JOC The Journal of Organic Chemistry

Article

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# Catalytic C−H Activation of Phenylethylamines or Benzylamines and Their Annulation with Allenes

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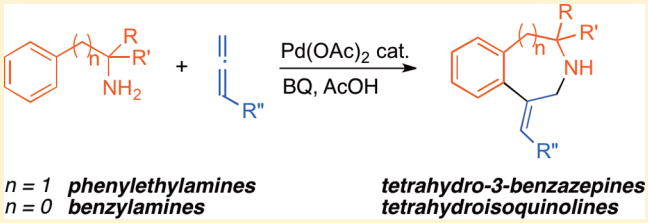
Supporting Information

**ABSTRACT:** Tetrahydro-3-benzazepines and tetrahydroisoquinolines are synthesized in one step from allenes and phenylethylamines or benzylamines, respectively. Mechanistically, it is assumed that activation of a C−H bond of an aromatic ring with Pd(II) occurs, directed by the primary amine, leading to the formation of a palladacycle into which an allene then undergoes insertion. The resulting $\pi$-allyl intermediate cyclizes to the products by an intramolecular allylic alkylation. The process is particularly useful with 2,3-butadienoates and amines having a quaternary carbon at the $\alpha$-position.




## INTRODUCTION

The use of allenes in the synthesis of highly functionalized molecules has increased over the past few years.[1] The 1,2-diene moiety confers on allenes a unique reactivity that has been applied in both organic and organometallic chemistry.[2] In particular, metal-catalyzed reactions of allenes have become a useful tool for the formation of C−C and C−X bonds.[3] However, transition-metal-catalyzed intermolecular reactions of aromatic substrates with unactivated C−H bonds and allenes has only recently been achieved with a variety of metals (Ir,[4] Re,[5] Pd,[6] and mainly Rh[7]). In all cases a carbonyl-derived directing group assists functionalization of the C−H bond (Scheme 1).

In 2011 we first reported on the use of primary amines as directing groups in C−H activation/carbonylation reactions under Pd(II) catalysis.[8] This result showed not only that the amino group can act as a director/activator group as other groups do but that it can also react further to form heterocyclic structures. Consequently, we envisaged that this group could also direct the carbopalladation of allenes through the formation of a palladacycle (**I**).[9] Since this carbopalladation would provide a reactive $\pi$-allyl intermediate (**II**), then because of its nucleophilic nature the amine would also undergo Tsuji−Trost allylic alkylation to cyclize to a 3-benzazepine skeleton (Scheme 2). Actually, it has been reported recently that the stoichiometric insertion reaction of allenes into the Pd−C bond of palladacycles of phenylethylamines (**I**) forms stable $\pi$-allyl intermediates (**II**) that can decompose to tetrahydro-3-benzapines under controlled conditions.[10] Tetrahydro-3-benzazepines are a family of compounds with interesting biological and pharmacological properties. This unique skeleton has also been found in several alkaloids.[11]

## RESULTS AND DISCUSSION

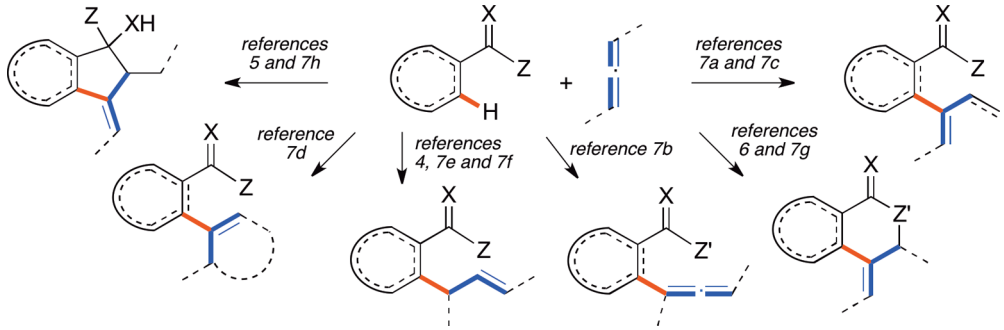
Since a metal-catalyzed method for their preparation is still lacking, we initially investigated the proposed reaction under conditions that were optimized for our carbonylation reaction.[8] After a short optimization process, the use of acetic acid as the solvent and benzoquinone (BQ) as the oxidant yielded optimal results. Under these conditions, we tried the insertion of ethyl 2,3-butadienoate (**1a**) into $\alpha$-quaternary primary amines **2** and their expected cyclization to tetrahydro-3-benzazepines **3** (Scheme 3). As shown in Table 1 and in accordance with our previous results for carbonylations,[8] greater steric hindrance at the quaternary carbon resulted in higher yields (see comparison of entries 1−3 and also 4 and 5).[12] Interestingly, an electron-withdrawing group is necessary to obtain good yields. Thus, replacement of a methyl group by a trifluoromethyl group resulted in a remarkably better yield (entries 5 and 6). It is also noteworthy that with this polarized allene, the addition of the amino group to the nonsymmetrical $\pi$-allyl intermediate is regioselective and only one regioisomer is obtained. Furthermore, good *Z* stereoselectivities are usually obtained (Table 1).[13]

Additionally, the cyclization process seems to be fast enough to prevent the primary amine from activating the remaining *ortho* C−H bond, thus preventing the formation of products

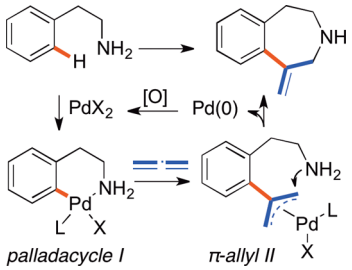
**Received:** July 22, 2014
**Published:** September 17, 2014

   dx.doi.org/10.1021/jo501658s | J. Org. Chem. 2014, 79, 9578−9585

**Scheme 1. C−H Activation with Allene Insertion**




**Scheme 2. Carbopalladation of Allene Followed by Allylic Alkylation**




**Scheme 3. Annulation of Allene 1a with α-Quaternary Primary Amines**

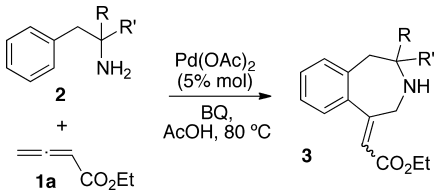


**Table 1. Reaction of Allene 1a with Primary Amines 2[a]**

| entry | amine | R | R′ | product | yield | Z:E |
|---|---|---|---|---|---|---|
| 1 | **2a** | $CO_2Me$ | Bn | **3a** | 86% | 83:17 |
| 2 | **2b** | $CO_2Me$ | Pr | **3b** | 76% | 90:10 |
| 3 | **2c** | $CO_2Me$ | Me | **3c** | 51% | 82:18 |
| 4 | **2d** | Me | Me | **3d** | 13% | >99:1 |
| 5 | **2e** | Pr | Me | **3e** | 18% | >99:1 |
| 6 | **2f** | Pr | $CF_3$ | **3f** | 73% | 87:13 |
| 7 | **2g** | $CO_2Et$ | $CO_2Et$ | **3g** | 83% | 83:17 |

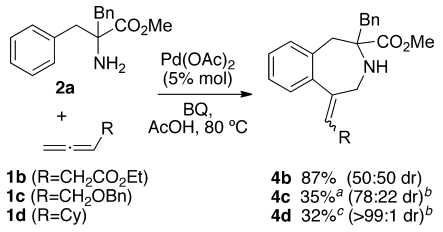
[a]Reaction conditions: amine (1.0 equiv), allene (1.2 equiv), benzoquinone (1.1 equiv), and $Pd(OAc)_2$ (5 mol %) in AcOH (0.12 M) at 80 °C for 30 min.

derived from the incorportation of two allene molecules, a common problem in some C−H activation protocols.

Other less polarized allenes were also explored (Scheme 4). Only with ethyl 3,4-pentadienoate (**1b**) were a high conversion and yield of benzazepine **4b** obtained. With other allenes (**1c** and **1d**) only low conversions were achieved. Again, only one regioisomer was observed as a mixture of *Z* and *E* olefins.[13]

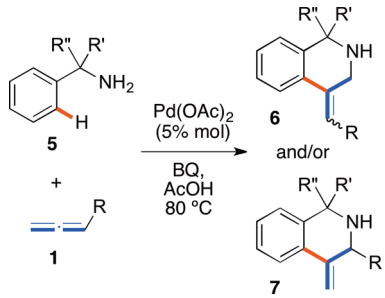
This approach could be also applied to the annulation of benzylamines with allenes to form six-membered rings that would provide access to tetrahydroisoquinolines (THIQs), a common scaffold present in many biologically active compounds (Scheme 5).[14] When methyl α-propylphenylglycinate (R′ = *n*-$C_3H_7$, R″ = $CO_2Me$, **5a**) reacted with conjugated

**Scheme 4. Annulation of Allenes 1b−d with Amine 2a**




[a]Yield based on **4c** used: 92%. [b]Z olefin as the major isomer. [c]Yield based on **4d** used: 72%.

**Scheme 5. Synthesis of Tetrahydroisoquinolines by Annulation of Benzylamines with Allenes**



allenes **1a** and **1f** under the same conditions, the corresponding THIQs **6a** and **6f** were obtained in good yields as single regio- and stereoisomers (Table 2, entries 1 and 6). However, when other allenes were used, significant amounts of the other regioisomer **7** were isolated (entries 2−5). The stereochemistry of the double bond was mainly *Z*.[13]

The performance of amines **5b−d** with allene **1a** was also explored (Scheme 6). The formation of tetrahydroisoquinolines

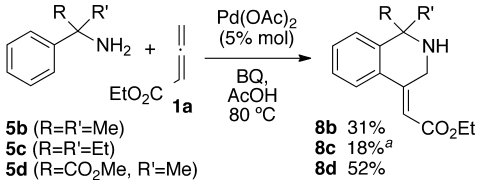
**Table 2. Annulation of Allenes 1a−f with Primary Amine 5a[a]**

| entry | allene | R | yield | 6:7 | dr (7) | Z:E[b] |
|---|---|---|---|---|---|---|
| 1 | **1a** | $CO_2Et$ | 77% | >99:1 | – | >99:1 |
| 2 | **1b** | $CH_2CO_2Et$ | 95% | 34:66 | 72:28 | 87:13 |
| 3 | **1c** | $CH_2OBn$ | 78% | 47:53 | 73:27 | 88:12 |
| 4 | **1d** | Cy | 53% | 40:60 | 70:30 | >99:1 |
| 5 | **1e** | $CH_2OTPS$ | 53% | 34:66 | 80:20 | 90:10 |
| 6 | **1f** | CN | 68% | >99:1 | – | >99:1 |

[a]Reaction conditions: amine (1.0 equiv), allene (1.2 equiv for **1a−e** and 3.0 equiv for **1f**), benzoquinone (1.1 equiv), and $Pd(OAc)_2$ (5 mol %) in AcOH (0.12 M) at 80 °C for 30 min. [b]Stereochemistry of the double bond in **6**.


dx.doi.org/10.1021/jo501658s | J. Org. Chem. 2014, 79, 9578−9585

**Scheme 6. Annulation of Amines 5b−d with Allene 1a**

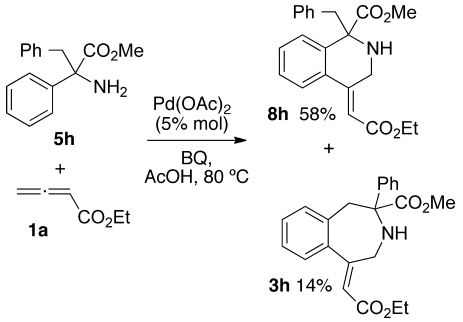



[a]Estimated yield based on **8c** used: 72%.

also showed the trend that was observed with benzazepines: an electron-withdrawing group at the $\alpha$-position of the amine is necessary for good yields.[12]

Finally, the relative rates of formation of six- and seven-membered rings were evaluated using methyl $\alpha$-benzylphenylglycinate (**5h**) (Scheme 7). According to our previous work,[8b]

**Scheme 7. Annulation of Allene 1a with Amine 5h**




the five-membered-ring palladacycle is preferred over the six-membered ring, and in this case it is also the more reactive one, leading to THIQ **8h** as the major product (87:13 *Z*/*E* mixture).[13]

## SUMMARY

We have developed a new approach to 3-benzoazepine or isoquinoline skeletons based on the reaction of terminal allenes with phenylethylamines or benzylamines, respectively. Allenes with an electron-withdrawing group such as an ester or nitrile afforded good to excellent yields and stereoselectivities. On the other hand, the amines need to be $\alpha$-disubstituted, preferably with electron-withdrawing groups.

## EXPERIMENTAL SECTION

All of the reactants were obtained from commercial sources and used as received. Solvents were distilled and dried before use. Column chromatography was performed on silica gel (230−400 mesh). Chemical shifts ($\delta$) are given in parts per million and coupling constants ($J$) in hertz. Amine **5b** and allenes **1a** and **1d** are commercially available. Amines **2a**,[8b] **2b**,[8b] **2c**,[8b] **2d**,[8b] **2g**,[18] **5c**,[19] **5d**,[8b] and **5h**[8b] and allenes **1b**,[15] **1c**,[16] and **1f**[17] were prepared according to previously published procedures.

**(Buta-2,3-dien-1-yloxy)(*tert*-butyl)diphenylsilane (1e).** TBDPSCl (6.70 mL, 25.77 mmol) was added dropwise to a solution of imidazole (2.340 g, 34.36 mmol) and propargyl alcohol (1.00 mL, 17.18 mmol) in anhydrous THF (30 mL). The resulting solution was stirred at rt overnight, and the reaction was quenched by the addition of a saturated solution of $NH_4Cl$ (15 mL). The phases were separated, and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure to obtain 4.598 g of a crude oil that was used in the next step without further purification. The crude oil and dicyclohexylamine (4.71 mL, 23.67 mmol) were added to a mixture of CuI (1.251 g, 6.58 mmol) and paraformaldehyde (1.012 g, 33.58 mmol) in dioxane (30 mL), and the mixture was heated at 100 °C for 4 h. The solvent was evaporated under reduced pressure, and the resulting crude material was purified by flash column chromatography (hexane/AcOEt 99:1) to obtain **1e** as a colorless oil (3.428 g, 11.114 mmol, 84%). $R_f$ (hexane/AcOEt 9:1) = 0.55; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.74−7.69 (m, 4H), 7.47−7.36 (m, 6H), 5.27 (quint, 1H, $J$ = 6.4 Hz), 4.74 (dt, 2H, $J$ = 6.5, 2.9 Hz), 4.25 (dt, 2H, $J$ = 6.2, 2.9 Hz), 1.05 (s, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 208.3, 135.7, 133.8, 129.8, 127.8, 90.8, 76.3, 62.1, 27.0, 26.7; **IR** (ATR, $cm^{-1}$) 2956, 2934, 2886, 2858, 1955, 1470, 1256, 1087, 776.

**2-Methyl-1-phenylpentan-2-amine (2e).** *2-Methyl-1-phenylpentan-2-ol (9).* Benzyl methyl ketone (2.003 g, 14.91 mmol) was added dropwise to a 0.5 M solution of allylmagnesium bromide in THF at 0 °C, and the mixture was stirred at 0 °C for 4 h. The reaction was quenched by the addition of a saturated solution of $NH_4Cl$, and the aqueous phase was extracted with AcOEt. The combined organic layer was washed with a saturated solution of NaCl, dried, and evaporated under reduced pressure to obtain 2.60 g of a crude material that was used in the next step without further purification. The crude material (0.500 g) and Pt/C catalyst (0.222 g, 0.057 mmol) were dissolved in AcOEt (25 mL). The suspension was flushed first with nitrogen and then with hydrogen and was stirred for 1 h at rt. The crude product was filtered through a short pad of Celite to obtain **9** as a colorless oil (0.416 g, 2.33 mmol, 82%). $R_f$ (hexane/AcOEt 4:1) = 0.41; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.34−7.20 (m, 5H), 2.79 (d, 1H, $J$ = 13.2 Hz), 2.73 (d, 1H, $J$ = 13.2 Hz), 1.48−1.43 (m, 4H), 1.15 (s, 3H), 0.94 (t, 3H, $J$ = 6.9 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 137.8, 130.7, 128.3, 126.5, 72.7, 48.2, 44.3, 26.6, 17.4, 14.8; **HRMS** (ESI+) calcd for $C_{12}H_{22}NO$ $[M + NH_4]^+$ 196.1696, found 196.1696.

*2-Chloro-N-(2-methyl-1-phenylpentan-2-yl)acetamide (10).* $H_2SO_4$ (0.57 mL, 10.10 mmol) was added dropwise to a solution of **9** (0.200 g, 1.12 mmol) and chloroacetonitrile (0.43 mL, 6.73 mmol) in 0.5 mL of acetic acid at 0 °C. The mixture was stirred for 5 h at rt. The mixture was poured into ice and extracted with $CH_2Cl_2$. The combined organic layers were washed with a saturated solution of $Na_2CO_3$ and brine and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane/AcOEt 95:5) to obtain **10** as a colorless solid (0.165 g, 0.651 mmol, 58%). $R_f$ (hexane/AcOEt 4:1) = 0.41; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.32−7.21 (m, 3H), 7.15−7.11 (m, 2H), 6.10 (bs, 1H), 3.95 (s, 2H), 3.16 (d, 1H, $J$ = 13.4 Hz), 2.93 (d, 1H, $J$ = 13.4 Hz), 1.89 (ddd, 1H, $J$ = 13.6, 12.0, 5.0 Hz), 1.57 (ddd, 1H, $J$ = 13.6, 12.1, 4.8 Hz), 1.46−1.31 (m, 2H), 1.28 (s, 3H), 0.94 (t, 3H, $J$ = 7.3 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 165.2, 137.3, 130.6, 128.2, 126.7, 57.4, 43.8, 43.1, 40.8, 24.1, 17.1, 14.5; **IR** (ATR, $cm^{-1}$) 3298, 2957, 2929, 1660, 1553, 1236, 702; **HRMS** (ESI+) calcd for $C_{14}H_{21}ClNO$ $[M + H]^+$ 254.1306, found 254.1302.

*2-Methyl-1-phenylpentan-2-amine (2e).* A solution of **10** (0.124 g, 0.49 mmol) and thiourea (0.045 g, 0.59 mmol) in a mixture of ethanol and acetic acid 5:1 (3 mL) was refluxed for 16 h. The reaction was quenched by the addition of a 1 M solution of NaOH, and the mixture was extracted with $CH_2Cl_2$. The organic layer was extracted with a 2 M solution of HCl, and the aqueous layer was basicified with solid NaOH and then extracted with $CH_2Cl_2$. The combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure to obtain **2e** as a colorless oil (0.070 g, 0.39 mmol, 80%). $R_f$ (hexane/AcOEt 4:1) = 0.10; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.31−7.16 (m, 5H), 2.64 (s, 2H), 1.46−1.39 (m, 2H), 1.37−1.30 (m, 2H), 1.22 (bs, 2H), 1.03 (s, 3H), 0.93 (t, 3H, $J$ = 7.0 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 138.4, 130.6, 128.0, 126.3, 52.1, 49.3, 45.4, 27.8, 17.4, 14.8; **HRMS** (ESI+) calcd for $C_{12}H_{20}N$ $[M + H]^+$ 178.1590, found 178.1591.

**2-Benzyl-1,1,1-trifluoropentan-2-amine (2f).** *1,1,1-Trifluoro-3-phenylpropan-2-one Oxime (11).* Trifluoromethyl benzyl ketone (1.00 mL, 6.23 mmol) was added to a solution of hydroxylamine hydrochloride (3.46 g, 49.79 mmol) and sodium acetate (4.09 g, 49.81 mmol) in a 5:1 water/ethanol mixture (25 mL), and the resulting mixture was refluxed for 1 h. The mixture was cooled to rt and extracted with $CH_2Cl_2$. The combined organic layers were dried over


dx.doi.org/10.1021/jo501658s | J. Org. Chem. 2014, 79, 9578−9585

anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane/AcOEt 9:1) to obtain **11** as a colorless solid (1.17 g, 5.76 mmol, 93%). **mp** = 38−40 °C (lit. 40−42 °C); $R_f$ (hexane/AcOEt 4:1) = 0.54; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 9.11 (bs, 1H), 7.33−7.22 (m, 5H), 3.87 (s, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 149.2 (q, $J_{CF}$ = 31.9 Hz), 134.1, 129.1, 128.8, 127.2, 120.9 (q, $J_{CF}$ = 274.6 Hz), 30.1; **IR** (ATR, $cm^{-1}$) 3300, 3100, 2920, 1700, 1600, 1450; **HRMS** (ESI+) calcd for $C_9H_9F_3NO$ $[M + H]^+$ 204.0631, found 204.0633.

*N-(2-Benzyl-1,1,1-trifluoropent-4-en-2-yl)hydroxylamine (**12**).* A 1 M solution of allylmagnesium bromide in $Et_2O$ (4.90 mL, 0.98 mmol) was added to a solution of **11** (0.208 g, 0.98 mmol) in anhydrous $Et_2O$, and the resulting solution was stirred at rt for 4 h. The reaction was quenched by the addition of a saturated solution of $NH_4Cl$, and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane/AcOEt 95:5) to obtain **12** as a colorless oil (0.204 g, 0.832 mmol, 85%). $R_f$ (hexane/AcOEt 4:1) = 0.44; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.35−7.23 (m, 5H), 5.85−5.72 (m, 1H), 5.27 (bs, 1H), 5.21−5.12 (m, 2H), 5.07 (bs, 1H), 3.26 (d, 1H, $J$ = 14.0 Hz), 2.88 (d, 1H, $J$ = 14.0 Hz), 2.44 (dd, 1H, $J$ = 14.6, 7.2 Hz), 2.29 (dd, 1H, $J$ = 14.6, 7.6 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 133.0 (q, $J_{CF}$ = 311.3 Hz), 131.0, 128.6, 128.3, 127.3, 127.2, 119.9, 66.0 (q, $J_{CF}$ = 22.8 Hz), 35.6 (q, $J_{CF}$ = 1.1 Hz), 35.5 (q, $J_{CF}$ = 1.2 Hz); **HRMS** (ESI+) calcd for $C_{12}H_{15}F_3NO$ $[M + H]^+$ 246.1100, found 246.1108.

*2-Benzyl-1,1,1-trifluoropentan-2-amine (**2f**).* Pt/C catalyst (0.160 g, 0.82 mmol) was added to a solution of **12** (0.200 g, 0.81 mmol) in AcOEt (25 mL). The resulting mixture was flushed first with nitrogen and then with hydrogen and was stirred for 1 h at rt. The mixture was filtered through a short pad of Celite to obtain 0.143 g of crude material that was used in the next step without further purification. The above crude material was added to a suspension of $LiAlH_4$ (0.124 g, 3.108 mmol) in anhydrous THF (10 mL) under a nitrogen atmosphere, and the mixture was stirred at rt for 48 h. The reaction was quenched by the addition of methanol, and the solvent was evaporated under reduced pressure. The crude material was partitioned between $CH_2Cl_2$ and a 2 M solution of HCl. The aqueous solution was extracted with $CH_2Cl_2$ and then basicified with solid NaOH. The aqueous layer was extracted again with $CH_2Cl_2$, and the combined organic layers were dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to obtain **2f** as a colorless oil (0.046 g, 0.197 mmol, 38%). $R_f$ (hexane/AcOEt 4:1) = 0.46; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40−7.22 (m, 5H), 2.89 (m, 2H), 1.59−1.41 (m, 4H), 1.37 (bs, 2H), 0.92 (t, 3H, $J$ = 6.8 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 135.5, 131.0, 128.3, 128.2 (q, $J_{CF}$ = 286.7 Hz), 127.1, 59.0 (q, $J_{CF}$ = 24.4 Hz), 40.1 (q, $J_{CF}$ = 1.4 Hz), 37.3, 16.8 (q, $J_{CF}$ = 1.4 Hz), 14.7; **HRMS** (ESI+) calcd for $C_{12}H_{17}F_3N$ $[M + H]^+$ 232.1308, found 232.1309.

**General Procedure for the Insertion Reaction.** Acetic acid was added to a mixture of the amine (1.0 equiv), the allene (1.2 equiv for **1a−e** and 3.0 equiv for **1f**), benzoquinone (1.1 equiv), and palladium acetate (5 mol %) to a concentration of 0.12 M. The reaction mixture was stirred for 30 min at 80 °C, and the crude material was filtered through a short pad of Celite. Acetic acid was evaporated under reduced pressure, and the crude material was dissolved in $CH_2Cl_2$ and washed with a 1 M solution of NaOH, water, and brine. The organic layer was dried over anhydrous $MgSO_4$ and evaporated, and the residue was purified by flash column chromatography. Complete separation of **3a−c**, **3f**, **3g**, and **4c** stereoisomeric mixtures was not accomplished, and only major stereoisomers were fully separated and characterized; for minor stereoisomers, only $^1$H NMR data are reported.

*(Z)-Methyl 2-Benzyl-5-(2-ethoxy-2-oxoethylidene)-2,3,4,5-tetrahydro-1H-benzo[d]azepine-2-carboxylate [(Z)-**3a**].* Compound (*Z*)-**3a** was obtained in 71% yield (0.104 g) as a colorless solid from 0.104 g of amine **2a**, 0.053 g of allene **1a**, 0.045 g of benzoquinone, 0.004 g of $Pd(OAc)_2$, and 3.5 mL of AcOH. $R_f$ (hexane/AcOEt 4:1) = 0.31; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40−7.15 (m, 7H), 7.11−7.06 (m, 2H), 5.93 (t, 1H, $J$ = 2.5 Hz), 4.39 (dd, 1H, $J$ = 20.5, 2.5 Hz), 4.19 (dd, 1H, $J$ = 20.8, 2.5 Hz), 4.19 (q, 2H, $J$ = 7.1 Hz), 3.62 (s, 3H), 3.16 (d, 1H, $J$ = 14.2 Hz), 2.99 (d, 1H, $J$ = 13.2 Hz), 2.97 (d, 1H, $J$ = 14.2 Hz), 2.85 (d, 1H, $J$ = 13.2 Hz), 1.88 (bs, 1H), 1.30 (t, 3H, $J$ = 7.1 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 175.1, 166.3, 164.8, 140.5, 136.1, 135.2, 130.1, 129.5, 129.2, 128.4, 127.9, 127.8, 127.1, 116.9, 66.4, 60.1, 52.0, 46.2, 43.4, 39.9, 14.5; **IR** (ATR, $cm^{-1}$) 3402, 2979, 2950, 1732, 1704, 1615, 1169, 730; **HRMS** (ESI+) calcd for $C_{23}H_{26}NO_4$ $[M + H]^+$ 380.1856, found 380.1860.

*(E)-Methyl 2-Benzyl-5-(2-ethoxy-2-oxoethylidene)-2,3,4,5-tetrahydro-1H-benzo[d]azepine-2-carboxylate [(E)-**3a**].* Compound (*E*)-**3a** was obtained in 15% yield (0.021 g) as a colorless solid from 0.104 g of amine **2a**, 0.053 g of allene **1a**, 0.045 g of benzoquinone, 0.004 g of $Pd(OAc)_2$, and 3.5 mL of AcOH. $R_f$ (hexane/AcOEt 4:1) = 0.18; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.32−7.04 (m, 9H), 5.96 (s, 1H), 4.02 (q, 2H, $J$ = 7.1 Hz), 3.77 (d, 1H, $J$ = 1.5 Hz), 3.76 (d, 1H, $J$ = 1.5 Hz), 3.63 (s, 3H), 3.18 (d, 1H, $J$ = 14.2 Hz), 3.03 (d, 2H, $J$ = 15.5 Hz), 2.86 (d, 1H, $J$ = 14.1 Hz), 1.11 (t, 3H, $J$ = 7.1 Hz).

*(Z)-Methyl 5-(2-Ethoxy-2-oxoethylidene)-2-propyl-2,3,4,5-tetrahydro-1H-benzo[d]azepine-2-carboxylate [(Z)-**3b**].* Compound (*Z*)-**3b** was obtained in 68% yield (0.102 g) as a colorless oil from 0.100 g of amine **2b**, 0.064 g of allene **1a**, 0.055 g of benzoquinone, 0.005 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 7:3) = 0.63; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38−7.28 (m, 3H), 7.10−7.05 (m, 1H), 5.91 (t, 1H, $J$ = 2.5 Hz), 4.34 (dd, 1H, $J$ = 20.6, 2.5 Hz), 4.19 (q, 2H, $J$ = 7.2 Hz), 4.14 (dd, 1H, $J$ = 21.0, 2.5 Hz), 3.75 (s, 3H), 3.10 (d, 1H, $J$ = 14.2 Hz), 2.85 (d, 1H, $J$ = 14.2 Hz), 1.88 (bs, 1H), 1.66−1.56 (m, 1H), 1.56−1.46 (m, 1H), 1.31 (t, 3H, $J$ = 7.1 Hz), 1.28−1.14 (m, 2H), 0.87 (t, 3H, $J$ = 7.3 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 175.9, 166.3, 165.1, 140.2, 135.5, 129.4, 129.2, 127.9, 127.7, 116.9, 64.9, 60.1, 52.3, 46.4, 39.7, 21.2, 17.6, 14.5, 14.4; **IR** (ATR, $cm^{-1}$) 3402, 2958, 1713, 1628, 1218, 1156, 1033, 731; **HRMS** (ESI+) calcd for $C_{19}H_{26}NO_4$ $[M + H]^+$ 332.1856, found 332.1860.

*(E)-Methyl 5-(2-Ethoxy-2-oxoethylidene)-2-propyl-2,3,4,5-tetrahydro-1H-benzo[d]azepine-2-carboxylate [(E)-**3b**].* Compound (*E*)-**3b** was obtained in 8% yield (0.012 g) as a colorless oil from 0.100 g of amine **2b**, 0.064 g of allene **1a**, 0.055 g of benzoquinone, 0.005 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 7:3) = 0.51; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.31−7.04 (m, 4H), 5.94 (s, 1H), 4.02 (q, 2H, $J$ = 7.1 Hz), 3.74 (m, 2H), 3.73 (s, 3H), 3.11 (d, 1H, $J$ = 14.2 Hz), 2.88 (d, 1H, $J$ = 14.2 Hz), 1.71−1.59 (m, 1H), 1.57−1.48 (m, 1H), 1.34−1.25 (m, 2H), 1.11 (t, 3H, $J$ = 7.1 Hz), 0.87 (t, 3H, $J$ = 7.3 Hz).

*(Z)-Methyl 5-(2-Ethoxy-2-oxoethylidene)-2-methyl-2,3,4,5-tetrahydro-1H-benzo[d]azepine-2-carboxylate [(Z)-**3c**].* Compound (*Z*)-**3c** was obtained in 42% yield (0.066 g) as a colorless oil from 0.100 g of amine **2c**, 0.073 g of allene **1a**, 0.063 g of benzoquinone, 0.006 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 7:3) = 0.27; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38−7.26 (m, 3H), 7.12−7.09 (m, 1H), 5.92 (t, 1H, $J$ = 2.4 Hz), 4.34 (dd, 1H, $J$ = 20.5, 2.5 Hz), 4.20 (q, 2H, $J$ = 7.1 Hz), 4.15 (dd, 1H, $J$ = 20.5, 2.6 Hz), 3.77 (s, 3H), 3.17 (d, 1H, $J$ = 14.1 Hz), 2.79 (d, 1H, $J$ = 14.1 Hz), 2.08 (bs, 1H), 1.31 (t, 3H, $J$ = 7.1 Hz), 1.26 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 176.6, 166.3, 164.7, 140.1, 135.2, 129.6, 129.2, 127.9, 127.8, 117.0, 61.3, 60.1, 52.5, 46.6, 40.4, 24.6, 14.5; **IR** (ATR, $cm^{-1}$) 3402, 2970, 1729, 1705, 1615, 1368, 1162, 1104, 728; **HRMS** (ESI+) calcd for $C_{17}H_{22}NO_4$ $[M + H]^+$ 304.1543, found 304.1549.

*(E)-Methyl 5-(2-Ethoxy-2-oxoethylidene)-2-methyl-2,3,4,5-tetrahydro-1H-benzo[d]azepine-2-carboxylate [(E)-**3c**].* Compound (*E*)-**3c** was obtained in 9% yield (0.014 g) as a colorless oil from 0.100 g of amine **2c**, 0.073 g of allene **1a**, 0.063 g of benzoquinone, 0.006 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 7:3) = 0.12; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.32−7.20 (m, 4H), 5.97 (s, 1H), 4.02 (q, 2H, $J$ = 7.1 Hz), 3.76 (s, 3H), 3.75 (m, 2H), 3.18 (d, 1H, $J$ = 14.2 Hz), 2.85 (d, 1H, $J$ = 14.2 Hz), 1.31 (s, 3H), 1.11 (t, 3H, $J$ = 7.1 Hz).

*(Z)-Ethyl 2-(4,4-Dimethyl-2,3,4,5-tetrahydro-1H-benzo[d]azepin-1-ylidene)acetate (**3d**).* Compound **3d** was obtained in 13% yield (0.022 g) as a brown oil from 0.102 g of amine **2d**, 0.095 g of allene **1a**, 0.081 g of benzoquinone, 0.008 g of $Pd(OAc)_2$, and 5.0 mL of AcOH. $R_f$ (hexane/AcOEt 7:3) = 0.12; **$^1$H NMR** (400 MHz, $CDCl_3$)


dx.doi.org/10.1021/jo501658s | J. Org. Chem. 2014, 79, 9578−9585

δ 7.37−7.27 (m, 3H), 7.08 (d, 1H, *J* = 7.3 Hz), 5.90 (t, 1H, *J* = 2.4 Hz), 4.25 (d, 2H, *J* = 2.2 Hz), 4.21 (q, 2H, *J* = 7.2 Hz), 2.62 (s, 2H), 2.19 (bs, 1H), 1.31 (t, 3H, *J* = 7.1 Hz), 1.13 (s, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 166.4, 139.4, 137.1, 129.6, 129.3, 128.6, 128.1, 127.3, 117.0, 60.1, 52.3, 45.2, 45.0, 27.5, 14.5; **HRMS** (ESI+) calcd for $C_{16}H_{22}NO_2$ $[M + H]^+$ 260.1645, found 260.1646.

*(Z)-Ethyl 2-(4-Methyl-4-propyl-2,3,4,5-tetrahydro-1H-benzo[d]-azepin-1-ylidene)acetate (**3e**).* Compound **3e** was obtained in 18% yield (0.020 g) as a colorless oil from 0.070 g of amine **2e**, 0.056 g of allene **1a**, 0.049 g of benzoquinone, 0.005 g of $Pd(OAc)_2$, and 3.5 mL of AcOH. $R_f$ (hexane/AcOEt 7:3) = 0.26; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.29−7.17 (m, 3H), 7.02−6.94 (m, 1H), 5.82 (t, 1H, *J* = 2.5 Hz), 4.19−4.15 (m, 2H), 4.13 (q, 2H, *J* = 7.1 Hz), 2.57 (d, 1H, *J* = 13.6 Hz), 2.48 (d, 1H, *J* = 13.6 Hz), 1.54 (bs, 1H), 1.33−1.27 (m, 4H), 1.24 (t, 3H, *J* = 7.1 Hz), 0.95 (s, 3H), 0.85 (t, 3H, *J* = 6.2 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 167.0, 166.4, 139.7, 137.0, 130.0, 129.2, 128.0, 127.2, 116.8, 77.2, 60.0, 54.7, 44.7, 44.0, 42.1, 24.3, 17.3, 14.9, 14.5; **IR** (ATR, $cm^{-1}$) 3402, 2957, 2930, 2871, 1706, 1162; **HRMS** (ESI+) calcd for $C_{18}H_{26}NO_2$ $[M + H]^+$ 288.1958, found 288.1957.

*(Z)-Ethyl 2-(4-Propyl-4-(trifluoromethyl)-2,3,4,5-tetrahydro-1H-benzo[d]azepin-1-ylidene)acetate [(Z)-**3f**].* Compound (*Z*)-**3f** was obtained in 64% yield (0.094 g) as a colorless oil from 0.101 g of amine **2f**, 0.061 g of allene **1a**, 0.053 g of benzoquinone, 0.005 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 9:1) = 0.33; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.41−7.29 (m, 3H), 7.16−7.10 (m, 1H), 5.90 (t, 1H, *J* = 2.5 Hz), 4.53 (dd, 1H, *J* = 20.8, 1.8 Hz), 4.39 (dd, 1H, *J* = 20.8, 2.5 Hz), 4.20 (q, 2H, *J* = 7.1 Hz), 3.21 (d, 1H, *J* = 14.1 Hz), 2.72 (d, 1H, *J* = 14.1 Hz), 1.58 (bs, 1H), 1.48−1.35 (m, 4H), 1.31 (t, 3H, *J* = 7.1 Hz), 0.84 (t, 3H, *J* = 6.1 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 166.2, 164.6, 139.9, 134.5, 130.2, 129.4, 128.5 (q, $J_{CF}$ = 289.7 Hz), 128.2, 127.9, 117.4, 61.1 (q, $J_{CF}$ = 23.8 Hz), 60.2, 45.7, 37.5, 35.9, 16.8 (q, $J_{CF}$ = 1.9 Hz), 14.7, 14.5; **IR** (ATR, $cm^{-1}$) 3402, 2966, 2875, 1703, 1613, 1369, 1140, 1111, 768; **HRMS** (ESI+) calcd for $C_{18}H_{23}F_3NO_2$ $[M + H]^+$ 342.1675, found 342.1676.

*(E)-Ethyl 2-(4-Propyl-4-(trifluoromethyl)-2,3,4,5-tetrahydro-1H-benzo[d]azepin-1-ylidene)acetate [(E)-**3f**].* Compound (*E*)-**3f** was obtained in 9% yield (0.013 g) as a colorless oil from 0.101 g of amine **2f**, 0.061 g of allene **1a**, 0.053 g of benzoquinone, 0.005 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.33−7.22 (m, 3H), 7.16−7.13 (m, 1H), 5.98 (t, 1H, *J* = 1.8 Hz), 4.01 (q, 2H, *J* = 7.1 Hz), 3.95 (d, 1H, *J* = 17.9 Hz), 3.75 (d, 1H, *J* = 17.9 Hz), 3.24 (d, 1H, *J* = 14.2 Hz), 2.70 (d, 1H, *J* = 14.2 Hz), 1.45−1.40 (m, 2H), 1.31−1.25 (m, 2H), 1.10 (t, 3H, *J* = 7.1 Hz), 0.86 (t, 3H, *J* = 6.2 Hz).

*(Z)-Diethyl 5-(2-Ethoxy-2-oxoethylidene)-4,5-dihydro-1H-benzo-[d]azepine-2,2(3H)-dicarboxylate [(Z)-**3g**].* Compound (*Z*)-**3g** was obtained in 69% yield (0.049 g) as a colorless oil from 0.060 g of amine **2g**, 0.032 g of allene **1a**, 0.027 g of benzoquinone, 0.003 g of $Pd(OAc)_2$, and 2.0 mL of AcOH. $R_f$ (hexane/AcOEt 7:3) = 0.14; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.36−7.32 (m, 1H), 7.30−7.25 (m, 2H), 7.12−7.08 (m, 1H), 5.91 (t, 1H, *J* = 2.5 Hz), 4.32 (d, 2H, *J* = 2.5 Hz), 4.29−4.15 (m, 6H), 3.34 (s, 2H), 1.30 (t, 3H, *J* = 7.1 Hz), 1.26 (t, 6H, *J* = 7.1 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 169.7, 166.2, 164.2, 139.9, 134.2, 129.4, 129.4, 128.0, 128.0, 117.3, 69.3, 62.2, 60.1, 45.7, 37.1, 14.4, 14.2; **IR** (ATR, $cm^{-1}$) 3401, 2980, 2934, 1730, 1705, 1615, 1282, 1167; **HRMS** (ESI+) calcd for $C_{20}H_{26}NO_6$ $[M + H]^+$ 376.1755, found 376.1760.

*(E)-Diethyl 5-(2-Ethoxy-2-oxoethylidene)-4,5-dihydro-1H-benzo-[d]azepine-2,2(3H)-dicarboxylate [(E)-**3g**].* Compound (*E*)-**3g** was obtained in 14% yield (0.010 g) as a colorless oil from 0.60 g of amine **2g**, 0.032 g of allene **1a**, 0.027 g of benzoquinone, 0.003 g of $Pd(OAc)_2$, and 2.0 mL of AcOH. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.28−7.10 (m, 4H), 5.94 (t, 1H, *J* = 1.7 Hz), 4.25 (q, 2H, *J* = 7.1 Hz), 4.21 (q, 2H, *J* = 7.1 Hz), 4.02 (q, 2H, *J* = 7.1 Hz), 3.83 (m, 2H), 3.38 (s, 2H), 1.28 (t, 6H, *J* = 7.1 Hz), 1.11 (t, 3H, *J* = 7.1 Hz).

*(Z)-Methyl 2-Benzyl-5-(3-ethoxy-3-oxopropylidene)-2,3,4,5-tetra-hydro-1H-benzo[d]azepine-2-carboxylate [(Z)-**4b**].* Compound (*Z*)-**4b** was obtained in 43% yield (0.063 g) as a yellow oil from 0.102 g of amine **2a**, 0.056 g of allene **1b**, 0.045 g of benzoquinone, 0.004 g of $Pd(OAc)_2$, and 3.5 mL of AcOH. $R_f$ (hexane/AcOEt 4:1) = 0.20; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.37−7.32 (m, 1H), 7.29−7.21 (m, 5H), 7.16−7.11 (m, 1H), 7.10−7.05 (m, 2H), 5.77 (tt, 1H, *J* = 7.1, 2.4 Hz), 4.16 (q, 2H, *J* = 7.2 Hz), 3.80−3.67 (m, 2H), 3.65 (s, 3H), 3.15−3.13 (m, 3H), 2.99 (t, 2H, *J* = 13.1 Hz), 2.83 (d, 1H, *J* = 13.2 Hz), 1.88 (bs, 1H), 1.27 (t, 3H, *J* = 7.0 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 175.5, 171.5, 144.9, 141.7, 136.3, 134.2, 130.1, 129.4, 128.3, 127.9, 127.6, 127.5, 127.0, 119.6, 65.8, 60.9, 52.0, 44.3, 43.9, 40.3, 33.6, 14.4; **HRMS** (ESI+) calcd for $C_{24}H_{28}NO_4$ $[M + H]^+$ 394.2013, found 394.2012.

*(E)-Methyl 2-Benzyl-5-(3-ethoxy-3-oxopropylidene)-2,3,4,5-tetra-hydro-1H-benzo[d]azepine-2-carboxylate [(E)-**4b**].* Compound (*E*)-**4b** was obtained in 44% yield (0.064 g) as a yellow oil from 0.102 g of amine **2a**, 0.056 g of allene **1b**, 0.045 g of benzoquinone, 0.004 g of $Pd(OAc)_2$, and 3.5 mL of AcOH. $R_f$ (hexane/AcOEt 4:1) = 0.16; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.31−7.13 (m, 9H), 5.81 (t, 1H, *J* = 7.4 Hz), 4.12 (q, 2H, *J* = 7.1 Hz), 3.69−3.65 (m, 2H), 3.60 (s, 3H), 3.37 (d, 1H, *J* = 13.1 Hz), 3.18 (d, 1H, *J* = 13.1 Hz), 3.09 (d, 2H, *J* = 7.4 Hz), 2.88 (d, *J* = 13.1 Hz), 2.85 (d, 1H, *J* = 13.1 Hz), 1.77 (bs, 1H), 1.24 (t, 3H, *J* = 6.3 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 172.1, 171.2, 144.4, 138.8, 136.3, 136.1, 135.7, 130.1, 130.0, 128.7, 128.6, 127.2, 127.1, 119.2, 64.9, 60.5, 51.9, 51.7, 46.5, 44.9, 34.8, 14.3; **HRMS** (ESI +) calcd for $C_{24}H_{28}NO_4$ $[M + H]^+$ 394.2013, found 394.2011.

*(Z)-Methyl 2-Benzyl-5-(2-(benzyloxy)ethylidene)-2,3,4,5-tetrahy-dro-1H-benzo[d]azepine-2-carboxylate [(Z)-**4c**].* Compound **4c** was obtained in 27% yield (0.043 g) as a yellow oil from 0.104 g of amine **2a**, 0.071 g of allene **1c**, 0.045 g of benzoquinone, 0.004 g of $Pd(OAc)_2$, and 3.5 mL of AcOH. $R_f$ (hexane/AcOEt 7:3) = 0.45; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.39−7.32 (m, 4H), 7.31−7.20 (m, 7H), 7.16−7.04 (m, 3H), 5.78 (t, 1H, *J* = 6.2 Hz), 4.56 (s, 2H), 4.15 (d, 2H, *J* = 6.0 Hz), 3.73 (d, 1H, *J* = 18.2 Hz), 3.64 (s, 3H), 3.63 (d, 1H, *J* = 18.2 Hz), 3.16 (d, 1H, *J* = 14.1 Hz), 3.00 (d, 1H, *J* = 13.1 Hz), 2.98 (d, 1H, *J* = 14.1 Hz), 2.81 (d, 1H, *J* = 13.2 Hz), 2.05 (bs, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 175.4, 144.9, 141.5, 138.3, 136.3, 134.3, 130.0, 129.4, 128.6, 128.3, 127.9, 127.8, 127.6, 127.6, 127.0, 124.8, 72.6, 66.2, 65.9, 51.9, 44.0, 43.9, 40.4; **HRMS** (ESI+) calcd for $C_{28}H_{30}NO_3$ $[M + H]^+$ 428.2220, found 428.2221.

*(E)-Methyl 2-Benzyl-5-(2-(benzyloxy)ethylidene)-2,3,4,5-tetrahy-dro-1H-benzo[d]azepine-2-carboxylate [(E)-**4c**].* Compound (*E*)-**4c** was obtained in 8% yield (0.013 g) as a yellow oil from 0.104 g of amine **2a**, 0.071 g of allene **1c**, 0.045 g of benzoquinone, 0.004 g of $Pd(OAc)_2$, and 3.5 mL of AcOH. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.30−7.22 (m, 10H), 7.18−7.15 (m, 4H), 5.84 (t, 1H, *J* = 7.0 Hz), 4.43 (s, 2H), 4.01 (m, 2H), 3.71 (m, 2H), 3.60 (s, 3H), 3.18 (d, 1H, *J* = 14.0 Hz), 3.02 (d, 1H, *J* = 14.0 Hz), 3.01 (d, 1H, *J* = 13.2 Hz), 2.86 (d, 1H, *J* = 13.2 Hz).

*(Z)-Methyl 2-Benzyl-5-(cyclohexylmethylene)-2,3,4,5-tetrahydro-1H-benzo[d]azepine-2-carboxylate (**4d**).* Compound **4d** was obtained in 32% yield (0.052 g) as a yellow oil from 0.113 g of amine **2a**, 0.065 g of allene **1d**, 0.055 g of benzoquinone, 0.005 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 4:1) = 0.60; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.31 (dd, 1H, *J* = 7.4, 1.4 Hz), 7.28−7.17 (m, 5H), 7.15−7.06 (m, 3H), 5.41 (dt, 1H, *J* = 9.6, 2.2 Hz), 3.81 (dd, 1H, *J* = 17.7, 2.3 Hz), 3.69 (dd, 1H, *J* = 17.6, 2.4 Hz), 3.65 (s, 3H), 3.16 (d, 1H, *J* = 14.0 Hz), 3.00 (d, 1H, *J* = 13.2 Hz), 2.97 (d, 1H, *J* = 14.0 Hz), 2.82 (d, 1H, *J* = 13.2 Hz), 2.29−2.17 (m, 1H), 1.90 (bs, 1H), 1.80−1.62 (m, 4H), 1.37−1.04 (m, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 175.7, 142.6, 139.6, 136.4, 135.1, 134.1, 130.1, 129.4, 128.3, 127.8, 127.5, 127.0, 126.9, 65.9, 51.9, 44.0, 43.8, 40.4, 36.9, 32.8, 32.7, 26.2, 26.1, 26.0; **IR** (ATR, $cm^{-1}$) 3402, 2920, 2848, 1731, 1448, 1216, 1175, 908, 730; **HRMS** (ESI+) calcd for $C_{26}H_{32}NO_2$ $[M + H]^+$ 390.2428, found 390.2427.

*(Z)-Methyl 4-(2-Ethoxy-2-oxoethylidene)-1-propyl-1,2,3,4-tetra-hydroisoquinoline-1-carboxylate (**6a**).* Compound **6a** was obtained in 77% yield (0.118 g) as a yellow oil from 0.100 g of amine **5a**, 0.065 g of allene **1a**, 0.057 g of benzoquinone, 0.004 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 7:3) = 0.22; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, 1H, *J* = 8.0 Hz), 7.52−7.44 (m, 1H), 7.40−7.32 (m, 1H), 7.31−7.26 (m, 1H), 6.33 (t, 1H, *J* = 1.6 Hz), 4.51 (dd, 1H, *J* = 17.2, 1.5 Hz), 4.27 (dd, 1H, *J* = 17.2, 1.9 Hz), 4.21 (q, 2H, *J* = 7.1 Hz), 3.74 (s, 3H), 2.13−2.04 (m, 1H), 1.97−1.88 (m, 1H), 1.38−1.24 (m,


dx.doi.org/10.1021/jo501658s | J. Org. Chem. 2014, 79, 9578−9585

2H), 1.32 (t, 3H, $J$ = 7.1 Hz), 0.91 (t, 3H, $J$ = 7.3 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 174.1, 166.5, 150.5, 139.0, 132.0, 129.9, 127.5, 126.8, 124.9, 111.5, 64.6, 60.0, 52.6, 42.4, 41.3, 17.6, 14.3, 14.2; **IR** (ATR, $cm^{-1}$) 3402, 2958, 2930, 2872, 1727, 1705, 1620, 1221, 1172, 1154, 729; **HRMS** (ESI+) calcd for $C_{18}H_{24}NO_4$ $[M + H]^+$ 318.1700, found 318.1694.

*Methyl 4-(3-Ethoxy-3-oxopropylidene)-1-propyl-1,2,3,4-tetrahydroisoquinoline-1-carboxylate (**6b**).* Compound **6b** was obtained as an 87:13 $Z$:$E$ mixture of stereoisomers in 32% yield (0.051 g) as a brown oil from 0.102 g of amine **5a**, 0.073 g of allene **1b**, 0.057 g of benzoquinone, 0.006 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 7:3) = 0.17; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.61 (m, 1H), 7.42 (m, 1H), 7.23 (m, 2H), 6.19 (t, 1H, $J$ = 7.3 Hz), 4.18 (q, 2H, $J$ = 7.1 Hz), 3.73 (m, 2H), 3.71 (s, 3H), 3.23 (dd, 2H, $J$ = 7.3, 2.2 Hz), 2.80 (bs, 1H), 2.10 (m, 1H), 1.91 (m, 1H), 1.31 (m, 2H), 1.27 (t, 3H, $J$ = 7.1 Hz), 0.90 (t, 3H, $J$ = 7.4 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 174.7, 171.6, 136.3, 134.4, 133.7, 127.5, 127.4, 126.9, 124.1, 114.6, 65.0, 61.0, 52.6, 42.0, 41.8, 33.6, 17.6, 14.4, 14.4; **HRMS** (ESI+) calcd for $C_{19}H_{26}NO_4$ $[M + H]^+$ 332.1856, found 332.1849.

*Methyl 3-(2-Ethoxy-2-oxoethyl)-4-methylene-1-propyl-1,2,3,4-tetrahydroisoquinoline-1-carboxylate (**7b-A**).* Diastereoisomer A of compound **7b** was obtained in 50% yield (0.080 g) as a brown oil from 0.102 g of amine **5a**, 0.073 g of allene **1b**, 0.057 g of benzoquinone, 0.006 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 7:3) = 0.53; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.52−7.41 (m, 2H), 7.26−7.20 (m, 2H), 5.42 (d, 1H, $J$ = 1.0 Hz), 4.94 (d, 1H, $J$ = 1.0 Hz), 4.16 (m, 2H), 3.94 (m, 1H), 3.72 (s, 3H), 2.82 (dd, 1H, $J$ = 15.1, 5.2 Hz), 2.64 (dd, 1H, $J$ = 15.1, 8.6 Hz), 2.56 (bs, 1H), 2.11 (ddd, 1H, $J$ = 14.0, 11.7, 4.4 Hz), 1.89 (ddd, 1H, $J$ = 14.0, 12.0, 4.5 Hz), 1.58−1.45 (m, 2H), 1.26 (t, 3H, $J$ = 7.1 Hz), 0.90 (t, 3H, $J$ = 7.4 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 174.2, 172.0, 143.8, 137.2, 134.2, 128.3, 127.5, 126.3, 125.4, 105.8, 65.6, 60.7, 52.8, 49.8, 41.5, 39.0, 18.3, 14.4, 14.3; **HRMS** (ESI+) calcd for $C_{19}H_{26}NO_4$ $[M + H]^+$ 332.1856, found 332.1848.

*Methyl 3-(2-Ethoxy-2-oxoethyl)-4-methylene-1-propyl-1,2,3,4-tetrahydroisoquinoline-1-carboxylate (**7b-B**).* Diastereoisomer B of compound **7b** was obtained in 13% yield (0.021 g) as a brown oil from 0.102 g of amine **5a**, 0.073 g of allene **1b**, 0.057 g of benzoquinone, 0.006 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 7:3) = 0.49; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.52 (m, 2H), 7.32−7.21 (m, 2H), 5.49 (d, 1H, $J$ = 1.0 Hz), 4.95 (d, 1H, $J$ = 1.0 Hz), 4.20 (q, 2H, $J$ = 7.1 Hz), 4.13 (m, 1H), 3.69 (s, 3H), 2.87 (dd, 1H, $J$ = 15.2, 4.6 Hz), 2.63 (dd, 1H, $J$ = 15.2, 8.2 Hz), 2.10 (m, 1H), 1.96 (m, 1H), 1.28 (t, 3H, $J$ = 7.1 Hz), 1.30−1.15 (m, 2H), 0.88 (t, 3H, $J$ = 7.3 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 175.4, 172.2, 143.6, 135.7, 134.5, 128.0, 127.5, 127.3, 124.8, 106.6, 65.2, 60.8, 52.6, 51.3, 43.3, 39.1, 17.0, 14.4, 14.3; **HRMS** (ESI+) calcd for $C_{19}H_{26}NO_4$ $[M + H]^+$ 332.1856, found 332.1847.

*Methyl 4-(2-(Benzyloxy)ethylidene)-1-propyl-1,2,3,4-tetrahydroisoquinoline-1-carboxylate (**6c**).* Compound **6c** was obtained as an 88:12 $Z$:$E$ mixture of stereoisomers in 37% yield (0.065 g) as a brown oil from 0.100 g of amine **5a**, 0.093 g of allene **1c**, 0.059 g of benzoquinone, 0.006 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 4:1) = 0.09; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.63−7.59 (m, 1H), 7.46−7.42 (m, 1H), 7.38−7.19 (m, 7H), 6.20 (t, 0.88H, $J$ = 6.6 Hz), 5.72 (t, 0.12H, $J$ = 6.6 Hz), 4.56 (s, 2H), 4.31 (d, 0.24H, $J$ = 6.6 Hz), 4.23 (dd, 1.76H, $J$ = 6.6, 2.1 Hz), 3.72 (s, 3H), 3.71 (d, 2H, $J$ = 3.5 Hz), 2.10 (bs, 1H), 2.10 (ddd, 1H, $J$ = 14.1, 11.5, 5.1 Hz), 1.92 (ddd, 1H, $J$ = 14.0, 11.7, 5.0 Hz), 1.37−1.28 (m, 2H), 0.90 (t, 3H, $J$ = 7.4 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 174.7, 138.2, 136.5, 134.8, 133.5, 128.5, 127.9, 127.8, 127.7, 127.3, 126.9, 124.2, 119.4, 72.5, 66.3, 65.0, 52.6, 42.0, 41.6, 17.6, 14.4; **IR** (ATR, $cm^{-1}$) 3402, 2956, 2870, 1728, 1455, 1364, 1217, 734; **HRMS** (ESI+) calcd for $C_{23}H_{28}NO_3$ $[M + H]^+$ 366.2064, found 366.2065.

*Methyl 3-((Benzyloxy)methyl)-4-methylene-1-propyl-1,2,3,4-tetrahydroisoquinoline-1-carboxylate (**7c**).* Compound **7c** was obtained in 41% yield (0.072 g) as a yellow oil from 0.100 g of amine **5a**, 0.093 g of allene **1c**, 0.059 g of benzoquinone, 0.006 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 4:1) = 0.28; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.55−7.47 (m, 2H), 7.32−7.15 (m, 7H), 5.49 (s, 1H), 5.02 (s, 1H), 4.53 (s, 2H), 3.72 (s, 3H), 3.68 (s, 3H), 2.47 (bs, 1H), 2.05 (ddd, 1H, $J$ = 14.1, 11.7, 4.4 Hz), 1.82 (ddd, 1H, $J$ = 14.1, 12.0, 4.6 Hz), 1.48−1.38 (m, 1H), 1.34−1.25 (m, 1H), 0.86 (t, 3H, $J$ = 7.4 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 174.1, 141.8, 138.3, 137.7, 134.0, 128.5, 128.0, 127.8, 127.7, 127.5, 125.7, 125.3, 107.9, 77.2, 73.5, 72.6, 65.5, 52.7, 52.6, 41.0, 18.4, 14.4; **IR** (ATR, $cm^{-1}$) 3402, 2954, 2859, 1731, 1428, 1395, 1220, 760; **HRMS** (ESI+) calcd for $C_{23}H_{28}NO_3$ $[M + H]^+$ 366.2064, found 366.2060.

*(Z)-Methyl 4-(Cyclohexylmethylene)-1-propyl-1,2,3,4-tetrahydroisoquinoline-1-carboxylate (**6d**).* Compound **6d** was obtained in 21% yield (0.033 g) as a brown oil from 0.103 g of amine **5a**, 0.073 g of allene **1d**, 0.058 g of benzoquinone, 0.006 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 4:1) = 0.45; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.60−7.55 (m, 1H), 7.43−7.39 (m, 1H), 7.22−7.17 (m, 2H), 5.87 (d, 1H, $J$ = 9.2 Hz), 3.76 (s, 2H), 3.72 (s, 3H), 3.00 (bs, 1H), 2.37−2.28 (m, 1H), 2.15−2.06 (m, 1H), 2.00−1.86 (m, 1H), 1.80−1.64 (m, 4H), 1.43−1.11 (m, 8H), 0.91 (t, 3H, $J$ = 7.3 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 174.8, 135.9, 134.6, 130.1, 129.5, 127.2, 126.9, 126.8, 123.7, 65.1, 52.6, 41.9, 41.5, 37.0, 33.4, 33.3, 26.1, 26.0, 26.0, 17.6, 14.4; **IR** (ATR, $cm^{-1}$) 3403, 2933, 2860, 1738, 1563, 1355, 1237; **HRMS** (ESI+) calcd for $C_{21}H_{30}NO_2$ $[M + H]^+$ 328.2271, found 328.2275.

*Methyl 3-Cyclohexyl-4-methylene-1-propyl-1,2,3,4-tetrahydroisoquinoline-1-carboxylate (**7d**).* Compound **7d** was obtained as a 7:3 mixture of diastereoisomers in 32% yield (0.051 g) as a brown oil from 0.103 g of amine **5a**, 0.073 g of allene **1d**, 0.058 g of benzoquinone, 0.006 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 4:1) = 0.64; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.51−7.43 (m, 1H), 7.30−7.20 (m, 3H), 5.44 (s, 0.7H), 5.40 (s, 0.3H), 4.97 (s, 1H), 3.76 (s, 2.1H), 3.62 (s, 0.9H), 3.60 (d, 0.3H, $J$ = 5.4 Hz), 3.28 (d, 0.7H, $J$ = 5.6 Hz), 2.17 (bs, 1H), 2.09−1.02 (m, 15H), 0.94 (t, 0.9H, $J$ = 7.3 Hz), 0.87 (t, 2.1H, $J$ = 7.4 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 175.8, 174.7, 143.7, 137.9, 136.3, 135.3, 127.8, 127.6, 127.5, 127.4, 126.4, 125.8, 125.5, 125.0, 109.2, 107.9, 65.2, 64.7, 60.4, 59.0, 52.6, 52.4, 42.2, 42.1, 41.1, 40.1, 31.1, 30.6, 28.5, 28.0, 26.8, 26.8, 26.7, 26.7, 26.6, 18.2, 17.2, 14.5, 14.4. **IR** (ATR, $cm^{-1}$) 3404, 2930, 2862, 1738, 1568, 1342, 1221; **HRMS** (ESI+) calcd for $C_{21}H_{30}NO_2$ $[M + H]^+$ 328.2271, found 328.2274.

*Methyl 4-(2-((tert-Butyldiphenylsilyl)oxy)ethylidene)-1-propyl-1,2,3,4-tetrahydroisoquinoline-1-carboxylate (**6e**).* Compound **6e** was obtained as a 90:10 $Z$:$E$ mixture of stereoisomers in 18% yield (0.045 g) as a brown oil from 0.105 g of amine **5a**, 0.179 g of allene **1e**, 0.059 g of benzoquinone, 0.006 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 4:1) = 0.35; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.72 (dd, 4H, $J$ = 7.8, 1.6 Hz), 7.59−7.53 (m, 1H), 7.45−7.37 (m, 7H), 7.25−7.21 (m, 2H), 6.18 (t, 0.95H, $J$ = 6.3 Hz), 5.71 (t, 0.05H, $J$ = 6.4 Hz), 4.51 (d, 0.1H, $J$ = 6.3 Hz), 4.42 (dd, 1.9H, $J$ = 6.2, 2.4 Hz), 3.71 (s, 2.85H), 3.69 (s, 0.15H), 3.53 (d, 2H, $J$ = 6.6 Hz), 2.08 (ddd, 1H, $J$ = 14.0, 11.6, 4.8 Hz), 1.89 (ddd, 1H, $J$ = 14.0, 11.8, 4.9 Hz), 1.37−1.29 (m, 2H), 1.07 (s, 9H), 0.90 (t, 3H, $J$ = 7.4 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 174.6, 136.6, 135.7, 135.7, 133.8, 133.8, 133.7, 132.3, 129.8, 129.8, 127.8, 127.8, 127.8, 127.8, 127.5, 127.3, 126.8, 124.2, 122.6, 77.2, 64.9, 60.9, 52.6, 41.9, 41.4, 27.0, 19.3, 17.7, 14.4; **IR** (ATR, $cm^{-1}$) 3402, 2956, 2929, 2855, 1728, 1427, 1219, 1110, 700; **HRMS** (ESI+) calcd for $C_{32}H_{40}NO_3Si$ $[M + H]^+$ 514.2772, found 514.2781.

*Methyl 3-(((tert-Butyldiphenylsilyl)oxy)methyl)-4-methylene-1-propyl-1,2,3,4-tetrahydroisoquinoline-1-carboxylate (**7e**).* Compound **7e** was obtained as a 4:1 mixture of diastereoisomers in 35% yield (0.087 g) as a brown oil from 0.105 g of amine **5a**, 0.179 g of allene **1e**, 0.059 g of benzoquinone, 0.006 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 4:1) = 0.54; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.77−7.66 (m, 4H), 7.59−7.54 (m, 1H), 7.47−7.21 (m, 9H), 5.55 (d, 0.8H, $J$ = 1.3 Hz), 5.48 (d, 0.2H, $J$ = 1.4 Hz), 5.08 (d, 0.8H, $J$ = 1.4 Hz), 4.78 (d, 0.2H, $J$ = 1.4 Hz), 4.14 (dd, 0.4H, $J$ = 5.5, 1.6 Hz), 4.01 (dd, 1.6H, $J$ = 4.5, 1.1 Hz), 3.75 (s, 2.4H), 3.70 (s, 0.6H), 3.68 (dd, 1H, $J$ = 5.1, 3.8 Hz), 2.11 (ddd, 1H, $J$ = 13.9, 11.6, 4.3 Hz), 1.85 (ddd, 1H, $J$ = 14.1, 11.9, 4.5 Hz), 1.59−1.47 (m, 1H), 1.41−1.32 (m, 1H), 1.02 (s, 9H), 0.91 (t, 3H, $J$ = 7.4 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 174.0, 142.2, 138.2, 135.8, 135.8, 135.8, 135.7, 134.9, 134.4, 133.6, 133.5, 129.8, 129.8, 127.9, 127.8, 127.8, 127.7, 127.6, 127.4, 127.3, 125.3, 125.2, 124.2, 108.2, 106.8, 77.2, 66.6, 66.4, 65.6, 64.9,


dx.doi.org/10.1021/jo501658s | J. Org. Chem. 2014, 79, 9578−9585

54.7, 54.3, 53.5, 52.6, 52.4, 43.6, 40.5, 26.9, 26.8, 26.7, 19.4, 19.4, 18.6, 17.1, 14.4, 14.4; **IR** (ATR, $cm^{-1}$) 3402, 2955, 2929, 2856, 1732, 1427, 1223, 1110, 700; **HRMS** (ESI+) calcd for $C_{32}H_{40}NO_3Si$ $[M + H]^+$ 514.2772, found 514.2778.

*(Z)-Methyl 4-(Cyanomethylene)-1-propyl-1,2,3,4-tetrahydroisoquinoline-1-carboxylate (**6f**).* Compound **6f** was obtained in 68% yield (0.088 g) as a yellow oil from 0.103 g of amine **5a**, 0.038 g of allene **1f**, 0.061 g of benzoquinone, 0.006 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 4:1) = 0.26; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.55 (m, 2H), 7.46−7.40 (m, 1H), 7.34−7.28 (m, 1H), 5.73 (t, 1H, $J$ = 1.2 Hz), 4.05 (d, 2H, $J$ = 1.3 Hz), 3.75 (s, 3H), 2.30 (bs, 1H), 2.09 (m, 1H), 1.95 (ddd, 1H, $J$ = 14.0, 9.7, 6.9 Hz), 1.38−1.23 (m, 2H), 0.91 (t, 3H, $J$ = 7.4 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 174.0, 154.9, 138.2, 131.2, 130.2, 127.8, 127.8, 124.4, 117.1, 89.8, 65.1, 52.9, 44.7, 41.9, 17.6, 14.3; **IR** (ATR, $cm^{-1}$) 3402, 2958, 2872, 2211, 1727, 1448, 1220, 730; **HRMS** (ESI+) calcd for $C_{16}H_{19}N_2O_2$ $[M + H]^+$ 271.1441, found 271.1446.

*(Z)-Ethyl 2-(1,1-Dimethyl-2,3-dihydroisoquinolin-4(1H)-ylidene)-acetate (**8b**).* Compound **8b** was obtained in 31% yield (0.053 g) as a brown oil from 0.094 g of amine **5b**, 0.094 g of allene **1a**, 0.084 g of benzoquinone, 0.008 g of $Pd(OAc)_2$, and 5.0 mL of AcOH. $R_f$ (hexane/AcOEt 3:2) = 0.20; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.55 (d, 1H, $J$ = 7.9 Hz), 7.33−7.12 (m, 3H), 6.22 (t, 1H, $J$ = 1.7 Hz), 4.33 (d, 2H, $J$ = 1.8 Hz), 4.14 (q, 2H, $J$ = 7.1 Hz), 1.39 (s, 6H), 1.25 (t, 3H, $J$ = 7.1 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 166.8, 152.2, 147.0, 131.4, 130.1, 126.7, 125.2, 125.0, 111.3, 60.1, 52.7, 42.6, 29.2, 14.5; **HRMS** (ESI+) calcd for $C_{15}H_{20}NO_2$ $[M + H]^+$ 246.1489, found 246.1492.

*(Z)-Ethyl 2-(1,1-Diethyl-2,3-dihydroisoquinolin-4(1H)-ylidene)-acetate (**8c**).* Compound **8c** was obtained in less than 18% yield (impure) as a brown oil from 0.092 g of amine **5c**, 0.080 g of allene **1a**, 0.068 g of benzoquinone, 0.006 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 7:3) = 0.21; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.65 (dd, 1H, $J$ = 7.9, 1.0 Hz), 7.34 (td, 1H, $J$ = 7.6, 1.3 Hz), 7.26−7.16 (m, 2H), 6.28 (t, 1H, $J$ = 1.9 Hz), 4.38 (d, 1H, $J$ = 1.9 Hz), 4.21 (q, 2H, $J$ = 7.1 Hz), 1.87 (dq, 2H, $J$ = 14.9, 7.5 Hz), 1.72 (dq, 2H, $J$ = 14.6, 7.4 Hz), 1.32 (t, 3H, $J$ = 7.1 Hz), 0.82 (t, 6H, $J$ = 7.4 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 166.8, 152.5, 144.7, 132.8, 129.7, 126.6, 125.8, 125.5, 111.2, 60.1, 57.8, 42.5, 30.9, 14.5, 8.3; **HRMS** (ESI+) calcd for $C_{17}H_{24}NO_2$ $[M + H]^+$ 274.1802, found 274.1799.

*(Z)-Methyl 4-(2-Ethoxy-2-oxoethylidene)-1-methyl-1,2,3,4-tetrahydroisoquinoline-1-carboxylate (**8d**).* Compound **8d** was obtained in 52% yield (0.074 g) as a colorless oil from 0.100 g of amine **5d**, 0.055 g of allene **1a**, 0.048 g of benzoquinone, 0.005 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 7:3) = 0.15; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.67 (d, 1H, $J$ = 7.8 Hz), 7.42−7.34 (m, 2H), 7.33−7.27 (m, 1H), 6.35 (t, 1H, $J$ = 1.7 Hz), 4.53 (dd, 1H, $J$ = 17.6, 1.6 Hz), 4.31 (dd, 1H, $J$ = 17.6, 2.0 Hz), 4.21 (q, 2H, $J$ = 7.1 Hz), 3.73 (s, 3H), 2.56 (bs, 1H), 1.71 (s, 3H), 1.32 (t, 3H, $J$ = 7.1 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 174.6, 166.6, 150.3, 139.9, 131.6, 130.1, 127.8, 126.6, 124.9, 111.9, 61.4, 60.2, 52.8, 43.0, 26.6, 14.4.

*Methyl 1-Benzyl-4-(2-ethoxy-2-oxoethylidene)-1,2,3,4-tetrahydroisoquinoline-1-carboxylate (**8h**).* Compound **8h** was obtained as a 87:13 *Z*:*E* mixture of stereoisomers in 58% yield (0.083 g) as a colorless solid from 0.100 g of amine **5h**, 0.055 g of allene **1a**, 0.048 g of benzoquinone, 0.005 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 4:1) = 0.30; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.78 (m, 1H), 7.69−7.65 (m, 1H), 7.47−7.41 (m, 1H), 7.34−7.29 (m, 1H), 7.27−7.22 (m, 3H), 7.17−7.13 (m, 2H), 6.34 (m, 0.15H), 6.31 (m, 0.85H), 4.55 (dd, 0.85H, $J$ = 16.7, 1.3 Hz), 4.45 (dd, 0.15H, $J$ = 20.6, 2.3 Hz), 4.24−4.15 (m, 3H), 3.69 (s, 2.55H), 3.65 (s, 0.45H), 3.64 (d, 1H, $J$ = 13.5 Hz), 3.17 (d, 1H, $J$ = 13.5 Hz), 2.29 (bs, 1H), 1.30 (t, 3H, $J$ = 7.1 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 173.7, 166.6, 150.3, 138.3, 135.7, 132.6, 130.5, 130.1, 128.4, 127.8, 127.8, 127.3, 125.0, 111.7, 64.9, 60.2, 52.6, 46.0, 42.3, 14.5; **IR** (ATR, $cm^{-1}$) 3402, 2979, 1703, 1619, 1370, 1158, 730; **HRMS** (ESI+) calcd for $C_{22}H_{24}NO_4$ $[M + H]^+$ 366.1700, found 366.1704.

*(Z)-Methyl 5-(2-Ethoxy-2-oxoethylidene)-2-phenyl-2,3,4,5-tetrahydro-1H-benzo[d]azepine-2-carboxylate (**3h**).* Compound **3h** was obtained in 14% yield (0.020 g) as a colorless solid from 0.100 g of amine **5h**, 0.055 g of allene **1a**, 0.048 g of benzoquinone, 0.005 g of $Pd(OAc)_2$, and 4.0 mL of AcOH. $R_f$ (hexane/AcOEt 4:1) = 0.37; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.51−7.46 (m, 2H), 7.40−7.17 (m, 6H), 6.82 (d, 1H, $J$ = 7.3 Hz), 5.94 (t, 1H, $J$ = 2.5 Hz), 4.30 (dd, 1H, $J$ = 20.5, 2.5 Hz), 4.23 (dd, 1H, $J$ = 20.5, 2.4 Hz), 4.17 (q, 2H, $J$ = 7.2 Hz), 3.69 (s, 3H), 3.69 (d, 1H, $J$ = 13.9 Hz), 3.11 (d, 1H, $J$ = 13.9 Hz), 1.29 (t, 3H, $J$ = 7.1 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 174.4, 166.3, 165.2, 141.1, 140.4, 135.1, 129.4, 129.1, 128.5, 127.8, 127.7, 127.7, 126.6, 116.8, 67.8, 60.1, 52.8, 46.0, 41.6, 14.5; **IR** (ATR, $cm^{-1}$) 3402, 2978, 1723, 1699, 1609, 1447, 1369, 1218, 1202, 730; **HRMS** (ESI+) calcd for $C_{22}H_{24}NO_4$ $[M + H]^+$ 366.1700, found 366.1705.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

$^1$H and $^{13}$C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors thank the Ministerio de Educación y Ciencia of Spain (CTQ2009-9692 and CTQ2009-11501) and CIBERobn for financial support. We thank the University of Barcelona for a fellowship to A.R.

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