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Design and Synthesis of 1-Benzazepine Derivatives by Strategic Utilization of Suzuki–Miyaura Cross-Coupling, Aza-Claisen Rearrangement and Ring-Closing Metathesis[‡]

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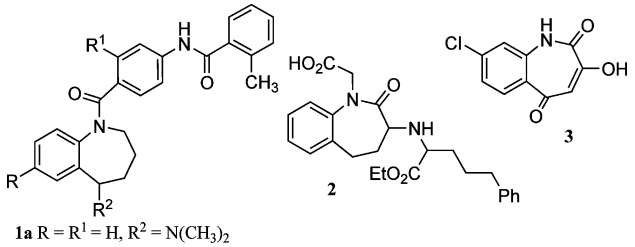
Keywords: Aza-Claisen rearrangement / 1-Benzazepine / Cross-coupling / Metathesis

A new and simple methodology has been realized for the synthesis of 7-substituted 2,3,4,5-tetrahydro-1-benzazepine derivatives with Suzuki–Miyaura cross-coupling, aza-Claisen rearrangement and ring-closing metathesis (RCM) the key steps. Here, *o*-allylacetanilide derivatives were obtained by Suzuki–Miyaura cross-coupling of the corresponding *o*-iodoacetanilides. The *o*-allylacetanilides, on *N*-allylation under phase-transfter catalysis conditions, provided diallyl derivatives as suitable precursors for RCM. These diallyl derivatives, on treatment with Grubbs' second-generation catalyst, gave the 1-benzazepine derivatives in moderate-to-good yields. These RCM products were found to be unstable and so they were hydrogenated to provide stable tetahydro-1-benzazepine derivatives **25**–**28**. 1*H*-1-Benzazepin-2-one derivatives **44** and **45** were synthesized following a similar sequence. In addition, the aza-Claisen rearrangement was utilized as a key step in the preparation of RCM precursor **17**.

Introduction

1-Benzazepine is an important fused heterocyclic moiety present as a key structural element in various biologically active molecules. For example, OPC-31260[1] (**1a**) and OPC-41061[2] (**1b**), potent orally effective non-peptide vasopressin V2-receptor antagonists, and Lotensin (Benzazepril) (**2**),[3] an ACE inhibitor used for the treatment of hypertension, have 1-benzazepine as a key structural element (Figure 1). Corbel et al. have reported various 1-benzazepine derivatives as ATP-dependent potassium channel antagonists.[4] 8-Chloro-3-hydroxy-1*H*-1-benzazepine-2,5-dione (**3**) acts as an antagonist at *N*-methyl-D-aspartate (NMDA) receptor glycine sites which could provide the means to treat neurodegenerative disorders associated with excitotoxicity.[5] Also, 1-benzazepine derivatives have found applications in cardiovascular diseases. Gottlieb and co-workers have carried out a dynamic and static conformational analysis of acylated tetrahydrobenzazepines by high-field NMR spectroscopy and molecular mechanics calculations.[6]



1a R = R^1 = H, R^2 = $N(CH_3)_2$
1b R = CH_3, R^1 = Cl, R^2 = OH

Figure 1. Biologically important compounds with 1-benzazepine as a key structural motif.

Numerous applications of 1-benzazepine derivatives in medicinal chemistry[7] have prompted organic chemists to develop new synthetic methodologies. Most of the methodologies developed for assembling 1-benzazepine derivatives involve the expansion of smaller rings, for example, by the reaction of indoles with dimethyl acetylenedicarboxylate[8] or ethyl cyanoacetate,[9] by the Beckman[10] or Schmidt[11] rearrangement of tetralones, by the treatment of 1,2-dihydroquinoline with dibromocarbene followed by dehydrobromination[12] or treatment with ethyl azidoformate[13] and by free-radical ring expansion of six-membered heterocycles to 1-benzazepines.[14] Recently, Pd-catalyzed reactions have also been employed in the synthesis of 1-benzazepine derivatives. In this regard, Quadir et al. reported the synthesis of 1-benzazepine derivatives by tandem Heck isomerisation and Buchwald–Hartwig aryl amination.[15a] The same group reported the synthesis of 1-benzazepine derivatives by the intramolecular Heck reaction[15b] and also prepared higher homologues of 1-benzazepine by RCM.[15c] Dykar and Markwitz achieved the synthesis of 1-benzazepine derivatives through Pd-catalyzed C–C and C–N bond-forming reactions.[16] As an alternative, Lete and co-workers reported the synthesis of 1-benzazepine derivatives, em-

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ploying Pd-catalyzed arylation and ring-closing metathesis (RCM) as the key steps.[17]

With the advent of well-defined ruthenium carbene complexes (**G-1**, **G-2** and **GH-3**, Figure 2),[18] metathesis has emerged as an important tool for carbon–carbon bond formation in organic synthesis. RCM[19] has received more attention in organic synthesis than other metathesis protocols. In addition, recent advances in metal-catalyzed coupling methods have allowed increasing usage of cross-coupling reactions in synthetic organic chemistry, for example, the Suzuki–Miyaura (SM)[20] cross-coupling reaction. Therefore a synergetic combination of these two powerful protocols for carbon–carbon bond formation has opened up various synthetic routes to complex targets.[21,22] Herein we would like to report a new route to 1-benzazepine derivatives involving the strategic use of SM cross-coupling, aza-Claisen rearrangement and RCM.

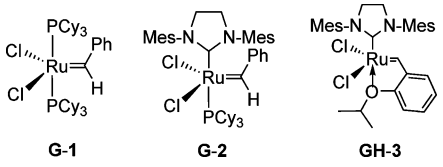


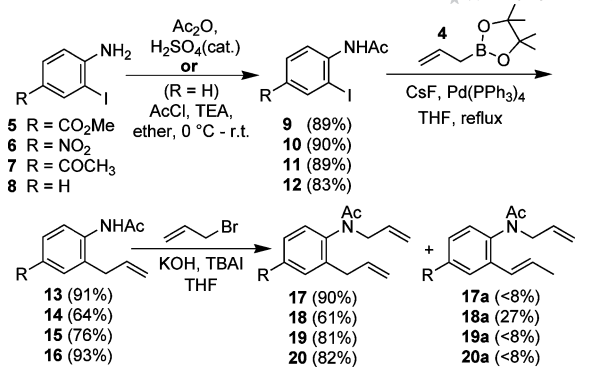
Figure 2. Ruthenium carbene metathesis catalysts.

Results and Discussion

Recently, we reported a new and simple methodology for the allylation of aromatic halides by the SM cross-coupling reaction between aromatic halides and allyl boronic acid pinacol cyclic ester **4**.[23] As a logical extension of this allylation strategy, we have also developed a new methodology for benzannulation that involves a combination of the SM cross-coupling reaction and RCM as the key steps. The required *o*-diallylarenes were obtained by SM cross-coupling of the corresponding *o*-diiodo derivatives.[22b] The *o*-diallyl derivatives were treated with Grubbs' catalyst **G-1** and in situ treatment of the RCM product with DDQ gave the benzannulated derivatives in good-to-excellent yields.

During the benzannulation strategy we prepared various 2-iodoaniline derivatives which prompted the development of the present strategy. Realization of this strategy requires protection of the free amine group to avoid complexation with ruthenium. Towards this goal, 4-methoxycarbonyl-2-iodoaniline (**5**) was treated with acetic anhydride in the presence of concd. sulfuric acid (catalytic, 1–2 drops)[24] to deliver the *N*-acetyl derivative **9** in 89% isolated yield (Scheme 1). When the *N*-acetyl derivative **9** was subjected to SM cross-coupling conditions for allylation using the allylboronate ester **4** as the coupling partner, the corresponding coupling product **13** was isolated in 91% yield.

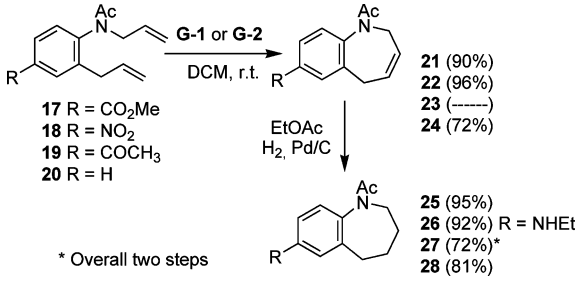
Our next goal was to carry out the *N*-allylation. To this end, the *o*-allylacetanilide derivative **13** was treated with allyl bromide under phase-transfer catalysis (PTC) conditions (KOH, TBAI, THF, room temp.)[25] to deliver the corresponding *N*-allyl derivative **17** in a very good yield (90%,



Scheme 1. Preparation of diallyl derivatives by the SM cross-coupling reaction as a key step.

Scheme 1). Here we would like to mention that in the reported procedure the authors carried out the reaction under sonication conditions. However, in our hands the reaction proceeded without sonication at room temperature. Moreover, under these reaction conditions, about 8–10% of the isomerized product **17a** was also observed.

Next the diallyl derivative **17** was treated with Grubbs' catalyst (**G-1**, 3 mol-%) in dry DCM. The reaction was complete within 1 h (TLC monitoring) and the 1-benzazepine derivative **21** was isolated in 90% yield (Scheme 2). Unfortunately the product **21** decomposed when kept at room temperature. We thought this may be due to the presence of a ruthenium impurity which might have been separated from the rest of the reaction mixture with compound **21** during purification by column chromatography. Therefore the reaction was repeated with Grubbs' second-generation catalyst (**G-2**, 3 mol-%). Although the product **21** was isolated in 90% yield, its decomposition could not be avoided. These observations indicated that the 1-benzazepine derivative **21** is unstable in the concentrated form at room temperature, but is stable in solution. To improve the stability of these compounds, hydrogenation of the RCM product **21** was attempted. Thus, the RCM product **21** was hydrogenated under Pd/C catalyst conditions in dry ethyl acetate to deliver the 1-acetyl-2,3,4,5-tetrahydro-1-benzazepine derivative **25** in 95% yield. The saturated product **25** was found to be stable.



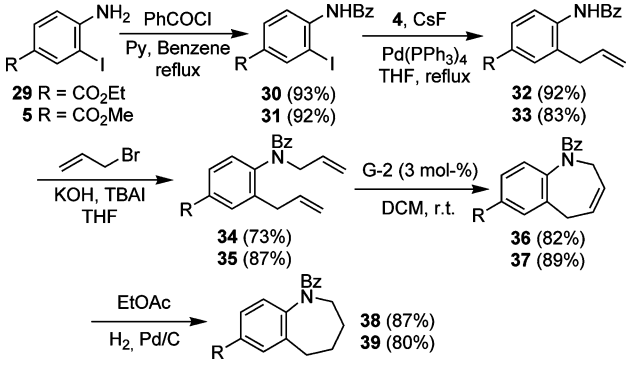
Scheme 2. Synthesis of 1-benzazepine derivatives by RCM and hydrogenation.

To generalize this methodology various other 7-substituted 1-acetyl-1-benzazepine derivatives were synthesized following the reaction sequences depicted in Scheme 1 and

Scheme 2. We are pleased to report that *N*-acetyl derivatives **10**–**12** were isolated in good-to-excellent yields. The allylated products **14**–**16** were also isolated in good yields (64–93%) under SM coupling conditions. Similarly, the diallyl products **18**–**20** were isolated in good-to-excellent (61–81%) yields under PTC conditions. It is worth mentioning that under PTC conditions for *N*-allylation of the nitro derivative **14**, the isomerized product **18a** was also isolated in 27% yield along with the desired product **18** in 61% yield.

The diallyl derivatives **18**–**20** were similarly treated with Grubbs' catalyst (**G-2**, 3 mol-%) in dry DCM to deliver the required RCM products **22**–**24** in moderate-to-good yields (72–96%). Unfortunately, the 1-benzazepine derivative **23** was found to be highly unstable and for this reason its isolation was found to be extremely difficult. Thus, the RCM product **23** was subjected in situ to hydrogenation conditions to deliver the saturated product **27** in good yield (72% yield after two steps). When the RCM product **22** was hydrogenated under Pd/C conditions using ethyl acetate as the solvent, the nitro group was also reduced in addition to the double bond. Moreover, the free amine group thus formed was protected as the *N*-ethyl derivative **26** which was confirmed by ^{1}H NMR as well as mass spectroscopic data. The RCM product **24** was found to be stable, possibly due to the absence of an electron-withdrawing group at the 7-position.

As the 1-benzazepine derivatives **21**–**23** with an *N*-acetyl protecting group are unstable, we thought of protecting the free amine group with different *N*-protecting groups to try to understand the factors affecting the stability of these compounds. Towards this goal, 2-iodoaniline derivative **29** was treated with benzoyl chloride in the presence of pyridine as base in dry benzene[26] to deliver the *N*-benzoyl derivative **30** in 93% isolated yield (Scheme 3). Allylation of the *N*-benzoyl derivative **30** under Suzuki cross-coupling conditions gave the product **32** in 92% yield. ^{1}H NMR analysis of the product **32** revealed that the product was contaminated with some side-product or impurity which was difficult to separate by silica gel column chromatography.

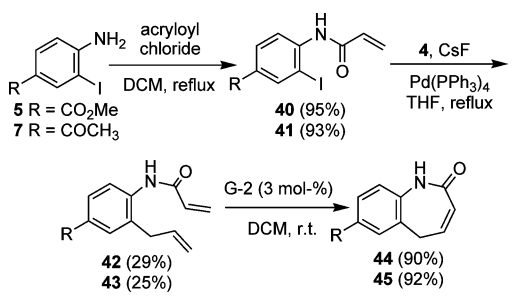


Scheme 3. Synthetic approach to 1-benzazepine derivatives with *N*-benzoyl protection.

When the allylated product **32** was subjected to *N*-allylation under PTC conditions, the diallyl derivative **34** was isolated in 73% yield. This reaction was difficult to monitor by TLC as the starting material and the product have the same R_f value. When the diallyl derivative **34** was subjected to RCM with the **G-2** catalyst, the reaction was complete after 1 h and the RCM product **36** was isolated in 82% yield. Similar reaction sequences were carried out with *o*-iodoaniline derivative **5** to provide the *N*-benzoyl derivative **31** in 92% yield, the allylated cross-coupling product **33** in 83% yield and the diallyl derivative **35** in 87% yield (Scheme 3). Furthermore, the RCM product **37** was isolated in 89% yield. The RCM products **36** and **37** were also found to be unstable and decomposed. A similar substrate having no electron-withdrawing group at the 7-position was prepared by Quadir et al. by RCM and they found this 1-benzazepine derivative to be very stable. Moreover, they provided an X-ray crystal structure of this compound.[15b] However, in our studies, compounds **36** and **37** have an electron-withdrawing group at the 7-position which may have a crucial effect on the stability of these products. Thus, unsaturated products were isolated (but not characterized) and immediate hydrogenation of these products furnished saturated derivatives **38** and **39** in 87% and 80% yields, respectively.

It appears that the instability of the RCM products may be due to the presence of two allylic CH_2 groups, one of which (C-5) is flanked by an aromatic ring and ethylene double bond, and also the two electron-withdrawing groups present at the 1- and 7-positions make the benzylic CH_2 group (C-5) amenable to aerial oxidation. Thus, we planned to protect the free amine with a protecting group containing an unsaturated moiety (e.g., an acryloyl group) which may also be a useful tether for the RCM sequence.

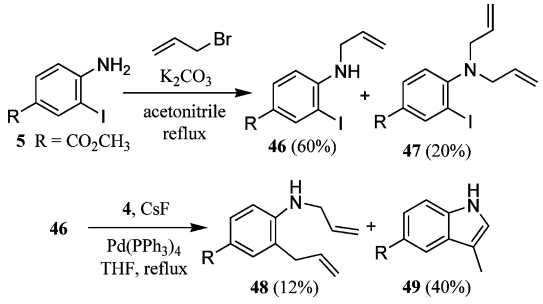
In this connection, the free amine of compound **5** was protected as the acryloyl by using a known literature procedure[27] to furnish the *N*-acryloyl derivative **40** in 95% yield (Scheme 4). However, when compound **40** was subjected to SM cross-coupling conditions to introduce the allyl group, the coupling product **42** was isolated in a low yield (29%). However, no other spot was observed in TLC other than the desired product. Treatment of the compound **42** with the **G-2** catalyst in dry DCM at room temperature delivered the 1-benzazepin-2-one derivative **44** in 90% yield as a white crystalline solid. Similar reaction sequences were applied to the 2-iodoaniline derivative **7** to deliver the *N*-acryloyl derivative **41** in 93% yield, the allylated cross-coupling product **43** in 25% yield and the RCM product **45** in



Scheme 4. Synthesis of 1-benzazepine-2-one derivatives without *N*-protection.

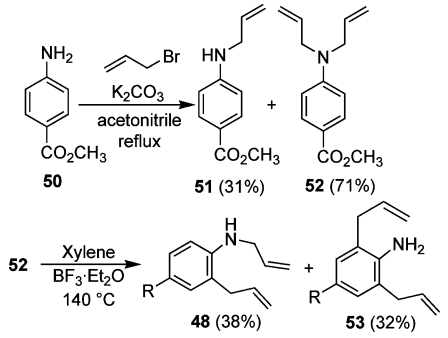
92% yield. Both the RCM products **44** and **45** are stable at room temperature.

As the *N*-protected derivatives **21**–**23** and **36**–**37** were found to be unstable, we thought of synthesizing the 1-benzazepine derivatives without a protecting group which in turn delivers 1-benzazepine derivatives with a free NH group. To this end, the *o*-iodoaniline derivative **5** was *N*-allylated using conventional allylation conditions (excess allyl bromide, K_2CO_3, acetonitrile, reflux) to give the monoallylated product **46** as well as the diallylated derivative **47** in 60 and 20% yields, respectively (based on 25% starting material recovered). When the monoallyl derivative **46** was subjected to SM cross-coupling conditions for the allylation, the desired coupling product **48** was isolated in 12% yield along with the 3-methylindole derivative **49** in 40% yield. The formation of the indole derivative **49** from *N*-alkenyl-2-haloanilines **46** under Pd-catalyzed conditions is very well documented in the literature (Scheme 5).[28]



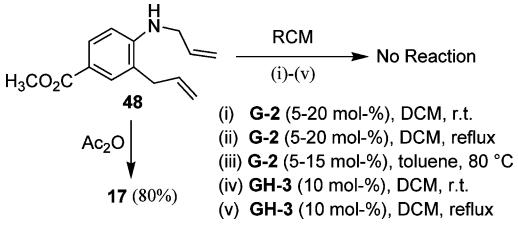
Scheme 5. Synthesis of 7-substituted 1*H*-1-benzazepine derivatives by SM cross-coupling.

As an alternate route for the synthesis of 1*H*-1-benzazepine derivatives, we thought the diallyl derivative **48** could be obtained by aromatic aza-Claisen rearrangement.[29] Towards this end, methyl 4-aminobenzoate (**50**) was treated with an excess of allyl bromide (2.5 equiv.) and K_2CO_3 as base in refluxing acetonitrile for 12 h to deliver the monoallyl derivative **51** as well as the diallyl derivative **52** in 31% and 52.4% yields, respectively (based on 10% starting material recovered, Scheme 6). When the diallylated derivative was heated in xylene in the presence of BF_3–Et_2O (1 equiv.) at 140 °C (oil bath) for 1.5 h,[29c] the desired aza-Claisen rearranged product **48** was obtained in 38% yield along with the doubly rearranged product **53** in 32% yield (based on 10% starting material recovered, Scheme 6). If the reaction was allowed to continue further until complete consumption of the starting material, the desired product **48** was converted into the undesired product **53** (TLC monitoring). Also, when undistilled xylene was used for the aza-Claisen rearrangement, TLC revealed the formation of a very complex reaction mixture. Thus, the use of freshly distilled xylene (over CaH_2) is crucial for effecting a smooth Claisen rearrangement. Also, the quantity of $BF_3{\cdot}Et_2O$ used plays an important role in this reaction. When 2 equiv. of $BF_3{\cdot}Et_2O$ was used, TLC revealed the formation of undesired compound **53** as the major product. We also observed a pronounced effect of temperature on the outcome of the Claisen rearrangement. When the reaction was carried out at a higher temperature (155–160 °C), undesired product **53** was exclusively observed (TLC monitoring).



Scheme 6. Synthesis of diallyl derivative **48** by the aza-Claisen rearrangement.

Next, the compound **48** was treated with the **G-2** catalyst under different reaction conditions (e.g., DCM, room temp.; DCM, reflux; toluene, 80 °C) and no RCM product was observed (Scheme 7). With the Grubbs–Hoveyda catalyst (**GH-3**), no reaction was observed when reaction was carried out in DCM at room temperature or at reflux. In view of these observations we concluded that the presence of the free NH group retarded the RCM due to complexation of the free lone-pair electrons on nitrogen with the Ru atom. Thus, the protection of the free NH group was considered. In this respect, when the diallyl derivative **48** was treated with LDA followed by MeI at –78 °C, no reaction was observed and the starting material was recovered. Also, we tried solvent-free and formalin-free Clarke's methylation conditions developed by Kosma and co-workers using paraformaldehyde and oxalic acid dihydrate at 100–110 °C.[30] However, TLC monitoring showed that the starting material undergoes further aza-Claisen rearrangement and is converted into compound **53**. When the diallyl derivative **48** was treated with acetic anhydride (no solvent) at room temperature for 12 h, the corresponding *N*-acetyl derivative **17** was isolated in 80% yield.



Scheme 7. Attempted RCM conditions and *N*-acetyl protection of the diallyl derivative **48**.

Conclusions

We have demonstrated a simple and useful strategy for the synthesis of 1-protected 2,3,4,5-tetrahydro-1-benzazepine derivatives that involves the SM cross-coupling reaction and RCM as key steps. 1*H*-1-Benzazepin-2-one derivatives

44 and **45** were also synthesized following a similar reaction sequence. The unsaturated derivatives **42** and **43** were obtained in lower yields under SM cross-coupling conditions. We also synthesized the RCM precursor **17** by aza-Claisen rearrangement followed by acetylation. In essence, a strategic combination of the SM cross-coupling reaction, aza-Claisen rearrangement and RCM has successfully been employed for the synthesis of 1-benzazepine derivatives. As 1-benzazepine derivatives are of medicinal importance, the compounds prepared here, along with the strategy reported, may find useful applications in drug discovery programs.

Experimental Section

General Remarks: Analytical TLC was performed on glass plates (10 × 5 cm) coated with silica gel G or GF 254 (containing 13% $CaSO_4$ as a binder). Visualization of the spots was achieved either by exposure to I_2 vapour or UV light. Column chromatography was performed on silica gel (100–200 mesh) usually with EtOAc and petroleum ether (b.p. 60–80 °C) mixtures as eluent. Melting points are uncorrected. ^1H and ^{13}C NMR spectroscopic data were recorded with a Varian VXR 300 or Varian VXR 400 spectrometer using TMS as the internal standard and $CDCl_3$ as solvent. The coupling constants (*J*) are given in Hertz (Hz). High-resolution mass spectroscopic data were recorded with a Q-ToF Micromass spectrometer. For all the reactions, anhydrous $MgSO_4$ or Na_2SO_4 was used as the drying agent after work-up.

All the commercial grade reagents were used without further purification. Grubbs' catalysts **G-1**, **G-2** and **GH-3** and allylboronate **4** were purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI, U.S.A.). 2-Iodoaniline derivatives **5**–**8**,[22b] *N*-acetyl derivatives **9**[24] and **12**,[31] *N*-benzoyl derivative **31**[26] and *N*-acryloyl derivative **40**[27] were prepared according to the reported procedures.

General Procedure for the *N*-Acetyl Protection of *o*-Iodoaniline Derivatives:[24] One drop of concd. H_2SO_4 was added to a stirred solution of the aniline derivative in acetic anhydride. The resulting mixture was stirred at room temp. for 5 min and then quenched with water and extracted with DCM (3 × 50 mL). The combined organic layers were washed with water, brine and dried with anhydrous sodium sulfate. The solvent was removed and the crude product was crystallized from ethanol to give the *N*-acetyl derivative as a crystalline solid.

General Procedure for Allylation by the Suzuki–Miyaura Cross-Coupling Reaction: In a three-necked round-bottomed flask equipped with a reflux condenser and nitrogen inlet/outlet, the iodo-derivative (1 equiv.), CsF (2 equiv.), $[Pd(PPh_3)_4]$ (6 mol-%) and dry THF (5 mL) were added. The resulting suspension was stirred at room temp. for 30 min. A solution of allylboronate **4** (2 equiv.) in THF (5 mL) was added to this suspension and the resulting mixture was heated at reflux. At the conclusion of the reaction (TLC monitoring), the reaction mixture was quenched with water and the usual work-up with DCM gave the crude product. The product was purified by silica gel column chromatography. Elution of the column with an appropriate petroleum ether/ethyl acetate mixture gave the desired product as a crystalline solid.

General Procedure for the *N*-Alkylation:[25] A solution of the starting material (1 equiv.) and allyl bromide (1.2 equiv.) in dry THF was added to a suspension of KOH (1.2 equiv.) and TBAI (2 equiv.) in dry THF (5 mL) over 2–3 min. The reaction mixture was stirred at room temp. At the conclusion of the reaction (TLC monitoring), the reaction mixture was quenched with water and the usual work-up with DCM gave the crude product which was purified by silica gel column chromatography. Elution of the column with petroleum ether/ethyl acetate gave the desired product.

General Procedure for Ring-Closing Metathesis: Grubbs' catalyst (3 mol-%) was added to a stirred solution of the diolefinic compound in dry DCM. The reaction mixture was stirred at room temp. At the conclusion of the reaction (TLC monitoring, 45–60 min), the solvent was removed and the crude product was purified by column chromatography. Elution of the column with petroleum ether/ethyl acetate gave the desired product.

General Procedure for Hydrogenation: Pd/C (10%, 20–40 mol-%) was added to a stirred solution of the RCM product in ethyl acetate (5 mL) and the resulting mixture was kept under hydrogen pressure (balloon pressure) for 24 h. The reaction mixture was filtered through a Celite pad which was washed with chloroform. The solvent was removed under reduced pressure to give the hydrogenated product.

General Procedure for *N*-Benzoyl Protection: Pyridine (1.5 equiv.) and benzoyl chloride (2 equiv.) were added to a stirred solution of *o*-iodoaniline (1 equiv.) in benzene and the resulting mixture was heated at reflux. At the conclusion of the reaction (TLC monitoring, nearly 5–6 h), the reaction mixture was quenched with water and extracted with chloroform (3 × 30 mL). The combined organic layers were washed with dilute HCL (20 mL) and brine. Then the solvent was evaporated and the residue was crystallized from ethanol to give the desired *N*-benzoyl derivative as a white crystalline solid.

General Procedure for *N*-Acryloyl Protection:[27] Acryloyl chloride was added to a stirred solution of the amine in dry DCM and the resulting mixture was heated at reflux for 14 h. The reaction mixture was quenched with water and extracted with DCM (3 × 20 mL). The combined organic layers were washed with water and brine and dried with anhydrous Na_2SO_4. The solvent was removed and the crude product was crystallized from ethanol to provide the desired product as a white crystalline solid.

Preparation of 2-Iodo-4-nitroacetanilide (10): 2-Iodoaniline derivative **6** (1.2 g, 4.5 mmol), acetic anhydride (8 mL) and concd. H_2SO_4 (1–2 drops) were treated as described in the general procedure and crystallization from ethanol gave the desired product **10** (1.25 g, 90%) as a pale yellow solid, m.p. 137–140 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 8.23 (dd, *J* = 2.4, 9.2 Hz, 1 H), 8.54 (d, *J* = 9.2 Hz, 1 H), 8.63 (d, *J* = 2.4 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 25.1, 87.4, 119.8, 124.9, 134.2, 143.4, 143.8, 168.6 ppm. HRMS (Q-ToF): calcd. for $C_8H_8N_2O_3I$ $[M + H]^+$ 306.9580; found 306.9581.

Preparation of 4-Acetyl-2-iodoacetanilide (11): 2-Iodoaniline derivative **7** (1.3 g, 4.98 mmol), acetic anhydride (5 mL) and concd. H_2SO_4 (1 drop) were treated as described in the general procedure to give the desired product **11** (1.34 g, 89%) as a pale yellow solid, m.p. 155–158 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 2.57 (s, 3 H), 7.67 (br. s, 1 H), 7.91 (dd, *J* = 1.6, 8.4 Hz, 1 H), 8.38 (d, *J* = 1.6 Hz, 1 H), 8.41 (d, *J* = 8.4 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 25.1, 26.5, 89.1, 120.2, 129.9, 134.1, 139.1, 142.2, 168.5, 195.6 ppm. HRMS (Q-ToF): calcd. for $C_{10}H_{11}NO_2I$ $[M + H]^+$ 303.9835; found 303.9845.

Preparation of 4-Methoxycarbonyl-2-(2-propenyl)acetanilide (13): *N*-Acetyl derivative **9** (100 mg, 0.31 mmol), CsF (95 mg, 0.62 mmol), $[Pd(PPh_3)_4]$ (22 mg, 6 mol-%) and allylboronate **4** (106 mg, 0.63 mmol) in THF (15 mL) were treated as described in the general procedure for allylation. At the conclusion of the reac-

tion (TLC monitoring, 12 h), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 30% ethyl acetate/petroleum ether gave the desired product **13** (66.0 mg, 90%) as a white solid, m.p. 123–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.17 (s, 3 H), 3.44 (d, J = 6.0 Hz, 2 H), 3.90 (s, 3 H), 5.14 (d, J = 17.2 Hz, 1 H), 5.24 (d, J = 10 Hz, 1 H), 5.93–6.02 (m, 1 H), 7.50 (br. s, 1 H), 7.87 (s, 1 H), 7.93 (dd, J = 2.0, 8.4 Hz, 1 H), 8.13 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 24.3, 36.7, 52.1, 117.3, 122.3, 126.1, 128.8, 129.1, 131.6, 135.6, 140.6, 166.7, 168.7 ppm. HRMS (Q-ToF): calcd. for $C_{13}H_{14}NO_3$ $[M + H]^+$ 256.0950; found 256.0954.

Preparation of 4-Nitro-2-(2-propenyl)acetanilide (14): *N*-Acetyl derivative **10** (200 mg, 0.65 mmol), CsF (200 mg, 1.3 mmol), $[Pd(PPh_3)_4]$ (45.3 mg, 6 mol-%) and allylboronate **4** (220 mg, 1.3 mmol) in THF (15 mL) were treated as described in the general procedure for allylation. At the conclusion of the reaction (TLC monitoring, 24 h), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 20% ethyl acetate/petroleum ether gave the desired product **14** (87.0 mg, 64%) as a white solid, m.p. 133–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 3.50 (dd, J = 6.0, 1.6 Hz, 2 H), 5.21 (dq, J = 17.2, 2.0, 1.6 1.2 Hz, 1 H), 5.33 (dq, J = 10.0, 1.6, 1.2, 1.2 Hz, 1 H), 5.95–6.04 (m, 1 H), 7.54 (br. s, 1 H), 8.09 (d, J = 2.4 Hz, 1 H), 8.15 (dd, J = 2.4, 8.8 Hz, 1 H), 8.34 (d, J = 8.8 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 24.8, 36.2, 118.4, 121.7, 123.5, 125.7, 128.7, 134.6, 142.4, 142.4, 143.7, 168.5 ppm. HRMS (Q-ToF): calcd. for $C_{11}H_{13}N_2O_3$ $[M + H]^+$ 221.0926; found 221.0931.

Preparation of 4-Acetyl-2-(2-propenyl)acetanilide (15): *N*-Acetyl derivative **11** (250 mg, 0.83 mmol), CsF (250 mg, 1.6 mmol), $[Pd(PPh_3)_4]$ (57.0 mg, 6 mol-%) and allylboronate **4** (277 mg, 1.6 mmol) in THF (15 mL) were treated as described in the general procedure for allylation. At the conclusion of the reaction (TLC monitoring, 16 h), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 25% ethyl acetate/petroleum ether gave the desired product **15** (135 mg, 76%) as a white solid, m.p. 126–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 3 H), 2.58 (s, 3 H), 3.45 (d, J = 6.0 Hz, 2 H), 5.12–5.26 (m, 2 H), 5.93–6.03 (m, 1 H), 7.59 (br. s, 1 H), 7.80 (s, 1 H), 7.84 (d, J = 8.4 Hz, 1 H), 8.15 (d, J = 7.2 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 24.4, 26.5, 36.6, 117.3, 122.4, 128.1, 129.2, 130.2, 133.2, 135.4, 140.7, 168.8, 197.4 ppm. HRMS (Q-ToF): calcd. for $C_{13}H_{16}NO_2$ $[M + H]^+$ 218.1181; found 218.1186.

Preparation of 2-(2-Propenyl)acetanilide (16): *N*-Acetyl derivative **12** (300 mg, 1.14 mmol), CsF (314 mg, 2.28 mmol), $[Pd(PPh_3)_4]$ (78.0 mg, 6 mol-%) and allylboronate **4** (386 mg, 2.28 mmol) in THF (15 mL) were treated as described in the general procedure for allylation. At the conclusion of the reaction (TLC monitoring, 22 h), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 15% ethyl acetate/petroleum ether gave the desired product **16** (187.0 mg, 93%) as a white crystalline solid, m.p. 91–94 °C (ref.[32] 87–89 °C).

Preparation of Diallyl Derivative 17: Allyl derivative **13** (50.0 mg, 0.214 mmol), KOH (13.2 mg, 0.23 mmol), TBAI (158 mg, 0.42 mmol) and allyl bromide (29.0 mg, 0.23 mmol) were treated as described in the general procedure for the *N*-alkylation. At the conclusion of the reaction (TLC monitoring, 3 h), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 20% ethyl acetate/petroleum ether gave the desired product **17** (53.0 mg, 90%) as a white solid, m.p. 52–53 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.76 (s, 3 H), 3.35 (d, J = 5.6 Hz, 2 H), 3.69–3.75 (m, 1 H, *N*-CH*H*-*cis*), 3.94 (s, 3 H), 4.68–4.74 (m, 1 H, *N*-C*H*H-*trans*), 5.03 (dq, J = 17.2, 1.6 1.2 Hz, 1 H), 5.10–5.10 (m 3 H), 5.82–5.93 (m, 2 H), 7.15 (d, J = 8.0 Hz, 1 H), 7.92 (dd, J = 8.0, 2.0 Hz, 1 H), 8.03 (d, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 22.6, 35.1, 51.7, 52.5, 117.8, 119.0, 128.8, 129.9, 130.4, 132.2, 132.5, 135.2, 138.2, 145.0, 166.4, 170.1 ppm. HRMS (Q-ToF): calcd. for $C_{16}H_{19}NO_3Na$ $[M + Na]^+$ 296.1263; found 296.1270.

Preparation of Diallyl Derivative 18: Allyl derivative **14** (100.0 mg, 0.46 mmol), KOH (28.0 mg, 0.5 mmol), TBAI (336 mg, 0.92 mmol) and allyl bromide (61.0 mg, 0.5 mmol) were treated as described in the general procedure for the *N*-alkylation. At the conclusion of the reaction (TLC monitoring, 4.5 h), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 3.5% ethyl acetate/petroleum ether gave the desired product **18** (72.0 mg, 61%) as a light-yellow low-melting solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.79 (s, 3 H), 3.41 (d, J = 6.0 Hz, 2 H), 3.75 (dd, J = 14.4, 7.6 Hz, 1 H), 4.73 (dd, J = 14.4, 6.0 Hz, 1 H), 5.27–5.02 (m, 4 H), 5.95–5.82 (m, 2 H), 7.28 (d, J = 8.8 Hz, 1 H), 8.13 (dd, J = 8.8, 2.4 Hz, 1 H), 8.24 (d, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 22.7, 35.2, 51.8, 118.9, 119.6, 122.8, 126.0, 130.9, 32.2, 134.2, 140.2, 146.7, 147.7, 169.6 ppm. HRMS (Q-ToF): calcd. for $C_{14}H_{16}N_2O_3$ $[M + H]^+$ 261.1231; found 261.1240.

Further elution of the column with 5% ethyl acetate/petroleum ether gave isomerized product **18a** (32 mg, 27%) as a yellow solid, m.p. 109–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.78 (s, 3 H), 1.97 (dd, J = 1.6, 6.4 Hz, 3 H), 4.67–4.72 (m, 1 H), 5.04 (dd, J = 1.2 16.8 Hz, 1 H), 5.12 (dd, J = 0.8, 10.0 Hz, 1 H), 5.80–5.90 (m, 2 H), 6.39 (dd, J = 1.6, 15.6 Hz, 1 H), 6.46–6.55 (m, 1 H), 7.24 (d, J = 8.4 Hz, 1 H), 8.08 (dd, J = 2.8, 8.4 Hz, 1 H), 8.24 (d, J = 2.8 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 19.1, 22.8, 51.6, 119.5, 121.8, 122.4, 124.2, 130.8, 132.2, 133.2, 137.8, 144.6, 147.8, 169.8 ppm. HRMS (Q-ToF): calcd. for $C_{14}H_{16}N_2O_3$ $[M + H]^+$ 261.1231; found 261.1235.

Preparation of Diallyl Derivative 19: Allyl derivative **15** (50.0 mg, 0.23 mmol), KOH (16.0 mg, 0.25 mmol), TBAI (170 mg, 0.46mmol) and allyl bromide (31.0 mg, 0.25 mmol) were treated as described in the general procedure for the *N*-alkylation. At the conclusion of the reaction (TLC monitoring, 4 h), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 15% ethyl acetate/petroleum ether gave the desired product **19** (48 mg, 81%) as a colourless thick liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.77 (s, 3 H), 2.62 (s, 3 H), 3.37 (d, J = 6.4 Hz, 2 H), 3.72 (dd, J = 14.4, 7.6 Hz, 1 H, *N*-CH_2-*cis*), 4.72 (dd, J = 14.4, 6.0 Hz, 1 H, *N*-CH_2-*trans*), 5.01–5.19 (m, 4 H), 5.83–5.95 (m, 2 H), 7.18 (d, J = 8.0 Hz, 1 H), 7.84 (dd, J = 8.0, 2.0 Hz, 1 H), 7.94 (d, J = 1.6 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 22.7, 26.8, 35.2, 51.8, 117.9, 119.1, 127.7, 130.2, 131.0, 132.6, 135.2, 137.2, 138.5, 145.3, 170.1, 197.5 ppm. HRMS (Q-ToF): calcd. for $C_{16}H_{20}NO_2$ $[M + H]^+$ 258.1494; found 258.1496.

Preparation of Diallyl Derivative 20: Allyl derivative **16** (56.0 mg, 0.33 mmol), KOH (22.3 mg, 0.39 mmol), TBAI (245 mg, 0.66mmol) and allyl bromide (48.0 mg, 0.39 mmol) were treated as described in the general procedure for the *N*-alkylation. At the con-

clusion of the reaction (TLC monitoring, 4 h), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 15% ethyl acetate/petroleum ether gave the desired product **20** (56 mg, 82%) as a colourless thick oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.76 (s, 3 H), 3.32 (d, J = 5. 6 Hz, 2 H), 3.71 (dd, J = 14.6, 7.6 Hz, 1 H, *N*-CH*H-cis*), 4.70 (dd, J = 14.6, 6.0 Hz, 1 H, *N*-C*H*H-*trans*), 5.02–5.13 (m 4 H), 5.84–5.94 (m, 2 H), 7.15 (d, J = 7.6 Hz, 1 H), 7.11–7.35 (m, 3 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 22.6, 35.2, 51.8, 117.1, 118.5, 127.6, 127.8, 128.5, 128.6, 129.4, 130.9, 132.9, 135.9, 137.6, 141.1, 170.7 ppm. HRMS (Q-ToF): calcd. for $C_{14}H_{18}NO$ $[M + H]^+$ 216.1388; found 216.1388.

Preparation of 1-Acetyl-7-methoxycarbonyl-2,5-dihydro-1-benzazepine (21): Diallyl derivative **17** (45 mg, 0.17 mmol) in dry DCM (5 mL) was treated with Grubbs' catalyst **G-2** (4.2 mg, 3 mol-%) as in the general procedure for RCM. At the conclusion of the reaction (TLC monitoring, 35 min), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 22% ethyl acetate/petroleum ether gave the desired product **21** (39.0 mg, 90%) as a white solid, m.p. 108–112 °C. (*Note*: *product decomposes when kept in concentrated form.*) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (s, 3 H), 3.13–3.07 (m, 1 H), 3.43–3.38 (m, 1 H), 3.81–3.77 (m, 1 H), 3.94 (s, 3 H), 5.41–5.36 (m, 1 H), 5.53–5.49 (m, 1 H), 5.80–5.74 (m, 1 H), 7.28 (d, J = 8.0 Hz, 1 H), 7.93 (d, J = 2.0 Hz, 1 H), 7.98 (dd, J = 2.4, 8.0 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 22.3, 31.9, 44.9, 52.5, 124.9, 127.0, 128.1, 129.5, 1130.2, 140.2, 146.5, 166.4, 169.6 ppm. HRMS (Q-ToF): calcd. for $C_{14}H_{16}NO_3$ $[M + H]^+$ 246.1130; found 246.1129.

Preparation of 1-Acetyl-7-nitro-2,5-dihydro-1-benzazepine (22): Diallyl derivative **18** (33.0 mg, 0.13 mmol) in dry DCM (5 mL) was treated with Grubbs' catalyst **G-2** (3.2 mg, 3 mol-%) as in the general procedure for RCM. At the conclusion of the reaction (TLC monitoring, 25 min), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 25% ethyl acetate/petroleum ether gave the desired product **22** (28.2 mg, 96%) as a liquid. (*Note*: *product decomposes when kept in concentrated form.*) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.88 (s, 3 H), 3.17 (m, 1 H), 3.38–3.43 (m, 1 H), 3.82–3.86 (m, 1 H), 5.40–5.45 (m, 1 H), 5.52–5.56 (m, 1 H), 5.75–5.81 (m, 1 H), 7.39 (d, J = 8.8 Hz, 1 H), 8.14 (d, J = 2.4 Hz, 1 H), 8.19 (dd, J = 2.4, 8.8 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 22.4, 31.9, 44.8, 123.3, 123.4, 124.4, 127.2, 129.1, 141.8, 1447.4, 148.1, 169.2 ppm. HRMS (Q-ToF): calcd. for $C_{12}H_{13}N_2O_3$ $[M + H]^+$ 233.0926; found 233.0931.

Preparation of 1-Acetyl-2,5-dihydro-1-benzazepine (24): Diallyl derivative **20** (29.0 mg, 0.13 mmol) in dry DCM (5 mL) was treated with Grubbs' catalyst **G-2** (2.3 mg, 3 mol-%) as described in the general procedure for RCM. At the conclusion of the reaction (TLC monitoring, 45 min), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 15% ethyl acetate/petroleum ether gave the desired product **24** (18 mg, 72%) as a while solid, m.p. 102–104 °C. (*Note*: *product decomposes when kept in concentrated form.*) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (s, 3 H), 2.97–3.03 (m, 1 H), 3.42 (d, J = 17.6 Hz, 1 H), 3.74–3.79 (m, 1 H), 5.32–5.39 (m, 1 H), 5.47–5.52 (m, 1 H), 5.72–5.79 (m, 1 H), 7.18–7.32 (m, 4 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 22.3, 32.0, 45.1, 124.5, 127.0, 127.8, 128.1, 128.5, 129.2, 139.9, 142.5, 170.2 ppm. HRMS (Q-ToF): calcd. for $C_{12}H_{14}NO$ $[M + H]^+$ 188.107; found 188.1076.

Preparation of 1-Acetyl-7-methoxycarbonyl-2,3,4,5-tetrahydro-1-benzazepine (25): The RCM product **21** (21.0 mg, 0.09 mmol) and Pd/C (10%) (34.5 mg, 20 mol-%) in ethyl acetate (5 mL) were treated as described in the general procedure for hydrogenation to give the desired product **25** (20.1 mg, 95%) as a thick colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24–1.30 (m, 2 H), 1.87 (s, 3 H), 2.04–1.71 (m, 2 H), 2.62–2.56 (m, 1 H), 2.81 (t, J = 4.8, 5.6 Hz, 2 H), 3.93 (s, 3 H), 4.73–4.70 (m, 1 H), 7.21 (d, J = 8.4 Hz, 1 H), 7.91, (dd, J = 2.0, 8.4 Hz, 1 H), 7.95 (d, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 22.8, 26.3, 28.9, 34.6, 47.1, 52.4, 127.9, 128.9, 129.7, 131.7, 140.9, 147.9, 166.6, 169.2 ppm. HRMS (Q-ToF): calcd. for $C_{14}H_{18}NO_3$ $[M + H]^+$ 248.1287; found 248.1287.

Preparation of 1-Acetyl-7-(ethylamino)-2,3,4,5-tetrahydro-1-benzazepine (26): The RCM product **22** (10.0 mg, 0.04 mmol) and Pd/C (10%,10.0 mg, 20 mol-%) in ethyl acetate (5 mL) were treated as described in the general procedure for hydrogenation to give the product **26** (9.3 mg, 92%) as a thick colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15–1.42 (m, 4 H), 1.77–1.98 (m, 6 H), 2.69 (t, J = 8.4 Hz, 1 H), 3.15 (q, J = 7.2 Hz, 2 H), 4.65 (d, J = 13.2 Hz, 1 H), 6.40–6.44 (m, 2 H), 6.90 (d, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 15.3, 22.7, 27.0, 29.2, 34.9, 38.7, 47.6, 110.5, 113.6, 128.4, 133.7, 141.5, 148.0, 170.6 ppm. HRMS (Q-ToF): calcd. for $C_{14}H_{21}N_2O$ $[M + H]^+$ 233.1654; found 233.1664.

Preparation of 1,7-Diacetyl-2,3,4,5-tetrahydro-1-benzazepine (27): Diallyl derivative **23** (12 mg, 0.05 mmol) in dry DCM (2 mL) was treated with Grubbs' catalyst **G-2** (2.0 mg, 3 mol-%) as in the general procedure for RCM. At the conclusion of the reaction (TLC monitoring), Pd/C (10%, 20 mg, 40 mol-%) and dry ethyl acetate (5 mL) were added to the same reaction vessel. The reaction mixture was then kept under a hydrogen pressure of 1 atm. (balloon pressure) for 24 h. After that, the reaction mixture was filtered through a Celite pad which was successively washed with chloroform (3 × 10 mL). The solvent was removed in vacuo to provide the desired product **27** (7.3 mg, overall 72% yield for two steps) as a thick liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38–1.40 (m, 1 H), 1.78–2.05 (m, 6 H), 2.56–2.62 (m, 4 H), 2.82 (t, J = 5.2 Hz, 2 H), 4.73 (d, J = 12.8 Hz, 1 H), 7.23 (d, J = 8.0 Hz, 1 H), 7.83 (dd, J = 1.6, 8.0 Hz, 1 H), 7.86 (d, J = 1.6 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 22.9, 26.4, 26.8, 29.0, 34.7, 47.2, 127.7, 128.1, 130.4, 136.7, 141.1, 148.1, 169.2, 197.5 ppm. HRMS (Q-ToF): calcd. for $C_{14}H_{18}NO_2$ $[M + H]^+$ 232.1338; found 232.1328.

Preparation of 1-Acetyl-2,3,4,5-tetrahydro-1*H*-benzazepine (28): The RCM product **24** (13.3 mg, 0.09 mmol) and Pd/C (10%, 30.0 mg, 20 mol-%) in ethyl acetate (5 mL) were treated as described in the general procedure for hydrogenation to give the desired product **28** (10.8 mg, 81%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$):[6] δ = 1.34–1.43 (m, 1 H), 1.76–2.00 (m, 4 H), 2.57–2.81 (m, 2 H), 7.13 (d, J = 3.2 Hz, 1 H), 7.22–7.27 (m, 2 H) ppm.

Preparation of Ethyl 4-Benzoylamino-3-iodobenzoate (30): *o*-Iodoaniline derivative **29** (600 mg, 2.06 mmol), pyridine (4 mL) and benzoyl chloride (434 mg, 3.0 mmol) in dry benzene (15 mL) were treated as described in the general procedure for *N*-benzoylation. At the conclusion of the reaction (TLC monitoring, 32 h), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product. Crystallization of the crude from ethanol (8 mL) gave the desired product **30** (760 mg, 93%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (t, J = 7.2 Hz, 3 H), 4.38 (q, J = 7.2 Hz, 2 H), 7.53–7.74 (m 3 H), 7.89

(dd, J = 1.2, 7.8 Hz, 2 H), 8.07 (dd, J = 1.6, 8.8 Hz, 1 H), 8.52 (br. s, 1 H), 8.50 (d, J = 1.6 Hz, 1 H), 8.62 (d, J = 8.8 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 14.5, 61.5, 88.9, 120.2, 127.4, 127.6, 129.3, 131.2, 132.8, 134.2, 140.3, 142.2, 164.9, 165.5 ppm. HRMS (Q-ToF): calcd. for $C_{16}H_{14}NIO_3Na$ $[M + Na]^+$ 417.9916; found 417.9921.

Preparation of Ethyl 4-Benzoylamino-3-(2-propenyl)benzoate (32): *N*-Benzoyl derivative **30** (250 mg, 0.63 mmol), CsF (191.0 mg, 1.26 mmol), $[Pd(PPh_3)_4]$ (44.0 mg, 6 mol-%) in THF (15 mL) and allylboronate **4** (212.0 mg, 1.3 mmol) in THF (5 mL) were treated as described in the general procedure for allylation. Elution of the column with 8% ethyl acetate/petroleum ether gave the desired product **32** (178.0 mg, 92%) as a white solid. (*Note: ^{1}H and ^{13}C NMR show that compound **32** is an inseparable mixture.*) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (t, J = 7.6 Hz, 3 H), 3.53 (d, J = 6.0 Hz, 2 H), 4.37 (q, J = 7.6 Hz, 2 H), 5.16 (dd, J = 1.2, 17.2 Hz, 1 H), 5.31 (dd, J = 2.0, 7.6 Hz, 1 H), 6.01–6.11 (m, 1 H), 7.47–7.58 (m, 3 H), 7.83–7.85 (m, 2 H), 7.92 (d, J = 2.4 Hz, 1 H), 8.02 (dd, J = 2.4, 8.8 Hz, 1 H), 8.18 (br. s, 1 H), 8.35 (d, J = 8.8 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 14.5, 37.2, 61.1, 117.8, 121.9, 126.6, 127.2, 128.4, 129.0, 129.5, 132.0, 132.3, 134.7, 135.6, 140.8, 165.6, 166.4 ppm. HRMS (Q-ToF): calcd. for $C_{19}H_{20}NO_3$ $[M + H]^+$ 310.1443; found 310.1451.

Preparation of Methyl 4-(Benzoylamino)-3-(2-propenyl)benzoate (33): *N*-Benzoyl derivative **31** (150 mg, 0.39 mmol), CsF (120 mg, 0.78 mmol), $[Pd(PPh_3)_4]$ (27 mg, 6 mol-%) in THF (15 mL) and allylboronate **4** (132 mg, 0.78 mmol) in dry THF (5 mL) were treated as described in the general procedure for allylation by the SM cross-coupling reaction. At the conclusion of the reaction (TLC monitoring, 4 h), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 9% ethyl acetate/petroleum ether gave the desired product **33** (96.5 mg, 83%) as a white solid, m.p. 111–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.51 (dd, J = 1.6, 4.4 Hz, 2 H), 3.91 (s, 3 H), 5.13–5.18 (dq, J = 1.6, 17.2 Hz, 1 H), 5.28–5.32 (dq, J = 1.6, 7.6 Hz, 1 H), 6.01–6.09 (m, 1 H), 7.48–7.52 (m, 3 H), 7.83–7.85 (m, 2 H), 7.93 (d, J = 2.0 Hz, 1 H), 8.00 (dd, J = 2.0, 8.4 Hz, 1 H), 8.19 (br. s, 1 H), 8.33 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 37.2, 52.2, 117.8, 121.9, 126.2, 127.2, 128.4, 129.0, 129.5, 132.0, 132.4, 134.7, 135.6, 140.9, 165.6, 166.8 ppm. HRMS (Q-ToF): calcd. for $C_{18}H_{18}NO_3$ $[M + H]^+$ 296.1287; found 296.1282.

Preparation of Ethyl 4-[Benzoyl(2-propenyl)amino]-3-(2-propenyl)-benzoate (34): Allyl derivative **32** (83.0 mg, 0.27 mmol), KOH (17.0 mg, 0.3 mmol), TBAI (198 mg, 0.5 mmol) and allyl bromide (35.0 mg, 0.3 mmol) were treated as described in the general procedure for the *N*-alkylation. Elution of the column with 8% ethyl acetate/petroleum ether gave the desired product **34** (68 mg, 73%) as a thick colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (t, J = 7.6 Hz, 3 H), 3.13–3.19 (m, 1 H), 3.32–3.38 (m, 1 H), 4.09–4.14 (m, 1 H), 4.32 (q, J = 7.6 Hz, 2 H), 4.73 (dd, J = 6.0, 14.4 Hz, 1 H), 5.06–5.17 (m, 4 H), 5.67–5.71 (m, 1 H), 5.97–6.03 (m, 1 H), 7.11–7.27 (m, 6 H), 7.77–7.82 (m, 2 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 14.4, 35.1, 53.3, 61.4, 117.9, 119.1, 127.8, 128.3, 128.6, 129.6, 129.9, 130.2, 132.1, 132.5, 135.3, 135.6, 137.5, 145.6, 166.0, 170.2 ppm. HRMS (Q-ToF): calcd. for $C_{22}H_{24}NO_3$ $[M + H]^+$ 350.1756; found 350.1764.

Preparation of Methyl 4-[Benzoyl(2-propenyl)amino]-3-(2-propenyl)-benzoate (35): Allyl derivative **33** (48 mg, 0.17 mmol), KOH (12.0 mg, 0.21 mmol), TBAI (130 mg, 0.34 mmol) and allyl bromide (26.0 mg, 0.21 mmol) were treated as described in the general procedure for the *N*-alkylation. At the conclusion of the reaction (TLC monitoring, 1.5 h), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 9% ethyl acetate/petroleum ether gave the desired product **35** (47.3 mg, 87%) as a colourless thick liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.13–3.19 (m, 1 H), 3.32–3.38 (m, 1 H), 3.87 (s, 3 H), 4.09–4.14 (m, 1 H), 4.73 (dd, J = 6.0, 14.4 Hz, 1 H), 5.06–5.17 (m, 4 H), 5.67–5.71 (m, 1 H), 5.97–6.03 (m, 1 H), 7.11–7.27 (m, 6 H), 7.77–7.82 (m, 2 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 35.1, 52.4, 53.3, 117.9, 119.1, 127.9, 128.4, 128.6, 129.5, 129.9, 130.2, 132.1, 132.4, 135.3, 135.5, 137.5, 145.7, 166.5, 170.2 ppm. HRMS (Q-ToF): calcd. for $C_{21}H_{222}NO_3$ $[M + H]^+$ 336.1600; found 336.1605

Preparation of Tetrahydro-1-benzazepine Derivative 38: Diallyl derivative **34** (27 mg, 0.077 mmol) in dry DCM (2 mL) was treated with Grubbs' catalyst (2.0 mg, 3 mol-%) as in the general procedure for RCM. At the conclusion of the reaction (TLC monitoring, 45 min), the solvent was removed and the crude product was purified by silica gel column chromatography. Elution of the column with 9% ethyl acetate/petroleum ether gave RCM product **36** (17.2 mg, 82%) which was used further without characterization.

Pd/C (10%, 20 mg, 40 mol-%) was added to a stirred solution of compound **36** (12.0 mg, 0.04 mmol) in dry ethyl acetate (5 mL). The reaction mixture was then kept under a hydrogen pressure of 1 atm. (balloon pressure) for 24 h. After that, the reaction mixture was filtered through a Celite pad which was successively washed with chloroform (3 × 10 mL). The solvent was removed in vacuo to provide the desired product **38** (10.6 mg, 87%) as a thick liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 (t, J = 7.2 Hz, 3 H), 1.41 (br. s, 1 H), 1.95 (br. s, 2 H), 2.10 (br. s, 1 H), 2.76 (br. s, 1 H), 2.99–3.02 (m, 2 H), 4.33 (q, J = 7.2 Hz, 2 H), 5.02 (br. s, 1 H), 6.66 (d, J = 8.0 Hz, 1 H), 7.15–7.25 (m, 5 H), 7.56 (d, J = 8.0 Hz, 1 H), 7.92 (d, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 14.5, 26.1, 29.6, 35.1, 47.8, 61.3, 128.1, 128.2, 128.4, 128.6, 129.0, 130.0, 131.6, 135.2, 139.3, 148.3, 166.2 ppm. HRMS (Q-ToF): calcd. for $C_{14}H_{18}NO_2$ $[M + H]^+$ 324.1600; found 324.1585.

Preparation of Tetrahydro-1-benzazepine Derivative 39: Diallyl derivative **35** (20 mg, 0.06 mmol) in dry DCM (2 mL) was treated with Grubbs' catalyst (1.5 mg, 3 mol-%) as in the general procedure for RCM. At the conclusion of the reaction (TLC monitoring, 40 min), the solvent was removed and the crude product was purified by silica gel column chromatography. Elution of the column with 9% ethyl acetate/petroleum ether gave RCM product **37** (16.2 mg, 89%) which was used further without characterization.

Pd/C (10%, 16.5 mg, 40 mol-%) was added to a stirred solution of compound **37** (12.0 mg, 0.04 mmol) in dry ethyl acetate (5 mL). The reaction mixture was then kept under a hydrogen pressure of 1 atm (balloon pressure) for 24 h. Then the reaction mixture was filtered through a Celite pad which was successively washed with chloroform (3 × 10 mL). The solvent was removed in vacuo to provide the desired product **39** (9.7 mg, 80%) as a thick liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (br. s, 1 H), 1.95 (br. s, 2 H), 2.10 (br. s, 1 H), 2.76 (br. s, 1 H), 2.99–3.03 (m, 2 H), 3.87 (s, 3 H), 5.03 (br. s, 1 H), 6.66 (d, J = 8.0 Hz, 1 H), 7.14–7.23 (m, 5 H), 7.55 (d, J = 8.0 Hz, 1 H), 7.92 (d, J = 1.6 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 26.1, 29.6, 35.1, 47.7, 52.9, 128.1, 128.2, 128.4, 128.7, 130.1, 131.6, 135.9, 139.4, 148.4, 166.6, 169.4 ppm. HRMS (Q-ToF): calcd. for $C_{19}H_{20}NO_3$ $[M + H]^+$ 310.1443; found 310.1431.

Preparation of 3-Iodo-4-(acrylamido)acetophenone (41): Aniline derivative **7** (180 mg, mmol) and acryloyl chloride (135.5 mg, mmol) in dry DCM were treated as described in the general procedure for *N*-acryloyl protection. At the conclusion of the reaction (TLC monitoring, 7 h), the reaction mixture was quenched with water and the usual work-up gave the crude. Crystallization of the crude product from ethanol gave the desired product **41** (180 mg, 93%) as a white crystalline solid, m.p. 148–150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.58 (s, 3 H), 5.90 (dd, J = 0.8, 16.8 Hz, 1 H), 6.34 (dd, J = 10.0, 16.8 Hz, 1 H), 6.50 (dd, J = 0.8, 16.8 Hz, 1 H), 7.82 (br. s, 1 H), 7.94 (dd, J = 2.4, 8.8 Hz, 1 H), 8.41 (d, J = 2.4 Hz, 1 H), 8.54 (d, J = 8.8 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 26.6, 89.5, 120.4, 129.2, 130.1, 131.2, 134.3, 139.2, 142.1, 163.7, 195.7 ppm. HRMS (Q-ToF): calcd. for $C_{11}H_{11}NIO_2$ $[M + H]^+$ 315.9835; found 315.9825.

Preparation of Diene 42: *N*-Acryloyl derivative **40** (70 mg, 0.21 mmol), CsF (64 mg, 0.42 mmol), $[Pd(PPh_3)_4]$ (12.1 mg, 6 mol-%) and allylboronate **4** (71 mg, 0.42 mmol) in dry THF (10 mL) were treated as described in the general procedure for allylation by the SM cross-coupling reaction. At the conclusion of the reaction (TLC monitoring, 5 h), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 17% ethyl acetate/petroleum ether gave the desired product **42** (15.2 mg, 29%) as a white solid, m.p. 146–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.47 (d, J = 6.0 Hz, 2 H), 3.91 (s, 3 H), 5.17 (dd, J = 1.4, 17.6 Hz, 1 H), 5.27 (dd, J = 1.4, 10.0 Hz, 1 H), 5.81 (d, J = 10 Hz, 1 H), 6.03 (m 1 H), 6.20 (dd, J = 15.6, 18.4 Hz, 1 H), 6.42 (d, J = 16.8 Hz, 1 H), 7.60 (br. s, 1 H), 7.89 (d, J = 2.0 Hz, 1 H), 7.96 (dd, J = 2.0, 8.4 Hz, 1 H), 8.25 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 37.2, 52.3, 117.7, 121.9, 126.3, 128.4, 129.5, 131.3, 131.9, 135.8, 140.7, 163.6, 166.8 ppm. HRMS (Q-ToF): calcd. for $C_{14}H_{16}NO_3$ $[M + H]^+$ 246.1130; found 246.1136.

Preparation of Diene 43: *N*-Acryloyl derivative **41** (80 mg, 0.25 mmol), CsF (77 mg, 0.5 mmol), $[Pd(PPh_3)_4]$ (11.7 mg, 4 mol-%) and allylboronate **4** (85 mg, 0.5 mmol) in dry THF (10 mL) were treated as described in the general procedure for the SM cross-coupling reaction. At the conclusion of the reaction (TLC monitoring, 5.5 h), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 22% ethyl acetate/petroleum ether gave the desired product **43** (14.3 mg, 25%) as a white solid, m.p. 128–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.59 (s, 3 H), 3.45 (dt, J = 1.6, 6.0 Hz, 2 H), 5.18 (dq, J = 1.6, 17.6 Hz, 1 H), 5.28 (dq, J = 1.6, 10.0 Hz, 1 H), 5.81 (dd, J = 0.8, 10.4 Hz, 1 H), 6.03–5.95 (m 1 H), 6.19 (dd, J = 10.4, 16.8 Hz, 1 H), 6.42 (dd, J = 0.8, 16.8 Hz, 1 H), 7.64 (br. s, 1 H), 7.82 (d, J = 2.0 Hz, 1 H), 7.88 (dd, J = 2.0, 8.0 Hz, 1 H), 8.30 (d, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 26.7, 37.3, 117.8, 121.8, 128.5, 128.7, 130.5, 131.2, 133.5, 137.5, 140.9, 163.6, 197.4 ppm. HRMS (Q-ToF): calcd. for $C_{14}H_{16}NO_2$ $[M + H]^+$ 230.1181; found 230.1188.

Preparation of Methyl 2-Oxo-2,5-dihydro-1*H*-benzazepine-7-carboxylate (44): The precursor **42** (8.0 mg, 0.03 mmol) and **G-2** (1.3 mg, 5 mol-%) in dry DCM were treated as described in the general procedure for the RCM reaction. At the conclusion of the reaction (TLC monitoring, 1.5 h), the solvent was removed to give the crude product which was purified by silica gel column chromatography. Elution of the column with 20% ethyl acetate/petroleum ether gave the desired product **44** (7.3 mg, 90%) as a white solid, m.p. 190–194 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.44 (d, J = 6.4 Hz, 2 H), 3.91 (s, 3 H), 6.01 (d, J = 10.8 Hz, 1 H), 6.66 (td, J = 4.0, 6.8, 10.8 Hz, 1 H), 7.15 (d, J = 8.0 Hz, 1 H), 7.85 (d, J = 1.6 Hz, 1 H), 7.90 (dd, J = 1.6, 8.0 Hz, 1 H), 9.80 (br. s, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 32.3, 52.5, 120.6, 125.7, 126.9, 129.5, 130.6, 131.0, 140.9, 141.9, 166.6, 168.5 ppm. HRMS (Q-ToF): calcd. for $C_{12}H_{12}NO_3$ $[M + H]^+$ 218.0817; found 218.0819.

Preparation of 7-Acetyl-2-oxo-2,5-dihydro-1-benzazepine (45): The precursor **43** (10.4 mg, 0.03 mmol) and G-2 (1.1 mg, 5 mol-%) in dry DCM were treated as described in the general procedure for RCM. At the conclusion of the reaction (TLC monitoring, 1.5 h), the solvent was removed to give the crude product which was purified by silica gel column chromatography. Elution of the column with 35% ethyl acetate/petroleum ether gave the desired product **45** (8.1 mg, 93%) as a white solid, m.p. 152–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.44 (d, J = 6.4 Hz, 2 H), 3.91 (s, 3 H), 6.01 (d, J = 10.8 Hz, 1 H), 6.66 (td, J = 4.0, 6.8, 10.8 Hz, 1 H), 7.15 (d, J = 8.0 Hz, 1 H), 7.85 (d, J = 1.6 Hz, 1 H), 7.90 (dd, J = 1.6, 8.0 Hz, 1 H), 9.80 (br. s, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 26.7, 32.4, 120.7, 125.7, 128.5, 129.3, 131.1, 134.1, 141.1, 141.9, 168.5, 196.9 ppm. HRMS (Q-ToF): calcd. for $C_{12}H_{12}NO_2$ $[M + H]^+$ 202.0868; found 202.0861.

Preparation of *N*-Allyl Derivative 46: 2-Iodoaniline derivative **5** (200 mg, 0.72 mmol), K_2CO_3 (100 mg, 0.73 mmol) and allyl bromide (88 mg, 0.74 mmol) were heated in dry acetonitrile (5 mL) at reflux for 4 d. Heating was then stopped, the reaction mixture allowed to cool to room temp. and then filtered through a Celite pad which was washed with ethyl acetate (3 × 25 mL). The solvent was removed and the crude product was purified by silica gel column chromatography. Elution of the column with 3% ethyl acetate/petroleum ether gave diallyl derivative **47** (22 mg, 12%) as a colourless liquid. Further elution of the column with 6% ethyl acetate/petroleum ether gave the monoallyl derivative **46** (102 mg, 60%) as a colourless liquid (based on 25% starting material recovered). Continued elution with 15% ethyl acetate/petroleum ether gave the starting material **5** (50 mg, 25%).

Spectral Data for Compound 46: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 3.87–3.91 (m, 2 H), 4.83 (br. s, 1 H), 5.12–5.31 (m, 2 H), 5.89–5.97 (m, 1 H), 6.50 (d, J = 8.8 Hz, 1 H), 7.87 (dd, J = 2.0, 8.8 Hz, 1 H), 8.35 (d, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 46.3, 51.9, 83.8, 109.4, 117.2, 120.1, 131.6, 133.7, 140.9, 150.5, 166.2 ppm. HRMS (Q-ToF): calcd. for $C_{11}H_{13}NO_2I$ $[M + H]^+$ 317.9991; found 317.9994.

Preparation of the Diallyl Derivative 48 by the SM Cross-Coupling Reaction: *N*-Allyl derivative **46** (59 mg, 0.18 mmol), CsF (52 mg, 0.37 mmol), $[Pd(PPh_3)_4]$ (6.5 mg, 3 mol-%) in dry THF (8 mL) and allylboronate **4** (62.5 mg, 0.37 mmol) in THF (15 mL) were treated as described in the general procedure for allylation. At the conclusion of the reaction (TLC monitoring, 48 h), the reaction mixture was quenched with water and the usual work-up using DCM gave the crude product which was charged onto a silica gel column. Elution of the column with 3% ethyl acetate/petroleum ether gave the desired product **48** (5.4 mg, 12%) as a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.32 (d, J = 6.0 Hz, 2 H), 3.83–3.85 (m, 5 H), 4.33 (br. s, 1 H), 5.09–5.28 (m, 4 H), 5.88–5.98 (m, 2 H), 6.58 (d, J = 8.4 Hz, 1 H), 7.74 (d, J = 2.0 Hz, 1 H), 7.84 (dd, J = 2.0, 8.4 Hz, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 36.5, 46.0, 51.7, 109.6, 116.8, 117.1, 118.4, 122.6, 130.4, 131.8, 134.5, 135.5, 150.1, 167.7 ppm. HRMS (Q-ToF): calcd. for $C_{14}H_{18}NO_2$ $[M + H]^+$ 232.1338; found 232.1347.

Further elution of the column with 5% ethyl acetate/petroleum ether gave the indole derivative **49** (14.2 mg, 40%) as a yellow solid,

m.p. 142–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$):[33] δ = 2.36 (d, J = 0.8 Hz, 3 H), 3.94 (s, 3 H), 7.02 (d, J = 0.8 Hz, 1 H), 7.33 (d, J = 8.4 Hz, 1 H), 7.89 (dd, J = 1.6, 8.4 Hz, 1 H), 8.21 (br. s, 1 H), 8.36 (s, 1 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 9.7, 52.0, 110.8, 113.4, 121.3, 122.1, 123.0, 123.4, 128.1, 139.0, 168.6 ppm.

Preparation of *N*-Allyl Derivative 51 and *N*,*N*-Diallyl Derivative 52: Methyl 4-aminobenzoate (**50**) (300 mg, 1.98 mmol) in acetonitrile (10 mL) was heated with allyl bromide (1 mL) in the presence of K_2CO_3 (0.98 g, 4.00 mmol) at 80 °C. After 12 h, the heating was stopped and the reaction mixture was filtered through a Celite pad and washed with ethyl acetate. The solvent was removed and the crude product was purified by silica gel column chromatography. Elution of the column with 4% ethyl acetate/petroleum ether gave the diallyl derivative **52** (240 mg, 52.4%) as a colourless thick liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 3.93 (dt, J = 1.6, 4.4 Hz, 4 H), 5.19–5.12 (m, 4 H), 5.79–5.87 (m, 2 H), 6.63 (d, J = 9.2 Hz, 2 H), 7.8 (d, J = 9.2 Hz, 2 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 51.6, 52.7, 111.1, 116.6, 117.4, 131.5, 132.5, 153.1, 167.5 ppm. HRMS (Q-ToF): calcd. for $C_{14}H_{18}NO_2$ $[M + H]^+$ 232.1338; found 232.1328.

Continued elution of the column with 7% ethyl acetate/petroleum ether gave the monoallyl derivative **51** (120 mg, 31%) as a white crystalline solid, m.p. 77–78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.82–3.84 (m, 5 H), 4.30 (br. s, 1 H), 5.17–5.21 (m, 1 H), 5.25–5.31 (m, 1 H), 5.87–5.96 (m, 1 H), 6.56 (d, J = 8.8 Hz, 2 H), 7.86 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 46.0, 51.7, 111.8, 116.9, 118.7, 131.7, 134.5, 151.9, 167.5 ppm. HRMS (Q-ToF): calcd. for $C_{11}H_{14}NO_2$ $[M + H]^+$ 192.1025; found 192.1021.

Preparation of Diallyl Derivative 48 by Aza-Claisen Rearrangement: $BF_3{\cdot}Et_2O$ (100 mg, 0.86 mmol) was added to a solution of diallyl derivative **52** (200 mg, 0.86 mmol) in freshly distilled xylene (5 mL), and the resulting mixture was heated at 140 °C in an oil bath for 1.5 h. The reaction was quenched with a saturated solution of sodium hydrogen carbonate and general work-up with chloroform gave the crude product which was purified by silica gel column chromatography. Elution of the column with 3% ethyl acetate/petroleum ether gave the starting material **52** (20 mg, 20%). Continued elution gave the desired diallyl derivative **48** (69 mg, 38%, based on starting material recovered) as a colourless liquid which turned yellow when kept open to air (^{1}H NMR spectroscopic data identical to those of the compound obtained by the SM cross-coupling reaction). Continued elution of the column with 5% ethyl acetate/petroleum ether gave side-product **53** (50 mg, 32%) as a colourless liquid that turned yellow. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.33 (dt, J = 1.6, 6.4 Hz, 4 H), 3.86 (s, 3 H), 4.15 (br. s, 2 H), 5.08–5.17 (m, 4 H), 5.90–5.97 (m, 2 H), 7.69 (s, 2 H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 36.7, 51.8, 116.9, 119.5, 123.1, 130.7, 135.4, 148.1, 167.6 ppm. HRMS (Q-ToF): calcd. for $C_{14}H_{18}NO_2$ $[M + H]^+$ 232.1338; found 232.1334

Preparation of the *N*-Acetyl Derivative 17 from Diallyl Derivative 48: Acetic anhydride (0.5 mL) was added to the diallyl derivative **48** (26 mg, 0.1 mmol) and the reaction mixture was stirred at room temp. At the conclusion of the reaction (TLC monitoring, 12 h), the reaction was quenched with water and extracted with DCM (2 × 20 mL). The solvent was removed in vacuo and the crude product was purified by silica gel column chromatography. Elution of the column with 15% ethyl acetate/petroleum ether gave the desired product **17** (25 mg, 80%) as a colourless liquid. ^{1}H NMR spectroscopic data was found to be identical to those of the compound prepared by a different route.

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