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(1*H*-Tetrazol-5-yl)-Allenes: Building Blocks for Tetrazolyl Heterocycles

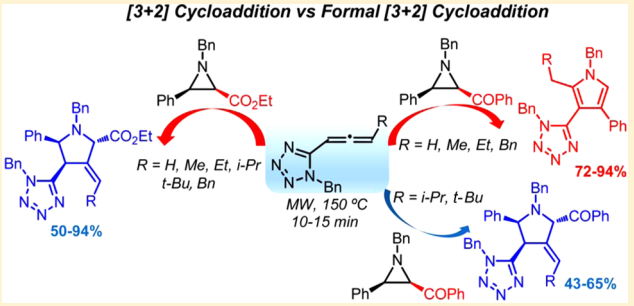
Ana L. Cardoso,[†] Marta S. C. Henriques,[‡] José A. Paixão,[‡] and Teresa M. V. D. Pinho e Melo*[,†]

[†]CQC and Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal

[‡]CFisUC and Department of Physics, University of Coimbra, 3004-516 Coimbra, Portugal

Supporting Information

ABSTRACT: (1*H*-Tetrazol-5-yl)-allenes have been prepared for the first time, and their reactivity toward aziridines explored. Reaction of a (1-benzyl-1*H*-tetrazol-5-yl)-phosphonium chloride and acyl chlorides in the presence of triethylamine afforded the target allenes via Wittig reaction of the *in situ* generated phosphorus ylide and ketenes. 1-(1-Benzyl-1*H*-tetrazol-5-yl)-propa-1,2-diene and 3-methyl-, 3-ethyl- and 3-benzyl derivatives undergo microwave-induced formal [3 + 2] cycloaddition with *cis*-*N*-benzyl-2-benzoyl-3-phenylaziridine, through C−N bond cleavage, to give selectively tetrasubstituted pyrroles. In contrast, with (1*H*-tetrazol-5-yl)-allenes bearing bulkier substituents at C-3, such as *i*-propyl or a *tert*-butyl, 4-methylenepyrrolidines were obtained exclusively via [3 + 2] cycloaddition of the *in situ* generated azomethine ylide. The latter allenes also gave 4-methylenepyrrolidines on reacting with *cis*-2-benzoyl-*N*-cyclohexyl-3-phenylaziridine, whereas with the other allenes, pyrroles were obtained as major products together with the formation of 4-methylenepyrrolidines. All the studied (1*H*-tetrazol-5-yl)-allenes reacted with *N*-benzyl-*cis*-3-phenylaziridine-2-carboxylate to give the corresponding 4-methylenepyrrolidines exclusively.

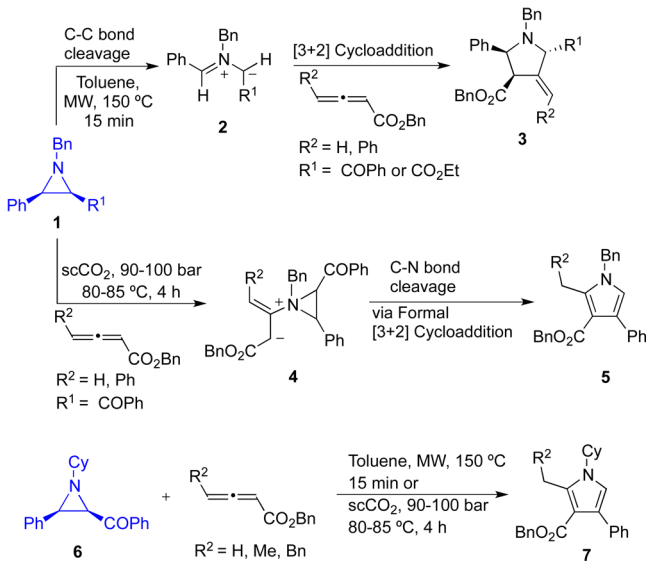


INTRODUCTION

Allenes featuring two cumulated double bonds show unique and varied reactivity, which makes them valuable and versatile building blocks in modern organic chemistry. In the last two decades, the chemistry of allenes experienced great advances and has been widely explored for various synthetic purposes.[1] The occurrence of allenic structures in a variety of natural products and pharmacologically active compounds has contributed largely to this.[2] Their synthetic potential in regio- and stereoselective transformations, as well as the possibility of selective axial to center chirality transfer as a route to chiral compounds, are also important factors. It is therefore not suprising that novel applications of allenes in areas such as natural product synthesis, catalytic asymmetric synthesis, and molecular materials have been recently reported.[3]

The chemistry of allenes has been one of our research topics.[4−8] Particularly interesting was the study on the reactivity of allenoates toward aziridines in organic solvents, under microwave irradiation (MW) or conventional heating,[7] and in supercritical carbon dioxide ($scCO_2$).[8] It was observed that aziridine-2-carboxylates react with allenoates to give 4-methylenepyrrolidines (e.g., **3**) exclusively, via 1,3-dipolar cycloaddition of the *in situ* generated azomethine ylides.[7] Interestingly, allenoates can also participate in [3 + 2] cycloaddition with 2-benzoylaziridines as the 2π component to afford 4-methylenepyrrolidines (e.g., **3**), but they can also react through formal [3 + 2] cycloaddition via aziridine C−N bond cleavage leading to functionalized pyrroles (e.g., **5**) (Scheme 1). The reaction outcome is influenced not only by the substitution pattern of the aziridines, which under the same reaction conditions determine the chemical behavior of the allenoates, but also by the reaction conditions. The microwave-induced reactions of *N*-benzyl-2-benzoyl-3-phenylaziridines and buta-2,3-dienoates in toluene led to site-, regio- and stereo-

Scheme 1. Reactivity of Allenoates Towards Aziridines



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selective synthesis of 4-methylenepyrrolidines. From the reaction with allenoates bearing bulkier C-4 substituents, 4-methylenepyrrolidines were also formed as minor products. *N*-Cyclohexyl-2-benzoyl-3-phenylaziridines reacted with buta-2,3-dienoates to give pyrroles as the major or exclusive product. Bulkier N-substituents on the aziridine ring favor the formal [3 + 2] cycloadditions with allenoates leading to selective formation of pyrroles.[7] In contrast, performing the same reactions under $scCO_2$ conditions affords pyrroles **5** as single products regardless of the aziridine N-substituent.[8] This study provided a synthethic methodology to pyrroles and methylenepyrrolidines which are important target molecules.[9,10]

Recently, we became interested in developing new synthetic routes to 5-substituted-1*H*-tetrazoles[11] which are used in medicinal chemistry as bioisosteres of carboxylic acids.[12] In this context, we envisaged that (1*H*-tetrazol-5-yl)-allenes could be particularly interesting building blocks for the synthesis of new nitrogen-containing five-membered heterocyles incorporating a tetrazole functionality. In this context, herein the synthesis of novel tetrazol-5-yl-allenes and their reactivity toward aziridines as a selective approach to functionalized methylenepyrrolidines and pyrroles are described.

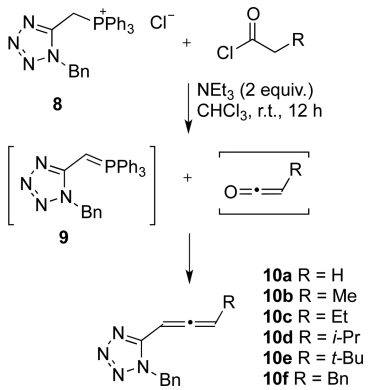
RESULTS AND DISCUSSION

The synthesis of the target (1*H*-tetrazol-5-yl)-allenes is outlined in Table 1. The required (1-benzyl-1*H*-tetrazol-5-yl)-phosphonium chloride **8** was previously synthesized via a three-step procedure starting from benzylamine and chloroacetyl chloride.[11f] The Wittig reaction between the phosphorus ylide **9**, formed from the phosphonium chloride **8** and triethylamine, and ketene, generated *in situ* from acetyl chloride (1 equiv) and triethylamine, gave the desired tetrazol-5-yl-allene **10a** in 38% yield (entry 1, Table 1). Treatment of ylide **9** with methylketene, isopropylketene, and benzylketene was carried out under the same reaction conditions and led to the formation of the corresponding allenes **10b**, **10d**, and **10f**, respectively, in moderate yields (entries 2−4, 40−49%, Table 1). To our delight, increasing the amount of acyl chloride from 1 to 2 equiv afforded allenes **10a**, **10b**, **10d**, and **10f** in significantly higher yields, ranging from 59% to 91% (entries 5, 6, 8, and 10, Table 1). However, using more than 2 equiv of the acyl chloride did not increase the yield further. Thus, the optimized reaction conditions were applied to the one-pot synthesis of allenes **10c** and **10e** bearing an ethyl and a *tert*-butyl substituent at C-3, respectively, which were isolated in high yields (entries 7 and 9, Table 1).

Having prepared (1*H*-tetrazol-5-yl)-allenes **10a−10f**, we set out to explore their reactivity toward aziridines. *cis*-1-Benzyl-2-benzoyl-3-phenylaziridine (**1a**) was synthesized following a known procedure,[13] and its chemical behavior under thermolysis in the presence of (1*H*-tetrazol-5-yl)-allene **10b** was studied (Table 2). Carriyng out the reaction in refluxing toluene for 1.5 h led to the formation of pyrrole **11a** as single product in 43% yield (entry 1). A slightly lower yield was observed (38%) when the reaction time was increased to 3 h, thus indicating the lack of stability of this heterocycle to prolonged heating (entry 2). Then, the microwave-induced reaction of aziridine **1a** with allene **10b** was studied (entries 3−7). It was observed that the best reaction conditions were achieved under microwave irradiation at 150 °C for 10 min, affording pyrrole **11a** in 85% yield (entry 4). The formation of pyrrole **11a** was surprising because in our previous studies,[7] aziridine **1a** reacted with various allenoates to give 4-methylenepyrrolidines exclusively (see Scheme 1). The only exception was observed in the reaction with benzyl 5-phenylpenta-2,3-dienoate which afforded a mixture of 1,3-dipolar and formal 1,3-dipolar cycloadducts.[7] Thus, these results demonstrate that the (1*H*-tetrazol-5-yl)-allenes and allenoates display a different reactivity toward 1-benzyl-2-benzoyl-3-phenylaziridine (**1a**) under the same reaction conditions.

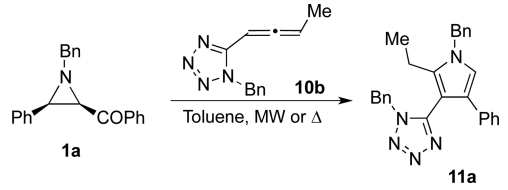
Under the optimized reaction conditions, we carried out the microwave-assisted reaction of aziridine **1a** with (1*H*-tetrazol-5-yl)-allenes **10c−10f** (Table 3). The reaction of allenes **10c** and **10d** gave the corresponding pyrrole derivatives **11c** (74%) and **11d** (60%) as single products (entries 1 and 3). Interestingly,

Table 1. One-pot Synthesis of (1*H*-Tetrazol-5-yl)-allenes 10a−f



entry	R	acyl chloride (equiv)	product (isolated yield)
1	H	1	**10a** (38%)
2	Me	1	**10b** (48%)
3	*i*-Pr	1	**10d** (49%)
4	Bn	1	**10f** (40%)
5	H	2	**10a** (59%)
6	Me	2	**10b** (91%)
7	Et	2	**10c** (66%)
8	*i*-Pr	2	**10d** (86%)
9	*t*-Bu	2	**10e** (73%)
10	Bn	2	**10f** (73%)

Table 2. Condition Screening for the Reaction of Aziridine 1a with Allene 10b



entry	reaction conditions	isolated yield
1	reflux, 1.5 h	43%
2	reflux, 3 h	38%
3	MW, 150 °C, 5 min	39%
4	MW, 150 °C, 10 min	85%
5	MW, 150 °C, 15 min	65%
6	MW, 160 °C, 10 min	75%
7	MW, 160 °C, 15 min	67%

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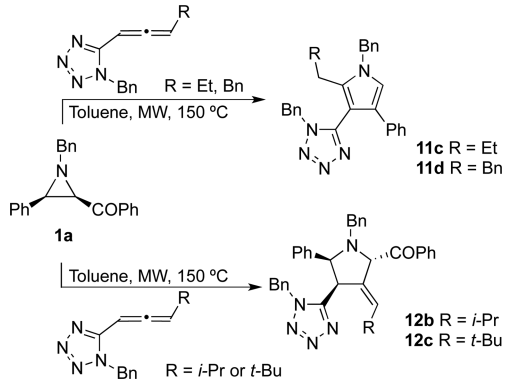
Table 3. Synthesis of Pyrroles and 4-Methylenepyrrolidines from Aziridine 1a and Allenes 10c−f

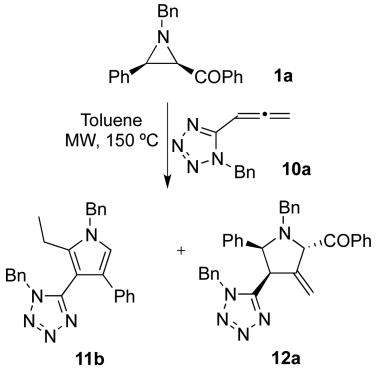


entry	R	reaction time (min)	product (isolated yield)
1	Et	10	**11c** (74%)
2	Et	15	**11c** (94%)
3	Bn	10	**11d** (60%)
4	Bn	15	**11d** (72%)
5	*i*-Pr	10	**12b** (53%)
6	*i*-Pr	15	**12b** (50%)
7	*t*-Bu	10	**12c** (57%)
8	*t*-Bu	15	**12c** (65%)

by increasing the reaction time from 10 to 15 min, we observed a significant enhancement in yields. Compounds **11c** and **11d** could be isolated 94% and 72% yield, respectively (entries 2 and 4). A different outcome was observed from the reaction of aziridine **1a** with the (1*H*-tetrazol-5-yl)-allenes **10**, bearing at C-3 an *i*-propyl or a *tert*-butyl substituent (entries 5−8). Using the optimized reaction conditions, 4-methylenepyrrolidines **12b** (53%) and **12c** (57%) were obtained selectively (entries 5 and 7). Carrying out these reactions with a longer reaction time (15 min) did not lead to relevant improvements (entries 6 and 8).

Exceptionally, the reaction of aziridine **1a** with 1-(1-benzyl-1*H*-tetrazol-5-yl)propa-1,2-diene (**10a**) gave a mixture of tetrasubstituted pyrrole **11b** and 4-methylenepyrrolidine **112a** (Scheme 2). Nevertheless, the microwave-irradiation at 150 °C for 15 min allowed the synthesis of pyrrole **11b** in high yield (89%), and 4-methylenepyrrolidine **12a** was isolated in only 5% yield.

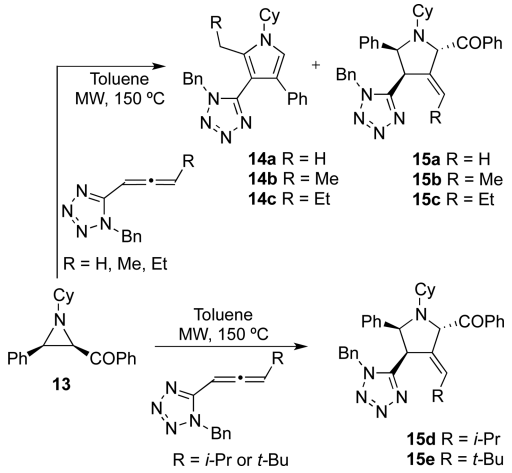
Scheme 2. Reactivity of Tetrazol-5-yl-allene 10a Towards Aziridine 1a



Reaction Time	Isolated Yields
10 min	**11b** (40%) **12a** (4%)
15 min	**11b** (89%) **12a** (5%)

Aiming to find whether the nature of the N-substituent of the 2-benzoyl-3-phenylaziridines is important in determining the outcome of the reaction with these (1*H*-tetrazol-5-yl)-allenes, the reactivity of *cis*-2-benzoyl-1-cyclohexyl-3-phenylaziridine[13] (**13**) was also investigated (Table 4). Aziridine **13** reacted with

Table 4. Synthesis of Pyrroles and Pyrrolidines from Aziridine 13 and (1*H*-Tetrazol-5-yl)-Allenes 10a−10e



entry	R	reaction time (min)	product (isolated yield)	
1	H	10	**14a** (57%)	**15a** (19%)
2	H	15	**14a** (57%)	**15a** (18%)
3	Me	10	**14b** (46%)	**15b** (16%)
4	Me	15	**14b** (69%)	**15b** (8%)
5	Et	10	**14c** (48%)	**15c** (16%)
6	Et	15	**14c** (37%)	**15c** (5%)
7	*i*-Pr	15	–	**15d** (50%)
8	*t*-Bu	10	–	**15e** (5%)
9	*t*-Bu	15	–	**15e** (30%)

allenes **10a−10c** under microwave irradiation to give the corresponding pyrroles **14a−14c** (48−69%) as major products together with the formation of pyrrolidines **15a−15c** (16−19%) (entries 1−6). As previously observed with aziridine **1a**, the reaction of **13** with tetrazol-5-yl-allenes **10d** and **10e**, bearing bulkier C-3 substituents, led to a different result, selectively affording 4-methylenepyrrolidines **15d** and **15e**, respectively, as single products (entries 7−9). However, 4-methylenepyrrolidine **15e** could only be obtained in moderate yield (30%). These results seem to indicate that bulkier C-3 substituents on the (1*H*-tetrazol-5-yl)-allenes hinder the formal [3 + 2] cycloaddition, favoring the 1,3-dipolar cycloaddition. Furthermore, the presence of a bulky group on the (1*H*-tetrazol-5-yl)-allenes has a higher impact on the reaction outcome than the bulkiness of the aziridine N-substituent.

We have previously proposed that pyrroles can be obtained from aziridines and allenoates via a formal [3 + 2] cycloaddition. This mechanim was reinforced by the isolation of a minor product, a pyrrole derivative containing a hydroxybenzyl side chain, which was formed from a proposed intermediate. Furthermore, the byproduct of these reactions, benzaldeyde, was also isolated.[7,8]

A similar mechanism could also explain the synthesis of pyrroles **11** and **14** (Scheme 3). Nucleophilic addition of the aziridine to the activated (1*H*-tetrazol-5-yl)-allene double bond gives intermediate **16**, followed by the intramolecular attack of the carbanion center on the aziridine ring, leading to the five-

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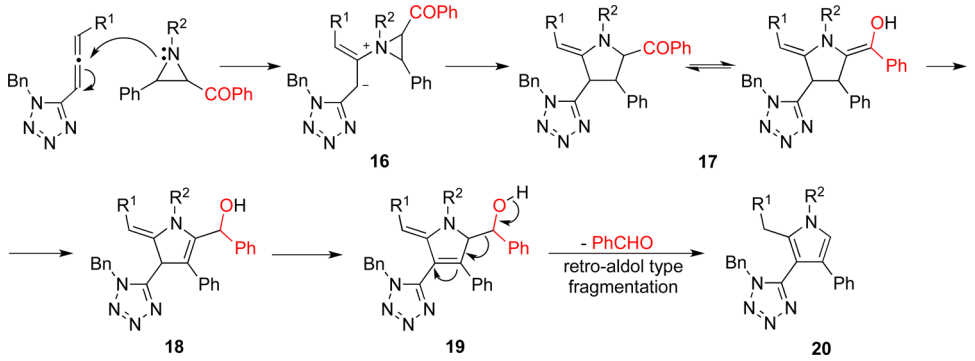
Scheme 3. Mechanism Proposal for the Formal [3 + 2] Cycloaddition of Aziridines with (1*H*-Tetrazol-5-yl)-Allenes



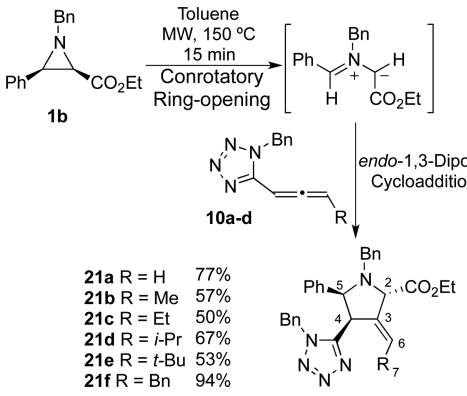
membered heterocycle **17** via C−N bond cleavage. Tautomerisms and retro-aldol-type fragmentation affords benzaldehyde and the target product **20**. Once again, benzaldeyde could be isolated from these reactions.

The reactivity of aziridines as masked zwitterionic intermediates has been previously reported. In fact, *N*-butyl- and *N*-alkenylaziridines react with dimethyl acetylene dicarboxylate to afford zwitterionic intermediates, which are converted into the corresponding dihydropyrroles through C−N bond cleavage.[14] On the other hand, the nucleophilic addition of N-substituted aziridines to arynes leading to zwitterionic intermediates has also been reported.[15]

It was previously observed that 3-phenylaziridine-2-carboxylates react with allenoates giving 4-methylenepyrrolidines exclusively.[7] Replacement of the benzoyl group by a carboxylate group at the aziridine ring favors the C−C bond cleavage leading to the generation of the corresponding azomethine ylide and the subsequent selective 1,3-dipolar cycloaddition. 3-Phenylaziridine-2-carboxylates showed the same reactivity pattern toward (1*H*-tetrazol-5-yl)-allenes.

In fact, the microwave-induced reaction of ethyl *N*-benzyl-*cis*-3-phenylaziridine-2-carboxylate **1b**[7] with (1*H*-tetrazol-5-yl)-allenes **10a−10f** gave 4-methylenepyrrolidines **21** in high yields in a site-, regio-, and stereoselective fashion (Scheme 4).

Scheme 4. Synthesis of 4-Methylenepyrrolidines from Aziridine 1b and (1*H*-Tetrazol-5-yl)-Allenes 10



The structural assignment of compound **21e** was supported by two-dimensional COSY, NOESY, HMQC, and HMBC spectra (see Supporting Information). In the NOESY spectrum H-4 shows connectivity with H-5, but no connectivity was observed between H-4 and H-2 or between H-5 and H-2. On the other hand, *tert*-butyl protons (H-7) show connectivity with H-4 but no connectivty with H-2, whereas H-6 shows connectivity with H-2, but no connectivity was observed with H-4 or H-5.

The reactivity of *N*-cyclohexyl-*cis*-3-phenylaziridine-2-carboxylate **22**[7] toward tetrazol-5-yl-allenes **10** was also explored (Scheme 5). Under microwave irradiation, the reaction of aziridine **22** with allenes **10a** and **10b** was site- and regioselective but not stereoselective. In both cases the corresponding 4-methylenepyrrolidines **23** were obtained as major products, but the stereoisomeric pyrrolidines **24** were also isolated. The formation of pyrrolidines **23** can be rationalized considering the conrotatory aziridine ring-opening leading to the corresponding azomethine ylide which participates in *endo* 1,3-dipolar cycloadditions with allenes **10a** and **10b**. Pyrrolidines **24** are the result of *exo* 1,3-dipolar cycloadditions. The structure of 4-methylenepyrrolidine **23a** was determined by X-ray crystallography allowing the complete stereochemistry assignment. The compound crystallizes in the noncentrosymmetric (albeit achiral) space group $P2_12_12$. Each unit cell contains two symmetry-independent molecules, one with *S*, *R*, *S* configuration for the chiral centers C-2, C-4, and C-5, respectively, the other with opposite chirality (see Supporting Information). The structural assignment of compound **24a** was supported by two-dimensional COSY, NOESY, and HMQC spectra (see Supporting Information). The NOESY spectrum of compound **24a** shows connectivity of H-2 with H-4, but no connectivity was observed between H-2 and H-5.

A different outcome was observed from the reaction of allenes **10c** and **10d** with aziridine **22**, which under the same reaction conditions gave selectively 4-methylenepyrrolidine **23c** and 4-methylenepyrrolidine **23d**, respectively, as single products albeit in moderate yield (Scheme 5).

CONCLUSION

An efficient one-pot synthesis of allenes bearing a (1*H*-tetrazol-5-yl)-substituent via Wittig reaction was reported. The reactivity of these (1*H*-tetrazol-5-yl)-allenes toward *N*-benzyl- and *N*-cyclohexyl-2-benzoyl-3-phenylaziridine under microwave irradiation provided selective routes to 3-(tetrazol-5-yl)-4-methylenepyrrolidines and 3-(tetrazol-5-yl)-pyrroles via 1,3-dipolar and formal 1,3-dipolar cycloadditions, respectively. It was observed that bulky C-3 substituents on the (1*H*-tetrazol-5-yl)-allenes hinder the formal [3 + 2] cycloaddition, thus favoring the 1,3-dipolar cycloaddition, and that the bulkiness of these C-3 substituents has a higher impact on the reaction outcome than the bulkiness of the aziridine N-substituent. Thus, (1*H*-tetrazol-5-yl)-allenes bearing bulkier substituents at C-3, such as *i*-propyl or a *tert*-butyl, gave 4-methyllenepyrro-

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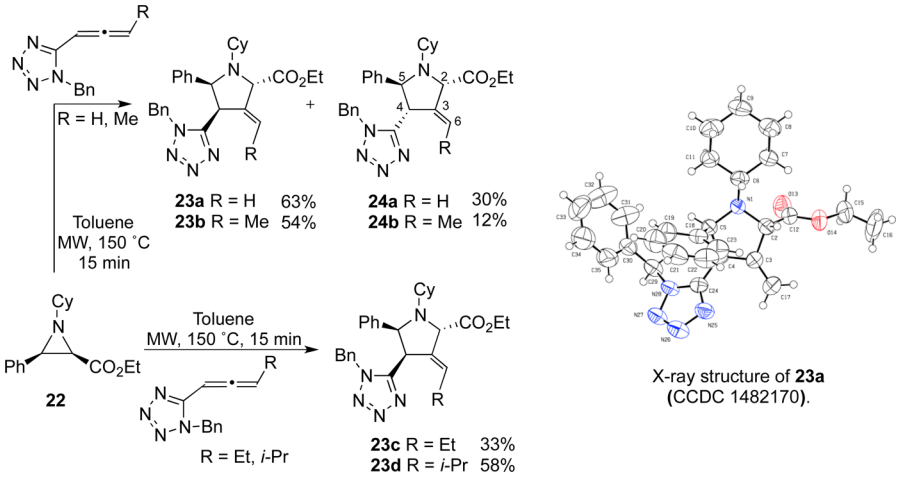
Scheme 5. Synthesis of Pyrrolidines from Aziridine 22 and (1*H*-Tetrazol-5-yl)-Allenes 10a−10d



lidines exclusively regardless of the aziridine N-substituent, whereas with other allenes, 3-(tetrazol-5-yl)-pyrroles were obtained as single or major products. Furthermore, the study demonstrated that the (1*H*-tetrazol-5-yl)-allenes and allenoates display a different reactivity pattern toward 2-benzoyl-3-phenylaziridines. *N*-Benzyl-*cis*-3-phenylaziridine-2-carboxylate reacted with all the studied (1*H*-tetrazol-5-yl)-allenes to give the corresponding 3-(tetrazol-5-yl)-4-methylenepyrrolidines exclusively.

EXPERIMENTAL SECTION

General Information. NMR spectra were run in $CDCl_3$ or DMSO-d_6 on a 400 MHz instrument and recorded at the following frequencies: proton (^{1}H, 400 MHz), carbon (^{13}C, 100 MHz). Chemical shifts are expressed in parts per million related to internal TMS and coupling constants (J) are in hertz. FT-IR spectra were recorded on a Fourier transform spectrometer with a Smart Orbit diamond crystal accessory. Microwave reactions were carried out on a microwave reactor CEM Focused Synthesis System Discover S-Class using closed 10 mL microwave vessels with the temperature-fixed mode. Reaction temperatures were measured during microwave heating by infrared surface detector. High-resolution mass spectra were performed by positive electrospray ionization on a TOF analyzer. Melting points were determined in open glass capillaries and are uncorrected. Thin-layer chromatography (TLC) analyses were performed using precoated silica gel plates. Flash column chromatography was performed with silica gel 60 as the stationary phase. Aziridines **1a**,[13] **1b**,[7b] **13**,[13] and **22**[7b] were prepared following procedures described in the literature. Tetrazol-5-yl phosphonium chloride **8** was synthesized via a three-step procedure previously reported.[11f]

General Experimental Method for the Synthesis of Tetrazol-5-yl-allenes (10a−10f). A solution of phosphonium salt **8** (5 mmol) and triethylamine (10 mmol) in dry $CHCl_3$ (50 mL) under nitrogen atmosphere was stirred at room temperature, while a solution of the appropriate acid chloride (5 mmol, Method A; 10 mmol, Method B) in dry $CHCl_3$ (2 mL) was added dropwise to it. After the addition, the mixture was stirred at room temperature for 12 h. The reaction mixture was washed with H_2O (3 × 50 mL), dried, and evaporated. The crude product was purified by flash column chromatography [ethyl acetate/hexane (1:2)] followed by recrystallization.

1-(1-Benzyl-1H-tetrazol-5-yl)propa-1,2-diene (***10a***). White solid, mp 74.1−76.0 °C (from ethyl acetate/hexane), 377 mg, 38% yield (method A), 585 mg, 59% yield (method B). IR 695, 715, 860, 1113, 1237, 1457, 1525, 1962 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (d, J = 6.8 Hz, 2H), 5.63 (s, 2H), 6.41 (t, J = 6.8 Hz, 1H), 7.13−7.15 (m, 2H), 7.34−7.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.0, 78.9, 81.2, 127.1, 128.7, 129.1, 133.6, 148.6, 212.2. HRMS (ESI) m/z calcd for $C_{11}H_{11}N_4$ $[M + H]^+$ 199.0978, found 199.0977.

1-(1-Benzyl-1H-tetrazol-5-yl)buta-1,2-diene (***10b***). White solid, mp 29.6-31.3 °C (from ethyl acetate/hexane), 509 mg, 48% yield (method A), 967 mg, 91% yield (method B). IR 691, 722, 881, 1119, 1244, 1418, 1526, 1954 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (dd, J = 3.6 Hz and J = 7.6 Hz, 3H), 5.62 (s, 2H), 5.62−5.67 (m, 1H), 6.37−6.39 (m, 1H), 7.08−7.10 (m, 2H), 7.32−7.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 50.9, 78.7, 92.3, 126.8, 128.5, 129.1, 133.8, 149.3, 209.4. HRMS (ESI) m/z calcd for $C_{12}H_{13}N_4$ $[M + H]^+$ 213.1134, found 213.1134.

1-(1-Benzyl-1H-tetrazol-5-yl)penta-1,2-diene (***10c***). White solid, mp 29.3−30.6 °C (from ethyl acetate/hexane), 747 mg, 66% yield (method B). IR 691, 718, 888, 1113, 1241, 1453, 1525, 1954 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 7.6 Hz, 3H), 2.01−2.09 (m, 2H), 5.63 (s, 2H), 5.75 (pseudo q, J = 6.4 Hz, 1H), 6.43−6.46 (m, 1H), 7.08−7.10 (m, 2H), 7.33−7.35 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6, 21.3, 50.9, 79.8, 99.1, 126.8, 128.5, 129.0, 133.8, 149.4, 208.4. HRMS (ESI) m/z calcd for $C_{13}H_{15}N_4$ $[M + H]^+$ 227.1291, found 227.1288.

1-(1-Benzyl-1H-tetrazol-5-yl)-4-methyl-penta-1,2-diene (***10d***). White solid, mp 54.6−56.1 °C (from ethyl acetate/hexane), 589 mg, 49% yield (method A), 1.03 g, 86% yield (method B). IR 694, 714, 870, 1114, 1236, 1453, 1518, 1950 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (d, J = 6.8 Hz, 3H), 1.01 (d, J = 6.8 Hz, 3H), 2.34−2.43 (m, 1H), 5.60 (d, J = 15.6 Hz, 1H), 5.65 (d, J = 15.6 Hz, 1H), 5.70 (t, J = 6.4 Hz, 1H), 6.45 (dd, J = 3.6 Hz and J = 6.4 Hz, 1H), 7.08−7.10 (m, 2H), 7.32−7.35 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 22.0, 28.0, 50.8, 80.2, 104.4, 126.8, 128.6, 129.1, 133.8, 149.4, 207.3. HRMS (ESI) m/z calcd for $C_{14}H_{17}N_4$ $[M + H]^+$ 241.1447, found 241.1446.

1-(1-Benzyl-1H-tetrazol-5-yl)-4,4-dimethyl-penta-1,2-diene (***10e***). White solid, mp 55.3−56.3 °C (from ethyl acetate/hexane), 928 mg, 73% yield (method B). IR 693, 722, 877, 1123, 1246, 1438, 1523, 1956 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 9H), 5.58 (d, J = 15.6 Hz, 1H), 5.67 (d, J = 15.6 Hz, 1H), 5.68 (d, J = 6.4 Hz, 1H), 6.45 (d, J = 6.4 Hz, 1H), 7.08−7.10 (m, 2H), 7.32−7.35 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.7, 32.9, 50.7, 80.6, 108.6, 126.8, 128.6, 129.1, 133.7, 149.5, 206.2. HRMS (ESI) m/z calcd for $C_{15}H_{19}N_4$ $[M + H]^+$ 255.1604, found 255.1603.

1-(1-Benzyl-1H-tetrazol-5-yl)-3-benzyl-propa-1,2-diene (***10f***). White solid, mp 71.9−72.6 °C (from ethyl acetate/hexane), 577 mg, 40% yield (method A), 1.05 g, 73% yield (method B). IR 692, 722, 868, 1122, 1240, 1452, 1530, 1963 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.37 (dd, J = 3.2 Hz and J = 7.2 Hz, 2H), 5.47 (d, J = 15.6 Hz, 1H), 5.55 (d, J = 15.6 Hz, 1H), 5.87 (pseudo t, J = 7.2 Hz, 1H), 6.40−6.43 (m, 1H), 6.40−6.43 (m, 1H), 6.99−7.01 (m, 2H), 7.14−7.15 (m, 2H), 7.20−7.35 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.4, 50.8, 79.8, 96.9, 126.8, 126.9, 128.4, 128.6, 128.7, 129.1, 133.7, 138.0, 149.1,

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208.9. HRMS (ESI) m/z calcd for $C_{18}H_{17}N_4$ $[M + H]^+$ 289.1447, found 289.1447.

General Experimental Methods for the [3 + 2] Cycloaddition of Aziridines with Tetrazol-5-yl-allenes. Method A: In a microwave reactor a suspension of the aziridine and allene in toluene (1 mL) was irradiated for the appropriate period of time with the temperature set to 150 °C. After cooling, the solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography [ethyl acetate/hexane (1:4)] followed by recrystallization.

Method B: A solution of the aziridine and allene in toluene (6 mL) was heated at reflux for the appropriated period of time in which the reaction was monitored by TLC. Then, the solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography [ethyl acetate/hexane (1:4)] followed by recrystallization.

*1-Benzyl-3-(1-benzyl-1H-tetrazol-5-yl)-2-ethyl-4-phenyl-1H-pyrrole (**11a**).* Prepared by method A or B from aziridine **1a** (100 mg, 0.32 mmol) and allene **8b** (0.48 mmol). Light yellow solid, 114 mg, 85% yield (method A), 58 mg, 43% yield (method B), mp 121.4−122.6 °C (from ethyl acetate/hexane). IR 696, 715, 1175, 1346, 1495, 1560 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.68 (t, J = 7.6 Hz, 3H), 2.40 (q, J = 7.6 Hz, 2H), 4.87 (s, 2H), 5.09 (s, 2H), 6.85−6.87 (m, 3H), 7.04−7.09 (m, 4H), 7.11−7.26 (m, 6H), 7.31−7.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 17.8, 50.6, 50.8, 101.3, 119.7, 123.9, 126.5, 126.6, 127.9, 128.0, 128.3, 128.5, 128.9, 129.1, 133.8, 134.5, 137.0, 138.1, 151.3. Anal. calcd for $C_{27}H_{25}N_5$: C, 77.30; H, 6.01; N, 16.69. Found: C, 77.30; H, 6.30; N, 16.64.

*1-Benzyl-3-(1-benzyl-1H-tetrazol-5-yl)-2-methyl-4-phenyl-1H-pyrrole (**11b**) and 5-Benzoyl-1-benzyl-3-(1-benzyl-1H-tetrazol-5-yl)-4-methylene-2-phenylpyrrolidine (**12a**).* Prepared by method A from aziridine **1a** (100 mg, 0.32 mmol) and allene **10a** (0.48 mmol) affording **11b** as a white solid, 116 mg, in 89% yield and **12a** as light yellow solid, 8 mg, in 5% yield.

*1-Benzyl-3-(1-benzyl-1H-tetrazol-5-yl)-2-methyl-4-phenyl-1H-pyrrole (**11b**).* Mp 147.3−148.5 °C (from ethyl acetate/hexane). IR 698, 738, 1072, 1454, 1495, 1550, 1601 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.89 (s, 3H), 4.90 (s, 2H), 5.05 (s, 2H), 6.81 (d, J = 7.2 Hz, 2H), 6.90 (s, 1H), 7.01−7.03 (m, 2H), 7.07−7.14 (m, 4H), 7.18−7.27 (m, 2H), 7.31−7.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.2, 50.8, 50.9, 102.2, 119.6, 123.9, 126.5, 126.6, 127.7, 127.9, 128.3, 128.5, 129.0, 129.1, 132.2, 134.0, 134.4, 136.7, 151.4. HRMS (ESI) m/z calcd for $C_{26}H_{24}N_5$ $[M + H]^+$ 406.2026, found 406.2026.

*5-Benzoyl-1-benzyl-3-(1-benzyl-1H-tetrazol-5-yl)-4-methylene-2-phenylpyrrolidine (**12a**).* Mp 173.6−175.1 °C (from ethyl acetate/hexane). IR 694, 738, 1072, 1454, 1495, 1550, 1601 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 3.66 (d, J = 13.2 Hz, 1H), 3.85 (d, J = 13.2 Hz, 1H), 4.29−4.40 (m, 2H), 4.66 (s, 1H), 4.79 (s, 1H), 5.16 (d, J = 16.0 Hz, 1H), 5.30 (d, J = 7.2 Hz, 1H), 5.64 (s, 1H), 6.97−7.00 (m, 2H), 7.18−7.20 (m, 5H), 7.24−7.34 (m, 10H), 7.48−7.51 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.5, 50.1, 50.9, 64.9, 69.6, 113.0, 127.2, 127.3, 128.0, 128.4, 128.6, 128.7, 128.8, 129.0, 129.2, 133.3, 136.9, 137.1, 137.9, 145.5, 154.8, 201.5. HRMS (ESI) m/z calcd for $C_{33}H_{30}N_5O$ $[M + H]^+$ 512.2444, found 512.2442.

*1-Benzyl-3-(1-benzyl-1H-tetrazol-5-yl)-2-propyl-4-phenyl-1H-pyrrole (**11c**).* Prepared by method A from aziridine **1a** (100 mg, 0.32 mmol) and allene **10c** (0.48 mmol). Light yellow solid, 130 mg, 94% yield, mp 140.3−141.9 °C (from ethyl acetate/hexane). IR 699, 758, 1144, 1213, 1453, 1570 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.64 (t, J = 7.2 Hz, 3H), 1.03−1.12 (m, 2H), 2.35 (q, J = 7.2 Hz, 2H), 4.86 (s, 2H), 5.08 (s, 2H), 6.85 (s, 1H), 6.86 (d, J = 8.0 Hz, 2H), 7.04−7.08 (m, 2H), 7.11−7.37 (m, 10H), 7.43−7.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 23.2, 26.5, 50.7, 50.8, 101.8, 119.7, 123.9, 126.6, 126.6, 127.9, 128.1, 128.3, 128.5, 128.9, 129.1, 133.8, 134.5, 136.9, 137.0, 151.3. Anal. calcd for $C_{28}H_{27}N_5$: C, 77.57; H, 6.28; N, 16.15. Found: C, 77.52; H, 6.40; N, 16.15.

*5-Benzoyl-1-benzyl-3-(1-benzyl-1H-tetrazol-5-yl)-4-(2-methylpropylidene)-2-phenylpyrrolidine (**12b**).* Prepared by method A from aziridine **1a** (100 mg, 0.32 mmol) and allene **10d** (0.48 mmol). Yellow solid, 94 mg, 53% yield, mp 172.0−173.1 °C (from ethyl acetate/hexane). IR 691, 722, 1132, 1220, 1452, 1494, 1670 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.24 (d, J = 6.0 Hz, 3H), 0.28 (d, J = 6.0 Hz, 3H), 0.74−0.78 (m, 1H), 3.62 (d, J = 13.2 Hz, 1H), 3.81 (d, J = 13.2 Hz, 1H), 3.89 (d, J = 15.2 Hz, 1H), 4.20 (d, J = 6.0 Hz, 1H), 4.79 (d, J = 10.0 Hz, 1H), 5.16 (d, J = 15.2 Hz, 1H), 5.32 (d, J = 6.0 Hz, 1H), 5.60 (s, 1H), 7.05−7.06 (m, 2H), 7.17 (br s, 3H), 7.24−7.30 (m, 11H), 7.40−7.48 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.8, 29.4, 42.5, 50.0, 50.6, 63.9, 69.6, 127.2, 127.8, 128.4, 128.5, 128.8, 129.0, 129.1, 132.9, 134.4, 134.7, 137.4, 137.6, 138.1, 154.6, 202.9. HRMS (ESI) m/z calcd for $C_{36}H_{36}N_5O$ $[M + H]^+$ 554.2914, found 554.2904.

*5-Benzoyl-1-benzyl-3-(1-benzyl-1H-tetrazol-5-yl)-4-(2,2-dimethylpropylidene)-2-phenylpyrrolidine (**12c**).* Prepared by method A from aziridine **1a** (100 mg, 0.32 mmol) and allene **10e** (0.48 mmol). White solid, 118 mg, 65% yield, mp 147.9−148.8 °C (from ethyl acetate/hexane). IR 688, 1132, 1213, 1452, 1676 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.32 (s, 9H), 3.55 (d, J = 13.2 Hz, 1H), 3.70 (d, J = 15.2 Hz, 1H), 3.77 (d, J = 13.2 Hz, 1H), 4.51 (d, J = 6.4 Hz, 1H), 4.75 (d, J = 15.2 Hz, 1H), 5.05 (s, 1H), 5.39 (d, J = 6.0 Hz, 1H), 5.65 (s, 1H), 7.10−7.12 (m, 2H), 7.15−7.22 (m, 6H), 7.26−7.29 (m, 7H), 7.32−7.38 (m, 4H), 7.43−7.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.3, 33.2, 42.3, 49.7, 50.5, 65.1, 70.6, 127.2, 128.4, 128.5, 128.7, 129.0, 129.1, 132.2, 132.8, 133.8, 137.6, 137.9, 138.1, 138.2, 154.9, 204.0. Anal. calcd for $C_{37}H_{37}N_5O$: C, 78.28; H, 6.57; N, 12.34. Found: C, 78.18; H, 6.58; N, 12.29.

*1-Benzyl-3-(1-benzyl-1H-tetrazol-5-yl)-2-ethyl-4-phenyl-1H-pyrrole (**11d**).* Prepared by method A from aziridine **1a** (100 mg, 0.32 mmol) and allene **10f** (0.48 mmol). White solid, 114 mg, 72% yield, mp 108.8−110.4 °C (from diethyl ether/hexane). IR 694, 720, 1029, 1182, 1208, 1453, 1495, 1603 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.36 (t, J = 8.4 Hz, 3H), 2.68 (t, J = 8.4 Hz, 3H), 4.86 (s, 2H), 4.88 (s, 2H), 6.87−6.89 (m, 5H), 7.03 (d, J = 6.8 Hz, 2H), 7.13−7.38 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8, 36.3, 50.7, 50.8, 102.2, 120.0, 123.9, 126.2, 126.5, 126.6, 126.7, 128.0, 128.3, 128.4, 128.6, 129.0, 129.2, 133.8, 134.5, 135.9, 136.9, 140.8, 151.3. Anal. calcd for $C_{33}H_{29}N_5$: C, 79.97; H, 5.90; N, 14.13. Found: C, 79.86, H, 5.99; N, 14.11.

*3-(1-Benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-2-methyl-4-phenyl-1H-pyrrole (**14a**) and 5-Benzoyl-3-(1-benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-4-methylene-2-phenylpyrrolidine (**15a**).* Prepared by method A from aziridine **13** (100 mg, 0.33 mmol) and allene **10a** (0.49 mmol) affording **14a** as a white solid, 74 mg, in 57% yield and **15a** as light yellow solid, 30 mg, in 19% yield.

*3-(1-Benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-2-methyl-4-phenyl-1H-pyrrole (**14a**).* Mp 158.0−159.5 °C (from ethyl acetate/hexane). IR 697, 720, 1199, 1265, 1449, 1595 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.24−1.34 (m, 1H), 1.40−1.49 (m, 2H), 1.62−1.81 (m, 4H), 1.91 (s, 3H), 1.91−1.99 (m, 4H), 3.73−3.80 (m, 1H), 4.86 (s, 2H), 6.79 (d, J = 6.8 Hz, 2H), 6.93 (s, 1H), 7.06−7.08 (m, 2H), 7.14−7.22 (m, 4H), 7.25−7.28 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.1, 25.4, 25.9, 34.2, 50.9, 55.8, 100.9, 115.1, 123.5, 126.3, 126.4, 127.9, 128.2, 128.4, 129.0, 131.1, 134.0, 134.8, 151.7. HRMS (ESI) m/z calcd for $C_{25}H_{28}N_5$ $[M + H]^+$ 398.2339, found 398.2333.

*Benzoyl-3-(1-benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-4-methylene-2-phenylpyrrolidine (**15a**).* Mp 64.3−66.0 °C (from ethyl acetate/hexane). IR 698, 721, 1074, 1212, 1448, 1595, 1654 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.84−1.21 (m, 5H), 1.41−1.73 (m, 5H), 2.61−2.66 (m, 1H), 4.76 (d, J = 8.4 Hz, 1H), 4.82 (d, J = 8.0 Hz, 1H), 5.05 (s, 1H), 5.22 (s, 1H), 5.34 (s, 2H), 5.76 (s, 1H), 6.79 (br s, 2H), 7.10−7.12 (m, 2H), 7.26−7.30 (m, 3H), 7.38−7.43 (m, 3H), 7.53−7.57 (m, 2H), 7.62−7.66 (m, 1H), 8.15 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0, 25.3, 25.7, 31.6, 33.5, 43.0, 50.8, 57.4, 67.4, 113.1, 127.8, 128.0, 128.1, 129.0, 129.1, 129.3, 133.4, 133.5, 135.8, 139.1, 143.0, 152.3, 200.9. HRMS (ESI) m/z calcd for $C_{32}H_{34}N_5O$ $[M + H]^+$ 504.2757, found 504.2746.

*3-(1-Benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-2-ethyl-4-phenyl-1H-pyrrole (**14b**) and 5-Benzoyl-3-(1-benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-4-ethylidene-2-phenylpyrrolidine (**15b**).* Prepared by method A from aziridine **13** (100 mg, 0.33 mmol) and allene **10b** (0.49 mmol) affording **14b** as a white solid, 94.5 mg, in 69% yield, and **15b** as light yellow solid, 13.5 mg, in 8% yield.

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*3-(1-Benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-2-ethyl-4-phenyl-1H-pyrrole (**14b**).* Mp 104.5−106.0 °C (from ethyl acetate/hexane). IR 698, 750, 960, 1204, 1451, 1570 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.73 (t, J = 7.6 Hz, 3H), 1.23−1.29 (m, 2H), 1.32−1.48 (m, 3H), 1.93−1.97 (m, 4H), 2.40 (q, J = 7.6 Hz, 2H), 3.76−3.83 (m, 1H), 4.83 (s, 2H), 6.82 (d, J = 6.8 Hz, 2H), 6.94 (s, 1H), 7.06−7.20 (m, 6H), 7.23−7.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 17.6, 25.4, 26.0, 34.8, 50.8, 55.5, 100.0, 115.3, 123.6, 126.3, 126.4, 128.2, 128.4, 129.1, 133.8, 134.9, 137.0, 151.6. HRMS (ESI) m/z calcd for $C_{26}H_{30}N_5$ $[M + H]^+$ 412.2495, found 412.2495.

*5-Benzoyl-3-(1-benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-4-ethylidene-2-phenylpyrrolidine (**15b**).* Mp 177.5−178.6 °C (from ethyl acetate/hexane). IR 692, 705, 972, 1219, 1446, 1499, 1667 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.63 (br s, 3H), 0.94−1.82 (m, 11H), 2.53−2.58 (m, 1H), 3.98 (d, J = 15.2 Hz, 1H), 4.18 (br s, 1H), 4.96 (d, J = 15.2 Hz, 1H), 5.26 (br s, 1H), 5.63 (br s, 1H), 5.88 (s, 1H), 6.99 (br s, 2H), 7.14−7.22 (m, 8H), 7.46−7.50 (m, 2H), 7.55−7.59 (m, 1H), 8.01 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 25.7, 25.9, 26.4, 30.3, 33.1, 42.2, 49.9, 56.2, 63.7, 67.3, 121.9, 127.9, 128.4, 128.7, 128.9, 129.0, 129.1, 132.9, 133.5, 136.8, 137.9, 138.7, 154.2, 206.4. HRMS (ESI) m/z calcd for $C_{33}H_{36}N_5O$ $[M + H]^+$ 518.2914, found 518.2911.

*3-(1-Benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-2-propyl-4-phenyl-1H-pyrrole (**14c**) and 5-Benzoyl-3-(1-benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-4-propylidene-2-phenylpyrrolidine (**15c**).* Prepared by method A from aziridine **13** (100 mg, 0.33 mmol) and allene **10c** (0.49 mmol) affording **14c** as a yellow solid, 67 mg, in 48% yield, and **15c** as light yellow solid, 28 mg, in 16% yield.

*3-(1-Benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-2-propyl-4-phenyl-1H-pyrrole (**14c**).* Mp 42.8−43.9 °C (from ethyl acetate/hexane). IR 695, 719, 1197, 1449, 1570 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.71 (t, J = 7.6 Hz, 3H), 0.84−1.44 (m, 5H), 1.66−1.80 (m, 4H), 1.92−2.00 (m, 4H), 2.35 (t, J = 7.6 Hz, 2H), 3.75−3.82 (m, 1H), 4.80 (s, 2H), 6.82 (d, J = 6.8 Hz, 2H), 6.94 (s, 1H), 7.06−7.08 (m, 2H), 7.10−7.27 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 23.4, 25.4, 26.0, 26.3, 34.8, 50.8, 55.6, 100.5, 115.3, 123.6, 126.4, 126.5, 128.2, 128.3, 128.4, 129.1, 133.8, 134.9, 135.7, 151.6. HRMS (ESI) m/z calcd for $C_{27}H_{32}N_5$ $[M + H]^+$ 426.2652, found 426.2647.

*5-Benzoyl-3-(1-benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-4-propylidene-2-phenylpyrrolidine (**15c**).* Mp 65.5−67.0 °C (from ethyl acetate/hexane). IR 703, 716, 1212, 1448, 1595, 1670 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.34 (t, J = 7.6 Hz, 3H), 0.86−1.93 (m, 13H), 2.62−2.67 (m, 1H), 4.03 (d, J = 15.6 Hz), 4.23 (d, J = 6.0 Hz, 1H), 5.05 (d, J = 15.6 Hz, 1H), 5.19 (pseudo t, J = 6.0 Hz, 1H), 5.68 (d, J = 6.4 Hz), 5.94 (s, 1H), 7.05 (br s, 3H), 7.18−7.65 (m, 10H), 8.07 (d, J = 8.0 Hz). HRMS (ESI) m/z calcd for $C_{34}H_{38}N_5O$ $[M + H]^+$ 532.3070, found 532.3054.

*5-Benzoyl-3-(1-benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-4-(2-methylpropylidene)-2-phenylpyrrolidine (**15d**).* Prepared by method A from aziridine **13** (100 mg, 0.33 mmol) and allene **10d** (0.49 mmol) affording **15d** as a yellow solid, 90 mg, in 50% yield. Mp 172.0−173.1 °C (from ethyl acetate/hexane). IR 691, 714, 1169, 1212, 1448, 1495, 1671 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.23 (d, J = 6.4 Hz, 3H), 0.31 (d, J = 6.4 Hz, 3H), 0.69−1.05 (m, 5H), 1.08−1.47 (m, 3H), 1.57−1.60 (m, 2H), 1.77 (br d, J = 12.4 Hz, 1H), 1.93 (br d, J = 11.2 Hz, 1H), 2.63−2.69 (m, 1H), 3.98 (d, J = 15.6 Hz, 1H), 4.22 (d, J = 6.4 Hz, 1H), 4.92 (d, J = 10.0 Hz, 1H), 5.10 (d, J = 15.6 Hz, 1H), 5.67 (d, J = 6.8 Hz, 1H), 5.91 (s, 1H), 7.04−7.06 (m, 2H), 7.22−7.26 (m, 3H), 7.29−7.31 (m, 5H), 7.52−7.56 (m, 2H) 7.61−7.64 (m, 1H), 8.03 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.7, 25.8, 26.0, 26.4, 29.5, 30.3, 33.0, 42.4, 49.9, 56.2, 63.6, 67.2, 127.8, 128.3, 128.7, 128.9, 129.0, 129.1, 132.9, 133.3, 133.9, 135.6, 137.2, 137.9, 154.9, 206.9. HRMS (ESI) m/z calcd for $C_{35}H_{40}N_5O$ $[M + H]^+$ 546.3227, found 546.3215.

*5-Benzoyl-3-(1-benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-4-(2,2-dimethylpropylidene)-2-phenylpyrrolidine (**15e**).* Prepared by method A from aziridine **13** (100 mg, 0.33 mmol) and allene **10e** (0.49 mmol) affording **15e** as a yellow solid, 55 mg, in 30% yield. Mp 173.2−175.0 °C (from ethyl acetate/hexane). IR 697, 705, 967, 1200, 1446, 1498, 1676 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.16 (s, 9H), 0.48−0.59 (m, 2H), 0.81−0.87 (m, 2H), 1.04−1.08 (m, 1H), 1.10−1.21 (m, 2H), 1.42−1.59 (m, 3H), 1.75−1.78 (m, 1H), 2.41−2.47 (m, 1H), 3.62 (d, J = 15.2 Hz, 1H), 4.36 (br s, 1H), 4.52 (d, J = 15.2 Hz, 1H), 5.03 (s, 1H), 5.64 (d, J = 6.4 Hz, 1H), 5.76 (s, 1H), 6.97 (br s, 2H), 7.11−7.12 (m, 8H), 7.37−7.41 (m, 2H), 7.45−7.49 (m, 1H), 7.89 (d, J = 7.6 Hz, 2H) . ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.8, 26.0, 26.5, 29.1, 30.1, 32.9, 33.2, 42.1, 49.7, 55.8, 64.4, 68.2, 128.5, 128.6, 128.7, 128.8, 128.9, 129.0, 132.2, 133.3, 134.5, 137.3, 137.8, 155.4, 208.4. HRMS (ESI) m/z calcd for $C_{36}H_{42}N_5O$ $[M + H]^+$ 560.3383, found 560.3367.

General Experimental Methods for the [3 + 2] Cycloaddition of *N*-Benzyl and *N*-Cyclohexyl-*cis*-3-phenylaziridines-2-carboxylates with Tetrazol-5-yl-allenes. In a microwave reactor, a suspension of the aziridine and allene in toluene (1 mL) was irradiated for 15 min with the temperature set to 150 °C. After cooling, the solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography [ethyl acetate/hexane (1:4)] followed by recrystallization.

*Ethyl 1-Benzyl-4-(1-benzyl-1H-tetrazol-5-yl)-3-methylene-5-phenylpyrrolidine-2-carboxylate (**21a**).* Prepared from aziridine **1b** (100 mg, 0.36 mmol) and allene **10a** (0.53 mmol) affording **21a** as a white solid, 133 mg, in 77% yield. Mp 151.0−151.9 °C (from ethyl acetate/hexane). IR 704, 749, 1018, 1115, 1247, 1452, 1496, 1716 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, J = 7.2 Hz, 3H), 3.82 (d, J = 14.0 Hz, 1H), 4.12−4.20 (m, 2H), 4.37 (br s, 1H), 4.45 (d, J = 15.6 Hz, 1H), 4.56 (s, 1H), 4.80 (s, 1H), 5.06 (d, J = 7.2 Hz, 1H), 5.18 (d, J = 15.6 Hz, 1H), 5.27 (s, 1H), 6.97−6.99 (m, 2H), 7.12−7.13 (m, 2H), 7.21−7.28 (m, 4H), 7.29−7.33 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 44.6, 50.1, 51.1, 60.7, 65.4, 69.4, 113.1, 127.2, 127.3, 127.9, 128.4, 128.6, 128.7, 129.1, 133.4, 136.7, 137.9, 144.2, 154.6, 171.5. HRMS (ESI) m/z calcd for $C_{29}H_{30}N_5O_2$ $[M + H]^+$ 480.2394, found 480.2384.

*Ethyl 1-Benzyl-4-(1-benzyl-1H-tetrazol-5-yl)-3-ethylidene-5-phenylpyrrolidine-2-carboxylate (**21b**).* Prepared from aziridine **1b** (100 mg, 0.36 mmol) and allene **10b** (0.53 mmol) affording **21a** as a white solid, 101 mg, in 57% yield. Mp 184.0−185.8 °C (from ethyl acetate/hexane). IR 701, 759, 1128, 1150, 1452, 1721 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.83 (d, J = 4.8 Hz, 3H), 1.21 (t, J = 6.8 Hz, 3H), 3.61 (d, J = 13.6 Hz, 1H), 3.73 (br s, 1H), 3.90 (br s, 1H), 4.11−4.14 (m, 3H), 4.54 (s, 1H), 5.07−5.12 (m, 2H), 5.67 (br s, 1H), 7.03 (br s, 2H), 7.26−7.31 (m, 13H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 14.4, 41.6, 50.0, 50.6, 60.4, 64.7, 69.5, 122.4, 127.2, 127.8, 128.4, 128.9, 129.1, 133.0, 136.4, 137.0, 138.0, 154.0, 172.2. Anal. calcd for $C_{30}H_{31}N_5O_2$: C, 73.00; H, 6.33; N, 14.19. Found: C, 72.84; H, 6.23; N, 14.14.

*Ethyl 1-Benzyl-4-(1-benzyl-1H-tetrazol-5-yl)-3-propylidene-5-phenylpyrrolidine-2-carboxylate (**21c**).* Prepared from aziridine **1b** (100 mg, 0.36 mmol) and allene **10c** (0.53 mmol) affording **21c** as a white solid, 91 mg, in 50% yield. Mp 168.5−169.9 °C (from ethyl acetate/hexane). IR 698, 707, 1029, 1130, 1451, 1495, 1718 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.47 (t, J = 7.6 Hz, 3H), 0.99−1.02 (m, 2H), 1.21 (t, J = 7.2 Hz, 3H), 3.62 (d, J = 14.0 Hz, 1H), 3.75 (d, J = 13.2 Hz, 1H), 3.90 (d, J = 14.0 Hz, 1H), 4.11−4.16 (m, 3H), 4.54 (s, 1H), 5.11 (br s, 1H), 5.57 (br s, 1H), 7.02−7.05 (m, 2H), 7.26−7.32 (m, 13H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 14.3, 22.6, 41.7, 49.9, 50.5, 60.4, 64.6, 69.4, 127.1, 127.7, 128.3, 128.4, 128.9, 129.1, 133.0, 134.9, 137.0, 138.1, 154.3, 172.2. HRMS (ESI) m/z calcd for $C_{31}H_{34}N_5O_2$ $[M + H]^+$ 508.2707, found 508.2714.

*Ethyl 1-Benzyl-4-(1-benzyl-1H-tetrazol-5-yl)-3-(2-methylpropylidene)-5-phenylpyrrolidine-2-carboxylate (**21d**).* Prepared from aziridine **1b** (100 mg, 0.36 mmol) and allene **10d** (0.53 mmol) affording **21d** as a white solid, 126 mg, in 67% yield. Mp 151.0−151.9 °C (from ethyl acetate/hexane). IR 702, 726, 1019, 1135, 1188, 1448, 1726 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.37 (d, J = 5.6 Hz, 3H), 0.46 (d, J = 5.6 Hz, 3H), 0.85−0.88 (m, 1H), 1.19 (t, J = 7.2 Hz, 3H), 3.64 (d, J = 14.0 Hz, 1H), 3.76 (d, J = 14.0 Hz, 1H), 3.89 (d, J = 15.2 Hz, 1H), 4.08−4.22 (m, 3H), 4.53 (s, 1H), 5.09−5.17 (m, 2H), 5.73 (d, J = 10.0 Hz, 1H), 7.05 (br s, 2H), 7.22−7.32 (m, 13H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.3, 22.0, 29.4, 41.7, 49.9, 50.5, 60.3, 64.4, 69.4, 127.1, 127.8, 128.3, 128.4, 128.8, 129.1, 133.0, 133.1, 134.4, 137.0, 138.1, 154.5, 172.2. HRMS (ESI) m/z calcd for $C_{32}H_{36}N_5O_2$ $[M + H]^+$ 522.2863, found 522.2843.

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*Ethyl 1-Benzyl-4-(1-benzyl-1H-tetrazol-5-yl)-3-(2,2-dimethylpropylidene)-5-phenylpyrrolidine-2-carboxylate (**21e**).* Prepared from aziridine **1b** (100 mg, 0.36 mmol) and allene **10e** (0.53 mmol) affording **21e** as a white solid, 102 mg, in 53% yield. Mp 181.0−183.0 °C (from ethyl acetate/hexane). IR 696, 704, 1121, 1151, 1182, 1449, 1735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.47 (s, 9H), 1.21 (t, J = 7.2 Hz, 3H), 3.69 (d, J = 15.2 Hz, 1H), 3.72 (d, J = 14.0 Hz, 1H), 4.04−4.10 (m, 1H), 4.19−4.27 (m, 1H), 4.43 (d, J = 6.0 Hz, 1H), 4.57 (s, 1H), 4.73 (d, J = 15.2 Hz, 1H), 5.17 (d, J = 6.0 Hz, 1H), 5.64 (s, 1H), 7.10−7.11 (m, 3H), 7.19−7.22 (m, 2H), 7.25−7.34 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 29.4, 33.2, 41.7, 49.6, 50.3, 60.2, 66.0, 70.4, 127.0, 128.2, 128.4, 128.7, 129.1, 131.6, 132.2, 137.2, 137.4, 138.1, 154.8, 172.5. HRMS (ESI) m/z calcd for $C_{33}H_{38}N_5O_2$ $[M + H]^+$ 536.3020, found 536.3012.

*Ethyl 1-Benzyl-4-(1-benzyl-1H-tetrazol-5-yl)-3-phenethylidene-5-phenylpyrrolidine-2-carboxylate (**21f**).* Prepared from aziridine **1b** (100 mg, 0.36 mmol) and allene **10f** (0.53 mmol) affording **21f** as a white solid, 195 mg, in 95% yield. Mp 133.0−134.2 °C (from ethyl acetate/hexane). IR 701, 746, 1114, 1183, 1453, 1494, 1720 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.13 (t, J = 7.2 Hz, 3H), 2.28−2.30 (m, 1H), 2.42−2.46 (m, 1H), 3.65 (d, J = 14.0 Hz, 1H), 3.77 (d, J = 14.0 Hz, 1H), 3.87 (d, J = 15.6 Hz, 1H), 4.08−4.13 (m, 2H), 4.21 (br s, 1H), 4.61 (s, 1H), 5.09 (d, J = 15.6 Hz, 1H), 5.16 (d, J = 4.4 Hz, 1H), 5.76 (br s, 1H), 6.67 (d, J = 6.4 Hz, 1H), 6.98−7.00 (m, 2H), 7.08−7.25 (m, 9H), 7.27−7.34 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 35.3, 41.9, 50.0, 50.5, 60.5, 64.7, 69.5, 126.1, 127.2, 127.7, 128.0, 128.3, 128.5, 129.0, 129.2, 132.8, 136.6, 136.9, 138.0, 138.6, 154.0, 172.0. Anal. Calcd for $C_{36}H_{35}N_5O_2$: C, 75.90; H, 6.19; N, 12.29. Found: C, 75.95; H, 6.22; N, 12.20.

*Ethyl 4-(1-Benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-3-methylene-5-phenylpyrrolidine-2-carboxylate (**23a**) and Ethyl 4-(1-Benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-3-methylene-5-phenylpyrrolidine-2-carboxylate (**24a**).* Prepared from aziridine **22** (100 mg, 0.37 mmol) and allene **10a** (0.55 mmol) affording **23a** as a yellow solid, 110 mg, in 63% yield and **24a** as a white solid, 52 mg, in 30% yield.

*Ethyl 4-(1-benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-3-methylene-5-phenylpyrrolidine-2-carboxylate (**23a**).* Mp 120.2−121.6 °C (from ethyl acetate/hexane). IR 698, 713, 895, 1179, 1307, 1454, 1747 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.84−1.27 (m, 6H), 1.31 (t, J = 7.2 Hz, 3H), 1.47−1.76 (m, 5H), 2.50−2.57 (m, 1H), 4.19−4.27 (m, 2H), 4.71 (d, J = 9.6 Hz, 2H), 4.81 (d, J = 7.6 Hz, 1H), 5.05 (s, 1H), 5.20 (d, J = 15.6 Hz, 1H), 5.32 (d, J = 15.6 Hz, 1H), 5.44 (s, 1H), 6.76 (br s, 2H), 7.09−7.11 (m, 3H), 7.17−7.20 (m, 2H), 7.37−7.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 24.1, 25.5, 25.8, 30.3, 32.4, 43.3, 50.6, 57.1, 61.1, 66.7, 66.9, 112.3, 127.7, 127.8, 127.9, 128.1, 128.9, 129.2, 133.5, 137.9, 143.5, 152.9, 174.5. Anal. calcd for $C_{28}H_{33}N_5O_2$: C, 71.31; H, 7.05; N, 14.85. Found: C, 71.41; H, 7.09; N, 14.81.

*Ethyl 4-(1-benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-3-methylene-5-phenylpyrrolidine-2-carboxylate (**24a**).* Mp 121.9−123.3 °C (from ethyl acetate/hexane). IR 694, 723, 895, 1165, 1315, 1449, 1752 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.80−1.24 (m, 4H), 1.24−1.31 (m, 1H), 1.36 (t, J = 7.2 Hz, 3H), 1.47−1.76 (m, 6H), 2.54−2.60 (m, 1H), 4.07 (d, J = 8.8 Hz, 1H), 4.23−4.33 (m, 2H), 4.51 (s, 1H), 4.71 (s, 1H), 4.87 (d, J = 15.6 Hz, 1H), 5.02 (d, J = 8.8 Hz, 1H), 5.18 (s, 1H), 5.40 (d, J = 15.6 Hz, 1H), 6.96−6.98 (m, 2H), 7.04−7.06 (m, 2H), 7.24−7.31 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 25.6, 26.0, 26.2, 29.5, 32.1, 49.8, 50.2, 56.3, 61.1, 65.6, 68.2, 110.0, 127.1, 127.4, 128.2, 128.6, 128.9, 129.0, 133.9, 140.1, 145.9, 153.9, 174.7. Anal. calcd for $C_{28}H_{33}N_5O_2.H_2O$: C, 68.69; H, 7.21; N, 14.30. Found: C, 68.62; H, 6.88; N, 14.26.

*Ethyl 4-(1-Benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-3-ethylidene-5-phenylpyrrolidine-2-carboxylate (**23b**) and Ethyl 4-(1-Benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-3-ethylidene-5-phenylpyrrolidine-2-carboxylate (**24b**).* Prepared from aziridine **22** (100 mg, 0.37 mmol) and allene **10b** (0.55 mmol) affording **23b** as a yellow solid, 97 mg, in 54% yield and **24b** as an oil, 22 mg, in 12% yield.

*Ethyl 4-(1-benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-3-ethylidene-5-phenylpyrrolidine-2-carboxylate (**23b**).* Mp 143.9−144.5 °C (from ethyl acetate/hexane). IR 705, 750, 1155, 1190, 1452, 1497, 1716 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.75−1.08 (m, 4H), 0.82 (d, J = 6.4 Hz, 3H), 1.30−1.36 (m, 1H), 1.32 (t, J = 7.2 Hz, 3H), 1.46−1.56 (m, 2H), 1.66−1.84 (m, 4H), 2.51−2.57 (m, 1H), 4.03 (d, J = 15.6 Hz, 1H), 4.16−4.24 (m, 3H), 4.78 (s, 1H), 4.99 (d, J = 15.6 Hz, 1H), 5.35 (d, J = 6.4 Hz, 1H), 5.67 (d, J = 6.0 Hz, 1H), 7.04 (br s, 2H), 7.15 (br s, 2H), 7.24−7.31 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 14.6, 25.7, 26.1, 26.4, 28.5, 32.0, 41.5, 49.8, 55.8, 60.6, 64.6, 66.7, 121.4, 127.8, 128.5, 128.9, 129.1, 133.0, 137.3, 137.5, 150.1, 176.3. Anal. calcd for $C_{29}H_{35}N_5O_2$: C, 71.72; H, 7.26; N, 14.42. Found: C, 71.66; H, 7.43; N, 14.58.

*Ethyl 4-(1-Benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-3-ethylidene-5-phenylpyrrolidine-2-carboxylate (**24b**).* IR 708, 730, 1151, 1186, 1454, 1719 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.64 (d, J = 7.6 Hz, 3H), 0.77−0.98 (m, 4H), 1.17−1.23 (m, 1H), 1.27 (t, J = 7.2 Hz, 3H), 1.39−1.72 (m, 6H), 2.46−2.52 (m, 1H), 3.85 (d, J = 6.4 Hz, 1H), 3.99 (d, J = 15.6 Hz, 1H), 4.16−4.26 (m, 2H), 4.51 (1H, s), 4.73 (d, J = 7.6 Hz, 1H), 5.27 (d, J = 15.6 Hz, 1H), 5.60 (d, J = 6.4 Hz, 1H), 6.81−6.83 (m, 2H), 7.17−7.20 (m, 6H), 7.28−7.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.2, 25.6, 25.9, 26.2, 29.5, 32.4, 46.8, 50.2, 56.5, 60.9, 66.5, 70.1, 121.6, 127.7, 128.6, 128.9, 129.2, 133.4, 135.9, 141.7, 154.4, 174.6. HRMS (ESI) m/z calcd for $C_{29}H_{36}N_5O_2$ $[M + H]^+$ 486.2863, found 486.2851.

*Ethyl 4-(1-benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-3-propylidene-5-phenylpyrrolidine-2-carboxylate (**23c**).* Prepared from aziridine **22** (100 mg, 0.37 mmol) and allene **10c** (0.55 mmol) affording **23c** as a white solid, 61 mg, in 33% yield. mp 132.1−133.8 °C (from ethyl acetate/hexane). IR 705, 720, 1123, 1149, 1243, 1438, 1498, 1731 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.50 (t, J = 7.2 Hz, 3H), 0.75−1.07 (m, 5H), 1.26−1.39 (m, 1H), 1.31 (t, J = 7.2 Hz, 3H), 1.45−1.55 (m, 2H), 1.66−1.74 (m, 3H), 1.82−1.85 (m, 1H), 2.53−2.58 (m, 1H), 4.01 (d, J = 15.6 Hz, 2H), 4.14 (d, J = 6.4 Hz, 1H), 4.16−4.23 (m, 2H), 4.78 (s, 1H), 5.02 (d, J = 15.6 Hz, 1H), 5.33 (d, J = 6.4 Hz, 1H), 5.54 (t, J = 6.0 Hz, 1H), 7.03 (br s, 2H), 7.24−7.27 (m, 2H), 7.28−7.32 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 14.2, 22.8, 25.7, 26.1, 26.4, 28.5, 32.0, 41.6, 49.8, 55.8, 60.5, 64.5, 66.7, 127.7, 128.3, 128.4, 128.9, 129.1, 133.0, 136.0, 137.3, 154.4, 176.3. HRMS (ESI) m/z calcd for $C_{30}H_{38}N_5O_2$ $[M + H]^+$ 500.3020, found 500.3004.

*Ethyl 4-(1-Benzyl-1H-tetrazol-5-yl)-1-cyclohexyl-3-(2-methylpropylidene)-5-phenylpyrrolidine-2-carboxylate (**23d**).* Prepared from aziridine **22** (100 mg, 0.37 mmol) and allene **10d** (0.55 mmol) affording **23d** as a white solid, 110 mg, in 58% yield. mp 131.4−132.3 °C (from ethyl acetate/hexane). IR 705, 751, 889, 1032, 1098, 1226, 1454, 1719 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.43 (d, J = 6.4 Hz, 6H), 0.73−1.08 (m, 6H), 1.29 (t, J = 7.2 Hz, 3H), 1.45−1.86 (m, 6H), 2.54−2.60 (m, 1H), 3.97 (d, J = 15.6 Hz, 2H), 4.13 (d, J = 6.0 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 4.77 (s, 1H), 5.08 (d, J = 15.6 Hz, 1H), 5.31−5.35 (m, 3H), 7.04 (br s, 3H), 7.24−7.28 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.1, 21.8, 25.7, 26.1, 26.4, 28.6, 29.4, 32.0, 41.6, 49.9, 55.8, 60.4, 64.5, 66.7, 127.7, 128.4, 128.9, 129.1, 133.0, 133.4, 134.2, 137.3, 154.7, 176.2. Anal. calcd for $C_{31}H_{39}N_5O_2$: C, 72.48; H, 7.65; N, 13.63. Found: C, 72.58; H, 7.53; N, 13.71.

X-ray Crystallography Structure Determination. X-ray data for compound **23a** were collected using a small single crystal and Mo Kα radiation. The crystallographic structure was solved by direct methods using SHELXT-2014/4.[16] Refinements were carried out with the SHELXL-2014/7 package.[17] All refinements were made by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms could be located on a difference Fourier synthesis; their positions were refined as riding on parent atoms with isotropic temperature factors using SHELXL-2014/7 defaults that constrain these atoms to idealized positions. X-ray data collection, processing parameters, and a summary of structure refinement results are presented in Table S1 (Supporting Information).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01679.

X-ray structural data for **23a** (CIF)

^1H and ^{13} NMR spectra for all new compounds (PDF)

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AUTHOR INFORMATION

Corresponding Author

*E-mail: tmelo@ci.uc.pt.

Notes

The authors declare no competing financial interest.

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