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**PAPER**

# The reaction of β-lactam carbenes with 3,6-dipyridyltetrazines: switch of reaction pathways by 2-pyridyl and 4-pyridyl substituents of tetrazines†

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The reactions of β-lactam carbenes with both 3,6-di(2-pyridyl)tetrazine and 3,6-di(4-pyridyl)tetrazine were studied. It was found that β-lactam carbenes reacted with 3,6-di(2-pyridyl)tetrazine to produce 5-triazolo[1,5-*a*]pyridylpyrrol-2-ones in good yields, while with 3,6-di(4-pyridyl)tetrazine, they afforded pyrido[*c*]cyclopenta[*b*]pyrrol-2-ones in moderate yields. Both reactions were proposed to follow cascade mechanisms containing a 3,6*a*-dipyridylpyrrolo[3,2-*c*]pyrazol-5-one intermediate. The different pathways of the transformation of pyrrolo[3,2-*c*]pyrazol-5-ones were switched by the 2- and 4-pyridyl substituents. This work not only provided a simple and efficient strategy for the construction of novel triazolo[1,5-*a*]pyridine and pyrido[*c*]cyclopenta[*b*]pyrrole derivatives, respectively, but also revealed two different thermal transformation patterns of 3*H*-pyrazole compounds.

## Introduction

β-Lactam carbenes, namely 2-azetidinone-4-ylidenes, were firstly generated from thermolysis of spiro[β-lactam-4,2′-oxadiazolines] by Warkentin and co-workers in the 1990's.[1,2] They investigated the reactions of β-lactam carbenes with both electron-rich and electron-deficient alkenes or alkynes to produce β-lactam-spiro-cyclopropane or β-lactam-spiro-cyclopropene derivatives, and demonstrated the β-lactam carbenes to be ambiphilic carbenes but with pronounced electrophilic activity.[3,4] We have been interested in the chemistry of β-lactam carbenes, not only in their ambiphilic reactivity but more importantly in their synthetic applications.[5–9] We demonstrated that β-lactam carbenes are unique intermediates in the construction of mono-, spiro- or fused heterocyclic compounds with or without a β-lactam moiety. For example, β-lactam carbenes underwent nucleophilic reaction toward aryl isocyanates to produce β-lactam-spiro-indole-2-ones.[5] On the other hand, β-lactam carbenes underwent electrophilic addition to aryl isonitriles to afford high yields of 2-(β-lactam-4-ylidene)indoles that rearranged into δ-carbolin-2-ones in the presence of an acid.[6] While the same carbenes reacted with alkyl isonitriles, 4-cyano or 4-carbamoyl substituted β-lactams were obtained depending on the alkyl groups of isonitriles.[7] Very recently, we found that the reaction of β-lactam carbenes with 3,6-diphenyl-1,2,4,5-tetrazines proceeded in a five-step cascade process to produce indeno[2,1-*b*]pyrrol-2-ones in good yields.[8] We envisioned that, by varying the aryl substituents of 3,6-diaryltetrazines, the reaction between β-lactam carbenes and 3,6-diaryltetrazines might be a general method for the synthesis of aryl-fused cyclopenta[*b*]pyrrol-2-one compounds. Thus, we undertook the current study on the reaction of β-lactam carbenes with 3,6-di(2-pyridyl)tetrazines and 3,6-di(4-pyridyl)tetrazines. Interestingly, the similar reactions of β-lactam carbenes with di(2-pyridyl)- and with di(4-pyridyl)tetrazines produced totally different products, 5-triazolo[1,5-*a*]pyridylpyrrol-2-ones or pyrido[*c*]cyclopenta[*b*]pyrrol-2-ones, *via* two different transformations of pyrrolo[3,2-*c*]pyrazol-5-one intermediates. Herein, we report our results.

## Results and discussion

We first studied the reaction of β-lactam carbenes with di(2-pyridyl)tetrazines. In practice, all β-lactam carbenes **2** are generated *in situ* by thermolysis of spiro[β-lactam-4,2′-oxadiazolines] **1**, which were prepared on the basis of Warkentin's method[1,2] and our previous report.[5,9] Since the optimal temperature for the generation of carbenes **2** from spiro-oxadiazolines **1** is around 100–110 °C according to Warkentin's reports[1–4] and our experience,[5–9] the reaction between 3,3-dimethyl-1-(*p*-methoxyphenyl)-2-azetidinone-4-ylidene **2c** and 3,6-di(2-pyridyl)tetrazine **3** (**2c** : **3** = 1 : 1) was initially examined in refluxing 1,4-dioxane, which produced 3,6*a*-di(2-pyridyl)pyrrolo[3,2-*c*]pyrazol-5-one **4c** as a major product in 40% yield along with 7% of minor product 5-triazolo[1,5-*a*]pyridylpyrrol-2-one **5c**. The spectroscopic analysis indicated that **4c** and **5c** were isomeric products derived from 1 + 1 addition of carbene **2c** with tetrazine **3** with the loss of one $N_2$ molecule. It was found that the reaction of β-lactam carbene **2c** with di(2-pyridyl)tetrazine **3** firstly yielded product **4c**, which was converted into **5c** in prolonged time under heating. Thus, the reaction conditions for the predominant formation of **4c** or **5c** were optimized by varying the ratio of starting materials,

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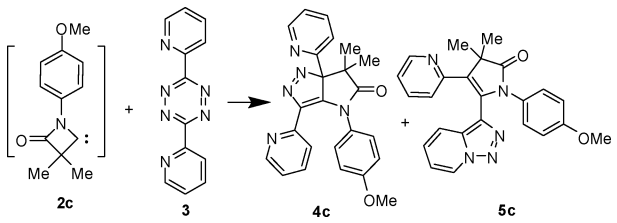
† Electronic supplementary information (ESI) available: NMR data and crystal structure data for compounds **4c**, **5c** and **8i**. CCDC reference numbers 844397–844399. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob06595e

**Table 1** Optimization of reaction conditions for the predominant formation of **4c** or **5c** from interaction of 3,3-dimethyl-1-(p-methoxyphenyl)-2-azetidinone-4-ylidene **2c** with 3,6-di(2-pyridyl)tetrazine **3**



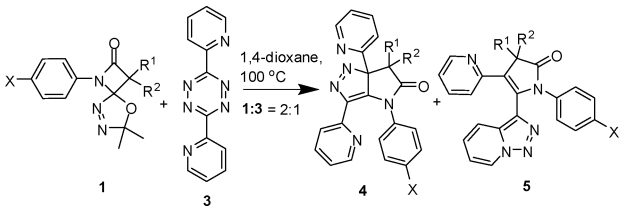

| | Reaction conditions | | | | Yield | |
|---|---|---|---|---|---|---|
| Entry | **1c** : **3** | Solvent | Temp. | Time (h) | **4c** | **5c** |
| 1 | 1 : 1 | 1,4-Dioxane | 100 | 9 | 40 | 7 |
| 2 | 1.5 : 1 | 1,4-Dioxane | 100 | 9 | 60 | 10 |
| 3 | 2 : 1 | 1,4-Dioxane | 100 | 5 | 70 | 15 |
| 4 | 1.5 : 1 | *n*-Heptane | 100 | 12 | 22 | 49 |
| 5 | 1.5 : 1 | Toluene | 100 | 9 | 50 | 11 |
| 6 | 1.5 : 1 | Toluene | 110 | 16 | 28 | 60 |
| 7 | 1.5 : 1 | 1,1,2-Trichloroethane | 110 | 24 | — | 43 |
| 8 | 1.5 : 1 | Xylene | 140 | 5 | — | 92 |

reaction temperature and solvents that were chemically inert towards carbenes **2** (Table 1). By using excess amount of carbene precursor **1c** (**1c** : **3** = 2 : 1) to promote the interaction of carbene with tetrazine and controlling both reaction time and temperature to inhibit the transformation of **4c** to **5c**, 70% yield of **4c** was obtained from the reaction in 1,4-dioxane at 100 °C (Table 1, entry 3). On the other hand, it was noted that increasing reaction temperature in toluene significantly improved the yield of **5c** (Table 1, entries 5 and 6). While further elevating reaction temperature in xylene, to our delight, product **5c** was obtained in 92% yield from the reaction conducted in refluxing xylene (Table 1, entry 8).

The generality of the reaction was studied, respectively, under the optimized conditions for the selective formation of products **4** or **5**. The reaction of β-lactam carbenes that were attached by different substituents with di(2-pyridyl)tetrazine **3** was firstly examined at 100 °C in 1,4-dioxane. As summarized in Table 2, the *N*-aryl group of β-lactam carbenes **2** showed little effects on the reaction. By keeping reaction temperature at 100 °C and time in 3.5–5 h, all reactions of *N*-phenyl, *N*-(4-methylphenyl), *N*-(4-methoxyphenyl), *N*-(4-chlorophenyl) and *N*-(4-bromophenyl) substituted β-lactam carbenes **2a–2e** with di(2-pyridyl)tetrazine **3** produced pyrrolo[3,2-*c*]pyrazol-5-ones **4a–4e** as major products in 70–83% yields, along with a small amount of byproducts **5a–5e** (Table 2, entries 1–5). However, the 3,3-alkyl substituents of carbene reactants have influence on the efficiency of both the reaction between carbenes **2** and tetrazine **3**, and the transformation from products **4** to **5**. For example, the reaction between 3,3-cyclohexyl-β-lactam carbene **2h** and tetrazine **3** proceeded somewhat more slower than that of methyl or/and ethyl substituted carbenes, probably due to the steric hindrance between two reactants (Table 2, entry 8). While all 3,3-dimethyl-β-lactam carbenes **2a–2e** reacted with tetrazine **3** to afford **4a–4e** as major products in good yields, the reaction of 3,3-diethyl- and 3-ethyl-3-methyl substituted carbenes **2f** and **2g** with **3** afforded **5f** and **5g**, respectively, as major products under the similar conditions, which indicated the isomerization of products **4f** and **4g** being faster than that of **4a–4e**. To selectively obtain compounds **5**, the reaction of β-lactam carbenes **2** with di(2-pyridyl)tetrazine **3** was then conducted under the optimized conditions for the formation of 5-triazolo[1,5-*a*]pyridylpyrrol-2-ones **5**. As indicated in Table 3, in refluxing xylene, all carbenes **2a–2h** bearing different substituents reacted with tetrazine **3** to afford pyrrol-2-ones **5** in good to excellent yields, although the reaction between 3,3-cyclohexyl substituted β-lactam carbene **2h** and tetrazine **3** proceeded more slowly than others.

Following the reaction of β-lactam carbenes **2** with di(2-pyridyl)tetrazine **3**, the behavior of carbenes **2** towards di(4-pyridyl)tetrazine **6** was also investigated. The optimized conditions for the reaction of carbenes **2** with di(2-pyridyl)tetrazine **3** were firstly employed in the reaction of β-lactam carbene **2c** with

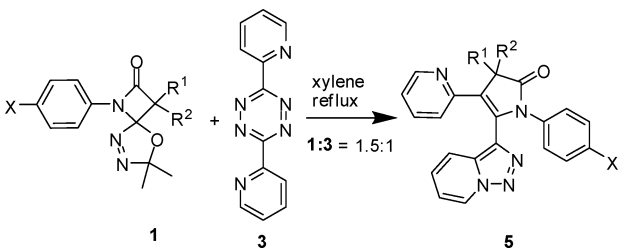
**Table 2** The reaction of spiro[β-lactam-4,2′-oxadiazolines] **1** and di(2-pyridyl)tetrazine **3** in 1,4-dioxane at 100 °C




| | | | | Yield (%) | |
|---|---|---|---|---|---|
| Entry | **1** | X, $R^1$, $R^2$ | Time (h) | **4** | **5** |
| 1 | **1a** | H, $CH_3$, $CH_3$ | 4 | **4a**: 83 | **5a**: 6 |
| 2 | **1b** | $CH_3$, $CH_3$, $CH_3$ | 4 | **4b**: 77 | **5b**: 10 |
| 3 | **1c** | $OCH_3$, $CH_3$, $CH_3$ | 5 | **4c**: 70 | **5c**: 15 |
| 4 | **1d** | Cl, $CH_3$, $CH_3$ | 3.5 | **4d**: 82 | —[a] |
| 5 | **1e** | Br, $CH_3$, $CH_3$ | 4 | **4e**: 73 | —[a] |
| 6 | **1f** | $CH_3$, $C_2H_5$, $C_2H_5$ | 3.5 | **4f**: 25 | **5f**: 55 |
| 7 | **1g** | $CH_3$, $CH_3$, $C_2H_5$ | 4 | **4g**: 37[b] | **5g**: 44 |
| 8 | **1h** | $CH_3$, $(CH_2)_5$ | 6 | **4h**: 88 | —[a] |

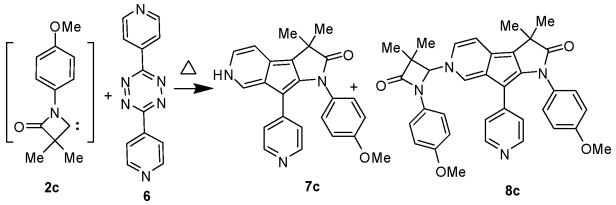
[a] A little amount of byproduct **5** was detected by TLC without isolation. [b] **4g** is a mixture of diastereomers that could not be separated by column chromatography.

**Table 3** The reaction of spiro[β-lactam-4,2′-oxadiazolines] **1** and di(2-pyridyl)tetrazine **3** in refluxing xylene




| | | | | Yield (%) |
|---|---|---|---|---|
| Entry | **1** | X, $R^1$, $R^2$ | Time (h) | **5** |
| 1 | **1a** | H, $CH_3$, $CH_3$ | 5 | **5a**: 87 |
| 2 | **1b** | $CH_3$, $CH_3$,$CH_3$ | 4 | **5b**: 83 |
| 3 | **1c** | $OCH_3$, $CH_3$, $CH_3$ | 4 | **5c**: 92 |
| 4 | **1d** | Cl, $CH_3$, $CH_3$ | 4 | **5d**: 91 |
| 5 | **1e** | Br, $CH_3$, $CH_3$ | 4 | **5e**: 80 |
| 6 | **1f** | $CH_3$, $C_2H_5$, $C_2H_5$ | 4 | **5f**: 82 |
| 7 | **1g** | $CH_3$, $CH_3$, $C_2H_5$ | 3 | **5g**: 90 |
| 8 | **1h** | $CH_3$, $(CH_2)_5$ | 12 | **5h**: 75 |

**Table 4** Reaction of β-lactam carbene **2c** with 3,6-di(4-pyridyl)tetrazine **6** under different conditions



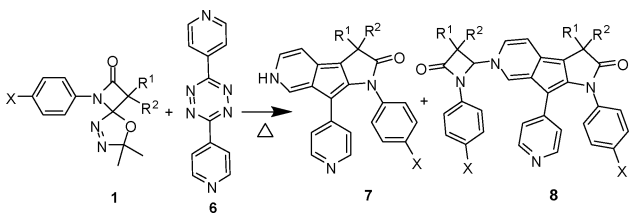

| | Reaction conditions | | | | Yield | |
|---|---|---|---|---|---|---|
| Entry | **1c** : **6** | Solvent | Temp. (°C) | Time (h) | **7c** | **8c** |
| 1 | 1.5 : 1 | 1,4-Dioxane | 100 | 12 | 36 | 61 |
| 2 | 2 : 1 | 1,4-Dioxane | 100 | 13 | 12 | 78 |
| 3 | 1.5 : 1 | Xylene | 140 | 6 | 42 | 21 |
| 4 | 1 : 1 | *n*-Heptane | 100 | 12 | 51[a] | — |
| 5 | 1.5 : 1 | *n*-Heptane | 100 | 12 | 65 | — |
| 6 | 1 : 1 | Toluene | 110 | 10 | 62[a] | 23 |
| 7 | 1.5 : 1 | Toluene | 110 | 10 | 65 | 31 |
| 8 | 1.5 : 1 | 1,1,2-Trichloroethane | 110 | 12 | 36 | 5 |

[a] When two reactants were employed in the ratio of 1 : 1, partial tetrazine **6** was not consumed.

di(4-pyridyl)tetrazine **6**. It was found that the reaction of **2c** with **6** (**2c** : **6** = 1.5 : 1) produced two compounds **7c** and **8c** with low selectivity in both refluxing 1,4-dioxane and xylene (Table 4, entries 1 and 3). After the spectroscopic analyses, product **7c** was identified as 3,3-dimethyl-1-(*p*-methoxyphenyl)-8-(4-pyridyl)pyrido[*c*]cyclopenta[*b*]pyrrol-2-one, and **8c** was a *N*-β-lactam substituted derivative of **7c**. Based on the structures of two products, product **8c** was apparently resulted from the N–H insertion of β-lactam carbene **2c** to product **7c**. We considered that if product **7c** could be removed from the reaction mixture during the reaction process, the formation of **8c** would be limited and then the yield of **7c** might be improved. It was noted that **7c** has very low solubility in many common organic solvents, such as heptane, toluene, dioxane, chloroform, ethyl acetate, acetone and ethanol. The use of low polarity solvents led to the precipitation of **7c** from solvent during reaction. Thus, the reaction of carbene **2c** with di(4-pyridyl)tetrazine **6** was examined in refluxing toluene and *n*-heptane, respectively. Although the reaction in toluene afforded a mixture of **7c** and **8c** in a ratio about 2 : 1 (Table 4, entry 7), product **7c** was obtained in 65% yield from the reaction in *n*-heptane and almost no **8c** was isolated (Table 4, entry 5). Comparing the reactions of carbene **2c** with tetrazine **6** (**2c** : **6** = 1.5 : 1) in dioxane, toluene and *n*-heptane, it was found that the reaction in dioxane or toluene gave higher total yields of products (**7c** + **8c**) than that in *n*-heptane, but with lower selectivity in the formation of **7c** *versus* **8c**. On the other hand, the reactions in toluene and *n*-heptane preferred to the formation of **7c**, while **8c** was isolated as major product in dioxane. The lower reactivity and higher selectivity of the reaction in *n*-heptane can be explained by the solubility of reactants or products in solvent. While the low solubility of di(4-pyridyl)tetrazine **6** in *n*-heptane decreased the reaction efficiency between carbene **2c** and tetrazine **6**, the non-solubility of product **7c** in *n*-heptane inhibited the reaction of carbene **2c** with **7c**. The reversed selectivity of reaction in dioxane and toluene was also attributed to the different solubilities of **7c** in these two solvents (Table 4, entries 1 and 7). Since 1,4-dioxane was the optimal solvent for the formation of product **8c** and it was derived from 2 + 1 addition of carbene **2c** with tetrazine **6**, two equivalents of **2c** were then employed to react with **6** in refluxing 1,4-dioxane, which improved the yield of **8c** to 78%.

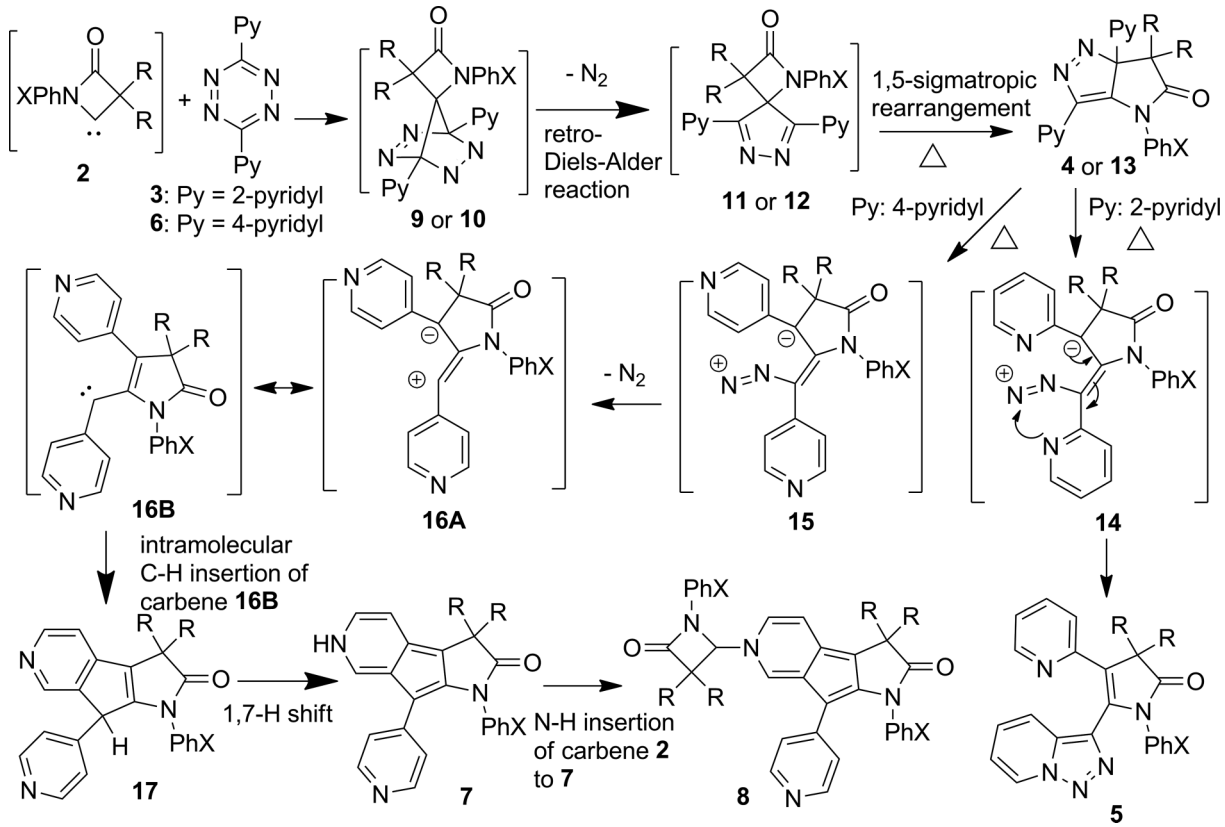
The generality of the reaction between β-lactam carbenes **2** bearing different substituents and di(4-pyridyl)tetrazine **6** was studied in refluxing *n*-heptane and 1,4-dioxane, respectively. It was found that the substituents of carbenes showed small influence on the reaction. As shown in Table 5, all carbenes **2** bearing different aryl and alkyl substituents on the β-lactam rings reacted with di(4-pyridyl)tetrazine **6** in refluxing *n*-heptanes to afford pyrido[*c*]cyclopenta[*b*]pyrrol-2-ones **7** in moderate yields. While

**Table 5** Reaction of β-lactam carbenes **2** with 3,6-di(4-pyridyl)tetrazine **6** in refluxing *n*-heptane or 1,4-dioxane




| | | | | | | | Yield (%) | |
|---|---|---|---|---|---|---|---|---|
| Entry | **1** | X, $R^1$, $R^2$ | **1** : **6** | Solvent | Temp. | Time (h) | **7** | **8** |
| 1 | **1a** | H, $CH_3$, $CH_3$ | 1.5 : 1 | *n*-Heptane | Reflux | 8 | **7a**: 65 | — |
| 2 | **1b** | $CH_3$, $CH_3$, $CH_3$ | 1.5 : 1 | *n*-Heptane | Reflux | 8 | **7b**: 63 | — |
| 3 | **1c** | $OCH_3$, $CH_3$, $CH_3$ | 1.5 : 1 | *n*-Heptane | Reflux | 8 | **7c**: 65 | — |
| 4 | **1d** | Cl, $CH_3$, $CH_3$ | 1.5 : 1 | *n*-Heptane | Reflux | 8 | **7d**: 60 | — |
| 5 | **1f** | $CH_3$, $C_2H_5$, $C_2H_5$ | 1.5 : 1 | *n*-Heptane | Reflux | 8 | **7f**: 56 | — |
| 6 | **1g** | $CH_3$, $CH_3$, $C_2H_5$ | 1.5 : 1 | *n*-Heptane | Reflux | 8 | **7g**: 51 | — |
| 7 | **1a** | H, $CH_3$, $CH_3$ | 2 : 1 | 1,4-Dioxane | Reflux | 13 | **7a**: 8 | **8a**: 57 |
| 9 | **1b** | $CH_3$, $CH_3$, $CH_3$ | 2 : 1 | 1,4-Dioxane | Reflux | 13 | **7b**: 7 | **8b**: 70 |
| 9 | **1c** | $OCH_3$, $CH_3$, $CH_3$ | 2 : 1 | 1,4-Dioxane | Reflux | 13 | **7c**: 12 | **8c**: 78 |
| 10 | **1d** | Cl, $CH_3$, $CH_3$ | 2 : 1 | 1,4-Dioxane | Reflux | 10 | **7d**: 14 | **8d**: 45 |
| 11 | **1i** | $OCH_3$, $C_2H_5$, $C_2H_5$ | 2 : 1 | 1,4-Dioxane | Reflux | 11 | — | **8i**: 79 |
| 12 | **1j** | $OCH_3$, $(CH_2)_4$ | 2 : 1 | 1,4-Dioxane | Reflux | 18 | **7j**: 5 | **8j**: 65 |




**Scheme 1** The proposed mechanisms for the reactions of β-lactam carbenes with 3,6-di(2-pyridyl)tetrazine and 3,6-di(4-pyridyl)tetrazine, respectively.



in refluxing 1,4-dioxane, the reaction of carbenes **2** with tetrazine **6** produced ***N***-β-lactam substituted pyrido[*c*]cyclopenta[*b*]pyrrol-2-ones **8** in 45–79% yields, along with a small amount of products **7**.

The structures of all products **4**, **5**, **7** and **8** were ascertained by spectroscopic methods. $^1$H NMR, MS and microanalysis indicated that both products **4** and **5** were the 1 + 1 adducts of β-lactam carbenes **2** and di(2-pyridyl)tetrazine **3** with the loss of one $N_2$ molecule, while products **7** were derived from the 1 + 1 addition of a carbene **2** and a di(4-pyridyl)tetrazine **6** with the loss of two $N_2$ molecules and products **8** were the 1 + 1 adducts of products **7** and carbenes **2**. Since the spectroscopic data did not allow full verification of the structures, the structures of **4c**, **5c** and **8i** were determined unambiguously by single crystal X-ray diffraction analysis†.

According to literature, the reactions of nucleophilic or ambiphilic carbenes with 3,6-disubstituted tetrazines generally proceed *via* a [4 + 1] cycloaddition followed by a retro [4 + 2] Diels–Alder cycloaddition to produce pyrazole derivatives.[10-13] In our previous study, we have demonstrated that the reaction of β-lactam carbenes with 3,6-diphenyltetrazines produce indeno[2,1-*b*]pyrrol-2-ones *via* the isolable β-lactam-spiro-pyrazole and pyrrolo[3,2-c]pyrazol-5-one intermediates.[8] However, it is surprising that the reactions of β-lactam carbenes **2** with 3,6-di(2-pyridyl)tetrazine **3** and 3,6-di(4-pyridyl)tetrazine **6** produce totally different types of products, the bicyclic 5-triazolo[1,5-*a*]pyridylpyrrol-2-ones **5** and tricyclic pyrido[*c*]cyclopenta[*b*]pyrrol-2-ones **7**, respectively. On the basis of our knowledge of the interaction between β-lactam carbenes **2** and 3,6-diphenyltetrazine, two cascade mechanisms are proposed, respectively, for the reactions of β-lactam carbenes **2** with 3,6-di(2-pyridyl)tetrazine **3** and 3,6-di(4-pyridyl)tetrazine **6**. As illustrated in Scheme 1, a [4 + 1] cycloaddition of β-lactam carbenes **2** with 3,6-di(2-pyridyl)tetrazine **3** or 3,6-di(4-pyridyl)tetrazine **6** forms the bridged compounds **9** or **10**, which are converted to β-lactam-spiro-pyrazoles **11** or **12** by a retro-Diels–Alder reaction. Under the heating condition, spiro-pyrazoles **11** or **12** undergo a 1,5-sigmatropic rearrangement to produce isolable 3,6*a*-di(2-pyridyl)pyrrolo[3,2-c]pyrazol-5-ones **4** or 3,6*a*-di(4-pyridyl)pyrrolo[3,2-c]pyrazol-5-ones **13**, respectively. The isomerization of pyrrolo[3,2-*c*]pyrazol-5-ones **4** to triazolo[1,5-*a*]pyridines **5** most probably proceeds *via* the breaking of pyrazole ring of **4** to form dipolar intermediates **14**. Intramolecular cyclization of **14** between the diazo species and the nearby nitrogen atom of pyridyl affords triazolo[1,5-*a*]pyridines **5**. In the reaction of carbenes **2** with 3,6-di(4-pyridyl)tetrazine **6**, the intermediates 3,6*a*-di(4-pyridyl)pyrrolo[3,2-*c*]pyrazol-5-ones **13** are unstable and have not been isolated. Decomposition of the pyrazole rings of pyrrolo[3,2-*c*]pyrazol-5-ones **13** with the loss of one $N_2$ molecule probably forms the carbene intermediates **16B**, which undergo an intramolecular insertion to the C–H bond of the pyridyl to afford pyrido[*c*]cyclopenta[*b*]pyrrol-2-ones **7**. Insertion of β-lactam carbenes **2** to the N–H bond of products **7** produced ***N***-β-lactam substituted pyrido[*c*]cyclopenta[*b*]pyrrol-2-ones **8**. The different transformations of pyrrolo[3,2-*c*]pyrazol-5-one intermediates **4** and **13** can be explained by the different stabilities and structures of the dipolar intermediates **14** and **15** derived from breaking of pyrazole ring of **4** and **13**. Since 2-pyridyl has a stronger electron-withdrawing inductive effect than

4-pyridyl group, the anions of intermediates **14** might be more stable than **15**. Meanwhile, the anions of **14** can be delocalized on the nitrogen atom of 2-pyridyl attached to the same carbon with the diazo group, and then catches the diazo species to form the triazole rings of products **5**. On the contrary, the less stable dipolar intermediates **15** releases a $N_2$ molecule to form carbene intermediates **16B**, which undergoes C–H insertion to the pyridyl to form the cyclopentadiene moieties of products **7**.

## Conclusions

In summary, we have studied the reactions of β-lactam carbenes with both 3,6-di(2-pyridyl)tetrazine and 3,6-di(4-pyridyl)tetrazine. Under the heating conditions, β-lactam carbenes reacted with 3,6-di(2-pyridyl)tetrazine to produce 5-triazolo[1,5-*a*]pyridylpyrrol-2-ones in good yields, while with 3,6-di(4-pyridyl)tetrazine, pyrido[*c*]cyclopenta[*b*]pyrrol-2-ones were obtained in moderate yields. Both reactions proceeded *via* a 3,6*a*-dipyridylpyrrolo[3,2-*c*]pyrazol-5-one intermediate. The transformation pathways of pyrrolo[3,2-*c*]pyrazol-5-one intermediates were switched by the 2-pyridyl or 4-pyridyl substituents, which led to the formation of totally different types of products. This work not only provided a simple and efficient strategy for the construction of novel triazolo[1,5-*a*]pyridine derivatives and the new pyrido[*c*]cyclopenta[*b*]pyrrole ring system, respectively, but also revealed two different thermal transformation patterns of 3*H*-pyrazole compounds that were regulated by their substituents.

## Experimental

Melting points are uncorrected. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) were recorded in the indicated solvents. J values are reported in Hz. IR spectra were recorded using an AVATAR 360 FT-IR spectrometer. Mass spectra were recorded on a Surveyor MSQ Plus (ESI) instrument and elemental analyses were performed on a GMBH Vario EL instrument. Column chromatography was performed using 200–300 mesh silica gel.

### General procedure for the reaction of β-lactam carbenes with 3,6-di(2-pyridyl)tetrazine in 1,4-dioxane

Under nitrogen atmosphere, the mixture of spiro[β-lactam-4,2′-oxadiazolines] **1**[1,2,5,9] (2 mmol) and 3,6-di(2-pyridyl)tetrazine **3**[14] (1 mmol) was heated in slightly refluxing 1,3-dioxane (50 mL) for 3.5–6 h (the time for each reaction was listed in Table 2). After removal of the solvent under vacuum, the residue was subject to chromatography on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate from 10 : 1 to pure ethyl acetate to give products 3,6*a*-di(2-pyridyl)pyrrolo[3,2-*c*]pyrazol-5-ones **4** in 25–88% yields and 5-triazolo[1,5-*a*]pyridylpyrrol-2-ones **5** in 6–55% yields. Products **4** or **5** were further purified by recrystallization in ethyl acetate and petroleum ether.

**6,6-Dimethyl-4-phenyl-3,6*a*-di(2-pyridyl)-6,6*a*-dihydropyrrolo-[3,2-*c*]pyrazol-5-one 4a.** 83%, mp 152–153 °C; IR $\nu$ (cm$^{-1}$) 1757, 1635, 1583, 1500; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.46 (d, $J$ = 4.1 Hz, 1H), 8.11 (d, $J$ = 4.2 Hz, 1H), 7.81 (d, $J$ = 8.0 Hz, 1H), 7.67 (td, $J$ = 7.8, 1.8 Hz, 1H), 7.56–7.61 (m, 2H), 7.38–7.40 (m, 3H), 7.36 (d, $J$ = 7.7, 3.1 Hz, 2H), 7.20 (dd, $J$ = 8.5, 4.8 Hz, 1H), 7.01 (dd, $J$ = 7.4, 4.9 Hz, 1H), 1.39 (s, 3H), 1.14 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 183.0, 161.3, 154.9, 149.7, 149.12, 149.07, 137.0, 136.3, 135.9, 134.0, 128.3, 127.3, 125.7, 123.6, 122.1, 121.7, 107.1, 55.04, 21.24, 18.95; MS (EI): 309 (55), 337 (100), 380 (45, M-1), 382 (35%, M+1). Anal. Calcd for $C_{23}H_{19}N_5O$: C 72.42, H 5.02, N 18.36; Found: C72.13, H 4.87, N 18.30.

**6,6-Dimethyl-3,6*a*-di(2-pyridyl)-4-*p*-tolyl-6,6*a*-dihydropyrrolo-[3,2-*c*]pyrazol-5-one 4b.** 77%, mp 119–120 °C; IR $\nu$ (cm$^{-1}$) 1755, 1638, 1583, 1514; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.46 (d, $J$ = 4.0 Hz, 1H), 8.17 (d, $J$ = 4.2 Hz, 1H), 7.74 (d, $J$ = 8.0 Hz, 1H), 7.66 (dt, $J$ = 7.6, 1.8 Hz, 1H), 7.59 (d, $J$ = 7.8 Hz, 1H), 7.55 (dd, $J$ = 7.8, 1.7 Hz, 1H), 7.14–7.21 (m, 5H), 7.02 (dd, $J$ = 6.8, 5.0 Hz, 1H), 2.41 (s, 3H), 1.38 (s, 3H), 1.13 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 183.1, 161.9, 154.9, 149.4, 149.0, 148.8, 137.4, 137.0, 136.3, 133.7, 133.3, 129.2, 129.0, 125.5, 123.6, 122.3, 121.8, 107.2, 55.1, 21.3, 21.2, 18.9; HRMS (ESI): 396.1823 (M+1), Anal. Calcd for $C_{24}H_{22}N_5O$: 396.1824 (M+1).

**4-(4-Methoxyphenyl)-6,6-dimethyl-3,6*a*-di(2-pyridyl)-6,6*a*-dihydropyrrolo[3,2-*c*]pyrazol-5-one 4c.** 70%, mp 162–163 °C; IR $\nu$ (cm$^{-1}$) 1773, 1628, 1582, 1512; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.47 (d, $J$ = 4.1 Hz, 1H), 8.19 (d, $J$ = 4.6 Hz, 1H), 7.77 (d, $J$ = 8.0 Hz, 1H), 7.66 (td, $J$ = 7.8, 1.6 Hz, 1H), 7.58 (d, $J$ = 7.8 Hz, 1H), 7.56 (td, $J$ = 7.8, 1.6 Hz, 1H), 7.20–7.22 (m, 3H), 7.02 (dd, $J$ = 7.4, 4.9 Hz, 1H), 6.90 (d, $J$ = 8.9 Hz, 2H), 3.85 (s, 3H), 1.37 (s, 3H), 1.12 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 183.4, 161.8, 158.8, 155.0, 149.8, 149.2, 149.0, 137.0, 135.9, 133.9, 129.5, 127.1, 123.6, 122.1, 121.7, 113.6, 107.0, 55.5, 54.9, 21.3, 18.9; MS (ESI): 412 (M+1). Anal. Calcd for $C_{24}H_{21}N_5O_2$: C 70.06, H 5.14, N 17.02; Found: C 69.87, H 5.51, N 16.95.

**4-(4-Chlorophenyl)-6,6-dimethyl-3,6*a*-di(2-pyridyl)-6,6*a*-dihydropyrrolo[3,2-*c*]pyrazol-5-one 4d.** 82%, mp 112–113 °C; IR $\nu$ (cm$^{-1}$) 1762, 1635, 1583, 1493; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.36 (d, $J$ = 4.1 Hz, 1H), 8.02 (d, $J$ = 4.5 Hz, 1H), 8.00 (d, $J$ = 8.0 Hz, 1H), 7.58–7.61 (m, 2H), 7.54 (d, $J$ = 7.9 Hz, 1H), 7.27 (d, $J$ = 8.7 Hz, 2H), 7.16 (d, $J$ = 8.7 Hz, 2H), 7.12 (dd, $J$ = 6.3, 1.0 Hz, 1H), 6.96 (dd, $J$ = 7.0, 5.0 Hz, 1H), 1.29 (s, 3H), 1.04 (s, 3H); $^{13}$C NMR (100 MHz, CDCl3) $\delta$ (ppm) 182.7, 160.7, 154.9, 149.6, 149.1, 149.1, 137.0, 136.1, 135.0, 134.2, 132.6, 128.2, 126.9, 123.8, 123.6, 122.0, 121.9, 107.2, 55.0, 21.2, 19.0; MS (CI): 416 (M+1); Anal. Calcd for $C_{23}H_{18}ClN_5O$: C 66.43, H 4.36, N 16.84; Found: C 66.53, H 4.79, N 16.75.

**4-(4-Bromophenyl)-6,6-dimethyl-3,6*a*-di(2-pyridyl)-6,6*a*-dihydropyrrolo[3,2-*c*]pyrazol-5-one 4e.** 73%, mp 145–146 °C; IR $\nu$ (cm$^{-1}$) 1770, 1627, 1583, 1488; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.43 (dd, $J$ = 4.7, 0.8 Hz, 1H), 8.12 (d, $J$ = 4.7 Hz, 1H), 8.06 (d, $J$ = 8.0 Hz, 1H), 7.68 (td, $J$ = 8.0, 1.8 Hz, 2H), 7.61 (d, $J$ = 7.9 Hz, 1H), 7.49 (dt, $J$ = 8.7, 2.8 Hz, 2H), 7.20–7.22 (m, 1H), 7.18 (dt, $J$ = 8.7, 2.9 Hz, 2H), 7.27 (ddd, $J$ = 7.5, 4.8, 1.0 Hz, 1H), 1.37 (s, 3H), 1.11 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 182.6, 160.7, 154.8, 149.4, 149.1, 148.9, 137.1, 136.4, 135.4, 134.0, 131.2, 127.2, 123.8, 123.7, 122.1, 122.0, 120.6, 107.2, 55.0, 21.20, 19.0; MS (EI): 44 (100), 417 (40), 459 (25%, M$^+$); Anal. Calcd for $C_{23}H_{18}BrN_5O$: C 60.01, H 3.94, N 15.21; Found: C 59.89, H 3.95, N 15.18.

**6,6-Diethyl-3,6*a*-di(2-pyridyl)-4-*p*-tolyl-6,6*a*-dihydropyrrolo[3,2-*c*]pyrazol-5-one 4f.** 25%, mp 145–146 °C; IR $\nu$ (cm$^{-1}$) 1765, 1632, 1582; $^1$H NMR (400 MHz, $CD_3COCD_3$) $\delta$ (ppm) 8.47 (dq,

$J$ = 4.7, 1.0 Hz, 1H), 8.07 (dt, $J$ = 8.0, 1.0, Hz, 1H), 7.94 (dq, $J$ = 4.8, 1.0 Hz, 1H), 7.81 (dt, $J$ = 8.0, 1.9, Hz, 1H), 7.73 (dt, $J$ = 7.5, 1.8 Hz, 1H), 7.58 (dt, $J$ = 8.0, 0.9 Hz, 1H), 7.35 (ddd, $J$ = 7.6, 4.8, 1.1 Hz, 1H), 7.15 (d, $J$ = 8.6 Hz, 2H), 7.03–7.06 (m, 3H), 2.35 (s, 3H), 1.95–2.02 (m, 1H), 1.77–1.85 (m, 1H), 1.38–1.47 (m, 1H), 1.11 (t, $J$ = 7.6 Hz, 3H), 0.90 (t, $J$ = 5.5 Hz, 3H), 0.87–0.93 (m, 1H); $^{13}$C NMR (100 MHz, $CD_3COCD_3$) $\delta$ (ppm) 180.9, 162.6, 155.2, 150.4, 149.0, 148.8, 137.5, 136.8, 136.1, 134.6, 133.3, 128.4, 126.0, 124.0, 123.2, 121.6, 121.4, 107.0, 63.0, 21.6, 20.3, 19.4, 7.8, 7.3; HRMS (TOF-ESI): 424.2125 (M+1); Anal. Calcd for $C_{26}H_{26}N_5O$: 424.2137 (M+1).

**3′,6*a*′-Di(2-pyridyl)-4′-*p*-tolyl-4′H-spiro[cyclohexane-1,6′-pyrrolo[3,2-*c*]pyrazol]-5′-one 4h.** 88%, 156–157 °C; IR $\nu$ (cm$^{-1}$) 1752, 1639, 1581; $^1$H NMR (400 MHz, $CD_3COCD_3$) $\delta$ (ppm) 8.47 (dq, $J$ = 4.8, 1.0 Hz, 1H), 8.05 (dd, $J$ = 8.0, 1.0, Hz, 1H), 7.95 (dq, $J$ = 4.7, 1.0 Hz, 1H), 7.83 (dt, $J$ = 7.9, 1.8, Hz, 1H), 7.72 (dt, $J$ = 7.6, 1.8 Hz, 1H), 7.58 (dt, $J$ = 8.0, 1.0 Hz, 1H), 7.35 (ddd, $J$ = 7.6, 4.8, 1.1 Hz, 1H), 7.15 (d, $J$ = 8.6 Hz, 2H), 7.08 (d, $J$ = 8.6 Hz, 2H), 7.05 (ddd, $J$ = 7.6, 4.8, 1.1 Hz, 1H), 2.36 (s, 3H), 1.71–1.82 (m, 4H), 1.62–1.64 (m, 1H), 1.34–1.55 (m, 5H); $^{13}$C NMR (100 MHz, $CD_3COCD_3$) $\delta$ (ppm) 181.5, 161.9, 155.2, 150.3, 149.1, 149.0, 137.4, 136.7, 136.1, 134.6, 133.2, 128.4, 126.0, 124.0, 123.7, 121.6, 121.5, 107.0, 60.4, 30.6, 25.5, 22.6, 22.03, 22.01, 20.4; HRMS (TOF-ESI): 436.2132 (M+1); Anal. Calcd for $C_{27}H_{26}N_5O$: 436.2137 (M+1).

### General procedure for the reaction of β-lactam carbenes 2 with 3,6-di(2-pyridyl)tetrazine 3 in xylene

Under nitrogen atmosphere, the mixture of spiro[β-lactam-4,2′-oxadiazolines] **1** (1.5 mmol) and 3,6-di(2-pyridyl)tetrazine **3** (1 mmol) was heated in refluxing xylene (50 mL) for 3–12 h. After removal of the solvent under vacuum, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate from 10 : 1 to pure ethyl acetate to give products 5-triazolo[1,5-*a*]pyridylpyrrol-2-ones **5** in 75–92% yields. Products **5** were further purified by recrystallization in ethyl acetate and petroleum ether.

**5-(3-[1,2,3]Triazolo[1,5-*a*]pyridyl)-3,3-dimethyl-1-phenyl-4-(2-pyridyl)pyrrol-2-one 5a.** 87%, mp 192–193 °C; IR $\nu$ (cm$^{-1}$) 1716, 1622, 1582, 1562, 1518; $^1$H NMR (400 MHz, $CD_3COCD_3$) $\delta$ (ppm) 8.86 (d, $J$ = 7.0 Hz, 1H), 8.56 (dt, $J$ = 3.9 Hz, 1H), 7.43 (d, $J$ = 7.8 Hz, 1H), 7.34 (dt, $J$ = 7.7, 1.9 Hz, 1H), 7.27 (dd, $J$ = 9.0, 6.6 Hz, 1H), 7.19–7.23 (m, 2H), 7.10–7.16 (m, 4H), 7.07 (ddd, $J$ = 7.5, 4.8 Hz, 1H), 6.82 (d, $J$ = 8.1 Hz, 1H), 1.68 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 182.1, 153.3, 149.0, 136.0, 135.0, 132.4, 130.8, 129.5, 128.7, 128.3, 127.2, 127.1, 126.4, 125.4, 124.1, 121.5, 117.4, 115.6, 49.48, 23.75; MS (ESI): 382(M+1); Anal. Calcd for $C_{23}H_{19}N_5O$: C 72.42, H 5.02, N 18.36; Found: C 72.04, H 4.68, N 18.17.

**5-(3-[1,2,3]Triazolo[1,5-*a*]pyridyl)-3,3-dimethyl-4-(2-pyridyl)-1-(*p*-tolyl)pyrrol-2-one 5b.** 83%, mp 184–185 °C; IR $\nu$ (cm$^{-1}$) 1733, 1619, 1584, 1513; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.61 (d, $J$ = 7.0 Hz, 1H), 8.56 (d, $J$ = 4.2 Hz, 1H), 7.19 (d, $J$ = 8.9 Hz, 1H), 7.07 (d, $J$ = 6.8 Hz, 1H), 7.04 (d, $J$ = 4.0 Hz, 2H), 7.00 (d, $J$ = 4.1 Hz, 2H), 6.91 (t, $J$ = 6.6 Hz, 1H), 6.85 (brs, 1H), 2.24 (s, 3H), 1.69 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 182.2, 153.5, 149.1, 137.0, 135.8, 132.4, 132.4, 130.8, 129.3, 128.5, 127.0, 126.2, 125.4, 124.0, 121.4, 117.5, 115.5, 49.4, 23.7, 21.1, 21.0; MS (EI): 180 (100), 230 (100), 396 (3%, M+1); Anal. Calcd for $C_{24}H_{21}N_5O$: C 72.89, H 5.35, N 17.71; Found: C 72.68, H 5.30, N 17.82.

**5-(3-[1,2,3]Triazolo[1,5-*a*]pyridyl)-1-(4-methoxyphenyl)-3,3-dimethyl-4-(2-pyridyl)pyrrol-2-one 5c.** 92%, mp 202–203 °C; IR $\nu$ (cm$^{-1}$) 1712, 1638, 1620, 1587, 1554, 1512; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.61 (d, $J$ = 7.0 Hz, 1H), 8.56 (d, $J$ = 4.1 Hz, 1H), 7.26–7.24 (m, 1H), 7.19 (d, $J$ = 9.0 Hz, 1H), 7.06–7.08 (m, 1H), 7.03 (dd, $J$ = 8.9, 1.9 Hz, 2H), 6.99 (t, $J$ = 6.8 Hz, 1H), 6.91 (td, $J$ = 6.9, 1.0 Hz, 1H), 6.83 (d, $J$ = 7.7 Hz, 1H), 6.73 (d, $J$ = 8.9 Hz, 2H), 3.71 (s, 3H), 1.69 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 182.5, 158.5, 153.5, 149.3, 135.6, 132.4, 130.8, 129.6, 128.5, 127.8, 126.3, 125.4, 123.8, 121.3, 117.4, 115.5, 114.0, 55.3, 49.3, 23.7; MS (ESI): 412 (M+1); Anal. Calcd for $C_{24}H_{21}N_5O_2$: C 70.06, H 5.14, N 17.02; Found: C 69.91, H 5.34, N 17.07.

**5-(3-[1,2,3]Triazolo[1,5-*a*]pyridyl)-1-(4-chlorophenyl)-3,3-dimethyl-4-(2-pyridyl)pyrrol-2-one 5d.** 91%, mp 208–209 °C; IR $\nu$ (cm$^{-1}$) 1720, 1620, 1583, 1526; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.63 (d, $J$ = 7.1 Hz, 1H), 8.58 (d, $J$ = 4.1 Hz, 1H), 7.27 (brs, 1H), 7.19 (d, $J$ = 8.6 Hz, 2H), 7.16 (d, $J$ = 9.0 Hz, 1H), 7.09 (d, $J$ = 6.6 Hz, 1H), 7.05 (d, $J$ = 8.7 Hz, 2H), 7.03 (brs, 1H), 6.94 (td, $J$ = 6.9, 1.1 Hz, 1H), 6.84 (brs, 1H), 1.68 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 182.0, 153.3, 149.4, 135.8, 133.7, 132.8, 132.3, 130.1, 129.9, 128.8, 128.4, 128.1, 126.6, 125.5, 124.0, 121.5, 117.3, 115.7, 49.5, 23.7; MS (CI): 416 (M+1); Anal. Calcd for $C_{23}H_{18}ClN_5O$: C 66.43, H 4.36, N 16.84; Found: C 66.52, H 4.60, N 16.84.

**5-(3-[1,2,3]Triazolo[1,5-*a*]pyridyl)-1-(4-bromophenyl)-3,3-dimethyl-4-(2-pyridyl)pyrrol-2-one 5e.** 80%, mp 205–206 °C; IR $\nu$ (cm$^{-1}$) 1720, 1635, 1583, 1561; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.56 (d, $J$ = 7.0 Hz, 1H), 8.50 (d, $J$ = 4.4 Hz, 1H), 7.27 (d, $J$ = 8.6 Hz, 2H), 7.20 (bs, 1H), 7.08 (d, $J$ = 8.9 Hz, 1H), 7.01(t, $J$ = 6.6 Hz, 1H), 6.95 (brs 1H), 6.92 (d, $J$ = 8.6 Hz, 2H), 6.87 (t, $J$ = 6.9 Hz, 1H), 6.76 (brs 1H), 1.61 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 181.9, 153.2, 149.3, 135.9, 134.2, 132.3, 131.8, 130.1, 129.8, 128.7, 128.0, 126.6, 125.6, 124.0, 121.6, 120.9, 117.3, 115.7, 49.5, 23.7; MS (ESI): 460 (M+1); Anal. Calcd for $C_{23}H_{18}BrN_5O$: C 60.01, H 3.94, N 15.21; Found: C 59.75, H 3.87, N 15.18.

**5-(3-[1,2,3]Triazolo[1,5-*a*]pyridyl)-3,3-diethyl-4-(2-pyridyl)-1-(*p*-tolyl)pyrrol-2-one 5f.** 82%; mp 182–183 °C, IR $\nu$ (cm$^{-1}$) 1712, 1623, 1585, 1514; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.53 (d, $J$ = 7.0 Hz, 1H), 8.48 (d, $J$ = 4.3 Hz, 1H), 7.15 (td, $J$ = 7.8, 1.8 Hz, 1H), 7.11 (d, $J$ = 7.9 Hz, 1H), 7.00 (ddd, $J$ = 8.8, 6.6, 0.8 Hz, 1H), 6.88–6.98 (m, 5H), 6.83 (td, $J$ = 6.9, 1.2 Hz, 1H), 6.79 (d, $J$ = 8.0 Hz, 1H), 2.21–2.26 (m, 2H), 2.16 (s, 3H), 1.92–1.97 (m, 2H), 0.91 (t, $J$ = 7.3 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 181.2, 153.8, 149.5, 137.1, 135.5, 133.0, 132.5, 132.4, 129.3, 128.7, 127.2, 126.3, 125.4, 125.1, 123.6, 121.1, 117.3, 115.4, 59.9, 30.1, 21.1, 9.3; MS (CI): 424 (M+1); Anal. Calcd for $C_{26}H_{25}N_5O$: C 73.74, H 5.95, N 16.54; Found: C 73.49, H 6.29, N 16.35.

**5-(3-[1,2,3]Triazolo[1,5-*a*]pyridyl)-3-ethyl-3-methyl-4-(2-pyridyl)-1-(*p*-tolyl)pyrrol-2-one 5g.** 90%, mp 161–162 °C; IR $\nu$ (cm$^{-1}$) 1713, 1635, 1619, 1582, 1514; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.53 (d, $J$ = 7.0 Hz, 1H), 8.48 (dd, $J$ = 4.8, 0.8 Hz, 1H), 7.16 (d, $J$ = 7.6, 1H), 7.11 (d, $J$ = 9.0 Hz, 1H), 7.00 (td, $J$ = 7.4, 0.7 Hz, 1H), 6.89–6.94 (m, 5H), 6.83(td, $J$ = 7.8, 1.1 Hz, 1H), 6.77

(d, $J$ = 7.9 Hz, 1H), 2.29–2.34 (m, 1H), 2.16 (s, 3H), 1.96–2.01 (m, 1H), 1.56 (s, 3H), 0.92 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 181.7, 153.6, 149.4, 137.0, 135.6, 132.4, 131.9, 129.3, 128.6, 127.3, 127.1, 126.3, 125.4, 125.4, 123.7, 121.2, 117.3, 115.5, 54.3, 30.6, 23.1, 21.0, 9.52; MS (CI): 410 (M+1); Anal. Calcd for $C_{25}H_{23}N_5O$: C 73.33, H 5.66, N 17.10; Found: C 73.45, H 5.44, N 17.16.

**3′-(3-[1,2,3]Triazolo[1,5-*a*]pyridyl)-4′-(2-pyridyl)-2-(*p*-tolyl)-spiro[cyclohexane-1,3′-pyrrol]-5′-one 5h.** 75%, mp 203–204 °C; IR $\nu$ ($cm^{-1}$) 1704, 1624, 1584, 1512; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.79 (d, $J$ = 4.1 Hz, 1H), 8.58 (dt, $J$ = 4.8, 0.9 Hz, 1H), 7.37 (dt, $J$ = 9.0, 1.0 Hz, 1H), 7.33 (td, $J$ = 7.8, 1.9 Hz, 1H), 7.22 (ddd, $J$ = 8.9, 6.8, 0.8 Hz, 1H), 7.04–7.09 (m, 2H), 7.01 (d, $J$ = 8.7 Hz, 2H), 6.98 (d, $J$ = 8.7 Hz, 2H), 6.82 (dd, $J$ = 8.0, 0.9 Hz, 1H), 2.53 (td, $J$ = 13.3, 4.2 Hz, 2H), 2.27 (tt, $J$ = 12.9, 3.7 Hz, 2H), 2.20 (s, 3H), 1.90 (d, $J$ = 13.2 Hz, 2H), 1.72–1.77 (m, 1H), 1.57 (dt, $J$ = 13.2, 3.6 Hz, 2H), 1.32 (qt, $J$ = 12.7, 3.7 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 180.9, 154.2, 149.1, 136.7, 135.9, 132.7, 132.4, 131.1, 129.3, 128.6, 126.9, 126.0, 125.6, 125.3, 125.3, 121.5, 117.6, 115.4, 52.0, 31.4, 25.20, 21.1, 20.3; MS (CI): 436 (M+1); Anal. Calcd for $C_{27}H_{25}N_5O$: C 74.46, H 5.79, N 16.08; Found: C 74.79, H 6.06, N 16.08.

### General procedure for the reaction of β-lactam carbenes 2 with 3,6-di(4-pyridyl)tetrazine 3 in *n*-heptane

Under nitrogen atmosphere, the mixture of spiro[β-lactam-4,2′-oxadiazolines] **1** (1.5 mmol) and 3,6-di(4-pyridyl)tetrazine **6** (1 mmol) was heated in refluxing *n*-heptane (50 mL) for 8 h. The yellow colored pyrido[*c*]cyclopenta[*b*]pyrrol-2-ones products **7** precipitated form the solvent during the reaction process. The crude products were then filtered and washed with chloroform, ethyl acetate, acetone and methanol to remove the soluble impurities. Products **7** can be further purified by recrystallization in DMSO and methanol.

**3,3-Dimethyl-1-phenyl-8-(4-pyridyl)pyrido[*c*]cyclopenta[*b*]pyrrol-2-one 7a.** 65%, mp 307–308 °C; IR $\nu$ ($cm^{-1}$) 3241, 1703, 1622, 1590; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 11.97 (s, 1H), 8.22 (s, 1H), 8.04 (d, $J$ = 5.9 Hz, 2H), 7.39 (d, $J$ = 5.9 Hz, 2H), 7.26–7.28 (m, 4H), 7.16–7.18 (m, 2H), 6.76 (d, $J$ = 6.0 Hz, 2H), 1.51 (s, 6H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 184.2, 148.2, 144.0, 142.3, 136.4, 128.6, 127.0, 126.3, 125.8, 124.2, 123.3, 122.9, 121.0, 112.0, 107.2, 94.0, 42.2, 25.0; HRMS (TOF-ESI): 354.1611 (M+1), Anal. Calcd for $C_{23}H_{20}N_3O$: 354.1606 (M+1).

**3,3-Dimethyl-8-(4-pyridyl)1-(*p*-tolyl)pyrido[*c*]cyclopenta[*b*]pyrrol-2-one 7b.** 62%; mp 312–313 °C; IR $\nu$ ($cm^{-1}$) 3244, 1714, 1619, 1597; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 11.94 (s, 1H), 8.21 (d, $J$ = 4.4 Hz, 1H), 8.05 (d, $J$ = 5.4 Hz, 2H), 7.39 (t, $J$ = 4.1 Hz, 1H), 7.26 (d, $J$ = 6.6 Hz, 1H), 7.07 (d, $J$ = 8.2 Hz, 2H), 7.04 (d, $J$ = 8.3 Hz, 2H), 6.77 (d, $J$ = 5.4 Hz, 2H), 2.29 (s, 3H), 1.49 (s, 6H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 184.3, 148.1, 144.2, 142.3, 136.4, 133.9, 129.0, 126.2, 125.7, 124.2, 123.3, 122.9, 121.0, 112.0, 107.2, 93.9, 42.1, 25.0, 20.6; MS (ESI): 368 (M+1). Anal. Calcd for $C_{24}H_{21}N_3O$: C 78.45, H 5.76, N 11.44; Found: C 78.13, H 5.56, N 11.19.

**3,3-Dimethyl-1-(4-methoxyphenyl)-8-(4-pyridyl)pyrido[*c*]cyclopenta[*b*]pyrrol-2-one 7c.** 65%; mp 302–303 °C; IR $\nu$ ($cm^{-1}$) 3244, 1698, 1621, 1592; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 11.92 (s, 1H), 8.18 (s, 1H), 8.05 (d, $J$ = 6.0 Hz, 2H), 7.37 (d, $J$ = 6.7 Hz, 1H), 7.24 (d, $J$ = 6.6 Hz, 1H), 7.06 (d, $J$ = 8.8 Hz, 2H), 6.81 (d, $J$ = 8.8 Hz, 2H), 6.77 (d, $J$ = 6.0 Hz, 2H) 3.72 (s, 3H), 1.47 (s, 6H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 184.5, 158.1, 148.1, 144.6, 142.2, 129.3, 127.8, 125.7, 124.1, 123.3, 122.9, 121.0, 113.9, 111.9, 107.1, 93.9, 55.4, 42.0, 25.0; MS (ESI): 384 (M+1). Anal. Calcd for $C_{24}H_{21}N_3O_2$: C 75.18, H 5.52, N 10.96; Found: C 74.98, H 5.91, N 10.72.

**1-(4-Chlorophenyl)-3,3-dimethyl-8-(4-pyridyl)pyrido[*c*]cyclopenta[*b*]pyrrol-2-one 7d.** 60%, mp 318–319 °C; IR $\nu$ ($cm^{-1}$) 3246, 1716, 1620, 1598; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 12.01 (s, 1H), 8.24 (d, $J$ = 6.1 Hz, 1H), 8.11 (d, $J$ = 6.0 Hz, 2H), 7.41 (t, $J$ = 5.9 Hz, 1H), 7.32 (dd, $J$ = 6.7, 2.0 Hz, 2H), 7.29 (d, $J$ = 6.6 Hz, 1H), 7.20 (dd, $J$ = 6.8, 2.0 Hz, 2H), 6.81 (dd, $J$ = 6.1, 1.4 Hz, 2H), 1.50 (s, 6H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 184.3, 148.2, 143.5, 142.3, 135.2, 131.1, 128.5, 127.9, 126.0, 124.1, 123.4, 123.0, 121.1, 111.9, 107.4, 93.9, 42.3, 25.0; HRMS (TOF-ESI): 388.1213, Anal. Calcd for $C_{23}H_{19}ClN_3O$: 388.1217 (M+1).

**3,3-Diethyl-8-(4-pyridyl)1-(*p*-tolyl)pyrido[*c*]cyclopenta[*b*]pyrrol-2-one 7f.** 56%, mp 303–304 °C; IR $\nu$ ($cm^{-1}$) 1717, 1619, 1595; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 11.97 (s, 1H), 8.19 (t, $J$ = 3.3 Hz, 1H), 8.01 (d, $J$ = 5.6 Hz, 2H), 7.36 (t, $J$ = 5.7 Hz, 1H), 7.14 (d, $J$ = 6.8 Hz, 1H), 7.05 (d, $J$ = 8.2 Hz, 2H), 6.96 (d, $J$ = 8.2 Hz, 2H), 6.76 (d, $J$ = 6.0 Hz, 2H), 2.25 (s, 3H), 1.93–2.01 (m, 2H), 1.75–1.83 (m, 2H), 0.63 (t, $J$ = 7.3 Hz, 6H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 183.3, 148.1, 146.2, 142.2, 136.4, 133.9, 129.1, 126.0, 125.5, 124.6, 123.9, 123.2, 121.1, 107.6, 107.4, 93.8, 52.9, 30.2, 20.6, 9.3; HRMS (TOF-ESI): 396.2072 (M+1), Anal. Calcd for $C_{26}H_{26}N_3O$: 396.2076 (M+1).

**3-Ethyl-3-methyl-8-(4-pyridyl)1-(*p*-tolyl)pyrido[*c*]cyclopenta[*b*]-pyrrol-2-one 7g.** 51%, mp 298–300 °C; IR $\nu$ ($cm^{-1}$) 1718, 1619, 1596; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 11.90 (s, 1H), 8.14 (d, $J$ = 6.0 Hz, 1H), 7.98 (d, $J$ = 6.0 Hz, 2H), 7.32 (t, $J$ = 5.8 Hz, 1H), 7.14 (d, $J$ = 6.6 Hz, 1H), 7.01 (d, $J$ = 8.2 Hz, 2H), 6.95 (d, $J$ = 8.2 Hz, 2H), 6.71 (dd, $J$ = 4.5, 1.4 Hz, 2H), 2.22 (s, 3H), 1.86–1.95 (m, 1H), 1.73–1.81 (m, 1H), 1.40 (s, 3H), 0.63 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 183.9, 148.1, 145.2, 142.3, 136.4, 133.9, 129.1, 126.1, 125.6, 124.4, 123.3, 121.5, 121.1, 109.8, 107.3, 93.9, 47.2, 31.6, 23.3, 20.62, 20.57, 9.5; HRMS (TOF-ESI): 382.1928 (M+1), Anal. Calcd for $C_{25}H_{24}N_3O$: 382.1919 (M+1).

### General procedure for the reaction of β-lactam carbenes 2 with 3,6-di(4-pyridyl)tetrazine 3 in 1,4-dioxane

Under nitrogen atmosphere, the mixture of spiro[β-lactam-4,2′-oxadiazolines] **1** (2 mmol) and 3,6-di(4-pyridyl)tetrazine **6** (1 mmol) was heated in refluxing 1,4-dioxane (50 mL) for 11–18 h. After the reaction mixture was cooled to room temperature, the small amount of yellow solids were filtered and washed with ethyl acetate, acetone and methanol to give the byproducts **7** in 5–14% yield. The filtrates were combined to remove the solvents under vacuum. The residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether, ethyl acetate and triethyl amine (10 : 5 : 1) to give products **8** in 45–79% yields.

**3,3-Dimethyl-6-(3,3-dimethyl-4-oxo-1-phenylazetidin-2-yl)-1-phenyl-8-(4-pyridyl)pyrido[*c*]cyclopenta[*b*]pyrrol-2-one 8a.** 57%; mp 289–290 °C; IR $\nu$ ($cm^{-1}$) 1772, 1725, 1627, 1596; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 8.25 (br, 1H), 7.97 (s, 2H), 7.43 (d, $J$ = 6.6 Hz, 1H), 7.32 (d, $J$ = 8.2 Hz, 2H), 7.26 (d, $J$ = 7.5 Hz, 2H), 7.18–7.22 (m, 4H), 7.06–7.11 (m, 3H), 6.66 (br, 2H), 6.34 (s, 1H), 1.44 (s, 6H), 1.41 (s, 3H), 0.89 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 184.0, 169.3, 148.2, 148.1, 145.4, 141.6, 136.1, 136.0, 129.5, 128.6, 127.2, 126.5, 125.1, 124.7, 123.5, 121.8, 116.9, 114.0, 107.6, 95.0, 77.7, 57.3, 42.1, 24.8, 21.2, 15.1; HRMS (TOF-ESI): 527.2458 (M+1), Anal. Calcd for $C_{34}H_{31}N_4O_2$: 527.2447 (M+1).

**6-(3,3-Dimethyl-4-oxo-1-(*p*-tolyl)azetidin-2-yl)-3,3-dimethyl-8-(4-pyridyl)1-(*p*-tolyl)pyrido[*c*]cyclopenta[*b*]pyrrol-2-one 8b.** 70%; mp 180–181 °C; IR $\nu$ ($cm^{-1}$) 1774, 1725, 1626, 1592; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 8.28 (br, 1H), 8.03 (s, 2H), 7.44 (d, $J$ = 5.8 Hz, 1H), 7.16–7.26 (m, 5H), 7.07 (d, $J$ = 8.1 Hz, 2H), 7.00 (d, $J$ = 8.1 Hz, 2H)), 6.72 (br, 2H), 6.36 (s, 1H), 2.28 (s, 3H), 2.24 (s, 3H), 1.48 (s, 6H), 1.45 (s, 3H), 0.93 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 184.0, 169.1, 148.1, 145.6, 141.6, 136.7, 134.0, 133.7, 133.6, 129.8, 129.1, 126.4, 125.1, 123.6, 121.8, 116.9, 114.0, 107.5, 94.9, 77.7, 57.2, 42.0, 24.8, 21.2, 20.6, 20.4, 15.2; HRMS (TOF-ESI): 555.2764 (M+1), Anal. Calcd for $C_{36}H_{35}N_4O_2$: 555.2760 (M+1).

**3,3-Dimethyl-6-[1-(4-methoxyphenyl)-3,3-dimethyl-4-oxo-azetidin-2-yl]-1-(4-methoxyphenyl)-8-(4-pyridyl)pyrido[*c*]cyclopenta[*b*]-pyrrol-2-one 8c.** 78%; mp 240–241 °C; IR $\nu$ ($cm^{-1}$) 1763, 1721, 1626, 1591; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 8.25 (br, 1H), 8.05 (d, $J$ = 3.5 Hz, 2H), 7.44 (d, $J$ = 7.0 Hz, 1H), 7.26 (d, $J$ = 9.0 Hz, 2H), 7.26 (br, 1H), 7.05 (d, $J$ = 8.8 Hz, 2H), 6.95 (d, $J$ = 8.9 Hz, 2H), 6.81 (d, $J$ = 8.9 Hz, 2H), 6.72 (br, 2H), 6.35 (s, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 1.48 (s, 6H), 1.46 (s, 3H), 0.93 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 184.2, 168.8, 158.4, 156.3, 148.2, 146.0, 141.6, 129.3, 128.9, 127.9, 125.1, 123.6, 121.8, 118.4, 114.7, 113.9, 107.4, 94.8, 77.9, 57.2, 55.4, 55.3, 41.9, 24.8, 21.2, 15.2; HRMS (TOF-ESI): 587.2662 (M+1), Anal. Calcd for $C_{36}H_{35}N_4O_4$: 587.2658 (M+1).

**1-(4-Chlorophenyl)-6-[1-(4-chlorophenyl)-3,3-dimethyl-4-oxo-azetidin-2-yl]-3,3-dimethyl-8-(4-pyridyl)pyrido[*c*]cyclopenta[*b*]pyrrol-2-one 8d.** 45%; mp 180–181 °C; IR $\nu$ ($cm^{-1}$) 1778, 1724, 1626, 1592; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 8.30 (br, 1H), 8.06 (s, 1H), 7.45 (d, $J$ = 6.9 Hz, 1H), 7.39 (d, $J$ = 8.7 Hz, 2H), 7.27 (d, $J$ = 9.1 Hz, 2H), 7.23 (d, $J$ = 7.8 Hz, 2H), 7.21 (br, 1H), 7.11 (d, $J$ = 8.6 Hz, 2H), 6.75 (br, 2H), 6.34 (s, 1H), 1.43 (s, 6H), 1.41 (s, 3H), 0.89 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 183.9, 169.3, 148.3, 144.9, 141.6, 135.0, 134.9, 131.5, 129.4, 128.6, 128.5, 128.1, 125.1, 123.7, 121.8, 118.6, 114.0, 107.7, 95.0, 77.9, 57.6, 42.2, 24.8, 21.2, 15.1; HRMS (TOF-ESI): 595.1647 (M+1), Anal. Calcd for $C_{34}H_{29}Cl_2N_4O_2$: 595.1668 (M+1).

**6-[3,3-Diethyl-1-(4-methoxyphenyl)-4-oxo-azetidin-2-yl]-3,3-diethyl-1-(4-methoxyphenyl)-8-(4-pyridyl)pyrido[*c*]cyclopenta[*b*]pyrrol-2-one 8i.** 79%; mp 168–169 °C; IR $\nu$ ($cm^{-1}$) 1765, 1722, 1625, 1591; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 8.32 (br, 1H), 8.06 (s, 2H), 7.47 (d, $J$ = 6.9 Hz, 1H), 7.28 (d, $J$ = 8.2 Hz, 2H), 7.15 (s, 1H), 6.99 (d, $J$ = 8.6 Hz, 2H), 6.96 (d, $J$ = 8.6 Hz, 2H), 6.81 (d, $J$ = 8.9 Hz, 2H), 6.73 (br, 1H), 6.45 (s, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 1.91–2.01 (m, 3 H), 1.77–1.85 (m, 3 H), 1.53 (br, 1H), 1.34 (br, 1H), 1.02 (t, $J$ = 7.2 Hz, 3H), 0.68–0.66 (m, 9H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 183.1, 168.2, 158.4, 156.4, 148.2, 147.8, 141.5, 129.0, 127.7, 125.6, 123.5, 122.8, 118.6, 114.7, 114.0, 109.8, 107.6, 94.7, 76.0, 64.4, 55.3, 55.2, 52.6, 30.0, 23.3, 19.6, 9.4, 8.3, 7.8; HRMS (TOF-ESI): 643.3291 (M+1), Anal. Calcd for $C_{40}H_{43}N_4O_4$: 643.3284 (M+1).

**6′-[1″-(4-Methoxyphenyl)-spiro[cyclopentane-1,3″-(4″-oxo-azetidin-2″-yl)]-1′-(4-methoxyphenyl)-8′-(4-pyridyl)spiro[cyclopentane-1,3′-pyrido[*c*]cyclopenta[*b*]pyrrol]-2′-one 8j.** 65%; mp 192–193 °C; IR $\nu$ ($cm^{-1}$) 1766, 1721, 1625, 1591; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 8.38 (br, 1H), 8.08 (s, 2H), 7.40 (s, 1H), 7.22 (d, $J$ = 9.0 Hz, 2H), 7.10 (d, $J$ = 6.2 Hz, 1H), 7.04 (d, $J$ = 8.7 Hz, 2H), 6.93 (d, $J$ = 8.8 Hz, 2H), 6.80 (d, $J$ = 8.8 Hz, 2H), 6.73 (br, 2H), 6.47 (s, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 2.25–2.31 (m, 1H), 1.92–2.10 (m, 10H), 1.41–1.73 (m, 4H), 1.04–1.09 (m, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 185.1, 169.6, 158.8, 156.7, 148.8, 147.2, 142.1, 129.8, 129.4, 128.4, 126.0, 124.2, 121.5, 118.8, 115.2, 115.0, 114.4, 108.2, 95.4, 78.9, 67.4, 55.9, 55.8, 52.4, 38.59, 38.56, 33.5, 27.9, 26.7, 26.6; HRMS (TOF-ESI): 639.2964 (M+1), Anal. Calcd for $C_{40}H_{39}N_4O_4$: 639.2971 (M+1).

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## Notes and references

1 M. Zoghbi and J. Warkentin, *J. Org. Chem.*, 1991, **56**, 3214–3215.
2 M. Zoghbi and J. Warkentin, *Can. J. Chem.*, 1993, **71**, 912–918.
3 M. Zoghbi and J. Warkentin, *Can. J. Chem.*, 1992, **70**, 2967–2971.
4 M. Zoghbi, S. E. Horne and J. Warkentin, *J. Org. Chem.*, 1994, **59**, 4090–4095.
5 Y. Cheng, B. Wang and L.-Q. Cheng, *J. Org. Chem.*, 2006, **71**, 4418–4427.
6 Y. Cheng and L.-Q. Cheng, *J. Org. Chem.*, 2007, **72**, 2625–2630.
7 L.-Q. Cheng and Y. Cheng, *Tetrahedron*, 2007, **63**, 9359–9364.
8 J. Xing, X.-R. Wang, C.-X. Yan and Y. Cheng, *J. Org. Chem.*, 2011, **76**, 4746–4752.
9 N. Shao, G.-X. Pang, C.-X. Yan, G.-F. Shi and Y. Cheng, *J. Org. Chem.*, 2011, **76**, 7458–7465.
10 A. Kümmell and G. Seitz, *Tetrahedron Lett.*, 1991, **32**, 2743–2746.
11 G. Frenzen, A. Kümmell, C. Meyer-Dulheuer and G. Seitz, *Chem. Ber.*, 1994, **127**, 1803–1806.
12 C. Gerninghaus, A. Kümmell and G. Seitz, *Chem. Ber.*, 1993, **126**, 733–738.
13 P. Imming, A. Kümmell and G. Seitz, *Heterocycles*, 1993, **35**, 299–304.
14 Y. F. Suen, H. Hope and M. H. Nantz, *J. Org. Chem.*, 2005, **70**, 8468–8471.