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Interaction of β-Lactam Carbenes with 3,6-Diphenyltetrazines: A Five-Step Cascade Reaction for the Direct Construction of Indeno[2,1-*b*]pyrrol-2-ones

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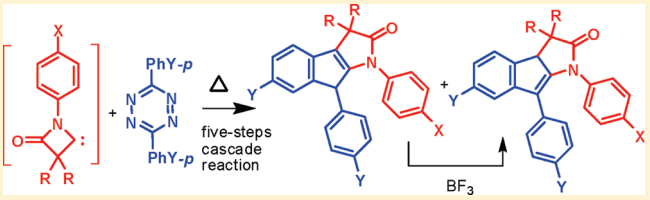
Supporting Information

ABSTRACT: A study of the nucleophilic addition of β-lactam carbenes to 3,6-diphenyltetrazines is reported. Instead of the formation of pyrazole derivatives like most reactions between nucleophilic or ambiphilic carbenes and 3,6-disubstituted tetrazines, β-lactam carbenes reacted with 3,6-diphenyltetrazines to produce indeno[2,1-*b*]pyrrol-2-ones in good yields. The reaction proceeds most probably through a five-step cascade process. This work has not only provided a one-pot operation for the efficient construction of mutisubstituted indeno[2,1-*b*]pyrrol-2-ones but also revealed the nucleophilicity of β-lactam carbenes.



Nucleophilic carbenes that are mainly *N*-heterocyclic carbenes have attracted continued interest from organic chemists because they are not only powerful ligands in the formation of metal complexes[1] but also useful organocatalysts[2] and versatile intermediates in organic synthesis.[3] For decades, nucleophilic carbenes have been developed into unique building blocks in the construction of a variety of novel heterocyclic and carbocyclic compounds. For example, the reaction of nucleophilic or ambiphilic carbenes with isocyanates has been utilized to prepare either indole-2-one[4] or imidazoline-2,4-dione derivatives[5] depending on the structures of both reactants. Cyclization between nucleophilic carbenes and vinyl ketenes affords a concise method for the preparation of cyclopentenones.[6] The stable dipolar adducts derived from *N*-heterocyclic carbenes and aryl isothiocyanates are versatile synthons in the construction of multifunctional pyrroles, thiophenes, spiro- or fused pyrroles, and thiophenes.[7] The three-component reactions of nucleophilic carbenes with activated alkynes and carbonyl compounds are a straightforward approach to mutisubstituted furans or fused furan derivatives.[8] Among the numerous reactions of *N*-heterocyclic and ambiphilic carbenes, those with 3,6-disubstituted 1,2,4,5-tetrazines generally proceeded via a [4 + 1] cycloaddition followed by reversion of [4 + 2] cycloaddition to produce substituted pyrazoles or spiro- or fused pyrazoles depending on the structures of both reactants.[9] Only one exception has been reported in which the substitution reaction of *N*-heterocyclic carbenes with 3,6-bis(3′,5′-dimethylpyrazolyl)-1,2,4,5-tetrazines afforded tetrazine derivatives.[10]

We have been interested in the chemistry of nucleophilic and ambiphilic carbenes for years.[7,11,12]Our interest in *N*-heterocyclic carbenes has led us to study the reactions of 2-azetidinone-4-ylidenes, a type of β-lactam carbenes pioneered by Warkentin in 1990s.[13] We have observed that β-lactam carbenes undergo both nucleophilic reaction with aryl isocyanates and electrophilic reaction with aryl isonitriles to produce spiro[azetidin-2-one-4,3′-indol-2′-ones] and 2-azetidinonylidene indoles, respectively.[12] Our previous works have indicated that β-lactam carbenes are unique intermediates in the construction of novel spiro- and fused heterocyclic compounds.[12] To gain insight into the ambident reactivity of β-lactam carbenes and to further explore their synthetic utility, we undertook the current investigate on the reaction of β-lactam carbenes with 3,6-diphenyl- and 3,6-bis-(4-substituted phenyl)tetrazines. We were delighted to discover that the reaction of β-lactam carbenes with 3,6-diphenyltetrazines proceeded in an unprecedented five-step cascade process to produce tricycle-fused indeno[2,1-*b*]pyrrol-2-ones in good yields.

We started this work with the examination of the reaction between 3,3-dimethyl-1-(*p*-methoxyphenyl)-2-azetidinon-4-ylidene **2c** and 3,6-diphenyltetrazine **3a**. In practice, all β-lactam carbenes **2** are generated in situ by thermolysis of spiro[β-lactam-4,2′-oxadiazolines] **1** following Warkentin's method.[13] Since the optimal temperature for the generation of carbenes **2** from spiro-oxadiazolines **1** is around 100−110 °C according to Warkentin's reports and our experience,[12,13] the reaction of **2c** with **3a** (**2c**:**3a** = 1.5:1) was examined at 100 °C in 1,4-dioxane, toluene and 1,1,2-trichloroethane that were chemically inert solvents toward carbenes. Surprisingly, instead of an envisaged pyrazole derivative as those derived from most reactions between nucleophilic or ambiphilic carbenes and 3,6-disubstituted tetrazines, the reaction of **2c** with **3a** produced two isomeric indeno[2,1-*b*]pyrrol-2-ones **4c** and **5c**. It was found that the reaction in

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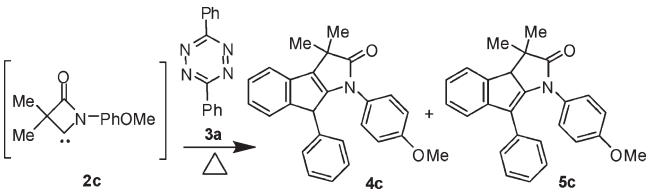
Table 1. Reaction of 3,3-Dimethyl-1-(*p*-methoxyphenyl)-2-azetidinone-4-ylidene 2c and 3,6-Diphenyltetrazine 3a under Different Conditions



				yield (%)	
entry	solvent	temp (°C)	time (h)	**4c**	**5c**
1	TCE[a]	100	5	9	48
2	dioxane	100	12	80	3
3	toluene	100	12	78	8
4	toluene	reflux	10	85	5
5	xylene	reflux	4	70	4

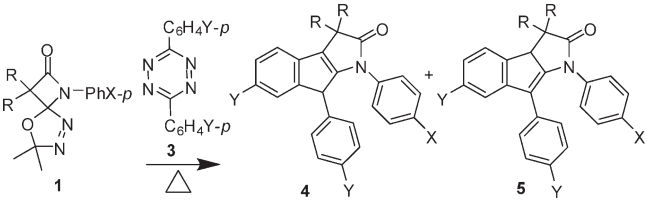
[a] TCE = 1,1,2-trichloroethane.

1,4-dioxane and toluene gave 78% and 80% yields of **4c**, respectively, along with 3% and 8% of **5c** (Table 1, entries 1 and 2). However, the use of 1,1,2-trichloroethane as solvent not only diminished the total yields of products but also reversed the selectivity between isomers **4c** and **5c**. The yield of major product **4c** was slightly improved to 85% from the reaction undergoing in refluxing toluene (Table 1, entry 4). Further elevation of reaction temperature in xylene led to a decrease in products.

The generality of the reaction was studied in refluxing toluene using spiro[β-lactam-4,2′-oxadiazolines] **1** and 3,6-bis(4-substituted phenyl)tetrazines **3**, both bearing different substituents. As summarized in Table 2, the *N*-aryl group of β-lactam carbenes **2** showed little effect on the reaction. All reactions of *N*-phenyl-, *N*-(4-methylphenyl)-, *N*-(4-methoxyphenyl)-, *N*-(4-chlorophenyl)-, and *N*-(4-bromophenyl)-substituted β-lactam carbenes **2a**−**e** with diphenyltetrazine **3a** proceeded equally efficiently to afford indeno[2,1-*b*]pyrrol-2-ones **4a**−**e** in 83−85% yields, along with a small amount of isomeric byproducts **5a**−**e** (Table 2, entries 1−5). On the contrary, the 3,3-alkyl substituents of carbene reactants did influence the efficiency of reaction. For example, the reactions of 3,3-diethyl-, 3,3-cyclopentyl-, and 3,3-cyclohexyl-2-azetidinon-4-ylidenes **2f**−**h** with bis(4-tolyl)tetrazine **3b** proceeded much slowly and produced lower total yields of products **4** and **5** than the reaction between 3,3-dimethyl-substituted carbene **2c** and tetrazine **3b** (Table 2, entries 10−13). The lower efficiency of the reactions between β-lactam carbenes **2** bearing bulky alkyl groups and diphenyltetrazines **3** can be best explained by the steric hindrance both in the addition of a carbene to tetrazine and in the transformation of reaction intermediates (vide infra). In comparison to carbene species that only influenced the efficiency of reactions, the structure of tetrazine reactants **3** not only determined the efficiency but also strongly influenced the outcomes of reactions. For instance, although β-lactam carbene **2a** reacted smoothly with diphenyl- (**3a**), bis(4-methylphenyl)- (**3b**), bis(4-chlorophenyl)- (**3d**), and bis(4-trifluoromethylphenyl)tetrazine (**3e**) to give products **4** or **5** in 82−88% yields (Table 2, entries 1, 6, 8, and 9), the reaction of **2a** with bis(4-methoxyphenyl)tetrazine **3c** proceeded much more slowly and produced product **4g** in only a moderate yield (63%) (Table 2, entry 7). On the other hand, while the carbenes **2** reacted with tetrazines **3a**−**c** substituted by phenyl, *p*-tolyl, and *p*-anisyl to produce isomers **4** as major products (Table 2, entries 1−7 and 10−13), the reactions of carbenes **2** with bis(*p*-chlorophenyl)tetrazine **3d** and bis(*p*-triflouromethylphenyl)tetrazine **3e** afforded isomers **5** under similar conditions (Table 2, entries 8 and 9). The lower reactivity of carbenes **2** to bis(*p*-anisyl)tetrazine **3c** was attributable to an electronic effect because the reaction was initiated by the nucleophilic addition of β-lactam carbenes **2** to diaryltetrazines **3** and the presence of strong electron-donating substituents of **3** deactivated the tetrazines **3** toward nucleophiles. It is intriguing that the substituents on tetrazines **3** strongly influenced the ratio of two isomeric products **4** and **5**. Most probably, the electronic effect of substituents of tetrazines **3** affected the speed of isomerization between products **4** and **5** (vide infra).

It was worth noting that some products **4** isomerized into their isomers **5** when they were dissolved in 1,1,2-trichloroethane or

Table 2. Reaction of Spiro[β-lactam-4,2′-oxadiazolines] 1 and Diaryltetrazines 3 under Optimized Conditions



						yield (%)	
entry	**1**	X, R, R	**3**	Y	time (h)	**4**	**5**
1	**1a**	H, CH_3, CH_3	**3a**	H	10	**4a**: 85	**5a**: 11
2	**1b**	CH_3, CH_3, CH_3	**3a**	H	10	**4b**: 84	**5b**: 7
3	**1c**	OCH_3, CH_3, CH_3	**3a**	H	10	**4c**: 85	**5c**: 5
4	**1d**	Cl, CH_3, CH_3	**3a**	H	10	**4d**: 83	**5d**: 12
5	**1e**	Br, CH_3, CH_3	**3a**	H	10	**4e**: 84	
6	**1a**	H, CH_3, CH_3	**3b**	CH_3	10	**4f**: 88	**5f**: 6[b]
7	**1a**	H, CH_3, CH_3	**3c**	OCH_3	31[a]	**4g**: 63	**5g**: 4[b]
8	**1a**	H, CH_3, CH_3	**3d**	Cl	10		**5h**: 86
9	**1a**	H, CH_3, CH_3	**3e**	CF_3	10		**5i**: 82
10	**1c**	OCH_3, CH_3, CH_3	**3b**	CH_3	10	**4j**: 88	**5j**: 6[b]
11	**1f**	OCH_3, Et, Et	**3b**	CH_3	24[a]	**4k**: 70	**5k**: 5[b]
12	**1g**	OCH_3, $(CH_2)_4$	**3b**	CH_3	24	**4l**: 74	—
13	**1h**	OCH_3, $(CH_2)_5$	**3b**	CH_3	31	**4m**: 65	5m: 5[b]

[a] In this reaction, a small amount of tetrazine **3c** or **3b** was not consumed. [b] The byproduct was isolated without full characterization.

Table 3. Isomerization of Products 4 to 5 under Different Conditions

entry	**4**	reaction conditions	yield of **5** (%)
1	**4a**	TCE, rt, 1 h	**5a**: 87
2	**4b**	TCE, rt, 1 h	**5b**: 86
3	**4c**	TCE, rt, 1 h	**5c**: 84
4	**4d**	TCE, rt, 1 h	**5d**: 82
5	**4c**	toluene, reflux, 24 h	**5c**: 88
6	**4c**	BF_3, toluene, rt, 0.5 h	**5c**: 84
7	**4g**	BF_3, toluene, rt, 0.5 h	**5g**: 89
8	**4k**	BF_3, toluene, rt, 5 h	**5k**: 65

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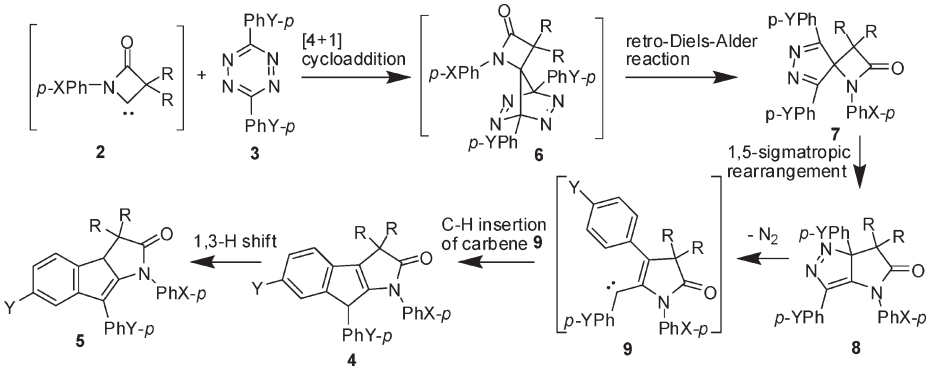
Scheme 1



deuterated chloroform or heated in refluxing toluene for a prolonged time. As shown in Table 3, **4a**−**d** dissolved in trichloroethane were converted into **5a**−**d** (82−87%) in 1 h at ambient temperature, while **4c** isomerized into **5c** (88%) when heated for 24 h in refluxing toluene. The isomerization of **4** to **5** at high temperature indicated that this is a thermal rearrangement. On the other hand, the transformation of **4a**−**5d** into **5a**−**d** in trichloroethane led us to propose that a trace amount of hydrochloride released from the solvent might accelerate the isomerization of **4**. To validate our hypothesis, aqueous HCl, TsOH hydrate, or HCl gas was added or bubbled into the solution of products **4** in 1,4-dioxane or toluene. However, instead of isomerizing into products **5**, compounds **4** were decomposed in the presence of a strong acid. A weaker Lewis acid was then utilized to promote the transformation of **4** to **5**. As expected, in the presence of BF_3, **4c**, **4g**, and **4k** were converted into **5c**, **5g**, and **5k** in 65−89% yields in toluene at room temperature (Table 3, entries 6−8). It was noted that the isomerization of 3,3-diethyl-substituted indeno[2,1-*b*]pyrrol-2-ones **4k** to **5k**, which was inefficient in refluxing toluene in the absence of an catalyst, occurred more slowly and produced a lower yield of **5k** than that of the 3,3-dimethyl-substituted analogue in the presence of BF_3. Taking these results into consideration, it is concluded that the isomerization of **4** to **5** is an acid-catalyzed thermal rearrangement.

The products **4** and **5** were fully characterized by spectroscopic data and microanalysis, which indicated that both **4** and **5** were the 1 + 1 combination of a carbene **2** and a tetrazine **3** with the loss of two N_2 molecules. Since the spectroscopic data did not allow full verification of the structures, to identify the products beyond doubt, the structures of **4c** and **5h** were determined unambiguously by single-crystal X-ray diffraction analysis (see the Supporting Information). The isomers **4** and **5** can be easily distinguished by their ^{1}H NMR spectra because the signal of cyclopentadienyl proton of **4** appeared around 5 ppm, while the proton attached to the cyclopentadiene ring of **5** resonated at about 4 ppm.

It was well documented that nucleophilic and ambiphilic carbenes reacted with 3,6-disubstituted tetrazines generally via a [4 + 1] cycloaddition followed by reversion of a [4 + 2] cycloaddition to produce pyrazole derivatives.[9] The current study revealed intriguingly the formation of indeno[2,1-*b*]pyrrol-2-ones **4** and **5** from β-lactam carbenes **2** and 3,6-diphenyltetrazines **3**. On the basis of the interaction pattern between nucleophilic carbenes and tetrazines,[9] a five-step cascade reaction was proposed for the formation of products **4**. As illustrated in Scheme 1, a [4 + 1] cycloaddition of β-lactam carbenes **2** with 3,6-diphenyltetrazines **3** forms the bridged compounds **6**, which are converted to β-lactam-spiropyrazoles **7** by the retro-Diels−Alder reaction. Under the heating conditions, spiro-pyrazoles **7** undergo a 1,5-sigmatropic rearrangement to produce pyrrolo[3,2-*c*]pyrazol-5-ones **8**. Decomposition of the pyrazole ring of **8** led to the formation of carbene intermediates **9**, which undergo an intramolecular insertion to the C−H bond of the phenyl to afford indeno[2,1-*b*]-pyrrol-2-ones **4**. A formal 1,3-H shift of cyclopentadienyl proton of **4** produces more extensively conjugated isomers **5**. To validate our proposed mechanism, the isolation of reaction intermediates was attempted. It was found that the reaction of β-lactam carbenes **2** with 3,6-diphenyltetrazines **3** initially formed two intermediates **7** and **8**. They were converted into products **4** and **5** over a prolonged time under heating. Since the yellow intermediate **7g** obtained from the reaction of carbene **2a** with bis(4-methoxyphenyl)tetrazine **3c** was much stable than those derived from other tetrazines, **7g** was isolated and identified as 3′5′-bis(4-methoxyphenyl)-3,3-dimethyl-1-phenylspiro[azetidine-2,4′-pyrazol]-4-one by spectroscopic data and single-crystal X-ray diffraction analysis (see the Supporting Information). To isolate intermediates **8**, the reactions of carbene **2a** with diphenyltetrazine **3a**, bis(*p*-chlorophenyl)tetrazine **3d**, and bis(*p*-triflouromethylphenyl)tetrazine **3e** were quenched in 1.5−2.5 h. Under these conditions, intermediates **8** were isolated along with the products **4** or **5**. Compound **8i** derived from bis(*p*-triflouromethylphenyl)-tetrazine **3e** can be separated from product **5i** by column chromatography. However, **8a** and **4a**, or **8h** and **5h**, have similar polarities that could not be separated by column chromatography. Fortunately, **8a** or **8h** was precipitated from the mixture of **8a** and **4a**, or **8h** and **5h**, dissolving in petroleum ether and ethyl ether. After structure determination by spectroscopic methods and single-crystal X-ray diffraction analysis of **8h**, compounds **8a**, **8h**, and **8i** were confirmed to be dihydropyrrolo[3,2-*c*]pyrazol-5-one derivatives (see the Supporting Information). The isolation of product **5** rather than **4** from the reaction of carbene **2a** with bis(4-chlorophenyl)tetrazine **3d** or bis(4-trifluoromethylphenyl)-tetrazine **3e** can be explained by the electronic effects of substituents bearing the cyclopentadiene ring of **4**. An electron-deficient substituent can enhance the acidity of the cyclopentadienyl proton of **4** and therefore probably promotes the 1,3-H shift of this proton. On the basis of the ^{1}H NMR analysis of the reaction mixture of **1a** with bis(chlorophenyl)tetrazine **3d** or with bis(4-trifluoromethylphenyl)tetrazine **3e**, product **4** could be

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detected while the reaction proceeded only for 1−2 h. These results support our proposed mechanism.

In summary, we have studied the nucleophilic reaction of 2-azetidinon-4-ylidenes, a type of ambiphilic β-lactam carbenes, with 3,6-diphenyltetrazines. In contrast to other nucleophilic and ambiphilic carbenes that reacted with 3,6-disubstituted tetrazines to form pyrazole derivatives, β-lactam carbenes reacted with 3,6-diphenyltetrazines to produce indeno[2,1-*b*]pyrrol-2-ones in good yields. The reaction proceeded most probably through a five-step cascade process. A few methods for the syntheses of indeno[2,1-*b*]pyrrole derivatives, such as the cycloaddition of carbamoyl cyanides with 1,3-butadiynes,[14a] a one-pot reaction of ninhydrin with triphenylphosphine, ammonium acetate, and dialkyl acetylenedicarboxylates,[14b] the reaction of 2-bromo-1-dicyanomethylene-3-indanone with aniline,[14c] have been documented in literature. However, no indeno[2,1-*b*]pyrrol-2-one or substituted indeno[2,1-*b*]pyrrol-2-ones have been reported. This work not only provided a simple and efficient method for the construction of mutisubstituted indeno[2,1-*b*]pyrrol-2-ones but also revealed the nucleophilic feature of β-lactam carbenes and demonstrated their application in organic synthesis.

EXPERIMENTAL SECTION

General Procedure for the Reaction of β-Lactam Carbenes with 3,6-Diaryltetrazines. Under nitrogen atmosphere, the mixture of spiro[β-lactam-4,2′-oxadiazolines] **1** (1.5 mmol) and 3,6-diphenyltetrazine **3a** or 3,6-bis(4-substitutedphenyl)tetrazines **3b**−**e** (1 mmol) was heated in refluxing toluene (30 mL) for 10−31 h until the tetrazines were totally consumed (Note: a small amount of tetrazine **3c** or **3b** was recovered from the reactions of **1a** with **3c** and **1f** with **3b**). 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 5:1 to give products **4** or **5**. Products **4** or **5** were further purified by recrystallization in ethyl acetate and petroleum ether.

3,3-Dimethyl-1,8-diphenyl-3,8-dihydroindeno[2,1-*b*]pyrrol-2-one (4a): 85% yield; mp 106−107 °C; IR ν (cm^{-1}) 1730, 1716, 1620, 1598; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.34−7.37 (m, 3H), 7.26 (t, J = 8.2 Hz, 2H), 7.22 (d, J = 7.6 Hz, 1H), 7.08−7.15 (m, 5H), 6.99−7.04 (m, 3H), 5.18 (s, 1H), 1.62 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 184.2, 151.7, 148.5, 139.4, 138.0, 136.9, 131.8, 129.4, 128.5, 128.0, 127.8, 127.0, 124.94, 124.85, 124.4, 118.2, 51.7, 46.1, 23.6, 23.2; MS (ESI) 352 (M + 1). Anal. Calcd for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99. Found: C, 85.26; H, 5.91; N, 3.95.

3,3-Dimethyl-8-phenyl-1-(*p*-tolyl)-3,8-dihydroindeno[2,1-*b*]pyrrol-2-one (4b): 84% yield; mp 140−141 °C; IR ν (cm^{-1}) 1721, 1617; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.34 (d, J = 7.4 Hz, 1H), 7.22 (d, J = 7.5 Hz, 1H), 7.19 (d, J = 8.3 Hz, 2H), 7.09−7.15 (m, 4H), 7.00−7.07 (m, 4H), 6.99 (dt, J = 7.5, 0.9 Hz, 1H), 5.12 (s, 1H), 2.23 (s, 3H), 1.61 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 184.4, 151.8, 148.5, 139.4, 138.1, 136.7, 134.3, 131.6, 130.0, 129.5, 128.5, 128.1, 127.9, 124.94, 124.89, 124.3, 118.1, 51.6, 46.1, 23.6, 23.1, 20.9; MS (ESI) 366 (M + 1). Anal. Calcd for $C_{26}H_{23}NO$: C, 85.45; H, 6.34; N, 3.83. Found: C, 85.27; H, 6.23; N, 3.81.

1-(4-Methoxyphenyl)-3,3-dimethyl-8-phenyl-3,8-dihydroindeno[2,1-*b*]pyrrol-2-one (4c): 85% yield; mp 143−144 °C; IR ν (cm^{-1}) 1720, 1619, 1512; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.33 (d, J = 7.4 Hz, 1H), 7.21 (dt, J = 7.5, 0.6 Hz, 1H), 7.09−7.17 (m, 6H), 7.01 (dd, J = 8.0, 1.9 Hz, 2H), 6.97 (dd, J = 7.5, 1.1 Hz, 1H), 6.79 (d, J = 9.0 Hz, 2H), 5.03 (s, 1H), 3.74 (s, 3H), 1.60 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 184.4, 159.0, 152.4, 148.5, 139.7, 138.1, 131.0, 129.7, 129.4, 128.5, 128.0, 127.8, 126.8, 124.9, 124.1, 118.0, 114.6, 55.6, 51.5, 46.0, 23.6, 23.1; MS (ESI) 382 (M + 1). Anal. Calcd for $C_{26}H_{23}NO_2$: C, 81.86; H, 6.08; N, 3.67. Found: C, 81.79; H, 6.13; N, 3.62.

1-(4-Chlorophenyl)-3,3-dimethyl-8-phenyl-3,8-dihydroindeno[2,1-*b*]pyrrol-2-one (4d): 83% yield; mp 121−122 °C; IR ν (cm^{-1}) 1721, 1712, 1620; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.41 (dd, J = 8.8, 1.9 Hz, 2H), 7.36 (d, J = 7.4 Hz, 1H), 7.27 (dd, J = 8.8, 2.0 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 7.09−7.16 (m, 4H), 7.06 (dd, J = 8.1, 1.6 Hz, 2H), 7.01 (t, J = 7.5 Hz, 1H), 5.22 (s, 1H), 1.62 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 184.1, 151.0, 148.5, 139.1, 137.7, 135.7, 132.2, 131.6, 129.52, 129.45, 128.5, 128.1, 127.9, 126.1, 124.9, 124.6, 118.3, 51.7, 46.1, 23.6, 23.1; MS (ESI) 386 (M + 1). Anal. Calcd for $C_{25}H_{20}ClNO$: C, 77.81; H, 5.22; N, 3.63. Found: C, 77.68; H, 5.28; N, 3.46.

1-(4-Bromophenyl)-3,3-dimethyl-8-phenyl-3,8-dihydroindeno[2,1-*b*]pyrrol-2-one (4e): 84% yield; mp 124−126 °C; IR ν (cm^{-1}) 1719, 1621, 1492; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.43 (d, J = 8.8 Hz, 2H), 7.35−7.38 (m, 3H), 7.24 (t, J = 7.5 Hz, 1H), 7.06−7.16 (m, 6H), 7.02 (t, J = 7.5 Hz, 1H), 5.23 (s, 1H), 1.62 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 184.0, 150.9, 148.5, 139.1, 137.7, 136.2, 132.4, 132.3, 129.5, 128.5, 128.1, 127.9, 126.4, 124.9, 124.6, 119.4, 118.3, 51.7, 46.1, 23.6, 23.1; MS (EI) 429 (M^+, 100). Anal. Calcd for $C_{25}H_{20}BrNO$: C, 69.78; H, 4.68; N, 3.25. Found: C, 69.67; H, 4.79; N, 3.19.

3,3,6-Trimethyl-1-phenyl-8-(*p*-tolyl)-3,8-dihydroindeno-[2,1-*b*]pyrrol-2-one (4f): 88% yield; mp 87−88 °C; IR ν (cm^{-1}) 1732, 1717, 1598; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.36 (d, J = 7.7 Hz, 2H), 7.28−7.22 (m, 3H), 7.12 (t, J = 7.4 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.94−6.90 (m, 5H), 5.11 (s, 1H), 2.24 (s, 3H), 2.16 (s, 3H), 1.59 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 184.1, 150.6, 149.0, 137.1, 137.0, 136.5, 135.1, 133.8, 131.8, 130.0, 129.4, 128.4, 128.3, 126.8, 125.8, 124.6, 117.8, 51.4, 46.0, 23.7, 23.2, 21.4, 21.0; MS (EI) 363 (90), 378 (100), 379 (M^+, 50). Anal. Calcd for $C_{27}H_{25}NO$: C, 85.45; H, 6.64; N, 3.69. Found: C, 85.28; H, 6.60; N, 3.56.

6-Methoxy-8-(4-methoxyphenyl)-3,3-dimethyl-1-phenyl-3,8-dihydroindeno[2,1-*b*]pyrrol-2-one (4g): 63% yield; mp 132−133 °C; IR ν (cm^{-1}) 1716, 1610, 1512; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.36 (d, J = 7.8 Hz, 2H), 7.27 (t, J = 8.2 Hz, 3H), 7.12 (t, J = 7.3 Hz, 1H), 6.94 (d, J = 8.6 Hz, 2H), 6.80 (dd, J = 8.1, 2.3 Hz, 1H), 6.76 (s, 1H), 6.68 (d, J = 8.6 Hz, 2H), 5.10 (s, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 1.59 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 184.2, 159.6, 158.2, 150.9, 149.4, 137.0, 132.1, 131.6, 129.8, 129.53, 129.45, 126.8, 124.6, 118.4, 114.8, 113.0, 112.0, 55.8, 55.4, 51.2, 46.1, 23.7, 23.2; MS (EI) 410 (100), 411 (M^+, 85). Anal. Calcd for $C_{27}H_{25}NO_3$: C, 78.81; H, 6.12; N, 3.40. Found: C, 78.52; H, 6.07; N, 3.24.

6-Chloro-8-(4-chlorophenyl)-3,3-dimethyl-1-phenyl-3,3a-dihydroindeno[2,1-*b*]pyrrol-2-one (5h): 86% yield; mp 202−203 °C; IR ν (cm^{-1}) 1745, 1729, 1640, 1600; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.34 (d, J = 7.5 Hz, 1H), 7.13−7.19 (m, 7H), 7.08 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 3.93 (s, 1H), 1.72 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 182.1, 150.4, 147.7, 134.92, 134.87, 133.9, 133.1, 130.2, 129.8, 128.7, 128.0, 126.9, 124.5, 124.2, 123.7, 119.8, 115.6, 59.0, 46.9, 23.7, 20.2; MS (EI) 43 (100), 201 (90), 227 (75), 418 (65), 419 (M^+, 55). Anal. Calcd for $C_{25}H_{19}Cl_2NO$: C, 71.44; H, 4.56; N, 3.33. Found: C, 71.36; H, 4.81; N, 3.10.

3,3-Dimethyl-1-phenyl-6-(trifluoromethyl)-8-(4-(trifluoromethyl)phenyl)-3,3a-dihydroindeno[2,1-*b*]pyrrol-2-one (5i): 82% yield; mp 184−185 °C; IR ν (cm^{-1}) 1744, 1730, 1636; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.53 (d, J = 7.7 Hz, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.41 (s, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.12−7.14 (m, 3H),

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7.07- 7.09 (m, 4H), 4.01 (s, 1H), 1.76 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 182.0, 149.0, 148.7, 140.2, 135.4, 134.7, 130.9, 130.5, 130.2, 129.9, 129.8, 129.5, 129.1, 128.8, 128.7, 128.4, 128.0, 127.2, 125.7, 125.3, 124.80, 124.76, 124.7, 123.6, 123.0, 122.6, 121.0, 120.9, 120.3, 119.9, 115.8, 115.2, 59.3, 47.0, 23.7, 20.4; MS (EI) 145 (100), 487 (M^+, 9). Anal. Calcd for $C_{27}H_{19}F_6NO$: C, 66.53; H, 3.93; N, 2.87. Found: C, 66.62; H, 3.99; N, 2.86.

1-(4-Methoxyphenyl)-3,3,6-trimethyl-8-(*p*-tolyl)-3,8-dihydroindeno[2,1-*b*]pyrrol-2-one (4j): 88% yield; mp 177−178 °C; IR ν (cm^{-1}) 1721, 1619, 1513; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.20 (d, J = 6.4 Hz, 1H), 7.18 (d, J = 8.9 Hz, 2H), 7.02 (d, J = 7.6 Hz, 1H), 6.95 (d, J = 8.0 Hz, 2H), 6.92 (s, 1H), 6.89 (d, J = 8.1 Hz, 2H), 6.79 (d, J = 9.0 Hz, 2H), 4.97 (s, 1H), 3.74 (s, 3H), 2.23 (s, 3H), 2.18 (s, 3H), 1.57 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 184.5, 158.8, 151.2, 149.1, 137.2, 136.7, 135.2, 133.6, 131.2, 130.1, 129.8, 128.38, 128.35, 126.5, 125.9, 117.7, 114.6, 55.7, 51.1, 46.0, 23.7, 23.1, 21.4, 21.0; MS (EI) 408 (100), 409 (M^+, 50). Anal. Calcd for $C_{28}H_{27}NO_2$: C, 82.12; H, 6.65; N, 3.42. Found: C, 82.03; H, 6.74; N, 3.30.

3,3-Diethyl-1-(4-methoxyphenyl)-6-methyl-8-(*p*-tolyl)-3,8-dihydroindeno[2,1-*b*]pyrrol-2-one (4k): 76% yield; mp 145−146 °C; IR ν (cm^{-1}) 1719, 1610, 1513; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.15 (d, J = 5.6 Hz, 1H), 7.13 (d, J = 6.9 Hz, 2H), 7.02 (d, J = 7.6 Hz, 1H), 6.95 (d, J = 8.0 Hz, 2H), 6.92 (s, 1H), 6.91 (d, J = 8.2 Hz, 2H), 6.80 (d, J = 8.9 Hz, 2H), 5.04 (s, 1H), 3.74 (s, 3H), 2.23 (s, 3H), 2.19 (s, 3H), 2.15−1.82 (m, 4H), 0.91 (t, J = 7.4 Hz, 3H), 0.76 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 183.5, 159.0, 154.0, 148.9, 137.3, 137.2, 135.2, 133.6, 130.0, 129.7, 128.6, 128.4, 126.9, 126.4, 125.9, 117.8, 114.7, 56.7, 55.7, 51.2, 21.4, 21.0, 10.2, 9.7; MS (EI) 407 (100), 436 (60), 437 (M^+, 40). Anal. Calcd for $C_{30}H_{31}NO_2$: C, 82.35; H, 7.14; N, 3.20. Found: C, 82.15; H, 7.03; N, 3.06.

1′-(4-Methoxyphenyl)-6′-methyl-8′-(*p*-tolyl)spiro[cyclopentane-1,3′-indeno[2,1-*b*]pyrrol]-2′-one (4l): 74% yield; mp 102−103 °C; IR ν (cm^{-1}) 1720, 1611, 1513; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.19 (d, J = 8.9 Hz, 2H), 7.11 (d, J = 7.6 Hz, 1H), 7.02 (d, J = 7.6 Hz, 1H), 6.95 (d, J = 8.0 Hz, 2H), 6.93 (s, 1H), 6.89 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 4.97 (s, 1H), 3.74 (s, 3H), 2.23 (s, 3H), 2.19 (s, 3H), 2.12−2.02 (m, 8H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 185.3, 158.7, 151.7, 149.2, 137.1, 136.5, 135.3, 133.5, 130.5, 130.0, 129.9, 128.4, 128.3, 126.5, 126.0, 117.7, 114.5, 55.6, 55.5, 51.0, 36.9, 36.4, 27.74, 27.68, 21.3, 21.0; MS (EI) 433 (100), 435 (M^+, 65). Anal. Calcd for $C_{30}H_{29}NO_2$: C, 82.73; H, 6.71; N, 3.22. Found: C, 82.69; H, 6.82; N, 3.13.

1′-(4-Methoxyphenyl)-6′-methyl-8′-(*p*-tolyl)spiro[cyclohexane-1,3′-indeno[2,1-*b*]pyrrol]-2′-one (4m): 65% yield; mp 142−143 °C; IR ν (cm^{-1}) 1725, 1599, 1513; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.32 (d, J = 7.7 Hz, 1H), 7.14 (d, J = 8.9 Hz, 2H), 7.04 (d, J = 7.7 Hz, 1H), 6.94 (d, J = 8.0 Hz, 2H), 6.92 (s, 1H), 6.87 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 4.92 (s, 1H), 3.74 (s, 3H), 2.23 (s, 3H), 2.18 (s, 3H), 1.67−2.00 (m, 10H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 182.5, 158.0, 151.6, 148.2, 136.7, 136.3, 134.4, 132.4, 129.6, 129.2, 128.8, 127.5, 127.4, 126.1, 125.0, 118.4, 113.7, 54.8, 50.5, 49.8, 32.8, 32.3, 25.0, 21.7, 21.6, 20.4, 20.1; MS (ESI) 450 (M + 1). Anal. Calcd for $C_{31}H_{31}NO_2$: C, 82.82; H, 6.95; N, 3.12. Found: C, 82.64; H, 6.74; N, 3.04.

General Procedure for the Isomerization of Compounds 4 to 5. *Method A.* Compounds **4a**−**d** (0.5 mmol) were stirred in trichloroethane (30 mL) for 0.5−1 h at room temperature. After removal of the solvent under vacuum, compounds **5a**−**d** were isolated by chromatography on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (10:1).

Method B. At room temperature, the solution of $Et_2O\cdot BF_3$ (0.25 mmol) in toluene (5 mL) was added dropwise to compounds **4** (0.5 mmol) in toluene (30 mL), and the mixture was stirred for a period of time until **4** was consumed (about 0.5−5 h). After removal of solvent under vacuum, compounds **5** were obtained by chromatography on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (10:1).

3,3-Dimethyl-1,8-diphenyl-3,3a-dihydroindeno[2,1-*b*]pyrrol-2-one (5a): 87% yield (method A); mp 165−166 °C; IR ν (cm^{-1}) 1735, 1721, 1643, 1596; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43 (d, J = 7.2 Hz, 1H), 7.28 (d, J = 3.2 Hz, 2H), 7.14−7.20 (m, 3H), 7.04−7.12 (m, 6H), 7.00 (dd, J = 7.6, 1.1 Hz, 2H), 3.94 (s, 1H), 1.71 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 182.4, 149.0, 145.4, 137.0, 135.3, 132.4, 128.6, 128.4, 127.64, 127.59, 126.9, 126.3, 124.3, 123.7, 123.4, 119.8, 117.8, 59.4, 46.9, 23.8, 20.1; MS (ESI) 352 (M + 1). Anal. Calcd for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99. Found: C, 85.22; H, 5.98; N, 3.93.

3,3-Dimethyl-8-phenyl-1-(*p*-tolyl)-3,3a-dihydroindeno-[2,1-*b*]pyrrol-2-one (5b): 86% yield (method A); mp 150−151 °C; IR ν (cm^{-1}) 1730, 1627, 1595; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41 (dd, J = 7.2, 0.6 Hz, 1H), 7.27 (d, J = 3.8 Hz, 2H), 7.14−7.19 (m, 1H), 7.05−7.13 (m, 3H), 6.98−7.01 (m, 4H), 6.90 (d, J = 8.2 Hz, 2H), 3.92 (s, 1H), 2.23 (s, 3H), 1.70 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 182.6, 149.1, 145.8, 137.0, 136.2, 132.8, 132.4, 129.0, 128.7, 127.6, 126.8, 124.4, 123.6, 123.4, 119.7, 117.6, 59.4, 46.7, 23.8, 21.0, 20.2; MS (ESI) 366 (M + 1). Anal. Calcd for $C_{26}H_{23}NO$: C, 85.45; H, 6.34; N, 3.83. Found: C, 85.34; H, 6.41; N, 3.75.

1-(4-Methoxyphenyl)-3,3-dimethyl-8-phenyl-3,3a-dihydroindeno[2,1-*b*]pyrrol-2-one (5c): 84% yield (method B); mp 173−174 °C; IR ν (cm^{-1}) 1724, 1634, 1513; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42 (d, J = 7.4 Hz, 1H), 7.27 (d, J = 3.9 Hz, 2H), 7.15−7.20 (m, 1H), 7.07−7.12 (m, 3H), 7.03 (dd, J = 6.8, 2.1 Hz, 2H), 7.00 (dd, J = 7.6, 1.5 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 3.93 (s, 1H), 3.73 (s, 3H), 1.71 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 182.7, 158.0, 149.1, 146.1, 136.9, 132.4, 128.8, 128.4, 127.63, 127.55, 126.8, 125.9, 123.6, 123.4, 119.6, 117.4, 113.7, 59.4, 55.5, 46.7, 23.8, 20.2; MS (ESI) 382 (M + 1). Anal. Calcd for $C_{26}H_{23}NO_2$: C, 81.86; H, 6.08; N, 3.67. Found: C, 81.77; H, 6.18; N, 3.59.

1-(4-Chlorophenyl)-3,3-dimethyl-8-phenyl-3,3a-dihydroindeno[2,1-*b*]pyrrol-2-one (5d): 82% yield (method A); mp 202−203 °C; IR ν (cm^{-1}) 1725, 1638; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43 (dd, J =7.3, 0.8 Hz, 1H), 7.28 (d, J = 4.2 Hz, 2H), 7.06 (d, J = 9.0 Hz, 2H), 7.11 (d, J = 9.0 Hz, 2H), 7.05−7.21 (m, 4H), 7.00 (dd, J = 6.6, 1.7 Hz, 2H), 3.92 (s, 1H), 1.71 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 182.3, 148.8, 144.7, 136.9, 133.8, 132.2, 131.5, 128.6, 128.5, 127.8, 127.7, 127.3, 125.3, 123.9, 123.4, 119.9, 118.3, 59.3, 46.9, 23.8, 20.1; MS (ESI) 386 (M + 1). Anal. Calcd for $C_{25}H_{20}ClNO$: C, 77.81; H, 5.22; N, 3.63. Found: C, 77.71; H, 5.35; N, 3.57.

3,3-Dimethyl-1-phenyl-6-methoxy-8-(*p*-methoxyphenyl)-3,3a-dihydroindeno[2,1-*b*]pyrrol-2-one (5g): 89% yield (method B); mp 129−130 °C; IR ν (cm^{-1}) 1723, 1647, 1607; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.29 (d, J = 8.0 Hz, 1H), 7.05−7.16 (m, 5H), 7.90 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 2.3 Hz, 1H), 6.69 (dd, J = 8.1, 2.4 Hz, 1H), 6.60 (d, J = 8.7 Hz, 2H), 3.86 (s, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 1.67 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 182.5, 160.9, 159.6, 151.7, 147.3, 136.7, 130.6, 130.1, 129.1, 126.8, 125.7, 125.3, 124.8, 117.8, 114.0, 109.4, 106.8, 59.2, 55.5, 47.4, 23.8, 20.2; HRMS (TOF-ESI) 412.1916 (M + 1), 412.1913 (M + 1).

3,3-Diethyl-1-(4-methoxyphenyl)-6-methyl-8-(*p*-tolyl)-3,3a-dihydroindeno[2,1-*b*]pyrrol-2-one (5k): 65% yield (method B); mp 120−121 °C; IR ν (cm^{-1}) 1723, 1641, 1596, 1512; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.22 (d, J = 7.5 Hz, 1H), 6.92 (dd, J = 6.8, 2.1 Hz, 2H), 6.86 (s, 1H), 6.82 (d, J = 7.5 Hz, 1H), 6.79 (d, J = 8.0 Hz, 2H), 6.74 (d, J = 8.1 Hz, 2H), 6.55 (dt, J = 9.0, 2.1 Hz, 2H), 4.00 (s, 1H), 3.59 (s, 3H), 2.17 (s, 3H), 2.10 (s, 3H), 1.86−1.90 (m, 2H), 1.29−1.44 (m, 2H), 1.08 (t, J = 7.5 Hz, 3H), 0.59 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 181.2, 159.1, 150.3, 149.2, 137.5, 136.8, 135.4,

130.9, 129.7, 129.6, 129.1, 127.3, 124.8, 124.4, 120.9, 116.4, 114.3, 55.7, 55.0, 28.2, 27.7, 21.6, 21.1, 10.0, 9.2; HRMS (TOF-ESI) 438.2429 (M + 1), 438.2433 (M + 1).

Procedure for the Isolation of Intermediate 7g. The mixture of spiro[β-lactam-4,2′-oxadiazoline] **1a** (1.5 mmol) and 3,6-bis-(*p*-methoxyphenyl)tetrazine **3c** (1 mmol) was heated at 100−110 °C in toluene (30 mL) for 8 h. After removal of the solvent under vacuum, the yellow compound **7g** was isolated from the mixture of products by chromatography on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate 3:1.

3′5′-Bis(4-methoxyphenyl)-3,3-dimethyl-1-phenylspiro-[azetidine-2,4′-pyrazol]-4-one (7g): 34% yield; mp 123−124 °C; IR ν (cm^{-1}) 1769, 1606, 1507; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.79 (d, J = 8.8 Hz, 4H), 7.43 (t, J = 8.0 Hz, 2H), 7.18−7.27 (m, 3H), 6.99 (d, J =9.0 Hz, 4H), 3.84 (s, 6H), 1.17 (s, 6H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 170.1, 168.8, 163.0, 138.6, 131.1, 129.8, 126.1, 125.8, 117.4, 115.5, 81.4, 64.1, 55.8, 21.3; MS (ESI) 439 (M^+). Anal. Calcd for $C_{27}H_{25}N_3O_3$: C, 73.78; H, 5.73; N, 9.56. Found: C, 73.64; H, 5.92; N, 9.54.

Procedure for the Isolation of Intermediates 8. The mixture of spiro[β-lactam-4,2′-oxadiazoline] **1a** (2 mmol) and diphenytetrazines **3a**, bis(4-chlorophenyl)tetrazine **3d**, or bis(4-trifluoromethylphenyl)tetrazine **3e** (1 mmol) was heated for 1.5−2.5 h in refluxing toluene (30 mL) (note: **1a** reacted with **3a** for 1.5 h, while **1a** reacted with **3d** or **3e** for 2.5 h). After removal of 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 5:1. Compounds **8i** and product **5i** were isolated in 32% and 53% yields, respectively, from the reaction of **1a** with bis(4-trifluoromethylphenyl)tetrazine **3e**. However, the compounds **8a** and **8h** could not be separated from product **4a** and **5h**, respectively, by chromatography. Finally, compound **8a**, or **8h**, was precipitated from the mixture of **8a** with **4a**, or **8h** with **5h**, in petroleum ether and ethyl ether.

3,6a-Diphenyl-6,6-dimethyl-4-phenyl-6,6a-dihydropyrrolo[3,2-*c*]pyrazol-5-one (8a): mp 118−119 °C; IR ν (cm^{-1}) 1752, 1626; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.59 (d, J = 8.7 Hz, 2H), 7.44−7.53 (m, 7H), 7.39 (t, J = 7.2 Hz, 1H), 7.32 (d, J = 7.0 Hz, 2H), 7.27 (t, J = 7.2 Hz, 1H), 7.20 (t, J = 7.0 Hz, 2H), 1.30 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 182.2, 156.5, 136.4, 136.0, 135.2, 130.8, 130.3, 129.7, 129.35, 129.30, 128.8, 128.7, 128.6, 125.5, 107.6, 56.0, 21.2, 20.3; HRMS (TOF-ESI) 380.1768 (M + 1), 380.1763 (M + 1).

3,6a-Bis(4-chlorophenyl)-6,6-dimethyl-4-phenyl-6,6a-dihydropyrrolo[3,2-*c*]pyrazol-5-one (8h): mp 147−148 °C; IR ν (cm^{-1}) 1758, 1656; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.60 (d, J = 8.7 Hz, 2H), 7.47−7.59 (m, 7H), 7.29 (dd, J = 6.6, 2.0 Hz, 2H), 7.23 (dd, J = 6.8, 2.1 Hz, 2H), 1.32 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 182.0, 156.9, 135.9, 135.0, 134.9, 124.4, 134.1, 130.8, 130.4, 130.3, 129.8, 129.5, 129.1, 128.9, 125.8, 107.1, 56.1, 21.1, 20.2; HRMS (TOF-ESI) 448.0987 (M + 1), 448.0983 (M + 1).

3,6a-Bis(4-trifluoromethylphenyl)-6,6-dimethyl-4-phenyl-6,6a-dihydropyrrolo[3,2-*c*]pyrazol-5-one (8i): 31% yield; mp 150−151 °C; IR ν (cm^{-1}) 1753, 1655; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.86 (s, 4H), 7.49−7.56 (m, 9H), 1.34 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 182.0, 158.5, 140.1, 135.9, 134.5, 133.9, 131.1, 130.8, 130.5, 130.2, 129.9, 129.8, 129.5, 129.4, 126.70, 126.66, 126.4, 126.3, 126.1, 125.69, 125.65, 123.7, 123.6, 107.5, 56.4, 21.2, 20.3; HRMS (TOF-ESI) 516.1506 (M + 1), 516.1511 (M + 1).

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR and ^{13}C NMR spectra of products **4**, **5**, **7g**, **8a**, **8h**, and **8i** excluding those byproducts without full characterization, ORTEP drawing of X-ray structures of compounds **4c**, **5h**, **7g**, and **8h** as well as single crystal data of **4c**, **5h**, **7g**, and **8h** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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