4-Substituted 2,3-Dihydroisoxazoles as Masked Azomethine Ylides: Access to Pyrrole Derivatives by 1,5- and 1,7-Dipolar Electrocyclizations of Enynyl Derivatives

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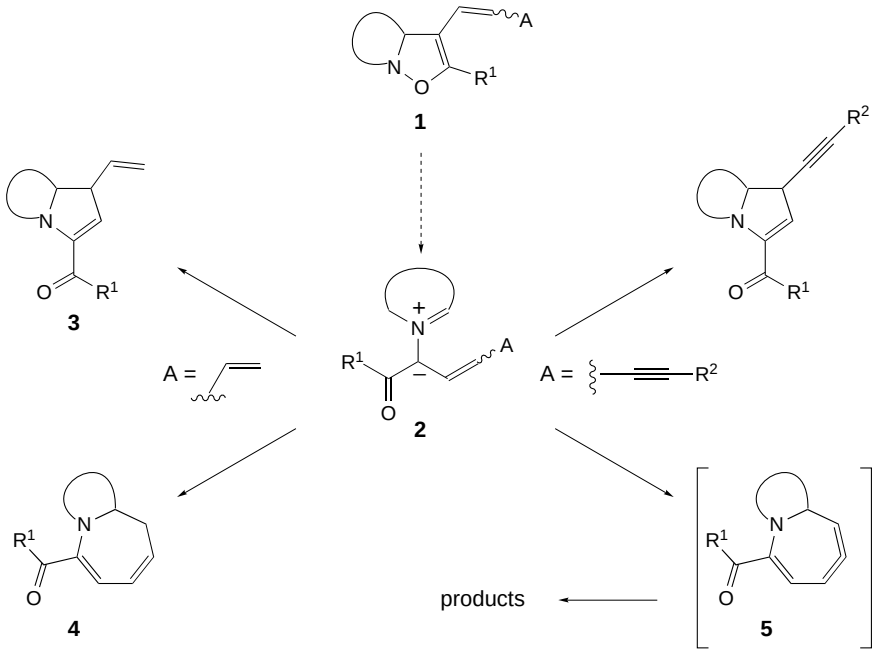
Dedicated to Professor Dr. *Horst Prinzbach* with best wishes on the occasion of his 70th birthday

The enynyl-substituted 2,3-dihydroisoxazoles ('isoxazolines') **9**–**14** were prepared by highly (*Z*)-selective *Peterson* olefination reaction from the corresponding carbaldehydes **6**–**8**. On short-time thermolysis (280–406°/10 s) the TMS derivatives **9**–**11** give rise to the annulated pyrrolines **18**–**20**, which, in some cases, suffer CH_4 elimination affording the pyrroles **15**–**17**. In contrast, thermolysis of the terminal alkyne derivatives **12**–**14** leads to the bicyclic compounds **21**–**23**. The reaction pathways are discussed on the basis of the formation of conjugated azomethine ylides as key intermediates, which either undergo a 1,5-cyclization to **18**–**20** or a 1,7-ring-closure affording cycloallene intermediates of type **V**, which are further transformed into the azepino pyrroles **21**–**23**.

Introduction. – In contrast to numerous successful 8π-cyclization reactions with conjugated 1,3-dipole systems like nitrile ylides, nitrile imines, diazo compounds, carbonyl ylides, azomethine imines, and nitrones, resulting in the formation of seven-membered heterocycles [1], surprisingly few applications are known with azomethine ylides as the dipolar component [1–4]. Whereas, in some reports, azomethine ylides have been postulated as reactive species in more complex, multistep rearrangements [5], three methods proved especially successful for the generation of the conjugated dipole systems as potential precursors of the anticipated seven-membered heterocycles: *i*) deprotonation of cycloimmonium salts [2], *ii*) H-shift in corresponding imines [3], and *iii*) reaction of conjugated aldehydes and *N*-substituted amino acids followed by decarboxylation [4]. We have recently shown that appropriately C(4)-substituted 2,3-dihydroisoxazoles of type **1** might also serve as precursors of azomethine ylides **2** (*Scheme 1*), affording the corresponding pyrrole and/or azepine derivatives **3**/**4** after a sequential transformation including *i*) cleavage of the weak N–O bond, *ii*) C–N bonding under formation of an aziridine ring, *iii*) C,C cleavage to **2**, and *iv* termination by either 1,5- or 1,7-dipolar electrocyclization [6].

Here we would like to disclose our latest results with examples of system **1** bearing a butenynyl group as a side chain, which eventually would give rise to the labile seven-membered vinyl cycloallene **5** after 8π-cyclization of the azomethine ylide **2** (A = $-C{\equiv}CR^2$) [7]. Analogous reactions have been performed with carbonyl ylides and nitrones as dipoles resulting in the remarkably efficient formation of simple and differently annulated vinyl furans [8] and acyl pyrroles/α-pyridons [9], respectively, after multistep rearrangements of the primarily formed seven-membered heterocycloallenes.

Scheme 1

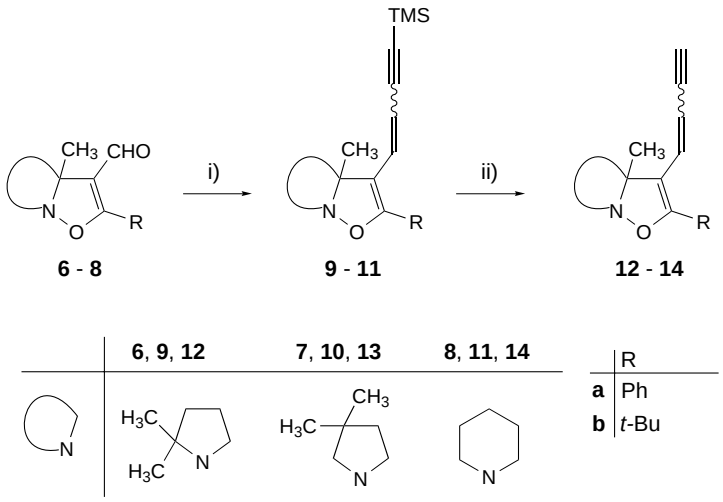


Results and Discussion. – The synthesis of the 2,3-dihydroisoxazole systems was accomplished by regioselective 1,3-dipolar cycloaddition of phenyl and *tert*-butyl prop-2-ynal to the corresponding nitrones as decribed in [6][7]. For introduction of the butenynyl function, the *Peterson* olefination [10] of the aldehydes **6**–**8** with bis(trimethylsilyl)propyne in the presence of $(i\text{-PrO})_4Ti$ proved to be the method of choice (*Scheme 2*) [11]. This olefination method gave high yields of the products **9**–**11** (*Table*), and the diastereoisomer ratios were in favor of the desired (*Z*)-isomers (6:1 to 50:1), as clearly indicated by the vicinal ^{1}H-NMR coupling constant of the olefinic protons ($J_{cis} \approx 12$ Hz, $J_{trans} \approx 16$ Hz). Protodesilylation of **9**–**11** with K_2CO_3 in MeOH afforded the terminal alkynes **12**–**14** (90–99% yield) with the (*Z*)/(*E*) ratio remaining unchanged.

The thermal reactions of the butenynyl-substituted compounds **9**–**14**[1]) were performed with *ca.* 10^{-2} M solutions in benzene under short-time thermolysis conditions at 280–406° with a contact time of *ca.* 10 s within the heating zone [8b]. This technique proved superior to other methods like flash-vacuum thermolysis or heating of solutions in an autoclave [12][13]. After purification and separation of the reaction mixture by flash chromatography, the product distribution for silylated *vs.* terminal alkynes turned out to be different. The silylated compounds **9**–**11** afforded the annulated pyrroles **15**–**17**, and the pyrrolines **18** and **19**, as well as the pyrrole **17** in the **b**-series with R = *t*-Bu

[1]) For simplicity, only the relevant (*Z*)-isomers of the enynyl dihydroisoxazoles are considered in the discussion.

Scheme 2



i) 1. TMS-C≡C–CH_2TMS, BuLi, $(i\text{-PrO})_4$Ti; 2. HCl. ii) K_2CO_3, MeOH, r.t.

Table 1. Peterson *Olefination of the Dihydroisoxazole-carbaldehydes* **6**–**8** *and Subsequent Hydrodesilylation* (yields [%] and (*Z*)/(*E*) ratio of **9**–**14**)

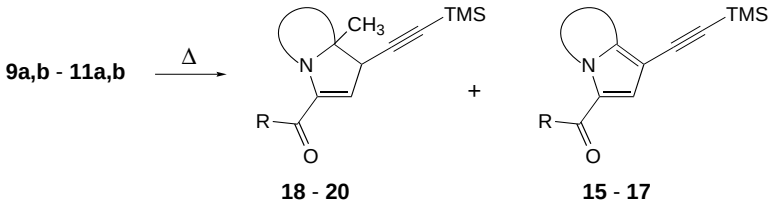
	9	**12**	(*Z*)/(*E*)	**10**	**13**	(*Z*)/(*E*)	**11**	**14**	(*Z*)/(*E*)
a	74	99	24 : 1	94	97	50 : 1	92	90	12 : 1
b	68	96	6 : 1	86	92	25 : 1	88	92	50 : 1

(*Scheme 3*). In contrast to the behavior of related butadienyl-substituted derivatives, which led to mixtures of the corresponding pyrrole and azepine systems [6][7] (**3** and **4**, resp., *Scheme 1*), only one product was obtained in our case. Their formation can be explained by a reaction pathway involving sequential rearrangement of the dihydroisoxazole moiety (**I**) into the acyl azidirine (**II**), and azomethine ylide (**III**), followed by a 1,5-dipolar electrocyclization leading to the dihydropyrroles **IV** as primary products (*Scheme 4*).

It has to be mentioned that, unlike the related carbonyl ylides, 6π-cyclizations of vinyl azomethine ylides are less common (for a review on 1,5-dipolar electrocyclizations, see [14]). Under the harsh reaction conditions, the benzoyl derivatives **18a**–**20a**, as well as **20b** suffer formal loss of CH_4 (type **IV** → **IX**, *Scheme 4*), a quite unusual elimination process which has been reported before, in a few cases [15]. Surprisingly, both the compounds **18b** and **19b**, obtained in 70–80% yield, were stable under the reaction conditions despite of their pivaloyl groups.

Contrary to the above results, treatment of the terminal alkynes **12**–**14** under short-time thermolysis conditions gave rise to structurally different products, namely the 1,2-annulated heterobicycles **21**–**23** (*Scheme 5*), consisting of both a pyrrole system and a cycloheptene or cyclooctene ring, respectively; only in the case of **12a** the 2,3-annulated isomer **24** was isolated as an additional product (see below). According to the analytical

Scheme 3



18 - 20 **15 - 17**

a: R = Ph
b: R = *t*-Bu

	18	**15**	**19**	**16**	**20**	**17**
a[a)]	–	45	–	23	–	26
b[b)]	72	–	79[c)]	–	–	38

[a]) 320°/10 s. [b]) 280°/10 s. [c]) On rising the temperature to 320°, the yield of **19b** decreased to 26%, and 5% of the pyrrole **16b** was isolated as a side-product.

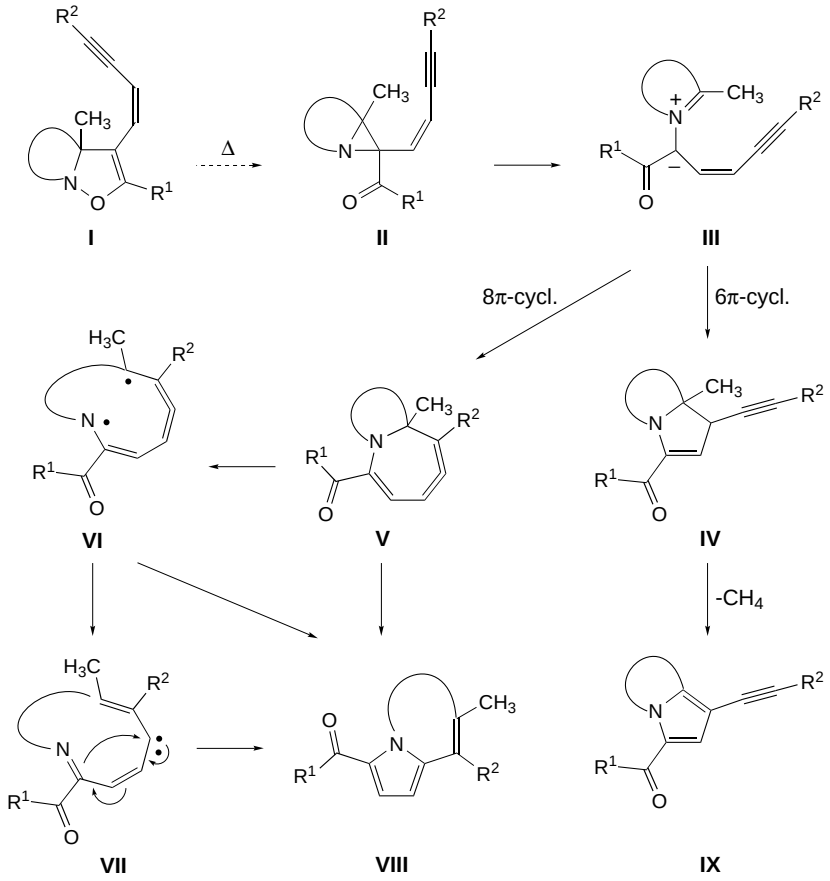
data, the reaction products are isomers of the starting dihydroisoxazoles. The final structure attribution to **21**–**23** is based on profound ^{1}H- and ^{13}C-NMR investigations including the HMBC technique for determining long range H,C correlations [16].

An indirect confirmation of the 1-azabicyclo[5.3.0]decatriene structure of the systems **21**, **22**, and their homologue **23** can be seen in the 2,3-annulated isomer **24**, which was formed together with **21a** in approximately equal amount during the thermolysis of **12a**. The isomer **24** was also obtained by thermal treatment of **21a**. This rearrangement might be explained by two consecutive 1,5-C migrations with the spiro compound **25** as an intermediate, followed by a final H-shift (**21a** → **25** → **26** → **24**, *Scheme 6*). Analogous transformations are known for some dipyrrolo[1,2-*a*:1′,2′-*d*]pyrazindiones [17].

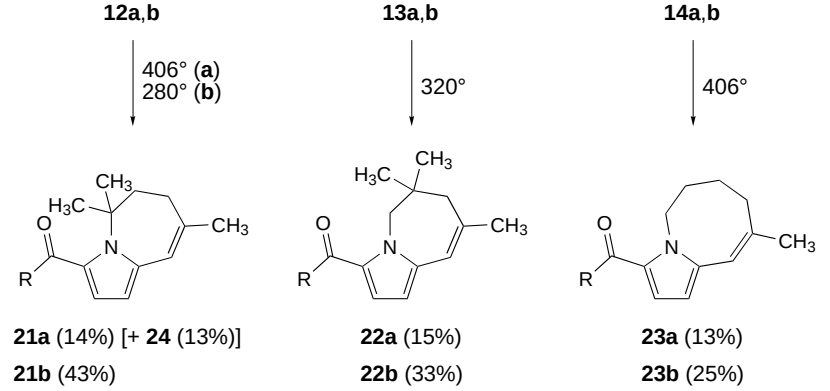
A mechanistic interpretation of the reactivity of the dihydroisoxazoles **9**–**11** and **12**–**14**, respectively, is given in *Scheme 4*, starting with compounds of general type **I**. After thermal activation, the known transformation into the aziridines **II** takes place with subsequent C–C bond cleavage and formation of the azomethine ylides **III** as central intermediates [18]. In the case of the silylated compounds (**9**–**11**) 6π-ring closure [14] then leads to the bicyclic dihydropyrrole derivatives **IV** which, in some cases and under forced conditions, undergo formal elimination of CH_4 to give **IX** [15]. Interestingly, a different deactivation process has to be suggested for the transformation of the terminal alkyne derivatives **12**–**14** at the stage of the azomethine ylides **III**. In those cases, annulated azepines **V**, possessing an allene functionality are formed[2]), which

[2]) Upon photolysis of **13a**, evidence for the intermediacy of a cyclic allene like **V** was obtained by the isolation of small amounts of a dimeric product probably formed by [2 + 2] cycloaddition of two allene moeties [7].

Scheme 4



Scheme 5

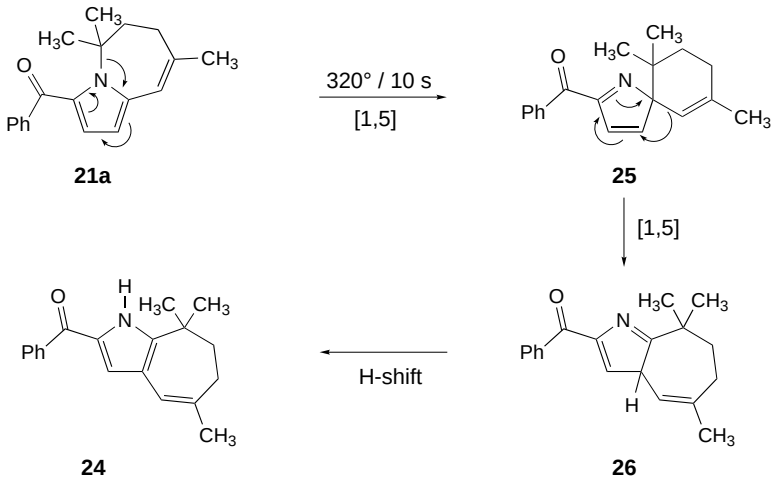


21a (14%) [+ **24** (13%)]
21b (43%)

22a (15%)
22b (33%)

23a (13%)
23b (25%)

Scheme 6



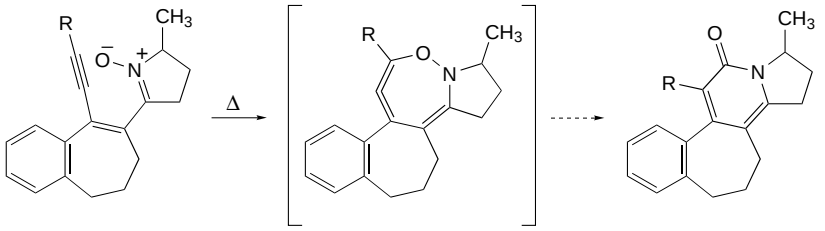
subsequently undergo further isomerization into the heterobicycles **VIII** by a formal 1,3-N shift. A possible pathway for the latter ring transformation includes a C–N bond cleavage to **VI** and either direct rebonding (**VI** → **VIII**) or electronic reorganization affording the carbene intermediates **VII** and leading to **VIII** by means of an electrocyclic 6π-ring closure. A similar mechanistic feature has been proposed for analogous cycloisomerizations with both appropriately conjugated carbonyl ylides [8] and nitrones as dipolar components [9]. Especially for the nitrone systems, strong support for the intermediacy of carbenes like **VII** has been obtained.

However, the question remains, why compounds **9**–**11** and **12**–**14** react in a different way by means of either 6π- or 8π-cyclization (*i.e.*, formation of type **IV**/**IX** *vs.* **VIII**). We assume that the bulky TMS group considerably slowes down the 8π-electrocyclization. Although the latter is usually very much favored compared to 6π-processes, particularly because of the more favorable stereoelectronic situation due to the helically distorted π-perimeter [1][2][8], steric factors exert a strong rate-decreasing influence on the formation of seven-membered rings of type **V**.

Evidence for the importance of steric effects on the 1,7-dipolar cyclization process have been obtained during experiments with structurally related nitrones. For instance, the reaction conditions for the transformation of the conjugated nitrones **27a**,**b** into the α-pyridone isomers **28a**,**b** – a reaction initiated by the rate-determining 1,7-dipolar ring closure to the cycloallenes **29a**,**b**, followed by several rearrangement steps – depend strongly on terminal substitution (*Scheme 7*). Whereas complete conversion for the silyl derivative **27a** needs 2 h at 220°, the reaction of **27b** is already finished after 15 min at 110° [19]. It has to be mentioned that in those cases a 1,5-cyclization process is not a productive alternative.

In line with the above discussion are the results with the 4-tolyl-substituted compound **30**, prepared from **12a** in high yield by *Sonogashira* coupling (*Scheme 8*) [20]. After short-time thermolysis and chromatographic purification of the reaction

Scheme 7



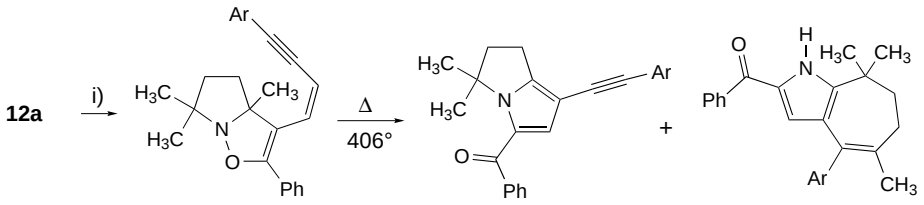
27 **29** **28a** (89%)

28b (92%)

a R = TBDMS: 220° / 2 h
b R = H : 110° / 15 min

mixture, two compounds were identified. The major component was the alkynyl pyrrole **31** and the minor one the cyclohepta[*b*]pyrrole **32**. With regard to the differently favored 1,5- and 1,7-electrocyclization processes, **30** as a precursor represents a borderline case between the terminal and the TMS-substituted alkyne derivatives, because the azomethine ylide intermediate reacts *via* both 6π- and 8π-cyclization resulting in the formation of **31** (**II** → **III** → **IV** → **IX**) and **32** (**II** → **III** → **V** → **VIII**, followed by two [1,5] sigmatropic rearrangements and one H-shift, as sketched in *Scheme 6*, respectively. Obviously, the steric demand of the 4-tolyl group is less significant compared to a TMS substituent.

Scheme 8



30 Ar = 4-MeC$_6$H$_4$ **31** (17%) **32** (7%)

i) 4-MeC$_6$H$_4$I, PdCl$_2$(PPh$_3$)$_2$, CuI, NEt$_3$, r.t., 98%.

The presence of bicyclic products of type **II** has been additionally confirmed in one case by independent thermolysis of the annulated aziridine **33**, which was obtained in pure form by photochemical transformation of **13a**. On short-time thermolysis of **33**, the annulated pyrrole **22a** was the only monomeric reaction product [7] (*Scheme 9*).

Conclusion. – With the successful transformation of conjugated dihydroisoxazoles into annulated pyrrole derivatives further examples have been added to previous work concerning the generation of intermediate azomethine ylides in intramolecular reaction pathways. Depending on the terminal substitution of the enynyl side-chains, either 6π- or 8π-electrocyclization reactions are involved as important product-determining steps.

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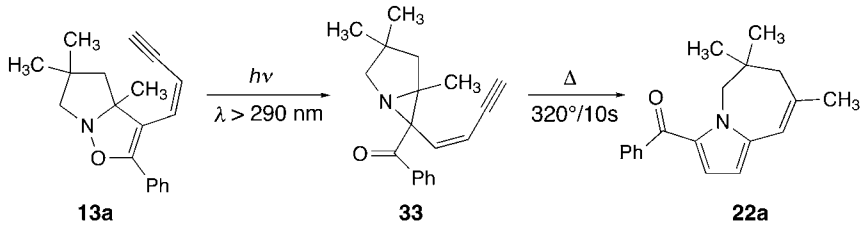
Scheme 9



Experimental Part

General. Products were isolated by flash chromatography (FC) on SiO_2 (*Silica 32–36*, *ICN Biomedicals*). TLC: SiO_2 *60 F-254*, 0.2 mm (*Merck*). Short-time thermolysis apparatus: a vertical, externally heated *Pyrex* tube (37 × 3 cm) packed with *Raschig* rings (*Pyrex*, 4 × 4 mm); packing height 18 cm, heating zone 30 cm; addition of the solutions through a dosing funnel (*Normag N 8056*) in a N_2 stream (flow rate 0.75 l/h), dropping rate 13 ml/h; temperature ±10°, contact time *ca*. 10 s [8b]. M.p.: uncorrected. UV: *Perkin Elmer Lamda 15*; in MeCN. IR: *Perkin-Elmer 297 Infracord*; in CCl_4. ^{1}H-NMR: *Bruker WM 250* (250 MHz), *WM 400* (400 MHz), and *DRX 500* (500 MHz); ^{13}C-NMR: *Bruker WM 400* (100 MHz) and *DRX 500* (125 MHz); $CDCl_3$ as solvent and TMS as internal standard. MS: *Finnigan MAT 44 S* (70 eV) with Datasystem *MAT SS 200*. Elemental analyses: *Perkin-Elmer Elemental Analyzer 240*.

General Procedure for the Preparation of the Enynyl-Substituted 2,3-Dihydroisoxazoles **9**–**11**. To a stirred soln. of 1,3-bis(trimethylsilyl)propyne (*ca*. 5–12 mmol) in 40 ml of dry THF was added under N_2 a soln. of BuLi in hexane (1 equiv.) at −25° to −30°. After stirring for 30 min, the mixture was cooled to −78°, treated with (i-PrO)$_4$Ti (1 equiv.) and stirred for an additional 15–20 min. At −78° the soln. of the aldehydes **6**–**8** (*ca*. 0.95 equiv.) in *ca*. 10 ml of dry THF was slowly added. After 30–45 min, the mixture was warmed to −30° or r.t., stirred for 30–60 min, hydrolyzed at −20° with 2N HCl, and extracted with Et_2O (3 × 20 ml). The org. phase was washed (sat. $NaHCO_3$ (2 × 80 ml) and NaCl solns.) and dried ($MgSO_4$). After concentration *in vacuo*, purification of the residue was accomplished by flash chromatography (SiO_2; cyclohexane/AcOEt 40:1 or 20:1). Due to the highly stereoselective formation of the required (*Z*)-isomers (see below), no further separation was performed. For obtaining pure (*E*)-isomers, iodide catalyzed (*Z*) → (*E*) isomerization can be applied.

*3a,4,5,6-Tetrahydro-3a,6,6-trimethyl-2-phenyl-3-[4-(trimethylsilyl)but-1-en-3-ynyl)]pyrrolo[1,2-*b*]isoxazole* ((*E*/*Z*)-**9a**). The reaction of a mixture of 1,3-bis(trimethylsilyl)propyne (2.63 g, 14.3 mmol), a 2.35M soln. of BuLi in hexane (14.3 mmol), (i-PrO)$_4$Ti (4.18 ml, 14.3 mmol) and **6a** (3.50 g, 13.9 mmol) in 62 ml of dry THF afforded 3.62 g (74%) of **9a** as a yellow oil ((*Z*)/(*E*) > 24:1). IR: 3054, 2963, 2130 (C≡C), 1597, 1492, 1447, 1347, 1250, 1114, 1071, 1006. UV: 251 (9200), 340 (15700). ^{1}H-NMR (250 MHz): 0.18 (*s*, Me_3Si); 1.22 (*s*, Me), 1.31 (*s*, 3 H, Me), 1.73 (*s*, 3 H, Me), 1.66–1.79 (*m*, CH_2), 2.03 (*m*, ^3J = 7, 1 H, CH_2), 2.51 (*dt*, ^2J = 13, ^3J = 7.5, 1 H, CH_2), 5.31 (*d*, ^3J = 12.6, HC=), 6.33 (*d*, ^3J = 12.6, HC=), 7.38 (*m*, 3 arom. H), 7.50 (m_c, 2 arom. H). ^{13}C-NMR (100 MHz): 0.1 (Me_3Si); 21.8 (Me); 28.3 (Me); 30.0 (Me); 36.3 (CH_2); 36.9 (CH_2); 68.3 (C_q); 77.2 (NC_q); 101.3 (≡*C*–Si(Me)$_3$); 102.0 (=CH); 105.4 (C≡); 115.5 (C_q=); 128.5 (arom. C); 128.9 (arom. C_q); 129.7 (arom. C); 130.9 (HC=); 156.8 (OC=). EI-MS: 351 (12, $M^{+\cdot}$], 336 (29), 281 (14), 266 (9), 105 (100), 77 (37). HR-MS: 351.2010 ($C_{22}H_{29}NOSi^+$; calc. 351.2018).

The data for (*E*)-**9a** were taken from a sample obtained as a red-brown oil in 87% yield after iodine/light-catalyzed isomerization of the (*Z*)-isomer: ^{1}H-NMR (250 MHz): 0.18 (*s*, Me_3Si); 1.18 (*s*, Me); 1.31 (*s*, Me); 1.55 (*s*, Me); 1.68–1.82 (*m*, CH_2); 1.85–1.93 (*m*, 1 H, CH_2), 2.43 (*m*, 1 H, CH_2), 5.55 (*d*, ^3J = 16.6, =CH); 6.79 (*d*, ^3J = 16.6, HC=); 7.38–7.43 (*m*, 3 arom. H); 7.50 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz): 0.1 (Me_3Si); 21.1 (Me); 28.3 (Me); 28.8 (Me); 34.9 (CH_2); 36.6 (CH_2); 68.9 (C_q); 76.5 (NC_q); 96.1 (≡*C*–$SiMe_3$); 103.8 (=CH); 105.8 (C≡); 115.6 (=C_q); 128.6 (arom. C); 128.6 (arom. C); 128.7 (arom. C_q); 129.7 (arom. C); 133.6 (HC=); 154.3 (OC=).

2-(tert-*Butyl)-3a,4,5,6-tetrahydro-3a,6,6-trimethyl-3-[4-(trimethylsilyl)but-1-en-3-ynyl)]pyrrolo[1,2-*b*]isoxazole* ((*Z*/*E*)-**9b**). The reaction of 1,3-bis(trimethylsilyl)propyne (1.77 g, 9.6 mmol), a 2.4M soln. of BuLi in hexane (11.1 mmol), (i-PrO)$_4$Ti (3.3 ml, 11.10 mmol), and **6b** (2.22 g, 9.36 mmol) in 66 ml of dry THF afforded 2.10 g (68%) of **9b** as a yellow oil ((*Z*)/(*E*) 6:1). IR: 2966, 2128, 1600, 1459, 1367, 1250, 1154, 1003. UV: 326

(5800), 249 (5700). ^{1}H-NMR (250 MHz): 0.18 (*s*, Me_3Si); 1.19 (*s*, Me); 1.22 (*s*, Me); 1.25 (*s*, *t*-Bu); 1.57 (*s*, Me); 1.66 (*t*, $^3J = 7$, 2 H−C(4)); 1.88 (*dt*, $^2J = 13$, $^3J = 7$, H−C(5)); 2.33 (*dt*, $^2J = 13$, $^3J = 7$, H−C(5)); 5.32 (*d*, $^3J = 12$, HC=); 6.44 (*d*, $^3J = 12$, =CH). ^{13}C-NMR (100 MHz): 0.1 (Me_3Si); 22.3 (Me); 28.1 (Me); 29.1 (*t*-Bu); 29.7 (Me); 33.6 (*t*-Bu); 36.2 (C(4)); 36.8 (C(5)); 68.2 (NC_q); 77.8 (NC_q); 100.1 (≡*C*−Me_3Si); 102.7 (=CH); 105.1 (C≡); 110.7 (C_q); 131.2 (=CH); 162.6 (CO). EI-MS: 331 (9, $M^{+\bullet}$), 316 (22), 261 (10), 246 (28), 204 (14), 176 (11), 75 (10), 73 (59), 57 (100). HR-MS: 331.2331 ($C_{20}H_{33}NOSi^+$; calc. 331.2331).

*3a,4,5,6-Tetrahydro-3a,5,5-trimethyl-2-phenyl-3-[4-(trimethylsilyl)but-1-en-3-ynyl]pyrrolo[1,2-*b*]isoxazole* ((*E*/*Z*)-**10a**). The reaction of the mixture of 1,3-bis(trimethylsilyl)propyne (2.21 g, 12.0 mmol), a 2.4M soln. of BuLi in hexane (12.0 mmol), (i-PrO)$_4$Ti (3.6 ml, 12.0 mmol) and **7a** (3.0 g, 11.67 mmol) in 52 ml of dry THF afforded 3.87 g (94%) of **10a** as an orange oil ((*Z*)/(*E*) >50:1).

Data of (*Z*)-**10a**: UV (MeCN): 334 (20000), 251 (7800). IR: 3070, 2950, 2840, 2130 (≡C), 1610, 1600, 1500, 1460, 1365, 1170, 1080. ^{1}H-NMR (250 MHz): 1.09 (*s*, Me); 1.23 (*s*, Me); 1.74 (*s*, Me); 1.92 (*dd*, $^2J = 13.6$, $^4J = 1.3$, H−C(4)); 2.34 (*d*, $^2J = 13.6$, H−C(4)); 2.88 (*d*, $^2J = 9.1$, 1 H−C(6)); 3.32 (*dd*, $^2J = 9.1$, $^4J = 1.3$, 1 H−C(6)); 5.35 (*d*, $^3J = 12.6$, C(3)−CH=C*H*); 6.39 (*d*, $^3J = 12.6$, C(3)−C*H*=CH); 7.39 (*m*, 3 arom. H); 7.48 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz): 28.1 (Me); 28.7 (Me), 29.4 (Me); 36.5 (C_q); 52.0 (CH_2); 69.1 (NCH_2); 76.9 (NC_q); 101.2 (≡C$SiMe_3$); 102.3 (C(8)); 105.4 (−C≡); 116.8 (C(3)); 128.5 (arom. C); 129.0 (arom. C); 129.4 (arom. C); 129.8 (H−C(7)); 131.1 (arom. C); 155.1 (OC=). EI-MS: 351 (46, $M^{+\bullet}$) 336 (43), 294 (52), 280 (59), 266 (22), 240 (12), 190 (36), 105 (100), 77 (61). HR-MS: 351.2021 ($C_{22}H_{29}NOSi^+$; calc. 351.2018).

Data of (E)-**10a**: IR: 3040, 2960, 2870, 2120 (C≡C), 1620, 1600, 1490, 1445, 1350, 1250, 1060. ^{1}H-NMR (250 MHz): 0.19 (*s*, Me_3Si); 1.08 (*s*, Me), 1.22 (*s*, Me); 1.55 (*s*, Me); 1.76 (*dd*, $^2J = 12.6$, $^4J = 1.4$, 1 H−C(4)); 2.26 (*d*, $^2J = 12.6$, 1 H−C(4)); 2.87 (*d*, $^2J = 9.1$, 1 H−C(6)); 3.34 (*dd*, $^2J = 9.1$, $^4J = 1.4$, 1 H−C(6)); 5.49 (*d*, $^3J = 16.7$, C(3)−CH=C*H*); 6.85 (*d*, $^3J = 16.7$, C(8)−C*H*=CH); 7.39–7.53 (*m*, 5 arom. H). ^{13}C-NMR (100 MHz): 27.7 (Me); 28.0 (Me); 28.1 (Me); 37.4 (C_q); 49.9 (CH_2); 69.5 (NCH_2); 76.4 (NC_q); 96.1 (≡*C*−$SiMe_3$), 104.2 (C(8)); 105.6 (C≡); 116.0 (C(3)); 128.5 (2 arom. C); 129.1 (arom. C_q); 129.6 (arom. C); 133.6 (C(7)); 152.1 (OC=). EI-MS: 351 (100, $M^{+\bullet}$), 336 (59), 294 (54), 280 (53), 278 (17), 266 (28), 246 (32), 240 (46), 220 (13), 190 (49), 176 (14), 105 (36).

*2-(*tert*-Butyl)-3a,4,5,6-tetrahydro-3a,5,5-trimethyl-3-[4-(trimethylsilyl)but-1-en-3-ynyl]pyrrolo[1,2-*b*]isoxazole* ((*Z*/*E*)-**10b**). The reaction of 1,3-bis(trimethylsilyl)propyne (1.56 g, 8.5 mmol), a 2.4M soln. of BuLi in hexane (9.0 mmol), (i-PrO)$_4$Ti (3.3 ml, 11.1 mmol), and **7b** (2.00 g, 8.46 mmol) in 63 ml of dry THF afforded 2.40 g (86%) of **10b** as an orange oil ((*Z*)/(*E*) 25:1).

Data of (Z)-**10b**: UV: 318 (17100), 249 (6200). IR: 2960, 2130, 1600, 1465, 1368, 1250, 1141, 1002. ^{1}H-NMR (250 MHz): 0.19 (*s*, Me_3Si); 1.07 (*s*, Me); 1.16 (*s*, Me); 1.23 (*s*, 9 H, *t*-Bu); 1.54 (*s*, Me); 1.74 (*dd*, $^2J = 13.1$, $^4J = 1.6$, 1 H, CH_2); 2.17 (*d*, $^2J = 13.1$, 1 H, CH_2); 2.70 (*d*, $^2J = 8.8$, 1 H, NCH_2); 3.14 (*dd*, $^2J = 8.8$, $^4J = 1.6$, 1 H, NCH_2); 5.34 (*d*, $^3J = 12.6$, =CH); 6.50 (*d*, $^3J = 12.6$, HC=). ^{13}C-NMR (100 MHz): 0.0 ($SiMe_3$); 28.1 (Me); 28.7 (Me); 29.0 (*Me*$_3$C); 29.2 (Me); 33.4 (Me$_3$*C*), 36.2; (C_q); 51.5 (CH_2); 68.6 (NCH_2); 76.9 (C(3a)); 100.3 (≡C−$SiMe_3$), 103.0 (=CH); 105.2 (C≡); 112.6 (C_q), 131.4 (=CH); 161.3 (C(2)). EI-MS: 331 (13, $M^{+\bullet}$), 316 (14), 274 (22), 232 (11), 218 (51), 177 (25), 73 (84), 57 (100). HR-MS: 331.2334 ($C_{20}H_{33}NOSi^+$; calc. 331.2331).

*4,5,6,7-Tetrahydro-3a-methyl-2-phenyl-3-[4-(trimethylsilyl)but-1-en-3-ynyl)]3a*H*-isoxazolo[2,3-*a*]pyridine* ((*Z*/*E*)-**11a**). The reaction of 1,3-bis(trimethylsilyl)propyne (3.64 g, 19.7 mmol), a 2.4M soln. of BuLi in hexane (19.73 mmol), (i-PrO)$_4$Ti (5.8 ml, 19.7 mmol), and **8a** (4.0 g, 16.4 mmol) in 90 ml of dry THF afforded 5.10 g (92%) of **11a** as a yellow oil ((*Z*)/(*E*) 12:1).

Data of (*Z*)-**11a**: UV: 337 nm (2100), 238 (12200). IR (mixture (*Z*/*E*)-**11a**): 3030, 2950, 2860, 2130, 1610, 1600, 1490, 1450, 1340, 1250, 1070, 1010. ^{1}H-NMR (250 MHz): 0.10 (*s*, Me_3Si); 1.58 (*s*, Me); 1.28 (*m*, 2 aliph. H); 1.52–1.78 (*m*, 3 aliph. H); 2.56 (*m*, 1 aliph. H); 2.89 (*m*, 1 H, NCH_2); 3.41 (*m*, 1 H, NCH_2); 5.50 (*d*, $^3J = 12.2$, C(3)−CH=C*H*); 6.37 (*d*, $^3J = 12.2$, C(3)−C*H*=CH); 7.35–7.44 (*m*, 3 arom. H); 7.60 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz): 0.1 (Me_3Si); 20.7 (CH_2); 23.5 (CH_2); 27.9 (Me); 32.6 (CH_2); 51.9 (NCH_2); 71.0 (NC_q); 101.4 (≡C−$SiMe_3$); 104.8 (C≡); 106.9 (HC=); 114.5 (C(3)); 128.3 (arom. C); 128.6 (arom. C_q); 129.5 (=CH); 132.5 (arom. C); 154.2 (OC=).

Data of (E)-**11a**: ^{1}H-NMR (250 MHz): 0.18 (*s*, Me_3Si); 1.26 (*s*, Me); 1.20–1.88 (*m*, 1 H−C(4), 2 H−C(5), 2 H−C(6)); 2.21 (*m*, 1 H−C(4)); 2.57 (*m*, 1 H−C(7)); 3.25 (*m*, 1 H−C(7)); 5.65 (*d*, $^3J = 16.5$, C(3)−CH=C*H*); 6.89 (*d*, $^3J = 16.5$, C(3)−C*H*=CH); 7.35–7.45 (*m*, 3 arom. H); 7.52 (*m*, 2 arom. H). EI-MS: 337 (14, $M^{+\bullet}$), 323 (14), 322 (53), 105 (100). HR-MS: 337.1861 ($C_{21}H_{27}NOSi^+$; calc. 337.1862).

2-(tert*-Butyl)-4,5,6,7-tetrahydro-3a-methyl-3-[4-(trimethylsilyl)but-1-en-3-ynyl]-3a*H*-isoxazolo[2,3-*a*]pyridine* ((*Z*/*E*)-**11b**). The reaction of 1,3-bis(trimethylsilyl)propyne (1.0 g, 5.4 mmol), a 2.4M soln. of BuLi in hexane (6 mmol), (i-PrO)$_4$Ti (2.05 ml, 7.0 mmol) and **8b** (1.12 g, 5.1 mmol) in 48 ml of dry THF afforded 1.43 g (88%) of **11b** as an orange oil ((*Z*)/(*E*) 50:1). UV: 310 (5900), 243 (7400). IR: 2960, 2856, 2144, 1605, 1452,

1250, 1106, 1013. ^{1}H-NMR (250 MHz): 0.16 (*s*, Me_3Si); 1.20 (*s*, *t*-Bu); 1.29 (*s*, Me); 1.33–1.53 (*m*, 2 CH_2); 1.61 (*m*, 1 H, CH_2); 1.97 (*m*, ^2J = 13, ^3J = 5, ^3J = 3, 1 H, CH_2); 2.83 (*ddd*, ^2J = 10, ^3J = 12, ^3J = 3, 1 H, NCH_2); 3.18 (*ddd*, ^2J = 10, ^3J = 3, ^3J = 1, 1 H, NCH_2); 5.60 (*d*, ^3J = 11.6, =CH); 6.23 (*d*, ^3J = 11.6, =CH). ^{13}C-NMR (100 MHz): 0.2 (Me_3Si); 20.8 (CH_2); 23.7 (CH_2); 28.0 (Me_3C), 28.4 (Me); 32.8 (CH_2); 33.0 (Me_3C), 51.5 (NCH_2); 71.1 (C(3a)); 99.9 (*C*$SiMe_3$); 104.3 (C≡); 109.1; 111.7 (=CH); 134.3 (=CH); 158.7 (C(2)). EI-MS: 317 (11, $M^{+\cdot}$), 302 (62), 260 (21), 246 (18), 232 (16), 218 (17), 204 (12), 176 (13), 73 (97), 57 (100). HR-MS: 317.2176 ($C_{19}H_{31}NOSi^+$; calc. 317.2175).

General Procedure for the Protodesilylation of **9**–**11**. A mixture of **9**–**11** (3–10 mmol) and 20–50 mg of dry K_2CO_3 in abs. MeOH (15–20 ml) was stirred for 24 h at r.t. under Ar in the dark. After the solvent was removed *in vacuo*, H_2O was added (50–100 ml), and the mixture was extracted with Et_2O (3 × 50–100 ml). The org. layer was washed with sat. NaCl soln., dried ($MgSO_4$), and concentrated *in vacuo*. Purification of the residue was accomplished by FC (SiO_2; cyclohexane/AcOEt 20:1). According to ^{1}H-NMR, the (*Z*)/(*E*) ratio of **12**–**14** remained unchanged.

*3-(But-1-en-3-ynyl)-3a,4,5,6-tetrahydro-3a,6,6-trimethyl-2-phenylpyrrolo[1,2-*b*]isoxazole* ((*Z*/*E*)-**12a**). The conversion of **9a** ((*Z*)/(*E*) 24:1; 3.56 g, 10.1 mmol) in 15 ml of dry MeOH and dry K_2CO_3 (50 mg) afforded after FC 2.80 g (99%) of ((*Z*/*E*)-**12a** as a red oil.

*Data of (*Z*)-***12a*** (obtained from (*Z*) → (*E*) isomerization): UV: 331 (17900), 252 (11000). IR: 3309 (≡CH), 3060, 2974, 2080 (C≡C), 1617, 1599, 1492, 1447, 1347, 1171. ^{1}H-NMR (250 MHz): 1.21 (*s*, Me); 1.31 (*s*, Me); 1.68–1.77 (*m*, CH_2); 1.71 (*s*, Me); 2.05 (*ddd*, ^2J = 13, ^3J = 7, ^3J = 6, 1 H, CH_2); 2.50 (*dt*, ^2J = 15, ^3J = 7.8, 1 H, CH_2); 3.22 (*dd*, ^4J = 2.7, ^5J = 0.8, ≡CH); 5.26 (*dd*, ^3J = 12.6, ^4J = 2.7, =CH); 6.38 (*dd*, ^3J = 12.6, ^5J = 0.8, =CH); 7.39 (*m*, 3 arom. H), 7.50 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz): 21.7 (Me); 28.2 (Me); 30.0 (Me); 36.2 (CH_2); 37.2 (CH_2); 68.3 (NC_q); 77.0 (NC_q); 83.7 (C≡); 83.9 (≡CH); 100.8 (=CH); 115.3 (=C_q); 128.5 (arom. C); 128.9 (arom. C); 128.9 (arom. C_q); 129.7 (arom. C); 131.7 (=CH); 156.2 (=CO). EI-MS: 279 (3, $M^{+\cdot}$), 264 (9), 209 (7), 180 (5), 139 (7), 115 (6), 105 (84), 77 (100). HR-MS: 279.1623 ($C_{19}H_{21}NO^+$; calc. 279.1623).

*Data of (*E*)-***12a***: IR: 3320 (H–C≡), 2980, 2100 (C≡C), 1630, 1600, 1490, 1450, 1355, 1260, 1170. ^{1}H-NMR (250 MHz): 1.20 (*s*, Me); 1.32 (*s*, Me); 1.70 (*s*, Me); 1.70–1.84 (*m*, 2 H, CH_2); 1.92 (*m*, ^3J = 6.7, ^2J = 12, 1 H, CH_2); 2.44 (*m*, ^3J = 7.7, ^3J = 8.8, ^2J = 12, 1 H, CH_2); 3.00 (*d*, ^4J = 2.4, HC≡); 5.48 (*dd*, ^3J = 16.6, ^4J = 2.4, HC=); 6.84 (*d*, ^3J = 16.6, HC=); 7.40 (*m*, 3 arom. H); 7.50 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz): 21.1 (Me); 28.2 (Me); 28.7 (Me); 34.9 (CH_2); 36.5 (CH_2); 68.8 (C_q); 76.4 (NC_q); 78.4 (HC≡); 84.2 (C≡); 102.5 (HC=); 115.2 (=C_q); 128.4 (arom. C); 128.5 (arom. C); 128.8 (arom. C_q); 129.7 (arom. C); 134.3 (HC=); 154.3 (OC=). EI-MS: 279 (12, $M^{+\cdot}$), 264 (23), 209 (21), 180 (11), 105 (100), 77 (48).

*3-(But-1-en-3-ynyl)-2-(*tert*-butyl)-3a,4,5,6-tetrahydro-3a,6,6-trimethylpyrrolo[1,2-*b*]isoxazole* ((*Z*/*E*)-**12b**). The reaction of **9b** ((*Z*)/(*E*) 6:1; 1.56 g, 4.70 mmol) in 18 ml of dry MeOH and dry K_2CO_3 (30 mg) afforded 1.18 g (96%) of (*Z*/*E*)-**12b** as an orange oil. The data are taken from the mixture of isomers.

*Data of (*Z*)-***12b***: UV: 314 (16100), 237 (7600). IR: 3310 (≡CH), 2972, 2083 (C≡C), 1602, 1459, 1367, 1341, 1150. ^{1}H-NMR (500 MHz): 1.18 (*s*, Me); 1.21 (*s*, Me); 1.25 (*s*, *t*-Bu); 1.54 (*s*, Me); 1.65 (*m*, 2 H–C(4)); 1.88 (*m*, ^2J = 13, 1 H–C(5)); 2.30 (*m*, ^2J = 13, ^3J = 7, 1 H–C(5)); 3.16 (*dd*, ^4J = 2.7, ^5J = 0.9, ≡CH); 5.30 (*dd*, ^3J = 12.5, ^4J = 2.7, C(3)–CH=C*H*); 6.50 (*dd*, ^3J = 12.5, ^5J = 0.9, C(3)–C*H*=CH). ^{13}C-NMR (100 MHz): 22.4 (Me); 28.2 (Me); 29.2 (*t*-Bu); 29.9 (Me); 36.3 (CH_2); 37.2 (CH_2); 68.4 (NC_q); 77.8 (≡CH); 83.0 (C≡); 102.3 (CH); 110.4 (=C_q); 132.4 (CH); 162.5 (OC=). EI-MS: 259 (26, $M^{+\cdot}$), 244 (60), 190 (39), 189 (36), 174 (100), 146 (95), 133 (30), 105 (21). HR-MS: 259.1934 ($C_{17}H_{25}NO^+$; calc. 259.1936).

*Data of (*E*)-***9b***: ^{1}H-NMR (500 MHz): 1.12 (*s*, Me); 1.24 (*s*, Me); 1.28 (*s*, *t*-Bu); 1.45 (*s*, Me); 1.71 (*m*, 2 H–C(4)); 1.82 (*m*, ^2J = 12, 1 H–C(5)); 2.35 (*m*, ^2J = 12, 1 H–C(5)); 2.97 (*dd*, ^4J = 2.2, ^5J = 0.5, ≡CH); 5.27 (*dd*, ^3J = 16.4, ^4J = 2.2, C(3)–CH=C*H*); 7.04 (*dd*, ^3J = 16.5, ^5J = 0.5, C(3)–C*H*=CH). ^{13}C-NMR (100 MHz): 21.3 (Me); 28.3 (Me); 29.0 (*t*-Bu); 29.6 (Me); 35.0 (CH_2); 36.6 (CH_2); 68.6 (C(6)); 77.5 (≡CH); 83.5 (≡C); 100.4 (CH); 110.1 (C(3a)); 134.5 (CH); 160.0 (C(2)).

*3-(But-1-en-3-ynyl)-3a,4,5,6-tetrahydro-3a,5,5-trimethyl-2-phenylpyrrolo[1,2-*b*]isoxazole* ((*E*/*Z*)-**13a**). The reaction of **10a** ((*Z*)/(*E*) 50:1; 3.15 g, 8.97 mmol) in 50 ml of dry MeOH and K_2CO_3 (50 mg) afforded 2.43 g (97%) of **13a** as a colorless solid.

*Data of (*Z*)-***13a***: UV: 324 (6300), 249 (8060), 233 (8270). IR: 3310 (≡CH), 3060, 2960, 2870, 2080 (C≡C), 1615, 1600, 1490, 1345, 1120. ^{1}H-NMR (250 MHz): 1.09 (*s*, Me); 1.22 (*s*, Me); 1.73 (*s*, Me); 1.88 (*dd*, ^2J = 13.4, ^4J = 1.2, 1 H–C(4)); 2.33 (*d*, ^2J = 13.4, 1 H–C(4)); 2.87 (*d*, ^2J = 9.1, 1 H–C(6)); 3.24 (*dd*, ^4J = 3, ^5J = 0.9, CH≡); 3.32 (*dd*, ^2J = 9.1, ^4J = 1.2, 1 H–C(6)); 5.30 (*dd*, ^3J = 12.5, ^4J = 3.0, C(3)–CH=C*H*); 6.44 (*dd*, ^3J = 12.5, ^5J = 0.9, C(3)–C*H*=CH); 7.40 (*m*, 3 arom. H); 7.48 (m_c, 2 arom. H). ^{13}C-NMR (100 MHz): 28.0 (Me); 28.6 (Me); 29.3 (Me); 36.3 (C(5)); 51.8 (CH_2); 68.9 (C(6)); 76.8 (C(3a)); 83.6 (C≡); 83.8 (≡CH); 101.2 (CH=); 116.2 (C(3)); 128.4 (arom. C); 128.9 (arom. C); 129.3 (arom. C); 129.8 (HC=); 131.9 (arom. C); 155.2 (OC=). EI-MS: 279

(49, $M^{+\cdot}$), 264 (32), 222 (76), 194 (56), 180 (16), 146 (24), 118 (54), 105 (100), 91 (24), 77 (87). HR-MS: 279.1629 ($C_{19}H_{21}NO^+$; calc. 279.1623).

*3-(But-1-en-3-ynyl)-2-(*tert*-butyl)-3a,4,5,6-tetrahydro-3a,5,5-trimethylpyrrolo[1,2-*b*]isoxazole* ((*Z*/*E*)-**13b**). The reaction of **10b** ((*Z*/*E*) 25:1; 1.70 g, 5.12 mmol) in 18 ml of dry MeOH and dry K_2CO_3 (35 mg) afforded 1.24 g (92%) of (*Z*/*E*)-**13b** as a yellow oil.

*Data of (*Z*)-***13b***: UV: 306 (7400), 234 (6800). IR: 3310 (≡CH), 2961, 2083 (C≡C), 1603, 1466, 1368, 1334, 1139. ^{1}H-NMR (500 MHz): 1.06 (*s*, Me); 1.16 (*s*, Me); 1.23 (*s*, *t*-Bu); 1.51 (*s*, Me); 1.70 (*dd*, ^2J = 13.2, ^4J = 1.4, 1 H–C(4)); 2.15 (*d*, ^2J = 13.2, 1 H–C(4)); 2.71 (*d*, ^2J = 8.8, 1 H–C(6)); 3.13 (*dd*, ^2J = 8.8, ^4J = 1.4, 1 H–C(6)); 3.15 (*dd*, ^4J = 2.7, ^5J = 0.9, CH≡); 5.33 (*dd*, ^3J = 12.5, ^4J = 2.7, C(3)–CH=C*H*), 6.56 (*dd*, ^3J = 12.5, ^5J = 0.9, C(3)–C*H*=CH). ^{13}C-NMR (100 MHz): 28.0 (Me); 28.7 (Me); 28.9 (*t*-Bu), 29.1 (Me); 33.3 (C_q); 36.0 (C_q); 51.2 (CH_2); 68.6 (C(6)); 83.0 (≡CH); 83.4 (≡C); 102.7 (CH); 112.0 (C(3)); 132.5 (CH); 160.9 (C(2)). EI-MS: 259 (13, $M^{+\cdot}$), 244 (10), 202 (33), 160 (12), 146 (100), 118 (33), 117 (11), 105 (15), 91 (16). HR-MS: 259.19342 ($C_{17}H_{25}NO^+$; calc. 259.19361).

*Data of (*E*)-***13b*** (obtained from (*Z*) → (*E*) isomerization): ^{1}H-NMR (500 MHz): 1.06 (*s*, Me); 1.18 (*s*, Me); 1.26 (*s*, *t*-Bu), 1.42 (*s*, Me); 1.68 (*dd*, ^2J = 12.4, ^4J = 1.3, 1 H–C(4)); 2.16 (*d*, ^2J = 12.4, 1 H–C(4)); 2.65 (*d*, ^2J = 9, 1 H–C(6)); 2.96 (*dd*, ^4J = 2.2, ^5J = 0.5, CH≡); 3.18 (*dd*, ^2J = 9, ^4J = 1.3, 1 H–C(6)); 5.19 (*dd*, ^3J = 16.4, ^4J = 2.2, C(3)–CH=C*H*); 7.08 (*dd*, ^3J = 16.4, ^5J = 0.5, C(3)–C*H*=CH).

*4,5,6,7-Tetrahydro-3a-methyl-2-phenyl-3-(but-1-en-3-ynyl)-3a*H*-isoxazolo[2,3-*a*]pyridine* ((*Z*/*E*)-**14a**). The conversion of **11a** ((*Z*/*E*) 12:1; 2.5 g, 7.4 mmol) in 74 ml of dry MeOH and dry K_2CO_3 (50 mg) afforded 1.77 g (90%) of (*Z*/*E*)-**14a**.

*Data of (*Z*)-***14a***: ^{1}H-NMR (250 MHz): 1.54 (*s*, Me); 1.20–1.76 (*m*, 5 H, 1 H–C(4), 2 H–C(5), 2 H–C(6)); 2.45 (m_c, 1 H–C(4)); 2.95 (m_c, 1 H–C(7)); 3.05 (*d*, ^4J = 2.7, CH≡); 3.40 (m_c, 1 H–C(7)); 5.47 (*dd*, ^3J = 11.9, ^4J = 2.7, CH=); 6.40 (*d*, ^3J = 11.9, CH=); 7.30–7.60 (*m*, 5 arom. H). ^{13}C-NMR (100 MHz): 23.5 (CH_2); 20.7 (CH_2); 27.9 (Me); 32.6 (CH_2); 52.0 (CH_2); 70.9 (C(3a)); 83.0 (C≡); 84.0 (C≡); 106.3 (CH=); 113.9 (C(3)); 128.3 (2 arom. C); 128.8 (arom. C_q); 129.4 (arom. C); 133.1 (CH=); 154.0 (C(2)).

*Data of (*E*)-***14a*** (obtained from (*Z*) → (*E*) isomerization): UV: 328 (11500), 231 (9500). IR: 3320, 2930, 2850, 2080, 1610, 1600, 1490, 1450, 1340, 1070, 1060. ^{1}H-NMR (250 MHz): 1.54 (*s*, Me); 1.20–1.76 (*m*, 1 H–C(4), 2 H–C(5), 2 H–C(6)); 2.45 (m_c, 1 H–C(4)); 2.95 (m_c, 1 H–C(7)); 3.01 (*d*, ^4J = 2.4, CH≡); 3.40 (m_c, 1 H–C(7)); 5.58 (*dd*, ^3J = 16.5, ^4J = 2.4, C(3)–CH=C*H*); 6.94 (*d*, ^3J = 16.5, C(3)–C*H*=CH); 7.30–7.69 (*m*, 5 arom. H). EI-MS: 265 (4, $M^{+\cdot}$), 250 (18), 106 (8), 105 (100), 77 (78). HR-MS: 265.1463 ($C_{19}H_{21}NO^+$; calc. 265.1467).

*4,5,6,7-Tetrahydro-3a-methyl-3-(but-1-en-3-ynyl)-2-(*tert*-butyl)-3a*H*-isoxazolo[2,3-*a*]pyridine* ((*Z*/*E*)-**14b**). The conversion of **11b** ((*Z*)/(*E*) 50:1; 0.97 g, 3.05 mmol) in 18 ml of dry MeOH and dry K_2CO_3 afforded 0.69 g (92%) of (*Z*/*E*)-**14b** as a red oil. UV: 299 (5600), 229 (8200). IR: 3310 (≡CH), 2938, 2089 (C≡C), 1609, 1453, 1360, 1106, 1017. ^{1}H-NMR (250 MHz): 1.19 (*s*, *t*-Bu); 1.27 (*s*, Me); 1.28–1.35 (*m*, 1 aliph. H); 1.41–1.51 (*m*, 3 aliph. H); 1.59–1.66 (*m*, 1 aliph. H); 1.89–1.95 (*m*, ^2J = 14, 1 aliph. H); 2.80 (*m*, ^2J = 11, ^3J = 10, ^3J = 3, 1 H, NCH_2); 3.13 (*dd*, ^4J = 2.4, ^5J = 1, ≡CH); 3.17 (*m*, ^2J = 11, ^3J = 5, ^3J = 2, 1 H, NCH_2); 5.59 (*dd*, ^3J = 11.5, ^4J = 2.4, =CH); 6.28 (*dd*, ^3J = 11.5, ^4J = 1, HC=). ^{13}C-NMR (100 MHz): 20.8 (CH_2); 23.7 (CH_2); 27.8 (*t*-Bu); 28.4 (Me); 32.7 (CH_2); 51.5 (NCH_2); 71.0 (C(3a)); 82.6 (C≡); 82.8 (≡CH); 108.6 ($=C_q$); 110.9 (=CH); 135.3 (CH=); 158.6 (C(2)). EI-MS: 245 (25, $M^{+\cdot}$), 230 (75), 188 (100), 174 (18), 160 (22), 146 (31), 118 (16), 91 (18). HR-MS: 245.1780 ($C_{16}H_{23}NO^+$; calc. 245.1780).

General Procedure of the Short-Time Thermolysis. 10^{-2}–10^{-3} M solns. of **9**–**14**, **30**[1]) in anh. benzene were slowly added through a heated column in a N_2 stream. The mixture was collected at 0° and concentrated *in vacuo*. After ^{1}H-NMR analysis of the raw material, purification was accomplished by FC (SiO_2; cyclohexane/AcOEt 50:1 or 100:1). In some cases, additional purification by MPLC (SiO_2; hexane/AcOEt 50:1) was performed.

Thermolysis of **9a**. The soln. of **9a** (60 mg, 0.17 mmol) in 20 ml of dry benzene at 320° afforded 26 mg (45%) of *{2,3-dihydro-3,3-dimethyl-7-[(trimetylsilyl)ethynyl]-1*H*-pyrrolizin-5-yl}phenylmethanone* (**15a**) as a yellow oil. IR: 3060, 2970, 2155 (C≡C), 1635 (CO), 1465, 1385, 1250, 1130, 1030. ^{1}H-NMR (250 MHz): 0.20 (*s*, Me_3Si); 1.69 (*s*, 2 Me); 2.42 (*t*, ^3J = 7.5, CH_2); 2.98 (*t*, ^3J = 7.5, CH_2); 6.81 (*s*, 1 H), 7.42 (*m*, 2 arom. H_m), 7.50 (*m*, 1 arom. H_p), 7.75 (*m*, 2 arom. H_o). ^{13}C-NMR (100 MHz): 1.2 (Me_3Si); 24.2 (CH_2); 27.9 (2 Me); 44.9 (Ar–CH_2); 67.3 (Me_3C), 94.9 (≡*C*$SiMe_3$); 98.4 (1 pyrrole C_q), 100.0 (C≡); 128.9 (C_q); 129.0 (arom. C); 130.2 (arom. C); 131.1 (pyrrole C); 132.3 (arom. C); 141.0 (C_q); 150.8 (C_q); 185.1 (CO). EI-MS: 335 (75, $M^{+\cdot}$), 320 (35), 280 (86), 105 (90), 77 (100). HR-MS: 335.1711 ($C_{21}H_{25}NOSi^+$; calc. 335.1705).

Thermolysis of **9b**. A soln. of **9b** (40 mg, 0.12 mmol) in 20 ml of dry benzene at 280° afforded after FC (neutral Al_2O_3, activity II–III; cyclohexane/AcOEt 100:1) 29 mg (72%) of *2,2-dimethyl-1-{2,3,7,7a-tetrahydro-*

*3,3,7a-trimethyl-1-[2-(trimethylsilyl)ethynyl]-1*H*-pyrrolizin-5-yl}propan-1-one* (**18b**) as a red oil. IR: 2965, 2168, 1676, 1477, 1367, 1250, 1158, 1070. ^{1}H-NMR (250 MHz): 0.15 (*s*, Me_3Si); 1.07 (*s*, Me); 1.22 (*s*, Me); 1.25 (*s*, *t*-Bu); 1.27 (*s*, Me); 1.51 (*ddd*, $^2J = 12.5$, $^3J = 9.1$, $^3J = 6.7$, 1 H, CH_2); 1.75–1.93 (*m*, CH_2); 2.32 (*ddd*, $^2J = 12.5$, $^3J = 9.1$, $^3J = 7.6$, 1 H, CH_2); 3.10 (*d*, $^3J = 3.3$, CH); 5.25 (*d*, $^3J = 3.3$, CH=). ^{13}C-NMR (100 MHz): 0.1 (Me_3Si); 25.5 (Me); 28.1 (Me_3C); 30.0 (Me); 31.0 (Me); 32.3 (CH_2); 42.6 (CH_2); 44.6 (Me_3C); 45.7 (CH); 62.7 (NC_q); 74.1 (NC_q); 91.1 (≡*C*$SiMe_3$); 104.5 (C≡); 112.5 (=CH); 146.6 (NC_q=); 207.1 (CO). EI-MS: 331 (100, $M^{+\cdot}$), 316 (71), 274 (13), 262 (51), 246 (22), 220 (18), 190 (49), 150 (20), 73 (57). HR-MS: 331.2331 ($C_{20}H_{33}NOSi^+$; calc. 331.2331).

Thermolysis of **10a**. A soln. of **10a** (302 mg, 0.86 mmol) in 85 ml of dry benzene at 320° afforded after FC (SiO_2; cyclohexane/AcOEt 3:1) as main product 69 mg (23%) of *2,3-dihydro-2,2-dimethyl-7-[(trimethylsilyl)ethynyl]-1*H*-pyrrolizin-5-yl](phenyl)methanone* (**16a**) as a brown oil. IR: 3060, 2980, 2900, 2150 (C≡C), 1625 (C=O), 1600, 1460, 1405, 1270, 1250, 1145. ^{1}H-NMR (250 MHz): 0.21 (*s*, Me_3Si); 1.30 (*s*, Me); 2.78 (*s*, CH_2); 4.18 (*s*, NCH_2); 6.88 (*s*, 1 pyrrole H); 7.40–7.57 (*m*, 3 arom. H); 7.81 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz): 0.2 (Me_3Si); 28.1 (2 Me); 39.5 (CH_2); 43.4 (C_q), 62.1 (NCH_2); 93.9 (≡*C*$SiMe_3$); 98.6 (pyrrole C_q); 99.2 (C≡); 126.3 (pyrrole C_q); 127.2 (pyrrole CH); 128.2 (arom. C); 128.9 (arom. C); 131.6 (arom. C); 139.1 (arom. C_q); 149.1 (pyrrole C_q); 184.7 (C=O). EI-MS: 335 (100, $M^{+\cdot}$), 320 (92), 280 (8), 152 (7), 149 (10), 113 (7), 105 (54), 77 (32), 73 (12). HR-MS: 355.1714 ($C_{21}H_{25}NOSi^+$; calc. 355.1705).

Thermolysis of **10b**. a) *At 280°*: A soln. of **10b** (39 mg, 0.12 mmol) in 17 ml of dry benzene at 280° afforded 31 mg (79%) of *2,2-dimethyl-1-{2,3,7,7a-tetrahydro-2,2,7a-trimethyl-1-[2-(trimethylsilyl)ethynyl]-1*H*-pyrrolizin-5-yl}propan-1-one* (**19b**) as a yellow oil. IR: 2960, 2146 (C≡C), 1669 (CO), 1461, 1366, 1250. ^{1}H-NMR (250 MHz): 0.16 (*s*, Me_3Si); 1.03 (*s*, Me); 1.14 (*s*, Me), 1.26 (*s*, *t*-Bu), 1.35 (*s*, Me); 1.46 (*d*, $^2J = 13.4$, 1 H, CH_2); 2.41 (*d*, $^2J = 13.4$, CH_2); 2.84 (*d*, $^2J = 11$, 1 H, NCH_2); 3.04 (*d*, $^2J = 11$, 1 H, NCH_2); 3.35 (*d*, $^3J = 3$, 1 H, CH); 5.47 (*d*, $^3J = 3$, HC=). ^{13}C-NMR (100 MHz): 0.1 (Me_3Si); 27.9 (Me_3C); 29.0 (Me); 29.3 (Me), 30.0 (Me); 40.4 (C_q); 44.2 (Me_3C), 47.3 (CH); 48.7 (CH_2); 65.2 (NCH_2); 73.4 (NC_q); 90.7 (≡*C*$SiMe_3$), 104.9 (C≡); 113.4 (=CH); 149.5 (NC=); 203.7 (CO). EI-MS: 331 (100, $M^{+\cdot}$), 316 (89), 261 (52), 258 (36), 246 (53), 230 (42), 205 (62), 177 (23), 162 (32), 73 (63). HR-MS: 331.2331 ($C_{20}H_{33}NOSi^+$; calc. 331.2331).

b) *At 320°*: A soln. of **10b** (60 mg, 0.18 mmol) in 25 ml of dry benzene at 320° afforded 16 mg (26%) of **19b** and 3 mg (5%) of *1-[2,3-dihydro-2,2-dimethyl-7-[(trimethylsilyl)ethynyl)-1*H*-pyrrolizin-5-yl]-2,2-dimethyl]propan-1-one* (**16b**) as orange oils. IR: 2962, 2152 (C≡C), 1639 (CO), 1458, 1365, 1249, 1189. ^{1}H-NMR (250 MHz): 0.22 (*s*, Me_3Si); 1.23 (*s*, 2 Me); 1.32 (*s*, *t*-Bu); 2.70 (*s*, CH_2); 4.07 (*s*, NCH_2); 7.07 (*s*, 1 pyrrole H). ^{13}C-NMR (100 MHz): 0.3 (Me_3Si); 28.1 (2 Me); 28.7 (Me_3C), 39.1 (CH_2); 43.0 (C_q); 43.1 (Me_3C), 63.0 (NCH_2); 93.6 (C≡); 97.8 (C_q); 99.6 (C≡); 123.5 (CH); 124.5 (C_q); 147.2 (NC_q), 196.7 (CO). EI-MS: 315 (22, $M^{+\cdot}$), 300 (5), 274 (10), 258 (100), 230 (6), 73 (25). HR-MS: 315.2019 ($C_{19}H_{29}NOSi^+$; calc. 315.2018).

Thermolysis of **11a**. A soln. of **11a** (300 mg, 0.89 mmol) in 90 ml of dry benzene at 320° afforded 73 mg (26%) of *(phenyl){5,6,7,8-tetrahydro-1-[(trimethylsilyl)ethynyl]-indolizin-3-yl}methanone* (**17a**) as an orange oil. IR: 2959, 2151 (C≡C), 1628 (CO), 1466, 1392, 1312, 1249, 1186, 1147. ^{1}H-NMR (250 MHz): 0.21 (*s*, Me_3Si); 1.86 (*m*, CH_2); 1.98 (*m*, CH_2); 2.90 (*t*, $^3J = 6$, CH_2); 4.44 (*t*, $^3J = 6$, NCH_2); 6.79 (*s*, 1 pyrrole H); 7.42–7.54 (*m*, 3 arom. H); 7.74 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz): 0.3 (Me_3Si); 19.4 (CH_2); 23.2 (CH_2); 23.3 (CH_2); 46.6 (NCH_2); 95.6 (≡*C*$SiMe_3$); 99.0 (pyrrole C_q), 102.6 (C≡); 125.4 (pyrrole CH); 128.1 (arom. C); 128.72 (pyrrole C_q); 129.1 (arom. C); 131.3 (arom. C); 140.1 (arom. C_q); 143.5 (arom. C_q); 185.4 (CO). EI-MS: 321 (100, $M^{+\cdot}$); 306 (69), 152 (14), 105 (74), 77 (52). HR-MS: 321.1554 ($C_{20}N_{23}NOSi^+$; calc. 321.1549).

Thermolysis of **11b**. A soln. of **11b** (82 mg, 0.12 mmol) in 20 ml of dry benzene at 280° afforded after FC (neutral Al_2O_3, activity II–III; cyclohexane/AcOEt 100:1) 30 mg (38%) of *2,2-dimethyl-1-{5,6,7,8-tetrahydro-[2-(trimethylsilyl)ethynyl]indolizin-3-yl}-propan-1-one* (**17b**) as a yellow oil. IR: 2959, 2147, 1638, 1466, 1447, 1361, 1309, 1249, 1153, 1103. ^{1}H-NMR (250 MHz): 0.23 (*s*, Me_3Si); 1.33 (*s*, *t*-Bu); 1.77–1.83 (*m*, CH_2); 1.87–1.93 (*m*, CH_2); 2.85 (*t*, $^3J = 6$, CH_2); 4.28 (*t*, $^3J = 6$, NCH_2); 7.09 (*s*, 1 pyrrole H). ^{13}C-NMR (100 MHz): 0.3 (Me_3Si); 19.3 (CH_2); 23.3 (CH_2); 23.6 (CH_2); 29.0 (Me_3C); 43.8 (Me_3C), 47.2 (NCH_2); 95.3 (≡*C*$SiMe_3$); 99.4 (C_q); 101.5 (C≡); 121.2 (CH); 126.8 (NC_q); 141.7 (NC_q); 197.3 (CO). EI-MS: 301 (17, $M^{+\cdot}$), 244 (100), 171 (10), 114 (7), 73 (24). HR-MS: 301.1863 ($C_{18}H_{27}NOSi^+$; calc. 301.1862).

Thermolysis of **12a**. A soln. of **12a** (183 mg, 0.65 mmol) in 70 ml of dry benzene at 406° afforded 32 mg (14%) of *6,7-dihydro-5,5,8-trimethyl-5*H*-pyrrolo[1,2-a]azepin-3-yl)(phenyl)methanone* (**21a**) as a yellow oil and 23 mg (13%) of *1,6,7,8-tetrahydro-(5,8,8-trimethylcyclohepta[b]pyrrol-2-yl)(phenyl)methanone* (**24**) as yellow crystals.

Data of **21a**: IR: 3060, 2973, 1635 (CO), 1578, 1463, 1347, 1320, 1228. ^{1}H-NMR (250 MHz): 1.77 (*s*, Me_2C); 1.89 (*d*, $^4J = 1.5$, Me); 2.06 (m_c, 2 H–C(6)); 2.44 (m_c, 2 H–C(7)); 5.88 (*d*, $^3J = 4$, 1 pyrrole H); 6.07 (*m*, $^4J = 0.9$, $^4J = 1.5$, H–C(9)); 6.39 (*d*, $^3J = 4$, 1 pyrrole H); 7.40 (*m*, 2 arom. H_m), 7.51 (m_c, 1 arom. H_p), 7.86 (*m*, 2 arom. H_o). ^{13}C-NMR (100 MHz): 25.6 (Me); 28.6 (2 Me); 32.2 (C(6)); 41.8 (C(7)); 60.9 (NC_q); 111.9 (C(2)); 117.9

(C(9)); 124.7 (C(1)); 127.9 (arom. C_m); 129.7 (arom. C_o); 131.7 (arom. C_p); 135.5 (C(3)); 138.3 (C(8)); 140.3 (arom. C_q); 140.6 (C(10)); 186.5 (CO). EI-MS: 279 (49, $M^{+\cdot}$), 236 (8), 224 (37), 174 (21), 105 (100), 77 (28). HR-MS: 279.1626 ($C_{19}H_{21}NO^+$; calc. 279.1623).

Data of **24**: M.p. 173–174° (Et_2O/pentane). IR: 3450, 3296, 3060, 2965, 1610, 1574, 1496, 1459, 1385, 1248, 1136. ^{1}H-NMR (500 MHz): 1.33 (*s*, 2 Me–C(8)); 1.78 (*ddd*, $^2J=12$, $^3J=6$, $^3J=4$, 2 H–C(7)); 1.83 (*d*, $^4J=1$, Me–C(5)); 2.36 (br. *t*, $^3J=6$, 2 H–C(6)); 6.00 (m_c, $^4J=1$, 1.3, H–C(4)); 6.57 (*d*, $^4J=2.7$, H–C(3)); 7.45 (*m*, 2 arom. H_m), 7.53 (*m*, 1 arom. H_p); 7.85 (*m*, 2 arom. H_o); 9.32 (NH). ^{13}C-NMR (125 MHz): 26.6 (Me); 28.6 (2 Me); 31.8 (C(6)); 35.3 (C(8)); 37.9 (C(7)); 118.3 (C(4)); 120.2 (C(3a)); 120.68 (C(3)); 127.9 (C(2)); 128.2 (arom. C); 128.8 (arom. C); 131.5 (arom. C_p), 135.6 (C(5)); 138.6 (arom. C_q); 145.4 (C(8a)); 183.9 (CO). EI-MS: 279 (100, $M^{+\cdot}$), 264 (91), 174 (10), 158 (16), 105 (81), 77 (24). Anal. calc. for $C_{19}H_{21}NO$ (279.38): C 81.68, H 7.58, N 5.01; found: C 81.56, H 7.47, N 4.90.

Thermolysis of **12b**. A soln. of **12b** (61 mg, 0.23 mmol) in 30 ml of dry benzene at 280° afforded 26 mg (43%) of *1-(6,7-dihydro-5,5,8-trimethyl-5*H*-pyrrolo[1,2-*a*]azepin-3-yl)2,2-dimethylpropan-1-one* (**21b**) as a yellow oil. IR: 2965, 1635 (CO), 1448, 1365, 1310, 1195, 1058. ^{1}H-NMR (400 MHz): 1.36 (*s*, *t*-Bu); 1.63 (*s*, Me_2C); 1.86 (*d*, $^4J=1$, Me); 2.00 (*m*, $^2J=1$, $^3J=6$, 2 H–C(6)); 2.39 (*m*, $^2J=12$, 2 H–C(7)); 5.87 (*d*, $^3J=4$, H–C(1)); 6.06 (*m*, $^4J=1$, H–C(9)); 6.61 (*d*, $^3J=4$, H–C(2)). ^{13}C-NMR (100 MHz): 5.4 (Me); 28.8 (Me_3C); 29.4 (2 Me); 32.5 (C(7)); 42.0 (C(6)); 44.6 (Me_3C); 60.5 (NC_q); 111.3 (C(1)); 116.6 (C(9)); 118.0 (C(2)); 136.0 (C(3)); 138.1 (C(8)); 146.9 (C(10)); 206.8 (CO). EI-MS: 259 (27, $M^{+\cdot}$), 202 (100), 186 (24), 160 (12), 146 (23), 118 (10). HR-MS: 259.1937 ($C_{17}H_{25}NO^+$; calc. 259.1936).

Thermolysis of **13a**. A soln. of **13a** (390 mg, 1.39 mmol) in 105 ml of dry benzene at 320° afforded 59 mg (15%) of **22a** as a yellow oil. IR: 3070, 3030, 2960, 2930, 2880, 1630 (C=O), 1470, 1390, 1325, 1245, 1050. ^{1}H-NMR (250 MHz): 1.06 (*s*, CMe_2), 1.94 (*d*, $^4J=1.5$, Me); 2.18 (*s*, CH_2); 4.44 (*s*, NCH_2); 5.98 (*d*, $^3J=4.3$, 1 pyrrole H); 6.20 (*m*, $^4J=1.2$, $^4J=1.5$, =CH); 6.73 (*d*, $^3J=4.3$, 1 pyrrole H); 7.46 (*m*, 3 arom. H); 7.78 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz): 26.9 (2 Me); 27.2 (Me); 36.5 (Me_2C); 49.6 (CH_2); 55.7 (NCH_2); 109.6 (CH); 116.1 (CH); 123.8 (CH); 128.0 (arom. C); 129.3 (arom. C); 131.1 (arom. C); 139.72 (arom. C_q), 140.8 (arom. C); 141.5 (C_q); 185.6 (C=O). EI-MS: 279 (44, $M^{+\cdot}$), 264 (16), 236 (19), 174 (9), 158 (6), 118 (10), 105 (100), 91 (15), 77 (78). HR-MS: 279.1617 ($C_{19}H_{21}NO^+$; calc. 279.1623).

Thermolysis of **13b**. A soln. of **13b** (60 mg, 0.23 mmol) in 30 ml of dry benzene at 320° afforded 20 mg (33%) of **22b** as a yellow oil. IR: 2962, 1634 (CO), 1459, 1365, 1306, 1195, 1074. ^{1}H-NMR (250 MHz): 1.01 (*s*, Me_2C), 1.35 (*s*, *t*-Bu); 1.93 (*d*, $^4J=1$, Me); 2.07 (*s*, CH_2); 4.25 (*s*, NCH_2); 5.94 (*d*, $^3J=4.1$, 1 pyrrole H); 6.16 (*m*, $^4J=1$, =CH); 6.98 (*d*, $^3J=4.1$, 1 pyrrole H). ^{13}C-NMR (100 MHz): 26.9 (Me); 27.0 (2 Me); 29.3 (Me_3C), 38.0 (Me_2C); 44.0 (Me_3C), 48.8 (CH_2); 55.6 (NCH_2); 108.3 (CH); 116.4 (CH); 118.9 (CH); 129.6 (C_q); 139.3 (C_q); 139.8 (C_q); 197.7 (C=O). EI-MS: 259 (19, $M^{+\cdot}$), 202 (100), 186 (7), 162 (6). HR-MS: 259.19342 ($C_{17}H_{25}NO^+$; calc. 259.19361).

Thermolysis of **14a**. A soln. of **14a** (200 mg, 0.75 mmol) in 80 ml of dry benzene at 406° afforded 25 mg (13%) of *(phenyl)(5,6,7,8-tetrahydro-9-methylpyrrolo[1,2-*a*]azocin-3-yl)methanone* (**23a**) as an orange oil. IR: 2932, 1662, 1625 (CO), 1577, 1473, 1350, 1280, 1046. ^{1}H-NMR (250 MHz): 1.55 (*m*, 2 H–C(7)); 1.92 (*d*, $^4J=1.3$, Me); 1.98 (m_c, 2 H–C(6)); 2.17 (*m*, 2 H–C(8)); 4.41 (*m*, NCH_2); 5.98 (*d*, $^3J=4.1$, H–C(1)); 6.12 (*q*, $^4J=1.3$, H–C(10)); 6.69 (*d*, $^3J=4.1$, H–C(2)); 7.41 (m_c, 2 arom. H_m), 7.46 (1 arom. H_p), 7.75 (*m*, 2 arom. H_o). ^{13}C-NMR (100 MHz): 21.1 (C(7)); 26.3 (Me); 29.6 (C(6)); 34.9 (C(8)); 45.1 (NCH_2); 108.2 (C(1)); 113.9 (C(10)); 23.5 (C(2)); 127.8 (arom. C); 129.1 (arom. C); 129.7 (C(3)); 130.8 (arom. C_p), 140.7 (arom. C_q); 141.2 (C(11)); 145.4 (C(9)); 185.3 (CO). EI-MS: 265 (25, $M^{+\cdot}$); 236 (11), 209 (99), 194 (28), 160 (12), 133 (35), 105 (100), 77 (88). HR-MS: 265.14658 ($C_{18}H_{19}NO^+$; calc. 265.14666).

Thermolysis of **14b**. A soln. of **14b** (51 mg, 0.208 mmol) in 25 ml of dry benzene at 406° afforded 34 mg (25%) of *2,2-dimethyl-1-(5,6,7,8-tetrahydro-9-methylpyrrolo[1,2-*a*]azocin-3-yl)propan-1-one* (**23b**) as a yellow oil. IR: 2931, 1683, 1634 (CO), 1457, 1395, 1344, 1279, 1058. ^{1}H-NMR (250 MHz): 1.36 (*s*, *t*-Bu); 1.48–1.57 (*m*, 2 H–C(7)); 1.87–1.95 (*m*, 2 H–C(6)); 1.91 (*d*, $^4J=1.3$, Me); 2.14 (m_c, $^3J=10$, $^3J=5$, 2 H–C(8)); 4.27 (m_c, $^3J=10$, $^3J=10$, $^3J=6$, NCH_2); 5.96 (*d*, $^3J=4.3$, H–C(1)); 6.09 (*q*, $^4J=1.3$, H–C(10)); 7.04 (*d*, $^3J=4.3$, H–C(2)). ^{13}C-NMR (100 MHz): 21.3 (C(7)); 26.3 (Me); 29.3 (*t*-Bu); 29.7 (C(6)); 35.0 (C(8)); 45.7 (NCH_2); 107.3 (C(1)); 114.4 (C(10)); 119.1 (C(2)); 127.5 (C(3)); 139.2 (C(11)); 144.8 (C(9)); 197.1 (CO). EI-MS: 245 (20, $M^{+\cdot}$), 188 (100), 172 (8), 160 (8), 133 (7), 118 (5), 91 (6). HR-MS: 245.1779 ($C_{16}H_{23}NO^+$; calc. 245.1780).

*3a,4,5,6-Tetrahydro-3a,6,6-trimethyl-3-[4-(4-methylphenyl)but-1-en-3-ynyl]-2-phenylpyrrolo[1,2-*b*]isoxazole* (**30**). To a mixture of **12a** (150 mg, 0.54 mmol) in 2 ml of dry Et_3N, 4-iodotoluene (164 mg, 0.75 mmol) and $PdCl_2(PPh_3)_2$ (38 mg, 0.054 mmol, 10 mol-%) was added CuI (5 mg, 0.03 mmol, 5 mol-%). The mixture was stirred under Ar in the dark for 3 h. After removing the catalyst by filtration and concentration of the soln. *in vacuo* the residue was purified by FC (SiO_2; cyclohexane/AcOEt 40:1) affording 194 mg (98%) of **30** as an

orange oil ((*Z*/*E*) > 24 :1). IR: 3060, 2973, 2185, 1618, 1597, 1508, 1447, 1345, 1243, 1110, 1068. UV: 359 (7600), 290 (8200), 242 (7700). ^{1}H-NMR (250 MHz): 1.22 (*s*, Me); 1.31 (*s*, Me); 1.71 (m_c, CH_2); 1.81 (*s*, Me); 2.11 (*ddd*, ^2J = 13, ^3J = 7, ^3J = 6, 1 H, CH_2); 2.36 (*s*, arom. Me); 2.62 (*dt*, ^2J = 13, ^3J = 8, 1 H, CH_2); 5.51 (*d*, ^3J = 12, CH=); 6.28 (*d*, ^3J = 12, CH=); 7.13 (*m*, ^3J = 7.6, 2 arom. H); 7.30 (*m*, ^3J = 7.6, 2 arom. H); 7.40 (*m*, 3 arom. H); 7.54 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz): 21.6 (Me); 21.7 (Me); 28.3 (Me); 29.8 (Me); 36.3 (CH_2); 36.4 (CH_2); 68.3 (NC_q); 77.2 (NC_q), 89.6 (≡C), 96.0 (C≡), 102.3 (=CH), 115.7 (=C_q), 120.9 (arom. C_q); 128.5 (arom. C); 128.9 (arom. C), 129.3 (arom. C); 129.6 (arom. C); 129.6 (arom. C); 131.0 (arom. C); 137.3 (=CH); 138.2 (arom. C_q); 156.2 (=CO). EI-MS: 369 (72, $M^{+\cdot}$), 354 (100), 326 (23), 298 (51), 264 (16), 208 (21), 105 (100), 77 (29). HR-MS: 369.2093 ($C_{26}H_{27}NO^+$; calc. 369.2093).

Thermolysis of **30**. A soln. of **30** (106 mg, 0.29 mmol) in 45 ml of dry benzene at 406° afforded after FC (SiO_2; cyclohexane/AcOEt 100 :1) 17 mg (17%) of *[2,3-dihydro-3,3-dimethyl-7-[2-(*p*-tolyl)ethynylpyrrolo-[1,2-*a*]pyrrol-5-yl](phenyl)methanone* (**31**) and 8 mg (8%) of *[1,6,7,8-tetrahydro-5,8,8-trimethyl-4-(*p*-tolyl)cyclohepta[*b*]pyrrol-2-yl](phenyl)methanone* (**32**) as yellow oils.

Data of **31**: IR: 3060, 2969, 2210 (C≡C), 1633 (C=O), 1508, 1464, 1384, 1261, 1136. ^{1}H-NMR (250 MHz): 1.72 (*s*, 2 Me); 2.34 (*s*, *Me*C_6H_4); 2.45 (*t*, ^3J = 7.4, CH_2); 3.03 (*t*, ^3J = 7.4, CH_2); 6.87 (*s*, 1 pyrrole H); 7.11 (m_c, ^3J = 8, 2 arom. H); 7.34 (*m*, ^3J = 8, 2 arom. H); 7.44 (*m*, 2 arom. H_m); 7.51 (*m*, 1 arom. H_p); 7.78 (*m*, 2 arom. H_o). ^{13}C-NMR (100 MHz): 21.5 (*Me*C_6H_4); 23.3 (CH_2); 27.1 (2 Me); 44.1 (CH_2); 66.4 (C_q); 82.5 (C≡*C*Ar); 89.5 (*C*≡CAr); 97.6 (C_q); 120.8 (arom. C_q); 120.8 (C_q); 128.1 (arom. C); 129.1 (arom. C); 129.3 (arom. C); 129.8 (arom. C); 131.3 (arom. C); 131.3 (arom. C); 137.8 (arom. C_q); 140.1 (aromat. C_q); 149.2 (C_q), 184.1 (C=O). EI-MS: 353 (100, $M^{+\cdot}$), 338 (10), 298 (90), 105 (14), 77 (8). HR-MS: 353.1777 ($C_{25}H_{23}NO^+$; calc. 353.1780).

Data of **32**: IR: 3448, 3293, 3054, 2923, 1611 (CO), 1574, 1495, 1452, 1383, 1268, 1137. ^{1}H-NMR (400 MHz): 1.43 (*s*, Me); 1.69 (*m*, Me−C(5)); 1.94 (*ddd*, ^2J = 12, 2 H−C(7)); 2.34 (*s*, *Me*C_6H_4); 2.38 (*ddd*, ^2J = 12, 2 H−C(6)); 6.10 (*d*, ^4J = 2.9, H−C(3)); 7.01 (m_c, ^3J = 8, 2 arom. H); 7.12 (m_c, ^3J = 8, 2 arom. H); 7.35 (*m*, 2 arom. H); 7.45 (*t*, 1 arom. H); 7.70 (*m*, 2 arom. H); 9.25 (NH). ^{13}C-NMR (125 MHz): 21.2 (*Me*C_6H_4); 23.2 (Me); 30.1 (2 Me); 32.7 (C(6)); 36.3 (C(8)); 41.5 (C(7)); 121.0 (C(3)); 124.1 (C(3a)); 127.6 (C(4)); 128.2 (CH); 128.7 (CH); 128.8 (CH); 129.6 (CH); 130.3 (arom. C); 131.4 (arom. C); 133.8 (C_q); 135.6 (C_q); 138.5 (arom. C); 140.0 (C(5)); 145.4 (C(8a)); 183.9 (CO). EI-MS: 369 (70, $M^{+\cdot}$), 354 (29), 326 (7), 313 (9), 264 (10), 119 (36), 105 (100), 77 (39). HR-MS: 369.2093 ($C_{26}H_{27}NO^+$; calc. 369.2093).

[6-(But-1-en-3-yn-6-yl)-2,2,5-trimethyl-1-azabicyclo[3.1.0]hex-6-yl](phenyl)methanone (**33**). A soln. of **13a** (663 mg, 2.37 mmol) in 260 ml of dry benzene at 20° was irradiated for 40 min with a high-pressure Hg lamp (*Hanau TQ 150*, 150 W) using a *Jena* filter (λ > 290 nm). After concentration of the soln., FC of the residue (neutral Al_2O_3, activity II – III; cyclohexene/AcOEt 40 :1 to 10 :1) afforded, besides unreacted **13a** (58 mg, 8%) and 22 mg (4%) of a dimer[2]), 154 mg (23%) of **33** as a colorless solid. UV: 244 (16500). IR: 3310 (≡C−H), 3060, 2960, 2870, 2800 (C≡C), 1700 (CO), 1685, 1660, 1600, 1450, 1365, 1020, 910, 695. ^{1}H-NMR (250 MHz): 0.99 (*s*, Me); 1.27 (*s*, Me); 1.31 (*s*, Me); 1.74 (*d*, ^2J = 13.7, 1 H−C(4)); 1.96 (*d*, ^2J = 13.7, 1 H−C(4)); 2.50 (*d*, ^2J = 12.2, 1 H−C(2)); 3.13 (*d*, ^2J = 12.2, 1 H, H−C(2)); 3.23 (*d*, ^4J = 2.1, CH≡; 5.92 (*dd*, ^3J = 11.0, ^4J = 2.1, CH=); 6.03 (*d*, ^3J = 11.0, CH=C); 7.45 (*m*, 3 arom. H); 7.83 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz): 21.5 (Me); 25.3 (Me); 30.83 (Me); 46.2 (CH_2); 48.8 (C_q); 58.6 (aziridine C); 59.8 (aziridine C); 63.5 (NCH_2); 79.2 (C≡); 86.2 (CH≡); 118.5 (CH=); 128.3 (arom. C); 129.0 (arom. C); 132.5 (arom. C); 135.5 (CH=); 137.5 (arom. C); 194.9 (CO). EI-MS: 279 (60, $M^{+\cdot}$), 264 (77), 262 (11), 250 (12), 222 (19), 194 (10), 174 (29), 158 (10), 118 (31), 105 (100), 78 (73), 77 (70). Anal. calc. for $C_{19}H_{21}NO$: C 81.68, H 7.58, N 5.01; found: C 81.58; H 7.62, N 4.92.

Thermolysis of **33**. A soln. of **33** (21 mg, 0.075 mmol) in 12 ml of dry benzene at 320° afforded after chromatographic purification 5 mg (24%) of **22a**.

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