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Synthesis of 2-Alkylidenepyrrolidines, Pyrroles, and Indoles by Condensation of Silyl Enol Ethers and 1,3-Bis-Silyl Enol Ethers with 1-Azido-2,2-dimethoxyethane and Subsequent Reductive Cyclization

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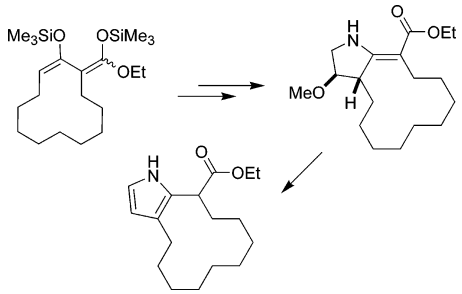

The condensation of 1,3-bis-silyl enol ethers with 1-azido-2,2-dimethoxyethane and subsequent reductive cyclization allowed an efficient regio- and diastereoselective synthesis of a variety of 2-alkylidene-4-methoxypyrrolidines. The thermal elimination of methanol resulted in the formation of functionalized pyrroles. Similarly, 2,3,3a,4,5,6-hexahydro-2,3-benzopyrroles were prepared and transformed into 4,5,6,7-tetrahydro-2,3-benzopyrroles. In contrast, treatment of 2-alkylidenepyrrolidines with trifluoroacetic acid resulted in formation of indoles by [4 + 2] cycloaddition and subsequent extrusion of a nitrogen atom.

Functionalized 2-alkylidenepyrrolidines represent versatile intermediates for the synthesis of pyrrolidines and fused heterocycles.[1,2] Numerous applications in the synthesis of natural products have been reported. For example, an efficient synthesis of mitomycin antitumor antibiotics relies on the cyclization of 2-alkylidenepyrrolidines attached to bromo-substituted quinones.[3a,b] Other synthetic applications include, for example, the synthesis of microsclerodermin E, carbapenam-3-carboxylic acid, the bridged pyrrolizidine core of asparagamine or camptothecin analogues.[3] 2-Alkylidenepyrrolidines represent direct precursors for the stereoselective synthesis of pyrrolidine substructures[4] by reduction[3f] of the exocyclic double bond. Pyrrolidines are present in a variety of alkaloids, such as hygrine, hygroline, or cuskhygrin, and in non-natural products used in the clinic (e.g., the vasodilator buflomedil).[4]

Synthetic approaches to 2-alkylidenepyrrolidines (exocyclic enamino esters) mainly rely on the use of *N*-

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heterocycles as starting materials. For example, the Eschenmoser method relies on the condensation of thiolactams with bromomethyl ketones or esters, followed by extrusion of sulfur.[5] Other syntheses include, for example, the reaction of lactim ethers with active methylene compounds,[6] the reaction of lactams or thiolactams with organometallic reagents[7] or the reaction of methyl bromoacetate with ω-mesylnitriles.[8] Synthetic methods, which include the formation of the *N*-heterocyclic moiety, are more rare. For example, 2-alkylidenepyrrolidines have been prepared by reaction of 1,3-dicarbonyl dianions with 1-bromo-2-chloroethane, nucleophilic substitution of the chloride by sodium azide and subsequent aza-Wittig reaction of the ω-azido-β-ketoester thus formed.[9] 2-Alkylidenepyrrolidines are available also by reaction of 1,3-dicarbonyl dianions with aziridines[10] and by ring transformations of lactones.[11]

Recently, we have reported[12] the synthesis of 2-alkylidenepyrrolidines by condensation of 1,3-dicarbonyl dianions with α-azidoketones, cyclization by Staudinger-aza-Wittig reaction,[13] and subsequent acid-mediated transformation of the products into functionalized pyrroles. Unfortunately, the preparative scope of this approach is limited to the use of α-azido*ketones*; the reaction of dianions with α-azido*aldehydes* resulted in the formation of complex mixtures. Herein, we report a solution of this problem based on what are, to the best of our knowledge, the first cyclocondensations of 1,3-bis-silyl enol ethers—electroneutral 1,3-dicarbonyl dianion equivalents[14,15]—with 1-azido-2,2-dimethoxyethane. These reactions allow a convenient synthesis of functionalized pyrrolidines and pyrroles which are not available from 1,3-dicarbonyl dianions[12] and from simple silyl enol ethers.[16] All products are formed with very good regioselectivity. In contrast, the preparative scope of the classic Knorr or Hantzsch procedures[17] is often limited by the formation of regioisomers. In addition, the preparation of alkyl-substituted derivatives can be problematic. Pyrroles[17,18] occur in a variety of natural products, such as the tetrapyrrol pigments bilirubin and porphobilinogen, and in a number of pharmaceuticals (e.g., the analgetic zomepirac).[19]

Results and Discussion

The $TiCl_4$-mediated condensation of simple silyl enol ethers with α-azidoketals has been reported.[16] However, the $TiCl_4$-mediated reaction of 1-azido-2,2-dimethoxyethane (**2**)[16] with 1,3-bis-silyl enol ether **1a** resulted in formation of a complex mixture, due to oxidative self-condensation of **1a** and decomposition. Based on our previous studies related to the reaction of 1,3-bis-silyl enol ethers with 1-chloro-2,2-dimethoxyethane, we turned to the use of the milder Lewis acid trimethylsilyltrifluoromethylsulfonate (Me_3SiOTf).[20,21] The Me_3SiOTf-mediated reaction of **1a** with **2** afforded the desired condensation product **3a** with good regio- and chemoselectivity (Scheme 1).

Treatment of a THF solution of **3a** with PPh_3 resulted in clean formation of the 2-alkylidenepyrrolidine **4a** (Scheme 1). The formation of **4a** proceeds by a domino Staudinger−aza-Wittig reaction and subsequent migration of the double bond into the exocyclic position. The double bond of **4a** was formed with good *Z*-selectivity, due to the formation of an intramolecular hydrogen bond N−H···O. The transformation of **4a** into the pyrrole **5a** was studied next. Treatment of a CH_2Cl_2 solution of **4a** with trifluoroacetic acid (TFA) resulted in formation of a complex mixture (Scheme 2, Table 2). The problem could be solved by reflux of a 1,4-dioxane solution of **4a** for 24 h to give the desired pyrrole **5a**. The product was formed by thermal extrusion of methanol and aromatization by migration of the exocyclic double bond.

To study the preparative scope of the new methodology, the substituents of the 1,3-bis-silyl enol ethers were systematically varied (Scheme 1, Table 1). The reaction of ester-derived dienes **1a**−**d** with 1-azido-2,2-dimethoxyethane (**2**) gave the open-chained azides **3a**−**d** which were transformed into the *Z*-configured 2-alkylidenepyrrolidines **4a**−**d**. Reflux of a 1,4-dioxane solution of **4a**−**d** gave the pyrroles **5a**−**d** in good yields. The reaction of **2** with 1,3-bis-silyl enol ether **1e**, prepared from benzoylacetone, gave **3e** which was transformed into the *Z*-configured 2-alkylidenepyrrolidine **4e**. Reflux of a 1,4-dioxane solution of **4e** afforded the pyrrole **5e** in good yield.

The reaction of **2** with **1f**−**o**, containing a substituent at the terminal carbon atom, gave the corresponding open-chained products **3f**−**o**. Treatment of **3f**−**o** with

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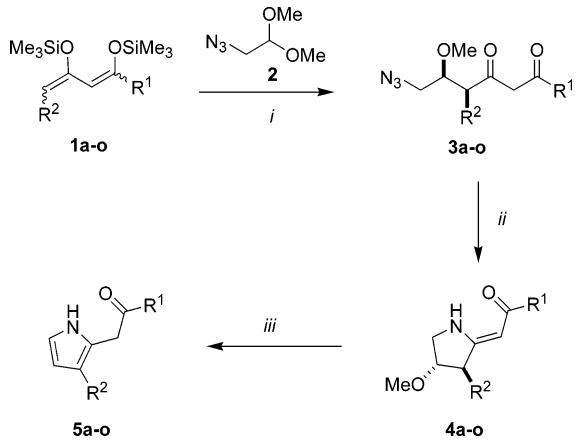
TABLE 1. Derivatives and Yields of Condensation Products 3 and Pyrrolidines 4 by Staudinger−aza-Wittig Reaction and Pyrroles 5 by Thermal Extrusion of Methanol

3, 4, 5	R^1	R^2	3[a] (%)	4[a] (%)	5[a] (%)	δ[b] (ppm)	δ[c] (ppm)	trans/cis[d]
a	OMe	H	48	81	76	4.55	170.5	
b	OEt	H	51	64	100	4.55	170.3	
c	O*i*Pr	H	47	74	100	4.53	169.9	
d	$O(CH_2)_2OMe$	H	44	74	98	4.61	170.2	
e	Ph	H	95	84	82	5.82	188.2	
f	OMe	Me	76	95	100	4.53	171.1	>98:2
g	OEt	Et	87	79	100	4.53	170.5	<2:98
h	OMe	OMe	63	66 (*trans*)	100	4.74	170.3	>98:2
				20 (*cis*)	100	4.76	170.3	<2:98
i	OEt	Allyl	60	94	*e*	4.56	171.0	>98:2
j	OEt	*n*Pr	82	86	100	4.53	170.8	>98:2
k	OEt	*n*Bu	83	93	100	4.53	170.8	>98:2
l	OEt	*n*Hex	86	98	100	4.53	170.6	>98:2
m	OEt	*n*Oct	82	86	*e*	4.53	170.7	>98:2
n	OEt	*n*Non	80	81	93	4.53	170.8	>98:2
o	OEt	*n*Dec	92	83	91	4.53	170.7	>98:2

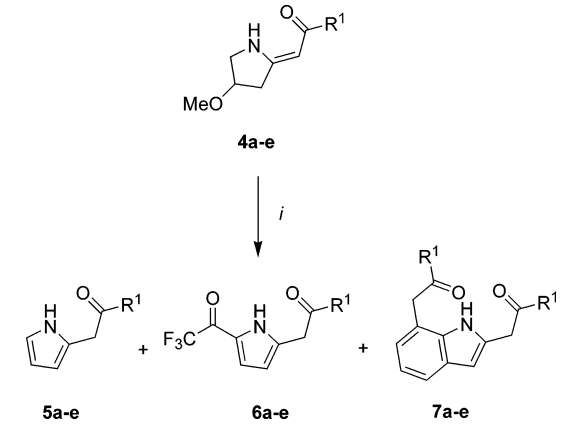
[a] Yields of isolated products. For all compounds **4a**−**o**: *Z*/*E* > 98:2 (configuration of the exocyclic double bond). [b] Chemical shift (^{1}H NMR, $CDCl_3$) of the hydrogen atom of the exocyclic double bond of **4**. [c] Chemical shift (^{13}C NMR, $CDCl_3$) of the carbonyl group of **4**. [d] Diastereomeric ratio (trans/cis) of **4f**−**o**. [e] Experiment (reflux, 1,4-dioxane or CH_2Cl_2) was not carried out.

SCHEME 1. Synthesis of 4a−o and 5a−o[a]



[a] Key: (i) 0.5 equiv of TMSOTf, CH_2Cl_2, −78 → +20 °C; (ii) PPh_3, 6 h, THF, 45 °C; (iii) reflux in 1,4-dioxane or CH_2Cl_2, 24 h.

SCHEME 2. Synthesis of 5a−e, 6a−e, and 7a−e[a]



[a] Key: (i) TFA, CH_2Cl_2, 20 °C, 24 h.

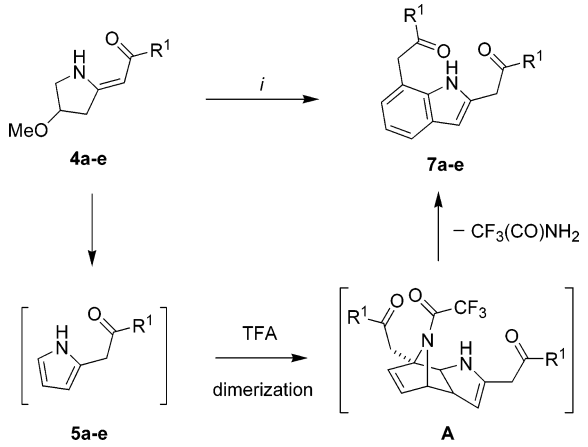
PPh_3 afforded the *Z*-configured 2-alkylidenepyrrolidines **4f**−**o**. All alkyl-substituted 2-alkylidenepyrrolidines **4f**,**g** and **4i**−**o** were formed with good *trans*-diastereoselectivity. In contrast, the reaction of **1h** with **2** afforded **3h** as a mixture of syn/anti diastereomers. The PPh_3-mediated cyclization of **3h** and chromatographic separation of the diastereomers afforded the *Z*-configured 3,4-dimethoxy-2-alkylidenepyrrolidines ***trans*-4h** and ***cis*-4h** in 66% and 20% yield, respectively. The 2-alkylidenepyrrolidines **4f**−**h**,**j**−**l**,**n**,**o** were transformed into the substituted pyrroles **5f**−**h**,**j**−**l**,**n**,**o** in good yields.

TABLE 2. Reaction of Pyrrolidines 4 with TFA: Derivatives and Yields of Pyrroles 5, Friedel−Crafts Acylation Products 6, and Indoles 7

5, 6, 7	R^1	5 (%)	6 (%)	7 (%)
a	OMe	32[b]	8[b]	49[a]
b	OEt	0	38[a]	54[a]
c	O*i*Pr	0	0	91[a]
d	$O(CH_2)_2OMe$	19	17[b]	45[a]
e	Ph	0	54[a]	0

[a] Yields of isolated products. [b] Calculated yields based on ^{1}H NMR integration of a mixture of **5** and **6**.

SCHEME 3. Possible Mechanism for the Formation of 7a−e



The configuration of the exocyclic double bond of 2-alkylidenepyrrolidines **4** was proven by NOESY experiments, X-ray structures and by comparison of the chemical shifts of the hydrogen atoms of the exocyclic double bond with those of related compounds (Table 1).[9,10,12] As expected, characteristic chemical shifts in the range of δ = 4.53−4.76 were observed for all *Z*-configured ester derived 2-alkylidenepyrrolidines. In addition, ester-derived and *Z*-configured 2-alkylidenepyrrolidines generally showed a characteristic carbonyl ^{13}C NMR resonance

in the range of $\delta = 169.9-171.1$. An independent proof of the configuration was established by crystal structure analyses of **4e**, **4f**, and ***cis*-4h**.

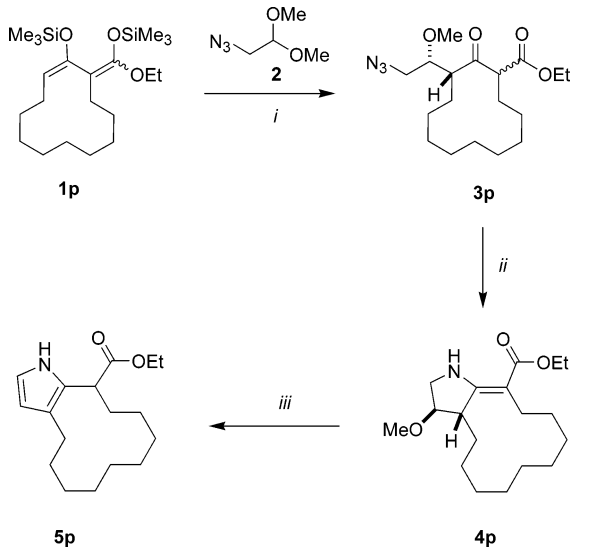
The crystal structure of **4f** revealed a *trans*-configuration of the methoxy and the methyl group. In fact, analysis of the coupling constants (Karplus) indicated that all alkyl-substituted pyrrolidines **4f**−**g**,**i**−**o** possess a *trans*-configuration. The excellent 1,2-diastereoselectivity can be explained based on known stereo-electronic considerations (comparison of acyclic extended transition states with minimized electrostatic repulsion).[20,21] The transition state leading to the *syn*-isomer of **3** is sterically favored over the one leading to the *anti*-isomer. Interestingly, the configuration of the terminal double bond of the 1,3-bis-silyl enol ether is irrelevant to the stereoselection. Inspection of the crystal lattice showed a dimeric structure containing two intermolecular hydrogen bonds N−H···O. The crystal structure of ***cis*-4h** established a *cis*-configuration of the two methoxy groups and the presence of a *Z*-configured exocyclic double bond.

The reaction of **4a**−**e** with trifluoroacetic acid (TFA) was studied next. Treatment of a CH_2Cl_2 solution of **4a** with TFA resulted in formation of an inseparable mixture of the pyrroles **5a** and **6a** and of the indole **7a** which could be isolated in pure form (49%) (Scheme 2, Table 2). The formation of pyrrole **6a** can be explained by Friedel−Crafts acylation of **5a** with TFA. The formation of large amounts of indole **7a** could be explained by dimerization of pyrrole **5a** to the [4 + 2] cycloadduct **A**, which subsequently aromatizes by acid-mediated extrusion of trifluoroacetamide (Scheme 3). The dimerization of pyrrole and 2-methylpyrrole, mediated by hydrogen chloride in ether or by sulfuric acid, was already noted in 1888.[22] Despite its synthetic usefulness, this transformation has not been systematically studied to date. The use of TFA/CH_2Cl_2 allows the synthesis of the functionalized (ester-substituted) indoles **7** which are not available by application of the original conditions reported (HCl or sulfuric acid).

The preparative scope of the reaction of 4-methoxy-2-alkylidenepyrrolidines with TFA was next studied. Treatment of a CH_2Cl_2 solution of **4b** with TFA resulted in formation of a separable mixture of pyrrole **6b** (38%) and indole **7b** (54%). The reaction of **4c** with TFA gave the indole **7c** in 91% yield. The reaction of **4d** with TFA afforded mainly the indole **7d** (45%) together with an inseparable mixture of pyrroles **5d** and **6d**. The reaction of **4e** with TFA gave the pyrrole **6e**. The structure of **6e** was independently confirmed by crystal structure analysis. Treatment of alkyl-substituted pyrroles, such as **4f**, with TFA resulted in the formation of an inseparable complex mixture.

The reaction of cyclic 1,3-bis-silyl enol ethers[23] with 1-azido-2,2-dimethoxyethane (**2**) was studied next (Scheme 4, Table 3). The reaction of **2** with **1p**, prepared from ethyl cyclododecan-1-one-2-carboxylate, afforded the condensation product **3p** with good 1,2-diastereoselectivity. Treatment of the latter with PPh_3 afforded the *trans*-configured 5,12-bicyclic pyrrolidine **4p**. Heating of **4p** in CH_2Cl_2 gave bicyclic **5p**. The structure of 5,12-bicyclic pyrrole **5p** was studied by crystal structure analysis. Inspection of the crystal lattice revealed, similar to **4f**, the presence of two intermolecular hydrogen bonds N−H···O and the formation of a dimer. The reaction of **2** with **1q**, prepared from ethyl cyclohexan-1-one-2-carboxylate, afforded the condensation product **3q**. Treatment of **3q** with PPh_3 afforded a separable mixture of the 5,6-bicyclic pyrrolidines ***cis*-4q** (73%) and ***trans*-4q** (15%). Heating ***trans*-4q** in 1,4-dioxane gave bicyclic **5q**. The reaction of **2** with **1r**, prepared from ethyl cyclooctan-1-one-2-carboxylate, afforded **3r**. The PPh_3-mediated cyclization of **3r** afforded the 5,8-bicyclic pyrrolidines ***cis*-4r** (14%) and ***trans*-4r** (76%). Heating ***cis*-4r** in 1,4-dioxane gave bicyclic **5r**. TFA treatment of ***trans*-4r** in CH_2Cl_2 gave the pyrrole **6f** (58%) by elimination of methanol and subsequent Friedel−Crafts acylation of the pyrrole moiety. The reaction of **2** with **1s**, prepared from ethyl 5-methylcyclohexan-1-one-2-carboxylate, afforded **3s** as a mixture of diastereomers. The PPh_3-mediated cyclization of **3s** gave pyrrolidine **4s** as a separable diastereomeric mixture. The relative configuration of the two diastereomers could not be unambiguously established. Based on analysis of the coupling constants and NOESY measurements, on analogy to the formation of **4q** and on the cyclization of dianions with 1,4-dibromo-2-butene,[24] we assume that diastereomers ***cis*-4s** (37%) and ***trans*-4s** (34%) possess the structure assigned. The TFA-mediated transformation of each diastereomer into **5s** failed, due to decomposition. The reaction of **2** with **1t**, prepared from methyl 6-phenylcyclohexan-1-one-2-carboxylate, afforded **3t**. Treatment of **3t** with PPh_3 afforded the 3-methoxyhexahydro-2,3-benzopyrrole **4t** as a separable mixture of two diastereomers. Heating **4t** in 1,4-dioxane gave bicyclic **5t** as an inseparable mixture of two diastereomers in good yield.

SCHEME 4. Synthesis of 4p and 5p[a]



[a] Key: (i) 0.5 equiv of TMSOTf, CH_2Cl_2, −78 → +20 °C, 58%; (ii) PPh_3, 3 h, THF, 80 °C, 98%; (iii) reflux in CH_2Cl_2 or 1,4-dioxane, 24 h, 100%.

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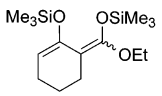
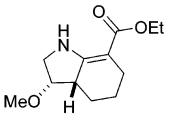
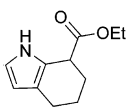
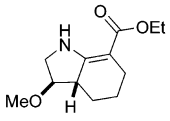
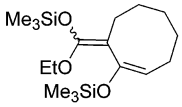
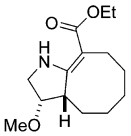
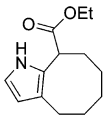
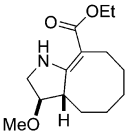
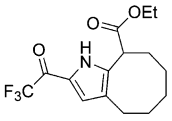
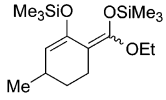
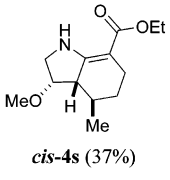
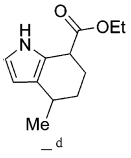
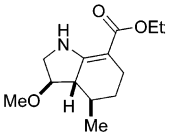
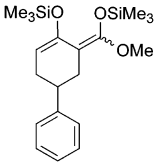
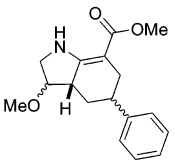
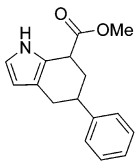
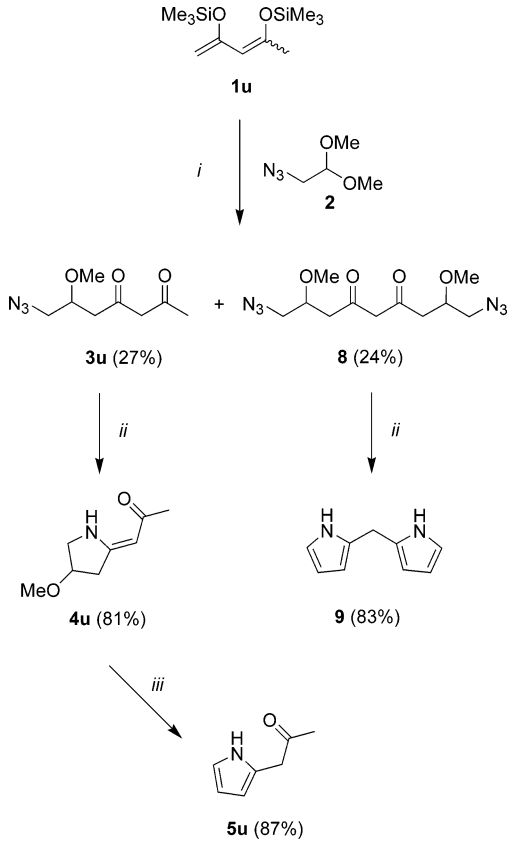
TABLE 3. Bicyclic Derivatives and Yields of Condensation Products 3 and Pyrrolidines 4 by Staudinger−aza-Wittig Reaction and Pyrroles 5 by Thermal Extrusion of Methanol

3-5	1	3[a]	4[a]	5[a]
q		48%	 ***cis*-4q** (73%)	 100%[b]
			 ***trans*-4q** (15%)	
r		65%	 ***cis*-4r** (14%)	 **5r** (83%)[b]
			 ***trans*-4r** (76%)	 **6f** (58%)[c]
s		96%	 ***cis*-4s** (37%)	 —[d]
			 ***trans*-4s** (34%)	
t		71%	 51%, 39%	 79%[b]

[a] Yields of isolated products. [b] Reflux, 1,4-dioxane (from *trans*-**4q**, *cis*-**4r** and diastereomeric mixture of **4t**). [c] TFA, CH_2Cl_2 (from *trans*-**4r**). [d] Experiment (reflux) was not carried out; TFA, CH_2Cl_2: 0%.

The reaction of 2,4-bis(trimethylsilyloxy)penta-1,3-diene (**1u**), prepared from acetylacetone, with 1-azido-2,2-dimethoxyethane (**2**) was studied next (Scheme 5). The reaction of **2** with **1u** afforded a separable mixture of the expected condensation product **3u** and of the double condensation product **8**. The latter was formed by reaction of **1u** with **2**, silyl migration and subsequent reaction with a second molecule of **2**. The use of an excess of **2** did not result in an increase of the yield of **8**. To the best of our knowledge, double condensations have been reported earlier for Me_3SiOTf-catalyzed reactions of 2-(trimethylsilyloxy)propene,[25] but not for the 1,3-bis-silyl enol ether **1u**. Treatment of **3u** with PPh_3 afforded the *Z*-configured 2-alkylidenepyrrolidine **4u**. Heating **4u** in 1,4-dioxane gave **5r**. Treatment of **8** with PPh_3 resulted in direct formation of the bis-pyrrole **9**.

SCHEME 5. Synthesis of 4u, 5u and 9[a]



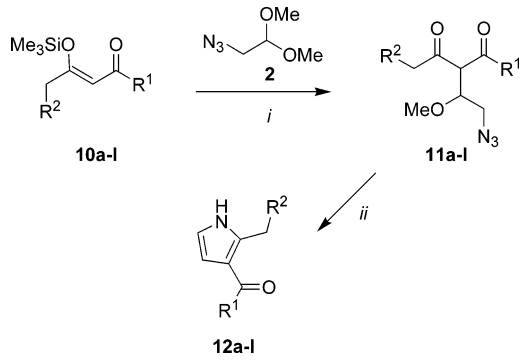
[a] Key: (i) 0.3 equiv of TMSOTf, CH_2Cl_2, −78 → +20 °C; (ii) PPh_3, 3 h, THF, 80 °C; (iii) reflux, 1,4-dioxane, 24 h.

The reaction of mono-silyl enol ethers with 1-azido-2,2-dimethoxyethane (**2**) was studied next (Scheme 6, Table 4). The reaction of **2** with silyl enol ethers **10a**−**l**, prepared from the corresponding 1,3-dicarbonyl compounds**,** gave the open-chained azides **11a**−**l**. Treatment of the latter with PPh_3 directly afforded the pyrroles **12a**−**l** in good yields. The structure of pyrrole **12b** was studied by crystal structure analysis. Inspection of the crystal lattice revealed the presence of intermolecular hydrogen bonds and the formation of a chain-type structure.

In summary, the cyclization of 1,3-bis-silyl enol ethers with 1-azido-2,2-dimethoxyethane allowed an efficient synthesis of a variety of 2-alkylidene-4-methoxypyrrolidines. The reactions proceeded with very good chemo-, regio- and 1,2-diastereoselectivity. Functionalized pyrroles were efficiently prepared by thermal elimination of methanol from 2-alkylidene-4-methoxypyrrolidines. In

(25) Mikami, K.; Ohmura, H. *Chem. Commun.* **2002**, 2626.

SCHEME 6. Synthesis of 11a–l and 12a–l[a]



[a] Key: (i) 0.5 equiv of TMSOTf, CH_2Cl_2, −78 → +20 °C; (ii) PPh_3, 3 h, THF, reflux.

TABLE 4. Derivatives and Yields of Condensation Products 11 and Pyrroles 12 by Staudinger–aza-Wittig Reaction

11, 12	R^1	R^2	11[a] (%)	12[a] (%)
a	OMe	H	50	85
b	OEt	H	50	91
c	$O(CH_2)_2OMe$	H		71[b]
d	Me	H	59	97
e	OEt	allyl		70[b]
f	OEt	Et		55[b]
g	OEt	*n*Pr		63[b]
h	OEt	*n*Bu		62[b]
i	OEt	*n*Hex	92	89
j	OEt	*n*Oct		65[b]
k	OEt	*n*Non		68[b]
l	OEt	*n*Dec		67[b]

[a] Yields of isolated products. [b] Yields of isolated products over two steps.

addition, the synthesis of pyrroles by cyclization of 1-azido-2,2-dimethoxyethane with monosilyl enol ethers, derived from 1,3-dicarbonyl compounds, was reported. The reaction of 2-alkylidene-4-methoxypyrrolidines with TFA resulted in the formation of functionalized indoles.

Experimental Section

1-Azido-2,2-dimethoxyethane (2).[16] Sodium azide (19.503 g, 300 mmol) and potassium iodide (3.320 g, 20 mmol) were added to a solution of 1-bromo-2,2-dimethoxyethane (823.64 mL, 200 mmol) in DMSO (140 mL) at room temperature. The reaction mixture was heated to 90 °C and stirred for 5 days at 90 °C. After cooling to room temperature, water (200 mL) and diethyl ether (200 mL) were added, the organic layer was separated and the aqueous layer was repeatedly extracted with diethyl ether (4 × 200 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and the filtrate was concentrated to dryness in vacuo. Product **2** was isolated without further purification as slightly yellow oil (22.31 g, 85%). For safety reasons, it is recommended to carry out the reaction on a small scale (2.0 g sodium azide, no decreasement of the yield was observed) and to use a safety shield. Although synthetic applications of **2** have been previously reported,[16] a procedure for its preparation was not provided. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.27 (d, J = 5.3 Hz, 2 H, CH_2N_3), 3.43 (s, 6 H, 2 × OCH_3), 4.48 (t, J = 5.3 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 51.66 (CH_2N_3), 54.25 (OCH_3), 103.08 (CH). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2995 (w), 2939 (m), 2837 (w, C–H), 2102 (s, N_3), 1444 (m), 1311 (w), 1275 (s), 1196 (m), 1129 (s), 1089 (s), 1064 (s), 1035 (m), 979 (w), 922 (w). MS (EI, 70 eV): m/z = 75 ($M^+ - CH_2N_3$, 100).

CAUTION: The handling of low-molecular weight azides is dangerous, due to their potentially explosive character. However, in our hands, neat **2** did not appear to be shock sensitive, the compound should be handled with great care. Neat azides must not be heated or distilled and all reactions should be carried out on a small scale. The use of a safety shield is highly recommended.

General Procedure for the Reaction of 1,3-Bis-silyl Enol Ethers (1) or Silyl Enol Ethers (10) with 1-Azido-2,2-dimethoxyethane (2). To a CH_2Cl_2 solution (10 mL/mmol) of **1** or **10** (1 equiv) and **2** (1.3 equiv) was added Me_3SiOTf (0.5 equiv) at −78 °C, and the solution was stirred for 2 h at −78 °C. The temperature of the reaction mixture was allowed to rise 20 °C during 14 h and the mixture was stirred for 3 h at 20 °C. To this solution a saturated aqueous solution of $NaHCO_3$ was added, the organic layer was separated and the aqueous layer was repeatedly extracted with dichloromethane. The combined organic extracts were dried over Na_2SO_4, filtered and the solvent of the filtrate was removed in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc) to give **3** or **11**.

6-Azido-5-methoxy-3-oxohexanoic Acid Methyl Ester (3a). Starting with **2** (1.705 g, 13 mmol), 1-methoxy-1,3-bis-trimethylsilanyloxybuta-1,3-diene (**1a**) (2.605 g, 10 mmol), and Me_3SiOTf (1.111 g, 5 mmol) in CH_2Cl_2 (100 mL), **3a** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a yellow oil (1.025 g, 48%). ^{1}H NMR ($CDCl_3$, 300 Hz): δ = 2.72 (dd, J = 17.1, 5.7 Hz, 1 H, CH_2), 2.89 (dd, J = 17.1, 6.9 Hz, 1 H, CH_2), 3.26 (dd, J = 12.9, 5.1 Hz, 1 H, CH_2N_3), 3.41 (s, 3 H, OCH_3), 3.46 (dd, J = 12.9, 4.2 Hz, 1 H, CH_2N_3), 3.50 (s, 2 H, CH_2), 3.75 (s, 3 H, OCH_3), 3.83–3.88 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 44.7, 49.5, 52.1, 52.5, 57.4, 75.7, 167.1, 200.4. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2955 (w), 2938 (w), 2104 (s), 1747 (s), 1276 (s), 1194 (m), 1181 (m), 1151 (m), 1114 (m), 1093 (m), 1042 (w). MS (EI, 70 eV): m/z = 201 (M^+ − Me, 7), 169 (39), 159 ($M^+ - CH_2N_3$, 65), 153 (5), 127 (95), 115 (14), 101 (97), 85 (100). Anal. Calcd. for $C_8H_{13}O_3N_3$ (215.209): C, 44.65; H, 6.09; N, 19.53. Found: C 45.46; H, 5.88; N, 19.53.

6-Azido-5-methoxy-3-oxohexanoic acid 2-Methoxyethyl Ester (3d). Starting with **2** (1.705 g, 13 mmol), 1-(2-methoxyethoxy)-1,3-bis-trimethylsilanyloxybuta-1,3-diene (**1d**) (3.085 g, 10 mmol), and Me_3SiOTf (1.111 g, 5 mmol) in CH_2Cl_2 (100 mL), **3d** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a yellow oil (1.145 g, 44%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.72 (dd, J = 12.9, 5.7 Hz, 1 H, CH_2), 2.90 (dd, J = 17.4, 6.9 Hz, 1 H, CH), 3.25 (dd, J = 12.9, 5.1 Hz, 1 H, CH_2N_3), 3.39 (s, 3 H, OCH_3), 3.41 (s, 3 H, OCH_3), 3.47 (dd, J = 12.9, 3.9 Hz, 1 H, CH_2N_3), 3.53 (s, 2 H, CH_2), 3.62 (t, J = 6.5 Hz, 2 H, $OCH_2CH_2OCH_3$), 3.87 (quint, J = 6.6 Hz, 1 H, CH), 4.31 (t, J = 6.9 Hz, 2 H, $OCH_2CH_2OCH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 44.4, 49.7, 52.6, 57.4, 58.7, 64.1, 70.0, 75.7, 166.7, 200.3. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2935 (w), 2103 (s), 1744 (s), 1717 (s), 1453 (w), 1411 (w), 1370 (m), 1316 (m), 1293 (s), 1253 (s), 1200 (m), 1182 (m), 1151 (m), 1129 (s), 1104 (m), 1037 (m). MS (EI, 70 eV): m/z = 203 ($M^+ - CH_2N_3$, 100), 184 (3), 145 (21), 127 (55), 112 (37).

6-Azido-5-methoxy-1-phenylhexane-1,3-dione (3e). Starting with **2** (1.705 g, 13 mmol), (1,3-bis-trimethylsilanyloxybuta-1,3-dienyl)benzene (**1e**) (3.066 g, 10 mmol), and Me_3SiOTf (1.111 g, 5 mmol) in CH_2Cl_2 (100 mL), **3e** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1.1) as a yellow oil (2.486 g, 95%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.60 (dd, J = 15, 3.0 Hz, 1 H, CH_2), 2.74 (dd, J = 15, 6.9 Hz, 1 H, CH_2), 3.30 (dd, J = 12.9, 5.4 Hz, 1 H, CH_2N_3), 3.44 (s, 3 H, OCH_3), 3.46 (dd, J = 12.9, 3.6 Hz, 1 H, CH_2N_3), 3.85–3.92 (m, 1 H, CH), 6.22 (s, 1 H, CH from enol form), 7.42 (d, J = 8.7 Hz, 2 H, 2 × CH from Ph), 7.52 (t, J = 8.0 Hz, 1 H, CH from Ph), 7.88 (d, J = 8.7 Hz, 2 H, 2 × CH from Ph), 16.11 (broad s, 1 H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 41.6, 53.1, 57.6, 77.2, 97.2, 126.9, 128.5, 132.4, 134.3, 183.1, 193.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2983 (w), 2934 (w), 2831 (w), 2102 (s), 1604 (s),

1574 (s), 1492 (m), 1459 (m), 1440 (m), 1363 (w), 1354 (w), 1291 (s), 1182 (w), 1150 (w), 1109 (m), 1083 (m), 766 (m), 698 (w, Ph). MS (EI, 70 eV): *m/z* = 205 ($M^+ - CH_2N_3$, 22), 174 (11), 161 (8), 147 (98), 105 (100).

6-Azido-5-methoxy-4-methyl-3-oxohexanoic Acid Methyl Ester (3f). Starting with **2** (1.705 g, 13 mmol), 1-methoxy-1,3-bis-trimethylsilanyloxypenta-1,3-diene (**1f**) (2.745 g, 10 mmol), and Me_3SiOTf (1.111 g, 5 mmol) in CH_2Cl_2 (100 mL), **3f** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1→ 1:1) as a yellow oil (2.177 g, 95%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.12 (dd, *J* = 40.2, 6.9 Hz, 3 H, CH_3), 2.97−3.11 (m, 1 H, CH), 3.15−3.65 (m, 1 H, CH_2N_3), 3.39 (s, 3 H, OCH_3), 3.49 (s, 2 H, CH_2), 3.50−3.65 (m, 1 H from CH_2N_3, and 1 H from CH), 3.77 (s, 3 H, OCH_3). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2983 (w), 2952 (m), 2940 (m), 2102 (s), 1748 (s), 1715 (s), 1653 (w), 1632 (w), 1454 (m), 1439 (m), 1406 (w), 1379 (w), 1346 (w), 1285 (m), 1261 (s), 1196 (m), 1180 (m), 1151 (m), 1098 (s), 1053 (m), 1017 (m). MS (EI, 70 eV): *m/z* = 173 ($M^+ - CH_2N_3$, 43), 99 (100). Anal. Calcd for $C_9H_{15}O_4N_3$ (229.236): C, 47.16; H, 6.60; N, 18.33. Found C, 46.55; H, 6.67; N, 18.09.

6-Azido-4-ethyl-5-methoxy-3-oxohexanoic Acid Ethyl Ester (3g). Starting with **2** (1.705 g, 13 mmol), 1-ethoxy-1,3-bis-trimethylsilanyloxyhexa-1,3-diene (**1g**) (3.026 g, 10 mmol), and Me_3SiOTf (1.111 g, 5 mmol) in CH_2Cl_2 (100 mL), **3g** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a yellow oil (2.512 g, 98%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 9.3 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.28 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.62 (quint, *J* = 7.4 Hz, 2 H, CH_2), 2.52 (t, *J* = 7.5 Hz, 1 H, CH), 2.91−3.06 (m, 1 H, CH_2N_3), 3.15−3.20 (m, 1 H, CH_2N_3), 3.40 (ds, *J* = 19.8 Hz, 3 H, OCH_3), 3.38−3.49 (m, 1 H, CH), 3.51 (ds, *J* = 17.1 Hz, 2 H, CH_2), 4.20 (q, *J* = 7.2 Hz, 2 H, OCH_2).

4-(2-Azido-1-methoxyethyl)-3-oxohept-6-enoic Acid Ethyl Ester (3i). Starting with **2** (1.967 g, 15 mmol), 1-ethoxy-1,3-bis-trimethylsilanyloxyhepta-1,3,6-triene (**1i**) (3.146 g, 10 mmol), and Me_3SiOTf (1.111 g, 5 mmol) in CH_2Cl_2 (100 mL), **3i** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a brownish oil (1.614 g, 60%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.28 (t, *J* = 7.2 Hz, 3 H, CH_3), 2.28−2.39 (m, 2 H, CH_2), 2.63−2.68 (m, 1 H, CH), 3.09−3.22 (m, 1 H, CH_2N_3), 3.37 (s, 3 H, OCH_3), 3.38−3.46 (m, 1 H, CH_2N_3), 3.48 (s, 2 H, CH_2), 3.49−3.57 (m, 1 H, CH), 4.10−4.24 (m, 1 H, OCH_2), 4.98−5.12 (m, 2 H, CH_2=CH), 5.63−5.84 (m, 1 H, CH=CH_2). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2982 (w), 2936 (w), 2102 (s), 1742 (s), 1717 (s), 1643 (w), 1444 (w), 1370 (w), 1306 (m), 1249 (s) 1180 (s), 1156 (s), 1100 (m), 1031 (m), 853 (w). MS (EI, 70 eV): *m/z* = 224 (M^+ − OEt, 3), 213 ($M^+ - CH_2N_3$, 100), 194 (4), 170 (16), 168 (3), 141 (13), 125 (85).

4-(2-Azido-1-methoxyethyl)-3-oxoheptanoic Acid Ethyl Ester (3j). Starting with **2** (1.967 g, 15 mmol), 1-ethoxy-1,3-bis-trimethylsilanyloxyhepta-1,3-diene (**1j**) (3.166 g, 10 mmol), and Me_3SiOTf (1.111 g, 5 mmol), in CH_2Cl_2 (100 mL), **3j** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a yellow oil (2.227 g, 82%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.28 (t, *J* = 7.2 Hz, 3 H, $OCHCH_3$), 1.22−1.35 (m, 2 H, CH_2), 1.56−1.62 (m, 2 H, CH_2), 3.01 (dt, *J* = 3.0, 8.4 Hz, 1 H, CH), 3.19 (dd, *J* = 13.5, 4.5 Hz, 1 H, CH_2N_3), 3.36 (s, 3 H, OCH_3), 3.43−3.50 (m, 1 H, CH_2N_3), 3.54 (s, 2 H, CH_2), 3.57 (dd, *J* = 13.5, 3.0 Hz, 1 H, CH), 4.20 (q, *J* = 7.2 Hz, 2 H, OCH_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 13.9, 14.0, 20.2, 30.2, 50.3, 51.6, 53.2, 58.0, 61.0, 82.0, 166.6, 205.3. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2962 (s), 2936 (s), 2874 (w), 2101 (s), 1745 (s), 1715 (s), 1647 (m), 1463 (m), 1411 (w), 1369 (m), 1301 (s), 1275 (s), 1238 (s), 1179 (m), 1156 (m), 1100 (s), 1034 (m). MS (EI, 70 eV): *m/z* = 226 (M^+ − OEt, 4), 215 ($M^+ - CH_2N_3$, 55), 184 (4), 142 (3), 127 (100).

3-(2-Azido-1-methoxyethyl)-2-oxocyclododecanecarboxylic Acid Ethyl Ester (3p). Starting with **2** (1.967 g, 15 mmol), 12-(ethoxytrimethylsilanyloxymethylene)-1-trimethylsilanyloxycyclododecene (**1p**) (3.967 g, 10 mmol), and Me_3SiOTf (1.111 g, 5 mmol) in CH_2Cl_2 (100 mL), **3p** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a yellow oil (2.065 g, 58%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.28 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.29−1.35 (m, 12 H, 6 × CH_2), 3.05−3.13 (m, 1 H, CH), 3.21−3.32 (m, 1 H, CH), 3.33, 3.47 (ds, 3H, OCH_3), 3.59 (dt, *J* = 13.2, 3.3 Hz, 1 H, CH_2N_3), 3.64−3.73 (m, 1 H, CH_2N_3), 3.95−4.03 (m, 1 H, CH), 4.17 (q, *J* = 7.2 Hz, 2 H, OCH_2). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2933 (s), 2867 (w), 2100 (s), 1743 (s), 1711 (s), 1469 (w), 1443 (w), 1291 (m), 1271 (m), 1250 (m), 1179 (m), 1154 (w), 1114 (m), 1099 (m), 1027 (m). MS (EI, 70 eV): *m/z* = 298 ($M^+ - CH_2N_3$, 100), 266 (5), 252 (95), 224 (9). Anal. Calcd for $C_{18}H_{31}O_4N_3$ (353.462): C, 61.17; H, 8.84; N, 11.89. Found: C, 61.33; H, 8.96; N, 11.64.

7-Azido-6-methoxyheptane-2,4-dione (3u). Starting with **2** (1.705 g, 13 mmol), 2,4-bis-trimethylsilanyloxypenta-1,3-diene (**1u**) (2.445 g, 10 mmol), and Me_3SiOTf (1.111 g, 5 mmol) in CH_2Cl_2 (100 mL), **3u** and **8** were isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as brownish oils (0.536 g, 27%; 0.582 g, 24%). ^1H NMR ($CDCl_3$, 300 MHz): δ= 2.07 (s, 3 H, CH_3), 2.46 (dd, *J* = 14.7, 6.0 Hz, 1 H, CH_2), 2.59 (dd, *J* = 14.7, 6.6 Hz, 1 H, CH_2), 3.28 (dd, *J* = 12.9, 5.4 Hz, 1 H, CH_2), 3.42 (s, 3 H, OCH_3), 3.43 (dd, *J* = 12.9, 3.9 Hz, 1 H, CH_2N_3), 3.78−3.86 (m, 1 H, CH), 5.55 (s, 1 H, CH=C), 15.39 (broad s, 1 H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_c= 24.5, 40.6, 53.0, 57.5, 77.0, 101.0, 190.6, 191.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2935 (m), 2102 (s), 1724 (w), 1708 (m), 1685 (w), 1618 (s), 1613 (s), 1562 (w), 1536 (w), 1458 (m), 1439 (m), 1426 (m), 1361 (m), 1293 (s), 1254 (m), 1195 (w), 1181 (w), 1152 (w), 1109 (m), 1036 (w). MS (EI, 70 eV): *m/z* = 184 (M^+ − Me, 98), 143 ($M^+ - CH_2N_3$, 80), 128 (92), 99 (100).

1,9-Diazido-2,8-dimethoxynonane-4,6-dione (8). ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.49 (ddd, *J* = 15, 6, 0.9 Hz, 2 H, CH_2), 2.61 (dd, *J* = 15, 6 Hz, 2 H, CH_2), 3.28 (dd, *J* = 12.9, 5.7 Hz, 2 H, CH_2-N_3), 3.43 (s, 6 H, 2 × OCH_3), 3.41−3.50 (m, 2 H, 2 × CH), 5.60 (s, 1 H, CH), 15.29 (broad s, 1 H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 40.7, 53.0, 57.6, 77.0, 101.8, 190.5. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3333 (br), 2935 (s), 2832 (w), 2101 (s), 1711 (s), 1668 (s), 1613 (s), 1442 (s), 1355 (s), 1291 (s), 1254 (s), 1195 (m), 1153 (m), 1039 (m), 931 (w), 844 (m). MS (EI, 70 eV): *m/z* = 298 (M^+, 100), 256 (10), 214 (22), 198 (80), 183 (26).

2-Acetyl-4-azido-3-methoxybutyric Acid Methyl Ester (11a). Starting with **2** (1.967 g, 15 mmol), 3-trimethylsilanyloxybut-2-enoic acid methyl ester (**10a**) (1.883 g, 10 mmol), and Me_3SiOTf (1.111 g, 5 mmol) in CH_2Cl_2 (100 mL), **11a** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a yellow oil (1.081 g, 50%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.27, 2.33 (ds, 3 H, CH_3), 3.23−3.40 (m, 1 H, CH_2−N_3), 3.44, 3.47 (ds, 3 H, OCH_3), 3.63 (dt, *J* = 13.2, 3.0 Hz, 1 H, CH_2−N_3), 3.73, 3.78 (ds, 3 H, OCH_3), 3.92 (dd, *J* = 9.6, 3.0 Hz, 1 H, CH), 3.99−4.03 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 3.6, 31.7, 51.1, 51.1, 52.8, 52.9, 58.5, 58.6, 60.2, 61.7, 78.5, 79.1, 167.6, 167.9, 201.0, 201.5. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2998 (w), 2956 (w), 2938 (w), 2105 (s), 1746 (s), 1720 (s), 1648 (w), 1438 (m), 1360 (m), 1260 (s), 1212 (m), 1197 (m), 1173 (m), 1150 (m), 1117 (m), 1096 (s), 1050 (w), 994 (w). MS (EI, 70 eV): *m/z* = 139 (M^+ − OMe, 14), 159 ($M^+ - CH_2N_3$, 3), 155 (1), 146 (3), 117 (79), 101 (6), 85 (85), 55 (9), 43 (100).

2-Acetyl-4-azido-3-methoxybutyric Acid Ethyl Ester (11b). Starting with **2** (1.967 g, 15 mmol), 3-trimethylsilanyloxybut-2-enoic acid ethyl ester (**10b**) (2.023 g, 10 mmol), and Me_3SiOTf (1.111 g, 5 mmol) in CH_2Cl_2 (100 mL), **11b** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a yellow oil (1.144 g, 50%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.29 (m, 3 H, CH_3), 2.27, 2.33 (ds, 3 H, CH_3), 3.25−3.37 (m, 1 H, CH_2−N_3), 3.41, 3.44 (ds, 3 H, OCH_3), 3.63 (m, 1 H, CH_2−N_3), 3.89 (dd, *J* = 8.7, 2.4 Hz, 1 H, CH), 3.99−4.04 (m, 1 H, CH), 4.17−4.26 (m, 2 H, OCH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 13.9, 14.0, 30.1, 31.2, 50.0, 50.9, 58.2, 58.3, 60.3, 61.7, 61.6, 61.7, 78.8, 166.8, 167.1, 200.8, 201.2. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2986 (w), 2939 (w), 2104 (s), 1742 (s), 1718 (s), 1642 (w), 1447 (w), 1366 (m), 1295 (s), 1256 (s), 1212 (m), 1179 (s), 1151 (m), 1115 (m), 1097 (s), 1044 (w), 1025 (w). MS (EI, 70

eV): *m/z* = 198 (M^+ − OMe, 1), 173 (M^+ − CH_2N_3, 2), 141 (1), 131 (84), 128 (3), 113 (2), 103 (26), 99 (3), 85 (100), 82 (2), 55 (6), 43 (68).

3-(2-Azido-1-methoxyethyl)pentane-2,4-dione (11d). Starting with **2** (0.786 g, 6.0 mmol), 4-trimethylsilanyloxypent-3-en-2-one (**10d**) (0.862 g, 5 mmol), and Me_3SiOTf (0.556 g, 2.5 mmol) in CH_2Cl_2 (100 mL), **11d** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 50:1 → 1:1) as a yellow oil (0.540 g, 59%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.21 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 3.17 (dd, *J* = 13.2, 3.6 Hz, 1 H, CH_2−N_3), 3.39 (s, 3 H, OCH_3), 3.63 (dd, *J* = 13.2, 3.0 Hz, 1 H, CH_2−N_3), 4.06 (dt, *J* = 9.3, 3.6 Hz, 1 H, CH), 4.15 (d, *J* = 9.3 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 30.6, 30.7, 50.4, 57.8, 69.2, 79.0, 201.2, 201.7. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2993 (w), 2938 (m), 2833 (w), 2104 (s), 1725 (s), 1703 (s), 1558 (m), 1423 (m), 1360 (s), 1276 (s), 1187 (m), 1153 (m), 1110 (s), 1197 (s), 1048 (w), 1024 (w), 956 (w), 930 (w), 579 (w). MS (EI, 70 eV): *m/z* = 199 (M^+, 2), 157 (2), 143 (9), 130 (1), 125 (3), 101 (58), 83 (15), 70 (5), 43 (100). Anal. Calcd for $C_8H_{13}O_3N_3$ (199.210): C, 48.24; H, 6.58; N, 21.09. Found: C, 48.70; H, 6.17; N, 21.30.

2-(2-Azido-1-methoxyethyl)-3-oxodecanoic Acid Ethyl Ester (11i). Starting with **2** (0.984 g, 7.5 mmol), 3-trimethylsilanyloxydec-2-enoic acid ethyl ester (**10i**) (1.432 g, 5.0 mmol), and Me_3SiOTf (0.556 g, 2.5 mmol) in CH_2Cl_2 (100 mL), **11i** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 5:1) as a yellow oil (2.058 g, 92%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.23−1.33 (m, 11 H, 4 × CH_2, OCH_2CH_3), 154−1.62 (m, 2 H, CH_2), 2.53 (t, *J* = 7.2 Hz, 2 H, CH_2), 3.15−3.37 (m, 1 H, CH_2-N_3), 3.38, 3.43 (ds, 3 H, OCH_3), 3.46−3.70 (m, 2 H, CH, CH_2-N_3), 4.20 (q, *J* = 7.2 Hz, 2 H, OCH_2), 4.15−4.23 (m, 1 H, CH). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2957 (s), 2930 (s), 2858 (s), 2120 (s), 1745 (s), 1717 (s), 1647 (w), 1463 (m), 1410 (w), 1371 (m), 1300 (s), 1234 (s), 1178 (s), 1158 (s), 1158 (m), 1126 (m), 1100 (s), 1033 (m). MS (EI, 70 eV): *m/z* = 257 (M^+ − N_3, 7), 196 (4), 185 (2), 169 (12), 143 (22), 130 (90), 127 (57), 114 (18), 102 (11), 85 (30), 70 (16), 57 (100), 43 (74). HRMS (ESI): calcd for $C_{15}H_{27}O_4N_3Na$ ($[M + Na]^+$) = 336.18993; found = 336.18912.

General Procedure for the Preparation of 2-Alkylidene-4-methoxypyrrolidines (4). To a THF-solution (10 mL/mmol) of **3** (1 equiv) was added triphenylphosphine (1.2 equiv) at room temperature. The reaction mixture was heated and stirred for 4 h at 80 °C. After cooling to 20 °C, the solvent was removed in vacuo and the residue was purified by chromatography (silica gel, *n*-hexane/EtOAc) to give **4**.

(4-Methoxypyrrolidin-2-ylidene)acetic Acid Methyl Ester (4a). Starting with **3a** (0.400 g, 1.86 mmol) and PPh_3 (0.585 g, 2.23 mmol) in THF (10 mL), **4a** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a yellow solid (0.257 g, 81%). Mp = 42.6 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.64 (dd, *J* = 17.1, 2.7 Hz, 1 H, CH_2), 2.77 (dd, *J* = 17.1, 6.3 Hz, 1 H, CH_2), 3.32 (s, 3 H, OCH_3), 3.56 (d, *J* = 10.5 Hz, 1 H, CH_2NH), 3.62 (s, 3 H, OCH_3), 3.60−3.68 (m, 1 H, CH_2NH), 4.05 (quint, *J* = 1.8 Hz, 1 H, CH), 4.55 (s, 1 H, CH=C), 7.82 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 38.2, 49.9, 52.1, 56.3, 76.9, 77.1, 163.8, 170.5. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3367 (m), 2982 (w), 2940 (m), 2881 (w), 1663 (s), 1603 (s), 1489 (m), 1458 (w), 1433 (w), 1340 (m), 1293 (m), 1225 (s), 1188 (m), 1152 (s), 1097 (s), 1045 (s), 904 (w), 782 (m). MS (EI, 70 eV): *m/z* = 171 (M^+, 87), 156 (4), 141 (15), 140 (100), 124 (17), 112 (28), 109 (22), 80 (41). Anal. Calcd for $C_8H_{13}O_3N$ (171.196): C, 56.13; H, 7.65; N, 8.18. Found: C, 55.76; H, 7.30; N, 8.01.

(4-Methoxypyrrolidin-2-ylidene)acetic Acid 2-Methoxyethyl Ester (4d). Starting with **3d** (0.300 g, 1.16 mmol) and PPh_3 (0.364 g, 1.39 mmol) in THF (30 mL), **4d** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a yellow solid (0.184 g, 74%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.64 (dd, *J* = 16.8, 2.7 Hz, 1 H, CH_2), 2.77 (dd, *J* = 17.1, 6.0 Hz, 1 H, CH_2), 3.32 (s, 3 H, OCH_3), 3.38 (s, 3 H, OCH_3), 3.53−3.60 (m, 2 H from OCH_2 and 1 H from CH_2NH), 3.66 (dd, *J* = 1.1, 5.4 Hz, 1 H, CH_2NH), 4.06 (quint, *J* = 3.0 Hz, 1 H, CH), 4.20 (t, *J* = 4.5 Hz, 2 H, OCH_2), 4.61 (s, 1 H, CH=C), 7.80 (broad s, 1 H, NH). ^{13}C ($CDCl_3$, 75 MHz): δ_C = 38.4, 52.3, 56.6, 59.0, 61.7, 71.1, 77.2, 77.7, 164.2, 170.2. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3384 (m), 2983 (w), 2970 (w), 2939 (w), 2921 (w), 2895 (m), 2846 (w), 2818 (w), 1658 (s), 1611 (s), 1491 (m), 1454 (w), 1371 (w), 1342 (w), 1295 (m), 1251 (s), 1235 (s), 1221 (s), 1201 (w), 1188 (w), 1164 (m), 1145 (m), 1129 (s), 1096 (s), 1078 (m), 1057 (s), 1044 (m), 774 (m), 709 (w), 655 (w). MS (EI, 70 eV): *m/z* = 215 (M^+, 29), 184 (21), 168 (4), 153 (20), 140 (100), 126 (6), 112 (60). The exact molecular mass *m/z* = 215.1158 ± 2 ppm [M^+] for $C_{10}H_{17}O_4N$ was confirmed by HRMS (EI, 70 eV).

2-(4-Methoxypyrrolidin-2-ylidene)-1-phenylethanone (4e). Starting with **3e** (2.000 g, 7.66 mmol) and PPh_3 (2.409 g, 9.19 mmol) in THF (70 mL), **4e** was isolated after chromatography (silica gel, *n*-Hex/EtOAc= 100:1 → 1:1) as a yellow solid (1.392 g, 84%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.80 (dd, *J* = 17.3, 28 Hz, 1 H, CH_2), 2.92 (dd, *J* = 17.5, 6.3 Hz, 1 H, CH_2), 3.35 (s, 3 H, OCH_3), 3.69 (dd, *J* = 11.8, 2.2 Hz, 1 H, CH_2NH), 3.79 (dd, *J* = 11.9, 5.3 Hz, 1 H, CH_2NH), 4.13 (quint, *J* = 2.8 Hz, 1 H, CH), 5.82 (s, 1 H, CH=C), 7.36−7.43 (m, 3 H, 3 × CH from Ph), 7.85−7.88 (m, 2 H, 2 × CH from Ph), 10.17 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 39.0, 52.8, 56.4, 76.5, 87.0, 126.9, 128.0, 130.4, 140.1, 166.5, 188.2. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3270 (w), 2994 (w), 2937 (m), 2880 (w), 2832 (w), 1609 (s), 1580 (s), 1523 (s), 1485 (s), 1457 (m), 1442 (w), 1410 (m), 1362 (m), 1342 (m), 1305 (s), 1288 (m), 1265 (s), 1240 (m), 1199 (w), 1178 (m), 1162 (m), 1092 (s), 1063 (w), 1039 (m), 1026 (w), 995 (w), 943 (w), 851 (m), 749 (s), 716 (s), 679 (m), 548 (w, Ph). MS (EI, 70 eV): *m/z* = 217 (M^+, 100), 202 (1), 186 (68), 140 (25), 112 (1), 80 (37), 77 (59). Anal. Calcd for $C_{13}H_{15}O_2N$ (217.267): C, 71.87; H, 6.96; N, 6.45. Found: C, 72.01; H, 7.41; N, 6.44.

(4-Methoxy-3-methylpyrrolidin-2-ylidene)acetic Acid Methyl Ester (4f). Starting with **3f** (2.000 g, 8.73 mmol) and PPh_3 (3.433 g, 13.1 mmol) in THF (70 mL), **4f** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a brownish oil (1.532 g, 95%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.19 (d, *J* = 7.5 Hz, 3 H, CH_3), 2.72−2.81 (m, 1 H, CH), 3.36 (s, 3 H, OCH_3), 3.43 (dd, *J* = 7.5, 3.6 Hz, 1 H, CH), 3.64 (s, 3 H,OCH_3), 3.66−3.76 (m, 2 H, CH_2NH), 4.53 (s, 1 H, CH=C), 7.72 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 16.6, 44.5, 50.1, 50.2, 57.1, 76.8, 84.3, 168.6, 171.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3373 (m), 2969 (w), 2954 (m), 2936 (m), 2903 (w), 2876 (w), 1737 (m), 1664 (s), 1604 (s), 1491 (w), 1458 (m), 1432 (m), 1314 (w), 1296 (w), 1257 (m), 1230 (s), 1203 (m), 1152 (s), 1106 (m), 1043 (m), 1018 (w), 784 (w). MS (EI, 70 eV): *m/z* = 185 (M^+, 100), 170 (1), 154 (92), 138 (12), 127 (17), 122(55). Anal. Calcd for $C_9H_{15}O_3N$ (185.223): C, 58.36; H, 8.16; N, 7.56. Found: C, 58.87; H, 7.56; N, 7.80.

(3-Ethyl-4-methoxypyrrolidin-2-ylidene)acetic Acid Ethyl Ester (4g). Starting with **3g** (1.000 g, 3.9 mmol) and PPh_3 (1.223 g, 4.7 mmol) in THF (50 mL), **4g** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a brownish oil (0.660 g, 79%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.99 (t, *J* = 4.2 Hz, 3 H, CH_3), 1.25 (t, *J* = 7.2 Hz, 3 H, OCH_2-CH_3), 1.39−1.53 (m, 1 H, CH_2), 1.58−1.66 (m, 1 H, CH_2), 2.63−2.66 (m, 1 H, CH), 3.33 (s, 3 H, OCH_3), 3.49 (dt, *J* = 10.8, 1.5 Hz, 1 H, CH), 3.67 (dd, *J* = 10.8, 5.4 Hz, 1 H, CH_2NH), 3.72−3.75 (m, 1 H, CH_2NH), 4.10 (dq, *J* = 1.5, 7.2 Hz, 2 H, OCH_2), 4.53 (s, 1 H, CH=C), 7.79 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 11.0, 14.4, 24.3, 50.8, 51.2, 56.1, 58.1, 77.4, 81.9, 167.4, 170.5. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3368 (m), 2971 (s), 2934 (s), 2901 (m), 2877 (m), 2827 (w), 1729 (w), 1659 (s), 1604 (s), 1491 (m), 1462 (m), 1368 (m), 1345 (w), 1311 (m), 1225 (s), 1246 (s), 1199 (s), 1149 (s), 1094 (s), 1050 (s), 783 (s). UV−vis (CH_2Cl_2, nm): λ_{max} (log ϵ) = 280 (4.16). MS (EI, 70 eV): *m/z* = 213 (M^+, 25), 185 (18), 182 (4), 154 (100), 136 (15), 107 (31). Anal. Calcd for $C_{11}H_{19}O_3N$ (213.276): C, 61.95; H, 8.98; N, 6.57. Found: C, 62.30; H, 8.32; N, 5.98.

(3-Allyl-4-methoxypyrrolidin-2-ylidene)acetic Acid Ethyl Ester (4i). Starting with **3i** (0.300 g, 1.11 g) and PPh_3 (0.351

g, 1.34 mmol) in THF (15 mL), **4i** was isolated after chromatography (silica gel, *n*-hex/EtOAc = 100:1 → 1:1) as a brownish oil (0.236 g, 94%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.26 (t, J = 7.2 Hz, 3 H, CH_3), 2.18−2.42 (m, 1 H, CH), 3.63−3.76 (m, 2 H, CH_2NH), 4.11 (dq, J = 1.5, 7.2 Hz, 2 H, OCH_2), 4.56 (s, 1 H, CH=C), 5.09−5.15 (m, 2 H, CH_2=CH), 5.76−5.88 (m, 1 H, CH=CH_2), 7.80 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 14.8, 35.9, 49.6, 51.0, 56.8, 58.7, 77.9, 81.7, 117.7, 134.9, 170.0, 171.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3367 (m), 2980 (s), 2934 (m), 2905 (m), 2829 (w), 1732 (s), 1661 (s), 1603 (s), 1488 (m), 1463 (m), 1444 (m), 1418 (w), 1369 (m), 1299 (s), 1245 (s), 1221 (s), 1183 (s), 1151 (s), 1099 (s), 1051 (s), 998 (w), 974 (w), 918 (m), 854 (m), 785 (w). MS (EI, 70 eV): m/z = 225 (M^+, 22), 194 (71), 180 (17), 151 (32), 120 (100). The exact molecular mass m/z = 225.1365 ± 2 ppm [M^+] for $C_{12}H_{19}O_3N$ was confirmed by HRMS (EI, 70 eV).

(4-Methoxy-3-propylpyrrolidin-2-ylidene)acetic Acid Ethyl Ester (4j). Starting with **3j** (0.350 g, 1.29 mmol) and PPh_3 (0.406 g, 1.55 mmol) in THF (15 mL), **4j** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a brownish oil (0.252 g, 86%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.98 (t, J = 6.6 Hz, 3 H, CH_3), 1.25 (t, J = 7.1 Hz, 3 H, OCH_2CH_3), 1.39−1.49 (m, 4 H, 2 × CH_2), 2.68−2.72 (m, 1 H, CH), 3.32 (s, 3 H, OCH_3), 3.49 (dt, J = 10.5, 1.5 Hz, 1 H, CH), 3.64−3.72 (m, 2 H, CH_2NH), 4.10 (dq, J = 1.5, 7.2 Hz, 2 H, OCH_2), 4.53 (s, 1 H, CH=C), 7.78 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 14.1, 14.7, 20.3, 34.0, 49.9, 51.0, 56.5, 58.5, 77.7, 82.7, 168.0, 170.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3367 (w), 2960 (m), 2934 (m), 2873 (w), 1661 (s), 1605 (s), 1489 (w), 1462 (w), 1369 (w), 1313 (w), 1286 (w), 1241 (s), 1220 (s), 1192 (m), 1149 (s), 1097 (m), 1050 (m), 783 (w). UV−vis (CH_2Cl_2, nm): λ_{max} (log ϵ) = 280 (4.18). MS (EI, 70 eV): m/z = 227 (M^+, 12), 196 (4), 182 (17), 167 (7), 154 (100). HRMS (ESI): calcd for $C_{12}H_{22}O_3N$ ([M + 1]$^+$) = 228.15997; found = 228.15923.

3-Methoxy-2,3,3a,4,5,6,7,8,9,10,11,12-dodecahydro-1*H*-cyclododeca[*b*]pyrrole-13-carboxylic Acid Ethyl Ester (4p). Starting with **3p** (1.900 g, 5.38 mmol) and PPh_3 (1.692 g, 6.45 mmol) in THF (10 mL), **4p** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a brownish oil (1.624 g, 98%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.23 (t, J = 7.2 Hz, 3 H, CH_3), 1.25−1.45 (m, 12 H, 6 × CH_2), 1.52−1.65 (m, 2 H, CH_2), 1.71−1.76 (m, 1 H, CH_2), 1.82−1.87 (m, 1 H, CH_2), 2.11−2.19 (m, 2 H, CH_2), 3.00 (dd, J = 9.2 Hz, 1 H, CH), 3.28 (s, 3 H, OCH_3), 3.53 (dd, J = 9.2 Hz, 1 H, CH), 3.58 (d, J = 4.6 Hz, 1 H, CH_2NH), 3.65 (dd, J = 18.4, 4.6 Hz, 1 H, CH_2-NH), 4.04−4.14 (m, 2 H, OCH_2), 8.04 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_c = 14.1, 21.1, 23.1, 24.1, 24.9, 25.6, 26.7, 27.9, 28.3, 37.3, 50.4, 50.7, 56.0, 58.6, 82.4, 90.3, 166.1, 175.3. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3355 (m), 2929 (s), 2860 (s), 1727 (s), 1656 (s), 1583 (s), 1468 (m), 1445 (m), 1367 (w), 1315 (w), 1296 (w), 1337 (s), 1226 (s), 1178 (s), 1146 (m), 1095 (s), 1049 (s). MS (EI, 70 eV): m/z = 309 (M^+, 29), 278 (100), 264 (9), 236 (4), 204 (51). The exact molecular mass m/z = 309.2304 ± 2 ppm [M^+] for $C_{18}H_{31}O_3N$ was confirmed by HRMS (EI, 70 eV).

1-(4-Methoxypyrrolidin-2-ylidene)propan-2-one (4u). Starting with **3u** (0.130 g, 0.653 mmol) and PPh_3 (0.188 g, 0.718 mmol) in THF (5 mL), **4u** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 50:1 → 1:1) as a yellow solid (1:1 mixture of product and PPh_3, calculated yield of product: 0.082 g, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.03 (s, 3 H, CH_3), 2.64 (dd, J = 17.1, 1.8 Hz, 1 H, CH_2), 2.78 (ddd, J = 17.1, 6.3, 0.6 Hz, 1 H, CH_2), 3.32 (s, 3 H, OCH_3), 3.60 (dd, J = 11.7, 2.4 Hz, 1 H, CH_2NH), 3.69 (dd, J = 11.7, 5.1 Hz, 1 H, CH_2NH), 4.06 (sept, J = 3.0 Hz, 1 H, CH), 5.12 (s, 1 H, CH=C), 9.68 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_c = 28.7, 38.6, 52.7, 56.5, 76.7, 90.5, 164.9, 195.4. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3297 (w), 2929 (m), 1624 (s), 1550 (s), 1504 (m), 1463 (w), 1438 (m), 1417 (w), 1361 (m), 1294 (m), 1252 (m), 1188 (s), 1097 (s), 21038 (w). MS (EI, 70 eV): m/z = 155 (M^+, 82), 140 (100), 124 (48), 80 (26), 68 (9). The exact molecular mass m/z = 155.0946 ± 2 ppm [M^+] for $C_8H_{13}O_2N$ was confirmed by HRMS (EI, 70 eV).

General Procedure for the Synthesis of Pyrroles (5). A solution of **4** in CH_2Cl_2 (10 mL/mmol) or in 1,4-dioxane (5 mL/mmol) was stirred at reflux for 24 h. After the solution was cooled to 20 °C, the solvent was removed in vacuo and the residue was purified by chromatography (silica gel, *n*-Hex/EtOAc) to give **5.**

(1*H*-Pyrrol-2-yl)acetic Acid Methyl Ester (5a). Starting with **4a** (0.100 g, 0.32 mmol) in 1,4-dioxane (10 mL), **5a** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 10:1) as a black oil (0.068 g, 76%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.69 (s, 2 H, CH_2), 3.72 (s, 3 H, OCH_3), 6.01 (m, 1 H, CH), 6.15 (m, 1 H, CH), 6.75 (m, 1 H, CH), 8.70 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_c = 33.0, 52.2, 107.4, 108.3, 115.0, 117.8, 171.6. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3382 (s), 2955 (m), 2926 (m), 1734 (s), 1646 (m), 1599 (w), 1574 (w), 1436 (s), 1343 (w), 1330 (w), 1260 (s), 1201 (m), 1150 (m), 1128 (m), 1095 (m), 1045 (w), 1024 (m), 796 (w), 723 (m). MS (EI, 70 eV): m/z = 139 (M^+, 33), 124 (2), 107 (5), 80 (100). The exact molecular mass m/z = 139.0633 ± 2 ppm [M^+] for $C_7H_9O_2N$ was confirmed by HRMS (EI, 70 eV).

(1*H*-Pyrrol-2-yl)acetic Acid 2-Methoxyethyl Ester (5d). Starting with **4d** (0.030 g, 0.14 mmol) in 1,4-dioxane (3 mL), **5d** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 10:1) as a black oil (0.025 g, 98%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.39 (s, 3 H, OCH_3), 3.60−3.63 (m, 2 H, OCH_2), 3.72 (s, 2 H, CH_2), 4.27−4.32 (m, 2 H, OCH_2), 6.02 (m, 1 H, CH), 6.14 (q, J = 3.0 Hz, 1 H, CH), 6.75 (m, 1 H, CH), 8.82 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 33.1, 58.8, 64.1, 70.1, 107.2, 108.1, 117.6, 122.9, 170.9. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3359 (m), 2932 (m), 2895 (m), 2825 (w), 1741 (s), 1643 (m), 1577 (w), 1452 (m), 1409 (m), 1369 (m), 1320 (s), 1264 (s), 1197 (s), 1178 (s), 1152 (s), 1227 (s), 1097 (s), 1037 (s), 861 (w), 790 (w), 728 (m). MS (EI, 70 eV): m/z = 183 (M^+, 25), 125 (11), 107 (46), 80 (100). The exact molecular mass m/z = 183.0895 ± 2 ppm [M^+] for $C_9H_{13}O_3N$ was confirmed by HRMS (EI, 70 eV).

1-Phenyl-2-(1*H*-pyrrol-2-yl)ethanone (5e). Starting with **4e** (0.026 g, 0.12 mmol) in 1,4-dioxane (5 mL), **5e** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a brownish solid (0.018 g, 82%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.32 (s, 2 H, CH_2), 6.07 (m, 1 H, CH),), 6.15 (dd, J = 6.0, 1.8 Hz, 1 H, CH), 6.76 (m, 1 H, CH), 7.44−7.50 (m, 2 H, 2 × CH of Ph), 7.55−7.60 (m, 1 H, CH of Ph), 7.99−8.03 (m, 2 H, 2 × CH from Ph), 8.85 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 36.9, 107.4, 108.2, 117.8, 123.9, 128.4, 128.7, 133.4, 136.3, 197.7. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3351 (s), 2902 (w), 1676 (s), 1587 (w), 1341 (m), 1285 (w), 1239 (m), 1215 (m), 999 (m), 796 (m), 742 (s), 731 (s), 690 (m), 600 (w). MS (EI, 70 eV): m/z = 185 (M^+, 33), 105 (79), 80 (100). The exact molecular mass m/z = 185.0841 ± 2 ppm [M^+] for $C_{12}H_{11}ON$ was confirmed by HRMS (EI, 70 eV).

(3-Methyl-1*H*-pyrrol-2-yl)acetic Acid Methyl Ester (5f). Starting with **4f** (0.300 g, 1.62 mmol) in CH_2Cl_2 (30 mL), **5f** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 10:1) as a brownish solid (0.248 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.04 (s, 3 H, CH_3), 3.60 (s, 2 H, CH_2), 3.71 (s, 3 H, OCH_3), 6.00 (t, J = 1.8 Hz, 1 H, CH), 6.67 (t, J = 1.8 Hz, 1 H, CH), 8.49 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 10.6, 30.9, 51.9, 109.7, 115.7, 116.4, 119.2, 171.7. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3353 (s), 2953 (w), 2922 (w), 1717 (s), 1448 (w), 1436 (m), 1401 (m), 1344 (m), 1290 (w), 1256 (m), 1224 (s), 1178 (m), 1099 (m), 986 (m), 848 (w), 787 (w), 721 (s), 592 (m), 568 (w). UV−vis (CH_2Cl_2, nm): λ_{max} (log ϵ) = 227 (3.65), 460 (2.39). MS (EI, 70 eV): m/z = 153 (M^+, 49), 138 (1), 94 (100), 80 (2). Anal. Calcd for $C_8H_{11}O_2N$ (153.181): C, 62.73; H, 7.24; N, 9.14. Found: C, 63.04; H, 7.82; N, 8.73.

(3-Ethyl-1*H*-pyrrol-2-yl)acetic Acid Ethyl Ester (5g). Starting with **4g** (0.120 g, 0.56 mmol) in CH_2Cl_2 (12 mL), **5g** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 1:1) as a brownish oil (0.102 g, 100%). ^{1}H NMR ($CDCl_3$,

300 MHz): δ = 1.16 (t, J = 7.5 Hz, 3 H, CH_3), 1.27 (t, J = 7.2 Hz, 3 H, OCH_2CH_3), 2.43 (q, J = 7.5 Hz, 2 H, CH_2), 3.59 (s, 2 H, CH_2), 4.17 (q, J = 7.2 Hz, 2 H, OCH_2), 6.05 (t, J = 1.8 Hz, 1 H, CH), 6.68 (t, J = 1.8 Hz, 1 H, CH), 8.53 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_c = 13.9, 15.4, 18.6, 31.1, 60.8, 107.8, 116.4, 118.5, 122.6, 171.2. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3392 (m), 2965 (m), 2933 (w), 2873 (w), 1730 (s), 1478 (w), 1460 (m), 1425 (w), 1401 (w), 1370 (m), 1331 (w), 1297 (m), 1251 (m), 1182 (m), 1139 (m), 1096 (w), 1030 (m), 724 (m). MS (EI, 70 eV): m/z = 181 (M^+, 37), 166 (5), 120 (3), 107 (100), 93 (23). The exact molecular mass m/z = 181.1103 ± 2 ppm [M^+] for $C_{10}H_{15}O_2N$ was confirmed by HRMS (EI, 70 eV).

(3-Propyl-1*H*-pyrrol-2-yl)acetic Acid Ethyl Ester (5j). Starting with **4j** (0.200 g, 0.88 mmol) in CH_2Cl_2 (20 mL), **5j** was isolated without further purification as a brownish oil (0.172 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.93 (t, J = 7.2 Hz, 3 H, CH_3), 1.27 (t, J = 7.2 Hz, 3 H, OCH_2CH_3), 1.55 (sextet, J = 7.5 Hz, 2 H, CH_2), 2.37 (t, J = 7.2 Hz, 2 H, CH_2), 3.59 (s, 2 H, CH_2), 4.17 (q, J = 7.2 Hz, 2 H, OCH_2), 6.03 (t, J = 2.7 Hz, 1 H, CH), 6.68 (t, J = 2.7 Hz, 1 H, CH), 8.56 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 14.15, 14.20, 24.5, 27.9, 31.4, 61.0, 108.7, 116.6, 119.2, 121.2, 171.5. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3393 (s), 2960 (s), 2931 (s), 2871 (m), 1731 (s), 1639 (w), 1461 (m), 1399 (w), 1371 (m), 1327 (m), 1303 (m), 1248 (s), 1231 (s), 1181 (s), 1140 (s), 1098 (m), 1067 (w), 1031 (s), 721 (m). MS (EI, 70 eV): m/z = 195 (M^+, 48), 180 (1), 166 (49), 122 (100). The exact molecular mass m/z = 195.1259 ± 2 ppm [M^+] for $C_{11}H_{17}O_2N$ was confirmed by HRMS (EI, 70 eV).

4,5,6,7,8,9,10,11,12,13-Decahydro-1*H*-cyclododeca[*b*]-pyrrole-13-carboxylic Acid Ethyl Ester (5p). Starting with **4p** (0.800 g, 2.59 mmol) in CH_2Cl_2 (40 mL), **5p** was isolated without further purification as a black solid (0.719 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.25 (t, J = 7.11 Hz, 3 H, CH_3), 1.18−1.43 (m, 12 H, 6×CH_2), 1.54−1.68 (m, 2 H, CH_2), 1.88−1.95 (m, 2 H, CH_2), 2.40−2.51 (m, 2 H, OCH_2), 3.84 (t, J = 7.5 Hz, 1 H, CH), 4.06−4.20 (m, 2 H, OCH_2), 6.00 (t, J = 2.7 Hz, 1 H, CH), 6.71 (t, J = 2.7 Hz, 1 H, CH), 8.39 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_c = 14.2, 22.1, 22.3, 22.5, 24.1, 24.16, 24.2, 24.7, 29.0, 32.7, 39.3, 60.8, 108.0, 117.2, 121.2, 124.6, 174.9. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3345 (s), 2928 (s), 2860 (m), 1721 (s), 1458 (w), 1232 (m), 1201 (m), 1153 (m). MS (EI, 70 eV): m/z = 277 (M^+, 100), 248 (1), 204 (100). UV−Vis (CH_2Cl_2, nm): λ_{max} (log ϵ) = 231 (3.71). The exact molecular mass m/z = 277.2042 ± 2 ppm [M^+] for $C_{17}H_{27}O_2N$ was confirmed by HRMS (EI, 70 eV). The structure was confirmed by X-ray crystallography.

1-(1*H*-Pyrrol-2-yl)propan-2-one (5u). Starting with **4u** (0.050 g, 0.32 mmol) in 1,4-dioxane (5 mL), **5u** was isolated after chromatography (silica gel, n-Hex/EtOAc = 10:1 → 1:1) as a brownish solid (0.034 g, 87%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3 H, CH_3), 3.74 (s, 2 H, CH_2), 6.00 (m, 1 H, CH), 6.15 (dd, J = 6.0, 3.0 Hz, 1 H, CH), 6.75 (m, 1 H, CH), 8.62 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 29.5, 42.1, 107.4, 108.3, 117.8, 123.8, 206.8. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3328 (s), 2912 (w), 1706 (s), 1427 (w), 1390 (w), 1358 (w), 1331 (w), 1286 (w), 1234 (w), 1168 (w), 1127 (w), 1029 (w), 799 (m), 758 (m), 728 (m), 607 (w), 561 (w). MS (EI, 70 eV): m/z = 123 (M^+, 22), 82 (100). The exact molecular mass m/z = 123.0684 ± 2 ppm [M^+] for C_7H_9ON was confirmed by HRMS (EI, 70 eV).

General Procedure for the TFA Reactions of Pyrrolidines (4). To a CH_2Cl_2 solution (20 mL/mmol) of **4** (1 equiv) was added TFA (13 equiv), and the solution was stirred for 24 h at 20 °C. The solvent was removed in vacuo and the residue was purified by chromatography (silica gel, n-hexane/EtOAc) to give **5**, **6**, and **7**.

5a-[5-(2,2,2-Trifluoroacetyl)-1*H*-pyrrol-2-yl]acetic Acid Methyl Ester (6a) and (7-Methoxycarbonylmethyl-1*H*-indol-2-yl)acetic Acid Methyl Ester (7a). Starting with **4a** (0.150 g, 0.88 mmol) and TFA (0.88 mL, 11.4 mmol) in CH_2Cl_2 (15 mL), **5**, **6a** and **7a** were isolated after chromatography (silica gel, n-Hex/EtOAc = 100:1 → 1:1) as black solid and brownish oil (0.047 g {0.039 g, 32%; 0.008 g, 4%}; 0.056 g, 49% = 85%). [Inseparable mixture of **5a/6a** = 4.5:1].

5a, 6a. [*Signals of **6a**] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.69 (s, 2 H, CH_2), 3.72 (s, 3 H, OCH_3), *3.77 (s, 2 H, CH_2), *3.78 (s, 3 H, OCH_3), 6.01 (m, 1 H, CH), 6.13−6.16 (m, 1 H, CH), *6.23 (m, 1 H, CH), 6.76 (m, 1 H, CH), 7.13 (m, 1 H, CH), 8.71 (broad s, 1 H, NH), *9.98 (broad s, 1 H, NH).^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = *32.9, 33.0, 52.1, *52.6, 107.4, 108.3, *112.3, 115.1, 117.8, *118.9, *122.0, *123.1, *125.8, *135.6, *169.7, 171.7. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3413 (w), 3298 (m), 2925 (w), 1746 (s), 1650 (s), 1437 (m), 1353 (m), 1261 (m), 1201 (s), 1145 (s), 1103 (w), 1062 (m), 1027 (w), 886 (w), 804 (m), 766 (m). MS (EI, 70 eV): m/z = *235 (M^+, 60), *176 (100), *166 (47), 139 (M^+, 1), 124 (1), 106 (52), 79 (36). The exact molecular mass m/z = 139.0633 ± 2 ppm [M^+] for $C_7H_9O_2N$ was confirmed by HRMS (EI, 70 eV).

7a. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.67 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.84 (s, 2 H, CH_2), 3.86 (s, 2 H, CH_2), 6.40 (m, 1 H, CH), 6.98 (d, J = 7.2 Hz, 1 H, CH), 7.11 (t, J = 7.2 Hz, 1 H, CH), 7.26 (d, J = 7.2 Hz, 1 H, CH), 8.76 (broad s, 1 H, NH).^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 33.7, 39.2, 51.9, 52.3, 100.3, 110.1, 120.7, 121.9, 125.4, 127.8, 130.5, 136.3, 171.0, 172.2. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3374 (w), 2954 (w), 1735 (s), 1641 (m), 1551 (w), 1437 (m), 1340 (w), 1262 (m), 1203 (m), 1161 (s), 1103 (w), 1045 (w), 1015 (w), 769 (w). MS (EI, 70 eV): m/z = 261 (M^+, 74), 215 (1), 202 (100), 166 (8), 143 (32), 115 (10). HRMS (ESI): calcd for $C_{14}H_{16}O_4N$ ([M + 1]$^+$) = 262.10793, found = 262.10718.

5d-[5-(2,2,2-Trifluoroacetyl)-1*H*-pyrrol-2-yl]acetic Acid 2-Methoxyethyl Ester (6d) and [7-(2-Methoxyethoxycarbonylmethyl)-1*H*-indol-2-yl]acetic Acid 2-Methoxyethyl Ester (7d). Starting with **4d** (0.050 g, 0.23 mmol) and TFA (0.23 mL, 3.02 mmol) in CH_2Cl_2 (5 mL), **5, 6d** and **7d** were isolated after chromatography (silica gel, n-Hex/EtOAc = 100:1 → 1:1) as black and brownish oils (0.019 g {0.008 g, 19%; 0.011 g, 17%}; 0.018, 45% = 81%). [Inseparable mixture of **5d/6d** = 1:1.4].

5d, 6d. [*Signals of **6d**] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.40 (s, 3 H, OCH_3), 3.42 (s, 3 H, OCH_3), 3.60−3.67 (m, 4 H, 2 × OCH_2), *3.72 (s, 2 H, CH_2), 3.80 (s, 2 H, CH_2), 4.27−4.30 (m, 2 H, OCH_2), 4.32−4.36 (m, 2 H, OCH_2), 6.02 (m, 1 H, CH), 6.12−6.15 (m, 1 H, CH), *6.23 (m, 1 H, CH), 6.75 (m, 1 H, CH), *7.13 (m, 1 H, CH), 8.78 (broad s, 1 H, NH), *10.18 (broad s, 1 H, NH). IR (neat, cm^{-1}): $\tilde{\nu}$ = 3375 (w), 3300 (m), 2978 (w), 2954 (w), 2926 (w), 2893 (w), 2856 (w), 1741 (m), 1653 (m), 1503 (w), 1452 (w), 1435 (w), 1407 (w), 1373 (w), 1342 (w), 1259 (m), 1192 (s), 1145 (s), 1102 (m), 1059 (m), 1034 (m), 883 (w), 804 (w), 765 (m), 731 (w). MS (EI, 70 eV): m/z = *279 (M^+, 1), *203 (11), 183 (M^+, 18), *176 (6), 107 (34), 80 (100). The exact molecular mass m/z = 183.0895 ± 2 ppm [M^+] for $C_9H_{13}O_3N$ was confirmed by HRMS (EI, 70 eV).

7d. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.35 (s, 3 H, OCH_3), 3.42 (s, 3 H, CH_3), 3.56−3.67 (m, 4 H, 2 × OCH_2), 3.88 (s, 2 H, CH_2), 3.89 (s, 2 H, CH_2), 4.23−4.26 (m, 2 H, OCH_2), 4.29−4.34 (m, 2 H, OCH_2), 6.42 (m, 1 H, CH), 6.99 (d, J = 7.2 Hz, 1 H, CH), 7.11 (t, J = 7.2 Hz, 1 H, CH), 7.26 (d, J = 7.2 Hz, 1 H, CH), 8.89 (broad s, 1 H, NH). IR (neat, cm^{-1}): $\tilde{\nu}$ = 3364 (w), 2928 (w), 1736 (s), 1643 (m), 1552 (w), 1441 (m), 1407 (m), 1376 (w), 1325 (w), 1254 (m), 1159 (s), 1129 (s), 1037 (m), 769 (w). MS (EI, 70 eV): m/z = 349 (M^+, 23), 199 (14), 167 (27), 143 (30), 141 (100), 114 (12), 104 (58). HRMS (ESI): calcd for $C_{18}H_{24}O_6N$ ([M + 1]$^+$) = 350.16036; found = 350.15946.

2,2,2-Trifluoro-1-[5-(2-oxo-2-phenylethyl)-1*H*-pyrrol-2-yl]ethanone (6e). Starting with **4e** (0.200 g, 0.92 mmol) and TFA (0.9 mL, 12.0 mmol) in CH_2Cl_2 (20 mL), **6e** was isolated after chromatography (silica gel, n-Hex/EtOAc = 100:1 → 1:1) as a black solid (0.139 g, 54%). Mp = 121.7 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.44 (s, 2 H, CH_2), 6.28 (dd, J = 3.9, 2.7 Hz, 1 H, CH), 7.16 (m, J = 2.0 Hz, 1 H, CH), 7.54 (m, 2 H, 2 × CH from Ph), 7.61−7.66 (m, 1 H, CH from Ph), 8.00−8.07 (m, 2 H, 2 × CH from Ph), 10.34 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_c = 36.5, 112.6, 115.2, 119.0, 122.0, 125.9,

128.4, 129.0, 134.1, 135.9, 136.7, 195.2. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3295 (m), 2962 (w), 2925 (w), 1692 (m), 1641 (s), 1559 (w), 1497 (w), 1448 (w), 1430 (w), 1406 (w), 1355 (w), 1332 (w), 1261 (m), 1187 (m), 1142 (s), 1098 (m), 1063 (m), 1024 (m), 883 (w), 794 (m), 758 (m), 687 (w). MS (EI, 70 eV): *m/z* = 281 (M^+, 4), 212 (5), 176 (4), 105 (100), 77 (45). HRMS (ESI): calcd for $C_{14}H_{11}O_2NF_3$ ($[M + 1]^+$) = 282.07419; found = 282.07346.

General Procedure for the Preparation of Pyrroles 9 and 12. To a THF solution (10 mL/mmol) of **11** (1 equiv) was added triphenylphosphine (1.2 equiv) at room temperature. The reaction mixture was heated and stirred for 4 h at 80 °C. After the mixture was cooled to 20 °C, the solvent was removed in vacuo and the residue was purified by chromatography (silica gel, *n*-hexane/EtOAc) to give **12**.

2-1*H*-Pyrrole-2-ylmethyl-1*H*-pyrrole (9). Starting with **8** (0.100 g, 0.34 mmol) and PPh_3 (0.198 g, 0.75 mmol) in THF (10 mL), **9** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 75:1 → 10:1) as a brownish solid (0.041 g, 83%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.97 (s, 2 H, CH_2), 6.02−6.042 (m, 2 H, 2 × CH), 6.14 (dd, *J* = 5.7, 2.7 Hz, 2 H, 2 × CH), 6.64 (dd, *J* = 4.2, 2.7 Hz, 2 H, 2 × CH), 6.64 (dd, *J* = 4.2, 2.7 Hz, 2 H, 2 × CH), 7.83 (broad s, 2 H, 2 × NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 26.4, 106.4, 108.4, 117.2, 129.0. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3333 (s), 2923 (w), 1631 (w), 1564 (w), 1468 (w), 1439 (w), 1425 (w), 1332 (w), 1261 (w), 1250 (w), 1183 (w), 1114 (m), 1094 (m), 1026 (m), 804 (m), 729 (s), 682 (w), 689 (w), 625 (w), 586 (m), 549 (w). MS (EI, 70 eV): *m/z* = 146 (M^+, 100), 80 (39), 67 (26). The exact molecular mass *m/z* = 146.0844 ± 2 ppm $[M^+]$ for $C_9H_{10}N_2$ was confirmed by HRMS (EI, 70 eV).

2-Methyl-1*H*-pyrrole-3-carboxylic Acid Methyl Ester (12a). Starting with **11a** (0.030 g, 0.14 mmol) and PPh_3 (0.044 g, 0.17 mmol) in THF (5 mL), **12a** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 5:1) as a brownish solid (0.017 g, 85%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.53 (s, 3 H, CH_3), 3.80 (s, 3 H, OCH_3), 6.55 (d, *J* = 2.7 Hz, 1 H, CH), 6.56 (d, *J* = 2.7 Hz, 1 H, CH), 8.23 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 13.2, 50.8, 110.4, 110.5, 115.8, 135.3, 166.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3312 (m), 2978 (s), 2952 (w), 2933 (w), 2867 (m), 1707 (s), 1680 (s), 1607 (w), 1580 (m), 1493 (w), 1452 (s), 1408 (w), 1381 (m), 1348 (w), 1329 (m), 1268 (m), 1226 (w), 1202 (m), 1177 (w), 1125 (s), 1076 (w), 1053 (w), 1026 (w), 900 (w), 844 (w), 790 (w), 726 (w). MS (EI, 70 eV): *m/z* = 139 (M^+, 46), 124 (19), 107 (100), 80 (33). The exact molecular mass *m/z* = 139.0633 ± 2 ppm $[M^+]$ for $C_7H_9O_2N$ was confirmed by HRMS (EI, 70 eV).

2-Methyl-1*H*-pyrrole-3-carboxylic Acid Ethyl Ester (12b). Starting with **11b** (0.100 g, 0.44 mmol) and PPh_3 (0.137 g, 0.52 mmol) in THF (10 mL), **12b** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 5:1) as a brownish solid (0.061 g, 91%). Mp = 64 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.34 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 2.52 (s, 3 H, CH_3), 4.27 (q, *J* = 7.2 Hz, 2 H, OCH_2), 6.56 (d, *J* = 2.4 Hz, 2 H, 2 × CH), 8.51 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 13.2, 14.5, 59.4, 110.4, 111.7, 15.7, 135.2, 165.8. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3294 (s), 2985 (m), 2938 (w), 2906 (w), 1697 (s), 1675 (s), 1578 (m), 1499 (m), 1447 (m), 1411 (m), 1369 (m), 1325 (s), 1267 (s), 1227 (w), 1201 (s), 1127 (s), 1095 (s), 1053 (s), 901 (m), 781 (m), 754 (m), 722 (m). MS (EI, 70 eV): *m/z* = 153 (M^+, 95), 124 (61), 108 (100). The exact molecular mass *m/z* = 153.0790 ± 2 ppm $[M^+]$ for $C_8H_{11}O_2N$ was confirmed by HRMS (EI, 70 eV).

1-(2-Methyl-1*H*-pyrrol-3-yl)ethanone (12d). Starting with **11d** (0.100 g, 0.55 mmol) and PPh_3 (0.172 g, 0.66 mmol) in THF (10 mL), **12d** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 30:1 → 2:1) as a brownish solid (0.066 g, 97%). Mp = 75 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.43 (s, 3 H, CH_3), 2.55 (s, 3 H, CH_3), 6.52−6.54 (m, 1 H, CH), 6.57−6.59 (m, 1 H, CH), 8.52 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 13.8, 28.3, 110.5, 115.9, 120.5, 135.4, 195.8. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3211 (s), 3110 (s), 3021 (m), 2981 (w), 2962 (m), 2926 (m), 2843 (w), 1636 (s), 1569 (s), 1491 (s), 1465 (s), 1402 (s), 1364 (s), 1333 (w), 1279 (m), 944 (m), 892 (m), 858 (w), 799 (w), 775 (w), 733 (m), 677 (w), 636 (w). MS (EI, 70 eV): *m/z* = 123 (M^+, 44), 107 (100) 94 (3), 80 (25), 66 (2), 43 (11). Anal. Calcd for C_7H_9ON (123.155): C, 68.27; H, 7.37; N, 11.37. Found: C, 68.12; H, 7.15; N, 11.53.

2-Heptyl-1*H*-pyrrole-3-carboxylic Acid Ethyl Ester (12i). Starting with **11i** (0.100 g, 0.33 mmol) and PPh_3 (0.105 g, 0.40 mmol) in THF (10 mL), **12i** was isolated after chromatography (silica gel, *n*-Hex/EtOAc = 100:1 → 5:1) as a brownish solid (0.069 g, 89%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.86 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.15−1.40 (m, 11 H, 4 × CH_2, CH_3), 1.50−1.64 (m, 2 H, CH_2), 2.92 (t, *J* = 7.5 Hz, 2 H, CH_2), 4.27 (q, *J* = 7.2 Hz, 2 H, OCH_2), 6.56 (d, *J* = 3.0 Hz, 1 H, CH), 6.58 (d, *J* = 3.3 Hz, 1 H, CH), 8.21 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 13.9, 14.3, 22.5, 27.3, 29.0, 29.3, 29.5, 31.7, 59.2, 110.9, 110.9, 115.8, 140.1, 165.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3324 (s), 2956 (s), 2928 (s), 2871 (m), 2857 (m), 1726 (m), 1702 (s), 1673 (s), 1574 (m), 1496 (m), 1466 (s), 1394 (m), 1370 (m), 1331 (m), 1297 (m), 1264 (m), 1197 (m), 1181 (m), 1128 (s), 1096 (w), 1077 (w), 1049 (m), 1028 (w), 902 (w), 790 (w), 724 (m). MS (EI, 70 eV): *m/z* = 237 (M^+, 40), 208 (18), 192 (12), 164 (39), 151 (38), 138 (6), 124 (100). Anal. Calcd for $C_{14}H_{23}O_2N$ (237.342): C, 70.85; H, 9.77; N, 5.90. Found: C, 70.47; H, 10.10; N, 5.91.

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Supporting Information Available: Details of the crystal structure determinations and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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