DOI: 10.1002/adsc.200800097

Diversity-Oriented Synthesis of Functionalized 1-Aminopyrroles by Regioselective Zinc Chloride-Catalyzed, One-Pot 'Conjugate Addition/Cyclization' Reactions of 1,3-Bis(silyl enol ethers) with 1,2-Diaza-1,3-butadienes

Vahuni Karapetyan,[a,b] Satenik Mkrtchyan,[a,b] Andreas Schmidt,[a] Orazio A. Attanasi,[c,*] Gianfranco Favi,[c] Fabio Mantellini,[c] Alexander Villinger,[a] Christine Fischer,[d] and Peter Langer[a,d,*]

[a] Institut für Chemie, Universität Rostock, Albert Einstein Str. 3a, 18059 Rostock, Germany
Fax: (+49)-381-498-6410; e-mail: peter.langer@uni-rostock.de
[b] Faculty of Chemistry, Yerevan State University, Alex Manoogian 1, 0025 Yerevan, Armenia
[c] Istituto di Chimica Organica, Università degli Studi di Urbino "Carlo Bo", Via I Maggetti 24, 61029 Urbino, Italy
[d] Leibniz-Institut für Katalyse an der Universität Rostock e.V., Albert Einstein Str. 29a, 18059 Rostock, Germany

Received: February 14, 2008; Published online: May 16, 2008

Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: In a convenient one-pot process, the easily accessible 1,2-diaza-1,3-butadienes and 1,3-bis(silyl enol ethers) are converted into the previously unknown functionalized 1-aminopyrroles and 1-amino-4,5,6,7-tetrahydroindoles. The domino reaction proceeds through a zinc chloride-catalyzed 'conjugate addition/cyclization' sequence.

Keywords: cyclizations; 1,2-diaza-1,3-butadienes; N-heterocycles; pyrroles; silyl enol ethers

Introduction

Pyrroles and pyrrolidines are present in many biologically active natural products, such as the porphyrins, phthalocyanines, various alkaloids, or vitamin B_{12}. A variety of synthetic compounds are of pharmacological relevance and are used in the clinic. This includes, for example, triprolidine, piracetam, anirolac, pyrvinium, fenpiclonil, pyrrolnitrin, stallimycin, tolmetin, zomepirac, clemizole, dextromoramide, prostaglandin $PGF_{2\alpha}$, vinblastine, vincristine, vincamine, reserpine, and perfluoroalkylpyrroles.[1] Oligo- and polypyrroles also represent important electronic materials, due to their high electroconductivity.[1,2] 1-Aminopyrroles also represent pharmacologically important heterocycles. Recently, 1-aminopyrroles have been employed as intermediates during the synthesis of analgesic[3] and NMDA receptor antagonists.[4] Whereas a variety of pyrrole syntheses are known, methods for the direct preparation of functionalized 1-aminopyrroles are rare.[5] Moreover, these approaches usually present significant limitations in terms of substitutent groups that can be introduced, the substitution pattern and/or the regioselectivity. Therefore, the development of new methods for the synthesis of these compounds is of considerable interest. The base-mediated conjugate addition of nucleophiles to α,β-unsaturated carbonyl compounds is of great synthetic utility.[6] Mukaiyama and co-workers were the first to report a Lewis acid-catalyzed variant of this reaction. These transformations, which proceed under mild conditions, rely on the use of silyl enol ethers as the nucleophiles.[7,8]

Recently, some of us reported[9] the synthesis of 1-aminopyrroles and 1-aminoindoles by one-pot 'conjugate addition/cyclization' reactions of simple silyl enol ethers with 1,2-diaza-1,3-butadienes.[10,11] 1,3-Bis(silyl enol ethers) represent electroneutral equivalents of 1,3-dicarbonyl dianions.[12] Like dianions, they generally react with electrophiles at their terminal carbon atom. One-pot cyclizations of 1,3-bis(silyl enol ethers) with oxalyl chloride,[13] 1,3-dielectrophiles,[14] pyrylium[15] and iminium salts,[16] and other electrophiles[12] have been reported. The Lewis acid-catalyzed condensation of 1,3-bis(silyl enol ethers) with 1,1-dimethoxy-2-azidoethane and subsequent cyclization allows a convenient synthesis of functionalized pyrroles.[17] Recently, we have reported a catalytic one-pot cyclization of 1,3-bis(silyl enol ethers) with 1,2-diaza-1,3-butadienes which provides a convenient and

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim WILEY InterScience DISCOVER SOMETHING GREAT

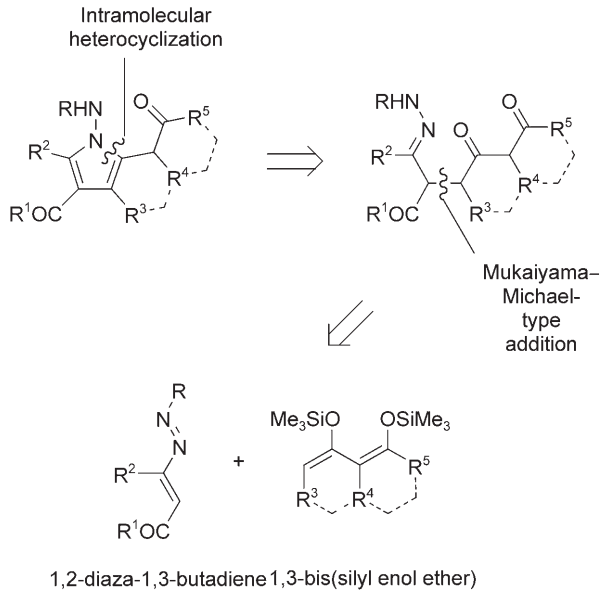


Figure 1. Retrosynthetic approach of pyrroles and tetrahydroindoles.

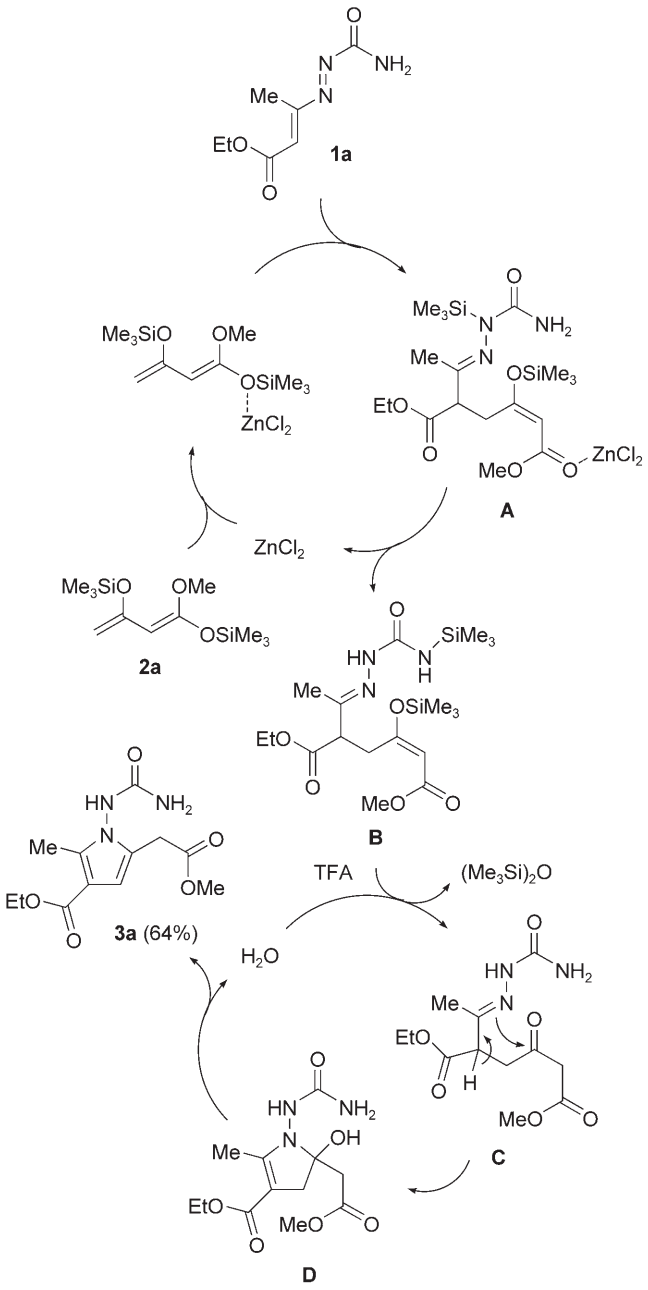
direct approach to a variety of functionalized 1-aminopyrroles.[18] Herein, we report full details of these studies. With regard to our preliminary communication,[18] the scope has been considerably extended. This synthetic strategy can be regarded as domino 'conjugate addition/cyclization' reactions, allowing the construction of 1-aminopyrrole rings in an efficient manner from easily available intermediates (see Figure 1).

It is noteworthy that these products are not readily available by other methods. Moreover, the presence of different groups in these systems confer an interesting contribution to this work, making them suitable as intermediates for more complex compounds.

Results and Discussion

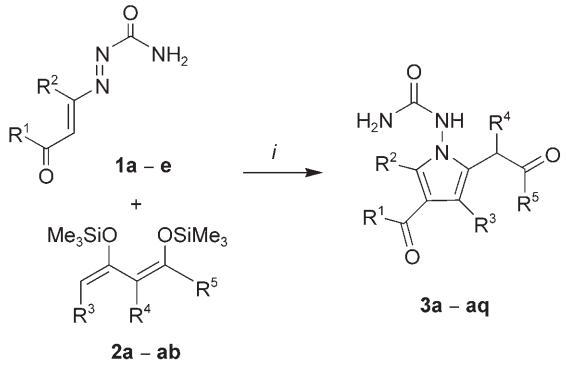
The 1,3-bis(silyl enol ether) **2a** was prepared from methyl acetoacetate in two steps.[19] The $ZnCl_2$-catalyzed reaction of **2a** with 1,2-diaza-1,3-butadiene **1a** and subsequent addition of trifluoroacetic acid (TFA) afforded the 1-aminopyrrole **3a** (Scheme 1). The best yields were obtained when $ZnCl_2$ and TFA were used as the catalyst and for protonation, respectively. The reaction was carried out following the protocol as previously reported for simple silyl enol ethers.[9]

The generally accepted mechanism for the Lewis acid-catalyzed conjugate addition of silyl enol ethers to Michael acceptors involves an activation of the latter by the Lewis acid.[20] Some of us earlier reported[9] mechanistic studies related to the reaction of simple silyl enol ethers (such as 1-methoxy-1-trimethylsilyloxyethene or 2,2-dimethyl-1-methoxy-1-trimethylsilyloxyethene) with 1,2-diaza-1,3-butadienes. In these studies, the progress of the reaction of **1a** with 1-methoxy-2-methyl-1-(trimethylsiloxy)-propene was directly monitored by NMR. In addition, a silylated open-chain intermediate could be successfully isolated and structurally characterized when the reaction was stopped immediately after the disappearance of the starting material (TLC control).[9] In fact, our previous studies suggested that the silyl enol ether rather than the diazadiene is activated by the Lewis acid. Accordingly, we assume that the regioselective forma-

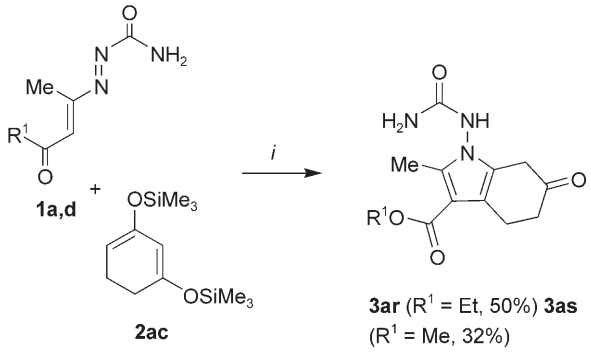


Scheme 1. Possible mechanism of the formation of 1-aminopyrrole **3a**; *i*: 1) $ZnCl_2$ (0.2 equiv.), CH_2Cl_2, 20 °C, 12 h; 2) TFA.

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 2. Synthesis of 1-aminopyrroles **3a–3aq**; *i*: 1) $ZnCl_2$ (0.2 equiv.), CH_2Cl_2, 20 °C, 12 h; 2) TFA.



Scheme 3. Synthesis of **3ar** and **3as**; *i*: 1) $ZnCl_2$ (0.2 equiv.), CH_2Cl_2, 20 °C, 12 h; 2) TFA.

tion of **3a** can be explained by $ZnCl_2$-catalyzed attack of the terminal carbon atom of **2a** at the terminal carbon of the azo-ene system of **1a** (Mukaiyama–Michael addition) to give intermediate **B**. In analogy to our previous studies,[9] the short-lived silylhydrazonic intermediate **A** is also hypothesized. The addition of TFA subsequently results in the cleavage of the silyl groups to give intermediate **C**. The latter undergoes an acid-catalyzed cyclization (by attack of the nitrogen atom to the carbonyl group) to give intermediate **D**. Subsequently, the acid-catalyzed elimination of a water molecule affords the final product **3a** (Scheme 1).

The addition/cyclization of various 1,3-bis(silyl enol ethers) **2a–ab** with 1,2-diaza-1,3-butadienes **1a–e** afforded the novel 1-aminopyrroles **3a–aq** (Scheme 2, Table 1). 1-Aminopyrroles were successfully prepared from 1,3-bis(silyl enol ethers) derived from β-keto esters (products **3a–d**, **3i–k**, **3m–ak**) or 1,3-diketones (**3e–h**, **3l**), from open-chained (**3a–w**, **3aj**, **3ak**, **3ao**, **3ap**) or cyclic 1,3-dicarbonyl compounds (**3x–3ai**), and from non-substituted (**3a–g**, **3j–n**, **3s**) or substituted 1,3-dicarbonyl compounds (**3h**, **i**, **3o–r**, **3t–w**, **3aj**, **3ak**, **3ao**, **3ap**). The cyclizations generally proceeded in moderate to excellent yield (except for **3aj**, **3ak**). The employment of the 7-membered cyclic bis(silyl enol ether) **2x**, of 1,1,1-trifluoro-2,4-bis(trimethylsilyloxy)-pentane-2,4-diene **2y**, and of methoxy-substituted diene **2z** proved to be unsuccessful. The failure of **2y** can be explained by its low reactivity. The failure of **2z** might be explained by compe-ting chelation of the Lewis acid by the additional methoxy group. Noteworthy, the employment of the amide **1e** failed.

The cyclization of 1,2-diaza-1,3-butadienes **1a** and **1d** with 1,3-bis(silyl enol ether) **2ac**, prepared from cyclohexane-1,3-dione, afforded the 1-amino-4,5,6,7-tetrahydroindol-6-ones **3ar** and **3as**, respectively (Scheme 3).

The structures of all products were established by spectroscopic methods. The structure of **3ai** was independently confirmed by X-ray crystal structure analysis (Figure 2).[21]

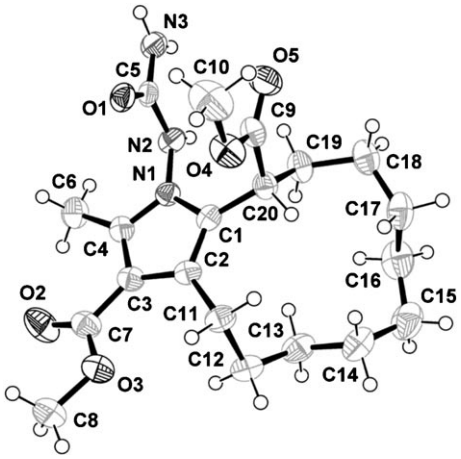


Figure 2. Ortep plot of **3ai**.

Conclusions

In conclusion, we have reported the regioselective synthesis of functionalized 1-aminopyrroles by $ZnCl_2$-catalyzed one-pot 'conjugate addition/cyclization' reactions of 1,3-bis(silyl enol ethers) with 1,2-diaza-1,3-butadienes. These reactions are easy to carry out, proceed under mild conditions and with high yields. It is noteworthy that the products are not directly available from the β-dicarbonyl compounds. In fact, previous investigations[5b,10a] have shown that the reactions between 1,2-diaza-1,3-butadiene and β-keto esters or 1,3-diketones proceed by base-catalyzed nucleophilic attack of the activated methylene group at the heterodiene system leading to regioisomeric 1-aminopyrroles. The 1-aminopyrroles prepared represent useful synthetic building blocks. For example, it has been reported previously that 1-aminopyrroles, including derivatives containing a urea moiety (similar to products **3a–as**), can be transformed into the corresponding pyrroles by reaction with $Cr_2(OAc)_4$,[22] KO-*t*-Bu/DMF,[23] or H_2/Raney Ni,[24] or by diazotation.[25]

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1. Synthesis of 1-aminopyrroles **3a–aq**.

1	2	3	R^1	R^2	R^3	R^4	R^5	Yield [%] of **3**[a]
a	**a**	**a**	OEt	Me	H	H	OMe	64
a	**b**	**b**	OEt	Me	H	H	OEt	92
a	**c**	**c**	OEt	Me	H	H	O-*i*-Bu	80
a	**d**	**d**	OEt	Me	H	H	O-*t*-Bu	81
a	**e**	**e**	OEt	Me	H	H	Me	56
a	**f**	**f**	OEt	Me	H	H	*t*-Bu	82
a	**g**	**g**	OEt	Me	H	H	Ph	60
a	**h**	**h**	OEt	Me	Me	H	Et	86
a	**i**	**i**	OEt	Me	Et	H	OMe	71
b	**b**	**j**	OMe	Et	H	H	OEt	60
c	**b**	**k**	O-*t*-Bu	Me	H	H	OEt	61
b	**e**	**l**	OMe	Et	H	H	Me	72
c	**j**	**m**	O-*t*-Bu	Me	H	H	$O(CH_2)_2OMe$	60
d	**j**	**n**	OMe	Me	H	H	$O(CH_2)_2OMe$	52
d	**k**	**o**	OMe	Me	*n*-Hex	H	OMe	65
c	**k**	**p**	O-*t*-Bu	Me	*n*-Hex	H	OMe	63
a	**l**	**q**	OEt	Me	Allyl	H	OMe	44
a	**m**	**r**	OEt	Me	*n*-Oct	H	OEt	47
a	**n**	**s**	OEt	Me	H	H	OBn	60
d	**o**	**t**	OMe	Me	*n*-Hept	H	OEt	75
a	**o**	**u**	OEt	Me	*n*-Hept	H	OEt	74
d	**p**	**v**	OMe	Me	*n*-Pr	H	OMe	97
a	**p**	**w**	OEt	Me	*n*-Pr	H	OMe	63
a	**q**	**x**	OEt	Me	H		$-(CH_2)_2O-$	50
d	**q**	**y**	OMe	Me	H		$-(CH_2)_2O-$	53
a	**r**	**z**	OEt	Me	$-(CH_2)_2-$		OMe	40
d	**r**	**aa**	OMe	Me	$-(CH_2)_2-$		OMe	35
a	**s**	**ab**	OEt	Me	$-(CH_2)_3-$		OEt	97
d	**s**	**ac**	OMe	Me	$-(CH_2)_3-$		OEt	87
a	**t**	**ad**	OEt	Me	$-CH_2CHMeCH_2-$		OMe	79
d	**t**	**ae**	OMe	Me	$-CH_2CHMeCH_2-$		OMe	61
a	**u**	**af**	OEt	Me	$-CHMeCH_2CH_2-$		OEt	49
d	**u**	**ag**	OMe	Me	$-CHMeCH_2CH_2-$		OEt	37
a	**v**	**ah**	OEt	Me	$-(CH_2)_9-$		OMe	42
d	**v**	**ai**	OMe	Me	$-(CH_2)_9-$		OMe	46
a	**w**	**aj**	OEt	Me	CH_2CH_2Cl	H	OEt	20
d	**w**	**ak**	OMe	Me	CH_2CH_2Cl	H	OEt	20
a	**x**	**al**	OEt	Me	$-(CH_2)_4-$		OMe	0
a	**y**	**am**	OEt	Me	H	H	CF_3	0
a	**z**	**an**	OEt	Me	OMe	H	OMe	0
a	**aa**	**ao**	OEt	Me	H	Me	OEt	45
a	**ab**	**ap**	OEt	Me	H	Et	OMe	40
e	**a**	**aq**	NMe_2	Me	H	H	OMe	0

[a] Isolated yields.

Experimental Section

General Comments

The spectroscopic data of all compounds are given in the supporting information.

General Procedure for the Synthesis of 1-Aminopyrroles 3 by Mukaiyama–Michael-Type Reactions of 1,3-Bis(silyl enol ethers) with 1,2-Diaza-1,3-butadienes

To a CH_2Cl_2 solution (12 mL) of 1,2-diaza-1,3-butadiene **1** (2.0 mmol) were added 1,3-bis(silyl enol ether) **2** (2.4 mmol) and freshly dried $ZnCl_2$ (0.055 g, 0.4 mmol) at 20 °C. The solution was stirred for 12 h at room temperature and subsequently TFA (0.3 mL) was added. The solvent was removed

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

under vacuum and the residue was purified by column chromatography (silica gel, heptane→heptane/EtOAc = 1:2).

Acknowledgements

We thank Mr. Gnuni Karapetyan for helpful discussions. Financial support from the State of Mecklenburg-Vorpommern (scholarships for A. S. and V. K.), from the DAAD (scholarship for S. M.) and from the Ministero dell'Università, dell'Istruzione e della Ricerca (MIUR) - Rome, Università degli Studi di Urbino "Carlo Bo" is gratefully acknowledged.

References

[1] a) R. J. Sundberg, in: *Comprehensive Heterocyclic Chemistry*, (Eds.: A. R. Katritzky, C. W. Rees), Pergamon Press, Oxford, **1984**, Vol. 4, p 314; b) G. W. Gribble, in: *Comprehensive Heterocyclic Chemistry II*, (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon-Elsevier Science, Amsterdam, **1996**, Vol. 2, Chapter 4.

[2] M. I. Goller, C. Barthet, G. P. McCarthy, R. Corradi, B. P. Newby, S. A. Wilson, S. P. Armes, S. Y. Luk, *Coll. Polym. Sci.* **1998**, *276*, 1010–1018.

[3] R. C. Effland, J. T. Klein, US Patent 4,546,105, **1985**; *Chem. Abstr.* **1986**, *104*, 186307.

[4] J. Kulagowski, J. Janusz, P. D. Leeson, UK Patent 2,265,372, **1993**; *Chem. Abstr.* **1993**, *120*, 134504.

[5] For select examples: a) G. S. Gadaginamath, A. S. Shyadligeri *Indian J. Chem. B* **2000**, *39*, 31–35; b) O. A. Attanasi, L. De Crescentini, G. Favi, P. Filippone, F. Mantellini, S. Santeusanio, *J. Org. Chem.* **2002**, *67*, 8178–8181; c) Y. Zhang, J. W. Herndon, *Org. Lett.* **2003**, *5*, 2043–2045.

[6] P. Perlmutter, *Conjugate Addition Reactions in Organic Synthesis*, Pergamon Press, Oxford, **1992**.

[7] a) K. Narasaka, K. Soai, T. Mukaiyama, *Chem. Lett.* **1974**, 1223–1224; b) K. Narasaka, K. Soai, Y. Aikawa, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 779–783; c) K. Saigo, M. Osaki, T. Mukaiyama, *Chem. Lett.* **1976**, 163–164; d) T. Mukaiyama, *Angew. Chem.* **1977**, *89*, 858–866; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 817–826; e) T. Mukaiyama, *Challenges in Synthetic Organic Chemistry*, (translated by E. Baldwin), Clarendon Press, Oxford, **1990**.

[8] a) T. Mukaiyama, S. Matsui, K. Homma, S. Kobayashi, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2687–2690; b) T. Sato, Y. Wakahara, J. Otera, H. Nozaki, *Tetrahedron* **1991**, *47*, 9773–9782, and references cited therein; c) S. Kobayashi, I. Hachiya, T. Takahori, *Tetrahedron Lett.* **1992**, *33*, 6815–6818; d) S. Mizukami, N. Kihara, T. Endo, *Tetrahedron Lett.* **1993**, *34*, 7437–7440; e) B. C. Ranu, M. Saha, S. Bhar, *Tetrahedron Lett.* **1993**, *34*, 1989–1990; f) C. LeRoux, H. Gaspard-Iloughmane, J. Dubac, J. Jaud, P. Vignaux, *J. Org. Chem.* **1993**, *58*, 1835–1839; g) C. L. Roux, H. Gaspard-Iloughmane, J. Dubac, *Bull. Soc. Chim. Fr.* **1993**, *130*, 832–842; h) G. Dujardin, J. M. Poirier, *Bull. Soc. Chim. Fr.* **1994**, *131*, 900–909; i) S. Kobayashi, S. Suda, M. Yamada, T. Mukaiyama, *Chem. Lett.* **1994**, 97–100; j) B. C. Ranu, M. Saha, S. Bhar, *J. Chem. Soc. Perkin Trans. 1* **1994**, 2197–2199; k) J. Otera, T. Sato, H. Nozaki, in: *Stereocontrolled Organic Synthesis*, (Ed.: B. M. Trost), IUPAC, Oxford, **1994**, pp 117–144; l) L. A. Telan, C.-D. Poon, S. A. Evans, Jr., *J. Org. Chem.* **1996**, *61*, 7455–7462; m) S. Sankararaman, R. Sudha, *J. Org. Chem.* **1999**, *64*, 2155–2157; n) K. Takasu, S.-J. Ueno, K. Inanaga, M. Ihara, *J. Org. Chem.* **2004**, *69*, 517–521; o) Z.-L. Shen, S. J. Ji, T.-P. Loh, *Tetrahedron Lett.* **2005**, *46*, 507–508.

[9] O. A. Attanasi, G. Favi, P. Filippone, S. Lillini, F. Mantellini, D. Spinelli, M. Stenta, *Adv. Synth. Catal.* **2007**, *349*, 907–915.

[10] a) O. A. Attanasi, L. De Crescentini, P. Filippone, F. Mantellini, S. Santeusanio, *Arkivoc* **2002**, *xi*, 274–292; b) O. A. Attanasi, L. De Crescentini, G. Favi, P. Filippone, F. Mantellini, S. Santeusanio, *J. Org. Chem.* **2004**, *69*, 2686–2692; c) O. A. Attanasi, G. Favi, P. Filippone, A. Golobič, B. Stanovnik, J. Svete, *J. Org. Chem.* **2005**, *70*, 4307–4313; d) O. A. Attanasi, G. Baccolini, C. Boga, L. De Crescentini, P. Filippone, F. Mantellini, *J. Org. Chem.* **2005**, *70*, 4033–4037; e) O. A. Attanasi, L. De Crescentini, G. Favi, P. Filippone, S. Lillini, F. Mantellini, S. Santeusanio, *Org. Lett.* **2005**, *7*, 2469–2471; f) O. A. Attanasi, G. Favi, P. Filippone, G. Giorgi, S. Lillini, F. Mantellini, F. R. Perrulli, *Synlett* **2006**, 2731–2734; g) O. A. Attanasi, L. De Crescentini, G. Favi, P. Filippone, A. Golobič, S. Lillini, F. Mantellini, *Synlett* **2006**, 2735–2738; h) O. A. Attanasi, P. Davoli, G. Favi, P. Filippone, A. Forni, G. Moscatelli, F. Prati, *Org. Lett.* **2007**, *9*, 3461–3464; i) O. A. Attanasi, G. Giorgi, G. Favi, P. Filippone, S. Lillini, F. R. Perrulli, S. Santeusanio, *Synlett* **2007**, 1691–1694; j) O. A. Attanasi, G. Giorgi, G. Favi, P. Filippone, S. Lillini, F. R. Perrulli, S. Santeusanio, *Synlett* **2007**, 1691–1694.

[11] a) K. N. Zelenin, V. A. Nikitin, N. M. Anodina, *Khim. Geterotsikl. Soedin.* **1973**, 124–128; b) S. Sommer, *Chem. Lett.* **1977**, 583–586; c) S. Sommer, *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 59–60; d) T. L. Gilchrist, R. Sanchez, R. C. Wasson, *J. Chem. Soc. Perkin Trans. 1* **1989**, 353–359; e) K. Banert, in: *Targets in Heterocyclic Systems – Chemistry and Properties*, (Eds.: O. A. Attanasi, D. Spinelli), Società Chimica Italiana, Rome, **1999**, Vol. 3, pp 1–32; f) S. Polanc, in: *Targets in Heterocyclic Systems – Chemistry and Properties*, (Eds.: O. A. Attanasi, D. Spinelli), Società Chimica Italiana, Rome, **1999**, Vol. 3, pp 33–92; g) R. K. Boeckman, Jr., P. Ge, J. E. Reed, *Org. Lett.* **2001**, *3*, 3647–3650; h) R. K. Boeckman, Jr., P. Ge, J. E. Reed, *Org. Lett.* **2001**, *3*, 3651–3653; i) M. Kim, H.-J. Gais, *J. Org. Chem.* **2006**, *71*, 4642–4650; j) D. Aparicio, O. A. Attanasi, P. Filippone, R. Ignacio, S. Lillini, F. Mantellini, F. Palacios, J. M. de Los Santos, *J. Org. Chem.* **2006**, *71*, 5897–5905.

[12] Review: P. Langer, *Synthesis* **2002**, 441–459.

[13] Review: P. Langer, *Synlett* **2006**, 3369–3381.

[14] Review: H. Feist, P. Langer, *Synthesis* **2007**, 327–347.

[15] Review: P. Langer, *Synlett* **2007**, 1016–1025.

[16] Review: P. Langer, *Eur. J. Org. Chem.* **2007**, 2233–2238.

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[17] E. Bellur, H. Görls, P. Langer, *J. Org. Chem.* **2005**, *70*, 4751–4761.
[18] A. Schmidt, V. Karapetyan, O. A. Attanasi, G. Favi, H. Görls, F. Mantellini, P. Langer, *Synlett* **2007**, 2965–2968.
[19] G. A. Molander, K. O. Cameron, *J. Am. Chem. Soc.* **1993**, *115*, 830–846.
[20] a) S. J. Blarer, W. B. Schweizer, D. Seebach, *Helv. Chim. Acta* **1982**, *65*, 1637–1654; b) M. Miyashita, T. Yanami, T. Kumazawa, A. Yoshikoshi, *J. Am. Chem. Soc.* **1984**, *106*, 2149–2156; c) D. Seebach, M. A. Brook, *Helv. Chim. Acta* **1985**, *68*, 319–324; d) T. Mukaiyama, M. Tamura, S. Kobayashi, *Chem. Lett.* **1986**, 1017–1020; e) M. A. Brook, D. Seebach, *Can. J. Chem.* **1987**, *65*, 836–850; f) for an example of electron transfer mechanism involving silyl ketene acetal and Lewis acid-coordinated Michael acceptor, see: T. Sato, Y. Wakahara, J. Otera, H. Nozaki, S. Fukuzumi, *J. Am. Chem. Soc.* **1991**, *113*, 4028–4030.
[21] CCDC 677345 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or can be ordered from the following address: Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223–1336–033 or deposit@ccdc.cam. ac.uk).
[22] a) G. R. Martinez, P. A. Grieco, C. V. Srinivasan, *J. Org. Chem.* **1981**, *46*, 3760–3761; b) G. R. Martinez, P. A. Grieco, E. Williams, K.-i. Kanai, C. V. Srinivasan, *J. Am. Chem. Soc.* **1982**, *104*, 1436–1438.
[23] G. Macaluso, G. Cusmano, G. Cirrincione, A. M. Almerico, P. Diana, *Heterocycles* **1991**, *32*, 1973–1981.
[24] a) G. Chelucci, M. Marchetti, *J. Heterocycl. Chem.* **1988**, *25*, 1135–1137; b) M. Satomura, *J. Org. Chem.* **1993**, *58*, 3757–3760.
[25] A. J. G. Baxter, J. Fuher, S. J. Teauge, *Synthesis* **1994**, 207–211.

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim