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Intramolecular Aza-Anti-Michael Addition of an Amide Anion to Enones: A Regiospecific Approach to Tetramic Acid Derivatives

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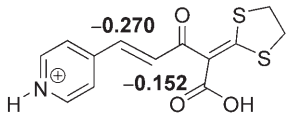
Abstract: A novel intramolecular aza-anti-Michael addition was disclosed in the one-pot reactions between 3-oxobutanamides and aryl (heteroaryl) aldehydes under basic conditions, in which amide anions regiospecifically attacked the α-carbon of an enone fragment, providing a new route to biologically important tetramic acid derivatives. An explanation for the unexpected regioselectivity is proposed based on the results of experiments and theoretical calculations, which is ascribed to (1) the conjugated and rigid molecular skeleton, and (2) proximity effects of the nucleophilic site and the enone α-carbon.

Keywords: amide anion; anti-Michael addition; enones; tetramic acids

Introduction

In recent years, some reactions known as the anti-Michael addition have been reported, in which the carbon-carbon and carbon-heteroatom bonds were formed regioselectively at the α-position of activated olefins.[1a] So far, some intelligent approaches for redirecting the regioselectivity of addition of a nucleophile from the classical β-addition mode to an α-addition have been developed. They include: 1) transition metal-catalyzed hydrocarbonation of an activated olefin;[1b] 2) addition of alkyllithium or -magnesium reagents to cinnamic acids, its esters, or primary or secondary amides, through a free radical mechanism;[2] 3) using a much stronger electron-withdrawing β-substituent, such as 2-/4-pyridinium and β,β-bis(trifluoromethyl) groups, to induce an umpolung of the carbon/carbon double bond of the α,β-unsaturated carbonyl system;[3] 4) directing an intramolecular oxo-anti-Michael addition using azide activation at the α-position of *o*-hydroxychalcones.[4] Different from the Morita–Baylis–Hillman[5] and α-formylation reactions[6] in which the α-C of activated olefins is nucleophilic, in an anti-Michael reaction the α-C of activated olefins acts as an electrophilic center. This change should bring new synthetic applications, for example, the ring size by an intramolecular anti-Michael addition would contain one carbon atom less than the normal Michael addition, and thus adds a new reaction to the repertoire of currently known processes.

During the course of our study of α-oxoketene *S,S*-acetal chemistry,[7] we reported an intramolecular oxo-anti-Michael reaction, in which the carboxyl acid oxygen could regioselectively attack the α-carbon of the β-(2-/4-pyridyl)-substituted enone fragment under acidic conditions, allowing the formation of tetronic acids.[8] However, in that case the anti-Michael addition occurred only in β-(2-/4-pyridyl)-substituted enone substrates; at the same time, the presence of a protonic acid appears indispensable, because the corresponding sodium carboxylate of 4-pyridyl-substituted enones failed in the cyclization reaction, which proved that the 2-/4-pyridinium induced the anti-Michael addition due to a strong $-C$ effect (negative conjugation effect). Indeed, our latest theoretical calculation on the intermediate (**i**) showed that the 4-pyridinium group led to an umpolung of the C/C double bond of the enone (Figure 1); therefore, this reaction should belong to the third type of anti-Michael additions described above.



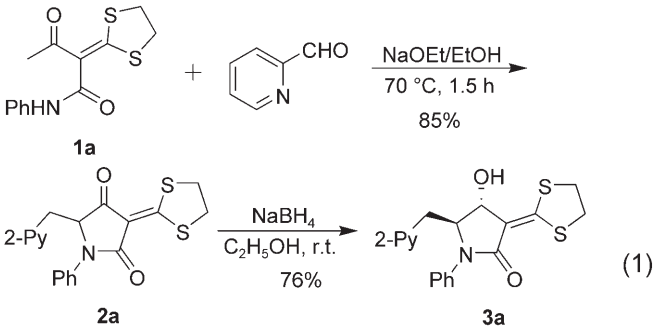
(**i**)

Figure 1. NBO charge distribution on the C/C double bond of pyridinium (**i**).

Herein, we report a new intramolecular anti-Michael reaction in which an amide anion exclusively attacks the α-carbon of enones under basic conditions, providing a regiospecific synthesis of biologically important tetramic acid (pyrrolidine-2,4-dione) derivatives. Importantly, the β-substituent in the enone fragment has a lower effect on the aza-anti-Michael addition than on the pyridinium-induced anti-Michael addition.[8] As part of these studies, we also explored the reason for the unexpected regioselectivity.

Results and Discussion

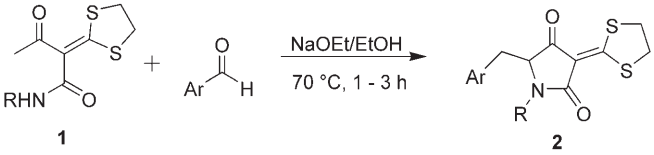
Initially, upon treatment of 2-(1,3-dithiolan-2-ylidene)-3-oxo-*N*-phenylbutanamide **1a** with pyridine-2-carboxyaldehyde in the presence of NaOEt in ethanol at 70 °C for 1.5 h, tetramic acid derivative **2a** was obtained in 85 % yield as the sole product, whose structure was confirmed by NMR spectral analysis of the corresponding 4-hydroxy derivative **3a** after reduction with $NaBH_4$ [Eq. (1)]. Other base systems (NaOH/EtOH, KOH/EtOH, NaOEt/DMF and NaH/DMSO) were tested, but NaOEt/EtOH was the most efficient and was selected for the following investigations. From the results listed in Table 1, it can be seen that both pyridine-4-carboxyaldehyde and pyridine-3-carboxyaldehyde smoothly reacted with **1a**, affording tetramic acids **2b** and **2c** in 78 % and 92 % yields, respectively (entries 1 and 2).



(1)

The structure of **2c** was unambiguously determined by X-ray diffraction analysis (Figure 2). In addition to pyridinecarboxyaldehydes, 3-nitrobenzaldehyde also participated in the one-pot reaction with **1a**, leading to tetramic acid **2d** in 86 % yield (entry 3). However, 2- and 4-nitrobenzaldehyde both failed in this cyclization process under identical and a variety of other conditions (for example, at reflux temperature or with *t*-BuOK as the base), and led to unidentified mixtures (entries 4 and 5). Notably, the one-pot reaction also occurred with 2-Cl- and 2,6-di-Cl-substituted benzaldehydes to give tetramic acids **2g** and **2l** in 80 and 82 % yields, respectively (entries 6 and 11). Furthermore, variation of R in **1** from aryl to alkyl groups (**1b**–**1e**) was also tolerated although slightly lower yields were observed in the cases of **1d** and **1e** (entries 7–10). The results exhibit the scope of the one-pot cyclization reactions with respect to a range of substrates. Thus, we present here a new and facile one-pot method for the synthesis of tetramic acids, a key structural unit in numerous biologically active natural and synthetic compounds.[9] Moreover, the introduction of a characteristic 1,3-dithiolan-2-ylidene group to the 3-position of tetramic acids is useful, since it has the potential to be converted into other functional groups such as thioesters,[10] 1,3-dithiolan-2-yl,[7f,g,11] enamines[7f,g,8] and aromatic rings[12] through ring opening, reduction, substitution and cycloaromatization reactions, respectively. Therefore, products **2** could act as a valuable synthetic scaffold in the preparation of natural and synthetic compounds with important biological and pharmacological activities.

Table 1. The one-pot reactions of compounds **1** with aldehydes.[a]



Entry	1	R	Ar	2	Yields [%][b]
1	**1a**	Ph	4-Pyridyl	**2b**	78
2	**1a**	Ph	3-Pyridyl	**2c**	92
3	**1a**	Ph	3-$NO_2C_6H_4$	**2d**	86
4	**1a**	Ph	2-$NO_2C_6H_4$	**2e**	0[c]
5	**1a**	Ph	4-$NO_2C_6H_4$	**2f**	0[c]
6	**1a**	Ph	2-ClC_6H_4	**2g**	80
7	**1b**	4-ClC_6H_4	2-Pyridyl	**2h**	89
8	**1c**	4-MeC_6H_4	2-Pyridyl	**2i**	83
9	**1d**	Bn	2-Pyridyl	**2j**	52
10	**1e**	Et	2-Pyridyl	**2k**	66
11	**1a**	Ph	2,6-$Cl_2C_6H_3$	**2l**	82

[a] 0.5 equivalent of NaOEt was used in all reactions.
[b] Isolated yields.
[c] No desired product was isolated.

Subsequently, a stepwise experiment was designed starting from compound **4** to determine what factors are responsible for the ring closure in the above one-pot reactions (Scheme 1). Acids **5** were first prepared by a Claisen–Schmidt condensation reaction between **4** and aldehydes,[13] followed by conversion to the resultant enone **6** by using a classical method. Subsequently, the cyclization of **6** was performed in the presence of NaOEt in ethanol, as expected leading to tetramic acids **2c**, **2e** and **2f** in high yields, respectively. From these results, it can be concluded that the intramolecular aza-anti-Michael addition of amide anion to the enone fragment of 3-oxo-pent-4-enam-

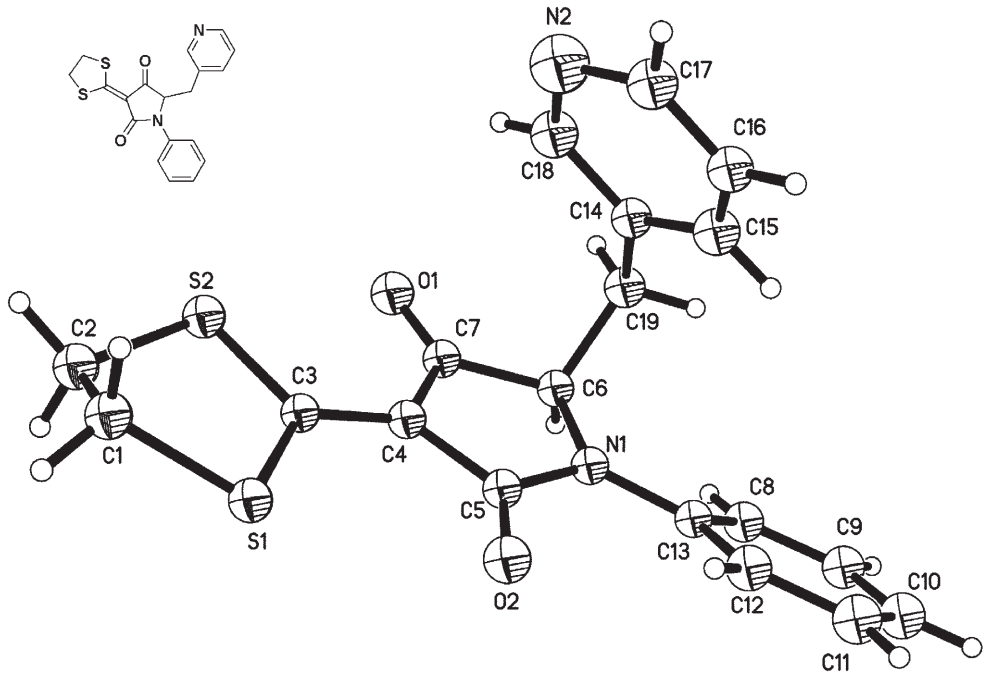
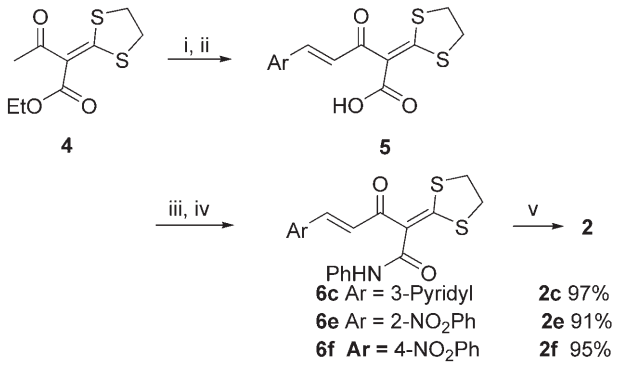


Figure 2. ORTEP drawing of molecule **2c.** Crystallographic data for the structure **2c** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-299148. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

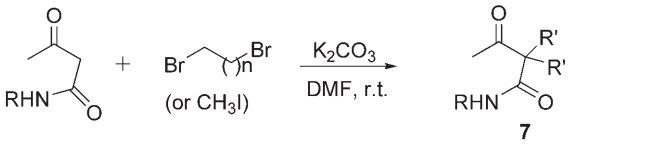


Scheme 1. *Reagents and Conditions*: (i) ArCHO, NaOH, C_2H_5OH, r.t. 6–9 h; (ii) HCl aqueous; (iii) $SOCl_2$, anhydrous CH_2Cl_2, reflux, 2 h; (iv) $PhNH_2$, CH_2Cl_2, reflux, 1.5 h; (v) NaOEt/C_2H_5OH, 70 °C, 1–2 h.

ides **6** is the ring-closure step. Further, successful preparation of **2e** and **2f** by this stepwise method suggests that the one-pot cyclizations of **1** with 2- and 4-nitrobenzaldehydes (Table 1, entries 4 and 5) failed in the Claisen–Schmidt condensation step. These results indicate that the one-pot reaction shown in Table 1 involves sequential Claisen–Schmidt condensation and intramolecular aza-anti-Michael addition to yield tetramic acids of type **2**.

According to Baldwin's guidelines on ring closure reactions,[14] there exist two allowed pathways in the ring closure of **6**, that is, *5-exo-trig* and *6-endo-trig*, respectively. It is known that the electron-withdrawing ability of pyridyl and substituted phenyl is far weaker than that of carbonyl group,[15] so the *6-endo-trig* pathway for the ring closure of **6** appears a much more reasonable choice,[16] however, no such products, i.e., Michael adducts, could be obtained in the cases where an enone substrate (or intermediate) **6** has an electron-withdrawing β-aryl group.[17] Therefore, we tried to elucidate the reason for the unexpected regioselectivity, and also to explore the scope and limitations of the one-pot reaction described above.

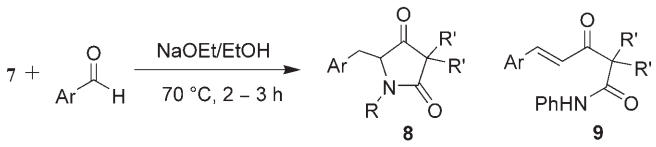
To examine the effect of conjugation between acetyl and carbamoyl units in amides **6**, compounds **7a–7c**, containing instead an sp^3 carbon atom at the 2-position, were prepared by reacting 3-oxo-*N*-phenylbutanamide with 1,4-dibromobutane, 1,2-dibromoethane and iodomethane in the presence of K_2CO_3 in DMF at ambient temperature, respectively (Scheme 2). Then, the reactions of **7** with selected aromatic aldehydes were carried out in the presence of NaOEt in ethanol. From these results listed in Table 2, it can be seen that a new group of tetramic acids **8** was successfully synthesized in good yields from the one-pot reactions between **7** and the corresponding pyridinecarboxyaldehydes (entries 1–3 and 6). The five-membered structure of products **8** was confirmed by NMR spectral analysis of the corresponding 4-hydroxy derivatives **3**. When reaction of



7a R = Ph, R',R' = $(CH_2)_4$ 94%
7b R = Ph, R',R' = $(CH_2)_2$ 87%
7c R = 4-MeC_6H_4, R' = CH_3 50%

Scheme 2.

Table 2. The reactions of compounds 7 with aldehydes.



Entry	7	Ar	8/9	Yields [%][a]
1	**7a**	4-Pyridyl	**8a**	85
2	**7a**	2-Pyridyl	**8b**	76
3	**7b**	4-Pyridyl	**8c**	89
4[b]	**7a**	2-Pyridyl	**8b/9a**	48 %/43 %
5	**7a**	3-$NO_2C_6H_4$	**9b**	94
6	**7c**	2-Pyridyl	**8d**	61

[a] Isolated yields based on **7**.
[b] Quenching the reaction at midway.

7a was quenched in the middle of the reaction with pyridine-2-carboxyaldehyde, **8b** and intermediate **9a** were isolated in 48 % and 43 % yields, respectively (entry 4), which indicated the formation of 3-spirotetramic acids **8** subjected to the same ring-closure mechanism as tetramic acids **2**. By contrast, reaction of 3-nitrobenzaldehyde with **7a** only afforded 94 % of **9b** under identical conditions (entry 5). These results indicate that the conjugation between the nucleophilic site and the electrophilic site appears not to be essential for the anti-Michael addition of amides **6**, but may have an accessory role because a much wider range of β-substituents was tolerated in the cyclization of substrates **6** than that in amides **9**. Also, the rigid skeleton of the species **6** should be considered as another beneficial factor since it can provide a constraint on the system[18] that forces the reaction to proceed with the observed regiochemistry, i.e., anti-Michael addition.

To rationalize the preference for the anti-Michael addition described above, we performed *ab initio* (HF/6-31G*) calculations on **6a** (**9a**) and its anion **6a**$^-$ (**9a**$^-$), respectively.[19] The NBO charge densities on α- and β-C in **6a** (**9a**) and anion **6a**$^-$ (**9a**$^-$) are schematically shown in Figure 3, from which it can be seen that α-C possesses more negative charge than β-C both in **6a** and **9a** owing to the much stronger electron-withdrawing ability of the carbonyl group than that of an aryl (heteroaryl) group. Upon removing the proton, a nearly equal NBO charge density is found on the two α- and β-C for the anion forms **6a**$^-$ and **9a**$^-$, respectively. This feature is in agreement with the anti-Michael additions. The umpolung on the C/C double bond of anion **6a**$^-$ might be due to the electron-donating effect of both amide anion and two alkylthio groups to the carbonyl of the enone system through their respective conjugated chains.[20] Besides, a remarkable decrease of negative charge density was observed at the α-carbon of unconjugated species **9a**$^-$, which suggests the steroelectronic effect between the N-nucleophile with the carbonyl as well as the alpha carbon of the enone system may exist.[4b] At the same time, the proximity effects[21] may also play a crucial role in the observed regioselectivity, namely the amide anion attacks the enone C/C double bond from the closer direction to α-C rather than β-C, hence the attack will be preferential to α-C, corresponding to the anti-Michael addition. Furthermore, the p orbital on the N atom of the HOMO is in the same phase as that of the α-C atom of the LUMO for the conformation of optimized anion **6a**$^-$ (**9a**$^-$), favoring anti-Michael addition. Additionally, the thermodynamic stability of the products of alpha and beta addition were calculated and compared. We found that the total energy of optimized **2a** (**8b**) is lower than that of corresponding Michael product by 9.977 (11.445) kcal mol^{-1}; therefore, the alpha addition product **2a** (**8b**) is also energetically stable.

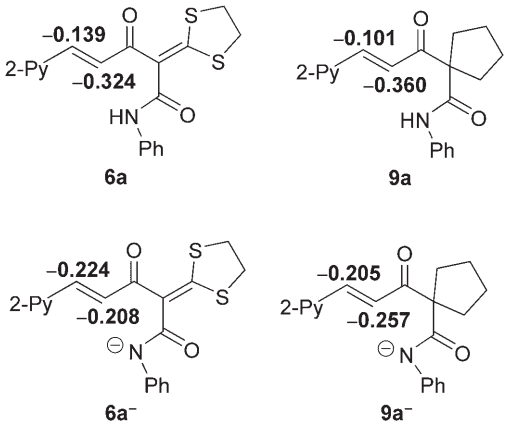


Figure 3. Comparison of the NBO charge distribution on α- and β-carbon of the enone fragment.

Conclusions

We have disclosed a novel intramolecular aza-anti-Michael addition of an amide anion to α,β-unsturated enones. As the key ring-closure step, a new route to biologically important tetramic acid derivatives has

been developed through the one-pot reactions between 3-oxobutanamides and aryl (heteroaryl) aldehydes under basic conditions. The reason for the observed regioselectivity in the ring-closure step was also explored through experiments and theoretical calculations, and mainly ascribed to (1) the conjugated and rigid molecular skeleton and (2) proximity effects of the nucleophilic site and the enone α-carbon. Our findings help define the structural prerequisites for an anti-Michael addition to an α,β-unsaturated enone system. Studies to further extend the intramolecular anti-Michael addition to other molecular systems are underway in our laboratory.

Experimental Section

Typical Procedures for the Syntheses of Tetramic Acids 2 *via* One-Pot Reaction (with 2a as an Example)

To a solution of 2-(1,3-dithiolan-2-ylidene)-3-oxo-*N*-phenylbutanamide **1a** (0.56 g, 2.0 mmol) and pyridine-2-carboxyaldehyde (0.24 mL, 2.5 mmol) in ethanol (6 mL) was added NaOEt (0.08 g, 1.0 mmol) in one portion at 0 °C. The reaction mixture was then heated to 70 °C and stirred for 1.5 h. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature, quenched with saturated aqueous NH_4Cl (25 mL), and vigorously stirred for another 15 min to allow the formation of a precipitate. Collection of the precipitate by filtration at reduced pressure followed by drying under vacuum afforded the product **2a** as a yellowish solid; yield: 0.62 g (85 %); mp 157–158 °C; ^{1}H NMR (DMSO-d_6, 500 MHz): $\delta = 3.13$ (dd, $J = 6.5$, 15.0 Hz, 1H), 3.20 (dd, $J = 4.0$, 15.0 Hz, 1H), 3.53–3.63 (m, 4H), 5.14 (dd, $J = 4.0$, 6.5 Hz, 1H), 6.81 (d, $J = 8.0$ Hz, 1H), 7.09–7.13 (m, 2H), 7.29–7.32 (m, 2H), 7.43 (d, $J = 7.5$ Hz, 2H), 7.47–7.50 (m, 1H), 8.35 (d, $J = 4.0$ Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz): $\delta = 191.7$ (C), 177.0 (C), 165.5 (C), 156.6 (C), 149.2 (CH), 137.3 (CH), 136.4 (C), 128.9 (CH), 125.0 (CH), 124.3 (CH), 123.2 (CH), 122.0 (C), 113.0 (CH), 63.5 (CH), 38.1 (CH_2), 37.8 (CH_2), 37.4 (CH_2); IR (KBr): $\nu = 1658$, 1594, 1517, 1489, 1436, 1372, 1274, 1205, 1149, 838, 775, 753, 610 cm^{-1}; ES-MS: $m/z = 369.3$ [$(M+1)$]$^+$; anal. calcd. for $C_{19}H_{16}N_2O_2S_2$: C 61.93, H 4.38, N 7.60; found: C 62.30, H 4.61, N 7.72.

Acknowledgements

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References

[1] For a review, see: a) E. Lewandowska, *Tetrahedron* **2007**, *63*, 2107–2122; b) J. G. Shim, J. C. Park, C. S. Cho, S. C. Shim, Y. Yamamoto, *Chem. Commun.* **2002**, 852–853.

[2] a) G. W. Klumpp, A. J. C. Mierop, J. J. Vrielink, A. Brugman, M. Schakel, *J. Am. Chem. Soc.* **1985**, *107*, 6740–6742; b) I. Crossland, *Acta Chem. Scand. B* **1975**, *29*, 468–470; c) M. J. Aurell, M. J. Bañuls, R. Mestres, E. Muñoz, *Tetrahedron* **2001**, *57*, 1067–1074.

[3] a) G. S. Ponticello, M. B. Freedman, C. N. Habecker, M. Katharine Holloway, J. S. Amato, R. S. Conn, J. J. Baldwin, *J. Org. Chem.* **1988**, *53*, 9–13; b) E. M. Coyanis, C. O. Della Védova, A. Haas, M. Winter, *J. Fluor. Chem.* **2002**, *117*, 185–192; c) R. Keese, C. Hinderling, *Synthesis* **1996**, 695–696.

[4] a) E. Patonay-Péli, G. Litkei, T. Patonay, *Synthesis* **1990**, 511–514. If no azide group is present at the α-position of enones, an exclusive intramolecular Michael addition will occur instead of the anti-Michael addition, please see: b) C. D. Johnson, *Acc. Chem. Res.* **1993**, *26*, 480.

[5] D. Basavaiah, A. J. Rao, T. Satyanarayana, *Chem. Rev.* **2003**, *103*, 811–891.

[6] E. R. Anabha, C. V. Asokan, *Synthesis* **2006**, 151–155.

[7] a) X. Bi, D. Dong, Q. Liu, W. Pan, L. Zhao, B. Li, *J. Am. Chem. Soc.* **2005**, *127*, 4578–4579; b) D. Dong, X. Bi, Q. Liu, F. Cong, *Chem. Commun.* **2005**, 3580–3582; c) X. Bi, D. Dong, Y. Li, Q. Liu, Q. Zhang, *J. Org. Chem.* **2005**, *70*, 10886–10889; d) L. Zhao, F. Liang, X. Bi, S. Sun, Q. Liu, *J. Org. Chem.* **2006**, *71*, 1094–1098; e) Y. Ouyang, D. Dong, H. Yu, Y. Liang, Q. Liu, *Adv. Synth. Catal.* **2006**, *348*, 206–210; f) F. Liang, J. Zhang, J. Tan, Q. Liu, *Adv. Synth. Catal.* **2006**, *348*, 1986–1990; g) J. Kang, F. Liang, S.-G. Sun, Q. Liu, X. Bi, *Org. Lett.* **2006**, *8*, 2547–2550.

[8] X. Bi, Q. Liu, S. Sun, J. Liu, W. Pan, L. Zhao, D. Dong, *Synlett* **2005**, 49–54.

[9] For reviews, see: a) A. Gossauer, *Prog. Chem. Org. Nat. Prod.* **2003**, *86*, 1–188; b) B. J. L. Royles, *Chem. Rev.* **1995**, *95*, 1981–2001. For selected recent examples, see: c) G. Lang, A. L. J. Cole, J. W. Blunt, M. H. G. Munro, *J. Nat. Prod.* **2006**, *69*, 151–153; d) A. R. Ratnayake, R. A. Davis, M. K. Harper, C. A. Veltri, C. D. Andjelic, L. R. Barrows, C. M. Ireland, *J. Nat. Prod.* **2005**, *68*, 104–107; e) D. M. Fitch, K. A. Evans, D. Chai, K. J. Duffy, *Org. Lett.* **2005**, *7*, 5521–5524; f) P. Huang, T.-J. Wu, Y.-P. Ruan, *Org. Lett.* **2003**, *5*, 4341–4344.

[10] S. K. Nair, R. Samuel, C. V. Asokan, *Synthesis* **2001**, 573–576.

[11] J. M. Mellor, S. R. Schofield, S. R. Korn, *Tetrahedron* **1997**, *53*, 17151–17162.

[12] a) P. J. Kocienski, A. Pontiroli, Q. Liu, *J. Chem. Soc., Perkin Trans. 1* **2001**, 2356–2366; b) S. Gill, P. J. Kocienski, A. Kohler, A. Pontiroli, Q. Liu, *Chem. Commun.* **1996**, 1743–1744.

[13] M. Wang, X. Xu, Q. Liu, L. Xiong, B. Yang, L. Gao, *Synth. Commun.* **2002**, *32*, 3437–3443.

[14] a) J. E. Baldwin, *J. Chem. Soc., Chem. Commun.* **1976**, 734–736; b) J. E. Baldwin, *Further Perspectives in Organic Chemistry*, A Ciba Foundation Symposium, Elsevier, Amsterdam, **1978**, p 85.

[15] P. G. Taylor, in: *The Chemistry of Double-Bonded Functional Groups*, *Supplement A3,* (Ed.: S. Patai), Wiley-VCH, Chichester, **1997**, Chapter 18, p 1105.
[16] For some examples of intramolecular aza-Michael addition, see: a) G. Bartoli, M. Bartolacci, A. Giuliani, E. Marcantoni, M. Massaccesi, E. Torregiani, *J. Org. Chem.* **2005**, *70*, 169–174; b) R. Ferraccioli, D. Carenzib, M. Catellani, *Tetrahedron Lett.* **2004**, *45*, 6903–6907; c) K. Takasu, S. Maiti, M. Ihara, *Heterocycles* **2003**, *59*, 51–54; d) T. Suwa, I. Shibata, K. Nishino, A. Baba, *Org. Lett.* **1999**, *1*, 1579–1581.
[17] In one case where the enone substrate **6m** has a β-4-methoxyphenyl, a complex mixture product was formed under the identical conditions as described in Scheme 1, from which an aza-Michael adduct **6m-i** was separated and confirmed by subsequent reduction and elimination reactions.
[18] B. K. Joseph, B. Verghese, C. Sudarsanakumar, S. Deepa, D. Viswam, P. Chandran, C. V. Asokan, *Chem. Commun.* **2002**, 736–737.
[19] For the calculation details, please see Supporting Information.
[20] a) R. Sugi, A. Yokoyama, T. Furuyama, M. Uchiyama, T. Yokozawa, *J. Am. Chem. Soc.* **2005**, *127*, 10172–10173; b) B. Negroni, A. Botrel, M. Hérail, A. Proutière, *J. Mol. Stru.* **1997**, *405*, 133–138.
[21] For a general discussion of the importance of the proximity of the reacting centers in intramolecular reactions, see: F. M. Menger, *Acc. Chem. Res.* **1985**, *18*, 128–134; F. M. Menger, *Acc. Chem. Res.* **1993**, *26*, 206–212.