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Domino Reaction of Acyclic α,α-Dialkenoylketene *S,S*-Acetals and Diamines: Efficient Synthesis of Tetracyclic Thieno[2,3-*b*]-thiopyran-Fused Imidazo[1,2-*a*]pyridine/Pyrido[1,2-*a*]pyrimidines

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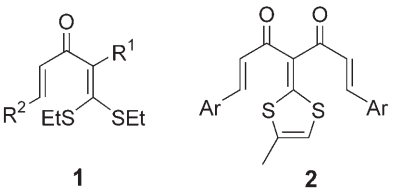
Abstract: A series of unusual fused tetraheterocyclic compounds **3**, consisting of a thiopyran (ring A), a thiophene (ring B), a pyridine (ring C), and an imidazole or a pyrimidine (ring D) core, with a bridgehead nitrogen and an angular methyl group, were successfully synthesized by a catalyst-free, one-pot, two-component domino reaction of 4-(4-methyl-1,3-dithiol-2-ylidene)-1,7-bis(aryl/heteroaryl)hepta-1,6-diene-3,5-dione **2** and diamines. In this reaction, up to five new bonds were formed accompanied by the C–S bond cleavage of the 1,3-dithiole ring of **2**, with water as the only by-product.

Keywords: α,α-dialkenoylketene *S,S*-acetals; diamines; domino reactions; fused polyheterocycles

Introduction

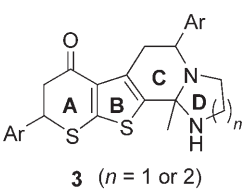
There has been increasing interest in highly efficient and environmentally acceptable synthetic methods in modern chemistry. In this context domino reactions have proven to be very effective and attractive.[1] The notable feature of a domino process is that bonds and new functionalities are constructed during the cascade, which, in turn, react further in subsequent steps under identical conditions to form new bonds and functionalities until termination leads to a stable final product. Clearly, the quality of a domino reaction is dependent on the number of bonds formed and the complexity of the product. The amounts of solvents, reagents, absorbents, and energy in domino reactions would be dramatically decreased compared to the conventional stepwise approach. On the other hand, the multi-step synthesis towards a complex compound is laborious and tedious, generating several equivalents of waste and salt as by-products. Hence, domino processes, in an environmentally benign and atom-economic fashion,[1,2] play an important role in organic syntheses, especially considering that certain complex compounds such as fused polyheterocycles[1,3,4] are of great significance and their synthesis still remains a challenge for chemists.

Over the past few decades, α-oxoketene *S,S*-acetals have emerged as versatile intermediates in organic synthesis.[5] During the course of our studies on the chemistry of functionalized ketene *S,S*-acetals,[6] we found that the easily available α-alkenoylketene *S,S*-acetals[7] showed promising structural features as novel organic intermediates in annulation reactions.[8] In particular, a new [5C+1C, (1N), (1S)] synthetic strategy has been recently developed for the construction of highly substituted phenolic rings,[8a] pyridones[8b] and thiopyran-4-ones[8c] relying upon the utilization of α-alkenoylketene *S,S*-acetals **1** as 1,5-bielectrophilic synthons. To explore the synthetic utility of the multi-functionalized α-alkenoylketene *S,S*-acetals, in our ongoing research, the analogue of **1**, namely 4-(4-methyl-1,3-dithiol-2-ylidene)-1,7-bisaryl/heteroarylhepta-1,6-diene-3,5-dione **2**, was synthesized and the reactions of **2** with 1,2/1,3-diamines were studied. As a result, a series of fused polyheterocycles **3**, with the structure of thieno[2,3-*b*]thiopyran-fused imidazo[1,2-*a*]pyridine/pyrido[1,2-*a*]pyrimidines, were prepared in one step by reacting acyclic **2** with 1,2-ethanediamine or 1,3-propanediamine at an elevated temperature in the open air.



1

2

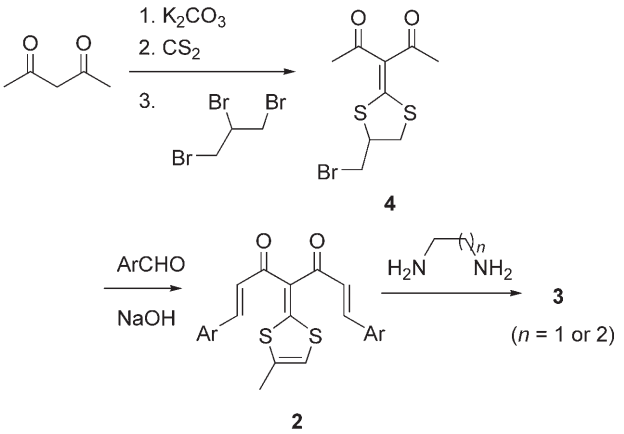


3 (*n* = 1 or 2)

Besides the high efficiency in the formation of multiple bonds and atom economy as a domino process, this reaction has the advantages: (1) the starting materials are readily available[8,9] and the reagents are cheap; (2) reaction proceeds smoothly under very mild conditions without introducing extra acid, base or metal catalyst; (3) it is an environmentally benign transformation due to the fact that only one molecule of water is released in the whole process; and (4) the thieno[2,3-*b*]thiopyran-fused imidazo[1,2-*a*]pyridine/pyrido[1,2-*a*]pyrimidine system **3**, to our best knowledge, represents a kind of new fused heterocycles containing a thiopyran (ring A), a thiophene (ring B), a pyridine (ring C), and an imidazole or a pyrimidine (ring D) core, furthermore, a bridgehead nitrogen and an angular methyl group are involved. Indeed, the present protocol provides a straightforward and effective pathway to construct nitrogen- and sulfur-containing heterocycles of type **3**, a relatively rare fused-ring system.

Results and Discussion

In our experiment, precursors **2** were synthesized by a two-step reaction starting from pentane-2,4-dione in excellent yields according to a similar procedure reported previously.[9] In the first step, pentane-2,4-dione reacted with CS_2 (1.1 equivs.) in the presence of K_2CO_3 (2.2 equivs.) in DMF for 1 h in an ice bath, followed by a dropwise addition of 1,2,3-tribromopropane to the reaction mixture and stirring overnight at room temperature. A yellow solid was obtained after pouring the reaction mixture into a large amount of ice-water. The only product was characterized as 3-(4-bromomethyl-[1,3]-dithiolan-2-ylidene)-pentane-2,4-dione **4** with an excellent yield of 91%. The second step was an aldol condensation of **4** with selected aryl aldehydes in the presence of NaOH.[10] The products, α,α-dialkenoylketene *S,S*-acetals **2**, were thus obtained in excellent yields (Table 1, entries 1–7) and the structure of **2** showed that the elimination of HBr took place, accompanied by the aldol condensation, to form the C=C double bonds of the 1,3-dithiol-2-ylidene moiety (Scheme 1).



Scheme 1. Domino process leading to polyheterocycles **3**.

In the following work we devoted our efforts to the study of the reaction of **2** with diamines.[8b] Initially the reaction of **2a** and 1,2-ethanediamine was investigated in varied solvents such as benzene, EtOH and THF, with the molar ratio of **2a** to 1,2-ethanediamine being 1:2.0. Unfortunately, there was no reaction in benzene and EtOH solution, and an incomplete reaction was observed in the case of THF as solvent. In another case when DMF was selected as the solvent, the reaction occurred and product **3a** was obtained in 23% isolated yield after purification of the reaction mixture by flash chromatography using petroleum ether-acetyl acetate (10:1, v/v) as eluent. Subsequently, the optimization of the reaction conditions, including solvents, reaction temperature, and reaction time for reaction of **2a** with 1,2-ethanediamine, was investigated. To our delight, after a series of experiments, acetonitrile was proved to be the best solvent and the yield of product **3a** reached 35% when the reaction

Table 1. Synthesis of **2** and **3**.

Entry	Ar	Time [h]	Substrate **2**	Yield[a] [%]	Diamine[b] A or B	Time [h]	Product **3**	Yield[a] [%]
1	C_6H_5	2.0	**2a**	91	A	3.5	**3a**	35
2	4-ClC_6H_4	3.0	**2b**	93	A	3.0	**3b**	38
3	4-FC_6H_4	2.5	**2c**	93	A	3.0	**3c**	42
4	4-$CH_3C_6H_4$	2.0	**2d**	90	A	3.5	**3d**	35
5	4-$CH_3OC_6H_4$	2.0	**2e**	90	A	3.5	**3e**	40
6	2-Pyridyl	3.0	**2f**	86	A	4.0	**3f**	32
7	2-Furanyl	2.5	**2g**	85	A	4.0	**3g**	33
8	C_6H_5	-	**2a**	-	B	3.0	**3h**	45
9	4-ClC_6H_4	-	**2b**	-	B	3.0	**3i**	46
10	4-FC_6H_4	-	**2c**	-	B	3.5	**3j**	42

[a] Isolated yields.
[b] A = 1,2-ethanediamine; B = 1,3-propanediamine.

of **2a** with 1,2-ethanediamine was performed in CH_3CN at elevated temperature (50 °C) for 3 h.

To extend the scope of this new procedure for the synthesis of the fused polyheterocycles, substrates **2b–e**, with electron-donating or electron-withdrawing groups on the phenyl rings, were then examined for their reactions with 1,2-ethanediamine under the optimized conditions. As a result, a series of products **3b–e** was obtained in moderate yields of 32–42 % (Table 1, entries 1–5). The substrates **2f** and **2g** which contained the heteroaromatic groups (2-pyridyl and 2-furanyl) were also allowed to react with 1,2-ethanediamine under identical conditions. Accordingly, pyridyl- and furanyl-substituted tetracycle compounds **3f** and **3g** were obtained. The reactions of **2** with 1,3-propanediamine also proceed smoothly under identical conditions as described above. For example, the reactions of **2a–2c** with 1,3-propanediamine gave the desired products **3h–3j** in 42–46 % yields (Table 1, entries 8–11). The structure of **3h** was established by single crystal X-ray diffraction analysis (Figure 1).[11]

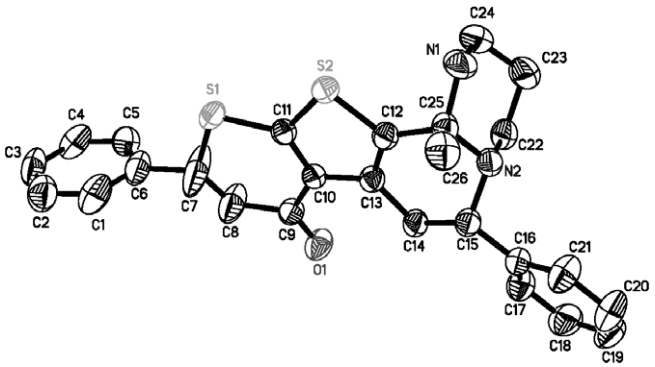
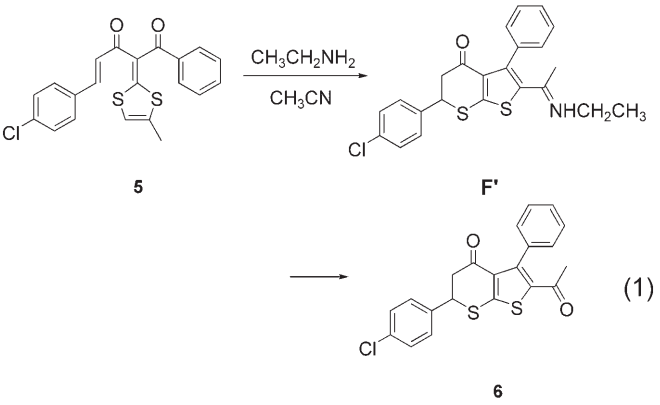


Figure 1. The ORTEP drawing of **3h**.

By reaction with 1,3-propanediamine, a tetracyclic system with three six-membered rings and one five-membered ring could be achieved. In the reaction with 1,2-ethanediamine, the resulting thieno[2,3-*b*]thiopyran-fused imidazo[1,2-*a*]pyridines **3a–3g** were composed by two six-membered rings and two five-membered rings. It has been reported that thieno[2,3-*b*]thiopyran (rings A and B)-containing sulfonamides may be used as novel topically active carbonic anhydrase inhibitors for the treatment of glaucoma.[12] On the other hand, imidazo[1,2-*a*]pyridine or pyrido[1,2-*a*]pyrimidines (rings C and D), as a kind of *N*-heterobicycle, have attracted considerable attention due to their wide range of biological and pharmacological activities.[13]

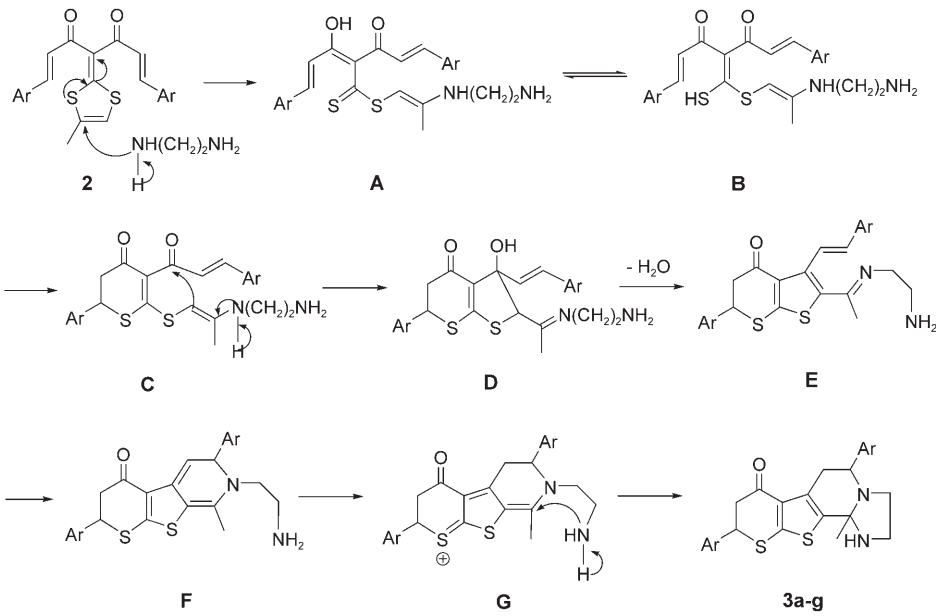
As a whole, this one-pot, two-component (**2** and a diamine) reaction without utilizing any other catalysts gives access to fused tetracyclic compounds **3** with water as the only by-product. During this cascade, one carbon-sulfur bond of the dithiole ring is cleaved and up to five bonds are newly formed. It should be noted that compounds 3 were obtained as a mixture of diastereomers since the molecules contain three chiral carbon atoms. Apparently, the domino synthetic strategy presented provides a convenient, atom-economic and environmentally friendly way to construct the complex tetracyclic compounds **3**. The wide generality of this process suggests its potential in the synthesis of this family of compounds and analogues.

In order to clarify the mechanism for the formation of **3**, a model reaction between compound **5**, 5-(4-chlorophenyl)-2-(4-methyl-1,3-dithiol-2-ylidene)-1-phenylpent-4-ene-1,3-dione, and a monoamine, for example, ethylamine was carried out [Eq. 1)]. As a



result, a useful product **6** (A + B ring) was obtained in 68 % yield. The acetyl group adjacent to the thiophene ring of **6** was formed *via* the hydrolysis of the imine E' (see Supporting Information).

On the basis of above results, a possible mechanism for the formation of thieno[2,3-*b*]thiopyran-fused imidazo[1,2-*a*]pyridine/pyrido[1,2-*a*]pyrimidines **3** is proposed and depicted in Scheme 2. Initially, due to the two strongly electron-withdrawing groups at the α-positions of the ketene *S*,*S*-acetals **2**, an S_NV (nucleophilic vinylic substitution) type reaction[14] occurs by attack of one of the amino groups of 1,2-ethanediamine to the vinyl carbon atom of 1,3-dithiole, leading to the fragmentation of the 1,3-dithiole ring and the formation of enamine intermediate **A**, in which the cleavage of the C–S bond is involved.[15] It was noticeable that, in all the experiments, the amine always attacks at the vinyl carbon atom connected with the methyl group of the 1,3-dithiole during this part of the S_NV reaction although the reason is currently not clear. Then, an intramolecular thio-Michael addition of intermediate **B** (a tautomer of **A**) takes place to furnish the thiopyran intermediate **C**.[7a,16] Next, the azatriene intermediate **E** would be formed by the reaction sequence of an intramolecular nucleophilic addition (**C**→**D**) and subsequent dehydration (**D**→**E**). The resulting intermediate **E**, which comprises a 6π



Scheme 2. Proposed mechanism for the domino reaction of **3** with diamine.

electron system, allows a 6π-azaelectrocyclization[17] to give tricyclic species **F**. Finally, the tetracyclic product **3** would be produced by the intramolecular aza-conjugate addition of the free amino group at the terminal carbon atom of the conjugated system of intermediate **G**.[17a]

Conclusions

In summary, a novel and highly efficient catalyst-free domino reaction of α,α-dialkenoylketene *S,S*-acetals **2** with 1,2-ethanediamine or 1,3-propanediamine, giving rise to the unusual tetracyclic thieno[2,3-*b*]thiopyran-fused imidazo[1,2-*a*]pyridine/pyrido[1,2-*a*]pyrimidines **3**, has been demonstrated. A possible mechanism involved in the ring closure cascade reactions, including an S_NV (addition-elimination) at an sp^2 carbon atom as the triggering step, the followed intramolecular thio-Michael addition, nucleophilic addition, 6π-azaelectrocyclization, and intramolecular aza-Michael addition, was proposed. The simplicity of manipulation, ready availability of the substrates, cheap reagents, and significant molecular complexity make this domino synthetic strategy attractive for academic research and other potential applications. It is predictable that this domino reaction will be extremely potent since diamines and similar binucleophiles are important synthetic reagents in numerous reactions. An extension of this work is in progress.

Experimental Section

Typical Procedure for the Preparation of 3h

To a solution of **2a** (390.5 mg, 1.0 mmol) in CH_3CN (10 mL) was added 1,3-propanediamine (148.2 mg, 2.0 mmol). The mixture was stirred at 50 °C for 3 h. After cooling to room temperature, the mixture was poured into water and the crude product was obtained by filtration, which was purified by flash chromatography (silica gel, petroleum ether: acetyl acetate = 10:1) to give rise to **3h** as a reddish solid. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K, TMS): $\delta = 1.48$ (m, 1H), 1.62 (m, 1H), 1.71 (s, 1.5H, Me), 1.74 (s, 1.5H, Me), 1.84 (broad, NH, 1H), 2.36 (m, 1H), 2.45 (m, 1H), 2.61 (m, 1H), 2.86 (m, 1H), 3.05 (m, 1H), 3.22 (m, 2H), 3.36 (m, 1H), 4.55 (m, 1H), 4.86 (m, 1H), 7.28 (m, 1H), 7.38 (m, 5H), 7.45 (m, 2H), 7.55 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 27.5$, 40.4, 40.9, 40.9, 46.6, 46.7, 49.4, 49.5, 58.1, 71.2, 71.3, 109.8, 127.0, 127.5, 127.9, 128.0, 128.2, 128.7, 129.0, 132.3, 132.4, 134.8, 134.9, 137.8, 138.9, 141.3, 151.0, 151.1, 190.1, 190.2; IR (KBr): $\nu = 3324$, 3029, 2930, 2826, 1656, 1451, 1199, 978, 896 cm^{-1}; MS (EI): calcd. $m/z = 446.15$, found 447.2 $[(M+1)]^+$; anal. calcd. for $C_{26}H_{26}N_2OS_2$: C 69.92, H 5.87, N 6.27; found: C 70.19, H, 5.75, N, 6.12.

Acknowledgements

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References

[1] Reviews: a) L. F. Tiete, *Chem. Rev.* **1996**, *96*, 115–136; b) S. E. Denmark, A. Thorarensen, *Chem. Rev.* **1996**, *96*, 137–165; c) M. Malacria, *Chem. Rev.* **1996**, *96*, 289–306; d) P. J. Parsons, C. S. Penkett, A. J. Shell, *Chem. Rev.* **1996**, *96*, 195–206; e) K. Neuschütz, J. Velker, R. Neier, *Synthesis* **1998**, 227–255; f) G. Poli, G. Giambastiani, A. Heumann, *Tetrahedron* **2000**, *56*, 5959–5989; g) A. J. McCarroll, J. C. Walton, *Angew. Chem.* **2001**, *113*, 2282–2307; *Angew. Chem. Int. Ed.* **2001**, *40*, 2224–2248; h) L. F. Tietze, U. Beifuss, *Angew. Chem.* **1993**, *105*, 134–170; *Angew. Chem. Int. Ed.* **1993**, *32*, 131–163; i) A. Bunce, *Tetrahedron* **1995**, *51*, 13103–13159; k) K. C. Nicolaou, T. Montagnon, S. A. Snyder, *Chem. Commun.* **2003**, 551–564; j) A. de Meijere, P. von Zezschwitz, S. Bräse, *Acc.Chem. Res.* **2005**, *38*, 413–422.

[2] a) S. A. A. El Bialy, H. Braun, L. F. Tietze, *Angew. Chem.* **2004**, *116*, 5505–5507; *Angew. Chem. Int. Ed.* **2004**, *43*, 5391–5393; b) H. Neumann, A. J. von Wanggelin, S. Klaus, D. Strübing, D. Gördes, M. Beller, *Angew. Chem.* **2003**, *115*, 4641–4645; *Angew. Chem. Int. Ed.* **2003**, *42*, 4503–4507; c) J. A. González-Vera, M. T. García-López, R. Herranz, *Org. Lett.* **2004**, *6*, 2641–2644; d) G. Cuny, M. Bois-Choussy, J. Zhu, *Angew. Chem.* **2003**, *115*, 4922–4925; *Angew. Chem. Int. Ed.* **2003**, *42*, 4774–4777; e) G. Giorgi, S. Miranda, P. López-Alvarado, C. Avendaño, J. Rodriguez, J. Carlos Menéndez, *Org. Lett.* **2005**, *7*, 2197–2200; f) C. H. Heathcock, *Angew. Chem.* **1992**, *104*, 675; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 665–681.

[3] B. M. Trost, *Science* **1991**, *254*, 1471.

[4] B. Alcaide, P. Almendros, *Curr. Med. Chem.* **2004**, *11*, 1921–1949.

[5] Reviews: a) R. K. Dieter, *Tetrahedron* **1986**, *42*, 3029–3096; b) H. Junjappa, H. Ila, C. V. Asokan, *Tetrahedron* **1990**, *46*, 5423–5506; c) H. Tla, H. Junjappa, O. Barun, *J. Organometal. Chem.* **2001**, *624*, 34–40.

[6] a) Y. Yin, M. Wang, Q. Liu, J. Hu, S. Sun, J. Kang, *Tetrahedron Lett.* **2005**, *46*, 4399–4402; b) S. Sun, Q. Zhang, Q. Liu, J. Kang, Y. Yin, D. Li, D. Dong, *Tetrahedron Lett.* **2005**, *46*, 6271–6274; c) D. Dong, Y. Liu, Y. Zhao, Y. Qi, Z. Wang, Q. Liu, *Synthesis* **2005**, 85–91; d) Q. Liu, G. Che, H. Yu, Y. Liu, J. Zhang, Q. Zhang, D. Dong, *J. Org. Chem.* **2003**, *68*, 9148–9150; e) Y. Liu, D. Dong, Q. Liu, Y. Qi, Z. Wang, *Org. Biomol. Chem.* **2004**, *2*, 28–30; f) S. Sun, Y. Liu, Q. Liu, Y. Zhao, D. Dong, *Synlett* **2004**, 1731–1734; g) Y.-L. Zhao, Q. Liu, J.-P. Zhang, Z.-Q. Liu, *J. Org. Chem.* **2005**, *70*, 6913–6917.

[7] a) R. Samuel, S. K. Nair, C. V. Asokan, *Synlett* **2000**, 1804–1806; b) B. K. Joseph, B. Verghese, C. Sudarsanakumar, S. Deepa, D. Viswam, P. Chandran, C. V. Asokan, *Chem. Commun.* **2002**, 736–737; c) X. Bi, Q. Liu, S. Sun, J. Liu, W. Pan, L. Zhao, D. Dong, *Synlett* **2005**, 49–54.

[8] 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, *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.

[9] a) M. Wang, X. Xu, Q. Liu, L. Xiong, B. Yang, L. Gao, *Synth. Comm.* **2002**, *32*, 3437–3443; b) E. B. Choi, I. K. Youn, C. S. Pak, *Synthesis* **1991**, 15–18.

[10] See Supporting Information.

[11] Crystal data for **3h**: $C_{26}H_{26}N_2OS_2$, $M=446.61$, monoclinic, space group $P21/n$, $a=14.065(4)$, $b=19.972(3)$, $c=8.359(1)$ Å, $\beta=105.596(3)$, $V=2261.6(5)$ Å^3, $Z=4$, $\rho_{calcd.}=1.312$, $T=293(2)$ K, 12677 reflections (4464 unique), 271 refined parameters, $R=0.072$ ($I>2\sigma(I)$), $wR_2=0.1766$ (all data). CCDC 271744 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.

[12] a) G. S. Ponticello, M. B. Freedman, C. N. Habecker, P. A. Lyle, H. Schwam, S. L. Varga, M. E. Christy, W. C. Randall, J. J. Baldwin, *J. Med. Chem.* **1987**, *30*, 591–597; b) G. D. Hartmann, W. Halczenko, J. D. Prugh, R. L. Smith, M. F. Sugrue, P. J. Mallorga, S. R. Michelson, W. C. Randall, H. Schwam, J. M. Sondey, *J. Med. Chem.* **1992**, *35*, 3027–3033; c) J. J. Baldwin, G. S. Ponticello, G. S. Anderson, M. E. Christy, M. A. Murcko, W. C. Randall, H. Schwam, M. F. Sugrue, J. B. Springer, P. Gautheron, J. Grove, P. Mallorga, M. P. Viader, B. M. McKeever, M. A. Navia, *J. Med. Chem.* **1989**, *32*, 2510–2513.

[13] a) G. Trapani, M. Franco, L. Ricciardi, A. Latrofa, G. Genchi, E. Sanna, F. Tuveri, E. Cagetti, G. Biggio, G. Liso, *J. Med. Chem.* **1997**, *40*, 3109; b) C. Hamdouchi, J. del Blas, M. del Prado, J. Gruber, B. A. Heinz, L. Vance, *J. Med. Chem.* **1999**, *42*, 50; c) A. Gangjee, O. Adair, S. F. Queener, *J. Med. Chem.* **1999**, *42*, 2447; d) A. Gangjee, O. Adair, S. F. Queener, *J. Med. Chem.* **2003**, *46*. 5074; e) A. Gangjee, O. Adair, S. F. Queener, *Bioorg. & Med. Chem.* **2001**, *9*, 2929.

[14] C. F. Bernasconi, *Tetrahedron* **1989**, *45*, 4017–4090.

[15] V. A. Ogurtsov, O. A. Rakitin, C. W. Rees, A. A. Smolentsev, P. A. Belyakov, D. G. Golovanov, K. A. Lyssenko, *Org. Lett.* **2005**, *7*, 791–794.

[16] S. K. Nair, R. Samuel, C. V. Asokan, *Synthesis* **2001**, *4*, 573–576.

[17] Examples of 6π-azaelectrocyclization: a) K. Tanaka, S. Katsumura, *J. Am. Chem. Soc.* **2002**, *124*, 9660–9661; b) K. Tanaka, S. Katsumura, *Org. Lett.* **2000**, *2*, 373–375; c) K. Tanaka, T. Kobayashi, H. Mori, S. Katsumura, *J. Org. Chem.* **2004**, *69*, 5906–5925; d) K. Tanaka, H. Mori, M. Yamamoto, S. Katsumura, *J. Org. Chem.* **2001**, *66*, 3099–3110; e) M. Alajarín, María-Mar Ortín, Pilar Sánchez-Andrada, Ángel Vidal, Delia Bautista, *Org. Lett.* **2005**, *7*, 5281–5284; f) A. R. de Lera, W. Reischl, W. H. Okamura, *J. Am. Chem. Soc.* **1989**, *111*, 4051–4063; g) D. F. Maynard, W. H. Okamura, *J. Org. Chem.* **1995**, *60*, 1763–1771.

