

Synthetic Methods

Brønsted Acid-Mediated Annulation of α -Oxo Ketene Dithioacetals with Pyrroles: Efficient Synthesis of Structurally Diverse Cyclopenta[*b*]pyrrolesXiaoge Yang,^[a] Kaikai Wu,^[a] Ping Wu,^[a] Jiping Chen,^[a] Chenglin Sun,^[a] and Zhengkun Yu^{*[a, b]}

Abstract: Brønsted acid-mediated annulation of internal olefins α -oxo ketene dithioacetals to pyrroles was efficiently achieved to afford cyclopenta[*b*]pyrroles. A pair of Brønsted acids with acid strengths, that is, trifluoroacetic acid, and *para*-toluenesulfonic acid hydrate, were applied to promote the annulation reactions. The resultant products were readily oxidized to sulfones by *meta*-chloroperoxybenzoic acid. Subsequent treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene gave desulfurized terminal olefins or [2+2] cycloaddition products from the desulfurized olefin intermediates. The present protocol provides facile access to structurally diverse cyclopenta[*b*]pyrrole derivatives under mild conditions.

The cyclopenta[*b*]pyrrole skeleton is a key structural motif in many biologically active and medicinally important molecules.^[1] For example, it is present in the macrotricyclic core of the complex molecule roseophilin^[1a] which exhibits potent cytotoxicity against K562 human erythroid leukemia and KB human epidermoid carcinoma cells,^[2] and also acts as the key backbone of the inhibitors of enzyme D-amino acid oxidase^[1b] and of other inhibitors^[1c] (Figure 1). Due to the increased interest in roseophilin among both biologists and chemists, synthe-

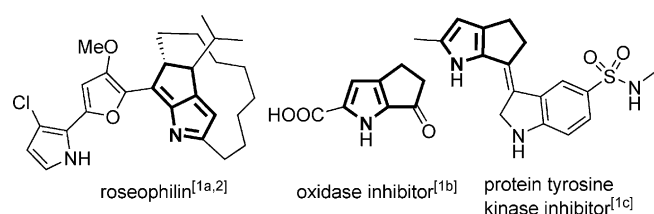


Figure 1. Selected cyclopenta[*b*]pyrrole-based bioactive molecules.

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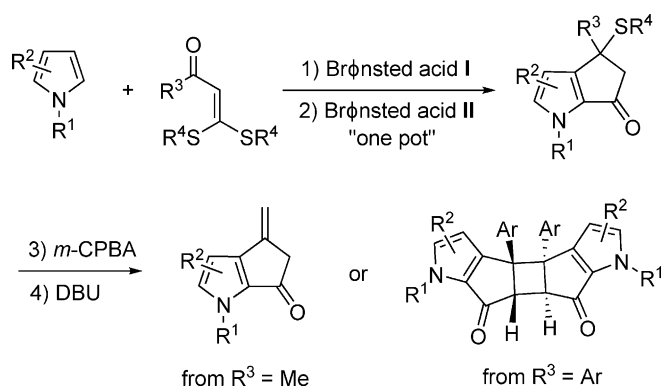
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sis of cyclopenta[*b*]pyrrole derivatives has recently been paid much attention. Acid-mediated Nazarov cyclization seems to be a straightforward route to access cyclopenta[*b*]pyrroles because Nazarov cyclization is a very versatile method to construct five-membered carbocycles.^[3] By means of this synthetic protocol, cyclopentenone-fused pyrroles were obtained from prefunctionalized pyrrolyl vinyl ketones.^[4] Platinum-catalyzed cascade cyclization/ring expansion of 2-alkynyl-1-azaspiro[2.3]-hexanes^[5a] and palladium-catalyzed annulation approach^[5b] afforded cyclopenta[*b*]pyrroles. Rhodium(I)-catalyzed hydroformylation of 1,4-diolefins in the presence of primary amines led to the same type of heterocyclic compounds.^[6] Multicomponent reactions involving 1,2-diketones,^[7a] enones, and enals^[7a,b] or β -alkynyl ketones^[7c,d] with primary amines, as well as organocatalytic processes using ketones and *N*-acylamino acids^[8] were applied for the same purpose. Polycyclic pyrrole derivatives have also been obtained by transition metal-catalyzed cyclization reactions.^[9]

Recently, α -oxo ketene dithioacetals have been demonstrated as potential C1–C3 building blocks in organic synthesis.^[10] During our ongoing investigation of the internal olefins of ketene dithioacetals,^[11] we found that Brønsted acid could mediate 3-olefination of indoles by α -oxo ketene dithioacetals through their C–S bond cleavage,^[12] and thus reasonably envisioned that α -oxo ketene dithioacetals might be used as the C3 building blocks to be annulated to a pyrrole core to establish a cyclopenta[*b*]pyrrole backbone. Herein, we report Brønsted acid-mediated annulation of α -oxo ketene dithioacetals to relatively simple pyrroles to access structurally diverse cyclopenta[*b*]pyrrole derivatives (Scheme 1).

Initially, the reaction of *N*-methylpyrrole (1a) with α -oxo ketene dithioacetal 4,4-bis(ethylthio)but-3-en-2-one (2a) was



Scheme 1. Synthesis and transformations of cyclopenta[*b*]pyrroles.

conducted to screen the reaction conditions (see the Supporting Information). In the presence of acetic acid (20 equiv) the reaction of **1 a** and **2 a** in a 1:1 molar ratio did not occur in dichloromethane at 30 °C over a period of 24 h. Under the same conditions, 10 mol% of *para*-toluenesulfonic acid hydrate (*p*-TsOH·H₂O) did not promote the reaction either, whereas use of 2 equivalents of *p*-TsOH·H₂O led to a complicated mixture and MeSO₃H (10 equiv) rendered formation of the target product, that is, cyclopenta[*b*]pyrrole **3 a**, in 7% yield. To our delight, 40 equivalents of trifluoroacetic acid (TFA) effected the desired reaction to form **3 a** in 31% yield. Formation of the target product seemed to depend greatly on the acid strengths of the Brønsted acid promoters. Among the tested solvents (dichloromethane, THF, toluene, and acetonitrile), dichloromethane acted as the most effective reaction medium to yield **3 a**. Water was found to facilitate the annulation reaction under a nitrogen atmosphere, and **3 a** was thus formed in 63% yield in the presence of 4 equivalents of water. Using an excess of pyrrole substrate (2 equiv) led to **3 a** in 79% yield. Reversal of the substrate ratio to **1 a**/**2 a** = 1:2 increased the yield of **3 a** to 83%. Performing the same reaction in 1,2-dichloroethane (DCE) at an elevated temperature of 40 °C afforded **3 a** in 88% yield (isolated in 65% yield). However, some reaction intermediates could not be transformed to the target product after the TFA-mediated reaction had continued for 24 h. To overcome this reaction barrier, both methanol and *p*-TsOH·H₂O were tested as additives to facilitate the late stage transformations of the reaction intermediates. After the above reaction had been carried out in the absence of water for 24 h, methanol was added and the reaction proceeded for another 2 h, giving **3 a** in 72% yield (isolated product), whereas addition of 0.5 mmol of *p*-TsOH·H₂O as the sole additive led to a decreased product yield. Surprisingly, use of a combination of methanol and *p*-TsOH·H₂O remarkably enhanced the yield of isolated **3 a** to 87%, adopting a relay pathway in which TFA promoted the reaction to partially form product **3 a** as well as the reaction intermediates, and *p*-TsOH·H₂O facilitated transformations of these intermediates to form the target product in the presence of methanol. The optimized reaction conditions were thus defined as the following: The reaction of **1 a** (0.3 mmol) and **2 a** (0.6 mmol) was carried out in the presence of TFA (12 mmol) in DCE (5 mL) at 40 °C for 24 h under a nitrogen atmosphere, and then MeOH (5 mL) and *p*-TsOH·H₂O (0.5 mmol) were added and the reaction was continued for another 2 h prior to workup.

Under the optimized conditions, the protocol's generality was explored (Table 1). Both *N*-methyl- and *N*-benzyl-substituted pyrroles efficiently underwent the reactions with α -acetyl ketene di(ethylthio)acetal **2 a** to give the target products **3 a** (87%) and **3 b** (82%), respectively, and *N*-phenylpyrrole reacted to form **3 c** in a lower yield (49%; Table 1, entries 1–3), whereas *N*-methyl-2-acetylpyrrole, *N*-tosyl- and *N*-Boc-substituted pyrroles did not exhibit any reactivity in the presence of **2 a**. Treatment of *N*-methyl-2-arylpyrroles with **2 a** under the stated conditions afforded **3 d–i** in 60–94% yields, and substituents such as methyl, chloro and fluoro are tolerated on the 2-aryl moieties of substrates **1** to obviously enhance the product yields (Table 1, entries 4–9). 3-Ethyl-*N*-methylpyrrole also reacted with

Table 1. Annulation of α -oxo ketene dithioacetals (**2**) to pyrroles (**1**)^[a]

Entry	2	3	Yield [%]
1		2 a	3 a , R ¹ = Me 87
2		2 a	3 b , R ¹ = Bn 82
3		2 a	3 c , R ¹ = Ph 49
4	2 a		3 d 74
5	2 a		3 e , X = Cl 94
6	2 a		3 f , X = Me 74
7	2 a		3 g , X = H 60
8	2 a		3 h , X = F 78
9	2 a		3 i , X = Cl 89
10	2 a		3 j 72
11		2 b	3 k 63
12		2 c , X = Cl	3 l , X = Cl 91
13		2 d , X = CF ₃	3 m , X = CF ₃ 76
14		2 c	3 n 72
15		2 e , X = H	3 o , X = H 57
16		2 f , X = F	3 p , X = F 52
17		2 g , X = Cl	3 q , X = Cl 68
18		2 h , X = Br	3 r , X = Br 68
19		2 i , X = I	3 s , X = I 65
20		2 j , X = CF ₃	3 t , X = CF ₃ 73
21		2 k , X = CN	3 u , X = CN 67
22		2 l	3 v 74
23		2 m	3 w 59

Table 1. (Continued)

Entry	2	3	Yield [%]
24	2n, X = Cl	3x, X = Cl	79
25	2o, X = Br	3y, X = Br	81
26	2n, X = Cl	3z, X = Cl	88
27	2o, X = Br	3z1, X = Br	79
28	2p	3z2	78
29	2p	3z3	62
30	2q	3z4, X = H	56
31	2q	3z5, X = Cl	49
32	2r	3z6	84
33	2s	3z7	87
34	2t	3z8	95

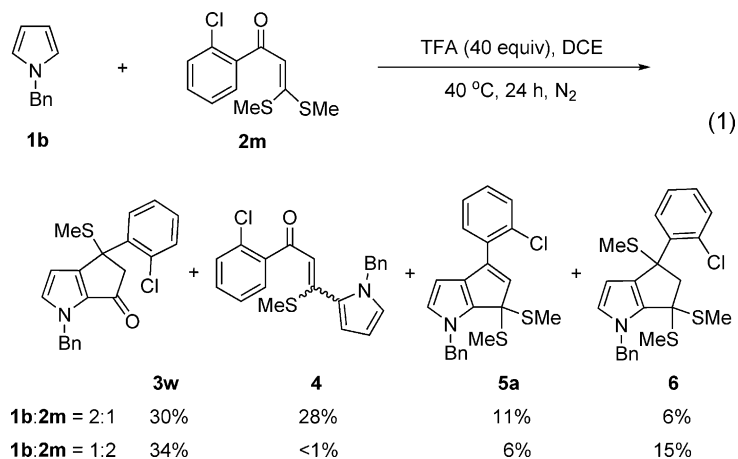
[a] Conditions: 1) **1** (0.3 mmol), **2** (0.6 mmol), TFA (12 mmol), DCE (5 mL), 40 °C, N₂, 24 h; then 2) *p*-TsOH·H₂O (0.5 mmol), MeOH (5 mL), 40 °C, N₂, 2 h. [b] Yield of isolated product.

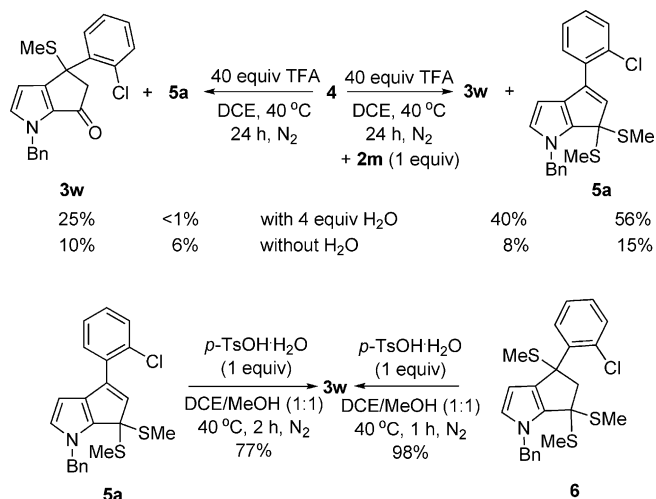
(95%; Table 1, entries 33 and 34), respectively. The molecular structures of cyclopenta[*b*]pyrroles **3** were further confirmed by X-ray crystallographic structural determination of **3z5** (see the Supporting Information). It is notable that acid-sensitive substrates, such as cinnamoyl ketene dithioacetals, *N*-H pyrroles and *N*-triisopropylsilyl pyrrole, underwent undesired reactions, giving no target products under the same conditions.

To elucidate the mechanism of the reaction of **1** and **2**, control experiments were performed. The reaction of *N*-benzyl pyrrole (**1b**) with α -oxo ketene dithioacetal **2m** was carried out in a 2:1 molar ratio in the presence of TFA (40 equiv) in dichloroethane at 40 °C for 24 h to give the target product **3w** (30%) and three separable intermediates **4** (28%), **5a** (11%), and **6** (6%), although **4** could not be isolated in the presence of excessive amount of **2m** [Eq. (1)]. Intermediates **5a** and **6** were unstable on silica gel and had to be isolated by means of basic alumina column chromatography. In a similar fashion, the reaction intermediate of type **5**, that is, **5b**, was isolated in 6% yield from the reaction of **1b** and **2q** in a 2:1 molar ratio. The molecular structures of **5b** and **6** were structurally characterized by X-ray crystallography (see the Supporting Information). Intermediate **4** was treated with trifluoroacetic acid (TFA) and water under the stated conditions to give the target product **3w** in 25% yield, and in the presence of α -oxo ketene dithioacetal **2m** (1 equiv) gave both **3w** (40%) and intermediate **5a** (56%; Scheme 2), suggesting that an excess of substrate **2** facilitated transformation of intermediate **4** by acting as a thiol equivalent.^[13] It should be noted that, under the same conditions, replacement of TFA by *p*-TsOH·H₂O (1 equiv) led to no reaction. With both *p*-TsOH·H₂O (1 equiv) and methanol as additives, intermediates **5a** and **6** were converted into **3w** in 77% and 98% yields, respectively, revealing that a strong Brønsted acid such as *p*-TsOH·H₂O could promote the efficient transformations of these intermediates with the aid of methanol. Although deprotection of dithioacetals has been well documented,^[14] the present case represents a new method to deprotect dithianes to the corresponding ketones.

A plausible annulation mechanism is proposed in Scheme 3. The reaction of **1** with **2** may be initiated by protonating the carbonyl oxygen of **2** to form carbocation **A** or direct protonation of the polarized C=C bond to generate carbocation **A'**,

2a to give **3j** (72%; Table 1, entry 10). The reactions of α -aroyl ketene di(ethylthio)acetals **2b–k** with *N*-benzyl and *N*-methylpyrroles produced the corresponding cyclopenta[*b*]pyrroles **3k–u** in 52–91% yields (Table 1, entries 11–21). Di(methylthio)acetals **2l–q** were also employed to react with various *N*-substituted pyrroles, affording the target products **3v–z5** (49–88%), and in most cases, compounds **3** were obtained in good to excellent yields (Table 1, entries 22–31). Interestingly, α -acetyl ketene di(benzylthio)acetal (**2r**) efficiently reacted with **1a** to form **3z6** in 84% yield (Table 1, entry 32). Variation of the aliphatic R³ group in substrates **2** to ethyl and *tert*-butyl led to the target products **3z7** (87%) and **3z8**

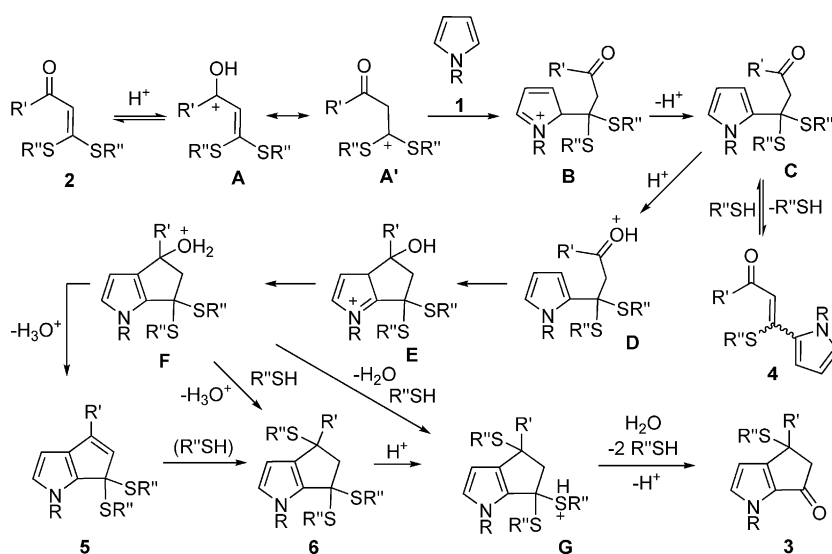




Scheme 2. Brønsted acid-mediated transformations of the reaction intermediates 4–6.

which is stabilized by the two adjacent electron-donating thioalkyls. Nucleophilic attack at the cationic carbon of **A'** by the C2 atom of pyrrole **1** generates species **B**, leading to intermediate **4** by loss of a proton and thiol R''SH from **C**. Species **C** is protonated to undergo electrophilic intramolecular cyclization to form **F**. Subsequent deprotonation and dehydration produces **5**, and addition of the in situ-generated thiol to **F** or **5** affords intermediate **6**. Brønsted acid-promoted deprotection of **6** or cascade thioalkylation/dethioacetalization of **F** gives the final product **3**.

Efforts were then made to prepare sulfur-free cyclopenta[*b*]pyrroles. By using *meta*-chloroperoxybenzoic acid (*m*-CPBA) as the oxidant,^[15] cyclopenta[*b*]pyrroles **3** were readily oxidized to the corresponding sulfones **7** and **9** in good to excellent yields (80–98%; Tables 2 and 3). Treatment of sulfones **7** obtained from the α -acetyl ketene dithioacetals with 1,8-diazabicy-



Scheme 3. Proposed annulation mechanism.

Table 2. Oxidation of **3** to sulfones (**7**) and sulfonyl elimination to **8**.^[a]

Entry	3 (R ¹ , R ² , R ⁴)	Yield [%] ^[b]	
		7	8
1	3a (Me, H, Et)	7a 93	8a 88
2	3z6 (Me, H, Bn)	7b 83	8a 92
3	3b (Bn, H, Et)	7c 85	8b 70
4	3v (Bn, H, Me)	7d 98	8b 79
5	3g (Me, 5-C ₆ H ₅ , Et)	7e 88	8c 90
6	3d (Me, 5-(<i>o</i> -MeC ₆ H ₄), Et)	7f 84	8d 93
7	3f (Me, 5-(<i>m</i> -MeC ₆ H ₄), Et)	7g 98	8e 80
8	3e (Me, 5-(<i>m</i> -ClC ₆ H ₄), Et)	7h 96	8f 75
9	3i (Me, 5-(<i>p</i> -ClC ₆ H ₄), Et)	7i 89	8g 99
10	3h (Me, 5-(<i>p</i> -FC ₆ H ₄), Et)	7j 97	8h 99
11	3j (Me, 4-Et, Et)	7k 96	8i 80

[a] Conditions for oxidation of **3** to give **7**: **3** (0.22 mmol), *m*-CPBA (0.66 mmol), CH₂Cl₂ (3 mL), RT, 1 h; conditions for sulfonyl elimination of **7** to give **8**: **7** (0.2 mmol), DBU (0.88 mmol), CH₂Cl₂ (2 mL), 35 °C, 22–70 h. [b] Yield of isolated product.

clo[5.4.0]undec-7-ene base (DBU; 4.4 equiv) in dichloromethane at 35 °C over a period of 22–70 h led to elimination of the sulfonyl moiety,^[16] affording cyclopenta[*b*]pyrrole-based terminal olefins **8** in 70–99% yields (Table 2). No obvious substituent effect was observed from *N*-benzyl, *m*-Me, *m*-Cl, or 4-Et (Table 2, entries 3, 4, 7, 8, and 11).

In a similar fashion, sulfones **9** were treated with DBU (Table 3). Unexpectedly, **9** readily underwent sulfonyl elimination with 1.2 equivalents of DBU, and the desired products **10** were not detected. 3-Arylindenones and cyclic enones have been known to undergo photodimerization in a confined environment^[17] or under heating conditions,^[18] and their [2+2] cycloaddition usually formed a mixture of head-to-tail and head-to-head photodimers, in which conversion of the substrates and selectivity of the dimeric products strongly depended on the reaction conditions. To our surprise, compounds **11** were directly formed from **9** in excellent yields up to 98% (Table 3), suggesting the instantaneous dimerization of the in situ-generated **10** upon exposure to daylight. The molecular structures of **11** were confirmed by the X-ray crystallographic structural determination of **11c** (see the Supporting Information). Further functionalization of **3r** and **3s** was achieved by means of Suzuki coupling with *p*-tolylboronic acid, affording **12** in 74%

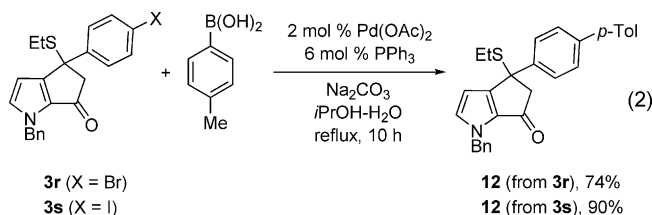
Table 3. Oxidation of **3** to sulfones (**9**) and sulfonyl elimination/[2+2] cycloaddition to **11**.^[a]

Entry	3 (R ¹ , R ² , Ar, R ⁴)	9	11
1	3z (Me, H, <i>m</i> -ClC ₆ H ₄ , Me)	9a	11a
2	3w (Bn, H, <i>o</i> -ClC ₆ H ₄ , Me)	9b	11b
3	3x (Bn, H, <i>m</i> -ClC ₆ H ₄ , Me)	9c	11c
4	3y (Bn, H, <i>m</i> -BrC ₆ H ₄ , Me)	9d	11d
5	3z2 (Bn, H, <i>p</i> -BrC ₆ H ₄ , Me)	9e	11e
6	3o (Bn, H, C ₆ H ₅ , Et)	9f	11f
7	3q (Bn, H, <i>p</i> -ClC ₆ H ₄ , Et)	9g	11g
8	3p (Bn, H, <i>p</i> -FC ₆ H ₄ , Et)	9h	11h
9	3m (Bn, H, <i>m</i> -CF ₃ C ₆ H ₄ , Et)	9i	11i
10	3z3 (Me, 4-Et, <i>p</i> -BrC ₆ H ₄ , Me)	9j	11j
11	3n (Me, 4-Et, <i>m</i> -ClC ₆ H ₄ , Et)	9k	11k

[a] Conditions for oxidation of **3** to give **9**: **3** (0.22 mmol), *m*-CPBA (0.66 mmol), CH₂Cl₂ (3 mL), RT, 1 h; conditions for sulfonyl elimination of **9** to give **11**: **9** (0.2 mmol), DBU (0.24 mmol), CH₂Cl₂ (2 mL), RT, 1 h. [b] Yield of isolated product.

and 90% yields, respectively [Eq. (2)], demonstrating a potential application of products **3**.

In conclusion, efficient synthesis of cyclopenta[*b*]pyrroles has been achieved by Brønsted acid-mediated annulation of α -oxo



ketene dithioacetals to *N*-substituted pyrroles. Further oxidation and sulfonyl elimination afforded structurally diverse cyclopenta[*b*]pyrroles. The present method provides a facile route to access cyclopenta[*b*]pyrrole derivatives under mild conditions.

Experimental Section

Typical procedure for annulation of pyrroles with α -oxo ketene dithioacetals

3a: Under a nitrogen atmosphere, to a solution of α -oxo ketene dithioacetal **2a** (114 mg, 0.6 mmol) in DCE (5 mL) were added pyrrole **1a** (24 mg, 0.3 mmol) and TFA (0.9 mL, 12 mmol). The mixture was stirred at 40 °C for 24 h and then MeOH (5 mL) and *p*-TsOH·H₂O (95 mg, 0.5 mmol) were successively added, and the reaction was continued at the same temperature for 2 h. After the mixture was allowed to cool to ambient temperature, water (20 mL) was added, and the resultant mixture was extracted with CH₂Cl₂ (3 × 15 mL). The combined organic phase was washed with saturated aqueous NaHCO₃ (10 mL), dried over anhydrous Na₂SO₄, and filtered, before volatiles were removed under reduced pres-

sure. The resulting residue was purified by column chromatography on silica gel [petroleum ether (60–90 °C)/AcOEt (15:1 v/v)] to afford **3a** as colorless oil (55 mg, 87%).

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Keywords: annulation · Brønsted acids · pyrroles · synthetic methods · thioacetals

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