DOI: 10.1002/ejoc.201001487

Sulfuric Acid-Catalyzed Regioselective Alkylation of Indoles and β-Naphthols with Ketene Dithioacetal-Based Allylic Alcohols

Mang Wang,*[a,b] Shaoguang Sun,[a] Deqiang Liang,[a] Bangyu Liu,[a] Ying Dong,[a] and Qun Liu*[a]

Keywords: Homogeneous catalysis / C-C coupling / Allylation / Regioselectivity / Indoles

A novel catalytic alkylation of indoles with allylic alcohols has been developed. Catalyzed by sulfuric acid (10 mol-%), the reaction between indoles **2** and allylic alcohols **1** based on ketene dithioacetal affords polyfunctionalized indoles **3** in good to excellent yields with high regioselectivities under mild conditions. The catalytic carbon–carbon coupling reaction provides a facile method for the environmentally benign functionalization of indoles with the advantages of good regiochemistry, atom efficiency, easily available catalyst, good yields and the synthetic potential of the polyfunctionalized indole products. Thus, further transformation of the resulting indoles **3** into pyridoindolone derivatives **4** was investigated. The efficiency of this carbon–carbon coupling reaction of **1** with **2** under the catalysis of sulfuric acid is due to the efficient formation of the reactive intermediate **I**, which is a carbocation that is strongly stabilized by two alkylthio groups at the terminal of the carbon–carbon double bond. The extension of this catalytic strategy to the synthesis of β-naphthols **5** was also achieved.

Introduction

The functionalization of indoles, especially through low cost, selective, and economically and environmentally friendly strategies, is of great synthetic importance for the preparation of pharmaceuticals, agrochemicals, and fine chemicals.[1] Among them, Lewis acid promoted Friedel–Crafts reactions have proved to be remarkably effective in the C3-alkylation of indoles under homogeneous, as well as heterogeneous, conditions.[2,3] In this field, although the alkylation of indoles with allyl halides, allyl acetates or allyl carbonates provides a valuable method for the direct allylation of indoles, these procedures generally suffer from problems associated with the regiochemistry of alkylation at the N1, C2 or C3 positions of the indole nucleus.[3]

Recently, the C–C coupling of alcohols as electrophiles with reactive carbon-centered nucleophiles has attracted the interest of many synthetic chemists due to the ready availability of starting materials, the atom efficiency, and the benign environmental nature.[4] However, the major limitation of these procedures is that either an excess of a protonic acid or a stoichiometric amount of a Lewis acid is required.[5] In the last years, a number of elegant methods involving metal complexes,[6] or metal salts[4a,7] as catalysts for the promotion of direct coupling between alcohols and nucleophiles have been developed, and some of these approaches have been successfully applied to the allylation of indoles.[6e,6g,6h] Brønsted acids are typically economical, benign, and easily available catalysts for organic reactions,[8] however, the coupling of alcohols with arenes in the presence of sub-stoichiometric loadings of Brønsted acids has been limited to the investigation of the allylation of indoles.[9]

During our ongoing research on ketene dithioacetal chemistry,[10,11] α-hydroxy ketene dithioacetals **1** were recognized as a type of reactive, functionalized allylic alcohol that could be used in the synthesis of useful compounds.[11,12] Taking into consideration the versatile reactivities of **1** as efficient electrophiles and the electron-rich indoles **2** as nucleohphiles, together with the importance of the functionalization of indoles, we decided to investigate the possibility of coupling **1** and **2** under the action of a range of available Brønsted acids as catalysts. To our delight, the reaction proceeded smoothly to afford the coupling products **3** in good to excellent yields with high regioselectivities in the presence of 10 mol-% of H_2SO_4 in acetonitrile at room temperature. The coupling products **3** were polyfunctionalized indoles that were successfully applied in the synthesis of pyridoindolone derivatives **4**. Additionally, the extension of this catalytic strategy to the synthesis of β-naphthols **5** was also achieved. In this paper, we wish to report this efficient, regioselective, and environmentally benign method for the allylation of indoles and β-naphthols using α-hydroxy ketene dithioacetals **1** as allylating agents under the catalysis of H_2SO_4.

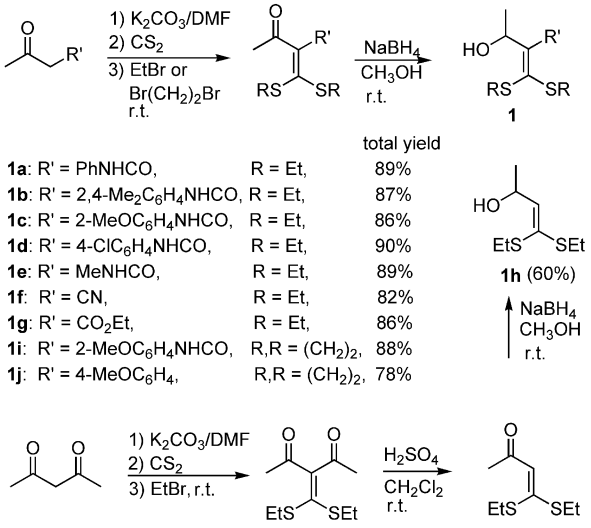
[a] Department of Chemistry, Northeast Normal University, Changchun 130024, P. R. of China
Fax: +86-431-85099759
E-mail: wangm452@nenu.edu.cn
liuqun@nenu.edu.cn
[b] State Key Laboratory of Fine Chemicals, Dalian University of Technology,
Dalian 116012, P. R. of China

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201001487.

Results and Discussion

Preparation of Starting Materials

According to the procedure reported previously, α-hydroxy ketene dithioacetals **1a**–**g**, **1i**, and **1j** were conveniently prepared in excellent yields through a two-step process involving the preparation of α-acetyl ketene dithioacetals (containing R′ = electron-withdrawing group or R′ = 4-$MeOC_6H_4$) starting from the corresponding active methylene compounds, carbon disulfide and alkyl halides in the presence of K_2CO_3, and sequential reduction of the corresponding α-acetyl ketene dithioacetals with $NaBH_4$.[11] For the preparation of substrate **1h** (R′ = H), an additional acid-promoted deacylation[13] was required before reduction of the α-acetyl ketene dithioacetal. The results are listed in Scheme 1.

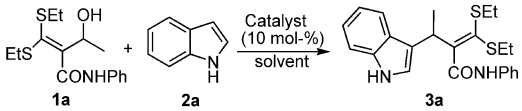


Scheme 1. Preparation of α-hydroxy ketene dithioacetals **1a**–**j**.

Optimization of Reaction Conditions for the Acid-Catalyzed Coupling of α-Hydroxy Ketene Dithioacetal 1a with Indole 2a

As an initial attempt, the reaction of 2-[bis(ethylthio)-methylene]-3-hydroxy-*N*-phenylbutanamide (**1a**; 1 mmol) with indole **2a** (1 mmol) catalyzed by 10 mol-% concentrated aqueous HCl, was carried out in acetonitrile (3 mL) at room temperature for 120 min (Table 1, entry 1). The reaction furnished a white solid in 65% yield after work-up and column chromatography of the resulting mixture. The product was characterized as 2-[bis(ethylthio)methylene]-3-(1*H*-indol-3-yl)-*N*-phenylbutanamide (**3a**) on the basis of its spectra and analytical data. The model reaction between **1a** and **2a** was then further examined to optimize the reaction conditions. As shown in Table 1, 10 mol-% concentrated aqueous H_2SO_4 could dramatically increase the yield of **3a** to 98% within 5 min (Table 1, entry 2). When organic acids were selected as catalyst, trifluoroacetic (TFA) and *p*-toluenesulfonic acid (PTSA) both gave the desired product in 79 and 90% yield, respectively, and required longer reaction times (Table 1, entries 3 and 4). Use of acetic acid afforded the product in only trace amounts, even after an extended reaction time (Table 1, entry 5). By comparison, coupling product **3a** was not be obtained in the absence of catalyst (Table 1, entry 6). Additionally, among the solvents tested (CH_3CN, tetrahydrofuran (THF), CH_2Cl_2, EtOH, and H_2O), acetonitrile proved to be the most efficient with respect to both the yield and reaction time (Table 1, entry 2 vs. entries 7–10).

Table 1. Optimization of conditions for the coupling between **1a** and **2a**.



Entry	Cat.	Solvent	Time [min]	Yield [%][a,b]
1	HCl	CH_3CN	120	65
2	H_2SO_4	CH_3CN	5	98
3	TFA	CH_3CN	240	79
4	PTSA	CH_3CN	30	90
5	AcOH	CH_3CN	720	trace[c]
6	–	CH_3CN	720	–[d]
7	H_2SO_4	THF	60	90
8	H_2SO_4	CH_2Cl_2	30	94
9	H_2SO_4	EtOH	720	–[d]
10	H_2SO_4	H_2O	720	–[d]

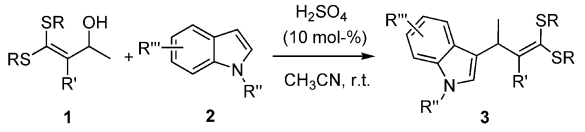
[a] Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), catalyst (0.1 mmol), solvent (3 mL), r.t. [b] Isolated yield. [c] Substrates **1a** and **2a** were recovered in 95 and 97%, respectively. [d] No reaction.

Sulfuric Acid-Catalyzed Coupling of α-Hydroxy Ketene Dithioacetals 1 with Indoles 2

Under the optimized conditions (Table 1, entry 2), the scope of the reaction was investigated. As described in Table 2, all α-hydroxy ketene diethyl thioacetals **1a**–**g** with a wide range of functional groups at the α-position, including *N*-aryl/alkyl carbonyl, cyano, and ethoxycarbonyl, reacted readily with indole **2a** to afford the coupling products **3** in excellent yields (Table 2, entries 1–7). In the case of **1h** (R = Et, R′ = H) as substrate, the reaction usually led to the formation of an unidentified mixture at room temperature. When the reaction of **1h** and **2a** was carried out at –40 °C, the desired product **3i** could be isolated in 78% yield (Table 2, entry 8). Similarly, α-hydroxy cyclic ketene dithioacetals **1i** (with an α-*N*-aryl carbonyl substituent) and **1j** (with an α-aryl substituent) also furnished the corresponding coupling product **3i** and **3j**, respectively, in high yield (Table 2, entries 9 and 10). The versatility of the above reaction was then demonstrated with the successful preparation of the corresponding coupling products **3** by treatment of various indoles **2** (1 mmol) with **1a** (1 mmol) under the catalysis of H_2SO_4. It was found that all the tested indoles **2** with substitutes at the 1-, 2-, 4-, and 5-positions were suitable substrates for the reaction, affording **3k**–**o** in

92–97% yields (Table 2, entries 11–15). It is noteworthy that these reactions were completed within 15 min to afford kinetically stable C3-allylated products, and no products allylated at either the C2 or N1 positions were detected in any of the cases. It is clear that the above results show a novel catalytic coupling with respect to a range of ketene dithioacetal-based allylic alcoholes **1** and indoles **2**. Thus, an efficient, environmental benign, and regioselective method for the allylation of indoles under very mild conditions has been developed.

Table 2. H_2SO_4-catalyzed coupling of α-hydroxy ketene dithioacetals **1** with indoles **2**.

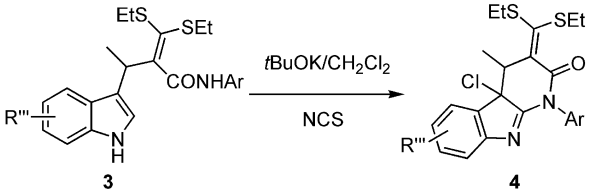


		R	R′	2	R′′	R′′′		Time [min]	Yield [%][a,b]
1	**1a**	Et	PhNHCO	**2a**	H	H	**3a**	5	98
2	**1b**	Et	2,4-$Me_2C_6H_3NHCO$	**2a**	H	H	**3b**	5	98
3	**1c**	Et	2-$MeOC_6H_4NHCO$	**2a**	H	H	**3c**	5	99
4	**1d**	Et	4-ClC_6H_4NHCO	**2a**	H	H	**3d**	10	95
5	**1e**	Et	MeNHCO	**2a**	H	H	**3e**	15	93
6	**1f**	Et	CN	**2a**	H	H	**3f**	5	94
7	**1g**	Et	CO_2Et	**2a**	H	H	**3g**	5	95
8	**1h**	Et	H	**2a**	H	H	**3h**	5	78[c]
9	**1i**	$(CH_2)_2$	2-MeC_6H_4NHCO	**2a**	H	H	**3i**	5	98
10	**1j**	$(CH_2)_2$	4-$MeOC_6H_4$	**2a**	H	H	**3j**	5	85[c]
11	**1c**	Et	2-$MeOC_6H_4NHCO$	**2b**	Et	H	**3k**	5	97
12	**1a**	Et	PhNHCO	**2c**	Et	2-Ph	**3l**	5	95
13	**1a**	Et	PhNHCO	**2d**	H	4-MeO	**3m**	15	92
14	**1a**	Et	PhNHCO	**2e**	H	5-MeO	**3n**	15	93
15	**1a**	Et	PhNHCO	**2f**	H	5-Br	**3o**	12	95

[a] Reaction conditions: **1** (1 mmol), **2** (1 mmol), conc. H_2SO_4 (0.1 mmol), CH_3CN (3 mL), r.t. [b] Isolated yields. [c] The reaction was performed at –40 °C.

Application of the Resulting Polyfunctionalized Indoles 3

As presented above, the H_2SO_4-catalyzed coupling reaction of **1** with **2** gives facile access to polyfunctionalized indoles. These functional groups can provide opportunities for further elaboration of these indoles. Thus, a simple cyclization of indoles **3** was examined in the presence of *N*-chlorosuccinimide (NCS) under basic conditions[14] for the synthesis of pyridoindolone derivatives **4**.[15] As summarized in Scheme 2, all the tested cyclizations of **3** furnished 3-[bis(ethylthio)methylene]-4a-chloro-4-methyl-1-aryl-4,4a-dihydro-1*H*-pyrido[2,3-*b*]indol-2(3*H*)-ones **4** in good to high yield. No dehydrochlorination product of **4** was isolated in any of the cases. Further attempts at the dehydrochlorination of **4** under basic conditions led to complex mixtures. Products **4** were well-characterized by their spectra and analytical data, and their structure was further established by X-ray diffraction studies of **4a** (Figure 1).[16]



	Ar	R'''		Time	*T*	Yield
3a	Ph	H	**4a**	5 min	r.t.	92%
3c	2-$MeOC_6H_4$	H	**4b**	10 min	r.t.	85%
3d	4-ClC_6H_4	H	**4c**	3 min	r.t.	78%
3m	Ph	4-MeO	**4d**	2 min	0 °C	70%
3n	Ph	5-MeO	**4e**	3 min	0 °C	72%
3o	Ph	5-Br	**4f**	5 min	r.t.	82%

Scheme 2. Synthesis of pyridoindolone derivatives **4** through the cyclization of **3** in the presence of NCS.

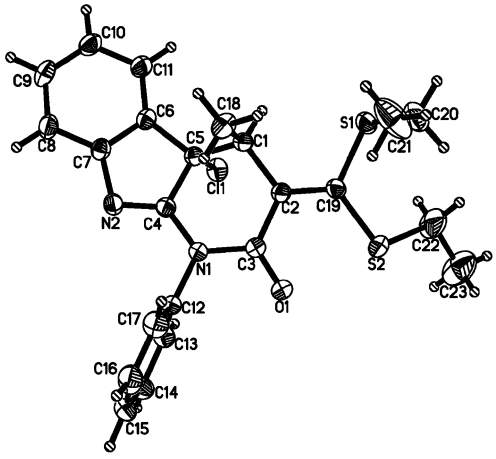
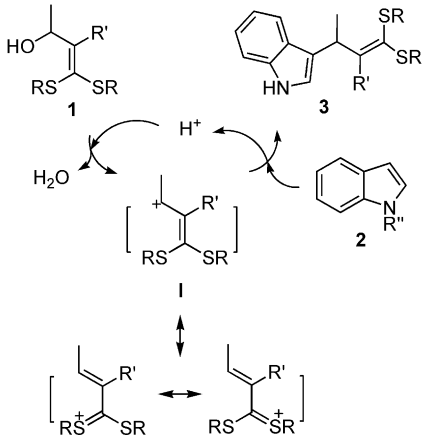


Figure 1. Molecular structure of **4a**.

Mechanism for the Sulfuric Acid-Catalyzed Coupling Reaction of α-Hydroxy Ketene Dithioacetals 1 with Indoles 2

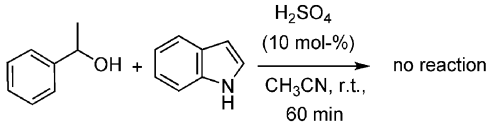
The H_2SO_4-catalyzed allylation of indoles described above represents a green and inexpensive catalytic process for the C–C coupling of alcohols as electrophiles with nucleophiles. It is widely known that the generation of a stable carbocation from a protonated alcohol is the most important issue in proton-catalyzed nucleophilic substitution of alcohols. Generally, an excess of a protonic acid is required for efficient activation of alcohols due to the poor leaving ability of the hydroxyl group.[5] In fact, the range of possible Brønsted acids as catalyst in sub-stoichiometric loadings for this procedure is rather limited.[4,9] Based on the nature of the functionalized ketene dithioacetals and on our previous work,[10,11] the efficient production of highly delocalized allylic carbocation **I**, which is stabilized by two alkythiol groups, plays an important role in the H_2SO_4-catalyzed C–C coupling reaction of α-hydroxy ketene dithioacetals **1** with indoles **2** in our experiments. As shown in Scheme 3, the coupling reaction starts with the formation of carbocation intermediate **I** by protonation and sequential dehy-

dration of **1** in the presence of H_2SO_4. Then, nucleophilic attack of indoles **2** on carbocation **I** leads to the coupling product **3**.



Scheme 3. Stable carbocation **I** as an intermediate in the H_2SO_4-catalyzed coupling of **1** with **2**.

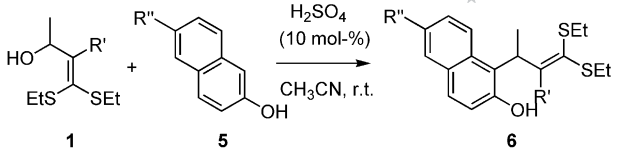
To discover the key role of the ketene dithioacetal functionality for these procedures, the reaction of 1-phenylethanol and indole was investigated (Scheme 4). In contrast to the H_2SO_4-catalyzed coupling reactions of α-hydroxy ketene dithioacetals **1** with indoles **2**, which were completed within 15 min (Table 2), no reaction was detected when 1-phenylethanol and indole were submitted to identical reaction conditions for 60 min; prolonging the reaction time to 240 min, led to only trace amounts of an unidentified compound (TLC analysis).



Scheme 4. H_2SO_4-catalyzed reaction of 1-phenylethanol and indole.

Sulfuric Acid-Catalyzed Coupling of α-Hydroxy Ketene Dithioacetals 1 with β-Naphthols 5

Recently, an $AlCl_3$ (1 equiv.) mediated C–C coupling reaction between α-hydroxy ketene dithioacetals **1** and β-naphthols **5** was realized in our laboratory, and an efficient synthesis of 3,4-disubstituted dihydrocoumarins was thus developed based on this synthetic strategy.[11c] To pursue a more efficient coupling between **1** and **5** and also to explore the scope of the catalytic coupling reaction of ketene dithioacetal-based allylic alcohols with nucleophiles, the H_2SO_4-catalyzed coupling of **1** with **5** was investigated. As expected, when the selected α-hydroxy ketene dithioacetals **1a** (or **1c**, **1f**, **1g**; 1 mmol) were reacted with β-naphthol **5a** (or **5b**; 1 mmol) in acetonitrile (3 mL) at room temperature in the presence of H_2SO_4 (10 mol-%), the coupling products **6a**–**e** were obtained in 65–82% isolated yields, respectively, within 4.5 h (Scheme 5).



	R'	R''	Time	Yield
6a:	PhNHCO	H	1 h	76%
6b:	2-$MeOC_6H_4NHCO$	H	1.5 h	82%
6c:	CN	H	0.5 h	80%
6d:	CO_2Et	H	4 h	65%
6e:	2-$MeOC_6H_4NHCO$	Br	4.5 h	74%

Scheme 5. H_2SO_4-catalyzed coupling of α-hydroxy ketene dithioacetals **1** with β-naphthols **5**.

Conclusions

This paper demonstrates an environmentally benign and regioselective H_2SO_4-catalyzed allylation of indoles and β-naphthols with ketene dithioacetal-based allylic alcohols. The reactions provide densely functionalized indoles and β-naphthols **3** and **6**, which are interesting building blocks in organic synthesis, from readily available starting materials **1** in good to excellent yields and in high regioselectivities under very mild reaction conditions. The preparation of pyridoindolone derivatives **4** was achieved by the cyclization of functionalized indoles **3** in the presence of NCS under the action of base. Future studies will focus on extending the scope of this catalytic C–C coupling reaction and on its synthetic applications in organic chemistry.

Experimental Section

General: All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel (300–400 mesh). All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). ^1H and ^{13}C NMR spectra were determined at ambient temperature with a Varian 500 MHz and 125/100 MHz spectrometer, respectively, using TMS as internal standard. All shifts are given in ppm. IR spectra (KBr) were recorded with a Magna-560 FTIR spectrophotometer in the range of 400–4000 cm^{-1}. Mass spectra were measured with an Agilient 1100 LCMsD spectrometer. Elemental analyses were obtained with a VarioEL analyzer. For X-ray analysis, compound **4a** (crystal dimension $0.22 \times 0.18 \times 0.15$ mm) was glued onto a glass fiber. Data were collected with a Bruker Smart Apex2 CCD diffractometer at 293 K using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and IP technique in the range $1.60° < \theta < 26.07°$.

Typical Procedure for the Coupling Reaction of 1 with 2. Compound 2a: To a solution of 2-[bis(ethylthio)methylene]-3-hydroxy-*N*-phenylbutanamide (**1a**; 311 mg, 1 mmol) and indole **2a** (117 mg, 1 mmol) in CH_3CN (3 mL) was added concentrated H_2SO_4 in CH_3CN (0.1 mL, 1 mol L^{-1}, 0.1 mmol) at room temperature. The reaction was allowed to proceed at room temperature and was complete within 5 min. The reaction was quenched with saturated aqueous $NaHCO_3$, and **3a** (402 mg, 98%) was collected as a white solid by filtration and dried in air.

Typical Procedure for the Synthesis of 4. Compound 4a: To a solution of **3a** (205 mg, 0.5 mmol) and *t*BuOK (224 mg, 2 mmol) in CH_2Cl_2 (5 mL) was added NCS (160 mg, 1.2 mmol). The reaction was allowed to proceed at room temperature and was complete within 5 min. The reaction mixture was poured into saturated aqueous NaCl (10 mL) and extracted with CH_2Cl_2 (3×, 10 mL). The combined organic extracts were washed with water, dried with anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/diethyl ether, 12:1) to give **4a** (203 mg, 92%) as a yellow solid.

Typical Procedure for the Coupling Reaction of 1 with 5. Compound 5a: To a solution of 2-[bis(ethylthio)methylene]-3-hydroxy-*N*-phenylbutanamide (**1a**; 311 mg, 1 mmol) and β-naphthol **5a** (144 mg, 1 mmol) in CH_3CN (3 mL) was added concentrated H_2SO_4 in CH_3CN (0.1 mL, 1 mol L^{-1}, 0.1 mmol) at room temperature. The reaction was allowed to proceed at room temperature and was complete in 1 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (pH 6), extracted with CH_2Cl_2 (3×, 8 mL) and the combined organic extracts were washed with water, dried with anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/diethyl ether, 80:1 then 40:1) to give **6a** (332 mg, 76%) as a white solid.

2-[Bis(ethylthio)methylene]-3-(1*H*-indol-3-yl)-*N*-phenylbutanamide (3a): White solid; m.p. 186–188 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.23 (t, J = 7.0 Hz, 3 H, CH_3), 1.42 (t, J = 7.0 Hz, 3 H, CH_3), 1.61 (d, J = 7.0 Hz, 3 H, CH_3), 2.70–2.75 (m, 1 H, SCH), 2.83–2.89 (m, 1 H, SCH), 2.95–2.97 (m, 2 H, SCH_2), 5.01 (q, J = 7.0 Hz, 1 H, CH), 6.22 (d, J = 3.0 Hz, 1 H, NH), 6.70 (d, J = 7.5 Hz, 3 H, 3× ArH), 6.94 (t, J = 7.5 Hz, 1 H, ArH), 7.09 (q, J = 7.5 Hz, 2 H, 2× ArH), 7.18 (t, J = 7.5 Hz, 1 H, ArH), 7.26 (t, J = 7.5 Hz, 1 H, ArH), 7.40 (d, J = 8.0 Hz, 1 H, ArH), 7.60 (d, J = 8.0 Hz, 1 H, ArH), 8.25 (s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7, 152.3, 137.3, 136.7, 130.0, 128.9 (2 C), 127.2, 124.3, 122.6, 122.3, 120.2, 120.0 (2 C), 118.4, 117.4, 112.0, 35.2, 27.8, 27.5, 18.7, 15.9, 15.0 ppm. IR (KBr): $\tilde{\nu}$ = 3396, 3298, 3057, 2976, 2361, 1659, 1512 cm^{-1}. $C_{23}H_{26}N_2OS_2$ (410.15): calcd. C 67.28, H 6.38, N 6.82; found C 67.10, H 6.26, N 6.80.

2-[Bis(ethylthio)methylene]-*N*-(2,4-dimethylphenyl)-3-(1*H*-indol-3-yl)butanamide (3b): Yellow solid; m.p. 114–116 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.21 (t, J = 7.0 Hz, 3 H, CH_3), 1.22 (s, 3 H, CH_3), 1.41 (t, J = 7.0 Hz, 3 H, CH_3), 1.65 (d, J = 7.0 Hz, 3 H, CH_3), 2.16 (s, 3 H, CH_3), 2.67–2.71 (m, 1 H, SCH), 2.88–2.95 (m, 2 H, SCH_2), 3.00–3.03 (m, 1 H, SCH), 5.04 (q, J = 7.0 Hz, 1 H, CH), 6.07 (s, 1 H, NH), 6.72 (s, 1 H, ArH), 6.84 (t, J = 8.0 Hz, 1 H, ArH), 6.86 (s, 1 H, ArH), 7.12 (t, J = 7.5 Hz, 1 H, ArH), 7.18 (t, J = 7.5 Hz, 1 H, ArH), 7.30 (d, J = 8.0 Hz, 1 H, ArH), 7.34 (d, J = 8.0 Hz, 1 H, ArH), 7.57 (d, J = 8.0 Hz, 1 H, ArH), 8.20 (s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7, 152.6, 136.9, 134.5, 133.0, 131.0, 129.9, 129.3, 127.2, 127.1, 122.4 (2 C), 122.2, 120.1, 118.5, 117.3, 112.0, 35.3, 27.8, 27.5, 21.0, 18.7, 16.6, 15.8, 15.1 ppm. IR (KBr): $\tilde{\nu}$ = 3416, 3277, 3060, 2971, 1647, 1513 cm^{-1}. $C_{25}H_{30}N_2OS_2$ (438.18): calcd. C 68.45, H 6.89, N 6.39; found C 68.30, H 6.82, N 6.41.

2-[Bis(ethylthio)methylene]-3-(1*H*-indol-3-yl)-*N*-(2-methoxyphenyl)-butanamide (3c): Yellowish solid; m.p. 162–164 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.20 (t, J = 7.5 Hz, 3 H, CH_3), 1.40 (t, J = 7.5 Hz, 3 H, CH_3), 1.64 (d, J = 7.0 Hz, 3 H, CH_3), 2.63–2.68 (m, 1 H, SCH), 2.85–2.95 (m, 2 H, SCH_2), 3.00–3.05 (m, 1 H, SCH), 3.28 (s, 3 H, CH_3), 5.06 (q, J = 7.0 Hz, 1 H, CH), 6.59 (d, J = 7.5 Hz, 1 H, ArH), 6.83 (t, J = 7.5 Hz, 1 H, ArH), 6.88 (t, J = 7.5 Hz, 1 H, ArH), 6.90 (s, 1 H, NH), 6.98 (s, 1 H, ArH), 7.15 (t, J = 7.5 Hz, 1 H, ArH), 7.21 (t, J = 7.5 Hz, 1 H, ArH), 7.32 (d, J = 8.0 Hz, 1 H, ArH), 7.64 (d, J = 8.0 Hz, 1 H, ArH), 8.09 (s, 1 H, NH), 8.28 (d, J = 8.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.5, 152.7, 147.8, 136.8, 129.8, 127.8, 127.1, 123.4, 122.2, 122.0, 121.0, 119.7, 119.4, 119.0, 117.5, 111.5, 109.9, 55.5, 35.1, 27.6, 27.5, 18.7, 15.7, 14.8 ppm. IR (KBr): $\tilde{\nu}$ = 3377, 3308, 3059, 2970, 2867, 1645, 1285 cm^{-1}. $C_{24}H_{28}N_2O_2S_2$ (440.16): calcd. C 65.42, H 6.41, N 6.36; found C 65.69, H 6.55, N 6.36.

2-[Bis(ethylthio)methylene]-*N*-(4-chlorophenyl)-3-(1*H*-indol-3-yl)-butanamide (3d): White solid; m.p. 208–210 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (t, J = 7.0 Hz, 3 H, CH_3), 1.42 (t, J = 7.0 Hz, 3 H, CH_3), 1.64 (d, J = 7.0 Hz, 3 H, CH_3), 2.71–2.74 (m, 1 H, SCH), 2.83–2.86 (m, 1 H, SCH), 2.98–3.00 (m, 2 H, SCH_2), 5.02 (q, J = 7.0 Hz, 1 H, CH), 6.16 (s, 1 H, NH), 6.50 (d, J = 8.5 Hz, 2 H, 2× ArH), 6.94 (s, 1 H, ArH), 7.04 (d, J = 8.5 Hz, 2 H, 2× ArH), 7.19 (t, J = 8.0 Hz, 1 H, ArH), 7.26 (t, J = 8.0 Hz, 1 H, ArH), 7.39 (d, J = 8.0 Hz, 1 H, ArH), 7.60 (d, J = 8.0 Hz, 1 H, ArH), 8.06 (s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.5, 152.0, 136.7, 136.0, 130.3, 129.1 (2 C), 128.9, 127.2, 122.8, 122.1, 120.9 (2 C), 120.4, 118.4, 117.7, 112.0, 35.1, 27.9, 27.5, 18.9, 15.9, 15.0 ppm. IR (KBr): $\tilde{\nu}$ = 3386, 3301, 3057, 2973, 1656, 1507, 1102 cm^{-1}. $C_{23}H_{25}ClN_2OS_2$ (444.11): calcd. C 62.07, H 5.66, N 6.29; found C 61.91, H 5.59, N 6.31.

2-[Bis(ethylthio)methylene]-3-(1*H*-indol-3-yl)-*N*-methylbutanamide (3e): White solid; m.p. 148–150 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.20 (t, J = 7.0 Hz, 3 H, CH_3), 1.37 (t, J = 7.0 Hz, 3 H, CH_3), 1.63 (d, J = 7.0 Hz, 3 H, CH_3), 2.43 (d, J = 4.5 Hz, 3 H, CH_3), 2.67–2.73 (m, 1 H, SCH), 2.80–2.84 (m, 1 H, SCH), 2.88–2.98 (m, 2 H, SCH_2), 4.59 (d, J = 4.5 Hz, 1 H, NH), 4.98 (q, J = 7.0 Hz, 1 H, CH), 7.06 (s, 1 H, ArH), 7.11 (t, J = 7.0 Hz, 1 H, ArH), 7.19 (t, J = 7.0 Hz, 1 H, ArH), 7.38 (d, J = 8.0 Hz, 1 H, ArH), 7.57 (d, J = 8.0 Hz, 1 H, ArH), 8.49 (s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.3, 152.7, 136.5, 128.9, 127.1, 122.3, 122.1, 119.7, 118.9, 118.0, 111.7, 35.0, 27.7, 27.4, 26.2, 19.3, 15.8, 15.0 ppm. IR (KBr): $\tilde{\nu}$ = 3415, 3217, 3049, 2967, 2922, 2868, 1645, 1255 cm^{-1}. $C_{18}H_{24}N_2OS_2$ (348.13): calcd. C 62.03, H 6.94, N 8.04; found C 62.31, H 6.99, N 8.06.

2-[Bis(ethylthio)methylene]-3-(1*H*-indol-3-yl)butanenitrile (3f): White solid; m.p. 111–112 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25 (t, J = 7.0 Hz, 3 H, CH_3), 1.35 (t, J = 7.0 Hz, 3 H, CH_3), 1.62 (d, J = 7.0 Hz, 3 H, CH_3), 2.85–2.89 (m, 2 H, SCH_2), 3.00–3.05 (m, 2 H, SCH_2), 4.83 (q, J = 7.0 Hz, 1 H, CH), 7.11 (t, J = 7.5 Hz, 1 H, ArH), 7.20 (t, J = 7.5 Hz, 2 H, 2× ArH), 7.37 (d, J = 8.0 Hz, 1 H, ArH), 7.60 (d, J = 8.0 Hz, 1 H, ArH), 8.13 (s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.0, 136.1, 126.5, 126.0, 122.1, 121.6, 119.4, 118.8, 117.3, 117.0, 111.4, 34.1, 29.3, 28.6, 19.1, 15.5, 14.6 ppm. IR (KBr): $\tilde{\nu}$ = 3389, 3050, 2969, 2207, 1454, 1226 cm^{-1}. $C_{17}H_{20}N_2S_2$ (316.11): calcd. C 64.52, H 6.37, N 8.85; found C 64.79, H 6.53, N 8.81.

Ethyl 2-[Bis(ethylthio)methylene]-3-(1*H*-indol-3-yl)butanoate (3g): White solid; m.p. 125 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.0 Hz, 3 H, CH_3), 1.20 (t, J = 7.0 Hz, 3 H, CH_3), 1.32 (t, J = 7.0 Hz, 3 H, CH_3), 1.60 (d, J = 7.0 Hz, 3 H, CH_3), 2.72 (q, J = 7.0 Hz, 2 H, SCH_2), 2.88 (q, J = 7.0 Hz, 2 H, SCH_2), 3.92 (q, J = 7.0 Hz, 2 H, OCH_2), 4.86 (q, J = 7.0 Hz, 1 H, CH), 7.05 (s, 1 H, NH), 7.09 (t, J = 7.5 Hz, 1 H, ArH), 7.16 (t, J = 7.5 Hz, 1 H, ArH), 7.32 (d, J = 8.0 Hz, 1 H, ArH), 7.60 (d, J = 8.0 Hz, 1 H, ArH), 7.95 (s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.8, 149.6, 136.1, 129.9, 127.2, 121.8, 121.3, 119.4, 119.2, 118.1, 110.8, 60.2, 34.5, 27.6, 26.9, 19.5, 15.5, 14.5, 13.6 ppm. IR (KBr): $\tilde{\nu}$ = 3344, 3051, 2970, 2925, 1697, 1297 cm^{-1}. $C_{19}H_{25}NO_2S_2$ (363.13): calcd. C 62.77, H 6.93, N 3.85; found C 62.58, H 6.86, N 3.83.

3-[4,4-Bis(ethylthio)but-3-en-2-yl]-1*H*-indole (3h): Red oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.21 (t, J = 7.5 Hz, 3 H, CH_3), 1.29 (t, J = 7.5 Hz, 3 H, CH_3), 1.46 (d, J = 7.0 Hz, 3 H, CH_3), 2.68–2.75 (m, 2 H, SCH_2), 2.81–2.90 (m, 2 H, SCH_2), 4.52 (q, J = 7.0 Hz, 1 H, CH), 6.30 (d, J = 9.5 Hz, 1 H, =CH), 7.00 (s, 1 H, NH), 7.12 (t, J = 7.5 Hz, 1 H, ArH), 7.20 (t, J = 7.5 Hz, 1 H, ArH), 7.37 (d, J = 8.0 Hz, 1 H, ArH), 7.68 (d, J = 8.0 Hz, 1 H, ArH), 7.96 (s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.0, 136.4, 127.4, 126.7, 122.0, 120.4, 120.1, 119.7, 119.2, 111.2, 32.7, 27.0, 26.8, 20.8, 15.4, 14.3 ppm. IR (KBr): $\tilde{\nu}$ = 3415, 3055, 2963, 2867, 1455, 1261 cm^{-1}. $C_{16}H_{21}NS_2$ (291.11): calcd. C 65.93, H 7.26, N 4.81; found C 65.74, H 7.12, N 4.88.

2-(1,3-Dithiolan-2-ylidene)-3-(1*H*-indol-3-yl)-*N*-*o*-tolylbutanamide (3i): Yellowish solid; m.p. 200–201 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.24 (s, J = 7.0 Hz, 3 H, CH_3), 1.75 (d, J = 7.0 Hz, 3 H, CH_3), 3.44–3.51 (m, 4 H, SCH_2 CH_2S), 4.65 (q, J = 7.0 Hz, 1 H, CH), 6.89 (m, 2 H, 2× ArH), 7.06–7.12 (m, 2 H, 2× ArH), 7.17 (s, 1 H, ArH), 7.21–7.24 (t, J = 8.0 Hz, 1 H, ArH), 7.37 (d, J = 8.0 Hz, 1 H, ArH), 7.44 (s, 1 H, NH), 7.62 (d, J = 8.0 Hz, 1 H, ArH), 7.68 (d, J = 8.0 Hz, 1 H, ArH), 8.24 (s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, [D$_6$-]DMSO): δ = 164.8, 137.6, 136.8, 130.8, 129.6, 127.1, 126.6, 124.8, 123.7, 123.6 (2 C), 122.4, 119.7 (2 C), 119.6, 116.8, 112.3, 39.0, 38.0, 36.9, 18.8, 17.1 ppm. IR (KBr): $\tilde{\nu}$ = 3284, 3203, 3047, 2965, 2919, 1618, 1515, 1245 cm^{-1}. $C_{22}H_{22}N_2OS_2$ (394.12): calcd. C 66.97, H 5.62, N 7.10; found C 67.12, H 5.72, N 7.09.

3-[1-(1,3-Dithiolan-2-ylidene)-1-(4-methoxyphenyl)propan-2-yl]-1*H*-indole (3j): Yellowish solid; m.p. 158–160 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.43 (d, J = 7.0 Hz, 3 H, CH_3), 3.25–3.28 (m, 2 H, SCH_2), 3.48–3.53 (m, 2 H, SCH_2), 3.71 (s, 3 H, CH_3), 4.43 (q, J = 7.0 Hz, 1 H, CH), 6.59–6.66 (m, 5 H, 4× ArH, NH), 7.11–7.15 (m, 1 H, ArH), 7.17–7.21 (m, 1 H, ArH), 7.32 (d, J = 7.5 Hz, 1 H, ArH), 7.83 (d, J = 7.5 Hz, 2 H, 2× ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.3, 136.2, 133.2, 132.9, 131.9, 130.7 (2 C), 127.4, 121.9, 121.2, 120.1, 119.4, 119.2, 112.9 (2 C), 110.8, 55.0, 39.6, 38.2, 37.2, 18.2 ppm. IR (KBr): $\tilde{\nu}$ = 3420, 3061, 2954, 2859, 1644, 1242 cm^{-1}. $C_{21}H_{21}NOS_2$ (367.11): calcd. C 68.63, H 5.76, N 3.81; found C 66.76, H 5.70, N 3.85.

2-[Bis(ethylthio)methylene]-3-(1-ethyl-1*H*-indol-3-yl)-*N*-(2-methoxyphenyl)butanamide (3k): Yellowish solid; m.p. 146–148 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.11 (t, J = 7.0 Hz, 3 H, CH_3), 1.18 (t, J = 7.0 Hz, 3 H, CH_3), 1.39 (t, J = 7.0 Hz, 3 H, CH_3), 1.66 (d, J = 7.0 Hz, 3 H, CH_3), 2.60–2.64 (m, 1 H, SCH), 2.84–2.92 (m, 2 H, SCH_2), 2.99–3.04 (m, 1 H, SCH), 3.24 (s, 3 H, OCH_3), 3.95–4.00 (m, 2 H, NCH_2), 5.06 (q, J = 7.0 Hz, 1 H, CH), 6.56 (d, J = 7.5 Hz, 1 H, ArH), 6.82–6.87 (m, 3 H, 3× ArH), 6.93 (s, 1 H, NH), 7.13 (t, J = 7.5 Hz, 1 H, ArH), 7.22 (t, J = 7.5 Hz, 1 H, ArH), 7.26–7.28 (m, 1 H, ArH), 7.62 (d, J = 7.5 Hz, 1 H, ArH), 8.29 (d, J = 7.5 Hz, 1 H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.1, 152.8, 147.3, 136.2, 128.6, 127.5, 127.4, 124.6, 122.9, 121.5, 120.6, 119.0 (2 C), 118.8, 116.0, 109.3, 109.2, 55.1, 40.8, 34.8, 27.2 (2 C), 18.6, 15.5, 15.0, 14.5 ppm. IR (KBr): $\tilde{\nu}$ = 3420, 3063, 2971, 2924, 2362, 1676, 1516 cm^{-1}. $C_{26}H_{32}N_2O_2S_2$ (468.19): calcd. C 66.63, H 6.88, N 5.98; found C 66.39, H 6.72, N 5.93.

2-[Bis(ethylthio)methylene]-3-(1-methyl-2-phenyl-1*H*-indol-3-yl)-*N*-phenylbutanamide (3l): White solid; m.p. 128–130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.17 (t, J = 7.5 Hz, 3 H, CH_3), 1.22 (t, J = 7.5 Hz, 3 H, CH_3), 1.47 (d, J = 7.5 Hz, 3 H, CH_3), 2.64–2.85 (m, 4 H, 2× SCH_2), 3.37 (s, 3 H, NCH_3), 4.96 (q, J = 7.0 Hz, 1 H, CH), 6.27 (s, 1 H, NH), 6.87 (d, J = 8.0 Hz, 2 H, ArH), 6.98 (t, J = 7.5 Hz, 1 H, ArH), 7.08 (t, J = 7.5 Hz, 1 H, ArH), 7.15 (t, J = 7.5 Hz, 2 H, 2× ArH), 7.21–7.31 (m, 4 H, 4× ArH), 7.40–7.42 (m, 3 H, 3× ArH), 7.76 (d, J = 8.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 152.4, 138.3, 137.4, 135.8, 132.3, 131.1, 128.9, 128.4 (2 C), 128.2 (2 C), 128.0, 127.1, 123.8, 121.7, 119.9, 119.8 (2 C), 119.6 (2 C), 113.0, 109.2, 36.3, 30.2, 27.5, 26.9, 19.4, 15.1, 14.5 ppm. IR (KBr): $\tilde{\nu}$ = 3407, 3053, 3019, 2962, 2923, 2864, 1672, 1594, 1502, 1465, 1433 cm^{-1}. $C_{30}H_{32}N_2OS_2$ (500.20): calcd. C 71.96, H 6.44, N 5.59; found C 72.05, H 6.36, N 5.56.

2-[Bis(ethylthio)methylene]-3-(4-methoxy-1*H*-indol-3-yl)-*N*-phenylbutanamide (3m): White solid; m.p. 216–218 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.20 (t, J = 7.0 Hz, 3 H, CH_3), 1.37 (t, J = 7.5 Hz, 3 H, CH_3), 1.57 (d, J = 7.0 Hz, 3 H, CH_3), 2.58–2.62 (m, 1 H, SCH), 2.77–2.81 (m, 1 H, SCH), 2.88–2.93 (m, 1 H, SCH), 3.02–3.07 (m, 1 H, SCH), 3.97 (s, 3 H, OCH_3), 5.08 (q, J = 6.5 Hz, 1 H, CH), 6.51–6.56 (m, 3 H, 3× ArH), 6.62 (d, J = 8.0 Hz, 2 H, 2× ArH), 6.90 (t, J = 7.5 Hz, 1 H, ArH), 6.97 (d, J = 8.0 Hz, 1 H, ArH), 7.05 (t, J = 8.0 Hz, 2 H, 2× ArH), 7.11 (t, J = 8.0 Hz, 1 H, ArH), 8.22 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, DMSO): δ = 166.6, 154.1, 152.7, 138.8, 137.5, 128.4 (2 C), 127.8, 123.2, 121.5, 121.4, 119.8 (2 C), 118.2, 116.4, 104.8, 98.9, 55.1, 35.2, 27.1, 26.1, 21.7, 15.5, 14.6 ppm. IR (KBr): $\tilde{\nu}$ = 3401, 3285, 3054, 2970, 2924, 1658, 1591, 1505, 1434 cm^{-1}. $C_{24}H_{28}N_2O_2S_2$ (440.16): calcd. C 65.42, H 6.41, N 6.36; found C 65.61, H 6.37, N 6.22.

2-[Bis(ethylthio)methylene]-3-(5-methoxy-1*H*-indol-3-yl)-*N*-phenylbutanamide (3n): White solid; m.p. 168–170 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (t, J = 7.5 Hz, 3 H, CH_3), 1.42 (t, J = 7.5 Hz, 3 H, CH_3), 1.60 (d, J = 7.0 Hz, 3 H, CH_3), 2.71–2.73 (m, 1 H, SCH), 2.85–2.88 (m, 1 H, SCH), 2.94–2.96 (m, 1 H, SCH), 3.00–3.02 (m, 1 H, SCH), 3.87 (s, 3 H, OCH_3), 4.98 (q, J = 7.0 Hz, 1 H, CH), 6.24 (s, 1 H, NH), 6.69 (s, 1 H, ArH), 6.75 (d, J = 7.5 Hz, 2 H, 2× ArH), 6.91–6.98 (m, 2 H, 2× ArH), 7.06–7.13 (m, 3 H, 3× ArH), 7.31 (d, J = 7.5 Hz, 1 H, ArH), 8.20 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 154.3, 151.9, 136.9, 131.5, 129.7, 128.6 (2 C), 126.9, 124.1, 122.9, 119.9 (2 C), 116.3, 112.6, 112.3, 99.7, 55.8, 34.9, 27.5, 27.2, 18.3, 15.5, 14.8 ppm. IR (KBr): $\tilde{\nu}$ = 3380, 3311, 3052, 3019, 2964, 2927, 2869, 2829, 1658, 1588, 1515, 1486, 1436 cm^{-1}. $C_{24}H_{28}N_2O_2S_2$ (440.16): calcd. C 65.42, H 6.41, N 6.36; found C 65.64, H 6.56, N 6.28.

2-[Bis(ethylthio)methylene]-3-(5-bromo-1*H*-indol-3-yl)-*N*-phenylbutanamide (3o): Yellow solid; m.p. 170–172 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25 (t, J = 7.5 Hz, 3 H, CH_3), 1.43 (t, J = 7.5 Hz, 3 H, CH_3), 1.63 (d, J = 7.5 Hz, 3 H, CH_3), 2.70–2.74 (m, 1 H, SCH), 2.84–2.88 (m, 1 H, SCH), 2.97–3.01 (m, 2 H, SCH_2), 4.97 (q, J = 6.5 Hz, 1 H, CH), 6.19 (s, 1 H, NH), 6.86 (d, J = 8.0 Hz, 2 H, 2× ArH), 6.94–6.99 (m, 2 H, 2× ArH), 7.14 (t, J = 7.5 Hz, 2 H, 2× ArH), 7.26 (t, J = 8.5 Hz, 1 H, ArH), 7.32–7.34 (m, 1 H, ArH), 7.76 (s, 1 H, ArH), 8.13 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 151.2, 136.8, 134.9, 130.4, 128.8 (2 C), 128.6, 124.9, 124.4, 123.3, 120.8, 120.0 (2 C), 116.6, 113.2, 112.9, 34.7, 27.7, 27.2, 18.4, 15.7, 14.8 ppm. IR (KBr): $\tilde{\nu}$ = 3391, 3257, 2968, 2921, 1653, 1596, 1560, 1522, 1437 cm^{-1}. $C_{23}H_{25}BrN_2OS_2$ (488.06): calcd. C 56.44, H 5.15, N 5.72; found C 56.62, H 5.24, N 5.68.

3-[Bis(ethylthio)methylene]-4a-chloro-4-methyl-1-phenyl-4,4a-dihydro-1*H*-pyrido[2,3-*b*]indol-2(3*H*)-one (4a): White solid; m.p. 182–184 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.94 (d, J = 7.0 Hz, 3 H, CH_3), 1.30 (t, J = 7.5 Hz, 3 H, CH_3), 1.42 (t, J = 7.0 Hz, 3 H, CH_3), 2.97–3.10 (m, 4 H, 2× SCH_2), 4.60 (q, J = 7.0 Hz, 1 H, CH), 7.17–7.21 (m, 1 H, ArH), 7.31–7.37 (m, 4 H, 4× ArH), 7.42–7.46 (m, 2 H, 2× ArH), 7.48–7.54 (m, 2 H, 2× ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.0, 161.9, 157.1, 153.5, 135.8, 134.7, 130.6, 129.7, 129.3 (2 C), 128.6, 128.2 (2 C), 125.0, 122.2, 120.3, 68.5, 43.0, 31.6, 29.6, 16.4, 15.1, 14.2 ppm. IR (KBr): $\tilde{\nu}$ =

3060, 2958, 2925, 2856, 1672, 1576, 1492, 1257 cm^{-1}. $C_{23}H_{23}ClN_2OS_2$ (442.09): calcd. C 62.35, H 5.23, N 6.32; found C 62.29, H 5.29, N 6.25.

3-[Bis(ethylthio)methylene]-4a-chloro-1-(2-methoxyphenyl)-4-methyl-4,4a-dihydro-1*H*-pyrido[2,3-*b*]indol-2(3*H*)-one (4b): Yellow solid; m.p. 156 °C (dec.). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.98 (d, J = 7.0 Hz, 3 H, CH_3), 1.30 (t, J = 7.0 Hz, 3 H, CH_3), 1.42 (t, J = 7.5 Hz, 3 H, CH_3), 2.97–3.11 (m, 4 H, 2× SCH_2), 3.77 (s, 3 H, OCH_3), 4.61 (q, J = 7.0 Hz, 1 H, CH), 7.03 (d, J = 7.0 Hz, 1 H, ArH), 7.08–7.11 (m, 1 H, ArH), 7.14–7.17 (m, 1 H, ArH), 7.29–7.35 (m, 3 H, 3× ArH), 7.40–7.46 (m, 2 H, 2× ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.9, 161.7, 155.5, 154.6, 153.9, 135.1, 130.5 (2 C), 130.4, 129.6, 124.9, 124.7, 122.2, 121.3, 120.2, 112.0, 68.6, 55.7, 43.5, 31.3, 29.6, 15.5, 15.3, 14.3 ppm. IR (KBr): $\tilde{\nu}$ = 3062, 2958, 2919, 2863, 1680, 1572, 1499, 1281 cm^{-1}. $C_{24}H_{25}ClN_2O_2S_2$ (472.10): calcd. C 60.94, H 5.33, N 5.92; found C 60.86, H 5.26, N 5.90.

3-[Bis(ethylthio)methylene]-4a-chloro-1-(4-chlorophenyl)-4-methyl-4,4a-dihydro-1*H*-pyrido[2,3-*b*]indol-2(3*H*)-one (4c): Yellow solid; m.p. 124 °C (dec.). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.90 (d, J = 7.0 Hz, 3 H, CH_3), 1.30 (d, J = 7.5 Hz, 3 H, CH_3), 1.40 (t, J = 7.5 Hz, 3 H, CH_3), 2.94–3.10 (m, 4 H, 2× SCH_2), 4.61 (q, J = 7.5 Hz, 1 H, CH), 7.18 (t, J = 7.5 Hz, 1 H, ArH), 7.28–7.37 (m, 4 H, 4× ArH), 7.46–7.48 (m, 3 H, 3× ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.7, 161.7, 157.8, 153.3, 134.6, 134.4, 134.3, 130.7, 129.6 (2 C), 129.5 (2 C), 129.3, 125.1, 122.3, 120.2, 68.4, 42.8, 31.7, 29.7, 16.4, 15.1, 14.2 ppm. IR (KBr): $\tilde{\nu}$ = 3061, 2958, 2923, 2864, 1660, 1573, 1487, 1273 cm^{-1}. $C_{23}H_{22}Cl_2N_2OS_2$ (476.06): calcd. C 57.86, H 4.64, N 5.87; found C 57.78, H 4.58, N 5.86.

3-[Bis(ethylthio)methylene]-4a-chloro-5-methoxy-4-methyl-1-phenyl-4,4a-dihydro-1*H*-pyrido[2,3-*b*]indol-2(3*H*)-one (4d): White solid; m.p. 164–166 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.95 (d, J = 7.0 Hz, 3 H, CH_3), 1.30 (t, J = 7.5 Hz, 3 H, CH_3), 1.43 (t, J = 7.5 Hz, 3 H, CH_3), 3.00–3.08 (m, 4 H, 2× SCH_2), 3.97 (s, 3 H, OCH_3), 4.81 (q, J = 7.0 Hz, 1 H, CH), 6.71 (d, J = 8.5 Hz, 1 H, ArH), 6.99 (d, J = 7.5 Hz, 1 H, ArH), 7.28–7.34 (m, 3 H, 3× ArH), 7.44 (d, J = 7.0 Hz, 1 H, ArH), 7.51 (t, J = 8.0 Hz, 2 H, 2× ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.5, 162.0, 157.0, 155.3, 154.9, 135.9, 132.2, 129.9, 129.3 (2 C), 128.5, 128.2 (2 C), 120.3, 113.2, 107.9, 69.2, 55.8, 41.8, 31.7, 29.6, 16.4, 15.1, 14.2 ppm. IR (KBr): $\tilde{\nu}$ = 2967, 2922, 1675, 1567, 1523, 1488 cm^{-1}. $C_{24}H_{25}ClN_2O_2S_2$ (472.10): calcd. C 60.94, H 5.33, N 5.92; found C 61.06, H 5.28, N 5.88.

3-[Bis(ethylthio)methylene]-4a-chloro-6-methoxy-4-methyl-1-phenyl-4,4a-dihydro-1*H*-pyrido[2,3-*b*]indol-2(3*H*)-one (4e): Yellow solid; m.p. 148–150 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.95 (d, J = 7.0 Hz, 3 H, CH_3), 1.30 (t, J = 7.5 Hz, 3 H, CH_3), 1.42 (t, J = 7.5 Hz, 3 H, CH_3), 2.98–3.08 (m, 4 H, 2× SCH_2), 3.84 (s, 3 H, OCH_3), 4.57 (d, J = 7.0 Hz, 1 H, CH), 6.82–6.83 (m, 1 H, ArH), 7.03 (d, J = 2.5 Hz, 1 H, ArH), 7.28 (d, J = 7.5 Hz, 1 H, ArH), 7.34 (d, J = 7.5 Hz, 2 H, 2× ArH), 7.43 (d, J = 7.5 Hz, 1 H, ArH), 7.51 (t, J = 7.5 Hz, 2 H, 2× ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 161.7, 157.6, 156.5, 146.6, 136.0, 135.9, 129.8, 129.2 (2 C), 128.4, 128.1 (2 C), 120.6, 114.7, 109.1, 68.5, 55.6, 42.9, 31.5, 29.5, 16.3, 15.0, 14.1 ppm. IR (KBr): $\tilde{\nu}$ = 3662, 2966, 2926, 1671, 1577, 1476, 1409 cm^{-1}. $C_{24}H_{25}ClN_2O_2S_2$ (472.10): calcd. C 60.94, H 5.33, N 5.92; found C 60.81, H 5.36, N 5.91.

3-[Bis(ethylthio)methylene]-6-bromo-4a-chloro-4-methyl-1-phenyl-4,4a-dihydro-1*H*-pyrido[2,3-*b*]indol-2(3*H*)-one (4f): White solid; m.p. 178–180 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.96 (d, J = 7.0 Hz, 3 H, CH_3), 1.30 (t, J = 7.5 Hz, 3 H, CH_3), 1.42 (t, J = 7.5 Hz, 3 H, CH_3), 2.97–3.10 (m, 4 H, 2× SCH_2), 4.59 (q, J = 7.0 Hz, 1 H, CH), 7.22 (d, J = 8.0 Hz, 1 H, ArH), 7.32 (d, J = 7.5 Hz, 2 H, 2× ArH), 7.44 (t, J = 7.0 Hz, 2 H, 2× ArH), 7.52 (t, J = 7.5 Hz, 2 H, 2× ArH), 7.59 (s, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1, 161.6, 157.8, 152.6, 136.8, 135.7, 133.5, 129.3 (2 C), 129.0, 128.7, 128.1 (2 C), 125.5, 121.6, 117.9, 68.1, 42.8, 31.7, 29.7, 16.4, 15.1, 14.2 ppm. IR (KBr): $\tilde{\nu}$ = 3434, 3082, 2962, 2922, 1672, 1613, 1570, 1491, 1449 cm^{-1}. $C_{23}H_{22}BrClN_2OS_2$ (520.00): calcd. C 52.93, H 4.25, N 5.37; found C 52.86, H 4.32, N 5.35.

2-[Bis(ethylthio)methylene]-3-(2-hydroxynaphthalen-1-yl)-*N*-phenylbutanamide (6a): White solid; m.p. 147–149 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.80 (t, J = 7.5 Hz, 3 H, CH_3), 1.27 (t, J = 7.5 Hz, 3 H, CH_3), 1.59 (d, J = 7.5 Hz, 3 H, CH_3), 2.46–2.50 (m, 1 H, SCH), 2.58–2.52 (m, 1 H, SCH), 2.72–2.75 (m, 2 H, SCH_2), 5.09 (q, J = 7.5 Hz, 1 H, CH), 7.12 (d, J = 9.0 Hz, 1 H, ArH), 7.24 (t, J = 8.0 Hz, 1 H, ArH), 7.32 (d, J = 7.5 Hz, 1 H, ArH), 7.43 (t, J = 7.5 Hz, 2 H, 2× ArH), 7.51 (t, J = 7.5 Hz, 2 H, 2× ArH), 7.62–7.65 (m, 3 H, 2× ArH, OH), 7.77 (d, J = 8.0 Hz, 1 H, ArH), 8.04 (d, J = 8.0 Hz, 1 H, ArH), 10.15 (s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.6, 152.5, 147.3, 136.8, 136.7, 133.0, 129.3 (2 C), 128.3, 128.8, 128.6, 126.3, 125.5, 122.2, 121.9, 121.2, 120.6, 120.5 (2 C), 35.0, 29.1, 27.5, 17.6, 15.0, 14.9 ppm. IR (KBr): $\tilde{\nu}$ = 3264, 3059, 2966, 2866, 1618, 1541 cm^{-1}. $C_{25}H_{27}NO_2S_2$ (437.15): calcd. C 68.61, H 6.22, N 3.20; found C 68.43, H 6.18, N 3.17.

2-[Bis(ethylthio)methylene]-3-(2-hydroxynaphthalen-1-yl)-*N*-(2-methoxyphenyl)butanamide (6b): White solid; m.p. 134–135 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.70 (t, J = 7.5 Hz, 3 H, CH_3), 1.27 (t, J = 7.5 Hz, 3 H, CH_3), 1.56 (t, J = 7.5 Hz, 3 H, CH_3), 2.41–2.45 (m, 1 H, SCH), 2.50–2.54 (m, 1 H, SCH), 2.64–2.69 (m, 1 H, SCH), 2.74–2.78 (m, 1 H, SCH), 3.93 (s, 3 H, OCH_3), 5.11 (q, J = 7.5 Hz, 1 H, CH), 6.96 (d, J = 8.0 Hz, 1 H, ArH), 7.06 (t, J = 8.0 Hz, 1 H, ArH), 7.13 (d, J = 8.5 Hz, 1 H, ArH), 7.16 (t, J = 8.0 Hz, 1 H, ArH), 7.31 (t, J = 7.5 Hz, 1 H, ArH), 7.51 (t, J = 7.5 Hz, 1 H, ArH), 7.62 (d, J = 8.5 Hz, 1 H, ArH), 7.76 (d, J = 8.0 Hz, 1 H, ArH), 8.05 (d, J = 8.5 Hz, 1 H, ArH), 8.16 (s, 1 H, OH), 8.50 (d, J = 7.5 Hz, 1 H, ArH), 10.34 (s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.7, 152.8, 148.5, 148.1, 136.9, 133.4, 129.1, 129.0, 128.8, 126.9, 126.5, 125.1, 122.4, 122.2, 121.6, 121.5, 121.1, 120.6, 110.5, 56.1, 35.2, 28.9, 27.7, 17.7, 14.9, 14.8 ppm. IR (KBr): $\tilde{\nu}$ = 3363, 3064, 2967, 1641. 1527 cm^{-1}. $C_{26}H_{29}NO_3S_2$ (467.16): calcd. C 66.78, H 6.25, N 3.00; found C 66.95, H 6.44, N 2.97.

2-[Bis(ethylthio)methylene]-3-(2-hydroxynaphthalen-1-yl)butanenitrile (6c): White solid; m.p. 171–172 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.0 Hz, 3 H, CH_3), 1.23 (t, J = 7.0 Hz, 3 H, CH_3), 1.68 (d, J = 7.0 Hz, 3 H, CH_3), 2.56–2.61 (m, 1 H, SCH), 2.75–2.81 (m, 3 H, SCH, SCH_2), 4.88 (q, J = 7.0 Hz, 1 H, CH), 5.80 (s, 1 H, OH), 7.02 (d, J = 8.0 Hz, 1 H, ArH), 7.33 (t, J = 7.5 Hz, 1 H, ArH), 7.51 (t, J = 7.5 Hz, 1 H, ArH), 7.64 (d, J = 8.5 Hz, 1 H, ArH), 7.77 (d, J = 8.0 Hz, 1 H, ArH), 8.09 (d, J = 8.5 Hz, 1 H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.0, 150.4, 132.6, 129.2, 129.1, 128.9, 126.7, 126.5, 122.8, 122.6, 121.7, 119.1, 118.7, 34.9, 29.8, 28.7, 19.0, 15.4, 15.1 ppm. IR (KBr): $\tilde{\nu}$ = 3295, 3068, 2963, 2930, 2215, 1625, 1514, 1302 cm^{-1}. $C_{19}H_{21}NOS_2$ (343.11): calcd. C 66.43, H 6.16, N 4.08; found C 66.65, H 6.21, N 4.15.

Ethyl 2-[Bis(ethylthio)methylene]-3-(2-hydroxynaphthalen-1-yl)-butanoate (6d): Colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.0 Hz, 3 H, CH_3), 1.24 (t, J = 7.0 Hz, 3 H, CH_3), 1.44 (t, J = 7.0 Hz, 3 H, CH_3), 1.48 (d, J = 7.5 Hz, 3 H, CH_3), 2.44–

2.49 (m, 1 H, SCH), 2.58–2.69 (m, 3 H, SCH, SCH_2), 4.44 (q, J = 7.0 Hz, 2 H, OCH_2), 5.06 (q, J = 7.5 Hz, 1 H, CH), 7.11 (d, J = 8.0 Hz, 1 H, ArH), 7.34 (t, J = 7.5 Hz, 1 H, ArH), 7.53 (t, J = 7.5 Hz, 1 H, ArH), 7.65 (d, J = 8.5 Hz, 1 H, ArH), 7.78 (d, J = 8.0 Hz, 1 H, ArH), 8.06 (d, J = 8.5 Hz, 1 H, ArH), 8.66 (s, 1 H, OH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.8, 152.0, 144.5, 136.9, 132.8, 129.0, 128.7, 128.6, 126.3, 122.4, 122.1, 120.8, 120.6, 62.4, 34.2, 28.3, 27.2, 17.4, 15.0, 14.7, 14.1 ppm. IR (KBr): $\tilde{\nu}$ = 3307, 3057, 2975, 2871, 1684, 1317 cm^{-1}. $C_{21}H_{26}O_3S_2$ (390.13): calcd. C 64.58, H 6.71; found C 64.33, H 6.61.

2-[Bis(ethylthio)methylene]-3-(6-bromo-2-hydroxynaphthalen-1-yl)-*N*-(2-methoxyphenyl)butanamide (6e): White solid; m.p. 117–119 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.67 (t, J = 7.0 Hz, 3 H, CH_3), 1.25 (t, J = 7.0 Hz, 3 H, CH_3), 1.51 (d, J = 7.5 Hz, 3 H, CH_3), 2.42–2.52 (m, 2 H, SCH_2), 2.62–2.66 (m, 1 H, SCH), 2.72–2.76 (m, 1 H, SCH), 3.92 (s, 3 H, OCH_3), 5.00 (q, J = 7.5 Hz, 1 H, CH), 6.95 (d, J = 8.5 Hz, 1 H, ArH), 7.05 (t, J = 8.0 Hz, 1 H, ArH), 7.11–7.17 (m, 2 H, 2× ArH), 7.53 (t, J = 8.5 Hz, 2 H, 2× ArH), 7.90 (t, J = 8.5 Hz, 2 H, 2× ArH), 8.15 (s, 1 H, OH), 8.48 (d, J = 8.0 Hz, 1 H, ArH), 10.53 (s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.3, 152.9, 148.2, 147.1, 137.0, 131.7, 130.4, 129.9, 129.2, 127.6, 126.5, 124.9, 123.9, 122.5, 121.2, 121.1, 120.3, 115.6, 110.1, 55.7, 34.8, 31.0, 28.5, 27.5, 17.3, 14.6 ppm. IR (KBr): $\tilde{\nu}$ = 3310, 2970, 2928, 1640, 1528, 1294 cm^{-1}. $C_{26}H_{28}BrNO_3S_2$ (545.07): calcd. C 57.14, H 5.16, N 2.56; found C 57.36, H 5.29, N 2.50.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectroscopic data of all compounds.

Acknowledgments

Financial support of this research by the National Natural Sciences Foundation of China (20972029/21072027), the Fundamental Research Funds for the Central Universities (NENU-STC08007) and the State Key Laboratory of Fine Chemicals (KF1003) is gratefully acknowledged.

[1] a) R. J. Sundberg, in: *The Chemistry of Indoles*, Academic Press, New York, **1970**; b) R. J. Sundberg, in: *The Chemistry of Indoles*, Academic Press, New York, **1996**; c) J. F. Austin, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2002**, *124*, 1172–1173; d) D. A. Evans, K. A. Scheidt, K. R. Frandrick, H. W. Lam, J. Wu, *J. Am. Chem. Soc.* **2003**, *125*, 10780–10781; e) M. Bandini, A. Melloni, A. Umani-Ronchi, *Angew. Chem. Int. Ed.* **2004**, *43*, 550–556; f) M. Rueping, B. J. Nachtsheim, S. A. Moreth, M. Bolte, *Angew. Chem. Int. Ed.* **2008**, *47*, 593–596; g) S.-L. You, Q. Cai, M. Zeng, *Chem. Soc. Rev.* **2009**, *38*, 2190–2201; h) F.-L. Sun, M. Zeng, Q. Gu, S.-L. You, *Chem. Eur. J.* **2009**, *15*, 8709–8712.

[2] a) H. Yamamoto, in: *Lewis Acids in Organic Synthesis*, Wiley-VCH, Weinheim, **2000**; b) J. C. Antilla, A. Klapars, S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 11684–11688.

[3] a) M. Bandini, A. Melloni, S. Tommasi, A. Umani-Ronchi, *Synlett* **2005**, 1199–1222; b) X. Zhu, A. Ganesan, *J. Org. Chem.* **2002**, *67*, 2705–2708; c) M. Bandini, A. Melloni, A. Umani-Ronchi, *Org. Lett.* **2004**, *6*, 3199–3202; d) M. Westermaier, H. Mayr, *Org. Lett.* **2006**, *8*, 4791–4794; e) S. Ma, S. Yu, Z. Peng, H. Guo, *J. Org. Chem.* **2006**, *71*, 9865–9868.

[4] a) M. Yasuda, T. Somyo, A. Baba, *Angew. Chem. Int. Ed.* **2006**, *45*, 793–794; b) G. Guillena, D. J. Ramón, M. Yus, *Angew. Chem. Int. Ed.* **2007**, *46*, 2358–2364.

[5] For example: a) G. C. Gullickson, D. E. Lewis, *Aust. J. Chem.* **2003**, *56*, 385–388; b) F. Bisaro, G. Prestat, M. Vitale, G. Poli, *Synlett* **2002**, 1823–1826; c) S. J. Coote, S. G. Davies, D. Middlemiss, A. Naylor, *Tetrahedron Lett.* **1989**, *30*, 3581–3584; d) A. A. Khalaf, R. M. Roberts, *J. Org. Chem.* **1972**, *37*, 4227–4235.

[6] See, for instance: a) F. Ozawa, H. Okamoto, S. Kawagishi, S. Yamamoto, T. Minami, M. Yoshifuji, *J. Am. Chem. Soc.* **2002**, *124*, 10968–10969; b) Y. Nishibayashi, M. Yoshikawa, Y. Inada, M. Hidai, S. Uemura, *J. Am. Chem. Soc.* **2002**, *124*, 11846–11847; c) B. D. Sherry, A. T. Radosevich, F. D. Toste, *J. Am. Chem. Soc.* **2003**, *125*, 6076–6077; d) M. Georgy, V. Boucard, J.-M. Campagne, *J. Am. Chem. Soc.* **2005**, *127*, 14180–14181; e) M. Kimura, M. Futamata, R. Mukai, Y. Tamaru, *J. Am. Chem. Soc.* **2005**, *127*, 4592–4593; f) Y. Nishibayashi, M. D. Milton, Y. Inada, M. Yoshikawa, I. Wakiji, M. Hidai, S. Uemura, *Chem. Eur. J.* **2005**, *11*, 1433–1451; g) B. M. Trost, J. Quancard, *J. Am. Chem. Soc.* **2006**, *128*, 6314–6315; h) M. Bandini, A. Eichholzer, *Angew. Chem. Int. Ed.* **2009**, *48*, 9533–9537.

[7] See, for instance: a) M. Yasuda, T. Saito, M. Ueba, A. Baba, *Angew. Chem. Int. Ed.* **2004**, *43*, 1414–1416; b) I. Iovel, K. Mertins, J. Kischel, A. Zapf, M. Beller, *Angew. Chem. Int. Ed.* **2005**, *44*, 3913–3916; c) J. Liu, E. Muth, U. Flörke, G. Henkel, K. Merz, J. Sauvageau, E. Schwake, G. Dyker, *Adv. Synth. Catal.* **2006**, *348*, 456–462; d) K. Mertins, I. Iovel, J. Kischel, A. Zapf, M. Beller, *Adv. Synth. Catal.* **2006**, *348*, 691–695.

[8] a) R. Sanz, D. Miguel, A. Martínez, J. M. Álvarez-Gutiérrez, F. Rodríguez, *Org. Lett.* **2007**, *9*, 2027–2030 and references cited therein b) T. Akiyama, *Chem. Rev.* **2007**, *107*, 5744–5758.

[9] For selective examples, see: a) K. J. P. A. Grieco Jr., *J. Chem. Soc., Chem. Commun.* **1993**, 510–512; b) R. Sanz, A. Martínez, D. Miguel, J. M. Álvarez-Gutiérrez, F. Rodríguez, *Adv. Synth. Catal.* **2006**, *348*, 1841–1845; c) S. Shirakawa, S. Kobayashi, *Org. Lett.* **2007**, *9*, 311–314.

[10] For selected examples in our group, see: a) Z. Fu, M. Wang, Y. Ma, Q. Liu, J. Liu, *J. Org. Chem.* **2008**, *73*, 7625–7630; b) Y. Ma, M. Wang, D. Li, B. Bekturhun, J. Liu, Q. Liu, *J. Org. Chem.* **2009**, *74*, 3116–3121; c) H.-J. Yuan, M. Wang, Y.-J. Liu, Q. Liu, *Adv. Synth. Catal.* **2009**, *351*, 112–116; d) Y. Liu, M. Wang, H. Yuan, Q. Liu, *Adv. Synth. Catal.* **2010**, *352*, 884–892; e) D. Liang, M. Wang, B. Bekturhun, B. Xiong, Q. Liu, *Adv. Synth. Catal.* **2010**, *352*, 1593–1599; f) M. Wang, F. Han, H. Yuan, Q. Liu, *Chem. Commun.* **2010**, *46*, 2247–2249.

[11] a) J. Liu, M. Wang, B. Li, Q. Liu, Y. Zhao, *J. Org. Chem.* **2007**, *72*, 4401–4405; b) J. Liu, F. Liang, Q. Liu, B. Li, *Synlett* **2007**, 156–160; c) C.-R. Piao, Y.-L. Zhao, X.-D. Han, Q. Liu, *J. Org. Chem.* **2008**, *73*, 2264–2269.

[12] a) A. D. Thomas, C. V. Asokan, *Tetrahedron Lett.* **2002**, *43*, 2273–2275; b) S. K. Nair, A. M. Jose, C. V. Asokan, *Synthesis* **2005**, 1261–1264.

[13] H. Yu, D. Dong, Y. Ouyang, Q. Liu, Y. Wang, *Lett. Org. Chem.* **2005**, *2*, 755–759.

[14] a) K. I. Booker-Milburn, M. Fedoulo, S. J. Paknoham, J. B. Strachan, J. L. Melville, M. Voyle, *Tetrahedron Lett.* **2000**, *41*, 4657–4661; b) R. Engqvist, J. Bergman, *Tetrahedron* **2003**, *59*, 9649–9653.

[15] S. R. Prakash, K. M. Cable, I. D. Correa, L. Fellows, S. Montgomery, J. J. Newman, L. Waterhouse, G. N. Wells, D. R. Sutherland, *J. Labelled Compd. Radiopharm.* **1995**, *36*, 993–1007.

[16] X-ray crystal data for **4a**: $C_{23}H_{23}ClN_2OS_2$; colorless; M = 443; orthorhombic; *Pna*2$_1$; a = 15.178 Å, b = 23.279 Å, c = 6.390 Å; V = 2257.8 Å^3; α = 90.00, β = 90.00, γ = 90.00; Z = 4; T = 293 K; F(000) = 928, R_1 = 0.0441, wR_2 = 0.1010. CCDC-793925 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.

Received: November 3, 2010
Published Online: March 14, 2011

