$\times 10^7$ M^{-1} s^{-1} for **1d**[27] but no measurable reaction (rate constant $<10^4$ M^{-1} s^{-1}) for **1c**.[28] A similar dependency of the reactivity of singlet aryl carbenes on para substituents has been described by Moss et al.[29]

It can be asked whether the carboxylation of carbenes **1** is a concerted reaction or not. For triplet carbenes **1a** and **1b**, there is no experimental evidence for the formation of an intermediate or carbene complex even if the carbene is isolated in pure CO_2. The small frequency shifts and line broadening of IR bands in CO_2 relative to Ar—which have been observed as well for singlet carbenes **1c** and **1d**—are attributed to unspecific matrix effects rather than to the formation of defined molecular complexes. On the other hand, we cannot exclude intermediates in the carboxylation of **1a** which are short-lived under the conditions of matrix isolation and rapidly rearrange to **2a**. The singlet–triplet gap ΔH_{ST} of **1a** in an unpolar solvent (isooctane) is 4.0 ± 0.3 kcal/mol[30] and therefore the thermal population of the excited singlet state is too small to account for the observed reactivity toward CO_2 at temperatures below 50 K. It is therefore reasonable to assume that the carboxylation of **1a** does not procede via thermally populated singlet **1a**. Crossover to the singlet manifold occurs at an unspecified stage along the reaction coordinate, and short-lived triplet diradicals having high ISC rates are possible intermediates.

The only hint for the formation of an ylide-type intermediate in the reaction of singlet carbenes **1c** and **1d** comes from the observation of a pale blue-green color when the carbenes are produced in the presence of CO_2. From our experiments there is no indication whether the colored compound is an intermediate on the path to oxiranones **2c** and **2d** or rather a side product. No colored product is observed during the carboxylation of **1a**.

In summary, this study suggests that the reactivity of carbenes **1** toward CO_2 is determined by their philicity rather than by their spin state. The reactivity is decreased by electron-withdrawing substituents, and the only products identified are oxiranones **2**. Short-lived triplet diradicals might be involved in the ISC, although there is no experimental evidence for the formation of these species.

Experimental Section

Diazo compounds **3a**[31] and **3b**[32] and diazirines **3c** and **3d**[33] have been synthesized according to literature procedures. The setup for matrix experiments has been described elsewhere.[16,34] Carbon dioxide (Messer Griesheim, 99.995%) was deposited at 80 K, yielding sufficiently transparent matrices and still matrix-isolated samples (the degree of matrix isolation was monitored by observing the line width of IR bands as function of the temperature of matrix deposition). The line width of IR bands increased during irradiation or annealing of the CO_2 matrices.

Other gases used were argon (Messer Griesheim, 99.9999%), oxygen (Messer Griesheim, 99.998%), $C^{18}O_2$, and $^{13}CO_2$ (MSD Isotopes 99.75% and 99.3% isotopic purity, respectively). Infrared spectra were recorded on a Bruker IFS 66 FT-IR spectrometer in the range 4000–450 cm^{-1}; the standard resolution was set to 1 cm^{-1}. Irradiation was performed by using a 500-W high-pressure mercury arc lamp, dichroic mirrors to preselect the range of irradiation, and appropriate cut-off filters.

Acknowledgment. Financial support was given by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. **1a**, 3129-17-7; **1b**, 3225-37-4; **1c**, 19807-41-1; **1d**, 102146-13-4; **2a**, 30436-19-2; **2c**, 138061-24-2; **2d**, 138061-25-3; **3a**, 883-40-9; **3b**, 932-97-8; **3c**, 4460-46-2; **3d**, 39184-67-3.

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Regioselective α-Methoxycarbonylsulfenylation of Ketones and Aldehydes: A Versatile Method for Preparation of Thiazolones, Thiadiazinones, and 3-Indolethiols[1]

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The characteristic properties of α-sulfenylcarbonyl compounds have led to the development of a number of useful transformations in organic synthesis.[3] In the area of heterocyclic chemistry, it is well documented that α-(acylthio)- and α-(cyanatothio)carbonyl compounds can serve as the precursor of 2-substituted thiazole derivatives (i.e., Hantzsch synthesis).[4] In addition, α-sulfenylcarbonyl compounds play also an important role in the synthesis of indole derivatives.[5]

In general, the most common method for the synthesis of α-sulfenylcarbonyl compounds involves the reaction of lithium enolates or trimethylsilyl enol ethers and organic disulfides,[5a-d] sulfenyl chlorides,[5a,e] or *S*-phenylthiosulfonates.[5b] Other methods for the synthesis of α-sulfenylcarbonyl compounds involve the reaction of α-halo ketones with thiolate anions or sulfenyl chlorides in the presence of zinc.[7] Methods for the synthesis of α-sulfenylated ketones include the reaction of 1,3,2-dioxophospholes[8] or α-diazoketones[9] with sulfenyl chlorides.

In this paper, we report a novel and regioselective α-methoxycarbonylsulfenylation of a variety of ketones and aldehydes employing (methoxycarbonyl)sulfenyl chloride **1**[10] as an electrophilic sulfenylating agent. Furthermore, the cyclization reactions of the resultant α-methoxycarbonylsulfenylated carbonyl compounds **2** with amines

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(2) Present address: Department of Organic Chemistry, Kwansei Gakuin University, Nishinomiya, Hyogo 662, Japan.
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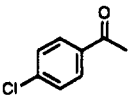
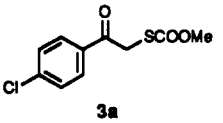
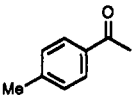
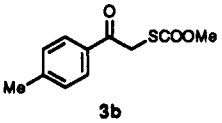
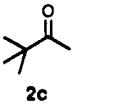
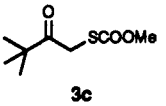
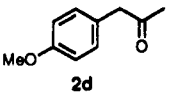
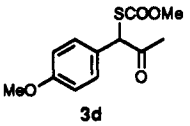
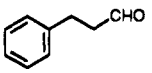
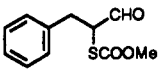
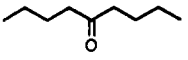
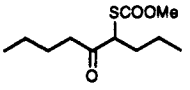
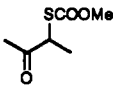
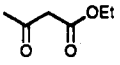
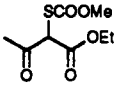
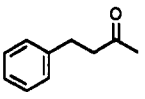
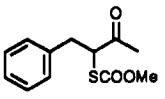
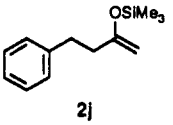
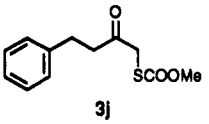
(10) Commercially available from Fluka Chemical Corp. Alternatively, methoxycarbonylsulfenyl chloride **1** can be easily prepared from chlorocarbonylsulfenyl chloride (commercially available from Aldrich Chemical Co.) and methanol. Zumach, V. G.; Kuhle, E. *Angew. Chem., Int. Ed. Engl.* **1970**, *82*, 63. Compound **1** has generally been used as a protecting agent for thiols. Greene, T. W. *Protective Groups in Organic Synthesis*; John Wiley and Sons: New York, 1981; p 214.

0022-3263/92/1957-1053$03.00/0

Table I. α-Methoxycarbonylsulfenylation of Carbonyl Compounds 2

entry	substrates	products	yield (%)	bp (mp) (°C)
1	 2a	 3a	72	(56–57)
2	 2b	 3b	68	(52–53)
3	 2c	 3c	65	75–78/12 mmHg
4	 2d	 3d	68	135–138/0.8 mmHg
5	 2e	 3e	62	180/0.8 mmHg[a]
6	 2f	 3f	74	102–104/0.9 mmHg
7	 2g	 3g	55	90–95/22 mmHg
8	 2h	 3h	72	92–94/0.8 mmHg
9	 2i	 3i	68	129–133/0.7 mmHg
10	 2j	 3j	73	135–138/0.8 mmHg

[a] Bulb to bulb distillation. [b] The reaction was carried out according to the known procedure.[5d]

and substituted hydrazines were found to offer efficient routes to a variety of important heterocyclic ring systems such as 2(3*H*)-thiazolones **4**,[11a] 1,3,4-(3*H*,6*H*)-thiadiazinones **5**,[11b] and 3-indolethiols[11c] as illustrated in the Scheme I. The α-[(methoxycarbonyl)sulfenyl]carbonyl moiety is incorporated in these compounds as shown by heavy lines.

Addition of the corresponding ketones (or aldehydes) **2** to 1 equiv of (methoxycarbonyl)sulfenyl chloride **1** in $CHCl_3$ at 25–35 °C for 24 h provided α-methoxycarbonylsulfenylated carbonyl compounds **3** in good yields. The structures of compounds **3** were confirmed by ^1H NMR, MS and IR spectral analyses (Experimental Section). The scope of the process is evident from Table I, which lists several examples of α-methoxycarbonylsulfenylated carbonyl compounds prepared by this methodology. In Table I, α-methoxycarbonylsulfenylation of ketones such as **2d**, **2g**, and **2i** proceeded in a thermodynamically controlled manner, affording the products **3d**, **3g**, and **3i**, respectively (entries 4, 7, and 9). On the other hand, the reaction of trimethylsilyl enol ether **2j**, derived from ketones **2i**, with **1** afforded **3j** in a 73% yield, which was sulfenylated at the terminal methyl group only, suggesting that this sulfenylation proceeds in a kinetically controlled manner (entry 10). Therefore, this sulfenylation occurs with good regioselectivity.

The α-methoxycarbonylsulfenylated carbonyl compounds **3** were used in the synthesis of various heterocyclic compounds. Treatment of **3a** with ammonium acetate (5.0 equiv) in AcOH at 80 °C for 3 h afforded product **4a** in 65% yield after silica gel chromatography. Compound **4a** was identical (mp, IR, and ^1H NMR) with the known 4-(4-chlorophenyl)-2(3*H*)-thiazolone which was prepared by the reaction of 2,4′-dichloroacetophenone and ethyl xanthamidate.[12] In a similar fashion, we prepared 4-substi-

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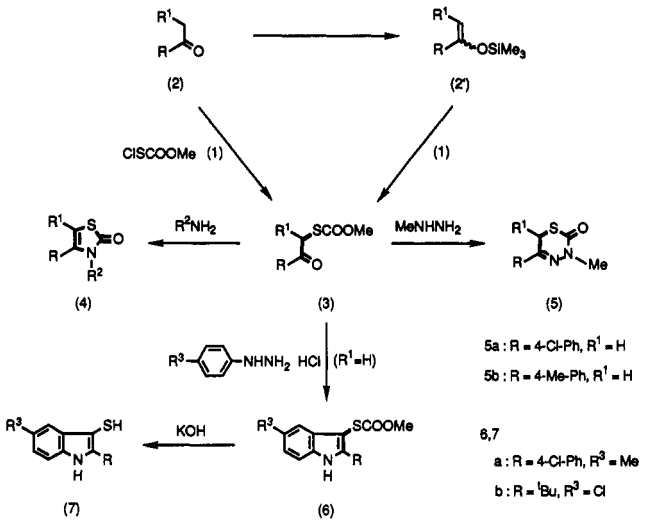
(12) Stevens, G.; Halamandaris, A.; Hopkinson, A. F. *J. Am. Chem. Soc.* **1958**, *80*, 5196.

Scheme I



tuted thiazolones **4b–f** via the route shown in Scheme I. Upon treatment with methylhydrazine in AcOH at 80 °C for 2 h, **3a,b** gave 1,3,4-(3*H*,6*H*)-thiadiazine-2-ones **5a,b** in 38 and 58% yields, respectively. Structural assignments for compounds **5a,b** were based on MS, IR, and ^{1}H NMR spectral data. In compound **5a**, the IR spectrum showed the presence of a carbonyl group at 1720 cm^{-1}. The ^{1}H NMR spectrum of **5a** showed a singlet peak (δ 3.90) for the methylene protons at C-6 which were different from that of **3a**. Elemental analysis and the mass spectrum (M^+) of **5a** were in agreement with the assigned structure. There has been considerable interest recently in the preparation and biological activity of these types of heterocyclic species.[14] The cyclocondensation of **3a,c** with phenylhydrazine hydrochlorides in AcOH for 3 h afforded none of 1,3,4-(3*H*,6*H*)-thiadiazin-2-one but instead gave 3-[(methoxycarbonyl)sulfenyl]indoles **6a,b** in 71 and 81% yields, respectively, via a (3,3)-sigmatropic rearrangement.[15] Compounds **6a,b** were smoothly converted into the corresponding 2-substituted 3-indolethiols **7a,b** in quantative yield by treatment with KOH (1.0 equiv) in methanol at rt.[15]

In summary, it was found that α-methoxycarbonylsulfenylated compound **3** can be prepared regioselectively from commercially available (methoxycarbonyl)sulfenyl chloride **1** and ketones (or aldehydes) **2**. These versatile intermediates serve as synthons for heterocycles containing thioester functionality, thiazolones, or thiadiazinones and for a facile introduction of a thiol group into the 3-position of the indole nucleus.

Experimental Section

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 60 MHz. Microanalytical data were provided by Sumika Analysis Center (Osaka).

General Procedure for the Preparation of α-(Methoxycarbonyl)sulfenyl Ketones (or Aldehydes) 3. To a stirred solution of ketones (or aldehydes) **2** (20 mmol) in $CHCl_3$ (20 mL) was added (methoxycarbonyl)sulfenyl chloride (2.53 g, 20 mmol) at rt, and the reaction mixture was allowed to stand for 24 h at 25–35 °C. The mixture was concentrated in vacuo yielding the crude only product which was purified by column chromatography on silica gel (entries 1 and 2) or by distillation (entries 3–10).

3a: IR (Nujol) 1720, 1700, 1160 cm^{-1}; MS m/z 244 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.15–7.90 (m, 4 H), 4.40 (s, 2 H), 3.80 (s, 3 H).

Anal. Calcd for $C_{10}H_9ClO_3S$: C, 49.09; H, 3.71. Found: C, 49.22; H, 3.72.

3b: IR (Nujol) 1720, 1700, 1160 cm^{-1}; MS m/z 244 (M^+); ^{1}H NMR ($CDCL_3$) δ 7.00–7.80 (m, 4 H), 4.25 (s, 2 H), 3.80 (s, 3 H), 2.50 (br s, 3 H).

Anal. Calcd for $C_{11}H_{12}O_3S$: C, 59.71; H, 5.47. Found: C, 59.79; H, 5.50.

3c: IR (neat) 1720, 1150 cm^{-1}; MS m/z 190 (M^+); ^{1}H NMR ($CDCl_3$) δ 3.90 (s, 2 H), 3.75 (s, 3 H), 1.20 (s, 9 H).

Anal. Calcd for $C_8H_{14}O_3S$: C, 50.52; H, 7.42. Found: C, 50.77; H, 7.71.

3d: IR (neat) 1720, 1160 cm^{-1}; MS m/z 254 (M^+): ^{1}H NMR ($CDCl_3$ δ 6.80–7.40 (m, 4 H), 5.30 (s, 1 H), 3.80 (s, 6 H), 2.25 (s, 3 H).

Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.67; H, 5.55. Found: C, 56.77; H, 5.71.

3e: IR (neat) 1740, 1720, 1150 cm^{-1}; MS m/z 212 (M^+); ^{1}H NMR ($CDCl_3$) δ 9.70 (d, J = 2 Hz, 1 H), 7.20–7.50 (m, 5 H), 3.80–4.45 (m, 1 H), 3.85 (s, 3 H), 2.80–3.70 (m, 2 H).

Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 59.98; H, 5.59.

3f: IR (neat) 1720, 1170 cm^{-1}; MS m/z 232 (M^+); ^{1}H NMR ($CDCl_3$) δ 4.10 (t, J = 7 Hz, 1 H), 3.80 (s, 3 H), 2.50–2.80 (m, 2 H), 1.00–2.00 (m, 14 H).

Anal. Calcd for $C_{11}H_{20}O_3S$: C, 56.87; H, 8.68. Found: C, 56.93; H, 8.70.

3g: IR (neat) 1720, 1170 cm^{-1}; MS m/z 162 (M^+); ^{1}H NMR ($CDCl_3$) δ 3.80–4.20 (q, J = 7 Hz, 1 H), 3.80 (s, 3 H), 2.20 (s, 3 H), 1.45 (d, J = 7 Hz, 3 H).

Anal. Calcd for $C_6H_{10}O_3S$: C, 44.43; H, 6.21. Found: C, 44.67; H, 6.41.

3h: IR (neat) 1740, 1610, 1160 cm^{-1}; MS m/z 220 (M^+); ^{1}H NMR ($CDCl_3$) δ 13.95 (br s, 0.75 H), 4.95 (s, 0.25 H), 4.25 (q, J = 7 Hz, 2 H), 3.82 (s, 0.75 H), 2.35 (s, 0.75 H), 2.35 (s, 2.25 H), 1.30 (t, J = 7 Hz, 3 H).

Anal. Calcd for $C_8H_{12}O_5S$: C, 43.63; H, 5.49. Found: C, 43.74; H, 5.70.

3i: IR (neat) 1720, 1160 cm^{-1}; MS m/z 238 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.20–7.40 (m, 5 H), 4.40 (t, J = 7 Hz, 1 H), 3.80 (s, 3 H), 2.94–4.30 (m, 2 H), 2.20 (s, 3 H).

Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92. Found: C, 60.55; H, 5.98.

3j: IR (neat) 1720, 1160 cm^{-1}; MS m/z 238 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.20–7.45 (m, 5 H), 3.85 (s, 2 H), 3.75 (s, 3 H), 2.75–3.00 (m, 4 H).

Anal. Calcd for $C_{12}H_{13}O_3S$: C, 60.48; H, 5.92. Found: C, 60.55; H, 5.94.

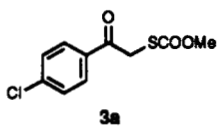
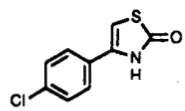
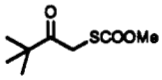
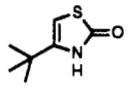
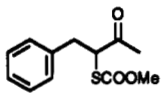
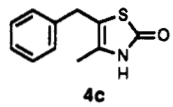
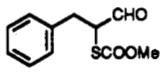
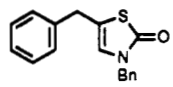
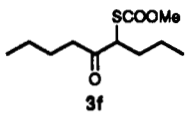
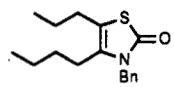
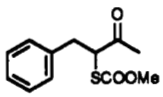
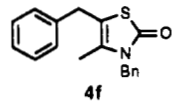
General Procedure for the Preparation of 4-Substituted 2(3*H*)-Thiazolones 4. A mixture of α-(methoxycarbonyl)sulfenyl ketones (or aldehydes) **3** (2 mmol) and ammonium acetate (benzylamine) (10 mmol) in AcOH (4 mL) was heated at 80 °C for 2 h and allowed to cool to rt. The crude reaction mixture was poured into 50 mL of ice–water and extracted with EtOAc. The organic phase was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated. The residual oil was chromatographed on silica gel using a 20% EtOAc–hexane mixture as eluent to give 4-substituted 2(3*H*)-thiazolones **4**. The yields, physical properties, and spectral data of **4** are shown in Table II. All the new products thus obtained gave correct elemental analyses (±0.3% for C, H, and N).

Reaction of 3a,b with Methylhydrazine. A solution containing **3a,b** (5 mmol) and methylhydrazine (0.23 g, 6 mmol) in AcOH (5 mL) was stirred at rt for 3 h. The mixture was poured into 50 mL of ice–water and extracted with EtOAc. The EtOAc extract was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated. The residue was recrystallized from *i*-PrOH–hexane to give 3-methyl-1,3,4(3*H*,6*H*)-thiadiazinones **5a,b** as white crystals. The yields, physical properties, and spectral data of **5a,b** are as follows.

5a: 38% yield; mp 157–159 °C; IR (Nujol) 1720 cm^{-1}; MS m/z 240 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.65 (d, J = 8 Hz, 2 H), 7.35 (d,

(13) See ref 3b, p 294.
(14) March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; p 1054.
(15) It is known that a thiol group can be introduced at the 3-position of indoles by reacting thiourea and indoline followed by hydrolysis: Marchesa, G. P.; Panzeri, E. *Chim. Ind. (Milan)* **1969**, *51*, 41; *Chem. Abstr.* **1969**, *70*, 77694. For a revent review on the synthesis of 3-indolylthioles, see: ref 10c, p 215.

Table II. Reaction of α-Methoxycarbonylsulfenylated Compounds 3 with Amines

substrates	amines	products	yield (%)	mp (°C)	MS (m/z)	IR (cm^{-1})	^1H NMR ($CDCl_3$/TMS)
 3a	NH_3	 4a	65	224–226 (224–225)[11]	221	1720	6.25 (s, 1 H), 7.10–7.60 (m, 4 H)
 3c	NH_3	 4b	57	117–119	157	1715	1.37 (s, 9 H), 5.60 (s, 1 H)
 3l	NH_3	 4c	69	oil	205	1721	2.00 (s, 3 H), 3.70 (s, 2 H), 7.00–7.40 (m, 5 H)
 3e	$BnNH_2$	 4d	72	78–79	281	1720	3.70 (d, J = 1 Hz, 2 H), 4.75 (s, 2 H), 6.17 (t, J = 1 Hz, 1 H), 7.00–7.50 (m, 10 H)
 3f	$BnNH_2$	 4e	70	oil	289	1730	0.90–1.20 (m, 6 H), 1.20–2.90 (m, 6 H), 2.20–2.70 (m, 4 H), 4.90 (s, 2 H), 7.20–7.40 (m, 5 H)
 3l	$BnNH_2$	 4f	59	oil	295	1720	2.00 (s, 3 H), 3.80 (s, 2 H), 4.95 (s, 2 H), 7.20–7.40 (m, 10 H)

J = 8 Hz, 2 H), 3.90 (s, 2 H), 3.50 (s, 3 H).

Anal. Calcd for $C_{10}H_9ClN_2OS$: C, 49.90; H, 3.77; N, 11.64. Found: C, 49.73; H, 3.77; N, 11.53.

5b: 58% yield; mp 94–95 °C; IR (Nujol) 1721 cm^{-1}; MS m/z 220 (M^+); ^1H NMR ($CDCl_3$) δ 7.66 (d, J = 8 Hz, 2 H), 7.35 (d, J = 8 Hz, 2 H), 3.90 (s, 2 H), 3.50 (s, 3 H).

Anal. Calcd for $C_{11}H_{12}N_2OS$: C, 59.98; H, 5.49; N, 12.72. Found: C, 60.06; H, 5.52; N, 12.69.

Reaction of 3a,c with Phenylhydrazines. In a similar fashion in the synthesis of 4, phenylhydrazines (1.0 equiv) were used in place of ammonium acetate to give 3-[(methoxycarbonyl)sulfenyl]indoles **6a,b**. The yields, physical properties, and spectral data of **6a,b** are as follows.

6a: 71% yield; mp 157–159 °C; IR (Nujol) 1720 cm^{-1}; MS m/z 331 (M^+); ^1H NMR ($CDCl_3$) δ 8.60–8.80 (br, s, 1 H), 7.05–7.60 (m, 7 H), 3.80 (s, 3 H), 2.40 (s, 3 H).

Anal. Calcd for $C_{17}H_{14}Cl\,NO_2S$: C, 61.53; H, 4.25; N, 4.21. Found: C, 61.50; H, 4.27; N, 4.35.

6b: 81% yield; mp 115–117 °C; IR (Nujol) 1723 cm^{-1}; MS m/z 297 (M^+); ^1H NMR ($CDCl_3$) δ 8.40–8.60 (br, s, 1 H), 7.50–7.80 (br s, 3 H), 3.80 (s, 3 H), 1.45 (s, 9 H).

Anal. Calcd for $C_{14}H_{16}ClNSO_2$: C, 56.47; H, 5.41; N, 4.70. Found: C, 56.48; N, 4.65.

Demethoxycarbonylation of 6a,b. A solution containing **6** (5 mmol) and potassium hydroxide (0.35 g, 6 mmol) in methanol (50 mL) was stirred at rt for 2 h. After the reaction was complete, the solution was neutralized with acetic acid and concentrated under reduced pressure. The residue was extracted with EtOAc (50 mL × 2), and the combined extracts were washed with water (30 mL), dried over $MgSO_4$, and evaporated. The crude product was recrystallized from *i*-PrOH to give 3-indolethiols **7** as white crystals. The yields, physical properties, and spectral data of **7a,b** are as follows.

7a: 98% yield; mp 157–159 °C; MS m/z 331 (M^+); ^1H NMR ($CDCl_3$) δ 8.60–8.80 (br s, 1 H), 7.05–7.60 (m, 7 H), 3.80 (s, 3 H), 2.40 (s, 3 H).

Anal. Calcd for $C_{15}H_{12}ClNS$: C, 65.80; H, 4.41; N, 5.11. Found: C, 65.94; H, 4.56; N, 5.06.

7b: 99% yield; mp 115–117 °C; MS m/z 297 (M^+); ^1H NMR ($CDCl_3$) δ 8.40–8.60 (br s, 1 H), 7.50–7.80 (br s, 3 H), 3.80 (s, 3 H), 1.45 (s, 9 H).

Anal. Calcd for $C_{12}H_{14}ClNS$: C, 60.11; H, 5.88; N, 5.83. Found: C, 60.18; H, 5.97; N, 5.99.

Registry No. **1**, 26555-40-8; **2a**, 99-91-2; **2b**, 122-00-9; **2c**, 75-97-8; **2d**, 122-84-9; **2e**, 104-53-0; **2f**, 502-56-7; **2g**, 78-93-3; **2h**, 141-97-9; **2i**, 2550-26-7; **2j**, 59417-89-9; **3a**, 65398-74-5; **3b**, 65398-72-3; **3c**, 137363-49-6; **3d**, 137363-50-9; **3e**, 137363-51-0; **3f**, 137363-52-1; **3g**, 137363-53-2; **3h**, 137363-54-3; **3i**, 137363-55-4; **3j**, 137363-56-5; **4a**, 2103-98-2; **4b**, 75820-45-0; **4c**, 137363-57-6; **4d**, 137363-58-7; **4e**, 137363-59-8; **4f**, 137393-31-8; **5a**, 137363-60-1; **5b**, 137363-61-2; **6a**, 137363-62-3; **6b**, 137363-63-4; **7a**, 137363-64-5; **7b**, 137363-65-6; (4-methylphenyl)hydrazine, 539-44-6; (4-chlorophenyl)hydrazine, 1073-69-4; methylhydrazine, 60-34-4.