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Unexpected Reactivity of the Burgess Reagent with Thiols: Synthesis of Symmetrical Disulfides

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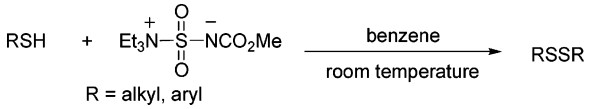

Reaction of the Burgess reagent with a series of aliphatic and aromatic thiols led to the corresponding symmetrical disulfides in high yields. No olefins were detected in the reactions of aliphatic thiols.

Since its discovery in the late 1960s, the Burgess reagent[1] has been used primarily for dehydration of secondary and tertiary alcohols and for the preparation of nitriles and carbamates.[2] Epoxides were thought to be inert to the action of the reagent until 2003 when we demonstrated that sulfamidates are easily prepared from its reaction with various oxiranes.[3] Since then, Nicolaou reported the synthesis of sulfamidates from diols as well as other compounds,[4] and the reagent is enjoying a renaissance in the exploration of new reactive options, including the first disclosure, published by us in 2006, of its asymmetric version and its application to the synthesis of chiral amino alcohol derivatives.[5] Extension of the reactivity studies to primary, secondary, and tertiary thiols was logical and has been suggested as a possible means of forming alkenes from such compounds.[6] We were, however, surprised to find no evidence of olefin or carbamate formation when we reacted decane-1-thiol (**1**) with 1 equivalent of the Burgess reagent. Instead, a nearly quantitative yield of disulfide **2** was isolated. Examination of other thiols (Table 1) reveals the reaction to be a general and high-yielding method, except for branched aliphatic thiols (entries 5 and 8), which react to afford both symmetrical disulfides[7] and trisulfides.[8]

The reaction of decane-1-thiol was optimized, as shown in Table 2, and we attempted to determine the mechanism of the reaction and to identify the reduced component in the sequence. Although the oxidation proceeded cleanly at 50 °C in 1 h, we found that higher yields could be obtained at room temperature in 1 h. The reaction was further accelerated by forming the thiolate anion first (entries 5−8, Table 2). The order of addition of the Burgess reagent and the thiol was shown to be inconsequential as long as there was a slight excess of the Burgess reagent. The use of polar solvents such as DMF (entry 4) hindered the rate of oxidation.

A tentative proposal—and at this stage speculative—for this transformation is shown in Scheme 1. In the first step the thiol reacts with the Burgess reagent either in an acid−base reaction to form thiolate **23** or via substitution to form inner salt **25**. Intermediates **25** or **27**, required for intramolecular E2 elimination, are likely to be protonated by mercaptans to generate thiosulfonyl carbamate **26**.[9] Instead, it is likely that thiosulfonyl carbamate **26** is attacked by either thiol or its conjugate base to form the disulfide and intermediate **28** or its tautomer **29**. We attempted to isolate compound **29** but were only able to characterize the triethylammonium salt **31** (in crystalline form), probably resulting from the immediate air oxidation of the labile intermediate **30**. NMR experiments in d_6-benzene showed the formation of a new species, which did not correspond to either

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(6) We are grateful to Prof. Graham J. Bodwell (Memorial University of Newfoundland), who suggested to us during the 12th LTOS Symposium in August 2006 that we examine the formation of alkenes from aliphatic thiols with the Burgess reagent.

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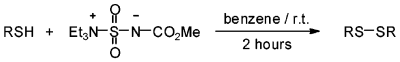
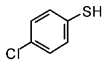
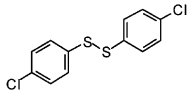
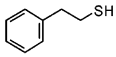
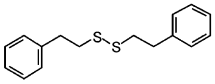
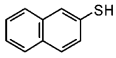
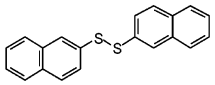
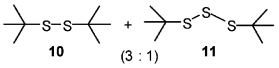
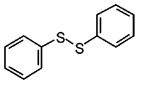
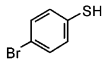
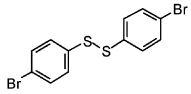
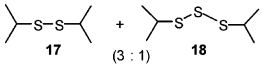
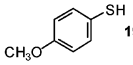
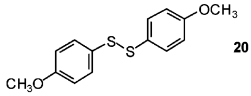
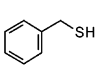
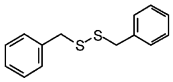
TABLE 1. Burgess Reagent Promoted Disulfide Formation[a]



entry	thiol		product		yield (%)
1	$CH_3(CH_2)_9SH$	1	$CH_3(CH_2)_9S-S(CH_2)_9CH_3$	2	95
2		3		4	93
3		5		6	92
4		7		8	90
5		9	 10 (3 : 1) 11		39
6		12		13	96
7		14		15	95
8		16	 17 (3 : 1) 18		85
9		19		20	90
10		21		22	93

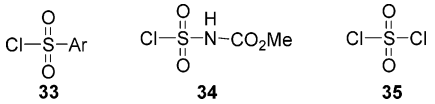
[a] Standard addition: thiol was added dropwise to the Burgess reagent.

the Burgess reagent or compound **31**. As the compound disappeared upon exposure to air, the formation of triethylammonium salt **31** was observed.

Various methods for the synthesis of symmetrical and unsymmetrical trisulfides have been developed by Harpp.[8a−d] Typical procedures include the alkoxide decomposition of sulfenylthiocarbonates,[8a] the reaction of thiols with sulfur dichloride to yield an intermediate thiosulfenyl chloride which reacts further with thiol to afford trisulfides,[8b] the reaction of disulfides with triphenylmethanesulfenyl chlorides with disulfides,[8c] and the reaction of thiols with triphenylmethanethiosulfenyl chloride to yield unsymmetrical trisulfides.[8d] By analogy with the mechanism proposed by Harpp,[8a−d] it is feasible that the sulfur atom of the newly formed disulfide is free to attack thiosulfonyl carbamate **26** to form a sulfonium salt. Loss of a stable carbocation by solvolysis (as in the case of 2-propanethiol and 2-methyl-2-propanethiol) would then lead to a symmetrical trisulfide, Scheme 1.[10]

That thiosulfamidates react rapidly with mercaptans is surprising, although a similar reaction has been observed for thiosulfonates. In 1988 Fuchs[11] reported the formation of disulfides from thiols and thiosulfonates. The reaction only took place when thiosulfonate formation was sufficiently slow, compared to the reaction of excess mercaptan with the thiosulfonate. When the more reactive sulfonyl bromides were used, the rate of sulfonylation was sufficiently fast and subsequent substitution leading to disulfides was not observed.

The electrophilic character of the Burgess reagent resembles that of a sulfuryl chloride. As it was difficult to compare the reactivity of sulfonyl chlorides such as **33** with sulfamidyl chlorides **34** and sulfuryl chloride **35**, we conducted a comparative study with decanethiol. Whereas the yield of disulfide is quantitative when Burgess reagent is used, it is formed in only 40% yield with sulfuryl chloride **35** after 1 h (Table 3). Leino[7f] reported the formation of symmetrical disulfides with sulfuryl chloride in methylene chloride and slower reactivity when the reaction was conducted in benzene. Although sulfonyl chlorides such as **33**[11] have been reported to oxidize thiols to disulfides, these reactions require the addition of a stoichiometric amount of a base such as triethylamine. The Burgess reagent requires no external base in its reactions with thiols to produce disulfides. The ease of preparation and the high yield of disulfides by this method compare favorably with those of other procedures in the literature.[7,12]



Experimental Section

General Procedure for the Formation of Disulfides. To a solution of Burgess reagent (1.05 equiv) in benzene (1 M) was added dropwise the corresponding thiol (1 equiv) dissolved in benzene at room temperature. The progress of the reaction was followed by GC/MS. After complete conversion of the starting material (approximately 30 min to 1 h), the reaction mixture was filtered through a plug of silica (hexanes). The crude product was either triturated with hexanes or purified by flash column chromatography.

Didecyl Disulfide (2) [CAS 10496-18-1]. Following the general procedure using decanethiol (0.59 mL, 2.86 mmol) as starting material gave 0.47 g of didecyl disulfide (95%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.70 (t, J = 7.2 Hz, 4H), 1.78−1.64 (m, 4H), 1.42−1.29 (m, 28H), 0.90 (t, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.2, 31.9, 29.6, 29.5, 29.3, 29.2, 28.8, 28.5, 22.7, 14.4; LRMS (EI) m/z 347 (M + 1, 25.4), 346 (M^+, 87.5), 278 (18.9), 206 (14.0), 173 (10.0), 140 (14.3), 139 (37.7), 125 (11.0), 101 (11.1), 97 (20.1), 96 (13.2), 95 (11.1), 91 (34.7), 87 (20.5), 85 (48.3), 84 (10.3), 83 (21.2), 71 (48.7), 70 (24.2), 69 (34.4), 68 (10.2), 67 (11.7), 60 (11.4), 57 (97.8), 56 (19.9), 55 (60.9), 47 (10.4), 45 (13.1), 43 (100.0), 42

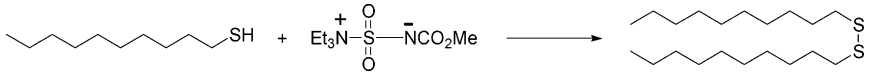
(9) The difference in acidity among alcohols ($pK_a \approx 16$), aliphatic thiols ($pK_a \approx 11$), and aromatic thiols ($pK_a \approx 6$) would not, at a first glance, lead to an assumption that the sulfamidate anion **27** would be completely protonated. This is not the case as demonstrated by the high yields of disulfides. Although it is possible for the E2 pathway to proceed even with 1% relative concentration of the active intermediate **27**, this pathway appears unfavorable. Even when a large excess of NaH (10 equiv) was used in the reaction media, ensuring a higher relative concentration of **27**, no alkenes were detected when aliquots were monitored by GC/MS.

(10) Following suggestions made by a reviewer, attempts to better define the mechanism of disulfide and trisulfide formation led us to examine reactions that also led to unsymmetrical disulfides. Benzanethiol and phenylethanethiol produced a statistical mixture of disulfides (2:1:1). In the reaction of benzanethiol and 2-methyl-2-propanethiol only benzyl disulfide was formed. Trisulfides were not detected as either intermediates or products in these reactions when aliquots were monitored by GC/MS. It is likely that the slower reactivity of branched thiols explains why no mixed disulfides were observed.

(11) Ranasinghe, M. G.; Fuchs, P. L. *Synth. Commun.* **1988**, *18*, 227.

(12) A reviewer pointed out that the cost of the Burgess reagent from Aldrich is $50−60 per gram and its use would be a more expensive alternative to the preparation of disulfides. However, the reagent is much cheaper when prepared fresh from chlorosulfonyl isocyanate ($1.5−2 per gram), methanol, and triethylamine.

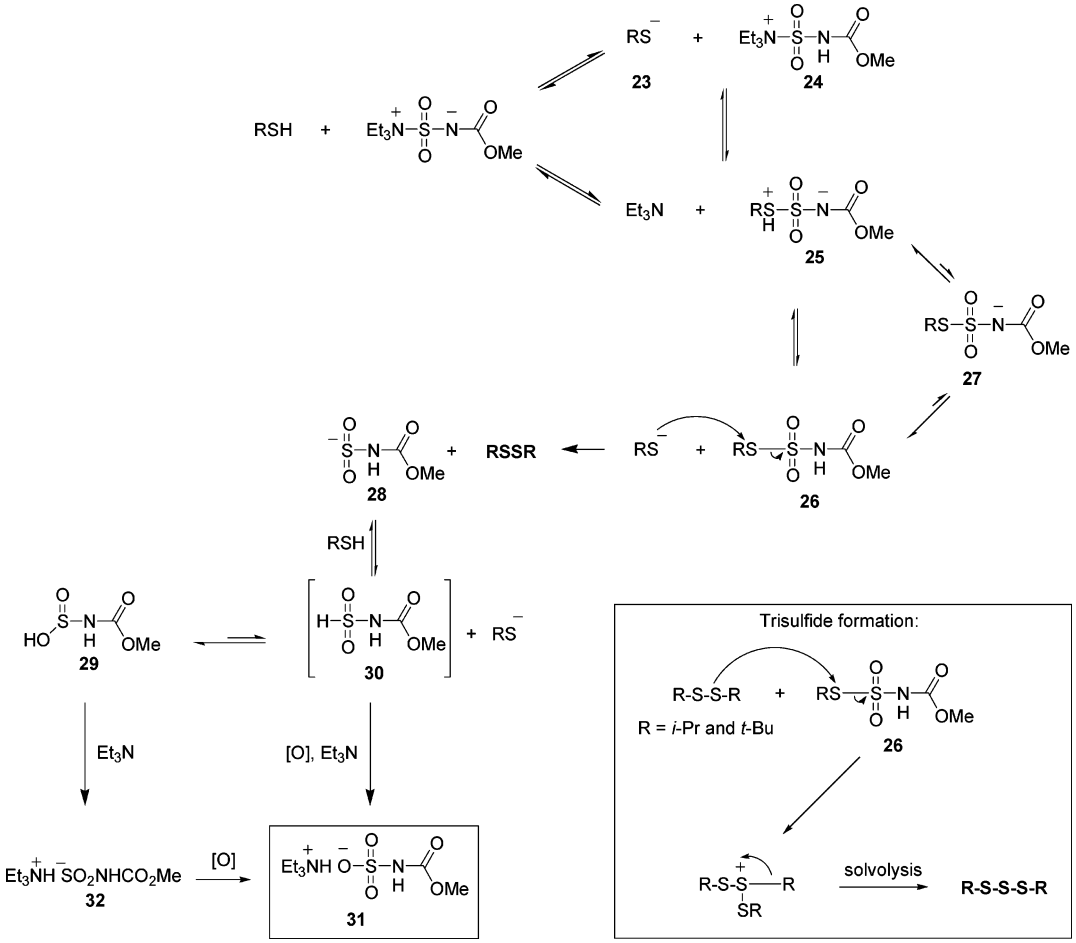
TABLE 2. Optimization Study for Decane-1-thiol



entry	amt of thiol (equiv)	amt of Burgess reagent (equiv)	conditions	addition order[a]	result[b]
1	1.0	1.05	benzene, rt, then 50 °C	standard	72% isolated yield (1 h)
2	1.0	1.05	benzene, rt	standard	95% isolated yield (1 h)
3	2.0	1.0	benzene, rt	standard	67% conversion (60 h)
4	1.0	1.05	DMF, rt	standard	50% conversion (24 h)
5	1.0	1.05	NaH, benzene, rt	standard	>95% conversion (30 min)
6	1.0	1.05	NaH, benzene, rt	inverse	>95% conversion (30 min)
7	1.0	1.05	NaH, benzene, 50 °C	standard	>95% conversion (30 min)
8	1.0	1.05	NaH, benzene, 50 °C	inverse	>95% conversion (30 min)

[a] Standard addition: thiol added dropwise to the Burgess reagent. Inverse addition: Burgess reagent added dropwise to the thiol. [b] GC/MS was used to measure conversion (%).

SCHEME 1. Suggested Mechanistic Options for the Oxidation of Thiols to Disulfides and Trisulfides with the Burgess Reagent



(12.1), 41 (49.9); HRMS (EI) *m*/*z* calcd for $C_{20}H_{42}S_2$ 346.2728, found 346.2727.

Bis(4-chlorophenyl) Disulfide (4) [CAS 1142-19-4]. Following the general procedure using 4-chlorobenzenethiol (0.207 g, 1.43 mmol) as starting material gave 0.190 g of bis(4-chlorophenyl) disulfide (93%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.38 (m, 4H), 7.30−7.24 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.1, 134.8, 134.5, 129.2; MS (EI) *m*/*z* 288 (M + 1, 37.5), 287 (M^+, 7.5), 286 (51.5), 145 (37.2), 144 (17.2), 143 (100.0), 108 (59.2), 99 (15.7), 84 (13.5), 75 (11.0), 73 (10.0), 69 (15.8), 63 (16.8); HRMS (EI) *m*/*z* calcd for $C_{12}H_8Cl_2S_2$ 285.9444, found 285.9444.

Bis(2-phenylethyl) Disulfide (6) [CAS 27846-22-6]. Following the general procedure using phenylethanethiol (0.192 mL, 1.43 mmol) as starting material gave 0.181 g of bis(2-phenylethyl) disulfide (92%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37−7.32 (m, 4H), 7.28−7.23 (m, 6H), 3.21−3.09 (m, 4H), 3.07−2.95 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 139.8, 128.6 (two overlapping signals), 128.5 (two overlapping signals), 126.5, 126.4, 40.2, 39.9, 35.7, 35.3; LRMS (EI) *m*/*z* 275 (M + 1, 2.5), 274 (M^+, 12.3), 105 (100.0), 77 (15.0); HRMS (EI) *m*/*z* calcd for $C_{16}H_{18}S_2$ 274.0850, found 274.0854.

Di-2-naphthalenyl Disulfide (8) [CAS 5586-15-2]. Following the general procedure using 2-naphthalenethiol (0.229 g, 1.43 mmol)

TABLE 3. Reactivity Comparison of Various Substituted Sulfuryl Chlorides and the Burgess Reagent in Benzene at Room Temperature

entry	reagent	time (h)	conversion[a] (%)
1	Burgess reagent	1	100
2	**33**	24	0
3	**34**	24	10
4	**35**	1	40

[a] Decane-1-thiol was used as the substrate (standard addition), and the conversion was determined by GC/MS.

as starting material gave 0.197 g of di-2-naphthalenyl disulfide (90%): mp 135−138 °C (ethyl acetate) (lit.[13] mp 137−138 °C); ^{1}H NMR (300 MHZ, $CDCl_3$) δ 7.96 (s, 2H), 7.8−7.4 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.3, 133.5, 132.5, 129.0, 127.8, 127.5, 126.7, 126.6, 126.2, 125.7; MS (EI) *m*/*z* 318 (100), 285 (3), 254 (8), 160 (41), 115 (43), 79 (10), 69 (9); HRMS (EI) *m*/*z* calcd for $C_{20}H_{14}S_2$ 318.0537, found 318.0532.

Di-*tert*-butyl Disulfide (10) [CAS 110-06-5] and Di-*tert*-butyl Trisulfide (11) [CAS 4253-90-1]. Following the general procedure using 2-methyl-2-propanethiol (0.130 g, 1.43 mmol) as starting material gave 0.050 g (39%) of a mixture of di-*tert*-butyl disulfide and di-*tert*-butyl trisulfide in ratio of 3 to 1: ^{1}H NMR (300 MHZ, $CDCl_3$) δ 1.31 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 46.2, 30.6.

Diphenyl Disulfide (13) [CAS 882-33-7]. Following the general procedure using benzenethiol (0.158 g, 1.43 mmol) as starting material gave 0.150 g of diphenyl disulfide (96%): mp 56−58 °C (CH_2Cl_2) (lit.[14] mp 58−60 °C, ethanol); ^{1}H NMR (300 MHZ, $CDCl_3$) δ 7.58−7.48 (m, 4H), 7.34−7.21 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 129.0, 127.5, 127.1; MS (EI) *m*/*z* 218 (100), 185 (6), 154 (8), 141 (12), 109 (96), 77 (12), 65 (30), 51 (12); HRMS (EI) *m*/*z* calcd for $C_{12}H_{10}S_2$ 218.0224, found 218.0222.

Bis(4-bromophenyl) Disulfide (15) [CAS 5335-84-2]. Following the general procedure using 4-bromobenzenethiol (0.300 g, 1.59 mmol) as starting material gave 0.287 g of bis(4-bromophenyl) disulfide (95%) as white needles after crystallization from $CHCl_3$: mp 94−95 °C ($CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 4H), 7.36 (d, J = 8.4 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.8, 132.2, 129.4, 121.6; MS *m*/*z* 378 (57), 377 (15), 376 (100), 374 (49), 190 (27), 189 (62), 188 (27), 187 (62), 140 (11), 109 (38), 108 (83), 82 (15), 69 (20), 63 (17); HRMS (EI) *m*/*z* calcd for $C_{12}H_8Br_2S_2$ 373.8434, found 373.8432.

Diisopropyl Disulfide (17) [CAS 4253-89-8] and Diisopropyl Trisulfide (18) [CAS 5943-34-0]. Following the general procedure using 2-propanethiol (0.200 g, 2.63 mmol) as starting material gave 0.179 g (85%) of a mixture of diisopropyl disulfide and diisopropyl trisulfide in a ratio of 2 to 1 as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.21 (sept, J = 6.6 Hz, 2H, trisulfide), 2.97 (sept, J = 6.6 Hz, 2H, disulfide), 1.37 (d, J = 6.6 Hz, 6H, trisulfide), 1.30 (d, J = 6.6 Hz, 6H, disulfide); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.1 (trisulfide), 41.5 (disulfide), 22.8 (trisulfide), 22.6 (disulfide); MS (EI) *m*/*z* 182 (17), 150 (27), 108 (29), 98 (10), 75 (12), 43 (100), 41 (21); HRMS (EI) *m*/*z* calcd for $C_6H_{14}S_2$ 150.0537, found 150.0539; HRMS (EI) *m*/*z* calcd for $C_6H_{14}S_3$ 182.0258, found 182.0254.

Bis(4-methoxyphenyl) Disulfide (20) [CAS 5335-87-5]. Following the general procedure using 4-methoxybenzenethiol (0.176 mL, 1.43 mmol) as starting material gave 0.180 g of bis(4-methoxyphenyl) disulfide (90%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.37 (m, 4H), 6.86−6.81 (m, 4H), 3.79 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 132.5, 128.3, 114.5, 55.3; LRMS (EI) *m*/*z* 279 (M + 1, 9.8), 278 (M^+, 51.7), 140 (25.4), 139 (100.0), 125 (12.1), 96 (12.4), 91 (14.3); HRMS (EI) *m*/*z* calcd for $C_{14}H_{14}O_2S_2$ 278.0435, found 278.0437.

Bis(phenylmethyl) Disulfide (22) [CAS 150-60-7]. Following the general procedure using benzenemethanethiol (0.169 mL, 1.43 mmol) as starting material gave 0.164 g of bis(phenylmethyl) disulfide (93%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.34 (m, 6H), 7.33−7.29 (m, 4H), 3.66 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.3, 129.4, 128.4, 127.4, 43.2; LRMS (EI) *m*/*z* 247 (M + 1, 3.0), 246 (M^+, 13.9), 91 (100.0); HRMS (EI) *m*/*z* calcd for $C_{14}H_{14}S_2$ 246.0537, found 246.0541.

Sulfo Methyl Ester Carbamic Acid Triethylammonium Salt (31). Compound **31** was isolated by diluting the crude reaction mixture with diethyl ether after following the general procedure. A white precipitate was formed which was filtered and dried under reduced pressure: mp 93−95 °C (Et_2O); IR (film) 3483, 3237, 2989, 2711, 2499, 1723, 1647, 1476, 1421, 1341, 1225, 1044, 948, 838 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.20 (br s, 1H), 7.15 (br s, 1H), 3.69 (s, 3H), 3.15−3.31 (m, 6H), 1.39 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 52.2, 46.4, 8.4; HRMS (FAB) *m*/*z* calcd for $(C_2H_5NO_5S\cdot 2C_6H_{15}N + H)^+$ 358.2376, found 358.2379. Anal. Calcd for $C_2H_5NO_5S\cdot C_6H_{15}N$: C, 37.49; H, 7.86; N, 10.96. Found: C, 37.67; H, 7.83; N, 10.76.

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Supporting Information Available: General procedure for the preparation of disulfides and ^{1}H and ^{13}C NMR spectra and characterization data for compounds **2**, **4**, **6**, **8**, **10**, **11**, **13**, **15**, **17**, **18**, **20**, **22**, and **31**. This material is available free of charge via the Internet at http://pubs.acs.org.

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