SYNTHESIS AND REACTION OF *S*-TRIMETHYLSILYLMETHYL CARBONIMIDODITHIOATE DERIVATIVES: SYNTHETIC EQUIVALENT OF THIOCARBONYL YLIDE

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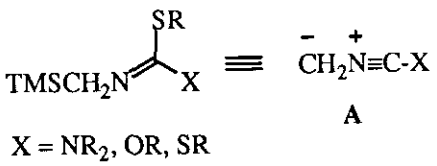
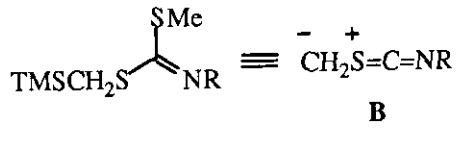
Abstract- *S*-Trimethylsilylmethyl carbonimidodithioate derivatives (**2**-**5**) prepared by an addition of trimethylsilylmethanethiol (**1**) toward the isothiocyanate followed by *S*-alkylation were found to react with various carbonyl compounds in the presence of fluoride ion to give oxathiolane derivatives (**6**-**9**) in moderate yields, in which the silylated carbonimidodithioate derivatives formally served as thiocarbonyl ylide equivalents.

Heterocyclic frameworks are found in many biologically active substances and are also involved in wide varieties of functionality materials. Therefore, further investigation of new heterocyclic systems and the development of new synthetic methodologies are desired. In order to construct the five-membered heterocycles, 1,3-dipolar [3 + 2] cycloaddition was considered to be the most efficient tool. In particular, the discovery of the mild desilylation method for generating the desired ylides has spurred the synthetic and the mechanistic studies on the reaction of the nonstabilized nitrogen, oxygen, and sulfur ylides.[1]



A

X = NR_2, OR, SR

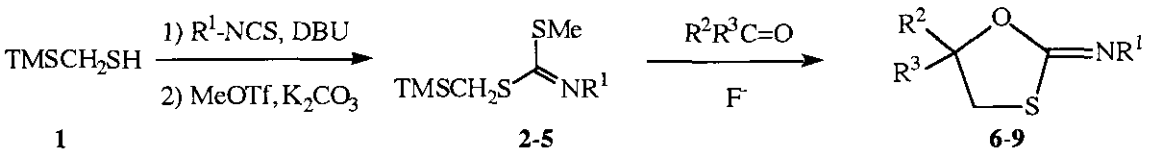


B

Recently, we reported the synthesis of *N*-trimethylsilylmethylated isothiourea, carbonimidothioate, and the corresponding dithioate derivatives and their fluoride-promoted reaction with various carbonyl compounds leading to the oxazoline derivatives, where the *N*-silylmethylated thioimidate derivatives served as amino-, alkoxy-, and alkylthionitrile ylide (**A**) equivalents, respectively.[2] We are now aiming at the utilization of *S*-silylmethylated carbonimidodithioate as a synthetic equivalent of the thiocarbonyl ylide (**B**). In this paper, we would like to describe the preparation of *S*-trimethylsilylmethyl carbonimidodithioate derivatives starting from trimethylsilylmethanethiol (**1**) and their reaction with a variety of carbonyl compounds in the presence of fluoride ion.

RESULTS AND DISCUSSION

When a reaction of trimethylsilylmethanethiol (**1**) with ethyl isothiocyanate was carried out in the presence of a catalytic amount of DBU, the corresponding thioxocarbamate was obtained quantitatively. As shown in Scheme 1, the thioxocarbamate, without purification, was treated with methyl triflate in the presence of potassium carbonate to give the desired methyl trimethylsilylmethyl *N*-ethylcarbonimidodithioate (**2**) in a quantitative yield (Table 1, entry 1). Phenyl and substituted phenyl isothiocyanates were also subjected to the above preparation to afford the corresponding *N*-arylcarbonimidodithioates (**3-5**) in high yields. The results are listed in Table 1.



1 **2-5** **6-9**

Scheme 1

Table 1. Preparation of Methyl Trimethylsilylmethyl Carbonimidodithioate Derivatives (**2-5**).

entry	R^1	Compd.	Yield (%)
1	Et	**2**	quant.
2	4-ClC_6H_4	**3**	80
3	Ph	**4**	81
4	4-$MeOC_6H_4$	**5**	quant.

Since these compounds (**2-5**) bear a sulfur atom and a good leaving group, methylthio portion, β and γ to the trimethylsilyl group, respectively, a formal 1,3-elimination of methylthiosilane would generate thiocarbonyl ylides. Recently, it was reported by Y. Tominaga *et al.* that a reaction of the corresponding *N*-(*p*-toluenesulfonyl)carbonimidodithioate with aldehydes gave thiiranes *via* the 1,3-dipolar cycloaddition of thiocarbonyl ylide to C=O double bond.[3]

We initially investigated the reaction of *N*-ethylcarbonimidodithioate (**2**) with various aldehydes. Thus, a solution of the compound (**2**), 4-chlorobenzaldehyde (2 equiv.), and cesium fluoride (2 equiv.) in DMF was stirred at room temperature for 15 h. After a usual workup, an analysis of the reaction mixture by means of ^{1}H NMR spectroscopy revealed the formation of an oxathiolane derivative (**6a**), a formal [3 + 2] cycloadduct, in 94% yield (run 1, Table 2).[4] The corresponding thiirane derivative could not be detected in the reaction mixture. Trying to purify the crude product by a column chromatography on silica gel, however, the isolated yield of the oxathiolane (**6a**) was at most 62%, probably due to its low stability in silica gel. The compound (**6a**) was obtained as an unseparable 80 : 20 mixture of diastereoisomers about

the imido double bond. As shown in the runs 2-6, changing the solvent and fluoride ion source did not give a significant improvement on the outcome of the reaction and the CsF-DMF system found to be the most effective in our case.

Table 2. Reaction of *S*-Trimethylsilylmethyl Carbonimidodithioates (**2**-**5**) with Carbonyl Compounds.

run	R^1	R^2	R^3	Fluoride	Solvent	Compd.	Yield, % (NMR)
1	Et	4-ClC_6H_4	H	CsF	DMF	**6a**	62 (94)
2	Et	4-ClC_6H_4	H	CsF	MeCN	**6a**	13 (31)
3	Et	4-ClC_6H_4	H	CsF	DME	**6a**	- [a] (8)
4	Et	4-ClC_6H_4	H	CsF	HMPA	**6a**	- [a] (17)
5	Et	4-ClC_6H_4	H	Bu_4NF	DMF	**6a**	- [a] (27)
6	Et	4-ClC_6H_4	H	KF[b]	DMF	**6a**	49 (58)
7	Et	Ph	H	CsF	DMF	**6b**	68
8	Et	4-MeC_6H_4	H	CsF	DMF	**6c**	52
9	Et	4-$MeOC_6H_4$	H	CsF	DMF	**6d**	trace
10	Et	4-$F_3CC_6H_4$	H	CsF	DMF	**6e**	59
11	Et	$Me(CH_2)_4$	H	CsF	DMF	**6f**	38
12	Et	Ph	Me	CsF	DMF	**6g**	12
13	Et	-$(CH_2)_5$-		CsF	DMF	**6h**	trace
14	4-ClC_6H_4	4-ClC_6H_4	H	CsF	DMF	**7a**	20
15[c]	4-ClC_6H_4	4-ClC_6H_4	H	CsF	DMF	**7a**	48
16[c]	4-ClC_6H_4	Ph	H	CsF	DMF	**7b**	44
17[c]	4-ClC_6H_4	4-MeC_6H_4	H	CsF	DMF	**7c**	36
18[c]	4-ClC_6H_4	4-$MeOC_6H_4$	H	CsF	DMF	**7d**	trace
19[c]	Ph	4-ClC_6H_4	H	CsF	DMF	**8**	33
20[c]	4-$MeOC_6H_4$	4-ClC_6H_4	H	CsF	DMF	**9**	66

a) Not determined

b) 18-Crown-6 (10 mol%) was added.

c) Ten equivalents of aldehydes were used.

Variations in both the *N*-substituents of the *S*-silylmethylated carbonimidodithioates and the nature of the carbonyl compounds were examined and the representative results are also compiled in Table 2. As shown in runs 7-10, most of aromatic aldehydes smoothly reacted with the carbonimidodithioate (**2**) to give the oxathiolanes (**6b**), (**6c**), and (**6e**) in moderate yields. However, we could not obtain the corresponding cycloadduct (**6d**) from 4-anisaldehyde although the ^1H NMR spectrum of the reaction mixture exhibited the formation of a small amount of the expected product. Aliphatic aldehyde and ketones could also be employed as carbonyl sources, even though the yields were not so high (runs 11-13).

We next investigated a similar reaction of *N*-arylcarbonimidodithioate derivatives (**3**-**5**). When a reaction of the *N*-(4-chlorophenyl)carbonimidodithioate (**3**) with 4-chlorobenzaldehyde (2 equiv.) in the presence of cesium fluoride (2 equiv.) was conducted at room temperature in DMF for 15 h, the expected oxathiolane derivative (**7a**) was isolated in 20% yield along with 22% yield of dimethyl *N*-(4-chlorophenyl)carbonimidodithioate (**10**) (run 14). We postulated that the compound (**10**) was formed by the hydrogen abstraction from the acidic methylene of the remaining carbonimidodithioate (**3**) by the intermediate carbanion. Accordingly, the presence of large excess of carbonyl compounds over the generating carbanion in the reaction mixture would enhance the formation of the desired cycloadduct. In fact, the use of ten equivalents of the aldehydes or slow addition of the carbonimidodithioate (**3**) to the reaction mixture changed the product ratio of **7a** : **10** from 39 : 61 to 62 : 38 or 54 : 46, respectively, and the isolated yield of the compound (**7a**) went up to 48% in the former case (run 15). The substituent effect of the aldehyde was similar to that in the reaction with *N*-ethylcarbonimidodithioate (**2**) (runs 16-18). Furthermore, treatments of *N*-phenyl- and *N*-(4-methoxyphenyl)carbonimidodithioates (**4**) and (**5**) with 4-chlorobenzaldehyde afforded the corresponding oxathiolane derivatives (**8**) and (**9**) in 33 and 66% yields, respectively (runs 19 and 20).

Consequently, the *S*-trimethylsilylmethyl carbonimidodithioate derivatives (**2**-**5**) readily available from trimethylsilylmethanethiol (**1**) and appropriate isothiocyanates were found to react with various carbonyl compounds to furnish the oxathiolane derivatives (**6**-**9**) in fair yields, where the *S*-silylmethylated carbonimidodithioates served as synthetic equivalents of thiocarbonyl ylides, *viz.* isothiocyanato ylides in these cases.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ solution on a Varian UNITY-400 spectrometer (399.97 MHz for ^{1}H, 100.58 MHz for ^{13}C). All chemical shifts are reported as δ values (ppm) relative to residual chloroform (7.26 ppm for ^{1}H) and the central peak of deuteriochloroform (77.00 ppm for ^{13}C). HRMS (EI) spectra were obtained on a JEOL JMS-AX-500 spectrometer with DA7000 data system using perfluorokerosene as an internal standard. Most of the starting materials and reagents were commercial products and were used as supplied. Solvents were dried by conventional methods and were distilled before use.

Preparation of Methyl Trimethylsilylmethyl Carbonimidodithioates (2-5)

For example, a preparation of methyl trimethylsilylmethyl *N*-(4-chlorophenyl)carbonimidodithioate (**3**) is demonstrated. A solution of trimethylsilylmethanethiol (**1**, 4.20 g, 35.0 mmol), 4-chlorophenyl isothiocyanate (5.81 g, 35.0 mmol), and a catalytic amount of DBU in ethanol (35 mL) was stirred at rt for 1 h. After removal of the solvent, the residue was extracted with $CHCl_3$ and the organic layer was washed with H_2O, dried over $MgSO_4$, and concentrated. The crude carbamate was dissolved in acetone (35 mL) and the chilled solution was treated with methyl triflate (11.5 g, 70.0 mmol) in the presence of K_2CO_3 (5.80 g, 42 mmol) overnight. After removal of the solvent, the residue was extracted with AcOEt and the organic layer was washed with H_2O, dried over $MgSO_4$, and chromatographed on silica gel.

Elution with hexane gave the carbonimidodithioate (**3**, 8.56 g, 80%) as an oil. ^{1}H NMR δ 0.11 (br s, 9 H), 2.31 (s, 2 H), 2.48 (s, 3 H), 6.81 and 7.27 (AA'BB'q, 4 H, *J* = 9 Hz). ^{13}C NMR δ -1.70, 15.01, 17.56, 121.89, 129.01, 129.04, 148.66, 165.16. HRMS *m/z* 303.0353 (M^+ calcd for $C_{12}H_{18}N^{35}ClSiS_2$ 303.0338). Anal. Calcd for $C_{12}H_{18}NClS_2Si$: C, 47.42; H, 5.97; N, 4.61. Found: C, 47.49; H, 5.78; N, 4.55.

Other carbonimidodithioate derivatives (**2**), (**4**), and (**5**) were similarly prepared. Yields are listed in Table 1 and the spectral data are as follows.

2: oil. ^{1}H NMR major isomer δ 0.10 (s, 9 H), 1.25 (t, 3 H, *J* = 7 Hz), 2.32 (s, 2 H), 2.34 (s, 3 H), 3.46 (q, 2 H, *J* = 7 Hz); minor isomer δ 0.13 (s, 9 H), 1.24 (t, 3 H, *J* = 7 Hz), 2.18 (s, 2 H), 2.55 (s, 3 H), 3.47 (q, 2 H, *J* = 7 Hz). ^{13}C NMR major isomer δ 1.87, 15.63, 15.73, 17.24, 47.35, 158.49; minor isomer δ 1.61, 14.50, 14.63, 16.58, 47.49, 157.52. HRMS *m/z* 221.0765 (M^+ calcd for $C_8H_{19}NSiS_2$ 221.0728).

4: oil. ^{1}H NMR δ 0.12 (br s, 9 H), 2.33 (br s, 2 H), 2.48 (s, 3 H), 6.87 (m, 2 H), 7.07 (m, 1 H), 7.31 (m, 2 H). ^{13}C NMR δ -1.70, 15.00, 17.52, 120.45, 123.67, 128.88, 150.14, 163.64. HRMS *m/z* 269.0733 (M^+ calcd for $C_{12}H_{19}NSiS_2$ 269.0728). Anal. Calcd for $C_{12}H_{19}NS_2Si$: C, 53.48; H, 7.11; N, 5.20. Found: C, 53.56; H, 7.04; N, 5.14.

5: oil. ^{1}H NMR δ 0.09 and 0.14 (2 br s, 9 H), 2.33 (br s, 2 H), 2.48 (s, 3 H), 3.80 (s, 3 H), 6.82 and 6.87 (AA'BB'q, 4 H, *J* = 9 Hz). ^{13}C NMR δ -1.69, 14.99, 17.39, 55.40, 114.27, 121.50, 143.21, 156.30. HRMS *m/z* 299.0879 (M^+ calcd for $C_{13}H_{21}NOSiS_2$ 299.0834). Anal. Calcd for $C_{13}H_{21}NOS_2Si$: C, 52.13; H, 7.07; N, 4.68. Found: C, 52.37; H, 7.08; N, 4.59.

Reaction of Methyl Trimethylsilylmethyl Carbonimidodithioates (2-5) with Carbonyl Compounds.

A reaction of *N*-ethylcarbonimidodithioate (**2**) with 4-chlorobenzaldehyde is representative. A mixture of the carbonimidodithioate (**2**, 111 mg, 0.50 mmol), 4-chlorobenzaldehyde (141 mg, 1.00 mmol), and CsF (152 mg, 1.00 mmol) in dry DMF (1 mL) was stirred at rt for 15 h. After an usual workup, the crude product was chromatographed on silica gel. Elution with a mixture of hexane and AcOEt (85 : 15) afforded the oxathiolane derivative **6a** (75.4 mg, 62%) as an oil. Although the compounds (**6a**) was obtained as an unseparable mixture of the diastereoisomers, the spectral data only for the major isomer were shown because the NMR signals corresponding to the minor isomer could not be assigned properly due to low intensity and overlapping of the signals. ^{1}H NMR δ 1.24 (t, 3 H, *J* = 7 Hz), 3.19 (dq, 1 H, *J* = 13 and 7 Hz), 3.22 (dq, 1 H, *J* = 13 and 7 Hz), 3.28 (dd , 1 H, *J* = 11 and 9 Hz), 3.62 (dd, 1 H, *J* = 11 and 6 Hz), 5.41 (dd, 1 H, *J* = 9 and 6 Hz), 7.33 and 7.57 (AA'BB'q, 4 H, *J* = 8 Hz). ^{13}C NMR δ 15.68, 38.02, 48.31, 80.73, 127.08, 128.88, 134.67, 136.08, 159.78. HRMS *m/z* 241.0310 (M^+ calcd for $C_{11}H_{12}NOClS$ 241.0328).

Reactions of other carbonyl compounds with carbonimidodithioates (**2-5**) were similarly carried out and the yields are summarized in Table 2. Physical and spectral data for the compounds (**6-10**) are as follows.

6b: oil. ^{1}H NMR δ 1.25 (t, 3 H, *J* = 7 Hz), 3.21 (dq, 1 H, *J* = 13 and 7 Hz), 3.24 (dq, 1 H, *J* = 13 and

7 Hz), 3.33 (dd, 1 H, J = 11 and 9 Hz), 3.63 (dd, 1 H, J = 11 and 6 Hz), 5.44 (dd, 1 H, J =9 and 6 Hz), 7.34-7.43 (m, 5 H). ^{13}C NMR δ 15.68, 38.06, 48.24, 81.54, 125.65, 128.57, 128.60, 137.52, 160.11. HRMS *m/z* 208.0835 [(M + 1)$^+$ calcd for $C_{11}H_{14}NOS$ 208.0796].

6c: oil. ^{1}H NMR δ 1.25 (t, 3 H, J = 7 Hz), 2.34 (s, 2 H), 3.19 (dq, 1 H, J = 13 and 7 Hz), 3.23 (dq, 1 H, J = 13 and 7 Hz), 3.32 (dd, 1 H, J = 11 and 9 Hz), 3.59 (dd, 1 H, J = 11 and 6 Hz), 5.41 (dd, 1 H, J = 9 and 6 Hz), 7.18 and 7.30 (AA'BB'q, 4 H, J = 8 Hz). ^{13}C NMR δ 15.76, 20.01, 38.16, 48.26, 81.70, 125.73, 129.31, 134.54, 138.57, 160.27. HRMS *m/z* 221.0911 (M$^+$ calcd for $C_{12}H_{15}NOS$ 221.0874).

6e: oil. ^{1}H NMR δ 1.26 (t, 3 H, J = 7 Hz), 3.21 (dq, 1 H, J = 13 and 7 Hz), 3.25 (dq, 1 H, J = 13 and 7 Hz), 3.31 (dd, 1 H, J = 11 and 9 Hz), 3.69 (dd, 1 H, J = 11 and 6 Hz), 5.51 (dd, 1 H, J = 9 and 6 Hz), 7.55 and 7.66 (AA'BB'q, 4 H, J = 8 Hz). ^{13}C NMR δ 15.68, 38.04, 48.41, 80.55, 123.84 (q, J = 271 Hz), 125.70 (q, J = 4 Hz), 125.98 (q, J = 4 Hz), 131.06 (q, J = 33 Hz), 141.57, 159.87. HRMS *m/z* 275.0636 (M$^+$ calcd for $C_{12}H_{12}NOF_3S$ 275.0592).

6f: oil. ^{1}H NMR δ 1.24 (t, 3 H, J = 7 Hz), 1.79 (s, 3 H), 3.16 (dq, 1 H, J = 13 and 7 Hz), 3.19 (dq, 1 H, J = 13 and 7 Hz), 3.53 and 3.58 (ABq, 2 H, J = 11 Hz), 7.26-7.46 (m, 5 H). ^{13}C NMR δ 15.84, 27.54, 43.00, 48.24, 86.68, 124.46, 127.83, 128.54, 143.26, 160.11. HRMS *m/z* 222.0977 [(M + 1)$^+$ calcd for $C_{12}H_{16}NOS$ 222.0953].

6g: oil. ^{1}H NMR δ 0.87 (t, 3 H, J = 7 Hz), 1.18 (t, 3 H, J = 7 Hz), 1.29 (m, 4 H), 1.40 (m, 1 H), 1.50 (m, 1 H), 1.63 (m, 1 H), 1.82 (m, 1 H), 3.03 (dd, 1 H, J = 11 and 9 Hz), 3.11 (dq, 1 H, J = 13 and 7 Hz), 3.14 (dq, 1 H, J = 13 and 7 Hz), 3.32 (dd, 1 H, J = 11 and 6 Hz), 4.39 (m, 1 H). ^{13}C NMR δ 13.76, 15.80, 22.37, 35.34, 31.49, 33.74, 36.10, 48.18, 81.17, 160.84. HRMS *m/z* 201.1163 (M$^+$ calcd for $C_{10}H_{19}NOS$ 201.1187).

7a: pale yellow powder, mp 111-114 ℃. ^{1}H NMR δ 3.37 (dd, 1 H, J = 11 and 10 Hz), 3.66 (dd, 1 H, J = 11 and 6 Hz), 5.61 (dd, 1 H, J = 10 and 6 Hz), 7.00 and 7.30 (AA'BB'q, 4 H, J = 9 Hz), 7.41 (s, 4 H). ^{13}C NMR δ 38.43, 82.42, 122.66, 127.25, 129.18, 129.31, 129.84, 135.16, 135.30, 147.34, 163.23. HRMS *m/z* 322.9981 (M$^+$ calcd for $C_{15}H_{11}NO^{35}Cl_2S$ 322.9938). Anal. Calcd for $C_{15}H_{11}NOCl_2S$: C, 55.57; H, 3.42; N, 4.32. Found: C, 55.76; H, 3.47; N, 4.30.

7b: pale yellow powder, mp 113-115 ℃. ^{1}H NMR δ 3.41 (dd, 1 H, J = 11 and 10 Hz), 3.65 (dd, 1 H, J = 11 and 6 Hz), 5.63 (dd, 1 H, J = 10 and 6 Hz), 6.96 and 7.30 (AA'BB'q, 4 H, J = 8 Hz), 7.38-7.48 (m, 5 H). ^{13}C NMR δ 38.42, 83.20, 122.73, 125.84, 128.91, 129.13, 129.24, 136.99, 147.58, 163.41. HRMS *m/z* 289.0323 (M$^+$ calcd for $C_{15}H_{12}NO^{35}ClS$ 289.0328). Anal. Calcd for $C_{15}H_{12}NOClS$: C, 62.17; H, 4.17; N, 4.83. Found: C, 61.96; H, 4.11; N, 4.96.

7c: pale yellow powder, mp 98-98 ℃. ^{1}H NMR δ 2.38 (s, 3 H), 3.40 (dd, 1 H, J = 11 and 10 Hz), 3.62 (dd, 1 H, J = 11 and 6 Hz), 5.60 (dd, 1 H, J = 10 and 6 Hz), 6.96 and 7.30 (AA'BB'q, 4 H, J = 9 Hz), 7.23 and 7.36 (AA'BB'q, 4 H, J = 9 Hz). ^{13}C NMR δ 21.13, 38.47, 83.36, 122.77, 125.90, 129.26, 129.59, 129.72, 133.91, 139.16, 147.64, 163.53. HRMS *m/z* 303.0457 (M$^+$ calcd for $C_{16}H_{14}NO^{35}ClS$ 303.0485).

8: pale yellow powder, mp 119-120 ℃. ^{1}H NMR δ 3.35 (dd, 1 H, J = 11 and 9 Hz), 3.64 (dd, 1 H, J = 11 and 6 Hz), 5.60 (dd, 1 H, J = 9 and 6 Hz), 7.02 (m, 2 H), 7.14 (m, 1 H), 7.35 (m, 2 H), 7.40 and

7.42 (AA'BB'q, 4 H, J = 9 Hz). ^{13}C NMR δ 38.35, 82.14, 121.25, 124.45, 127.25, 129.12, 129.17, 135.04, 135.60, 148.85, 165.55. HRMS *m/z* 289.0296 (M^+ calcd for $C_{15}H_{12}NO^{35}ClS$ 289.0328). Anal. Calcd for $C_{15}H_{12}NOClS$: C, 62.17; H, 4.17; N, 4.83. Found: C, 62.27; H, 4.15; N, 4.73.

9: pale yellow powder, mp 130–135 ℃. ^{1}H NMR δ 3.34 (dd, 1 H, J = 11 and 10 Hz), 3.63 (dd, 1 H, J = 11 and 6 Hz), 3.81 (s, 3 H), 5.58 (dd, 1 H, J = 10 and 6 Hz), 6.89 and 6.98 (AA'BB'q, 4 H, J = 9 Hz), 7.40 and 7.42 (AA'BB'q, 4 H, J = 9 Hz). ^{13}C NMR δ 38.36, 55.43, 82.00, 114.47, 122.24, 127.25, 129.09, 134.97, 135.61, 142.05, 156.72, 162.43. HRMS *m/z* 319.0430 (M^+ calcd for $C_{16}H_{14}NO_2{}^{35}ClS$ 319.0434). Anal. Calcd for $C_{16}H_{14}NO_2ClS$: C, 60.09; H, 4.41; N, 4.38. Found: C, 60.12; H, 4.53; N, 4.43.

10: oil. ^{1}H NMR δ 2.50 (s, 6 H), 6.81 and 7.27 (AA'BB'q, 4 H, J = 9 Hz). ^{13}C NMR δ 14.90, 121.84, 129.04, 129.22, 148.52, 163.57. HRMS *m/z* 232.9877 [M^+ calcd for $C_9H_{10}N^{37}ClS_2$ 332.9912).

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