Generation and Characterization of 1,3-Di-*t*-butyl- and 1,3-Di-*t*-butyl-4,6-dimethylthieno[3,4-*c*]thiophenes

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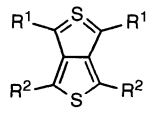
1,3-Di-*t*-butyl- and 1,3-di-*t*-butyl-4,6-dimethylthieno[3,4-*c*]thiophenes (**1g** and **1h**) are generated by Pummerer dehydration of the corresponding sulfoxides (**4** and **5**, respectively) in boiling acetic anhydride and can be trapped with *N*-phenylmaleimide (NPM). Both *endo*- and *exo*-adducts are formed from **1g** and NPM, while only *exo*-adduct is formed from **1h** and NPM. Reduction and isomerization of the starting materials occur in the reactions of **4** and **5** with trifluoroacetic anhydride. The reaction of **5** with trifluoroacetic anhydride in the presence of 2,6-lutidine also gives 4,6-di-*t*-butyl-1-(trifluoroacetylmethylene)-3-methyl-1*H*,3*H*-thieno[3,4-*c*]thiophene.

Thieno[3,4-*c*]thiophenes, so-called "nonclassical" thienothiophenes, have been attracting much attention.[1] Thieno[3,4-*c*]thiophene (**1a**)[2] and its dimethyl (**1b**)[3] and bis(methoxycarbonyl) (**1c**)[3] derivatives were generated and characterized by trapping experiments with *N*-phenylmaleimide. On the other hand, tetraphenyl- (**1d**),[4] tetrakis(alkylthio)- (**1f**),[5] and tetra-2-thienylthieno[3,4-*c*]thiophenes (**1e**)[6] were successfully synthesized as isolable compounds. These isolable thieno[3,4-*c*]thiophenes owe their stability to resonance and electron-withdrawing effects of the substituents.[5b] However, there is no report on thieno[3,4-*c*]thiophenes stabilized by the steric protection with bulky substituents (kinetic stabilization). We report here the generation and characterization of thieno[3,4-*c*]thiophenes carrying bulky substituents.

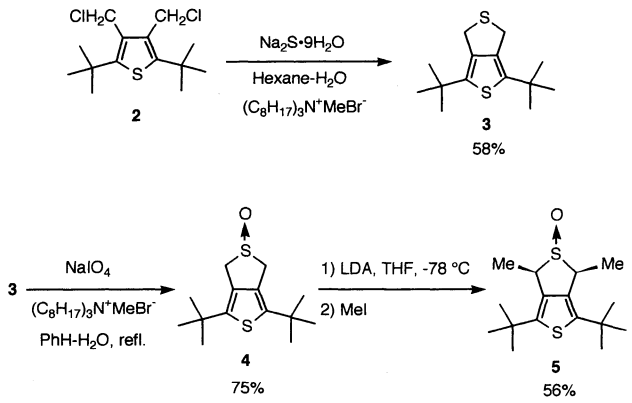


1a: $R^1=R^2=H$
1b: $R^1=Me$, $R^2=H$
1c: $R^1=CO_2Me$, $R^2=H$
1d: $R^1=R^2=Ph$
1e: $R^1=R^2=2$-Thienyl
1f: $R^1=R^2=SR$
1g: $R^1=H$, $R^2=t$-Bu
1h: $R^1=Me$, $R^2=t$-Bu

Results and Discussion

We first attempted the synthesis of tetra-*t*-butyl derivative (**1**: $R^1=R^2=t$-Bu) by the method of Cava.[4] However, the precursor, tetrapivaloylethane, could not be obtained by the coupling of the bromide and the sodium salt of dipivaloylmethane probably due to the steric hindrance.

We therefore turned the target to 1,3-dialkyl-4,6-di-*t*-butylthieno[3,4-*c*]thiophene. Thus, 2,5-di-*t*-butyl-3,4-bis(chloromethyl)thiophene (**2**)[7] was chosen as the starting compound. The reaction of **2** with Na_2S afforded 4,6-di-*t*-butyl-1*H*,3*H*-thieno[3,4-*c*]thiophene (**3**) in 58% yield, which was oxidized with $NaIO_4$ in refluxing benzene–water in the presence of $(C_8H_{17})_3N^+MeBr^-$ to give the sulfoxide **4** in 75% yield. Dilithiation of **4** with 2.2 equiv of lithium diisopropylamide at −78 °C followed by treatment with iodomethane gave 4,6-di-*t*-butyl-1,3-dimethyl-1*H*,3*H*-thieno[3,4-*c*]thiophene 2-oxide (**5**) in 56% yield. The sulfoxide **5** was the sole isomer obtained, although three isomers are likely to be formed. In the ^1H NMR two methyl groups of **5** are equivalent, indicating that the methyl groups are in cis geometry each other. Their stereochemistry relative to the sulfinyl group was determined to be cis by comparison of the ^1H NMR spectra of **5** and its isomer obtained by the reaction described later.[9] Quenching of the lithiated **5** with isopropyl bromide resulted in the formation of a complex mixture.



Pummerer dehydration of sulfoxides **4** and **5** with acetic anhydride or trifluoroacetic anhydride was investigated to prepare the corresponding thieno[3,4-*c*]thiophenes. Dehydration of **4** in boiling acetic anhydride in the presence of *N*-phenylmaleimide (NPM) yielded expected two adducts **6** and **7** in 8 and 79% yields, respectively. The assignment of **6** and **7** was performed by the comparison of their ^1H NMR spectra;[1b] the α-protons to the imide carbonyls of the endo adduct **6** appear at lower field (δ=4.13) than those of the exo adduct **7** (δ=3.46) because of the deshielding effect

of the bridged sulfur. The formation of the adducts **6** and **7** indicates the generation of 1,3-di-*t*-butylthieno-[3,4-*c*]thiophene (**1g**) as the reactive intermediate. It is apparent that both the regioselectivity of the addition and the high *exo*/*endo* selectivity (Table 1) are due to the steric hindrance of 1,3-di-*t*-butyl groups of **1g**. When the dehydration of **4** was done without NPM, only an intractable mixture was obtained. Next, dehydration of **4** was examined with trifluoroacetic anhydride in the presence of 2,6-lutidine in CH_2Cl_2[10] to carry out the dehydration at lower temperatures. The reaction at 0 °C, however, gave a complex mixture, from which a sulfide **3** was isolated in 26% yield. Although it seemed that the product **3** might be formed by the hydrogen abstraction of **1g** from the solvent, no deuterium was introduced into **3** when the reaction was carried out in $CDCl_3$. Moreover, no adduct was obtained in the presence of NPM or dimethyl acetylenedicarboxylate. It is known that reduction of sulfoxides by trifluoroacetic anhydride takes place in the presence of reducing agents such as iodide anion,[11] dimethyl sulfide,[12] and hydrogen sulfide.[13] In the present case, therefore, the material formed during the reaction must exert as the reducing agent.

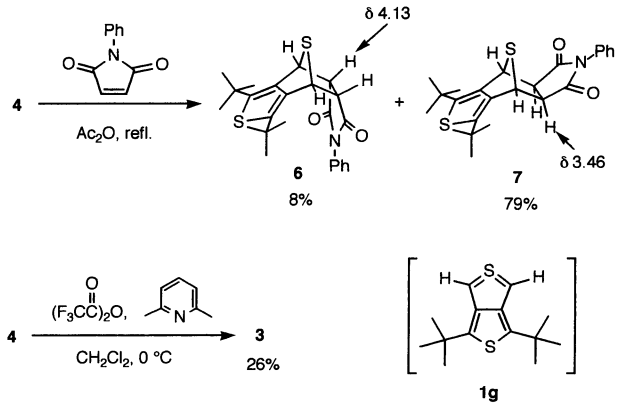
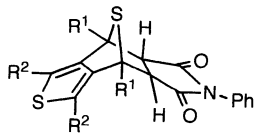


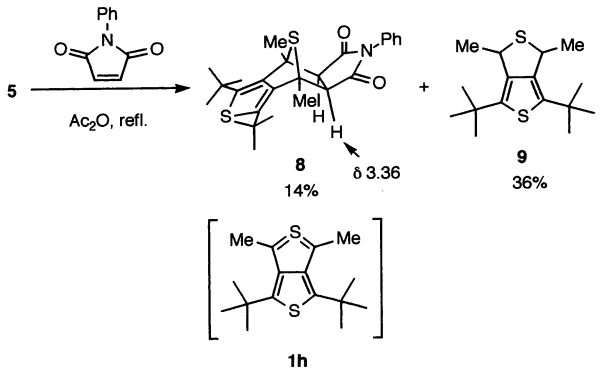
Table 1. The Chemical Shifts of the α-Protons to Imide Carbonyls and the Formation Ratio of *exo*/*endo* of NPM Adducts



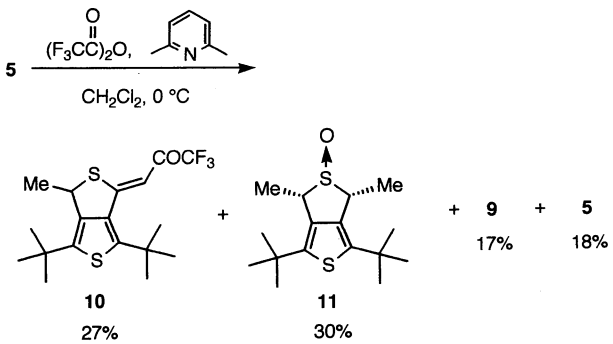
R^1	R^2	δ		Formation ratio	Ref.
		endo	*exo*	*exo*/*endo*	
H	H	4.21	3.52	1.8	2
Me	H	3.91	3.30	2.4	3
H	CO_2Me	4.27	3.52	4.2	3
SEt	SEt	4.27	3.24	3.6	5d
Th[a]	Th[a]	4.99	4.26	8.8	6
H	*t*-Bu	4.13	3.46	9.9	b)

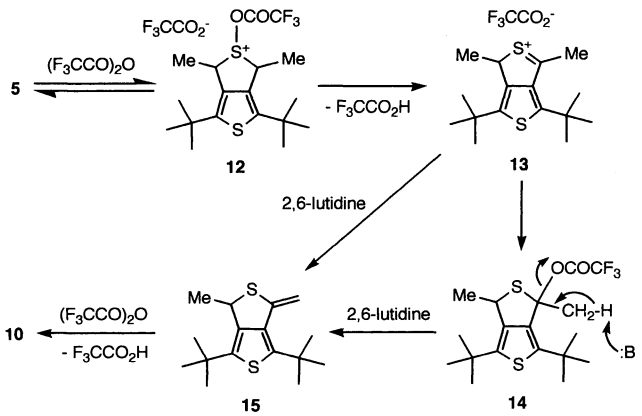
a) 2-Thienyl. b) This work.

Pummerer dehydration of sulfoxide **5** in boiling acetic anhydride in the presence of NPM yielded the desired adduct **8** (14%) and a reduction product **9** (36%). The formation of the adduct indicates the generation of 1,3-di-*t*-butyl-4,6-dimethylthieno[3,4-*c*]thiophene (**1h**) as the intermediate. The structure of **8** was assigned to the *exo*-adduct by the ^1H NMR spectrum. The signal due to the α-protons to the imide carbonyls appears at δ=3.36, which is comparable with those of other *exo*-adducts reported so far (Table 1). Although it is difficult to specify the position of the addition only by the ^1H NMR spectrum, it is natural to assume that the addition takes place at the less crowded 4,6-positions.



On the other hand, dehydration of **5** with trifluoroacetic anhydride and 2,6-lutidine in dichloromethane at 0 °C gave an unexpected alkene **10** (27%), the reduction product **9** (17%), and the isomer (**11**, 30%) of the starting sulfoxide along with recovery of **5** (18%). During the reaction, no color change indicative of the formation of the desired thieno[3,4-*c*]thiophene (**1h**), which is anticipated to be a highly colored compound, was not observed. The formation of the alkene **10** is speculated as shown in Scheme 1. The Pummerer rearrangement of **5** would proceed through a sulfonium ion **12** and then a carbonium ion (**13**) stabilized by the adjacent sulfur atom. Either elimination of trifluoroacetic acid from the Pummerer rearrangement product **14** or deprotonation from the carbonium ion **13** catalized by 2,6-lutidine gives rise to an exomethylene compound **15**, which





Scheme 1.

further reacts with trifluoroacetic anhydride to yield **10**.[14] The reaction without 2,6-lutidine to avoid the formation of **15** gave **9** (33%), **11** (30%), and **5** (18%). The elimination of the methine proton of **13** or **14** should provide the desired thieno[3,4-*c*]thiophene (**1h**), but the large steric hindrance around the methine proton seems to prevent the desired reaction.

In conclusion new thieno[3,4-*c*]thiophenes **1g** and **1h** were generated from the corresponding sulfoxides **4** and **5** and their generation was confirmed by trapping experiments. Steric protection with two *t*-butyl and two methyl groups (**1h**) is not sufficient to make the thieno[3,4-*c*]thiophene isolable. It is necessary to introduce more bulky alkyl groups into appropriate positions for isolation of a sterically stabilized thieno-[3,4-*c*]thiophene.

Experimental

General. Melting points were determined on a MEL-TEMP capillary tube apparatus and are uncorrected. ^{1}H NMR spectra were obtained on a Bruker AM400 (400 MHz) or a JEOL FX-90Q (90 MHz) spectrometer and ^{13}C NMR spectra on a Bruker AM400 (100.6 MHz) or a JEOL FX-90Q (22.49 MHz) spectrometer using $CDCl_3$ as the solvent and chemical shifts are expressed in parts per million from Me_4Si as an internal standard. IR spectra were taken on a Hitachi 270-50 spectrometer. UV-vis absorption spectra were taken on a Hitachi 340 spectrometer. Low- and high-resolution mass spectra were measured with a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode. Dry column chromatography was performed with using a 1:5 mixture of Merck Kieselgel 60 F_{254} (70—230 mesh) and Merck Kieselgel 60 (70—230 mesh) packed in a seamless cellulose tubing and visualized with a 254-nm UV lamp. Elemental analyses were performed by Chemical Analysis Center of Saitama University, for which we thank Professor M. Sato, Mr. M. Kubo, and Mrs. E. Morikubo.

4,6-Di-*t*-butyl-1*H*,3*H*-thieno[3,4-*c*]thiophene (3). To a solution of 2,5-di-*t*-butyl-3,4-bis(chloromethyl)thiophene (**2**)[7] (1.01 g, 3.44 mmol) in hexane (50 ml) were added a solution of $Na_2S \cdot 9H_2O$ (1.83 g, 7.62 mmol) in water (20 ml) and a small amount of $(C_8H_{17})_3N^+CH_3Cl^-$. The mixture was stirred at room temperature for 5 h and then water and ether were added. The ethereal layer was separated, washed with water, dried over anhydrous $MgSO_4$, and evaporated. The pale yellow oil was subjected to dry column chromatography (silica gel, CCl_4) to yield **3** (512 mg, 58%): Colorless crystals, mp 117—118 °C (MeOH); ^{1}H NMR ($CDCl_3$) δ=1.34 (18H, s) and 3.90 (4H, s); ^{13}C NMR δ=30.5 (CH_2), 31.2 (CH_3), 34.4 (C), 139.4 (C), and 139.8 (C); MS *m/z* (rel intensity) 254 (M^+; 34) and 239 (100). Found: C, 66.09; H, 8.50%. Calcd for $C_{47}H_{22}S_2$: C, 66.08; H, 8.71%.

4,6-Di-*t*-butyl-1*H*,3*H*-thieno[3,4-*c*]thiophene 2-Oxide (4). To a solution of 4,6-di-*t*-butyl-1*H*,3*H*-thieno[3,4-*c*]thiophene (**3**) (103 mg, 0.40 mmol) in benzene (20 ml) were added a solution of $NaIO_4$ (112 mg, 0.52 mmol) in water (5 ml), a small amount of $(C_8H_{17})_3N^+CH_3Cl^-$, and methanol (15 ml). The mixture was refluxed for 17 h and allowed to cool to room temperature. The mixture was extracted with benzene and the extract was washed with water, dried over anhydrous $MgSO_4$ and evaporated. The residue was purified with dry column chromatography (silica gel, CH_2Cl_2–Et_2O 9:1) to provide the desired sulfoxide **4** (82 mg, 75%): Colorless crystals, mp 170—171 °C (hexane–CCl_4); ^{1}H NMR δ=1.36 (18H, s), 3.78 (2H, d, *J*=15.4 Hz), and 4.23 (2H, d, *J*=15.4 Hz); ^{13}C NMR δ=31.7, 34.6, 54.0, 131.3, and 145.9; IR (KBr) 1042 cm^{-1} (S=O); MS *m/z* (rel intensity) 270 (M^+; 33) and 207 (100). Found: C, 61.90; H, 8.11%. Calcd for $C_{14}H_{22}OS_2$: C, 62.17; H, 8.20%.

4,6-Di-*t*-butyl-1,3-dimethyl-1*H*,3*H*-thieno[3,4-*c*]thiophene 2-Oxide (5). A solution of sulfoxide **4** (266 mg, 0.98 mmol) in THF (5 ml) was added dropwise to a solution of lithium diisopropylamide, prepared from diisopropylamine (0.3 ml, 2.14 mmol) and butyllithium (1.62 M, 1.4 ml, 2.27 mmol) (1 M=1 mol dm^{-3}) in THF (5 ml), at −78 °C under argon. Iodomethane (0.3 ml, 4.82 mmol) was added after stirring for 7 min at this temperature and the mixture was stirred for additional 30 min. The resulting mixture was allowed to warm to room temperature and then water and ether were added. The ethereal extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by dry column chromatography (silica gel, Et_2O) to give the desired sulfoxide **5** (164 mg, 56%): Colorless crystals, mp 161—162 °C (hexane); ^{1}H NMR δ=1.39 (18H, s), 1.60 (6H, d, *J*=7.7 Hz), and 3.95 (2H, q, *J*=7.7 Hz); ^{13}C NMR δ=18.3, 32.4, 35.2, 61.2, 140.2, and 144.9; IR (KBr) 1050 cm^{-1} (S=O); MS *m/z* (rel intensity) 298 (M^+; 30) and 235 (100). Found: C, 64.25; H, 8.59%. Calcd for $C_{16}H_{26}OS_2$: C, 64.38; H, 8.78%.

Dehydration of 4,6-Di-*t*-butyl-1*H*,3*H*-thieno[3,4-*c*]thiophene 2-Oxide (4). (1) In Acetic Anhydride in the Presence of *N*-Phenylmaleimide (NPM). A solution of sulfoxide **4** (54 mg, 0.20 mmol) and NPM (34.6 mg, 0.20 mmol) in acetic anhydride (5 ml) was heated at reflux under N_2 for 1 h. After removal of the solvent under reduced pressure, the residue was subjected to dry column chromatography (silica gel, CH_2Cl_2) to yield *endo*-adduct **6** (7 mg, 8%) and *exo*-adduct **7** (67 mg, 79%).

6: Colorless crystals, mp 223—224 °C decomp (hexane–CH_2Cl_2); ^{1}H NMR δ=1.34 (18H, s), 4.13 (2H, t, *J*=2.2 Hz), 5.12 (2H, t, *J*=2.3 Hz), 6.74 (2H, m), and 7.35 (3H, m); ^{13}C NMR δ=32.7 (q), 35.5 (s), 52.2 (d), 54.7 (d), 127.2 (d), 129.1 (d), 129.2 (d), 131.4 (s), 137.6 (s), 142.2 (s), and 173.7 (s); IR (KBr) 1718 cm^{-1} (C=O); MS *m/z* (rel intensity) 425 (M^+; 18), 252 (100), and 237 (98). Found: *m/z* 425.1475. Calcd for $C_{24}H_{27}NO_2S_2$: M, 425.1484.

7: Colorless crystals, 258—259 °C decomp (hexane–CH_2Cl_2); ^{1}H NMR δ=1.40 (18H, s), 3.46 (2H, s), 5.02 (2H, s), 7.26 (2H, m), and 7.48 (3H, m); ^{13}C NMR δ=32.0 (q), 34.5 (s), 52.2 (d), 53.0 (d), 126.6 (d), 128.9 (d), 129.2 (d), 132.0 (s), 139.5 (s), 141.4 (s), and 174.9 (s); IR (KBr) 1724 cm^{-1} (C=O); MS *m/z* (rel intensity) 425 (M^+; 17), 252 (88) and 237 (100). Found: *m/z* 425.1512. Calcd for $C_{24}H_{27}NO_2S_2$: M, 425.1484.

(2) In Trifluoroacetic Anhydride in the Presence of 2,6-Lutidine. To a solution of sulfoxide **4** (54.4 mg, 0.20 mmol) in CH_2Cl_2 (2 ml) were added trifluoroacetic anhydride (0.05 ml) and 2,6-lutidine (0.03 ml, 0.26 mmol) at 0 °C under nitrogen. The mixture was stirred for 2 h at 0 °C and for 15 h at room temperature and quenched by addition of 1.2 M HCl. The mixture was extracted with CH_2Cl_2 and the extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated. The residue was subjected to dry column chromatography (silica gel, CCl_4) to provide **3** (13.5 mg, 26%) and the starting material (22 mg, 49%).

Dehydration of 4,6-Di-*t*-butyl-1,3-dimethyl-1*H*,3*H*-thieno-[3,4-*c*]thiophene 2-Oxide (5). (1) In Acetic Anhydride in the Presence of NPM. A solution of sulfoxide **5** (46 mg, 0.15 mmol) and NPM (27 mg, 0.16 mmol) in acetic anhydride (5 ml) was refluxed under argon for 24 h. The solution was allowed to cool to room temperature and the solvent was removed under reduced pressure. The residue was subjected to dry column chromatography (silica gel, CH_2Cl_2) to give *exo*-adduct **8** (10 mg, 14%) and **9** (16 mg, 36%).

8: Colorless crystals, mp 250—251 °C decomp (hexane–CH_2Cl_2); ^{1}H NMR δ=1.47 (18H, s), 2.23 (6H, s), 3.36 (2H, s), 7.28 (2H, d, *J*=7.5 Hz), 7.41 (1H, t, *J*=7.5 Hz), and 7.49 (2H, d, *J*=7.7 Hz); ^{13}C NMR δ=19.7 (q), 32.8 (q), 34.0 (s), 58.2 (d), 62.3 (s), 126.7 (d), 128.8 (d), 129.2 (d), 132.0 (s), 137.7 (s), 147.3 (s), and 173.5 (s); MS *m/z* (rel intensity) 453 (M^+; 2) and 283 (100). Found: *m/z* 453.1779. Calcd for $C_{26}H_{31}NO_2S_2$: M, 453.1796.

9: Colorless crystals, mp 89—90 °C (MeOH); ^{1}H NMR δ=1.36 (18H, s), 1.79 (6H, d, *J*=6.9 Hz), and 4.21 (2H, q, *J*=6.9 Hz); ^{13}C NMR δ=28.7 (q), 32.3 (q), 35.1 (s), 40.2 (d), 139.6 (s), and 145.3 (s); MS *m/z* (rel intensity) 282 (M^+; 30) and 267 (100). Found: C, 67.86; H, 9.06%. Calcd for $C_{16}H_{26}S_2$: C, 68.02; H, 9.28%.

(2) In Trifluoroacetic Anhydride in the Presence of 2,6-Lutidine. To a solution of sulfoxide **5** (52 mg, 0.17 mmol) in CH_2Cl_2 (10 ml) were added trifluoroacetic anhydride (0.5 ml) and 2,6-lutidine (0.1 ml, 0.86 mmol) at 0 °C under argon. The solution was stirred at this temperature for 1.5 h and quenched by addition of 1.2 M HCl. The mixture was extracted with CH_2Cl_2 and the extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated. The residue was subjected to dry column chromatography (silica gel, CCl_4 and then Et_2O) to provide **9** (8.4 mg, 17%), alkene **10** (18 mg, 27%), and isomer **11** (16 mg, 30%).

10: Yellow crystals, mp 118—119 °C (hexane); ^{1}H NMR δ=1.45 (9H, s), 1.57 (9H, s), 1.69 (3H, d, *J*=6.9 Hz), 4.50 (1H, q, *J*=7.0 Hz), and 7.26 (1H, s); ^{13}C NMR δ=25.0 (q), 30.3 (q), 32.1 (q), 32.3 (s), 35.1 (s), 41.4 (d), 105.8 (d), 117.2 (q, J_{CF}=288.4 Hz, q), 138.2 (s), 141.3 (s), 147.0 (s), 151.2 (s), 165.6 (s), and 177.4 (t, J_{CF}=33.4 Hz, t); IR (KBr) 1660 cm^{-1} (C=O); UV (MeCN) 370 (log ε 4.37), 313 (4.07), and 252 nm (4.01); MS *m/z* (rel intensity) 376 (M^+; 81), 361 (89), and 319 (100). Found: *m/z* 376.1353. Calcd for $C_{18}H_{23}OF_3S_2$: M, 376.1343.

11: Colorless crystals, mp 176—177 °C (hexane); ^{1}H NMR δ=1.40 (18H, s), 1.49 (6H, d, *J*=7.3 Hz), and 4.29 (2H, q, *J*=7.3 Hz); ^{13}C NMR δ=13.8, 32.2, 35.1, 51.1, 133.4, and 146.3; IR (KBr) 1068 cm^{-1} (S=O); MS *m/z* (rel intensity) 298 (M^+; 100) and 235 (100). Found: *m/z* 298.1428. Calcd for $C_{16}H_{26}OS_2$: M, 298.1425.

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