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Heteroarylthiomethylsilanes. Synthesis and Application to Heteroarylthiomethylation of Carbonyl Compounds [1]

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ABSTRACT

Heteroarylthiomethyltrimethylsilanes bearing a 2-pyridyl, 2-imidazolyl, 5-tetrazolyl, or 2-pyrimidinyl group, readily prepared by the reaction of heteroarylmercaptans with halomethyltrimethylsilane in the presence of a base, are synthetic equivalents of heteroarylthiomethyl anions, otherwise inaccessible, and are effective reagents for the introduction of a heteroarylthiomethyl group at a carbonyl carbon atom in the presence of a catalytic amount of tetrabutylammonium fluoride.

INTRODUCTION

Introduction of heteroaryl and organosulfur moieties to organic molecules is important from the viewpoint of not only organic synthesis but also their biological and pharmacological activities, and various methods have been developed [2]. In the previous articles, we described how arylthiomethylation and alkylthiomethylation can be achieved by using organosilicon compounds under mild conditions [3]. However, heteroarylthiomethylations are almost unknown or else have been carried out only under considerably strong basic conditions [4,5]. As a part of a program aimed at exploring a new class of heteroarylthiomethyl anions and an extension of our studies on the fluoride ion-promoted reaction of organosilicon compounds [6], we report herein a convenient and mild method for the introduction of heteroarylthiomethyl groups into carbonyl compounds using heteroarylthiomethyltrimethylsilanes promoted by the fluoride ion.

RESULTS AND DISCUSSION

The starting heteroarylthiomethylsilanes **2a–d** were readily prepared by the condensation of each heteroarylmercaptan **1** with iodomethyltrimethylsilane or chloromethyltrimethylsilane in the presence of a base, as shown in Equations 1 and 2. Reaction of lithium 2-pyridinylthiolate, prepared from 2-mercaptopyridine and butyllithium, with iodomethyltrimethylsilane in THF gave **2a** in 97% yield (Method A). This method was not necessarily suitable for the synthesis of other heteroarylthiomethylsilanes (**2b–2d**), such as the 2-imidazolyl, 2-pyrimidinyl, and 5-tetrazolyl derivatives. Thus, 2-pyrimidiylthiomethyltrimethylsilane (**2c**) was obtained in only 67% yield according to the procedure. However, when a heteroarylmercaptan was mixed with chloromethyltrimethylsilane in the presence of sodium hydroxide in ethanol and the mixture was refluxed for 1 day with stirring (Method B) [7], the corresponding product was obtained in almost quantitative yield. (Equation 2)

$$\mathrm{ArSH} + \mathrm{BuLi} \xrightarrow[\mathrm{THF},-78^{\circ}\mathrm{C}]{} \mathrm{ArSLi} \qquad (1)$$

$$\textbf{1a},\ \mathrm{Ar} = 2\text{-Pyridyl} \xrightarrow[\mathrm{RT},\ 7\ \mathrm{h}]{\mathrm{ICH_2SiMe_3}} \mathrm{ArSCH_2SiMe_3}\ \textbf{2a},\ 97\%$$

Dedicated to Prof. Adrian Gibbs Brook on the occasion of his seventieth birthday.

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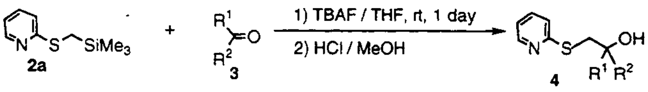
TABLE 1 Reaction of **2a** with Carbonyl Compounds Catalyzed by TBAF[a]



Entry	Carbonyl Compound 3a–l			Product 4a–l	
		R^1	R^2		% Yield[b]
1	**3a**	C_6H_5	H	**4a**	70
2	**3b**	p-$CH_3OC_6H_4$	H	**4b**	76
3	**3c**	2,6-$Cl_2C_6H_3$	H	**4c**	80
4	**3d**	p-$CH_3C_6H_4$	H	**4d**	57
5	**3e**	p-NCC_6H_4	H	**4e**	55[c]
6	**3f**	$C_{10}H_7$	H	**4f**	51
7	**3g**	p-ClC_6H_4	H	**4g**	93
8	**3h**	o-BrC_6H_4	H	**4h**	51
9	**3i**	*tert*-Bu	H	**4i**	47
10	**3j**	CH_3CH_2	H	**4j**	30
11	**3k**	$(CH_3)_2CH$	H	**4k**	30
12	**3l**	C_6H_5	C_6H_5	**4l**	31

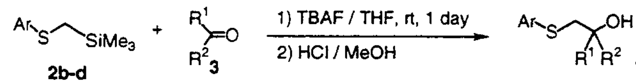
[a]All reactions were carried out in the presence of 10 mol% of TBAF in THF at RT for 1 day under nitrogen.
[b]Yield after isolation by column chromatography.
[c]One equivalent of TBAF was used.

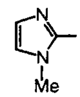
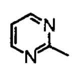
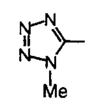
$$\text{ArSH} + \text{ClCH}_2\text{SiMe}_3 \xrightarrow[\text{reflux, 1 day}]{\text{NaOH/EtOH}} \text{ArSCH}_2\text{SiMe}_3 \qquad (2)$$

1b, Ar = 2-(1-Me-Imidazolyl) **2b**, 100%
c, Ar = 2-Pyrimidinyl **c**, 94%
d, Ar = 5-(1-Me-Tetrazolyl) **d**, 100%

2-Trimethylsilylmethylthiopyridine (2-TMSCH$_2$SPy) (**2a**) reacts smoothly with various carbonyl compounds, including aromatic and aliphatic aldehydes and ketones, promoted by the fluoride ion to give the corresponding adducts **4** (Equation 3). A catalytic amount of tetrabutylammonium fluoride (TBAF) (10 mol%) is enough to promote 2-pyridinylthiomethylation except for the reaction with *p*-cyanobenzaldehyde (**3e**). In the case of *p*-cyanobenzaldehyde (**3e**), one equivalent of TBAF was required for the complete consumption of the substrate. The results are listed in Table 1. Some significant features of the present reaction are as follows. (1) Various aromatic and aliphatic substrates can undergo the reaction to give the corresponding β-hydroxyalkyl heteroaryl sulfides **4** under mild and almost neutral conditions. (2) Various functional groups, such as methoxyl, cyano, chloro, and bromo, remain intact under the reaction conditions. (3) The heteroarylthiomethylation is rather slow in the cases of aromatic aldehydes bearing an electron-withdrawing substituent and one equivalent of the catalyst is required to complete the reaction.

TABLE 2 Reaction of **2b–d** with Carbonyl Compounds Catalyzed by TBAF[a]



Entry	Substrate 2	Carbonyl Compound 3			Product 4	
	Ar-		R^1	R^2	%Yield[b]	
1	 2b	3a	C_6H_5	H	70	4m
2		3b	p-$CH_3OC_6H_4$	H	28	4n
3		3c	2,6-$Cl_2C_6H_3$	H	61	4o
4		3d	p-$CH_3C_6H_4$	H	77	4p
5		3f	$C_{10}H_7$	H	57	4q
6		3j	CH_3CH_2	H	53	4r
7	 2c	3a	C_6H_5	H	40	4s
8		3b	p-$CH_3OC_6H_4$	H	50	4t
9		3c	2,6-$Cl_2C_6H_3$	H	58	4u
10		3f	$C_{10}H_7$	H	38	4v
11	 2d	3a	C_6H_5	H	31	4w[c]

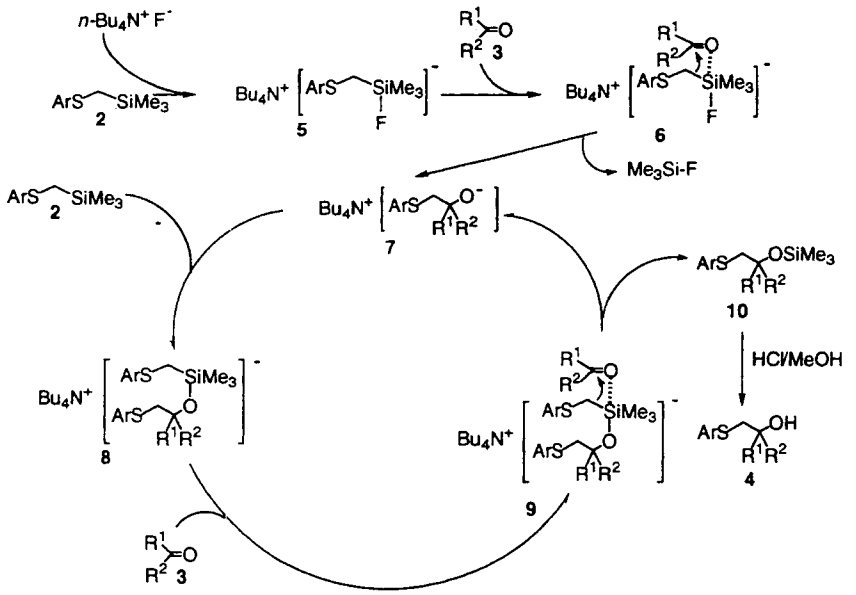
[a]All reactions were carried out in the presence of 10 mol% of TBAF in THF at RT for 1 day under nitrogen.
[b]Yield after isolation by column chromatography.
[c]An equivalent of TBAF was used.

Other heteroarylthiomethylsilanes, such as 1-methyl-2-trimethylsilylmethylthioimidazole (**2b**), 2-trimethylsilylmethylthiopyrimidine (**2c**), and 1-methyl-5-trimethylsilylmethylthiotetrazole (**2d**) are also good reagents for the introduction of a heteroarylthiomethyl group into a carbonyl group to afford the corresponding β-hydroxyalkyl heteroaryl sulfides, otherwise inaccessible, as summarized in Table 2.

$$\underset{\textbf{2b–d}}{\text{ArSCH}_2\text{SiMe}_3} + \underset{\textbf{3}}{\text{R}^1\text{R}^2\text{C=O}} \xrightarrow[\text{2)HCl/MeOH}]{\text{1)TBAF/THF RT 1 day}} \underset{\textbf{4}}{\text{ArSCH}_2\text{CR}^1\text{R}^2(\text{OH})} \qquad (3)$$

A catalytic cycle shown in Scheme 1 reasonably explains the entire process for this heteroarylthiomethylation using **2** and other fluoride ion-promoted alkylation of carbonyl compounds known previously [3]. At the first stage, the fluoride ion attacks the silicon atom of **2** to form a pentacoor-

SCHEME 1



dinate silicate **5**, not a free anion, $ArSCH_2$-, without desilylation [8]. A carbonyl compound **3** coordinates to the silicon atom of **5** as a sixth ligand which now reveals Lewis acidity to form a hexacoordinate silicate **6** the carbonyl carbon being activated to be more electrophilic. The nucleophilically activated heteroarylthiomethyl group in **6** is transferred to the carbonyl carbon to give tetrabutylammonium alkoxide **7** as a catalytic species for the next step, together with the release of fluorotrimethylsilane. The tetrabutylammonium alkoxide **7**, thus formed, is a key intermediate in the catalytic cycle and activates both **2** and **3** (similar to the role of TBAF at the first stage) to afford a silyl ether **10** of an addition product **4** via **8** and **9**, with regeneration of the catalyst **7**, as shown in Scheme 1. Thus, the catalytic cycle is completed. After acid methanolysis of **10**, the corresponding β-hydroxyalkyl heteroaryl sulfide **4** is obtained. Both the substituent effect on the aromatic ring of **3** observed in this work and the retention of the stereochemistry [3d] are reasonably explained by this scheme.

Thus, readily available, storable, and stable heteroarylthiomethylsilanes **2** are the first important reagents to be used as heteroarylthiomethyl anion equivalents for easy, and mild addition to carbonyl groups of aldehydes and ketones.

EXPERIMENTAL

The IR spectra were recorded on a Shimadzu IR-460 spectrometer. The NMR spectra were determined on a JEOL-JMN-EX-270 spectrometer using TMS (tetramethylsilane) as an internal standard. MS spectra were recorded on a Shimadzu QP2000 spectrometer. The microanalyses were performed at the Analytical Center of the University of Tsukuba. Ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. All experiments were carried out under an argon atmosphere. Purification of the products was carried out by thin layer chromatography (TLC) and column chromatography on silica gel. Unless otherwise noted, chemicals were purchased from commercial suppliers and used without further purification.

Synthesis of Heteroarylthiomethyltrimethylsilanes **2**

Method A. A butyllithium-hexane solution (1.6 M, 9.3 mL, 16 mmol) was added to a solution of 2-mercaptopyridine (1.67 g, 15 mmol) in tetrahydrofuran (40 mL) at −78°C, and the resulting solution was stirred for 10 minutes. The temperature of the resulting mixture was raised to RT, and iodomethyltrimethylsilane (4.5 mL, 30 mmol) was added to this solution with stirring. After the reaction mixture had been stirred for 7 hours at an ambient temperature, hydrolysis of the reaction mixture, ether extraction from the aqueous layer and usual successive workup procedures were carried out. After evaporation of the solvent, the residue was distilled to give a product **2a** (2.90 g, 14.5 mmol) as a colorless oil in 97% yield. Bp 100°C (1 mm Hg).

Method (B). Chloromethyltrimethylsilane (2.1 mL, 15 mmol) was added to 2-mercapto-1-methylimidazole **1b** (1.78 g, 15 mmol) and sodium hydroxide (0.6 g, 15 mmol) in ethanol (30 mL), and the mixture was stirred at reflux for 1 day. After removal of ethanol by evaporation, hydrolysis of the reaction mixture, ether extraction and usual

successive workup procedures were carried out. After evaporation of the solvent, the residue was distilled to give a product **2b** (3 g, 15 mmol) as a colorless oil in quantitative yield. Bp 130°C (1 mm Hg). Similarly, **2c** and **2d** were prepared from the corresponding starting materials in 94 and 100% yields, respectively. Spectral data of **2** are as follows.

2a. Bp 100°C (1 mm Hg). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.13 (s, 9H), 2.35 (s, 2H), 6.90 (t, J = 4.9 Hz, 1H), 7.17 (d, J = 2.3 Hz, 1H), 7.37 (t, J = 2.3 Hz, 1H), 8.40 (d, J = 4.9 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ −1.8 (q), 15.1 (t), 118.7 (d), 121.0 (d), 135.4 (d), 149.0 (d), 161.1 (s); IR (neat) 3445 (w), 2895 (m), 1581 (s), 1556 (s), 1454 (s), 1415 (s), 1391 (m), 1251 (s), 1136 (s), 860 (s), 756 (s), 723 (s) cm^{-1}; MS m/z 197 (M^+, 1.3), 182 (100), 150 (16), 78 (27), 73 (59), 45 (34). Anal. found: C, 54.77; H, 7.66; N, 7.10. Calcd for $C_9H_{15}NSSi$: C, 54.55; H, 7.59; N, 7.13.

2b. Bp 130°C (1 mm Hg). ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.05 (s, 9H), 2.21 (s, 2H), 3.37 (s, 3H), 6.69 (d, J = 0.99 Hz, 1H), 6.82 (d, J = 0.99 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ −2.3 (q), 18.4 (d), 32.4 (q), 121.4 (d), 128.3 (d), 143.9 (s); IR (neat) 2955 (s), 1460 (s), 1418 (m), 1391 (m), 1280 (s), 1249 (s), 859 (s), 754 (m), 734 (m), 694 (m) cm^{-1}; MS m/z 200 (M^+, 7), 185 (100), 96 (23), 95 (29), 73 (53), 59 (26), 45 (31). Anal. found: C, 47.52; H, 7.94; N, 14.04. Calcd for $C_8H_{16}N_2SSi$: C, 47.95; H, 8.05; N, 13.98.

2c. Bp 120°C (1 mm Hg). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.06 (s, 1H), 2.31 (s, 2H), 6.85 (t, J = 5.0 Hz, 1H), 8.41 (d, J = 5.0 Hz, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ −1.8 (q), 16.0 (t), 115.9 (d), 156.8 (d), 173.8 (s); IR (neat) 2955 (m), 1568 (s), 1542 (s), 1381 (s), 1248 (s), 1208 (s), 1186 (s), 866 (s), 794 (m), 772 (m), 743 (m), 698 (m), 629 (m) cm^{-1}; MS m/z 198 (M^+, 3), 183 (100), 73 (63), 45 (24). Anal. found: C, 48.42; H, 7.05; N, 14.17. Calcd for $C_8H_{14}N_2SSi$: C, 48.44; H, 7.11; N, 14.12.

2d. Bp 155°C (0.8 mm Hg). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.10 (s, 9H), 2.53 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ −2.1 (q), 17.6 (d), 33.1 (q), 156.1 (s); IR (neat) 2955 (m), 1471 (m), 1410 (s), 1280 (m), 1253 (s), 1172 (m), 862 (s), 701 (s) cm^{-1}; MS m/z 202 (M^+, 1), 187 (22), 113 (57), 73 (100), 59 (27), 45 (27), 43 (39). Anal. found: C, 35.87; H, 6.86; N, 27.93. Calcd. for $C_6H_{14}N_4SSi$: C, 35.61; H, 6.97; N, 27.69.

General Procedure for Heteroarylthiomethylation of **3**

A mixture of a sulfide **2** (0.5 mmol) and a carbonyl compound (1.5 mmol) was stirred at room temperature in THF (2 mL) for 1 day, after addition of tetrabutylammonium fluoride (0.05 mmol). After treatment of the reaction mixture with methanol (1 mL), including hydrochloric acid (1 M, 5 drops), ether extraction and usual successive workup procedures were carried out. After the solvent had been evaporated, the β-hydroxyheteroaryl sulfides **4** were purified by TLC on silica gel. The spectral data of **4** are as follows.

4a. Bp 200°C (1 mm Hg). ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.33 (dd, J = 7.6, 14.5 Hz, 1H), 3.44 (dd, J = 3, 14.5 Hz, 1H), 5.01 (dd, J = 3, 7.6 Hz), 6.23 (brs, 1H), 6.91 (t, J = 4.9 Hz, 1H), 7.14–7.41 (m, 7H), 8.30 (d, J = 4.9 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 40.3 (t), 73.7 (d), 119.6 (d), 122.5 (d), 125.2 (d), 126.4 (d), 127 (d), 127.9 (d), 136.2 (d), 143.5 (s), 148.4 (d), 158.6 (s); IR (neat) 3335 (m), 3185 (m), 3050 (m), 1581 (s), 1557 (m), 1494 (m), 1454 (s), 1416 (s), 1150 (m), 1127 (s), 1061 (m), 987 (m), 759 (s), 728 (m), 699 cm^{-1}(s). Anal. found: C, 67.56; H, 5.68; N, 6.10. Calcd for $C_{13}H_{13}NOSi$: C, 67.50; H, 5.66; N, 6.06.

4b. ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.38 (dd, J = 7.3, 14.8 Hz, 1H), 3.46 (dd, J = 3.3, 14.8 Hz, 1H), 3.79 (dd, J = 3.3, 7.3 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 7.02–7.07 (m, 1H), 7.27 (d, J = 7.9 Hz, 1H), 7.36 (d, J = 8.8 Hz, 2H), 7.47–7.53 (m, 1H), 8.40 (d, J = 4.3 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 40.6 (t), 55.1 (q), 73.8 (d), 113.5 (d), 119.9 (d), 122.8 (d), 126.9 (d), 135.9 (d), 136.5 (s), 148.6 (d), 158.8 (s), 159 (s); IR ($CHCl_3$) 3340 (m), 3005 (m), 1610 (m), 1584 (m), 1512 (s), 1457 (m), 1417 (m), 1248 (s), 1169 (m), 1127 (m), 1034 (m) cm^{-1}.

4c. Mp 104–106°C (recrystallized from hexane/ethyl acetate). ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.23 (dd, J = 3.6, 14.9 Hz, 1H), 4.16 (dd, J = 10.2, 14.9 Hz, 1H), 5.70 (dd, J = 3.6, 10.2 Hz, 1H), 6.15 (brs, 1H), 7.03–7.14 (m, 2H), 7.27–7.31 (m, 3H), 7.48–7.55 (m, 1H), 8.41 (d, J = 5 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 35.5 (t), 72.8 (d), 120.0 (d), 122.8 (d), 128.9 (d), 129.3 (d), 134.6 (d), 136.5 (s), 137.1 (s), 148.6 (d), 158.9 (s); IR (KBr) 3120 (s), 1580 (s), 1436 (s), 1440 (s), 1127 (s), 1083 (m), 1046 (s), 995 (m), 911 (w), 781 (s), 751 (s), 731 (m) cm^{-1}. Anal. found: C, 52.03; H, 3.80; N, 4.95. Calcd for $C_{13}H_{11}NOSCl_2$: C, 52.01; H, 3.69; N, 4.67.

4d. ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.24 (s, 3H), 3.29 (dd, J = 7.3, 14.8 Hz, 1H), 3.38 (dd, J = 3.3, 14.8 Hz, 1H), 4.95 (dd, J = 3.3, 7.3 Hz, 1H), 5.84 (brs, 1H), 6.91–6.97 (m, 1H), 7.06 (d, J = 7.9 Hz, 2H), 7.14–7.38 (m, 3H), 7.40–7.43 (m, 1H), 8.29–8.32 (m, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 21.1 (q), 40.8 (t), 74.2 (d), 119.9 (d), 122.9 (d), 125.7 (d), 128.9 (s), 136.6 (d), 136.9 (d), 140.8 (d), 148.7 (d), 158.9 (s), 159.1 (s); IR ($CHCl_3$) 3180 (m), 3005 (s), 1581 (s), 1510 (w), 1457 (s), 1414 (s), 1146 (s), 1073 (m), 819 (m), 685 (w) cm^{-1}.

4e. ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.37 (dd, J = 6.9, 15.2 Hz, 1H), 3.57 (dd, J = 3, 15.2 Hz, 1H), 5.19 (dd, J = 3, 6.9 Hz, 1H), 7.11–7.16 (m, 1H), 7.32–7.40 (m, 1H), 7.55–7.66 (m, 5H), 8.44 (d, J = 4.3 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 40.6 (t), 73.5 (d), 111 (d), 120.5 (d), 123.3 (d), 126.7 (s), 132.1 (d), 137.2 (d), 148.3 (d), 149.1 (s), 158.5 (s); IR (neat) 3050 (s), 2915 (s), 2225 (s), 1719 (s), 1581 (s), 1558

(m), 1504 (m), 1455 (s), 1416 (s), 1278 (s), 1126 (s), 1071 (m), 834 (m), 758 (s), 725 (m), 559 (s) cm^{-1}.

4f. ^1H NMR (270 MHz, $CDCl_3$) δ 3.45 (dd, J = 7.9, 15 Hz, 1H), 3.69 (dd, J = 2.3, 15 Hz, 1H), 5.86 (dd, J = 2.3, 7.9 Hz, 1H), 7.04 (m, 1H), 7.27 (d, J = 7.9 Hz, 1H), 7.44–7.55 (m, 5H), 7.77 (d, J = 7.9 Hz, 1H), 7.85–7.89 (m, 2H), 8.13 (d, J = 8.3 Hz, 1H), 8.45 (d, J = 4.9 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 40.1 (t), 71.2 (d), 120 (d), 122.8 (d), 122.9 (d), 123.4 (d), 125.4 (s), 125.9 (s), 127.8 (d), 128.9 (d), 130.1 (d), 133.7 (d), 136.6 (d), 139 (s), 148.7 (d), 159.0 (s); IR ($CHCl_3$) 3165 (m), 3050 (m), 1582 (s), 1559 (m), 1453 (m), 1414 (m), 1226 (m), 1084 (m), 800 (m) cm^{-1}.

4g. ^1H NMR (270 MHz, $CDCl_3$) δ 3.33 (dd, J = 7.3, 14.9 Hz, 1H), 3.47 (dd, J = 3, 14.9 Hz, 1H), 5.06 (dd, J = 3, 7.3, 1H), 6.49 (brs, 1H), 7.03–7.08 (m, 1H), 7.26–7.38 (m, 5H), 7.47–7.53 (m, 1H), 8.38 (d, J = 4.6 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 40.7 (t), 73.6 (d), 120.1 (d), 122.9 (d), 127.2 (d), 128.2 (d), 132.8 (s), 136.6 (d), 142.3 (s), 148.7 (d), 158.7 (s).

4h. ^1H NMR (270 MHz, $CDCl_3$) δ 3.43 (dd, J = 6.8, 15.2 Hz, 1H), 3.56 (dd, J = 2.6, 15.2 Hz, 1H), 5.41 (dd, J = 2.6, 6.8 Hz, 1H), 7.05–7.15 (m, 2H), 7.25–7.36 (m, 2H), 7.49–7.55 (m, 2H), 7.34 (dd, J = 1.7, 7.9 Hz, 1H), 8.41 (d, J = 4.3 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 38.9 (t), 73.6 (d), 120.3 (d), 121.6 (d), 123.1 (d), 127.4 (d), 128.6 (d), 128.9 (d), 132.5 (s), 136.8 (d), 142.5 (s), 148.7 (d), 159.4 (s).

4i. ^1H NMR (270 MHz, $CDCl_3$) δ 1 (s, 9H), 3.24 (m, 2H), 3.52 (m, 1H), 5.69 (brs, 1H), 7–7.07 (m, 1H), 7.27–7.33 (m, 1H), 7.45–7.65 (m, 1H), 8.37–8.39 (m, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 25.8 (q), 34.8 (s), 35.6 (t), 81.1 (d), 119.9 (d), 123 (d), 136.9 (d), 148.3 (d), 159.5 (s); IR (neat) 3350 (s), 2945 (s), 2930 (s), 1581 (s), 1558 (m), 1478 (s), 1450 (s), 1416 (s), 1362 (m), 1279 (m), 1126 (s), 1073 (m), 1013 (m), 898 (m), 757 (s), 738 (m) cm^{-1}.

4j. ^1H NMR (270 MHz, $CDCl_3$) δ 1 (t, J = 7.6 Hz, 3H), 1.51–1.72 (m, 2H), 3.22 (dd, J = 6.9, 14.9 Hz, 1H), 3.38 (dd, J = 2.6, 14.9 Hz, 1H), 3.87 (ddd, J = 2.6, 2.9, 6.2 Hz, 1H), 5.81 (brs, 1H), 7.04–7.09 (m, 1H), 7.28–7.34 (m, 1H), 7.51–7.58 (m, 1H), 8.38–8.40 (m, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 10.1 (q), 29.6 (d), 38.1 (t), 73.1 (d), 120 (d), 123.1 (d), 137 (d), 148.2 (d), 159.2 (s).

4k. ^1H NMR (270 MHz, $CDCl_3$) δ 0.96 (d, J = 6.9 Hz, 3H), 1.02 (d, J = 6.6 Hz, 3H), 1.77–1.93 (m, 1H), 3.24 (dd, J = 6.9, 14.9 Hz, 1H), 3.32 (dd, J = 2.9, 14.9 Hz, 1H), 3.60–3.66 (m, 1H), 5.75 (brs, 1H), 7.01–7.06 (m, 1H), 7.27–7.38 (m, 1H), 7.48–7.55 (m, 1H), 8.36 (d, J = 5 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 17.9 (q), 18.7 (q), 33.6 (d), 36.3 (t), 77.2 (d), 119.9 (d), 123 (d), 136.8 (d), 148.4 (d), 159.3 (s); IR (neat) 3360 (s), 2950 (s), 1582 (s), 1558 (m), 1450 (s), 1416 (s), 1147 (s), 1043 (m), 995 (m), 756 (s) cm^{-1}.

4l. ^1H NMR (270 MHz, $CDCl_3$) δ 4.04 (s, 2H), 7.04 (m, 1H), 7.25–7.35 (m, 6H), 7.45–7.54 (m, 6H), 8.40 (d, J = 5 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 44 (t), 77.9 (d), 104.2 (d), 120.2 (d), 123.1 (d), 126.2 (d), 126.8 (d), 128.1 (s), 136.7 (d), 146.9 (s), 159.3 (s); IR (KBr) 3420 (s), 3140 (s), 1582 (s), 1553 (s), 1488 (m), 1452 (s), 1414 (s), 1280 (m), 1129 (s), 1075 (m), 1042 (m), 997 (s), 756 (s), 729 (m), 701 (s), 638 (m) cm^{-1}.

4m. mp 66–67°C (recrystallized from hexane/ethyl acetate). ^1H NMR (270 MHz, $CDCl_3$) δ 3.25 (dd, J = 7.3, 14.5 Hz, 1H), 3.32 (dd, J = 3.6, 14.5 Hz, 1H), 3.53 (s, 3H), 5.09 (dd, J = 3.6, 7.3 Hz, 1H), 6.86 (d, J = 1.3 Hz, 1H), 6.97 (d, J = 1.3 Hz; 1H), 7.3 (m, 5H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 33.3 (q), 42.5 (t), 74.3 (d), 122.1 (d), 125.8 (d), 127.2 (d), 127.9 (d), 128.1 (d), 142.8 (s), 143.6 (s); IR (KBr) 3150 (s), 2830 (m), 1459 (s), 1403 (m), 1287 (m), 1083 (m), 1056 (s), 748 (s), 713 (s) cm^{-1}. Anal. found: C, 61.40; H, 6.19; N, 11.87. Calcd for $C_{12}H_{14}N_2OS$: C, 61.51; H, 6.02; N, 11.96.

4n. ^1H NMR (270 MHz, $CDCl_3$) δ 3.25 (dd, J = 6.9, 14.5 Hz, 1H), 3.31 (dd, J = 4, 14.5 Hz, 1H), 3.57 (s, 3H), 3.79 (s, 3H), 5.06 (dd, J = 4, 6.9 Hz, 1H), 5.89 (brs, 1H), 6.84–6.89 (m, 3H), 7.00 (d, J = 1.3 Hz, 1H), 7.34 (d, J = 8.6 Hz, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 33.5 (q), 42.6 (t), 55.2 (q), 74.2 (d), 113.6 (d), 122.1 (d), 127 (d), 130 (d), 135.9 (s), 143 (s), 158.8 (s); IR (neat) 3325 (s), 2915 (m), 1612 (s), 1576 (s), 1511 (s), 1451 (s), 1415 (s), 1300 (m), 1248 (s), 1176 (s), 1124 (s), 1030 (s), 833 (s), 759 (s) cm^{-1}.

4o. ^1H NMR (270 MHz, $CDCl_3$) δ 3.26 (dd, J = 3.3, 14.5 Hz, 1H), 3.58 (s, 3H), 3.95 (dd, J = 9.9, 14.5 Hz, 1H), 5.47 (dd, J = 3.3, 9.9 Hz, 1H), 6.89 (d, J = 1.3 Hz, 1H), 7 (d, J = 1.3 Hz, 1H), 7.10–7.28 (m, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 33.6 (q), 37.7 (t), 72.8 (d), 122.1 (d), 128.3 (d), 128.9 (d), 129.2 (d), 134.6 (s), 137.1 (s), 142.8 (s); IR ($CHCl_3$) 3115 (s), 3005 (s), 2855 (m), 1690 (m), 1580 (s), 1465 (s), 1427 (s), 1277 (m), 1186 (m), 1129 (m), 1086 (s), 690 (m) cm^{-1}.

4p. ^1H NMR (270 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.24 (dd, J = 6.9, 14.5 Hz, 1H), 3.30 (dd, J = 3.6, 14.5 Hz, 1H), 3.54 (s, 3H), 5.07 (dd, J = 3.6, 6.9 Hz, 1H), 6.87 (d, J = 1.3 Hz, 1H), 6.98 (d, J = 1.3 Hz, 1H), 7.14 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 21 (q), 33.4 (q), 42.6 (t), 74.4 (d), 122.1 (d), 125.8 (s), 128.1 (d), 128.9 (d), 136.8 (d), 140.8 (s), 142.9 (s); IR (neat) 3165 (s), 3015 (m), 2850 (m), 1515 (m), 1460 (s), 1410 (m), 1298 (s), 1128 (m), 1068 (s), 820 (m), 731 (s), 689 (m) cm^{-1}.

4q. ^1H NMR (270 MHz, $CDCl_3$) δ 3.38 (dd, J = 7.3, 14.9 Hz, 1H), 3.48 (dd, J = 2.6, 14.9 Hz, 1H), 3.52 (s, 3H), 5.89 (dd, J = 2.6, 7.3 Hz, 1H), 6.87 (d, J = 1.3 Hz, 1H), 6.90 (brs, 1H), 7.03 (d, J = 1.3 Hz, 1H), 7.41–7.50 (m, 3H), 7.74 (d, J = 8.3 Hz, 1H), 7.82–7.86 (m, 2H), 7.94–7.97 (m, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 33.5 (q), 41.8 (t), 71.6 (d), 122.3 (d), 122.7 (d), 123.7 (d), 125.3 (s), 125.5 (s), 126.1 (d), 127.9 (d), 129 (d), 130 (d), 133.7 (d), 139 (s), 143 (s); IR (neat) 3130 (s), 2920 (s), 1592 (w), 1512 (s), 1459 (s), 1410 (m), 1329 (w), 1280 (s), 1129 (m), 1080 (s),

1237 (w), 1216 (w), 1129 (m), 1080 (s), 926 (m), 804 (s), 782 (s), 747 (s), 691 (m), 627 (w) cm^{-1}.

4r. ^1H NMR (270 MHz, $CDCl_3$) δ 0.97 (t, J = 7.6 Hz, 3H), 1.49–1.70 (m, 2H), 3.03 (dd, J = 7.3, 14.5 Hz, 1H), 3.18 (dd, J = 2.6, 14.5 Hz, 1H), 3.59 (s, 3H), 3.86 (ddd, J = 2.6, 7.3, 12.5 Hz, 1H), 6.88 (d, J = 1.3 Hz, 1H), 6.95 (d, J = 1.3 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 9.9 (q), 29.6 (t), 33.4 (q), 40 (t), 73.3 (d), 122 (d), 128.2 (d), 142.9 (s); IR (neat) 3325 (s), 3205 (s), 2050 (s), 1512 (m), 1456 (s), 1413 (m), 1374 (m), 1280 (s), 1126 (s), 1800 (m), 1050 (m), 1024 (m), 977 (m), 925 (w), 739 (m), 680 (m) cm^{-1}.

4s. ^1H NMR (270 MHz, $CDCl_3$) δ 3.38 (dd, J = 8.3, 14.5 Hz, 1H), 3.57 (dd, J = 3, 14.5 Hz, 1H), 4.31 (brs, 1H), 5.08 (dd, J = 3, 8.3 Hz, 1H), 7.02 (t, J = 5 Hz, 1H), 7.25–7.47 (m, 5H), 8.52 (d, J = 5 Hz, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 40.3 (t), 73.8 (d), 116.7 (d), 125.7 (s), 127.5 (d), 128.3 (d), 143 (s), 157.1 (d), 172.3 (s).

4t. ^1H NMR (270 MHz, $CDCl_3$) δ 3.38 (dd, J = 8.3, 14.5 Hz, 1H), 3.53 (dd, J = 3.3, 14.5 Hz, 1H), 3.80 (s, 3H), 4.07 (brs, 1H), 5.03 (dd, J = 3.3, 8.3 Hz, 1H), 6.89 (d, J = 8.6 Hz, 2H), 7.02 (t, J = 5 Hz, 1H), 7.36 (d, J = 8.6 Hz, 2H), 8.52 (d, J = 5 Hz, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 40.5 (t), 55.2 (q), 73.5 (d), 113.7 (d), 116.8 (d), 127 (s), 135.3 (d), 157.2 (d), 159.1 (s), 172.5 (s); IR (neat) 3330 (s), 2990 (s), 2830 (m), 1612 (s), 1587 (m), 1566 (s), 1513 (s), 1464 (m), 1382 (s), 1303 (m), 1246 (s), 1198 (s), 1173 (s), 1108 (w), 1061 (m), 1032 (s), 995 (m), 833 (s), 806 (m), 771 (s), 750 (s), 633 (m) cm^{-1}.

4u. ^1H NMR (270 MHz, $CDCl_3$) δ 3.38 (dd, J = 8.6, 14.8 Hz, 1H), 3.79 (dd, J = 2.6, 14.5 Hz, 1H), 5.85 (dd, J = 2.6, 8.6 Hz, 1H), 4.65 (brs, 1H), 7.01 (t, J = 5 Hz, 1H), 7.51 (m, 3H), 7.83 (m, 3H), 8.24 (d, J = 5 Hz, 1H), 8.54 (d, J = 5 Hz, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 39.9 (t), 70.5 (d), 116.8 (t), 122.9 (d), 123 (d), 125.5 (d), 126.1 (d), 128.1 (s), 128.3 (s), 128.9 (d), 130.1 (d), 133.7 (d), 138.6 (s), 157.2 (d), 172.5 (s).

4v. Mp 132–134°C. ^1H NMR (270 MHz, $CDCl_3$) δ 3.39 (dd, J = 4.6, 14.5, 1H), 4.11 (dd, J = 9.2, 14.5 Hz, 1H), 4.73 (brs, 1H), 5.76 (dd, J = 4.6, 9.2 Hz, 1H), 7.02 (t, J = 5 Hz, 1H), 7.11–7.17 (m, 1H), 7.28–7.31 (m, 2H), 8.52 (d, J = 5 Hz, 2H); IR (KBr) 3215 (s), 1567 (s), 1436 (s), 1404 (m), 1200 (m), 1139 (m), 1082 (m), 1043 (s), 775 (s) cm^{-1}.

4w. ^1H NMR (270 MHz, $CDCl_3$) δ 3.32 (brs, 1H), 3.51 (dd, J = 8.3, 14 Hz, 1H), 3.74 (dd, J = 3.6, 14 Hz, 1H), 3.91 (s, 3H), 5.15 (dd, J = 3.6, 8.3 Hz, 1H), 7.27–7.44 (m, 5H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 33.5 (q), 41.8 (t), 72.7 (d), 125.8 (d), 128.2 (d), 128.6 (d), 141.8 (d), 156.1 (s).

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