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Novel formation of indoles and 3,1-benzoxazines from *o*-alkenylanilides and dimethyl(methylthio)sulfonium trifluoromethanesulfonate

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Abstract—The reaction of dimethyl(methylthio)sulfonium trifluoromethanesulfonate (DMTST) with *o*-allylphenol gave 2-methylthiomethyl-2,3-dihydrobenzofuran in 97% yield. The reaction of DMTST with *N*-tosyl-*o*-isopropenylanilide followed by the addition of aq sodium carbonate afforded *N*-tosyl-3-methylindole in 88% yield, whereas *N*-tosyl-*o*-vinylanilide afforded *N*-tosylindoline in 85% yield.

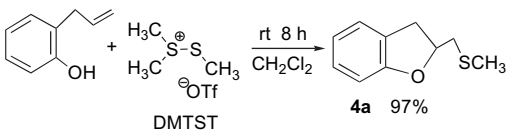
1. Introduction

Dimethyl(methylthio)sulfonium tetrafluoroborate (DMTSF) is a useful reagent for the synthesis of cyclic ethers or amines.[1] On the other hand, dimethyl(methylthio)sulfonium trifluoromethanesulfonate (DMTST) has been found to be a good reagent for the synthesis of glycosides.[2] Previously, we have synthesized vinylphosphonium salts by reacting alkenes with DMTST and triphenylphosphine.[3] However, to our knowledge, there is no report on the synthesis of indoles (**1**) by intramolecular thioamination using DMTST. Indoles **1** are very important compounds because of their synthetic and pharmacological utility. Recent methods include the intramolecular cyclization of amino-substituted Fischer chromium carbenes,[4] the reaction of NBS with vinylic anilides,[5] and the palladium-catalyzed intramolecular arylacylation of aryl iodide.[6] We have reported a novel method for the synthesis of *N*-tosylindoles (**1**) and benzazetines (**2**) from *o*-alkenylanilides (**3**) and DMTST.[7] However, the reactivity of **2** led to structural ambiguity of benzazetines. We report herein the full details of the synthesis of indoles **1**, dihydrobenzofuran (**4**), and 3,1-benzoxazines (**5**) from DMTST and **3**.

2. Results and discussion

2.1. Synthesis of 2-methylthio-2,3-dihydrobenzofuran and indoles

In our previous work on the synthesis of *exo*-methylenedihydrobenzofuran, which involved reacting *o*-hydroxybenzyltriphenylphosphonium bromide with butyllithium followed by the addition of paraformaldehyde, the yield was only 50%.[8] Thus, other methods were desirable for the synthesis of dihydrobenzofurans (**4**). Capozzi et al. reported the synthesis of 2-methylthiomethyl-2,3-dihydrobenzofuran (**4a**) by reacting bis(methylthio)methylsulfonium hexachloroantimonate (BMTSH) with *o*-allylphenol followed by the addition of aq sodium carbonate, in 59% yield.[9] However, this salt is very hygroscopic and relatively difficult to synthesize. Thus, we first tried to synthesize benzofuran **4a** by reacting DMTST with *o*-allylphenol. Treatment of *o*-allylphenol with DMTST in dichloromethane for 8 h at rt resulted in the formation of benzofuran **4a** in 97% yield (Scheme 1). The present method has some advantages for the synthesis of BMTSH, which was prepared in situ and treated with *o*-allylphenol without any further operation.



Scheme 1.

Since this method proved to be a good procedure for intramolecular cyclization using DMTST, we applied it to the synthesis of indoles **1** via intramolecular cyclization of *o*-alkenylanilides **3**, which were easily synthesized from *o*-alkenylnitrobenzenes (**6**).[10] Starting *o*-alkenylanilides **3** were synthesized from the following one- or three-step method from commercially available *o*-nitrobenzaldehyde or *o*-isopropenylaniline (Scheme 2).

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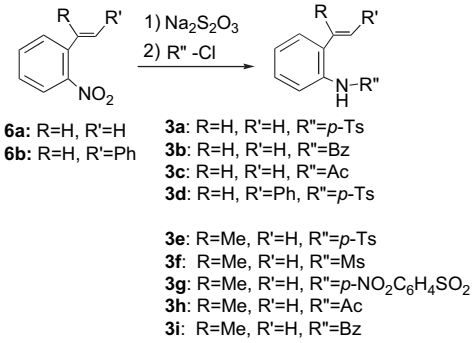
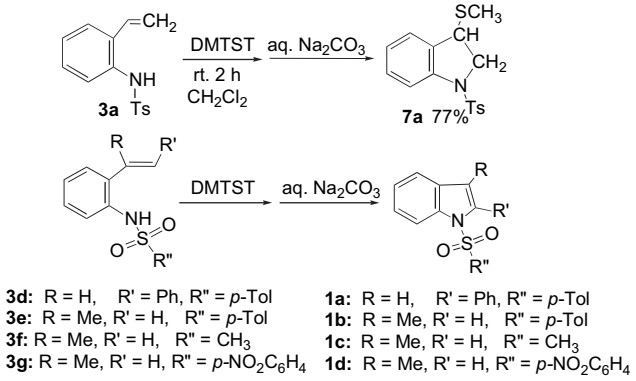


Scheme 2.

Treatment of DMTST with *o*-aminostyrene resulted in the formation of a complex mixture of unidentified products, suggesting that primary anilines did not afford the cyclized products. When *o*-vinyl-*N*-*p*-tosylanilide (**3a**) was chosen as substrate, 3-methylthio-*N*-tosylindoline (**7a**) was obtained in 77% yield. The structure was confirmed from its NMR spectrum. A typical AB_2 pattern (4.2, 3.9 and 4.2 ppm) was observed at the *N*-methylene and methine regions of its proton NMR spectrum, which was similar to that of *N*-acetyl-3-methylindoline (3.52, 3.58, and 4.21 ppm).[11] Additionally, when *o*-isopropenyl-*N*-*p*-tosylanilide (**3e**) was reacted with 2 equiv of DMTST in acetonitrile at rt for 8 h, 3-methyl-*N*-*p*-tosylindole (**1b**) was directly formed in 86% yield. When this reaction was carried out at 0 °C, only 45% of **1b** was obtained. Other substituted alkenyl-*N*-sulfonylamides (**3d**, **3f**, and **3g**) also reacted with DMTST at rt to afford the corresponding *N*-sulfonylindoles (**1a**, **1c**, and **1d**) in good yields (Scheme 3). The results are summarized in Table 1. Cappozzi et al. synthesized 2-methylthio-3-methylindole in only 36% yield by the reaction of **3e** with BMTSH,[12] whereas **1b** was not isolated, suggesting that the reactivity toward **3e** between DMTST and BMTSH is quite different. Further treatment of initially formed **1b** with BMTST might result in the formation of methylthiolated product. Thus, thioamination was achieved for the synthesis of indoles from *o*-alkenylanilides **3d**–**3g** and DMTST.



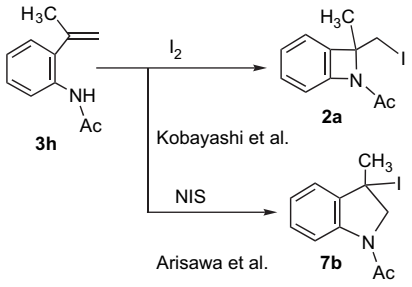
Scheme 3.

2.2. Synthesis of 4*H*-3,1-benzoxazines 5

We then applied this method to the synthesis of *N*-benzoylindoles. The reaction of *o*-isopropenylacetanilide (**3h**) with iodine and with *N*-iodosuccinimide (NIS) was already reported by Kobayashi et al.[13] and Arisawa et al.,[5] respectively. The reaction of **3h** with iodine gave 2-iodomethyl-2-methyl-*N*-acetylbenzazetine (**2a**),[13] whereas the reaction with NIS gave 3-iodo-3-methyl-*N*-acetylindoline (**7b**) (Scheme 4).[5]

Table 1. Reaction of DMTST with *N*-tosylalkenylanilides **3**

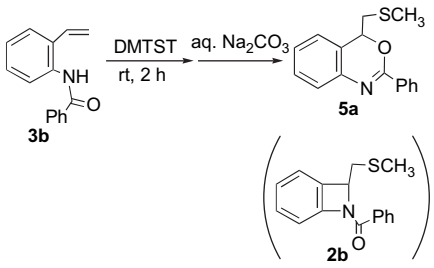
Substrate	Solvent	Time	Temperature	Product	Yield (%)
3d	CH_3CN	8	rt	**1a**	65
3e	CH_3CN	8	rt	**1b**	86
3e	CH_2Cl_2	8	rt	**1b**	92
3e	CH_2Cl_2	14	0	**1b**	45
3e	CH_2Cl_2	3	rt	**1b**	65
3f	CH_2Cl_2	14	rt	**1c**	95
3g	CH_2Cl_2	14	rt	**1d**	86



Scheme 4.

We are interested in the difference in reactivity between these active halogen reagents and DMTST. The reaction of *o*-vinylbenzanilide (**3b**) with DMTST at rt followed by the addition of aq sodium carbonate gave colorless crystals. At first, we thought that this compound was 2-methylthiomethyl-*N*-benzoylbenzazetine (**2b**), because the spectroscopic nature of **2b** was similar to that reported by Kobayashi et al.[13] Its NMR spectrum showed methylene double doublet signals at 2.85 and 3.05 ppm. The methine carbon signal of **2b** resonated at 75.7 ppm, which was quite different from the reported value (51.6 ppm) of the methine signal of *N*-acetyl-3-(2-hydroxypropan-2-yl)indoline, suggesting that the structure is not an indoline derivative.[14] The amide carbonyl carbon generally resonates in the range of 160–180 ppm,[15] whereas the amide carbonyl carbon of **2b** resonated at 159.8 ppm. In general, simple benzo-fused four-membered heterocyclic compounds easily react with dienophiles or dimerize to give more stable cyclic heterocycles than four-membered ones, e.g., the thermolysis of benzoselenates afforded dimerized products.[16] Thus, we performed the thermolysis of the product in refluxing toluene in the presence of DMAD, but recovered the starting compound unchanged, suggesting that the four-membered structure might not be correct. Since the C=N carbon of 2-phenyl-3,1-benzoxazine resonated at 157.4 ppm,[17] we concluded that the exact structure of this compound should not be benzoazetine **2b** but 4-methylthiomethyl-2-phenyl-3,1-benzoxazine (**5a**) (Scheme 5).

Finally, the molecular structure of **5a** was confirmed by X-ray crystallographic analysis and the ORTEP drawing is shown in Figure 1.[18]



Scheme 5.

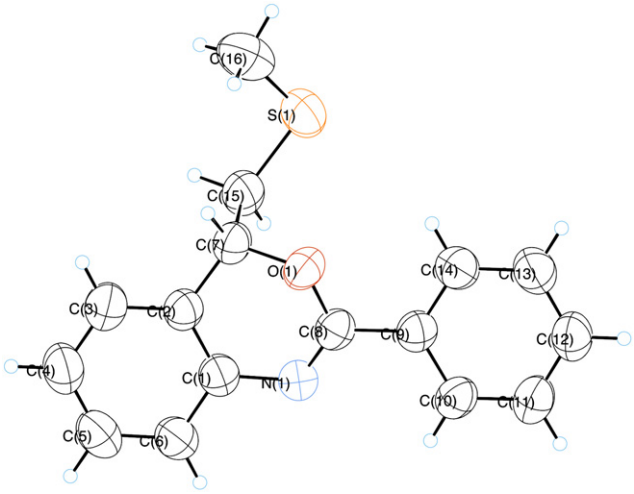
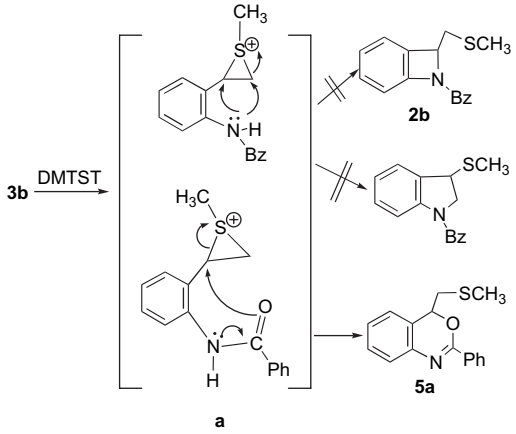


Figure 1. ORTEP drawing of 3,1-benzoxazine **5a**.

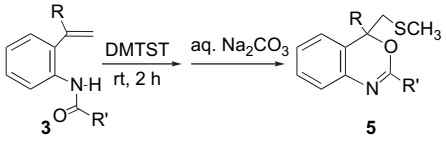
Selected bond lengths and angles: O1–C7 1.445(3) Å, O1–C8 1.370(4) Å, N1–C1 1.414(4) Å, N1–C8, 1.271(4) Å, C1–C2 1.382(5) Å, C2–C7 1.503(4). C8–O1–C7 116.6(3)°, C8–N1–C1 117.0(3)°, C2–C1–C6 119.7(3)°, C1–C2–C7 117.2(3)°, O1–C7–C2 109.7(2)°, N1–C8–O1 125.1(3)°.

These results clearly show that activated intermediate (**a**) was attacked by acyl oxygen at the benzyl position, which is more cationic than the β-position, to afford not benzazetine **2b** but the less strained six-membered heterocycle, 3,1-benzoxazine **5a** (Scheme 6). Other reactions were carried out in a similar manner. The results are shown in Table 2. Actually, Capozzi et al. found that a similar reaction of **3h** and **3i** with BMTSH gave **5c** and **5d** in high yields.[19]



Scheme 6.

Table 2. Reaction of **3** with DMTST



	R	R′	Solvent	Time (h)	Product			
						R	R′	Yield (%)
3b	H	Ph	CH_3CN	12	**5a**	H	Ph	91
3b	H	Ph	CH_2Cl_2	12	**5a**	H	Ph	90
3c	H	Me	CH_2Cl_2	8	**5b**	H	Me	92
3h	Me	Me	CH_3CN	8	**5c**	Me	Me	93
3h	Me	Me	CH_2Cl_2	8	**5c**	Me	Me	90
3i	Me	Ph	CH_2Cl_2	8	**5d**	Me	Ph	90

3. Conclusion

We have developed a simple method for the synthesis of indoles, 3,1-benzoxazines and quinolines, using DMTST as a double-bond activating reagent, which resulted in the intramolecular cyclization of 2-alkenoylanilines. Thus, the regioselective and chemoselective syntheses of indoles **1** and 3,1-benzoxazines **5** were achieved by the use of *o*-alkenylanilides and DMTST.

4. Experimental

4.1. General

Flash chromatography was carried out by Merck Kieselgel 60 (230–400 mesh). Thin layer chromatography (TLC) was carried out on commercially available pre-coated aluminum plates (Merck silica Kieselgel 60 F_{254}). All solvents were distilled before use, and no further treatment was carried out. NMR spectra were measured on a Varian Innova-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C). The melting points were uncorrected.

4.2. Materials

Dimethyl disulfide, methyl triflate, *o*-allylphenol, *o*-nitrobenzaldehyde, and *o*-isopropenylaniline are commercially available. DMTST was synthesized by a reported procedure.[3] *o*-Alkenylanilides **3a**–**3i** were synthesized by the reported procedure.[10,22]

4.3. Reaction of *o*-allylphenol with DMTST

To a solution of dimethyl disulfide (282 mg, 3.0 mmol) in dichloromethane (5 mL) was added a solution of methyl triflate (492 mg, 3.0 mmol) in one portion. After stirring for 30 min, *o*-allylphenol (200 mg, 1.5 mmol) in dichloromethane (5 mL) was added dropwise at rt. After stirring for 2 h, aq Na_2CO_3 (5%, 5 mL) was added to the reaction mixture and separated. The dichloromethane layer was dried over magnesium sulfate, filtered, and evaporated to give 2-methylthiomethyl-2,3-dihydrobenzofuran (**4a**) (260 mg, 1.45 mmol). Colorless oil; The spectral data were identical with the reported value.[9] ^{1}H NMR ($CDCl_3$) δ=2.20 (SCH_3), 2.78 (dd, 1H, J=6.8 and 14.0 Hz, C*H*HSMe), 2.87

(dd, 1H, J=6.8 and 14.0 Hz, CH*H*SMe), 3.04 (dd, 1H, J=7.2 and 16.0 Hz, CHH), 3.73 (dd, 1H, J=8.4 and 16.0 Hz, CHH), 4.95 (dt, 1H, J=6.8 and 8.8 Hz, CH), 6.78 (d, 1H, J=8.0 Hz, Ar), 6.85 (dd, 1H, J=7.6 and 8.0 Hz, Ar), 7.10 (dd, 1H, J=7.6 and 8.0 Hz, Ar), 7.15 (d, 1H, J=8.8 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ=16.52 (SCH_3), 35.10 (CH_2), 39.37 (CH_2), 82.14 (CH), 109.50 (Ar), 120.68 (Ar), 125.13 (Ar), 126.39 (Ar), 128.20, 159.33 (Ar).

4.4. Reaction of *o*-vinyl-*N*-*p*-tosylanilide (3a) with DMTST

To a solution of DMTST (516 mg, 2.0 mmol) in dichloromethane (5 mL) was added a solution of *o*-vinyl-*N*-*p*-tosylanilide **3a** (153 mg, 1.0 mmol) in dichloromethane (5 mL) at rt. After stirring for 8 h, the reaction mixture was washed with 10% of aq sodium carbonate (10 mL) and separated. The water layer was extracted with dichloromethane (5 mL×2) and the combined extract was dried over magnesium sulfate, filtered, and evaporated to give pale yellow crystals, which was chromatographed over silica gel by elution with hexane to afford colorless oil of 3-methylthio-*N*-tosylindoline (**7a**) (246 mg, 0.77 mmol). ^{1}H NMR ($CDCl_3$) δ=1.72 (s, 3H, SCH_3), 2.37 (s, 3H, CH_3), 3.90 (dd, 1H, J=9.6 and 15.2 Hz, CHH), 4.18–4.24 (m, 2H, CH_2 and CH), 7.01 (dd, 1H, J=8.0 and 7.6 Hz, Ar), 7.20–7.27 (m, 5H, Ts and Ar), 7.66 (d, 1H, J=8.0 Hz, Ar), 7.70 (d, 2H, J=8.4 Hz, Ts). ^{13}C NMR ($CDCl_3$) δ=11.89 (SCH_3), 21.76 (Ts), 43.96 (CH), 56.79 (CH_2), 114.78 (Ar), 124.23 (Ar), 125.77 (Ar), 127.59 (Ts), 129.33 (Ar), 129.94 (Ts), 130.93 (Ts), 133.96 (Ar), 142.20 (Ar), 144.55 (Ts). Anal. found: C, 60.23; H, 5.39; N, 4.36. Calcd for $C_{16}H_{17}NO_2S_2$: C, 60.16; H, 5.36; N, 4.38.

4.5. Reaction of *o*-isopropenyl-*N*-*p*-tosylanilide (3e) with DMTST

To a solution of DMTST (516 mg, 2.0 mmol) in dichloromethane (5 mL) was added a solution of *o*-isopropenyl-*N*-*p*-tosylanilide **3e** (167 mg, 1.0 mmol) in dichloromethane (5 mL) at rt. After stirring for 8 h, the reaction mixture was washed with 10% of aq sodium carbonate (10 mL) and separated. The water layer was extracted with dichloromethane (5 mL×2) and the combined extract was dried over magnesium sulfate, filtered, and evaporated to give colorless solid, which was chromatographed over silica gel by elution with hexane–dichloromethane (1:1) to afford colorless plates of 3-methyl-*N*-tosylindole (**1b**) (265 mg, 0.92 mmol). Mp 112–114 °C (lit.[20] mp 114–115 °C). ^{1}H NMR ($CDCl_3$) δ=2.22 (s, 3H, CH_3), 2.29 (s, 3H, TsMe), 7.16 (d, 2H, J=8.0 Hz, Ts), 7.20 (t, 1H, J=8.4 Hz, Ar), 7.30 (t, 1H, J=8.0 Hz, Ar), 7.43 (d, 1H, J=8.0 Hz, Ar), 7.73 (d, 2H, J=8.0 Hz, Ts), 7.98 (d, 1H, J=8.4 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ=9.91 (Me), 21.74 (TsMe), 113.89 (Ar), 118.83 (Ar), 119.61 (Ar), 123.20 (Ar), 123.29 (Ar), 124.79 (Ar), 126.95 (Ts), 130.00 (Ts), 132.02 (Ar), 135.49 (Ar), 135.64 (Ts), 144.88 (Ts).

The following reactions were carried out in a similar manner.

2-Phenyl-*N*-*p*-toluenesulfonylindole **1a**: colorless oil; spectral data were identical with the reported value.[21]

3-Methyl-*N*-methanesulfonylindole **1c**: colorless oil; spectral data were identical with the reported value.[22] ^{1}H NMR ($CDCl_3$) δ=2.30 (s, 3H, CH_3), 3.03 (s, 3H, Ms), 7.20 (s, 1H, Ar), 7.29–7.40 (m, 2H, Ar), 7.56 (d, 1H, J=8.0 Hz, Ar), 7.90 (d, 1H, J=8.1 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ=9.89 (Me), 40.42 (Ms), 113.39 (Ar), 119.81 (Ar), 119.91 (Ar), 123.16 (Ar), 123.52 (Ar), 125.12 (Ar), 131.98 (Ar), 135.55 (Ar).

3-Methyl-*N*-*p*-nitrobenzenesulfonylindole (**1d**): Mp 132–134 °C. ^{1}H NMR ($CDCl_3$) δ=2.25 (s, 3H, CH_3), 7.23–7.28 (m, 2H, Ar), 7.34 (dd, 1H, J=7.6 and 8.0 Hz, Ar), 7.46 (d, 1H, J=7.6 Hz, Ar), 8.00 (d, 1H, J=7.6 Hz, Ar), 8.02 (d, 2H, J=8.4 Hz, *p*-NO_2Ar), 8.25 (d, 2H, J=8.4 Hz, *p*-NO_2Ar). ^{13}C NMR ($CDCl_3$) δ=9.97 (CH_3), 119.80 (Ar), 120.05 (Ar), 120.71 (Ar), 122.71 (Ar), 124.09 (Ar), 124.65 (*p*-NO_2Ar), 125.49 (Ar), 128.20 (*p*-NO_2Ar), 132.24 (Ar), 135.36 (Ar), 143.59 (*p*-NO_2Ar), 150.72 (*p*-NO_2Ar). Anal. found: C, 56.87; H, 3.88; N, 8.88. Calcd for $C_{15}H_{12}NO_4S$: C, 56.95; H, 3.82; N, 8.86.

4.6. One-pot synthesis of 1b

To a solution of dimethyl disulfide (0.282 g, 3.0 mmol) in dichloromethane (5 mL) was added a solution of methyl triflate (0.492 g, 3.0 mmol) in one portion. After stirring for 30 min, **3e** (0.167 g, 1.0 mmol) in dichloromethane (5 mL) was added dropwise to this solution at rt. After stirring for 5 h, the reaction mixture was washed with 10% of aq sodium carbonate (10 mL) and separated. The water layer was extracted with dichloromethane (5 mL×2) and the combined extract was dried over magnesium sulfate, filtered, and evaporated to give colorless solid, which was chromatographed over silica gel by elution with hexane–dichloromethane (1:1) to afford colorless plates of 3-methyl-*N*-tosylindole (**1b**) (259 mg, 0.90 mmol).

4.7. Reaction of *o*-vinylbenzanilide with DMTST

To a solution of DMTST (516 mg, 2.0 mmol) in dichloromethane (5 mL) was added a solution of *o*-vinylbenzanilide **3b** (223 mg, 1.0 mmol) in dichloromethane (5 mL) at rt. After stirring for 8 h, the reaction mixture was washed with 10% of aq sodium carbonate (10 mL) and separated. The water layer was extracted with dichloromethane (5 mL×2) and the combined extract was dried over magnesium sulfate, filtered, and evaporated to give colorless solid, which was chromatographed over silica gel by elution with hexane–dichloromethane (1:1) to afford colorless crystals of 2-phenyl-4-methylthiomethyl-3,1-benzoxazine (**5a**) (255 mg, 0.95 mmol). Mp 51–53 °C. ^{1}H NMR ($CDCl_3$) δ=2.10 (s, 3H, SMe), 2.85 (dd, 1H, J=5.6 and 14.0 Hz, CH_2), 3.05 (dd, 1H, J=7.6 and 14.0 Hz, CH_2), 5.56 (dd, 1H, J=5.6 and 7.6 Hz, CH), 7.09–7.55 (m, 8H, Ar), 8.18 (dd, 1H, J=1.2 and 8.4 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ=16.86 (SMe), 40.49 (CH_2), 75.68 (CH), 124.74, 125.30, 126.60, 128.37, 128.51, 129.51, 131.72, 132.74, 139.71 (Ar), 156.56 (C=O). Anal. found: C, 70.64; H, 5.90; N, 5.03. Calcd for $C_{16}H_{15}NOS$: C, 71.34; H, 5.61; N, 5.20.

Other reactions were carried out in a similar manner.

2-Methyl-4-methylthiomethyl-3,1-benzoxazine (**5b**): colorless oil; ^{1}H NMR ($CDCl_3$) δ=2.10 (s, 3H, SMe), 2.15 (s, 3H, Me), 2.82 (dd, 1H, J=5.6 and 13.2 Hz, CH_2), 2.97

(dd, 1H, J=7.6 and 13.2 Hz, CH_2), 5.41 (dd, 1H, J=5.6 and 7.6 Hz, CH), 7.05 (d, 1H, J=7.6 Hz, Ar), 7.13 (d, 1H, J=8.0 Hz, Ar), 7.18 (dd, 1H, J=7.6 and 8.0 Hz, Ar), 7.28 (dd, 1H, J=7.6 and 8.0 Hz). ^{13}C NMR ($CDCl_3$) δ=16.90 (SMe), 21.82 (Me), 40.85 (CH_2), 75.86 (CH), 123.81 (Ar), 124.37 (Ar), 124.62 (Ar), 126.45 (Ar), 129.42 (Ar), 138.57 (Ar), 159.86 (C=N). MS: found: 207; calcd for $C_{11}H_{13}NOS$ M^+ 207. Anal. found: C, 58.40; H, 6.76; N, 6.63. Calcd for $C_{11}H_{13}NOS(+H_2O)$. C, 58.64; H, 6.32; N, 6.76.

2-Methyl-4-methylthiomethyl-4-methyl-3,1-benzoxazine (**5c**): pale yellow oil (99 mg, 0.045 mmol, 90%). ^{1}H NMR ($CDCl_3$) δ=1.73 (s, 3H, SMe), 1.92 (s, 3H, Me), 2.13 (s, 3H, =C–CH_3), 2.84 (d, 1H, J=14.0 Hz, CH_2), 2.97 (d, 1H, J=14.0 Hz, CH_2), 7.06–7.19 (m, 3H, Ar), 7.26 (dd, 1H, J=6.8 and 7.6 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ=17.86 (SMe), 22.06 (Me), 26.58 (=C-CH_3), 46.24 (CH_2), 80.80 (q-C), 123.59 (Ar), 124.44 (Ar), 126.52 (Ar), 128.00 (Ar), 129.14 (Ar), 138.66 (Ar), 160.01 (N=C). Anal. found: C, 65.24; H, 7.02; N, 5.99. Calcd for $C_{12}H_{15}NOS$: C, 65.12; H, 6.83; N, 6.33.

2-Methyl-4-methylthiomethyl-4-phenyl-3,1-benzoxazine (**5d**): pale yellow oil; ^{1}H NMR ($CDCl_3$) δ=1.85 (s, 3H, SMe), 1.90 (s, 3H, Me), 2.94 (d, 1H, J=14.0 Hz, CH_2), 3.06 (d, 1H, J=14.0 Hz, CH_2), 7.16–7.24 (m, 2H, Ar), 7.32 (br, 2H, Ar), 7.40–7.53 (m, 3H, Ar), 8.17 (br d, 2H, J=8.0 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ=18.04 (SMe), 25.97 (Me), 45.70 (CH_2), 80.91 (q-C), 123.63 (Ar), 125.37 (Ar), 126.80 (Ar), 128.21 (Ar), 128.48 (Ar), 128.96 (Ar), 129.21 (Ar), 131.63 (Ar), 132.93 (Ar), 139.29 (Ar), 156.68 (N=C). Anal. found: C, 71.95; H, 6.18; N, 4.92. Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; N, 4.94.

4.8. Crystal data for 5a

Crystal data for **5a**: $C_{16}H_{15}NOS$. Crystallized from hexane. Cu Kα radiation. M=269.366, a=5.680(2) Å, b=12.1510(4) Å, c=19.3270(6) Å, V=1401.548 Å, T=298 K, orthorhombic, space group=$P2_12_12_1$, Z=4, 4399 measured reflections, 2418 independent reflections, R=0.0567, wR=0.1791 for 2085 observed reflections, R=0.0640 for all reflections. Reflection data were obtained at 298 K on a DIP-3200 X-ray diffractometer (Bruker AXS Co. Ltd.) with an imaging plate, Cu Kα radiation, and Ni filter.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.05.111.

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