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ONE-POT SYNTHESIS OF 3-OXO-2*H*,4*H*-1,4-BENZOTHAZINE-2-CARBONITRILE DERIVATIVES *VIA* CYCLIZATION OF METHYL {[2-(CYANOMETHYL)SULFANYL]PHENYL}CARBAMATE

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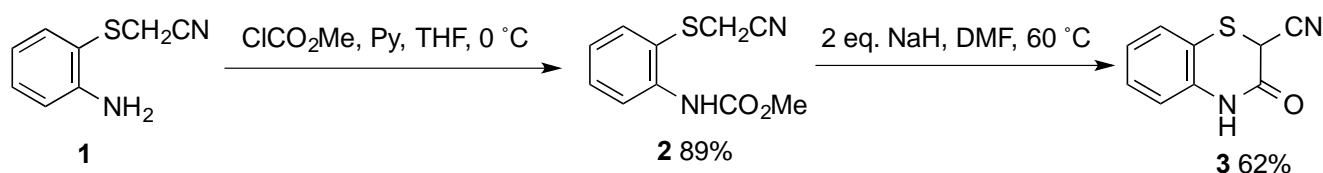
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Abstract – A facile method for the synthesis of 3-oxo-2*H*,4*H*-1,4-benzothiazine-2-carbonitrile (2-cyano-2*H*-1,4-benzothiazin-3(4*H*)-one) derivatives has been developed. Sodium hydride-mediated cyclization of methyl {[2-(cyanomethyl)sulfanyl]phenyl}carbamate, which can be easily prepared from commercially available 2-aminobenzenethiol in two steps, allows the synthesis of 3-oxo-2*H*,4*H*-1,4-benzothiazine-2-carbonitrile and its 2-mono- and 2,4-di-alkylated derivatives in one-pot.

The 2*H*-1,4-benzothiazin-3(4*H*)-one core has attracted considerable synthetic effort¹ since it occurs in many therapeutic agents.² Some 3-oxo-2*H*,4*H*-1,4-benzothiazine-2-carbonitrile (2-cyano-2*H*-1,4-benzothiazin-3(4*H*)-one) derivatives have been prepared and reported to be of potent use for Ca antagonists and blood platelet aggregation inhibitors.³ It has also been reported that some 3-oxo-2*H*,4*H*-1,4-benzothiazine-2-carbonitrile 1,1-dioxides, which have been prepared by cyclization of ethyl {[2-(cyanomethyl)sulfonyl]phenyl}carbamates with sodium hydroxide, are important precursors for the synthesis of potential activators of ATP sensitive potassium channels.⁴ However, there have been only few reports on the general synthesis of 3-oxo-2*H*,4*H*-1,4-benzothiazine-2-carbonitriles. In this paper, we wish to demonstrate a new strategy for the preparation of this type of 2*H*-1,4-benzothiazin-3(4*H*)-ones. 3-Oxo-2*H*,4*H*-1,4-benzothiazine-2-carbonitrile (**3**) and its 2-mono- (**4**) and 2,4-di-alkylated derivatives (**5**) and (**6**) can be prepared by sodium hydride-mediated cyclization of methyl {[2-(cyanomethyl)-

sulfanyl]phenyl} carbamate (**2**).⁵ These new 2*H*-1,4-benzothiazin-3(4*H*)-one derivatives may be of biological importance.

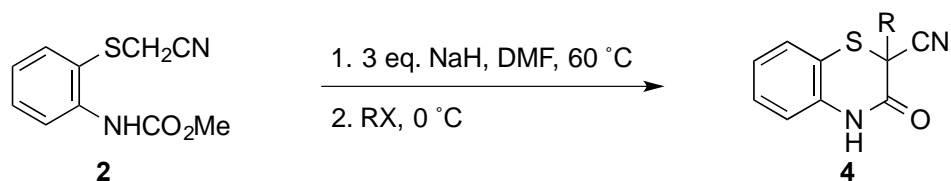
The procedure we have developed for the synthesis of 3-oxo-2*H*,4*H*-1,4-benzothiazine-2-carbonitrile (**3**) is illustrated in Scheme 1. 2-[(2-Aminophenyl)sulfanyl]acetonitrile (**1**) could be easily obtained from commercially available 2-aminobenzenethiol according to the reported procedure.^{6,7} First, compound (**1**) was *N*-methoxycarbonylated with methyl chloroformate in THF in the presence of pyridine at 0 °C to give methyl {[2-(cyanomethyl)sulfanyl]phenyl} carbamate (**2**) in 89% yield. Treatment of this carbamate with two equivalents of sodium hydride in DMF at 60 °C provided, after aqueous work up and subsequent purification by column chromatography on silica gel, the desired product (**3**) in 62% yield.



Scheme 1

With the reaction conditions for the formation of **3** in hand, we turned our attention to the introduction of substituents to the 2- and/or 4-positions of the 4*H*-1,4-benzothiazin-3(2*H*)-one ring. As shown in Scheme 2, after compound (**2**) was treated with three equivalents of sodium hydride under the above conditions, the reaction mixture was cooled to 0 °C and alkyl halides were added. The alkylation at the 2-position proceeded smoothly at this temperature, and the desired 2-alkylated products (**4**) were obtained in the yields compiled in Table 1. When two equivalents of sodium hydride were used in the reaction with methyl iodide, products (**4a**) was obtained in only 24% yield along with **3** (30%). An inactivated alkyl halide, such as *n*-butyl bromide, proved to be usable in the present procedure to give the corresponding desired product (**4b**), albeit in a rather decreased yield (Entry 2). (Methylsulfanyl)methylation could also be achieved by using chloromethyl methyl sulfide to give the corresponding product (**4e**) in a moderate yield (Entry 5). Unfortunately, however, when electron-withdrawing group (EWG)-activated haloalkanes, such as 2-bromoacetonitrile and *tert*-butyl 2-bromoacetates, were used, the reactions resulted in the formation of intractable mixtures of products, from which no corresponding desired products could be isolated. These results are probably due to reactions arising from deprotonation of α -hydrogen of these halides with sodium methoxide generated during the cyclization of **2**.

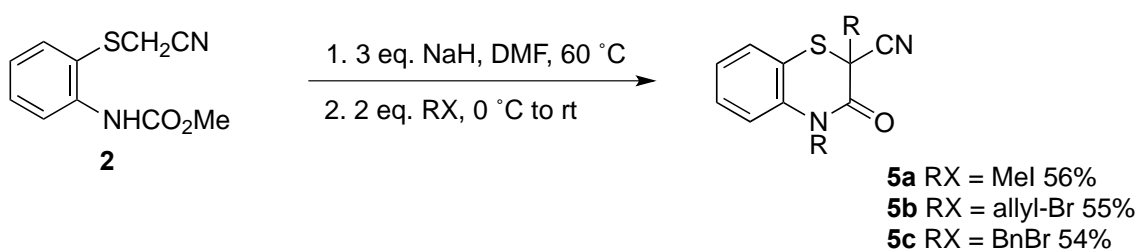
One-pot preparation of 2,4-dialkyl-3-oxo-2*H*,4*H*-1,4-benzothiazine-2-carbonitriles **5** were easily accomplished, as depicted in Scheme 3. Treatment of compound **2** with three equivalents of sodium hydride as above was followed by addition of two equivalents of alkyl halides at 0 °C and the reaction temperature was raised to room temperature to furnish the expected products in moderate yields.



Scheme 2

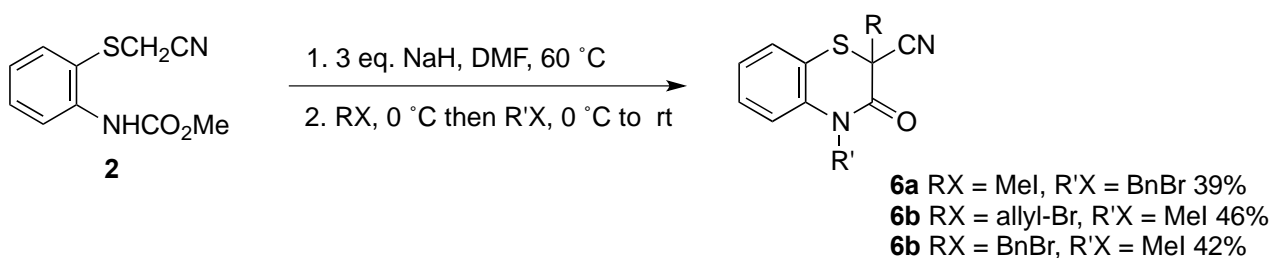
Table 1. Preparation of 2-alkylated 3-oxo-2*H*,4*H*-1,4-benzothiazine-2-carbonitriles (**4**)

| Entry | RX | 4 | Yield/% ^a |
|-------|---------------------------------------|-----------|----------------------|
| 1 | MeI | 4a | 60 |
| 2 | <i>n</i> -BuBr | 4b | 36 |
| 3 | CH ₂ =CHCH ₂ Br | 4c | 55 |
| 4 | BnBr | 4d | 57 |
| 5 | MeSCH ₂ Cl | 4e | 43 |

^a Yields of isolated products.

Scheme 3

To demonstrate the utility of the present cyclization, we next attempted to introduce the different alkyl groups to the 2- and 4-positions in one-pot, as illustrated in Scheme 4. Thus, compound (**2**) was treated with three equivalents of sodium hydride as above and the first alkylation at the 2-position was achieved immediately at 0 °C. The second alkylation at the 4-position was performed by adding the second alkyl halides at the same temperature and subsequent raising the reaction temperature to room temperature to give the desired products, 2,4-dialkylated 3-oxo-2*H*,4*H*-benzothiazine-2-carbonitriles (**6**), albeit in low-to-moderate yields. The somewhat lower yields compared to those of compounds (**5**) are due to the second alkylation with excesses of the first alkyl halides.



Scheme 4

To conclude, the results reported above demonstrate that non-, 2-, and 2,4-di-substituted 3-oxo-2*H*,4*H*-1,4-benzothiazine-3-carbonitriles can be conveniently synthesized by sodium hydride-mediated cyclization of methyl {[2-(cyanomethyl)sulfanyl]phenyl} carbamate, easily derived from commercially available 2-aminobenzenethiol. Although the yields of the products are not so good, the ready availability of the reactants and the reagents as well as the easy operations under mild reaction conditions makes the present method attractive.

EXPERIMENTAL

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were recorded with a PerkinElmer Spectrum 65 FTIR spectrophotometer. ¹H and ¹³C NMR spectra were recorded using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 and 125 MHz, respectively. High-resolution MS spectra were measured by a Thermo Scientific Exactive spectrometer. Elemental analyses were performed with an Elementar Vario EL II instrument. TLC was carried out on Merck Kieselgel 60 PF₂₅₄. Column chromatography was performed using WAKO GEL C-200E. All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

Starting Materials. 2-[(2-Aminophenyl)sulfanyl]acetonitrile (**1**) was prepared according to the reported procedure.⁶ All other chemicals used in this study were commercially available.

Methyl {[2-(cyanomethyl)sulfanyl]phenyl} carbamate (2**).** To a stirred solution of **1** (1.7 g, 10 mmol) in THF (40 mL) containing pyridine (0.80 g, 10 mmol) at 0 °C was added ClCO₂Me (0.96 g, 10 mmol) dropwise. After 10 min, saturated aqueous NH₄Cl (50 mL) was added and the mixture was extracted with AcOEt (3 × 30 mL). The combined extracts were washed with H₂O (3 × 30 mL) and brine (40 mL), dried (Na₂SO₄), and concentrated by evaporation. The residual solid was recrystallized to give **2** (2.0 g, 89%); a white solid; mp 102–104 °C (hexane/CH₂Cl₂); IR (KBr) 3353, 2248, 1736 cm⁻¹; ¹H NMR (CDCl₃) δ 3.43 (s, 2H), 3.81 (s, 3H), 7.09 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 7.46 (td, *J* = 7.4, 1.1 Hz, 1H), 7.66 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.83 (br s, 1H), 8.22 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 21.6, 52.6, 115.9, 117.9, 119.3, 123.8, 132.1, 136.8, 140.3, 153.6. HR-MS (DART, positive). Calcd for C₁₀H₁₁N₂O₂S (M+H): 223.0541. Found: *m/z* 223.0532.

3-Oxo-2*H*,4*H*-1,4-benzothiazine-2-carbonitrile (3**).** To a stirred suspension of NaH (60% in mineral oil; 0.12 g, 3.0 mmol) in DMF (3 mL) at 0 °C was added a solution of **2** (0.22 g, 1.0 mmol) in DMF (2 mL) dropwise. After evolution of H₂ gas had ceased, the mixture was heated at 60 °C for 1 h. Saturated aqueous NH₄Cl (15 mL) was added to the cooled mixture and the resulting mixture was extracted with AcOEt (3 × 15 mL). The combined extracts were washed with H₂O (3 × 15 mL) and brine (20 mL), dried (Na₂SO₄), and concentrated by evaporation. The residual solid was recrystallized to give **3** (0.12 g, 62%);

a pale-yellow solid; mp 141–143 °C (hexane/CH₂Cl₂); IR (KBr) 3200, 2242, 1679 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ 5.48 (s, 1H), 7.08–7.12 (m, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 11.32 (br s, 1H); ¹³C NMR (DMSO-*d*₆) δ 30.6, 114.9, 115.5, 117.9, 124.1, 128.3, 128.5, 136.2, 158.3. HR-MS (DART, negative). Calcd for C₉H₅N₂OS (M–H): 189.0123. Found: *m/z* 189.0122. Anal. Calcd for C₉H₆N₂OS: C, 56.83; H, 3.18; N, 14.73; S, 16.85. Found: C, 56.56; H, 3.16; N, 14.82; S, 16.90.

Typical Procedure for the Preparation of 2-Alkylated 3-Oxo-2*H*,4*H*-1,4-benzothiazine-2-carbonitriles (4). **2-Methyl-3-oxo-2*H*,4*H*-1,4-benzothiazine-2-carbonitrile (4a).** Compound (1) (0.22 g, 1.0 mmol) was treated with NaH (60% in mineral oil; 0.12 g, 3.0 mmol) as described for the preparation of 3. After the reaction mixture was cooled to 0 °C, MeI (0.14 g, 1.0 mmol) was added. After 10 min, the mixture was worked up as described for the preparation of 3. The residue was purified by column chromatography on SiO₂ (Et₂O/hexane 1:1) to give 4a (0.12 g, 60%); a white solid; mp 151–153 °C (hexane/CH₂Cl₂); IR (KBr) 3201, 2231, 1683 cm⁻¹; ¹H NMR (CDCl₃) δ 1.94 (s, 3H), 7.06 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.14 (ddd, *J* = 8.0, 7.4, 1.1 Hz, 1H), 7.32 (ddd, *J* = 8.0, 7.4, 1.1 Hz, 1H), 7.38 (dd, *J* = 8.0, 1.1 Hz, 1H), 9.49 (br s, 1H); ¹³C NMR (CDCl₃) δ 20.0, 37.9, 116.9, 117.0, 117.8, 124.9, 128.2, 128.8, 135.2, 161.5. HR-MS (DART, positive). Calcd for C₁₀H₉N₂OS (M+H): 205.0435. Found: *m/z* 205.0430.

2-Butyl-3-oxo-2*H*,4*H*-1,4-benzothiazine-2-carbonitrile (4b): a white solid; mp 146–148 °C (hexane/CH₂Cl₂); IR (KBr) 3200, 2231, 1685 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ 0.86 (t, *J* = 7.4 Hz, 3H), 1.31–1.36 (m, 2H), 1.45–1.55 (m, 2H), 1.84–1.90 (m, 1H), 2.14–2.21 (m, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.33 (td, *J* = 7.4, 1.1 Hz, 1H), 7.46 (dd, *J* = 7.4, 1.1 Hz, 1H), 11.40 (br, s 1H); ¹³C NMR (DMSO-*d*₆) δ 13.7, 21.7, 27.1, 32.0, 40.0, 43.3, 115.1, 116.6, 117.6, 124.2, 128.3, 128.8, 159.9. HR-MS (DART, positive). Calcd for C₁₃H₁₅N₂OS (M+H): 247.0905. Found: *m/z* 247.0898.

3-Oxo-2-(prop-2-enyl)-2*H*,4*H*-1,4-benzothiazine-2-carbonitrile (4c): a white solid; mp 148–150 °C (hexane/CH₂Cl₂); IR (KBr) 3202, 2235, 1690, 1643 cm⁻¹; ¹H NMR (CDCl₃) δ 2.79 (dd, *J* = 14.3, 7.4 Hz, 1H), 3.09 (dd, *J* = 14.3, 7.4 Hz, 1H), 5.34 (d, *J* = 11.5 Hz, 1H), 5.37 (d, *J* = 4.0 Hz, 1H), 5.93–6.01 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.32 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 9.49 (s, 1H); ¹³C NMR (CDCl₃) δ 37.5, 43.2, 115.6, 116.4, 117.7, 122.0, 125.0, 128.4, 128.8, 129.5, 135.0, 161.0. HR-MS (DART, positive). Calcd for C₁₂H₁₁N₂OS (M+H): 231.0592. Found: *m/z* 231.0583. Anal. Calcd for C₁₂H₁₀N₂OS: C, 62.59; H, 4.38; N, 12.16; S, 13.92. Found: C, 62.35; H, 4.38; N, 12.26; S, 13.84.

3-Oxo-2-(phenylmethyl)-2*H*,4*H*-1,4-benzothiazine-2-carbonitrile (4d): a pale-yellow solid; mp 186–188 °C (hexane/CH₂Cl₂); IR (KBr) 3202, 2233, 1687 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ 3.19 (d, *J* = 14.3 Hz, 1H), 3.55 (d, *J* = 14.3 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.13 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.31–7.39 (m, 6H), 7.43 (d, *J* = 8.0 Hz, 1H), 11.49 (br s, 1H); ¹³C NMR (DMSO-*d*₆) δ 37.5, 44.5, 115.0, 116.1, 117.6,

124.3, 128.0, 128.3, 128.4, 128.8, 130.4, 133.3, 136.0, 159.6. HR-MS (DART, negative). Calcd for $C_{16}H_{11}N_2OS$ (M-H): 279.0592. Found: m/z 279.0601. Anal. Calcd for $C_{16}H_{12}N_2OS$: C, 68.55; H, 4.31; N, 9.99; S, 11.44. Found: C, 68.48; H, 4.33; N, 10.12; S, 11.65.

2-[(Methylsulfonyl)methyl]-3-oxo-2H,4H-1,4-benzothiazine-2-carbonitrile (4e): a white solid; mp 130–132 °C (hexane/ CH_2Cl_2); IR (KBr) 3193, 2233, 1686 cm^{-1} ; 1H NMR (DMSO- d_6) δ 2.26 (s, 3H), 3.22 (d, $J = 14.3$ Hz, 1H), 3.39 (d, $J = 14.3$ Hz, 1H), 7.10–7.14 (m, 2H), 7.34 (dd, $J = 8.0, 7.4$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 1H); 11.44 (br s, 1H); ^{13}C NMR (DMSO- d_6) δ 17.0, 36.4, 40.0, 45.1, 115.1, 117.6, 124.3, 128.3, 128.8, 135.8, 158.9. HR-MS (DART, positive). Calcd for $C_{11}H_{11}N_2OS_2$ (M+H): 251.0313. Found: m/z 251.0313.

Typical Procedure for the Preparation of 2,4-Dialkylated 3-Oxo-2H,4H-1,4-benzothiazine-2-carbonitriles (5). **2,4-Dimethyl-3-oxo-2H,4H-1,4-benzothiazine-2-carbonitrile (5a).** Compound (1) (0.22 g, 1.0 mmol) was treated with NaH (60% in mineral oil; 0.12 g, 3.0 mmol) as described for the preparation of 3. After the reaction mixture was cooled to 0 °C, MeI (0.28 g, 2.0 mmol) was added and stirring was continued for 10 min at rt. The resulting mixture was worked up as described for the preparation of 3. The residue was purified by column chromatography on SiO_2 to give 5a (0.12 g, 56%); a yellow oil; R_f 0.54 (Et₂O/hexane 1:1); IR (KBr) 2232, 1679 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.92 (s, 3H), 3.53 (s, 3H), 7.15 (t, $J = 7.4$ Hz, 1H), 7.19 (d, $J = 7.4$ Hz, 1H), 7.39 (t, $J = 7.4$ Hz, 1H), 7.43 (d, $J = 7.4$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.5, 33.8, 38.3, 117.1, 118.1, 119.6, 124.5, 128.86, 128.88, 139.2, 160.9. HR-MS (DART, positive). Calcd for $C_{11}H_{11}N_2OS$ (M+H): 219.0592. Found: m/z 219.0587.

3-Oxo-2,4-bis(prop-2-enyl)-2H,4H-1,4-benzothiazine-2-carbonitrile (5b): a colorless oil; R_f 0.27 (Et₂O/hexane 1:5); IR (neat) 2232, 1682, 1645 cm^{-1} ; 1H NMR ($CDCl_3$) δ 2.81 (dd, $J = 14.3, 7.4$ Hz, 1H), 3.14 (dd, $J = 14.3, 6.9$ Hz, 1H), 4.37 (d, $J = 15.4$ Hz, 1H), 4.88 (d, $J = 15.4$ Hz, 1H), 5.22 (d, $J = 17.8$ Hz, 1H), 5.27 (d, $J = 10.3$ Hz, 1H), 5.36 (d, $J = 12.0$ Hz, 2H), 5.90–6.02 (m, 2H), 7.15 (t, $J = 7.4$ Hz, 1H), 7.23 (d, $J = 8.6$ Hz, 1H), 7.35 (dd, $J = 8.0, 7.4$ Hz, 1H), 7.43 (d, $J = 7.4$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 37.6, 43.4, 49.2, 115.9, 116.7, 118.1, 119.0, 121.8, 124.7, 128.9, 129.0, 130.0, 131.3, 138.6, 159.8. HR-MS (DART, positive). Calcd for $C_{15}H_{15}N_2OS$ (M+H): 271.0905. Found: m/z 271.0898.

3-Oxo-2,4-bis(phenylmethyl)-2H,4H-1,4-benzothiazine-2-carbonitrile (5c): a yellow solid; mp 130–132 °C (hexane/ CH_2Cl_2); IR (KBr) 2232, 1682 cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.35 (d, $J = 14.3$ Hz, 1H), 3.76 (d, $J = 14.3$ Hz, 1H), 5.05 (d, $J = 16.6$ Hz, 1H), 5.50 (d, $J = 16.6$ Hz, 1H), 7.06 (dd, $J = 8.0, 7.4$ Hz, 1H), 7.12 (d, $J = 8.6$ Hz, 1H), 7.22–7.39 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 38.9, 45.3, 50.2, 115.9, 118.3, 119.0, 124.7, 126.0, 127.5, 128.3, 128.6, 128.9, 129.0, 129.2, 130.4, 133.1, 135.8, 138.6, 160.6. HR-MS (DART, positive). Calcd for $C_{23}H_{19}N_2OS$ (M+H): 371.1218. Found: m/z 371.1203. Anal. Calcd for $C_{23}H_{18}N_2OS$: C, 74.57; H, 4.90; N, 7.56; S, 8.65. Found: C, 74.35; H, 4.94; N, 7.64; S, 8.85.

Typical Procedure for the Preparation of 2,4-Dialkylated 3-Oxo-2*H*,4*H*-1,4-benzothiazine-2-carbonitriles (6). 2-Methyl-3-oxo-4-(phenylmethyl)-2*H*,4*H*-1,4-benzothiazine-2-carbonitrile (6a).

Compound (1) (0.22 g, 1.0 mmol) was treated with NaH (60% in mineral oil; 0.12 g, 3.0 mmol) as described for the preparation of 3. After the reaction mixture was cooled to 0 °C, MeI (0.14 g, 1.0 mmol) was added. After 10 min, BnBr (0.17 g, 1.0 mmol) was added and stirring was continued for 10 min at rt. The resulting mixture was then worked up as described for the preparation of 3 to give a residue, which was purified by column chromatography on SiO₂ to give 6a (0.12 g, 60 %); a yellow oil; *R*_f 0.27 (AcOEt/hexane 1:4); IR (neat) 2231, 1683 cm⁻¹; ¹H NMR (CDCl₃) δ 1.95 (s, 3H), 4.98 (d, *J* = 16.6 Hz, 1H), 5.47 (d, *J* = 16.6 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 2H), 7.22–7.26 (m, 3H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 1H); ¹³C NMR (CDCl₃) δ 20.3, 38.4, 50.2, 117.1, 118.5, 124.7, 125.9, 126.0, 127.5, 128.9, 129.0, 130.4, 135.8, 138.7, 160.8. HR-MS (DART, positive). Calcd for C₁₇H₁₅N₂OS (M+H): 295.0905. Found: *m/z* 295.0899.

4-Methyl-3-oxo-2-(prop-2-enyl)-2*H*,4*H*-1,4-benzothiazine-2-carbonitrile (6b): a yellow oil; *R*_f 0.24 (AcOEt/hexane 1:4); IR (neat) 2228, 1679, 1646 cm⁻¹; ¹H NMR (CDCl₃) δ 2.79 (dd, *J* = 14.3, 7.4 Hz, 1H), 3.12 (dd, *J* = 14.3, 7.4 Hz, 1H), 3.53 (s, 3H), 5.33 (d, *J* = 5.2 Hz, 1H), 5.36 (s, 1H), 5.93–6.01 (m, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.6 Hz, 1H), 7.39 (ddd, *J* = 8.6, 7.4, 1.7 Hz, 1H), 7.42 (td, *J* = 7.4, 1.7 Hz, 1H); ¹³C NMR (CDCl₃) δ 33.8, 37.8, 43.5, 115.9, 118.0, 119.0, 121.7, 124.5, 128.9, 129.1, 130.0, 139.0, 160.3. HR-MS (DART, positive). Calcd for C₁₃H₁₃N₂OS (M+H): 245.0748. Found: *m/z* 245.0736.

4-Methyl-3-oxo-2-(phenylmethyl)-2*H*,4*H*-1,4-benzothiazine-2-carbonitrile (6c): a yellow oil; *R*_f 0.24 (AcOEt/hexane 1:5); IR (neat) 2236, 1675 cm⁻¹; ¹H NMR (CDCl₃) δ 3.21 (d, *J* = 14.8 Hz, 1H), 3.48 (s, 3H), 3.60 (d, *J* = 14.8 Hz, 1H), 7.05 (td, *J* = 7.4, 1.1 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 7.27–7.32 (m, 7H); ¹³C NMR (CDCl₃) δ 33.8, 39.1, 45.3, 115.9, 117.9, 118.8, 124.5, 128.2, 128.6, 128.9, 129.2, 130.4, 133.1, 139.0, 160.6. HR-MS (DART, positive). Calcd for C₁₇H₁₅N₂OS (M+H): 295.0905. Found: *m/z* 295.0900.

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REFERENCES AND NOTES

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