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**ONE-POT SYNTHESIS OF 2-(1,4-DIHYDRO-2*H*-3,1-BENZOTHAZIN-2-YLIDENE)PROPANEDIOIC ACID DERIVATIVES BY THE REACTION OF 2-(1-BROMOALKYL)PHENYL ISOTHIOCYANATES WITH PROPANEDIOIC ACID DERIVATIVES USING SODIUM HYDRIDE**

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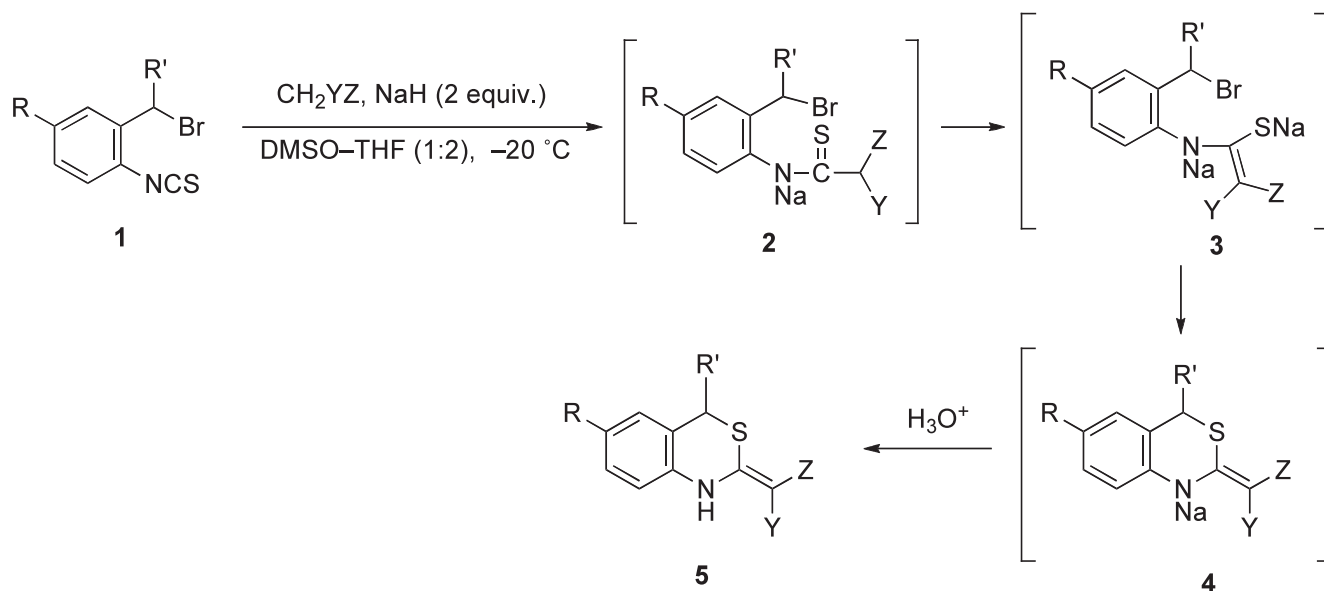
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**Abstract** – An efficient one-pot procedure for the preparation of 2-(1,4-dihydro-2*H*-3,1-benzothiazin-2-ylidene)propanedioic acid derivatives from 2-(1-bromoalkyl)phenyl isothiocyanates with propanedioic (malonic) acid derivatives, such as propanedinitrile, ethyl cyanoacetates, 3-oxo-3-(pyrrolidin-1-yl)propanenitrile and diethyl propanedioate, has been developed. The reactions are carried out in the presence of two equivalents of sodium hydride at –20 °C to give the desired products.

2-(1,4-Dihydro-2*H*-3,1-benzothiazin-2-ylidene)propanedioic acid derivatives are attractive heterocycles as some compounds having the 1,4-dihydro-2*H*-3,1-benzothiazin-2-ylidene structure have been reported to possess pharmacological activities.<sup>1</sup> However, few general methods for the preparation of 2-(1,4-dihydro-2*H*-3,1-benzothiazin-2-ylidene)propanedioic acid derivatives have been elaborated, though a synthesis of ethyl 2-cyano-2-(4-oxo-1,4-dihydro-2*H*-3,1-benzothiazin-2-ylidene)acetate by the reaction of ethyl 2-isothiocyanatobenzoate with methyl cyanoacetates in the presence of Et<sub>3</sub>N has been reported by Basheer and Rappoport.<sup>2</sup> In this article, we wish to describe a facile one-pot procedure for the synthesis of 2-(1,4-dihydro-2*H*-3,1-benzothiazin-2-ylidene)propanedioic acid derivatives by the reaction of 2-(1-bromoalkyl)phenyl isothiocyanates with propanedioic (malonic) acid derivatives using sodium hydride as a base under mild conditions.

The one-pot synthesis was conducted by the process depicted in Scheme 1. The starting isothiocyanates (**1**) were easily obtained by benzylic bromination of commercially available 2-alkylphenyl isothiocyanates with *N*-bromosuccinimide (NBS). Compounds (**1**) were allowed to react with propanedioic acid derivatives, such as propanedinitrile, ethyl cyanoacetate, 3-oxo-3-(pyrrolidin-1-yl)-

propanenitrile and diethyl propanedioate, in the presence of two equivalents of sodium hydride in DMSO/THF at  $-20\text{ }^{\circ}\text{C}$ . The stabilized carbanions, generated from propanedioic acid derivatives and the first equivalent of sodium hydride, attack on the isothiocyanato carbon to generate the intermediates (**2**). Then, the second equivalent of sodium hydride abstracts the methine proton, activated by the two electron withdrawing groups and the thiocarbonyl group, to generate the dianion intermediates (**3**). Intramolecular substitution of bromide with thioenolate sulfur provides 1-sodio-3,1-benzothiazine intermediates (**4**). The usual aqueous workup and subsequent recrystallization of the crude products afforded the desired products (**5**). The results are compiled in Table 1. For example, the reaction of 2-(bromomethyl)phenyl isothiocyanate (**1a**) with propanedinitrile proceeded cleanly and smoothly to yield the corresponding desired product (**5a**) in good yield (Entry 1). At a higher temperature ( $0\text{ }^{\circ}\text{C}$ ) a rather complicated mixture of products was obtained and the yield of the desired product (**5a**) dropped to 22% (data not shown in Table 1). The reactions in THF using two equivalents of sodium hydride and in DMSO/THF using an equivalent of sodium hydride both gave considerably complicated reaction mixtures as judged by TLC analyses. Although ethyl cyanoacetate, 3-oxo-3-(pyrrolidin-1-yl)propanenitrile, and diethyl propanedioate are also usable in the reactions with **1a**, the yields of the corresponding products (**5b-d**) were moderate (Entries 2-4, respectively).



The use of 2-bromomethyl-4-chlorophenyl isothiocyanate (**1b**) provided the corresponding products (**5f-h**) in yields comparable to those of using **1a** (Entries 6–8). While the reaction of 2-bromomethyl-4-methoxyphenyl isothiocyanate (**1c**) with propanedinitrile led to the formation of rather intractable mixture of products, from which only moderate yield of the expected product (**5i**) was isolated

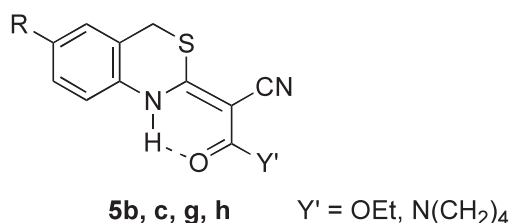
(Entry 9), that using 2-(1-bromoethyl)phenyl isothiocyanate (**1d**) proceeded uneventfully to give the corresponding products (**5j**) in relatively good yield (Entry 10).

**Table 1.** Preparation of 2-(1,4-dihydro-2*H*-3,1-benzothiazin-2-ylidene)propanedioic acid derivatives (**5**)

Entry	<b>1</b>	Y	Z	<b>5</b>	Yield/% <sup>a</sup>
1	<b>1a</b> (R = R' = H)	CN	CN	<b>5a</b>	82
2	<b>1a</b>	CO <sub>2</sub> Et	CN	<b>5b</b>	55
3	<b>1a</b>	CON(CH <sub>2</sub> ) <sub>4</sub>	CN	<b>5c</b>	57
4	<b>1a</b>	CO <sub>2</sub> Et	CO <sub>2</sub> Et	<b>5d</b>	42
5	<b>1a</b>	COCH <sub>3</sub>	CO <sub>2</sub> Et	<b>5e</b> <sup>b</sup>	22
6	<b>1b</b> (R = Cl, R' = H)	CN	CN	<b>5f</b>	82
7	<b>1b</b>	CO <sub>2</sub> Et	CN	<b>5g</b>	54
8	<b>1b</b>	CON(CH <sub>2</sub> ) <sub>4</sub>	CN	<b>5h</b>	56
9	<b>1c</b> (R = OMe, R' = H)	CN	CN	<b>5i</b>	45
10	<b>1d</b> (R = H, R' = Me)	CN	CN	<b>5j</b>	72

<sup>a</sup> Yields of isolated products. <sup>b</sup> A mixture of stereoisomers was obtained.

When the reaction was carried out using ethyl cyanoacetate or 3-oxo-3-(pyrrolidin-1-yl)propanenitrile, only *E*-isomer was obtained in each case (Entries 2, 3, 7, and 8). As depicted in Figure 1, this exclusive formation of *E*-isomers ascribed to the stabilization due to the hydrogen bonding between the NH hydrogen and the carbonyl oxygen in each case. As can be seen in EXPERIMENTAL section, the C=O stretching bands of these products are observed at considerably decreased wavenumbers and the chemical shifts of NH protons appear in much lower magnetic field ( $\delta$  12.23–13.60) than those of 2-(1,4-dihydro-2*H*-3,1-benzothiazin-2-ylidene)propanedinitriles (**5a**, **5f**, **5i**, and **5j**). Ethyl 3-oxobutanoate proved to be usable in the present reaction, but the reaction with **1a** provided the product (**5e**) as a mixture of stereoisomers in much lower yields than those using the above propanedioic acid derivatives (Entry 5).



**Figure 1**

In conclusion, we have developed an efficient one-pot synthesis of 2-(1,4-dihydro-2*H*-3,1-benzothiazin-2-ylidene)propanedioic acid derivatives by the reaction of 2-(1-bromoalkyl)phenyl isothiocyanates with propanedioic acid derivatives under mild reaction conditions. Notable advantages of the present method

are: i) simplicity of the procedure, ii) mild reaction conditions, and iii) easy availability of the starting materials.

## EXPERIMENTAL

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were recorded with a Perkin–Elmer Spectrum65 FTIR spectrophotometer.  $^1\text{H}$  NMR spectra were recorded using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 MHz or a JEOL LA400FT NMR spectrometer operating at 400 MHz.  $^{13}\text{C}$  NMR spectra were recorded using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz. High-resolution MS spectra (DART, positive) were measured by a Thermo Scientific Exactive spectrometer. TLC was carried out on Merck Kieselgel 60 PF<sub>254</sub>. 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.** 1-Bromomethyl-2-isothiocyanatobenzene (**1a**)<sup>3</sup> and 3-oxo-3-(pyrrolidin-1-yl)propanenitrile<sup>4</sup> were prepared according to the appropriate reported procedures. All other chemicals used in this study were commercially available.

**1-Bromoalkyl-2-isothiocyanatobenzenes (1b), (1c), and (1d).** These compounds were prepared from the respective 1-alkyl-2-isothiocyanatobenzenes according to the procedure reported for the preparation of **1a** from 1-isothiocyanato-2-methylbenzene.<sup>3</sup>

**1-Bromomethyl-5-chloro-2-isothiocyanatobenzene (1b):**<sup>5</sup> yield: 67%; a white solid; mp 57–59 °C (hexane–CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr) 2069 cm<sup>-1</sup>;  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.45 (s, 2H), 7.21 (d,  $J$  = 8.4 Hz, 1H), 7.29 (dd,  $J$  = 8.4, 2.3 Hz, 1H), 7.40 (d,  $J$  = 2.3 Hz, 1H). Anal. Calcd for C<sub>8</sub>H<sub>5</sub>BrClNS: C, 36.60; H, 1.92; N, 5.33. Found: C, 36.58; H, 1.93; N, 5.16.

**1-Bromomethyl-2-isothiocyanato-5-methoxybenzene (1c):** yield: 57%; a white solid; mp 74–76 °C (hexane–CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr) 2135, 1608 cm<sup>-1</sup>;  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.82 (s, 3H), 4.47 (s, 2H), 6.83 (dd,  $J$  = 9.2, 3.1 Hz, 1H), 6.90 (d,  $J$  = 3.1 Hz, 1H), 7.20 (d,  $J$  = 9.2 Hz, 1H). Anal. Calcd for C<sub>9</sub>H<sub>8</sub>BrNOS: C, 41.88; H, 3.12; N, 5.43. Found: C, 41.68; H, 3.19; N, 5.30.

**1-(1-Bromoethyl)-2-isothiocyanatobenzene (1d):** yield: 60%; a colorless liquid;  $R_f$  0.50 (hexane); IR (KBr) 2097 cm<sup>-1</sup>;  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  1.99 (d,  $J$  = 6.9 Hz, 3H), 5.38 (q,  $J$  = 6.9 Hz, 1H), 7.19–7.25 (m, 3H), 7.48–7.51 (m, 1H). Anal. Calcd for C<sub>9</sub>H<sub>8</sub>BrNS: C, 44.64; H, 3.33; N, 5.78. Found: C, 44.58; H, 3.38; N, 5.71.

**Typical Procedure for the Preparation of 2-(1,4-Dihydro-2H-3,1-benzothiazin-2-ylidene)malonic Acid Derivatives (5). 2-(1,4-Dihydro-2H-3,1-benzothiazin-2-ylidene)-1,3-propanedinitrile (5a).** To a stirred suspension of NaH (60% in mineral oil; 80 mg, 2.0 mmol) in DMSO–THF (6 mL; 1:2, v/v) at –20

°C was added  $\text{CH}_2(\text{CN})_2$  (66 mg, 1.0 mmol) dropwise. After evolution of  $\text{H}_2$  gas had ceased, compound (**1a**) (0.23 g, 1.0 mmol) was added, and then stirring was continued for 30 min at the same temperature before saturated aqueous  $\text{NH}_4\text{Cl}$  (15 mL) was added. The mixture was extracted with AcOEt ( $3 \times 10$  mL) and the combined extracts were washed with water ( $2 \times 10$  mL) and brine (10 mL), dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated by evaporation. The residual solid was recrystallized from hexane– $\text{CH}_2\text{Cl}_2$  to give **5a** (0.17 g, 82%); a white solid; mp 223–225 °C; IR (KBr) 3247, 3212, 2217, 2197, 1624  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.01 (s, 2H), 7.11 (d,  $J = 7.8$  Hz, 1H), 7.23–7.26 (m, 2H), 7.36–7.40 (m, 1H), 8.64 (br, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  28.47, 50.06, 113.79 (two overlapped Cs), 118.13, 119.98, 126.36, 127.69, 129.64, 135.23, 168.63. HR MS (DART, positive). Calcd for  $\text{C}_{11}\text{H}_8\text{N}_3\text{S}$  (M+H): 214.0439. Found:  $m/z$  214.0425. Anal. Calcd for  $\text{C}_{11}\text{H}_7\text{N}_3\text{S}$ : C, 61.95; H, 3.31; N, 19.70. Found: C, 61.91; H, 3.34; N, 19.62.

**Ethyl (E)-2-Cyano-2-(1,4-dihydro-2H-3,1-benzothiazin-2-ylidene)acetate (5b)**: a pale-yellow solid; mp 127–129 °C (hexane– $\text{CH}_2\text{Cl}_2$ ); IR (KBr) 3286, 3223, 2203, 1649, 1611  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.36 (t,  $J = 7.3$  Hz, 3H), 3.99 (s, 2H), 4.29 (q,  $J = 7.4$  Hz, 2H), 7.02 (d,  $J = 7.8$  Hz, 1H), 7.17–7.19 (m, 2H), 7.30–7.34 (m, 1H), 12.23 (br s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.28, 27.93, 61.13, 73.32, 116.93, 118.31, 119.44, 125.65, 127.57, 129.19, 135.36, 166.73, 167.61. HR MS (DART, positive). Calcd for  $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}_2\text{S}$  (M+H): 261.0697. Found:  $m/z$  261.0681. Anal. Calcd for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ : C, 59.98; H, 4.56; N, 10.76. Found: C, 60.01; H, 4.64; N, 10.49.

**(E)-2-(1,4-Dihydro-2H-3,1-benzothiazin-2-ylidene)-3-oxo-3-(pyrrolidin-1-yl)propanenitrile (5c)**: a pale-yellow solid; mp 185–187 °C (hexane– $\text{CH}_2\text{Cl}_2$ ); IR (KBr) 3284, 2184, 1611, 1575  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.91–1.95 (m, 4H), 3.56 (br s, 2H), 3.81 (br s, 2H), 3.96 (s, 2H), 6.99 (dd,  $J = 7.6$  Hz, 1H), 7.11–7.16 (m, 2H), 7.29 (d,  $J = 8.4$  Hz, 1H), 13.50 (br s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  23.92, 26.74, 28.16, 47.20, 48.85, 73.74, 118.45, 119.23, 120.08, 124.94, 127.31, 128.97, 136.05, 165.80, 166.03. HR MS (DART, positive). Calcd for  $\text{C}_{15}\text{H}_{16}\text{N}_3\text{OS}$  (M+H): 286.1014. Found:  $m/z$  286.1024. Anal. Calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_3\text{OS}$ : C, 63.13; H, 5.30; N, 14.73. Found: C, 63.08; H, 5.29; N, 14.70.

**Diethyl 2-(1,4-Dihydro-2H-3,1-benzothiazin-2-ylidene)-1,3-propandioate (5d)**: a pale-yellow solid; mp 76–79 °C (hexane– $\text{CH}_2\text{Cl}_2$ ); IR (KBr) 3254, 1666, 1640, 1602  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.33 and 1.34 (2t,  $J = 7.3$  Hz each, combined 6H), 3.78 (s, 2H), 4.26 and 4.28 (2q,  $J = 7.3$  Hz each, combined 4H), 6.98 (d,  $J = 7.8$  Hz, 1H), 7.08–7.15 (m, 2H), 7.27 (d,  $J = 7.8$  Hz, 1H), 12.59 (br s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.01, 14.22, 28.31, 60.34, 60.83, 93.39, 118.13, 121.12, 124.42, 126.88, 128.55, 136.52, 164.02, 166.89, 168.49. HR MS (DART, positive). Calcd for  $\text{C}_{15}\text{H}_{18}\text{NO}_4\text{S}$  (M+H): 308.0956. Found:  $m/z$  308.0972. Anal. Calcd for  $\text{C}_{15}\text{H}_{17}\text{NO}_4\text{S}$ : C, 58.61; H, 5.57; N, 4.56. Found: C, 58.71; H, 5.82; N, 4.60.

**Ethyl 2-(1,4-Dihydro-2H-3,1-benzothiazin-2-ylidene)-3-oxobutanoate (5e)**: a mixture of stereoisomers ( $E:Z = ca. 1:9$ ); a pale-yellow solid; mp 96–112 °C; IR (KBr) 3276, 1692, 1614  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.37 and 1.39 (2t,  $J = 6.9$  Hz each, combined 3H), 2.43 (s, 0.3H), 2.47 (s, 2.7H), 3.69 (s, 0.2H),

3.79 (s, 1.8H), 4.31 and 4.34 (2q,  $J = 6.9$  Hz each, combined 2H), 7.03 (d,  $J = 8.0$  Hz, 1H), 7.13–7.17 (m, 2H), 7.27–7.31 (m, 1H), 13.22 (br s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.30, 28.29, 28.86, 30.60, 31.60, 60.48, 60.78, 102.31, 103.09, 118.30, 118.97, 121.00, 125.15, 125.49, 126.92, 128.27, 128.61, 135.96, 167.45, 167.94, 196.03. HR MS (DART, positive). Calcd for  $\text{C}_{14}\text{H}_{16}\text{NO}_3\text{S}$  (M+H): 278.0851. Found:  $m/z$  278.0837. Anal. Calcd for  $\text{C}_{14}\text{H}_{15}\text{NO}_3\text{S}$ : C, 60.63; H, 5.45; N, 5.05. Found: C, 60.42; H, 5.62; N, 5.02.

**2-(6-Chloro-1,4-dihydro-2H-3,1-benzothiazin-2-ylidene)-1,3-propanedinitrile (5f):** a yellow solid; mp 253–255 °C (hexane–THF); IR (KBr) 3243, 3199, 2220, 2199, 1622  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.98 (s, 2H), 7.04 (d,  $J = 8.4$  Hz, 1H), 7.25 (d,  $J = 2.3$  Hz, 1H), 7.36 (dd,  $J = 8.4, 2.3$  Hz, 1H), 8.54 (br s, 1H);  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  26.95, 50.11, 114.32, 115.90, 121.01, 123.77, 127.17, 128.52, 129.45, 135.18, 167.99. HR MS (DART, positive). Calcd for  $\text{C}_{11}\text{H}_7\text{ClN}_3\text{S}$  (M+H): 248.0049. Found:  $m/z$  248.0068. Anal. Calcd for  $\text{C}_{11}\text{H}_6\text{ClN}_3\text{S}$ : C, 53.34; H, 2.44; N, 16.96. Found: C, 53.23; H, 2.52; N, 16.81.

**Ethyl (E)-2-(6-Chloro-1,4-dihydro-2H-3,1-benzothiazin-2-ylidene)-2-cyanoacetate (5g):** a pale-yellow solid; mp 135–136 °C (hexane– $\text{CH}_2\text{Cl}_2$ ); IR (KBr) 3171, 2213, 1653, 1612  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.35 (t,  $J = 7.6$  Hz, 3H), 3.95 (s, 2H), 4.29 (q,  $J = 7.6$  Hz, 2H), 6.96 (d,  $J = 8.4$  Hz, 1H), 7.19 (d,  $J = 2.3$  Hz, 1H), 7.30 (dd,  $J = 8.4, 2.3$  Hz, 1H), 12.27 (br s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  14.28, 27.71, 61.34, 74.16, 119.47, 121.06, 127.56, 128.67, 129.23, 130.61, 134.11, 166.20, 167.57. HR MS (DART, positive). Calcd for  $\text{C}_{13}\text{H}_{12}\text{ClN}_2\text{O}_2\text{S}$  (M+H): 295.0308. Found:  $m/z$  295.0323. Anal. Calcd for  $\text{C}_{13}\text{H}_{11}\text{ClN}_2\text{O}_2\text{S}$ : C, 52.97; H, 3.76; N, 9.50. Found: C, 52.90; H, 3.82; N, 9.43.

**(E)-2-(6-Chloro-1,4-dihydro-2H-3,1-benzothiazin-2-ylidene)-3-oxo-3-(pyrrolidin-1-yl)propanenitrile (5h):** a pale-yellow solid; mp 204–206 °C (hexane– $\text{CH}_2\text{Cl}_2$ ); IR (KBr) 3385, 2187, 1614, 1567  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.91–1.95 (m, 4H), 3.55–3.81 (m, 4H), 3.92 (s, 2H), 6.92 (d,  $J = 8.4$  Hz, 1H), 7.15 (d,  $J = 2.3$  Hz, 1H), 7.25 (dd,  $J = 8.4, 2.3$  Hz, 1H), 13.60 (br s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25.15, 26.75, 27.93, 47.69, 49.29, 74.38, 118.89, 119.59, 121.64, 127.30, 128.99, 129.84, 134.77, 165.56, 165.63. HR MS (DART, positive). Calcd for  $\text{C}_{15}\text{H}_{15}\text{ClN}_3\text{OS}$  (M+H): 320.0624. Found:  $m/z$  320.0614. Anal. Calcd for  $\text{C}_{15}\text{H}_{14}\text{ClN}_3\text{OS}$ : C, 56.33; H, 4.41; N, 13.14. Found: C, 56.26; H, 4.48; N, 13.08.

**2-(6-Methoxy-1,4-dihydro-2H-3,1-benzothiazin-2-ylidene)-1,3-propanedinitrile (5i):** a white solid; mp 250–251 °C (hexane– $\text{CH}_2\text{Cl}_2$ ); IR (KBr) 3254, 3212, 2217, 2200, 1626  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.82 (s, 3H), 3.96 (s, 2H), 6.75 (d,  $J = 2.3$  Hz, 1H), 6.90 (dd,  $J = 8.4, 2.3$  Hz, 1H), 7.05 (d,  $J = 8.4$  Hz, 1H), 8.70 (br s, 1H);  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  27.54, 48.26, 55.56, 112.51, 114.10, 114.81, 116.38, 120.59, 123.19, 129.60, 157.11, 167.31. HR MS (DART, positive). Calcd for  $\text{C}_{12}\text{H}_{10}\text{N}_3\text{OS}$  (M+H): 244.0544. Found:  $m/z$  244.0551. Anal. Calcd for  $\text{C}_{12}\text{H}_9\text{N}_3\text{OS}$ : C, 59.24; H, 3.73; N, 17.27. Found: C, 59.13; H, 3.81; N, 17.22.

**2-(4-Methyl-1,4-dihydro-2H-3,1-benzothiazin-2-ylidene)-1,3-propanedinitrile (5j):** a pale-yellow solid; mp 215–217 °C (hexane– $\text{CHCl}_3$ ); IR (KBr) 3245, 3208, 2219, 2195, 1620  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500

MHz, DMSO- $d_6$ )  $\delta$  1.47 (d,  $J = 7.6$  Hz, 3H), 4.56 (q,  $J = 7.6$  Hz, 1H), 7.23 (t,  $J = 7.6$  Hz, 1H), 7.30 (d,  $J = 7.6$  Hz, 1H), 7.34 (t,  $J = 7.6$  Hz, 1H), 7.37 (d,  $J = 7.6$  Hz, 1H), 11.89 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  21.88, 37.08, 49.74, 114.64, 116.21, 119.75 (two overlapped Cs), 126.17, 126.53, 128.72, 134.99, 166.37. HR MS (DART, positive). Calcd for  $\text{C}_{12}\text{H}_{10}\text{N}_3\text{S}$  (M+H): 228.0595. Found:  $m/z$  228.0587. Anal. Calcd for  $\text{C}_{12}\text{H}_9\text{N}_3\text{S}$ : C, 63.41; H, 3.99; N, 18.49. Found: C, 63.16; H, 4.01; N, 18.19.

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