SYNTHESIS OF 3,1-BENZOTHIAZINES FROM 2-ALKENYL- AND 2-ALKYNYLANILIDES AND LAWESSON REAGENT

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Abstract – Reaction of 2-vinylacetanilide with P₄S₁₀ gave 2-vinylthioacetanilide, whereas reaction of 2-vinylacetanilide with Lawesson reagent (LR) afforded 2,4-dimethyl-4H-3,1-benzothiazine in 62% yield. Reaction of 2-alkynylanilides with LR gave 4-exomethylene-4H-3,1-benzothiazines in good yields.

INTRODUCTION

4H-3,1-Benzothiazines (1) are important compounds because of their biological and structural appeal. 4H-3,1-Benzothiazine derivatives with aromatic substituents at positions 2 and/or 4 exhibit many kinds of biological activities¹ and are of interest for the production of recording materials and use in photographic and laser techniques.² Moreover, they are valuable building blocks and can be used for the synthesis of indole derivatives in particular.³ Recent methods include the reaction of 2-alkenylanilides (2) having electron-withdrawing groups with LR,⁴ the reaction of 2-hydroxyalkylanilides with LR,⁵ the reaction of 2-alkynythioformanilides with DBU,⁶ the reaction of 2-alkynylaniline with isothiocyanate,⁷ and the Friedel-Crafts reaction of isothiocyanate.⁸ However, there is no report on the direct synthesis of benzothiazines from 2-alkynylanilides (3). These results prompted us to investigate the reaction of 2-alkenylanilides 2 having electron-donating groups and 2-alkynylanilides 3 with LR, to find out whether the corresponding intramolecular cyclization would proceed or not. Herein, we describe a new approach to the synthesis of 4H-3,1-benzothiazines 1 and 4-exomethylene-4H-3,1-benzothiazines (4) based on a thionation process followed by a cyclization process from 2-alkenyl- and 2-alkynylanilides.

RESULTS AND DISCUSSION

2-Alkenylanilides 2 with electron-withdrawing groups (CO₂Me and CN) underwent thionation and intramolecular cyclization to give 3,1-benzothiazines.⁴ As the intramolecular cyclization did not proceed by using 2-alkynylformanilide and P₄S₁₀ as the thionation reagent,⁶ we first attempted to react 2-alkenylnilide 2 with P₄S₁₀ or LR to investigate the possibility of tandem thionation and intramolecular cyclization.
Treatment of 2-vinylacetanilide (2a) with $P_4S_{10}$ in refluxing pyridine (6 h) resulted in the formation of 2-vinylthioacetanilide (5a) in 66% yield (Table 1, Entry 1). When the reaction was carried out by using LR as the thionation reagent, starting 2a was recovered almost quantitatively (Entry 2). The reaction of 2a with LR in refluxing chloroform also recovered starting 2a (Entry 3). However, when toluene was used as the solvent (refluxing for 12 h), 2,4-dimethyl-3,1-benzothiazine (1a) was obtained in 62% yield.

**Table 1. Reaction of 2a with thionation reagent**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Thionation Reagent</th>
<th>Solvent</th>
<th>Time / h</th>
<th>5a (yield /%)</th>
<th>1a (yield /%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$P_4S_{10}$ (0.5 eq)</td>
<td>pyridine</td>
<td>6</td>
<td>66</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>LR (0.5 eq)</td>
<td>pyridine</td>
<td>6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>LR (0.5 eq)</td>
<td>CHCl$_3$</td>
<td>8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>LR (0.5 eq)</td>
<td>THF</td>
<td>12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>LR (0.5 eq)</td>
<td>toluene</td>
<td>12</td>
<td>0</td>
<td>62</td>
</tr>
</tbody>
</table>

From these results, the optimum conditions for tandem thionation and intramolecular cyclization of 2 were judged to be LR (0.5 eq) in refluxing toluene. We then tried the reaction by using anilide (2b-2f) prepared from commercially available isopropenylaniline as substrates under these reaction conditions (Scheme 1). The reaction of 2-isopropenylacetanilide (2b) with LR gave 2-isopropenylthioacetanilide (5b) and 2,4,4-trimethyl-$4H$-3,1-benzothiazine (1b) in 19% and 68% yields, respectively (Table 2, Entry 1). When the reaction was carried out in refluxing toluene for 12 h, 1b was isolated in 89% yield (Entry 2). Other isopropenylanilides 2c-2f also afforded benzothiazines 1c-1f in good yields (Entries 3-6).

**Scheme 1**
<table>
<thead>
<tr>
<th>Entry</th>
<th>Anilide</th>
<th>Time/h</th>
<th>Thioanilide</th>
<th>Thiazine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2b</td>
<td>4</td>
<td>5b</td>
<td>1b 68</td>
</tr>
<tr>
<td>2</td>
<td>2b</td>
<td>12</td>
<td>5b</td>
<td>1b 89</td>
</tr>
<tr>
<td>3</td>
<td>2c</td>
<td>12</td>
<td>5c</td>
<td>1c 89</td>
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<tr>
<td>4</td>
<td>2d</td>
<td>12</td>
<td>5d</td>
<td>1d 53</td>
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<td>5</td>
<td>2e</td>
<td>15</td>
<td>5e</td>
<td>1e 84</td>
</tr>
<tr>
<td>6</td>
<td>2f</td>
<td>18</td>
<td>5f</td>
<td>1f 91</td>
</tr>
</tbody>
</table>

Thus, the thionation and intramolecular cyclization of anilides 2 with LR afforded 3,1-benzothiazines 1 in moderate to good yields.

Previously, we have reported the synthesis of 3,1-benzoxazines by active halogen mediated intramolecular cyclization of 2-alkenylanilides. As thioanilides are more nucleophilic than the corresponding anilides, the formation of 3,1-benzothiazines by intramolecular cyclization would proceed without any activating reagents. Although the two-step synthesis of 4-alkenyl-3,1-benzothiazine was accomplished by the reaction of 2-alkynylformanilides with P₄S₁₀ followed by the addition of DBU, the sequential thionation and cyclization of 2-alkynylanilides 3 was not reported. The only reported example was the reaction of anilides 3 with phenylisothiocyanates, which afforded 2-imino-3,1-benzothiazines, and 2-imino substituents were required. Thus, we then tried to react anilide 3 with LR to find out whether tandem thionation and cyclization would proceed. Starting 2-alkynylanilides 3 were synthesized by the acylation of 2-alkynylanilines, which were easily synthesized by the Sonogashira coupling reaction. Treatment of [2-(2-phenylethynyl)phenyl]benzanilide (3a) with LR (0.5 eq) at rt for 36 h resulted in the almost recovery of 3a (Scheme 2, Table 3, Entry 1). When 1 eq of LR was used, small amount of 2-(phenylethynyl)thiobenzanilide (6a) was formed (Entry 2). When the reaction was carried out in refluxing toluene for 5 h, (Z)-4-benzylidene-2-phenyl-4H-3,1-benzothiazine (4a) were obtained in 82% yield (Entry 3). When P₄S₁₀ was used as the thionation reagent, thioanilide 6a was obtained in 42% yield and further cyclization did not proceed (Entry 4). It is noteworthy that isolated 6a was allowed to react with 0.1 eq of LR in refluxing toluene to afford 4a in 85% yield.
As the optimum conditions for tandem thionation and intramolecular cyclization would be LR (0.5 eq) in refluxing toluene, we then applied these conditions to a variety of 2-alkynylanilides (3b-3i) (Scheme 3). The results are shown in Table 4. The reaction of 3b with LR in refluxing toluene for 12 h gave 3,1-benzothiazine 4b in 57% yield (Entry 2).

$$\text{H} \quad \text{R} \quad \text{N} \quad \text{R'} \quad \text{O} \quad \text{LR} \quad \text{R} \quad \text{NH} \quad \text{R'} \quad \text{S} \quad \text{H} \quad \text{toluene} \quad \text{reflux}$$

3a: R = Ph, R' = Ph
3b: R = n-Bu, R' = Ph
3c: R = t-Bu, R' = Ph
3d: R = Ph, R' = Me
3e: R = Ph, R' = Et
3f: R = Ph, R' = p-Tol
3g: R = Ph, R' = p-Anis
3h: R = Ph, R' = p-ClC₆H₄
3i: R = Ph, R' = p-CF₃C₆H₄

4a: R = Ph, R' = Ph
4b: R = n-Bu, R' = Ph
4c: R = t-Bu, R' = Ph
4d: R = Ph, R' = Me
4e: R = Ph, R' = Et
4f: R = Ph, R' = p-Tol
4g: R = Ph, R' = p-Anis
4h: R = Ph, R' = p-ClC₆H₄
4i: R = Ph, R' = p-CF₃C₆H₄

Scheme 3

Table 4. Reaction of anilide 3 with LR

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkynylanilide 3</th>
<th>Time /h</th>
<th>4</th>
<th>Yield / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3a</td>
<td>5</td>
<td>4a</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>3b</td>
<td>12</td>
<td>4b</td>
<td>57</td>
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<tr>
<td>3</td>
<td>3c</td>
<td>48</td>
<td>4c</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>3d</td>
<td>23</td>
<td>4d</td>
<td>72</td>
</tr>
<tr>
<td>5</td>
<td>3e</td>
<td>18</td>
<td>4e</td>
<td>77</td>
</tr>
<tr>
<td>6</td>
<td>3f</td>
<td>7</td>
<td>4f</td>
<td>80</td>
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<td>7</td>
<td>3g</td>
<td>5</td>
<td>4g</td>
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<td>8</td>
<td>3h</td>
<td>24</td>
<td>4h</td>
<td>71</td>
</tr>
<tr>
<td>9</td>
<td>3i</td>
<td>48</td>
<td>4i</td>
<td>68</td>
</tr>
</tbody>
</table>
When a sterically hindered anilide, such as 2-(3,3-dimethyl-1-butynyl)phenylacetanilide 3c, was used as substrate, prolonged reaction time is required (48 h) (Entry 3). Electron-donating groups, such as a methoxy or a methyl group, at para position gave relatively high yields of benzothiazines 4f and 4g (Entries 6 and 7). Electron-withdrawing groups at para position 3h-3i gave moderate yields of products 4h and 4i (Entries 8 and 9).

The reaction would proceed as follows: LR reacted with anilide 3a to afford to give the corresponding thioanilide 6a. Thiocarbonyl sulfur of 6a intramolecularly attacked triple bond to afford cyclized prodct, which finally produced 4a (Scheme 4).

The stereochemistry of 4 was determined from proton NMR spectra. The exo-alkene signal of 4c appeared at 6.14 ppm. The reported example of (Z)-benzylideneisochromene showed a signal at 6.32 ppm assignable to the exo-alkene proton, which is similar to 4c.11 NOESY spectrum of 4c shows the correlation between exomethylene proton and 5-H proton (Figure 1). Fortunately, as single crystals of 4c were obtained, the X-ray crystallographic analysis of 4c could be performed. As shown in Figure 2, stereochemistry of 4c has Z-form.
In summary, 2-vinylacetanilide 2a reacted with P₄S₁₀ to afford thioacetanilide 5a, whereas the reaction of anilides 2 with LR gave 3,1-benzothiazines 1 in good yields. The reaction of 2-alkynylanilides 3 with LR in refluxing toluene gave 4-methylene-3,1-benzothiazines 4 in good yields. We have successfully synthesized 3,1-benzothiazines from 2-alkenylanilides and 2-alkynylanilides by thionation and intramolecular cyclization in one-pot operation.

**EXPERIMENTAL**

**General**

All chemicals were obtained from commercial suppliers and were used without further purification. NMR spectra (¹H at 400 MHz; ¹³C at 100 MHz) were recorded in CDCl₃, and chemical shifts are expressed in ppm relative to internal TMS for ¹H- and ¹³C-NMR. Melting points were uncorrected.

**Material**

All reagents (2-isopropenylaniline, LR, and P₄S₁₀) were purchased from TCI or Aldrich. 2-Vinylaniline was synthesized by reduction of 2-nitrostyrene with Sn/HCl. 2-Alkynylanilines were synthesized by Sonogashira coupling reaction. 2-Vinylanilides were synthesized by the method reported in the literature. 2-Alkynylanilides were synthesized by the reaction of 2-alkynylanilines with acyl chlorides. Followings are new compounds. Compound 3c: colorless needles; ¹H NMR (CDCl₃) δ = 1.38 (s, 9H, t-Bu), 7.03 (dd, 1H, J = 7.6 Hz and 7.6 Hz, Ar), 7.32 (dd, 1H, J = 7.6 Hz and 7.6 Hz, Ar), 7.40 (d, 1H, J = 7.6 Hz, Ar), 7.48-7.57 (m, 3H, Ar), 7.94 (d, 2H, J = 6.8 Hz, Ar), 8.58 (d, 1H, J = 8.4 Hz, Ar), 8.86 (br, 1H, NH). MS (GC): Calcd for C₁₉H₁₉NO: 277.15. Found; 277.87 (M⁺). Compound 3e: colorless needles. ¹H NMR (CDCl₃) δ = 1.28 (dd, 3H, J = 7.4 Hz and 7.6 Hz, CH₃), 2.46 (dt, 2H, J = 7.6 Hz and 7.6 Hz, CH₂), 7.05 (dd, 1H, J = 7.6 Hz and 7.6 Hz, Ar), 7.34-7.40 (m, 4H, Ar), 7.49-7.55 (m, 3H, Ar), 8.04 (br, 1H, NH), 8.44 (d, 1H, J = 8.0 Hz, Ar). MS (GC): Calcd for C₁₉H₁₉NO: 249.12. Found; 248.97 (M⁺). Compound 3f: colorless needles. ¹H NMR (CDCl₃) δ = 2.43 (s, 3H, CH₃), 7.09 (dd, 1H, J = 7.6 Hz and 7.6 Hz, Ar), 7.27 (d, 2H, J = 8.0 Hz, Ar), 7.40-7.44 (m, 3H, Ar), 7.85 (d, 2H, J = 8.0 Hz, Ar), 8.62 (d, 1H, J = 8.8 Hz, Ar), 8.93 (br, 1H, NH). MS (GC): Calcd for C₂₂H₁₇NO: 311.13. Found; 310.97 (M⁺). Compound 3g: colorless needles. ¹H NMR (CDCl₃) δ = 3.88 (s, 3H, OCH₃), 6.96 (d, 2H, J = 8.8 Hz, Ar), 7.09 (dd, 1H, J = 7.4 Hz and 7.6 Hz, Ar), 7.39-7.41 (m, 3H, Ar), 7.53-7.57 (m, 3H, Ar), 7.92 (d, 2H, J = 8.8 Hz, Ar), 8.09 (d, 1H, J = 8.8 Hz, Ar), 8.60 (d, 1H, J = 8.4 Hz, Ar), 8.88 (br, 1H, NH). MS (ESI): Calcd for C₂₂H₁₇NO₂: 327.13. Found; 352.64 (M +2+ Na⁺). Compound 3h: colorless needles. ¹H NMR (CDCl₃) δ = 7.12 (dd, 1H, J = 7.6 Hz and 7.6 Hz, Ar), 7.41-7.43 (m, 3H, Ar), 7.45 (d, 2H, J = 8.4 Hz, Ar), 7.52-7.56 (m, 3H, Ar), 7.74 (d, 1H, J = 8.8 Hz, Ar), 7.89 (d, 1H, J = 8.4 Hz, Ar), 8.58 (d, 1H, J = 8.4 Hz, Ar), 8.88 (br, 1H, NH). MS (ESI): Calcd for
C$_{21}$H$_{14}$ClNO: 331.08. Found; 356.53 (M +2+ Na$^+$). Compound 3i: colorless needles. $^1$H NMR (CDCl$_3$) δ = 7.14 (dd, 1H, J = 7.6 Hz and 7.6 Hz, Ar), 7.41-7.46 (m, 4H, Ar), 7.52-7.58 (m, 3H, Ar), 7.74 (d, 2H, J = 8.0 Hz, Ar), 8.06 (d, 2H, J = 8.0 Hz, Ar), 8.60 (d, 1H, J = 8.4 Hz, Ar), 8.93 (br, 1H, NH). MS (GC): Calcd for C$_{22}$H$_{14}$F$_3$NO; 365.10. Found; 364.85(M$^+$).

**Reaction of 2-vinylacetanilide 2a with P$_4$S$_{10}$ in refluxing pyridine**

To a solution of 2-vinylacetanilide 2a (0.081 g, 0.50 mmol) in pyridine (5 mL) was added P$_4$S$_{10}$ (0.056 g, 0.25 mmol) in one portion. After refluxing for 6 h, the reaction mixture was washed with water and extracted with EtOAc (7 mL x 3). The combined extract was washed with water, dried over sodium sulfate, filtered, and evaporated to give pale brown oil, which was chromatographed over alumina by elution with hexane:EtOAc (1:1) to afford pale yellow oil of 2-vinylthioacetanilide 5a (0.056 g, 0.32 mmol, 64%). 5a: yellow oil; (lit., yellow oil) (rotational isomeric mixture) $^1$H NMR (CDCl$_3$) δ = 2.39 (s, 3H, CH$_3$), 2.76 (s, 3H), 5.39 (d, 1H, J$_{cis}$ = 11.2 Hz, =C=H), 5.44 (d, 1H, J$_{cis}$ = 11.2 Hz, =C=H), 5.74 (d, 1H, J$_{trans}$ = 17.6 Hz, =CH), 5.80 (d, J$_{trans}$ = 17.6 Hz, =CH), 6.64 (dd, 1H, J = 11.2 and 17.6 Hz, =CH), 7.16-7.62 (m, 4H, Ar), 8.52 (br, 1H, NH), 9.22 (br, 1H, NH).

$^{13}$C NMR (CDCl$_3$) 5a: δ = 30.33 (CH$_3$), 118.32 (=CH$_2$), 126.92, 127.47, 128.66, 129.26 (Ar), 131.47 (=CH), 134.77, 135.75, (Ar), 205.85 (C=S).

5a*: δ = 34.83 (CH$_3$), 117.47 (=CH$_2$), 128.56, 127.86, 128.50, 129.08, 132.06 (=CH), 134.31, 136.42 (Ar), 202.61 (C=S).

**Reaction of 2a with LR in toluene**

To a solution of 2-vinylacetanilide 2a (0.081 g, 0.50 mmol) in toluene (5 mL) was added LR (0.10 g, 0.25 mmol) in one portion. After refluxing for 12 h, the reaction mixture was filtered through short silica gel column, and evaporated to give brown oil, which was chromatographed over silica gel by elution with hexane:EtOAc (1:1) to afford pale yellow oil of 2,4-dimethyl-4$^H$-3,1-benzothiazine 1a (0.053 g, 0.30 mmol, 60%). 1a: yellow oil; (lit., yellow oil) (rotational isomeric mixture) $^1$H NMR (CDCl$_3$) δ = 1.44 (d, 3H, J = 7.2 Hz, CH$_3$), 2.42 (s, 3H, CH$_3$), 4.04 (dt, 1H, J = 7.0 Hz and 7.2 Hz, CH), 7.10 (d, 1H, J = 7.2 Hz, Ar), 7.22-7.26 (m, 1H, Ar), 7.31-7.33 (m, 2H, Ar). $^{13}$C NMR (CDCl$_3$) 5a*: δ = 30.33 (CH$_3$), 118.32 (=CH$_2$), 126.92, 127.47, 128.66, 129.26 (Ar), 131.47 (=CH), 134.77, 135.75, (Ar), 205.85 (C=S). 5a*: δ = 34.83 (CH$_3$), 117.47 (=CH$_2$), 128.56, 127.86, 128.50, 129.08, 132.06 (=CH), 134.31, 136.42 (Ar), 202.61 (C=S).

Other reactions were carried out in a similar manner.

2-Isopropenylthioacetanilide (5b): colorless needles: mp 84-86 °C (rotational isomeric mixture); $^1$H NMR (CDCl$_3$) δ = 2.04 (s, 3H, =CCH$_3$), 2.06 (s, 3H, =CCH$_3$), 2.47 (s, 3H, CH$_3$), 2.66 (s, 3H, CH$_3$), 5.00 (s, 1H, =CH), 5.02 (s, 1H, =CH), 5.32 (s, 1H, =CH), 5.33 (s, 1H, =CH), 7.10-7.37 (m, 5H + 4H, Ar), 8.21 (d, 1H, J = 8.0 Hz, Ar), 8.68 (br, 1H, NH), 8.80 (br, 1H, NH). $^{13}$C NMR (CDCl$_3$) 5b*: δ = 23.58 (CH$_3$), 30.08(CH$_3$), 116.99 (=CH$_2$), 126.91, 127.55, 128.54, 129.65, 135.24 (=CH), 140.02, 142.68 (Ar), 200.65
\(5b\): \(\delta = 24.09 \ (\text{CH}_3), \ 35.92 \ (\text{CH}_3), \ 118.08 \ (=\text{CH}_2), \ 126.01, \ 127.22, \ 128.40, \ 128.57 \ (\text{Ar}), \ 135.07 \ (=\text{CH}), \ 138.25, \ 142.46, \ (\text{Ar}), \ 204.69 \ (\text{S}=\text{C})\). Anal. Calcd for C\(_{11}\)H\(_{13}\)NS: C, 69.07; H, 6.85; N, 7.32. Found: C, 68.99; H, 6.77; N, 7.70.

2,4,4-Trimethyl-4\(H\)-3,1-benzothiazine \((1b)\), yellow oil: \(^1\)H NMR (CDCl\(_3\)) \(\delta = 1.59 \ (s, 6\text{H}, \text{CH}_3), \ 2.41 \ (s, \ 3\text{H}, \text{CH}_3), \ 7.26-7.37 \ (m, 4\text{H}, \text{Ar})\). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta = 28.37 \ (\text{CH}_3), \ 29.46 \ (2\times \text{CH}_3), \ 43.44 \ (\text{C}(\text{CH}_3)_2), \ 121.16, \ 127.44, \ 127.91, \ 128.00, \ 130.13, \ 143.13 \ (\text{Ar}), \ 161.18 \ (\text{C}=\text{N})\). HRMS: Calcd for C\(_{11}\)H\(_{13}\)NS; 191.0769. Found; \((\text{M}^+)^\) 191.0772.

4,4-Dimethyl-2-phenyl-4\(H\)-3,1-benzothiazine \((1c)\) (0.11 g, 0.44 mmol, 89%). \(1c\): yellow oil, \(^1\)H NMR (CDCl\(_3\)) \(\delta = 1.68 \ (s, 6\text{H}, 2\times \text{CH}_3), \ 7.34-7.41 \ (m, 3\text{H}, \text{Ar}), \ 7.48-7.51 \ (m, 3\text{H}, \text{Ar}), \ 7.55 \ (d, \ J= 8.0 \text{ Hz}, \text{Ar}), \ 8.15 \ (d, 2\text{H}, J = 7.6 \text{ Hz}, \text{Ar})\). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta = 29.11 \ (2\times \text{CH}_3), \ 43.54 \ (\text{C}(\text{CH}_3)_2), \ 121.49, \ 127.89, \ 128.13, \ 128.28, \ 128.33, \ 128.70, \ 131.15, \ 131.59, \ 138.61, \ 143.93 \ (\text{Ar}), \ 161.09 \ (\text{C}=\text{N})\). HRMS: Calcd for C\(_{16}\)H\(_{15}\)NS; 253.0925. Found; \((\text{M}^+)^\) 253.0934.

4,4-Dimethyl-2-(\(p\)-tolyl)-4\(H\)-3,1-benzothiazine \((1d)\). yellow oil, \(^1\)H NMR (CDCl\(_3\)) \(\delta = 1.66 \ (s, 6\text{H}, \text{CH}_3), \ 2.41 \ (s, 3\text{H}, \text{CH}_3), \ 7.25-7.39 \ (m, 5\text{H}, \text{Ar}), \ 7.52 \ (d, \ J = 7.8 \text{ Hz}, \text{Ar}), \ 8.04 \ (d, \ 2\text{H}, J = 6.4 \text{ Hz}, \text{Ar})\). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta = 21.75 \ (\text{CH}_3), \ 29.09 \ (2\times \text{CH}_3), \ 43.49 \ (\text{C}(\text{CH}_3)_2), \ 121.47, \ 127.85, \ 128.03, \ 128.06, \ 128.32, \ 129.44, \ 131.24, \ 135.99, \ 142.07, \ 144.05 \ (\text{Ar}), \ 161.00(\text{C}=\text{N})\). HRMS: Calcd for C\(_{17}\)H\(_{17}\)NS; 267.1082. Found; \((\text{M}^+)^\) 267.1083.

4,4-Dimethyl-2-(\(p\)-anisyl)-4\(H\)-3,1-benzothiazine \((1e)\). yellow oil, \(^1\)H NMR (CDCl\(_3\)) \(\delta = 1.67 \ (s, 6\text{H}, \text{CH}_3), \ 3.88 \ (s, 3\text{H}, \text{OCH}_3), \ 6.98 \ (d, 2\text{H}, J = 8.8 \text{ Hz}, \text{Ar}), \ 7.17 \ (d, 1\text{H}, J = 7.6 \text{ Hz}, \text{Ar}), \ 7.26-7.40 \ (m, 2\text{H}, \text{Ar}), \ 7.52 \ (d, 1\text{H}, J = 7.6 \text{ Hz}, \text{Ar}), \ 8.12 \ (d, 2\text{H}, J = 8.8 \text{ Hz}, \text{Ar})\). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta = 27.75 \ (\text{CH}_3), \ 54.40 \ (\text{OCH}_3), \ 112.83, \ 120.21, \ 126.41, \ 126.63, \ 126.68, \ 128.90, \ 129.64, \ 129.86, \ 142.41, \ 159.80 \ (\text{Ar}), \ 161.55(\text{C}=\text{N})\). HRMS: Calcd for C\(_{17}\)H\(_{17}\)NOS; 283.1031. Found; 283.1027 (\text{M}^+).

4,4-Dimethyl-2-(\(p\)-chlorophenyl)-4\(H\)-3,1-benzothiazine \((1f)\). yellow oil, \(^1\)H NMR (CDCl\(_3\)) \(\delta = 1.66 \ (s, 6\text{H}, \text{CH}_3), \ 7.37-7.40 \ (m, 3\text{H}, \text{Ar}), \ 7.44 \ (d, 2\text{H}, J = 8.4 \text{ Hz}, \text{Ar}), \ 7.52 \ (d, 1\text{H}, J = 7.6 \text{ Hz}, \text{Ar}), \ 8.09 \ (d, 2\text{H}, J = 8.4 \text{ Hz}, \text{Ar})\). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta = 27.80 \ (\text{CH}_3), \ 42.38 \ (\text{C}(\text{CH}_3)_2), \ 54.40 \ (\text{OCH}_3), \ 112.83, \ 120.21, \ 126.41, \ 126.63, \ 126.68, \ 128.90, \ 129.64, \ 129.86, \ 142.41, \ 159.80 \ (\text{Ar}), \ 161.55(\text{C}=\text{N})\). HRMS: Calcd for C\(_{16}\)H\(_{14}\)ClNS; 287.0535. Found; 287.0530 (\text{M}^+).

**Reaction of N-[2-(2-phenylethynyl)phenyl]benzanilide 3a with P\(_4\)S\(_{10}\)**

To a solution of benzanilide 3a (0.15 g, 0.50 mmol) in toluene (5 mL) was added P\(_4\)S\(_{10}\) (0.055 g, 0.25 mmol) in one portion. After refluxing for 15 h, the reaction mixture was washed with water and extracted with EtOAc (7 mL x 3). The combined extract was washed with water, dried over sodium sulfate, filtered, and evaporated to give pal brown oil, which was chromatographed over alumina gel by elution with hexane:EtOAc (10:1) to afford yellow crystals of N-[2-(2-phenylethynyl)phenyl]-
thiobenzanilide 6a (0.12 g, 0.38 mmol, 76%). 6a: yellow needles, mp 90-92 °C. 1H NMR (CDCl3) δ = 7.22-7.55 (m, 11H, Ar), 7.62 (d, 1H, J = 7.6 Hz, Ar), 7.96 (br, 2H, Ar), 10.03 (br, 1H, NH). 13C NMR (CDCl3) δ = 84.48 (q, C), 98.24 (q, C), 115.75 (q, C), 119.35 (q, C), 121.18 (q, C), 122.23 (q, C), 126.06, 127.02, 128.95, 129.37, 131.54, 131.65, 132.12, 140.25, 144.05 (Ar), 196.75 (C=S). Anal. Calcd for C21H15NS: C, 80.48; H, 4.82; N, 4.47. Found: C, 81.10; H, 4.87; N, 5.10. Analytical data of 7a was little bit off, however, spectral data of which clearly support the structure.

**Reaction of N-[2-(2-phenylethynyl)phenyl]propionamide 3e with LR**

To a solution of propionamide 3e (0.12 g, 0.50 mmol) in toluene (5 mL) was added LR (0.10 g, 0.25 mmol). After refluxing for 18 h, the reaction mixture was filtered through short silica gel column, and evaporated to give a pale brown oil, which was chromatographed over silica gel by elution with hexane:EtOAc (5:1) to give yellow oil of (Z)-4-benzylidene-2-ethyl-4H-3,1-benzothiazine (4e) (0.10 g, 0.38 mmol). 4e: yellow oil, 1H NMR (CDCl3) δ = 1.28 (t, 3H, J = 7.6 Hz, CH3), 2.57 (q, 2H, J = 7.6 Hz, CH2), 7.03 (s, 1H, =CH), 7.30-7.35 (m, 2H, Ar), 7.40-7.47 (m, 6H, Ar), 7.61 (d, 1H, J = 7.6 Hz, Ar). 13C NMR (CDCl3) δ = 12.10 (CH3), 34.77 (CH2), 121.83 (=CH), 124.38, 124.87, 126.64, 127.66, 128.45, 128.52, 129.09, 129.41, 129.91, 136.02, 142.43 (Ar), 164.02 (C=N). HRMS: Calcd for C17H15NS; 265.0925. Found; 265.0924 (M+).

Other reactions were carried out in a similar manner.

(Z)-4-Benzylidene-2-phenyl-4H-3,1-benzothiazine (4a): yellow oil, 1H NMR (CDCl3) δ = 7.13 (s, 1H, =CH), 7.32-7.57 (m, 11H, Ar), 7.66 (d, 1H, J = 8.0 Hz, Ar), 8.05 (d, 2H, J = 8.2 Hz, Ar). 13C NMR (CDCl3) δ = 122.45 (CH), 124.54, 126.11, 126.22, 127.77, 127.81, 128.60, 128.72, 128.83, 129.64, 129.68, 129.97, 131.77, 136.03, 137.69, 143.13 (Ar), 158.10 (C=N). HRMS: Calcd for C21H15NS; 313.0925. Found; 313.0924 (M+).

(Z)-4-Pentylidene-2-phenyl-4H-3,1-benzothiazine (4b): yellow oil, 1H NMR (CDCl3) δ = 0.94 (t, 3H, J = 7.2 Hz, CH3), 1.40-1.54 (m, 4H, 2CH2), 2.30 (dd, 2H, J = 7.2 Hz and 7.6 Hz, CH2), 6.09 (dd, 1H, J = 7.2 Hz and 7.2 Hz, =CH), 7.27 (dd, 1H, J = 7.6 Hz and 8.2 Hz, Ar), 7.36 (dd, 1H, J = 7.6 Hz and 8.2 Hz, Ar), 7.45-7.51 (m, 5H, Ar), 8.08 (d, 2H, J = 8.2 Hz, Ar). 13C NMR (CDCl3) δ = 12.95 (CH3), 21.38, 27.55, 30.06 (CH2), 120.99 (=CH), 122.48, 123.30, 125.99, 126.33, 127.23, 127.48, 127.99, 128.25, 130.32, 136.73, 141.77 (Ar), 157.57 (C=N). HRMS: Calcd for C19H19NS; 293.1238. Found; 293.0236 (M+).

(Z)-4-t-Butylmethylene-2-phenyl-4H-3,1-benzothiazine (4c): yellow needles: mp: 84-85 °C. 1H NMR (CDCl3) δ = 1.35 (s, 9H, 3CH3), 6.14 (s, 1H, =CH), 7.30 (dd, 1H, J = 6.4 Hz and 7.6 Hz, Ar), 7.36 (dd, 1H, J = 6.4 Hz and 7.6 Hz, Ar), 7.45-7.52 (m, 5H, Ar), 8.08 (d, 2H, J = 7.6 Hz, Ar). 13C NMR (CDCl3) δ = 30.15 (3CH3), 33.75 (C(CH3)3), 122.84, 123.48 (Ar), 124.32 (=CH), 127.91, 128.58, 128.84, 129.05, 129.18, 131.70, 138.01, 139.45, 143.25 (Ar), 158.81 (C=N). EI-MS: Calcd for C19H19NS; 293. Found;
X-Ray crystallographic data for 4c: Mr = 293.41, a = 11.512(8) Å, b = 12.053(8) Å, c = 24.029(16) Å, V = 3218(4) Å³, T = 293 K, monoclinic, space group P2₁/a, Z = 8, 6342 dependent reflections, R1 = 0.0575, wR2 = 0.1278. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre. Deposition number CCDC-815982.

(Z)-4-Benzylidene-2-methyl-4H-3,1-benzothiazine (4d): yellow oil, ¹H NMR (CDCl₃) δ = 2.36 (s, 3H, CH₃), 7.02 (s, 1H, =CH), 7.30-7.46 (m, 8H, Ar), 7.61 (d, 1H, J = 7.8 Hz, Ar). ¹³C NMR (CDCl₃) δ = 27.90 (CH₃), 121.51 (=CH), 124.39, 124.88, 126.56, 127.74, 128.52, 128.78, 128.91, 129.40, 129.96, 135.95, 142.40 (Ar), 158.91(C=N). HRMS: Calcd for C₁₆H₁₃NS; 251.0769. Found; 251.0776 (M⁺).

(Z)-4-Benzylidene-2-(p-tolyl)-4H-3,1-benzothiazine (4f): yellow needles: mp146-148 °C, ¹H NMR (CDCl₃) δ = 2.41 (s, 3H, CH₃), 7.12 (s, 1H, =CH), 7.24-7.26 (m, 2H, Ar), 7.31-7.39 (m, 2H, Ar), 7.43-7.47 (m, 3H, Ar), 7.53-7.57 (m, 3H, Ar), 7.64 (d, 1H, J = 8.0 Hz, Ar), 7.94 (d, 2H, J = 8.0 Hz, Ar). ¹³C NMR (CDCl₃) δ = 21.83 (CH₃), 122.52 (=CH), 124.53, 126.06, 126.29, 127.74, 128.56, 128.57, 128.58, 129.53, 129.65, 129.91, 135.00, 136.08, 142.28, 143.23 (Ar), 158.01 (C=N). EI-MS: Calcd for C₂₁H₁₇NS; 327. Found; (M⁺) 327. Anal. Calcd for C₂₁H₁₇NS: C, 80.47; H, 5.42; N, 4.21. Found: C, 80.70; H, 5.23; N, 4.28.

(Z)-4-Benzylidene-2-(p-methoxyphenyl)-4H-3,1-benzothiazine (4g): yellow needles: mp124-126 °C, ¹H NMR (CDCl₃) δ = 3.86 (s, 3H, OCH₃), 6.94 (d, 2H, J = 6.8 Hz, Ar), 7.12 (s, 1H, =CH), 7.34-7.38 (m, 2H, Ar), 7.43-7.47 (m, 3H, Ar), 7.52 (dd, 3H, J = 7.6 Hz and 8.0 Hz, Ar), 7.63 (d, 1H, J = 7.6 Hz, Ar), 7.80 (d, 2H, J = 8.4 Hz, Ar). ¹³C NMR (CDCl₃) δ = 55.68 (OCH₃), 114.14 (Ar), 122.48 (=CH), 124.55, 126.05, 126.37, 127.74, 128.56, 128.35, 128.35, 129.39, 129.51, 129.68, 129.90, 130.32, 136.13, 143.36, 157.38 (Ar), 162.71 (C=N). EI-MS: Calcd for C₂₂H₁₇NOS; 343. Found; 343 (M⁺). Anal. Calcd for C₂₂H₁₇NOS: C, 76.94; H, 4.99; N, 4.08. Found: C, 76.85; H, 5.05; N, 4.28.

(Z)-4-Benzylidene-2-(p-chlorophenyl)-4H-3,1-benzothiazine (4h): yellow needles, mp 153-155 °C, ¹H NMR (CDCl₃) δ = 7.13 (s, 1H, =CH), 7.33-7.48 (m, 7H, Ar), 7.51-7.53 (m, 3H, Ar), 7.65 (d, 1H, J = 7.6 Hz, Ar), 7.99 (d, 2H, J = 8.4 Hz, Ar). ¹³C NMR (CDCl₃) δ = 121.14 (=CH), 124.55, 126.05, 126.37, 127.74, 128.56, 128.35, 128.35, 129.51, 129.68, 129.90, 130.32, 136.13, 143.36, 157.38 (Ar), 162.71 (C=N). EI-MS: Calcd for C₂₁H₁₄ClNS; 347. Found; 347 (M⁺). Anal. Calcd for C₂₁H₁₄ClNS: C, 72.51; H, 4.06; N, 4.03. Found: C, 72.53; H, 4.10; N, 4.23.

(Z)-4-Benzylidene-2-(p-trifluoromethylphenyl)-4H-3,1-benzothiazine (4i): yellow oil, ¹H NMR (CDCl₃) δ = 7.14 (s, 1H, =CH), 7.34-7.57 (m, 8H, Ar), 7.66-7.71 (m, 3H, Ar), 8.16 (d, 2H, J = 8.4 Hz, Ar). ¹³C NMR (CDCl₃) δ = 122.38 (=CH), 124.55, 125.31 (Ar), 125.64 (q, J = 15.0 Hz, CF₃), 126.74, 127.95, 127.97, 128.61, 129.37, 129.55, 129.85, 130.07, 132.96, 133.28, 135.77, 140.69, 142.74 (Ar), 156.49
(C=N). HRMS: Calcd for C_{22}H_{14}F_{3}NS; 381.0799. Found; 381.0791 (M^+).

REFERENCES