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ScienceDirect
Tetrahedron 64 (2008) 1002–1011
Tetrahedron

# Novel β-lactam condensed 3-thiaquinolines: an efficient synthesis and structural characterization

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Received 18 June 2007; revised 10 September 2007; accepted 27 September 2007
Available online 2 October 2007

Dedicated to Professor Csaba Szántay on the occasion of his 80th birthday

**Abstract**—Quinoline analog 2-aryl-4*H*-3,1-benzothiazine derivatives **8**–**13**, obtained by the condensation of *o*-aminobenzyl chloride **1** with substituted thiobenzamides **2**–**7**, were transformed to azeto[2,1-*a*][3,1]benzothiazin-1-one derivatives **18**–**23a**,**b**,**c** and **24d**,**e** by reaction with the corresponding substituted acetyl chlorides **14**–**17** in the presence of triethylamine. The structures of the new molecules were determined by NMR spectroscopy and electron ionization (EI) mass spectrometry. The typical $EI^+$ mass spectrometric fragmentations of **8**–**13** and **18**–**23a**,**b**,**c** and **24d**,**e** are discussed in detail.


## 1. Introduction

Since the discovery of penicillin, β-lactams (including penicillins, cephalosporins, monobactams, and carbapenems) have become a major class of antibacterial agents. Because of their widespread use, bacterial resistance has developed into a major health problem worldwide over the past few decades.[1] This has motivated growing interest in the preparation and biological evaluation of new types of β-lactams.[2] Moreover, some derivatives possess various other useful pharmacological effects. They include, for example, inhibitors of human leucocyte elastase,[3] cholesterol acyl transferase,[4] and thrombin.[5] From a synthetic aspect, azetidin-2-one derivatives are versatile intermediates in the construction of complex heterocycles,[6] non-proteogenic amino acid derivatives, peptides, and peptide turn mimetics.[7–9] They can be utilized in the synthesis of different natural compounds, such as apiosporamide or taxol derivatives.[10,11] In the former compounds, which contain a relatively strained β-lactam structural unit, the reaction with nucleophilic reagents usually takes place at the N1–C2 bond. Further, some β-lactam derivatives (e.g., α-halo-β-lactams) are versatile synthons furnishing a wide variety of functionalized lactams.[12,13]

The reaction most widely used for the construction of azetidinone rings is the [2+2] ketene–imine cycloaddition reaction, the Staudinger reaction.[2] Several variants of this reaction have been described, in which the ketene is formed in situ from precursors.[2,14–16] In most cases, the reactions occur at low temperature and cis selectivity is observed.[2]

In an earlier paper,[17] we investigated the mechanism of the reactions between differently substituted 4-thia analogs of isoquinolines, 4*H*- and 2*H*-1,3-benzothiazine derivatives and substituted acetyl chlorides. The selectivities of the reactions and the stereochemistry of the linearly or angularly condensed β-lactams formed were also extensively studied.[18–20] During our investigations of the reactivity of the monochloro-β-lactams prepared, we developed a ring-transformation method for the synthesis of 2-methoxycarbonyl-3-aryl-4,5-dihydro-1,4-benzothiazepines.[21] We recently extended this ring-enlargement reaction to the preparation of 2,3-disubstituted 4,1-benzothiazepines. When the monochloro-β-lactam derivative 2-chloro-2a-phenyl-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (**18a**) was treated with sodium ethoxide in dry ethanol at ambient temperature, two products were obtained: 3-ethoxycarbonyl-2-phenyl-3,5-dihydro-4,1-benzothiazepine and 3-ethoxycarbonyl-2-phenyl-1,5-dihydro-4,1-benzothiazepine, which are in a tautomeric relationship to each other. Surprisingly these, 4,1-benzothiazepines could be separated by column chromatography and they manifested the rare phenomenon of desmotropy.[22]

*Keywords*: Sulfur, nitrogen heterocycles; β-Lactams; NMR spectroscopy; Mass spectrometry.
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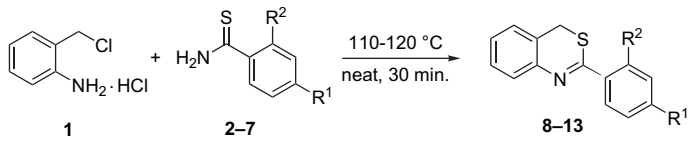
doi:10.1016/j.tet.2007.09.079




**2, 8**: $R^1 = R^2 = H$; **3, 9**: $R^1 = Cl$, $R^2 = H$; **4, 10**: $R^1 = CH_3$, $R^2 = H$; **5, 11**: $R^1 = H$, $R^2 = Cl$; **6, 12**: $R^1 = H$, $R^2 = CH_3$; **7, 13**: $R^1 = H$, $R^2 = OCH_2CH_3$

**Scheme 1**. Preparation of starting 4*H*-3,1-benzothiazine derivatives **8–13**.

As a continuation of our investigations in the field of sulfur- and nitrogen-containing condensed-skeleton heterocycles[23–25] and azetobenzothiazines,[17–20] our current aim was the preparation and structure analysis of different regioisomeric 3-thioquinoline analog, azeto[1,2-*a*][3,1]benzothiazin-1-one derivatives, which could be useful intermediates in 4,1-benzothiazepine desmotrope pairs.[22]

## 2. Results and discussion

### 2.1. Synthesis

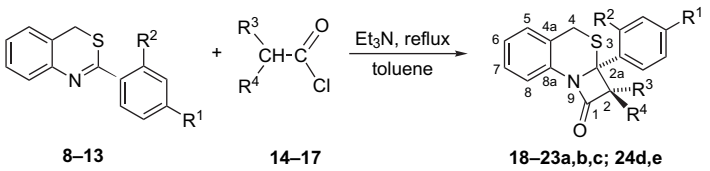
The starting 2-aminobenzyl chloride hydrochloride (**1**) was obtained by the treatment of 2-aminobenzyl alcohol with thionyl chloride.[26] Fusion of **1** with thiobenzamides **2–7** provided the key intermediate 4*H*-3,1-benzothiazine derivatives **8–13** in moderate to good yields (Scheme 1).[27] As concerns this type of compounds, it is worthy of mention that some 2-(2,4-dihydroxyphenyl)-4*H*-3,1-benzothiazines were recently demonstrated to display excellent activities against the human breast cancer T47D line and strong antifungal effects against certain strains of molds, yeasts, and dermatophytes.[28]

For the preparation of our target β-lactam derivatives, we set out to use the Staudinger reaction. The reaction of **8** with chloroacetyl chloride (**14**) in dichloromethane in the presence of triethylamine failed at room temperature. When the reaction was carried out in refluxing benzene,[18] azeto[2,1-*a*][3,1]benzothiazin-1-one derivative **18a** was obtained in good yield. Similarly, **18b**,**c**, **19–23a**,**b**,**c**, and **24d**,**e** were prepared under the conditions given in Section 4 and in Scheme 2 by the reaction of 4*H*-3,1-benzothiazine derivatives **8–13** with the corresponding acid chlorides **14–16**. When α-chloro phenylacetyl chloride (**17**) was used as ketene source, a diastereomeric mixture of **24d** and **24e** was obtained. The NMR spectrum of the crude product of the latter reaction revealed a 73:27 mixture of **24d** and **24e** (Scheme 2).[29]

### 2.2. NMR spectroscopy

The $^1H$ and $^{13}C$ NMR signals were assigned via the information achieved from the DQF-COSY, HSQC (or CH-Shift), and HMBC (or COLOC) spectra. Measurements were made at various temperatures; the presented assignments usually relate to the temperatures at which the signals were sharpest. In cases where full assignment was possible at room temperature (+25 °C) and at low temperature (−60 °C), the results are presented for both (Tables 1 and 2 in Supplementary data).

The starting compounds **10–13** (**8**,**9** were reported previously[27]) gave sharp signals and the interpretation of their NMR spectra was straightforward. The heterocyclic skeleton can be assumed to be planar because of the shape of the H-4 signal. Both of these protons exhibit the same chemical shift and the signal is a singlet. For compounds **18–23a**,**b**,**c** and **24d**,**e**, the formation of a four-membered β-lactam ring makes the structures non-planar and H-4 are no longer magnetically equivalent: two doublets are observed, with a $^1H$–$^1H$ coupling constant of approximately 16 Hz. NOE difference spectra were also measured in order to establish the spatial structures of the molecules. However, only very limited NOE correlations were observed. Typically, NOE was detected from H-4 to H-5, which can serve as further confirmation of the assignment, but it does not furnish information on the 3D structure. When H-4 were irradiated, no enhancement of the 2a-aryl ring protons was observed. Further, no NOE was seen from H-2 to the 2a-aryl protons (structures **a** and **c**). Accordingly, it can be assumed that H-2 and 2a-aryl are trans to each other, and thus 2a-aryl is cis to 2-Cl (**a**) or 2-Ph (**c**), as expected for the Staudinger reaction.[2]




**8**: $R^1 = R^2 = H$;
**9**: $R^1 = Cl$, $R^2 = H$;
**10**: $R^1 = CH_3$, $R^2 = H$;
**11**: $R^1 = H$, $R^2 = Cl$
**12**: $R^1 = H$, $R^2 = CH_3$;
**13**: $R^1 = H$, $R^2 = OCH_2CH_3$

**14**: $R^3 = Cl$, $R^4 = H$;
**15**: $R^3 = Cl$, $R^4 = Cl$;
**16**: $R^3 = Ph$, $R^4 = H$;
**17**: $R^3 = Ph$, $R^4 = Cl$

**18,24**: $R^1 = R^2 = H$; **19**: $R^1 = Cl$, $R^2 = H$;
**20**: $R^1 = CH_3$, $R^2 = H$; **21**: $R^1 = H$, $R^2 = Cl$;
**22**: $R^1 = H$, $R^2 = CH_3$; **23**: $R^1 = H$, $R^2 = OCH_2CH_3$
**a**: $R^3 = Cl$, $R^4 = H$; **b**: $R^3 = Cl$, $R^4 = Cl$;
**c**: $R^3 = Ph$, $R^4 = H$; **d**: $R^3 = Cl$, $R^4 = Ph$
**e**: $R^3 = Ph$, $R^4 = Cl$

**Scheme 2**. Synthesis of azeto[2,1-*a*][3,1]benzothiazin-1-one derivatives (**18–23**)**a–c** and **24d**,**e**.

Another noteworthy difference for compounds **18**–**23a**,**b**,**c** and **24d**,**e** as compared with the starting compounds is the restricted rotation of the Ph substituents, which demonstrate a significant broadening of the NMR signals. The compounds are divided below into subsets, structures behaving similarly being discussed together.

**2.2.1. Structures containing unsubstituted or *p*-substituted 2a-aryl rings 18–20a,b,c.** The NMR signals for 2-Cl and 2,2-di-Cl-substituted compounds (**a** and **b**) were markedly broadened at room temperature (25 °C). As the temperature was decreased to −60 °C, the signals sharpened and individual signals were detected for each 2a-aryl proton and carbon. This indicates that the rotation of the 2a-aryl group is hindered at room temperature and totally restricted at low temperature, where no symmetric signals are observed although the aryl group is symmetric. Higher temperatures (up to +55 °C) were also tried for **18b**. The signals proved to be sharper than that at room temperature and the signals for 2a-Ph were symmetric, indicating faster rotation of this Ph group. The effect of mono- or di-Cl substitution did not seem to play an essential role in the hindered rotational behavior. The 2-Ph-substituted compounds (**c**) exhibited interesting properties. At room temperature, relatively sharp signals were observed and both aryl groups (2a-aryl and 2-Ph) exhibited symmetric signals. From this, it can be concluded that 2-Ph presents less steric hindrance for the rotation of 2a-aryl than does the 2-Cl substituent. When the temperature was lowered, the signals first broadened and then sharpened again, and at −60 °C rather sharp signals were observed. The interesting feature is that the signals for the 2a-aryl substituent were non-symmetric, while those for the 2-Ph substituent were symmetric. This shows that the rotation of the 2a-aryl group is totally restricted, but the rotation of 2-Ph is still fast on the NMR time-scale. This is an intriguing case where two aryl groups situated on vicinal carbons display very different rotational behavior.

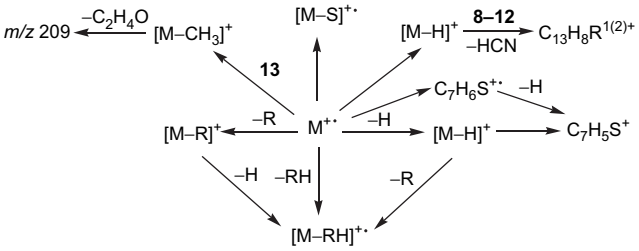
**2.2.2. Structures with *o*-substituted 2a-aryl rings 21–23a,b,c.** For the 2-Cl and 2,2-di-Cl-substituted compounds (**a** and **b**), sharp signals were observed at room temperature. This indicates that the 2a-aryl group rotates either very slowly or fast on the NMR time-scale, because the *o*-substituted 2a-aryl is not symmetric and the decision cannot be made on the basis of the symmetry of the NMR signals. We expected the former possibility, since *ortho* substitution is more likely to hinder the rotation as compared with *para* substitution. To check on this expectation, we also measured these compounds at low temperatures. As no signal broadening or other significant changes were observed, the rotation can be considered to have stopped even at room temperature. For compounds **21c** and **22c**, the signals were clearly broadened at room temperature (not so much as to prevent the assignment at room temperature). This is in harmony with the above conclusion that 2-Ph allows the 2a-aryl to rotate more freely. The signals remained relatively broadened at low temperature, and the situation with sharp signals and stopped rotation well below the coalescence was not achieved. Compound **23c** behaved like Cl-substituted compounds **23a** and **23b**, giving sharp signals at all temperatures. The *o*-$OCH_2CH_3$ substituent is apparently so bulky that it does not permit rotation at all. However, it should be noted that the 2-Ph group in the **c** compounds gave symmetric signals in each case.

**2.2.3. Compounds 24d and 24e.** The NMR results on these two diastereomers were rather similar. In both cases, very broad and unassignable signals were observed at room temperature. When the temperature was decreased, the signals sharpened, but remained markedly broad. At −60 °C, the signals were sharp enough to allow measurement of the 2D spectra and the assignment of the signals. As a common feature, the aryl ring at position 2a gave non-symmetric signals (rotation stopped), whereas the Ph at position 2 gave symmetric signals. The latter were still very broad at −60 °C for **24d**. For **24e**, they were sharper, which resembles the situation in, for example, **18c**. It may therefore be supposed that for **24e** the Ph substituent corresponds to $R^3$.

In conclusion, it may be stated that the 2-Ph substituent exhibits less steric hindrance for the rotation of the 2a-aryl group than do the 2-Cl or 2,2-di-Cl substituents. Further, depending on the substitution of the 2a-aryl group, its rotation may be restricted or not. However, regardless of the 2a-aryl group, the rotation of the 2-Ph group is not hindered.

## 2.3. Mass spectra

The mass spectra of the compounds studied nicely confirmed the proposed structures. The molecular ions of **8**–**13** form the base peaks of the spectra, whereas for the other compounds they correspond to the ion $A^{+\bullet}$=$[M-R^1(R^2)C{=}C{=}O]^{+\bullet}$ (Scheme 3), with the exception of compounds **23a,b,c** where the *o*-$OC_2H_5$ group assumes a predominating role and the base peak of **23a**,**b** corresponds to $[M-OC_2H_5]^+$ and that of **23c** apparently to $[M-PhC{=}C{=}O]^+$, *m*/*z* 270. In fact, the latter ion was fairly strong for all compounds where $R^3$=Ph (Table 6 in Supplementary data) and its relative abundance (RA) varied from 28% for **18c** to 83% for **23c** when corrected for the $^{13}C$ influence of the ion $A^{+\bullet}$, $[M-PhCH{=}C{=}O]^{+\bullet}$.



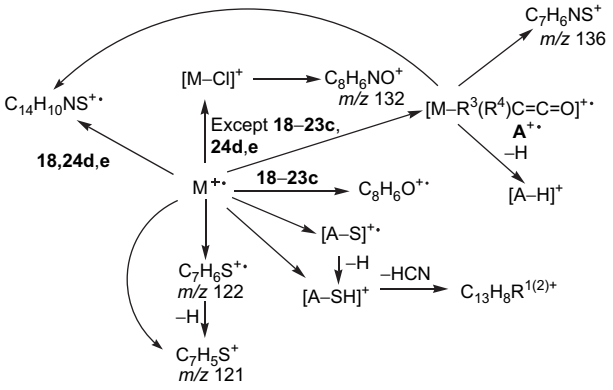

**Scheme 3**. Main (common) fragmentations of **8**–**13**.

**2.3.1. 4*H*-3,1-Benzothiazine derivatives 8–13.** As a whole, the fragmentation of 3,1-benzothiazines **8**–**13** is fairly straightforward (Scheme 3 and Table 3 in Supplementary data).

All of them gave a moderate $[M-H]^+$ peak except **13** (RA 2%). Similarly, they all furnished moderate or fair amounts of $[M-R^{1(2)}]^+$ (6–60%) and $[M-R^{1(2)}H]^{+\bullet}$ (5–29%). The highest relative abundance (RA) was observed for the *o*-Cl derivative **11**, where the Cl can obviously abstract hydrogen most easily. Similarly, they all exhibited $[M-S]^{+\bullet}$ (RA 6–14%) and $[M-SH]^+$ (RA 6–79%). The latter ion was strongest for **12** and **13**, with *o*-$CH_3$ or *o*-$OC_2H_5$, respectively, where the S atom can easily abstract an hydrogen atom from these *ortho* substituents. All of compounds **8**–**13** also yielded clear $M^{2+}$ peaks (Table 3 in Supplementary data),

and clear ions $[C_{13}H_8R^{1(2)}]^+$, formed from $[M-SH]^+$ through the loss of HCN, except for **13**, where the ion with the same nominal mass corresponds to $[M-CH_3-C_2H_4O]^+$ instead. The last two common ions are $C_7H_6S^{+\bullet}$ and $C_7H_5S^+$ with *m/z* 122 and 121, respectively, the former of which is obtained directly from the molecular ion and the latter from the ion $[M-H]^+$ but both are also formed via some secondary ions. *ortho* Substitution (**11**–**13**) clearly increases the fragmentation in comparison with the unsubstituted or *p*-substituted derivatives (**8**–**10**), the higher mass fragments resulting mainly from primary fragmentations or fragmentations after the loss of a hydrogen atom (Table 4 in Supplementary data).

**2.3.2. Azeto[1,2-*a*][3,1]benzothiazin-1-one derivatives 18–23a,b,c and 24d,e.** The common fragmentations are summarized in Scheme 4 and Table 5 in Supplementary data. All 2-Cl and 2,2-di-Cl-substituted compounds lose Cl, this loss being weakest for *p*-Cl derivatives, strongest for *o*-Cl and moderate for those derivatives without a Cl substituent on the Ph ring. Obviously the loss of Cl occurs from C-2 and from the *ortho* position of the aryl substituent (or *o*-Cl enhances the loss of Cl from C-2), whereas the *p*-Cl substitution hinders this loss.




**Scheme 4**. Main (primary) fragmentations of **18–23a**,**b**,**c** and **24d**,**e**.

The base peak always corresponds to $A^{+\bullet}=[M-R^3(R^4)C{=}C{=}O]^{+\bullet}$, even in the case of **21c**, if it is taken into account that its $^{13}C$ counterpart is responsible for *m/z* 260 being the base peak. In fact, $A^{+\bullet}$ corresponds to the regeneration of **8**–**13**. All of **18**–**23a**,**b**,**c** and **24d**,**e** gave moderate peaks for $[A-H]^+$, $[A-S]^{+\bullet}$, and $[A-SH]^+$ (Scheme 4 and Table 5 in Supplementary data), the latter two of which were very much enhanced for *o*-$CH_3$-substituted **22a**,**b**,**c**, and also $[A-S]^{+\bullet}$ for *o*-$OC_2H_5$-substituted **23a**,**b**,**c**. The interesting ions include $C_{13}H_8R^{1(2)+}$ (cf. also Table 3 in Supplementary data), formed from $[A-SH]^+$ similarly as in the case of **8**–**13**, through loss of HCN. $C_7H_6S^+$ and $C_7H_5S^+$ (Table 5 in Supplementary data) were also typical for the 4*H*-3,1-benzothiazines (Table 3 in Supplementary data).

There were a few ions, which were common for most or all of these compounds. The ion *m/z* 224 appeared in all the spectra, although it is a primary fragment only for compounds **18**, **24d** and **24e** and was very weak for compounds **20**. All 2-Ph substituted derivatives **18**–**23c** exhibited the ion $C_8H_6O^{+\bullet}$, the counter ion of $A^{+\bullet}$, i.e., this ion is resonance-stabilized by the Ph group (Tables 5 and 6 in Supplementary data).

Similarly, the ion *m/z* 132, $C_8H_6NO^+$, was present for all of the compounds, although it was relatively or very weak for **18**–**23c** and **24d**,**e**. One route to this ion is via $[M-Cl]^+$, which was missing from the latter compounds, this possibly being a reason for the weakness of the former ion. $C_7H_6NS^+$, *m/z* 136 (Table 6 in Supplementary data), was present for most of the compounds (RA 5–20%), but very weak or missing for **18**–**23c** and **24d**,**e** (RA 0–4%). One route to this ion is via $A^{+\bullet}$, but Cl substitution, and especially *o*-Cl **21a**,**b**,**c**, obviously enhances this process.

A few more fragmentations may be mentioned. Compounds **22a**,**b** readily lost *o*-$CH_3$ and **23a**,**b** *o*-$OC_2H_5$, to give very strong $[M-CH_3]^+$ or $[M-OC_2H_5]^+$ (Table 6 in Supplementary data). Compounds **18b**, **21**–**23b** all gave the ion *m/z* 299 corresponding to $[M-HCl]^{+\bullet}$ (**18b**), $[M-Cl-Cl]^{+\bullet}$ (**21b**,**23b**) and $[M-CH_3-Cl]^+$ (**22b**) (see Table 6 in Supplementary data); in fact, **20b** and **20a**, **22a**, **23a** also gave moderate peaks (*m/z* 313, 279, 279, and 309, respectively) corresponding to $[M-HCl]^{+\bullet}$. Compounds **18**–**23c** and **24d**,**e** in turn furnished the ion *m/z* 210 (**18c** and **20c** only a weak one), $C_{14}H_{10}S^+$, obtained via a concerted mechanism from the intermediate $[M-C_8H_6NOS]^+$, e.g., $C_{14}H_{10}SCl^+$ for **24d** and **24e**. The other ions listed in Table 6 in Supplementary data are characteristic only of the compounds they represent. Elemental compositions were determined for several of them by means of accurate mass measurements, as indicated in the table.

Three more ions deserve special mention: *m/z* 204, $C_{15}H_{10}N^+$, for **21a**,**b** and for **22a**,**b**,**c**, *m/z* 180, $C_{13}H_{10}N^+$, for **23a**,**b**,**c** and *m/z* 155 for **19a**,**b**,**c** and **21a**,**b**,**c**, $C_7H_4SCl^+$. As shown by the *B*/*E* and $B^2/E$ metastability studies, the first is formed via the loss of Cl from the intermediate $C_{15}H_{14}NCl^+$ for **21a**,**b** and from $A^{+\bullet}$ for **22a**,**b**,**c**. The second originates from the intermediate $C_{14}H_{10}NO^+$, and the third from $[M-Cl]^+$ and $A^{+\bullet}$.

## 3. Conclusion

This paper has described the syntheses of 3-thiaquinoline analog 2-aryl-4*H*-3,1-benzothiazine derivatives **8**–**13** and their transformation to azeto[2,1-*a*][3,1]benzothiazin-1-one derivatives **18**–**23a**,**b**,**c** and **24d**,**e**. Their structures were confirmed by $^1H$ and $^{13}C$ NMR spectroscopy and electron ionization (EI) mass spectrometry and their fragmentation behavior under EI is discussed in some detail. The β-lactams obtained are useful starting materials for the preparation of 4,1-benzothiazepine derivatives, which exhibit the rare phenomenon of desmotropy. Further investigations on the syntheses of these desmotrope pairs are under way.

## 4. Experimental

### 4.1. General methods

Melting points were determined on a Kofler micro melting apparatus and are uncorrected. Elemental analyses were

performed with a Perkin–Elmer 2400 CHNS elemental analyser. IR spectra were recorded in KBr pellets with a UNICAM SP 100 double beam spectrometer. Merck Kieselgel 60$F_{254}$ plates were used for TLC: the eluent was *n*-hexane–ethyl acetate 9:1. *o*-Aminobenzyl alcohol was purchased from Fluka. Thiobenzamides were prepared by sulfurization from the corresponding benzamides, using the Lawesson reagent.[30] Compounds **8** and **9** were prepared by the given general procedure; their physical data were identical to the published data.[27]

### 4.2. NMR spectroscopy

NMR spectra were acquired with a Bruker Avance 500 spectrometer operating at 500.13 MHz for $^1$H and at 125.77 MHz for $^{13}$C, or with a JEOL JNM-L-400 spectrometer operating at 399.78 MHz for $^1$H and at 100.54 MHz for $^{13}$C. The spectra were recorded at variable temperatures (from −60 °C to +55 °C) in $CDCl_3$ (see Tables 1 and 2 in Supplementary data). Proton and carbon spectra were referenced internally to the TMS (tetramethylsilane) signal at 0.00 ppm.

1D proton spectra consisting of 32k data points were acquired with normal single-pulse excitation and a 45° flip angle. 1D carbon spectra consisting of 65k data points were acquired with normal single-pulse excitation, broad-band proton decoupling, a 45° flip angle and spectral widths of 30 kHz, and with 0.3–1.0 Hz exponential weighting applied prior to Fourier transformation. NOE difference experiments were carried out with saturation times of 6–8 s, and enhancements were expressed as a percentage, integrated with respect to the irradiated spin (set to −100%). 2D heteronuclear one-bond correlation experiments were performed by using either carbon-detected CH-shift correlations with partial homonuclear decoupling in the f1 dimension (Jeol spectrometer) or proton-detected HSQC with gradient selection (Bruker). Long-range heteronuclear correlation experiments included either carbon-detected COLOC (Jeol) or proton-detected HMBC with gradient selection (Bruker). The one-bond coupling constant was 145 Hz and the long-range coupling constants were 8–10 Hz in proton–carbon correlation spectra. 2D homonuclear H,H-correlation experiments were performed by using phase-sensitive double quantum filtered COSY. The spectral widths of the 2D spectra were optimized from the 1D spectra. All spectra were recorded with standard pulse sequences.

### 4.3. Mass spectrometry

The 70 eV low-resolution spectra were recorded with a VG ZABSpec instrument equipped with an OPUS V3.3 data system. The samples were introduced through a solids-inlet system, which was slightly heated to improve evaporation. The accelerating voltage was 8 kV, the temperature of the source was 433 K, and the trap current was 200 μA. The accurate mass measurements were performed at a resolution of 8000–10,000 (10% valley definition) by a voltage scanning technique, using perfluorokerosene as a reference compound. To clarify the fragmentation pathways, B/E scans (FFR1) were also applied. The demonstration of some parent ions also required the use of $B^2/E$ spectra. For linked scans, the resolution was 2000–2500.

### 4.4. General procedure for the preparation of 4*H*-3,1-benzothiazine derivatives 8–13 from 2-aminobenzyl chloride hydrochloride (1)

To a stirred and cooled (10–15 °C) mixture of thionyl chloride (6.5 mL, 89 mmol) and chloroform (30 mL), 2-aminobenzyl alcohol (5 g, 41 mmol) dissolved in chloroform (100 mL) was added dropwise over 1 h. After the addition, the reaction was stirred for a further 1 h at room temperature and then evaporated (50 °C). The crystalline residue was taken up in diethyl ether (40 mL), filtered and washed with diethyl ether (2×40 mL). Compound **1** was used without further purification.

For the transformation of compound **1**, the method of El-Desoky[27] was used with slight modifications, as follows. 2-Aminobenzyl chloride hydrochloride (**1**) (15 mmol) was thoroughly mixed with the appropriate thioamide (**2**–**7**) (15 mmol) and the mixture was maintained at 110–120 °C for 30 min. To the melt, $CHCl_3$ (30 mL) was added and the solid formed was suspended. To the suspension, water was added (10 mL) and the water phase was made just alkaline with 10% NaOH solution under intensive shaking. The organic layer was separated, extracted with water (30 mL), dried ($Na_2SO_4$), filtered, and evaporated. The residues thus obtained were purified by column chromatography with *n*-hexane–ethyl acetate 9:1 as eluent to give **8**–**13**. Benzothiazine derivatives **8** and **9** are known compounds.[27]

**4.4.1. 2-(4-Methylphenyl)-4*H*-3,1-benzothiazine (10).** Pale-yellow crystalline powder, mp: 104–106 °C (from diisopropyl ether), lit.[31] mp: 109–110 °C, yield 82%. Anal. Calcd for $C_{15}H_{13}NS$ (239.34): C, 75.28; H, 5.47; N, 5.85; S, 13.40. Found: C, 75.11; H, 5.29; N, 5.89; S, 13.26. $\nu_{max}$ (KBr disc) 1546, 1431, 1192, 1050, 1029, 937, 771, 752, 709, 643 cm$^{-1}$. $^1$H NMR $\delta$ ($CDCl_3$, 25 °C): 8.03 (m, 2H, 2′,6′-H), 7.43 (m, 1H, 8-H), 7.36 (m, 1H, 7-H), 7.26 (m, 2H, 3′,5′-H), 7.24 (m, 1H, 6-H), 7.15 (m, 1H, 5-H), 3.98 (s, 2H, 4-H), 2.41 (s, 3H, $CH_3$) ppm. $^{13}$C NMR $\delta$ ($CDCl_3$, 25 °C): 161.0 (2-C), 144.5 (8a-C), 142.0 (4′-C), 135.3 (1′-C), 129.2 (3′-C), 129.2 (5′-C), 128.4 (7-C), 128.2 (2′-C), 128.2 (6′-C), 127.4 (6-C), 126.9 (8-C), 126.8 (5-C), 119.8 (4a-C), 28.6 (4-C), 21.5 ($CH_3$) ppm. MS (EI): $M^{+\bullet}$=239 (100).

**4.4.2. 2-(2-Chlorophenyl)-4*H*-3,1-benzothiazine (11).** Pale-yellow crystalline powder, mp: 51–53 °C (from diisopropyl ether), yield 74%. Anal. Calcd for $C_{14}H_{10}ClNS$ (259.75): C, 64.73; H, 3.88; N, 5.39; S, 12.34. Found: C, 64.58; H, 4.02; N, 5.46; S, 12.50. $\nu_{max}$ (KBr disc) 1605, 1574, 1538, 1502, 1486, 1448, 1408, 1304, 1253, 1196, 1170, 1105, 1012, 948, 890, 855, 820, 790, 758, 707, 638 cm$^{-1}$. $^1$H NMR $\delta$ ($CDCl_3$, 25 °C): 7.56 (m, 1H, 6′-H), 7.46 (m, 1H, 3′-H), 7.42 (m, 1H, 8-H), 7.37 (m, 1H, 7-H), 7.34 (m, 1H, 4′-H), 7.33 (m, 1H, 5′-H), 7.29 (m, 1H, 6-H), 7.15 (m, 1H, 5-H), 4.06 (s, 2H, 4-H) ppm. $^{13}$C NMR $\delta$ ($CDCl_3$, 25 °C): 160.3 (2-C), 143.6 (8a-C), 138.1 (1′-C), 132.4 (2′-C), 130.8 (4′-C), 130.4 (6′-C), 130.4 (3′-C), 128.6 (7-C), 128.3 (6-C), 127.1 (5-C), 127.1 (8-C), 126.8 (5′-C), 118.7 (4a-C), 29.1 (4-C) ppm. MS (EI): $M^{+\bullet}$=259 (100).

**4.4.3. 2-(2-Methylphenyl)-4*H*-3,1-benzothiazine (12).** Pale-yellow crystalline powder, mp: 52–53 °C (from diisopropyl ether), lit.[31] mp: 54.5–56 °C, yield 46%. Anal. Calcd

for $C_{15}H_{13}NS$ (239.34): C, 75.28; H, 5.47; N, 5.85; S, 13.40. Found: C, 75.56; H, 5.31; N, 5.67; S, 13.32. $\nu_{max}$ (KBr disc) 1665, 1602, 1550, 1478, 1451, 1380, 1291, 1248, 1188, 1121, 1096, 1037, 965–835, 761, 708, 667 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, 25 °C): 7.59 (m, 1H, 6′-H), 7.41 (m, 1H, 8-H), 7.36 (m, 1H, 7-H), 7.32 (m, 1H, 4′-H), 7.28 (m, 1H, 6-H), 7.26 (m, 2H, 3′,5′-H), 7.16 (m, 1H, 5-H), 4.06 (s, 2H, 4-H), 2.54 (s, 3H, $CH_3$) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, 25 °C): 162.7 (2-C), 143.9 (8a-C), 138.5 (1′-C), 136.9 (2′-C), 131.1 (3′-C), 130.0 (6′-C), 129.9 (4′-C), 128.5 (7-C), 127.9 (6-C), 127.1 (5-C), 126.9 (8-C), 125.7 (5′-C), 118.5 (4a-C), 29.1 (4-C), 20.4 ($CH_3$) ppm. MS (EI): $M^{+\bullet}$=239 (100).

**4.4.4. 2-(2-Ethoxyphenyl)-4*H*-3,1-benzothiazine (13).** Pale-yellow crystalline powder, mp: 62−64 °C (from diisopropyl ether), yield 76%. Anal. Calcd for $C_{16}H_{15}NOS$ (269.36): C, 71.34; H, 5.61; N, 5.20; S, 11.90. Found: C, 71.42; H, 5.70; N, 5.36; S, 12.02. $\nu_{max}$ (KBr disc) 1596, 1580, 1542, 1490, 1478, 1448, 1391, 1292, 1257, 1238, 1189, 1117, 1038, 960–870, 780–720, 708, 670, 652, 628 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, 25 °C): 7.75 (m, 1H, 6′-H), 7.40 (m, 1H, 8-H), 7.37 (m, 1H, 4′-H), 7.35 (m, 1H, 7-H), 7.25 (m, 1H, 6-H), 7.15 (m, 1H, 5-H), 7.03 (m, 1H, 5′-H), 6.96 (m, 1H, 3′-H), 4.14 (q, $J$=7.8 Hz, 2H, $CH_3$–$CH_2$), 3.89 (s, 2H, 4-H), 1.45 (t, $J$=7.8 Hz, 3H, $CH_3$–$CH_2$) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, 25 °C): 160.6 (2-C), 156.6 (2′-C), 144.0 (8a-C), 131.1 (4′-C), 129.4 (6′-C), 129.0 (1′-C), 128.3 (7-C), 127.6 (6-C), 126.8 (8-C), 126.7 (5-C), 120.7 (5′-C), 120.1 (4a-C), 112.7 (3′-C), 64.6 ($CH_2$), 28.7 (4-C), 14.8 ($CH_3$) ppm. MS (EI): $M^{+\bullet}$=269 (100).

### 4.5. General procedure for azetobenzothiazines 18–23a,b,c and 24d,e

To a stirred solution of the 4*H*-3,1-benzothiazine derivatives **8–13** (2.0 mmol) in anhydrous benzene (10 mL) (**18a**,**b**, **19a**,**b**, **22a**,**b**, **21a** and **20b** for 12h; **21b**, **23b** for 8h and **20a**, **23a** for 4h) or toluene (**18c**, **19c**, **20c**, **22c** and **24d**,**e** for 4h and **21c**, **23c** for 12h), the appropriate acid chloride derivative **14–17** (3.0 mmol) was added. The solution was refluxed and triethylamine (0.4 mL, 3.0 mmol) in anhydrous toluene or benzene (20 mL) was added dropwise over 4 h at reflux. The addition of appropriate acid chloride derivative **14–17** (3.0 mmol) and triethylamine (0.4 mL, 3.0 mmol) was repeated one or two more times under the same conditions as above. The reaction mixture was then cooled and extracted with brine (20 mL), and the organic layer was dried with $Na_2SO_4$. After evaporation, the residue was taken up in benzene (5 mL) and passed through a short column of silica, the solvent was evaporated off, and the oily residue crystallized on trituration with ethanol.

**4.5.1. (2*R**,2a*S**)-2-Chloro-2a-phenyl-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (18a).** White crystalline powder, mp: 118–120 °C (from methanol), yield 52%. Anal. Calcd for $C_{16}H_{12}ClNOS$ (301.79): C, 63.68; H, 4.01; N, 4.64; S, 10.63. Found: C, 63.39; H, 3.87; N, 4.71; S, 10.82. $\nu_{max}$ (KBr disc) 1770, 1598, 1577, 1492, 1455, 1408, 1354, 1300, 1250, 1217, 1165, 1066, 1027, 1014, 972, 942, 926, 885, 857, 840, 756, 739, 695 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, −60 °C): 7.90 (m, 1H, 8-H), 7.70 (m, 1H, 2′-H), 7.54 (m, 1H, 3′-H), 7.46 (m, 1H, 7-H), 7.42 (m, 1H, 4′-H), 7.30 (m, 1H, 5′-H), 7.23 (m, 1H, 5-H), 7,22 (m, 1H, 6-H), 7,17 (m, 1H, 6′-H), 5.38, (s, 1H, 2-H), 3.76 (d, $J$=16.5 Hz, 1H, 4-H), 3.60 (d, $J$=16.5 Hz, 1H, 4-H) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, −60 °C): 159.6 (1-C), 135.8 (1′-C), 132.6 (8a-C), 129.0 (4′-C), 128.8 (3′-C), 128.6 (5-C), 128.6 (7-C), 127.7 (2′-C), 127.6 (5′-C), 126.6 (6′-C), 124.8 (6-C), 120.5 (4a-C), 120.2 (8-C), 70.1 (2a-C), 66.8 (2-C), 30.0 (4-C) ppm. MS (EI): $M^{+\bullet}$=301 (22).

**4.5.2. 2,2-Dichloro-2a-phenyl-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (18b).** White crystalline powder, mp: 152–154 °C (from methanol–chloroform), yield 72%. Anal. Calcd for $C_{16}H_{11}Cl_2NOS$ (336.24): C, 57.15; H, 3.30; N, 4.17; S, 9.54. Found: C, 56.89; H, 3.49; N, 4.08; S, 9.48. $\nu_{max}$ (KBr disc) 1788, 1572, 1488, 1448, 1354, 1219, 1186, 1160, 1097, 1078, 1060, 1036, 963, 948, 858, 848, 817, 776, 758, 717, 692, 674, 649 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, −60 °C): 7.88 (m, 1H, 8-H), 7.83 (m, 1H, 2′-H), 7.56 (m, 1H, 3′-H), 7.47 (m, 1H, 7-H), 7.43 (m, 1H, 4′-H), 7.28 (m, 1H, 5′-H), 7.26 (m, 1H, 6-H), 7,23 (m, 1H, 5-H), 7,10 (m, 1H, 6′-H), 3.82 (d, $J$=16.4 Hz, 1H, 4-H), 3.46 (d, $J$=16.4 Hz, 1H, 4-H) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, −60 °C): 157.5 (1-C) 136.1 (1′-C), 131.8 (8a-C), 129.4 (4′-C), 129.1 (3′-C), 128.9 (5-C), 128.7 (7-C), 127.7 (5′-C), 127.2 (2′-C), 126.0 (6′-C), 125.5 (6-C), 121.7 (4a-C), 120.2 (8-C), 88.4 (2-C), 79.9 (2a-C), 29.5 (4-C) ppm. MS (EI): $M^{+\bullet}$=335 (24).

**4.5.3. (2*R**,2a*R**)-2,2a-Diphenyl-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (18c).** White crystalline powder, mp: 156–158 °C (from methanol), yield 86%. Anal. Calcd for $C_{22}H_{17}NOS$ (343.44): C, 76.94; H, 4.99; N, 4.08; S, 9.34. Found: C, 76.74; H, 4.88; N, 4.02; S, 9.25. $\nu_{max}$ (KBr disc) 1768, 1597, 1578, 1492, 1455, 1415, 1350, 1337, 1239, 1198, 1167, 995–855, 755, 732, 696, 660 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, −60 °C): 8.00 (m, 1H, 8-H), 7.48 (m, 1H, 7-H), 7.27 (m, 1H, 5-H), 7.22 (m, 1H, 6-H), 7.17 (m, 3H, 3″,4″,5″-H), 7.13* (m, 1H, 5′-H), 7.11 (m, 1H, 4′-H), 7.10* (m, 1H, 6′-H), 7.08* (m, 1H, 3′-H), 7.06* (m, 1H, 2′-H), 7.04 (m, 2H, 2″,6″-H), 5.06 (s, 1H, 2-H), 3.74 (d, $J$=16.4 Hz, 1H, 4-H), 3.56 (d, $J$=16.4 Hz, 1H, 4-H) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, −60 °C): 164.7 (1-C) 137.2 (1′-C), 133.5 (8a-C), 131.2 (1″-C), 129.3 (2″,6″-C), 128.6 (5-C), 128.5 (7-C), 128.3 (3″,5″-C), 128.2* (3′-C), 128.0 (4″-C), 127.7 (4′-C), 127.0* (2′-C), 127.0* (5′-C), 126.3* (6′-C), 124.0 (6-C), 120.1 (8-C), 120.9 (4a-C), 69.9 (2a-C), 68.9 (2-C), 28.9 (4-C) ppm (*assignment uncertain). MS (EI): $M^{+\bullet}$=343 (6).

**4.5.4. (2*R**,2a*S**)-2-Chloro-2a-(4-chlorophenyl)-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (19a).** White crystalline powder, mp: 195–196 °C (from methanol), yield 59%. Anal. Calcd for $C_{16}H_{11}Cl_2NOS$ (336.24): C, 57.15; H, 3.30; N, 4.17; S, 9.54. Found: C, 56.87; H, 3.42; N, 4.12; S, 9.67. $\nu_{max}$ (KBr disc) 1778, 1582, 1493, 1456, 1408, 1360, 1302, 1248, 1217, 1172, 1091, 1070, 1012, 972, 947, 918, 887, 856, 828, 782, 757, 740, 658, 632 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, 25 °C): 7.87 (m, 1H, 8-H), 7.40 (m, 1H, 7-H), 7.36 (m, 2H, 2′,6′-H), 7.33 (m, 2H, 3′,5′-H), 7.17 (m, 1H, 5-H), 7.16 (m, 1H, 6-H), 5.27 (s, 1H, 2-H), 3.72 (d, $J$=16.5 Hz, 1H, 4-H), 3.58 (d, $J$=16.5 Hz, 1H, 4-H) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, 25 °C): 159.3 (1-C), 135.1 (4′-C), 135.0 (1′-C), 133.0 (8a-C),

128.9 (2′,6′-C), 128.8 (7-C), 128.6 (5-C), 128.6 (3′,5′-C), 124.9 (6-C), 120.6 (8-C), 120.5 (4a-C), 69.9 (2a-C), 67.3 (2-C), 20.2 (4-C) ppm. MS (EI): $M^{+\bullet}$=335 (23).

**4.5.5. 2a-(4-Chlorophenyl)-2,2-dichloro-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (19b).** White crystalline powder, mp: 132–134 °C (from methanol–chloroform), yield 75%. Anal. Calcd for $C_{16}H_{10}Cl_3NOS$ (370.38): C, 51.84; H, 2.72; N, 3.78; S, 8.65. Found: C, 52.02; H, 2.59; N, 3.74; S, 8.49. $\nu_{max}$ (KBr disc) 1790, 1597, 1579, 1492, 1456, 1403, 1364, 1302, 1228, 1167, 1094, 1035, 1010, 942, 886, 854, 815, 765, 748, 669 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, −60 °C): 7.86 (m, 1H, 8-H), 7.80 (m, 1H, 2′-H), 7.52 (m, 1H, 3′-H), 7.46 (m, 1H, 7-H), 7.27 (m, 1H, 6-H), 7.24 (m, 2H, 5,5′-H), 7.04 (m, 1H, 6′-H), 3.84 (d, $J$=16.5 Hz, 1H, 4-H), 3.46 (d, $J$=16.5 Hz, 1H, 4-H) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, −60 °C): 157.3 (1-C), 135.2 (4′-C), 134.8 (1′-C), 131.6 (8a-C), 129.4 (3′-C), 128.9 (5-C), 128.8 (2′-C), 128.8 (7-C), 127.8 (5′-C), 127.5 (6′-C), 125.7 (6-C), 121.4 (4a-C), 120.8 (8-C), 88.2 (2-C), 79.4 (2a-C), 29.4 (4-C) ppm. MS (EI): $M^{+\bullet}$=369 (24).

**4.5.6. (2*R**,2a*R**)-2a-(4-Chlorophenyl)-2-phenyl-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (19c).** White crystalline powder, mp: 184–186 °C (from methanol–chloroform), yield 89%. Anal. Calcd for $C_{22}H_{16}ClNOS$ (377.89): C, 69.92; H, 4.27; N, 3.71; S, 8.49. Found: C, 70.11; H, 4.16; N, 3.70; S, 8.31. $\nu_{max}$ (KBr disc) 1765, 1580, 1490, 1452, 1400, 1348, 1230, 1198, 1169, 1088, 1065, 1008, 930–770, 752, 720, 695 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, −60 °C): 7.99 (m, 1H, 8-H), 7.48 (m, 1H, 7-H), 7.27 (m, 1H, 5-H), 7.22 (m, 1H, 6-H), 7.20 (m, 3H, 3″,4″,5″-H), 7.08* (m, 1H, 2′-H), 7.03* (m, 1H, 6′-H), 7.03 (m, 2H, 2″,6″-H), 7,02* (m, 2H, 3′,5′-H), 5.06 (s, 1H, 2-H), 3.74 (d, $J$=16.4 Hz, 1H, 4-H), 3.52 (d, $J$=16.4 Hz, 1H, 4-H) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, −60 °C): 164.5 (1-C), 136.0 (4′-C), 133.2 (1′-C), 133.3 (8a-C), 130.8 (1″-C), 129.2 (2″,6″-C), 128.7 (5-C), 128.6* (3′-C), 128.5 (7-C), 128.5 (3″,5″-C), 128.5* (5′-C), 128.2 (4″-C), 127.6* (6′-C), 127.0* (2′-C), 124.2 (6-C), 120.7 (4a-C), 120.1 (8-C), 69.4 (2a-C) 68.9 (2-C), 28.9 (4-C) ppm (*assignment uncertain). MS (EI): $M^{+\bullet}$=377 (6).

**4.5.7. (2*R**,2a*S**)-2-Chloro-2a-(4-methylphenyl)-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (20a).** White crystalline powder, mp: 196–198 °C (from methanol–ethyl acetate), yield 57%. Anal. Calcd for $C_{17}H_{14}ClNOS$ (315.82): C, 64.65; H, 4.47; N, 4.44; S, 10.15. Found: C, 64.82; H, 4.62; N, 4.40; S, 10.23. $\nu_{max}$ (KBr disc) 1772, 1580, 1490, 1455, 1400, 1361, 1300, 1220, 1170, 1095, 1072, 1018, 975, 920, 882, 840, 815, 798, 755, 740, 695 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, 25 °C): 7.87 (m, 1H, 8-H), 7.39 (m, 1H, 7-H), 7.30 (m, 2H, 2′,6′-H), 7.16 (m, 2H, 3′,5′-H), 7.15 (m, 1H, 5-H), 7.14 (m, 1H, 6-H), 5.26 (s, 1H, 2-H), 3.69 (d, $J$=16.0 Hz, 1H, 4-H), 3.60 (d, $J$=16.0 Hz, 1H, 4-H), 2.35 (s, 3H, $CH_3$) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, 25 °C): 159.6 (1-C), 139.0 (4′-C), 133.3 (8a-C), 133.2 (1′-C), 129.0 (3′,5′-C), 128.6 (7-C), 128.6 (5-C), 127.4 (2′,6′-C), 124.7 (6-C), 120.8 (4a-C), 120.6 (8-C), 70.4 (2a-C), 67.4 (2-C), 29.3 (4-C), 21.2 ($CH_3$) ppm. MS (EI): $M^{+\bullet}$=315 (30).

**4.5.8. 2,2-Dichloro-2a-(4-methylphenyl)-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (20b).** White crystalline powder, mp: 154–156 °C (from methanol–ethyl acetate), yield 61%. Anal. Calcd for $C_{17}H_{13}Cl_2NOS$ (350.26): C, 58.29; H, 3.74; N, 4.00; S, 9.15. Found: C, 58.62; H, 3.39; N, 4.15; S, 9.22. $\nu_{max}$ (KBr disc) 1775, 1610, 1580, 1492, 1455, 1365, 1300, 1223, 1182, 1171, 1155, 1086, 1040, 1030, 1018, 972, 947, 885, 860, 850–740, 671 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, −60 °C): 7.87 (m, 1H, 8-H), 7.71 (m, 1H, 2′-H), 7.46 (m, 1H, 7-H), 7.36 (m, 1H, 3′-H), 7.25 (m, 1H, 6-H), 7.21 (m, 1H, 5-H), 7.07 (m, 1H, 5′-H), 6.98 (m, 1H, 6′H), 3.81 (d, $J$=16.6 Hz, 1H, 4-H), 3.46 (d, $J$=16.6 Hz, 1H, 4-H), 2.38 (s, 3H, $CH_3$) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, −60 °C): 157.5 (1-C), 139.6 (4′-C), 133.1 (1′-C), 131.8 (8a-C), 129.9 (3′-C), 128.9 (5-C), 128.6 (7-C), 128.2 (5′-C), 127.1 (2′-C), 126.1 (6′-C), 125.5 (6-C), 121.7 (4a-C), 120.8 (8-C), 88.4 (2-C), 80.0 (2a-C), 29.6 (4-C), 21.4 ($CH_3$) ppm. MS (EI): $M^{+\bullet}$=349 (26).

**4.5.9. (2*R**,2a*R**)-2a-(4-Methylphenyl)-2-phenyl-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (20c).** White crystalline powder, mp: 128–130 °C (from methanol), yield 81%. Anal. Calcd for $C_{23}H_{19}NOS$ (357.47): C, 77.28; H, 5.36; N, 3.92; S, 8.97. Found: C, 77.11; H, 5.10; N, 3.87; S, 9.13. $\nu_{max}$ (KBr disc) 1769, 1597, 1575, 1492, 1452, 1358, 1240, 1162, 1092, 1070, 1025, 970–718, 695 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, 25 °C): 7.97 (m, 1H, 8-H), 7.40 (m, 1H, 7-H), 7.18 (m, 1H, 5-H), 7.13 (m, 1H, 6-H), 7.11 (m, 3H, 3″,4″,5″-H), 7.03 (m, 2H, 2″,6″-H), 6.98 (m, 2H, 2′,6′-H), 6.84 (m, 2H, 3′,5′-H), 4.96 (s, 1H, 2-H), 3.65 (d, $J$=16.5 Hz, 1H, 4-H), 3.55 (d, $J$=16.5 Hz, 1H, 4-H), 2.16 (s, 3H, $CH_3$) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, 25 °C): 164.4 (1-C), 137.5 (4′-C), 134.6 (1′-C), 134.1 (8a-C), 131.8 (1″-C), 129.5 (2″,6″-C), 128.5 (5-C), 128.4 (7-C), 128.4 (3′,5′-C), 128.3 (3″,5″-C), 127.9 (4″-C), 127.0 (2′,6′-C), 123.9 (6-C), 121.3 (4a-C), 120.5 (8-C), 70.2 (2a-C), 69.6 (2-C), 29.3 (4-C), 21.0 ($CH_3$) ppm. MS (EI): $M^{+\bullet}$=357 (4).

**4.5.10. (2*R**,2a*S**)-2-Chloro-2a-(2-chlorophenyl)-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (21a).** White crystalline powder, mp: 153–156 °C (from methanol), yield 66%. Anal. Calcd for $C_{16}H_{11}Cl_2NOS$ (336.24): C, 57.15; H, 3.30; N, 4.17; S, 9.54. Found: C, 57.59; H, 3.12; N, 4.09; S, 9.12. $\nu_{max}$ (KBr disc) 1788, 1602, 1582, 1567, 1495, 1470, 1458, 1431, 1412, 1360, 1300, 1277, 1236, 1218, 1158, 1080, 1050, 1039, 1012, 967, 910, 890–820, 750–695, 672 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, 25 °C): 7.84 (m, 1H, 8-H), 7.49 (m, 1H, 3′-H), 7.42 (m, 1H, 7-H), 7.32 (m, 1H, 4′-H), 7.20 (m, 2H, 5,6-H), 7.15 (m, 1H, 5′-H), 7.01 (m, 1H, 6′-H), 5.36 (s, 1H, 2-H), 3.72 (d, $J$=16.6 Hz, 1H, 4-H), 3.60 (d, $J$=16.6 Hz, 1H, 4-H) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, 25 °C): 160.4 (1-C), 133.7 (1′-C), 133.4 (8a-C), 132.8 (2′-C), 131.5 (3′-C), 130.2 (4′-C), 128.7 (7-C), 128.4 (5-C), 127.9 (6′-C), 126.2 (5′-C), 125.1 (6-C), 120.9 (8-C), 120.7 (4a-C), 70.1 (2a-C), 67.0 (2-C), 29.0 (4-C) ppm. MS (EI): $M^{+\bullet}$=335 (18).

**4.5.11. 2a-(2-Chlorophenyl)-2,2-dichloro-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (21b).** White crystalline powder, mp: 187–188 °C (from methanol–chloroform), yield 79%. Anal. Calcd for $C_{16}H_{10}Cl_3NOS$ (370.38): C, 51.84; H, 2.72; N, 3.78; S, 8.65. Found: C, 51.59; H, 2.95; N, 3.60; S, 8.88. $\nu_{max}$ (KBr disc) 1790, 1602, 1580, 1493, 1468, 1457, 1430, 1365, 1300, 1272, 1224, 1200, 1176, 1130, 1088, 1045, 965, 944, 886, 860, 831, 808, 770–705, 672, 638 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$,

25 °C): 7.84 (m, 1H, 8-H), 7.52 (m, 1H, 3′-H), 7.43 (m, 1H, 7-H), 7.33 (m, 1H, 4′-H), 7.24 (m, 1H, 6-H), 7.20 (m, 1H, 5-H), 7.14 (m, 1H, 5′-H), 6.98 (m, 1H, 6′H), 3.76 (d, $J$=16.5 Hz, 1H, 4-H), 3.47 (d, $J$=16.5 Hz, 1H, 4-H) ppm. $^{13}$C NMR $\delta$ ($CDCl_3$, 25 °C): 158.1 (1-C), 134.7 (1′-C), 133.0 (8a-C), 132.9 (2′-C), 131.6 (3′-C), 130.4 (4′-C), 128.8 (7-C), 128.6 (5-C), 127.2 (6′-C), 126.1 (5′-C), 125.7 (6-C), 121.8 (4a-C), 121.1 (8-C), 88.2 (2-C), 79.5 (2a-C), 29.4 (4-C) ppm. MS (EI): $M^{+\bullet}$=369 (19).

**4.5.12. (2*R**,2a*R**)-2a-(2-Chlorophenyl)-2-phenyl-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (21c).** White crystalline powder, mp: 225–228 °C (from methanol–chloroform), yield 78%. Anal. Calcd for $C_{22}H_{16}ClNOS$ (377.89): C, 69.92; H, 4.27; N, 3.71; S, 8.49. Found: C, 69.67; H, 4.11; N, 3.76; S, 8.52. $\nu_{max}$ (KBr disc) 1771, 1600, 1579, 1492, 1468, 1452, 1405, 1350, 1275, 1225, 1200, 1170, 1148, 1080, 1029, 960, 951, 885, 861, 845, 780–730, 719, 692 $cm^{-1}$. $^1$H NMR $\delta$ ($CDCl_3$, 25 °C): 7.93 (m, 1H, 8-H), 7.43 (m, 1H, 7-H), 7.22 (m, 1H, 5-H), 7.19 (m, 1H, 6-H), 7.17 (m, 1H, 4″-H), 7.15 (m, 1H, 6′-H), 7.11 (m, 4H, 4′,5′,3″,5″-H), 7.07 (m, 1H, 3′-H), 7.03 (m, 2H, 2″,6″-H), 4.96 (s, 1H, 2-H), 3.69 (d, $J$=16.5 Hz, 1H, 4-H), 3.59 (d, $J$=16.5 Hz, 1H, 4-H) ppm. $^{13}$C NMR $\delta$ ($CDCl_3$, 25 °C): 165.4 (1-C), 134.8 (2′-C), 134.2 (8a-C), 132.2 (1′-C), 131.5 (1″-C), 131.1 (3′-C), 130.4 (2″,6″-C), 129.4 (4′-C), 128.5 (7-C), 128.4 (6′-C), 128.3 (5-C), 128.1 (4″-C), 127.7 (3″,5″-C), 125.8 (5′-C), 124.4 (6-C), 121.2 (4a-C), 120.9 (8-C), 69.8 (2a-C) 69.6 (2-C), 29.0 (4-C) ppm. MS (EI): $M^{+\bullet}$=377 (17).

**4.5.13. (2*R**,2a*S**)-2-Chloro-2a-(2-methylphenyl)-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (22a).** White crystalline powder, mp: 120–123 °C (from methanol–ethyl acetate), yield 47%. Anal. Calcd for $C_{17}H_{14}ClNOS$ (315.82): C, 64.65; H, 4.47; N, 4.44; S, 10.15. Found: C, 64.36; H, 4.61; N, 4.53; S, 10.22. $\nu_{max}$ (KBr disc) 1782, 1600, 1580, 1483, 1456, 1362, 1300, 1240, 1217, 1200, 1170, 1096, 1062, 1032, 1010, 914, 857, 842, 800, 778, 752, 719, 698, 630 $cm^{-1}$. $^1$H NMR $\delta$ ($CDCl_3$, 25 °C): 7.87 (m, 1H, 8-H), 7.42 (m, 1H, 7-H), 7.27 (m, 1H, 3′-H), 7.26 (m, 1H, 4′-H), 7.18 (m, 2H, 5,6-H), 7.04 (m, 1H, 5′-H), 6.91 (m, 1H, 6′-H), 5.31 (s, 1H, 2-H), 3.68 (d, $J$=16.5 Hz, 1H, 4-H), 3.58 (d, $J$=16.5 Hz, 1H, 4-H), 2.51 (s, 3H, $CH_3$) ppm. $^{13}$C NMR $\delta$ ($CDCl_3$, 25 °C): 159.9 (1-C), 136.1 (1′-C), 133.7* (8a-C), 133.7* (2′-C), 132.2 (3′-C), 129.0 (4′-C), 128.6 (7-C), 128.4 (5-C), 126.7 (6′-C), 125.2 (5′-C), 124.9 (6-C), 120.9 (4a-C), 120.7 (8-C), 70.7 (2a-C), 66.7 (2-C), 29.1 (4-C), 21.4 ($CH_3$) ppm (*assignment uncertain). MS (EI): $M^{+\bullet}$=315 (38).

**4.5.14. 2,2-Dichloro-2a-(2-methylphenyl)-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (22b).** White crystalline powder, mp: 146–148 °C (from methanol–ethyl acetate), yield 52%. Anal. Calcd for $C_{17}H_{13}Cl_2NOS$ (350.26): C, 58.29; H, 3.74; N, 4.00; S, 9.15. Found: C, 58.06; H, 3.92; N, 4.24; S, 9.32.$\nu_{max}$ (KBr disc) 1872, 1578, 1492, 1450, 1370, 1302, 1223, 1173, 1150, 1088, 1040, 973, 946, 884, 860–740, 674 $cm^{-1}$. $^1$H NMR $\delta$ ($CDCl_3$, 25 °C): 7.86 (m, 1H, 8-H), 7.43 (m, 1H, 7-H), 7.30 (m, 1H, 3′-H), 7.27 (m, 1H, 4′-H), 7.22 (m, 1H, 6-H), 7.18 (m, 1H, 5-H), 7.02 (m, 1H, 5′-H), 6.87 (m, 1H, 6′H), 3.73 (d, $J$=16.5 Hz, 1H, 4-H), 3.46 (d, $J$=16.5 Hz, 1H, 4-H), 2.51 (s, 3H, $CH_3$) ppm. $^{13}$C NMR $\delta$ ($CDCl_3$, 25 °C): 157.7 (1-C), 136.4 (1′-C), 134.9 (2′-C), 133.2 (8a-C), 132.5 (3′-C), 129.2 (4′-C), 128.7 (7-C), 128.6 (5-C), 125.9 (6′-C), 125.5 (6-C), 125.1 (5′-C), 122.1 (4a-C), 121.1 (8-C), 88.3 (2-C), 80.4 (2a-C), 29.6 (4-C), 21.4 ($CH_3$) ppm. MS (EI): $M^{+\bullet}$=349 (56).

**4.5.15. (2*R**,2a*R**)-2a-(2-Methylphenyl)-2-phenyl-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (22c).** White crystalline powder, mp: 198–200 °C (from methanol–ethyl acetate), yield 71%. Anal. Calcd for $C_{23}H_{19}NOS$ (357.47): C, 77.28; H, 5.36; N, 3.92; S, 8.97. Found: C, 76.96; H, 5.54; N, 3.78; S, 8.81. $\nu_{max}$ (KBr disc) 1764, 1604, 1578, 1492, 1454, 1409, 1349, 1300, 1265, 1238, 1200, 1167, 1095, 1057, 1030, 970–850, 786, 755, 720, 700 $cm^{-1}$. $^1$H NMR $\delta$ ($CDCl_3$, 25 °C): 7.95 (m, 1H, 8-H), 7.43 (m, 1H, 7-H), 7.21 (m, 1H, 5-H), 7.17 (m, 1H, 6-H), 7.16 (m, 1H, 4″-H), 7.09 (m, 3H, 4′,3″,5″-H), 7.04 (m, 1H, 6′-H), 7.00 (m, 1H, 5′-H), 6.97 (m, 2H, 2″,6″-H), 6.86 (m, 1H, 3′-H), 4.89 (s, 1H, 2-H), 3.66 (d, $J$=16.4 Hz, 1H, 4-H), 3.57 (d, $J$=16.4 Hz, 1H, 4-H), 1.98 (s, 3H, $CH_3$) ppm. $^{13}$C NMR $\delta$ ($CDCl_3$, 25 °C): 165.0 (1-C), 135.6 (2′-C), 134.8 (1′-C), 134.5 (8a-C), 131.8 (3′-C), 131.7 (1″-C), 130.1 (2″,6″-C), 128.4 (7-C), 128.4 (5-C), 128.3 (4′-C), 128.2 (4″-C), 127.9 (3″,5″-C), 127.1 (6′-C), 124.8 (5′-C), 124.2 (6-C), 121.4 (4a-C), 120.8 (8-C), 70.5 (2a-C), 69.3 (2-C), 29.2 (4-C), 21.0 ($CH_3$) ppm. MS (EI): $M^{+\bullet}$=357 (16).

**4.5.16. (2*R**,2a*S**)-2-Chloro-2a-(2-ethoxyphenyl)-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (23a).** White crystalline powder, mp: 177–179 °C (from methanol–chloroform), yield 65%. Anal. Calcd for $C_{18}H_{16}ClNO_2S$ (345.84): C, 62.51; H, 4.66; N, 4.05; S, 9.27. Found: C, 62.44; H, 4.75; N, 3.99; S, 9.19. $\nu_{max}$ (KBr disc) 1782, 1598, 1582, 1489, 1460, 1448, 1388, 1345, 1287, 1253, 1155, 1121, 1056, 1042, 928, 882, 856, 840, 822, 798, 767, 750, 698 $cm^{-1}$. $^1$H NMR $\delta$ ($CDCl_3$, 25 °C): 7.82 (m, 1H, 8-H), 7.40 (m, 1H, 7-H), 7.32 (m, 1H, 4′-H), 7.19 (m, 1H, 5-H), 7.18 (m, 1H, 6-H), 6.96 (m, 1H, 3′-H), 6.84 (m, 1H, 6′-H), 6.80 (m, 1H, 5′-H), 5.25 (s, 1H, 2-H), 4.23 (m, 1H, C$H_2$–$CH_3$), 4.07 (m, 1H, C$H_2$–$CH_3$), 3.72 (d, $J$=16.5 Hz, 1H, 4-H), 3.69 (d, $J$=16.5 Hz, 1H, 4-H), 1.51 (t, $J$=7.2 Hz, 3H, $CH_3$) ppm. $^{13}$C NMR $\delta$ ($CDCl_3$, 25 °C): 160.9 (1-C), 155.3 (2′-C), 133.8 (8a-C), 130.4 (4′-C), 128.5 (7-C), 128.4 (5-C), 126.7 (6′-C), 124.8 (6-C), 124.5 (1′-C), 121.0 (4a-C), 120.8 (8-C), 119.5 (5′-C), 112.4 (3′-C), 69.2 (2a-C), 67.0 (2-C), 64.0 ($CH_2O$), 29.1 (4-C), 14.8 ($CH_3$) ppm. MS (EI): $M^{+\bullet}$=245 (55).

**4.5.17. 2,2-Dichloro-2a-(2-ethoxyphenyl)-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (23b).** White crystalline powder, mp: 187–191 °C (from methanol–ethyl acetate), yield 70%. Anal. Calcd for $C_{18}H_{15}Cl_2NO_2S$ (380.29): C, 56.85; H, 3.89; N, 3.68; S, 8.43. Found: C, 56.69; H, 4.12; N, 3.61; S, 8.22. $\nu_{max}$ (KBr disc) 1778, 1598, 1582, 1492, 1455, 1362, 1289, 1254, 1165, 1130, 1109, 1073, 1047, 927, 883, 855, 810, 770–710, 672 $cm^{-1}$. $^1$H NMR $\delta$ ($CDCl_3$, 25 °C): 7.81 (m, 1H, 8-H), 7.40 (m, 1H, 7-H), 7.33 (m, 1H, 4′-H), 7.20 (m, 1H, 6-H), 7.19 (m, 1H, 5-H), 6.98 (m, 1H, 3′-H), 6.78 (m, 1H, 6′-H), 6.77 (m, 1H, 5′-H), 4.25 (m, 1H, C$H_2$–$CH_3$), 4.13 (m, 1H, C$H_2$–$CH_3$), 3.74 (d, $J$=16.5 Hz, 1H, 4-H), 3.58 (d, $J$=16.5 Hz, 1H, 4-H), 1.58 (t, $J$=7.2 Hz, 3H, $CH_3$) ppm. $^{13}$C NMR $\delta$ ($CDCl_3$, 25 °C): 158.7 (1-C), 155.5 (2′-C), 133.3 (8a-C), 130.6 (4′-C), 128.6 (5-C), 128.5 (7-C), 125.8 (6′-C), 125.5

(1′-C), 125.4 (6-C), 122.2 (4a-C), 121.1 (8-C), 119.4 (5′-C), 112.3 (3′-C), 88.4 (2-C), 78.6 (2a-C), 64.2 ($CH_2O$-C), 29.6 (4-C), 14.8 ($CH_3$) ppm. MS (EI): $M^{+\bullet}$=379 (46).

**4.5.18. (2*R**,2a*R**)-2a-(2-Ethoxyphenyl)-2-phenyl-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (23c).** White crystalline powder, mp: 175–178 °C (from methanol–ethyl acetate), yield 86%. Anal. Calcd for $C_{24}H_{21}NO_2S$ (387.50): C, 74.39; H, 5.46; N, 3.61; S, 8.27. Found: C, 74.36; H, 5.60; N, 3.58; S, 8.12. $\nu_{max}$ (KBr disc) 1762, 1600, 1578, 1493, 1454, 1409, 1392, 1356, 1288, 1247, 1170, 1128, 1109, 1095, 1060, 1048, 945, 920, 885, 790–725, 700, 671 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, 25 °C): 7.93 (m, 1H, 8-H), 7.41 (m, 1H, 7-H), 7.22 (m, 1H, 5-H), 7.16 (m, 1H, 6-H), 7.11 (m, 2H, 4′,4″-H), 7.08 (m, 2H, 3″,5″-H), 6.97 (m, 2H, 2″,6″-H), 6.95 (m, 1H, 6′-H), 6.74 (m, 1H, 5′-H), 6.47 (m, 1H, 3′-H), 4.86 (s, 1H, 2-H), 3.81 (m, 1H, C*H*$_2$–$CH_3$), 3.71 (d, *J*=16.7 Hz, 1H, 4-H), 3.66 (d, *J*=16.7 Hz, 1H, 4-H), 3.16 (m, 1H, C*H*$_2$–$CH_3$), 1.35 (t, *J*=7.2 Hz, 3H, $CH_3$) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, 25 °C): 165.8 (1-C), 154.5 (2′-C), 134.6 (8a-C), 132.4 (1″-C), 129.8 (2″,6″-C), 129.6 (4′-C), 128.4 (5-C), 128.3 (7-C), 127.7 (4″-C), 127.3 (3″,5″-C), 127.2 (6′-C), 125.5 (1′-C), 124.1 (6-C), 121.4 (4a-C), 120.7 (8-C), 119.1 (5′-C), 111.4 (3′-C), 69.5 (2-C), 68.9 (2a-C), 62.7 ($CH_2O$–C), 29.2 (4-C), 14.71 ($CH_3$) ppm. MS (EI): $M^{+\bullet}$=387 (15).

**4.5.19. (2*R**,2a*S**)-2-Chloro-2,2a-diphenyl-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (24d).** White crystalline powder, mp: 151–156 °C [compound **24d** was separated from **24e** by column chromatography with *n*-hexane–benzene 1:1 ($R_f$ 0.39), followed by *n*-hexane–benzene 1:2 as eluent ($R_f$ 0.45)], yield 72%. Anal. Calcd for $C_{21}H_{16}ClNOS$ (377.89): C, 69.92; H, 4.27; N, 3.71; S, 8.49. Found: C, 69.55; H, 4.49; N, 3.74; S, 8.62. $\nu_{max}$ (KBr disc) 1779, 1600, 1581, 1492, 1445, 1367, 1302, 1245, 1218, 1172, 1108, 1090, 1070, 1039, 1025, 952, 938, 862, 840, 823, 793, 741, 714, 702, 692 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, −60 °C): 8.00 (m, 1H, 8-H), 7.98 (m, 1H, 2′-H), 7.69 (m, 2H, 2″,6″-H), 7.63 (m, 1H, 3′-H), 7.52 (m, 3H, 3″,4″,5″-H), 7.48 (m, 1H, 7-H), 7.46 (m, 1H, 4′-H), 7.35 (m, 1H, 5′-H), 7.27 (m, 1H, 6′-H), 7.21 (m, 1H, 6-H), 7.13 (m, 1H, 5-H), 3.60 (d, *J*=16.5 Hz, 1H, 4-H), 3.42 (d, *J*=16.5 Hz, 1H, 4-H) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, −60 °C): 161.5 (1-C), 137.0 (1′-C), 132.8 (1″-C), 132.1 (8a-C), 129.8 (3″,5″-C), 129.1 (3′-C), 129.0 (4″-C), 128.8 (5-C), 128.8 (4′-C), 128.5 (7-C), 127.7 (5′-C), 127.7 (2″,6″-C), 127.2 (2′-C), 126.9 (6′-C), 125.1 (6-C), 121.0 (4a-C), 120.6 (8-C), 80.1 (2-C), 77.4 (2a-C), 29.6 (4-C) ppm. MS (EI): $M^{+\bullet}$=377 (11).

**4.5.20. (2*R**,2a*R**)-2-Chloro-2,2a-diphenyl-2,2a-dihydro-2*H*,4*H*-azeto[1,2-*a*][3,1]benzothiazin-1-one (24e).** White crystalline powder, mp: 218–226 °C [compound **24d** was separated from **24e** by column chromatography with *n*-hexane–benzene 1:1 ($R_f$ 0.24), followed by *n*-hexane–benzene 1:2 as eluent ($R_f$ 0.30)], yield 17%. Anal. Calcd for $C_{21}H_{16}ClNOS$ (377.89): C, 69.92; H, 4.27; N, 3.71; S, 8.49. Found: C, 69.61; H, 4.66; N, 3.80; S, 8.69. $\nu_{max}$ (KBr disc) 1780, 1600, 1582, 1493, 1445, 1365, 1300, 1244, 1218, 1172, 1110, 1090, 1071, 1040, 1026, 951, 939, 862, 840, 822, 793, 744, 714, 699 $cm^{-1}$. $^1H$ NMR $\delta$ ($CDCl_3$, −60 °C): 7.99 (m, 1H, 8-H), 7.67 (m, 1H, 2′-H), 7.47 (m, 1H, 7-H), 7.35 (m, 2H, 2″,6″-H), 7.22 (m, 1H, 6-H), 7.21 (m, 2H, 5,3′-H), 7.15 (m, 3H, 3″,4″,5″-H), 7.07 (m, 1H, 4′-H), 6.94 (m, 1H, 5′-H), 6.87 (m, 1H, 6′-H), 3.79 (d, *J*=16.5 Hz, 1H, 4-H), 3.43 (d, *J*=16.5 Hz, 1H, 4-H) ppm. $^{13}C$ NMR $\delta$ ($CDCl_3$, −60 °C): 161.5 (1-C), 136.5 (1′-C), 133.7 (1″-C), 132.4 (8a-C), 129.8 (5″-C), 128.9* (5-C), 128.8* (4″-C), 128.5* (3′-C), 128.4* (7-C), 128.3 (10-C), 128.0 (3″-C), 127.7 (6″-C), 127.5 (2″-C), 127.2 (2′-C), 127.2 (5′-C), 126.4 (6′-C), 125.0 (6-C), 122.0 (4a-C), 120.9 (8-C), 82.1 (2-C), 78.8 (2a-C), 29.4 (4-C) ppm (*assignment uncertain). MS (EI): $M^{+\bullet}$=377 (11).

## Acknowledgements

The authors express their thanks to the Hungarian Scientific Research Foundation (OTKA), and to Ms. E. Juhász Dinya for technical assistance. We are indebted to Professor G. Dombi for measuring the IR spectra.

## Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.09.079.

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