Photochemical [3+2] Cycloaddition of 2′-Vinyl-2*H*-1,4-benzothiazin-3(4*H*)-one-2-spirocyclopropanes Catalyzed by Diphenyl Dichalcogenides

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2′-Vinyl-2*H*-1,4-benzothiazin-3(4*H*)-one-2-spirocyclopropanes (1) were irradiated with a tungsten lamp at room temperature in the presence of a catalytic amount of diphenyl dichalcogenide to provide 1,2-dioxolane derivatives (3) in good yields. Diphenyl diselenide was more effective than diphenyl disulfide as a radical source. The photochemical [3+2] cycloaddition of 1b with electron-deficient alkenes proceeded smoothly under reflux in benzene to give spiro-cyclopentanes (5). Spiro-cyclopentenes (6) were formed by the photochemical [3+2] cycloaddition of 1b with alkynes.

Key words vinylcyclopropane; benzothiazinone; photochemical [3+2] cycloaddition; chalcogen radical

Pharmacologically active benzothiazinone derivatives include semotiadil, a Ca^{2+} antagonist,[1] and SPR-210, an aldose reductase inhibitor.[2] In a previous paper we have described the synthesis and transformation of tricyclic benzothiazinium salts bearing a bridgehead sulfur atom as part of a program to synthesize benzothiazinone derivatives possessing unusual skeletons,[3] such as benzothiazinones bonded with spirovinylcyclopropane. The vinylcyclopropane unit has been subjected to a variety of chemical transformations.[4] We have also explored the novel transformation of 1-(electron-withdrawing group)-1-sulfenyl-substituted 2-vinylcyclopropanes[5] and the chemical behavior of 2′-vinyl-2*H*-benzothiazine-2-spirocyclopropan-3(4*H*)-ones in acidic media.[6] Photochemical reactions are one of the methods available for transformation of vinylcyclopropanes, and Feldman and co-workers have extensively investigated [3+2] cycloaddition of vinylcyclopropanes catalyzed by chalcogen radicals (Fig. 1).[7]

Bertrand and co-workers applied radical [3+2] cycloaddition to the synthesis of bicyclic lactones, lactams and ketones.[8] We recently reported photochemical thiylation of 2′-vinyl-2*H*-benzothiazine-2-spirocyclopropan-3(4*H*)-ones[9] and next intended to synthesize new 2*H*-benzothiazin-3(4*H*)-one derivatives by photochemical [3+2] cycloaddition of vinylcyclopropanes. This paper describes the transformation of 2′-vinyl-2*H*-benzothiazin-3(4*H*)-one-2-spirocyclopropanes by photochemical [3+2] cycloaddition with oxygen, alkenes and alkynes to give 2*H*-benzothiazin-3(4*H*)-ones with a spiro five-membered ring.

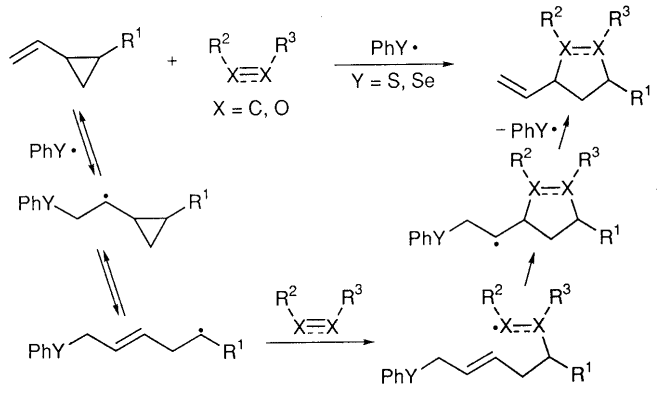

Fig. 1

Results and Discussion

2′-Vinyl-2*H*-benzothiazine-2-spirocyclopropan-3(4*H*)-ones (**1**) and 2′-vinyl-2*H*-benzothiazine-2-spirocyclopropan-3(4*H*)-one 1-oxides (**2**) were irradiated under a tungsten lamp at room temperature in the presence of a catalytic amount of diphenyl dichalcogenide (Chart 1, Table 1). 1,2-Dioxolane derivatives (**3**) were obtained as a mixture of diastereomers in good to high yields from benzothiazinones **1** (entries 1—4). Although **3a** and **3c** (R^1 = Me) were isolated as stable prisms (recrystallized from ether–hexane), **3b** was unstable and was converted to the β-ketol (**4**) in quantitative yield by treatment with silica gel.[7c] Diphenyl diselenide was slightly more effective than

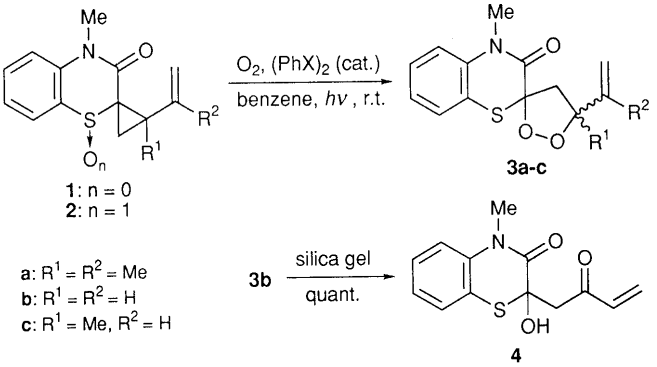

Chart 1

Table 1. Dioxolane Formation by Photochemical Oxygenation of Vinylcyclopropanes **1** and **2**

Entry	Cyclopropane	X	Time (h)	Product (% yield)
1	**1a**	Se	40	**3a** (94)[a]
2	**1a**	S	40	**3a** (88)[a]
3	**1b**	Se	12	**3b** (70)[b]
4	**1c**	Se	40	**3c** (95)[a]
5	**2a**	Se	40	Complex mixture
6	**2c**	Se	40	Complex mixture

a) Isolated yield. A mixture of diastereomers (1 : 1, estimated by the ^{1}H-NMR spectra). *b*) Crude yield. A mixture of diastereomers (9 : 1, estimated from the ^{1}H-NMR spectrum). The crude **3b** was converted to the heteroacetal **4** in quantitative yield by treatment with silica gel.

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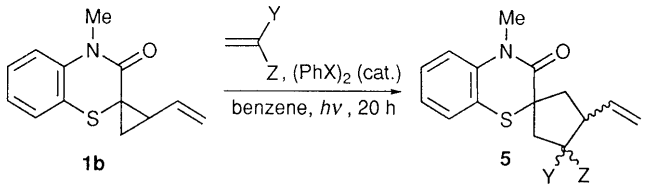


5a: Y = CO_2Me, Z = H
5b: Y = CO_2Et, Z = H
5c: Y = CN, Z = H
5d: Y = CN, Z = Cl
5e: Y = CHO, Z = H

Chart 2

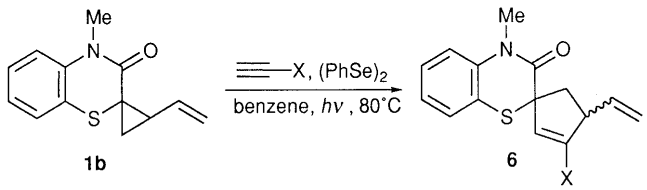
Table 2. Cyclopentane Formation by Photochemical [3+2] Cycloaddition of Vinylcyclopropane **1b** with Alkenes

Entry	X	Y	Z	Temp. (°C)	Product (% yield)[a]	Isomeric ratio
1	Se	CO_2Me	H	0	**5a** (13)	1.0:1.9:5.1:1.3[c]
2	Se	CO_2Me	H	20	**5a** (38)	1.0:2.3:5.1:1.3[c]
3	Se	CO_2Me	H	80	**5a** (91)	1.0:1.9:5.1:1.3[c]
4[b]	Se	CO_2Me	H	80	**5a** (85)	1.0:2.4:2.8:1.0[c]
5	S	CO_2Me	H	80	**5a** (20)	1.0:4.4:2.3:1.0[c]
6	Se	CO_2Et	H	80	**5b** (85)	1.0:2.0:3.4:0.7[c]
7	Se	CN	H	80	**5c** (94)	1.0:1.5:1.1:0.8[d]
8	Se	CN	Cl	80	**5d** (88)	1.0:1.7:1.9:0.9[d]
9	Se	CHO	H	80	**5e** (85)	1.0:1.5[d]
10	Se	CH_2Br	H	80	No Reaction	
11	Se	OEt	H	80	No Reaction	

a) Isolated yield. *b*) CH_3CN was used as a solvent. *c*) Inseparable mixtures of diastereomers were obtained. The ratio was estimated from the ^{1}H-NMR spectra. *d*) Separated ratio.

diphenyl disulfide as a radical source (entries 1, 2). In contrast with the reactions of benzothiazinones **1**, oxygenation of benzothiazinone 1-oxides **2** was unsuccessful, giving a complex mixture (entries 5, 6). Stabilization of a radical intermediate by the capto-dative structure[10] of **1** would promote addition of a chalcogen radical to the vinylcyclopropane and ring-opening processes.

Photochemical [3+2] cycloaddition of **1b** with some alkenes was examined (Chart 2, Table 2). Reactions were carried out by the use of 15 eq of alkenes and a catalytic amount of diphenyl dichalcogenide in benzene under nitrogen for 20 h by irradiation with a tungsten lamp. Spiro cyclopentane derivatives (**5**) were obtained from the reactions with activated alkenes (entries 1—9). The yields of **5a** were improved by raising the reaction temperature (entries 1—3). Use of diphenyl diselenide gave a considerably better result than that of diphenyl disulfide (entries 3, 5). Spiro cyclopentane derivatives bearing an ester group (**5a**, **5b**) were obtained as inseparable mixtures of diastereomers (entries 1—6). The ratios were estimated from the ^{1}H-NMR spectra. The ratio of the four diastereomers was changed slightly by the use of acetonitrile as a solvent (entries 3, 4). The four diastereomers could be isolated in the cases of the cyano derivatives (**5c**, **5d**) (entries 7, 8). The reaction with acrolein gave only two separable diastereomers (entry 9). In all cases, stereoselectivity was low. Reactions with allyl bromide and ethyl vinyl ether provided no cycloaddition product (entries 10, 11).



6a: X = CO_2Me
6b: X = CO_2Et

Chart 3

Table 3. Cyclopentene Formation in Photochemical [3+2] Cycloaddition of Vinylcyclopropane **1b** with Alkynes

Entry	X	$(PhSe)_2$ (eq.)	Time	Product (% yield)[a]	Isomeric ratio[b]
1	CO_2Me	0.1	20 h	**6a** (28)	1.0:2.0
2	CO_2Et	0.1	20 h	**6b** (30)	1.0:2.0
3	CO_2Et	0.1	4 d	**6b** (34)	1.0:3.0
4	CO_2Et	1	20 h	**6b** (66)	1.0:1.8
5	Ph	0.1	20 h	No Reaction	

a) Isolated yield. *b*) An inseparable mixture of diastereomers. The ratio was estimated from the ^{1}H-NMR spectra.

Photochemical [3+2] cycloaddition of **1b** was examined by the use of 15 eq of alkynes and diphenyl diselenide in benzene at 80 °C under nitrogen (Chart 3, Table 3). Reactions with methyl and ethyl propiolates in the presence of 0.1 eq of diphenyl diselenide for 20 h gave spiro cyclopentene derivatives (**6**) as an inseparable mixture of diastereomers in low yields (entries 1, 2). Prolonged reaction time (4 d) did not improve the yield of **6b** (entry 3). Compound **6b** was provided in good yield by the use of 1 eq of diphenyl diselenide (entry 4). Use of phenylacetylene gave no cycloaddition products (entry 5).

In conclusion, we studied the radical [3+2] cycloadditions of vinylcyclopropanes which are spiro-bound with a benzothiazine ring. Diphenyl diselenide was more effective as a radical initiator of the cycloaddition than diphenyl disulfide. The capto-dative structure presumably accelerates addition of a chalcogen radical to the vinylcyclopropane by stabilization of a radical intermediate. The reactions proceeded without azobisisobutyronitrile and with a weak tungsten lamp.[7] This transformation of the vinylcyclopropanes is applicable to the synthesis of new 2*H*-benzothiazin-3(4*H*)-one derivatives with a spiro five-membered ring which are of pharmacologically interest, since some benzothiazinones[1,2] possess potent pharmacological activity.

Experimental

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra of solids (KBr) and liquids (NaCl) were recorded on a JASCO IRA-100 spectrophotometer. ^{1}H-NMR spectra were recorded on a JEOL GX-270 (270 MHz) or a JEOL EX-400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. ^{13}C-NMR spectra and nuclear Overhauser effects (NOEs) were obtained on a JEOL EX-400 spectrometer. Mass spectra were recorded on a JEOL JMS-D 300 spectrometer with a direct-insertion probe at 70 eV. Elemental analyses of new compounds were performed by a Yanaco CHN Corder MT-5. All chromatographic isolations were accomplished with either Kieselgel 60 (Merck) or BW-127ZH (Fuji Silysia) for column chromatography or Kieselgel 60 PF_{254} containing gypsum (Merck) for preparative TLC.

Photochemical Oxygenation of Vinylcyclopropanes (1, 2) General Procedure A stirred solution of a vinylcyclopropane (0.5 mmol) and a catalytic amount of diphenyl diselenide (16 mg, 0.1 mmol) in dry benzene (1 ml) was irradiated with a tungsten lamp (60 W) at room temperature for 40 h. The reaction mixture was evaporated under reduced pressure and the residue was purified by preparative TLC with ethyl acetate–hexane (1 : 5) to give a dioxolane **3**. The reaction conditions and the yields are summarized in Table 1.

5′-Isopropenyl-4,5′-dimethyl-2*H*-1,4-benzothiazin-3(4*H*)-one-2-spiro-3′-1′,2′-dioxolane (**3a**): Colorless prisms as a 1 : 1 mixture of diastereomers (ether–hexane), mp 95—96 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.53, 1.55 (each 3H, s, Me), 1.85, 1.87 (each 3H, s, Me), 2.38, 2.62, 3.81, 4.22 (each 1H, d, J=13 Hz, 4′-H), 3.50, 3.54 (each 3H, s, NMe), 4.95, 4.96, 5.07, 5.13 (each 1H, s, olefinic H), 7.04—7.11 (total 4H, m, ArH), 7.25—7.39 (total 4H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 18.7 (q), 19.1 (q), 23.5 (q), 23.6 (q), 33.3 (q), 33.4 (q), 52.1 (t), 52.2 (t), 88.0 (s), 88.6 (s), 88.7 (s), 88.8 (s), 111.6 (t), 112.3 (t), 117.6 (d), 117.8 (d), 120.4 (s), 120.7 (s), 123.6 (d), 123.7 (d), 127.4 (d), 127.5 (d), 128.6 (d), 128.7 (d), 138.7 (s), 138.8 (s), 144.8 (s), 145.4 (s), 159.6 (s), 160.3 (s). MS m/z (rel. int. %): 291 (M^+, 25), 165 (100). IR (KBr) cm^{-1}: 1670 (C=O). *Anal.* Calcd for $C_{15}H_{17}NO_3S$: C, 61.83; H, 5.88; N, 4.81. Found: C, 61.83; H, 5.87; N, 4.86.

4-Methyl-5′-vinyl-2*H*-1,4-benzothiazin-3(4*H*)-one-2-spiro-3′-1′,2′-dioxolane (**3b**): Crude product after decantation with hexane. Colorless oil as a 9 : 1 mixture of diastereomers. ^{1}H-NMR ($CDCl_3$) δ: isomer$_{major}$: 2.38 (1H, dd, J=13, 8 Hz, 4′-H), 3.53 (3H, s, NMe), 4.01 (1H, dd, J=13, 7 Hz, 4′-H), 4.90—4.98 (1H, m, 5′-H), 5.37 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.47 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.85 (1H, ddd, J=17, 11, 7 Hz, C$\underline{H}$=CH$_2$), 7.04—7.16 (2H, m, ArH), 7.25—7.38 (2H, m, ArH); isomer$_{minor}$: 2.78 (1H, dd, J=13, 8 Hz, 4′-H), 3.53 (3H, s, NMe), 3.80 (1H, dd, J=13, 5 Hz, 4′-H), 4.90—4.98 (1H, m, 5′-H), 5.31 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.39 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.99 (1H, ddd, J=17, 10, 7 Hz, C$\underline{H}$=CH$_2$), 7.04—7.16 (2H, m, ArH), 7.25—7.38 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: isomer$_{major}$: 33.2 (q), 49.1 (t), 83.8 (d), 88.2 (s), 117.7 (d), 121.9 (t), 123.8 (d), 127.6 (d), 128.7 (d), 131.7 (d), 134.1 (s), 138.6 (s), 160.0 (s); isomer$_{minor}$: 33.3 (q), 48.0 (t), 83.1 (d), 86.9 (s), 117.4 (d), 119.8 (t), 120.3 (d), 127.6 (d), 129.1 (d), 130.6 (d), 136.6 (s), 138.8 (s), 160.4 (s). MS m/z (rel. int. %): 263 (M^+, 23), 166 (100). IR (NaCl) cm^{-1}: 1660 (C=O). HR-MS Calcd for $C_{13}H_{13}NO_3S$: 263.0616. Found: 263.0605.

4,5′-Dimethyl-5′-vinyl-2*H*-1,4-benzothiazin-3(4*H*)-one-2-spiro-3′-1′,2′-dioxolane (**3c**): Colorless prisms as a 1 : 1 mixture of diastereomers (ether–hexane), mp 115—116 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.53, 1.55 (each 3H, s, Me), 2.38, 2.55, 3.83, 4.03 (each 1H, d, J=13 Hz, 4′-H), 3.52, 3.54 (each 3H, s, NMe), 5.21, 5.27 (each 1H, d, J_{cis}=11 Hz, CH=C$\underline{H}_2$), 5.39 (total 2H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 6.04 (total 2H, dd, J=11, 17 Hz, C$\underline{H}$=CH$_2$), 7.04—7.12 (total 4H, m, ArH), 7.25—7.38 (total 4H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 22.6 (q), 22.8 (q), 33.3 (q×2), 53.0 (t), 53.3 (t), 86.3 (s), 86.5 (s), 88.0 (s), 88.4 (s), 115.1 (t), 116.5 (t), 117.6 (d), 117.7 (d), 120.3 (s), 120.5 (s), 123.7 (d×2), 127.5 (d×2), 128.6 (d×2), 138.1 (d), 138.7 (s), 138.8 (s), 139.3 (d), 159.8 (s), 160.3 (s). MS m/z (rel. int. %): 277 (M^+, 17%), 165 (100). IR (KBr) cm^{-1}: 1665 (C=O). *Anal.* Calcd for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45; N, 5.05. Found: C, 60.36; H, 5.44; N, 5.05.

Conversion of Dioxolane 3b to β-Ketol 4 with Silica Gel The crude dioxolane **3b** (92 mg, 0.35 mmol) was filtered through silica gel with ethyl acetate–hexane (1 : 4) to give a β-ketol **4** (92 mg) in quantitative yield.

2-Hydroxy-4-methyl-2-(2-oxo-3-butenyl)-2*H*-1,4-benzothiazin-3-(4*H*)-one (**4**): Pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 3.18, 3.39 (each 1H, d, J=16 Hz, 1′-H), 3.52 (3H, s, NMe), 5.62 (1H, br s, OH), 5.97 (1H, dd, J_{cis}=10, J_{gem}=1 Hz, CH=C$\underline{H}_2$), 6.32 (1H, dd, J_{trans}=17, J_{gem}=1 Hz, CH=C$\underline{H}_2$), 6.45 (1H, dd, J=17, 10 Hz, C$\underline{H}$=CH$_2$), 7.03—7.16 (2H, m, ArH), 7.12—7.36 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 33.5 (q), 43.7 (t), 88.2 (s), 117.7 (d), 120.6 (s), 124.1 (d), 127.8 (d), 129.3 (d), 130.9 (t), 136.8 (d), 139.4 (s), 165.1 (s), 200.2 (s). MS m/z (rel. int. %): 263 (M^+, 10), 166 (100). IR (NaCl) cm^{-1}: 3380 (OH), 1660 (amide and ketone). HR-MS Calcd for $C_{13}H_{13}NO_3S$: 263.0616. Found: 263.0628.

Photochemical [3+2] Cycloaddition of Vinylcyclopropane 1b General Procedure A stirred solution of the vinylcyclopropane **1b** (116 mg, 0.5 mmol), an alkene (7.5 mmol) and a catalytic amount of diphenyl diselenide (16 mg, 0.1 mmol) in degassed dry benzene (7 ml) was irradiated with a tungsten lamp (60 W) under nitrogen at 80 °C for 20 h. The reaction mixture was cooled and evaporated under reduced pressure and the residue was purified by preparative TLC with ethyl acetate–hexane (1 : 8) for **5a** and **5b** or with benzene–chloroform (3 : 1) for **5c—5e**. The reaction conditions and the yields are summarized in Table 2.

Methyl 3,4-Dihydro-4-methyl-3-oxo-4′-vinyl-1,4-benzothiazine-2-spiro-1′-cyclopentane-3′-carboxylate (**5a**): Fraction 1, colorless oil as a 1.0 : 1.9 mixture of diastereomers. ^{1}H-NMR ($CDCl_3$) δ: isomer$_{major}$: 1.88 (1H, dd, J=13, 8 Hz, 5′-H), 2.18 (1H, dd, J=14, 8 Hz, 2′-H), 2.42 (1H, dd, J=13, 7 Hz, 5′-H), 2.62 (1H, dd, J=14, 8 Hz, 2′-H), 3.06 (1H, dq, J=7, 8 Hz, 4′-H), 3.19 (1H, q, J=8 Hz, 3′-H), 3.47 (3H, s, NMe), 3.63 (3H, s, OMe), 4.97—5.05 (2H, m, CH=C$\underline{H}_2$), 5.78 (1H, ddd, J=17, 10, 8 Hz, C$\underline{H}$=CH$_2$), 7.00—7.07 (2H, m, ArH), 7.23—7.38 (2H, m, ArH); isomer$_{minor}$: 1.93 (1H, dd, J=14, 7 Hz, 5′-H), 2.02 (1H, dd, J=14, 9 Hz, 2′-H), 2.06 (1H, dd, J=14, 11 Hz, 5′-H), 2.76 (1H, q, J=9 Hz, 3′-H), 2.89 (1H, dd, J=14, 9 Hz, 2′-H), 3.21 (1H, dddd, J=11, 9, 8, 7 Hz, 4′-H), 3.48 (3H, s, NMe), 3.67 (3H, s, OMe), 5.01—5.09 (2H, m, CH=C$\underline{H}_2$), 5.75 (1H, ddd, J=17, 10, 8 Hz, C$\underline{H}$=CH$_2$), 7.00—7.07 (2H, m, ArH), 7.23—7.38 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: isomer$_{major}$: 33.0 (q), 38.1 (t), 41.8 (t), 46.0 (d), 48.2 (d), 49.9 (s), 51.5 (q), 116.3 (t), 116.9 (d), 123.1 (s), 123.2 (d), 127.1 (d), 128.5 (d), 137.1 (d), 139.8 (s), 169.3 (s), 173.6 (s); isomer$_{minor}$: 33.0 (q), 39.1 (t), 41.4 (t), 46.7 (d), 49.4 (d), 50.8 (s), 51.5 (q), 115.8 (t), 117.1 (d), 122.7 (s), 127.3 (d), 128.8 (d), 129.7 (d), 138.1 (d), 140.0 (s), 169.8 (s), 174.1 (s). MS m/z (rel. int. %): 317 (M^+, 100), 286 (M^+−OMe, 16), 258 (M^+−CO_2Me, 16). IR (NaCl) cm^{-1}: 1735 (C=O), 1660 (C=O). HR-MS Calcd for $C_{17}H_{19}NO_3S$: 317.1085. Found: 317.1078. Fraction 2, colorless oil as a 5.1 : 1.3 mixture of diastereomers. ^{1}H-NMR ($CDCl_3$) δ: isomer$_{major}$: 1.89 (1H, dd, J=14, 9 Hz, 2′-H), 1.89 (1H, dd, J=14, 5 Hz, 5′-H), 2.54 (1H, dd, J=14, 8 Hz, 5′-H), 2.63 (1H, dd, J=14, 9 Hz, 2′-H), 3.15—3.35 (2H, m, 3′- and 4′-H), 3.48 (3H, s, NMe), 3.62 (3H, s, OMe), 5.00 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.07 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.75 (1H, ddd, J=17, 10, 8 Hz, C$\underline{H}$=CH$_2$), 6.99—7.09 (2H, m, ArH), 7.23—7.34 (2H, m, ArH); isomer$_{minor}$: 1.56 (1H, dd, J=14, 9 Hz, 2′-H), 1.94 (1H, dd, J=14, 7 Hz, 5′-H), 2.33 (1H, dd, J=14, 11 Hz, 5′-H), 2.86 (1H, dd, J=14, 9 Hz, 2′-H), 2.88 (1H, ddt, J=11, 8, 7 Hz, 4′-H), 2.94 (1H, dt, J=8, 9 Hz, 3′-H), 3.47 (3H, s, NMe), 3.64 (3H, s, OMe), 5.00 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.07 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.71—5.80 (1H, m, C$\underline{H}$=CH$_2$), 6.99—7.09 (2H, m, ArH), 7.23—7.34 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: isomer$_{major}$: 33.0 (q), 36.4 (t), 39.6 (t), 44.6 (d), 47.0 (d), 51.4 (q), 51.7 (s), 116.3 (t), 117.3 (d), 122.4 (s), 123.1 (d), 127.3 (d), 128.8 (d), 136.9 (d), 140.2 (s), 168.5 (s), 173.1 (s); isomer$_{minor}$: 33.0 (q), 39.3 (t), 41.5 (t), 47.2 (d), 49.0 (d), 50.5 (s), 52.2 (q), 115.6 (t), 117.2 (d), 122.5 (s), 123.1 (d), 127.3 (d), 128.6 (d), 138.9 (d), 140.0 (s), 169.0 (s), 173.7 (s). MS m/z (rel. int. %): 317 (M^+, 100), 286 (M^+−OMe, 12), 258 (M^+−CO_2Me, 7). IR (NaCl) cm^{-1}: 1735 (C=O), 1660 (C=O). HR-MS Calcd for $C_{17}H_{19}NO_3S$: 317.1085. Found: 317.1080.

Ethyl 3,4-Dihydro-4-methyl-3-oxo-4′-vinyl-1,4-benzothiazine-2-spiro-1′-cyclopentane-3′-carboxylate (**5b**): Fraction 1, colorless oil as a 1 : 2 mixture of diastereomers. ^{1}H-NMR ($CDCl_3$) δ: isomer$_{major}$: 1.22 (3H, t, J=7 Hz, Me), 1.88 (1H, dd, J=13, 8 Hz, 5′-H), 2.18 (1H, dd, J=14, 8 Hz, 2′-H), 2.42 (1H, dd, J=13, 7 Hz, 5′-H), 2.60 (1H, dd, J=14, 8 Hz, 2′-H), 3.06 (1H, dq, J=7, 8 Hz, 4′-H), 3.15 (1H, q, J=8 Hz, 3′-H), 3.47 (3H, s, NMe), 4.06—4.12 (2H, m, OCH$_2$), 4.99 (1H, d, J_{cis}=11 Hz, CH=C$\underline{H}_2$), 5.03 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.79 (1H, ddd, J=17, 10, 8 Hz, C$\underline{H}$=CH$_2$), 7.00—7.07 (2H, m, ArH), 7.22—7.38 (2H, m, ArH); isomer$_{minor}$: 1.23 (3H, t, J=7 Hz, Me), 1.93 (1H, dd, J=14, 7 Hz, 5′-H), 2.02 (1H, dd, J=14, 9 Hz, 2′-H), 2.06 (1H, dd, J=14, 11 Hz, 5′-H), 2.63 (1H, q, J=9 Hz, 3′-H), 2.88 (1H, dd, J=14, 9 Hz, 2′-H), 3.21 (1H, dddd, J=11, 9, 8, 7 Hz, 4′-H), 3.48 (3H, s, NMe), 4.10—4.16 (2H, m, OC$\underline{H}_2$), 4.98 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.06 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.75 (1H, ddd, J=17, 10, 8 Hz, C$\underline{H}$=CH$_2$), 7.00—7.07 (2H, m, ArH), 7.22—7.38 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: isomer$_{major}$: 14.6 (q), 33.0 (q), 38.1 (t), 41.8 (t), 46.0 (d), 48.1 (d), 49.9 (s), 60.3 (t), 116.3 (t), 116.9 (d), 123.1 (s), 123.2 (d), 127.1 (d), 128.4 (d), 137.1 (d), 139.8 (s), 169.8 (s), 173.1 (s); isomer$_{minor}$: 14.6 (q), 33.0 (q), 38.1 (t), 41.8 (t), 46.0 (d), 48.1 (d), 49.9 (s), 60.3 (t), 116.3 (t), 116.9 (d), 123.1 (s), 123.2 (d), 127.1 (d), 128.4 (d), 137.1 (d), 139.8 (s), 169.8 (s), 173.1 (s). MS m/z (rel. int. %): 331 (M^+, 100), 286 (M^+−OEt, 25), 258 (M^+−CO_2Et, 21). IR (NaCl) cm^{-1}: 1730 (C=O), 1660 (C=O). HR-MS Calcd for $C_{18}H_{21}NO_3S$: 331.1242. Found: 331.1253. Fraction 2, colorless oil as a 3.4 : 0.7 mixture of diastereomers. ^{1}H-NMR ($CDCl_3$) δ: isomer$_{major}$: 1.21 (3H, t, J=7 Hz, Me), 1.88 (2H, dd, J=14, 7 Hz, 2′- and 5′-H), 2.54 (1H, dd, J=14, 8 Hz, 5′-H), 2.70 (1H, dd, J=14, 9 Hz, 2′-H), 3.19—3.31 (2H, m, 3′- and 4′-H), 3.48 (3H, s, NMe), 4.08 (2H, q, J=7 Hz, OCH$_2$), 5.00 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.07 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.78 (1H, ddd, J=17, 10, 8 Hz, C$\underline{H}$=CH$_2$), 6.99—7.08 (2H,

m, ArH), 7.24—7.34 (2H, m, ArH); isomer$_{minor}$: 1.21 (3H, t, J=7 Hz, Me), 1.56 (1H, dd, J=14, 9 Hz, 2′-H), 2.03 (1H, dd, J=14, 7 Hz, 5′-H), 2.42 (1H, dd, J=14, 11 Hz, 5′-H), 2.86 (1H, dd, J=14, 9 Hz, 2′-H), 2.88 (1H, ddt, J=11, 8, 7 Hz, 4′-H), 3.01 (1H, dt, J=8, 9 Hz, 3′-H), 3.47 (3H, s, NMe), 4.12 (2H, q, J=7 Hz, OCH_2), 4.99 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.07 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.79 (1H, ddd, J=17, 10, 7 Hz, C$\underline{H}$=CH_2), 6.99—7.08 (2H, m, ArH), 7.24—7.33 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: isomer$_{major}$: 14.2 (q), 33.0 (q), 36.4 (t), 39.7 (t), 44.6 (d), 47.0 (d), 52.2 (s), 60.4 (t), 116.3 (t), 117.3 (d), 122.5 (s), 123.1 (d), 127.3 (d), 128.8 (d), 136.9 (d), 140.2 (s), 168.6 (s), 172.7 (s); isomer$_{minor}$: 14.2 (q), 33.0 (q), 39.4 (t), 41.5 (t), 47.4 (d), 49.1 (d), 50.6 (s), 60.5 (t), 115.6 (t), 117.2 (d), 122.5 (s), 123.1 (d), 127.3 (d), 128.7 (d), 139.0 (d), 140.1 (s), 169.0 (s), 173.2 (s). MS m/z (rel. int. %): 331 (M^+, 100), 286 (M^+−OEt, 22), 258 (M^+−CO_2Et, 11). IR (NaCl) cm^{-1}: 1730 (C=O), 1660 (C=O). HR-MS Calcd for $C_{18}H_{21}NO_3S$: 331.1242. Found: 331.1256.

3,4-Dihydro-4-methyl-3-oxo-4′-vinyl-1,4-benzothiazine-2-spiro-1′-cyclopentane-3′-carbonitrile (**5c**): Fraction 1, colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.55 (1H, dd, J=14, 10 Hz, 5′-H), 2.16 (1H, dd, J=14, 7 Hz, 2′-H), 2.48 (1H, dd, J=14, 11 Hz, 2′-H), 2.45—2.98 (3H, m, 3′-, 4′-, 5′-H), 3.49 (3H, s, NMe), 5.16 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.24 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.73 (1H, ddd, J=17, 10, 8 Hz, C$\underline{H}$=CH_2), 7.03—7.11 (2H, m, ArH), 7.26—7.33 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 33.2 (q), 33.8 (d), 39.5 (t), 41.3 (t), 48.5 (d), 50.2 (s), 117.4 (d), 117.9 (t), 119.8 (s), 121.7 (s), 123.6 (d), 127.8 (d), 128.8 (d), 136.2 (d), 139.9 (s), 168.3 (s). MS m/z (rel. int. %): 284 (M^+, 76), 192 (100). IR (NaCl) cm^{-1}: 2250 (CN), 1660 (C=O). HR-MS Calcd for $C_{16}H_{16}N_2OS$: 284.0983. Found: 284.0992. Fraction 2, colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.96—2.02 (3H, m, 5′-H×2 and 2′-H), 2.69—2.78 (1H, m, 3′-H), 2.73 (1H, dd, J=14, 9 Hz, 2′-H), 2.80—3.18 (1H, m, 4′-H), 3.47 (3H, s, NMe), 5.15 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.24 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.71 (1H, ddd, J=17, 10, 7 Hz, C$\underline{H}$=CH_2), 7.04—7.09 (2H, m, ArH), 7.26—7.32 (1H, m, ArH), 7.35—7.40 (1H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 33.1 (q), 34.2 (d), 39.6 (t), 41.2 (t), 47.8 (d), 50.5 (s), 117.3 (d), 118.0 (t), 120.3 (s), 121.9 (s), 123.7 (d), 127.7 (d), 128.9 (d), 135.6 (d), 139.7 (s), 168.6 (s). MS m/z (rel. int. %): 284 (M^+, 100). IR (NaCl) cm^{-1}: 2250 (CN), 1655 (C=O). HR-MS Calcd for $C_{16}H_{16}N_2OS$: 284.0983. Found: 284.0988. Fraction 3, colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.92 (1H, dd, J=14, 7 Hz, 5′-H), 2.08 (1H, dd, J=15, 8 Hz, 2′-H), 2.39 (1H, dd, J=14, 10 Hz, 5′-H), 2.85 (1H, dd, J=15, 7 Hz, 2′-H), 3.12—3.21 (1H, m, 3′-H), 3.26—3.32 (1H, m, 4′-H), 3.49 (3H, s, NMe), 5.19—5.24 (2H, m, CH=C$\underline{H}_2$), 5.92 (1H, ddd, J=18, 11, 8 Hz, C$\underline{H}$=CH_2), 7.03—7.11 (2H, m, ArH), 7.26—7.34 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 33.2 (q), 33.3 (d), 38.5 (t), 39.7 (t), 44.0 (d), 51.7 (s), 117.5 (d), 118.3 (t), 119.4 (s), 121.7 (s), 123.5 (d), 127.8 (d), 128.9 (d), 135.4 (d), 140.0 (s), 167.7 (s). MS m/z (rel. int. %): 284 (M^+, 100). IR (NaCl) cm^{-1}: 2250 (CN), 1660 (C=O). HR-MS Calcd for $C_{16}H_{16}N_2OS$: 284.0983. Found: 284.0983. Fraction 4, yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.90 (1H, dd, J=14, 10 Hz, 5′-H), 2.11 (1H, dd, J=14, 5 Hz, 2′-H), 2.48 (1H, dd, J=14, 7 Hz, 5′-H), 2.85 (1H, dd, J=14, 8 Hz, 2′-H), 2.96 (1H, ddt, J=10, 8, 7 Hz, 4′-H), 3.21 (1H, ddd, J=8, 7, 5 Hz, 3′-H), 3.48 (3H, s, NMe), 5.18 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.24 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.73 (1H, ddd, J=17, 10, 8 Hz, C$\underline{H}$=CH_2), 7.03—7.10 (2H, m, ArH), 7.26—7.33 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 33.1 (q), 34.2 (d), 39.7 (t), 42.1 (t), 45.6 (d), 49.6 (s), 117.1 (d), 118.3 (t), 119.8 (s), 122.2 (s), 123.6 (d), 127.5 (d), 128.7 (d), 135.5 (d), 139.6 (s), 168.9 (s). MS m/z (rel. int. %): 284 (M^+, 82), 192 (100). IR (NaCl) cm^{-1}: 2250 (CN), 1660 (C=O). HR-MS Calcd for $C_{16}H_{16}N_2OS$: 284.0983. Found: 284.0991.

3′-Chloro-3,4-dihydro-4-methyl-3-oxo-4′-vinyl-1,4-benzothiazine-2-spiro-1′-cyclopentane-3′-carbonitrile (**5d**): Fraction 1, colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.96 (1H, dd, J=14, 12 Hz, 5′-H), 2.73 (1H, d, J=15 Hz, 2′-H), 2.81 (1H, dd, J=14, 7 Hz, 5′-H), 3.01 (1H, d, J=15 Hz, 2′-H), 3.06 (1H, dt, J=12, 7 Hz, 4′-H), 3.50 (3H, s, NMe), 5.33 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.36 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.89 (1H, ddd, J=17, 10, 7 Hz, C$\underline{H}$=CH_2), 7.08—7.11 (2H, m, ArH), 7.32 (1H, dt, J=8, 1 Hz, ArH), 7.42 (1H, dd, J=8, 1 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 33.4 (q), 40.3 (t), 47.3 (s), 50.6 (t), 56.5 (d), 60.0 (s), 117.4 (d), 117.4 (s), 121.3 (t), 121.6 (s), 123.9 (d), 127.9 (d), 129.1 (d), 131.7 (d), 139.6 (s), 168.0 (s). MS m/z (rel. int. %): 318 (M^+, 78), 283 (M^+−Cl, 30), 139 (100). IR (NaCl) cm^{-1}: 2260 (CN), 1665 (C=O). HR-MS Calcd for $C_{16}H_{15}ClN_2OS$: 318.0594. Found: 318.0582. Fraction 2, colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.93 (1H, dd, J=14, 6 Hz, 5′-H), 2.57 (1H, dd, J=14, 13 Hz, 5′-H), 2.60 (1H, d, J=16 Hz, 2′-H), 3.43 (1H, ddd, J=13, 7, 6 Hz, 4′-H), 3.51 (3H, s, NMe), 3.53 (1H, d, J=16 Hz, 2′-H), 5.32 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.33 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.85 (1H, ddd, J=17, 10, 7 Hz, C$\underline{H}$=CH_2), 7.06—7.13 (2H, m, ArH), 7.30—7.38 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 33.4 (q), 37.6 (t), 49.4 (s), 51.7 (t), 53.7 (d), 62.2 (s), 117.7(d), 118.0 (s), 120.8 (t), 121.7 (s), 123.7 (d), 128.1 (d), 129.0 (d), 131.7 (d), 140.0 (s), 167.0 (s). MS m/z (rel. int. %): m/z 318 (M^+, 87), 306 (100), 283 (M^+−Cl, 43). IR (NaCl) cm^{-1}: 2260 (CN), 1660 (C=O). HR-MS Calcd for $C_{16}H_{15}ClN_2OS$: 318.0594. Found: 318.0617. Fraction 3, colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 2.15 (1H, t, J=13 Hz, 5′-H), 2.56 (1H, d, J=16 Hz, 2′-H), 2.58 (1H, dd, J=13, 7 Hz, 5′-H), 3.17 (1H, dt, J=13, 7 Hz, 4′-H), 3.48 (1H, d, J=16 Hz, 2′-H), 3.50 (3H, s, NMe), 5.29 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.31 (1H, d, J_{cis}=11 Hz, CH=C$\underline{H}_2$), 5.81 (1H, ddd, J=17, 11, 7 Hz, C$\underline{H}$=CH_2), 7.05—7.12 (2H, m, ArH), 7.26—7.40 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 33.4 (q), 40.4 (t), 48.1 (s), 50.8 (t), 55.0 (d), 62.8 (s), 117.3 (d), 117.5 (s), 120.9 (t), 121.7 (s), 123.8 (d), 127.8 (d), 128.9 (d), 131.8 (d), 139.5 (s), 168.2 (s). MS m/z (rel. int. %): 318 (M^+, 56), 283 (M^+−Cl, 100). IR (NaCl) cm^{-1}: 2250 (CN), 1655 (C=O). HR-MS Calcd for $C_{16}H_{15}ClN_2OS$: 318.0594. Found: 318.0575. Fraction 4, colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 2.05 (1H, dd, J=14, 6 Hz, 5′-H), 2.27 (1H, dd, J=14, 12 Hz, 5′-H), 2.33 (1H, d, J=15 Hz, 2′-H), 3.31 (1H, ddd, J=12, 8, 6 Hz, 4′-H), 3.50 (3H, s, NMe), 3.82 (1H, d, J=15 Hz, 2′-H), 5.31 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.34 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.89 (1H, ddd, J=17, 10, 7 Hz, C$\underline{H}$=CH_2), 7.05—7.12 (2H, m, ArH), 7.30—7.37 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 33.4 (q), 39.0 (t), 48.8 (s), 50.4 (t), 55.5 (d), 60.4 (s), 116.9 (s), 117.6 (d), 121.1 (t), 121.6 (s), 123.7 (d), 128.0 (d), 129.0 (d), 131.6 (d), 139.8 (s), 167.1 (s). MS m/z (rel. int. %): 318 (M^+, 100), 283 (M^+−Cl, 18). IR (NaCl) cm^{-1}: 2260 (CN), 1665 (C=O). HR-MS Calcd for $C_{16}H_{15}ClN_2OS$: 318.0594. Found: 318.0577.

3′-Chloro-3,4-dihydro-4-methyl-3-oxo-4′-vinyl-1,4-benzothiazine-2-spiro-1′-cyclopentane-3′-carbaldehyde (**5e**): Fraction 1, pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.97 (1H, dd, J=14, 7 Hz, 5′-H), 2.04 (1H, dd, J=13, 6 Hz, 2′-H), 2.18 (1H, dd, J=14, 11 Hz, 5′-H), 2.72 (1H, dd, J=13, 10 Hz, 2′-H), 2.74 (1H, dddd, J=11, 10, 6, 2 Hz, 3′-H), 3.10—3.17 (1H, m, 4′-H), 3.48 (3H, s, NMe), 5.05 (1H, d, J_{cis}=10 Hz , CH=C$\underline{H}_2$), 5.12 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.80 (1H, ddd, J=17, 10, 8 Hz, C$\underline{H}$=CH_2), 7.02—7.09 (2H, m, ArH), 7.24—7.34 (2H, m, ArH), 9.65 (1H, d, J=2 Hz, CHO). ^{13}C-NMR ($CDCl_3$) δ: 33.1 (q), 35.2 (t), 41.2 (t), 44.0 (d), 51.8 (s), 56.0 (d), 116.3 (t), 117.3 (d), 122.1 (s), 123.5 (d), 127.5 (d), 129.0 (d), 138.2 (d), 140.0 (s), 168.9 (s), 201.4 (s). MS m/z (rel. int. %): 287 (M^+, 100). IR (NaCl) cm^{-1}: 2825, 2730 (aldehyde C–H), 1720 (CHO), 1660 (C=O). HR-MS Calcd for $C_{16}H_{17}NO_2S$: 287.0980. Found: 287.0974. Fraction 2, pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.65 (1H, dd, J=13, 10 Hz, 5′-H), 1.97 (1H, dd, J=14, 8 Hz, 2′-H), 2.54 (1H, dd, J=14, 9 Hz, 2′-H), 2.71 (1H, dd, J=13, 8 Hz, 5′-H), 2.80—2.88 (1H, m, 3′-H), 2.94—3.04 (1H, m, 4′-H), 3.47 (3H, s, NMe), 5.04 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.19 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.78 (1H, ddd, J=17, 10, 7 Hz, C$\underline{H}$=CH_2), 7.01—7.09 (2H, m, ArH), 7.25—7.35 (2H, m, ArH), 9.64 (1H, d, J=2 Hz, CHO). ^{13}C-NMR ($CDCl_3$) δ: 33.0 (q), 36.0 (t), 42.6 (t), 44.8 (d), 50.6 (s), 56.0 (d), 116.2 (t), 117.2 (d), 122.4 (s), 123.4 (d), 127.4 (d), 128.6 (d), 138.6 (d), 139.9 (s), 169.2 (s), 201.7 (s). MS m/z (rel. int. %): 287 (M^+, 47), 192 (100). IR (NaCl) cm^{-1}: 2825, 2730 (aldehyde C–H), 1720 (CHO), 1660 (C=O). HR-MS Calcd for $C_{16}H_{17}NO_2S$: 287.0980. Found: 287.0970.

Photochemical [3+2] Cycloaddition of the Vinylcyclopropane 1b General Procedure A stirred solution of the vinylcyclopropane **1b** (116 mg, 0.5 mmol), an alkyne (7.5 mmol) and a catalytic amount of diphenyl diselenide (16 mg, 0.1 mmol) in degassed dry benzene (7 ml) was irradiated with a tungsten lamp (60 W) under nitrogen at 80 °C for 20 h. The reaction mixture was cooled and evaporated under reduced pressure and the residue was purified by preparative TLC with ethyl acetate–hexane (1 : 8). The reaction conditions and the yields are summarized in Table 3.

Methyl 3,4-Dihydro-4-methyl-3-oxo-4′-vinyl-1,4-benzothiazine-2-spiro-1′-cyclopent-2′-ene-3′-carboxylate (**6a**): Fraction 1, pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 2.23 (1H, dd, J=14, 8 Hz, 5′-H), 2.65 (1H, dd, J=14, 6 Hz, 5′-H), 3.49 (3H, s, NMe), 3.70 (3H, s, OMe), 3.78—3.83 (1H, m, 4′-H), 5.05 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.14 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.87 (1H, ddd, J=17, 10, 8 Hz, C$\underline{H}$=CH_2), 6.46 (1H, d, J=2 Hz, 2′-H), 7.03—7.12 (2H, m, ArH), 7.26—7.35 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 33.1 (q), 39.4 (t), 47.4 (d), 51.6 (q), 56.5 (s), 115.9 (t), 117.5 (d), 121.9 (s), 123.6 (d), 127.5 (d), 128.8 (d), 138.4 (d), 139.5 (d), 139.7 (s), 141.1 (s), 164.4 (s), 166.3 (s). MS m/z (rel. int.

%): 315 (M^+, 100), 284 ($M^+ - OMe$, 10). IR (NaCl) cm^{-1}: 1730 (C=O), 1665 (C=O), 1265 (C–O). HR-MS Calcd for $C_{17}H_{17}NO_3S$: 315.0929. Found: 315.0917. Fraction 2, pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.86 (1H, dd, J=14, 3 Hz, 5′-H), 3.15 (1H, dd, J=14, 9 Hz, 5′-H), 3.49 (3H, s, NMe), 3.69 (3H, s, OMe), 3.78—3.81 (1H, m, 4′-H), 5.07 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.16 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.96 (1H, ddd, J=17, 10, 8 Hz, C$\underline{H}$=CH_2), 6.45 (1H, d, J=1 Hz, 2′-H), 7.04—7.11 (2H, m, ArH), 7.24—7.44 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 33.1 (q), 39.4 (t), 48.0 (d), 51.6 (q), 56.4 (s), 115.9 (t), 117.4 (d), 121.8 (s), 123.6 (d), 127.5 (d), 128.7 (d), 139.0 (d), 139.2 (d), 139.6 (s), 141.2 (s), 164.3 (s), 167.0 (s). MS m/z (rel. int. %): 315 (M^+, 100). IR (NaCl) cm^{-1}: 1720 (C=O), 1660 (C=O), 1255 (C–O). HR-MS Calcd for $C_{17}H_{17}NO_3S$: 315.0929. Found: 315.0920.

Ethyl 3,4-Dihydro-4-methyl-3-oxo-4′-vinyl-1,4-benzothiazine-2-spiro-1′-cyclopent-2′-ene-3′-carboxylate (**6b**): Fraction 1, yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.25 (3H, t, J=7 Hz, Me), 2.23 (1H, dd, J=14, 8 Hz, 5′-H), 2.63 (1H, dd, J=14, 6 Hz, 5′-H), 3.49 (3H, s, NMe), 3.78—3.83 (1H, m, 4′-H), 4.16 (2H, q, J=7 Hz, OCH_2), 5.04 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.13 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.87 (1H, ddd, J=17, 10, 8 Hz, C$\underline{H}$=CH_2), 6.46 (1H, d, J=2 Hz, 2′-H), 7.02—7.11 (2H, m, ArH), 7.26—7.35 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 14.1 (q), 33.1 (q), 39.5 (t), 47.4 (d), 56.5 (s), 60.6 (t), 115.8 (t), 117.5 (d), 121.9 (s), 123.5 (d), 127.5 (d), 128.7 (d), 138.4 (d), 139.1 (d), 139.7 (s), 141.4 (s), 164.0 (s), 166.9 (s). MS m/z (rel. int. %): 329 (M^+, 100), 284 ($M^+ - OEt$, 14). IR (NaCl) cm^{-1}: 1720 (C=O), 1665 (C=O). HR-MS Calcd for $C_{18}H_{19}NO_3S$: 329.1085. Found: 329.1081. Fraction 2, yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.24 (3H, t, J=7 Hz, Me), 1.87 (1H, dd, J=14, 3 Hz, 5′-H), 3.14 (1H, dd, J=14, 9 Hz, 5′-H), 3.49 (3H, s, NMe), 3.77—3.81 (1H, m, 4′-H), 4.08—4.19 (2H, m, OCH_2), 5.06 (1H, d, J_{cis}=10 Hz, CH=C$\underline{H}_2$), 5.17 (1H, d, J_{trans}=17 Hz, CH=C$\underline{H}_2$), 5.64 (1H, ddd, J=17, 10, 8 Hz, C$\underline{H}$=CH_2), 6.45 (1H, d, J=1 Hz, 2′-H), 7.03—7.11 (2H, m, ArH), 7.22—7.29 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 14.4 (q), 33.5 (q), 39.8 (t), 48.4 (d), 56.8 (s), 61.0 (t), 116.2 (t), 117.7 (d), 122.2 (s), 123.9 (d), 127.8 (d), 129.0 (d), 139.2 (d), 139.4 (d), 139.9 (s), 141.9 (s), 164.2 (s), 167.3 (s). MS m/z (rel. int. %): 329 (M^+, 77), 284 ($M^+ - OEt$, 13), 191 (100). IR (NaCl) cm^{-1}: 1720 (C=O), 1655 (C=O), 1230 (C–O). HR-MS Calcd for $C_{18}H_{19}NO_3S$: 329.1085. Found: 329.1092.

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