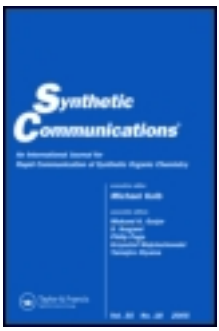

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BENZODIAZEPINE ANALOGUES. PART 8.[1] TRIMETHYLSILYL AZIDE MEDIATED SCHMIDT REARRANGEMENT of THIOFLAVANONE and THIOCHROMANONE PRECURSORS.

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ABSTRACT: The synthesis and Schmidt rearrangment of a series of thioflavanone analogues to benzothiazepinone derivatives is described.

Various benzothiazepinones, including the clinically useful analogues thiazesim and diltiazem, have been shown to exhibit pharmacological activity.[1-3] In previous communications,[4] we have reported the synthesis and mass spectrometric analysis of benzoxazepinone, benzodioxepinone and benzodiazepinone systems. The conformational preferences and receptor binding affinities of these compounds are being examined and, for comparative purposes, sulphur-containing analogues were required.

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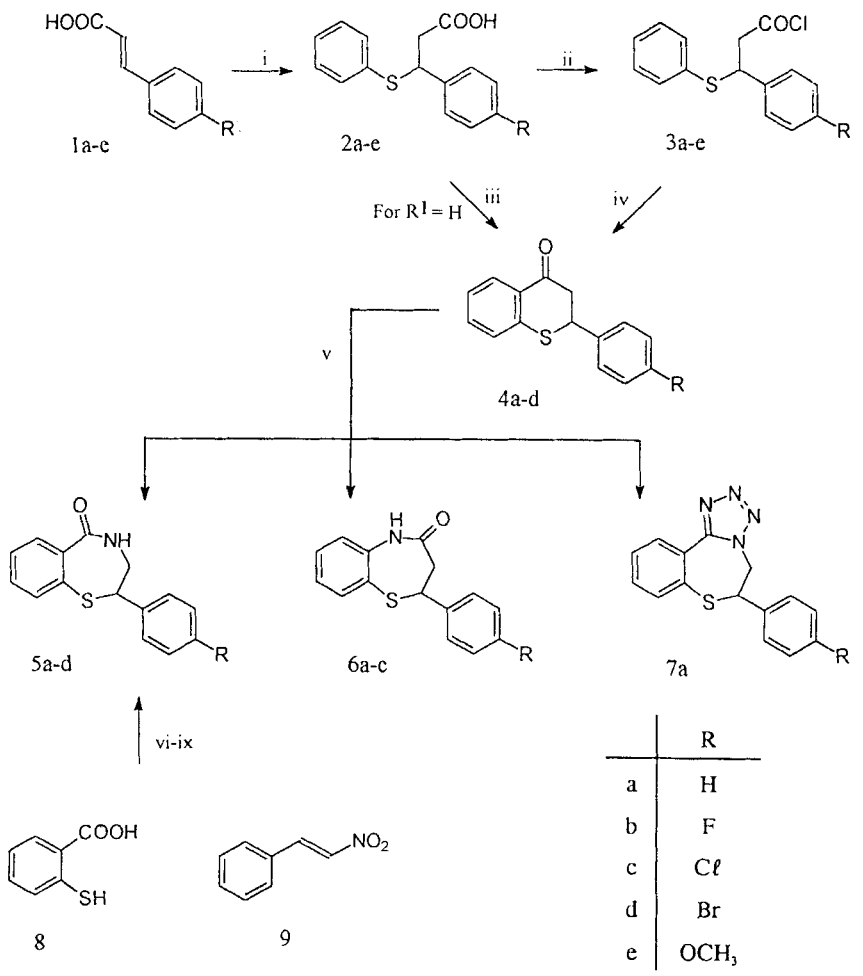
Both cyclisation and ring-expansion approaches to the synthesis of benzothiazepinones have been described. For example, 2-aminothiophenol has been condensed with 3-bromopropanoic acids [5] and with cinnamic and related α,β-unsaturated acids.[6] In analogous condensations, reaction of 2-nitrothiophenols with 3-bromopropanoic acid [5] afforded nitro intermediates, resolution, reduction and cyclisation of which provided access to optically active 2,3-dihydro-1,5-benzothiazepin-4(5*H*)-ones.[7] Alternative, ring-expansion approaches *via* Schmidt or Beckmann rearrangement of thiochromanone or thioflavanone precursors have also been reported.[8-10] Lévai,[10] for example, obtained a *ca* 1:1 mixture of 2-phenyl-2,3-dihydro-1,4-benzothiazepin-5(4*H*)-one **5a** and its 1,5-regioisomer **6a** by treating thioflavanone **4a** with sodium azide in acid medium. In our synthesis of benzothiazepinones, we have largely followed a ring-expansion strategy to access the regioisomeric products **5a-d** and **6a-c** from the thioflavanones **4a-d** (Scheme 1).

The thioflavanones **4a-d** were obtained *via* a modification of Arndt's procedure.[11] Conjugate addition of thiophenol to the cinnamic acids **1a-e** gave, as expected, the corresponding 3-(phenylmercapto)propanoic acids **2a-e** (Scheme 1) but, while $POC\ell_3$-catalysed cyclisation of the parent system **2a** proceeded smoothly to afford thioflavanone **4a**, attempted extension of the method to the acids **2b-e** proved unsuccessful. Use of polyphosphoric acid or concentrated sulphuric acid [12] also failed to effect cyclisation to the expected products and, consequently, the 3-(phenylmercapto)propanoic acids **2a-e** were



	R
a	H
b	F
c	Cℓ
d	Br
e	OCH_3

Reagents: i) PhSH, HBr, CH_3CO_2H, heat; ii) $SOC\ell_2$, $CHC\ell_3$, heat; iii) $POC\ell_3$, heat; iv) $A\ell C\ell_3$, heat; v) TMS-N_3, CF_3CO_2H; vi) CH_3CH_2OH, heat; vii) $SOC\ell_2$, $CHC\ell_3$, heat; viii) $SnC\ell_2 . 2H_2O$, CH_3OH - CH_3CO_2H, heat; ix) Heat.

SCHEME 1

converted to the corresponding acid chlorides **3a-e** using thionyl chloride. The required thioflavanones **4a-d** were then obtained by Friedel-Crafts cyclisation of the crude acid chlorides, using equimolar quantities of aluminium chloride as catalyst. The failure of compound **2e** to undergo cyclisation may have been due to co-ordination of the 4′-methoxy group with the catalyst.[13]

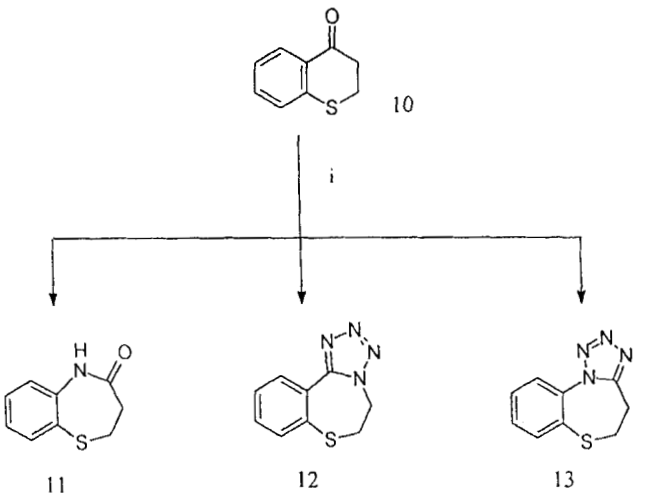
Schmidt rearrangement of the thioflavanones **4a-d** was then achieved using trimethylsilyl azide (TMS-N_3) in trifluoroacetic acid,[14] rather than the hydrazoic acid systems used by previous researchers. Trace quantities of the tetrazolo-1,4-benzothiazepines **7a-d** were detected in the reaction mixtures, but isolation was only possible in the case of the parent system **7a**. The formation of both 1,4- and 1,5-regiosomeric benzothiazepinones is somewhat surprising since, in our previous studies, trimethylsilyl azide mediated Schmidt rearrangement of flavanones [4a] and 2-arylquinolones [4f] has proceeded *regioselectively* to afford the corresponding 1,4-products only. In Baeyer-Villiger reactions of flavanones, however, we have noted [4c] a reversal of this regioselectivity with exclusive formation of the 1,5-benzodioxepin-2-ones, and kinetic studies have been undertaken to explain the observed trends.[15] The parent 1,4-benzothiazepin-5(4*H*)-one **5a** was shown to be identical to the product obtained following the reported [2] condensation of thiosalicyclic acid **8** with β-nitrostyrene **9**. The most striking differences between the ^{1}H NMR spectra of the 1,4-benzothiazepin-5(4*H*)-ones **5**, their 1,5-analogues **6** and tetrazolo derivatives **7** lie in the aliphatic region (*ca* δ 3 - 5 ppm), the methylene multiplets shifting progressively downfield as the

adjacent functionality changes from CO (**6a**; *ca* δ 3) to NH (**5a**; *ca* δ 3.5) and, finally, to the tetrazolo moeity (**7a**; *ca* δ 5), the signal multiplicity, in each case, reflecting the diastereotopicity of the methylene protons.

Wünsch *et al.*[8] have shown that hydrazoic acid mediated Schmidt rearrangement of thiochromanones affords both 1,4- and 1,5-benzothiazepinones. Treatment of thiochromanone **10** with trimethylsilyl azide in trifluoroacetic acid, however, afforded 2,3-dihydro-1,5-benzothiazepin-4(5*H*)-one **11** together with the regioisomeric tetrazolo derivatives **12** and **13** (Scheme 2); none of the 1,4-benzothiazepinone was isolated. The [5,1-*d*]tetrazolo derivative **13** has been obtained previously *via* nitrosation of 2,3-dihydro-1,5-benzothiazepin-4-yl-hydrazine,[16] but the [1,5-*d*]tetrazolo analogue **12** is new. The benzothiazepinone **11** is readily distinguished from the tetrazolo products **12** and **13** by both their IR (the lactam moiety in compound **11** giving rise to characteristic NH and CO absorption bands) and their NMR spectra [the C=O ^{13}C signal, for example, appearing significantly downfield (δ 173.9 ppm) of the C=N signals (*ca.* 153 ppm.)].

EXPERIMENTAL

^1H And ^{13}C NMR spectra were obtained for solutions in $CDC\ell_3$ on a Bruker AMX 400 spectrometer and were typically referenced using the solvent peaks (δ_H 7.25 and δ_C 77.0 ppm). Low resolution MS spectra were recorded on



Reagents: i) TMS-N_3, CF_3CO_2H.

SCHEME 2

a Hewlett-Packard 5988A mass spectrometer and high resolution analyses were performed on a Kratos double focusing magnetic sector instrument (Cape Technikon Mass Spectrometry Unit).

The 3-(phenylmercapto)propanoic acids **2a-e** were prepared by reacting the corresponding cinnamic acids **1a - e** with thiophenol,[11] and cyclised *via* the crude acid chlorides **3a-d** to the 4′-substituted thioflavanones **4a-d**. Thioflavanone **4a** was also obtained by direct cyclisation of the acid **2a** as described by Arndt.[11] Formation of the ring-expanded products **5**, **6** and **7** was achieved by treating the thioflavanones **4** with trimethylsilyl azide in trifluoroacetic acid; the known

1,4-benzothiazepinone **5a** was also obtained directly from thiosalicyclic acid **8** and β-nitrostyrene **9**.[2] The experimental procedures are illustrated by the following examples.

*2-Phenyl-2,3-dihydro-4*H*-1-benzothiopyran-4-one* **4a**.— A stirred mixture of 3-phenyl-3-(phenylmercapto)propanoic acid **2a** (10.0 g, 38.8 mmol) and $SOC\ell_2$ (5.49 g, 46.5 mmol) in chloroform (30 ml) was boiled under reflux for 30 min. The mixture was evaporated *in vacuo* and the crude acid chloride **3a** was taken up in CS_2 (10 ml) and added dropwise to a stirred suspension of $A\ell C\ell_3$ (5.21 g, 46.6 mmol) in CS_2 (25 ml) at 0-5°C. The mixture was then boiled under reflux for 30 minutes, cooled and poured slowly with shaking into a mixture of crushed ice (40 g) and $HC\ell$ (20 ml). The product was extracted with $CHC\ell_3$ (3 x 30 ml) and the combined organic extracts were washed, sequentially, with 10% aq. NaOH (2 x 20 ml) and water (2 x 20 ml), and then dried (anhyd. $MgSO_4$). The solvent was removed by evaporation *in vacuo* and the residue was purified by flash chromatography (on silica; elution with benzene) to afford 2-phenyl-2,3-dihydro-4*H*-1-benzothiopyran-4-one **4a** (4.46 g, 48%), m.p. 54-56°C (from CS_2-hexane) (lit.[11] 55 - 56°C); δ_H (400 MHz, $CDC\ell_3$) 3.20 and 3.31 (2H, 2 x dd, CH_2), 4.72 (1H, dd, 2-H), 7.18-7.43 (8H, ArH) and 8.15 (1H, dd, 5-H); δ_C (100 MHz, $CDC\ell_3$) 45.5 (C-3), 47.7 (C-2), 125.2 (C-8), 127.2 (C-6), 127.4 (C-2′ and C-6′), 128.4 (C-4′), 129.0 (C-3′ and C-5′), 129.2 (C-5), 130.4 (C-4a), 133.6 (C-7), 138.4 (C-1′), 142.1 (C-8a) and 194.3 (C-4); ν_{max} (KBr) 1673 (C=O) cm^{-1}; *m/z* 240 (M^+, 31.6%) and 136 (100%).

*2-Phenyl-2,3-dihydro-1,4-benzothiazepin-5(4*H*)-one* **5a**, *2-phenyl-2,3-dihydro-1,5-benzothiazepin-4(5*H*)-one* **6a** and *6-phenyl-5,6-dihydrotetrazolo[1,5-*d*][1,4]-benzothiazepine* **7a**.— Trimethylsilyl azide (1.44 g, 12.5 mmol) was added dropwise to a stirred solution of 2-phenyl-2,3-dihydro-4*H*-1-benzothiopyran-4-one **4a** (2.0 g, 8.3 mmol) in trifluoroacetic acid (25 mℓ) at room temperature under N_2. After stirring for *ca* 3d., the solvent was evaporated *in vacuo*, and the residue purified by flash chromatography [elution with EtOAc-hexane (3:2)] to afford three fractions, *viz.*,

(i) 2-phenyl-2,3-dihydro-1,4-benzothiazepin-5(4*H*)-one **5a** (0.85 g, 40%), m.p. 186°C (from EtOH) (lit.,[2] 186-188°C); δ_H (400 MHz, $CDC\ell_3$) 3.37 and 3.57 (2H, 2 x m, CH_2), 4.61 (1H, dd, 2-H) and 7.20-7.80 (10H, NH and ArH); δ_C (100 MHz, $CDC\ell_3$) 47.5 (C-3), 56.2 (C-2), 127.3 (C-2′ and C-6′), 128.0 (C-9), 128.8 (C-3′ and C-5′), 129.2 (C-4′), 129.9 (C-7), 130.2 (C-5a), 131.7 (C-6), 134.3 (C-8), 139.9 (C-1′), 141.2 (C-9a) and 172.5 (C-5); ν_{max} (KBr) 3310 (NH) and 1750 (C=O) cm^{-1}; *m/z* 255 (M^+, 52.1%) and 226 (100%); and

(ii) 2-phenyl-2,3-dihydro-1,5-benzothiazepin-4(5*H*)-one **6a** (0.63 g, 20%), m.p. 176°C (from EtOH) (lit.,[10] 180-181°C); δ_H (400 MHz, $CDC\ell_3$) 2.86 (2H, m, CH_2), 4.89 (1H, dd, 2-H), 7.17-7.65 (9H, ArH) and 8.20 (1H, br s, NH); δ_C (100 MHz, $CDC\ell_3$) 41.5 (C-3), 53.2 (C-2), 123.2 (C-9), 126.4 (C-2′ and C-6′), 126.7 (C-5a and C-7), 127.8 (C-4′), 128.8 (C-3′ and C-5′), 130.2 (C-6), 135.9 (C-8), 141.3 (C-1′), 143.3 (C-9a) and 172.1 (C-4); ν_{max} (KBr) 3220 (NH) and 1650 (C=O) cm^{-1}; and

(iii) *6-phenyl-5,6-dihydrotetrazolo[1,5-d][1,4]benzothiazepine* **7a** (0.51 g, 22%), m.p. 124°C (from EtOH) (Found: M^+, 280.0780. $C_{15}H_{12}N_4S$ requires *M*, 280.0783); δ_H (400 MHz, $CDC\ell_3$) 4.71 (1H, dd, 2-H), 4.88 and 5.04 (2H, 2 x dd, CH_2), 7.30-8.14 (9H, ArH); δ_C (100 MHz, $CDC\ell_3$) 53.5 (C-3), 54.7 (C-2), 127.1 (C-2′ and C-6′), 128.0 (C-5a), 128.8 (C-9), 129.3 (C-3′, C-4′ and C-5′), 131.2 (C-7), 132.1 (C-8), 134.2 (C-1′), 134.2 (C-6), 138.6 (C-9a) 154.2 (C-5); ν_{max} (KBr) 1600 (C=N) cm^{-1}; *m/z* 280 (M^+, 97.4%) and 148 (100%).

Compounds **2a** [m.p. 84-86 °C (lit.[11] 85-86°C)], **6b** [m.p. 184°C (lit.[6] 179°C], **6c** [m.p. 206°C (lit.[17] 204-205°C)], **11** [m.p. 216°C (lit.[8] 215 - 216°C)] and **13** [m.p. 130 - 132°C (lit.[16] 140°C)] are known. Analytical data for other, new compounds prepared in this study are as follows.

3-(4-Fluorophenyl)-3-(phenylmercapto)propanoic acid **2b** (7.4 g, 88.5%), m.p. 94-96°C (from hexane) (Found: M^+, 276.0641. $C_{15}H_{13}SO_2F$ requires *M*, 276.0620); δ_H (400 MHz, $CDC\ell_3$) 2.90 and 2.98 (2H, 2 x dd, CH_2), 4.58 (1H, dd, 3-H), 6.92-7.30 (9H, ArH) and 11.0 (1H, br s, CO_2H); δ_C (100 MHz, $CDC\ell_3$) 40.6 (C-2), 48.0 (C-3), 115.4 ($^2J_{CF}$ 21.1 Hz, C-3′ and C-5′), 128.1 (C-4′′), 129.0 (C-2′′ and C-6′′), 129.2 ($^3J_{CF}$ 8.0 Hz, C-2′ and C-6′), 133.0 (C-1′′), 133.7 (C-3′′ and C-5′′), 135.9 ($^4J_{CF}$ 3.0 Hz, C-1′), 162.1 ($^1J_{CF}$ 246.5 Hz, C-4′) and 176.6 (C-1); ν_{max} (KBr) 1700 (C=O) cm^{-1}; *m/z* 276 (M^+, 17.1%) and 125 (100%).

3-(4-Chlorophenyl)-3-(phenylmercapto)propanoic acid **2c** (5.55 g, 87%), mp. 102-104°C (from hexane) (Found: M^+, 292.0302. $C_{15}H_{13}SO_2{}^{35}C\ell$ requires *M*, 292.0324); δ_H (400 MHz, $CDC\ell_3$) 2.90 and 2.95 (2H, 2 x dd, CH_2), 4.55 (1H, dd, 3-H), 7.10-7.38 (9H, ArH) and 10.9 (1H, br s, CO_2H); δ_C (100 MHz, $CDC\ell_3$) 40.4 (C-2), 48.1 (C-3), 128.2 (C-4''), 128.7 (C-2' and (C-6'), 129.0 (C-3' and C-5'), 129.0 (C-2'' and C-6''), 132.8 (C-1'), 133.4 (C-4'), 133.7 (C-3'' and C-5''), 138.8 (C-1'') and 176.3 (C-1); ν_{max} (KBr) 1700 (C=O) cm^{-1}; *m/z* 292 [M^+ ($^{35}C\ell$), 17.9%] and 141 (100%).

3-(4-Bromophenyl)-3-(phenylmercapto)propanoic acid **2d** (4.0 g, 90%), m.p. 108°C (from hexane) (Found M^+, 335.9817. $C_{15}H_{13}SO_2{}^{79}Br$ requires *M*, 335.9820); δ_H (400 MHz, $CDC\ell_3$) 2.89 and 2.97 (2H, 2 x dd, CH_2), 4.53 (1H, dd, 3-H), 7.04-7.41 (9H, ArH) and 10.7 (1H, br s, CO_2H); δ_C (100 MHz, $CDC\ell_3$) 40.3 (C-2), 48.1 (C-3), 121.5 (C-4'), 128.2 (C-4''), 129.0 (C-2' and C-6'), 129.3 (C-2'' and C-6''), 131.6 (C-3' and C-5'), 132.8 (C-1'), 133.7 (C-3'' and C-5''), 139.3 (C-1'') and 176.3 (C-1); ν_{max} (KBr) 1705 (C=O) cm^{-1}; *m/z* 336 [M^+(^{79}Br), 11.8%] and 185 (100%).

3-(4-Methoxyphenyl)-3-(phenylmercapto)propanoic acid **2e** (13.2 g, 88%), m.p. 88-90°C (from hexane) (Found: M^+, 288.0804. $C_{16}H_{16}SO_3$ requires *M*, 288.0819); δ_H (400 MHz, $CDC\ell_3$) 2.93 and 2.98 (2H, 2 x dd, CH_2), 3.76 (3H, s, OCH_3), 4.60 (1H, dd, 3-H), 6.79-7.34 (9H, ArH) and 10.45 (1H, s, CO_2H); δ_C (100 MHz, $CDC\ell_3$) 40.8 (C-2), 48.0 (C-3), 55.2 (OCH_3), 113.9 (C-3' and

C-5′), 127.8 (C-4′′), 128.7 (C-2′ and C-6′), 128.8 (C-2′′ and C-6′′), 132.1 (C-1′), 133.3 (C-3′′ and C-5′′), 133.6 (C-1′′), 158.9 (C-4′) and 176.9 (C-1); ν_{max} (KBr) 1700 (C=O) cm^{-1}; *m/z* 288 (M^+, 6.1%) and 137 (100%).

*2-(4-Fluorophenyl)-2,3-dihydro-4*H*-1-benzothiopyran-4-one* **4b** (1.96 g, 42%), m.p. 94-96°C (from CS_2-hexane) (Found: M^+, 258.0488. $C_{15}H_{11}SOF$ requires *M*, 258.0515); δ_H (400 MHz, $CDC\ell_3$) 3.18 and 3.27 (2H, 2 x dd, CH_2), 4.71 (1H, dd, 2-H), 7.03-7.43 (7H, ArH) and 8.14 (1H, dd, 5-H); δ_C (100 MHz, $CDC\ell_3$) 44.7 (C-3), 46.8 (C-2), 115.9 ($^2J_{CF}$ 22.1 Hz, C-3′ and C-5′), 125.3 (C-8), 127.2 (C-6), 129.1 ($^3J_{CF}$ 8.1 Hz, C-2′ and C-6′), 129.2 (C-5), 130.4 (C-4a), 133.7 (C-7), 134.3 ($^4J_{CF}$ 3.0 Hz, C-1′), 141.8 (C-8a), 162.5 ($^1J_{CF}$ 247.5 Hz, C-4′) and 194.1 (C-4); ν_{max} (KBr) 1675 (C=O) cm^{-1}; *m/z* 258 (M^+, 32.1%) and 136 (100%).

*2-(4-Chlorophenyl)-2,3-dihydro-4*H*-1-benzothiopyran-4-one* **4c** (2.2 g, 48%), m.p. 111-113°C (from CS_2-hexane) (Found: M^+, 274.0212. $C_{15}H_{11}SO^{35}C\ell$ requires *M*, 274.0220); δ_H (400 MHz, $CDC\ell_3$) 3.18 and 3.27 (2H,2 x dd,CH_2), 4.68 (1H, dd, 2-H), 7.02-7.43 (7H, ArH) and 8.13 (1H, dd, 5-H); δ_C (100 MHz, $CDC\ell_3$) 44.7 (C-3), 46.5 (C-2), 125.4 (C-8), 127.2 (C-6), 128.8 (C-2′ and C-6′), 129.2 (C-3′ and C-5′), 129.2 (C-5), 130.4 (C-4a), 133.7 (C-7), 134.3 (C-4′), 137.0 (C-1′), 141.6 (C-8a) and 193.9 (C-4); ν_{max} (KBr) 1670 (C=O) cm^{-1}; *m/z* 274 [$M^+(^{35}C\ell)$, 27.0%] and 136 (100%).

2-(4-Bromophenyl)-2,3-dihydro-4H-1-benzothiopyran-4-one **4d** (1.74 g, 44%), m.p. 152-154°C (from CS_2-hexane) (Found: M^+, 317.9698. $C_{15}H_{11}SO^{79}Br$ requires *M*, 317.9715); δ_H (400 MHz, $CDC\ell_3$) 3.18 and 3.27 (2H, 2 x dd, CH_2), 4.67 (1H, dd, 2-H), 7.12-7.51 (7H, ArH) and 8.14 (1H, dd, 5-H); δ_C (100 MHz, $CDC\ell_3$) 44.8 (C-3), 46.5 (C-2), 122.4 (C-4′), 125.4 (C-8), 127.2 (C-6), 129.1 (C-2′ and C-6′), 129.2 (C-5), 130.4 (C-4a), 132.1 (C-3′ and C-5′), 133.7 (C-7), 137.5 (C-1′), 141.5 (C-8a) and 193.9 (C-4); ν_{max} (KBr) 1675 (C=O) cm^{-1}; *m/z* 318 [$M^+(^{79}Br)$, 56.2%] and 136 (100%).

2-(4-Fluorophenyl)-2,3-dihydro-1,4-benzothiazepin-5(4H)-one **5b** (0.34 g, 35%), m.p. 188°C (from EtOH) (Found: M^+, 273.0627. $C_{15}H_{12}NOSF$ requires *M*, 273.0623); δ_H (400 MHz, $CDC\ell_3$) 3.34 and 3.57 (2H, 2 x m,CH_2), 4.61 (1H, dd, 2-H) and 6.96-7.74 (9H, ArH and NH); δ_C (100 MHz, $CDC\ell_3$) 47.6 (C-3), 55.4 (C-2), 115.7 ($^2J_{CF}$ 21.1 Hz, C-3′ and C-5′), 129.0 ($^3J_{CF}$ 8.1 Hz, C-2′ and C-6′), 129.4 (C-9), 128.0 (C-5a), 128.0 (C-7), 131.7 (C-6), 134.3 (C-8), 136.9 ($^4J_{CF}$ 3.0 Hz, C-1′), 129.8 (C-9a), 162.3 ($^1J_{CF}$ 247.5 Hz, C-4′) and 172.4 (C-5); ν_{max} (KBr) 3305 (NH) and 1745 (C=O) cm^{-1}; *m/z* 273 (M^+, 73,2%) and 244 (100%).

2-(4-Chlorophenyl)-2,3-dihydro-1,4-benzothiazepin-5(4H)-one **5c** (0.53 g, 33%), m.p. 122°C (from EtOH) (Found: M^+, 289.0340. $C_{15}H_{12}NOS^{35}C\ell$ requires *M*, 289.0327); δ_H (400 MHz, $CDC\ell_3$) 3.30 and 3.55 (2H, 2 x m, CH_2), 4.57 (1H, dd, 2-H), 7.20-7.73 (8H, ArH) and 8.21 (1H, t, NH); δ_C (100 MHz, $CDC\ell_3$) 47.4 (C-3), 55.4 (C-2), 128.6 (C-2′ and C-6′), 129.0 (C-3′ and C-5′), 129.7 (C-9), 129.8 (C-5a), 130.1 (C-7), 131.8 (C-6), 133.9 (C-4′), 134,3 (C-8), 139.5

(C-1′), 139.7 (C-9a) and 172.2 (C-5); ν_{max} (KBr) 3300 (NH) and 1750 (C=O) cm^{-1}; *m/z* 289 [$M^+(^{35}C\ell)$, 91.2%] and 260 (100%).

2-(4-Bromophenyl)-2,3-dihydro-1,4-benzothiazepin-5(4H)-one **5d** (0.36 g, 28%), m.p. 144°C (from EtOH) (Found: M^+, 332.9818. $C_{15}H_{12}NOS^{79}Br$ requires *M*, 332.9823); δ_H (400 MHz, $CDC\ell_3$) 3.33 and 3.56 (2H, 2 x m, CH_2), 4.56 (1H, dd, 2-H), 6.91 (1H, br s, NH) and 7.18-7.76 (8H, ArH); δ_C (100 MHz, $CDC\ell_3$) 47.3 (C-3), 55.5 (C-2), 122.0 (C-4′), 129.0 (C-2′ and C-6′), 129.5 (C-9), 129.8 (C-5a), 130.1 (C-7), 131.8 (C-6), 132.0 (C-3′ and C-5′), 134.3 (C-8), 139.7 (C-1′), 140.0 (C-9a) and 172.2 (C-5); ν_{max} (KBr) 3350 (NH) and 1745 (C=O) cm^1; *m/z* 333 [$M^+(^{79}Br)$, 40.3%] and 197 (100%).

*5,6-Dihydrotetrazolo[1,5-*d*][1,4]benzothiazepine* **12** (1.87 g, 30%), m.p. 108°C (from EtOH) (Found: M^+, 204.0462. $C_9H_8N_4S$ requires *M*, 204.0470); δ_H (400 MHz, $CDC\ell_3$) 2.68 (2H, m, 2-CH_2), 4.44 (2H, m, 3-CH_2), 7.44-7.66 (3H, ArH) and 8.52 (1H, dd, 6-H); δ_C (100 MHz, $CDC\ell_3$) 33.1 (C-3), 50.8 (C-2), 125.6 (C-5a), 128.4 (C-9), 131.5 (C-7), 132.0 (C-6), 132.8 (C-8), 135.4 (C-9a) and 154.0 (C-5); ν_{max} (KBr) 1610 (C=N) cm^{-1}; *m/z* 204 (M^+, 92.3%) and 148 (100%).

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