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A facile synthesis and highly atom economic 1,3-dipolar cycloaddition of hexahydropyrido[3,4-*c*][1,5]benzothiazepines with nitrile oxide: stereoselective formation of hexahydro-[1,2,4]oxadiazolo[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepines

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Abstract—A series of new 2-methyl-11-aryl-4-[(*E*)-arylmethylidene]-1,2,3,4,11,11a-hexahydropyrido[3,4-*c*][1,5]benzothiazepines were obtained by the reaction of *o*-aminothiophenol and (*E*)-1-methyl-3,5-bis(arylidene)-4-piperidones in the presence of a catalytic amount of acetic acid under solvent-free microwave irradiation. These dipolarophiles undergo a highly atom economic 1,3-dipolar cycloaddition with nitrile oxide to afford a series of novel 6-methyl-1-phenyl-8-aryl-4-[(*E*)-arylmethylidene]-4,5,6,7,7a,8-hexahydro[1,2,4]oxadiazolo[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepines stereoselectively.

1. Introduction

The 1,3-dipolar cycloaddition constitutes a versatile synthetic methodology for the construction of five-membered ring heterocycles.[1] In particular, the 1,3-dipolar cycloaddition of nitrile oxides to C=N bond affords oxadiazoles, which have important pharmaceutical properties.[2] Apart from being highly potent and selective inhibitors of human tryptase,[3] compounds with 1,2,4-oxadiazole sub-structure are present in glycogen phosphorylase, which is responsible for the conversion of glycogen into glucose,[4] dopamine ligands,[5] serotoninergic (5-HT3) antagonists[6] and muscarinic agonists.[7] 1,2,4-Oxadiazoles also display antikinetoplastid,[8] anti-inflammatory and antimicrobial[9] activities. [1,5]Benzothiazepines also find a unique place in drug discovery programmes as they display a wide range of biological activities such as antibacterial,[10] antifeedant,[11] analgesic,[12] anticonvulsant,[13] calcium antagonists,[14] enzyme inhibitors,[15] endogenous natriuretic factors[16] and as potential central nervous system agents.[17] Compounds with the piperidine sub-structure are also widely prevalent in many biologically important systems.[18]

The above importance of 1,2,4-oxadiazoles, piperidines and [1,5]benzothiazepines and our interest in the synthesis of novel heterocycles[19] lead us to report in this paper, a highly atom economic and stereoselective synthesis of a series of new [1,2,4]oxadiazolo[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepines **3**, with potential biological value, via a nitrile oxide cycloaddition to a series of new 2-methyl-11-aryl-4-[(*E*)-arylmethylidene]-1,2,3,4,11,11a-hexahydropyrido[3,4-*c*][1,5]benzothiazepines **2** synthesised under solvent-free microwave irradiation. It is pertinent to note that atom economic transformations[20] are of paramount importance, as they minimise the waste rendering them eco-friendly and hence attractive from the viewpoint of green chemistry. Further, there are only a few studies available in the literature on the 1,3-dipolar cycloaddition of nitrile oxides to [1,5]benzothiazepines[13,21] and the present study is the first report on (i) the synthesis of the dipolarophile **2** and (ii) the 1,3-dipolar cycloaddition of nitrile oxide to benzothiazepines fused to another heterocycle.

2. Results and discussion

The reaction of *o*-aminothiophenol and (*E*)-1-methyl-3,5-bis-(arylidene)-4-piperidones **1** (Scheme 1) under solvent-free microwave irradiation afforded a series of new 2-methyl-11-aryl-4-[(*E*)-arylmethylidene]-1,2,3,4,11,11a-hexahydropyrido[3,4-*c*][1,5]benzothiazepines. Appropriately substituted **1** and *o*-aminothiophenol in a 1:1 molar ratio in presence of a catalytic amount of acetic acid were mixed thoroughly in an open glass tube. This tube was partially immersed in a silica bath and irradiated in a microwave oven at maximum

Keywords: Benzothiazepine; Piperidone; 1,3-Dipolar cycloaddition; Nitrile oxide.
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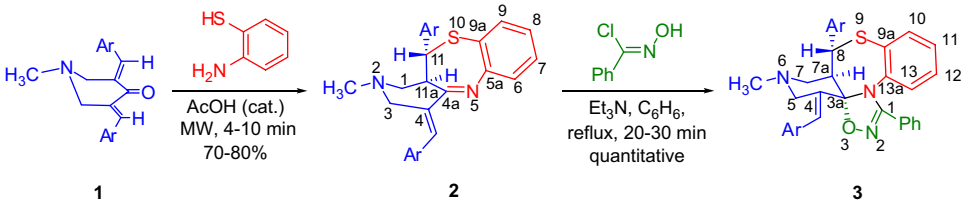


Scheme 1. Synthesis of [1,5]benzothiazepines **2** and **3**.

Table 1. Synthesis of [1,5]benzothiazepines **2** and **3**

Compds	Microwave method		Conventional method		Compds	Yield[b] (%)
	Time (min)	Yield[a] (%)	Time (h)	Yield (%)		
2a	6	80	10	30	**3a**	94
2b	8	79	10	28	**3b**	96
2c	8	75	10	25	**3c**	95
2d	8	70	10	21	**3d**	98
2e	10	70	11	23	**3e**	95
2f	4	80	10	27	**3f**	96
2g	6	72	10	25	**3g**	95
2h	8	75	11	24	**3h**	96
2i	6	80	11	26	**3i**	94
2j	6	75	10	25	**3j**	97

[a] Yield after recrystallisation.
[b] Yield after column purification.

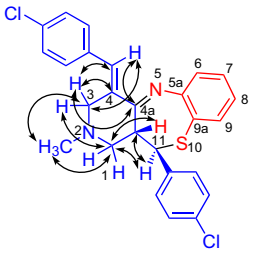


Figure 1. Selected HMBC correlations of **2b**.

power level under atmospheric pressure for the time given in Table 1. The reaction was monitored (TLC) after every 1 min of irradiation. The temperature of the silica bath after complete irradiation was found to be ~85 °C (as measured by stirring the silica bath with a thermometer). After completion of the reaction (TLC), the yellow solid was recrystallised from ethanol to obtain pure **2** in 70–80% yield (Table 1). This reaction in either ethanol or methanol at reflux with a few drops of acetic acid took several hours for less than 30% conversion, while refluxing in acetic acid alone led to complete decomposition of the reaction mixture.

The [1,5]benzothiazepines **2a–j** were characterised by ^{1}H, ^{13}C, 2D NMR spectroscopic data and X-ray crystallographic studies. Selected HMBC correlations of **2b** are given in Figure 1. As **2** has two stereocentres, two diastereomers are possible with H-11 and H-11a in either a cis or trans relationship. Molecular mechanics calculations (MM+) employing Polak-Ribiere algorithm of Hyperchem 7.5 show that the trans isomer is more stable, as it has less energy (26.4 kcal/mol) than the cis isomer (33.9 kcal/mol). The MM+ energy-minimised structure of **2g** (Fig. 2a) reveals that (i) the thiazepine and piperidine rings adopt a boat and a half chair conformation, respectively; (ii) in the trans isomer, H-11 and H-11a have a dihedral angle of 167.8° in consonance with the observed J value of 12 Hz between these protons and (iii) H-11a has almost equal dihedral angles, 63.2° and 55.7°, with each of the 1-CH_2 protons in accord with the triplet multiplicity of H-11a corresponding to the J value of 3 Hz. The structure of **2g** determined from a single crystal X-ray study (Fig. 3) is in excellent agreement with that deduced from NMR spectroscopic data. The dihedral angles obtained from the structure derived from X-ray studies [174.3° (H-11 and H-11a), 67.7° and 51.5° (H-11a and two 1-CH_2)] also agree well with that obtained from molecular modelling. These results of NMR spectroscopic and X-ray studies show that **2** adopts almost the same conformation in solution and solid state.

The 1,3-dipolar cycloaddition of nitrile oxide, generated in situ from benzohydroximinoyl chloride and triethylamine, with 2-methyl-11-aryl-4-[(*E*)-arylmethylidene]-1,2,3,4,11,11a-hexahydropyrido[3,4-*c*][1,5]benzothiazepines **2a–j** affords

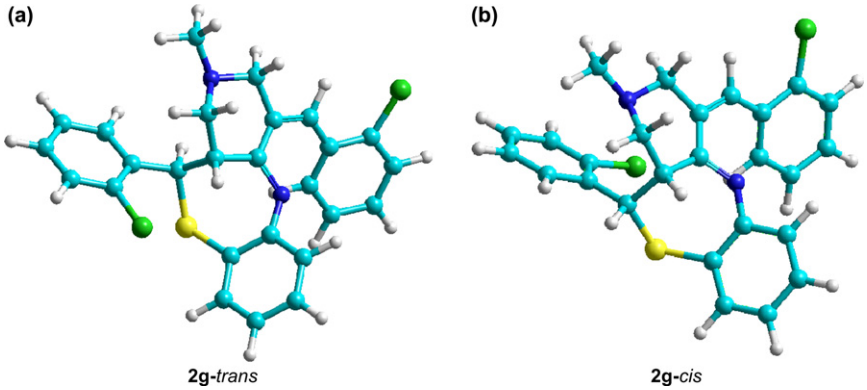


Figure 2. MM^{+} optimised geometry for **2g**-*trans* and **2g**-*cis*.

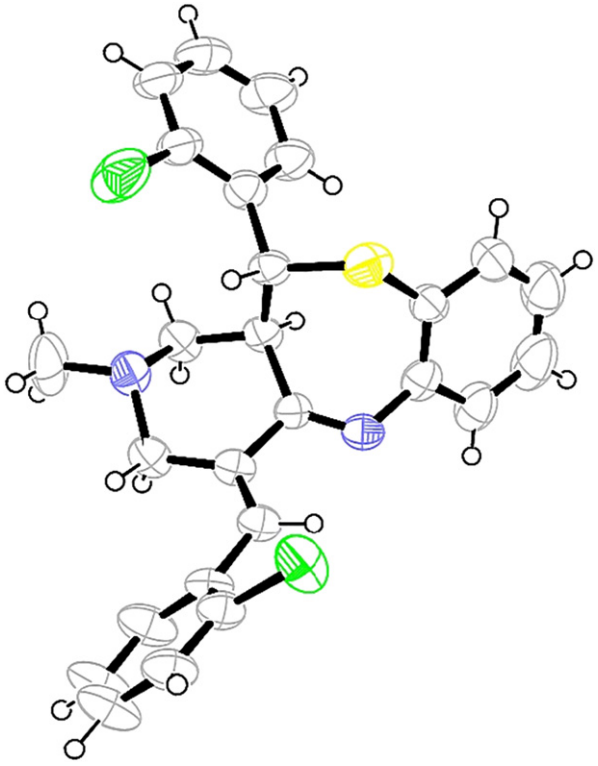


Figure 3. ORTEP diagram of **2g**.

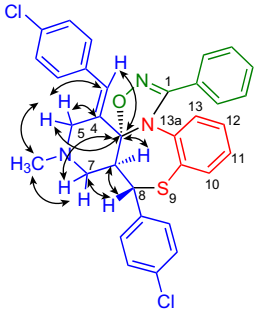


Figure 4. Selected HMBC correlations of **3b**.

novel 6-methyl-1-phenyl-8-aryl-4-[(*E*)-arylmethylidene]-4,5,6,7,7a,8-hexahydro[1,2,4]oxadiazolo[5,4-*d*]pyrido[3,4-*c*]-[1,5]benzothiazepines **3a–j** (Scheme 1). This reaction is complete in 20–30 min affording **3** almost quantitatively, except for the slight loss of the product that occurs during column chromatography (Table 1). The triethylamine hydrochloride formed during the reaction can be filtered, neutralised and reused. Hence the only waste generated in this reaction is hydrochloric acid and the atom economy of the reaction is very high, i.e. 94%.

The structure of [1,2,4]oxadiazolo[5,4-*d*]pyrido[1,5]benzothiazepines (**3a–j**) was elucidated using ^{1}H, ^{13}C and 2D NMR spectra as described for **3b**. The doublet at 4.71 ppm (J=10.8 Hz) is assigned to H-8 on the basis of its multiplicity. Further, H-8 shows HMBC correlations (Fig. 4) with a methylenic and a methine carbon (inferred from the DEPT spectra) at 53.1 and 44.3 ppm, respectively, assigning them to C-7 and C-7a. The doublet at 2.39 ppm (J=10.5 Hz) due to H-7a and the doublet at 2.76 ppm (J=11.7 Hz) due to one of the 7-CH_2 hydrogens are assigned from C,H-COSY correlations. The other 7-CH_2 hydrogen overlaps with the N–CH_3 signal at 2.20–2.27 ppm. That the signals 3.81 (d, J=12.3 Hz) and 3.29 (d, J=12.0 Hz) arise from 5-CH_2 is evident from their HMBC correlations with C-4 at 133.0 ppm, benzylidene carbon at 127.5 ppm and the quaternary carbon (C-3a) at 100.1 ppm. The signals at 54.1, 46.7 and 45.3 ppm are assigned to C-5, C-8 and N–CH_3 carbons, respectively, from their C,H-COSY correlations. The benzylidene hydrogen appears as a singlet at 7.49 ppm, whereas the aromatic ring hydrogens appear as a multiplet in the range 6.76–7.81 ppm.

The structure of **3** determined from the single crystal X-ray crystallographic and NMR spectroscopic studies is in good agreement. The ORTEP diagrams of **3b** and **3c** (Fig. 5) show that (i) the piperidine and the thiazepine rings adopt a chair and boat conformation, respectively, and (ii) the nitrile oxide cycloaddition occurs from the less hindered side of **2** enabling facial selectivity (Scheme 2).

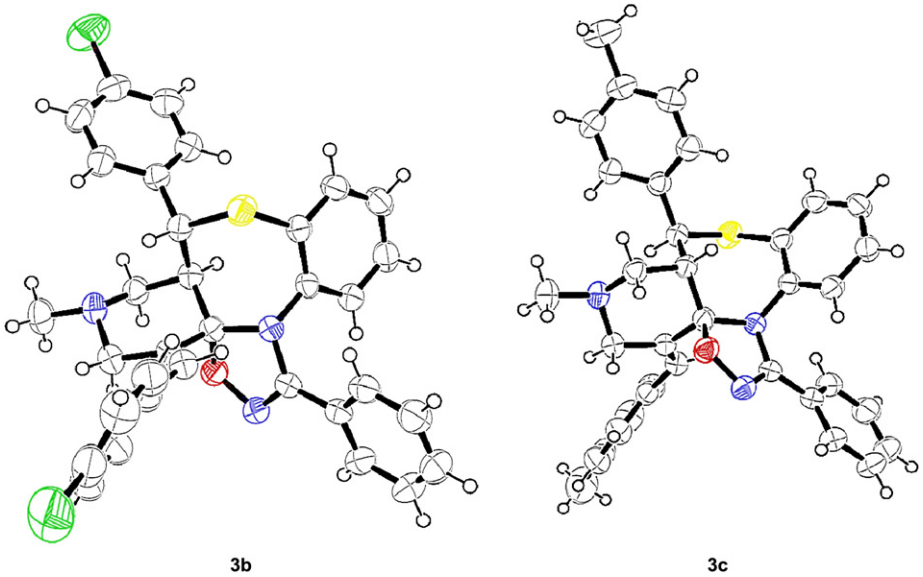
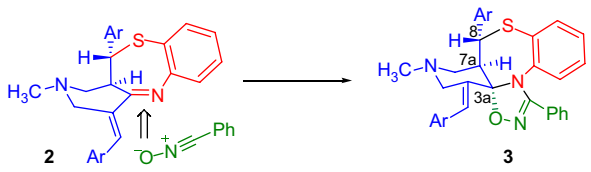


Figure 5. ORTEP diagrams of **3b** and **3c**.



Scheme 2. Diastereofacialselective cycloaddition of nitrile oxide to **2**.

A comparison of the X-ray structures of **2g** and **3b** (Fig. 3) discloses that, except for the presence of an oxadiazole ring in **3**, stereochemical features of both **2** and **3** remain similar. The cycloaddition of nitrile oxide to **2** is also chemoselective, as it is found that even when an excess of nitrile oxide is employed, further cycloaddition of nitrile oxide to the benzylidene of **3** does not occur. This is presumably ascribable to the steric hindrance for the cycloaddition on both the faces of the benzylidene C═C bond of **3** by (i) the C_{7a}–C_8 and C_{3a}–O bonds, which are orientated axially on opposite faces with reference to the piperidine ring system and (ii) the aryl ring of the benzylidene, which is twisted from the plane of the C═C bond (Figs. 3b and 5).

3. Conclusions

The present study describes a highly atom economic protocol for the stereoselective synthesis of a series of new [1,2,4]oxadiazolo[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepines via nitrile oxide cycloaddition. The dipolarophiles, pyrido[3,4-*c*][1,5]benzothiazepines, employed in this study are also newly synthesised under solvent-free microwave irradiation. Further investigations on the synthetic utility of **2** in the construction of novel heterocycles are under progress in our research group.

4. Experimental

4.1. General

The melting points were measured in open capillary tubes and are uncorrected. The ^{1}H, ^{13}C and the 2D NMR spectra were recorded on a Bruker (Avance) 300 MHz NMR instrument using TMS as internal standard and $CDCl_3$ as solvent. Standard Bruker software was used throughout. Chemical shifts are given in parts per million (δ-scale) and the coupling constants are given in hertz. An IFB microwave oven (Model: Electron) operating at 230 V and 50 Hz with consumption of 1000 W with microwave power maximum level of 600 W and microwave frequency of 2450 MHz was employed for the irradiation done in this work. Silica gel-G plates (Merck) were used for TLC analysis with a mixture of petroleum ether (60–80 °C) and ethyl acetate as eluent. IR spectra were recorded on a JASCO FTIR instrument (KBr). Elemental analyses were performed on a Perkin–Elmer 2400 Series II Elemental CHNS analyser. Molecular mechanics calculations (MM+) employing Polak-Ribiere algorithm were performed using Hyperchem 7.5. The samples **3b** and **3c** obtained from column chromatography were recrystallised in a 10:1 mixture of ethyl acetate/dichloromethane, while **2g** was recrystallised from ethanol to obtain crystals suitable for X-ray studies. X-ray diffraction data of **2g** were collected on Enraf–Nonius (CAD4) diffractometer with Mo Kα (λ=0.71073 Å) radiation with a scan range of $2.09° \leq \theta \leq 24.97°$, whereas the X-ray diffraction data of **3b** and **3c** were collected on CCD area detector with Mo Kα (λ=0.71073 Å) radiation and the scan range was $1.39° \leq \theta \leq 26.12°$ and $1.39° \leq \theta \leq 26.03°$, respectively.

4.2. Synthesis of 2-methyl-11-aryl-4-(arylmethylidene)-1,2,3,4,11,11a-hexahydro-pyrido[3,4-*c*][1,5]benzothiazepines (2)

Conventional method: A mixture of *o*-aminothiophenol (1 mmol), (*E*)-1-methyl-3,5-bis(arylidene)-4-piperidone (1 mmol) and acetic acid (1 mL) was heated at reflux in ethanol or methanol (15 mL) for a time period given in Table 1. The solvent was evaporated under reduced pressure and the benzothiazepine was separated through a silica column using petroleum ether/ethyl acetate (12:1 v/v mixture) as eluent.

Microwave method: A mixture of *o*-aminothiophenol (1 mmol), (*E*)-1-methyl-3,5-bis(arylidene)-4-piperidone (1 mmol) and a catalytic amount of acetic acid (30 mol %) was thoroughly mixed in a glass tube, the tube containing the mixture partially immersed in a silica bath in a microwave oven and irradiated for the appropriate time interval as shown in Table 1 at the maximum power level (600 W). The progress of the reaction was monitored after every 1 min of irradiation by TLC with petroleum ether/ethyl acetate (4:1 v/v mixture) as eluent. After each irradiation, the reaction mixture was cooled to room temperature and mixed well. After completion of the reaction (TLC), the solid mass was washed with water, dried and recrystallised from ethanol to obtain pure **2**.

4.2.1. 2-Methyl-11-phenyl-4-(phenylmethylidene)-1,2,3,4,11,11a-hexahydropyrido[3,4-*c*][1,5]benzothiazepine (2a). Obtained as yellow solid (0.273 g, 80%), mp 199–200 °C; R_f (petroleum ether/EtOAc, 4:1) 0.65; found: C, 78.85; H, 6.17; N, 7.15. $C_{26}H_{24}N_2S$ requires C, 78.75; H, 6.10; N, 7.06%; ν_{max}(KBr) 1604, 1562, 1488, 1446 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.70 (1H, d, *J* 1.5 Hz, C═C*H*), 7.11–7.61 (14H, m, Ar), 5.10 (1H, d, *J* 12.0 Hz, 11-C*H*), 4.10 (1H, d, *J* 13.5 Hz, 3-CH_2), 3.18 (1H, dd, *J* 13.5, 2.7 Hz, 3-CH_2), 3.11 (1H, dt, *J* 11.7, 3.0 Hz, 11a-C*H*), 2.21–2.25 (5H, m, N–CH_3 and 1-CH_2); δ_C (75 MHz, $CDCl_3$) 171.7, 152.4, 144.1, 136.5, 135.5, 133.8, 133.4, 130.7, 130.3, 129.1, 128.7, 128.5, 128.2, 127.0, 126.4, 124.0, 63.2, 58.6, 55.9, 47.0, 46.5.

4.2.2. 11-(4-Chlorophenyl)-4-[(4-chlorophenyl)methylidene]-2-methyl-1,2,3,4,11,11a-hexahydropyrido[3,4-*c*]-[1,5]benzothiazepine (2b). Obtained as yellow solid (0.257 g, 79%), mp 194–195 °C; R_f (petroleum ether/EtOAc, 4:1) 0.65; found: C, 67.00; H, 4.68; N, 6.11. $C_{26}H_{22}Cl_2N_2S$ requires C, 67.09; H, 4.76; N, 6.02%; ν_{max}(KBr) 1621, 1558, 1488, 1452 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.64 (1H, s, C═C*H*), 7.10–7.58 (12H, m, Ar), 5.07 (1H, d, *J* 12.0 Hz, 11-C*H*), 4.02 (1H, d, *J* 14.1 Hz, 3-CH_2), 3.14 (1H, dd, *J* 14.1, 2.4 Hz, 3-CH_2), 3.05 (1H, dt, *J* 12.0, 3.1 Hz, 11a-C*H*), 2.21–2.29 (5H, m, N–CH_3 and 1-CH_2); δ_C (75 MHz, $CDCl_3$) 171.1, 152.2, 142.5, 135.4, 134.9, 134.5, 134.1, 133.8, 132.1, 131.9, 130.5, 129.3, 129.0, 128.3, 126.5, 125.9, 123.5, 62.3, 58.4, 55.7, 46.9, 46.6.

4.2.3. 2-Methyl-11-(4-methylphenyl)-4-[(4-methylphenyl)methylidene]-1,2,3,4,11,11a-hexahydropyrido[3,4-*c*][1,5]benzothiazepine (2c). Obtained as yellow solid (0.250 g, 75%), mp 186–187 °C; R_f (petroleum ether/EtOAc, 4:1) 0.65; found: C, 79.29; H, 6.59; N, 6.63. $C_{28}H_{28}N_2S$ requires C, 79.20; H, 6.65; N, 6.60%; ν_{max}(KBr) 1619, 1556, 1509, 1450 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.67 (1H, s, C═C*H*), 7.07–7.59 (12H, m, Ar), 5.07 (1H, d, *J* 12.0 Hz, 11-C*H*), 4.07 (1H, d, *J* 14.1 Hz, 3-CH_2), 3.17 (1H, dd, *J* 14.1, 2.0 Hz, 3-CH_2), 3.09 (1H, dt, *J* 12.0, 3.0 Hz, 11a-C*H*), 2.38 (3H, s, Ar-CH_3), 2.31 (3H, s, Ar-CH_3), 2.20–2.25 (5H, m, N–CH_3 and 1-CH_2); δ_C (75 MHz, $CDCl_3$) 171.8, 152.5, 141.2, 138.5, 137.9, 135.5, 133.8, 133.4, 133.1, 130.7, 130.2, 129.8, 129.4, 126.9, 126.4, 125.5, 124.1, 63.1, 58.7, 56.0, 46.9, 46.6, 21.8, 21.5.

4.2.4. 11-(4-Methoxyphenyl)-4-[(4-methoxyphenyl)-methylidene]-2-methyl-1,2,3,4,11,11a-hexahydropyrido[3,4-*c*][1,5]benzothiazepine (2d). Obtained as yellow solid (0.228 g, 70%), mp 180–182 °C; R_f (petroleum ether/EtOAc, 4:1) 0.35; found: C, 73.73; H, 6.11; N, 6.10. $C_{28}H_{28}N_2O_2S$ requires C, 73.65; H, 6.18; N, 6.14%; ν_{max}(KBr) 1670, 1598, 1508, 1455, 1348 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.76 (1H, s, C═C*H*), 7.03–7.55 (12H, m, Ar), 5.07 (1H, d, *J* 12.1 Hz, 11-C*H*), 4.09 (1H, d, *J* 14.3 Hz, 3-CH_2), 3.85 (6H, s, Ar-OCH_3), 3.18 (1H, dd, *J* 14.3, 2.0 Hz, 3-CH_2), 3.04 (1H, dt, *J* 12.1, 3.0 Hz, 11a-C*H*), 2.22–2.25 (5H, m, N–CH_3 and 1-CH_2); δ_C (75 MHz, $CDCl_3$) 171.8, 152.4, 160.6, 159.9, 136.5, 135.5, 133.1, 132.7, 132.4, 130.1, 129.3, 128.4, 128.1, 126.4, 125.5, 124.0, 114.5, 114.4, 62.8, 58.7, 56.0, 55.7, 55.6, 47.1, 46.6.

4.2.5. 11-(4-Fluorophenyl)-4-[(4-fluorophenyl)methylidene]-2-methyl-1,2,3,4,11,11a-hexahydropyrido[3,4-*c*][1,5]benzothiazepine (2e). Obtained as yellow solid (0.233 g, 70%), mp 203–204 °C; R_f (petroleum ether/EtOAc, 4:1) 0.65; found: C, 72.26; H, 5.07; N, 6.42. $C_{26}H_{22}F_2N_2S$ requires C, 72.20; H, 5.13; N, 6.48%; ν_{max}(KBr) 1598, 1565, 1506, 1452 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.65 (1H, s, C═C*H*), 6.94–7.60 (12H, m, Ar), 5.09 (1H, d, *J* 12.0 Hz, 11-C*H*), 4.05 (1H, d, *J* 14.0 Hz, 3-CH_2), 3.15 (1H, dd, *J* 14.0, 2.4 Hz, 3-CH_2), 3.04 (1H, dt, *J* 12.0, 3.1 Hz, 11a-C*H*), 2.22–2.25 (5H, m, N–CH_3 and 1-CH_2); δ_C (75 MHz, $CDCl_3$) 171.3, 152.3, 62.3, 58.4, 55.7, 47.1, 46.6.

4.2.6. 11-(3-Fluorophenyl)-4-[(3-fluorophenyl)methylidene]-2-methyl-1,2,3,4,11,11a-hexahydropyrido[3,4-*c*][1,5]benzothiazepine (2f). Obtained as yellow solid (0.266 g, 80%), mp 148–150 °C; R_f (petroleum ether/EtOAc, 4:1) 0.65; found: C, 72.12; H, 5.20; N, 6.41. $C_{26}H_{22}F_2N_2S$ requires C, 72.20; H, 5.13; N, 6.48%; ν_{max}(KBr) 1590, 1555, 1500, 1465 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.65 (1H, s, C═C*H*), 6.90–7.61 (12H, m, Ar), 5.08 (1H, d, *J* 12.0 Hz, 11-C*H*), 4.06 (1H, d, *J* 13.8 Hz, 3-CH_2), 3.15 (1H, dd, *J* 13.8, 2.1 Hz, 3-CH_2), 3.07 (1H, d, *J* 12.0 Hz, 11a-C*H*), 2.23–2.31 (5H, m, N–CH_3 and 1-CH_2); δ_C (75 MHz, $CDCl_3$) 170.6, 151.8, 62.2, 58.0, 55.3, 46.5, 46.2.

4.2.7. 11-(2-Chlorophenyl)-4-[(2-chlorophenyl)methylidene]-2-methyl-1,2,3,4,11,11a-hexahydropyrido[3,4-*c*]-[1,5]benzothiazepine (2g). Obtained as yellow solid (0.234 g, 72%), mp 172–173 °C; R_f (petroleum ether/EtOAc, 4:1) 0.30; found: C, 67.14; H, 4.71; N, 6.07. $C_{26}H_{22}Cl_2N_2S$ requires C, 67.09; H, 4.76; N, 6.02%; ν_{max}(KBr) 1623, 1562, 1444, 1359 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.79 (1H, s, C═C*H*), 7.09–7.75 (12H, m, Ar), 5.79 (1H, d, *J* 12.0 Hz, 11-C*H*), 3.89 (1H, d, *J* 14.0 Hz, 3-CH_2), 3.19 (1H, dt, *J* 12.0, 3.3 Hz, 11a-C*H*), 3.10 (1H, dd, *J* 14.0, 2.4 Hz, 3-CH_2), 2.21–2.29 (5H, m, N–CH_3 and 1-CH_2); δ_C (75 MHz, $CDCl_3$) 170.8, 152.6, 141.4, 136.0, 135.6, 135.3, 134.9, 132.7, 131.3, 130.5, 130.2, 130.1, 130.0, 129.7, 129.0, 127.8, 127.3, 126.6, 126.3, 125.7, 123.1, 58.3, 57.6, 56.1, 46.9, 46.4.

4.2.8. 2-Methyl-11-(2-methylphenyl)-4-[(2-methylphenyl)methylidene]-1,2,3,4,11,11a-hexahydropyrido[3,4-*c*][1,5]benzothiazepine (2h). Obtained as yellow solid (0.251 g, 75%), mp 173–174 °C; R_f (petroleum ether/EtOAc, 4:1) 0.65; found: C, 79.15; H, 6.71; N, 6.53. $C_{28}H_{28}N_2S$ requires C, 79.20; H, 6.65; N, 6.60%; ν_{max}(KBr) 1617, 1594, 1556, 1486 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.73 (1H, s, C═C*H*), 7.11–7.54 (12H, m, Ar), 5.49 (1H, d, *J* 12.1 Hz, 11-C*H*), 3.92 (1H, d, *J* 14.1 Hz, 3-CH_2), 3.17 (1H, d, *J* 12.1 Hz, 11a-C*H*), 2.99 (1H, dd, *J* 14.1, 2.4 Hz, 3-CH_2), 2.43 (3H, s, Ar-CH_3), 2.37 (3H, s, Ar-CH_3), 2.14–2.21 (5H, m, N–CH_3 and 1-CH_2); δ_C (75 MHz, $CDCl_3$) 171.8, 152.6, 142.6, 138.5, 135.9, 135.6, 135.1, 133.8, 132.5, 130.6, 130.5, 130.3, 129.9, 128.7, 127.7, 127.1, 126.2, 126.1, 125.8, 125.6, 123.8, 58.4, 57.8, 56.1, 47.5, 46.4, 20.6, 19.9.

4.2.9. 2-Methyl-11-(2-thienyl)-4-[2-thienylmethylidene]-2,3,11,11a-tetrahydropyrido[3,4-*c*][1,5]benzothiazepine (2i). Obtained as yellow solid (0.273 g, 80%), mp 184–185 °C; R_f (petroleum ether/EtOAc, 4:1) 0.50; found: C, 64.60; H, 4.99; N, 6.81. $C_{22}H_{20}N_2S_3$ requires C, 64.67; H, 4.93; N, 6.86%; ν_{max}(KBr) 1603, 1577, 1554, 1488 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.92 (1H, s, C═C*H*), 6.86–7.58 (10H, m, Ar), 5.39 (1H, d, *J* 8.4 Hz, 11-C*H*), 4.23 (1H, d, *J* 14.8 Hz, 3-CH_2), 3.21 (1H, dd, *J* 15.0, 2.4 Hz, 3-CH_2), 2.98 (1H, dt, *J* 8.4, 3.0 Hz, 11a-C*H*), 2.35–2.39 (5H, m, N–CH_3 and 1-CH_2); δ_C (75 MHz, $CDCl_3$) 170.0, 152.5, 147.5, 139.9, 136.0, 131.9, 130.5, 130.4, 129.0, 128.0, 126.7, 126.0, 125.5, 125.2, 124.8, 124.6, 122.9, 58.8, 58.5, 55.7, 48.0, 46.7.

4.2.10. 11-(1-Naphthyl)-4-[(1-naphthyl)methylidene]-2-methyl-1,2,3,4,11,11a-hexahydropyrido[3,4-*c*][1,5]benzothiazepine (2j). Obtained as yellow solid (0.239 g, 75%), mp 139–141 °C; R_f (petroleum ether/EtOAc, 4:1) 0.65; found: C, 82.30; H, 5.60; N, 5.72. $C_{34}H_{28}N_2S$ requires C, 82.22; H, 5.68; N, 5.64%; ν_{max}(KBr) 1620, 1560, 1550, 1490 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.29 (1H, s, C═C*H*), 7.19–8.26 (18H, Ar), 6.20 (1H, d, *J* 11.7 Hz, 11-C*H*), 4.00 (1H, d, *J* 12.0 Hz, 3-CH_2), 3.34 (1H, dd, *J* 11.7, 2.1 Hz, 1-CH_2), 3.10 (1H, dd, *J* 12.3, 2.1 Hz, 3-CH_2), 2.18 (1H, d, *J* 12.3 Hz, 11a-C*H*), 1.97 (3H, s, N–CH_3); δ_C (75 MHz, $CDCl_3$) 171.4, 152.3, 140.6, 135.6, 135.1, 133.6, 133.2, 131.2, 130.8, 130.1, 128.9, 128.6, 128.5, 128.0, 127.6, 126.5, 126.3, 126.2, 125.9, 125.8, 125.7, 125.4, 125.2, 123.1, 58.2, 56.5, 55.5, 47.9, 45.7.

4.3. Synthesis of 6-methyl-1-phenyl-8-aryl-4-[(*E*)-arylmethylidene]-4,5,6,7,7a,8-hexahydro[1,2,4]oxadiazolo[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepines (3)

General procedure: 2-Methyl-11-aryl-4-[(*E*)-arylmethylidene]-1,2,3,4,11,11a-hexahydro-pyrido[3,4-*c*][1,5]benzothiazepine (**2**, 1 mmol) and benzohydroximinoyl chloride

(1 mmol) were dissolved in benzene (15 mL). Triethylamine (1 mmol) was added to the mixture and heated at reflux until the reaction goes to completion (TLC) for 20–30 min. Then the triethylamine hydrochloride was filtered off, the solvent removed and the residue purified by a column with silica gel using petroleum ether/ethyl acetate (90:10 v/v) mixture.

4.3.1. 6-Methyl-1,8-diphenyl-4-[(*E*)-phenylmethylidene]-4,5,6,7,7a,8-hexahydro-[1,2,4]oxadiazolo[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepine (3a). Obtained as colourless solid (0.244 g, 94%), mp 193–194 °C; R_f (petroleum ether/EtOAc, 4:1) 0.77; found: C, 76.93; H, 5.60; N, 8.08. $C_{33}H_{29}N_3OS$ requires C, 76.86; H, 5.67; N, 8.15%; ν_{max}(KBr) 1560, 1469, 1355, 1282 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.76–7.83 (19H, m, Ar), 7.57 (1H, s, C=C*H*), 4.75 (1H, d, *J* 10.8 Hz, 8-C*H*), 3.91 (1H, d, *J* 12.0 Hz, 5-CH_2), 3.31 (1H, d, *J* 12.3 Hz, 5-CH_2), 2.75 (1H, d, *J* 11.7 Hz, 7-CH_2), 2.46 (1H, d, *J* 10.8 Hz, 7a-C*H*), 2.28 (1H, d, *J* 11.4 Hz, 7-CH_2), 2.20 (3H, s, N–CH_3); δ_C (75 MHz, $CDCl_3$) 158.5, 144.7, 144.0, 136.6, 136.5, 132.2, 130.9, 129.8, 129.2, 129.0, 128.7, 128.2, 127.5, 127.2, 127.1, 127.0, 126.5, 125.3, 124.7, 123.9, 100.5, 54.2, 53.2, 47.5, 45.3, 44.4.

4.3.2. 8-(4-Chlorophenyl)-4-[(*E*)-(4-chlorophenyl)methylidene]-6-methyl-1-phenyl-4,5,6,7,7a,8-hexahydro[1,2,4]oxadiazolo[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepine (3b). Obtained as colourless solid (0.242 g, 96%), mp 219–220 °C; R_f (petroleum ether/EtOAc, 4:1) 0.77; found: C, 67.87; H, 4.60; N, 7.27. $C_{33}H_{27}Cl_2N_3OS$ requires C, 67.80; H, 4.66; N, 7.19%; ν_{max}(KBr) 1562, 1488, 1467, 1351 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.76–7.81 (17H, m, Ar), 7.49 (1H, s, C=C*H*), 4.71 (1H, d, *J* 10.8 Hz, 8-C*H*), 3.81 (1H, d, *J* 12.3 Hz, 5-CH_2), 3.29 (1H, d, *J* 12.0 Hz, 5-CH_2), 2.76 (1H, d, *J* 11.7 Hz, 7-CH_2), 2.39 (1H, d, *J* 10.5 Hz, 7a-C*H*), 2.20–2.27 (4H, m, N–CH_3 and 7-CH_2); δ_C (75 MHz, $CDCl_3$) 158.4, 144.6, 142.4, 136.5, 134.8, 133.1, 133.0, 132.9, 131.0, 130.5, 130.1, 129.0, 128.9, 128.4, 128.2, 127.6, 127.5, 126.3, 125.5, 124.2, 124.0, 100.1, 54.1, 53.1, 46.7, 45.3, 44.3.

4.3.3. 6-Methyl-8-(4-methylphenyl)-4-[(*E*)-(4-methylphenyl)methylidene]-1-phenyl-4,5,6,7,7a,8-hexahydro[1,2,4]oxadiazolo[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepine (3c). Obtained as colourless solid (0.244 g, 95%), mp 208–209 °C; R_f (petroleum ether/EtOAc, 4:1) 0.77; found: C, 77.39; H, 6.21; N, 7.69. $C_{35}H_{33}N_3OS$ requires C, 77.31; H, 6.12; N, 7.73%; ν_{max}(KBr) 1562, 1509, 1465, 1353 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.75–7.82 (17H, m, Ar), 7.53 (1H, s, C=C*H*), 4.72 (1H, d, *J* 10.8 Hz, 8-C*H*), 3.91 (1H, d, *J* 12.0 Hz, 5-CH_2), 3.29 (1H, d, *J* 12.0 Hz, 5-CH_2), 2.74 (1H, dd, *J* 11.7, 2.4 Hz, 7-CH_2), 2.43 (1H, d, *J* 10.5 Hz, 7a-C*H*), 2.35 (3H, s, Ar-CH_3), 2.27–2.32 (4H, m, 7-CH_2 and Ar-CH_3), 2.19 (3H, s, N–CH_3); δ_C (75 MHz, $CDCl_3$) 158.5, 144.8, 141.1, 136.9, 136.6, 133.6, 131.6, 130.8, 129.7, 129.4, 129.2, 128.9, 128.8, 128.6, 127.5, 126.8, 126.5, 125.2, 124.8, 123.8, 100.6, 54.2, 53.3, 47.2, 45.3, 44.4, 21.3, 21.1.

4.3.4. 4-[4-[(*E*)-(4-Methoxyphenyl)methylidene]-6-methyl-1-phenyl-6,7,7a,8-tetrahydro[1,2,4]oxadiazolo[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepin-8(5*H*)yl]phenylmethylether (3d). Obtained as colourless solid (0.247 g, 98%), mp 170–171 °C; R_f (petroleum ether/EtOAc, 4:1) 0.60; found: C, 72.95; H, 5.87; N, 7.38. $C_{35}H_{33}N_3O_3S$ requires C, 73.02; H, 5.78; N, 7.30%; ν_{max}(KBr) 1561, 1515, 1489, 1355 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.53–7.81 (17H, m, Ar), 7.48 (1H, s, C=C*H*), 4.70 (1H, d, *J* 11.2 Hz, 8-C*H*), 3.90 (1H, d, *J* 12.0 Hz, 5-CH_2), 3.81 (3H, s, Ar-OCH_3), 3.78 (3H, s, Ar-OCH_3), 3.28 (1H, d, *J* 12.3 Hz, 5-CH_2), 2.73 (1H, d, *J* 11.7 Hz, 7-CH_2), 2.39 (1H, d, *J* 11.2 Hz, 7a-C*H*), 2.28 (1H, d, *J* 12.0 Hz, 7-CH_2), 2.20 (3H, s, N–CH_3); δ_C (75 MHz, $CDCl_3$) 158.7, 158.6, 158.4, 144.7, 136.8, 136.3, 131.8, 131.5, 130.8, 129.6, 128.9, 128.4, 127.9, 127.4, 126.5, 123.7, 118.1, 115.2, 113.6, 113.0, 100.6, 55.3, 55.2, 54.1, 53.2, 46.9, 45.2, 44.5.

4.3.5. 8-(4-Fluorophenyl)-4-[(*E*)-(4-fluorophenyl)methylidene]-6-methyl-1-phenyl-4,5,6,7,7a,8-hexahydro[1,2,4]oxadiazolo[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepine (3e). Obtained as colourless solid (0.243 g, 95%), mp 184–185 °C; R_f (petroleum ether/EtOAc, 4:1) 0.77; found: C, 71.91; H, 5.01; N, 7.68. $C_{33}H_{27}F_2N_3OS$ requires C, 71.85; H, 4.93; N, 7.62%; ν_{max}(KBr) 1600, 1508, 1469, 1351 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.76–7.82 (17H, m, Ar), 7.50 (1H, s, C=C*H*), 4.74 (1H, d, *J* 10.5 Hz, 8-C*H*), 3.83 (1H, d, *J* 12.0 Hz, 5-CH_2), 3.30 (1H, d, *J* 12.0 Hz, 5-CH_2), 2.76 (1H, dd, *J* 11.7, 2.1 Hz, 7-CH_2), 2.40 (1H, d, *J* 10.8 Hz, 7a-C*H*), 2.21–2.28 (4H, m, N–CH_3 and 7-CH_2), δ_C (75 MHz, $CDCl_3$) 157.4, 143.7, 138.8, 135.5, 99.2, 53.0, 52.1, 45.7, 44.2, 43.5.

4.3.6. 8-(3-Fluorophenyl)-4-[(*E*)-(3-fluorophenyl)methylidene]-6-methyl-1-phenyl-4,5,6,7,7a,8-hexahydro[1,2,4]oxadiazolo[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepine (3f). Obtained as colourless solid (0.246 g, 96%), mp 159–160 °C; R_f (petroleum ether/EtOAc, 4:1) 0.77; found: C, 71.89; H, 4.85; N, 7.56. $C_{33}H_{27}F_2N_3OS$ requires C, 71.85; H, 4.93; N, 7.62%; ν_{max}(KBr) 1610, 1581, 1469, 1442 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.65–7.81 (17H, m, Ar), 7.51 (1H, s, C=C*H*), 4.73 (1H, d, *J* 10.5 Hz, 8-C*H*), 3.84 (1H, d, *J* 12.0 Hz, 5-CH_2), 3.30 (1H, d, *J* 12.0 Hz, 5-CH_2), 2.77 (1H, dd, *J* 11.7, 2.1 Hz, 7-CH_2), 2.40 (1H, d, *J* 10.5 Hz, 7a-C*H*), 2.26 (1H, d, *J* 12.0 Hz, 7-CH_2), 2.22 (3H, s, N–CH_3); δ_C (75 MHz, $CDCl_3$) 158.4, 146.3, 144.6, 136.6, 133.3, 100.0, 54.1, 53.1, 46.9, 45.3, 44.3.

4.3.7. 8-(2-Chlorophenyl)-4-[(*E*)-(2-chlorophenyl)methylidene]-6-methyl-1-phenyl-4,5,6,7,7a,8-hexahydro[1,2,4]oxadiazolo[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepine (3g). Obtained as colourless solid (0.238 g, 95%), mp 164–165 °C; R_f (petroleum ether/EtOAc, 4:1) 0.35; found: C, 67.71; H, 4.75; N, 7.10. $C_{33}H_{27}Cl_2N_3OS$ requires C, 67.80; H, 4.66; N, 7.19%; ν_{max}(KBr) 1560, 1467, 1440, 1349 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.50–7.84 (17H, m, Ar), 7.59 (1H, s, C=C*H*), 5.53 (1H, d, *J* 10.2 Hz, 8-C*H*), 3.61 (1H, d, *J* 12.0 Hz, 5-CH_2), 3.23 (1H, d, *J* 12.0 Hz, 5-CH_2), 2.76 (1H, d, *J* 11.7 Hz, 7-CH_2), 2.54 (1H, d, *J* 10.5 Hz, 7a-C*H*), 2.26 (1H, d, *J* 12.0 Hz, 7-CH_2), 2.20 (3H, s, N–CH_3); δ_C (75 MHz, $CDCl_3$) 158.6, 145.0, 140.5, 136.9, 135.3, 134.4, 133.9, 133.5, 130.9, 130.8, 130.0, 129.4, 128.9, 128.5, 127.9, 127.7, 126.9, 126.6, 126.3, 125.2, 124.1, 123.9, 100.1, 54.6, 53.3, 45.2, 43.7, 42.9.

4.3.8. 6-Methyl-8-(2-methylphenyl)-4-[(*E*)-(2-methylphenyl)methylidene]-1-phenyl-4,5,6,7,7a,8-hexahydro[1,2,4]oxadiazolo[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepine (3h). Obtained as colourless solid (0.247 g, 96%), mp 150–151 °C; R_f (petroleum ether/EtOAc, 4:1) 0.77; found: C,

77.25; H, 6.05; N, 7.80. $C_{35}H_{33}N_3OS$ requires C, 77.31; H, 6.12; N, 7.73%; ν_{max}(KBr) 1579, 1465, 1445, 1349 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.53–7.83 (17H, m, Ar), 7.55 (1H, s, C=C*H*), 5.18 (1H, d, *J* 10.5 Hz, 8-C*H*), 3.61 (1H, d, *J* 11.7 Hz, 5-CH_2), 3.22 (1H, d, *J* 12.0 Hz, 5-CH_2), 2.73 (1H, d, *J* 11.4 Hz, 7-CH_2), 2.56 (1H, d, *J* 10.5 Hz, 7a-C*H*), 2.41 (3H, s, Ar-CH_3), 2.32 (3H, s, Ar-CH_3), 2.24 (1H, d, *J* 11.4 Hz, 7-CH_2), 2.16 (3H, s, N–CH_3); δ_C (75 MHz, $CDCl_3$) 158.5, 144.9, 142.1, 137.0, 136.8, 136.1, 135.6, 132.1, 130.9, 130.4, 129.8, 129.2, 129.0, 128.2, 127.5, 127.3, 126.7, 126.5, 126.4, 125.5, 125.2, 125.1, 124.3, 123.9, 100.5, 54.7, 53.4, 45.1, 44.3, 42.4, 20.3, 19.7.

4.3.9. 6-Methyl-1-phenyl-8-(2-thienyl)-4-[(*E*)-2-thienylmethylidene]-4,5,6,7,7a,8-hexahydro[1,2,4]oxadiazolo-[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepine (3i). Obtained as colourless solid (0.243 g, 94%), mp 179–180 °C; R_f (petroleum ether/EtOAc, 4:1) 0.77; found: C, 66.07; H, 4.85; N, 8.03. $C_{29}H_{25}N_3OS_3$ requires C, 66.00; H, 4.77; N, 7.96%; ν_{max}(KBr) 1600, 1499, 1461, 1350 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.70–7.81 (15H, m, Ar), 7.53 (1H, s, C=C*H*), 5.01 (1H, d, *J* 10.5 Hz, 8-C*H*), 4.20 (1H, d, *J* 12.6 Hz, 5-CH_2), 3.32 (1H, d, *J* 12.3 Hz, 5-CH_2), 2.82 (1H, dd, *J* 11.7, 2.4 Hz, 7-CH_2), 2.45 (1H, d, *J* 11.7 Hz, 7-CH_2), 2.31–2.36 (4H, m, N–CH_3 and 7a-C*H*); δ_C (75 MHz, $CDCl_3$) 158.2, 147.1, 144.6, 138.6, 137.2, 130.9, 130.5, 130.0, 129.0, 128.8, 127.5, 127.0, 126.4, 126.1, 125.3, 124.2, 124.1, 123.9, 123.6, 121.5, 100.4, 54.2, 53.5, 46.1, 45.4, 43.4.

4.3.10. 6-Methyl-8-(1-naphthyl)-4-[(*E*)-2-naphthylmethylidene]-1-phenyl-4,5,6,7,7a,8-hexahydro[1,2,4]-oxadiazolo[5,4-*d*]pyrido[3,4-*c*][1,5]benzothiazepine (3j). Obtained as colourless solid (0.240 g, 97%), mp 173–174 °C; R_f (petroleum ether/EtOAc, 4:1) 0.77; found: C, 80.05; H, 5.34; N, 6.89. $C_{41}H_{33}N_3OS$ requires C, 79.97; H, 5.40; N, 6.82%; ν_{max}(KBr) 1581, 1467, 1441, 1353 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.80–8.36 (23H, m, Ar), 8.07 (1H, s, C=C*H*), 5.89 (1H, d, *J* 9.9 Hz, 8-C*H*), 3.74 (1H, d, *J* 12.0 Hz, 5-CH_2), 3.35 (1H, d, *J* 12.0 Hz, 5-CH_2), 2.78–2.81 (2H, m, 7-CH_2), 2.24 (1H, d, *J* 9.9 Hz, 7a-C*H*), 2.00 (3H, s, N–CH_3); δ_C (75 MHz, $CDCl_3$) 158.5, 145.0, 139.8, 137.1, 133.9, 133.7, 133.4, 132.4, 131.2, 130.9, 130.0, 129.0, 128.7, 128.3, 127.7, 127.6, 126.9, 126.4, 126.0, 125.8, 125.3, 124.8, 124.0, 123.1, 122.6, 100.7, 54.5, 53.7, 45.0, 44.7, 41.4.

4.4. X-ray crystal structure determination of 2g

The unit cell was measured by centering 25 reflections and refined by full-matrix least-square on F^2. Empirical formula $C_{26}H_{22}Cl_2N_2S$; formula weight 465.42; crystal system triclinic; space group *PT*. The unit cell dimensions are *a*=7.935(3) Å, *b*=10.206(4) Å, *c*=14.933 Å, α=76.58°, β=86.48°, γ=79.15°, *V*=1155.2(8) $Å^3$, *Z*=2, D_{calcd}=1.338 Mg/m^3, μ=0.388 mm^{-1}, *T*=293(2) K, *F*(000)=484. Number of reflections collected were 5023, number of independent reflections were 4067 (R_{int}=0.0359), R_1=0.0542, wR_2=0.1219 for final *R* indices [$I>2\sigma(I)$], R_1=0.1653, wR_2=0.1607 on all data. CCDC number is 609323.

4.5. X-ray crystal structure determination of 3b

The unit cell was measured by centering 5350 reflections and refined by full-matrix least-square on F^2. Empirical formula $C_{33}H_{27}Cl_2N_3OS$; formula weight 584.54; crystal system triclinic; space group *P*-1. The unit cell dimensions are *a*=9.0275(16) Å, *b*=11.390(2) Å, *c*=14.739(3) Å, α=86.522(3)°, β=84.749(3)°, γ=74.016(3)°, *V*=1449.8(4) $Å^3$, *Z*=2, D_{calcd}=1.339 Mg/m^3, μ=0.328 mm^{-1}, *T*=298(2) K, *F*(000)=608. Number of reflections collected were 5669, number of independent reflections were 4585 (R_{int}=0.0191), R_1=0.0457, wR_2=0.1128 for final *R* indices [$I>2\sigma(I)$], R_1=0.0568, wR_2=0.1197 on all data. CCDC number is 632029.

4.6. X-ray crystal structure determination of 3c

The unit cell was measured by centering 5160 reflections and refined by full-matrix least-square on F^2. Empirical formula $C_{35}H_{33}N_3OS$; formula weight 543.70; crystal system triclinic; space group *P*-1. The unit cell dimensions are *a*=9.0800(10) Å, *b*=11.3724(13) Å, *c*=14.7418(17) Å, α=86.222(2)°, β=83.695(2)°, γ=74.354(2)°, *V*=1455.9(3) $Å^3$, *Z*=2, D_{calcd}=1.240 Mg/m^3, μ=0.144 mm^{-1}, *T*=298(2) K, *F*(000)=576. Number of reflections collected were 5670, number of independent reflections were 4465 (R_{int}=0.0205), R_1=0.0464, wR_2=0.1178 for final *R* indices [$I>2\sigma(I)$], R_1=0.0593, wR_2=0.1258 on all data. CCDC number is 632030.

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Supplementary data

Supplementary data (^1H, ^{13}C, DEPT, H,H-COSY, C,H-COSY and HMBC spectra of compounds **2b** and **3b**) associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.05.097.

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