Tetrahedron: *Asymmetry* 27 (2016) 973–979

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Stereoselective 1,3-dipolar cycloadditions of thioketones to carbohydrate-derived nitrones

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ARTICLE INFO

Article history:
Received 16 July 2016
Accepted 2 August 2016
Available online 28 August 2016

ABSTRACT

A series of cycloaliphatic thioketones was reacted with selected enantiopure nitrones bearing carbohydrate-derived moieties leading to 1,4,2-oxathiazolidine derivatives in a highly stereoselective manner. Analysis of spectroscopic data supplemented by X-ray diffraction analysis of the major products confirmed the anti-configuration in the series derived from D-glyceraldehyde and L-erythrose-functionalized nitrones bearing a sugar moiety at the C atom. In the case of the model benzaldehyde-derived nitrone decorated at the N atom with carbohydrate auxiliary, and also for a L-erythrose-derived cyclic nitrone, in the reaction with sterically crowded 2,2,4,4-tetramethyl-3-thioxocyclobutanone the exclusive formation of single diastereoisomeric products was observed indicating an excellent steric match of the substrates. Dissociation constants of selected (3+2)-cycloadducts were determined by ^{1}H NMR spectroscopy.

1. Introduction

Over the last few decades, both aromatic and cycloaliphatic thioketones have attracted considerable attention as extremely reactive dipolarophiles (so-called "superdipolarophiles") towards diverse 1,3-dipoles such as diazoalkanes, thiocarbonyl *S*-methanides, and nitrones.[1] It is well documented, that they react with 1,3-dipoles yielding the corresponding five-membered sulfur heterocycles.[2] For example, 1,3-dithiolanes, 1,2,4-trithiolanes, 1,4,2-dithiazolidines, 1,3-oxathiolanes, and 1,3-thiazolidines are available by (3+2)-cycloaddition reactions, which are believed to occur via a concerted pathway. However, in recent publications the reactions of aryl/hetaryl and dihetaryl thioketones with some diazoalkanes and with thiocarbonyl ylides were shown to proceed via diradical stepwise mechanisms.[3] Reactions of thioketones with nitrones have been studied, and 1,4,2-oxathiazolidines are reported as products formed with complete regioselectivity.[4–6] However, this type of products derived from *c*-aryl/alkyl nitrones undergo dissociation in solution and form an equilibrium with the starting materials as reported by Black and Watson,[4a] and also by Huisgen et al.[1a] Only in the case of fluorinated nitrones[5] and their analogues bearing a diphenylphosphinoyl[6] moiety was a remarkable stability of the cycloadducts observed.

On the other hand, carbohydrate-derived nitrones are attractive chiral 1,3-dipoles widely applied not only for the (3+2)-cycloadditions but also for other reactions leading to *N*,*O*-heterocycles with diverse ring size.[7] In addition, they are useful starting materials for reactions with nucleophiles, particularly with Grignard reagents and lithiated organyls.[8] To the best of our knowledge, (3+2)-cycloadditions of enantiopure nitrones with thioketones have not been reported. Thus, in continuation of our studies aimed at the synthesis and applications of thioketones in organic synthesis[9] we became interested in chiral 1,4,2-oxathiazolidines. Herein we report on the highly stereoselective additions of selected cycloaliphatic thioketones **1a–d** depicted in Figure 1 with a model enantiopure D-glyceraldehyde and L-erythrose-derived nitrones.

2. Results and discussion

For the test experiments with cycloaliphatic thioketones **1**, enantiopure D-glyceraldehyde derived nitrone **2** was selected as a model compound (Fig. 2).[10] In a typical procedure, a solution of **1a** in THF was added dropwise to a slight excess of **2** (1.1 equiv) in dry THF, at room temperature, and after only a few minutes, the characteristic red colour of starting thioketone **1a** completely disappeared indicating the end of reaction. The crude reaction mixture was examined by ^{1}H NMR which showed two sets of signals located at 4.33 (d_{br}, $J \approx 9.1$ Hz) ppm and 4.26 (d, $J = 8.7$ Hz) ppm attributed to C(3)-*H* of the expected 1,4,2-oxathiazolidine products of type **6** as a diastereomeric mixture in a 96:4 ratio (Scheme 1,

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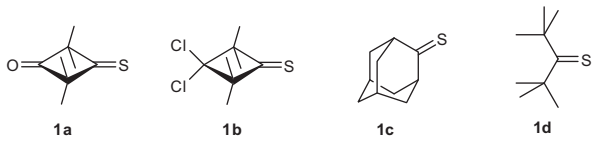


Figure 1. Thioketones **1a–d** selected for the study on (3+2)-cycloadditions with enantiopure nitrones.

Table 1). Similar excellent facial selectivity (97:3 ratio) was noticed for the reactions of thioketone **1b** and adamantanethione **1c**. Moreover, the sterically crowded di-*tert*-butyl thioketone **1d** also provided the corresponding product, however only in a ca. 3:1 ratio, after a remarkably longer reaction time of 30 min. It is a rather unexpected result as this bulky thioketone reacts only with small 1,3-dipoles such as diazomethane.[11] Major components of the crude 1,4,2-oxathiazolidines **6a–d** were easily separated by standard column chromatography, and isolated as colourless materials, fairly stable in the pure state. Although the structure of new enantiopure 1,4,2-oxathiazolidines **6** were confirmed by NMR techniques supplemented by MS and elemental analysis, the absolute configurations of the newly generated stereogenic centers could not be assigned by spectroscopic analysis. Fortunately, the absolute configuration of *anti*-**6c** was confirmed by a single crystal X-ray structure measurements (Fig. 3). Since characteristic shift patterns in ^{1}H and ^{13}C NMR spectra for both series of diastereoisomeric products **6a–d** were observed, the *anti*-configuration of major components could be assigned as well.

In order to gain more insight into the influence of steric hindrance caused by substituents attached to 1,3-dioxolane moiety of the nitrone on the stereochemical outcome, a series of L-erythrose-derived nitrones **3–5** was selected for further studies. The parent L-erythrose-derived *N*-glycosylhydroxylamine, a known 'masked nitrone' **3**, was prepared by condensation of the respective lactol with neat *N*-benzylhydroxylamine as described.[12] Subsequent trapping of the hydroxyl group in **3** under standard silylation conditions, performed in the presence of DMAP and imidazole, afforded nitrones **4** and **5** in fair yields of ca. 70%.[13] Attempted synthesis of 1,4,2-oxathiazolidine **7a** under standard reaction conditions using nitrone **3** and thioketone **1a** provided after 30 min a complex mixture of desired products (*anti*-/*syn*-configured products in a 55:45 ratio), contaminated with unconsumed substrates (ca. 26%). Neither longer reaction times (up to 24 h at rt) nor decrease of the reaction temperatures led to completion of the reaction, which indicates a mismatch of the substrates resulting in significant shift of the equilibrium towards the reaction partners. In contrast, the reactions of both silylated analogues **4** and **5** provided target compounds **8a** and **9a** in excellent yields (>97%) and high *anti*-diastereoselectivity (dr ratio 81:19; Table 1, entries 6 and 7). Apparently, the steric pressure by *cis*-substitution at the backbone 1,3-oxolane moiety of the starting nitrones **4** and **5** has some negative effect on the stereoselectivity. The absolute configurations at the newly generated stereogenic centers in **7–9** was tentatively assigned based on the NMR spectra; the characteristic shift patterns of the signals attributed to the 1,4,2-oxathiazolidine and the 1,3-dioxolane moieties nicely matched to those observed for products in D-glyceraldehyde series. For example, in the ^{1}H NMR spectra of **9a**, the diagnostic shifts and coupling constant values of $J = 8.5$ Hz (3.95 ppm, for *syn*-**9a**), and of $J = 9.9$ Hz (4.10 ppm, for *anti*-**9a**) were observed (Fig. 4). As expected for concerted processes, no influence of the solvents used on the reaction outcome could be observed; thus, similar results with respect to the chemical yield and to the ratio of isomers were noticed for the reactions performed at ambient conditions in THF, CH_2Cl_2, and toluene. On the other hand, some impact of the reaction temperature on the diastereomeric ratio was observed. Whereas the reaction performed in refluxing THF provided *anti*-/*syn*-configured products in 71:29 ratio, slightly enhanced diastereoselectivity (83:17) was observed for the reaction run at −10 °C (Table 1, entry 7).

In continuation, benzaldehyde-derived nitrone **10**[14] functionalized at the N atom with a carbohydrate auxiliary was reacted with thioketones **1a** and **1b** to afford the corresponding products **11a** and **11b**, respectively, in excellent yield and diastereoselectivity of >99:1 (Scheme 2). Similar to our previous report on the application of the aforementioned nitrone in the synthesis of 1,2-oxazines,[15] the signals of the benzylic protons assigned to C(3) of the 1,4,2-oxathiazolidine ring appear as singlets (at 6.03 and 5.89 ppm for **11a** and **11b**, respectively). Hence, due to unhindered rotation of the auxiliary moiety the absolute configuration could not be assigned by NOE experiments. Fortunately, the X-ray analysis of **11a** unambiguously indicated the 7(*S*)-configuration of the product (Fig. 5). Again, the absolute configuration in dichloro-analogue **11b** was assumed based on the characteristic patterns in the NMR spectra of the series. Finally, the reaction of selected cyclic nitrone **12**[16] with model thioketone **1a** was performed to afford 1,4,2-oxathiazolidine **13a** as sole products in 92% yield. Apparently, the presence of the fused 1,3-oxolane moiety in **12** favours exclusive addition of the thioketone from the less hindered back side. The presence of an uncoupled signal (singlet at 4.91 ppm) in the ^{1}H NMR spectrum of **13a**, attributed to 3b′-H of the polycyclic skeleton strongly supports the proposed absolute configuration at the newly generated stereogenic center.

Almost all tested reactions went virtually to completion as evidenced by the loss of the coloured thioketone (with the exception of that with nitrone **3** and **1a**), and fairly stable cycloadducts were isolated. However, partial cycloreversion was observed by ^{1}H NMR for $CDCl_3$ solutions stored for a longer time at room temperature. For example, a sample of enantiomerically pure anti-**6a** reached equilibrium after 24 h, and the initial mixture of 1,4,2-oxathiazolidines **6a** (*anti*-/*syn*- 96:4 ratio) accompanied by a small amounts of the starting materials was formed. Similar monitoring of pure *anti*-**9a** and *syn*-**9a** showed, that each of diastereomers provided the initial mixture of *anti*-**9a**/*syn*-**9a** (81:19 ratio) after only a few days. By analogy to previous reports,[1a,6] dissociation constants of selected (3+2)-cycloadducts were determined by ^{1}H NMR spectroscopy and the results are summarized in Table 2. The collected data for the D-glyceraldehyde series revealed, that adamantane-derived product **6c** is more stable than 3-oxocyclobutane derivative **6a** and its dichloro analogue **6b** by factors of 3.7 and 2.5, respectively. On the other hand, the dissociation constant of **6d** is two orders of magnitude higher than those determined for **6a–c**. Presumably, the presence of two *tert*-butyl groups in **6d** favours cycloreversion process due to

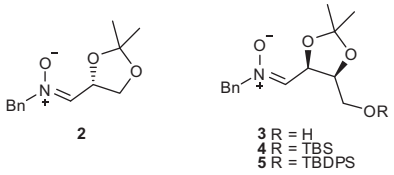
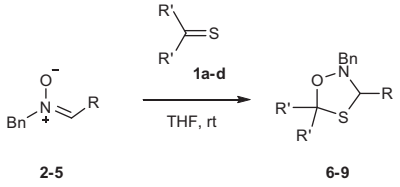
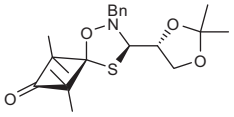
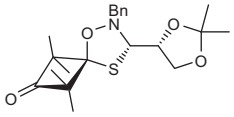
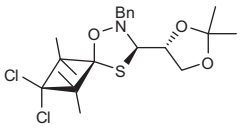
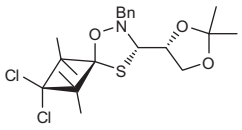
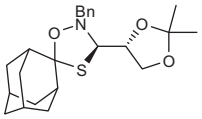
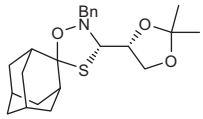
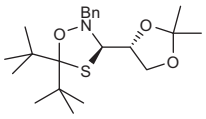
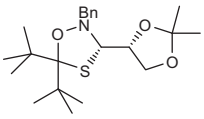
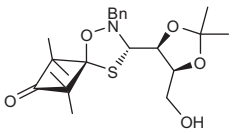
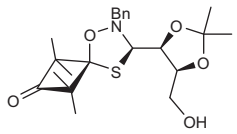
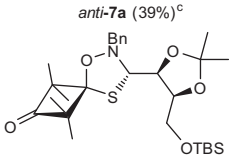
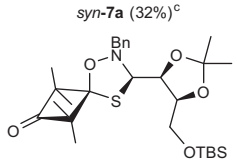
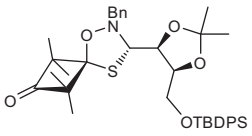
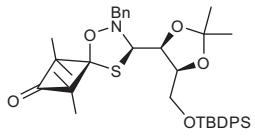


Figure 2. D-Glyceraldehyde and L-erythrose-derived nitrones **2** and **3–5**.



Scheme 1. (3+2)-Cycloadditions of thioketones **1** to nitrones **2–5** leading to 1,4,2-oxathiazolidine derivatives **6–9**.

Table 1
Synthesis of 1,4,2-oxathiazolidines **6**–**9**; *reaction conditions*: thione **1a**–**d** (1.0 mmol), nitrone **2**–**5** (1.1 mmol), THF, rt, 5–30 min

Entry	*anti*-/*syn*-[a]	Products	
1	96:4		
		anti-**6a** (88%)[b]	*syn*-**6a** (4%)[c]
2	97:3		
		anti-**6b** (92%)[b]	*syn*-**6b** (3%)[c]
3	97:3		
		anti-**6c** (83%)[b]	*syn*-**6c** (3%)[c]
4	76:24		
		anti-**6d** (11%)[b] (60%)[c]	*syn*-**6d** (19%)[c]
5	55:45[d]		
		anti-**7a** (39%)[c]	*syn*-**7a** (32%)[c]
6	81:19		
		anti-**8a** (51%)[b]	*syn*-**8a** (18%)[c]
7	71:29[e] 81:19[f] 83:17[g]		
		anti-**9a** (74%)[b]	*syn*-**9a** (9%)[b]

[a] Ratio of *anti*-/*syn*-products in a crude reaction mixture.
[b] Yield of isolated purified material.
[c] Yield estimated by ^{1}H NMR spectroscopic analysis of crude reaction mixture.
[d] In an equilibrium with starting materials: **7a**:**3**:**1a** in ca. 6:1:1 ratio.
[e] THF, reflux, 5 min.
[f] THF, rt, 20 min.
[g] THF, −10 °C, 30 min.

remarkable steric repulsion, which in the case of **6a** and **6b** is to some extent overcompensated for by decrease of the cyclobutane ring strain. Finally, the analysis of K_{diss} in 3-oxocyclobutane series **a** demonstrate that the stability of (3+2)-cycloadducts follows the order **6a** > **13a** > **11a**, which very likely relates to increase of the ring strain in tricyclic system, and to the steric hindrance around the *S*,*O*-acetal group caused by chiral auxiliary, respectively.

3. Conclusions

The presented study showed that enantiopure carbohydrate-derived nitrones smoothly undergo (3+2)-cycloaddition reactions with cycloaliphatic thioketones to give 1,4,2-oxathiazolidines with complete regioselectivity, high yield, and good to excellent diastereoselectivity. Chromatographic separation of crude products enabled isolation of the major diastereomers, and in two cases, the absolute configuration at the newly generated stereogenic centers was unambiguously established by means of single-crystal X-ray diffraction analysis. Remarkably, isolated products are stable in the pure state, however, in $CDCl_3$ solutions at room temperature, an equilibration with starting materials was evidenced. These enantiomerically pure products are the first examples of chiral 1,4,2-oxathiazolidines prepared by (3+2)-cycloaddition with thioketones, and nicely supplements earlier reports on this topic.

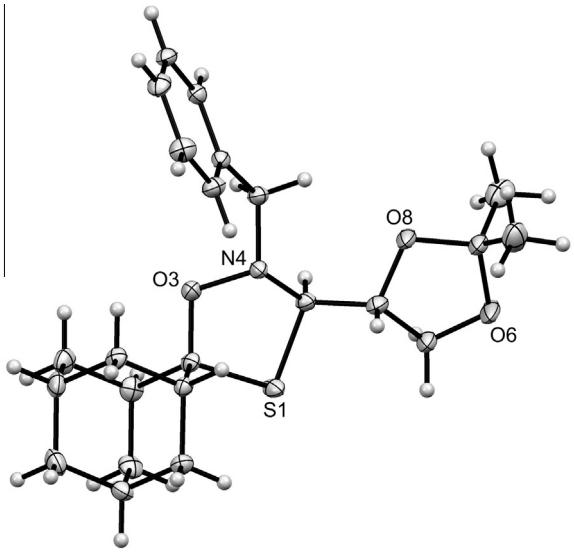
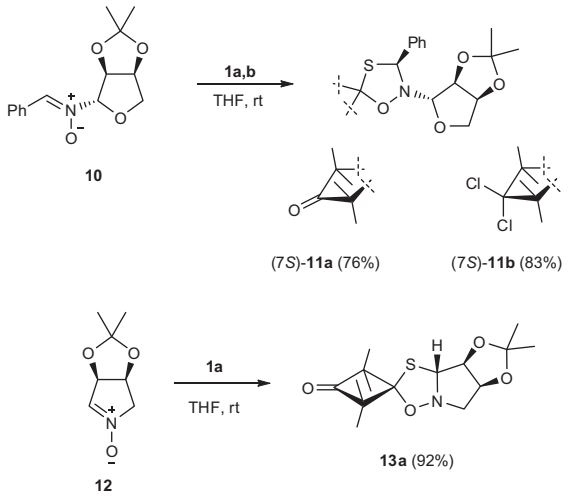


Figure 3. A view of the molecular structure of compound *anti*-**6c**. Displacement ellipsoids are drawn at the 50% probability level. X-ray data collected at the ambient temperature 100 K.



Scheme 2. Synthesis of 1,4,2-oxathiazolidines (7*S*)-**11a**,**b** and **13a**.

4. Experimental

4.1. General

Solvents were purchased and used as received without further purification. Nitrones **2**,[10] **3**,[12] **4**–**5**,[13] **10**,[14] and **12**[16] were prepared following the literature reports. 2,2,4,4-Tetramethyl-3-thioxocyclobutanone **1a**, 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione **1b**, and adamantanethione **1c** were obtained by thionation of the corresponding ketones with P_2S_{10} in pyridine according to literature;[17] for di(*tert*-butyl)thioketone **1d** a protocol involving reaction of di(*tert*-butyl)ketimine lithium salt with CS_2 was applied.[18] Products were purified by standard chromatography column on silica gel (230–400 mesh, Merck or Fluka) or by flash chromatography using Reveleris X2 (Grace) system. Unless stated otherwise, yields refer to analytically pure samples. NMR spectra were recorded with Bruker AVIII 600 instrument. Chemical shifts are reported relative to solvent residual peaks (^{1}H NMR: δ = 7.26 ppm [$CDCl_3$]; ^{13}C NMR: δ = 77.0 ppm [$CDCl_3$]). For detailed peak assignments 2D spectra were measured (COSY, HMQC, HMBC). IR spectra were measured with a FTIR NEXUS spectrometer (as KBr pellets or thin films). MS were performed with a Finnigan MAT-95 or with a Varian 500-MS LC Ion Trap instruments. Optical rotations were

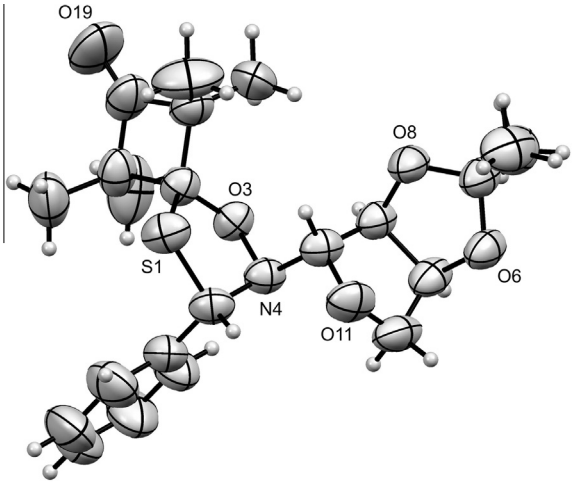


Figure 5. A view of the molecular structure of compound (7*S*)-**11a**. Displacement ellipsoids are drawn at the 50% probability level. X-ray data collected at the ambient temperature 293 K.

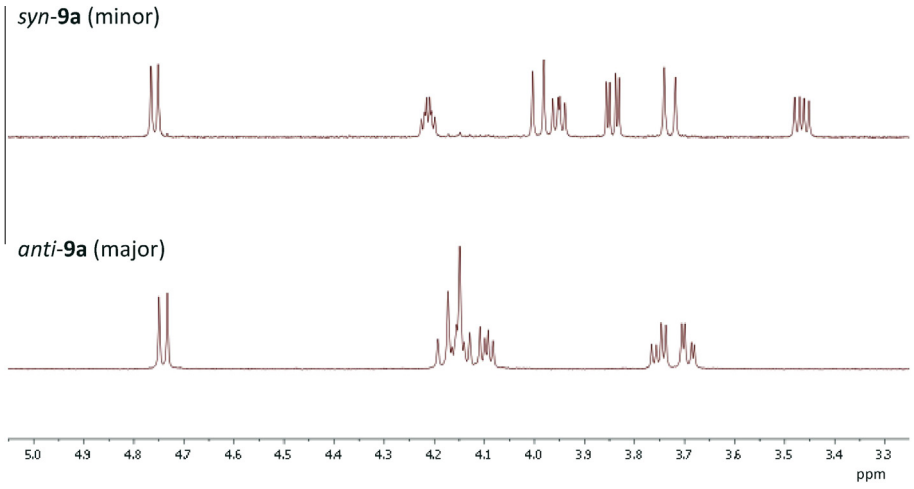


Figure 4. Diagnostic part of the ^{1}H NMR spectra of *syn*-**9a** (upper) and *anti*-**9a** (bottom).

Table 2
Dissociation constants of cycloadducts **6a–d**, **11a**, and **13a**[a]

Entry	Adduct(s)	$K_{diss} \times 10^5$ [mol L^{-1}]
1	**6a**	0.827
2	**6b**	0.561
3	**6c**	0.223
4	**6d**	75.86
5	**11a**	24.25
6	**13a**	4.784

[a] Determined by ^{1}H NMR at 25 °C; initial concentration of starting materials c = 0.050 mol L^{-1}.

determined with an Anton Paar MCP 500 polarimeter at the temperatures indicated. Elemental analyses were obtained with a Vario EL III (Elementar Analysensysteme GmbH) instrument. Melting points were determined in capillaries with a MEL-TEMP II apparatus (Aldrich) or with a polarizing optical microscope (Opta-Tech), and are uncorrected. Single crystal X-ray data[19] were collected with a Bruker SMART APEX II CCD diffractometer (Cu Kα radiation, λ = 1.54178 Å, 30 W Incoatec Microfocus Source IμS with Montel optics); the structure solution and refinement was performed by using Shelxs-97[20] and Shelxl-2014.[21]

4.1.1. General procedure for the synthesis of 1,4,2-oxathiazolidines

To a solution of the respective nitrone (1.1 mmol) in dry THF (3 mL) a solution of thione **1** (1.0 mmol) in THF (1 mL) was added dropwise and the stirring was continued at room temperature until the starting thione was fully consumed (TLC monitoring, SiO_2, petroleum ether/EtOAc 20:1). The solvent was removed under reduced pressure, and the resulting was filtered through short silica gel pad (SiO_2, hexanes/EtOAc 3:1). Crude 1,4,2-oxathiazolidine derivative was purified on chromatography column.

4.1.2. (4′*R*,7*R*)-6-Benzyl-7-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)-1,1,3,3-tetramethyl-5-oxa-8-thia-6-azaspiro[3.4]octan-2-one *anti*-6a

5 min; crude product (377 mg, 96%) containing mixture of *anti*- and *syn*-products in a 96:4 ratio, respectively, was purified on chromatography column (SiO_2, petroleum ether/EtOAc 10:1) to give *anti*-**6a** (343 mg, 88%) as a thick colourless oil; $[\alpha]_D^{20}$ = −78.5 (*c* 0.88, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.08 (s, 3H, 2′-Me), 1.22, 1.24, 1.29, 1.31 (4 s, 3H each, 1-Me$_2$, 3-Me$_2$), 1.31 (s, 3H, 2′-Me), 3.76 (dd, J = 4.6, 8.9 Hz, 1H, 5′-H), 3.97–4.04 (m, 1H, 4′-H), 4.01 (d, J = 11.9 Hz, 1H, C*H*$_2$Ph), 4.07 (dd, J = 6.5, 8.9 Hz, 1H, 5′-H), 4.20 (d, J = 11.9 Hz, 1H, C*H*$_2$Ph), 4.33 (d$_{br}$, $J \approx$ 9.1 Hz, 1H, 7-H), 7.28–7.31, 7.33–7.36, 7.41–7.43 (3 m, 1H, 2H, 2H, Ph) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 18.5, 20.5, 22.4, 25.0 (4 q, 4 Me), 25.4, 26.5 (2 q, 2′-*Me*$_2$), 61.3 (t, *C*H$_2$Ph), 65.5, 66.6 (2 s, C-1, C-3), 67.3 (t, C-5′), 76.2 (d, C-7), 77.1 (d, C-4′), 103.8 (s, C-4), 110.7 (s, C-2′), 128.0, 128.5, 129.7, 135.4 (3 d, s, Ph), 219.6 (C=O) ppm; IR (film): ν = 3085–2865 (=C—H, C—H), 1790 (C=O), 1455, 1390, 1070, 1030 (C—O) cm^{-1}; ESI-MS (*m*/*z*): 414 (100, [M+Na]$^+$); elemental analysis calcd (%) for $C_{21}H_{29}NO_4S$ (391.5): C 64.42, H 7.47, N 3.58, S 8.19; found: C 64.15, H 7.43, N 3.46, S 7.90.

Selected data for *syn*-**6a** (in a mixture with *anti*-**6a**): ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.24, 1.28, 1.32, 1.33, 1.37 (5 s, 3H each), 3.50 (dd, J = 6.5, 8.8 Hz, 1H, 5′-H), 3.89 (dt, $J \approx$ 5.8, 8.8 Hz, 1H, 5′-H), 3.95, 4.12 (2 d, J = 11.7 Hz, 1H each, C*H*$_2$Ph), 4.26 (d, J = 8.7 Hz, 1H, 7-H) ppm, other signals overlap with those of *anti*-**6a**; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 18.6, 20.8, 22.3, 25.1, 25.2, 26.7 (6 q, 6 Me), 61.5 (t, *C*H$_2$Ph), 65.6, 66.7 (2 s, C-1, C-3), 67.7 (t, C-5′), 76.1, 77.7 (2 d, C-7, C-4′), 104.5 (s, C-4), 109.6 (s, C-2′), 128.3, 128.8, 129.5, 135.2 (3 d, s, Ph), 219.7 (C=O) ppm.

4.1.3. (4′*R*,7*R*)-6-Benzyl-2,2-dichloro-7-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)-1,1,3,3-tetramethyl-5-oxa-8-thia-6-azaspiro[3.4]octane *anti*-6b

5 min; crude product (433 mg, 97%) containing mixture of *anti*- and *syn*-products in a 97:3 ratio, respectively, was purified on chromatography column (SiO_2, petroleum ether/EtOAc 15:1) to give *anti*-**6b** (411 mg, 92%) as a colourless solid; mp 111–113 °C; $[\alpha]_D^{20}$ = −80.4 (*c* 0.86, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.05, 1.29 (2 s, 3H each, 2′-Me$_2$), 1.34, 1.36, 1.42, 1.43 (4 s, 3H each, 1-Me$_2$, 3-Me$_2$), 3.72 (dd, J = 4.8, 8.9 Hz, 1H, 5′-H), 3.96–3.99 (m, 1H, 4′-H), 3.98 (d, J = 11.9 Hz, 1H, C*H*$_2$Ph), 4.03 (dd, J = 6.5, 8.9 Hz, 1H, 5′-H), 4.14 (d, J = 11.9 Hz, 1H, C*H*$_2$Ph), 4.23 (d, J = 9.1 Hz, 1H, 7-H), 7.26–7.29, 7.31–7.34, 7.38–7.42 (3 m, 1H, 2H, 2H, Ph) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 23.0, 24.6, 25.4, 28.0 (4 q, 4 Me), 26.0, 26.6 (2 q, 2′-*Me*$_2$), 59.4, 59.7 (2 s, C-1, C-3), 61.1 (t, *C*H$_2$Ph), 67.2 (t, C-5′), 76.0 (d, C-7), 76.8 (d, C-4′), 98.4 (s, C-2), 105.5 (s, C-4), 110.6 (s, C-2′), 127.9, 128.4, 129.7, 135.4 (3 d, s, Ph) ppm; IR (KBr): ν = 3065–2855 (=C—H, C—H), 1450, 1255, 1225, 1145, 1070 (C—O) cm^{-1}; ESI-MS (*m*/*z*): 447 (21, [M+H]$^+$), 446 (100, [M]$^+$); elemental analysis calcd (%) for $C_{21}H_{29}Cl_2NO_3S$ (446.4): C 56.50, H 6.55, N 3.14, S 7.18; found: C 56.36, H 6.65, N 3.07, S 7.31.

Selected data for *syn*-**6b** (in a mixture with *anti*-**6b**): ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.18, 1.32, 1.38, 1.47 (4 s, 3H each), 3.33 (dd, J = 5.6, 8.8 Hz, 1H, 5′-H), 3.77 (dt, $J \approx$ 5.9, 8.8 Hz, 1H, 5′-H), 3.82, 4.01 (2 d, J = 11.7 Hz, 1H each, C*H*$_2$Ph) ppm, other signals overlap with those of *anti*-**6b**; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 23.1, 25.0, 25.1, 25.9, 26.7, 28.3 (6 q, 6 Me), 59.6, 59.9 (2 s, C-1, C-3), 61.5 (t, *C*H$_2$Ph), 67.8 (t, C-5′), 75.9, 77.3 (2 d, C-7, C-4′), 100.0 (s, C-2), 106.7 (s, C-4), 109.6 (s, C-2′), 128.8, 129.1, 129.5, 135.2 (3 d, s, Ph) ppm.

4.1.4. (3′*R*,4″*R*)-Spiro{adamantane-2,5′-[2′-benzyl-3′-(2″,2″-dimethyl-1″,3″-dioxolan-4″-yl)-[1,4,2]oxathiazolidine} *anti*-6c

20 min; crude product (374 mg, 93%) containing mixture of *anti*- and *syn*-products in a 97:3 ratio, respectively, was purified on chromatography column (SiO_2, petroleum ether/EtOAc 20:1) to give *anti*-**6c** (333 mg, 83%) as a colourless solid; mp 89–91 °C; $[\alpha]_D^{20}$ = −78.3 (*c* 0.44, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.14, 1.30 (2 s, 3H each, 2″-Me$_2$), 1.53–1.62, 1.68–1.94, 2.04–2.10 (3 m, 2H, 8H, 3H, Ad), 2.23 (m$_c$, 1H, Ad), 3.72 (dd, J = 5.4, 8.9 Hz, 1H, 5″-H), 4.06 (dd, J = 6.5, 8.9 Hz, 1H, 5″-H), 4.21 (d, J = 13.0 Hz, 1H, C*H*$_2$Ph), 4.26 (ddd, J = 5.4, 6.5, 9.1Hz, 1H, 4″-H), 4.33 (d, J = 9.1 Hz, 1H, 3′-H), 4.40 (d, J = 13.0 Hz, 1H, C*H*$_2$Ph), 7.23–7.26, 7.29–7.33, 7.41–7.44 (3 m, 1H, 2H, 2H, Ph) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 25.5, 26.6 (2 q, 2 Me), 26.0, 26.7, 34.1, 34.7, 37.2, 38.0, 38.1, 41.9, 42.2 (2 d, 5 t, 2 d, Ad), 61.8 (t, *C*H$_2$Ph), 67.6 (t, C-5″), 76.91 (d, C-4″), 76.95 (d, C-3′), 106.5 (s, spiro-C), 110.5 (s, C-2″), 127.3, 128.2, 129.1, 137.2 (3 d, s, Ph) ppm; IR (KBr): ν = 3085–2860 (=C—H, C—H), 1450, 1370, 1225, 1065 (C—O) cm^{-1}; ESI-MS (*m*/*z*): 424 (100, [M+Na]$^+$), 402 (11, [M]$^+$); elemental analysis calcd (%) for $C_{23}H_{31}NO_3S$ (401.6): C 68.79, H 7.78, N 3.49, S 7.99; found: C 68.71, H 7.75, N 3.47, S 8.03. Suitable crystals for an X-ray crystal structure determination were obtained from hexane solution by slow evaporation of the solvent.

Selected data for *syn*-**6c** (in a mixture with *anti*-**6c**): ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.25, 1.29 (2 s, 3H each, 2″-Me$_2$), 3.49 (dd, J = 5.1, 8.8 Hz, 1H, 5″-H), 4.01 (dd, J = 6.2, 8.8 Hz, 1H, 5″-H), 4.13 (ddd, J = 5.1, 6.2, 8.7 Hz, 1H, 4″-H) ppm, other signals overlap with those of *anti*-**6c**; ^{13}C NMR ($CDCl_3$, 151 MHz): selected signals δ = 63.0 (t, *C*H$_2$Ph), 67.8 (t, C-5″), 77.8 (d, C-3′), 108.7, 109.5 (2 s, spiro-C, C-2″), 127.9, 128.5, 129.3, 136.6 (3 d, s, Ph) ppm.

4.1.5. (3*R*,4′*R*)-2-Benzyl-3-(2′2′-dimethyl-1′,3′-dioxolan-4′-yl)-5,5-bis(*tert*-butyl)-[1,4,2]oxathiazolidine *anti*-6d

30 min; crude product was filtered through a short silica gel plug (petroleum ether/EtOAc 10:1) to give **6d** (311 mg, 79%) as a

mixture of *anti*- and *syn*-products in a 76:24 ratio, respectively. Attempted separation by standard column chromatography enabled isolation of a small sample of *anti*-**6d** (42 mg, 11%) as a colourless oil; $[\alpha]_D^{20} = -41.2$ (*c* 0.23, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ = 1.08, 1.16 (2 s, 9H each, 2 *t*Bu), 1.37, 1.46 (2 s, 3H each, 2 Me), 3.79 (dd, *J* = 7.2, 8.4 Hz, 1H, 5′-H), 3.85 (d, *J* = 13.8 Hz, 1H, C*H*$_2$Ph), 4.06 (d, *J* = 7.9 Hz, 1H, 3-H), 4.07 (dd, *J* = 6.4, 8.4 Hz, 1H, 5′-H), 4.35 (ddd, *J* = 6.4, 7.2, 7.9 Hz, 1H, 4′-H), 4.56 (d, *J* = 13.8 Hz, 1H, C*H*$_2$Ph), 7.23–7.27, 7.29–7.32, 7.38–7.41 (3 m, 1H, 2H, 2H, Ph) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 25.7, 26.7 (2 q, 2 Me), 29.8, 30.5, 43.7, 44.5 (2 q, 2 s, 2 *t*Bu), 61.2 (t, *C*H$_2$-Ph), 68.3 (t, C-5′), 75.8 (d, C-3), 76.3 (d, C-4′), 107.4 (s, C-5), 110.2 (s, C-2′), 126.9, 127.8, 129.7, 137.6 (3 d, s, Ph) ppm; IR (film): ν = 3080–2865 (=C—H, C—H), 1450, 1370, 1220, 1070 (C—O) cm^{-1}; CI-MS (*m*/*z*): 394 (71, $[M+H]^+$), 292 (100); elemental analysis calcd (%) for $C_{22}H_{35}NO_3S$ (393.2): C 67.14, H 8.96, N 3.56, S 8.15; found: C 67.13, H 8.93, N 3.45, S 8.08.

Selected data for *syn*-**6d** (in a mixture with *anti*-**6d**): ^1H NMR ($CDCl_3$, 600 MHz): δ = 1.05, 1.17 (2 s, 9H each, 2 *t*Bu), 1.25, 1.36 (2 s, 3H each, 2 Me), 3.81 (d, *J* = 13.7 Hz, 1H, C*H*$_2$Ph), 4.15 (dd, *J* = 6.6, 8.1 Hz, 1H, 5′-H), 4.31–4.35 (m, 2H, 3-H, 5′-H), 4.42 (d, *J* = 13.7 Hz, 1H, C*H*$_2$Ph), 4.49 (td, *J* ≈ 2.9, 7.0 Hz, 1H, 4′-H), other signals overlap with those of *anti*-**6d**; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 24.8, 26.2 (2 q, 2 Me), 29.6, 30.4, 43.9, 44.2 (2 q, 2 s, 2 *t*Bu), 61.7 (t, *C*H$_2$Ph), 65.4 (t, C-5′), 72.8 (d, C-3), 74.6 (d, C-4′), 106.8 (s, C-5), 109.1 (s, C-2′), 127.0, 127.9, 129.4, 137.5 (3 d, s, Ph) ppm.

4.1.6. Synthesis of 1,4,2-oxathiazolidines 7a

30 min; crude reaction mixture (99% recovery of the mass) was analyzed by NMR spectroscopy; the ^1H NMR spectrum taken in $CDCl_3$ revealed the presence of an equilibrated mixture containing starting materials (**1a** and **3**, ~13% each) and the products *anti*-**7a** and *syn*-**7a** (74%, in ca. 55:45 ratio, respectively). Attempted separation of the products by chromatography techniques was in vain. ESI-MS (*m*/*z*): 422 (3, $[M+H]^+$), 266 (54, $[M-\mathbf{1a}]^+$), 91 (100, $[Bn]^+$); Selected data for *anti*-**7a** (in a mixture with *syn*-**7a**, **1a**, and **3**): ^1H NMR ($CDCl_3$, 600 MHz): δ = 3.68 (dd, *J* = 5.3, 12.0 Hz, 1H, 5′-CH_2O), 3.76 (dd, *J* = 3.9, 12.0 Hz, 1H, 5′-CH_2O), 4.57 (d, *J* = 9.8 Hz, 1H, 7-H) ppm; Selected data for *syn*-**7a** (in a mixture with *anti*-**7a**, **1a**, and **3**): ^1H NMR ($CDCl_3$, 600 MHz): δ = 2.94 (dd, *J* = 6.7, 11.9 Hz, 1H, 5′-CH_2O), 3.24 (dd, *J* = 4.8, 11.9 Hz, 1H, 5′-CH_2O), 4.71 (d, *J* = 10.0 Hz, 1H, 7-H) ppm.

4.1.7. (4′*S*,5′*S*,7*S*)-6-Benzyl-7-[2′,2′-dimethyl-5′-(*tert*-butyldimethylsiloxymethyl)-1′,3′-dioxolan-4′-yl]-1,1,3,3-tetramethyl-5-oxa-8-thia-6-azaspiro[3.4]octan-2-one *anti*-8a

20 min; crude reaction mixture was filtered through short silica gel plug (CH_2Cl_2) and the solvents were removed to give **8a** (520 mg, 97%) as a mixture of *anti*- and *syn*-products in a 81:19 ratio, respectively. Major product *anti*-**8a** (273 mg, 51%) was isolated by column chromatography (SiO_2, petroleum ether/Et_2O 5:1) as a colourless solid; mp 66–68 °C; $[\alpha]_D^{20} = +56.7$ (*c* 0.55, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ = −0.05, −0.02, 0.84 (3 s, 3H, 3H, 9H, TBS), 1.22, 1.23, 1.26, 1.28, 1.30, 1.34 (6 s, 3H each, 6 Me), 3.67–3.73 (m, 2H, 5′-C*H*$_2$O), 4.05–4.11 (m, 3H, 4′-H, 5′-H, C*H*$_2$-Ph), 4.19 (d, *J* = 12.1 Hz, 1H, C*H*$_2$Ph), 4.67 (d, *J* = 9.5 Hz, 1H, 7-H), 7.25–7.32, 7.39–7.42 (2 m, 3H, 2H, Ph) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = −5.6, −5.4 (2 q, 2 Me, TBS), 18.3, 25.9 (s, q, *t*Bu), 18.7, 20.5, 22.1, 25.2, 25.6, 27.6 (6 q, 6 Me), 61.0 (t, *C*H$_2$Ph), 61.7 (t, 5′-*C*H$_2$O), 65.3, 66.6 (2 s, C-1, C-3), 72.6 (d, C-7), 77.3, 78.5 (2 d, C-4′, C-5′), 102.2 (s, C-4), 108.7 (s, C-2′), 127.8, 128.4, 129.5, 135.7 (3 d, s, Ph), 220.1 (s, C=O) ppm; IR (KBr): ν = 3060–2855 (=C—H, C—H), 1790 (C=O), 1250, 1145, 1030 (C—O) cm^{-1}; ESI-MS (*m*/*z*): 537 (42, $[M+H]^+$), 536 (100, $[M]^+$); elemental analysis calcd (%) for $C_{28}H_{45}NO_5SSi$ (535.8): C 62.76, H 8.47, N 2.61, S 5.98; found: C 62.53, H 8.43, N 2.73, S 5.81.

Selected data for *syn*-**8a** (in a mixture with *anti*-**8a**): ^1H NMR ($CDCl_3$, 600 MHz): δ = −0.09, −0.03, 0.82 (3 s, 3H, 3H, 9H, TBS), 1.20, 1.28, 1.32, 1.33 (4 s, 3H each, 4 Me), 3.28 (dd, *J* = 5.7, 11.3 Hz, 1H, 5′-C*H*$_2$O), 3.61 (dd, *J* = 3.8, 11.3 Hz, 1H, 5′-C*H*$_2$O), 3.96 (dd, *J* = 2.4, 5.7 Hz, 1H, 5′-H), 3.97 (d, *J* = 12.5 Hz, 1H, C*H*$_2$Ph), 4.85 (d, J = 8.6 Hz, 1H, 7-H) ppm, other signals overlap with those of *anti*-**8a**.

4.1.8. Synthesis of 1,4,2-oxathiazolidines 9a

20 min; crude products (647 mg, 98%, *anti*/*syn* 81:19) were separated by flash chromatography (SiO_2, petroleum ether/EtOAc 95:5) to give *syn*-**9a** (59 mg, 9%, first eluted) and *anti*-**9a** (488 mg, 74%, second eluted) as a colourless oils.

4.1.9. (4′*S*,5′*S*,7*R*)-6-Benzyl-7-[2′,2′-dimethyl-5′-(*tert*-butyldimethylsiloxymethyl)-1′,3′-dioxolan-4′-yl]-1,1,3,3-tetramethyl-5-oxa-8-thia-6-azaspiro[3.4]octan-2-one *syn*-9a

$[\alpha]_D^{20} = -28.5$ (*c* 0.95, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ = 1.02 (s, 9H, *t*Bu), 1.12, 1.23, 1.26, 1.31 (4 s, 3H each, 1-Me_2, 3-Me_2), 1.34, 1.42 (2 s, 3H each, 2′-Me_2), 3.47 (dd, *J* = 6.1, 11.2 Hz, 1H, 5′-CH_2O), 3.73 (d, *J* = 13.3, 1H, C*H*$_2$Ph), 3.85 (dd, *J* = 3.8, 11.2 Hz, 1H, 5′-CH_2O), 3.95 (dd, *J* = 6.1, 8.5 Hz, 1H, 4′-H), 3.99 (d, *J* = 13.3, 1H, C*H*$_2$Ph), 4.21 (td, *J* = 3.8, 6.1 Hz, 1H, 5′-H), 4.76 (d, *J* = 8.5 Hz, 1H, 7-H), 7.11–7.15, 7.18–7.21, 7.24–7.29, 7.33–7.36, 7.39–7.42, 7.58–7.60, 7.63–7.65 (7 m, 3H, 2H, 2H, 3H, 1H, 2H, 2H, 3 Ph) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 18.7, 26.9 (s, q, *t*Bu), 19.2, 20.9, 22.1, 24.9 (4 q, 1-Me_2, 3-Me_2), 25.3, 27.7 (2 q, 2′-Me_2), 61.2 (t, *C*H$_2$Ph), 62.5 (t, 5′-*C*H$_2$O), 65.6, 66.8 (2 s, C-1, C-3), 74.6 (d, C-7), 77.8 (d, C-4′), 78.2 (d, C-5′), 104.1 (s, C-4), 108.3 (s, C-2′), 127.56, 127.58, 127.7, 128.5, 128.7, 129.63, 129.65, 133.2, 133.5, 135.4, 135.67, 135.71 (7 d, 3 s, 2 d, 3 Ph), 220.2 (s, C=O) ppm; IR (film): ν = 3070–2860 (=C—H, C—H), 1790 (C=O), 1460, 1380, 1250, 1215, 1115 (C—O) cm^{-1}; ESI-MS (*m*/*z*): 682 (100, $[M+Na]^+$), 660 (12, $[M]^+$); elemental analysis calcd (%) for $C_{38}H_{49}NO_5SSi$ (659.3): C 69.16, H 7.48, N 2.12; found: C 69.25, H 7.54, N 1.95.

4.1.10. (4′*S*,5′*S*,7*S*)-6-Benzyl-7-[2′,2′-dimethyl-5′-(*tert*-butyldimethylsiloxymethyl)-1′,3′-dioxolan-4′-yl]-1,1,3,3-tetramethyl-5-oxa-8-thia-6-azaspiro[3.4]octan-2-one *anti*-9a

$[\alpha]_D^{20} = +19.6$ (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ = 1.00 (s, 9H, *t*Bu), 1.20, 1.22, 1.27, 1.30 (4 s, 3H each, 1-Me_2, 3-Me_2), 1.21, 1.34 (2 s, 3H each, 2′-Me_2), 3.69 (dd, *J* = 3.7, 11.5 Hz, 1H, 5′-CH_2O), 3.75 (dd, *J* = 5.3, 11.5 Hz, 1H, 5′-CH_2O), 4.10 (dd, *J* = 5.9, 9.9 Hz, 1H, 4′-H), 4.14 (ddd, *J* = 3.7, 5.3, 5.9 Hz, 1H, 5′-H), 4.14, 4.18 (d, *J* = 12.2 Hz, 1H each, C*H*$_2$Ph), 4.74 (d, *J* = 9.9 Hz, 1H, 7-H), 7.27–7.32, 7.33–7.44, 7.61–7.63, 7.68–7.70 (4 m, 3H, 8H, 2H, 2H, 3 Ph) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 18.6, 26.8 (s, q, *t*Bu), 19.1, 20.4, 22.2, 25.2 (4 q, 1-Me_2, 3-Me_2), 25.5, 27.6 (2 q, 2′-Me_2), 61.2 (t, *C*H$_2$Ph), 62.6 (t, 5′-*C*H$_2$O), 65.2, 66.6 (2 s, C-1, C-3), 72.6 (d, C-7), 77.3 (d, C-5′), 78.6 (d, C-4′), 102.2 (s, C-4), 108.9 (s, C-2′), 127.6, 127.7, 127.8, 128.4, 129.5, 129.6, 129.7, 132.9, 133.0, 135.70, 135.73, 135.75 (7 d, 2 s, d, s, d, 3 Ph), 220.0 (s, C=O) ppm; IR (film): ν = 3075–2850 (=C—H, C—H), 1785 (C=O), 1460, 1380, 1250, 1220, 1215, 1115, 1080 (C—O) cm^{-1}; ESI-MS (*m*/*z*): 682 (100, $[M+Na]^+$); elemental analysis calcd (%) for $C_{38}H_{49}NO_5SSi$ (659.3): C 69.16, H 7.48, N 2.12, S 4.26; found: C 69.04, H 7.49, N 2.10, S 4.15.

4.1.11. (3a′*S*,4′*S*,6a′*S*,7*S*)-6-(2′,2′-Dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4′-yl)-1,1,3,3-tetramethyl-7-phenyl-5-oxa-8-thia-6-azaspiro[3.4]octan-2-one (7*S*)-11a

10 min; crude product (7*S*/7*R* >99:1) was filtered through short silica gel plug (petroleum ether/EtOAc 15:1) to give (7*S*)-**11a** (319 mg, 76%) as a colourless solid; mp 115–116 °C; $[\alpha]_D^{20} = -54.5$ (*c* 0.78, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ = 0.84, 0.92, 1.26, 1.36 (4 s, 3H each, 1-Me_2, 3-Me_2), 1.36, 1.50 (2 s, 3H each,

2′-Me_2), 4.00–4.04 (m, 2H, 6′-H_2), 4.71 (s, 1H, 4′-H), 4.93 (dd, J = 3.2, 6.1 Hz, 1H, 6a′-H), 5.13 (d, J = 6.1 Hz, 1H, 3a′-H), 6.03 (s, 1H, 7-H), 7.23–7.27, 7.30–7.34, 7.47–7.49 (3 m, 1H, 2H, 2H, Ph) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 18.3, 20.1, 22.6, 24.5 (4 q, 1-Me_2, 3-Me_2), 24.9, 26.3 (2 q, 2′-Me_2), 64.9, 67.1 (2 s, C-1, C-3), 72.3 (d, C-7), 74.1 (t, C-6′), 80.4 (d, C-6a′), 83.5 (d, C-3a′), 96.8 (d, C-4′), 104.4 (s, C-4), 112.3 (s, C-2′), 127.0, 127.7, 128.1, 140.0 (3 d, s, Ph), 220.1 (s, C=O) ppm; IR (KBr): ν = 3090–2880 (=C—H, C—H), 1795 (C=O), 1455, 1380, 1210, 1095, 1050, 1035 (C—O) cm^{-1}; ESI-MS (m/z): 442 (100, [M+Na]$^+$); elemental analysis calcd (%) for $C_{22}H_{29}NO_5S$ (419.2): C 62.98, H 6.97, N 3.34, S 7.64; found: C 62.85, H 6.97, N 3.26, S 7.46. Suitable crystals for an X-ray crystal structure determination were obtained from petroleum ether solution by slow evaporation of the solvent.

4.1.12. (3a′*S*,4′*S*,6a′*S*,7*S*)-6-(2′,2′-Dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4′-yl)-1,1,3,3-tetramethyl-7-phenyl-5-oxa-8-thia-6-azaspiro[3.4]octan-2-one (7*S*)-11b

10 min; crude product (7*S*/7*R* >99:1) was filtered through short silica gel plug (petroleum ether/EtOAc 15:1) to give (7*S*)-**11b** (394 mg, 83%) as a colourless solid; mp 129–131 °C; $[\alpha]_D^{20}$ = −58.5 (c 0.80, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.90, 1.10, 1.40, 1.49 (4 s, 3H each, 1-Me_2, 3-Me_2), 1.37, 1.50 (2 s, 3H each, 2′-Me_2), 4.01 (m_c, 2H, 6′-H_2), 4.62 (s, 1H, 4′-H), 4.91-4.93 (m, 1H, 6a′-H), 5.11 (d_{br}, $J \approx$ 6.1 Hz, 1H, 3a′-H), 5.89 (s, 1H, 7-H), 7.23–7.26, 7.29–7.32, 7.42–7.45 (3 m, 1H, 2H, 2H, Ph) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 22.5, 26.3, 26.8, 27.5 (4 q, 1-Me_2, 3-Me_2), 24.0, 25.0 (2 q, 2′-Me_2), 58.9, 60.4 (2 s, C-1, C-3), 72.1 (d, C-7), 74.2 (t, C-6′), 80.6 (d, C-6a′), 83.1 (d, C-3a′), 96.9 (d, C-4′), 98.7 (s, C-2), 106.1 (s, C-4), 112.3 (s, C-2′), 127.1, 127.8, 128.2, 139.6 (3 d, s, Ph) ppm; IR (KBr): ν = 3085–2870 (=C—H, C—H), 1380, 1210, 1095, 1055 (C—O) cm^{-1}; ESI-MS (m/z): 497 (13, [M+Na]$^+$), 474 (100, [M]$^+$); elemental analysis calcd (%) for $C_{22}H_{29}Cl_2NO_4S$ (474.4): C 55.69, H 6.16, N 2.95, S 6.76; found: C 55.70, H 6.35, N 2.75, S 6.97.

4.1.13. (3a′*S*,3b′*R*,7a′*S*)-Spiro[(1,1,3,3-tetramethyl-2-oxocyclobutane)-4,5′-[2′,2′-dimethyl-tetrahydro-1′,3′,6′-trioxa-4′-thia-6a′-azacyclopenta[*a*]pentalene] 13a

15 min; crude product was purified by column on silica gel (petroleum ether/EtOAc 6:1) to give **13a** (288 mg, 92%) as a single diastereoisomer; colourless solid; mp 45–47 °C; $[\alpha]_D^{20}$ = +118.0 (c 0.62, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.24, 1.26, 1.27 (3 s, 6H, 3H, 3H, 4 Me), 1.32, 1.52 (2 s, 3H each, 2′-Me_2), 3.28 (dd, J = 5.1, 11.4 Hz, 1H, 7′-H), 3.47 (d_{br}, $J \approx$ 11.4 Hz, 1H, 7′-H), 4.80 (d_{br}, $J \approx$ 6.6 Hz, 1H, 3a′-H), 4.91 (pseudo-t, $J \approx$ 6.4 Hz, 1H, 7a′-H), 4.91 (s, 1H, 3b′-H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 19.0, 20.0, 23.0, 24.0 (4 q, 4 Me), 24.9, 26.4 (2 q, 2′-Me_2), 59.7 (t, C-7′), 64.6, 67.4 (2 s, C-1, C-3), 78.6 (d, C-7a′), 80.1 (d, C-3b′), 80.9 (d, C-3a′), 104.8 (s, spiro-C), 112.3 (s, C-2′), 219.3 (s, C=O) ppm; IR (KBr): ν = 2990–2860 (=C—H, C—H), 1780 (C=O), 1460, 1380, 1205, 1060, 1030, 1010 (C—O) cm^{-1}; CI-MS (m/z): 314 (2, [M+H]$^+$), 158 (100), 142 (36); elemental analysis calcd (%) for $C_{15}H_{23}NO_4S$ (313.1): C 57.48, H 7.40, N 4.47, S 10.23; found: C 57.54, H 7.48, N 4.46, S 10.21.

Acknowledgements

Support of this work by the National Science Center, Cracow, Poland, in the framework of the Maestro grant (project number 2012/06A/ST5/00219) is gratefully acknowledged.

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