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3-Oxo-3-thia-2-azabicyclo[2.2.1]hept-5-en-2-carboxylates: the first isolation and characterization

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ABSTRACT

Methyl and benzyl 3-oxo-3-thia-2-azabicyclo[2.2.1]hept-5-en-2-carboxylate were isolated at rt and characterized for the first time. Both *endo* and *exo*-isomers were observed. Under suitable experimental conditions (stoichiometric amount of sodium acetate, −40 °C or sodium borohydride/methyl iodide) ring opening of these compounds gave the corresponding thiosulfonates or methyl sulfides, respectively.

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The substitution of carbon atom with sulfur atom in pharmacologically active molecules has attracted large interest, for different reasons, such as the synthesis of bioisosteres, the collection of information on the mode of action, to enhance the pharmacological activity, and for the elimination of the side effects. The [4 + 2] cycloaddition reaction between dienes and *N*-sulfinyl dienophiles[1,2] allowed to synthesize the sulfur homologues of compound A (Fig. 1), versatile building blocks for the synthesis of different pharmacologically active molecules, such as homoallylic amines, vicinal amino alcohols,[3] vicinal amines, amino sugars,[4,5] and natural products.[6,7]

As a further contribution to this synthetic strategy, in a previous work our research group prepared 4-aminocyclopent-2-ene-1-sulfonic acid **5**, its cyclohexene homologous **9** and some sulfinamide derivatives (**6–8**) (Scheme 1).[8,9]

Compounds **5–9** were obtained in good yields by Hetero Diels-Alder cycloaddition/ring opening sequence using some nucleophiles such as OH^-(aq), benzylamine, pyrrolidine, some aminoacids, and a deprotonated carbamate: lithium methoxycarbonylamide.

It is to be noted that in spite of wide chemical interest and potential applications of a bicyclic compound like **3**, there is neither a protocol so far for its isolation, nor a spectroscopic evidence of its formation. The presence of cycloadduct **3** as an intermediate was assumed only on the basis of the formation of derivatives. On the other hand, the instability of a similar bicyclic system (compound **B**, Fig. 1), also at low temperature, is reported.[10]

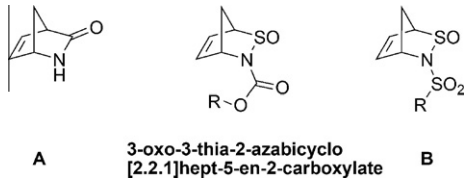
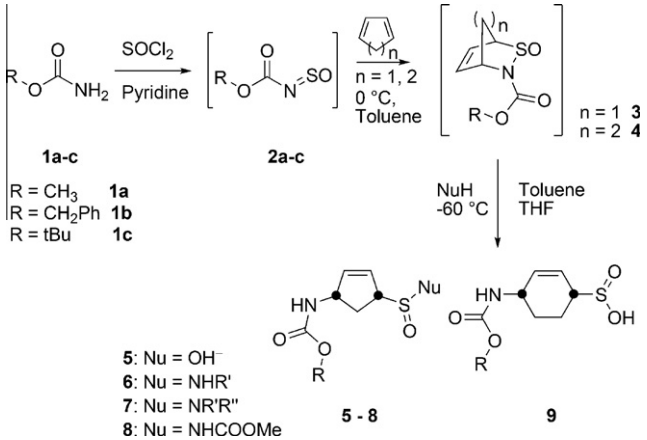


Figure 1. Compound **A** is commercially available; compound **B** was never isolated at rt.



Scheme 1. Opening of the sulfinamide bond with NaOH and amines.

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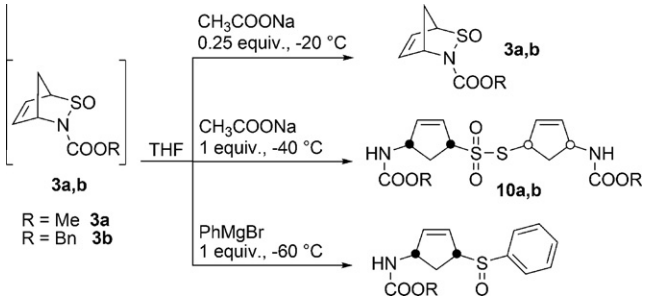
However, taking into account the synthetic importance of this intermediate, we tried to find a way to isolate it and to determine the real stability.

Starting from our experience, we knew that: (1) the sulfinamide bond can be cleaved under acidic and basic conditions; (2) a little amount of pyridinium chloride remains in the flask during the work-up of *N*-sulfinyl carbamate **2**, and which is never completely removed with the double filtration during the work-up of the first synthetic step; (3) the homologous compound **4** can be isolated with a simple phosphate buffer at pH = 7.[11,12] Knowing all these features we tried the use of phosphate buffer also to attempt the isolation of compound **3**, but we recovered the starting carbamate. What we needed was something that could neutralize the solution but it must not be a nucleophile toward compound **3**. We decided to use an aqueous solution of sodium acetate. By varying the amount of this reagent and temperature, we found that with small quantity of sodium acetate (0.25 equiv) at −20 °C it is possible to isolate the cycloadduct **3**[13] in ~60% of yield (Fig. 2); while with stoichiometric amount and a lower reaction temperature (−40 °C) we isolated a new derivative: thiosulfonate **10** (Scheme 2).[14]

The explanation of the first result was attributed to the fact that acetate in a small amount acts as a buffer together with the residual pyridinium chloride. Mass spectra (MS and MS^2), mono-, and bi-dimensional NMR experiments (^1H, ^{13}C, HSQC, COSY) were recorded to confirm the structure of **3**. As shown in Figure 2, by ^1H-NMR it is possible to see two isomers of compound **3**. Signals were assigned to the *exo*-adduct (red dots) and the *endo*-adduct (blue dots), respectively, in analogy to homologous **4**,[12] and on the basis of anisotropic cone of the sulfinyl group.



Scheme 2. Variation of the sodium acetate gives different results.

To reach a final structural confirmation of the isolated product, compound **3** was treated with phenyl magnesium bromide to give a well known product, methyl 4-(phenylsulfinyl)cyclopent-2-enylcarbamate (Scheme 2).[7,8] With the NMR experiments we also found that in few hours at rt the product disappears as the cycloaddition reaction is reversible; while at −18 °C in the freezer after 1 week the *endo*-adduct was transformed in part into the starting materials, in part into the *exo*-adduct (Fig. 2).

To find the explanation of the second result (Scheme 2) we performed the reaction using sodium acetate-^{18}O. The obtained thiosulfonate mainly shows in ESI-MS a molecular ion at 383 *m/z*, due to the incorporation of three ^{18}O atoms. MS^2 spectrometry of this ion gives a signal at 244 *m/z*, due to the neutral loss of 139 amu. (Scheme 3) The same neutral loss has been observed with **3a** containing only ^{16}O. MS^3 spectrometry of 244 gives a signal at 162 *m/z* assigned to a neutral loss of $^{18}OS_2$.

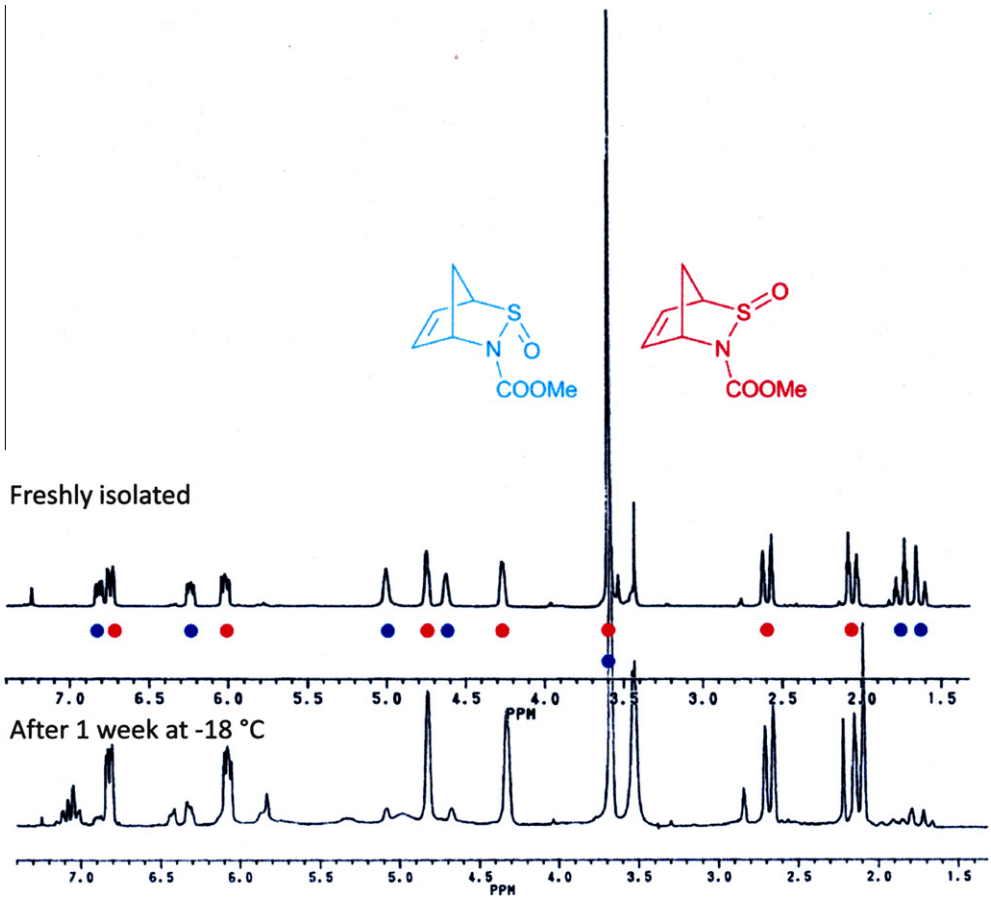
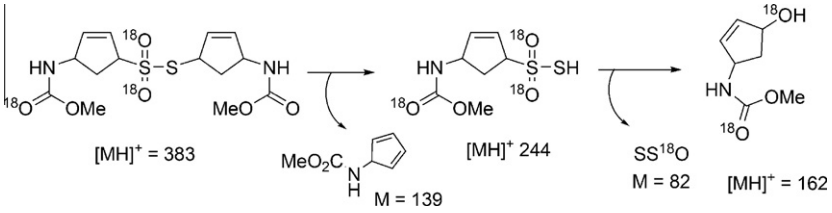


Figure 2. The signals of *exo* (red) and *endo* (blue) isomers can be distinguished by the colored spots. Spectra were recorded at rt.



Scheme 3. ESI-MS spectroscopy of ^{18}O-thiosulfonate **10**.

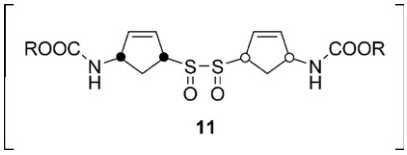
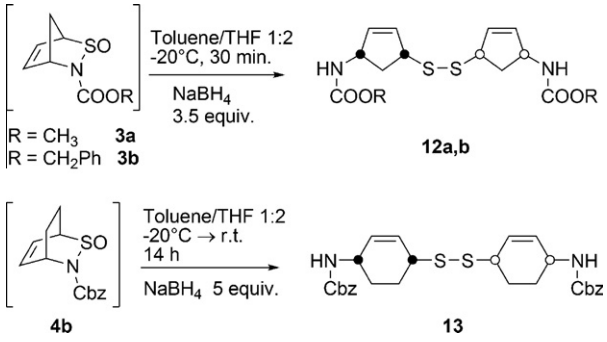
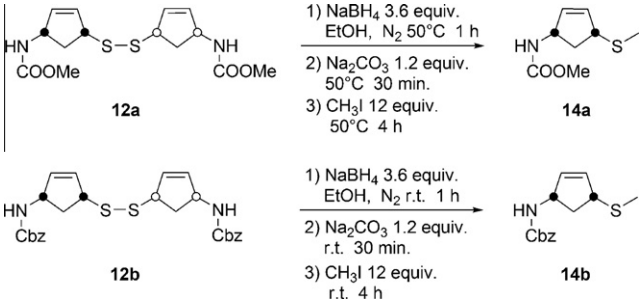


Figure 3. α-disulfoxide **11** was never isolated.



Scheme 4. The sulfinamide bond can be cleaved also by $NaBH_4$.



Scheme 5. Disulfides **12a,b** can be easily transformed into the methyl thioether **14a,b**.

We think that acetate is involved in the reaction both in the formation of an α-disulfoxide **11**, never isolated (Fig. 3), and maybe in the rearrangement to the compound **10**. As reported in the literature,[15–19] alkyl-α-disulfoxides are stable only at low temperature and they rearrange to thiosulfonates by raising the temperature to rt. Recently, Ishii et al.,[20] succeeded in the isolation of some *vic*-disulfoxides, but the S(O)–S(O) moiety is constrained in a five-membered-ring system.

Trying to understand if this type of reactivity could be extended to other dihydrothiazine derivatives, we synthesized the homologous **4b**,[11,12] but we found that in any case the sulfinamide does not react with sodium acetate to give the corresponding thiosulfonate, neither changing the temperature nor prolonging the time of reaction.

After these two significant results, we have further developed the reactivity of the sulfinamides **3** and **4**. In particular, with an excess of sodium borohydride it is possible to obtain disulfides **12**[21] and **13**[22] respectively (Scheme 4). As shown in the scheme, homologous **4** needs more time and higher temperature to give the same result. At last we transformed compounds **12a** and **12b** into the methyl thioether derivatives **14a** and **14b**[23] using a well know procedure[24] in order to confirm the structure of the disulfides (Scheme 5).

In conclusion this work remarks the different stability between compounds **3** and **4**. In fact, some of the reactions shown above are possible only with compound **3** due to its angular tension, while other reactions are possible also for compound **4**, but with higher temperature and longer time. So varying the amount of sodium acetate we isolated for the first time pure compound **3** for some hours at rt, otherwise it is possible to isolate new thiosulfonate **10**. At last we synthesized new disulfides **12** and **13** and methylthioether **14**.

Acknowledgments

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13. Melting points were determined with a Kofler hot stage and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 27 °C ($CDCl_3$), unless otherwise stated, with a Bruker AC200 MHz instrument operating at 200.13 and 50.33 MHz respectively. Chemical shifts are reported in ppm from internal TMS. The ^{1}H NMR data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, brs = broad singlet, coupling constants in Hz. Mass spectra were recorded in the positive or negative ion mode with a LCQ-DECA Thermo instrument by using electrospray ionization. All solvents were previously dried according to standard procedures. Analytical TLC was performed on silica gel 60 F254 plates. Flash column chromatography was carried out on silica gel (0.040–0.063 mm). Dicyclopentadiene was freshly distilled with a Vigreux column in order to obtain cyclopentadiene monomer that was collected at 0 °C and rapidly added inside the reaction flask.
*General preparation method for the compounds **3a** and **3b*** In a two neck round bottom flask carbamate (4.0 mmol) was dissolved in dry Et_2O (25 mL). Rapidly it was made vacuum and then was added N_2, and it was repeated two times again. The mixture was cooled to 0 °C with an ice bath, and, if necessary, was added other Et_2O (2 mL). $SOCl_2$ was added first (0.30 mL, 4.2 mmol) rapidly and then pyridine (0.66 mL, 8.2 mmol) slowly for 1.5 h. The mixture was stirred at 0 °C for 2 h. After this time, the precipitate was rapidly filtered off with a double filtration and the solvent was evaporated first under reduced pressure without warming and then with high vacuum pump keeping the flask at 0 °C.

The residue (clear yellow oil) was dissolved in a dry and previously cooled toluene (5 mL) and was added freshly distilled cyclopentadiene monomer (0.21 mL, 3.2 mmol). The mixture was stirred at 0 °C for 20 h. After this time, the reaction was diluted with dry THF (10 mL) previously cooled, and the temperature was lowered to −20 °C. Slowly drop by drop for 15 min, under stirring, was slowly added CH_3COONa (65 mg, 0.8 mmol) dissolved in the minimum amount of H_2O. The reaction was stirred for another 15 min at −20 °C. After this time the solvents were removed without warming the flask. The residue was dissolved with DCM (30 mL) and quickly washed with H_2O (3 × 10 mL). The organic phase was dried over Na_2SO_4, filtered and evaporated under reduced pressure.

*(endo/eso) Methyl 3-oxo-3-thia-2-azabicyclo[2.2.1]hept-5-en-2-carboxylate (**3a**):* yellow oil (0.43 g, 57%), that deteriorates in a few hours at room temperature. ^{1}H-NMR: δ 1.64 (dt, *J* = 10.5, 1.1, 1H, H5b *endo*), 1.78 (dt, *J* = 10.5, 2.4, 1H, H5a *endo*), 2.08 (dt, *J* = 10.5, 2.4, 1H, H5b *exo*), 2.61 (dt, *J* = 10.5, 1.1, 1H, H5a *exo*), 3.61 (s, 6 H, $COOCH_3$ *endo+exo*), 4.27 (brs, 1H, H1 *exo*), 4.65 (brs, 1H, H1 *endo*), 4.75 (brs, 1H, H4 *exo*), 5.02 (brs, 1H, H4 *endo*), 6.00–6.10 (m, 1H, H3 *exo*), 6.21–6.31 (m, 1H, H3 *endo*), 6.72–6.79 (m, 1H, H2 *exo*), 6.81–6.90 (m, 1H, H2 *endo*). ^{13}C-NMR: δ 45.2, 53.3, 62.5, 73.0, 130.7, 145.3, 155.9. MS(ESI): *m*/*z* = 210 $[M+Na]^+$.

*(endo/eso) Benzyl 3-oxo-3-thia-2-azabicyclo[2.2.1]hept-5-en-2-carboxylate (**3b**):* yellow oil (0.54 g, 55%), that deteriorates in a few hours at room temperature. ^{1}H-NMR: δ 1.79 (dt, *J* = 10.5, 1.2, 1H, H5b *endo*), 1.92 (dt, *J* = 10.5, 2.3, 1H, H5a *endo*), 2.21 (dt, *J* = 10.5, 2.4, 1H, H5b *exo*), 2.83 (dt, *J* = 10.5, 1.2, 1H, H5a *exo*), 4.42 (brs, 1H, H1 *exo*), 4.74 (brs, 1H, H1 *endo*), 4.82 (brs, 1H, H4 *exo*), 4.96 (brs, 1H, H4 *endo*), 5.21 (s, 4H, OCH_2Ph *endo+exo*), 6.11–6.21 (m, 1H, H3 *exo*), 6.40–6.50 (m, 1H, H3 *endo*), 6.88–6.98 (m, 1H, H2 *exo*), 6.97–7.07 (m, 1H, H2 *endo*) 7.33 (s, 10H, Ph *exo+endo*). MS(ESI): *m*/*z* = 264 $[M+H]^+$, 286 $[M+Na]^+$.

14. *General preparation method for the compounds **10a** and **10b*** A solution of unisolated compound **3** (estimated about 3.2 mmol) in dry toluene (5 mL) at 0 °C, prepared as reported above, was diluted with dry THF (10 mL) previously cooled and the temperature was lowered to −40 °C. Slowly drop by drop for 15 min, under stirring, was added CH_3COONa (0.26 g, 3.2 mmol) dissolved in the minimum amount of H_2O. The reaction was stirred for another 15 min at −40 °C. After this time the mixture was evaporated without heating the flask. The residue was dissolved in $CHCl_3$ (50 mL) and washed with H_2O (3 × 15 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel (Et_2O/EtOAc 1:3).

*S-4-(Methoxycarbonylamino)cyclopent-2-enyl 4-(methoxycar-bonylamino)-cyclopent-2-ene-1-sulfonothioate (**10a**):* yellow oil (0.80 g, 68%). ^{1}H-NMR: δ 1.93 (dt, *J* = 15.4, 4.6, 1H, *cis* H5'), 2.12 (dt, *J* = 15.4, 3.4, 1H, *cis* H5), 2.67 (dt, *J* = 15.4, 7.7, 1H, *trans* H5), 2.97 (dt, *J* = 15.4, 7.7, 1H, *trans* H5'), 3.65 (s, 6H, OCH_3), 4.31–4.46 (m, 1H, H1'), 4.66–4.83 (m, 1H, H1), 4.83–4.98 (m, 2H, H4'+H4), 5.88–5.98 (m, H3+H3'), 6.15–6.25 (m, 2H, H2+H2'). ^{13}C-NMR: δ 29.5, 32.7, 32.9, 52.1, 53.8, 54.0, 75.5, 125.7, 131.9, 135.6, 135.7, 156.0. MS(ESI): *m*/*z* = 377 $[M+H]^+$, 399 $[M+Na]^+$. $C_{14}H_{20}N_2O_6S_2$ (376): calcd C 44.67; H 5.35; N 7.44; found C 44.81; H 5.12; N 7.53.

*S-4-(Benzyloxycarbonylamino)cyclopent-2-enyl 4-(benzyloxycar-bonylamino)-cyclopent-2-ene-1-sulfonothioate (**10b**):* yellow oil (1.09 g, 65%). ^{1}H-NMR: δ 1.88 (dt, *J* = 15.0, 3.6, 1H, *cis* H5'), 2.09 (dt, *J* = 15.5, 3.6, 1H, *cis* H5), 2.62 (dt, *J* = 15.5, 8.3, 1H, *trans* H5), 2.93 (dt, *J* = 15.0, 8.3, 1H, *trans* H5'), 4.26–4.40 (m, 1H, H1'), 4.65–4.82 (m, 1H, H1), 4.96–5.03 (m, 2H, H4+H4'), 5.03 (s, 4H, OCH_2Ph), 5.85–5.92 (m, 2H, H3+H3'), 6.14–6.21 (m, 2H, H2+H2') 7.28 (s, 10H, Ph). ^{13}C-NMR: δ 29.5, 32.7, 33.0, 53.8, 54.0, 66.9, 75.0, 127.1, 127.6, 128.4, 128.9, 132.3, 132.7, 132.9, 136.4, 156.6. MS(ESI): *m*/*z* = 529 $[M+H]^+$, 551 $[M+Na]^+$. $C_{26}H_{28}N_2O_6S_2$ (528): calcd C 59.07; H 5.34; N 5.30; found C 59.24; H 5.18; N 5.67.

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21. *General preparation method for the compounds **12a** and **12b**.* A solution of unisolated compound **3** (estimated about 3.2 mmol) in dry toluene (5 mL) at 0 °C, prepared as reported above, was diluted with dry THF (10 mL) previously cooled, and the temperature was lowered to −20 °C. Slowly drop by drop for 15 min, under stirring, was added $NaBH_4$ (0.42 g, 11.2 mmol) dissolved in the minimum amount of dry THF, then the mixture was stirred for 1 h at 0 °C. After this time the reaction was quenched with 1 mL of H_2O and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (50 mL) and washed with H_2O (3 × 15 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel (petroleum ether/EtOAc 1:1).

*Dimethyl 4,4′-disulfanediylbis(cyclopent-2-ene-4,1-diyl)dicarba-mate (**12a**):* white solid (0.84 g, 77%); mp: 145–146 °C; ^{1}H-NMR: δ 1.72 (tt*, *J* = 14.1, 3.3, 2H, *cis* H5), 2.78 (dt, *J* = 15.1, 6.7, 2H, *trans* H5), 3.68 (s, 6H, OCH_3), 3.78–3.86 (m, 2H, H4), 4.67–4.85 (m, 2H, H1), 5.85 (s, 4H, H2+H3). ^{13}C-NMR: δ 39.1, 54.3, 54.9, 55.6, 133.9, 134.3, 156.0. MS(ESI): *m*/*z* = 367 $[M+Na]^+$. $C_{14}H_{20}N_2O_4S_2$ (344): calcd C 48.82; H 5.85; N 8.13; found C 48.93; H 5.69; N 8.36. *With 400 MHz instrument this signal appears as two doublets of triplets.

*Dibenzyl 4,4′-disulfanediylbis(cyclopent-2-ene-4,1-diyl)dicarba-mate (**12b**):* white solid (1.19 g, 75%); mp: 95–98 °C; ^{1}H-NMR: δ 1.74 (tt*, *J* = 15.4, 4.4, 2H, *cis* H5), 2.78 (dt, *J* = 15.4, 8.9, 2H, *trans* H5), 3.80–3.88 (m, 2H, H4), 4.72–4.90 (m, 2H, H1), 5.13 (s, 4H, OCH_2Ph), 5.86 (s, 4H, H2+H3), 7.37 (s, 10H, Ph). ^{13}C-NMR: δ 30.2, 39.0, 54.4, 66.8, 128.0, 128.1, 128.4, 134.1, 134,3, 136.4, 156.8. MS(ESI): *m*/*z* = 497 $[M+H]^+$, 519 $[M+Na]^+$. $C_{26}H_{28}N_2O_6S_2$ (496): calcd C 62.88; H 5.68; N 5.64; found C 62.97; H 5.72; N 5.51. *With a 400 MHz instrument this signal appears as two doublets of triplets.

22. *Dibenzyl 4,4′-disulfanediylbis(cyclohex-2-ene-4,1-diyl)dicarbamate (**13**):* A solution of unisolated **4b**[11] (2.9 mmol) in dry toluene (5 mL) at 0 °C was diluted with dry THF (10 mL) previously cooled, and the temperature was lowered to −20 °C. Slowly drop by drop for 15 min, under stirring, was added $NaBH_4$ (0.55 g, 14.5 mmol) dissolved in the minimum amount of dry THF. The reaction was stirred for 14 h raising the temperature from −20 °C to rt. After this time the reaction was quenched with 1 mL of H_2O and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (50 mL) and washed with H_2O (3 × 15 mL). The organic phase was dried over Na_2SO_4, filtered and evaporated obtaining **13** as a white solid (1.06 g, 70%). mp: 121–122 °C; ^{1}H-NMR: δ 1.66–2.14 (m, 8H, H5+H6), 3.37–3.50 (m, 2H, H4), 4.14–4.29 (m, 2H, H1), 5.08 (s, 4H, OCH_2Ph) 5.27 (s, 4H, H2+H3), 7.30 (s, 10H, Ph). ^{13}C-NMR: δ 25.9, 26.0, 66.4, 127.7, 127.8, 128.2, 128.4, 131.7, 136.2, 155.6. MS(ESI): *m*/*z* = 525 $[M+H]^+$, 547 $[M+Na]^+$. $C_{28}H_{32}N_2O_4S_2$ (524): calcd C 64.09; H 6.15; N 5.34; found C 64.36; H 6.09; N 5.56.

23. *General preparation method for the compounds **14a** and **14b*** In a solution of compound **10** (1.2 mmol) in dry EtOH (10 mL) at rt under N_2, was added $NaBH_4$ (0.16 g, 4.32 mmol) dissolved in the minimum amount of dry EtOH, and the reaction was stirred for 1 h. After this time was added Na_2CO_3 fine powder (0.14 g, 1.3 mmol) and stirred for 30 min. Finally was added CH_3I (0.90 mL, 14.4 mmol) and stirred for 4 h. At the end of the reaction, the solvent was evaporated and the residue was dissolved in $CHCl_3$ (50 mL) and washed with H_2O (3 × 15 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel (petroleum ether/EtOAc 3:1).

*Methyl 4-(methylthio)cyclopent-2-enylcarbamate (**14a**):* yellow oil (0.14 g, 62%). ^{1}H-NMR: δ 1.61 (dt, *J* = 14.5, 5.7, 1H, *cis* H5), 2.16 (s, 3H, SCH_3), 2.71 (dt, *J* = 14.5, 8.6, 1H, *trans* H5), 3.64 (s, 3H, OCH_3), 3.77–3.88 (m, 1H, H4), 4.64–4.82 (m, 1H, H1) 5.73–5.88 (m, 2H, H2 + H3). ^{13}C-NMR: δ 13.7, 39.1, 46.8, 52.0, 53.6, 132.8, 134.8, 156.1. MS(ESI): *m*/*z* = 188 $[M+H]^+$, 210 $[M+Na]^+$. $C_8H_{13}NO_2S$ (187): calcd C 51.31; H 7.00; N 7.48; found C 51.23; H 7.46; N 7.34.

*Benzyl 4-(methylthio)cyclopent-2-enylcarbamate (**14b**):* yellow oil (0.20 g, 65%). ^{1}H-NMR: δ 1.68 (dt, *J* = 15.6, 3.9, 1H, *cis* H5), 2.14 (s, 3H, SCH_3), 2.78 (dt, *J* = 15.6, 8.4, 1H, *trans* H5), 3.66–3.74 (m, 1H, H4), 4.4.76–4.85 (m, 1H, H1), 5.12 (s, 2H, OCH_2Ph), 5.78–5.98 (m, 2H, H2 + H3) 7.33 (s, 5H, Ph). ^{13}C-NMR: δ 13.9, 38.9, 48.8, 56.0, 66.7, 128.1, 128.2, 128.5, 132.7, 134.8, 136.1, 156.6. MS(ESI): *m*/*z* = 286 $[M+Na]^+$. $C_{14}H_{17}NO_2S$ (263): calcd C 63.85; H 6.51; N 5.32; found C 64.03; H 6.38; N 5.41.

24. Roberts-Bleming, S. J.; Davies, G. L.; Kalaji, M.; Murphy, P. J.; Celli, A. M.; Donati, D.; Ponticelli, F. *J. Org. Chem.* **2003**, *68*, 7115–7118.