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Facile Access to Bicyclic Sultams with Methyl 1-Sulfonylcyclopropane-1-carboxylate Moieties[‡]

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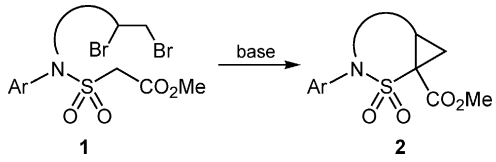
N-(2,3-Dibromopropyl)- and *N*-(3,4-dibromobutyl)(methoxycarbonyl)methanesulfanilides upon treatment with potassium carbonate in DMF furnish methyl 3-aryl-2,2-dioxo-2-thia-3-azabicyclo[*n*.1.0]alkane-1-carboxylates in yields ranging from 54 to 84 % (10 examples). The starting materials were obtained by sulfonylation of *N*-alkenylanilines with methyl (chlorosulfonyl)acetate and subsequent bromination. For the *N*-alkenylanilines (10 examples, 60–77 % yield) an efficient new synthesis employing a 2-nitrophenylsulfonyl substituent as a protective as well as an activating group has been developed. The 4-methoxyphenyl (PMP) group could easily be removed from the sultam nitrogen atom by treatment with cerium(IV) ammonium nitrate.

Introduction

Earlier on, our group has reported intermolecular reactions between sulfonamides, obtained from different anilines and alkyl 2-(chlorosulfonyl)acetates, with a wide range of alkylating agents.[1] As it turned out, cyclodialkylation of such sulfonamides with 1,ω-dibromides constitutes an efficient route to five-, six- and seven-membered sultams with an α-methoxycarbonyl group. Here we report the results of our investigation concerning analogous intramolecular cyclodialkylations occurring in *N*-(ω-1,ω-dibromoalkyl)-(methoxycarbonyl)methanesulfanilides **1** (Scheme 1).



Scheme 1. Concept for the intramolecular cyclodialkylation of methoxycarbonylmethanesulfanilides.

Results and Discussion

The acyclic *N*-(ω-1,ω-dibromoalkyl)(methoxycarbonyl)-methanesulfanilides of type **1** were prepared from the corresponding *N*-(ω-alkenyl)(methoxycarbonyl)methanesulfanilides, which were obtained from the corresponding *N*-alkenylanilines. Initially, the parent *N*-allylaniline (**5a**) was prepared by allylation of formanilide (**3**) and subsequent deformylation in 78 % overall yield (Scheme 2). A more convenient general access to *N*-(ω-alkenyl)anilines, avoiding the use of sodium hydride, was developed starting from 2-nitrobenzenesulfanilides **7** obtained from the sulfonyl chloride **6** and the respective aniline. Alkylation of compounds **7** with allyl, homoallyl and 4-pentenyl bromides afforded the *N*-(2-nitrophenylsulfonyl)anilines **8**, **9** and **11**, respectively, from which the protective and at the same time activating 2-nitrophenylsulfonyl group could cleanly be removed by treatment with thiophenol/potassium carbonate in DMF. The yields over all three steps in this sequence ranged from 61 to 77 % (Scheme 2, Table 1).

N-Alkenylanilines **5**, **10** and **12** reacted smoothly with methyl (chlorosulfonyl)acetate[2] to give the corresponding sulfonamides **13**–**15** in good yields (Scheme 3 and Table 2).

Addition of bromine to the C=C double bonds in sulfamides **13**–**15** occurred quantitatively to give the corresponding dibromoalkyl derivatives **16**, **18**, **20** in virtually pure form according to their ^{1}H NMR spectra. Upon treatment with potassium carbonate in DMF, the (dibromoalkyl)sulfonamides **16** and **18** underwent intramolecular cyclodialky-

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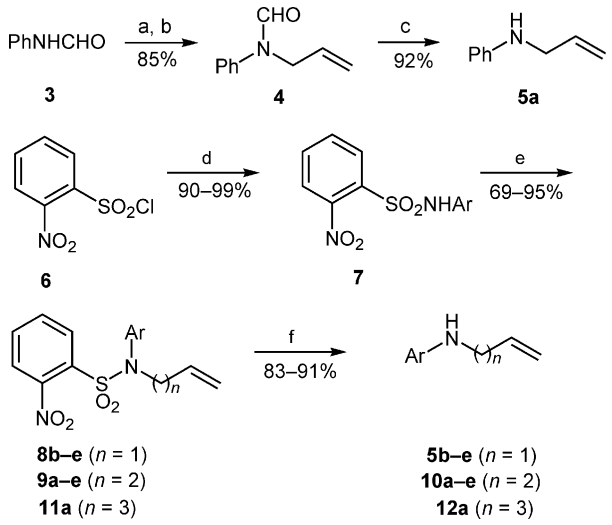
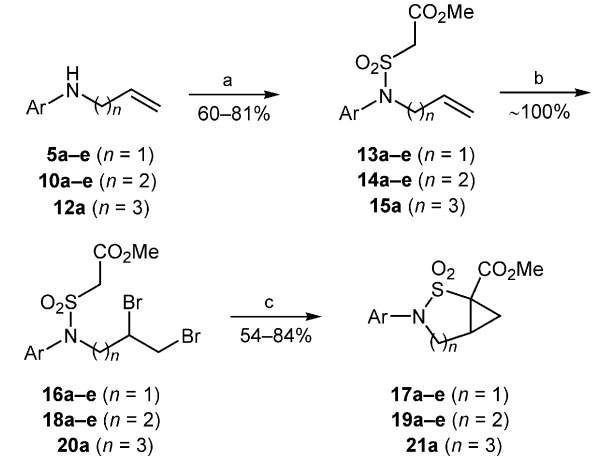


Scheme 2. Preparation of various *N*-alkenylanilines. For further details see Table 1. (a) NaH, THF, reflux, 4 h; (b) allylBr, THF, reflux, 3 h; (c) aq. HCl, 60 °C, 1 h; (d) $ArNH_2$, AcONa, 50% aq. EtOH; (e) $CH_2{=}CH(CH_2)_nBr$, K_2CO_3, DMF; **7** → **8**: room temp., 2 h; **7** → **9**, **11**: 40 °C, 12 h; (f) PhSH, K_2CO_3, DMF, 40 °C, 3 h.

Table 1. Preparation of various *N*-alkenylanilines (see Scheme 2).

Ar	Product	% Yield[a]
4-MeC_6H_4	**5b**	75
2,6-$Me_2C_6H_3$	**5c**	76
4-ClC_6H_4	**5d**	75
4-$MeOC_6H_4$	**5e**	77
Ph	**10a**	60
4-MeC_6H_4	**10b**	65
2,6-$Me_2C_6H_3$	**10c**	70
4-ClC_6H_4	**10d**	61
4-$MeOC_6H_4$	**10e**	61
Ph	**12a**	61

[a] Over 3 steps.



Scheme 3. Transformation of *N*-alkenylanilines to bicyclic sultams. For further details see Table 2. (a) $ClSO_2CH_2CO_2Me$, Py, MeCN, 10 °C; (b) Br_2, CH_2Cl_2, 0 °C, 30 min; (c) K_2CO_3, DMF, 50 °C, 4 h (15 h for sultams **19**).

Table 2. Transformation of *N*-alkenylanilines to bicyclic sultams (see Scheme 3).

Ar	Product	% Yield	Product	% Yield
Ph	**13a**	74	**17a**	80
4-MeC_6H_4	**13b**	73	**17b**	83
2,6-$Me_2C_6H_3$	**13c**	81	**17c**	76
4-ClC_6H_4	**13d**	76	**17d**	68
4-$MeOC_6H_4$	**13e**	74	**17e**	73
Ph	**14a**	65	**19a**	63
4-MeC_6H_4	**14b**	70	**19b**	54
2,6-$Me_2C_6H_3$	**14c**	60	**19c**	84
4-ClC_6H_4	**14d**	78	**19d**	60
4-$MeOC_6H_4$	**14e**	74	**19e**	58
Ph	**15a**	70	**21a**	–[a]

[a] Complex mixture of products.

lation of their C,H-acidic positions to yield the bicyclic sultams **17**, **19**. While the reactions of dibromides **16** leading to the cyclopropane-annelated five-membered sultams **17** were complete within 2 h, without any noticeable influence of the aryl substituents on the yield and reaction time, the homologous starting materials **18** required longer reaction times (12 h) and furnished the cyclopropane-annelated six-membered sultams **19** mostly in lower yields. It is noteworthy, that for the 2,6-dimethylaniline derivatives **17c** and **19c**, analogues of which were found to be most reactive in the intermolecular cyclodialkylations,[1] the reaction times were the shortest. Under the established conditions, the dibromoalkyl derivative **20a** obtained by bromine addition to the *N*-pentenylaniline derivative **15a** gave a complex mixture from which the expected 2-thia-3-azabicyclo[5.1.0]octane derivative **21a** could not be isolated.

The structure of the sultam **17a** was proved by X-ray crystallography (see Figure 1). In the crystal, the 2-thia-3-azabicyclo[3.1.0]hexane skeleton adopts a flattened boat conformation, as is frequently observed for bicyclo[3.1.0]-hexane derivatives.[4] The interplanar angle between the three- and five-membered rings is 110.4°, and the nitrogen corner of the five-membered ring is bent by an angle of 34.3° towards the three-membered ring. The C=C bond distal to the two electron-withdrawing groups is shorter [147.5(2) pm] than the two proximal bonds [152.0(2) and 152.6(2) pm], a typical effect caused by electron-withdrawing substituents on a cyclopropane ring.[5] The coordination around the nitrogen is virtually trigonally planar.

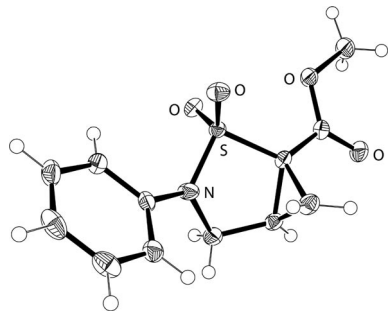
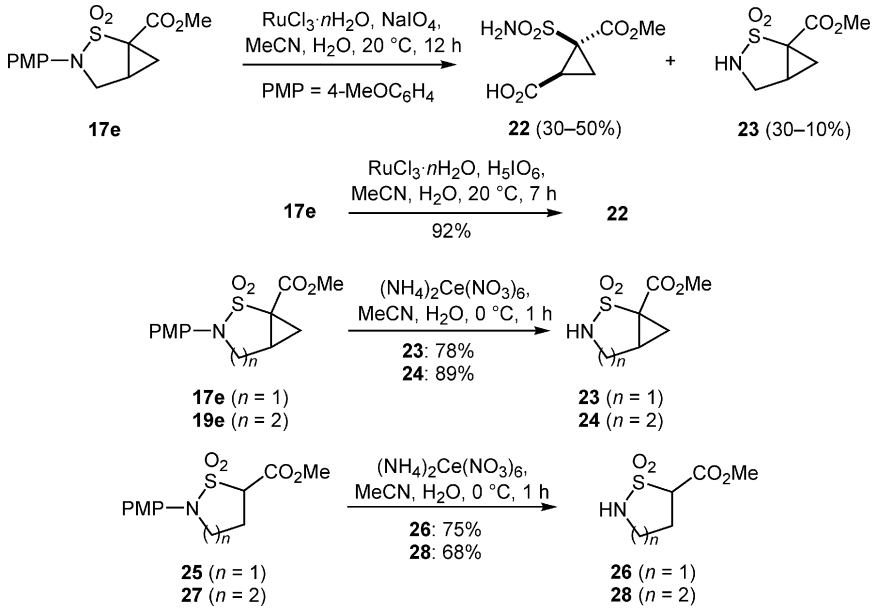


Figure 1. Structure of methyl 2,2-dioxo-3-phenyl-2-thia-3-azabicyclo[3.1.0]hexane-1-carboxylate (**17a**) in the crystal.[3]



Scheme 4. Oxidative removal of the PMP group from several sultams under various conditions.

The bisacceptor-substituted cyclopropane ring in the bicyclic sultams **17** turned out to be rather resistant towards attack by common nucleophiles.[6] Thus, the compound **17a** was recovered unchanged after treatment with thiophenol/potassium carbonate in DMF at 50 °C for 2 d.

In an attempt to prepare sultams of type **17** without an aryl group on nitrogen, the *N*-(4-methoxyphenyl) derivative **17e** was treated with RuO_4 generated in situ from $RuCl_3$ and two different co-oxidants.[7] However, treatment of sultam **17e** with $RuCl_3$ and $NaIO_4$ gave the sulfamoyl-substituted monomethyl cyclopropane-1,2-dicarboxylate **22** as the main product and the *N*-dearylated sultam **23** in inacceptable low yield (10%). After a systematic optimization of the reaction conditions, with changes of the quantity of co-oxidant and the rate of its addition to the reaction mixture, the sultam **23** was eventually obtained in 30% yield (Scheme 4). Treatment of sultam **17e** with $RuCl_3$ and periodic acid instead of sodium periodate as the co-oxidant, furnished compound **22** as the single product in excellent yield (92%).

The removal of *N*-(4-methoxyphenyl) groups from carboxamides has previously been achieved with cerium(IV) ammonium nitrate (CAN) under mild conditions,[8] but to the best of our knowledge, there have been no reports concerning the analogous cleavage of *N*-(4-methoxyphenyl)sulfonamides. Yet, the same conditions as applied for *N*-(4-methoxyphenyl)-substituted carboxamides can be used to remove the PMP group from the bicyclic **17e**, **19e** as well as the monocyclic sultams **25**, **27**[1] with good to excellent yields (68–89%) of the products **23**, **24**, **26** and **28**, respectively.

Conclusions

Cyclizing intramolecular dialkylation of *N*-(ω-1,ω-dibromoalkyl)(methoxycarbonyl)methanesulfanilides readily leads to bicyclic sultams containing 1-methoxycarbonyl-1-sulfamoylcyclopropane moieties annelated to five- and six-membered rings. These compounds essentially are conformationally rigidified γ-aminobutyric and δ-aminovaleric acid derivatives which ought to be useful for incorporation in small peptide mimetics after oxidative removal of the *N*-(4-methoxyphenyl) group and cleavage of the ester moiety.

Experimental Section

General Remarks: All reagents were used as purchased without further purification. The solvents were purified and dried prior to use according to conventional methods. ^1H and ^{13}C NMR spectra were recorded at ambient temperature with a Bruker AM 250 instrument at 250.13 (^1H) and 62.90 (^{13}C and DEPT) MHz and Bruker DPX 300 instrument at 300.13 (^1H) and 75.54 (^{13}C and DEPT) MHz. Chemical shifts (δ) are given in ppm relative to resonances of solvents (^1H: δ = 7.26 for $CHCl_3$ and δ = 2.50 ppm for [D$_5$]DMSO; ^{13}C: δ = 77.0 for $CDCl_3$ and δ = 39.7 ppm for [D$_6$]DMSO). Coupling constants (J) are given in Hz. Multiplicities of signals are described as follows: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet. The multiplicities of signals in ^{13}C NMR spectra were determined by the DEPT technique. Mass spectra were recorded with a Finnigan MAT 95 spectrometer. Chromatographic separation was carried out on Merck silica gel 60 (0.063–0.200 mm). Analytical TLC was performed on Macherey–Nagel ready-to-use plates AluGram® Sil G/UV$_{254}$. Detection was achieved by development with molybdatophosphoric acid solution (5% in ethanol). Melting points (uncorrected) were determined in capillaries with a Büchi 510 apparatus. Elemental analyses of solid compounds: Mikroanalytisches Laboratorium des Instituts für Organische und Biomolekulare Chemie der Georg-August-Universität, Göttingen.

***N*-Allylaniline (5a):** A solution of formanilide (**3**) (113.5 g, 0.95 mol) in THF (200 mL) was added slowly to a stirred suspension of NaH (60% dispersion in oil, 40.0 g, 1.00 mol) in anhydrous THF (300 mL), and the reaction mixture was heated at reflux for

4 h. Then allyl bromide (121.0 g, 1.00 mol) was added, and the mixture was heated at reflux for an additional 3 h, cooled to room temp. and diluted with water (200 mL). The organic layer was separated, washed with brine (2 × 75 mL), dried with Na_2SO_4 and the solvents evaporated in vacuo. A mixture of residual crude *N*-allylformanilide (**4**) thus obtained and 10% HCl (335 mL) was stirred at 70 °C for 1 h, cooled to 0 °C and made strongly alkaline by careful addition of solid NaOH. The mixture was extracted with Et_2O (3 × 80 mL), the combined organic layers washed with brine, dried with Na_2SO_4 and concentrated, the residue was distilled in vacuo to afford *N*-allylaniline (**5a**) 99.1 g (92%) as a colorless oil; b.p. 65–70 °C (2 Torr); lit.[9] b.p. 115 °C (23 Torr).

General Procedure for the Synthesis of *N*-Aryl-2-nitrobenzenesulfonamides 7a–e (GP1): 2-nitrobenzenesulfonyl chloride (**6**) (33.2 g, 150 mmol) was added in small portions to a vigorously stirred mixture of the respective aniline (180 mmol) and NaOAc (17.2 g, 210 mmol) in 50% aq. MeOH (150 mL) over a period of 30 min. The mixture was then stirred at 60 °C for 1 h, cooled to room temp., diluted with water (600 mL) and acidified to pH 2 with concd. HCl. The precipitate was filtered off, washed thoroughly with water and recrystallized from EtOAc/hexane to afford the corresponding 2-nitrobenzenesulfonanilide. According to GP1 the following sulfonamides were prepared:

2-Nitro-*N*-phenylbenzenesulfonamide (7a): Yield 41.3 g (99%), colorless solid, m.p. 117–119 °C; lit.[10] m.p. 118–120 °C.

***N*-(4-Methylphenyl)-2-nitrobenzenesulfonamide (7b):** Yield 41.6 g (95%), slightly yellow solid, m.p. 117–118 °C; lit.[11] m.p. 114–116 °C.

***N*-(2,6-Dimethylphenyl)-2-nitrobenzenesulfonamide (7c):** Yield 42.7 g (93%), colorless solid, m.p. 163–165 °C; lit.[11] m.p. 163–164 °C.

***N*-(4-Chlorophenyl)-2-nitrobenzenesulfonamide (7d):** Yield 45.4 g (97%), slightly green solid, m.p. 124–125 °C; lit.[12] m.p. 123–124 °C.

***N*-(4-Methoxyphenyl)-2-nitrobenzenesulfonamide (7e):** Yield 41.6 g (90%), gray solid, m.p. 106–107 °C; lit.[12] m.p. 106–108 °C.

General Procedure for the Preparation of *N*-Alkenyl-*N*-aryl-2-nitrobenzenesulfonamides 8, 9, 11 (GP2): A mixture of the respective *N*-aryl-2-nitrobenzenesulfonamide (**7**) (50.0 mmol), the respective alkenyl bromide (55.0 mmol) and anhydrous K_2CO_3 (10.4 g, 75.0 mmol) in DMF (50 mL) was stirred at the given temperature for the stated time (see Scheme 2). The mixture was poured into water (350 mL) and extracted with CH_2Cl_2 (3 × 75 mL). The combined organic phases were washed with water (5 × 100 mL), dried with $MgSO_4$ and concentrated in vacuo. The solid residue was purified by recrystallization from EtOAc/hexane to afford the corresponding sulfonamide. According to GP2 the following sulfonamides were prepared:

***N*-Allyl-*N*-(4-methylphenyl)-2-nitrobenzenesulfonamide (8b):** Yield 14.4 g (87%), slightly yellow solid, m.p. 124–125 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 3 H, CH_3), 4.36 (dt, J = 1.2, 6.5 Hz, 2 H, NCH_2), 5.06–5.14 (m, 2 H, CH=CH_2), 5.81 (ddt, J = 6.4, 10.3, 16.7 Hz, 1 H, CH=CH_2), 7.02–7.12 (m, 4 H, ArH), 7.44–7.69 (m, 4 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (CH_3), 55.2 (NCH_2), 119.1 (CH=CH$_2$), 123.9 (CH=CH_2), 129.5 (2 C, CH-Ar), 130.0 (2 C, CH-Ar), 131.2 (CH-Ar), 132.1 (CH-Ar), 132.3 (C-Ar), 133.1 (CH-Ar), 133.7 (CH-Ar), 135.1 (C-Ar), 138.6 (C-Ar), 148.1 (C-Ar) ppm. MS (EI, 70 eV): *m*/*z* (%) = 332 (3) [M^+], 146 (100), 130 (23), 117 (22). $C_{16}H_{16}N_2O_4S$ (332.4): calcd. C 57.82, H 4.85, N 8.43; found C 57.74, H 4.71, N 8.22.

***N*-(But-3-enyl)-*N*-phenyl-2-nitrobenzenesulfonamide (9a):** Yield 13.1 g (79%), slightly yellow solid, m.p. 74–76 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.23 (q, J = 7.2 Hz, 2 H, NCH_2CH_2), 3.87 (t, J = 7.2 Hz, 2 H, NCH_2), 5.02–5.10 (m, 2 H, CH=CH_2), 5.69–5.85 (m, 1 H, CH=CH_2), 7.19–7.23 (m, 3 H, ArH), 7.32–7.34 (m, 2 H, ArH), 7.44–7.47 (m, 2 H, ArH), 7.60–7.64 (m, 2 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 33.1 (NCH_2CH_2), 51.6 (NCH_2), 117.5 (CH=CH$_2$), 123.8 (CH=CH_2), 128.6 (CH-Ar), 129.5 (2 C, CH-Ar), 129.7 (2 C, CH-Ar), 131.1 (CH-Ar), 131.8 (CH-Ar), 132.0 (C-Ar), 133.7 (CH-Ar), 134.4 (CH-Ar), 137.7 (C-Ar), 148.1 (C-Ar) ppm. MS (EI, 70 eV): *m*/*z* (%) = 332 (2) [M^+], 291 (62), 186 (100), 105 (44), 77 (24). $C_{16}H_{16}N_2O_4S$ (332.4): calcd. C 57.82, H 4.85, N 8.43; found C 57.63, H 4.70, N 8.29.

***N*-(But-3-enyl)-*N*-(4-methylphenyl)-2-nitrobenzenesulfonamide (9b):** Yield 14.2 g (82%), slightly yellow solid, m.p. 96–97 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.23 (q, J = 7.1 Hz, 2 H, NCH_2CH_2), 2.34 (s, 3 H, CH_3), 4.36 (t, J = 7.1 Hz, 2 H, NCH_2), 5.02–5.09 (m, 2 H, CH=CH_2), 5.69–5.85 (m, 1 H, CH=CH_2), 7.05–7.14 (m, 4 H, ArH), 7.42–7.51 (m, 2 H, ArH), 7.58–7.67 (m, 2 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.2 (CH_3), 33.1 (NCH_2CH_2), 51.6 (NCH_2), 117.4 (CH=CH$_2$), 123.8 (CH=CH_2), 129.5 (2 C, CH-Ar), 130.1 (2 C, CH-Ar), 131.1 (CH-Ar), 132.0 (CH-Ar), 132.1 (C-Ar), 133.6 (CH-Ar), 134.5 (CH-Ar), 135.0 (C-Ar), 138.7 (C-Ar), 148.1 (C-Ar) ppm. MS (EI, 70 eV): *m*/*z* (%) = 346 (6) [M^+], 305 (65), 186 (27), 119 (100), 91 (24). $C_{17}H_{18}N_2O_4S$ (346.4): calcd. C 58.94, H 5.24, N 8.09; found C 58.73, H 5.04, N 8.09.

General Procedure for the Synthesis *N*-Alkenylanilines 5, 10, 12 (GP3): A mixture of the respective *N*-alkenyl-*N*-aryl-2-nitrobenzenesulfonamide (44.0 mmol), thiopenol (11.0 g, 100.0 mmol) and anhydrous K_2CO_3 (19.3 g, 140.0 mmol) in DMF (50 mL) was stirred at 40 °C for 4 h. The mixture was poured into water (350 mL) and extracted with Et_2O (3 × 100 mL). The ethereal phase was washed with water (5 × 100 mL), then treated with 3 M HCl (3 × 100 mL) to extract the amine hydrochloride into the aqueous phase. The latter was washed with Et_2O (2 × 50 mL), then made strongly alkaline by carefull addition of solid NaOH. The mixture was extracted with Et_2O (3 × 70 mL), the combined extracts were washed with water (100 mL), brine (50 mL) and dried with $MgSO_4$. The solvent was removed in vacuo on a rotary evaporator, the crude product distilled in vacuo (in some cases the crude amine was used in the next step without purification) to afford the corresponding *N*-alkenylaniline. According to GP3 the following amines were prepared.

***N*-Allyl-4-methylaniline (5b):**[12] Yield 5.88 g (91%), colorless oil, b.p. 105–109 °C (2 Torr).

***N*-Allyl-2,6-dimethylaniline (5c):**[13] Yield 6.60 g (87%), colorless oil.

***N*-Allyl-4-chloroaniline (5d):**[14] Yield 6.53 g (84%), colorless oil, b.p. 110–114 °C (2 Torr).

***N*-Allyl-4-methoxyaniline (5e):**[14] Yield 7.01 g (90%), reddish oil.

***N*-(But-3-enyl)aniline (10a):**[15] Yield 5.29 g (85%), colorless oil.

***N*-(But-3-enyl)-4-methylaniline (10b):**[16] Yield 5.47 g (83%), colorless oil.

***N*-(But-3-enyl)-2,6-dimethylaniline (10c):** Yield 6.62 g (90%), colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.28 (s, 6 H, 2 CH_3), 2.31–2.40 (m, 2 H, NCH_2CH_2), 3.07 (dt, J = 0.7, 6.7 Hz, 3 H, HNCH_2), 5.11–5.22 (m, 2 H, CH=CH_2), 5.77–5.94 (m, 1 H, CH=CH_2), 6.81 (t, J = 7.5 Hz, 1 H, 4-ArH), 7.00 (d, J = 7.8 Hz, 2 H, 3,5-ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 18.7 (2 C, CH_3), 35.3 (NCH_2CH_2), 47.4 (NCH_2), 117.1 (CH=CH$_2$), 121.7

(CH-Ar), 128.9 (2 C, CH-Ar), 129.2 (2 C, C-Ar), 136.2 (*C*H=CH_2), 146.2 (C-Ar) ppm. MS (EI, 70 eV): *m*/*z* (%) = 175 (8) [M^+], 134 (100), 105 (12).

***N*-(Pent-4-enyl)aniline (12a):**[17] Yield 5.47 g (86%), colorless oil.

General Procedure for the Synthesis of Methyl 2-(*N*-Alkenyl-*N*-arylsulfamoyl)acetates 13–15 (GP4): A solution of methyl (chlorosulfonyl)acetate (5.18 g, 30.0 mmol) in anhydrous acetonitrile (30 mL) was slowly added at 10 °C to a solution of the respective alkenylaniline (33.0 mmol) and pyridine (2.84 g, 36.0 mmol) in anhydrous acetonitrile (75 mL). Then the reaction mixture was stirred at 30 °C for 1 h, diluted with water (250 mL), acidified with concentrated HCl to pH 2 and extracted with CH_2Cl_2 (3 × 75 mL). The combined organic phases were washed with 5% HCl (2 × 50 mL), brine (50 mL) and dried with anhydrous $MgSO_4$. The solvents were removed in vacuo with a rotary evaporator, and the corresponding sulfonamide was used in the next step without purification. According to GP4 the following sulfonamides were prepared:

Methyl 2-(*N*-Allyl-*N*-phenylsulfamoyl)acetate (13a):[1] Yield 5.97 g (74%), slightly yellow oil, R_f = 0.32 (EtOAc/hexane, 1:2).

Methyl 2-[*N*-Allyl-*N*-(4-methylphenyl)sulfamoyl]acetate (13b): Yield 6.23 g (73%), slightly yellow oil, R_f = 0.34 (EtOAc/hexane, 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3 H, CCH_3), 3.83 (s, 3 H, OCH_3), 3.98 (s, 2 H, SO_2CH_2), 4.32 (dt, *J* = 1.2, 6.3 Hz, 2 H, NCH_2), 5.07–5.15 (m, 2 H, CH=CH_2), 5.79 (ddt, *J* = 6.3, 10.2, 16.5 Hz, 1 H, C*H*=CH_2), 7.19–7.22 (m, 2 H, ArH), 7.30–7.34 (m, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0 (CCH_3), 53.0 (OCH_3), 54.3 (CH_2), 55.4 (CH_2), 118.7 (CH=*C*H_2), 129.0 (2 C, CH-Ar), 130.0 (2 C, CH-Ar), 133.1 (*C*H=CH_2), 135.5 (C-Ar), 138.4 (C-Ar), 163.9 (CO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 283 (75) [M^+], 252 (18), 145 (100), 130 (95), 119 (61), 105 (46), 91 (96), 77 (56), 65 (95), 41 (95).

Methyl 2-[*N*-(But-3-enyl)-*N*-phenylsulfamoyl]acetate (14a): Yield 5.66 g (65%), colorless oil, R_f = 0.37 (EtOAc/hexane, 1:2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.21 (q, *J* = 7.1 Hz, 2 H, NCH_2CH_2), 3.78–3.84 (m, 5 H), 3.94 (s, 2 H, SO_2CH_2), 5.00–5.07 (m, 2 H, CH=CH_2), 5.65–5.81 (m, 1 H, C*H*=CH_2), 7.36–7.47 (m, 5 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 33.4 (NCH_2CH_2), 52.2 (CH_2), 53.2 (OCH_3), 54.2 (CH_2), 117.5 (CH=*C*H_2), 128.6 (CH-Ar), 129.5 (2 C, CH-Ar), 129.7 (2 C, CH-Ar), 134.4 (*C*H=CH_2), 138.2 (C-Ar), 164.1 (CO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 283 (2) [M^+], 242 (64), 146 (10), 118 (18), 105 (100), 77 (72), 51 (24), 41 (36).

Methyl 2-[*N*-(But-3-enyl)-*N*-(4-methylphenyl)sulfamoyl]acetate (14b): Yield 6.24 g (70%), colorless oil, R_f = 0.38 (EtOAc/hexane, 1:2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.16–2.25 (m, 2 H, NCH_2CH_2), 2.37 (s, 3 H, CCH_3), 3.78 (t, *J* = 7.0 Hz, 2 H, NCH_2), 3.82 (s, 3 H, OCH_3), 3.94 (s, 2 H, SO_2CH_2), 4.97–5.06 (m, 2 H, CH=CH_2), 5.64–5.81 (m, 1 H, C*H*=CH_2), 7.19–7.23 (m, 2 H, ArH), 7.32–7.36 (m, 2 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.2 (CCH_3), 33.4 (NCH_2CH_2), 52.2 (CH_2), 53.2 (OCH_3), 54.1 (CH_2), 117.4 (CH=*C*H_2), 129.2 (2 C, CH-Ar), 130.3 (2 C, CH-Ar), 134.4 (*C*H=CH_2), 135.5 (C-Ar), 138.7 (C-Ar), 164.1 (CO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 297 (4) [M^+], 256 (100), 119 (90), 91 (14).

Methyl 2-[*N*-(Pent-4-enyl)-*N*-phenylsulfamoyl]acetate (15a): Yield 6.24 g (70%), colorless oil, R_f = 0.42 (EtOAc/hexane, 1:2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.57 (quintett, *J* = 7.3 Hz, 2 H, NCH_2CH_2), 2.02–2.12 (m, *J* = 7.3 Hz, 2 H, $NCH_2CH_2CH_2$), 3.75 (t, *J* = 7.2 Hz, 2 H, NCH_2) 3.82 (s, 3 H, OCH_3), 3.94 (s, 2 H, SO_2CH_2), 4.91–5.00 (m, 2 H, CH=CH_2), 5.72 (ddt, *J* = 6.6, 10.2, 16.8 Hz, 1 H, C*H*=CH_2), 7.31–7.49 (m, 5 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 28.1 (CH_2), 30.4 (CH_2), 52.3 (CH_2), 53.2 (OCH_3), 54.1 (CH_2), 115.4 (CH=*C*H_2), 128.5 (CH-Ar), 129.3 (2 C, CH-Ar), 129.7 (2 C, CH-Ar), 137.4 (*C*H=CH_2), 138.4 (C-Ar), 164.0 (CO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 297 (1) [M^+], 242 (28), 160 (78), 118 (21), 106 (100), 77 (26), 55 (10).

General Procedure for the Synthesis of Sultams 17, 19 (GP5): A solution of bromine (3.40 g, 23.0 mmol) in CH_2Cl_2 (20 mL) was slowly added at 0 °C to a solution of the respective sulfonamide **13**, **14** or **15** (22.0 mmol) in CH_2Cl_2 (70 mL), and the mixture was stirred for an additional 30 min, then washed with water (30 mL), 10% Na_2SO_3 (2 × 30 mL), brine (30 mL) and dried with anhydrous Na_2SO_4. The solvents were removed in vacuo with a rotary evaporator, and the crude dibromide was used in the next step without any additional purification.

A solution of the respective dibromide **16**, **18** or **20** (22.0 mmol) in DMF (50 mL) was added at 50 °C within 3 h to a suspension of K_2CO_3 (9.52 g, 69.0 mmol) in DMF (100 mL) , and the mixture was stirred at this temperature for an additional 1 h. Then the DMF was removed in vacuo, the residue dissolved in CH_2Cl_2 (150 mL), the solution washed with water (75 mL) and 10% HCl (3 × 75 mL), water (50 mL) and brine (50 mL). The organic phase was dried with anhydrous $MgSO_4$ and concentrated in vacuo with a rotary evaporator. The crude product was recrystallized from EtOAc/hexane (the sultams **19a**–**e** were purified by flash chromatography) to give the corresponding methyl 3-aryl-2,2-dioxo-2-thia-3-azabicyclo[*n*.1.0]alkane-1-carboxylate. According to GP5 the following sultams were prepared.

Methyl 2,2-Dioxo-3-phenyl-2-thia-3-azabicyclo[3.1.0]hexane-1-carboxylate (17a): Yield 4.70 g (80%), colorless solid, m.p. 108–109 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.89 (dd, *J* = 5.7, 8.2 Hz, 1 H, 6-H), 2.12 (t, *J* = 5.8 Hz, 1 H, 6′-H), 2.68 (m, 1 H, 5-H), 3.65 (d, *J* = 9.7 Hz, 1 H, 4-H), 3.91 (s, 3 H, OCH3), 3.98 (dd, *J* = 3.5, 9.7 Hz, 1 H, 4′-H), 7.20–7.42 (m, 5 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 (C-6), 22.8 (C-5), 42.5 (C-1), 45.7 (C-4), 53.5 (OCH_3), 123.1 (2 C, CH-Ar), 126.4 (CH-Ar), 129.4 (2 C, CH-Ar), 136.2 (C-Ar), 165.7 (CO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 267 (38) [M^+], 144 (27), 104 (74), 91 (13), 77 (100), 59 (15), 51 (36), 39 (31). $C_{12}H_{13}NO_4S$ (267.3): calcd. C 53.92, H 4.90, N 5.24; found C 54.00, H 5.00, N 5.24.

Methyl 3-(4-Methylphenyl)-2,2-dioxo-2-thia-3-azabicyclo[3.1.0]hexane-1-carboxylate (17b): Yield 5.06 g (83%), slightly yellow solid, m.p. 125–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.86 (dd, *J* = 5.8, 8.1 Hz, 1 H, 6-H), 2.10 (t, *J* = 5.8 Hz, 1 H, 6′-H), 2.33 (s, 3 H, CCH3), 2.65 (ddd, *J* = 3.6, 6.1, 8.0 Hz, 1 H, 5-H), 3.58 (d, *J* = 9.7 Hz, 1 H, 4-H), 3.89 (s, 3 H, OCH3), 3.93 (dd, *J* = 3.4, 9.7 Hz, 1 H, 4′-H), 7.15–7.23 (m, 4 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 (C-6), 20.8 (CH_3), 22.8 (C-5), 42.2 (C-1), 46.0 (C-4), 53.4 (OCH_3), 123.7 (2 C, CH-Ar), 129.9 (2 C, CH-Ar), 133.2 (C-Ar), 136.6 (C-Ar), 165.7 (CO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 281 (100) [M^+], 158 (35), 91 (72), 65 (26), 39 (20). $C_{13}H_{15}NO_4S$ (281.3): calcd. C 55.47, H 5.57, N 4.89; found C 55.50, H 5.37, N 4.98.

Methyl 2,2-Dioxo-3-phenyl-2-thia-3-azabicyclo[4.1.0]heptane-1-carboxylate (19a): Yield 6.65 g (63%), colorless solid, m.p. 120–121 °C, R_f = 0.14 (EtOAc/hexane, 1:2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.76 (dd, *J* = 5.6, 9.4 Hz, 1 H, 7-H), 1.87 (dd, *J* = 5.6, 7.5 Hz, 1 H, 7′-H), 2.22–2.56 (m, 3 H), 3.58 (ddd, *J* = 5.1, 7.3, 13.5 Hz, 1 H, 4-H), 3.87 (s, 3 H, OCH_3), 4.10 (ddd, *J* = 6.4, 8.2, 13.5 Hz, 1 H, 4′-H), 7.22–7.39 (m, 5 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.9 (C-6), 22.5 (C-5), 27.3 (C-6), 44.5 (C-1), 49.8 (C-4), 53.5 (OCH_3), 126.2 (2 C, CH-Ar), 127.1 (CH-Ar), 129.2 (2 C, CH-Ar), 140.4 (C-Ar), 167.8 (CO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 281 (36)

[M+], 105 (100), 77 (10). $C_{13}H_{15}NO_4S$ (281.3): calcd. C 55.50, H 5.37, N 4.98; found C 55.49, H 5.33, N 5.25.

Methyl 3-(4-Methylphenyl)-2,2-dioxo-2-thia-3-azabicyclo[4.1.0]heptane-1-carboxylate (19b): Yield 3.25 g (54%), colorless solid, m.p. 74–75 °C, R_f = 0.18 (EtOAc/hexane, 1:2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.77 (dd, J = 5.7, 9.7 Hz, 1 H, 7-H), 1.92 (dd, J = 5.7, 7.6 Hz, 1 H, 7′-H), 2.18–2.52 (m, 3 H), 2.33 (s, 3 H, CCH_3), 3.49 (ddd, J = 5.2, 7.1, 13.6 Hz, 1 H, 4-H), 3.86 (s, 3 H, OCH_3), 4.11 (ddd, J = 6.3, 8.2, 13.6 Hz, 1 H, 4′-H), 7.12–7.22 (m, 4 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.7 (C-7), 20.9 (CH_3), 22.4 (C-5), 27.2 (C-6), 44.5 (C-1), 49.9 (C-4), 53.5 (OCH_3), 126.3 (2 C, CH-Ar), 129.9 (2 C, CH-Ar), 137.2 (C-Ar), 137.7 (C-Ar), 167.9 (CO) ppm. MS (EI, 70 eV): m/z (%) = 295 (68) [M+], 119 (100), 91 (20). $C_{14}H_{17}NO_4S$ (295.4): calcd. C 56.93, H 5.80, N 4.74; found C 56.90, H 5.71, N 4.91.

***t*-2-Methoxycarbonyl-2-sulfamoyl-*r*-1-cyclopropanecarboxylic Acid (22):** Periodic acid (6.81 g, 30 mmol) and $RuCl_3 \cdot nH_2O$ (27 mg, 0.09 mmol, 3 mol-%) were added to a solution of the sultam **17e** (891 mg, 3 mmol) in a mixture of CH_2Cl_2 (15 mL), MeCN (15 mL) and H_2O (25 mL), and the mixture was stirred vigorously at room temp. for 10 h. The reaction mixture was extracted with EtOAc (3 × 30 mL), the combined organic phases were dried with $MgSO_4$ and filtered through a short pad of silica gel. The solvents were removed in vacuo with a rotary evaporator, and the solid residue was recrystallized from EtOAc/hexane to afford the carboxylic acid **22** (615 mg, 92%) as a colorless solid, m.p. 142–144 °C. ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 1.78 (dd, J = 5.8, 8.0 Hz, 1 H, 3-H), 1.95 (dd, J = 5.8, 7.7 Hz, 1 H, 3′-H), 1.85 (t, J = 7.8 Hz, 1 H, 1-H), 3.78 (s, 3 H, OCH_3), 6.85 (s, 2 H, NH_2) ppm. ^{13}C NMR (250 MHz, [D$_6$]DMSO): δ = 18.3 (CH), 31.1 (CH), 48.2 (C), 53.3 (OCH_3), 167.0 (NH CO), 167.3 (CO) ppm. MS (ESI): m/z (%) = 445 [2 M – H+], 222 (100) [M – H+]. $C_6H_9NO_6S$ (223.2): calcd. C 32.29, H 4.06, N 6.28; found C 31.98, H 3.84, N 6.21.

General Procedure for the Oxidative Cleavage of the 4-Methoxyphenyl Group with Ceric Ammonium Nitrate (CAN) (GP6): A solution of CAN (12.08 g, 22.05 mmol) in water (80 mL) was slowly added to a stirred solution of the respective sultam (7 mmol) in MeCN (100 mL) kept at 0 °C, and the mixture was stirred for an additional 1 h, then diluted with water (200 mL) and extracted with EtOAc (5 × 50 mL). The organic phase was washed with 10% Na_2SO_3 (100 mL), water (50 mL), brine (50 mL) and dried with $MgSO_4$. The solvents were evaporated in vacuo with a rotary evaporator, and the crude product was purified by flash chromatography followed by recrystallization from EtOAc/hexane. According to GP6 the following sultams were prepared:

Methyl 2,2-Dioxo-2-thia-3-azabicyclo[3.1.0]hexane-1-carboxylate (23): Yield 1.04 g (78%); colorless solid, m.p. 119–120 °C; R_f = 0.08 (EtOAc/hexane, 1:2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.74 (t, J = 6.6 Hz, 1 H, 6-H), 1.86 (t, J = 7.3 Hz, 1 H, 6′-H), 2.58–2.65 (m, 1 H, 5-H), 3.33 (dd, J = 6.4, 12.4 Hz, 1 H, 4-H), 3.52 (ddd, J = 3.1, 8.2, 12.3 Hz, 1 H, 4′-H), 3.86 (s, 3 H, OCH_3), 4.79 (t, J = 6.2 Hz, 1 H, NH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 22.7 (C-6), 28.8 (C-5), 40.6 (C-4), 42.9 (C-1), 53.5 (OCH_3), 166.2 (CO) ppm. MS (EI, 70 eV): m/z (%) = 191 (100) [M+], 160 (58), 126 (16), 95 (96), 67 (72), 59 (30), 41 (54). $C_6H_9NO_4S$ (191.2): calcd. C 37.69, H 4.74, N 7.33; found C 37.91, H 4.57, N 7.09.

Methyl 2,2-Dioxo-2-thia-3-azabicyclo[4.1.0]heptane-1-carboxylate (24): Yield 554 mg (89%), slightly yellow solid, m.p. 108–109 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.65–1.76 (m, 2 H), 1.85–1.98 (m, 1 H), 2.12–2.25 (m, 1 H), 2.39–2.50 (m, 1 H), 3.21–3.33 (m, 1 H), 3.44–3.60 (m, 1 H), 3.84 (s, 3 H, OCH_3), 4.12 (dd, J = 4.8, 8.2 Hz, 1 H, NH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.0 (C-7), 23.0 (C-5), 26.7 (C-6), 41.5 (C-1), 41.7 (C-4), 53.5 (OCH_3), 168.1 (CO) ppm. MS (EI, 70 eV): m/z (%) = 205 (26) [M+], 177 (20), 174 (28), 145 (40), 126 (16), 113 (100), 112 (44), 81 (56), 53 (41). $C_7H_{11}NO_4S$ (205.2): calcd. C 40.97, H 5.40, N 6.82; found C 41.30, H 5.16, N 6.99.

Methyl 2,2-Dioxo-1,2-thiazolidine-5-carboxylate (26): Yield 269 mg (75%), colorless solid, m.p. 110–111 °C. ^{1}H NMR (250 MHz, [D$_6$]-DMSO): δ = 2.36–2.61 (m, 2 H), 3.02–3.26 (m, 2 H), 3.73 (s, 3 H, OCH_3), 4.02 (dd, J = 7.2, 8.8 Hz, 1 H, 6-H), 7.06 (t, J = 7.0 Hz, 1 H, NH) ppm. ^{13}C NMR (250 MHz, [D$_6$]DMSO): δ = 28.1 (C-4), 39.7 (C-3), 52.6 (OCH_3), 60.8 (C-5), 165.7 (CO) ppm. MS (DCI): m/z = 197 [M + NH_4+]. $C_5H_9NO_4S$ (179.2): calcd. C 33.51, H 5.06, N 7.82; found C 33.71, H 4.78, N 8.07.

Methyl 2,2-Dioxo-1,2-thiazinane-6-carboxylate (28): Yield 656 mg (68%), colorless solid, m.p. 104–105 °C. ^{1}H NMR (250 MHz, [D$_6$]-DMSO): δ = 1.52–1.75 (m, 2 H), 2.15–2.26 (m, 2 H), 3.17–3.25 (m, 2 H), 3.76 (s, 3 H, OCH_3), 3.89 (dd, J = 5.5, 9.3 Hz, 1 H, 6-H), 7.00 (t, J = 7.1 Hz, 1 H, NH) ppm. ^{13}C NMR (250 MHz, [D$_6$]-DMSO): δ = 22.9 (CH_2), 26.7 (CH_2), 44.4 (C-3), 52.1 (OCH_3), 62.9 (C-6), 165.5 (CO) ppm. MS (DCI): m/z = 211 [M + NH_4+]. $C_6H_{11}NO_4S$ (193.2): calcd. C 37.30, H 5.74, N 7.25; found C 37.63, H 5.50, N 7.04.

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[1] V. A. Rassadin, A. A. Tomashevskiy, V. V. Sokolov, A. A. Potekhin, *Khim. Geterosikl. Soedin.* **2008**, 605–617; *Chem. Heterocycl. Compd. Engl. Transl.* **2008**, *44*, 474–485.

[2] G. H. Wee, B. Liu, L. Zhang, *J. Org. Chem.* **1992**, *57*, 4404–4414.

[3] Crystals of methyl 2,2-dioxo-3-phenyl-2-thia-3-azabicyclo[3.1.0]hexane-1-carboxylate (**17a**) were grown by slow evaporation of their solution in a CH_2Cl_2/Et_2O/hexane mixture and measured on a Stoe IPDS II two circle diffractometer using graphite-monochromated Mo-K_α radiation. The structure solutions and refinements on F^2 were performed with the SHELXL-97 program. The hydrogen atoms were located in difference Fourier maps and refined as riding groups with the 1.2-fold isotropic displacement parameter of the corresponding C atom. **17a**: $C_{12}H_{13}NO_4S$ (267.29), crystal size: 0.1–0.3 mm, T 133(2) K, monoclinic, a = 10.3899(7), b = 6.0821(3), c = 19.3059(15) Å, α = 90, β = 104.531(6), γ = 90°, V = 1180.96(13) Å^3, Z = 4, space group $P2_1/n$, ρ = 1.503 g cm^{-3}, μ = 0.280 mm^{-1}, intensities measured: 17057 ($2\theta_{max}$ = 49.52°), independent 1982 (R_{int} = 0.0339), 215 parameters refined, R_1 = 0.0279 for 1896 reflections with $I > 2\sigma(I)$, wR_2 (all data) = 0.0691, Gof = 1.076, maximum and minimum residual electron densities 0.347 and –0.294 e Å^{-3}. CCDC-713449 contains the crystallographic data (excluding structure factors). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[4] See e.g.: S. I. Kozhushkov, R. Langer, D. S. Yufit, J. A. K. Howard, H. Schill, D. Demus, K. Miyazawa, A. de Meijere, *Eur. J. Org. Chem.* **2004**, 289–303.

[5] F. H. Allen, *Acta Crystallogr., Sect. B* **1980**, *36*, 81–96.

[6] For a review on nucleophilic additions to bis-acceptor-substituted cyclopropanes, see: S. Danishefsky, *Acc. Chem. Res.* **1979**, *12*, 66–72.

[7] L. S. M. Miranda, M. L. A. A. Vasconcellos, *Synthesis* **2004**, *11*, 1767–1770.

[8] a) R. E. Mewshawand, T. J. Commons, *J. Antibiot.* **1987**, *11*, 1563–1571; b) D. R. Kronenthal, C. Y. Han, M. K. Taylor, *J. Org. Chem.* **1982**, *47*, 2765–2768.
[9] W. F. Cockburn, R. A. W. Johnstone, T. S. Stevens, *J. Chem. Soc.* **1960**, 3340–3346.
[10] V. V. Sokolov, A. N. Butkevich, V. N. Yuskovec, A. A. Tomashevskii, A. A. Potekhin, *Russ. J. Org. Chem.* **2005**, *41*, 1023–1035.
[11] J. H. Freeman, E. C. Wagner, *J. Org. Chem.* **1951**, *16*, 815–837.
[12] M. Utsunomiya, Y. Myamoto, J. Ipposhi, T. Ohshima, K. Mashima, *Org. Lett.* **2007**, *9*, 3371–3374.
[13] M. Moreno-Manas, L. Morral, R. Pleixats, *J. Heterocycl. Chem.* **1997**, *34*, 241–246.
[14] G. Bartoli, *Tetrahedron Lett.* **1988**, *29*, 2251–2254.
[15] W. Bao, Y. Zhang, *Synth. Commun.* **1997**, *27*, 615–620.
[16] A. R. Katritzky, N. Shobana, P. A. Harris, *Organometallics* **1992**, *11*, 1381–1384.
[17] M. J. Szymonifka, J. V. Heck, *Tetrahedron Lett.* **1989**, *30*, 2869–2872.

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