Reactions of Pyridine Analogues of Aza-*ortho*-xylylenes Generated from 1,3-Dialkylpyridosultams

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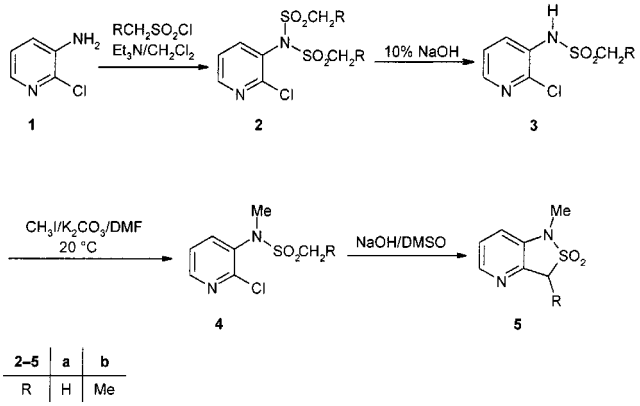
2,3-Dihydro-3-imino-2-methylenepyridines, generated by thermal extrusion of SO_2 from 1,3-dialkyl-1,3-dihydroisothiazolo[4,3-*b*]pyridine 2,2-dioxides (1,3-dialkylpyridosultams), underwent [1,5] hydrogen shifts, which led to 3-alkylamino-2-vinylpyridine derivatives. Cycloalkanespiro-3-pyridosultams **12**, which were easily obtained by alkylation of pyridosultams with α,ω-dihaloalkanes, gave, in a similar reaction, 3-alkylamino-2-cycloalkenylpyridine derivatives **14** in good yields. Cyclobutanespiro-3-pyridosultam **12b**, after thermal extrusion of SO_2, formed cyclobutenyl derivative **14b**, which underwent a ring-opening reaction to form butadiene derivative **15**. The latter can be trapped with dienophiles, for example, *N*-phenylmaleimide.

Introduction

Aza-*ortho*-xylylenes (6-methylene-2,4-cyclohexadien-1-imines) are potential building blocks for the construction of condensed heterocyclic systems.[1] These reactive 1-azadienes enter the Diels–Alder reaction leading to 1,2,3,4-tetrahydroquinoline derivatives. In recent years we have developed a method for the generation of aza-*ortho*-xylylenes by thermal extrusion of SO_2 from 1,2-benzisothiazoline 2,2-dioxide derivatives[2] and applied it to the generation of practically unknown pyridine analogues of aza-*ortho*-xylylenes.[3] The only known methods of generation of heterocyclic analogues of aza-*ortho*-xylylenes involve thermal 1,4-elimination of water from 3-amino-2-(1-hydroxyalkyl)pyridine under flash vacuum thermolysis (FVT) conditions,[4] thermal (FVT) 1,5-elimination of hydrogen chloride from imidochloride derived from 4-amino-3-methylpyridine[5] or base-induced 1,4-elimination of hydrogen fluoride from 3-amino-4-(trifluoromethyl)quinoline.[6] In one of our previous papers we described the generation of pyridine analogues of aza-*ortho*-xylylenes by thermal extrusion of SO_2 from easily available 1,3-dihydroisothiazolo[4,3-*b*]pyridine 2,2-dioxides (pyridosultams)[3] and applied them to reactions with various dienophiles. For example, the Diels–Alder reaction of *N*-phenylmaleimide (NPMI) with aza-*ortho*-xylylene generated from *N*-methylpyridosultam at 215 °C gave the corresponding tetrahydro[1,5]naphthyridine derivative in good yield.[3] Similarly, *N*-methyl-3-phenylpyridosultam extruded SO_2 in boiling toluene and formed aza-*ortho*-xylylene that reacted with 1,4-naphthoquinone to give the corresponding Diels–Alder cycloaddition product.[7] Aza-*ortho*-xylylene generated from *N*-(5-pent-1-enyl)pyridosultam underwent an intramolecular Diels–Alder reaction with its terminal double bond, to form 5,6,6a,7,8,9-hexahydropyrrolo[1,2-*a*][1,5]naphthyridine.[3]

Now we report on the results of our studies on the reactions of aza-*ortho*-xylylene analogues generated from 3-alkyl derivatives of pyridosultams.

Pyridosultams are easily available from 3-amino-2-chloropyridine (**1**) and alkanesulfonyl chlorides by the following sequence of reactions: bis-*N*-sulfonylation, desulfonylation, *N*-alkylation and cyclization (Scheme 1). Since the sulfonylation of **1** with one mol of methanesulfonyl chloride led to an inseparable mixture of mono- and disulfonylated products **2** and **3**, we developed a procedure in which the aminopyridine **1** was disulfonylated, after which one of the sulfonyl groups was removed under basic conditions; this gave the monosulfonylated product **3** in high yield. The monosulfonamide was then *N*-alkylated with an alkyl halide in the presence of K_2CO_3 in dimethylformamide. Finally, the cyclization of the *N*-alkylsulfonamide **4** in the presence of solid NaOH or *t*BuOK in DMSO gave pyridosultam **5** in good yield.



Scheme 1

This procedure, starting with ethanesulfonyl chloride, makes 1,3-dimethylpyridosultam **5b** accessible, and can be extended to other 3-alkyl-substituted derivatives, with the corresponding commercially available alkanesulfonyl chlorides as starting materials. In the synthesis of 1,3-dimethylpyridosultam, the final cyclization should be carried out

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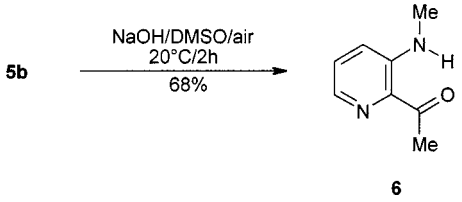
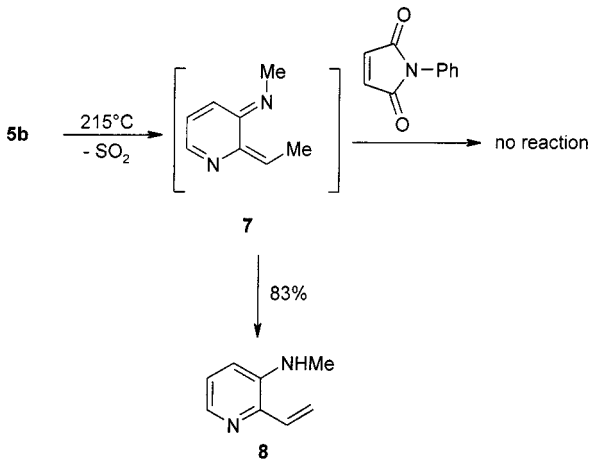
under anaerobic conditions, since the anion of the formed sultam **5b** is oxidised in the presence of air to pyridinyl-ethanone derivative **6**. In an independent experiment, we found that 1,3-dimethylpyridosultam **5b** is oxidised to 1-[3-(methylamino)-2-pyridyl]-ethanone (**6**) in 68% yield when stirred with NaOH in DMSO for 2 h in air (Scheme 2). Autooxidation of anions derived from benzosultams was used previously for the synthesis of benzophenones[8] and 2*H*-isoindoles.[9]



Scheme 2

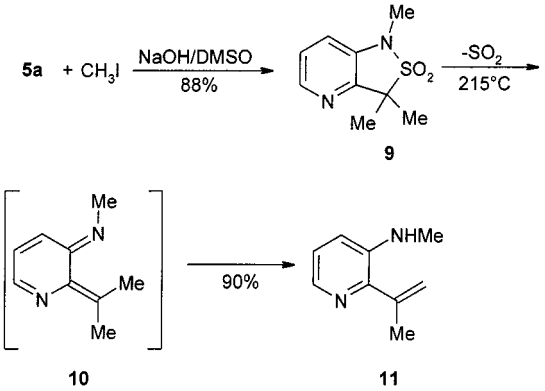
The attempts to obtain 1,3-dialkylpyridosultams by monoalkylation of the 1-alkylpyridosultam with alkyl halides were unsuccessful because of a subsequent alkylation reaction of the desired product. For example, the reaction of 1-methylpyridosultam **5a** with one mol of methyl iodide in various base–solvent systems (NaOH/DMSO, *t*BuOK/DMF) led to a mixture of mono- and dialkylated products and unchanged starting material. Therefore, the procedure described above employing alkanesulfonyl chlorides, as exemplified by the reaction with ethanesulfonyl chloride, seems to be more convenient for this purpose.

Attempts to introduce aza-*ortho*-xylylene **7** derived from the pyridosultam **5b** in the Diels–Alder reaction with NPMI were unsuccessful. After both reagents were heated in boiling 1,2,4-trichlorobenzene (TCB, 215 °C), a complex mixture was formed in which the cycloaddition product was not detected. GC-MS analysis revealed the presence of a product whose molecular mass corresponded to the loss of sulfur dioxide [M – 64] from the starting compound **5b**. When this reaction was performed in the absence of a dienophile, the product was isolated and identified as *N*-methyl-*N*-(2-vinyl-3-pyridyl)amine (**8**). The formation of this compound was a result of [1,5] hydrogen shift in the intermediate azaxylylene **7** (Scheme 3).



Scheme 3

We carried out the alkylation of *N*-methylpyridosultam in order to synthesize 3,3-dialkylpyridosultams. In most cases, the alkylation was complete within 15 min in NaOH/DMSO at room temperature. Thus, when *N*-methylpyridosultam **5a** and methyl iodide were dissolved in DMSO and stirred with finely powdered NaOH for 30 min at room temperature, the expected 3,3-dimethyl derivative **9** was obtained in 88% yield. The sultam **9**, when refluxed in 1,2,4-trichlorobenzene for 15 min, gave *N*-(2-isopropenyl-3-pyridyl)-*N*-methylamine (**11**) in 90% yield (Scheme 4).

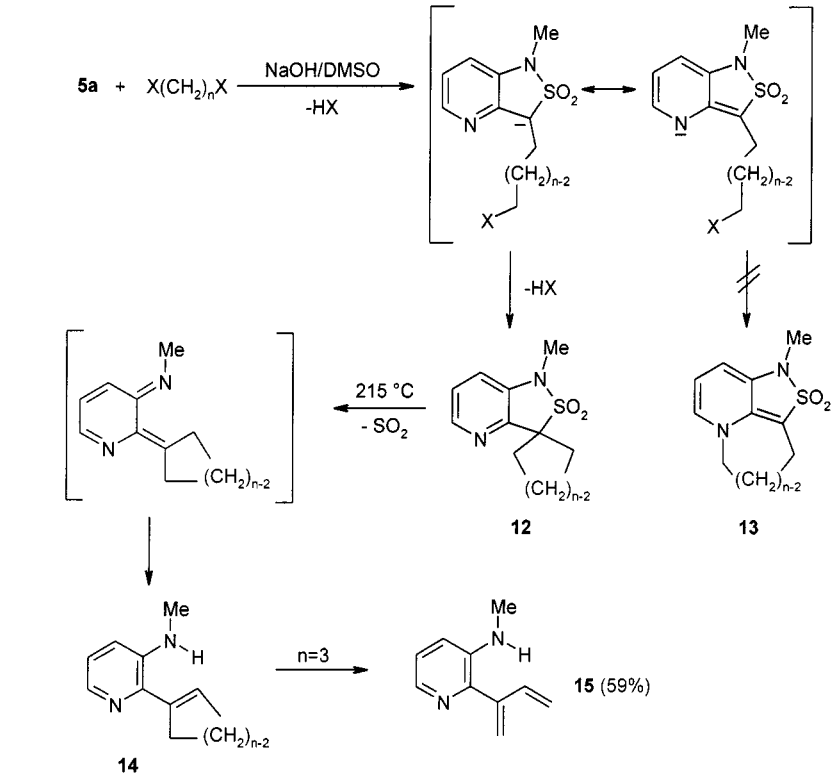


Scheme 4

Alkylation of *N*-methylpyridosultam with homologous C_2–C_6 α,ω-dihaloalkanes gave the corresponding cycloalkanospiro-3-pyridosultams **12** in good yields (Scheme 5).

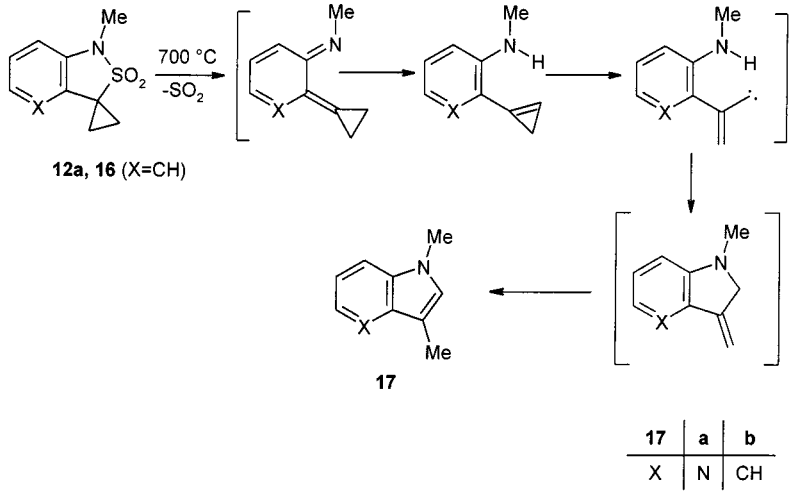
It is noteworthy that the ambident carbanions formed in these reactions are not *N*-alkylated, but only *C*3-alkylated. It was proved by the NMR spectra of the obtained products. For example, alkylation of the pyridosultam **5a** with 1,5-dibromopentane gave the spirocyclohexano compound **12d**. In the ^{13}C NMR spectrum of this product, there were only four signals in the aliphatic region. The alternative compound **13d,** if formed, would have exhibited five signals in the same region of the ^{13}C NMR spectrum.

The thermal extrusion of SO_2 from cycloalkanospiropyridosultams **12c**–**12e** in boiling trichlorobenzene was completed in 15 min and gave the corresponding 2-cycloalkenylpyridine derivatives **14c**–**14e** in very good yields. Only in the case of cyclopropanospiropyridosultam **12a** did no extrusion occur, and after prolonged heating at 215 °C, this compound remained unchanged. The experiments in a pyrolytic oven attached to the GC-MS system revealed that this compound extruded SO_2 at 500–650 °C; a mixture of products resulted and, for the main product, the structure of 1,3-dimethyl-1*H*-pyrrolo[3,2-*b*]pyridine (**17a**) was assigned. This was supported by the results of an analogous reaction of cyclopropanospirobenzosultam **16** in which the main product was identified as 1,3-dimethylindole (**17b**). These compounds were possibly formed as shown in Scheme 6. After the extrusion of SO_2, a [1,5] sigmatropic shift occurred, followed by a well precedented isomerization of cyclopropene to vinylcarbene,[10,11] which inserted into the



n	X	Sultam (yield %)	Cycloalkene (yield %)
2	Br	**12a** (92)	**14a** (0)
3	I	**12b** (88)	**14b** (0) [**15**(59)]
4	Br	**12c** (88)	**14c** (86)
5	Br	**12d** (76)	**14d** (93)
6	Br	**12e** (42)	**14e** (92)

Scheme 5

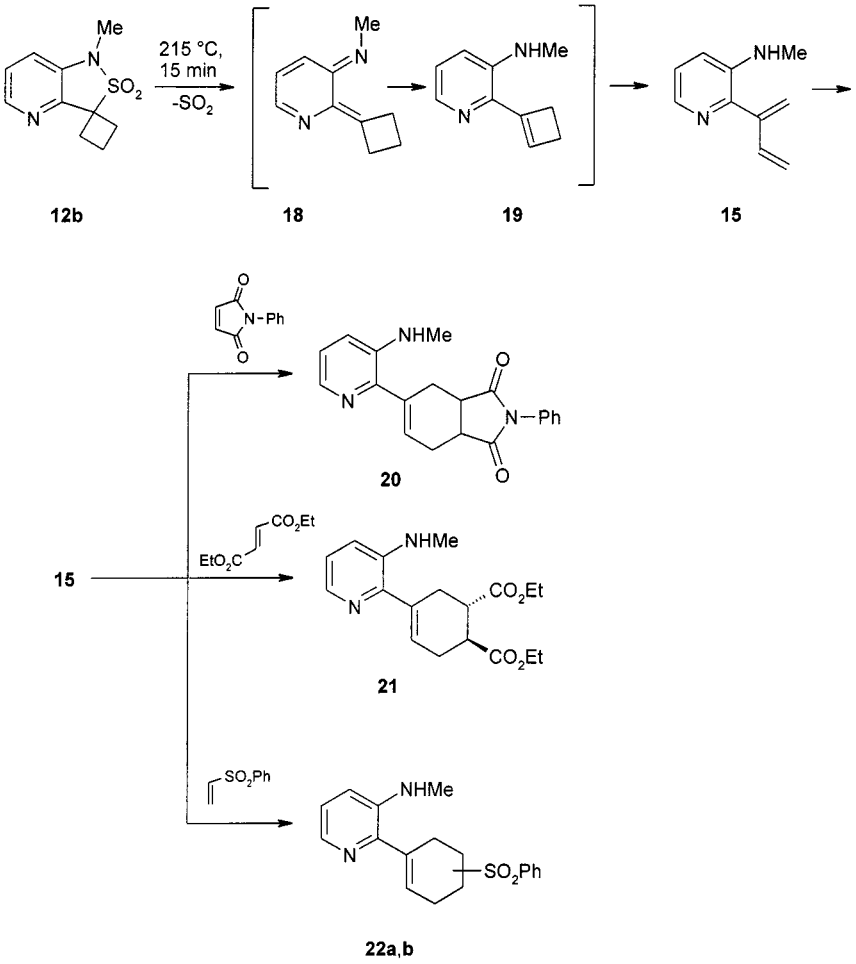


17	a	b
X	N	CH

Scheme 6

N–H bond. Finally, an isomerization of the exocyclic double bond led to the observed compounds **17a**,**b**.

In the case of cyclobutanospiropyridosultam **12b**, the extrusion of SO_2 proceeded very easily and *N*-[2-(1-cyclobutenyl)-3-pyridyl]-*N*-methylamine **19**, resulting from [1,5] hydrogen shift in the intermediate azaxylylene **18**, underwent electrocyclic opening of the cyclobutene ring, giving, finally, *N*-methyl-*N*-[2-(1-methyleneallyl)-3-pyridyl]amine (**15**).

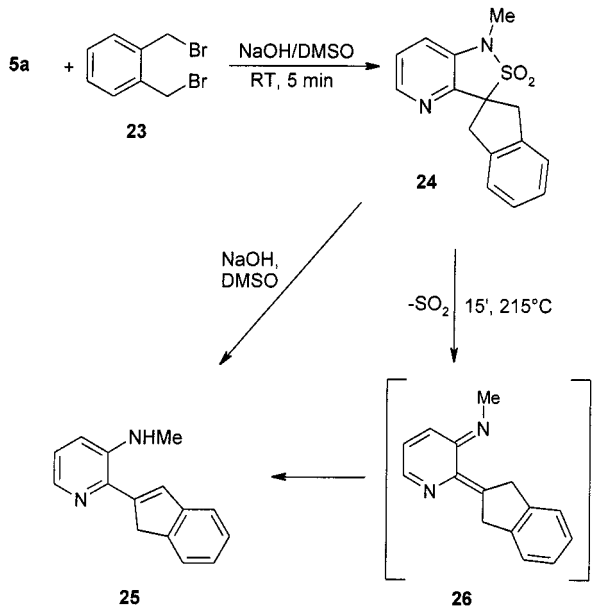


Scheme 7

When the thermal extrusion of SO_2 from the sultam **12b** was performed in the presence of *N*-phenylmaleimide, a [4+2] cycloaddition to the formed butadiene **15** occurred and the *N*-[2-(1-cyclohexenyl)-3-pyridyl]-*N*-methylamine **20** was formed (Scheme 7). The addition of the butadiene **15** to dimethyl fumarate, leading to diester **21**, proceeded similarly. In the reaction of **15** with phenyl vinyl sulfone, an inseparable mixture of two isomeric phenylsulfonylcyclohexene derivatives **22a**,**b** was formed.

Alkylation of *N*-methylpyridosultam **5a** with 1,2-bis(bromomethyl)benzene (**23**) under standard conditions (NaOH, DMSO, room temp, 1 h) gave a mixture of the expected alkylation product **24** and *N*-[2-(1*H*-inden-2-yl)-3-pyridyl]-*N*-methylamine (**25**). The latter was formed as a result of base-induced elimination of SO_2 from the spiroindane derivative **24**. However, when the alkylation was carried out for 5 min, the expected spiroindane derivative **24** was formed in 81% yield. In boiling TCB it gave the corresponding aza-*ortho*-xylylene **26**, which, after [1,5] hydrogen shift, formed the indene derivative **25** in high yield (Scheme 8).

The described reactions gave easy access to substituted 3-amino-2-vinylpyridine derivatives which may be used for the synthesis of azaindole derivatives,[12] analogously to the



Scheme 8

synthesis of indoles by ring closure of 2-vinylaniline derivatives.[13,14]

Experimental Section

Melting points are uncorrected. – ^{1}H NMR spectra were obtained with Bruker AMX (500 MHz) and Varian Gemini (200 MHz) instruments with TMS as internal standard. Coupling constants are given in Hz. – Mass spectra (electron impact, 70 eV) were obtained on an AMD 604 (AMD Intectra GmbH, Germany) instrument. HRMS were measured in the presence of perfluorokerosene as the reference compound. – Column chromatography was performed with silica gel 240–400 mesh (Merck). – All starting materials and solvents were commercial and were used without purification.

General Procedure for the Synthesis of *N*-(2-Chloro-3-pyridyl)alkanesulfonamides 3: To a solution of 3-amino-2-chloropyridine (**1**, 10.3 g, 0.08 mol) and triethylamine (18.0 g, 0.18 mol) dissolved in dichloromethane (80 mL) and cooled to 5 °C, the solution of alkanesulfonyl chloride (0.18 mol) in dichloromethane (40 mL) was added dropwise, with stirring; the temperature was kept below 10 °C. After the addition, the reaction mixture was stirred for 2 h at room temperature, and was then evaporated to dryness under reduced pressure. Aqueous NaOH (10%, 320 mL, 0.8 mol) was added to the residue, and the mixture was stirred for 30 min to complete dissolution. Then the solution was neutralized with aqueous HCl to pH = 7, was saturated with Na_2SO_4, and extracted several times with ethyl acetate. The extracts were combined, dried ($MgSO_4$), and evaporated. The product was purified by crystallization from hexane/ethyl acetate and some of the product was isolated by column chromatography of the filtrate. The following compounds were obtained:

***N*-(2-Chloro-3-pyridyl)methanesulfonamide (3a):** Yield: 14.9 g, 72 mmol (90%), m.p. 94–95 °C (from EtOH). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.09 (s, 3 H), 7.20 (broad s, 1 H), 7.32 (dd, *J* = 8.1 Hz, *J* = 4.7 Hz, 1 H), 8.00 (dd, *J* = 8.1 Hz, *J* = 1.8 Hz, 1 H), 8.24 (dd, *J* = 4.7 Hz, *J* = 1.8 Hz, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 41.1, 124.2, 131.2, 131.5, 142.9, 146.2. – MS (70 eV); *m*/*z* (%): 208 (22) [M + 2$^+$], 206 (62) [M$^+$], 129 (35), 128 (65), 127 (100), 100 (39), 92 (38), 65 (12), 39 (30). – HRMS ($C_6H_7{}^{35}ClNSO_2$): calcd. 205.9917; found 205.9926. – $C_6H_7ClN_2O_2S$ (206.7): calcd. C 34.87, H 3.41, N 13.56; found C 34.85, H 3.78, N 13.37. – Also 0.41 g (4%) of 3-amino-2-chloropyridine was regenerated.

***N*-(2-Chloro-3-pyridyl)ethanesulfonamide (3b):** Yield: 12.0 g, 54 mmol (68%), m.p. 70–72 °C (from EtOH). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.43 (t, *J* = 7.4 Hz, 3 H), 3.18 (q, *J* = 7.4 Hz, 2 H), 7.00 (broad s, 1H), 7.31 (dd, *J* = 8.1 Hz, *J* = 4.8 Hz, 1 H), 8.04 (dd, *J* = 8.1 Hz, *J* = 1.7 Hz, 1 H), 8.22 (dd, *J* = 4.8 Hz, *J* = 1.7 Hz, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 8.7, 47.8, 124.1, 129.8, 131.8, 142.0, 145.9. – MS (70 eV); *m*/*z* (%): 222 (12) [M + 2$^+$], 220 (33) [M$^+$], 130 (32), 128 (100), 127 (30), 100 (12), 92 (50), 65 (21), 39 (26). – HRMS ($C_7H_9{}^{35}ClN_2O_2S$): calcd. 220.0073; found 220.0077. – $C_7H_9ClN_2O_2S$ (220.7): calcd. C 38.10, H 4.11, N 12.69, S 14.53; found C 38.25, H 4.28, N 12.60, S 14.68.

General Procedure for *N*-Methylation of Sulfonamides: The solution of *N*-(2-chloro-3-pyridyl)alkanesulfonamide **3** (0.01 mol), methyl iodide (2.13 g, 0.015 mol), and tetrabutylammonium bromide (0.32 g, 0.001 mol) in DMF (20 mL) was stirred with K_2CO_3 (10 g) at room temp. The progress of the reaction was monitored by TLC. When the starting sulfonamide disappeared, the reaction mixture was poured into a solution of Na_2SO_4. The product was extracted with ethyl acetate and dried with $MgSO_4$. After evaporation of the solvent, the crude product was used in the next step without further purification. The following compounds were obtained:

***N*-(2-Chloro-3-pyridyl)-*N*-methylmethanesulfonamide (4a)**: Yield: quantitative, m.p. 93–95 °C (from EtOH). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.04 (s, 3 H), 3.29 (s, 3 H), 7.32 (dd, *J* = 7.8 Hz, *J* = 4.7 Hz, 1 H), 7.82 (dd, *J* = 7.9 Hz, *J* = 1.8 Hz, 1 H), 8.35 (dd, *J* = 4.7 Hz, *J* = 1.8 Hz, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 38.1, 40.3, 124.0, 135.7, 141.9, 149.7, 150.7. – MS (70 eV); *m*/*z* (%): 222 (24) [M + 2$^+$], 220 [M$^+$] (65), 185 (67), 143 (34), 142 (29), 141 (100), 128 (19), 126 (42), 105 (52), 100 (17), 78 (82). – HRMS ($C_7H_9ClN_2O_2S$): calcd. 220.0073; found 220.0057. – $C_7H_9ClN_2O_2S$ (220.7): calcd. C 38.10, H 4.11, N 12.69, S 14.53; found C 38.08, H 4.29, N 12.69, S 14.32.

***N*-(2-Chloro-3-pyridyl)-*N*-methylethanesulfonamide (4b):** Yield: 84% (oil). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.49 (t, *J* = 7.4 Hz, 3 H), 3.21 (q, *J* = 7.4 Hz, 2 H), 3.36 (s, 3H), 7.32 (dd, *J* = 7.9 Hz, *J* = 4.7 Hz, 1 H), 7.89 (dd, *J* = 7.9 Hz, *J* = 1.9 Hz, 1 H), 8.32 (dd, *J* = 4.7 Hz, *J* = 1.9 Hz, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 8.6, 38.7, 48.2, 124.0, 136.0, 142.0, 149.6, 150.7. – MS (70 eV); *m*/*z* (%): 236 (17) [M + 2$^+$], 234 (45) [M$^+$], 199 (39), 143 (34), 142 (48), 141 (100), 126 (29), 105 (54), 78 (65), 39 (23). – HRMS ($C_8H_{11}{}^{35}ClN_2O_2S$): calcd. 234.0230; found 234.0230.

General Procedure for the Synthesis of Pyridosultams 5: Potassium *tert*-butoxide (2.24 g, 20 mmol) was added to a stirred solution of *N*-(2-chloropyridine)-*N*-methylalkanesulfonamide **4** (7 mmol) in DMSO (20 mL). The reaction mixture was stirred for 40 min at room temp, was then poured into the solution of NH_4Cl, and was saturated with solid Na_2SO_4. The product was extracted with ethyl acetate and dried with $MgSO_4$. After evaporation of the solvent, the product was purified by column chromatography. The following compounds were obtained:

1-Methyl-1,3-dihydroisothiazolo[4,3-*b*]pyridine 2,2-Dioxide (*N*-Methylpyridosultam) (5a): Yield: 63%, m.p. 148–150 °C (hexane/ethyl acetate). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.15 (s, 3 H), 4.46 (s, 2 H), 6.98 (dd, *J* = 8.1 Hz, *J* = 1.3 Hz, 1 H), 7.26 (dd, *J* = 8.1 Hz, *J* = 5.1 Hz, 1 H), 8.18 (dd, *J* = 5.1 Hz, *J* = 1.3 Hz, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 26.7, 52.6, 115.9, 124.7, 138.6, 140.3, 143.0. – MS (70 eV); *m*/*z* (%): 184 (58) [M$^+$], 120 (24), 119 (100), 105 (18), 92 (8), 79 (14). – HRMS ($C_7H_8N_2O_2S$): calcd. 184.0307; found 184.0322. – $C_7H_8N_2O_2S$ (184.2): calcd. C 45.65, H 4.35, N 15.22; found C 45.65, H 4.36, N 15.14.

1,3-Dimethyl-1,3-dihydroisothiazolo[4,3-*b*]pyridine 2,2-Dioxide (1,3-Dimethylpyridosultam) (5b): The reaction was carried out under argon. Yield: 70%; m.p. 75–76 °C (from EtOH). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.80 (d, *J* = 7.1 Hz, 3 H), 3.18 (s, 3 H), 4.39 (q, *J* = 7.1 Hz, 1 H), 7.00 (dd, *J* = 8.1 Hz, *J* = 1.3 Hz, 1 H), 7.27 (dd, *J* = 8.1 Hz, *J* = 5.0 Hz, 1 H), 8.21 (dd, *J* = 5.0 Hz, *J* = 1.3 Hz, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 12.2, 26.7, 57.4, 115.9, 124.6, 137.7, 143.1, 144.9. – MS (70 eV); *m*/*z* (%): 198 (37) [M$^+$], 134 (47), 133 (90), 119 (100), 106 (11), 92 (16), 66 (11), 39 (22). – HRMS ($C_8H_{10}N_2O_2S$): calcd. 198.0463; found 198.0461. – $C_8H_{10}N_2O_2S$ (198.2): calcd. C 48.47, H 5.08, N 14.13; found C 48.44, H 4.95, N 14.24, S 16.00.

The Reaction of 1,3-Dimethylpyridosultam (5) with NaOH/DMSO in Air: 1,3-Dimethylpyridosultam (**5b**, 0.50 g, 2.5 mmol) was stirred with NaOH (1 g) in DMSO (5 mL) at 20 °C until the substrate disappeared (2 h). The reaction mixture was then poured into an aqueous solution of NH_4Cl and was extracted with ethyl acetate. After purification by column chromatography (hexane/ethyl acet-

ate), 1-[3-(methylamino)-2-pyridyl]ethanone (**6**) was obtained. Yield 0.23g (68%), yellow crystals, m.p. 83–86 °C (hexane/ethyl acetate). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.73 (s, 3 H), 2.93 (d, *J* = 5.1 Hz, 3 H), 7.07 (dd, *J* = 8.7 Hz, *J* = 1.2 Hz, 1 H), 7.31 (dd, *J* = 8.8 Hz, *J* = 4.2 Hz, 1 H), 7.96 (dd, *J* = 4.2 Hz, *J* = 1.2 Hz, 1 H), 8.56 (broad s, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 27.6, 29.4, 119.3, 129.1, 134.6, 136.0, 148.5, 204.5. – MS (70 eV); *m*/*z* (%): 150 (100) [M^+], 149 (39), 135 (49), 133 (19), 107 (62), 93 (17), 79 (52). – HRMS ($C_8H_{10}N_2O$): calcd. 150.0793; found 150.0794. – $C_8H_{10}N_2O$ (150.2): calcd. C 63.98, H 6.71, N 18.65; found C 63.52, H 7.04, N 18.30. – IR (KBr): ν = 3343 (s, N–H), 1651 (vs, C=O).

General Procedure for Alkylation of *N*-Methylpyridosultam (5a): To a solution of *N*-methylpyridosultam (**5a**, 1 mmol) and methyl iodide (0.30 g, 2.1 mmol) or the corresponding α,ω-dialkyl halide (1.1 mmol) in DMSO (20 mL), finely ground NaOH (0.80 g, 20 mmol) was added. The reaction was stirred for 30 min, then it was poured into the solution of NH_4Cl, and then this mixture was saturated with Na_2SO_4. The product was extracted with ethyl acetate and dried. After evaporation of the solvent, the product was purified by column chromatography. The following compounds were obtained:

1,3,3-Trimethyl-1,3-dihydroisothiazolo[4,3-*b*]pyridine 2,2-Dioxide; (1,3,3-Trimethyl)pyridosultam (9): Yield: 88%; m.p. 95–97 °C (ethyl acetate). – ^{1}H NMR (200 MHz, $CDCl_3$): 1.74 (s, 6 H), 3.16 (s, 3 H), 7.00 (dd, *J* = 8.1 Hz, *J* = 1.3 Hz, 1 H), 7.24 (dd, *J* = 8.1 Hz, *J* = 5.0 Hz, 1 H), 8.20 (dd, *J* = 5.0 Hz, *J* = 1.3 Hz, 1 H). – ^{13}C NMR($CDCl_3$): 21.6, 26.7, 61.6, 116.1, 124.4, 136.4, 143.0, 149.3. – MS (70 eV); *m*/*z* (%): 212 (29) [M^+], 148 (20), 147 (44), 133 (100), 39 (16). – HRMS ($C_9H_{12}N_2O_2S$): calcd. 212.0620; found 212.0620. – $C_9H_{12}N_2O_2S$ (212.3): calcd. C 50.93, H 5.70, N 13.20, S 15.10; found C 50.95, H 5.70, N 13.14, S 15.12.

Cyclopropanospiro-3′-(1′-methyl-1′,3′-dihydroisothiazolo[4,3-*b*]pyridine) 2′,2′-Dioxide (12a): Yield: 92%; m.p. 110–112 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.81–1.85 (m, 2 H), 2.01–2.04 (m, 2 H), 3.22 (s, 3 H), 6.94 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1 H), 7.16 (dd, *J* = 8.0 Hz, *J* = 5.0 Hz, 1 H), 8.07 (dd, *J* = 5.0 Hz, *J* = 1.3 Hz, 1 H). – ^{13}C NMR ($CDCl_3$) δ = 16.7, 27.3, 43.1, 114.8, 123.5, 137.5, 142.6, 144.4. – MS (70 eV); *m*/*z* (%): 210 (77) [M^+], 162(7), 144(5), 145(100), 131(32), 119(33), 118(29), 117(22), 104(17). – HRMS ($C_9H_{10}N_2O_2S$): calcd. 210.0463; found 210.0458. – $C_9H_{10}N_2O_2S$ (210.3): calcd. C 51.41, H 4.79, N 13.32, S 15.25; found C 51.32, H 4.73, N 13.34, S 15.35.

Cyclobutanospiro-3′-(1′-methyl-1′,3′-dihydroisothiazolo[4,3-*b*]pyridine) 2′,2′-Dioxide (12b): Yield: 88%, m.p. 90–91 °C (hexane/ethyl acetate). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.20–2.29 (m, 1 H), 2.30–2.39 (m, 1 H), 2.66–2.73 (m, 2 H), 3.01–3.9 (m, 2 H), 3.13 (s, 3 H), 6.91 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1 H), 7.21 (dd, *J* = 8.0 Hz, *J* = 5.0 Hz, 1 H), 8.23 (dd, *J* = 5.0 Hz, *J* = 1.3 Hz, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 15.8, 27.0, 29.4, 63.7, 115.5, 124.5, 136.7, 143.2, 147.4. – MS (70 V) *m*/*z* (%): 224 (75) [M^+], 196 (100), 159 (67), 145 (42), 132 (74), 131 (67). – HRMS ($C_{10}H_{12}N_2O_2S$): calcd. 224.0620; found 224.0620. – $C_{10}H_{12}N_2O_2S$ (224.3): calcd. C 53.55, H 5.39, N 12.49, S 14.29; found C 53.40, H 5.41, N 12.33, S 14.05.

Cyclopentanospiro-3′-(1′-methyl-1′,3′-dihydroisothiazolo[4,3-*b*]pyridine) 2′,2′-Dioxide (12c): Yield: 88%; m.p. 56–57 °C (hexane/ethyl acetate). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.9–2.1 (m, 4 H), 2.1–2.3 (m, 2 H), 2.6–2.8 (m, 2 H), 6.94 (dd, *J* = 8.1 Hz, *J* = 1.3 Hz, 1 H), 7.19 (dd, *J* = 8.1 Hz, *J* = 5.0 Hz, 1 H), 8.17 (dd, *J* = 5.0 Hz, *J* = 1.3 Hz, 1 H). – ^{13}C NMR($CDCl_3$): δ = 26.5, 26.9, 35.0, 72.0, 115.7, 124.1, 136.9, 143.0, 149.1. – MS (70 eV); *m*/*z* (%): 238 (35) [M^+], 197 (23), 174 (27), 173 (46), 159 (18), 146 (100), 145 (45), 133 (16), 132 (13), 131 (34). – HRMS ($C_{11}H_{14}N_2O_2S$): calcd. 238.0776 found: 238.0784. – $C_{11}H_{14}N_2O_2S$ (238.3): calcd. C 55.44, H 5.92, N 11.76; found C 55.35, H 6.05, N 11.64.

Cyclohexanospiro-3′-(1′-methyl-1′,3′-dihydroisothiazolo[4,3-*b*]pyridine) 2′,2′-Dioxide (12d): Yield: 76%; m.p. 105–107 °C (hexane/ethyl acetate). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.40–1.63 (m, 1 H), 1.74–2.00 (m, 5 H), 2.02–2.20 (m, 2H), 2.24–2.40 (m, 2 H), 3.17 (s, 3 H), 6.97 (dd, *J* = 8.0 Hz, *J* = 1.4 Hz, 1 H), 7.23 (dd, *J* = 8.0 Hz, *J* = 5.0 Hz, 1 H), 8.20 (dd, *J* = 5.0 Hz, *J* = 1.4 Hz, 1 H). – ^{13}C NMR($CDCl_3$): δ = 22.7, 25.2, 26.7, 31.2, 65.5, 115.9, 124.1, 136.4, 142.7, 149.1. – MS (70 eV); *m*/*z* (%): 252 (21) [M^+], 197 (12), 188 (19), 187 (43), 173 (15), 160 (29), 159 (100), 146 (21), 145 (41), 133 (10), 131 (14). – HRMS ($C_{12}H_{16}N_2O_2S$): calcd. 252.0933; found 252.0921. – $C_{12}H_{16}N_2O_2S$ (252.3): calcd. C 57.12, H 6.39, N 11.10, S 12.71; found C 56.93, H 6.50, N 11.04, S 12.93.

Cycloheptanospiro-3′-(1′-methyl-1′,3′-dihydroisothiazolo[4,3-*b*]pyridine) 2′,2′-Dioxide (12e): Yield: 42%; m.p. 107–108 °C (hexane/ethyl acetate). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.60–2.10 (m, 8 H), 2.13–2.30 (m, 2 H), 2.45–2.60 (m, 2 H), 3.15 (s, 3 H), 6.98 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1 H), 7.23 (dd, *J* = 8.0 Hz, *J* = 5.0 Hz, 1 H), 8.20 (dd, *J* = 5.0 Hz, *J* = 1.3 Hz, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 23.9, 26.7, 31.3, 33.5, 68.5, 116.0, 124.0, 136.0, 142.7, 150.6. – MS (70 eV); *m*/*z* (%): 266 (19) [M^+], 202(13), 201(15), 197(12), 187(19), 173(32), 160(20), 159(100), 146(41), 145(29), 133(15), 131(18). – HRMS ($C_{13}H_{18}N_2O_2S$): calcd. 266.1089; found 266.1087. – $C_{13}H_{18}N_2O_2S$ (266.4): calcd. C 58.62, H 6.81, N 10.52, S 12.04; found C 58.46, H 6.95, N 10.38, S 12.2.

Indano-2-spiro-3′-(1′-methyl-1′,3′-dihydroisothiazolo[4,3-*b*]pyridine) 2′,2′-Dioxide (24): Reaction time: 5 min. Yield: 81%; m.p. 185–186 °C (ethyl acetate). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.20 (s, 3 H), 3.61 (d, *J* = 17.1 Hz, 2 H), 4.02 (d, *J* = 17.1 Hz, 2 H), 7.03 (dd, *J* = 8.0 Hz, *J* = 1.4 Hz, 1 H), 7.27 (dd, *J* = 8.0 Hz, *J* = 5.0 Hz, 1 H), 7.26–7.30 (m, 4 H), 8.21 (dd, *J* = 5.0 Hz, *J* = 1.4 Hz, 1 H). – ^{13}C NMR($CDCl_3$): δ = 27.0, 40.7, 71.6, 116.0, 124.6, 124.9, 128.1, 137.0, 139.5, 143.3, 147.9. – MS (70 eV); *m*/*z* (%): 286 (10) [M^+], 222 (55), 221 (100), 207 (26), 206 (14), 205 (12). – HRMS ($C_{15}H_{14}N_2O_2S$): calcd. 286.0776; found 286.0759. – $C_{15}H_{14}N_2O_2S$ (286.4): calcd. C 62.92, H 4.93, N 9.78, S 11.12; found C 62.82, H 4.94, N 9.62, S 11.30.

General Procedure for the Thermal Extrusion of SO_2 from Pyridosultams: Pyridosultam (1 mmol) was refluxed in trichlorobenzene (10 mL) for 15 min. The reaction mixture was then subjected to column chromatography. Trichlorobenzene was eluted with hexane/ethyl acetate (10:1) and then the product with hexane/ethyl acetate (1:1). The following compounds were obtained:

***N*-Methyl-*N*-(2-vinyl-3-pyridyl)amine (8):** Yield: 83% (oil). – ^{1}H NMR ($CDCl_3$): δ = 2.89 (s, 3 H), 5.54 (dd, *J* = 11.0 Hz, *J* = 2.0 Hz, 1 H), 6.20 (dd, *J* = 17.2 Hz, *J* = 2.0 Hz, 1 H), 6.87 (dd, *J* = 17.2 Hz, *J* = 11.0 Hz, 1 H), 6.94 (dd, *J* = 8.2 Hz, *J* = 1.4 Hz, 1 H), 7.13 (dd, *J* = 8.2 Hz, *J* = 4.6 Hz, 1 H), 8.02 (dd, *J* = 4.6 Hz, *J* = 1.4 Hz, 1 H). – ^{13}C NMR($CDCl_3$): δ = 30.9, 117.5, 119.6, 132.9, 131.9, 138.3, 142.2, 143.0. – MS (70 eV); *m*/*z* (%): 134 (79) [M^+], 133 (39), 119 (100), 106 (9), 92 (24), 79 (11), 65 (15), 39 (24). – HRMS ($C_8H_{10}N_2$): calcd. 134.0844; found 134.0843.

***N*-(2-Isopropenyl-3-pyridyl)-*N*-methylamine (11):** Yield: 90% (oil). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.16 (dd, *J* = 1.2 Hz, *J* = 1.4 Hz, 3 H), 2.82 (d, *J* = 5.1 Hz, 3 H), 4.4 (broad s, 1 H), 5.26 (dq, *J* = 1.8 Hz, *J* = 1.2 Hz, 1 H), 5.46 (dq, *J* = 1.8 Hz, *J* = 1.4 Hz, 1 H), 6.88 (dd, *J* = 8.3 Hz, *J* = 1.4 Hz, 1 H), 7.07 (dd, *J* = 8.3 Hz, *J* = 4.6 Hz, 1 H), 7.95 (dd, *J* = 4.6 Hz, *J* = 1.4 Hz, 1 H) –

^{13}C NMR($CDCl_3$): δ = 23.4, 30.9, 116.3, 116.6, 123.2, 137.1, 142.4, 143.5, 147.3. – MS (70 eV); *m/z* (%): 148 (65) [M^+], 147 (51), 133 (100), 132 (14), 118 (14), 39 (11). – HRMS ($C_9H_{12}N_2$): calcd. 148.1001; found 148.1021.

***N*-Methyl-*N*-[2-(1-methyleneallyl)-3-pyridyl]amine (15):** Yield: 60% (oil). – ^{1}H NMR (200 MHz, $CDCl_3$): 2.84 (d, *J* = 3.6 Hz, 3 H), 4.02 (broad s, 1 H), 4.96 (br. d, *J* = 17.4 Hz, 1 H), 5.20 (br. d, *J* = 10.5 Hz, 1 H), 5.38–5.40 (m, 1 H), 5.61–5.63 (m, 1 H), 6.63 (dd, *J* = 17.4 Hz, *J* = 10.5 Hz, 1 H), 6.95 (dd, *J* = 8.2 Hz, *J* = 1.3 Hz, 1 H), 7.17 (dd, *J* = 8.2 Hz, *J* = 4.7 Hz, 1 H), 7.53 (dd, *J* = 4.7 Hz, *J* = 1.3 Hz, 1 H). – ^{13}C NMR ($CDCl_3$): 30.1, 115.9, 117.3, 120.0, 123.1, 136.3, 137.1, 142.6, 144.0, 145.1. – MS (70 eV); *m/z* (%): 160 (69) [M^+], 159 (76), 146 (11), 145 (100), 144 (35), 143 (18), 132 (15), 131 (30), 130 (82), 118 (23), 117 (29), 79 (14), 78 (12), 77 (12), 66 (11), 39 (17). – HRMS ($C_{10}H_{12}N_2$): calcd. 160.1001; found 160.0998.

***N*-[2-(1-Cyclopentenyl)-3-pyridyl]-*N*-methylamine (14c):** Yield: 86%, m.p. 103–104 °C (ethyl acetate). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.04–1.88 (m, 2 H), 2.66–2.53 (m, 2 H), 2.91–2.78 (m, 5 H), 4.44 (broad s, 1 H), 6.20–6.15 (m; 5 lines, 1 H), 6.86 (dd, *J* = 8.2 Hz, *J* = 1.5 Hz, 1 H), 7.01 (dd, *J* = 8.2 Hz, *J* = 4.6 Hz, 1 H), 7.94 (dd, *J* = 4.6 Hz, *J* = 1.5 Hz, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 23.3, 31.0, 34.8, 36.4, 116.5, 122.8, 130.6, 137.4, 142.8, 143.3, 143.6. – MS (70 eV); *m/z* (%): 174 (100) [M^+], 173 (52), 159 (21), 158 (14), 146 (70), 145 (50), 132 (15), 131 (42), 66 (10). – HRMS ($C_{11}H_{14}N_2$): calcd. 174.1157; found 174.1152. – $C_{11}H_{14}N_2$ (174.3): calcd. C 75.82, H 8.10, N 16.08; found C 75.50, H 8.02, N 15.99.

***N*-[2-(1-Cyclohexenyl)-3-pyridyl]-*N*-methylamine (14d):** Yield: 93%, m.p. 115–116 °C (ethyl acetate). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.68–1.90 (m, 4 H), 2.16–2.30 (m, 2 H), 2.32–2.46 (m, 2 H), 2.85 (d, *J* = 5.1 Hz, 3 H), 4.35 (broad s, 1 H), 5.95–6.02 (m, 1 H), 6.89 (dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 1 H), 7.08 (dd, *J* = 8.1 Hz, *J* = 4.8 Hz, 1 H), 7.96 (dd, *J* = 4.8 Hz, *J* = 1.4 Hz, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 22.7, 23.5, 25.6, 28.4, 31.0, 116.4, 122.8, 128.4, 136.7, 137.2, 142.5, 148.5. – MS (70 eV); *m/z* (%): 188 (73) [M^+], 187 (55), 173 (15), 160 (26), 159 (100), 146 (22), 145 (50), 131 (15). – HRMS ($C_{12}H_{16}N_2$): calcd. 188.1314; found 188.1332. – $C_{12}H_{16}N_2$ (188.3): calcd. C 76.56, H 8.57, N 14.88; found C 76.50, H 8.50, N 14.65.

***N*-[2-(1-Cycloheptenyl)-3-pyridyl]-*N*-methylamine (14e):** Yield: 92%, m.p. 89–90 °C (ethyl acetate). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.60–1.80 (m, 4 H), 1.80–1.95 (m, 2 H), 2.30–2.40 (m, 2 H), 2.50–2.60 (m, 2 H), 2.84 (d, *J* = 4.4 Hz, 3 H), 4.21 (broad s, 1 H), 6.15 (t, *J* = 6.4 Hz, 1 H), 6.86 (dd, *J* = 8.1, *J* = 1.4 Hz, 1 H), 7.04 (dd, *J* = 8.1 Hz, *J* = 4.7 Hz, 1 H), 7.93 (dd, *J* = 4.7 Hz, *J* = 1.4 Hz, 1 H). – ^{13}C NMR($CDCl_3$): δ = 27.7, 28.2, 29.5, 31.0, 32.9, 33.6, 116.5, 122.7, 134.0, 137.2, 142.2, 142.9, 150.2. – MS (70 eV); *m/z* (%): 202 (47) [M^+], 201 (19), 187 (14), 173 (24), 160 (17), 159 (100), 146 (33), 145 (26), 131 (14). – HRMS ($C_{13}H_{18}N_2$): calcd. 202.1470; found 202.1461.

***N*-[2-(1*H*-Inden-2-yl)-3-pyridyl]-*N*-methylamine (25):** Yield: 90% (oil). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.94 (d, *J* = 4.9 Hz, 3 H), 4.10 (s, 2 H), 4.65 (broad s, 1 H), 7.03 (dd, *J* = 8.2 Hz, *J* = 1.4 Hz, 1 H), 7.14 (dd, *J* = 8.2 Hz, *J* = 4.5 Hz, 1 H), 7.22–7.42 (m, 3 H), 7.45–7.52 (m, 1 H), 7.60–7.54 (m, 1 H), 8.10 (dd, *J* = 4.5 Hz, *J* = 1.5 Hz, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 31.2, 42.3, 117.3, 121.9, 123.2, 124.3, 125.9, 127.0, 130.0, 138.2, 141.7, 143.7, 144.2, 145.5, 146.4. – MS (70 eV); *m/z* (%): 222 (93) [M^+], 221 (100), 219 (13), 207 (32), 206 (22), 205 (16). – HRMS ($C_{15}H_{14}N_2$): calcd. 222.1157; found 222.1152.

Thermal Extrusion of SO_2 from Cyclobutanespiro-3′-pyridosultam (17) in the Presence of Dienophiles. – General Procedure: Pyridosultam (**17**, 0.4 mmol) and a dienophile (0.7 mmol) were refluxed in trichlorobenzene (5 mL) for 30 min. The reaction mixture was passed through a chromatography column. Trichlorobenzene was eluted with hexane/ethyl acetate (10:1) and then the product was eluted with hexane/ethyl acetate (1:1). The following compounds were obtained:

From *N*-Phenylmaleimide: 5-[3-(Methylamino)-2-pyridyl]-2-phenyl-3a,4,7,7a-tetrahydro-1*H*-isoindole 1,3(2*H*)-Dioxide (20): Yield: 81%, m.p. 151–152 °C (ethyl acetate). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.53 (dddd, *J* = 15.9 Hz, *J* = 6.5 Hz, *J* = 3.8 Hz, *J* = 2.3 Hz, 1 H), 2.72 (d, *J* = 4.9 Hz, 3 H), 2.78 (dddd, *J* = 15.7 Hz, *J* = 7.4 Hz, *J* = 2.3 Hz, *J* = 2.3 Hz, 1 H), 2.88 (ddd, *J* = 15.9, *J* = 6.5 Hz, *J* = 3.1 Hz, 1 H), 3.14 (dd, *J* = 15.7 Hz, *J* = 3.1 Hz, 1 H), 3.35 (ddd, *J* = 9.3 Hz, *J* = 7.4 Hz, *J* = 3.1 Hz, 1 H), 3.43 (ddd, *J* = 9.3 Hz, *J* = 6.5 Hz, *J* = 3.1 Hz, 1 H), 4.20 (q, *J* = 4.9 Hz, 1 H), 6.34 (ddd, *J* = 6.5 Hz, *J* = 3.8 Hz, *J* = 2.3 Hz, 1 H), 6.86 (dd, *J* = 8.2 Hz, *J* = 1.3 Hz, 1 H), 7.05 (dd, *J* = 8.2 Hz, *J* = 4.6 Hz, 1 H), 7.24–7.27 (m, 2 H), 7.34–7.38 (m, 1 H), 7.42–7.46 (m, 2 H), 7.95 (dd, *J* = 4.6 Hz, *J* = 1.4 Hz, 1 H). – ^{13}C NMR($CDCl_3$): δ = 25.3, 28.0, 30.8, 39.7, 40.5, 117.1, 123.6, 126.8, 127.6, 129.1, 129.6, 132.5, 137.7, 138.7, 142.6, 144.9, 179.5. – MS (70 eV); *m/z* (%): 333 (81) [M^+], 332 (30), 318 (10), 186 (23), 185 (68), 171 (14), 169 (21), 160 (19), 159 (50), 146 (100), 145 (46) 131 (12). – HRMS ($C_{20}H_{19}N_3O_2$): calcd. 333.1477; found 333.1452.

From Dimethyl Fumarate: Dimethyl *trans*-4-[3-(Methylamino)-2-pyridyl]-4-cyclohexene-1,2-dicarboxylate (21): Yield: 91%; m.p. 102.5–103.5 °C (ethyl acetate/hexane 1:1). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.40–2.48 (m, 1 H), 2.52– 2.64 (m, 2 H), 2.80–2.87 (m, 4 H), 3.03 (ddd, *J* = 10.0 Hz, *J* = 10.0 Hz, *J* = 5.8 Hz, 1 H), 3.12 (ddd, *J* = 10.0 Hz, *J* = 10.0 Hz, *J* = 5.5 Hz, 1 H), 3.70 (s, 3 H), 3.73 (s, 3 H), 4.35 (broad s, 1 H), 5.97–6.00 (m, 1 H), 6.87 (dd, *J* = 8.2 Hz, *J* = 1.1 Hz, 1 H), 7.06 (dd, *J* = 8.2 Hz, *J* = 4.7 Hz, 1 H), 7.91 (dd, *J* = 4.7 Hz, *J* = 1.3 Hz, 1 H). – ^{13}C NMR($CDCl_3$): δ = 28.3, 30.4, 30.8, 41.2, 42.0, 52.49, 52.54, 116.7, 123.4, 125.7, 135.1, 137.3, 142.8, 146.1, 175.4. – MS (70 eV); *m/z* (%): 304 (37) [M^+], 273 (8), 246 (16), 245 (100), 218 (16), 185 (48), 169 (13), 159 (32), 145 (12). – HRMS ($C_{16}H_{20}N_2O_4$): calcd. 304.1423; found 304.1417,

From Phenyl Vinyl Sulfone: After reflux for 10 min, an inseparable mixture of *N*-methyl-*N*-{2-[5-(phenylsulfonyl)-1-cyclohexyl]-3-pyridyl}amine (**22a**) and *N*-methyl-*N*-{2-[4-(phenylsulfonyl)-1-cyclohexyl]-3-pyridyl}amine (**22b**) formed. Yield: 52% (isomers ratio 7:2 according to HPLC). – MS (70 eV); *m/z* (%): 328 (14) [M^+], 187 (100), 185 (95), 171 (12), 169 (11), 159 (18), 145 (22), 77 (10), 43 (47). – HRMS ($C_{16}H_{20}N_2O_4$): calcd. 328.1245; found 328.1231.

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