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ORIGINAL PAPER

Organocatalytic one-pot synthesis of functionalized 1,3-oxathiolanes and 1,3-thiazolidines

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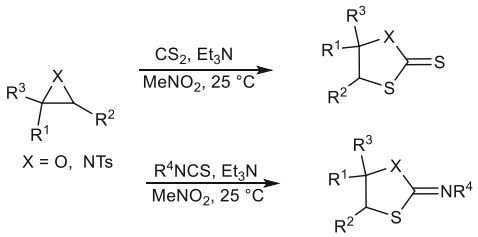
Abstract An efficient organocatalytic approach for the synthesis of 1,3-oxathiolanes and 1,3-thiazolidines is reported. In this methodology, conjugated base of nitromethane was employed as a potential organocatalyst to promote cyclization reaction between strained heterocyclic compounds and heterocumulenes at ambient conditions.

Graphical abstract



Keywords Heterocycles · One-pot reaction · Strained heterocycle · Organocatalytic · Heterocumulene

Introduction

Three-membered heterocyclic rings are valuable building block due to their ability to function as carbon electrophiles [1, 2]. These substrates undergo nucleophilic attack with heterocumulenes either at C-2 or C-3 position to afford corresponding heterocyclic compounds [3–6]. The extent of regioselectivity depends mainly on operating conditions and ring substituents [7, 8]. Furthermore, most of these nucleophilic ring opening (NRO) transformations rely on catalysts such as metal catalysts [9, 10] or organocatalysts to accomplish the desired transformation [11]. The advantages of organocatalysts include their lack of sensitivity to moisture and oxygen, low cost, and low toxicity, although their catalytic efficiency is usually lower than in metal-catalyzed processes in terms of turnover number. 1,3-Oxathiolane and 1,3-thiazolidine derivatives are found in a wide range of bioactive compounds [12, 13]. In recent years, several different methods for the synthesis of these heterocycles have been reported [14–17]. Hou has also disclosed a concise procedure for the construction of 1,3-thiazolidines using organophosphines [18]. These results encouraged us to examine alternative conditions for the synthesis of 1,3-thiazolidines and 1,3-oxathiolanes in the presence of Et_3N in nitromethane ($MeNO_2$).

Results and discussion

The reaction was initially examined using CS_2 (**1**) and 2-methyloxirane (**2a**) in the presence of pyridine as a base. Stirring in $MeNO_2$ at ambient conditions for 6 h gave 5-methyl-1,3-oxathiolane-2-thione (**3a**) in 69 % yield. To develop the reaction conditions a variety of bases and solvents were examined (Table 1). No reaction took place in the absence of a base even at higher temperatures. Among the bases examined, Et_3N gave the best result. The yield was almost unchanged by the reducing amount of Et_3N to 10 mol % (Table 1). Other solvents, such as THF, MeCN, DMF, hexane, and H_2O were also examined; however, no transformation occurred in the absence of $MeNO_2$ (Table 1). It could be deduced that $MeNO_2$ involves in reaction progress beyond acting as the solvent.

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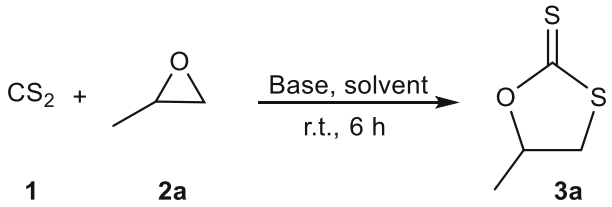
Table 1 Optimization of reaction conditions



Entry	Base	Solvent	**3a**[a] Yield/%
1	Et_3N	$MeNO_2$	94
2	Et_3N	$MeNO_2$	96[b]
3	Et_3N	$EtNO_2$	79
4	Et_3N	DMF	–
5	Pyridine	$MeNO_2$	69
6	DMAP	$MeNO_2$	10
7	DBU	$MeNO_2$	72
8	DABCO	$MeNO_2$	43

[a] Reaction conditions: **1** (3 mmol), **2a** (1.0 mmol), base (10 mol %), solvent (2 cm^3), 25 °C for 6 h

[b] 1.0 mmol of Et_3N was used

Finally, optimal results for this transformation were obtained when 10 mol % of Et_3N in $MeNO_2$ (2 cm^3) was used, furnishing **3a** in 94 % yield. The *trans*-structure of product was determined by the coupling constant of the two bridgehead hydrogens (**3a**, $J = 11.4$ Hz).

We next sought to explore the scope of the reaction (Table 2) using a wide range of oxiranes. Ring opening of alkyl-substituted oxiranes proceeded with good yields (Table 2). However, no reaction took place in the presence of cyclopentene and cyclooctene oxide as the oxirane sources due to the high strain energy of the product. Oxirane derived from cyclohexene gave excellent yield while cyclopentene oxide only afforded the product in moderate yield (Table 2). In the presence of alkyl-substituted oxiranes, the attack occurred exclusively at the terminal position, though styrene oxide gave benzylic-attacked product in high yield (Table 2). Isothiocyanates **4** were also examined and exhibited similar reactivity pattern to that observed with CS_2. In all cases, the corresponding 1,3-oxathiolane-2-imine was obtained in good yield together with 3–8 % of hydrolyzed isothiocyanate. These products could be easily removed due to their different solubility from **5** (Table 2).

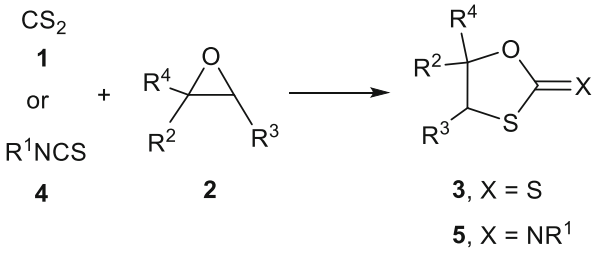
The reaction condition described above could also be extended to those with aziridines **6** (Table 3), providing corresponding heterocycles **7** or **8** in acceptable yields. However, aziridines **6** required longer reaction times to accomplish the transformation.

The structures of the products were confirmed by spectroscopic analyses. For example, the ^1H NMR spectrum of **3a** showed characteristic (AB)X spin system for the CH_2-CH H-atoms, together with a doublet for the methyl group. The ^{13}C NMR spectrum of **3a** exhibited 4 signals in agreement with the proposed structure. The characteristic signal at 227 ppm belongs to the C-S double bond.

Although the mechanistic details of the formation of the products are not known, a plausible rationalization is proposed in Scheme 1. It is conceivable that the reaction starts with the formation of intermediate **11**, followed by addition of oxirane to generate ring-opened intermediate **12**. Cyclization of this adduct leads to formation of the intermediate **13**, which is converted to **3a** by elimination of the conjugated base of $MeNO_2$. However, another possibility could involve the attack of **10** to heterocumulenes.

In conclusion, we have described an organocatalytic approach for the synthesis of functionalized 1,3-oxathiolanes and 1,3-thiazolidines. The reaction was completely regio-selective and in all cases only one regio-isomer was detected in NMR analyses. Electronic and steric variations of the substrates showed no appreciable change in the efficiency of the transformation. Several functional groups such as methyl methacrylate, alkoxy, phenoxy, allyl, and halide could be well tolerated. Using this procedure, a simple etheric extraction would suffice to isolate the pure product.

Table 2 Synthesis of functionalized 1,3-oxathiolanes



Entry	4	R^1	2	R^2, R^3, R^4	3[a] yield/%	5[b] yield/%
1	**4a**	Ph	**2a**	Me, H	**3a**, 95	**5a**, 91
2	**4a**	Ph	**2b**	Et, H, H	**3b**, 93	**5b**, 90
3	**4a**	Ph	**2c**	Ph, H, H	**3c**, 94[c]	**5c**, 92[c]
4	**4a**	Ph	**2d**	$(CH_3)_2CHOCH_2$, H, H	**3d**, 94	**5d**, 90
5	**4a**	Ph	**2e**	Ph, Ph, H (*cis*)	**3e**, 96	**5e**, 94
6	**4a**	Ph	**2f**	$PhOCH_2$, H	**3f**, 94	**5f**, 91
7	**4a**	Ph	**2g**	$CH_2CCH_3COOCH_2$, H, H	**3g**, 97	**5g**, 95
8	**4a**	Ph	**2h**	$CH_2CHCH_2OCH_2$, H, H	**3h**, 90	**5h**, 87
9	**4a**	Ph	**2i**	$ClCH_2$, H, H	**3i**, 86	**5i**, 82
10	**4a**	Ph	**2j**	C_3H_7, CH_3, H	**3j**, 94	**5j**, 92
11	**4a**	Ph	**2k**	$-(CH_2)_4-$, H	**3k**, 92	**5k**, 92
12	**4a**	Ph	**2l**	$-(CH_2)_5-$, H	**3l**, 56	**5l**, 53
13	**4b**	4-Me-C_6H_4	**2f**	$PhOCH_2$, H, H		**5m**, 92
14	**4c**	4-MeO-C_6H_4	**2d**	$(CH_3)_2CHOCH_2$, H, H		**5n**, 91
15	**4d**	$(CH_3)_2CH$	**2f**	$PhOCH_2$, H, H		**5o**, 86

[a] Reaction conditions: **1** (3.0 mmol), **2** (1.0 mmol), Et_3N (10 mol %), $MeNO_2$ (2 cm^3), 25 °C for 6 h

[b] Reaction conditions: **4** (1.0 mmol), **2** (1.0 mmol), Et_3N (10 mol %), $MeNO_2$ (2 cm^3), 25 °C for 6 h

Experimental

Epoxides, CS_2, nitromethane, bases, and solvents were obtained from Merck and were used without further purification. *N*-Tosylaziridines were prepared using the literature procedures [19]. M.p.: Electrothermal-9100 apparatus. IR Spectra: Shimadzu IR-460 spectrometer. ^1H and ^{13}C NMR spectra: Bruker DRX-500 AVANCE instrument; in $CDCl_3$ at 500.1 and 125.7 MHz, resp; δ in ppm, J in Hz. EI-MS (70 eV): Finnigan-MAT-8430 mass spectrometer. Elemental analyses (C, H, N) were performed with a Heraeus CHN-O-Rapid analyzer. The results agreed favorably with the calculated values.

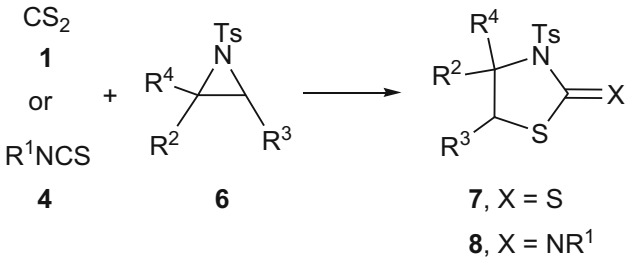
General procedure for the preparation of 3, 5, 7, and 8

To a stirred solution of heterocumulene (1–3 mmol) and strained heterocycle (1 mmol), 0.01 g Et_3N (10 mol %) in 3 cm^3 $MeNO_2$ was added. The mixture was stirred for 6–10 h at 25 °C. After completion of the reaction (monitored by TLC), 5 cm^3 of cold diethyl ether was added to the reaction mixture. Separation of etheric layer and removing of solvent under vacuo gave the pure title products. All the known compounds gave satisfactory spectroscopic values and are analog to spectroscopic data reported in literature [14, 16, 18].

5-Methyl-5-propyl-1,3-oxathiolane-2-thione (**3j**, $C_7H_{12}OS_2$)

The crude product was purified by cold etheric extraction affording 0.16 g (94 %) **3j**. Yellow oil; IR (KBr): $\bar{\nu}$ = 3038, 2981, 1626, 1541, 1347, 1336, 1108 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.95 (t, ^3J = 6.4 Hz, Me), 1.21 (s, Me), 1.29–1.38 (m, 2 CH_2), 3.35 (d, ^2J = 11.4 Hz, CH), 3.49 (d, ^2J = 11.4 Hz, CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 13.5 (CH_2), 14.2 (Me), 23.5 (Me), 41.1 (CH_2), 52.9 (CH_2), 84.3 (C), 228.2 (C) ppm; EI-MS (70 eV): *m*/*z* (%) = 176 (M^+, 5), 160 (22), 116 (45), 100 (63), 85 (100), 76 (78).

Table 3 Synthesis of functionalized 1,3-thiazolidines

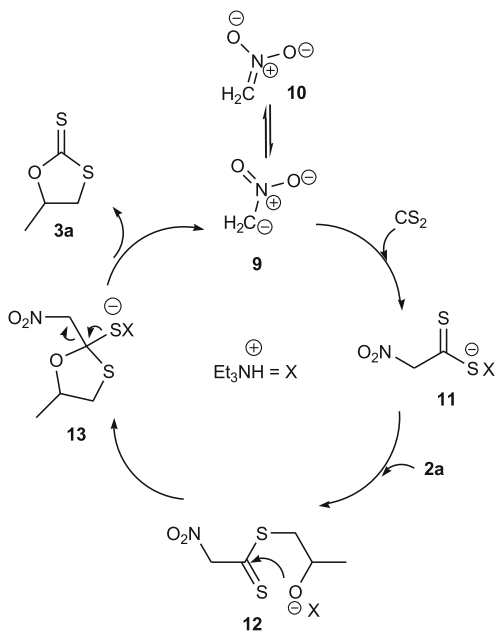


Entry	4	R^1	6	R^2, R^3, R^4	7[a] yield/%	8[b] yield/%
1	**4a**	Ph	**6a**	Ph, Ph, H	**7a**, 89	**8a**, 85
2	**4a**	Ph	**6b**	H, Ph, H	**7b**, 90	**8b**, 88
3	**4a**	Ph	**6c**	Bn, H, H	**7c**, 93[c]	**8c**, 89
4	**4a**	Ph	**6d**	C_4H_9, H, H	**7d**, 95	**8d**, 86
5	**4a**	Ph	**6e**	C_5H_{11}, CH_3, H	**7e**, 82	**8e**, 81
6	**4a**	Ph	**6f**	H, H, H	**7f**, 96	**8f**, 94
7	**4a**	Ph	**6g**	$TMSCH_2CH_2$, H, H	**7g**, 95	**8g**, 89
8	**4a**	Ph	**6h**	$BnOCH_2$, H, H	**7h**, 90	**8h**, 87
9	**4a**	Ph	**6i**	$-(CH_2)_4-$, H	**7i**, 86	**8i**, 82
10	**4a**	Ph	**6j**	$-(CH_2)_5-$, H	**7j**, 51	**8j**, 47
11	**4b**	4-Me-C_6H_4	**6k**	Bn, H, H		**8k**, 89
12	**4d**	$(CH_3)_2CH$	**6l**	Bn, H, H		**8l**, 75

[a] Reaction conditions: **1** (3 mmol), **6** (1.0 mmol), Et_3N (10 mol %), $MeNO_2$ (2 cm^3), 25 °C for 10 h

[b] Reaction conditions: **4** (1 mmol), **6** (1.0 mmol), Et_3N (10 mol %), $MeNO_2$ (2 cm^3), 25 °C for 10 h

Scheme 1



Hexahydro-3aH-cyclohepta[d][1,3]oxathiole-2-thione (**3l**, $C_8H_{12}OS_2$)

The crude product was purified by cold etheric extraction affording 0.10 g (56 %) **3l**. Yellow oil; IR (KBr): $\bar{\nu}$ = 3041, 2971, 1631, 1547, 1326, 1309, 1107 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.35–2.18 (m, 10H), 2.91–2.94 (m, CH), 4.08–4.11 (m, CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 23.2 (CH_2), 26.5 (CH), 30.1 (CH_2), 30.8 (CH_2), 32.6 (CH_2), 51.8 (CH), 82.1 (CH), 227.9 (C) ppm; EI-MS (70 eV): *m/z* (%) = 188 (M^+, 9), 112 (68), 96 (41), 76 (79) 54 (100).

N-(4,5-Diphenyl-1,3-oxathiolan-2-ylidene)benzenamine (**5e**, $C_{21}H_{17}NOS$)

The crude product was purified by cold etheric extraction affording 0.31 g (94 %) **5e**. Pale yellow solid; m.p.: 112-115 °C; IR (KBr): $\bar{\nu}$ = 3025, 2967, 1610, 1547, 1330, 1323, 1113 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 4.41 (s, CH), 5.76 (s, CH), 7.11–7.35 (m, 15 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 44.9 (CH), 70.1 (CH), 123.1 (2 CH), 127.3 (CH), 127.6 (CH), 128.1 (2 CH), 128.5 (2 CH), 128.7 (CH), 129.5 (2 CH), 129.8 (2 CH), 131.1 (2 CH), 135.6 (C), 137.5 (C), 148.9 (C), 162.5 (C) ppm;

EI-MS (70 eV): *m/z* (%) = 331 (M^+, 2), 196 (53), 177 (37), 119 (62), 77 (100).

N-(5-Methyl-5-propyl-1,3-oxathiolan-2-ylidene)benzenamine (**5j**, $C_{13}H_{17}NOS$)

The crude product was purified by cold etheric extraction affording 0.22 g (92 %) **5j**. Pale yellow oil; IR (KBr): $\bar{\nu}$ = 3038, 2970, 1617, 1548, 1321, 1310, 1108 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, ^3J = 6.1 Hz, Me), 1.24 (s, Me), 1.27–1.36 (m, 2 CH_2), 3.32 (d, ^2J = 11.0 Hz, CH), 3.45 (d, ^2J = 11.0 Hz, CH), 6.91 (d, ^3J = 6.8 Hz, 2 CH), 7.11 (t, ^3J = 6.5 Hz, CH), 7.28 (t, ^3J = 6.4 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 13.2 (CH_2), 14.9 (Me), 24.2 (Me), 39.6 (CH_2), 43.2 (CH_2), 73.9 (C), 121.7 (2 CH), 126.1 (CH), 129.6 (2 CH), 147.3 (C), 164.8 (C) ppm; EI-MS (70 eV): *m/z* (%) = 235 (M^+, 6), 119 (58), 117 (36), 85 (63), 77 (100).

N-[5-(Phenoxymethyl)-1,3-oxathiolan-2-ylidene]propan-2-amine (**5p**, $C_{13}H_{17}NO_2S$)

The crude product was purified by cold etheric extraction affording 0.22 g (86 %) **5p**. Pale yellow oil; IR (KBr): $\bar{\nu}$ = 3025, 2970, 1644, 1548, 1340, 1314, 1109 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.13 (d, ^3J = 6.7 Hz, 2 Me), 3.11–3.15 (m, CH), 3.26-3.32 (m, CH_2), 4.31–4.35 (m, CH_2), 4.93-4.98 (m, CH), 6.89 (d, ^3J = 6.7 Hz, 2 CH), 7.05 (t, ^3J = 6.3 Hz, CH), 7.17 (d, ^3J = 6.8 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 20.1 (2 Me), 36.2 (CH_2), 48.9 (CH), 69.3 (CH_2), 81.3 (CH), 114.1 (2 CH), 121.3 (CH), 129.8 (2 CH), 159.8 (C), 167.1 (C) ppm; EI-MS (70 eV): *m/z* (%) = 251 (M^+, 7), 134 (45), 118 (52), 77 (100), 58 (69).

4,5-Diphenyl-3-tosylthiazolidine-2-thione (**7a**, $C_{22}H_{19}NO_2S_3$)

The crude product was purified by cold etheric extraction affording 0.38 g (89 %) **7a**. Pale yellow solid; m.p.: 113–115 °C; IR (KBr): $\bar{\nu}$ = 3035, 2978, 1637, 1548, 1341, 1308, 1111 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, Me), 4.42 (s, CH), 5.28 (s, CH), 7.08–7.28 (m, 10 CH), 7.33 (d, ^3J = 6.5 Hz, 2 CH), 7.85 (d, ^3J = 6.7 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 23.5 (Me), 54.3 (CH), 68.7 (CH), 126.1 (CH), 126.8 (CH), 127.4 (2 CH), 127.8 (2 CH), 128.1 (2 CH), 128.4 (2 CH), 129.1 (2 CH), 130.0 (2 CH), 135.2 (C), 140.2 (C), 141.7 (C), 145.7 (C), 201.7 (C) ppm; EI-MS (70 eV): *m/z* (%) = 425 (M^+, 5), 270 (26), 170 (69), 155 (52), 91 (42), 77 (100).

4-Methyl-4-pentyl-3-tosylthiazolidine-2-thione (**7e**, $C_{16}H_{23}NO_2S_3$)

The crude product was purified by cold etheric extraction affording 0.29 g (82 %) **7e**. Pale yellow oil; IR (KBr): $\bar{\nu}$ = 3037, 2967, 1638, 1551, 1344, 1312, 1108 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.09 (t, ^3J = 6.9 Hz, Me), 1.28 (s, Me), 1.41–1.63 (m, 3 CH_2), 1.81 (t, ^3J = 6.7 Hz, CH_2), 2.31 (s, Me), 3.41 (d, ^2J = 11.3 Hz, CH), 3.54 (d, ^2J = 11.3 Hz, CH), 7.33 (t, ^3J = 6.9 Hz, 2 CH), 7.82 (d, ^3J = 6.5 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 15.1 (Me), 21.3 (Me), 22.4 (CH_2), 24.0 (CH_2), 25.6 (Me), 35.7 (CH_2), 37.4 (CH_2), 56.1 (CH_2), 84.1 (C), 126.9 (2 CH), 131.4 (2 CH), 135.8 (C), 142.1 (C), 202.0 (C) ppm; EI-MS (70 eV): *m/z* (%) = 357 (M^+, 10), 202 (21), 170 (69), 155 (57), 113 (100), 77 (43).

3-Tosylthiazolidine-2-thione (**7f**, $C_{10}H_{11}NO_2S_3$)

The crude product was purified by cold etheric extraction affording 0.26 g (96 %) **7f**. Pale yellow oily solid; IR (KBr): $\bar{\nu}$ = 3025, 2961, 1642, 1553, 1344, 1310, 1109 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.26 (s, Me), 3.46 (t, ^3J = 7.1 Hz, CH_2), 4.60 (t, ^3J = 7.0 Hz, CH_2), 7.31 (d, ^3J = 6.7 Hz, 2 CH), 7.81 (d, ^3J = 6.2 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 24.4 (Me), 36.2 (CH_2), 60.1 (CH_2), 127.0 (2 CH), 130.0 (2 CH), 135.9 (C), 141.0 (C), 201.1 (C) ppm; EI-MS (70 eV): *m/z* (%) = 273 (M^+, 1), 197 (36), 170 (100), 155 (69), 118 (41), 91 (58).

4-[2-(Trimethylsilyl)ethyl]-3-tosylthiazolidine-2-thione (**7g**, $C_{15}H_{23}NO_2S_3Si$)

The crude product was purified by cold etheric extraction affording 0.35 g (95 %) **7g**. Pale yellow solid; m.p.: 98-100 °C; IR (KBr): $\bar{\nu}$ = 3051, 2973, 1644, 1551, 1346, 1312, 1112 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.04 (s, 3 Me), 0.70 (t, ^3J = 6.8 Hz, CH_2), 1.72–1.76 (m, CH_2), 2.35 (s, Me), 3.46–3.49 (m, CH_2), 5.12–5.16 (m, CH), 7.32 (d, ^3J = 6.5 Hz, 2 CH), 7.81 (d, ^3J = 6.7 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 0.3 (3 Me), 13.4 (CH_2), 24.4 (Me), 27.0 (CH_2), 41.2 (CH_2), 65.1 (CH), 126.1 (2 CH), 130.3 (2 CH), 136.8 (C), 142.6 (C), 198.6 (C) ppm; EI-MS (70 eV): *m/z* (%) = 373 (M^+, 5), 218 (22), 170 (100), 155 (67), 91 (43).

4-[(Benzyloxy)methyl]-3-tosylthiazolidine-2-thione (**7h**, $C_{18}H_{19}NO_3S_3$)

The crude product was purified by cold etheric extraction affording 0.35 g (90 %) **7h**. Pale yellow solid; m.p.: 119–121 °C; IR (KBr): $\bar{\nu}$ = 3051, 2972, 1647, 1551, 1342, 1308, 1106 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.31 (s, Me), 3.26–3.38 (m, CH_2), 4.48–4.71 (m, 2 CH_2), 5.31–5.35 (m, CH), 7.11–7.25 (m, 5 CH), 7.32 (d, ^3J = 7.1 Hz, 2 CH), 7.81 (d, ^3J = 6.7 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 24.1 (Me), 36.9 (CH_2), 68.3 (CH), 73.7 (CH_2), 80.4 (CH_2), 126.2 (2 CH), 127.0 (CH), 128.3 (2 CH), 129.9 (2 CH), 131.4 (2 CH), 135.8 (C), 136.3 (C), 142.1 (C), 201.1 (C) ppm; EI-MS (70 eV): *m/z* (%) = 393 (M^+, 2), 238 (37), 170 (72), 155 (69), 91 (100), 77 (59).

N-(4,5-Diphenyl-3-tosylthiazolidin-2-ylidene)benzenamine (**8a**, $C_{28}H_{24}N_2O_2S_2$)

The crude product was purified by cold etheric extraction affording 0.41 g (85 %) **8a**. Pale yellow solid; m.p.: 134–

136 °C; IR (KBr): $\bar{\nu}$ = 3046, 2981, 1623, 1548, 1338, 1305, 1109 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.32 (s, Me), 4.62 (s, CH), 5.38 (s, CH), 7.08-7.31 (m, 15 CH), 7.35 (d, ^3J = 6.7 Hz, 2 CH), 7.83 (d, ^3J = 6.9 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 24.0 (Me), 45.1 (CH), 69.6 (CH), 121.2 (2 CH), 126.0 (CH), 127.1 (2 CH), 128.0 (2 CH), 128.2 (CH), 128.5 (CH), 128.7 (2 CH), 129.0 (2 CH), 129.5 (2 CH), 130.3 (2 CH), 132.5 (2 CH), 135.2 (C), 140.8 (C), 142.1 (C), 143.1 (C), 149.4 (C), 164.2 (C) ppm; EI-MS (70 eV): *m/z* (%) = 484 (M^+, 2), 330 (42), 329 (11), 170 (72), 155 (52), 77 (100).

N-(4-Benzyl-3-tosylthiazolidin-2-ylidene)benzenamine (**8c**, $C_{23}H_{22}N_2O_2S_2$)

The crude product was purified by cold etheric extraction affording 0.38 g (89 %) **8c**. Pale yellow solid; m.p.: 100-102 °C; IR (KBr): $\bar{\nu}$ = 3046, 2978, 1644, 1542, 1346, 1312, 1110 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.34 (s, Me), 2.79–2.85 (m, 2 CH), 3.41–3.47 (m, 2 CH), 5.13–5.16 (m, CH), 7.08–7.29 (m, 10 CH), 7.31 (d, ^3J = 6.8 Hz, 2 CH), 7.83 (d, ^3J = 6.4 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 24.3 (Me), 35.9 (CH_2), 43.7 (CH_2), 67.9 (CH), 121.8 (2 CH), 125.3 (CH), 126.7 (2 CH), 127.1 (CH), 127.6 (2 CH), 128.0 (2 CH), 129.8 (2 CH), 131.4 (2 CH), 135.0 (C), 136.3 (C), 142.3 (C), 149.0 (C), 164.7 (C) ppm; EI-MS (70 eV): *m/z* (%) = 422 (M^+, 5), 267 (18), 155 (69), 91 (100), 77 (58).

N-(3-Tosylthiazolidin-2-ylidene)benzenamine (**8f**, $C_{16}H_{16}N_2O_2S_2$)

The crude product was purified by cold etheric extraction affording 0.31 g (94 %) **8f**. Pale yellow solid; m.p.: 86–88 °C; IR (KBr): $\bar{\nu}$ = 3037, 2977, 1652, 1549, 1342, 1311, 1110 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.24 (s, Me), 3.49 (t, ^3J = 6.7 Hz, CH_2), 4.72 (t, ^3J = 6.5 Hz, CH_2), 7.10 (d, ^3J = 6.9 Hz, 2 CH), 7.18–7.29 (m, 3 CH), 7.32 (d, ^3J = 6.5 Hz, 2 CH), 7.81 (d, ^3J = 6.9 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 24.1 (Me), 34.9 (CH_2), 59.8 (CH_2), 121.1 (2 CH), 126.0 (CH), 128.2 (2 CH), 130.2 (2 CH), 131.7 (2 CH), 135.8 (C), 142.2 (C), 149.5 (C), 164.9 (C) ppm; EI-MS (70 eV): *m/z* (%) = 207 (M^+, 2), 170 (61), 155 (48), 91 (39), 77 (100).

*N-[4-[2-(Trimethylsilyl)ethyl]-3-tosylthiazolidin-2-ylidene]-benzenamine (**8g**, $C_{21}H_{28}N_2O_2S_2Si$)*

The crude product was purified by cold etheric extraction affording 0.38 g (89 %) **8g**. Pale yellow solid; m.p.: 116–118 °C; IR (KBr): $\bar{\nu}$ = 3048, 2970, 1648, 1544, 1343, 1311, 1116 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.08 (s, 3 Me), 0.79 (t, ^3J = 7.1 Hz, CH_2), 1.70–1.74 (m, CH_2), 2.32 (s, Me), 3.39–3.45 (m, CH_2), 5.08–5.12 (m, CH), 7.13 (d, ^3J = 6.9 Hz, CH), 7.18 (t, ^3J = 7.0 Hz, 2 CH), 7.25 (d, ^3J = 6.4 Hz, 2 CH), 7.34 (d, ^3J = 6.8 Hz, 2 CH), 7.83 (d, ^3J = 6.5 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 0.5 (3 Me), 10.8 (CH_2), 24.1 (Me), 29.3 (CH_2), 36.6 (CH_2), 62.3 (CH), 120.3 (2 CH), 126.7 (CH), 128.0 (2 CH), 130.6 (2 CH), 131.4 (2 CH), 135.2 (C), 141.4 (C), 149.48 (C), 165.8 (C) ppm; EI-MS (70 eV): *m/z* (%) = 432 (M^+, 2), 277 (21), 170 (45), 155 (78), 77 (100).

N-[4-[(Benzyloxy)methyl]-3-tosylthiazolidin-2-ylidene]-benzenamine (**8h**, $C_{24}H_{24}N_2O_3S_2$)

The crude product was purified by cold etheric extraction affording 0.39 g (87 %) **8h**. Pale yellow solid; m.p.: 132–134 °C; IR (KBr): $\bar{\nu}$ = 3052, 2972, 1652, 1551, 1344, 1310, 1109 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.34 (s, Me), 3.32–3.48 (m, CH_2), 4.51–4.79 (m, 2 CH_2), 5.26–5.29 (m, CH), 7.11–7.29 (m, 10 CH), 7.31 (d, ^3J = 6.7 Hz, 2 CH), 7.82 (d, ^3J = 6.3 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 24.2 (Me), 34.5 (CH_2), 69.9 (CH), 71.2 (CH_2), 81.1 (CH_2), 121.3 (2 CH), 127.1 (CH), 127.5 (2 CH), 128.1 (CH), 129.1 (2 CH), 129.6 (2 CH), 130.1 (2 CH), 131.4 (2 CH), 135.0 (C), 137.4 (C), 143.4 (C), 149.9 (C), 165.7 (C) ppm; EI-MS (70 eV): *m/z* (%) = 452 (M^+, 2), 297 (18), 170 (70), 155 (51), 91 (100), 77 (62).

N-(4-Benzyl-3-tosylthiazolidin-2-ylidene)-4-methylbenzenamine (**8k**, $C_{24}H_{24}N_2O_2S_2$)

The crude product was purified by cold etheric extraction affording 0.39 g (89 %) **8k**. Pale yellow solid; m.p.: 101–103 °C; IR (KBr): $\bar{\nu}$ = 3046, 2977, 1652, 1550, 1343, 1310, 1107 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.29 (s, Me), 2.32 (s, Me), 2.73–2.80 (m, 2 CH), 3.35–3.43 (m, 2 CH), 5.15–5.19 (m, CH), 7.10 (d, ^3J = 6.7 Hz, 2 CH), 7.15–7.28 (m, 7 CH), 7.33 (d, ^3J = 6.5 Hz, 2 CH), 7.85 (d, ^3J = 6.9 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 23.2 (Me), 24.5 (Me), 36.5 (CH_2), 40.3 (CH_2), 68.1 (CH), 123.1 (2 CH), 126.0 (CH), 127.1 (2 CH), 127.5 (2 CH), 128.0 (2 CH), 130.6 (2 CH), 132.1 (2 CH), 135.1 (C), 135.7 (C), 139.2 (C), 141.6 (C), 148.3 (C), 165.2 (C) ppm; EI-MS (70 eV): *m/z* (%) = 436 (M^+, 2), 128 (23), 170 (38), 155 (45), 91 (100), 77 (63).

N-(4-Benzyl-3-tosylthiazolidin-2-ylidene)propan-2-amine (**8l**, $C_{20}H_{24}N_2O_2S_2$)

The crude product was purified by cold etheric extraction affording 0.29 g (75 %) **8l**. Pale yellow solid; m.p.: 67–69 °C; IR (KBr): $\bar{\nu}$ = 3046, 2977, 1652, 1544, 1349, 1311, 1108 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.15 (d, ^3J = 7.0 Hz, 2 Me), 2.32 (s, Me), 2.78–2.89 (m, 2 CH), 3.20–3.41 (m, 3 CH), 5.11–5.14 (m, CH), 7.07 (d, ^3J = 6.4 Hz, 2 CH), 7.19 (t, ^3J = 7.1 Hz, CH), 7.25 (d, ^3J = 6.7 Hz, 2 CH), 7.31 (d, ^3J = 6.5 Hz, 2 CH), 7.82 (d, ^3J = 6.7 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 21.1 (2 Me), 24.2 (Me), 37.1 (CH_2), 41.5 (CH_2), 49.2 (CH), 67.3 (CH), 125.2 (CH), 126.7 (2 CH), 127.3 (2 CH), 128.1 (2 CH), 130.3 (2 CH), 135.8 (C), 137.5 (C), 142.1

(C), 164.7 (C) ppm; EI-MS (70 eV): *m*/*z* (%) = 388 (M^+, 1), 233 (31), 170 (58), 155 (46), 91 (100), 77 (62).

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