Organo-catalytic synthesis of 1,3-thiazole derivatives

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An efficient synthesis of 1,3-thiazolidine derivatives has been achieved in which 2-pyridinecarboxaldehyde oxime was employed as a base catalyst to effect cyclisation between aziridines and CS_2 in DMF at 40 °C. A similar reaction between aziridines and thiocyanates yielded 1,3-thiazoline-2-imine derivatives

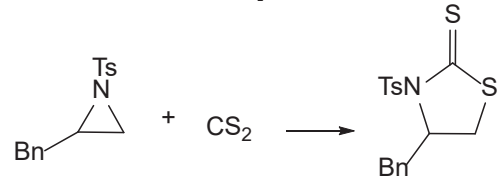
Keywords: 1,3-thiazoline-2-imine, thyiocyanates, aziridine, carbon disulphide, 1,3-thiazolidine

Aziridines (ethylene imines) are important building blocks due to their high potential for applications in the fields of organic synthesis. They allow for convenient access to amines,[1] amino alcohols,[2] diamines,[3] and other useful amine derivatives.[4–6] Moreover, many transformations of aziridines with heterallenes to form the corresponding N-containing heterocycles have been well documented.[7–9] Most of these ring-opening reactions rely on a catalyst to give the desired heterocyclic compounds in good yields.[10–13] Hou and coworkers have utilised organophosphines to promote the cyclisation reaction between three-membered heterocycles and heteroallenes.[14] Additionally, nitromethane has also been employed to mediate ring opening of three-membered heterocycles in reaction with heteroallenes at ambient conditions.[15] However, we were especially interested in a report by Yavari and coworker in which a useful organo-catalytic route to form 1,3-oxathiolene-2-imines from epoxides and thiocyanates used 2-pyridinecarboxaldehyde oxime as the basic catalyst,[16] as we planned to carry out a study of the analogous reaction between thiocyanates and aziridine using the same catalyst. We here report on that reaction and, as a simpler variant, the reaction between carbon disulphide and aziridine to form two types of 1,3-thiazole derivatives.

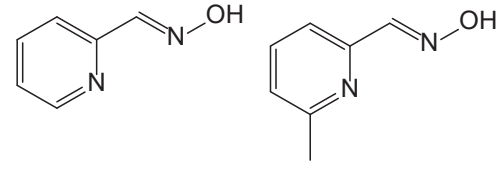
Results and discussion

The reaction was initially examined using 2-benzyl-1-tosylaziridine (**1a**) and CS_2 (**2**) in the presence of MeONa (10% mol). Stirring in THF at 40 °C for 4 h afforded 4-benzyl-3-tosylthiazolidine-2-thione (**3a**) in 42% yield (Table 1, entry 1). To optimise the reaction conditions a variety of solvents and catalysts were examined and the results are shown in Table 1. Among the solvents examined, DMF was superior to other solvents (entry 12). Reaction in an apolar solvent like toluene led to a very low conversion (entry 7). Reaction conducted in a protic solvent gave the desired product in a moderate yield, most likely due to the lower nucleophilicity of ethoxide ion in a protic solvent (entry 11). Ethers and a chlorinated solvent were not efficient in this transformation (entries 8, 9, and 10). Polar-aprotic solvents improved the yield appreciably, an outcome we attribute to the greater solubility power towards polar compounds (entries 12 and 13). Reaction conducted in H_2O resulted in a very low conversion (entry 14). No reaction took place in the absence of the catalyst even at higher temperatures (not shown in Table 1). Tetrabutylammonium methoxide achieved a higher conversion, most likely due to better solubility in organic solvent than that of MeONa (entry 4). Catalyst screening showed that 2-pyridinecarboxaldehyde oxime **L1** afforded the desired product in excellent 94% yield (entry 12), but the 6-methyl analogue **L2** afforded the desired product in a lower yield of 76% (entry 5). It could be deduced that the steric issue on catalyst structure influences the reaction progress. Pyridine *N*-oxide failed to promote the desired reaction and resulted in a complicated mixture (entry 2). It is worth mentioning that no reaction took place at ambient conditions even for longer reaction times.

Table 1 Optimisation of the reaction conditions (catalyst, solvent) for the preparation of 4-benzyl-3-tosyl-1,3-thiazolidine-2-thione **3a** from 2-benzyl-1-tosylaziridine **1a** and CS_2 **2a**[a]



1a **2** **3a**



L1 **L2**

Entry	Catalyst	Solvent	Yield/%
1	MeONa	THF	42
2	pyridine N-oxide	DMF	–
3	MeONa	DMF	80
4	Bu_4NOMe	DMF	89
5	L_2	DMF	76
6	L_1	CS_2	74
7	L_1	toluene	5
8	L_1	dioxane	34
9	L_1	THF	40
10	L_1	CH_2Cl_2	25
11	L_1	EtOH	51
12	L_1	DMF	94
13	L_1	DMSO	89
14	L_1	H_2O	13

[a]Reaction conditions: **1a** (1.0 mmol), **2** (2.0 mmol), catalyst (20 mol%), and solvent (3 mL) at 40 °C for 4 h.

The scope of this methodology was then evaluated using substituted aziridines and the results are shown in Table 2. Alkyl substituted aziridines **1b**–**e** gave exclusively the products of terminal-attack (entries 2–5). The difference in reactivity of aryl-substituted aziridines was reflected in the reaction of 2-phenyl-1-tosylaziridine **1f**, where the attack occurred exclusively at the benzylic position due to the influence of

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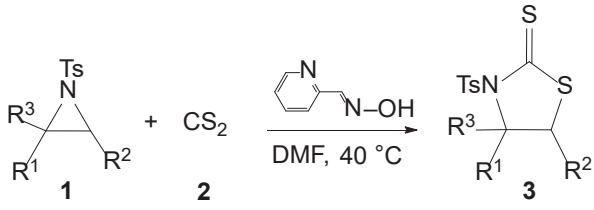
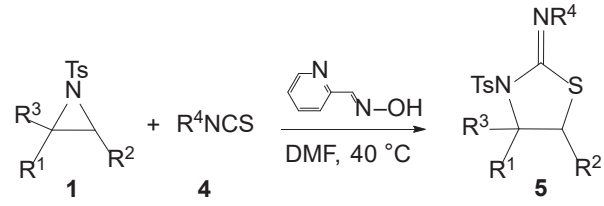
Table 2 Yields of a series of 3-tosyl-1,3-thiazolidine-2-thione derivatives **3a–k** (R^1, R^2, R^3 = various) prepared from mono- and disubstituted 1-tosylaziridines **1a–k** (R^1, R^2, R^3 = various) and CS_2 **2a**[a]



Entry	Aziridine	R^1,R^2, R^3	Product, Yield/%
1	**1a**	Bn, H, H	**3a**, 94
2	**1b**	*n*-C_3H_7, H, Me	**3b**, 89
3	**1c**	*n*-C_4H_9, H, H	**3c**, 85
4	**1d**	*n*-C_5H_{11}, CH_3, H	**3d**, 78
5	**1e**	*n*-C_6H_{13}, H, H	**3e**, 87
6	**1f**	H, Ph, H	**3f**, 98
7	**1g**	Me, Ph, H	**3g**, 87
8	**1h**	Ph, CO_2Me, H	**3h**, 89
9	**1i**	-$(CH_2)_4$-,H	**3i**, 98
10	**1j**	-$(CH_2)_5$-,H	**3j**, 52
11	**1k**	*n*-C_3H_7, *n*-C_3H_7, H	**3k**, 94

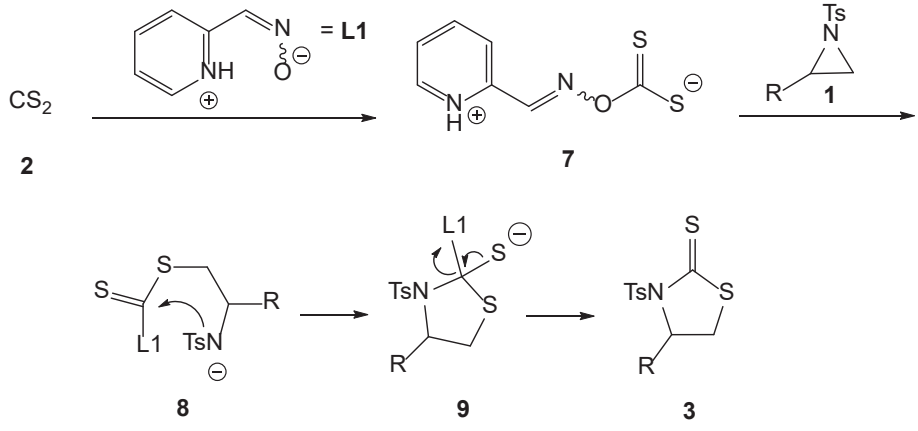
[a]Reaction conditions: **1** (1.0 mmol), **2** (2.0 mmol), L_1 (20 mol%), in DMF (3 mL) at 40 °C for 4 h.

Table 3 Yields of a series of 3-tosyl-1,3-thiazoline-2-imine derivatives **5a–e** (R^1, R^2, R^3, R^4 = various) prepared from mono- and disubstituted 1-tosylaziridines **1a**,**b**,**f**,**i** (R^1, R^2, R^3 = various) and either of two thiocyanates 4 (R^4 = Ph, *i*-Pr)



Entry	Aziridine	Isothiocyanate	R^4	R^1,R^2, R^3	Product, Yield/%
1	**1a**	**4a**	Ph	Bn, H, H	**5a**, 91
2	**1a**	**4b**	*i*-Pr	Bn, H, H	**5b**, 87
3	**1b**	**4b**	*i*-Pr	*n*-C_3H_7, H, Me	**5c**, 84
4	**1f**	**4b**	*i*-Pr	H, Ph, H	**5d'**, 90
5	**1i**	**4b**	*i*-Pr	-$(CH_2)_4$-,H	**5e**, 86

[a]Reaction conditions: **1** (1.0 mmol), **4** (1.0 mmol), L_1 (20 mol%), and DMF (3 mL) at 40 °C for 7.



Scheme 1 Plausible mechanism for the formation of 3.

electronic and steric effects (entry 6). The *gem*-disubstituted aziridine **1b** gave the desired product in good yield (entry 2). Among the aziridines derived from cycloalkenes **1i**,**j**, only the cyclohexene derivative afforded the desired product in a good yield (entry 9). The regioselectivity of the reaction is in accordance with that of aziridines with other nucleophiles reported in the literature.[17–19]

To extend the scope of this transformation, isothiocyanates **4** were also examined and exhibited a similar reactivity pattern to that observed with CS_2, as shown in Table 3. Good yields of 1,3-thiazoline-2-imines were obtained from both aryl **4a** (entry 1) and alkyl isothiocyanates **4b** (entries 2–5). However, a longer reaction time (7 h) was required to accomplish the transformation. No product derived from the hydrolysis of isothiocyanate was detected in NMR analyses.

The structures of **3a**–**k** and **5a**–**e** were confirmed by spectroscopic analyses. For example, the ^{1}H NMR spectrum of **3a** showed a characteristic (AB)X spin system for the CH_2–CH group, together with a singlet for the methyl group. The ^{13}C NMR spectrum of **3a** exhibited 17 signals in agreement with the proposed structure. The mass spectrum of **3a** displayed the molecular ion peak at *m*/*z* 363. The ^{1}H NMR spectrum of **5a** also showed a characteristic (AB)X spin system for the CH_2–CH group, together with a singlet for the methyl group. The ^{13}C NMR spectrum of **5a** exhibited 23 signals in agreement with the proposed structure. The mass spectrum of **5a** displayed the molecular ion peak at *m*/*z* 422.

Although the mechanistic details of the formation of compounds **3** are not known, a plausible rationalisation is proposed in Scheme 1. Note that no reaction took place using 2-pyridinecarboxaldehyde oxime ethyl ether and benzaldehyde oxime even for longer reaction times. These results suggest that the reaction starts presumably with the attack of **L1** upon CS_2 (**2**) to give **7**, which adds to aziridine **1** to generate **8**. Cyclisation of this intermediate leads to **9** which affords **3** by elimination of **L1**.

Conclusion

We have developed a facile organo-catalytic approach for the synthesis of 1,3-thiazole derivatives. The reaction is completely regioselective as shown by NMR analyses. This methodology did not suffer from the limitations of previous reports such as costly catalyst,[14] extra dry solvent,[14] strong base,[16] and low yield. Electronic and steric variations of the substrates showed no appreciable change in the efficiency of the transformation.

Using this procedure, a simple ether extraction is used to isolate the pure product.

Experimental

All chemicals used in this work except the aziridines were purchased from Merck and were used without further purification. We prepared *N*-tosylaziridines using the literature procedures.[20] Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyser. Mass spectra were recorded on a Finnigan-MAT 8430 spectrometer operating at an ionisation potential of 70 eV. IR spectra were measured on a Shimadzu IR-460 spectrometer (the samples were dissolved in $CHCl_3$). ^{1}H NMR and ^{13}C NMR spectra were measured with a Bruker DRX-500 Avance spectrometer at 500.1 and 125.8 MHz, respectively. NMR spectra were obtained for solutions in $CDCl_3$ using TMS as the internal standard. Chemical shifts (δ) are given in ppm and coupling constants (*J*) are given in Hz.

Synthesis of compounds **4***; general procedure*

A mixture of 2-pyridinecarboxaldehyde oxime (20 mol%, 24 mg) and CS_2 or a thicyanate (1–2 mmol) in DMF (3 mL) was heated to 40 °C. Aziridine (1 mmol) was then added to the resulting mixture in one portion. The reaction mixture was then stirred for 4–7 h at 40 °C until the substrate disappeared. Afterwards, the mixture was poured in H_2O (5 mL) and the pH was adjusted to 3 by addition of concentrated HCl. The mixture was extracted with EtOAc (3 × 6 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give crude products. If solid, the crude product was further purified by recrystallisation from ether. The catalyst could be recovered for another run by recrystallisation from EtOH–CH_2Cl_2.

4-Benzyl-3-tosylthiazolidine-2-thione (**3a**)

The crude product was purified by recrystallisation from ether affording 0.35 g (94%) **3a**. M.p. 86–88.5 °C; IR: ν 3017, 2987, 1629, 1589, 1465, 1248, 1309, 1148 cm^{-1}; ^{1}H NMR: δ 2.38 (s, Me), 2.92 (m, CH), 3.10 (dd, ^2J = 6.9 Hz, ^3J = 7.2 Hz, CH), 3.30 (dd, ^2J = 7.1 Hz, ^3J = 4.6 Hz, CH), 3.45 (dd, ^2J = 7.1 Hz, ^3J = 12.1 Hz, CH), 4.93–4.99 (m, CH), 7.11 (t, ^3J = 6.0 Hz, CH), 7.17 (d, ^3J = 6.8 Hz, 2 CH), 7.24–7.37 (m, 4 CH), 7.82 (d, ^3J = 7.0 Hz, 2 CH); ^{13}C NMR: δ 23.1 (Me), 34.9 (CH_2), 39.4 (CH_2), 67.8 (CH), 127.0 (CH), 128.9 (2 CH), 129.2 (2 CH), 129.5 (2 CH), 130.1 (2 CH), 135.6 (C), 138.9 (C), 143.6 (C), 198.2 (C); EI-MS (70 eV): *m*/*z* (%) 363 (M$^+$, 3), 171 (63), 155 (34), 91 (100), 77 (52), 43 (44), 34 (18). Anal. calcd for $C_{17}H_{17}NO_2S_3$ (363.52): C, 56.17, H, 4.71; N, 3.85, S, 26.46; found: C, 56.43, H, 4.93; N, 3.95, S, 26.43%.

4-Methyl-4-propyl-3-tosylthiazolidine-2-thione (**3b**)

The crude product was purified by recrystallisation from ether affording 0.29 g (89%) **3b**. Yellow oil; IR: ν 2983, 2970, 1634, 1594, 1473, 1236, 1324, 1132 cm^{-1}; ^{1}H NMR: δ 0.96 (t, ^3J = 6.4 Hz, Me), 1.28 (s, Me), 1.32–1.49 (m, CH_2CH_2), 2.36 (s, Me), 3.31–3.46 (m, CH_2), 7.43 (d, ^3J = 6.9 Hz, 2 CH), 7.82 (d, ^3J = 6.7 Hz, 2 CH); ^{13}C NMR: δ 15.8 (Me), 16.0 (CH_2), 20.1 (Me), 23.7 (Me), 40.4 (CH_2), 45.6 (CH_2), 78.2 (C), 129.6 (2 CH), 130.5 (2 CH), 134.6 (C), 143.8 (C), 197.9 (C); EI-MS (70 eV): *m*/*z* (%) 329 (M$^+$, 2), 253 (28), 171 (41), 131 (78), 91 (42), 98 (100), 43 (47). Anal. calcd for $C_{14}H_{19}NO_2S_3$ (329.50): C, 51.03, H, 5.81; N, 4.25, S, 29.19; found: C, 51.14, H, 5.97; N, 4.42, S, 29.36%.

4-Butyl-3-tosylthiazolidine-2-thione (**3c**)

The crude product was purified by recrystallisation from ether affording 0.28 g (85%) **3c**. M.p. 72–73 °C; IR: ν 2980, 2954, 1648, 1590, 1463, 1245, 1320, 1122 cm^{-1}; ^{1}H NMR: δ 0.98 (t, ^3J = 6.4 Hz, Me), 1.39–1.50 (m, CH_2CH_2), 1.85–1.92 (m, CH_2), 2.34 (s, Me), 3.26 (dd, ^2J = 7.3 Hz, ^3J = 6.7 Hz, CH), 3.37 (dd, ^2J = 6.3 Hz, ^3J = 11.7 Hz, CH), 4.87 (m, CH), 7.40 (d, ^3J = 6.9 Hz, 2 CH), 7.81 (d, ^3J = 6.7 Hz, 2 CH); ^{13}C NMR: δ 15.6 (Me), 22.0 (CH_2), 23.5 (Me), 28.4 (CH_2), 30.0 (CH_2), 34.2 (CH_2), 78.0 (CH_2), 128.2 (2 CH), 130.3 (2 CH), 136.0 (C), 142.9 (C), 198.2 (C); EI-MS (70 eV): *m*/*z* (%) 329 (M$^+$, 6), 171 (34), 155 (78), 133 (57), 99 (100), 43 (40). Anal. calcd for $C_{14}H_{19}NO_2S_3$ (329.50): C, 51.03, H, 5.81; N, 4.25, S, 29.19; found: C, 51.18, H, 5.97; N, 4.38, S, 29.22%.

5-Methyl-4-pentyl-3-tosylthiazolidine-2-thione (**3d**)

The crude product was purified by washing with cold ether affording 0.28 g (78%) **3d**. Yellow oil; IR: ν 2980, 2954, 1648, 1590, 1463, 1325, 1244, 1120 cm^{-1}; ^{1}H NMR: δ 0.94 (t, ^3J = 6.8 Hz, Me), 1.32–1.47 (m, 3 CH_2), 1.53 (d, ^3J = 6.5 Hz, Me), 1.78–1.82 (m, CH_2), 2.34 (s, Me), 3.79–3.84 (m, CH), 4.84–4.88 (m, CH), 7.41 (d, ^3J = 6.9 Hz, 2 CH), 7.84 (d, ^3J = 6.7 Hz, 2 CH); ^{13}C NMR: δ 13.2 (Me), 15.0 (Me), 19.5 (CH_2), 20.4 (CH_2), 23.4 (Me), 28.2 (CH_2), 33.5 (CH_2), 51.0 (CH), 68.3 (CH_2), 128.3 (2 CH), 130.7 (2 CH), 135.2 (C), 143.4 (C), 197.5 (C); EI-MS (70 eV): *m*/*z* (%) 357 (M$^+$, 1), 171 (43), 155 (100), 112 (73), 91 (61), 43 (31). Anal. calcd for $C_{16}H_{23}NO_2S_3$ (357.55): C, 53.75, H, 6.48; N, 3.92, S, 26.90; found: C, 53.89, H, 6.64; N, 4.11, S, 26.93%.

4-Hexyl-3-tosylthiazolidine-2-thione (**3e**)

The crude product was purified by re-crystallisation from ether affording 0.31 g (87%) **3e**. M.p. 77–80 °C; IR: ν 3023, 2984, 2963, 1652, 1585, 1457, 1322, 1278, 1117 cm^{-1}; ^{1}H NMR: δ 0.93 (t, ^3J = 6.4 Hz, Me), 1.30–1.45 (m, 4 CH_2), 1.83–1.86 (m, CH_2), 2.37 (s, Me), 3.22–3.36 (m, CH_2), 4.91–4.94 (m, CH), 7.40 (d, ^3J = 6.6 Hz, 2 CH), 7.82 (d, ^3J = 6.9 Hz, 2 CH); ^{13}C NMR: δ 13.6 (Me), 21.4 (CH_2), 22.7 (CH_2), 23.5 (Me), 29.2 (CH_2), 31.1 (CH_2), 33.8 (CH_2), 36.1 (CH_2), 70.1 (CH), 128.9 (2 CH), 130.2 (2 CH), 135.6 (C), 143.2 (C), 198.2 (C); EI-MS (70 eV): *m*/*z* (%) 357 (M$^+$, 1), 171 (51), 155 (100), 112 (76), 91 (44). Anal. calcd for $C_{16}H_{23}NO_2S_3$ (357.55): C, 53.75, H, 6.48; N, 3.92, S, 26.90; found: C, 53.79, H, 6.56; N, 3.99, S, 26.98%.

5-Phenyl-3-tosylthiazolidine-2-thione (**3f**)

The crude product was purified by recrystallisation from ether affording 0.34 g (98%) **3f**. M.p. 116–118 °C; IR: ν 3012, 2988, 2973, 1662, 1590, 1448, 1319, 1283, 1109 cm^{-1}; ^{1}H NMR: δ 2.36 (s, Me), 4.64–4.69 (m, CH), 4.81–4.87 (m, CH_2), 7.18–7.42 (m, 7 CH), 7.82 (d, ^3J = 7.1, 2 CH); ^{13}C NMR: δ 21.7 (Me), 62.5 (CH), 68.5 (CH_2), 127.7 (CH), 128.8 (2 CH), 129.2 (2 CH), 130.3 (2 CH), 130.7 (2 CH), 136.7 (C), 139.4 (C), 146.6 (C), 198.1 (C); EI-MS (70 eV): *m*/*z* (%) 349 (M$^+$, 6), 171 (49), 155 (80), 104 (63), 91 (56), 77 (100), 54 (36). Anal. calcd for $C_{16}H_{15}NO_2S_3$ (349.49): C, 54.99, H, 4.33; N, 4.01, S, 27.52; found: C, 55.11, H, 4.48, N, 4.18, S, 27.51%.

4-Methyl-5-phenyl-3-tosylthiazolidine-2-thione (**3g**)

The crude product was purified by recrystallisation from ether affording 0.32 g (87%) **3g**. M.p. 93–95 °C; IR: ν 3028, 2976, 2960, 1653, 1587, 1456, 1330, 1276, 1124 cm^{-1}; ^{1}H NMR: δ 1.17 (d, ^3J = 6.1, Me), 2.35 (s, Me), 4.32–4.39 (m, CH), 4.67 (d, ^3J = 6.7, CH), 7.14–7.40 (m, 7 CH), 7.81 (d, ^3J = 6.5, 2 CH); ^{13}C NMR: δ 14.2 (Me), 23.5 (Me), 57.1 (CH), 62.4 (CH), 125.0 (CH), 128.1 (2 CH), 128.9 (2 CH), 129.1 (2 CH), 130.3 (2 CH), 134.3 (C), 137.1 (C), 143.8 (C), 197.7 (C); EI-MS (70 eV): *m*/*z* (%) 363 (M$^+$, 5), 171 (44), 155 (79), 118 (67), 91 (51), 77 (100). Anal. calcd for $C_{17}H_{17}NO_2S_3$ (363.52): C, 56.17, H, 4.71, N, 3.85, S, 26.46; found: C, 56.23, H, 4.79; N, 3.87, S, 26.52%.

Methyl 5-phenyl-2-thioxo-3-tosylthiazolidine-4-carboxylate (**3h**)

The crude product was purified by recrystallisation from ether affording 0.36 g (89%) **3h**. M.p. 105–107 °C; IR: ν 3031, 2973, 1743, 1652, 1590, 1461, 1327, 1260, 1128 cm^{-1}; ^{1}H NMR: δ 2.36 (s, Me), 3.59 (s, MeO), 4.89 (d, ^3J = 10.9, CH), 5.19 (d, ^3J = 10.8, CH), 7.16 (d, ^3J = 6.8, CH), 7.22 (d, ^3J = 6.6, 2 CH), 7.27–7.41 (m, 4 CH), 7.82 (d, ^3J = 6.9, 2 CH); ^{13}C NMR: δ 23.4 (Me), 54.6 (MeO), 56.4 (CH), 70.2 (CH), 127.3 (CH), 128.2 (2 CH), 128.6 (2 CH), 128.9 (2 CH), 130.9 (2 CH), 134.5 (C), 139.5 (C), 144.1 (C), 169.2 (C), 198.1 (C); EI-MS (70 eV): *m*/*z* (%) 407 (M$^+$, 7), 171 (51), 162 (68), 155 (71), 78 (46), 77 (100), 54 (28). Anal. calcd for $C_{18}H_{17}NO_4S_3$ (407.53): C, 53.05, H, 4.20; N, 3.44, S, 23.60; found: C, 53.11, H, 4.29; N, 3.42, S, 23.61%.

Hexahydro-3-tosyl[1,3]benzothiazole-2(3H)-thione (**3i**)

The crude product was purified by recrystallisation from ether affording 0.32 g (98%) **3i**. M.p. 181–182 °C; IR: ν 3020, 2964, 1645, 1579, 1449, 1313, 1268, 1121 cm^{-1}; ^{1}H NMR: δ 1.42–2.19 (m, 8 H), 2.34 (s, Me), 3.14–3.22 (m, CH), 4.01–4.05 (m, CH), 7.40 (d, ^3J = 6.7, 2 CH), 7.84 (d, ^3J = 6.9, 2 CH); ^{13}C NMR: δ 21.9 (CH_2), 23.4 (Me), 26.2 (CH_2), 27.8 (CH_2), 32.1 (CH_2), 53.5 (CH), 68.1 (CH), 128.4 (2 CH), 130.0 (2 CH), 135.1 (C), 143.9 (C), 198.9 (C); EI-MS (70 eV): *m*/*z* (%) 327 (M$^+$, 7), 171 (58), 155 (100), 91 (64), 82

(71), 54 (60). Anal. calcd for $C_{14}H_{17}NO_2S_3$ (327.49): C, 51.35, H, 5.23; N, 4.28, S, 29.37; found: C, 51.42, H, 5.32; N, 4.33, S, 29.36%.

Octahydro-3-tosylcyclohepta[d]thiazole-2-thione (**3j**)

The crude product was purified by recrystallisation from ether affording 0.18 g (52%) **3j**. M.p. 178 °C (decomp.); IR: ν 3025, 2977, 1631, 1569, 1463, 1341, 1122 cm^{-1}; ^1H NMR: δ 1.36–2.16 (m, 10 H), 2.36 (s, Me), 3.68–3.74 (m, CH), 4.73–4.79 (m, CH), 7.81 (d, ^3J = 6.7, 2 CH), 7.83 (d, ^3J = 6.8, 2 CH); ^{13}C NMR: δ 22.1 (CH_2), 24.5 (Me), 25.2 (CH_2), 26.0 (CH_2), 31.3 (CH_2), 34.7 (CH_2), 52.5 (CH), 73.1 (CH), 128.7 (2 CH), 130.2 (2 CH), 134.5 (C), 143.7 (C), 199.4 (C); EI-MS (70 eV): *m/z* (%) 341 (M^+, 5), 265 (23), 171 (48), 155 (100), 96 (78), 91 (54), 54 (44). Anal. calcd for $C_{15}H_{19}NO_2S_3$ (341.51): C, 52.75, H, 5.61; N, 4.10, S, 28.17; found: C, 52.89, H, 5.79; N, 4.23, S, 28.21%.

4,5-Dipropyl-3-tosylthiazolidine-2-thione (**3k**)

The crude product was purified by recrystallisation from ether affording 0.34 g (94%) **3l**. Oily solid; IR: ν 3011, 2967, 1633, 1577, 1478, 1345, 1122 cm^{-1}; ^1H NMR: δ 0.94–2.11 (m, 14 H), 2.34 (s, Me), 3.50–3.58 (m, CH), 4.76–4.84 (m, CH), 7.41 (d, ^3J = 6.8, 2 CH), 7.82 (d, ^3J = 6.9 Hz, 2 CH); ^{13}C NMR: δ 13.8 (Me), 15.0 (Me), 21.3 (CH_2), 22.9 (CH_2), 23.7 (Me), 30.2 (CH_2), 31.6 (CH_2), 53.1 (CH), 66.8 (CH), 128.7 (2 CH), 130.6 (2 CH), 135.1 (C), 143.5 (C), 197.8 (C); EI-MS (70 eV): *m/z* (%) 357 (M^+, 5), 281 (29), 171 (67), 155 (100), 112 (71), 91 (53), 54 (32). Anal. calcd for $C_{16}H_{23}NO_2S_3$ (357.55): C, 53.75, H, 6.48; N, 3.92, S, 26.90; found: C, 53.89, H, 6.64; N, 4.08, S, 26.98%.

N-(4-Benzyl-3-tosylthiazolidin-2-ylidene)benzenamine (**5a**)

The crude product was purified by recrystallisation from ether affording 0.39 g (91%) **5a**. M.p. 118–120 °C; IR: ν 3011, 2967, 1643, 1577, 1478, 1345, 1122 cm^{-1}; ^1H NMR: δ 2.34 (s, Me), 2.96–3.42 (m, 4 CH), 4.81–4.85 (m, CH), 6.72 (d, ^3J = 6.8, 2 CH), 7.08 (t, ^3J = 6.5, CH), 7.26–7.41 (m, 9 CH), 7.82 (d, ^3J = 6.9 Hz, 2 CH); ^{13}C NMR: δ 23.5 (Me), 34.3 (CH_2), 39.7 (CH_2), 68.1 (CH), 120.1 (2 CH), 124.4 (CH), 126.1 (CH), 128.0 (2 CH), 128.4 (2 CH), 129.2 (2 CH), 130.4 (2 CH), 131.6 (2 CH), 135.5 (C), 138.6 (C), 143.9 (C), 149.4 (C), 156.2 (C); EI-MS (70 eV): *m/z* (%) 422 (M^+, 5), 155 (69), 135 (46), 118 (64), 91 (100), 77 (81), 54 (32). Anal. calcd for $C_{23}H_{22}N_2O_2S_2$ (422.56): C, 65.37, H, 5.25; N, 6.63, S, 15.18; found: C, 56.42, H, 5.31; N, 6.67, S, 15.22%.

N-(4-Benzyl-3-tosylthiazolidin-2-ylidene)propan-2-amine (**5b**)

The crude product was purified by recrystallisation from ether affording 0.34 g (87%) **5b**. M.p. 78–81 °C; IR: ν 3018, 2978, 1658, 1560, 1468, 1322, 1108 cm^{-1}; ^1H NMR: δ 0.96 (6 H, d, ^3J = 6.4 Hz, 2 Me), 2.32 (s, Me), 3.33–3.41 (m, 2 CH_2), 3.61–3.65 (H, m, CH), 4.56–4.61 (m, CH), 7.12–7.35 (m, 5 CH), 7.40 (d, ^3J = 6.7 Hz, 2 CH), 7.83 (d, ^3J = 6.6 Hz, 2 CH); ^{13}C NMR: δ 21.5 (2 Me), 23.5 (Me), 34.3 (CH_2), 39.1 (CH_2), 49.0 (CH), 67.3 (CH), 125.1 (CH), 127.2 (2 CH), 128.4 (2 CH), 128.9 (2 CH), 130.1 (2 CH), 135.7 (C), 137.1 (C), 144.0 (C), 155.9 (C); EI-MS (70 eV): *m/z* (%) 388 (M^+, 5), 155 (64), 118 (76), 101 (50), 91 (100), 77 (60), 54 (32). Anal. calcd for:$C_{20}H_{24}N_2O_2S_2$ (388.55): C, 61.82, H, 6.23; N, 7.21, S, 16.51; found: C, 61.96, H, 6.37; N, 7.36, S, 16.50%.

N-(4-Methyl-4-propyl-3-tosylthiazolidin-2-ylidene)propan-2-amine (**5c**)

The crude product was purified by recrystallisation from ether affording 0.30 g (84%) **5c**. Oily solid; IR: ν =3034, 2976, 1652, 1562, 1486, 1331, 1116 cm^{-1}; ^1H NMR: δ 0.93–0.98 (9 H, m, 3 Me), 1.22 (s, Me), 1.33–1.69 (m, 2 CH_2), 2.34 (s, Me), 3.21–3.38 (m, CH_2), 3.62–3.66 (m, CH), 7.41 (d, ^3J = 6.5 Hz, 2 CH), 7.82 (d, ^3J = 6.3 Hz, 2 CH); ^{13}C NMR: δ 13.4 (Me), 17.8 (CH_2), 21.7 (Me), 22.4 (2 Me), 23.6 (Me), 36.1 (CH_2), 45.1 (CH_2), 49.2 (CH), 74.3 (C), 128.1 (2 CH), 129.8 (2 CH), 134.1 (C), 143.6(C), 165.1 (C); EI-MS (70 eV): *m/z* (%) 354 (M^+, 5), 155 (89), 101 (76), 91 (48), 84 (100), 54 (32). Anal. calcd for $C_{17}H_{26}N_2O_2S_2$ (354.53): C, 57.59, H, 7.39; N, 7.90, S, 18.09; found: C, 57.72, H, 7.50; N, 7.92, S, 18.18%.

N-(5-Phenyl-3-tosylthiazolidin-2-ylidene)propan-2-amine (**5d**)

The crude product was purified by recrystallisation from ether affording 0.34 g (90%) **5d**. M.p. 89–91 °C; IR: ν 3034, 2989, 1654, 1563, 1488, 1324, 1119 cm^{-1}; ^1H NMR: δ 0.96 (d, ^3J = 6.5 Hz, 2 Me), 2.31 (s, Me), 3.63–3.68 (m, CH), 4.30–4.35 (m, CH), 4.58–4.64 (m, CH_2), 7.11 (d, ^3J = 6.8, 2 CH), 7.15–7.30 (m, 3 CH), 7.41 (d, ^3J = 6.4 Hz, 2 CH), 7.82 (d, ^3J = 6.6 Hz, 2 CH); ^{13}C NMR: δ 21.3 (2 Me), 23.5 (Me), 49.3 (CH), 57.9 (CH), 63.4 (CH_2), 127.1 (CH), 127.6 (2 CH), 128.3 (2 CH), 129.6 (2 CH), 130.1 (2 CH), 134.1 (C), 141.4 (C), 143.5 (C), 156.2 (C); EI-MS (70 eV): *m/z* (%) 374 (M^+, 5), 171 (45), 155 (76), 104 (51), 110 (65), 77 (100), 54 (32). Anal. calcd for $C_{19}H_{22}N_2O_2S_3$ (374.52): C, 60.93, H, 5.92; N, 7.48, S, 17.12; found: C, 61.11, H, 6.11; N, 7.64, S, 17.19%.

N-(Hexahydro-3-tosylbenzo[d]thiazol-2(3H)-ylidene)propan-2-amine (**5e**)

The crude product was purified by recrystallisation from ether affording 0.30 g (86%) **5e**. M.p. 158–160 °C; IR: ν 3011, 2977, 1645, 1561, 1482, 1321, 1109 cm^{-1}; ^1H NMR: δ 0.94 (d, ^3J = 6.4, 2 Me), 1.32–2.24 (m, 8 CH), 2.34 (s, Me), 3.63–3.67 (m, CH), 3.80–3.85 (m, CH), 4.75–4.79 (m, CH), 7.42 (d, ^3J = 6.8, 2 CH), 7.83 (d, ^3J = 6.4 Hz, 2 CH); ^{13}C NMR: δ 21.5 (2 Me), 22.4 (CH_2), 23.6 (Me), 27.4 (CH_2), 29.1 (CH_2), 30.2 (CH_2), 42.6 (CH), 50.3 (CH), 67.1 (CH), 128.1 (2 CH), 130.3 (2 CH), 134.6 (C), 144.2 (C), 165.3 (C); EI-MS (70 eV): *m/z* (%) 352 (M^+, 5), 251 (35), 171 (61), 155 (100), 82 (60), 91 (48), 54 (32). Anal. calcd for $C_{17}H_{24}N_2O_2S_2$ (352.50): C, 57.92, H, 6.86; N, 7.95, S, 18.19; found: C, 58.30, H, 6.93; N, 8.10, S, 18.28%.

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