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Efficient Pyrrolidine Catalyzed Cycloaddition of Aziridines with Isothiocyanates, Isoselenocyanates and Carbon Disulfide "On Water"

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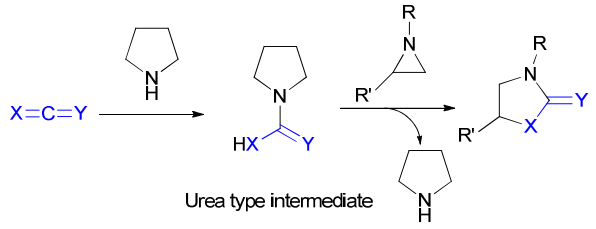
The cycloaddition of aziridines with isothiocyanates, isoselenocyanates and carbon disulfide has been described using pyrrolidine as catalyst on water at moderate temperature. This protocol features the use of commercial amine as catalyst and water as solvent affording potential route for the construction of five membered heterocycles in high yields.

Introduction

Water is the most abundant, cheap, safe and environmentally benign solvent in nature. Development of effective methods for the use of water as a reaction medium for organic synthesis has thus received much attention in recent years.[1-3] The cycloaddition of aziridines with isothiocyanates affords efficient approach for the construction of functionalized five membered heterocycles that are important in biological and medicinal sciences.[4] For examples, Pd,[5] Ni,[6] Fe,[3t] Zn,[7] PBu_3,[8] NaI,[9] HBF_4[10] and Ph_4SbBr[11] based systems have been studied for the reaction of aziridines with carbodiimides, carbon disulfide, isocyanates, isothiocyantes or isoselenocycantes as catalyst or stoichiometric reagents. Herein, we wish to report an efficient pyrrolidine catalyzed cycloaddition reaction of aziridines with isothiocyanates, isoselenocyanates and carbon disulfide on water at moderate temperature under air.[12] The reaction occurs in aqueous suspension via a urea type intermediate affording a potential route for the construction of five membered heterocycles under mild reaction conditions (Scheme 1).

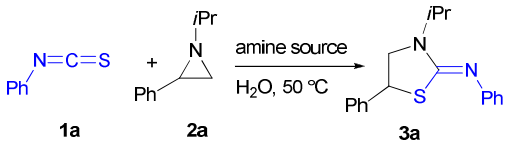


Scheme 1 Amine catalyzed cycloaddition of aziridine with heterocumulenes via urea type intermediate.

Results and discussion

First, the reaction conditions were optimized employing phenyl isothiocyanate (**1a**) and 1-isopropyl-2-phenylaziridine (**2a**) as model substrates in the presence of various amine catalysts on water at varied temperature (Table 1). Gratifyingly, the reaction occurred to give the desired thiazolidin-2-ylidene (**3a**) in 46% yield when the substrates **1a** and **2a** were stirred with 25 mol% pyrrolidine for 12 h on water at ambient conditions (entry 1). Increasing the reaction temperature to 50 °C led to completion of the process in 6 h with 97% yield (entry 2). In a set of screened amine catalysts, pyrrolidine, morpholine, piperidine, L-proline, *N*-methylaniline, diisopropylamine, *N*-Boc pyrrolidine, triethylamine, DBU, $NaHCO_3$ and K_2CO_3, the former afforded the superior results (entries 2-13). Control experiments confirmed that without the amine catalyst the reaction produced **3a** after 12 h in <9% yield (entry 14-15).

Table 1 Optimization of the reaction conditions[a]



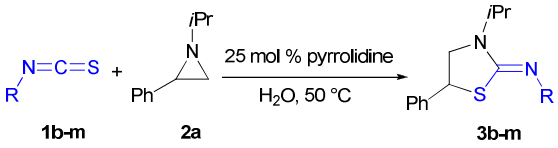
1a **2a** **3a**

Entry	Catalyst	*T* (°C)	*t* (h)	Yield **3a** (%)[b]
1	pyrrolidine	28	12	46
2	pyrrolidine	50	6	97
3	morpholine	50	6	36
4	piperidine	50	6	38
5	L-proline	50	6	75
6	*N*-methylaniline	50	6	25
7	diisopropylamine	50	6	20
8	*N*-Boc-pyrrolidine	50	6	9
9	triethylamine	50	6	9
10	DBU	50	6	15
11	$NaHCO_3$	50	6	12
12	K_2CO_3	50	6	13
13	pyrrolidine	50	10	86[c]
14	-	50	12	9
15	-	28	12	4

[a] Reaction conditions. **1a** (0.5 mmol), **2a** (0.5 mmol), catalyst (25 mol %), H_2O (1.0 mL), 50 °C, air. [b] Determined by 400 MHz ^{1}H NMR. [c] 20 mol % of catalyst used. DBU = 1,8-diazabicyclo[5.4.0]-undec-7-ene

With the optimal conditions in hand, the generality of the protocol was studied for the reactions of a series of substituted isothiocyanates with aziridine **2a** (Table 2). The reactions were efficient to afford the target products in high yields. For examples, isothiocyanates **1b-h** having 2-methoxy, 2-methyl, 3-fluoro, 4-ethyl, 4-methoxy, 4-methyl and 4-nitro substituents in the phenyl ring underwent reaction to give the heterocycles **3b-h** in 69-88% yields. Likewise, the substrates **1i-k** bearing 2,4-, 3,4- and 3,5-dimethyl substituents readily underwent reaction to provide the target products **3i-k** in 79-85% yields. Furthermore, aliphatic isothiocyanate **1l** was compatible affording the target heterocycle **3l** in 70% yield. Similarly, 1-naphthyl isothiocyanate **1m** underwent reaction to give the desired **3m** in 82% yield.

Table 2 Pyrrolidine-catalyzed cycloaddition of substituted isothiocyanates with aziridine **2a**[a]

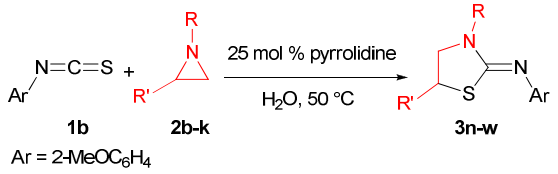


1b-m **2a** **3b-m**

Entry	Isothio-cyanate	R	*t* (h)	Product (Yield, %)[b]
1	**1b**	2-MeOC$_6$H$_4$	7.0	**3b** (73)
2	**1c**	2-MeC$_6$H$_4$	8.5	**3c** (71)
3	**1d**	3-FC$_6$H$_4$	5.5	**3d** (69)
4	**1e**	4-EtC$_6$H$_4$	9.5	**3e** (80)
5	**1f**	4-MeOC$_6$H$_4$	10.5	**3f** (88)
6	**1g**	4-MeC$_6$H$_4$	9.5	**3g** (82)
7	**1h**	4-NO$_2$C$_6$H$_4$	10.0	**3h** (75)
8	**1i**	2,4-Me$_2$C$_6$H$_3$	10.0	**3i** (79)
9	**1j**	3,4-Me$_2$C$_6$H$_3$	10.5	**3j** (81)
10	**1k**	3,5-Me$_2$C$_6$H$_3$	9.0	**3k** (85)
11	**1l**	*α*-methylbenzyl	9.5	**3l** (70)
12	**1m**	1-naphthyl	9.0	**3m** (82)

[a] Reaction conditions. **1b-m** (0.5 mmol), **2a** (0.5 mmol), H_2O (1.0 mL), 50 °C, air. [b] Yield of isolated product.

Table 3 Pyrrolidine-catalyzed cycloaddition of isothiocyanate **1b** with substituted aziridines[a]



1b **2b-k** **3n-w**

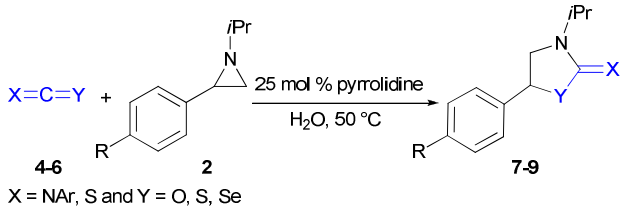
Ar = 2-MeOC$_6$H$_4$

Entry	Aziridine	R	R'	*t* (h)	Product (Yield, %)[b]
1	**2b**	allyl	Ph	9.5	**3n** (70)
2	**2c**	Bn	Ph	10.5	**3o** (78)
3	**2d**	*n*-Bu	Ph	6.5	**3p** (83)
4	**2e**	cyclohexyl	Ph	8.5	**3q** (69)
5	**2f**	Ts	Ph	12.0	**3r** n.d.
6	**2g**	*i*Pr	4-BrC$_6$H$_4$	9.0	**3s** (85)
7	**2h**	*i*Pr	4-FC$_6$H$_4$	10.5	**3t** (74)
8	**2i**	*i*Pr	4-MeOC$_6$H$_4$	5.0	**3u** (89)
9	**2j**	*i*Pr	4-MeC$_6$H$_4$	6.0	**3v** (77)
10	**2k**	*i*Pr	2,4-Me$_2$C$_6$H$_3$	8.5	**3w** (73)

[a] Reaction conditions. **1b** (0.5 mmol), **2b-k** (0.5 mmol), H_2O (1.0 mL), 50 °C, air. [b] Yield of isolated product. n.d. = not detected.

Next, the reactions of substituted aziridines **2b-k** with isothiocyanate **1b** were examined and the results are summarized in table 3. For examples, aryl aziridines **2b-e** having allyl, benzyl, *n*-butyl and cyclohexyl substituents on the nitrogen atom underwent reaction to give the corresponding cycloaddition products **3n-q** in 69-83% yields, whereas 1-tosyl-2-phenyl-aziridine **2f** showed no reaction and the starting materials were recovered intact. Furthermore, the substrates **2g-k** having electrons donating and electron withdrawing substituents such as 4-bromo, 4-fluoro, 4-methoxy, 4-methyl and 2,4-dimethyl groups readily underwent reaction to furnish the thiazolidin-2-ylidenes **3s-w** in 73-89% yields.

Table 4 Pyrrolidine-catalyzed cycloaddition of isoselenocyanates and carbon disulfide with substituted aziridines[a]



4-6 **2** **7-9**

X = NAr, S and Y = O, S, Se

Entry	Substrate	X	Y	R	*t* (h)	Product (Yield, %)[b]
1	**4**	N(4-ClC$_6$H$_4$)	O	H	3.5	**7** n.d.
2	**5a**	N(Ph)	Se	H	4.0	**8a** (91)
3	**5b**	N(2-MeOC$_6$H$_4$)	Se	H	2.5	**8b** (80)
4	**5c**	N(3-MeC$_6$H$_4$)	Se	H	4.5	**8c** (83)
5	**5d**	N(4-ClC$_6$H$_4$)	Se	H	3.5	**8d** (89)
6	**5e**	N(4-MeOC$_6$H$_4$)	Se	H	6.0	**8e** (85)
7	**6**	S	S	H	8.0	**9a** (73)
8	**6**	S	S	Br	9.5	**9b** (85)
9	**6**	S	S	MeO	5.5	**9c** (81)
10	**6**	S	S	Me	7.0	**9d** (77)

[a] Reaction conditions. **4-5** (0.5 mmol) or **6** (2.5 mmol) , **2** (0.5 mmol), H_2O (1.0 mL), 50 °C, air. [b] Yield of isolated product. n.d. = not detected.

Finally, the reactions of isocyanate **4**, isoselenocyanates **5a-e** and carbon disulfide **6** with aziridines, were investigated (Table 4). However, isocyanate **4** showed no reaction and the starting materials were recovered intact (entry 1). In contrast, isoselenocyanates **5a-e** readily underwent reaction with aziridine **2a** to afford the target products **8a-e** in 80-91% yield. Likewise, carbon disulfide **6** underwent reaction with aziridines **2a**, **2g**, **2i** and **2j** to furnish the heterocycles **9a-d** in 73-85% yields.

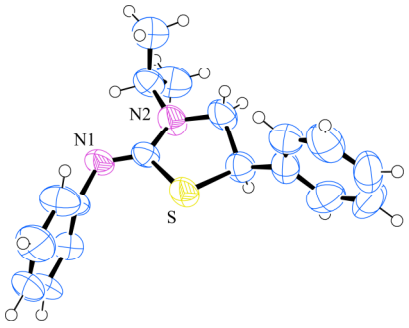
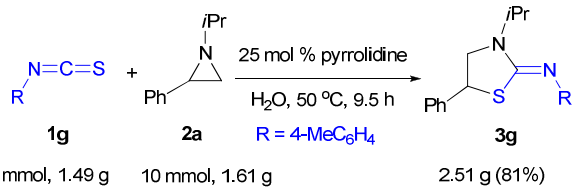
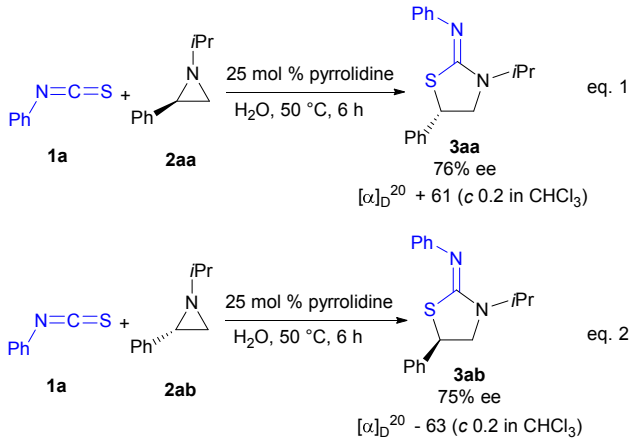


Fig. 1 ORTEP diagram of (*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)aniline (**3ab**). Thermal ellipsoids are drawn at a 50 % probability level (CCDC-1025804).

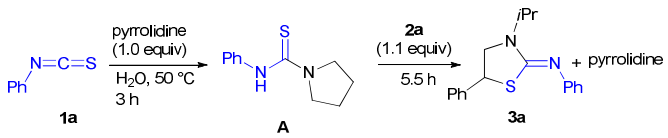
To reveal the scale up of the process, the reaction of **1g** with **2a** was studied (Scheme 2). As above, the reaction occurred to afford **3g** in 81% yield. This result clearly suggests that the protocol may be employed on the gram scale synthesis of the target heterocycles.



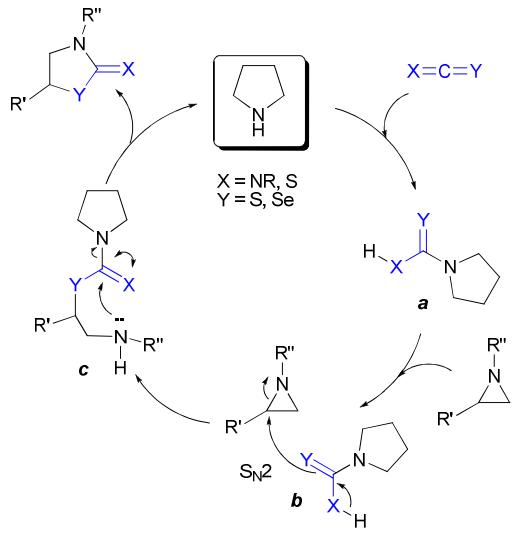
Scheme 2 Gram scale synthesis.



Scheme 3 Reaction of chiral aziridines.



Scheme 4 Urea type intermediate.



Scheme 5 Proposed catalytic cycle.

To gain insight into mechanism, optically active aziridines **2aa** and **2ab** having opposite configurations were reacted with isothiocyanate **1a** under the optimized reaction conditions (eq. 1 and 2). The reactions proceeded readily to yield the target heterocycles with inverted configurations (Scheme 3). These results suggest that the reaction involves S_N2 pathway. The absolute configuration of **3ab** was confirmed by single crystal X-ray analysis (Fig. 1). Furthermore, we were able to isolate and characterize the reactive urea type intermediate **A** when a 1:1 mixture of isothiocyanate **1a** and pyrrolidine were reacted (Scheme 4). The isolated intermediate **A** readily underwent reaction with aziridine **2a** to give the target product **3a**. These results suggest that the reaction of pyrrolidine with heterocumulene can yield the reactive urea type intermediate ***a*** that may proceed reaction with aziridine via intermediate ***b*** (S_N2) to afford ***c***. The intramolecular cyclization of ***c*** may then give the target heterocycles and the catalyst to complete the catalytic cycle (Scheme 5).

Conclusions

In summary, we have developed an efficient and simple organocatalytic protocol for the (3+2)-cycloaddition reaction of isothiocyanates, isoselenocyanates and carbon disulfide with aziridines under mild conditions. The features of this process include the use of commercial pyrrolidine as the catalyst and involvement of urea type intermediate. These studies can open a new further development of the cycloaddition of isothiocyanates, isoselenocyanates and carbon disulfide with a variety of substrates.

Acknowledgements

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Experimental

General information

All reactions were performed in pure water (>5 MΩ cm @ 25 °C, total organic content < 30 ppb) obtained from Elix water purification system. Amines and alkenes were purchased from Aldrich and used as received. Selenium (99.9%) and amino acids were purchased from SRL. Aziridines[13] and heterocumulenes[3t] were prepared according to the reported procedure. The reactions were monitored by analytical TLC on Merck silica gel G/GF 254 plates. The column chromatography was performed with Rankem silica gel (60-120 mesh). NMR (^{1}H and ^{13}C) spectra were recorded on DRX-400 Varian and Bruker Avance III 600 spectrometers. The data have been accounted as follows: chemical shifts (δ ppm) (multiplicity, coupling constant (Hz), integration). The abbreviations for multiplicity are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets. Chemical shifts (δ) are reported relative to residual solvent signals ($CHCl_3$, 7.24 ppm for ^{1}H NMR and 77.23 ppm for ^{13}C NMR). Melting points were determined with a Büchi B-545 apparatus and are uncorrected. Elemental analyses were recorded using Perkin Elmer CHNS analyzer. Optical rotation was determined by using Perkin Elmer-343 Polarimeter. FT-IR spectra were

recorded using Perkin Elmer IR spectrometer. HPLC analysis was carried out using Waters-2489 with Daicel Chiralcel OJ, OJ-H columns using isopropanol and hexane as eluent.

General procedure for the cycloaddition of aziridines with isothiocyanates and isoselenocyanates. Isothiocyanate or isoselenocyanate (0.5 mmol), aziridine (0.5 mmol) and pyrrolidine (0.125 mmol) were stirred in H_2O (1 mL) at 50 °C under air (Table 1-4). The progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. The reaction mixture was then cooled to room temperature and extracted with diethyl ether (3 x 10 mL). The organic layer was washed with water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent on a rotary evaporator gave a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate as eluent.

General procedure for the cycloaddition of aziridines with carbon disulfide. Carbon disulfide (2.5 mmol) was added portion wise for 0.5 h to a stirred solution of aziridine (0.5 mmol) and pyrrolidine (0.125 mmol) were stirred in H_2O (1 mL) at 50 °C under air and the stirring continued for the appropriate time (Table 4). The progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. The reaction mixture was then cooled to room temperature and extracted with diethyl ether (3 x 10 mL). The organic layer was washed with water (5 mL). Drying (Na_2SO_4) and evaporated on a rotary evaporator to give a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate as eluent.

(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)aniline 3a. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.60; colorless solid; yield 86% (127 mg); mp 108-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 2H), 7.32-7.22 (m, 5H), 7.02-6.96 (m, 3H), 4.69-4.64 (m, 2H), 3.86 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.54 (dd, *J* = 10.0, 7.6 Hz, 1H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 152.3, 139.3, 128.8, 128.2, 127.5, 123.0, 122.2, 52.9, 46.7, 46.3, 20.0, 19.1; FT-IR (KBr) 3075, 3034, 2964, 2934, 2856, 1613, 1584, 1178, 1061, 855, 766 cm^{-1}; Anal. Calcd for $C_{18}H_{20}N_2S$: C, 72.93; H, 6.80; N, 9.45; S, 10.82. Found: C, 72.85; H, 6.82; N, 9.48; S, 10.85; Compound **3aa**: $[\alpha]_D^{20}$ = + 61.0 (*c* 0.2 in $CHCl_3$); HPLC analysis: 76% ee [Daicel CHIRALCEL OJ column, hexane/*i*PrOH = 85:15, flow rate: 1 mL /min, λ = 215 nm, t_R = 12.72 min (major), 18.24 min (minor)]; Compound **3ab**: $[\alpha]_D^{20}$ = - 63.0 (*c* 0.2 in $CHCl_3$); HPLC analysis: 75% ee [Daicel CHIRALCEL OJ column, hexane/*i*PrOH = 85:15, flow rate: 1 mL /min, λ = 215 nm, t_R = 12.66 min (minor), 17.21 min (major)].

(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-2 methoxyaniline 3b. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.54; colorless solid; yield 73% (118 mg); mp 107-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.32-7.23 (m, 3H), 7.00-6.96 (m, 1H), 6.92-6.90 (m, 1H), 6.86-6.82 (m, 2H), 4.75-4.68 (m, 1H), 4.64 (t, *J* = 7.2 Hz, 1H), 3.87 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.80 (s, 3H), 3.54 (dd, *J* = 9.6, 7.6 Hz, 1H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 151.8, 141.7, 139.6, 128.7, 128.0, 127.5, 123.9, 123.0, 120.7, 111.6, 55.8, 53.2, 46.5, 46.4, 19.9, 19.1; FT-IR (KBr) 3056, 3032, 2973, 2947, 2926, 2867, 1623, 1585, 1493, 1187, 1064, 1024, 747 cm^{-1}; Anal. Calcd for $C_{19}H_{22}N_2OS$: C, 69.90; H, 6.79; N, 8.58; S, 9.82. Found: C, 69.98; H, 6.77; N, 8.55; S, 9.84.

(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-2-methylaniline 3c. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; yield 71% (110 mg); mp 74-75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.32-7.25 (m, 3H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 4.68-4.62 (m, 2H), 3.86 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.54 (dd, *J* = 9.6, 8.0 Hz, 1H), 2.20 (s, 3H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.25 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7, 151.1, 139.6, 130.6, 130.2, 128.9, 128.2, 127.5, 126.4, 123.2, 121.4, 53.3, 46.7, 46.5, 20.0, 19.1, 18.2; FT-IR (KBr) 3058, 3023, 2971, 2929, 2870, 1626, 1591, 1488, 1456, 1401, 1362, 1243, 1212, 1179, 1110, 1066, 939 cm^{-1}; Anal. Calcd for $C_{19}H_{22}N_2S$: C, 73.51; H, 7.14; N, 9.02; S, 10.33. Found: C, 73.59; H, 7.13; N, 8.99; S, 10.29.

(*Z*)-3-Fluoro-*N*-(3-isopropyl-5-phenylthiazolidin-2-ylidene)aniline 3d. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.54; colorless solid; yield 69% (108 mg); mp 91-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.36 (m, 2H), 7.32-7.23 (m, 3H), 7.17-7.13 (m, 1H), 6.77-6.74 (m, 1H), 6.72-6.65 (m, 2H), 4.68-4.61 (m, 2H), 3.84 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.53 (dd, *J* = 9.6, 7.6 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (d, $^1J_{CF}$ = 243.4 Hz), 158.5, 154.1 (d, $^3J_{CF}$ = 9.9 Hz), 139.0, 129.9 (d, $^3J_{CF}$ = 9.9 Hz), 128.9, 128.3, 127.5, 118.0, 109.7 (d, $^2J_{CF}$ = 16.8 Hz), 109.5 (d, $^2J_{CF}$ = 17.5 Hz) , 52.9, 46.8, 46.4, 20.0, 19.1; FT-IR (KBr) 3061, 3028, 2975, 2925, 2856, 1618, 1588, 1482, 1402, 1254, 1228, 1182, 1126, 1057, 963 cm^{-1}; Anal. Calcd for $C_{18}H_{19}FN_2S$: C, 68.76; H, 6.09; N, 8.91; S, 10.20. Found: C, 68.86; H, 6.07; N, 8.89; S, 10.23.

(*Z*)-4-Ethyl-*N*-(3-isopropyl-5-phenylthiazolidin-2-ylidene)aniline 3e. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.56; colorless solid; yield 80% (130 mg); mp 63-64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.33-7.26 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 4.70-4.63 (m, 2H), 3.85 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.54 (dd, *J* = 10.0, 7.6 Hz, 1H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.23-1.18 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 149.9, 139.3, 138.6, 128.8, 128.2, 128.1, 127.5, 121.9, 52.9, 46.6, 46.2, 28.3, 20.0, 19.0, 15.7; FT-IR (KBr) 3067, 3020, 2964, 2923, 2861, 1618, 1594, 1504, 1474, 1453, 1404, 1244, 1208, 1194, 1066, 848 cm^{-1}; Anal. Calcd for $C_{20}H_{24}N_2S$: C, 74.03; H, 7.46; N, 8.63; S, 9.88. Found: C, 73.93; H, 7.49; N, 8.67; S, 9.91.

(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-4-methoxybenzenamine 3f.[3t] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.53; colorless liquid; yield 88% (144 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2H), 7.31-7.22 (m, 3H), 6.91 (d, *J* = 9.2 Hz, 2H), 6.79 (d, *J* = 9.2 Hz, 2H), 4.68-4.60 (m, 2H), 3.83 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.71 (s, 3H), 3.52 (dd, *J* = 9.6, 7.6 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 155.7, 145.4, 139.2, 128.8, 128.1, 127.5, 123.1, 114.1, 55.4, 53.0, 46.7, 46.4, 20.0, 19.1; FT-IR (neat) 3032, 2970, 2934, 2871, 2059, 1870, 1614, 1504, 1455, 1402, 1364, 1290, 1237, 1179, 1126, 1103, 1066, 1035, 937 cm^{-1}; Anal. Calcd for $C_{19}H_{22}N_2OS$: C, 69.90; H, 6.79; N, 8.58; S, 9.82. Found: C, 69.98; H, 6.77; N, 8.55; S, 9.84.

(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-4-methylbenzenamine 3g.[3t] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.55; colorless solid; yield 82% (127 mg); mp 89-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.33-7.26 (m, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 4.69-4.62 (m, 2H), 3.84 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.53 (dd, *J* = 9.6, 8.0 Hz, 1H), 2.27 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 149.8, 139.3, 132.2, 129.4, 128.8, 128.1, 127.5, 121.9, 52.9, 46.7, 46.3, 21.0, 20.0, 19.1; FT-IR (KBr) 3025, 2971, 2928, 2870, 1624, 1602, 1505, 1470, 1454, 1402, 1363, 1270, 1242, 1212, 1191, 1126, 1106, 1066, 1030, 938 cm^{-1} Anal. Calcd for $C_{19}H_{22}N_2S$: C, 73.51; H, 7.14; N, 9.02; S, 10.33. Found: C, 73.62; H, 7.11; N, 8.98; S, 10.29.

(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-4-nitroaniline 3h. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.45; yellow solid; yield 75% (128 mg); mp 68-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.39-7.28 (m, 5H), 7.04 (d, *J* = 8.8 Hz, 2H), 4.72 (t, *J* = 7.6 Hz, 1H), 4.70-4.63 (m, 1H), 3.91 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.60 (dd, *J* = 10.0, 8.0 Hz, 1H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 158.3, 142.6, 138.5, 128.8, 128.3, 127.2, 124.8, 122.4, 52.8, 46.8, 46.6, 19.7, 19.1; FT-IR (KBr) 3063, 3038, 2973, 2926, 2869, 2852, 1614, 1571, 1498, 1328, 1218, 1185, 1162, 1108, 1066, 850 cm^{-1}; Anal. Calcd for $C_{18}H_{19}N_3O_2S$: C, 63.32; H, 5.61; N, 12.31; S, 9.39. Found: C, 63.40; H, 5.60; N, 12.34; S, 9.36.

(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-2,4-dimethylaniline 3i. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; yield 79% (128 mg); mp 69-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.32-7.25 (m, 3H), 6.94 (s, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 4.68-4.61 (m, 2H), 3.85 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.52 (t, *J* = 8.4 Hz, 1H), 2.24 (s, 3H), 2.17 (s, 3H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.24 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 148.5, 139.7, 132.4, 131.0, 130.2, 128.8, 128.1, 127.5, 126.9, 121.2, 53.2, 46.6, 46.5, 21.0, 19.9, 19.1, 18.1; FT-IR (KBr) 3063, 2967, 2926, 2844, 1626, 1605, 1492, 1470, 1397, 1242, 1206, 1192, 1166, 1117, 1064, 929 cm^{-1}; Anal. Calcd for $C_{20}H_{24}N_2S$: C, 74.03; H, 7.46; N, 8.63; S, 9.88. Found: C, 74.13; H, 7.44; N, 8.59; S, 9.84.

(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-3,4-dimethylaniline 3j. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.56; colorless solid; yield 81% (131 mg); mp 96-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.34-7.27 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.71-4.63 (m, 2H), 3.84 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.53 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.21 (s, 3H), 2.19 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 150.0, 139.3, 136.8, 130.8, 129.9, 128.7, 128.0, 127.5, 123.4, 119.1, 52.8, 46.6, 46.2, 20.0, 19.9, 19.2, 19.0; FT-IR (KBr) 3060, 3025, 2973, 2852, 1618, 1594, 1493, 1467, 1454, 1234, 1180, 1149, 1060, 966, 827 cm^{-1}; Anal. Calcd for $C_{20}H_{24}N_2S$: C, 74.03; H, 7.46; N, 8.63; S, 9.88. Found: C, 74.11; H, 7.44; N, 8.60; S, 9.85.

(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-3,5-dimethylbenzenamine 3k. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; yield 85% (138 mg); mp 74-75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.34 (m, 1H), 7.38-7.31 (m, 5H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.68 (s, 1H), 4.78-4.71 (m, 1H), 4.68 (t, *J* = 7.6 Hz, 1H), 3.87 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.57 (dd, *J* = 9.6, 8.0 Hz, 1H), 2.33 (s, 6H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.29 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 152.0, 139.2, 138.1, 128.7, 128.0, 127.4, 124.6, 119.7, 52.7, 46.6, 46.2, 21.3, 19.9, 18.9; FT-IR (KBr) 3029, 2971, 2927, 2867, 1614, 1455, 1402, 1362, 1289, 1240, 1210, 1143, 1068, 1027, 953 cm^{-1}; Anal. Calcd for $C_{20}H_{24}N_2S$: C, 74.03; H, 7.46; N, 8.63; S, 9.88. Found: C, 73.95; H, 7.45; N, 8.67; S, 9.93.

(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-1-phenylethanamine 3l. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.49; pale yellow liquid; yield 70% (113 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.37 (m, 4H), 7.35-7.25 (m, 5H), 7.21-7.16 (m, 1H), 4.63-4.56 (m, 2H), 4.29 (q, *J* = 6.4 Hz, 1H), 3.69 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.41 (dd, *J* = 9.6, 7.2 Hz, 1H), 1.46 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 147.2, 140.1, 128.8, 128.1, 128.0, 127.5, 126.5, 126.3, 64.1, 52.7, 46.6, 46.2, 25.9, 19.7, 18.9; FT-IR (neat) 3049, 3029, 2917, 2858, 1633, 1588, 1489, 1451, 1312, 1258, 1183, 1074, 1025, 908 cm^{-1}; Anal. Calcd for $C_{20}H_{24}N_2S$: C, 74.03; H, 7.46; N, 8.63; S, 9.88. Found: C, 74.14; H, 7.44; N, 8.59; S, 9.83.

(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)naphthalen-1-amine 3m. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.56; colorless solid; yield 82% (142 mg); mp 102-103 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 3.6 Hz, 1H), 7.69-7.68 (m, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.35-7.33 (m, 2H), 7.28-7.25 (m, 3H), 7.19 (t, *J* = 7.2 Hz, 2H), 7.15-7.12 (m, 1H), 6.95 (d, *J* = 6.6 Hz, 2H), 4.80-4.78 (m, 1H), 4.55 (t, *J* = 7.2 Hz, 1H), 3.81 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.49 (dd, *J* = 9.6, 7.8 Hz, 1H), 1.27 (d, *J* = 6.6 Hz, 3H), 1.23 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.2, 148.9, 139.4, 134.5, 128.9, 128.2, 127.9, 127.5, 126.0, 125.1, 124.1, 123.0, 116.2, 53.2, 46.8, 46.6, 20.2, 19.4; FT-IR (KBr) 3050, 3020, 2969, 2916, 2870, 2848, 1604, 1568, 1501, 1456, 1386, 1276, 1242, 1215, 1174, 1063, 1038, 926 cm^{-1}; Anal. Calcd for $C_{22}H_{22}N_2S$: C, 76.26; H, 6.40; N, 8.08; S, 9.26. Found: C, 76.20; H, 6.41; N, 8.11; S, 9.28.

(*Z*)-*N*-(3-Allyl-5-phenylthiazolidin-2-ylidene)-2-methoxyaniline 3n. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.54; yellow liquid; yield 70% (113 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.32-7.26 (m, 3H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 6.4 Hz, 2H), 5.99-5.89 (m, 1H), 5.27-5.19 (m, 2H), 4.71 (t, *J* = 7.2 Hz, 1H), 4.21-4.18 (m, 2H), 3.86-3.84 (m, 1H), 3.81 (s, 3H), 3.57 (t, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 151.8, 141.4, 139.2, 133.0, 128.7, 128.1, 127.6, 124.1, 122.9, 120.8, 118.0, 111.8, 58.2, 55.9, 49.3, 46.7; FT-IR (neat) 3064, 3025, 3006, 2952, 2924, 2832, 1627, 1586, 1493, 1466, 1453, 1399, 1247, 1173, 1110, 1046, 1027, 1005,

927 cm^{-1}; Anal. Calcd for $C_{19}H_{20}N_2OS$: C, 70.34; H, 6.21; N, 8.63; S, 9.88. Found: C, 70.42; H, 6.19; N, 8.60; S, 9.85.

(*Z*)-*N*-(3-Benzyl-5-phenylthiazolidin-2-ylidene)-2-methoxyaniline 3o. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; yield 78% (117 mg); mp 87-88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.38-7.35 (m, 4H), 7.31-7.25 (m, 4H), 7.05-7.02 (m, 2H), 7.00-6.91(m, 2H), 4.90 (d, *J* = 14.8, 1H), 4.80 (d, *J* = 14.8, 1H), 4.70 (t, *J* = 7.6, 1H), 3.88 (s, 3H), 3.78 (dd, *J* = 10.0, 7.6 Hz, 1H), 3.52 (dd, *J* = 10.0, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 151.9, 141.5, 139.1, 137.2, 128.8, 128.7, 128.6, 128.1, 127.6, 127.5, 124.1, 122.9, 120.9, 111.8, 57.9, 56.0, 50.2, 46.8; FT-IR (KBr) 3080, 3061, 3025, 2990, 2960, 2916, 2867, 1624, 1585, 1493, 1452, 1407, 1360, 1240, 1213, 1152, 1110, 1023, 920 cm^{-1}; Anal. Calcd for $C_{23}H_{22}N_2OS$: C, 73.76; H, 5.92; N, 7.48; S, 8.56. Found: C, 73.69; H, 5.94; N, 7.51; S, 8.53.

(*Z*)-*N*-(3-Butyl-5-phenylthiazolidin-2-ylidene)-2-methoxyaniline 3p. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.61; colorless solid; yield 83% (141 mg); mp 71-72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.33-7.26 (m, 3H), 7.02-6.98 (m, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.87 (t, *J* = 6.4 Hz, 2H), 4.67 (t, *J* = 7.6 Hz, 1H), 3.88 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.81 (s, 3H), 3.63-3.57 (m, 3H), 1.68-1.63 (m, 2H), 1.42 (q, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 151.8, 141.8, 139.5, 128.7, 128.0, 127.5, 123.9, 123.0, 120.7, 111.7, 58.6, 55.8, 46.7, 46.2, 29.3, 20.2, 14.0; FT-IR (KBr) 3064, 3001, 2956, 2924, 2857, 2829, 1628, 1582, 1495, 1457, 1403, 1293, 1248, 1225, 1176, 1101, 1046, 1027, 988 cm^{-1}; Anal Calcd for $C_{20}H_{24}N_2OS$: C, 70.55; H, 7.10; N, 8.23; S, 9.42. Found: C, 70.65; H, 7.09; N, 8.20; S, 9.38.

(*Z*)-*N*-(3-Cyclohexyl-5-phenylthiazolidin-2-ylidene)-2-methoxyaniline 3q. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.59; yellow liquid; yield 69% (126 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.32-7.26 (m, 3H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.88-6.85 (m, 2H), 4.61 (t, *J* = 6.8 Hz, 1H), 4.36-4.31 (m, 1H), 3.91 (t, *J* = 8.8 Hz, 1H), 3.81 (s, 3H), 3.59 (t, *J* = 8.0 Hz, 1H), 2.03-1.65 (m, 5H), 1.48-1.06 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 151.8, 141.8, 139.8, 128.7, 128.0, 127.4, 123.9, 123.3, 120.8, 111.8, 55.9, 54.5, 54.3, 46.6, 30.5, 29.7, 25.8, 25.7, 25.6; FT-IR (neat) 3060, 3020, 2937, 2851, 2829, 1628, 1583, 1493, 1466, 1401, 1302, 1231, 1173, 1111, 1046, 1028, 910, 891, 806 cm^{-1}; Anal. Calcd for $C_{22}H_{26}N_2OS$: C, 72.09; H, 7.15; N, 7.64; S, 8.75. Found: C, 72.00; H, 7.13; N, 7.66; S, 8.71.

(*Z*)-*N*-(5-(4-Bromophenyl)-3-isopropylthiazolidin-2-ylidene)-2-methoxyaniline 3s. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.57; colorless solid; yield 85% (172 mg); mp 79-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.01-6.98 (m, 1H), 6.92-6.85 (m, 3H), 4.73-4.70 (m, 1H), 4.56 (t, *J* = 6.8 Hz, 1H), 3.87 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.81 (s, 3H), 3.50 (dd, *J* = 9.2, 6.4 Hz, 1H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 151.7, 141.6, 139.1, 131.8, 129.2, 124.1, 123.0, 121.9, 120.8, 111.7, 55.9, 53.2, 46.5, 45.8, 19.7, 19.3; FT-IR (KBr) 3050, 3004, 2968, 2927, 2845, 2823, 1627, 1585, 1490, 1467, 1399, 1275, 1260, 1235, 1177, 1110, 1061, 934 cm^{-1}; Anal. Calcd for $C_{19}H_{21}BrN_2OS$: C, 56.30; H, 5.22; N, 6.91; S, 7.91. Found: C, 56.38; H, 5.20; N, 6.89; S, 7.87.

(*Z*)-*N*-(5-(4-Fluorophenyl)-3-isopropylthiazolidin-2-ylidene)-2-methoxyaniline 3t. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.55; colorless solid; yield 74% (127 mg); mp 120-121 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2H), 7.02-6.99 (m, 3H), 6.92 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.87-6.85 (m, 2H), 4.74-4.72 (m, 1H), 4.62 (t, *J* = 6.6 Hz, 1H), 3.87 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.82 (s, 3H), 3.51 (dd, *J* = 9.6, 7.2 Hz, 1H), 1.28 (d, *J* = 6.6 Hz, 3H), 1.23 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 161.2 ((d, $^1J_{CF}$ = 215.3 Hz), 151.8, 141.6, 135.7, 135.6, 129.3 (d, $^3J_{CF}$ = 8.0 Hz), 124.1, 123.1, 120.9, 115.8 (d, $^2J_{CF}$ = 21.3 Hz), 111.8, 56.0, 53.5, 46.5, 45.9, 19.9, 19.3 ; FT-IR (KBr) 3053, 3034, 2965, 2927, 2861, 2834, 1625, 1585, 1510, 1493, 1466, 1240, 1224, 1174, 1114, 1026, 939 cm^{-1}; Anal. Calcd for $C_{19}H_{21}FN_2OS$: C, 66.25; H, 6.15; N, 8.13; S, 9.31. Found: C, 66.32; H, 6.13; N, 8.16; S, 9.35.

(*Z*)-*N*-(3-Isopropyl-5-(4-methoxyphenyl)thiazolidin-2-ylidene)-2-methoxyaniline 3u. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.51; yellow liquid; yield 89% (159 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.87-6.83 (m, 4H), 4.76-4.72 (m, 1H), 4.64 (t, *J* = 7.2 Hz, 1H), 3.86 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.54 (dd, *J* = 9.6, 7.8 Hz, 1H), 1.29 (d, *J* = 6.6 Hz, 3H), 1.25 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 152.1, 131.4, 128.8, 124.3, 123.4, 120.9, 120.8, 114.2, 111.9, 56.1, 55.5, 53.8, 46.7, 46.4, 20.1, 19.2; FT-IR (neat) 3061, 2969, 2932, 2834, 1623, 1585, 1512, 1493, 1463, 1355, 1254, 1177, 1029, 928 cm^{-1}; Anal. Calcd for $C_{20}H_{24}N_2O_2S$: C, 67.38; H, 6.79; N, 7.86; S, 8.99. Found: C, 67.30; H, 6.81; N, 7.83; S, 9.03.

(*Z*)-*N*-(3-Isopropyl-5-(*p*-tolyl)thiazolidin-2-ylidene)-2-methoxyaniline 3v. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.56; colorless solid; yield 77% (131 mg); mp 117-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.98 (t, *J* = 6.8 Hz, 1H), 6.91 (d, *J* = 6.8 Hz, 1H), 6.85 (d, *J* = 6.8 Hz, 2H), 4.72-4.69 (m, 1H), 4.61 (t, *J* = 6.8 Hz, 1H), 3.84 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.80 (s, 3H), 3.51 (dd, *J* = 9.2, 8.0 Hz, 1H), 2.30 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 151.9, 141.7, 137.9, 136.5, 129.5, 127.5, 124.0, 123.1, 120.8, 111.8, 56.0, 53.5, 46.6, 46.5, 21.2, 20.0, 19.2; FT-IR (KBr) 3040, 3009, 2973, 2923, 2848, 2834, 1629, 1586, 1492, 1469, 1450, 1402, 1260, 1236, 1220, 1180, 1158, 1111, 1062, 1045, 1025, 820 cm^{-1}; Anal. Calcd for $C_{20}H_{24}N_2OS$: C, 70.55; H, 7.10; N, 8.23; S, 9.42. Found: C, 70.65; H, 7.09; N, 8.20; S, 9.38.

(*Z*)-*N*-(5-(2,4-Dimethylphenyl)-3-isopropylthiazolidin-2-ylidene)-2-methoxyaniline 3w. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.57; colorless solid; yield 73% (129 mg); mp 84-85 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d,

J = 7.8 Hz, 1H), 7.03-6.98 (m, 2H), 6.95 (s, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 2H), 4.88 (t, *J* = 7.2 Hz, 1H), 4.76-4.74 (m, 1H), 3.85 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.82 (s, 3H), 3.57 (dd, *J* = 9.6, 7.8 Hz, 1H), 2.29 (s, 3H), 2.28 (s, 3H), 1.30 (d, *J* = 6.6 Hz, 3H), 1.27 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 151.9, 141.7, 137.5, 135.5, 134.4, 131.3, 127.3, 126.7, 123.9, 123.1, 120.8, 111.7, 55.9, 52.1, 46.5, 42.3, 21.1, 19.9, 19.6, 19.2; FT-IR (KBr) 3058, 2970, 2924, 2859, 2831, 1624, 1585, 1493, 1464, 1402, 1362, 1257, 1236, 1177, 1113, 1046, 1028, 934 cm^{-1}; Anal. Calcd for $C_{21}H_{26}N_2OS$: C, 71.15; H, 7.39; N, 7.90; S, 9.04. Found: C, 71.22; H, 7.37; N, 7.93; S, 9.00.

(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)benzenamine 8a.[3t] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.67; yellow liquid; yield 91% (156 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.31-7.22 (m, 5H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 2H), 4.78-4.72 (m, 2H), 3.85 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.65 (dd, *J* = 10.4, 8.0 Hz, 1H), 1.26 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 153.1, 140.0, 128.5, 128.3, 127.4, 127.2, 122.8, 121.3, 53.4, 46.8, 41.6, 19.6, 19.0; FT-IR (neat) 3058, 3027, 2971, 2929, 2869, 1614, 1590, 1489, 1454, 1402, 1363, 1243, 1205, 1185, 1163, 1126, 1069, 1024 cm^{-1}; Anal. Calcd for $C_{18}H_{20}N_2Se$: C, 62.97; H, 5.87; N 8.16. Found: C, 63.07; H, 5.83; N, 8.19.

((*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)-2-methoxybenzenamine 8b.[3t] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.60; colorless solid; yield 80% (149 mg); mp 107-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.27-7.18 (m, 3H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 2H), 4.83-4.80 (m, 1H), 4.72 (t, *J* = 7.2 Hz, 1H), 3.83 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.76 (s, 3H), 3.63 (dd, *J* = 10.4, 7.6 Hz, 1H), 1.26 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 151.6, 142.7, 140.2, 128.4, 127.5, 127.4, 123.9, 122.0, 120.6, 111.5, 55.6, 54.0, 47.1, 41.8, 19.8, 19.1; FT-IR (KBr) 3026, 2970, 2923, 2870, 1623, 1586, 1493, 1464, 1400, 1363, 1236, 1204, 1184, 1112, 1047, 1027 cm^{-1}; Anal. Calcd for $C_{19}H_{22}N_2OSe$: C, 61.12; H, 5.94; N, 7.50. Found: C, 61.19; H, 5.90; N, 7.47.

(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)-3-methylbenzenamine 8c.[3t] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.62; colorless liquid; yield 83% (148 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.29-7.19 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.85-6.80 (m, 3H), 4.81-4.77 (m, 1H), 4.72 (t, *J* = 6.8 Hz, 1H), 3.80 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.62 (dd, *J* = 10.4, 8.0 Hz, 1H), 2.30 (s, 3H), 1.28 (d, *J* = 4.8 Hz, 3H), 1.26 (d, *J* = 4.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 153.2, 140.1, 138.3, 128.5, 127.6, 127.5, 123.8, 122.3, 118.3, 53.6, 47.0, 41.8, 21.3, 19.9, 19.2; FT-IR (neat) 3030, 2971, 2927, 2862, 1613, 1593, 1455, 1400, 1362, 1282, 1207, 1185, 1069 cm^{-1}; Anal. Calcd for $C_{19}H_{22}N_2Se$: C, 63.86; H, 6.21; N, 7.84. Found: C, 63.87; H, 6.23; N, 7.80.

(*Z*)-4-Chloro-*N*-(3-isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)benzenamine 8d.[3t] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; yellow liquid; yield 89% (168 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.30-7.22 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 4.78-4.68 (m, 2H), 3.84 (dd, *J* = 10.4, 6.8 Hz, 1H), 3.65 (dd, *J* = 10.4, 8.0 Hz, 1H), 1.24 (t, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 151.8, 139.8, 128.7, 128.6, 128.0, 127.8, 127.4, 123.0, 53.8, 47.2, 42.2, 19.8, 19.2; FT-IR (neat) 3061, 3029, 2972, 2930, 2870, 1614, 1585, 1485, 1404, 1364, 1274, 1243, 1205, 1185, 1162, 1088, 1068, 1009 cm^{-1}; Anal. Calcd for $C_{18}H_{19}ClN_2Se$: C, 57.23; H, 5.07; N, 7.42. Found: C, 57.31; H, 5.08; N, 7.39.

(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)-4-methoxybenzenamine 8e.[3t] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.57; yellow liquid; yield 85% (159 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.33-7.25 (m, 3H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.82-4.75 (m, 2H), 3.86 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.73 (s, 3H), 3.67 (dd, *J* = 10.4, 7.6 Hz, 1H), 1.31 (d, *J* = 4.8 Hz, 3H), 1.29 (d, *J* = 4.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 155.7, 146.8, 140.2, 128.6, 127.6, 127.5, 122.3, 113.9, 55.1, 53.7, 47.1, 41.8, 19.8, 19.2; FT-IR (neat) 3031, 2971, 2870, 2833, 1614, 1504, 1464, 1401, 1363, 1294, 1239, 1205, 1185, 1067, 1035, 981 cm^{-1}; Anal. Calcd for $C_{19}H_{22}N_2OSe$: C, 61.12; H, 5.94; N, 7.50. Found: C, 61.05; H, 5.96; N, 7.54.

3-Isopropyl-5-phenylthiazolidine-2-thione 9a. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.56; colorless liquid; yield 73% (87 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.25 (m, 5H), 5.21-5.14 (m, 1H), 4.79 (dd, *J* = 7.6, 6.8 Hz, 1H), 4.28 (dd, *J* = 11.6, 8.4 Hz, 1H), 3.94 (dd, *J* = 11.6, 6.8 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 138.9, 129.1, 128.5, 127.2, 58.4, 49.6, 47.2, 19.6, 19.2; FT-IR (neat) 3056, 3031, 2972, 2930, 2873, 1668, 1601, 1472, 1430, 1367, 1300, 1275, 1239, 1201, 1184, 1076, 1029, 973 cm^{-1}; Anal. Calcd for $C_{12}H_{15}NS_2$: C, 60.72; H, 6.37; N, 5.90; S, 27.02. Found: C, 60.63; H, 6.38; N, 5.93; S, 27.06.

5-(4-Bromophenyl)-3-isopropylthiazolidine-2-thione 9b. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.52; colorless solid; yield 85% (134 mg); mp 69-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 7.46 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.18-5.11 (m, 1H), 4.71 (dd, *J* = 8.0, 6.4 Hz, 1H), 4.26 (dd, *J* = 11.6, 8.4 Hz, 1H), 3.87 (dd, *J* = 11.6, 6.4 Hz, 1H), 1.23 (d, *J* = 7.2 Hz, 3H), 1.17 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 138.1, 132.1, 128.8, 122.3, 58.2, 49.6, 46.4, 19.4, 19.2; FT-IR (KBr) 3042, 2970, 2923, 2867, 1663, 1610, 1582, 1510, 1481, 1432, 1369, 1301, 1241, 1199, 1182, 1072, 1029, 1008, 823 cm^{-1}; Anal. Calcd for $C_{12}H_{14}BrNS_2$: C, 45.57; H, 4.46; N, 4.43; S, 20.28. Found: C, 45.65; H, 4.44; N, 4.40; S, 20.32.

3-Isopropyl-5-(4-methoxyphenyl)thiazolidine-2-thione 9c. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; colorless solid; yield 81% (108 mg); mp 62-63 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 7.27 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.23-5.13 (m, 1H), 4.74 (t, *J* = 8.0 Hz, 1H), 4.22 (dd, *J* = 11.6, 8.0 Hz, 1H), 3.88 (dd, *J* = 11.6, 6.8 Hz, 1H), 3.77

(s, 3H), 1.24 (d, J = 6.8 Hz, 3H), 1.18 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 159.3, 130.5, 128.2, 114.7, 58.3, 55.1, 49.3, 46.5, 19.3, 19.0; FT-IR (KBr) 3009, 2975, 2948, 2925, 2898, 2828, 1662, 1607, 1509, 1480, 1465, 1433, 1369, 1303, 1280, 1250, 1200, 1175, 1075, 1033, 831 cm^{-1}; Anal. Calcd for $C_{13}H_{17}NOS_2$: C, 58.39; H, 6.41; N, 5.24; S, 23.98. Found: C, 58.50; H, 6.40; N, 5.21; S, 23.94.

3-Isopropyl-5-(*p*-tolyl)thiazolidine-2-thione 9d. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.49; colorless liquid; yield 77% (97 mg); ^{1}H NMR (400 MHz, $CDCl_3$) 7.25 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 5.20-5.13 (m, 1H), 4.77 (t, J = 8.0 Hz, 1H), 4.26 (dd, J = 11.6, 8.4 Hz, 1H), 3.91 (dd, J = 11.6, 6.8 Hz, 1H), 2.31 (s, 3H), 1.24 (d, J = 6.8 Hz, 3H), 1.19 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 138.2, 135.7, 129.6, 127.0, 58.3, 49.5, 46.9, 21.0, 19.5, 19.1; FT-IR (neat) 3017, 2972, 2927, 2873, 1654, 1610, 1512, 1472, 1431, 1360, 1297, 1239, 1185, 1076, 1036, 816 cm^{-1}; Anal. Calcd for $C_{13}H_{17}NS_2$: C, 62.11; H, 6.82; N, 5.57; S, 25.50. Found: C, 62.21; H, 6.80; N, 5.54; S, 25.45.

***N*-Phenylpyrrolidine-1-carbothioamide A.**[16] Phenyl isothiocyanate (0.5 mmol) and pyrrolidine (0.5 mmol) were stirred in H_2O (1 mL) for 3 h at 50 ºC under air. Then, the reaction mixture was then cooled to room temperature and extracted with dichloromethane (3 x 10 mL). The organic layer was washed with water (5 mL). Drying (Na_2SO_4) and evaporated on a rotary evaporator to give a colorless solid; yield 95% (98 mg); mp 121-122 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) 7.34-7.30 (m, 4H), 7.19-7.16 (m, 1H), 6.91(s, 1H), 3.66 (s, 4H), 2.01 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 139.4, 128.4, 125.8, 125.6, 52.2, 25.7; FT-IR (KBr) 3249, 3038, 2953, 2933, 2867, 1593, 1538, 1496, 1459, 1407, 1342, 1356, 1302, 1291, 1222, 949, 854, 725, 696 cm^{-1}; Anal. Calcd for $C_{18}H_{20}N_2S$: C, 64.04; H, 6.84; N, 13.58; S, 15.54. Found: C, 64.12; H, 6.82; N, 13.55; S, 15.51.

Notes and references

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† Electronic Supplementary Information (ESI) available: NMR (^{1}H, ^{13}C) spectra of the products. See DOI: 10.1039/b000000x/

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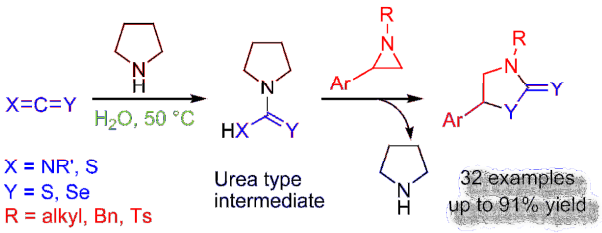

The cycloaddition of aziridines with isothiocyanates, isoselenocyanates and carbon disulfide has been described using pyrrolidine as catalyst on water at moderate temperature. This protocol features the use of commercial amine as catalyst and water as solvent affording potential route for the construction of five membered heterocycles in high yields.