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Aerobic intramolecular aminothiocyanation of unactivated alkenes promoted by *in situ* generated iodine thiocyanate

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ABSTRACT

Aerobic intramolecular aminothiocyanation of unactivated alkenes has been developed by *in situ* generated iodine thiocyanate under open-flask conditions. This protocol provides a concise and efficient method for synthesizing SCN-containing pyrrolidine, piperidine and indoline derivatives with isolated yields of up to 87%. Furthermore, mixing iodine and sodium thiocyanate with oxygen afforded iodine thiocyanate (ISCN) and dithiocyanatoiodate $[I(SCN)_2]^-$ which were testified by liquid chromatography mass spectrometry. A mechanistic investigation indicates that iodonium ion and sulfonium ion intermediates might be involved in this transformation.

1. Introduction

Thiocyanate compounds are especially important, not only as core moiety of complex compound existing in natural products, biologically active chemicals, pharmaceuticals and functional materials,[1] but also as key precursors in synthesizing thioheterocycles, thioesters, thiols and thiosulfonates.[2] For example, Prasad's group has used pyran-2-ones with thiocyanates for the synthesis of intermedia compounds, then via sulfenylation obtain human immunodeficiency virus-1 (HIV) protease inhibitors.[3] Undoubtedly, it is very promising method to install SCN group into molecules using low toxicity and wide available of the thiocyanate salts as thiocyanation reagent. Over the past several decades, alkynes, aromatics and carbonyl compounds under different oxidative conditions have successfully accessed to SCN-containing compounds.[4] In recent years, the difunctionalization of alkenes with thiocyanates affording SCN-containing compounds has been reported.[5–7] For examples, Liu's group reported a convenient way of trifluoromethylthiocyanation of alkenes by copper catalysis, using trimethylsilyl isothiocyanate as thiocyanating reagent and Togni reagent as trifluoromethyl source.[6] In 2016, Egami reported that chlorothiocyanation adducts was gave by alkenes with trimethylsilyl isothiocyanate and 1-chloro-1,2-benziodoxol-3-(*H*)-one.[7] Guo's group reported a route towards synthesis of SCN-containing dihydrofurans and lactones by tandem radical cyclization of olefinic compounds.[8]

In 2004, Gataullin et al. utilized N-benzyl-2-(2-cyclohexenyl)-aniline to produce the corresponding 1-thiocyanato derivatives via aminothiocyanation in the presence of iodine and sodium dicarbonate, however the synthesis of pyrrolidine, piperidine and indoline derivatives has not been exploited through aminothiocyanation.[9] It is well-known that the iodine-participated addition of alkenes proceeds through iodonium intermediate, whereas the mechanism involving some possible more reactive species under air condition, remains unknown and undiscovered in this aminothiocyantion. Herein we would like to report an intramolecular aminothiocyanation of unactivated alkenes with *in situ* generated iodine thiocyanate ISCN or its anion complex $[I(SCN)_2]^-$. In this article, the formation of species ISCN and $[I(SCN)_2]^-$ are discovered utilizing liquid chromatography mass spectrometry (LC-MS) detection and thus the yields of aminothiocyanation products were improved significantly.

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0040-4020/

2. Results and discussion

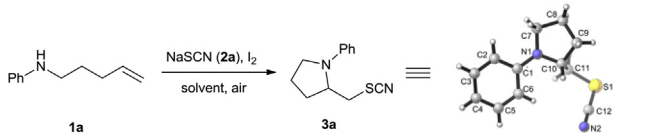
(1- At the outset of our investigation, we selected the N-(pent-4-en-1-yl)aniline 1a as the model substrate and available sodium thiocyanate 2a as the thiocyanation reagent (Table 1). Firstly, various solvents were screened; as a result the usage of MeCN led to form desired product 3a in 32% yield with conversion value of 70% in the presence of 2 equivalents of iodine at room temperature for 8 h (entry 1). Fortunately, the structure of 3a was confirmed convincingly through single-crystal X-ray diffraction analysis. When aminothiocyanation was carried out in DCM and DCE, 3a was generated only in 6% and 9% yields with conversions of 99% and 34%, respectively (entries 2 and 3). Subsequently, aprotic solvents such as methanol and ethanol were evaluated, and the desired aminothiocyanation products were afforded in low yields of 31% and 17%, respectively (entries 4 and 5). When Et_2O and THF were used as solvents, the yields were 14% and 41% respectively (entries 6 and 7). When EtOAc was utilized as a solvent, 3a was improved to 44% yield (entry 8). It was worth to note that NIS replacing I_2 as an iodine source resulted in the same level of reactivity under the same conditions (see supporting information). The amount of iodine was investigated; as a result the amount of iodine increased to 3.5 equivalents resulted in the better yield (80%), then more or less amount of iodine is detrimental to this aminothiocyanation (entries 9–11). Moreover, the amount of sodium thiocyanate was optimized; as a result either decreasing or increasing the equivalents of sodium thiocyanate reduced the yield (entries 12 and 13). When 3 mL or 5 mL of acetic ether was added, the yield of 3a decreased slightly (entries 14 and 15). The effects of reaction temperatures were examined as well, and the best results were observed when the temperature was elevated to 50 °C, while either raising or lowering the temperature led to lower yields (entries 16–18).

To make further explorations, the product **3a** was obtained in 76% yield in argon atmosphere (entry 19). As a contrast, **3a** was gave in 90 or 92% yields, respectively in air or in pure oxygen atmosphere (entries 17 and 20), which indicates that the oxygen improved animothiocyanation of unactivated alkenes. Accordingly, the mixture of sodium thiocyanate and iodine were stirred in a round-bottom flask under open-flask conditions at 50 °C for 8 h, the reaction solution were detected by liquid chromatography mass spectrometry, and species ISCN (**I**) and $[I(SCN)_2]^-$ (**II**) were observed: the cation model of $[NaI(SCN)]^+$ is found 224.1 (calcd: 223.8), and the radical cation models of $[I(SCN)_2]^{+\bullet}$ are found 266.1 (calcd: 265.8) with Na^+ and 282.2 (calcd: 281.8) with K^+ (Fig. 1). The complex of iodine and sodium thiocyanate was able to afford $[I_2(SCN)]^-$ which complexed with thiocyanates under oxidation condition by oxygen affording iodine thiocyanate (**I**),[10] then the complex of ISCN (**I**) and SCN^- afforded $[I(SCN)_2]^-$.[11] Accordingly, N-(pent-4-en-1-yl)aniline was subjected to the reaction mixture of I_2 and NaSCN, however the same level of yield was observed (Table 1, entry 21). So the addition subsequence of feedstocks has no effect to this reaction.

A series of commercially available inorganic as well as organic thiocyanates were investigated, and results revealed that thiocyanate sources had an effect on the reactivity of this reaction (Table 2). NH_4SCN (**2b**) gave a close level of reactivity to NaSCN (entry 1), KSCN (**2c**) generated the desired product in a relatively low yield of 75% (entry 2), whereas no reaction was observed when CuSCN (**2d**) was employed as the SCN source (entry 3). Organic thiocyanates such as guanidine thiocyanate (**2e**), 1-butyl-3-methylimidazolium thiocyanate (**2f**) and tetrabutylammonium thiocyanate (**2g**) were attempted as well, and the aminothiocyanation products were afforded in 78–80% yields (entries 4–6).

With the optimal conditions for aminothiocyanation in hand, the scope of the reaction was investigated, as the results summarized in Table 3. Different substitutions such as alkyl, alkoxy, trifluoromethoxy and halogen on benzene ring of anilines were explored; as a result *ortho*-methyl substitution **3b** was not obtained

Table 1
Optimization of reaction conditions.[a]



Entry	Solvent	NaSCN (eq.)	I_2 (eq.)	T (°C)	Conv.[b] (%)	Yield[b] (%)
1	MeCN	3	2	rt	70	32
2	DCM	3	2	rt	99	6
3	DCE	3	2	rt	34	9
4	MeOH	3	2	rt	99	31
5	EtOH	3	2	rt	99	17
6	Et_2O	3	2	rt	99	14
7	THF	3	2	rt	99	41
8	EtOAc	3	2	rt	99	44
9	EtOAc	3	3	rt	99	73
10	EtOAc	3	3.5	rt	99	80
11	EtOAc	3	4	rt	99	76
12	EtOAc	2.5	3.5	rt	99	73
13	EtOAc	3.5	3.5	rt	99	78
14	EtOAc	3	3.5	rt	99	77[c]
15	EtOAc	3	3.5	rt	99	75[d]
16	EtOAc	3	3.5	40	99	82
17	EtOAc	3	3.5	50	99	90
18	EtOAc	3	3.5	60	99	85
19	EtOAc	3	3.5	50	99	76[e]
20	EtOAc	3	3.5	50	99	92[f]
21	EtOAc	3	3.5	50	99	90[g]

[a] Conditions: **1a** (0.5 mmol), NaSCN (specified) and I_2 (specified) in solvent (4 mL) at rt for 8 h under air.
[b] Yield determined by ^1H NMR using mesitylene as an internal standard.
[c] 3 mL of EtOAc.
[d] 5 mL of EtOAc.
[e] The reaction was performed in argon atmosphere.
[f] The reaction was performed in oxygen atmosphere.
[g] NaSCN and I_2 were stirred for 1 h in EtOAc, then **1a** was added to the mixing solvent.

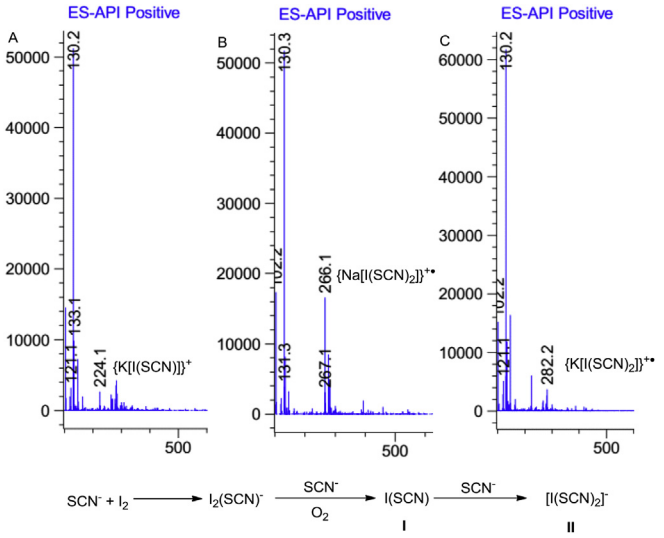
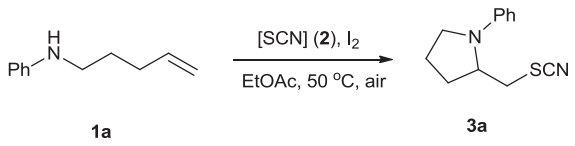
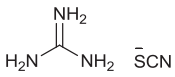
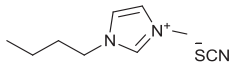
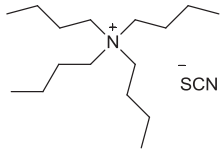


Fig. 1. Capture of Iodine thiocyanate (ISCN) and dithiocyanatoiodate $[I(SCN)_2]^-$ by LC-MS.

Table 2
Investigation of thiocyanates.[a]



1a 3a

Entry	[SCN] (2)	Conv[b] (%)	Yield[b] (%)
1	NH_4SCN	99	87
2	KSCN	99	75
3	CuSCN	–	0
4		99	78
5		99	78
6		99	80

[a] Conditions: **1a** (0.5 mmol), **2** (1.5 mmol) and iodine (1.75 mmol) in EtOAc (4 mL) at 50 °C for 8 h under air.
[b] Yield determined by ^{1}H NMR using mesitylene as an internal standard.

presumably due to steric effects of methyl group, while *para*-substitutions (**3d** and **3e**) provided higher reactivities and *meta*-substitution gave median yield such as **3c** (62%) and **3f** (41%), respectively. Methoxyl and trifluoromethyl substitutions (**3g** and **3h)** resulted in the yields of 41% and 70%, respectively. For halogen substitutions, a similar trend was demonstrated: *para*-substituents (**3i**, **3k** and **3m**) present higher reactivities than that of *meta*-halogen substituted ones (**3j**, **3l** and **3n**), where *meta*-iodine substituent **3n** gave moderate yield of 39% and *para*-chloro substituent **3k** afforded the best yield of 92%. Naphthylamine was employed as a substrate, and the corresponding N-naphthyl pyrrole **3o** was obtained in 73% yield. Substitutions on the alkenyl group were investigated as well; as a result α-methyl substituent led to the generation of α,α′-disubstituted pyrrolidine derivatives **3p** in excellent yield of 92% and β,β-diphenyl substituent gave rise to γ,γ-diphenyl substituted pyrrole **3q** in 33% yield. When benzylamine such as N-benzyl-2,2-diphenylpent-4-en-amine was utilized as a substrate, **3r** was gave in 36% yield. Considering the piperidine ring acted as a common motif in natural and piperidine derivatives exhibited an extensive range of biological interests,[12] several SCN-containing piperidine derivative (**3s**-**3u**) was afforded. However, aliphatic and cyclic olefin amine substrates were disabled to give the aminothiocyanation products (**3v** and **3w)**. Moreover, it was showed that the replacement of iodine by N-Iodosuccinimide also gave desired products, such as **3a**, **3e**, **3f**, and **3k** in lower yield of 75%, 59%, 40%, and 65%, respectively.

To further expand the general utility of this strategy, the *o*-allylanilines were considered as substrates, and under the optimal conditions (For detailed optimization, see Supporting Information) indoline derivatives having alkyl **5a**, aryl **5b**, heterocyclic **5c**, and fused ring **5d** substituents were afforded in moderate yield range of 30–52% at the temperature of 70 °C, utilizing NaSCN as thiocyanating source in the presence of iodine (Table 4), while for *para*-fluoro-substituted allylaniline **4e**, the reaction resulted in difficult-to-separate product and the content of corresponding product **5e** were calculated in 64% ^{1}H NMR yield. Interestingly, the silica-gel column chromatography afforded **5e** in isolated yield of 23% through recrystallization with the mixture of dichloromethane and petro ether.

Following the same procedure, both azidation and cyanation were executed. Unfortunately, **1a** with sodium azide (eq. (1)) or trimethylsilyl cyanide (eq. (2)) did not afford corresponding aminoazidation and aminocyanation products, whereas iodide **7** was obtained in 53% and 72% yields,[13] respectively (Scheme 1). It was also indicated that either azidation or cyanation is deactivated in these conditions.

To clarify the mechanism, several controlled experimentals were conducted (Scheme 2). The products **3a** were obtained in 88% and 72% yields when the reaction were carried out in dark (eq. (3) and eq. (4)). No TEMPO-involved product was detected when the reaction was carried out in the presence of TEMPO (eq. (5)). But the yield of **3a** dropped possibly due to the consumption of I_2 by TEMPO,[14] and the results could possibly rule out the radical process. In the absence of iodine, there is no aminothiocyanation product to be observed, which suggests iodine is important for the reaction (eq. (6)). The reaction of iodide **7** under optimal reaction conditions without iodine also afforded compound **3a** (eq. (7)), suggesting the easy-to-exchange nature of iodine in the presence of sodium thiocyanate.

Based on these experimental results, a plausible mechanistic pathway for the aminothiocyanation is proposed, depicted as in Scheme 3. Firstly iodonium ion **6** was generated from interaction of I_2 (path a) or ISCN (path b) with alkene, while sulfonium ion **8** was formed through the attack of sulfur in ISCN to alkene. The former proceeded tandem aminoiodination and bimolecular substitution between SCN^- and I to generate **3a** and the latter gave rise to **3a** just via an intramolecular nucleophilic attack.

3. Conclusion

(3- In summary, a concise and efficient aminothiocyanation of unactivated alkenes with sodium thiocyanate under mild conditions have developed. This aerobic intramolecular aminothiocyanation of alkenes provides a facile access to a series of new compounds SCN-containing pyrrolidine, piperidine dindoline derivatives. By utilization of LC-MS, the active species ISCN and $I(SCN)_2^-$ were captured and provided an insight to clarify the aminothiocyantion mechanism via an iodonium ion or sulfonium intermediates.

4. Experimental section

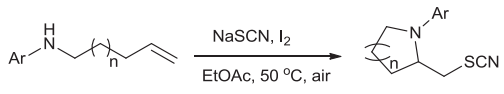
4.1. General information

(4- The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution at 500 (125) MHz spectrometer at 20–25 °C. ^{1}H NMR spectra were reported in parts per million using TMS ($\delta = 0.00$ ppm) as an internal standard. ^{13}C NMR spectra were reported in parts per million using solvent $CDCl_3$ ($\delta = 77.2$ ppm) as an internal standard. High-resolution mass spectra (HRMS) electrospray ionization (ESI) was carried out on a UPLC-Q-ToF MS spectrometer. All reagents were purchased from commercial suppliers and used as received. All experiments were conducted in the atmosphere. Column chromatography and thin-layer chromatography (TLC) which was used to monitor the reactions were performed on silica gel.

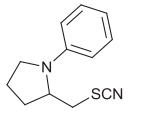
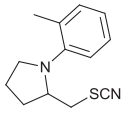
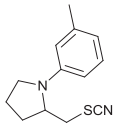
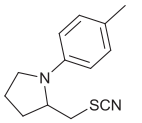
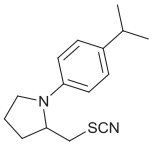
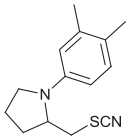
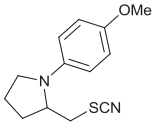
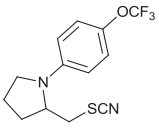
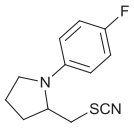
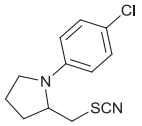
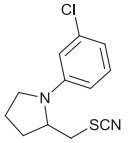
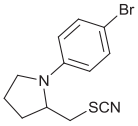
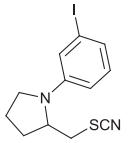
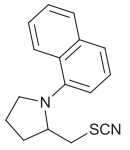
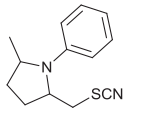
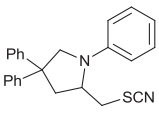
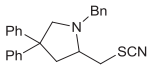
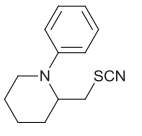
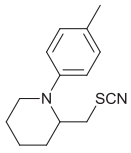
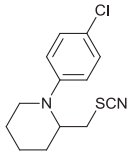
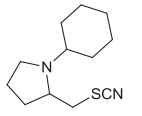
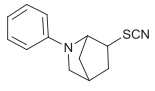
4.2. General procedure for the cyclization of olefinic amine compounds with NaSCN

(5- To a round-bottom flask was charged with compunds 1

Table 3
Scope of aminothiocyanation of alkenes.[a]



1 **3**

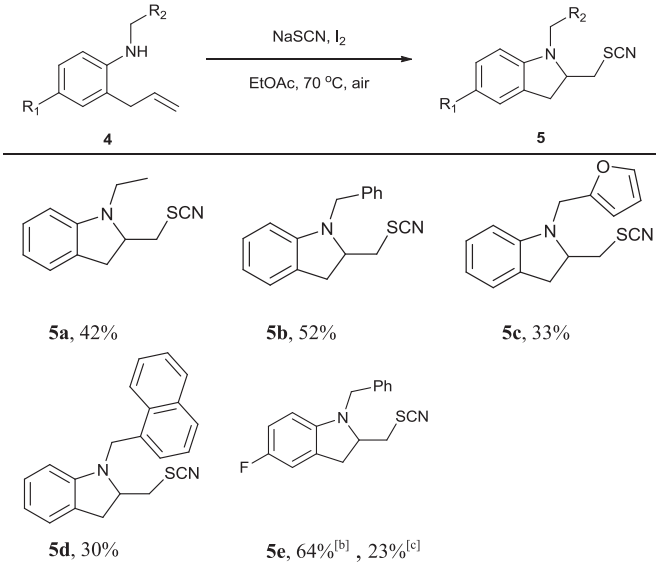
 **3a**, 90%[b] (85%)[c]	 **3b**, 0%	 **3c**, 62% (54%)
 **3d**, 85% (78%)	 **3e**, 75% (69%)	 **3f**, 41% (34%)
 **3g**, 41% (32%)	 **3h**,70% (63%)	 **3i**, 75% (68%)
 **3j**, 72% (65%)	 **3k**, 92% (87%)	 **3l**, 75% (60%)
 **3m**, 77% (66%)	 **3n**, 39% (28%)	 **3o**, 73% (61%)
 **3p**, 92% (83%) (dr=1:25)	 **3q**, 33% (21%)	 **3r**, 36% (24%)
 **3s**, 53% (42%)	 **3t**, 56% (52%)	 **3u**, 58% (54%)
 **3v**, 0%	 **3w**, 0%	

[a] Conditions: **1** (0.5 mmol), NaSCN (1.5 mmol) and I_2 (1.75 mmol) in EtOAc (4 mL) at 50 °C for 8 h under air.

[b] Yield determined by ^{1}H-NMR using mesitylene as an internal standard.

[c] Isolated yield in parentheses.

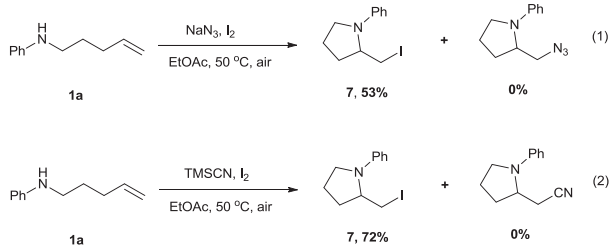
Table 4
Aminothiocyanation of different *o*-allylanilines.[a]



[a] Conditions: **4** (0.5 mmol), NaSCN (1.5 mmol) and I_2 (1.75 mmol) in EtOAc (4 mL) at 70 °C for 8 h under air.

[b] Yield determined by ^{1}H-NMR using mesitylene as an internal standard.

[c] Isolated yield by recrystallization.



Scheme 1. Approach to azidation and cyanation products.

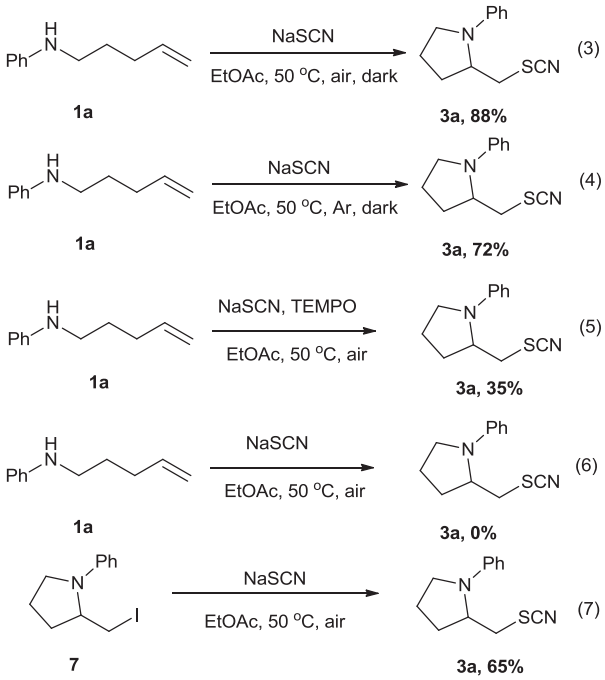
(0.5 mmol), EtOAc (4 mL) NaSCN (1.5 mmol) and I_2 (1.75 mmol) successively. Then the resulting mixture was stirred under open-flask conditions at 50 °C (oil bath temperature) for 8 h. The reaction was quenched with saturated solution of $Na_2S_2O_3$. The organic phase was separated, and the aqueous layer was extracted with EtOAc (5 mL × 3). The combined organic solution was dried with Mg_2SO_4 and concentrated in vacuo. The resulting residue was purified by a column chromatography to give the corresponding products **3** in yields as listed in Table 3.

*4.2.1. 1-Phenyl-2-(thiocyanatomethyl)pyrrolidine (**3a**)*

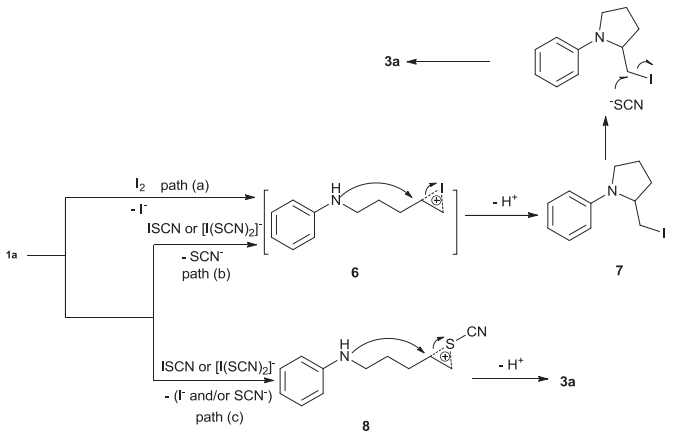
White solid; 85% yield, 93 mg; mp 67–71 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.24 (m, 2H), 6.75 (t, J = 7.5 Hz, 1H), 6.62 (d, J = 8.0 Hz, 2H), 4.14–4.10 (m, 1H), 3.55–3.51 (m, 1H), 3.31–3.27 (m, 1H), 3.25–3.19 (m, 1H), 2.77 (dd, J = 13.5, 9.5 Hz, 1H), 2.13–2.01 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 129.8, 117.3, 112.4, 112.2, 58.5, 49.0, 39.3, 35.6, 30.0, 23.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{15}N_2S$ 219.0951, found 219.0953.

*4.2.2. 2-(Thiocyanatomethyl)-1-(m-tolyl)pyrrolidine (**3c**)*

Brown oil; 54% yield, 63 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, J = 8.0 Hz, 1H), 6.60 (d, J = 7.5 Hz, 1H), 6.47–6.45 (m, 2H), 4.12 (t, J = 9.0 Hz, 1H), 3.55–3.51 (m, 1H), 3.31 (dd, J = 13.0, 1.0 Hz, 1H), 3.22 (q, J = 8.5 Hz, 1H), 2.77 (dd, J = 13.5, 9.5 Hz, 1H), 2.35 (s, 3H), 2.21–2.00 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 139.5, 129.6, 118.2, 112.9, 112.4, 109.4, 58.5, 49.0, 35.6, 30.0, 23.3, 22.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ for $C_{13}H_{17}N_2S$ 233.1107, found 233.1108.



Scheme 2. Controlled experiments.



Scheme 3. Proposed reaction mechanisms.

*4.2.3. 2-(Thiocyanatomethyl)-1-(p-tolyl)pyrrolidine (**3d**)*

White solid; 78% yield, 90 mg; mp 59–62 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09–7.07 (m, 2H), 6.57–6.54 (m, 2H), 4.11–4.06 (m, 1H), 3.54–3.50 (m, 1H), 3.30–3.27 (m, 1H), 3.22–3.17 (m, 1H), 2.82–2.78 (m, 1H), 2.27 (s, 3H), 2.22–2.01 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 130.2, 126.4, 112.5, 112.3, 58.6, 49.3, 35.9, 30.0, 23.4, 20.5. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ for $C_{13}H_{17}N_2S$ 233.1107, found 233.1117.

*4.2.4. 1-(4-Isopropylphenyl)-2-(thiocyanatomethyl) pyrrolidine (**3e**)*

Brown oil; 69% yield, 90 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, J = 8.0 Hz, 2H), 6.57 (d, J = 8.5 Hz, 2H), 4.07 (t, J = 8.0 Hz, 1H), 3.50 (t, J = 8.5 Hz, 1H), 3.27 (d, J = 13.0 Hz, 1H), 3.18 (dd, J = 17.0, 9.0 Hz, 1H), 2.85–2.80 (m, 1H), 2.74 (dd, J = , 13.0, 9.5 Hz, 1H), 2.16–2.00 (m, 4H), 1.21 (d, J = 6.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 137.6, 127.5, 112.4, 112.0, 58.6, 49.1, 35.7, 33.2, 30.0, 24.4, 24.3, 23.3. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ for $C_{15}H_{21}N_2S$ 261.1420, found 261.1425.

*4.2.5. 1-(3,4-Dimethylphenyl)-2-(thiocyanatomethyl)pyrrolidine (**3f**)*

White solid; 34% yield, 42 mg; mp 64–72 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (d, J = 8.0 Hz, 1H), 6.46 (s, 1H), 6.39 (d, J = 8.5 Hz, 1H), 4.07 (t, J = 7.5 Hz, 1H), 3.53–3.49 (m, 1H), 3.28 (q, J = 13.0 Hz, 1H), 3.17 (dd, J = 8.5, 17.0 Hz, 1H), 2.27 (dd, J = 13.0, 9.5 Hz, 1H), 2.24 (s, 3H), 2.17 (s, 3H), 2.14–2.00 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 114.7, 137.9, 130.7, 125.3, 113.9, 112.6, 109.7, 58.6, 49.3, 36.0, 30.0, 23.4, 20.5, 18.7. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ for $C_{14}H_{19}N_2S$ 247.1264, found 247.1271.

*4.2.6. 1-(4-Methoxyphenyl)-2-(thiocyanatomethyl)pyrrolidine (**3g**)*

Light yellow oil; 32% yield, 40 mg; mp 67–72 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89–6.86 (m, 2H), 6.61–6.58 (m, 2H), 4.06–4.02 (m, 1H), 3.77 (s, 3H), 3.53–3.50 (m, 1H), 3.29–3.25 (m, 1H) 3.16 (dd, J = 16.5, 8.5 Hz, 1H), 2.81(dd, J = 13.5, 9.5 Hz, 1H), 2.21–2.00 (m, 4H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 141.1115.4, 113.2, 112.6, 58.8, 56.0, 49.8, 36.1, 30.1, 23.5. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ for $C_{13}H_{17}N_2OS$ 249.1056, found 249.1050.

*4.2.7. 2-(Thiocyanatomethyl)-1-(4-(trifluoromethoxy)phenyl) pyrrolidine (**3 h**)*

Light yellow oil; 63% yield, 95 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, J = 8.0 Hz, 2H), 6.57 (d, J = 8.0 Hz, 2H), 4.10 (t, J = 8.0 Hz, 1H), 3.53–3.50 (m, 1H), 3.28–3.19 (m, 2H), 2.74 (t, J = 11.0, 3.0 Hz, 1H), 2.21–2.02 (m, 4H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 140.4, 122.9, 120.9 (d, J = 254 Hz), 112.2, 58.8, 49.2, 35.3, 30.0, 23.3. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ for $C_{13}H_{14}F_3N_2OS$ 303.0774, found 303.0781.

*4.2.8. 1-(4-Fluorophenyl)-2-(thiocyanatomethyl)pyrrolidine (**3i**)*

White solid; 68% yield, 81 mg; mp 44–45 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (t, J = 9.0 Hz, 2H), 6.55–6.52 (m, 2H), 4.10 (t, J = 8.5 Hz,1H), 3.52–3.50 (m, 1H), 3.25 (dd, J = 13.5, 1.5 Hz, 1H), 3.17 (q, J = 8.0 Hz, 1H), 2.77 (dd, J = 13.0, 9.0 Hz, 1H), 2.22–2.00 (m, 4H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 154.8, 143.0, 116.2(d, J = 22.5 Hz), 112.8 (d, J = 7.5 Hz), 112.4, 58.8, 49.6, 35.7, 30.1, 23.4. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ for $C_{12}H_{14}FN_2S$ 237.0856, found 237.0867.

*4.2.9. 1-(3-Fluorophenyl)-2-(thiocyanatomethyl)pyrrolidine (**3j**)*

White solid; 65% yield, 77 mg; mp 55–58 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (dd, J = 15.5, 8.5 Hz, 1H), 6.43 (td, J = 8.5, 1.5 Hz, 1H), 6.38 (dd, J = 8.0, 1.5 Hz, 1H), 6.30–6.27 (m, 1H), 4.10–4.07 (m, 1H), 3.51–3.47 (m, 1H), 3.27–3.18 (m, 2H), 2.77 (dd, J = 13.5, 9.5 Hz, 1H), 2.22–2.01 (m, 4H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.3 (d, J = 241.3 Hz), 147.9 (d, J = 11.3 Hz), 130.8 (d, J = 10.0 Hz), 112.2, 107.8 (d, J = 1.3 Hz), 103.7 (d, J = 21.3 Hz), 99.4 (d, J = 25.0 Hz), 58.6, 49.0, 35.2, 29.9, 23.2. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ for $C_{12}H_{14}FN_2S$ 237.0856, found 237.0856.

*4.2.10. 1-(4-Chlorophenyl)-2-(thiocyanatomethyl)pyrrolidine (**3k**)*

White solid; 87% yield, 110 mg; mp 73–75 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, J = 9.0 Hz, 2H), 6.53 (d, J = 9.0 Hz, 2H), 4.07 (t, J = 9.0 Hz, 1H), 3.50 (dd, J = 10.0, 2.5 Hz, 1H), 3.25–3.16 (m, 1H), 2.75 (dd, J = 13.5, 9.5 Hz, 1H), 2.22–2.02 (m, 4H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 129.8, 122.1113.2, 112.2, 58.6, 49.1, 36.3, 30.0, 23.3. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ for $C_{12}H_{13}ClN_2S$ 253.0561, found 253.0571.

*4.2.11. 1-(3-Chlorophenyl)-2-(thiocyanatomethyl)pyrrolidine (**3l**)*

White solid; 75% yield, 95 mg; mp 54–55 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, J = 8.0 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 6.57 (s, 1H), 6.49 (dd, J = 10.0, 1.5 Hz, 1H), 4.11–4.08 (m, 1H), 3.52–3.48 (m, 1H), 3.26–3.19 (m, 2H), 2.77 (dd, J = 23.0, 9.5 Hz, 1H), 2.22–2.02 (m, 4H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 135.5, 130.7, 117.2, 112.22, 112.16, 110.3, 58.6, 49.0, 35.3, 30.0, 23.2. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ for $C_{12}H_{14}ClN_2S$ 253.0561, found 253.0571.

*4.2.12. 1-(4-Bromophenyl)-2-(thiocyanatomethyl)pyrrolidine (**3m**)*

White solid; 66% yield, 98 mg; mp 85–89 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 8.0 Hz, 2H), 6.49 (d, J = 7.5 Hz, 2H), 4.07 (t, J = 15.0 Hz, 1H), 3.50–3.47 (m, 1H), 3.25–3.16 (m, 2H), 2.75 (dd, J = 12.5, 9.5 Hz,1H), 2.22–2.04 (m, 4H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 132.4, 113.8, 112.2, 109.2, 58.6, 49.1, 35.3, 30.0, 23.3. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ for $C_{12}H_{14}BrN_2S$ 297.0056, found 297.0063.

*4.2.13. 1-(3-Iodophenyl)-2-(thiocyanatomethyl)pyrrolidine (**3n**)*

Brown oil; 28% yield, 48 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, J = 7.5 Hz, 1H), 6.97–6.93 (m, 2H), 6.57 (dd, J = 9.5, 1.5 Hz, 1H), 4.08 (t, J = 9.0 Hz, 1H), 3.50–3.46 (m, 1H), 3.25–3.17 (m, 2H), 2.76 (dd, J = 22.5, 9.5 Hz,1H), 2.21–2.00 (m, 4H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 131.1, 126.2, 121.0, 112.2, 111.4, 95.9, 58.4, 48.9, 35.2, 29.9, 23.2. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ for $C_{12}H_{14}IN_2S$ 344.9917. found 344.9921.

*4.2.14. 1-(Naphthalen-1-yl)-2-(thiocyanatomethyl)pyrrolidine (**3o**)*

Brown oil; 61% yield, 82 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16–8.14 (m, 1H), 7.84–7.82 (m,1H), 7.58 (d, J = 8.0 Hz,1H),7.49 (t, J = 3.5 Hz, 2H), 7.41 (t, J = 8.0 Hz, 1H), 7.13 (d, J = 7.5 Hz, 1H), 4.20–4.16 (m, 1H), 3.86–3.82 (m, 1H), 3.27–3.24 (m, 1H), 3.20–3.16 (m, 1H), 2.95–2.91 (m, 1H), 2.41–2.34 (m, 1H), 2.13–1.89 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 135.0, 130.3, 128.4, 126.2, 125.9, 125.86, 125.55, 124.2, 124.1, 115.0, 113.7, 58.5, 56.8, 38.7, 30.3, 24.1. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ for $C_{16}H_{17}N_2S$ 269.1107, found 269.1116.

4.2.15. 2-Methyl-1-phenyl-5-(thiocyanatomethyl)pyrrolidine (**3p**)

White solid; 83% yield, 96 mg; mp 66–67 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.23 (m, 2H), 6.72 (t, *J* = 7.0 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 4.21 (t, *J* = 8.0 Hz, 1H), 4.14–4.09 (m, 1H), 3.27 (d, *J* = 13.5 Hz, 1H), 2.61 (dd, *J* = 22.5, 9.5 Hz,1H), 2.38–2.30 (m, 1H), 2.22–2.14 (m, 1H), 2.04 (dd, *J* = 12.5, 7.0 Hz, 1H), 1.75 (dd, *J* = 12.5, 7.0 Hz, 1H), 1.25 (d, *J* = 11.0 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 129.8, 116.9, 113.9, 112.3, 57.5, 53.6, 34.4, 30.3, 27.4, 18.0. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ for $C_{13}H_{17}N_2S$ 233.1107, found 233.1108.

4.2.16. 1,4,4-Triphenyl-2-(thiocyanatomethyl)pyrrolidine (**3q**)

White solid; 21% yield, 39 mg; mp 177–183 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.33 (m, 3H), 7.31–7.25 (m, 5H), 7.25–7.20 (m, 4H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.97 (t, *J* = 6.5 Hz, 1H), 4.30 (d, *J* = 12.5 Hz, 1H), 3.99 (d, *J* = 11.0 Hz, 1H), 3.31 (t, *J* = 10.5 Hz, 1H), 3.31–3.28 (m, 3H), 2.55 (t, *J* = 12.5 Hz, 1H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 146.5, 144.6, 129.6, 128.8, 128.7, 128.4, 127.0, 126.8, 126.6, 121.4, 117.7, 110.4, 58.8, 56.5, 48.2, 42.4, 41.9. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ for $C_{24}H_{23}N_2S$ 371.1577, found 371.1594.

4.2.17. 1-Benzyl-4,4-diphenyl-2-(thiocyanatomethyl)pyrrolidine (**3r**)

White solid; 24% yield, 46 mg; mp 156–159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.34 (m, 2H), 7.31–7.29 (m, 7H), 7.23–7.22 (m, 2H), 7.19–7.15 (m, 2H), 7.09 (d, *J* = 6.5 Hz, 2H), 3.65–3.56 (m, 3H), 3.21 (d, *J* = 6.5 Hz, 1H), 3.14 (t, *J* = 10.5 Hz, 1H), 2.92 (d, *J* = 12.5 Hz, 1H), 2.42 (t, J = 12.0, 1H), 2.37–2.31 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 144.6, 137.4, 129.4, 128.64, 128.58, 128.55, 128.4, 127.7, 126.7, 126.6, 126.3, 110.6, 62.7, 61.8, 59.2, 48.1, 42.7, 41.8. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ for $C_{25}H_{25}N_2S$ 385.1733, found 385.1738.

4.2.18. 1-Phenyl-2-(thiocyanatomethyl)piperidine (**3s**)

Brown oil; 42% yield, 49 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.91 (t, *J* = 7.0 Hz, 1H), 4.06–4.02 (m, 1H), 3.32–3.28 (m, 1H), 3.20–3.16 (m, 1H), 3.04 (dd, *J* = 12.5, 9.0 Hz, 1H), 3.00–2.94 (m, 1H), 1.93–1.88 (m, 2H), 1.74–1.60 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.1, 129.6, 120.9, 118.2, 112.8, 56.1, 46.0, 33.6, 27.0, 25.2, 19.8. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ for $C_{13}H_{17}N_2S$ 233.1107, found 233.1101.

4.2.19. 2-(Thiocyanatomethyl)-1-(p-tolyl)piperidine (**3t**)

Light yellow oil; 52% yield, 64 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 3.91–3.83 (m, 1H), 3.17–3.10 (m, 2H), 3.05–3.00 (m, 1H), 2.98–2.91 (m, 1H), 2.28 (s, 3H), 1.92–1.84 (m, 2H), 1.74–1.58 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 131.0, 130.1, 119.2, 113.0, 56.5, 47.7, 34.2, 27.4, 25.3, 20.7, 20.3. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ for $C_{14}H_{19}N_2S$ 247.1264, found 247.1275.

4.2.20. 1-(4-Chlorophenyl)-2-(thiocyanatomethyl)piperidine (**3u**)

Yellow oil; 54% yield, 72 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 4.02–3.97 (m, 1H), 3.26 (dt, *J* = 12.5, 3.5 Hz, 1H), 3.17–3.12 (m, 1H), 3.03–2.97 (m, 1H), 2.94 (td, *J* = 10.0, 3.0 Hz, 1H), 1.96–1.84 (m, 2H), 1.75–1.51 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 129.4, 125.4, 119.0, 112.5, 56.1, 45.6, 33.2, 26.7, 24.9, 19.4. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ for $C_{13}H_{16}ClN_2S$ 267.0717, found 267.0711.

4.3. General procedure for the cyclization of 2-allylaniline compounds with NaSCN

To a round-bottom flask was charged with compunds 1 (0.5 mmol), EtOAc (4 mL) NaSCN (1.5 mmol) and I_2 (1.75 mmol) successively. Then the resulting mixture was stirred under open-flask conditions at 70 °C (oil bath temperature) for 8 h. The reaction was quenched with saturated solution of $Na_2S_2O_3$. The organic phase was separated, and the aqueous layer was extracted with EtOAc (5 × 3 mL). The combined organic solution was dried with Mg_2SO_4 and concentrated in vacuo. The residue was purified by a column chromatography to give the corresponding products **5** in yields as listed in Table 4.

4.3.1. 1-Ethyl-2-(thiocyanatomethyl)indoline (**5a**)

Brown oil; 42% yield, 46 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11–7.10 (m, 2H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 4.08–4.03 (m, 1H), 3.37–3.28 (m, 4H), 3.18–3.10 (m, 1H), 2.96 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.14 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 128.0, 127.9, 124.7, 119.0, 112.8, 108.3, 61.4, 41.4, 38.3, 34.3, 11.2. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ for $C_{12}H_{15}N_2S$ 219.0951, found 219.0959.

4.3.2. 1-Benzyl-2-(thiocyanatomethyl)indoline (**5b**)

White oil; 52% yield, 72 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.27 (m, 5H), 7.10 (t, *J* = 7.0 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 4.38 (d, *J* = 16.0 Hz, 1H), 4.30 (d, *J* = 16.0 Hz, 1H), 4.06–4.00 (m, 1H), 3.36 (dd, *J* = 16.0, 9.5 Hz, 1H), 3.18 (d, *J* = 5.0 Hz, 2H), 3.01 (dd, J = 16.0, 8.5, Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 138.0, 129.0, 128.1, 127.7, 127.6, 127.4, 124.7, 119.1, 112.7, 108.1, 63.4, 52.6, 38.4, 34.4. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ for $C_{17}H_{17}N_2S$ 281.1107, found 218.1104.

4.3.3. 1-(Furan-2-ylmethyl)-2-(thiocyanatomethyl)indoline (**5c**)

White solid; 33% yield, 45 mg; mp 59–62 °C. 1H NMR (500 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.30 (s, 1H), 6.22 (s, 1H), 4.50 (d, *J* = 16.5 Hz, 1H), 4.40 (d, *J* = 16.5 Hz, 1H), 3.93 (d, *J* = 6.0 Hz, 1H), 3.73 (d, *J* = 12.0 Hz, 1H), 3.50 (dd, *J* = 12.0, 6.5 Hz, 1H), 3.32 (dd, *J* = 16.5, 4.5 Hz, 1H), 3.05 (dd, *J* = 16.5, 6.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 143.5, 142.4, 130.0, 128.2, 118.4, 118.3, 112.3, 111.8, 110.5, 108.2, 53.5, 48.1, 43.2, 34.4. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ for $C_{15}H_{15}N_2OS$ 271.0900, found 271.0904.

4.3.4. 1-(Naphthalen-1-ylmethyl)-2-(thiocyanatomethyl)indoline (**5d**)

Light yellow solid; 30% yield, 50 mg; mp 125–138 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 25.5, 5.5 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 4.5 Hz, 2H), 7.43–7.38 (m, 2H), 7.06 (s, 2H), 6.74 (t, *J* = 7.0 Hz, 1H), 6.61 (d, *J* = 15.0 Hz, 1H), 4.94 (q, *J* = 16.5 Hz, 2H), 3.97 (s, 1H), 3.74 (d, *J* = 12.5 Hz, 1H), 3.52–3.49 (m, 1H), 3.43 (d, *J* = 17.0 Hz, 1H), 3.16 (d, *J* = 14.5 Hz, 1H). ^{13}C NMR (125 MHz, CDCl3) δ 144.3, 134.1, 132.0, 131.2, 130.0, 129.1, 128.5, 128.2, 125.7, 126.5, 126.1, 124.5, 122.9, 118.2, 118.1, 112.3, 111.6, 53.5, 53.3, 43.3, 34.6. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ for $C_{21}H_{19}N_2S$ 331.1264, found 331.1268.

4.3.5. 1-Benzyl-5-fluoro-2-(thiocyanatomethyl)indoline (**5e**)

White solid; 23% yield, 35 mg; mp 74–83 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.28 (m, 5H), 6.81 (d, *J* = 7.0 Hz, 1H), 6.72 (t, *J* = 9.0 Hz, 1H), 6.25 (dd, *J* = 4.0 Hz, 1H), 4.32 (d, *J* = 16.0 Hz, 1H), 4.23 (d, *J* = 16.0 Hz, 1H), 4.04–3.99 (m, 1H), 3.35–3.30 (m, 1H) 3.18–3.17 (m, 2H), 2.98 (dd, *J* = 16.5, 8.5 Hz, 1H). ^{13}C NMR (125 MHz, CDCl3) δ 158.1, 156.2, 148.1, 137.7, 129.0, 127.8, 127.6, 113.9 (d, *J* = 12.5 Hz), 112.6, 112.3 (d, *J* = 25.0 Hz), 108.5 (d, *J* = 5.0 Hz), 63.9, 53.3, 38.3,

34.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ for $C_{17}H_{16}FN_2S$ 299.1013, found 299.1011.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2018.04.023.

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