DOI: 10.1002/ejoc.200700462

Synthesis and Rearrangement of 1,2,3-Triheteroaryl(aryl)-Substituted Aziridines

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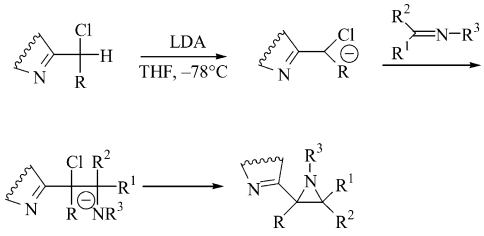
Keywords: Aziridines / Enamines / Rearrangement / Carbanions / Nitrogen heterocycles

Aziridines carrying three (or two) heteroaryl groups with electron-withdrawing effects were synthesised with sufficient diastereoselectivity. The *cis* aziridines are susceptible to ring opening and rearrangement when the formation of secondary enamines in stable hexacyclic structures with a N–H···N hydrogen bond is possible.

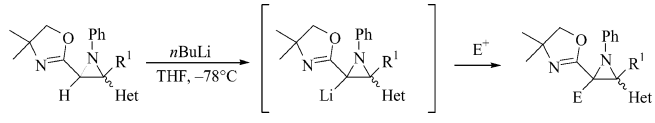
Introduction

The great interest in the synthesis and reactivity of aziridines, one of the most valuable three-membered ring systems in modern synthetic chemistry, is due to their widely recognised versatility as significant intermediates for the synthesis of biologically and pharmacologically active compounds.[1,2] Recently, a review on the ability of this small heterocycle to undergo ring-opening reactions with a wide variety of nucleophiles was reported.[3] The synthesis of amino acids,[4] azasugars,[5] chiral ligands,[6] natural products[7] and more generally, nitrogen-containing organic compounds are some of the main synthetic applications. Moreover, further potential applications are possible with aziridines containing heterocyclic substituents, which are capable of freeing masked carbonyl functionalities.[8] Many synthetic approaches for the synthesis of aziridines have been reported in the literature, including reactions between nitrenes and olefins[9] or between carbenes and imines.[10] Those involving the cyclisation of β-amino alcohols seem to be particularly interesting.[11] Preparative methodologies for chiral aziridines have also been extensively reviewed.[1a,12] Our research group has recently developed methodology for a simple, diasteroselective synthesis of several heterocycle-substituted aziridines on the basis of the Darzens reaction between α-chloroalkyl heterocycles and imines[13] (Scheme 1).



Scheme 1.

The functionalisation of these three-membered rings through the generation of the aziridinyl anion at C2 or C3, and then reaction with electrophilic groups to form more complex aziridines is also very interesting. Many studies have been reported concerning the stability and reactivity of aziridines and aziridinyl anions.[14] It has been reported that the presence of an electron-withdrawing group, such as a *para*-tolylsulfonyl group, at the aziridine nitrogen atom is crucial for the stabilisation of the developing negative charge during the reaction and so for the ring-opening reaction to occur. Aziridine and aziridinyl anion binding α-azaheterocycles (EWG groups) at C2 and/or C3 seem fairly stable, particularly when one of these is the oxazoline.[2b,14] In fact, the diastereoselective functionalisation of aziridines by formation of aziridinyllithiums and quenching with electrophiles has been reported (Scheme 2).



Scheme 2.

In contrast, we think it would be interesting to study aziridines substituted with more electron-withdrawing groups, such as a heteroaryl moiety, and particularly those carrying a third azaheterocycle on the nitrogen atom. According to the results of the literature,[15] the stability of such an aziridine ring could change and, under basic conditions, result in ring opening. Recently, we discovered that 1,2,3-triheterocycle-substituted aziridines carrying the nonaromatic oxazoline heterocycle at C2 were easily and stereoselectively obtained and also functionalised by the formation, with strong base, of stable aziridinyl anions and coupling with electrophiles, as described in Scheme 2.[16] To further clarify the

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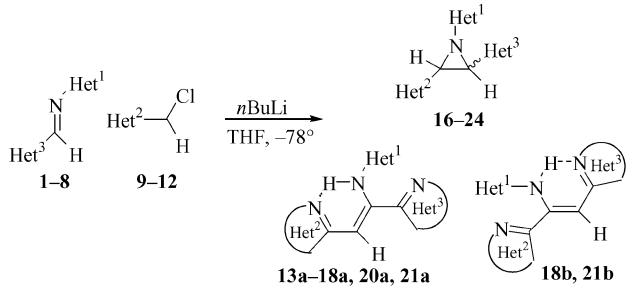
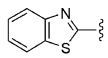
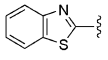
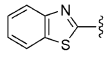
possibility of synthesis and stability of this strained ring, we now report the notable and unexpected results we acquired from the synthesis of 1,2,3-triheteroaryl- and 1-phenyl-2,3-diheteroaryl-substituted aziridines.

Results and Discussion

Darzens methodology was used for the construction of the aziridine rings as summarised in Table 1. Already known (*E*)-heteroarylimines **3**, **5**[17], **6**, **7**[18] and **8**,[19] unknown **1**, **2** and **4** and chloromethyl heteroaryl compounds **9**–**12** were prepared as described in the Experimental Section. 2-Chloromethyl pyridine **9** was lithiated with *n*BuLi in THF at –78 °C under an atmosphere of nitrogen and added to imine **3**. The reaction mixture was gradually warmed to room temperature and then stirred overnight (13–15 h). After quenching with aqueous ammonium chloride, only **13a** was isolated in good yield; the structure of which corresponded to a secondary enamine on the basis of spectroscopic data; whereas no trace amounts of aziridine were found (Table 1, Entry 1). Stable enamine **14a** was also isolated as a pure product from the reaction of 2-chloromethylpyridinyllithium, derived from deprotonation of **9**, with imine **4** (Table 1, Entry 2), whereas enamine **15a** was isolated when α-chloromethyl-4-methylthiazolyllithium, derived from **11**, was treated with imine **5** (Table 1, Entry 3). The configuration of the enamino moiety (*Z*) and the conformation (s-*cis*) of the obtained compounds were established by NMR spectroscopic studies and by comparison with **21a**, which was obtained in the analogous reaction of 2-chloromethylpyridinyllithium with imine **7** (Table 1, Entry 9), and whose X-ray data[20] also showed a hexacyclic structure with a strong intramolecular N–H···N hydrogen bond (Figure 1).

Table 1. Coupling reaction between heteroarylimines **1**–**8** and chloromethyl heteroaryl compounds **9**–**12**.



Entry		Het[1]	Het[2]	Het[3]	Total yield % [a]	Product distribution (%)[b]			
1	**3**				65	–	–	**13a**	–
2	**4**				41	–	–	**14a**	–
3	**5**				66	–	–	**15a**	–
4	**2**				65	(*R**,*S**)-**16** (56)	(*R**,*R**)-**16** (31)	**16a** (13)	–
5	**2**				65	(*R**,*S**)-**17** (72)	(*R**,*R**)-**17** (26)	**17a** (2)	–
6	**1**				92	(*R**,*S**)-**18** (70)	–	**18a** (15)	**18b** (15)
7	**3**				90	(*R**,*S**)-**19** (35)	(*R**,*R**)-**19** (65)	–	–
8	**6**	Ph			75	–	(*R**,*R**)-**20** (25)	**20a** (75)	–
9	**7**	Ph			80	(*R**,*S**)-**21** (11)	(*R**,*R**)-**21** (61)	**21a** (25)	**21b** (3)
10	**8**	Ph			79	(*R**,*S**)-**22** (12)	(*R**,*R**)-**22** (88)	–	–
11	**8**	Ph			94	–	(*R**,*R**)-**23** (100)	–	–
12	**6**	Ph			85	(*R***S**)-**24** (50)	(*R***R**)-**24** (50)	–	–

[a] Isolated yields. [b] Diastereomeric ratios evaluated by GC and ^{1}H NMR spectroscopy.

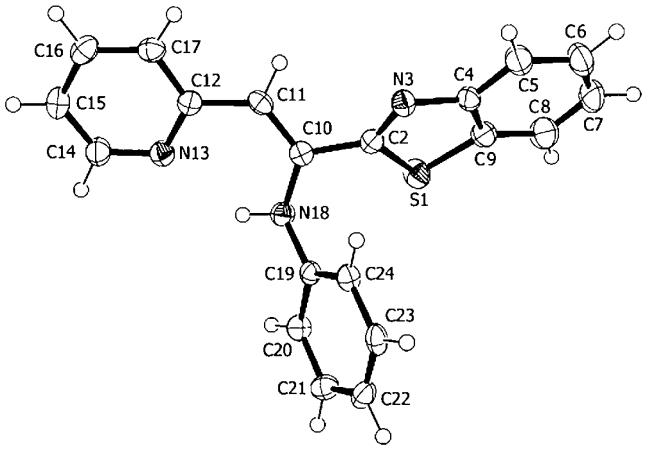
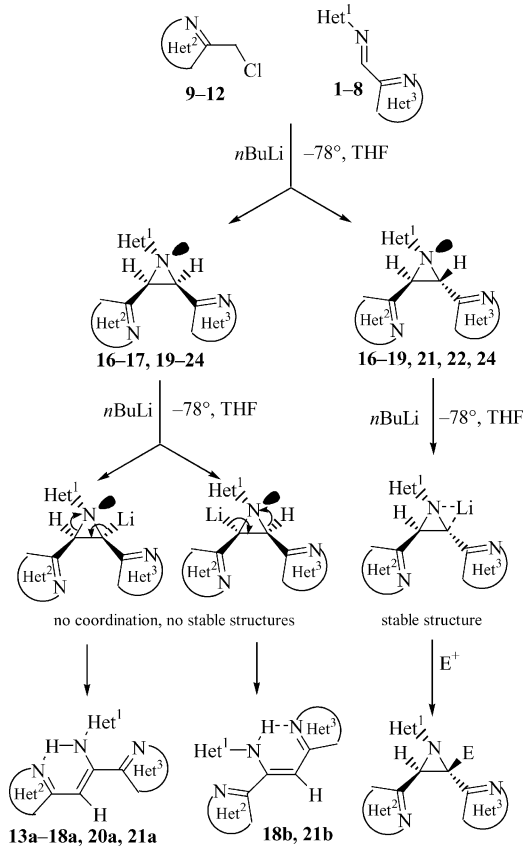


Figure 1. Plot of one independent molecule of compound **21a** with numbering scheme. Ellipsoids at 50% probability level, H atoms not to scale.

To the best of our knowledge, only two examples with similar structures have been reported: (1) the [2+2] cycloaddition reaction of an oxazolinyl alkylamide with dimethyl fumarate[21] and (2) the reaction of azaenolates of 2-alkyloxa(thia)zolines with imidoyl chlorides.[22] The ^{1}H NMR chemical shift (11.10–11.70 ppm) for the enamine hydrogen of our compounds was in accordance with those from the literature.

When 2-chloromethylpyridinyllithium was treated with imine **2**, under the same reaction conditions, stable aziridine **16** was isolated in two diastereomeric forms [(*R**,*S**)/(*R**,*R**), 56:31] and the product of its own rearrangement **16a** (13%; Table 1, Entry 4). 2-Chloromethylbenzothiazolyllithium, derived from deprotonation of **10**, was also treated with imine **2**, with the same reaction time and under the same conditions, and produced aziridine **17** in two diastereomeric forms [(*R**,*S**)/(*R**,*R**), 72:26] and enamine **17a** (2%; Table 1, Entry 5). A greater quantity of enamine was isolated when the same 2-chloromethylbenzothiazolyllithium was coupled with imine **1** (Table 1, Entry 6). Apart from aziridine **18** in the diastereomeric forms (*R**,*S**), two enamines, **18a** and **18b**, were isolated in an equal ratio. Aziridine and enamine were also formed together when a phenyl group was bound at the nitrogen atom of starting imine **6** or **7** (Table 1, Entries 8, 9). The complete analysis of the results reported in Table 1 indicates that the aziridine, with at least two heterocycles at C2 and C3, is not stable and, under basic conditions, has a propensity to undergo deprotonation at C2 or at C3 because of the groups with stronger electron-withdrawing capabilities that are connected to them. The stability of the aziridinyllithium that is formed is linked to the possibility to coordinate the Li^+ from the aziridine nitrogen atom. This occurs if the aziridinyl anion is produced from the *trans* structure, and therefore, the ring opening occurs with difficulty and does not rearrange; moreover, in the presence of an electrophile, it can be captured. Instead, the lack of coordination with the Li^+ ion in the aziridinyl anion produced from the *cis* structure causes ring opening and rearrangement in a very stable enamine structure. In any case, we think the presence of a nearby α-aza functionality is important for rearrangement and for stabilisation of the hexacyclic structure through the formation of an N–H···N hydrogen bond (Scheme 3). Indeed, ring opening and rearrangement did not occur when it was possible for deprotonation to take place on the C atom bearing Het^3, which has an α-aza group with strong electron-withdrawing effects: only a mixture of *cis* and *trans* aziridines was isolated, and in the absence of an α-aza group on Het^2, enamine coordination through the construction of a hexacyclic structure was impossible (Table 1, Entries 7, 12). At last, under the conditions listed in Table 1, Entry 11, the possibility for rearrangement did not exist, and the aziridine was isolated in good yield; the lack of an α-aza group at C2 and C3 did not favour deprotonation and the possible formation of the hexacyclic system with a strong N–H–N hydrogen bond.



Scheme 3.

As confirmation of our hypothesis, when 2-chloromethylpyridinyllithium was treated with imine **7** (e.g., Table 1, Entry 9) and the reaction was quenched after just 20 min, only aziridines (*R**,*S**)-**21** and (*R**,*R**)-**21** were isolated (10:90 ratio, 50% yield) and no trace amounts of enamines **21a** and **21b** were observed. Aziridine (*R**,*S**)-**21** was then deprotonated with *n*BuLi at –78 °C in THF and quenched after 2 h with D_2O. The starting material deuterated at C2 and C3 was recovered, which points out the high stability of the *trans* aziridinyl anion. Under the same conditions, aziridine (*R**,*R**)-**21** was transformed completely into en-

amines **21a** and **21b**, which points out the tendency of the *cis* aziridinyl anion to undergo rearrangement.

Conclusions

We prepared aziridines with good diastereoselectivity and carrying three (or two) heteroaryl groups with strong electron-withdrawing effects. The *cis* aziridines are susceptible to ring opening and rearrangement when the formation of secondary enamines in stable hexacyclic structures with a N–H···N hydrogen bond is granted. The formation of these compounds is unprecedented in organic synthesis and could reveal a variety of interests.

Experimental Section

General Remarks: *n*-Butyllithium (*n*BuLi) was a commercial solution in hexanes (Aldrich) and was titrated with *N*-pivaloyl-*o*-toluidine prior to use.[23] THF, triethylamine, 4-formylmorpholine, 2-pyridinecarboxaldehyde, 3-pyridinecarboxaldehyde, 4-pyridinecarboxaldehyde, 4-methylthiazole, 2-aminothiazole, methanesulfonyl chloride, 2-aminopyridine, 3-aminopyridine, 2-aminothiophenol, glycolic acid, 2-(chloromethyl)pyridine hydrochloride and 4-(chloromethyl)pyridine hydrochloride were of commercial grade (Aldrich) and used without further purification. Aniline and benzaldehyde were of commercial grade (Aldrich) and purified by distillation prior to use. Substrate **10** was obtained by reaction of 2-aminothiophenol with glycolic acid and subsequent halogenation.[24] Compound **11** was prepared by formylation of 4-methylthiazole, reduction of the so-obtained 2-thiazolylaldehyde and subsequent halogenation, following reported synthetic protocols.[13b] Petroleum ether refers to the 40–60 °C boiling fraction. The ^{1}H and the ^{13}C NMR spectra were recorded with a Bruker Avance 400 apparatus (400.13 and 100.62 MHz, for ^{1}H and ^{13}C, respectively) with $CDCl_3$ as the solvent and TMS as an internal standard (δ = 7.24 ppm for ^{1}H spectra; δ = 77.0 ppm for ^{13}C spectra). The IR spectra were recorded with an FTIR spectrophotometer Digilab Scimitar Series FTS 2000. GC–MS analyses were performed with an Agilent Technologies 6850 series II gas chromatograph (5% phenylpolymethylsiloxane capillary column, 30 m, 0.25 mm i.d.), equipped with a 5973 Network mass-selective detector operating at 70 eV. The electrospray ionisation [HRMS (ESI)] experiments were carried out in a hybrid QqTOF mass spectrometer (PE SCIEX-QSTAR) equipped with an ion-spray ionisation source. MS (+) spectra were acquired by direct infusion (5 μL min^{-1}) of a solution containing the appropriate sample (10 pmol μL^{-1}) dissolved in a solution 0.1% acetic acid, methanol/water (50:50) at the optimum ion voltage of 4800 V. The nitrogen gas flow was set at 30 psi (pounds per square inch) and the potentials of the orifice, the focusing ring and the skimmer were kept at 30, 50 and 25 V relative to ground, respectively. Melting points were determined with an Electrothermal melting point apparatus and are uncorrected. TLC was performed on Merck silica gel plates with F-254 indicator; viewing was by UV light (254 nm). Flash chromatography was performed with Merck 230–400 mesh silica gel by using petroleum ether/diethyl ether (Et_2O) or ethyl acetate (AcOEt) mixtures as eluants. All reactions involving air-sensitive reagents were performed under an atmosphere of nitrogen in oven-dried glassware by using syringe/septum cap techniques.

General Procedure for the Preparation of Heteroarylimines 1–8: Heteroarylimines **1**–**8** were prepared by dehydration reaction of the appropriate amine (1 mmol) with the corresponding aldehyde (1 mmol) in anhydrous Et_2O, in the presence of molecular sieves (Aldrich, 4 A°, 1.6 mm pellets, 7 g) for 7–16 h, following the protocol of Taguchi.[25]

***N*-[(1*E*)-Pyridin-2-ylmethylene]pyridin-3-amine (1):** Yield: 114 mg (62.5%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.36 (dd, J = 5.2, 8.0 Hz, 1 H), 7.39–7.42 (m, 1 H), 7.58–7.61 (m, 1 H), 7.83 (t, J = 7.7 Hz, 1 H), 8.21 (d, J = 7.7 Hz, 1 H), 8.52 (d, J = 4.7 Hz, 1 H), 8.57 (d, J = 2.0 Hz, 1 H), 8.62 (s, 1 H), 8.74 (d, J = 4.7 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 122.1, 123.7, 125.5, 127.7, 136.7, 143.0, 146.8, 147.8, 149.8, 154.0, 162.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3059, 2984, 1632, 1588, 1476, 1438, 1418 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 183 (91) [M]$^+$, 182 (100), 155 (86), 130 (21), 105 (25), 78 (70). HRMS (ESI): calcd. for $C_{11}H_{10}N_3$ 184.17130 [M + H]$^+$; found 184.17129.

***N*-[(1*E*)-Pyridin-4-ylmethylene]pyridin-2-amine (2):** Yield: 115 mg (63%), yellow solid. M.p. 46–48 °C (petroleum ether). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.36 (dd, J = 4.8, 8.3 Hz, 1 H), 7.55–7.58 (m, 1 H), 7.77 (d, J = 6.0 Hz, 2 H), 8.48 (s, 1 H), 8.52–8.55 (m, 2 H), 8.79 (d, J = 6.0 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 122.2, 123.7, 127.8, 142.1, 142.5, 146.7, 148.1, 150.7, 159.7 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3059, 2986, 1632, 1600, 1560, 1476, 1417, 1320, 1229, 1185 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 183 (100) [M]$^+$, 182 (84), 155 (10), 105 (42), 78 (74). HRMS (ESI): calcd. for $C_{11}H_{10}N_3$ 184.17130 [M + H]$^+$; found 184.17127.

***N*-[(1*E*)-Pyridin-2-ylmethylene]thiazol-2-amine (4):** Yield: 110 mg (58.3%), yellow solid. M.p. 71.6–73.1 °C (petroleum ether). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.29 (d, J = 3.4 Hz, 1 H), 7.39–7.43 (m, 1 H), 7.74 (d, J = 3.4 Hz, 1 H), 7.83 (t, J = 6.8 Hz, 1 H), 8.26 (d, J = 7.8 Hz, 1 H), 8.75 (d, J = 4.3 Hz, 1 H), 9.08 (s, 1 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 119.0, 122.9, 125.8, 136.6, 141.8, 150.0, 153.4, 163.6, 172.0 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3059, 2994, 1625, 1609, 1499, 1470, 1215, 1138 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 189 (100) [M]$^+$, 188 (55), 162 (35), 105 (24), 78 (20). HRMS (ESI): calcd. for $C_9H_8N_3S$ 190.12774 [M + H]$^+$; found 190.12771.

General Procedure for the Preparation of Compounds 13–24: To a stirred mixture of imine **1**–**8** (1.0 mmol) and **9**–**12** (1.0 mmol) in THF (10 mL) was added dropwise *n*BuLi (2.5 M in hexane, 0.6 mL, 1.5 mmol) at –78 °C under an atmosphere of nitrogen. After 20 min the resulting mixture was warmed slowly to room temperature and then, after overnight, quenched with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with Et_2O (3 × 20 mL), and the combined organic layer was dried with anhydrous Na_2SO_4 and concentrated in vacuo. The crude mixture was flash-chromatographed (silica gel, petroleum ether/Et_2O, 2:8 for **13a**; 4:6 for **15a**, **20**–**24**; 1:9 for **16**–**19**; petroleum ether/AcOEt, 4:6 for **14a**) to afford pure products **13**–**24** (41–90%).

[1-(4-Methylthiazol-2-yl)-2-pyridin-2-ylvinyl]pyridin-2-ylamine (13a): Yield: mg 191 (65%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.43 (s, 3 H), 638–6.40 (m, 2 H), 6.65–6.68 (m, 1 H), 6.83 (s, 1 H), 6.97–7.00 (m, 1 H), 7.16–7.19 (m, 1 H), 7.31 (td, J = 2.0, 8.2 Hz, 1 H), 7.54 (td, J = 1.0, 7.7 Hz, 1 H), 8.11 (d, J = 4.0 Hz, 1 H), 8.51 (d, J = 4.0 Hz, 1 H), 11.31 (br. s, exchanges with D_2O, 1 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 17.3, 110.1, 112.7, 115.1, 116.2, 120.4, 124.6, 136.3, 137.0, 137.8, 148.1, 148.3, 153.1, 155.5, 156.7, 166.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3350 (br.), 3058, 2965, 2828, 2806, 1621, 1593, 1499, 1472, 1437, 1305, 1257, 1151 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 294 (18) [M]$^+$, 293 (10), 216 (100), 144 (9), 78 (25). HRMS (ESI): calcd. for $C_{16}H_{15}N_4S$ 295.10195 [M + H]$^+$; found 295.10190.

(1,2-Dipyridin-2-ylvinyl)thiazol-2-ylamine (14a): Yield: 115 mg (41%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 6.17 (s, 1 H), 6.58 (d, J = 3.6 Hz, 1 H), 7.08 (dd, J = 6.0, 7.4 Hz, 1 H), 7.18–7.23 (m, 2 H), 7.30 (dd, J = 6.0, 7.4 Hz, 1 H), 7.58 (d, J = 7.9 Hz, 1 H), 7.64 (td, J = 1.8, 7.9 Hz, 1 H), 7.69 (td, J = 1.9, 7.9 Hz, 1 H), 8.60 (d, J = 4.5 Hz, 1 H), 8.70 (d, J = 4.6 Hz, 1 H), 11.18 (br. s, exchanges with D_2O, 1 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 108.7, 111.1, 120.3, 123.4, 123.9, 124.2, 136.3, 136.5, 138.8, 144.3, 147.8, 149.7, 154.2, 156.9, 165.2 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3297 (br.), 3061, 2958, 1632, 1590, 1521, 1469, 1373, 1159 cm^{-1}. GC–MS (70 eV): m/z (%) = 280 (35) $[M]^+$, 247 (90), 202 (100), 78 (38) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{13}N_4S$: 281.08629, $[M + H]^+$; found 281.08627

[1,2-Bis(4-methylthiazol-2-yl)vinyl]thiazol-2-ylamine (15a): Yield: 211 mg (66%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.49 (s, 3 H), 2.50 (s, 3 H), 6.46 (s, 1 H), 6.70 (d, J = 3.5 Hz, 1 H), 6.78 (s, 1 H), 7.00 (s, 1 H), 7.28 (d, J = 3.5 Hz, 1 H), 11.21 (br. s, exchanges with D_2O, 1 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 17.2, 103.47, 103.50, 112.3, 116.1, 136.7, 139.0, 153.3, 153.8, 162.2, 163.9, 164.5 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3225 (br.), 3116, 2980, 2927, 2863, 1617, 1522, 1443, 1263, 1156, 1112 cm^{-1}. GC–MS (70 eV): m/z (%) = 320 (94) $[M]^+$, 319 (47), 287 (100), 222 (96). HRMS (ESI): calcd. for $C_{13}H_{13}N_4S$ 321.03049 $[M + H]^+$; found 321.03048.

2-(1-Pyridin-3-yl-3-pyridin-4-ylaziridin-2-yl)pyridine (16)

(*R,*S**)-16:** Yield: 100 mg (36.4%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.81 (d, J = 2.6 Hz, 1 H), 4.18 (d, J = 2.6 Hz, 1 H), 6.99–7.05 (m, 2 H), 7.13–7.16 (m, 1 H), 7.29 (d, J = 5.9 Hz, 2 H), 7.43 (d, J = 7.8 Hz, 1 H), 7.67 (td, J = 1.7, 7.8 Hz, 1 H), 8.03–8.04 (m, 1 H), 8.14 (dd, J = 1.7, 4.4 Hz, 1 H), 8.37 (d, J = 4.4 Hz, 1 H), 8.58 (d, J = 5.9 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 45.9, 50.7, 121.9, 122.7, 123.1, 124.1, 127.6, 136.5, 142.7, 143.4, 144.2, 145.9, 149.2, 149.8, 152.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3079, 3036, 2967, 2929, 2856, 1602, 1590, 1479, 1424 cm^{-1}. GC–MS (70 eV): m/z (%) = 274 (11) $[M]^+$, 273 (7), 196 (100), 181 (21), 169 (16), 78 (35). HRMS (ESI): calcd. for $C_{17}H_{15}N_4$ 275.12985 $[M + H]^+$; found 275.12981.

(*R,*R**)-16:** Yield: 55 mg (20%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.75 (d, J = 6.7 Hz, 1 H), 3.94 (d, J = 6.7 Hz, 1 H), 7.03 (t, J = 7 Hz, 1 H), 7.17–7.24 (m, 4 H), 7.35 (d, J = 7.5 Hz, 1 H), 7.47 (t, J = 7.5 Hz, 1 H), 8.29 (d, J = 4.2 Hz, 1 H), 8.36–8.42 (m, 4 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 47.6, 49.7, 121.9, 122.6, 122.7, 123.7, 127.1, 136.2, 142.5, 143.8, 144.9, 149.0, 149.38, 149.45, 154.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3061, 3038, 2972, 1601, 1587, 1479, 1405, 1275 cm^{-1}. GC–MS (70 eV): m/z (%) = 274 (21) $[M]^+$, 196 (100), 181 (15), 169 (12), 92 (17), 78 (15). HRMS (ESI): calcd. for $C_{17}H_{15}N_4$ 275.12985 $[M + H]^+$; found 275.12980.

Pyridin-3-yl-(2-pyridin-2-yl-1-pyridin-4-yl-vinyl)amine (16a): Yield: 23 mg (8.5%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 5.81 (s, 1 H), 6.80 (d, J = 8.2 Hz, 1 H), 6.98 (dd, J = 4.7, 8.1 Hz, 1 H), 7.06 (dd, J = 5.2, 6.6 Hz, 1 H), 7.18 (d, J = 8.1 Hz, 1 H), 7.37 (d, J = 5.9 Hz, 2 H), 7.64 (td, J = 1.7, 7.9 Hz, 1 H), 8.10 (d, J = 3.6 Hz, 1 H), 8.20 (d, J = 2.6 Hz, 1 H), 8.54 (d, J = 4.2 Hz, 1 H), 8.58 (d, J = 5.9 Hz, 2 H), 11.72 (br. s, exchanges with D_2O, 1 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 107.3, 119.9, 122.2, 123.1, 123.8, 127.1, 136.4, 138.5, 142.3, 142.5, 144.5, 145.2, 147.6, 150.1, 157.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3250 (br.), 3060, 2965, 2929, 1626, 1594, 1471, 1414, 1262 cm^{-1}. GC–MS (70 eV): m/z (%) = 274 (19) $[M]^+$, 273 (30), 196 (100), 182 (15), 169 (22), 78 (43). HRMS (ESI): calcd. for $C_{17}H_{15}N_4$ 275.12985 $[M + H]^+$; found 275.12987.

2-(3-Pyridin-4-yl-1-pyridin-3-ylaziridin-2-yl)benzothiazole (17)

(*R,*S**)-17:** Yield: 155 mg (47%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.10 (d, J = 2.2 Hz, 1 H), 4.18 (d, J = 2.2 Hz, 1 H), 7.06–7.13 (m, 2 H), 7.23 (d, J = 5.5 Hz, 2 H), 7.39 (t, J = 7.5 Hz, 1 H), 7.47 (t, J = 7.5 Hz, 1 H), 7.87 (d, J = 7.9 Hz, 1 H), 7.90 (d, J = 8.1 Hz, 1 H), 8.21–8.28 (m, 2 H), 8.59 (d, J = 5.5 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 47.2, 48.3, 121.6, 121.9, 123.2, 123.4, 125.6, 126.5, 127.8, 134.8, 142.7, 143.1, 143.9, 144.5, 150.0, 153.1, 164.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3064, 3037, 2987, 1602, 1480, 1426, 1245 cm^{-1}. GC–MS (70 eV): m/z (%) = 330 (37) $[M]^+$, 252 (100), 148 (11), 78 (10). HRMS (ESI): calcd. for $C_{19}H_{15}N_4S$ 331.10195 $[M + H]^+$; found 331.10191.

(*R,*R**)-17:** Yield: 56 mg (17%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.90 (d, J = 6.5 Hz, 1 H), 4.19 (d, J = 6.5 Hz, 1 H), 7.25–7.29 (m, 1 H), 7.33 (t, J = 8.0 Hz, 1 H), 7.41–7.47 (m, 4 H), 7.66 (d, J = 7.9 Hz, 1 H), 7.93 (d, J = 8.1 Hz, 1 H), 8.40 (dd, J = 1.1, 4.6 Hz, 1 H), 8.50–8.52 (m, 3 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 46.9, 48.2, 121.5, 122.7, 122.8, 123.7, 125.2, 126.1, 127.0, 134.6, 142.1, 142.4, 145.4, 147.8, 149.6, 153.3, 166.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3065, 3039, 2966, 1605, 1585, 1479, 1427, 1241 cm^{-1}.GC–MS (70 eV): m/z (%) = 330 (30) $[M]^+$, 252 (100), 148 (12), 78 (9). HRMS (ESI): calcd. for $C_{19}H_{15}N_4S$ 331.10195 $[M + H]^+$; found 331.10189.

(2-Benzothiazol-2-yl-1-pyridin-4-yl-vinyl)pyridin-3-yl-amine 17a: Yield: 1.0%. GC–MS (70 eV): m/z (%) = 330 (60) $[M]^+$, 329 (55), 252 (100), 196 (50), 78 (40).

2-(3-Pyridin-2-yl-1-pyridin-3-ylaziridin-2-yl)benzothiazole [(*R,*S**)-18]:** Yield: 212 mg (64%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.16 (d, J = 2.6 Hz, 1 H), 4.70 (d, J = 2.6 Hz, 1 H), 7.03–7.06 (m, 1 H), 7.13–7.16 (m, 2 H), 7.38 (t, J = 7.4 Hz, 1 H), 7.48 (t, J = 8.5 Hz, 2 H), 7.67 (td, J = 1.5, 7.6 Hz, 1 H), 7.86 (d, J = 8.0 Hz, 1 H), 7.97 (d, J = 8.0 Hz, 1 H), 8.12–8.16 (m, 2 H), 8.40 (d, J = 4.5 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 45.4, 51.0, 121.7, 122.9, 123.0, 123.1, 123.9, 125.3, 126.3, 127.7, 134.8, 136.5, 142.9, 143.7, 143.8, 149.4, 152.4, 153.5, 167.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3063, 2988, 2857, 1591, 1480, 1425, 1241 cm^{-1}. GC–MS (70 eV): m/z (%) = 330 (80) $[M]^+$, 329 (90), 297 (17), 281 (15), 252 (52), 196 (100), 182 (45). HRMS (ESI): calcd. for $C_{19}H_{15}N_4S$ 331.10195 $[M + H]^+$; found 331.10190.

(2-Benzothiazol-2-yl-1-pyridin-2-yl-vinyl)pyridin-3-yl-amine (18a): Yield: 45 mg (14%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 6.31 (s, 1 H), 6.96–6.98 (m, 1 H), 7.04–7.07 (m, 1 H), 7.26–7.34 (m, 2 H), 7.40 (d, J = 7.8 Hz, 1 H), 7.46 (td, J = 1.1, 7.4 Hz, 1 H), 7.64 (td, J = 1.7, 7.8 Hz, 1 H), 7.82 (d, J = 8.0 Hz, 1 H), 7.94 (d, J = 8.2 Hz, 1 H), 8.17 (dd, J = 1.1, 4.6 Hz, 1 H), 8.22 (d, J = 2.6 Hz, 1 H), 8.68 (dd, J = 1.1, 4.8 Hz, 1 H) 11.18 (br. s, exchanges with D_2O, 1 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 100.3, 121.3, 121.7, 123.2, 123.7, 123.8, 124.3, 126.2, 127.7, 133.4, 136.6, 138.3, 143.0, 143.3, 147.2, 150.8, 153.4, 153.7, 166.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3249 (br.), 3064, 2964, 1621, 1584, 1470, 1435, 1292, 1121 cm^{-1}. GC–MS (70 eV): m/z (%) = 330 (43) $[M]^+$, 329 (58), 281 (9), 252 (100), 238 (33), 207 (16) cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{15}N_4S$ 331.10195 $[M + H]^+$; found 331.10197.

(1-Benzothiazol-2-yl-2-pyridin-2-yl-vinyl)pyridin-3-yl-amine (18b): Yield: 45 mg (14%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 6.59 (s, 1 H), 7.02–7.12 (m, 3 H), 7.30 (d, J = 8.0 Hz, 1 H), 7.39 (t, J = 7.2 Hz, 1 H), 7.50 (t, J = 8.0 Hz, 1 H), 7.67 (td, J = 1.8, 7.8 Hz, 1 H), 7.81 (d, J = 8.0 Hz, 1 H), 8.06 (d, J = 8.0 Hz, 1 H), 8.13 (dd, J = 1.4, 4.0 Hz, 1 H), 8.31 (d, J = 2.6 Hz, 1 H), 8.56 (d, J = 4.6 Hz, 1 H), 11.37 (br. s, exchanges with D_2O, 1 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 110.4, 120.8, 121.7, 123.3, 123.6, 124.7, 125.6, 126.4, 127.0, 135.6, 136.6, 139.3, 139.4, 142.5, 142.8, 147.9, 153.2, 156.6, 165.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3243 (br.), 3063, 2990, 1622, 1588, 1499, 1470, 1434, 1257 cm^{-1}. GC–MS (70 eV): m/z (%) = 330 (45) $[M]^+$, 329 (57), 281 (30), 252 (100), 238 (38), 207

(55) cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{15}N_4S$ 331.10195 $[M + H]^+$; found 331.10196.

2-[2-(4-Methyl-1,3-thiazol-2-yl)-3-pyridin-4-ylaziridin-1-yl]pyridine (19)

(*R,*S**)-19:** Yield: 93 mg (31.5%), oil. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 4.17 (d, J = 2.8 Hz, 1 H), 4.27 (d, J = 2.8 Hz, 1 H), 6.64 (d, J = 8.1 Hz, 1 H), 6.78 (s, 1 H), 6.90 (dd, J = 5.3, 6.4 Hz, 1 H), 7.19 (d, J = 5.8 Hz, 2 H), 7.43 (td, J = 1.7, 9.1 Hz, 1 H), 8.28 (d, J = 5.0 Hz, 1 H), 8.52 (d, J = 5.8 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 16.9, 46.9, 48.1, 114.0, 116.6, 118.9, 122.0, 137.3, 144.7, 148.4, 149.7, 153.2, 158.8, 163.9 ppm. IR (film): $\tilde{\nu}$ = 3077, 2924, 1591, 1468, 1431, 1300, 797, 735 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 294 (24) $[M]^+$, 293 (14), 216 (100), 201 (44), 196 (61), 78 (60), 51 (27). HRMS (ESI): calcd. for $C_{16}H_{14}N_4S$ 295.09392 $[M + H]^+$; found 295.09392.

(*R,*R**)-19:** Yield: 201 mg (68.5%), oil. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 4.08 (d, J = 6.4 Hz, 1 H), 4.27 (d, J = 6.4 Hz, 1 H), 6.68 (s, 1 H), 7.05 (dd, J = 5.1, 7.0 Hz, 1 H), 7.12 (d, J = 8.1 Hz, 1 H), 7.39 (d, J = 4.7 Hz, 2 H), 7.64 (td, J = 1.8, 7.9 Hz, 1 H), 8.33 (d, J = 4.7 Hz, 1 H), 8.49 (d, J = 5.7 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 16.8, 46.4, 47.5, 113.8, 115.6, 119.8, 123.1, 138.1, 143.2, 148.5, 149.2, 153.1, 162.6, 164.6 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3072, 3030, 2923, 1592, 1469, 1433, 1285, 1147, 823, 789, 743 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 294 (22) $[M]^+$, 293 (12), 216 (100), 201 (35), 196 (56), 78 (40), 51 (14). HRMS (ESI): calcd. for $C_{16}H_{14}N_4S$ 295.09392 $[M + H]^+$; found 295.09392.

2-(1-Phenyl-3-pyridin-2-ylaziridin-2-yl)pyridine [(*R,*R**)-20]:** Yield: 51 mg (18.7%), yellow solid. M.p. 109.5–110.3 °C (petroleum ether). ^1H NMR (400.13 MHz, $CDCl_3$): δ = 4.17 (s, 2 H), 6.75 (d, J = 7.6 Hz, 2 H), 6.86 (t, J = 7.4 Hz, 1 H), 7.07 (t, J = 7.6 Hz, 2 H), 7.12–7.16 (m, 2 H), 7.31 (d, J = 7.6 Hz, 2 H), 7.61 (td, J = 1.7, 7.7 Hz, 2 H), 8.49 (d, J = 4.4 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 49.4, 120.7, 121.9, 122.3, 122.6, 128.5, 136.2, 148.3, 149.2, 155.7 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3063, 2970, 1592, 1490, 1474, 1437 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 273 (4) $[M]^+$, 195 (100), 167 (17), 92 (27). HRMS (ESI): calcd. for $C_{18}H_{16}N_3$ 274.13458 $[M + H]^+$; found 274.13455.

(1,2-Dipyridin-2-yl-vinyl)phenylamine (20a): Yield: 153 mg (56.2%), yellow solid. M.p. 110.8–112.0 °C (petroleum ether). ^1H NMR (400.13 MHz, $CDCl_3$): δ = 6.17 (s, 1 H), 6.70 (dd, J = 3.7, 8.7 Hz, 2 H), 6.82 (t, J = 7.4 Hz, 1 H), 6.96–7.00 (m, 1 H), 7.07–7.11 (m, 2 H), 7.17–7.22 (m, 2 H), 7.37 (dd, J = 1.0, 8.9 Hz, 1 H), 7.51–7.59 (m, 2 H), 8.51 (dd, J = 4.1, 4.9 Hz, 1 H), 8.66–8.67 (m, 1 H), 11.48 (br. s, 1 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 106.6, 119.2, 120.7, 121.0, 122.7, 123.5, 123.9, 128.7, 136.0, 142.9, 146.1, 147.5, 149.5, 155.7, 158.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3190 (br.), 3085, 3058, 2962, 2928, 1628, 1590, 1498, 1467, 1388 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 273 (20) $[M]^+$, 272 (20), 195 (100), 181 (57), 77 (41), 51 (25). HRMS (ESI): calcd. for $C_{18}H_{16}N_3$ $[M + H]^+$ 274.13458; found 274.13454.

2-(1-Phenyl-3-pyridin-2-ylaziridin-2-yl)benzothiazole (21)

(*R,*S**)-21:** Yield: 29.6 mg (9%), yellow solid. M.p. 93.7–95.6 °C. ^1H NMR (400.13 MHz): δ = 4.10 (d, J = 2.3 Hz, 1 H), 4.60 (d, J = 2.3 Hz, 1 H), 6.84 (d, J = 7.8 Hz, 2 H), 6.91 (t, J = 7.2 Hz, 1 H), 7.10–7.18 (m, 3 H), 7.31–7.38 (m, 2 H), 7.46 (t, J = 7.8 Hz, 1 H), 7.63 (td, J = 1.5, 7.8 Hz, 1 H), 7.83 (d, J = 7.8 Hz, 1 H), 7.98 (d, J = 7.8 Hz, 1 H), 8.45 (d, J = 4.4 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 46.2, 51.7, 120.7, 121.0, 121.7, 122.7, 122.9, 123.0, 125.1, 126.1, 128.7, 135.0, 136.3, 147.2, 149.3, 153.68, 153.7, 168.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3065, 2990, 2928, 1597, 1490, 1437 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 329 (11) $[M]^+$, 251 (63), 195 (100), 167 (18), 92 (27), 77 (48), 51 (26). HRMS (ESI): calcd. for $C_{20}H_{16}N_3S$ 330.10668 $[M + H]^+$; found 330.10666.

(*R,*R**)-21:** Yield: 161 mg (49%), oil. ^1H NMR (400.13 MHz): δ = 4.04 (d, J = 6.5 Hz, 1 H), 4.16 (d, J = 6.5 Hz, 1 H), 7.06–7.12 (m, 2 H), 7.15–7.18 (m, 2 H), 7.27–7.33 (m, 3 H), 7.38–7.42 (m, 1 H), 7.57–7.65 (m, 2 H), 7.74 (d, J = 7.7 Hz, 1 H), 7.94 (d, J = 8.3 Hz, 1 H), 8.49 (dd, J = 0.9, 1.5 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 47.2, 50.7, 119.8, 121.4, 122.6, 122.7, 122.8, 123.8, 124.8, 125.8, 129.4, 135.0, 136.1, 149.4, 152.0, 153.5, 154.4, 167.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3067, 2982, 1595, 1490, 1437, 1409 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 329 (15) $[M]^+$, 251 (74), 195 (100), 167 (17), 92 (22), 77 (47), 51 (26). HRMS (ESI): calcd. for $C_{20}H_{16}N_3S$ 330.10668 $[M + H]^+$; found 330.10665.

(1-Benzothiazol-2-yl-2-pyridin-2-ylvinyl)phenylamine (21a): Yield 65.8 mg (20%), yellow solid. M.p. 128.6–130.8 °C (petroleum ether). ^1H NMR (400.13 MHz): δ = 6.48 (s, 1 H), 6.80–6.84 (m, 3 H), 6.98 (dd, J = 0.8, 5.0 Hz, 1 H), 7.08 (dd, J = 2.2, 7.2 Hz, 2 H), 7.20 (d, J = 7.9 Hz, 1 H), 7.28 (t, J = 7.1 Hz, 1 H), 7.41 (t, J = 7.1 Hz, 1 H), 7.55 (td, J = 1.8, 7.7 Hz, 1 H), 7.70 (d, J = 8.0 Hz, 1 H), 8.01 (d, J = 8.0 Hz, 1 H), 8.46 (d, J = 4.4 Hz, 1 H), 11.13 (br. s, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 109.2, 111.2, 117.2, 119.5, 121.9, 123.4, 124.5, 125.3, 126.1, 128.9, 135.9, 136.3, 140.2, 142.8, 147.9, 153.0, 157.0, 167.2 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3238, 3062, 3009, 2960, 2928, 1620, 1591, 1498, 1470, 1262 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 329 (35) $[M]^+$, 328 (21), 251 (56), 237 (100), 194 (29), 135 (17), 77 (79), 51 (30). HRMS (ESI): calcd. for $C_{20}H_{16}N_3S$ 330.10668 $[M + H]^+$; found 330.10663.

(2-Benzothiazol-2-yl-1-pyridin-2-ylvinyl)phenylamine (21b): Compound characterized only by ^1H NMR as it was isolated in low quantity containing an inseparable mixture of the two isomers (**21a+21b**). Yield: 2.4%. ^1H NMR (400.13 MHz): δ = 6.19 (s, 1 H), 6.73 (d, J = 7.5 Hz, 2 H), 6.83–6.87 (m, 2 H), 7.09 (t, J = 7.5 Hz, 2 H), 7.17–7.21 (m, 2 H), 7.35 (td, J = 0.9, 7.1 Hz, 1 H), 7.50 (td, J = 1.6, 7.6 Hz, 1 H), 7.73 (t, J = 7.6 Hz, 1 H), 7.83 (d, J = 8.0 Hz, 1 H), 8.60 (d, J = 4.9 Hz, 1 H), 11.05 (br. s, 1 H) ppm.

2-(1-Phenyl-3-pyridin-3-ylaziridin-2-yl)pyridine (22)

(*R,*S**)-22:** Yield: 26 mg (9.5%), oil. ^1H NMR (400.13 MHz): δ = 3.77 (d, J = 2.7 Hz, 1 H), 3.94 (d, J = 2.7 Hz, 1 H), 6.67 (dd, J = 0.8, 7.4 Hz, 2 H), 6.82 (t, J = 7.4 Hz, 1 H), 7.03 (t, J = 7.8 Hz, 2 H), 7.08–7.12 (m, 2 H), 7.27–7.30 (m, 2 H), 7.58 (td, J = 1.7, 7.8 Hz, 1 H), 8.41 (td, J = 0.8, 7.4 Hz, 2 H), 8.55 (d, J = 1.8 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 46.3, 50.2, 120.7, 122.3, 122.4, 122.5, 123.0, 128.7, 131.9, 134.2, 136.4, 147.6, 148.8, 149.2, 149.5, 155.3 ppm. IR (film): $\tilde{\nu}$ = 3056, 2925, 1592, 1489, 1435, 1025 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 273 (15) $[M]^+$, 272 (21), 195 (30), 181 (100), 167 (20), 77 (41), 51 (23). HRMS (ESI): calcd. for $C_{18}H_{16}N_3$ 274.13458 $[M + H]^+$; found 274.13455.

(*R,*R**)-22:** Yield: 190 mg (69.5%), oil. ^1H NMR (400.13 MHz): δ = 3.65 (d, J = 6.5 Hz, 1 H), 3.79 (d, J = 6.5 Hz, 1 H), 6.94–7.05 (m, 5 H), 7.19–7.23 (m, 3 H), 7.39 (td, J = 1.5, 7.7 Hz, 1 H), 7.52 (dt, J = 1.6, 7.8 Hz, 1 H), 8.29 (dd, J = 1.3, 4.7 Hz, 1 H), 8.35 (d, J = 4.9 Hz, 1 H), 8.53 (d, J = 1.8 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 46.4, 49.4, 119.7, 121.7, 122.1, 122.6, 123.2, 129.2, 131.0, 135.2, 135.9, 148.3, 149.0, 149.3, 153.0, 155.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3058, 2926, 1593, 1489, 1436, 1266, 1026 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 273 (23) $[M]^+$, 272 (16), 195 (100), 181 (38), 167 (20), 168 (20), 92 (21), 77 (21), 51 (11). HRMS (ESI): calcd. for $C_{18}H_{16}N_3$ 274.13458 $[M + H]^+$; found 274.13452.

3-(1-Phenyl-3-pyridin-4-ylaziridin-2-yl)pyridine [(*R,*R**)-23]:** Yield: 257 mg (94%), yellow solid. M.p. 172.2–173.8. ^1H NMR (400.13 MHz): δ = 3.59 (d, J = 6.5 Hz, 1 H), 3.65 (d, J = 6.5 Hz,

1 H), 7.00–7.06 (m, 4 H), 7.13 (dd, J = 1.3, 4.6 Hz, 2 H), 7.25 (td, J = 2.0, 7.4 Hz 2 H), 7.46 (dt, J = 1.7, 7.9 Hz, 1 H), 8.33–8.36 (m, 3 H), 8.52 (d, J = 2.1 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 46.7, 47.5, 119.8, 122.6, 122.9, 123.5, 129.4, 130.6, 135.0, 144.3, 148.9, 149.4, 149.5, 153.0 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3078, 2986, 2973, 1600, 1489, 1404, 1275 cm^{-1}. GC–MS (70 eV): *m/z* (%) = 273 (63) $[M]^+$, 272 (93), 195 (23), 181 (28), 168 (100), 77 (100), 51 (57). HRMS (ESI): calcd. for $C_{18}H_{16}N_3$ 274.13458 $[M + H]^+$; found 274.13453.

2-(1-Phenyl-3-pyridin-4-ylaziridin-2-yl)pyridine (24)

(*R,*S**)-24:** Yield: 116 mg (42.5%), yellow solid. M.p. 113.8–115.2 °C (petroleum ether). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.74 (d, J = 2.5 Hz, 1 H), 3.93 (d, J = 2.5 Hz, 1 H), 6.64 (d, J = 7.5 Hz, 2 H), 6.83 (t, J = 7.3 Hz, 1 H), 7.01–7.11 (m, 5 H), 7.26 (d, J = 7.8 Hz, 1 H), 7.57 (td, J = 1.6, 7.7 Hz, 1 H), 8.37 (d, J = 4.0 Hz, 1 H), 8.44 (d, J = 5.9 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 46.9, 50.9, 120.5, 122.2, 122.3, 122.5, 122.8, 128.7, 136.3, 145.9, 147.5, 149.2, 149.5, 154.6 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3063, 2973, 2930, 1598, 1491, 1437, 1277 cm^{-1}. GC–MS (70 eV): *m/z* (%) = 273 (11) $[M]^+$, 272(7), 195 (100), 181 (24), 167 (20), 92 (29), 77 (34), 51 (24). HRMS (ESI): calcd. for $C_{18}H_{16}N_3$ 274.13458 $[M + H]^+$; found 274.13455.

(*R,*R**)-24:** Yield: 116 mg (42.5%), yellow solid. M.p. 108.3–109.5 °C (petroleum ether). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.63 (d, J = 6.7 Hz, 1 H), 3.83 (d, J = 6.7 Hz, 1 H), 6.99–7.06 (m, 4 H), 7.19–7.27 (m, 5 H), 7.45 (td, J = 1.6, 7.7 Hz, 1 H), 8.33 (dd, J = 1.2, 4.8 Hz, 2 H), 8.36 (d, J = 4.9 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 47.7, 49.9, 119.8, 121.9, 122.4, 122.8, 123.4, 129.3, 136.1, 144.7, 149.3, 149.4, 152.9, 154.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3064, 2987, 2967, 1599, 1489, 1419, 1268, 1148 cm^{-1}. GC–MS (70 eV): *m/z* (%) = 273 (11) $[M]^+$, 195 (100), 181 (29), 167 (22), 92 (32), 77 (42), 51 (31). HRMS (ESI): calcd. for $C_{18}H_{16}N_3$ 274.13458 $[M + H]^+$; found 274.13455.

Acknowledgments

This work was carried out under the framework of the National Project "Stereoselezione in Sintesi Organica. Metodologie ed Applicazioni" supported by the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR, Rome). We would like to thank also the University of Lecce and the CINMPIS (Consorzio Interuniversitario Nazionale Metodologie e Processi Innovativi di Sintesi) for their financial support.

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[20] X-ray crystallographic data for **21a**: $C_{20}H_{15}N_3S$, T = 123 K, $0.22 \times 0.16 \times 0.13$ mm^3, yellow, prismatic crystal, triclinic, space group $P\bar{1}$, a = 11.155(2) Å, b = 11.671(2) Å, c = 13.575(2) Å, α = 82.32(2)°, β = 74.05(2)°, γ = 75.25(2)°, V = 1639.4(5) Å^3, Z = 4, $D_{calcd.}$ = 1.335 g cm^{-3}, λ (Mo-K_α) = 0.71073 Å, μ (Mo-K_α) = 0.203 mm^{-1}. Data collection: Bruker SMART APEX diffractometer, Oxford low temperature device, data collection blow 2θ = 55°, 16357 data collected, 7519 independent, 4549 observed [$I > 2\sigma(I)$]. The structure was solved by *SIR*2002 (M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Cryst.* **2003**, 36, 1103), and refined on F^2 by SHELX97 (G. M. Sheldrick, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**). Final R = 0.0484, wR = 0.0867, on observed data, goodness-of-fit = 0.950, $-0.29 < \Delta\rho < 0.24$ e Å^{-3}. The crystal structure of **21a** contains two independent molecules; their conformations are similar, in spite of some geometrical parameters differing significantly. In particular, the intramolecular distance N18···N13 (hydrogen bonded) is 2.804(2) Å and 2.741(2) Å in the two independent molecules. Other quite significant differences are, for example, the torsion angles S1–C2–C10–N18 and C2–C10–N18–C19, whose values are 37.5(2), 23.4(2) and 47.9(3), 57.1(3)°, respectively, for the two independent molecules. CCDC-638681 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Received: May 22, 2007
Published Online: October 11, 2007

