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Exploiting the σ-phylic properties of cationic gold(I) catalysts in the ring opening reactions of aziridines with indoles†

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A study on the S_N2-type ring opening reactions of aziridines with indoles as nucleophiles is reported. Under gold(I) catalysis a great variety of tryptamine derivatives were prepared in good to excellent yields with complete stereocontrol when chiral aziridines were used. We demonstrated that cationic gold(I) catalysts are superior Lewis acids to the previously reported group 3, 12 and 13 metals in terms of catalyst loading and reaction yields. Moreover, complete regioselectivity was observed for 2-phenyl-*N*-tosylaziridine; whereas, regioselectivity up to 10 : 1 ratio was observed with 2-methyl-*N*-tosylaziridine. Finally, a preliminary study on the dearomatization reactions giving rise to pyrroloindolines is also reported.

Introduction

Aziridine nucleophilic ring-opening reactions have been recognized for a long time as a precious and reliable tool to introduce a CCN motif in a huge number of substrates.[1] In the specific case of the indole nucleus, regioselective nucleophilic ring-opening of aziridines led to the formation of tryptamine derivatives, chemically synthesized or naturally occurring drugs/alkaloids with well-defined and significant biological effects.[2] However, reported examples with indoles as nucleophiles are relatively rare and involve aziridines bearing an electron withdrawing group at nitrogen (activated aziridines) under (Lewis) acidic catalysis.[3] In particular, the regiochemical outcome for reactions involving C2 monosubstituted aziridines largely depends on the substitution pattern (Scheme 1).

For example, indoles add regioselectively at the benzylic position of C2 aryl substituted aziridines under $LiClO_4$,[3h] and $Sc(OTf)_3/Zn(OTf)_2$ catalysis,[3a] or in the presence of an excess of BF_3 [3i] (Scheme 1, eqn (1)). Moving to alkyl substituted aziridines, mixtures of both conceivable regioisomers are isolated using $Zn(OTf)_2$ [3c] as a catalyst, and only one report of regioselective reaction in the presence of an excess of BF_3 has been reported until now[3i] (Scheme 1, eqn (2)). Besides, aziridines 2-carboxylate have been involved in the synthesis of tryptophan derivatives using 1 equivalent of $Sc(ClO_4)_3$,[3j] $Sc(OTf)_3$ [3b] or $Y(OTf)_3$ [3d] as a promoter (Scheme 1, eqn (3)). From the data reported in Scheme 1, it should be noted that working with chiral C2 substituted aziridines, enantiomeric pure compounds can be obtained, suggesting the involvement of a S_N2-type mechanism for the ring-opening reaction.[3i,c] Clearly, enantiomeric pure derivatives have been obtained in C3 selective ring opening reactions of enantiomeric pure C2 substituted aziridines.[3b,d,j] Furthermore, several of the reported reactions suffer from some drawbacks, *i.e.*, they are performed in the presence of at least a stoichiometric amount of Lewis acids, require an excess of aziridine/indole substrates and/or are limited in scope.

On the other hand, indole is one of the most extensively explored heterocyclic nuclei. A plethora of synthetic methodologies have been developed for the assembly of the indole core[4] as well as for the functionalization of the preformed nucleus.[5] This latter goal has been mainly achieved on the pyrrole moiety with electrophiles, exploiting the enamine-type reactivity at the C3 carbon atom and the nucleophilic properties of the nitrogen atom, and, to a lesser extent, with nucleophiles, reversing the natural reactivity by the insertion of suitable substituents at nitrogen or at C2/C3 positions.

Other interconnected and fascinating research areas encompass the dearomative manipulation of the preformed indole ring[6] for the synthesis of the indolenine core and the cyclization/cycloaddition reactions for the synthesis of polycyclic indole derivatives,[4e,h,k,7] either common scaffolds in naturally occurring and bioactive compounds. Over the last few years, the effectiveness of all these transformations has been notably enhanced through the development of new catalytic and organocatalytic processes.

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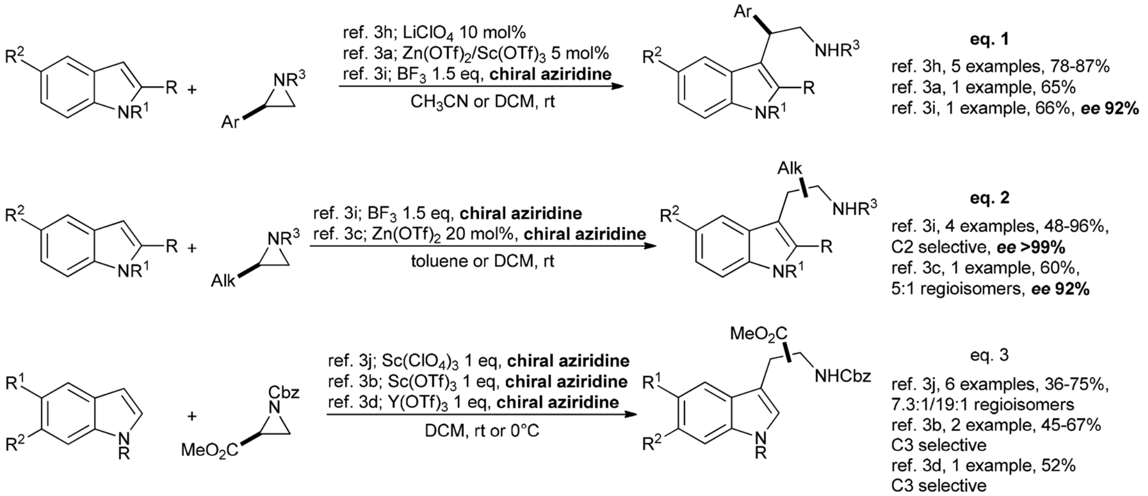
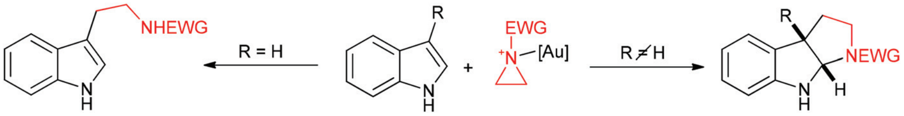


Scheme 1 Previously reported results on the ring opening reactions of aziridines with indoles.



Scheme 2 Planned gold(I) catalyzed reactions.

Considering these results and in step with our latest research reports on the synthesis of polycyclic indoles[8] and indole derivatives[9] under gold catalysis, we recognized gold-activated aziridines as suitable electrophiles for the simple functionalization and the dearomative reactions of indoles for the synthesis of β-indolylamines and fused pyrrolo[2,3-*b*] indoles, respectively (Scheme 2).

Formation of stable complexes *via N*-coordination of aziridines with *in situ* generated triphenylphosphine gold(I) triflate ($AuPPh_3OTf$) has been recently described by Lorenz and co-workers.[10] These complexes are quite stable and can be isolated and characterized under standard laboratory conditions. Moreover, in 2007 Wu and co-workers published a gold(III) chloride/silver triflate catalyzed ring-opening reaction of aziridines with furan and electron-rich arenes.[11] Thus, in the presence of 1–5% of $AuCl_3$ and 3–15% of AgOTf in nitromethane at room temperature, the reaction affords the corresponding β-aryl(furyl)amines in good to excellent yields. Moreover, several papers dealing with the σ-phylic properties of gold species have been recently published.[8*a*,12]

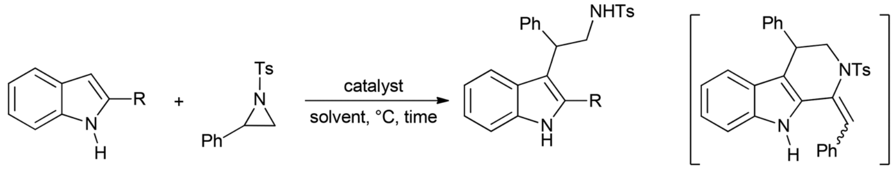
Results

We started our investigations testing the reactivity of indoles **1a** and **1h** with racemic 2-phenyl-*N*-tosylaziridine (**2a**), under conventional Lewis acid, organic acid and gold catalyses. A comprehensive review of the reaction conditions we tested is summarized in Table 1.

We choose to survey the reactivity of 2-alkynylindole **1h**, besides simple and commercially available **1a**, to verify the feasibility of a domino process involving nucleophilic addition of an indole to an aziridine and subsequent hydroamination of the triple bond (Table 1, compound in brackets). However, under the tested reaction conditions, this compound has never been isolated or detected in the crude reaction mixtures. When the reaction works toward the formation of the desired compounds **3**, the isolated regioisomers arose from the C2 selective ring-opening of the aziridine, compounds **3a** and **3h**. The structure of **3a** was elucidated *via* 1D and 2D NMR experiments.[13] Initially, for comparison, we tested several conventional Lewis acids under catalytic conditions (15 mol%, entries 1–3). Instead, boron trifluoride was used under the conditions reported in ref. 3*i* (entry 4). These first attempts, however, led to the formation of the desired product in poor or moderate yields. Similar results were obtained in the presence of trifluoroacetic acid as the catalyst, whereas phosphoric acid (1,1′-binaphthyl-2,2′-diyl hydrogenphosphate) proved essentially ineffective, entries 5 and 6. Thus, gold(III) chloride, in the presence of silver triflate as an activating agent, was tested under the reaction conditions reported by Wu,[11] entry 7. In this case, **3a** was obtained in 23% yield. 5 mol% silver triflate, silver triflimidate or cationic gold(I) species proved more effective, entries 8–14, and compounds **3a** and **3h** were isolated in 45–98% yields, with [Au(JohnPhos)NTf_2] as the catalyst of choice.

With these results in hand, we initially choose to test the scope of the reaction under the conditions reported in Table 1,

Table 1 Optimization studies for the formation of tryptamine derivatives **3a** and **3h**



1a, R = Ph
1h, R = ≡—Ph
2a
3a, R = Ph
3h, R = ≡—Ph

Entry[a]	Indole	Eq. of **2a**	Catalyst (mol%)	Solvent	*T*, °C	Time, h	Yield, %
1	**1a**	1.1	$In(OTf)_3$ (15 mol%)	DCM	rt, 40	20	42
2	**1a**	1.1	$Sc(OTf)_3$ (15 mol%)	DCM	rt, 40	20	21
3	**1h**	1.5	$Zn(NTf_2)_2$ (15 mol%)	DCE	rt, 60	20	48
4	**1a**	0.6	$BF_3·OEt_2$ (1.5 eq.)	DCM	−20	0.2	54
5	**1h**	1.5	TfOH (5 mol%)	DCE	rt	1.5	51
6	**1h**	1.5	BDHP (5 mol%)[b]	DCE	80	20	Traces
7	**1a**	1.1	$AuCl_3$ (5 mol%), AgOTf (15 mol%)	CH_3NO_2	rt	24	23
8	**1h**	1.5	AgOTf (5 mol%)	DCM	rt, 40	20	50
9	**1a**	1.5	$AgNTf_2$ (5 mol%)	DCE	80	24	45
10	**1h**	1.5	$[Au(PPh_3)OTf]$ (5 mol%)	DCE	80	0.5	61
11	**1h**	1.5	$[Au(IPr)SbF_6]$ (5 mol%)	DCE	80	0.5	79
12	**1h**	1.5	$[Au(JohnPhos)NTf_2]$ (5 mol%)	DCE	80	0.5	87
13	**1h**	1.5	$[Au(PPh_3)NTf_2]$ (5 mol%)	DCE	80	0.5	80
14	**1a**	**1.1**	**$[Au(JohnPhos)NTf_2]$ (5 mol%)**	**DCE**	**80**	**4.5**	**98**

[a] Entries 1–3, 5–14: reaction conditions: to a solution of indole (0.3 mmol) and aziridine (*n* equiv.) in the appropriate solvent (2 mL, 0.15 M), a catalyst was added and the mixture was stirred for the stated time and temperature. Entry 4, see ref. 3*i*. [b] BDHP = 1,1′-binaphthyl-2,2′-diyl hydrogenphosphate.

entry 14, changing the substituent array on the indole nucleus (Scheme 3).

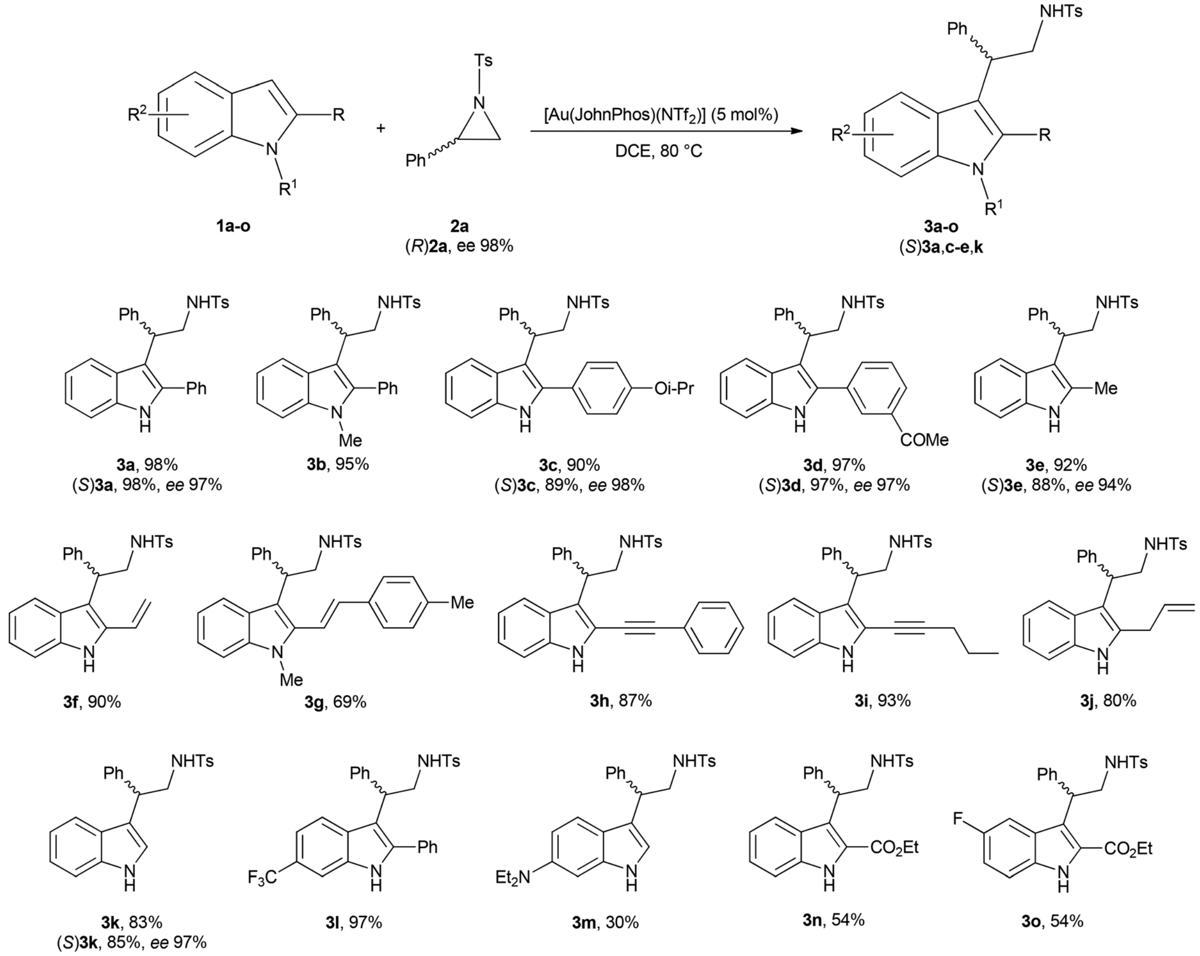
Product yields ranged from very good to excellent when the reaction was performed with 2-aryl, 2-alkyl, 2-vinyl, 2-alkynyl and 2-allyl indoles (**1a**, **1c–f**, **1h–j**), with *N*-Me protected indoles **1b** and **1g** and with indole itself (**1k**). The introduction of an EWG on the indole phenyl moiety is well tolerated (**1l**), whereas in the presence of an EDG, indole **1m**, or when an ethoxycarbonyl group is linked at C2 of the indole nucleus, indoles **1n** and **1o**, the corresponding tryptamine derivatives **3m–o** were obtained in moderate yields. Moreover, the reactions of indoles **1a,c–e,k** were repeated in the presence of (*R*)-2-phenyl-*N*-tosylaziridine ((*R*)**2a**) yielding the corresponding optically active compounds (*S*)**3a,c–e,k** in enantiomeric excesses comparable to that of the starting aziridine.

Next, we turned our attention to the aziridine nucleus testing the reactivity of *N*-tosylaziridine (**2b**) (Scheme 4).

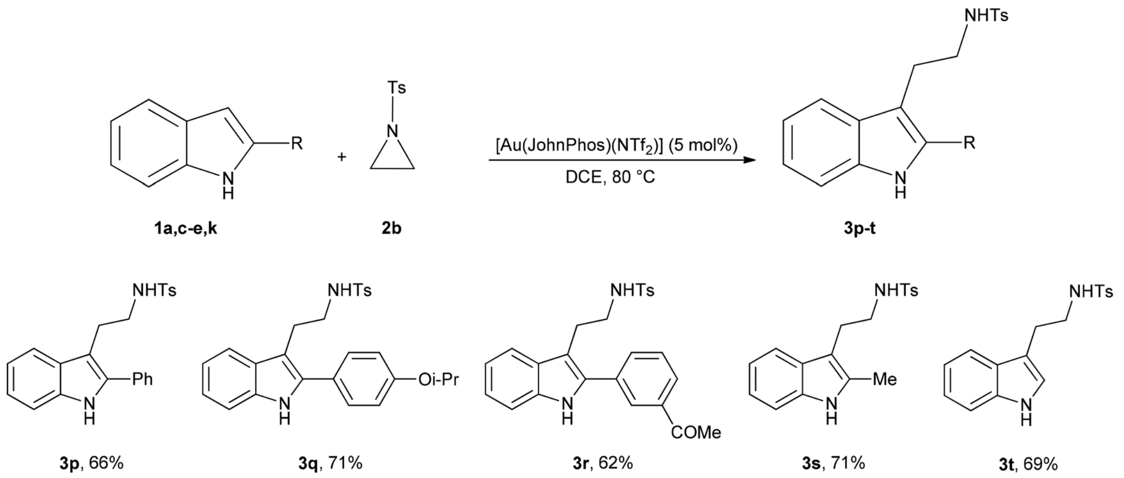
The reaction works well also with the unsubstituted *N*-tosylaziridine (**2b**). Tryptamines **3p–t** were obtained in 62–71% yield using a slight excess (1.2 equivalents) of thermally fragile **2b**. Working with a larger excess of **2b** (1.5 or 2.0 equivalents) resulted in the isolation of dirty reaction products, contaminated by inseparable tarry decomposition compounds arising from **2b**.

Then, we focused on the ring opening reactions of racemic 2-methyl-*N*-tosylaziridine (**2c**) with indoles **1** (Table 2).

Generally, quite unsatisfactory results were obtained working with 2-methyl-*N*-tosylaziridine **2c**. The first three experiments (entries 1–3), performed with indoles **1a,c,e** under standard reaction conditions, resulted in the isolation in excellent overall yields of an inseparable mixture of both conceivable regioisomeric tryptamines **3u–w** and **3′u–w** in 2 : 1 ratios. As reported in the Introduction, regioselectivity in the ring-opening reaction of activated 2-alkylaziridines, using indoles as nucleophiles, is still a challenging objective and only one example of a regioselective reaction has been reported until now in the presence of an excess (1.5 equiv.) of boron trifluoride etherate.[3i] Thus, we performed the reaction between **1a** and **2c** under the conditions reported by Farr and co-workers (entry 4) attaining **3u** and **3′u** in a 12 : 1 ratio. Next, with the aim to improve the regioisomeric ratios between **3** and **3′** under catalytic conditions, we tested several cationic gold(I) complexes varying both the ligands and the counterions (entries 5–8) achieving quite disappointing results. Better results could be obtained in the presence of simple gold(I) salts such as gold(I) triflate, generated *in situ* by mixing equimolecular amounts of gold(I) chloride and silver triflate. Thus, the reaction gave rise to compounds **3u** and **3′u** in a 7 : 1 ratio (entry 9). The yield and regioisomeric ratio comparable to those obtained with boron trifluoride could be obtained working in the presence of 2 equivalents of indole **1a** (entry 10). A brief screening on the nature of silver salts was then performed revealing that AuCl/$AgSbF_6$ and AuCl/$AgNTf_2$ were the catalysts of choice to achieve **3u** and **3′u** in 70% yield and 7 : 1 ratio (entries 11 and 12). A control experiment performed with silver triflate as the catalyst failed to give the desired



Scheme 3 Reaction scope with 2-phenyl-*N*-tosylaziridines **2a** and (*R*)**2a**.

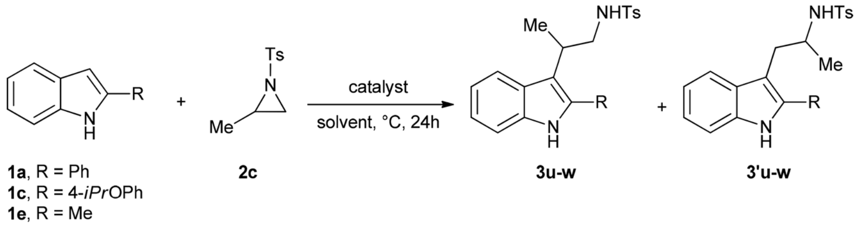


Scheme 4 Reaction scope with *N*-tosylaziridine **2b**.

compound (entry 13). Structures and ratios between the two regioisomers were assigned *via* NMR analysis.[13] A control reaction between indole **1a** and aziridine (*S*)**2c** under the reaction conditions reported in Table 2, entry 12 resulted in the isolation of a mixture of (*R*)**3u** (94% ee) and **3′u** in 68% overall yield (10 : 1 ratio) (Scheme 5).

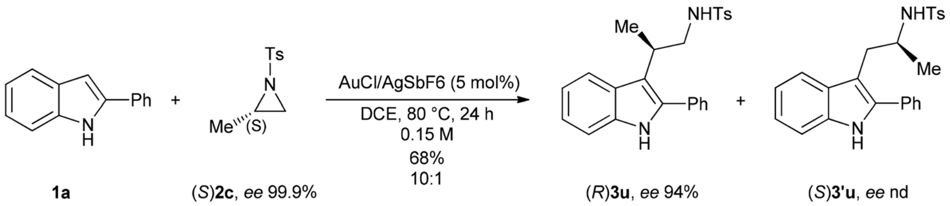
Moreover, several additional experiments were performed with indole **1a** and aziridines **2d–f** (Scheme 6).

Table 2 Ring-opening reactions of 2-methyl-*N*-tosylaziridine (**2c**) with indoles **1**

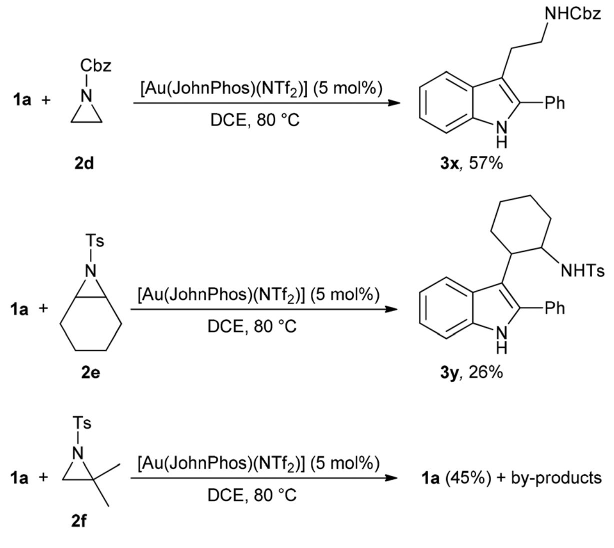


Entry[a]	Indole	Catalyst (mol%)	Solvent	*T*, °C	Overall yield, %	Ratio 3/3′
1	**1a**	[Au(JohnPhos)(NTf_2)] (5 mol%)	DCE	80	98	2 : 1
2	**1c**	[Au(JohnPhos)(NTf_2)] (5 mol%)	DCE	80	86	2 : 1
3	**1e**	[Au(JohnPhos)(NTf_2)] (5 mol%)	DCE	80	92	2 : 1
4	**1a**	$BF_3 \cdot OEt_2$ (1.5 equiv.)	DCM	20	55	12 : 1
5	**1a**	[Au(JohnPhos)(SbF_6)(CH_3CN)] (5 mol%)	DCE	80	91	1.5 : 1
6	**1a**	[Au(PPh_3)(NTf_2)] (5 mol%)	DCE	80	31	1.5 : 1
7	**1a**	[Au(IPr)(NTf_2)] (5 mol%)	DCE	80	99	2 : 1
8	**1a**	[Au(IPr)(SbF_6)(CH_3CN)] (5 mol%)	DCE	80	96	2 : 1
9	**1a**	AuCl/AgOTf (5 mol%)	DCE	80	27	7 : 1
10	**1a**	AuCl/AgOTf (5 mol%)	DCE	80	46	10 : 1
11	**1a**	AuCl/$AgNTf_2$ (5 mol%)	DCE	80	70	7 : 1
12	**1a**	AuCl/$AgSbF_6$ (5 mol%)	DCE	80	70	7 : 1
13	**1a**	AgOTf (5 mol%)	DCE	80	—	—

[a] Entries 1–3, 5–9: reaction conditions: to a solution of indole (0.3 mmol) and aziridine (1.1 equiv.) in DCE (2 mL, 0.15 M), a catalyst was added and the mixture was stirred for the stated time and temperature. Entry 4: see ref. 3*i*. Entries 10–13: reaction conditions: to a solution of indole (0.3 mmol) and aziridine (0.15 equiv.) in DCE (2 mL, 0.15 M), a catalyst was added and the mixture was stirred at 80 °C for 24 h.



Scheme 5 Gold(I) catalyzed reaction of indole **1a** and aziridine (*S*)**2c**.



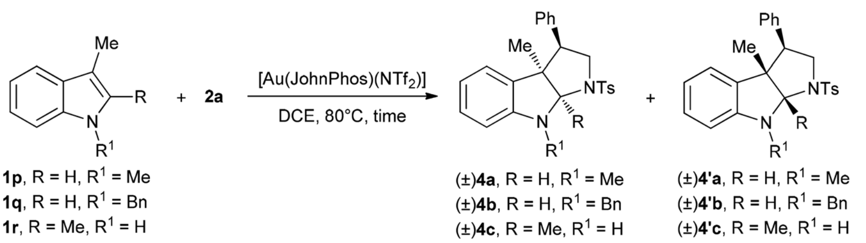
Scheme 6 Gold(I) catalyzed reaction of indole **1a** and aziridines **2d–f**.

Under standard reaction conditions indole **1a** reacts with aziridines **2d** and **2e** giving rise to tryptamines **3x,y** in low to moderate yields, besides unreacted **1a**. Moreover, the same reaction performed in the presence of aziridine **2f** resulted in the isolation of unreacted **1a** (45%) alongside a mixture of unidentified compounds.

Finally, we want to report our preliminary results on the dearomative domino addition/annulation reactions between *N*,3-dimethylindole **1p**, *N*-benzyl-3-methylindole **1q**, 2,3-dimethylindole **1r** and 3-allyl-*N*-methylindole **1s** with aziridines **2a** and **2b**, under cationic [Au(JohnPhos)(NTf_2)] gold(I) catalysis (Scheme 7).

Excellent results on related dearomative reactions, involving unsubstituted aziridines,[14] symmetrically C2/C3 substituted aziridines[15] or C2 substituted aziridines,[16] have been recently reported.

Under cationic gold(I) catalysis, the dearomatization reactions of indoles **1p–r** with aziridine **2a** proceeded in moderate



R = H, R^1 = Me
overall yield 68%
ratio **4a**:**4'a** 60:40

R = H, R^1 = Bn
overall yield 63%
ratio **4b**:**4'b** 45:55

R = Me, R^1 = H
overall yield 55%
ratio **4c**:**4'c** 70:30

Entry	Indole	1p/1s:2b	[M]	T, °C	t, h	Yield, %
1	1p	1:1.2	0.15	80	42	18
2	1p	1:1.2	0.15	120	24	28
3	1p	1:1.2	0.15	120[a]	1	29
4	1p	1:1.2	0.15	150[a]	1	39
5	1p	1:2	0.15	150[a]	1	29
6	1p	2:1	0.30	150[a]	1	45
7	1p	2:1	0.60	150[a]	1	55
8	1s	2:1	0.60	150[a]	1	45

[a] Under microwaves irradiation

Scheme 7 Dearomative domino addition/annulation reactions.

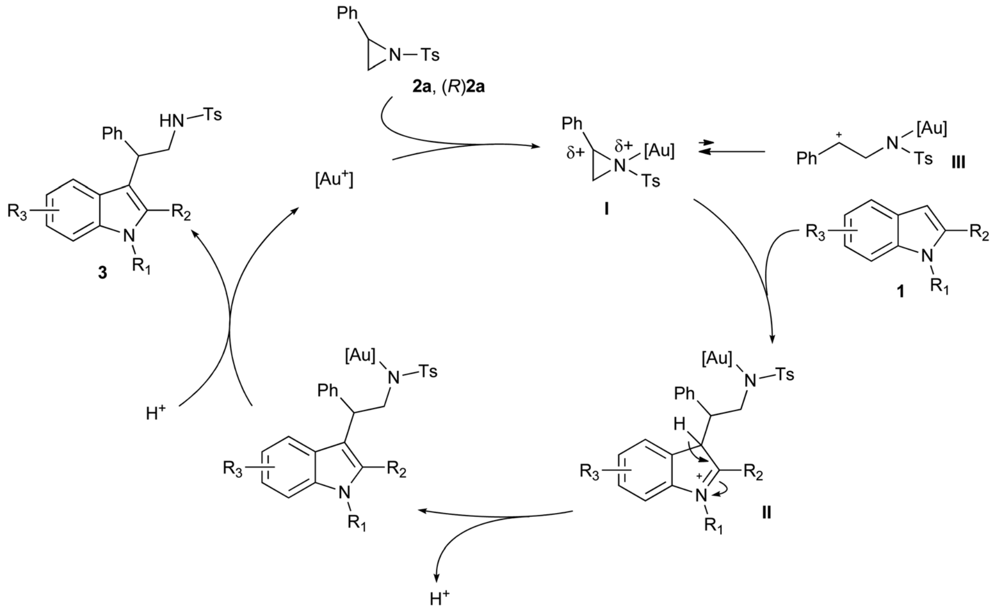
yields giving rise to the corresponding diastereoisomeric dihydropyrroloindolines (±)**4a–c** and (±)**4′a–c** as racemic mixtures. Diastereoisomers (±)**4a**/(±)**4′a** and (±)**4c**/(±)**4′c** could be separated by column chromatography and the structures were established by comparison with the reported data[16] for (±)**4a** and (±)**4′a** and by 2D NOESY experiments for (±)**4c** and (±)**4′c**. Diastereoisomers (±)**4b**/(±)**4′b** were characterized as a mixture *via* NMR and by comparison with the reported data.[16] Reactions with indoles **1p,q** were repeated also in the presence of chiral aziridine (*R*)**2a** giving rise to enantiomeric enriched diastereoisomers **4a** (96% ee), **4′a** (96% ee)/**4b** (99% ee) and **4′b** (99% ee). **4a**/**4′a** and **4b**/**4′b** were evaluated as mixtures *via* chiral HPLC analysis, after chromatographic purification.[13,17]

Working with indole **1p** and aziridine **2b**, the indoline **4d** was obtained in 55% yield after optimization of the reaction conditions. In particular, the reactions performed under standard conditions (ratio indole/aziridine 1 : 1.2, 0.15 M solution in dichloroethane) at 80 and at 120 °C under conventional heating or at temperatures ranging from 120 to 150 °C under microwave irradiation gave unsatisfactory results (yields 18–39%, Scheme 7, entries 1–4). A brief optimization study on the reagent ratios and reaction concentrations revealed that doubling the equivalents of **2b** has no effect on the product yield (Scheme 7, entry 5). On the other hand, working with two equivalents of indole **1p**, at 0.3 M and 0.6 M concentrations, the desired compound could be isolated in 45% and 55% yields, respectively (Scheme 7, entries 6 and 7). Under optimized reaction conditions, 3-allyl-*N*-methylindole (**1s**) was tested in the dearomative reaction giving rise to indoline **4e** in 45% yield.

Discussion

As a general remark it can be stated that cationic gold(I) complexes are active catalysts in the ring-opening reactions of activated aziridine with indoles as nucleophiles. In particular, [Au(JohnPhos)NTf$_2$] is the catalyst of choice for the ring-opening reactions performed with 2-phenyl-*N*-tosylaziridine **2a**. Thus, the nucleophilic attack of indoles **1a–o**, through the C3 carbon atom, occurs regioselectively at the C2 of the aziridine ring, yielding the corresponding tryptamine derivatives **3a–o** in excellent yields with a catalyst loading of only 5 mol%. Moreover, the ring-opening reactions provide racemic mixtures when performed with achiral aziridine **2a** and is stereospecific employing the chiral aziridine (*R*)**2a** as the starting material. Based on these experimental results and literature reports, a reaction mechanism can be postulated for the ring-opening reactions of **2a** and (*R*)**2a** with indoles **1** (Scheme 8). Therefore, azaphilic[10,18] activation of aziridine by a cationic gold(I) catalyst produces an activated complex (**I**). Then indole **1** attacks regioselectively at the benzylic carbon of **I** producing a new intermediate **II** *via* a Friedel–Crafts-type reaction. Rearomatization and protodeauration steps conclude the catalytic cycle affording **3** and restoring the catalyst.

The stereospecificity attained with (*R*)**2a** accounts for the intermediacy of a strongly polarized species like **I**, reacting with **1** *via* the S_N2-type mechanism. Besides, the intermediacy of a zwitterionic species **III**, Scheme 8, can be disregarded as it would provide racemic **3** by S_N1-type mechanism. Unfortunately, the same regioselectivity was not observed in the ring-opening reactions involving 2-methyl-*N*-tosylaziridine (**2b**) under [Au(JohnPhos)NTf$_2$] catalysis. As reported in the literature and confirmed by our experiments (see Table 2), boron trifluoride is able to almost regioselectively address the nucleophilic attack at the more hindered carbon atom of the aziridine ring. It seems that an excess of a hard Lewis acid like boron trifluoride is essential to establish a strong interaction within both reacting substrates and to trigger the reaction toward the C2 selective ring-opening reaction path.[3i,19] Instead, cationic gold(I) complexes in a catalytic amount



Scheme 8 Proposed reaction mechanism.

weakly interact with the aziridine nitrogen, and in the absence of a strong directing group like a phenyl ring in aziridine **2a**, the reaction outcomes are driven by steric and electronic issues making possible two opposite reaction paths. Both of them involve the ring-opening reaction of aziridine **2b**, respectively, at C2 and C3, affording mixtures of both conceivable tryptamines **3** and **3′**. In line with these observations, it is worth noting that using 5 mol% of more electrophilic naked cationic gold salts improves the regioisomeric ratio between **3u** and **3′u**. Importantly, the [Au(JohnPhos)NTf_2] catalyst proves effective also in the dearomative reactions of C3 substituted indoles. In this latter case, a reaction intermediate analogous to **II**, Scheme 8, evolves by intramolecular amination reaction and regeneration of the catalyst.

Conclusions

In this work we established the high efficiency of a cationic gold(I) catalyst [Au(JohnPhos)(NTf_2)] in the ring opening reactions of 2-phenyl-*N*-tosylaziridine **2a** and (*R*)**2a** with indoles as nucleophiles. In particular, we gathered a large collection of tryptamine derivatives in high yields, with complete stereochemical control and at a catalyst loading of only 5 mol%. To the best of our knowledge, only sporadic examples of related Lewis acid catalyzed reactions have been reported until now.[3h,a,i] Furthermore, it should be pointed out that, depending on the nature of the Lewis acid employed, previously reported reactions could suffer from lack of stereocontrol due to racemization of the starting aziridine during the reaction course.[16a] The results obtained with **2a**, besides those obtained with *N*-tosylaziridine itself (**2b**), represent the key strength of our work. In contrast, less exciting results have been achieved with 2-methyl-*N*-tosylaziridine (**2c**) and in the dearomative domino addition/annulation reactions. In the first case, we observed a lack of regiochemical control even if nearly quantitative reaction yields could be obtained. Dearomative reactions giving rise to pyrroloindoline derivatives, besides excellent stereocontrol, present several drawbacks. Moderate yields and low diastereoselection are the main weak points that must be addressed and further efforts in these directions are ongoing in our laboratory. Also the results reported for aziridines **2d–f** in Scheme 6 could represent a good starting point for further investigations.

Experimental

General experimental details

All chemicals and solvents are commercially available and were used after distillation or treatment with drying agents. Silica gel F254 thin-layer plates were employed for thin-layer chromatography (TLC). Silica gel 40–63 micron per 60 Å was employed for flash column chromatography. Melting points were measured with a Perkin-Elmer DSC 6 calorimeter at a heating rate of 5 °C min^{-1} and are uncorrected. ^1H and ^{13}C-NMR spectra were determined with a Varian-Gemini 200, a Bruker 300 or 500 Avance spectrometer at room temperature in $CDCl_3$, CD_2Cl_2 or d_6-acetone with residual solvent peaks as the internal reference. The APT sequence was used to distinguish the methine and methyl carbon signals from those arising from methylene and quaternary carbon atoms. Two-dimensional NMR experiments were performed, where appropriate, to aid the assignment of structures. Low-resolution MS spectra were recorded with a Thermo-Finnigan LCQ advantage AP electrospray/ion trap equipped instrument using a syringe pump device to directly inject sample solutions. Microwave promoted reactions were performed with a single-mode Personal Chemistry microwave synthesizer "Emrys Creator," using sealed glass vessels. The temperature was detected with an infrared sensor. Indoles **1a**, **1e**, **1k**, **1n**, **1o**, **1p**, **1r** are commercially available and were used without any further purification. Indoles **1b–d**, and **1l** are known compounds and were prepared as reported in the literature.[9,20] Indoles **1q** and **1s** are known compounds and were prepared according to literature procedures.[21] Indole **1h**[22] and indoles **1i** and **1j**[23] were prepared according to the procedures reported in ref. 9 and 20 (see below). Indoles **1f** and **1g** were prepared as reported in ref. 24 and 8*b*, respectively.[24,8b] Indole **1m** is a new compound and was prepared as reported below. Aziridines **2a–f** are known compounds and were prepared according to standard procedures.[25] $AuCl_3$, AuCl[Au(PPh_3)Cl], [Au(JohnPhos)Cl], [Au(IPr)Cl], $AgNTf_2$, AgOTf, $In(OTf)_3$, $Zn(NTf)_2$ and TfOH were purchased from commercial suppliers and used as received, the rest of the gold catalysts were prepared according to literature procedures.[26]

Preparation and characterization data for compounds 1h–j,m

2-(Phenylethynyl)-1*H*-indole (1h).[22] Ethyl 2-(phenylethynyl)-1*H*-indole-1-carboxylate[20] (0.84 g, 2.9 mmol) was dissolved in MeOH (20 mL). Solid K_2CO_3 (0.40 g, 2.9 mmol) was added and the mixture stirred for 2 h at 40 °C. Then the solvent was removed in vacuum and the residue was dissolved in H_2O/EtOAc 1 : 1 (50 mL). The two phases were separated and the aqueous layer was extracted with EtOAc (2 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuum to yield 2-(phenylethynyl)-1*H*-indole (**1h**) (0.59 g, 94%) as a yellow solid. **^{1}H-NMR** (200 MHz, CD_2Cl_2): δ 8.39 (s, 1H), 7.59 (m, 3H), 7.40 (m, 4H), 7.27 (t, J = 6.9 Hz, 1H), 7.15 (t, J = 7.3 Hz, 1H), 6.87 (s, 1H). **^{13}C-NMR** (50 MHz, CD_2Cl_2): δ 136.5 (C), 131.6 (2 × CH), 128.9 (CH), 128.7 (2 × CH), 128.0 (C), 123.8 (CH), 122.8 (C), 120.9(CH), 120.7 (CH), 119.0 (C), 111.0 (CH), 108.8 (CH), 92.6 (C), 81.8 (C). **ESI-MS** *m*/*z* 218 (M + H^+, 100). Data are in agreement with those reported in ref. 22.

2-(Pent-1-yn-1-yl)-1*H*-indole (1i). To a well stirred solution of ethyl 2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate[20] (1.0 g, 2.96 mmol) and pent-1-yne (0.24 g, 3.55 mmol) in dry DMF (12 mL), $Pd(PPh_3)_4$ (4 mol%, 132 mg, 0.12 mmol), CuI (2 mol%, 11.3 mg, 0.06 mmol) and Et_3N (8.25 mL, 59.2 mmol) were added. The mixture was then stirred at room temperature until the disappearance of starting materials (*ca.* 1 h) and then diluted with 0.1 M HCl (100 mL). The aqueous phase was extracted with EtOAc (3 × 50 mL); the combined organic phases were washed with brine (1 × 50 mL), dried over Na_2SO_4, filtered and concentrated in vacuum. Purification by column chromatography (Hex/EtOAc 98 : 2) yielded ethyl 2-(pent-1-yn-1-yl)-1*H*-indole-1-carboxylate (0.72 g, 95%) as a yellow oil. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 8.13 (d, J = 8.2 Hz, 1H), 7.48 (m, 1H), 7.37–7.17 (m, 2H), 6.82 (s, 1H), 4.51 (q, J = 7.1 Hz, 2H), 2.48 (t, J = 7.1 Hz, 2H), 1.68 (sextet, J = 7.1 Hz, 2H), 1.49 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7.3 Hz, 3H). Ethyl 2-(pent-1-yn-1-yl)-1*H*-indole-1-carboxylate (0.72 g, 2.82 mmol) was dissolved in MeOH (19 mL). Solid K_2CO_3 (0.39 g, 2.82 mmol) was added and the mixture was stirred for 2 h at 40 °C. After that time, the solvent was removed in vacuum and the residue was dissolved in H_2O/EtOAc 1 : 1 (50 mL). The two phases were separated and the aqueous layer was extracted with EtOAc (2 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuum to yield 2-(pent-1-yn-1-yl)-1*H*-indole (**1i**) (0.49 g, 94%) as a brown wax. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.56 (m, 1H), 7.35–7.02 (m, 3H), 6.66 (d, J = 1.3 Hz, 1H), 2.44 (t, J = 7.0 Hz, 2H), 1.63 (sextet, J = 7.1 Hz, 2H), 1.07 (t, J = 7.3 Hz, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ 136.0 (C), 128.1 (C), 123.2 (CH), 120.8 (CH), 120.5 (CH), 119.8 (C), 110.8 (CH), 107.7 (CH), 93.9 (C), 73.4 (C), 22.3 (CH_2), 21.8 (CH_2), 13.8 (CH_3). **ESI-MS** *m*/*z* 182 (M − H^+, 100).

2-Allyl-1*H*-indole (1j).[23] Ethyl 2-allyl-1*H*-indole-1-carboxylate[20] (0.25 g, 1.11 mmol) was dissolved in MeOH (8 mL) and K_2CO_3 (0.15 g, 1.11 mmol) was added. The mixture was stirred for 30 min at 40 °C. After that time, the solvent was removed in vacuum and the residue was dissolved in H_2O/EtOAc 1 : 1 (15 mL). The two phases were separated and the aqueous layer was extracted with EtOAc (2 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in a vacuum to yield 2-allyl-1*H*-indole (**1j**) (0.11 g, 60%) as a white solid. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.54 (d, J = 6.8 Hz, 1H), 7.36–7.00 (m, 3H), 6.28 (s, 1H), 6.00 (m, 1H), 5.21 (m, 2H), 3.55 (d, J = 6.3 Hz, 2H). Data are in agreement with those reported in ref. 23.

***N*,*N*-Diethyl-1*H*-indol-6-amine (1m).** A solution of 2 M NaOH (3.7 mL, 7.49 mmol) was added to a stirring solution of 6-(*N*,*N*-diethylamino)-1-(phenylsulfonyl)-1*H*-indole[27] (200 mg, 0.61 mmol) in 7 mL of MeOH and heated at 85 °C under a nitrogen atmosphere. The reaction mixture was stirred for 24 h until no more starting product was detectable by TLC analysis. Methanol was removed under reduced pressure and the crude product was poured into H_2O (25 mL) and extracted with EtOAc (4 × 20 mL), washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and then the residue was purified by flash chromatography over a silica gel column using Hex/EtOAc (7 : 3) to afford *N*,*N*-diethyl-1*H*-indol-6-amine (**1m**) (95 mg, 83%) as pale brown oil. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.47 (d, J = 9.1 Hz, 1H), 7.01 (m, 1H), 6.78 (m, 2H), 6.42 (m, 1H), 3.36 (q, J = 7.0 Hz, 4H), 1.16 (t, J = 7.0 Hz, 6H). **^{13}C-NMR** (C_6D_6, 50 MHz): δ 145.2 (C), 138.0 (C), 121.7 (CH), 121.3 (CH), 120.9 (C), 110.7 (CH), 102.4 (CH), 96.3 (CH), 45.7 (2 × CH_2), 12.7 (2 × CH_3). **ESI-MS** *m*/*z* 189 (M + H^+, 100).

Preparation and characterization data for compounds 3a–t, (*S*)3a, (*S*)3c–e, (*S*)3k, 3x,y

Representative procedure for gold(I)-catalyzed ring opening of *N*-tosyl aziridines (procedure A). To a N_2-flushed solution of indoles **1a–o** (1.0 equiv.) and *N*-tosyl aziridine **2a**, (*R*)**2a** or **2b** (1.1 or 1.2 equiv.) in DCE (0.15 M), [Au(JohnPhos)(NTf_2)] (5 mol%) was added and the mixture was stirred at 80 °C for

0.5–5 h. The solvent was then removed in vacuum and the residue was purified by column chromatography (SiO_2) to yield the corresponding products **3a–t**, (*S*)**3a**, (*S*)**3c–e**, (*S*)**3k**.

4-Methyl-*N*-(2-phenyl-2-(2-phenyl-1*H*-indol-3-yl)ethyl)benzenesulfonamide (3a). Procedure A was followed using 2-phenyl-1*H*-indole (**1a**) (58 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (**2a**) (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3a** (137 mg, 98%) as a white solid (m.p.: 165–167 °C). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.54–7.38 (m, 8H), 7.32–7.09 (m, 9H), 6.97 (t, *J* = 7.5 Hz, 1H), 4.49 (dd, *J* = 10.7, 6.1 Hz, 1H), 4.24 (dd, *J* = 9.1, 2.8 Hz, 1H), 3.84–3.62 (m, 2H), 2.42 (s, 3H). **^{1}H NMR** (300 MHz, $CDCl_3$ + D_2O): δ 7.54–7.38 (m, 8H), 7.32–7.09 (m, 9H), 6.97 (t, *J* = 7.5 Hz, 1H), 4.49 (dd, *J* = 10.7, 6.1 Hz, 1H), 3.80 (dd, *J* = 12.2, 6.1 Hz, 1H), 3.70 (dd, *J* = 10.9, 12.0 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 143.4 (C), 141.9 (C), 138.0 (C), 136.5 (C), 136.4 (C), 132.4 (C), 129.8 (2 × CH), 129.1 (2 × CH), 128.9 (2 × CH), 128.8 (2 × CH), 128.6 (CH), 127.9 (2 × CH), 127.3 (C), 127.2 (2 × CH), 126.9 (CH), 122.7 (CH), 120.4 (CH), 120.3 (CH), 111.8 (CH), 109.7 (C), 46.9 (CH_2), 42.5 (CH), 21.8 (CH_3). **ESI-MS** *m*/*z* 465 ($M - H^+$, 100). Calcd for $C_{29}H_{26}N_2O_2S$ [466.59]: C 74.65, H 5.62, N 6.00; found C 74.38, H 5.78, N 5.86.

(*S*)-4-Methyl-*N*-(2-phenyl-2-(2-phenyl-1*H*-indol-3-yl)ethyl)benzenesulfonamide ((*S*)3a). Procedure A was followed using (*R*)-2-phenyl-1-tosylaziridine ((*R*)**2a**). (*S*)**3a** was obtained in 98% yield and 97% ee. (*S*)**3a** was analyzed *via* chiral-HPLC in comparison with racemic **3a**, see the ESI† (HPLC section) for details.

4-Methyl-*N*-(2-(1-methyl-2-phenyl-1*H*-indol-3-yl)-2-phenylethyl)benzenesulfonamide (3b). Procedure A was followed using 1-methyl-2-phenyl-1*H*-indole (**1b**) (62 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (**2a**) (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3b** (137 mg, 95%) as a white thick oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 7.55–7.12 (m, 17H), 6.95 (t, *J* = 7.0 Hz, 1H), 4.25 (dd, *J* = 10.6, 6.6 Hz, 1H), 3.72–3.51 (m, 5H), 2.44 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 143.6 (C), 142.2 (C), 140.9 (C), 137.8 (C), 136.6 (C) 131.5 (C), 131.2 (2 × CH), 130.0 (2 × CH), 129.0 (CH), 128.9 (2 × CH), 128.8 (2 × CH), 128.0 (2 × CH), 127.5 (2 × CH), 126.9 (CH), 126.2 (C), 122.3 (CH), 120.2 (CH), 120.1 (CH), 110.3 (C), 110.2 (CH), 46.9 (CH_2), 42.8 (CH), 31.3 (CH_3), 21.9 (CH_3). **ESI-MS** *m*/*z* 503 [$M + Na^+$, 100]. Calcd for $C_{30}H_{28}N_2O_2S$ [480.63]: C 74.97, H 5.87, N 5.83; found C 75.29, H 5.71, N 5.97.

***N*-(2-(2-(4-Isopropoxyphenyl)-1*H*-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide (3c).** Procedure A was followed using 2-(4-isopropoxyphenyl)-1*H*-indole (**1c**) (75.4 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (**2a**) (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3c** (142 mg, 90%) as a white solid (m.p.: 75–78 °C). **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.50–7.36 (m, 3H), 7.32–7.08 (m, 11H), 6.97–6.85 (m, 3H), 4.59 (hept, *J* = 6.0 Hz, 1H), 4.45 (dd, *J* = 10.7, 6.2 Hz, 1H), 4.22 (dd, *J* = 9.0, 2.9 Hz, 1H), 3.84–3.55 (m, 2H), 2.40 (s, 3H), 1.39 (d, *J* = 6.2 Hz, 3H), 1.37 (d, *J* = 6.0 Hz, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ 158.5 (C), 143.3 (C), 142.0 (C), 138.0 (C), 136.5 (C), 136.3 (C), 130.1 (2 × CH), 129.8 (2 × CH), 128.8 (2 × CH), 127.9 (2 × CH), 127.4 (C), 127.2 (2 × CH), 126.9 (CH), 124.4 (C), 122.4 (CH), 120.3 (CH), 120.1 (CH), 116.3 (2 × CH), 111.4 (CH), 109.1 (C), 70.3 (CH), 46.8 (CH_2), 42.4 (CH), 22.3 (CH_3), 22.2 (CH_3), 21.7 (CH_3). **ESI-MS** *m*/*z* 523 [$M - H^+$, 100]. Calcd for $C_{32}H_{32}N_2O_3S$ [524.67]: C 73.25, H 6.15, N 5.34; found: C 73.02, H 6.27, N 5.49.

(*S*)-*N*-(2-(2-(4-Isopropoxyphenyl)-1*H*-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide ((*S*)3c). Procedure A was followed using (*R*)-2-phenyl-1-tosylaziridine ((*R*)**2a**). (*S*)**3c** was obtained in 89% yield and 98% ee. (*S*)**3c** was analyzed *via* chiral-HPLC in comparison with racemic **3c**, see the ESI† (HPLC section) for details.

***N*-(2-(2-(3-Acetylphenyl)-1*H*-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide (3d).** Procedure A was followed using 1-(3-(1*H*-indol-2-yl)phenyl)ethanone (**1d**) (70.6 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (**2a**) (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 7 : 3) yielded **3d** (148 mg, 97%) as a yellowish solid (m.p.: 77–79 °C). **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 8.92 (s, 1H), 7.89 (m, 2H), 7.64–7.05 (m, 14H), 6.96 (t, *J* = 7.2, 1H), 4.48 (m, 2H), 3.75 (m, 2H), 2.42 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 198.2 (C), 143.5 (C), 141.8 (C), 137.7 (C), 136.8 (C), 136.7 (C), 136.6 (C), 133.3 (CH), 133.0 (C), 129.8 (2 × CH), 129.3 (CH), 128.9 (2 × CH), 128.9 (CH), 128.0 (2 × CH), 127.3 (C), 127.2 (2 × CH), 127.1 (CH), 122.9 (CH), 120.5 (CH), 120.3 (CH), 112.0 (CH), 110.4 (C), 47.1 (CH_2), 43.0 (CH), 26.8 (CH_3), 21.7 (CH_3). 1 CH_{ar} is overlapping probably with 2 × CH at 128.0. **ESI-MS** *m*/*z* 507 [$M - H^+$, 100]. Calcd for $C_{31}H_{28}N_2O_3S$ [508.63]: C 73.20, H 5.55, N 5.51; found: C 73.58, H 5.41, N 5.62.

(*S*)-*N*-(2-(2-(3-Acetylphenyl)-1*H*-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide ((*S*)3d). Procedure A was followed using (*R*)-2-phenyl-1-tosylaziridine ((*R*)**2a**). (*S*)**3d** was obtained in 97% yield and 97% ee. (*S*)**3d** was analyzed *via* chiral-HPLC in comparison with racemic **3d**, see the ESI† (HPLC section) for details.

4-Methyl-*N*-(2-(2-methyl-1*H*-indol-3-yl)-2-phenylethyl)benzenesulfonamide (3e). Procedure A was followed using 2-methyl-1*H*-indole (**1e**) (39.4 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (**2a**) (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3e** (112 mg, 92%) as a white solid (m.p.: 147–150 °C). **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.31–7.08 (m, 9H), 6.90 (t, *J* = 7.4 Hz, 1H), 4.41 (dd, *J* = 10.4, 6.1 Hz, 1H), 4.33 (dd, *J* = 8.9, 2.9 Hz, 1H), 3.84 (ddd, *J* = 12.1, 9.1, 6.2, 1H), 3.61 (ddd, *J* = 12.1, 10.6, 3.2, 1H), 2.45 (s, 3H), 2.33 (s, 3H). **^{1}H-NMR** (200 MHz, $CDCl_3$ + D_2O): δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.31–7.08 (m, 9H), 6.90 (t, *J* = 7.4 Hz, 1H), 4.41 (dd, *J* = 10.5, 6.1 Hz, 1H), 4.33 (dd, *J* = 8.9, 2.9 Hz, 1H), 3.83 (dd, *J* = 12.1, 6.1, 1H), 3.60 (dd, *J* = 12.1, 10.6, 1H), 2.45 (s, 3H), 2.32 (s, 3H). ^{13}**C NMR** (50 MHz, CDCl$_3$): *δ* 143.7 (C), 141.7 (C), 136.7 (C), 135.8 (C), 133.9 (C), 130.0 (2 × CH), 128.8 (2 × CH), 127.9 (2 × CH), 127.3 (2 × CH), 127.2 (C), 126.8 (CH), 121.4 (CH), 119.8 (CH), 118.9 (CH), 111.1 (CH), 109.2 (C), 46.6 (CH$_2$), 42.3 (CH), 21.8 (CH$_3$), 12.2 (CH$_3$). **ESI-MS** *m*/*z* 403 [M − H$^+$, 100]. Calcd for $C_{24}H_{24}N_2O_2S$ [404.52]: C 71.26, H 5.98, N 6.93; found: C 71.48, H 6.02, N 6.80.

4-Methyl-*N*-(2-phenyl-2-(2-vinyl-1*H*-indol-3-yl)ethyl)benzenesulfonamide (3f). Procedure A was followed using ethyl 2-vinyl-1*H*-indole (**1f**) (42.9 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (**2a**) (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf$_2$)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 3 : 1) yielded **3f** (112 mg, 90%) as a white solid (m.p.: 130–132 °C). ^{1}**H-NMR** (200 MHz, CDCl$_3$): *δ* 8.23 (s, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.32–7.14 (m, 10H), 6.88 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 6.69 (dd, *J* = 17.5, 11.3 Hz, 1H), 5.52 (d, *J* = 17.6 Hz, 1H), 5.28 (d, *J* = 11.3 Hz, 1H), 4.49 (dd, *J* = 10.3, 6.1 Hz, 1H), 4.30 (dd, *J* = 8.7, 3.4 Hz, 1H), 3.87 (m, 1H), 3.62 (m, 1H), 2.43 (s, 3H). ^{13}**C-NMR** (50 MHz, CDCl$_3$): *δ* 143.6 (C), 141.1 (C), 136.9 (C), 136.7 (C), 134.3 (C), 129.9 (2 × CH), 128.8 (2 × CH), 127.8 (2 × CH), 127.3 (2 × CH), 127.2 (C), 126.9 (CH), 125.3 (CH), 123.4 (CH), 120.3 (CH), 120.1 (CH), 113.6 (CH$_2$), 113.0 (C), 111.3 (CH), 46.5 (CH$_2$), 41.8 (CH), 21.8 (CH$_3$). **ESI-MS** *m*/*z* 439 [M + Na$^+$, 100]. Calcd for $C_{25}H_{24}N_2O_2S$ [416.54]: C 72.09, H 5.81, N 6.73; C 72.37, H 5.88, N 6.72.

(*E*)-4-Methyl-*N*-(2-(1-methyl-2-(4-methylstyryl)-1*H*-indol-3-yl)-2-phenylethyl)benzenesulfonamide (3g). Procedure A was followed using ethyl (*E*)-1-methyl-2-(4-methylstyryl)-1*H*-indole (**1g**) (74.2 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (**2a**) (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf$_2$)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3g** (108 mg, 69%) as a yellow wax. ^{1}**H-NMR** (200 MHz, CDCl$_3$): *δ* 7.55 (d, *J* = 8.3 Hz, 2H), 7.37–7.10 (m, 14H), 6.94 (m, 2H), 6.64 (d, *J* = 16.5 Hz, 1H), 4.58 (dd, *J* = 10.5, 6.3 Hz, 1H), 4.30 (dd, *J* = 8.8, 3.1 Hz, 1H), 3.84–3.59 (m, 5H), 2.39 (s, 3H), 2.34 (s, 3H). ^{13}**C-NMR** (50 MHz, CDCl$_3$): *δ* 143.4 (C), 142.2 (C), 138.6 (C), 138.1 (C), 137.7 (C), 136.7 (C), 135.7 (CH), 134.1 (C), 129.8 (2 × CH), 129.7 (2 × CH), 128.9 (2 × CH), 128.0 (2 × CH), 127.3 (2 × CH), 126.9 (CH), 126.8 (2 × CH), 126.6 (C), 122.4 (CH), 120.1 (CH), 119.8 (CH), 115.7 (CH), 110.7 (C), 109.8 (CH), 47.0 (CH$_2$), 43.2 (CH), 31.1 (CH$_3$), 21.6 (CH$_3$), 21.5 (CH$_3$). ESI-MS *m*/*z* 519 [M − H$^+$, 100]. Calcd for $C_{33}H_{32}N_2O_2S$ [520.68]: C 76.12, H 6.19, N 5.38; found C 76.23, H 6.02, N 5.49.

4-Methyl-*N*-(2-phenyl-2-(2-(phenylethynyl)-1*H*-indol-3-yl)ethyl)benzenesulfonamide (3h). Procedure A was followed using 2-(phenylethynyl)-1*H*-indole (**1h**) (65.2 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (**2a**) (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf$_2$)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3h** (128 mg, 87%) as a yellowish solid (m.p.: 190–192 °C). ^{1}**H-NMR** (200 MHz, d_6-Acetone): *δ* 10.59 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.57–7.41 (m, 8H), 7.39–7.09 (m, 7H), 6.99 (t, *J* = 7.0 Hz, 1H), 6.49 (t, *J* = 5.5 Hz, 1H), 4.74 (t, *J* = 8.0 Hz, 1H), 4.08–3.80 (m, 2H), 2.34 (s, 3H). ^{13}**C-NMR** (50 MHz, d_6-Acetone): *δ* 143.0 (C), 142.6 (C), 138.4 (C), 136.9 (C), 131.3 (2 × CH), 129.7 (2 × CH), 128.9 (2 × CH), 128.5 (2 × CH), 128.2 (2 × CH), 127.1 (2 × CH), 126.8 (C), 126.6 (CH), 123.5 (CH), 123.0 (C), 121.4 (C), 119.9 (CH), 119.5 (CH), 116.8 (C), 111.5 (CH), 95.0 (C), 82.3 (C), 46.8 (CH$_2$), 43.5 (CH), 20.7 (CH$_3$). 1 CH$_{ar}$ is missing, probably overlapping. **ESI-MS** *m*/*z* 489 [M − H$^+$, 100]. Calcd for $C_{31}H_{26}N_2O_2S$ [490.62]: C 75.89, H 5.34, N 5.71; found: C 76.22, H 5.28, N 5.93.

4-Methyl-*N*-(2-(2-(pent-1-yn-1-yl)-1*H*-indol-3-yl)-2-phenylethyl)benzenesulfonamide (3i). Procedure A was followed using 2-(pent-1-yn-1-yl)-1*H*-indole (**1i**) (55 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (**2a**) (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf$_2$)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 5 : 1) yielded **3i** (127 mg, 93%) as a white solid (m.p.: 126–128 °C). ^{1}**H-NMR** (200 MHz, CDCl$_3$): *δ* 8.06 (s, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.31–7.07 (m, 9H), 6.92 (t, *J* = 6.7 Hz, 2H), 4.48 (m, 2H), 3.80 (dd, *J* = 8.1, 6.3 Hz, 2H), 2.47–2.29 (m, 5H), 1.71–1.53 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H). ^{13}**C-NMR** (50 MHz, CDCl$_3$): *δ* 143.4 (C), 141.4 (C), 137.2 (C), 135.9 (C), 129.8 (2 × CH), 128.8 (2 × CH), 128.0 (2 × CH), 127.3 (2 × CH), 127.0 (CH), 126.5 (C), 123.6 (CH), 120.3 (CH), 119.3 (CH), 118.4 (C), 118.0 (C), 111.1 (CH), 97.4 (C), 72.7 (C), 46.5 (CH$_2$), 43.0 (CH), 22.2 (CH$_2$), 21.8 (CH$_3$), 21.7 (CH$_2$), 13.9 (CH$_3$). **ESI-MS** *m*/*z* 455 [M − H$^+$, 100]. Calcd for $C_{28}H_{28}N_2O_2S$ [456.60]: C 73.65, H 6.18, N 6.14; C 73.37, H 6.12, N 6.26.

***N*-(2-(2-Allyl-1*H*-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide (3j).** Procedure A was followed using ethyl 2-allyl-1*H*-indole (**1j**) (47.2 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (**2a**) (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf$_2$)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 7 : 3) yielded **3j** (103 mg, 80%) as a white wax. ^{1}**H NMR** (200 MHz, CDCl$_3$): *δ* 7.99 (s, 1H), 7.60 (d, *J* = 8.2, 2H), 7.37–7.03 (m, 10H), 6.89 (t, *J* = 7.5, 1H), 5.87 (m, 1H), 5.2–5.05 (m, 2H), 4.42 (dd, *J* = 10.4, 6.2 Hz, 1H), 4.31 (dd, *J* = 9.0, 3.4 Hz, 1H), 3.82 (m, 1H), 3.59 (m, 1H), 3.42 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H). ^{13}**C NMR** (50 MHz, CDCl$_3$): *δ* 143.6 (C), 141.5 (C), 136.9 (C), 136.0 (C), 135.2 (C), 134.7 (CH), 129.9 (2 × CH), 128.7 (2 × CH), 127.9 (2 × CH), 127.3 (2 × CH), 127.2 (C), 126.8 (CH), 121.7 (CH), 119.9 (CH), 119.3 (CH), 117.9 (C), 111.2 (CH), 109.7 (CH), 46.6 (CH$_2$), 42.2 (CH), 31.0 (CH$_2$), 21.7 (CH$_3$). **ESI-MS** *m*/*z* 429 [M − H$^+$, 100]. Calcd for $C_{26}H_{26}N_2O_2S$ [430.57]: C 72.53, H 6.09, N 6.51; found: C 72.87, H 5.99, N 6.61.

***N*-(2-(1*H*-Indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide (3k).** Procedure A was followed using 1*H*-indole (**1k**) (51.4 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (**2a**) (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf$_2$)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3k** (100 mg, 83%) as a white solid (m.p.: 185–188 °C). ^{1}**H-NMR** (200 MHz, DMSO-d_6): *δ* 10.86 (s, 1H), 7.62 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.39–7.05 (m, 10H), 7.00 (t, *J* = 8.2 Hz, 1H), 6.85 (t, *J* = 7.9 Hz, 1H), 4.27 (t, *J* = 7.7 Hz, 1H), 3.35–3.19 (m, 2H), 2.32 (s, 3H). ^{13}**C-NMR** (50 MHz, DMSO-d_6): *δ* 143.6 (C), 143.1 (C), 138.3 (C), 136.9 (C), 130.2

(2 × CH), 128.9 (2 × CH), 128.7 (2 × CH), 127.2 (2 × CH), 127.1 (C), 126.8 (CH), 122.8 (CH), 121.7 (CH), 119.0 (CH), 116.1 (C), 112.1 (CH), 48.2 (CH_2), 43.3 (CH), 21.6 (CH_3). **ESI-MS** *m*/*z* 391 [M − H^+, 100]. Calcd for $C_{23}H_{22}N_2O_2S$ [390.50]: C 70.74, H 5.68, N 7.17; found C 70.99, H 5.75, N 7.01.

***(S)*-*N*-(2-(1*H*-Indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide ((*S*)3k).** Procedure A was followed using (*R*)-2-phenyl-1-tosylaziridine ((*R*)**2a**). (*S*)**3k** was obtained in 85% yield and 97% ee. (*S*)**3k** was analyzed *via* chiral-HPLC in comparison with racemic **3k**, see the ESI† (HPLC section) for details.

4-Methyl-*N*-(2-phenyl-2-(2-phenyl-6-(trifluoromethyl)-1*H*-indol-3-yl)ethyl)benzenesulfonamide (3l). Procedure A was followed using 2-phenyl-6-(trifluoromethyl)-1*H*-indole (**1l**) (78.4 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (**2a**) (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3l** (156 mg, 97%) as a white solid (m.p.: 201–203 °C). **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 8.64 (s, 1H), 7.68 (s, 1H), 7.46–7.34 (m, 7H), 7.32–6.99 (m, 9H), 4.49 (dd, *J* = 10.7, 6.0 Hz, 1H), 4.13 (m, 1H), 3.69 (m, 2H), 2.40 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ 143.6 (C), 141.2 (C), 140.6 (C), 136.4 (C), 135.3 (C), 131.6 (C), 129.8 (2 × CH), 129.5 (C), 129.2 (2 × CH), 129.1 (CH), 129.0 (2 × CH), 128.9 (2 × CH), 127.8 (2 × CH), 127.1 (2 × CH), 125.2 (q, *J* = 271 Hz, C), 124.6 (q, *J* = 32 Hz, C), 120.4 (CH), 116.9 (q, *J* = 3.5 Hz, CH), 110.5 (C), 109.1 (q, *J* = 4.3 Hz, CH), 46.8 (CH_2), 42.2 (CH), 21.6 (CH_3). **ESI-MS** *m*/*z* 533 [M − H^+, 100]. Calcd for $C_{30}H_{25}F_3N_2O_2S$ [534.60]: C 67.40, H 4.71, N 5.24; found: C 67.76; H 4.80, N 5.31.

***N*-(2-(6-(Diethylamino)-1*H*-indol-3-yl)ethyl)-4-methylbenzenesulfonamide (3m).** Procedure A was followed using *N*,*N*-diethyl-1*H*-indol-6-amine (**1m**) (56.50 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (90.2 mg, 0.33 mmol) (**2a**) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3m** (41 mg, 30%) as a white solid (m.p.: 54–56 °C). **^{1}H NMR** (C_6D_6, 200 MHz): δ 7.45 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.19–7.12 (m, 3H), 6.98–6.89 (m, 4H), 6.58 (d, *J* = 8.1 Hz, 2H), 6.26–6.22 (m, 2H), 5.41 (t, *J* = 7.0 Hz, 1H), 4.73 (bs, 1H), 3.94–3.84 (m, 1H), 3.47–3.36 (m, 1H), 2.77 (q, *J* = 7.0 Hz, 4H), 1.83 (s, 3H), 0.86 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (C_6D_6, 50 MHz): δ 145.0 (C), 142.3 (C), 140.9 (C), 137.3 (C), 135.1 (C), 129.3 (2 × CH), 129.0 (2 × CH), 127.1 (2 × CH), 126.8 (C), 126.7 (2 × CH), 124.6 (CH), 121.6 (C), 120.4 (CH), 116.1 (CH), 102.3 (CH), 49.5 (CH_2), 45.8 (2 × CH_2), 40.7 (CH), 20.9 (CH_3), 12.8 (2 × CH_3). 1 CH_{ar} is missing, probably overlapping. **ESI-MS** *m*/*z* 484 [M + Na^+, 100], 462 [M + H^+, 60]. Calcd for $C_{27}H_{31}N_3O_2S$: C 70.25, H 6.77, N 9.10; found C 70.15, H 6.53, N 9.07.

Ethyl 3-(2-(4-methylphenylsulfonamido)-1-phenylethyl)-1*H*-indole-2-carboxylate (3n). Procedure A was followed using ethyl 1*H*-indole-2-carboxylate (**1n**) (56.7 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (**2a**) (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3n** (75 mg, 54%) as a white solid (m.p.: 175–177 °C). **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 9.19 (s, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.32–7.10 (m, 9H), 6.91 (t, *J* = 7.0 Hz, 1H), 5.39 (dd, *J* = 10.0, 6.1 Hz, 1H), 4.88 (m, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.00–3.70 (m, 2H), 2.39 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ 162.3 (C), 143.4 (C), 141.1 (C), 136.9 (C), 136.4 (C), 129.7 (2 × CH), 128.7 (2 × CH), 127.9 (2 × CH), 127.2 (2 × CH), 126.9 (CH), 126.5 (C), 125.7 (CH), 124.8 (C), 122.0 (CH), 121.9 (C), 120.8 (CH), 112.5 (CH), 61.6 (CH_2), 46.6 (CH_2), 41.6 (CH), 21.7 (CH_3), 14.5 (CH_3). **ESI-MS** *m*/*z* 461 [M − H^+, 100]. Calcd for $C_{26}H_{26}N_2O_4S$ [462.56]: C 67.51, H 5.67, N 6.06; found: 67.88, H. 5.52, N. 6.19.

Ethyl 5-fluoro-3-(2-(4-methylphenylsulfonamido)-1-phenylethyl)-1*H*-indole-2-carboxylate (3o). Procedure A was followed using ethyl 5-fluoro-1*H*-indole-2-carboxylate (**1o**) (62.2 mg, 0.3 mmol), 2-phenyl-1-tosylaziridine (**2a**) (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3o** (75 mg, 54%) as a white solid (m.p.: 125–127 °C). **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 9.27 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.35–7.12 (m, 7H), 6.99 (td, *J* = 9.0, 2.4 Hz, 1H), 6.78 (dd, *J* = 9.9, 2.3 Hz, 1H), 5.33 (dd, *J* = 5.9, 10.4 Hz, 1H), 4.90 (m, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.89 (dt, *J* = 12.7, 6.4 Hz, 1H), 3.69 (td, *J* = 11.8, 4.6 Hz, 1H), 2.40 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 162.0 (C), 157.8 (d, J_{C-F} = 237 Hz, C), 143.5 (C), 140.7 (C), 136.7 (C), 133.0 (C), 129.8 (2 × CH), 128.8 (2 × CH), 127.8 (2 × CH), 127.1 (2 × CH), 127.0 (CH), 126.4 (C), 121.7 (d, J_{C-F} = 5.5 Hz, C), 114.9 (d, J_{C-F} = 27 Hz, CH), 113.5 (d, J_{C-F} = 9.4 Hz, CH), 106.3 (d, J_{C-F} = 24 Hz, CH), 61.7 (CH_2), 46.2 (CH_2), 41.3 (CH), 21.7 (CH_3), 14.5 (CH_3). **ESI-MS** *m*/*z* 479 [M − H^+, 100]. Calcd for $C_{26}H_{25}FN_2O_4S$ [480.55]: C 64.98, H 5.24, N 5.83; found: C 64.72, H 5.38, N 5.91.

4-Methyl-*N*-(2-(2-phenyl-1*H*-indol-3-yl)ethyl)benzenesulfonamide (3p). Procedure A was followed using 2-phenyl-1*H*-indole (**1a**) (58 mg, 0.3 mmol), 1-tosylaziridine (**2b**) (71 mg, 0.36 mmol, 1.2 equiv.) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3p** (77 mg, 66%) as a white solid (m.p.: 129–130 °C). **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.51–7.33 (m, 7H), 7.27–7.03 (m, 4H), 4.40 (t, *J* = 6.0 Hz, 1H), 3.26 (m, 2H), 3.07 (m, 2H), 2.39 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ 143.4 (C), 137.1 (C), 136.1(C), 135.9 (C), 132.8 (C), 129.8 (2 × CH), 129.2 (2 × CH), 128.8 (C), 128.4 (2 × CH), 128.2 (CH), 127.2 (2 × CH), 122.8 (CH), 120.2 (CH), 119.0 (CH), 111.2 (CH), 108.6 (C), 43.4 (CH_2), 25.2 (CH_2), 21.7 (CH_3). **ESI-MS** *m*/*z* 389 [M − H^+, 100]. Calcd for $C_{23}H_{22}N_2O_2S$ [390.50]: C 70.74, H 5.68, N 7.17; found C 70.95, H 5.56, N 7.01.

***N*-(2-(2-(4-Isopropoxyphenyl)-1*H*-indol-3-yl)ethyl)-4-methylbenzenesulfonamide (3q).** Procedure A was followed using 2-(4-isopropoxyphenyl)-1*H*-indole (**1c**) (75.3 mg, 0.3 mmol), 1-tosylaziridine (**2b**) (71 mg, 0.36 mmol, 1.2 equiv.) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3q** (96 mg, 71%) as a white solid (m.p.: 54–55 °C). **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.44–7.31 (m, 4H), 7.22–7.01 (m, 4H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.59 (hept, *J* = 6.0 Hz, 1H), 4.41 (t, *J* = 6.1 Hz, 1H), 3.26 (m, 2H), 3.04 (m, 2H), 2.39 (s, 3H), 1.38 (d, *J* = 6.1 Hz, 6H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ 158.1 (C), 143.3 (C), 137.1 (C), 136.1 (C), 135.9 (C), 129.8 (2 × CH), 129.6 (2 × CH), 128.9 (C), 127.2 (2 × CH), 124.8 (C), 122.4 (CH), 120.1 (CH), 118.7 (CH), 116.4 (2 × CH), 111.1 (CH), 107.7 (C), 70.3 (CH), 43.4 (CH_2), 25.2 (CH_2), 22.3 (CH_3), 21.7 (CH_3). **ESI-MS** *m*/*z* 447 [M − H^+, 100]. Calcd for $C_{26}H_{28}N_2O_3S$ [448.58]: C 69.62, H 6.29, N 6.25; found C 69.86, H 6.32, N 6.18.

***N*-(2-(2-(3-Acetylphenyl)-1*H*-indol-3-yl)ethyl)-4-methylbenzenesulfonamide (3r).** Procedure A was followed using 1-(3-(1*H*-indol-2-yl)phenyl)ethanone (**1d**) (70.6 mg, 0.3 mmol), 1-tosylaziridine (**2b**) (71 mg, 0.36 mmol, 1.2 equiv.) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 7 : 3) yielded **3r** (80 mg, 62%) as a yellowish solid (m.p.: 52.5–54 °C). **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 8.59 (s, 1H), 8.06 (m, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.62–7.30 (m, 5H), 7.27–7.01 (m, 4H), 4.80 (t, *J* = 6.1 Hz, 1H), 3.27 (m, 2H), 3.08 (m, 2H), 2.58 (s, 3H), 2.37 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ 198.4 (C), 143.5 (C), 137.8 (C), 137.1 (C), 136.3 (C), 134.7 (C), 133.3 (C), 132.8 (CH), 129.8 (2 × CH), 129.5 (CH), 128.7 (C), 127.9 (CH), 127.8 (CH), 127.2 (2 × CH), 123.1 (CH), 120.3 (CH), 119.1 (CH), 111.5 (CH), 109.3 (C), 43.5 (CH_2), 26.9 (CH_3), 25.5 (CH_2), 21.7 (CH_3). **ESI-MS** *m*/*z* 431 [M − H^+, 100]. Calcd for $C_{25}H_{24}N_2O_3S$ [432.53]: C 69.42, H 5.59, N 6.48; found C 69.83, H 5.47, N 6.22.

4-Methyl-*N*-(2-(2-methyl-1*H*-indol-3-yl)ethyl)benzenesulfonamide (3s). Procedure A was followed using 2-methyl-1*H*-indole (**1e**) (39.4 mg, 0.3 mmol), 1-tosylaziridine (**2b**) (71 mg, 0.36 mmol, 1.2 equiv.) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3s** (70 mg, 71%) as a white wax. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.33–7.16 (m, 4H), 7.14–6.96 (m, 2H), 4.31 (t, *J* = 6.2 Hz, 1H), 3.22 (m, 2H), 2.90 (m, 2H), 2.40 (s, 3H), 2.35 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ 143.5 (C), 137.1 (C), 135.6 (C), 132.7 (C), 129.8 (2 × CH), 128.4 (C), 127.2 (2 × CH), 121.4 (CH), 119.6 (CH), 117.8 (CH), 110.7(CH), 107.3 (C), 43.4 (CH_2), 24.9 (CH_2), 21.7 (CH_3), 11.8 (CH_3). **ESI-MS** *m*/*z* 327 [M − H^+, 65]. Calcd for $C_{18}H_{20}N_2O_2S$ [328.43]: C 65.83, H 6.14, N 8.53; found C 66.11, H 6.00, N 8.77.

***N*-(2-(1*H*-Indol-3-yl)ethyl)-4-methylbenzenesulfonamide (3t).** Procedure A was followed using 1*H*-indole (**1k**) (35.1 mg, 0.3 mmol), 1-tosylaziridine (**2b**) (71 mg, 0.36 mmol, 1.2 equiv.) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 9 : 1) yielded **3t** (65 mg, 69%) as a white wax. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.64 (d, *J* = 8.3 Hz, 3H), 7.45–6.92 (m, 7H), 4.38 (t, *J* = 5.9 Hz, 1H), 3.28 (m, 2H), 2.93 (m, 2H), 2.40 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ 143.5 (C), 137.1 (C), 136.7 (C), 129.8 (2 × CH), 127.2 (2 × CH), 122.9 (CH), 122.4 (CH), 119.7 (CH), 118.7 (CH), 111.8 (C), 111.6 (CH), 43.3 (CH_2), 25.7 (CH_2), 21.7 (CH_3). **ESI-MS** *m*/*z* 313 [M − H^+, 100]. Calcd for $C_{17}H_{18}N_2O_2S$ [314.40]: C 64.94, H 5.77, N 8.91; found C 65.19, H 5.83, N 8.87.

Benzyl (2-(2-phenyl-1*H*-indol-3-yl)ethyl)carbamate (3x). Procedure A was followed using 2-phenyl-1*H*-indole (**1a**) (58 mg, 0.3 mmol), benzyl aziridine-1-carboxylate (**2d**) (64 mg, 0.36 mmol, 1.2 equiv.) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 9 : 1) yielded **3x** (63 mg, 57%) as a white solid (m.p.: 46–48 °C). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.69–7.12 (m, 14H), 5.05 (s, 1H), 4.84 (t, *J* = 6.0 Hz, 1H), 3.53 (q, *J* = 6.8 Hz, 2H), 3.13 (t, *J* = 7.1 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 156.6 (C), 136.9 (C), 136.1 (C), 135.7 (C), 133.1 (C), 129.2 (C), 129.2 (2 × CH), 128.7 (CH), 128.3 (4 × CH), 128.2 (2 × CH), 128.1 (CH), 122.7 (CH), 120.1 (CH), 119.3 (CH), 111.2 (CH), 109.8 (C), 66.7 (CH_2), 41.8 (CH_2), 25.3 (CH_2). **ESI-MS** *m*/*z* 393 [M + Na^+, 75], 371 [M + H^+, 100]. Calcd for $C_{24}H_{22}N_2O_2$ [370.44]: C 77.81, H 5.99, N 7.56; found C 77.69, H 5.87, N 7.68.

4-Methyl-*N*-(2-(2-phenyl-1*H*-indol-3-yl)cyclohexyl)benzenesulfonamide (3y). Procedure A was followed using 2-phenyl-1*H*-indole (**1a**) (58 mg, 0.3 mmol), 7-tosyl-7-azabicyclo[4.1.0]-heptane (**2e**) (91 mg, 0.36 mmol, 1.2 equiv.) and [Au(JohnPhos)-(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3y** (35 mg, 26%) as a white wax. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.51–7.39 (m, 5H), 7.29–7.18 (m, 2H), 7.15–7.08 (m, 3H), 6.84–6.77 (m, 3H), 4.15 (m, 1H), 3.43 (m, 1H), 2.83 (ddd, *J* = 12.2, 10.8, 4.1, 1H), 2.52 (m, 1H), 2.30 (s, 3H), 1.88 (m, 3H), 1.30 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 142.6 (C), 136.4 (2 × C), 136.0 (C), 132.7 (C), 129.3 (2 × CH), 129.2 (2 × CH), 129.0 (2 × CH), 128.6 (CH), 126.6 (2 × CH), 122.1 (CH), 120.3 (CH), 119.7 (CH), 112.5 (C), 111.3 (CH), 56.3 (CH), 41.7 (CH), 35.0 (CH_2), 32.5 (CH_2), 26.2 (CH_2), 25.3 (CH_2), 21.8 (CH_3) (one quaternary carbon is missing, probably overlapped with one negative signal, CH). **ESI-MS** *m*/*z* 444 [M + H^+, 100]. Calcd for $C_{27}H_{28}N_2O_2S$ [444.59]: C 72.94, H 6.35, N 6.30; found C 72.86, H 6.12, N 6.41.

Representative procedures for the ring opening reactions of 2-methyl-*N*-tosyl aziridine (2c and (*S*)2c) – see Table 2 for details

Table 2, entries 1–3 general procedure. To a N_2-flushed solution of indoles **1a,c,e** (1.0 equiv.) and 2-methyl-*N*-tosyl aziridine (**2c**) (1.1 equiv.) in DCE (0.15 M), [Au(JohnPhos)(NTf_2)] (5 mol%) was added and the mixture was stirred at 80 °C for 24 h. The solvent was then removed in vacuum and the residue was purified by column chromatography (SiO_2) to yield the corresponding products **3u–w**/**3′u–w** as inseparable mixtures.

4-Methyl-*N*-(2-(2-phenyl-1*H*-indol-3-yl)propyl)benzenesulfonamide (3u) and 4-methyl-*N*-(1-(2-phenyl-1*H*-indol-3-yl)propan-2-yl)benzenesulfonamide (3′u). The general procedure was followed using 1*H*-indole **1a** (39.0 mg, 0.2 mmol), aziridine **2c** (46.5 mg, 0.22 mmol) and [Au(JohnPhos)(NTf_2)] (7.75 mg, 0.01 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded

3u/**3′u** (79.3 mg, 98%) in a 2 : 1 ratio as a white solid. The ratio and identity of the two regioisomers were established *via* 1D and 2D NMR analysis. See the copy of the original spectra enclosed in the ESI.† ESI-MS *m*/*z* 403 [M − H$^+$, 100]. Reported data are in agreement with those reported in the literature.[3i]

***N*-(2-(2-(4-Isopropoxyphenyl)-1*H*-indol-3-yl)propyl)-4-methylbenzenesulfonamide (3v) and *N*-(1-(2-(4-isopropoxyphenyl)-1*H*-indol-3-yl)propan-2-yl)-4-methylbenzenesulfonamide (3′v).** The general procedure was followed using 1*H*-indole **1c** (75.4 mg, 0.3 mmol), aziridine **2c** (69.7 mg, 0.33 mmol) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3v**/**3′v** (120 mg, 86%) in a 2 : 1 ratio as a pink solid. The ratio and identity of the two regioisomers were established by analogy with **3u**/**3′u** *via* ^{1}H NMR analysis. See the copy of the original spectra enclosed in the ESI.† ESI-MS *m*/*z* 461 [M − H$^+$, 100].

4-Methyl-*N*-(2-(2-methyl-1*H*-indol-3-yl)propyl)benzenesulfonamide (3w) and 4-methyl-*N*-(1-(2-methyl-1*H*-indol-3-yl)propan-2-yl)benzenesulfonamide (3′w). The general procedure was followed using 1*H*-indole **1e** (39.5 mg, 0.3 mmol), aziridine **2c** (69.7 mg, 0.33 mmol) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 8 : 2) yielded **3w**/**3′w** (94.4 mg, 92%) in a 2 : 1 ratio as a pink thick oil. The ratio and identity of the two regioisomers were established by analogy with **3u**/**3′u** *via* ^{1}H NMR analysis. See the copy of the original spectra enclosed in the ESI.† ESI-MS *m*/*z* 341 [M − H$^+$, 100].

Table 2, entry 4. To a solution of 1*H*-indole **1a** (58.0 mg, 0.3 mmol) and aziridine **2c** (42.3 mg, 0.2 mmol) in DCM (1 mL) boron trifluoride etherate (0.04 mL, 0.3 mmol) was added at room temperature over a period of 10 min. The solution was stirred for 24 h and was quenched with 5% aqueous $NaHCO_3$ solution (1 mL). The two phases were separated and the aqueous layer was extracted with DCM (2 × 1 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuum. Purification by column chromatography (Hex/EtOAc 8 : 2) yielded **3u** and **3′u** (43 mg, 55%) as inseparable mixture in a 12 : 1 ratio as a white solid. Reported data refer to major isomers and are in agreement with those reported in ref. 3*i*. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.49–7.30 (m, 9H), 7.26–7.15 (m, 3H), 6.99 (t, *J* = 7.3 Hz, 1H), 4.18 (d, *J* = 7.1 Hz, 1H), 3.32 (m, 3H), 2.40 (s, 3H), 1.39 (d, *J* = 5.9 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 143.2 (C), 136.7 (C), 136.5 (2 × C), 132.8 (C), 129.7 (2 × CH), 129.1 (2 × CH), 129.0 (2 × CH), 128.4 (CH), 127.1 (2 × CH), 126.7 (C), 122.5 (CH), 120.0 (CH), 119.9 (CH), 112.9 (C), 111.5 (CH), 48.1 (CH_2), 31.8 (CH), 21.7 (CH_3), 19.0 (CH_3). **ESI-MS** *m*/*z* 427 [M + Na$^+$, 100].

Table 2, entry 12. To a N_2-flushed solution of AuCl (2.3 mg, 0.01 mmol) and $AgSbF_6$ (3.4 mg, 0.01 mmol) in DCE (1.33 mL), indole **1a** (77.3 mg, 0.4 mmol) and aziridine **2c** (42.3 mg, 0.20 mmol) were added and the mixture was stirred for 24 h at 80 °C. The solvent was then removed in vacuum and the residue was purified by column chromatography (Hex/EtOAc 8 : 2) yielding **3u**/**3′u** (51 mg, 70%) as an inseparable mixture in a 7 : 1 ratio as a white solid. The ratio and identity of the two regioisomers were established *via* ^{1}H NMR analysis and are in agreement with those reported in ref. 12. See the enclosed copy of the original spectra. The same reaction was performed using (*S*)-2-methyl-1-tosylaziridine ((*S*)**2c**). The purified reaction mixture was analyzed *via* chiral-HPLC, see the ESI† (HPLC section) for details.

Preparation and characterization data for compounds (±)4a–d and (±)4′a–c

(±)-3a,8-Dimethyl-3-phenyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole ((±)4a and (±)4′a). Procedure A was followed using 1,3-dimethyl-indole (**1p**) (87.1 mg, 0.6 mmol), aziridine **2a** (197 mg, 0.72 mmol) and [Au(JohnPhos)(NTf_2)] (23.3 mg, 0.03 mmol) in DCE (4 mL). Purification of the crude product by column chromatography (Hex/DCM 1 : 1) yielded progressively (±)**4a** and (±)**4′a** (170 mg, overall yield 68%, ratio 60 : 40) as white solids (m.p.: (±)**4a** 115–117.2 °C; (±)**4′a** 173–176 °C). (±)**4a:**[16] **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.29–7.23 (m, 3H), 7.05 (dt, *J* = 7.7, 1.3 Hz, 1H), 6.85 (d, *J* = 6.2, 2H), 6.39 (d, *J* = 7.8 Hz, 1H), 6.31 (t, *J* = 7.4 Hz, 1H), 5.60 (d, *J* = 7.4 Hz, 1H), 5.40 (s, 1H), 3.80 (dd, *J* = 12.2, 6.5 Hz, 1H), 3.42 (t, *J* = 12.4 Hz, 1H), 3.07 (s, 3H), 2.76 (dd, *J* = 12.6, 6.5 Hz, 1H), 2.50 (s, 3H), 1.31 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 151.2 (C), 144.2 (C), 137.6 (C), 136.1 (C), 130.3 (2 × CH), 129.2 (2 × CH), 129.0 (C), 128.8 (CH), 128.3 (2 × CH), 127.9 (CH), 127.7 (2 × CH), 125.8 (CH), 116.8 (CH), 105.4 (CH), 91.5 (CH), 57.1 (C), 55.4 (CH), 51.6 (CH_2), 31.7 (CH_3), 26.4 (CH_3), 22.0 (CH_3). **ESI(+)-MS** (*m*/*z* %): 441 (100) [M + Na]$^+$. Calcd for $C_{25}H_{26}N_2O_2S$ [418.56]: C 71.74, H 6.26, N 6.69; found C.71.92, H 6.16, N 6.85. (±)**4′a:**[16b] **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.38–7.24 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.96 (dd, *J* = 6.6, 2.9 Hz, 2H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.56 (dd, *J* = 7.1, 3.5 Hz, 2H), 5.10 (s, 1H), 3.89–3.76 (m, 2H), 3.61 (dd, *J* = 11.0, 8.0 Hz, 1H), 3.06 (s, 3H), 2.50 (s, 3H), 0.53 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 149.5 (C), 144.4 (C), 135.7 (C), 135.5 (C), 133.0 (C), 130.2 (2 × CH), 129.1 (2 × CH), 129.0 (CH), 128.5 (2 × CH), 128.2 (2 × CH), 127.8 (CH), 122.7 (CH), 118.2 (CH), 107.9 (CH), 94.8 (CH), 54.5 (C), 52.9 (CH_2), 52.4 (CH), 33.2 (CH_3), 22.0 (CH_3), 16.9 (CH_3). **ESI-MS** *m*/*z* 419 [M + H$^+$, 100]. Calcd for $C_{25}H_{26}N_2O_2S$ [418.56]: C 71.74, H 6.26, N 6.69; found: C 71.88, H 6.02, N 6.98.

8-Benzyl-3a-methyl-3-phenyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole ((±)4b and (±)4′b). Procedure A was followed using indole **1p** (132.7 mg, 0.6 mmol), aziridine **2a** (196.8 mg, 0.72 mmol) and [Au(JohnPhos)(NTf_2)] (23.3 mg, 0.03 mmol) in DCE (4 mL). Purification of the crude product by column chromatography (Hex/EtOAc 9 : 1) yielded (±)**4b** and (±)**4′b** as an inseparable mixture (187 mg, overall yield 63%, ratio 60 : 40, white solid). (±)**4b**[13,14]/(±)**4′b**: **^{1}H-NMR** (300 MHz, $CDCl_3$): by comparison with NMR data in ref 16*b*, signals marked in blue and red can be attributed to (±)**4b** and (±)**4′b**, respectively. Signals in black are superimposed hydrogens. δ 7.76 (m, 4H), 7.46–7.20 (m, 20H), 7.08 (dt, *J* = 1.6, 7.5 Hz, 1H), 7.03–6.94 (m, 3H), 6.87 (dd, *J* = 1.6, 7.7 Hz, 2H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.60 (dd, *J* = 1.6, 7.3 Hz, 1H), 6.42 (d, *J* = 7.9 Hz, 1H), 6.35 (d, *J* = 7.9 Hz, 1H), 6.30 (dt, *J* = 0.8, 7.4 Hz, 1H), 5.60 (dd, *J* = 1.1, 7.4 Hz, 1H), 5.52 (s, 1H), 5.45 (s, 1H), 4.77 (AB, *J* = 16.2 Hz, 2H), 4.75 (AB, *J* = 16.5 Hz, 2H), 3.81–3.90 (m, 3H), 3.53 (t, *J* = 9.3 Hz, 1H), 3.53 (t, *J* = 12.6 Hz, 1H), 2.79 (dd, *J* = 12.7, 6.4 Hz, 1H), 2.48 (s, 3H), 2.46 (s, 3H), 1.27 (s, 3H), 0.58 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): *δ* 150.3, 148.7, 144.2, 144.1, 139.2, 138.9, 137.3, 136.00, 135.7, 135.2, 132.9, 130.1, 130.0, 129.1 129.0, 128.8, 128.7, 128.7, 128.6, 128.4, 128.2, 128.0, 127.7, 127.6, 127.6, 127.4, 127.2, 127.0, 126.0, 122.5, 117.9, 116.7, 108.0, 105.6, 92.5, 90.1, 57.1, 55.5, 54.8, 52.8, 52.7, 51.4, 49.9, 48.3, 29.9, 26.66, 21.9, 17.0. **ESI-MS** *m*/*z* 495 [M + H$^+$, 100].

(±)-3a,8a-Dimethyl-3-phenyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole ((±)4c and (±)4′c). Procedure A was followed using 2,3-dimethyl-1*H*-indole (**1r**) (43.6 mg, 0.3 mmol), aziridine **2a** (90.2 mg, 0.33 mmol) and [Au(JohnPhos)(NTf_2)] (11.6 mg, 0.015 mmol) in DCE (2 mL). Purification of the crude product by column chromatography (Hex/EtOAc 98 : 2–9 : 1–8 : 2) yielded progressively (±)**4′c** and (±)**4c** (69 mg, overall yield 55%, ratio (±)**4c**/(±)**4′c** 70 : 30) as white solids (m.p.: (±)**4c** 177–179 °C; (±)**4′c** 145–147 °C). (±)**4c**: **^{1}H-NMR** (300 MHz, $CDCl_3$): *δ* 7.72 (d, *J* = 8.1 Hz, 2H), 7.41–6.95 (m, 8H), 6.56 (t, *J* = 7.8 Hz, 1H), 6.46 (t, *J* = 7.3 Hz, 1H), 5.92 (d, *J* = 7.4 Hz, 1H), 5.42 (bs, 1H), 3.58–3.32 (m, 3H), 2.39 (s, 3H), 1.84 (s, 3H), 1.22 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): *δ* 148.2 (C), 143.3 (C), 139.1 (C), 137.6 (C), 135.6 (C), 129.7 (2 × CH), 129.6 (2 × CH), 128.3 (2 × CH), 127.9 (CH), 127.7 (CH), 127.3 (2 × CH), 126.1 (CH), 118.4 (CH), 109.2 (CH), 91.9 (C), 59.5 (C), 51.4 (CH), 50.6 (CH_2), 23.5 (CH_3), 22.7 (CH_3), 21.7 (CH_3). **ESI-MS** *m*/*z* 419 [M + H$^+$, 100]. Calcd for $C_{25}H_{26}N_2O_2S$ [418.56]: C 71.74, H 6.26, N 6.69; found: C 71.95, H 6.02, N 6.81. (±)**4′c**: **^{1}H-NMR** (300 MHz, $CDCl_3$): *δ* 7.80 (d, *J* = 8.3 Hz, 2H), 7.32–7.23 (m, 5H), 7.15–7.08 (m, 2H), 7.06 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.99 (d, *J* = 6.8 Hz, 1H), 6.76 (dt, *J* = 7.4, 0.8 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 5.26 (bs, 1H), 3.70 (dd, *J* = 7.5, 2.1 Hz, 1H), 3.47 (m, 2H), 2.43 (s, 3H), 1.72 (s, 3H), 0.93 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): *δ* 146.9 (C), 143.6 (C), 139.3 (C), 137.3 (C), 135.0 (C), 129.9 (2 × CH), 129.1 (2 × CH), 128.7 (CH), 128.5 (2 × CH), 127.9 (2 × CH), 127.5 (CH), 122.8 (CH), 119.4 (CH), 109.5 (CH), 92.3 (C), 59.8 (C), 52.6 (CH_2), 51.6 (CH), 24.1 (CH_3), 21.9 (CH_3), 19.7 (CH_3). **ESI-MS** *m*/*z* 419 [M + H$^+$, 100]. Calcd for $C_{25}H_{26}N_2O_2S$ [418.56]: C 71.74, H 6.26, N 6.69; found: C 71.90, H 6.11, N 6.58.

Reactions between indoles 1p,q and aziridine (*R*)2a. The reactions between indoles **1p,q** and aziridine (*R*)**2a** were performed as reported above for the reactions with racemic **2a**. The crude reaction mixtures were purified through a short pad of silica gel giving rise to pure mixtures of **4a**/**4′a** and **4b**/**4′b** which were evaluated *via* chiral HPLC analysis, in comparison with racemic (±)**4a**/(±)**4′a** and (±)**4b**/(±)**4′b**, respectively, see the ESI† (HPLC section) for details.

(±)-(3a,8a-*cis*)-3a,8-Dimethyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole ((±)4d). Entry 7, Scheme 7. In a nitrogen flushed vial a solution of aziridine **2b** (39.5 mg, 0.2 mmol) and [Au(JohnPhos)(NTf_2)] (7.7 mg, 0.01 mmol) in DCE (0.6 mL) was prepared. Then a solution of indole **1p** (58.1 mg, 0.4 mmol) in DCE (0.7 mL) was added and the mixture was stirred for 1 min under nitrogen. The vial was then sealed and heated at 150 °C for 1 h in a single-mode microwave synthesizer. The solvent was removed at reduced pressure and the resulting crude product was purified by flash column chromatography, affording indoline (±)**4d** (38 mg, 55%) as a white wax. **^{1}H-NMR** (200 MHz, $CDCl_3$): *δ* 7.78 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.40 (d, *J* = 7.8 Hz, 1H), 5.12 (s, 1H), 3.61–3.47 (m, 1H), 3.13–2.95 (m, 4H), 2.45 (s, 3H), 1.93 (ddd, *J* = 12.4, 5.8, 2.7 Hz, 1H), 1.39 (m, 1H), 1.14 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): *δ* 150.2 (C), 143.8 (C), 137.1 (C), 133.4 (C), 130.0 (2 × CH), 128.7 (CH), 127.5 (2 × CH), 122.1 (CH), 117.9 (CH), 106.2 (CH), 91.3 (CH), 53.3 (C), 48.7 (CH_2), 39.7 (CH_2), 31.6 (CH_3), 24.6 (CH_3), 21.7 (CH_3). **ESI-MS** *m*/*z* 365 [M + Na$^+$, 38]. Calcd for $C_{19}H_{22}N_2O_2S$ [342.46]: C 66.64, H 6.48, N 8.18; found: C 66.86, H 6.33, N 8.01.

(±)-(3a,8a-*cis*)-3a-Allyl-8-methyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole ((±)4e). Entry 8, Scheme 7. In a nitrogen flushed vial a solution of aziridine **2b** (39.5 mg, 0.2 mmol) and [Au(JohnPhos)(NTf_2)] (7.7 mg, 0.01 mmol) in DCE (0.6 mL) was prepared. Then a solution of indole **1s** (68.5 mg, 0.4 mmol) in DCE (0.7 mL) was added and the mixture was stirred for 1 min under nitrogen. The vial was then sealed and heated at 150 °C for 1 h in a single-mode microwave synthesizer. The solvent was removed at reduced pressure and the resulting crude product was purified by flash column chromatography, affording indoline (±)**4e** (33 mg, 45%) as a white wax. **^{1}H-NMR** (300 MHz, CD_2Cl_2): *δ* 7.77 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.10 (td, *J* = 7.7, 1.3 Hz, 1H), 6.94 (dd, *J* = 7.3.1.3 Hz, 1H), 6.65 (td, *J* = 7.3, 1.0 Hz, 1H), 6.40 (dd, *J* = 7.9, 0.7 Hz, 1H), 5.42 (m, 1H), 5.16 (s, 1H), 4.97 (m, 1H), 4.92 (m, 1H), 3.60 (m, 1H), 2.96 (m, 4H), 2.47 (s, 3H), 2.30 (m, 1H), 2.06 (m, 1H), 1.87 (m, 1H), 1.42 (m, 1H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): *δ* 151.1 (C), 144.1 (C), 137.1 (C), 134.1 (CH), 131.6 (C), 130.1 (2 × CH), 128.7 (CH), 127.4 (2 × CH), 122.8 (CH), 118.1 (C), 117.5 (CH), 105.8 (CH), 88.4 (CH), 57.3 (C), 48.4 (CH_2), 42.7 (CH_2), 37.8 (CH_2), 31.3 (CH_3), 21.5 (CH_3). **ESI-MS** *m*/*z* 391 [M + Na$^+$, 100]. Calcd for $C_{21}H_{24}N_2O_2S$ [368.49]: C 68.45, H 6.56, N 7.60; found: C 68.40, H 6.59, N 7.55.

Notes and references

1 (*a*) G. Callebaut, T. Meiresonne, N. De Kimpe and S. Mangelinckx, *Chem. Rev.*, 2014, **114**, 7954; (*b*) P.-A. Wang, *Beilstein J. Org. Chem.*, 2013, **9**, 1677; (*c*) R. Chawla, A. K. Singh and L. D. S. Yadav, *RSC Adv.*, 2013, **3**, 11385; (*d*) S. Stanković, M. D'hooghe, S. Catak, H. Eum, M. Waroquier, V. Van Speybroeck, N. De Kimpe and H.-J. Ha, *Chem. Soc. Rev.*, 2012, **41**, 643; (*e*) S. H. Krake and S. C. Bergmeier, *Tetrahedron*, 2010, **66**, 7337; (*f*) P. Lu, *Tetrahedron*, 2010, **66**, 2549; (*g*) G. S. Singh, M. D'hooghe and N. De Kimpe, *Chem. Rev.*, 2007, **107**, 2080.

2 (*a*) M. Ishikura, T. Abe, T. Choshi and S. Hibino, *Nat. Prod. Rep.*, 2015, **32**, 1389; (*b*) S. Lancianesi, A. Palmieri and M. Petrini, *Chem. Rev.*, 2014, **114**, 7108; (*c*) A. N. Da Silva and S. J. Tepper, *CNS Drugs*, 2012, **26**, 823; (*d*) D. G. Barceloux, in *Medical Toxicology of Drug Abuse*, John Wiley & Sons, Inc., Hoboken, 2012, pp. 193–199; (*e*) D. Zhang, H. Song and Y. Qin, *Acc. Chem. Res.*, 2011, **44**, 447; (*f*) A. J. Kochanowska-Karamyan and M. T. Hamann, *Chem. Rev.*, 2010, **110**, 4489; (*g*) G. Blay, J. R. Pedro and C. Vila, in *Catalytic Asymmetric Friedel-Crafts Alkylations*, ed. M. Bandini and A. Umani-Ronchi, Wiley-VCH, Weinheim, 2009, pp. 223–270.

3 Selected recent examples: (*a*) M. K. Ghorai, D. P. Tiwari and N. Jain, *J. Org. Chem.*, 2013, **78**, 7121; (*b*) I. Tirotta, N. L. Fifer, J. Eakins and C. A. Hutton, *Tetrahedron Lett.*, 2013, **54**, 618; (*c*) J. Cockrell, C. Wilhelmsen, H. Rubin, A. Martin and J. B. Morgan, *Angew. Chem., Int. Ed.*, 2012, **51**, 9842; (*d*) Y. Li, E. Hayman, M. Plesescu and S. R. Prakash, *Tetrahedron Lett.*, 2008, **49**, 1480; (*e*) H. M. Kaiser, W. F. Lo, A. M. Riahi, A. Spannenberg, M. Beller and M. K. Tse, *Org. Lett.*, 2006, **8**, 5761; (*f*) T. Hudlicky, U. Rinner, K. J. Finn and I. Ghiviriga, *J. Org. Chem.*, 2005, **70**, 3490; (*g*) U. Rinner, T. Hudlicky, H. Gordon and G. R. Pettit, *Angew. Chem., Int. Ed.*, 2004, **43**, 5342; (*h*) J. S. Yadav, B. V. S. Reddy and G. Parimala, *J. Chem. Res., Synop.*, 2003, 78; (*i*) R. N. Farr, R. J. Alabaster, J. Y. L. Chung, B. Craig, J. S. Edwards, H. W. Gibson, G.-J. Ho, G. R. Humphrey, S. A. Johnson and E. J. J. Grabowski, *Tetrahedron: Asymmetry*, 2003, **14**, 3503; (*j*) T. Nishikawa, S. Kajii, K. Wada, M. Ishikawa and M. Isobe, *Synthesis*, 2002, 1658; (*k*) J. S. Yadav, B. V. S. Reddy, S. Abraham and G. Sabitha, *Tetrahedron Lett.*, 2002, **43**, 1565.

4 For selected recent reviews and books on indole synthesis see: (*a*) G. Bartoli, R. Dalpozzo and M. Nardi, *Chem. Soc. Rev.*, 2014, **43**, 4728; (*b*) G. Abbiati, F. Marinelli, E. Rossi and A. Arcadi, *Isr. J. Chem.*, 2013, **53**, 856; (*c*) M. Platon, R. Amardeil, L. Djakovitch and J.-C. Hierso, *Chem. Soc. Rev.*, 2012, **41**, 3929; (*d*) S. Cacchi and G. Fabrizi, *Chem. Rev.*, 2011, **111**, PR215; (*e*) R. Vicente, *Org. Biomol. Chem.*, 2011, **9**, 6469; (*f*) S. Cacchi, G. Fabrizi and A. Goggiamani, *Org. Biomol. Chem.*, 2011, **9**, 641; (*g*) S. A. Patil, R. Patil and D. D. Miller, *Curr. Med. Chem.*, 2011, **18**, 615; (*h*) J. Barluenga, F. Rodríguez and F. J. Fañanás, *Chem. – Asian J.*, 2009, **4**, 1036; (*i*) N. T. Patil and Y. Yamamoto, *Chem. Rev.*, 2008, **108**, 3395; (*j*) K. Krüger, A. Tillack and M. Beller, *Adv. Synth. Catal.*, 2008, **350**, 2153; (*k*) L. Ackermann, *Synlett*, 2007, 507; (*l*) G. R. Humphrey and J. T. Kuethe, *Chem. Rev.*, 2006, **106**, 2875; (*m*) S. Cacchi and G. Fabrizi, *Chem. Rev.*, 2005, **105**, 2873; (*n*) G. Zeni and R. C. Larock, *Chem. Rev.*, 2004, **104**, 2285; (*o*) *Modern Heterocyclic Chemistry*, ed. J. Barluenga and C. Valdés, Wiley-VCH Verlag GmbH & Co. KGaA, 2011, pp. 377–531.

5 For selected recent reviews and books on indole functionalization see: (*a*) R. Dalpozzo, *Chem. Soc. Rev.*, 2015, **44**, 742; (*b*) M. Shiri, *Chem. Rev.*, 2012, **112**, 3508; (*c*) M. Bandini, *Org. Biomol. Chem.*, 2013, **11**, 5206; (*d*) G. Broggini, E. M. Beccalli, A. Fasana and S. Gazzola, *Beilstein J. Org. Chem.*, 2012, **8**, 1730; (*e*) T. Lindel, N. Marsch and S. K. Adla, *Top. Curr. Chem.*, 2012, **309**, 67; (*f*) C. C. J. Loh and D. Enders, *Angew. Chem., Int. Ed.*, 2012, **51**, 46; (*g*) N. Batail, M. Genelot, V. Dufaud, L. Joucla and L. Djakovitch, *Catal. Today*, 2011, **173**, 1; (*h*) M. Bandini, *Chem. Soc. Rev.*, 2011, **40**, 1358; (*i*) E. M. Beck and M. J. Gaunt, *Top. Curr. Chem.*, 2010, **292**, 85; (*j*) A. Palmieri, M. Petrini and R. R. Shaikh, *Org. Biomol. Chem.*, 2010, **8**, 1259; (*k*) G. Bartoli, G. Bencivenni and R. Dalpozzo, *Chem. Soc. Rev.*, 2010, **39**, 4449; (*l*) M. Bandini and A. Eichholzer, *Angew. Chem., Int. Ed.*, 2009, **48**, 9608; (*m*) L. Joucla and L. Djakovitch, *Adv. Synth. Catal.*, 2009, **351**, 673; (*n*) *Catalytic Asymmetric Friedel–Crafts Alkylations*, ed. M. Bandini and A. Umani-Ronchi, Wiley-VCH, Weinheim, 2009; (*o*) B. Thomas, T. B. Poulsen and K. A. Jørgensen, *Chem. Rev.*, 2008, **108**, 2903.

6 For selected recent reviews on indole dearomatization see: (*a*) W. Zi, Z. Zuo and D. Ma, *Acc. Chem. Res.*, 2015, **48**, 702; (*b*) Q. Ding, X. Zhou and R. Fan, *Org. Biol. Chem.*, 2014, **12**, 4807. For selected recent examples on indole dearomatization see: (*c*) W. Zi, H. Wu and F. D. Toste, *J. Am. Chem. Soc.*, 2015, **137**, 3225; (*d*) C. Liu, Q. Yin, L.-X. Dai and S.-L. You, *Chem. Commun.*, 2015, **51**, 5971; (*e*) M. Jia, M. Monari, Q.-Q. Yang and M. Bandini, *Chem. Commun.*, 2015, **51**, 2320; (*f*) Y.-C. Zhang, J.-J. Zhao, F. Jiang, S.-B. Sun and F. Shi, *Angew. Chem., Int. Ed.*, 2014, **53**, 13912; (*g*) M. Mari, S. Lucarini, F. Bartoccini, G. Piersanti and G. Spadoni, *Beilstein J. Org. Chem.*, 2014, **10**, 1991; (*h*) M. Jia, G. Cera, D. Perrotta, M. Monari and M. Bandini, *Chem. – Eur. J.*, 2014, **20**, 9875; (*i*) H. Li, R. P. Hughes and J. Wu, *J. Am. Chem. Soc.*, 2014, **136**, 6288; (*j*) H. Yin, T. Wang and N. Jiao, *Org. Lett.*, 2014, **16**, 2302; (*k*) L. Han, C. Liu, W. Zhang, X.-X. Shi and S.-L. You, *Chem. Commun.*, 2014, **50**, 1231.

7 For selected recent reviews on polycyclic indole synthesis see: (*a*) L.-Q. Lu, J.-R. Chen and W.-J. Xiao, *Acc. Chem. Res.*, 2012, **45**, 1278. For selected recent papers on polycyclic indole synthesis see: (*b*) C. N. Rao, D. Lentz and H.-U. Reissig, *Angew. Chem., Int. Ed.*, 2015, **54**, 2750; (*c*) J. Gao, Y. Shao, J. Zhu, J. Zhu, H. Mao, X. Wang and X. Lv, *J. Org. Chem.*, 2014, **79**, 9000; (*d*) R. K. Arigela, R. Kumar, S. Samala, S. Gupta and B. Kundu, *Eur. J. Org. Chem.*, 2014, 6057; (*e*) C. R. Reddy, U. Dilipkumarand and M. D. Reddy, *Org. Lett.*, 2014, **16**, 3792; (*f*) S. Das, R. L. Harde, D. E. Shelke, N. Khairatkar-Joshi, M. Bajpai, R. S. Sapalya, H. V. Surve, G. S. Gudi, R. Pattem, D. B. Behera, B. J. Satyawan and A. Thomas, *Bioorg. Med. Chem. Lett.*, 2014, **24**, 2073; (*g*) S. He, R. P. Hsung, W. R. Presser, Z.-X. Ma and B. J. Haugen, *Org. Lett.*, 2014, **16**, 2180; (*h*) T. Wang, S. Shi, D. Pflaesterer, E. Rettenmeier, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Chem. – Eur. J.*, 2014, **20**, 292.

8 (*a*) V. Pirovano, M. Dell'Acqua, D. Facoetti, S. Rizzato, G. Abbiati and E. Rossi, *Eur. J. Org. Chem.*, 2013, 6267;

(*b*) V. Pirovano, L. Decataldo, E. Rossi and R. Vicente, *Chem. Commun.*, 2013, **49**, 3594; (*c*) E. Rossi, V. Pirovano, M. Negrato, G. Abbiati and M. Dell'Acqua, *Beilstein J. Org. Chem.*, 2015, **11**, 1997; (*d*) V. Pirovano, E. Arpini, M. Dell'Acqua, R. Vicente, G. Abbiati and E. Rossi, *Adv. Synth. Catal.*, 2016, **358**, 403.

9 V. Pirovano, D. Facoetti, M. Dell'Acqua, E. Della Fontana, G. Abbiati and E. Rossi, *Org. Lett.*, 2013, **15**, 3812.

10 I.-P. Lorenz, C. Krinninger, R. Wilberger, R. Bobka, H. Piotrowski, M. Warchhold and H. Nöth, *J. Organomet. Chem.*, 2005, **690**, 1986.

11 X. Sun, W. Sun, R. Fan and J. Wu, *Adv. Synth. Catal.*, 2007, **349**, 2151.

12 (*a*) J. J. Hirner, K. E. Roth, Y. Shi and S. A. Blum, *Organometallics*, 2012, **31**, 6843; (*b*) Y.-Q. Zhang, Z.-H. Chen, Y.-Q. Tu, C.-A. Fan, F.-M. Zhang, A.-X. Wang and D.-Y. Yuan, *Chem. Commun.*, 2009, 2706; (*c*) S. Miaskiewicz, J.-M. Weibel, P. Pale and A. Blanc, *Org. Lett.*, 2016, **18**, 844; (*d*) M. Hoffmann, J.-M. Weibel, P. de Fremont, P. Pale and A. Blanc, *Org. Lett.*, 2014, **16**, 908; (*e*) N. Kern, M. Hoffmann, A. Blanc, J.-M. Weibel and P. Pale, *Org. Lett.*, 2013, **15**, 836; (*f*) N. Kern, A. Blanc, S. Miaskiewicz, M. Robinette, J.-M. Weibel and P. Pale, *J. Org. Chem.*, 2012, **77**, 4323; (*g*) N. Kern, A. Blanc, J.-M. Weibel and P. Pale, *Chem. Commun.*, 2011, **47**, 6665.

13 See the ESI† for details.

14 M. Nakagawa and M. Kawahara, *Org. Lett.*, 2000, **2**, 953.

15 (*a*) D. Yang, L. Wang, F. Han, D. Li, D. Zhao, Y. Cao, Y. Ma, W. Kong, Q. Sun and R. Wang, *Chem. – Eur. J.*, 2014, **20**, 16478; (*b*) L. Wang, D. Yang, F. Han, D. Li, D. Zhao and R. Wang, *Org. Lett.*, 2015, **17**, 176.

16 (*a*) Y.-M. Huang, C.-W. Zheng, L. Pan, Q.-W. Jin and G. Zhao, *J. Org. Chem.*, 2015, **80**, 10710; (*b*) Z. Chai, Y.-M. Zhu, P.-J. Yang, S. Wang, S. Wang, Z. Liu and G. Yang, *J. Am. Chem. Soc.*, 2015, **137**, 10088.

17 The stereochemistry of the indoline products was tentatively assigned by analogy with the results reported by Zhao *et al.* (ref. 16*a*). Thus, they synthesized almost pure (*S*,*S*,*S*)**3a**, (*R*,*R*,*R*)**3a** and (*S*,*S*,*S*)**3b** whose structures were established by single-crystal X-ray diffraction.

18 (*a*) J. J. Hirner, K. E. Roth, Y. Shi and S. A. Blum, *Organometallics*, 2012, **31**, 6843; (*b*) N. Kern, A. Blanc, S. Miaskiewicz, M. Robinette, J.-M. Weibel and P. Pale, *J. Org. Chem.*, 2012, **77**, 4323.

19 M. K. Ghorai, A. Kumar and D. Prakash Tiwari, *J. Org. Chem.*, 2010, **75**, 137.

20 E. Rossi, G. Abbiati, V. Canevari, E. Magri and G. Celentano, *Synthesis*, 2006, 299.

21 (*a*) C. Shao, G. Shi, Y. Zhang, S. Pan and X. Guan, *Org. Lett.*, 2015, **17**, 2652; (*b*) J. S. Yadav, B. V. S. Reddy, P. Muralikrishna Reddy and Ch. Srinivas, *Tetrahedron Lett.*, 2002, **43**, 5185; (*c*) I. Usui, S. Schmidt, M. Keller and B. Breit, *Org. Lett.*, 2008, **10**, 1207.

22 M. Nagamochi, Y.-Q. Fang and M. Lautens, *Org. Lett.*, 2007, **9**, 2955.

23 T. Pei, Y.-C. Chen, P. G. Dormer and I. W. Davies, *Angew. Chem., Int. Ed.*, 2008, **47**, 4231.

24 J. Waser, B. Gaspar, H. Nambu and E. M. Carreira, *J. Am. Chem. Soc.*, 2006, **128**, 11693.

25 (*a*) R. A. Craig, N. R. O'Connor, A. F. G. Goldberg and B. M. Stoltz, *Chem. – Eur. J.*, 2014, **20**, 4806; (*b*) Y. Pei, K. Brade, E. Brule, L. Hagberg, F. Lake and C. Moberg, *Eur. J. Org. Chem.*, 2005, 2835; (*c*) T. A. Moss, D. M. Barber, A. F. Kyle and D. J. Dixon, *Chem. – Eur. J.*, 2013, **19**, 3071; (*d*) M. Žinić, S. Alihodžić and V. Škarić, *J. Chem. Soc., Perkin Trans. 1*, 1993, 21; (*e*) H. Rubin, J. Cockrell and J. B. Morgan, *J. Org. Chem.*, 2013, **78**, 8865; (*f*) N. Hsueh, G. J. Clarkson and M. Shipman, *Org. Lett.*, 2015, **17**, 3632.

26 (*a*) N. Mézailles, L. Ricard and F. Gagosz, *Org. Lett.*, 2005, **7**, 4133; (*b*) L. Ricard and F. Gagosz, *Organometallics*, 2007, **26**, 4704.

27 M. Dell'Acqua, L. Ronda, R. Piano, S. Pellegrino, F. Clerici, E. Rossi, A. Mozzarelli, M. L. Gelmi and G. Abbiati, *J. Org. Chem.*, 2015, **80**, 10939.