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Asymmetric Iodocyclization Catalyzed by Salen–$Cr^{III}Cl$: Its Synthetic Application to Swainsonine

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Abstract: The previously developed enantioselective iodocyclization of γ-hydroxy-*cis*-alkenes required 30 mol% of (*R*,*R*)-salen–Co^{II} complex as chiral catalyst and 0.75 equivalent of *N*-chlorosuccinimide (NCS) as activator to produce 2-substituted tetrahydrofurans with 61 to 90% *ee*. Due to the considerable loading amount of the Co^{II} complex, another more effective catalyst was pursued by screening (*R*,*R*)-salen–transition metal complexes. When 10 mol% of the catalysts were applied with 0.5 equivalent of NCS, a higher level of stereoselectivity was attained with the corresponding $Cr^{III}Cl$ (84% *ee*), $Mn^{II}Cl$ (52% *ee*) and Co^{II} complexes (66% *ee*). Refinement of the conditions established a novel catalytic enantioselective iodocyclization protocol using iodine in the presence of 7 mol% of (*R*,*R*)-salen–$Cr^{III}Cl$ complex activated by 0.7 equivalent of NCS in toluene to induce 74 to 93% *ee*.

Keywords: asymmetric catalysis · cyclization · enantioselectivity · swainsonine

Introduction

Electrophile-mediated cyclization is one of the most reliable ways to form heterocycles.[1] The prime concern in the cyclization involves the stereoselectivity which is dictated by the facial differentiation of olefinic double bonds. The most preceptive facial differentiation techniques have been invented in asymmetric epoxidation,[2] dihydroxylation,[3] aminohydroxylation[4] and hydrogenation.[5] While the stereochemistry issue in electrophile-promoted cyclization has mainly focused on diastereoselectivity utilizing preexisting stereogenic centers in substrates,[6] enantioselective versions have seldom been investigated. The latter examples cover selenocyclization with chiral organoselenyl reagents,[7] mercuriocyclization with Hg^{II} carboxylates[8] and Hg^{II}–bisoxazoline complexes,[9] iodocyclization with iodonium ion amine complexes[10] and with *N*-iodosuccinimide in the presence of Ti^{IV}–Binol complexes,[11] and chlorohydroxylation with Pd^{II}–Binap complexes.[12] Most of them have their separate drawbacks such as stoichiometric use of expensive chiral reagents, low enantioselectivity and lack of substrate generality. We have been engaged in efforts to evolve the catalytic asymmetric electrophile-promoted cyclization. Planning of the proposed cyclization study led us to deliberate several controlling factors such as substrate structures, how to accelerate the asymmetric cyclization, how to impose chiral environments, electrophilic species and how to suppress the racemic background reaction. In this context, we documented a highly enantioselective iodoetherification of γ-hydroxy-*cis*-alkenes using iodine in the presence of salen–Co^{II} complex and *N*-chlorosuccinimide (NCS).[13] Since our reported method requires a relatively considerable amount of the complex (30 mol%) for high stereoselectivity, we have endeavored to exploit more efficient catalysts in terms of their loading quantities as well as enantioselectivity.

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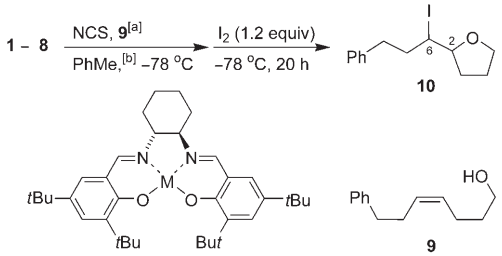
Results and Discussion

The search for the new catalyst was initiated by scouting a series of (*R*,*R*)-salen–metal complexes in the presence of NCS in the iodocyclization of the model substrate **9**. Thereby, **9** was cyclized using iodine in the presence of 10 mol% of the catalysts **1**–**8** activated by 0.5 equivalent of NCS. As disclosed in Table 1, the experimental data reveal that while

Table 1. Iodocyclization of **9** using (*R*,*R*)-salen–M complexes **1**–**8** (10 mol%) with NCS (0.5 equiv).



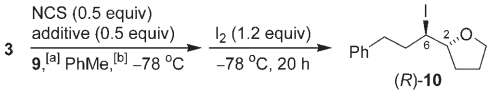
Entry	(*R*,*R*)-salen–M	Yield [%][c]	*ee* [%][d,e]
1	**1**	63 (30)	0
2	**2**	70 (21)	4 (2*R*,6*R*)
3	**3**	89 (7)	84 (2*R*,6*R*)
4	**4**	89 (6)	52 (2*R*,6*R*)
5	**5**	49 (50)	13 (2*S*,6*S*)
6	**6**	87 (5)	66 (2*R*,6*R*)
7	**7**	38 (52)	9 (2*S*,6*S*)
8	**8**	60 (38)	0
9[f]	**3**	93 (5)	86 (2*R*,6*R*)

[a] [**9**] = 10 mM. [b] Distilled from Na before use. [c] Values in parentheses refer to the recovery of starting material. [d] Determined by HPLC analysis using DAICEL OD-H. [e] Absolute configurations in parentheses. [f] PhMe was used without drying.

the Al^{III}, Ti^{IV}, Fe^{III}, Ni^{II} and Cu^{II} complexes delivered poor stereoselectivities (entries 1, 2, 5, 7 and 8), high % *ee* values were acquired with the Cr^{III} and Co^{II} complexes (entries 3 and 6), and a moderate value with the Mn^{III} complex (entry 4). It turned out that (*R*,*R*)-salen–Cr^{III}Cl complex **3** realized the highest asymmetric induction as well as the highest chemical conversion (entry 3). In addition, the cyclization was found to proceed a little more rewardingly in wet toluene than in dry solvent (entry 9). It is worthwhile mentioning that the major stereoisomer induced by the catalysts **5** and **7** is enantiomeric to that by the catalysts **2**–**4** and **6**.

With the prospective catalyst **3** in hand, the iodocyclization conditions were optimized by adjusting the amounts of **3** and NCS, additives, and the concentration. The representative outcomes are outlined in Table 2. The quantity of the chiral complex **3** was varied from 0.5 to 20 mol% in the presence of 0.5 equivalent of NCS. The enantioselectivity increased when amount of the catalyst was augmented (entries 1–3), reaching the maximum level with 7 mol% (entry 3), and slightly decreased with 15 mol% or more (entry 5). The optimal NCS amount was calibrated to gain a marginally increased 87% *ee* value with 0.7 equivalent consistently (entry 6). Another improvement was endeavored by addition of K_2CO_3 or $NaHCO_3$ to result in essentially the same stereoselectivity with a similar chemical yield, but a little inferior enantioselectivity was observed with Cs_2CO_3 (entries 7 and 8). Further improvement was attempted by concentration variation. However, while the enantioselectivity was marginally improved in more dilute solution, higher

Table 2. Iodocyclization of **9** using (*R*,*R*)-salen–Cr^{III}Cl complex **3** with NCS and additive (0.5 equiv).



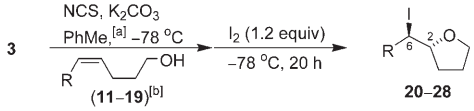
Entry	**3** (mol%)	Additive	Yield [%][c]	*ee* [%]
1	2	–	84 (12)	73
2	5	–	87 (10)	84
3	7	–	90 (6)	86
4	10	–	92 (5)	86
5	15	–	90 (5)	84
6[d]	7	–	88 (9)	87
7[d]	7	Cs_2CO_3	87 (9)	84
8[d]	7	K_2CO_3 or $NaHCO_3$	89 (6)	88
9[d,e]	7	K_2CO_3	96	83

[a] [**9**] = 10 mM. [b] Used without drying. [c] Values in parentheses refer to the recovery of starting material. [d] 0.7 equiv of NCS. [e] [**9**] = 15 mM.

concentration had a deleterious effect on the stereoinduction (entry 9).

The established iodocyclization conditions (entry 8 in Table 2) were applied to several γ-hydroxy-*cis*-alkenes **11**–**19**. The results are summarized in Table 3. While most of

Table 3. Iodocyclization of **11**–**19** using (*R*,*R*)-salen–Cr^{III}Cl complex **3** (7 mol%) with NCS (0.7 equiv) and K_2CO_3 (0.5 equiv).



11, 20: R = CH_2Ph **14, 23**: R = Et **17, 26**: R = *i*Bu
12, 21: R = $(CH_2)_3Ph$ **15, 24**: R = *n*Pr **18, 27**: R = $(CH_2)_3OTr$
13, 22: R = Me **16, 25**: R = *i*Pr **19, 28**: R = $(CH_2)_4N_3$

Entry	Substrate	Product	Yield [%][c]	*ee* [%][d]
1	**9**	(*R*)-**10**	89 (6)	88 (86)
2	**11**	**20**	43 (56)	75 (61)[e,f]
3	**12**	**21**	94 (2)	85 (84)[g]
4	**13**	**22**	94 (3)	74 (67)[f,h]
5	**14**	**23**	93 (2)	88 (82)[f,h]
6	**15**	**24**	92 (4)	89 (85)[h]
7	**16**	**25**	92 (2)	89 (73)[h]
8	**17**	**26**	90 (3)	87 (71)[h]
9	**18**	**27**	90 (8)	93 (90)[i]
10	**19**	**28**	90 (2)	91[f,j]

[a] Used without drying. [b] [substrate] = 10 mM. [c] Values in parentheses refer to the recovery of starting material. [d] Numbers in parentheses refer to the % *ee* values in the iodocyclization using 30 mol% of (*R*,*R*)-salen–Co^{II} complex with 0.75 equiv of NCS and [substrate] = 8 mM. [e] Determined by HPLC analysis using DAICEL OD-H. [f] The absolute configuration was not determined. [g] Determined by HPLC analysis of reductively deiodinated product of **21** using DAICEL OD-H. [h] Determined by GC analysis using CHIRALDEX B-DM. [i] Determined by HPLC analysis of detritylated product of **27** using DAICEL AD-H. [j] Determined by HPLC analysis using DAICEL AD-H.

the substrates displayed high stereoselectivity (around 90% *ee*), somewhat diminished % *ee* values were observed with benzyl alkenol **11** and methyl alkenol **13** (entries 2 and 4).

Even though it is difficult to propose a working model of the asymmetric iodocyclization at present, probably the sterically less demanding small methyl substituent might be attributed to the lower enantioselectivity of **13**. In the case of **11**, the proximity of the phenyl group to the olefinic double bond seemed to exert an adverse effect on the stereoselectivity although the reason is unclear. All of the tested substrates produced higher asymmetric induction with the complex **3** than with the complex **6**. The enantioselectivity increments range from 1 to 16%. It is manifest that the Cr^{III} catalyst system is more effective than Co^{II}.

Although enough experimental evidence has not been accumulated to explain the function of our developed catalytic system in the asymmetric iodocyclization, it is envisioned that NCS reacts with iodide anion to release ICl slowly, which is complexed with the catalyst to activate ICl further. Possibly, the slow generation of ICl is crucial to minimize the background reaction, and the complex between ICl and the catalyst exists as a zwitterion-like species such as $[I^+]$-$[(R,R)$-salen–$Cr^{III}Cl]^-$, the iodonium cation of which resides near the right nitrogen due to the left axial hydrogen at the ring junction (Figure 1). Another conceivable NCS function

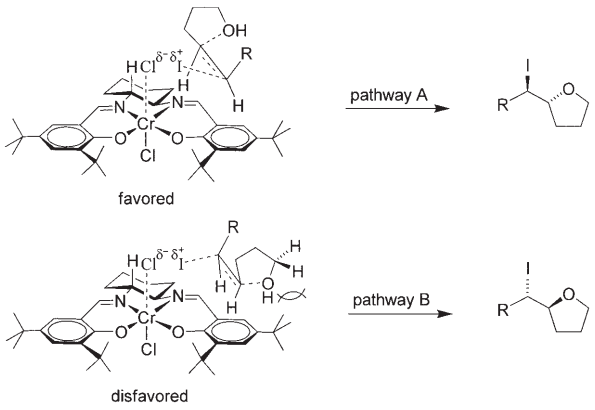
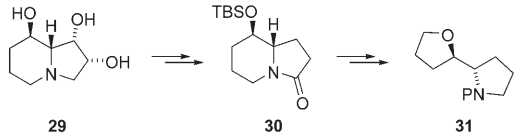


Figure 1. A plausible pathway of the iodocyclization.

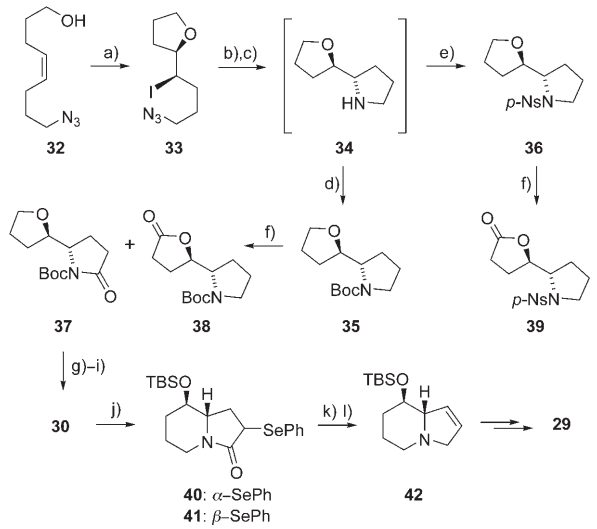
is oxidation of Cr^{III} to higher oxidation state(s) to enhance its Lewis acidity, which activates iodine itself to drive the iodocyclization to some extent. The conjecture can explain why 0.7 equivalents of NCS is enough for the cyclization. The skewed side-on approach model is suggested as the rationale of the iodocyclization enantioselectivity.[14] In the model, the substrate approaches the complex through the right trough between the cyclohexane and the aryl ring, and its hydroxypropyl group stays away from the aryl ring due to the steric congestion from the *tert*-butyl group in the transition state of the tetrahydrofuranyl ring formation. The rudimentary scenario favors pathway A over pathway B to procure the observed enantiomerically enriched tetrahydrofurans.

The potential synthetic utility of the developed protocol led us to pursue asymmetric synthesis of swainsonine **29**.[15] The indolizidine alkaloid was envisioned to be elaborated from pyrrolidinone **30**, which would be conceivably derived from intermediate **31** (Scheme 1). Our synthetic strategy for



Scheme 1. Retrosynthetic analysis of swainsonine **29**.

the target molecule would culminate in preparation of **31** using our developed asymmetric iodocyclization, and the unprecedented chemoselective oxidation of **31** to the corresponding lactam or lactone depending on the *N*-protecting group. The synthesis commenced with the iodocyclization of the azido alkenol **32** to afford the azido tetrahydrofuran **33** with 90% *ee* in 86% yield along with 7% of recovered **32** (Scheme 2). The azido group of **33** was reduced with stan-



Scheme 2. Synthesis of swainsonine **29**. a) **3**, NCS, I_2, K_2CO_3, PhMe, −78°C, 86% (90% *ee*); b) $SnCl_2$, PhSH, Et_3N, MeCN, room temperature; c) NaOAc, EtOH, reflux; d) Boc_2O, $NaHCO_3$, H_2O, MeOH, room temperature, 80% (for steps b–d); e) *p*-NsCl, NaOH, H_2O, EtOH, room temperature, 64% (for steps b, c and e); f) $RuCl_3{\cdot}3H_2O$, $NaIO_4$, CCl_4, H_2O, MeCN, room temperature, 65% for **37**, 21% for **38**, 65% for **39** (based on 15% of recovered **36**); g) TMSI, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0°C; h) TBSOTf, 2,6-lutidine, CH_2Cl_2, 0°C; i) NaH, THF, 0°C, 88% (for steps g–i); j) LDA (3 equiv), PhSeBr (1equiv), THF, −78°C, then 2,6-di-*tert*-butyl-4-methylphenol, −78°C, 74% (**40**/**41** 3:1); k) $LiAlH_4$, $AlCl_3$, THF, −78°C, 97%; l) $NaIO_4$, $NaHCO_3$, H_2O, MeOH, 0°C, 91%. NCS = *N*-chlorosuccinimide, Boc = *tert*-butoxycarbonyl, *p*-Ns = *p*-nitrobenzenesulfonyl, TMS = trimethylsilyl, TBS = *tert*-butyldimethylsilyl, Tf = trifluoromethanesulfonyl, LDA = lithium diisopropylamide.

nous chloride[16] and the resulting amino iodide was cyclized under basic conditions. The crude bicyclic tetrahydrofuranyl pyrrolidine **34** was protected to furnish carbamate **35** and sulfonamide **36**[17] in 80% and 64% overall yield from **33**, respectively. When **35** and **36** were subjected to the similar oxidation conditions using ruthenium chloride in the pres-

ence of $NaIO_4$,[18] the former gave 65% of the pyrrolidinone **37** along with 21% of lactone **38**, and the latter yielded 65% of lactone **39** based on 15% of recovered **36**. Some of the observed side products seemed to stem from the oxidation of the tertiary carbons. Among the screened protecting groups including *p*-toluenesulfonyl, benzyloxycarbonyl, trifluoroacetyl and 2,2,2-trichloroethoxycarbonyl groups, *tert*-butoxycarbonyl and *p*-nitrobenzenesulfonyl groups elicited the best chemoselectivity.

For the synthesis of swainsonine **29**, **37** was treated with TMSI[19] in the presence of BF_3–etherate to open the tetrahydrofuranyl ring (Scheme 2). The resultant hydroxyl iodide was silylated, the carbamate group of which was concomitantly deprotected, and then cyclized to render the requisite indolizidinone **30** in 88% overall yield. To install the olefinic double bond in the pyrrolidinone ring, **30** was phenylselenylated using one equivalent of LDA to give rise to a 1:1 mixture of the α-stereoisomer **40** and the β-stereoisomer **41**. Since later oxidative elimination of the phenylselenylated derivative from **41** proceeded inefficiently, the phenylselenylation was carried out using three equivalents of LDA and one equivalent of PhSeBr followed by quenching with 2,6-di-*tert*-butyl-4-methylphenol to provide a 3:1 mixture of **40** and **41** in 74% combined yield along with 21% of recovered **30**. After separation, **40** was reduced to indolizidine with alane generated in situ from $LiAlH_4$ and $AlCl_3$,[20] and oxidatively eliminated to produce the known indoline **42** in 88% overall yield, which was readily converted to swainsonine **29** via stereoselective dihydroxylation.[21]

Conclusion

In conclusion, we have discovered a more efficient iodocyclization of γ-hydroxy-*cis*-alkenes using 7 mol% of salen–$Cr^{III}Cl$ complex rather than the previously reported 30 mol% of salen–Co^{II} complex, in which significantly less of the catalyst has been loaded and higher enantioselectivity has been attained. Also, the synthetic value of the developed iodocylcization has been demonstrated in the synthesis of an indolizidine alkaloid, swainsonine, in which another distinctive process is considered as chemoselective oxidation of **35** and **36**.

Experimental Section

General methods: NMR spectra were obtained on Bruker Avance 400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) and measured in $CDCl_3$. Chemical shifts were recorded in ppm relative to internal standard $CDCl_3$, and coupling constants were reported in Hz. The high resolution mass spectra were recorded on VG Autospec Ultima spectrometer. The enantioselectivities were determined by HPLC or GC analysis. HPLC measurements were done on a RAININ model equipped with SD-200 pump, DVW-100 detector (D-Star Instruments) measured at 254 nm, and chiral column such as DAICEL OD-H and DAICEL AD-H. Eluting solvent was a mixture of 2-propanol and hexane. GC was measured on Donam DS-6200 GC with Chiraldex B-DM. All reactions were carried out in oven-dried glassware under a N_2 atmosphere. While toluene employed in the iodocyclization was used directly from the stock bottle (Junsei, EP grade) without purification, all other solvents were distilled from the indicated drying reagents right before use: Et_2O and THF (Na/benzophenone), CH_2Cl_2 (P_2O_5), MeCN (CaH_2) and DMF (CaH_2). The normal work-up included extraction, drying over Na_2SO_4 and evaporation of volatile materials in vacuo. Purifications by column chromatography were performed using Merck silica gel 60 (230–400 mesh). Additional intermediates available in the Supporting Information.

Representative procedure for the asymmetric iodocyclization: To a mixture of K_2CO_3 (66 mg, 0.48 mmol), NCS (90 mg, 0.66 mmol) and (*R*,*R*)-salen–$Cr^{III}Cl$ (42 mg, 0.066 mmol) were added toluene (114 mL) and alcohol **32** (162 mg, 0.96 mmol) dissolved in toluene (6 mL) at room temperature. After cooling down the mixture to −78 °C, iodine (288 mg, 1.14 mmol) was added to it as solid in a portion. The resulting mixture was stirred at −78 °C for 20 h and then quenched with 10% aqueous $Na_2S_2O_5$ (100 mL). Normal work-up with Et_2O (3×30 mL) followed by column chromatography (Et_2O/hexane 1:5) gave azide **33** (243 mg, 86%) along with the starting alcohol (15 mg, 9%). **33**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.07–3.95 (m, 1H), 3.95–3.91 (m, 1H), 3.82–3.80 (m, 1H), 3.71–3.70 (m, 2H), 3.32–3.29 (t, 2H, J=5.6 Hz), 1.95–1.71 (m, 6H), 1.69–1.57 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 82.2, 69.0, 50.6, 40.9, 33.5, 30.8, 29.3, 26.2 ppm; HRMS(EI): *m*/*z*: calcd for $C_8H_{14}IN_3O$: 295.0182 $[M]^+$, found: 295.0205.

(*R*)-2-((*R*)-1-Iodo-3-phenylpropyl)tetrahydrofuran (10): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.17 (m, 5H), 4.04–4.00 (m, 1H), 3.93 (td, 1H, J=8.2, 6.8 Hz), 3.82 (td, 1H, J=7.8, 5.8 Hz), 3.73 (td, 1H, J=7.2, 4.7 Hz), 3.01–2.95 (m, 1H), 2.74–2.67 (m, 1H), 2.20–2.13 (m, 1H), 2.05–1.84 (m, 4H), 1.71–1.62 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.8, 128.6, 128.5, 126.1, 82.4, 69.0, 41.6, 37.9, 35.7, 30.9, 26.2 ppm; HRMS (EI): *m*/*z*: calcd for $C_{13}H_{17}IO$: 316.0330 $[M]^+$, found: 316.0358.

(*R*)-2-((*R*)-1-Iodo-2-phenylethyl)tetrahydrofuran (20): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.19 (5H, m), 4.32–4.28 (m, 1H), 4.02–3.98 (m, 1H), 3.84–3.80 (m, 1H), 3.55–3.49 (m, 1H), 3.37–3.31 (td, 1H, J=8.5, 6.4 Hz), 3.25–3.19 (td, 1H, J=8.9, 5.3 Hz), 2.04–1.57 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.8, 129.1, 128.4, 126.7, 80.4, 69.1, 43.6, 42.7, 31.7, 26.1 ppm; HRMS (EI): *m*/*z*: calcd for $C_{12}H_{15}IO$: 302.0168 $[M]^+$, found: 302.0140.

(*R*)-2-((*R*)-1-Iodo-4-phenylbutyl)tetrahydrofuran (21): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.16 (m, 5H), 4.13–4.08 (m, 1H), 3.95 (td, 1H, J=8.2, 6.8 Hz), 3.81 (td, 1H, J=7.8, 5.7 Hz), 3.71 (td, 1H, J=7.1, 4.7 Hz), 2.71–2.56 (m, 2H), 2.05–1.89 (m, 5H), 1.79–1.64 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.8, 128.4, 128.3, 125.9, 82.4, 68.9, 42.1, 35.9, 35.0, 31.5, 30.9, 26.2 ppm; HRMS (EI): *m*/*z*: calcd for $C_{14}H_{19}IO$: 330.0481 $[M]^+$, found: 330.0421.

(*R*)-2-((*R*)-1-Iodoethyl)tetrahydrofuran (22): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.19–4.12 (m, 1H), 3.93 (td, 1H, J=8.1, 6.9 Hz), 3.82 (td, 1H, J=7.7, 5.8 Hz), 3.73–3.70 (m, 1H), 2.05–1.91 (m, 3H), 1.86 (d, 3H, J=7 Hz), 1.65–1.60 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 83.5, 68.9, 31.9, 30.2, 26.3, 24.1 ppm; HRMS (EI): *m*/*z*: calcd for $C_6H_{11}IO$: 225.9855 $[M]^+$, found: 225.9888.

(*R*)-2-((*R*)-1-Iodopropyl)tetrahydrofuran (23): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.03–3.98 (m, 1H), 3.92 (td, 1H, J=8.2, 6.8 Hz), 3.79 (td, 1H, J=7.8, 5.7 Hz), 3.74 (td, 1H, J=7.2, 4.9 Hz), 2.07–1.62 (m, 6H), 1.04 ppm (t, 3H, J=7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 82.3, 68.8, 44.7, 30.7, 29.7, 26.2, 14.6 ppm; HRMS (EI): *m*/*z*: calcd for $C_7H_{13}IO$: 240.0011 $[M]^+$, found: 240.0003.

(*R*)-2-((*R*)-1-Iodobutyl)tetrahydrofuran (24): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.09–4.06 (m, 1H), 3.92 (td, 1H, J=8.2, 6.8 Hz), 3.79 (td, 1H, J=7.8, 5.7 Hz), 3.71 (td, 1H, J=7.2, 4.8 Hz), 2.03–1.79 (m, 4H), 1.71–1.54 (m, 3H), 1.43–1.33 (m, 1H), 0.90 ppm (t, 3H, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 82.4, 68.9, 42.2, 38.3, 30.8, 26.2, 23.0, 13.2 ppm; HRMS (EI): *m*/*z*: calcd for $C_8H_{15}IO$: 254.0168 $[M]^+$, found: 254.0158.

(*R*)-2-((*R*)-1-Iodo-2-methylpropyl)tetrahydrofuran (25): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.08–4.04 (m, 1H), 3.90 (td, 1H, J=8.2, 6.9 Hz), 3.79–3.68 (m, 2H), 2.03–1.85 (m, 3H), 1.61–1.52 (m, 1H), 1.30–1.23 (m, 1H), 0.97 ppm (dd, 6H, J=13.7, 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ

= 81.7, 67.9, 54.8, 32.8, 31.6, 26.1, 23.8, 20.9 ppm; HRMS (EI): *m/z*: calcd for $C_8H_{15}IO$: 254.0168 $[M]^+$, found: 254.0143.

(*R*)-2-((*R*)-1-Iodo-3-methylbutyl)tetrahydrofuran (26): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.13–4.06 (m, 1H), 3.94–3.92 (m, 1H), 3.82–3.79 (q, 1H, J=5.8 Hz), 3.67–3.66 (m, 1H), 2.02–2.00 (m, 2H), 1.93–1.86 (m, 3H), 1.70–1.65 (m, 1H), 1.33–1.31 (m, 1H), 0.95–0.93 (d, 3H, J=6.5 Hz), 0.84–0.82 pppm (d, 3H, J=6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 82.5, 68.9, 45.1, 41.2, 31.1, 28.1, 26.2, 23.1, 20.6 ppm; HRMS (EI): *m/z*: calcd for $C_9H_{17}IO$: 268.0324 $[M]^+$, found: 268.0298.

(*R*)-2-((*R*)-1-Iodo-4-(trityloxy)butyl)tetrahydrofuran (27): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.43 (m, 6H), 7.32–7.23 (m, 9H), 4.08–4.03 (m, 1H), 3.95 (td, 1H, J=8.1, 6.8 Hz), 3.82 (td, 1H, J=7.8, 5.8 Hz), 3.71 (td, 1H, J=7.1, 4.8 Hz), 3.16–3.06 (m, 2H), 2.08–1.88 (m, 6H), 1.77–1.63 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2, 128.6, 127.7, 126.8, 86.4, 82.3, 68.8, 62.5, 42.4, 33.4, 30.9, 30.2, 26.2 ppm; HRMS (EI): *m/z*: calcd for $C_{27}H_{29}IO_2$: 512.1212 $[M]^+$, found: 512.1197.

(*R*)-2-((*R*)-5-Azido-1-iodopentyl)tetrahydrofuran (28): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.37–5.33 (m, 2H), 3.61–3.58 (t, 2H, J=6.5 Hz), 3.24–3.22 (t, 2H, J=6.9 Hz), 2.10–2.01 (m, 4H), 1.62–1.53 (m, 4H), 1.43–1.38 pppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 129.7, 129.6, 62.4, 51.3, 32.5, 28.3, 26.6, 26.5, 23.5 ppm; HRMS (EI): *m/z*: calcd for $C_9H_{16}IN_3O$: 309.0338 $[M]^+$, found: 309.0372.

(*S*)-*tert*-Butyl 2-((*R*)-tetrahydrofuran-2-yl)pyrrolidine-1-carboxylate (35) and (*S*)-1-(4-nitrophenylsulfonyl)-2-((*R*)-tetrahydrofuran-2-yl)pyrrolidine (36): To a mixture of $SnCl_2$ (413 mg, 2.18 mmol) and PhSH (0.9 mL, 8.72 mmol) in acetonitrile (3 mL) was added Et_3N (0.91 mL, 6.54 mmol) in an ice bath dropwise. Subsequently, azide **33** (429 mg, 1.45 mmol) was injected to the resulting solution in the ice bath dropwise over 10 min. After stirring the mixture at room temperature for 30 min, the volatile materials were evaporated in vacuo and the residue was dissolved in 2 M aqueous NaOH (5 mL). Normal work-up with CH_2Cl_2 (3×5 mL) yielded the crude iodo amine. All the crude amine was heated at reflux with NaOAc·hydrate (1.37 g) in EtOH (5 mL) for one day. EtOH was evaporated in vacuo and the residue was filtered through celite (500 mg) with CH_2Cl_2 (15 mL). Removal of the volatile materials under reduced pressure gave the cyclized product **34**. After dissolving the crude pyrrolidine **34** in MeOH (5 mL), Boc_2O (381 mg, 1.74 mmol) and saturated aqueous $NaHCO_3$ (2 mL) were added and the resulting solution was stirred at room temperature for 5 h. The following normal work-up with EtOAc (3×5 mL) and chromatographic purification (EtOAc/hexane 1:4) afforded the Boc-protected pyrrolidine **35** (280 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90–3.88 (m, 1H), 3.77–3.72 (m, 2H), 3.64–3.62 (m, 1H), 3.32–3.30 (m, 1H), 3.25–3.22 (m, 1H), 1.87–1.80 (m, 4H), 1.76–1.53 (m, 4H), 1.37 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 80.1, 78.9, 68.2, 60.2, 46.6, 28.9, 28.4, 26.3, 25.64, 23.6 ppm; HRMS (EI): *m/z*: calcd for $C_{13}H_{23}NO_3$: 241.1678 $[M]^+$, found: 241.1702.

The crude pyrrolidine **34** obtained from **33** (429 mg, 1.45 mmol) was stirred with *p*-NsCl (384 mg, 1.74 mmol) in a mixture of 1 M aqueous NaOH (3 mL) and Et_2O (3 mL) at room temperature for a day. Normal work-up with EtOAc (3×3 mL) and chromatographic separation (EtOAc/hexane 1:4) furnished the nosyl-protected pyrrolidine **36** (300 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35–8.32 (d, 2H, J= 7.0 Hz), 8.02–7.99 (d, 2H, J=7.9 Hz), 4.01–3.98 (ddd, 1H, J=1.4, 1.0, 5.1 Hz), 3.83–3.78 (m, 2H), 3.74–3.71 (m, 1H), 3.40–3.36 (m, 1H), 3.28–3.26 (m, 1H), 2.00–1.95 (m, 1H), 1.91–1.86 (m, 4H), 1.75–1.71 (m, 1H), 1.57–1.47 (m, 1H), 1.25–1.19 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.9, 144.5, 128.6, 124.2, 80.4, 68.6, 63.5, 49.2, 28.8, 26.7, 25.7, 24.4 ppm; HRMS (EI): *m/z*: calcd for $C_{14}H_{18}N_2O_5S$: 326.0936 $[M]^+$, found: 326.0942.

(*S*)-*tert*-Butyl 2-oxo-5-((*R*)-tetrahydrofuran-2-yl)pyrrolidine-1-carboxylate (37): **35** (280 mg, 1.16 mmol) was dissolved in a mixture of CCl_4 (20 mL), MeCN (20 mL) and H_2O (30 mL), and $NaIO_4$ (1.98 g, 9.28 mmol) and $RuCl_3{\cdot}3H_2O$ (5 mg, 0.023 mmol) were added. After 12 h at room temperature, normal work-up with CH_2Cl_2 (3×10 mL) and chromatographic separation (EtOAc/hexane 1:1) gave rise to lactam **37** (192 mg, 65%) and lactone **38** (62 mg, 21%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.17–4.12 (m, 2H), 3.80–3.78 (m, 1H), 3.71–3.69 (m, 1H), 2.68–2.62 (m, 1H), 2.37–2.32 (m, 1H), 1.97–1.86 (m, 5H), 1.57–1.53 (m, 1H), 1.49 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.8, 150.2, 82.8, 79.7, 68.7, 60.4, 32.5, 28.3, 28.1, 25.9, 18.7 ppm; HRMS (EI): *m/z*: calcd for $C_{13}H_{21}NO_4$: 255.1471 $[M]^+$, found: 255.1454.

(*R*)-5-((*S*)-1-(4-Nitrophenylsulfonyl)pyrrolidin-2-yl)dihydrofuran-2(3*H*)-one (39): To **36** (300 mg, 0.93 mmol) dissolved in a mixture of CCl_4 (18 mL), MeCN (18 mL) and H_2O (27 mL) were added $NaIO_4$ (1.59 g, 7.44 mmol) and $RuCl_3{\cdot}3H_2O$ (4 mg, 0.018 mmol). After one day at room temperature, normal work-up with CH_2Cl_2 (3×10 mL) followed by chromatographic purification (EtOAc/hexane 1:1) provided lactone **39** (207 mg, 65%) along with 15% of the recovered **36** (45 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (dd, 2H, J=6.9, 1.8 Hz), 8.00 (dd, 2H, J= 6.9, 1.9 Hz), 4.67–4.65 (m, 1H), 3.85–3.83 (m, 1H), 3.42–3.39 (m, 1H), 3.24–3.21 (m, 1H), 2.58–2.53 (m, 2H), 2.38–2.33 (m, 1H), 2.16–2.14 (m, 1H), 1.91–1.87 (m, 2H), 1.61–1.57 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.4, 150.2, 143.4, 128.6, 124.5, 81.1, 62.7, 49.2, 28.4, 26.5, 24.9, 24.2 ppm; HRMS (EI): *m/z*: calcd for $C_{14}H_{16}N_2O_6S$: 340.0729 $[M]^+$, found: 340.0747.

(8*R*,8a*S*)-8-(*tert*-Butyldimethylsilyloxy)hexahydroindolizin-3(5*H*)-one (30): TMSI (0.48 mL, 3.38 mmol) and $BF_3{\cdot}OEt_2$ (0.18 mL, 1.69 mmol) were injected to **37** (505 mg, 1.69 mmol) in CH_2Cl_2 (4 mL) in an ice bath. After removal of the bath, the mixture was stirred at room temperature for 3 h and then quenched with saturated aqueous NH_4Cl (5 mL). Normal work-up with EtOAc (3×5 mL) yielded the crude iodo alcohol. To the crude alcohol in CH_2Cl_2 (4 mL) were added TBSCl (509 mg, 3.38 mmol) and 2,6-lutidine (0.39 mL, 3.38 mmol) cooled in an ice bath. The reaction mixture was stirred at room temperature for 2 h, quenched with saturated aqueous NH_4Cl (5 mL) and worked up with EtOAc (3× 4 mL) to supply the crude iodo silyl ether. After addition of NaH (135 mg, 60% oil dispersion, 3.38 mmol) to the crude silyl ether in an ice bath, the mixture was stirred in the bath for 30 min and quenched with saturated aqueous NH_4Cl (3 mL). Normal work-up with EtOAc (3× 3 mL) and the subsequent chromatographic purification produced indolizidinone **30** (401 mg, 88% overall yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.02–3.98 (m, 1H), 3.18–3.14 (m, 2H), 2.53–2.47 (m, 1H), 2.36–2.34 (m, 2H), 2.25–2.23 (m, 1H), 2.02–1.97 (m, 1H), 1.72–1.68 (m, 2H), 1.40–1.35 (m, 2H), 0.86 (s, 9H), 0.04 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.9, 74.3, 62.9, 39.3, 33.8, 30.2, 25.6, 23.2, 22.9, 17.9, −4.0, −4.7 ppm; HRMS (EI) calcd for $C_{14}H_{27}NO_2Si$: *m/z*: 269.1811 $[M]^+$, found: 269.1817.

(2*S*,8*R*,8a*S*)-8-(*tert*-Butyldimethylsilyloxy)-2-(phenylselanyl)hexahydroindolizin-3(5*H*)-one (40): LDA solution was freshly prepared by dropwise addition of *n*BuLi (2.5 M in THF, 1.79 mL, 4.47 mmol) to diisopropylamine (0.63 mL, 4.47 mmol) in THF (3 mL) at −78 °C. To the LDA solution was injected **30** (401 mg, 1.49 mmol) dissolved in THF (2 mL) at −78 °C. After 1 h, PhSeBr (351 mg, 1.49 mmol) in THF (1 mL) was added and stirred at that temperature for another one hour. Then, the mixture was quenched with 2,6-di-*tert*-butyl-4-methylphenol (1.5 g, 6.8 mmol) and stirred at −78 °C for 10 min. After addition of saturated aqueous NH_4Cl (10 mL), normal work-up with EtOAc (3×5 mL) followed by column chromatography (EtOAc/hexane 1:3) afforded the α-phenylselenyl indolizidinone **40** (354 mg, 56%) and the β-phenylselenyl indolizidinone **41** (115 mg, 18%) along with **30** (84 mg, 21%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.97–3.93 (dd, 1H, J=8.5, 4.6 Hz), 3.81–3.78 (dd, 1H, J=6.2, 2.6 Hz), 3.06–3.03 (m, 1H), 2.66–2.60 (m, 1H), 2.36–2.38 (m, 1H), 2.26–2.20 (m, 2H), 1.88–1.82 (m, 1H), 1.66–1.60 (m, 1H), 1.26–1.20 (m, 1H), 0.83 (s, 9H), 0.00 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.7, 135.9, 129.1, 128.4, 127.6, 73.9, 61.3, 40.6, 39.9, 33.7, 31.3, 25.6, 23.1, 17.8, −4.0, −4.6 ppm; HRMS (EI): *m/z*: calcd for $C_{20}H_{31}NO_2SeSi$: 425.1289 $[M]^+$, found: 425.1265.

(8*R*,8a*S*)-8-(*tert*-Butyldimethylsilyloxy)-3,5,6,7,8,8a-hexahydroindolizine (42): Alane was freshly prepared by dropwise addition of $LiAlH_4$ (1.0 M in THF, 3 mL, 3.0 mmol) to $AlCl_3$ (134 mg, 1.0 mmol) in THF (3 mL) at 0 °C. To **40** (200 mg, 0.47 mmol) dissolved in THF (2 mL) was injected the alane solution (5.7 mL, 0.94 mmol) dropwise at −78 °C. The mixture was stirred for 1 h, and then quenched with H_2O (0.11 mL), 15% aqueous NaOH (0.11 mL) and H_2O (0.33 mL) in sequence at that temperature. After 5 min, EtOAc (5 mL) and celite (1 g) were added at room temperature. The resulting mixture was stirred for 2 h and filtered

through celite (1 g) with EtOAc (15 mL). Evaporation of the volatile materials in vacuo followed by chromatographic purification (EtOAc/hexane 1:10) furnished the corresponding indolizidine (187 mg, 97%).

To the indolizidine (187 mg, 0.46 mmol) dissolved in a 10:1 mixture of MeOH and H_2O (5.5 mL) were added $NaIO_4$ (197 mg, 0.92 mmol) and $NaHCO_3$ (20 mg, 0.24 mmol) in an ice bath, and the mixture was reacted in the bath for 30 min. After addition of saturated aqueous NH_4Cl (5 mL), normal work-up with EtOAc (3×5 mL) and the subsequent chromatographic separation (EtOAc/hexane 1:1) gave **42** (106 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.04–6.03 (br d, 1H, J=5.2 Hz), 5.88–5.85 (dddd, 1H, J=2.0, 2.0, 2.0, 1.8 Hz), 3.64–3.60 (dddd, 1H, J=12.5, 4.2, 1.7, 1.6 Hz), 3.44–3.41 (ddd, 1H, J=10.3, 9.4, 4.3 Hz), 3.24–3.20 (m, 1H), 2. 91–2.88 (br d, 1H, J=10.8 Hz), 2.84 (br s, 1H), 2.40–2.32 (m, 1H), 1.91–1.65 (m, 1H), 1.65–1.60 (m, 2H), 1.26–1.21 (m, 1H), 0.87 (s, 9H), 0.04 (s, 3H), 0.03 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.6, 128.6, 74.1, 72.0, 57.9, 48.9, 34.4, 25.8, 24.5, 18.1, −4.2, −4.7 ppm; HRMS (EI): m/z: calcd for $C_{14}H_{27}NOSi$: 253.1862 $[M]^+$, found: 253.1887.

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