Synthesis S. T. Bugde et al. Paper

Protecting-Group-Directed Regio- and Stereoselective Oxymercuration–Demercuration: Synthesis of Piperidine Alkaloids Containing 1,2- and 1,3-Amino Alcohol Units

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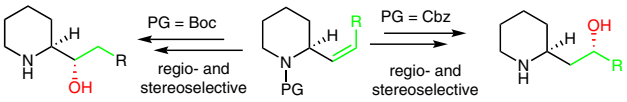

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Abstract An efficient synthesis of naturally occurring 1,2- and 1,3-amino alcohol unit containing 2-substituted piperidine alkaloids and their analogues has been developed from L-pipecolinic acid. The protocol describes the regio- and stereoselective oxymercuration–demercuration of 2-alkenyl piperidines based on protecting groups to give piperidine alkaloids as a key step.

Key words oxymercuration, stereoselectivity, oxazolidinone, piperidines, pipecolinic acid

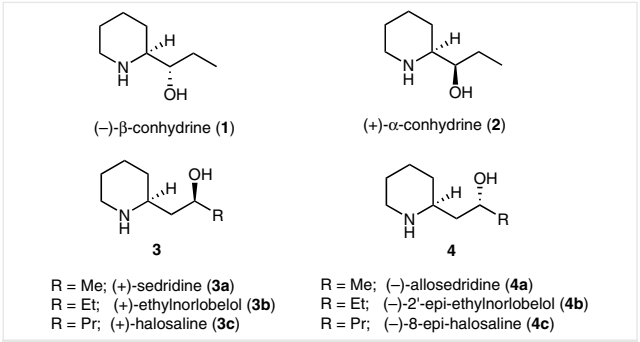
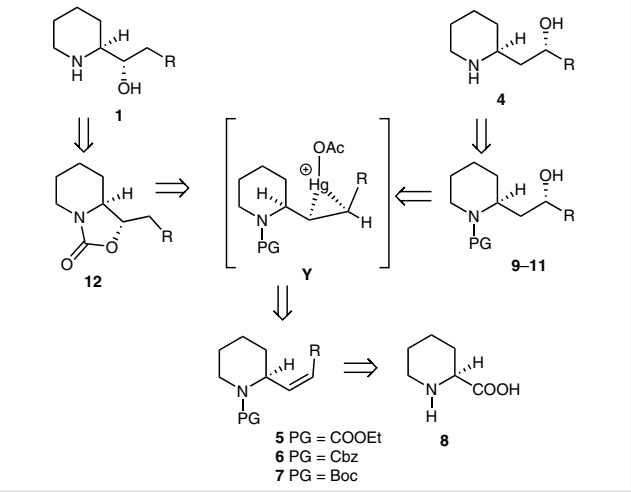


Figure 1 Natural 2-substituted piperidine alkaloids

Amino alcohols having 1,2- and 1,3-relationships are compounds of special interest as ligands in various metal-mediated reactions.[1] This spatial relationship is also found in several natural products.[2] Conhydrines **1** and **2** are piperidine alkaloids of the hemlock family, isolated from the plant *Conium Maculatum L.*[3] (+)-Sedridine **3a**, (–)-allosedridine **4a**, (+)-ethylnorlobelol **3b**, (–)-2′-*epi*-ethylnorlobelol **4b**, (+)-halosaline **3c**, and (–)-8-*epi*-halosaline **4c** have been isolated from different *sedum* species and are therefore called sedum alkaloids (Figure 1).[4] Considerable attention has focused on their synthesis during the last decade due to their biological activities, which includes anti-Alzheimer, anti-viral and anti-bacterial action.[5] Although a plethora of routes are reported for the synthesis of hydroxyalkyl piperidines,[6] the development of new efficient strategies for the synthesis of these alkaloids and their analogues remains desirable.

Asymmetric synthesis using easily available chiral precursors has a great advantage of built-in chirality; however, the challenge of regioselective and stereoselective generation of the next stereocenter still needs to be met. We had earlier reported a regioselective Wacker oxidation for the synthesis of naturally occurring pyrrolidine alkaloids containing a 1,3-oxyamino unit.[7] Recently, we developed a Henry–Nef reaction protocol for the synthesis of naturally occurring 1,3-amino alcohols containing pyrrolidine as well as piperidine rings.[8] In a continuation of this work, we report herein regioselective and stereoselective oxymercuration–demercuration for the synthesis of hydroxyl piperidine alkaloids containing the 1,3- and 1,2-amino alcohol units.[9] A regioselective functionalization by the oxy-mercuration of β,γ-unsaturated urethanes was disclosed earlier by Krow and Fan for the synthesis of γ-ketourethanes.[9h] Diastereoselective intramolecular azamercurations for the synthesis of (+)-pseudohygroline has been reported by Perlmutter and co-workers.[9i]

We conceptualized that protecting group directed regio- and stereoselective oxymercuration–demercuration of olefins **5**–**7** (Scheme 1), which could be obtained from commercially available L-pipecolinic acid (**8**), may give access to both 1,3- and 1,2-amino alcohol unit containing alkaloids **1**–**4**. It was anticipated that $Hg(OAc)_2$ would add stereoselectively from the less hindered side of olefins **5**–**7** to form the mercurinium ion intermediates **Y**, which then could be attacked by the water (nucleophile) regio-

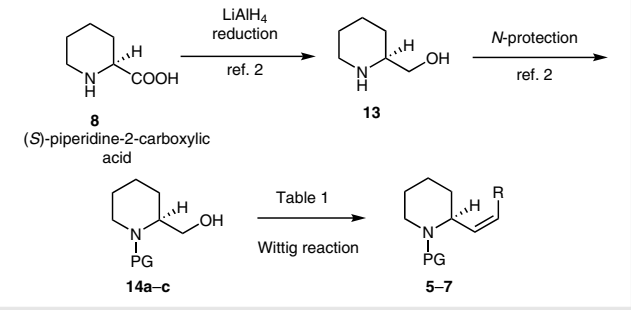


Scheme 1 Retrosynthetic approach

selectively, depending on the size of the protecting group, leading to 1,3-aminoalcohols **9**–**11**; if the protecting group participates in an intramolecular fashion,[10–12] it may lead to oxazolidinones **12** regio- and stereosectively. Oxazolidinones **12** then could be hydrolyzed to give 1,2-amino alcohols (–)-β-conhydrines **1** while alcohols **9**–**11** would provide natural alkaloids **4**. The minor diastereomers could then be similarly converted into other natural products **2** and **3**.

To test the hypothesis we started with L-pipecolinic acid, which was first reduced with $LiAlH_4$ and then protected with a carboethoxy group (Scheme 2). Further oxidation with Dess–Martin periodinane (DMP) and subsequent Wittig olefination provided the required olefin **5** (Table 1, entry 1). Wittig reaction of unstabilized ylides are known to provide *Z*-olefins, and the geometry of the product obtained **5** was found to be *Z* based on its ^1H NMR data.

Once olefin **5a** was in hand, it was first subjected to oxymercuration using 1.1 equiv $Hg(OAc)_2$ in THF/H_2O (1:1) until the yellow color persisted. Demercuration using NaOH and $NaBH_4$ afforded a mixture of two diastereomers in 1:1.7 ratio. The selectivity was marginally increased to 1:2 by the



Scheme 2 Synthesis of 2-alkenyl piperidines

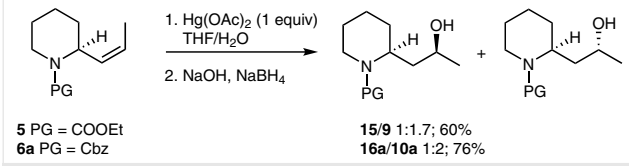
Table 1 Synthesis of 2-Alkenyl Piperidines[a]

Entry	Protecting group **14a–c**	Phosphonium salt	R	Product	Yield (%)[b]
1	-COOEt	$C_2H_5PPh_3^+Br^-$	Me	**5**	63
2	-Cbz	$C_2H_5PPh_3^+Br^-$	Me	**6a**	71
3	-Cbz	$C_3H_7PPh_3^+Br^-$	Et	**6b**	66
4	-Cbz	$C_4H_9PPh_3^+Br^-$	Pr	**6c**	72
5	-Cbz	$C_6H_{13}PPh_3^+Br$	Pent	**6d**	59
6	-Boc	$C_2H_5PPh_3^+Br^-$	Me	**7a**	72
7	-Boc	$C_3H_7PPh_3^+Br^-$	Et	**7b**	61
8	-Boc	$C_4H_9PPh_3^+Br^-$	Pr	**7c**	55
9	-Boc	$C_6H_{13}PPh_3^+Br^-$	Pent	**7d**	63

[a] Reaction conditions: **14a** (1.0 equiv), $NaHCO_3$ (1.5 equiv), DMP (1.5 equiv) in CH_2Cl_2 (20 mL), 0 °C, then to phosphonium salt (1 equiv) in THF (20 mL), *n*-BuLi (1 equiv) at 0 °C, then, aldehyde (1 equiv).
[b] Isolated yield.

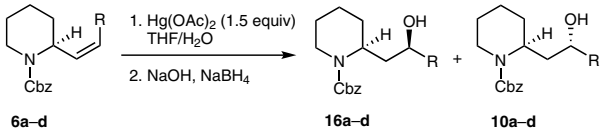
use of the Cbz protecting group (Scheme 3). Hence for further studies, the Cbz protecting group was chosen, because it is much easier to remove than the COOEt group.

An optimal yield of 88% was obtained for **6a** when 1.5 equiv $Hg(OAc)_2$ was used (Table 2, entry 1). We elaborated this methodology for a series of *Z*-alkenes **6b**–**d**. It was observed that as the size of the alkyl group increased, the yield of the oxymercuration–demercuration reaction diminished while the stereoselectivity for the *syn* isomer (Table 2) increased from 1:2 to 1:4.1. The configuration of



Scheme 3 Oxymercuration–demercuration reaction of olefin **5** and **6a**

Table 2 Oxymercuration–Demercuration of *N*-Cbz Protected Alkenes[a]



Entry	**6**	Product **16a–d/10a–d**	Time (h)	Yield (%) **16a–d/10a–d** (combined)[b]	Ratio **16a–d/10a–d**
1	**6a**	R = Me	24	29/59 (88)	1:2
2	**6b**	R = Et	24	14/52 (66)	1:3.7
3	**6c**	R = Pr	24	14/53 (67)	1:3.8
4	**6d**	R= Pent	24	9/31 (55)	1:4.1

[a] Reaction conditions: **6** (1 equiv), $Hg(OAc)_2$ (1.5 equiv), H_2O/THF (1:1, 12 mL) at r.t., then 3 N NaOH (2 mL), 0.5 N $NaBH_4$ (3 mL) at 0 °C for 1 h.
[b] Isolated yield.

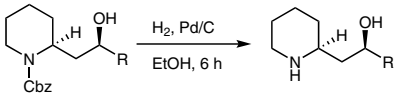
the products was assigned by comparison with published NMR data, and the optical rotation of the antipodes, and further confirmed by conversion into the natural products.

The targeted natural products and their analogues were then synthesized from their respective starting compounds. (+)-Sedridine **3a** and (–)-allosedridine **4a** were synthesized by removal of the *N*-Cbz group through hydrogenation in 95 and 92% yield, respectively. (+)-Ethylnorlobelol **3b** and (–)-2′-*epi*-ethylnorlobelol **4b** were similarly synthesized from **16b** and **10b**, respectively. (+)-Halosaline **3c**, (–)-8-*epi*-halosaline **4c**, **3d**, and **4d** were obtained from their respective starting compounds (Table 3 and Table 4).

After accomplishing the synthesis of piperidine alkaloids containing the 1,3-amino alcohol unit, we set out to synthesize conhydrine **1**, which is an alkaloid containing the 1,2-amino alcohol unit. When **7a** was subjected to oxymercuration–demercuration using 1.5 equiv $Hg(OAc)_2$, oxazolidinone **12a** was obtained regioselectively and with complete diastereoselectivity in 33% yield. The yield increased to 77% when 1 equiv $Hg(OAc)_2$ was employed. Similar Boc group participation has been utilized to obtain oxazolidinones by halo-induced cyclization recently by Paisuwan et al.,[10a] using $SnCl_4$ catalysts by Alcaide et al.,[10b] and earlier by Fisher and Overman.[10c] Brocherieux-Lanoy et al.[10d] reported $TiCl_4$ and Colombo et al.[10e] $InCl_3$ for oxazinone formation. Comins et al. and Cipolla et al. reported the participation of the Cbz group for iodolactonisation reactions.[11,12] Suga et al. have shown participation of the *N*-methyl carbamate group in [2+4] cycloaddition reactions for oxazinone synthesis.[13]

Similarly, oxymercuration–demercuration of alkenes **7b–d** gave oxazolidinones **12b–d**. Increasing the length of the side-arm chain had no effect on the formation of oxazolidinones and yields, which were consistently satisfactory (Table 5). Basic hydrolysis of these oxazolidinones furnished (–)-β-conhydrine **1a** and its analogues in 73–78% yield (Table 6).

Table 3 Synthesis of 1,3-Amino Alcohol Alkaloids[a]

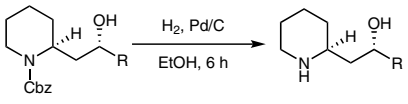


16a–d **3a–d**

Entry	16	Product	Yield (%)[b]
1	**16a**	**3a**; R = Me; (+)-sedridine	95
2	**16b**	**3b**; R = Et; (+)-ethylnorlobelol	84
3	**16c**	**3c**; R = Pr; (+)-halosaline	92
4	**16d**	**3d**; R = Pent; (+)-**3d**	92

[a] Reaction conditions: **16** (1.0 equiv), Pd/C(10% w/w), EtOH (15 mL) at r.t. under H_2 pressure (40 psi) Parr hydrogenator for 6 h.
[b] Isolated yield.

Table 4 Synthesis of 1,3-Amino Alcohol Alkaloids[a]

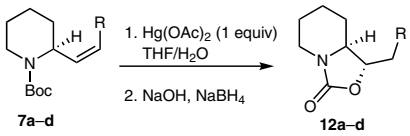


10a–d **4a–d**

Entry	10	Product	Yield (%)[b]
1	**10a**	**4a**; R = Me; (–)-allosedridine	92
2	**10b**	**4b**; R = Et; (–)-2′-*epi*-ethylnorlobelol	88
3	**10c**	**4c**; R = Pr; (–)-8-*epi*-halosaline	96
4	**10d**	**4d**; R = Pent; (–)-**4d**	94

[a] Reaction conditions: **10** (1.0 equiv), Pd/C(10% w/w), EtOH (15 mL) at r.t. under H_2 pressure (40 psi) Parr hydrogenator for 6 h.
[b] Isolated yield.

Table 5 Oxymercuration of *N*-Boc Protected Alkenes[a]

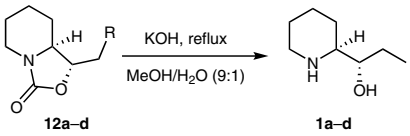


7a–d **12a–d**

Entry	7	12	Time (h)	Yield (%)[b]
1	**7a**	**12a**	4	77
2	**7b**	**12b**	4	73
3	**7c**	**12c**	4	71
4	**7d**	**12d**	4	76

[a] Reaction conditions: **7** (1 equiv), $Hg(OAc)_2$ (1 equiv), H_2O/THF (1:1, 12 mL) at r.t., then 3 N NaOH (2 mL), 0.5 N $NaBH_4$ (3 mL) at 0 °C for 1 h.
[b] Isolated yield.

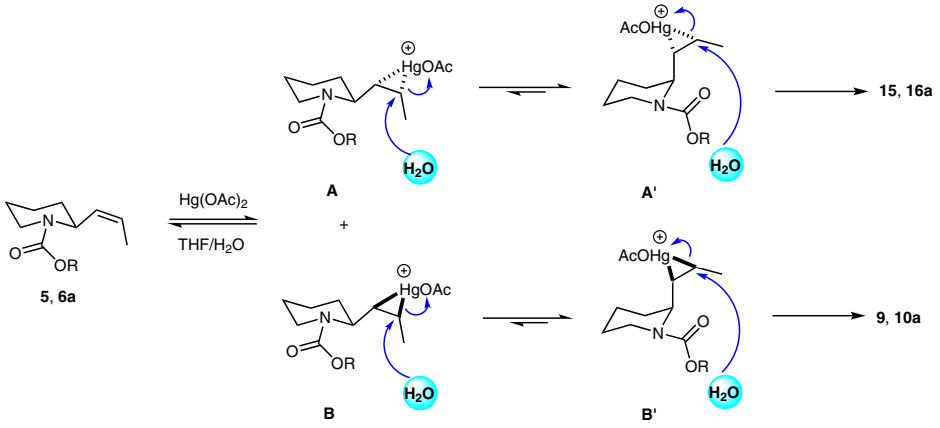
Table 6 Synthesis (–)-β-Conhydrine and Analogues[a]



12a–d **1a–d**

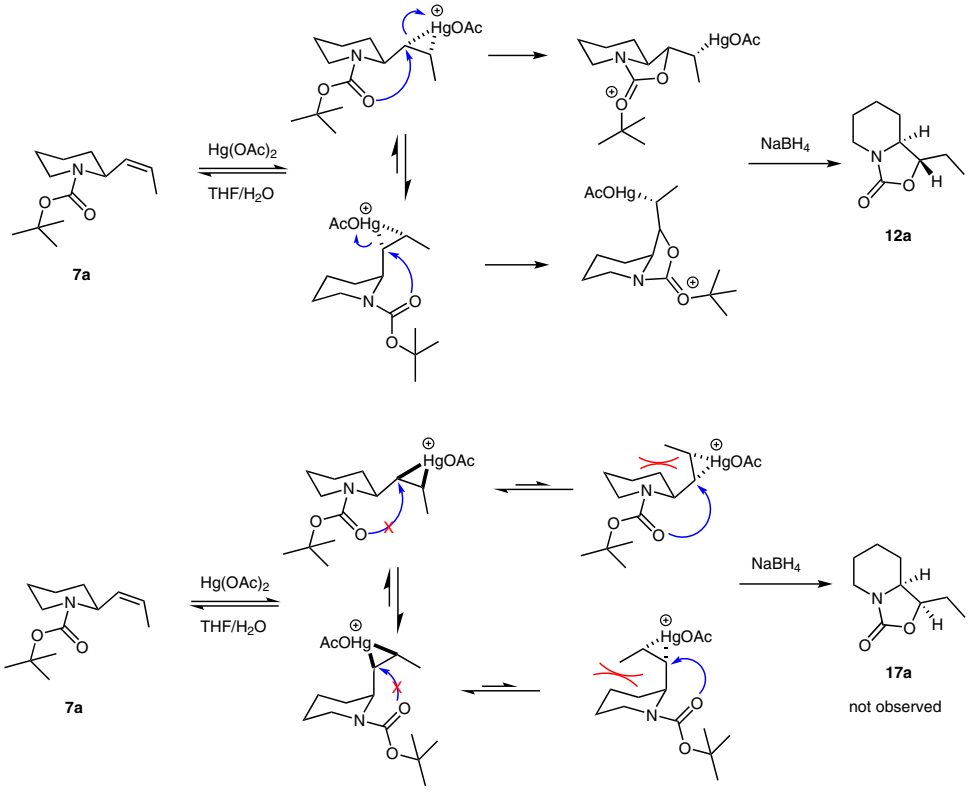
Entry	12	Product	Yield (%)[b]
1	**12a**	**1a**; (–)-β-conhydrine	71
2	**12b**	**1b**; R = Et	83
3	**12c**	**1c**; R = Pr	76
4	**12d**	**1d**; R = Pent	71

[a] Reaction conditions: **12** (1 equiv), KOH (20 equiv), MeOH/H_2O (10 mL, 9:1) was heated at reflux for 24 h.
[b] Isolated yield.



Scheme 4 Plausible mechanism for formation of 1,3-amino alcohols

A speculative mechanism to account for the formation of the 1,3-amino alcohols is depicted in Scheme 4 and for the 1,2-alcohols in Scheme 5. Alkenes **5** and **6a** react with $Hg(OAc)_2$ to form reversibly mercurinium ions **A**(**A′**) and **B**(**B′**). Nucleophilic attack by water on **A**(**A′**) and **B**(**B′**) then provided **15**, **16a**, and **9**, **10a** after demercuration (Scheme 4). The low ratio of selectivity suggests that both **A** and **B** mercurinium ion intermediates are formed in almost equal proportions. In the case of alkene **7**, the Boc protecting group participates in an intramolecular fashion because of its proximity, and loses isobutylene to form oxazolidinone **12a** regioselectively after demercuration. The fact that formation of the isomer **17a** was not observed could be due to the disfavored pathway because of significant steric interactions in the transition state, as depicted in Scheme 5.



Scheme 5 Plausible mechanism for formation of 1,2-amino alcohols

In summary, the oxymercuration–demercuration reaction was successfully employed to synthesize natural 2-substituted hydroxyl alkyl piperidines (+)-sedridine, (–)-allosedridine, (+)-ethylnorlobelol, (–)-2′-*epi*-ethylnorlobelol, (+)-halosaline, (–)-8-*epi*-halosaline (–)-β-conhydrine and their analogues. The synthesis of 1,3-amino alcohols was achieved by employing *N*-benzyloxycarbamates of L-pipecolinic acid, and 1,2-amino alcohols were prepared from *N*-*tert*-butyloxycarbamates. The remarkable protecting group directed switchable regio- and stereoselectivity of oxymercuration–demercuration of the internal alkene is noteworthy. Further studies for such protecting group directed hydroboration will be undertaken soon.

Chemicals and solvents were purchased from commercial suppliers and purified where required. Column chromatography was performed on silica gel (60–120 mesh) and on basic alumina. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded with a Bruker AVANCE III instrument. Chemical shifts are given in ppm relative to residual solvent peak. DEPT experiments were used to find the multiplicities of carbon signals. Optical rotations were measured using sodium D line (589 nm) with a Rudolph Autopol IV. Infrared spectra were recorded with a Shimadzu FTIR instrument. High-resolution mass spectra (HRMS) were recorded with a Micro Mass ES-QTOF mass spectrometer.

I. Oxidation-Wittig Reaction; General Procedure

To a mixture of N-protected pipecolinol **14a–c** (4.8 mmol, 1 equiv), and $NaHCO_3$ (7.2 mmol, 1.5 equiv) in CH_2Cl_2 (20 mL) at 0 °C under N_2 atmosphere was added Dess–Martin periodinane (7.2 mmol, 1.5 equiv). The reaction mixture was stirred at r.t. for 30 min. The reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL) and washed with saturated $NaHCO_3$ solution (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed in vacuo to give the crude pipecolinal, which was used for further reactions without purification. To a three-neck round-bottom flask containing the phosphonium salt (4.8 mmol, 1 equiv) in THF (20 mL) under N_2 atmosphere, was added *n*-butyllithium (4.8 mmol, 1 equiv) dropwise by syringe at 0 °C. A dark-orange color was obtained. The reaction mixture was stirred for 10 min and pipecolinal (4.8 mmol, 1 equiv) in THF (2 mL) was added by syringe and stirred further for 2 h. The reaction was quenched with 2 N NH_4Cl (20 mL) solution. The reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed with brine (2 × 10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (60–120 mesh) using EtOAc/hexanes to afford products **5–7**.

(*Z*)-Ethyl 2-(Prop-1-enyl)piperidine-1-carboxylate (5)

Yield: 0.92 g (58%); colorless liquid; $[\alpha]_D^{27}$ +4.1 (*c* = 0.68, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.72 (t, *J* = 9.2, 1.2 Hz, 1 H), 5.54–5.59 (m, 1 H), 5.09 (t, *J* = 6.4 Hz, 1 H), 4.09–4.16 (m, 2 H), 4.00 (d, *J* = 14.0 Hz, 1 H), 2.90 (dt, *J* = 11.2, 2.4 Hz, 1 H), 1.56–1.70 (m, 9 H), 1.25 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.5, 127.6, 126.3, 61.0, 47.7, 39.8, 30.2, 25.5, 19.4, 14.6, 13.1.

IR (KBr): 2935, 1693, 1427, 1255 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{19}NO_2Na$: 220.1314; found: 220.1314.

(*Z*)-Benzyl 2-(Prop-1-enyl)piperidine-1-carboxylate (6a)[14a]

Yield: 1.02 g (71%); colorless liquid; $[\alpha]_D^{27}$ +9.6 (*c* = 1.9, $CHCl_3$) {ref.[14a] $[\alpha]_D$ +14.6 (*c* = 1.9, $CHCl_3$)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.35 (m, 5 H), 5.72 (t, *J* = 10.4 Hz, 1 H), 5.54–5.58 (m, 1 H), 5.07 (d, *J* = 12.4 Hz, 1 H), 5.02 (d, *J* = 12.4 Hz, 1 H), 4.06 (d, *J* = 13.6 Hz, 1 H), 2.95 (dt, *J* = 13.6, 2.8 Hz, 1 H), 1.53–1.71 (m, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.3, 137.0, 128.4, 127.8, 127.8, 127.5, 66.9, 52.2, 48.0, 40.0, 30.3, 25.5, 19.4, 13.2.

IR (KBr): 3024, 2937, 1693, 1427 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{21}NO_2Na$: 282.1470; found: 282.1470.

(*Z*)-Benzyl 2-(But-1-enyl)piperidine-1-carboxylate (6b)

Yield: 0.859 g (66%); colorless liquid; $[\alpha]_D^{27}$ +6.8 (*c* = 2.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19–7.27 (m, 5 H), 5.57–5.62 (m, 1 H), 5.36–5.41 (m, 1 H), 5.05 (d, *J* = 12.4 Hz, 1 H), 5.01 (d, *J* = 12.4 Hz, 1 H), 3.98 (dd, *J* = 14.0, 3.6 Hz, 1 H), 2.89 (dt, *J* = 12.8, 2.8 Hz, 1 H), 2.00 (t, *J* = 7.2 Hz, 2 H), 1.51–1.56 (m, 6 H), 1.36–1.39 (m, 1 H), 0.84 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 137.0, 134.1, 128.4, 127.8, 125.9, 66.9, 48.2, 39.9, 30.6, 25.5, 20.9, 19.4, 14.1.

IR (KBr): 2935, 2864, 1693, 1421 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{23}NO_2Na$: 296.1626; found: 296.1626.

(*Z*)-Benzyl 2-(Pent-1-enyl)piperidine-1-carboxylate (6c)

Yield: 0.861 g (72%); colorless liquid; $[\alpha]_D^{27}$ +14.3 (*c* = 1.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.28 (m, 5 H), 5.63 (tt, *J* = 5.6, 1.6 Hz, 1 H), 5.38–5.41 (m, 1 H), 5.06 (d, *J* = 12.4 Hz, 1 H), 5.03 (d, *J* = 12.4 Hz, 1 H), 3.98 (d, *J* = 13.2 Hz, 1 H), 2.88 (dt, *J* = 12.8, 3.2 Hz, 1 H), 1.97 (q, *J* = 7.2 Hz, 2 H), 1.52–1.59 (m, 6 H), 1.36–1.38 (m, 1 H), 1.26 (q, *J* = 7.2 Hz, 2 H), 0.77 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 136.9, 132.3, 128.4, 127.8, 126.5, 66.9, 48.2, 39.9, 30.6, 29.6, 25.5, 22.6, 19.4, 13.8.

IR (KBr): 2935, 1693, 1421, 1263 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{25}NO_2Na$: 310.1783; found: 310.1783.

(*Z*)-Benzyl 2-(Hept-1-enyl)piperidine-1-carboxylate (6d)[14b]

Yield: 0.902 g (59%); colorless liquid; $[\alpha]_D^{27}$ +17.2 (*c* = 2.07, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.28 (m, 5 H), 5.59–5.64 (m, 1 H), 5.38–5.41 (m, 1 H), 5.03 (s, 2 H), 3.98 (d, *J* = 10.4 Hz, 1 H), 2.89 (dt, *J* = 13.2, 2.8 Hz, 1 H), 1.98 (d, *J* = 6.0 Hz, 2 H), 1.51–1.63 (m, 6 H), 1.13–1.24 (m, 7 H), 0.79 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 137.0, 128.4, 127.8, 126.3, 66.9, 48.2, 39.9, 31.5, 30.6, 29.2, 27.5, 25.5, 22.5, 19.4, 14.0.

IR (KBr): 2931, 1697, 1421, 1255 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{29}NO_2Na$: 338.2096; found: 338.2096.

(*Z*)-*tert*-Butyl 2-(Prop-1-enyl)piperidine-1-carboxylate (7a)[14c,14d]

Yield: 0.89 g (72%); colorless liquid; $[\alpha]_D^{27}$ +7.3 (*c* = 0.3, $CHCl_3$) {ref.[14d] $[\alpha]_D^{26}$ +13.7 (*c* = 0.3, $CHCl_3$)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.70 (t, *J* = 9.2 Hz, 1 H), 5.52–5.56 (m, 1 H), 5.03 (t, *J* = 5.2 Hz, 1 H), 3.95 (d, *J* = 15.2 Hz, 1 H), 2.85 (dt, *J* = 13.2, 2.0 Hz, 1 H), 1.53–1.71 (m, 9 H), 1.45 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 128.0, 125.8, 79.1, 47.7, 39.6, 30.3, 28.4, 25.6, 19.5, 13.2.

IR (KBr): 2976, 1693, 1415 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{23}NO_2Na$: 248.1626; found: 248.1626.

(*Z*)-*tert*-Butyl 2-(But-1-enyl)piperidine-1-carboxylate (7b)

Yield: 0.805 g (61%); colorless liquid; $[\alpha]_D^{27}$ +3.7 (*c* = 1.72, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.83 (dt, *J* = 10.8, 2.0 Hz, 1 H), 5.34–5.41 (m, 1 H), 4.94 (t, *J* = 7.2 Hz, 1 H), 3.87 (dd, *J* = 12.8, 3.6 Hz, 1 H), 2.79 (dt, *J* = 13.2, 2.8 Hz, 1 H), 2.01–2.11 (m, 2 H), 1.48–1.61 (m, 6 H), 1.38 (s, 9 H), 0.91 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7, 133.5, 126.3, 79.1, 47.9, 39.5, 30.7, 28.5, 25.6, 20.9, 19.5, 14.2.

IR (KBr): 2974, 1693, 1415, 1166 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{25}NO_2Na$: 262.1783; found: 262.1783.

(*Z*)-*tert*-Butyl 2-(Pent-1-enyl)piperidine-1-carboxylate (7c)

Yield: 0.773 g (55%); colorless liquid; $[\alpha]_D^{27}$ +14.4 (*c* = 1.9, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.61 (dt, *J* = 8.4, 1.6 Hz, 1 H), 5.36–5.40 (m, 1 H), 4.95 (br s, 1 H), 3.87 (dd, *J* = 13.2, 2.4 Hz, 1 H), 2.79 (dt, *J* = 13.6, 3.2 Hz, 1 H), 2.01 (q, *J* = 8.4 Hz, 2 H), 1.51–1.53 (m, 4 H), 1.30–1.38 (m, 13 H), 0.84 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7, 131.8, 127.0, 79.1, 47.9, 39.5, 30.6, 29.6, 28.4, 25.6, 22.7, 19.5, 13.8.

IR (KBr): 2960, 1693, 1417, 1166 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{27}NO_2Na$: 276.1939; found: 276.1939.

(*Z*)-*tert*-Butyl 2-(Hept-1-enyl)piperidine-1-carboxylate (7d)

Yield: 0.99 g (63%); colorless liquid; $[\alpha]_D^{27}$ +17.1 (*c* = 1.67, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.60 (dt, *J* = 10.8, 2.0 Hz, 1 H), 5.34–5.41 (m, 1 H), 4.94 (t, *J* = 6.8 Hz, 1 H), 3.87 (dd, *J* = 16.4, 2.8 Hz, 1 H), 2.79 (dt, *J* = 13.6, 2.8 Hz, 1 H), 2.03 (dq, *J* = 7.2, 2.0 Hz, 2 H), 1.45–1.61 (m, 6 H), 1.38 (s, 9 H), 1.38–1.21 (m, 6 H), 0.81 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7, 132.1, 126.1, 79.1, 47.9, 39.5, 31.5, 30.6, 29.3, 28.5, 27.6, 25.6, 22.5, 19.5, 14.0.

IR (KBr): 2931, 1693, 1454, 1166 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{31}NO_2Na$: 304.2252; found: 304.2252.

II. Oxymercuration–Demercuration for Preparation of 9, 15, 10a–d and 16a–d; General Procedure

To a solution of $Hg(OAc)_2$ (3.5 mmol, 1.5 equiv) in H_2O/THF (1:1, 12 mL), was added a solution of alkenes **5**, **6a–d** or **7a–d** (2.3 mmol, 1 equiv) in THF (2 mL) at r.t. and the mixture was stirred until the yellow color disappeared. The reaction mixture was cooled to 0 °C. Aq NaOH (3 N, 3 equiv) and aq. $NaBH_4$ (0.5 M, 2 equiv) were added and the mixture was stirred for 1 h. The reaction mixture was then extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (60–120 mesh) using EtOAc/hexanes to afford products **9**, **15**, **10a–d** or **16a–d**.

Ethyl (*S*)-2-((*S*)-2-Hydroxypropyl)piperidine-1-carboxylate (9)[8]

Yield: 0.125 g (19%); colorless liquid; $[\alpha]_D^{28}$ –16.0 (*c* = 0.04, $CHCl_3$) {ref.[8] $[\alpha]_D^{28}$ –16.0 (*c* = 0.04, $CHCl_3$)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.47 (br s, 1 H), 4.14–4.22 (m, 3 H), 4.00 (d *J* = 12.0 Hz, 1 H), 3.55 (br s, 1 H), 2.73 (t, *J* = 13.2 Hz, 1 H), 2.00 (t, *J* = 12.8 Hz, 1 H), 1.38–1.73 (m, 7 H), 1.25–1.28 (m, 4 H), 1.19 (t, *J* = 4.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 63.2, 61.6, 47.0, 39.2, 39.1, 29.2, 25.4, 19.1, 14.5.

IR (KBr): 3455, 2900, 1690 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{21}NO_3Na$: 238.1419; found: 238.1419.

Ethyl (*S*)-2-((*R*)-2-Hydroxypropyl)piperidine-1-carboxylate (15)[8]

Yield: 0.262 g (40%); colorless liquid; $[\alpha]_D^{28}$ –56.4 (*c* = 0.2, $CHCl_3$) {ref.[8] $[\alpha]_D^{28}$ –56.8 (*c* = 0.2, $CHCl_3$)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.38 (br s, 1 H), 4.13 (q, *J* = 6.8 Hz, 2 H), 4.00 (d, *J* = 8.8 Hz, 1 H), 3.81 (d, *J* = 4.8 Hz, 1 H), 2.87 (t, *J* = 12.8 Hz, 1 H), 1.85 (br s, 1 H), 1.55–1.60 (m, 6 H), 1.40 (d, *J* = 12.4 Hz, 1 H), 1.21–1.27 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 65.9, 61.3, 48.5, 39.6, 39.2, 29.2, 25.4, 23.4, 18.9, 14.6.

IR (KBr): 3502, 2985, 1690, 1670 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{21}NO_3Na$: 238.1419; found: 238.1419.

(*S*)-Benzyl 2-((*S*)-2-Hydroxypropyl)piperidine-1-carboxylate (16a)[8]

Yield: 0.188 g (29%); colorless liquid; $[\alpha]_D^{23}$ –19.3 (*c* = 0.21, $CHCl_3$) {ref.[8] $[\alpha]_D^{26}$ –28.5 (*c* = 2.920, $CHCl_3$)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.36 (m, 5 H), 5.17 (d, *J* = 12.4 Hz, 1 H), 5.12 (d, *J* = 12.4 Hz, 1 H), 4.53 (d, *J* = 6.8 Hz, 1 H), 4.14 (br s, 1 H), 4.03 (d, *J* = 13.6 Hz, 1 H), 3.53 (br s, 1 H), 2.75 (t, *J* = 13.2 Hz, 1 H), 2.00 (t, *J* = 13.6 Hz, 1 H), 1.50–1.75 (m, 7 H), 1.19 (d, *J* = 5.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 136.6, 128.5, 128.4, 128.1, 127.9, 68.6, 67.5, 47.3, 39.3, 37.1, 29.4, 29.2, 25.5, 19.2, 10.5.

IR (KBr): 3456, 2933, 2864, 1693, 1425 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{23}NO_3Na$: 300.1576; found: 300.1576.

(*S*)-Benzyl 2-((*S*)-2-Hydroxybutyl)piperidine-1-carboxylate (16b)[8]

Yield: 0.073 g (14%); colorless liquid; $[\alpha]_D^{25}$ –23.3 (*c* = 0.21, $CHCl_3$) {ref.[8] $[\alpha]_D^{26}$ –27.9 (*c* = 0.8, $CHCl_3$)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.31 (m, 5 H), 5.12 (d, *J* = 12.4 Hz, 1 H), 5.05 (d, *J* = 12.0 Hz, 1 H), 4.45 (br s, 1 H), 3.98 (d, *J* = 12.4 Hz, 1 H), 3.14 (br s, 1 H), 2.67 (dt, *J* = 13.6, 2.4 Hz, 1 H), 1.94 (dt, *J* = 14.0, 2.0 Hz, 1 H), 1.33–1.59 (m, 8 H), 1.09–1.21 (m, 1 H), 0.86 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 136.6, 128.1, 127.9, 68.5, 67.4, 47.2, 39.2, 37.1, 29.4, 25.4, 19.1, 10.4.

IR (KBr): 3455, 2922, 2861, 1696 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{25}NO_3Na$: 314.1732; found: 314.1732.

(*S*)-Benzyl 2-((*S*)-2-Hydroxypentyl)piperidine-1-carboxylate (16c)

Yield: 0.096 g (14%); colorless liquid; $[\alpha]_D^{20}$ –28.4 (*c* = 0.76, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.30 (m, 5 H), 5.13 (d, *J* = 12.4 Hz, 1 H), 5.04 (d, *J* = 12.0 Hz, 1 H), 4.46 (d, *J* = 10.8 Hz, 1 H), 3.97 (d, *J* = 10.8 Hz, 1 H), 3.22 (br s, 1 H), 2.68 (dt, *J* = 13.2, 2.4 Hz, 1 H), 1.93 (dt, *J* = 14.0, 1.6 Hz, 1 H), 1.36–1.58 (m, 10 H), 1.27 (t, *J* = 8.8 Hz, 2 H), 1.13 (dt, *J* = 11.2, 3.2 Hz, 1 H), 0.82 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 136.6, 128.5, 128.0, 127.8, 67.4, 66.9, 47.3, 39.3, 38.9, 37.5, 29.4, 25.4, 19.2, 19.1, 14.1.

IR (KBr): 3468, 2935, 1693, 1427 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{27}NO_3Na$: 328.1889; found: 328.1889.

(*S*)-Benzyl 2-((*S*)-2-Hydroxyheptyl)piperidine-1-carboxylate (16d)

Yield: 0.056 g (9%); colorless liquid; $[\alpha]_D^{25}$ –23.0 (*c* = 0.60, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19–7.29 (m, 5 H), 5.12 (d, *J* = 10.8 Hz, 1 H), 5.05 (d, *J* = 10.8 Hz, 1 H), 4.44 (br s, 1 H), 2.64 (dt, *J* = 13.6, 2.4 Hz, 1 H), 3.99 (d, *J* = 12.4 Hz, 1 H), 3.21 (br s, 1 H), 1.92 (dt, *J* = 14.0, 2.0 Hz, 1 H), 1.13–1.57 (m, 15 H), 0.81 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.4, 156.8, 128.5, 128.1, 67.4, 67.2, 47.3, 39.3, 37.6, 36.7, 32.0, 29.4, 25.8, 25.4, 22.6, 19.1, 14.0.

IR (KBr): 3462, 2934, 1693, 1425 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{31}NO_3Na$: 356.2202; found: 356.2202.

(*S*)-Benzyl 2-((*R*)-2-Hydroxypropyll)piperidine-1-carboxylate (10a)[8,14e]

Yield: 0.37 g (59%); colorless liquid; $[\alpha]_D^{25}$ –49.7 (*c* = 0.65, $CHCl_3$) {ref.[14e] $[\alpha]_D^{22}$ –52.3 (*c* = 1.275, $CHCl_3$)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.36 (m, 5 H), 5.15 (d, *J* = 12.4 Hz, 1 H), 5.10 (d, *J* = 12.4 Hz, 1 H), 4.41 (d, *J* = 5.6 Hz, 1 H), 4.04 (d, *J* = 10.4 Hz, 1 H), 3.82 (br s, 1 H), 2.90 (t, *J* = 12.8 Hz, 1 H), 1.81–1.88 (m, 1 H), 1.25–1.67 (m, 8 H), 1.18 (d, *J* = 4.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9, 136.8, 128.3, 128.2, 128.1, 128.0, 127.9, 71.4, 67.1, 48.9, 39.6, 37.6, 30.3, 29.2, 25.5, 18.9, 10.0.

IR (KBr): 3441, 2933, 2864, 1693, 1425 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{23}NO_3Na$: 300.1576; found: 300.1576.

(*S*)-Benzyl 2-((*R*)-2-Hydroxybutyl)piperidine-1-carboxylate (10b)[8]

Yield: 0.279 g (52%); light-yellow liquid; $[\alpha]_D^{22}$ –45.2 (*c* = 0.21, $CHCl_3$) {ref.[8] $[\alpha]_D^{26}$ –46.8 (*c* = 0.13, $CHCl_3$)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.29 (m, 5 H), 5.07 (d, *J* = 12.4 Hz, 1 H), 5.03 (d, *J* = 12.4 Hz, 1 H), 4.36–4.39 (m, 1 H), 3.96 (d, *J* = 12.0 Hz, 1 H), 3.46 (br s, 1 H), 2.83 (t, *J* = 12.8 Hz, 1 H), 2.19 (br s, 1 H), 1.32–1.71 (m, 10 H), 0.83 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.8, 136.8, 128.4, 127.9, 127.9, 71.4, 67.1, 48.9, 39.6, 37.6, 30.3, 29.1, 25.4, 18.9, 10.0.

IR (KBr): 3450, 3933, 1693, 1423 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{25}NO_3Na$: 314.1732; found: 314.1732.

(*S*)-Benzyl 2-((*R*)-2-Hydroxypentyl)piperidine-1-carboxylate (10c)

Yield: 0.363 g (53%); colorless liquid; $[\alpha]_D^{22}$ –42.4 (*c* = 1.27, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19–7.28 (m, 5 H), 5.07 (d, *J* = 12.4 Hz, 1 H), 5.04 (d, *J* = 12.4 Hz, 1 H), 4.37 (q, *J* = 5.6 Hz, 1 H), 3.97 (d, *J* = 13.2 Hz, 1 H), 3.56 (br s, 1 H), 2.82 (dt, *J* = 13.2, 4.4 Hz, 1 H), 1.81 (br s, 1 H), 1.54–1.59 (m, 6 H), 1.32–1.36 (m, 4 H), 0.82 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.8, 136.7, 128.4, 127.9, 127.8, 69.6, 67.1, 48.8, 39.7, 39.6, 37.8, 28.9, 25.4, 18.9, 18.8, 14.0.

IR (KBr): 3450, 2933, 1693, 1425, 1265 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{27}NO_3Na$: 328.1889; found: 328.1889.

(*S*)-Benzyl 2-((*R*)-2-Hydroxyheptyl)piperidine-1-carboxylate (10d)

Yield: 0.188 g (31%); colorless liquid; $[\alpha]_D^{22}$ –36.7 (*c* = 0.78, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.29 (m, 5 H), 5.07 (d, *J* = 12.4 Hz, 1 H), 5.03 (d, *J* = 12.4 Hz, 1 H), 4.37 (t, *J* = 5.2 Hz, 1 H), 3.97 (d, *J* = 12.0 Hz, 1 H), 3.55 (br s, 1 H), 2.83 (dt, *J* = 13.2, 2.0 Hz, 1 H), 2.1 (br s, 2 H), 1.64–1.69 (m, 1 H), 1.53–1.59 (m, 5 H), 1.35–1.38 (m, 4 H), 1.19–1.25 (m, 5 H), 0.81 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 136.8, 128.4, 127.8, 70.1, 67.1, 48.9, 39.6, 37.9, 37.6, 31.8, 29.2, 25.3, 25.4, 22.6, 18.9, 14.0.

IR (KBr): 3439, 2931, 1693, 1427 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{31}NO_3Na$: 356.2202; found: 356.2202.

III. Oxymercuration–Demercuration for Preparation of 12a–d; General Procedure

To a solution of $Hg(OAc)_2$ (2.3 mmol, 1 equiv) in H_2O/THF (1:1, 12 mL), were added a solution of alkenes **7a–d** (2.3 mmol, 1 equiv) in THF (2 mL) at r.t. and the mixture was stirred until the yellow color disappeared. The reaction mixture was cooled to 0 °C. Aq NaOH (3 N, 3 equiv) and aq $NaBH_4$ (0.5 M, 2 equiv) was added and the mixture was stirred for 1 h. The reaction mixture was extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (60–120 mesh) using EtOAc/hexanes to afford products **12a–d**.

1-Ethyltetrahydro-1*H*-oxazolo[3,4-*a*]pyridin-3(5*H*)-one (12a)[6i,14f]

Yield: 0.172 g (77%); colorless liquid; $[\alpha]_D^{20}$ –29.4 (*c* = 0.31, $CHCl_3$) {ref.[14f] $[\alpha]_D^{20}$ –33.2 (*c* = 0.4, $CHCl_3$)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.00 (q, *J* = 6.8 Hz, 1 H), 3.85 (dd, *J* = 10.8, 2.8 Hz, 1 H), 3.23–3.26 (m, 1 H), 2.79 (t, *J* = 12.4 Hz, 1 H), 1.71–1.92 (m, 5 H), 1.25–1.45 (m, 3 H), 1.01 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7, 81.9, 59.4, 41.1, 30.5, 27.0, 24.2, 22.6, 9.0.

IR (KBr): 2939, 2879, 1745, 1427 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_9H_{15}NO_2Na$: 192.1000; found: 192.1000.

1-Propyltetrahydro-1*H*-oxazolo[3,4-*a*]pyridin-3(5*H*)-one (12b)

Yield: 0.257 g (73%); colorless liquid; $[\alpha]_D^{20}$ –34.0 (*c* = 0.22, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.95–3.99 (m, 1 H), 3.78 (td, *J* = 13.2, 2.4 Hz, 1 H), 3.10–3.15 (m, 1 H), 2.72 (dt, *J* = 12.4, 3.2 Hz, 1 H), 1.61–1.85 (m, 4 H), 1.18–1.57 (m, 6 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7, 80.6, 59.8, 41.1, 36.1, 30.4, 24.2, 22.6, 18.1, 13.8.

IR (KBr): 2937, 1753, 1444, 1244 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{17}NO_2Na$: 206.1157; found: 206.1157.

1-Butyltetrahydro-1*H*-oxazolo[3,4-*a*]pyridin-3(5*H*)-one(12c)

Yield: 0.27 g (71%); colorless liquid; $[\alpha]_D^{20}$ –34.0 (*c* = 0.31, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.04 (dq, *J* = 5.6, 2.0 Hz, 1 H), 3.85 (dd, *J* = 13.2, 4.8 Hz, 1 H), 3.19–3.23 (m, 1 H), 2.78 (dt, *J* = 12.8, 3.6 Hz, 1 H), 1.91 (d, *J* = 11.2 Hz, 1 H), 1.83 (d, *J* = 13.2 Hz, 1 H), 1.61–1.74 (m, 4 H), 1.35–1.46 (m, 6 H), 0.93 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 80.7, 59.8, 41.1, 33.7, 30.4, 26.8, 24.2, 22.3, 22.3, 13.8.

IR (KBr): 2935, 1759, 1446, 1244 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{19}NO_2Na$: 220.1313; found: 220.1313.

1-Hexyltetrahydro-1*H*-oxazolo[3,4-*a*]pyridin-3(5*H*)-one (12d)

Yield: 0.302 g (76%); colorless liquid; $[\alpha]_D^{20}$ –31.9 (*c* = 0.83, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.03 (q, *J* = 7.2 Hz, 1 H), 3.85 (d, *J* = 14.4 Hz, 1 H), 3.20 (dt, *J* = 11.2, 2.8 Hz, 1 H), 2.78 (dt, *J* = 12.8, 3.2 Hz, 1 H), 1.90 (d, *J* = 9.6 Hz, 1 H), 1.83 (d, *J* = 12.8 Hz, 1 H), 1.61–1.71 (m, 3 H), 1.28–1.47 (m, 11 H), 0.88 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7, 80.8, 59.8, 41.1, 34.1, 31.6, 30.5, 28.9, 24.7, 24.2, 22.6, 22.2, 14.0.

IR (KBr): 2931, 1759, 1444, 1244 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{23}NO_2Na$: 248.1626; found: 248.1626.

IV. Deprotection of Benzyl Carbamates by Hydrogenation; General Procedure

Compounds **10a–d** and **16a–d** in EtOH (15 mL) were stirred with 10% Pd/C (10% w/w) under H_2 atmosphere (40 psi) for 6 h using a Parr hydrogenator at r.t. The reaction mixture was filtered, washed with EtOH and then concentrated to give compounds **3a–d** and **4a–d**.

(+)-Sedridine (3a)[15a]

Yield: 0.074 g (95%); yellow solid; mp 82–83 °C (ref.[6j] 82–83 °C); $[\alpha]_D^{25}$ +26.3 (*c* = 0.57, EtOH) {ref.[15a] $[\alpha]_D$ +26.2 (*c* = 0.85, EtOH)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.00 (br s, 1 H), 4.50 (br s, 1 H), 4.15–4.18 (m, 1 H), 3.26 (d, *J* = 12.4 Hz, 1 H), 3.06–3.11 (m, 1 H), 2.72 (dt, *J* = 12.0, 3.2 Hz, 1 H), 1.58–1.69 (m, 7 H), 1.41–1.45 (m, 1 H), 1.21 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.9, 54.5, 45.9, 42.6, 30.1, 24.1, 23.6, 23.5.

IR (KBr): 3381, 2964, 1556, 1404 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_8H_{17}NOH$: 144.1388; found: 144.1388.

(+)-Ethylnorlobelol (3b)[15a]

Yield: 0.023 g (84%); light-yellow crystalline solid; mp 61–62 °C (ref.[15a] 61 °C); $[\alpha]_D^{26}$ +16.1 (*c* 0.23, EtOH) {ref.[15a] $[\alpha]_D$ +17.5 (0.80, EtOH)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.87 (br s, 1 H), 3.56–3.67 (m, 2 H), 3.40–3.43 (m, 1 H), 3.23–3.24 (m, 1 H), 2.80–2.83 (m, 1 H), 1.17–1.93 (m, 10 H), 0.90 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 69.6, 54.8, 46.2, 40.6, 30.4, 30.4, 24.6, 23.9, 10.1.

IR (KBr): 3329, 2934, 1460, 1265 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_9H_{19}NOH$: 158.1545; found: 158.1545.

(+)-Halosaline (3c)

Yield: 0.030 g (92%); white solid; mp 79–80 °C; $[\alpha]_D^{25}$ +20.5 (*c* = 0.05, EtOH) {ref.[15b] for *R*,*R*-isomer, (–)-halosaline $[\alpha]_D^{25}$ –24.5 (*c* = 0.86, EtOH)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89–3.93 (m, 1 H), 3.35 (d, *J* = 12.4 Hz, 1 H), 3.18–3.23 (m, 1 H), 2.76 (dt, *J* = 12.0, 4.4 Hz, 1 H), 1.25–1.86 (m, 12 H), 0.84 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 66.5, 54.7, 44.9, 39.5, 39.4, 28.8, 22.7, 22.2, 18.9, 14.0.

IR (KBr): 3273, 2933, 1454, 1126 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{21}NOH$: 172.1701; found: 172.1701.

(*S*)-1-((*S*)-Piperidin-2-yl)heptan-2-ol (3d)[15c]

Yield: 0.024 g (92%); white solid; mp 64–65 °C; $[\alpha]_D^{23}$ +6.9 (*c* = 0.14, EtOH) {ref.[15c] $[\alpha]_D^{22}$ +9.0 (*c* = 0.7, EtOH)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.95 (br s, 1 H), 3.39 (d, *J* = 12.4 Hz, 1 H), 3.23 (d, *J* = 9.6 Hz, 1 H), 2.78–2.81 (m, 1 H), 2.37 (br s, 2 H), 1.74–1.89 (m, 6 H), 1.37–1.44 (m, 4 H), 1.18–1.23 (m, 6 H), 0.82 (t, *J* = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.0, 54.7, 45.3, 40.1, 37.5, 31.8, 29.3, 25.4, 23.0, 22.9, 22.6, 14.0.

IR (KBr): 3441, 2929, 1460, 1263 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{25}NOH$: 200.2014; found: 200.2014.

(–)-Allo-sedridine (4a)[15a]

Yield: 0.072 g (92%); yellow solid; mp 62–63 °C (ref.[6j] mp 61.5–63 °C); $[\alpha]_D^{25}$ –21.6 (*c* = 0.32, MeOH) {ref.[8] $[\alpha]_D$ –16.4 (*c* = 0.80, MeOH)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.07–4.11 (m, 2 H), 3.32 (d, *J* = 13.2 Hz, 1 H), 3.06 (t, *J* = 10.4 Hz, 1 H), 2.78–2.83 (m, 1 H), 1.73–1.88 (m, 5 H), 1.50–1.59 (m, 3 H), 1.20 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.5, 57.8, 45.1, 42.4, 30.7, 24.3, 23.4, 22.9.

IR (KBr): 3350, 2945, 1604, 1436 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_8H_{17}NOH$: 144.1388; found: 144.1388.

(–)-2′-*epi*-Ethylnorlobelol (4b)[15a]

Yield: 0.076 g (96%); white crystalline solid; mp 52–53 °C; $[\alpha]_D^{25}$ –10.2 (*c* = 0.98, EtOH) {ref.[15a] $[\alpha]_D$ –6.6 (*c* = 0.8, EtOH)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76–3.82 (m, 1 H), 3.39 (d, *J* = 12.8 Hz, 1 H), 3.15 (br s, 1 H), 2.86 (t, *J* = 10.8 Hz, 1 H), 1.73–1.95 (m, 8 H), 1.40–1.45 (m, 3 H), 0.87 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 73.4, 58.0, 45.3, 40.8, 32.0, 31.0, 24.6, 23.4, 9.9.

IR (KBr): 3334, 2931, 1612, 1452 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_9H_{19}NOH$: 158.1545; found: 158.1545.

(–)-8-*epi*-Halosaline (4c)[15b]

Yield: 0.024 g (96%); white solid; mp 37–38 °C; $[\alpha]_D^{25}$ –11.4 (*c* = 1.1, MeOH) {ref.[15b] $[\alpha]_D^{25}$ –12.1 (*c* = 0.45, MeOH)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.75–3.77 (m, 1 H), 3.67 (br s, 2 H), 3.00 (dd, *J* = 14.8, 1.2 Hz, 1 H), 2.71 (t, *J* = 9.2 Hz, 1 H), 2.55 (dt, *J* = 12.0, 1.6 Hz, 1 H), 1.74–1.77 (m, 1 H), 1.58 (dt, *J* = 13.6, 2.0 Hz, 2 H), 1.11–1.46 (m, 9 H), 0.84 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 72.5, 58.1, 45.9, 42.3, 40.3, 34.0, 26.9, 24.3, 18.6, 14.1.

IR (KBr): 3311, 2929, 1444, 1124 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{21}NOH$: 172.1701; found: 172.1701.

(*R*)-1-((*S*)-Piperidin-2-yl)heptan-2-ol (4d)

Yield: 0.059 g (94%); white solid; mp 56–57 °C; $[\alpha]_D^{25}$ –14.9 (*c* = 0.8, EtOH).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.87 (br s, 2 H), 3.76 (d, *J* = 4.4 Hz, 1 H), 3.02 (d, *J* = 12.8 Hz, 1 H), 2.71 (t, *J* = 10.0 Hz, 1 H), 2.56 (t, *J* = 12.8 Hz, 1 H), 1.76 (d, *J* = 12.0 Hz, 1 H), 1.58 (t, *J* = 13.6 Hz, 2 H), 1.15–1.46 (m, 13 H), 0.81 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.6, 57.4, 44.8, 40.1, 38.2, 31.6, 29.3, 25.1, 22.3, 21.9, 13.9.

IR (KBr): 3394, 2949, 2858, 1454, 1128 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{25}NOH$: 200.2014; found: 200.2014.

V. Hydrolysis of Oxazolidinones; General Procedure

KOH (20 equiv) was added to a stirred solution of oxazolidinones **12a–d** (1 equiv) in MeOH/H_2O (9:1, 10 mL) and the mixture was heated at reflux for 12 h. The reaction mixture was then cooled and concentrated under reduced pressure. The residue was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue was purified by column chromatography on basic alumina using $CHCl_3$/MeOH to afford products **1a–d**.

(–)-β-Conhydrine (1a)[15d]

Yield: 0.12 g (71%); mp 67–68 °C (ref.[15d] mp 68–70 °C); $[\alpha]_D^{25}$ –32.4 (*c* = 0.68, $CHCl_3$) {ref.[15d] $[\alpha]_D^{25}$ –34.5 (*c* = 1, $CHCl_3$)}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.17 (dt, *J* = 8.0, 3.2 Hz, 1 H), 3.04 (d, *J* = 11.2 Hz, 1 H), 2.53 (dt, *J* = 9.2, 2.8 Hz, 1 H), 2.26- 2.34 (m, 3 H), 1.78 (dt, *J* = 4.8, 3.2 Hz, 1 H), 1.75 (br s, 1 H), 1.49–1.60 (m, 2 H), 1.26–1.33 (m, 3 H), 1.06–1.10 (m, 1 H), 0.91 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 75.5, 60.8, 46.3, 28.9, 26.5, 26.3, 24.3, 9.9.

IR (KBr): 3298, 2931, 2854, 1450 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_8H_{17}NOH$: 144.1388; found: 144.1388.

(*S*)-1-((*S*)-Piperidin-2-yl)butan-1-ol (1b)

Yield: 0.12 g (83%); white crystalline solid; mp 63–64 °C; $[\alpha]_D^{22}$ –19.2 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.23 (dt, *J* = 8.8, 4.4 Hz, 1 H), 3.02 (dd, *J* = 11.6, 2.4 Hz, 1 H), 2.52 (dt, *J* = 12.0, 2.8 Hz, 1 H), 2.28 (dt, *J* = 6.4, 3.2 Hz, 1 H), 1.75 (m, 1 H), 2.05 (br s, 2 H), 1.26–1.74 (m, 8 H), 1.07 (dq, *J* = 11.2, 4.0 Hz, 1 H), 0.86 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 73.5, 61.3, 46.4, 35.8, 29.0, 26.0, 24.3, 19.0, 14.1.

IR (KBr): 3323, 3070, 2937, 1442 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_9H_{19}NOH$: 158.1545; found: 158.1545.

(*S*)-1-((*S*)-Piperidin-2-yl)pentan-1-ol (1c)

Yield: 0.197 g (76%); yellow thick liquid; $[\alpha]_D^{21}$ –13.8 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.21 (dt, *J* = 7.6, 2.8 Hz, 1 H), 3.03 (dd, *J* = 12.0, 2.8 Hz, 1 H), 2.51 (dt, *J* = 12.0, 3.2 Hz, 1 H), 2.28 (dt, *J* = 7.2, 2.8 Hz, 1 H), 1.24–1.76 (m, 12 H), 1.06 (dq, *J* = 10.8, 4.0 Hz, 1 H), 0.84 (t, *J* = 11.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 73.9, 61.3, 46.4, 33.3, 29.1, 27.9, 26.2, 24.4, 22.8, 14.0.

IR (KBr): 3315, 3170, 2931, 1454 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{21}NOH$: 172.1701; found: 172.1701.

(*S*)-1-((*S*)-Piperidin-2-yl)heptan-1-ol (1d)

Yield: 0.189 g (71%); yellow thick liquid; $[\alpha]_D^{21}$ –14.0 (*c* = 0.52, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.21 (t, *J* = 12.8 Hz, 1 H), 3.01 (dd, *J* = 13.6, 2.4 Hz, 1 H), 2.52 (dt, *J* = 12.0, 2.8 Hz, 1 H), 2.28 (dt, *J* = 9.6, 3.2 Hz, 1 H), 1.21–1.74 (m, 16 H), 1.05 (dq, *J* = 12.0, 4.0 Hz, 1 H), 0.81 (t, *J* = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 73.8, 61.3, 46.4, 33.6, 31.8, 29.4, 29.0, 26.1, 25.7, 24.4, 22.6, 14.1.

IR (KBr): 3315, 3169, 2929, 1442 cm^{-1}.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{25}NOH$: 200.2014; found: 200.2014.

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Supporting Information

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