Protecting group directed regio- and stereoselective oxymercuration–demercuration: Synthesis of piperidine alkaloids containing 1,2- and 1,3-amino alcohol unit

Sandesh T. Bugde\textsuperscript{a}, Prajesh S. Volvoikar\textsuperscript{a} and Santosh G. Tilve\textsuperscript{a,b}

\textsuperscript{a} Department of Chemistry, Goa University, Taleigao Plateau, Goa 403206, India

\textsuperscript{b} Organic Chemistry Department, RUDN University, 6 Miklukcho-Maklaya str., Moscow 117198, Russian Federation

* E-mail: stilve@unigoa.ac.in
Copies of the $^1$H NMR, $^{13}$C NMR and selected HRMS Spectra.

(Z)-Ethyl-2-(prop-1-enyl)piperidine-1-carboxylate (5) $^1$H NMR CDCl$_3$

(Z)-Ethyl-2-(prop-1-enyl)piperidine-1-carboxylate (5) $^{13}$C NMR CDCl$_3$
(Z)-Ethyl-2-(prop-1-enyl)piperidine-1-carboxylate (5) $^{13}$C DEPT CDCl$_3$

(Z)-Benzyl-2-(prop-1-enyl)piperidine-1-carboxylate (6a) $^1$H NMR CDCl$_3$
(Z)-Benzyl-2-(prop-1-enyl)piperidine-1-carboxylate (6a) $^{13}$C NMR CDCl$_3$

![NMR spectrum]

(Z)-Benzyl-2-(prop-1-enyl)piperidine-1-carboxylate (6a) $^{13}$C DEPT CDCl$_3$

![DEPT spectrum]
(Z)-Benzyl-2-(but-1-en-1-yl)piperidine-1-carboxylate (6b) $^1$H NMR CDCl$_3$

\[
\text{Chemical Structure Image}
\]

(Z)-Benzyl-2-(but-1-en-1-yl)piperidine-1-carboxylate (6b) $^{13}$C NMR CDCl$_3$

\[
\text{Chemical Structure Image}
\]
(Z)-Benzyl-2-(but-1-en-1-yl)piperidine-1-carboxylate (6b) $^{13}$C DEPT CDCl$_3$

(Z)-Benzyl-2-(pent-1-enyl)piperidine-1-carboxylate (6c) $^1$H NMR CDCl$_3$
(Z)-Benzyl-2-(pent-1-ynyl)piperidine-1-carboxylate (6c) $^{13}$C NMR CDCl$_3$

(Z)-Benzyl-2-(pent-1-ynyl)piperidine-1-carboxylate (6c) $^{13}$C DEPT CDCl$_3$
(Z)-Benzyl-2-(hept-1-enyl)piperidine-1-carboxylate (6d) $^1$H NMR CDCl$_3$

\[ \text{(Z)-Benzyl-2-(hept-1-enyl)piperidine-1-carboxylate (6d) $^1$H NMR CDCl$_3$} \]

\[ \text{(Z)-Benzyl-2-(hept-1-enyl)piperidine-1-carboxylate (6d) $^{13}$C NMR CDCl$_3$} \]

S8
(Z)-Benzyl-2-(hept-1-enyl)piperidine-1-carboxylate (6d) $^{13}$C DEPT CDCl$_3$

(Z)-tert-Butyl-2-(prop-1-enyl)piperidine-1-carboxylate (7a) $^1$H NMR CDCl$_3$
(Z)-tert-Butyl-2-(prop-1-enyl)piperidine-1-carboxylate (7a) $^{13}$C NMR CDCl$_3$

![NMR spectrum of (Z)-tert-Butyl-2-(prop-1-enyl)piperidine-1-carboxylate (7a) $^{13}$C NMR CDCl$_3$](image1)

(Z)-tert-Butyl-2-(prop-1-enyl)piperidine-1-carboxylate (7a) $^{13}$C DEPT CDCl$_3$

![DEPT spectrum of (Z)-tert-Butyl-2-(prop-1-enyl)piperidine-1-carboxylate (7a) $^{13}$C DEPT CDCl$_3$](image2)
(Z)-tert-Butyl-2-(but-1-enyl)piperidine-1-carboxylate (7b) $^1$H NMR CDCl$_3$

(7b)

(7b)

(7b)

(7b)

(Z)-tert-Butyl-2-(but-1-enyl)piperidine-1-carboxylate (7b) $^{13}$C NMR CDCl$_3$
(Z)-\textit{tert}-Butyl-2-(but-1-enyl)piperidine-1-carboxylate (7b) $^{13}$C DEPT CDCl$_3$

(Z)-\textit{tert}-Butyl-2-(pent-1-enyl)piperidine-1-carboxylate (7c) $^1$H NMR CDCl$_3$
(Z)-

$\text{tert-Butyl-2-}(\text{pent-1-eny})\text{piperidine-1-carboxylate (7c)}$ $^{13}\text{C NMR CDCl}_3$

$\text{DEPT CDCl}_3$

(Z)-

$\text{tert-Butyl-2-}(\text{pent-1-eny})\text{piperidine-1-carboxylate (7c)}$ $^{13}\text{C DEPT CDCl}_3$
(Z)-tert-Butyl-2-(hept-1-enyl)piperidine-1-carboxylate (7d) 1H NMR CDCl₃

(Z)-tert-Butyl-2-(hept-1-enyl)piperidine-1-carboxylate (7d) 13C NMR CDCl₃
(Z)-tert-Butyl-2-(hept-1-enyl)piperidine-1-carboxylate (7d) $^{13}$C DEPT CDCl$_3$

Ethyl-(S)-2-((S)-2-hydroxypropyl)piperidine-1-carboxylate (9) $^1$H NMR CDCl$_3$
Ethyl-(S)-2-((S)-2-hydroxypropyl)piperidine-1-carboxylate (9) $^{13}$C NMR CDCl$_3$

![13C NMR spectrum of Ethyl-(S)-2-((S)-2-hydroxypropyl)piperidine-1-carboxylate (9) in CDCl$_3$.]

Ethyl-(S)-2-((S)-2-hydroxypropyl)piperidine-1-carboxylate (9) $^{13}$C DEPT CDCl$_3$

![13C DEPT spectrum of Ethyl-(S)-2-((S)-2-hydroxypropyl)piperidine-1-carboxylate (9) in CDCl$_3$.]
Ethyl-(S)-2-((R)-2-hydroxypropyl)piperidine-1-carboxylate (15) $^1$H NMR CDCl$_3$

Ethyl-(S)-2-((R)-2-hydroxypropyl)piperidine-1-carboxylate (15) $^{13}$C NMR CDCl$_3$
Ethyl-(S)-2-((R)-2-hydroxypropyl)piperidine-1-carboxylate (15) $^{13}$C DEPT CDCl$_3$

(S)-Benzyl-2-((S)-2-hydroxypropyl)piperidine-1-carboxylate (16a) $^1$H NMR CDCl$_3$
(S)-Benzyl-2-((S)-2-hydroxypropyl)piperidine-1-carboxylate (16a) $^{13}$C NMR CDCl$_3$

(S)-Benzyl-2-((S)-2-hydroxypropyl)piperidine-1-carboxylate (16a) $^{13}$C DEPT CDCl$_3$
(S)-Benzyl-2-((S)-2-hydroxybutyl)piperidine-1-carboxylate (16b) \(^1\)H NMR CDCl\(_3\)

\[
\begin{align*}
\text{\textit{16b}} \\
\end{align*}
\]

((S)-Benzyl-2-((S)-2-hydroxybutyl)piperidine-1-carboxylate (16b) \(^{13}\)C NMR CDCl\(_3\)

\[
\begin{align*}
\text{\textit{16b}} \\
\end{align*}
\]
(S)-Benzyl-2-((S)-2-hydroxybutyl)piperidine-1-carboxylate (16b) $^{13}$C DEPT CDCl$_3$

(S)-Benzyl-2-((S)-2-hydroxypentyl)piperidine-1-carboxylate (16c) $^1$H NMR CDCl$_3$
(S)-Benzyl-2-((S)-2-hydroxypentyl)piperidine-1-carboxylate (16c) $^{13}$C NMR CDCl$_3$
(S)-Benzyl-2-((S)-2-hydroxypentyl)piperidine-1-carboxylate (16c) $^{13}$C DEPT CDCl$_3$

![S-Benzy](image1)

(S)-Benzyl-2-((S)-2-hydroxyheptyl)piperidine-1-carboxylate (16d) $^1$H NMR CDCl$_3$

![S-Benzy](image2)
(S)-Benzyl-2-(((S)-2-hydroxyheptyl)piperidine-1-carboxylate (16d) $^{13}$C NMR CDCl$_3$

(S)-Benzyl-2-(((S)-2-hydroxyheptyl)piperidine-1-carboxylate (16d) $^{13}$C DEPT CDCl$_3$
(S)-Benzyl-2-((R)-2-hydroxypropyll)piperidine-1-carboxylate (10a) $^1$H NMR CDCl₃

(S)-Benzyl-2-((R)-2-hydroxypropyll)piperidine-1-carboxylate (10a) $^{13}$C NMR CDCl₃
(S)-Benzyl-2-((R)-2-hydroxypropyl)piperidine-1-carboxylate (10a) $^{13}$C DEPT CDCl$_3$

(S)-Benzyl-2-((R)-2-hydroxybutyl)piperidine-1-carboxylate (10b) $^1$H NMR CDCl$_3$
(S)-Benzyl-2-((R)-2-hydroxybutyl)piperidine-1-carboxylate (10b) $^{13}$C NMR CDCl$_3$

(S)-Benzyl-2-((R)-2-hydroxybutyl)piperidine-1-carboxylate (10b) $^{13}$C DEPT CDCl$_3$
(S)-Benzyl-2-((R)-2-hydroxypentyl)piperidine-1-carboxylate (10c) $^1$H NMR CDCl$_3$

(S)-Benzyl-2-((R)-2-hydroxypentyl)piperidine-1-carboxylate (10c) $^{13}$C NMR CDCl$_3$
(S)-Benzyl-2-((R)-2-hydroxypentyl)piperidine-1-carboxylate (10c) $^{13}$C DEPT CDCl$_3$

(S)-Benzyl-2-((R)-2-hydroxyheptyl)piperidine-1-carboxylate (10d) $^1$H NMR CDCl$_3$
1-Ethyltetrahydro-1H-oxazolo[3,4-a]pyridin-3(5H)-one (12a) $^1$H NMR CDCl$_3$
1-Ethyltetrahydro-1H-oxazolo[3,4-a]pyridin-3(5H)-one (12a) $^{13}$C DEPT CDCl$_3$

1-Propyltetrahydro-1H-oxazolo[3,4-a]pyridin-3(5H)-one (12b) $^1$H NMR CDCl$_3$
1-Propyltetrahydro-1H-oxazolo[3,4-a]pyridin-3(5H)-one (12b) $^{13}$C NMR CDCl$_3$

1-Propyltetrahydro-1H-oxazolo[3,4-a]pyridin-3(5H)-one (12b) $^{13}$C DEPT CDCl$_3$
1-Butyltetrahydro-1H-oxazolo[3,4-a]pyridin-3(5H)-one (12c) $^{13}$C NMR CDCl$_3$

---

1-Butyltetrahydro-1H-oxazolo[3,4-a]pyridin-3(5H)-one (12c) $^{13}$C NMR CDCl$_3$
1-Butyltetrahydro-1H-oxazolo[3,4-a]pyridin-3(5H)-one (12c) $^{13}$C DEPT CDCl$_3$

1-Hexyltetrahydro-1H-oxazolo[3,4-a]pyridin-3(5H)-one (12d) $^1$H NMR CDCl$_3$
1-Hexyltetrahydro-1\textit{H}-oxazolo[3,4-\textit{a}]pyridin-3(5\textit{H})-one (12d) $^{13}$C NMR CDCl$_3$

1-Hexyltetrahydro-1\textit{H}-oxazolo[3,4-\textit{a}]pyridin-3(5\textit{H})-one (12d) $^{13}$C DEPT CDCl$_3$
(+)-Sedridine (3a) $^1$H NMR CDCl$_3$

(+)-Sedridine (3a) $^{13}$C NMR CDCl$_3$
(+)-Sedridine (3a) $^{13}$C DEPT CDCl$_3$

(+)-Ethynlorlobelol (3b) $^1$H NMR CDCl$_3$
(+)-Ethynorlobelol (3b) $^{13}$C NMR CDCl$_3$

(+)-Ethynorlobelol (3b) $^{13}$C DEPT CDCl$_3$
(+)-Halosaline (3c) $^1$H NMR CDCl$_3$

![NMR spectrum of (+)-Halosaline (3c) $^1$H NMR CDCl$_3$]

(+)-Halosaline (3c) $^{13}$C NMR CDCl$_3$

![NMR spectrum of (+)-Halosaline (3c) $^{13}$C NMR CDCl$_3$]
(+)-Halosaline (3c) $^{13}$C DEPT CDCl$_3$

(5)-1-((S)-Piperidin-2-yl)heptan-2-ol (3d) $^1$H NMR CDCl$_3$
((S)-1-((S)-Piperidin-2-yl)heptan-2-ol (3d) $^{13}$C NMR CDCl$_3$

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image1}
\caption{(S)-1-((S)-Piperidin-2-yl)heptan-2-ol (3d) $^{13}$C NMR CDCl$_3$}
\end{figure}

(S)-1-((S)-Piperidin-2-yl)heptan-2-ol (3d) $^{13}$C DEPT CDCl$_3$

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image2}
\caption{(S)-1-((S)-Piperidin-2-yl)heptan-2-ol (3d) $^{13}$C DEPT CDCl$_3$}
\end{figure}
(-)-Allo-sedridine (4a) $^1$H NMR CDCl$_3$

(-)-Allo-sedridine (4a) $^{13}$C NMR CDCl$_3$
(-)-Allo-sedridine (4a) $^{13}$C DEPT CDCl$_3$

\[ \text{SB-13-14-SED DEPT CDCl$_3$} \]

\[ \text{\includegraphics[width=0.7\textwidth]{allosedridine_13C_nmr}} \]

(-)-2’-epi-Ethynorlobelol (4b) $^1$H NMR CDCl$_3$

\[ \text{SB-13-31-SED RE CDCl$_3$ NMR} \]

\[ \text{\includegraphics[width=0.7\textwidth]{epiethynorlobelol_1H_nmr}} \]
(-)-2’-epi-Ethynorlobelol (4b) $^{13}$C NMR CDCl$_3$

(-)-2’-epi-Ethynorlobelol (4b) $^{13}$C DEPT CDCl$_3$
(-)-8-epi-Halosaline (4c) $^1$H NMR CDCl$_3$

(-)-8-epi-Halosaline (4c) $^{13}$C NMR CDCl$_3$
(-)-8-epi-Halosaline (4c) $^{13}$C DEPT CDCl$_3$

$^{1}$H NMR CDCl$_3$

(R)-1-((S)-Piperidin-2-yl)heptan-2-ol (4d) $^{1}$H NMR CDCl$_3$
(R)-1-((S)-Piperidin-2-yl)heptan-2-ol (4d) \(^{13}\)C NMR CDCl\(_3\)

![NMR spectrum of (R)-1-((S)-Piperidin-2-yl)heptan-2-ol (4d) in CDCl\(_3\)]

\[(R)-1-((S)-Piperidin-2-yl)heptan-2-ol (4d) \(^{13}\)C DEPT CDCl\(_3\)]

![DEPT spectrum of (R)-1-((S)-Piperidin-2-yl)heptan-2-ol (4d) in CDCl\(_3\)]
(-)-β-Conhydrine (1a) $^1$H NMR CDCl$_3$

(-)-β-Conhydrine (1a) $^{13}$C NMR CDCl$_3$
(-)-\(\beta\)-Conhydrine (1a) \(^{13}\)C DEPT CDCl\(_3\)

(\(S\))-1-((\(S\))-Piperidin-2-yl)butan-1-ol (1b) \(^1\)H NMR CDCl\(_3\)
(S)-1-((S)-Piperidin-2-yl)butan-1-ol (1b) $^{13}$C NMR CDCl$_3$

(S)-1-((S)-Piperidin-2-yl)butan-1-ol (1b) $^{13}$C DEPT CDCl$_3$
(S)-1-((S)-Piperidin-2-yl)pentan-1-ol (1c) $^1$H NMR CDCl$_3$

\[
\text{H NMR CDCl}_3
\]

(\text{S})-1-((\text{S})-Piperidin-2-yl)pentan-1-ol (1c) $^{13}$C NMR CDCl$_3$

\[
\text{C NMR CDCl}_3
\]
(S)-1-((S)-Piperidin-2-yl)pentan-1-ol (1c) $^{13}$C DEPT CDCl$_3$

(5)-1-((S)-Piperidin-2-yl)heptan-1-ol (1d) $^1$H NMR CDCl$_3$
(S)-1-((S)-Piperidin-2-yl)heptan-1-ol (1d) $^{13}$C NMR CDCl$_3$

(S)-1-((S)-Piperidin-2-yl)heptan-1-ol (1d) $^{13}$C DEPT CDCl$_3$
Selected HRMS spectra
SB-c2 9 (0.233) AM (Cen.2, 64.50, At=5434, 0.550, 28.9, 90, 0, 16); Cen (S)

Mol For = C18H27NO3Na
Calcd Mass = 328.1899 (M+Na)
**SB-c3**

**SB-c3 4 (0.096) AM (Cen.2, 25.00, Ar, 5434, 0.556, 28.030, LS 10): Cm (3.6)

328 1889**

- **Mol For = C18H27NO3Na**
- **Calcd Mass = 328.1889 (M+Na)**

![Chemical Structure](image)

**Mass Spectrogram**

- **M/z**
  - 328.4030
  - 329.2010
  - 320.2302
  - 519.6336

**S58**
Mol For = C20H31NO3Na
Calcd Mass = 356.2202 (M+Na)
Mol For = C20H31NO3Na
Calcd Mass = 356.2202 (M+Na)
Mol For = C12H25NOH
Calcd Mass = 260.2014 (M+H)
Mol For = C12H25NOH
Calcld Mass = 200.2014 (M+H)
Mol For = C11H16NO2Na
Calcd Mass = 220.1313 (M+Na)

COOEt
Mol. For = C10H21NOH
Calcd. Mass = 172.1701 (M+H)
Mol. For = C14H25NO2Na
Calcd Mass = 262.1783 (M+Na)
SB-g2

SB-g2 1 (0.041) AM (Cen, 2, 99.00, Ar, 0.54, 0.56, 28.02, 0.52, LS 10); Sm (SG, 4x6.00); Cn (1.31)

206.1157

Mol. For = C10H17NO2Na
Calcd. Mass = 206.1157 (M+Na)
MOI. FOR = C9H19NOH
Calcd. Mass = 158.1545 (M+H)
Mol. For = C17H31NO2Na
Calcd. Mass = 304.2252 (M+Na)

BOC
Mol. For = C13H23NO2Na
Calcd. Mass = 248.1626 (M+Na)
SB-h3
SB-h3 12 (0.286) AM (Cem.2. 0.10, Ar.5434.0.556.28.0.05, LS 10); Sm (SG. 4x6.00); Sb (4.45.00); Cm (3.24)
200.2014

Mol. For = C12H25NOH
Calcd. Mass = 200.2014 (M+H)