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General Synthetic Techniques

The following reagents were used as received: Ph$_3$P (triphenylphosphine, Aldrich), DEAD (diethyl azodicarboxylate solution, 40 wt. % in toluene, Aldrich), Z-L-serine (carbobenzyloxy-L-serine, Aldrich), Mg turnings (Aldrich), 5-bromo-1-pentene (Aldrich), CuBr$_2$SMe$_2$ (copper (I) bromide dimethyl sulfide complex, Aldrich), mCPBA (3-chloroperbenzoic acid, <77%, Aldrich), Pd(OH)$_2$/C (20 wt. % loading, Aldrich). All solvents were of HPLC grade and purchased from Fisher. For anhydrous reactions CH$_2$Cl$_2$ was pre-dried with CaCl$_2$ and freshly distilled over P$_2$O$_5$; THF was freshly distilled from sodium; glassware was dried at 100 °C for at least 24 hours. Anhydrous reactions were performed under argon. Flash chromatography was carried out using silica gel (230-400 mesh, Fisher). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance 500 MHz and 360 MHz spectrometers. Deuterated solvents were purchased from Aldrich.

Synthetic Procedures and Characterization Data

**Synthesis of N-(benzyloxy carbonyl)-L-serine-$\beta$-lactone (1).**

$$\text{O} \quad \text{NHCbz} \quad \text{N}$$

To a stirred solution of Ph$_3$P (5.48 g, 20.9 mmol) in anhydrous THF (100 mL) at -78 °C was added a solution of DEAD (40 wt. % in toluene; 9.52 mL, 20.9 mmol) dropwise over 10 min. A solution of Z-L-serine (5 g, 20.9 mmol) in 20 mL of anhydrous THF was added dropwise to the above mixture over 30 min. The mixture was stirred for 20 min at -78 °C and then for 3 hours at rt. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel (hexane:ethyl acetate (3:2)) to afford 1 (2.63 g).
g, 57%) as a white solid: [\alpha]_{D}^{23} = -27.4^\circ\ (c\ 1,\ \text{CH}_3\text{CN});\ \text{mp} 133-134^\circ\text{C};\ R_{f}\text{(hexane: ethyl acetate (1:1))} = 0.5;\n
\text{H NMR (360 MHz, CDCl}3\) \delta 4.37-4.45 (m, 2H, -CHC\text{H}_2\text{O-}),\ 5.07-5.15 (m, 3H, -NHCHCOO- and -NHCH}_2\text{Ph}),\ 5.51 (bs, 1H, -\text{NH}-),\ 7.29-7.38 (m, 5H, -\text{Ph});\n
\text{C NMR (CDCl}3\) \delta 59.93, 66.59, 68.07, 128.59, 128.78, 128.87, 135.69, 155.28, 168.92;\n
HRMS (ESI) \text{m/z calcd. for C}_{11}\text{H}_{11}\text{NO}_4 (\text{M}^+) : 221.0688,\text{ found: 221.0690.}\n
\text{Synthesis of (S)-2-(N-benzyloxycarbonyl)amino-7-octenoic acid (2).}\n
\text{Grignard reagent was prepared by dropwise addition of 5-bromo-1-pentene (11.24 g, 75.4 mmol) in 20 mL of anhydrous ethyl ether to Mg turnings (2.2 g, 90.5 mmol) in 5 mL of anhydrous ethyl ether at a rate adjusted to maintain a gentle reflux. The suspension was stirred for another 15 min after the addition of 5-bromo-1-pentene was complete.}\n
\text{To the solution of I (2.0 g, 9.0 mmol) and CuBr•SMe}_2\ (0.47 g, 2.3 mmol) in 60 mL of anhydrous THF was added Grignard reagent over 5 min at -78^\circ\text{C}. The mixture was then stirred for 2 hours at -23^\circ\text{C} and 1.5 hours at rt. The reaction was quenched by addition of 0.5 M HCl. 10 mL of methanol were added via syringe and the mixture was stirred for additional 20 min under argon. The black precipitate was filtered through a pad of Celite and the solution was concentrated \text{in vacuo}. The residue was chromatographed on silica gel using a gradient elution system (hexane: ethyl acetate (1:1) \rightarrow ethyl acetate \rightarrow \text{MeOH}). Two fractions were collected which correspond to 2: Carboxylic acid (eluted with hexane:EtOAc (1:1) ) and carboxylate (eluted with MeOH). The fractions were combined and the solvent was removed \text{in vacuo} to give 2 (1.13 g, 43%) as a pale yellow oil: [\alpha]_{D}^{23} = +10.4^\circ\ (c\ 1.0,\ \text{MeOH});\n
\text{H NMR (360 MHz, CDCl}3\) \delta 1.31-1.47 (m, 4H, -CH}_2\text{C\text{H}_2\text{C\text{H}_2\text{CH}_2-}),\ 1.61-1.74 (m, 1H, -NHCHCH}_2\text{CH}_2-\text{),}\ 1.76-1.95 (m, 1H, -NHCHCH}_2\text{CH}_2-\text{),}\ 1.96-2.08 (m, 2H, -CH}_2\text{CH}_2\text{CH=CH}_2\text{),}\ 4.38 (brq, J = 5.2 Hz, 1H, -NHCHCOO-),\ 4.90-5.01 (m, 2H, -CH=\text{CH}_2\text{),}\ 5.04-5.17 (m, 2H, -NHCH}_2\text{Ph),}\ 5.28 (brd, J = 8.0 Hz, 1H, -\text{NH}-),\ 5.75 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H, -CH}_2\text{CH=CH}_2\text{),}\ 7.29-7.38 (m, 5H, \text{Ph});\n
\text{C NMR (CDCl}3\) \delta 24.57, 28.30, 32.17, 33.34, 53.72, 67.17, 114.68, 128.08, 128.21, 128.39, 128.53, 136.11, 138.39, 156.14, 177.18;\n
HRMS (ESI) \text{m/z calcd. for C}_{16}\text{H}_{22}\text{NO}_4 (\text{M}^+) : 292.1548,\text{ found: 292.1535.}
Synthesis of (2S, 7RS)-2-(N-benzyloxycarbonyl)amino-7,8-epoxyoctanoic acid.

Compound 2 (1 g, 3.4 mmol) was dissolved in 100 mL of anhydrous CH₂Cl₂ and mCPBA (0.92 g, 4.1 mmol, <77%) dissolved in 20 mL of anhydrous CH₂Cl₂ was added dropwise at 0 °C under argon. The mixture was stirred for 18 hours and the solvent was removed in vacuo. The mixture was chromatographed on silica gel: The unreacted starting materials were removed using EtOAc and then the pure product was washed off by EtOAc:MeOH (3:2). The solvent was removed in vacuo to afford a mixture of diastereomers of Cbz-protected 3 (0.81 g, 77 %) as a pale yellow oil: ¹H NMR (360 MHz, CD₃OD) δ 1.38-1.58 (m, 6H, -CH₂CH₂CH₂CH₂-), 1.60-1.71 (m, 1H, -NHCHCH₂CH₂-), 1.77-1.89 (m, 1H, -NHCHCH₂CH₂-), 2.44 (dd, J = 4.9 Hz, 2.7 Hz, 1H, -NHC₂H₂O), 2.70 (dd, J = 4.9, 4.1 Hz, 1H, -NHC₂H₂O), 2.85-2.90 (m, 1H, -NHC₂H₂O), 4.07-4.14 (m, 1H, -NHCHCOO-), 5.07 (dd, J = 17.6, 12.5 Hz, 2H, -NHCH₂Ph), 7.24-7.37 (m, 5H, Ph);
¹³C NMR (CD₃OD) δ 26.75, 26.79, 33.47, 33.50, 47.88, 53.46, 56.52, 67.66, 128.97, 129.10, 129.59, 138.43, 158.62, 178.58;
HRMS (ESI) m/z calcd. for C₁₆H₂₂NO₅ (M+H)⁺: 308.1497, found: 308.1484.

Synthesis of (2S, 7RS)-2-amino-7,8-epoxyoctanoic acid (3).

To 8 mg of Pd(OH)₂/C in 10 mL of MeOH was added (2S, 7RS)-2-(N-benzyloxycarbonyl)amino-7,8-epoxyoctanoic acid (0.78 g, 2.5 mmol) dissolved in 5 mL of MeOH. Hydrogen balloon was attached and the black suspension was stirred for 25 min. Even though the deprotection reaction was not complete after 25 min, it was stopped to prevent the formation of (2S)-2-amino-7-hydroxyoctanoic acid. The Cbz-protected 3 and 3 were separated by chromatography on silica gel (EtOAc: MeOH (1:1)) to give 3 (0.32 g, 72%) as a white solid: mp 160-163 °C (decomposition);
$^1$H NMR (360 MHz, D$_2$O) $\delta$ 1.39-1.95 (m, 8H, -CH$_2$CH$_2$CH$_2$CH$_2$), 2.73 (app t, $J = 3.8$ Hz, 1H, $\text{CH}_2$), 2.97 (app t, $J = 4.3$ Hz, 1H, $\text{CH}_2$), 3.16-3.21 (m, 1H, $\text{CH}_2$), 3.75 (t, $J = 6.0$ Hz, 1H, -NHCCHCOO-);

$^{13}$C NMR (D$_2$O) $\delta$ 24.06, 24.85, 30.51, 31.07, 48.24, 54.03, 54.81, 175.36;

HRMS (ESI) $m/z$ calcd. for C$_8$H$_{15}$NO$_3$Na (M+Na)$^+$: 196.0950, found: 196.0954.

Anal. calcd. for C$_8$H$_{15}$NO$_3$: C, 55.47; H, 8.73; N, 8.09. Found: C, 55.34; H, 8.71; N, 8.16.
$^1$H NMR of N-(benzylxycarbonyl)-L-serine-β-lactone (I).
$^{13}$C NMR of N-(benzylxycarbonyl)-L-serine-$\beta$-lactone (1).
'H NMR of (S)-2-(N-benzyloxycarbonyl)amino-7-octenoic acid (2).
$^{13}$C NMR of (S)-2-(N-benzyloxycarbonyl)amino-7-octenoic acid (2).
$^1$H NMR of (2S, 7RS)-2-(N-benzyloxycarbonyl)amino-7,8-epoxyoctanoic acid.
$^{13}$C NMR of (2S, 7RS)-2-(N-benzyloxycarbonyl)amino-7,8-epoxyoctanoic acid.
$^1$H NMR of (2S, 7RS)-2-amino-7,8-epoxyoctanoic acid (3).
$^{13}$C NMR of (2S, 7RS)-2-amino-7,8-epoxyoctanoic acid (3).