**ADDENDUM I:** SELECTED $^1$H NMR SPECTRA

Note:

$^1$H NMR data was processed with *Felix* version 95.0 NMR data processing program, from Biosym Technologies Inc., on a Silicon Graphics *Indigo* R3000 workstation, running Irix version 5.3 as the operating system.

X-Axis = ppm downfield from TMS
Addendum I: Selected $^1$H NMR spectra

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Compound 5
Addendum I: Selected 1H NMR spectra

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Compound 18
Addendum I: Selected 1H NMR spectra

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Compound 9
Addendum I: Selected $^1$H NMR spectra

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Compound 6a
Addendum I: Selected $^1H$ NMR spectra

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Compound 11
Addendum I: Selected $^1$H NMR spectra

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Compound 12
Addendum I: Selected $^1$H NMR spectra

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Compound 13
Addendum I: Selected $^1$H NMR spectra

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Compound 4
Addendum I: Selected $^1$H NMR spectra

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Compound 17
Addendum I: Selected $^1$H NMR spectra

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Compound 39
Addendum I: Selected $^1$H NMR spectra

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Compound 92
Addendum I: Selected $^1$H NMR spectra

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Compound 94
Addendum I: Selected $^1$H NMR spectra

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Compound 95
Addendum I: Selected $^1$H NMR spectra

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Compound 96
Addendum I: Selected 1H NMR spectra

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Compound 97
Addendum I: Selected $^1H$ NMR spectra

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Compound 98
Addendum I: Selected 1H NMR spectra

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Compound 101
Addendum I: Selected 1H NMR spectra

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Compound 105
Addendum I: Selected 1H NMR spectra

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Compound 106
Addendum I: Selected 1H NMR spectra

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Compound 107
Addendum I: Selected 1H NMR spectra

Compound 108

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222
Addendum I: Selected 1H NMR spectra

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Compound 112
Addendum I: Selected 1H NMR spectra

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Compound 118
Addendum I: Selected $^1H$ NMR spectra

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Compound 114
Addendum I: Selected 1H NMR spectra

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Compound 124
Addendum I: Selected 1H NMR spectra

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Compound 121
Addendum I: Selected 1H NMR spectra

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Compound 126
1D-proton difference NOE experiments were conducted. The $T_1$ relaxation times for the protons involved in the experiment were calculated via inverse recovery experiments. The mixing times for the NOE experiments were maximized in order to observe maximum NOE to about 2/3 of the $T_1$ relaxation measured.

NOEs observed: H-2$\alpha$ (δ 3.95 ppm) to H-2$\beta$ (δ 3.57 ppm), H-2$\alpha$ (δ 3.95 ppm) to H-4 (δ 4.02 ppm), H-4 (δ 4.02 ppm) to H-14 (δ 5.09 ppm), H-4 (δ 4.02 ppm) to H-13 (δ 2.20 ppm), H-13 (δ 2.20 ppm) to H-4 (δ 4.02 ppm), H-13 (δ 2.20 ppm) to H-11 (δ 2.15 ppm), H-12 (δ 3.88 ppm) to H-11 (δ 2.15 ppm), H-12 (δ 3.88 ppm) to H-2$\beta$ (δ 3.57 ppm).

The absence of an NOE between H-12 and H-13, which was seen for compound 100, confirms the R relative stereochemistry of the hydroxyl at C-12.
2. Compound 94

1D-proton difference NOE experiments were conducted. The T¹ relaxation times for the protons involved in the experiment were calculated via inverse recovery experiments. The mixing times for the NOE experiments were maximized in order to observe maximum NOE to about 2/3 of the T¹ relaxation measured.

NOEs observed: H-2α (δ 4.82 ppm) to H-2β (δ 4.52 ppm), H-2β (δ 4.52 ppm) to H-2α (δ 4.82 ppm), H-2α (δ 4.82 ppm) to H-15 (δ 2.39 ppm), H-14 (δ 5.17 ppm) to H-15 (δ 2.39 ppm), H-14 (δ 5.17 ppm) to H-18 (δ 1.72 ppm), H-6 (δ 4.35 ppm) to H-16 (δ 0.92 ppm).

The absence of an NOE from H-6 to H-15 confirms the R relative stereochemistry at C-6.
3. **Compound 96**

1D-proton difference NOE experiments were conducted. The $T_1$ relaxation times for the protons involved in the experiment were calculated via inverse recovery experiments. The mixing times for the NOE experiments were maximized in order to observe maximum NOE to about 2/3 of the $T_1$ relaxation measured.

NOEs observed: H-2$\alpha$ ($\delta$ 4.01 ppm) to H-2$\beta$ ($\delta$ 3.64 ppm), H-2$\beta$ ($\delta$ 3.64 ppm) to H-2$\alpha$ ($\delta$ 4.01 ppm), H-2$\alpha$ ($\delta$ 4.01 ppm) to H-14 ($\delta$ 2.83 ppm), H-14 ($\delta$ 2.83 ppm) to H-2$\alpha$ ($\delta$ 4.01 ppm), H-14 ($\delta$ 2.83 ppm) to H-15 ($\delta$ 2.25 ppm), H-15 ($\delta$ 2.25 ppm) to H-14 ($\delta$ 2.83 ppm), H-14 ($\delta$ 2.83 ppm) to H-18 ($\delta$ 1.03 ppm), H-14 ($\delta$ 2.83 ppm) to H-16 ($\delta$ 0.57 ppm).

An NOE observed between H-2$\alpha$ and H-14 confirms the R relative stereochemistry at C-14. The absence of an NOE between H-6 and H-15 supports the assignment of the R relative stereochemistry for C-6.
4. Compound 99

1D-proton difference NOE experiments were conducted. The $T_1$ relaxation times for the protons involved in the experiment were calculated via inverse recovery experiments. The mixing times for the NOE experiments were maximized in order to observe maximum NOE to about 2/3 of the $T_1$ relaxation measured.

NOEs observed: H-2$\alpha$ ($\delta$ 5.67 ppm) to H-2$\beta$ ($\delta$ 4.51 ppm), H-2$\beta$ ($\delta$ 4.51 ppm) to H-2$\alpha$ ($\delta$ 5.67 ppm), H-2$\beta$ ($\delta$ 4.51 ppm) to H-6 ($\delta$ 4.30 ppm), H-6 ($\delta$ 4.30 ppm) to H-7$\beta$ ($\delta$ 1.41 ppm), H-2$\alpha$ ($\delta$ 5.67 ppm) to H-14 ($\delta$ 2.93 ppm), H-14 ($\delta$ 2.93 ppm) to H-15 ($\delta$ 2.20 ppm), H-15 ($\delta$ 2.20 ppm) to H-14 ($\delta$ 2.93 ppm).

An NOE observed between H-2$\alpha$ and H-14 confirms the R relative stereochemistry for the C-14 at the epoxide functionality. The absence of an NOE between H-6 and H-15 supports the R relative stereochemistry assignment at C-6.
5. **Compound 100**

1D-proton difference NOE experiments were conducted. The $T_1$ relaxation times for the protons involved in the experiment were calculated via inverse recovery experiments. The mixing times for the NOE experiments were maximized in order to observe maximum NOE to about 2/3 of the $T_1$ relaxation measured.

Observed NOEs: H-2$\alpha$ (δ 4.05 ppm) to H-2$\beta$ (δ 3.69 ppm), H-2$\beta$ (δ 3.69 ppm) to H-2$\alpha$ (δ 4.05 ppm), H-4 (δ 4.10 ppm) to H-13 (δ 2.11 ppm), H-13 (δ 2.11 ppm) to H-4 (δ 4.10 ppm), H-12 (δ 4.08 ppm) to H-13 (δ 2.11 ppm), H-13 (δ 2.11 ppm) to H-12 (δ 4.08 ppm).

An NOE observed between H-12 and H-13, which was absent on compound 91, confirms the S relative stereochemistry assignment for C-12.
1D-proton difference NOE experiments were conducted. The T<sup>1</sup> relaxation times for the protons involved in the experiment were calculated via inverse recovery experiments. The mixing times for the NOE experiments were maximized in order to observe maximum NOE to about 2/3 of the T<sup>1</sup> relaxation measured.

Observed NOEs: H-4 (δ 4.16 ppm) to H-14 (δ 5.14 ppm), H-4 (δ 4.16 ppm) to H-13 (δ 2.39 ppm), H-13 (δ 2.39 ppm) to H-4 (δ 4.16 ppm), H-13 (δ 2.39 ppm) to H-10α (δ 1.98 ppm), H-13 (δ 2.39 ppm) to H-11 (δ 4.83 ppm), H-11 (δ 4.83 ppm) to H-13 (δ 2.39 ppm), H-10α (δ 1.98 ppm) to H-11 (δ 4.83 ppm), H-10β (δ 3.06 ppm) to H-16 (δ 1.23 ppm).

An NOE observed between H-3 and H-11, which was not seen for compound 124, confirms the S relative stereochemistry assignment for C-11. This assignment is further supported by the observation of NOEs between H-10α and H-13 and between H-10α and H-11.
2. Compound 121

1D-proton difference NOE experiments were conducted. The $T_1$ relaxation times for the protons involved in the experiment were calculated via inverse recovery experiments. The mixing times for the NOE experiments were maximized in order to observe maximum NOE to about 2/3 of the $T_1$ relaxation measured.

NOEs observed: H-2$\alpha$ ($\delta$ 4.01 ppm) to H-2$\beta$ ($\delta$ 3.58 ppm), H-2$\beta$ ($\delta$ 3.58 ppm) to H-2$\alpha$ ($\delta$ 4.01 ppm), H-4 ($\delta$ 4.03 ppm) to H-2$\alpha$ ($\delta$ 4.01 ppm), H-4 ($\delta$ 4.03 ppm) to H-14 ($\delta$ 5.09 ppm), H-4 ($\delta$ 4.03 ppm) to H-13 ($\delta$ 2.64 ppm), H-13 ($\delta$ 2.64 ppm) to H-4 ($\delta$ 4.03 ppm), H-12 ($\delta$ 3.86 ppm) to H-11 ($\delta$ 4.21 ppm).

An NOE observed between H-11 and H-12 confirms the cis relative stereochemistry assigned for the diol and the absence of NOEs between H-13 and H-11 or between H-13 and H-12 supports the S* assignment for C-12 and the R* relative stereochemistry assignment for C-11. These assignments are further supported by comparison with the results for the NOE experiments conducted on the trans diol 126.
3. Compound 122

1D-proton difference NOE experiments were conducted. The $T_1$ relaxation times for the protons involved in the experiment were calculated via inverse recovery experiments. The mixing times for the NOE experiments were maximized in order to observe maximum NOE to about 2/3 of the $T_1$ relaxation measured.

NOEs observed: H-2α ($\delta$ 4.12 ppm) to H-2β ($\delta$ 3.42 ppm), H-2β ($\delta$ 3.42 ppm) to H-2α ($\delta$ 4.12 ppm), H-4 (δ 4.14 ppm) to H-14 (δ 5.18 ppm), H-4 (δ 4.14 ppm) to H-13 (δ 2.31 ppm), H-13 (δ 2.31 ppm) to H-4 (δ 4.14 ppm), H-10β (δ 1.85 ppm) to H-11 (δ 5.10 ppm), H-12 (δ 4.81 ppm) to H-2α (δ 4.12 ppm).

An NOE observed between H-2 and H-12 confirms the S relative stereochemistry assigned for C-12. The absence of NOEs between H-12 and H-13 and between H-11 and H-13 further supports the assignment.
4. Compound 124

A 2D-proton-proton NOESY experiment was conducted on compound 124. NOEs reported are those corresponding to the cross peaks observed on the 2D-experiment.

NOEs observed (cross peaks): H-2α (δ 4.10 ppm) to H-2β (δ 3.79 ppm), H-4 (δ 4.25 ppm) to H-13 (δ 2.64 ppm), H-6α (δ 2.25 ppm) to H-6β (δ 2.53 ppm), H-10β (δ 2.17 ppm) to H-11 (δ 4.23 ppm), H-10α (δ 2.20 ppm) to H-10β (δ 2.17 ppm).

The absence of a cross peak between H-11 and H-13 supports the R relative stereochemistry assignment at C-11. This assignment was further supported by comparison with the results obtained for compound 112.
5. Compound 126

1D-proton difference NOE experiments were conducted. The $T_1$ relaxation times for the protons involved in the experiment were calculated via inverse recovery experiments. The mixing times for the NOE experiments were maximized in order to observe maximum NOE to about 2/3 of the $T_1$ relaxation measured.

Observed NOEs: $H-2\alpha (\delta 3.73 \text{ ppm})$ to $H-2\beta (\delta 4.05 \text{ ppm})$, $H-2\beta (\delta 4.05 \text{ ppm})$ to $H-2\alpha (\delta 3.73 \text{ ppm})$, $H-2\beta (\delta 4.05 \text{ ppm})$ to $H-11 (\delta 4.19 \text{ ppm})$, $H-4 (\delta 4.07 \text{ ppm})$ to $H-13 (\delta 2.51 \text{ ppm})$, $H-13 (\delta 2.51 \text{ ppm})$ to $H-4 (\delta 4.07 \text{ ppm})$, $H-11 (\delta 4.19 \text{ ppm})$ to $H-10\beta (\delta 1.88 \text{ ppm})$, $H-12 (\delta 4.03 \text{ ppm})$ to $H-13 (\delta 2.51 \text{ ppm})$, $H-13 (\delta 2.51 \text{ ppm})$ to $H-12 (\delta 4.03 \text{ ppm})$, $H-4 (\delta 4.07 \text{ ppm})$ to $H-14 (\delta 5.09 \text{ ppm})$.

An NOE observed between $H-2\beta$ and $H-11$ confirms the $R$ relative stereochemistry assignment at C-11 and an NOE observed between $H-12$ and $H-13$ confirms the $R$ relative stereochemistry assignment at C-12. These assignments are further supported by comparison with the results obtained for compound 121.