

The Impact of LR-HSQMBC Very Long-Range Heteronuclear Correlation Data on Computer-Assisted Structure Elucidation

SUPPLEMENTAL INFORMATION

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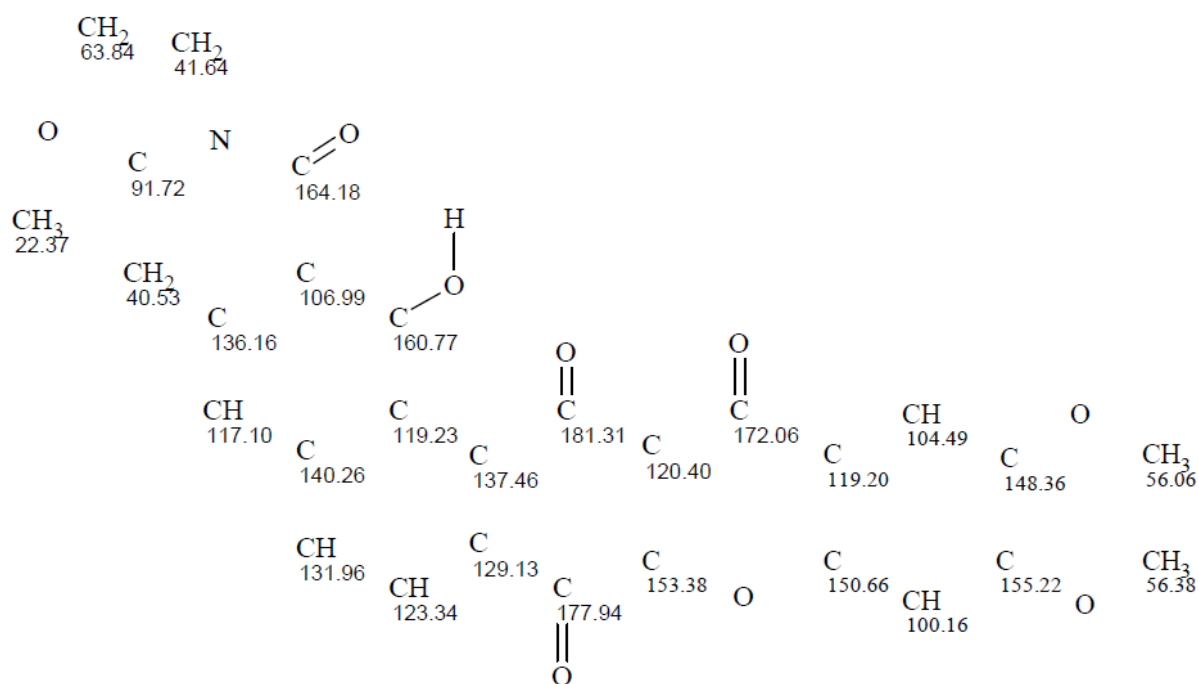
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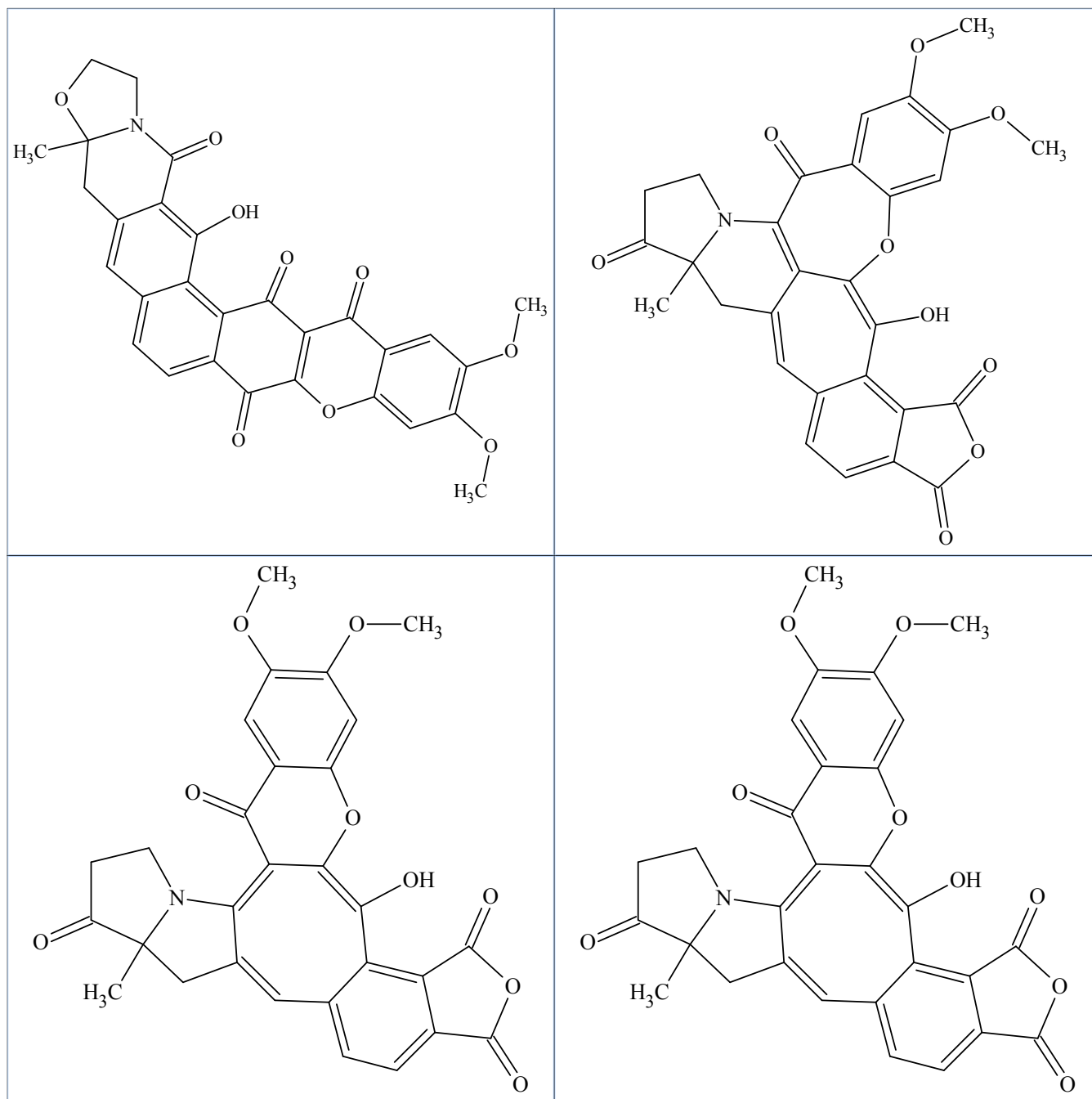
- S1. Molecular connectivity diagram from Figure 1. Pg . 2.
- S2. Structure Elucidator CASE program output when the cervinomycin A₂ calculation was done using HMBC and 4 Hz LR-HSQMBC data. Only 4 structure were generated in a calculation lasting 37 h. Pg 3.
- S3. Long-range heteronuclear correlations observed in the 2 Hz optimized LR-HSQMBC spectrum of staurosporine (**2**). Correlations are color-coded as a function of the correlation path length. Pg. 4.
- S4. Structure Elucidator CASE program output when the staurosporine calculation was done using ¹H-¹³C and ¹H-¹⁵N HMBC data, IDR-HSQC-TOCSY, 2 Hz optimized LR-HSQMBC, 1,1-ADEQUATE, and dual optimized inverted ¹J_{CC} 1,n-ADEQUATE data. The calculation lasted 0.2 s and generated 24 structures. Pg. 5.

S1. Molecular connectivity diagram from Figure 1.

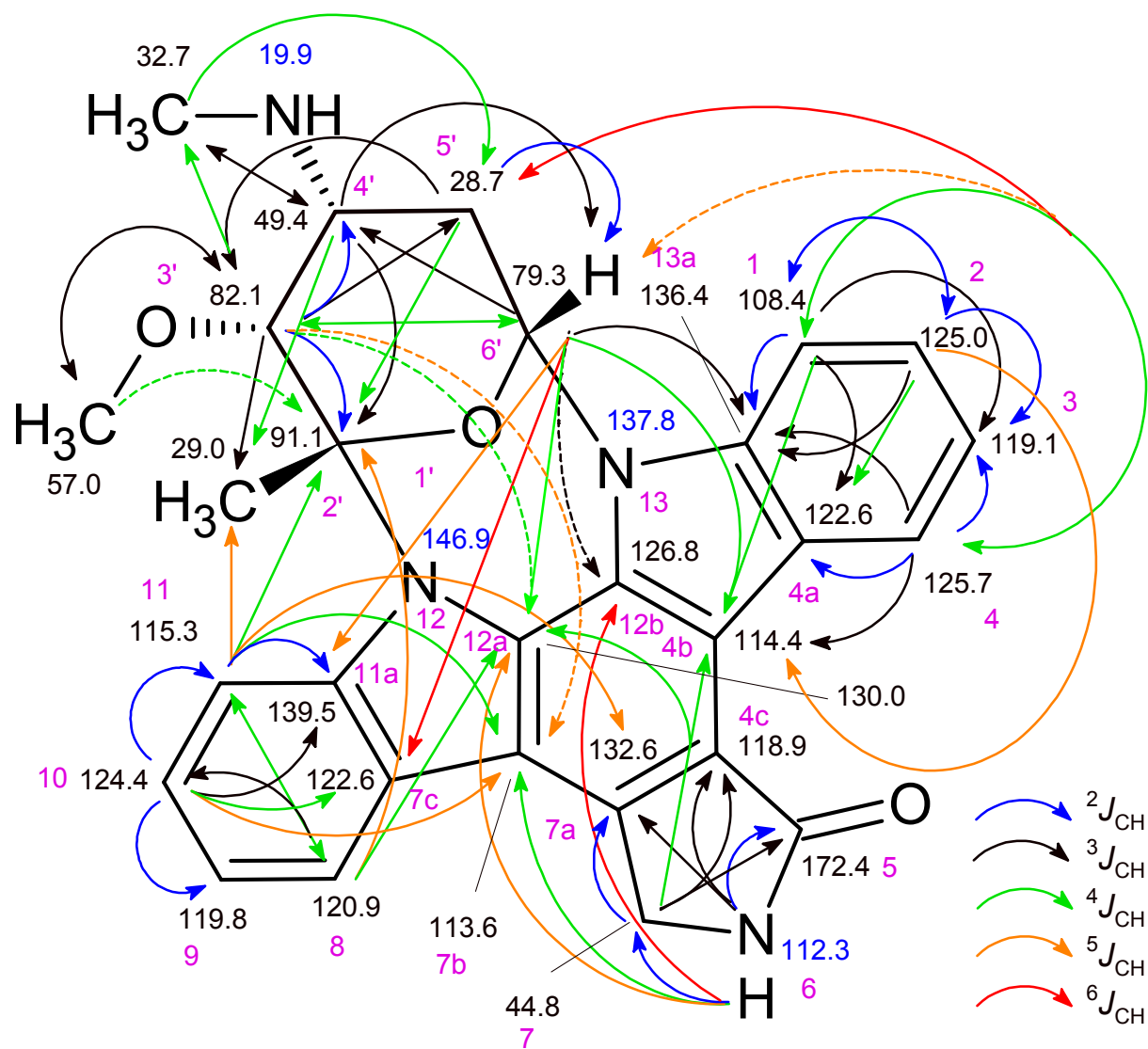


The complete ensemble of long-range heteronuclear correlations in the 4 Hz HMBC and 4 and 2 Hz optimized LR-HSQMBC of cervinomycin A₂ are shown in: R. T. Williamson, A. V. Buevich, G. E. Martin, T. Parella, *J. Org. Chem.*, **2014**, *79*, 3387.

S2. Structure Elucidator CASE program output when the cervinomycin A₂ calculation was done using 8 and 4 Hz optimized ¹H-¹³C HMBC and 4 Hz optimized LR-HSQMBC data. A total of 4 structures were generated in a 37 h calculation (shown below). Structures are rank ordered based on congruence between calculated and experimental ¹³C chemical shifts. When the 2 Hz optimized LR-HSQMBC data were substituted for the 4 Hz optimized LR-HSQMBC data in the program input, 7 structures were generated by the program in 150 s. When both 4 and 2 Hz optimized LR-HSQMBC data were included in the program input file, only a single structure was generated in a 104 s calculation.

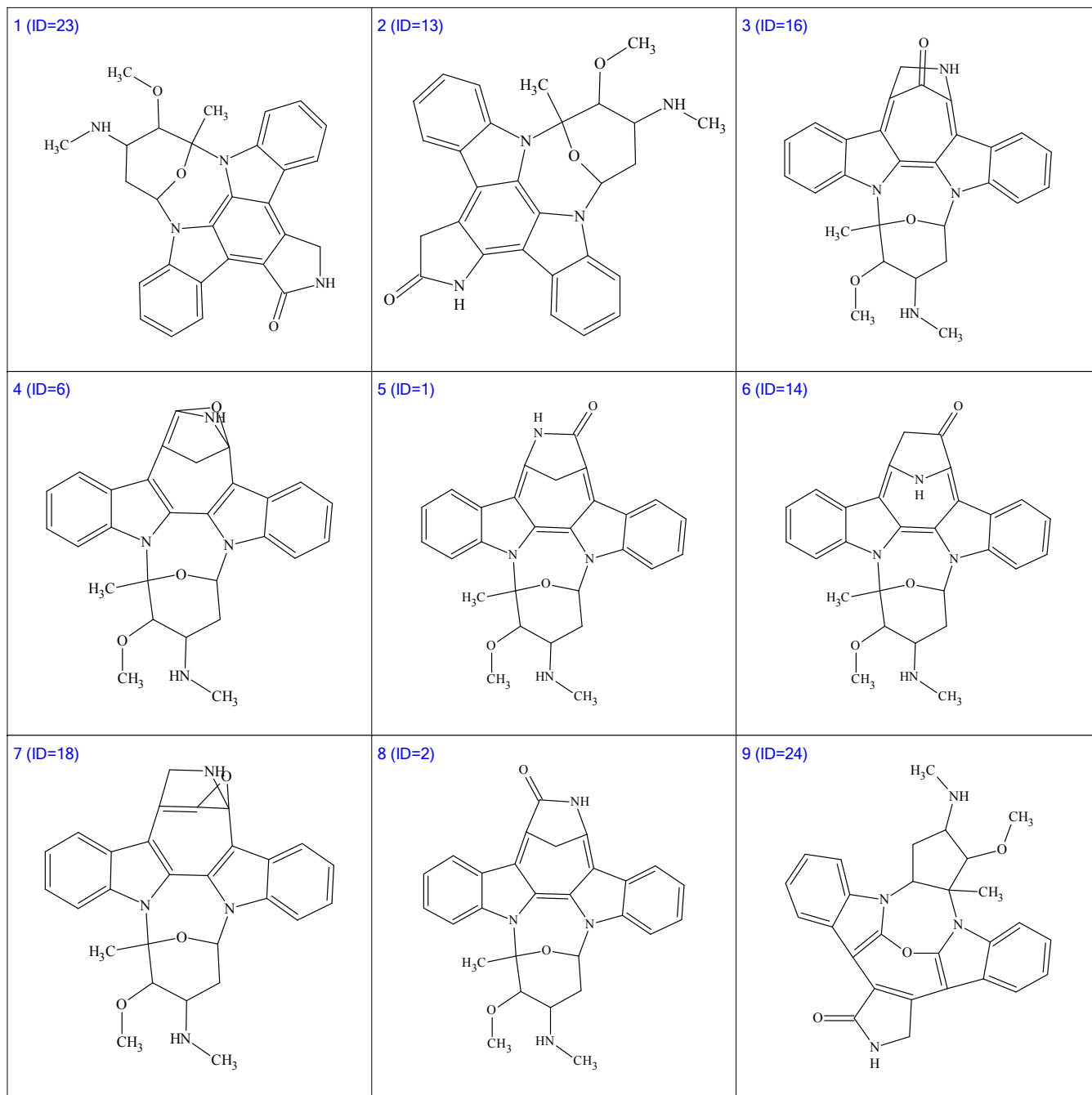


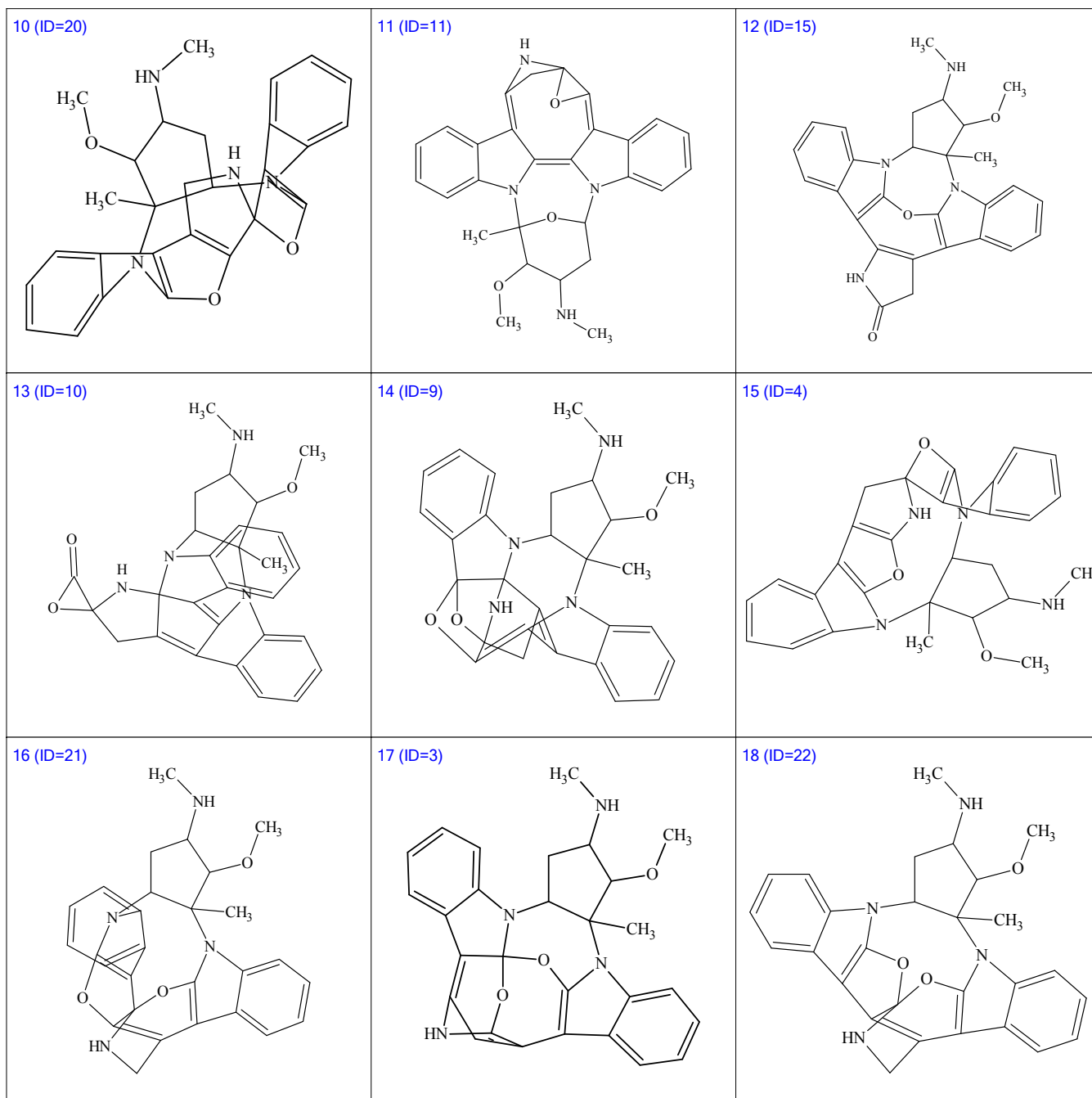
S3. Long-range heteronuclear correlations observed in the 2 Hz optimized LR-HSQMBC spectrum of staurosporine (**2**). Correlations are color-coded as a function of the correlation path length. When more than one coupling path was possible, the shorter pathlength is indicated.



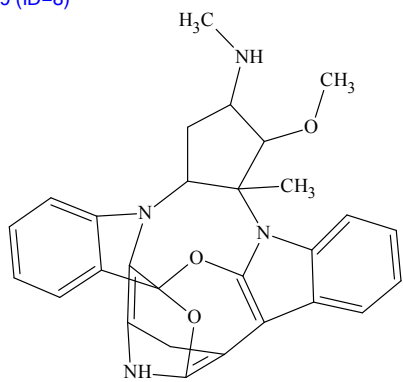
^1H - ^{13}C and ^1H - ^{15}N HMBC, 1,1-ADEQUATE, and dual optimized inverted $^1J_{\text{CC}}$ correlations for staurosporine (**2**) were previously reported (see: M. M. Senior, R. T. Williamson, and G. E. Martin, *J. Nat. Prod.*, **2013**, 76, 2088).

S4. Structure Elucidator CASE program output when the staurosporine calculation was done using ^1H - ^{13}C and ^1H - ^{15}N HMBC data, IDR-HSQC-TOCSY, 2 Hz optimized LR-HSQMBC, 1,1-ADEQUATE, and dual optimized inverted $^1J_{\text{CC}}$ 1,n-ADEQUATE data. The calculation lasted 0.2 s and generated 24 structures. Structures are rank ordered based on congruence between calculated and experimental ^{13}C chemical shifts.

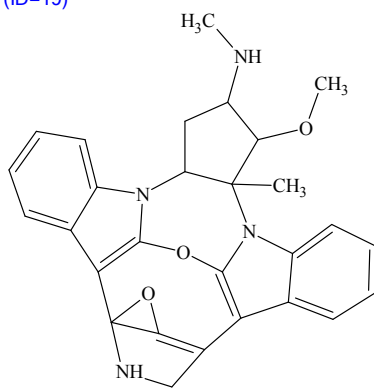




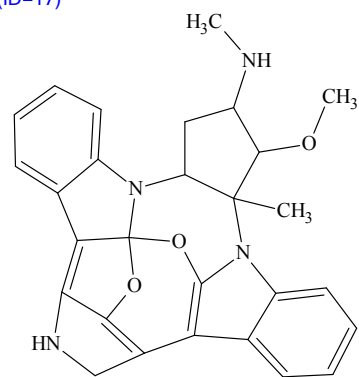
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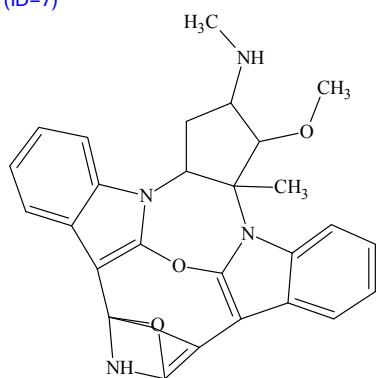
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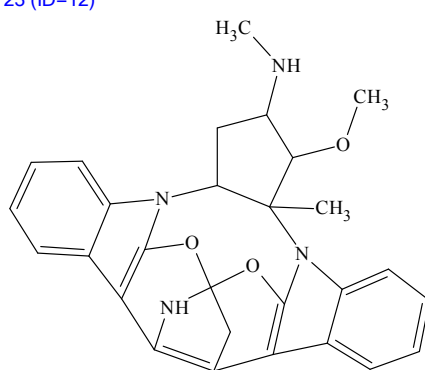
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22 (ID=7)



23 (ID=12)



24 (ID=5)

