

## Supplementary Materials:

### Azaphilones Pigments from the Fungus *Penicillium hirayamae*

Coralie Pavesi <sup>1</sup>, Victor Flon <sup>2</sup>, Grégory Genta-Jouve <sup>3</sup>, Elodie Pramila <sup>4</sup>, Alexandre Escargueil <sup>4</sup>, Adeel Nasir <sup>5</sup>, Tristan Montier <sup>5,6</sup>, Xavier Franck <sup>2,\*</sup> and Soizic Prado <sup>1,\*</sup>

<sup>1</sup> Muséum National d'Histoire Naturelle, Unité Molécules de Communication et Adaptation des Micro-organismes, UMR 7245, CP 54, 57 rue Cuvier, 75005 Paris, France

<sup>2</sup> Normandie Université, CNRS, UNIROUEN, INSA Rouen, COBRA (UMR 6014 & FR 3038), 76000 Rouen, France

<sup>3</sup> UAR3456 CNRS LEEISA, Laboratoire Ecologie, Evolution, Interactions des Systèmes Amazoniens, Centre de Recherche de Montabo, IRD, 275 Route de Montabo, CEDEX BP 70620, 97334 Cayenne, France

<sup>4</sup> Sorbonne University INSERM U938, Centre de Recherche Saint-Antoine, 75012 Paris, France

<sup>5</sup> Brest University, INSERM, Etablissement Français du Sang, Unité Génétique Génomique Fonctionnelle et Biotechnologie, UMR 1078, 29200 Brest, France

<sup>6</sup> Centre Hospitalier Régional Universitaire de Brest, Service de Génétique Médicale et de Biologie de la Reproduction, Centre de Référence des Maladies Rares "Maladies Neuromusculaires", 29200 Brest, France

\* Correspondence: xavier.franck@insa-rouen.fr (X.F.); soizic.prado@mnhn.fr (S.P.)

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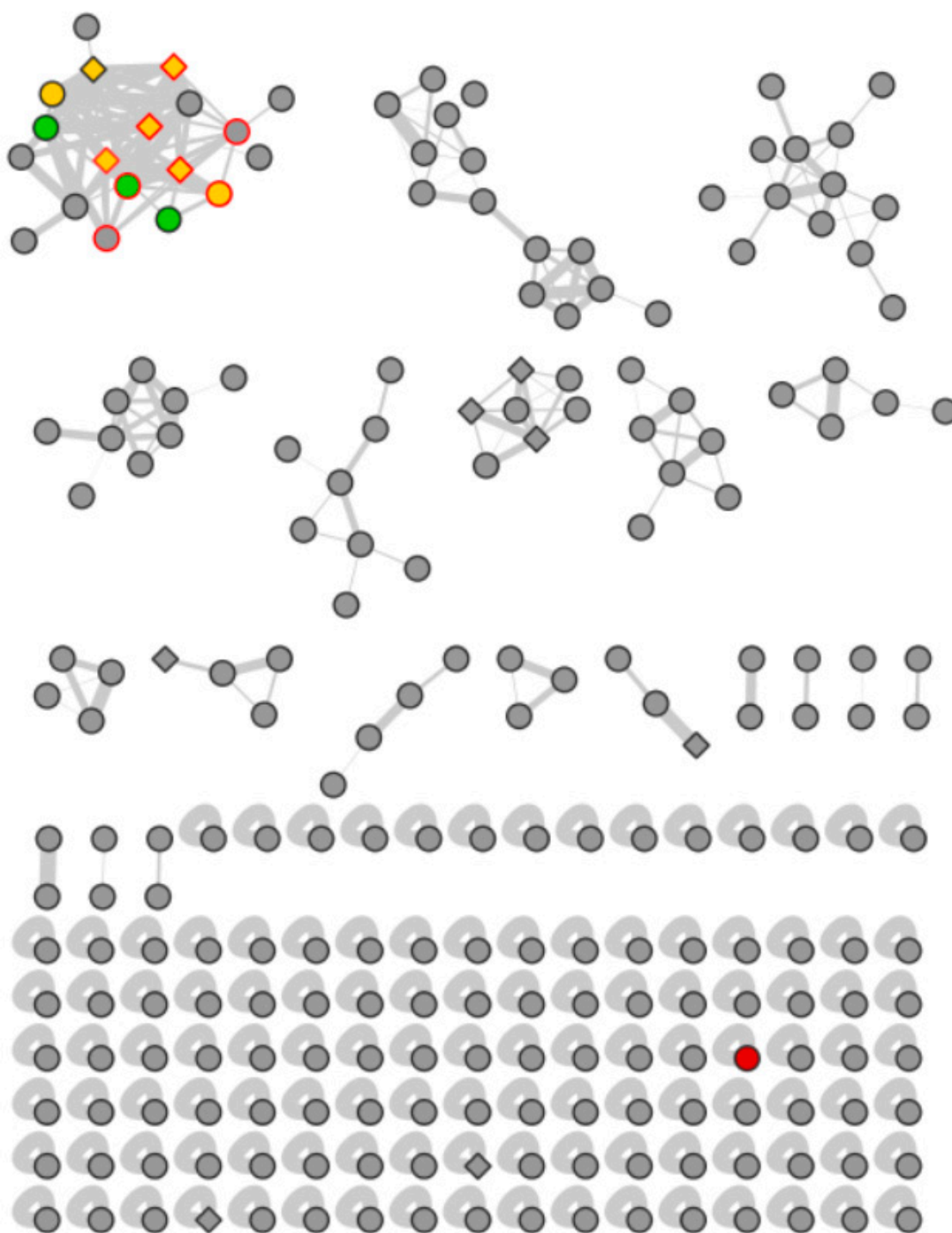


Figure S1. Full molecular network of *P. hirayamae* crude extract. Cluster of azaphilones is highlighted in yellow (known azaphilones), green (new azaphilones). Diamond indicates azaphilones identified in GNPS database and red square those identified thanks to Sirius 5.5.5. Sclerotiorin was also identified on the molecular networking and is represented as a self-loop in red.

## 1. Penazaphilone J

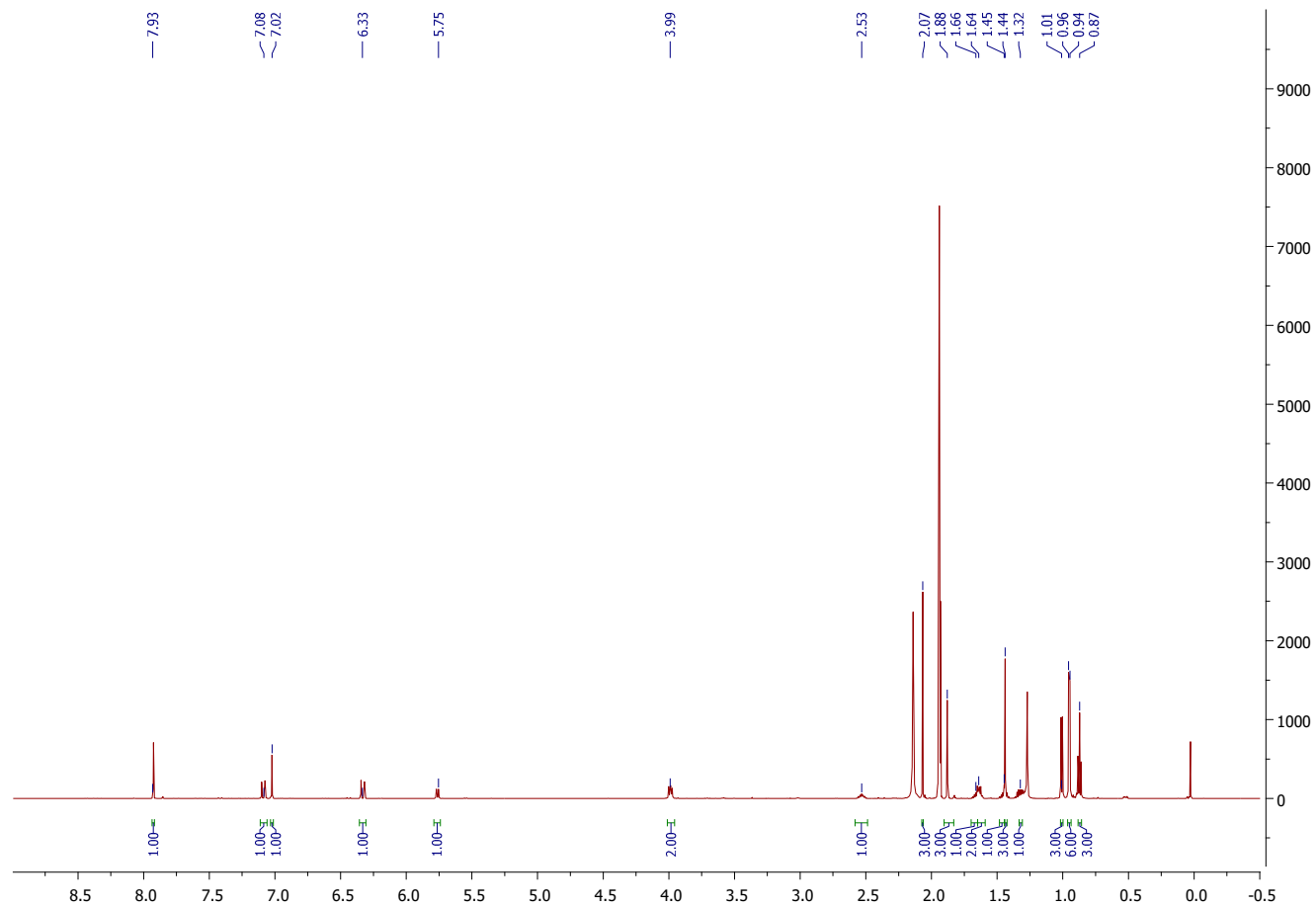


Figure S2.  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{CN}$ ) of penazaphilone J

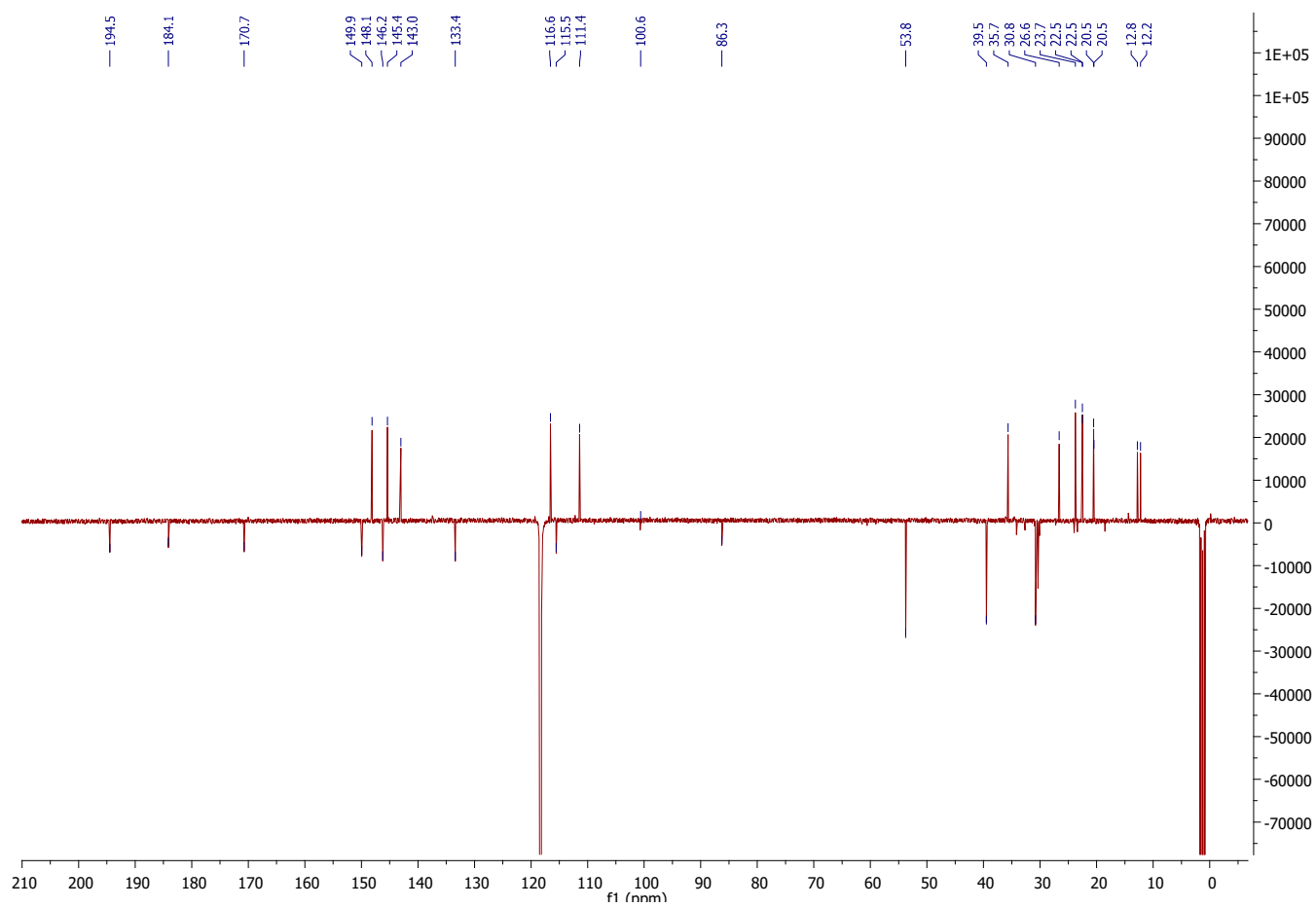


Figure S3. 1D NMR (600 MHz, CD<sub>3</sub>CN) DEPT Q of of penazaphilone J

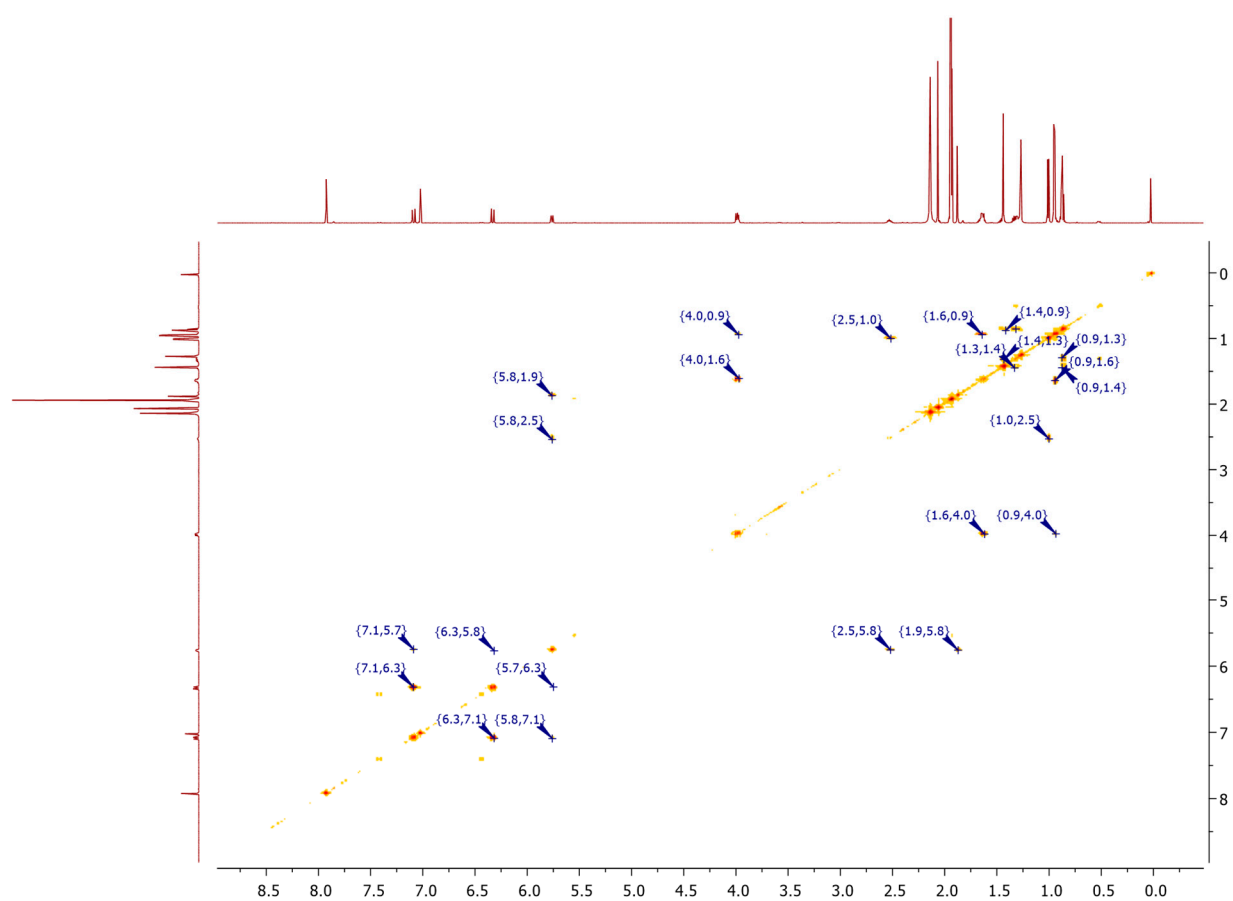


Figure S4 2D NMR (600 MHz,  $\text{CD}_3\text{CN}$ ) COSY of penazaphilone J

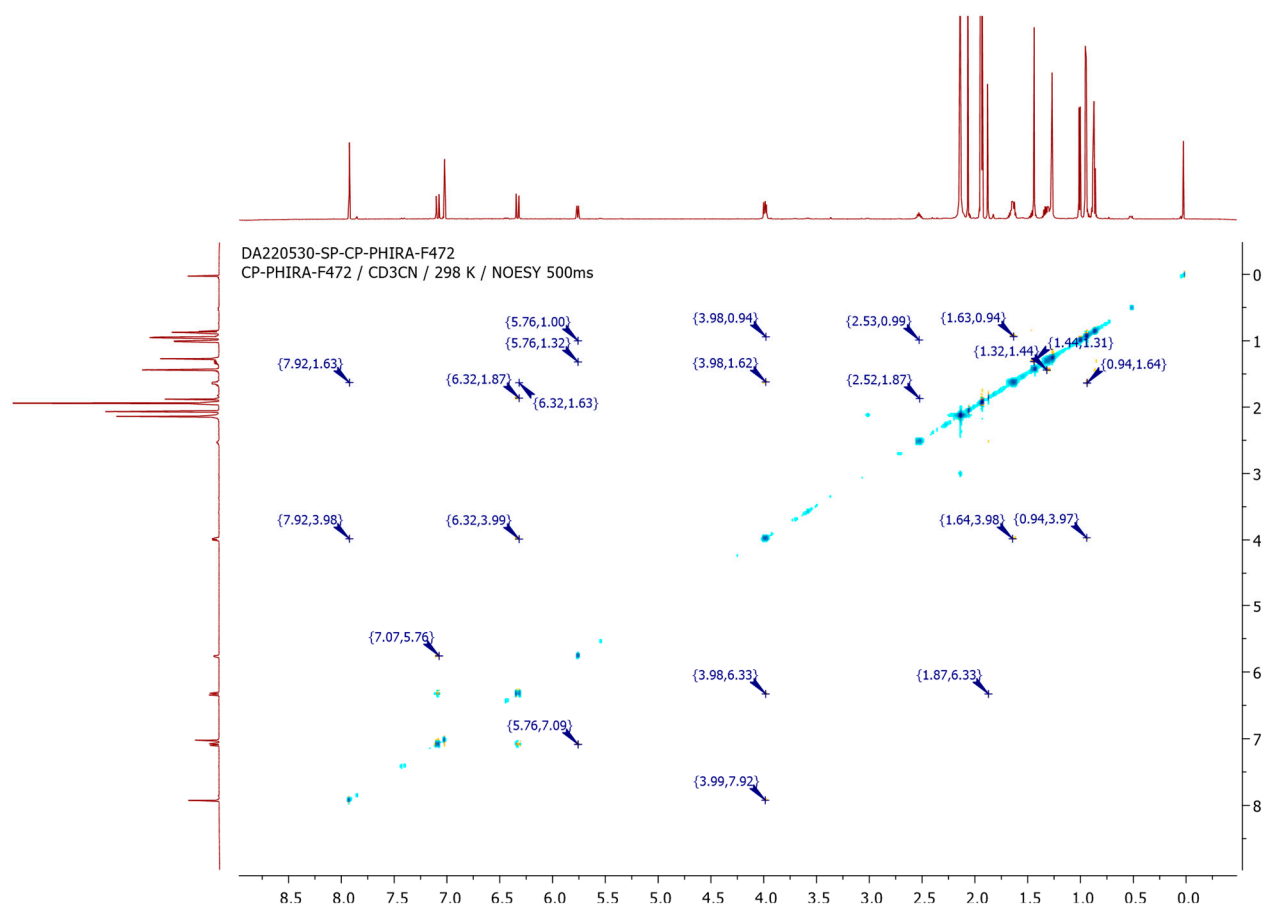


Figure S5 2D NMR NOESY (600 MHz, CD<sub>3</sub>CN) of penazaphilone J

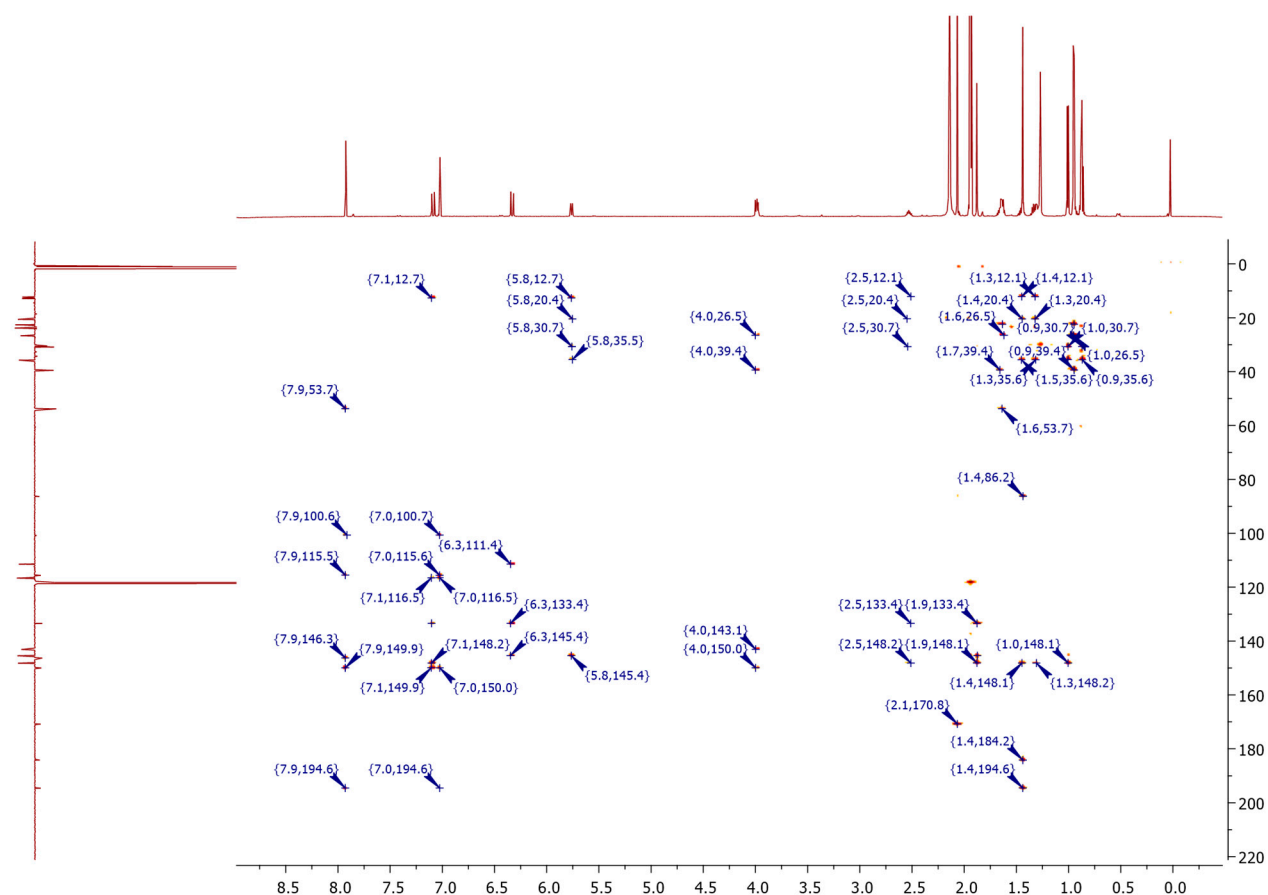


Figure S6 2D NMR (600 MHz, CD<sub>3</sub>CN) HMBC of penazaphilone J

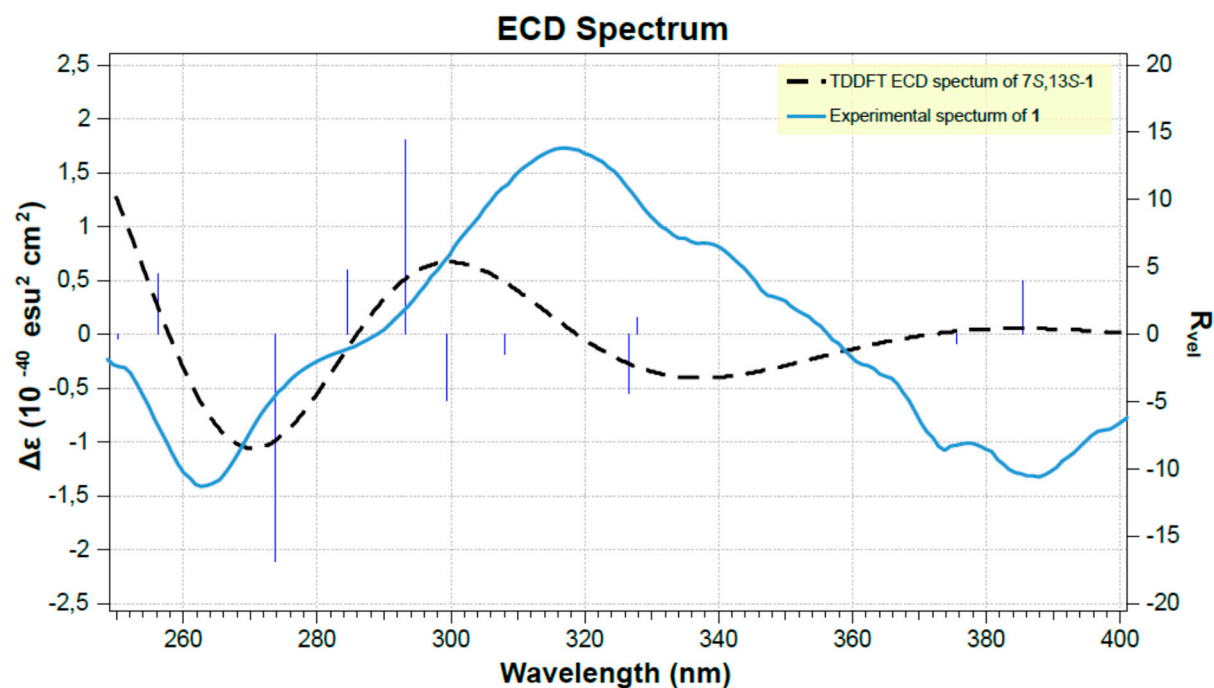


Figure S7. Comparison of the experimental ECD spectrum of **1** and calculated ECD spectrum for the (7S, 13S) stereoisomer.



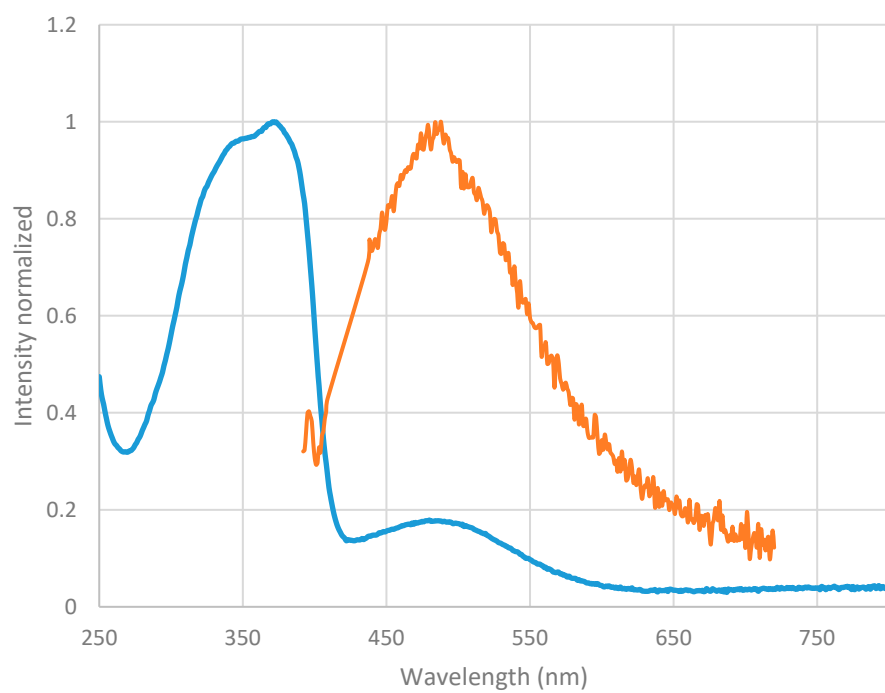


Figure S8 Absorption (in blue) and emission (in orange) spectra of penazaphilone J

Stokes shift  $\Delta\lambda = 116$  nm

## 2. Penazaphilone K

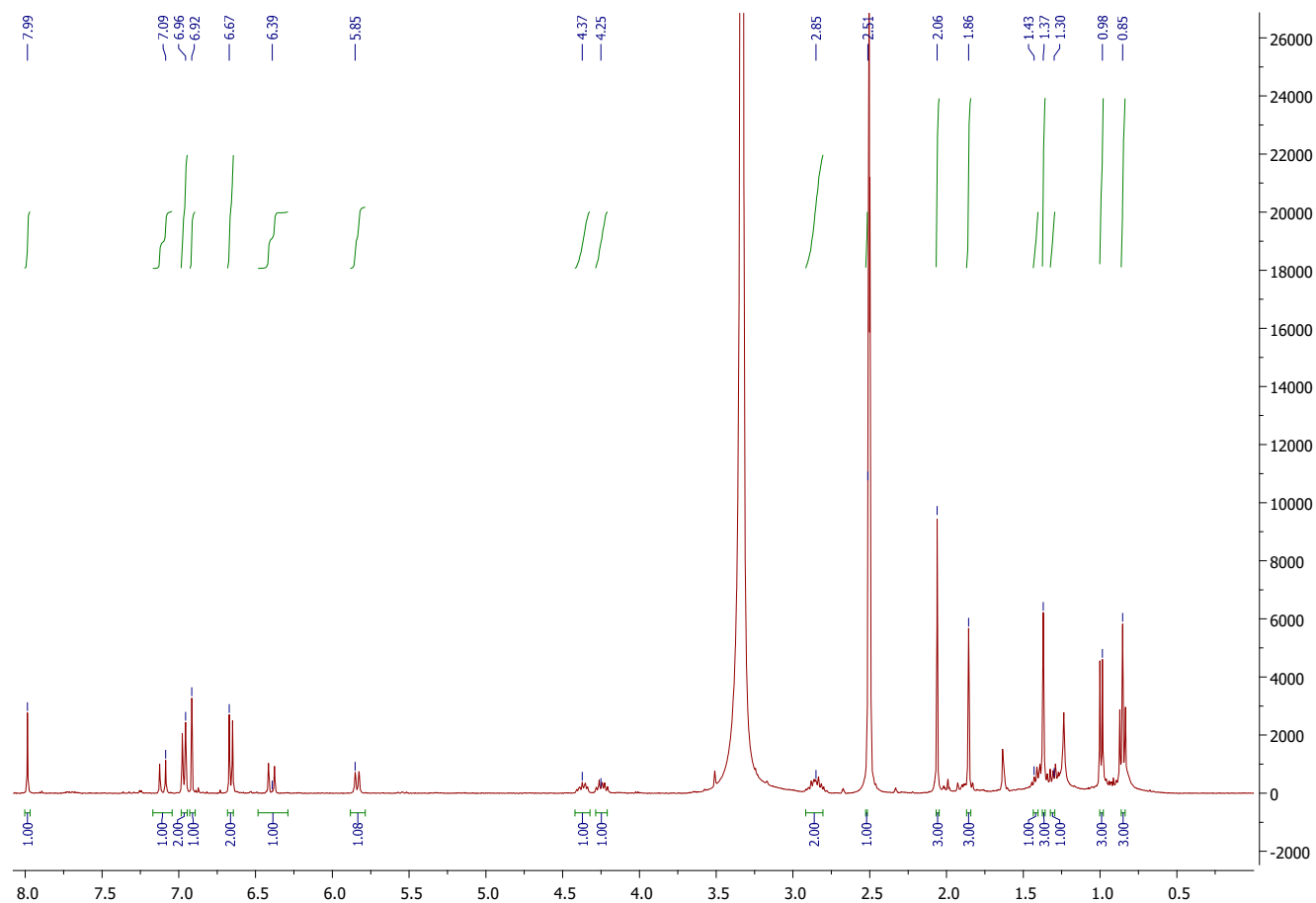


Figure S9 <sup>1</sup>H 1D NMR (600 MHz, DMSO-*d*<sub>6</sub>) penazaphilone K

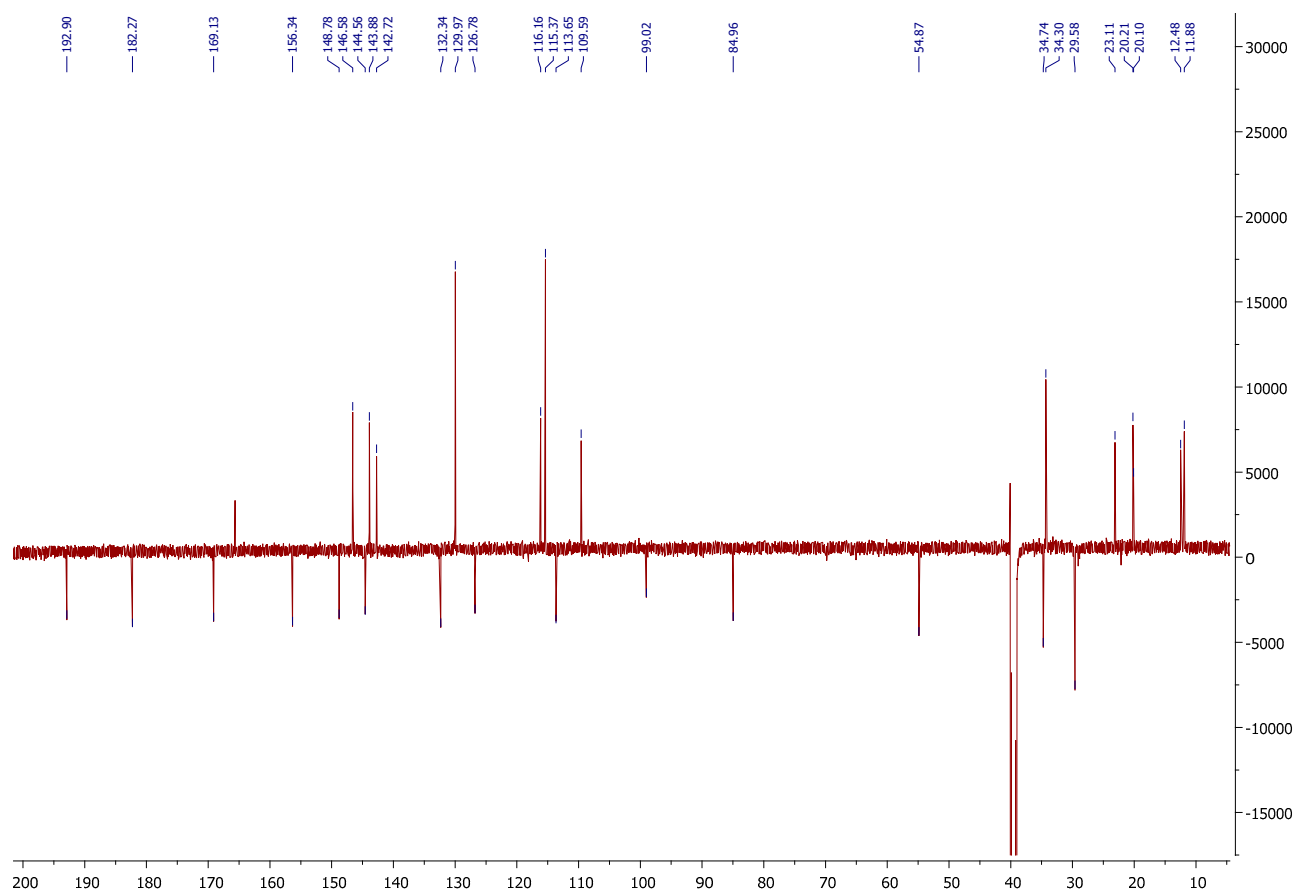
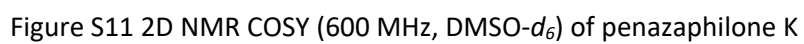


Figure S10 1D NMR DEPT Q (600 MHz, DMSO- $d_6$ ) of penazaphilone K



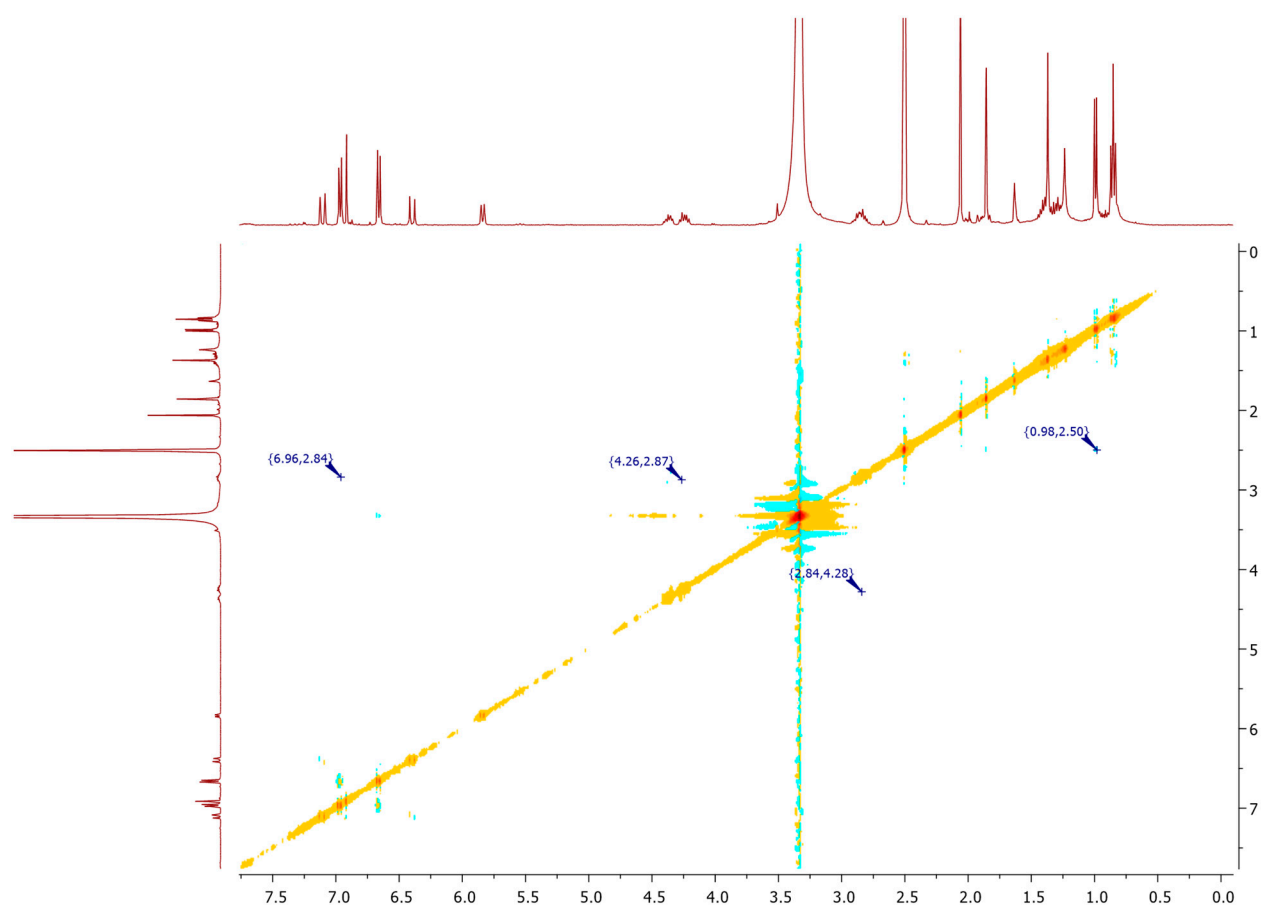


Figure S12 2D NMR NOESY (600 MHz, DMSO- $d_6$ ) of penazaphilone K

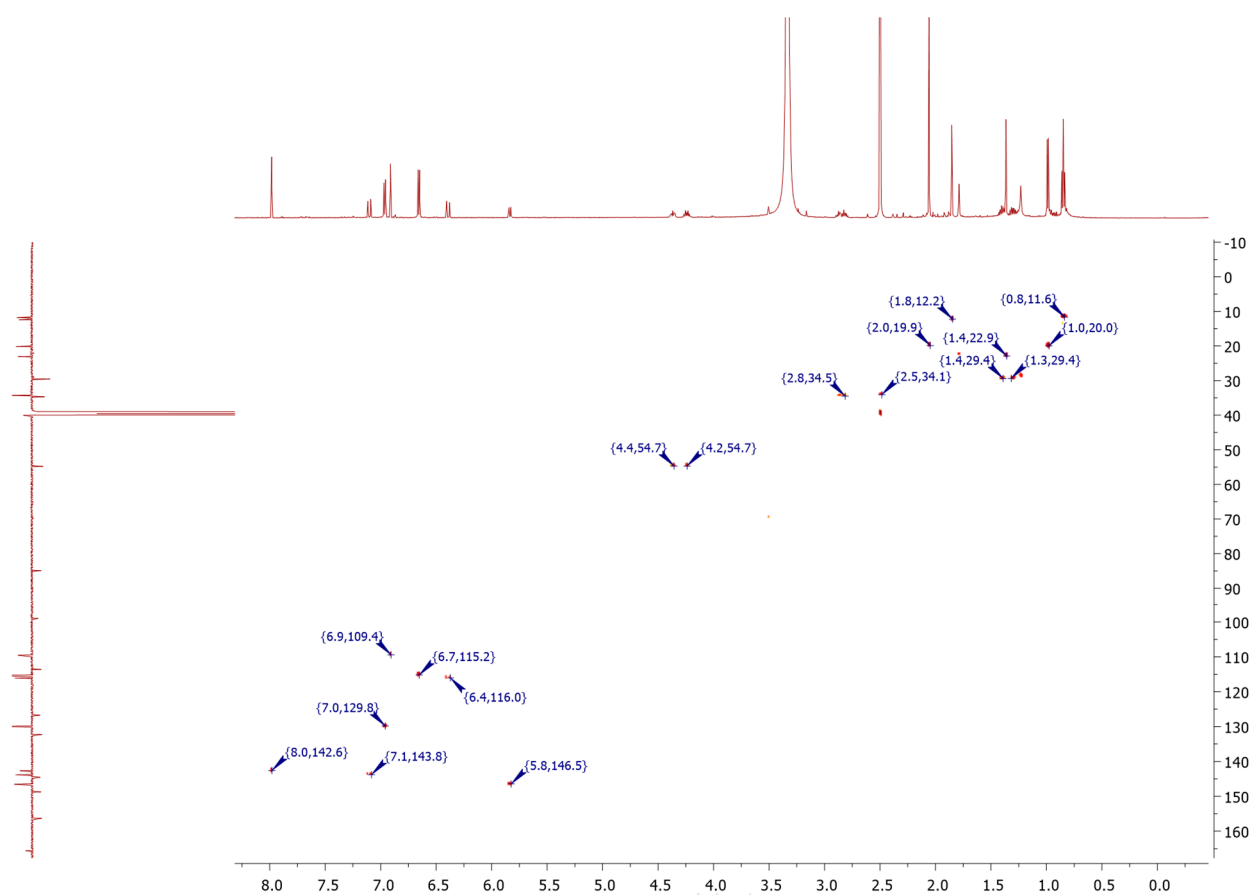


Figure S13 2D NMR HSQC (600 MHz, DMSO- $d_6$ ) penazaphilone K

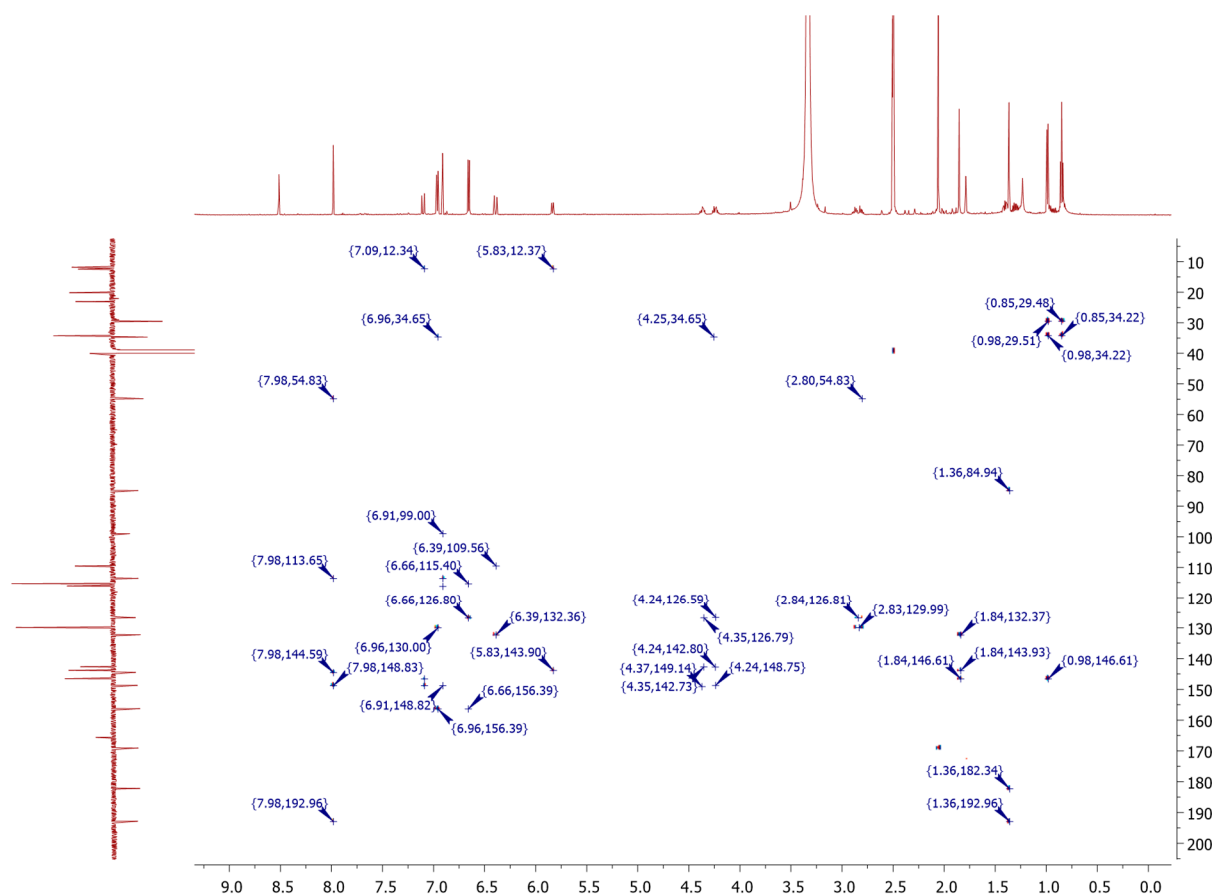


Figure S14 2D NMR HMBC (600 MHz,  $\text{DMSO}-d_6$ ) penazaphilone K

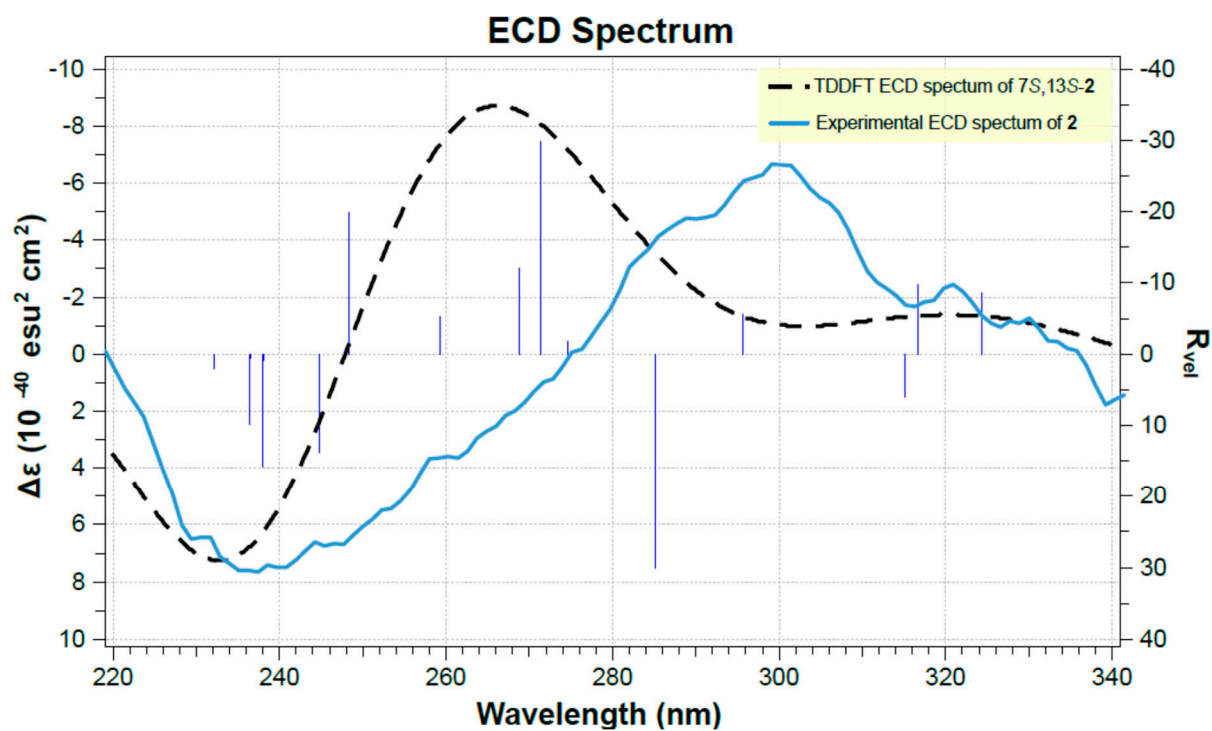


Figure S15. Comparison of the experimental ECD spectrum of **2** and calculated ECD spectrum for the (7S, 13S) stereoisomer

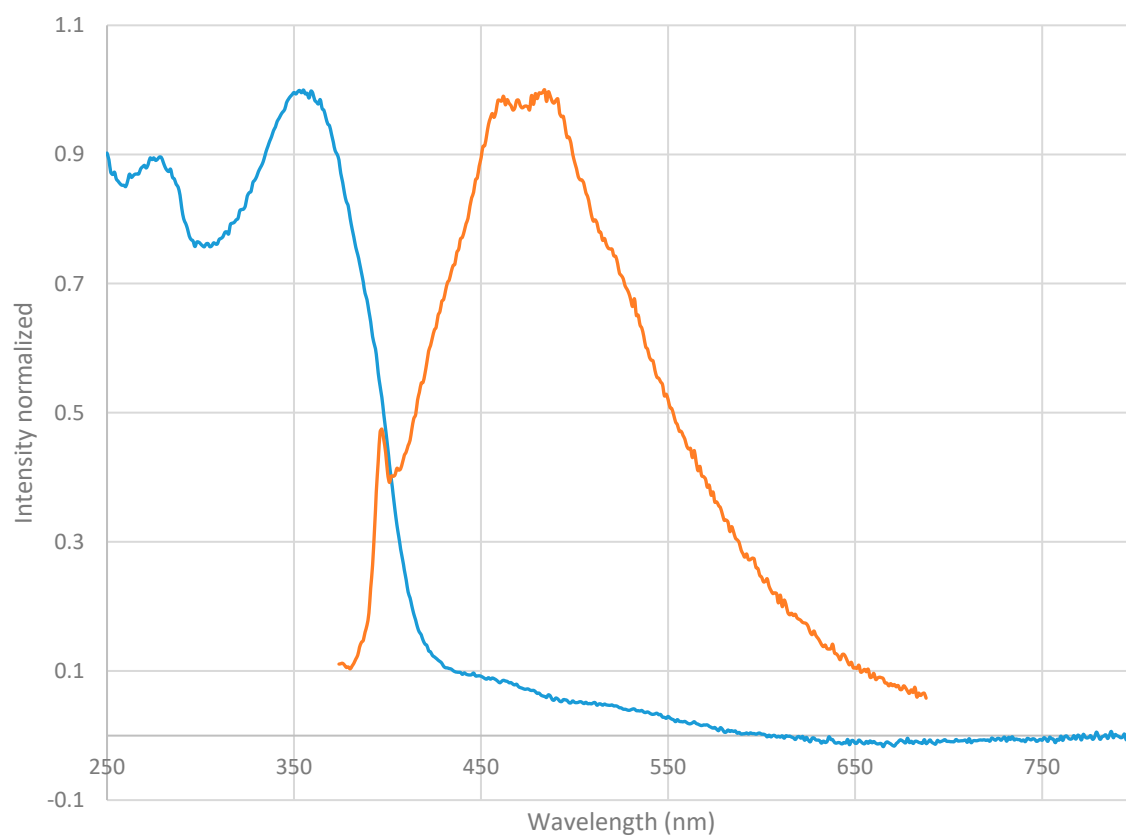


Figure S16 Absorption (in blue) and emission (in orange) spectra of penazaphilone K

Stokes shift  $\Delta\lambda = 106$  nm



### 3. Penazaphilone L

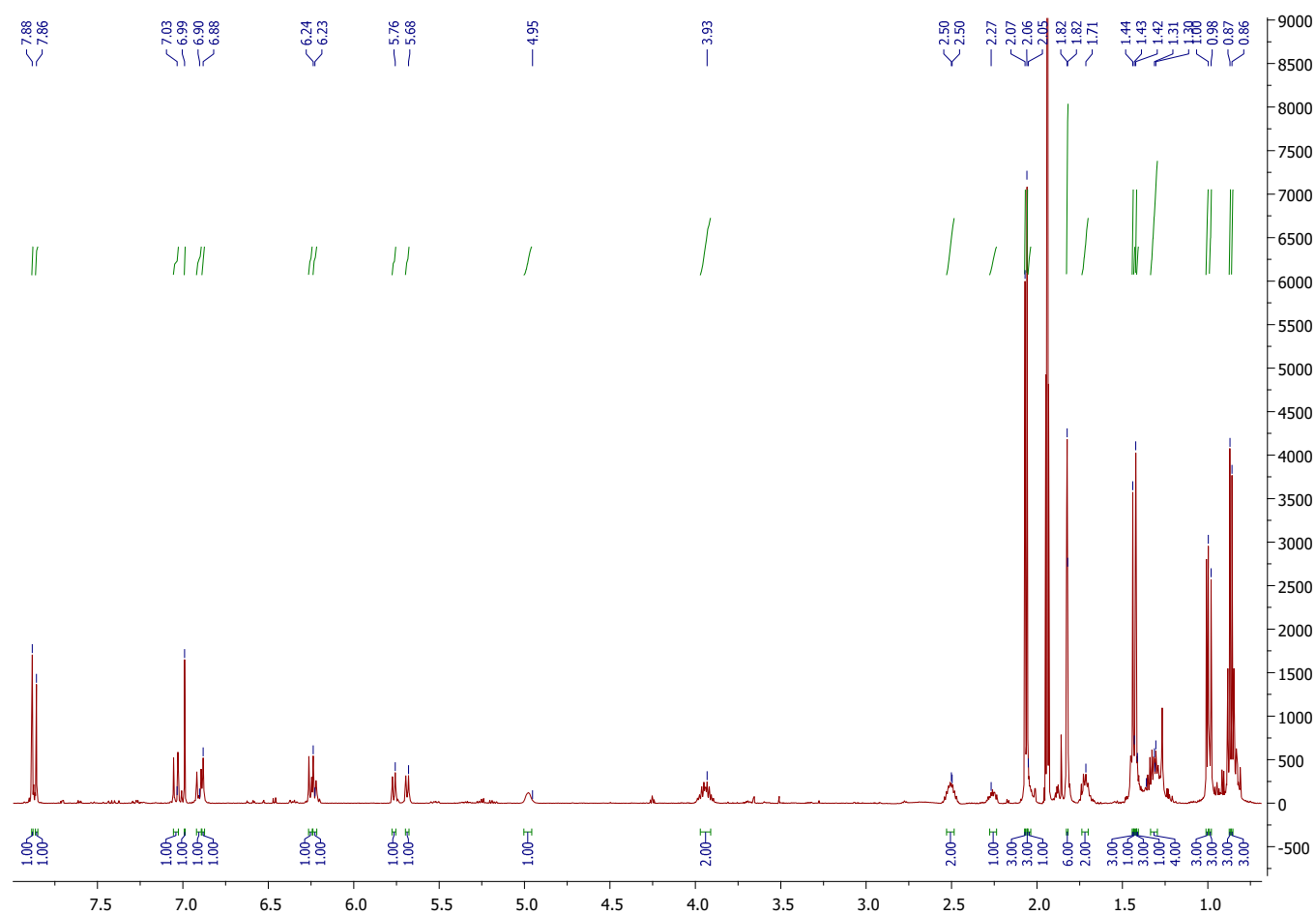


Figure S17 1D  $^1\text{H}$  NMR (600MHz,  $\text{CD}_3\text{CN}$ ) of penazaphilone L

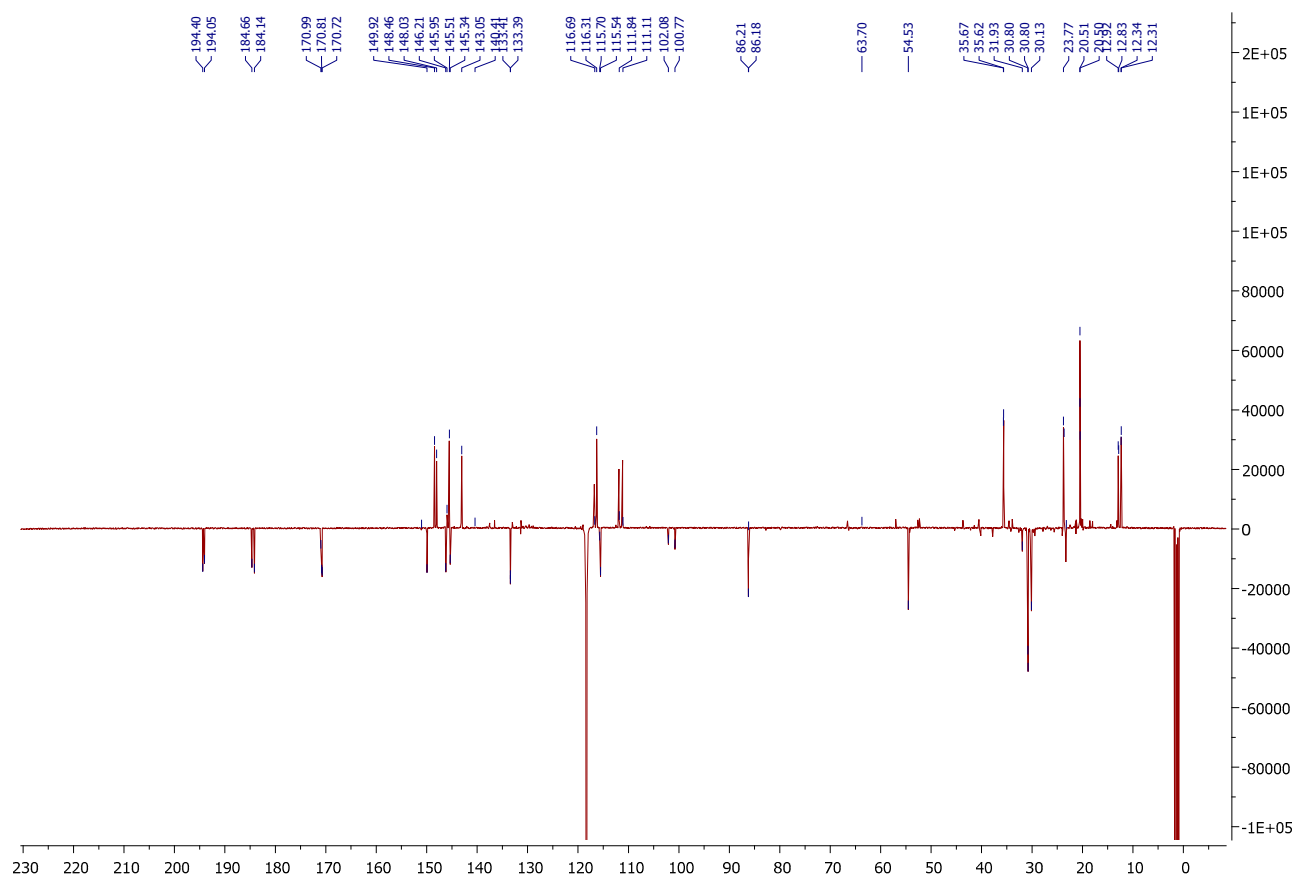


Figure S18 1D NMR DEPTQ (600MHz, CD<sub>3</sub>CN) of penazaphilone L

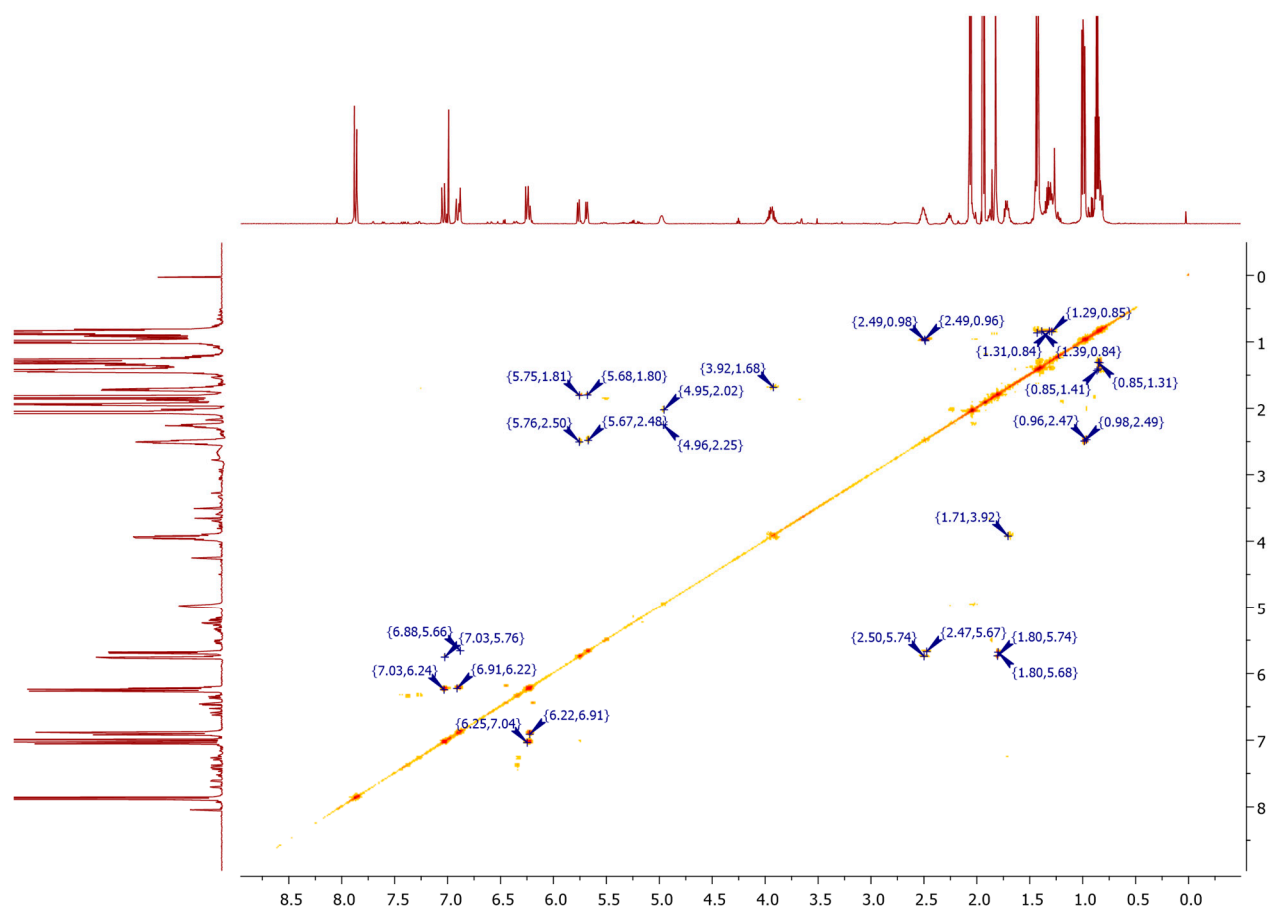


Figure S19 2D NMR COSY (600MHz,  $\text{CD}_3\text{CN}$ ) of penazaphilone L

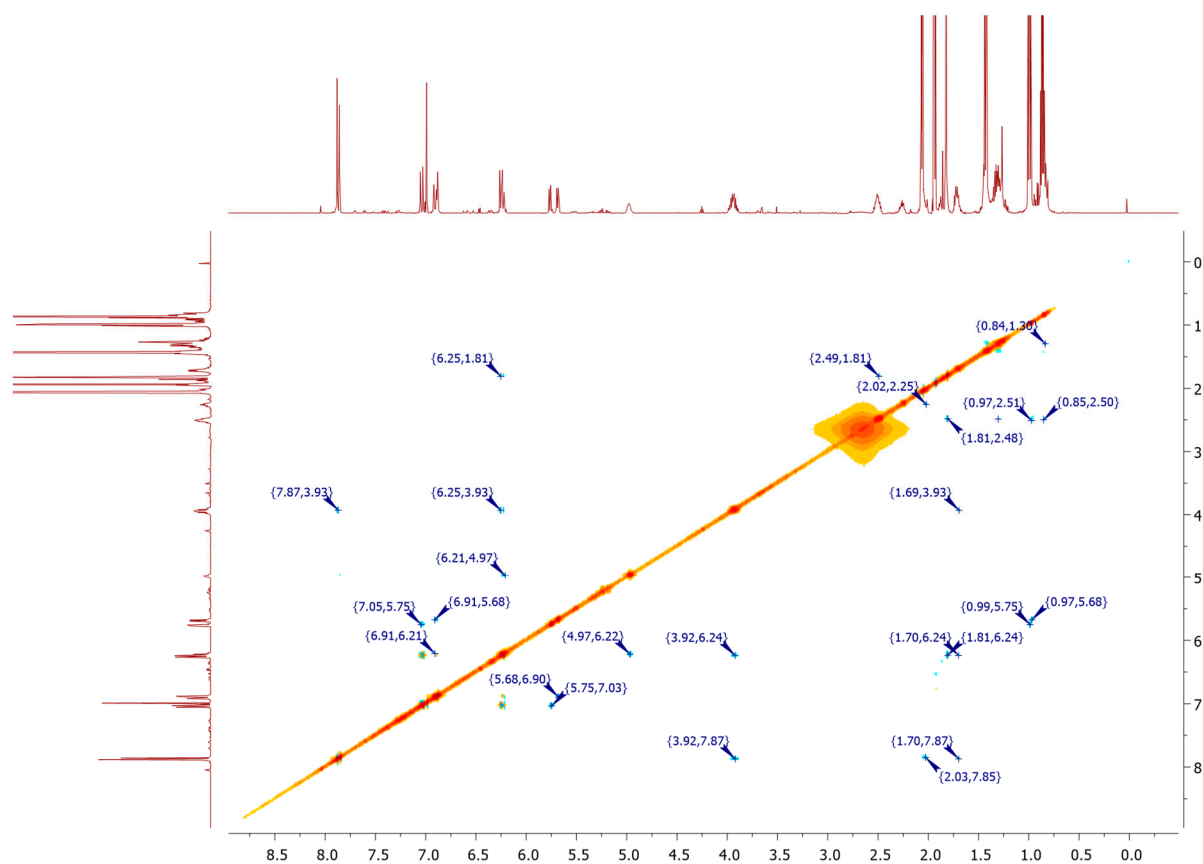


Figure S20 2D NMR NOESY (600MHz,  $\text{CD}_3\text{CN}$ ) of penazaphilone L

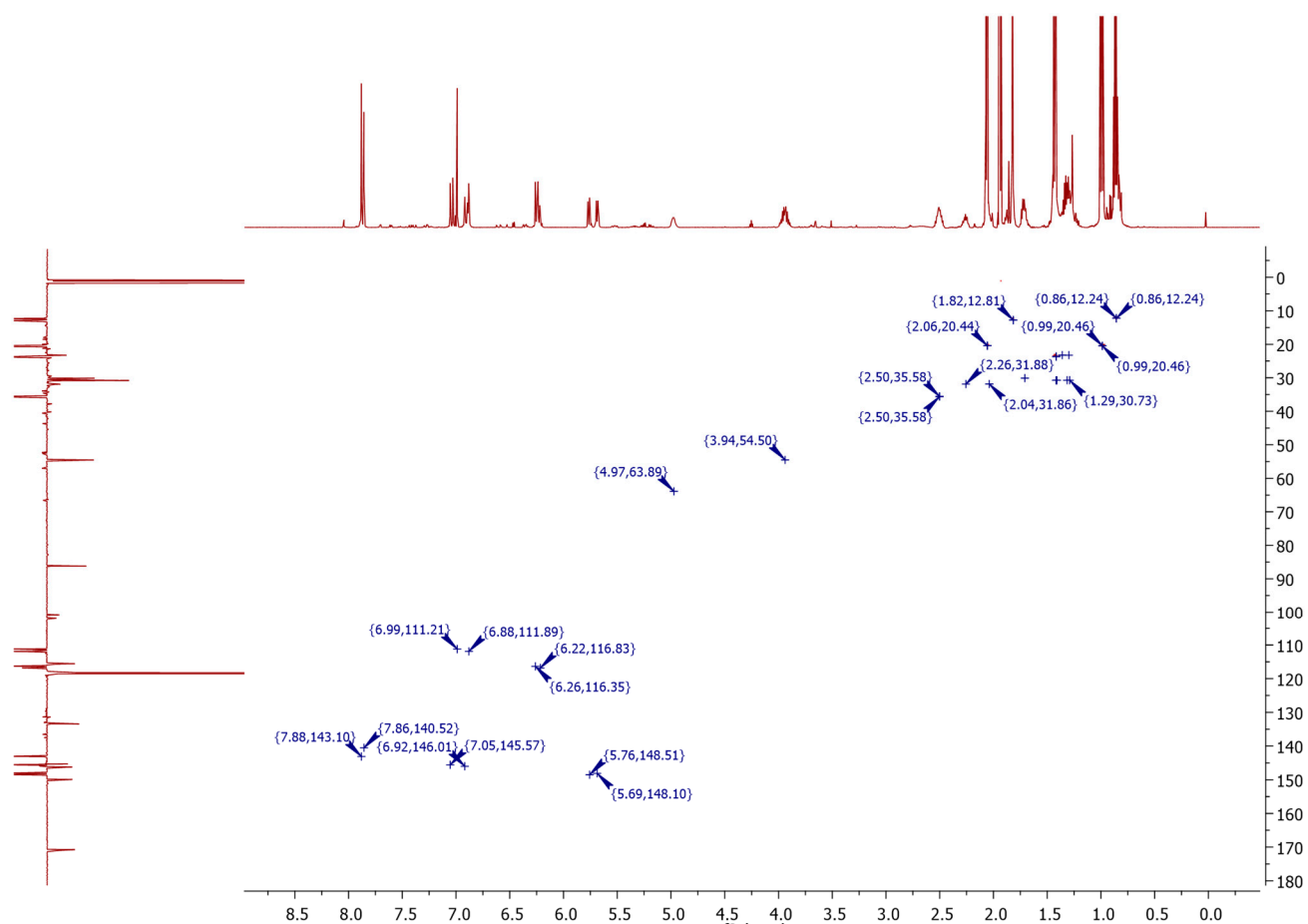


Figure S21 2D NMR HSQC (600MHz,  $\text{CD}_3\text{CN}$ ) of penazaphilone L

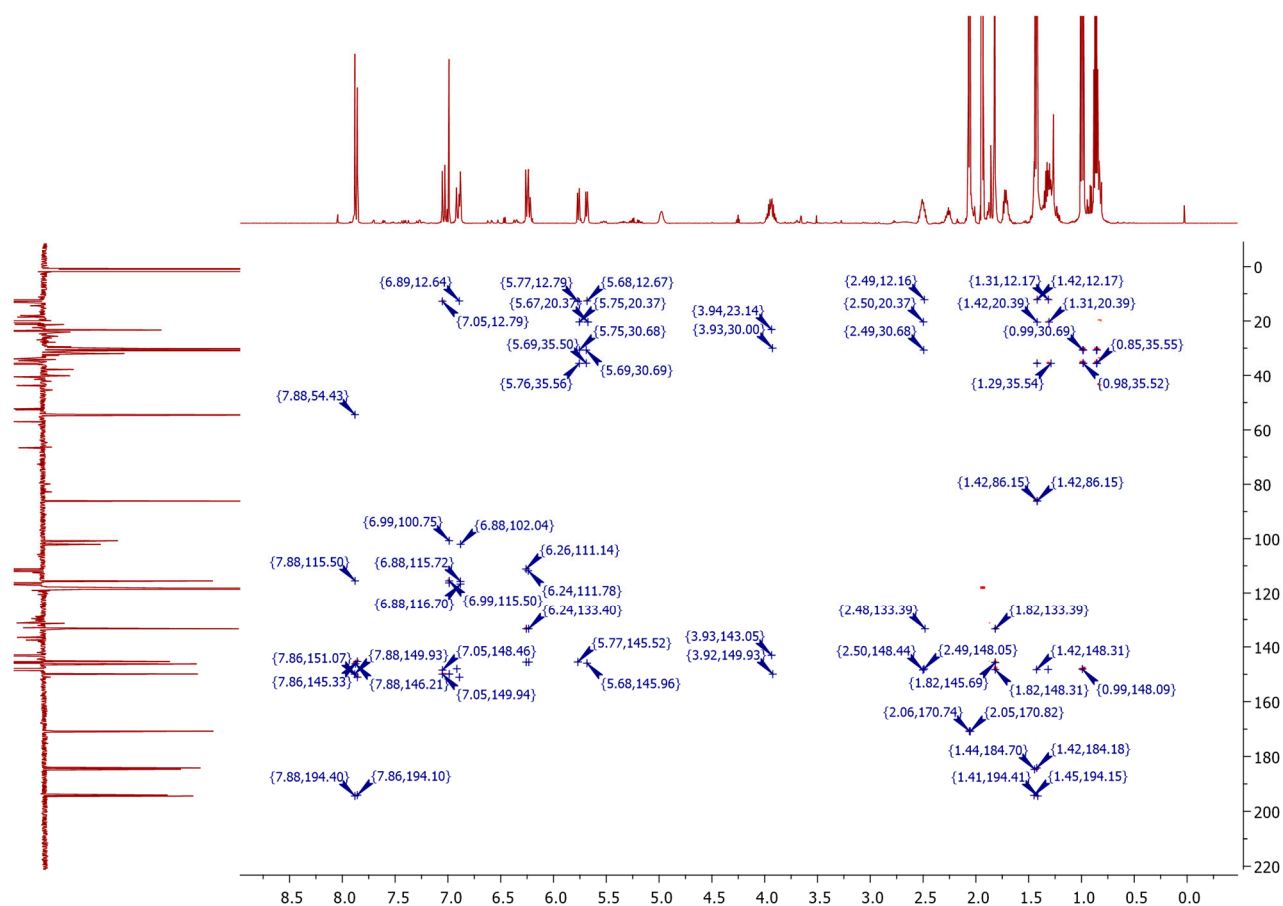


Figure S22 2D NMR HMBC (600MHz, CD<sub>3</sub>CN) of penazaphilone L

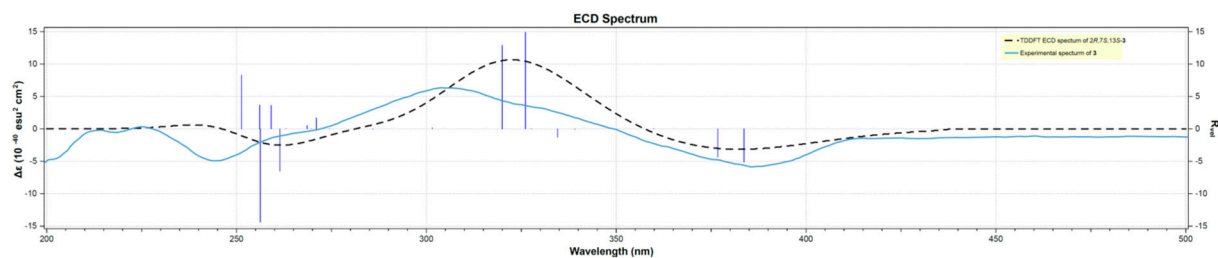


Figure S23. Comparison of the experimental ECD spectrum of 3 and calculated ECD spectrum for the (2'R, 7S, 7''S, 13S, 13''S) stereoisomer

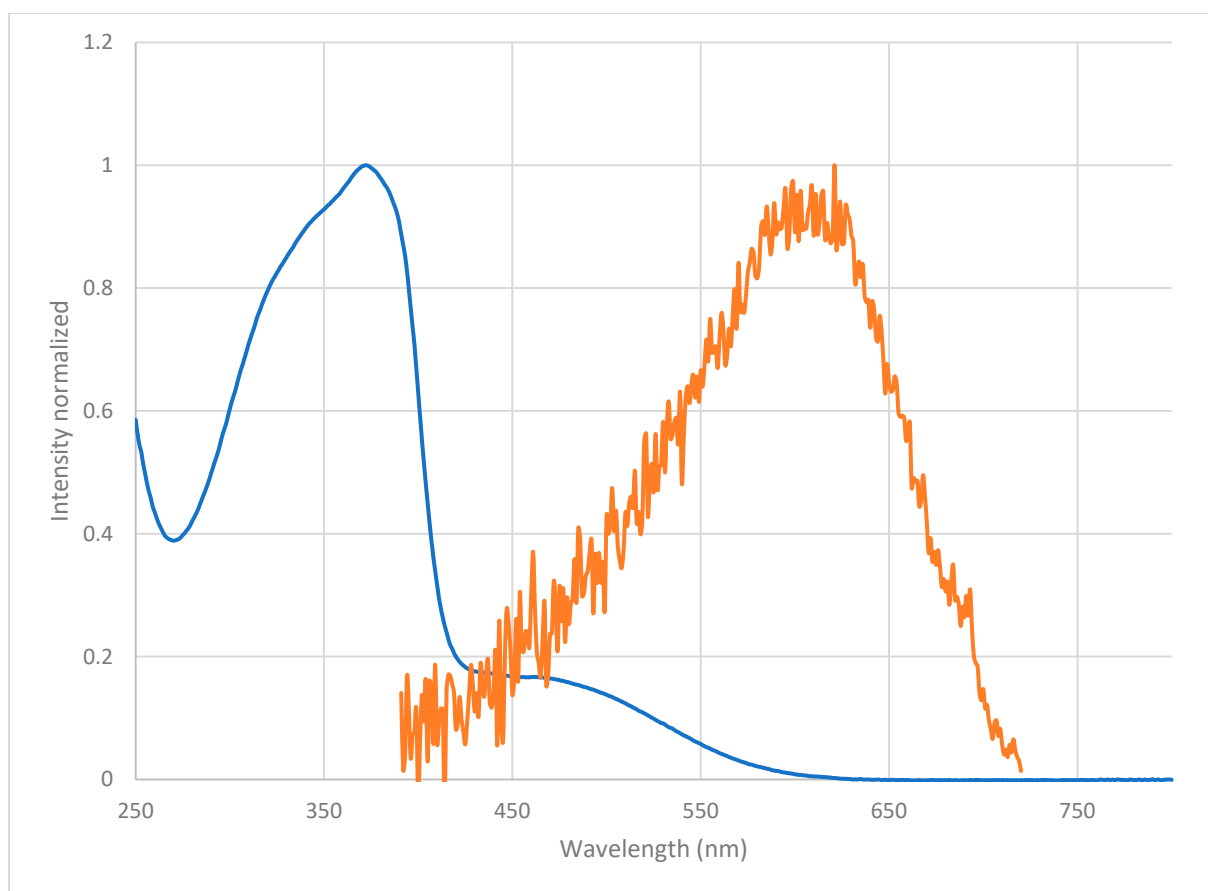


Figure S24 Absorption (in blue) and emission (in orange) spectra of penazaphilone L

Stokes shift  $\Delta\lambda = 131$  nm