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## Supplementary Material

### Photoinduced Cycloadditions in the Diversity-Oriented Synthesis Toolbox: Increasing Complexity with Straightforward Postphotochemical Modifications

*Weston J. Umstead, Olga A. Mukhina, N. N. Bhuvan Kumar and Andrei G. Kutateladze\**

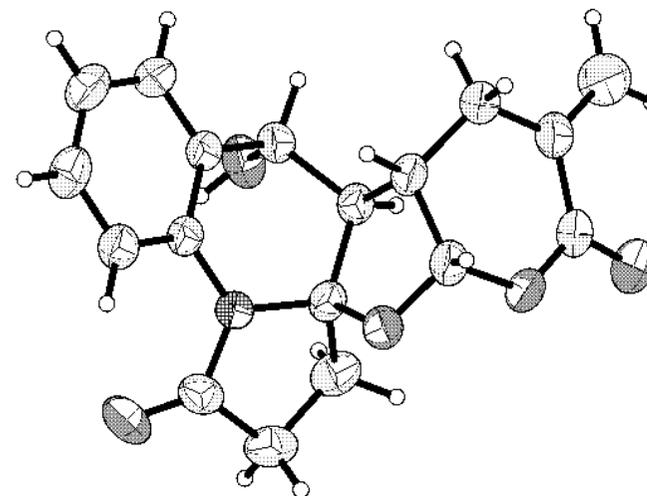
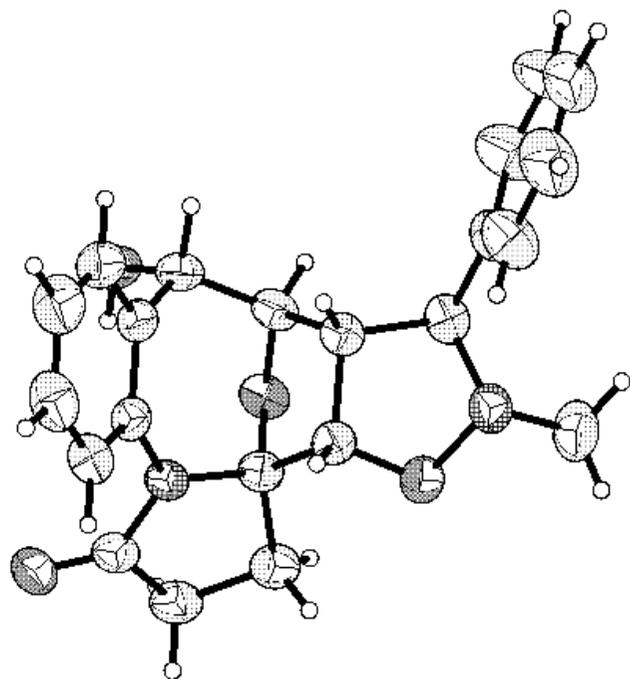
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Xray structures of compounds 7 and 12''

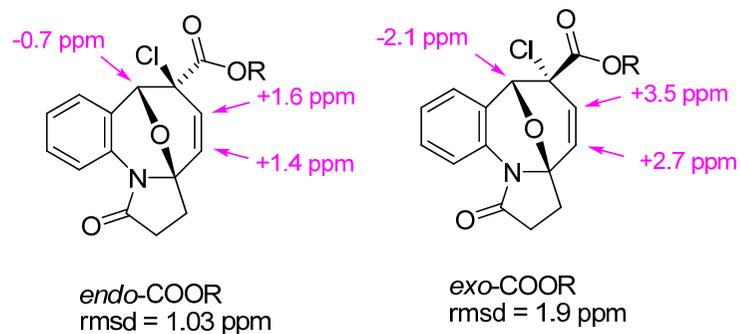


7



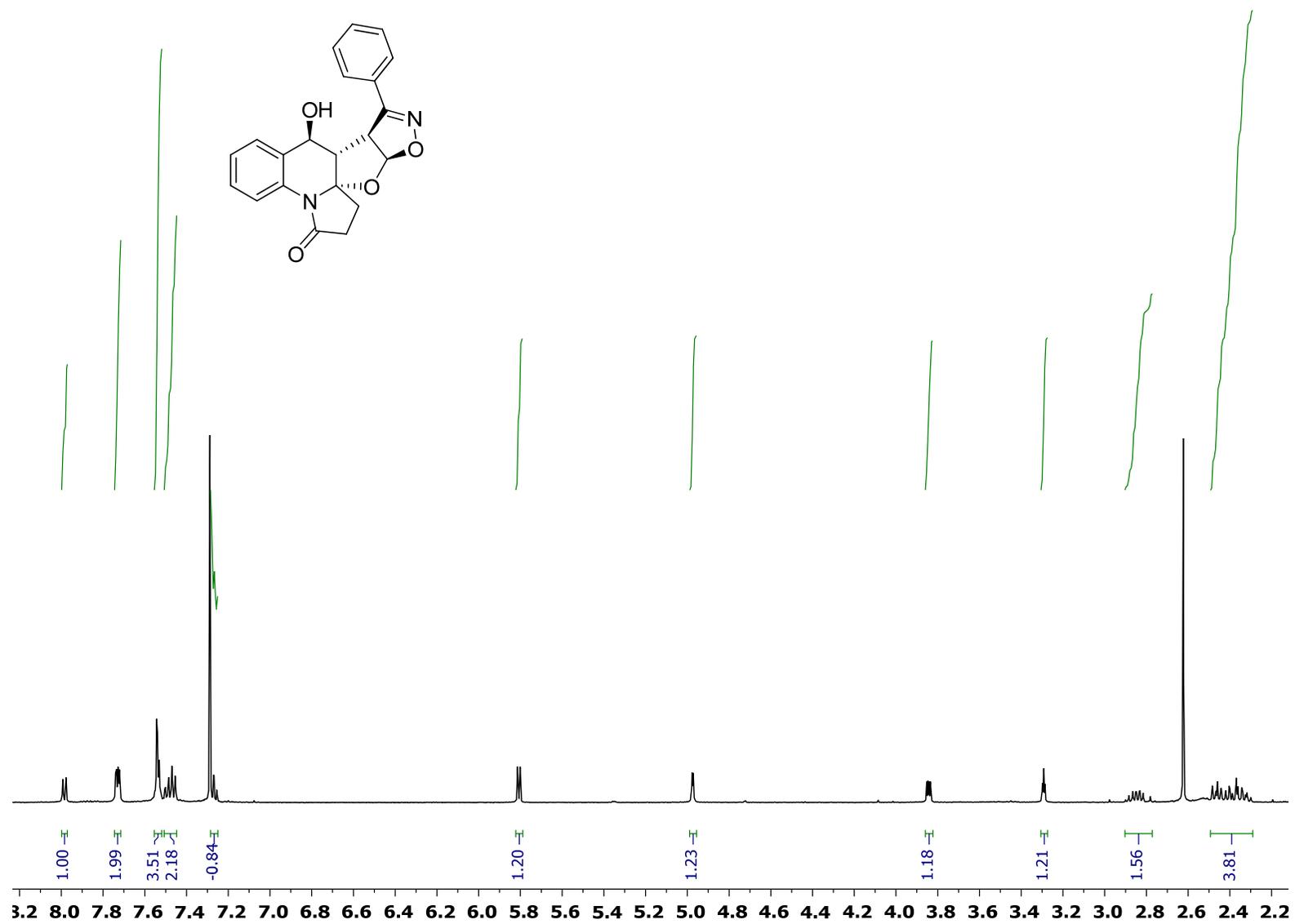
## $^{13}\text{C}$ NMR chemical shifts of compound **9**

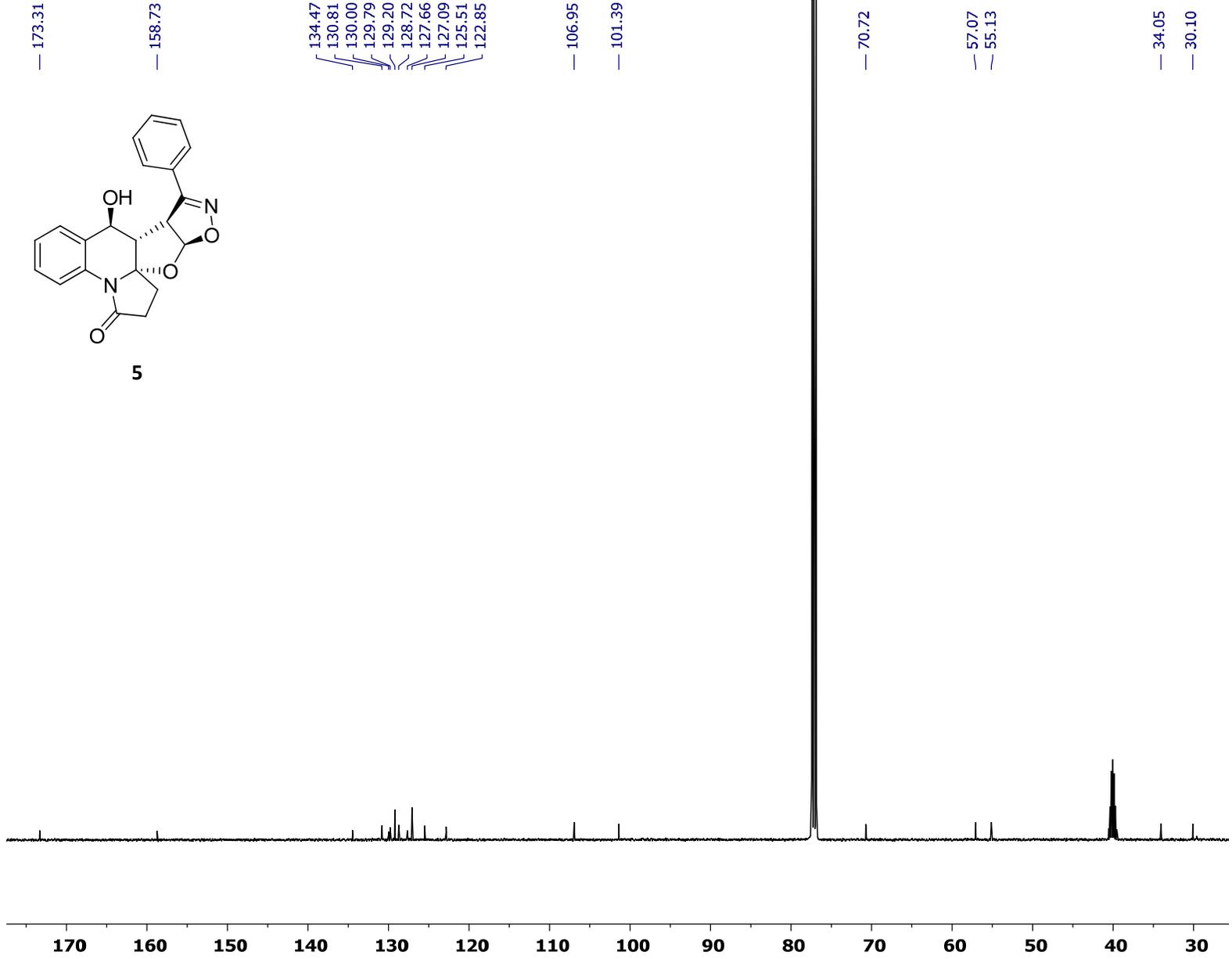
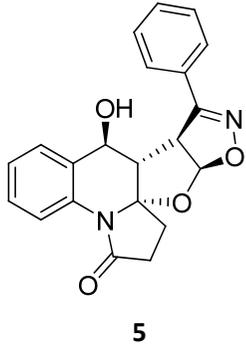
$^{13}\text{C}$  NMR chemical shifts were calculated at the b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) level of theory for both *exo*-COOR and *endo*-COOR stereoisomers of  $\alpha$ -chloroester **9** and linearly corrected for the experimental chemical shift values. Figure S1 shows that the rmsd for the *endo* isomer was twice better than that of the *exo* isomer. The largest deviations were associated with the carbons most proximal to the C(Cl)COOR moiety.

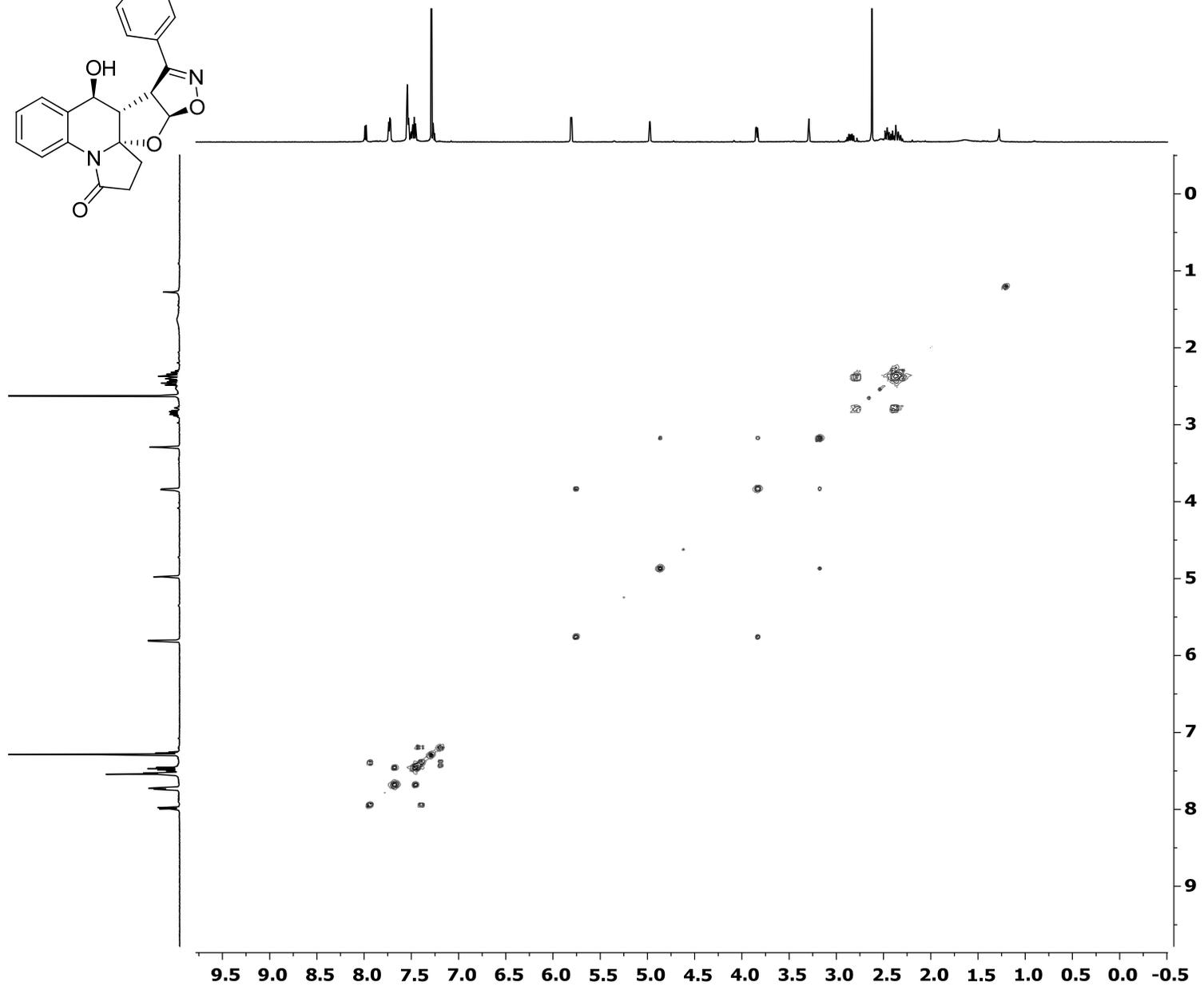
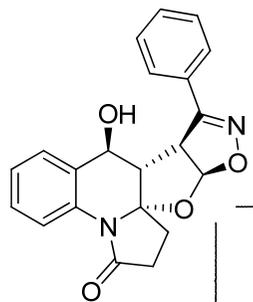


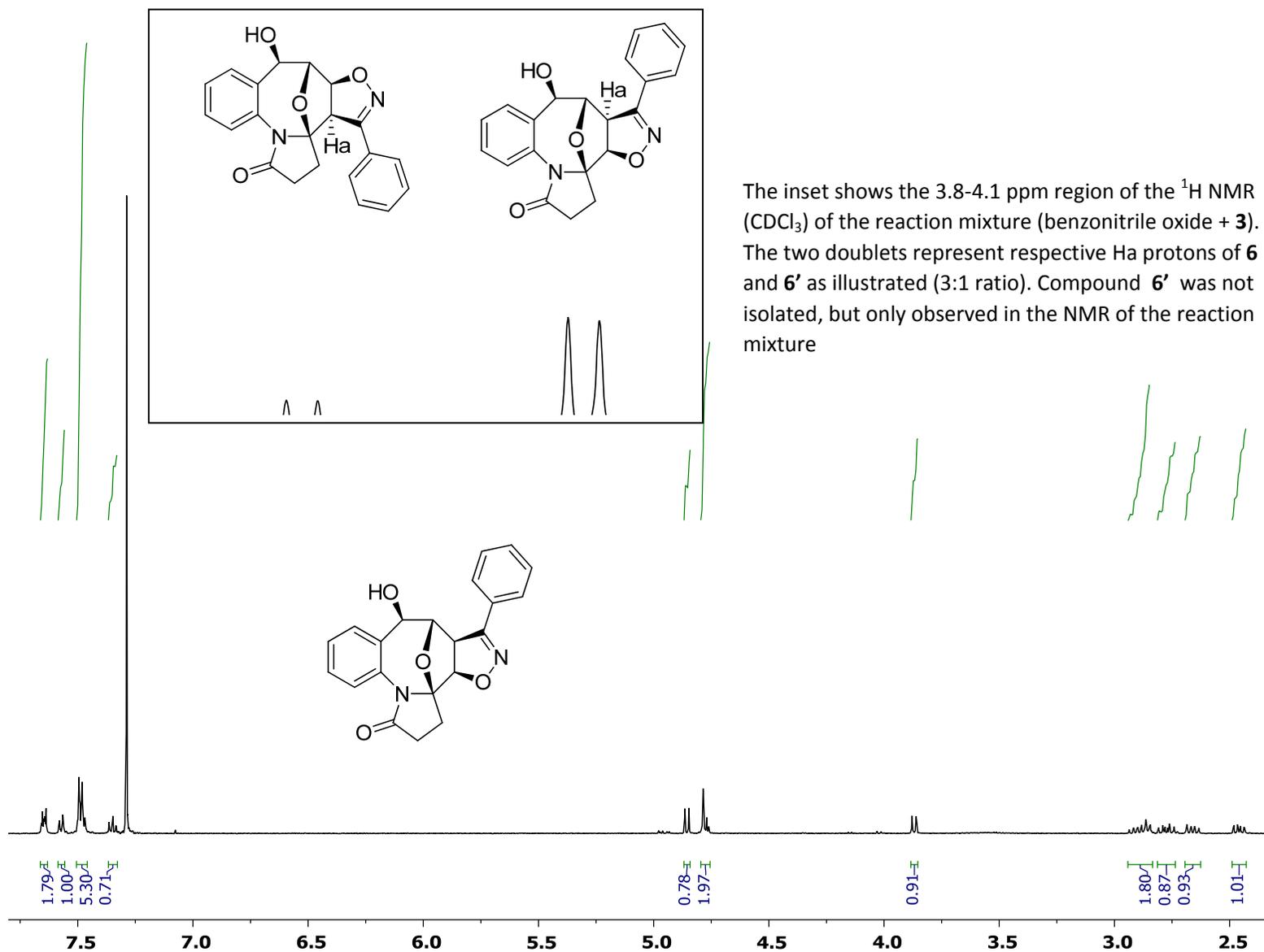
**Figure S1.**  $^{13}\text{C}$  NMR chemical shifts computed for the *endo*-COOR stereoisomer fit experimental values much better (the largest deviations are shown in magenta).

# NMR spectra of the products

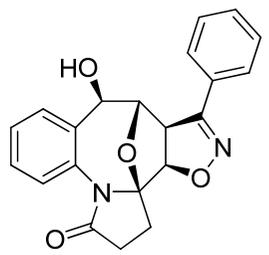




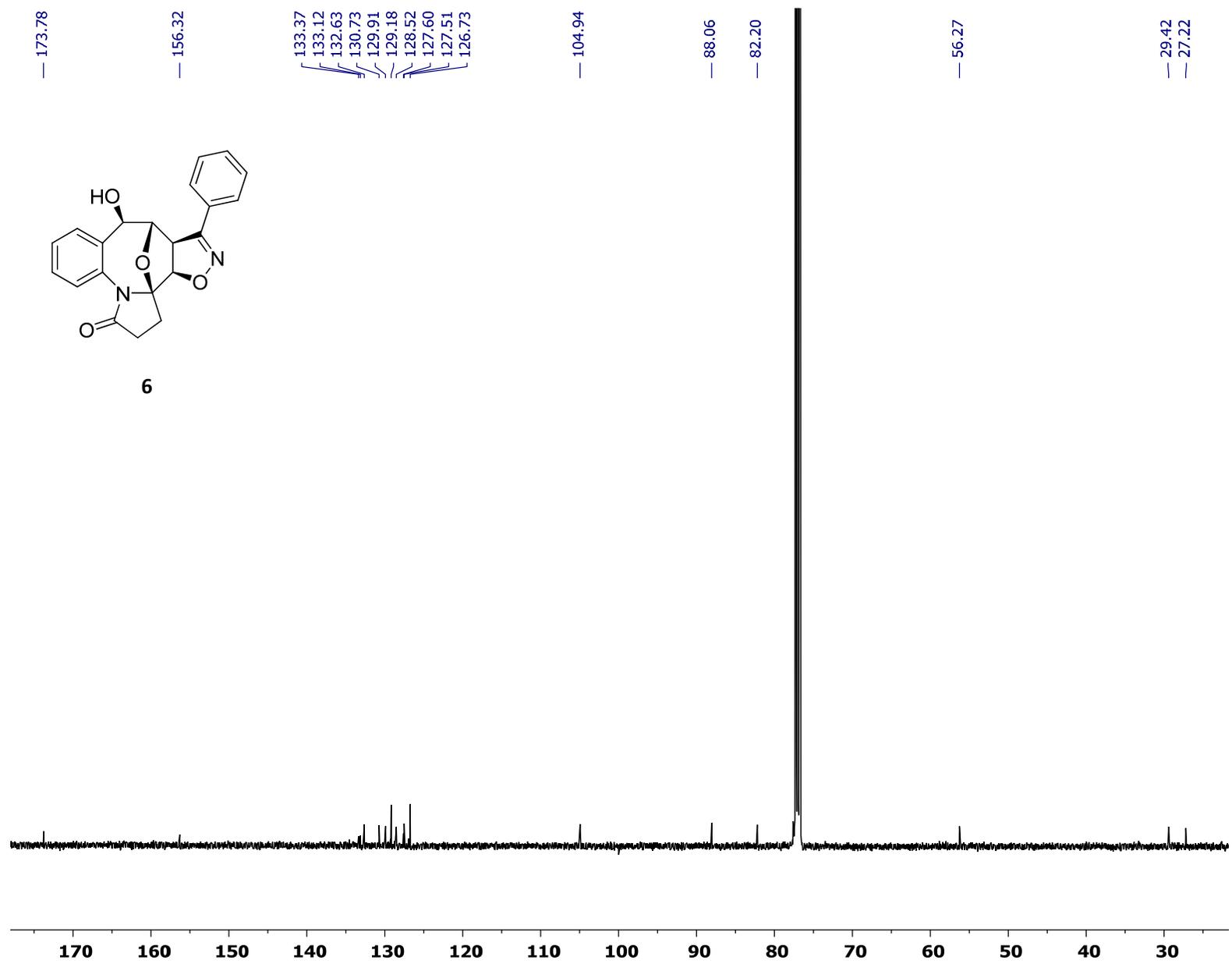


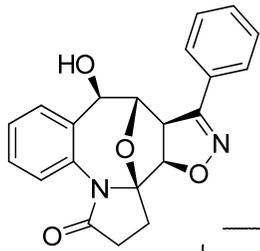


The inset shows the 3.8-4.1 ppm region of the  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) of the reaction mixture (benzotrile oxide + **3**). The two doublets represent respective Ha protons of **6** and **6'** as illustrated (3:1 ratio). Compound **6'** was not isolated, but only observed in the NMR of the reaction mixture

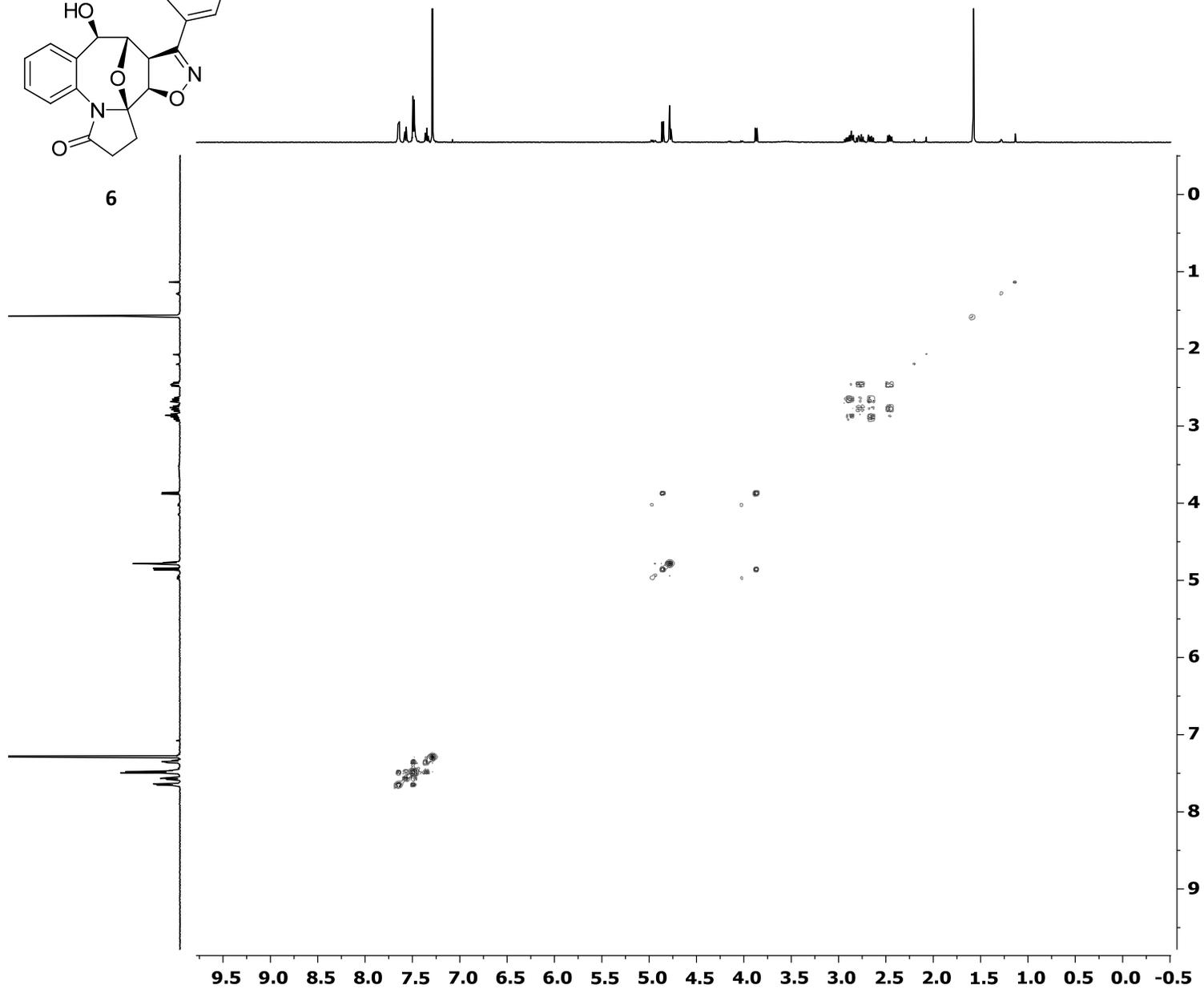


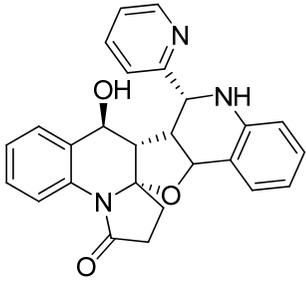
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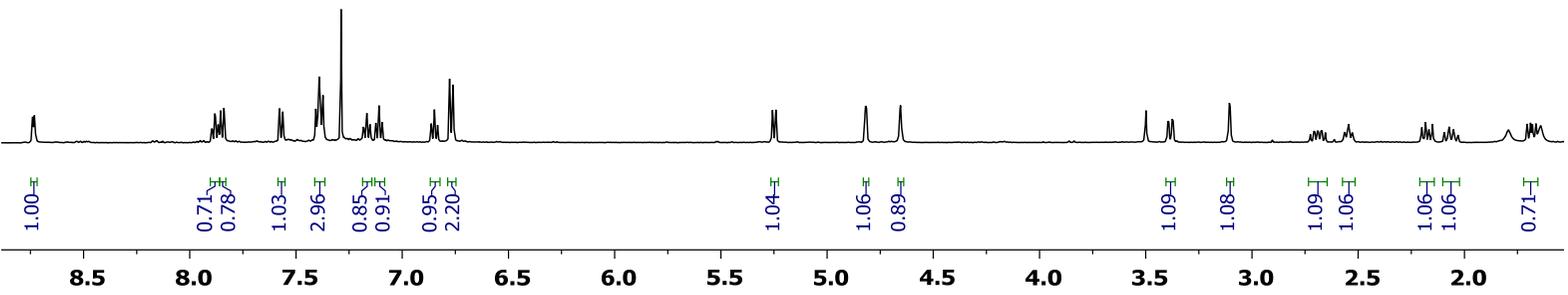
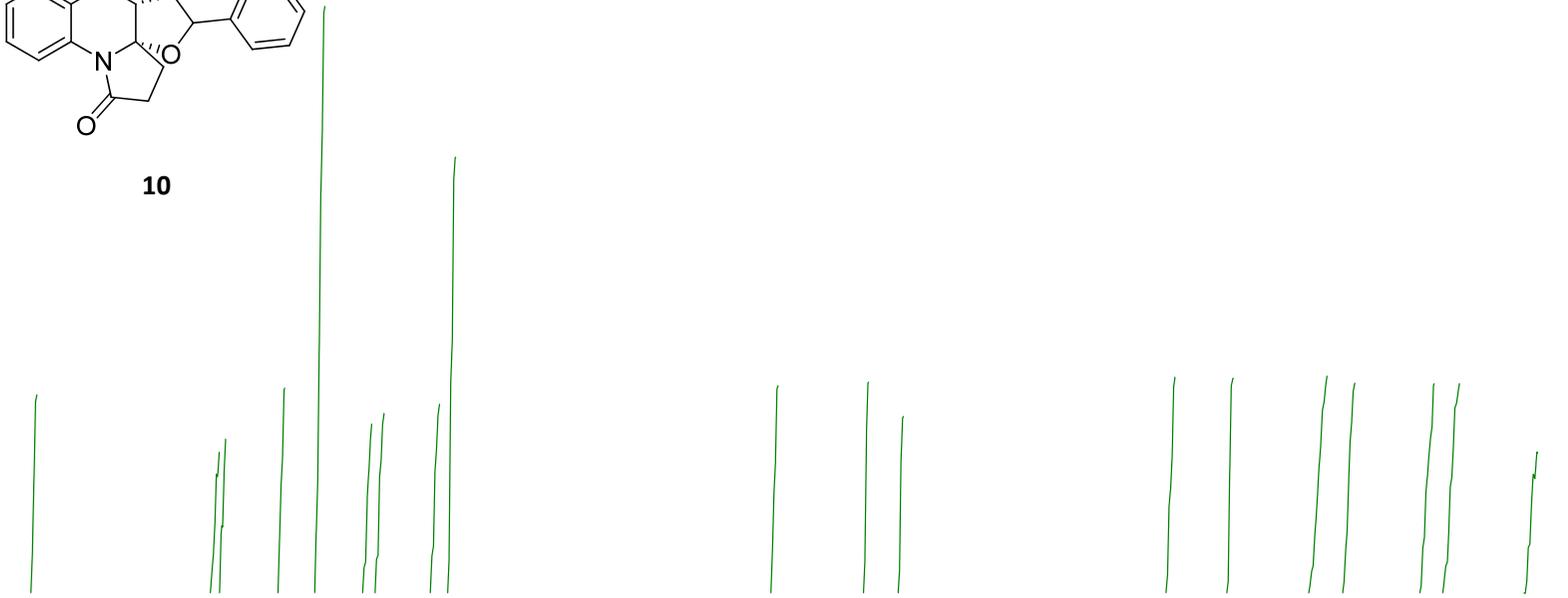


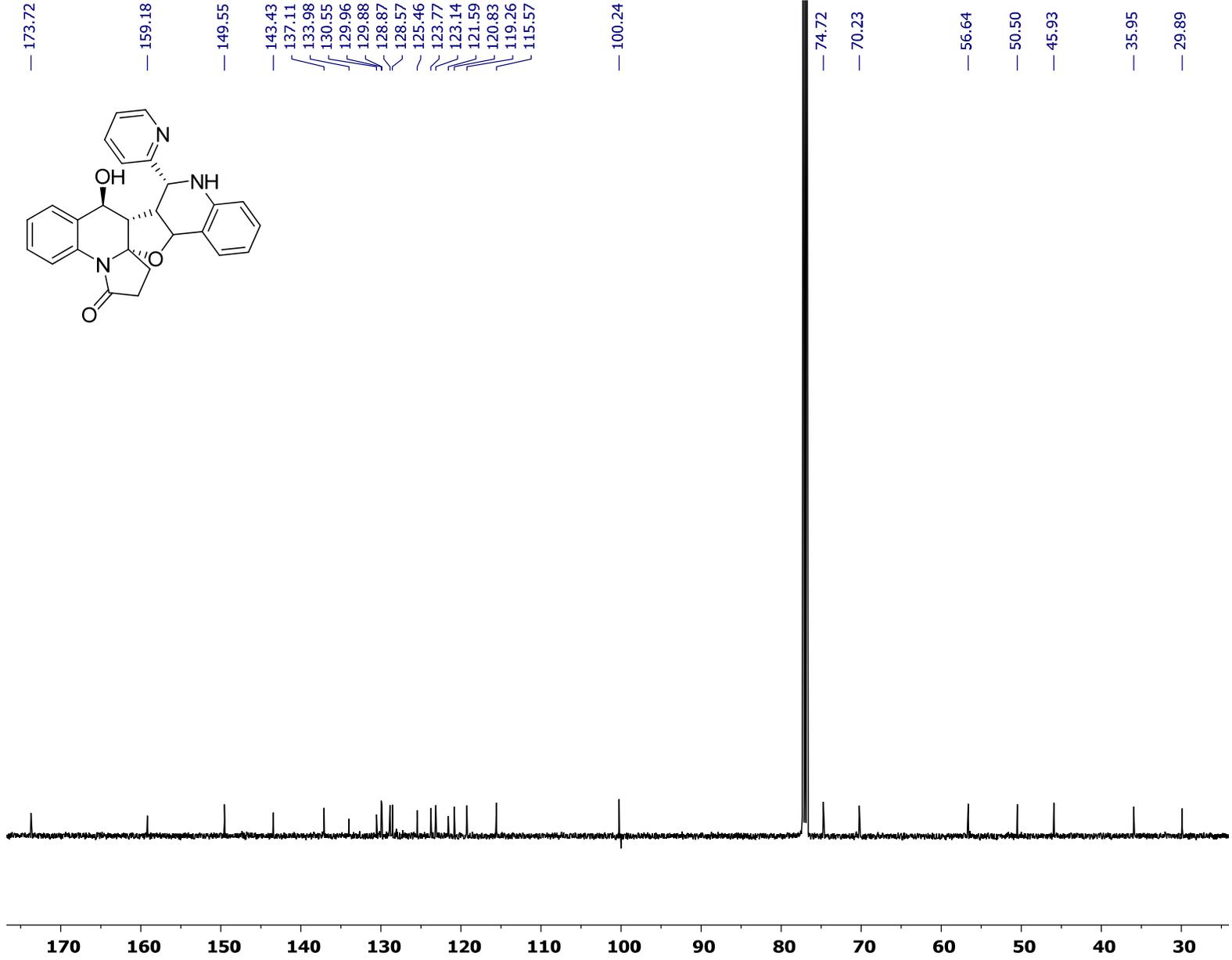
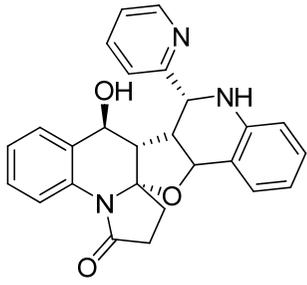
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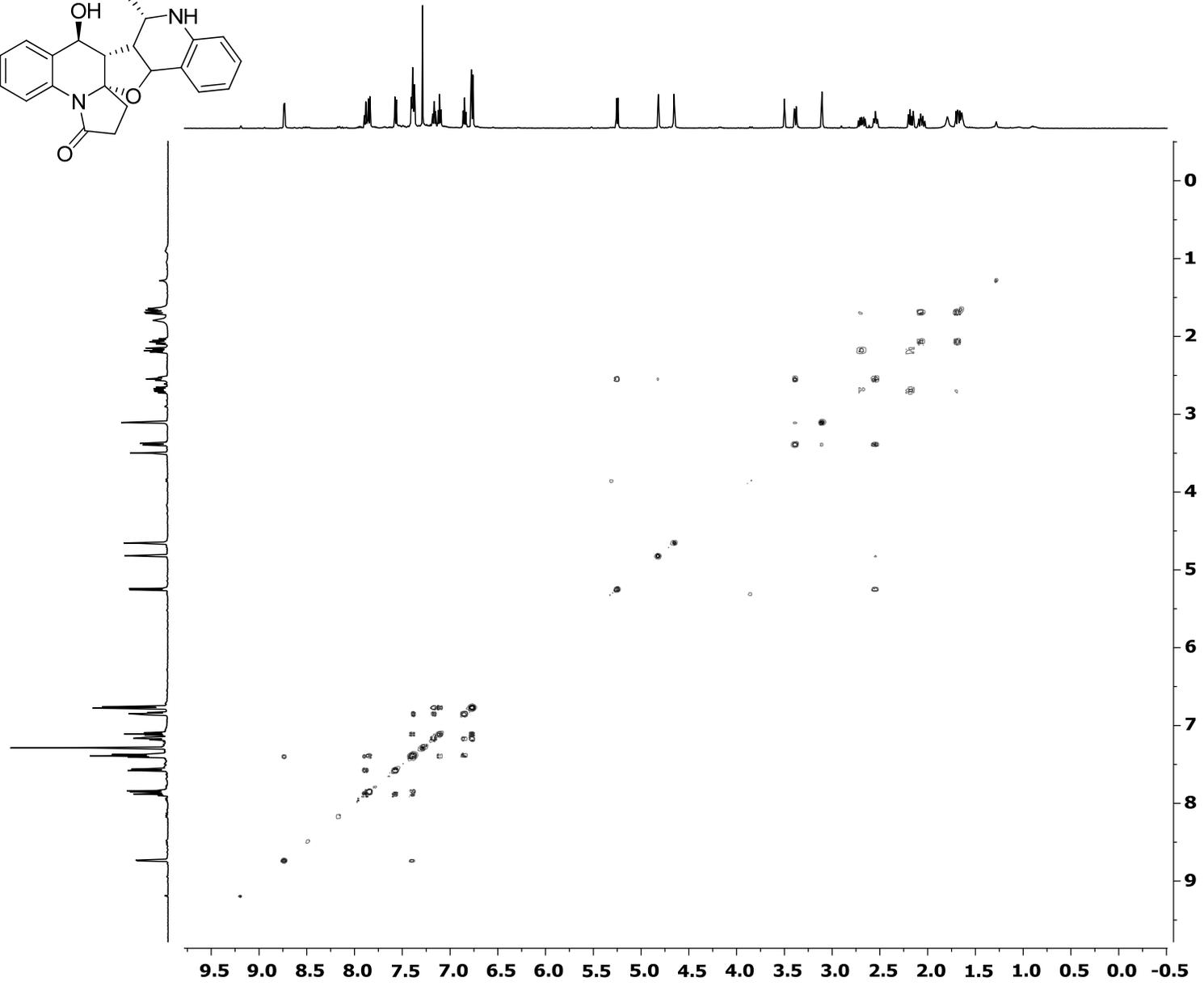
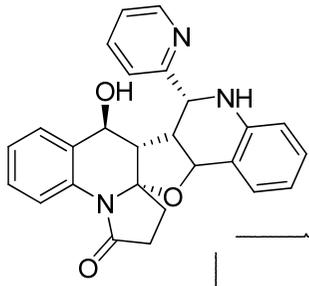


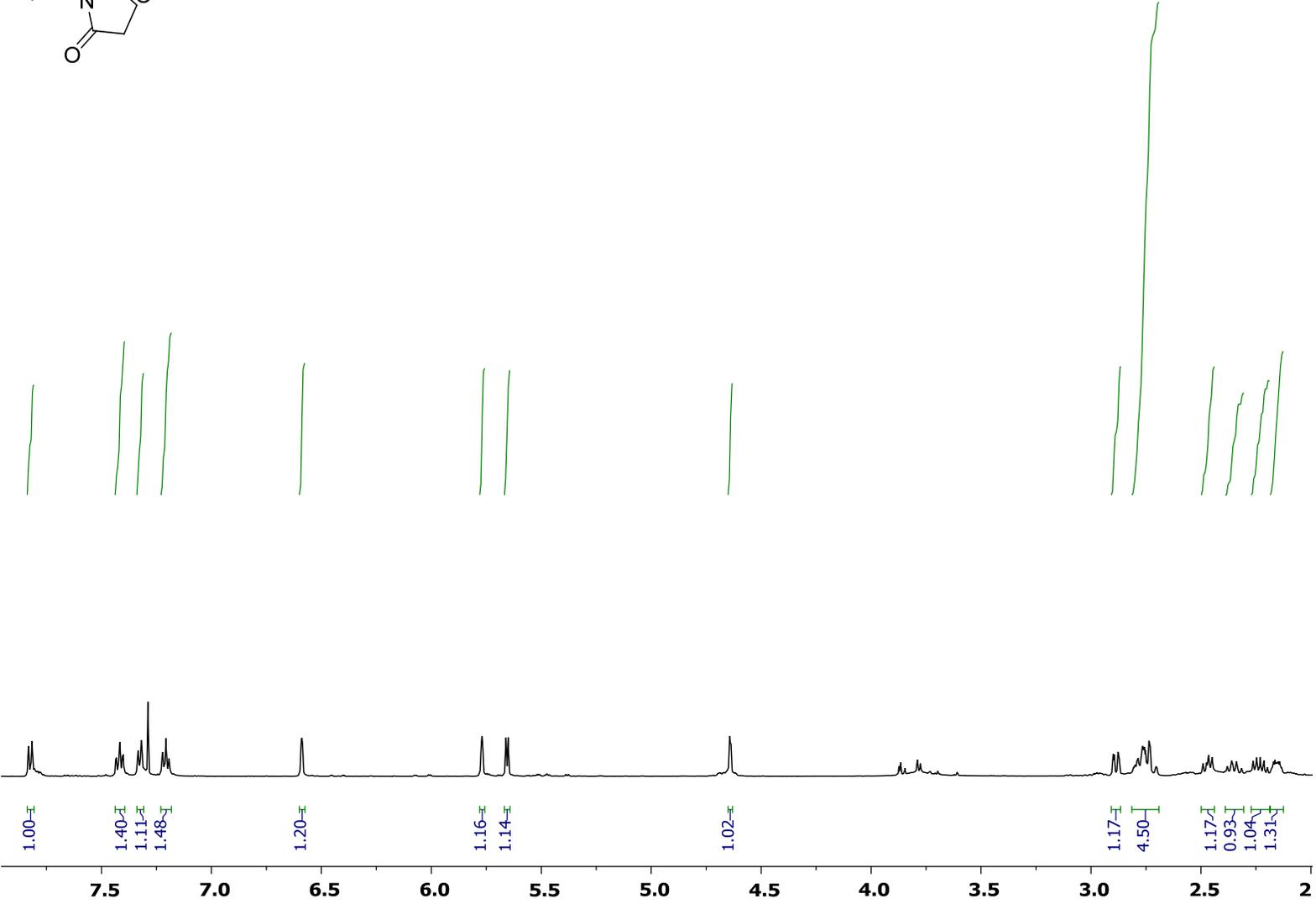
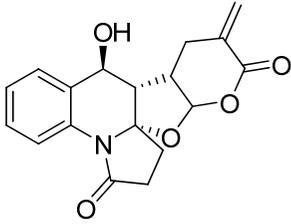


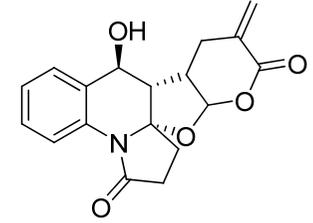
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173.72  
173.70

163.47

133.43  
130.89  
130.04  
130.01  
129.82  
129.29  
125.85  
123.77

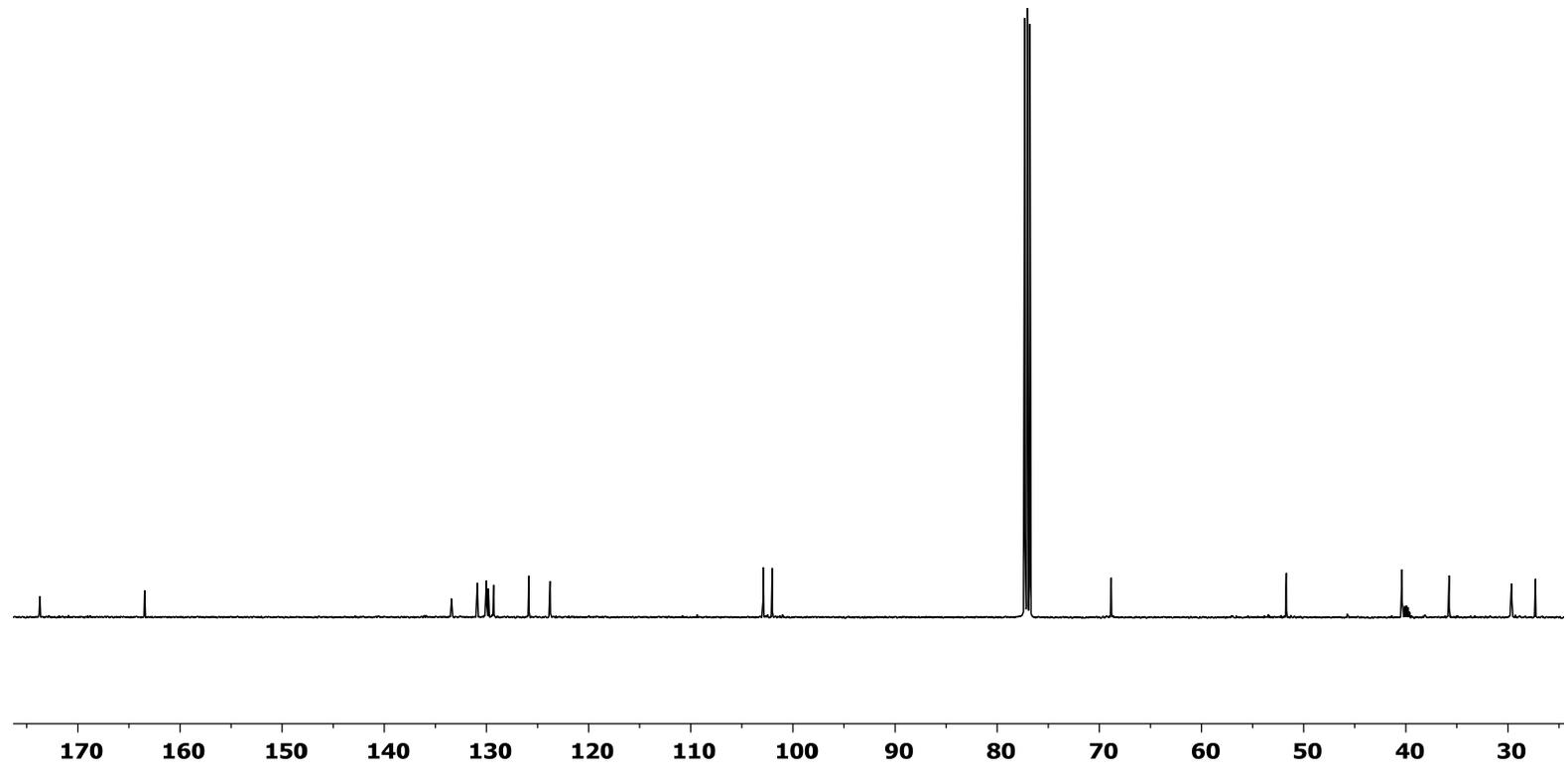
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102.02

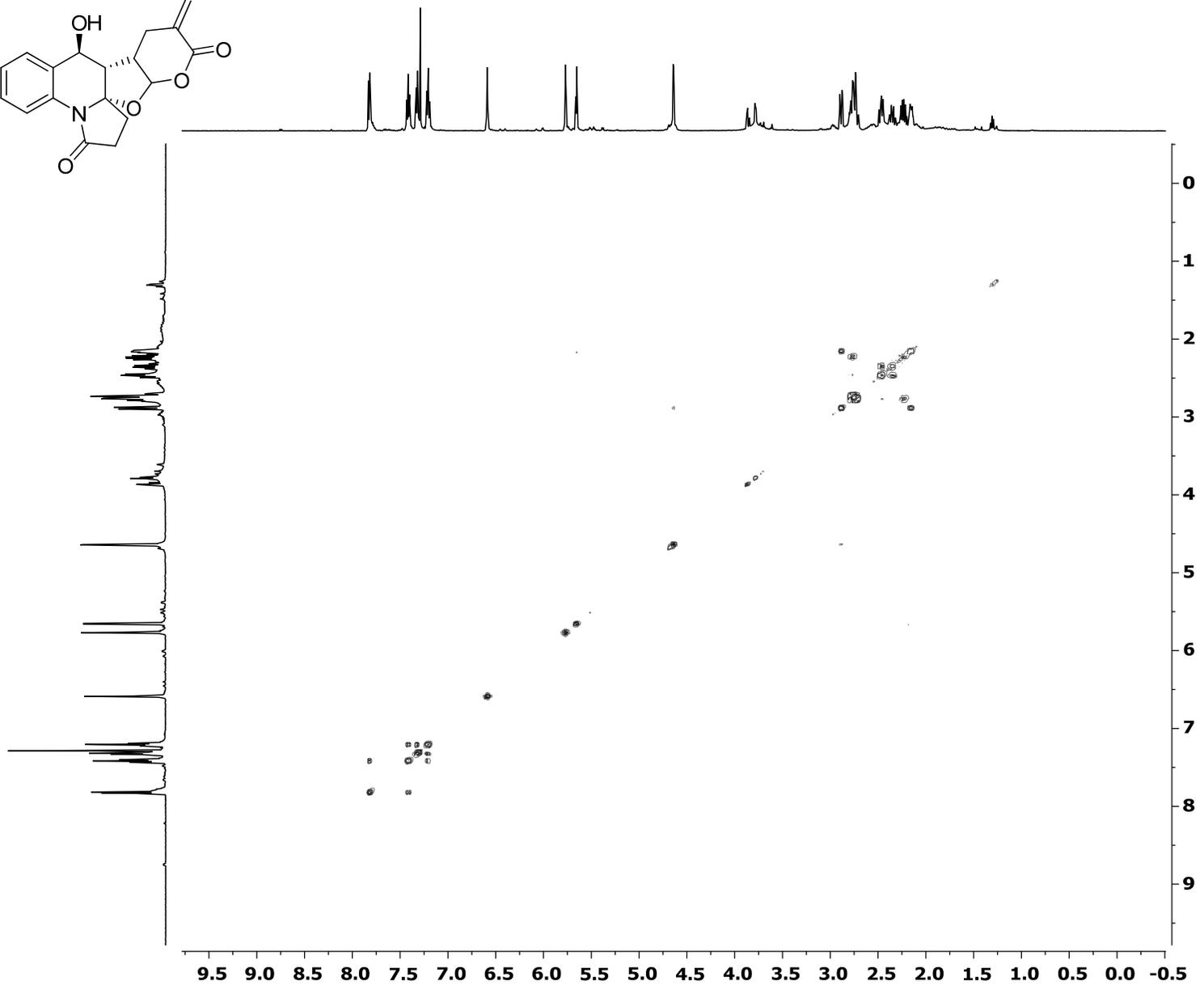
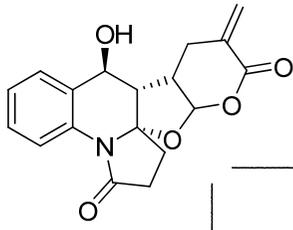
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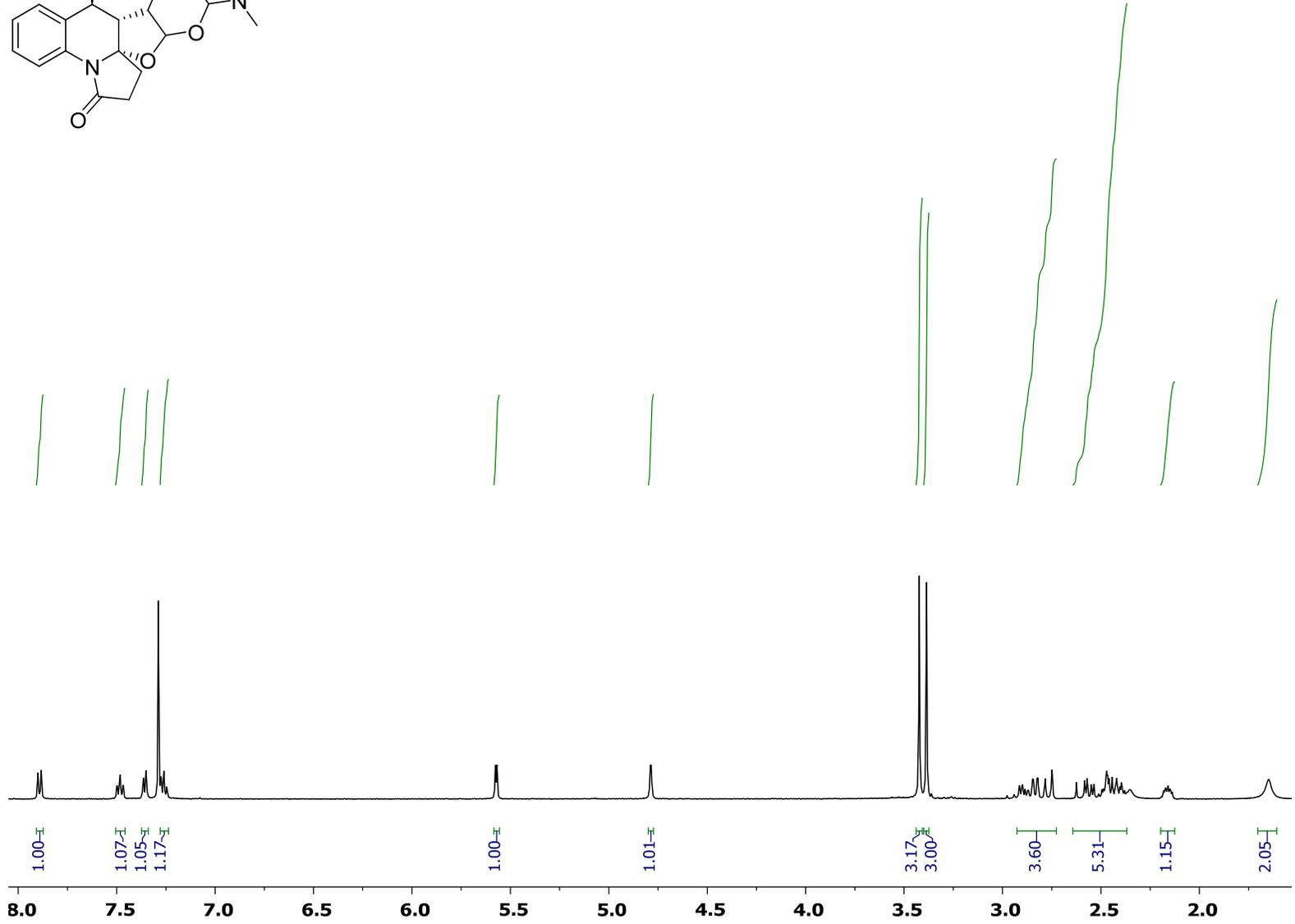
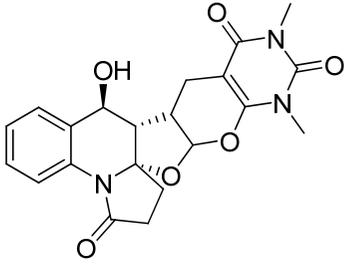
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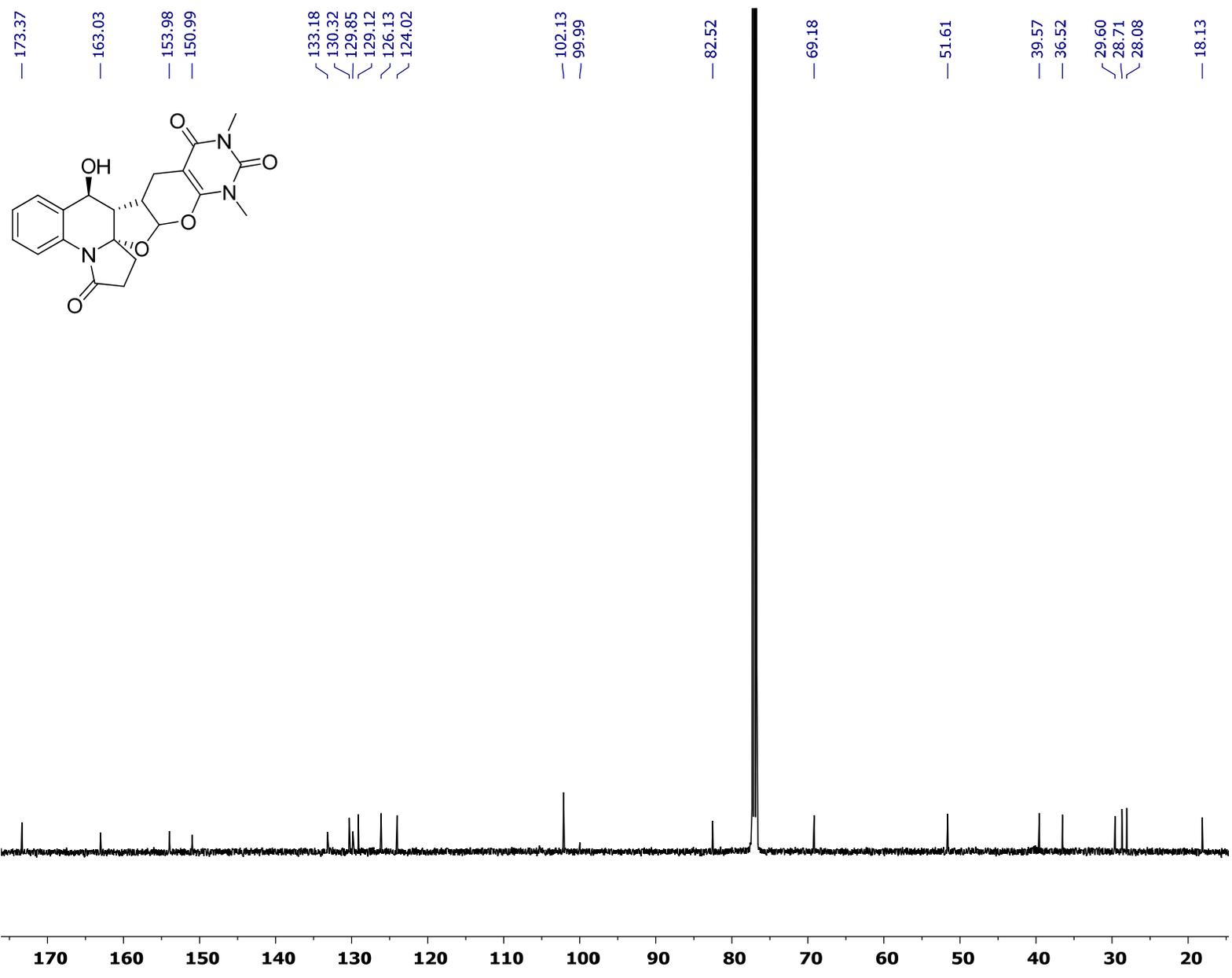
40.37  
35.76

29.65  
27.31









— 173.37

— 163.03

— 153.98

— 150.99

— 133.18

— 130.32

— 129.85

— 129.12

— 126.13

— 124.02

— 102.13

— 99.99

— 82.52

— 77.00

— 69.18

— 51.61

— 39.57

— 36.52

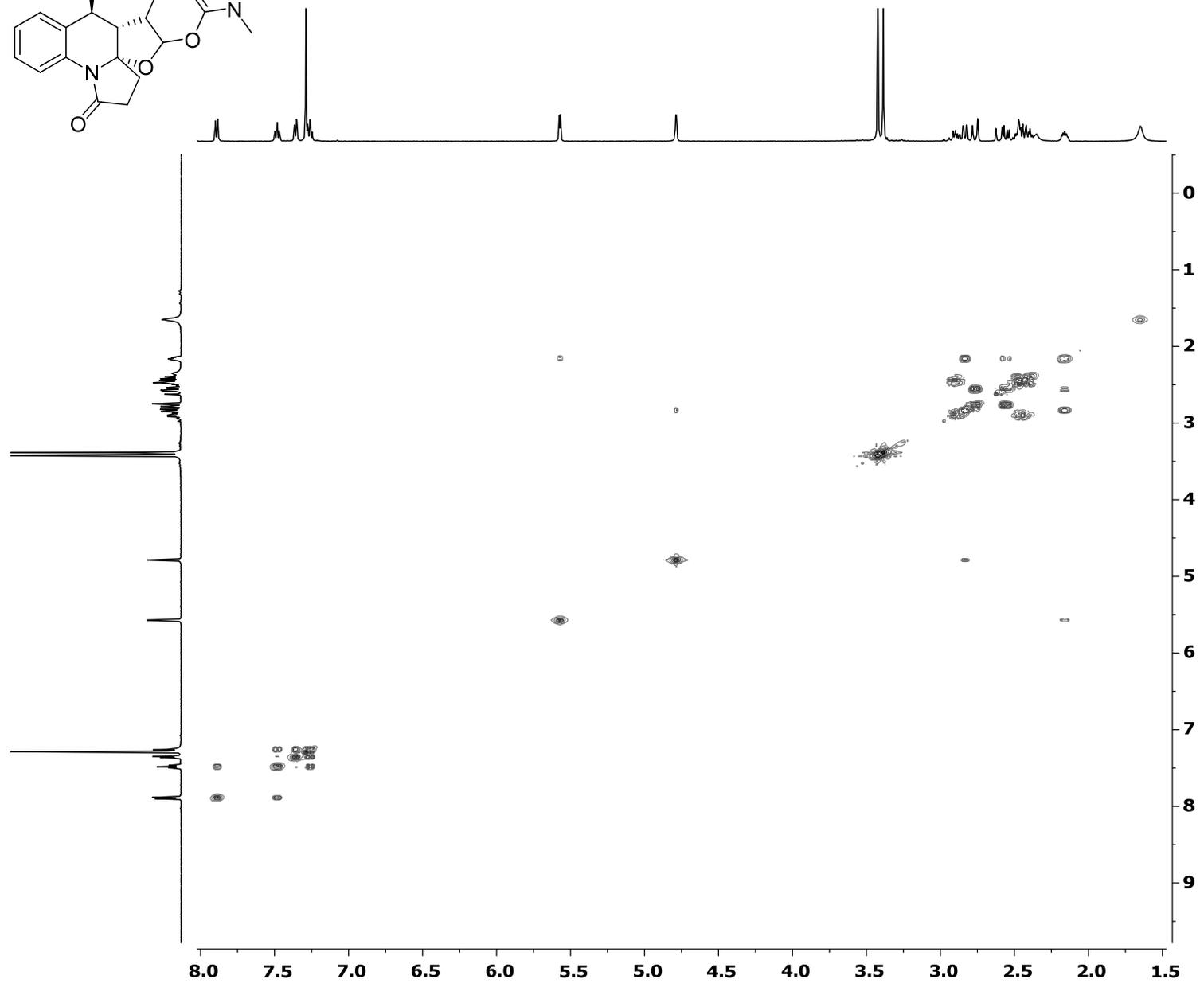
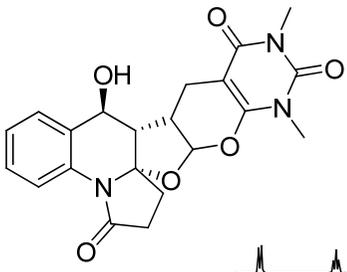
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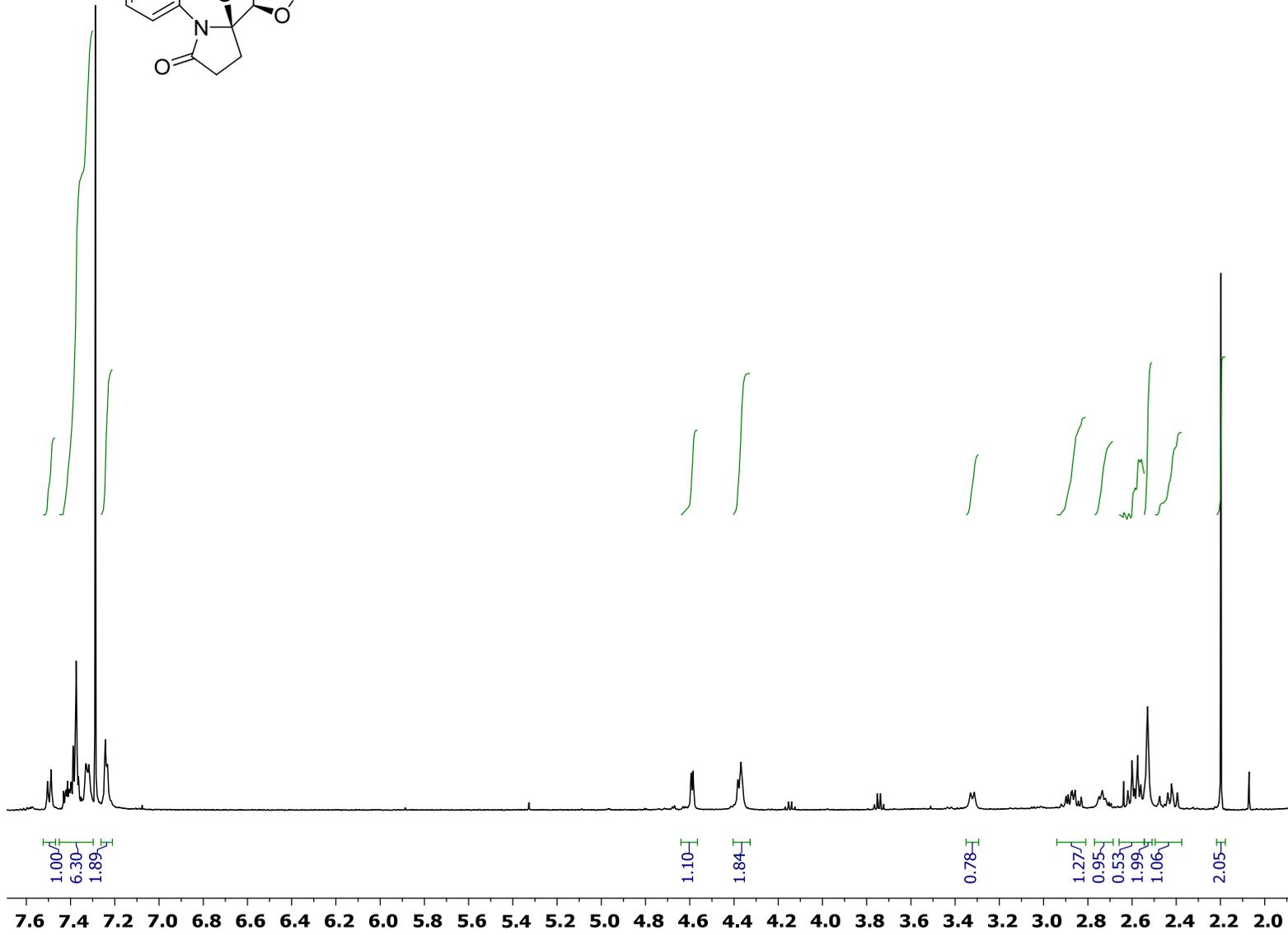
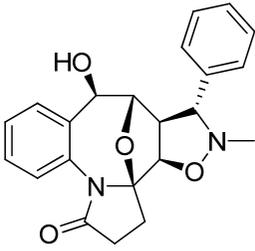
— 28.71

— 28.08

— 18.13

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20





— 173.95

134.01  
133.57  
132.45  
129.46  
129.07  
128.66  
128.22  
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127.11

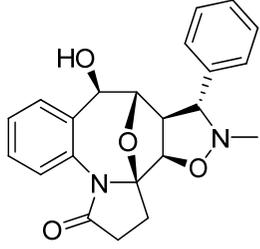
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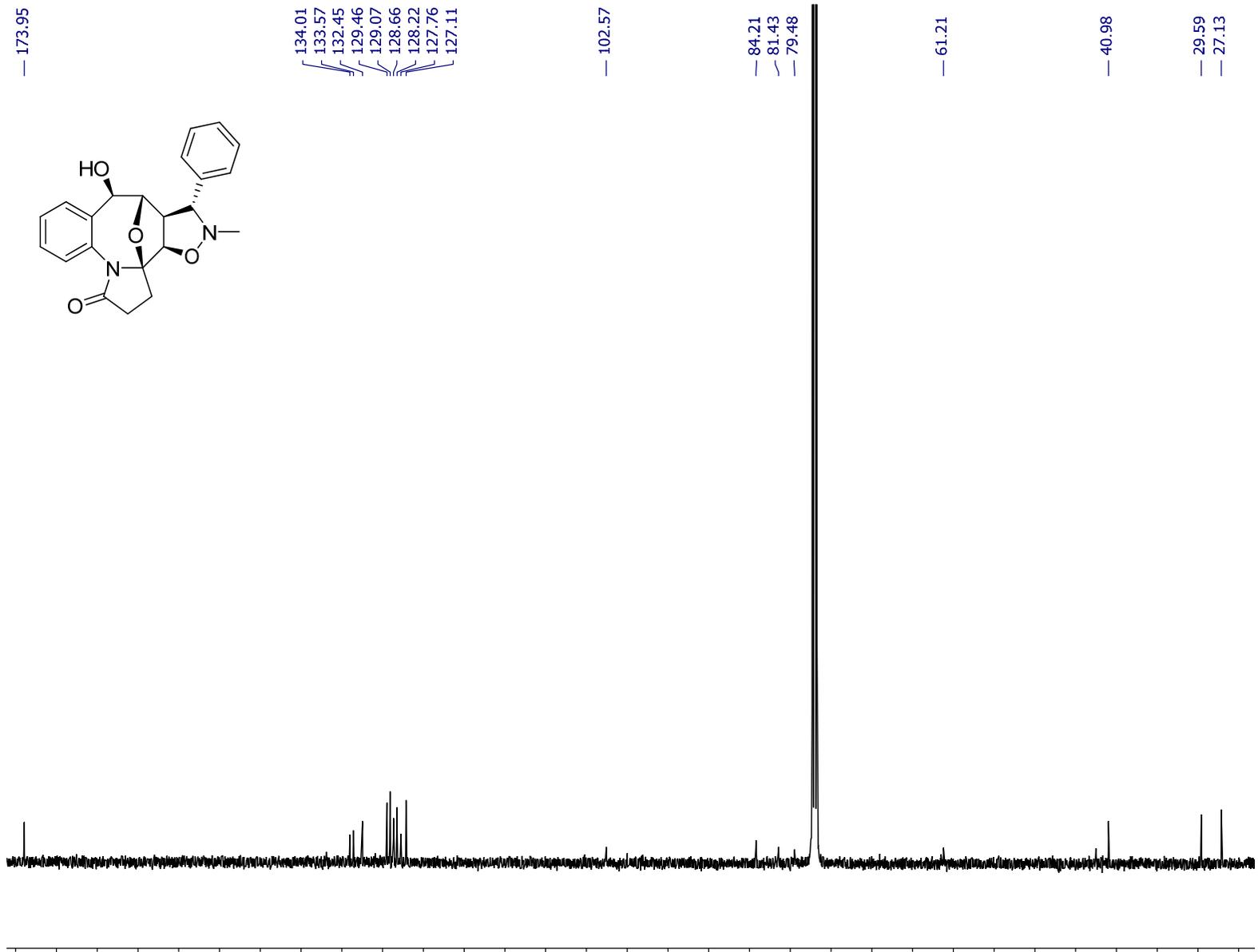
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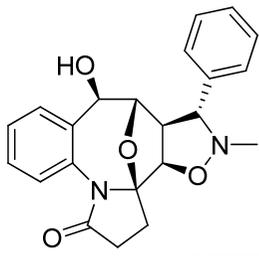
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— 27.13

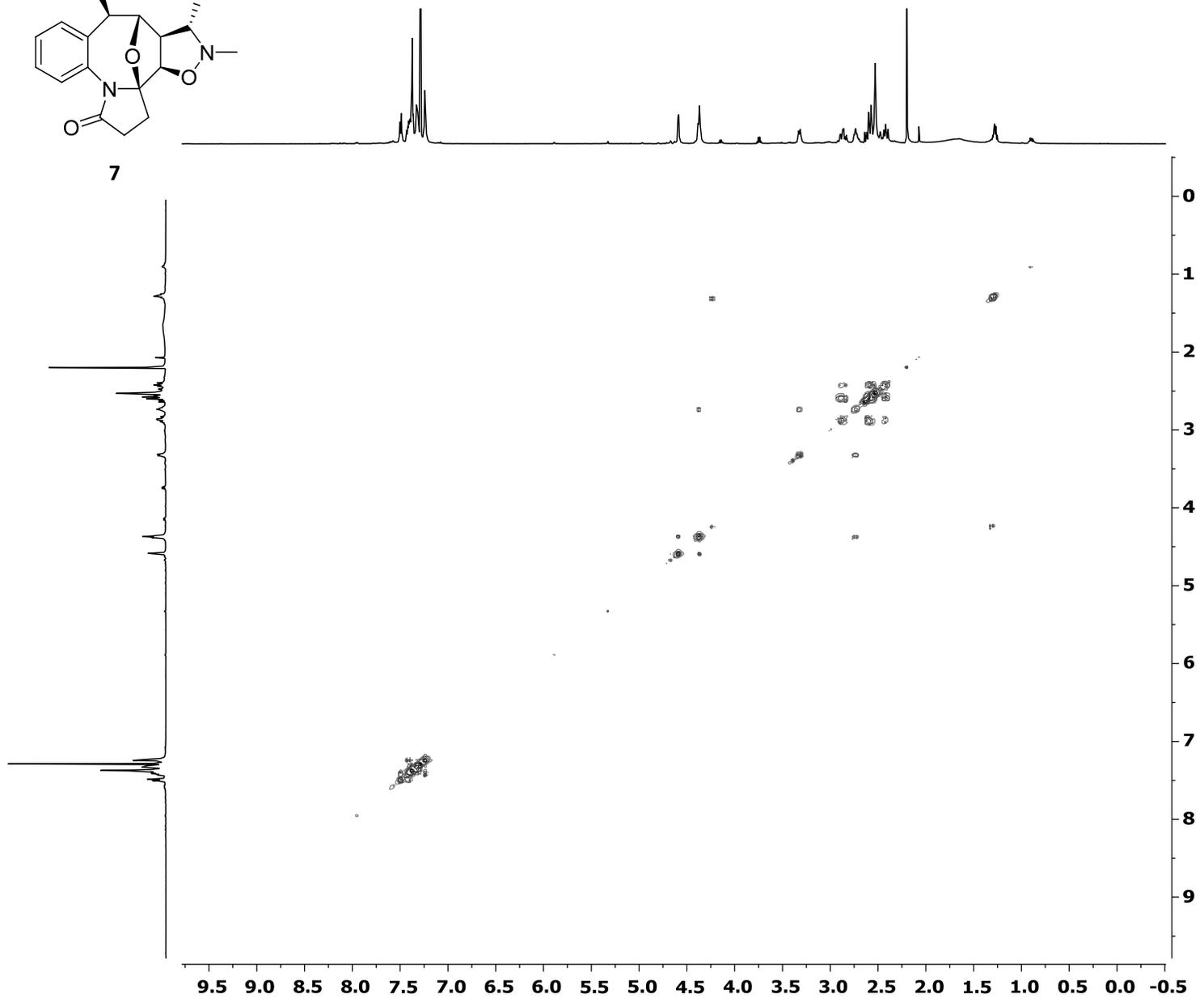


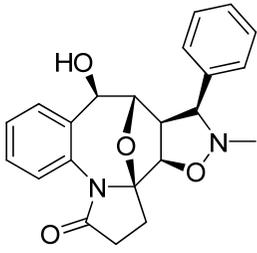
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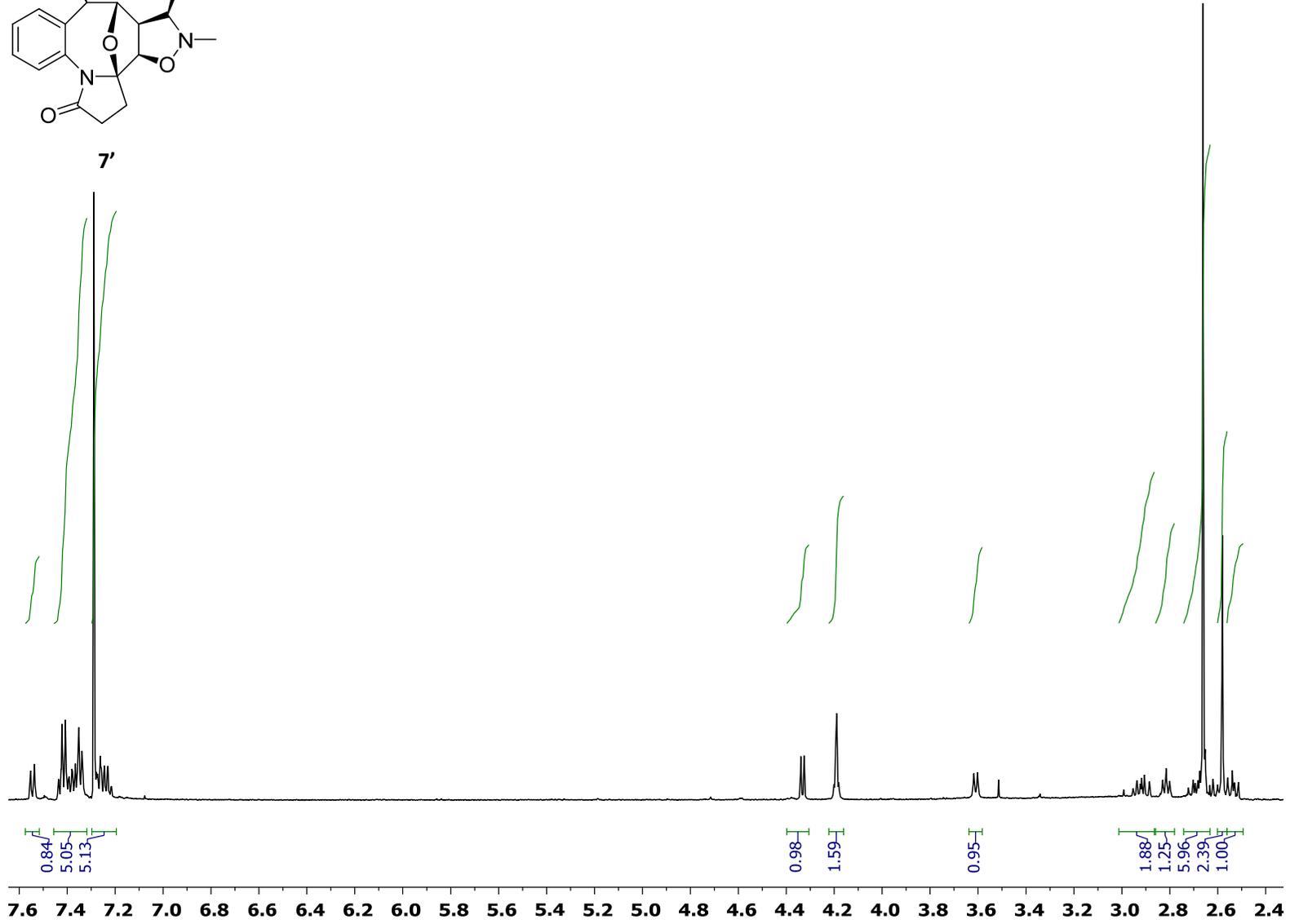


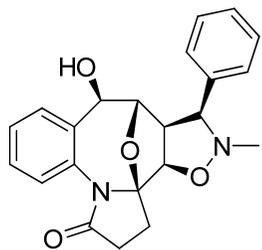
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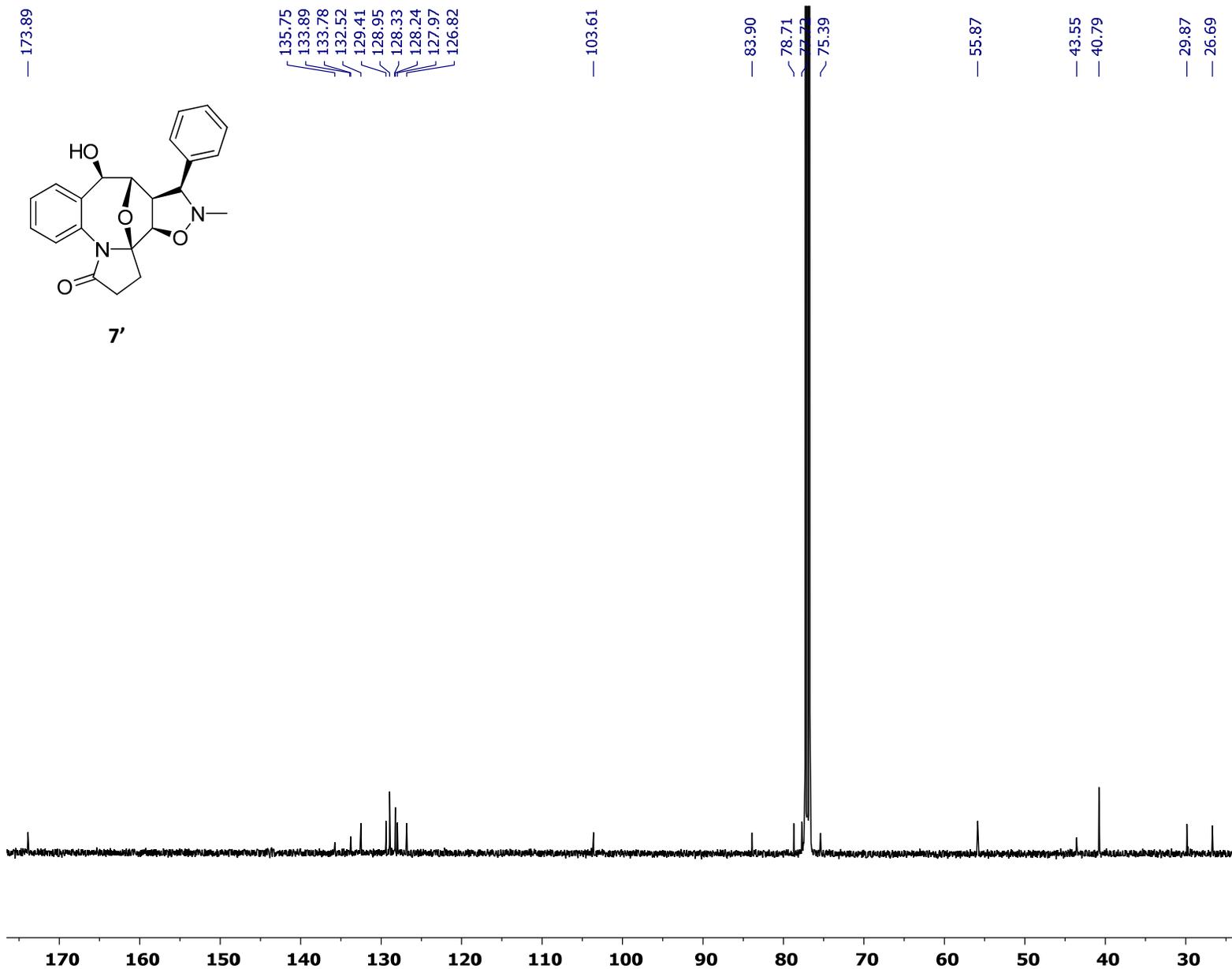


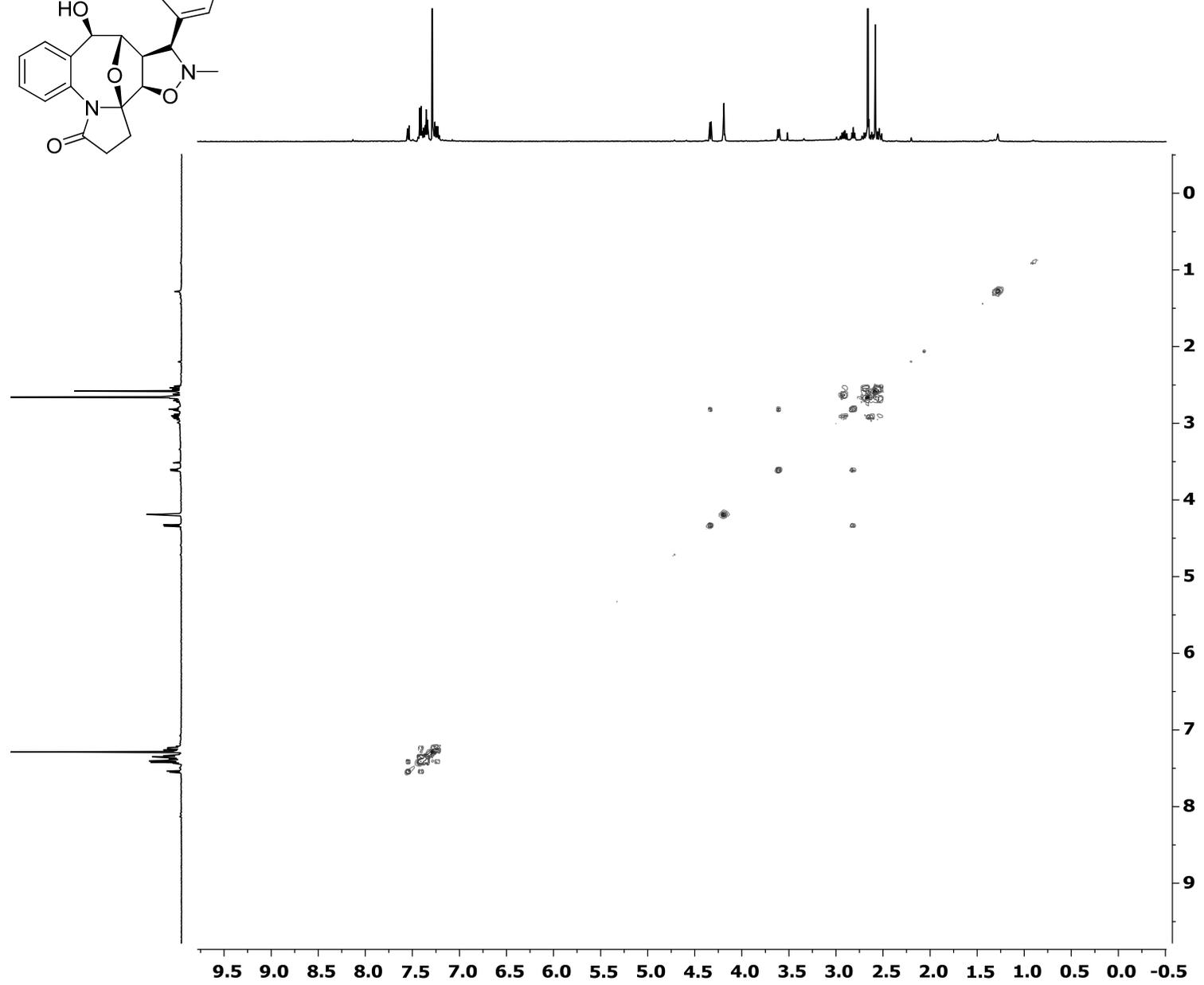
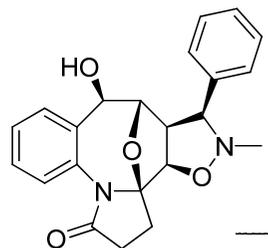
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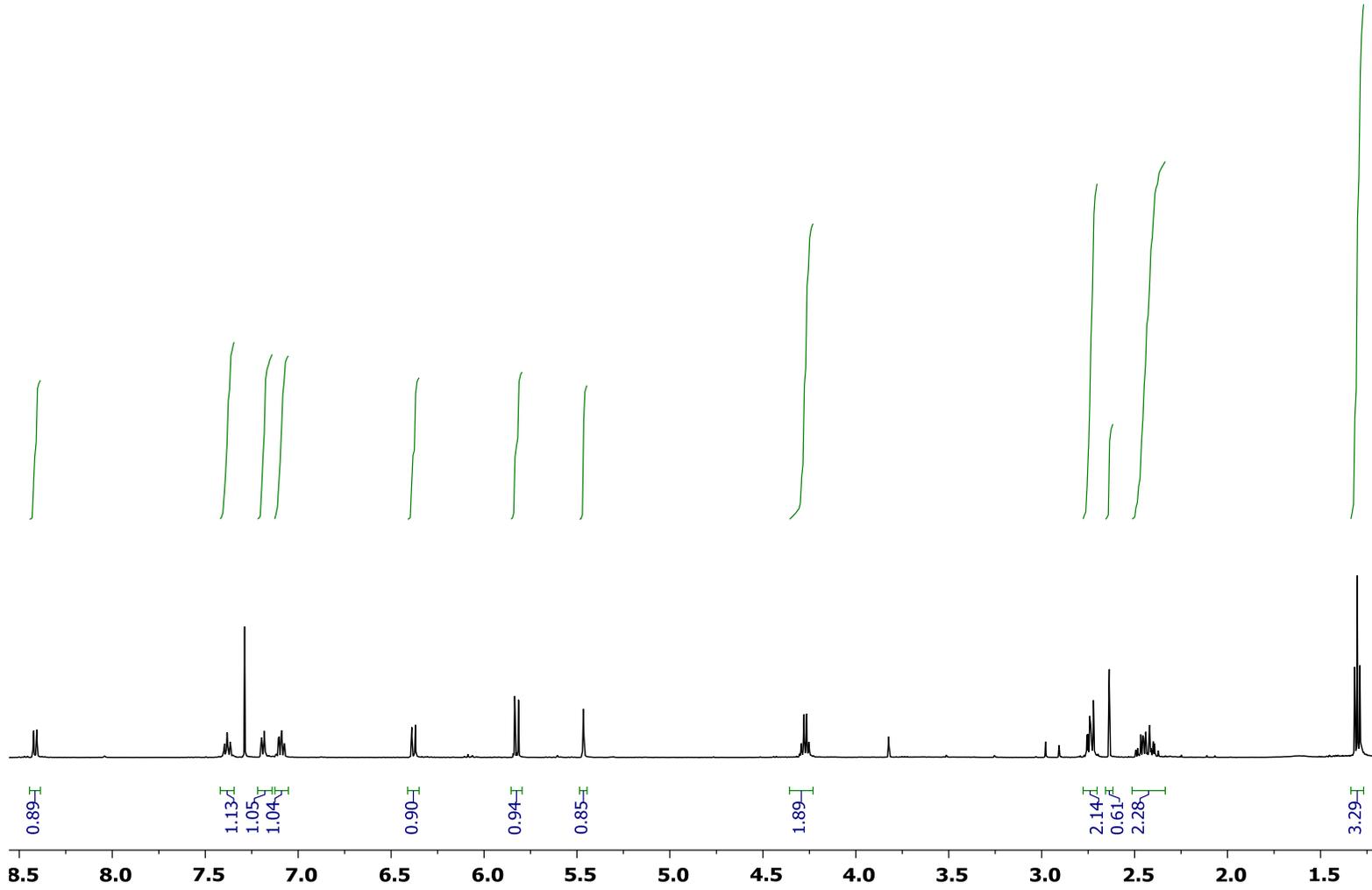
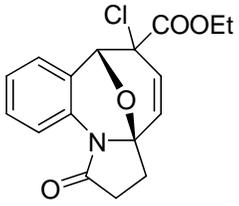




7'







— 170.83  
— 167.34

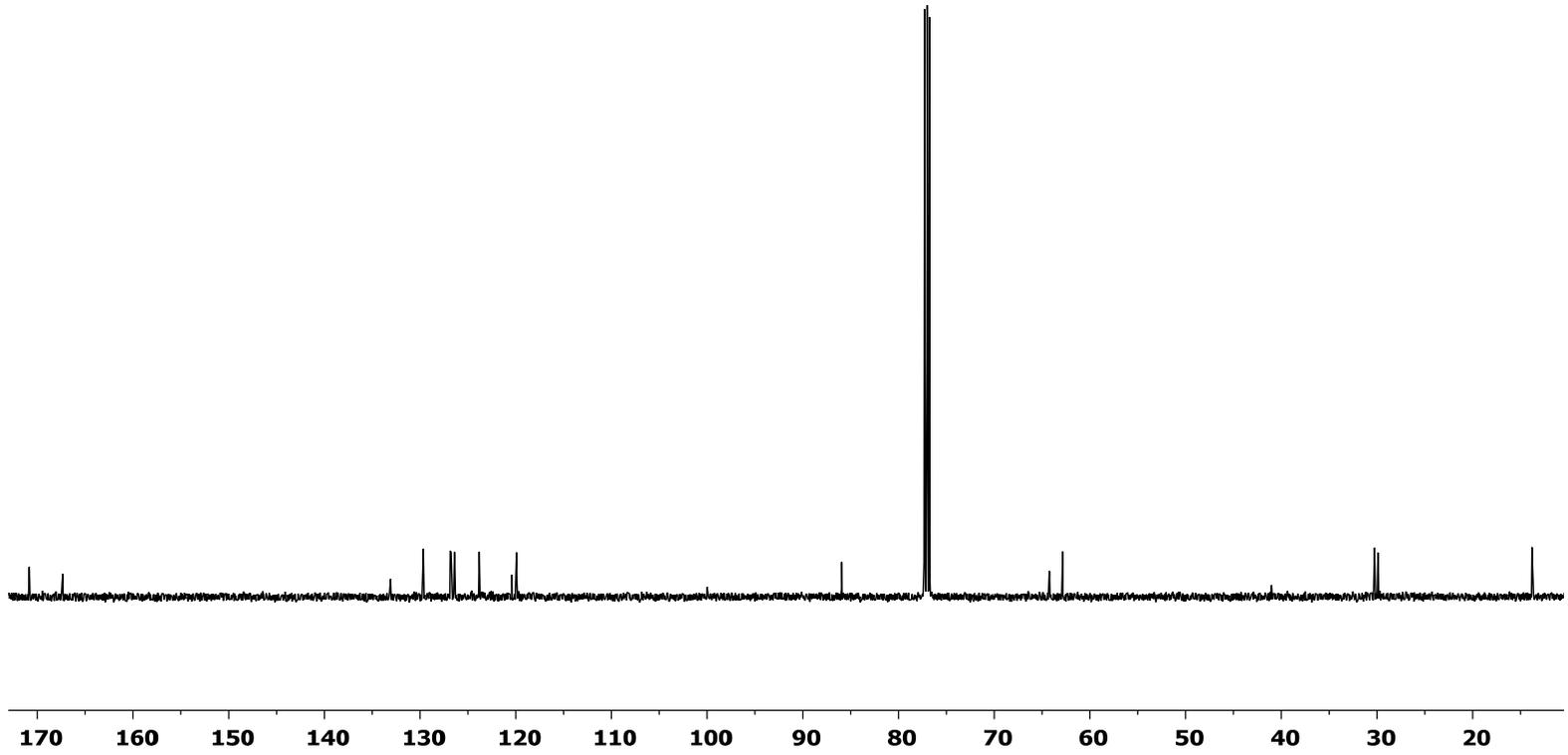
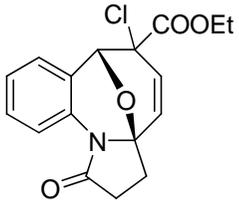
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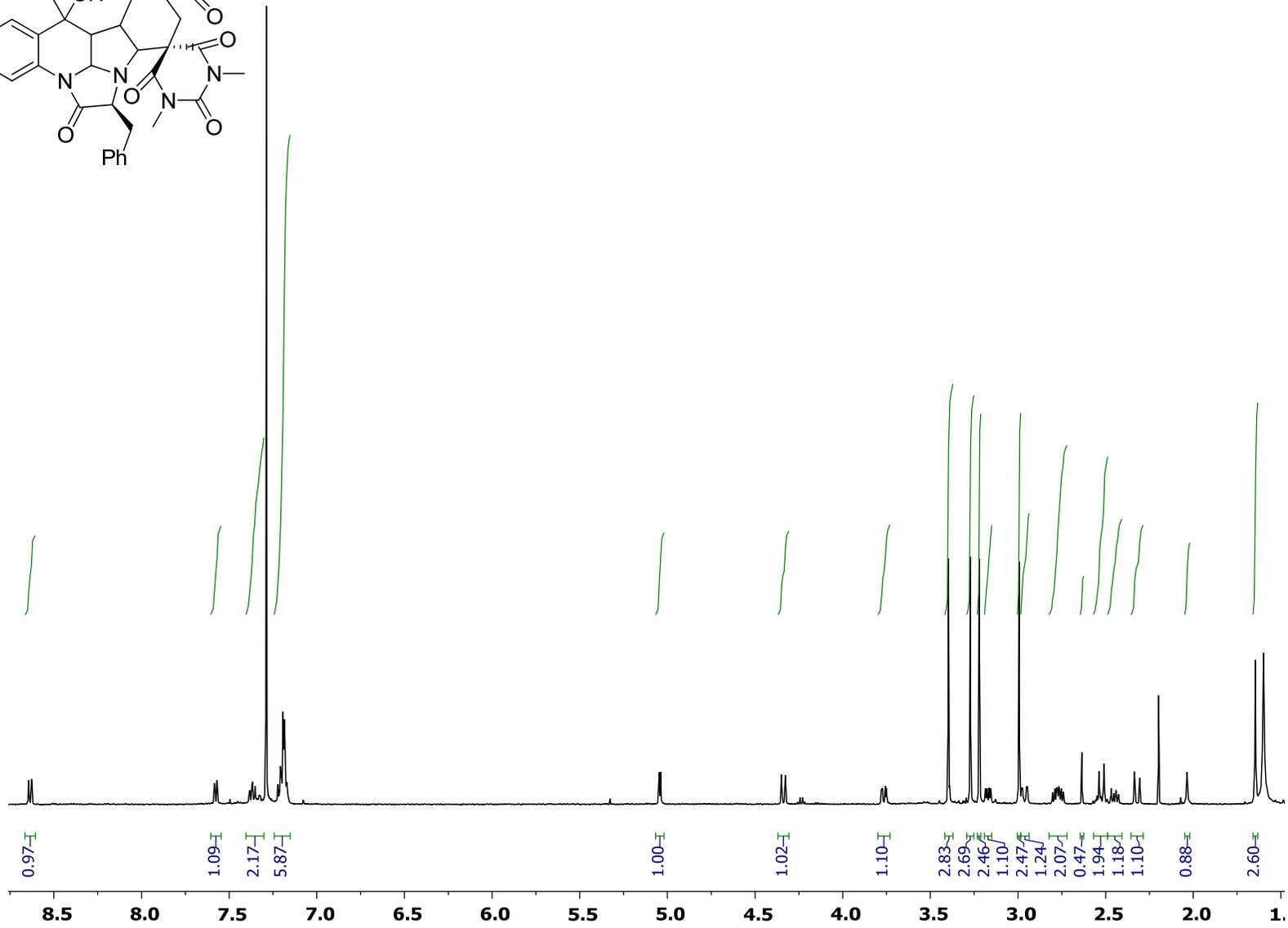
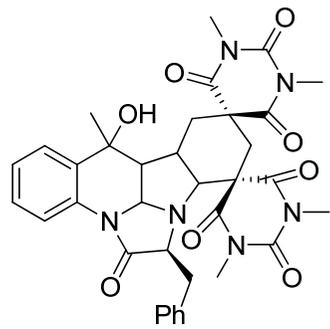
— 85.94

✓ 64.23  
✓ 62.85

✓ 30.26  
✓ 29.89

— 13.80





173.56  
172.11  
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170.73  
170.62

150.66  
150.25

138.20  
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130.42  
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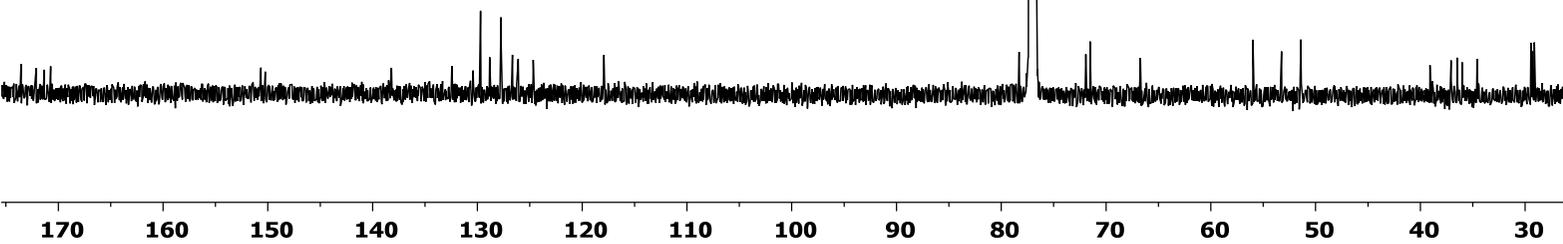
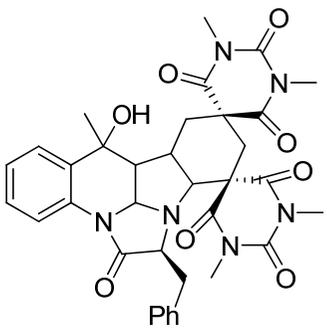
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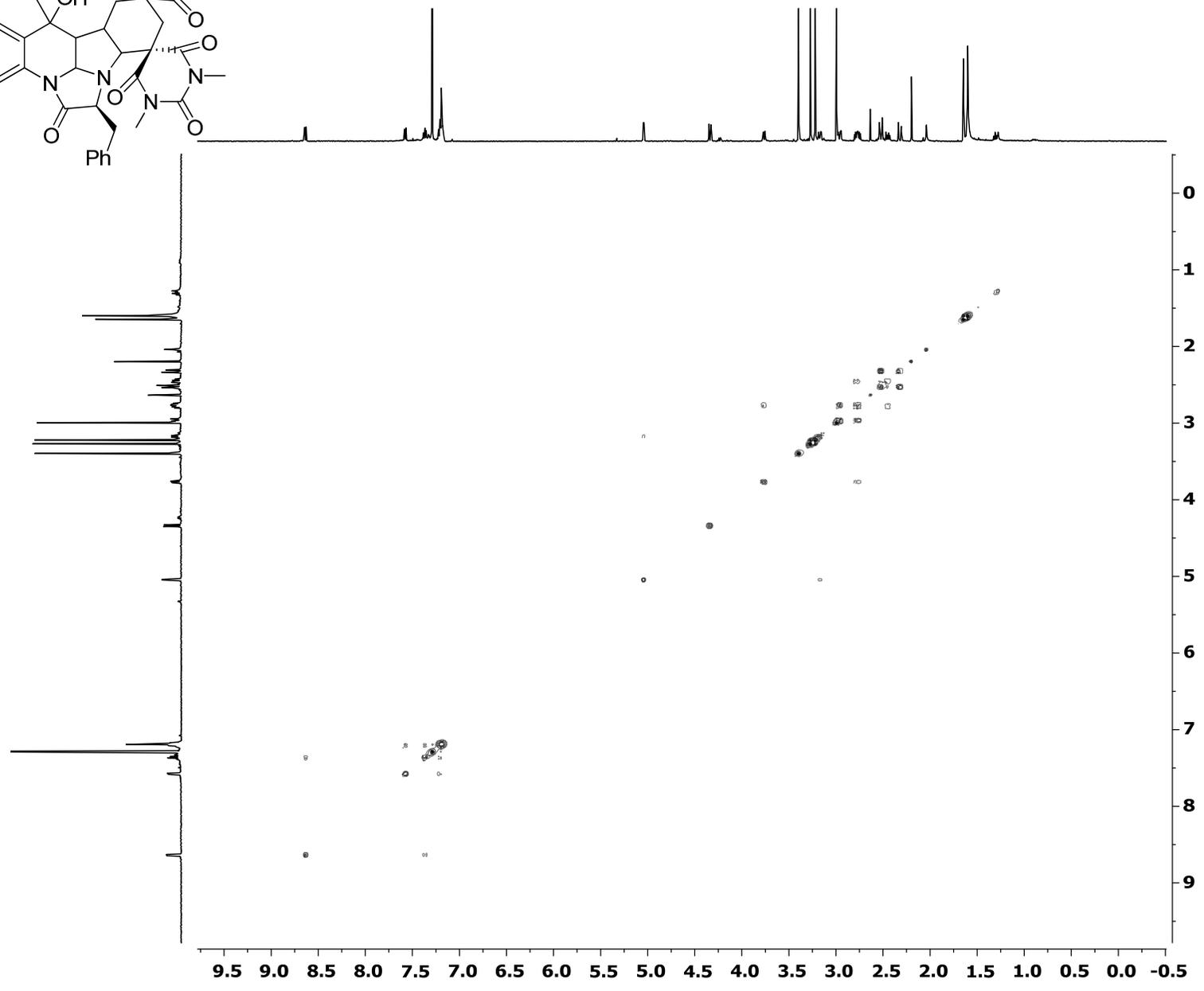
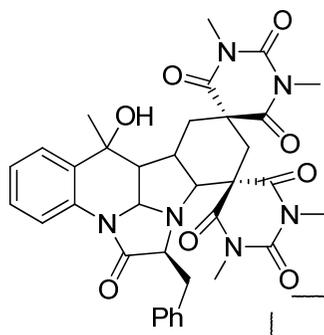
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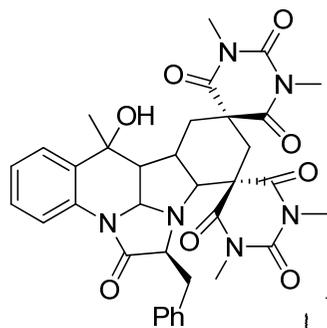
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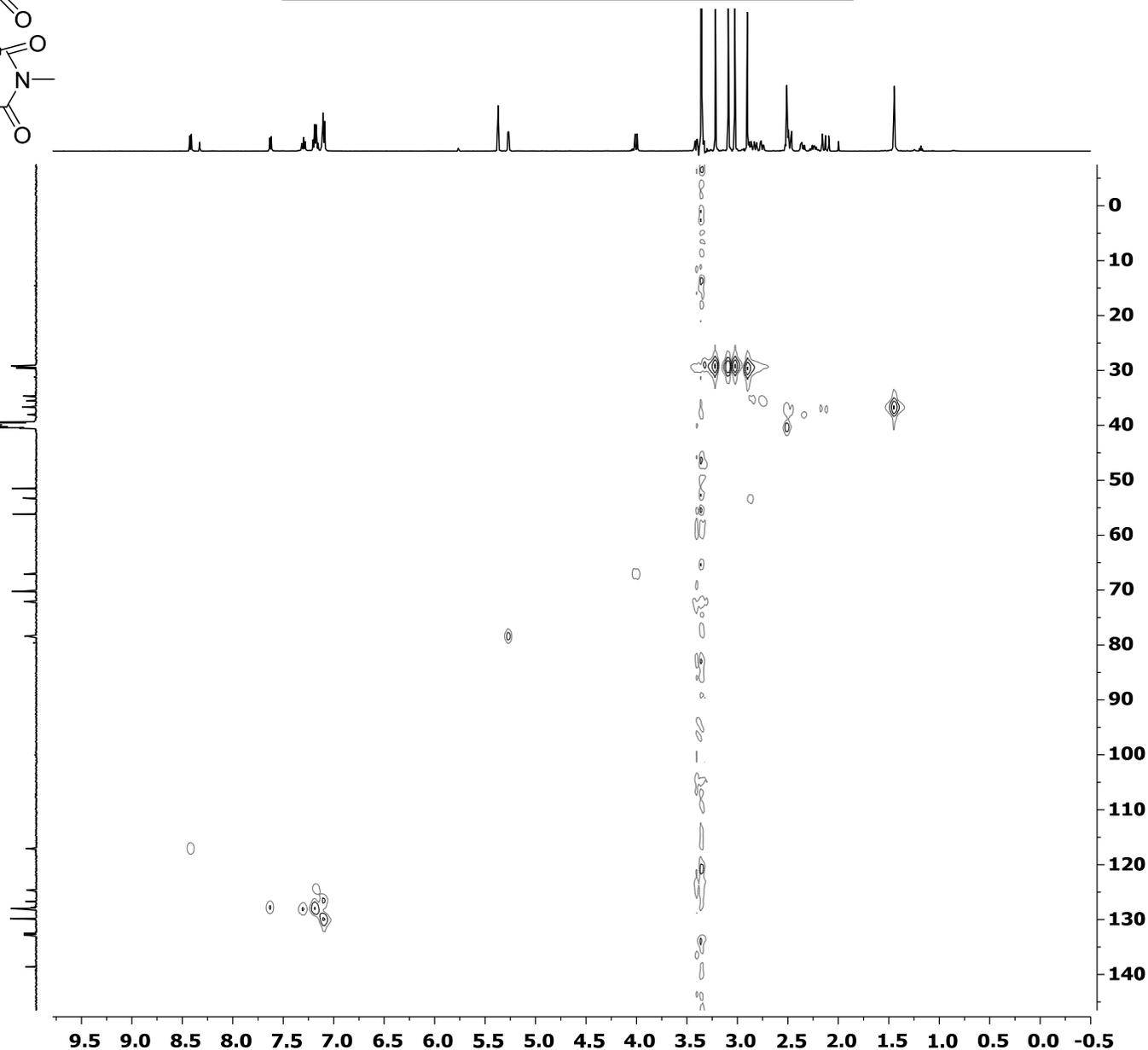


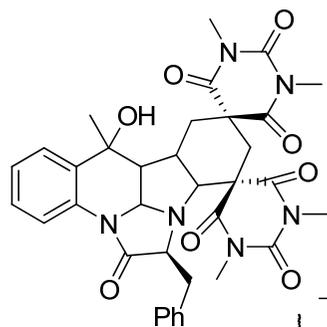




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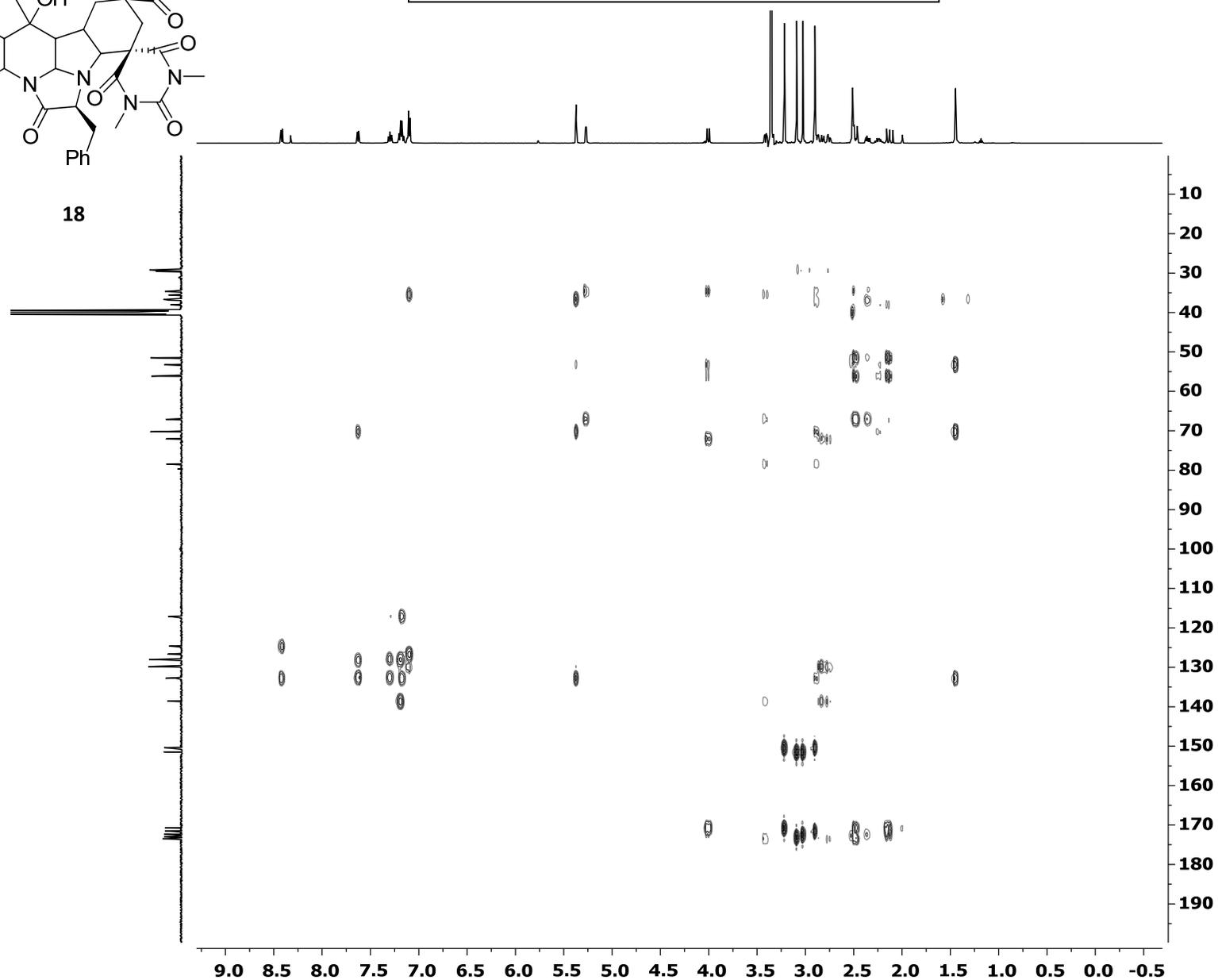
HMQC spectrum

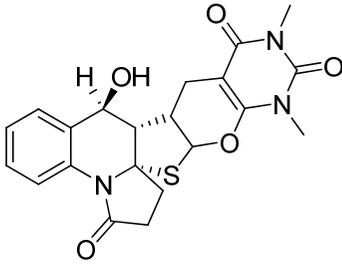




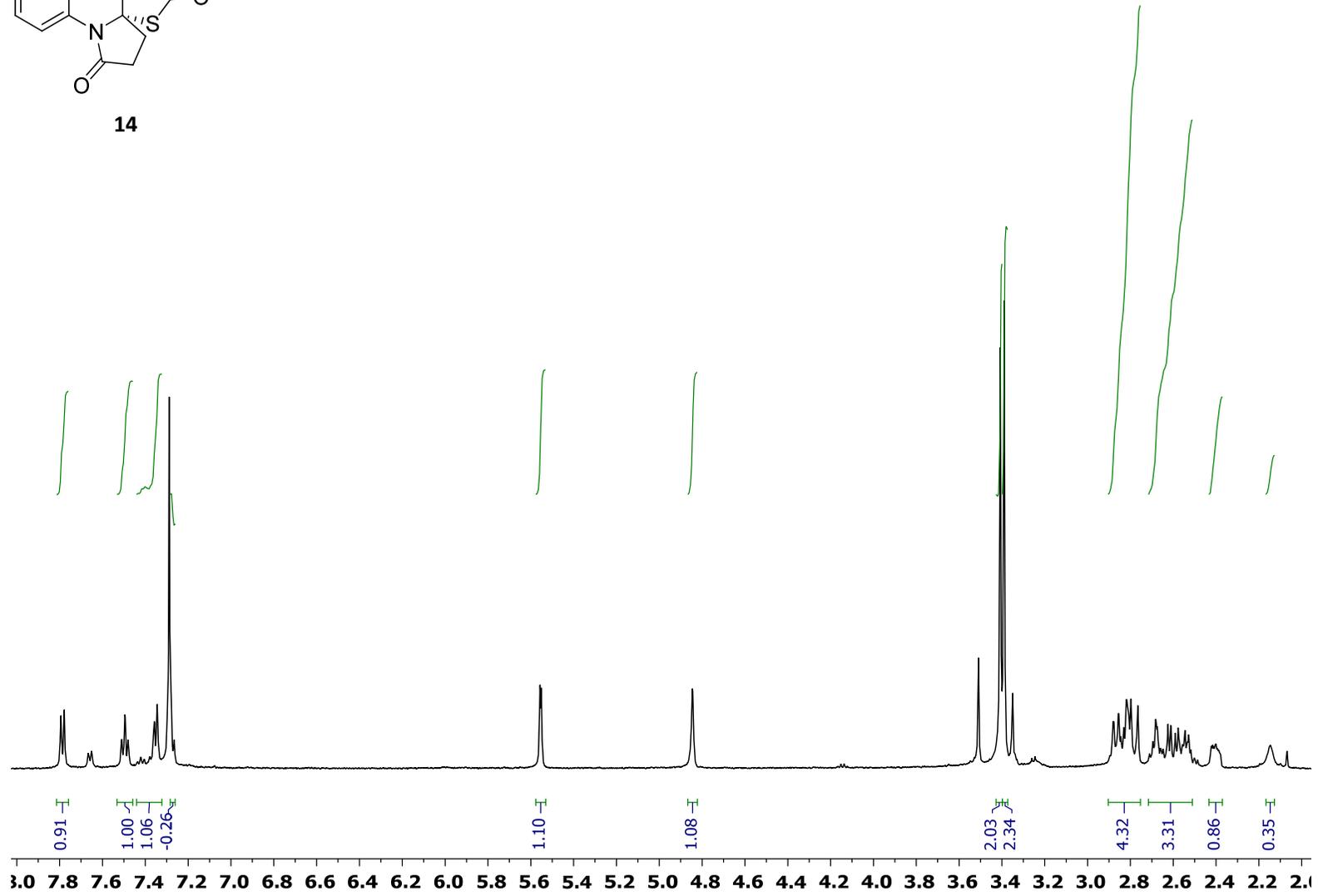
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HMBC spectrum





14



— 171.83  
— 163.07  
— 154.46  
— 150.85

∩ 133.48  
∩ 130.94  
∩ 130.36  
∩ 128.89  
∩ 126.42  
∩ 124.45

∩ 88.81  
∩ 84.99  
∩ 82.90

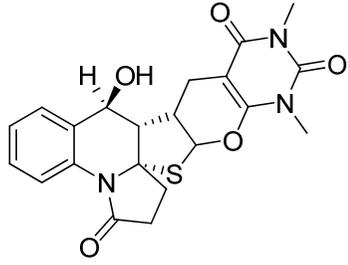
— 70.42

— 56.25

— 45.39  
— 42.41

∩ 30.72  
∩ 28.73  
∩ 28.12

— 20.30



14

