Electronic Supplementary Information

When crown ethers finally click: novel, click-assembled, fluorescent enantiopure pyridino-crown ether-based chemosensors – and an *N*-2-aryl-1,2,3-triazole containing one

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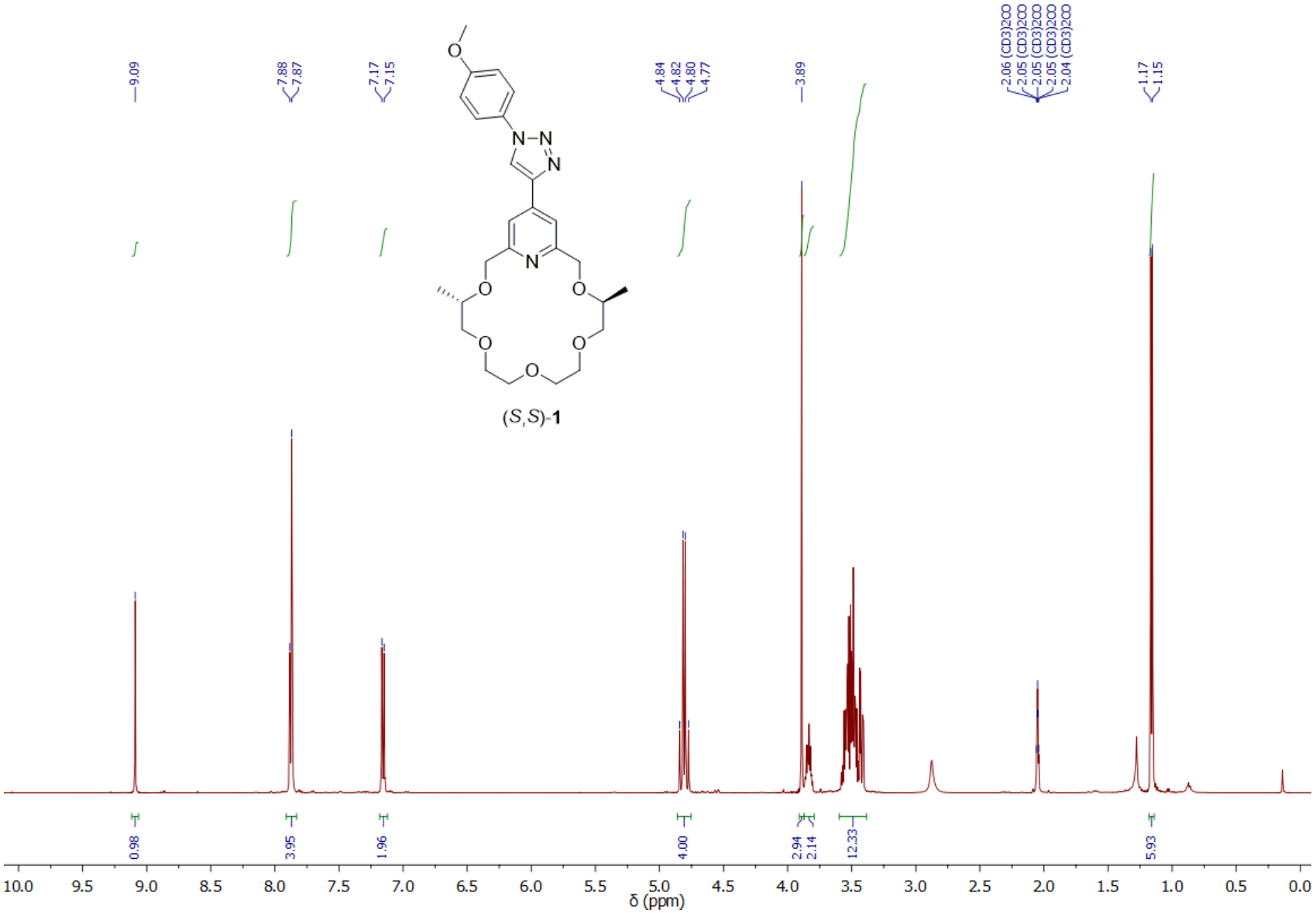

Figure S1. ^{1}H NMR spectrum of (*S*,*S*)-**1** (acetone-d_6, 500 MHz)

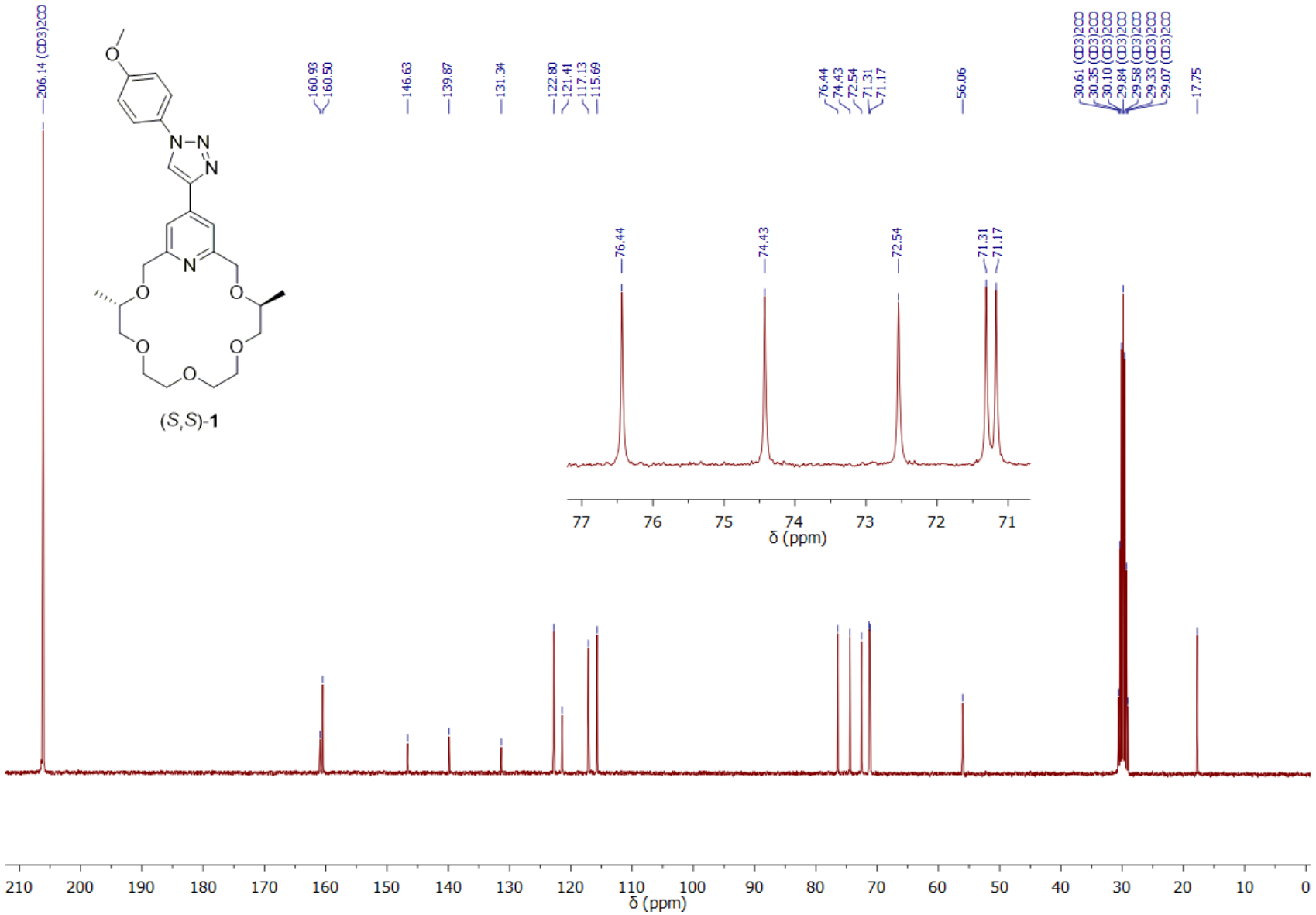

Figure S2. ^{13}C NMR spectrum of (*S*,*S*)-**1** (acetone-d_6, 75.5 MHz)

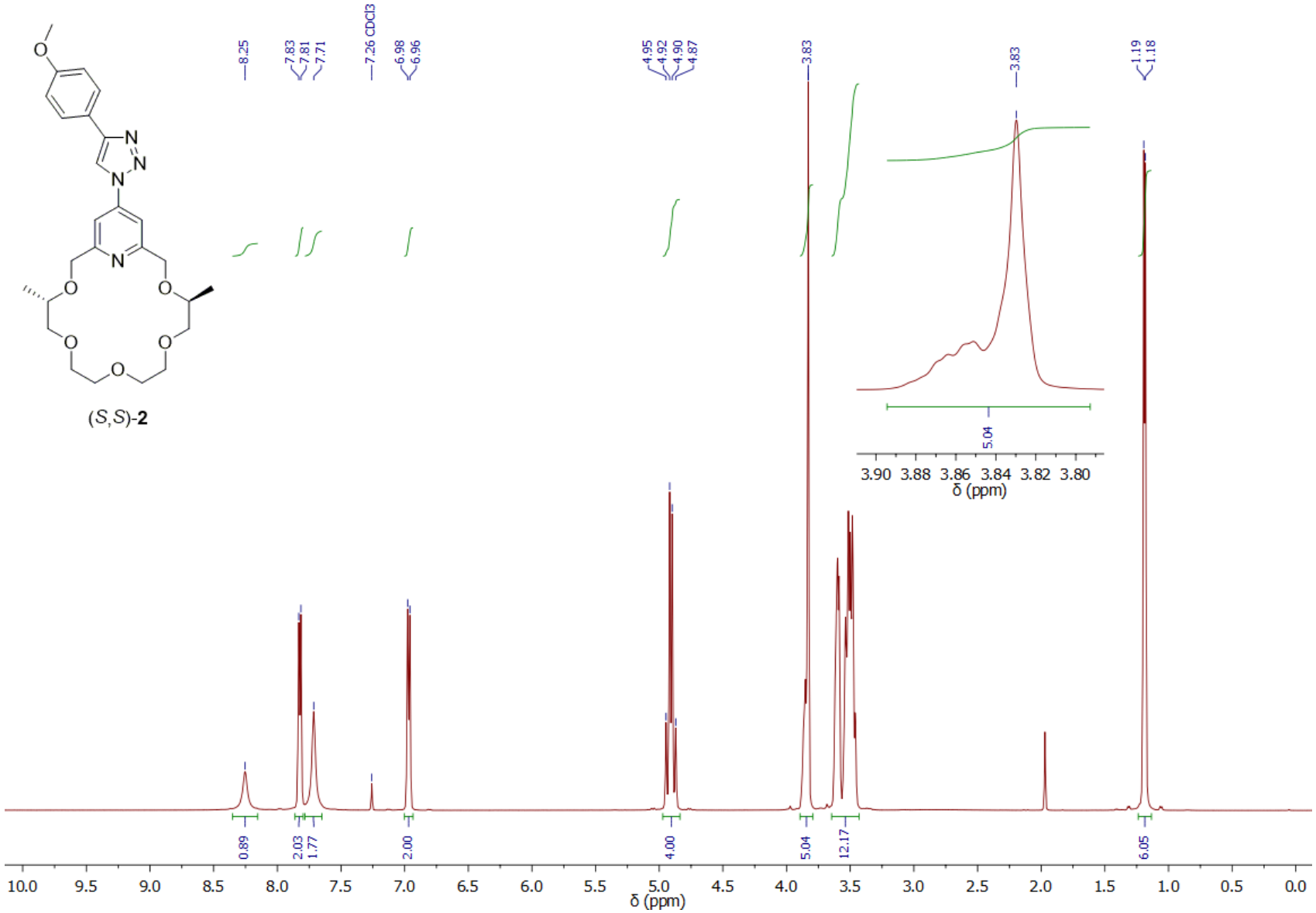

Figure S3. ^{1}H NMR spectrum of (*S*,*S*)-**2** ($CDCl_3$, 500 MHz)

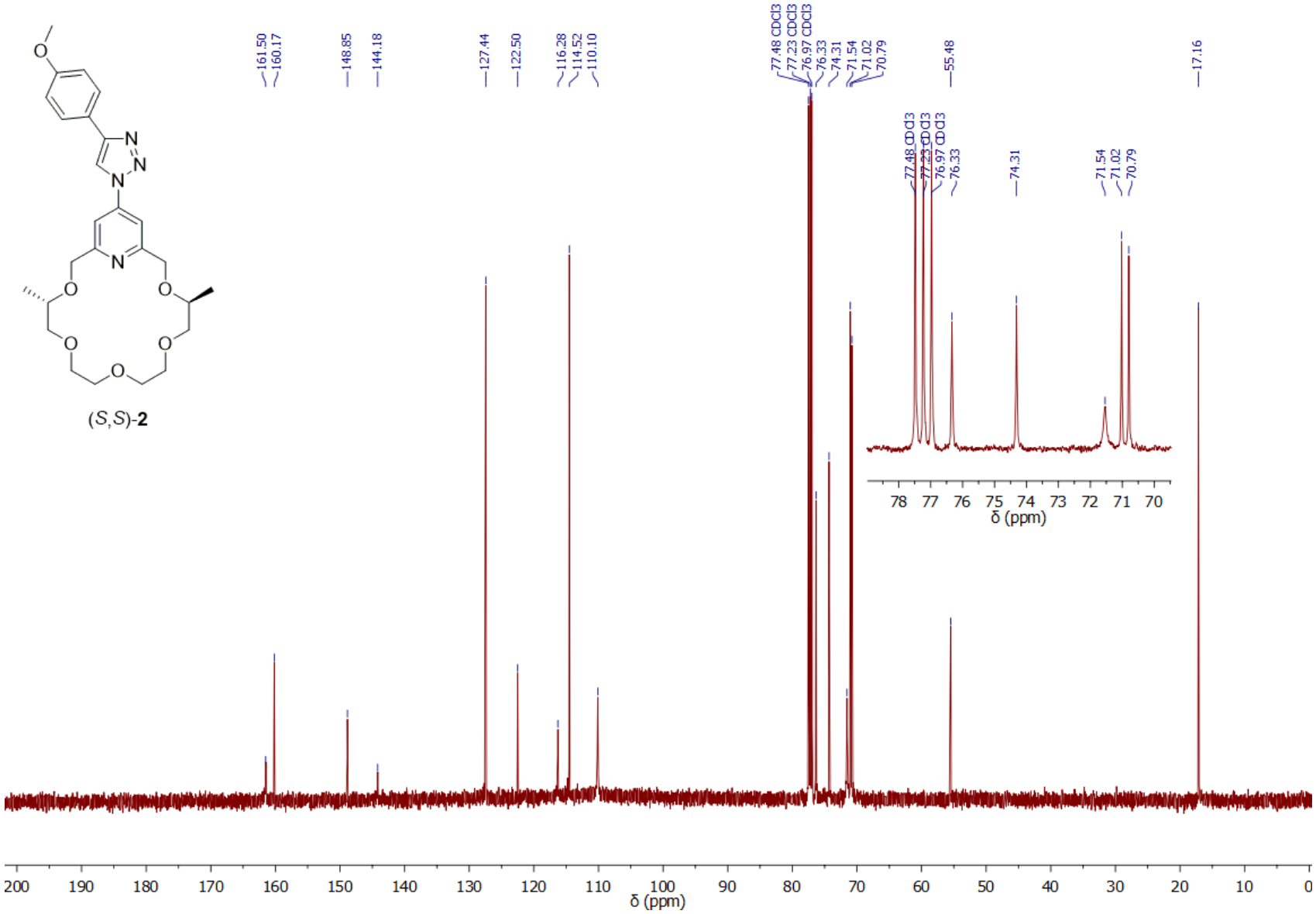

Figure S4. ^{13}C NMR spectrum of (*S*,*S*)-**2** ($CDCl_3$, 125 MHz)

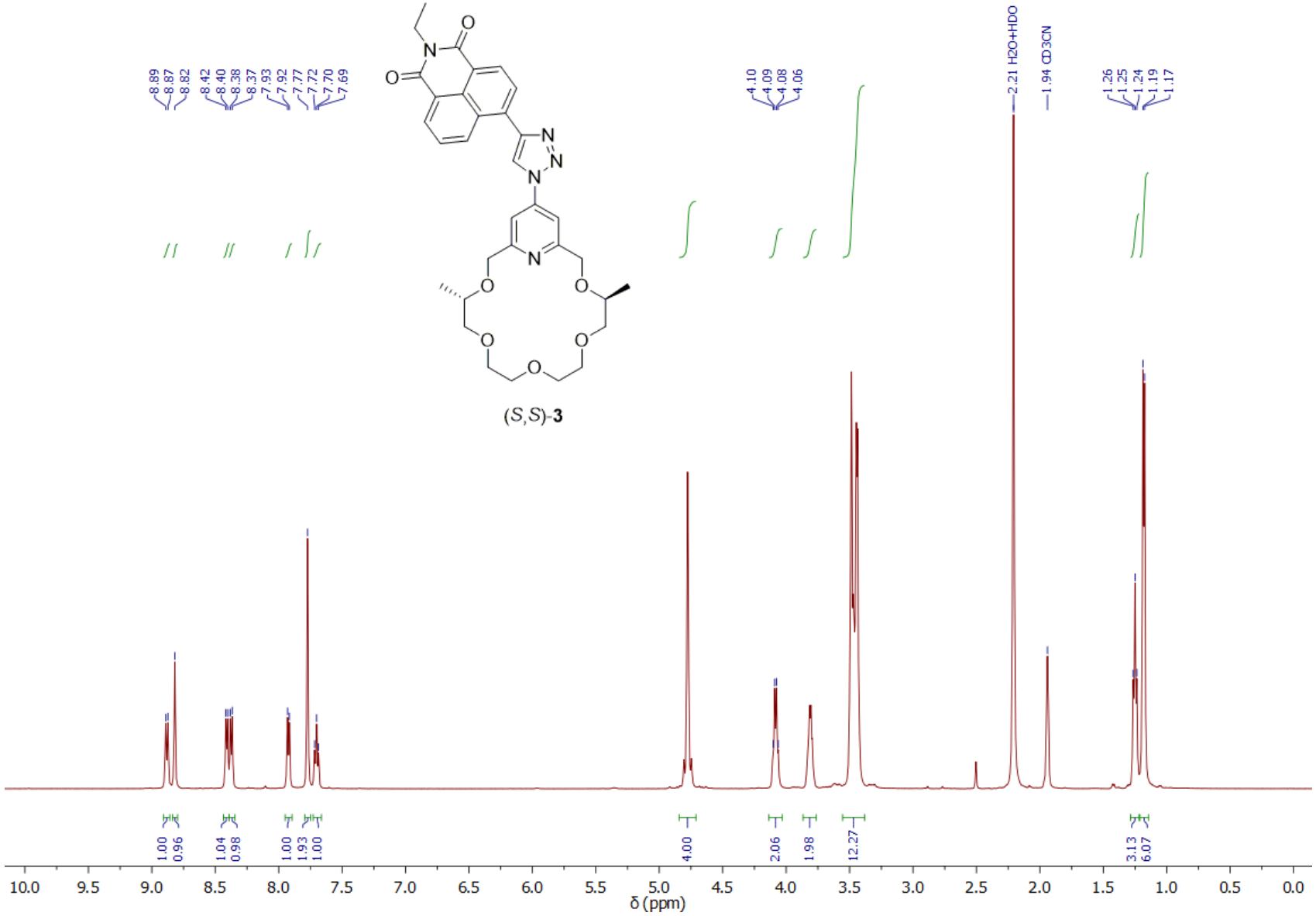

Figure S5A. ^{1}H NMR spectrum of (*S*,*S*)-**3** (CD_3CN, 500 MHz)

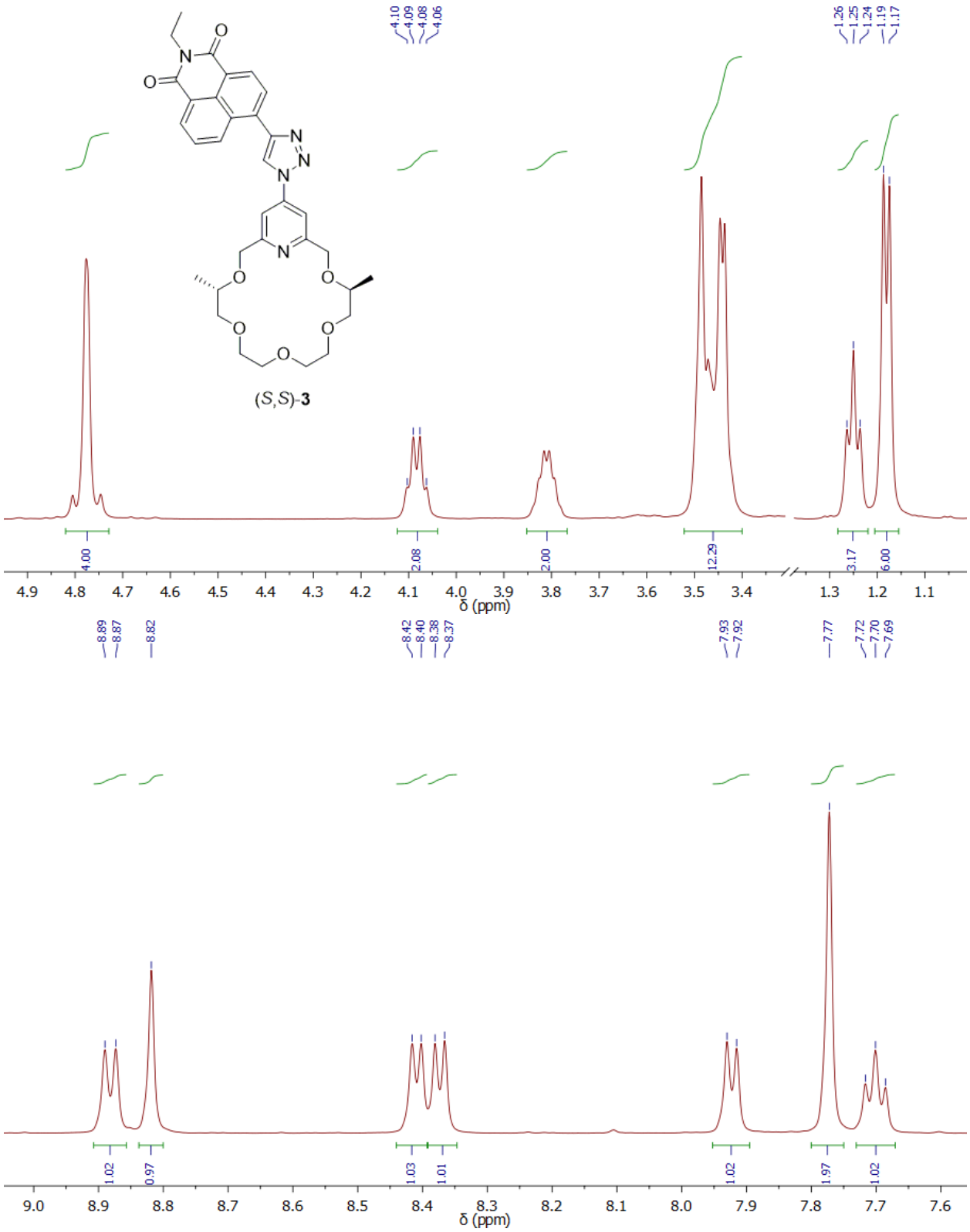

Figure S5B. Parts of the ^{1}H NMR spectrum of (*S*,*S*)-**3** (CD_3CN, 500 MHz)

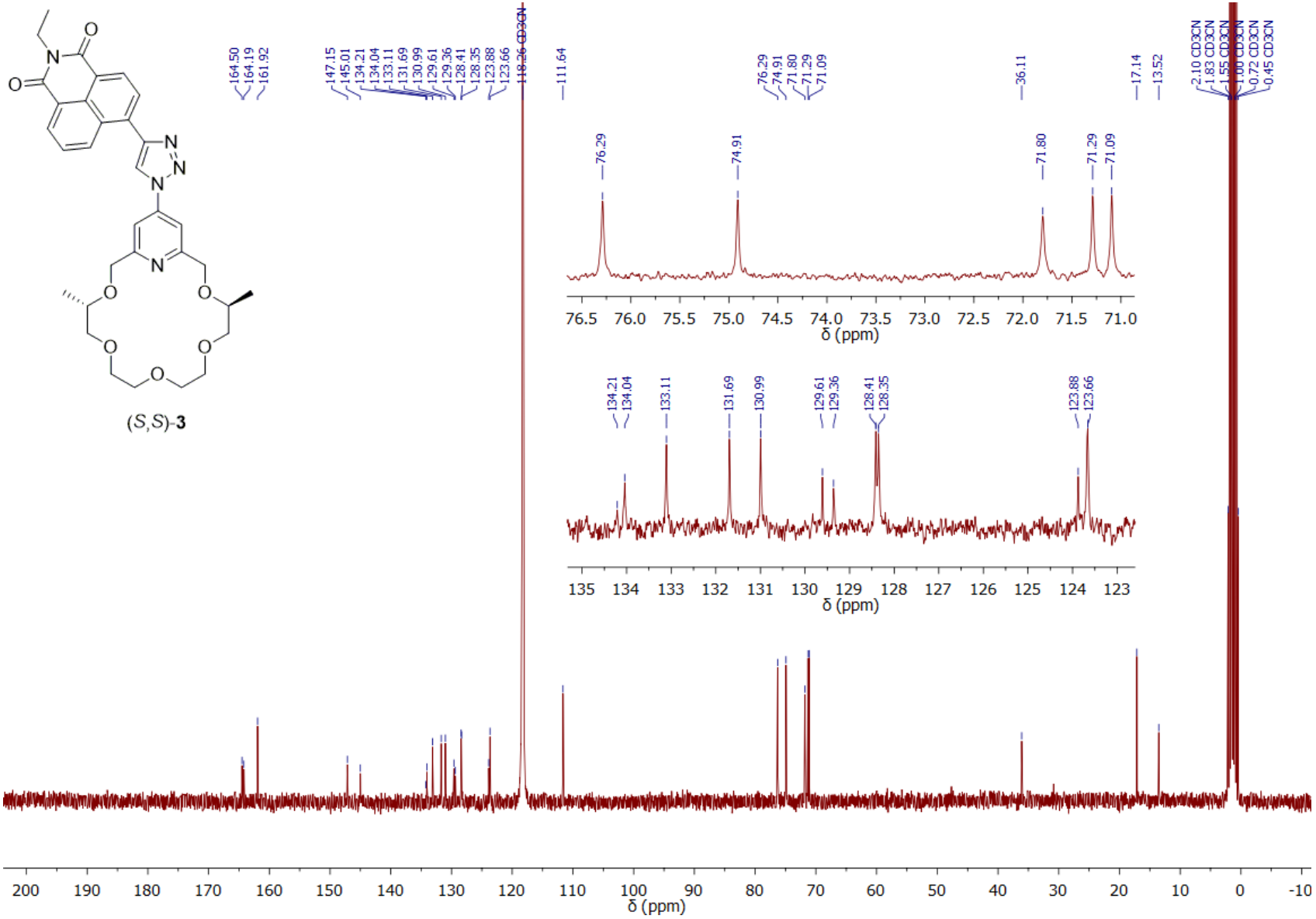

Figure S6. ^{13}C NMR spectrum of (*S*,*S*)-**3** (CD_3CN, 125 MHz)

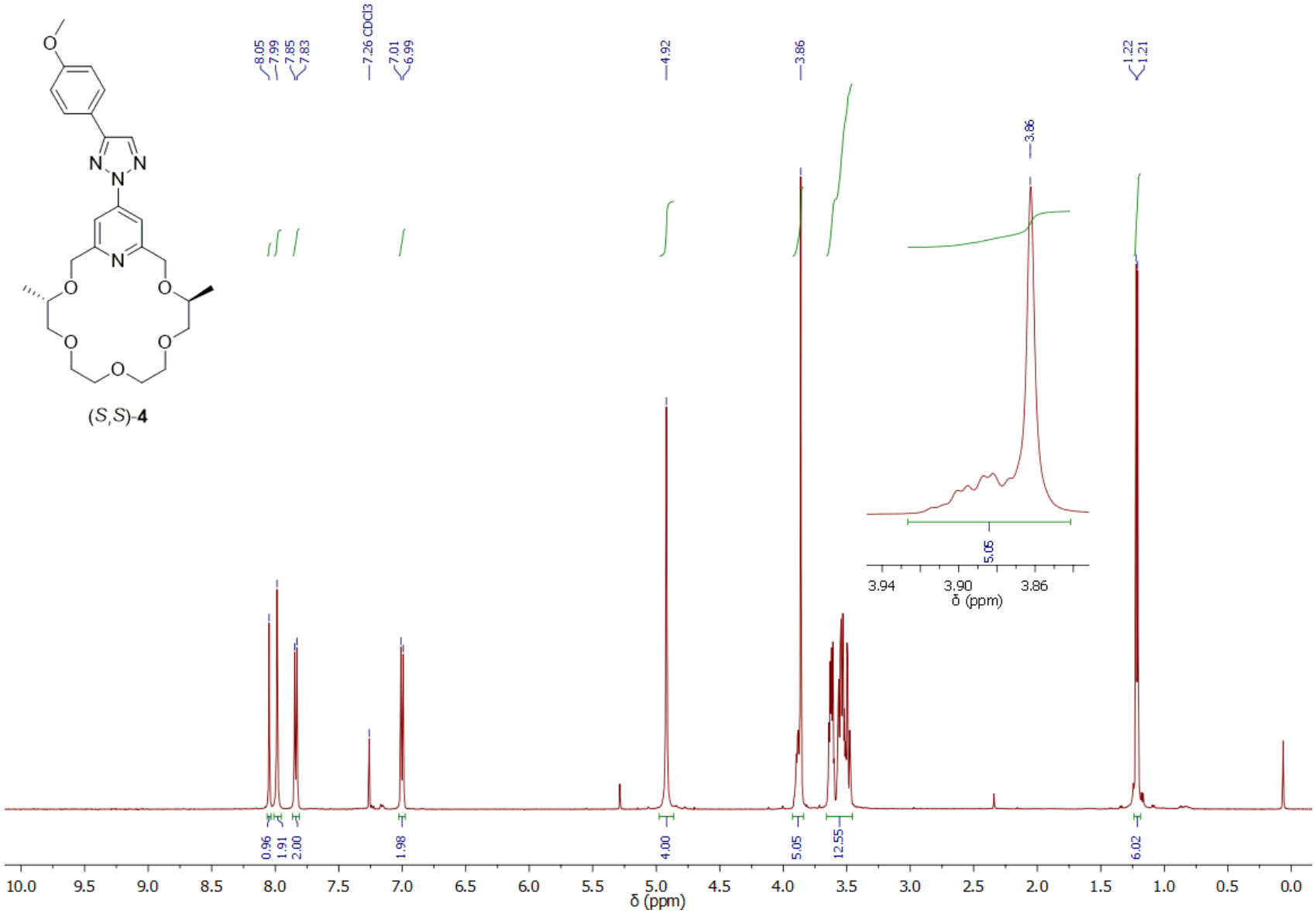

Figure S7. ^{1}H NMR spectrum of (*S*,*S*)-**4** ($CDCl_3$, 500 MHz)

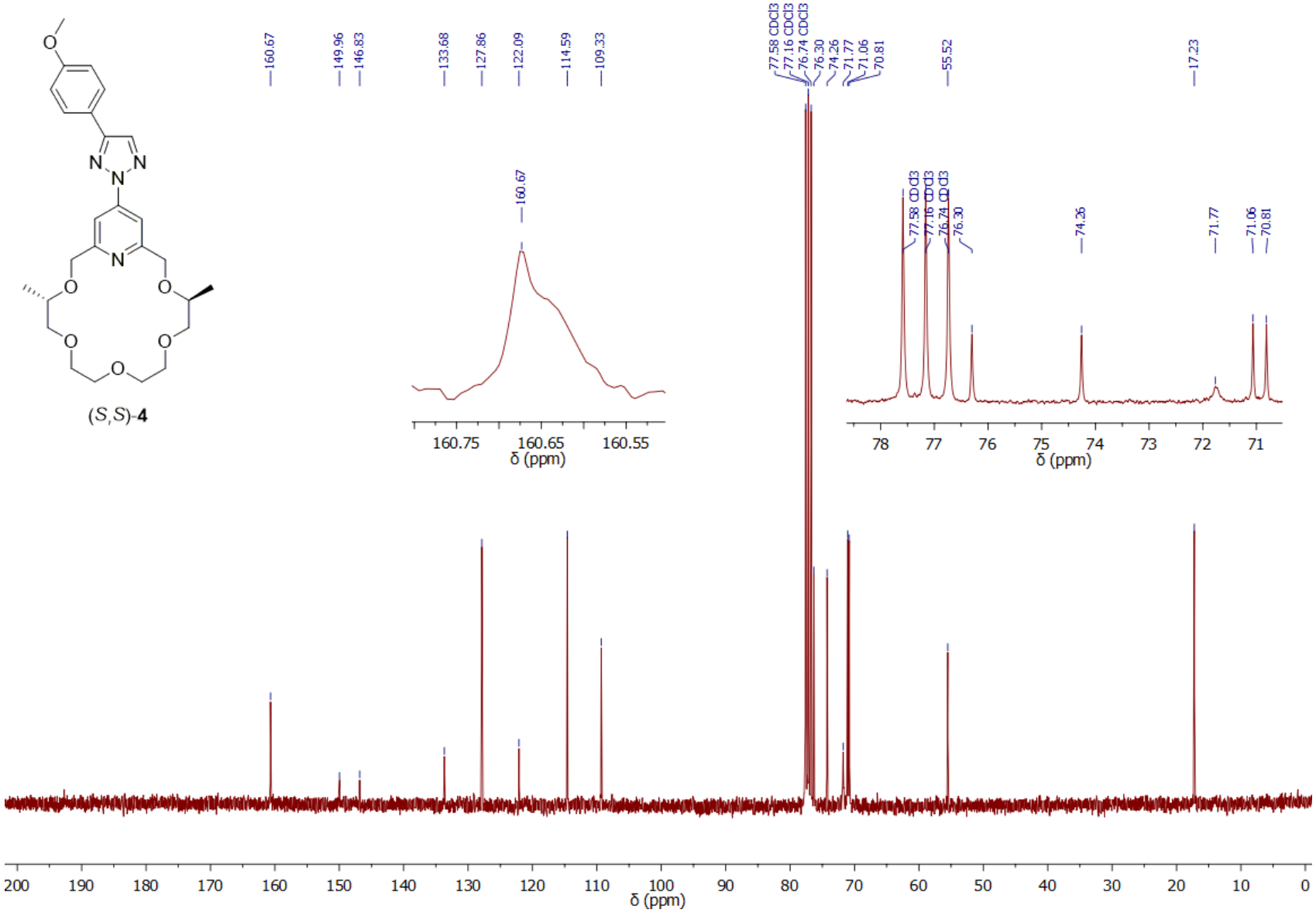

Figure S8. ^{13}C NMR spectrum of (*S*,*S*)-**4** ($CDCl_3$, 125 MHz)

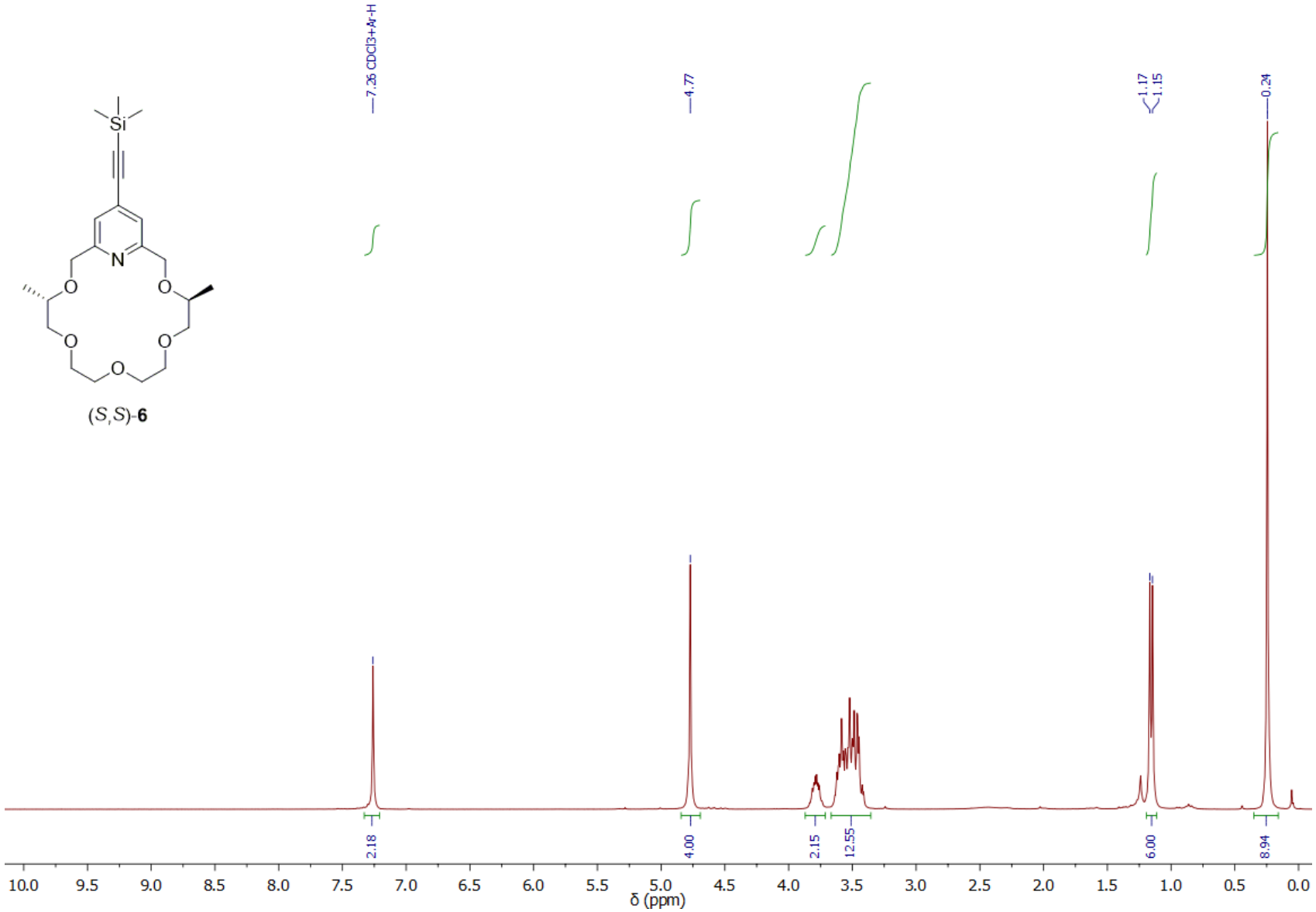

Figure S9. ^{1}H NMR spectrum of (*S*,*S*)-**6** ($CDCl_3$, 300 MHz)

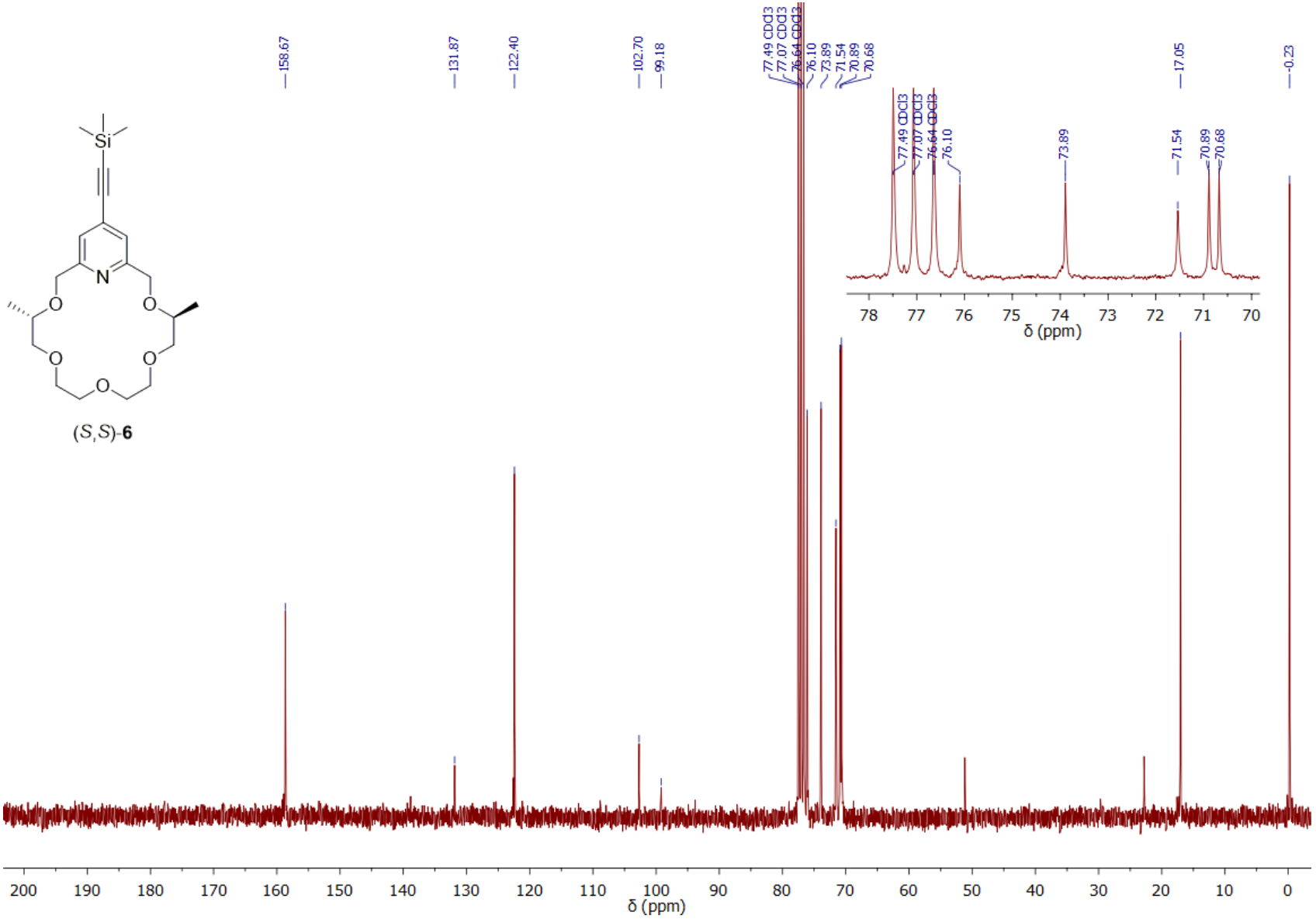

Figure S10. ^{13}C NMR spectrum of (*S*,*S*)-**6** ($CDCl_3$, 75.5 MHz)

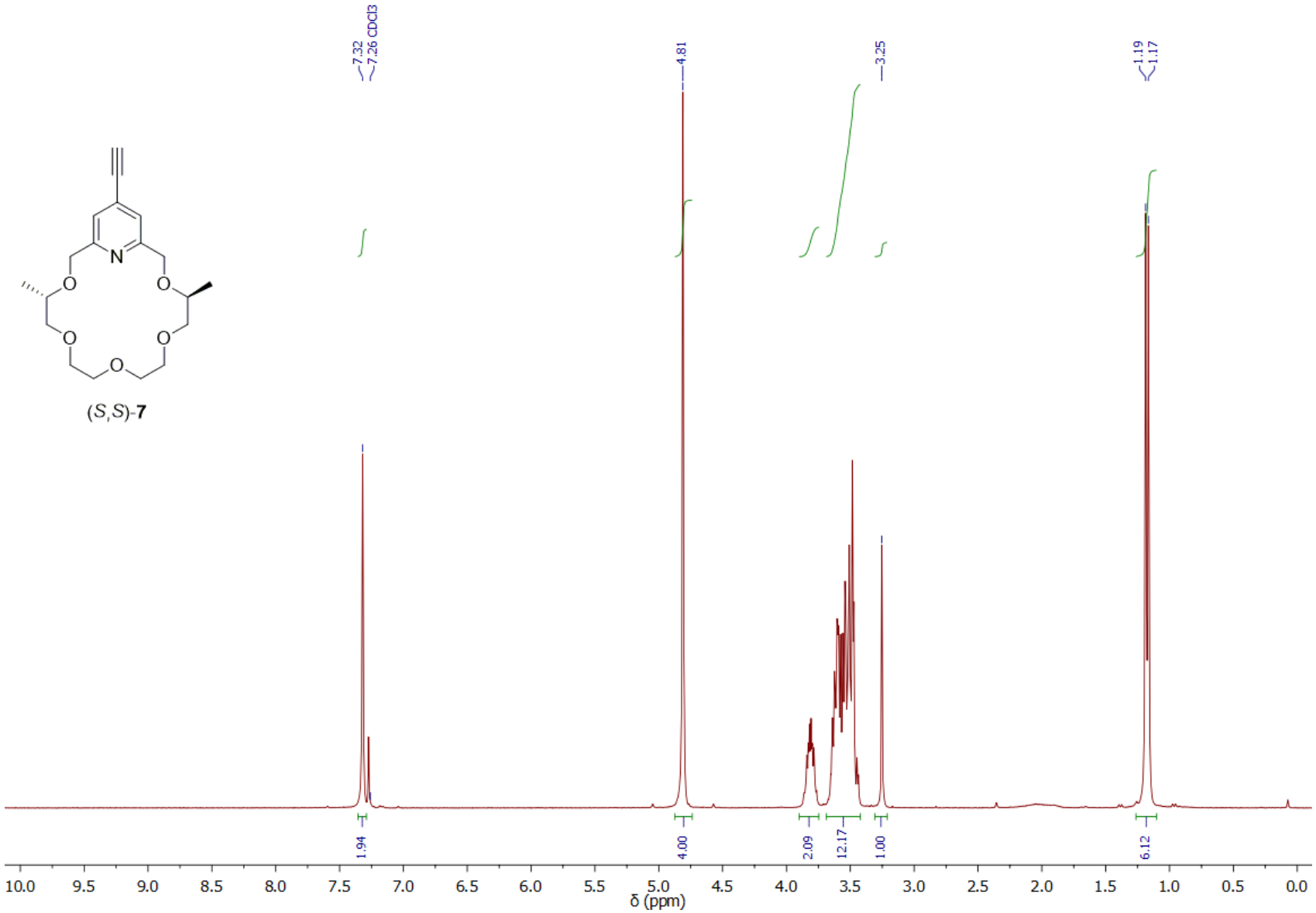

Figure S11. ^{1}H NMR spectrum of (*S*,*S*)-**7** ($CDCl_3$, 500 MHz)

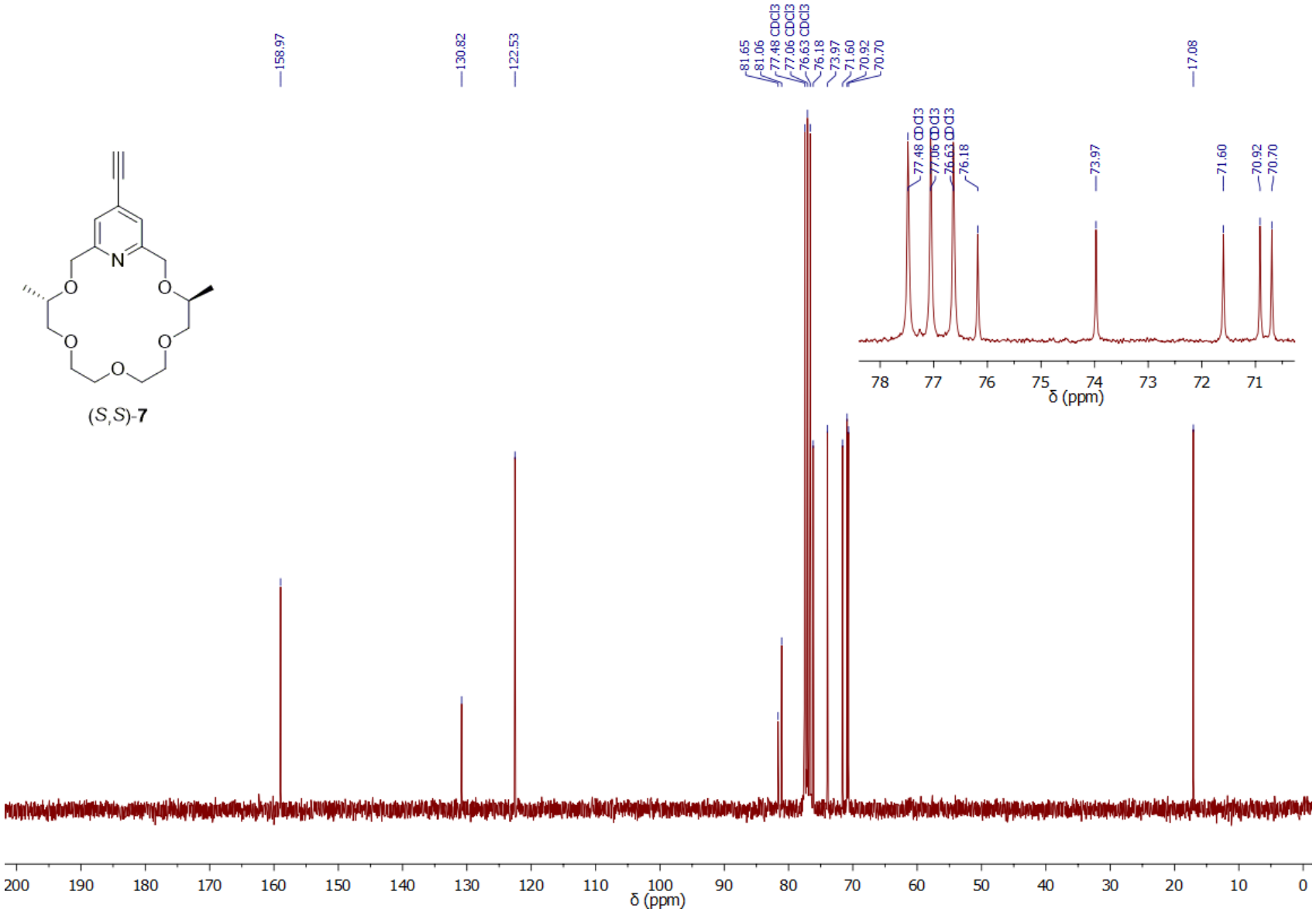

Figure S12. ^{13}C NMR spectrum of (*S*,*S*)-**7** ($CDCl_3$, 75.5 MHz)

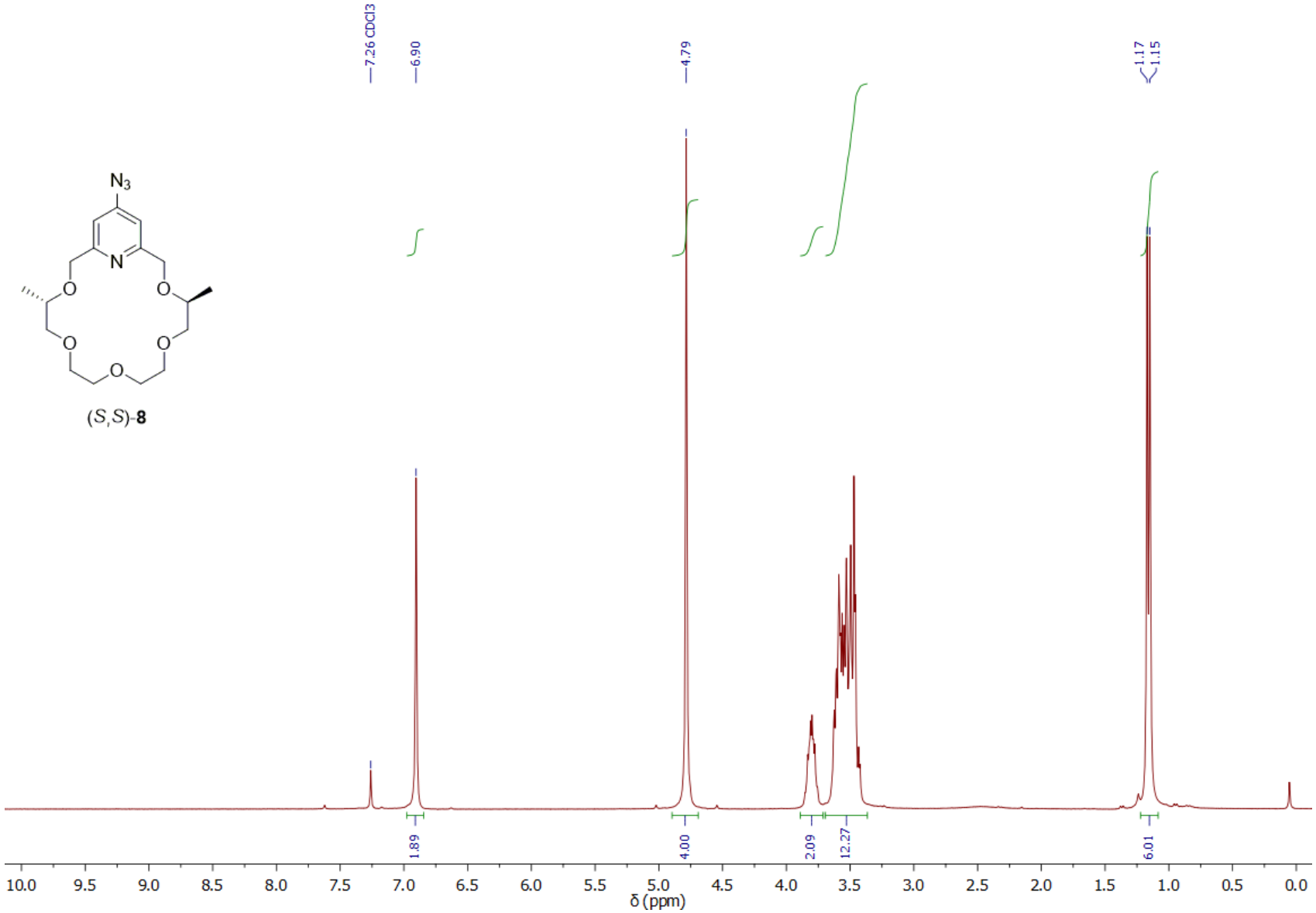

Figure S13. ^{1}H NMR spectrum of (*S*,*S*)-**8** ($CDCl_3$, 300 MHz)

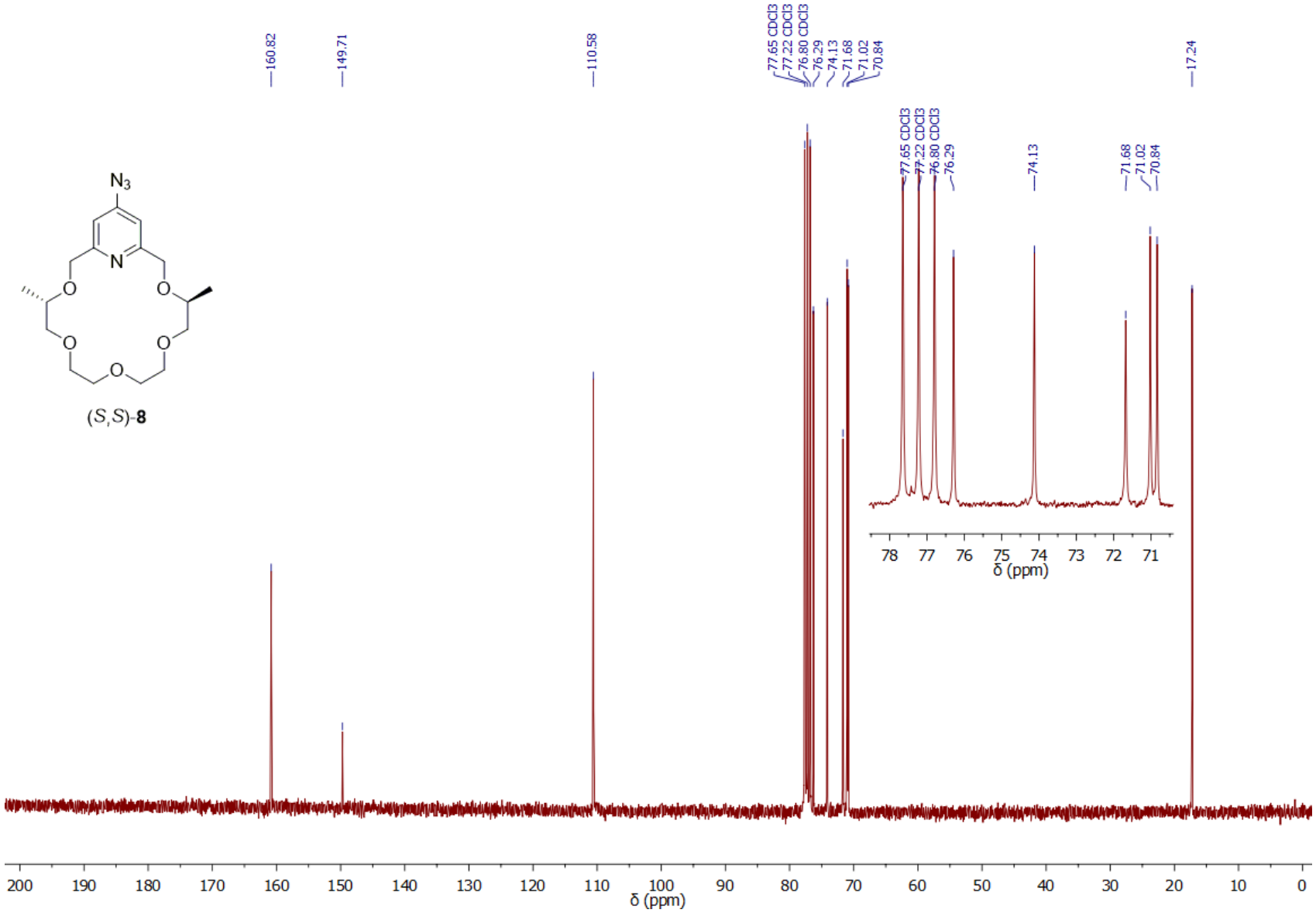

Figure S14. ^{13}C NMR spectrum of (*S*,*S*)-**8** ($CDCl_3$, 75.5 MHz)

Evaluation of 2D NMR spectra of (*S*,*S*)-**1**–(*S*,*S*)-**3**

2D ROESY and HMBC spectra were recorded for further support of structures (*S*,*S*)-**1**–(*S*,*S*)-**3**. The ROESY spectrum of ligand (*S*,*S*)-**2** showed a cross-peak between the triazole proton (8.25 ppm) and pyridine proton (7.71 ppm). Similarly, the triazole proton (8.82 ppm) and pyridine proton (7.77 ppm) of ligand (*S*,*S*)-**3** gave a ROE signal. These interactions could not be detected for the corresponding 1,5-isomers.

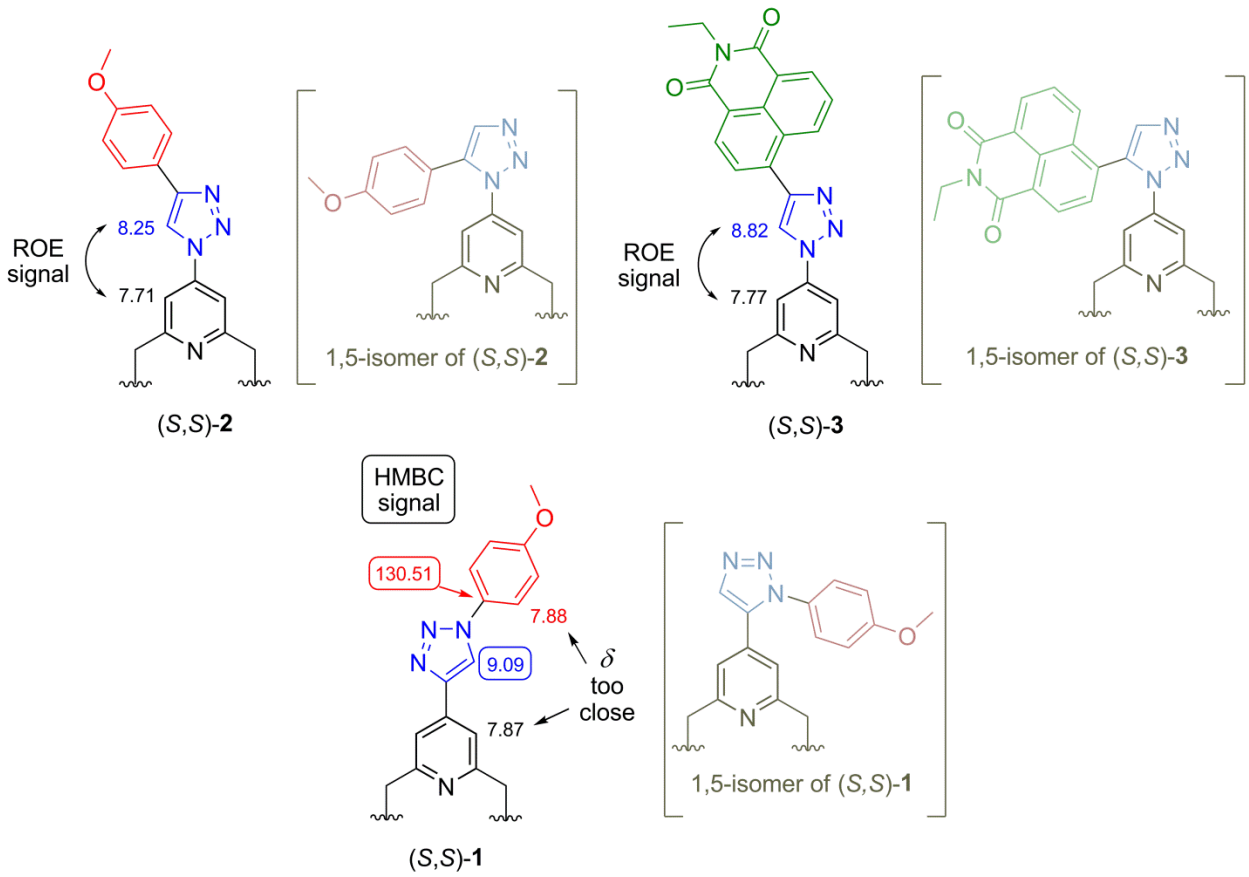

Figure S15. Parts of the structures of sensor molecules (*S*,*S*)-**1**–(*S*,*S*)-**3** with proton and carbon signal values (ppm) used for verifying the structures by 2D NMR techniques

In the case of ligand (*S*,*S*)-**1**, a ROE signal between the triazole proton (9.09 ppm) and phenyl proton (7.88 ppm) as well as the absence of a cross-peak between the pyridine proton (7.87 ppm) and phenyl proton (7.88 ppm) would support structure (*S*,*S*)-**1** and exclude its 1,5-isomer, but due to the very similar chemical shifts (7.87 and 7.88 ppm), these interactions could not be evaluated. Therefore, a HMBC spectrum was recorded. A weak HMBC signal between

the triazole proton (9.09 ppm) and phenyl carbon (131.34 ppm) confirmed structure (*S*,*S*)-**1**, because this correlation would not be expected for its 1,5-isomer through a four-bond distance. Furthermore, the predicted chemical shifts (by ACD/Spectrus software) for the triazole carbons of (*S*,*S*)-**1** are 121.96 ppm (C5) and 146.70 ppm (C4), in contrast to 134.28 ppm (C5) and 141.32 ppm (C4) for its 1,5-isomer. Thus, the corresponding measured values of 121.41 ppm (C5) and 146.63 ppm (C4) also suggest structure (*S*,*S*)-**1**.