Supporting Information

Stereoselective Synthesis of Bicyclo[6.1.0]nonene Precursors of the Bioorthogonal Reagents sTCO and BCN

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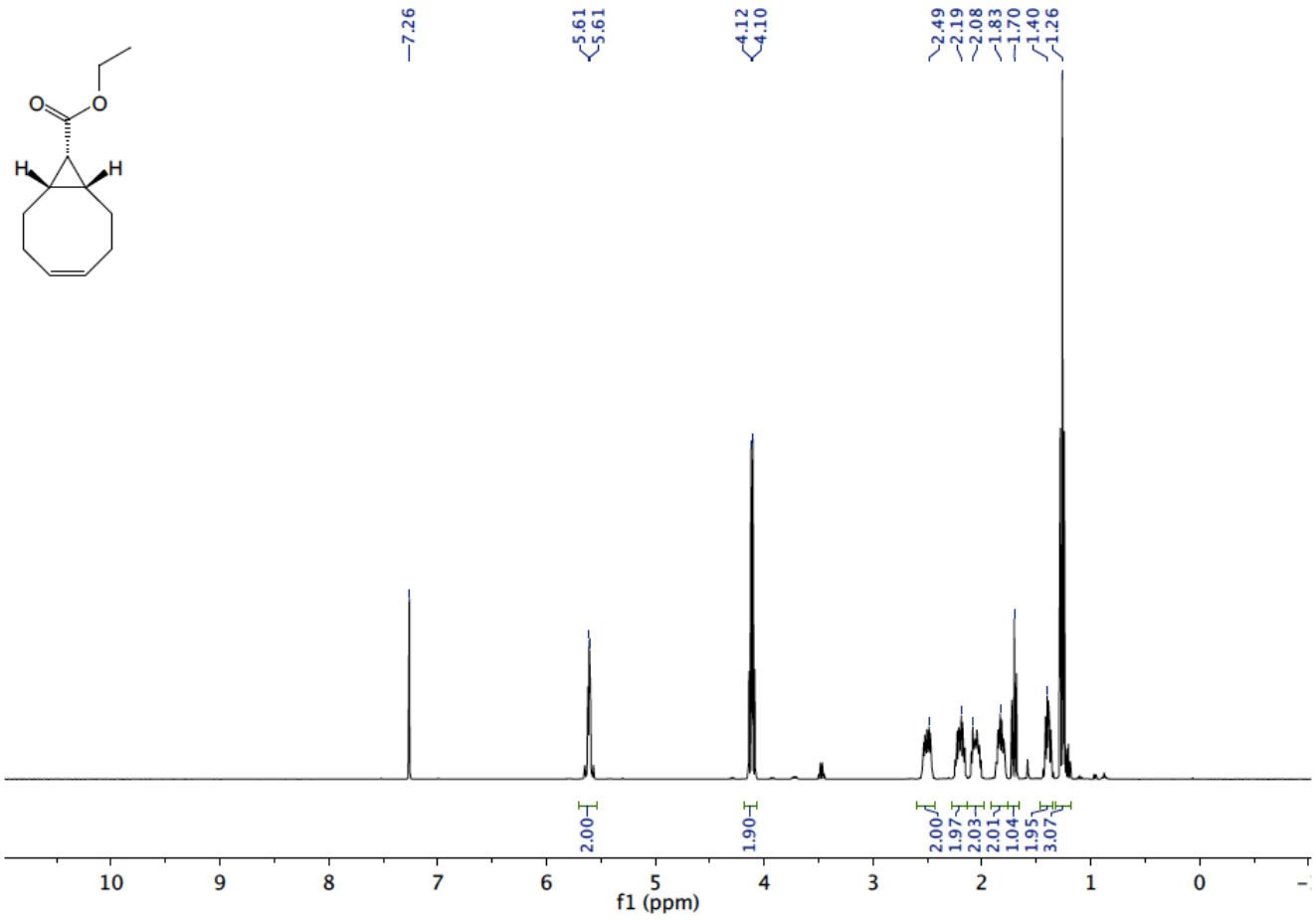
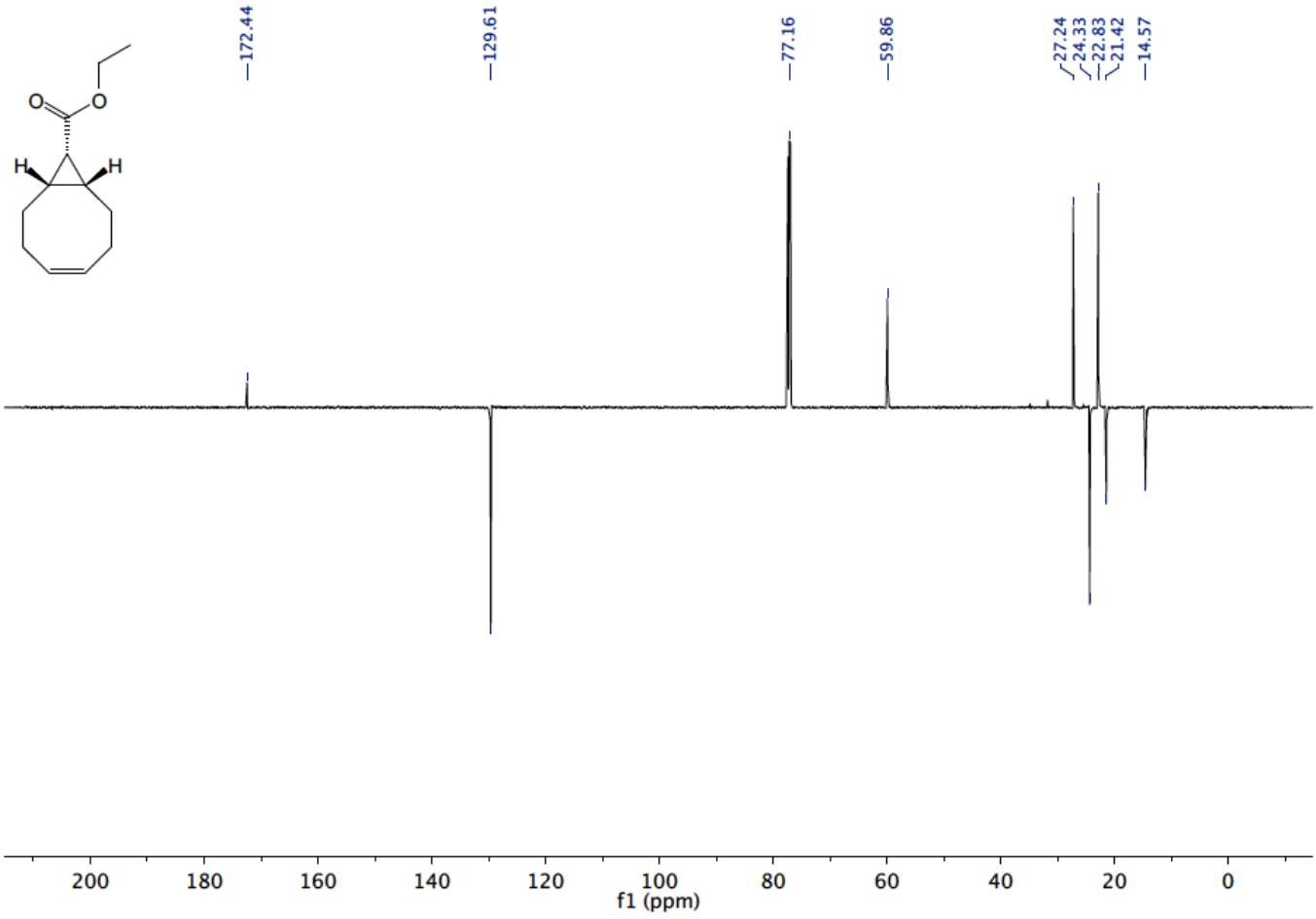
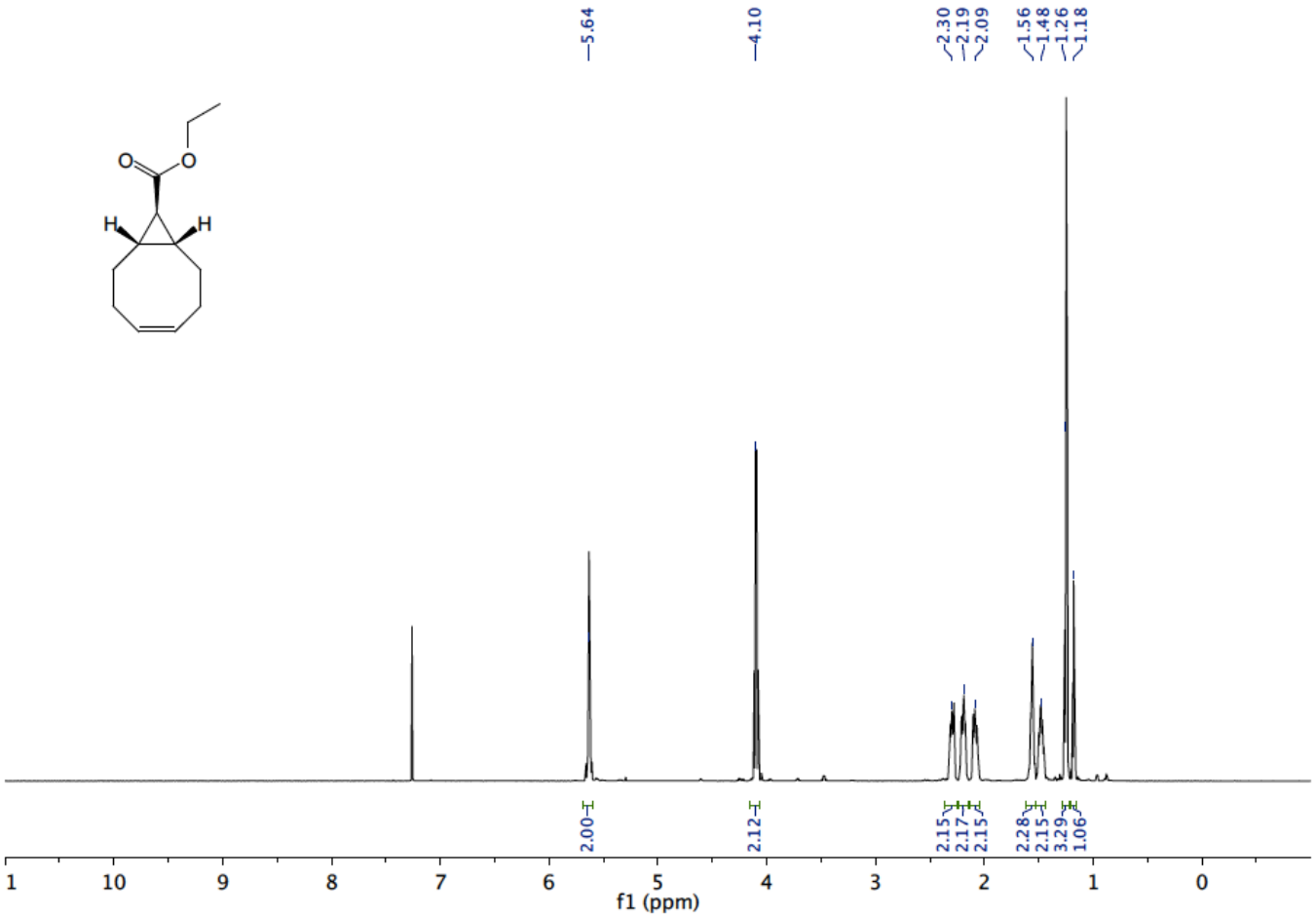
^{1}H NMR spectrum of **3-*syn*** (400 MHz, $CDCl_3$)



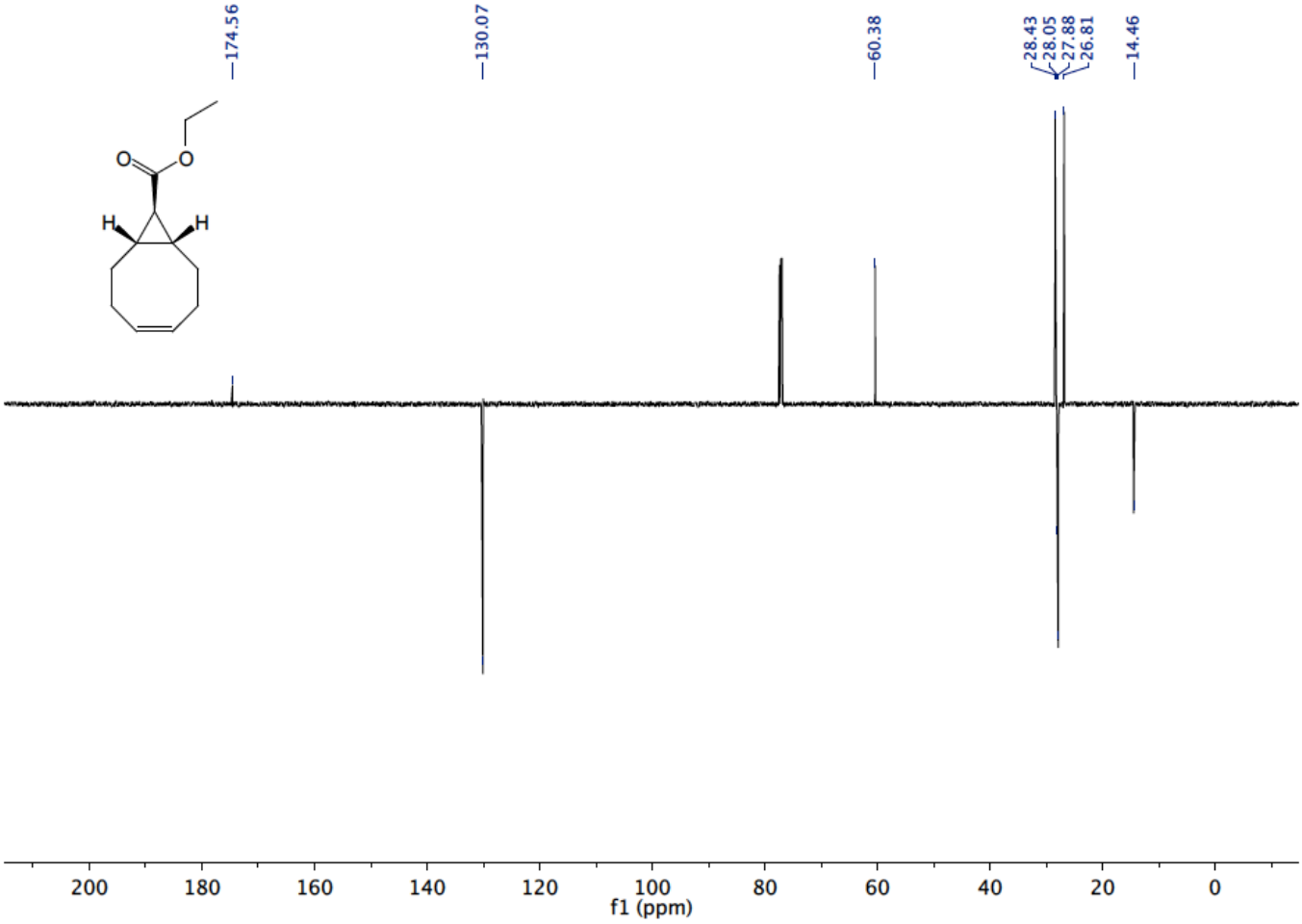
^{13}C NMR spectrum of **3-*syn*** (150 MHz, $CDCl_3$)



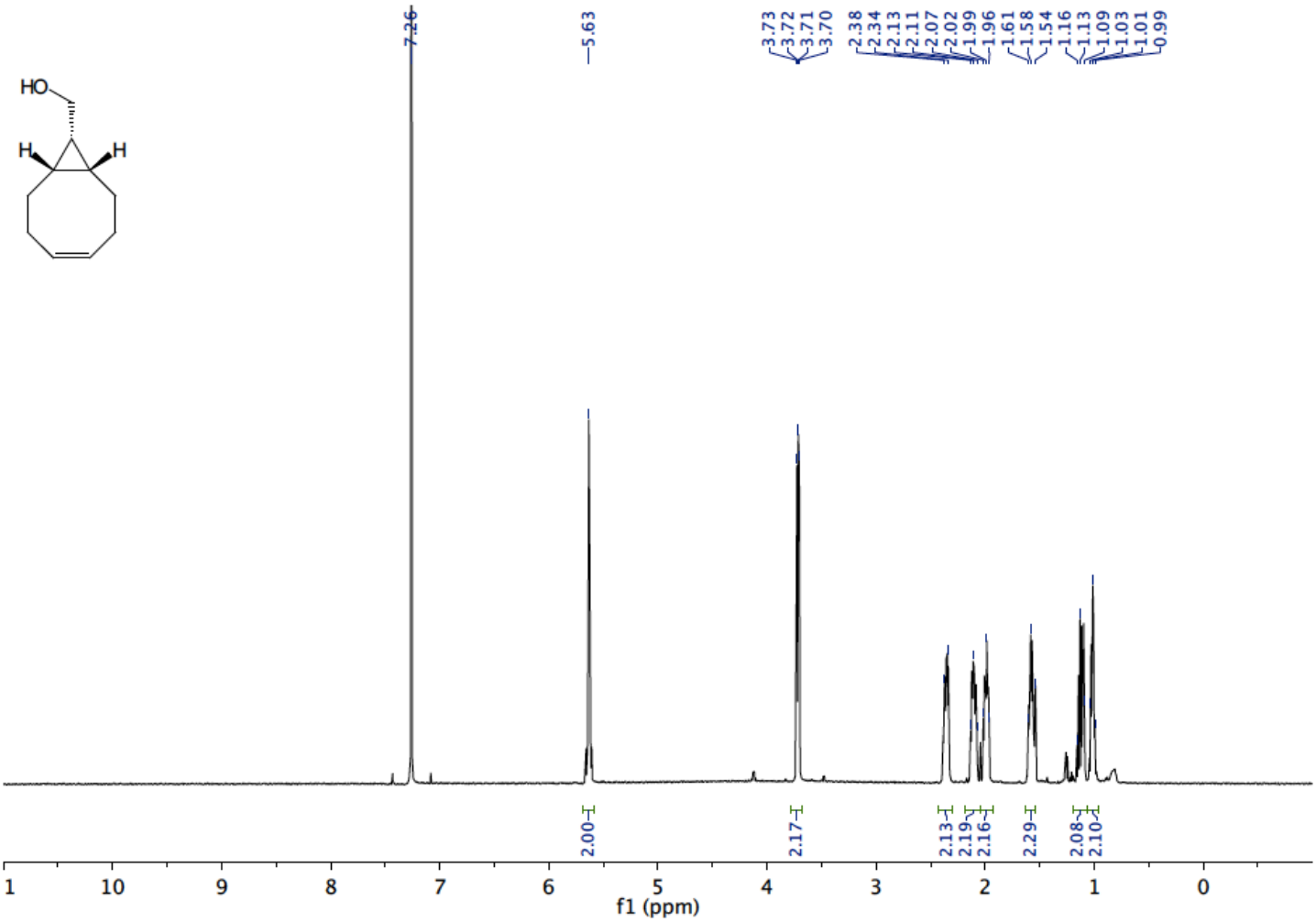
^{1}H NMR spectrum of **3-*anti*** (600 MHz, $CDCl_3$)



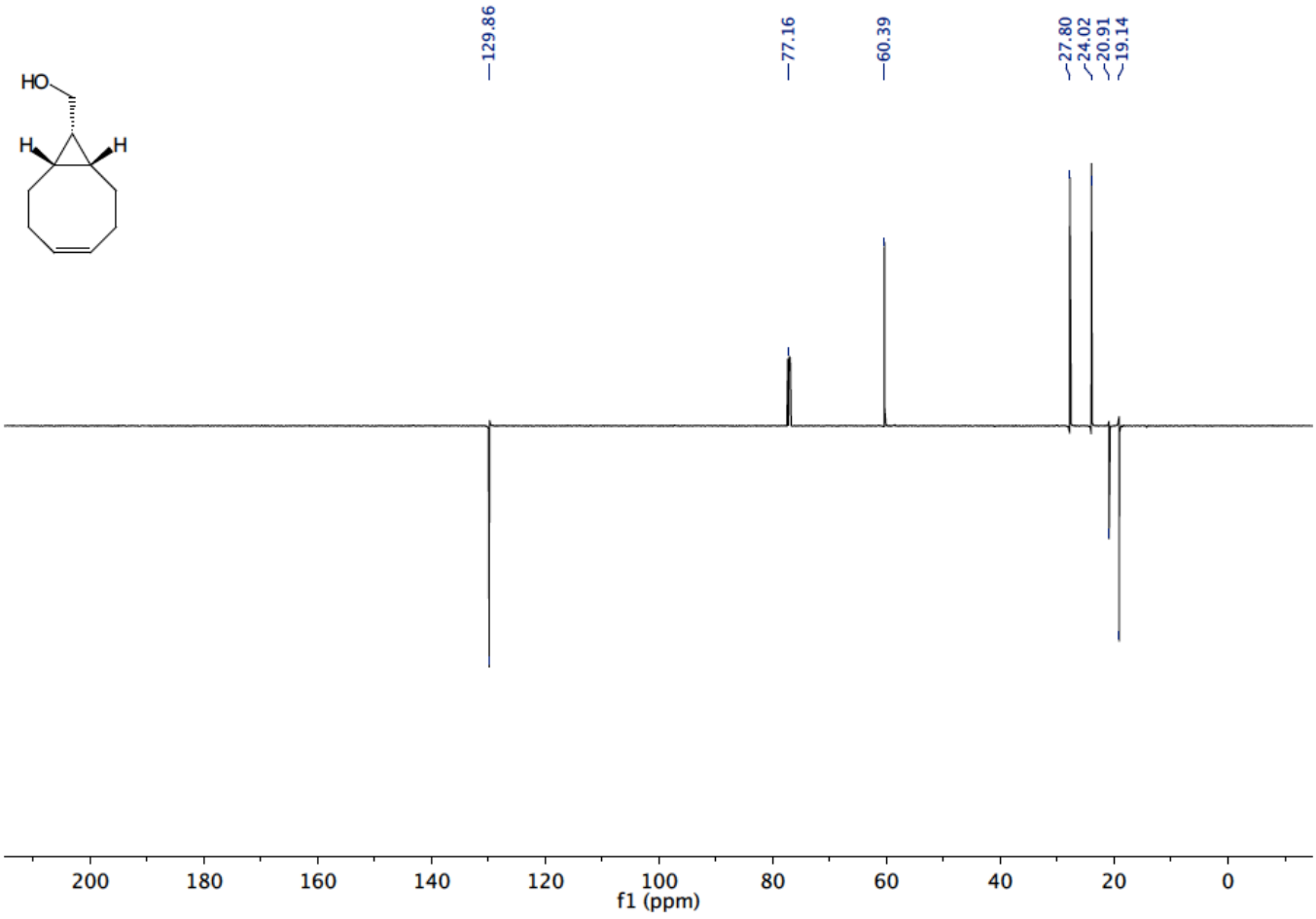
^{13}C NMR spectrum of **3-*anti*** (150 MHz, $CDCl_3$)



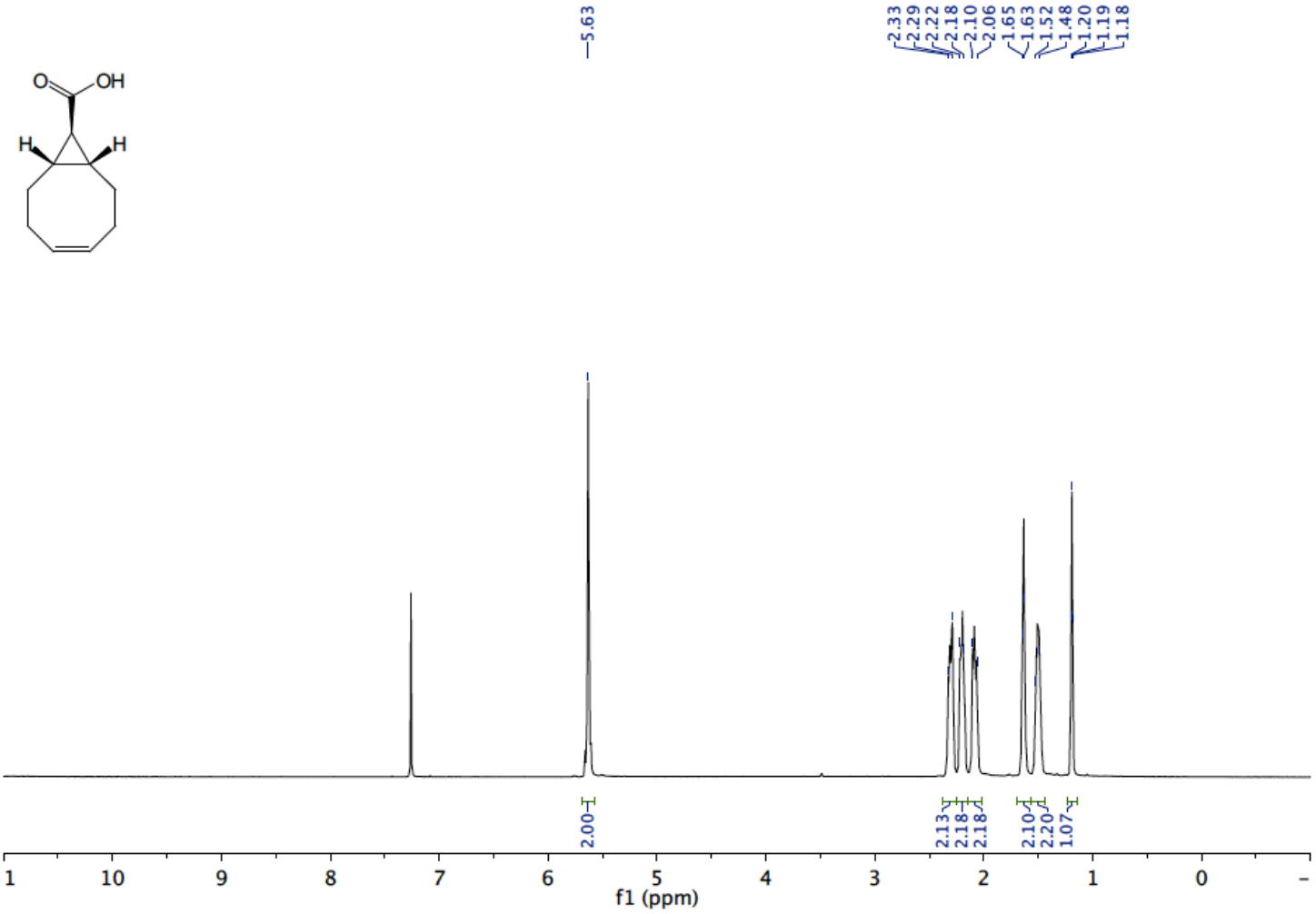
^{1}H NMR spectrum of **5** (600 MHz, $CDCl_3$)



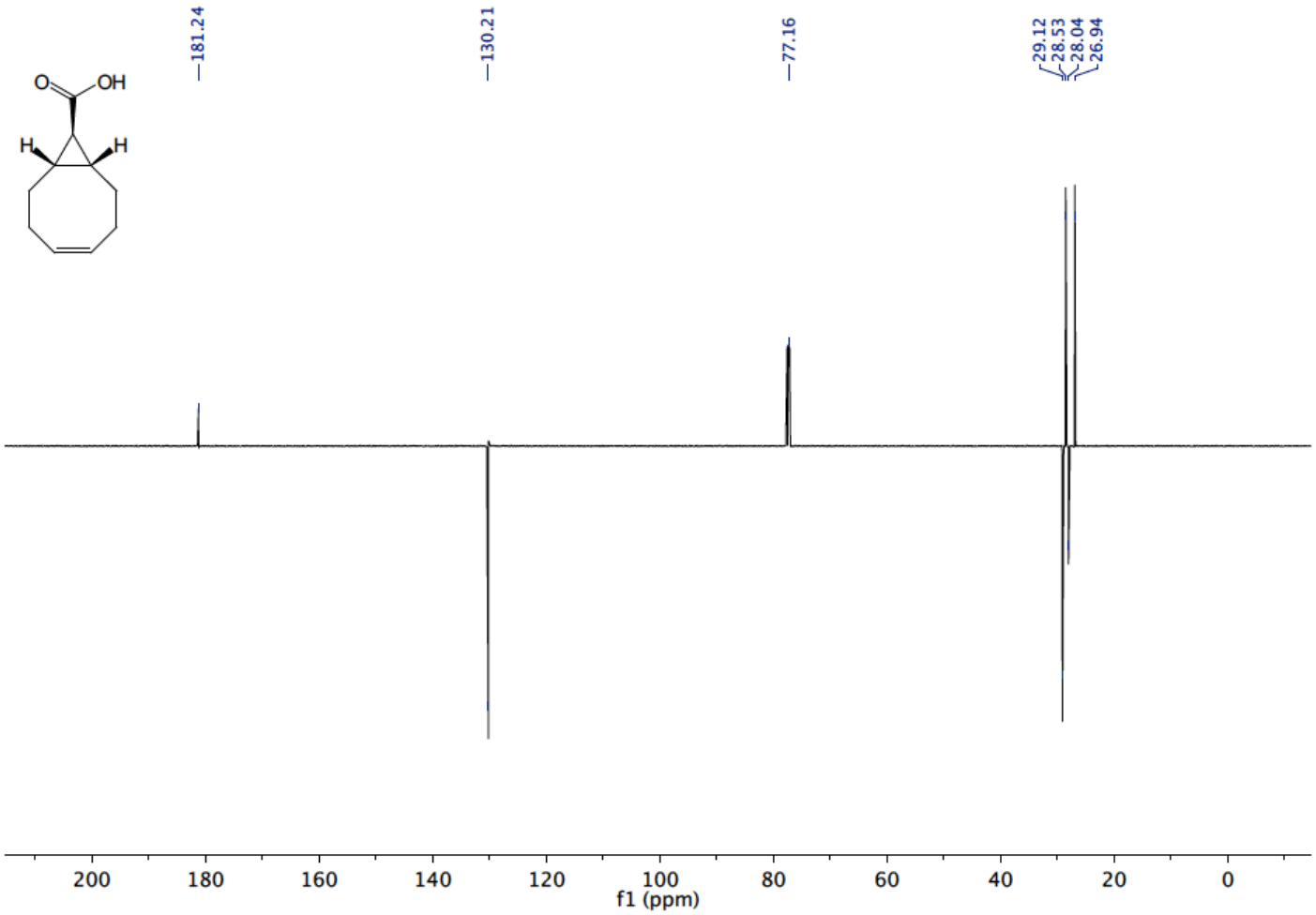
^{13}C NMR spectrum of **5** (150 MHz, $CDCl_3$)



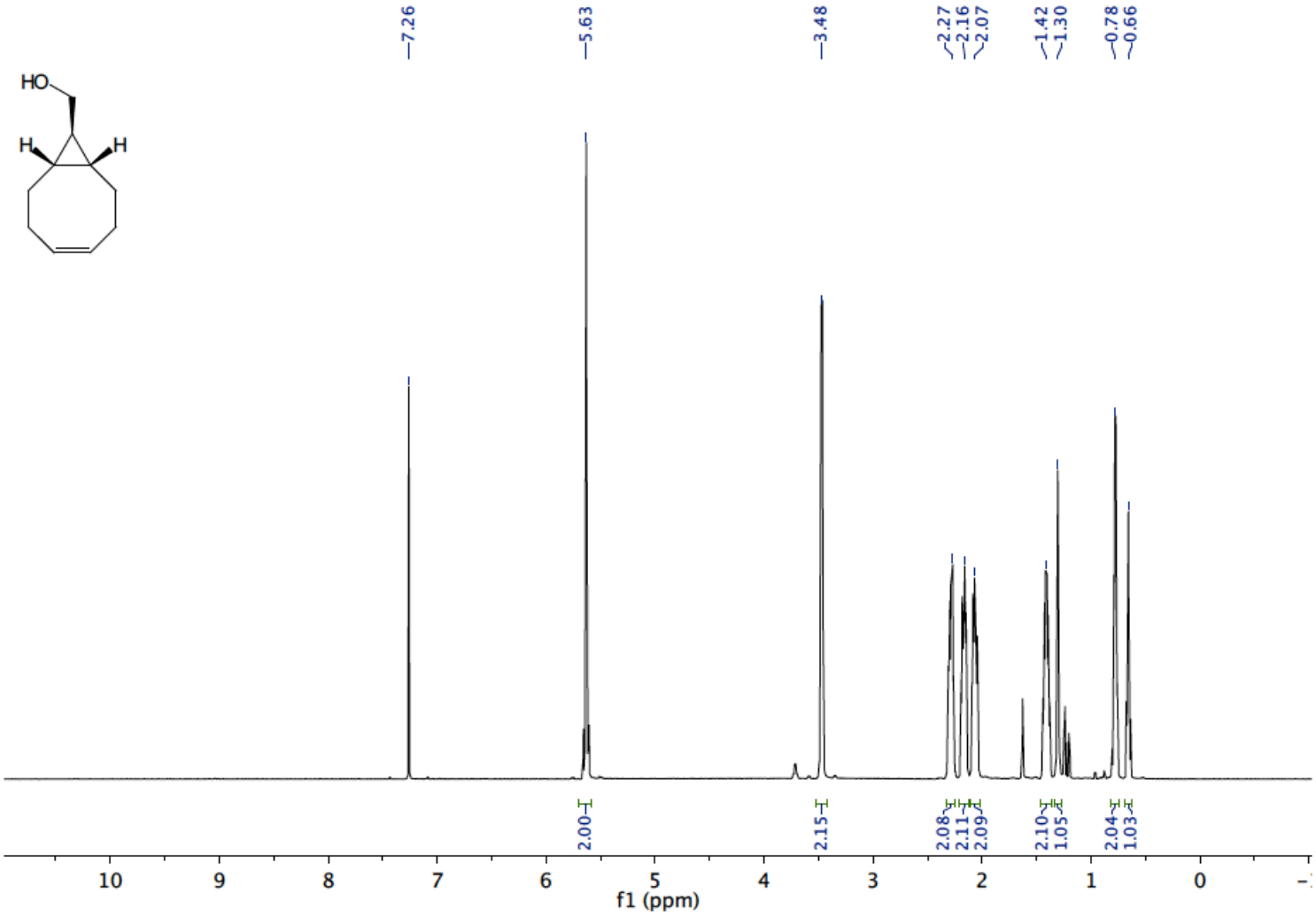
^{1}H NMR spectrum of **6** (600 MHz, $CDCl_3$)



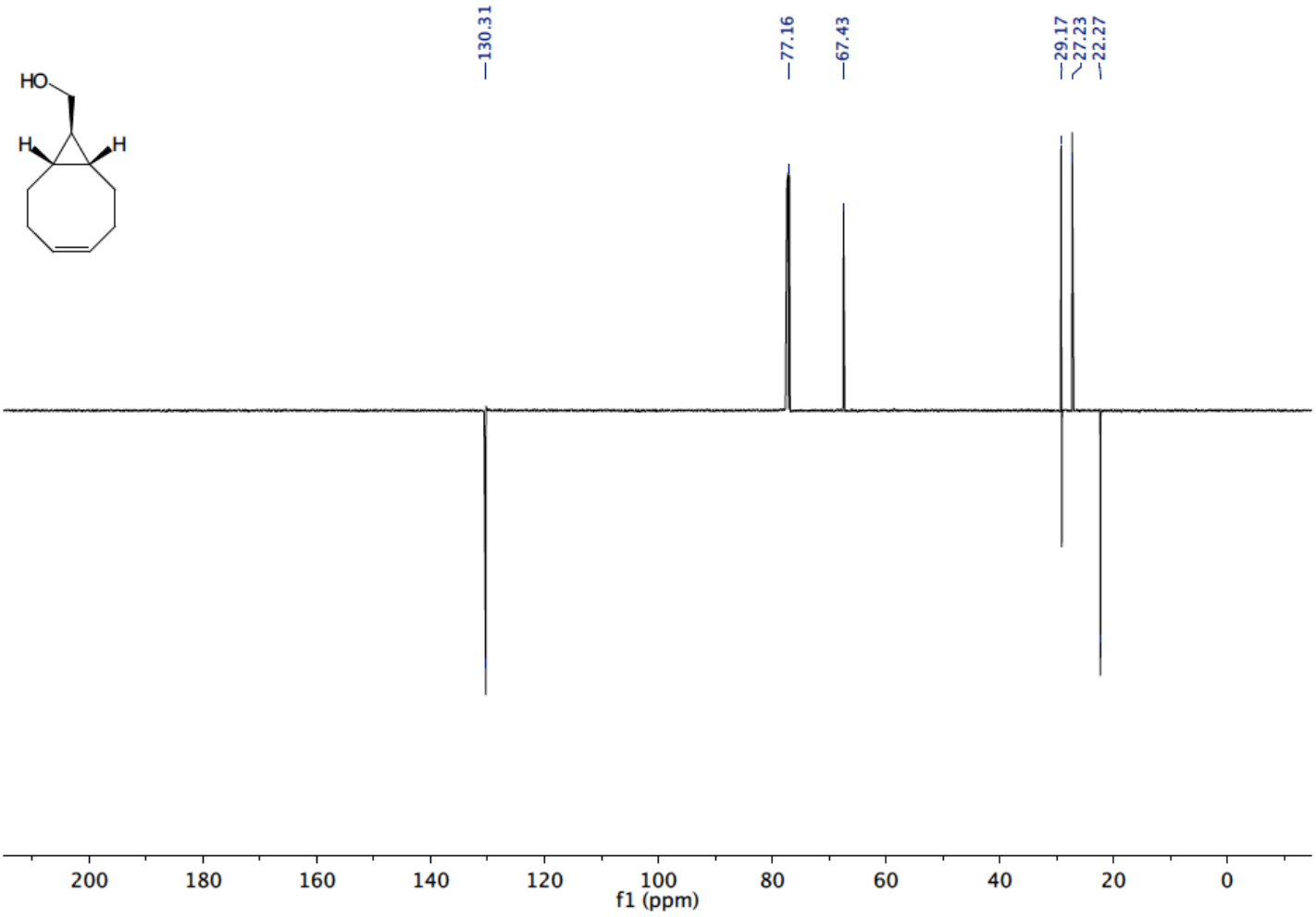
^{13}C NMR spectrum of **6** (150 MHz, $CDCl_3$)



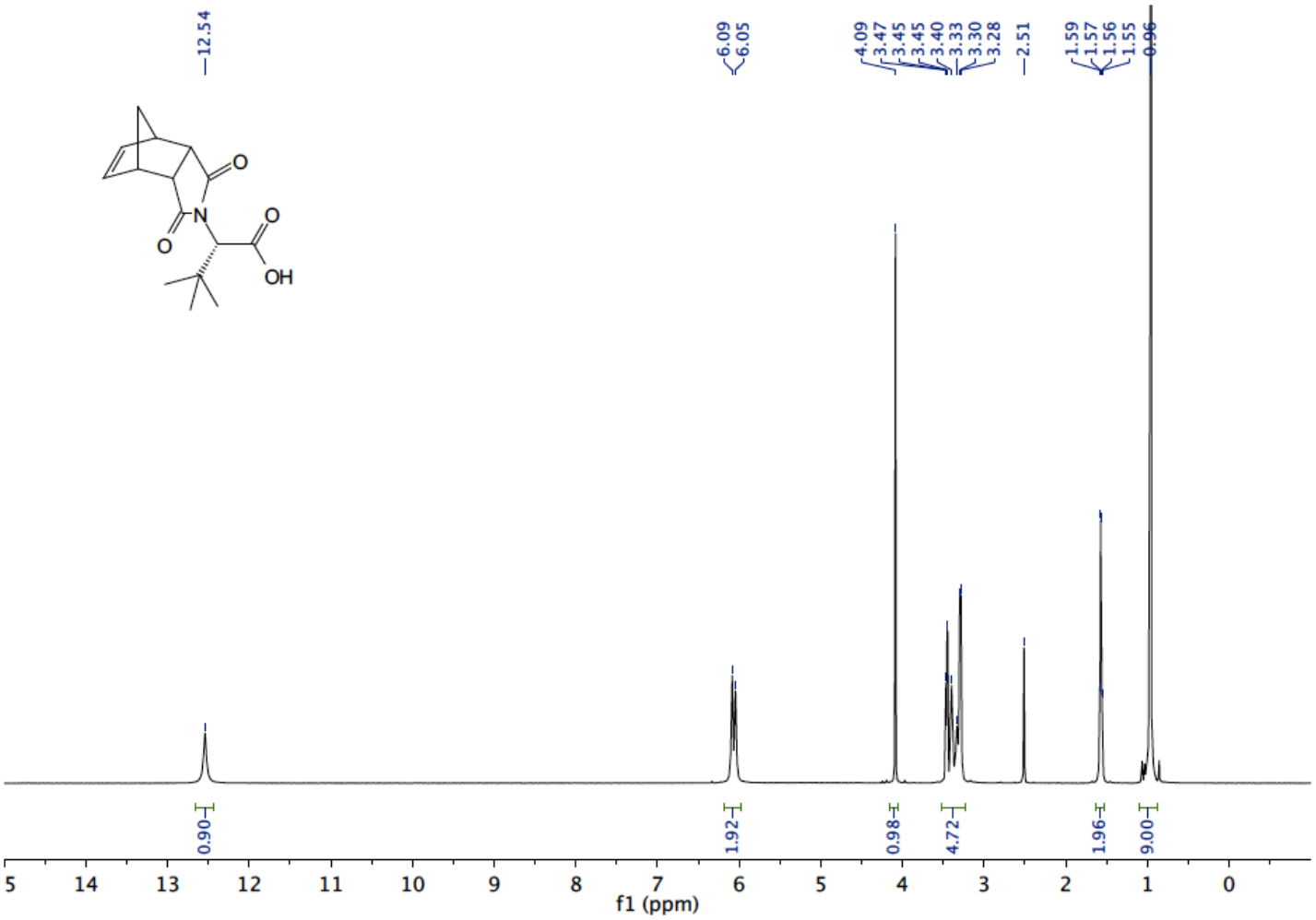
^{1}H NMR spectrum of **4** (600 MHz, $CDCl_3$)



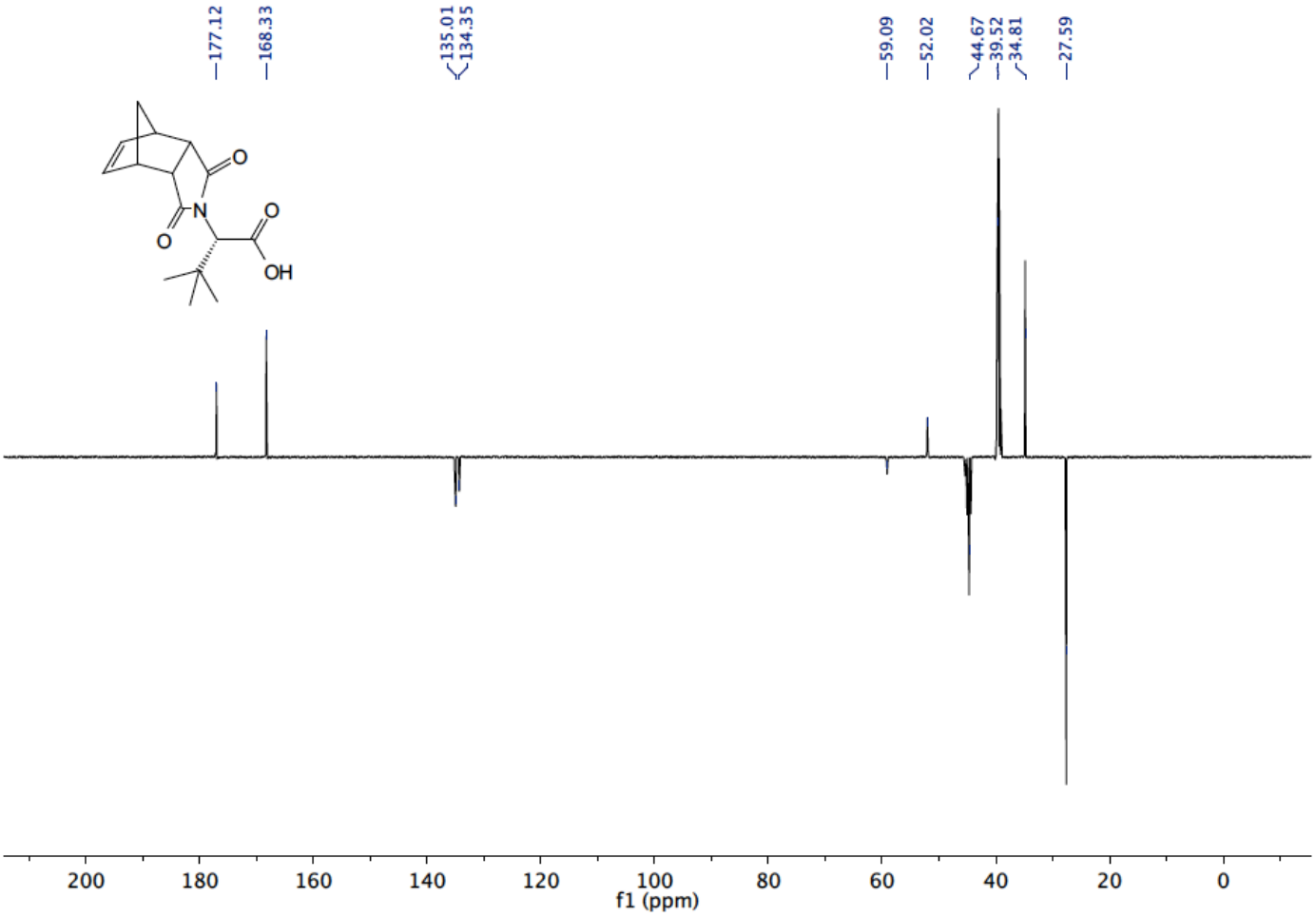
^{13}C NMR spectrum of **4** (150 MHz, $CDCl_3$)



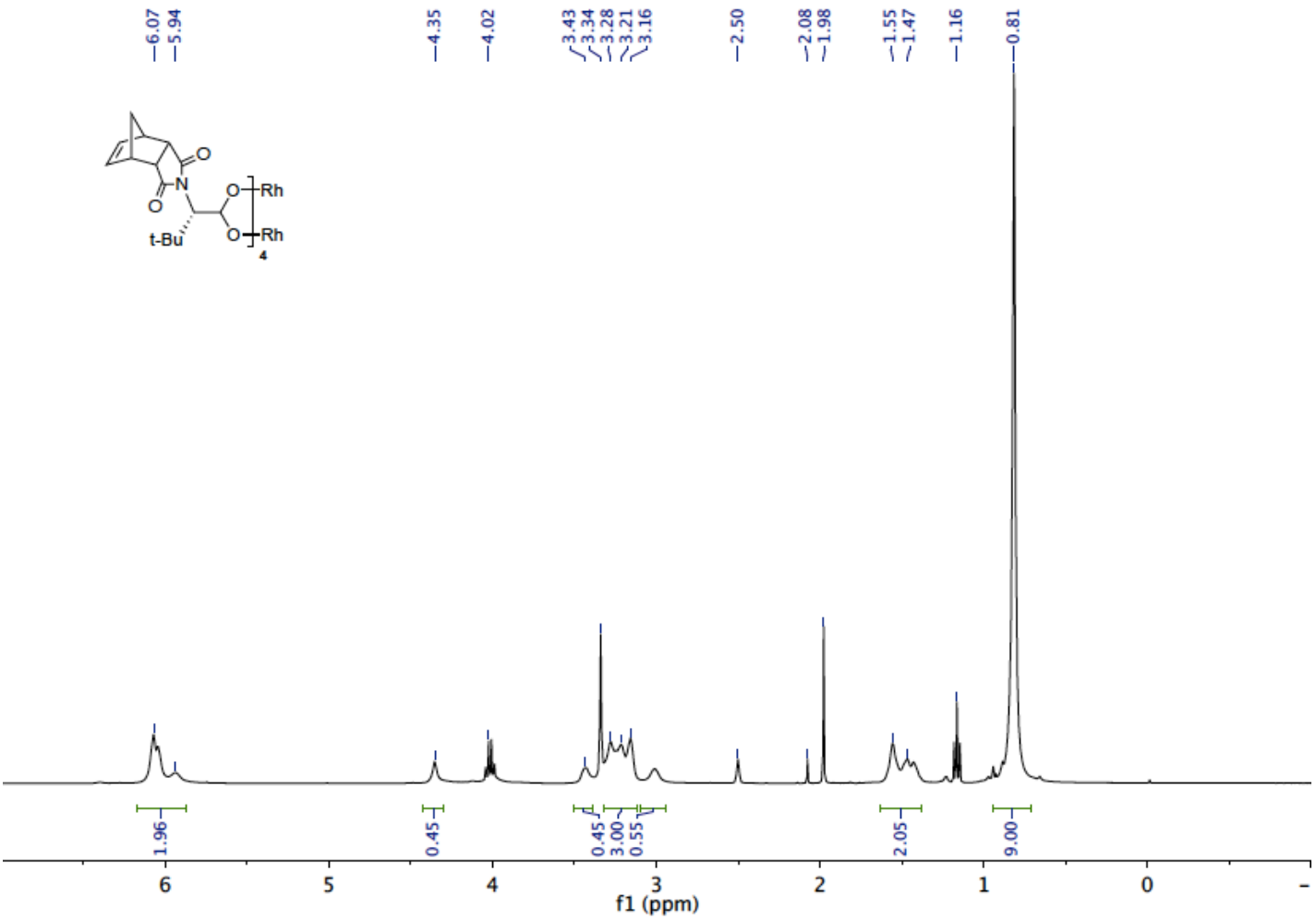
^{1}H NMR spectrum of **(*S*)-BHTL** (600 MHz, $(CD_3)_2SO$)



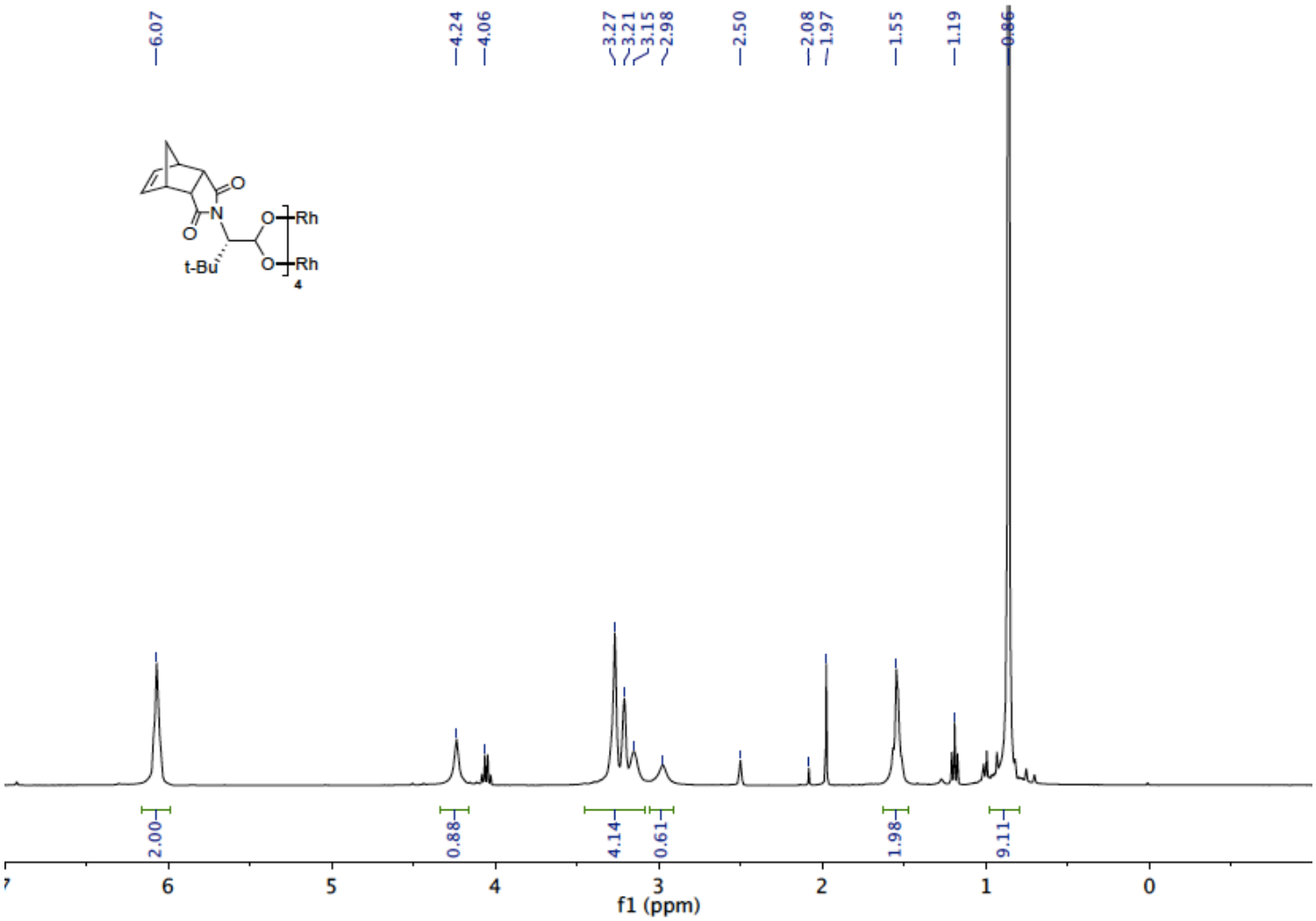
^{13}C NMR spectrum of **(*S*)-BHTL** (150 MHz, $(CD_3)_2SO$)



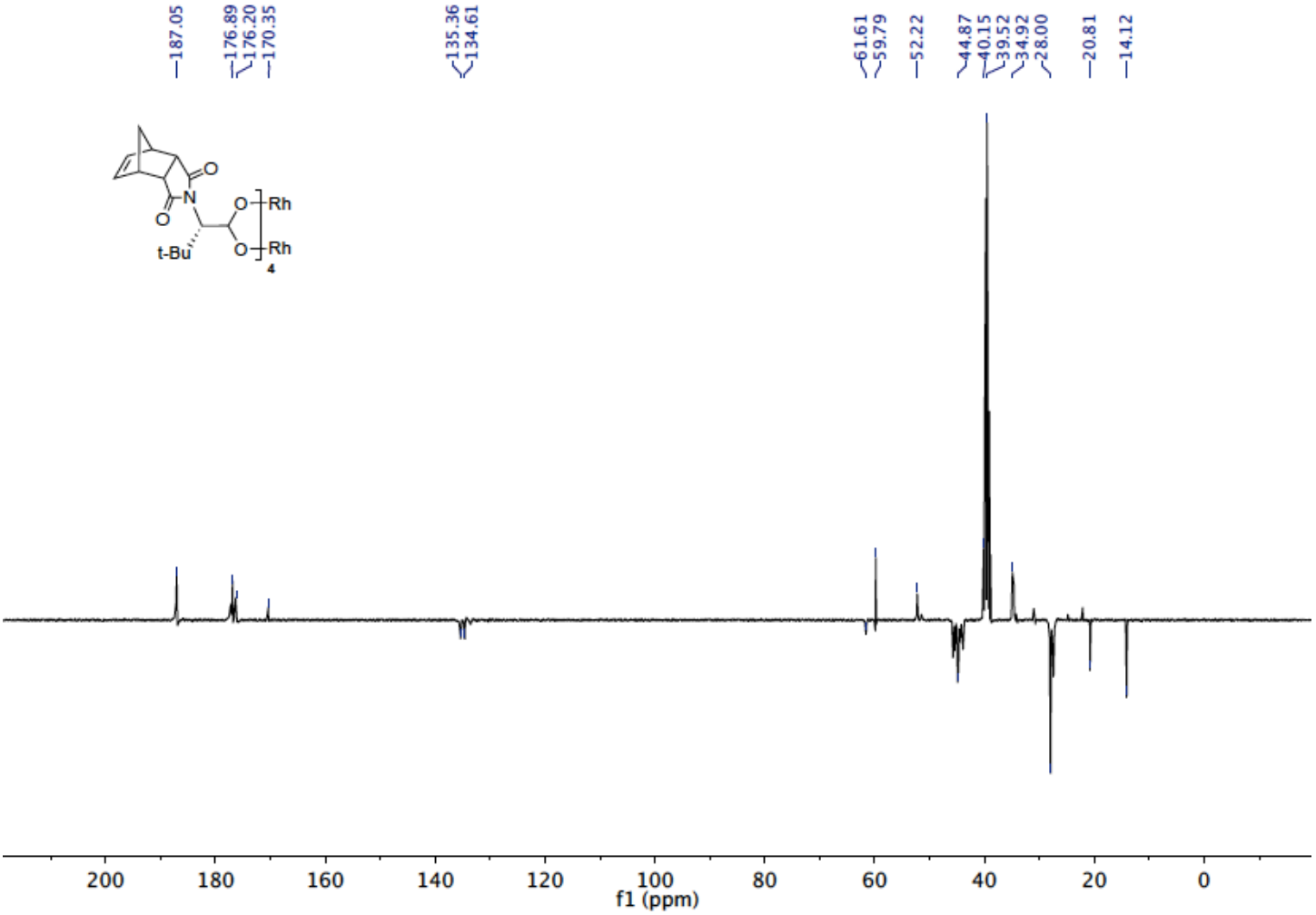
^{1}H NMR spectrum of **Rh_2(*S*-BHTL)$_4$**, room temperature (400 MHz, $(CD_3)_2SO$)



^{1}H NMR spectrum of **Rh_2(*S*-BHTL)$_4$** 360K (400MHz, $(CD_3)_2SO$)



^{13}C NMR spectrum of **Rh_2(*S*-BHTL)$_4$** (600MHz, $(CD_3)_2SO$)



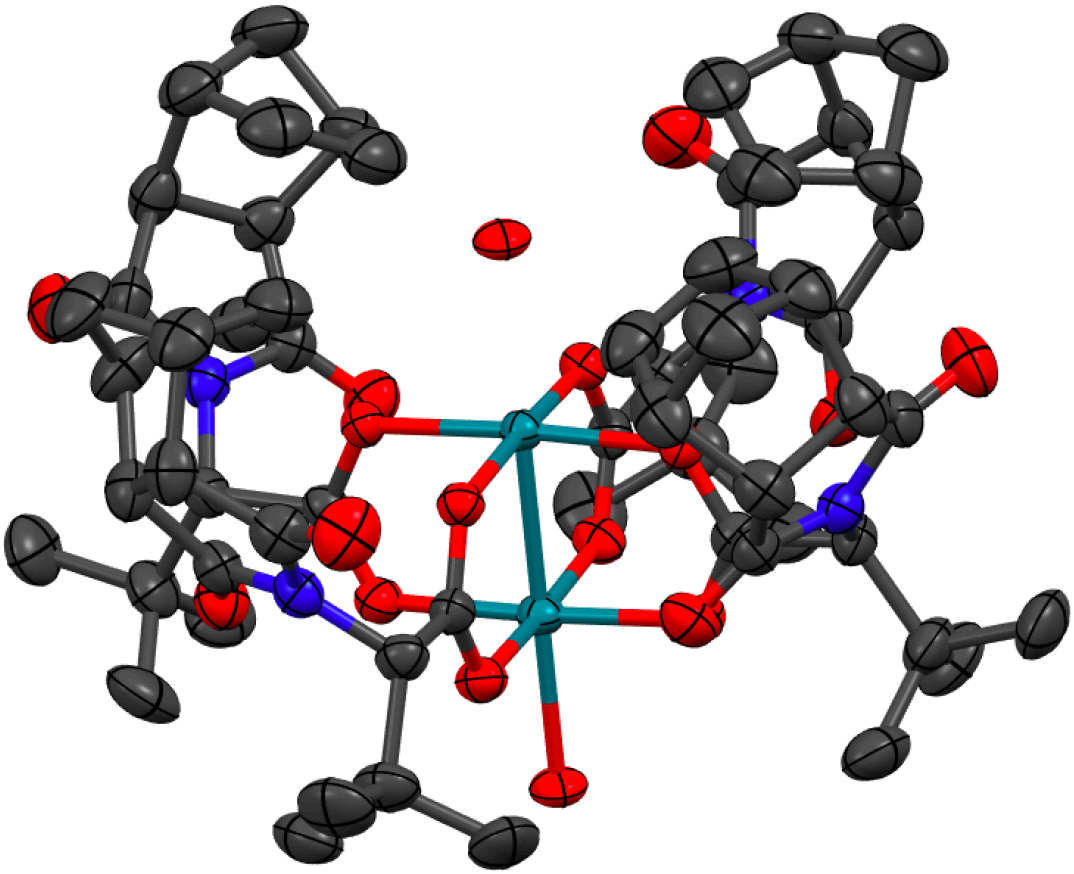


Fig S1. X-ray structure of Rh_2(*S*-BHTL)$_4$ (50% probability ellipsoids)