CHEMISTRY
AN ASIAN JOURNAL

Supporting Information

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Highly Enantioselective Reactions of Configurationally Labile Epimeric Diamine Complexes of Lithiated *S*-Benzyl Thiocarbamates

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NMR analyses

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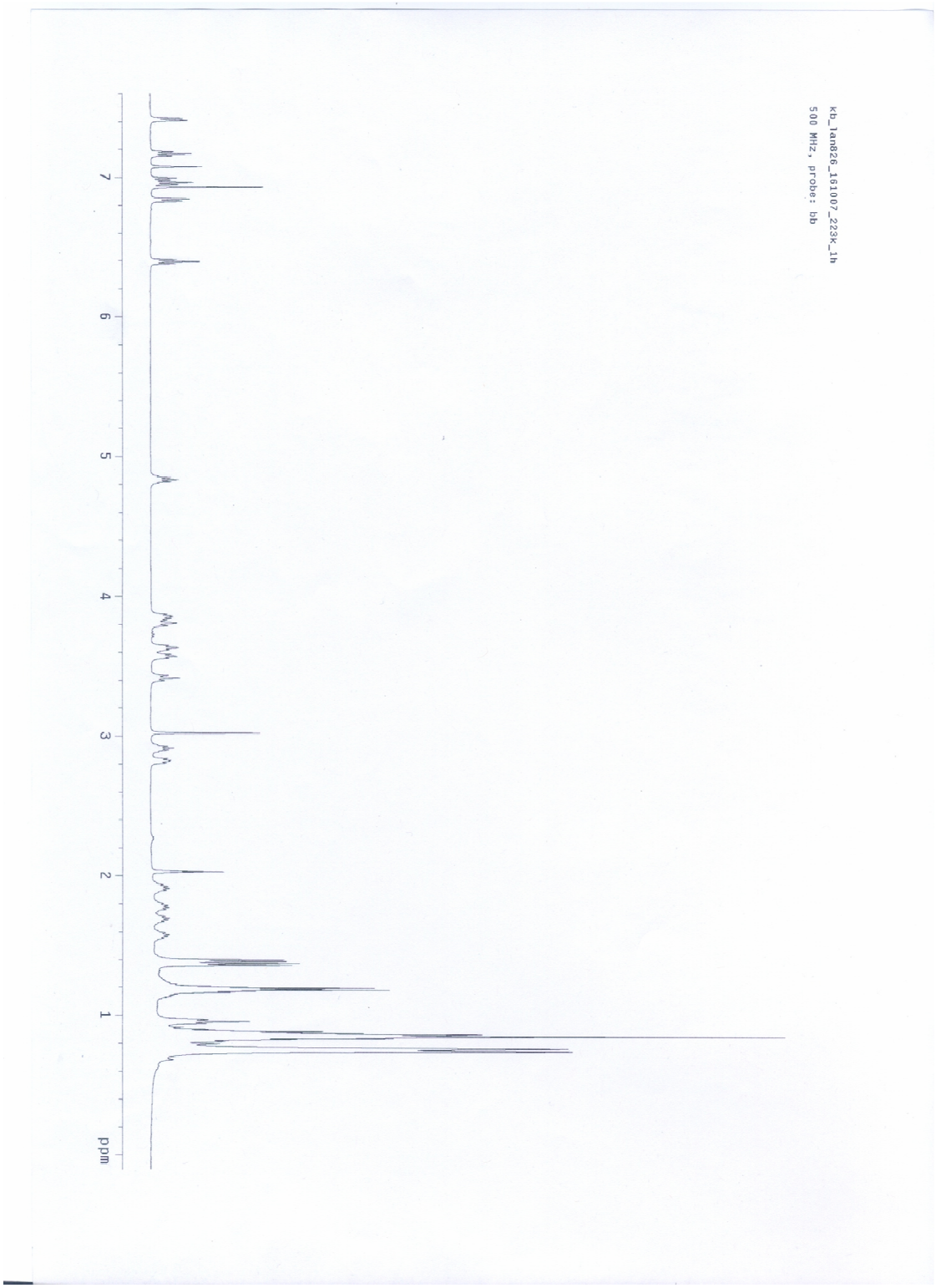
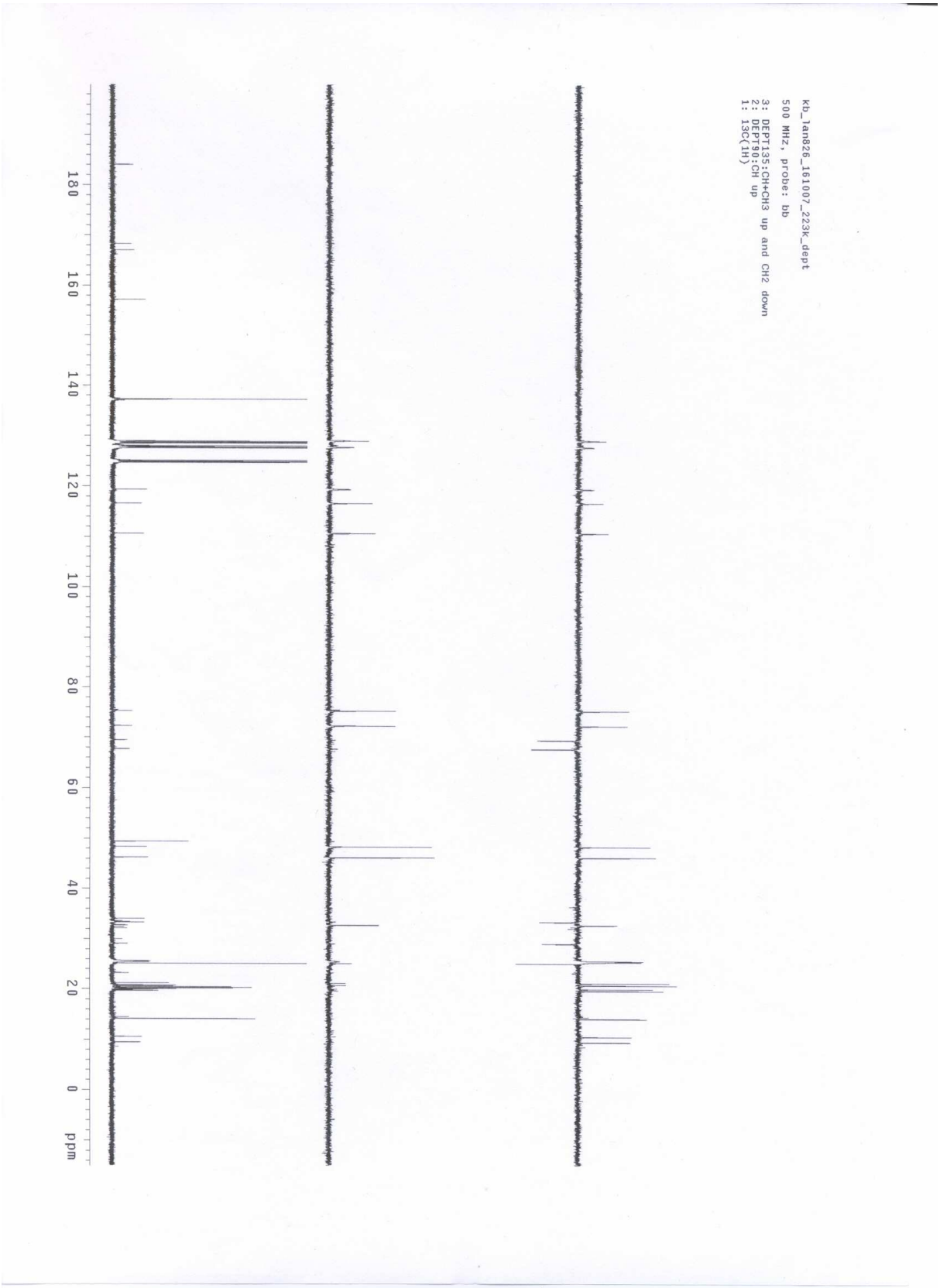
X-ray crystal structure analyses

Important NMR spectra of the lithium complexes (R_C)-16•18:

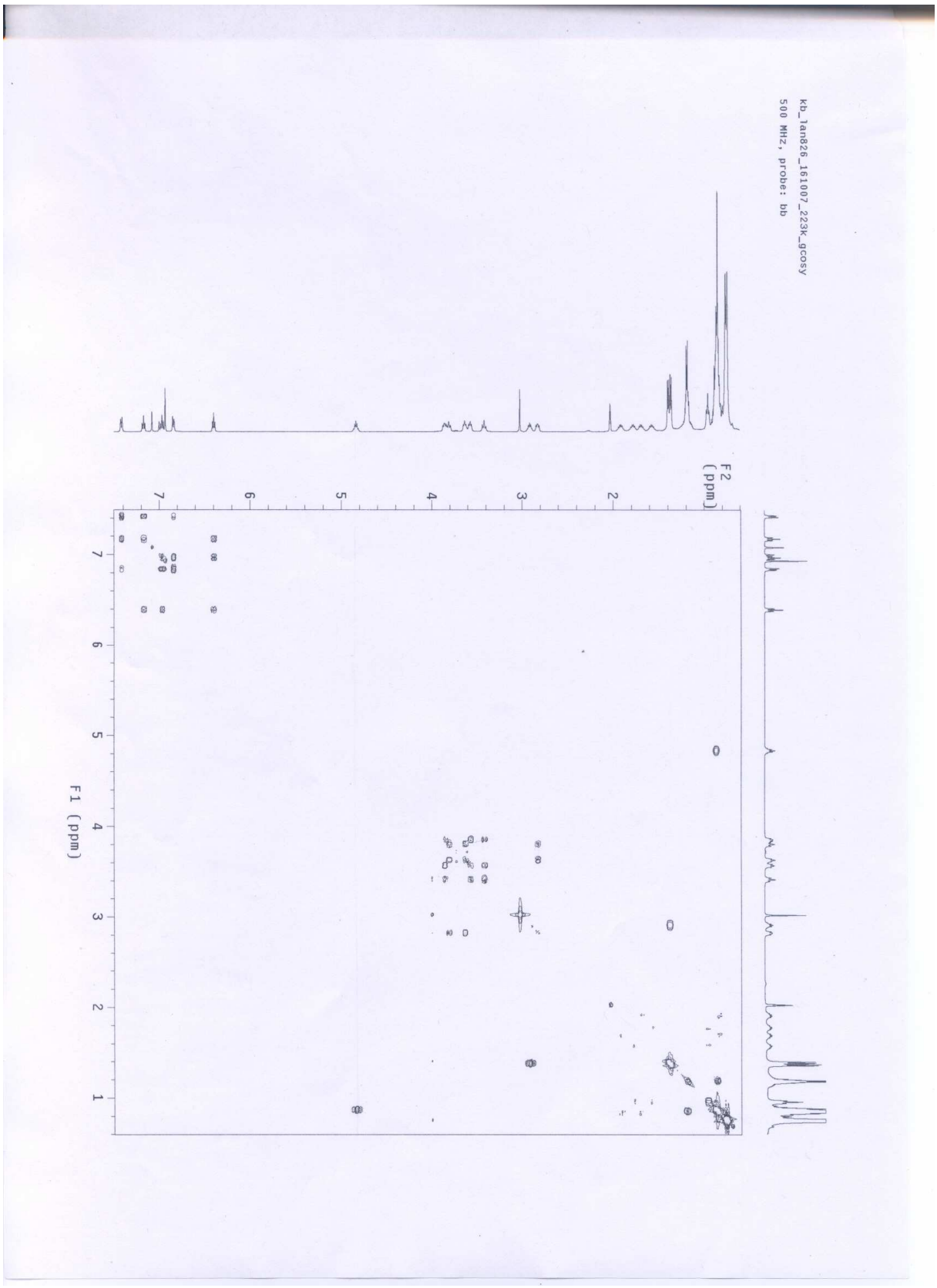
^{1}H NMR spectrum of (R_C)-**16•18** after epimerisation at −50 °C (500 MHz, toluene-d_8):



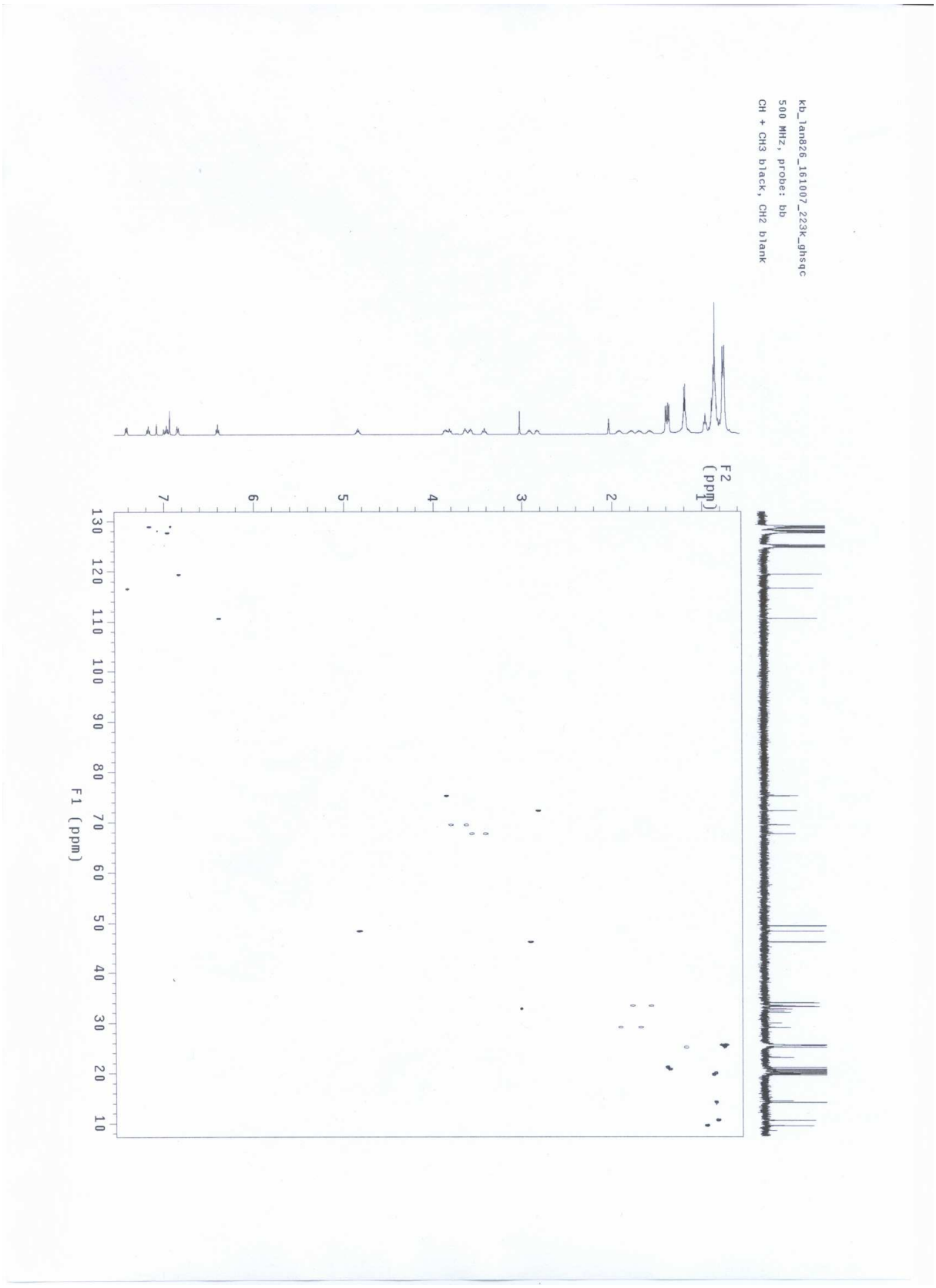
^{13}C NMR spectrum of (R_C)-**16•18** after epimerisation at −50 °C (500 MHz, toluene-d_8):



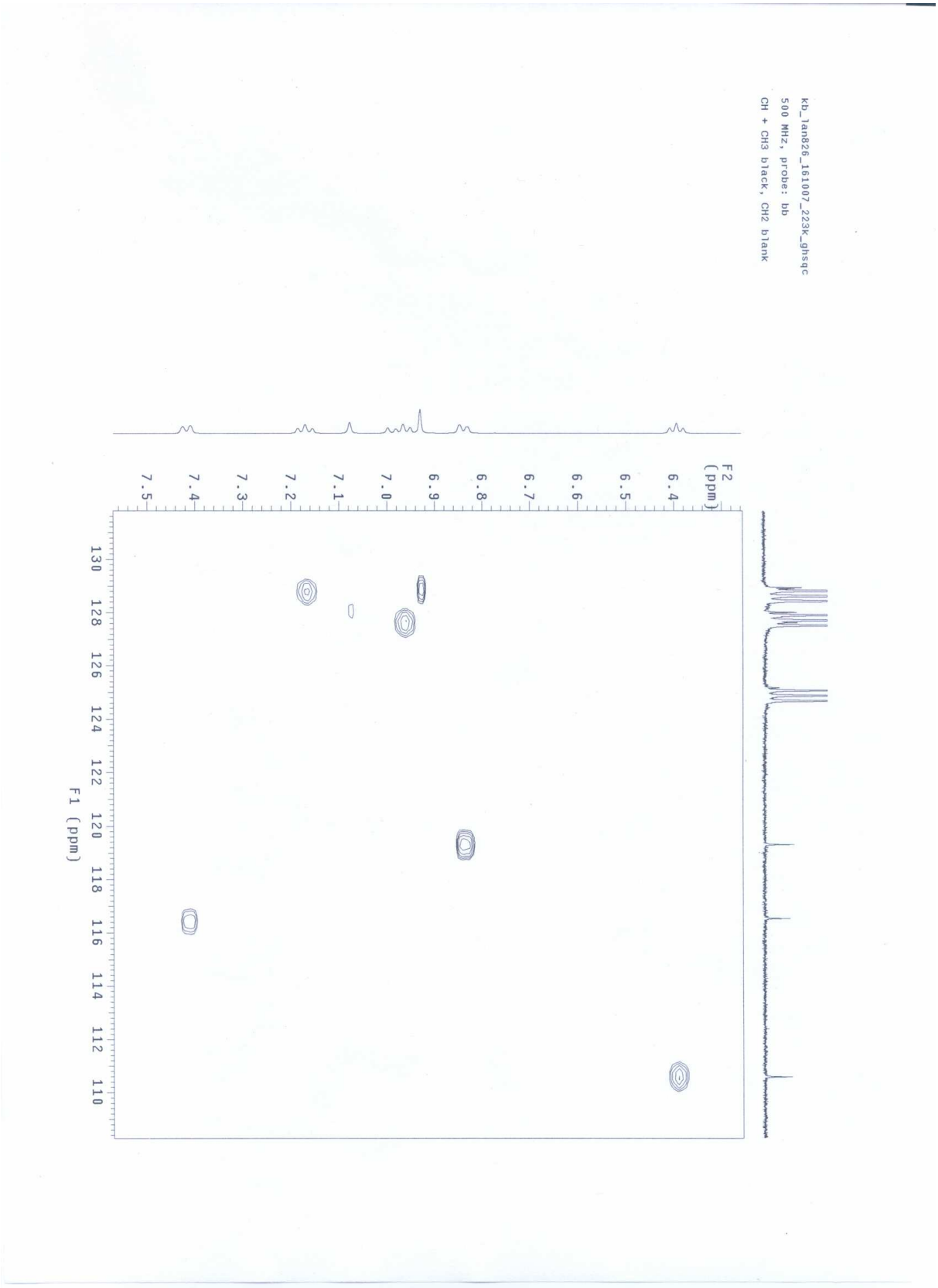
gcosy NMR spectrum of (R_C)-**16•18** after epimerisation at −50 °C (500 MHz, toluene-d_8):



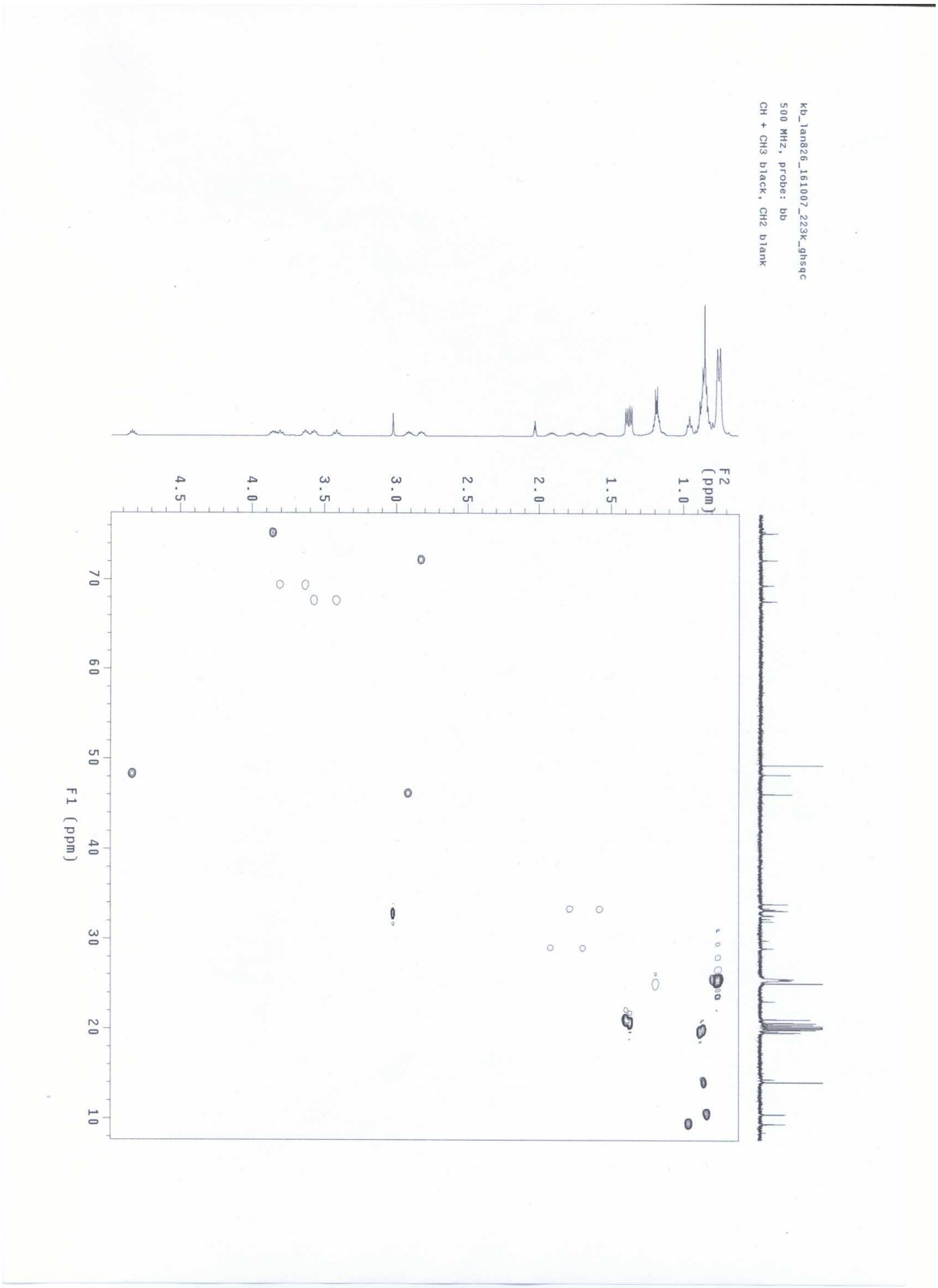
ghsqc NMR spectrum (full) of (R_C)-**16•18** after epimerisation at −50 °C (500 MHz, toluene-d_8):



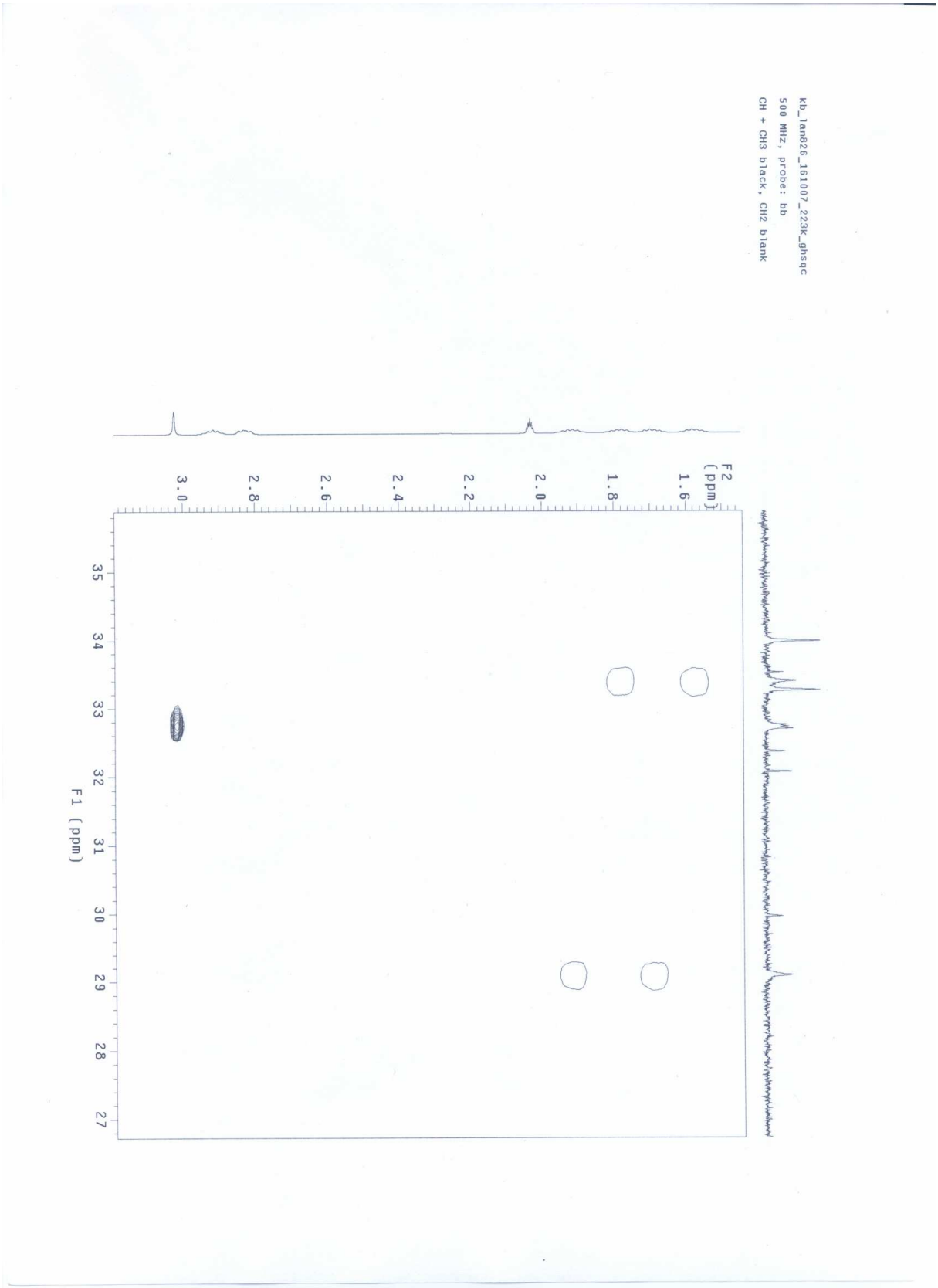
ghsqc NMR spectrum (zoom 1) of (R_C)-**16•18** after epimerisation at −50 °C (500 MHz, toluene-d_8):



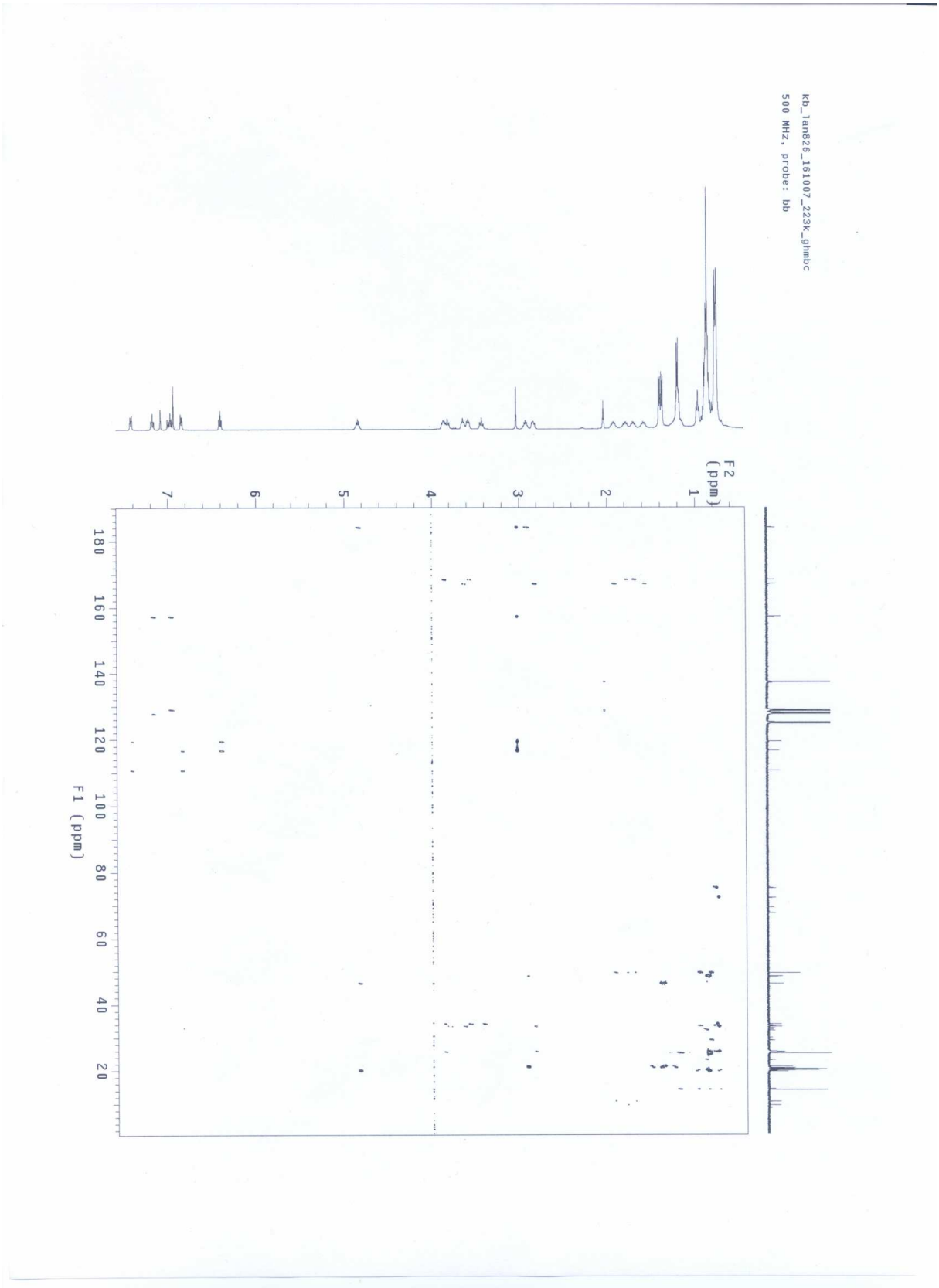
ghsqc NMR spectrum (zoom 2) of (R_C)-**16•18** after epimerisation at −50 °C (500 MHz, toluene-d_8):



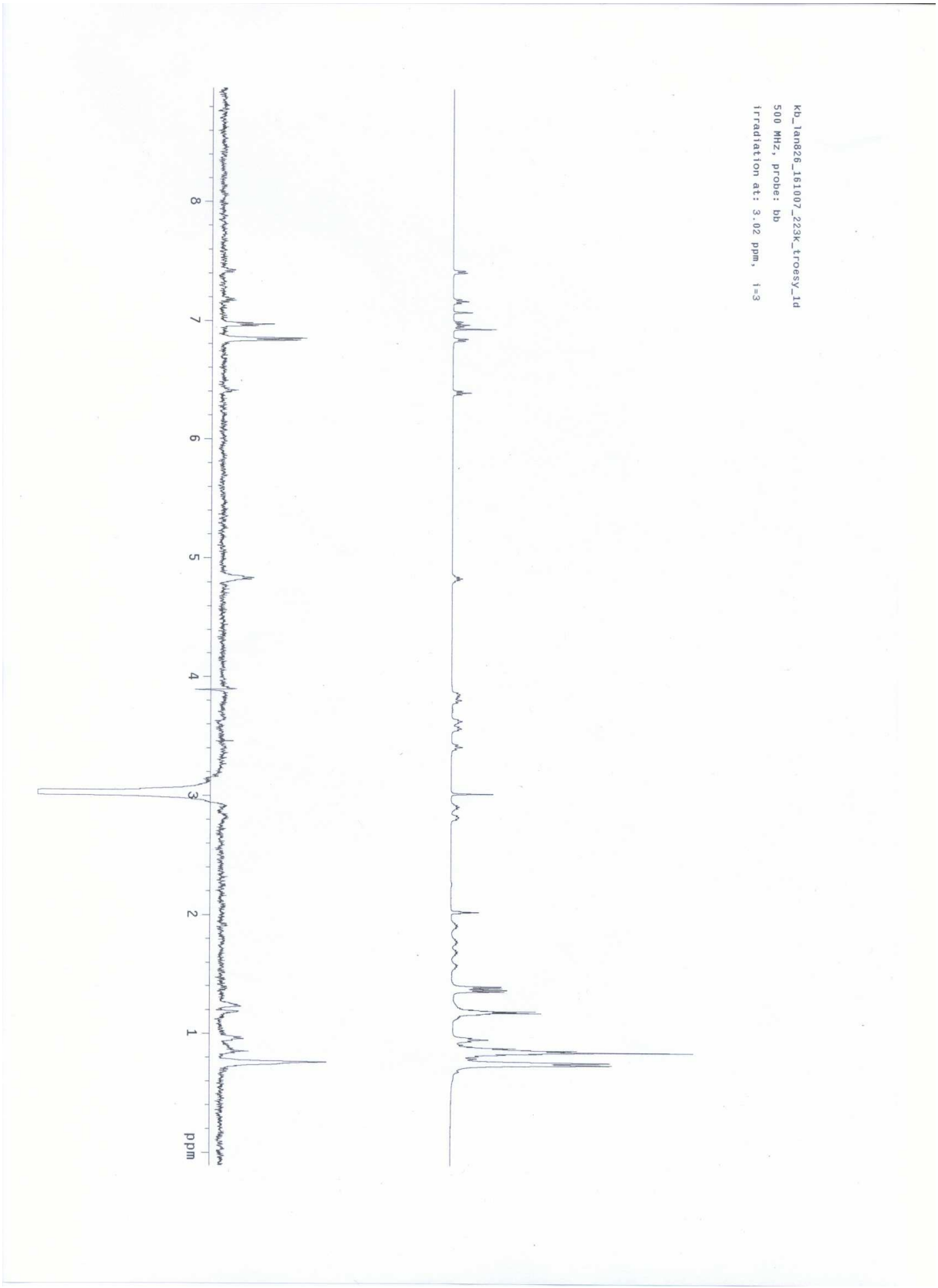
ghsqc NMR spectrum (zoom 3) of (R_C)-**16•18** after epimerisation at −50 °C (500 MHz, toluene-d_8):



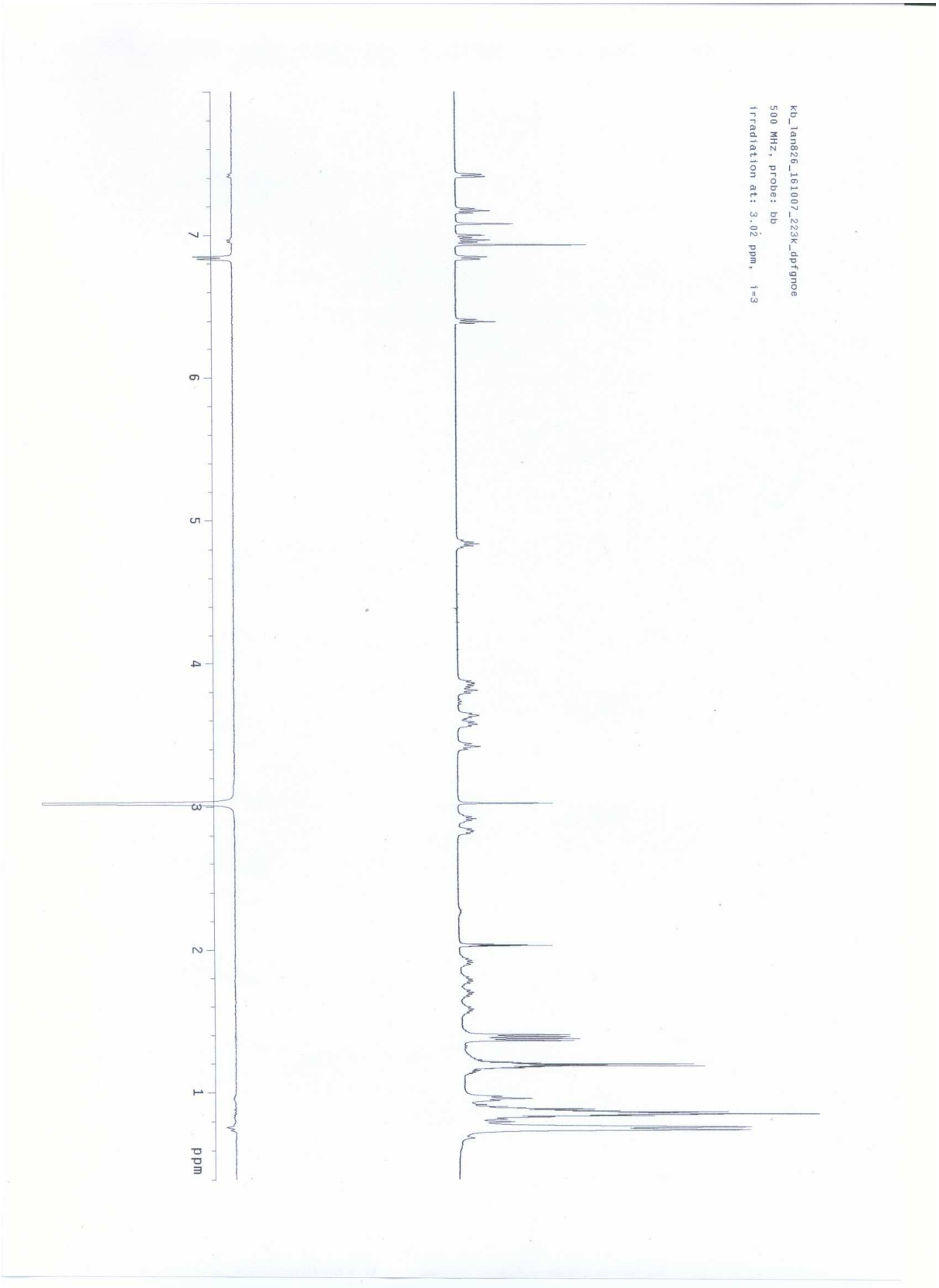
ghmbc NMR spectrum of (R_C)-**16•18** after epimerisation at −50 °C (500 MHz, toluene-d_8):



roesy-1d NMR spectrum of (R_C)-**16•18** after epimerisation at −50 °C (500 MHz, toluene-d_8):



NOE experiment[1] of (R_C)-**16•18** after epimerisation at −50 °C (500 MHz, toluene-d_8); selective irradiation on the signal of the benzylic proton (3.02 ppm):



[1] DPFGSE-NOE: K. Scott, J. Stonehouse, J. Keeler, T.-L. Hwang, A. J. Shaka, *J. Am. Chem. Soc*. **1995**, *117*, 4199-4200.

^{1}H NMR of H-3 of the minor epimer (S_C)-16•18, indicating the epimerisation process over time (interval 5 min.) by decaying: