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Primary Cycloalkylimines

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Electronic Supplementary Information

Contents

General. NMR spectra were recorded on Bruker Avance 400 MHz spectrometer. Spectra were recorded in deuterochloroform referenced to $CHCl_3$ (^1H, 7.26 ppm) or $CDCl_3$ (^{13}C, 77.16 ppm), or CD_2Cl_2 (^1H, 5.33 ppm) or CD_2Cl_2 (^{13}C, 53.5 ppm),. Chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hertz. The following abbreviations are used to describe multiplicity: s-singlet, d-doublet, q-quadruplet, sept-septet, m-multiplet, and br.-broad. Infrared spectra were recorded with the sample condensed at 77 K on a NaCl window of a homemade cryostat with a Nicolet Avatar 320 FT-IR spectrometer.

Preparation of Imines 1b-1f. Imines **1b**-**1f** were synthesized by vaporization *in vacuo* (0.1 mbar) of the corresponding α-aminonitrile **2b**-**2f** on powdered KOH heated to 90°C. The equipment consisted of a substrate inlet, a reactor (Φ: 3 cm, L: 30 cm) filled in half-section with powdered KOH (28 g, 0.5 mol) and heated to 90 °C, a cold finger filled with liquid nitrogen and a connection to the pump with a valve. The α-aminonitrile (0.2 g) was slowly vaporized on KOH and the formed products were trapped on the cold finger. A cosolvent (0.6 mL) can be added for analysis by NMR spectroscopy. When all the precursor was vaporized, the cold finger was isolated from the vacuum line and dry nitrogen gas was introduced, the liquid nitrogen was flushed under a stream of air, and products and solvent were collected in the NMR tube placed at the base of the cold finger. The presence of a few percent or traces of the corresponding ketone with the very hygroscopic cycloalkylimines cannot be avoided in the NMR tubes. In the case of the very reactive compound **1b**, due to the presence of butanenitrile isomer and trimer, the purity did not exceed 75%.

Hexahydro-2,4,6-tricyclobutyl-1,3,5-triazine 3b. Yield: 76 %. ^1H NMR ($CDCl_3$, 400 MHz , 296 K) δ 1.46 (s brd, 3H, NH) ; 1.42 (s brd, 4H, CH_2) ; 1.82 (tt, 6H, $^3J_{HH}$ = 7.0 Hz, $CH_2C{=}N$) ; 2.02 (t, 12H, $^3J_{HH}$ = 7.0 Hz, $CH_2C{=}N$). ^{13}C NMR ($CDCl_3$, 100 MHz, 296 K) δ 14.5 (t, $^1J_{CH}$ = 135.5 Hz, CH_2), 36.5 ($^1J_{CH}$ = 135.3 Hz, $\underline{C}H_2CN$), 70.1 (s, N-C-N). HRMS. $[M+H]^+$ ($C_{12}H_{22}N_3$). m/z (th.): 208.18082. m/z (found): 208.1810.

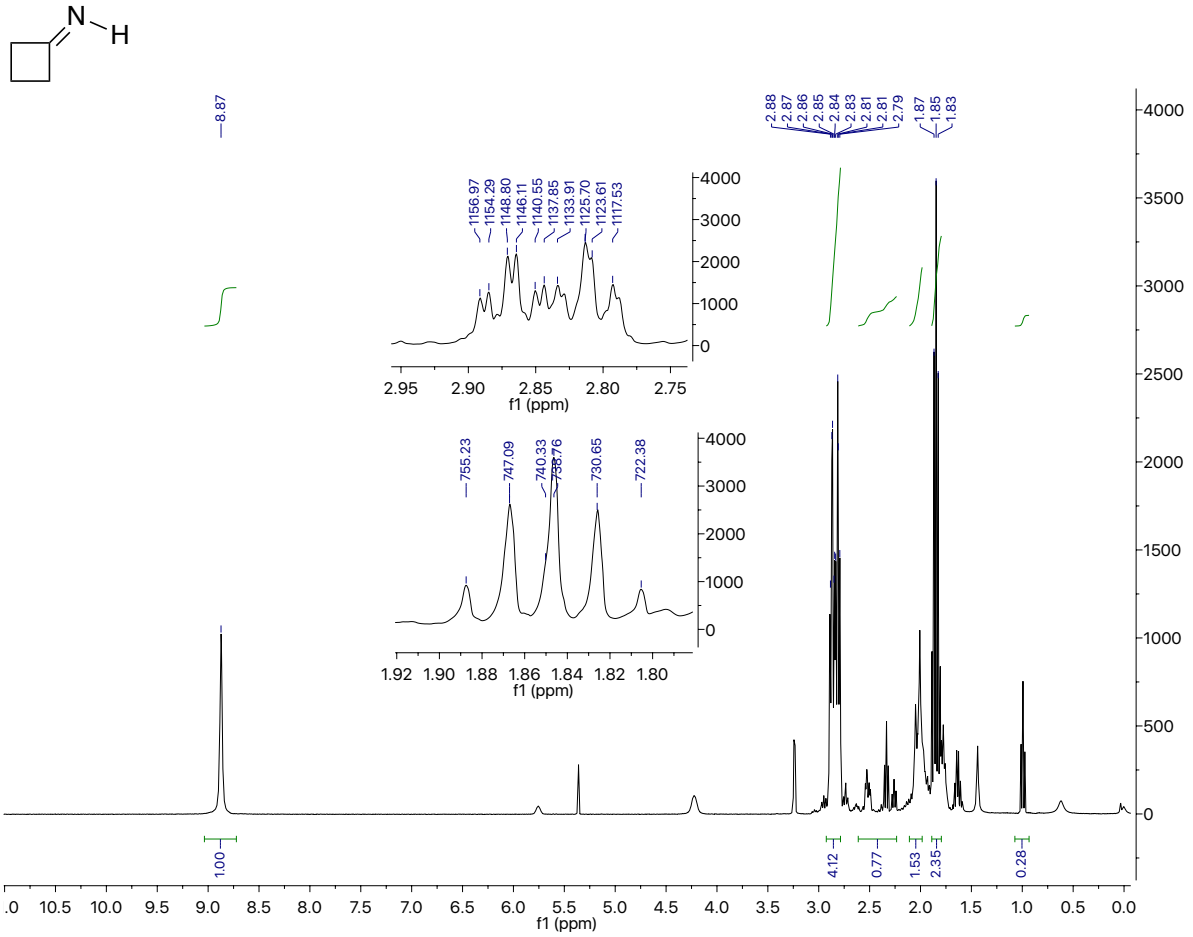


Figure S1. ^{1}H NMR spectrum (CD_2Cl_2, 193 K) of imine **1b** and n-butanenitrile.

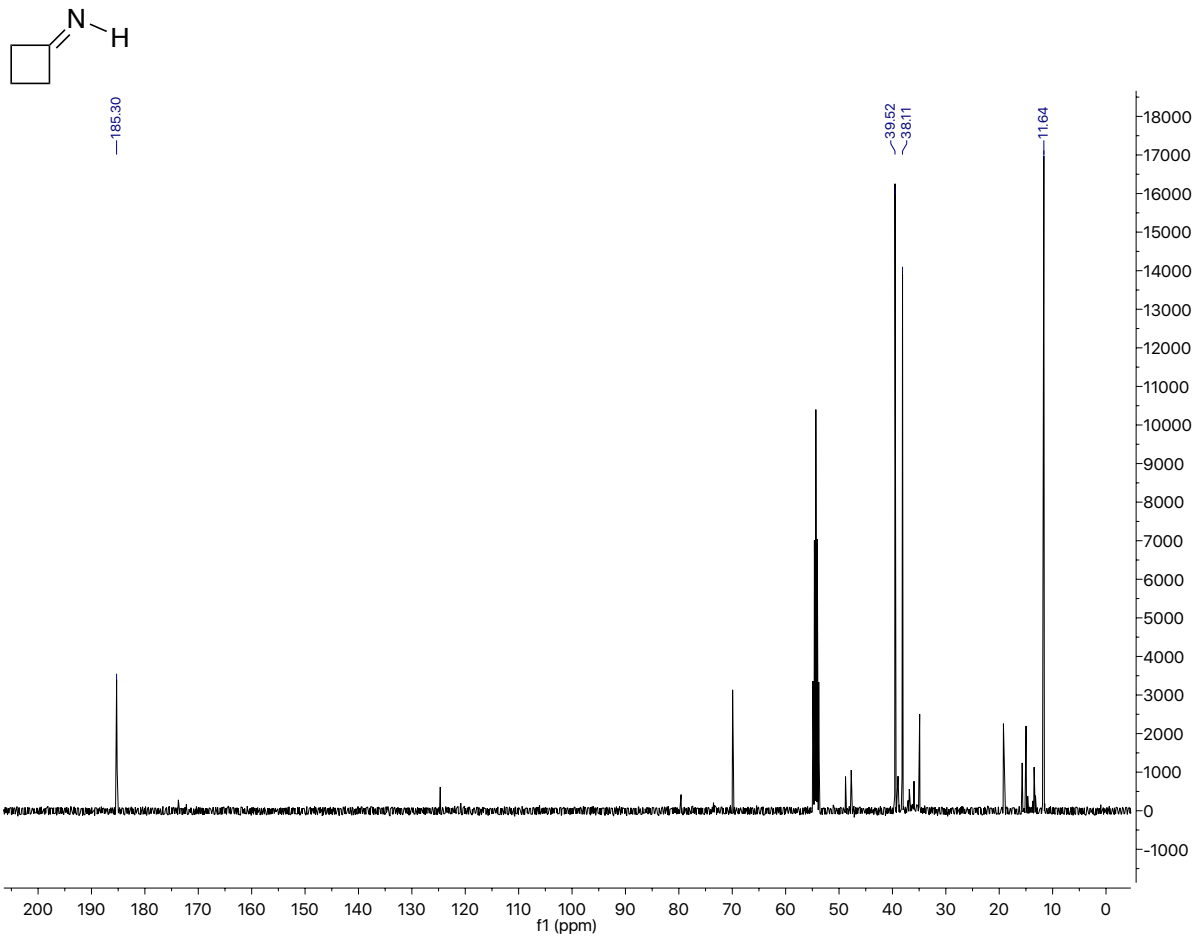


Figure S2. ^{13}C NMR spectrum (CD_2Cl_2, 193 K) of imine **1b** and n-butanenitrile.

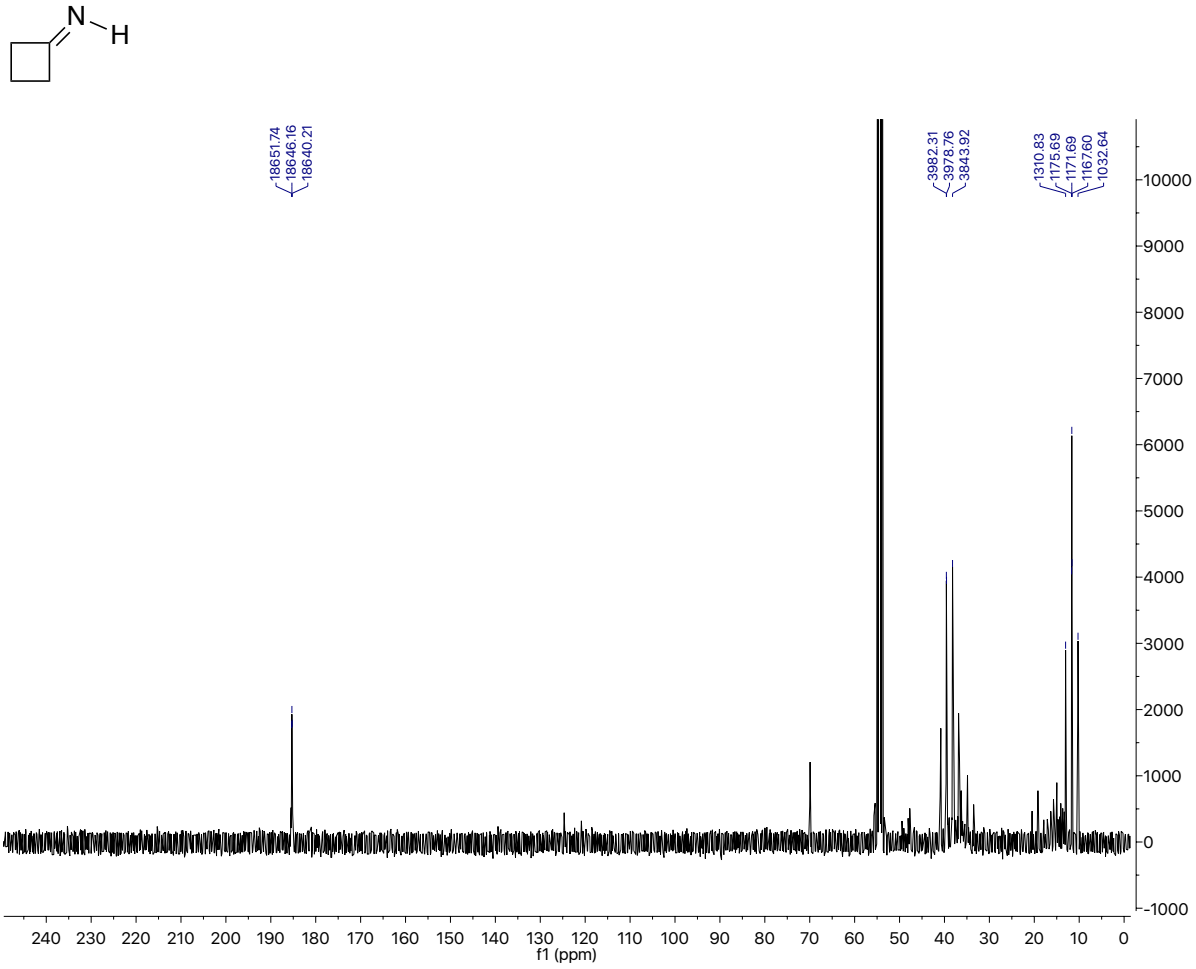
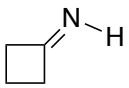


Figure S3. ^{1}H-coupled ^{13}C NMR spectrum (CD_2Cl_2, 193 K) of imine **1b**.



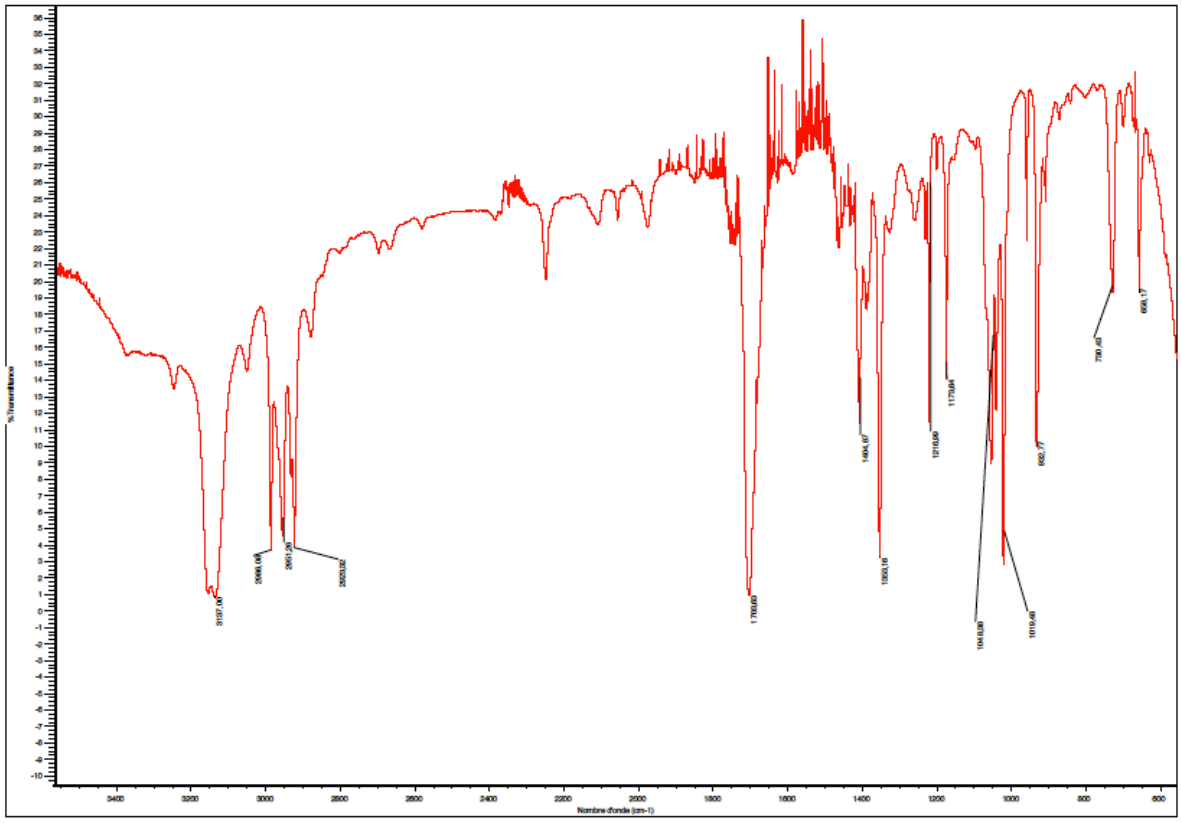


Figure S4. Infrared spectrum (film, 77K) of imine **1b** with small amounts of butanenitrile.

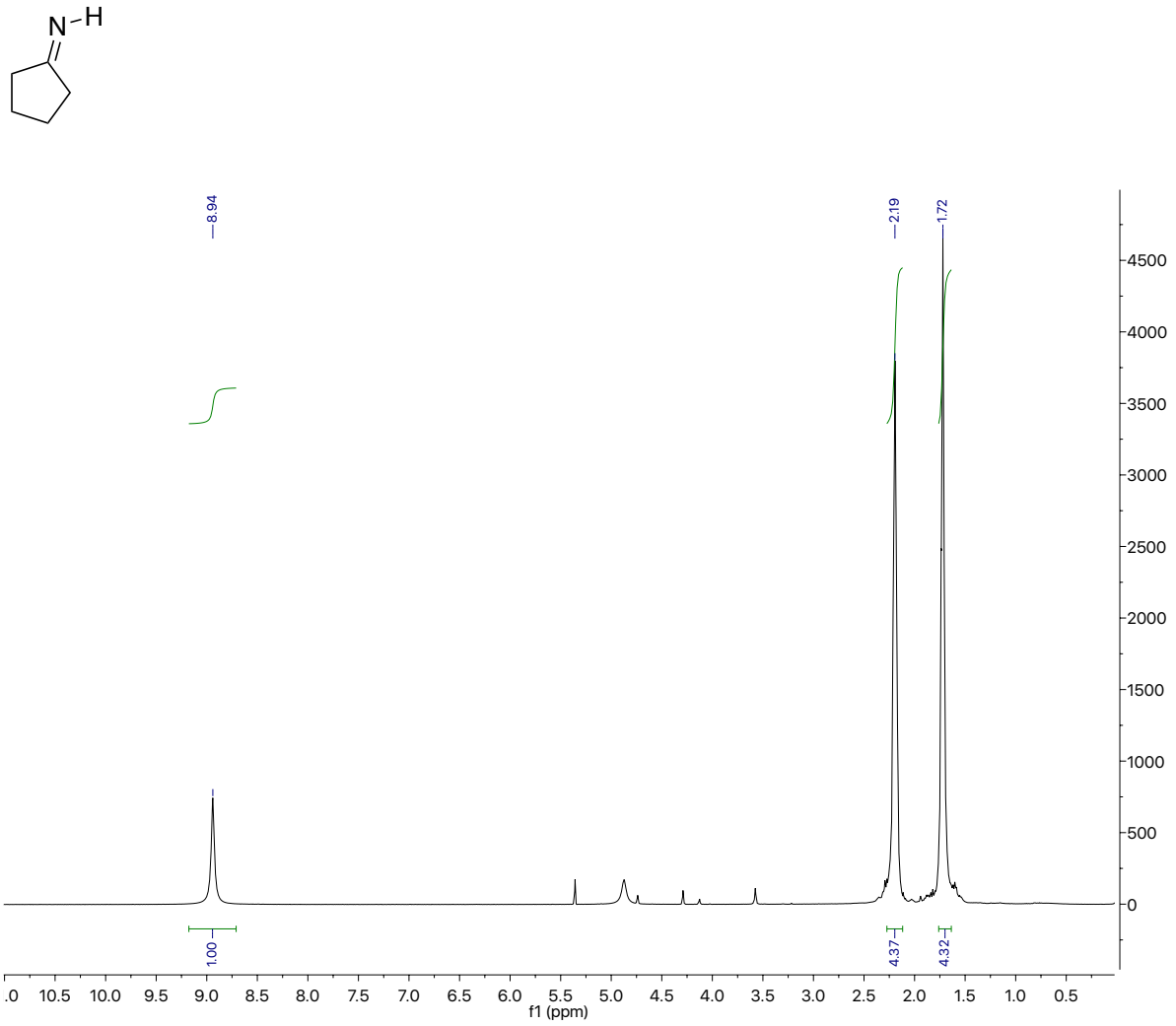


Figure S5. ^{1}H NMR spectrum (CD_2Cl_2, 193 K) of imine **1c.**

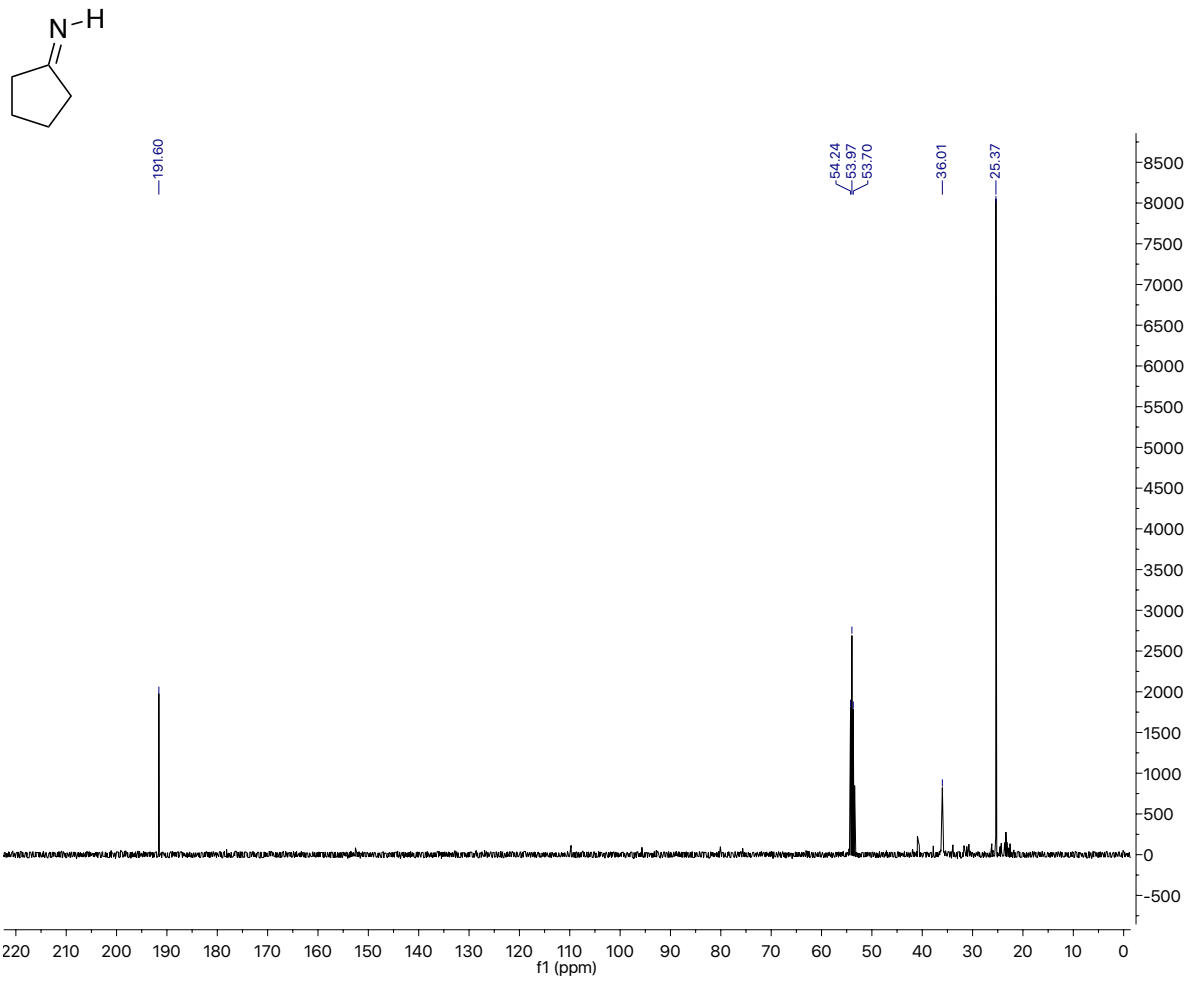
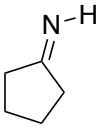


Figure S6. ^{13}C NMR spectrum (CD_2Cl_2, 296 K) of imine **1c.**



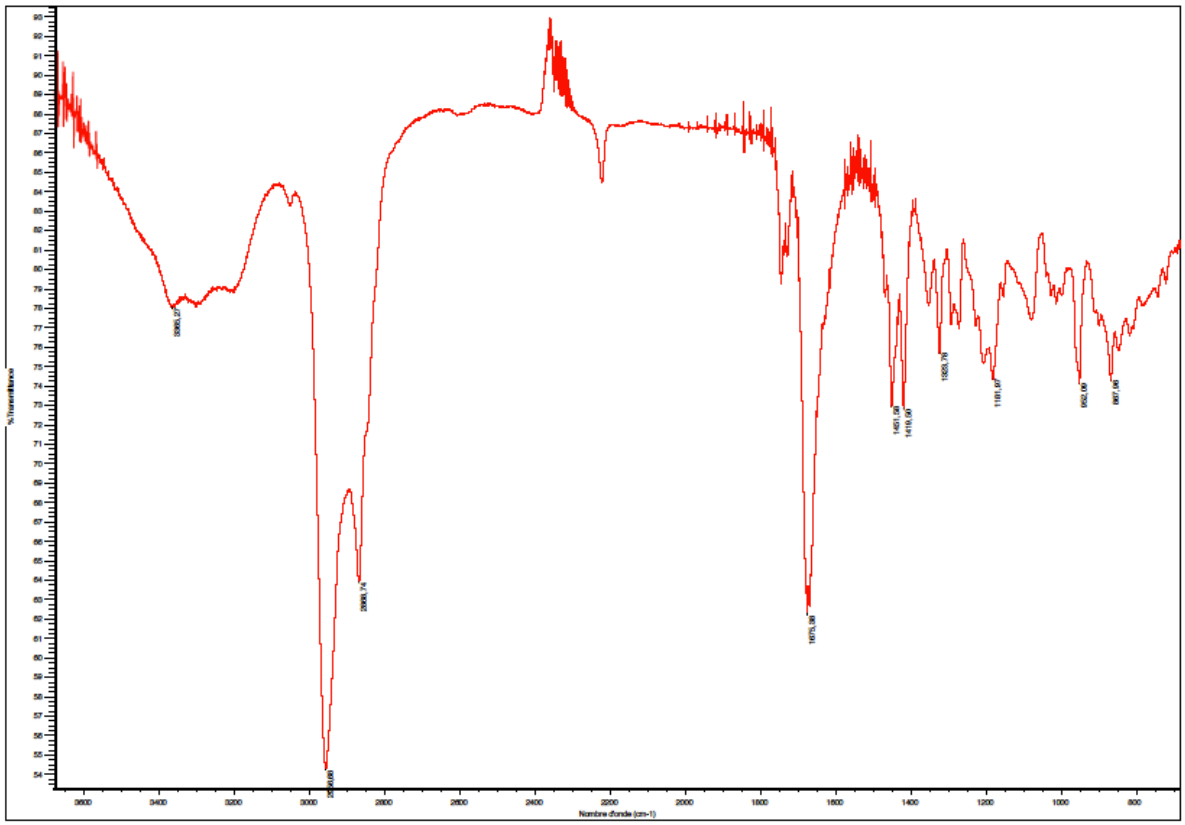


Figure S7. Infrared spectrum (film) of imine **1c.**

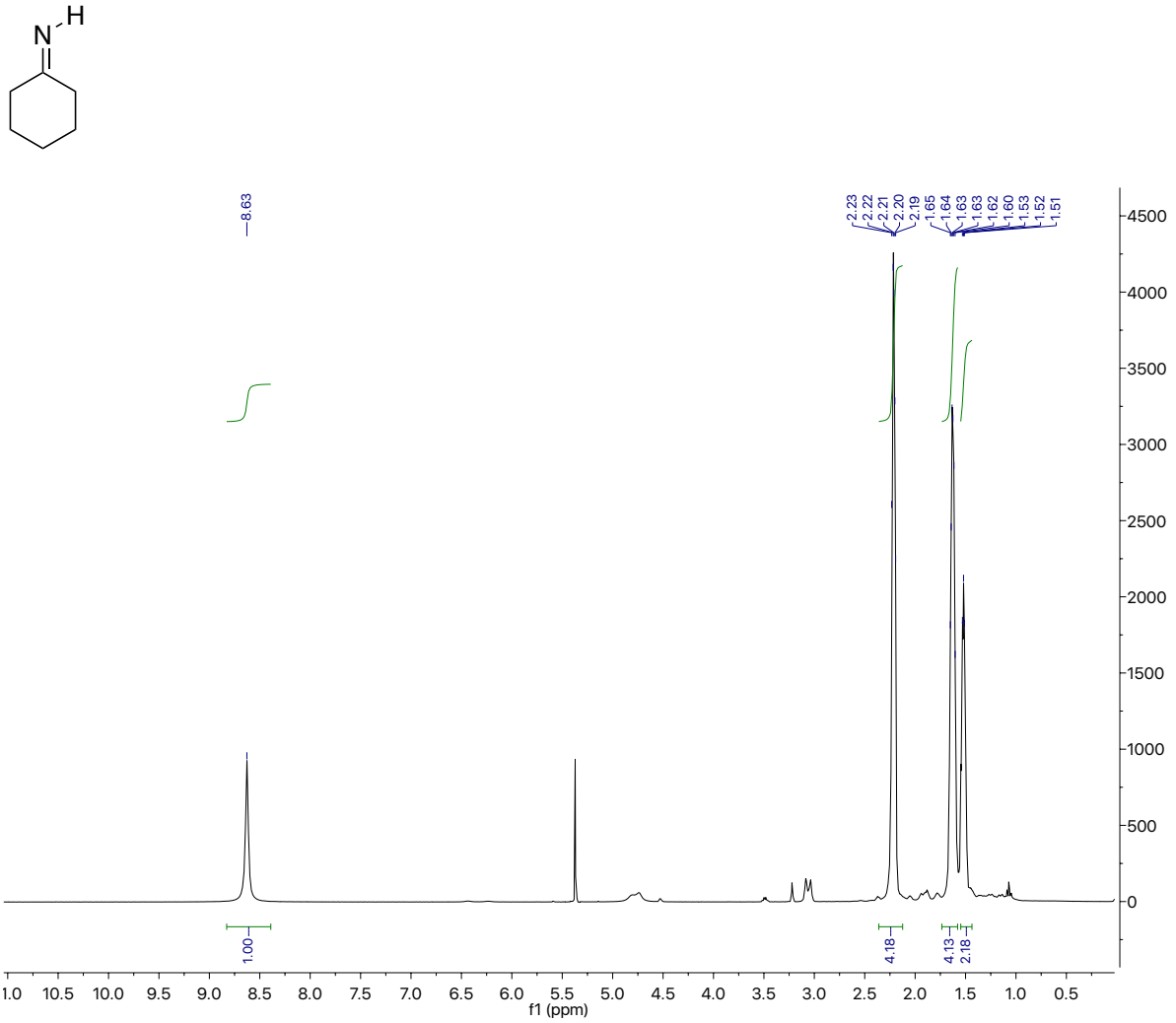


Figure S8. ^{1}H NMR spectrum (CD_2Cl_2, 193 K) of Imine **1d.**

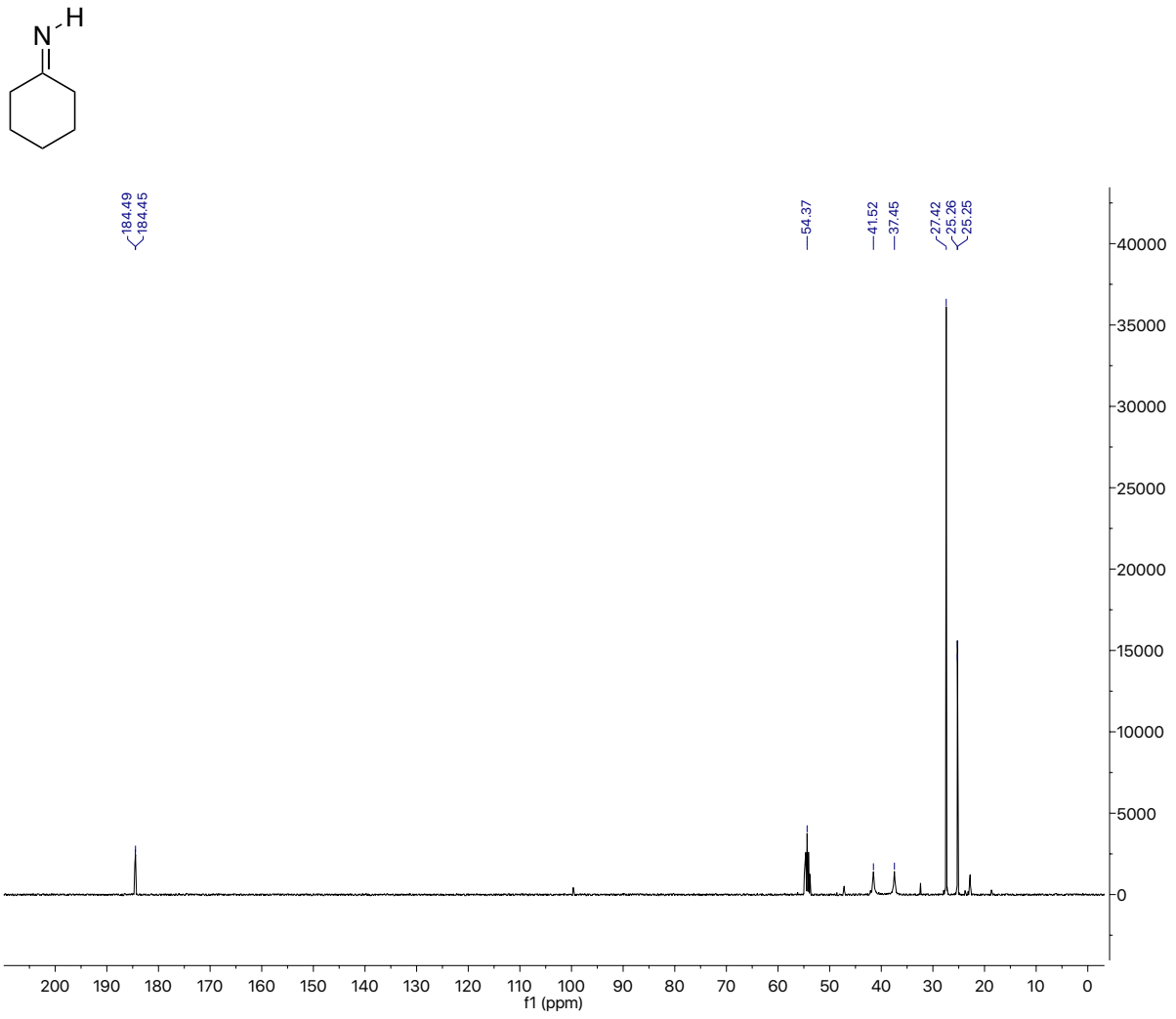
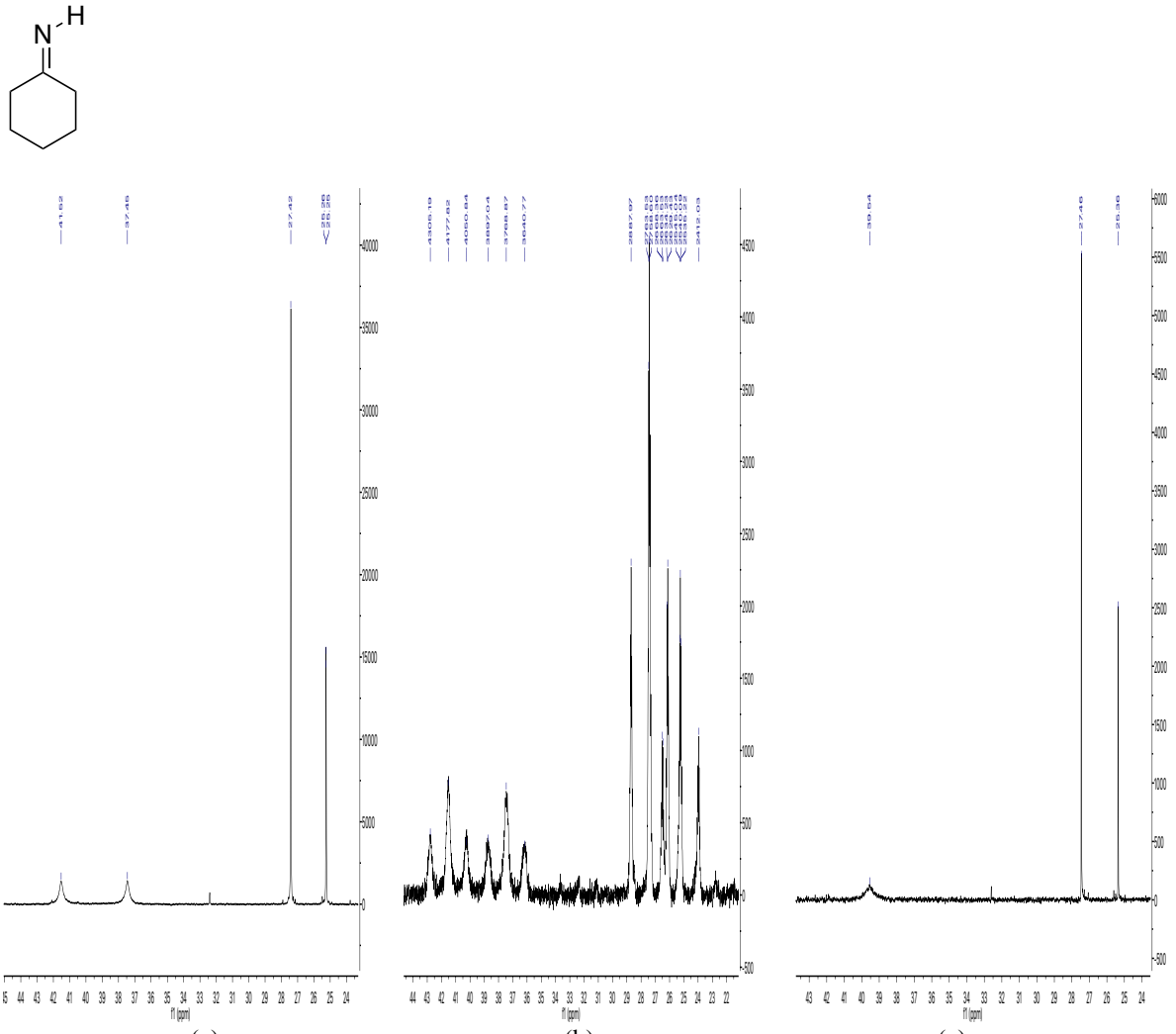
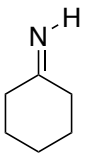


Figure S9. ^{13}C NMR spectrum (CD_2Cl_2, 193 K) of Imine **1d.**



(a) (b) (c)

Figure S10. Imine **1d** (CD_2Cl_2): (a) ^{1}H-decoupled ^{13}C NMR spectrum (193 K). (b) ^{1}H-coupled ^{13}C NMR spectrum (193 K). (c) ^{1}H-decoupled ^{13}C NMR spectrum (273K).



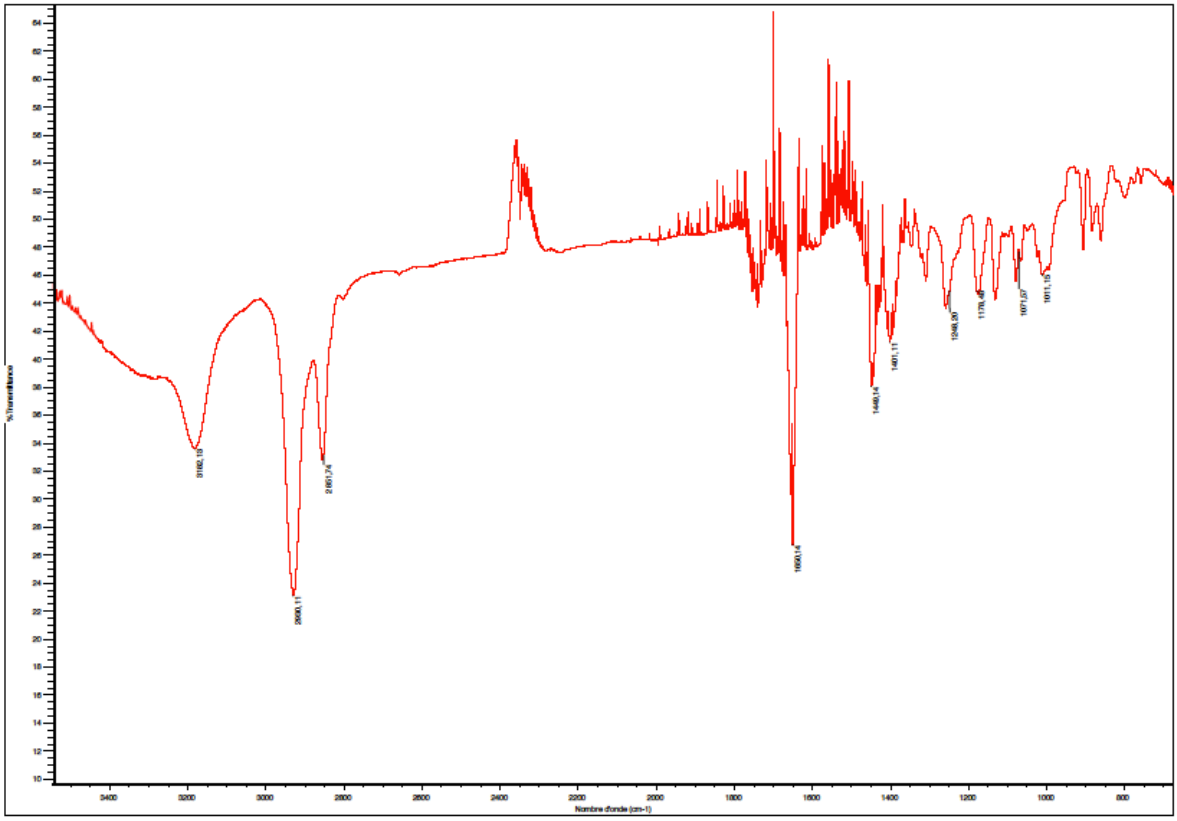


Figure S11. Infrared Spectrum (film, 77 K) of imine **1d**.

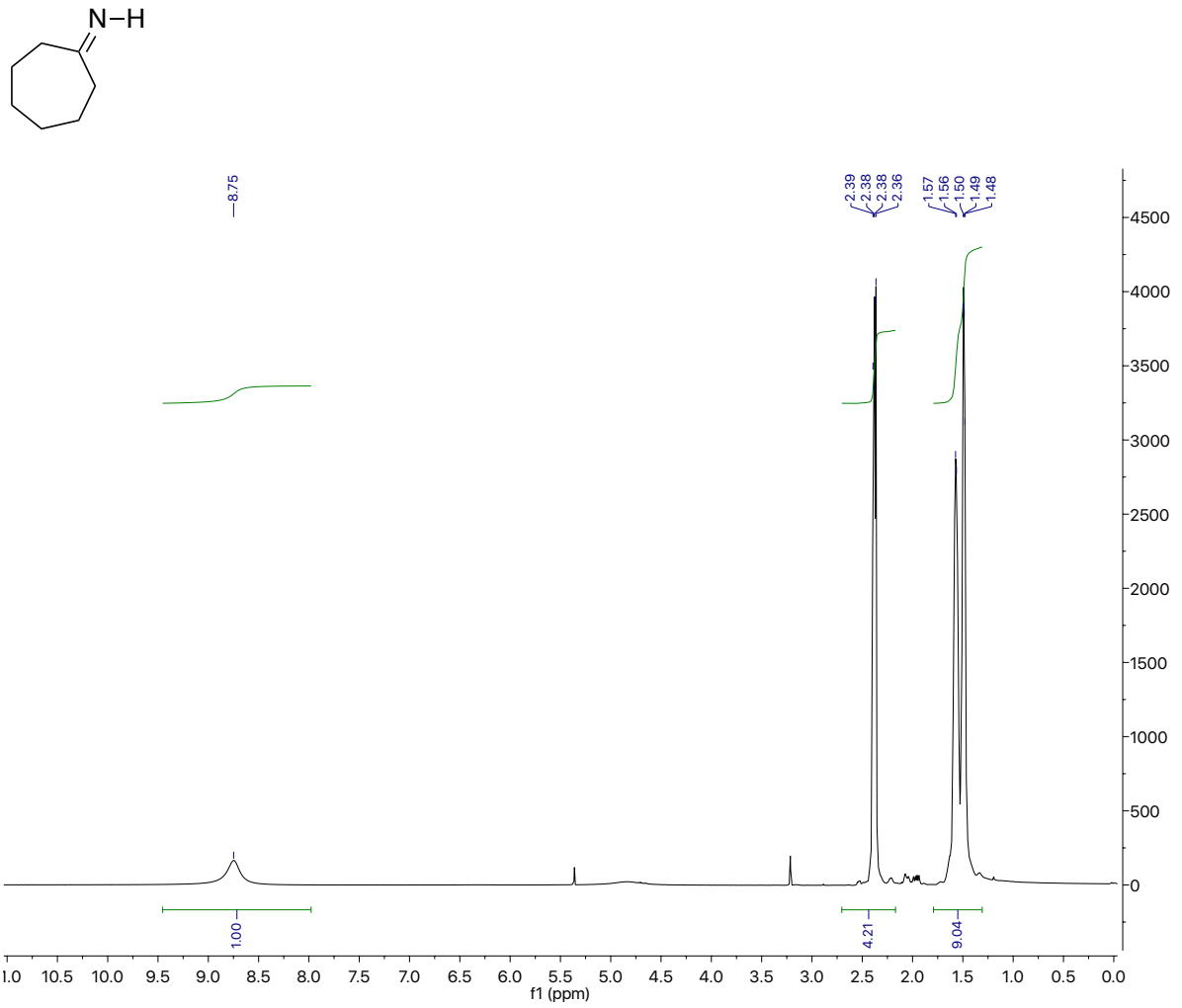


Figure S12. ^{1}H NMR (CD_2Cl_2, 193 K) of imine **1e.**

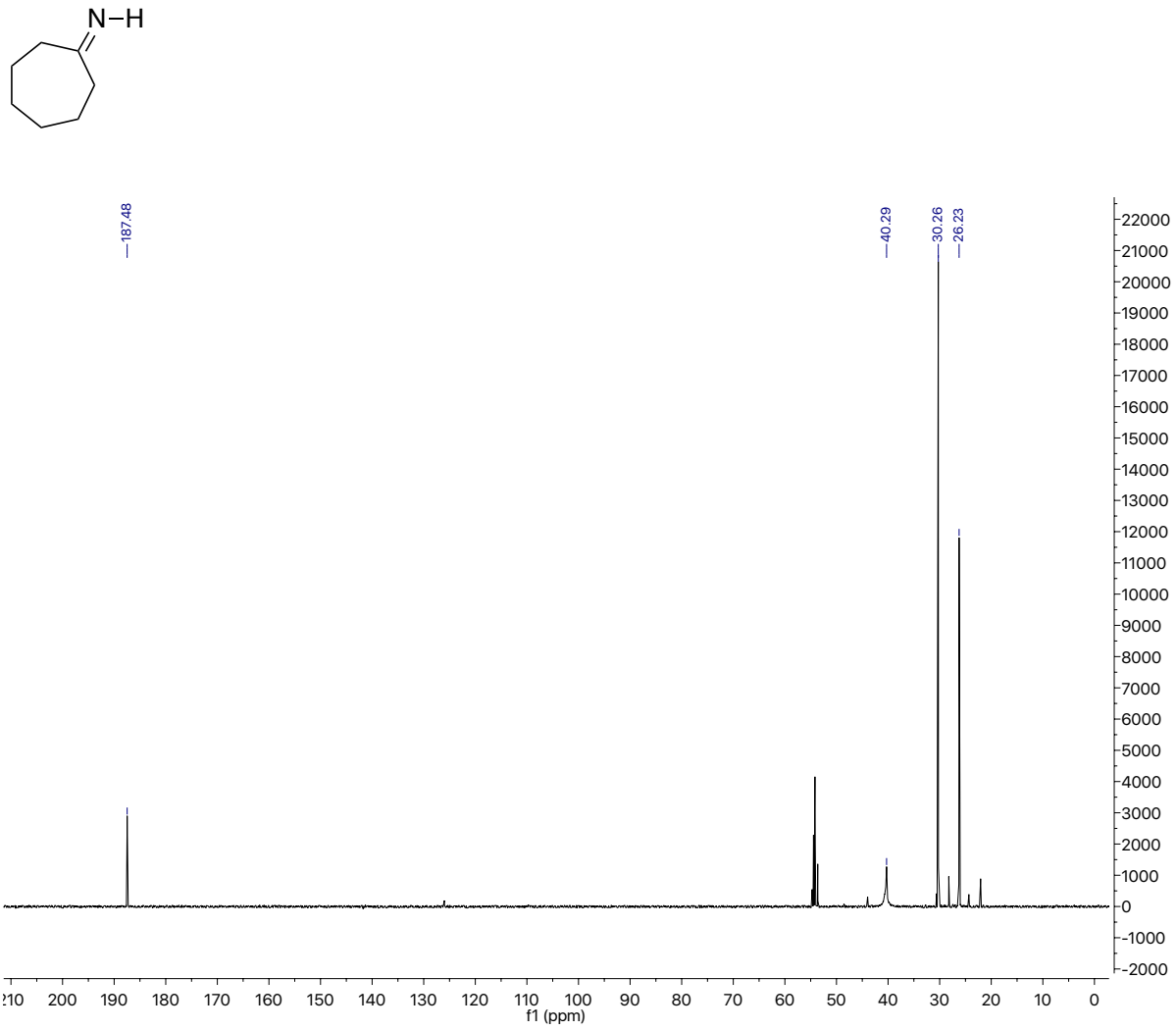
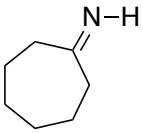


Figure S13. ^{13}C NMR spectrum (CD_2Cl_2, 193 K) of imine **1e.**



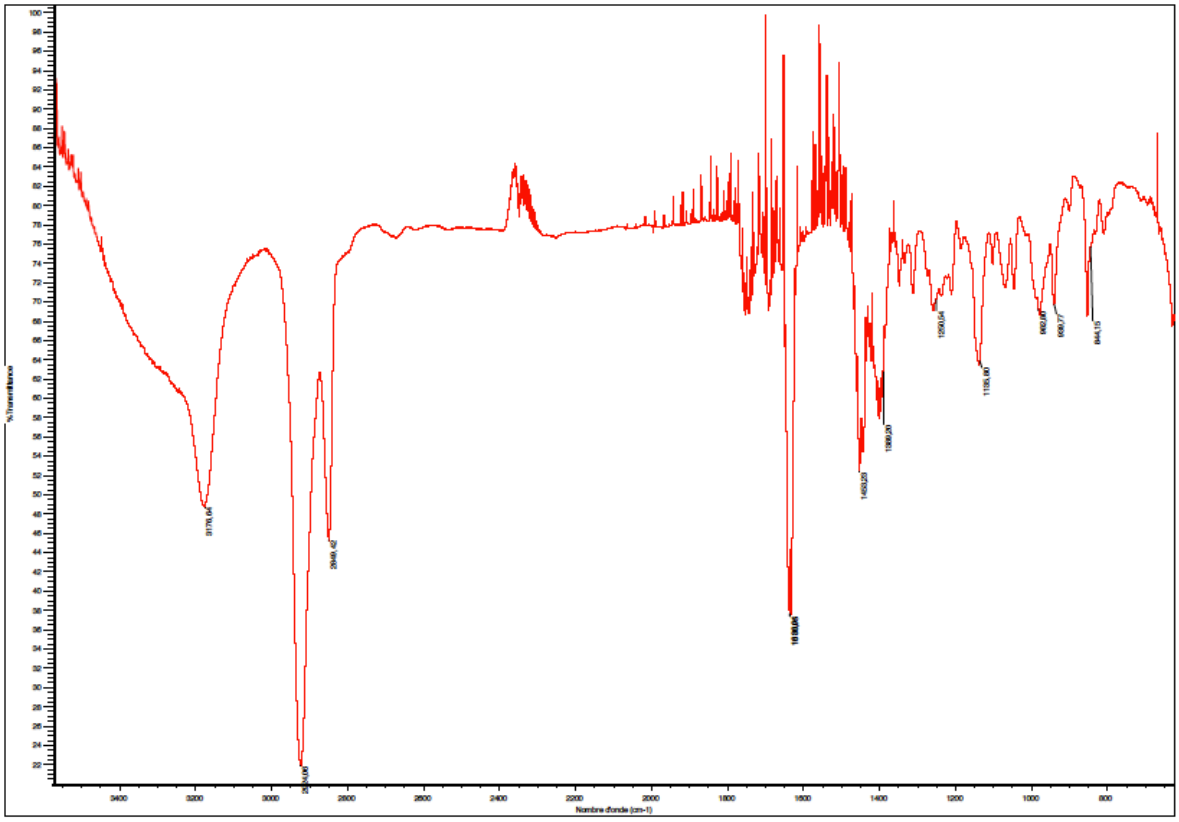


Figure S14. Infrared spectrum (film 77K) of imine **1e.**

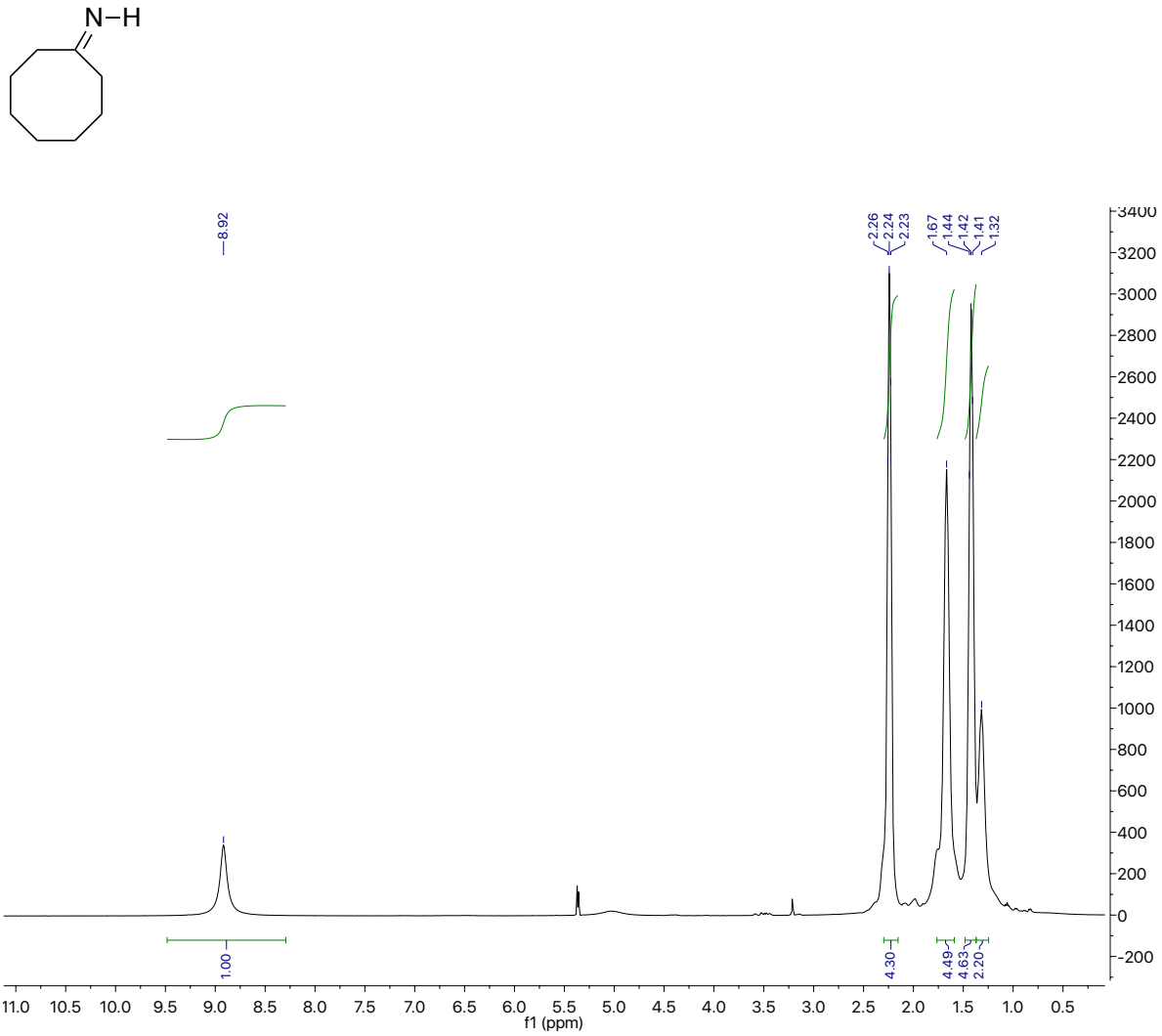


Figure S15. ^{1}H NMR spectrum (CD_2Cl_2, 193 K) of Imine **1f.**

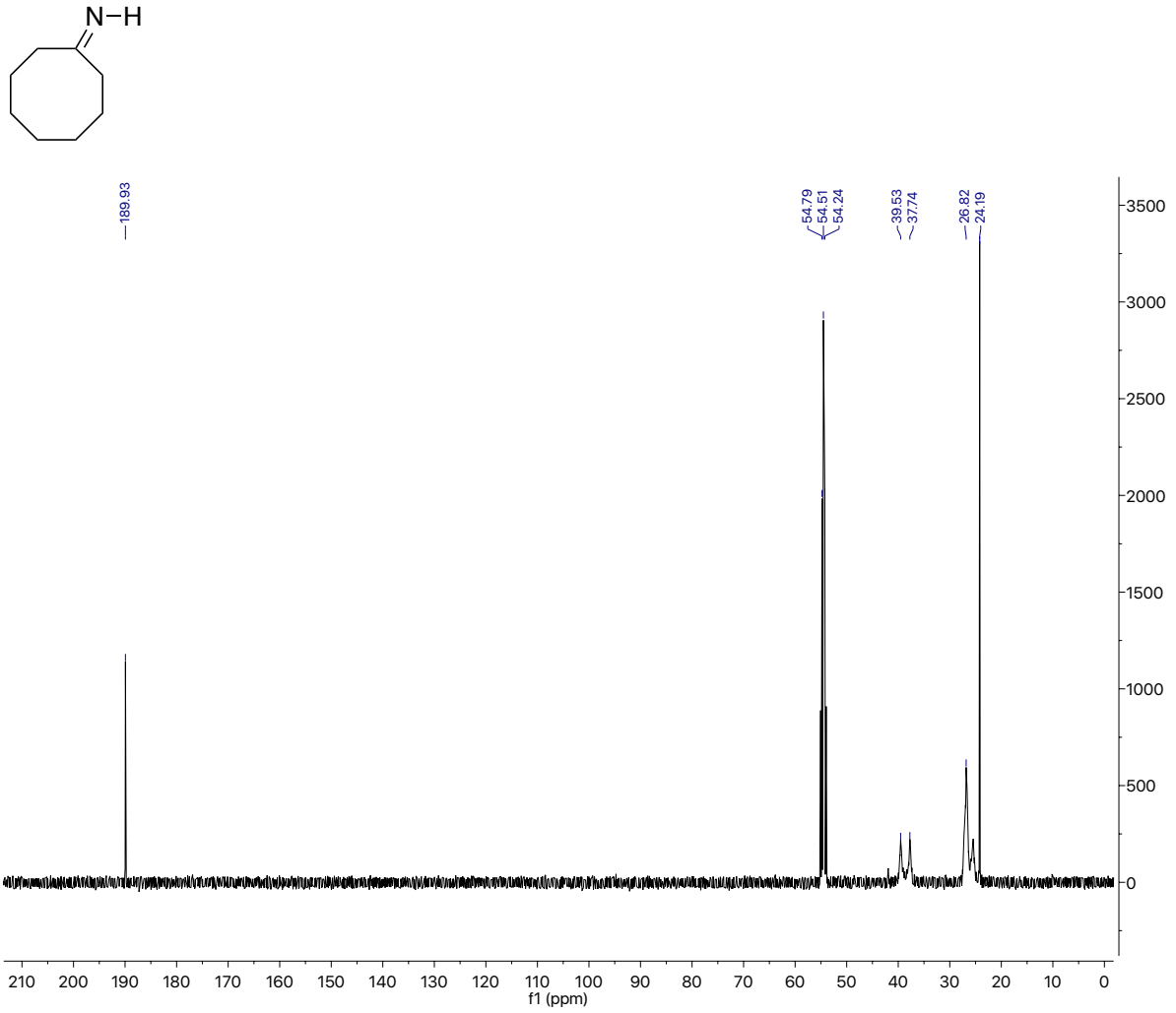


Figure S16. ^{13}C NMR spectrum (CD_2Cl_2, 183 K) of imine **1f.**

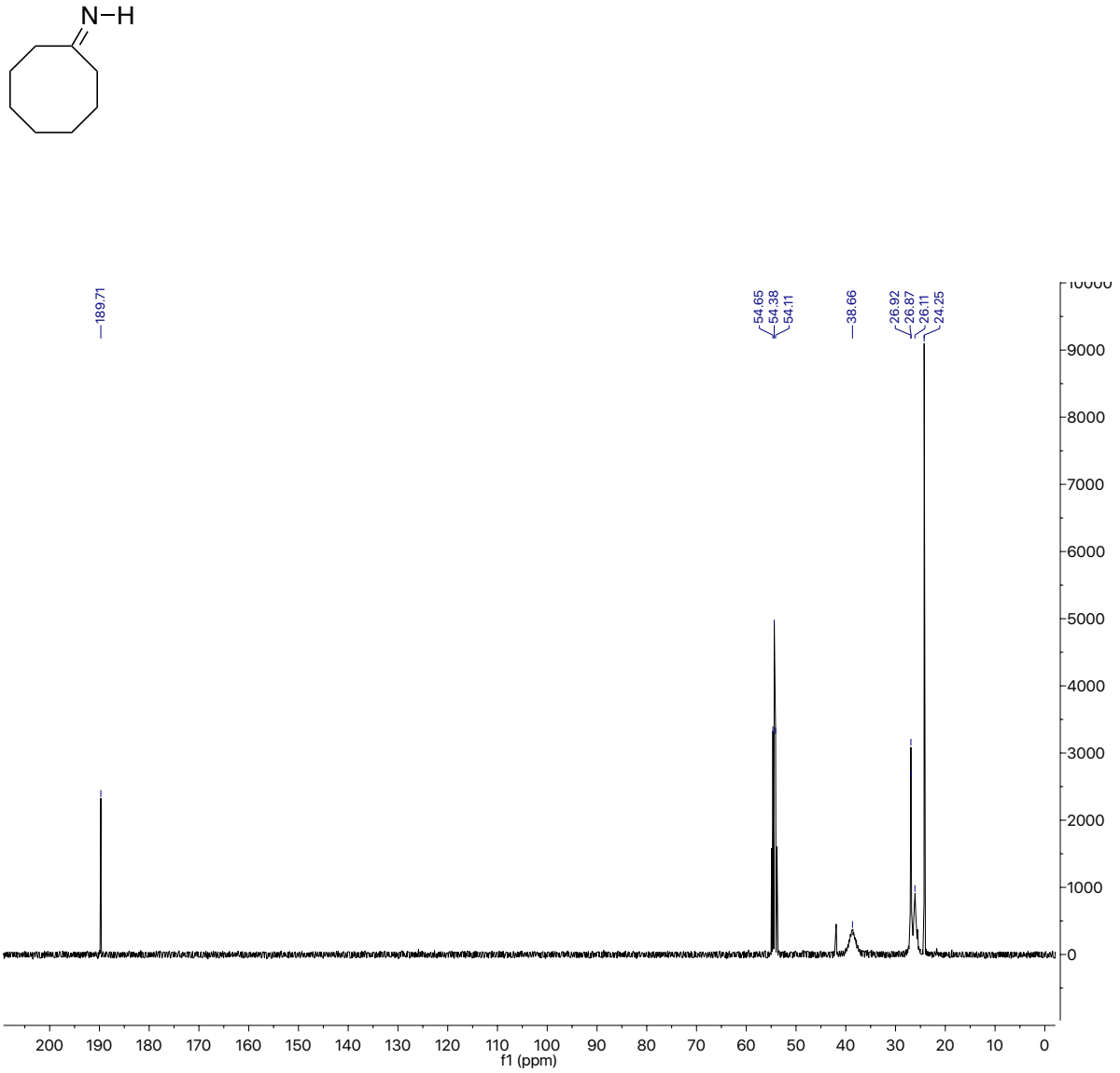


Figure S17. ^{13}C NMR spectrum (CD_2Cl_2, 273 K) of imine **1f.**

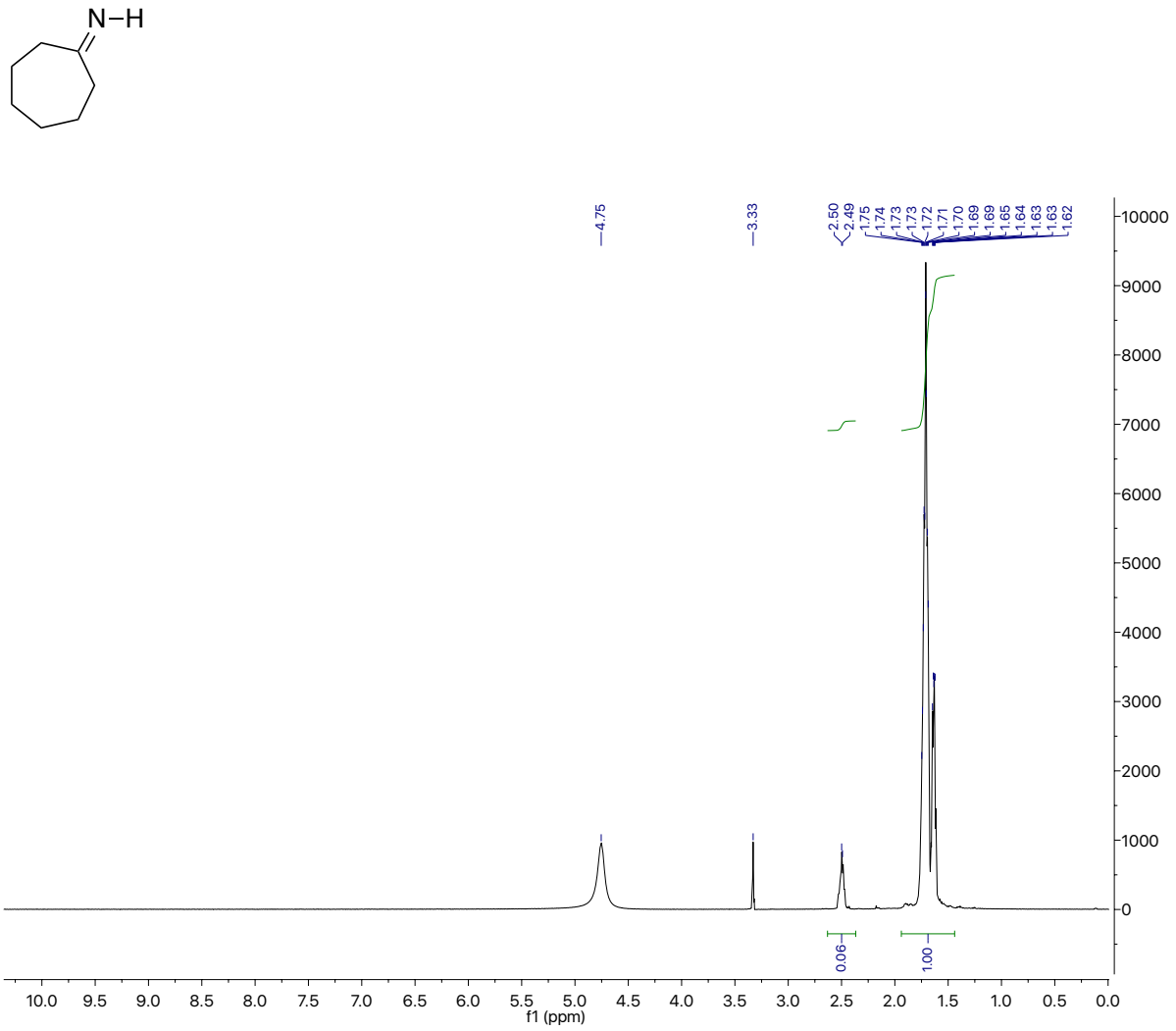


Figure S18. ^{1}H NMR spectrum of tetradeuterated imine **1e** in CD_3OD.

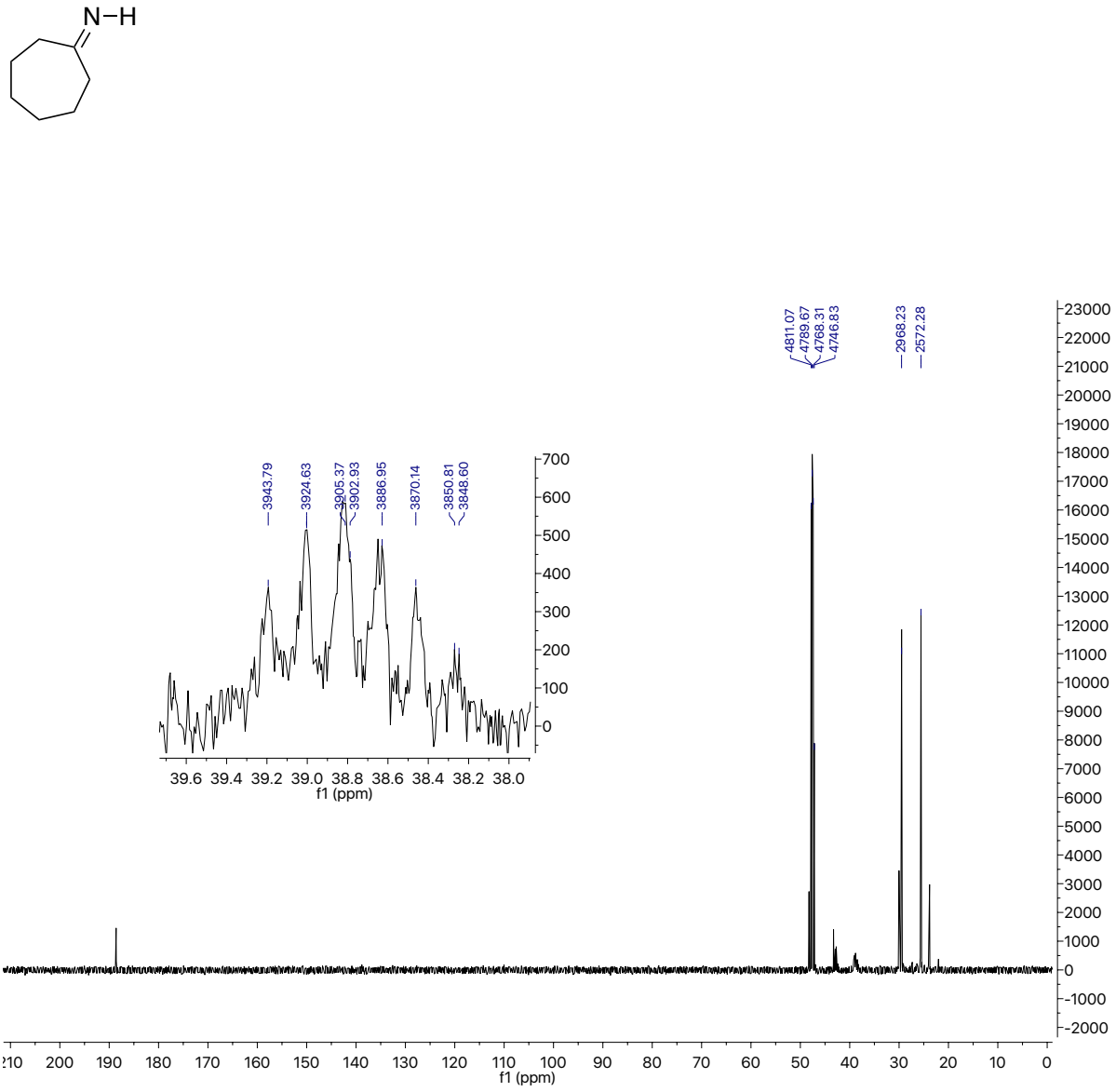


Figure S19. ^{13}C NMR spectrum of tetradeuterated imine **1e** in CD_3OD.

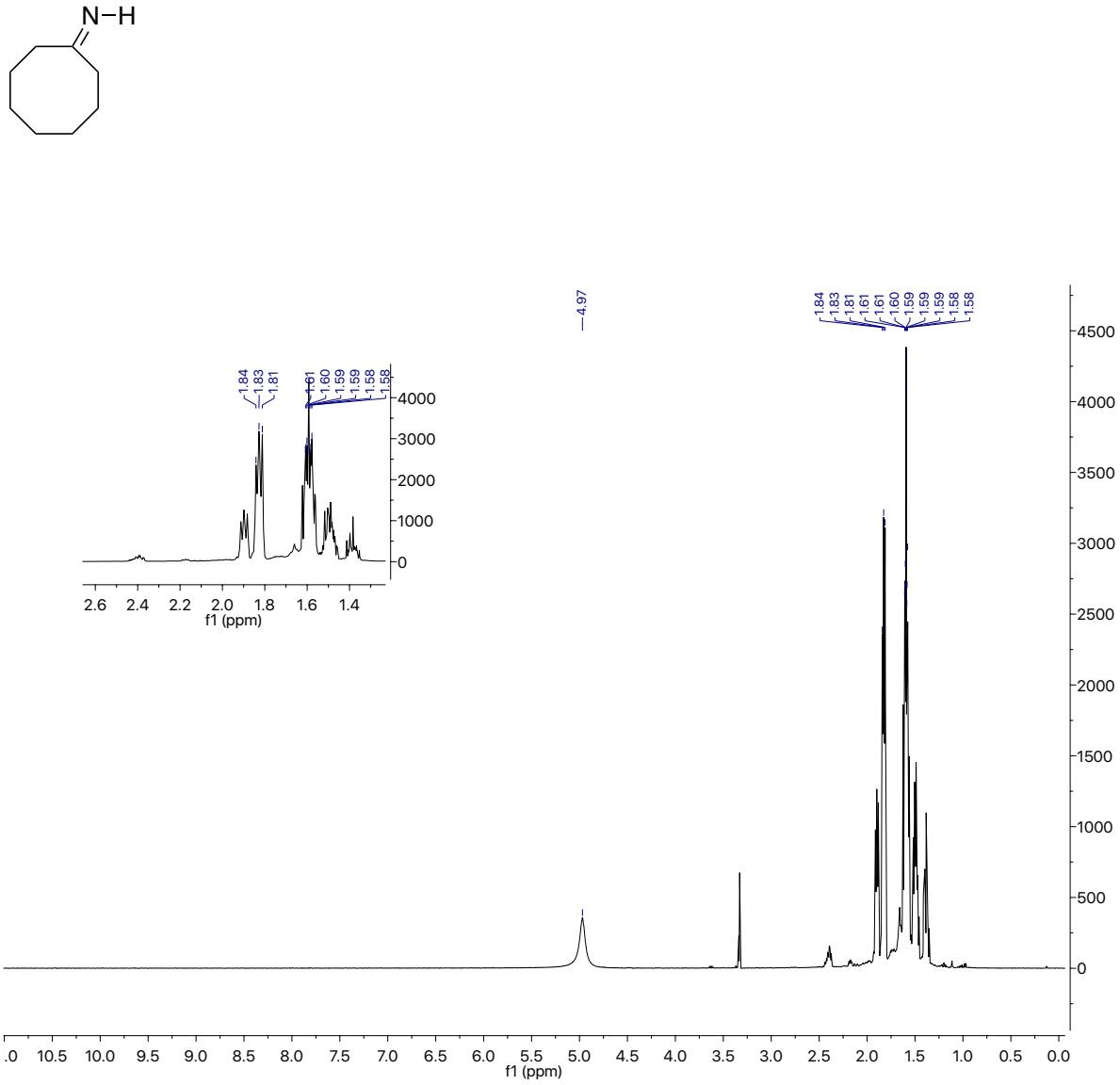


Figure S20. ^{1}H NMR spectrum of tetradeuterated imine **1f** in CD_3OD.

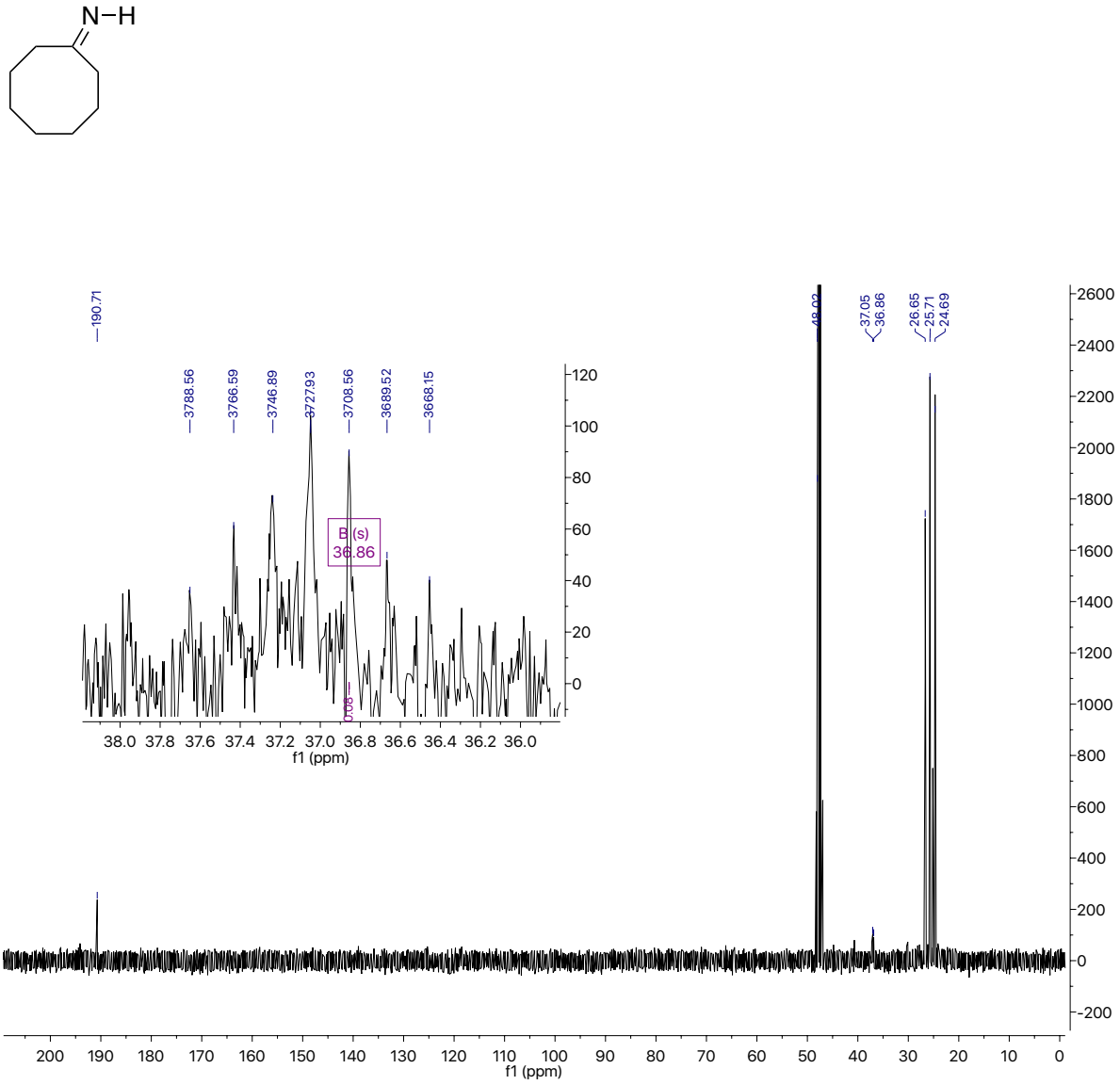


Figure S21. ^{13}C NMR spectrum of tetradeuterated imine **1f** in CD_3OD.