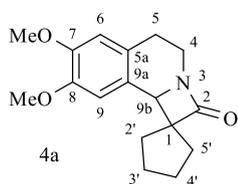


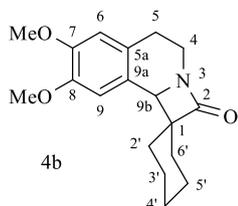
Reaction of methyl bromocycloalkanecarboxylates with zinc and dihydroisoquinoline derivative

Elena A. Nikiforova, Nikolay F. Kirillov, Vladislav S. Melekhin and Pavel A. Slepukhin

The IR spectra of compounds **4a-c** and **6** from mulls in mineral oil were measured on a Spectrum Two PerkinElmer Fourier spectrometer. The ^1H NMR (400 MHz) and ^{13}C (100 MHz) spectra of these compounds were recorded on a Bruker Avance III HD 400 instrument in CDCl_3 with HMDS as an internal standard.

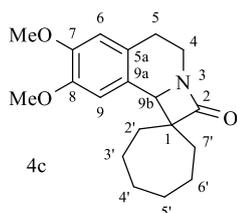


7,8-Dimethoxy-5,9b-dihydro-2H,4H-spiro[azeto[2,1-a]isoquinoline-1,1'-cyclopentan]-2-one **4a**. Yield 3.28 g (57%), mp 85–86 °C. IR (ν , cm^{-1}): 1738 ($\text{C}=\text{O}$). ^1H NMR, δ , ppm: 1.26–2.24 m [8H, $(\text{CH}_2)_4$], 2.54 dd (1H, C^5H , J 14.8 Hz, 3.2 Hz), 2.86 dt (1H, C^5H , J 12.4 Hz, 3.6 Hz), 2.95 dt (1H, C^4H , J 13.6 Hz, 6.0 Hz), 4.03 dd (1H, C^4H , J 12.4 Hz, 6.0 Hz), 3.85 s (3H, MeO), 3.86 s (3H, MeO), 4.33 s (1H, C^{9b}H), 6.44 s (1H, H^{Ar}), 6.63 s (1H, H^{Ar}). ^{13}C NMR, δ , ppm: 24.6, 25.4, 28.0, 28.4, 65.3 ($\text{C}^{\text{cyclopentane}}$), 33.6 (C^5), 36.5 (C^4), 55.4 (MeO), 55.6 (MeO), 61.0 (C^{9b}), 109.3, 112.1, 124.7, 126.2, 147.5, 147.8 (C^{Ar}), 177.0 (CO). Found (%): C 70.95; H 7.42; N 4.96. Calc. for $\text{C}_{17}\text{H}_{21}\text{NO}_3$ (%): C 71.06; H 7.37; N 4.87.

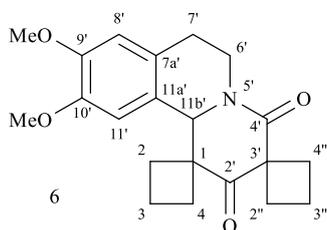


7,8-Dimethoxy-5,9b-dihydro-2H,4H-spiro[azeto[2,1-a]isoquinoline-1,1'-cyclohexan]-2-one **4b**. Yield 3.80 g (63%), mp 129–130 °C⁹. IR (ν , cm^{-1}): 1737

(C=O). ^1H NMR, δ , ppm: 1.06–2.12 m [10H, $(\text{CH}_2)_5$], 2.53 dd (1H, C^5H , J 15.6 Hz, 3.2 Hz), 2.79 dt (1H, C^5H , J 12.4 Hz, 3.6 Hz), 2.94 dt (1H, C^4H , J 15.6 Hz, 6.0 Hz), 4.01 dd (1H, C^4H , J 13.2 Hz, 6.0 Hz), 3.84 s (3H, MeO), 3.86 s (3H, MeO), 4.20 s (1H, C^{9b}H), 6.53 s (1H, H^{Ar}), 6.60 s (1H, H^{Ar}). ^{13}C NMR, δ , ppm: 22.7, 23.9, 25.6, 28.9, 33.7, 60.0 ($\text{C}^{\text{cyclohexane}}$), 28.6 (C^5), 36.8 (C^4), 56.0 (MeO), 56.3 (MeO), 60.5 (C^{9b}), 110.6, 112.6, 124.7, 127.2, 147.9, 148.4 (C^{Ar}), 176.6 (CO). Found (%): C 71.90; H 7.63; N 4.83. Calc. for $\text{C}_{18}\text{H}_{23}\text{NO}_3$ (%): C 71.73; H 7.69; N 4.65.



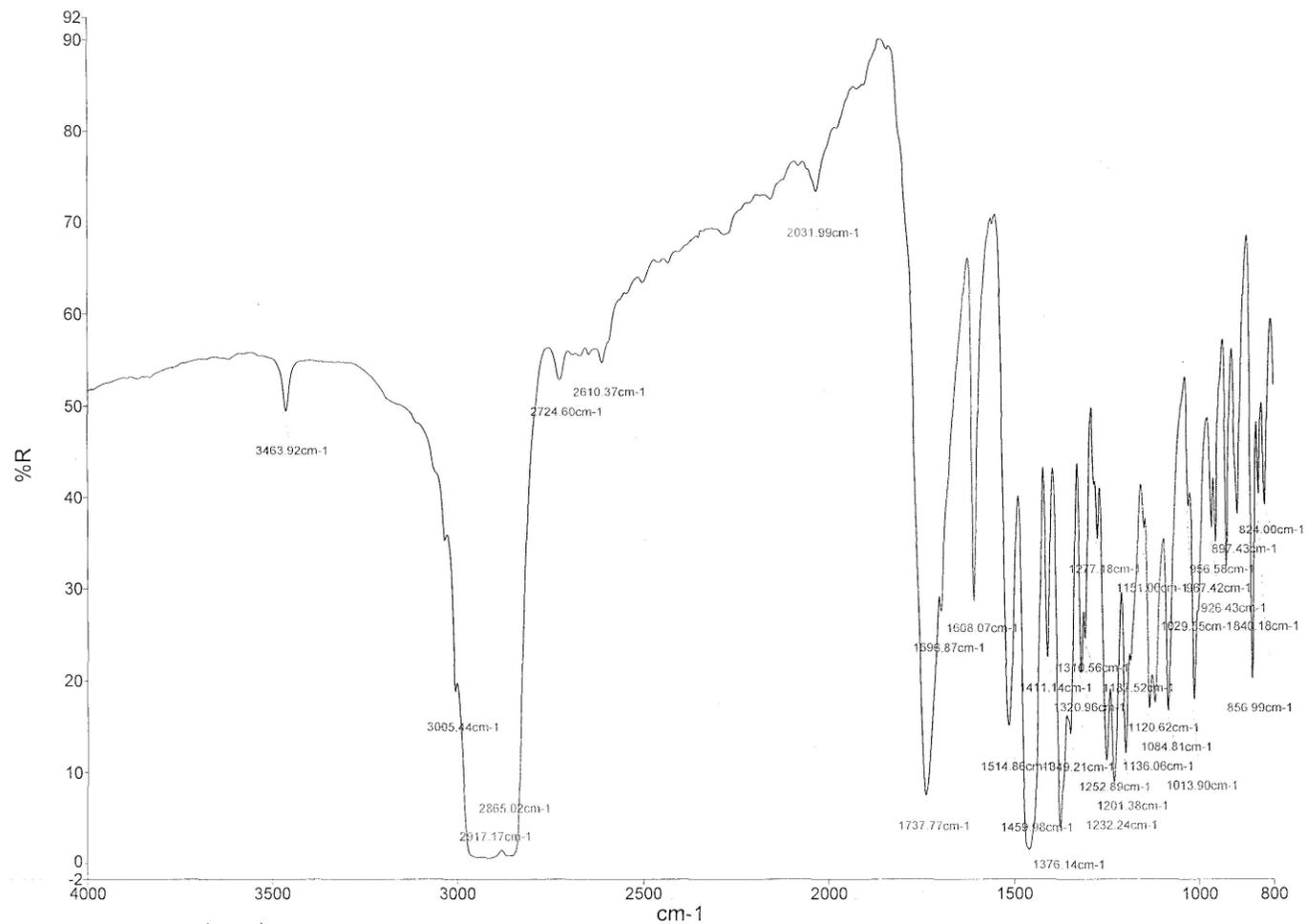
7,8-Dimethoxy-5,9b-dihydro-2H,4H-spiro[azeto[2,1-a]isoquinoline-1,1'-cycloheptan]-2-one **4c**. Yield 3.78 g (60%), mp 99–100 °C. IR (ν , cm^{-1}): 1756 (C=O). ^1H NMR, δ , ppm: 1.21–2.23 m [12H, $(\text{CH}_2)_6$], 2.51 dd (1H, C^5H , J 15.2 Hz, 3.2 Hz), 2.79 dt (1H, C^5H , J 12.4 Hz, 3.6 Hz), 2.90 dt (1H, C^4H , J 13.6 Hz, 6.0 Hz), 3.98 dd (1H, C^4H , J 12.8 Hz, 6.0 Hz), 3.83 s (3H, MeO), 3.84 s (3H, MeO), 4.23 s (1H, C^{9b}H), 6.49 s (1H, H^{Ar}), 6.60 s (1H, H^{Ar}). ^{13}C NMR, δ , ppm: 23.6, 24.4, 29.8, 29.9, 30.8, 35.6, 63.0 ($\text{C}^{\text{cycloheptane}}$), 28.7 (C^5), 36.8 (C^4), 56.0 (MeO), 56.2 (MeO), 61.9 (C^{9b}), 110.4, 112.6, 125.0, 127.1, 148.0, 148.3 (C^{Ar}), 176.9 (CO). Found (%): C 72.48; H 8.06; N 4.57. Calc. for $\text{C}_{19}\text{H}_{25}\text{NO}_3$ (%): C 72.35; H 7.99; N 4.44.



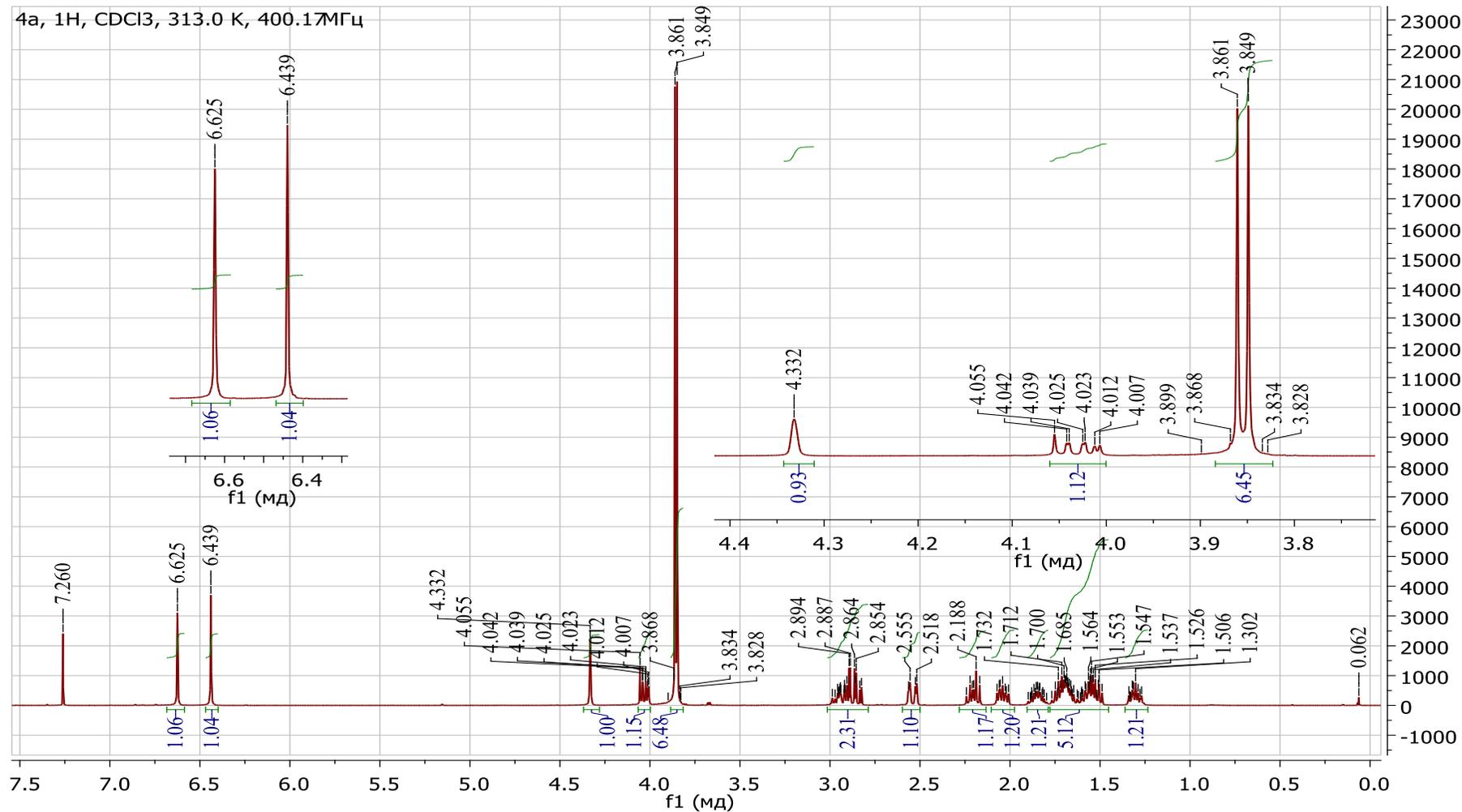
9',10'-Dimethoxy-7',11b'-dihydro-2'H,4'H,6'H-dispiro[cyclobutane-1,1'-pyrido[2,1-a]isoquinoline-3',1''-cyclobutane]-2',4'-dione **6**. Yield 2.56 g (36%) (for the reaction with a ratio $\mathbf{1d}/\mathbf{2} = 1:1$), 4.83 g (68%) (for the reaction with a ratio

1d/2 = 2,5:1), mp 162–163 °C. IR (ν , cm^{-1}): 1704, 1658 (C=O). ^1H NMR, δ , ppm: 1.20 – 2.88 m [15H, 2(CH₂)₃, C^{7'}H₂, C^{6'}H], 4.03 dt (1H, C^{6'}H, J 10.4 Hz, 6.0 Hz), 3.87 s (3H, MeO), 3.90 s (3H, MeO), 4.65 s (1H, C^{11b'}H), 6.63 s (1H, H^{Ar}), 6.72 s (1H, H^{Ar}). ^{13}C NMR, δ , ppm: 15.5, 15.8, 23.0, 26.2, 29.7, 32.4, 54.1, 55.4 (2 C^{cyclobutane}), 26.6 (C^{7'}), 40.0 (C^{6'}), 56.1 (MeO), 56.4 (MeO), 58.0 (C^{11b'}), 112.0, 112.3, 123.6, 130.1, 147.5, 148.8 (C^{Ar}), 170.8 (C^{4'}O), 209.6 (C^{2'}O). Found (%): C 71.05; H 7.16; N 4.11. Calc. for C₂₁H₂₅NO₄ (%): C 70.96; H 7.09; N 3.94.

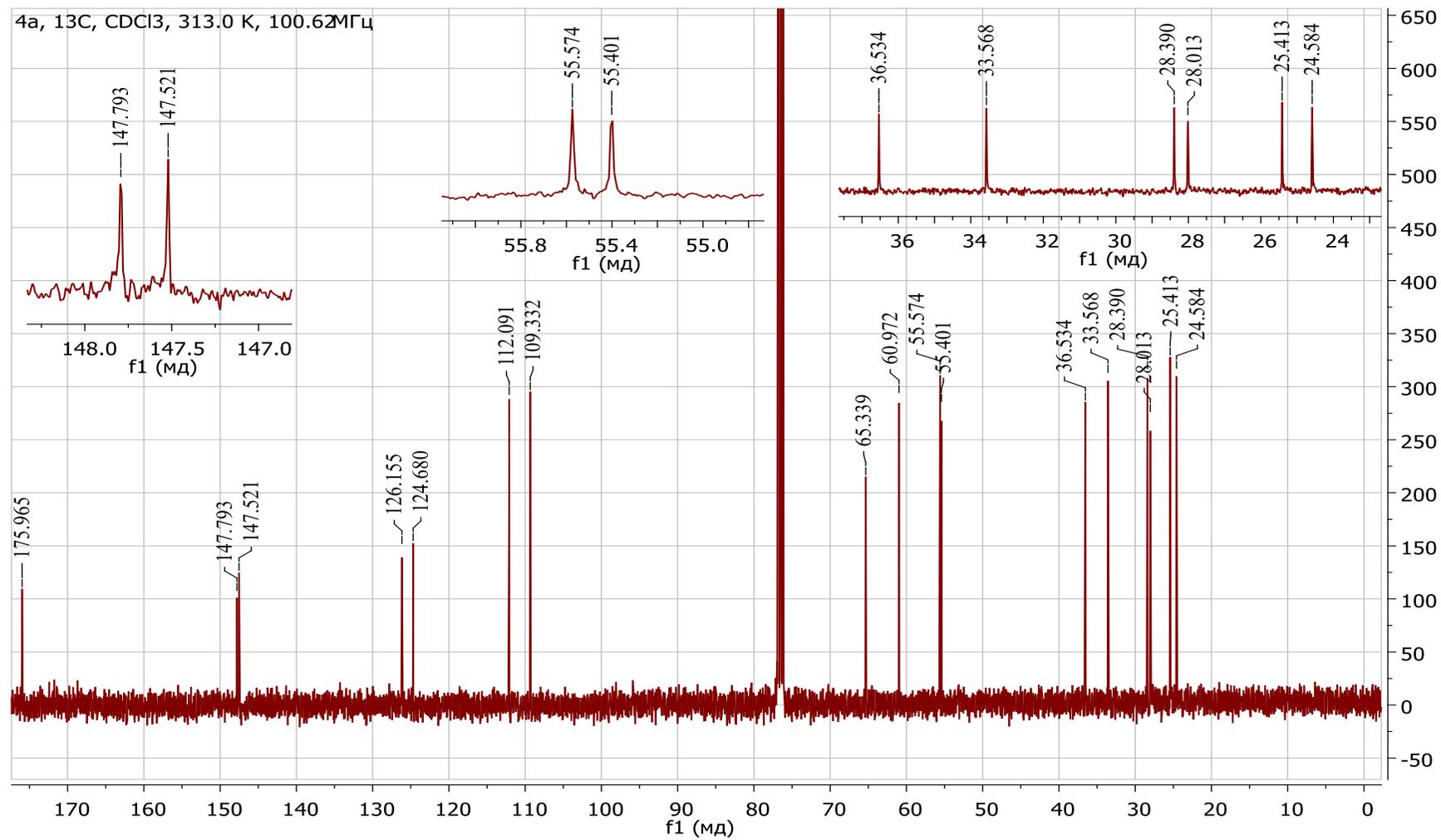
IR Spectrum (mulls in mineral oil) of **4a**



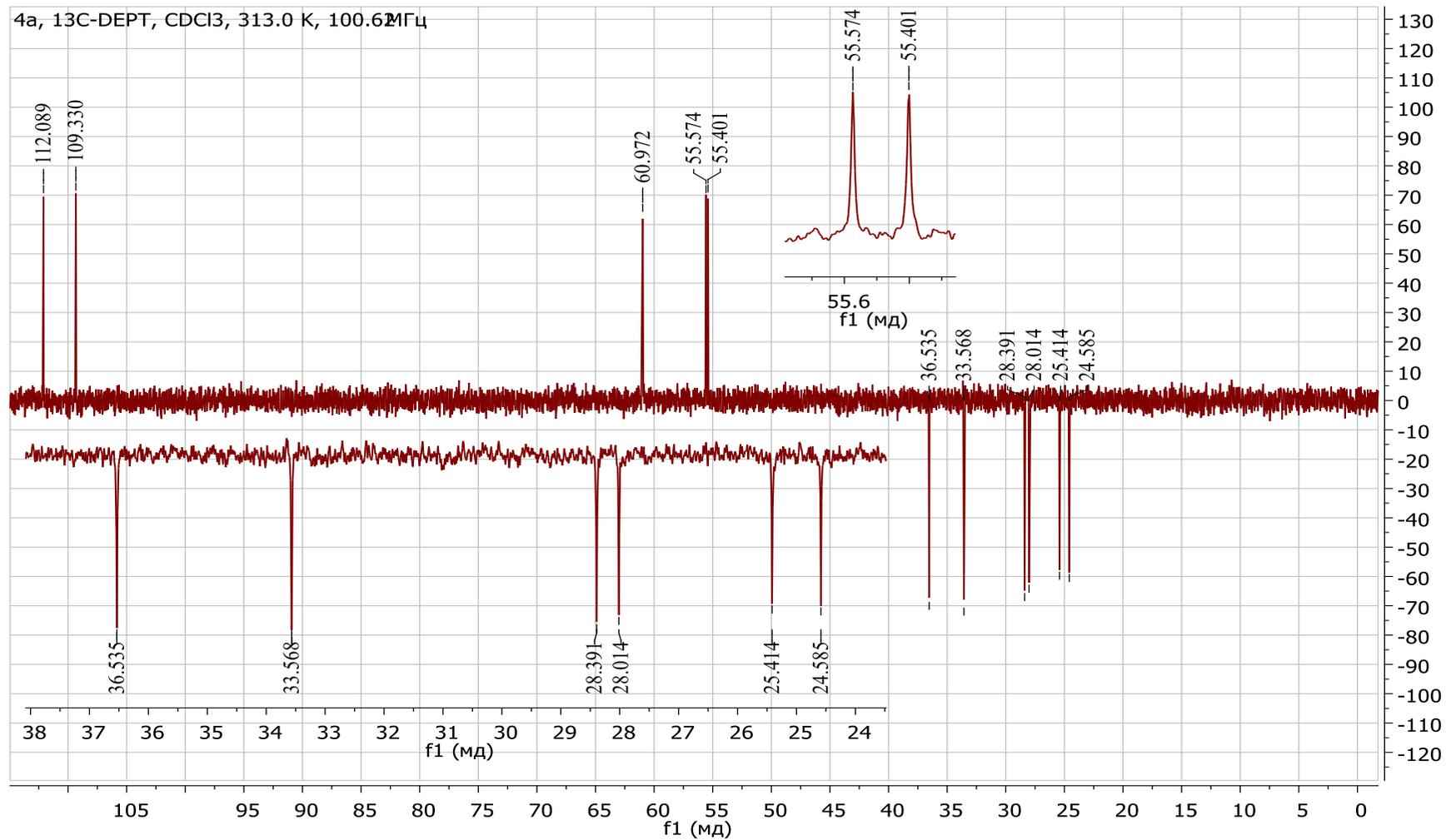
¹H NMR Spectrum (CDCl₃, 400 MHz) of **4a**



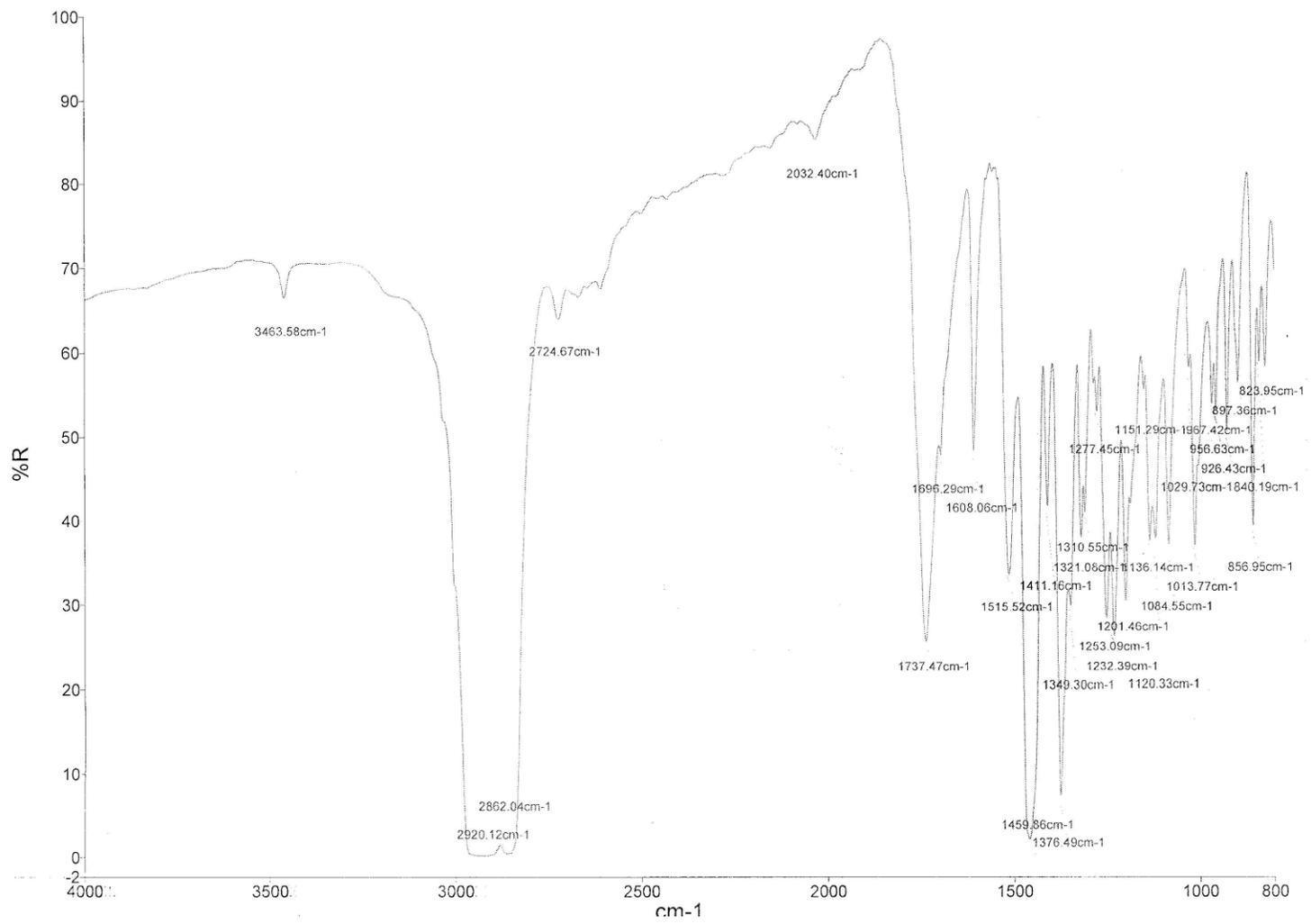
^{13}C NMR Spectrum (CDCl_3 , 100 MHz) of **4a**



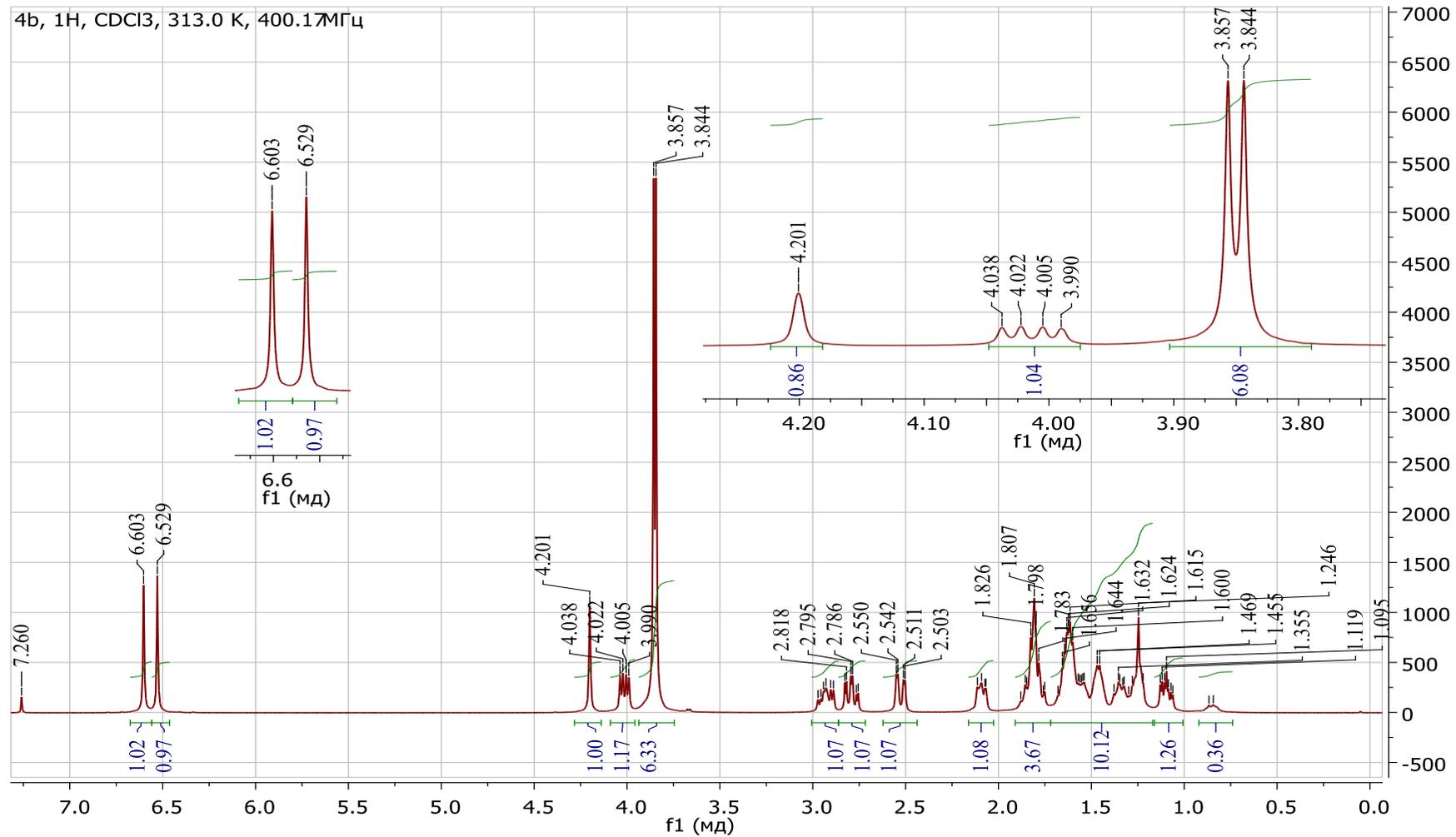
^{13}C -DEPT NMR Spectrum (CDCl_3 , 100 MHz) of **4a**



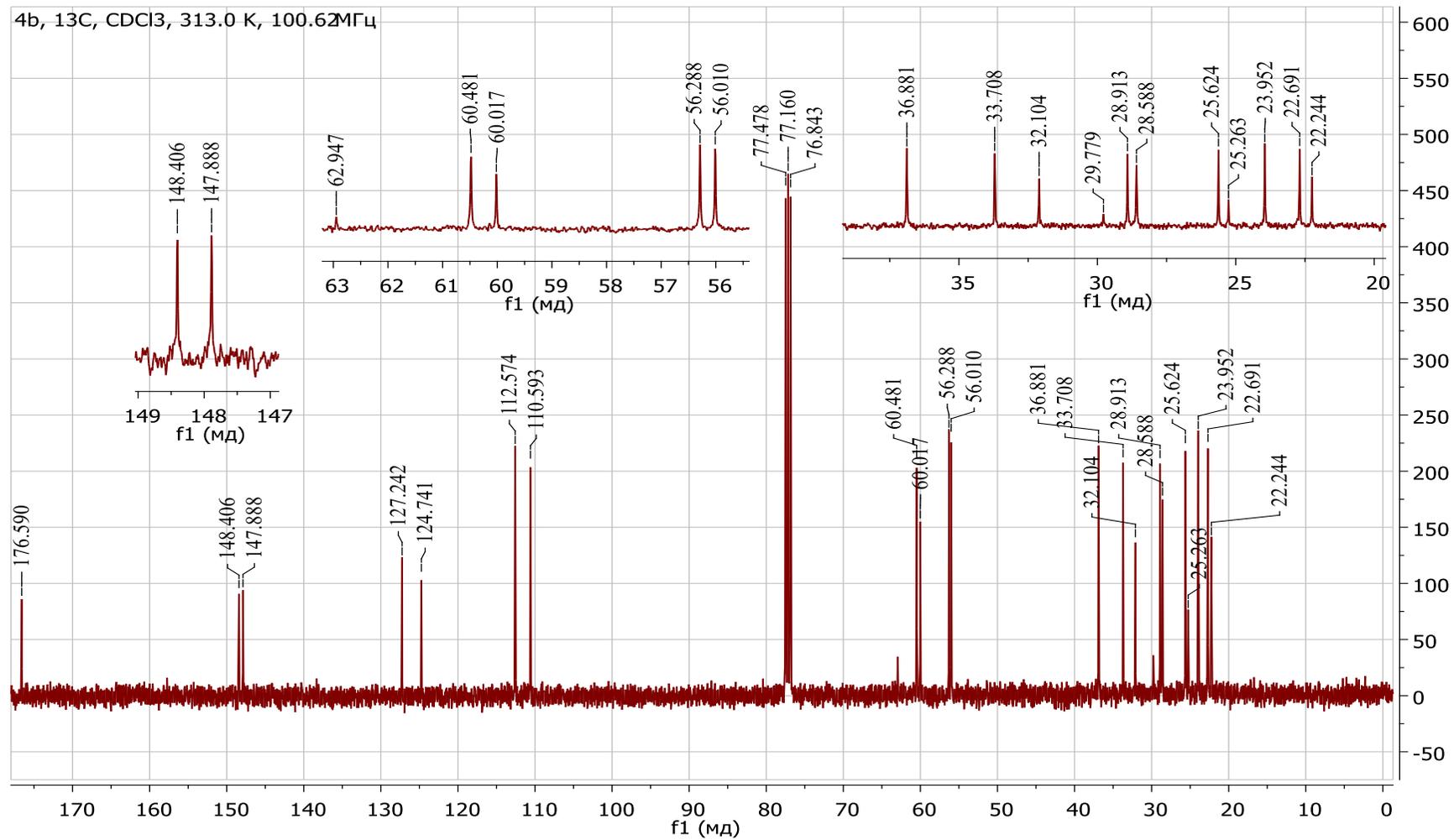
IR Spectrum (mulls in mineral oil) of **4b**



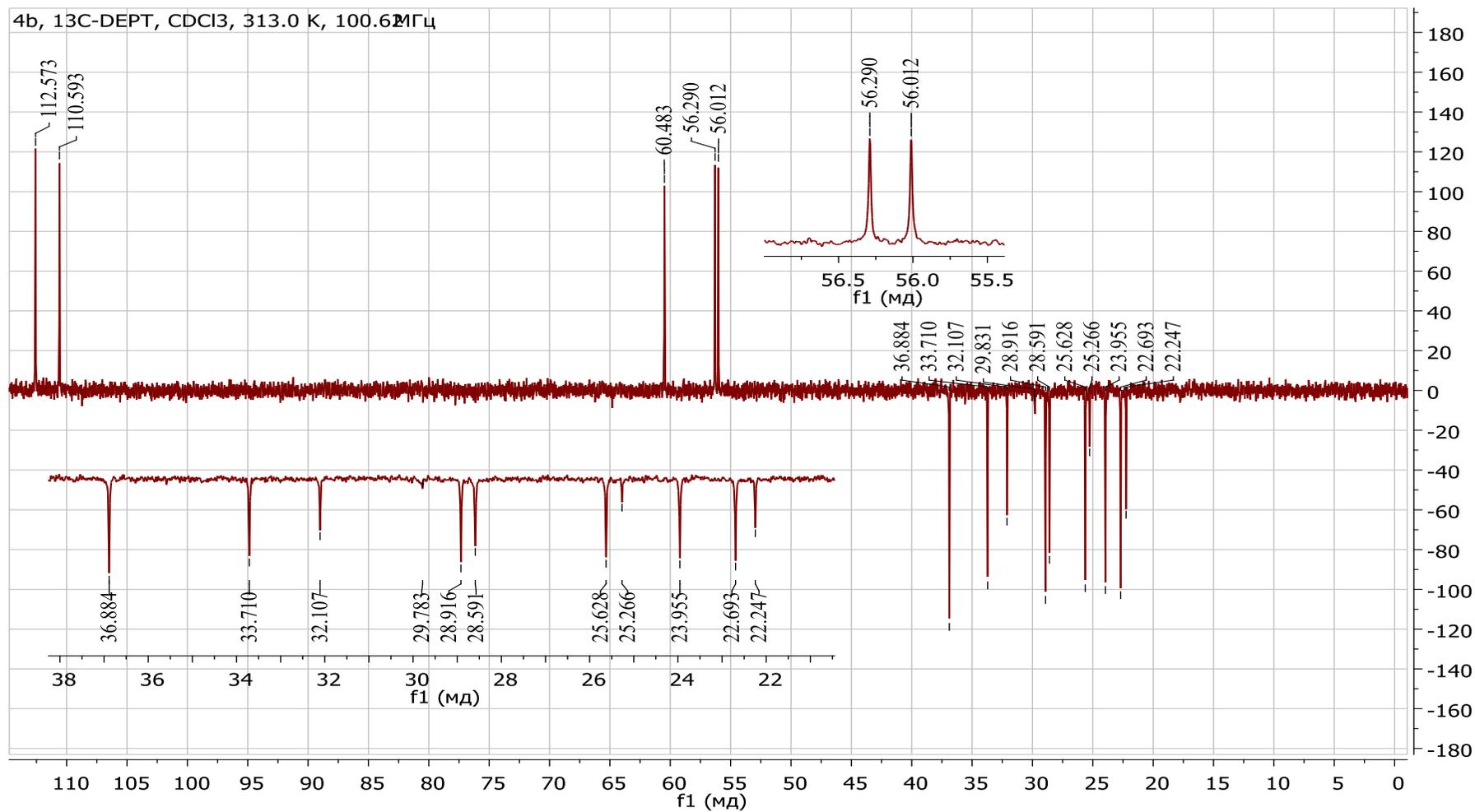
^1H NMR Spectrum (CDCl_3 , 400 MHz) of **4b**



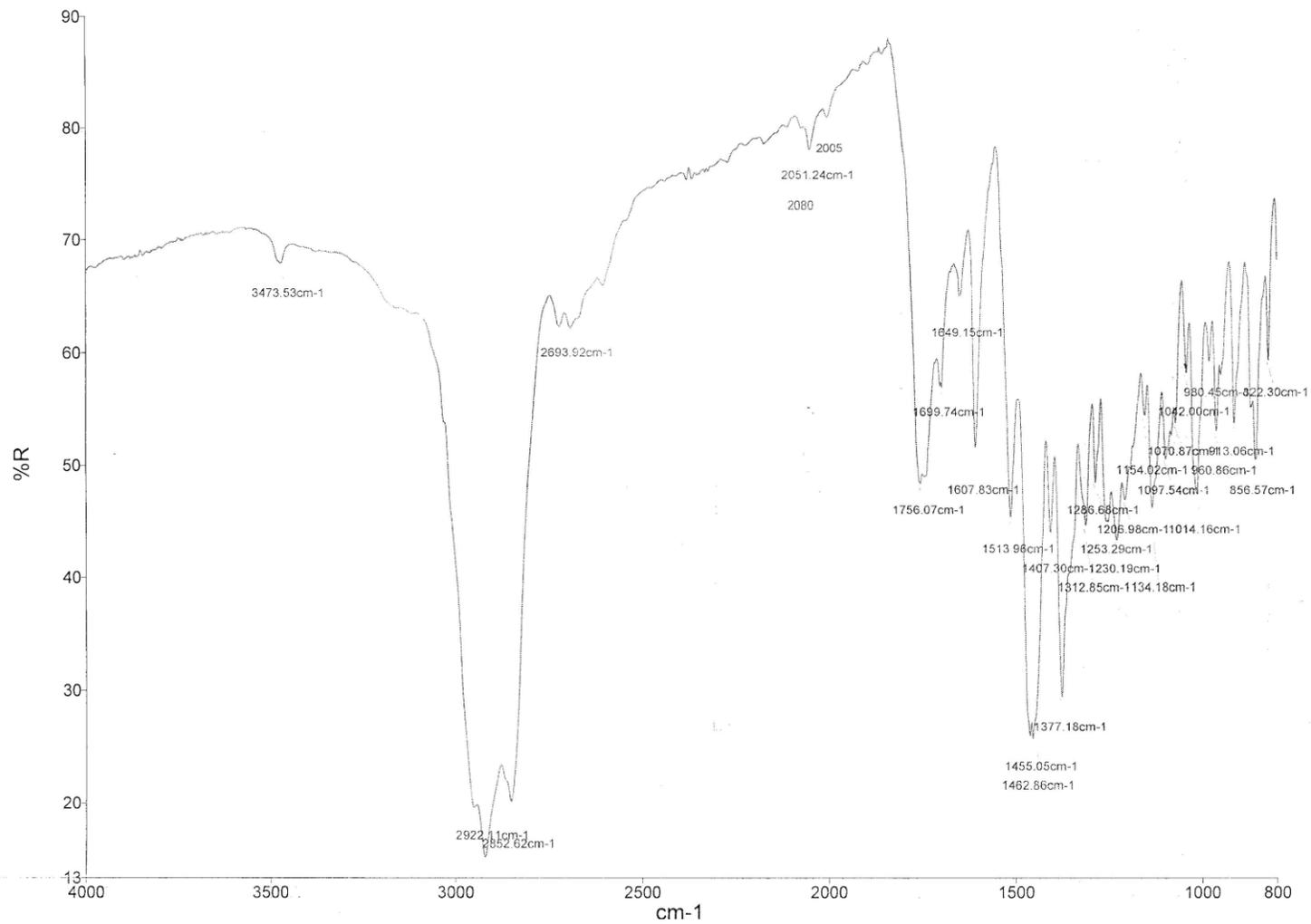
¹³C NMR Spectrum (CDCl₃, 100 MHz) of **4b**



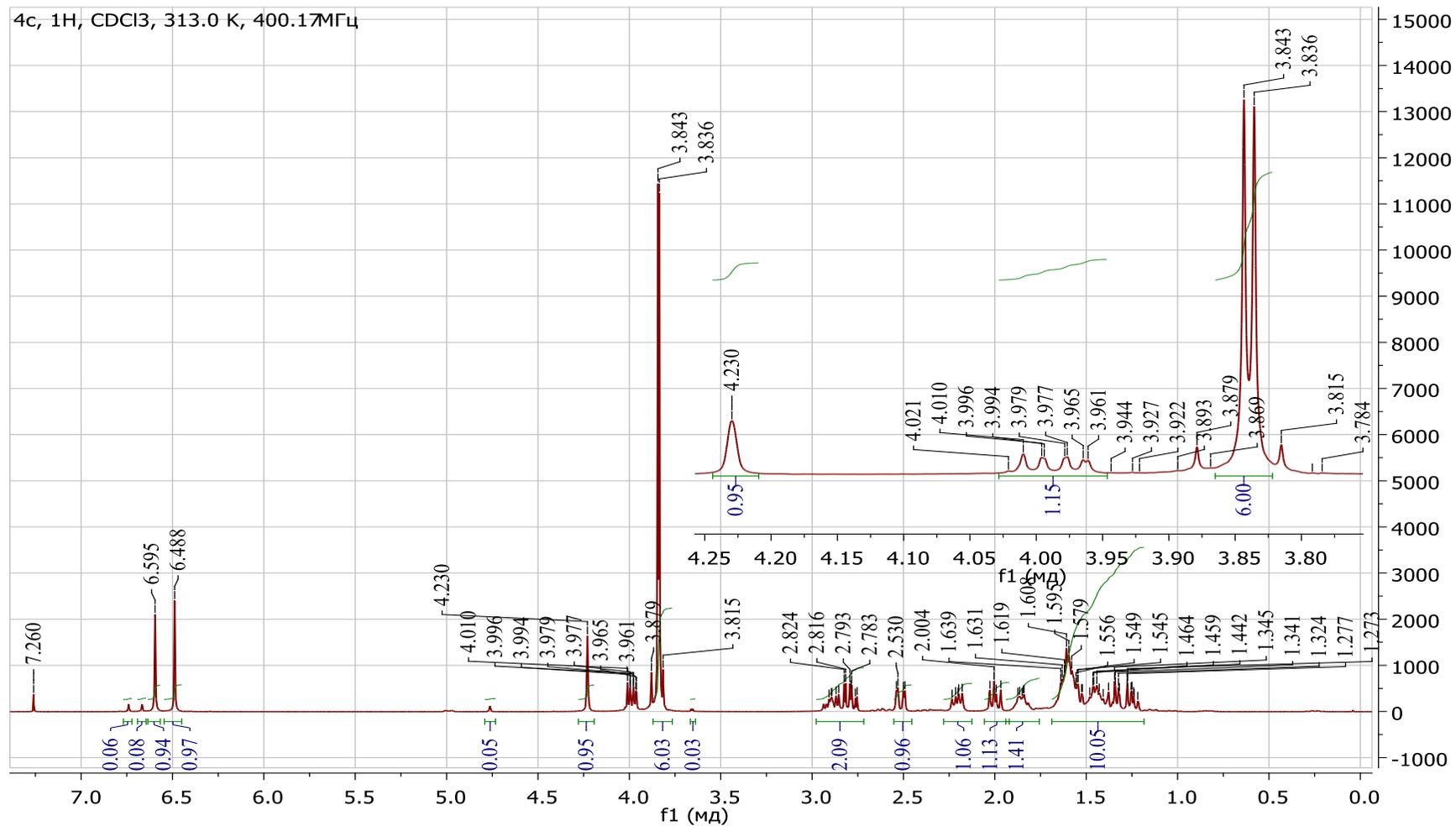
¹³C-DEPT NMR Spectrum (CDCl₃, 100 MHz) of **4b**



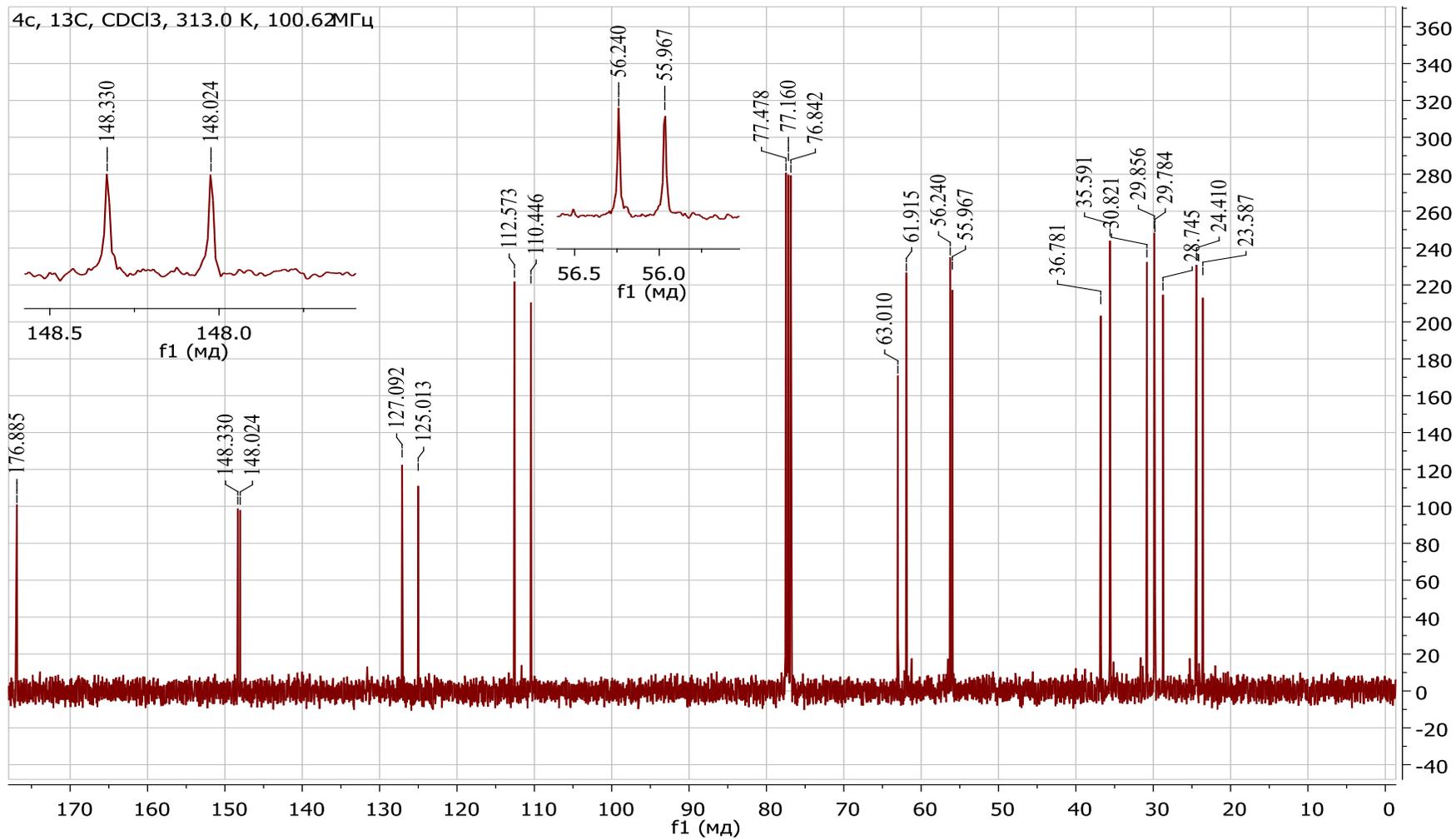
IR Spectrum (mulls in mineral oil) of 4c



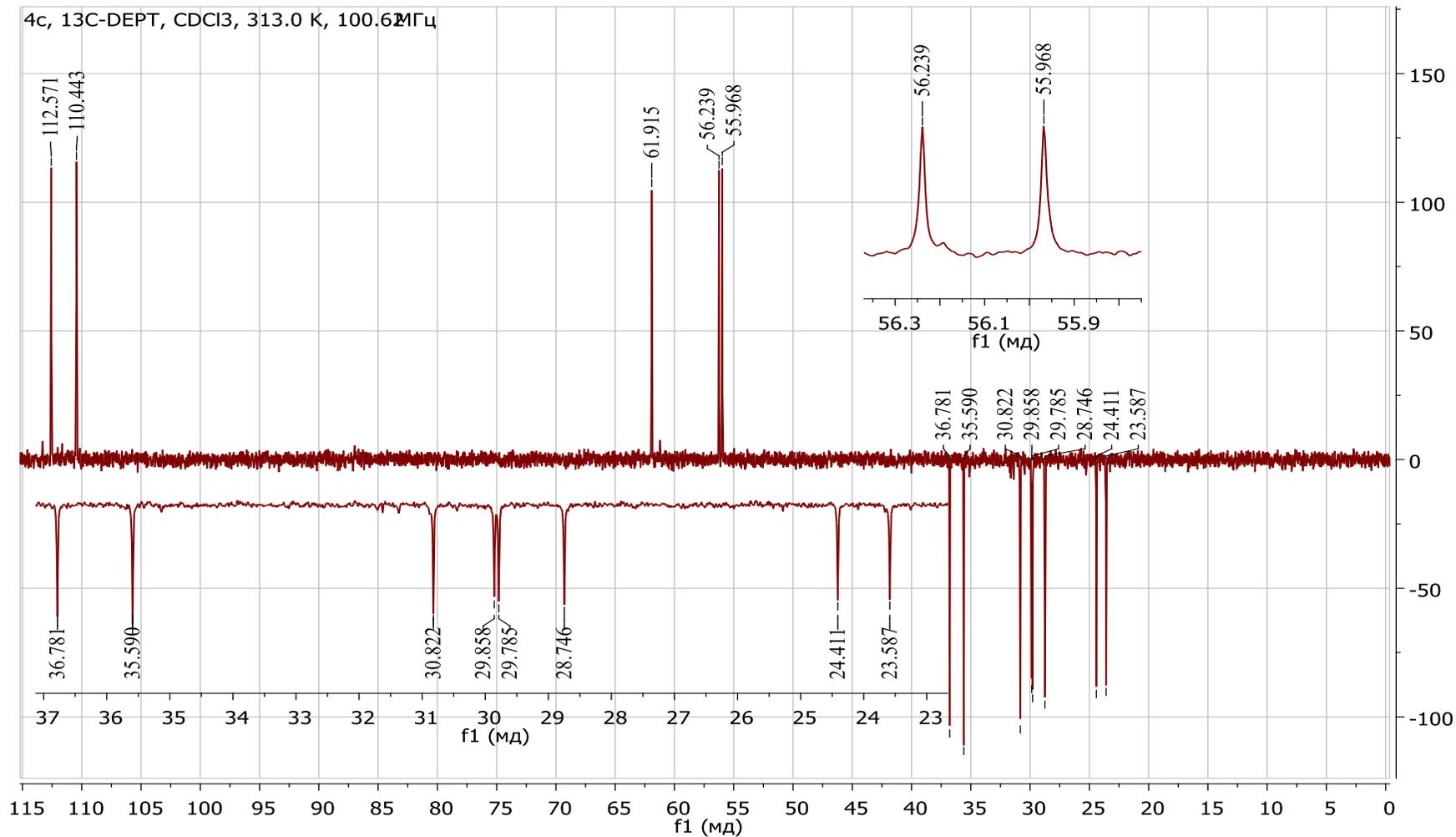
¹H NMR Spectrum (CDCl₃, 400 MHz) of **4c**



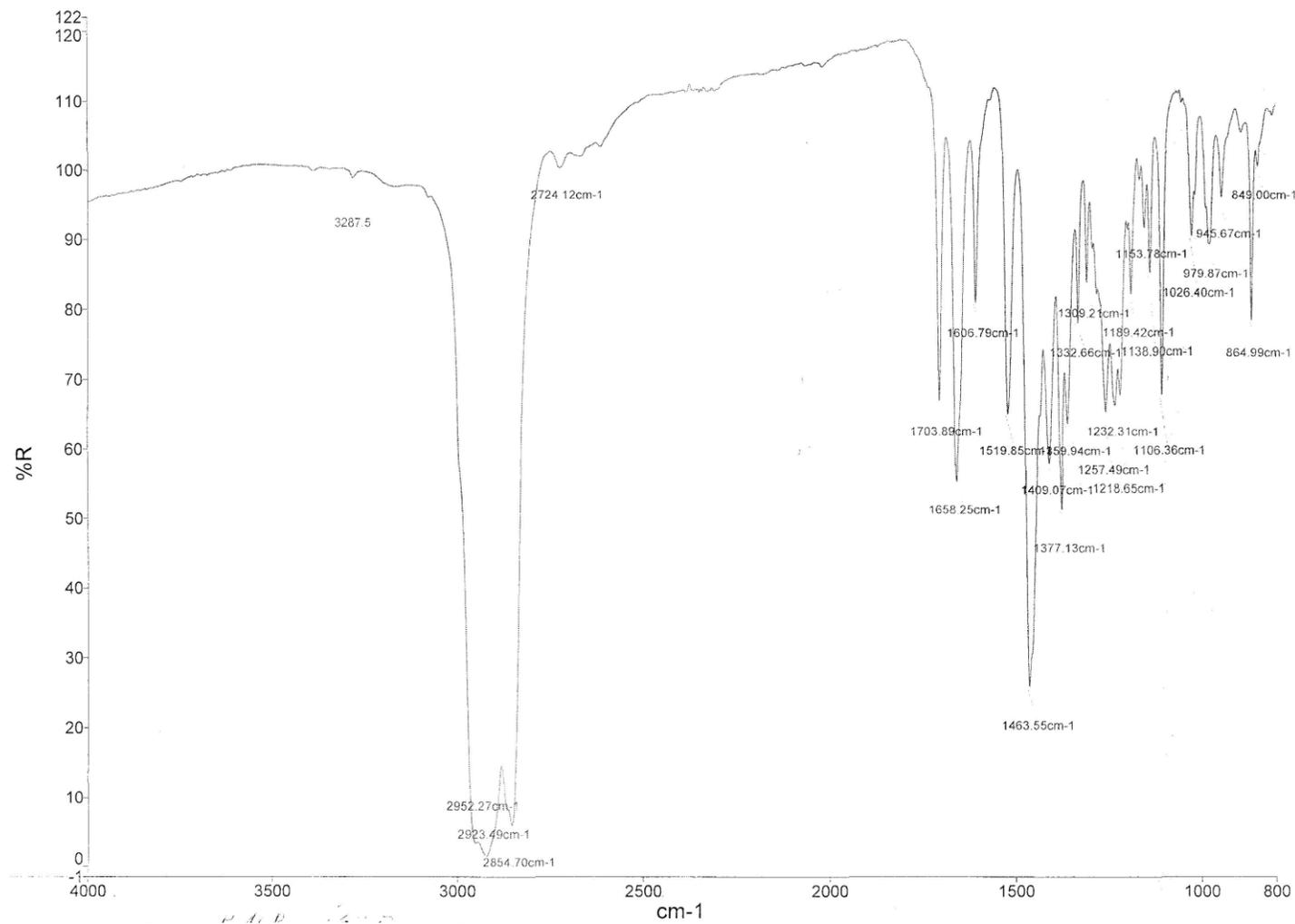
¹³C NMR Spectrum (CDCl₃, 100 MHz) of **4c**



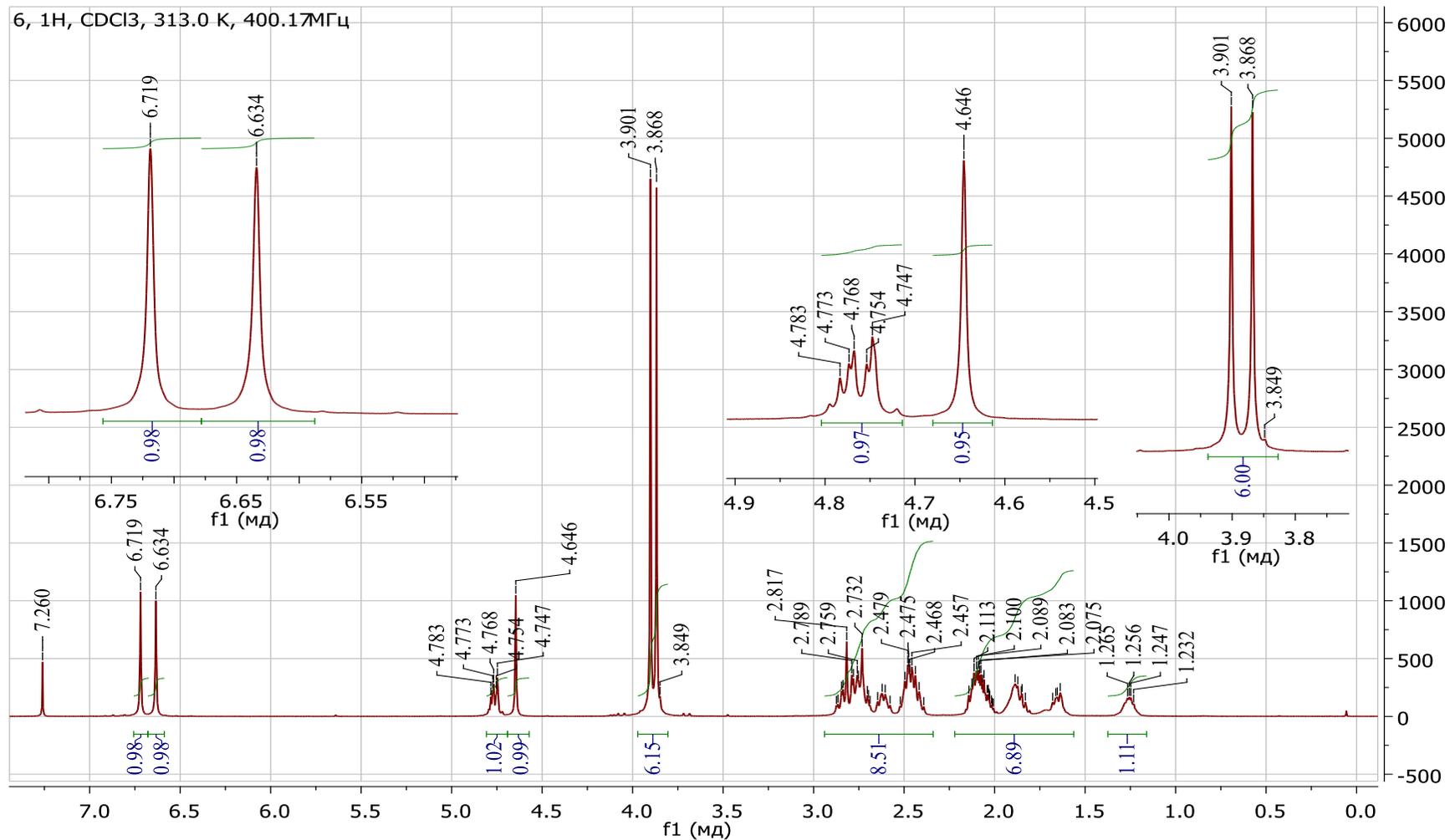
¹³C-DEPT NMR Spectrum (CDCl₃, 100 MHz) of **4c**



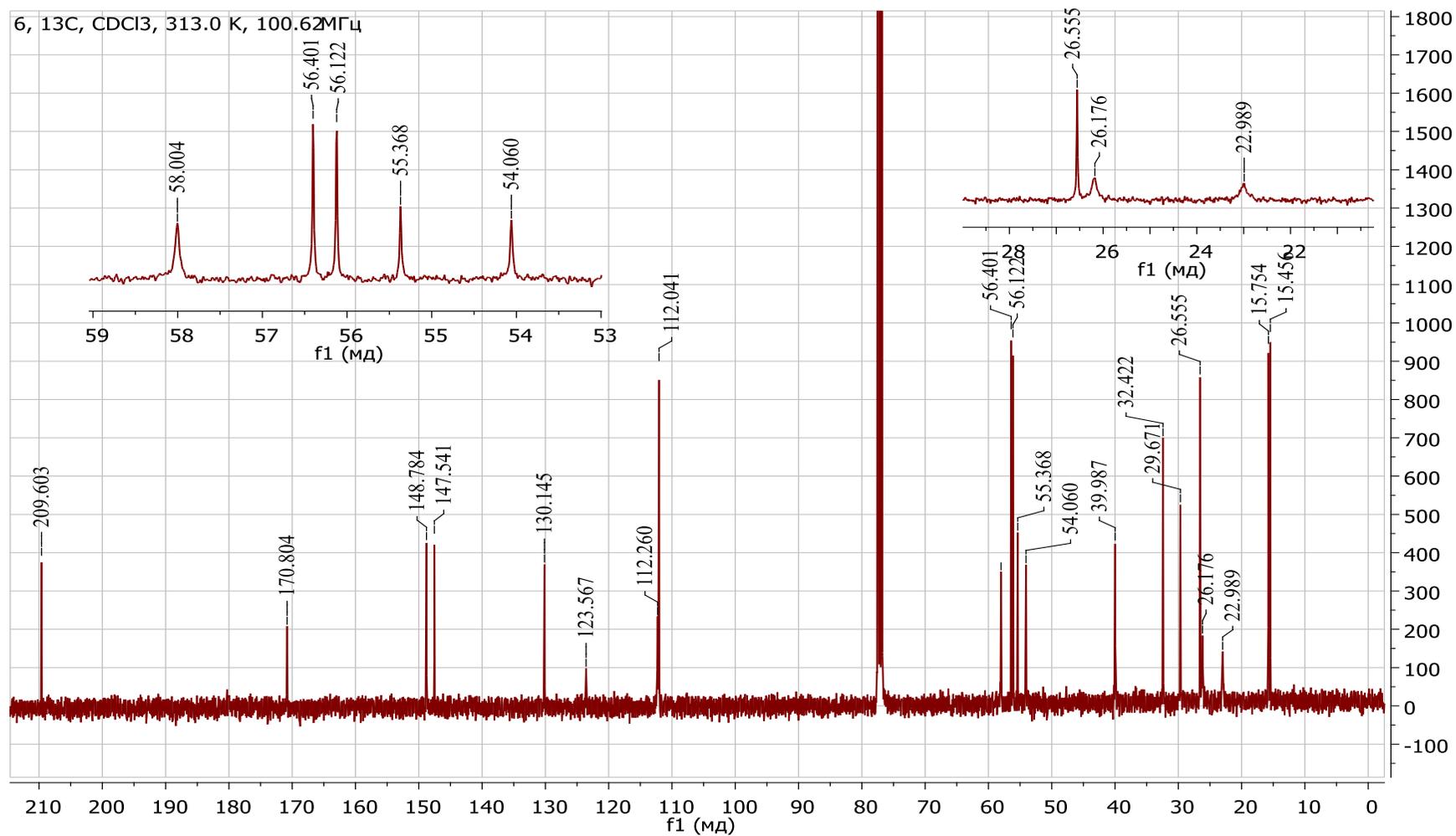
IR Spectrum (mulls in mineral oil) of **6**



¹H NMR Spectrum (CDCl₃, 400 MHz) of **6**



¹³C NMR Spectrum (CDCl₃, 100 MHz) of **6**



¹³C-DEPT NMR Spectrum (CDCl₃, 100 MHz) of **6**

