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Dinuclear copper(II) complex with novel N,N',N'',O-tetradentate Schiff base ligand containing trifluoromethylpyrazole and hydrazone moieties

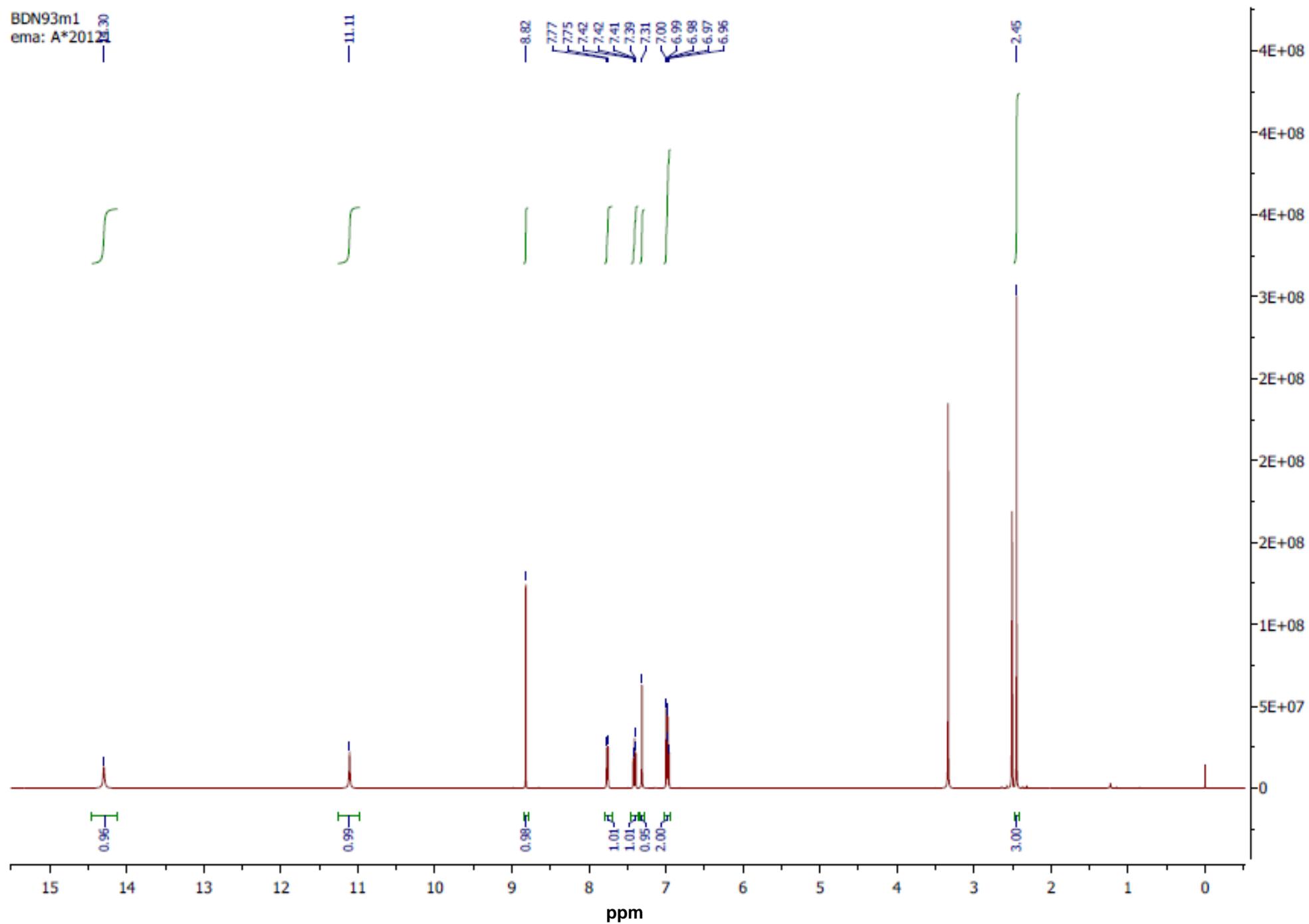
**Denis N. Bazhin, Yulia S. Kudyakova, Pavel A. Slepukhin, Yanina V. Burgart,
Natalia N. Malysheva, Alisa N. Kozitsina, Alla V. Ivanova, Artem S. Bogomyakov
and Victor I. Saloutin**

All reagents and solvents were commercially sourced and used without further purification. The ^1H , ^{19}F , ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer (500 MHz) with TMS as internal standard. Melting points were obtained on a Stuart SMP3 apparatus in open capillaries. IR diffuse-reflectance spectra were recorded with a Perkin-Elmer Spectrum One FTIR instrument in the range 400–4000 cm^{-1} . Elemental analysis was performed using a Perkin Elmer PE 2400 Series II analyzer. Reactions were monitored by thin layer chromatography (TLC) with 0.20 mm Alugram Sil G/UV₂₅₄ pre-coated silica gel plates (60 F254).

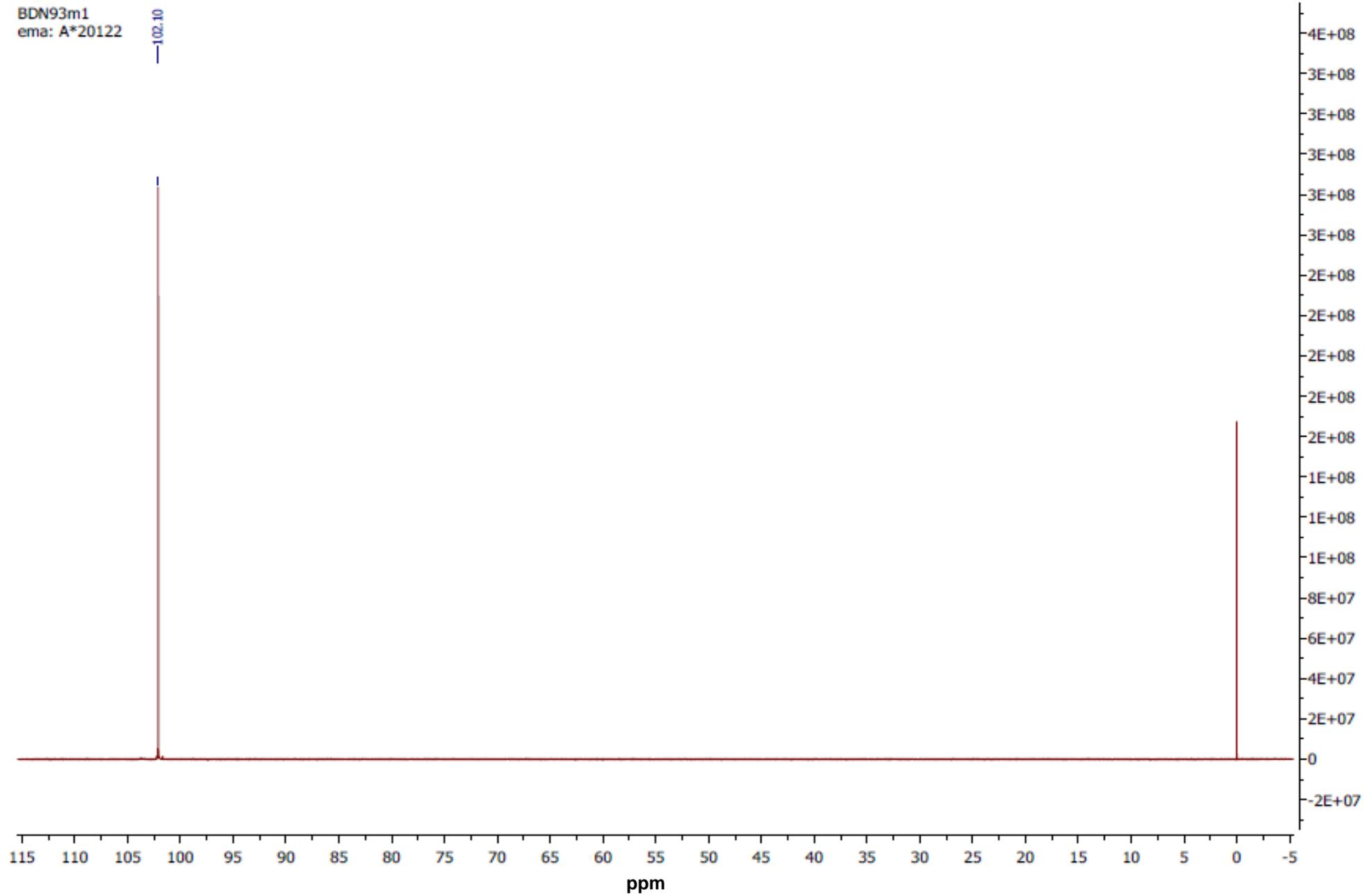
Synthesis of the ligand 3. Salicylaldehyde (1.1 ml, 10 mmol) was added to the solution of pyrazole **2** (1.92 g, 10 mmol) in ethanol (15 ml) and the resulting mixture was stirred at room temperature for 2 h. The precipitate formed was filtered off and recrystallized from ethyl acetate to give ligand **3** as pale yellow solid, yield 2.58 g (87%), m.p. 217–218 °C. IR (DRA, ν/cm^{-1}): 3348 (OH), 3145 (NH), 3049 (arC–H), 2987, 2753 (C–H), 1626, 1591, 1559 (C=N, NH, C=C), 1493 (arC–C), 1274–1124 (C–F). ^1H NMR (500 MHz, DMSO- d_6): δ = 2.45 (s, 3H, Me), 6.96–7.00 (m, 2H, C₆H₄), 7.31 (s, 1H, C₆H₄), 7.39–7.42 (m, 1H, C₆H₄), 7.75–7.77 (m, 1H, pyrazole), 8.82 (s, 1H, H–C=N), 11.11 (br.s, 1H, OH), 14.30 (br. s., 1H, NH). ^{19}F NMR (470 MHz, DMSO- d_6 /C₆F₆): δ = 102.10 (s, CF₃). ^{13}C NMR (125 MHz, DMSO- d_6): δ = 15.26, 105.37, 116.44, 118.44, 119.56, 121.50 (q, $^2J_{\text{CF}}$ = 268 Hz), 130.63, 133.17, 141.50 (q, $^3J_{\text{CF}}$ = 37 Hz), 142.29, 155.75, 158.61, 160.66. Calcd. for C₁₃H₁₁F₃N₄O: C 52.68, H 3.75, N 18.86, F 19.27. Found: C 52.71, H 3.74, N 18.91, F 19.24.

Synthesis of complex 4. The ligand **3** (1.48 g, 5 mmol) was suspended in ethanol (20 ml) at room temperature. Then the copper(II) chloride dihydrate (1.02 g, 6 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. The precipitate formed was filtered off, recrystallized from ethanol and washed with hot hexane to give complex **4** as dark green crystalline, yield 1.30 g (71%), m.p. >350 °C (decomp.). IR (DRA, ν/cm^{-1}): 3063 (arC–H), 3021 (C–H), 1619, 1568, 1527 (C=N, C=C), 1464 (arC–C), 1247–1140 (C–F), 556 (Cu–N), 472 (Cu–O). Calcd. for C₂₆H₂₀Cu₂F₆N₈O₃: C 42.57, H 2.75, N 15.28, F 15.54. Found: C 42.53, H 2.68, N 15.31, F 15.58.

Compound 3, ¹H NMR (500 MHz, [D₆]DMSO)

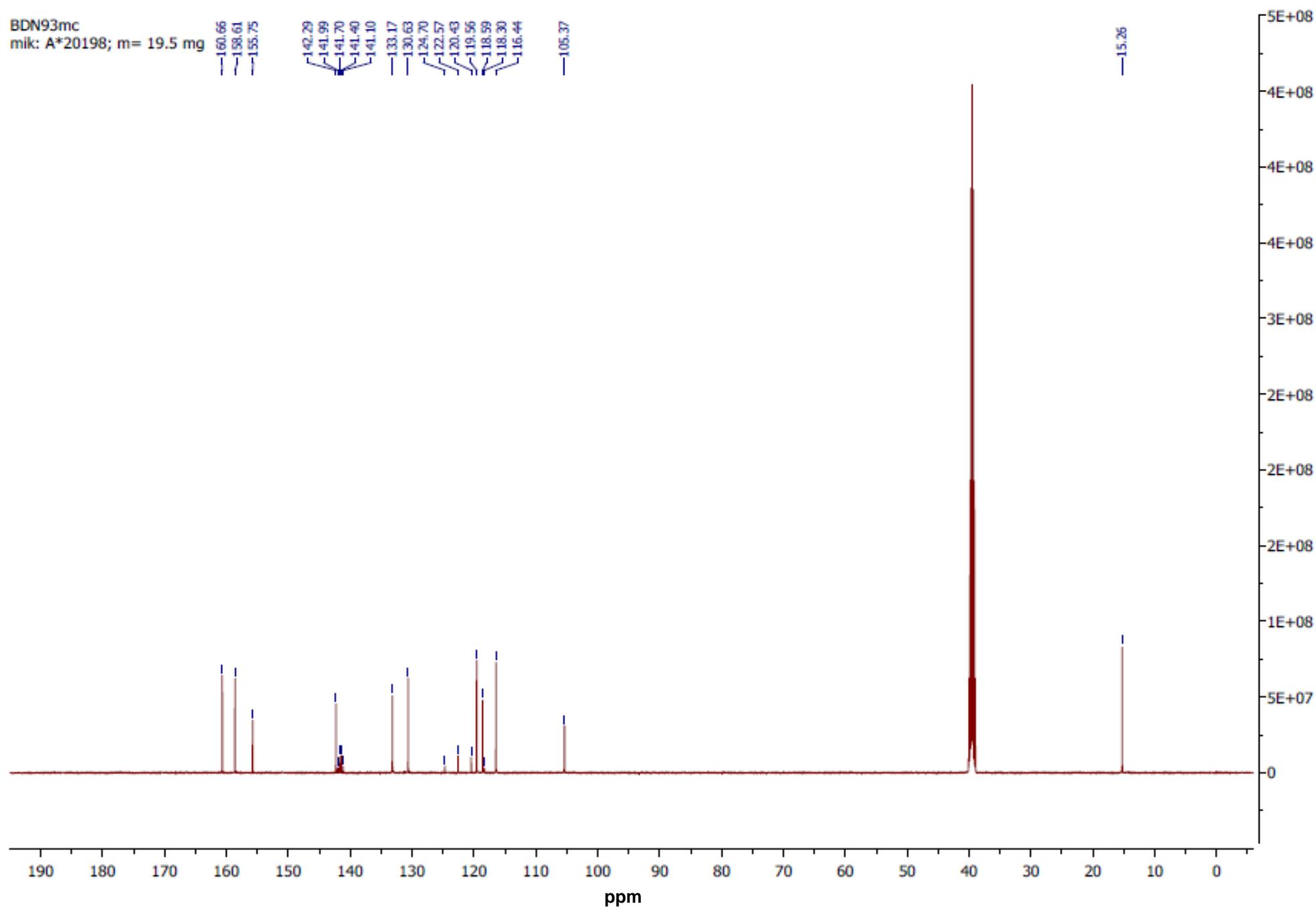


Compound 3, ^{19}F NMR (470 MHz, $[\text{D}_6]\text{DMSO}$)

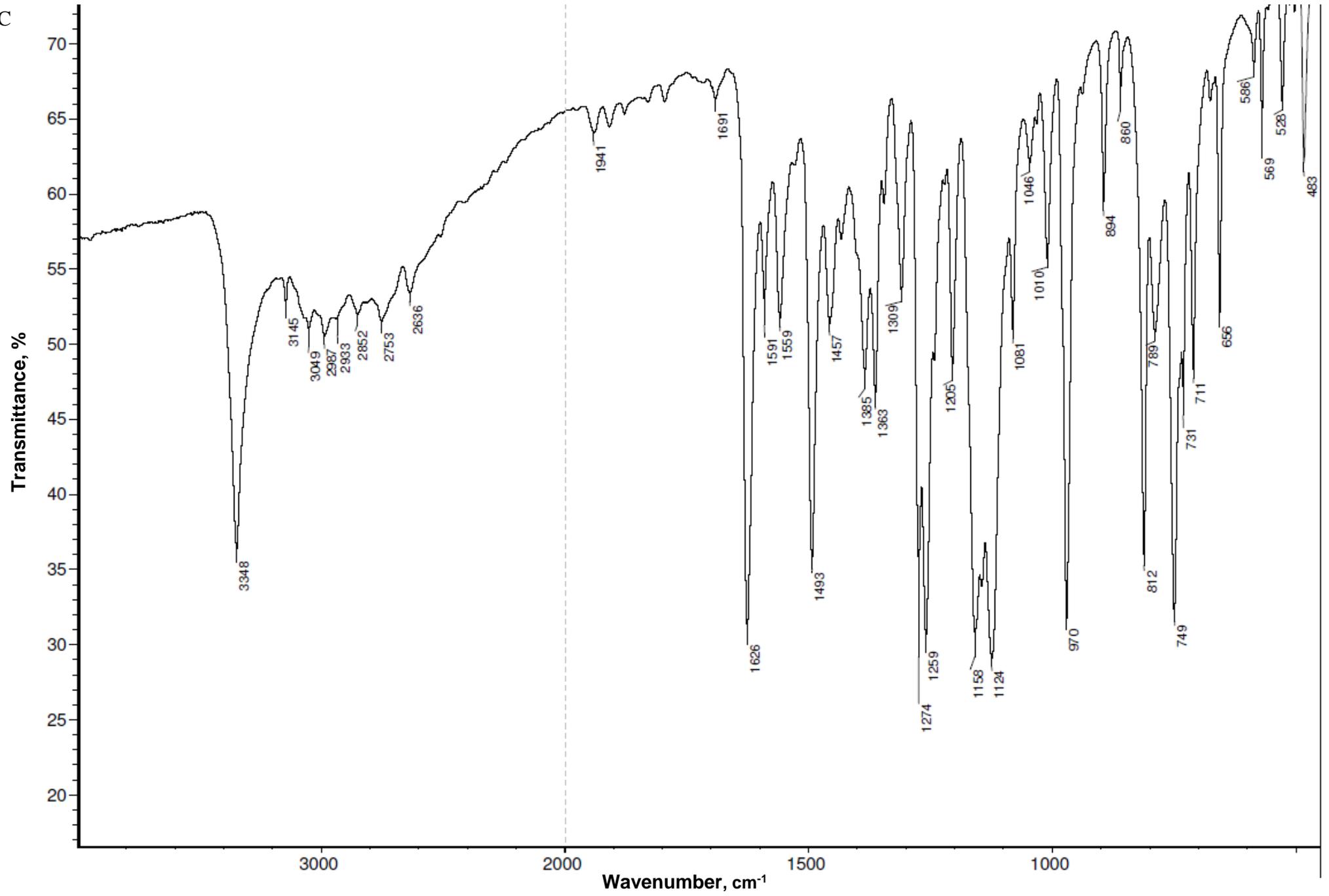


Compound 3, ¹³C NMR (125 MHz, [D6]DMSO)

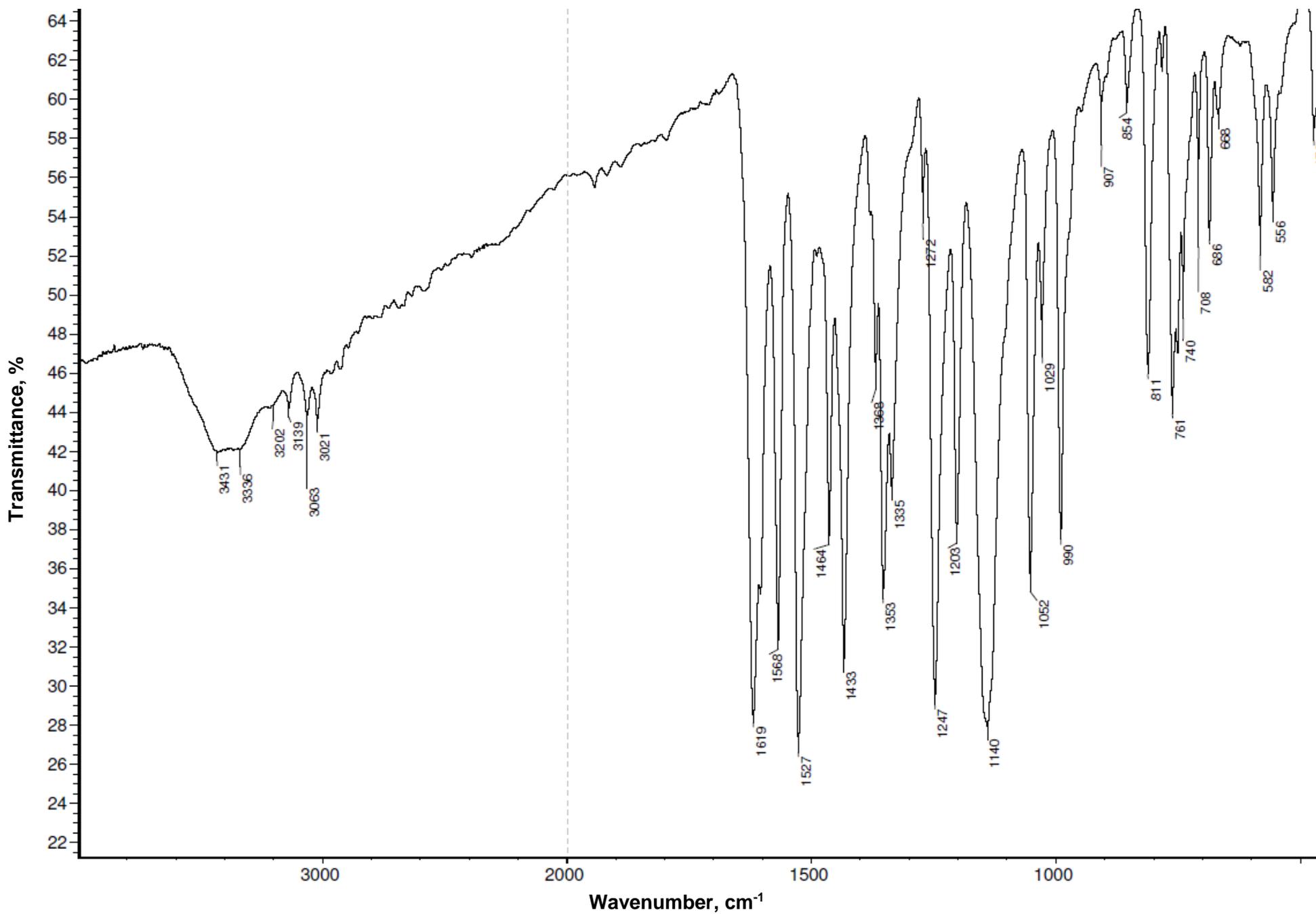
BDN93mc
mik: A*20198; m= 19.5 mg



C



Complex 4, solid-state IR spectrum



The conformation of the resulting N_3O_2 coordination unit is distorted square-pyramidal, as revealed by the structural parameter τ_5 (Addison *et al.*, 1984), which is defined as $\tau = (\beta - \alpha) / 60$ where β and α are the two greatest angles of the coordinated atom. For an ideal square-pyramidal coordination, τ is 0, whereas for ideal trigonal-bipyramidal coordination, τ becomes 1.0. In the dinuclear copper (II) complex **4**, the largest angles are $\beta_1 = 168.83(11)^\circ$ for N3—Cu1—O2 , $\beta_2 = 169.78(11)^\circ$ for N2—Cu2—O1 , and $\alpha_1 = 150.18(12)^\circ$ for N8—Cu1—N1 , $\alpha_2 = 151.50(12)^\circ$ for N6—Cu2—N4 (Figure S1, Table S1). Thus, τ is 0.31, its value is close to square-pyramidal geometry, but indicates a distortion. The central Cu1 atom forms the coordination polyhedra with O2, N3, N8 and N1 atoms providing the basal plane, and O3 atom occupying the apical position. The coordination polyhedra of Cu2 center is formed by O1, N2, N6 and N4 atoms of basal plane and apical O3 atom of bridging water molecule (Figure S2).

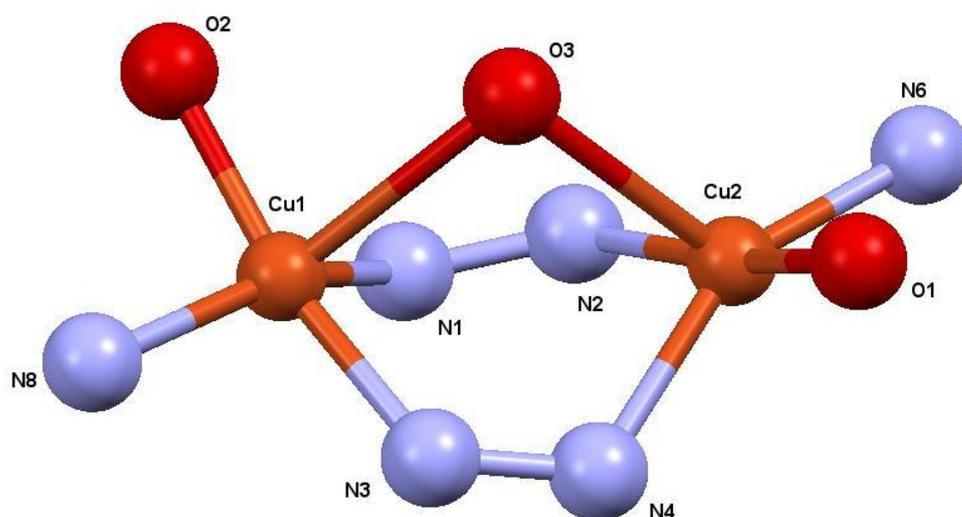


Figure S1 Coordination environment of Cu1 and Cu2 centers in the complex **4**.

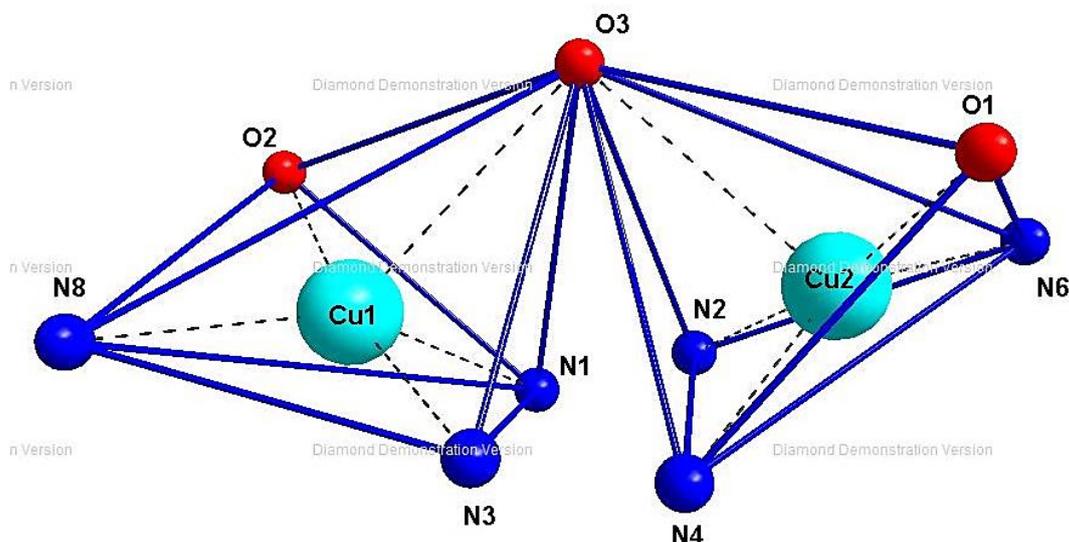


Figure S2 Coordination polyhedra of Cu1 and Cu2 centers in the complex **4**.

Table S1 Geometric parameters of the five-coordinated copper(II) centers in complex **4**.

Bond	Å	Bond	Å
Cu1 – O3	2.407(2)	Cu2 – O3	2.452(2)
Cu1 – O2	1.878(2)	Cu2 – O1	1.880(2)
Cu1 – N1	2.042(3)	Cu2 – N4	2.055(3)
Cu1 – N3	1.926(3)	Cu2 – N2	1.933(3)
Cu1 – N8	1.988(2)	Cu2 – N6	1.992(2)
Angle	°	Angle	°
N3 – Cu1 – O2	168.83(11)	N2 – Cu2 – O1	169.78(11)
N8 – Cu1 – N1	150.18(12)	N6 – Cu2 – N4	151.50(12)
N8 – Cu1 – O3	122.60(10)	N6 – Cu2 – O3	124.05(10)
O2 – Cu1 – O3	86.10(10)	O1 – Cu2 – O3	86.47(10)
O2 – Cu1 – N1	88.60(11)	O1 – Cu2 – N4	88.54(11)
N3 – Cu1 – N8	90.17(10)	N2 – Cu2 – N6	90.02(11)
N3 – Cu1 – O3	82.76(10)	N2 – Cu2 – O3	83.36(10)
N3 – Cu1 – N1	91.52(11)	N2 – Cu2 – N4	91.51(11)
N1 – Cu1 – O3	87.13(10)	N4 – Cu2 – O3	84.39(10)
O2 – Cu1 – N8	95.27(10)	O1 – Cu2 – N6	94.80(10)