Supporting Information

Shape-Persistent Ruthenium (II)- and Iron (II)-Bisterpyridine Metallodendrimers: Synthesis, Traveling-Wave Ion-Mobility Mass Spectrometry, and Photophysical Properties

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1. ESI mass spectra, ESI-TWIM MS plots, and drift time distributions of Ru(II) complex **G0**.

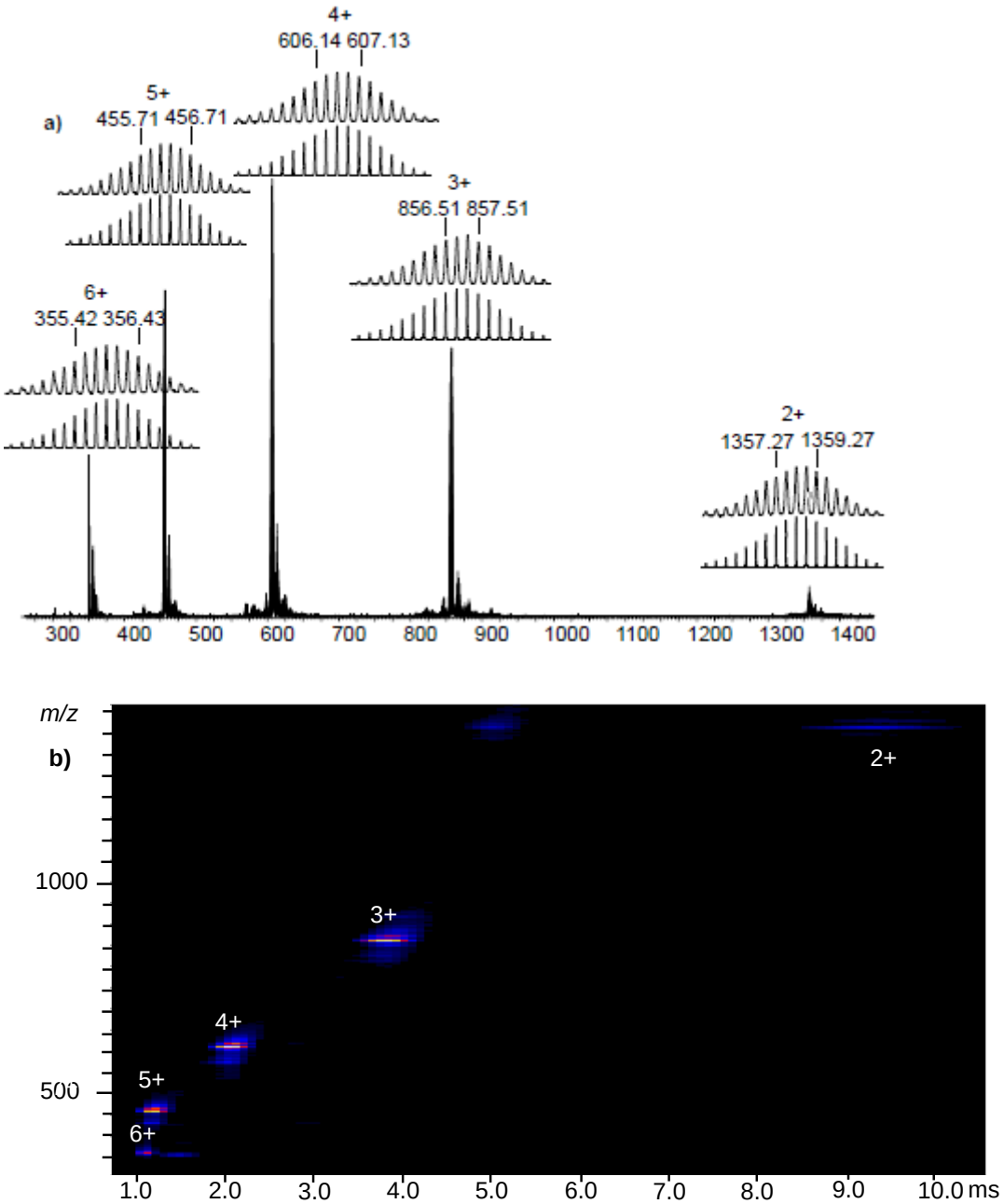
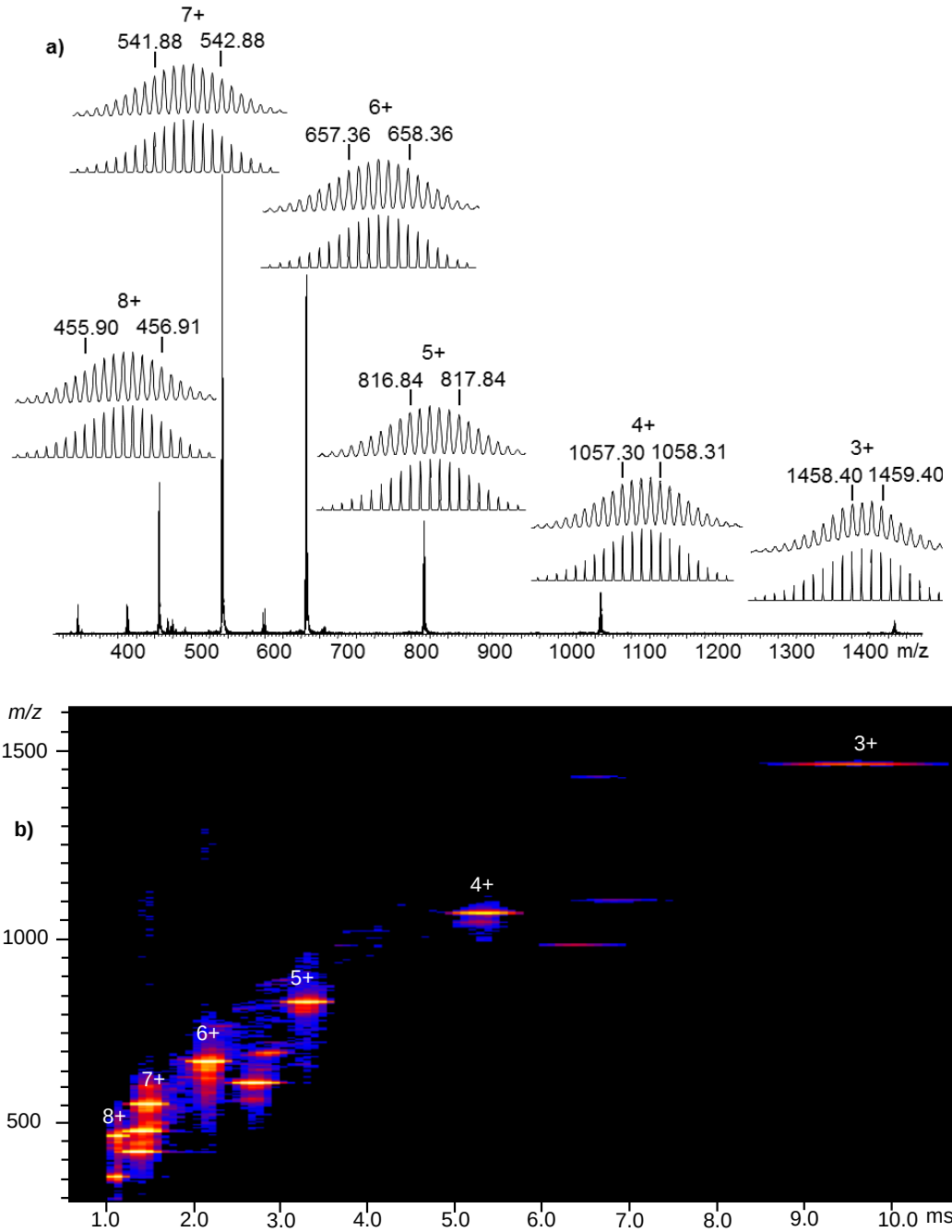


Figure S1. (a) ESI mass spectrum of **G0.** The insets in the mass spectrum show experimental (top) and calculated (bottom) isotope distributions**.** (b) Two-dimensional ESI-TWIM MS plot (mass-to-charge ratio *vs.* drift time) of **G0** measured at a traveling wave velocity of 350 m/s and traveling wave height of 8.5 V. The charge states of intact assemblies are marked.

2. ESI MS, ESI-TWIM MS plots, drift time distributions, and gradient tandem MS of Ru(II)/Fe(II) complex **G1Ru4Fe1**.



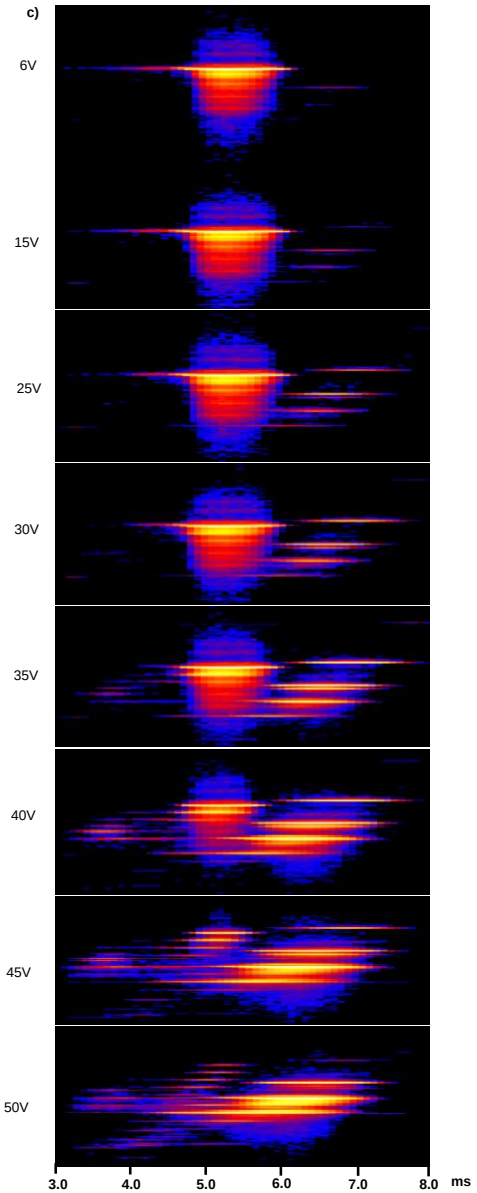


Figure S2. (a) ESI MS of **G1Ru4Fe1.** The insets in the mass spectrum show experimental (top) and calculated (bottom) isotope distributions**.** (b) Two-dimensional ESI-TWIM MS plot (mass-to-charge ratio *vs.* drift time) of **G1Ru4Fe1** measured at a traveling wave velocity of 350 m/s and a traveling wave height of 8.5 V. The charge states of intact assemblies are marked. (c) Two-dimensional ESI gMS^2 TWIM plot of *m/z* 1058 (4+) from **G1Ru4Fe1** (PF_6^-, as counterion). The *m/z*-1058 ion was mass-selected by the Q analyzer and subjected to CAD with Ar atoms in the trap cell at collision energies varying between 6-50 eV. The ions exiting the trap were separated by size through the TWIM device at a traveling wave velocity of 350 m/s and a traveling wave height of 8.5 V, and the separated ions were transferred to the ToF region for *m/z* analysis. The plots display a narrow *m/z* window around *m/z* 1058 to show how the intensity of the assembly **G1Ru4Fe1** (PF_6^-, as counterion) is depleted as it undergoes increasingly energetic collisions.

3. Gradient tandem MS of Ru(II) complexes **G1Ru5**.

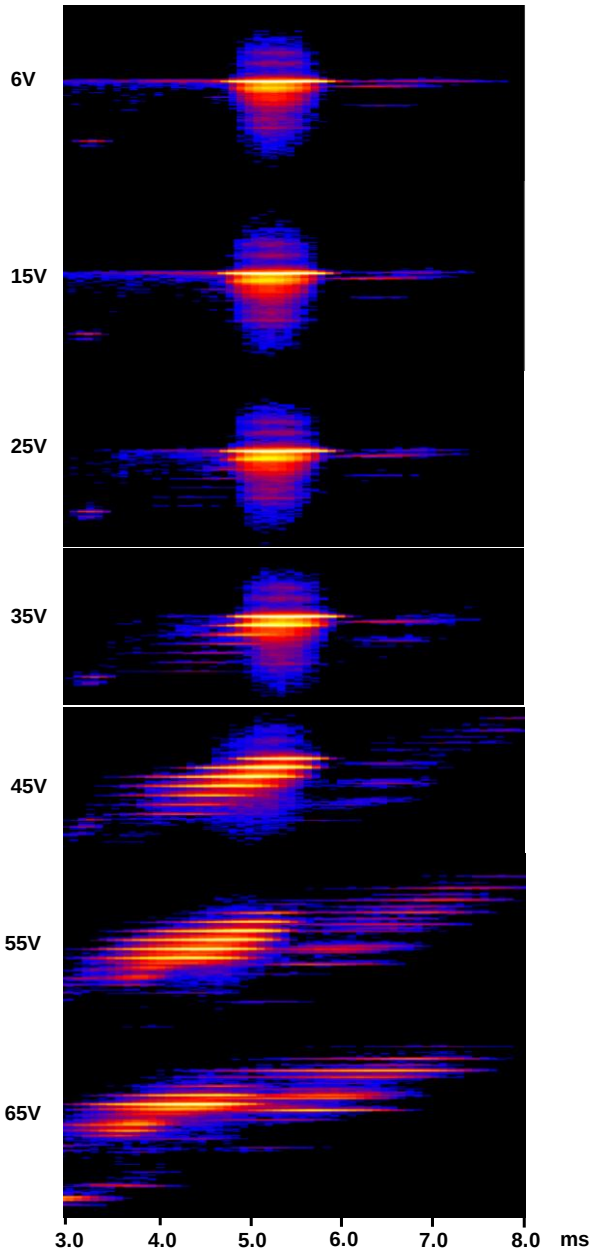
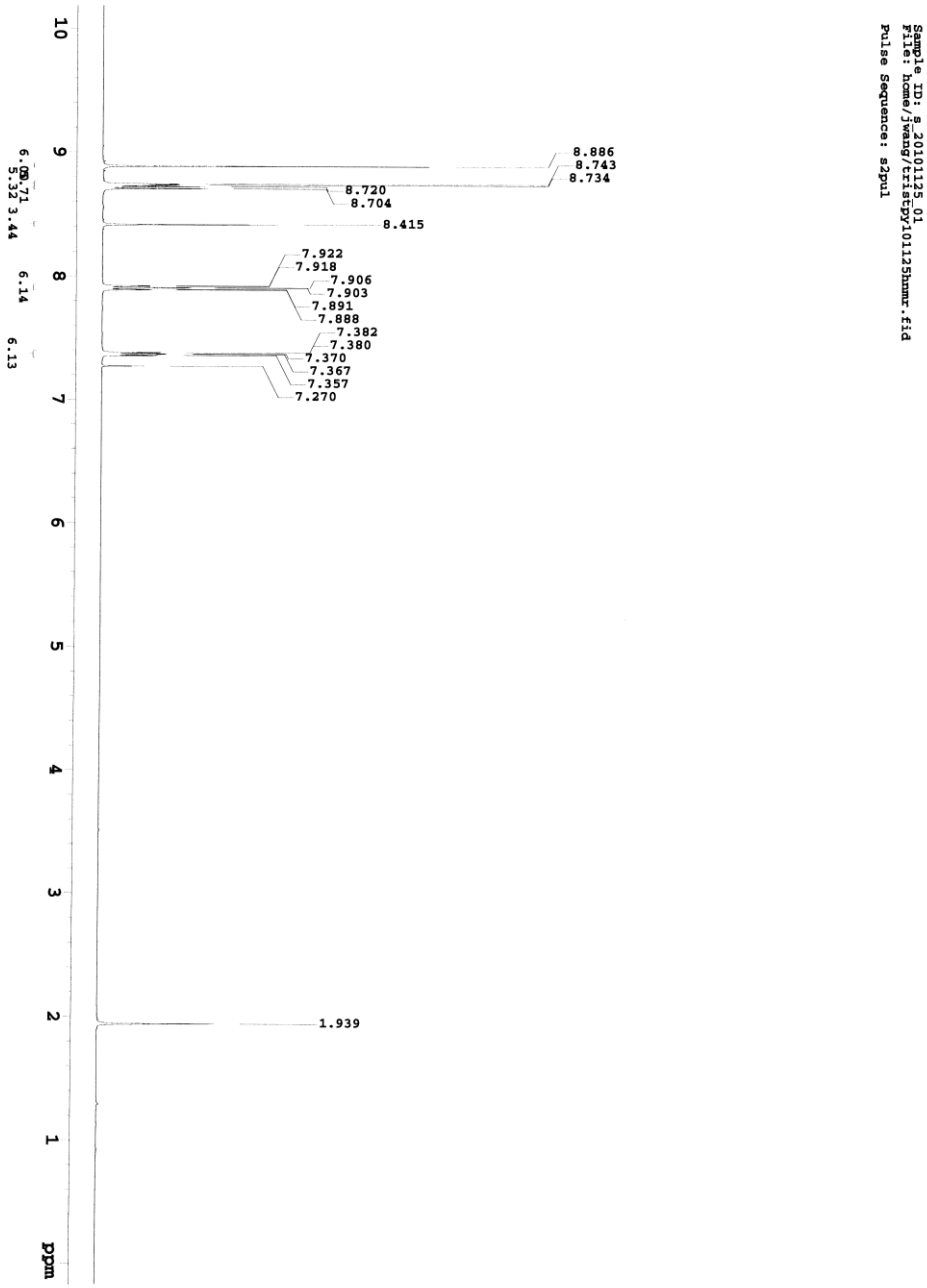
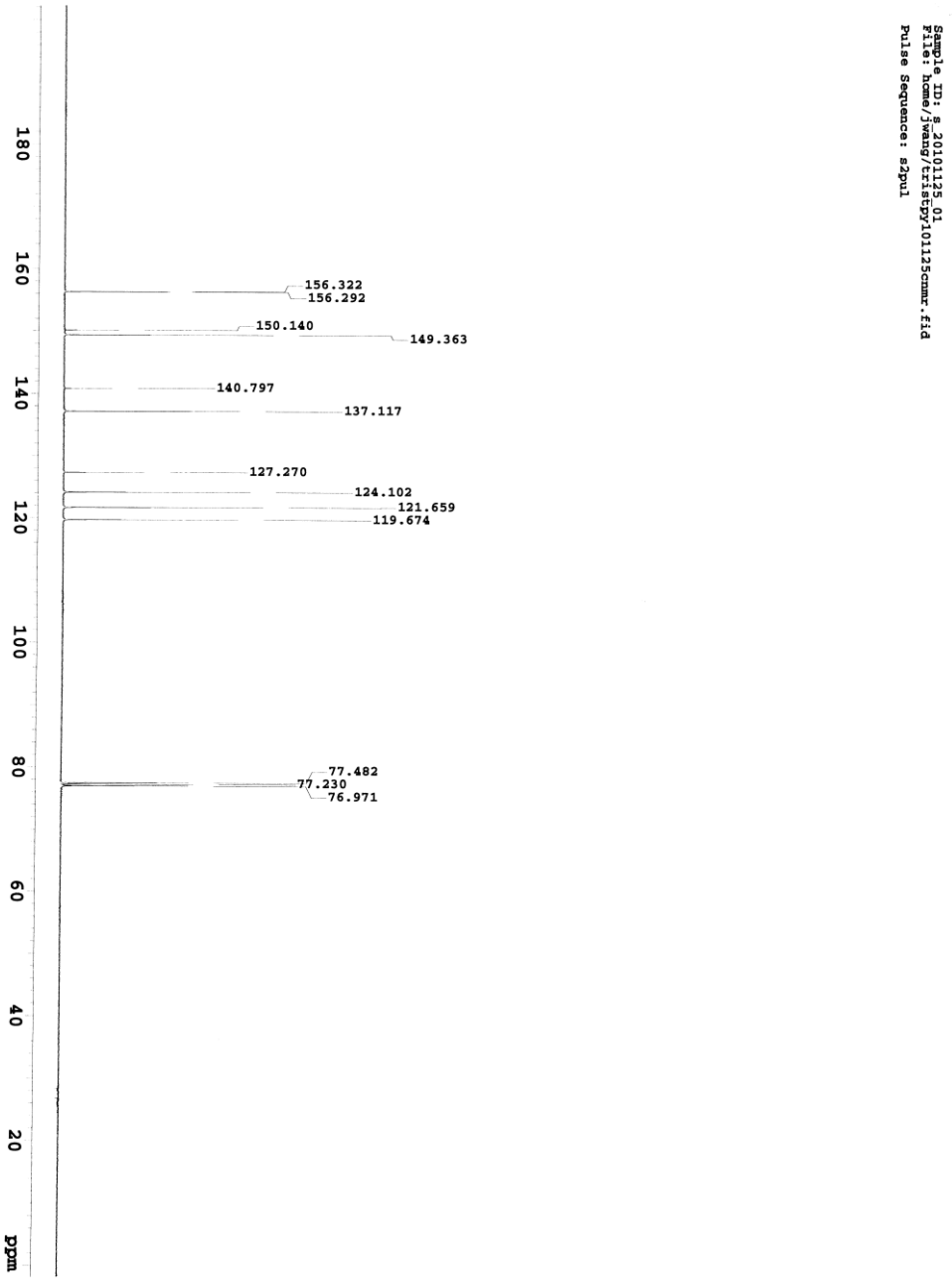


Figure S3. Two-dimensional ESI gMS^2 TWIM plot of *m/z* 1069 (4+) from **G1Ru5** (PF_6^-, as counterion). The *m/z*-1069 ion was mass-selected by the Q analyzer and subjected to CAD with Ar atoms in the trap cell at collision energies varying between 6-65 eV. The ions exiting the trap were separated by size through the TWIM device at a traveling wave velocity of 350 m/s and a traveling wave height of 8.5 V, and the separated ions were transferred to the ToF region for *m/z* analysis. The plots display a narrow *m/z* window around *m/z* 1069 to show how the intensity of the assembly **G1Ru5** (PF_6^-, as counterion) is depleted as it undergoes increasingly energetic collisions.

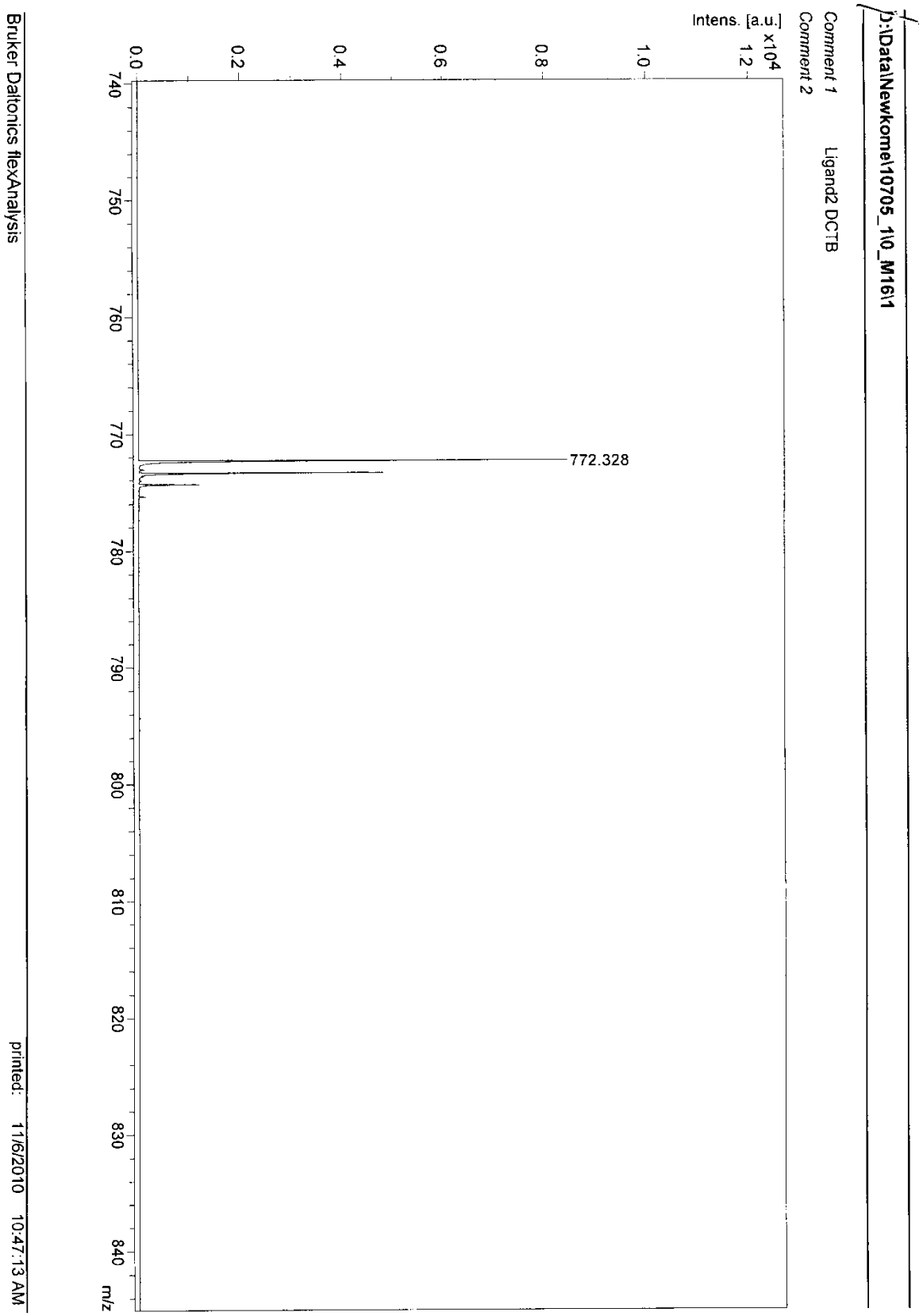
4. ^{1}H NMR, ^{13}C NMR, MALDI-ToF MS, and COSY NMR spectra of the ligands and metallo-structures**.**



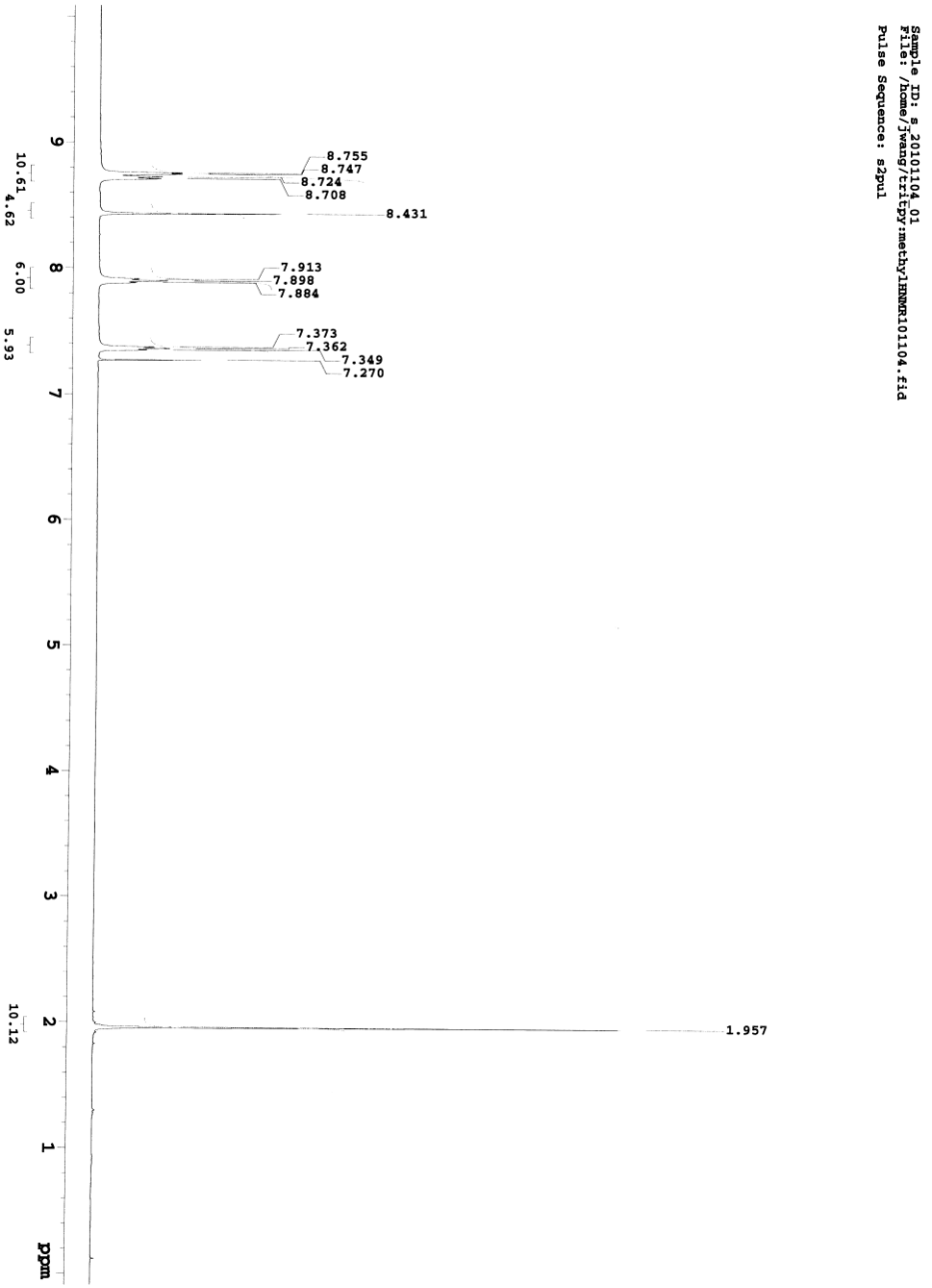
^{1}H NMR spectrum of **T3**.



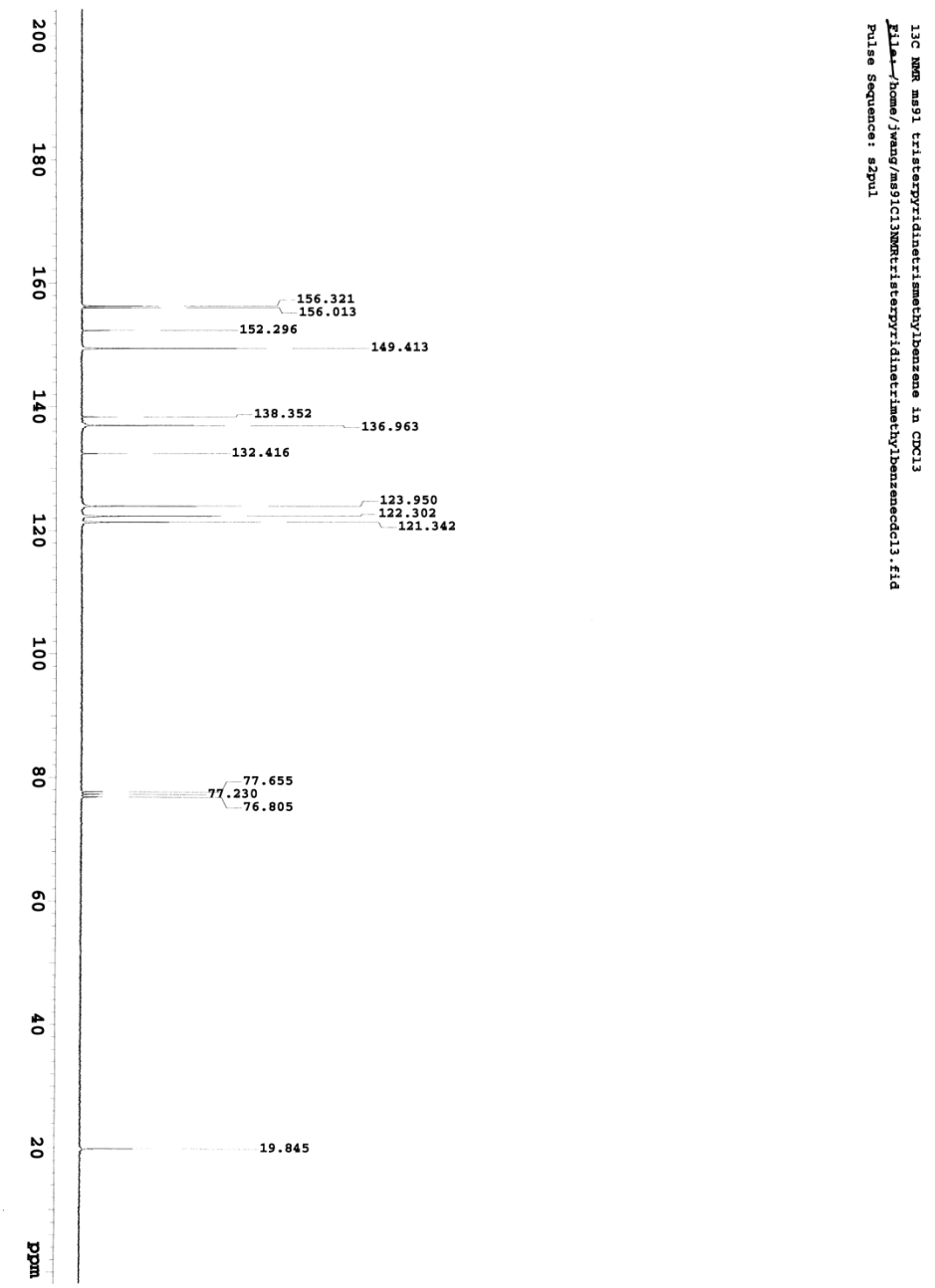
^{13}C NMR spectrum of **T3**.



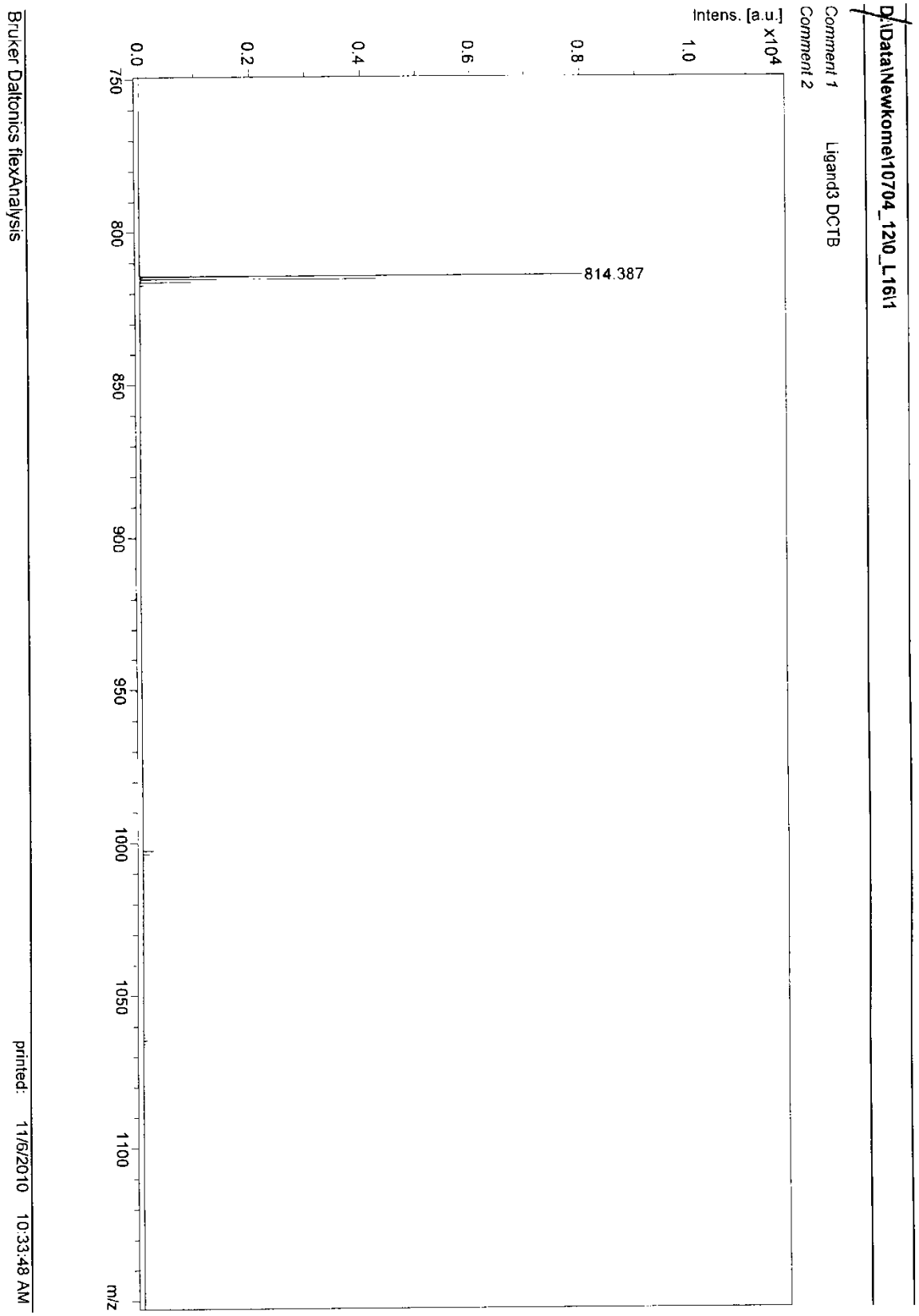
MALDI-ToF mass spectrum of **T3**.



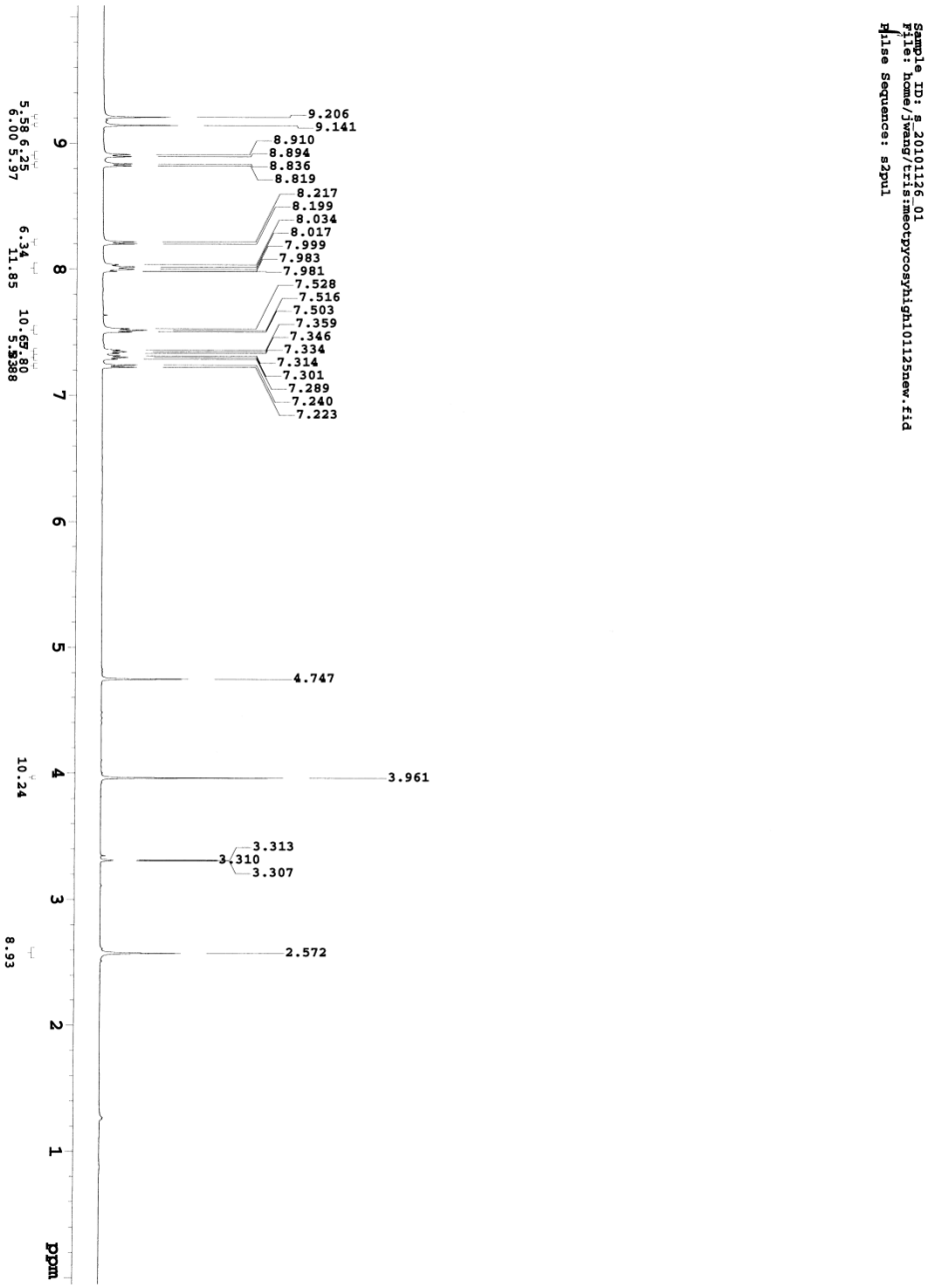
^{1}H NMR spectrum of **MT3**.



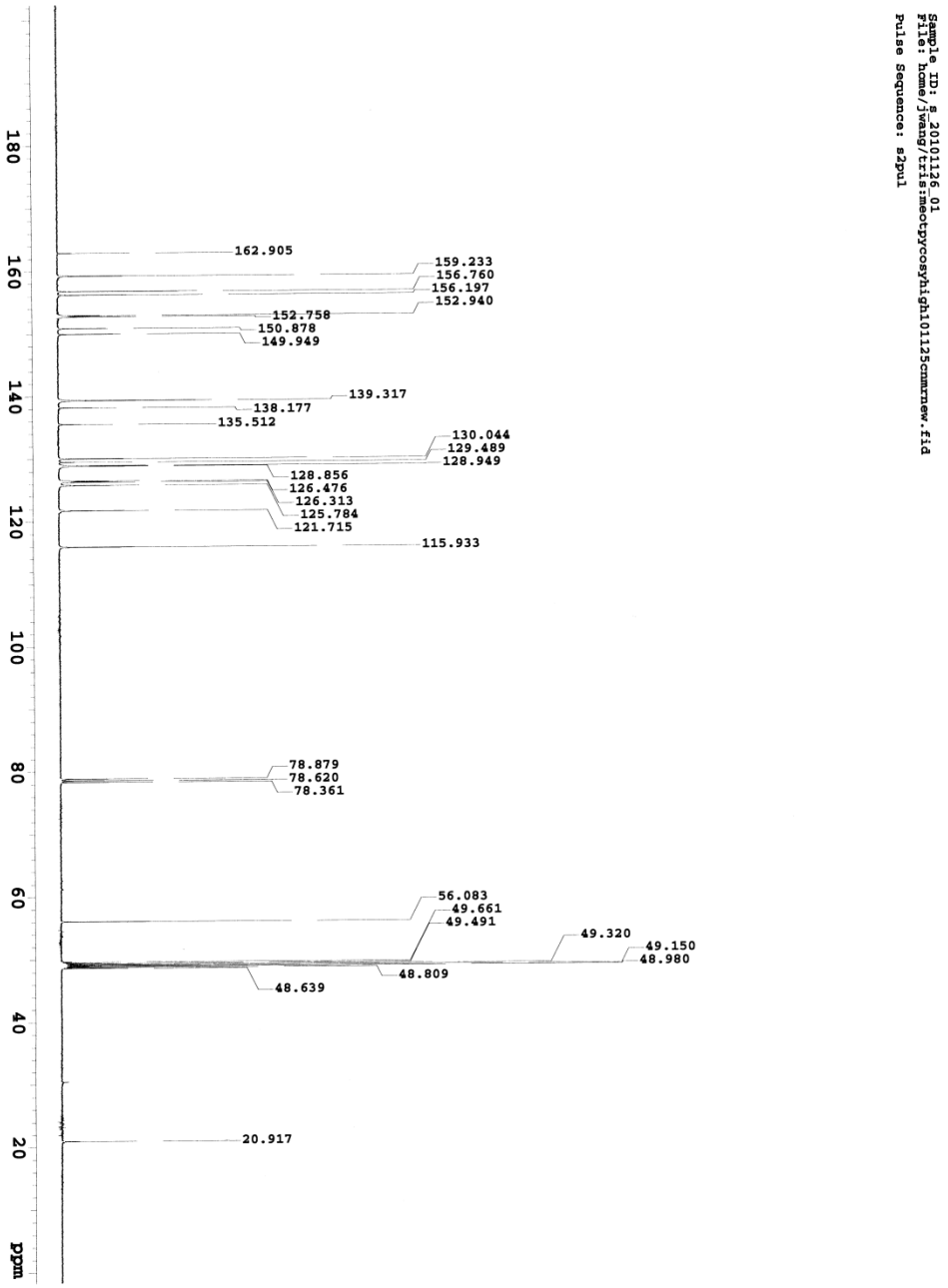
^{13}C NMR spectrum of **MT3**



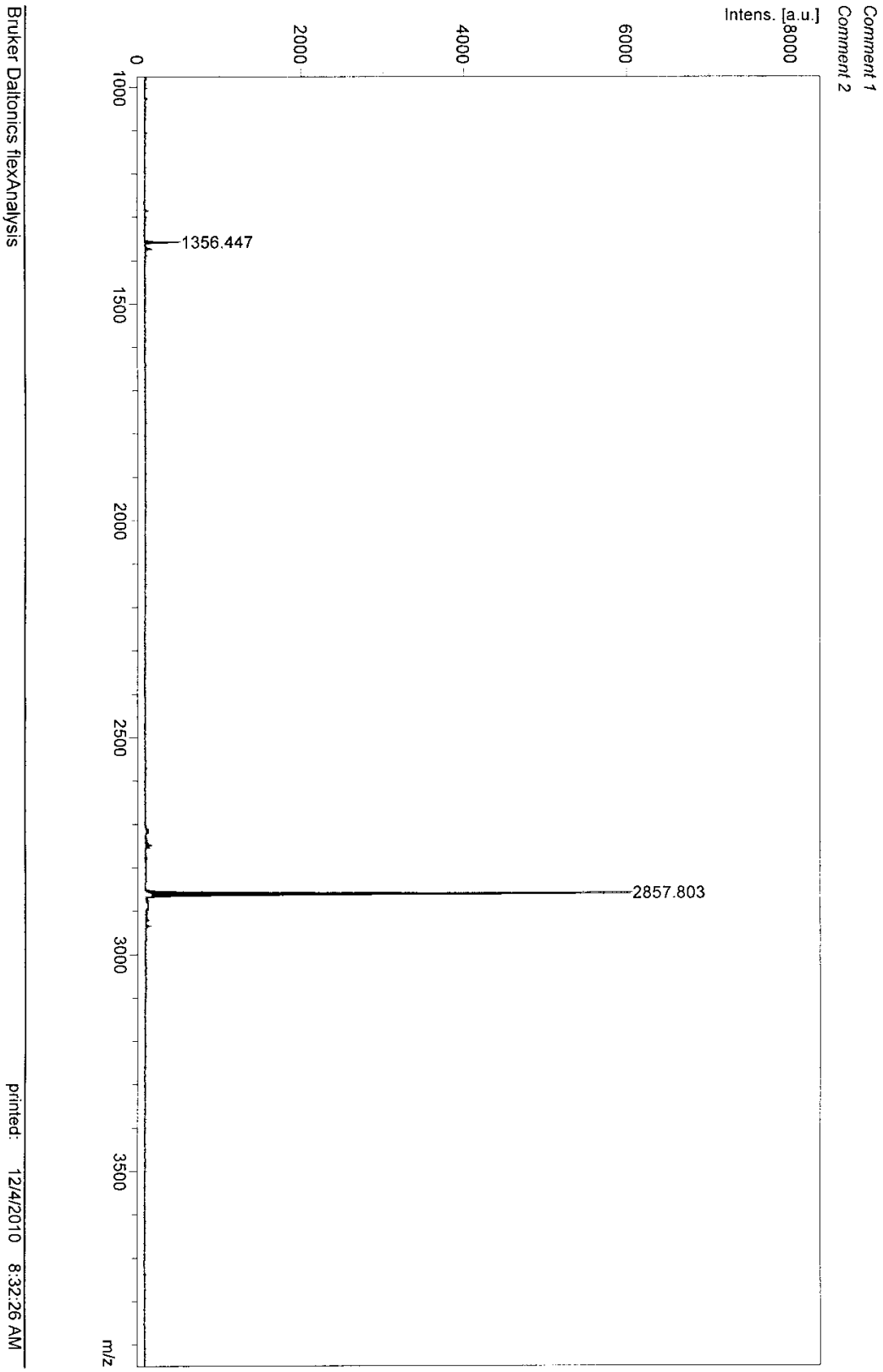
MALDI-ToF mass spectrum of **MT3**.



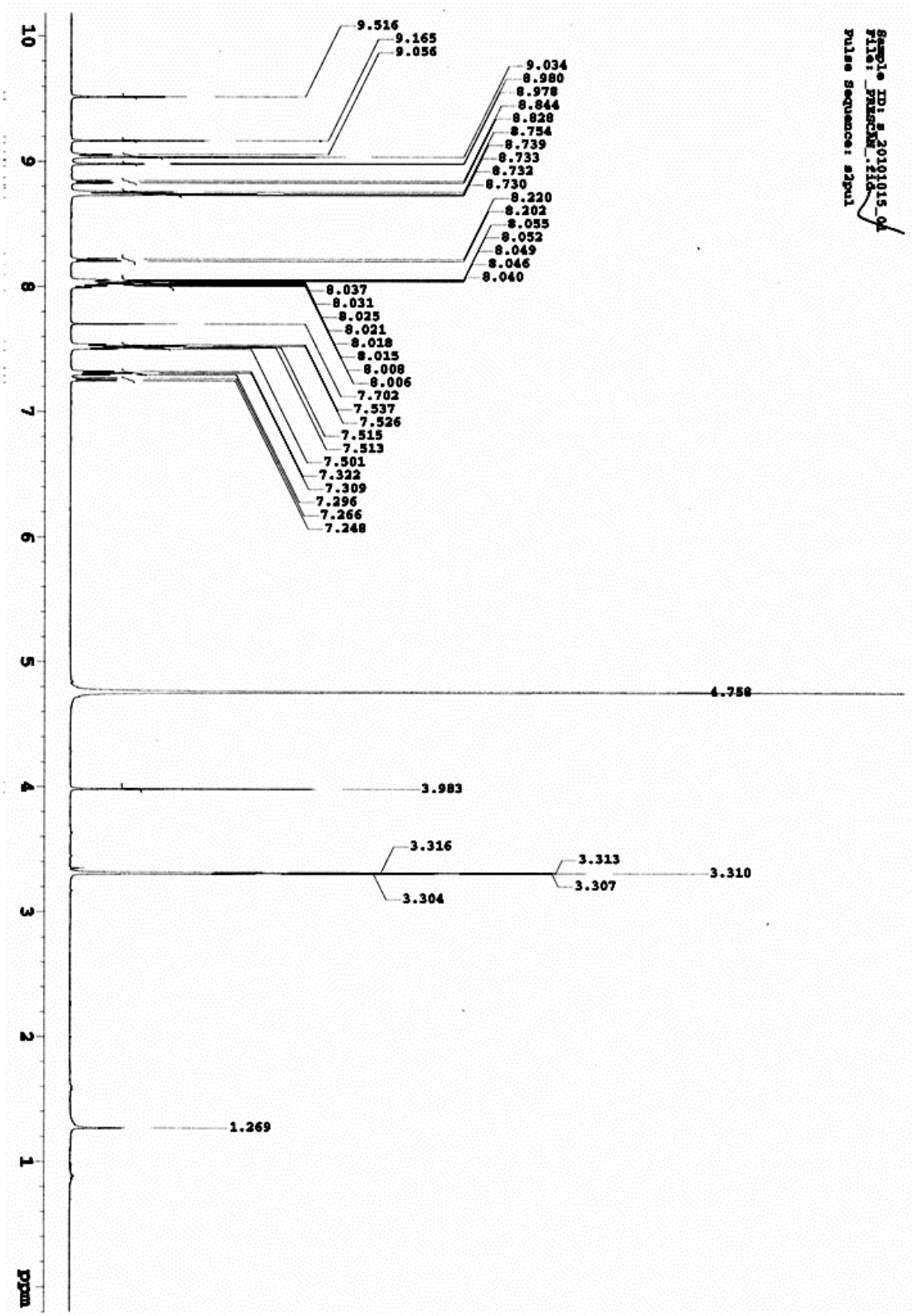
^{1}H NMR spectrum of **G0**.



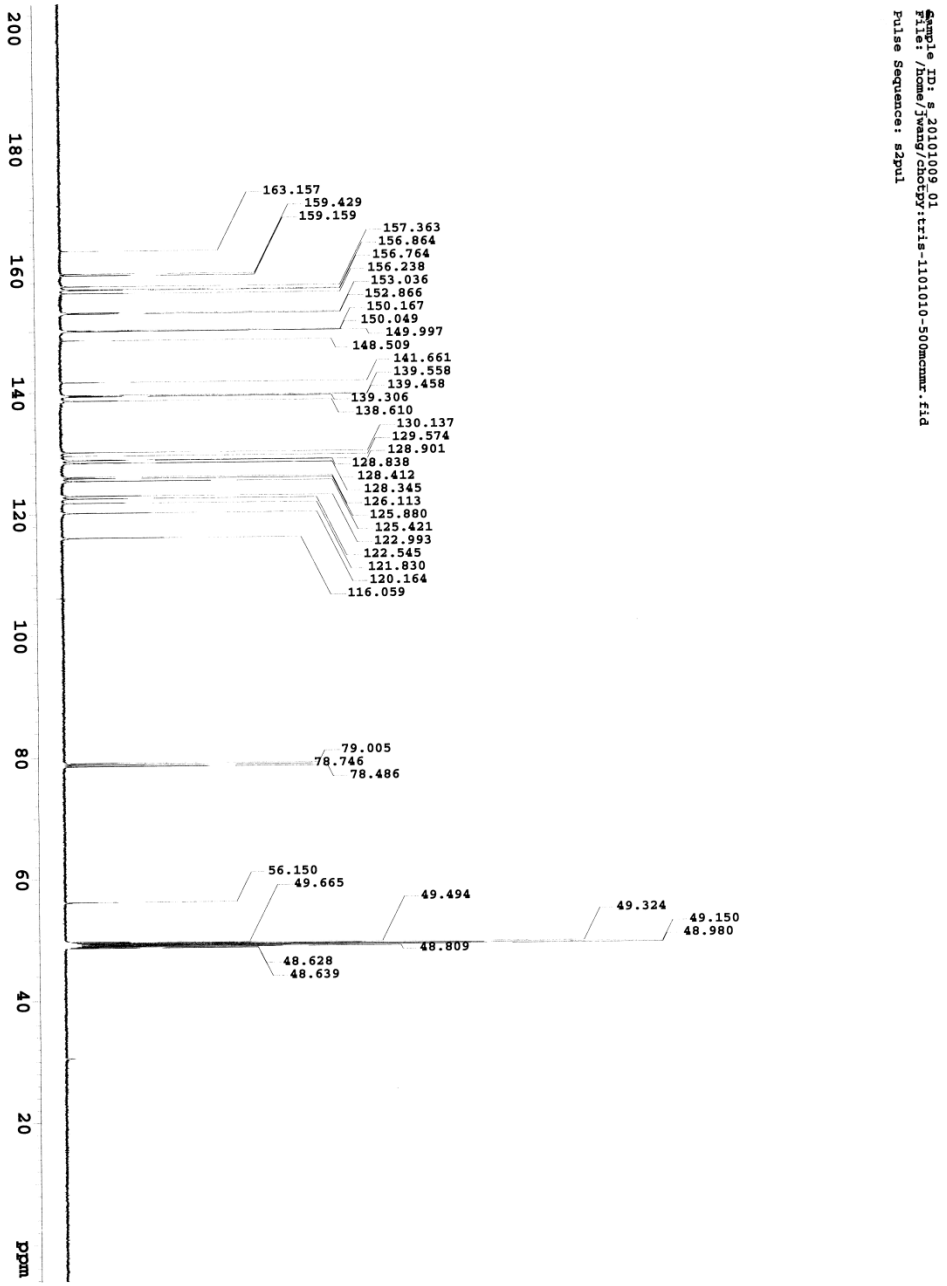
^{13}C NMR spectrum of **G0**.



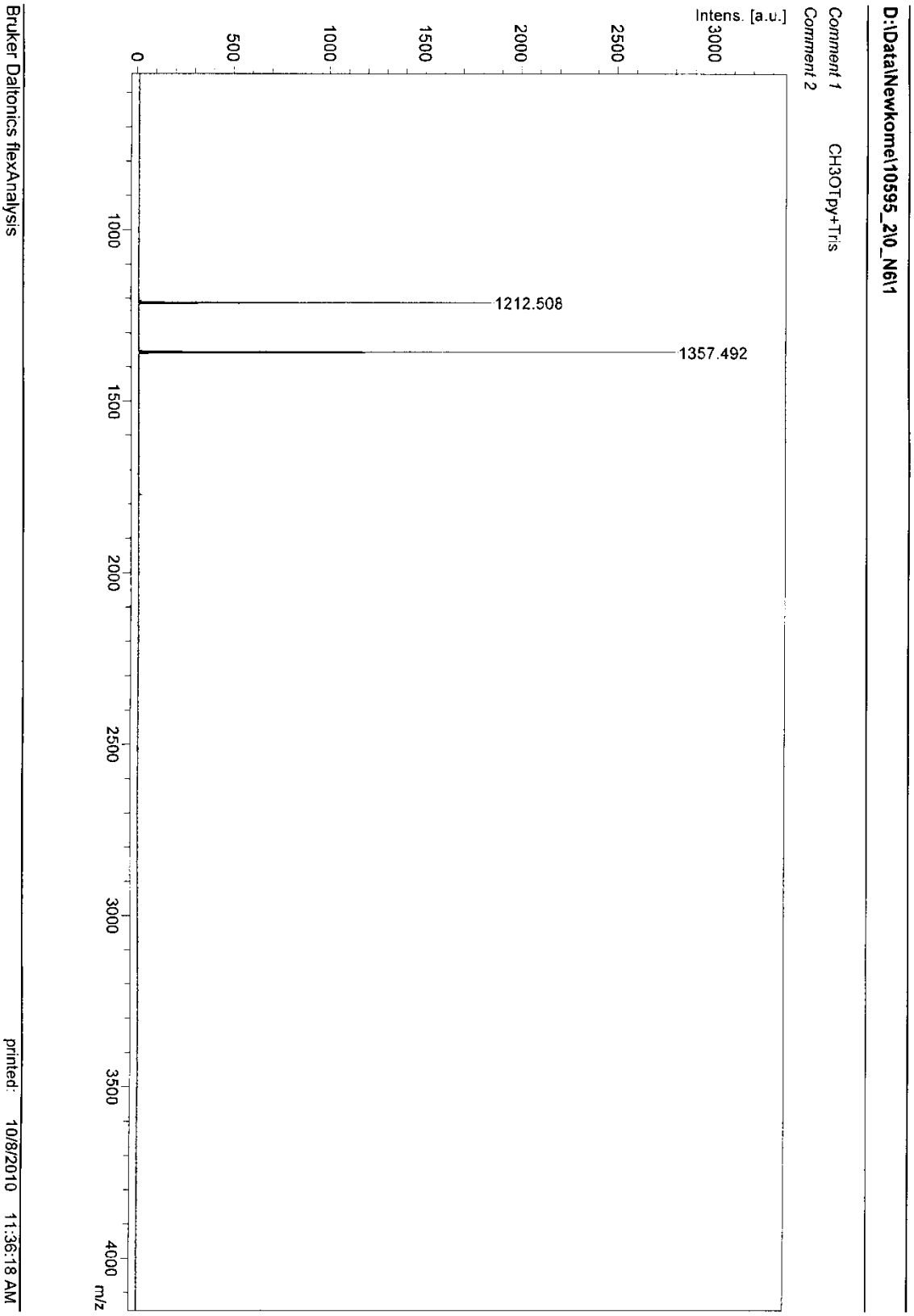
MALDI-ToF mass spectrum of **G0**.



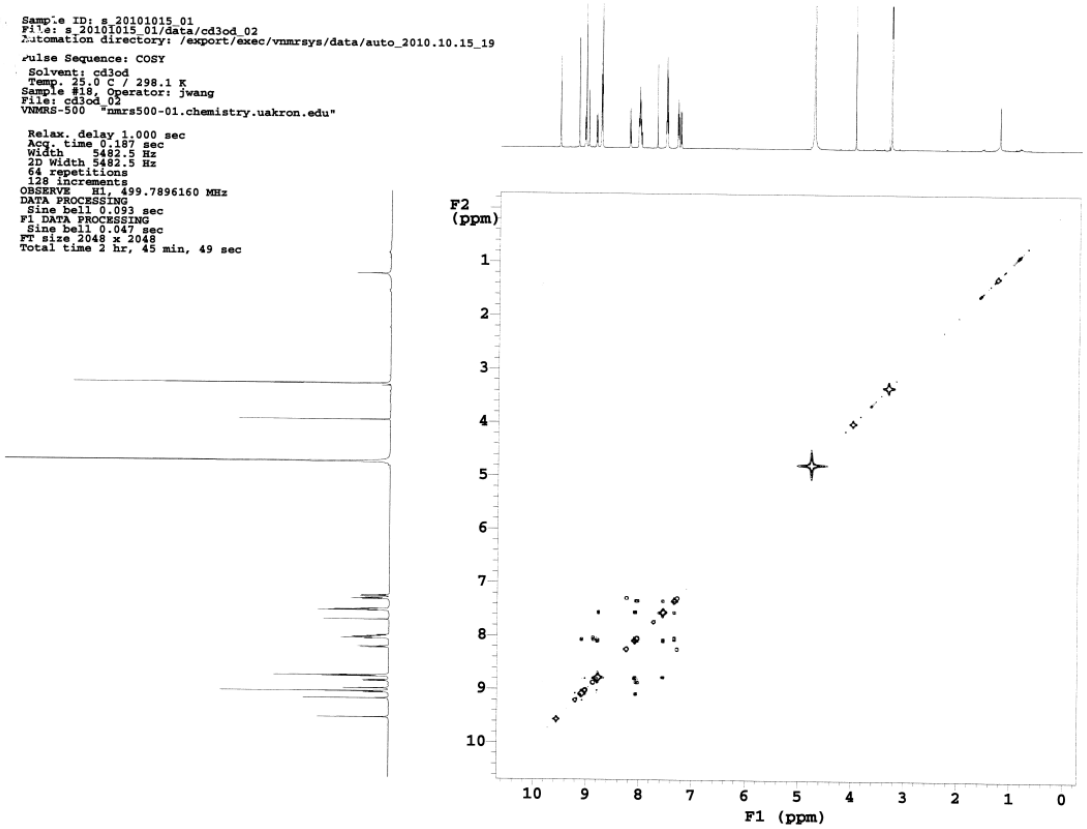
^{1}H NMR spectrum of **T2Ru1**.



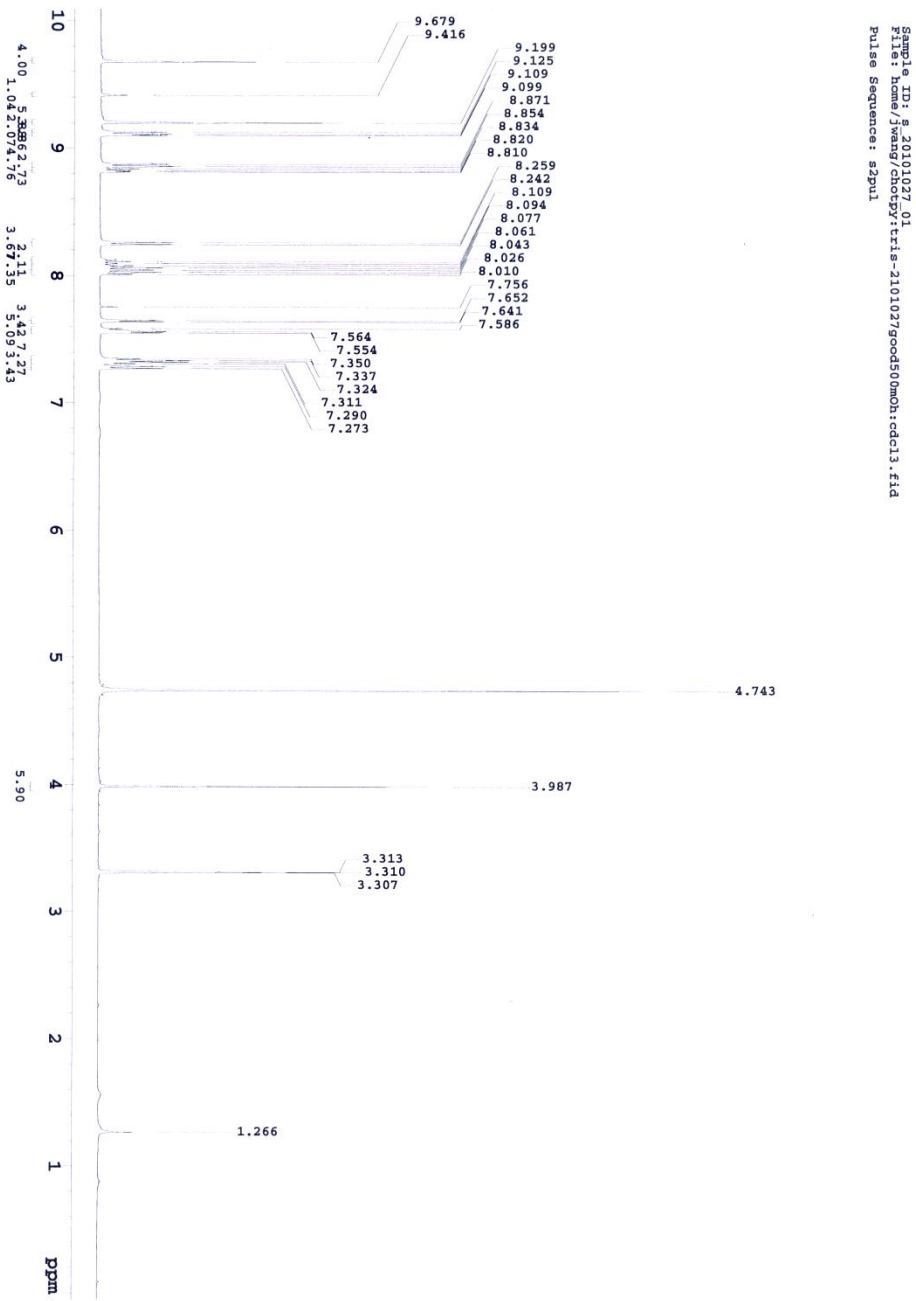
^{13}C NMR spectrum of **T2Ru1**.



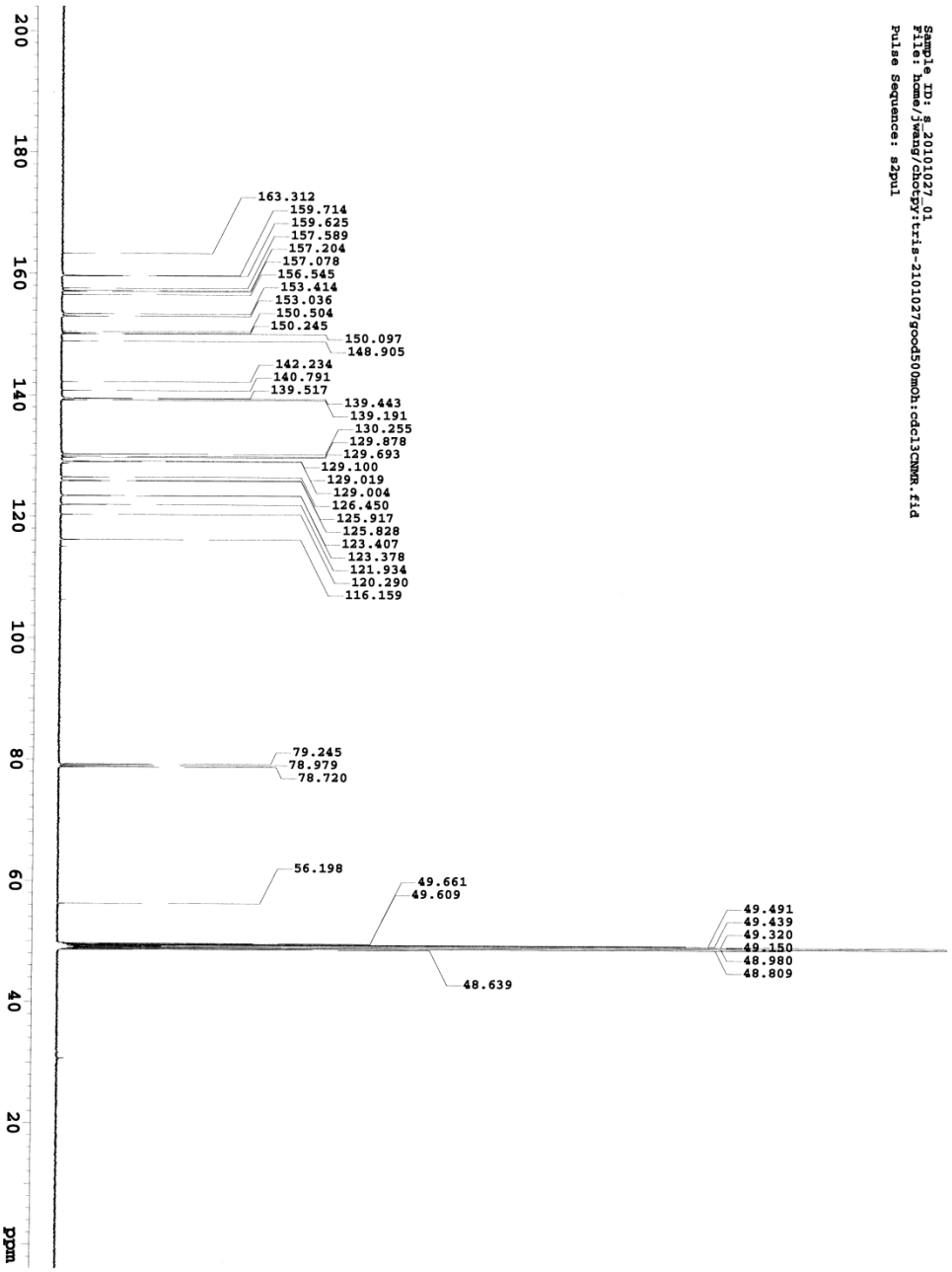
MALDI-ToF mass spectrum of **T2Ru1**.



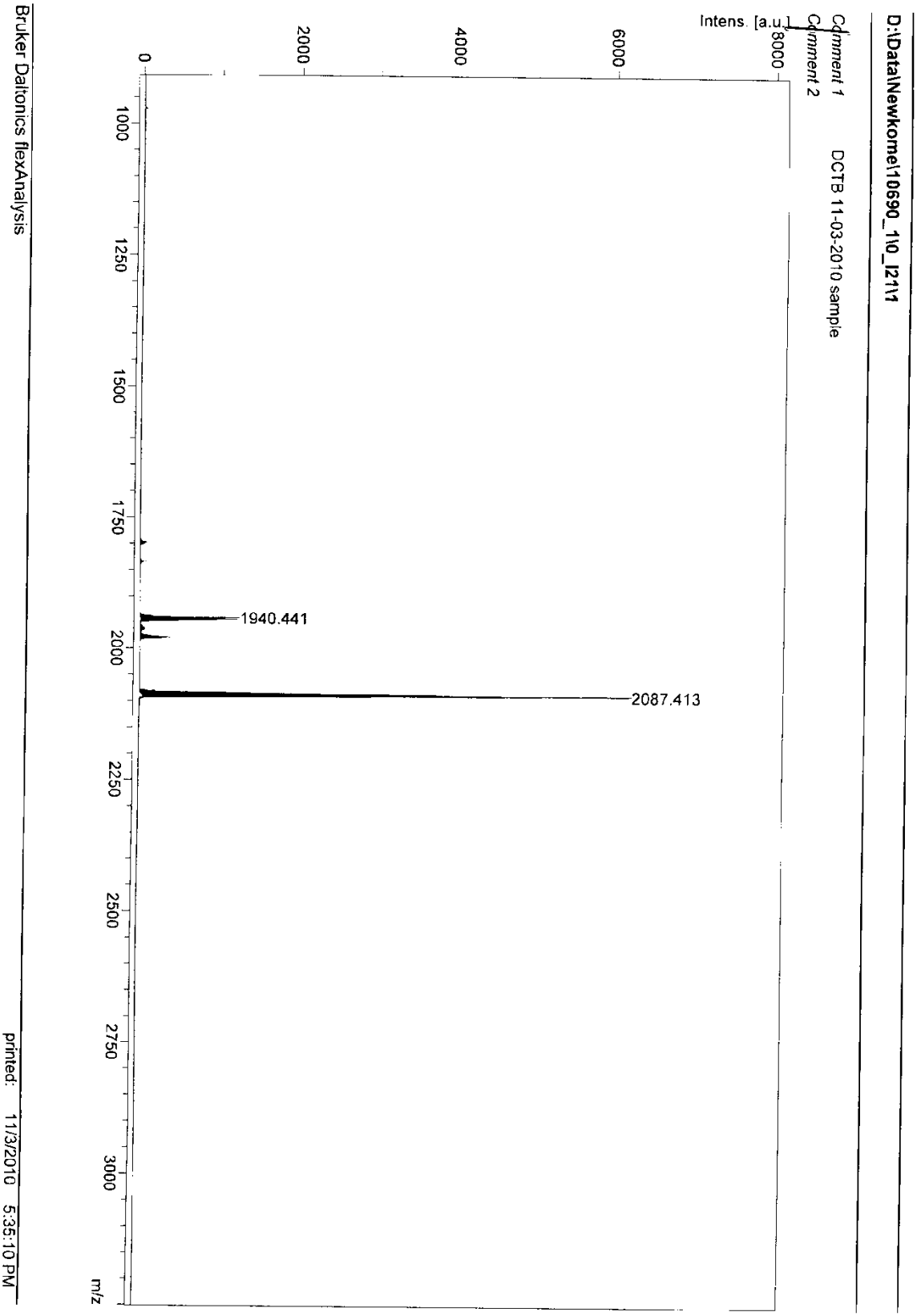
COSY NMR spectrum of **T2Ru1**.



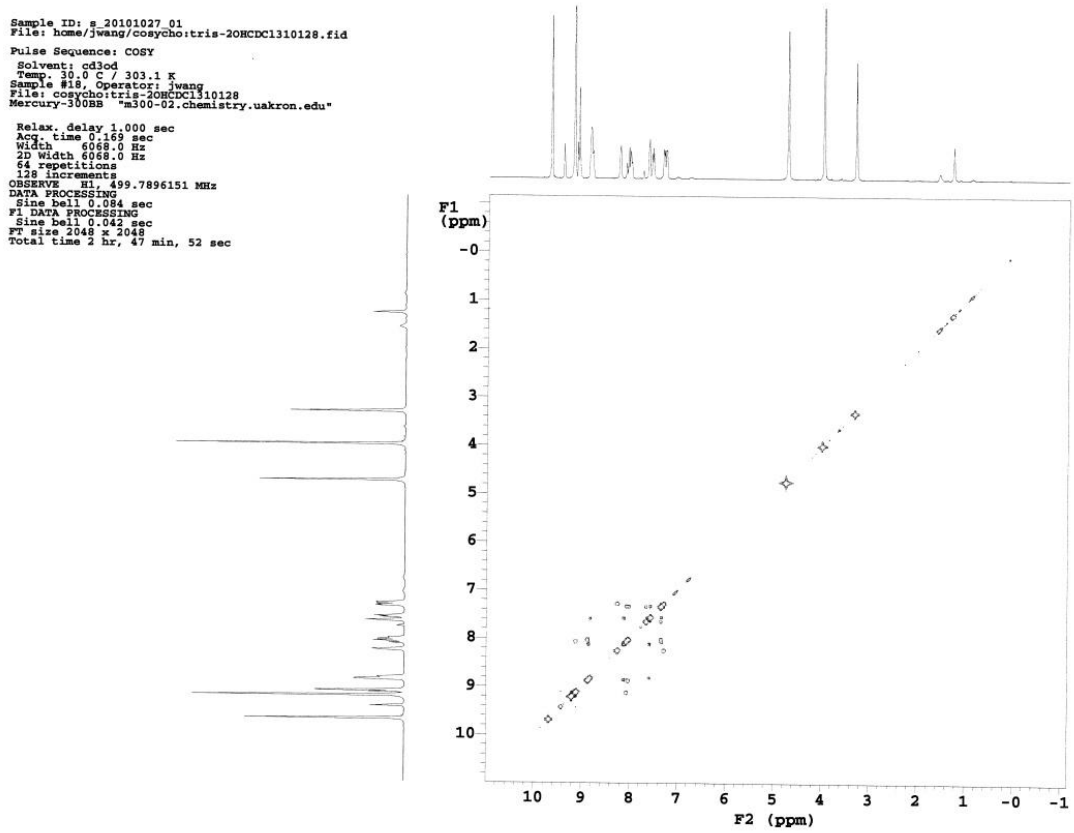
^{1}H NMR spectrum of **T1Ru2**.



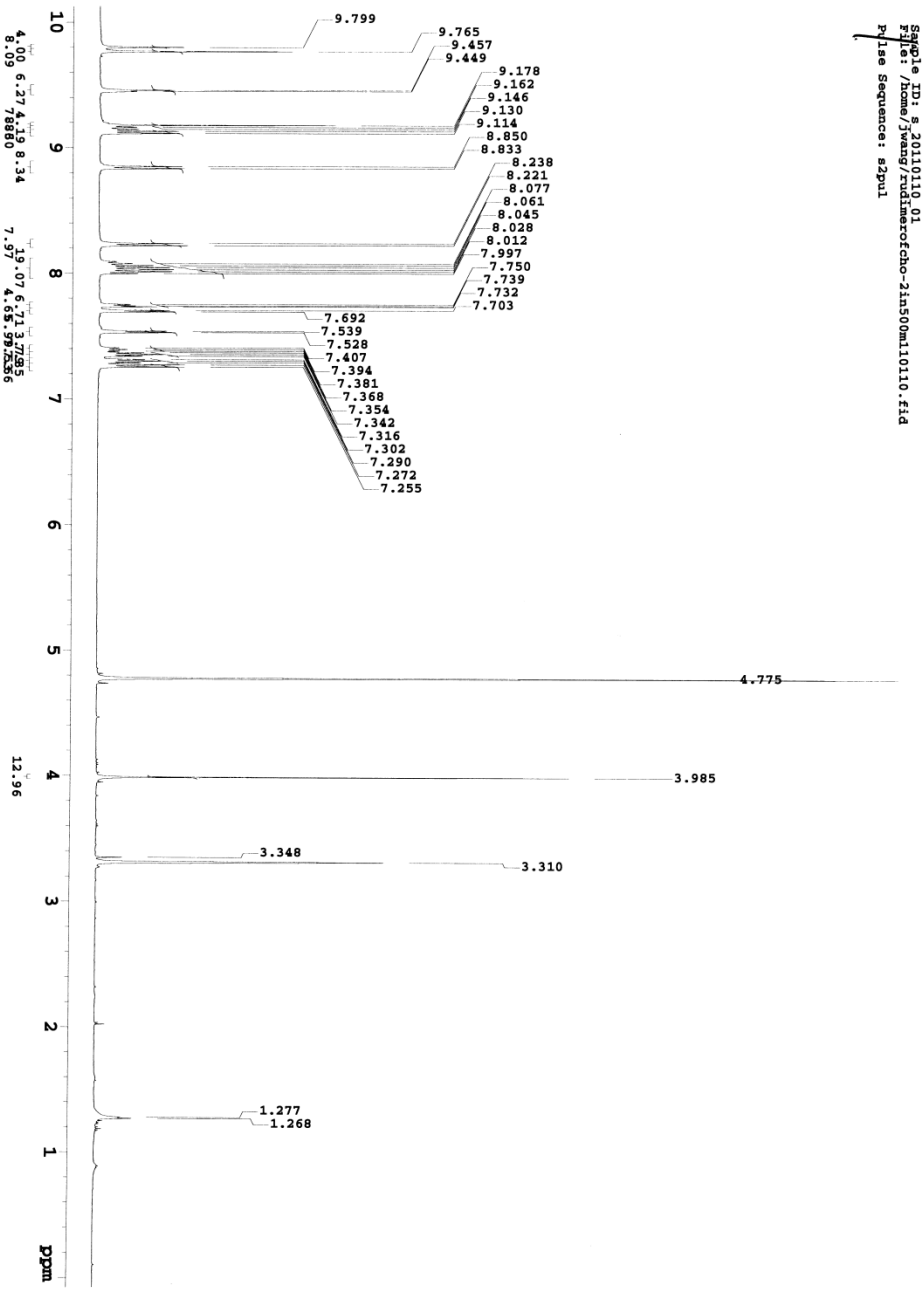
^{13}C NMR spectrum of **T1Ru2**.



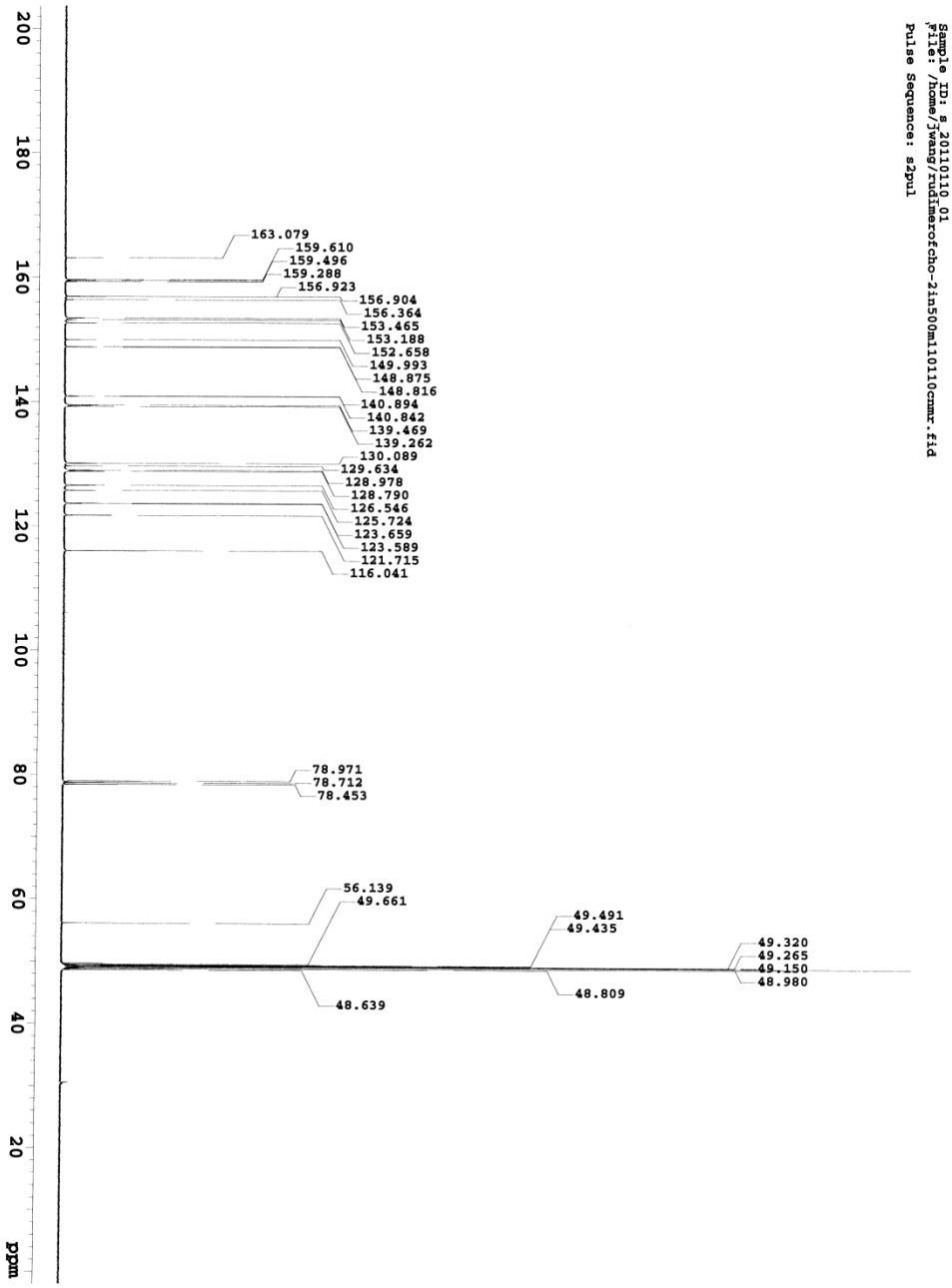
MALDI-ToF mass spectrum of **T1Ru2**.



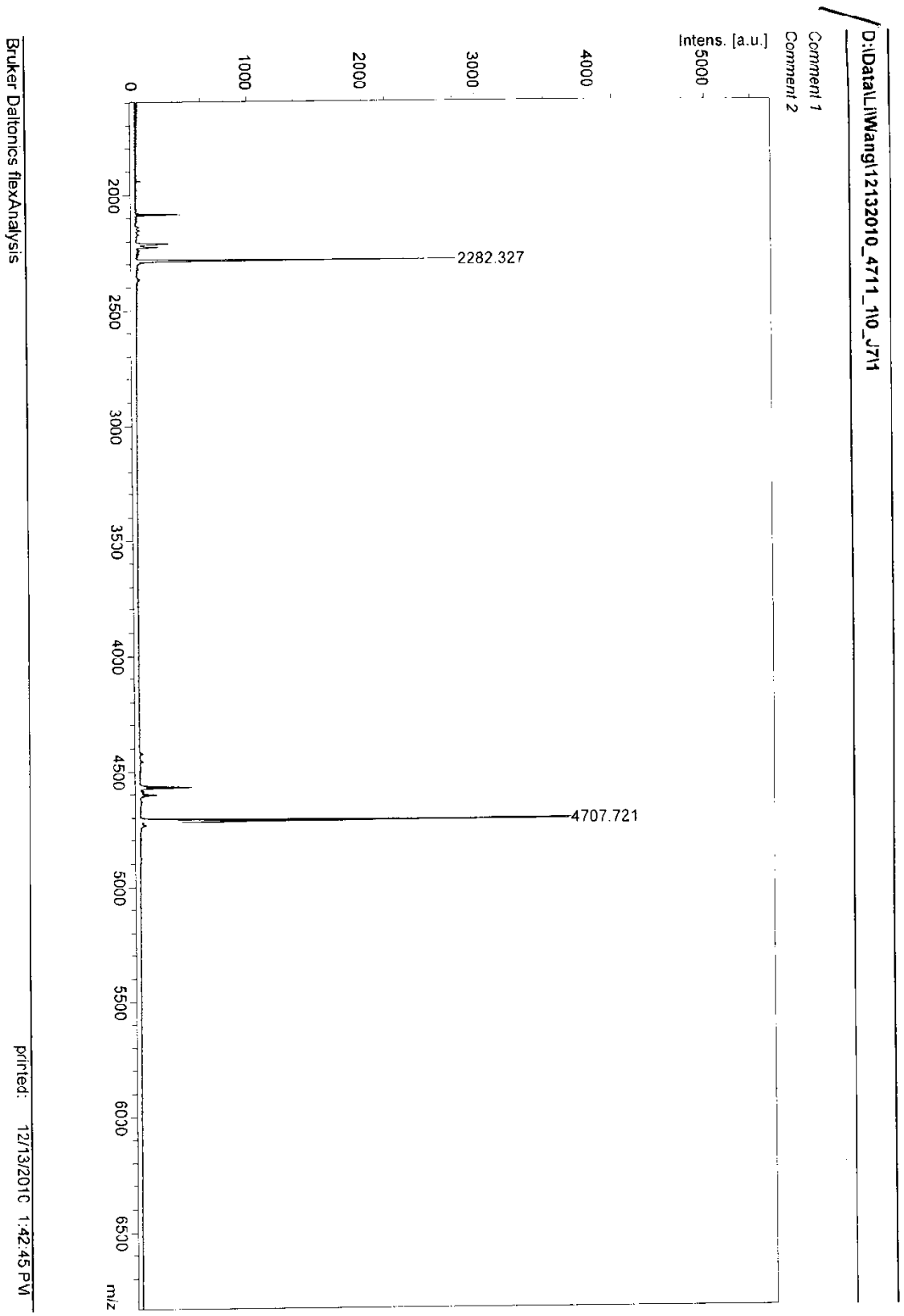
COSY NMR spectrum of **T1Ru2**.



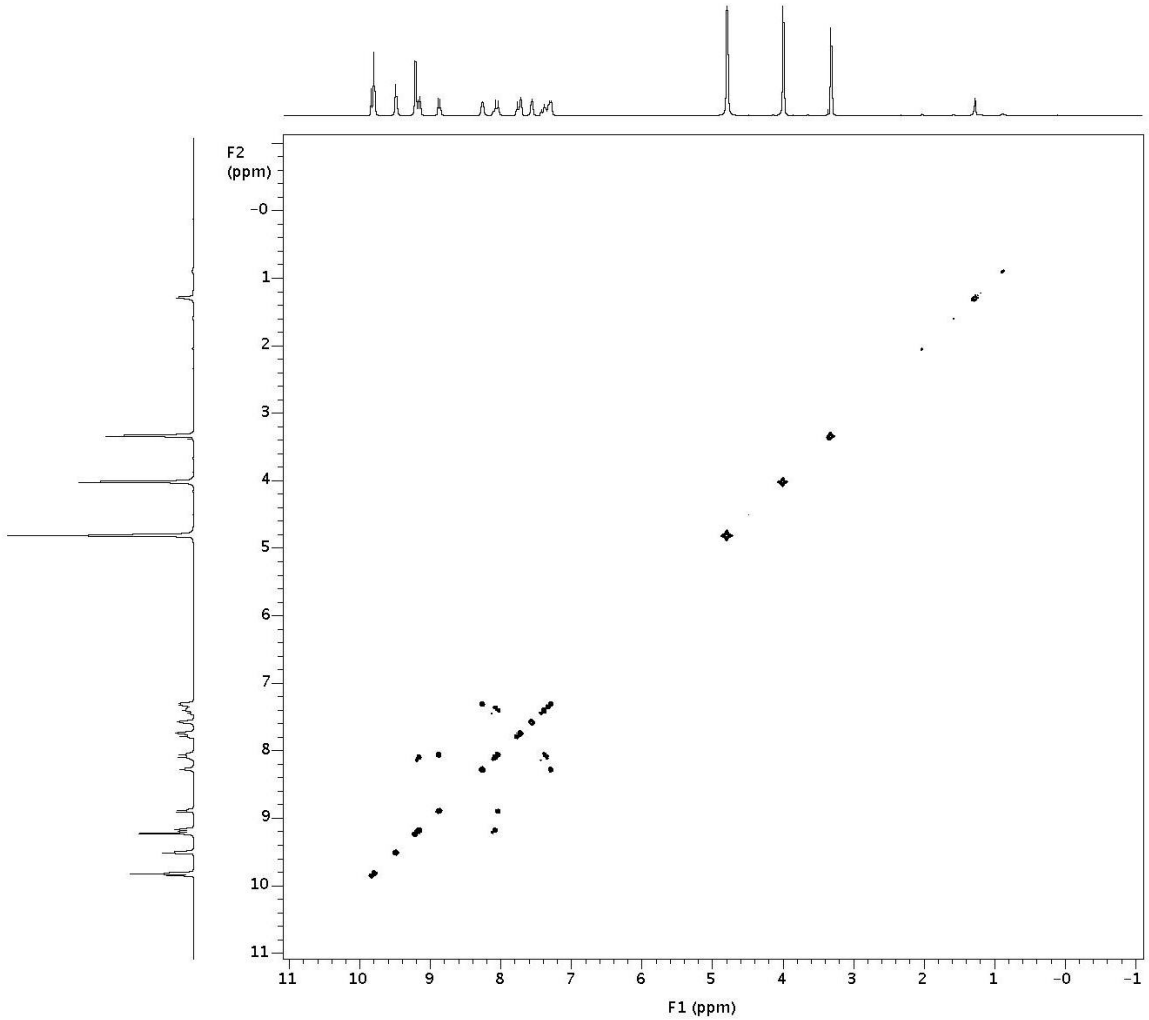
^{1}H NMR spectrum of **G1Ru5**.



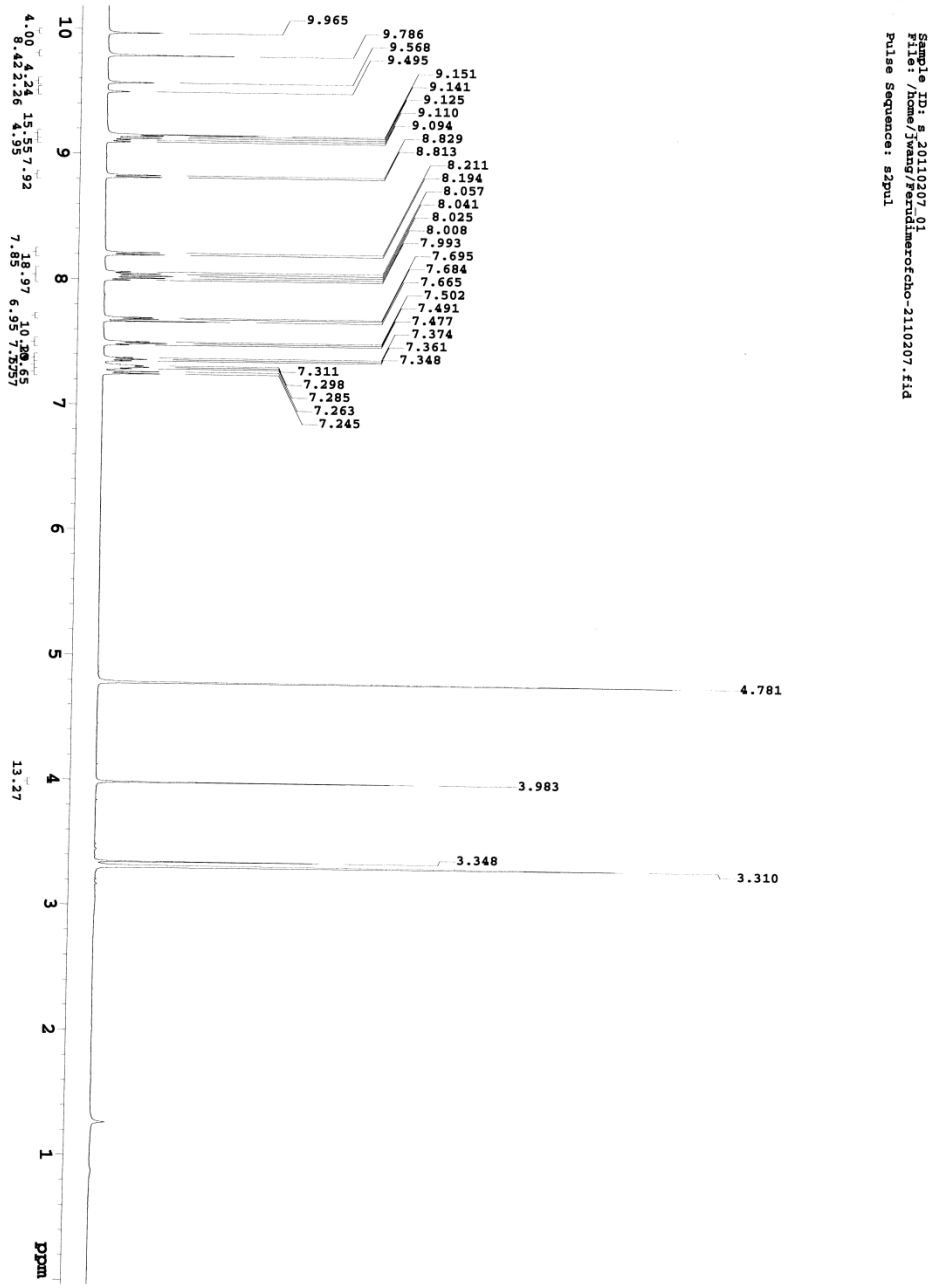
^{13}C NMR spectrum of **G1Ru5**.



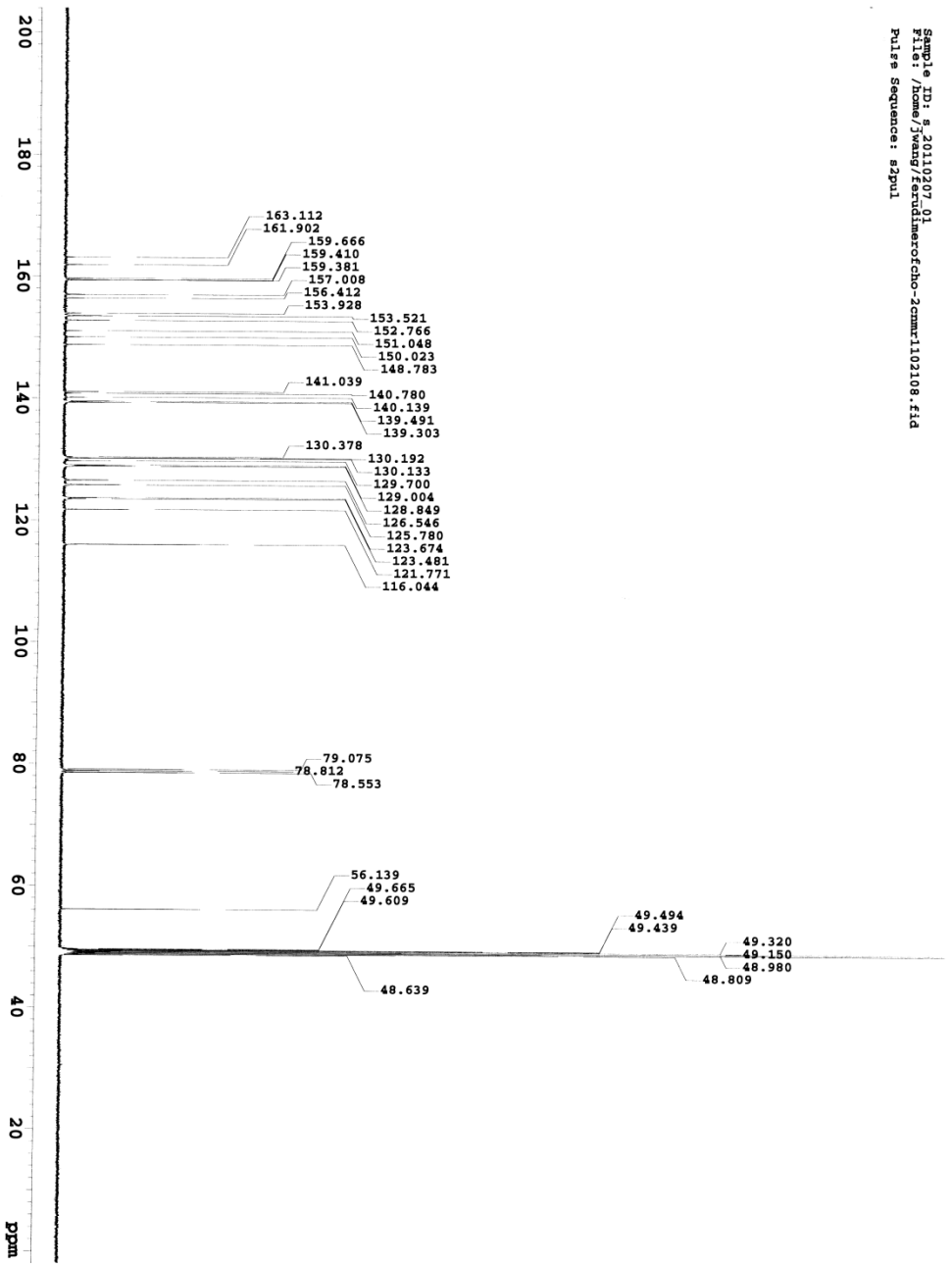
MALDI-ToF mass spectrum of **G1Ru5**.



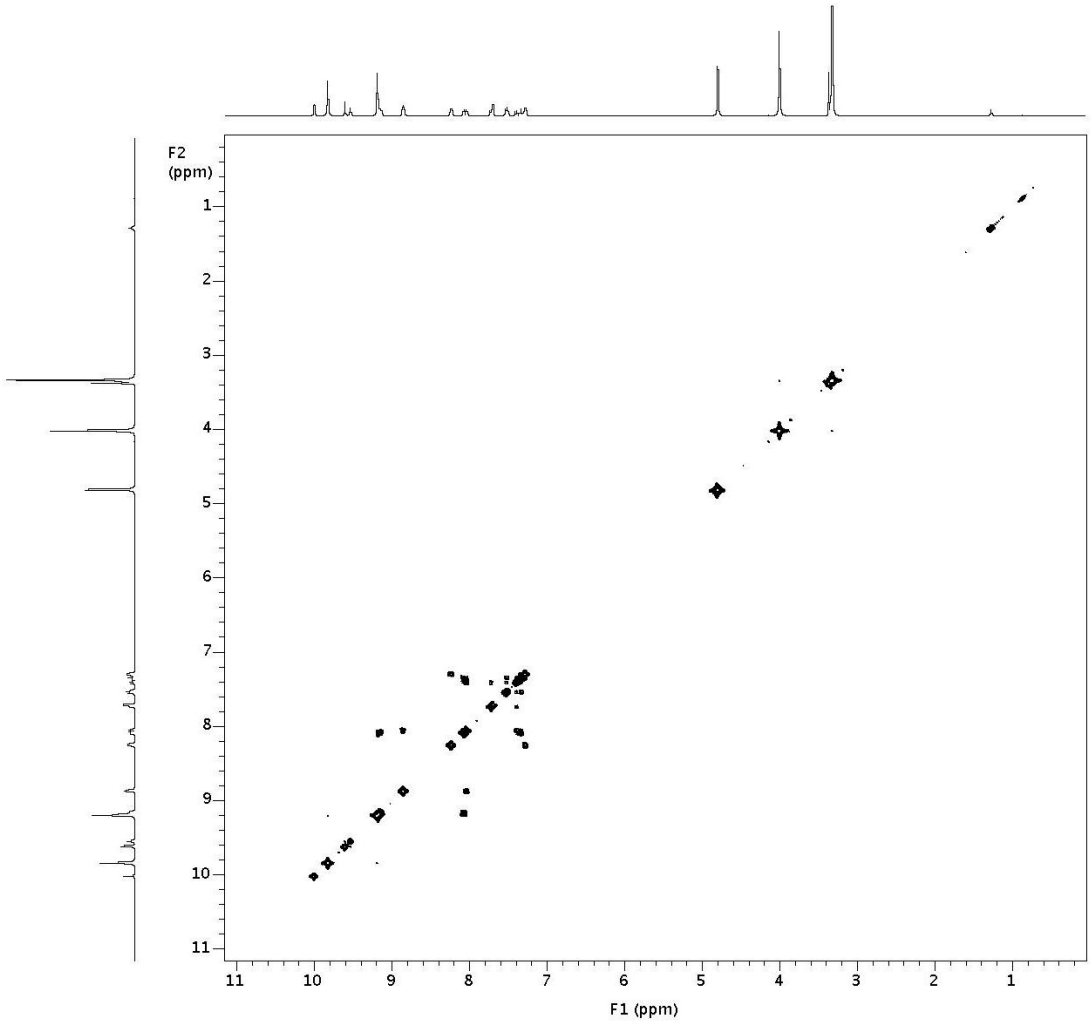
COSY NMR spectrum of **G1Ru5**.



^{1}H NMR spectrum of **G1Ru4Fe1**.



^{13}C NMR spectrum of **G1Ru4Fe1**.



COSY NMR spectrum of **G1Ru4Fe1**.

5. Pertinent X-ray data for **G0** and **MT3**.

Diffraction data for **MT3** were collected at T=100K on a Nonius KappaCCD diffractometer equipped with Mo Kα radiation (λ=0.71073 Å). Refinement was by full-matrix least squares using SHELXL, with H atoms in idealized positions, and one Me group having its H atoms disordered into two sets of positions. Crystal data for **MT3**: $C_{54}H_{39}N_9 \cdot 2\ CHCl_3$, monoclinic space group C2/c, a=16.380(3), b=13.469(2), c=22.139(4) Å, β=95.722(6)˚, V=4860.0(14) $Å^3$, T=100.0(5) K , Z=4, ρ_{calcd}=1.439 g cm^{-3}, μ(MoKα)=0.40 mm^{-1}. A total of 32,549 data was collected at θ=30.5˚, R_{int}=0.026. Refinement yielded R=0.044 for 5849 data with I>2σ(I) of 7390 unique data and 324 refined parameters. The molecule lies on a crystallographic twofold axis.

Diffraction data for **G0** were collected at T=100K on a Bruker CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ=0.71073 Å). The structure of **G0** which lies about a threefold rotation axis was refined by full-matrix least squares using SHELXTL, with H atoms in idealized positions. Crystal data for **G0**: $C_{120}H_{90}N_{18}O_3Ru_3$, $6(NO_3) \cdot 12\ CH_3OH$, trigonal space group R3c, a =31.823(7), b=31.823(7), c=21.495(5) Å (hexagonal axes), V=18851(8) $Å^3$, T=100(2) K, Z=6, ρ_{calcd}=1.528 g cm^{-3}, μ(MoKα)=0.448 mm^{-1}. A total of 37,791 data was collected to θ=23.5˚, R_{int}=0.124. Refinement yielded R=0.0603 and an absolute structure parameter (Flack) of 0.32(6) for 3126 data with I>2σ(I) of 4121 unique data and 472 refined parameters. Contribution to the structure factors

from the disordered solvent and one of the two independent nitrate ions was removed for refinement using the SQUEEZE technique.