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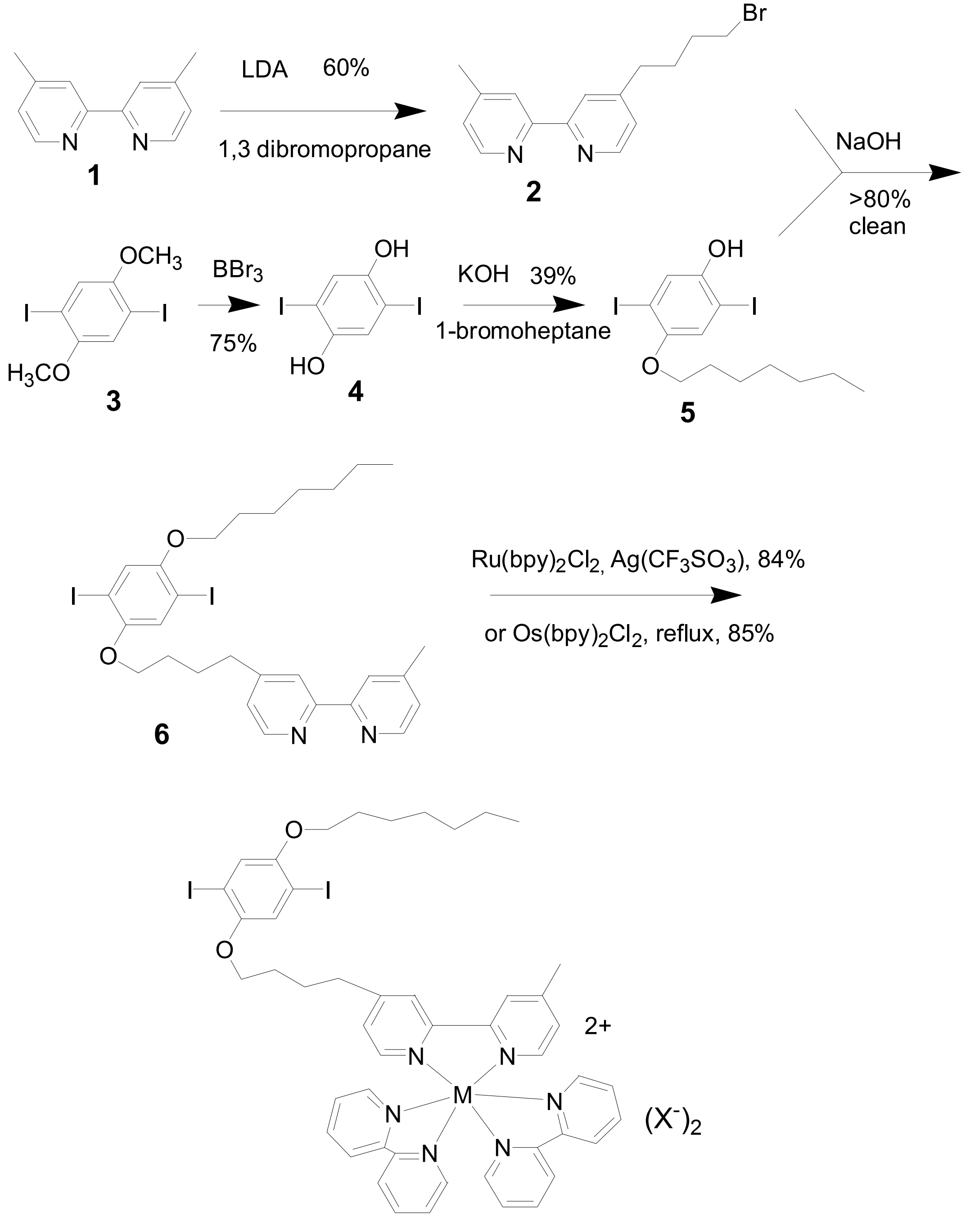
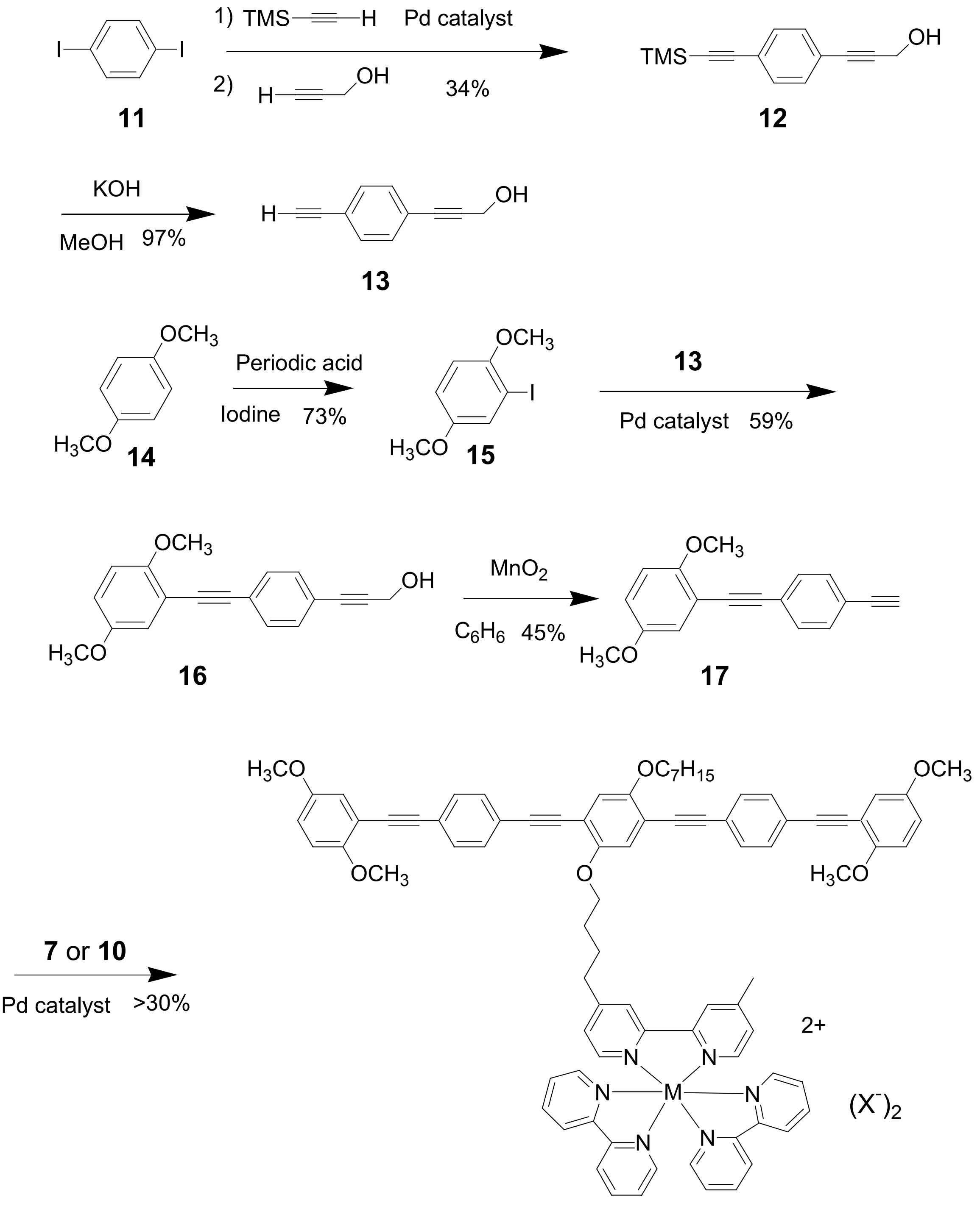
Scheme 1



7 : M = Ru, X = $CF_3SO_3^-$

10 : M = Os, X = PF_6^-

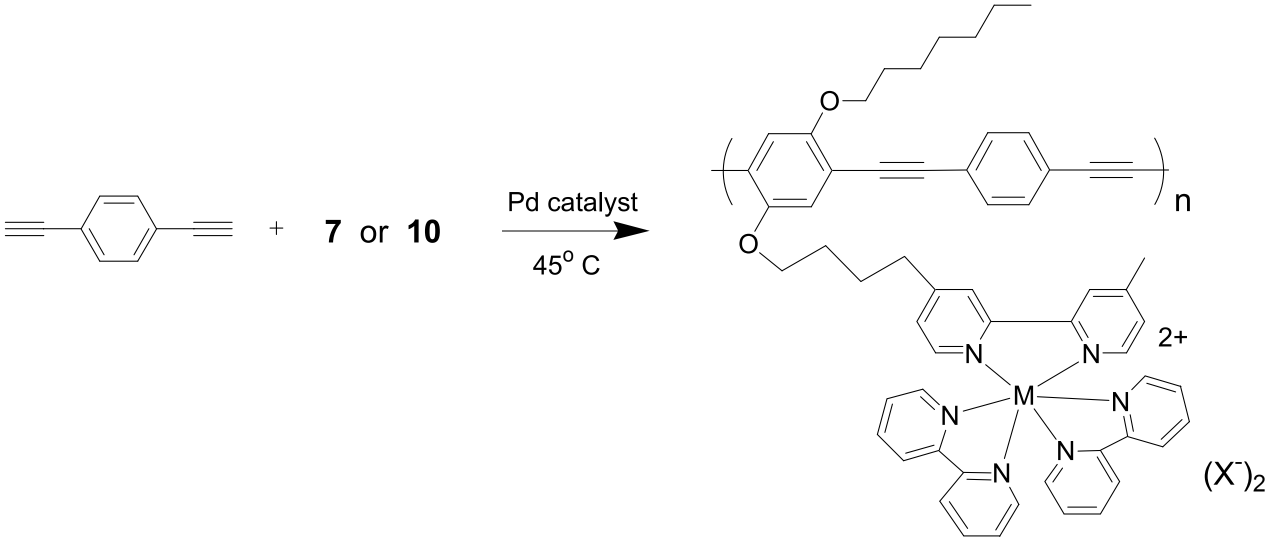
Scheme 2



M-Ru : M = Ru, X = $CF_3SO_3^-$

M-Os : M = Os, X = PF_6^-

Scheme 3



P-Ru : M = Ru, X = $CF_3SO_3^-$

P-Os : M = Os, X = PF_6^-

Synthesis and Characterization of Metal-Oligomers and Polymers

Materials. Solvents and chemicals used for synthesis were of reagent grade and used without purification unless noted. Silica gel (Merck, 230-400 mesh) was used for chromatography. NMR spectra were obtained on a Varian 300-MHz spectrometer.

4-methyl-4'-(4-bromobutyl)-2,2'-bipyridine (2). This compound was prepared by modification of literature procedures.[1-4] A solution of LDA was prepared by adding 6 mL of 2.5 M butyllithium (14.5 mmol) in hexane dropwise to diisopropyl amine (2.3 mL, 16.2 mmol) in 5 mL of THF at –78° C. After stirring the solution for 15 min, a solution of 4,4'-dimethyl-2,2'-bipyridine **(1)** (2.4 g, 13 mmol) dissolved in 60 mL of THF was added. The resulting dark brown mixture was stirred for 2 hr at –78° C, then stirred at 0°C for 0.5 hr. Then 1,3-dibromopropane (13.2 mL, 130mmol) in 70 mL of THF was added dropwise over one hour, during which time the solution's color changed first to green and then to yellow. The reaction solution was stirred overnight at ambient temperature. After this time, solvent and excess 1,3-dibromopropane were removed under reduced pressure. The resulting residue was purified by gradient column chromatography on alumina (hexanes/CH_2Cl_2 70/30 at the beginning, then polarity increasing gradually, hexanes/ CH_2Cl_2/acetone 40/55/5 at the end). The product was obtained as a white solid, yield 2.4g (60%).

Spectral Data: ^{1}H NMR ($CDCl_3$, ppm) δ 1.79–1.98 (br, m, 4H), 2.40 (s, 3H), 2.70 (t, 2H), 3.40 (t, 2H), 7.11 (d, 2H), 8.21 (s, 2H), 8.56 (d, 1H), 8.57 (d, 1H); ^{13}C NMR ($CDCl_3$, ppm) 21.1, 28.6, 32.0, 33.2, 34.4, 121.0, 121.9, 123.7, 124.6, 148.0, 148.7, 148.9, 151.6, 155.7, 156.0.

2,5-diiodo-1,4-hydroquinone (4). This compound was prepared by modification of literature procedures.[5, 6] Boron tribromide (12.8 mL, 12.8 mmol) was added dropwise to a cold (–78° C) solution of 2,5-dimethoxy-1,4-diiodobenzene **(3)** (2 g, 5.12 mmol) in CH_2Cl_2 (20 mL). The resulting solution was stirred at ambient temperature for 40 hr, and then poured into ice water. The product precipitated, and the crude solid was recrystallized in a mixture of THF and hexane to afford 1.4 g of the pure product (yield: 75%).

Spectral Data: ^{1}H NMR (acetone-d, ppm) δ 7.30 (s, 2H), 8.80 (s, 2H); ^{13}C NMR (acetone-d, ppm) 84.3, 125.0, 151.7.

4-Heptyloxy-2,5-diiodophenol (5). This compound was prepared by modification of a literature procedure.[5] To a solution of compound **4** (5 g,13.8 mmol) in DMSO (35 mL) was added potassium hydroxide powder (2.32 g, 41.4 mmol). A solution of 1-bromoheptane (2.47 g, 13.8 mmol) in DMSO (7.5 mL) was added immediately. The resulting mixture was stirred at ambient temperature overnight and then it was poured into water. A solid (mainly the bis-heptyloxy-substituted by-product) was removed by filtration, and the filtrate was neutralized to pH = 7 by addition of hydrochloric acid. The dark brown product that precipitated was collected by filtration, and then recrystallized in hexanes to afford the pure product (yield 2.5 g, 39%).

Spectral Data: ^{1}H NMR ($CDCl_3$, ppm) δ 0.90 (t, 3H), 1.19-1.4 (br, m, 6H), 1.49 (quintet, 2H), 1.79 (quintet, 2H), 3.89 (t, 2H), 4.9 (br, 1H), 7.00 (s, 1H), 7.40 (s, 1H); ^{13}C NMR ($CDCl_3$, ppm) 14.1, 22.6, 26.0, 29.0, 29.1, 31.8, 70.3, 84.4, 87.6, 120.8, 124.7, 149.7, 152.6.

4-[4-(4-Heptyloxy-2,5-diiodophenoxy)butyl]-4'-methyl-2,2'-bipyridine (6). This compound was prepared by modification of a literature procedure.[5] Compound 2 (1.66 g, 3.61 mmol), 5 (1 g, 3.38 mmol) and powdered NaOH (0.39 g, 9.84 mmol) were dissolved in 33 mL of DMF. The color of the solution turned light red from light yellow after 10 minutes of heating at 75° C. The mixture was stirred for 6 hr at 75° C. At this time, a small aliquot was removed from the reaction mixture, dropped into water and extracted with CH_2Cl_2. The solvent was removed by vacuum, and ^{1}H NMR of the resulting solid indicated that the reaction was complete based on the absence of a resonance at 3.4 ppm (due to the -CH_2-Br protons in 2). Subsequently, 50 mL of water was added to the reaction mixture, and the aqueous solution was extracted with a large amount of CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate and then evaporated to afford the crude product. Purification was accomplished by gradient column chromatography on silica gel. The elution was begun with hexanes/THF 95/5 and the polarity was gradually increased to hexanes/THF 80/20. The pure product was obtained as white, microcrystalline material, yield 2.0 g (90%).

Spectral Data: ^{1}H NMR ($CDCl_3$, ppm) δ 0.85 (t, J=6.9 Hz, 3H), 1.27 (m, 6H), 1.44 (quintet, 2H), 1.72-1.92 (m, 6H), 2.39 (s, 3H), 2.75(t, J=7.5 Hz, 2H), 3.87 (t, J=6.3 Hz, 2H), 3.90 (t, J=6.0 Hz, 2H), 7.08 (d, J=5.1 Hz, 1H), 7.11 (s, 2H), 7.13 (d, J=5.7 Hz, 1H), 8.18 (s, 1H), 8.23 (s, 1H), 8.49 (d, J=5.1 Hz, 1H), 8.52 (d, J=5.1 Hz, 1H); ^{1}H NMR (acetone-d, ppm) δ 0.90 (t, 3H), 1.32 (m, 6H), 1.51 (quintet, 2H), 1.79 (quintet , 2H), 1.90 (quintet, 2H), 2.00 (quintet, 2H), 2.42 (s, 3H), 2.88 (t, 2H), 4.00 (t, 2H), 4.10 (t, 2H), 7.22 (d, 1H), 7.29 (d, 1H), 7.30 (s, 1H), 7.33 (s, 1H), 8.30 (s, 1H), 8.40 (s, 1H), 8.50 (d, 1H), 8.55 (d, 1H); ^{13}C NMR ($CDCl_3$, ppm) 14.1, 21.1, 22.5, 25.9, 26.7, 28.6, 28.9, 29.0, 31.7, 34.9, 69.7, 70.1, 86.2, 121.3, 122.0, 122.5, 122.6, 123.8, 124.6, 148.1, 148.7, 148.9, 152.1, 152.5, 152.8, 155.8, 155.9. Mass spec. (FAB, high resolution) calc'd for $C_{28}H_{35}N_2O_2I_2$ (M+H) 685.07880, found 685.07879.

Compound 7. This compound was prepared via modification of literature procedures.[5, 7, 8] $Ru(bpy)_2Cl_2$ (0.38g, 0.78mmol) was dissolved in 320 mL acetone, then $Ag(CF_3SO_3)$ (0.8g, 3.1 mmol) was added. The solution changed to a red-wine color. The reaction mixture was refluxed for 2 hrs and during this time a precipitate formed. The reaction mixture was filtered through Celite to remove AgCl. A solution of compound 6 (0.38 g, 0.55 mmol) in 25 mL of 2-methoxy ethanol wad added, and the reaction was stirred at reflux overnight, and monitored by thin layer chromatography. When TLC indicated that the reaction was complete, the solvents were removed by vacuum. The residue was then purified by gradient chromatography on silica gel (eluant: hexenes/methylene chloride 80/20 at the beginning, then gradually increasing polarity, methylene chloride/acetonitrile 70/30 at the end). The red-orange fluorescent fraction was collected and the solvent was evaporated to afford the pure product as a red microcrystalline solid, yield 0.65 g (84%).

Spectral Data (see Figures S-1 – S-3): ^{1}H NMR (acetone-d, ppm) δ 0.90 (t, 3H), 1.28 – 1.42 (m, 6H), 1.54 (quintet, 2H), 1.79 (quintet, 2H), 1.88 (quintet, 2H), 2.00 (quintet, 2H), 2.58 (s, 3H), 3.01 (t, J=7.5 Hz, 2H), 4.03 (t, J=6.3 Hz, 2H), 4.06 (t, J=5.4 Hz, 2H), 7.33 (s, 2H), 7.42 (d, J=6.3 Hz, 1H), 7.50 (d, J=6.3 Hz, 1H), 7.57 (m, 4H), 7.83 (d, J=6.3 Hz, 1H), 7.89 (d, J=6.3 Hz, 1H), 8.04 (m, 4H), 8.19 (t, J=6.3 Hz, 4H), 8.79 (s, 1H), 8.83 (s, 1H), 8.85 (d, J=6.3 Hz, 4H); ^{1}H

NMR ($CDCl_3$, ppm) δ 0.84 (t, J=6.9 Hz, 3H), 1.22-1.35 (m, 6H), 1.44 (quintet, J=6.6 Hz, 2H), 1.74 (quintet, J=6.6 Hz, 2H), 1.83 (quintet, J=6.3 Hz, 2H), 1.94 (quintet, J=6.9 Hz, 2H), 2.52 (s, 3H), 2.91 (t, J=7.2 Hz, 2H), 3.87 (t, J=6.3 Hz, 2H), 3.92 (t, J=5.4 Hz, 2H), 7.11 (s, 1H), 7.13 (s, 1H), 7.21 (d, J=5.7 Hz, 1H), 7.27 (d, J=6.0 Hz, 1H), 7.39-7.52 (m, 6H), 7.62-7.72 (m, 4H), 7.98 (t, J=7.5 Hz, 4H), 8.40 (d, J= 4.8 Hz, 2H), 8.56 (d, J=8.3 Hz, 4H); ^{13}C NMR (acetone-d_6, ppm) δ 14.4, 21.1, 23.2, 26.7, 27.4, (three peaks between 29 and 31 are hidden in the solvent acetone peaks), 32.5, 35.2, 70.4, 70.8, 86.9, 120.0, 123.4, 123.6, 124.3, 125.3, 126.2, 128.6, 129.4, 138.7, 151.2, 151.6, 151.9, 152.5, 153.6, 153.8, 155.3, 157.5, 157.7, 158.1; ^{13}C NMR ($CDCl_3$, ppm) 14.1, 21.3, 22.6, 25.9, 26.4, 28.5, 28.9, 29.1, 31.7, 34.7, 69.6, 70.3, 86.4, 112.0, 118.6, 122.6, 122.7, 124.6, 125.5, 128.0, 129.0, 138.0, 150.2, 150.3, 150.4, 151.1, 152.4, 152.9, 154.6, 156.1, 156.3, 156.6. Mass spec. (electrospray, high resolution) calc'd for $C_{49}H_{50}O_5N_6F_3I_2RuS$ (M+) 1247.0658, found 1247.0466.

Compound 10. Compound **6** (0.1 g, 0.146 mmol) and $Os(bpy)_2Cl_2$ (0.082 g, 0.151 mmol) were combined in 15 mL of ethylene glycol and the solution was refluxed under nitrogen for 40 hr. The reaction was cooled to room temperature and then it was poured into 20 mL of saturated aqueous NH_4PF_6 solution whereupon the dark green PF_6^- salt of the complex precipitated. The mixture was cooled in a refrigerator overnight, and the product was collected by filtration, washed with water several times, and then dried to afford the pure compound, yield 180 mg (86%).

Spectral Data (see Figures S-4 – S-7): ^1H NMR (acetone-d_6, ppm) δ 0.89 (t, J=6.9 Hz, 3H), 1.22-1.42 (m, 6H), 1.54 (quintet, J=6.9 Hz, 2H), 1.79 (quintet, J=7.5 Hz, 2H), 1.86 (quintet, J=6.9 Hz, 2H), 1.99 (quintet, J=7.8 Hz, 2H), 2.64 (s, 3H), 3.04 (t, J=6.9 Hz, 2H), 4.03 (t, J=6.0 Hz, 2H), 4.06 (t, J=6.0 Hz, 2H), 7.32 (s, 1H), 7.34 (s, 1H), 7.44 (m, 4H), 7.76 (d, J=6.3 Hz, 1H), 7.81 (d, J=5.7 Hz, 1H), 7.99 (m, 4H), 8.69 (s, 1H), 8.74 (s, 1H), 8.78 (d, J=7.8 Hz, 4H); ^{13}C NMR (acetone-d, ppm) 14.4, 21.1, 23.4, 26.8, 27.7, (three peaks between 29 and 31 are hidden in the acetone peaks), 32.6, 35.1, 70.5, 70.9, 87.0, 123.5, 123.7, 125.5, 126.3, 129.2, 129.9, 138.0, 150.8, 151.0, 151.2, 151.7, 151.8, 153.6, 154.8, 159.5, 160.2. Mass spec. (electrospray, high resolution) calc'd for $C_{48}H_{50}O_2N_6F_6I_2OsP$ (M^+) 1333.1340, found 1333.1442.

Compound 12. This compound was prepared via modification of literature procedures.[9, 10] 1,4-diiodo-benzene (**11**) (14 g, 42.4 mmol) was dissolved in 85 mL of THF, 50 mL of diisopropyl-amine was added, the solution was degassed for 15 min with argon flow. Then trimethylsilyl acetylene (6 mL, 42.4 mmol), $Pd(PPh_3)_2Cl_2$ (0.89 g, 1.27 mmol) and CuI (0.81 g, 4.24 mmol) were added under nitrogen. The reaction mixture was stirred for 2 hr under reflux, and the color was yellow. Then 2-propyne-1-ol (3 mL, 50.8 mmol) was added dropwise with a syringe, and the color of the solution immediately turned black. The reaction mixture was stirred overnight at reflux. After this time, the reaction mixture was filtered through Celite to remove solids. The filtrate was evaporated and purified by silica gel chromatography (eluant: CH_2Cl_2/hexane 4/1). Yield, 3.3 g (34 %).

Compound 13. A mixture of compound **12** (3.3 g, 14.4 mmol), KOH (3.2 g, 57.8 mmol) in a mixture of water (13 mL), methanol (24 mL) and THF (29 mL) was stirred for 6 hr at room temperature. After this time, the solvents were evaporated, the residue was extracted with ethyl ether, washed with 0.5 M of HCl solution, and then with saturated $NaHCO_3$ solution. Evaporation of ether afforded the product, yield 2.2 g (97%).

Spectral Data: ^{1}H NMR ($CDCl_3$, ppm) δ 3.18 (s, 1H), 4.48 (s, 2H), 7.40 (dd, 4H).

Compound 16. Compound **13** (0.75 g, 4.8 mmol) and 2-iodo-1,4-dimethoxybenzene[9] (**15**) (1.34 g, 5.1 mmol) were dissolved in 24 mL of THF. Diisopropylamine (9 mL) was added, the solution was degassed for 30 min with argon, and then $Pd(PPh_3)_2Cl_2$ (0.067g, 0.096mmol) and CuI (0.046g, 0.24 mmol) were added under nitrogen. The reaction mixture was stirred overnight at 70° C, and it exhibited a blue fluorescence. The reaction mixture was cooled and filtered to remove solids through Celite and then purified by chromatography on silica, yield 0.82 g (59%).

Spectral Data: ^{1}H NMR ($CDCl_3$, ppm) δ 2.95 (br, 1H), 3.95 (s, 3H), 4.05 (s, 3H), 4.68 (s, 2H), 7.02 (dd, 2H), 7.22 (s, 1H), 7.57 (d, 2H), 7.68 (dd, 4H); ^{13}C NMR ($CDCl_3$, ppm) 51.3, 55.6, 56.3, 85.0, 87.4, 89.1, 92.8, 111.9, 112.4, 115.8, 117.9, 122.1, 123.3, 131.4, 153.0, 154.3.

Compound 17. This compound was prepared via modification of a literature procedure.[10] Compound **16** (1.5 g, 5.1 mmol), ground potassium hydroxide (1.44 g, 25.6 mmol) and manganese dioxide (4.46 g, 51.3 mmol, precipitated active) were placed in 50 mL of benzene. The mixture was stirred 6 hr at ambient temperature. The reaction mixture was filtered and it was purified by column chromatography on silica gel, yield 0.6g (45%).

Spectral Data: ^{1}H NMR ($CDCl_3$, ppm) δ 3.18 (s, 1H), 3.76 (s, 3H), 3.86 (s,3H), 6.82 (dd, 2H), 7.02 (d, 1H), 7.47 (dd, 4H); ^{13}C NMR ($CDCl_3$, ppm) 55.7, 56.4, 78.8, 83.3, 87.7, 92.7, 112.0, 112.4, 116.0, 118.0, 121.7, 123.8, 131.5, 131.9, 153.1, 154.4.

M-Ru. Compound **7** (0.054 g, 0.039 mmol) and compound **17** (0.021 g, 0.080 mmol) were dissolved in 9 mL of THF and 5 mL of diisopropylamine, the solution was degassed for 30 min with argon flow and then $Pd(PPh_3)_2Cl_2$ (0.002 g, 0.0027 mmol) and CuI (0.001 g, 0.0054 mmol) were added under argon. The reaction mixture was stirred overnight at 70° C. The solvents were then evaporated, and added a minimal amount of CH_2Cl_2 was added to dissolve the crude product. Diethyl ether was subsequently added to precipiate the desired product. The precipitate was recovered by centerfugation and decantation. The precipitate was then washed several times with diethyl ether to afford the pure product, yield 20 mg (30%).

Spectral Data (see Figures S-8 – S-13): ^{1}H NMR (acetone-d, ppm) δ 0.88 (t, 3H), 1.33 (m, 6H), 1.43 (m, 2H), 1.60 (quintet, J=7.8 Hz, 2H), 1.86 (quintet, J=7.5 Hz, 2H), 1.96 (m, 2H), 2.56 (s, 3H), 3.06 (t, J=7.2 Hz, 2H), 3.79 (s, 3H), 3.80 (s, 3H), 3.83 (s, 3H), 3.87 (s, 3H), 4.12 (t, J=6.0 Hz, 2H), 4.20 (t, 2H); 7.02 (m, 4H+2H), 7.19 (s, 2H), 7.38 (m, 3H) 7.48 (m, 3H), 7.58 (m, 8H), 7.80 (m, 2H), 8.03 (m, 4H), 8.18 (m, 4H), 8.76 (m, 4H+2H); ^{13}C NMR (acetone-d, ppm) 14.9, 19.8, 21.9, 23.8, 27.4, (three peaks between 29 and 31 hide in the peaks of acetone), 33.2, 36.0, 56.8, 57.2, 70.2, 70.7, 89.5, 89.7, 93.7, 113.8, 115.2, 115.6, 117.4, 118.1, 119.3, 119.5, 124.5, 124.7, 125.2, 125.9, 126.0, 126.6, 129.3, 130.0, 132.9, 139.3, 151.8, 152.1, 152.4, 153.0, 153.2, 154.8, 154.9, 155.3, 155.9, 156.0, 158.0, 158.1, 158.6. Mass spec. (electrospray, high resolution) calc'd for $C_{85}H_{76}O_9N_6F_3RuS$ (M^+) 1515.4406, found: 1515.4539.

M-Os. This compound was prepared according the method described above for **M-Ru**, except that **10** was used in place of **7**. The final product was further purified by silica column chromatography a gradient (CH_2Cl_2/CH_3CN 90/10 to CH_2Cl_2/CH_3CN 70/30), yield 40 mg (42%).

Spectral Data (see Figures S-14 – S-17): ^{1}H NMR (acetone-d, ppm) δ 0.88 (t, J=6.6 Hz, 3H), 1.33 (m, 6H), 1.43 (m, 2H), 1.60 (quintet, J=7.8 Hz, 2H), 1.86 (quintet, J=7.5 Hz, 2H), 1.96 (m, 2H), 2.61 (s, 3H), 3.08 (t, J=7.2 Hz, 2H), 3.79 (s, 3H), 3.82 (s, 3H), 3.87 (s, 3H), 4.11 (t, J=6.0 Hz, 2H), 4.19 (t, 2H); 7.02 (m, 4H+2H), 7.18 (d, J=3.0 Hz, 2H), 7.38 (m, 3H) 7.46 (m, 4H), 7.48 (m, 3H), 7.57 (m, 4H), 7.70 (m, 2H), 7.90 (m, 4H), 7.96 (m, 4H), 8.71 (m, 4H+2H); ^{13}C NMR (acetone-d, ppm) 14.5, 21.1, 23.3, 26.9, 28.1, (three peaks between 29 and 31 hide in the peaks of acetone), 32.7, 35.3, 56.1, 56.7, 69.7, 70.2, 89.2, 93.3, 95.4, 113.3, 114.7, 115.0, 116.9, 117.6, 118.7, 119.0, 124.0, 125.5, 126.2, 129.2, 129.9, 132.4, 138.0, 150.9, 151.4, 151.5, 151.8, 154.3, 154.8, 154.9, 155.4, 155.6, 159.3, 159.6, 160.3. Mass spec. (electrospray, high resolution) calc'd for $C_{84}H_{76}O_6N_6F_6P_1Os$ (M^+) 1601.5038, found: 1601.5089.

Ru-P. Compound **7** (0.10 g, 0.072 mmol) and 1,4-diethynylbenzene[11] **(**0.0095 g, 0.034 mmol) were dissolved in 7 mL of DMF and 4 mL of diisopropylamine and the solution was degassed with argon for 0.5 hr. Then $Pd(PPh_3)_2Cl_2$ (0.0025 mg, 0.0036 mmol) and CuI (0.0014 g, 0.0072 mmol) were added under argon. The reaction was stirred and maintained at 45° C for 12 hr. The polymer was precipitated from the reaction mixture by pouring the DMF/diisopropylamine solution into vigorously stirring methanol that had previously been cooled to -78° C. The polymer was collected by filtration. It was further purified by re-dissolving into DMF and precipitation from cold methanol, yield after purification 80 mg (73%). The purified polymer was soluble only in DMF and DMSO. In addition, the material could not be taken to dryness, because it would not re-dissolve after drying. Thus, the polymer was stored in the dark as a suspension in methanol solution. GPC analysis was repeatedly attempted using $CHCl_3$/DMF mixtures, but the polymer did not elute from the column.

Spectral Data (see supporting Figure S-18): ^{1}H NMR (DMF-d_7, ppm) δ 0.89 (s, br, 3H, –CH_3), 1.29 (m, 6H, -CH_2-), 1.57 (br, 2H, -CH_2-), 1.85 (br, 2H, -CH_2-), 2.01 (br, 4H, -CH_2-), 2.60 (s, 3H, Ar-CH_3), 3.02 (partially obscured by DMF peak, s, 2H, Ar-CH_2-), 4.18 (m, 4H, -O-CH_2-), 7.35 (br, 2H, bpy), 7.48 (br, 2H, Ar), 7.63 (m, 4H+4H, bpy+Ar), 7.83 (s, br, 2H, bpy), 8.0 (br, 4H, bpy, obscured by DMF peak), 8.24 (s, br, 4H, bpy), 8.98 (br, 6H, bpy).

Os-P. This polymer was prepared, purified and stored as described above for **Ru-P**. It was also obtained in 75% yield.

Spectral Data (see supporting Figure S-19): ^{1}H NMR (DMF-d_7/DMSO-d_6 mixture) δ 0.88 (br, 3H, -CH_3), 1.30 (m, br, 6H, -CH_2-), 1.56 (br, 2H, -CH_2-), 1.82 (br, 2H, -CH_2-), 1.98 (br, 4H, -CH_2-), 2.66 (s, 3H, Ar-CH_3), 3.04 (br, 2H, Ar-CH_2-), 4.10 (m, 4x2H, -O-CH_2-), 7.36 (br, 2H+2H, bpy and Ar), 7.50 (br, 4H, bpy), 7.65 (br, 4H, Ar), 7.82 (br, 4H+2H, bpy), 8.0 (br, 4H, bpy, hide in a big peak of DMF-d), 8.89 (br, 6H, bpy).

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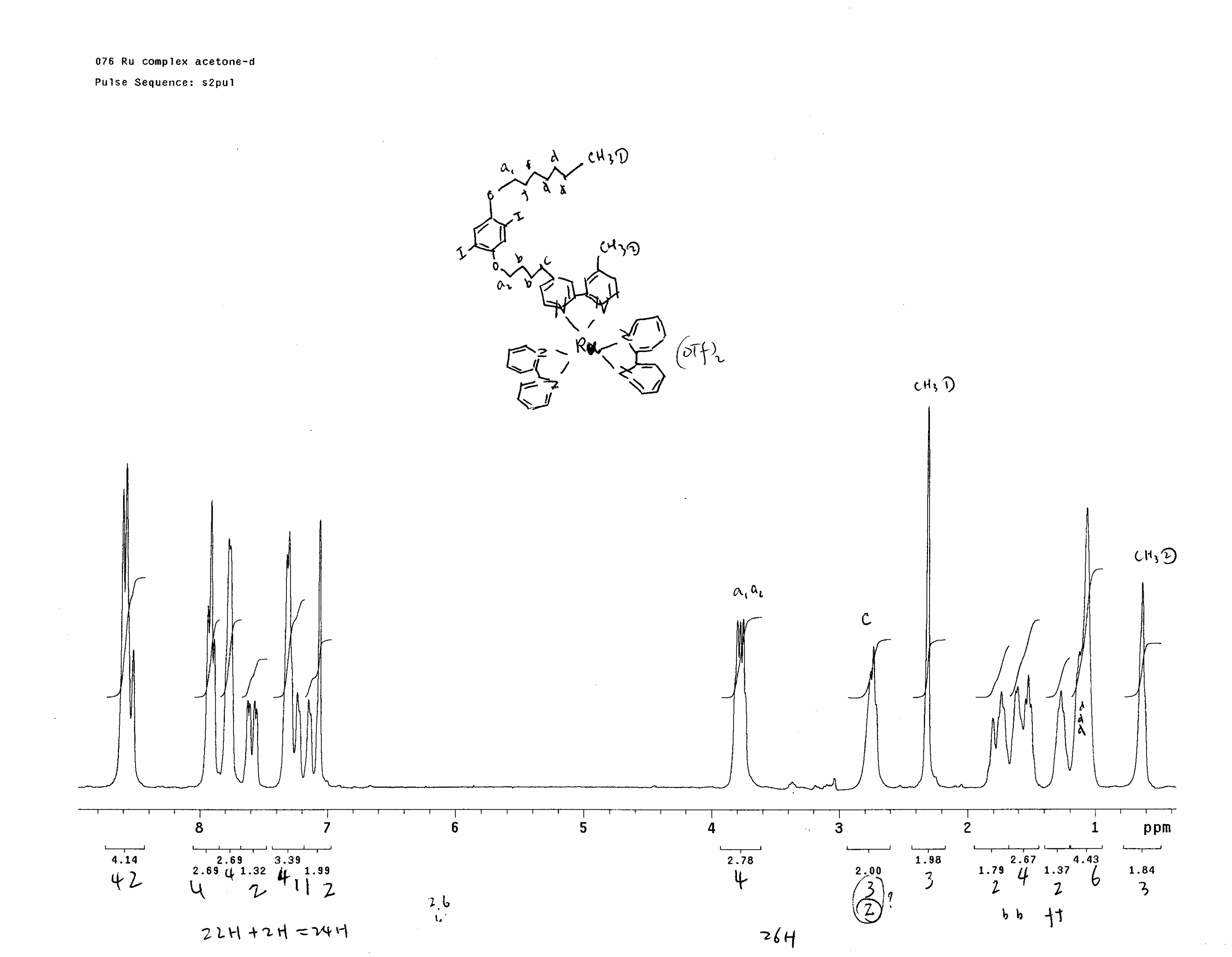
076 Ru complex acetone-d
Pulse Sequence: s2pul
a1
a2
b
c
d
f
CH3 ①
CH3 ②
I
O
N
Ru
(OTf)2
a1 a2
c
CH3 ①
CH3 ②
8
7
6
5
4
3
2
1
ppm
4.14
2.69
2.69
1.32
3.39
1.99
2.78
2.00
1.98
1.79
2.67
1.37
4.43
1.84
42
4
4
2
4
1
1
2
4
3
2
?
3
2
4
2
6
3
b b
f f
22H + 2H = 24H
2.6
26H

Figure S-1

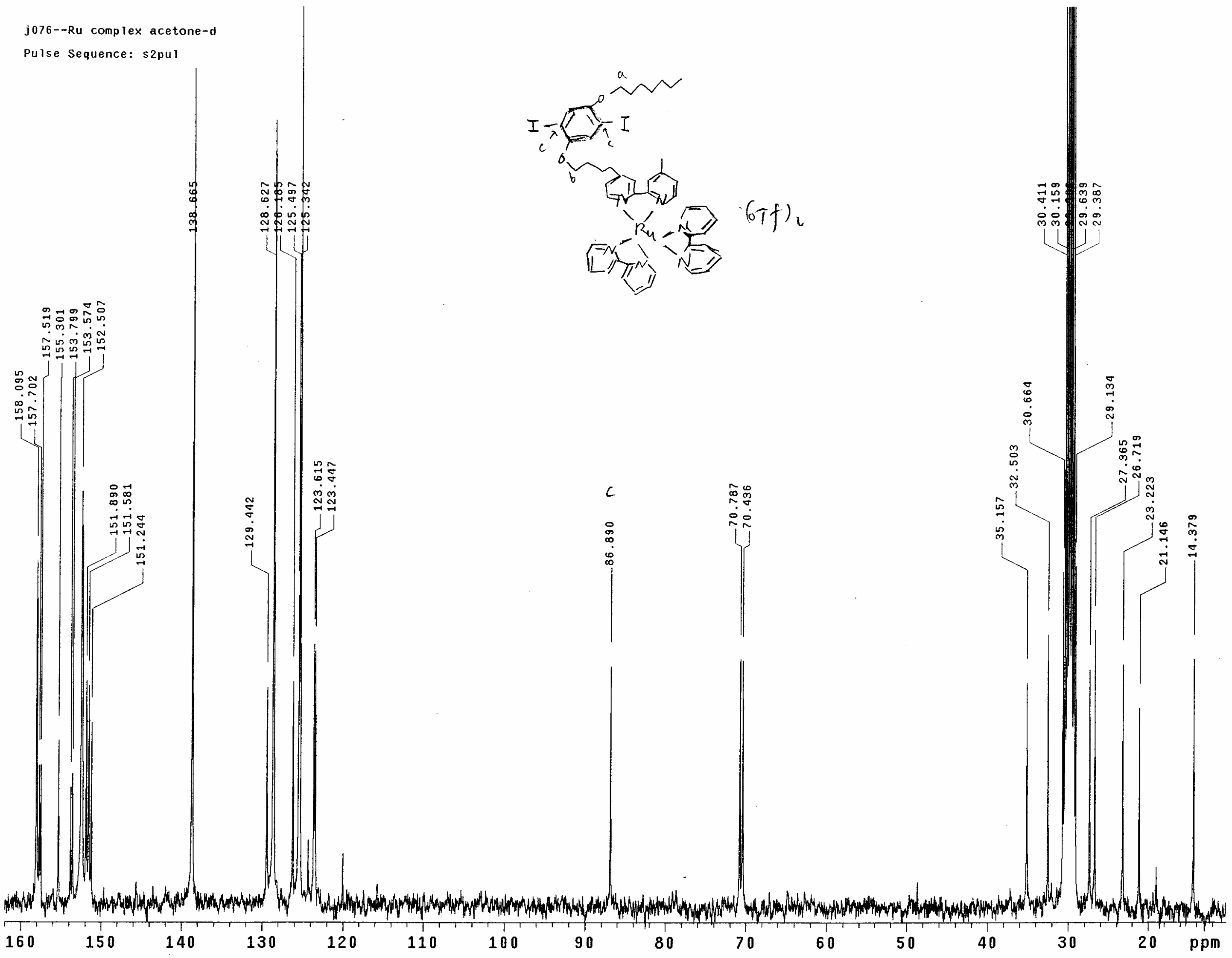
j076--Ru complex acetone-d
Pulse Sequence: s2pul
a
o
I
I
c
c
c
o
b
N
N
Ru
N
N
N
N
(OTf)2
158.095
157.702
157.519
155.301
153.799
153.574
152.507
151.890
151.581
151.244
138.665
129.442
128.627
128.185
125.497
125.342
123.615
123.447
c
86.890
70.787
70.436
35.157
32.503
30.664
30.411
30.159
29.639
29.387
29.134
27.365
26.719
23.223
21.146
14.379
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

Figure S-2

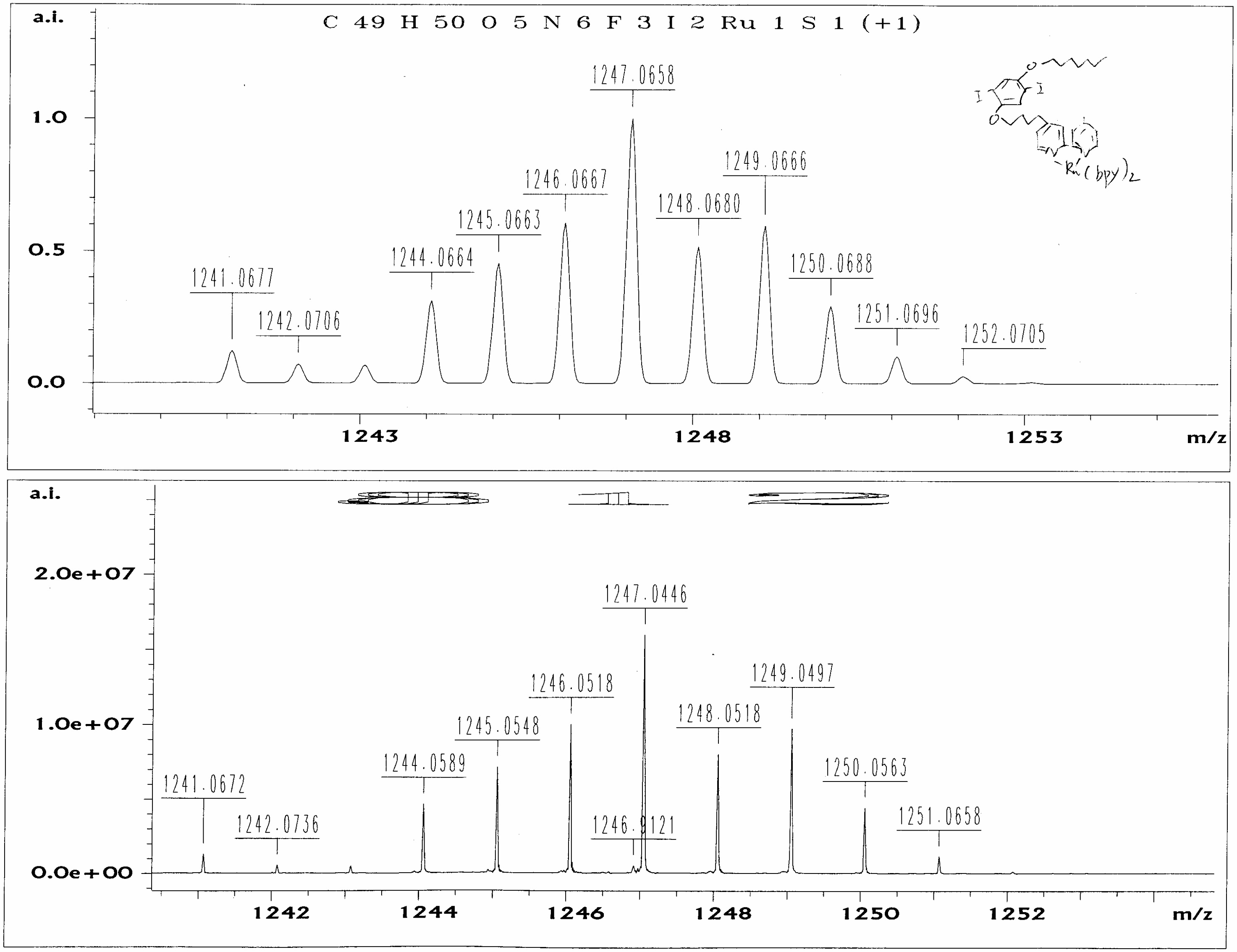
a.i.
C 49 H 50 O 5 N 6 F 3 I 2 Ru 1 S 1 (+1)
1.0
0.5
0.0
1241.0677
1242.0706
1244.0664
1245.0663
1246.0667
1247.0658
1248.0680
1249.0666
1250.0688
1251.0696
1252.0705
1243
1248
1253
m/z
I
I
O
O
Ru(bpy)2
a.i.
2.0e+07
1.0e+07
0.0e+00
1241.0672
1242.0736
1244.0589
1245.0548
1246.0518
1246.9121
1247.0446
1248.0518
1249.0497
1250.0563
1251.0658
1242
1244
1246
1248
1250
1252
m/z

Figure S-3

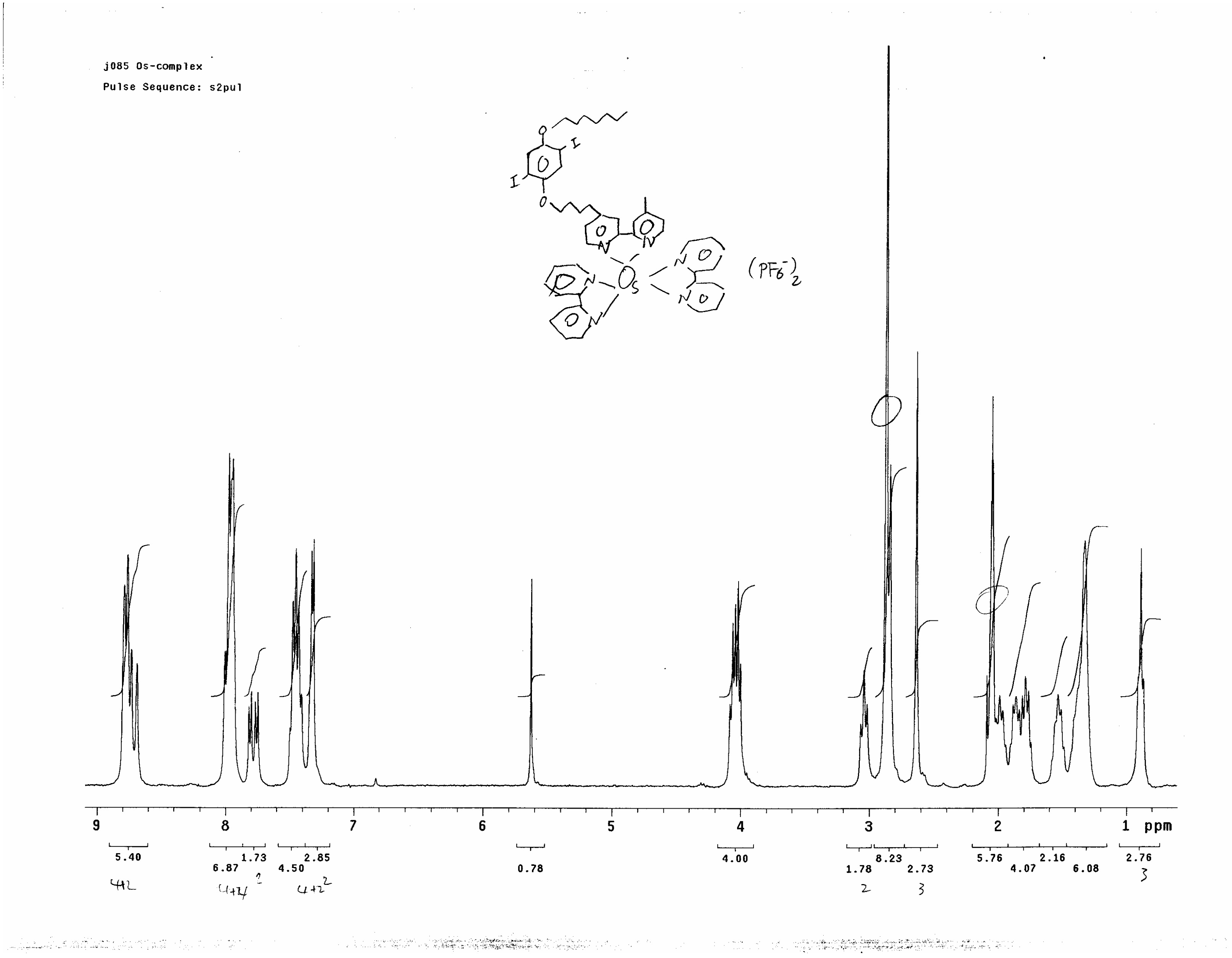
j085 Os-complex
Pulse Sequence: s2pul
I
I
O
O
N
N
Os
$(PF_6^-)_2$
9
8
7
6
5
4
3
2
1 ppm
5.40
6.87
1.73
4.50
2.85
0.78
4.00
1.78
8.23
2.73
5.76
4.07
2.16
6.08
2.76
4+2
4+4
2
4+2
2
3
3

Figure S-4

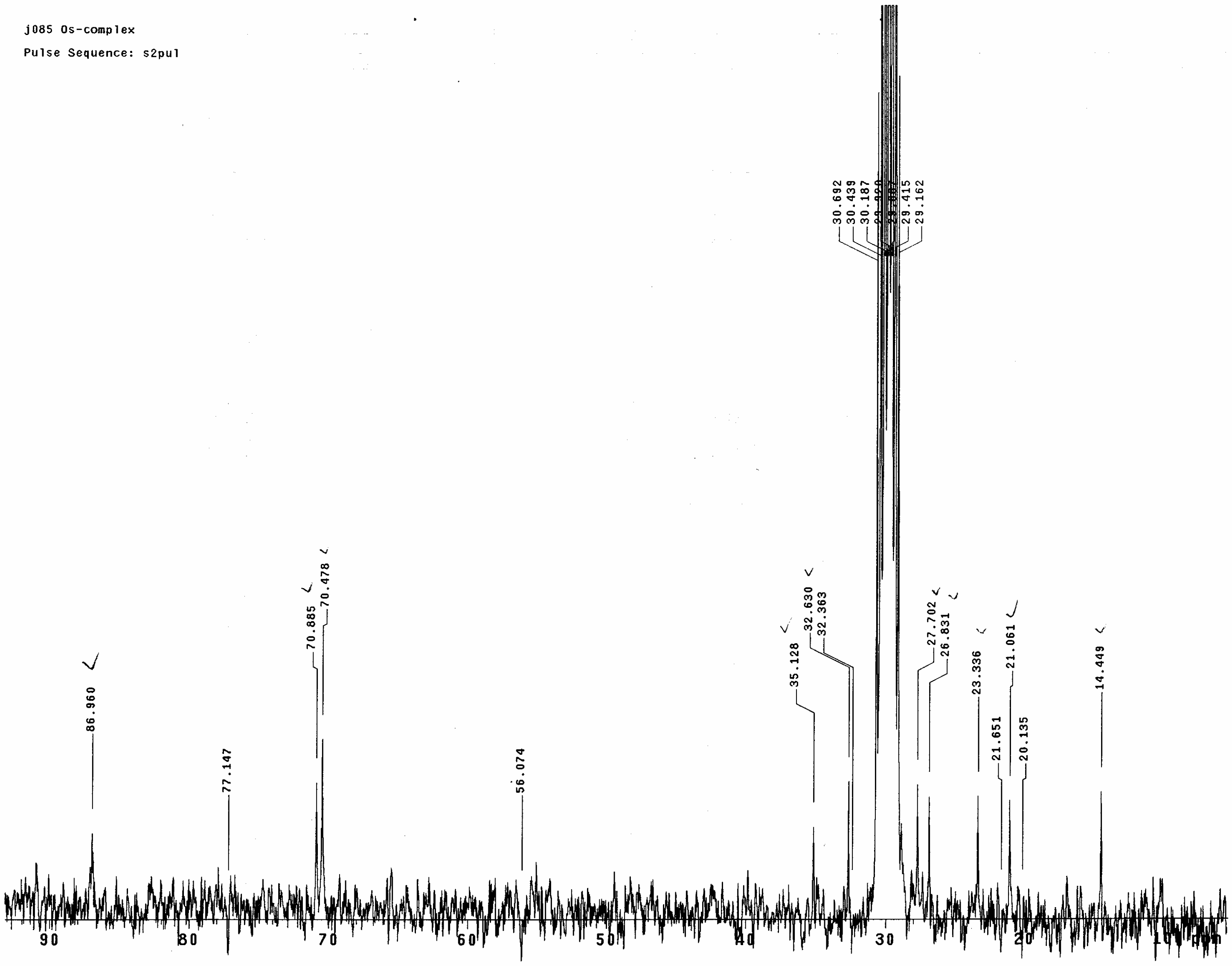
j085 Os-complex
Pulse Sequence: s2pul
86.960
77.147
70.885
70.478
56.074
35.128
32.630
32.363
30.692
30.439
30.187
29.415
29.162
27.702
26.831
23.336
21.651
21.061
20.135
14.449
90
80
70
60
50
40
30
20
10 ppm

Figure S-5

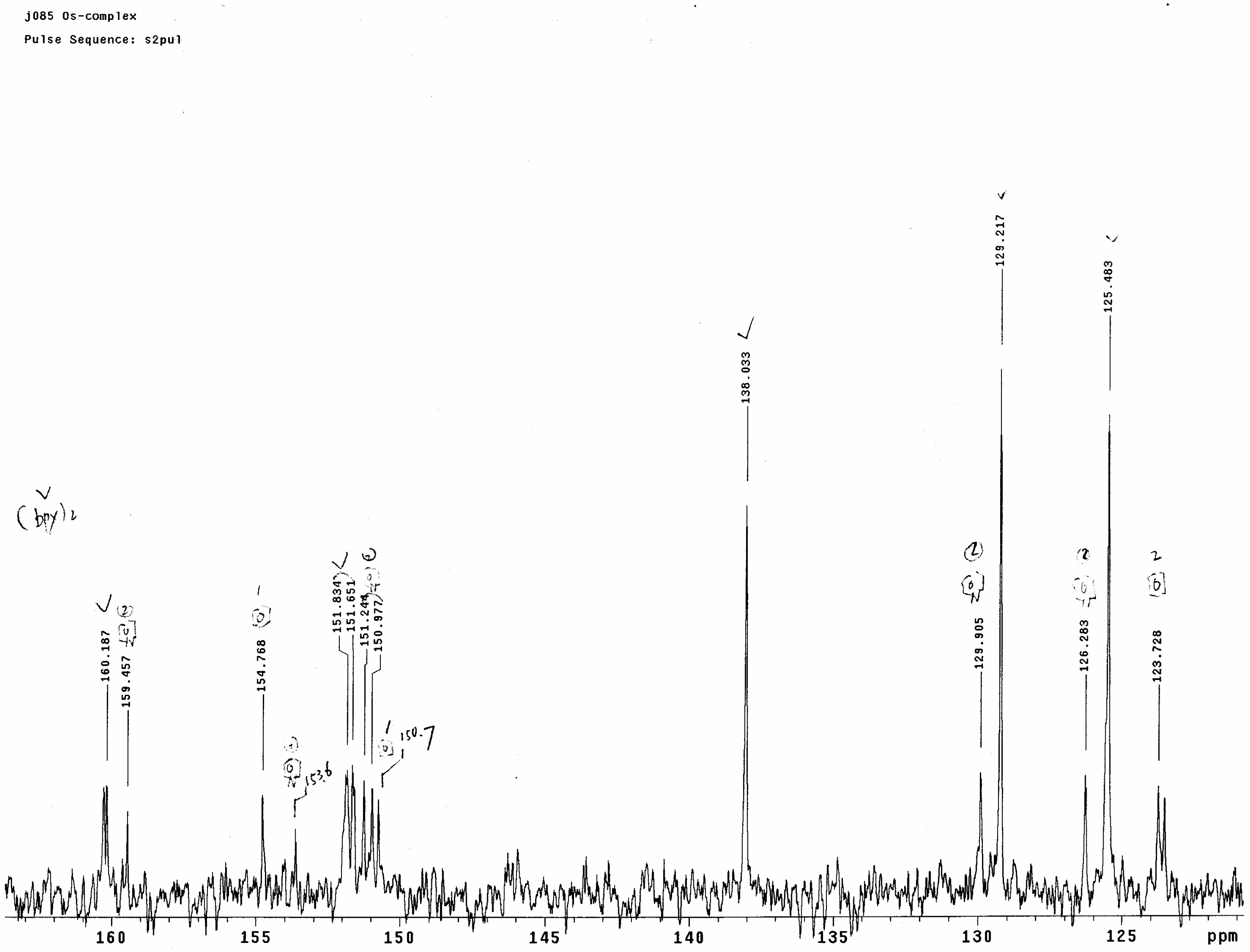
j085 Os-complex
Pulse Sequence: s2pul
(bpy)2
160.187
159.457
154.768
153.6
151.834
151.651
151.244
150.977
150.7
138.033
129.905
129.217
126.283
125.483
123.728
160
155
150
145
140
135
130
125
ppm

Figure S-6

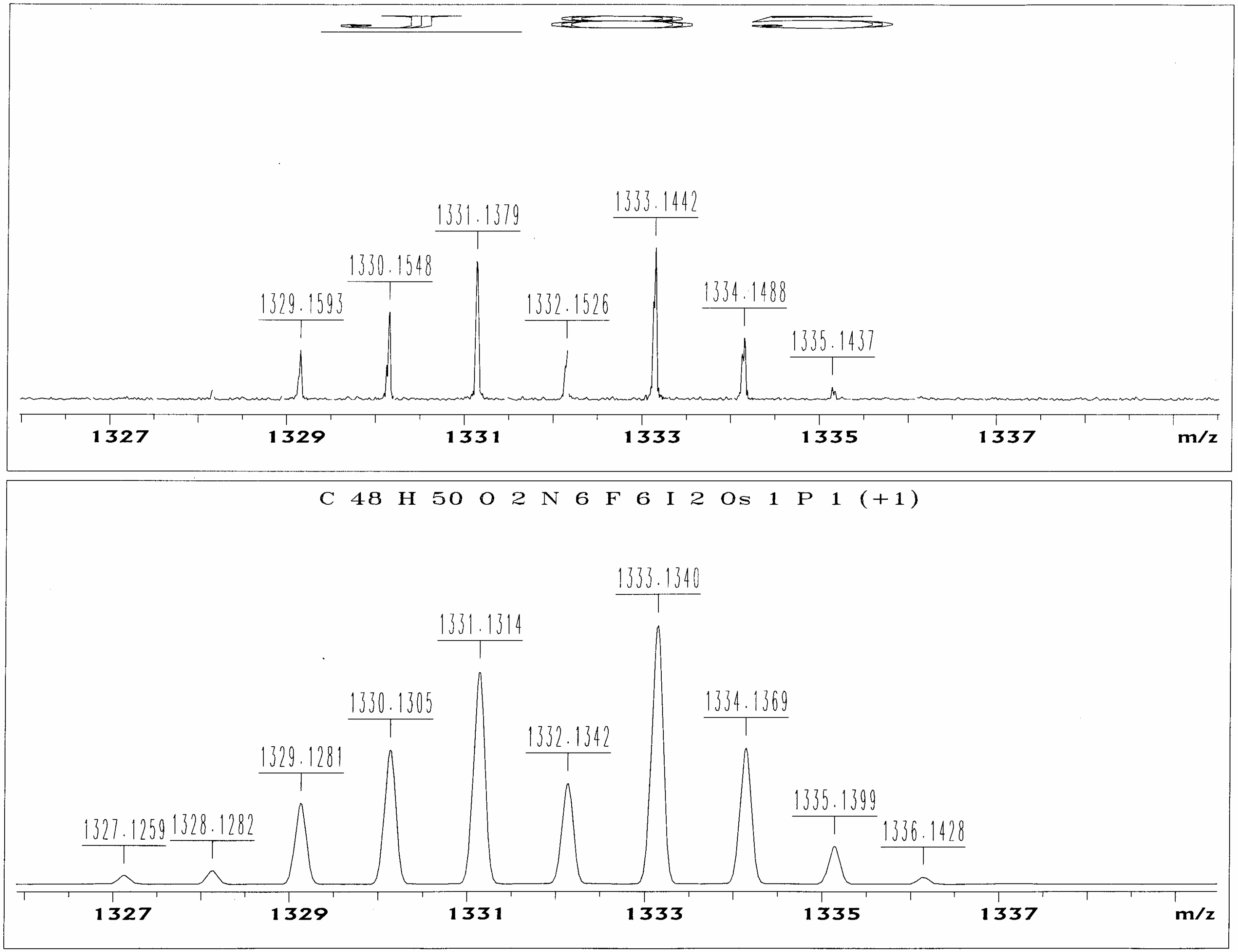
1331.1379
1333.1442
1330.1548
1329.1593
1332.1526
1334.1488
1335.1437
1327
1329
1331
1333
1335
1337
m/z
C 48 H 50 O 2 N 6 F 6 I 2 Os 1 P 1 (+1)
1333.1340
1331.1314
1330.1305
1332.1342
1334.1369
1329.1281
1335.1399
1327.1259
1328.1282
1336.1428
1327
1329
1331
1333
1335
1337
m/z

Figure S-7

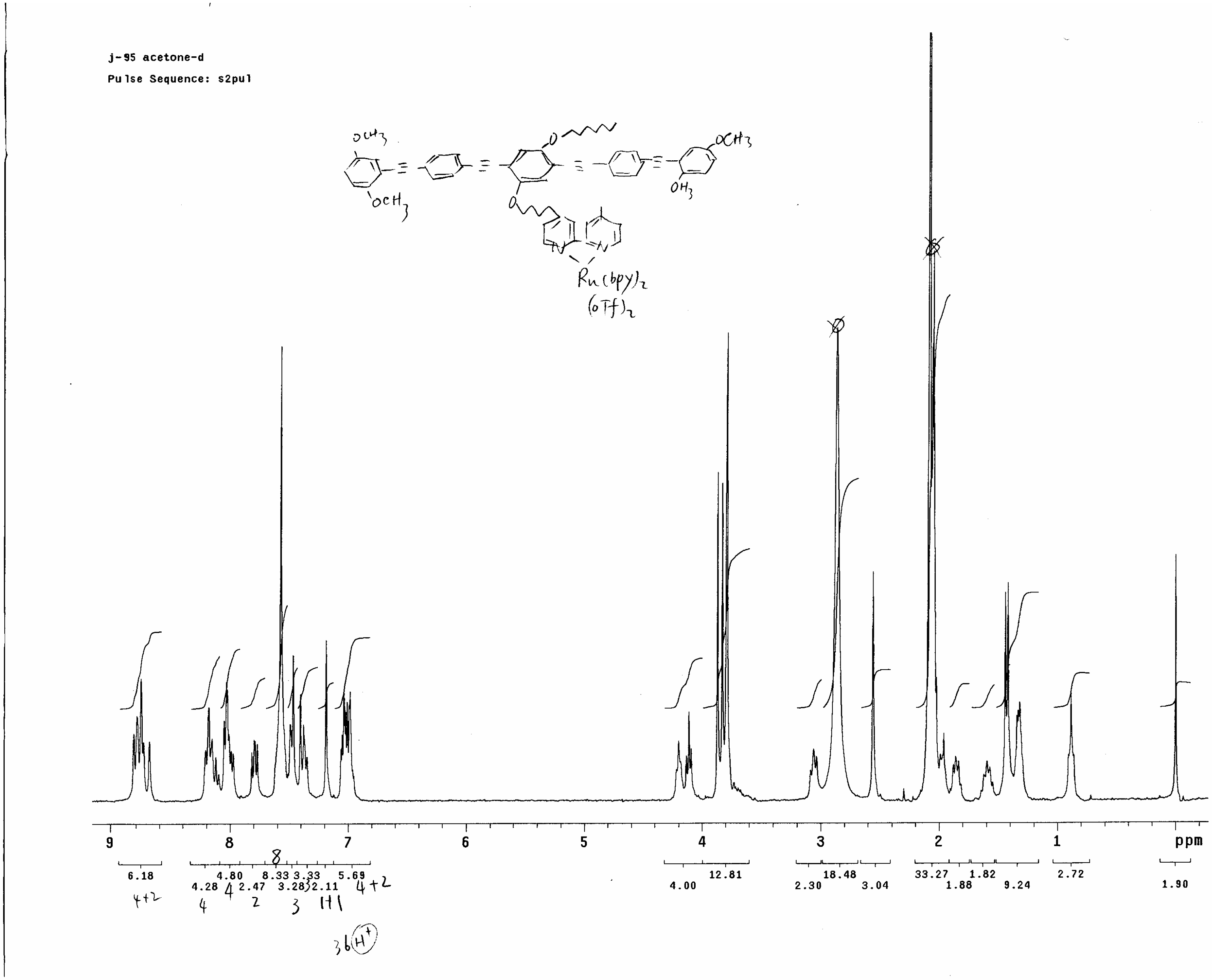
j-95 acetone-d
Pulse Sequence: s2pul
OCH3
OCH3
O
OCH3
OH3
O
N
N
Ru(bpy)2
(OTf)2
9
8
7
6
5
4
3
2
1
ppm
6.18
4.80
4.28
8.33
2.47
3.33
3.28
3.28
2.11
5.69
4.00
12.81
18.48
2.30
3.04
33.27
1.82
1.88
9.24
2.72
1.90
4+2
4
4
2
8
3
1H1
4+2
36(H+)

Figure S-8

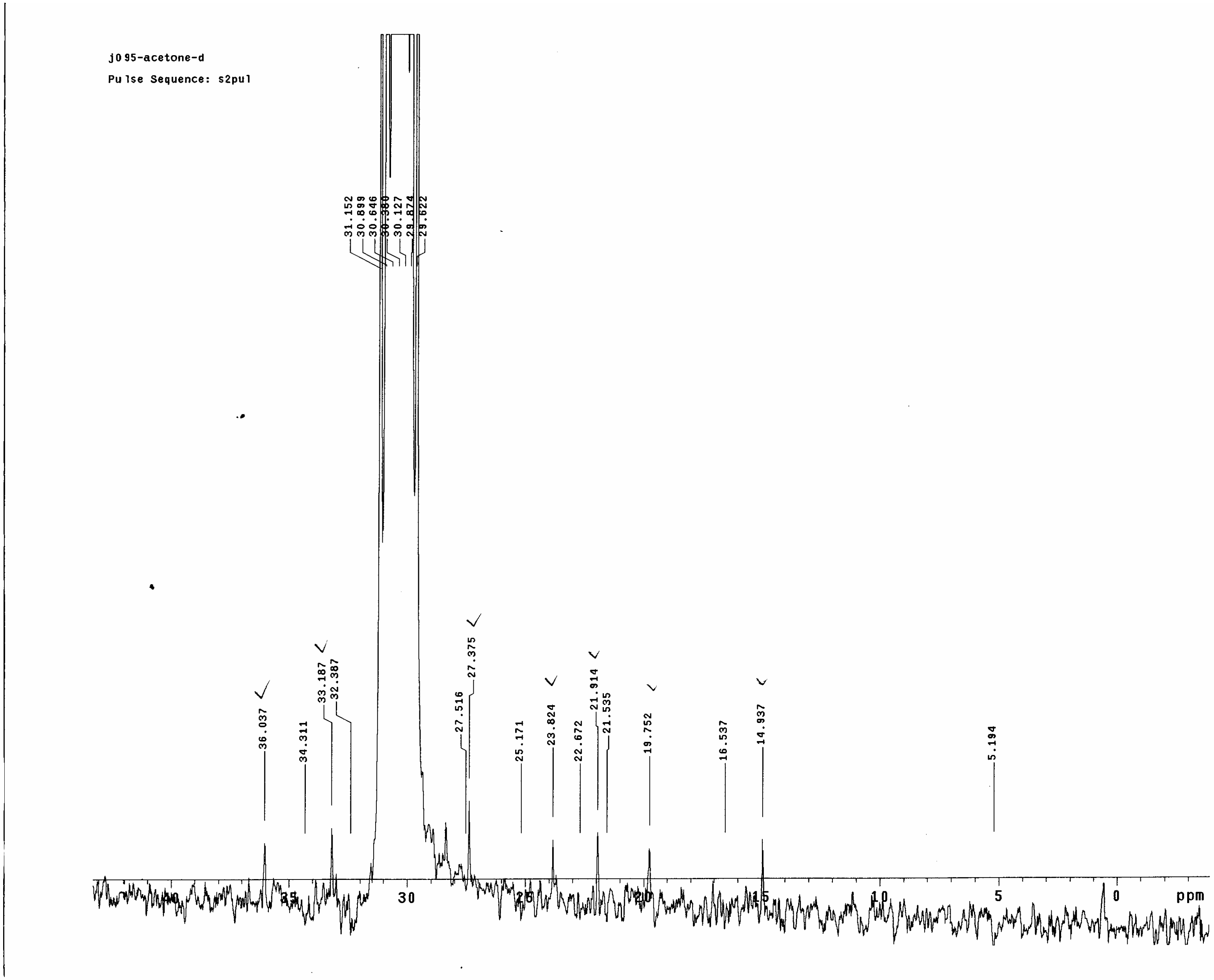
j095-acetone-d
Pulse Sequence: s2pul
31.152
30.899
30.646
30.380
30.127
29.874
29.622
36.037
34.311
33.187
32.387
27.516
27.375
25.171
23.824
22.672
21.914
21.535
19.752
16.537
14.937
5.194
35
30
25
20
15
10
5
0
ppm

Figure S-9

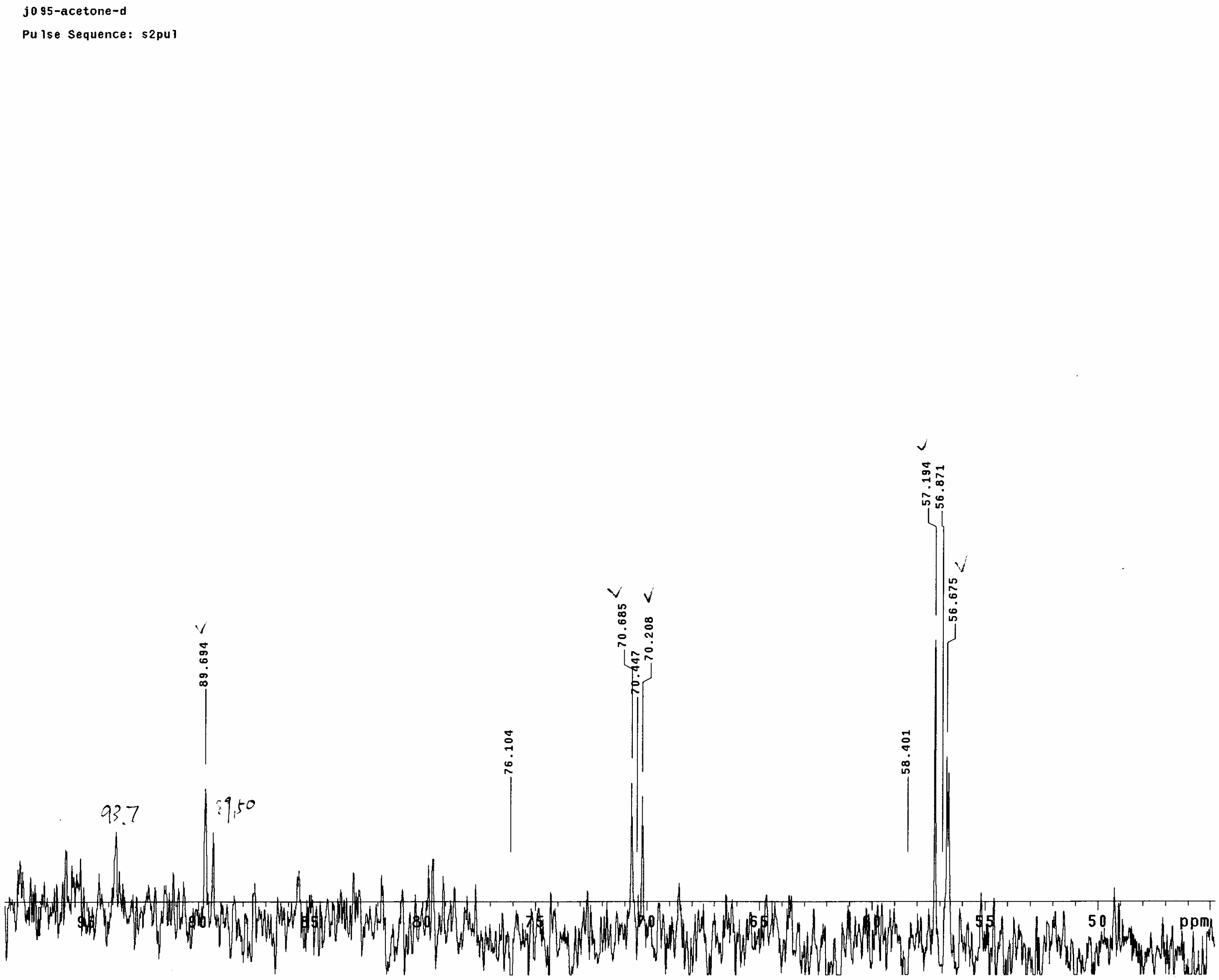
j095-acetone-d
Pulse Sequence: s2pul
89.694
76.104
70.685
70.447
70.208
58.401
57.194
56.871
56.675
93.7
89.50
95
90
85
80
75
70
65
60
55
50
ppm

Figure S-10

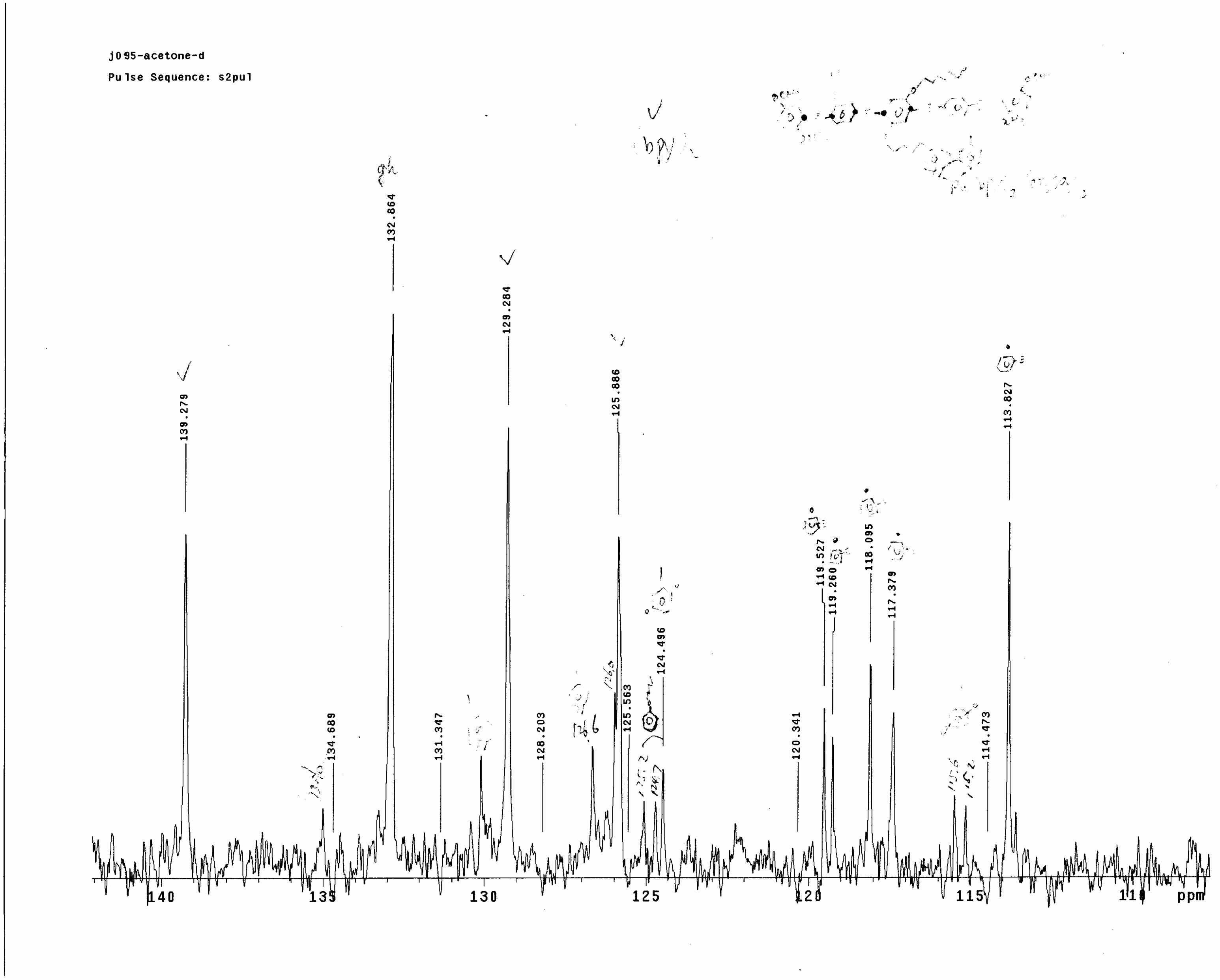
j095-acetone-d
Pulse Sequence: s2pul
139.279
134.689
132.864
ph
131.347
129.284
128.203
126
125.886
125.563
bpy
124.496
120.341
119.527
119.260
118.095
117.379
114.473
113.827
140
135
130
125
120
115
110
ppm

Figure S-11

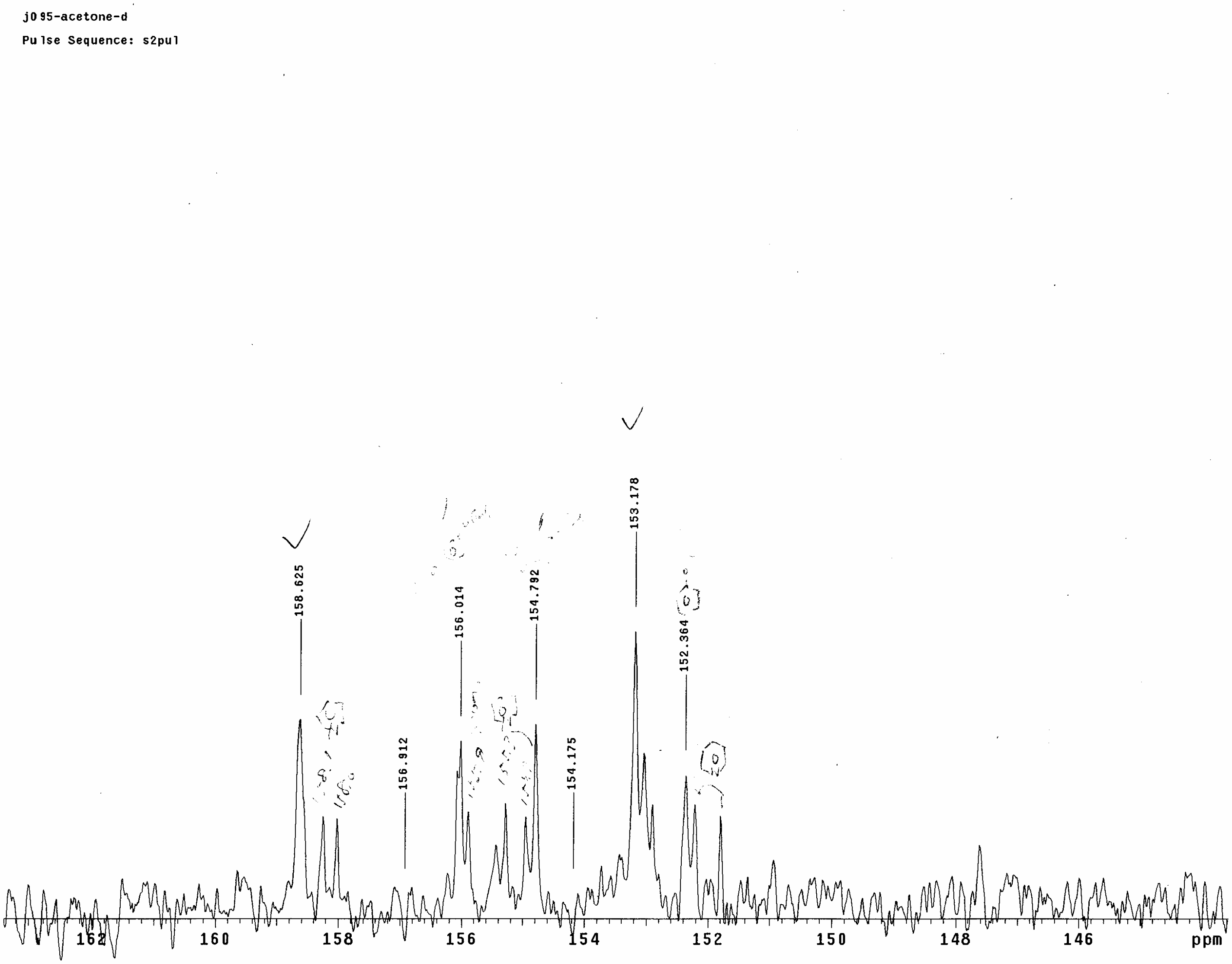
j095-acetone-d
Pulse Sequence: s2pul
158.625
156.912
156.014
154.792
154.175
153.178
152.364
162
160
158
156
154
152
150
148
146
ppm

Figure S-12

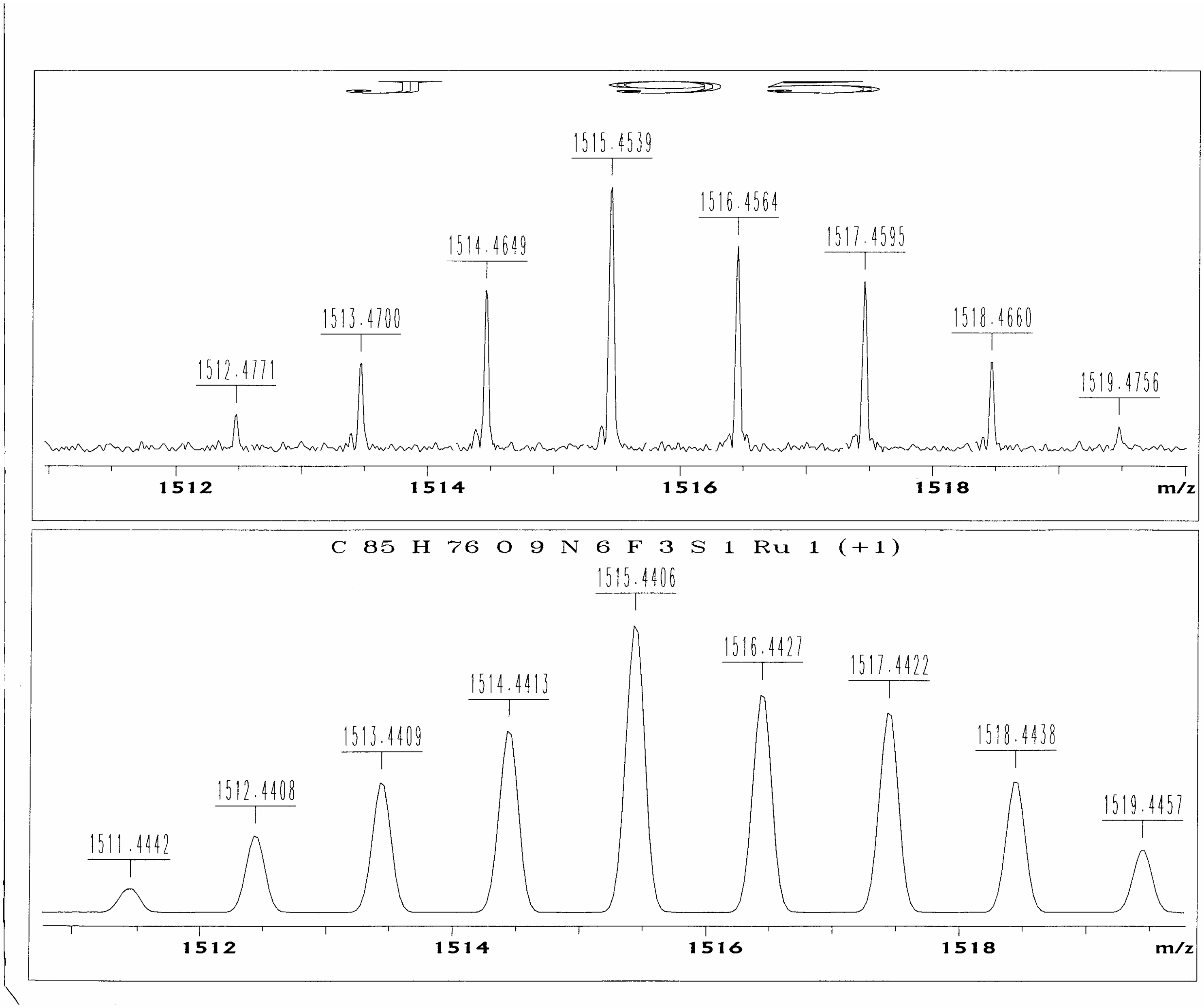
1512.4771
1513.4700
1514.4649
1515.4539
1516.4564
1517.4595
1518.4660
1519.4756
1512
1514
1516
1518
m/z
C 85 H 76 O 9 N 6 F 3 S 1 Ru 1 (+1)
1511.4442
1512.4408
1513.4409
1514.4413
1515.4406
1516.4427
1517.4422
1518.4438
1519.4457
1512
1514
1516
1518
m/z

Figure S-13

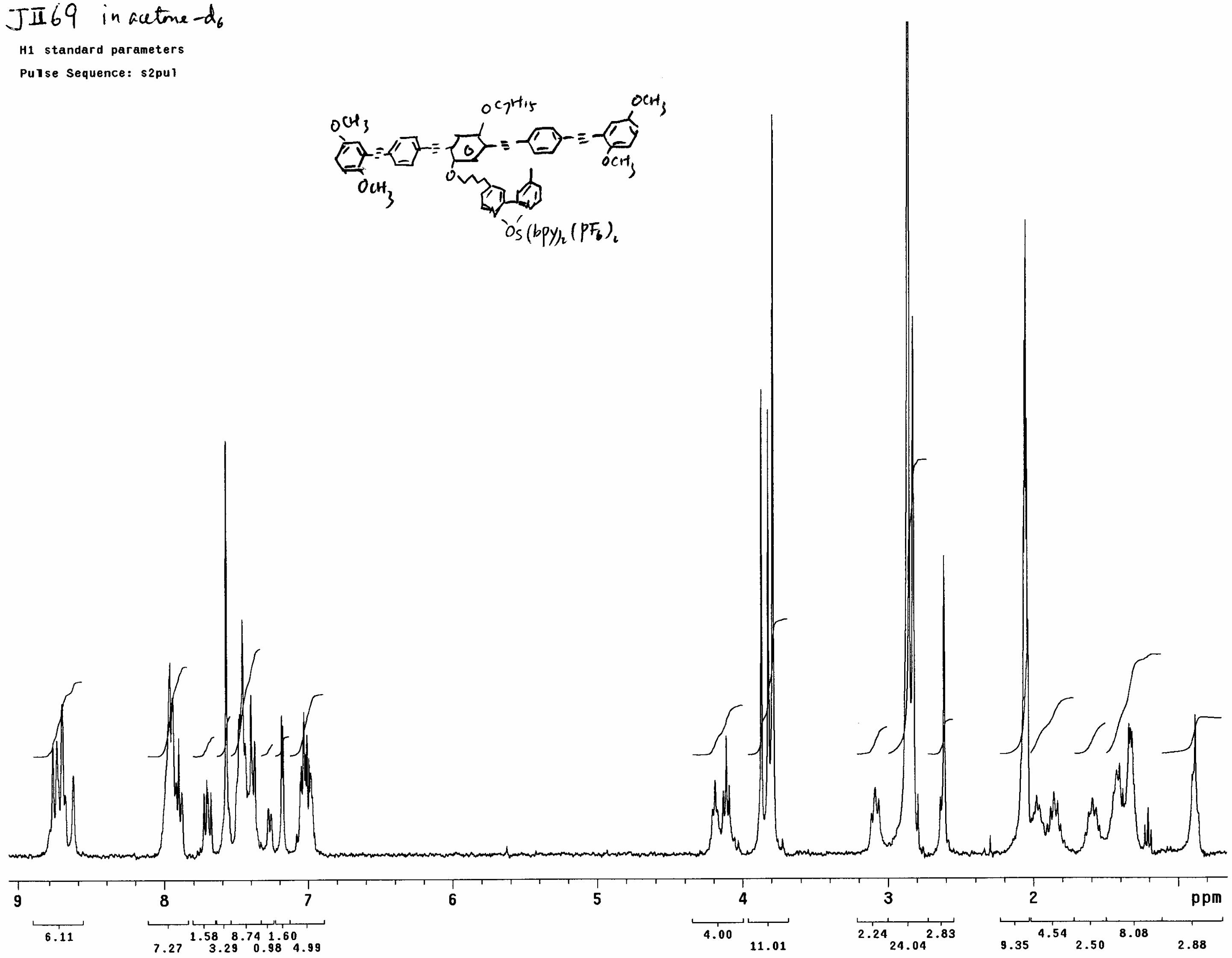
JII69 in acetone-d_6
H1 standard parameters
Pulse Sequence: s2pul
OCH3
OC7H15
OCH3
OCH3
OCH3
O
Os(bpy)2(PF6)2
9
8
7
6
5
4
3
2
ppm
6.11
7.27
1.58
3.29
8.74
0.98
1.60
4.99
4.00
11.01
2.24
24.04
2.83
9.35
4.54
2.50
8.08
2.88

Figure S-14

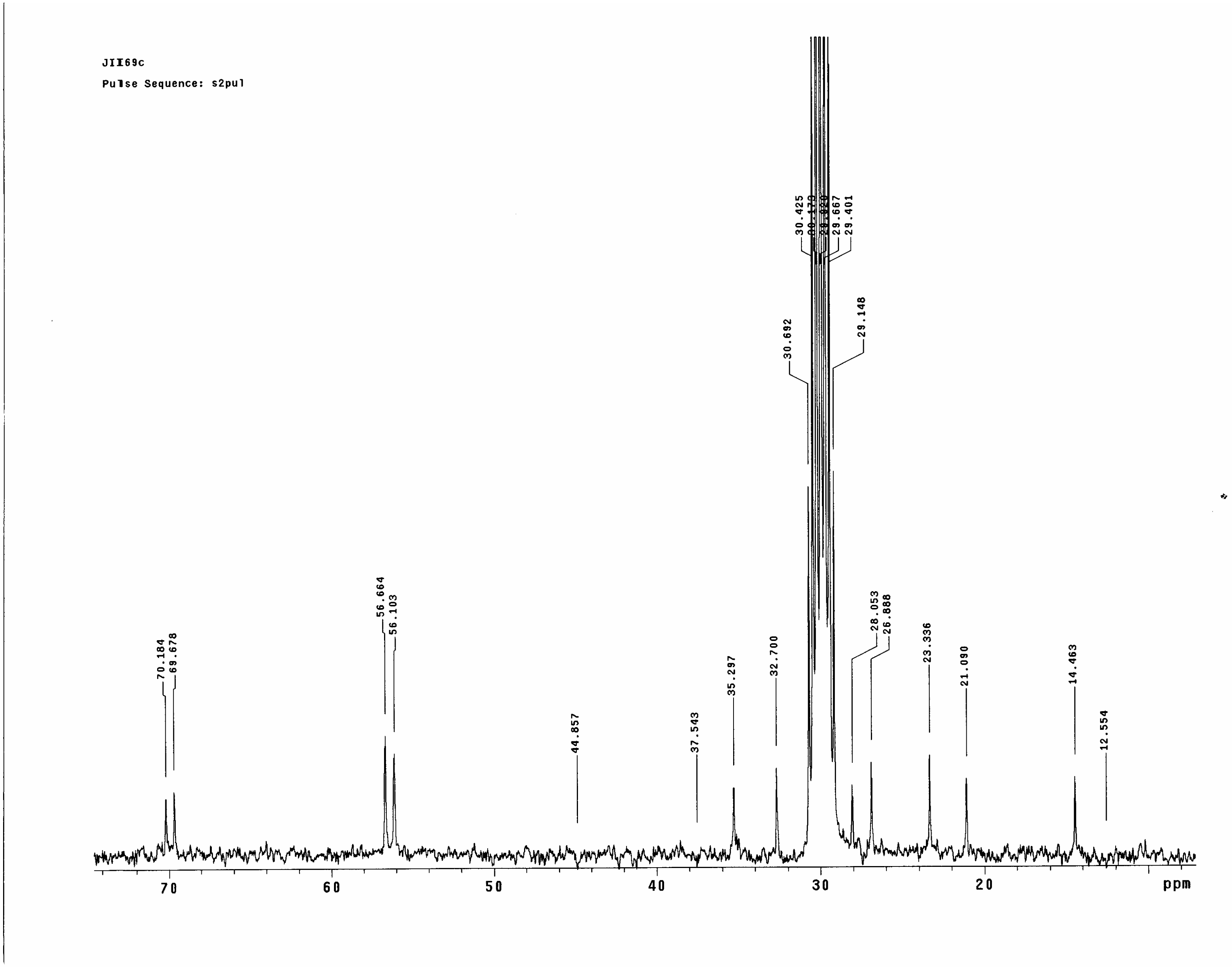
JII69c
Pulse Sequence: s2pul
70.184
69.678
56.664
56.103
44.857
37.543
35.297
32.700
30.692
30.425
30.173
29.920
29.667
29.401
29.148
28.053
26.888
23.336
21.090
14.463
12.554
70
60
50
40
30
20
ppm

Figure S-15

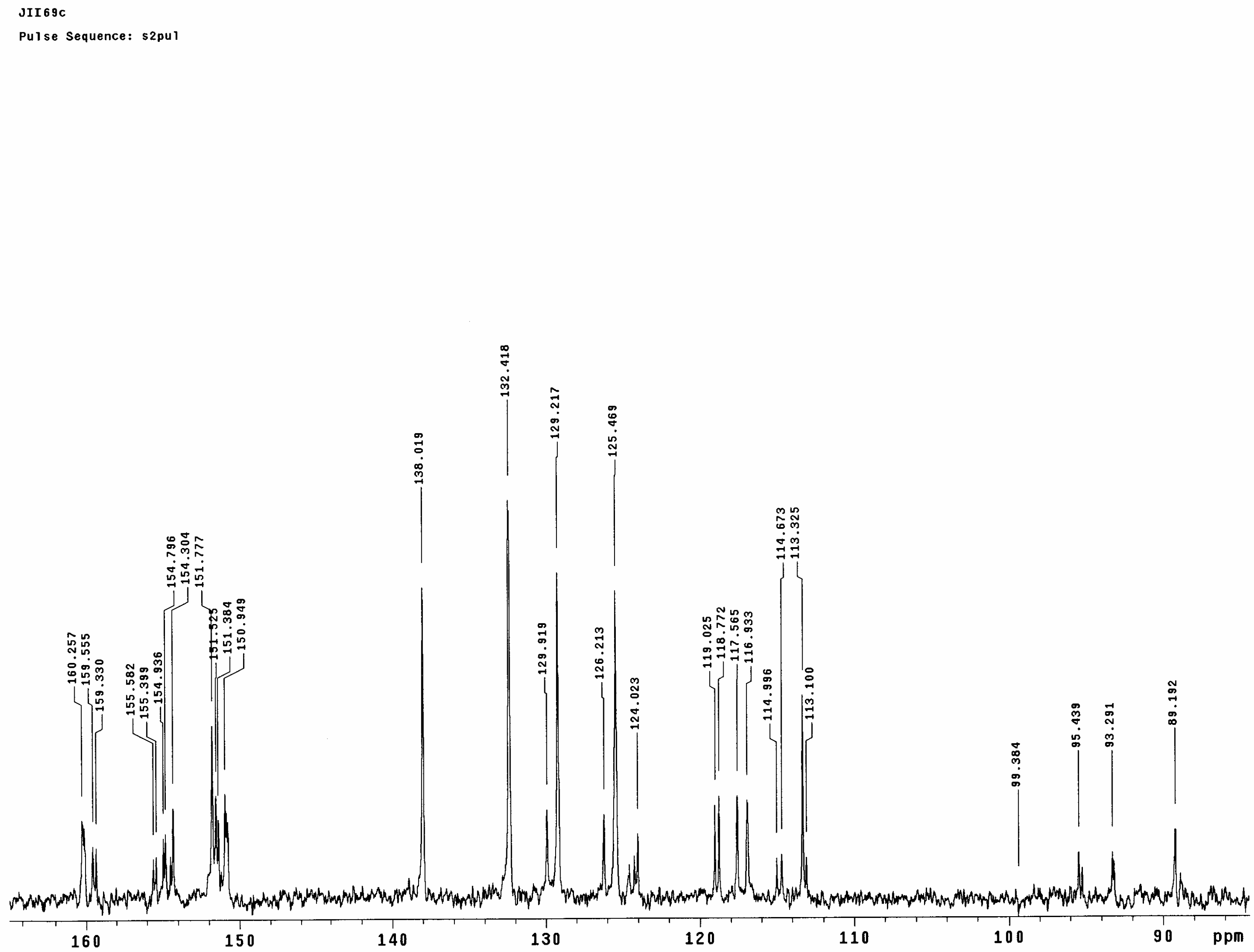
JII69c
Pulse Sequence: s2pul
160.257
159.555
159.330
155.582
155.399
154.936
154.796
154.304
151.777
151.525
151.384
150.949
138.019
132.418
129.919
129.217
126.213
125.469
124.023
119.025
118.772
117.565
116.933
114.996
114.673
113.325
113.100
99.384
95.439
93.291
89.192
160
150
140
130
120
110
100
90
ppm

Figure S-16

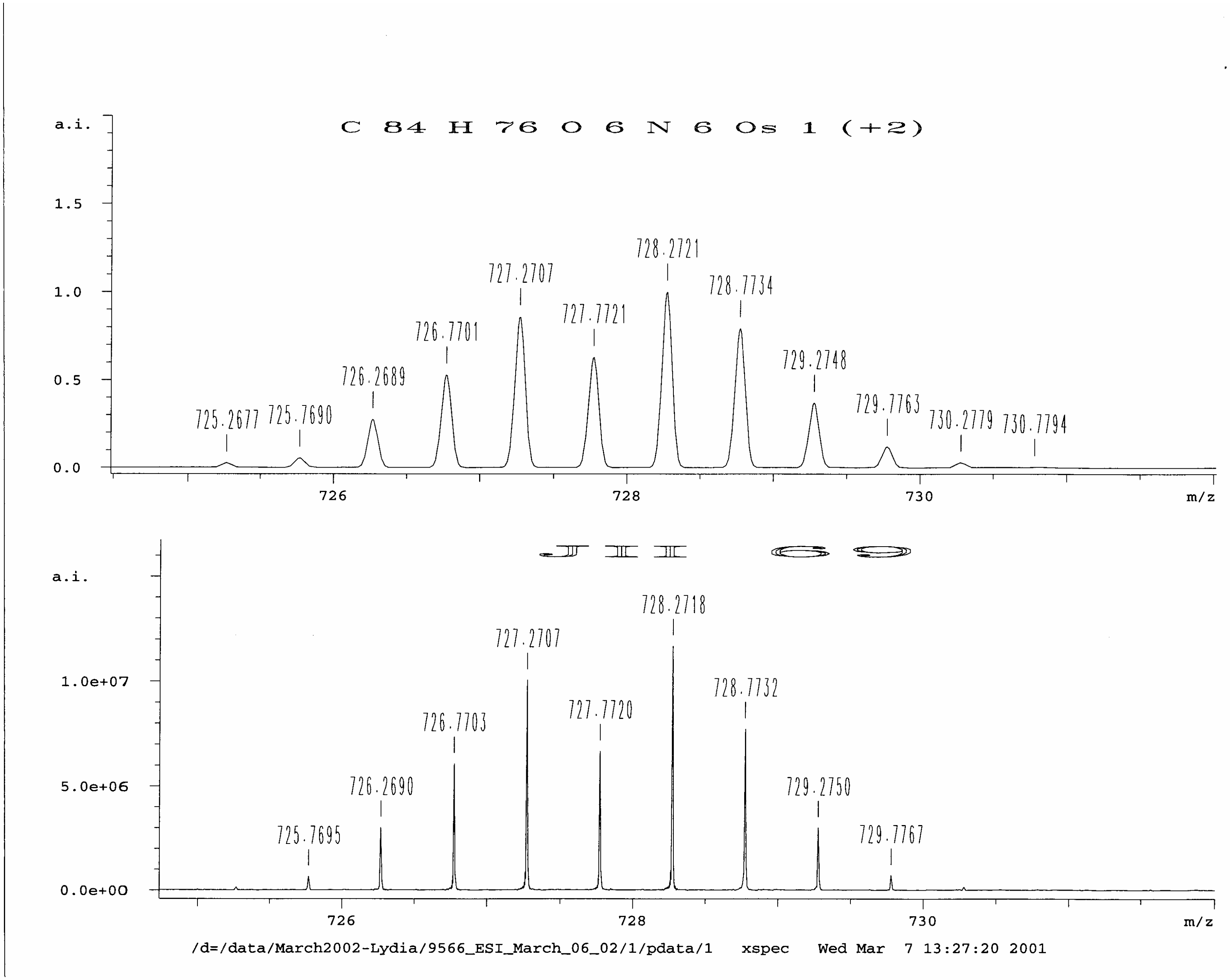
C 84 H 76 O 6 N 6 Os 1 (+2)
a.i.
1.5
1.0
0.5
0.0
725.2677
725.7690
726.2689
726.7701
727.2707
727.7721
728.2721
728.7734
729.2748
729.7763
730.2779
730.7794
726
728
730
m/z
JII 69
a.i.
1.0e+07
5.0e+06
0.0e+00
725.7695
726.2690
726.7703
727.2707
727.7720
728.2718
728.7732
729.2750
729.7767
726
728
730
m/z
/d=/data/March2002-Lydia/9566_ESI_March_06_02/1/pdata/1 xspec Wed Mar 7 13:27:20 2001

Figure S-17

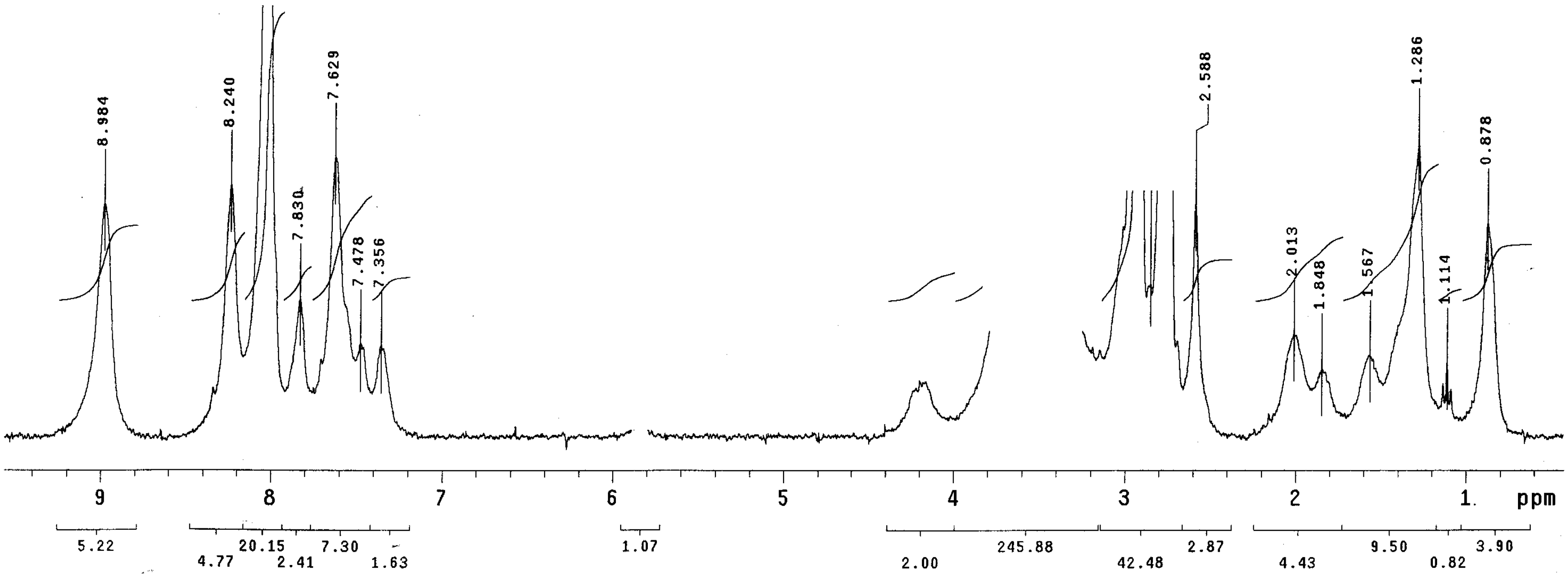
8.984
8.240
7.830
7.629
7.478
7.356
2.588
2.013
1.848
1.567
1.286
1.114
0.878
9
8
7
6
5
4
3
2
1.
ppm
5.22
4.77
20.15
2.41
7.30
1.63
1.07
2.00
245.88
42.48
2.87
4.43
9.50
0.82
3.90

Figure S-18

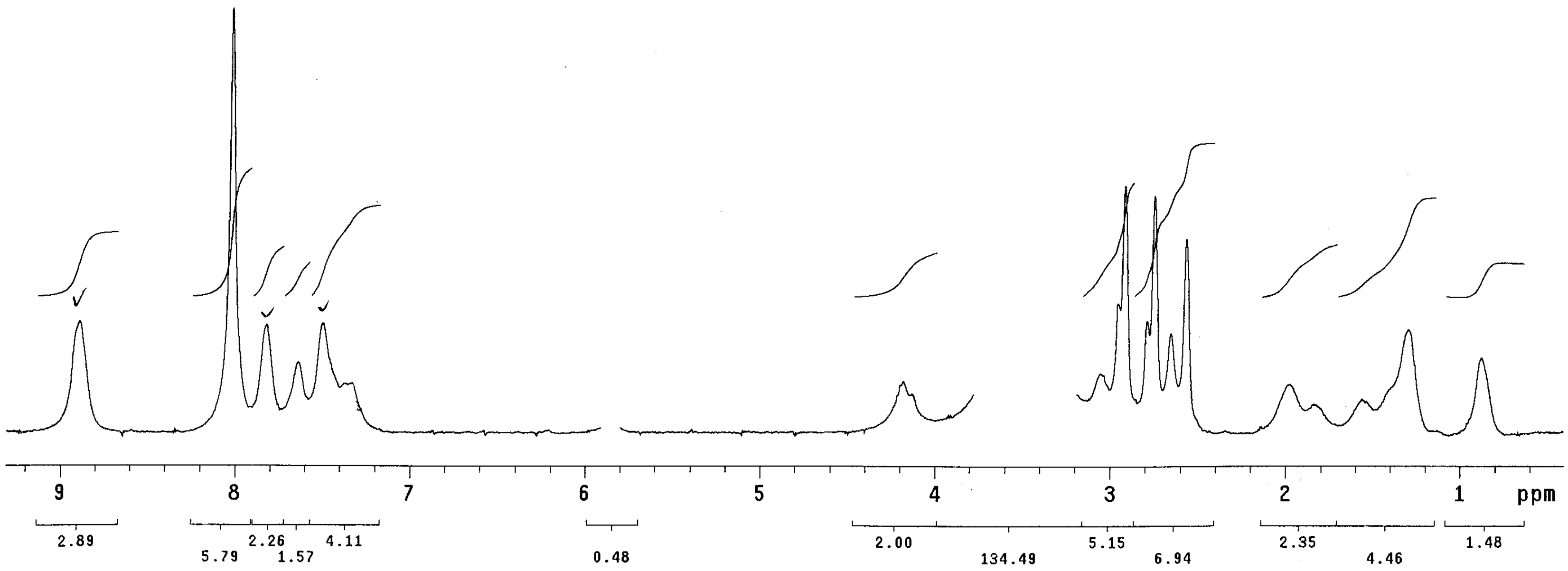
9
8
7
6
5
4
3
2
1
ppm
2.89
5.79
2.26
1.57
4.11
0.48
2.00
134.49
5.15
6.94
2.35
4.46
1.48

Figure S-19

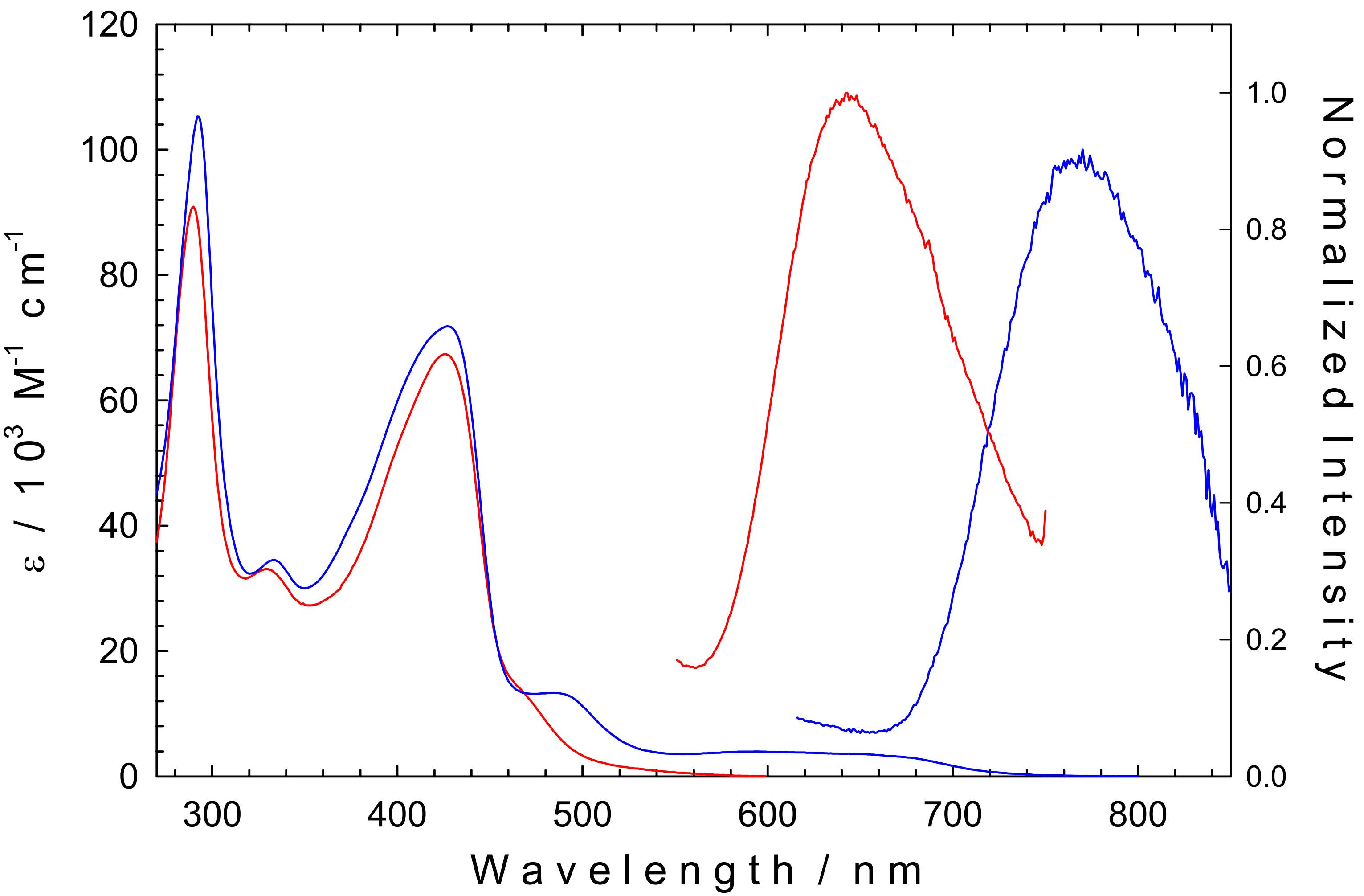
120
100
80
60
40
20
0
ε / 10^3 M^{-1} cm^{-1}
300
400
500
600
700
800
Wavelength / nm
1.0
0.8
0.6
0.4
0.2
0.0
Normalized Intensity

Figure S-20

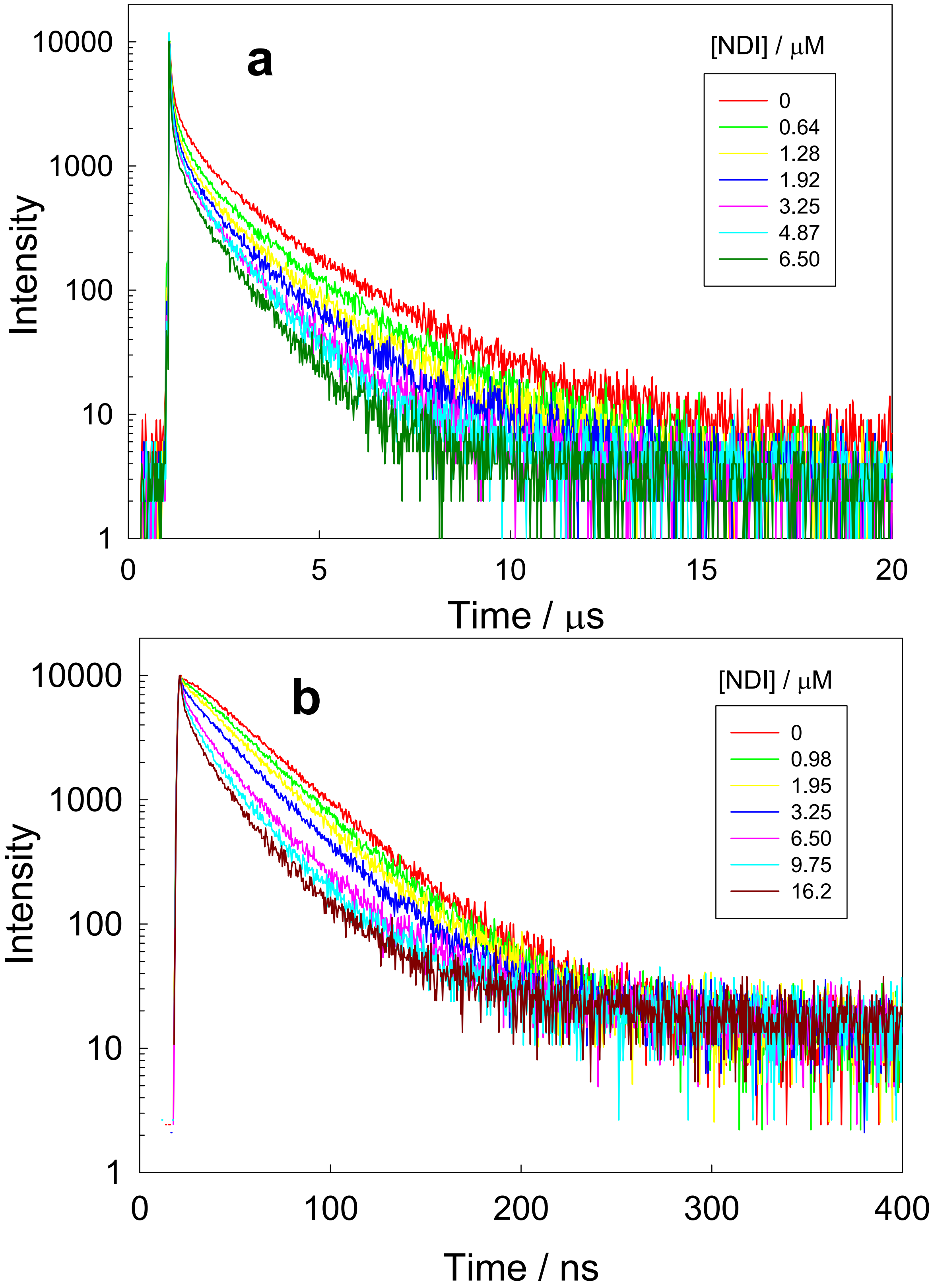
a
[NDI] / μM
0
0.64
1.28
1.92
3.25
4.87
6.50
Intensity
10000
1000
100
10
1
0
5
10
15
20
Time / μs
b
[NDI] / μM
0
0.98
1.95
3.25
6.50
9.75
16.2
Intensity
10000
1000
100
10
1
0
100
200
300
400
Time / ns

Figure S-21

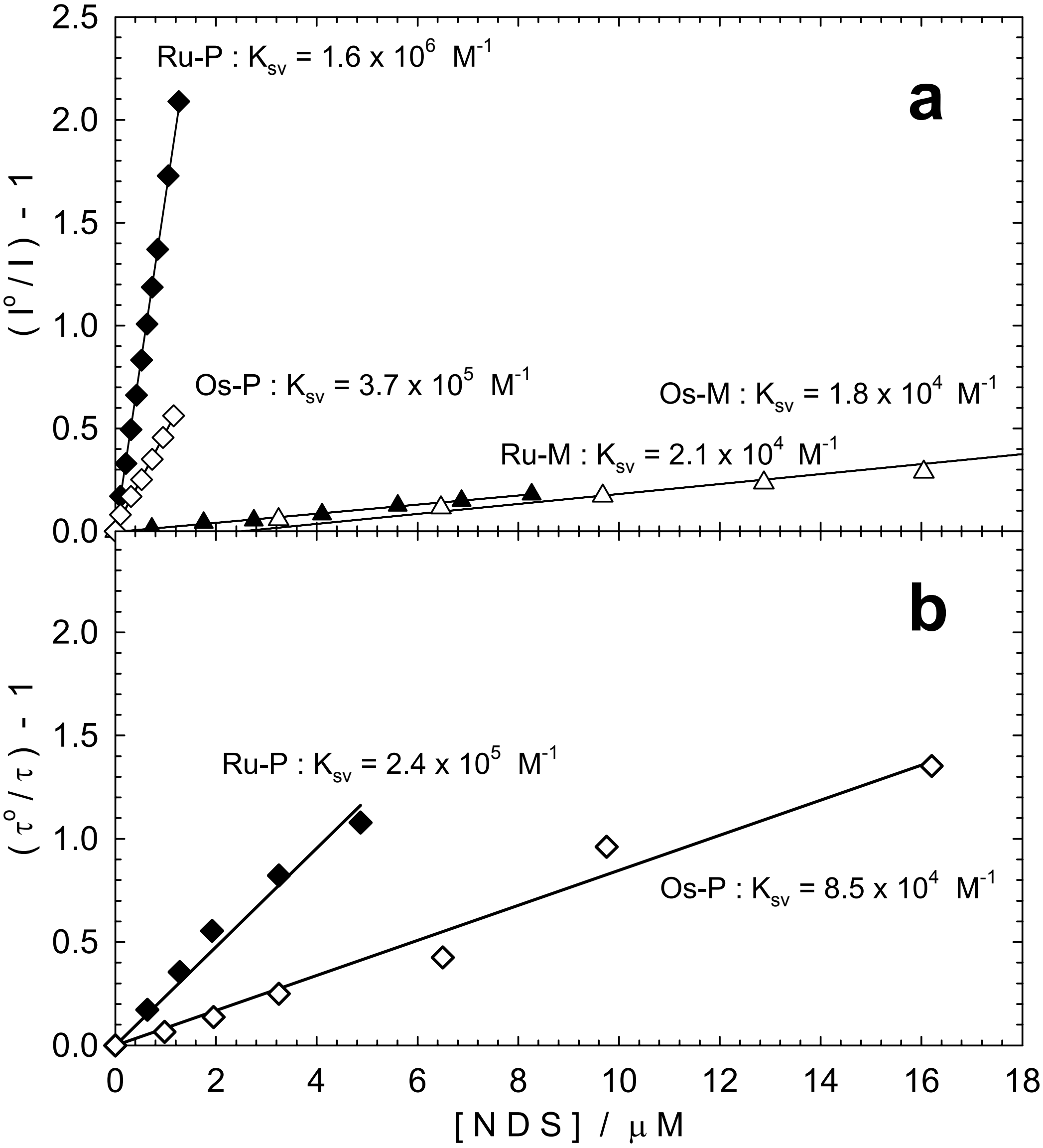
a
b
Ru-P : K_{sv} = 1.6 x 10^6 M^{-1}
Os-P : K_{sv} = 3.7 x 10^5 M^{-1}
Os-M : K_{sv} = 1.8 x 10^4 M^{-1}
Ru-M : K_{sv} = 2.1 x 10^4 M^{-1}
Ru-P : K_{sv} = 2.4 x 10^5 M^{-1}
Os-P : K_{sv} = 8.5 x 10^4 M^{-1}
(I^o / I) - 1
(τ^o / τ) - 1
[N D S] / μ M
0.0
0.5
1.0
1.5
2.0
2.5
0
2
4
6
8
10
12
14
16
18

Figure S-22