SUPPORTING INFORMATION

Rigid Cross-conjugated Macrocycles: A Cyclic Alternative to 4,4'-Bipyridines in Supramolecular Chemistry

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1. Synthetic procedures and characterization for compounds **3 a-b**, **5 a-b** and **7 a-b**.
2. ^{1}H NMR spectra for **6**.
3. ^{1}H, ^{13}C, and *g*HMQC NMR spectra for **7a-b**.
4. ESI MS for **7a**.
5. X-ray crystallographic details for **7a**.

General. Reagents were purchased reagent grade from commercial suppliers and used without further purification. THF was distilled from sodium/benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2. 3,5-Diethynyl pyridine[1] and **2a-b**[2] were prepared as previously reported. Evaporation and concentration *in vacuo* was achieved at H_2O-aspirator pressure. All Pd-catalyzed coupling reactions were performed in standard, dry glassware under an inert atmosphere of N_2. A positive pressure of N_2 was essential to the success of all Pd-catalyzed reactions. Degassing of solvents was accomplished by vigorously bubbling N_2 through the solutions for greater than 45 min. Column chromatography: Aluminum oxide, neutral, Brockman 1, 150 mesh from *Aldrich Chemical Company, Inc*. Thin Layer Chromatography (TLC): Aluminum sheets coated with *aluminum oxide N/UV$_{254}$* from *Macherey-Nagel*: visualization by UV light. M.p.: *Gallencamp* apparatus; uncorrected. UV/Vis spectra: *Varian Cary 400* at rt; λ_{max} in nm (ε in L M^{-1} cm^{-1}). Fluorescence spectra: *Photon Technology International* instrument at rt; Solvent: dry, degassed CH_2Cl_2. IR spectra: *Nic-Plan IR Microscope* (as solids). ^1H- and ^{13}C-NMR: *Varian Gemini* 300 or 500 and *Bruker* 300 instruments at rt in CD_2Cl_2 or $CDCl_3$; solvent peaks (5.32 and 7.24 ppm for ^1H and 53.80 and 77.00 ppm for ^{13}C, respectively) as reference. ES MS (*m/z*): *Micromass Zabspec oaTOF* or *PE Biosystems Mariner TOF* instruments; solvent: 3:1, MeOH:toluene or CH_3NO_2. MALDI MS (*m/z*): *PE Voyager Elite* instrument in reflectron mode with delayed extraction; Matrix: 1,8,9-trihydroxyanthracene; solvent: CH_2Cl_2.

Tetrayne 3a: $Pd(PPh_3)_4$ (50 mg, 0.04 mmol) and CuI (25 mg, 0.13 mmol) were sequentially added to a degassed solution of diethynyl pyridine **1** (134 mg, 1.05 mmol), vinyl triflate **2a** (630 mg, 2.10 mmol) and Et_2NH (4 mL) in THF (80 mL). The reaction mixture was stirred at rt for 30 min until TLC analysis indicated the disappearance of **1**. Sat'd NH_4Cl and diethyl ether were added and the organic phase was washed with two further portions of sat'd NH_4Cl and dried over anh. $MgSO_4$. Flash chromatography on alumina (hexanes/CH_2Cl_2, 2:1) yielded **3a** (356 mg, 79%) as a white solid: mp 71-72 °C; R_f = 0.4 (hexanes/CH_2Cl_2, 2:1); UV/Vis (CH_2Cl_2) 297 (30700) nm; IR (µscope) 2959, 2904, 2210, 2151, 1577 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.21 (s, 18H), 2.08 (s, 12H), 7.78 (br s, 1H), 8.54 (br s, 2H); ^{13}C NMR (75.5 MHz, APT, CD_2Cl_2) δ -0.01, 23.03, 23.06, 87.54, 90.17, 97.13, 101.22, 101.24, 120.37, 140.30, 150.86, 158.26; ES MS (MeOH/toluene) *m/z* (rel. intensity): 428.2 ($[M + H]^+$, 100); ES HRMS *m/z* calcd. ($C_{27}H_{34}NSi_2$, M + H) 428.2230, found 428.2226.

Tetrayne 3b: $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) and CuI (20 mg, 0.10 mmol) were sequentially added to a degassed solution of diethynyl pyridine **1** (70 mg, 0.55 mmol), vinyl triflate **2b** (504 mg, 1.08 mmol) and Et_2NH (1.5 mL). The reaction flask was sealed under N_2 and heated for 24 hours at 55 °C. After cooling to rt, sat'd NH_4Cl and diethyl ether were added and the organic phase was washed with two further portions of sat'd NH_4Cl and dried over anh. $MgSO_4$. Flash chromatography on alumina (hexanes/CH_2Cl_2, 2:1) yielded **3b** (254 mg, 61%) as a clear solid: mp 118-121 °C; R_f = 0.4 (hexanes/CH_2Cl_2, 2:1); UV/Vis (CH_2Cl_2) 259 (48800), 348 (41700) nm; IR (µscope) 3081, 2910, 2205, 2151, 1536 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 0.60 (q, J = 7.8 Hz, 12H), 0.95 (t, J = 7.8 Hz, 18H), 7.33-7.51 (m, 21H), 8.30 (d, J = 2.0 Hz, 2H); ^{13}C NMR (75.5 MHz, APT, CD_2Cl_2) δ 4.54, 7.56, 87.68, 92.79, 96.74, 101.76, 104.00, 120.10, 128.10, 128.18, 129.23, 129.26, 130.60, 130.66, 139.97, 140.16, 140.55, 150.99, 158.57; ES MS (MeOH/toluene) *m/z* (rel. intensity): 760.4 ($[M + H]^+$, 100); ES HRMS *m/z* calcd. ($C_{53}H_{54}NSi_2$, M + H) 760.3795, found 760.3792.

Macrocycle 5a: Trimer **3a** (154 mg, 0.36 mmol) was dissolved in wet MeOH/THF (50 mL) and desilylated by treating with K_2CO_3 and stirring at rt for 1 h. Ether and sat'd NH_4Cl were added to the reaction mixture and the organic phase was washed with two further portions of sat'd NH_4Cl and dried over anh. $MgSO_4$. Solvent was removed under reduced pressure and the deprotected trimer **4a** was used without any further purification. The deprotected polyyne was oxidatively coupled in dry CH_2Cl_2 (350 mL) in the presence of air, TMEDA (1.0 mL, 6.6 mmol), and CuI (520 mg, 2.73 mmol) for 90 min. at rt. Ether and sat'd NH_4Cl were added to the reaction mixture and the organic phase was washed with two further portions of sat'd NH_4Cl and dried over anh. $MgSO_4$. The solvent was removed under reduced pressure to yield an off-white solid. Macrocycle **5a** was not isolated due to the extremely limited solubility of this crude reaction product.

Macrocycle 5b: Trimer **3b** (82 mg, 0.12 mmol) was dissolved in THF (50 mL), treated with 2 drops of TBAF, and stirred at rt for 30 min. Ether and sat'd NH_4Cl were added to the reaction mixture and the organic phase was washed with two further portions of sat'd NH_4Cl and dried over anh. $MgSO_4$. Solvent was removed under reduced pressure and the deprotected trimer **4b** was used without any further purification. The deprotected polyyne was oxidatively coupled in dry CH_2Cl_2 (220 mL) in the presence of air, TMEDA (0.35 mL, 2.3 mmol), and CuI (175 mg, 0.92 mmol) for 3 h at rt followed by 12 h at 4 °C. Ether and sat'd NH_4Cl were added to the reaction mixture and the organic phase was washed with two further portions of sat'd NH_4Cl and dried over anh. $MgSO_4$. Precipitation from CH_2Cl_2 yielded **5b** (29 mg, 51%) as a bright yellow solid the was not sufficiently soluble for meaningful ^{13}C NMR anaylsis: mp 172 °C (decomposition); UV/Vis (CH_2Cl_2) 260 (72600), 363 (88800), 401 (sh, 43400) nm; IR (µscope) 3052, 2210, 1583, 1513 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.31-7.48 (m, 40H), 7.83 (t, J = 1.9 Hz, 2H), 8.13 (d, J = 1.9 Hz, 4H); ES MS (MeOH/toluene) *m/z* (rel. intensity): 1059.4 ($[M + H]^+$, 43); ES HRMS *m/z* calcd. ($C_{82}H_{47}N_2$, M+H) 1059.3734, found 1059.3738.

Macrocycle porphyrin assembly 7a: The crude product mixture containing macrocycle **5a** (155 mg) was added to a solution of Ru porphyrin **6** (200 mg, 0.25 mmol) in CH_2Cl_2 (2 mL). Flash chromatography on alumina (hexanes/CH_2Cl_2, 1:1) yielded **7a** (152 mg, 39% overall from **3a**) as a burgundy solid: mp 132 °C (decomposition); UV/Vis (CH_2Cl_2) 294 (134800), 414 (535600), 534 (46500), 570 (20000); IR (µscope) 3126, 2866, 2210, 1916, 1806, 1575 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 1.30 (d, *J* = 1.9 Hz, 4H), 1.84 (s, 12H), 2.00 (s, 12H), 2.70 (s, 24H), 6.04 (t, *J* = 1.7 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 8H), 7.57 (d, *J* = 7.8 Hz, 8H), 7.90 (dd, *J* = 7.8, 1.9 Hz, 8H), 8.11 (dd, *J* = 7.8, 1.9 Hz, 8H), 8.64 (s, 16H); ^{13}C NMR (125.3 MHz, CD_2Cl_2) δ 21.53, 23.16, 23.45, 75.66, 78.07, 85.45, 88.83, 99.65, 118.09, 122.03, 127.30, 127.61, 132.08, 134.44 (2×), 137.40, 137.79, 139.82, 144.03, 145.08, 160.99, 181.08; ES MS (CH_3NO_2) *m/z* (rel. intensity): 2160 ($[M + H]^+$, 3), 1361 ($[M – porphyrin]^+$, 21), 798 ($[porphyrin]^+$, 100), 563 ([**5a** + H]$^+$, 92)[3].

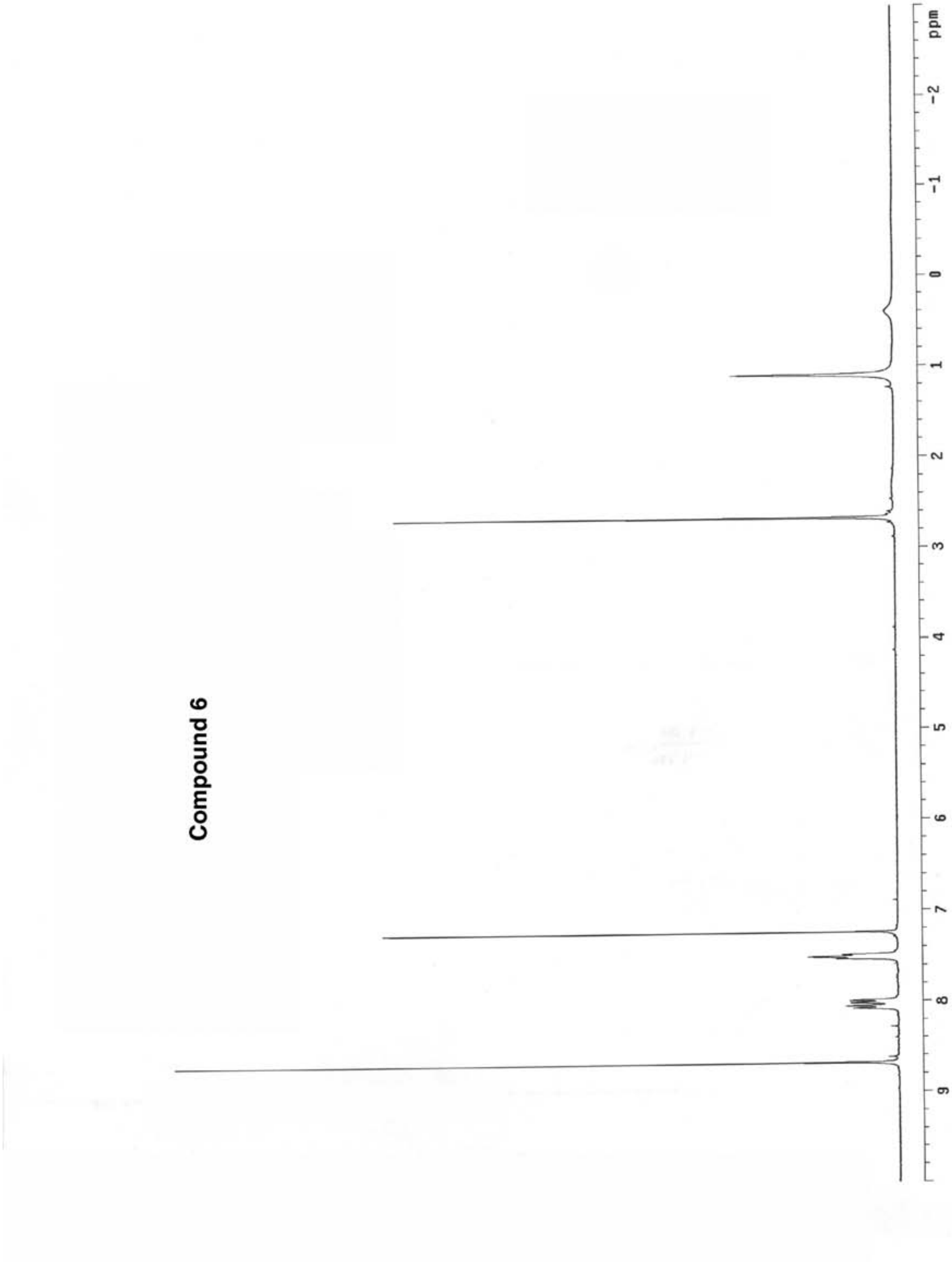
Macrocycle porphyrin assembly 7b: Macrocycle **5b** (10 mg, 0.009 mmol) was added to a solution of Ru porphyrin **6** (15 mg, 0.019 mmol) in CH_2Cl_2 (2 mL) and the assembly product crystallized upon concentration to give **7b** (15 mg, 60%) as a bright red solid: mp 266 °C (decomposition); UV/Vis (CH_2Cl_2) 363 (101200), 413 (493200), 534 (35800), 568 (9200) nm; IR (µscope) 3021, 1949, 1529, 1512, 1493 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 1.12 (br s, 4H), 2.65 (s, 24H), 6.08 (br s, 2H), 7.02 - 7.43 (m, 48H), 7.53 (d, *J* = 7.7 Hz, 8H), 7.76 (d, *J* = 7.7 Hz, 8H), 8.05 (d, *J* = 7.7 Hz, 8H), 8.58 (s, 16H); ^{13}C NMR (125.3 MHz, APT, CD_2Cl_2) δ 21.54, 76.41, 81.31, 85.40, 90.52, 99.23, 117.62, 121.89, 127.53, 127.56, 128.22, 128.31, 129.71, 130.09, 130.48, 132.14, 134.44, 134.47, 137.28, 139.02, 139.63, 139.78, 143.94, 145.34, 160.40, missing CO peak; ES MS (CH_3NO_2) *m/z* (rel. intensity): 1856 ($[M + H – porphyrin]^+$, 4), 1059 ([**5b** + H]$^+$, 34), 770 ([**6** – CO]$^+$, 100); MALDI MS: 1829 ($[M + H – porphyrin – CO]^+$).

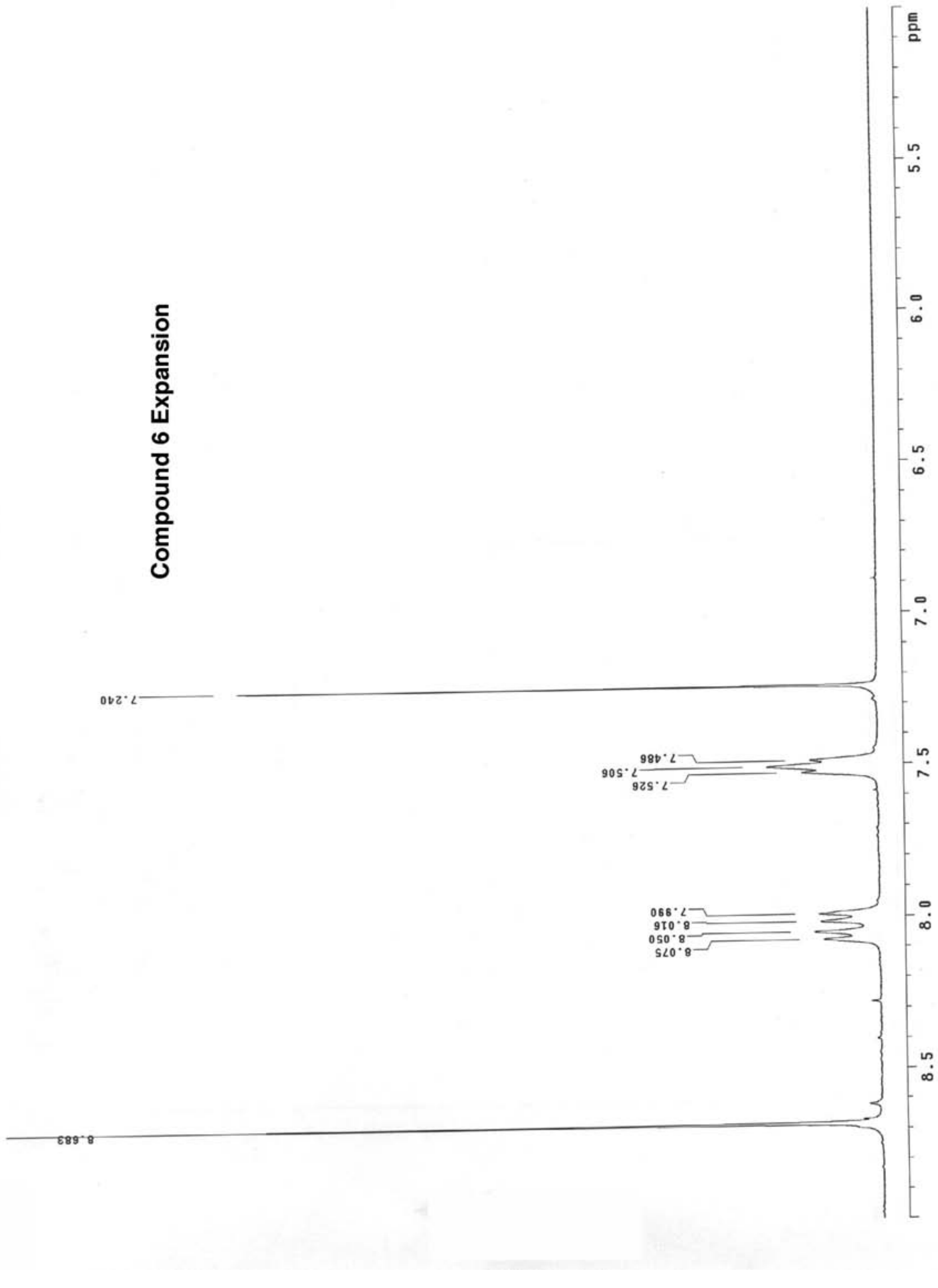
References:

1) Ng, Siu Choon; Novak, Igor; You, Xiaomei; Huang, Wei. *J. Phys. Chem. A* **1998**, *102,* 904 – 908.
2) Stang, P. J.; Fisk, T. E. *Synthesis* **1979**, 438 - 440.
3) Note: Comparison of the theoretical isotopic distribution patterns with those peaks observed at *m/z* 2160 and 1361 suggests that both the protonated and radical cation species are present in the sample. The isotopic distribution patterns observed are consistent with two overlapping distributions. The peaks observed at *m/z* 798 and 563 mass units, however, are attributed solely to the radical cation and protonated fragments, respectively. Several attempts were made to improve the intensity of the $(M+H)^+$ peak (by varying the applied voltage, using different combinations of

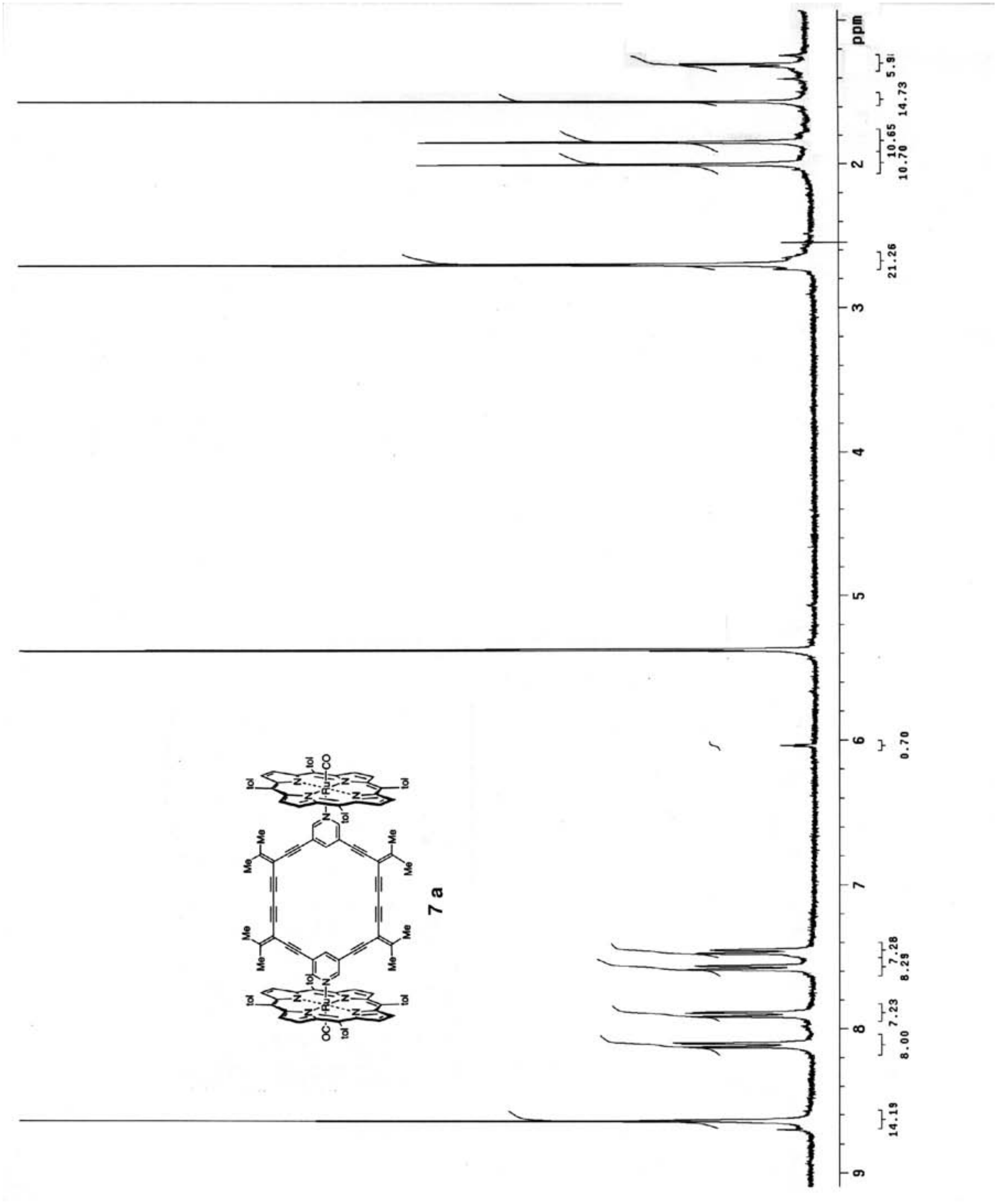
solvents and by lowering the temperature) but all attempts resulted in a loss of sensitivity and no significant gains in intensity.

Compound 6





Compound 6 Expansion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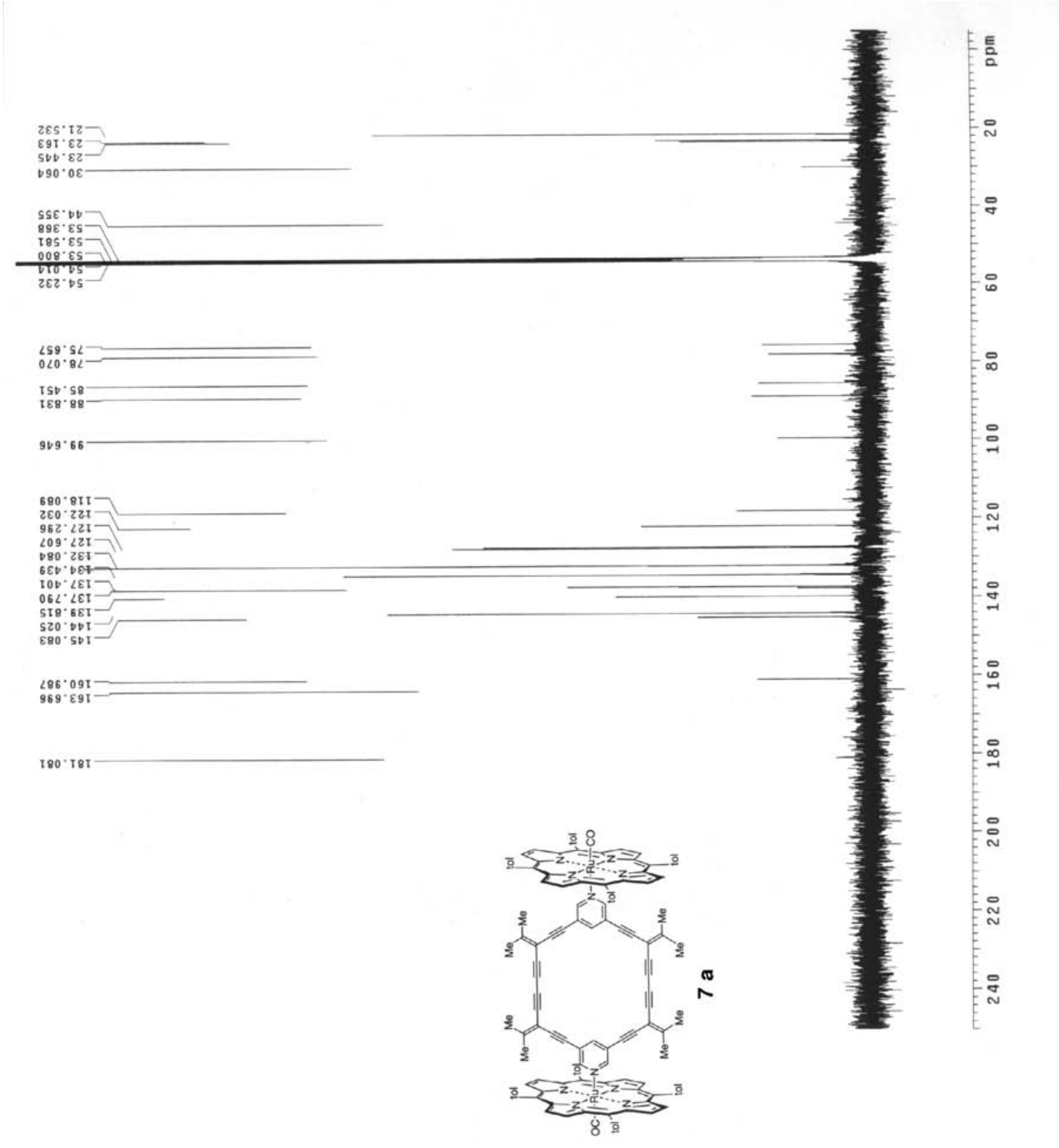
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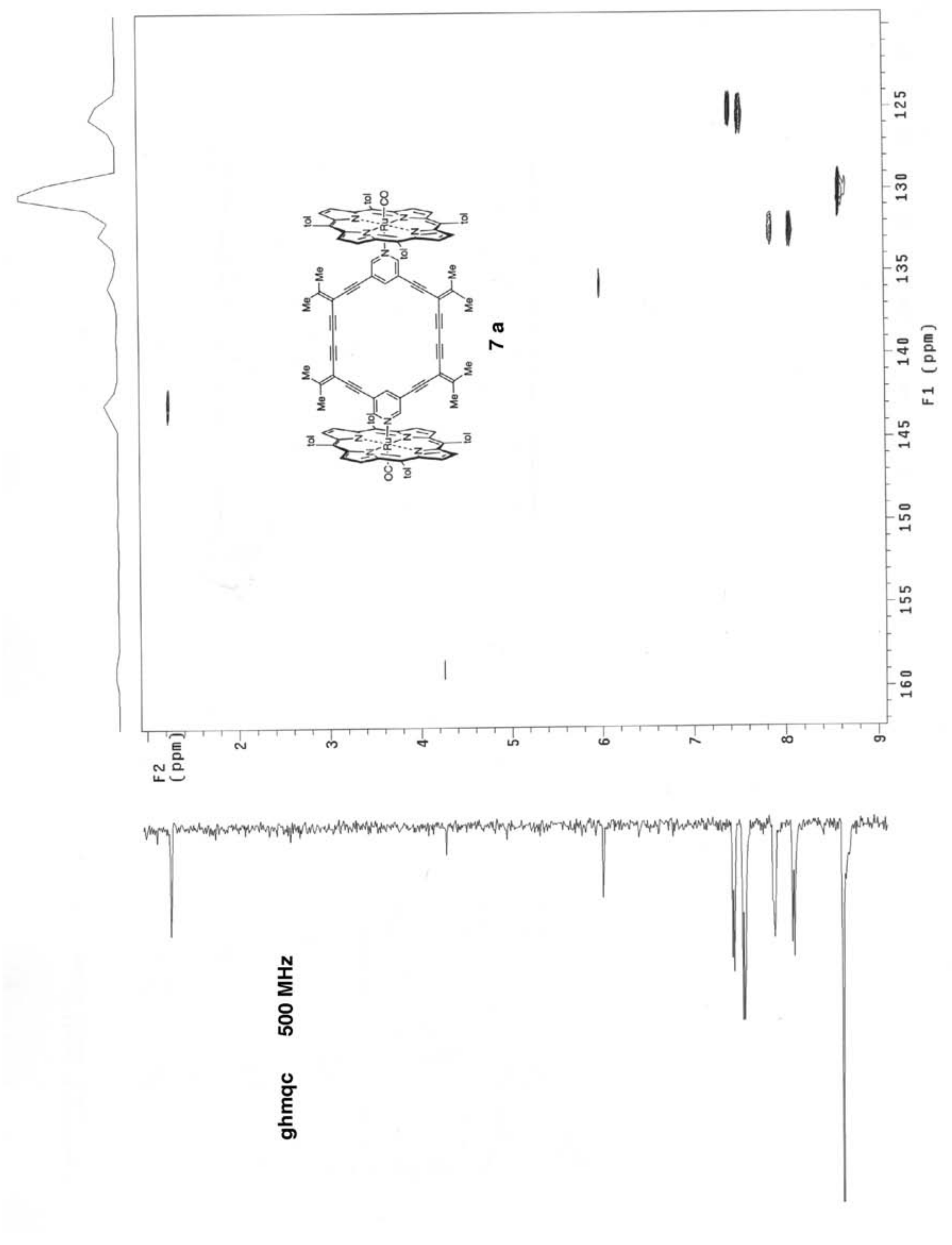
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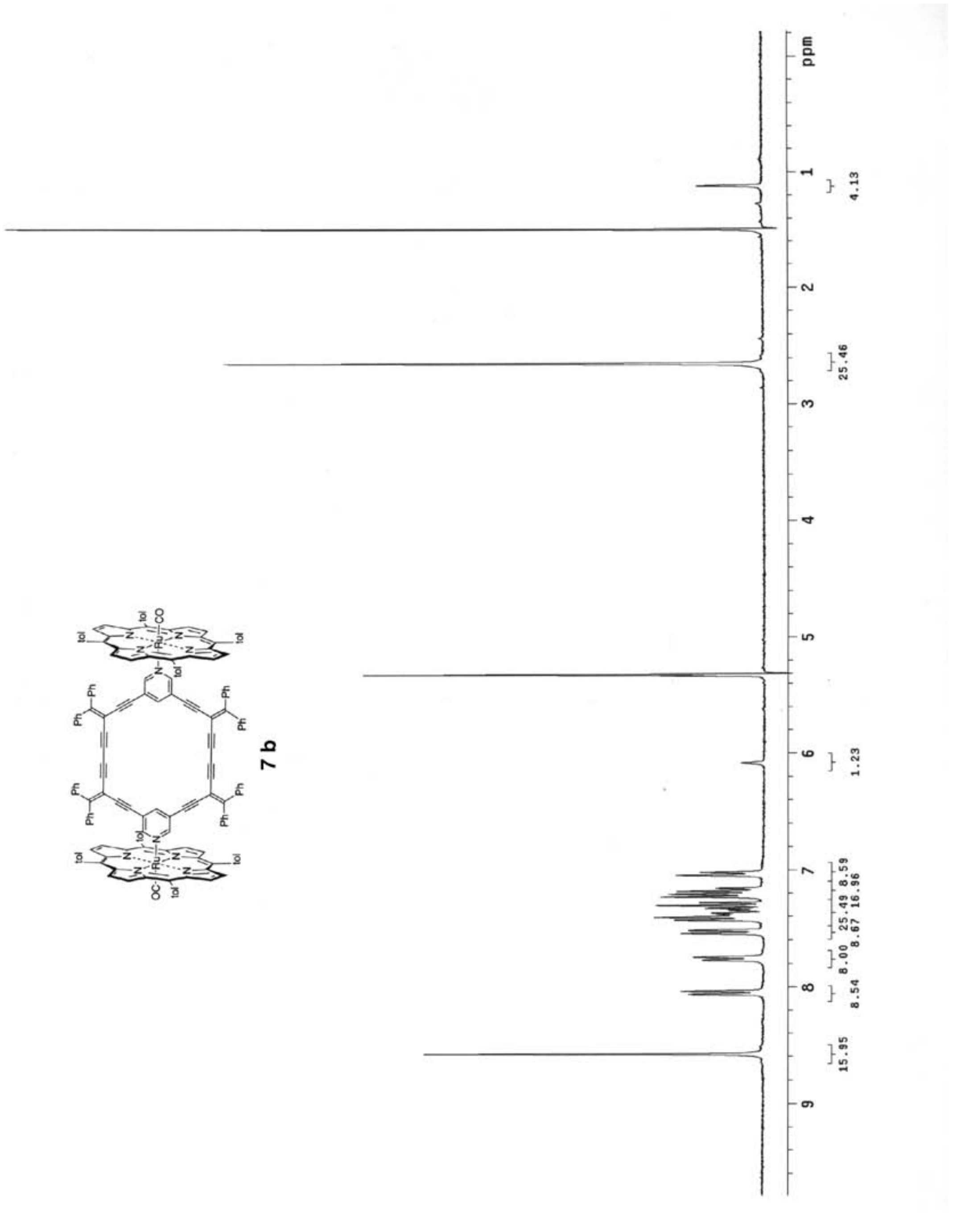
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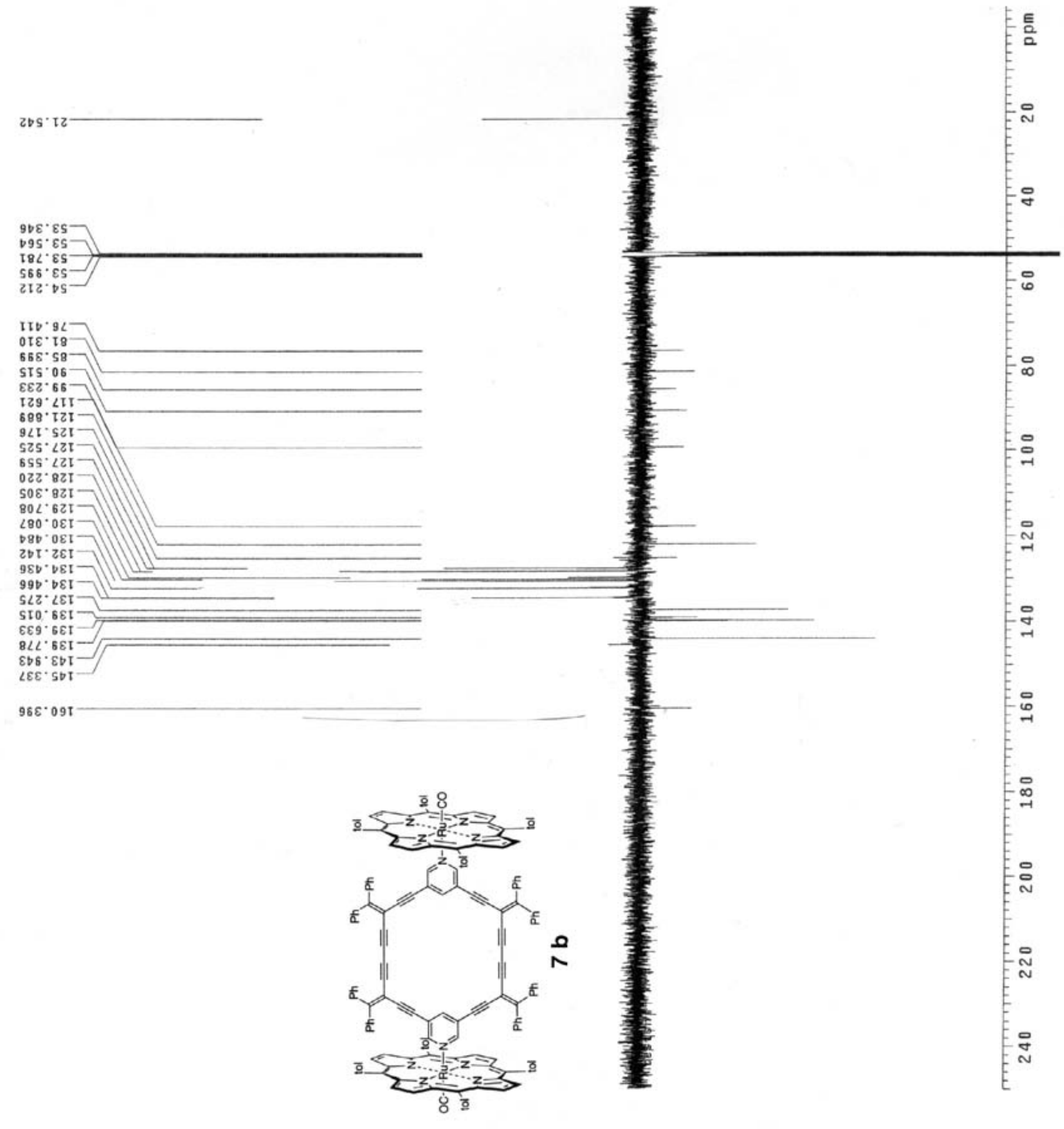
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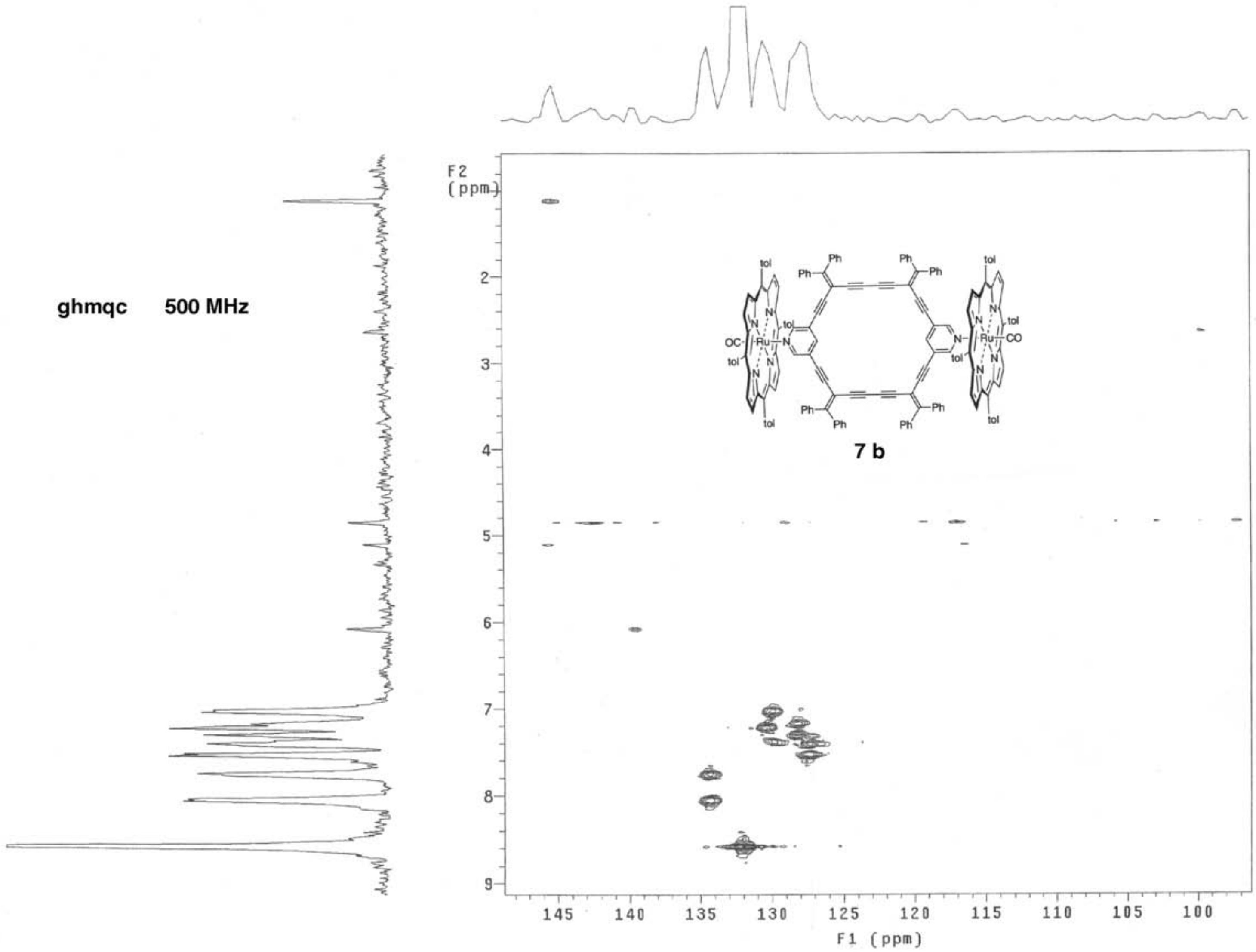
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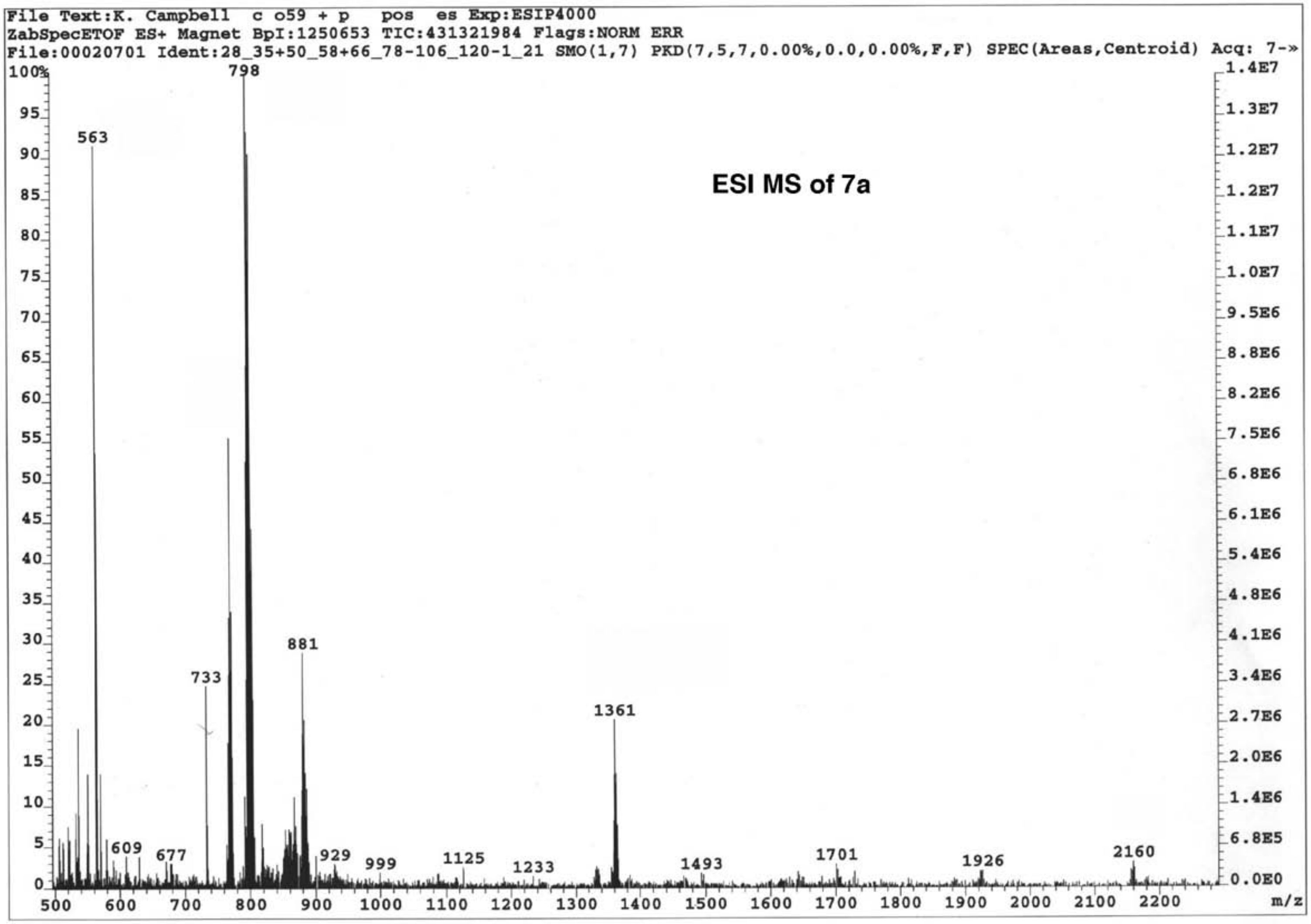
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