Supplementary Material (ESI) for Chemical Communications

Chemical Communications

A [2]Rotaxane-based ^{1}H NMR Spectroscopic Probe for the Simultaneous Determination of Physiologically Important Metal Ions in Solution

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SUPPORTING INFORMATION

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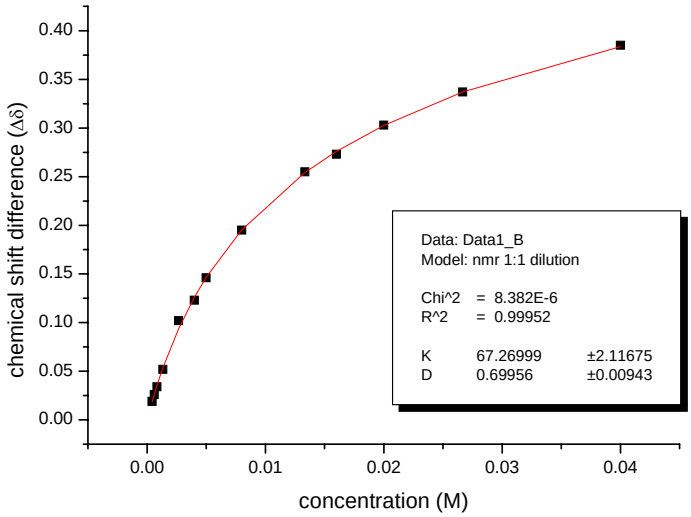
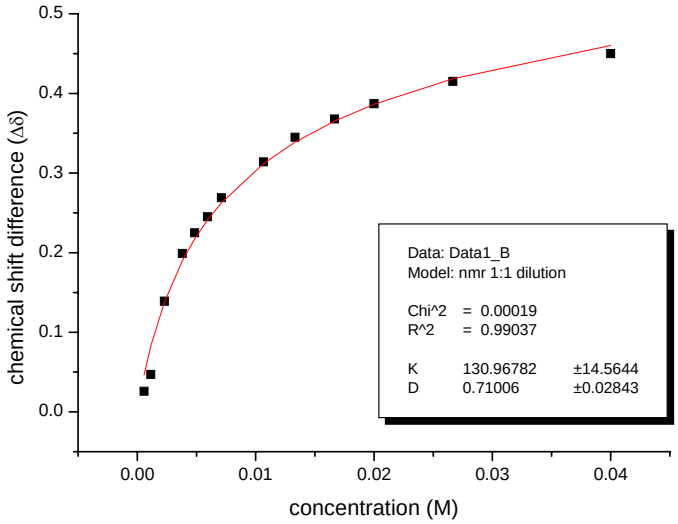
2-H_2·$4PF_6$: A solution of the dibromide **1** (34 mg, 0.1 mmol), BPX26C6 (65 mg, 0.15 mmol), and TFA (29 L, 0.4 mmol) in $MeNO_2$ (1 mL) was stirred at room temperature for 10 min. PPh_3 (79 mg, 0.3 mmol) was added and the reaction mixture was stirred for 12 h at ambient temperature. The solvent was evaporated under reduced pressure; the solid residue was dissolved in MeCN (1 mL) and subjected to filtration. Saturated aqueous NH_4PF_6 (5 mL) was added to the solution and the organic solvent was evaporated under reduced pressure. The precipitate was washed sequentially with water (5 mL), ether (5 mL), and CH_2Cl_2 (50 mL) to give **2**-H_2·$4PF_6$ as a white powder (77 mg, 45%). M.p.: >256 °C (dec.); ^{1}H NMR (400 MHz, CD_3CN): δ = 3.55–3.62 (m, 8H), 3.62–3.77 (m, 8 H), 4.03 (br, 8 H), 4.93 (d, *J* = 15.6 Hz, 4 H), 6.28 (br, 8 H), 7.50–7.60 (m, 4 H), 7.54–7.88 (m, 24 H), 7.94–8.02 (m, 6 H), 8.24 (s, 2 H) ppm; ^{13}C NMR (100 MHz, CD_3CN): δ = 28.0 (*J*(P,C) = 50.1 Hz), 70.3, 71.2, 73.2, 116.9, 117.7, 125.0, 128.5, 131.4, 131.6, 134.8, 134.9, 136.8, 137.7, 144.8 ppm; HR-MS (ESI): $C_{72}H_{73}N_2O_6P_4^+$ ([**2**-H·$2PF_6$]$^+$) calcd *m/z* 1413.4227; found *m/z* 1413.4228.

2·$2PF_6$: Triethylamine (20 μL, 0.143 mmol) was added to a solution of **2**-H_2·$4PF_6$ (83 mg, 49 μmol) in MeCN. The resulting mixture was stirred at room temperature for 10 min and recrystallized through vapor diffusion with MeCN/isopropyl ether to give colorless crystals (66 mg, 96%). M.p.: >238 °C (dec.); ^{1}H NMR (400 MHz, CD_3CN): δ = 3.26–3.44 (m, 16 H), 4.09 (s, 8 H), 4.56 (d, *J* = 15.2 Hz, 4 H), 6.45 (s, 8 H), 7.09 (d, *J* = 8 Hz, 2 H), 7.59–8.05 (m, 34 H) ppm; ^{13}C NMR (100 MHz, CD_3CN): δ = 28.3 (*J*(P,C) = 48.6 Hz), 69.1, 71.0, 73.0, 117.7, 118.6, 123.7, 128.3, 131.1, 131.3, 134.9 135.0, 136.3, 137.7, 150.2 ppm; HR-MS (ESI): $C_{72}H_{72}N_2O_6P_2^{2+}$ ([**2**]$^{2+}$) calcd *m/z* 561.2427; found *m/z* 561.2421

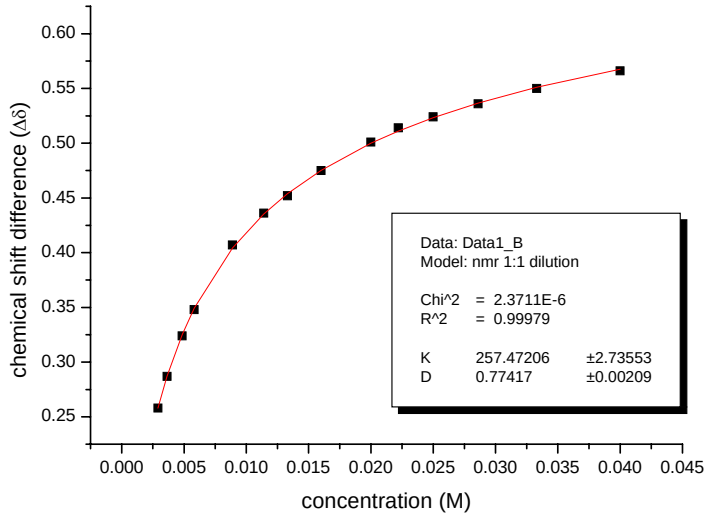
The Complexation of BPX26C6 and BP-H_2·2PF_6 in CD_3CN Dilution Isotherm



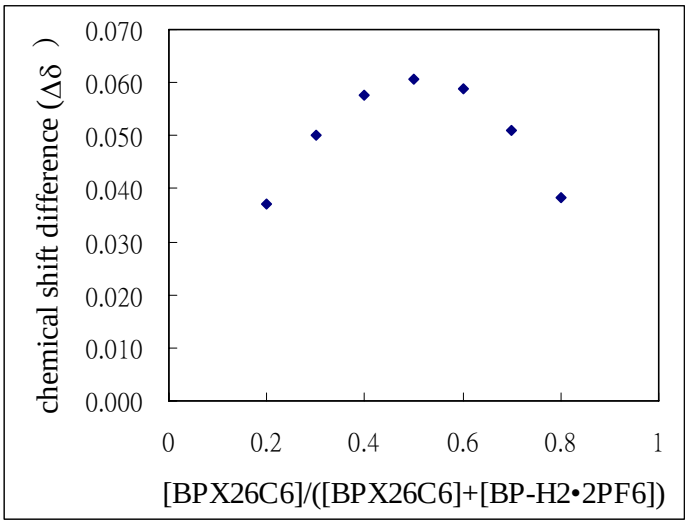
The Complexation of BPX26C6 and BP-H_2·2PF_6 in CD_3NO_2 Dilution Isotherm



The Complexation of BPX26C6 and BP-H_2·2PF_6 in $CD_3CN/CDCl_3$ (1:1)
Dilution Isotherm



The Complexation of BPX26C6 and BP-H_2·2PF_6 in CD_3CN
Job Plot



([BPX26C6]+[BP-H_2·2PF_6]) = 5.0 mM

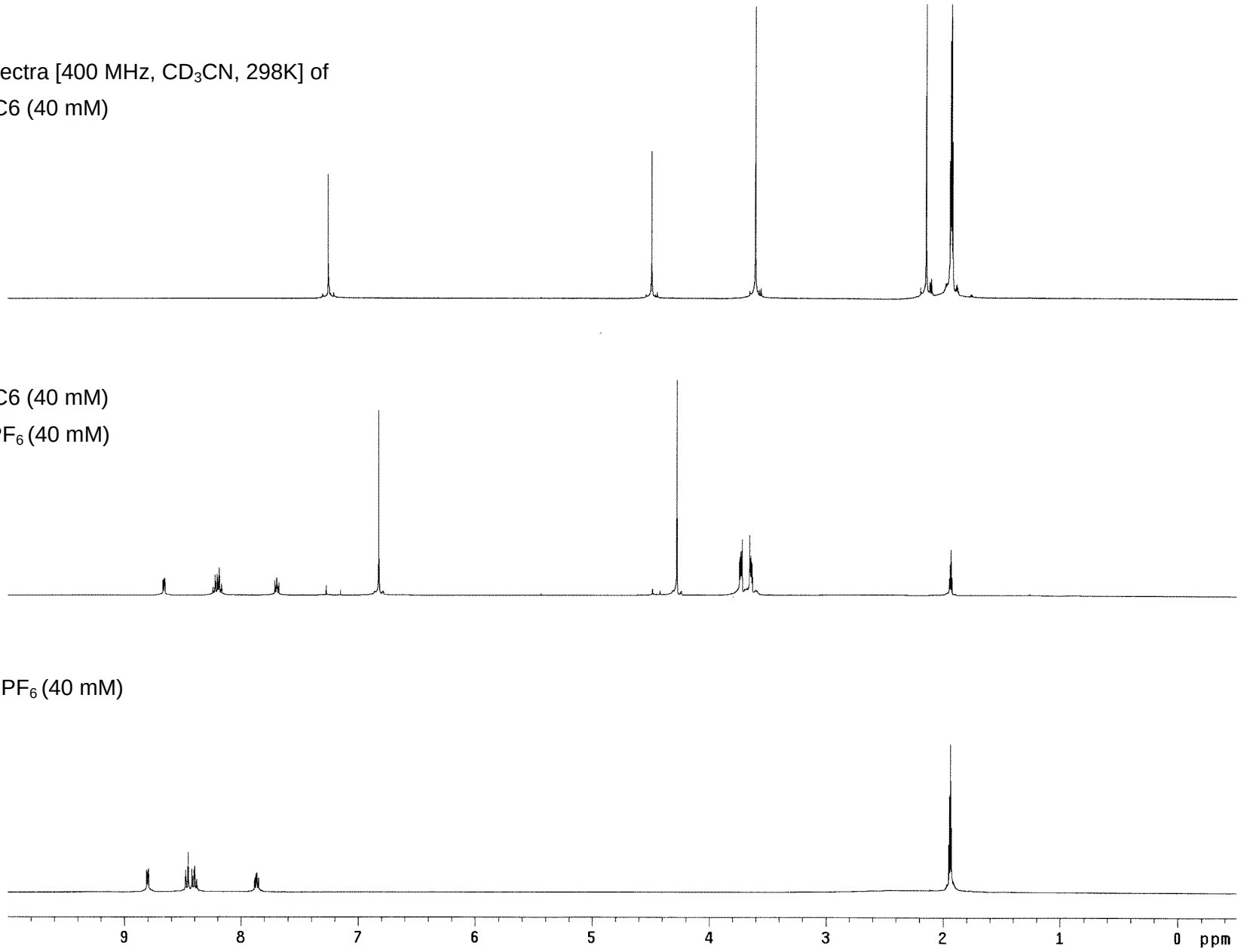
Using the signal of free BPX26C6 at δ 7.27 as the reference

^{1}H NMR spectra [400 MHz, CD_3CN, 298K] of

(a) BPX26C6 (40 mM)

(b) BPX26C6 (40 mM)
+ BP-H_2·2PF_6 (40 mM)

(c) BP-H_2·2PF_6 (40 mM)

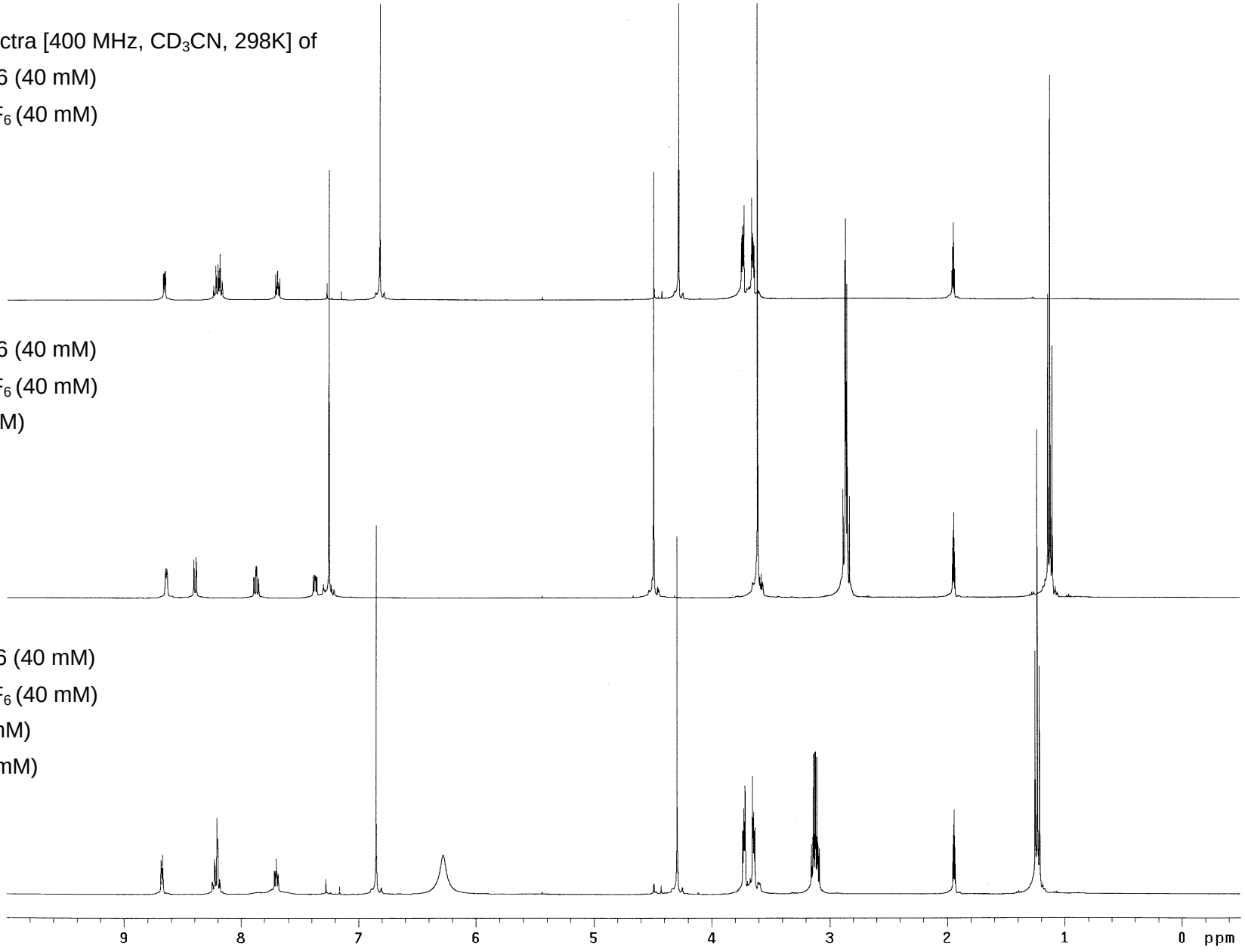


^{1}H NMR spectra [400 MHz, CD_3CN, 298K] of

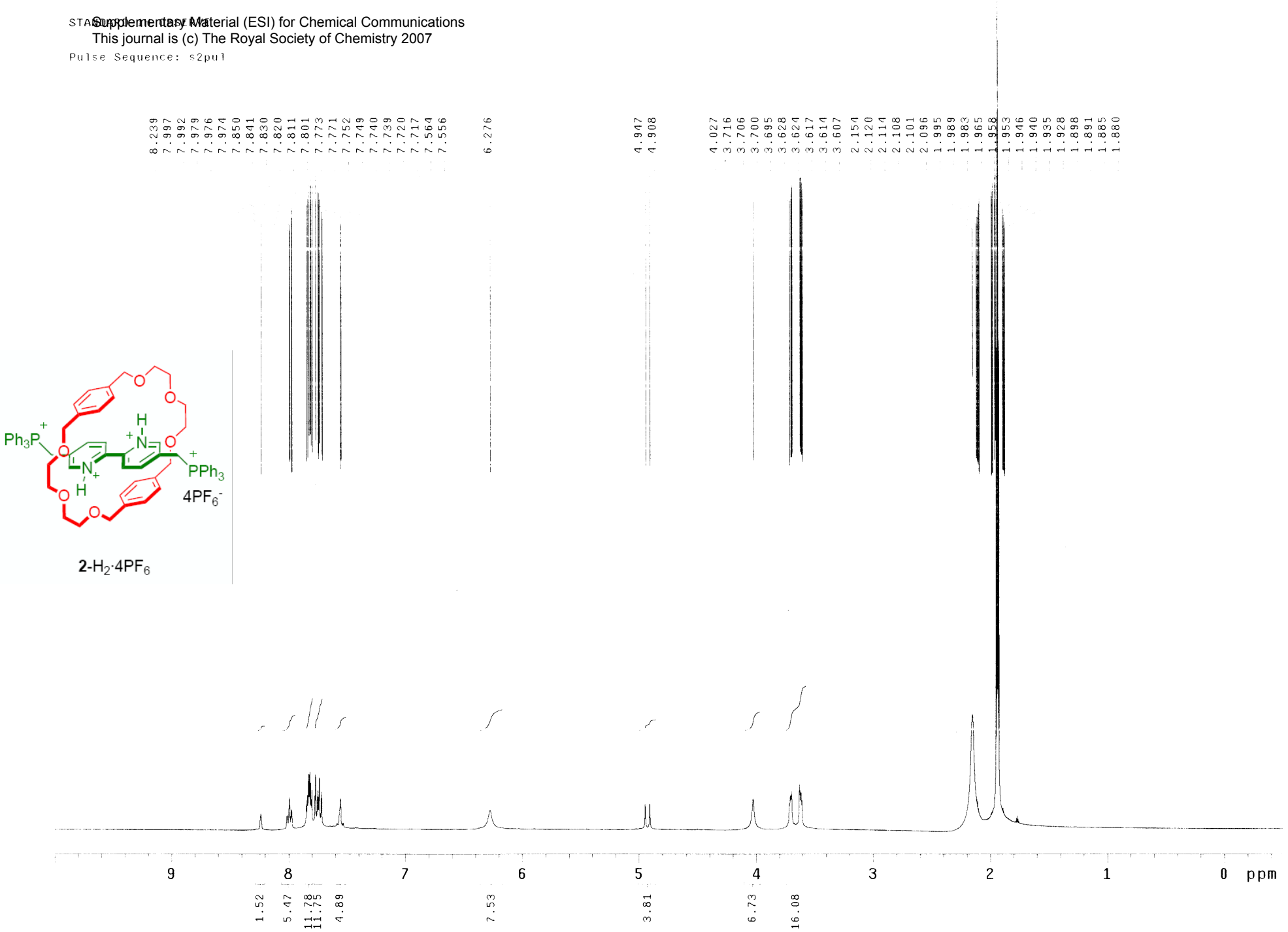
(a) BPX26C6 (40 mM)
+ BP-H_2·2PF_6 (40 mM)

(b) BPX26C6 (40 mM)
+ BP-H_2·2PF_6 (40 mM)
+ Et_3N (80mM)

(c) BPX26C6 (40 mM)
+ BP-H_2·2PF_6 (40 mM)
+ Et_3N (80 mM)
+ TFA (160 mM)



Pulse Sequence: s2pul

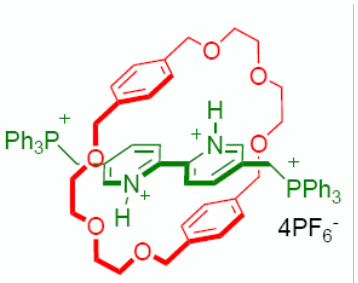


2-H_2·4PF_6

CNG960112
sprH2 C13
CD3CN

Pulse Sequence: s2pul

144.846
137.656
136.766
134.934
134.835
131.567
131.445
128.527
124.992
118.151
117.718
116.851
73.228
71.237
70.340
28.237
27.736
2.006
1.800
1.595
1.390
1.185
0.980
0.774

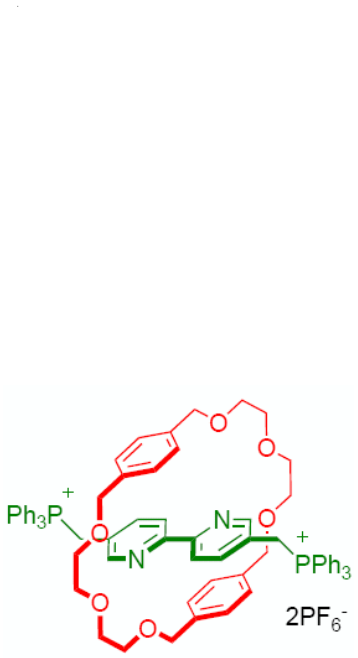


2-H_2·4PF_6

160 140 120 100 80 60 40 20 0 ppm

CNG951227
spr crystal
CD3CN

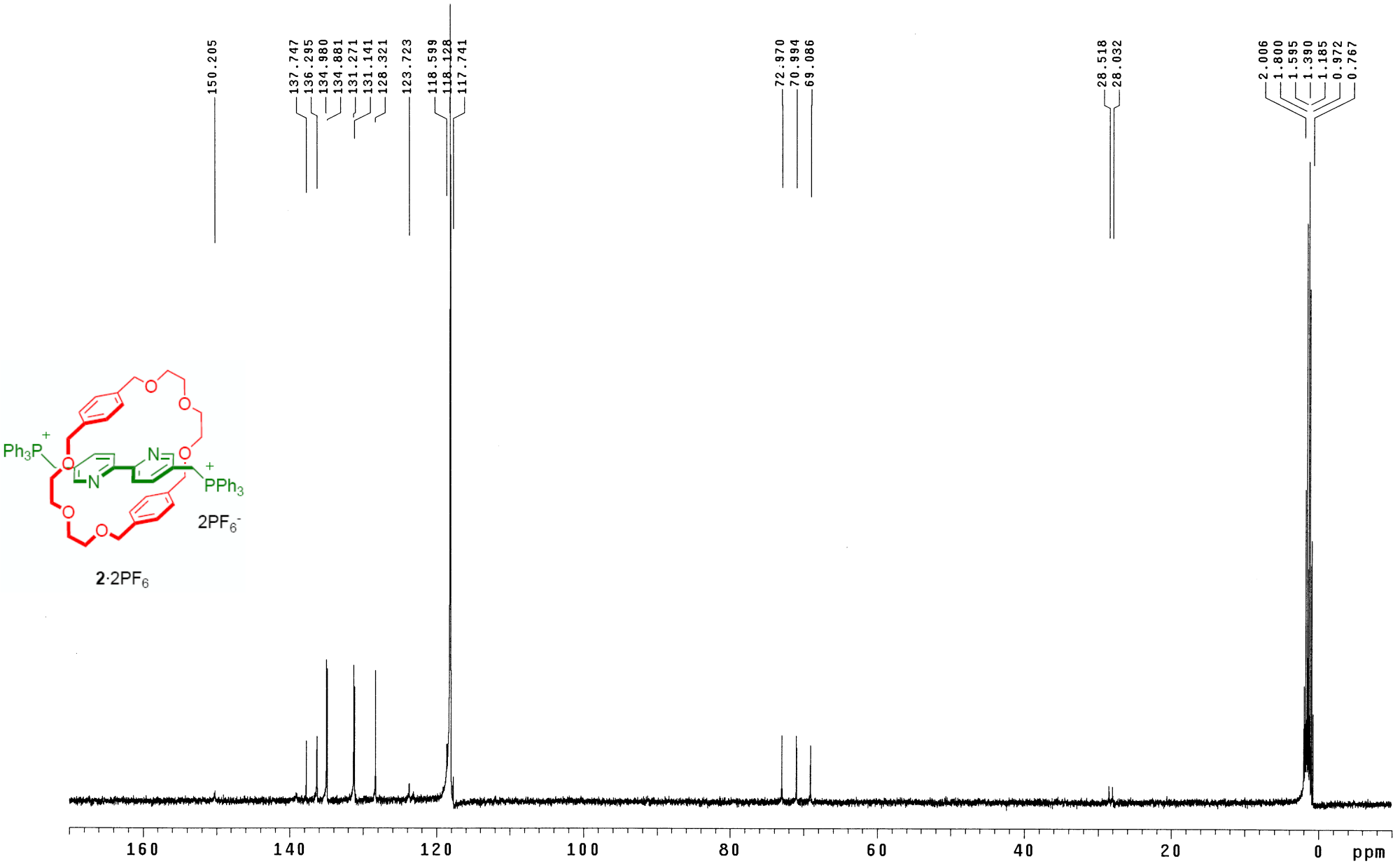
Pulse Sequence: s2pul



2·2PF$_6$

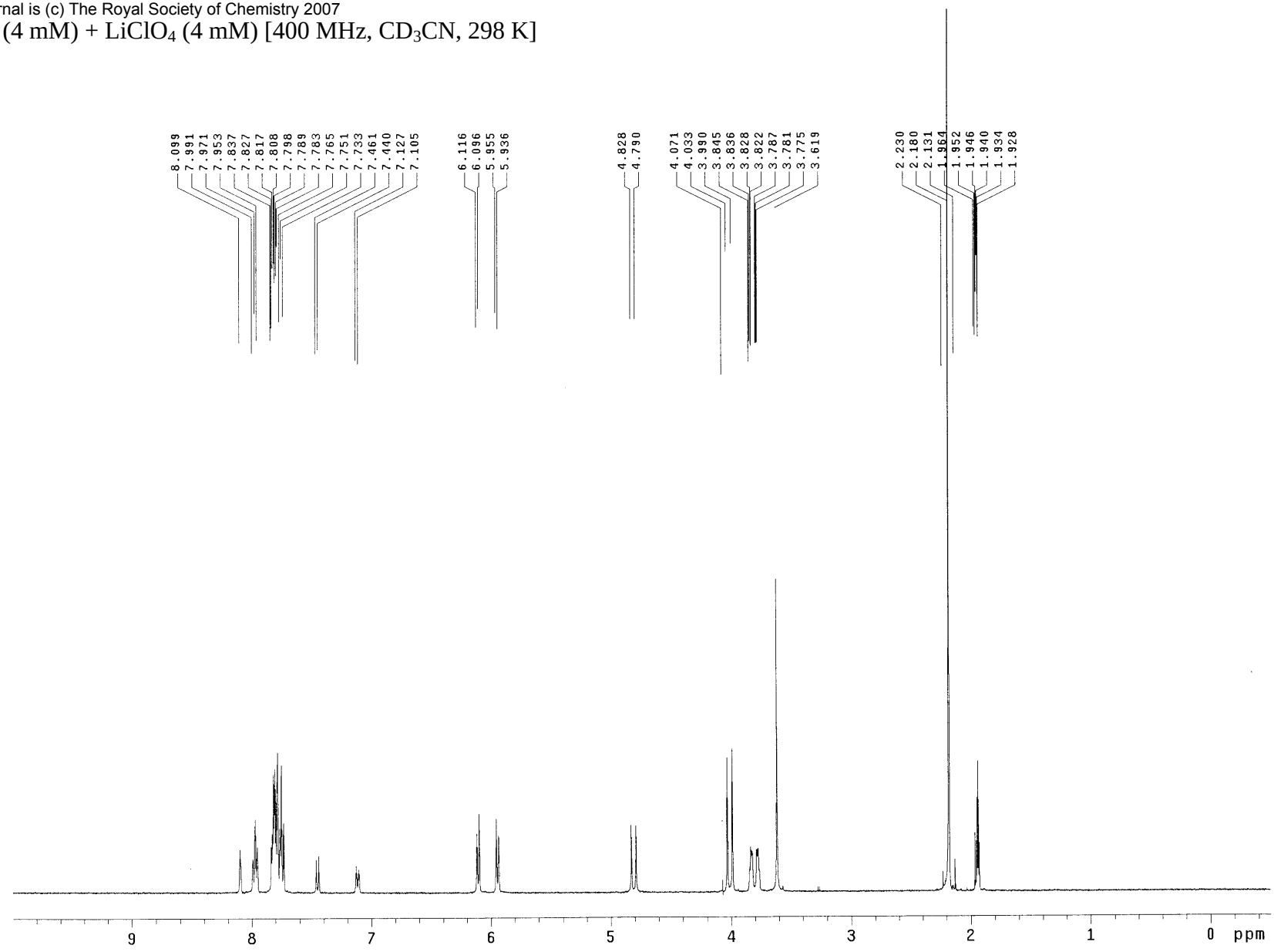
24 Time

Pulse Sequence: s2pul

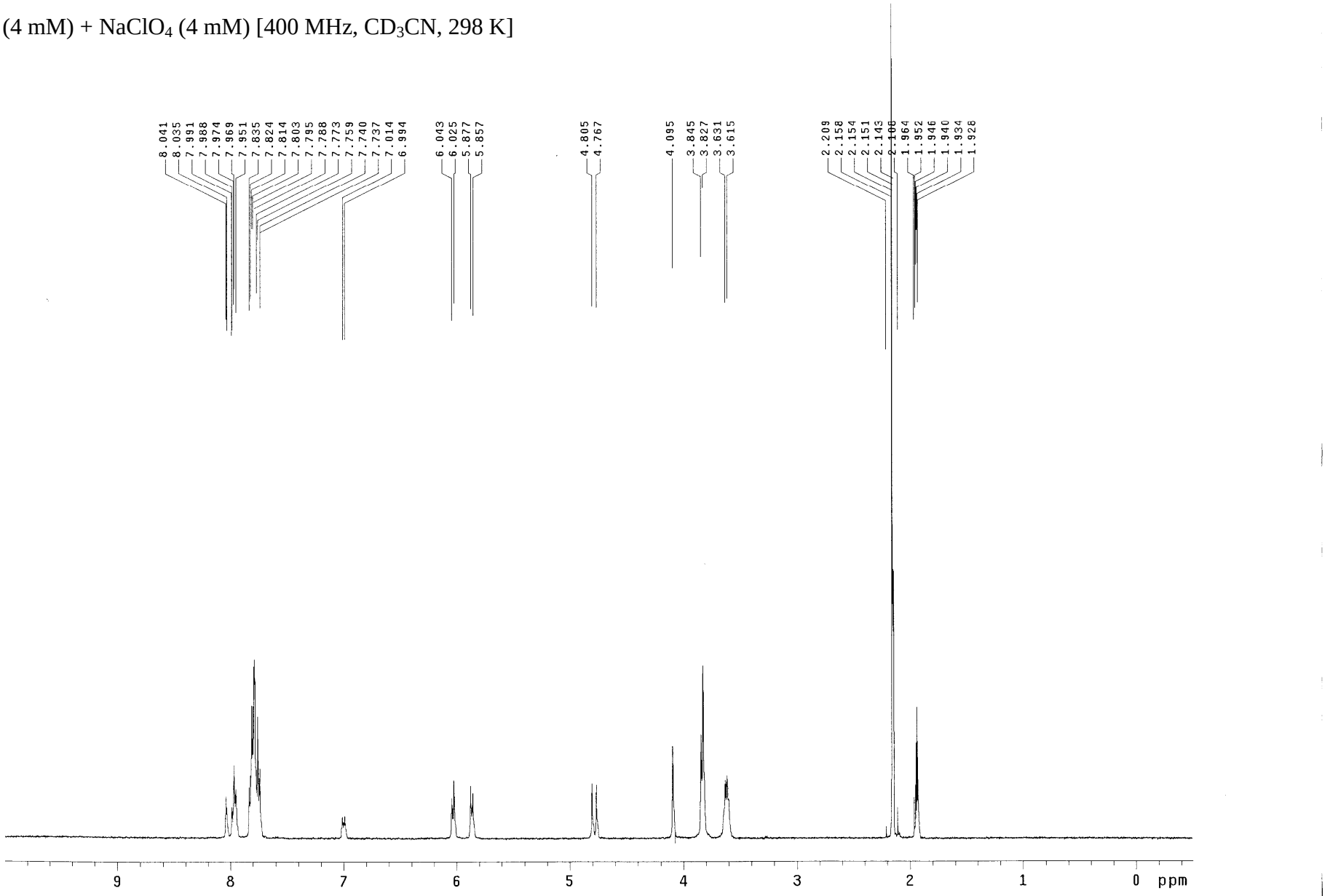


2·2PF$_6$

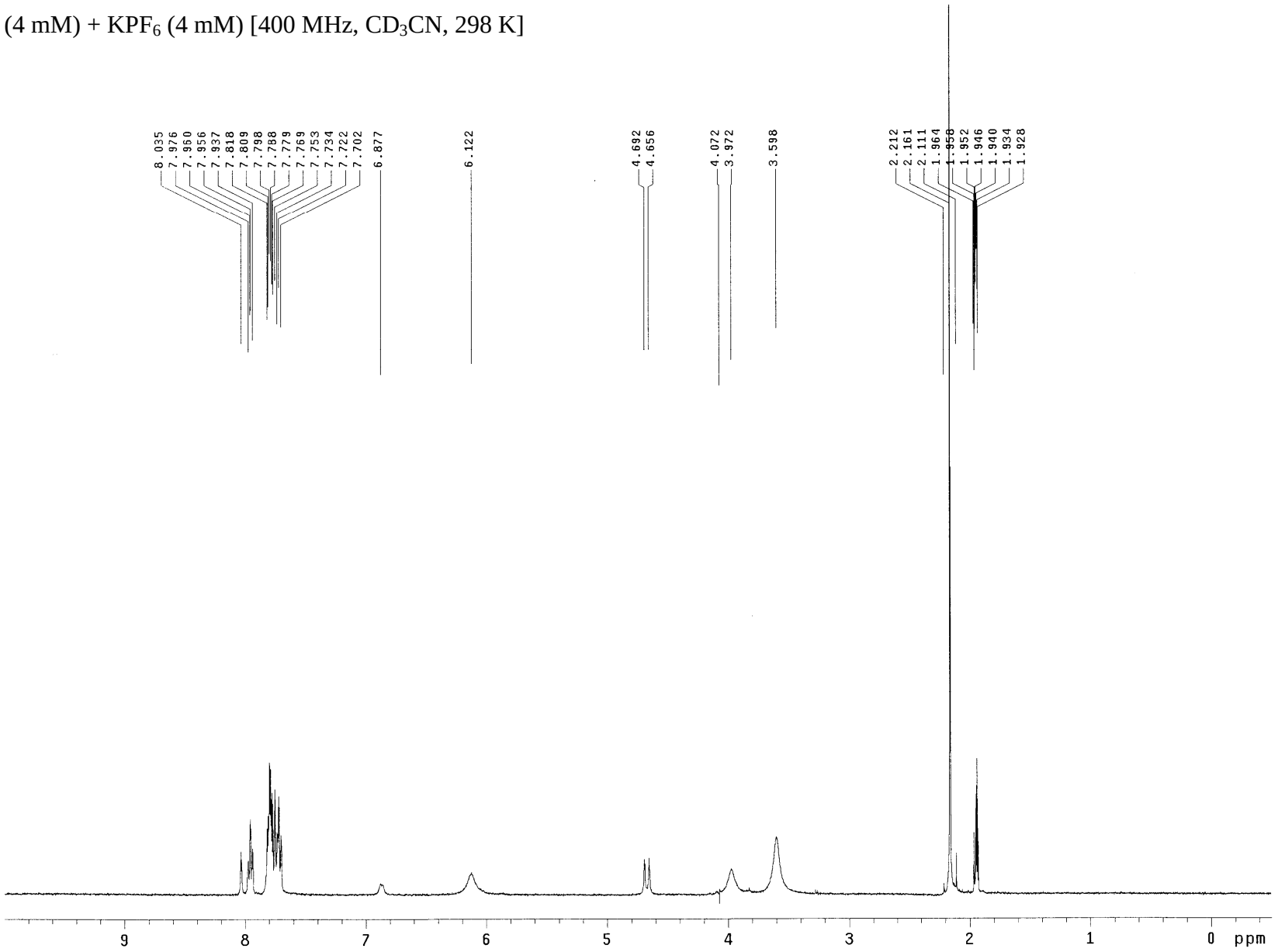
$2{\cdot}2PF_6$ (4 mM) + $LiClO_4$ (4 mM) [400 MHz, CD_3CN, 298 K]



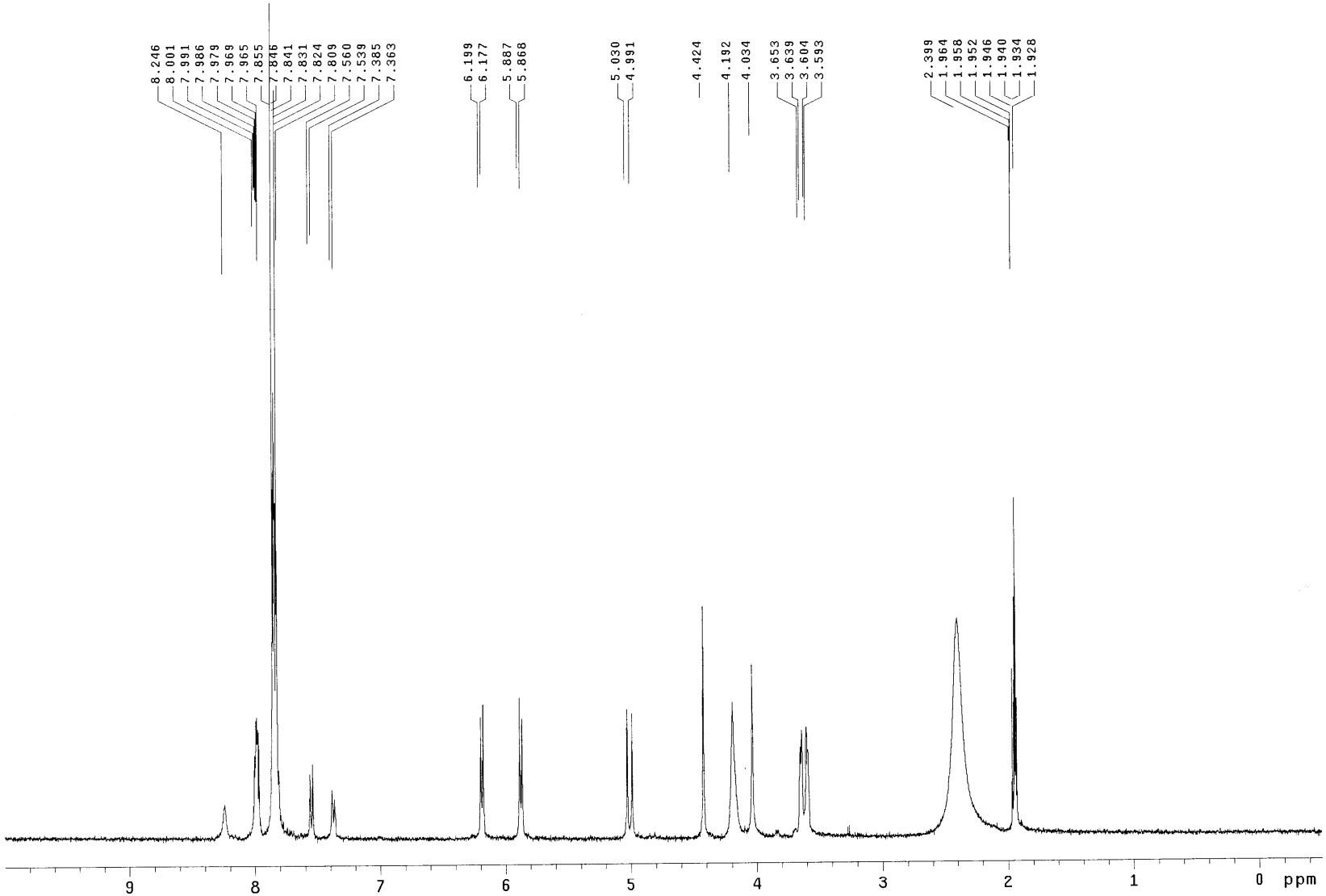
2·2PF_6 (4 mM) + $NaClO_4$ (4 mM) [400 MHz, CD_3CN, 298 K]



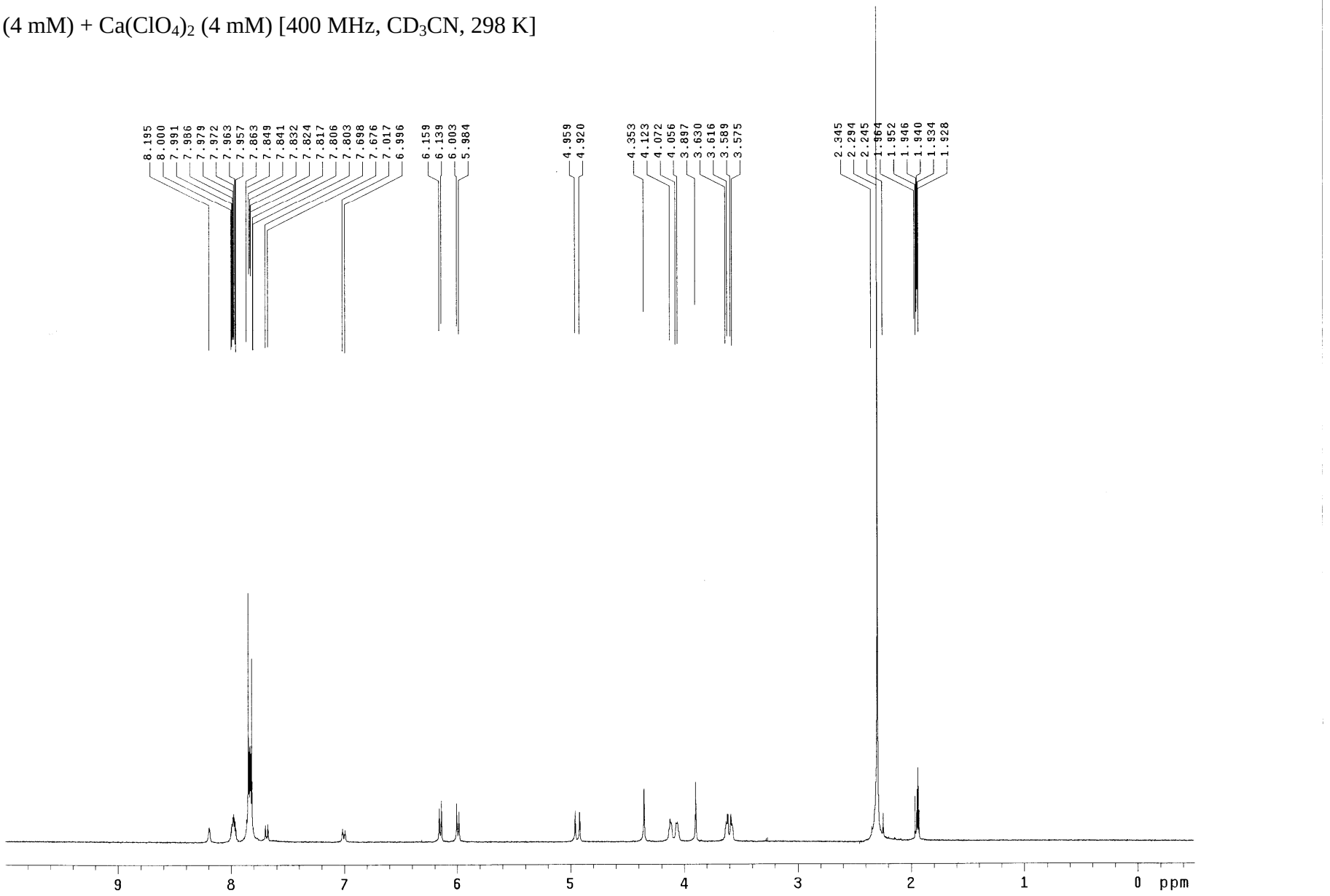
$2{\cdot}2PF_6$ (4 mM) + KPF_6 (4 mM) [400 MHz, CD_3CN, 298 K]



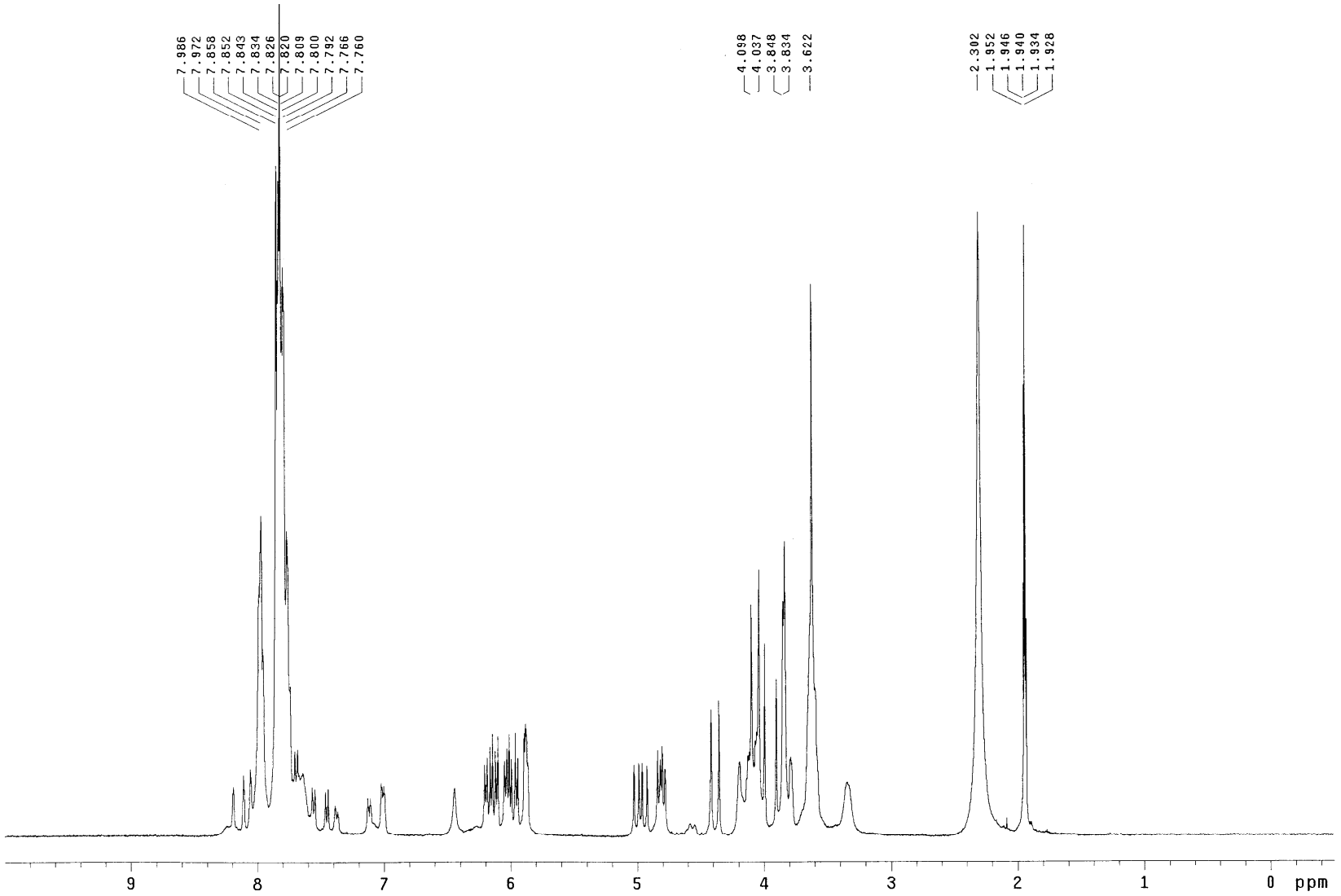
2·2PF_6 (4 mM) + $Mg(ClO_4)_2$ (4 mM) [400 MHz, CD_3CN, 298 K]



2·2PF_6 (4 mM) + $Ca(ClO_4)_2$ (4 mM) [400 MHz, CD_3CN, 298 K]

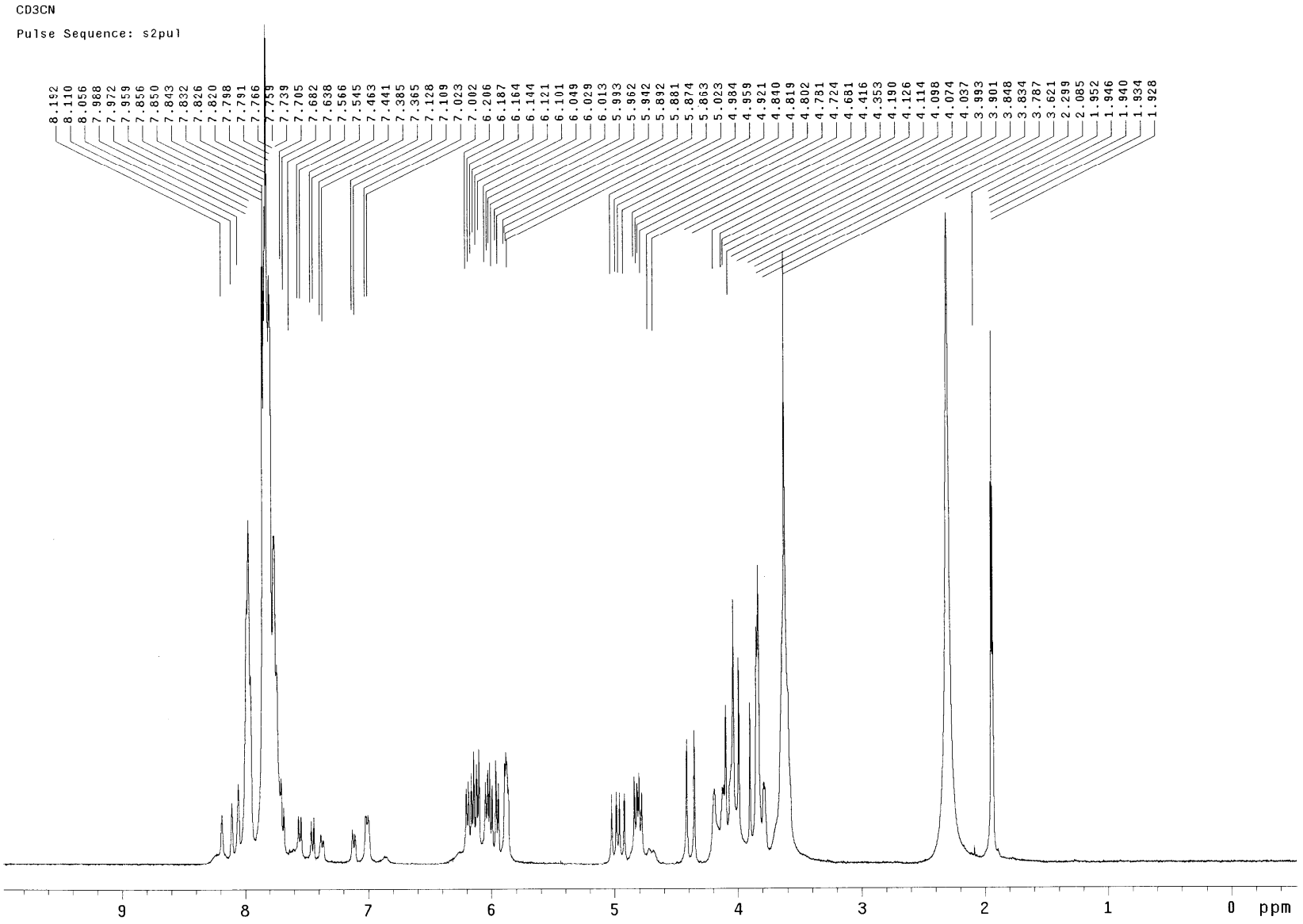


$2{\cdot}2PF_6$ (20 mM) + $LiClO_4$ (4 mM) + $NaClO_4$ (4 mM) + $Mg(ClO_4)_2$ (4 mM) + $Ca(ClO_4)_2$ (4 mM)
[400 MHz, CD_3CN, 298 K]



2·2PF_6 (20 mM) + $LiClO_4$ (4 mM) + $NaClO_4$ (4 mM) + KPF_6 (4 mM) + $Mg(ClO_4)_2$ (4 mM) + $Ca(ClO_4)_2$ (4 mM)

[400 MHz, CD_3CN, 298 K]



Partial ^{1}H NMR spectra [400 MHz, CD_3CN, 298K] of