Supplementary Material (ESI) for Chemical Communications

Supporting Information

Oxidation of poly(enetetramine)s:

A new strategy for the synthesis of conjugated polyelectrolytes

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Synthetic and Analytical Details

Spectra

Chromatograms

Materials and Methods. Anion exchange for the 1,1′,3,3′-tetra-*n*-butyl diiodide salts[1] of benzobis(imidazolium), 2,2′- and 5,5′-bibenzimidazolium was effected *via* treatment with Me_2SO_4 using methodology previously established for **M1**.[2] Poly(1,1′,3,3′-tetra-*n*-butyl-2,2′-benzobisimidazolylidene) (**1**) and poly(1,1′,3,3′-tetra-*n*-butyl-5,5′-bibenzimidazoylidene) (**2**) were prepared as previously described.[1] All reactions were performed under an inert atmosphere of nitrogen or argon using standard Schlenk or glovebox techniques. Solvents were dried and purified by distillation from CaH_2 (CH_2Cl_2) or sodium (THF). All other reagents were purchased from commercial sources and used as received. NMR spectra were recorded at 22 °C on a 300 MHz Varian Unity, a 400 MHz or a 600 MHz Varian Mercury spectrometer. Chemical shifts for ^1H and ^{13}C NMR spectra are expressed in ppm relative to residual solvent (d_5-DMSO in DMSO-d_6, 2.49 ppm and 39.5 ppm for ^1H and ^{13}C, respectively). ^{13}C NMR spectra were routinely run with broadband decoupling. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 or a VG analytical ZAB2-E instrument and are reported as m/z. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a Mettler-Toledo TGA/SDTA851^e and DSC823^e, respectively, under an atmosphere of nitrogen at a temperature scan rate of 10 °C min^{-1}.

Molecular Weight Determinations. Intrinsic viscosities [η] were measured at 35 °C in a Cannon-Manning viscometer *via* serial dilutions of the polymeric analyte in DMF solution containing 0.1 M LiBr. The Mark-Houwink parameters for polybenzimidazole ($K = 1.35 \times 10^{-2}$, $\alpha = 0.733$)[3] were used to estimate the M_w values for polymers **P1'**, **P1**, **P2'**, and **P2**. Vapor pressure osmometry (VPO) was performed on a Knauer K-7000 using the EuroOsmo 7000 package. Each polymer was measured at multiple concentrations in DMF at 90 °C and compared to a polystyrene standard, enabling estimation of M_w values. Mass spectra were acquired on a

Varian 902-MS MALDI-FT Mass Spectrometer equipped with a 12 T magnet and a pulsed Nd:YAG laser (New Wave Research Orion). Polymer samples were deposited between layers of 2,5-dihydroxybenzoic acid using standard spotting techniques. Values for M_w were obtained using established methodology.[4] Gel permeation chromatography (GPC) was performed on a Viscotek system equipped with a VE 1122 pump, a VE 7510 degasser, two fluorinated polystyrene columns (I-MBHW-3078 and I-MBLMW-3078) thermostatted to 30 °C (using a ELDEX CH 150 column heater) and arranged in series, a Viscotek 270 Dual Detector (light scattering detector and differential viscometer), and a VE 3580 refractive index detector using 10 mM lithium formate in formic acid as the eluent.

General Spectroscopic Considerations. UV-visible absorption and fluorescence emission spectra were recorded on a Perkin-Elmer Lambda 35 spectrophotometer and a PTI QuantaMaster 4L fluorimeter, respectively. All measurements were made with matched 6Q Spectrosil quartz cuvettes (Starna) with 1 cm path lengths and 3.0 mL sample solution volumes, and were performed in aqueous solutions, with the exception of **P1'** and **P2'** (DMF). Polymers **P1** and **P2** were soluble in water, up to mM concentrations. Beer's law measurements were performed at 25 °C using 10, 20, 30 and 40 µM sample concentrations. Emission spectra were acquired using 1.0 µM solutions of fluorophore. Quantum yields were determined relative to 1.0 µM quinine sulfate in 0.1 *N* H_2SO_4 ($\Phi = 0.546$, for **M1**, **M2** and **L**)[5] or 0.10 µM fluorescein in 0.1 *N* NaOH ($\Phi = 0.95$, for **P1** and **P2**).[6]

[1,1′,3,3′-Tetra-*n*-butyl-2,2′-bibenzimidazolium]$(MeSO_4)_2$ (L). Addition of I_2 (100 mg, 0.39 mmol) to 1,1′,3,3′-tetra-*n*-butyl-2,2′-bibenzimidazolylidene (110 mg, 0.16 mmol) in 5 mL THF resulted in an immediate color change from bright yellow to dark orange. After stirring the reaction mixture for 2 h at ambient temperature, the solvent was removed under reduced pressure. The resulting red solid was then washed with Et_2O and dried under vacuum to afford the bis(iodide) salt of **L**. After suspending this crude material in 5 mL of CH_2Cl_2, Me_2SO_4 (30 µL, 0.39 mmol) was added and the resulting slurry was allowed to stir for 24 h at ambient temperature. Removal of solvent under reduced pressure afforded 70 mg (63% yield) of the desired compound as a yellow waxy solid. ^{1}H NMR (400 MHz): δ 8.37 (m, 4H, 4,4′,7,7′-*H*), 7.96 (m, 4H, 5,5′,6,6′-*H*), 4.53 (t, J = 8 Hz, 8H, $NCH_2(CH_2)_2CH_3$), 3.36 (s, 6H, CH_3SO_4), 1.80 (m, 8H, $NCH_2CH_2CH_2CH_3$), 1.35 (m, 8H, $N(CH_2)_2CH_2CH_3$), 0.86 (m, 12H, $N(CH_2)_3CH_3$) ppm. ^{13}C NMR (100 MHz): δ 133.3, 128.8, 115.5, 97.3, 52.8, 47.3, 31.2, 19.1, 13.6 ppm. HRMS for $[\mathbf{L} - 2MeSO_4]^{2+}$: Calcd, 230.1778; found, 230.1782. UV/vis: λ_{max} = 289 nm, $\varepsilon = 1.15 \times 10^4$ M^{-1} cm^{-1}. Fluorescence: λ_{em} = 353 nm, Φ = 0.089.

General procedure for the oxidation of poly(enetetramine)s. Addition of I_2 to a solution of poly(enetetramine) in 5 mL THF resulted an immediate color change from dark red to dark orange. After allowing the reaction to stir for 2 h at ambient temperature, the solvent was removed under reduced pressure. The resulting solid was then washed with Et_2O and dried under vacuum to afford the desired poly(benzimidazolium) iodide salt as a powder.

Poly{[1,1′,3,3′-tetra-*n*-butyl-2,2′-dehydrobenzobis(imidazolium)](I)$_2$} (P1'). Following the general procedure, 253 mg of I_2 (1.0 mmol) and 177 mg of **1** (0.45 mmol) afforded 171 mg (60% yield) of **P1'** as a brown-orange powder. ^{1}H NMR (400 MHz): δ 10.44–10.26 (m, 0.125H, Ar*H*), 9.74–9.56 (m, 0.25H, Ar*H*), 9.56–9.40 (m, 0.25H, Ar*H*), 9.40–9.26 (m, 0.125H, Ar*H*), 9.26–9.02 (m, 0.5H, Ar*H*), 8.98–8.82 (m, 0.125H, Ar*H*), 8.28–8.02 (m, 0.5H, Ar*H*), 7.92 (br, 0.125H, Ar*H*), 5.62–5.50 (m, 0.125H, NCH_2), 5.24–4.38 (m, 6H, NCH_2), 4.30–4.20 (m, 0.125H, NCH_2), 4.20–4.02 (m, 1H, NCH_2), 4.00–3.90 (m, 0.25H, NCH_2), 3.88–3.68 (m, 0.25H, NCH_2), 3.44–3.22 (m, 0.25H, NCH_2), 2.16–1.64 (m, 8H, NCH_2CH_2), 1.58–1.24 (m, 8H, $N(CH_2)_2CH_2$), 1.08–0.80 (m, 12H, N(CH_2)$_3$C*H*$_3$) ppm. T_g = 48 °C. T_d = 166 °C (75% mass loss). Intrinsic viscosity [η] = 9.6 mL^{-1} g. M_w (technique) = 7.8 kDa (η), 2.69 kDa (MALDI), 2.2 kDa (VPO). UV/vis: λ_{max} = 360 nm, ε = 2.40 × 10^4 M^{-1} cm^{-1}. Fluorescence: none observed.

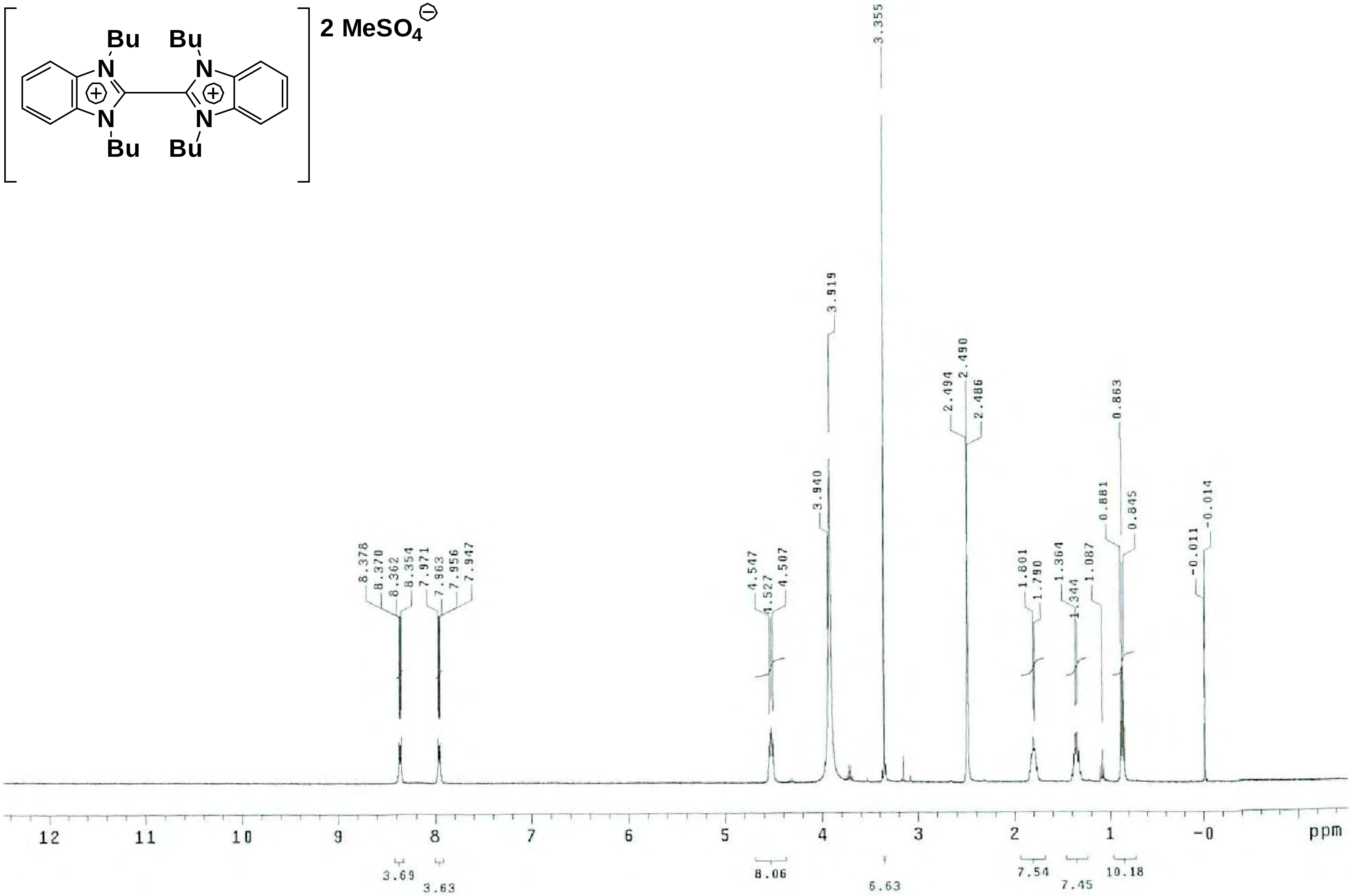
Poly{[1,1′,3,3′-tetra-*n*-butyl-2,2′-dehydro-5,5’-bibenzimidazolium](I)$_2$} (P2'): Following the general procedure, 253 mg of I_2 (1.0 mmol) and 250 mg of **2** (0.50 mmol) afforded 231 mg (64% yield) of **P2'** as a dark red solid. ^{1}H NMR (300 MHz): δ 8.92–8.78 (1H, Ar*H*), 8.72–8.52 (m, 2.5H, Ar*H*), 8.52–8.10 (m, 2H, Ar*H*), 7.96–7.76 (m, 0.5H, Ar*H*), 4.68 (br, 7.5H, NC*H*$_2$), 4.48–4.30 (m, 0.5H, NC*H*$_2$), 1.91 (br, 8H, NCH$_2$C*H*$_2$), 1.46 (br, 7H, N(CH_2)$_2$C*H*$_2$), 1.29 (br, 1H, N(CH_2)$_2$C*H*$_2$), 1.06–0.82 (m, 12H, N(CH_2)$_3$C*H*$_3$) ppm. T_g = 103 °C. T_d = 202 °C (64% mass loss). Intrinsic viscosity [η] = 5.8 mL^{-1} g. M_w (technique) = 3.9 kDa (η), 4.25 kDa (MALDI), 3.6 kDa (VPO). UV/vis: λ_{max} = 351 nm, ε = 2.04 × 10^4 M^{-1} cm^{-1}. Fluorescence: none observed.

General procedure for anion exchange. Dimethyl sulfate was added to solid poly(benzimidazolium) iodide and the resulting slurry was heated to 100 °C for 12 h. The reaction was then quenched through the addition to excess Et_2O to induce precipitation of crude poly(benzimidazolium) methylsulfate as a powder.

Poly{[1,1′,3,3′-tetra-*n*-butyl-2,2′-dehydrobenzobis(imidazolium)](MeSO$_4$)$_2$} (P1): Following the general procedure, 5 mL of Me_2SO_4 (53 mmol) and 171 mg of **P1'** (0.27 mmol) afforded 148 mg of **P1** (89% yield) as a golden solid after trituration with Et_2O followed by drying under reduced pressure. ^{1}H NMR (400 MHz): δ 9.46–8.89 (s, 5H, Ar*H*), 8.19 (s, 1H, Ar*H*), 8.13 (s, 0.5H, Ar*H*), 8.10 (s, 1.5H, Ar*H*), 4.90–4.40 (10H, NC*H*$_2$), 3.36 (5H, C*H*$_3$SO$_4$), 2.10–1.70 (12H, NCH$_2$C*H*$_2$), 1.55–1.25 (12H, N(CH_2)$_2$C*H*$_2$), 1.00–0.85 (12H, N(CH_2)$_3$C*H*$_3$) ppm. ^{13}C NMR (100 MHz): δ 153.9, 131.6, 129.0, 125.4, 92.6, 64.9, 52.8, 47.2, 31.0, 29.5, 19.3, 15.2, 13.6 ppm. T_g = 73 °C. T_d = 259 °C (70% mass loss). Intrinsic viscosity [η] = 9.3 mL^{-1} g.

M_w (method) = 7.4 (η), 2.40 kDa (MALDI), 2.0 kDa (VPO) kDa, 14.5 kDa (PDI = 1.7) (GPC). UV/vis: λ_{max} = 341 nm, ε = 1.23 × 10^4 M^{-1} cm^{-1}. Fluorescence: λ_{em} = 501 nm, Φ = 0.20.

Poly{[1,1′,3,3′-tetra-*n*-butyl-2,2′-dehydro-5,5′-bibenzimidazolium]($MeSO_4$)$_2$} (P2): Following the general procedure, 5 mL of Me_2SO_4 (53 mmol) and 231 mg of **P2'** (0.35 mmol) afforded 195 mg of **P2** (83% yield) as a waxy orange solid after trituration with isopropanol and hexanes followed by drying under reduced pressure. ^{1}H NMR (300 MHz): δ 9.00–8.20 (9H, Ar*H*), 4.69 (br, 8H, NC*H*$_2$), 3.29 (s, 6H, C*H*$_3$SO$_4$), 1.90 (br, 8H, NCH$_2$C*H*$_2$), 1.45 (br, 8H, N(CH$_2$)$_2$C*H*$_2$), 1.00–0.80 (m, 12H, N(CH$_2$)$_3$C*H*$_3$) ppm. ^{13}C NMR (150 MHz): δ 161.7, 139.1, 136.8, 134.3, 133.8, 133.2, 129.4, 128.7, 126.2, 116.5, 116.2, 114.2, 113.8, 112.1, 68.6, 62.0, 52.7, 49.3, 48.6, 47.6, 34.4, 34.2, 31.5, 31.3, 30.9, 30.8, 25.4, 24.7, 23.1, 22.0, 21.6, 19.3, 19.1, 13.9, 13.6, 92.6, 64.9, 52.8, 47.2, 31.0, 29.5, 19.3, 15.2, 13.6 ppm. T_g = 105 °C. T_d = 323 °C (61% mass loss). Intrinsic viscosity [η] = 5.7 mL^{-1} g. M_w (method) = 3.8 kDa (η), 2.56 kDa (MALDI), 2.3 kDa (VPO), 21.6 (PDI = 1.8) (GPC). UV/vis: λ_{max} = 336 nm, ε = 2.04 × 10^4 M^{-1} cm^{-1}. Fluorescence: λ_{em} = 473 nm, Φ = 0.18.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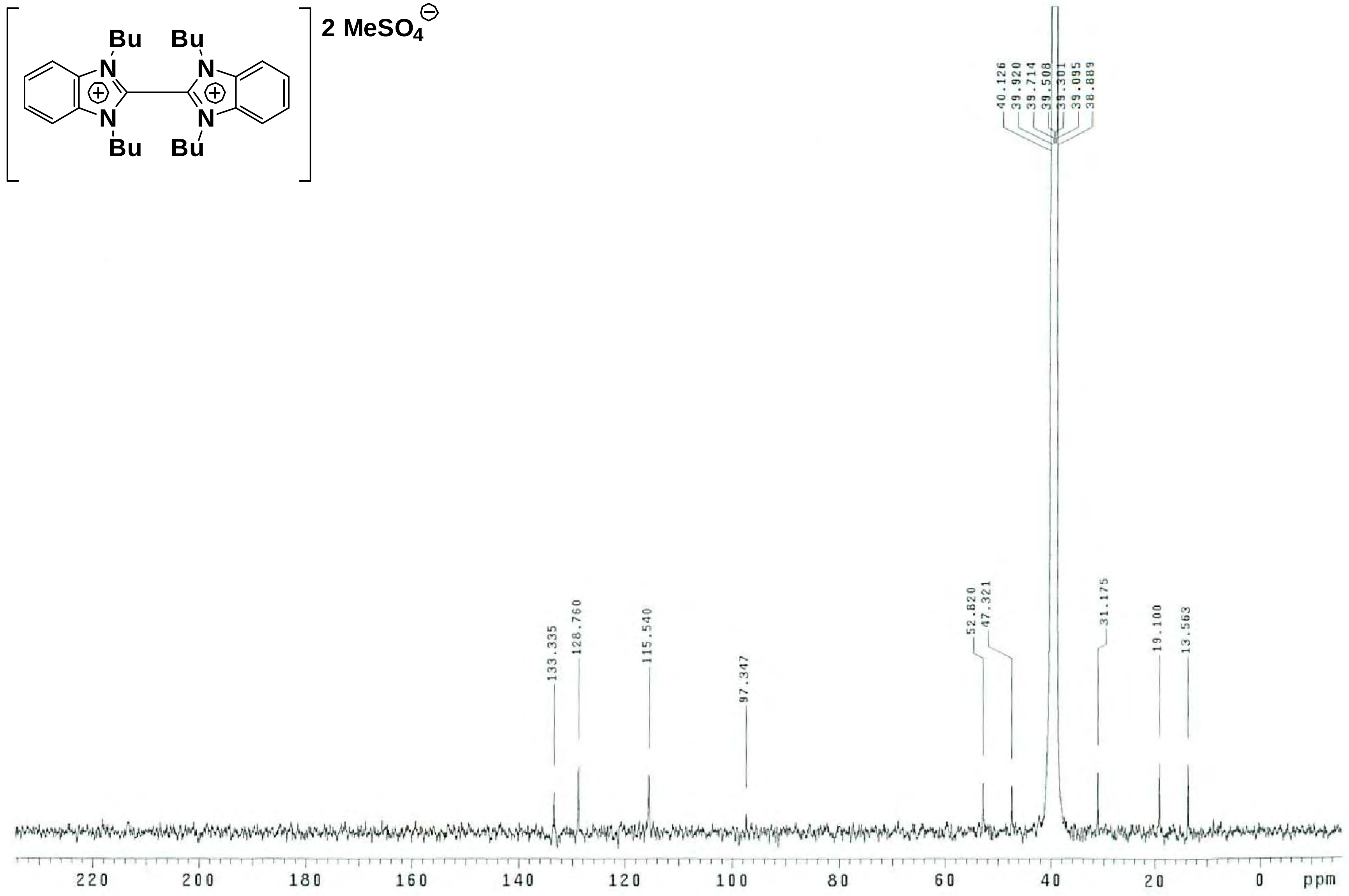
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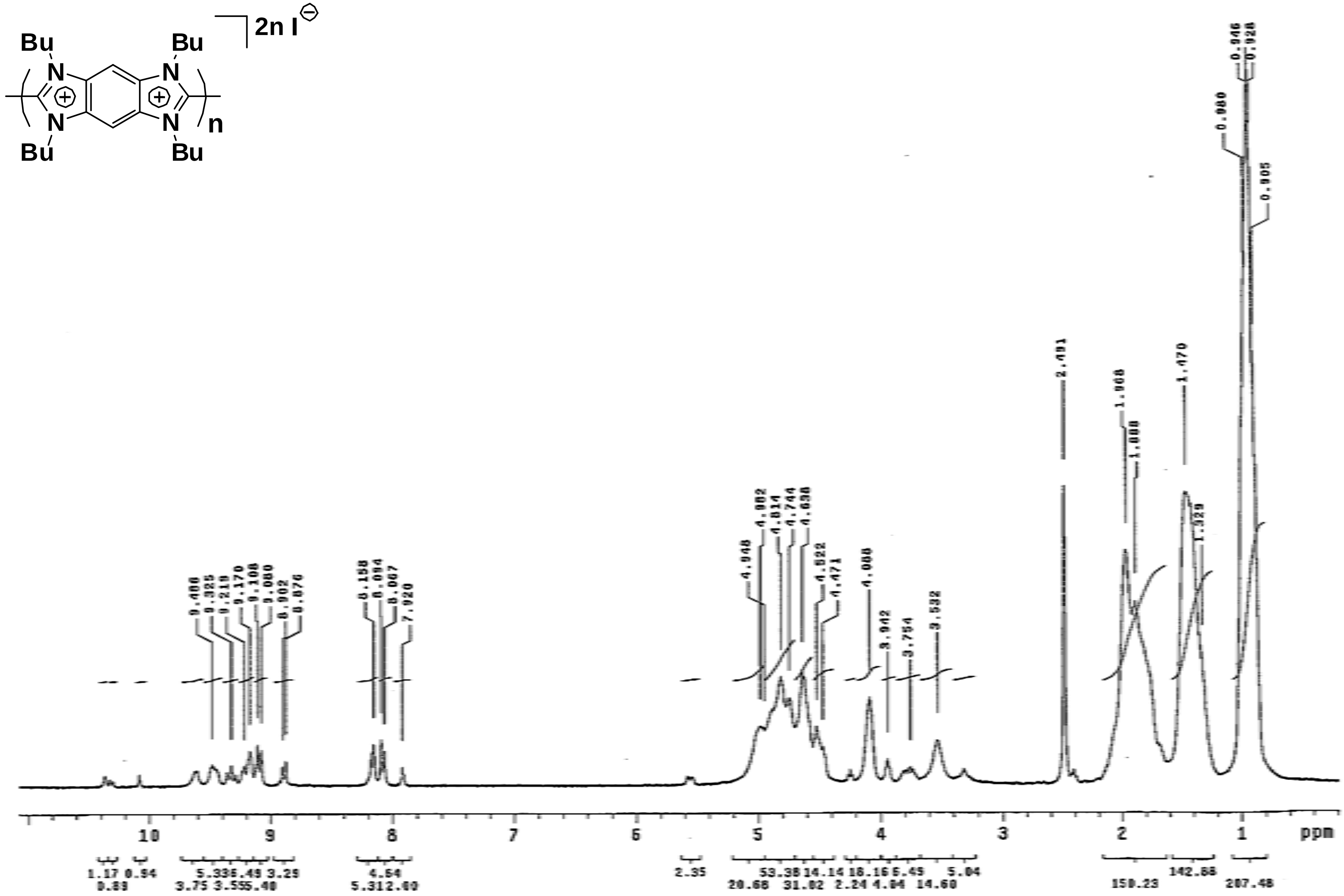
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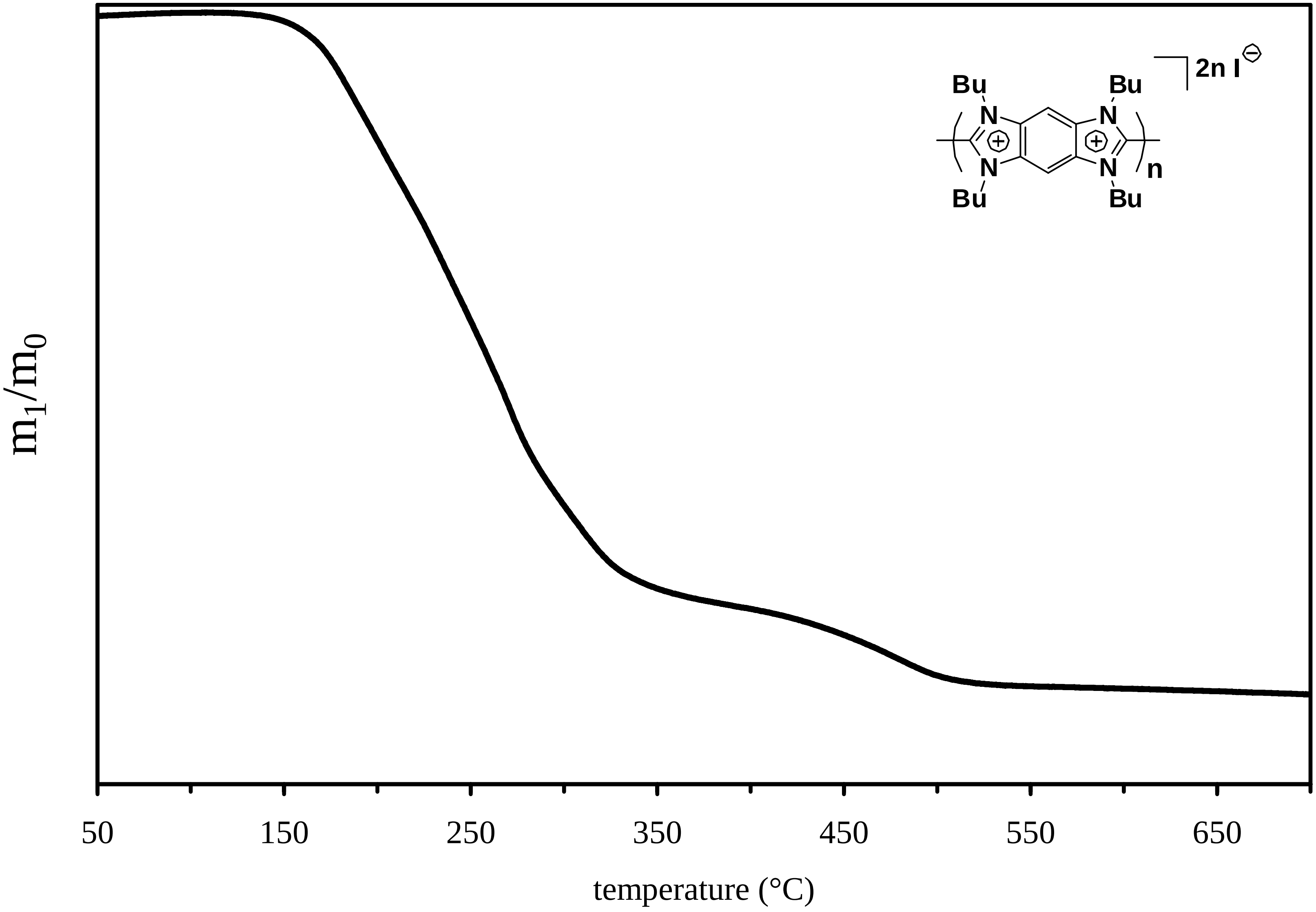
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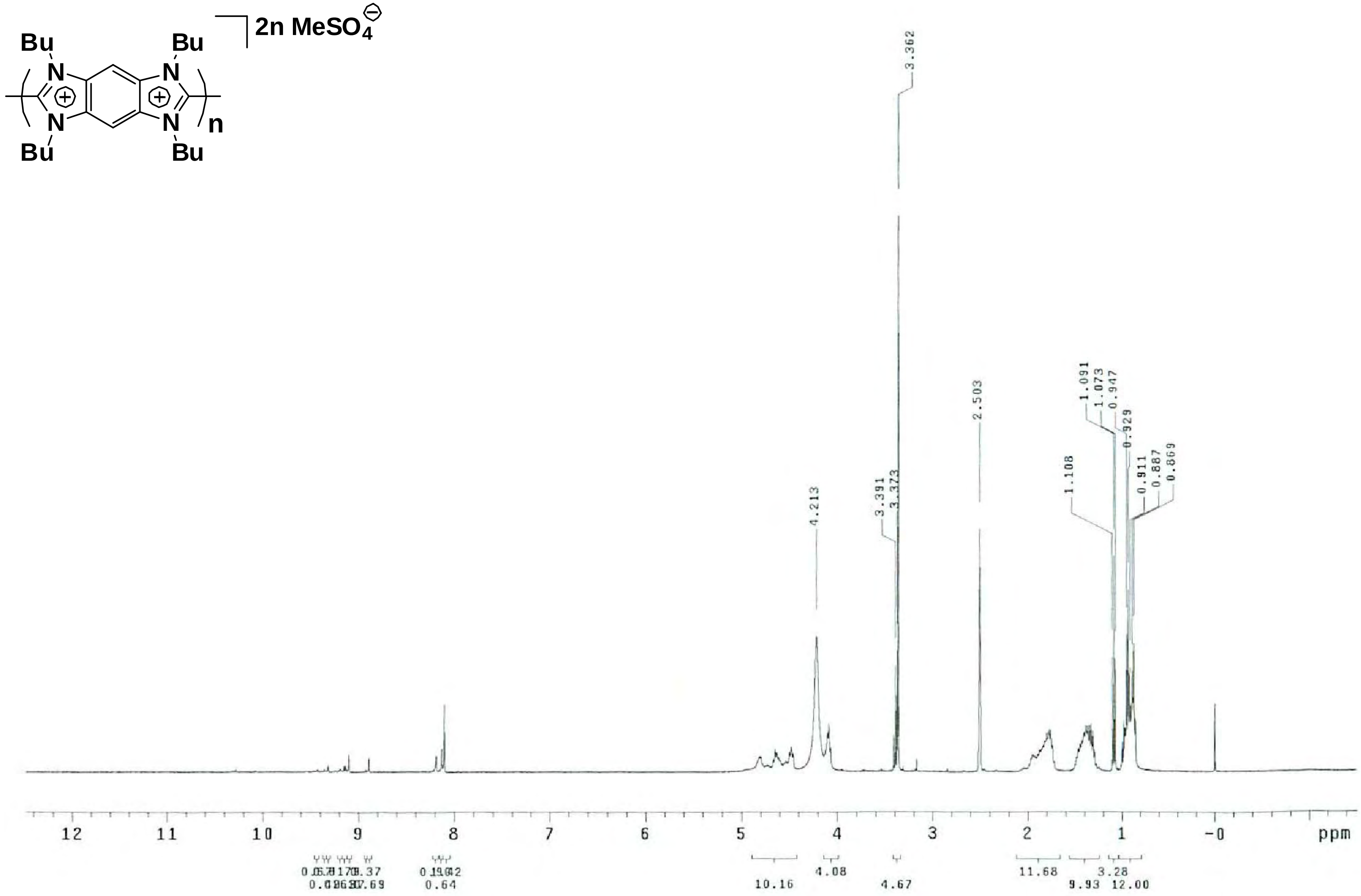
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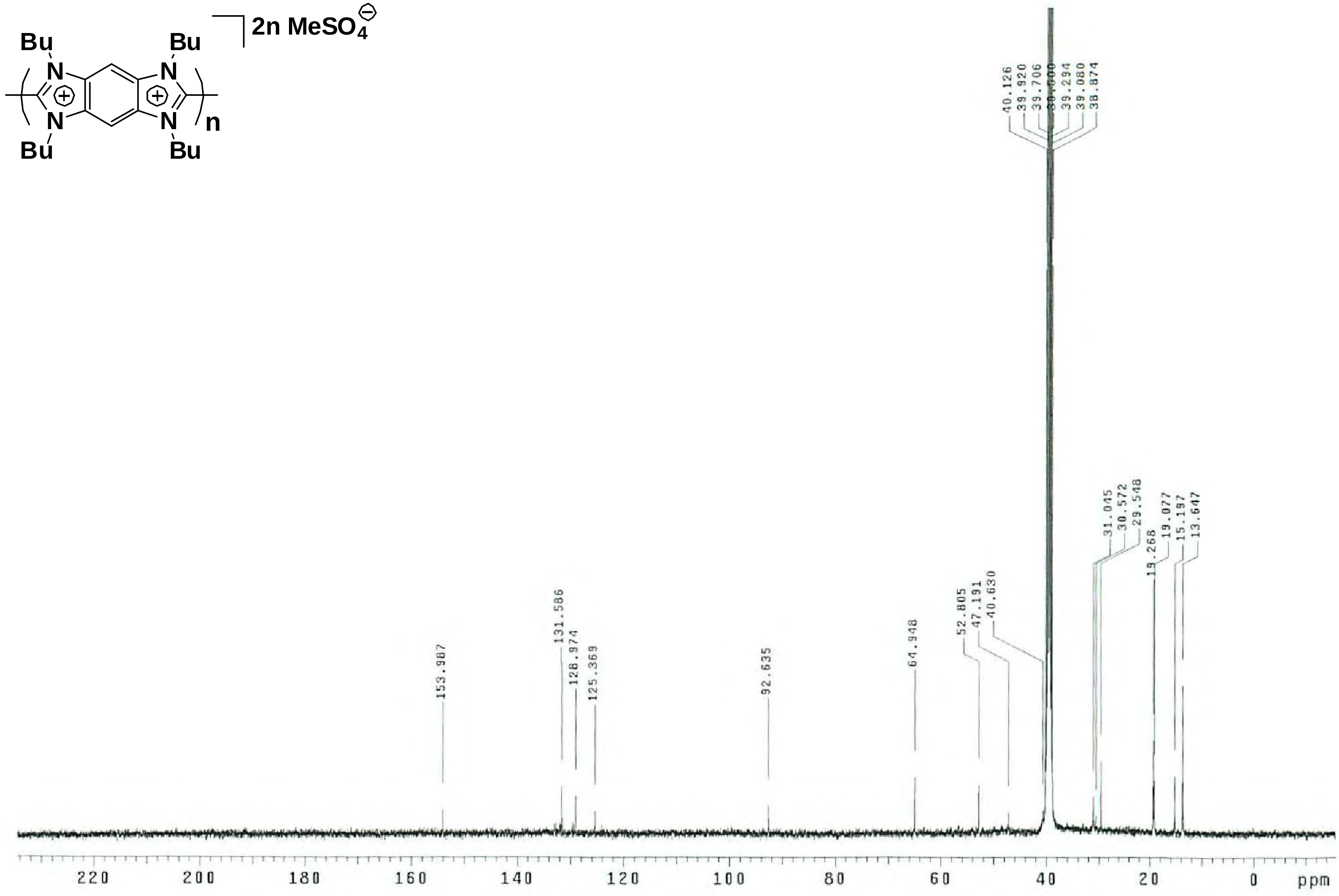
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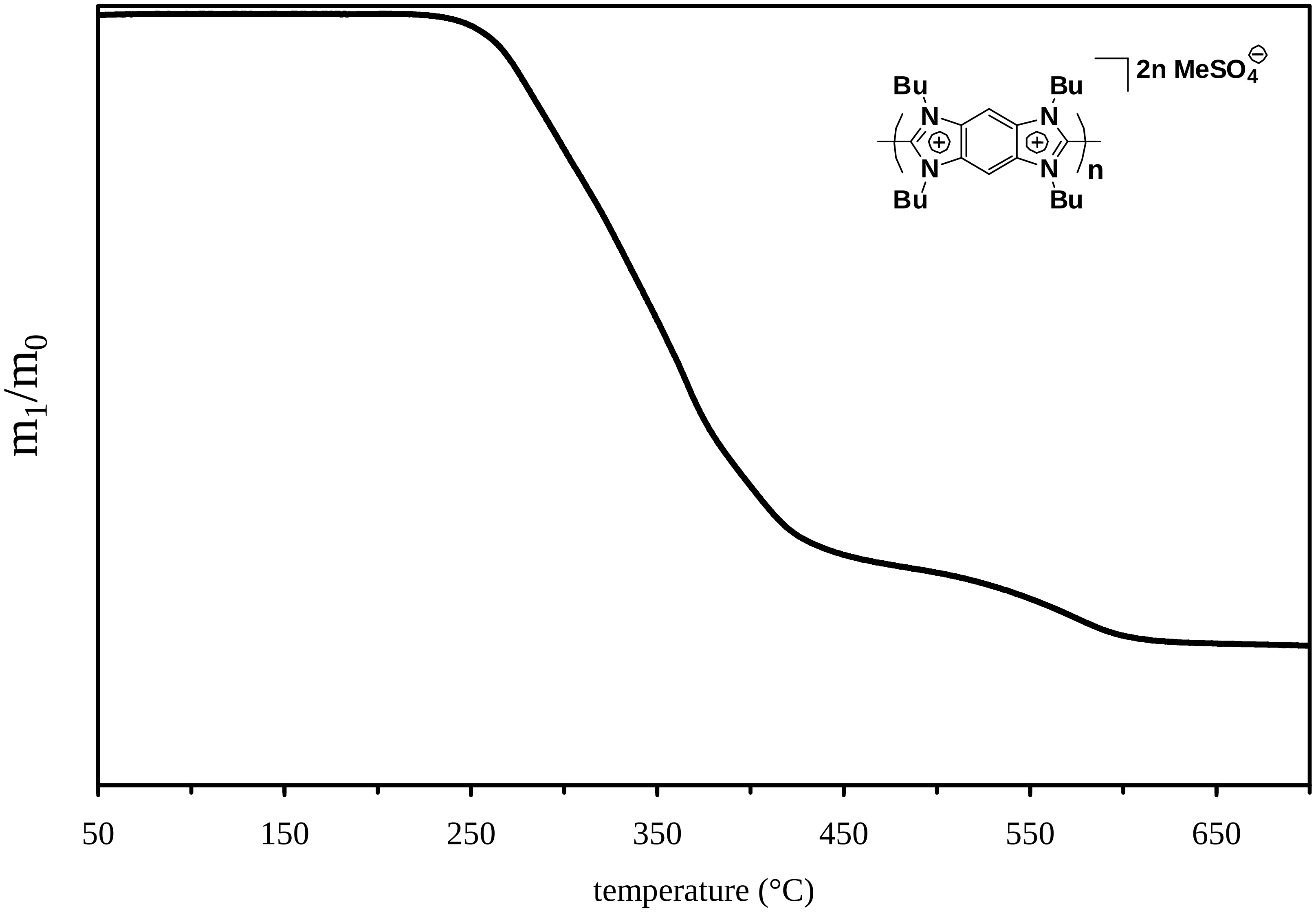
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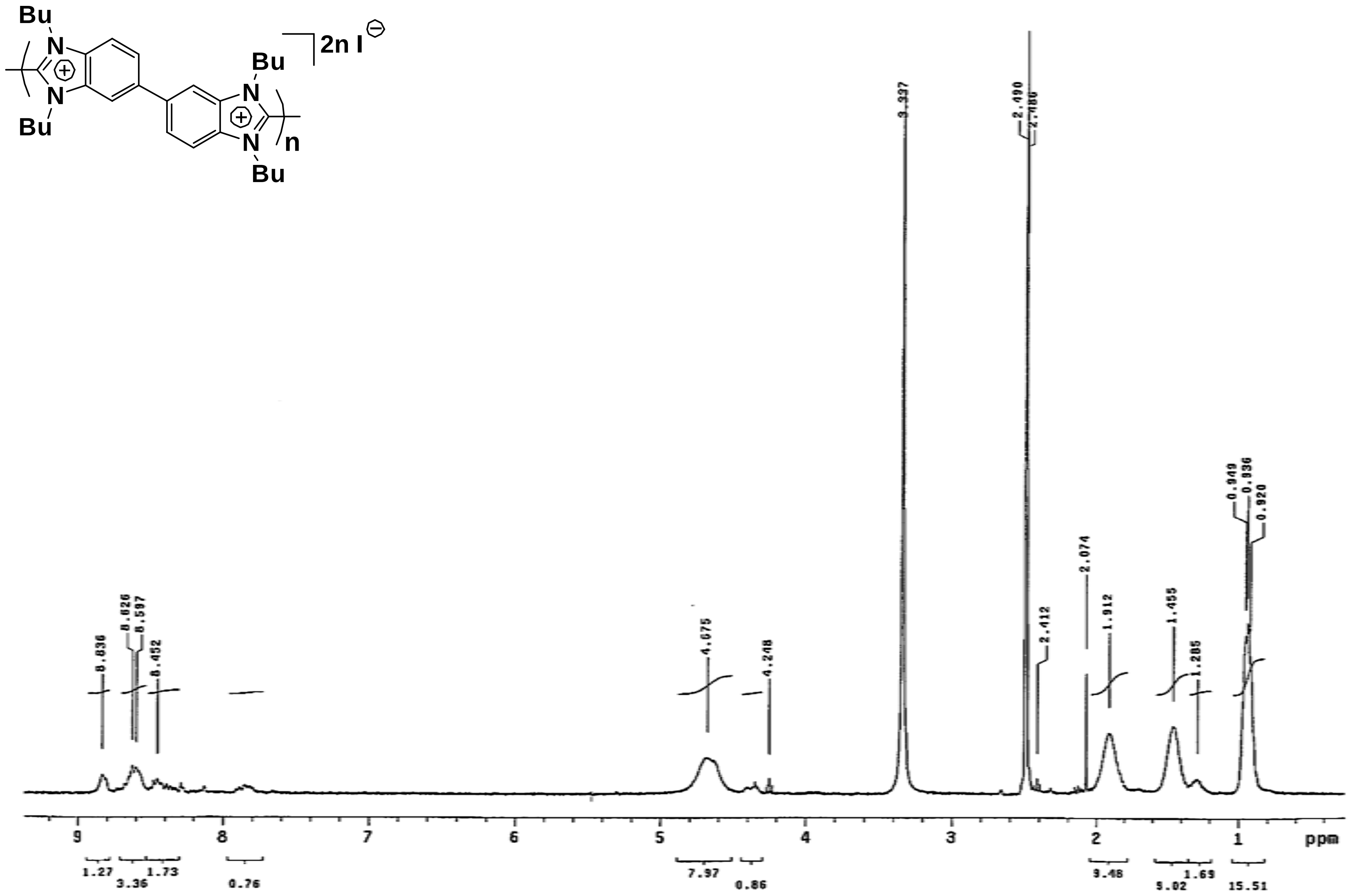
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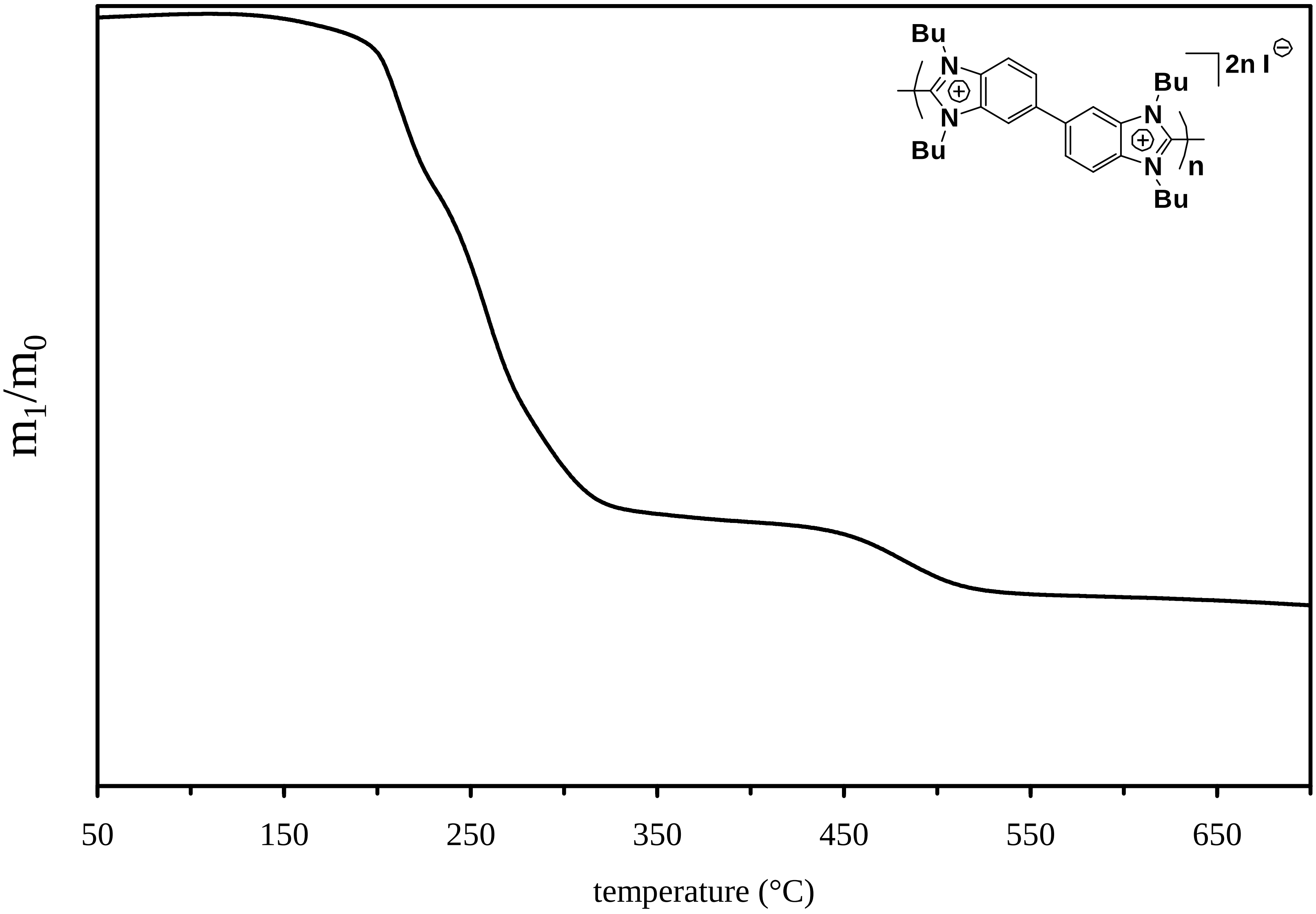
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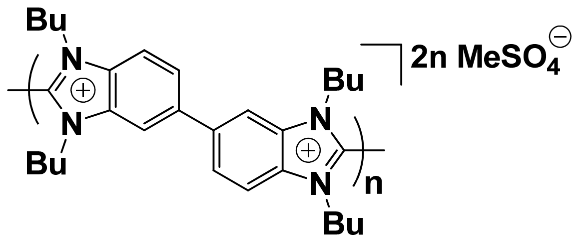
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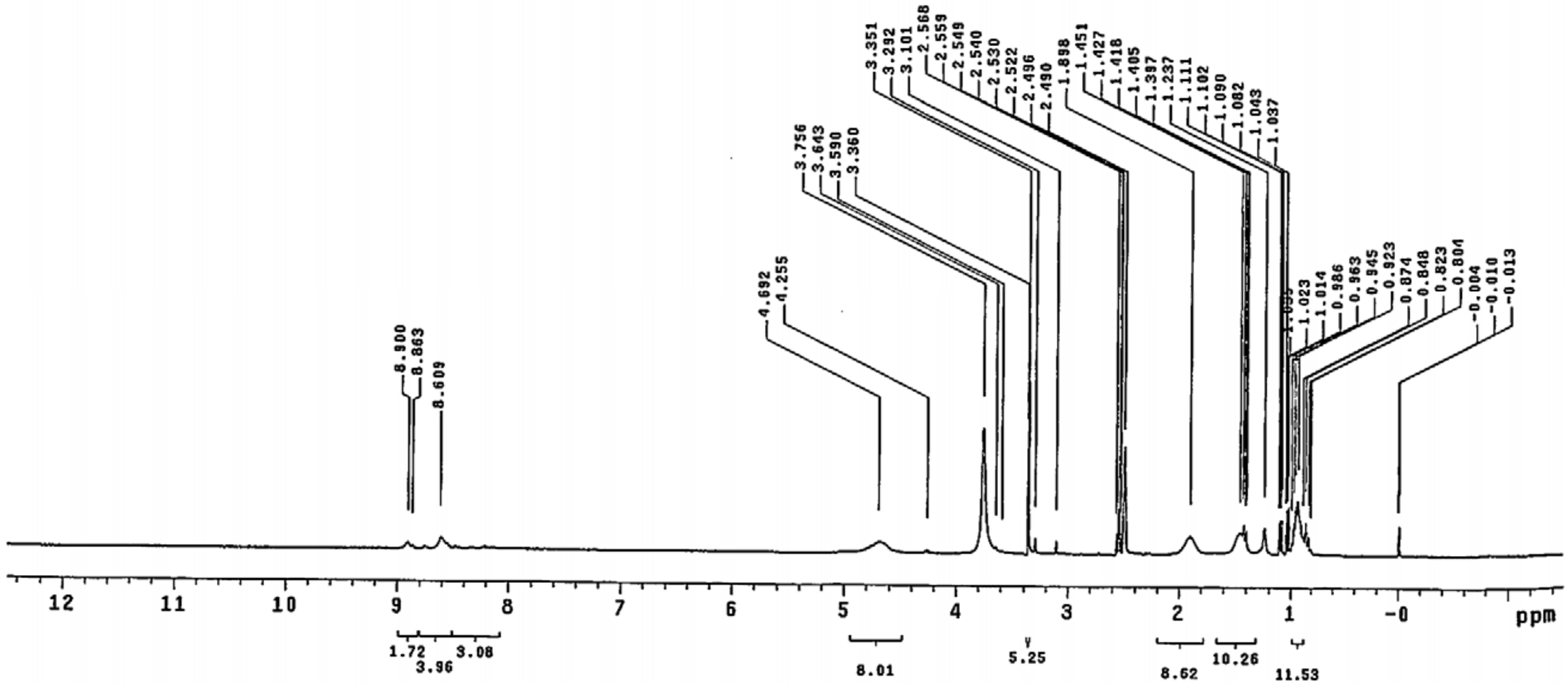
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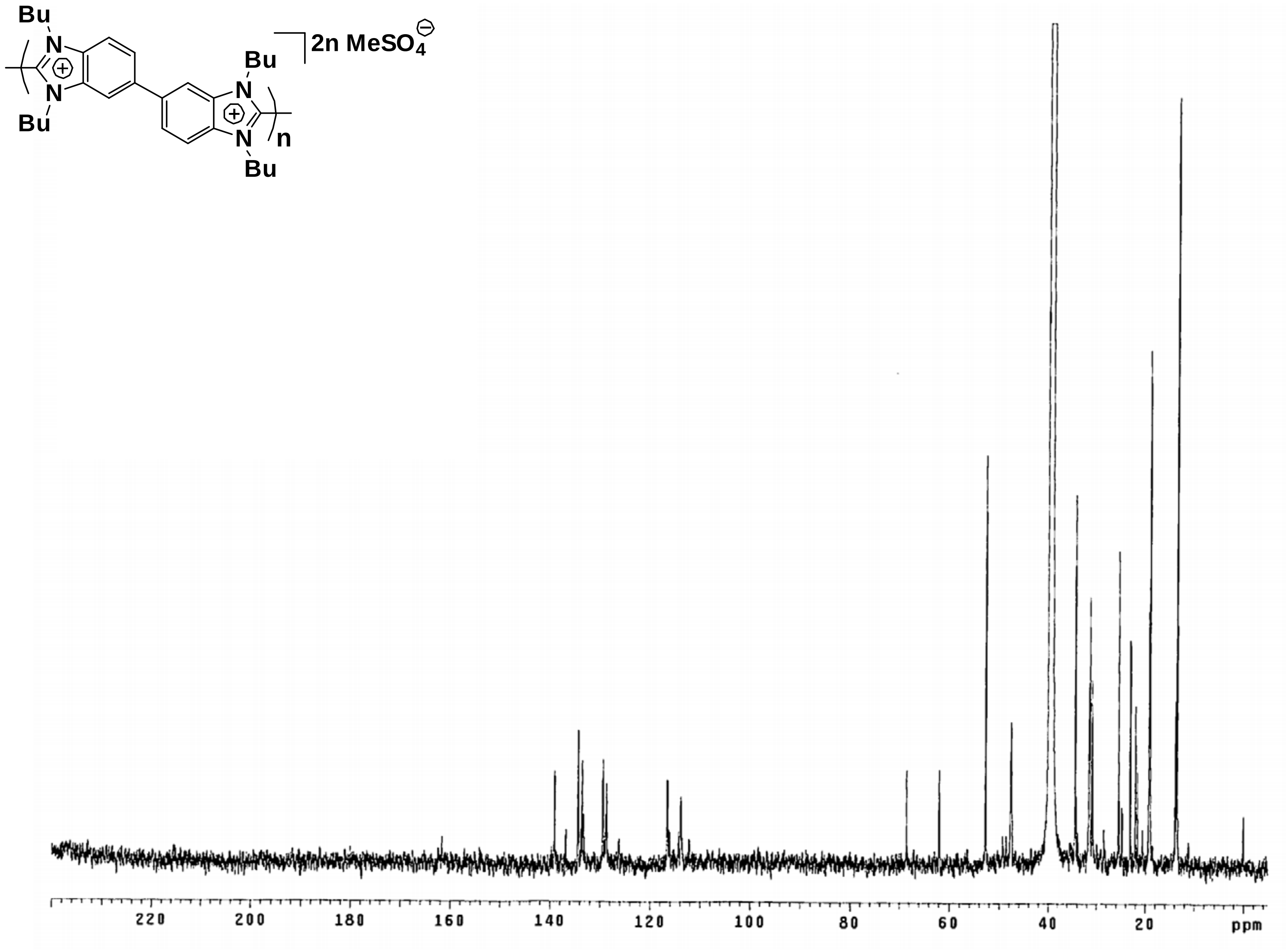
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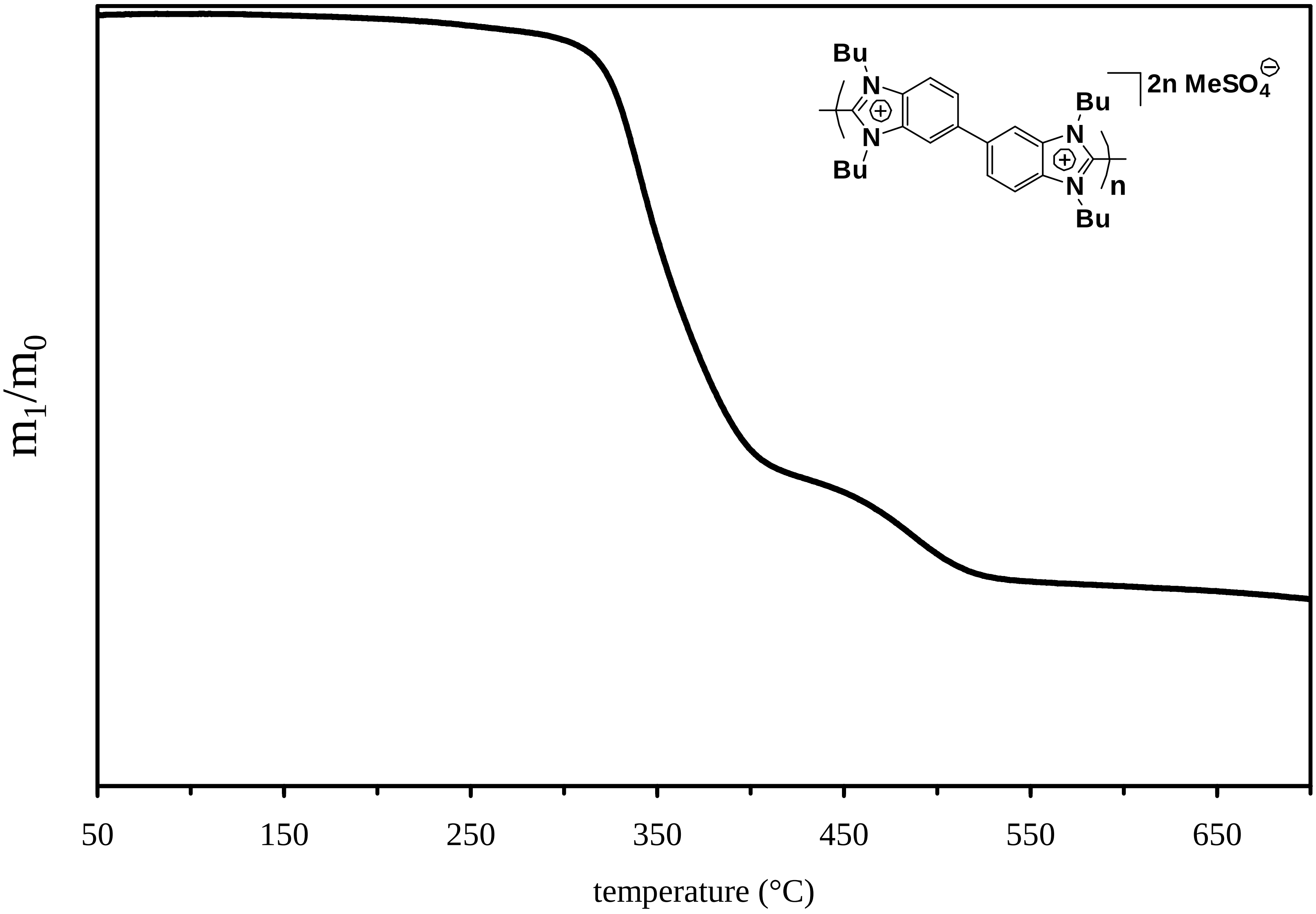
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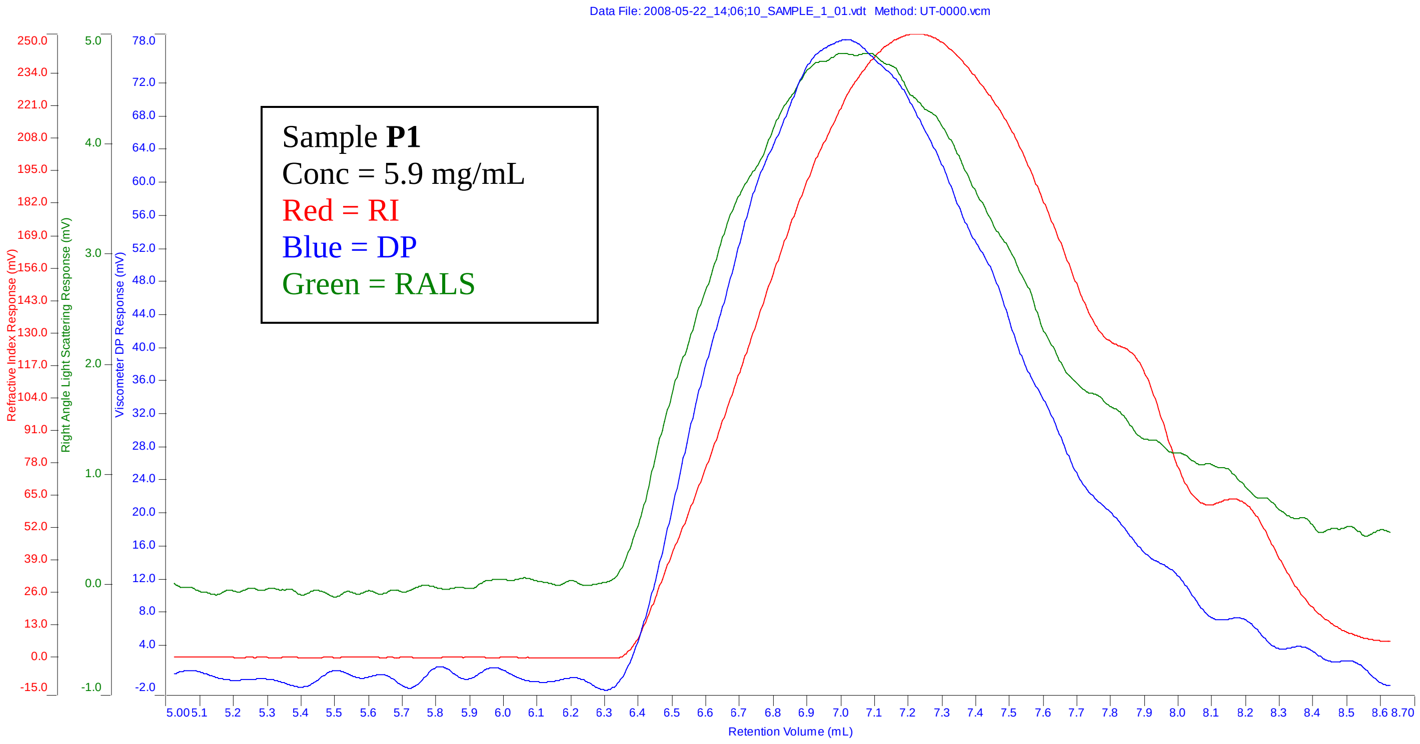
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182.0
169.0
156.0
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130.0
117.0
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26.0
13.0
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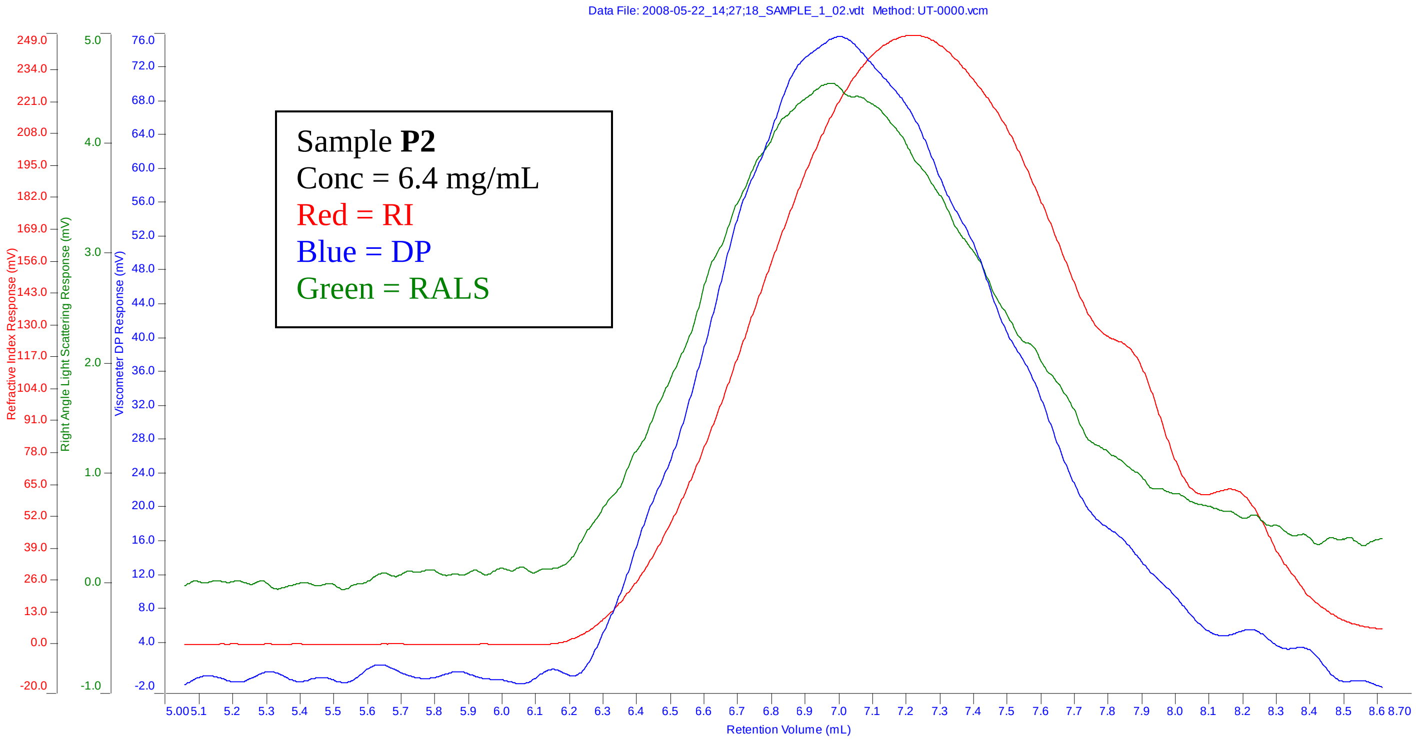
Data File: 2008-05-22_14;27;18_SAMPLE_1_02.vdt Method: UT-0000.vcm
Sample **P2**
Conc = 6.4 mg/mL
Red = RI
Blue = DP
Green = RALS
Refractive Index Response (mV)
249.0
234.0
221.0
208.0
195.0
182.0
169.0
156.0
143.0
130.0
117.0
104.0
91.0
78.0
65.0
52.0
39.0
26.0
13.0
0.0
-20.0
Right Angle Light Scattering Response (mV)
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
Viscometer DP Response (mV)
76.0
72.0
68.0
64.0
60.0
56.0
52.0
48.0
44.0
40.0
36.0
32.0
28.0
24.0
20.0
16.0
12.0
8.0
4.0
-2.0
5.00 5.1 5.2 5.3 5.4 5.5 5.6 5.7 5.8 5.9 6.0 6.1 6.2 6.3 6.4 6.5 6.6 6.7 6.8 6.9 7.0 7.1 7.2 7.3 7.4 7.5 7.6 7.7 7.8 7.9 8.0 8.1 8.2 8.3 8.4 8.5 8.6 8.70
Retention Volume (mL)

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