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Supporting Information

Photovoltaic performance of an ultra small band gap polymer

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Experimental

General

^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz NMR spectrometer. Molecular weights were determined using size exclusion chromatography in HPLC-grade *o*-dichlorobenzene at 80°C against polystyrene standards on a Polymer Laboratories-GPC 120 high temperature chromatograph, a PD 2040 high-temperature light scattering detector, and a Midas autosampler. A mixed-C 300 × 7.5 mm column was used, together with a pre-column. The flow rate was 1 ml/min and the injection volume 100 μl .

UV-vis absorption spectra were measured with a Perkin-Elmer Lambda 900 spectrometer. Cyclic voltammetry (scan rate = 100 mV/s) was performed on an Autolab PGSTAT30 potentiostat in a three-electrode single-compartment cell using *o*-

dichlorobenzene containing 0.1 M TBAPF₆ (Fluka) as electrolyte. The working electrode was platinum disk, the counter electrode a platinum wire, and the reference electrode Ag/AgCl. Potentials are relative to Fc/Fc⁺.

The photovoltaic devices were prepared by spin coating EL-grade PEDOT:PSS onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Philips Research). The photoactive layer was deposited by spin coating from the appropriate solvent. The counter electrode of LiF (1 nm) and aluminum (100 nm) was deposited by vacuum evaporation at 5 x 10⁻⁶ mbar. The active area of the cells was 0.17 cm². *J-V* characteristics were measured under ~75 mW/cm² white light from a tungsten-halogen lamp using a Keithley 2400 source meter. Short circuit currents under AM1.5 conditions were obtained from the spectral response and convolution with the solar spectrum.

Tapping Mode AFM was measured in a NanoScope Dimension 3100 microscope (Veeco, Digital Instruments) using PPP-NCHR probes (Nanosensors).

Methyl-3,5-di(ethylhexyloxy)benzoate (1) A solution of methyl-3,5-dihydroxybenzoate (**1**) (5.0 g, 30.7 mmol), 1-bromo-2-ethylhexane (14.38 g, 74.5 mmol) and K₂CO₃ (20.93 g, 151.0 mmol) in CH₃CN (150 ml) was prepared. The reaction mixture was refluxed for 16 hrs and subsequently quenched by addition of demineralized water (200 ml). The aqueous phase was extracted with CH₂Cl₂ (4x 100 ml). The combined organic layers were dried over Na₂SO₄ and the remaining solvent was evaporated. Purification by chromatography on silica gel (hexane:CH₂Cl₂) afforded 10.74 g of a colorless oil (92% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.16 (d, 2H, *J* = 2.5 Hz), 6.65 (t, 1H, *J* = 2.2 Hz), 3.90 (s, 3H), 3.87 (dd, 4H, *J* = 4.5 Hz, *J* = 1.5 Hz), 1.72 (m, 2H),

1.55-1.36 (m, 8H), 1.35-1.27 (m, 8H), 0.96-0.85 (m, 12 H). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3): δ 167.0, 160.4, 131.7, 107.5, 106.5, 70.7, 52.2, 39.4, 30.5, 29.1, 23.8, 23.0, 14.1, 11.1. Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{O}_3$: C, 76.55; H, 10.71; O, 12.75. Found: C, 68.64; H, 9.96. GC-MS ($M_w = 392.58$): $m/z = 392.40$ [M^+].

1,2-Bis[3,5-di(2-ethylhexyloxy)phenyl]ethanedione (2) To a solution of Na (0.58 g, 25.2 mmol) in ether (40 ml), compound (1) (4.82 g, 12.3 mmol), dissolved in ether (20 ml), was added dropwise during 10 minutes. After 16 hrs the reaction mixture was cooled to $-78\text{ }^\circ\text{C}$ and SOCl_2 (3 ml, 41.4 mmol) was slowly added. The mixture was allowed to reach room temperature. After 6 hrs, the reaction was quenched by careful addition of ice/water (50 ml). The aqueous phase was extracted with CHCl_3 (3x 100 ml). The combined organic layers were dried over Na_2SO_4 and the remaining solvent was evaporated. Purification by chromatography on silica gel (hexane: CH_2Cl_2) resulted in 1.66 g of a yellow oil (37% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.05 (d, 4H, $J = 2.2$ Hz), 6.73 (t, 2H, $J = 2.2$ Hz), 3.86 (dd, 8H, $J = 5.5$ Hz, $J = 2.2$ Hz), 1.70 (m, 4H), 1.53-1.35 (m, 16H), 1.34-1.24 (m, 16H), 0.94-0.85 (m, 24H). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3): δ 194.4, 160.8, 134.5, 107.8, 70.8, 39.4, 30.5, 29.1, 23.8, 23.0, 14.1, 11.1. Anal. Calcd for $\text{C}_{46}\text{H}_{74}\text{O}_6$: C, 76.41; H, 10.32; O, 13.28. Found: C, 73.74; H, 9.72. MALDI-TOF MS ($M_w = 722.55$): $m/z = 723.61$ [M^+].

1,4-Dibromo-2,1,3-benzothiadiazole (4) To a solution of 2,1,3-benzothiadiazole (3) (9.95 g, 73.1 mmol) in aqueous HBr (48%, 50 ml), bromine (37.30 g, 233.4 mmol) was added dropwise during 1h. An additional amount of aqueous HBr (30 ml) was added to

commence stirring. The reaction mixture was refluxed for 2.5 h and subsequently filtrated (while hot). The filtrate was thoroughly washed with demineralized water and dissolved in ether (800 ml). The organic phase was washed with demineralized water (3x 200 ml), dried over Na₂SO₄ and the remaining solvent was evaporated. Recrystallization from MeOH afforded 16.56 g of white needles (77% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.73 (s, 2H). ¹³C-NMR (400 MHz, CDCl₃): δ 152.9, 132.3, 113.9. Anal. Calcd for C₆Br₂N₄O₄S: C, 24.52; H, 0.69; Br, 54.36; N, 9.53; S, 10.91. Found: C, 24.42; H, 0.39; N, 9.20. GC-MS (M_w = 293.97): m/z = 293.90 [M⁺]. m.p. = 187 °C.

1,4-Dibromo-5,6-dinitro-2,1,3-benzothiadiazole (5) A mixture of concentrated H₂SO₄ (100 ml) and fuming HNO₃ (100 ml) was cooled to 0 °C. To keep the temperature below 5 °C, compound (4) (5.22 g, 17.8 mol) was added in small portions. After stirring for 6 h at 0 °C, the reaction mixture was poured out into ice/water (300 ml). The precipitate was filtrated and washed with water. Purification by chromatography on silica gel (solid deposition) (EtOAc:heptane, 1:4) gave 1.83 g of (5) as a beige solid (27% yield). ¹³C-NMR (400 MHz, CDCl₃): δ 151.4, 144.9, 110.3. Anal. Calcd for C₆Br₂N₄O₄S: C, 18.77; Br, 41.62; N, 14.59; O, 16.67; S, 8.35. Found: C, 18.69; N, 14.10. MALDI-TOF MS (M_w = 383.80): m/z = 383.84 [M]. m.p. = 201 °C.

1,4-Di(2-thienyl)-5,6-dinitro-2,1,3-benzothiadiazole (6) To a solution of (5) (3.80 g, 9.90 mmol) and 2-tributylstannylthiophene (9.06 g, 24.3 mmol) in THF (150 ml), Pd(PPh₃)₂Cl₂ (338 mg, 0.48 mmol) was added. The reaction mixture was refluxed for 16 h, after which it was cooled to room temperature and concentrated to allow precipitation

from hexane. After filtration and washing with hexane, recrystallization from toluene afforded 3.10 g of an orange solid (80% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.75 (dd, 2H, J = 5.1Hz, J = 0.7Hz), 7.52 (dd, 2H, J = 4.7Hz, J = 1.1Hz), 7.25 (m, 2H). ¹³C-NMR (400 MHz, CDCl₃): δ 152.2, 141.9, 131.4, 131.0, 129.5, 128.0, 121.5. Anal. Calcd for C₁₄H₁₀N₄S₃: C, 43.07; H, 1.55; N, 14.35; O, 16.39; S, 24.64. Found: C, 43.67; H, 0.76; N, 13.57. MALDI-TOF MS (M_w = 389.95): m/z = 390.02 [M⁻].

1,4-Di(2-thienyl)-5,6-diamino-2,1,3-benzothiadiazole (7) To a solution of (6) (502 mg, 1.29 mmol) in acetic acid (40 ml), iron dust (878 mg, 15.72 mmol) was added. The reaction mixture was heated to 80 °C. After 5 h, demineralized water (100 ml) was added to the mixture and the product was extracted with ether (3x 100 ml). The ethereal phase was dried over Na₂SO₄ en the solvent was evaporated resulting in 416 mg of a brown solid (98% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.57 (dd, 2H, J = 5.5Hz, J = 1.1Hz), 7.37 (dd, 2H, J = 3.3Hz, J = 1.1Hz), 7.26 (t, 2H, J = 4.7Hz), 4.39 (br, 4H). ¹³C-NMR (400 MHz, CDCl₃): δ 150.9, 139.3, 135.2, 128.5, 127.5, 127.2, 107.2. Anal. Calcd for C₁₄H₁₀N₄S₃: C, 50.89; H, 3.05; N, 16.95; S, 29.11. Found: C, 50.79; H, 2.65; N, 17.05. MALDI-TOF MS (M_w = 330.01): m/z = 330.05 [M⁺].

4,7-Bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole-5,6-diamine (8) In the dark, a solution of (7) (459 mg, 1.39 mmol) in THF (20 ml) was prepared. After cooling the mixture to 0 °C, NBS (497 mg, 2.80 mmol) was added in one portion. After 4 h, NBS (54 mg, 0.3 mmol) was added. After an additional 2 h, demineralized water (50 ml) was added to the reaction mixture. The product was extracted with CHCl₃ (4x 100 ml) and

dried over Na₂SO₄. The remaining solvent was evaporated. Purification by chromatography on silica gel (CHCl₃) afforded 411 mg of **(8)** as a green solid (61% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.20 (d, 2H, J = 3.7Hz), 7.12 (d, 2H, J = 4.7Hz), 4.40 (br, 4H). ¹³C-NMR (400 MHz, CDCl₃): δ 150.4, 139.4, 136.9, 130.2, 128.9, 114.2, 106.6. Anal. Calcd for C₁₄H₈Br₂N₄S₃: C, 34.44; H, 1.65; Br, 32.73; N, 11.48; S, 19.70. Found: C, 34.57; H, 1.52; N, 10.91. MALDI-TOF MS (M_w = 487.83): m/z = 487.80 [M⁺].

4,9-Bis(5-bromo-2-thienyl)-6,7-bis{di(2-ethylhexyloxy)phenyl}[1,2,5]thiadiazolo[3,4-g]quinoxaline (9) To solution of **(8)** (80 mg, 0.16 mmol) in 25 ml of ethanol, **(2)** (123 mg, 0.17 mmol) was added. The reaction mixture was refluxed for 5 days. The remaining solvent was evaporated and purification by chromatography on silica gel (CH₂Cl₂:heptane, 1:2) afforded 112 mg of **(9)** as a green sticky solid (58% yield). ¹H-NMR (400 MHz, CDCl₃): δ 8.91 (d, 2H, J = 4.2Hz), 7.23 (d, 2H, J = 4.3Hz), 6.96 (d, 4H, J = 2.2Hz), 6.58 (t, 2H, J = 2.2Hz), 3.80 (dd, 8H, J = 5.8Hz, J = 1.3Hz), 1.71-1.66 (m, 4H), 1.52-1.25 (m, 32H), 0.94-0.89 (m, 24H). ¹³C-NMR (400 MHz, CDCl₃): δ 160.3, 153.6, 151.4, 139.0, 137.4, 134.1, 133.4, 129.6, 120.6, 120.4, 108.8, 104.6, 70.8, 39.3, 30.6, 29.1, 23.9, 23.1, 14.1, 11.2. Anal. Calcd for C₁₄H₈Br₂N₄S₃: C, 34.44; H, 1.65; Br, 32.73; N, 11.48; S, 19.70. Found: not determined. MALDI-TOF MS (M_w = 1174.35): m/z = 1174.11 [M⁺].

PBTTQ (10) A solution of Ni(cod)₂ (69 mg, 0.25 mmol) and bypyridine (37 mg, 0.24 mmol) in toluene (3 ml) was heated to 80 °C. Subsequently, **(9)** (102 mg, 0.09 mmol)

was added in one portion. An additional amount of toluene (3 ml) was added to get all of the monomer in solution. After 20 hrs a mixture of MeOH/Acetone/0.1 M HCl (1:1:1, 100 ml) was added and was left to stir for 2 hrs. The polymer was precipitated in MeOH and filtered through a Soxhlet thimble. The polymer was fractionated by Soxhlet extraction using MeOH, hexane, CH₂Cl₂, and CHCl₃ respectively. The polymer was obtained in 56 mg as a yellowish solid (64% yield). ¹H-NMR (400 MHz, CDCl₃): δ 8.74 (br, 2H), 7.04 (br, 2H), 6.83 (br, 4H), 6.57 (br, 2H), 3.74 (br, 8H), 1.54 (br, 4H), 1.28 (br, 32H), 0.89 (br, 24H). GPC (o-DCB at 80 °C): $M_w = 58500$ g/mol, $M_n = 9300$ g/mol, PDI = 6.3.

Optical properties

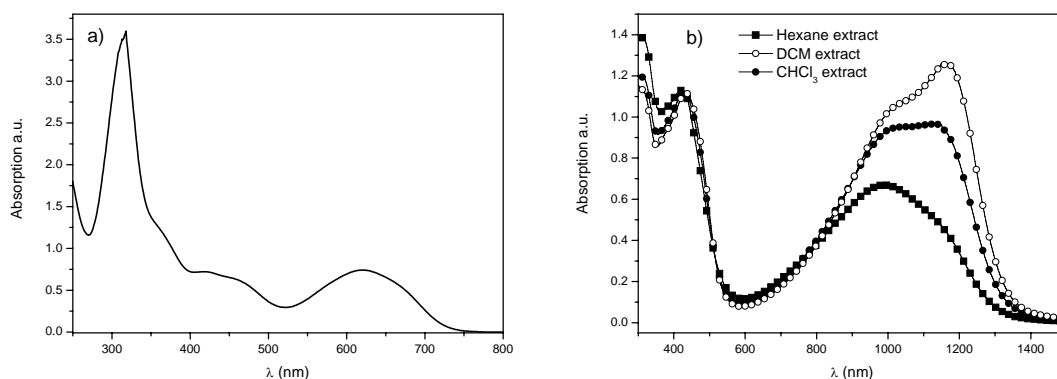


Figure S1. Absorption spectra of (a) the monomer of PBTTQ and (b) the different fractions obtained by Soxhlet extraction measured in *o*-dichlorobenzene.

Cyclic Voltammetry

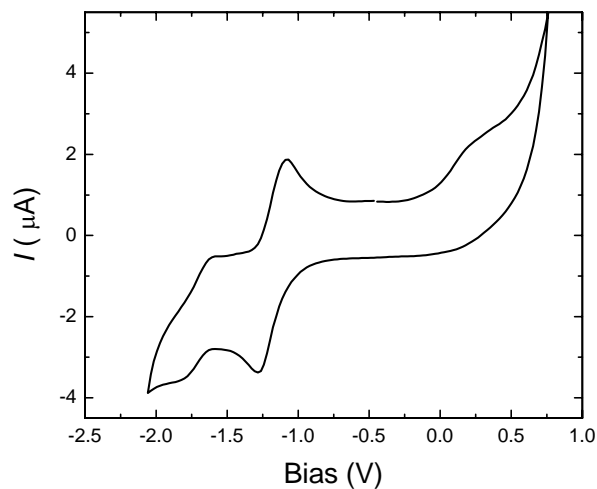


Figure S2. Cyclic voltammogram of PBTTQ recorded in *o*-dichlorobenzene solution (vs. Fc/Fc^+) containing 0.1 M TBAPF_6 (scan rate = 100 mV/s, concentration 2×10^{-3} M based on monomer units).

GPC results

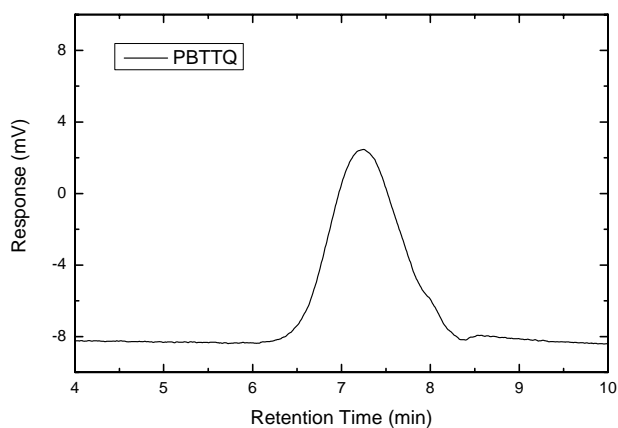
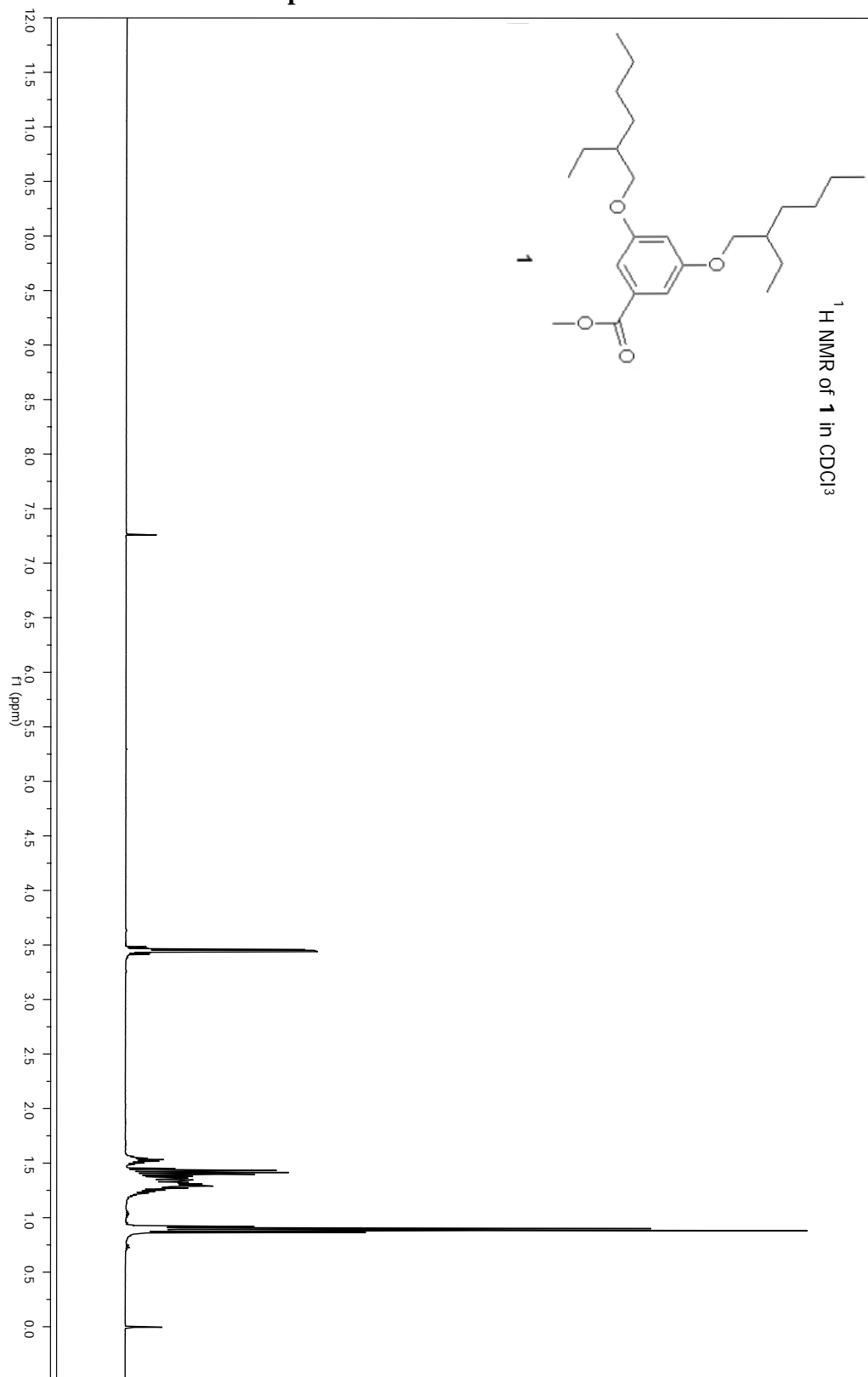
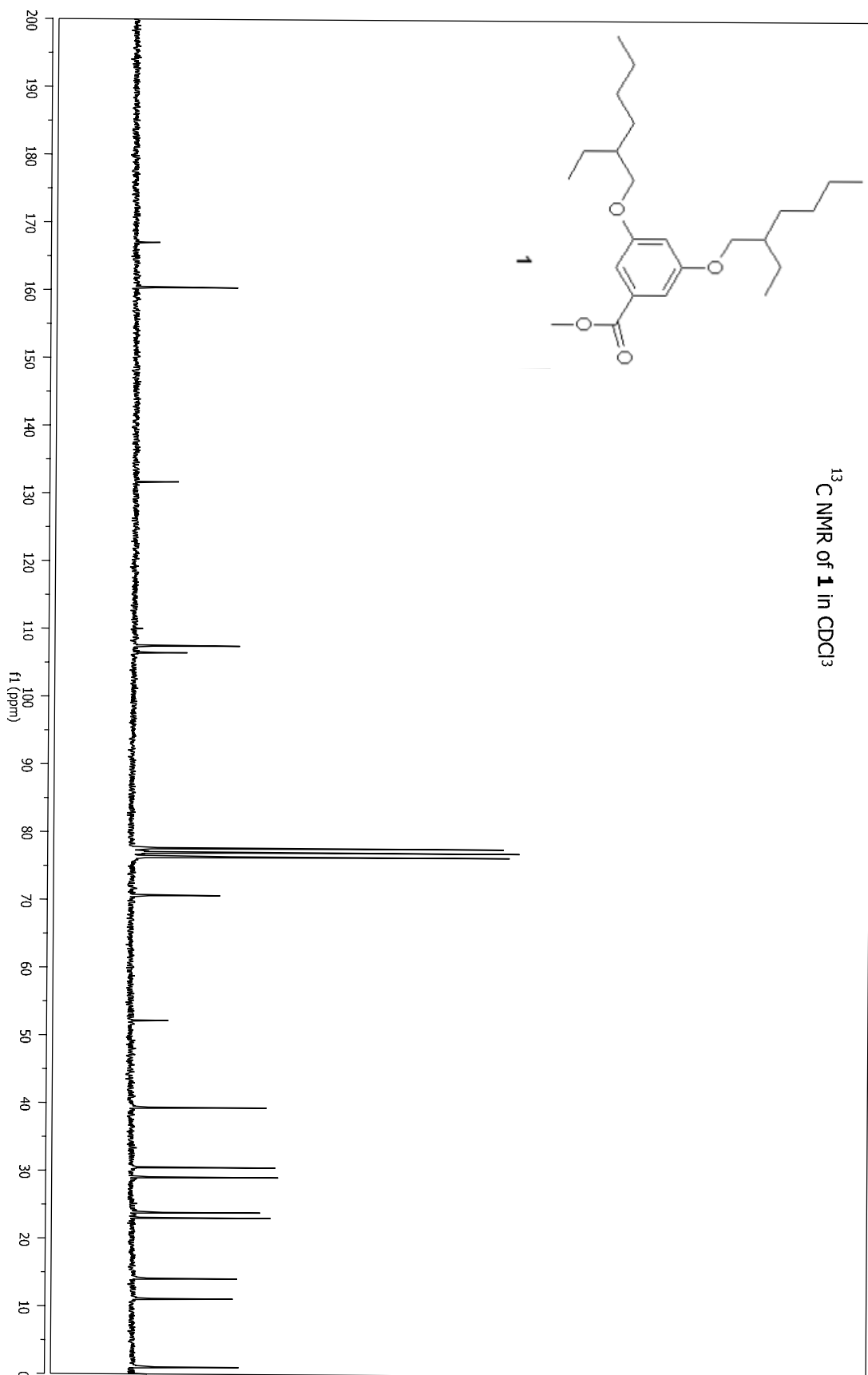


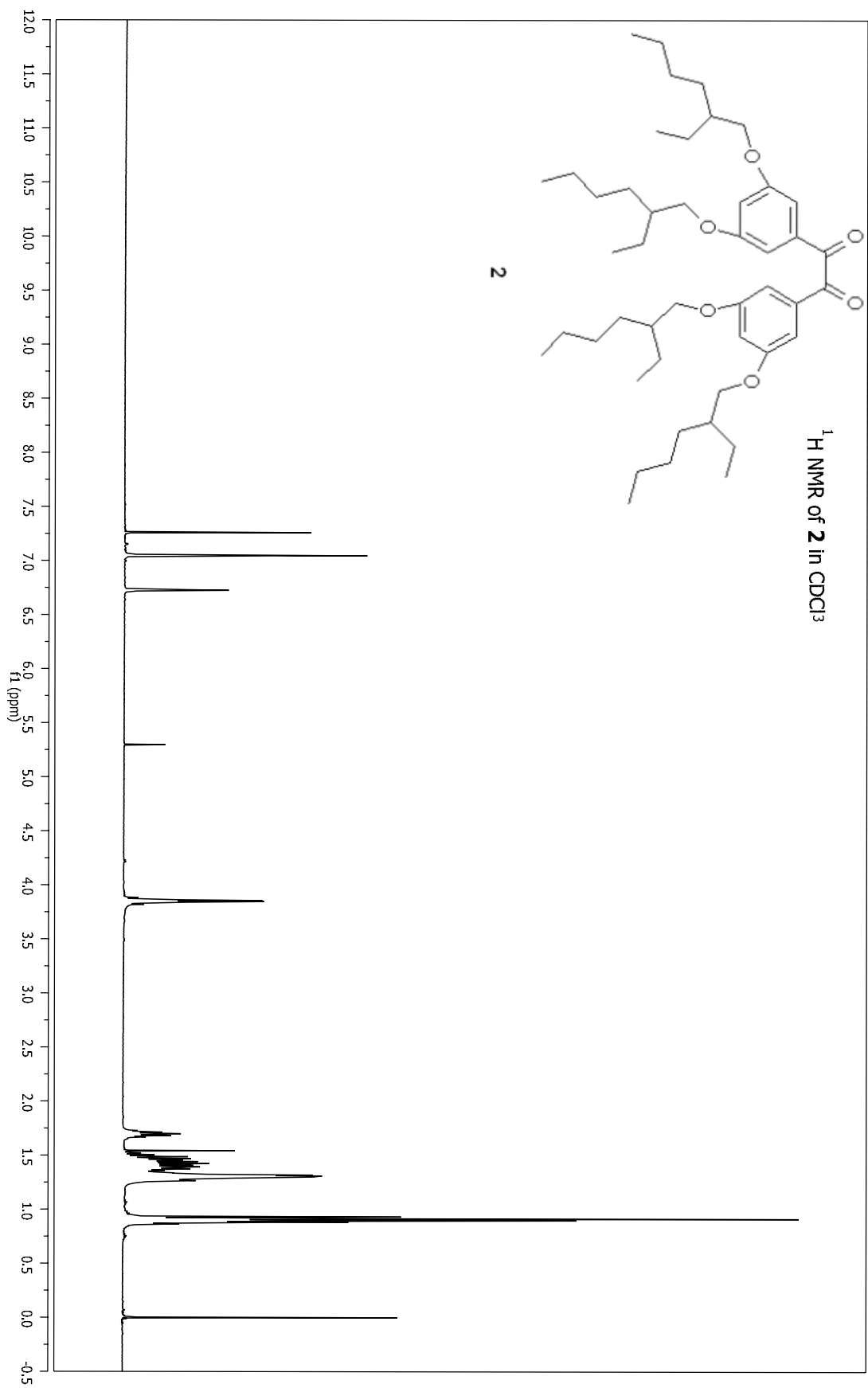
Figure S3. GPC trace of PBTTQ measured (Refractive Index) at 80 °C in *o*-dichlorobenzene.

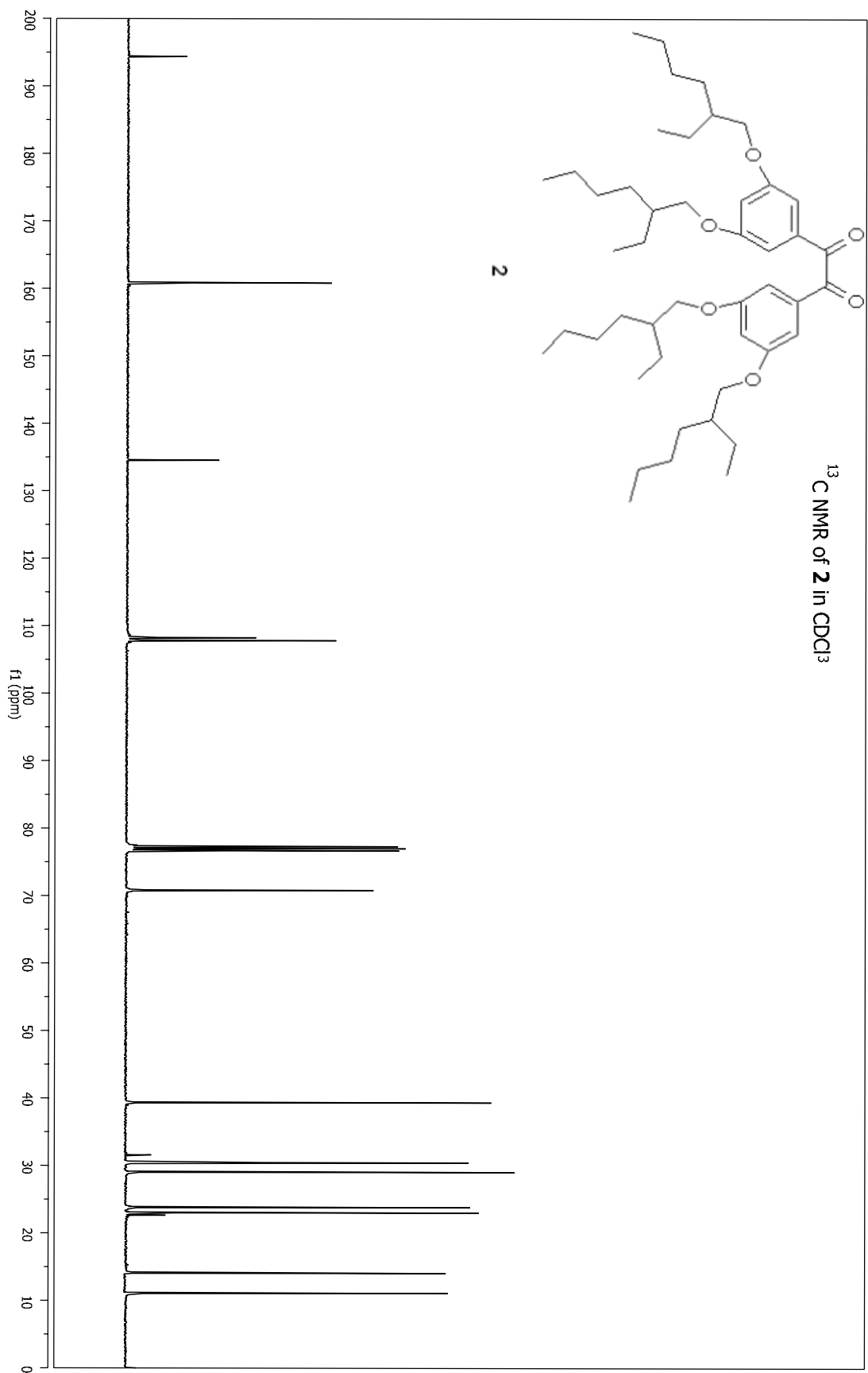
$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra

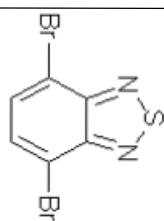


¹³C NMR of **1** in CDCl₃



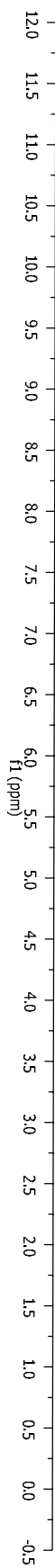




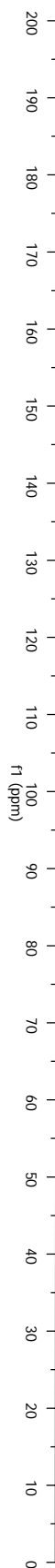
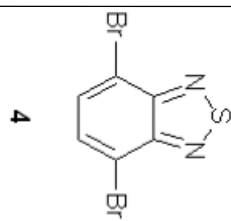


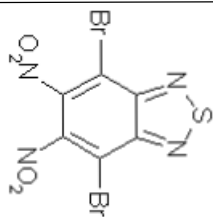
4

¹H NMR of **4** in CDCl₃

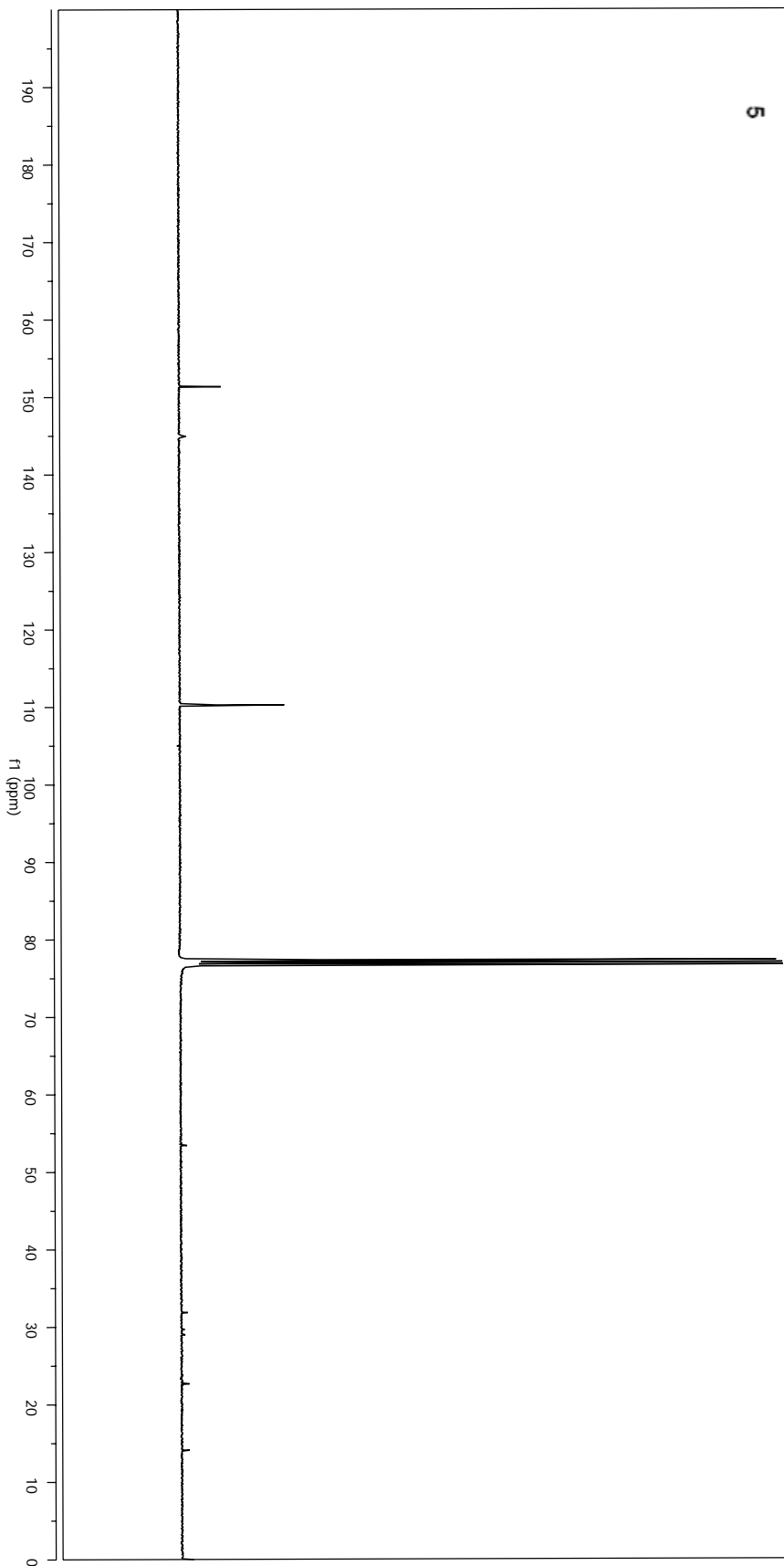


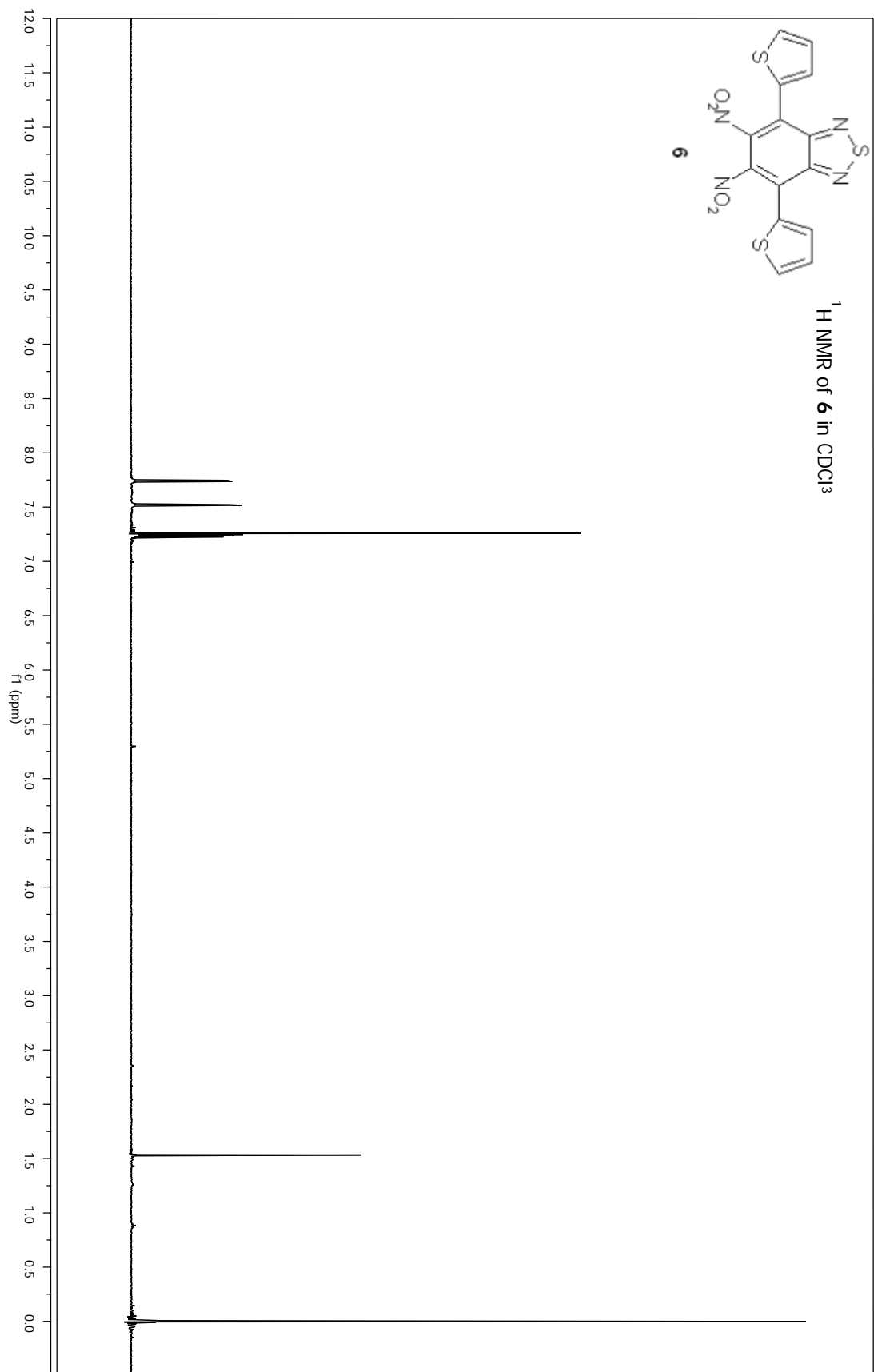
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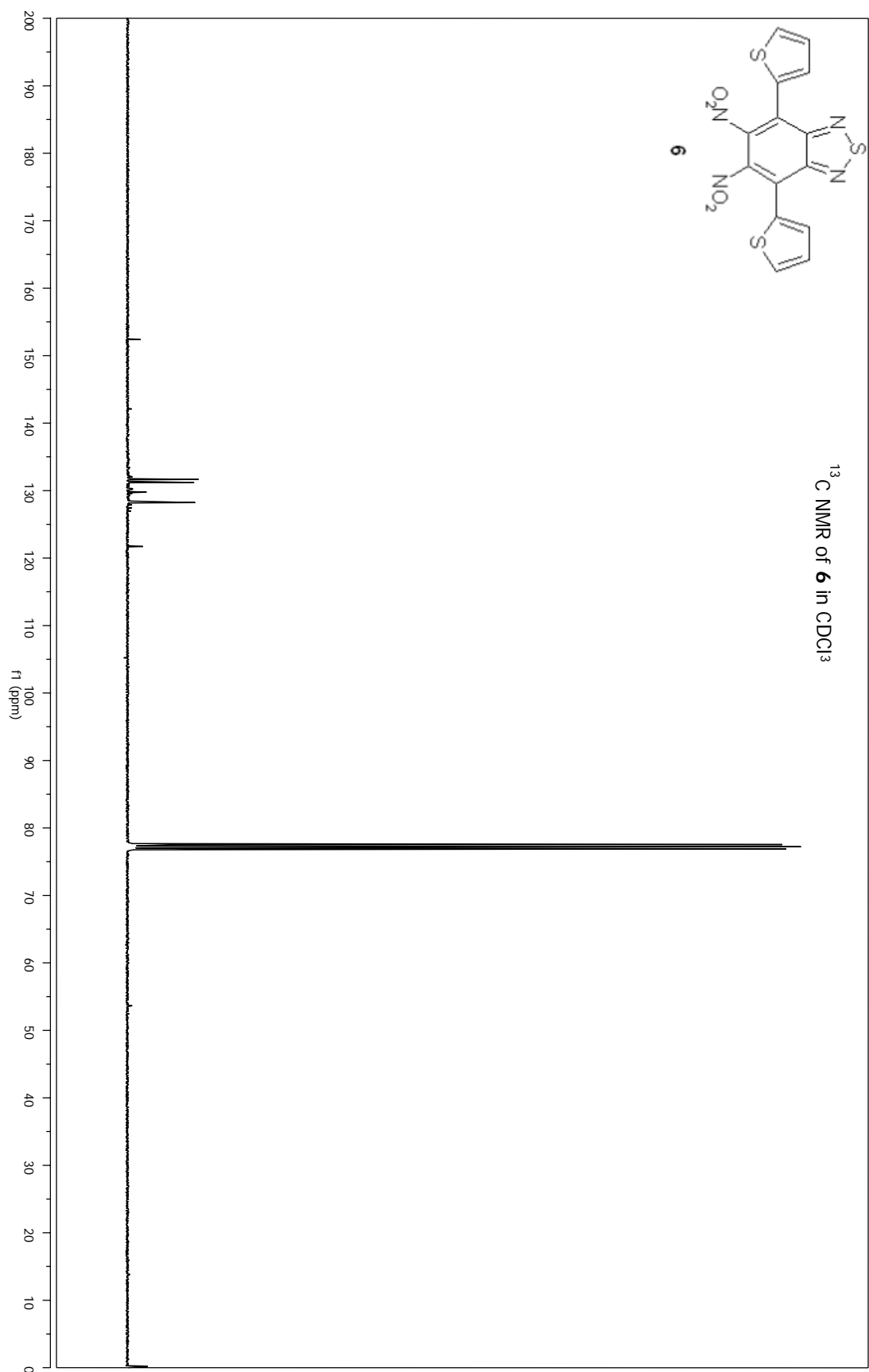


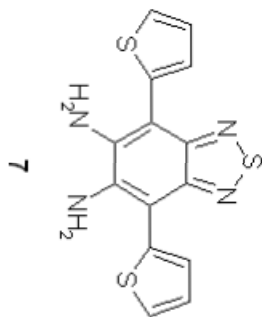


¹³C NMR of **5** in CDCl₃

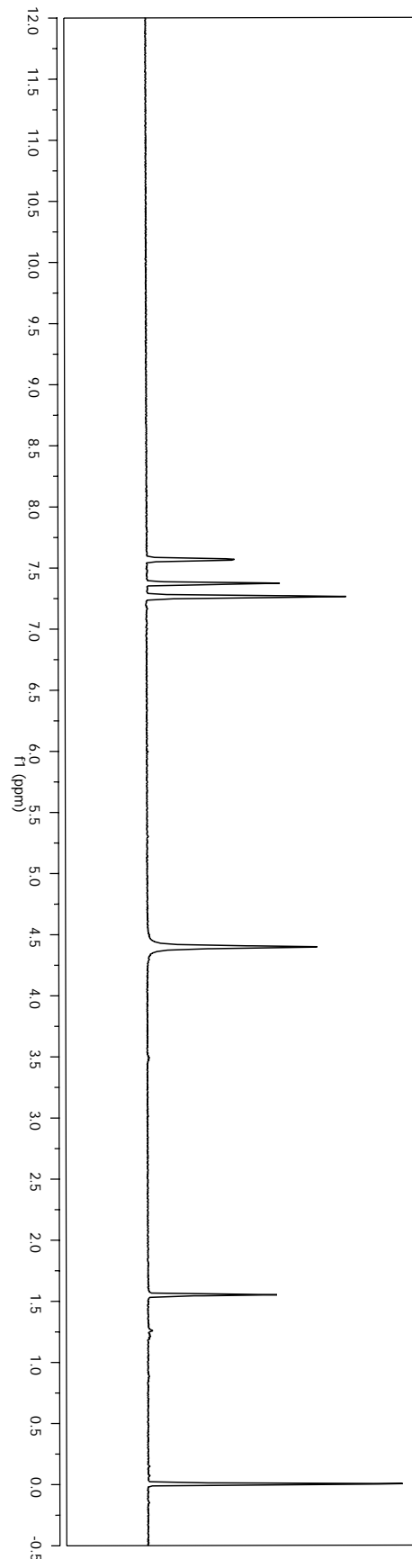


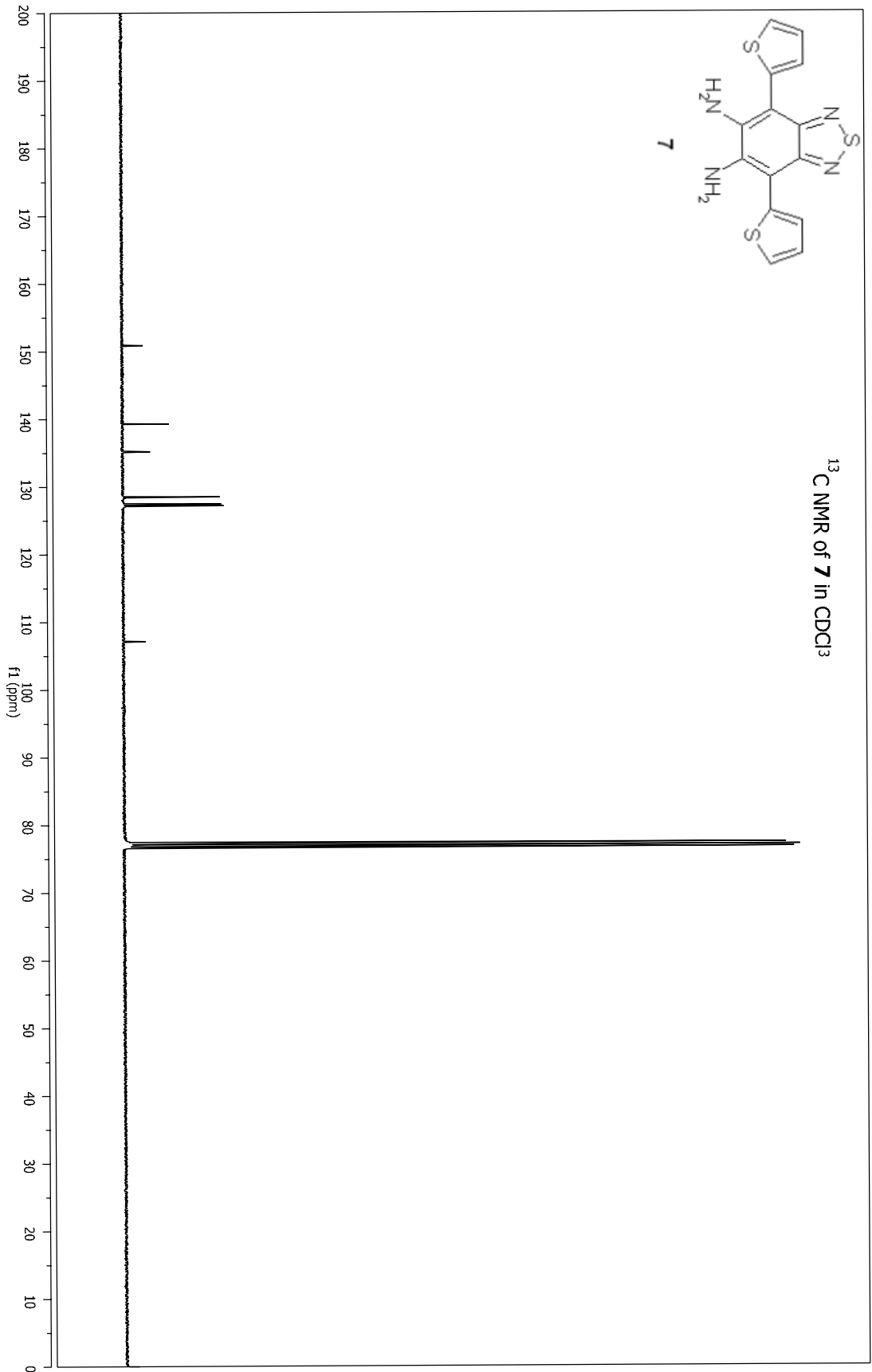


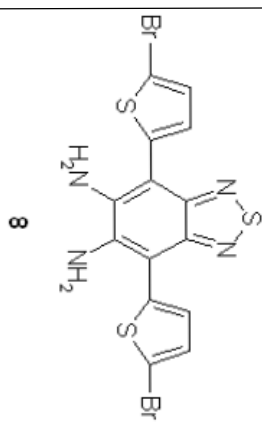




¹H NMR of **7** in CDCl₃







¹H NMR of **8** in CDCl₃

