Supporting Information

A Diels-Alder Crosslinkable Host Polymer for Improved PLED Performance: The Impact on Solution Processed Doped Device and Multilayer Device Performance

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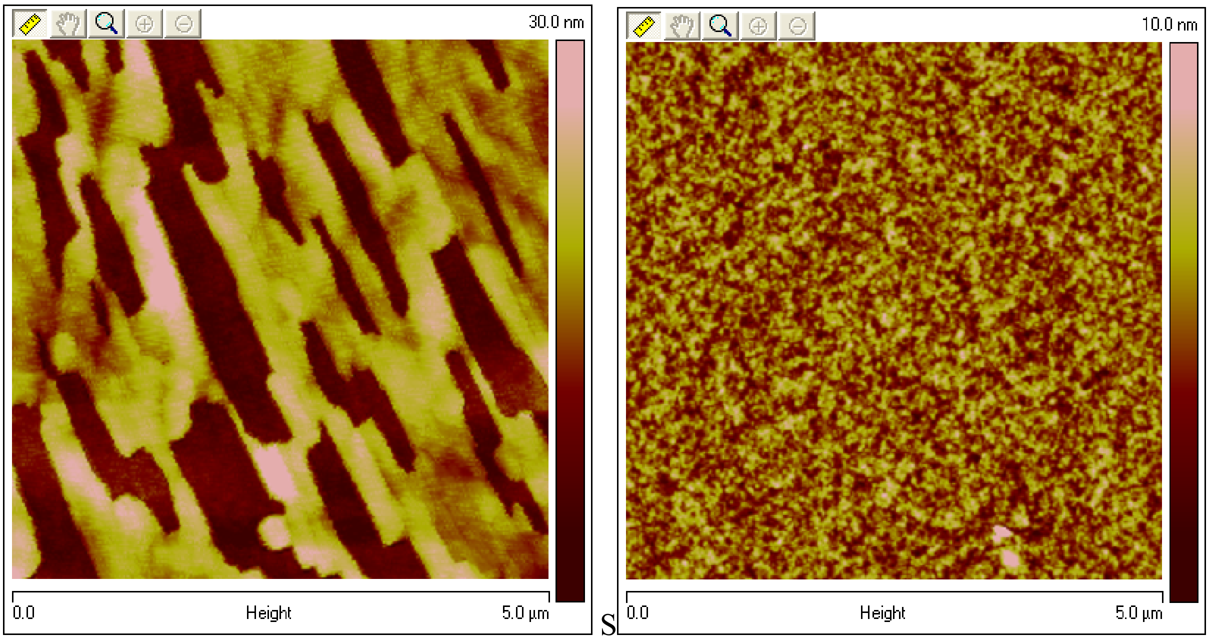


Figure S1. AFM images of PFOX:PC blend films before (left) and after (right) thermally induced crosslinking.

Synthetic Details S1. Synthesis of Compound **4** and **PFO(X)**.

2,7-dibromo-9,9-bis(6-bromohexyl)-9H-fluorene (4) – A two-neck round bottom flask with air condenser was charged with aqueous KOH (150 mL, 50 wt. %), tetrabutylammonium bromide (0.796 g, 2.46 mmol), and 2,7-dibromofluorene (4.000 g, 12.35 mmol). The mixture was placed in an oil bath preheated to 70 °C after which 1,6-dibromohexane (20 mL, 129.96 mmol) was added in one portion. The reaction was stirred for 45 minutes, then cooled to room temperature and extracted with CH_2Cl_2 (4 x 50 mL). The combined organic extracts were washed with aqueous HCl (1 M, 2 x 50 mL), water (50 mL), and brine (50 mL), then dried over $MgSO_4$, filtered, and solvent removed under reduced pressure. The resulting clear, light-orange oil was dissolved in a minimum amount of hexanes and chromatographed on silica eluting with a gradient of 100% hexanes to 9:1 hexanes/CH_2Cl_2. The second eluted compound was collected as a white crystalline solid after removal of solvent (5.203 g, 65%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (dd, 2H, J = 0.5 Hz, 8.0 Hz), 7.46 (dd, 2H, J = 1.8 Hz, 8.0 Hz), 7.43 (dd, 2H, J = 0.5 Hz, 1.8 Hz), 3.297 (t, 4H, J = 6.9 Hz), 1.92 (m, 4H), 1.67 (m, 4H), 1.20 (m, 4H), 1.09 (m, 4H), 0.57 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.1, 139.0, 130.3, 126.0, 121.5, 121.2, 55.6, 40.1, 32.6, 27.8, 23.5. HRMS (GC-EI) calculated for $C_{25}H_{30}Br_4$ M^+ 645.9081, found m/z 645.9066. Anal. Calcd.: C 46.19; H, 4.65; N, 0.00; found C, 46.33; H, 4.49; N, 0.00.

PFO(X) – In a 50 mL Schlenk tube was combined **2** (0.450 g, 0.66 mmol), **1** (0.422 g, 0.66 mmol), K_2CO_3 (1.817 g, 13.15 mmol), toluene (6 mL), water (6 mL), and aliquot 336 (2 drops). The biphasic system was degassed with three freeze-pump-thaw cycles, then backfilled with nitrogen and warmed to room temperature. Tetrakistrisphenylphosphine palladium(0) (0.008 g, 0.01 mmol) was added and the reaction degassed three more times, then backfilled with nitrogen, warmed to room temperature, and heated to 70 °C for 48 hours. At this point, phenyl boronic acid pinacol ester (1 small scoop, obtained from Aldrich) was added and the endcapping reaction allowed to proceed for 24 hours, followed by injection of bromobenzene (0.2 mL) and the final endcapping step allowed to continue for a final 24 hours. Upon cooling to room temperature the crude polymer was precipitated into rapidly stirring methanol and collected by suction filtration on a nylon membrane (20 μm porosity). The crude polymer was further purified by Soxhlet extraction with methanol (24 hours), hexane (24 hours), and chloroform (4 hours). The chloroform fraction was reduced in volume to approximately 15 mL and a small amount of palladium scavenger (diethylammonium diethyldithiocarbamate) added. After stirring for 1 hour, the polymer was reprecipitated into rapidly stirring methanol and isolated by suction filtration as a grey-colored fibrous solid (0.493 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, 4H, *J* = 7.8 Hz), 7.65 (m, 8H), 7.32 (dd, 2H, *J* = 0.9, 1.8 Hz), 6.26 (m, 2H, *J* = 1.8, 3.1 Hz), 6.21 (d, 2H, *J* = 3.0 Hz), 4.33 (s, 4H), 3.32 (t, 4H, *J* = 6.6 Hz), 2.08 (br m, 4H), 1.40 (m, 4H), 1.11 (br m, 36 H), 0.79 (m, 10H). Anal. Calcd.: C 83.98; H, 9.03; N, 0.00; found C, 83.61; H, 9.05; N, 0.00. GPC M_n = 38 047 g/mol; M_w = 71 061 g/mol; PDI = 1.87.

Figure S2. ^{1}H NMR spectrum of compound **PFO(X)**.

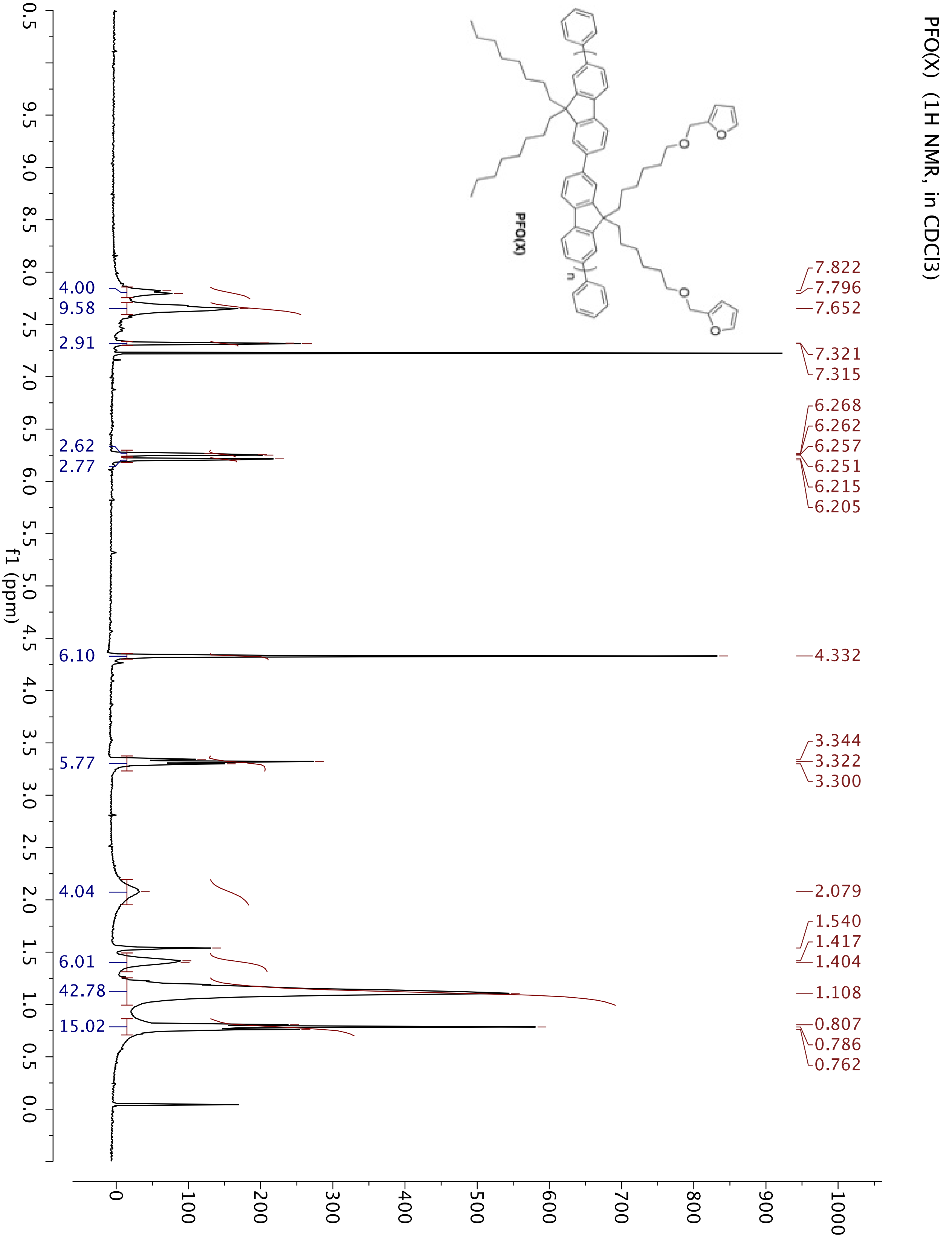


Figure S3. ^{1}H NMR spectrum of **bE-BTD(X)**.

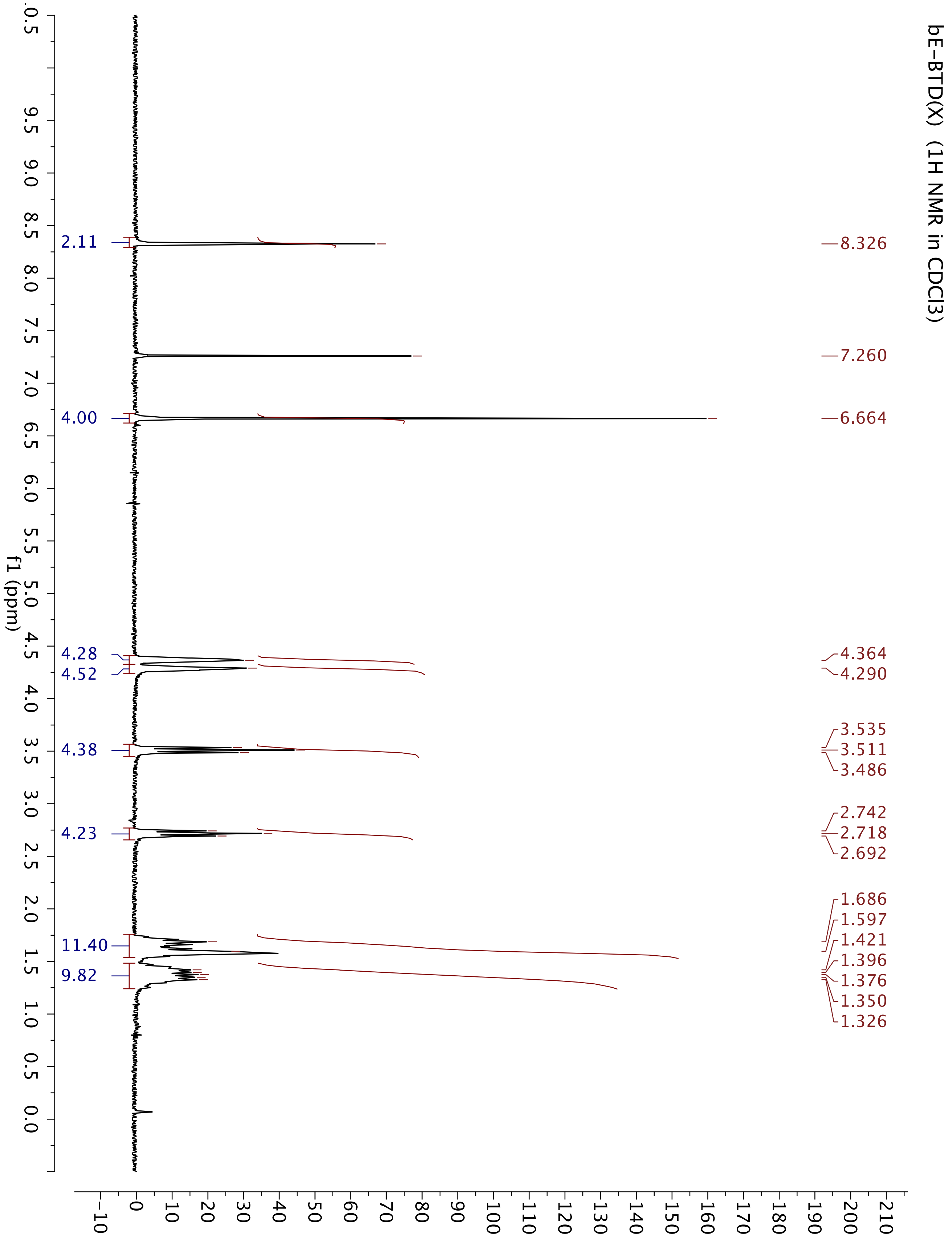


Figure S4. ^{13}C NMR spectrum of **bE-BTD(X)**.

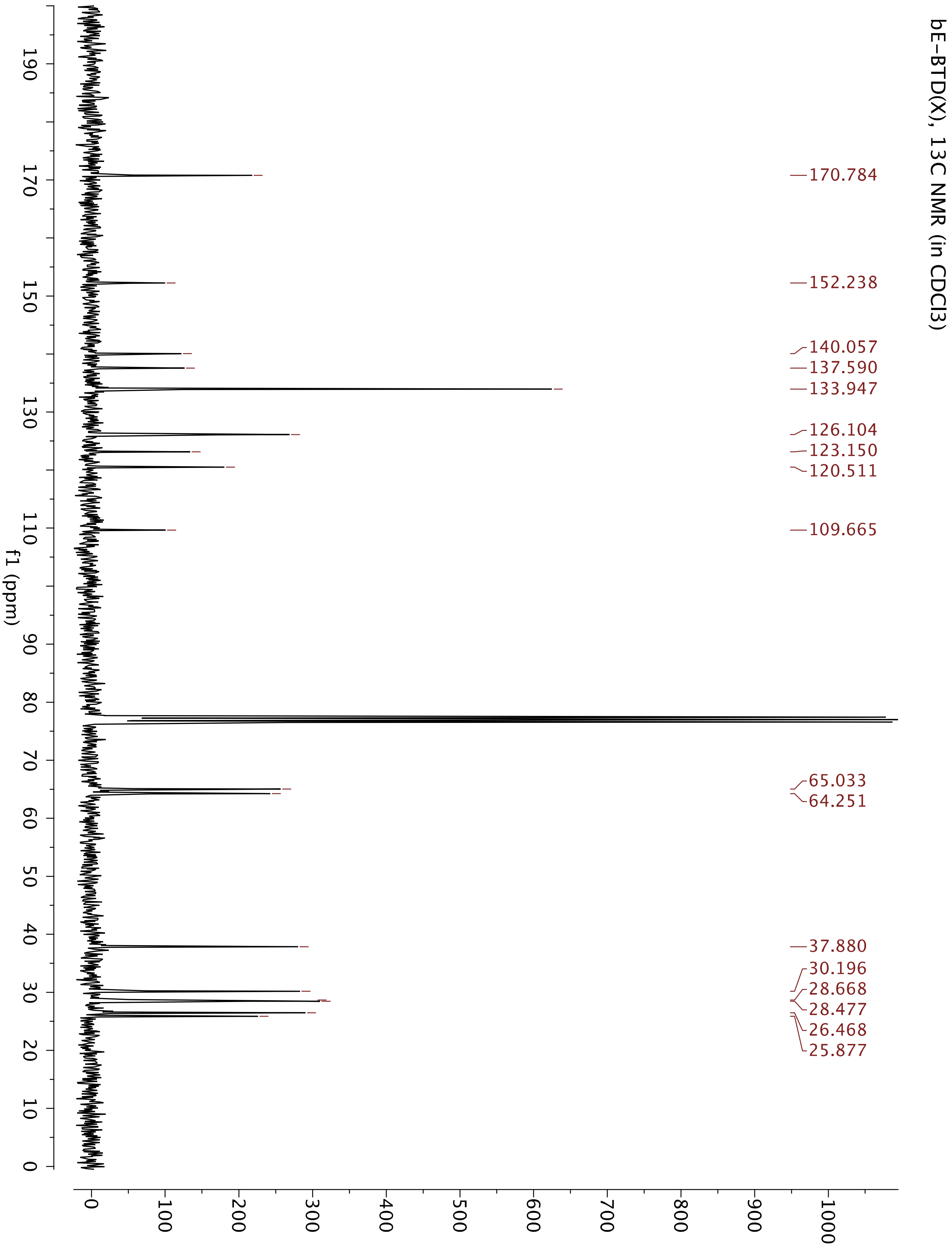


Figure S5. ^{1}H NMR spectrum of compound **2**.

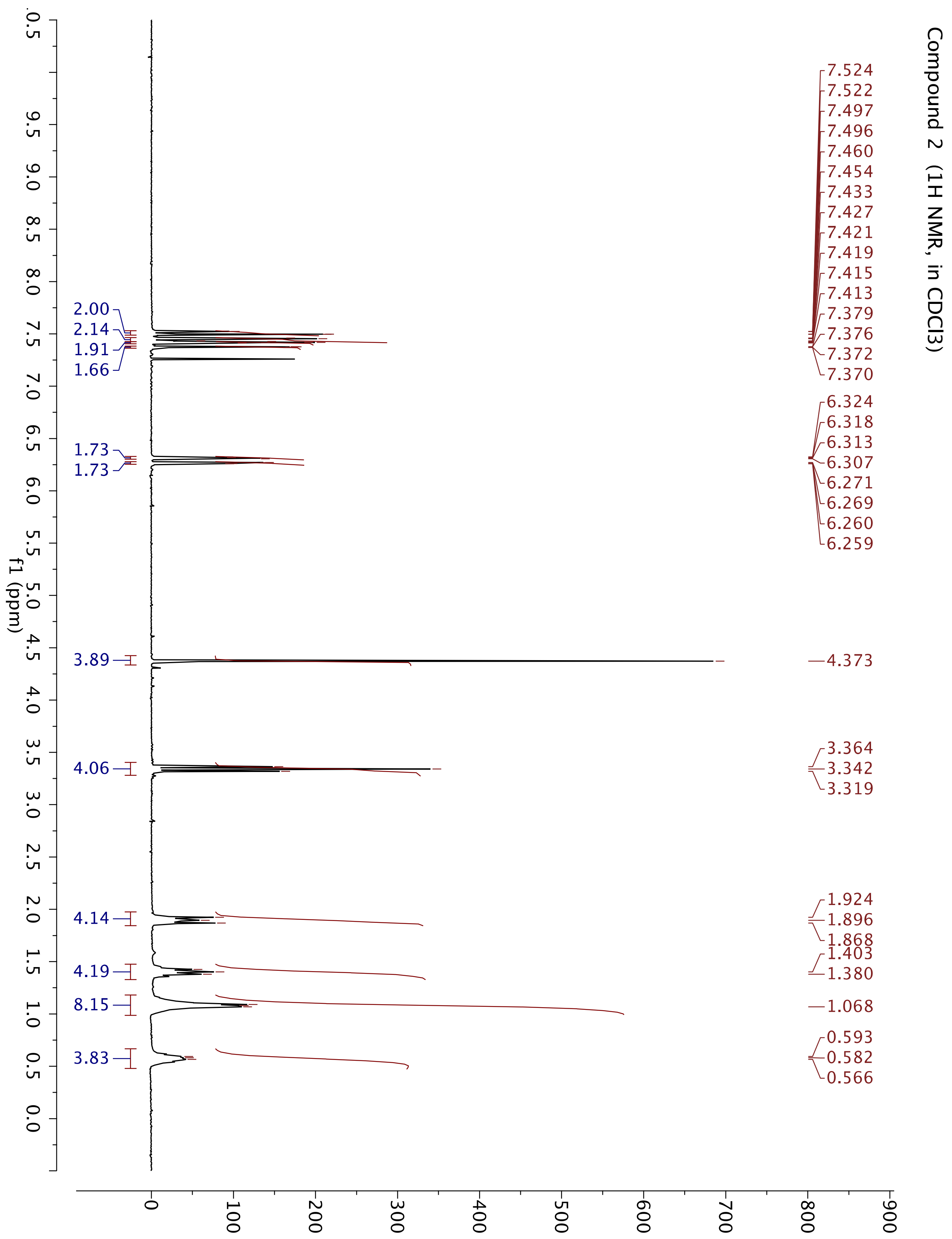


Figure S6. ^{13}C NMR spectrum of compound **2**.

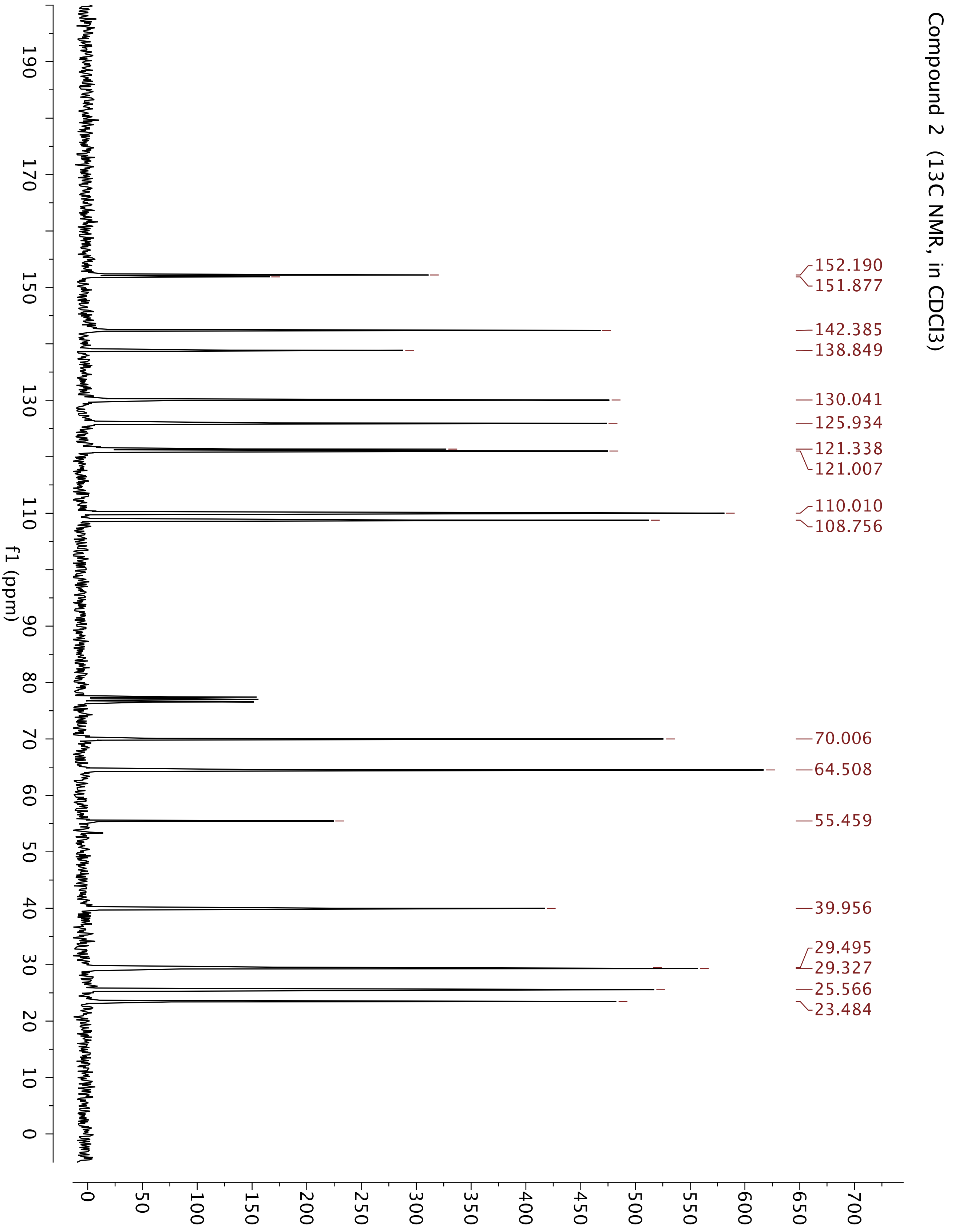


Figure S7. ^{1}H NMR spectrum of compound **4**.

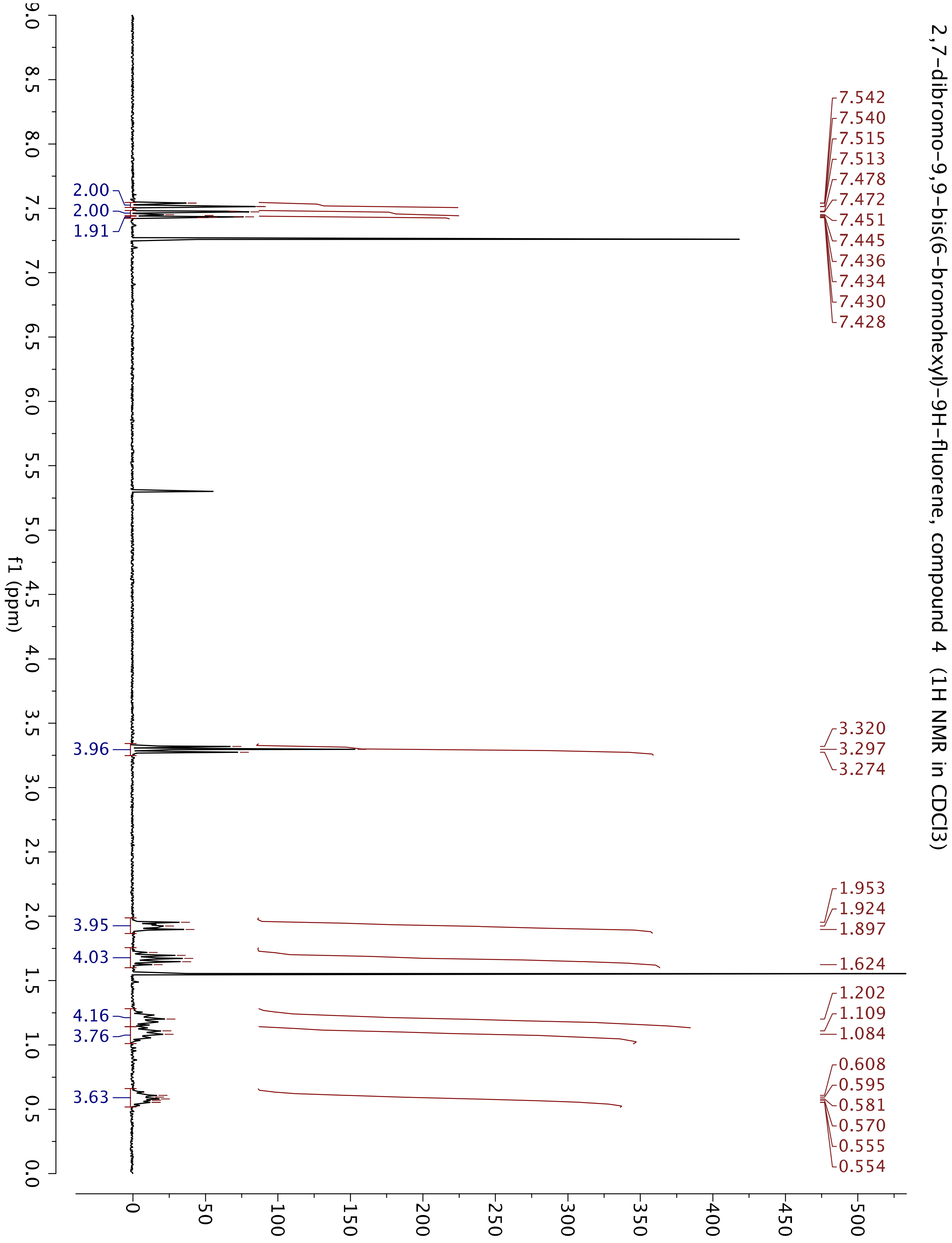


Figure S8. ^{13}C NMR spectrum of compound **4**.

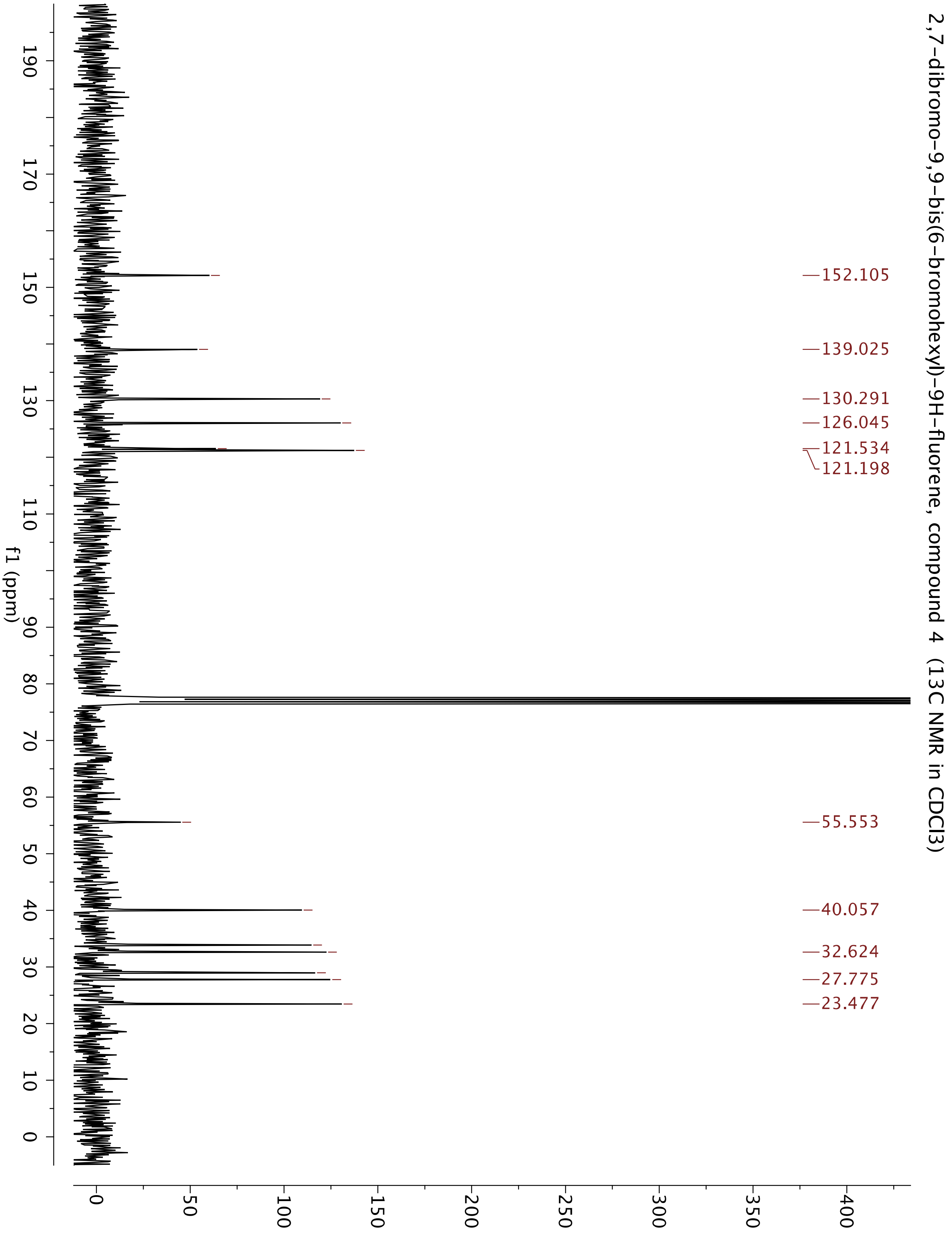


Figure S9. ^{1}H NMR spectrum of compound **9**.

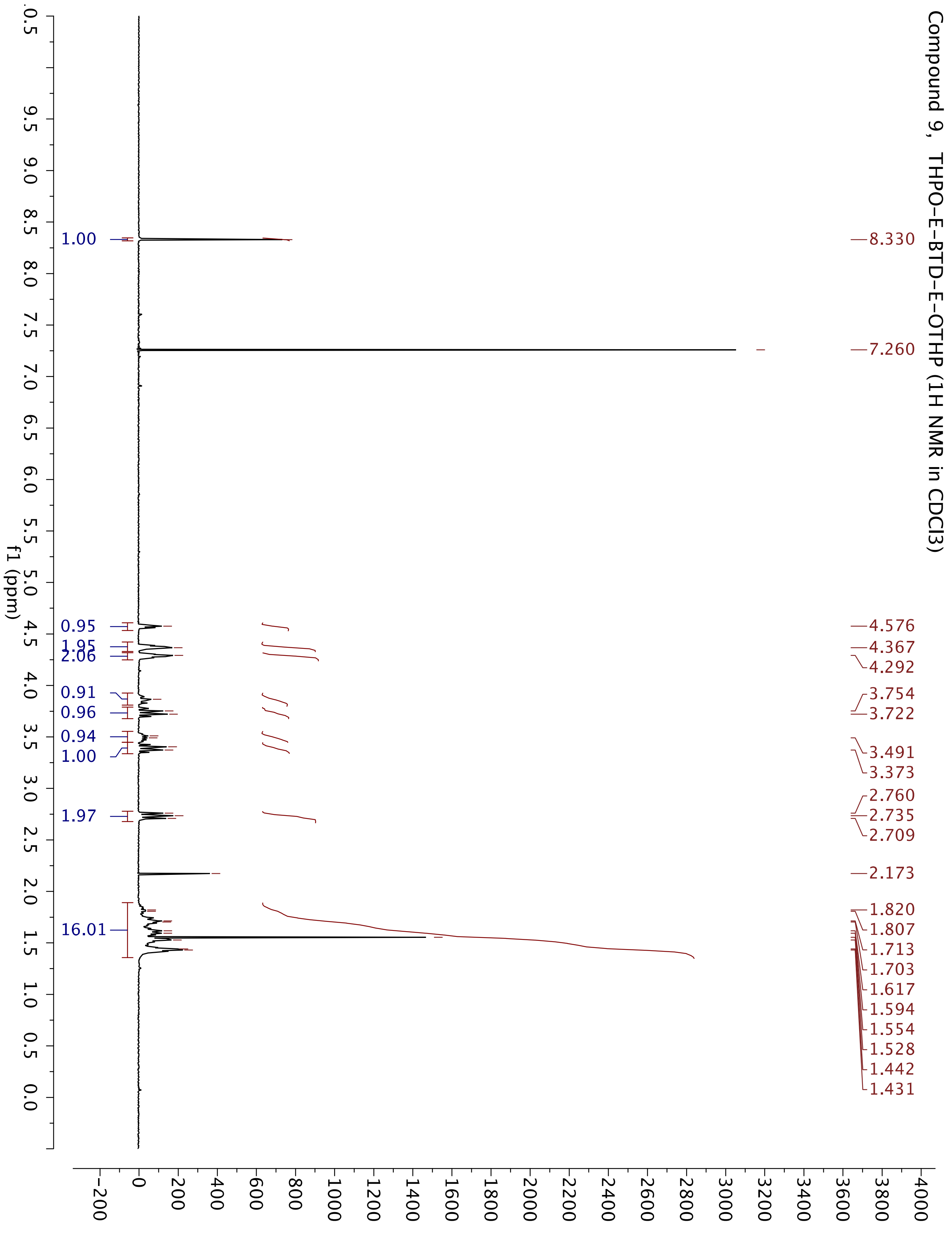


Figure S10. ^{13}C NMR spectrum of compound **9**.

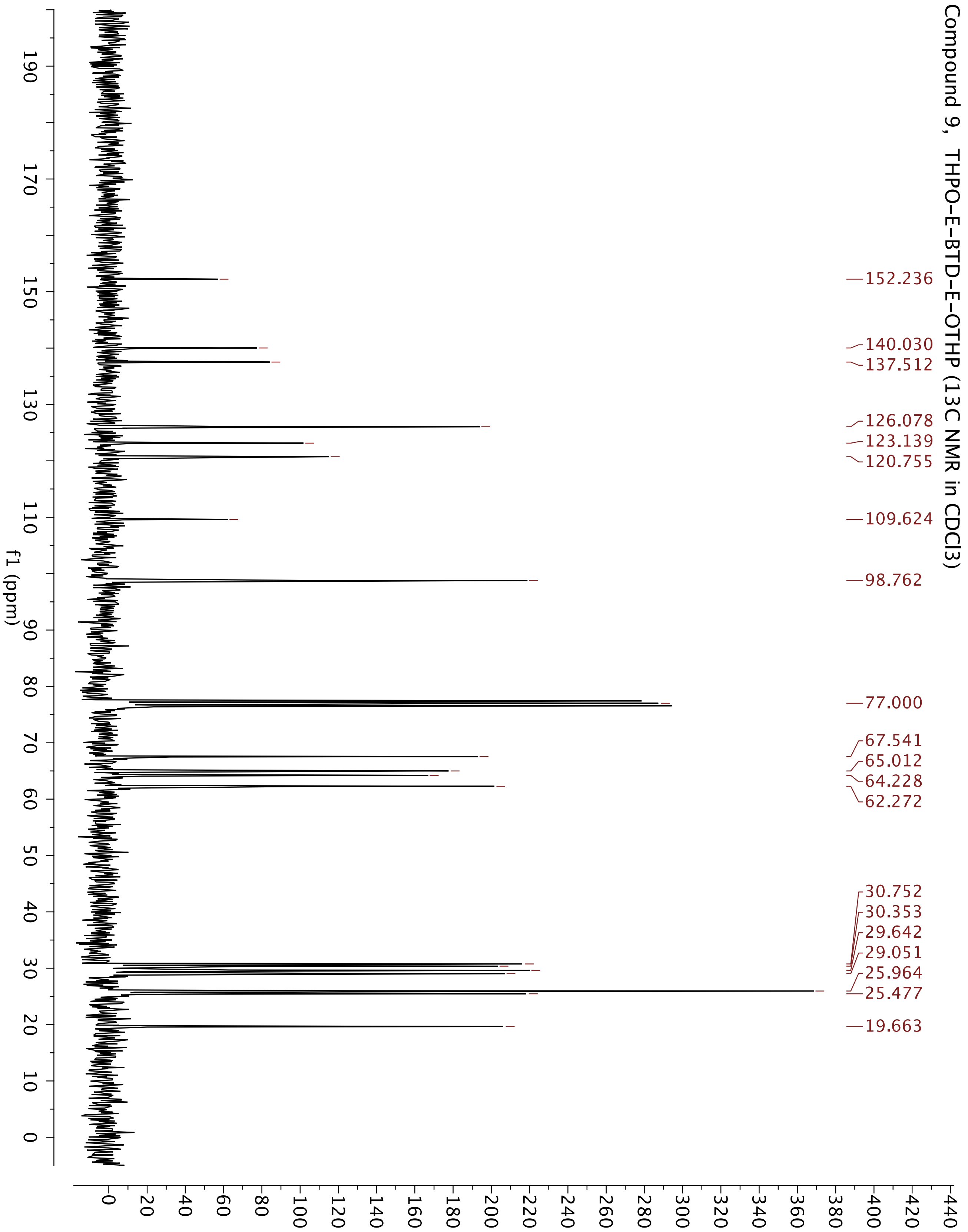
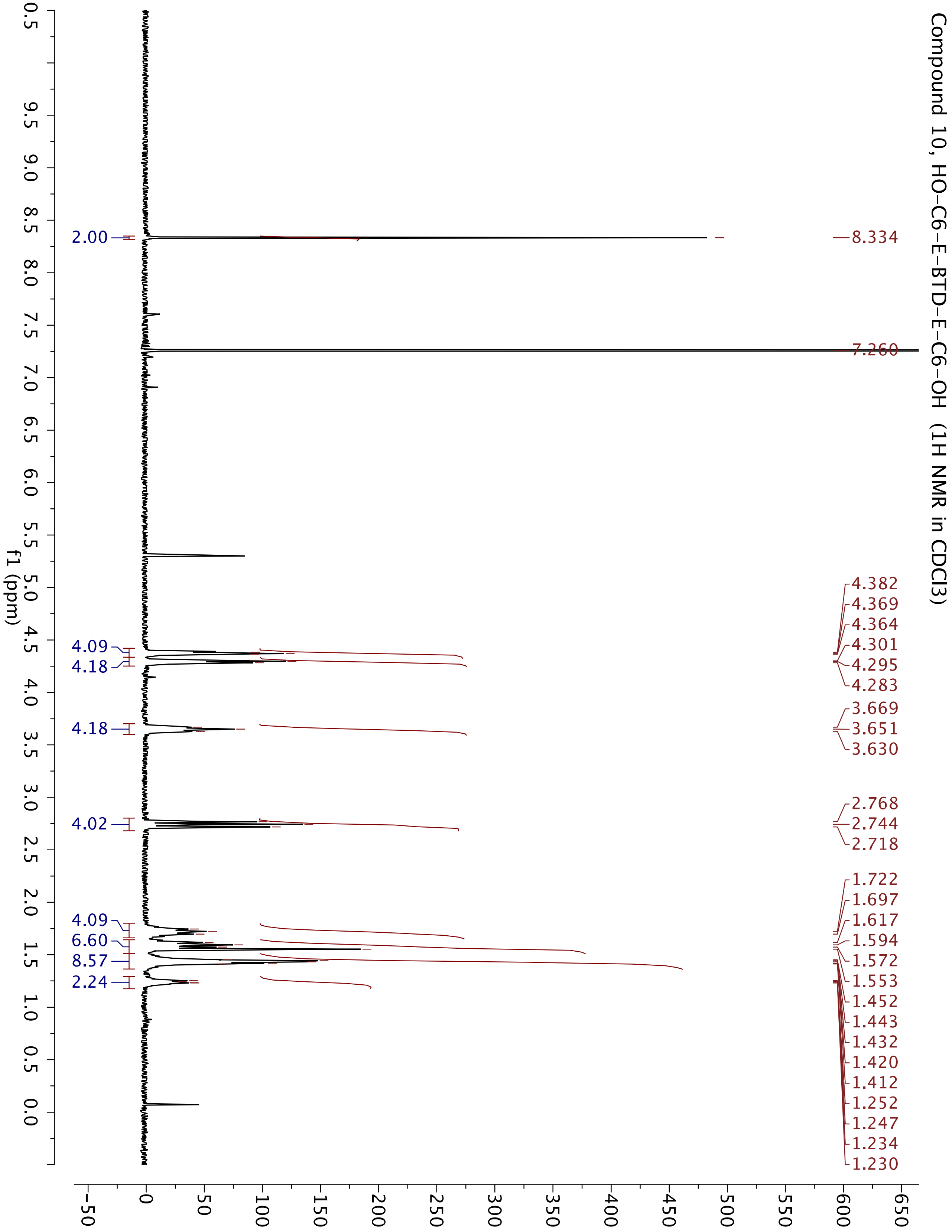


Figure S11. ^{1}H NMR spectrum of compound **10**.



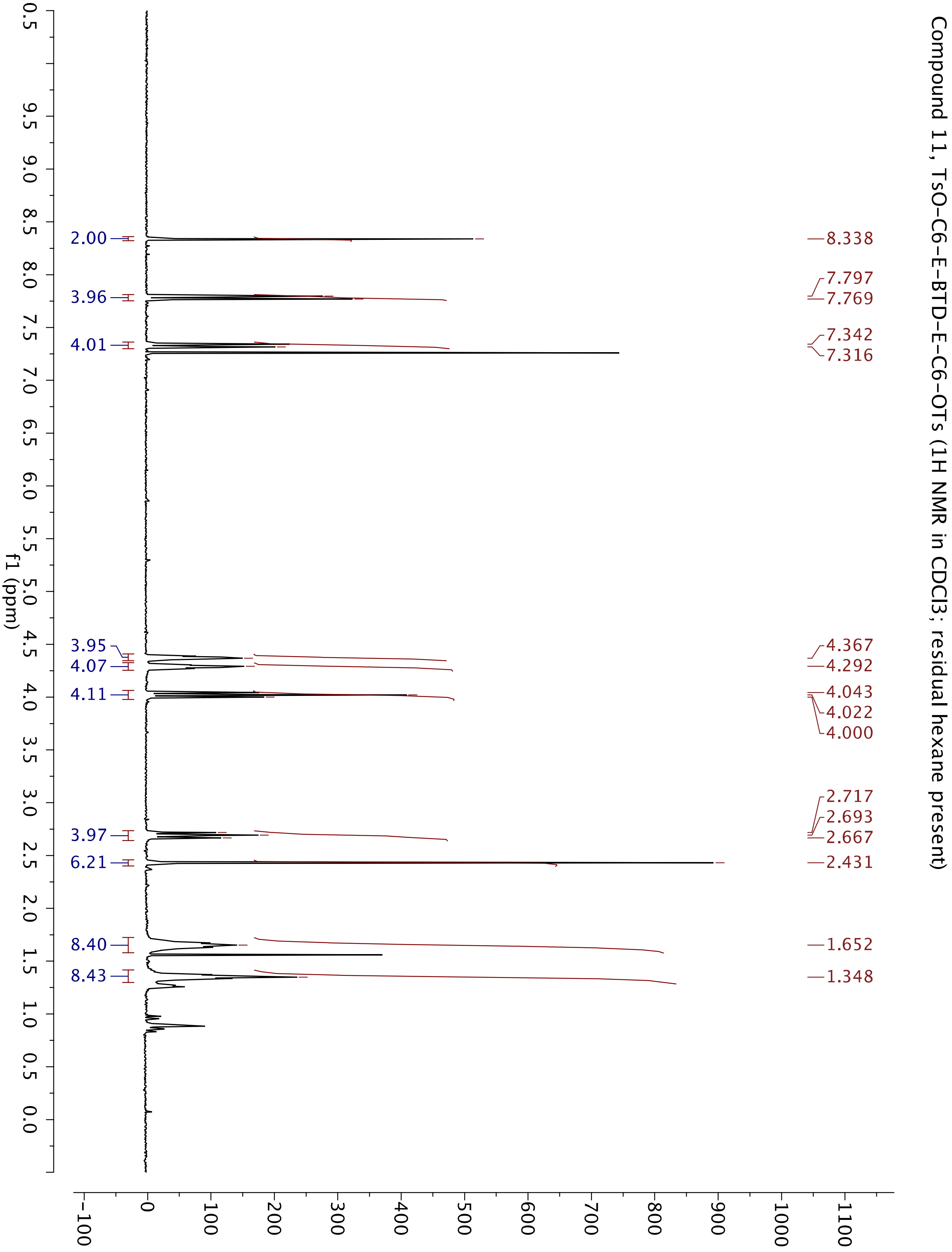


Figure S12. ^{1}H NMR spectrum of compound **11**.

Figure S13. ^{13}C NMR spectrum of compound **11**.

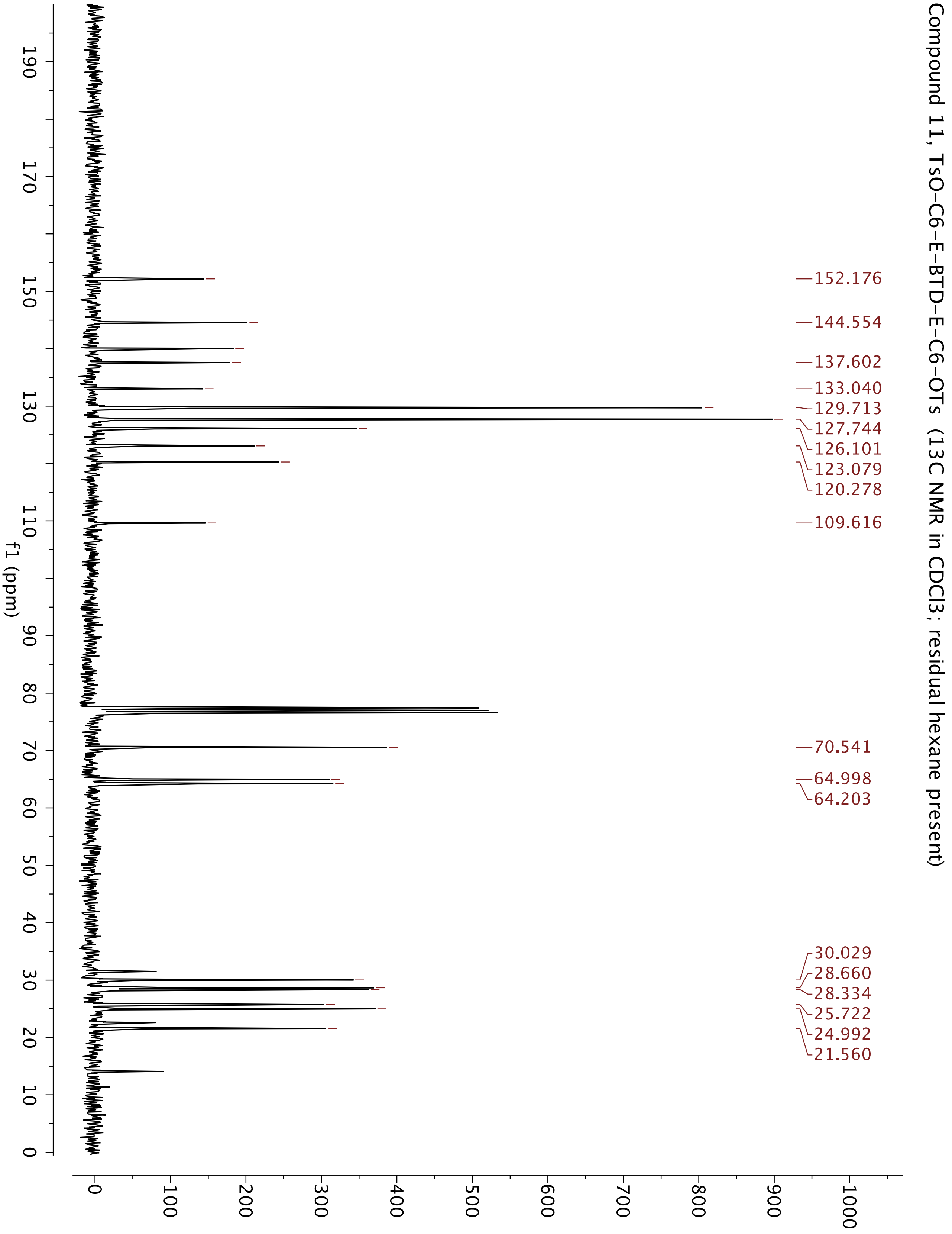


Figure S14. ^{1}H NMR spectrum of compound **PC**.

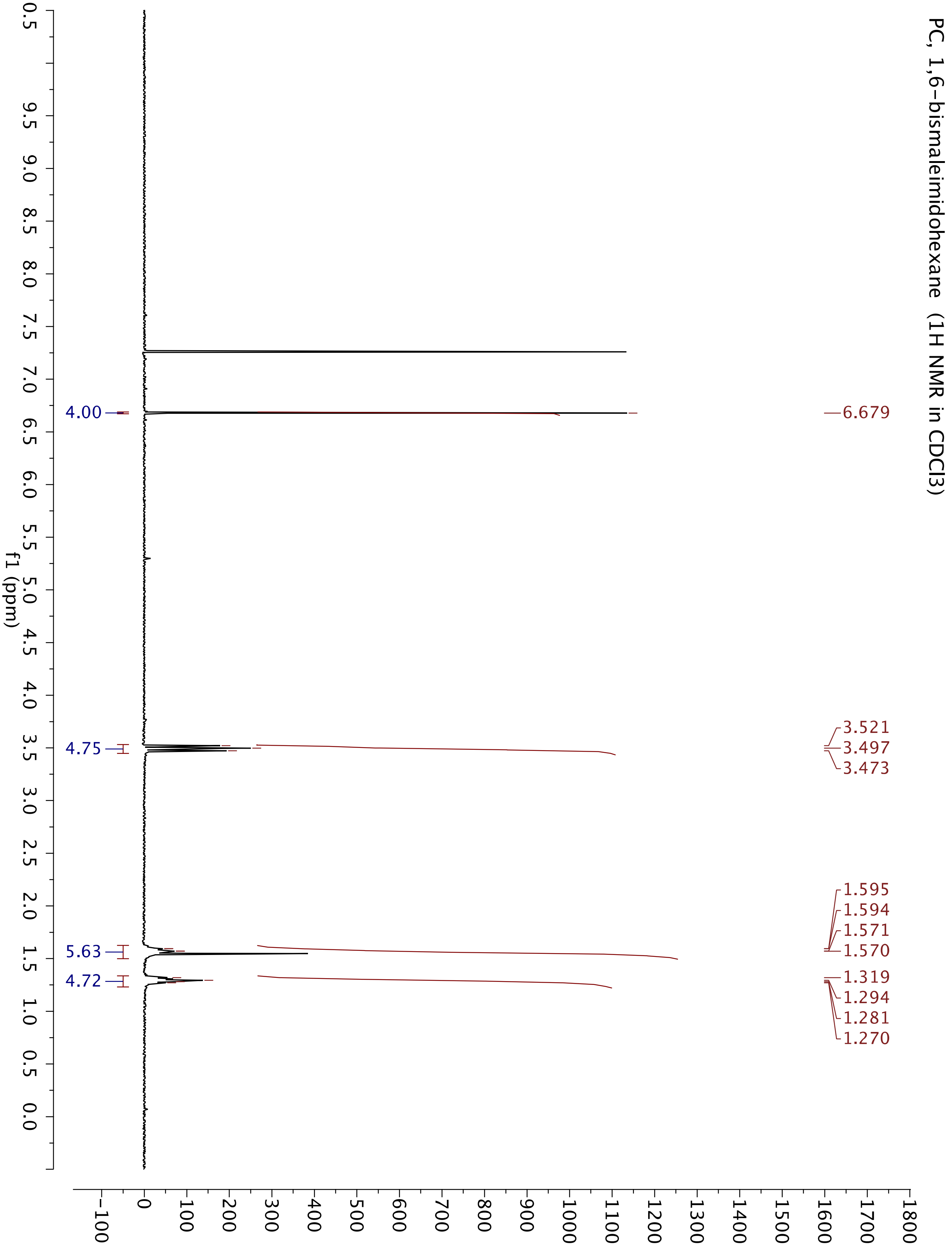


Figure S15. Current density vs. voltage curves for non-crosslinked **bE-BTD(X)** doped **PFO(X)** devices with no **PC**.

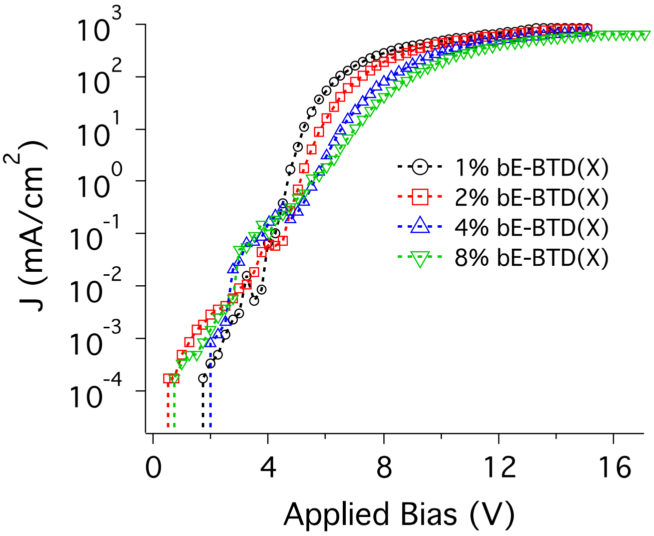


Figure S16. Current density vs. voltage curves for crosslinked **bE-BTD(X)** doped **PFO(X)/PC** devices with no ETL (a) and with an ETL consisting of **TAZ** doped in **PFO** (b).