

Catalytic Synthesis of Conjugated Azopolymers from Aromatic Diazides

Supporting Information

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1. General Information

General Considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under an atmosphere of N₂. Solvents were dried and degassed by passing through a column of activated alumina and sparging with Ar gas. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and stored over activated 3 Å molecular sieves prior to use. All other reagents and starting materials were purchased from commercial vendors and used without further purification unless otherwise noted. Liquid reagents were degassed and stored over activated 3 Å molecular sieves prior to use. The (*i*-PrNDI)Ni₂(C₆H₆) complex (**1**), was prepared according to previously reported procedures.¹

Physical Methods. ¹H NMR spectra were collected at room temperature on a Bruker Avance-III 800, Bruker AV-III-400-HD, Bruker DRX 500 MHz, or Varian Inova300 spectrometer. ¹H and ¹³C NMR spectra are reported in parts per million relative to tetramethylsilane, using the residual solvent resonances as an internal standard. UV-vis measurements were acquired on an Agilent Cary 6000i UV-Vis-nIR spectrophotometer using a 1-cm two-window quartz cuvette. High-resolution mass data were obtained using a 6320 Ion Trap MS system. GPC data were obtained using a EcoSEC HLC-8321GPC/HT with a refractive index (RI) detector at 50 °C or a TOSOH ECOSEC HLC-8320 GPC run at 180 °C. IR data were collected on a Thermo Nicolet 6700 FT-IR spectrometer with an MCT-A detector and a KBr beam splitter with a range of 800–4500 cm⁻¹. Emission spectra were collected using an Edinburgh Instruments FLS980 Steady State Fluorescence Spectrometer with a xenon lamp. Thermogravimetric analysis was collected using a TA Instrument Q50 TGA instrument with a heating rate of 20 °C·min⁻¹ under an N₂ atmosphere.

Spectroelectrochemistry Experiments. Spectroelectrochemistry data for **10** were obtained using a CHI 660E Potentiostat and a Flame Vis-NIR Fiber Optic Spectrometer Ocean Optics spectrometer. Electrochemical measurements of **15** were performed using a Gamry Interface 1000 Potentiostat. Cyclic voltammograms were acquired using a glassy carbon working electrode (3 mm diameter disk) under an atmosphere of N₂. The potentials were internally referenced to the reversible Fc/Fc⁺ couple.

Photoswitching Experiments. An in-house irradiation setup was built using a TENMA 72-2685 power supply, a 3D printed holder for a 1-cm UV-Vis cuvette bearing 3 unmounted LEDs. Two light sources were used: 395 nm (6 mW at 20mA) and 555 nm (1 mW at 20 mA) from Thorlabs, Newton, NJ, USA. The irradiance is 18 mW/cm² for the 395 nm LED unit and 3 mW/cm² for the 555 nm LED unit.

X-Ray Crystallography. Single Crystal XRD Data Collection. A single crystal of **17a** was coated with a trace of fomblin oil, affixed onto a MiTeGen micromesh mount and transferred to the goniometer head of a Bruker Quest diffractometer with kappa geometry, an I-μ-S microsource X-ray tube, laterally graded multilayer (Goebel) mirror single crystal for monochromatization, a Photon3 CMOS area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Cu Kα radiation (λ = 1.54178 Å) at 100 K. Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3.²

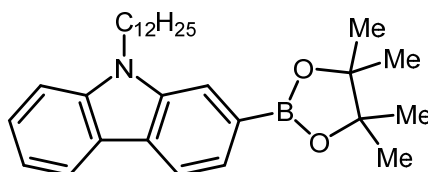
The space group was assigned and the structure solved by direct methods using XPREP within the SHELXTL suite of programs³ from an integration using only the major domain. The structure was refined using the hklf 5 routine by full matrix least squares against F^2 with all reflections of component 1 (including the overlapping ones), using Shelxl2016⁴ using the graphical interface Shelxle⁵ resulting in a BASF value of 0.392(1).

H atoms were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 Å for aromatic C-H, 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH₂ and CH₃ moieties, and 0.84 Å for O-H bonds, respectively. Methyl H and hydroxyl atoms were allowed to rotate but not to tip to best fit the experimental electron density. $U_{\text{iso}}(\text{H})$ values were set to a multiple of $U_{\text{eq}}(\text{C})$ with 1.5 for CH₃, and 1.2 for C-H units, respectively. Additional data collection and refinement details, including description of disorder and/or twinning (where present) can be found in Section 13.

Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2054149 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2. Synthesis of Organoazides

SAFETY NOTE: Organoazides are high energy molecules, and they can be thermally unstable and shock sensitive. In order to minimize explosion hazards, care should be taken to avoid organoazides with low C-to-N ratios (generally C-to-N ratios >3 are recommended), limit scale to the extent possible, and store organoazides in solution. We did not encounter any specific safety concerns with the organoazides used in these studies. TGA studies were carried out using diazides **S10** and **2**.

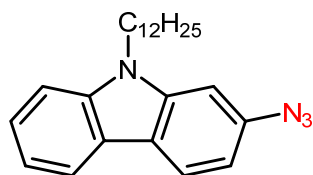


9-dodecyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (S1). This procedure is based on a modified literature procedure.⁶ In an N₂ filled glovebox, a Schlenk tube was charged with 2-bromo-9-dodecyl-9H-carbazole⁷, (0.50 g, 1.2 mmol, 1.0 equiv), Pd(dppf)Cl₂ (0.16 g, 0.22 mmol, 0.18 equiv), bis(pinacolato)diboron (0.37 g, 1.5 mmol, 1.2 equiv), KOAc (1.4 g, 15 mmol, 12 equiv), and 1,4-dioxane (33 mL). The reaction vessel was sealed, removed from the glovebox, and heated at 80 °C for 16 h. After cooling to room temperature, the reaction mixture was filtered through celite, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, 30% CH₂Cl₂/hexanes, R_f = 0.4). The product was isolated as a colorless oil (0.32 g, 57% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.17 – 8.11 (m, 2H), 7.91 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.27 – 7.22 (m, 1H), 4.36 (t, *J* = 7.4 Hz, 2H), 1.95 – 1.86 (m, 2H), 1.43 (s, 12H), 1.28 (m, 18H), 0.91 (t, *J* = 7.0 Hz, 3H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 141.0, 140.0, 126.2, 125.4, 125.1, 124.9, 122.6, 120.8, 119.6, 118.7, 115.1, 108.9, 83.8, 43.0, 32.0, 29.6, 29.1, 27.3, 25.2, 25.0, 24.9, 22.7, 14.1.

HRMS (APCI): calcd for C₃₀H₄₅NO₂B¹⁰ [M + H]⁺: 461.3574; found: 461.3562

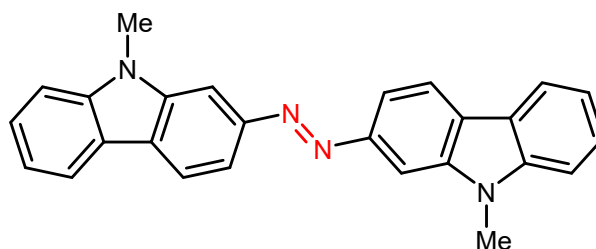


2-azido-9-dodecyl-9H-carbazole (4b). This procedure is based on a modified literature procedure.⁸ NaN₃ (0.068 g, 1.0 mmol, 1.5 equiv) and Cu(OAc)₂ (0.013 g, 0.069 mmol, 0.10 equiv) were added to a solution of **S1** (0.32 g, 0.69 mmol, 1.0 equiv) in a mixture of CHCl₃ (5.7 mL) and MeOH (5.7 mL). The reaction was heated at 55 °C and stirred under air for 24 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, 100% hexanes, R_f = 0.8). The product was isolated as an off-white solid (0.18 g, 70% yield).

¹H NMR (800 MHz, CDCl₃) δ 8.05 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.25 (t, J = 7.3 Hz, 1H), 7.01 (s, 1H), 6.95 (d, 1H), 4.26 (t, J = 7.3 Hz, 2H), 1.90 – 1.84 (m, 2H), 1.39 – 1.24 (m, 18H), 0.89 (t, J = 7.2 Hz, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 141.3, 140.8, 137.7, 125.5, 122.5, 121.4, 120.3, 120.0, 119.2, 110.2, 108.7, 99.0, 43.1, 31.8, 29.5, 29.5, 29.4, 29.3, 29.3, 28.8, 27.2, 22.6, 14.1.

HRMS (APCI): calcd for C₂₄H₃₂N₄ [M + H]⁺: 377.2700; found: 377.2704

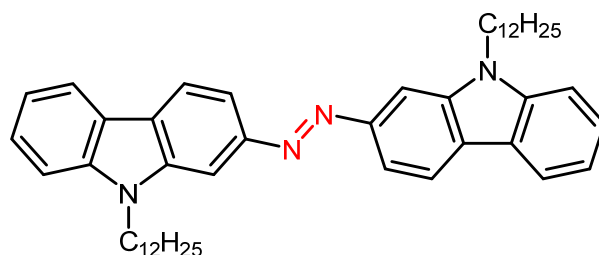


(E)-1,2-bis(9-methyl-9H-carbazol-2-yl)diazene (5a). This procedure is based on a modified literature procedure.⁹ In an N₂ filled glovebox, a 20-mL vial was charged with **4a** (0.044 g, 0.20 mmol, 1.0 equiv), toluene (4.0 mL), and a magnetic stir bar. While stirring, **1** (7.0 mg, 0.010 mmol, 5 mol%) dissolved in toluene (1.0 mL) was added to the reaction vial. The vial was sealed, and the reaction mixture was stirred at room temperature. After 2 h, the reaction vial was opened to air, and the crude mixture was directly loaded onto a column (SiO₂, 5% EtOAc/hexanes, R_f = 0.3) for purification. The product was isolated as an orange solid. Run 1: 0.033 g, 44% yield; Run 2: 0.035 g, 44% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, J = 8.3 Hz, 2H), 8.14 (d, J = 7.8 Hz, 2H), 8.07 (s, 2H), 7.97 (d, J = 8.0 Hz, 2H), 7.53 (m, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.30 – 7.27 (m, 2H), 3.97 (s, 6H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 151.3, 142.5, 141.4, 126.6, 125.1, 122.4, 120.9, 120.6, 119.4, 115.3, 108.7, 102.8, 29.3.

HRMS (APCI): calcd for C₂₆H₂₁N₄ [M + H]⁺: 389.1761; found: 389.1765



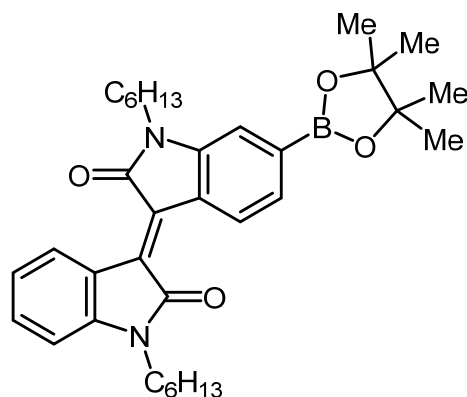
(E)-1,2-bis(9-dodecyl-9H-carbazol-2-yl)diazene (5b). This procedure is based on a modified literature procedure.⁹ In an N₂ filled glovebox, a 20-mL vial was charged with **4b** (0.075 g, 0.20 mmol, 1.0 equiv), toluene (4.0 mL), and a magnetic stir bar. While stirring, **1** (7.0 mg, 0.010 mmol, 5 mol%) dissolved in toluene (1.0 mL) was added to the reaction vial. The vial was sealed, and the reaction mixture was stirred at room temperature. After 2 h, the reaction vial was opened to air, and the crude mixture was directly loaded onto a column (SiO₂, 2% EtOAc/hexanes, R_f = 0.2) for purification. The product was isolated as a yellow solid. Run 1: 0.066 g, 95% yield; Run 2: 0.066 g, 95% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.3 Hz, 2H), 8.16 (d, *J* = 7.8 Hz, 2H), 8.09 (d, *J* = 1.6 Hz, 2H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.49 (m, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 4.41 (t, *J* = 7.3 Hz, 4H), 1.96 (p, *J* = 7.4 Hz, 4H), 1.50 – 1.42 (m, 4H), 1.41 – 1.34 (m, 4H), 1.33 – 1.22 (m, 28H), 0.89 (t, *J* = 6.8 Hz, 6H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 151.2, 141.8, 140.7, 126.4, 125.0, 122.4, 120.8, 120.5, 119.2, 114.1, 108.9, 104.0, 43.2, 31.8, 29.6, 29.5, 29.4, 29.3, 29.0, 27.3, 22.6, 14.1.

UV–Vis–NIR (C₆H₅Cl, 0.143 mM): λ_{max}, nm (ε, M⁻¹ cm⁻¹): 302 (1800), 398 (4900).

HRMS (APCI): calcd for C₄₈H₆₅N₄ [M + H]⁺: 697.5204 ; found: 697.5207

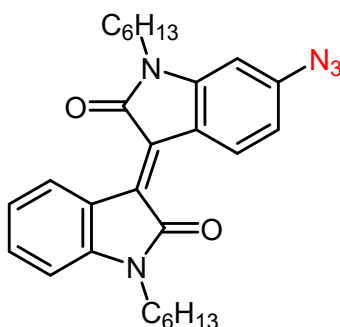


(E)-1,1'-dihexyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[3,3'-biindolinylidene]-2,2'-dione (S2). This procedure is based on a modified literature procedure.⁶ In an N₂ filled glovebox, a Schlenk tube was charged with (E)-6-bromo-1,1'-dihexyl-[3,3'-biindolinylidene]-2,2'-dione¹⁰ (0.16 g, 0.31 mmol, 1.0 equiv), Pd(dppf)Cl₂ (0.041 g, 0.057 mmol, 0.18 equiv), bis(pinacolato)diboron (0.12 g, 0.47 mmol, 1.5 equiv), KOAc (0.092 g, 0.94 mmol, 3.0 equiv), and 1,4-dioxane (6.2 mL). The reaction vessel was sealed, removed from the glovebox, and heated at 80 °C for 16 h. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, 10% Et₂O/hexanes, R_f = 0.2). The product was isolated as a red solid (0.14 g, 81% yield).

¹H NMR (400 MHz, CDCl₃) δ 9.18 (d, 1H), 9.14 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 7.9, 1.0 Hz, 1H), 7.34 (t, 1H), 7.16 (s, 1H), 7.03 (t, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 3.78 (p, *J* = 15.2, 7.4 Hz, 4H), 1.76 – 1.66 (m, 4H), 1.37 (s, 12H), 1.35 – 1.22 (m, 12H), 0.91 – 0.86 (m, 6H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 167.7, 167.6, 144.8, 143.8, 134.2, 133.4, 132.4, 130.0, 128.9, 128.7, 124.2, 122.0, 121.6, 113.0, 107.8, 84.0, 40.0, 39.9, 31.4, 27.4, 27.3, 26.6, 26.6, 24.8, 22.5, 13.9, 13.9.

HRMS (APCI): calcd for C₃₄H₄₅B¹⁰N₂O₄ [M + H]⁺: 556.3581; found: 556.3571

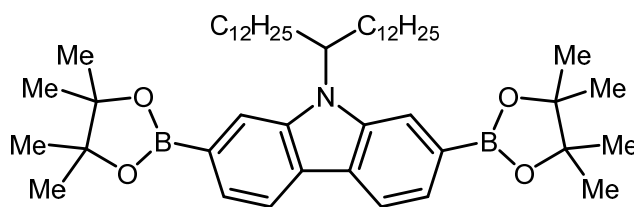


(E)-6-azido-1,1'-dihexyl-[3,3'-biindolinylidene]-2,2'-dione (S3). This procedure is based on a modified literature procedure.⁸ NaN₃ (0.060 g, 0.93 mmol, 1.5 equiv) and Cu(OAc)₂ (0.011 g, 0.062 mmol, 0.10 equiv) were added to a solution of **S1** (0.34 g, 0.62 mmol, 1.0 equiv) in a mixture of CHCl₃ (5.0 mL) and MeOH (5.0 mL). The reaction was heated at 55 °C and stirred under air for 24 h. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, 10% Et₂O/hexanes, R_f = 0.3). The product was isolated as a deep red solid. (0.14 g, 48% yield).

¹H NMR (500 MHz, CDCl₃) δ 9.23 (d, *J* = 8.6 Hz, 1H), 9.14 (d, *J* = 8.0 Hz, 1H), 7.33 (t, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.68 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.36 (d, *J* = 2.2 Hz, 1H), 3.79 – 3.70 (m, 4H), 1.68 (m, 4H), 1.44 – 1.35 (m, 4H), 1.35 – 1.27 (m, 8H), 0.91 – 0.85 (m, 6H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 168.2, 167.9, 146.5, 144.6, 143.8, 132.5, 132.2, 131.6, 129.8, 122.1, 121.7, 118.7, 111.9, 107.9, 99.1, 98.9, 40.2, 40.1, 31.5, 27.5, 26.7, 22.5, 14.0.

HRMS (APCI): calcd for C₂₈H₃₃N₅O₂ [M + H]⁺: 472.2707 found: 472.2717

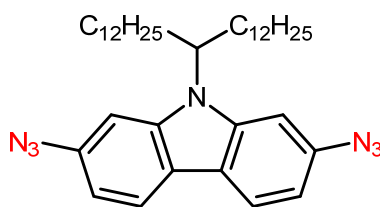


9-(pentacosan-13-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (S4). This procedure is based on a modified literature procedure.⁶ In an N₂ filled glovebox, a Schlenk tube was charged with 2,7-dibromo-9-(pentacosan-13-yl)-9H-carbazole¹¹, (1.0 g, 1.5 mmol, 1.0 equiv), Pd(dppf)Cl₂ (0.39 mg, 0.53 mmol, 0.35 equiv), bis(pinacolato)diboron (0.90 mg, 3.6 mmol, 2.4 equiv), KOAc (1.7 g, 18 mmol, 12 equiv), and 1,4-dioxane (40 mL). The reaction vessel was sealed, removed from the glovebox, and heated at 80 °C for 16 h. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, 50% CH₂Cl₂/hexanes, R_f = 0.4). The product was isolated as a yellow oil (0.64 g, 56% yield).

¹H NMR (800 MHz, CDCl₃) δ 8.14 (d, J = 24.3, 2H), 8.04 (s, 1H), 7.90 (s, 1H), 7.74 – 7.63 (m, 2H), 4.75 – 4.67 (m, 1H), 2.40 – 2.30 (m, 2H), 2.00 – 1.93 (m, 2H), 1.41 (s, 24H), 1.33 – 1.09 (m, 38H), 1.02 – 0.97 (m, 2H), 0.88 (t, J = 7.2 Hz, 6H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 141.9, 138.6, 128.3, 126.0, 124.6, 124.5, 119.96, 119.65, 118.0, 115.4, 83.6, 56.3, 33.8, 31.8, 29.6, 29.5, 29.5, 29.4, 29.3, 29.3, 26.7, 24.9, 22.6, 14.0.

HRMS (APCI): calcd for C₄₉H₈₁B₁₀N₂O₄ [M + H]: 769.6461; found: 769.6446

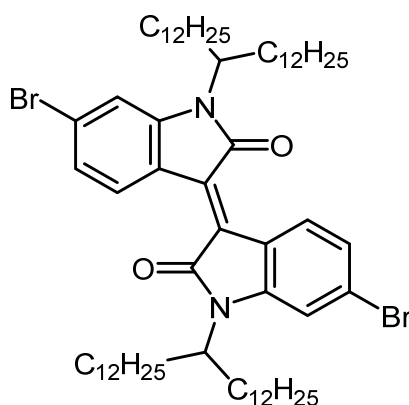


2,7-diazido-9-(pentacosan-13-yl)-9H-carbazole (2). This procedure is based on a modified literature procedure.⁸ NaN₃ (0.13 g, 2.0 mmol, 3.0 equiv) and Cu(OAc)₂ (0.024 g, 0.13 mmol, 0.20 equiv) were added to a solution of **S4** (0.51 g, 0.66 mmol, 1.0 equiv) in a mixture of CHCl₃ (3.3 mL) and MeOH (3.3 mL). The reaction was heated at 55 °C and stirred under air for 24 h. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, 100% hexanes, R_f = 0.6). The product was isolated as a yellow oil (0.29 g, 73% yield).

¹H NMR (800 MHz, CDCl₃) δ 7.98 (dd, J = 28.7, 8.3 Hz, 2H), 7.12 (s, 1H), 6.97 – 6.90 (m, 3H), 4.45 – 4.38 (m, 1H), 2.25 – 2.14 (m, 2H), 1.93 – 1.82 (m, 2H), 1.30 – 1.08 (m, 38H), 1.01 – 0.94 (m, 2H), 0.87 (t, J = 7.2 Hz, 6H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 143.3, 139.7, 137.6, 137.0, 128.3, 121.0, 120.8, 119.7, 110.5, 110.4, 102.0, 99.4, 56.7, 33.4, 31.8, 29.5, 29.5, 29.4, 29.3, 29.2, 26.6, 22.6, 14.1.

HRMS (APCI): calcd for C₃₇H₅₈N₇ [M + H]: 600.4748; found: 600.4752

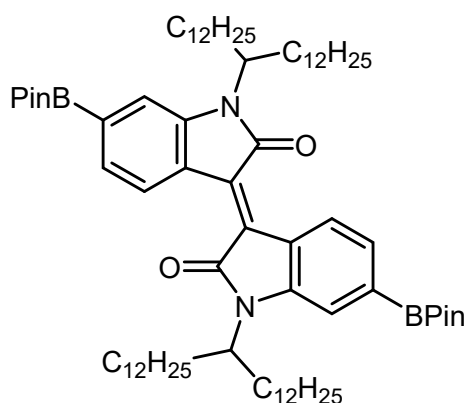


(E)-6,6'-dibromo-1,1'-di(pentacosan-13-yl)-[3,3'-biindolinylidene]-2,2'-dione (S5). This procedure is based on a modified literature procedure.¹² 6,6'-dibromoisindigo¹² (0.42 g, 1.0 mmol, 1.0 equiv) and Cs₂CO₃ (0.98 g, 3.0 mmol, 3.0 equiv) were added to a reaction flask and sealed. The reaction vessel was sparged with N₂ to remove air. Anhydrous N,N-Dimethylformamide (10 mL) was added, and the mixture was heated at 70 °C. After 30 minutes of heating, pentacosan-13-yl 4-methylbenzenesulfonate¹³ (1.2 g, 2.2 mmol, 2.2 equiv) dissolved in anhydrous N,N-dimethylformamide (10.0 mL) was added, and the reaction was allowed to stir for 16 h at 70 °C. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, hexanes, R_f = 0.2). The product was isolated as a deep red solid (0.56 g, 50% yield).

¹H NMR (800 MHz, CDCl₃) δ 9.06 (s, 2H), 7.23 – 6.90 (m, 4H), 4.64 (s, 1H), 3.69 (s, 1H), 2.26 (s, 1H), 1.92 (s, 3H), 1.75 (m, 4H), 1.38 – 1.13 (m, 80H), 0.89 (t, *J* = 7.2 Hz, 12H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 168.1, 144.6, 130.9, 126.4, 124.7, 120.5, 113.1, 52.5, 31.9, 31.9, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 26.6, 22.6, 14.1.

HRMS (APCI): calcd for C₆₆H₁₀₉Br₂N₂O₂ [M + H]⁺: 1119.6850; found: 1119.6866

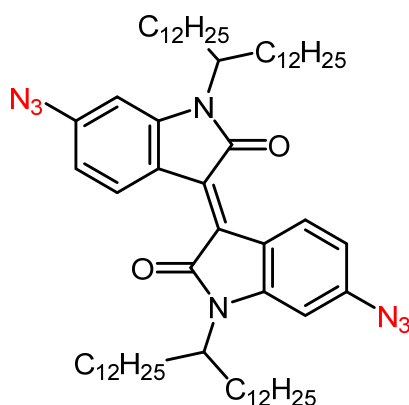


(E)-1,1'-di(pentacosan-13-yl)-6,6'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[3,3'-biindolinylidene]-2,2'-dione (S6). This procedure is based on a modified literature procedure.⁶ In an N₂ filled glovebox, a Schlenk tube was charged with **S5** (0.56 g, 0.50 mmol, 1.0 equiv), Pd(dppf)Cl₂ (0.022 g, 0.030 mmol, 0.060 equiv), bis(pinacolato)diboron (0.38 g, 1.5 mmol, 3.0 equiv), KOAc (0.29 g, 3.0 mmol, 6.0 equiv), and 1,4-dioxane (10.0 mL). The reaction vessel was sealed, removed from the glovebox, and heated at 80 °C for 16 h. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, 20% CH₂Cl₂/hexanes, R_f = 0.25). The product was isolated as a deep red solid (0.49 g, 80% yield).

¹H NMR (400 MHz, CDCl₃) δ 9.09 (s, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.26 (s, 3H), 4.64 (s, 1H), 3.88 (s, 1H), 2.40 – 1.90 (m, 4H), 1.82 – 1.66 (m, 4H), 1.36 (s, 24H), 1.32 – 1.15 (m, 80H), 0.86 (t, *J* = 7.0 Hz, 12H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 168.0, 142.9, 133.6, 128.5, 124.3, 115.2, 83.9, 52.3, 32.0, 31.8, 29.6, 29.6, 29.5, 29.4, 29.3, 26.7, 24.8, 22.6, 14.1.

HRMS (APCI): calcd for C₇₈H₁₃₃B₁₀N₂O₄ [M + H]⁺: 1215.0381; found: 1215.0417

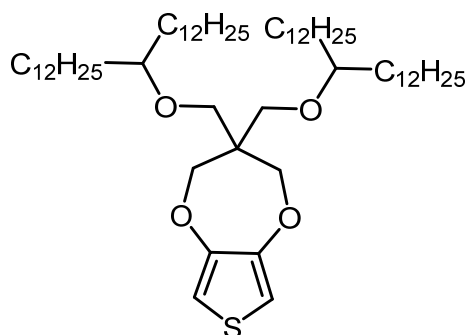


(E)-6,6'-diazido-1,1'-di(pentacosan-13-yl)-[3,3'-biindolinylidene]-2,2'-dione (S7). This procedure is based on a modified literature procedure.⁸ NaN₃ (0.036 g, 0.56 mmol, 3.0 equiv) and Cu(OAc)₂ (7.0 mg, 0.037 mmol, 0.20 equiv) were added to a solution of **S6** (0.23 g, 0.19 mmol, 1.0 equiv) in a mixture of CHCl₃ (3.5 mL) and MeOH (3.5 mL). The reaction was heated at 55 °C and stirred under air for 16 h. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, 10% CH₂Cl₂/hexanes, R_f = 0.3). The product was isolated as a deep red solid (0.098 g, 50% yield).

¹H NMR (500 MHz, CDCl₃) δ 9.17 (s, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 6.55 (s, 2H), 4.64 (s, 1H), 3.68 (s, 1H), 2.26 (s, 1H), 1.90 (s, 3H), 1.78 – 1.67 (m, 4H), 1.37 – 1.14 (m, 80H), 0.87 (t, *J* = 6.9 Hz, 12H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 168.7, 145.2, 143.5, 131.1, 131.1, 118.8, 111.5, 101.1, 52.4, 31.9, 29.9, 29.6, 29.6, 29.5, 29.4, 26.7, 23.0, 22.7, 14.1.

HRMS (APCI): calcd for C₆₆H₁₀₉N₈O₂ [M + H]⁺: 1045.8668; found: 1045.8696

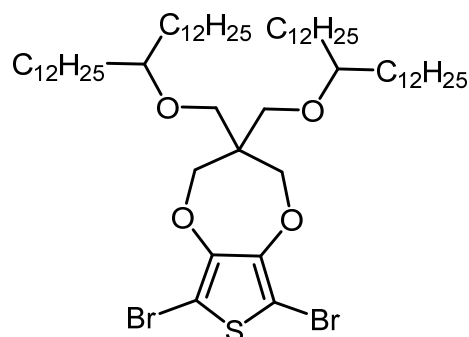
**3,3-bis((pentacosan-13-yloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (S8).**

This procedure is based on a modified literature procedure.¹⁴ A round-bottom flask was charged with NaH (0.11 g, 4.4 mmol, 3.0 equiv) and pentacosan-13-ol¹³ (1.2 g, 3.2 mmol, 2.1 equiv). The solution was sparged with N₂ to remove air. Anhydrous N,N-dimethylformamide (6.0 mL) was added to the flask, and the reaction mixture was heated at 70 °C. After 6 h, 3,3-bis(bromomethyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine¹⁴ (0.50 g, 1.5 mmol, 1.0 equiv) was added as a solid, and the reaction mixture was allowed to stir at 70 °C for 48 h. After cooling to room temperature, the reaction mixture was added to 200 mL of sat. NaCl (aq). The crude product was extracted with three portions of diethyl ether, and the combined organic phases were washed with three portions of water. The organic phase was dried using Na₂SO₄ then concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, 15% CH₂Cl₂/hexanes, R_f = 0.3). The product was isolated as a white solid (0.65 g, 48% yield).

¹H NMR (400 MHz, CDCl₃) δ 6.43 (s, 2H), 4.01 (s, 4H), 3.50 (s, 4H), 3.23 – 3.12 (m, 2H), 1.50 – 1.36 (m, 8H), 1.26 (s, 80H), 0.88 (t, *J* = 6.7 Hz, 12H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 149.7, 104.7, 67.7, 47.8, 34.1, 33.6, 31.9, 29.9, 29.7, 29.6, 29.6, 29.3, 25.3, 22.6, 22.3, 14.1, 14.0.

HRMS (APCI): calcd for C₅₉H₁₁₃O₄S [M + H]⁺: 917.8354; found: 917.8342

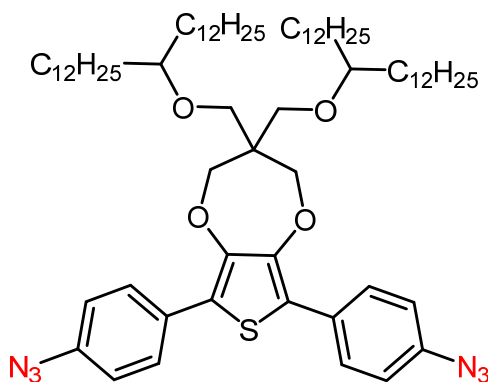


6,8-dibromo-3,3-bis((pentacosan-13-yloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (S9). This procedure is based on a modified literature procedure.¹⁴ A round bottom flask was charged with **S8** (0.30 g, 0.33 mmol, 1.0 equiv) and NBS (0.17 g, 0.98 mmol, 3.0 equiv). The flask was sparged with N₂, and CHCl₃ (6.0 mL) was added under N₂. The reaction was allowed to stir at room temperature for 16 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography (SiO₂, 10% CH₂Cl₂/hexanes, R_f = 0.4). The product was isolated as a white solid (0.33 g, 94% yield).

¹H NMR (500 MHz, CDCl₃) δ 4.09 (s, 4H), 3.53 (s, 4H), 3.21 – 3.15 (m, 2H), 1.49 – 1.23 (m, 88H), 0.88 (t, *J* = 6.9 Hz, 12H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 147.3, 90.9, 67.9, 48.2, 33.8, 32.1, 30.1, 29.9, 29.9, 29.6, 25.5, 22.9, 14.3.

HRMS (APCI): calcd for C₅₉H₁₁₀Br₂O₄S [M + H]⁺: 1073.6564; found: 1073.6551

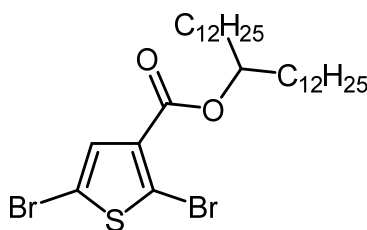


6,8-bis(4-azidophenyl)-3,3-bis((pentacosan-13-yloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (S10). This procedure is based on a modified literature procedure.¹⁵ In an N₂ filled glovebox, a Schlenk tube was charged with **S9** (0.19 g, 0.18 mmol, 1.0 equiv), 2-(4-azidophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane¹⁶ (0.095 g, 0.39 mmol, 2.2 equiv), tris(o-methoxyphenyl)phosphine (0.015 g, 0.042 mmol, 0.24 equiv), K₃PO₄ (0.23 g, 1.1 mmol, 6.0 equiv), Pd₂(dba)₃ (0.019 g, 0.021 mmol, 0.12 equiv), Aliquat 336 (1 drop), and toluene (6.1 mL). The Schlenk tube was sealed and removed from the glovebox. Under N₂, degassed H₂O (0.90 mL) was added. The reaction was allowed to stir at room temperature for 4 h. The reaction mixture was then diluted with CH₂Cl₂ and washed with water (2 × 50 mL). The organic phase was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, 20% CH₂Cl₂/hexanes, R_f = 0.4). The product was isolated as an off-white solid. (0.12 g, 60% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.8 Hz, 4H), 7.02 (d, *J* = 8.8 Hz, 4H), 4.16 (s, 4H), 3.58 (s, 4H), 3.26 – 3.16 (m, 2H), 1.43 (s, 8H), 1.26 (s, 80H), 0.87 (t, *J* = 6.8 Hz, 12H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 146.4, 138.2, 129.9, 127.8, 119.1, 118.3, 80.0, 73.9, 67.7, 47.9, 33.6, 31.9, 29.9, 29.7, 29.6, 29.3, 25.3, 22.6, 14.1.

HRMS (APCI): calcd for C₇₁H₁₁₈N₆O₄S [M + H]⁺: 1151.9008; found: 1151.8990

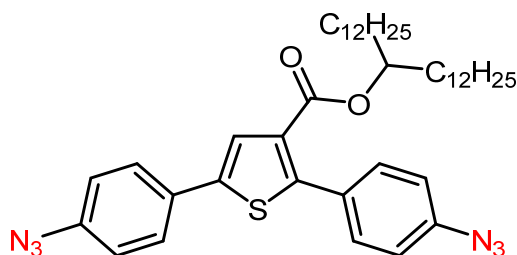


Pentacosan-13-yl 2,5-dibromothiophene-3-carboxylate (S11). This procedure is based on a modified literature procedure.¹⁷ A round-bottom flask was charged with 2,5-dibromothiophene-3-carboxylic acid¹⁷ (0.37 g, 1.0 mmol, 1.0 equiv), 4-Dimethylaminopyridine (0.37 g, 3.0 mmol, 3.0 equiv), pentacosan-13-ol¹³ (0.86 g, 3.0 mmol, 3.0 equiv), and *N,N'*-dicyclohexylcarbodiimide (0.62 g, 3.0 mmol, 3.0 equiv). The reaction vessel was sparged with N₂, and CH₂Cl₂ (10 mL) was added to the reaction flask. The reaction was allowed to stir at room temperature for 48 h. The resulting mixture was filtered through celite, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, 10% Et₂O/hexanes). The product was isolated as a white semi-solid. (0.46 mg, 72% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.33 (s, 1H), 5.13 – 5.01 (m, 1H), 1.68 – 1.57 (m, 4H), 1.26 (d, *J* = 6.5 Hz, 40H), 0.88 (m, 6H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 160.7, 132.5, 131.9, 118.9, 111.3, 76.0, 34.8, 34.2, 32.1, 31.8, 29.8, 29.8, 29.7, 29.7, 29.5, 28.4, 25.5, 22.9, 22.8, 20.8, 14.3, 11.6.

HRMS (APCI): calcd for C₃₀H₅₂Br₂O₂S [M + H]⁺: 635.2128; found: 635.2123

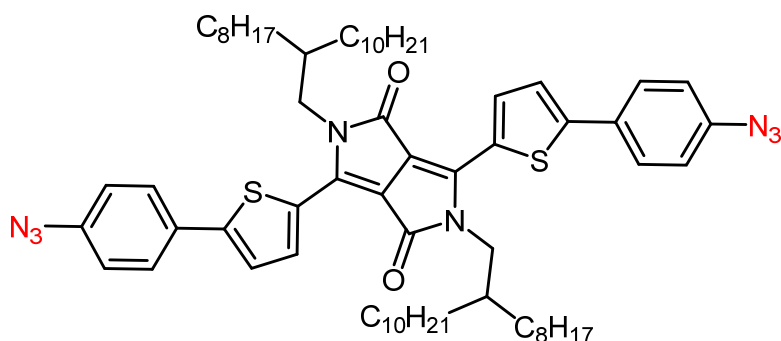


Pentacosan-13-yl 2,5-bis(4-azidophenyl)thiophene-3-carboxylate (S12). This procedure is based on a modified literature procedure.¹⁵ In an N₂ filled glovebox, a Schlenk tube was charged with **S11** (0.20 g, 0.31 mmol, 1.0 equiv), 2-(4-azidophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane¹⁶ (0.17 g, 0.69 mmol, 2.2 equiv), tris(o-methoxyphenyl)phosphine (0.027 g, 0.075 mmol, 0.24 equiv), K₃PO₄ (0.40 g, 1.9 mmol, 6.0 equiv), Pd₂(dba)₃ (0.035 g, 0.038 mmol, 0.12 equiv), Aliquat 336 (1 drop), and toluene (11 mL). The Schlenk tube was sealed and removed from the glovebox. Under N₂, degassed H₂O (1.6 mL) was added. The reaction was allowed to stir at room temperature for 4 h. The reaction mixture was then diluted with CH₂Cl₂ and washed with water (2 × 50 mL). The organic phase was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, 10% CH₂Cl₂/hexanes, R_f = 0.2). The product was isolated as a yellow solid. (0.13 g, 57% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.68 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 4H), 5.00 (m, 1H), 1.51 (d, *J* = 6.5 Hz, 4H), 1.26 (s, 40H), 0.89 (t, *J* = 6.8 Hz, 6H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 162.9, 148.3, 141.5, 140.6, 139.9, 131.5, 130.3, 130.1, 129.9, 127.2, 125.6, 119.7, 118.6, 75.2, 34.1, 32.0, 29.8, 29.8, 29.7, 29.7, 29.5, 25.4, 22.8, 14.2.

HRMS (APCI): calcd for C₄₂H₆₀N₆O₂S [M + H]⁺: 712.4493; found: 712.4495



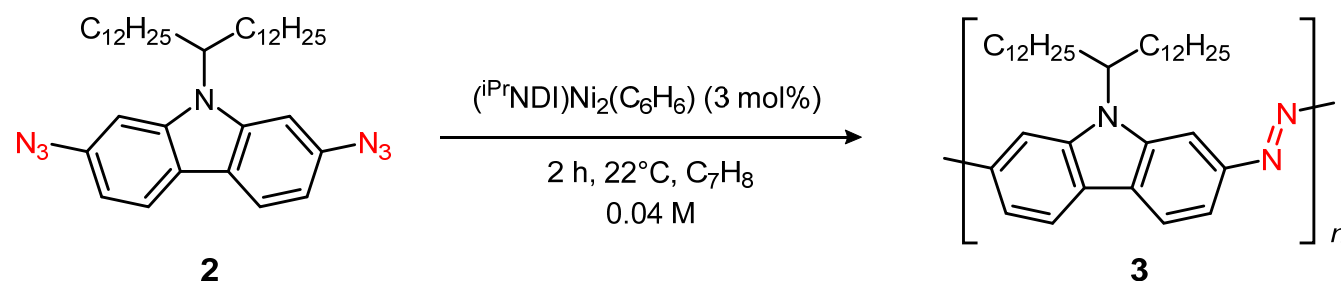
3,6-bis(5-(4-azidophenyl)thiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (S13). This procedure is based on a modified literature procedure.¹⁵ In an N₂ filled glovebox, a Schlenk tube was charged with 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione¹⁸ (0.25 g, 0.25 mmol, 1.0 equiv), 2-(4-azidophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane¹⁶ (0.13 g, 0.54 mmol, 2.2 equiv), tris(*o*-methoxyphenyl)phosphine (0.042 g, 0.12 mmol, 0.48 equiv), K₃PO₄ (0.63 g, 2.9 mmol, 12.0 equiv.), Pd₂(dba)₃ (0.054 g, 0.059 mmol, 0.24 equiv), Aliquat 336 (1 drop), and toluene (8.5 mL). The Schlenk tube was sealed and removed from the glovebox. Under N₂, degassed H₂O (1.2 mL) was added. The reaction was allowed to stir at room temperature for 4 h. The reaction mixture was then diluted with CH₂Cl₂ and washed with water (2 × 50 mL). The organic phase was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, 30% CH₂Cl₂/hexanes, R_f = 0.1). The product was isolated as a deep blue oil. (0.15 g, 54% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.92 (d, *J* = 4.1 Hz, 2H), 7.72 – 7.61 (m, 4H), 7.42 (d, *J* = 4.1 Hz, 2H), 7.08 (s, 4H), 4.06 (d, *J* = 7.7 Hz, 4H), 1.97 (s, 2H), 1.28 (m, 64H), 0.85 (s, 12H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 161.6, 148.4, 140.4, 139.6, 136.7, 130.0, 128.7, 127.4, 124.2, 119.6, 108.2, 46.2, 37.9, 31.9, 31.8, 31.3, 30.0, 29.6, 29.6, 29.5, 29.3, 29.3, 26.3, 22.6, 22.6, 14.0.

HRMS (APCI): calcd for C₆₆H₉₄N₈O₂S₂ [M + H]⁺: 1095.7014; found: 1095.7001

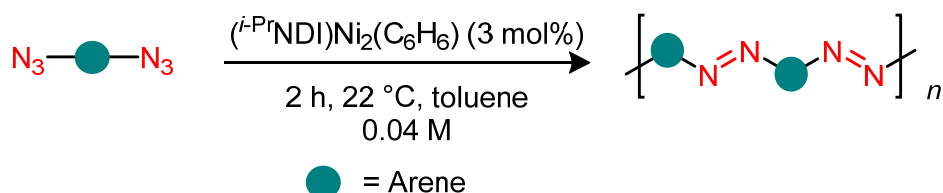
3. Reaction Optimization Studies



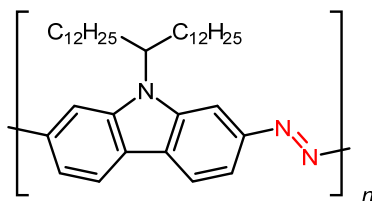
Standard procedure. This procedure is based on a modified literature procedure.⁹ In an N_2 filled glovebox, a 2-dram vial equipped with a stir bar was charged with **2** (10.0 mg, 0.017 mmol, 1.0 equiv) and toluene (0.30 mL). Catalyst **1** (0.36 mg, 0.50 μmol , 3 mol %) dissolved in C_7H_8 (0.12 mL) was added to the stirring diazide solution. The reaction was allowed to stir for 2 h at room temperature. The reaction was quenched by exposure to air. MeOH (1.0 mL) and CH_2Cl_2 (1.0 mL) were added sequentially. The resulting suspension was sonicated and gravity filtered. The red solid was washed sequentially with Et_2O (20.0 mL) and CH_2Cl_2 (20.0 mL) to remove any low molecular weight material. The solid was allowed to air dry then collected and dried further under vacuum. Monomer conversions for entries 3 and 5 were determined by ^1H NMR. For entry 8 the polymer was purified using a Soxhlet apparatus. The product was washed sequentially with MeOH, hexanes, and CHCl_3 then extracted with $\text{C}_6\text{H}_5\text{Cl}$.

entry	deviation from Standard Conditions	conversion of 2	M_n (kg/mol)	M_w (kg/mol)	$\bar{M}_n$	X_n
1	none	>99%	20.5	58.7	2.9	37.7
2	purification by Soxhlet extraction ($\text{C}_6\text{H}_5\text{Cl}$)	>99%	42.1	92.5	2.2	77.6
3	1 mol% of 1	31%	–	–	–	–
4	5 mol% of 1	>99%	28.2	98.5	3.5	51.8
5	[2] = 0.02 M	79%	–	–	–	–
6	[2] = 0.08 M	>99%	35.2	104.2	3.0	64.7
7	60 °C	>99%	69.0	295.9	4.3	126.9
8	THF instead of toluene	>99%	8.6	18.6	2.1	15.8

4. Azopolymer Synthesis and Characterization



General procedure. In an N₂ filled glovebox, a microwave vial was charged with a solution of the diazide (1.0 equiv) dissolved in toluene and a magnetic stir bar. A solution of catalyst **1** (3 mol%) dissolved in toluene was added to the stirring diazide solution (0.04 M final concentration of the diazide). The vial was sealed, and the reaction mixture was stirred at room temperature. After 2 h, the reaction vial was opened to air and methanol was added to precipitate the product. After sonication, the crude mixture was added to a thimble and purified in a Soxhlet apparatus (see below for wash and extraction solvents). Isolated polymers were obtained after drying under vacuum.



PolyAzoCarbazole (3).¹⁹ Synthesized according to the general procedure using **2** (0.10 g, 0.17 mmol, 1.0 equiv), toluene (4.2 mL), and **1** (3.6 mg, 5.0 μmol, 3 mol%). Soxhlet wash solvents: MeOH, hexanes, then CHCl₃. Extraction solvent: C₆H₅Cl. PolyAzoCarbazole (**3**) was isolated as a red solid. (0.061 g, 61% yield).

¹H NMR (400 MHz, 100 °C, toluene-*d*₈) δ 8.47 (s, 2H), 8.16 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.3 Hz, 2H), 4.70 (s, 1H), 2.52 – 2.36 (m, 2H), 1.97 – 1.83 (m, 2H), 1.32 – 1.09 (m, 40H), 0.86 (t, 6H).

UV–Vis–NIR (C₆H₅Cl, 0.0326 mM): λ_{max}, nm (ε, M⁻¹ cm⁻¹): 440 (sh), 470 (sh), 503 (15,000), 538 (17,000).

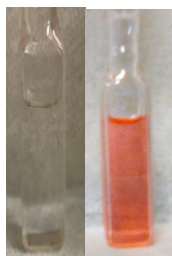
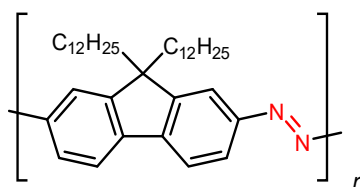
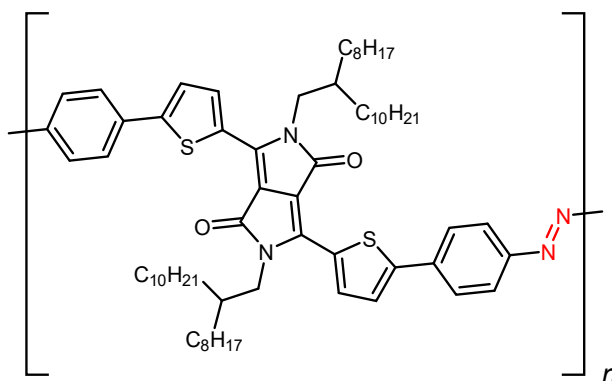


Figure S1. Photo of **2** (left) and **3** (right) in C₆H₅Cl.



PolyAzoFluorene (6). Synthesized according to the general procedure using 2,7-diazo-9,9-didodecyl-9*H*-fluorene⁹ (0.10 g, 0.17 mmol, 1.0 equiv), toluene (4.3 mL), and **1** (3.7 mg, 5.1 μ mol, 3 mol%). Soxhlet wash solvents: MeOH then hexanes. Extraction solvent: $CHCl_3$. PolyAzoFluorene (**6**) was isolated as an orange solid. (0.082 g, 82% yield). Spectral match those previously reported.⁹

UV-Vis-NIR (C_6H_5Cl , 0.0566 mM): λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$): 336 (1,700) 450 (sh), 484 (17,000) 520 (18,000)



PolyAzoTDPP (7). Synthesized according to the general procedure using **S13** (0.10 g, 0.091 mmol, 1.0 equiv), toluene (2.3 mL), and **1** (2.0 mg, 2.7 μ mol, 3 mol%). Soxhlet wash solvents: MeOH then hexanes. Extraction solvent: $CHCl_3$. PolyAzoTDPP (**7**) was isolated as a green solid. (0.077 g, 77% yield).

^1H NMR (400 MHz, toluene- d_8) δ 9.44 – 9.15 (m, 2H), 7.93 (d, J = 8.1 Hz, 3H), 7.62 (d, J = 8.4 Hz, 3H), 4.20 (s, 4H), 2.21 (s, 2H), 1.60 – 1.22 (m, 64H), 0.93 – 0.86 (m, 12H).

UV-Vis-NIR (C_6H_5Cl , 0.0385 mM): λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$): 334 (1,300) 426 (3,500), 664 (8,600), 746 (sh)



Figure S2. Photo of **S13** (left) and **7** (right) in C_6H_5Cl .

PolyAzoThiophene (8). Synthesized according to the general procedure using **S12** (0.10 g, 0.14 mmol, 1.0 equiv), toluene (3.5 mL), and **1** (3.1 mg, 4.2 μ mol, 3 mol%). Soxhlet wash solvents: MeOH then hexanes. Extraction solvent: CHCl_3 . PolyAzoThiophene (**8**) was isolated as an orange solid. (0.081 g, 81% yield).

^1H NMR (400 MHz, 100 $^\circ\text{C}$, toluene- d_8) δ 8.05 (s, 2H), 7.97 (s, 3H), 7.72 (s, 2H), 7.58 (s, 2H), 5.23 (s, 1H), 1.68 – 1.44 (m, 4H), 1.31 (s, 40H), 0.90 (s, 6H).

UV-Vis-NIR ($\text{C}_6\text{H}_5\text{Cl}$, 0.0135 mM): λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 427 (15,000)

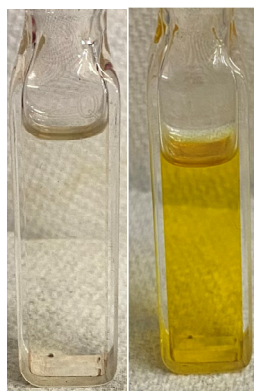
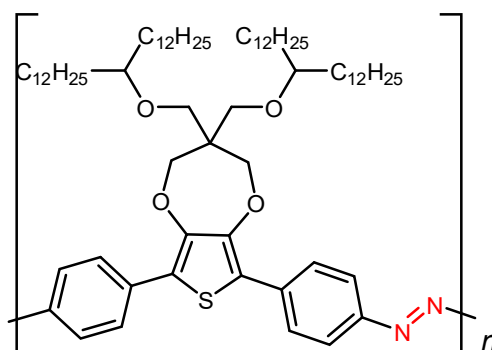


Figure S3. Photo of **S12** (left) and **8** (right) in $\text{C}_6\text{H}_5\text{Cl}$.



PolyAzoProDOT (9). Synthesized according to the general procedure using **S10** (0.10 g, 0.087 mmol, 1.0 equiv), toluene (2.2 mL), and **1** (1.9 mg, 2.6 μ mol, 3 mol%). Soxhlet wash solvent: MeOH. Extraction solvent: hexanes. PolyAzoProDOT (**9**) was isolated as a red solid. (0.097 g, 97% yield).

^1H NMR (400 MHz, 50 $^\circ\text{C}$, CDCl_3) δ 8.04 – 7.86 (m, 8H), 4.27 (s, 4H), 3.65 (s, 4H), 3.31 – 3.23 (m, 2H), 1.57 – 1.45 (m, 8H), 1.37 – 1.23 (m, 80H), 0.88 (t, 12H).

UV-Vis-NIR ($\text{C}_6\text{H}_5\text{Cl}$, 0.0456 mM): λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 514 (20,000), 543 (sh)

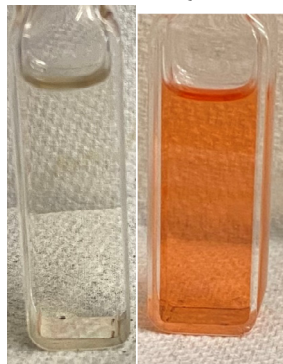
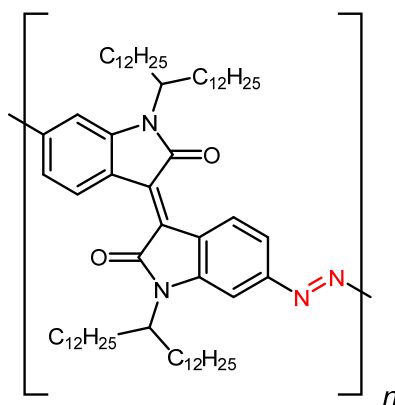


Figure S4. Photo of **S10** (left) and **9** (right) in $\text{C}_6\text{H}_5\text{Cl}$.



PolyAzolisoindigo (10). Synthesized according to the general procedure using **S7** (0.098 g, 0.094 mmol, 1.0 equiv), toluene (2.3 mL), and **1** (6.8 mg, 9.4 μ mol, 10 mol%). Soxhlet wash solvents: MeOH then hexanes. Extraction solvent: CHCl₃. PolyAzolisoindigo (**10**) was isolated as a green solid. (0.091 g, 93% yield).

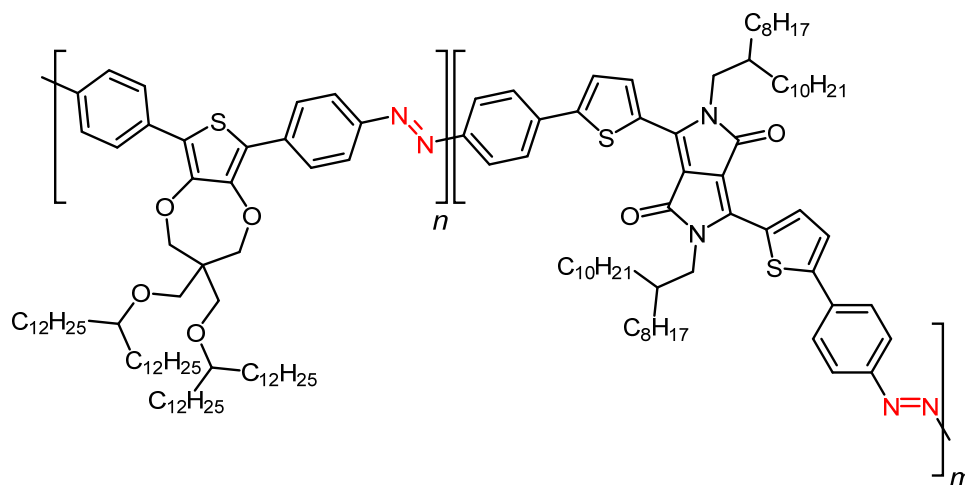
¹H NMR (400 MHz, 100 °C, toluene-*d*₈) δ 9.81 (s, 2H), 7.91 – 7.50 (m, 4H), 4.52 (s, 2H), 2.19 (s, 4H), 1.77 (s, 4H), 1.31 (s, 80H), 0.89 (s, 12H).

UV-Vis-NIR (C₆H₅Cl, 0.0606 mM): λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 381 (sh), 481 (17,000), 664 (25,000), 709 (26,000).



Figure S5. Photo of **S7** (left) and **10** (right) in C₆H₅Cl.

Copolymerization Experiments



ProDOT/TDPP copolymerization at 1:1 (11). In an N₂ filled glovebox, a 2-dram vial was charged with a magnetic stir bar, **S10** (0.010 g, 8.7 μmol, 1.0 equiv), **S13** (0.010 g, 9.1 μmol, 1.0 equiv) and toluene (0.22 mL). Catalyst **1** (3.9 mg, 0.55 μmol, 3 mol% total) dissolved in toluene (0.22 mL) was added to the stirring solution of the diazides. The vial was sealed, and the reaction mixture was stirred at room temperature. After 2 h, the reaction vial was opened to air, and MeOH was added to precipitate the product. After sonication, the crude material was filtered, and the precipitate was washed with Et₂O (10.0 mL) and CH₂Cl₂ (10.0 mL). The solid was allowed to air dry then collected and dried further under vacuum to yield the product as a dark purple solid. (0.021 g, >99% yield). Ratio of ProDOT (**9**) to TDPP (**7**) by ¹H NMR integration (1:1.04).

UV-Vis-NIR (C₆H₅Cl, 0.0187 mM): λ_{max}, nm (ε, M⁻¹ cm⁻¹): 327 (sh), 442 (sh), 534 (7,900), 659 (sh), 710 (13,000)



Figure S5. Photo of **11** in C₆H₅Cl.

ProDOT/TDPP copolymerization at 3:1 (12). In an N₂ filled glovebox, a 2-dram vial was charged with a magnetic stir bar, **S10** (0.015 g, 13.0 μ mol, 1.0 equiv), **S13** (5.0 mg, 4.6 μ mol, 0.35 equiv) and toluene (0.22 mL). Catalyst **1** (3.9 mg, 0.55 μ mol, 3 mol% total) dissolved in toluene (0.22 mL) was added to the stirring solution of the diazides. The vial was sealed, and the reaction mixture was stirred at room temperature. After 2 h, the reaction vial was opened to air, and MeOH was added to precipitate the product. After sonication, the crude material was filtered, and the precipitate was washed with Et₂O (10.0 mL) and CH₂Cl₂ (10.0 mL). The solid was allowed to air dry then collected and dried further under vacuum to yield the product as a purple solid. (0.021 g, >99% yield). Ratio of ProDOT (**9**) to TDPP (**7**) by ¹H NMR integration (2.6:1).

UV-Vis-NIR (C₆H₅Cl, 0.0351 mM): λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 521 (11,000), 644 (sh), 692 (6,300)

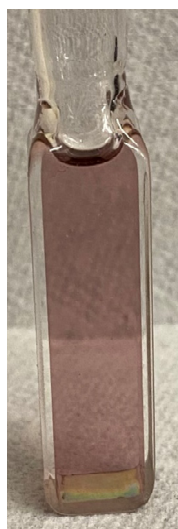
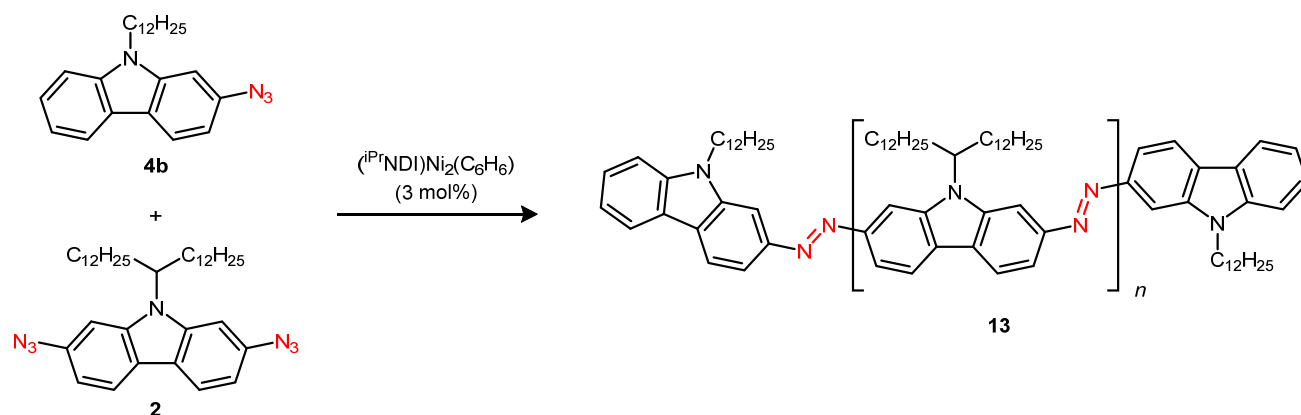


Figure S6. Photo of **12** in C₆H₅Cl.

5. Endcapping Experiments

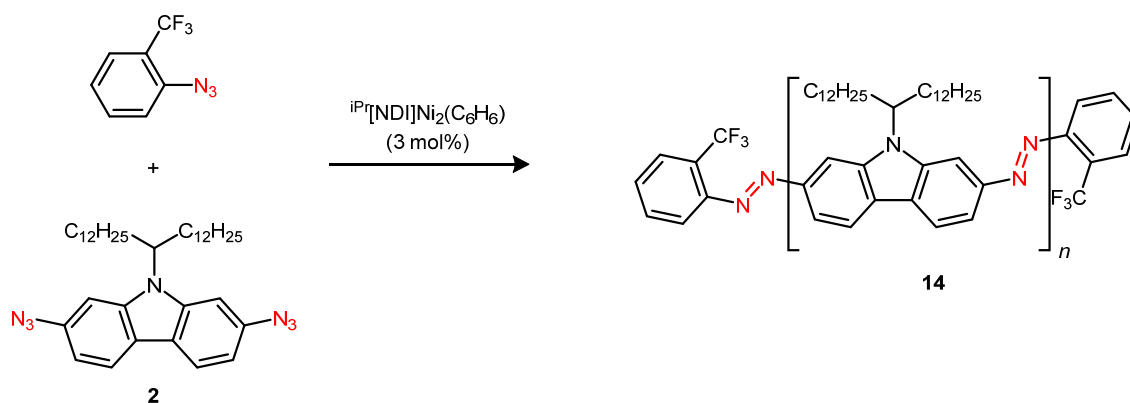


Carbazole end group incorporation (13). In an N_2 filled glovebox, a 2-dram vial was charged with a magnetic stir bar, **2** (0.015 g, 0.025 mmol, 1.0 equiv), **4b** (0.50 mg, 1.3 μmol , 0.050 equiv) and toluene (0.50 mL). Catalyst **1** (0.60 mg, 0.69 μmol , 3 mol %) dissolved in toluene (0.13 mL) was added to the stirring solution of the azides. The vial was sealed, and the reaction mixture was stirred at room temperature. After 2 h, the reaction vial was opened to air, and MeOH (3.0 mL) was added to precipitate the product. After sonication, the crude material was filtered, and the precipitate was washed with Et_2O (10.0 mL) and CH_2Cl_2 (10.0 mL). The solid was allowed to air dry then collected and dried further under vacuum to yield the product as a red solid (0.010 g, 67% yield). Ratio of repeat units to end groups by ^1H NMR integration (17:1).

^1H NMR of **13** end group (400 MHz, 100 $^\circ\text{C}$, toluene- d_8) δ 7.97 (d, J = 7.9 Hz, 1H), 4.02 (br s, 2H).

^1H NMR of **13** repeat unit (400 MHz, 100 $^\circ\text{C}$, toluene- d_8) δ 8.47 (s, 2H), 8.16 (d, J = 8.7 Hz, 2H), 8.09 (d, J = 8.8 Hz, 2H), 4.70 (s, 1H), 2.42 (s, 2H), 1.89 (s, 2H), 1.19 (d, J = 33.8 Hz, 40H), 0.86 (d, J = 7.2 Hz, 6H).

UV-Vis-NIR ($\text{C}_6\text{H}_5\text{Cl}$, 0.0428 mM): λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 435 (sh), 465 (sh), 499 (21,000), 532 (22,000).



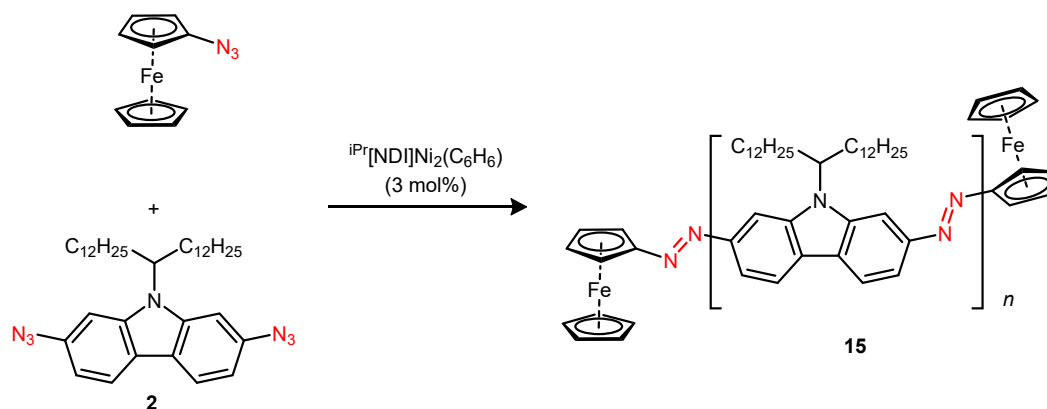
2-(trifluoromethyl)phenyl end group incorporation (14). In an N₂ filled glovebox, a 2-dram vial was charged with a magnetic stir bar, **2** (0.015 g, 0.025 mmol, 1.0 equiv), 2-(trifluoromethyl)phenyl azide⁹ (0.20 mg, 1.3 μmol, 0.050 equiv) and toluene (0.50 mL). Catalyst **1** (0.60 mg, 0.69 μmol, 3 mol %) dissolved in toluene (0.13 mL) was added to the stirring solution of the azides. The vial was sealed, and the reaction mixture was stirred at room temperature. After 2 h, the reaction vial was opened to air, and MeOH (3.0 mL) was added to precipitate the product. After sonication, the crude material was filtered, and the precipitate was washed with Et₂O (10.0 mL) and CH₂Cl₂ (10.0 mL). The solid was allowed to air dry then collected and dried further under vacuum to yield the product as a red solid (8.9 mg, 60% yield). Ratio of repeat units to end groups by ¹H NMR integration (30:1).

¹H NMR of **14** end group (400 MHz, 100 °C, toluene-*d*₈) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H)

¹H NMR of **14** repeat unit (400 MHz, 100 °C, toluene-*d*₈) δ 8.47 (s, 2H), 8.16 (d, *J* = 8.7 Hz, 2H), 8.09 (d, *J* = 8.8 Hz, 2H), 4.70 (s, 1H), 2.42 (s, 2H), 1.89 (s, 2H), 1.19 (d, *J* = 33.8 Hz, 40H), 0.86 (d, *J* = 7.2 Hz, 6H).

¹⁹F NMR of **14** (376 MHz, 100 °C, toluene-*d*₈) δ -58.8.

UV-Vis-NIR (C₆H₅Cl, 0.0428 mM): λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 435 (sh), 465 (sh), 499 (17,000), 532 (18,000).

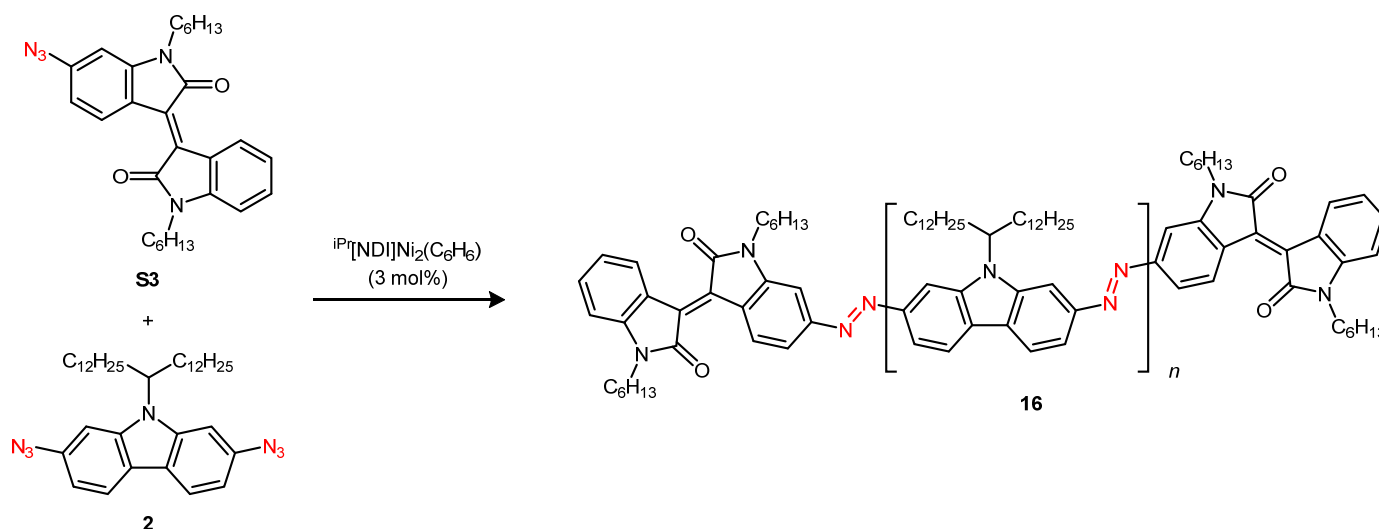


Ferrocene end group incorporation (15). In an N_2 filled glovebox, a 2-dram vial was charged with a magnetic stir bar, **2** (0.015 g, 0.025 mmol, 1.0 equiv.), azidoferrocene⁹ (0.30 mg, 1.3 μmol , 0.050 equiv.) and toluene (0.50 mL). Catalyst **1** (0.60 mg, 0.69 μmol , 3 mol %) dissolved in toluene (0.13 mL) was added to the stirring solution of the azides. The vial was sealed, and the reaction mixture was stirred at room temperature. After 2 h, the reaction vial was opened to air, and MeOH (3.0 mL) was added to precipitate the product. After sonication, the crude material was filtered, and the precipitate was washed with Et_2O (10.0 mL) and CH_2Cl_2 (10.0 mL). The solid was allowed to air dry then collected and dried further under vacuum to yield the product as a red solid (9.1 mg, 60% yield). Ratio of repeat units to end groups by ^1H NMR integration (34:1).

^1H NMR of **15** end group (400 MHz, 100 $^\circ\text{C}$, toluene- d_8) δ 5.15 (t, J = 2.0 Hz, 2H), 4.31 (t, J = 2.0 Hz, 2H), 4.10 (s, 5H).

^1H NMR of **15** repeat unit (400 MHz, 100 $^\circ\text{C}$, toluene- d_8) δ 8.47 (s, 2H), 8.16 (d, J = 8.7 Hz, 2H), 8.09 (d, J = 8.8 Hz, 2H), 4.70 (s, 1H), 2.42 (s, 2H), 1.89 (s, 2H), 1.19 (d, J = 33.8 Hz, 40H), 0.86 (d, J = 7.2 Hz, 6H).

UV-Vis-NIR ($\text{C}_6\text{H}_5\text{Cl}$, 0.0551 mM): λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 432 (sh), 468 (sh), 501 (6,200), 533 (7,200).



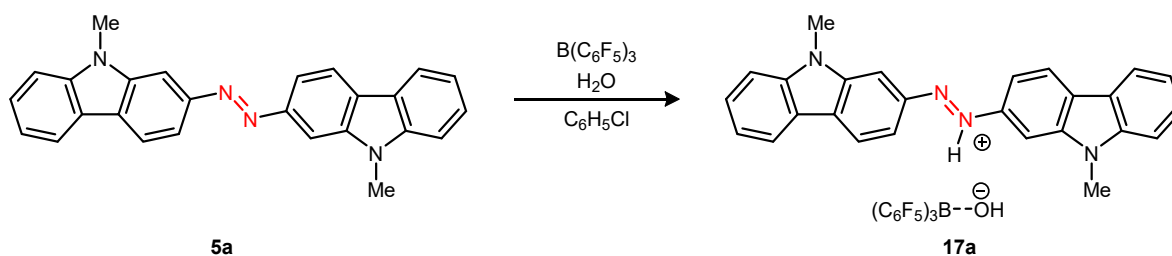
Isoindigo end group incorporation (16). In an N_2 filled glovebox, a 2-dram vial was charged with a magnetic stir bar, **2** (0.015 g, 0.025 mmol, 1.0 equiv.), **S3** (0.60 mg, 1.3 μmol , 0.050 equiv.) and toluene (0.50 mL). Catalyst **1** (0.60 mg, 0.69 μmol , 3 mol %) dissolved in toluene (0.13 mL) was added to the stirring solution of the azides. The vial was sealed, and the reaction mixture was stirred at room temperature. After 2 h, the reaction vial was opened to air, and MeOH (3.0 mL) was added to precipitate the product. After sonication, the crude material was filtered, and the precipitate was washed with Et_2O (10.0 mL) and CH_2Cl_2 (10.0 mL). The solid was allowed to air dry then collected and dried further under vacuum to yield the product as a red solid (11.0 mg, 73% yield). Ratio of repeat units to end groups by ^1H NMR integration (37:1).

^1H NMR of **16** end group (400 MHz, 100 $^\circ\text{C}$, toluene- d_8) δ 9.83 (br s, 1H), 9.62 (br s, 1H), 3.65 (br s, 2H).

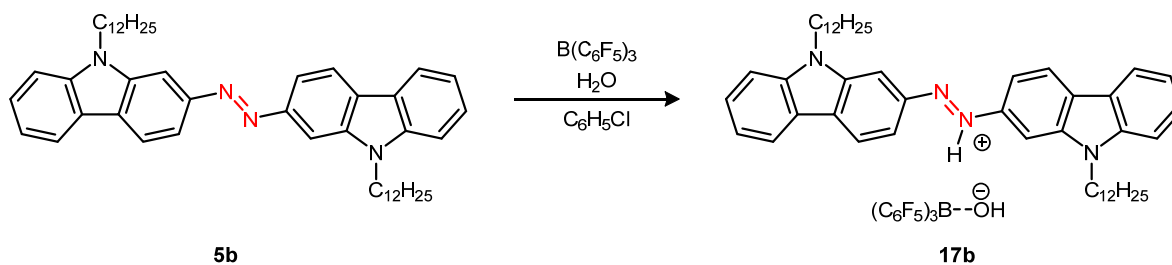
^1H NMR of **16** repeat unit (400 MHz, 100 $^\circ\text{C}$, toluene- d_8) δ 8.47 (s, 2H), 8.16 (d, $J = 8.7$ Hz, 2H), 8.09 (d, $J = 8.8$ Hz, 2H), 4.70 (s, 1H), 2.42 (s, 2H), 1.89 (s, 2H), 1.19 (d, $J = 33.8$ Hz, 40H), 0.86 (d, $J = 7.2$ Hz, 6H).

UV-Vis-NIR ($\text{C}_6\text{H}_5\text{Cl}$, 0.0612 mM): λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 432 (sh), 468 (sh), 501 (23,000), 534 (24,000)

6. Lewis Acid Experiments



Azocarbazole B(C₆F₅)₃/H₂O adduct (17a). An NMR tube was charged with **5a** (2.0 mg, 5.2 μmol, 1.0 equiv) dissolved in C₆H₅Cl (0.40 mL). B(C₆F₅)₃ (10.0 mg, 0.020 mmol, 3.8 equiv) was added as a solid to solution, resulting in an immediate color change to deep blue. C₆H₅Cl (0.10 mL) was layered on top of the solution followed by pentane (0.70 mL). The solvents were allowed to mix for 7 days, and single crystals suitable for X-ray diffraction were obtained.



Azocarbazole B(C₆F₅)₃/H₂O adduct (17b). A vial was charged with **5b** (2.0 mg, 2.9 μmol, 1.0 equiv) and C₆H₅Cl (0.40 mL). B(C₆F₅)₃ (10.0 mg, 0.020 mmol, 3.8 equiv) was added as a solid to solution, resulting in a color change to deep blue.

¹H NMR (300 MHz, CDCl₃) δ 8.16 (t, *J* = 8.7 Hz, 4H), 8.08 (d, *J* = 1.7 Hz, 2H), 7.89 (d, *J* = 8.6, 2H), 7.61 (t, *J* = 7.7 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 4.34 (t, *J* = 7.2 Hz, 4H), 1.91 (t, *J* = 7.3 Hz, 4H), 1.35 (s, 8H), 1.24 (d, *J* = 8.1 Hz, 28H), 0.85 (t, *J* = 6.6 Hz, 6H).

¹⁹F NMR (282 MHz, CDCl₃) δ -136.98 (d), -159.12 (t, *J* = 20.3 Hz), -165.28 (t).

UV-Vis-NIR (C₆H₅Cl, 0.143mM): λ_{max}, nm (ε, M⁻¹ cm⁻¹): 316 (3,200), 626 (11,000)

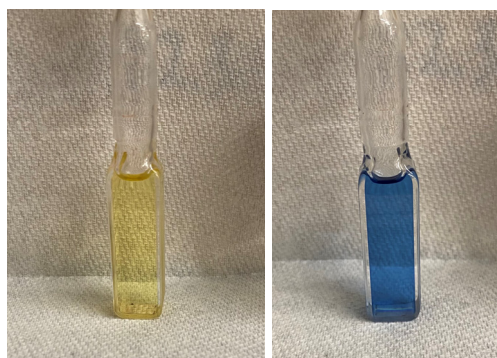


Figure S7. Photo of **5b** in C₆H₅Cl before (left) and after (right) addition of excess B(C₆F₅)₃.

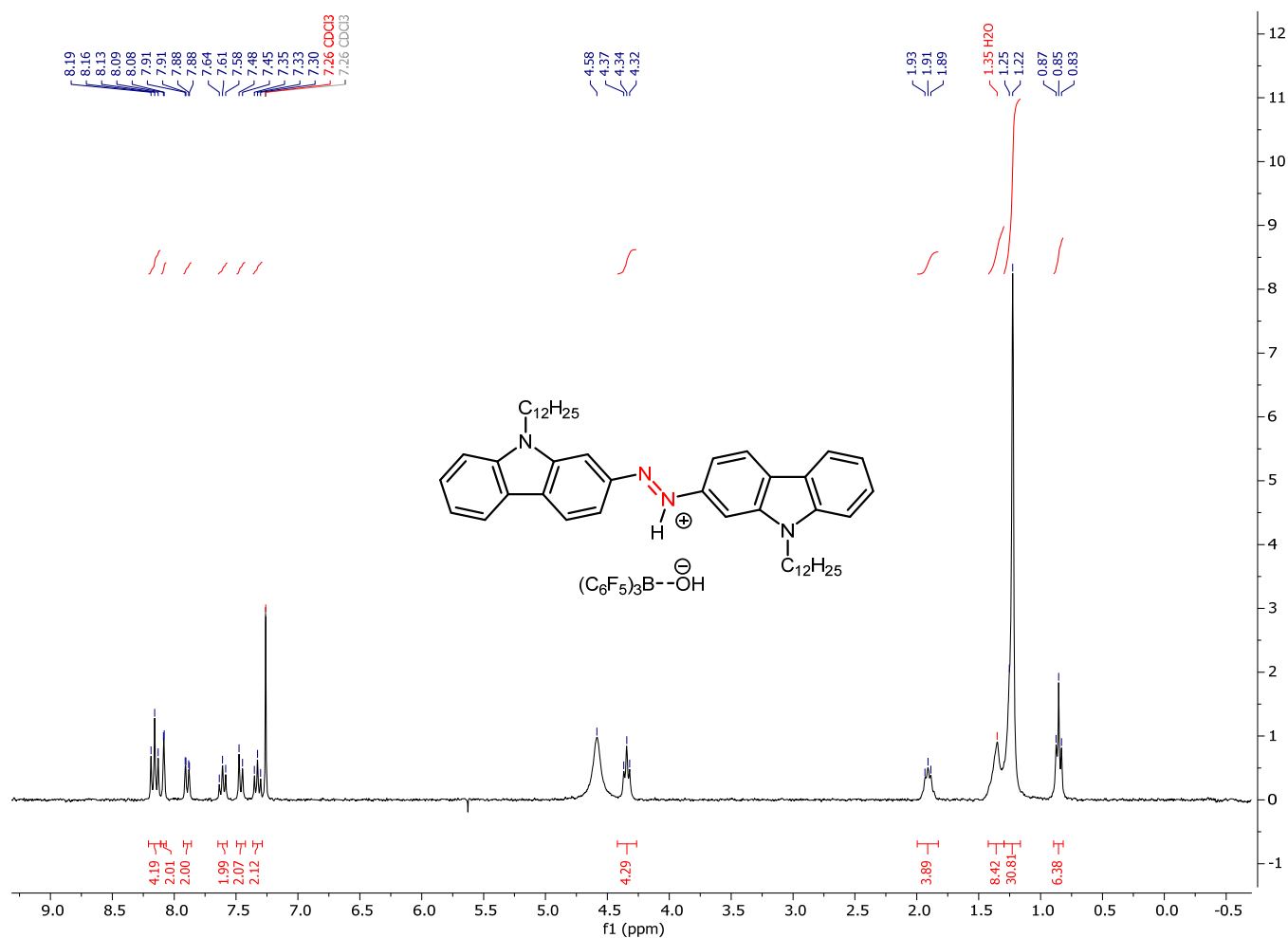


Figure S8. ^1H NMR spectrum of **17b** (300 MHz, $CDCl_3$).

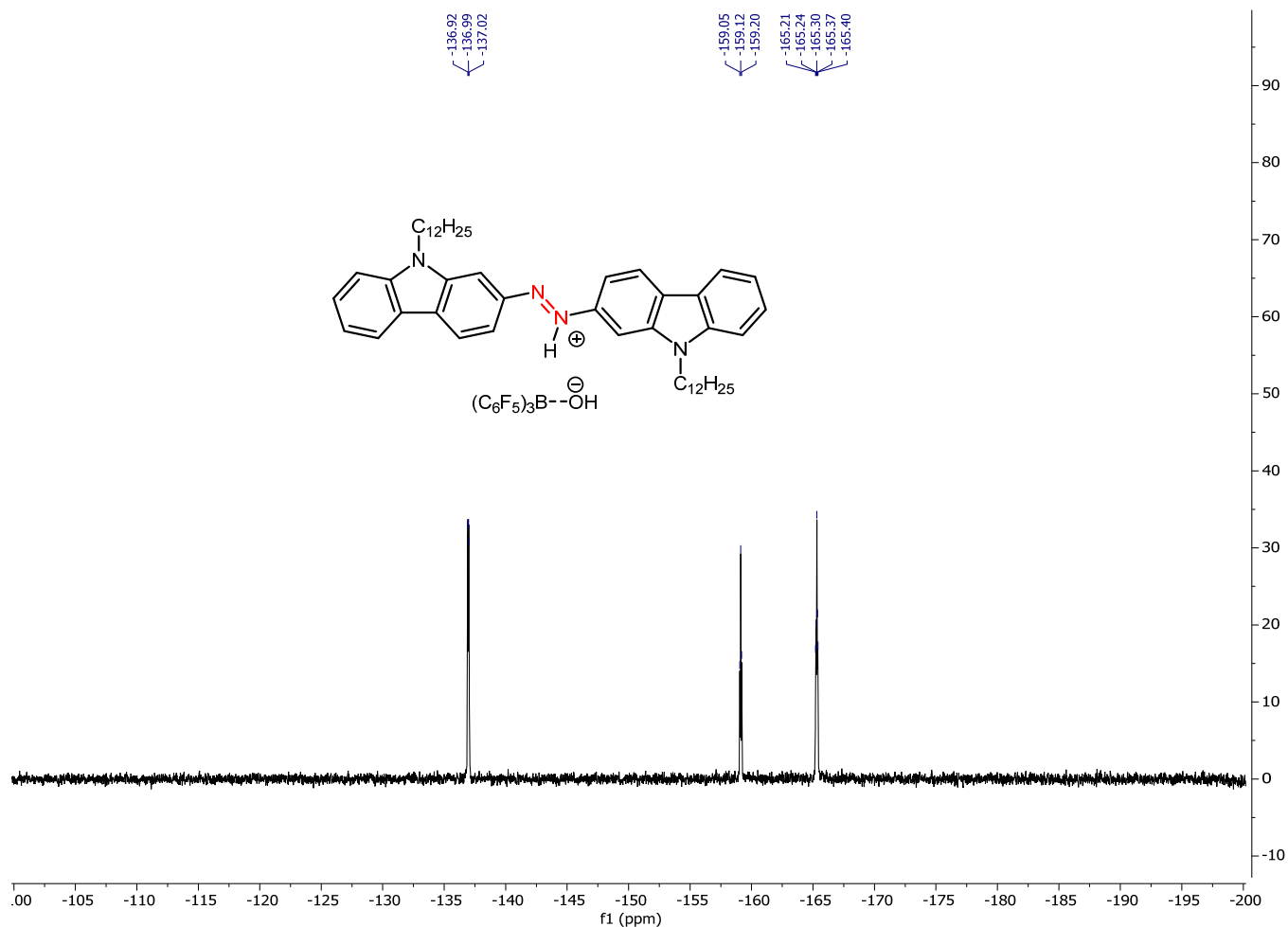


Figure S9. ¹⁹F NMR spectrum of **17b** (282 MHz, CDCl₃).

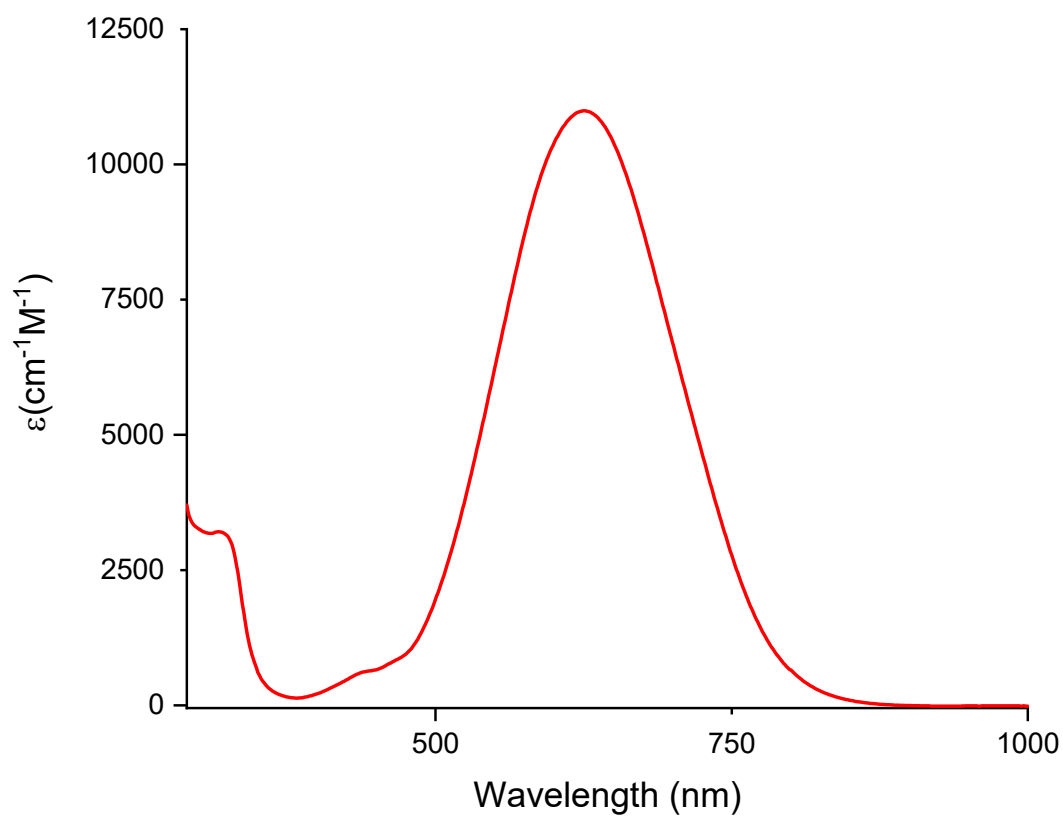


Figure S10. UV-Vis spectrum of **17b** (0.143mM) in C₆H₅Cl.

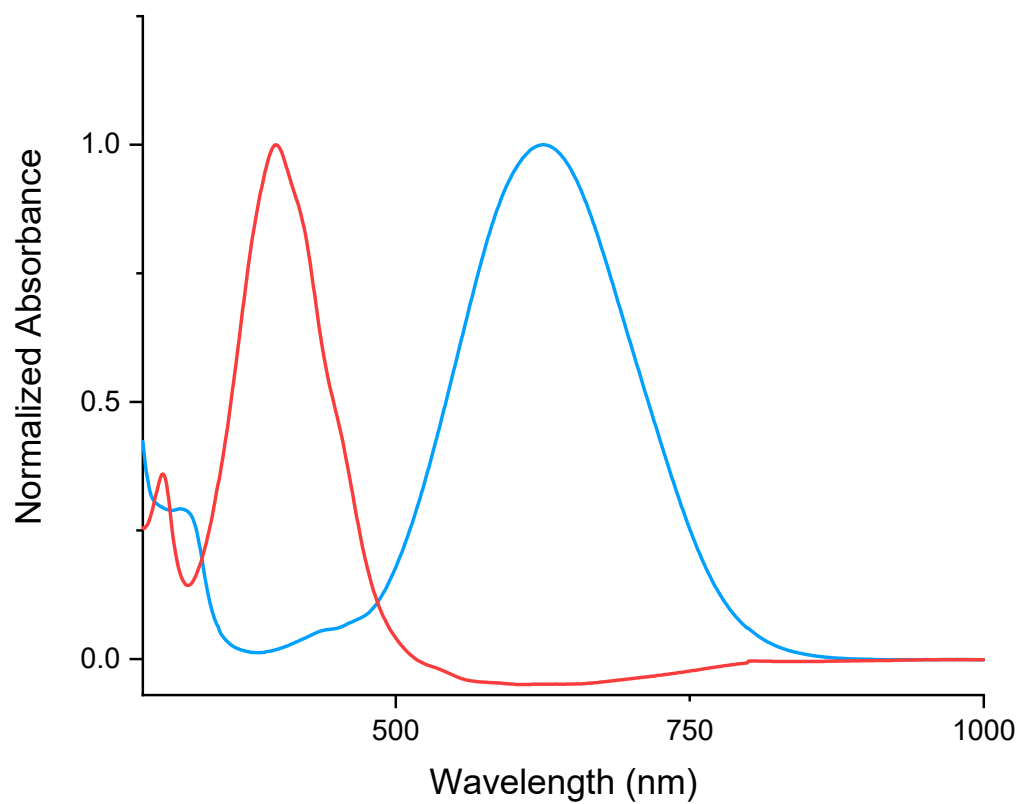
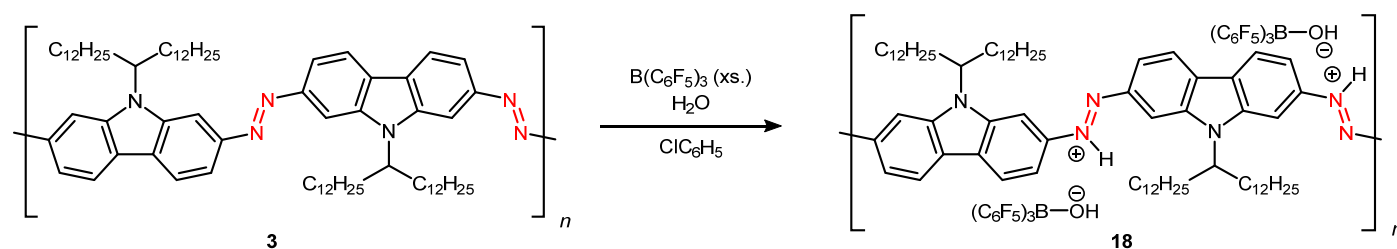


Figure S11. Normalized UV-Vis spectrum of **5b** (red) and **17b** (blue) in C₆H₅Cl.



UV Vis titration of **3 using B(C₆F₅)₃ (**18**).** A vial was charged with **3** (0.4 mg, 0.73 μmol, 1.0 equiv) and C₆H₅Cl (20 mL). An aliquot (3 mL) was taken, and B(C₆F₅)₃ (0.15 M in 1.0 mL) was titrated into the solution of **3**.

¹H NMR of **18** (400 MHz, 100 °C, toluene-*d*₈) δ 8.44 (s, 2H), 8.08 (q, *J* = 8.9 Hz, 4H), 6.03 (ddt, *J* = 14.2, 7.0, 3.6 Hz, 2H), 4.68 (s, 1H), 2.41 (s, 2H), 1.92 (s, 2H), 1.20 (d, *J* = 23.2 Hz, 40H), 0.91 – 0.82 (m, 6H).

UV–Vis–NIR of **18** (C₆H₅Cl, 0.0326 mM): λ_{max}, nm (ε, M⁻¹ cm⁻¹): 411 (4,400), 748 (sh), 821 (18,000)

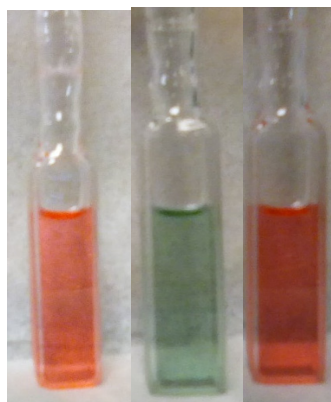


Figure S12. Pictures of (from left to right) **3**, **18** (after 0.151 M addition of B(C₆F₅)₃) and **18** after 1 drop pyridine in C₆H₅Cl.

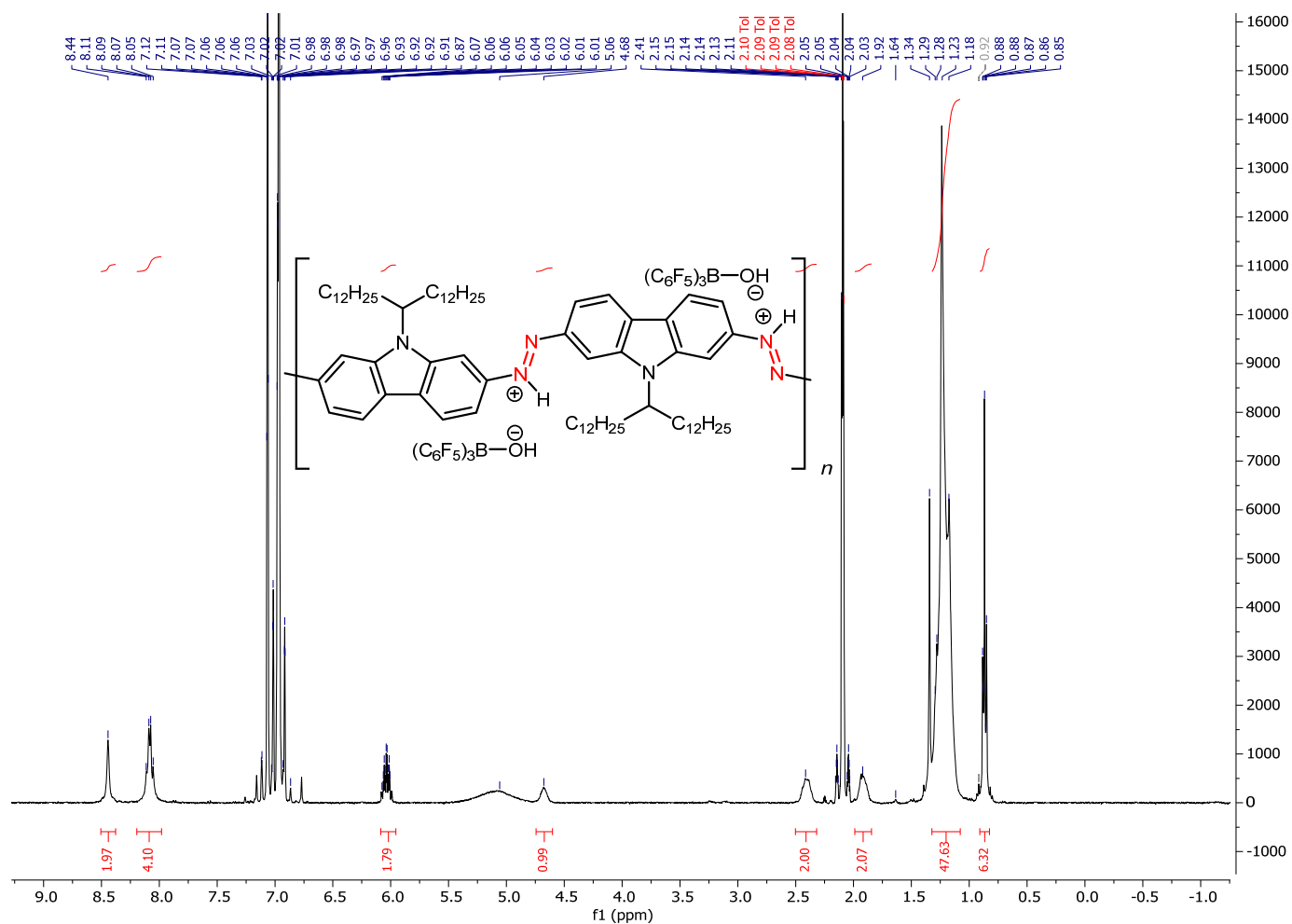


Figure S13. ^1H NMR spectrum of **18** (400 MHz, 100 $^\circ\text{C}$, toluene- d_8).

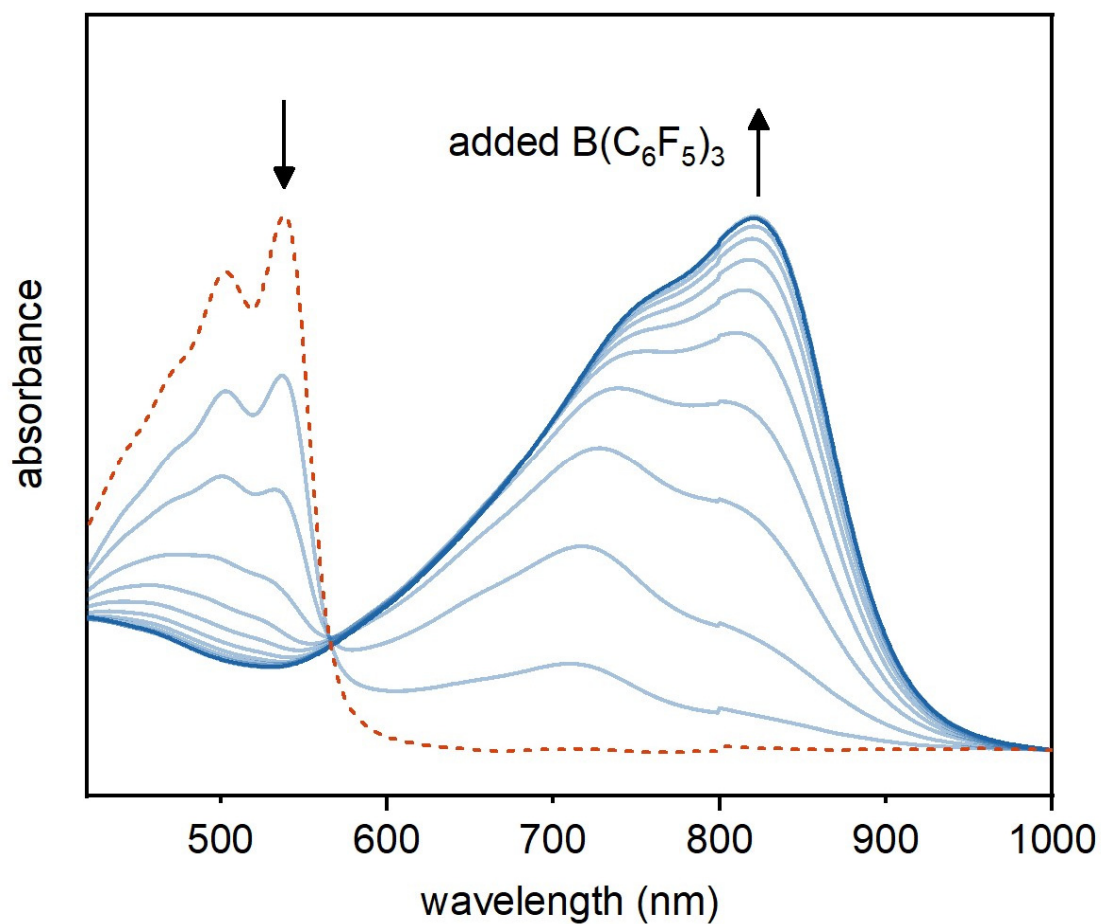


Figure S14. UV-Vis titration of $\text{B}(\text{C}_6\text{F}_5)_3$ (0.15 M) into **3** (0.0326 mM) in $\text{C}_6\text{H}_5\text{Cl}$.

7. Cyclic Voltammetry

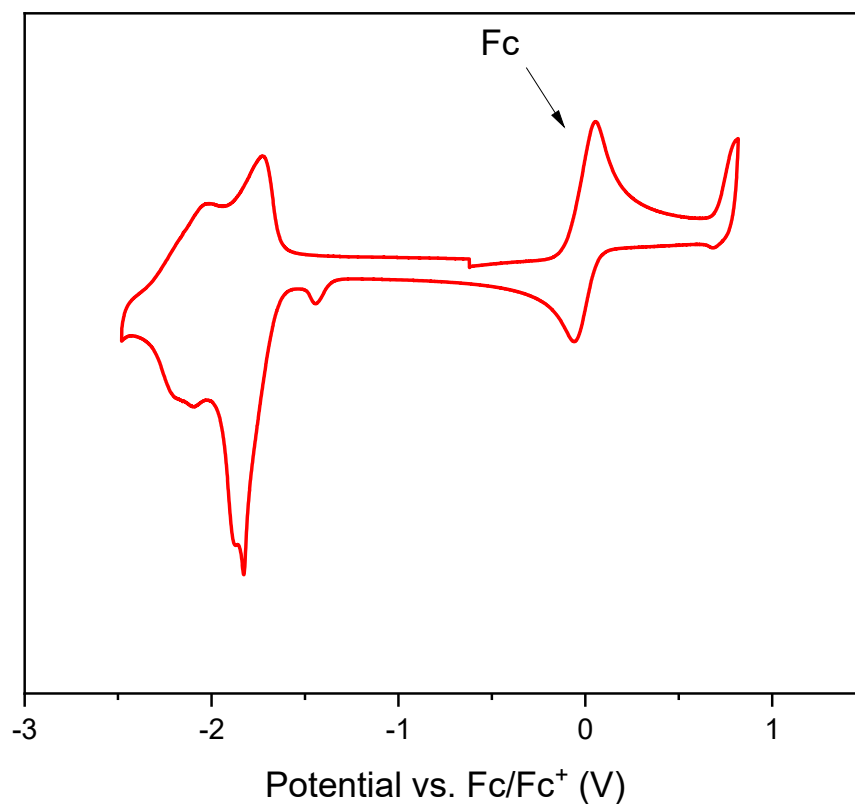


Figure S15. Cyclic voltammogram of **3**. The voltammogram was taken by heating a solution of **3** and dropping it onto a glassy carbon working electrode. Supporting electrolyte: 0.3 M TBAPF₆ in THF; 100 mV/s scan rate. Scans were started at the open-circuit potential and scanned in the anodic direction.

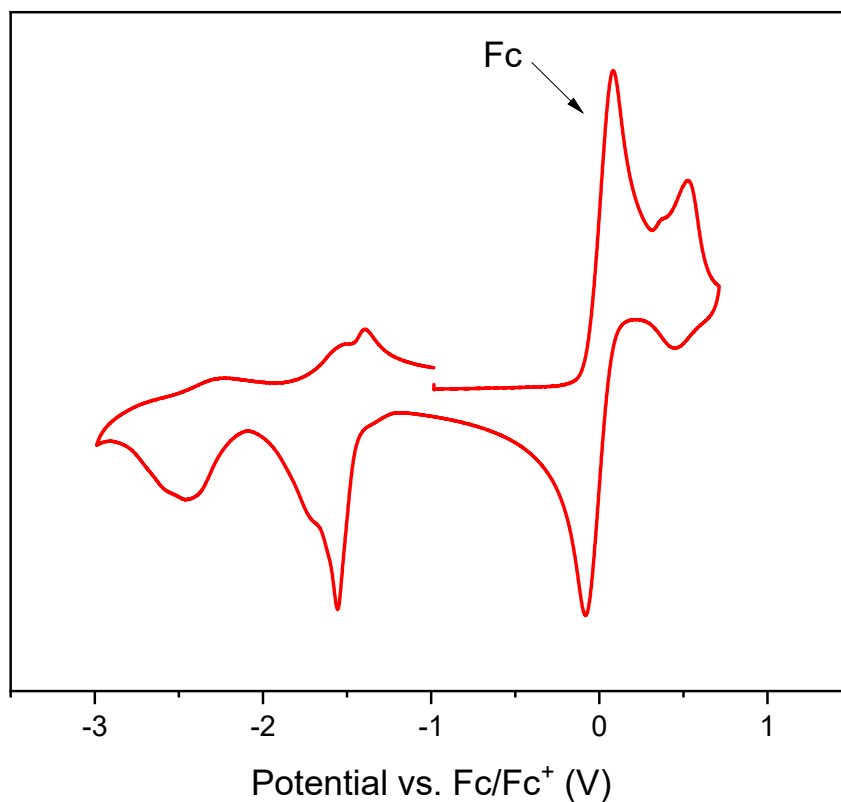


Figure S16. Cyclic voltammogram of **7**. The voltammogram was taken by heating a solution of **7** and dropping it onto a glassy carbon working electrode. Supporting electrolyte: 0.3 M TBAPF₆ in THF; 100 mV/s scan rate. Scans were started at the open-circuit potential and scanned in the anodic direction.

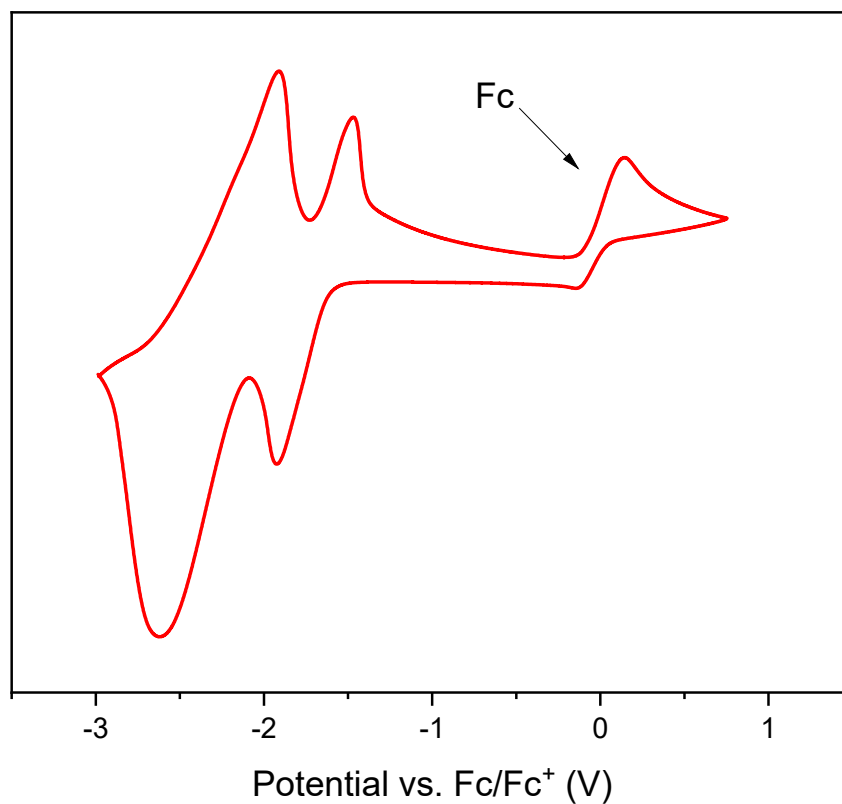


Figure S17. Cyclic voltammogram of **8**. The voltammogram was taken by heating a solution of **8** and dropping it onto a glassy carbon working electrode. Supporting electrolyte: 0.3 M TBAPF₆ in THF; 100 mV/s scan rate. Scans were started at the open-circuit potential and scanned in the anodic direction.

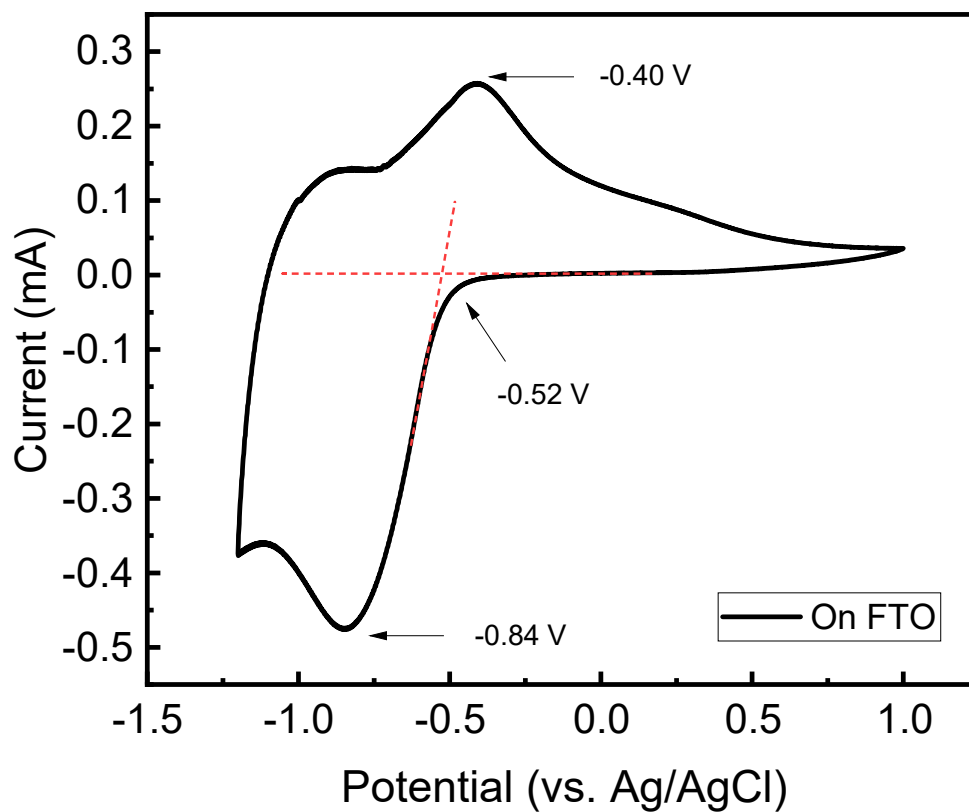


Figure S18. Cyclic voltammogram for a thin film of **10** spin coated on FTO/glass substrate. Voltammograms taken in a 0.2 M TBAPF₆ in propylene carbonate (PC) with a 50 mV/s scan rate. The $E_{1/2}$ value for **10** is -0.62V vs. Ag/AgCl.

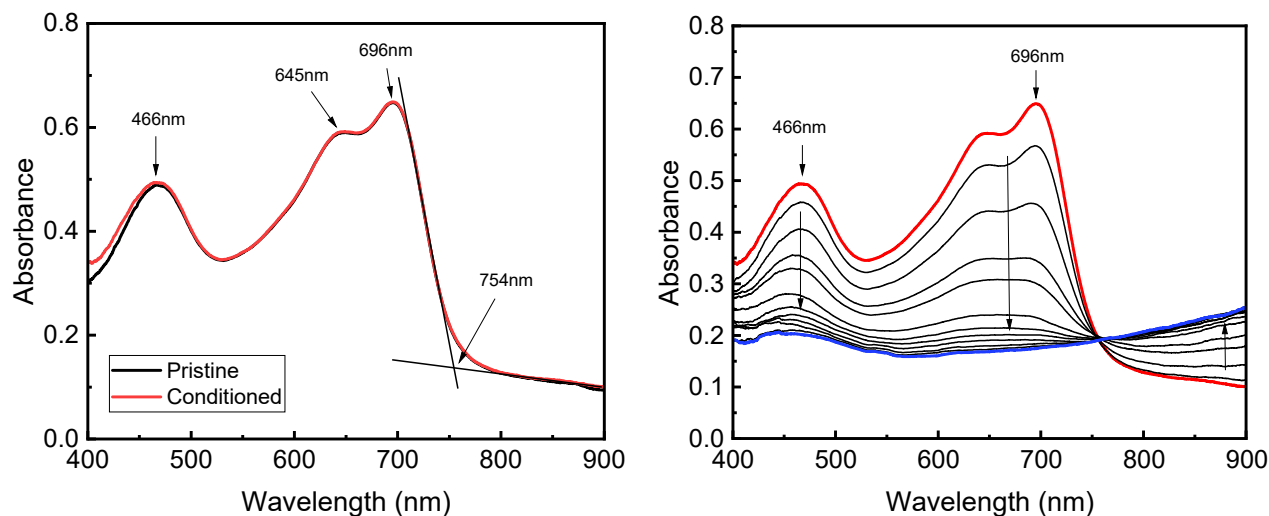


Figure S19. Spectroelectrochemistry for a thin film of **10** spin coated onto FTO/glass substrate in 0.2 M TBAPF₆/Propylene carbonate. UV-Vis Spectra of pristine film and electrochemical conditioned film (left). Spectroelectrochemistry of **10** (red) subjected to 20 mV potential increments from -0.4 V to -0.7 V vs Ag/AgCl (right). The polymer film bleaches at -0.7 V (blue).

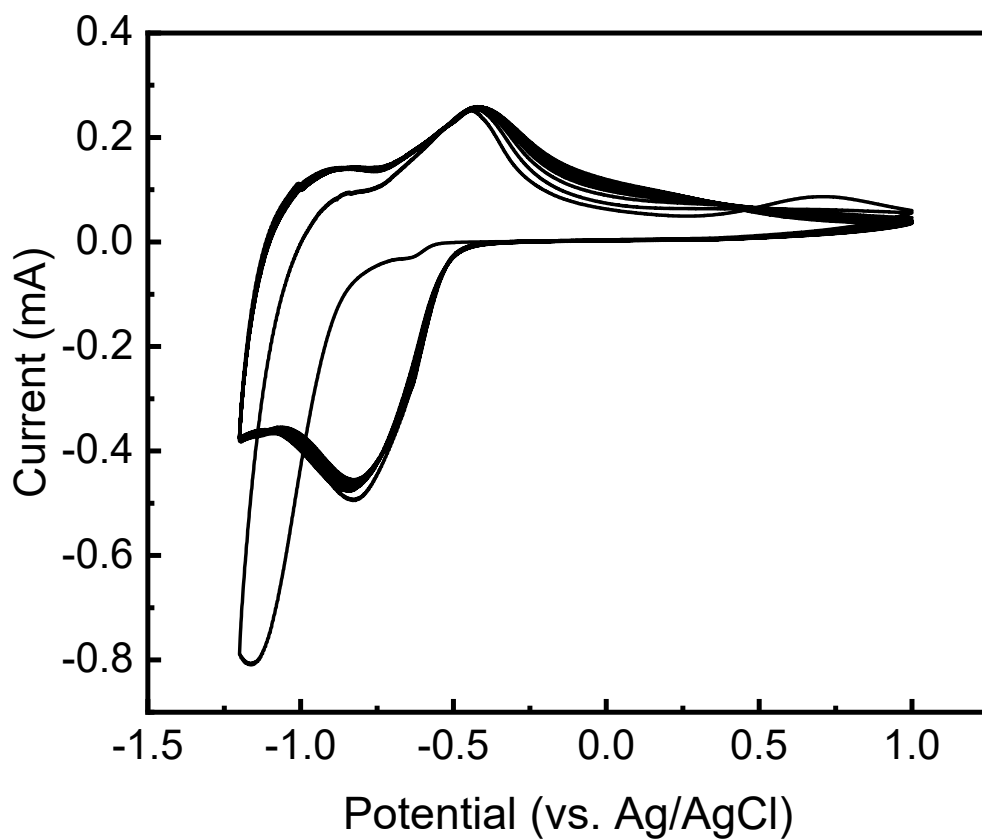


Figure S20. Cyclic voltammogram of **10** deposited on Fluorine-doped tin oxide (FTO) substrate after 10 continuous cycles under N₂ atmosphere. Voltammograms taken in a 0.2 M TBAPF₆ in propylene carbonate (PC) with a 50 mV/s scan rate. The $E_{1/2}$ value for **10** is -0.62V vs. Ag/AgCl.

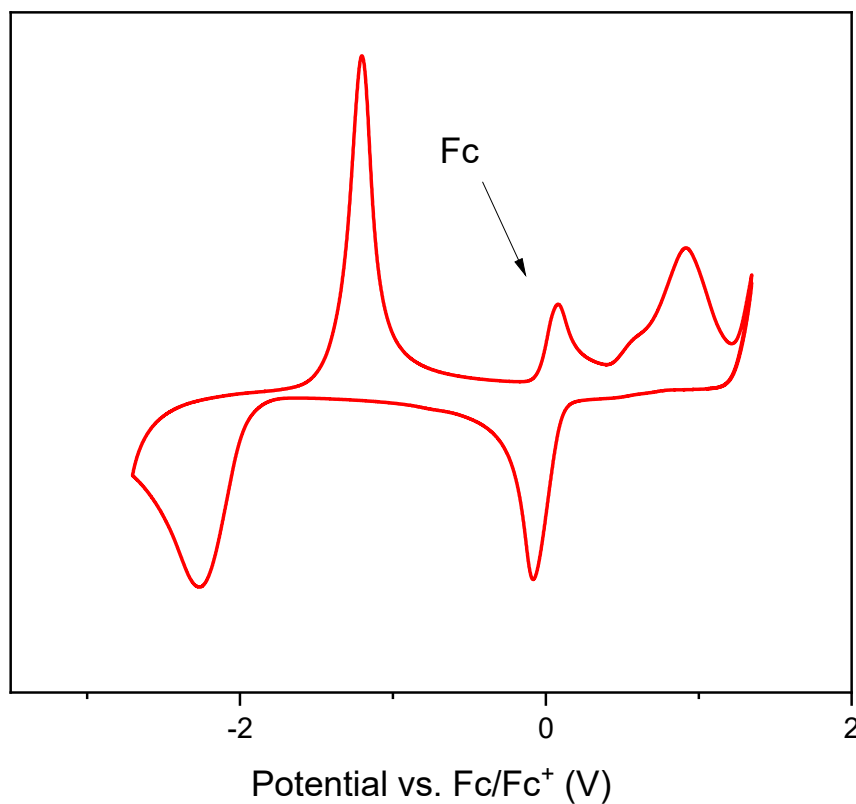


Figure S21. Cyclic voltammogram of **11**. The voltammogram was taken by heating a solution of **11** and dropping it onto a glassy carbon working electrode. Supporting electrolyte: 0.3 M TBAPF₆ in THF; 100 mV/s scan rate. Scans were started at the open-circuit potential and scanned in the anodic direction.

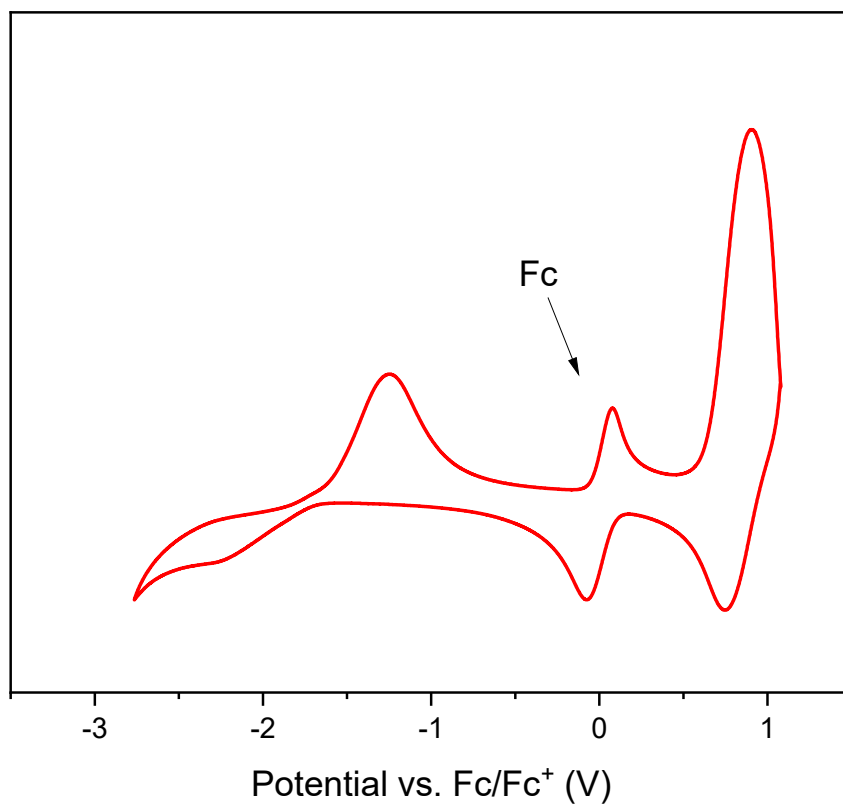


Figure S22. Cyclic voltammogram of **12**. The voltammogram was taken by heating a solution of **12** and dropping it onto a glassy carbon working electrode. Supporting electrolyte: 0.3 M TBAPF₆ in THF; 100 mV/s scan rate. Scans were started at the open-circuit potential and scanned in the anodic direction.

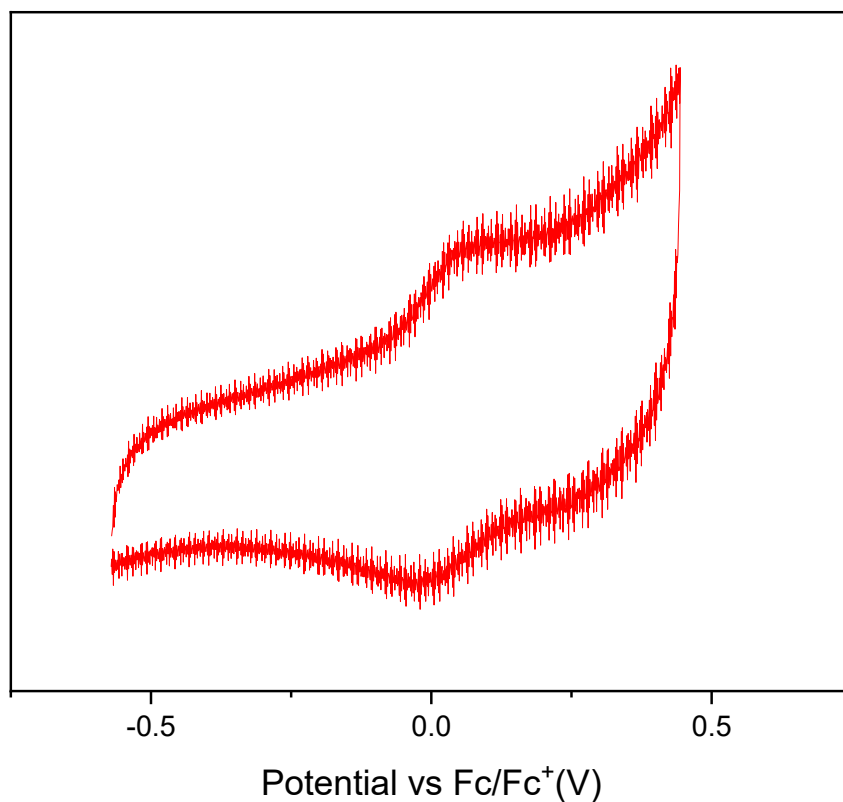
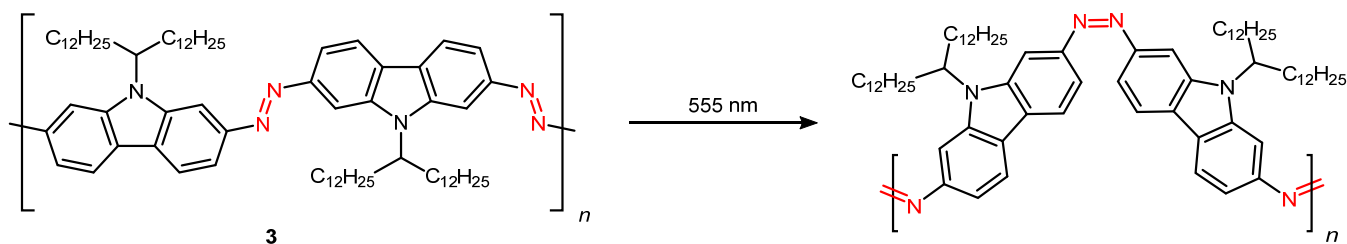


Figure S23. Cyclic voltammogram isolated in the ferrocene couple for **15**. The voltammogram was taken by heating a solution of **15** and dropping it onto a glassy carbon working electrode. Supporting electrolyte: 0.3 M TBAPF₆ in THF; 100mV/s scan rate. Scans were started at the open-circuit potential and scanned in the cathodic direction. The $E_{1/2}$ value for **15** is 0.02 V vs. Fc/Fc⁺.

8. Photoswitching Experiments



PolyAzoCarbazole (3). A vial was charged with **3** (0.4 mg) and $\text{C}_6\text{H}_5\text{Cl}$ (20 mL). An aliquot (3 mL) was added to a cuvette, irradiated for 30 s at 555 nm, and quickly transferred to a UV-Vis instrument to obtain measurements.

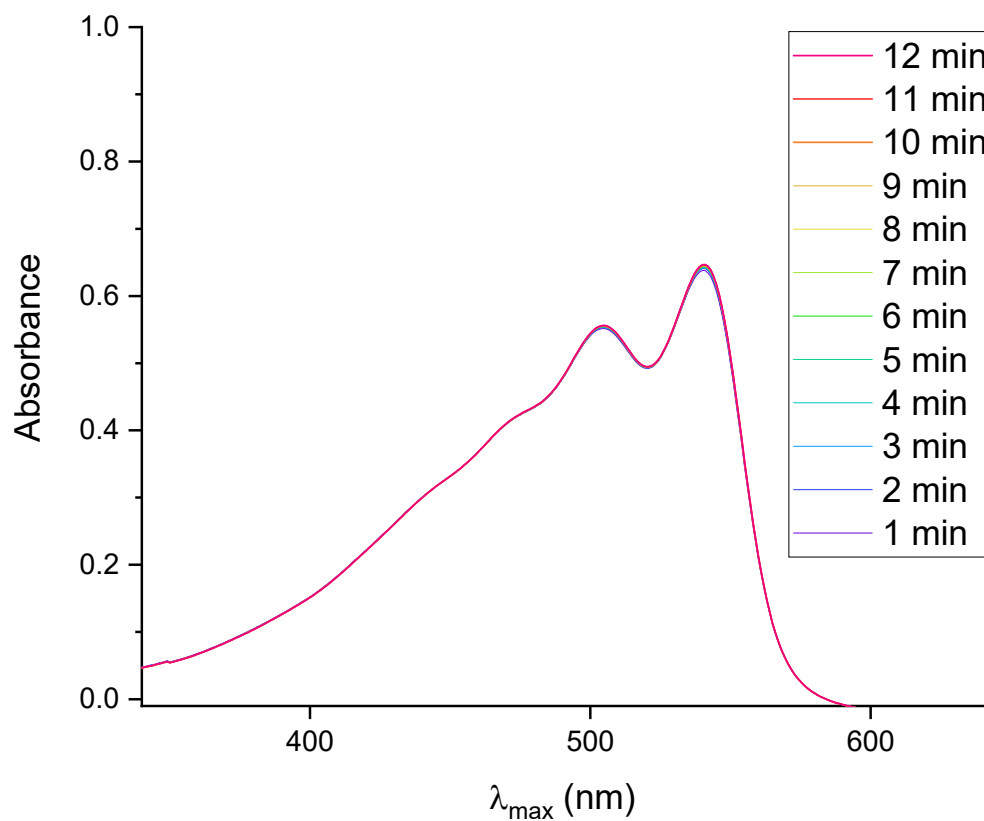
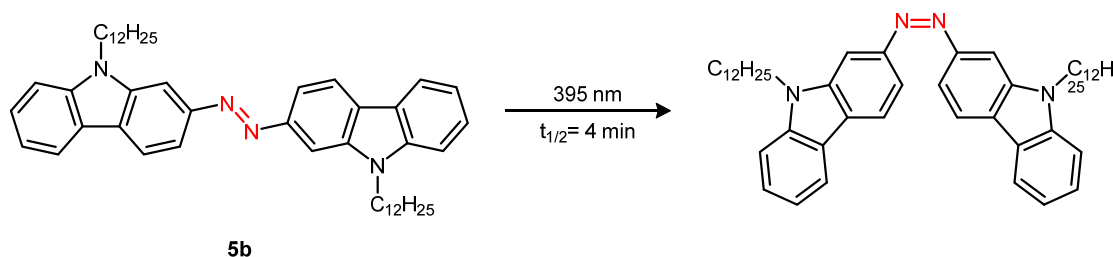


Figure S24. UV-Vis spectrum of photoisomerization of **3** (0.0326 mM) in $\text{C}_6\text{H}_5\text{Cl}$.



Azocarbazole (5b). A vial was charged with **5b** (0.4 mg) and CH₂Cl₂ (20 mL). An aliquot (3 mL) was added to a cuvette, irradiated for 30 s at 395 nm, and quickly transferred to a UV-Vis instrument to obtain measurements.

UV-Vis-NIR (CH₂Cl₂, 0.028 mM): λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 264 (62,000), 303 (25,000), 393 (18,000).

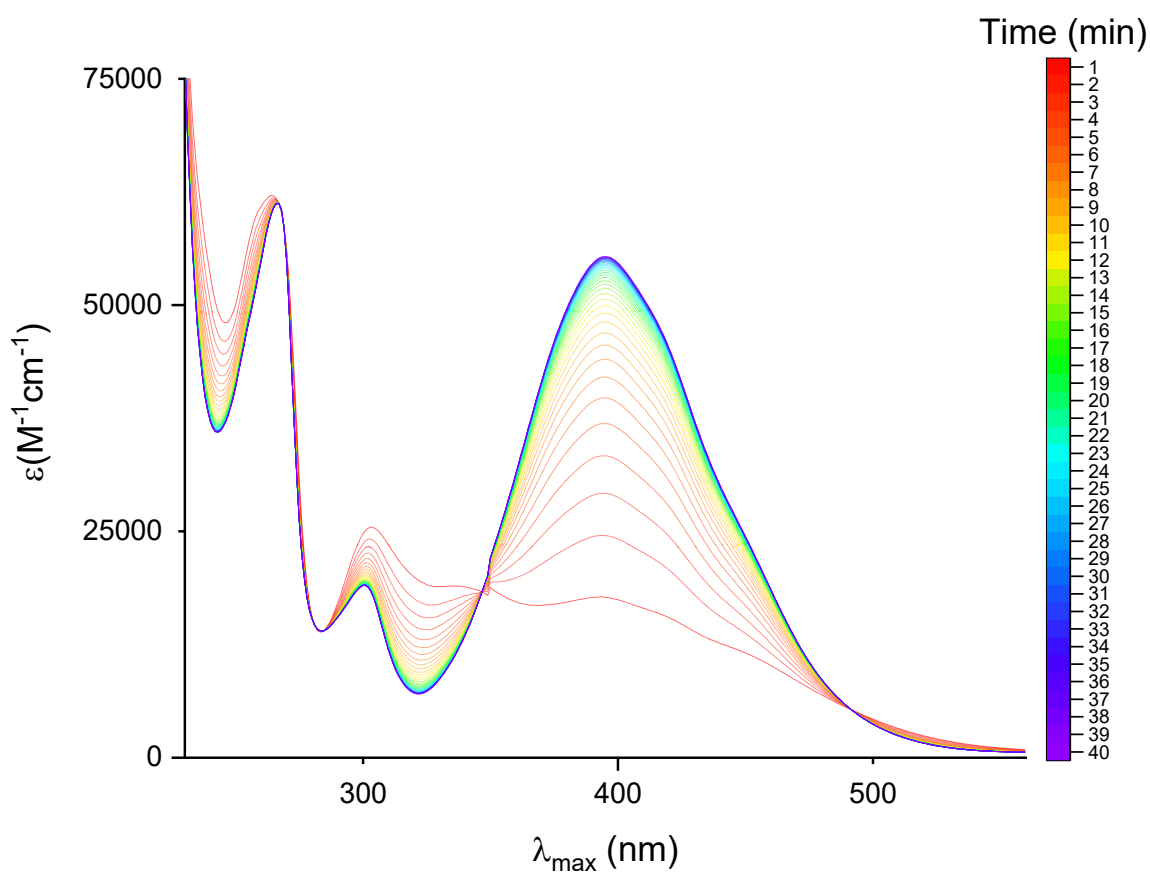


Figure S25. UV-Vis spectrum of photoisomerization of **5b** (0.028 mM) in CH₂Cl₂.

9. Thermogravimetric Analysis

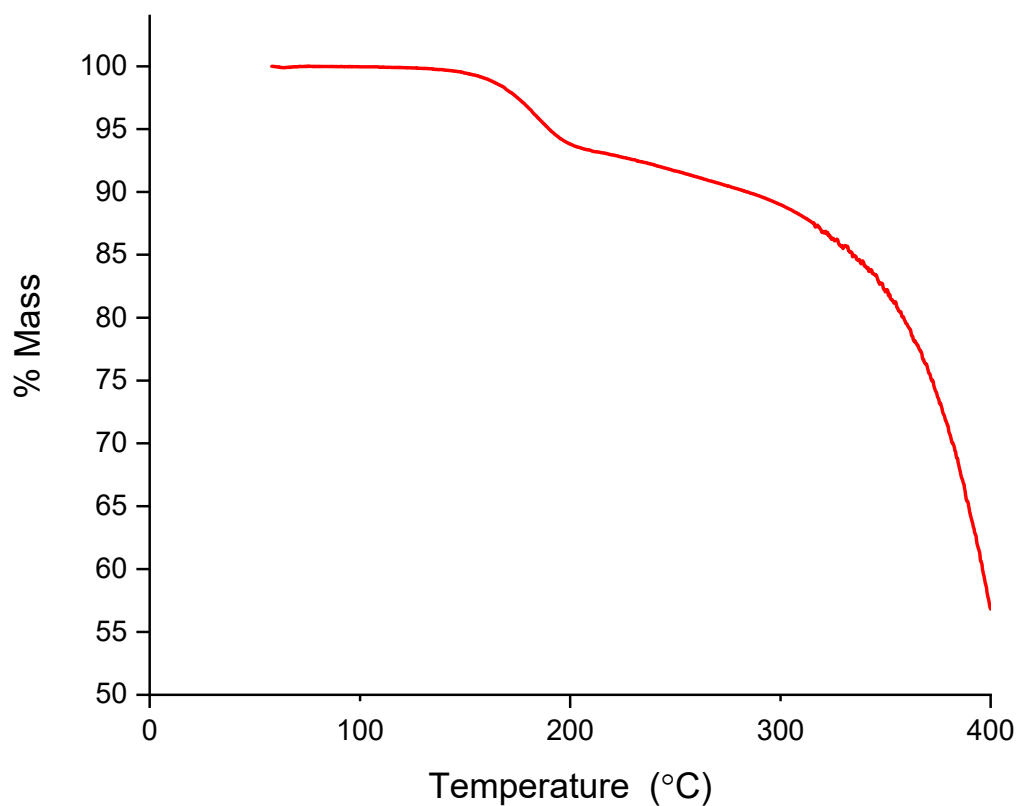


Figure S26. Thermogravimetric analysis of **S10** at 20°C per minute.

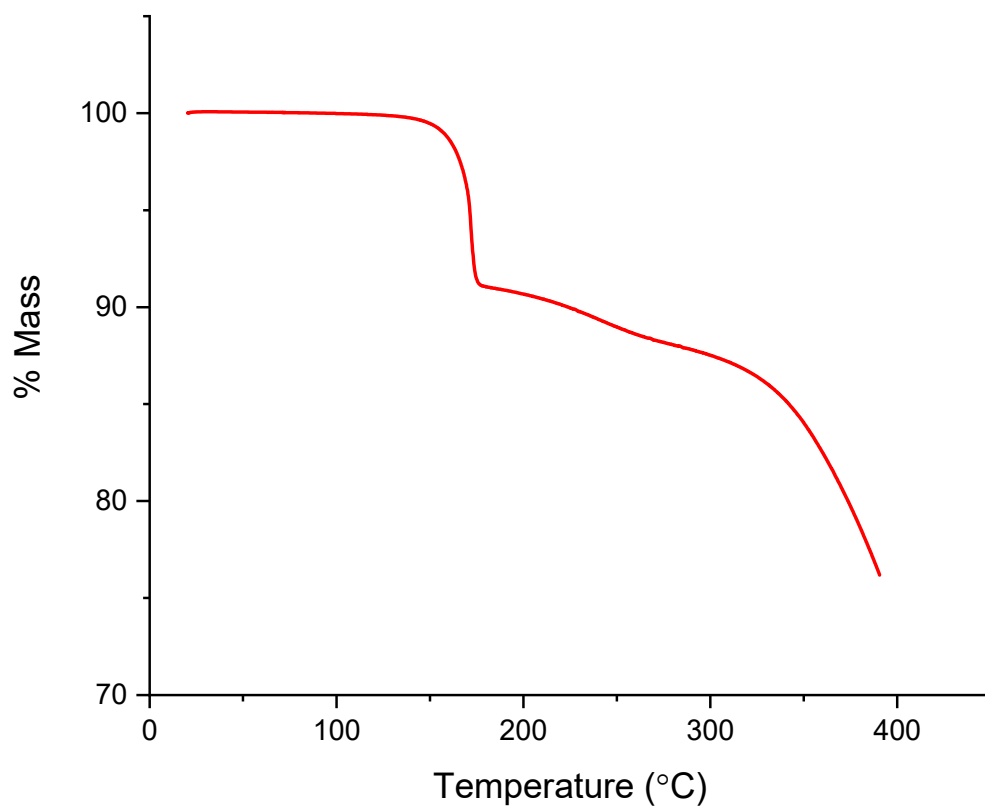


Figure S27. Thermogravimetric analysis of **2** at 20°C per minute.

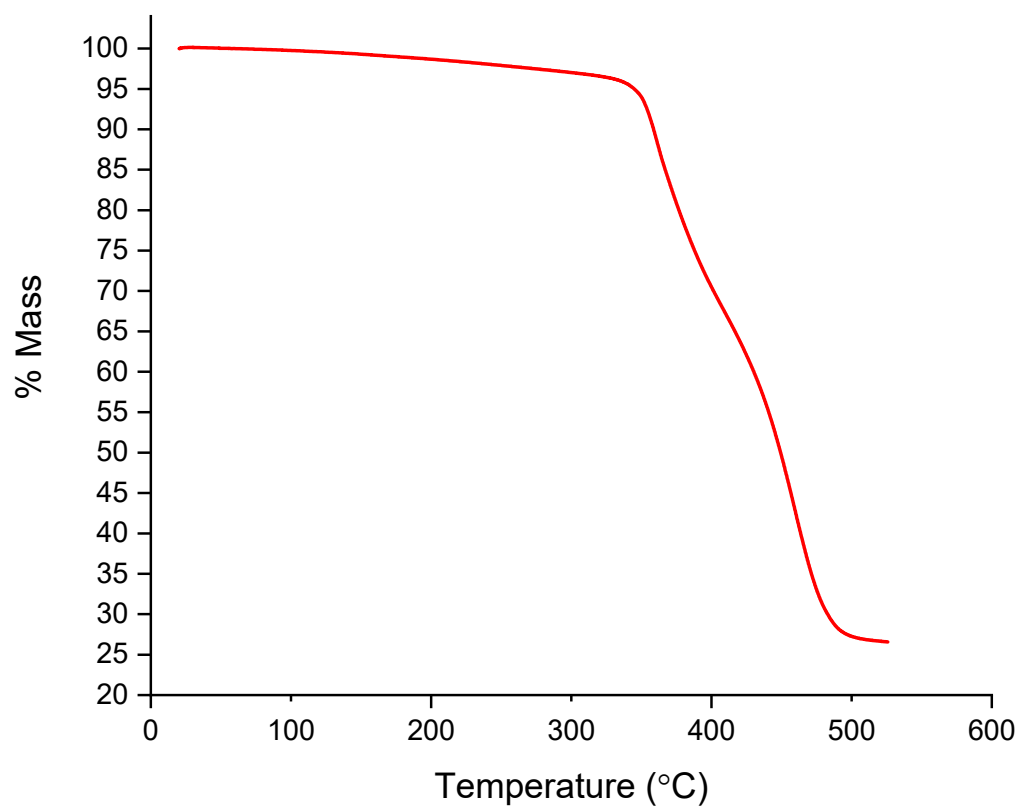


Figure S28. Thermogravimetric analysis of **3** at 20°C per minute.

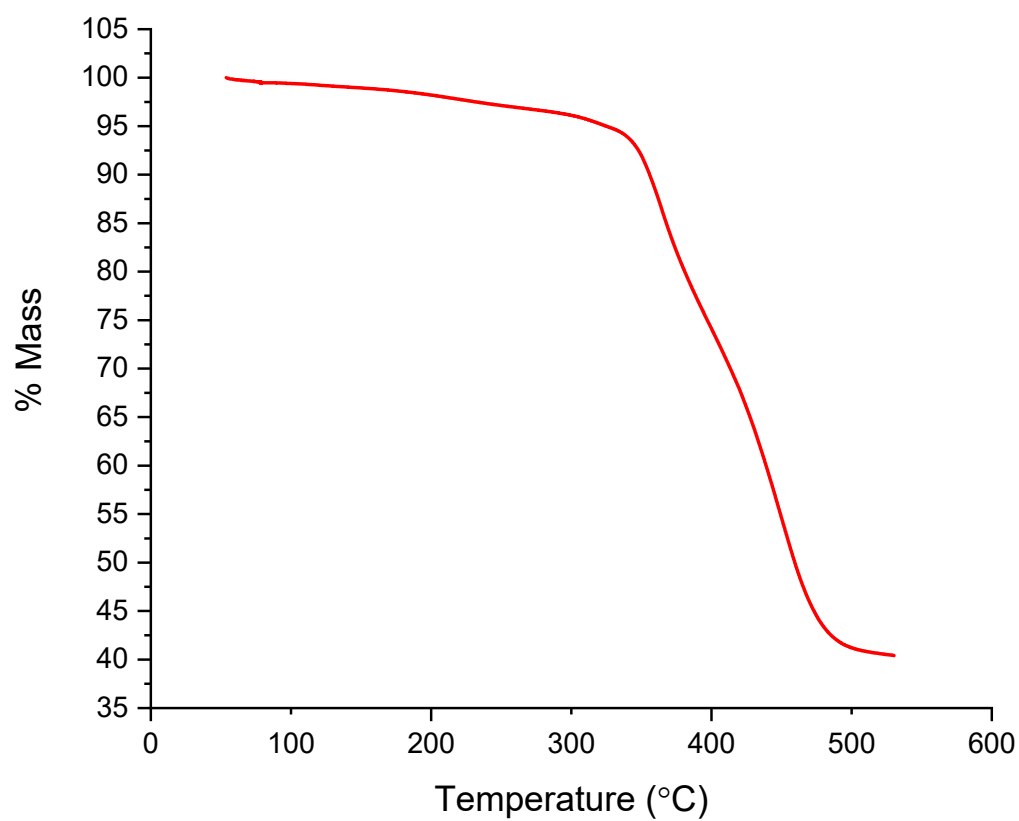


Figure S29. Thermogravimetric analysis of **10** at 20°C per minute.

10. Emission Spectra

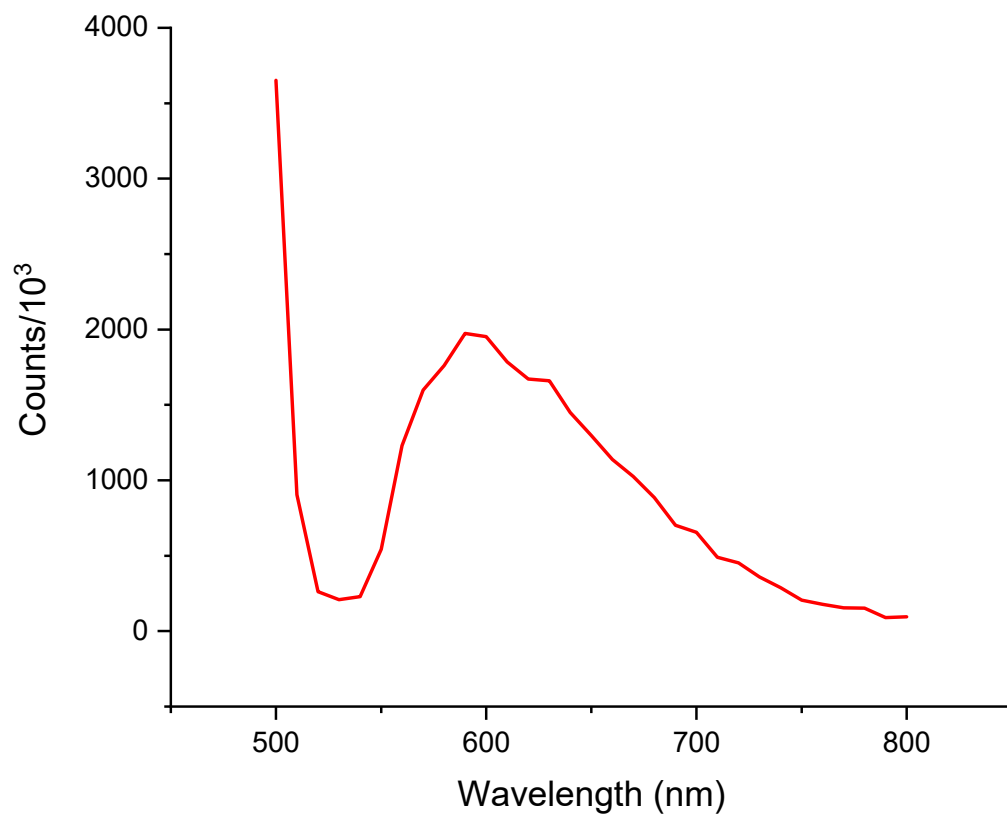


Figure S30. Emission spectrum of **3** (0.046 mM) at 503 nm in C₆H₅Cl.

11. NMR Spectra

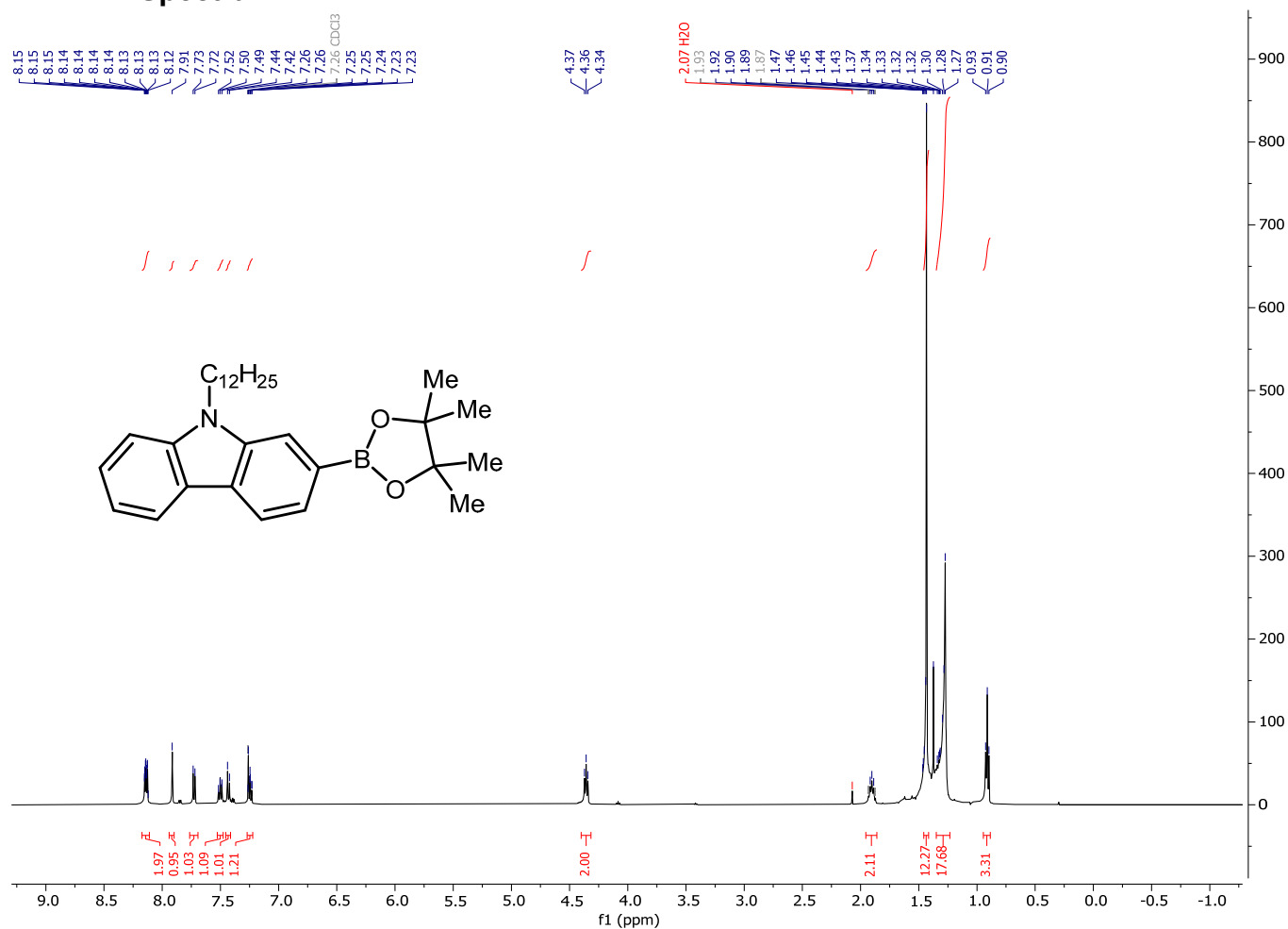


Figure S31. ¹H NMR spectrum of **S1** (500 MHz, CDCl₃).

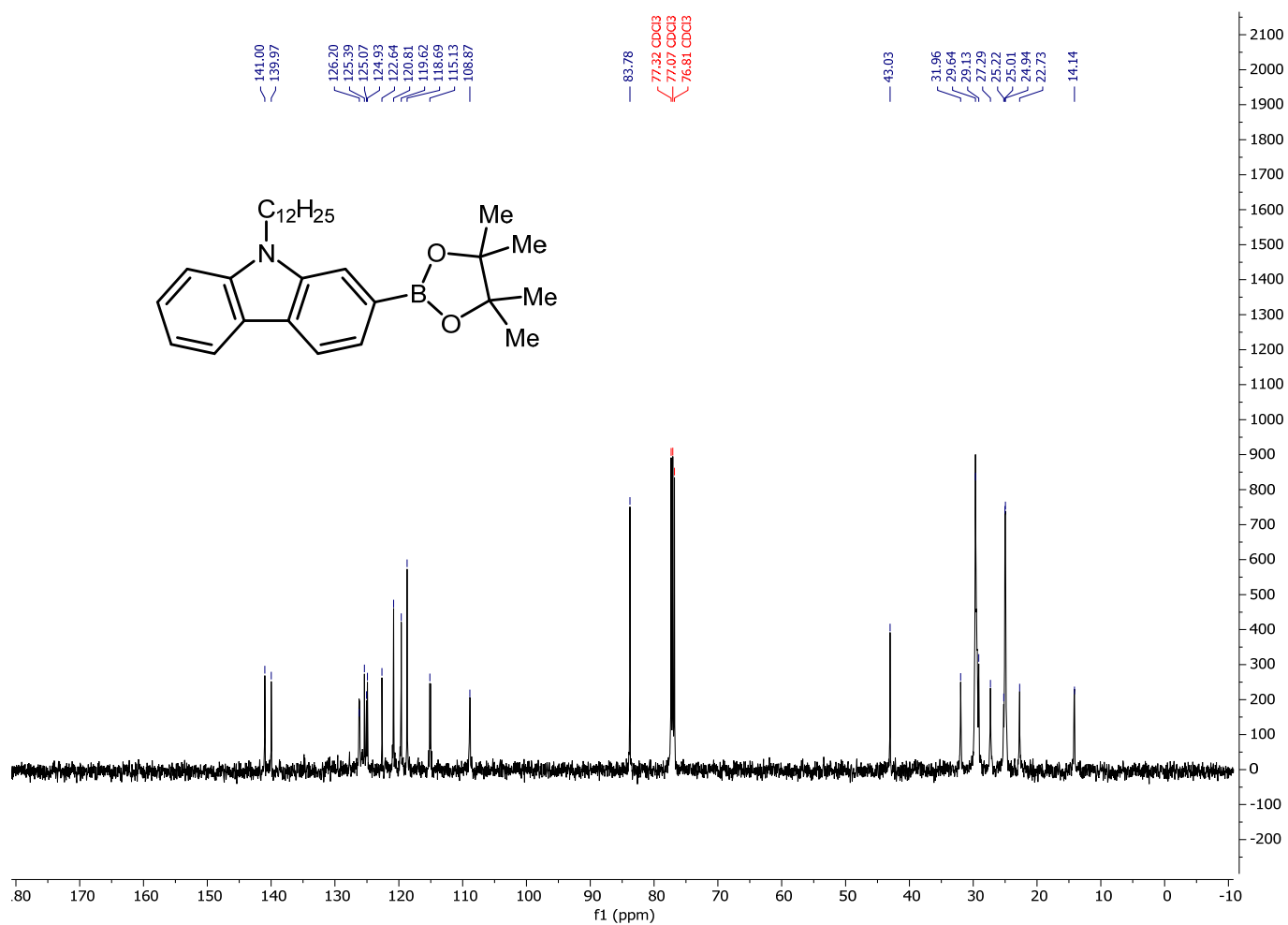


Figure S32. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **S1** (126 MHz, CDCl_3).

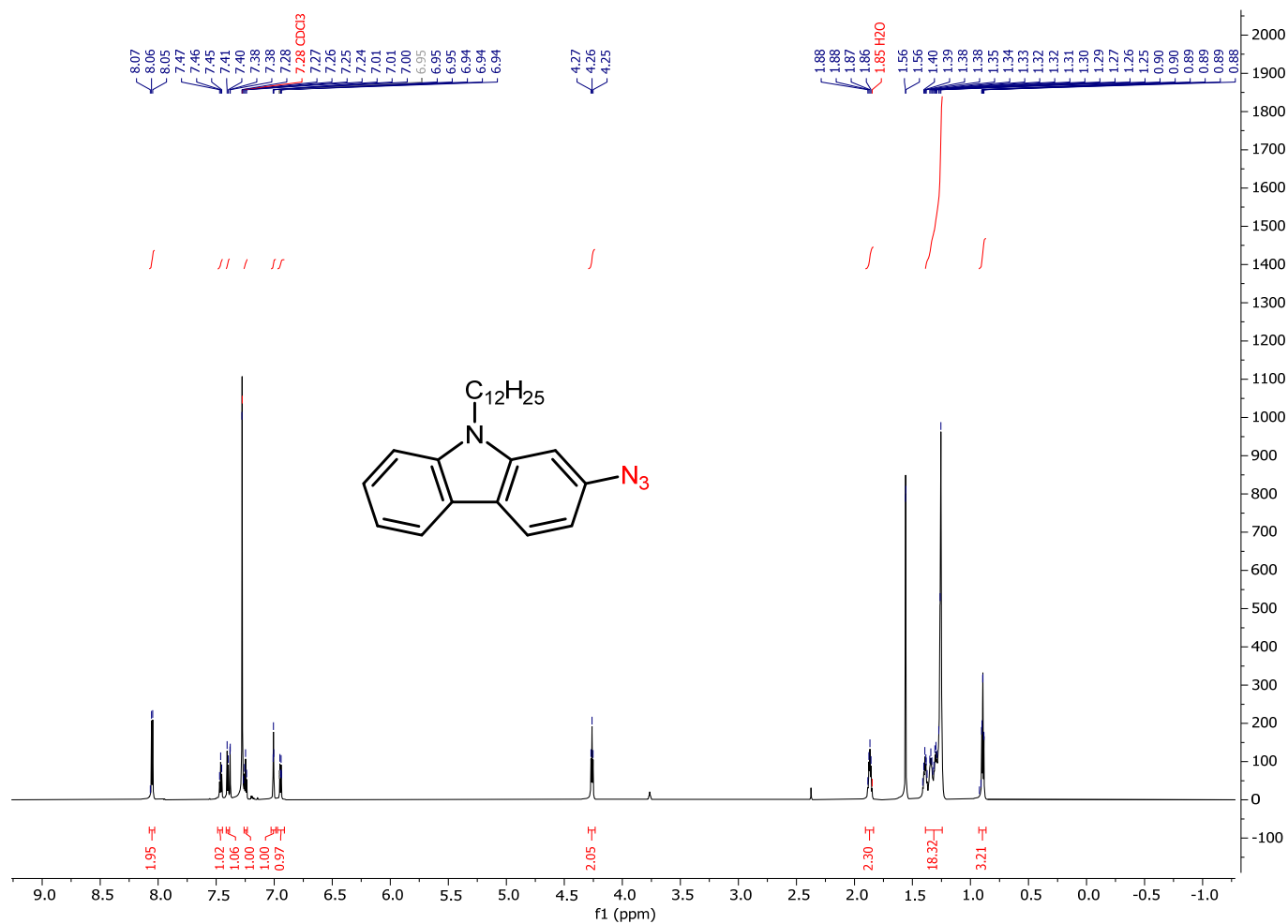


Figure S33. ^1H NMR spectrum of **4b** (800 MHz, CDCl_3).

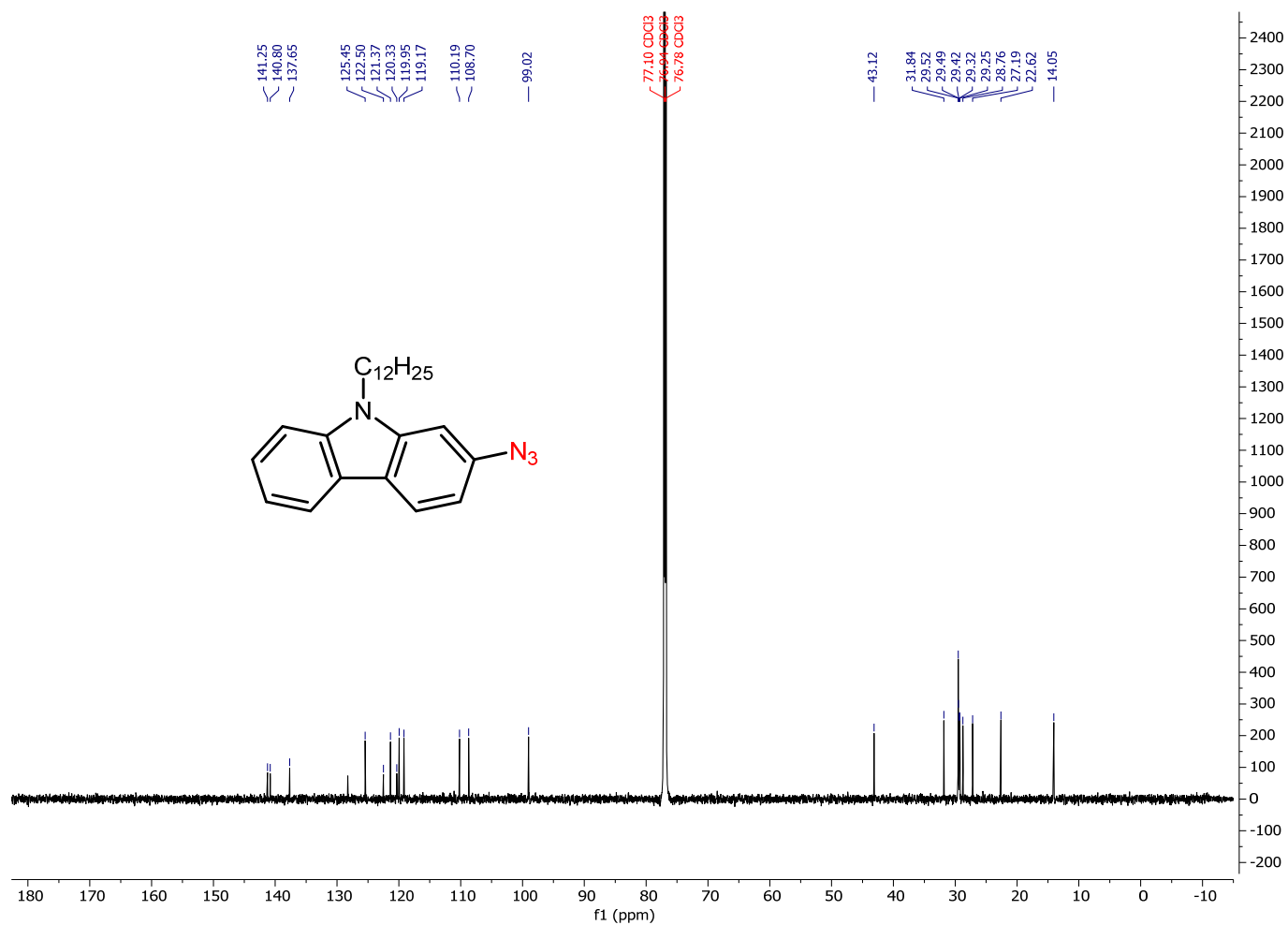


Figure S34. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4b** (201 MHz, CDCl_3).

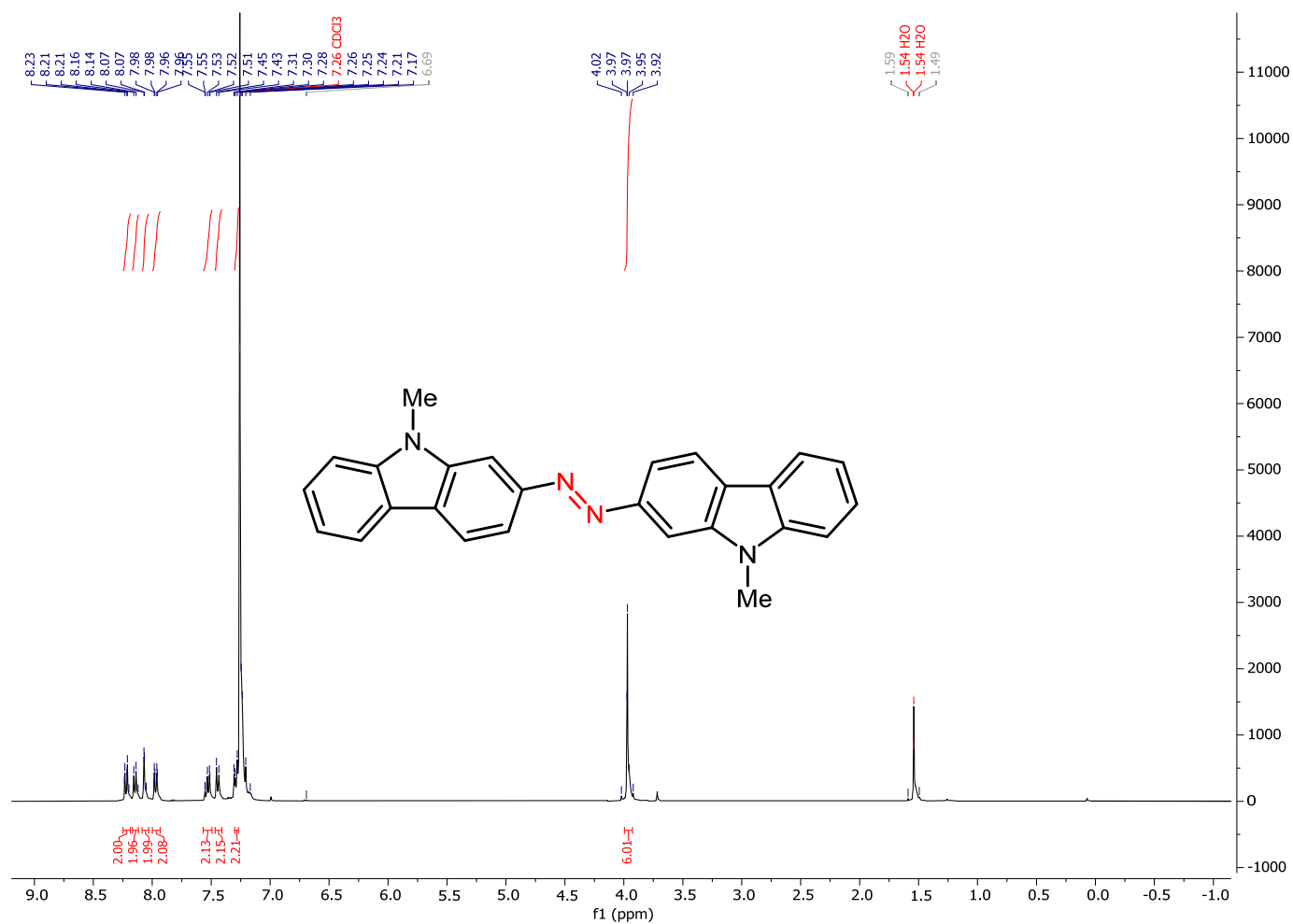


Figure S35. ¹H NMR spectrum of **5a** (400 MHz, CDCl₃).

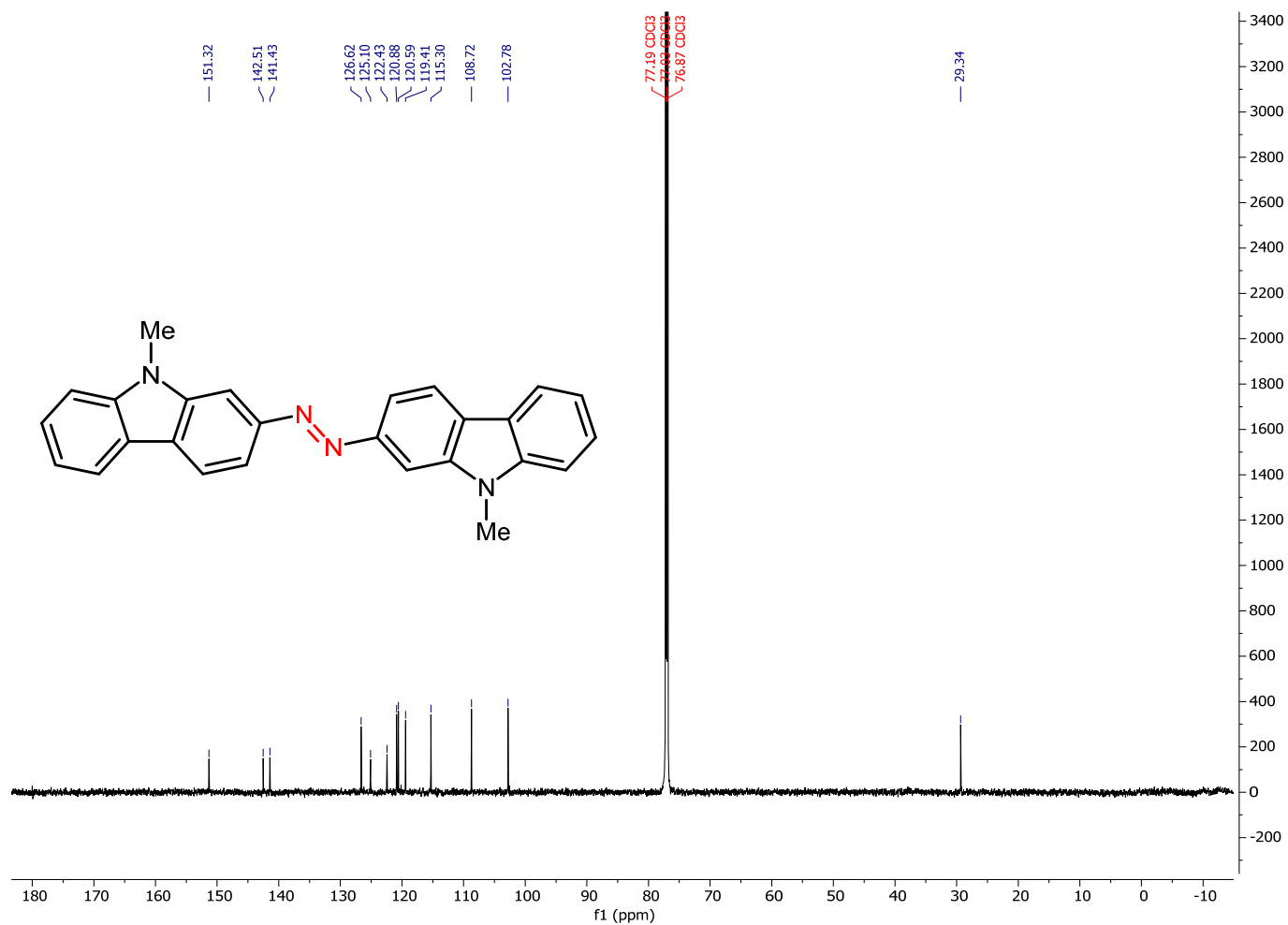


Figure S36. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5a** (201 MHz, CDCl_3).

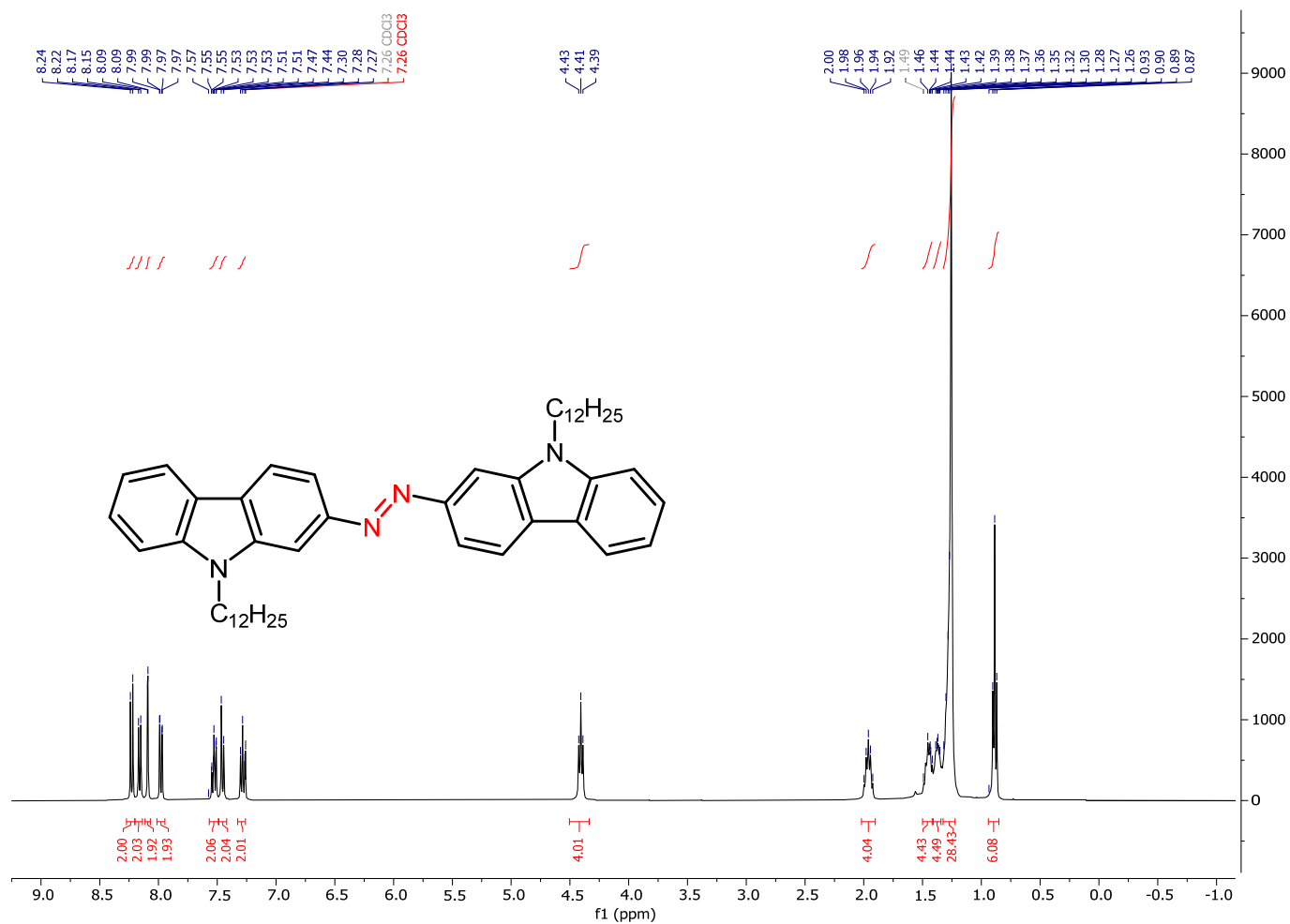


Figure S37. ¹H NMR spectrum of **5b** (400 MHz, CDCl₃).

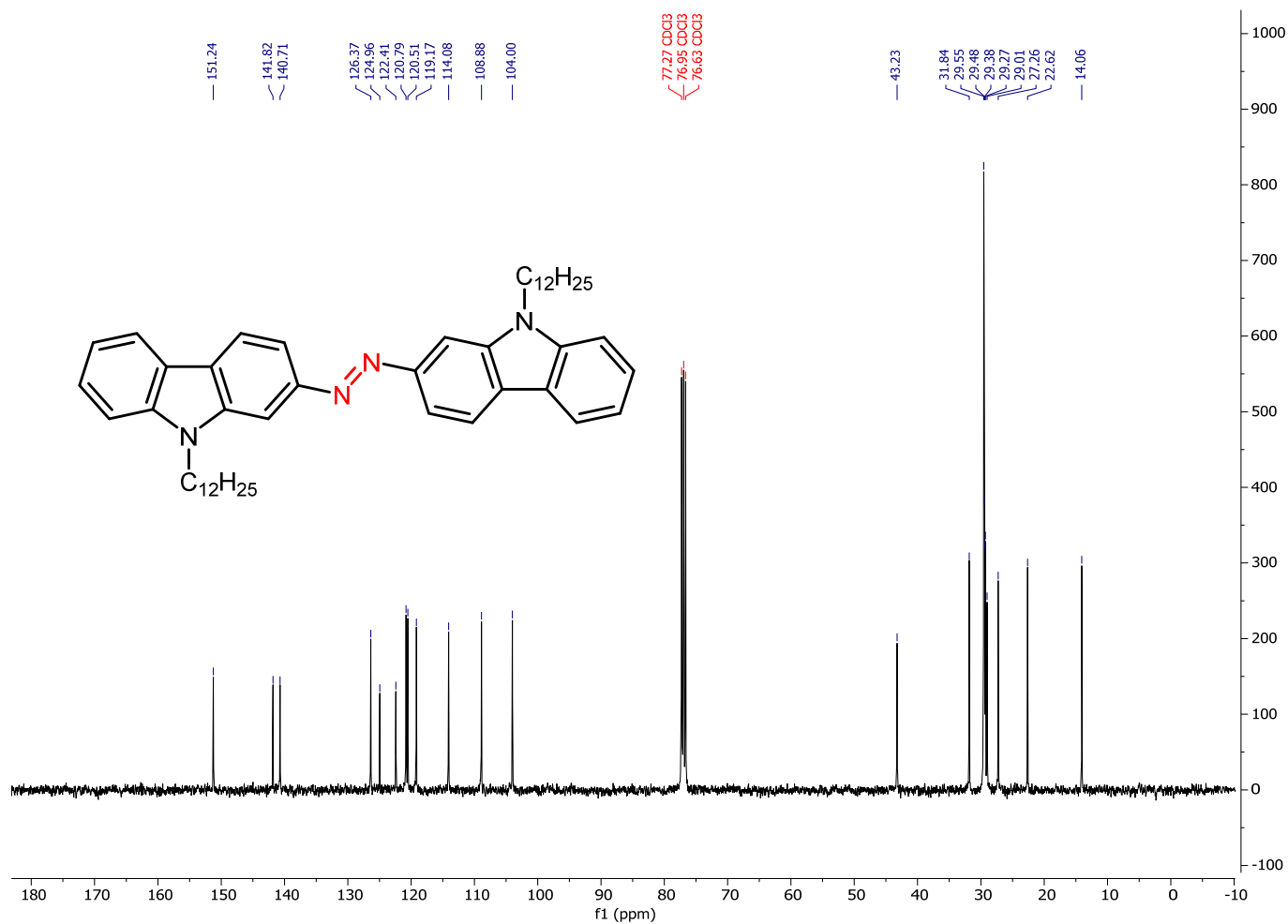


Figure S38. ¹³C{¹H} NMR spectrum of **5b** (126 MHz, CDCl₃).

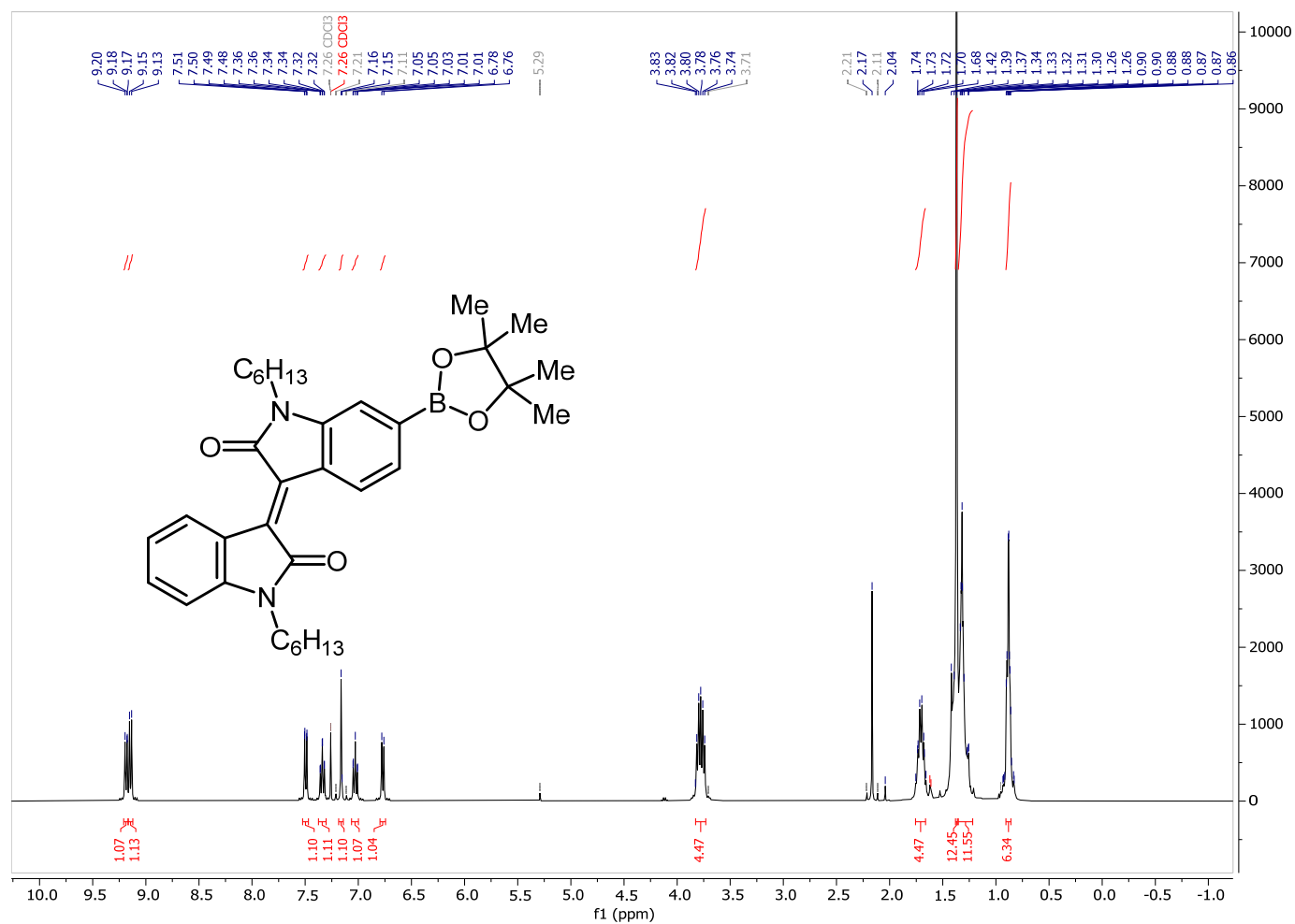


Figure S39. ¹H NMR spectrum of **S2** (400 MHz, CDCl₃).

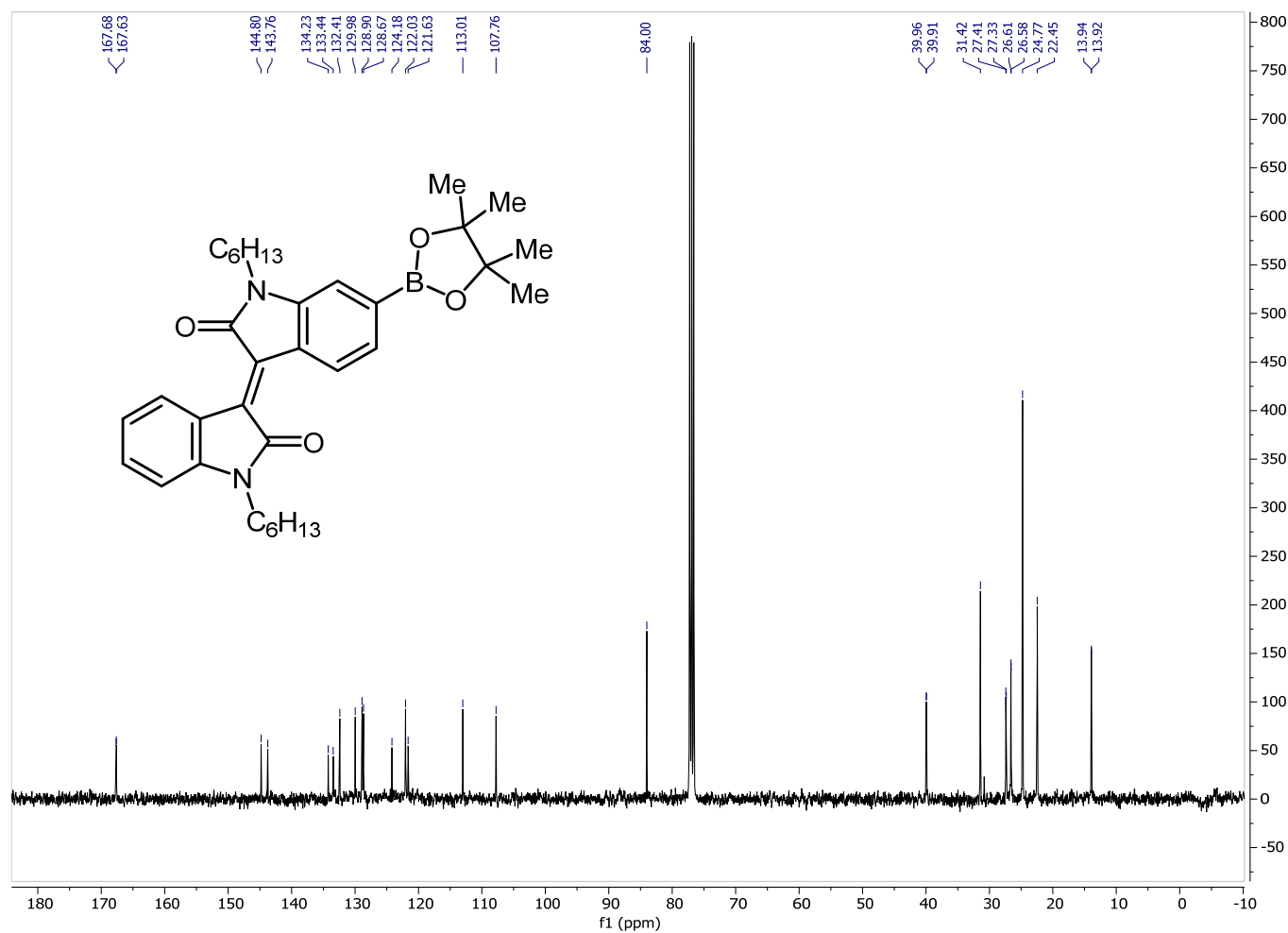


Figure S40. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **S2** (101 MHz, CDCl_3).

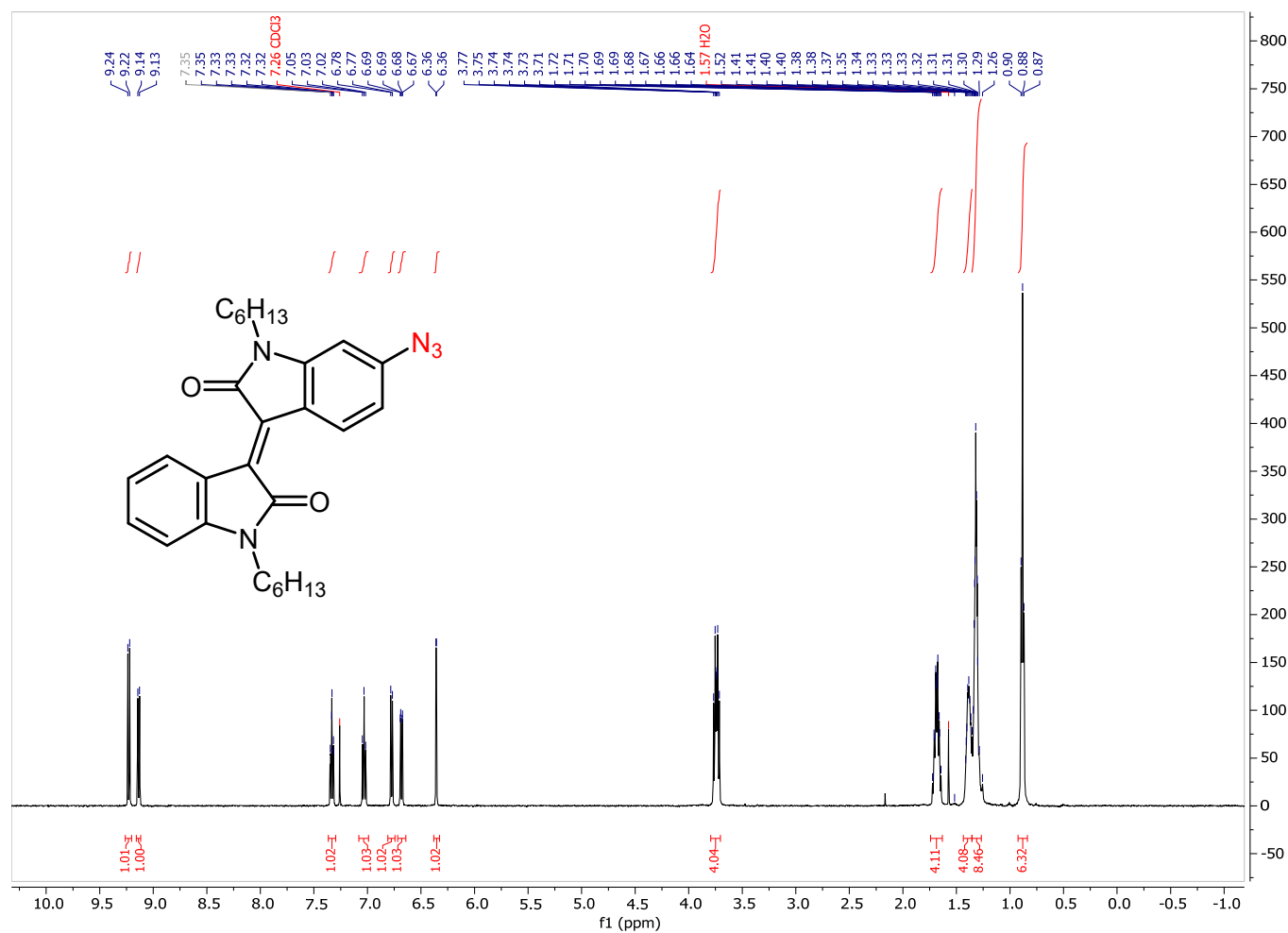


Figure S41. ^1H NMR spectrum of **S3** (500 MHz, CDCl_3).

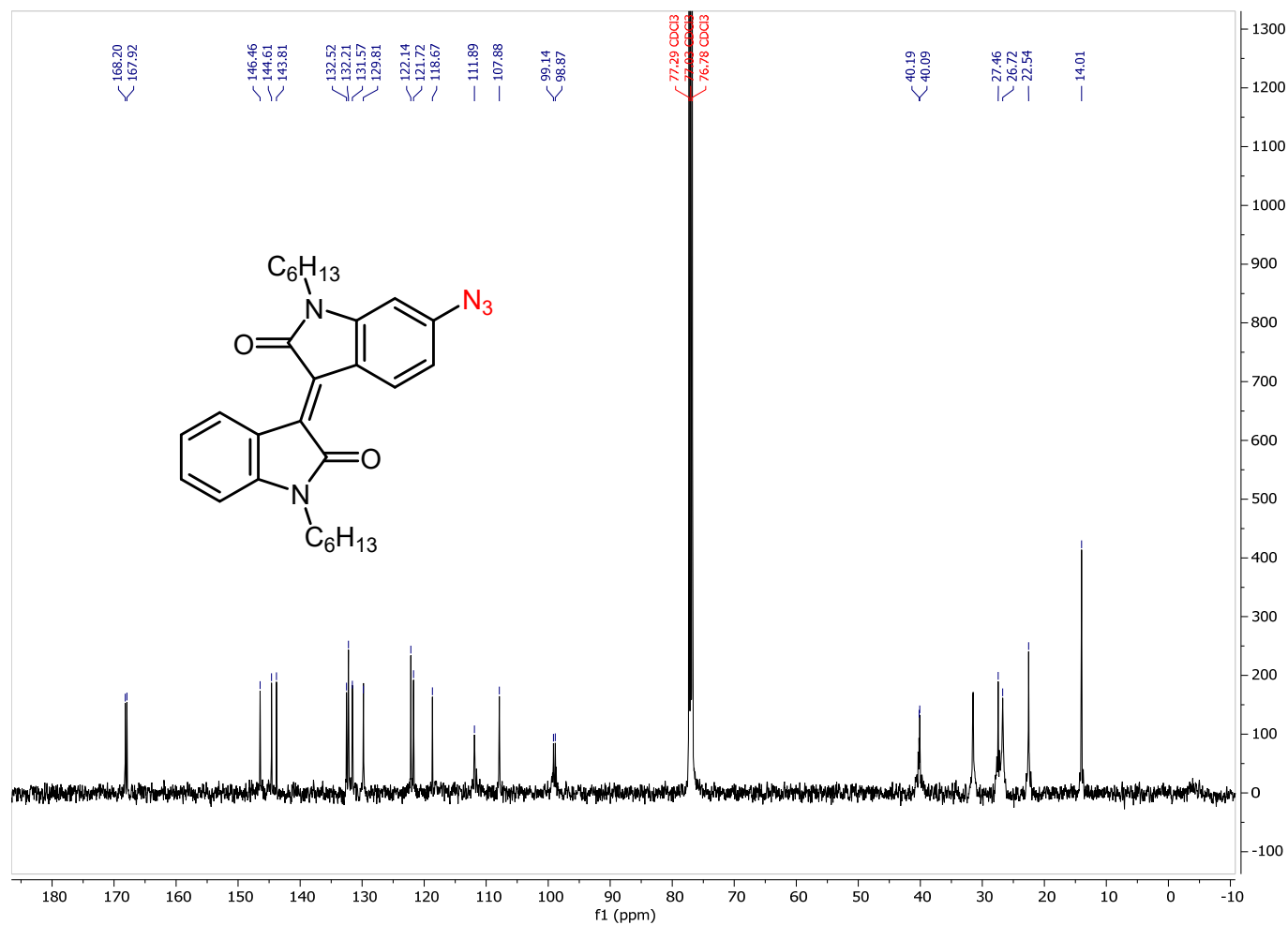


Figure S42. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of S3 (126 MHz, CDCl_3).

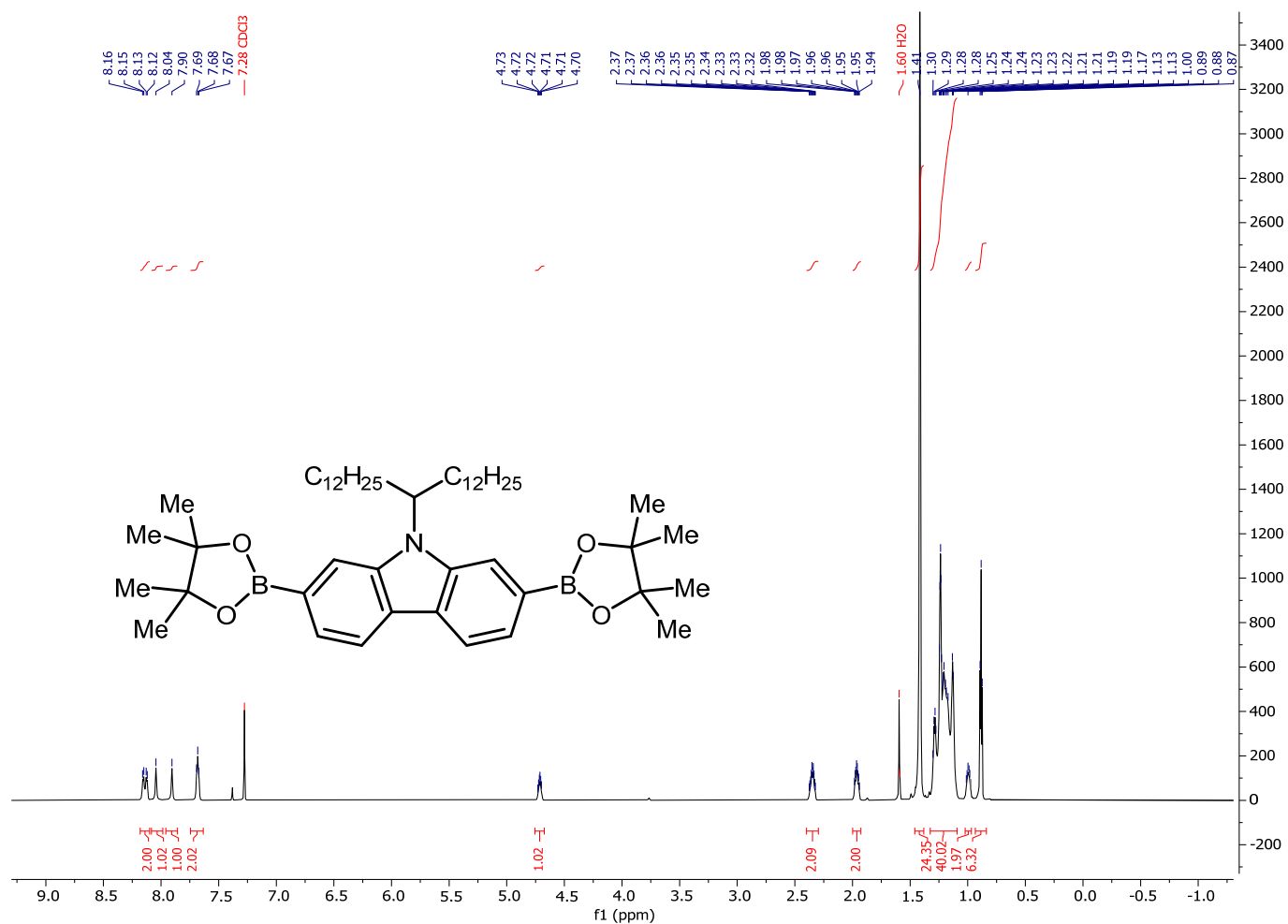


Figure S43. ¹H NMR spectrum of **S4** (800 MHz, CDCl₃).

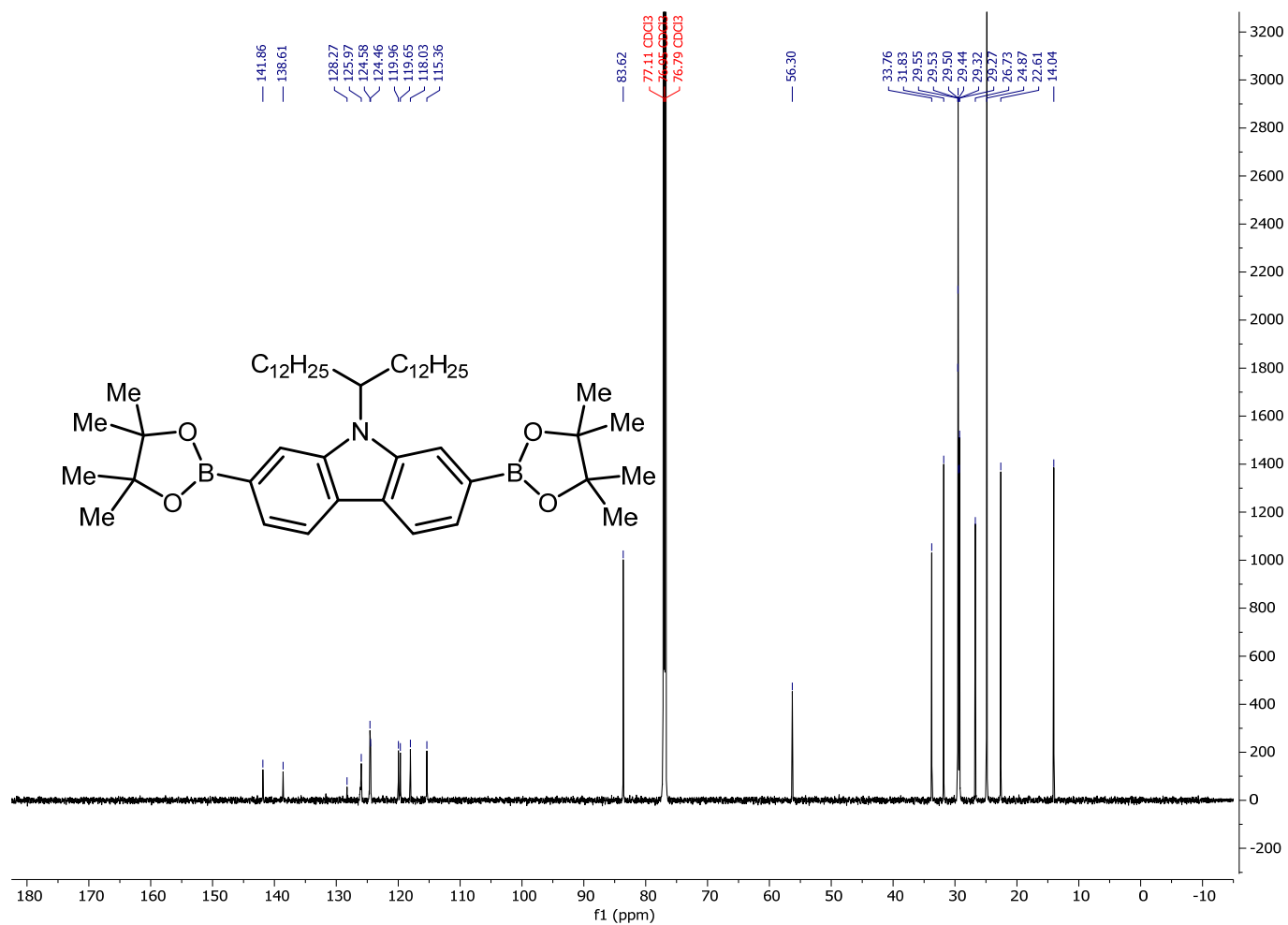


Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **S4** (201 MHz, CDCl_3).

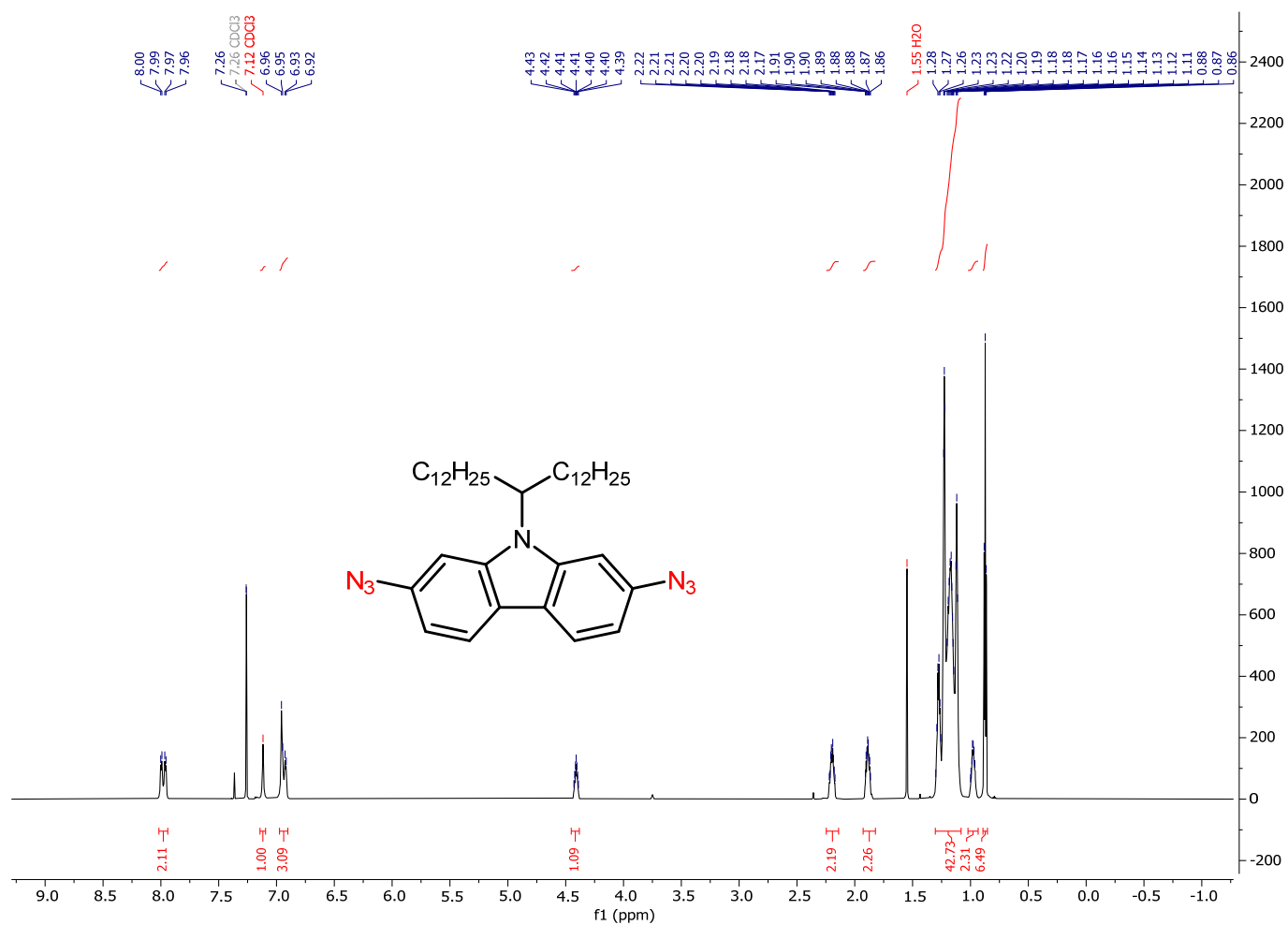


Figure S45. ¹H NMR spectrum of **2** (800 MHz, CDCl₃).

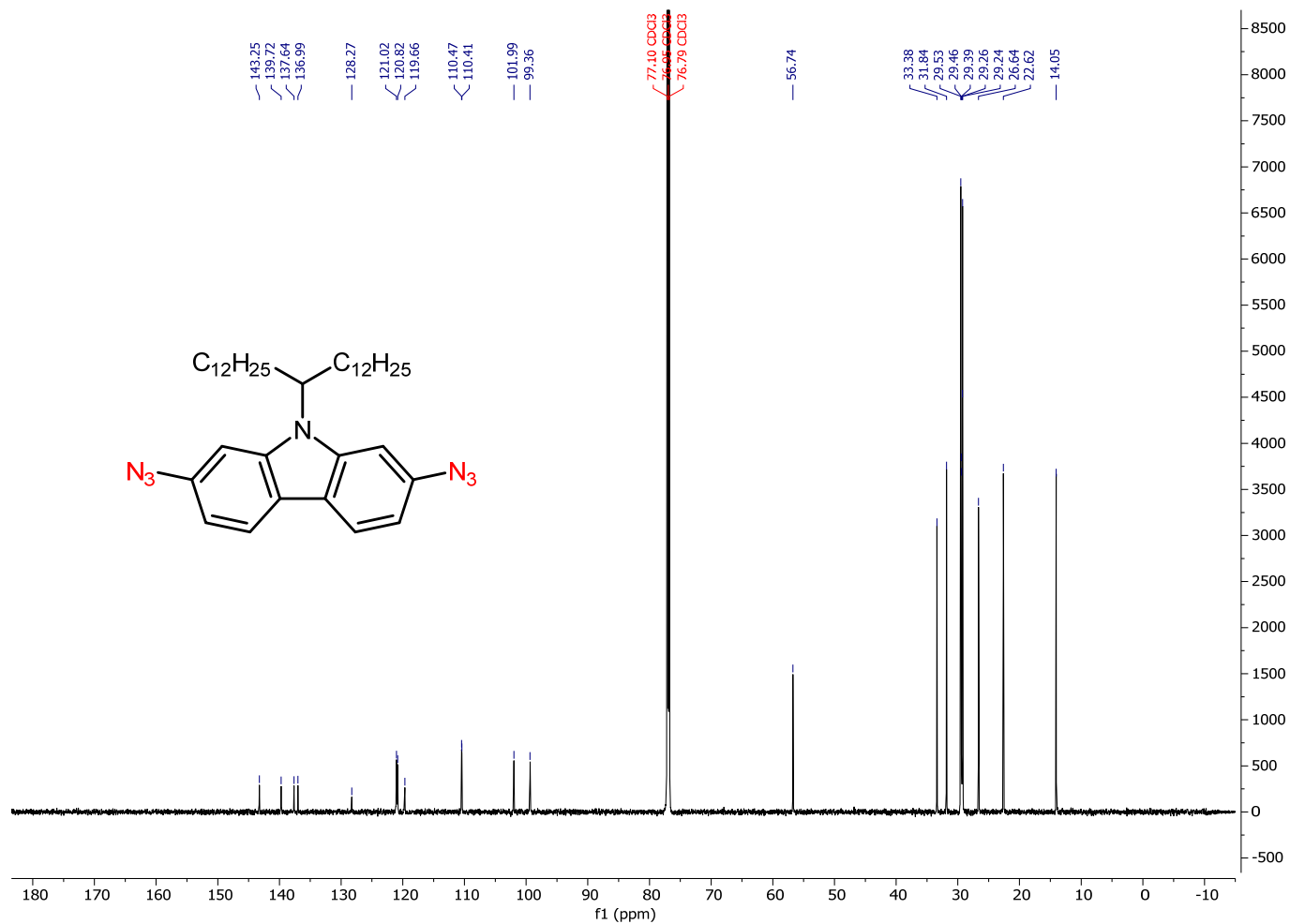


Figure S46. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2 (201 MHz, CDCl_3).

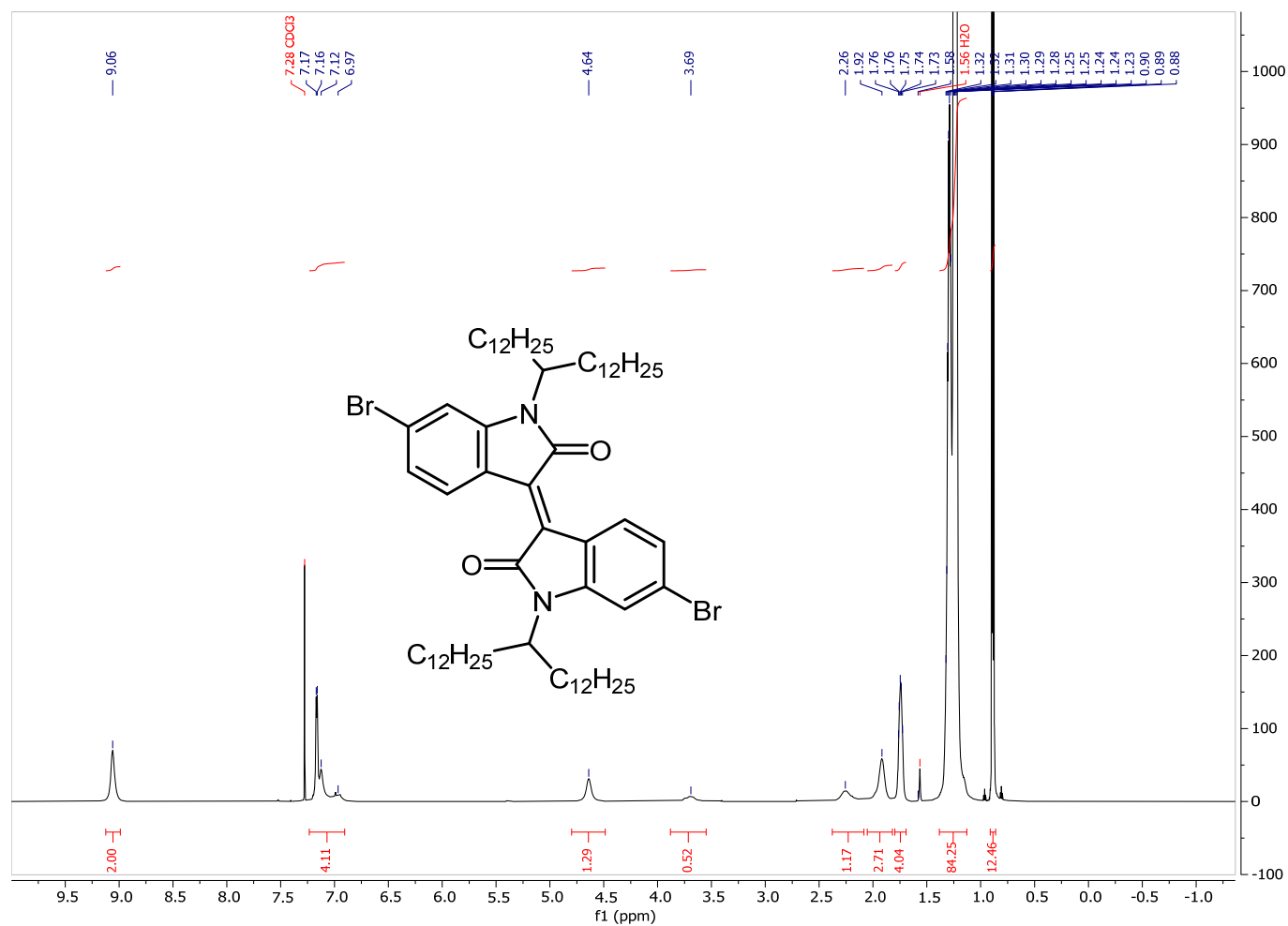


Figure S47. ^1H NMR spectrum of S5 (300 MHz, CDCl_3).

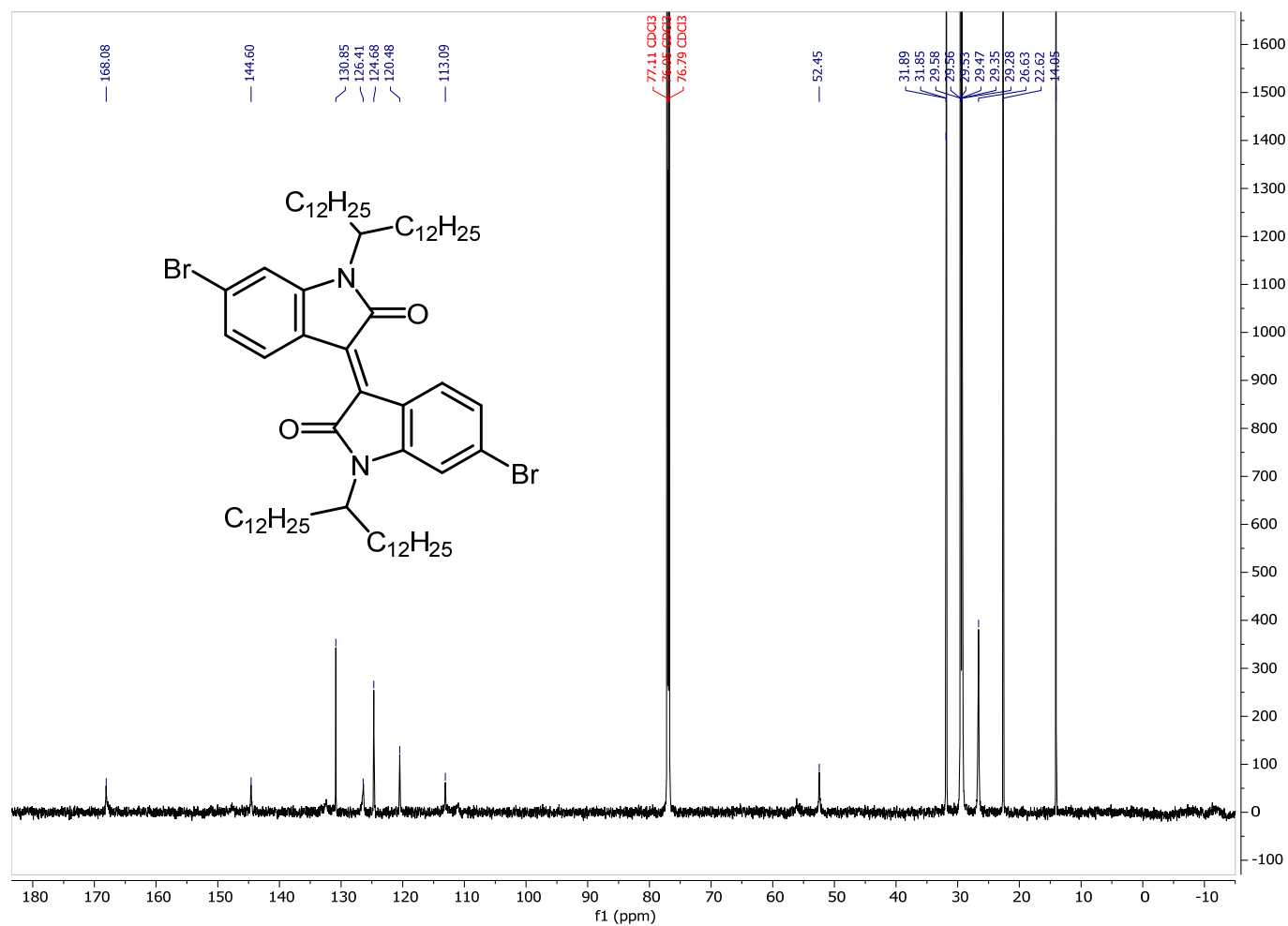


Figure S48. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of S5 (201 MHz, CDCl_3).

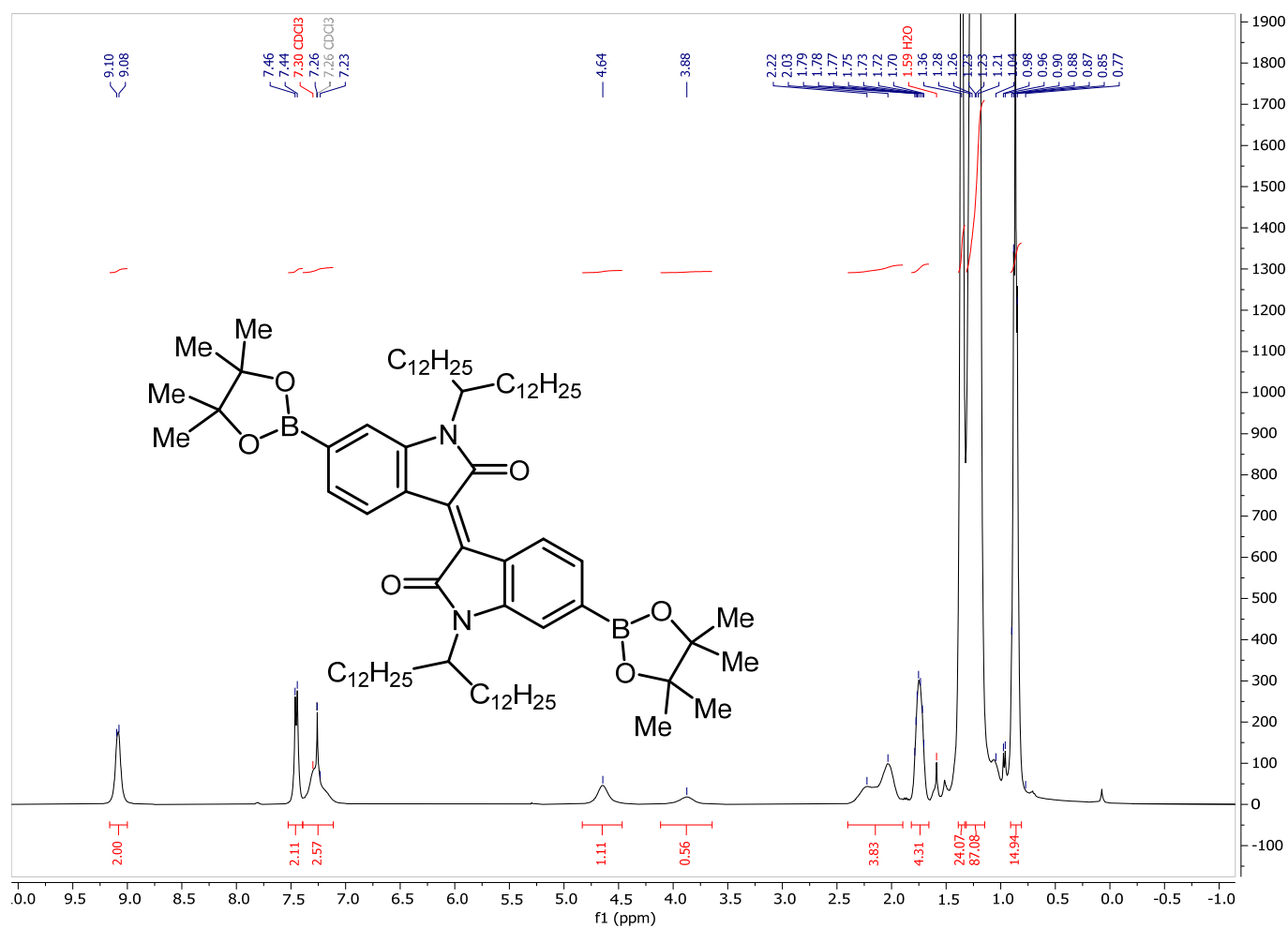


Figure S49. ^1H NMR spectrum of **S6** (400 MHz, $CDCl_3$).

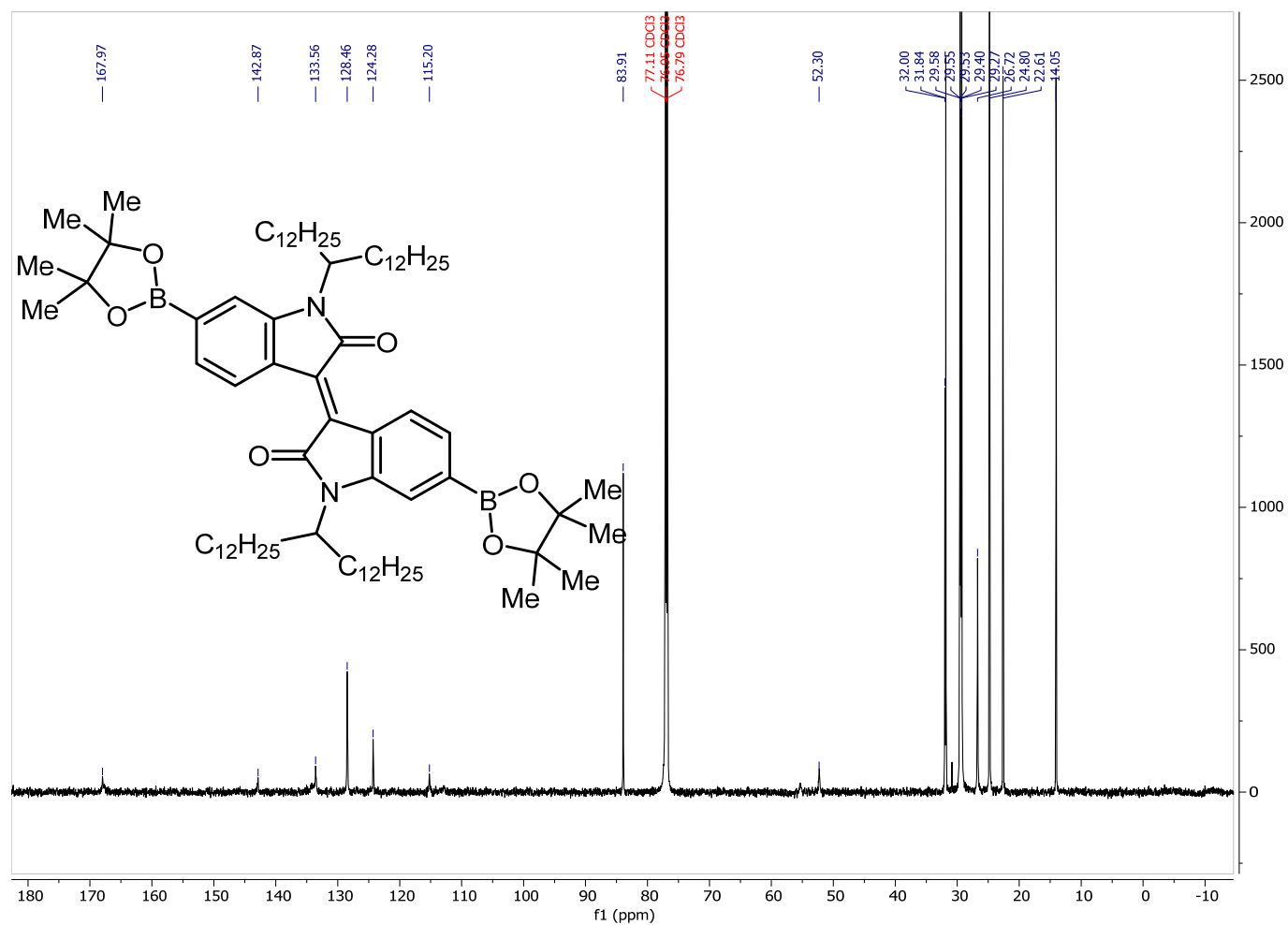


Figure S50. ¹³C{¹H} NMR spectrum of S6 (201 MHz, CDCl₃).

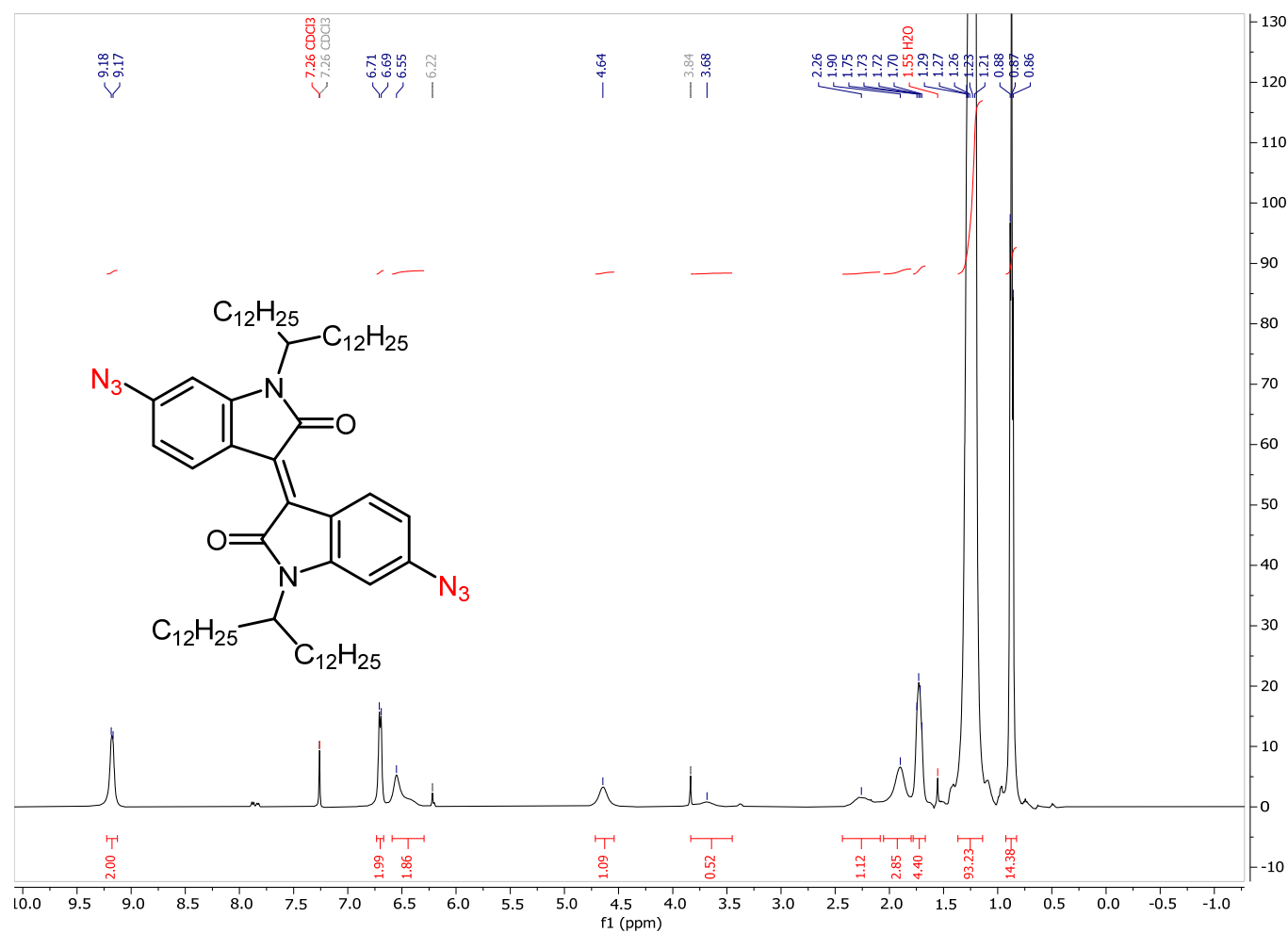


Figure S51. ¹H NMR spectrum of **S7** (500 MHz, CDCl₃).

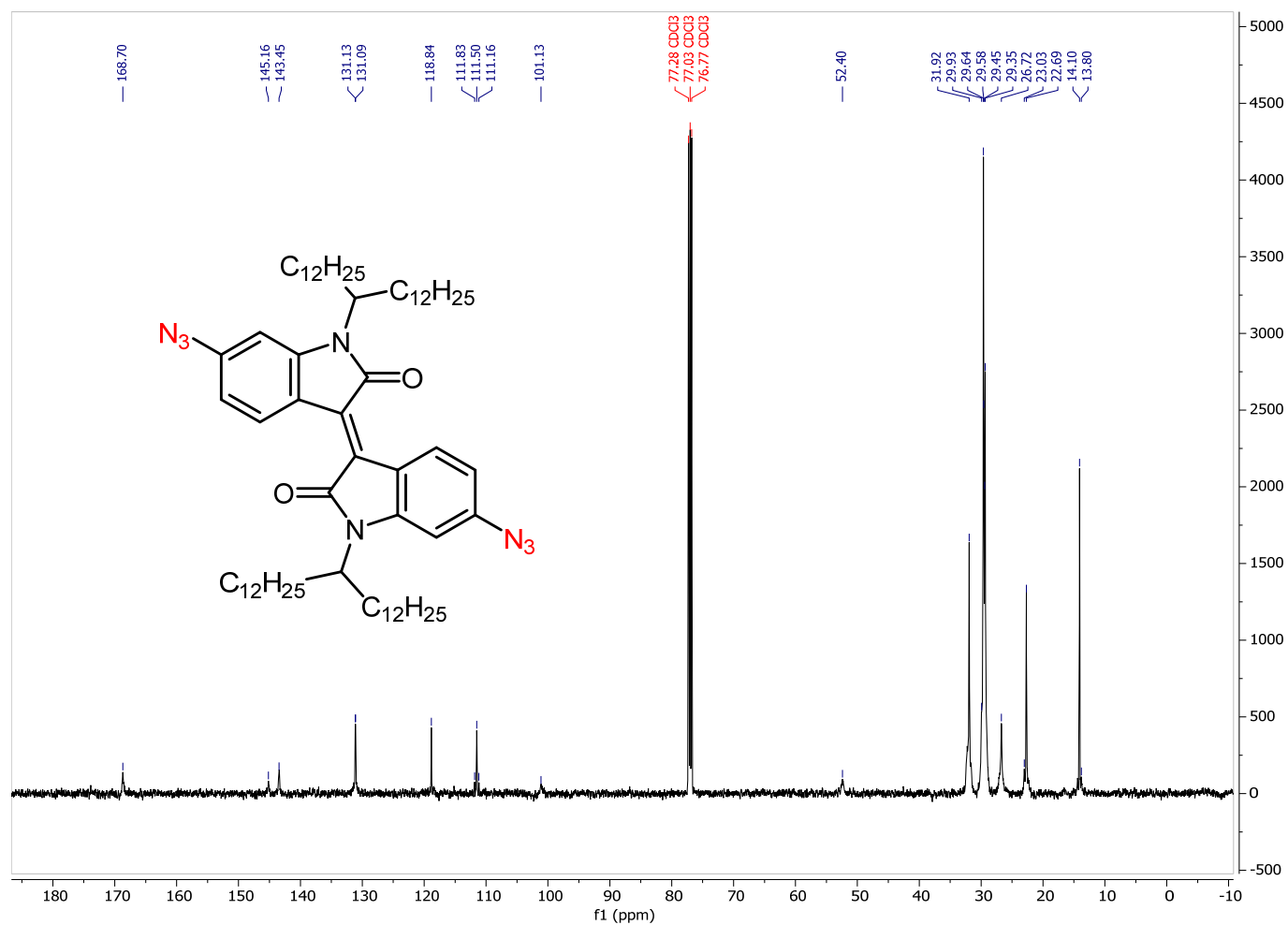


Figure S52. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **S7** (126 MHz, CDCl_3).

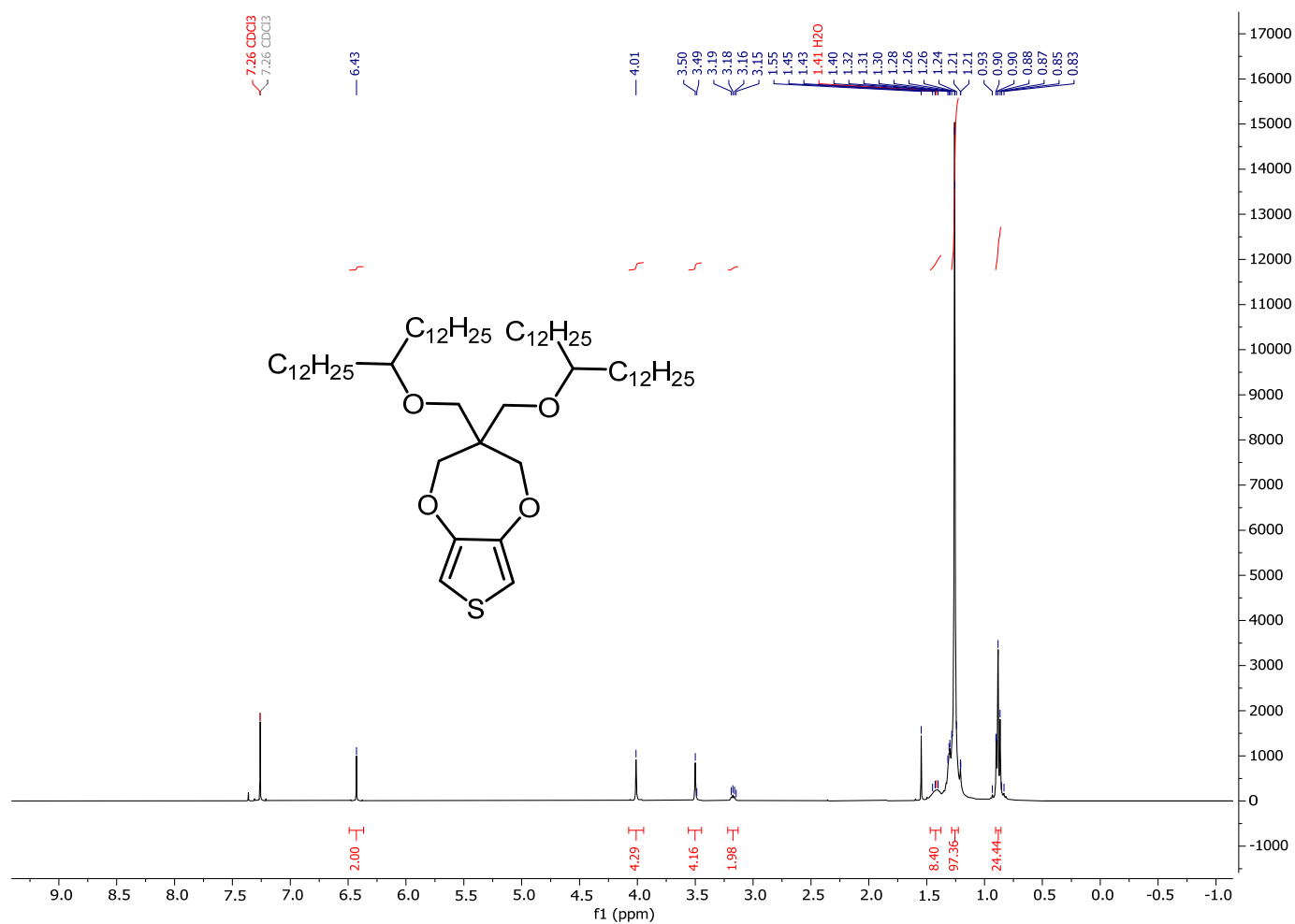


Figure S53. ¹H NMR spectrum of **S8** (400 MHz, CDCl₃).

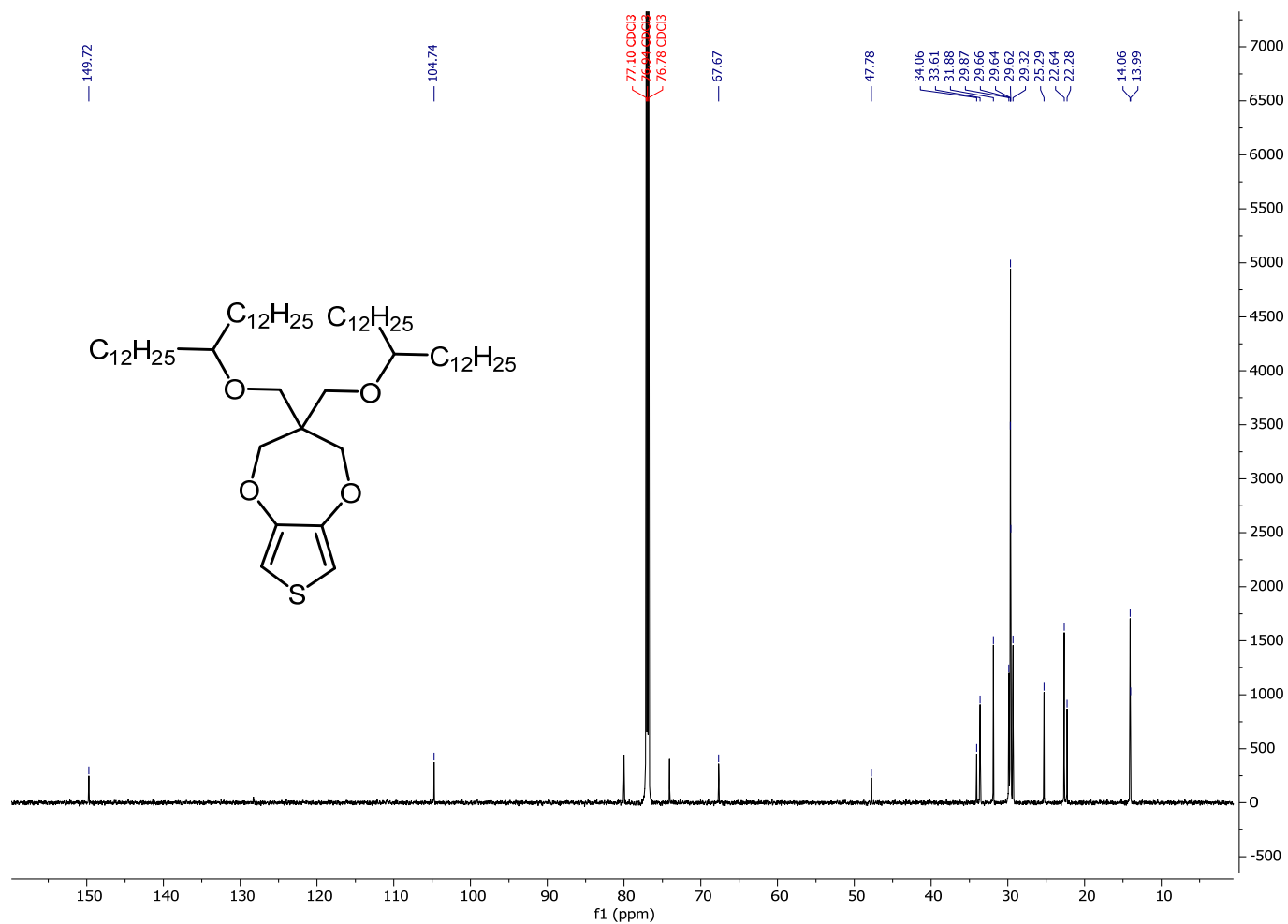


Figure S54. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **S8** (201 MHz, CDCl_3).

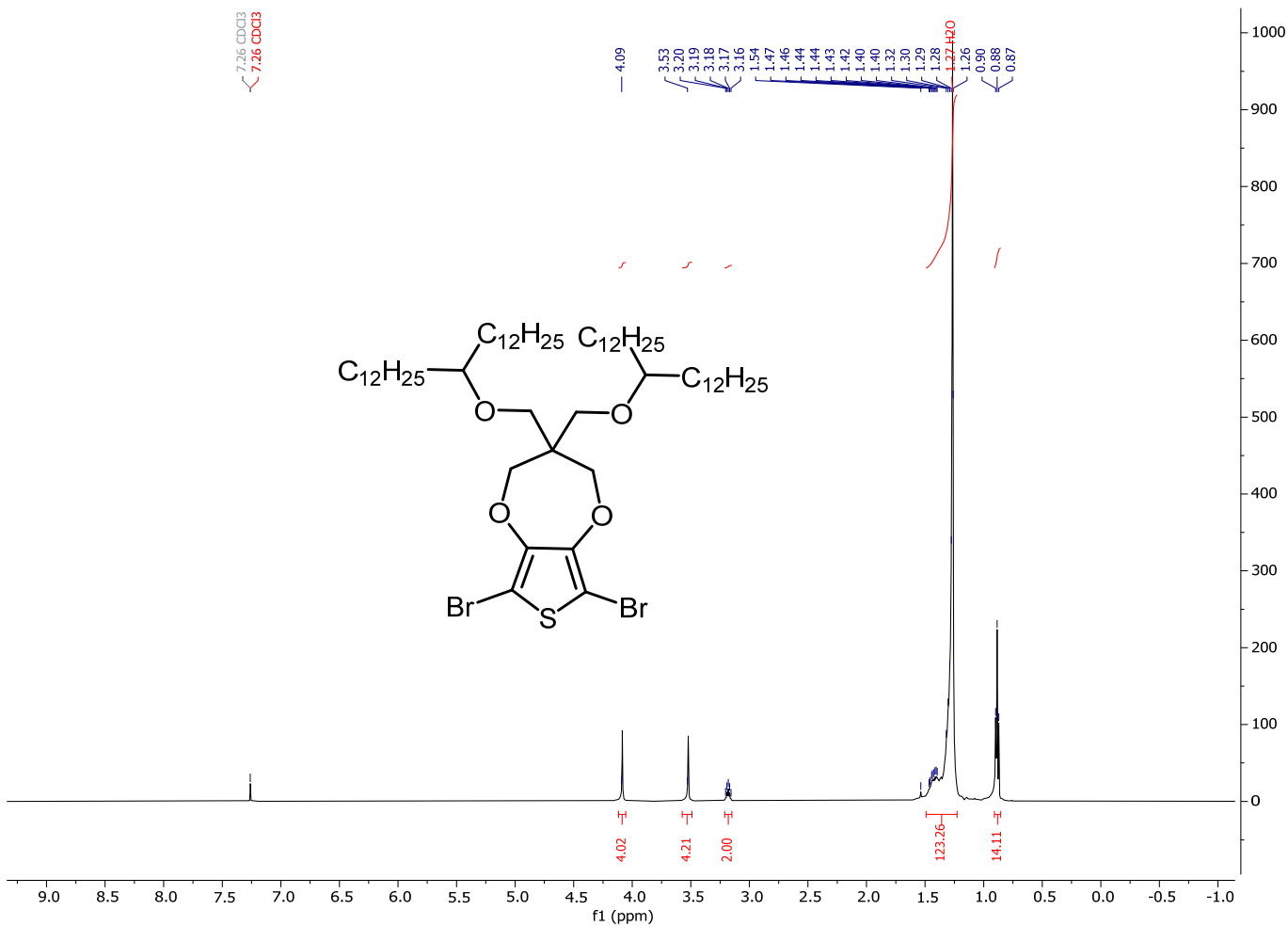


Figure S55. ^1H NMR spectrum of **S9** (400 MHz, CDCl_3).

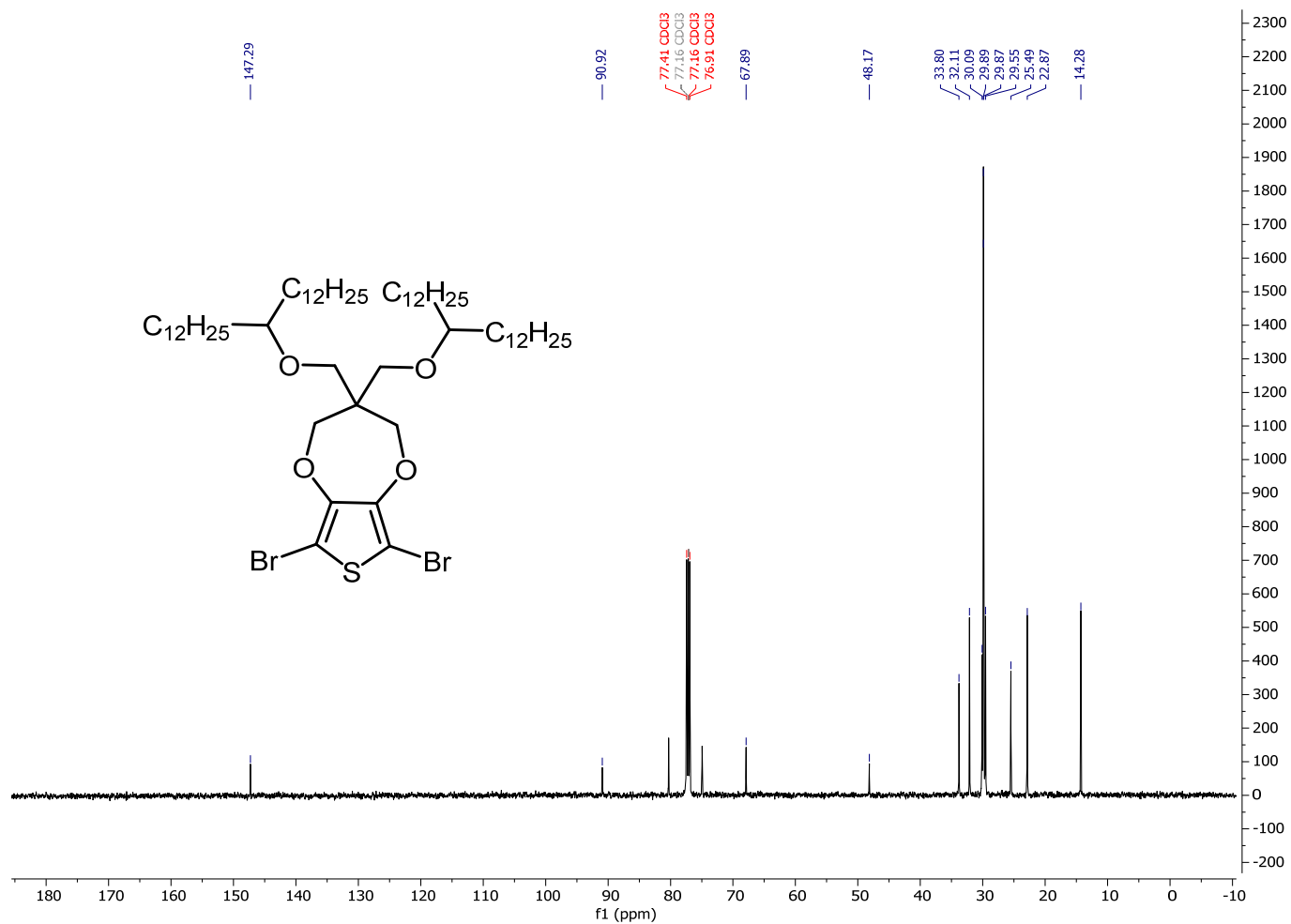


Figure S56. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **S9** (101 MHz, CDCl_3).

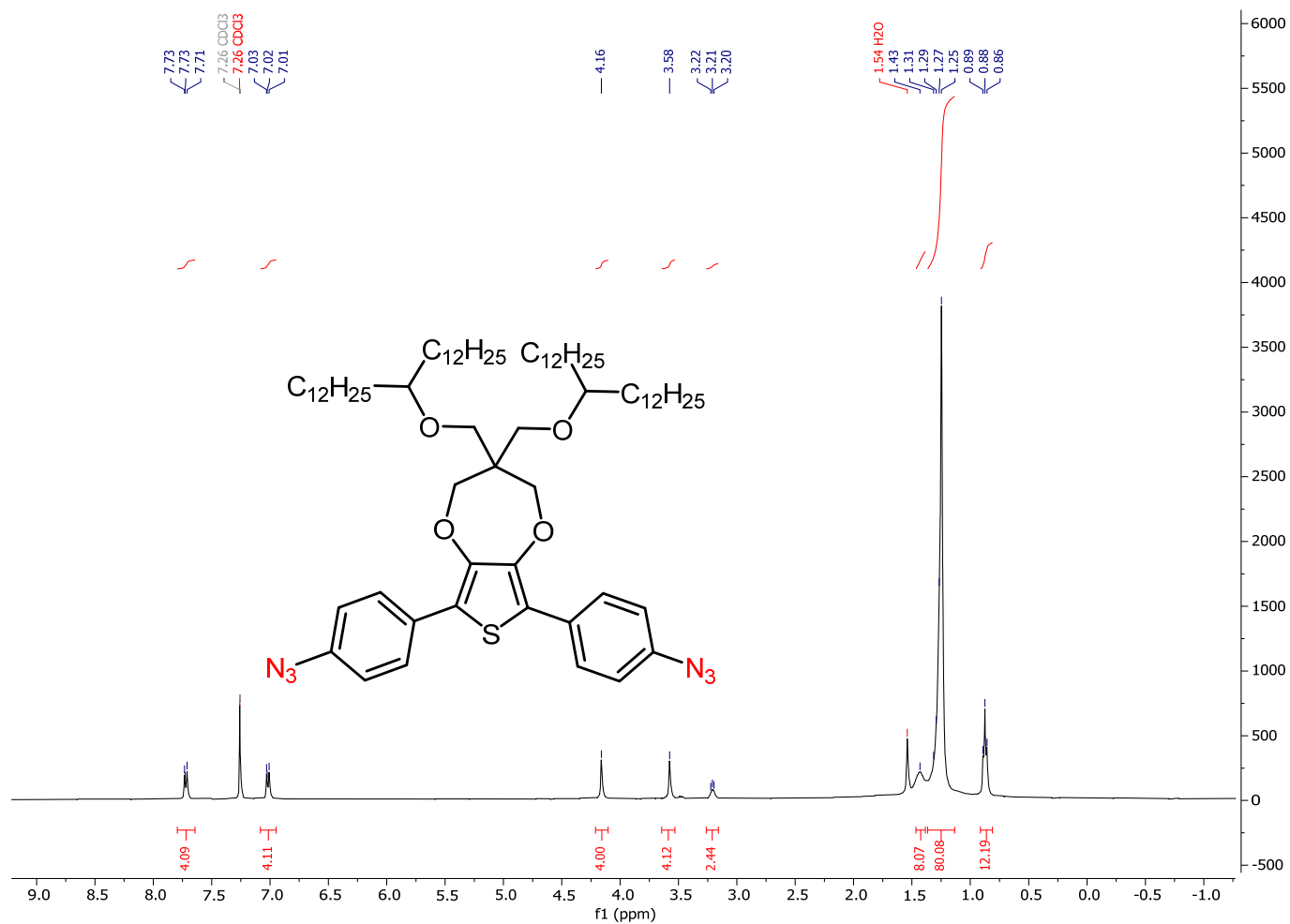


Figure S57. ¹H NMR spectrum of **S10** (400 MHz, CDCl₃).

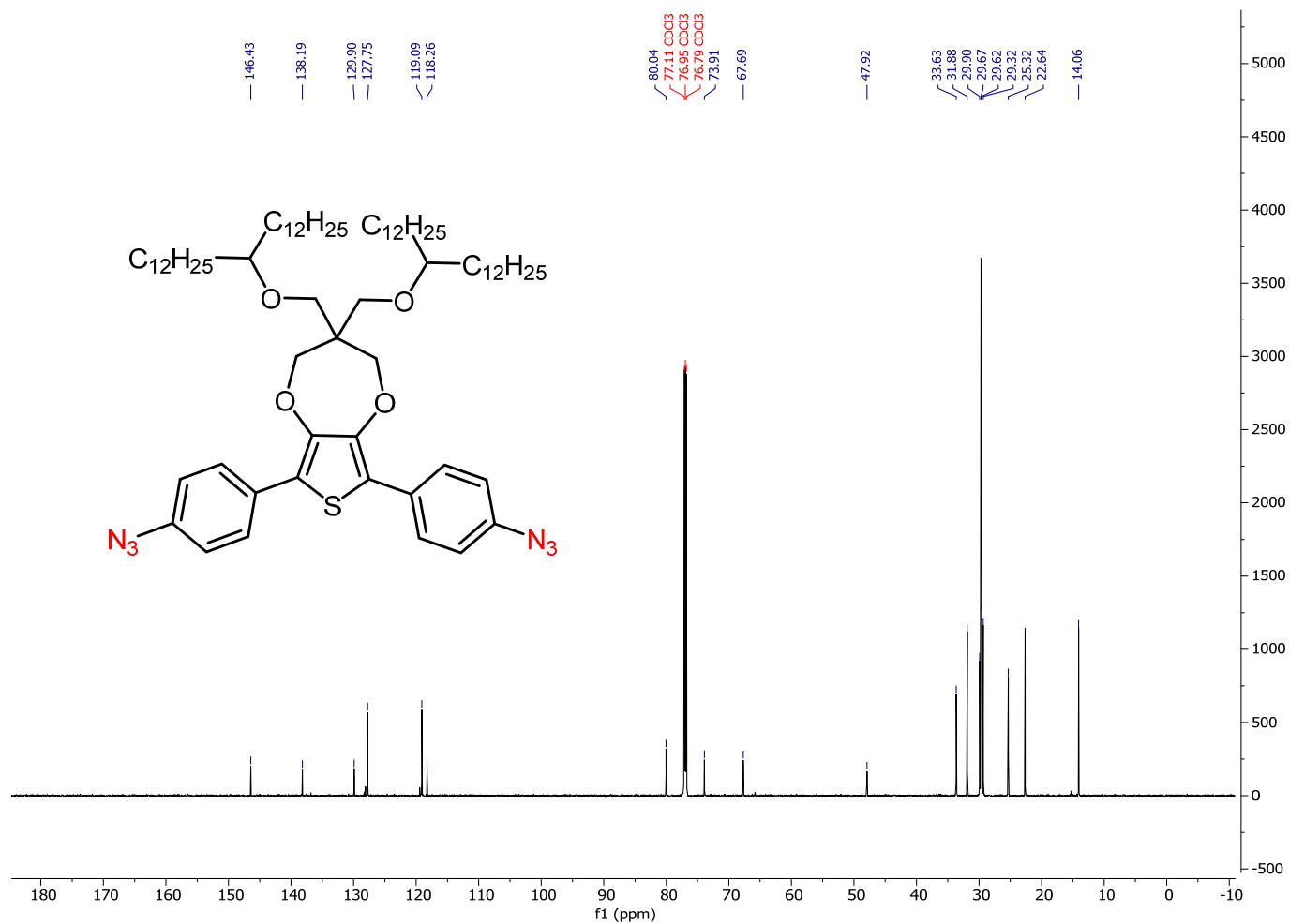


Figure S58. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **S10** (201 MHz, CDCl_3).

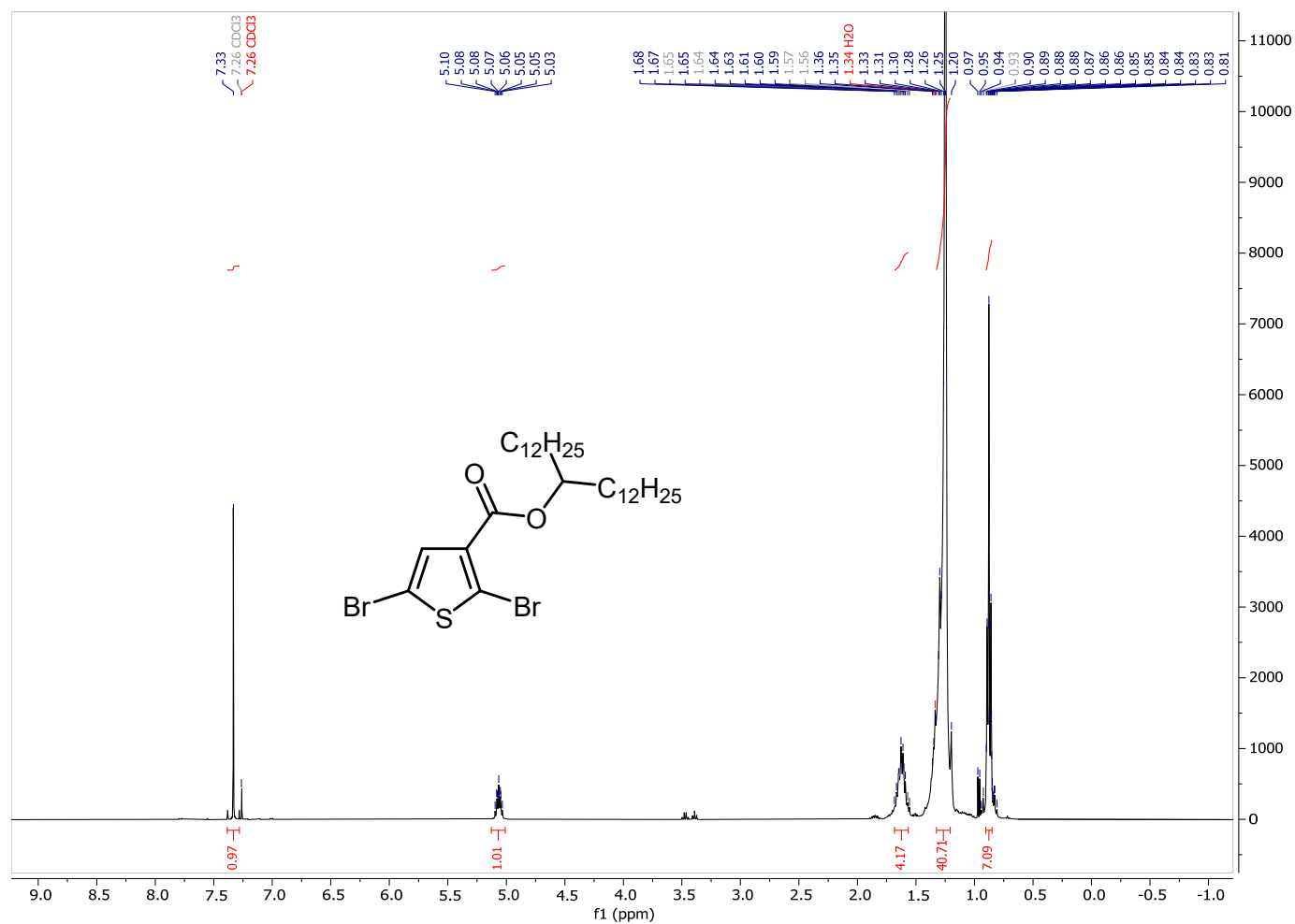


Figure S59. ¹H NMR spectrum of **S11** (400 MHz, CDCl₃).

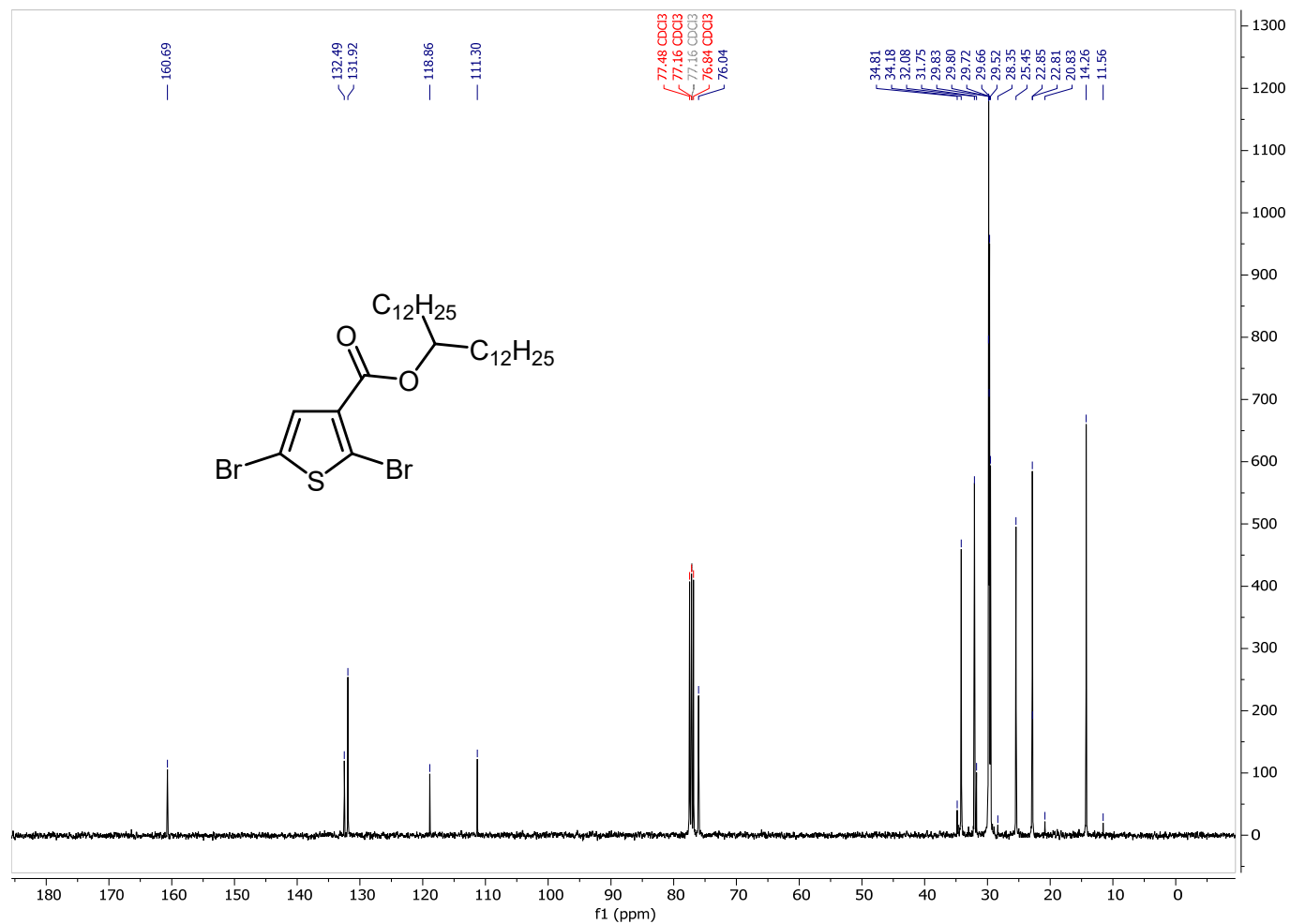


Figure S60. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **S11** (101 MHz, CDCl_3).

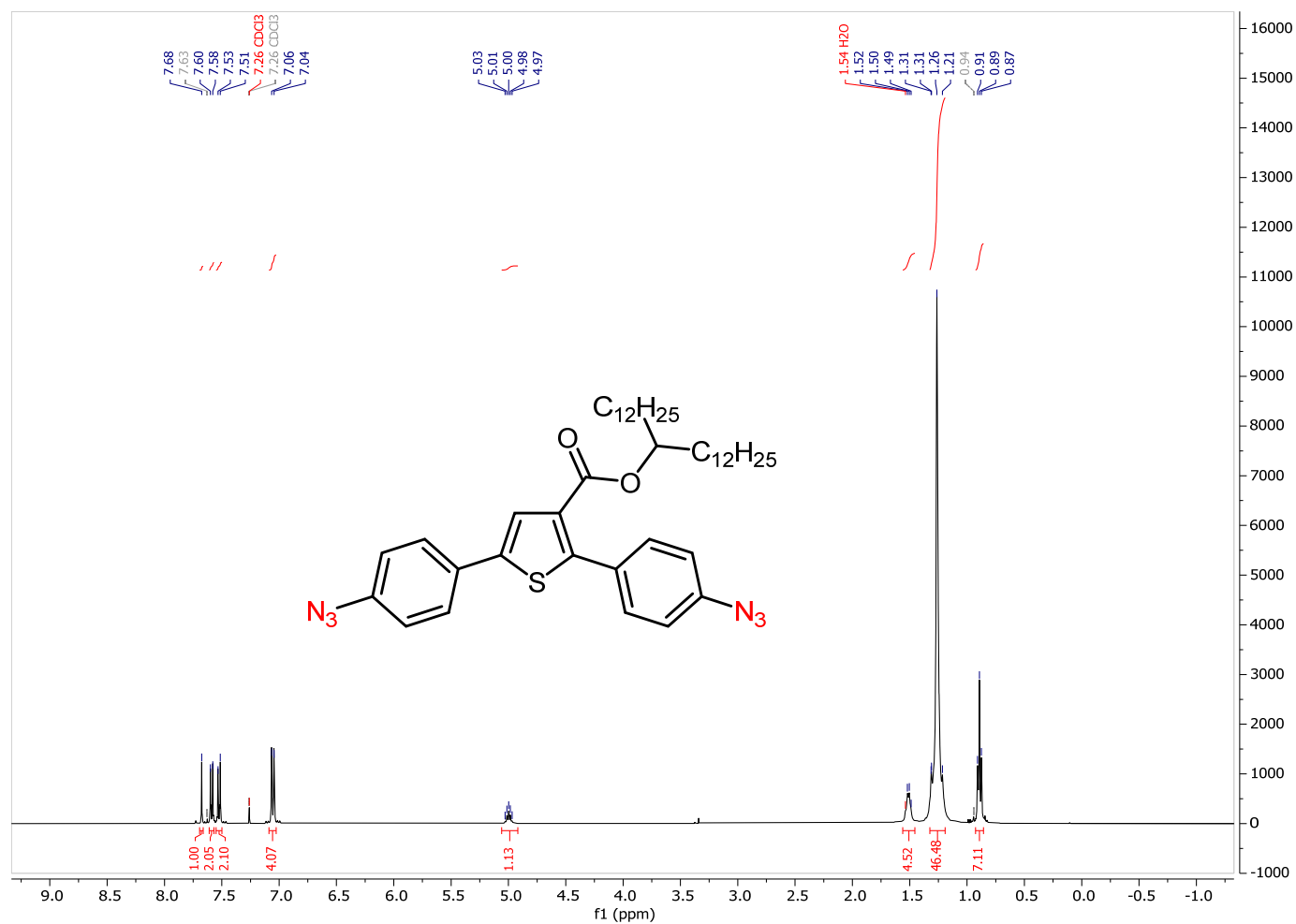


Figure S61. ¹H NMR spectrum of **S12** (400 MHz, CDCl₃).

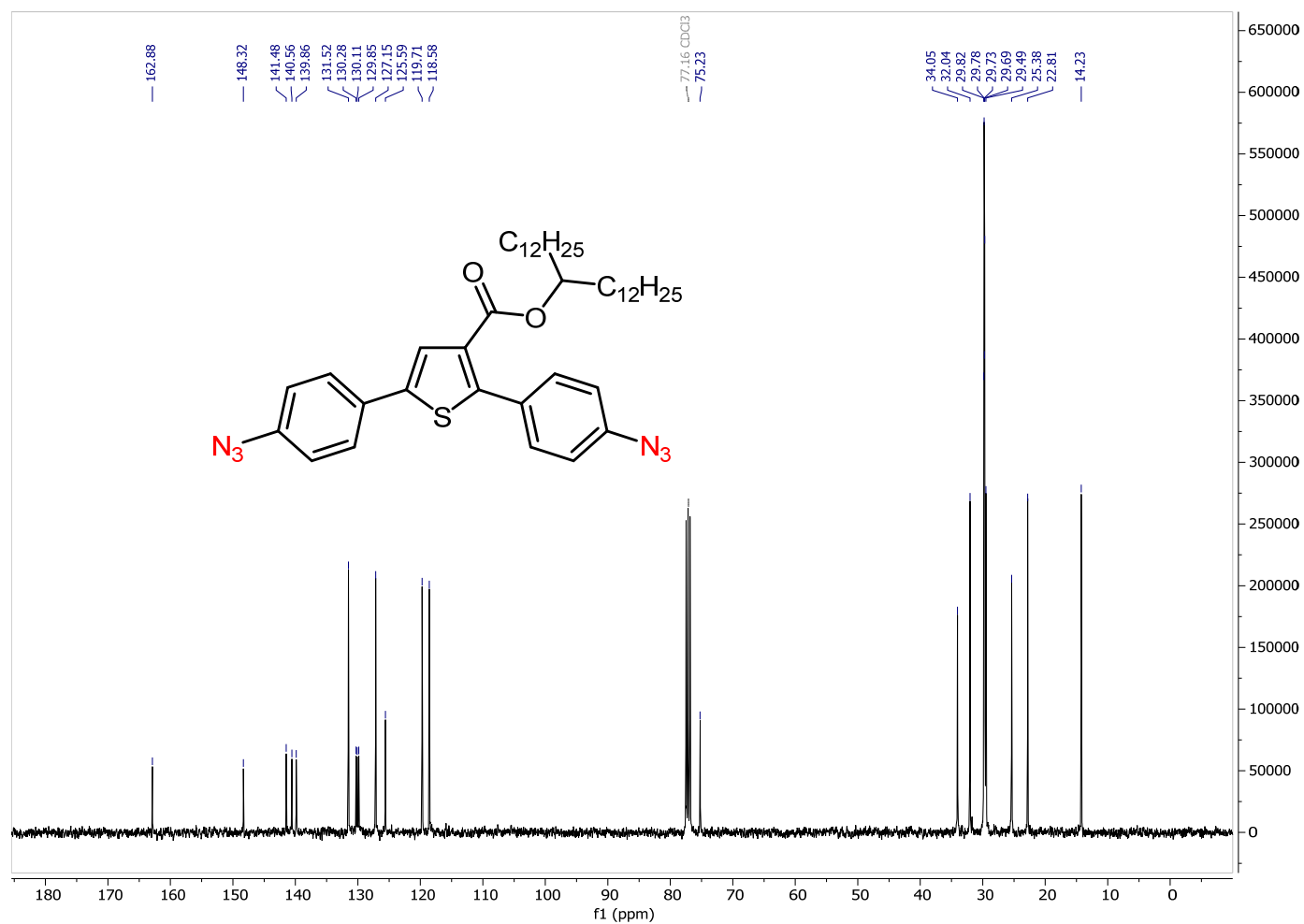


Figure S62. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **S12** (101 MHz, CDCl_3).

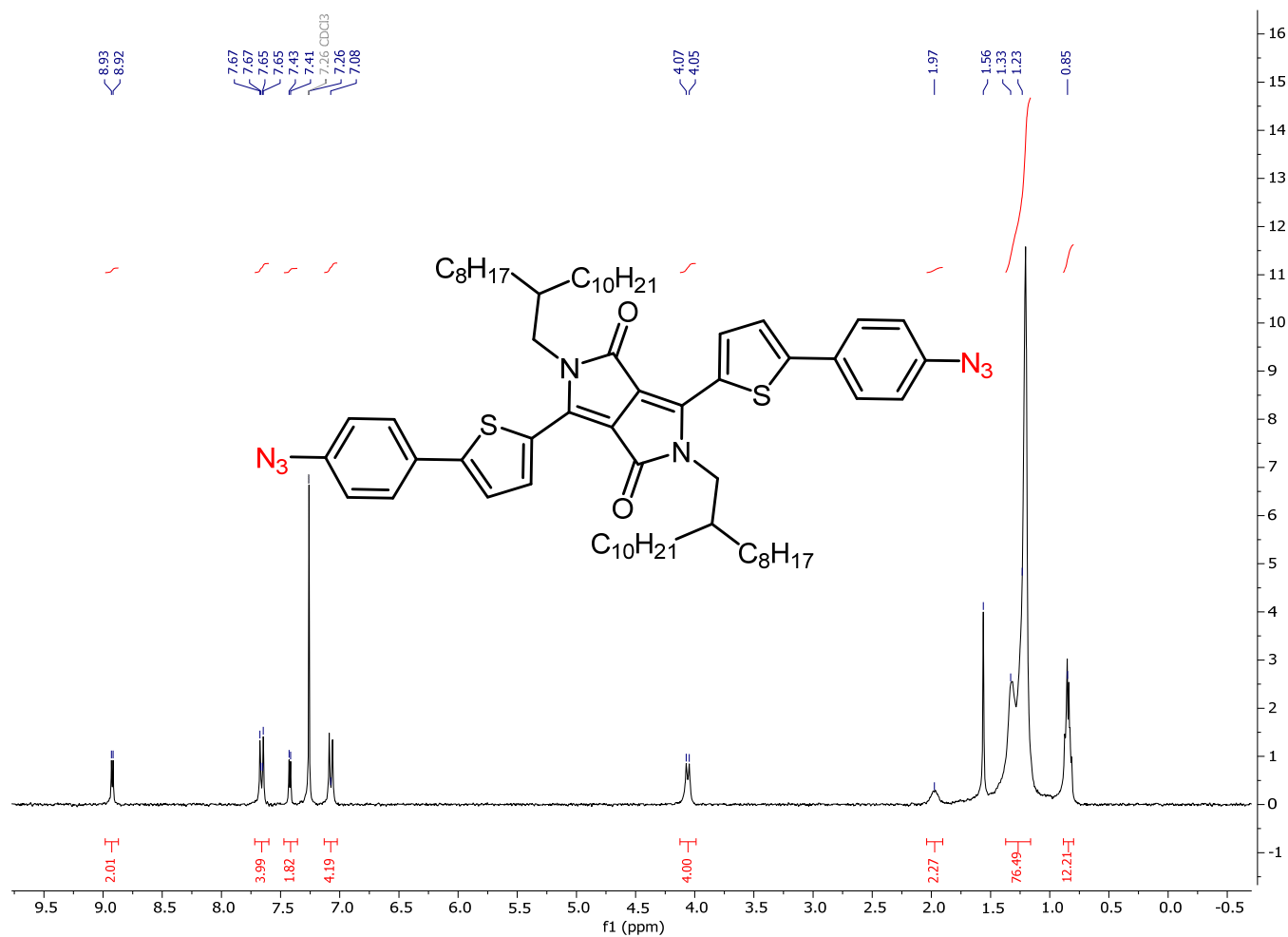


Figure S63. ¹H NMR spectrum of **S13** (300 MHz, CDCl₃).

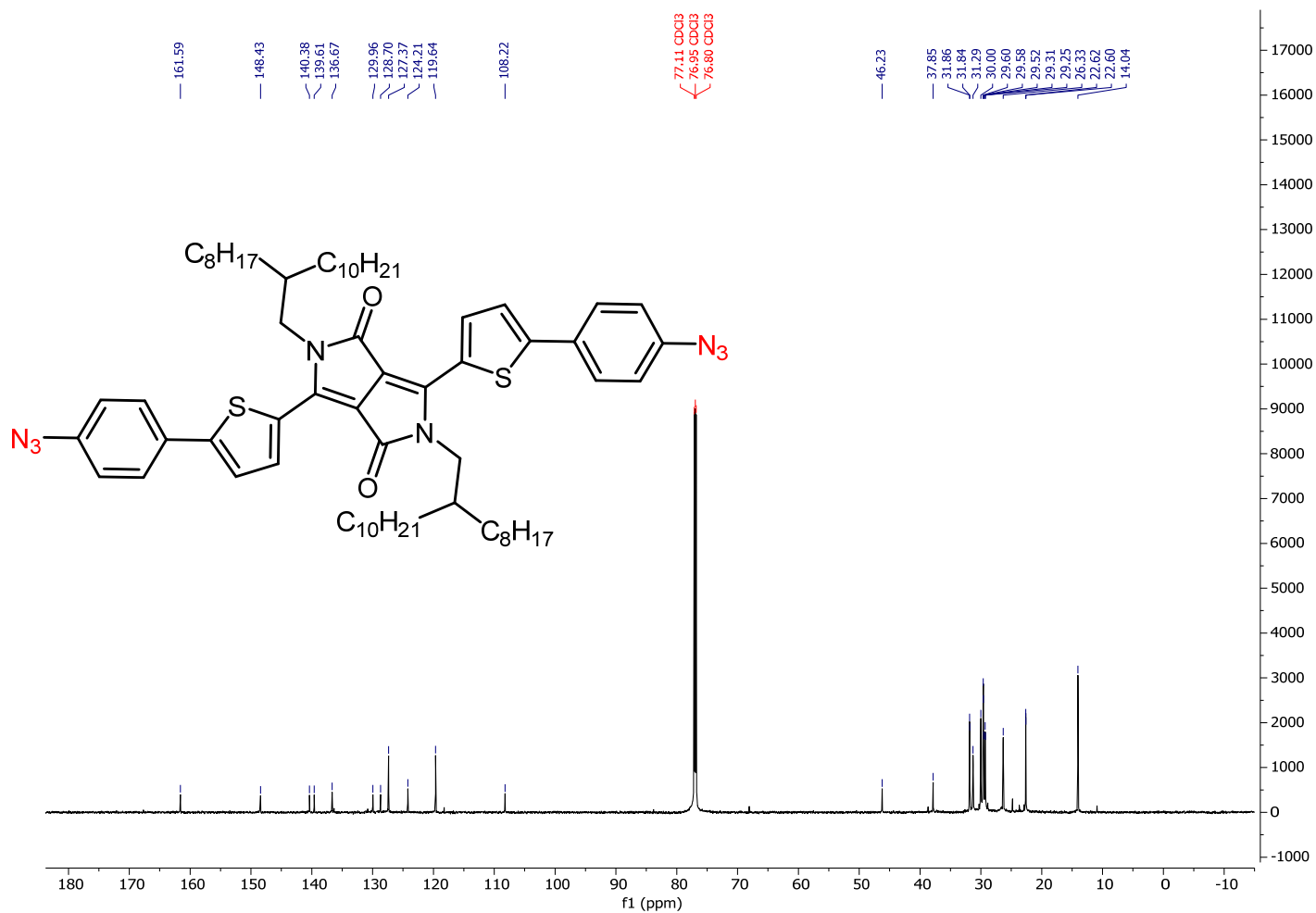


Figure S64. ¹³C{¹H} NMR spectrum of **S13** (201 MHz, CDCl₃).

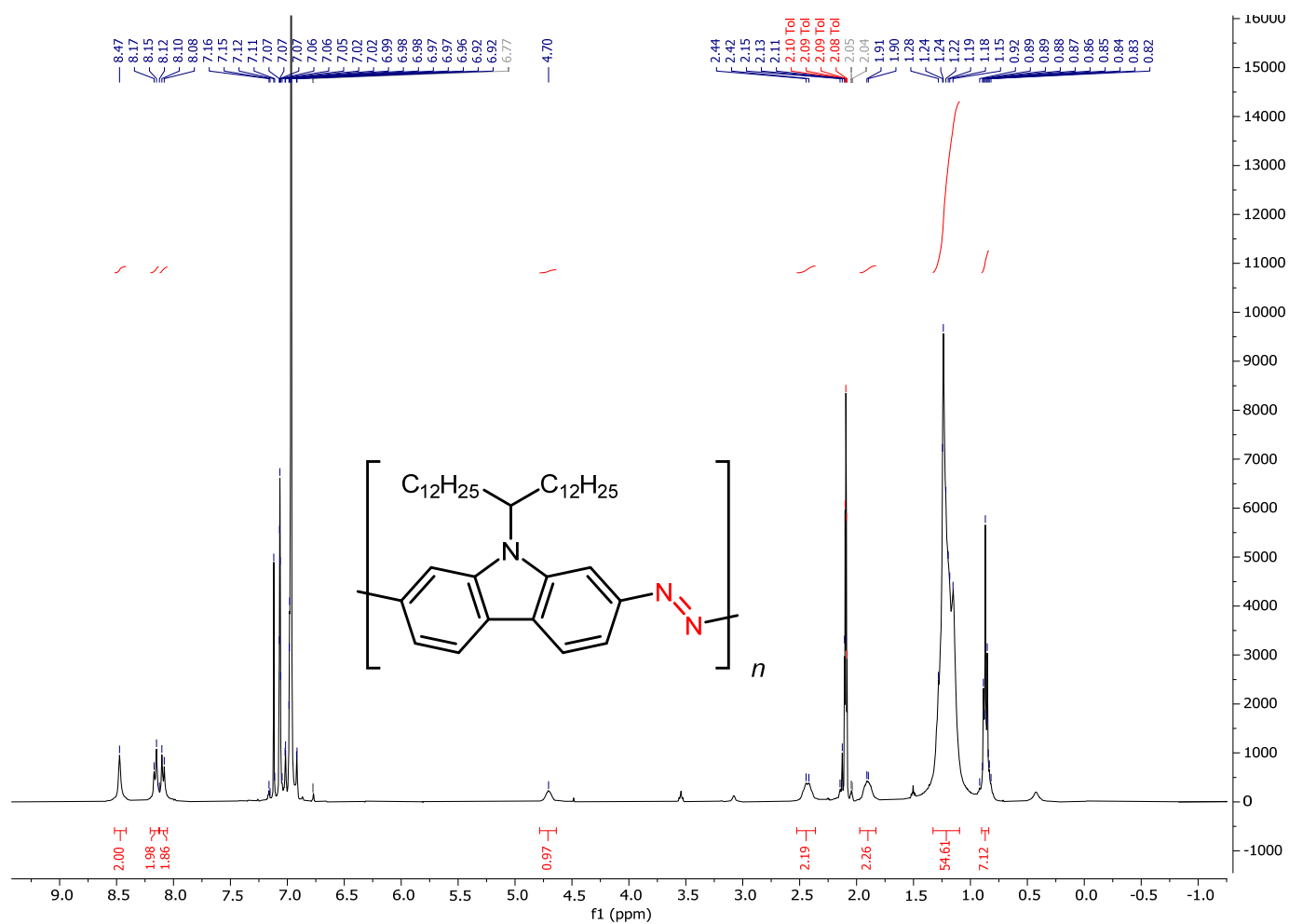


Figure S65. ^1H NMR spectrum of **3** (400 MHz, 100°C , $\text{toluene-}d_8$).

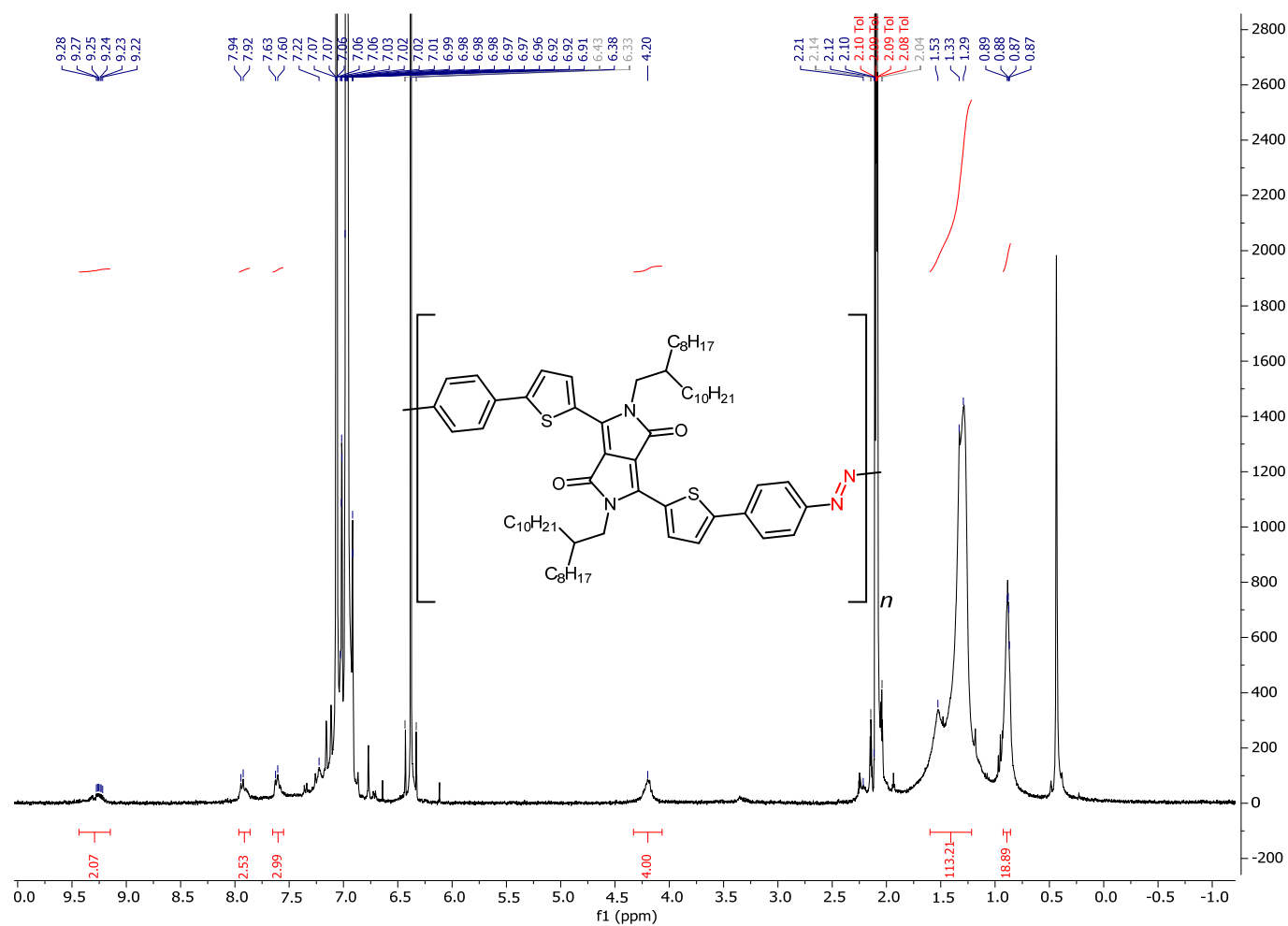


Figure S66. ^1H NMR spectrum of **7** (400 MHz, 100 °C, $\text{toluene-}d_8$).

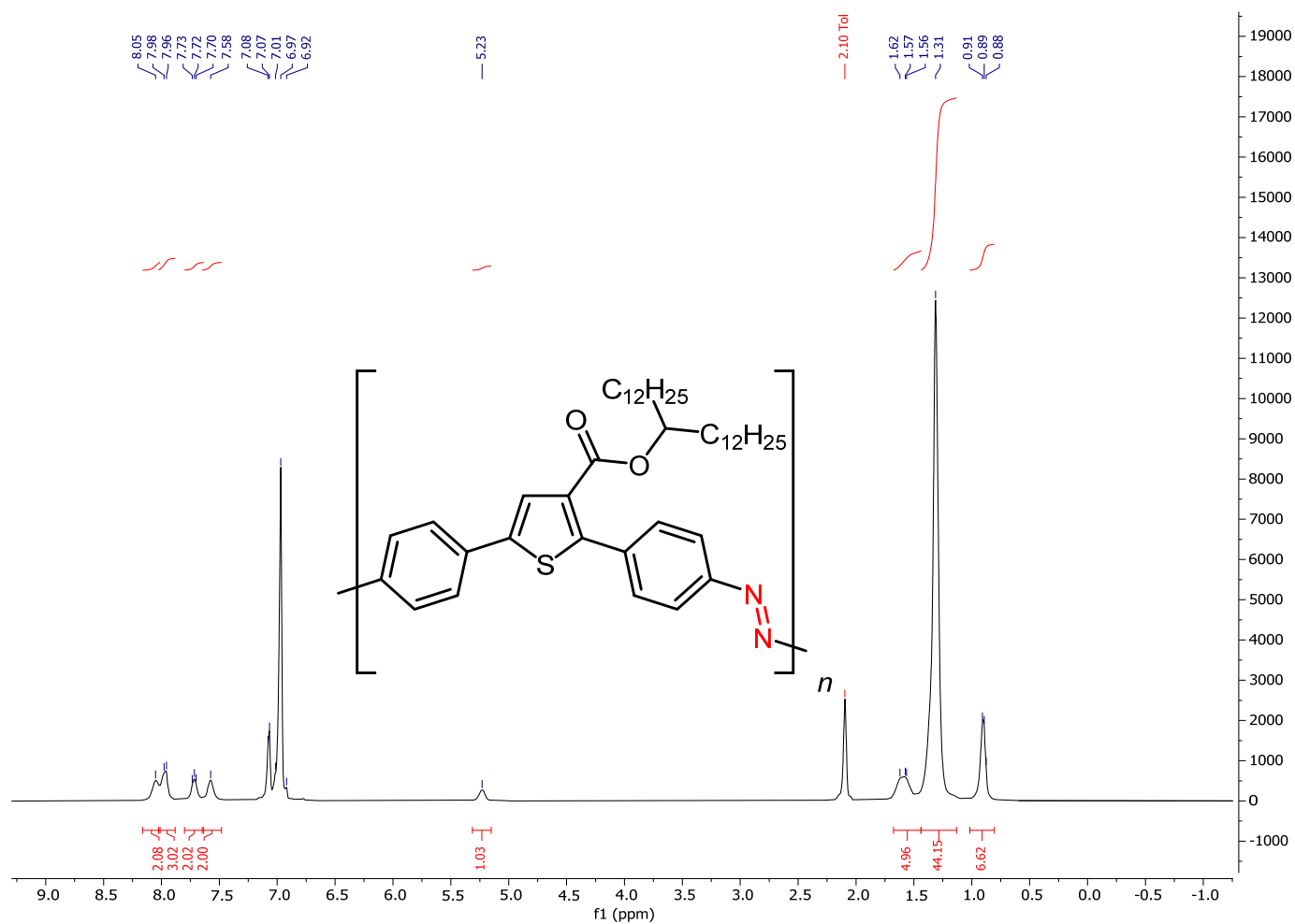


Figure S67. ¹H NMR spectrum of **8** (400 MHz, 100 °C, toluene-*d*₈).

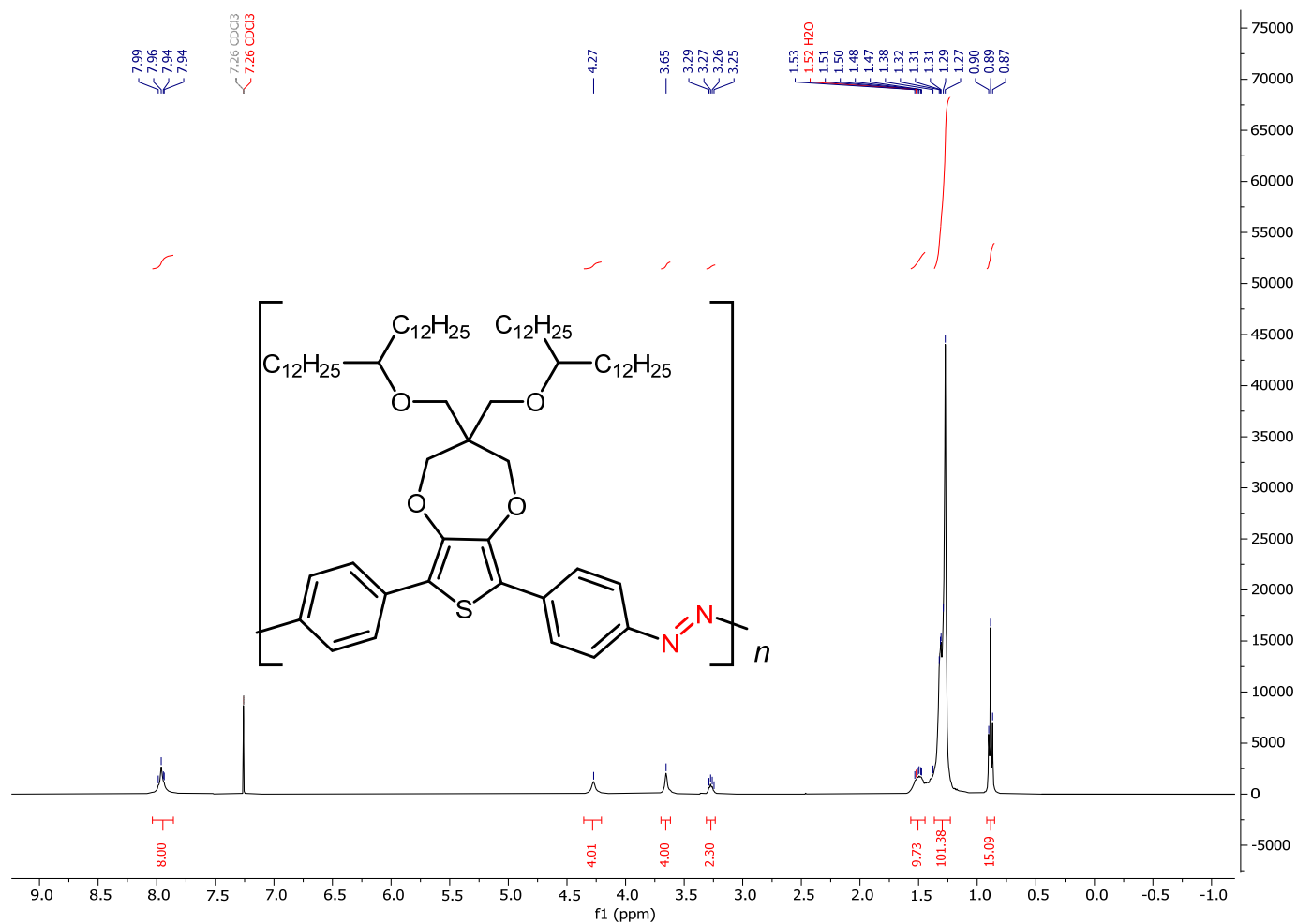


Figure S68. ¹H NMR spectrum of **9** (400 MHz, 50°C, CDCl₃).

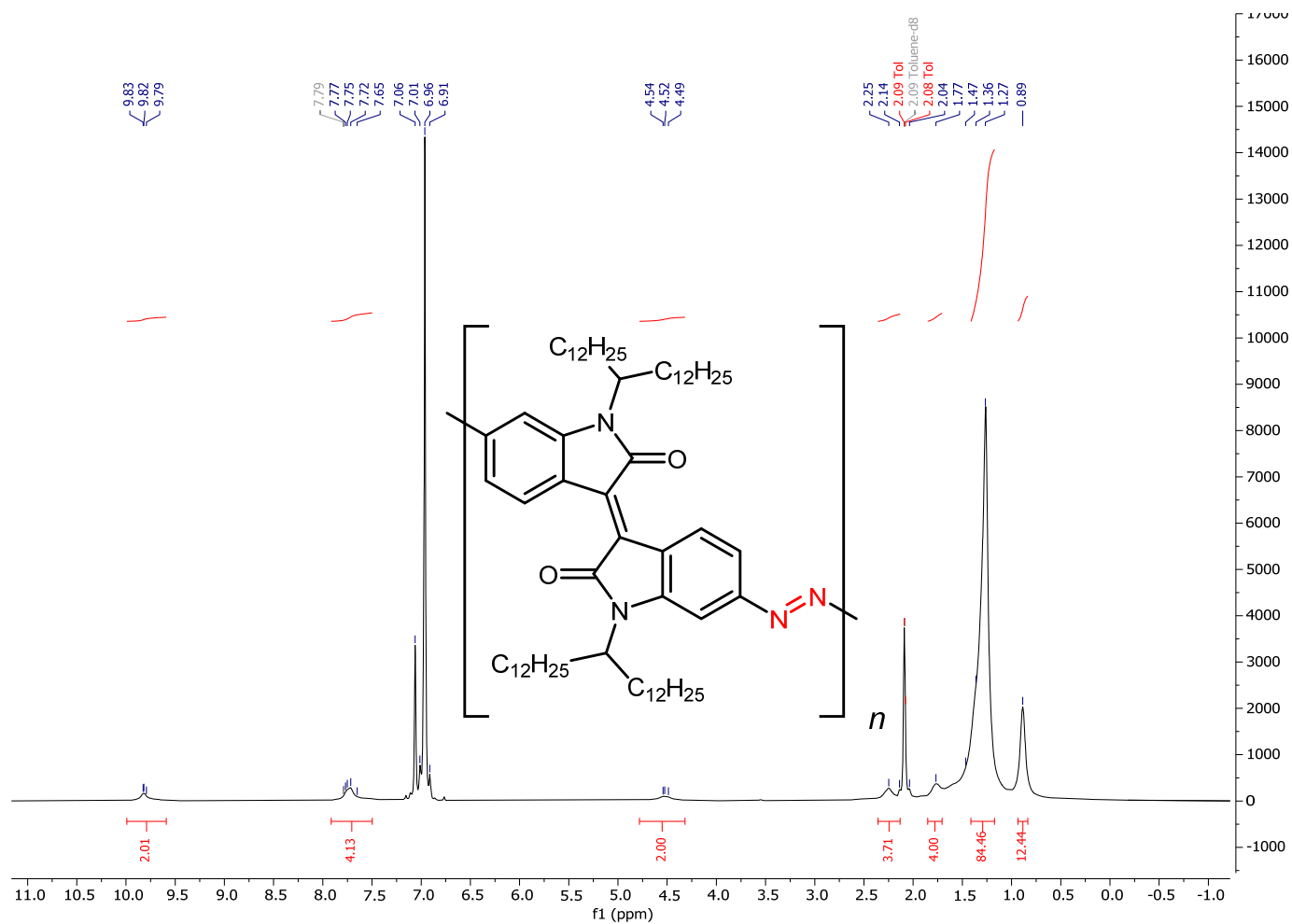


Figure S69. ¹H NMR spectrum of **10** (400 MHz, 100 °C, toluene-*d*₈).

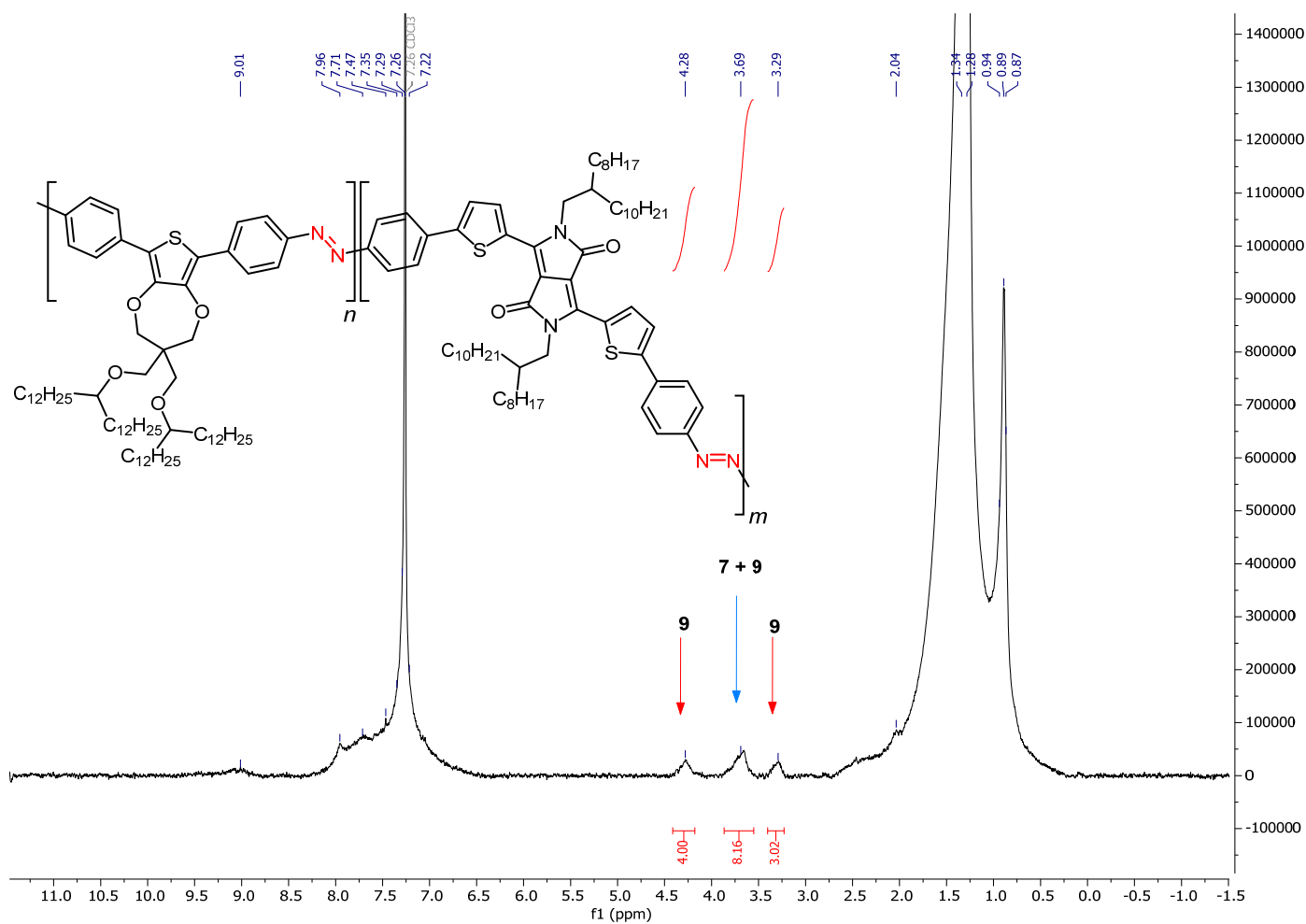


Figure S70. ¹H NMR spectrum of **11** (500 MHz, 50 °C, CDCl₃).

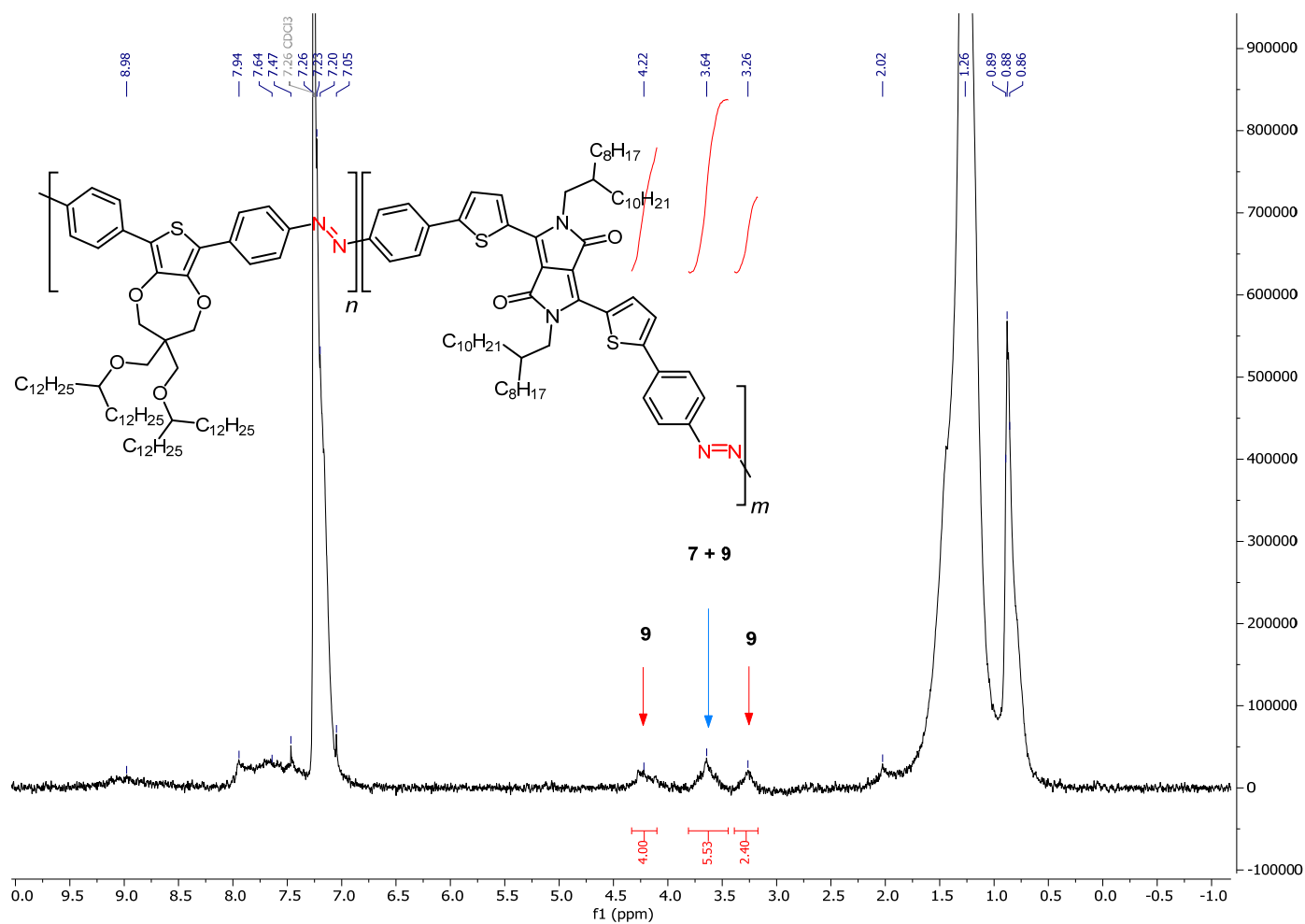


Figure S71. ^1H NMR spectrum of **12** (500 MHz, 50°C , CDCl_3).

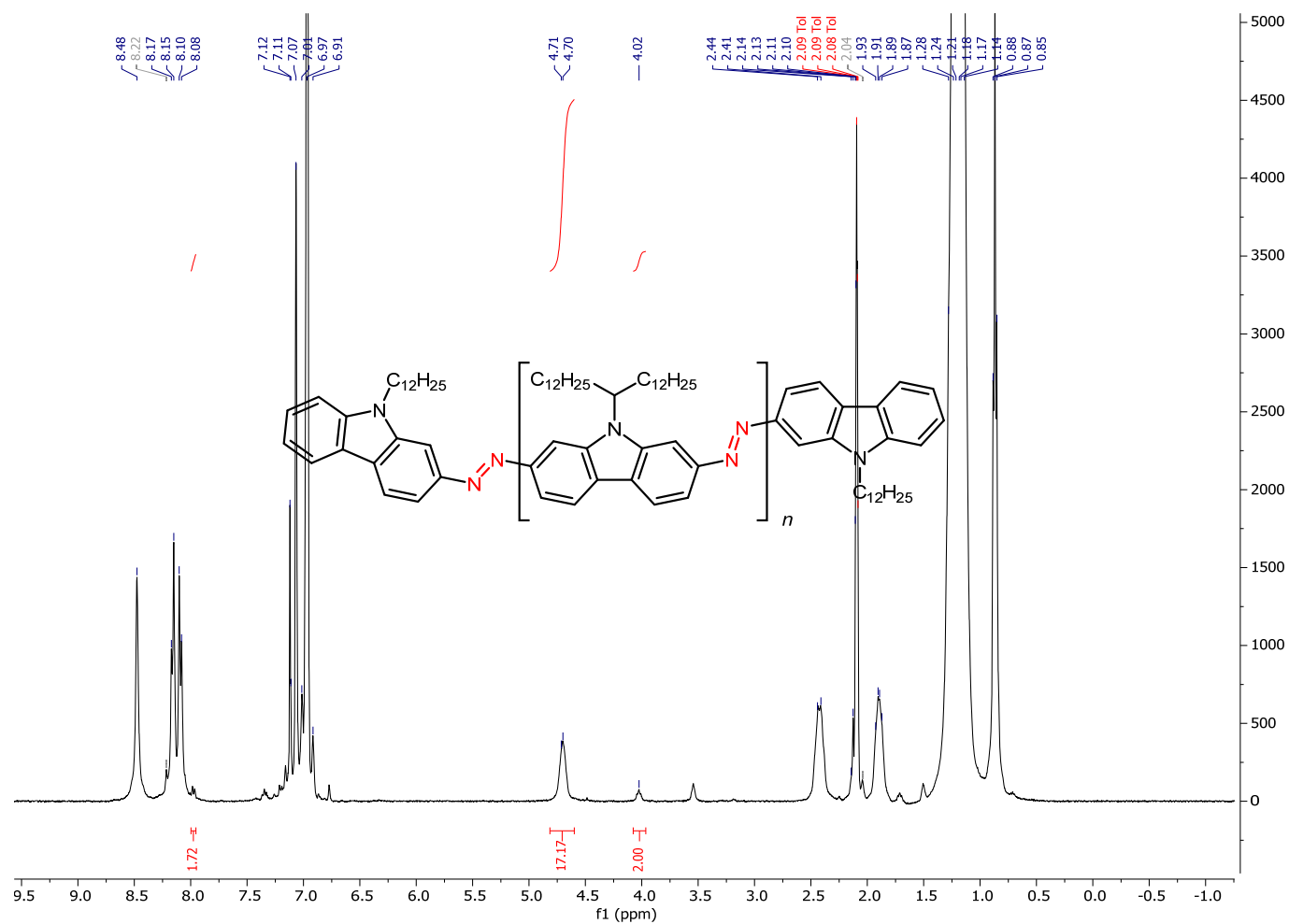


Figure S72. ^1H NMR spectrum of **13** (400 MHz, 100 °C, toluene- d_8).

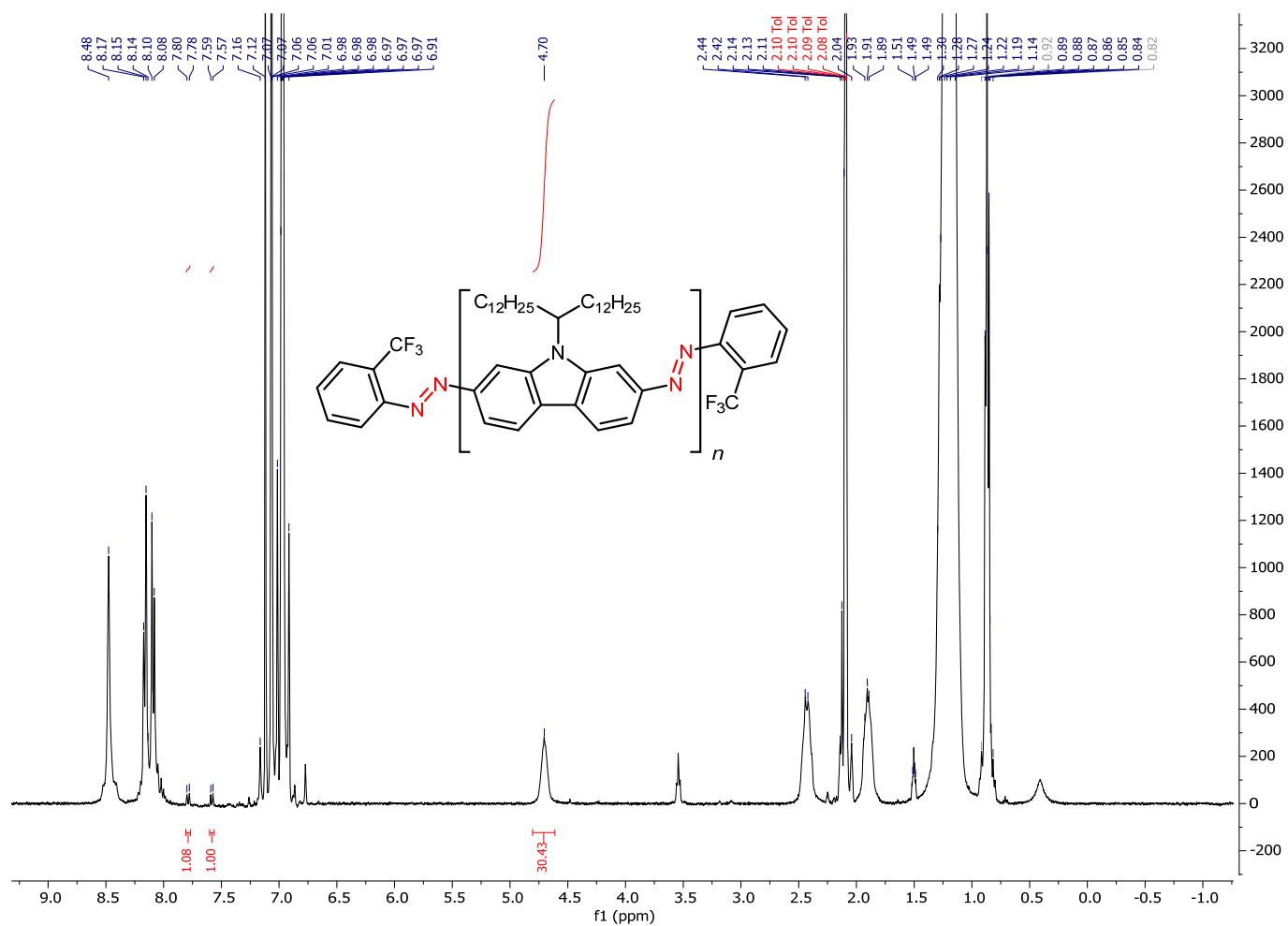


Figure S73. ^1H NMR spectrum of **14** (400 MHz, $100\text{ }^\circ\text{C}$, toluene- d_8).

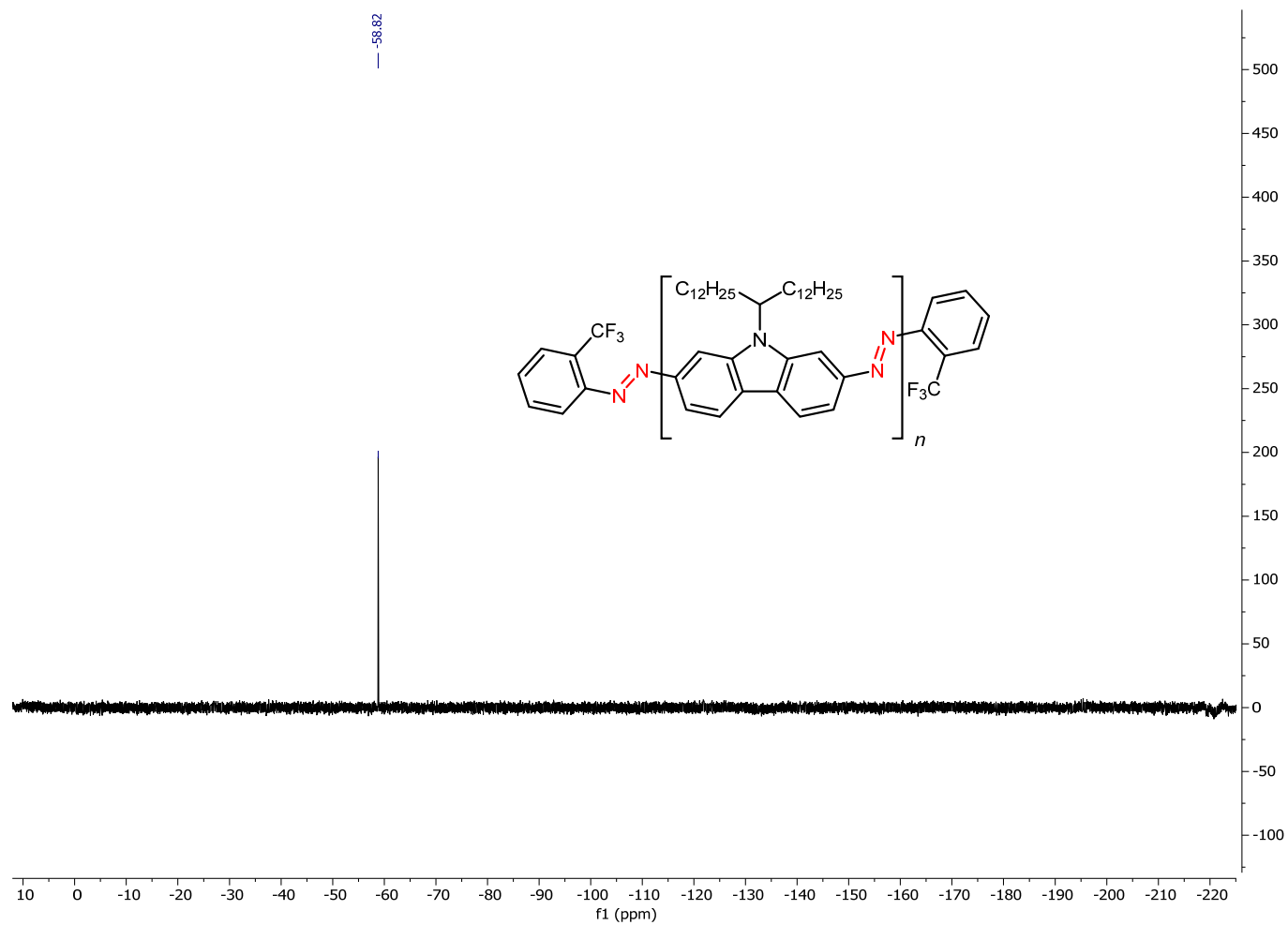


Figure S74. ^{19}F NMR spectrum of **14** (376 MHz, 100 °C, toluene- d_8).

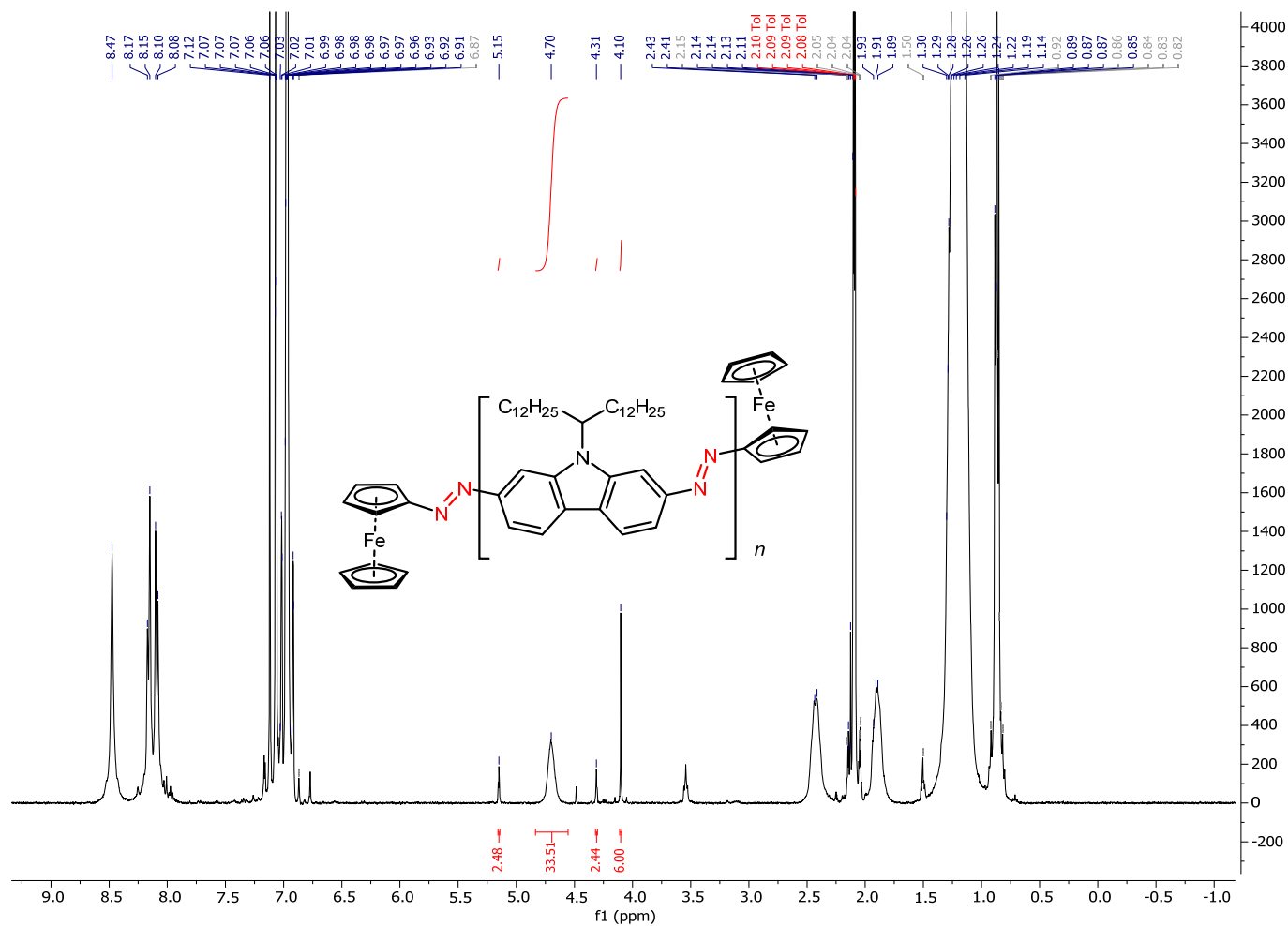


Figure S75. ^1H NMR spectrum of **15** (400 MHz, 100°C , $\text{toluene-}d_8$).

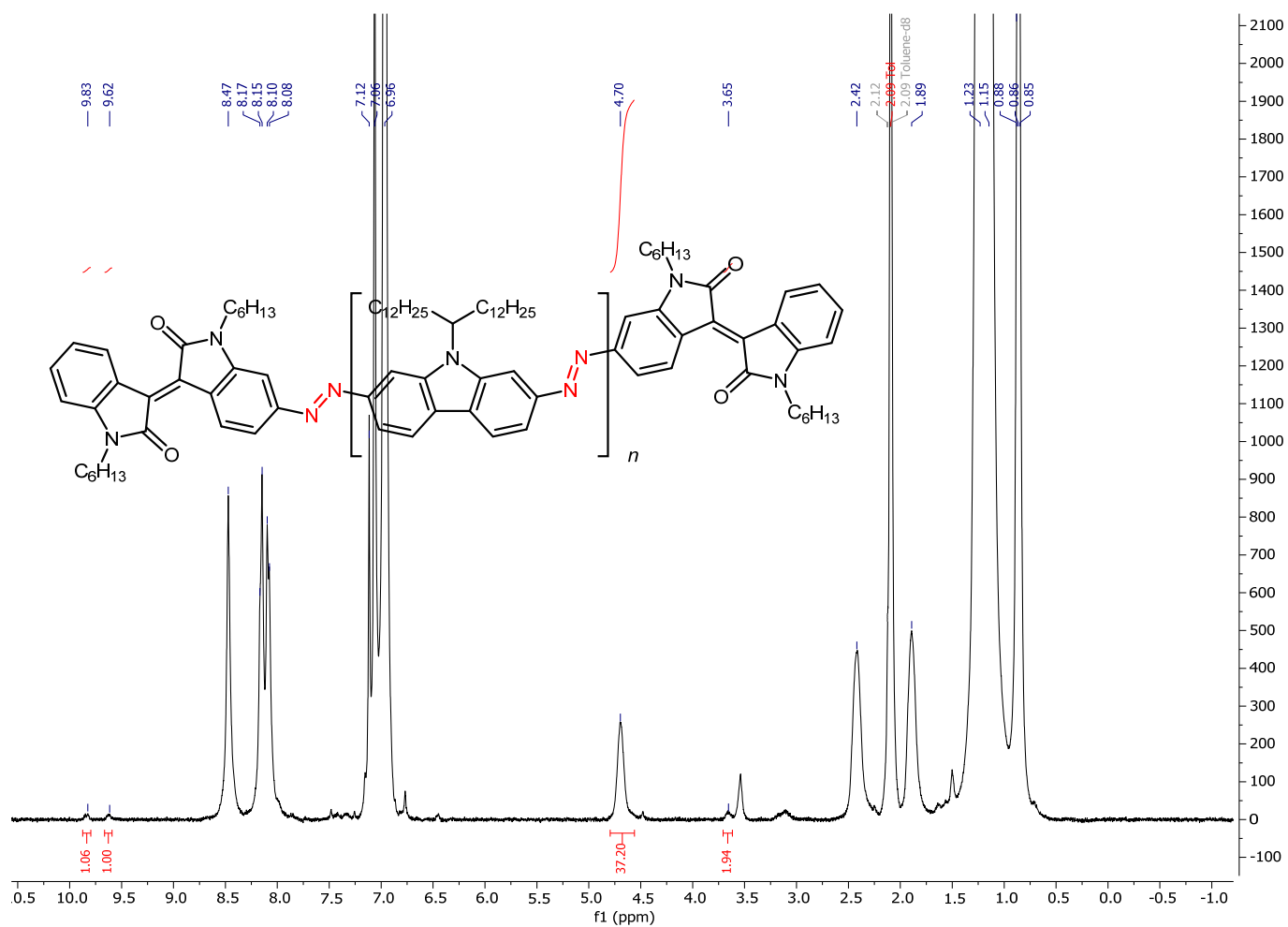


Figure S76. ¹H NMR spectrum of **16** (400 MHz, 100 °C, toluene-*d*₈).

12. UV-Vis Spectroscopy

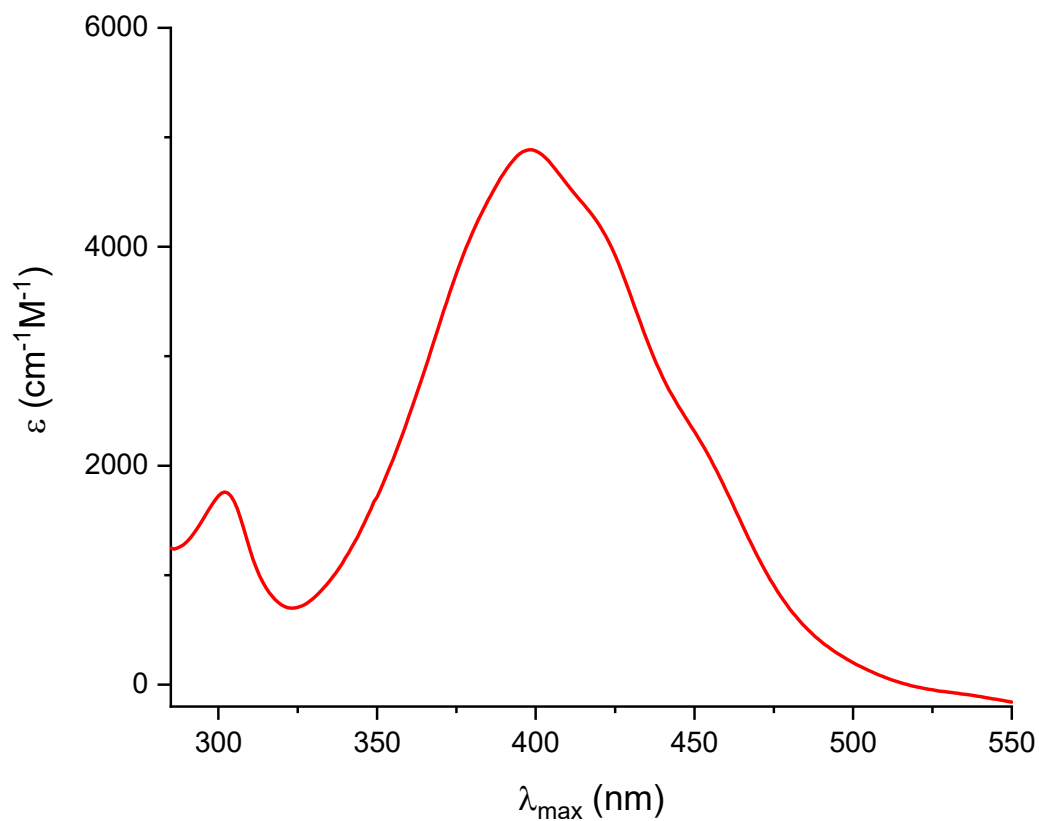


Figure S77. UV-Vis spectrum of **5b** (0.143 mM) in $\text{C}_6\text{H}_5\text{Cl}$.

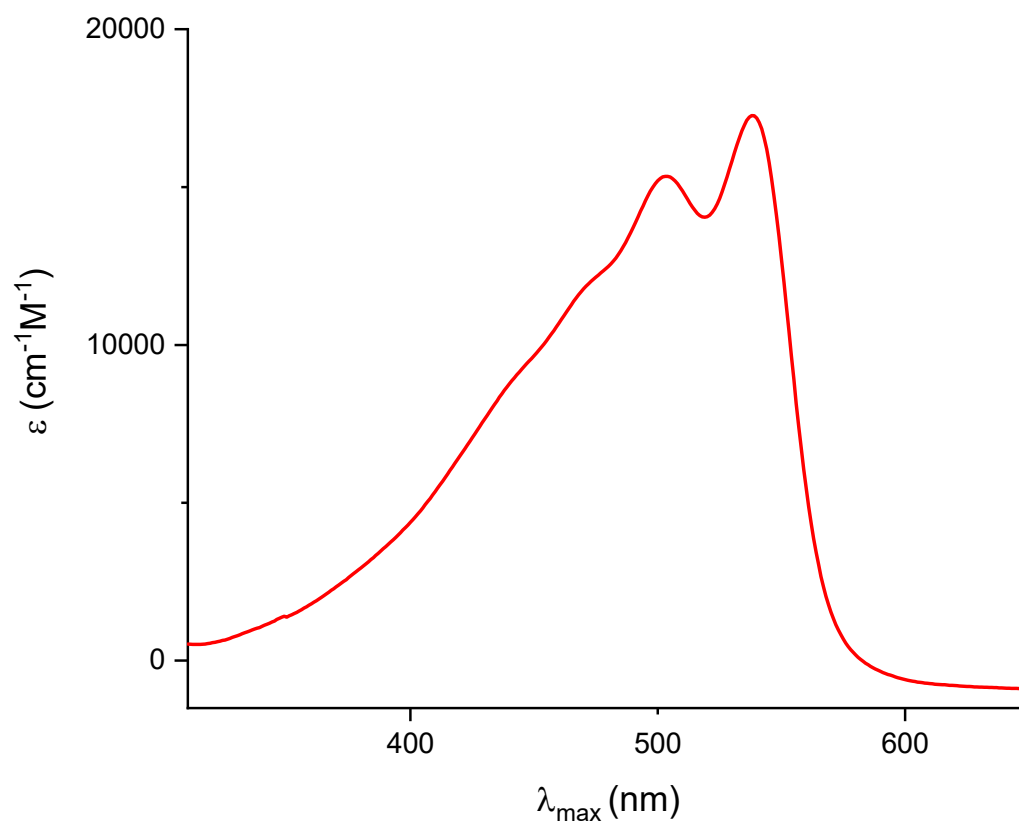


Figure S78. UV-Vis spectrum of **3** (0.0326 mM) in C₆H₅Cl.

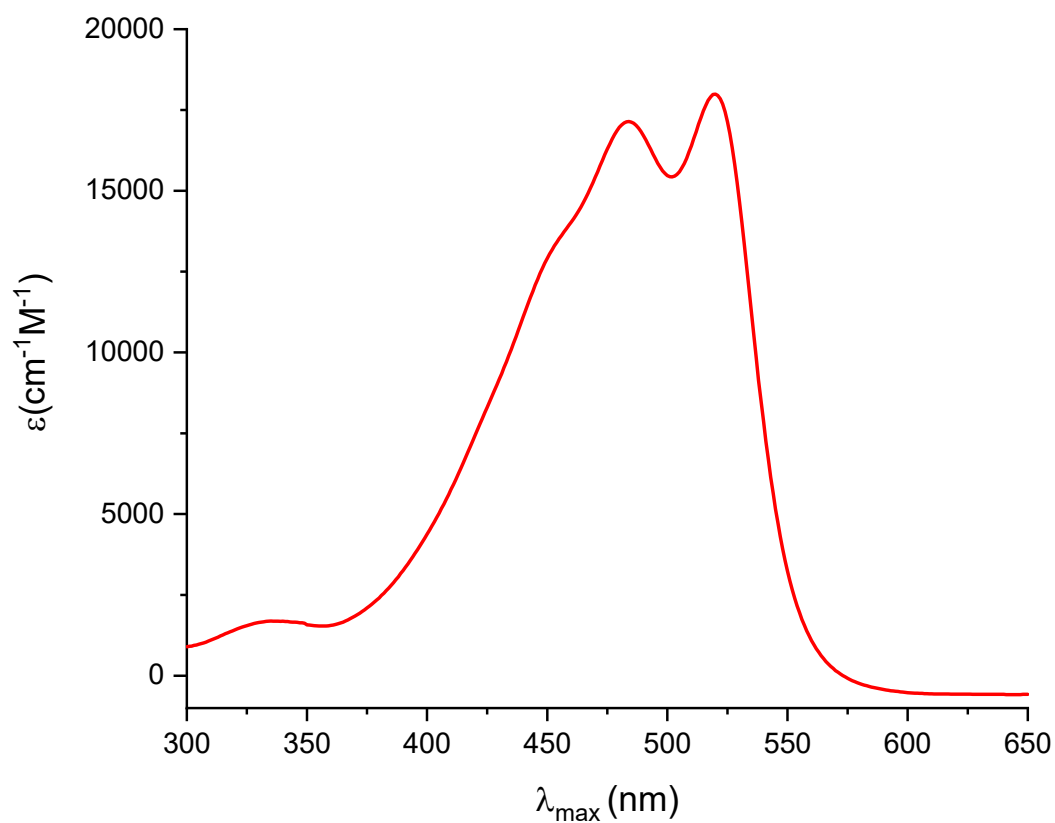


Figure S79. UV-Vis spectrum of **6** (0.0566 mM) in $\text{C}_6\text{H}_5\text{Cl}$.

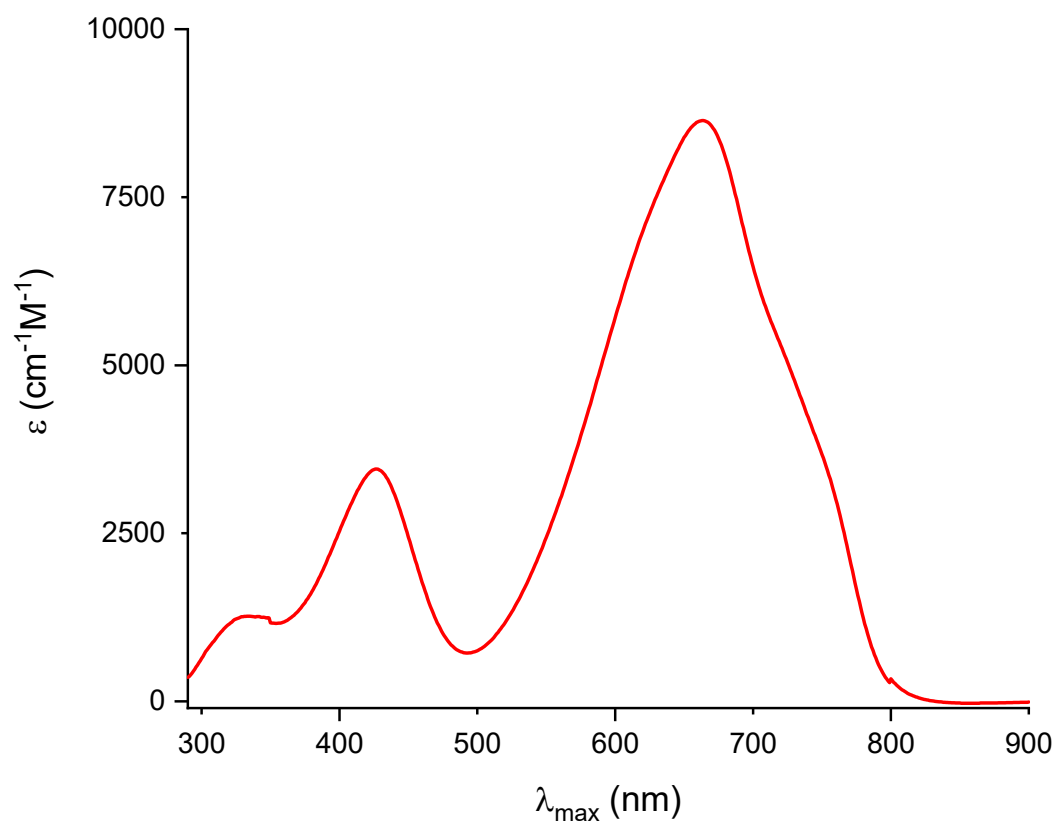


Figure S80. UV-Vis spectrum of **7** (0.0385 mM) in C₆H₅Cl.

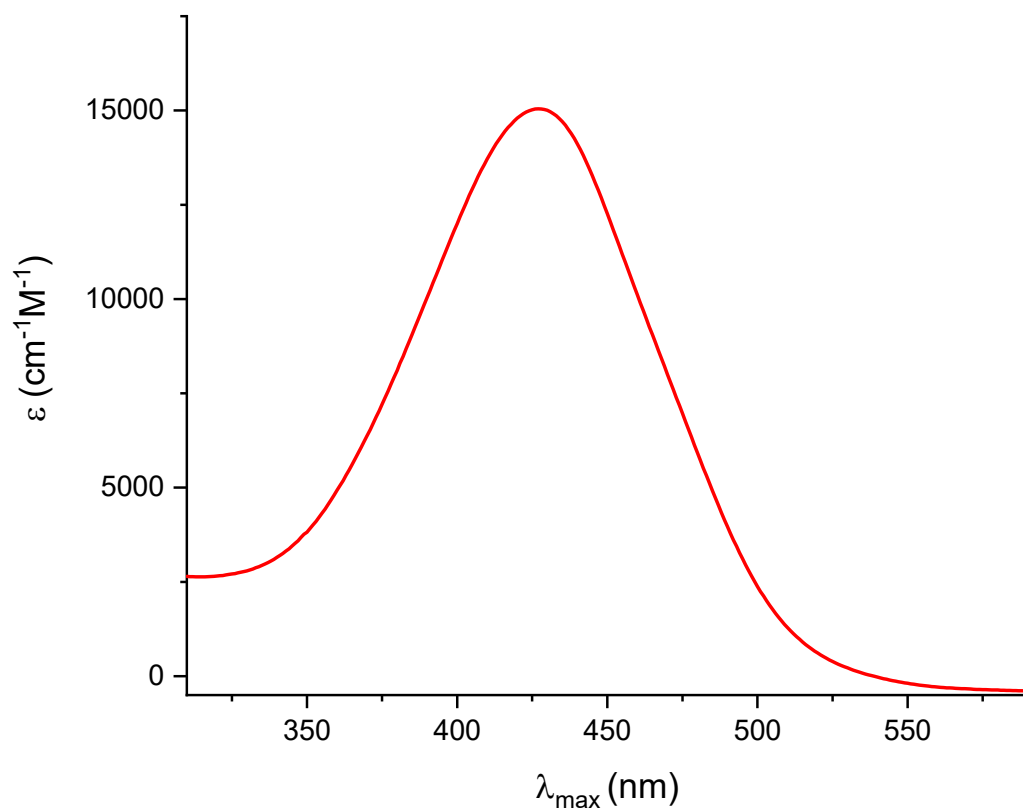


Figure S81. UV-Vis spectrum of **8** (0.0135 mM) in C₆H₅Cl.

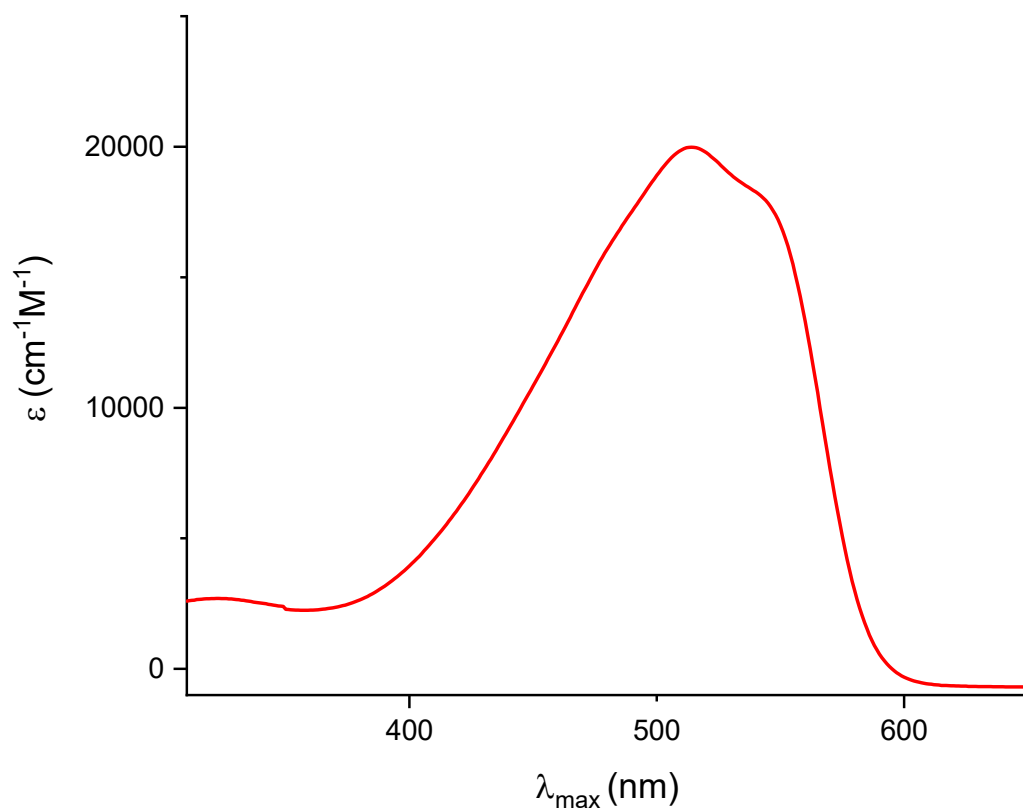


Figure S82. UV-Vis spectrum of **9** (0.0456 mM) in $\text{C}_6\text{H}_5\text{Cl}$.

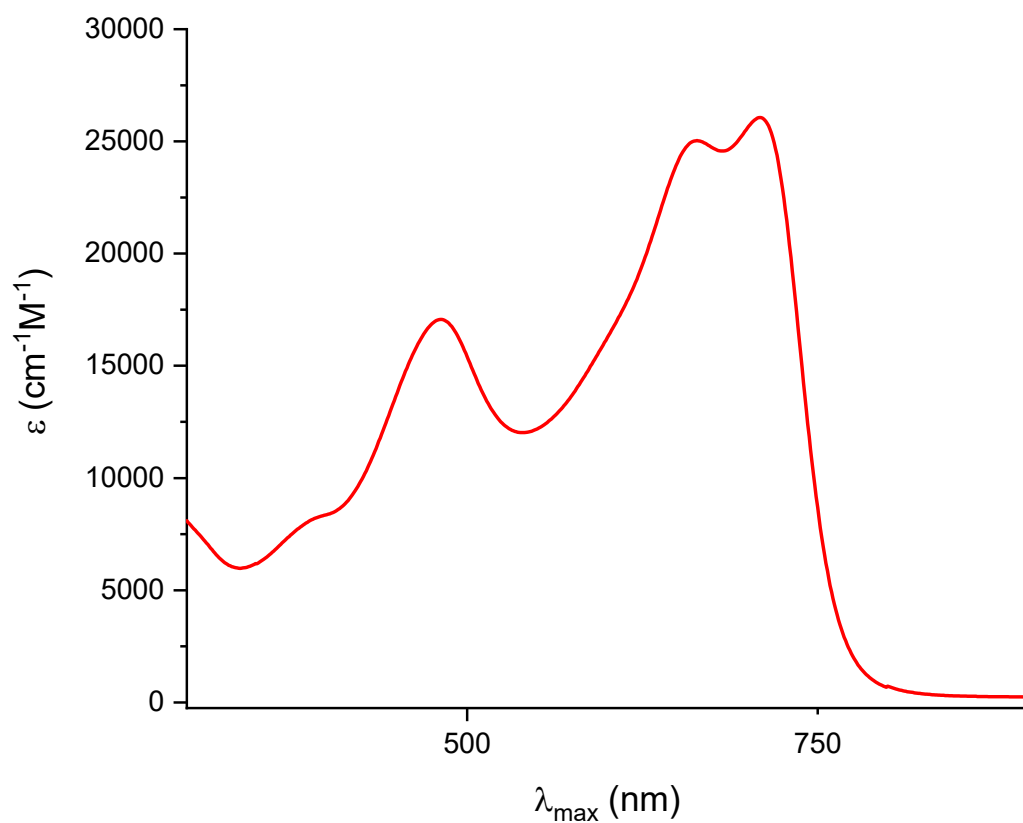


Figure S83. UV-Vis spectrum of **10** (0.0606 mM) in $\text{C}_6\text{H}_5\text{Cl}$.

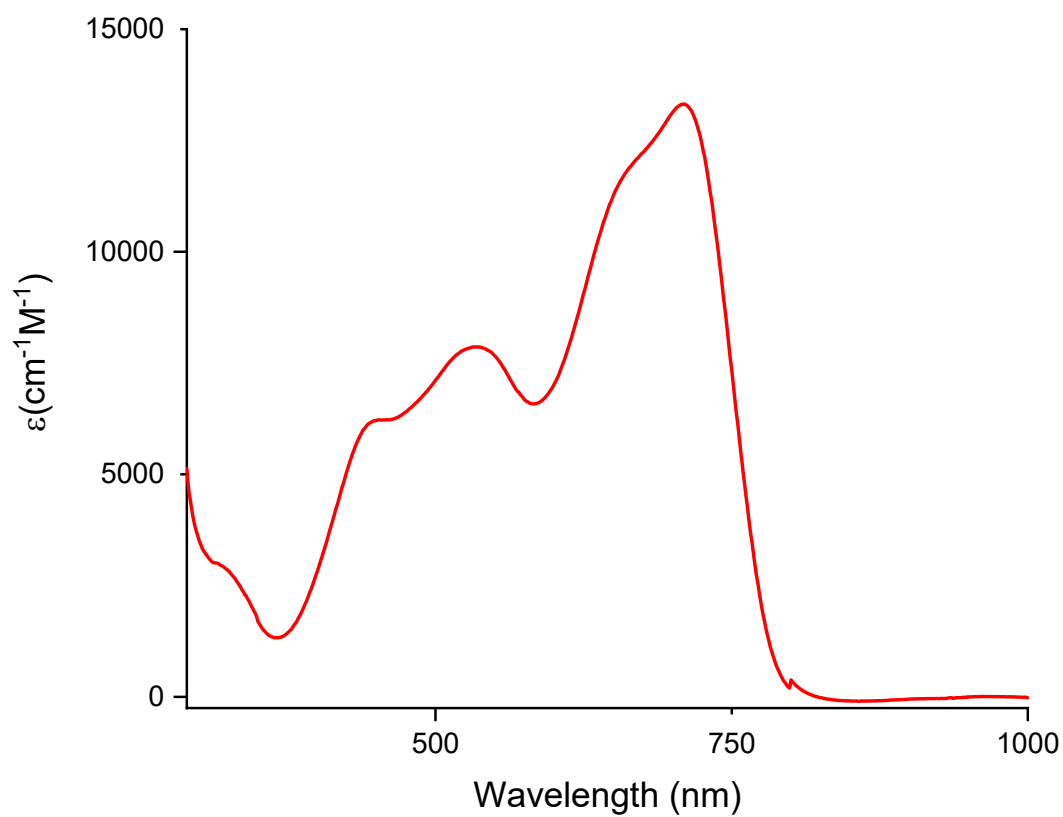


Figure S84. UV-Vis spectrum of **11** (0.0187 mM) in $\text{C}_6\text{H}_5\text{Cl}$.

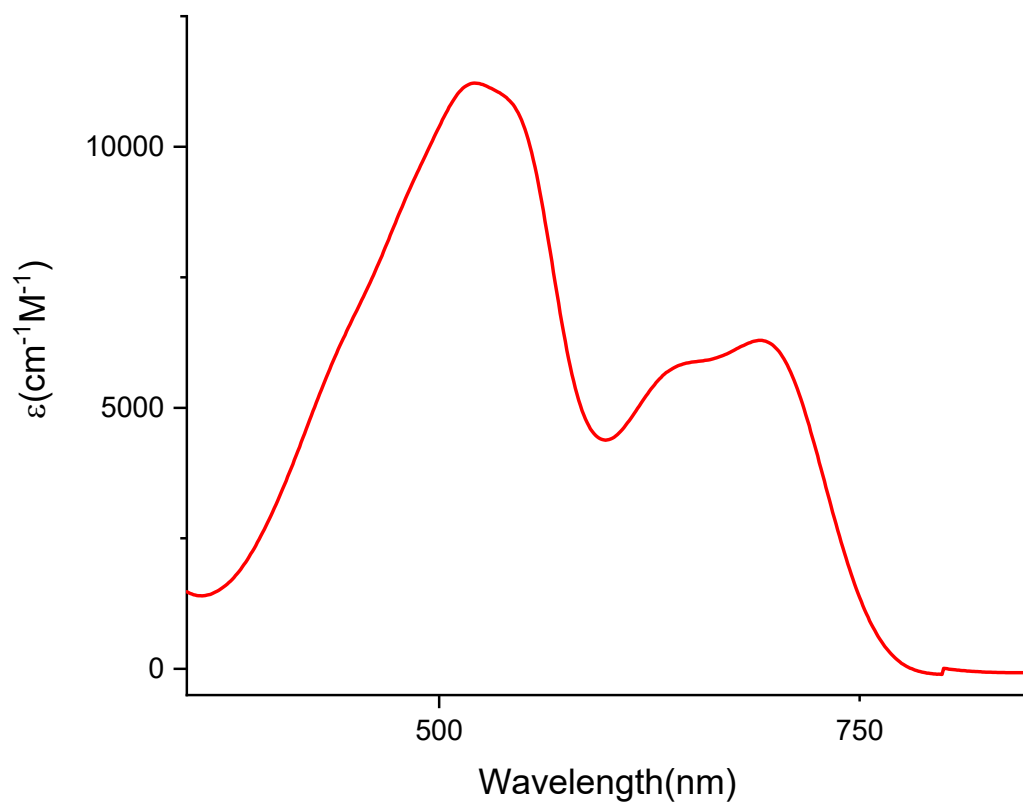


Figure S85. UV-Vis spectrum of **12** (0.0351 mM) in $\text{C}_6\text{H}_5\text{Cl}$.

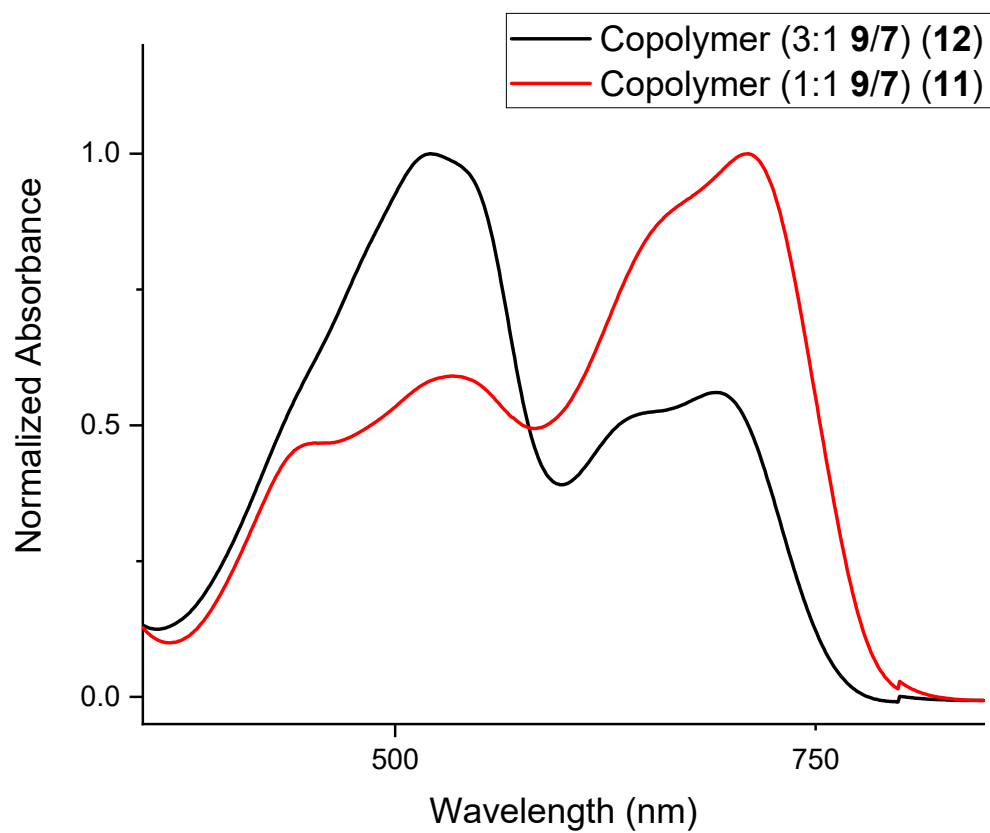


Figure S86. UV-Vis spectrum of **11** and **12** overlaid in C₆H₅Cl.

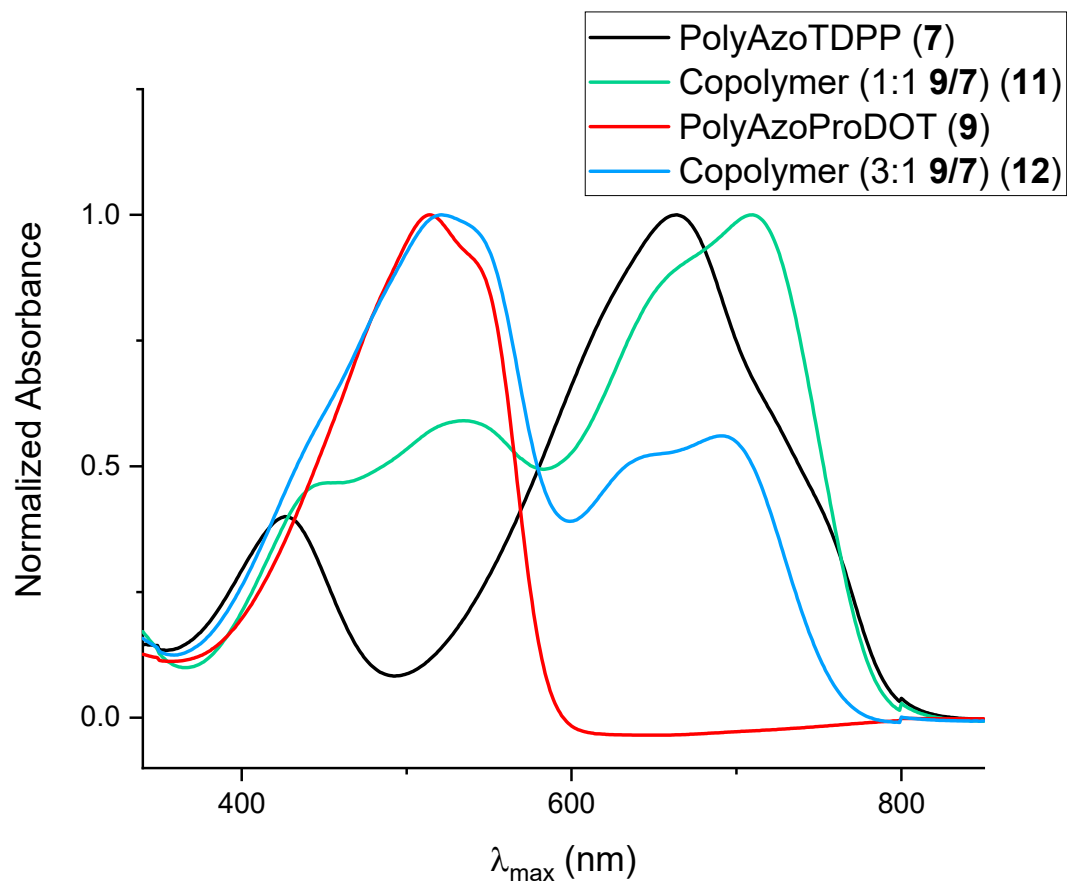


Figure S87. UV-Vis spectrum of **7**, **9**, **11** and **12** overlaid in C₆H₅Cl.

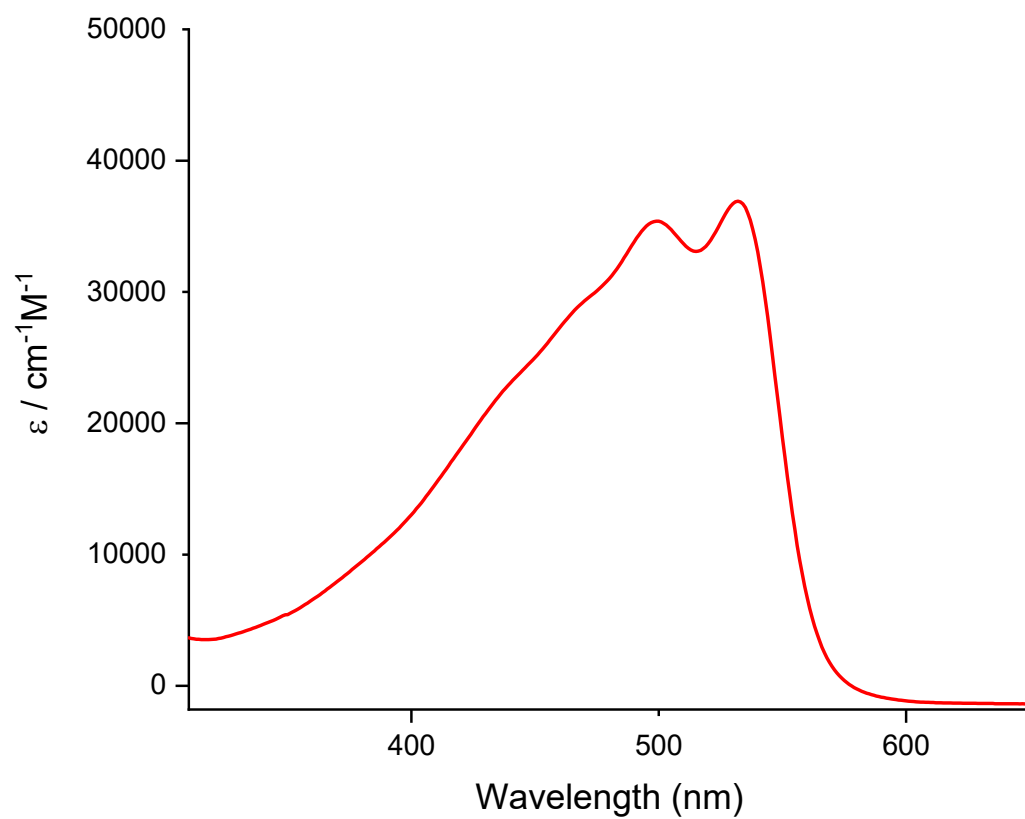


Figure S88. UV-Vis spectrum of **13** (0.0428 mM) in $\text{C}_6\text{H}_5\text{Cl}$.

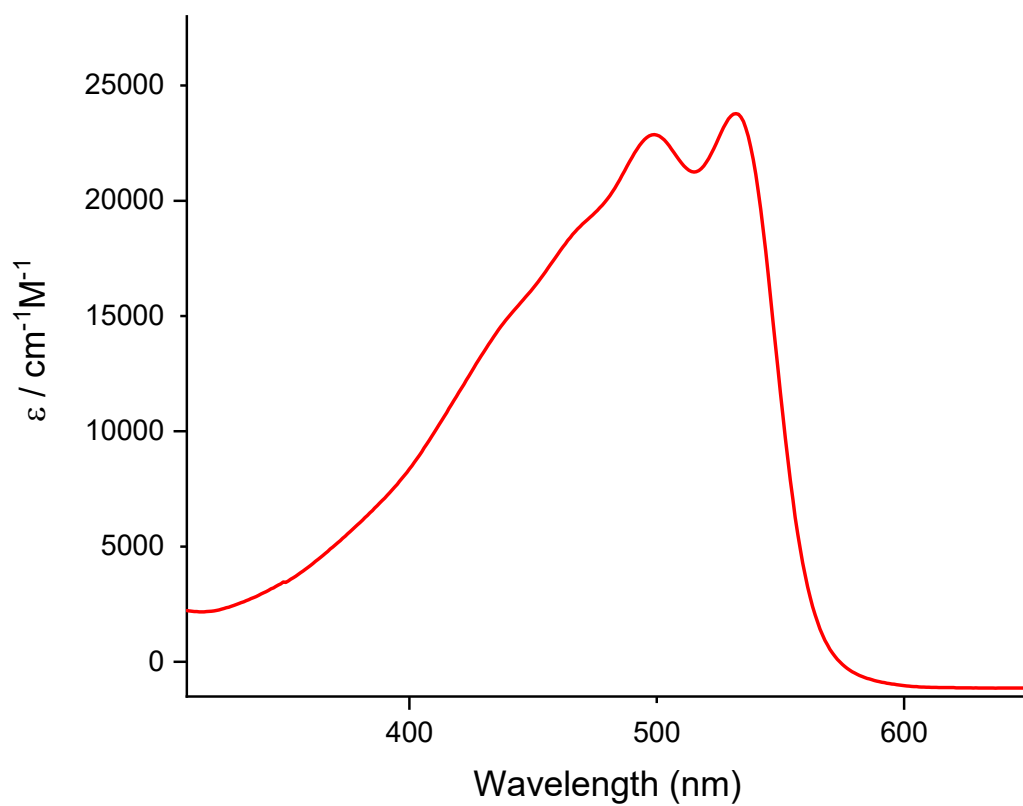


Figure S89. UV-Vis spectrum of **14** (0.0428 mM) in $\text{C}_6\text{H}_5\text{Cl}$.

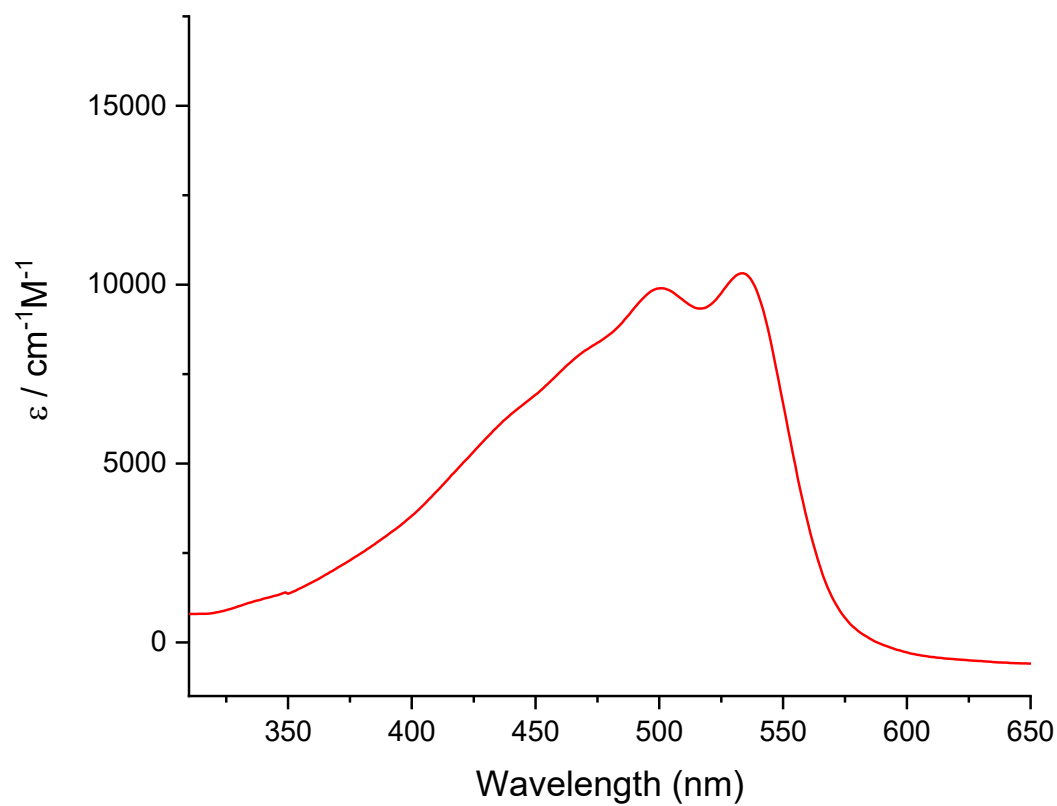


Figure S90. UV-Vis spectrum of **15** (0.0551 mM) in $\text{C}_6\text{H}_5\text{Cl}$.

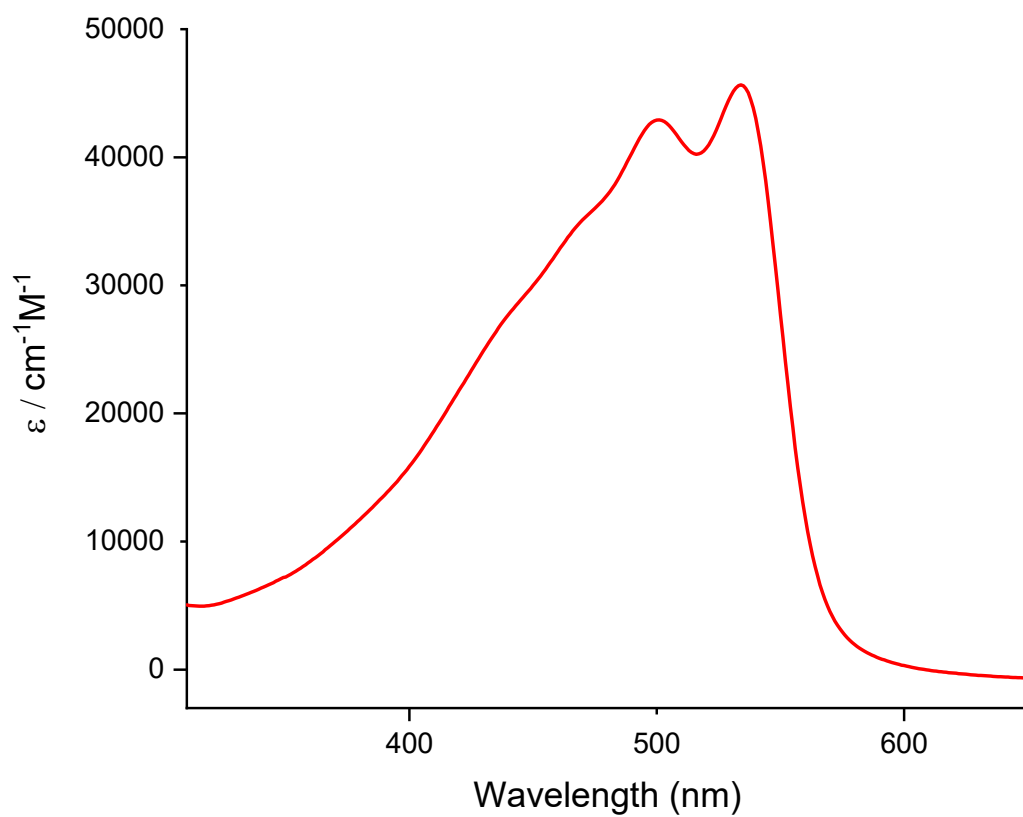


Figure S91. UV-Vis spectrum of **16** (0.0612 mM) in $\text{C}_6\text{H}_5\text{Cl}$.

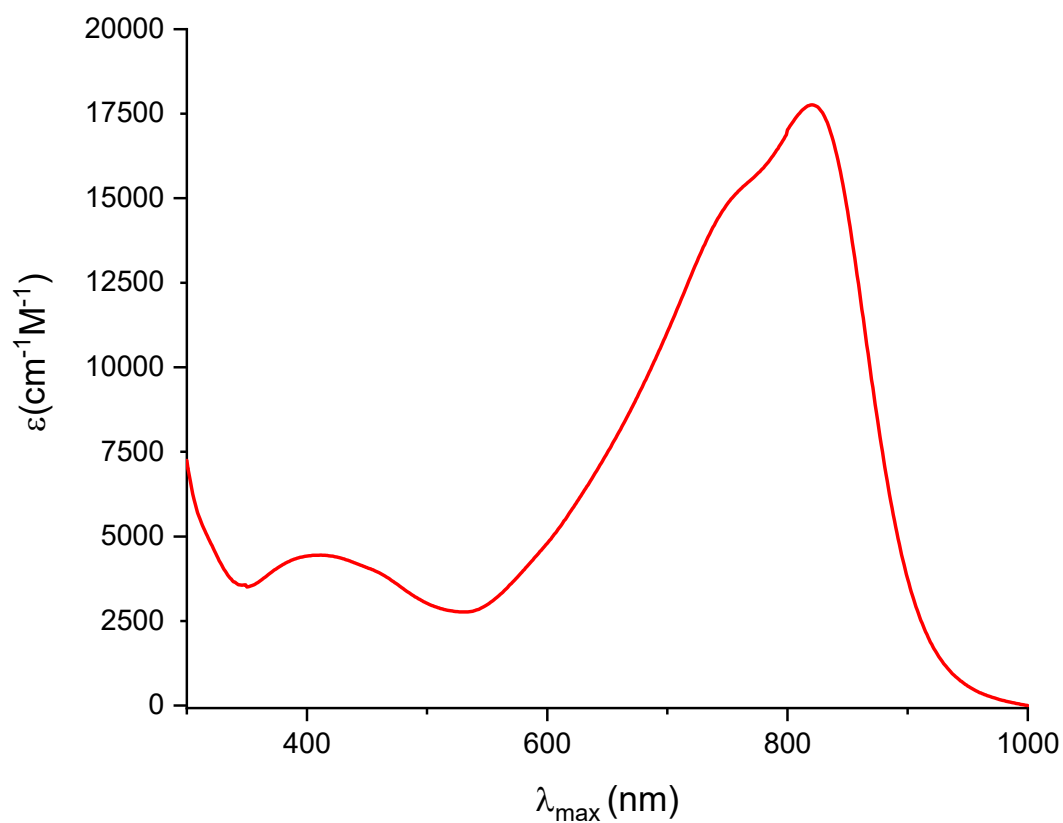
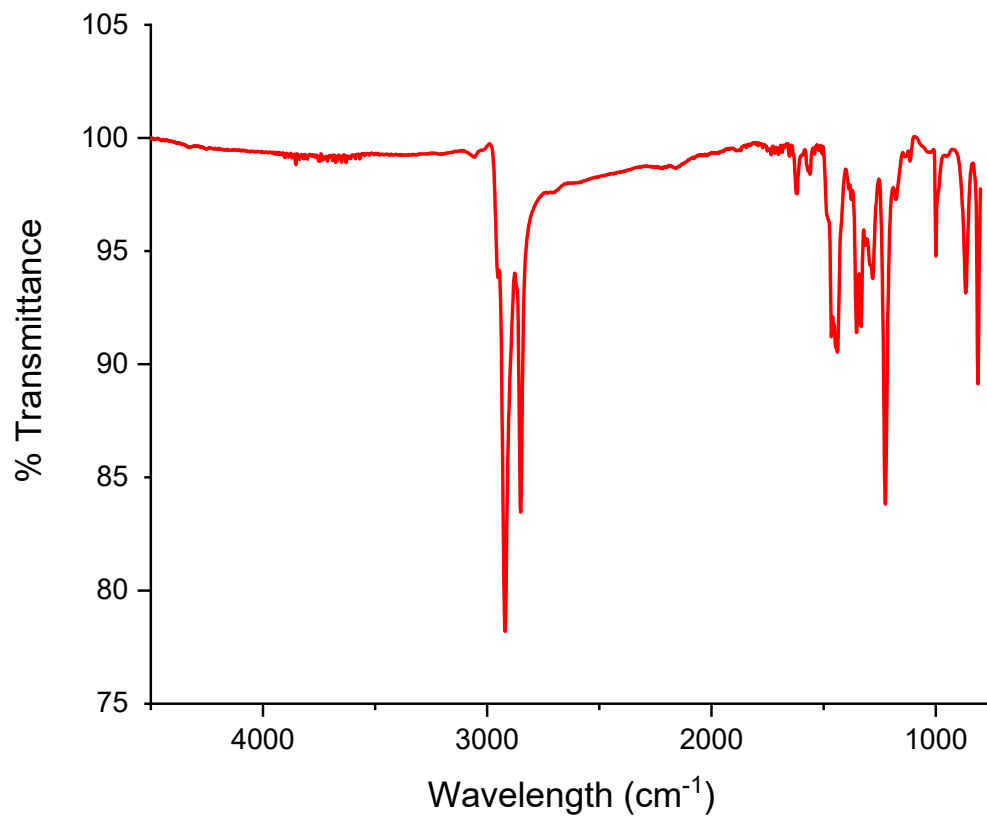


Figure S92. UV-Vis spectrum of **18** (0.0326 mM) in $\text{C}_6\text{H}_5\text{Cl}$.

13. IR Spectra

**Figure S93.** FT-IR spectrum of **3**.

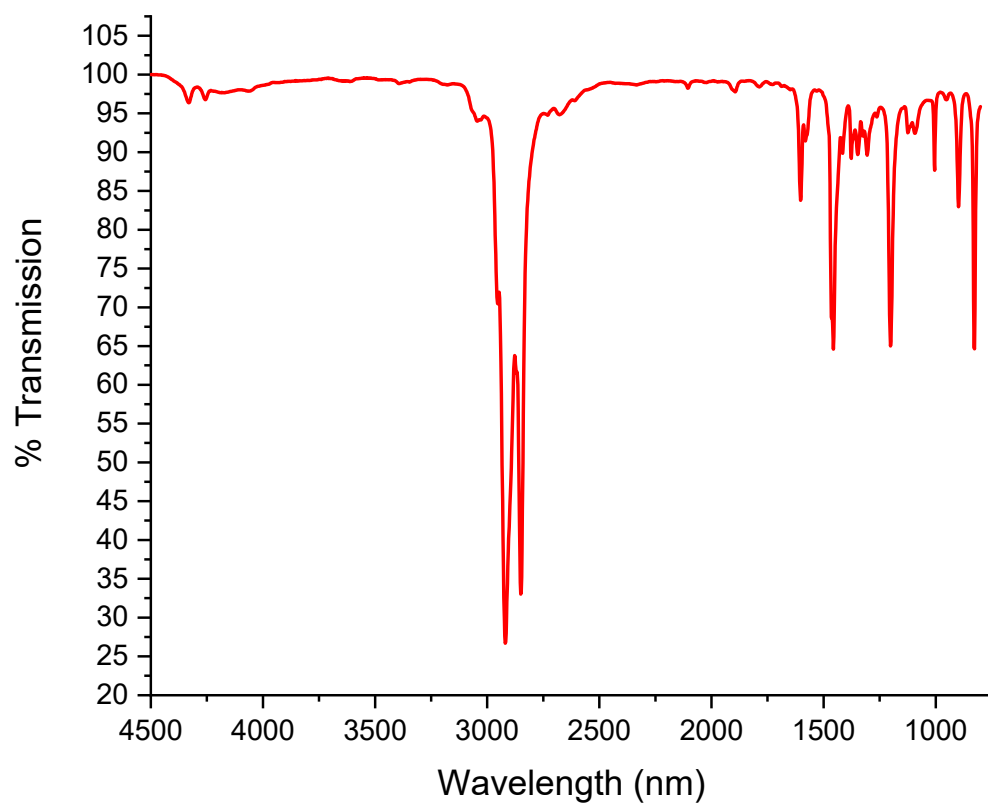


Figure S94. FT-IR spectrum of **6**.

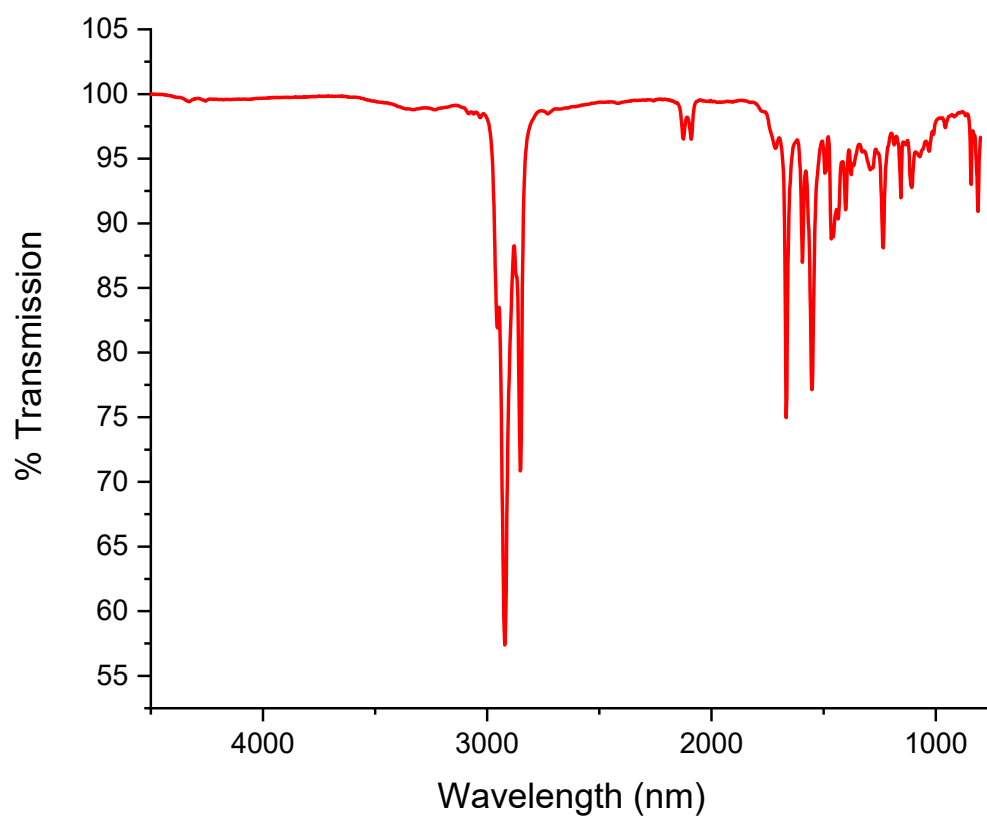


Figure S95. FT-IR spectrum of **7**.

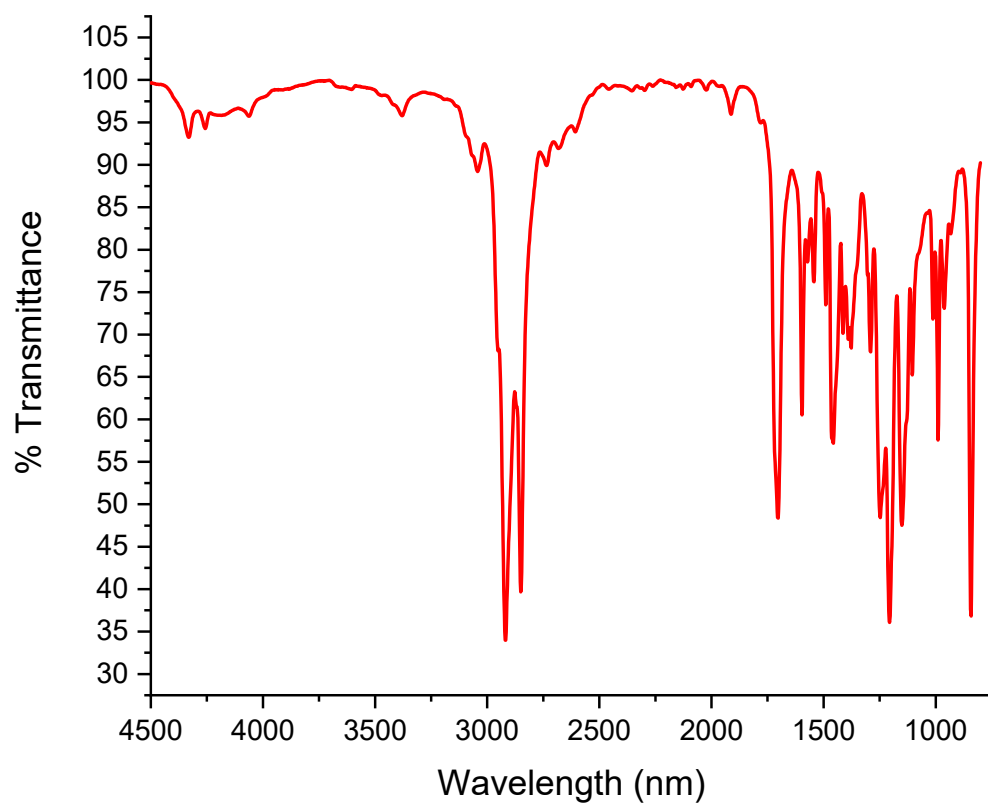


Figure S96. FT-IR spectrum of **8**.

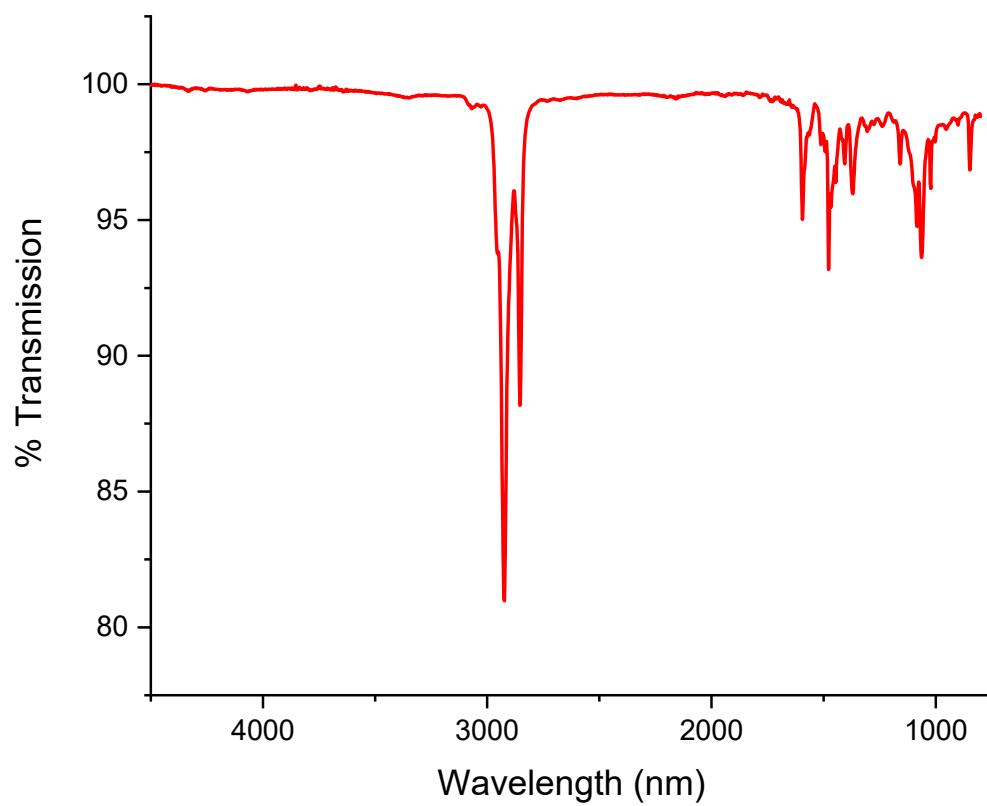


Figure S97. FT-IR spectrum of **9**.

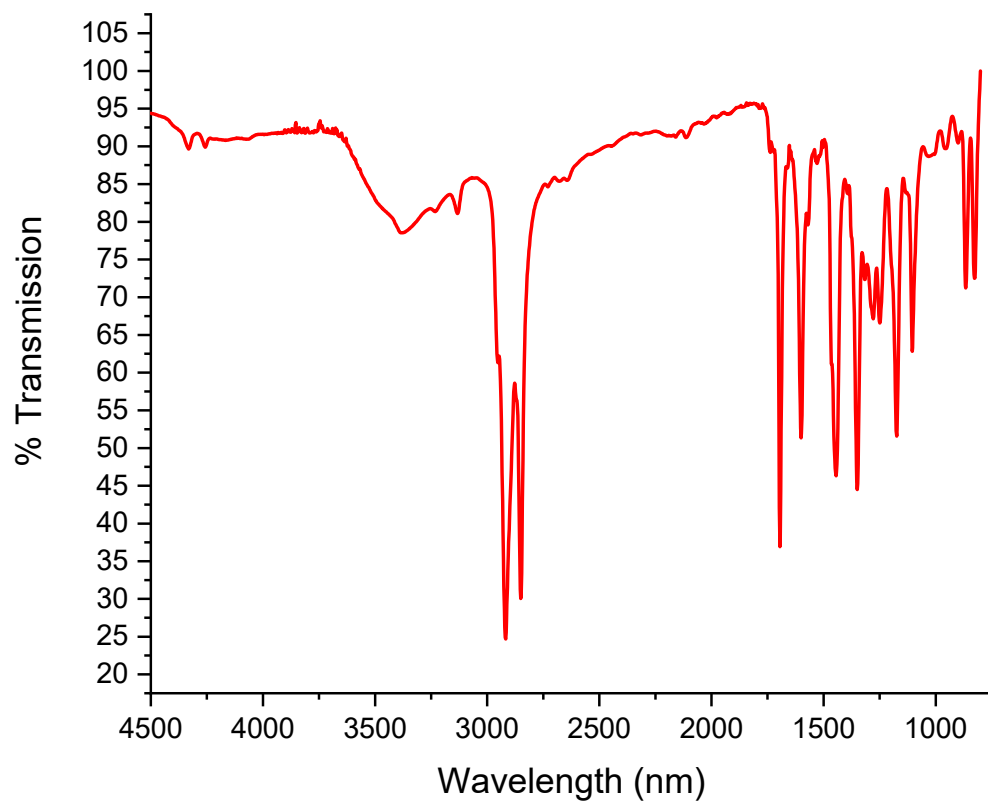


Figure S98. FT-IR spectrum of **10**.

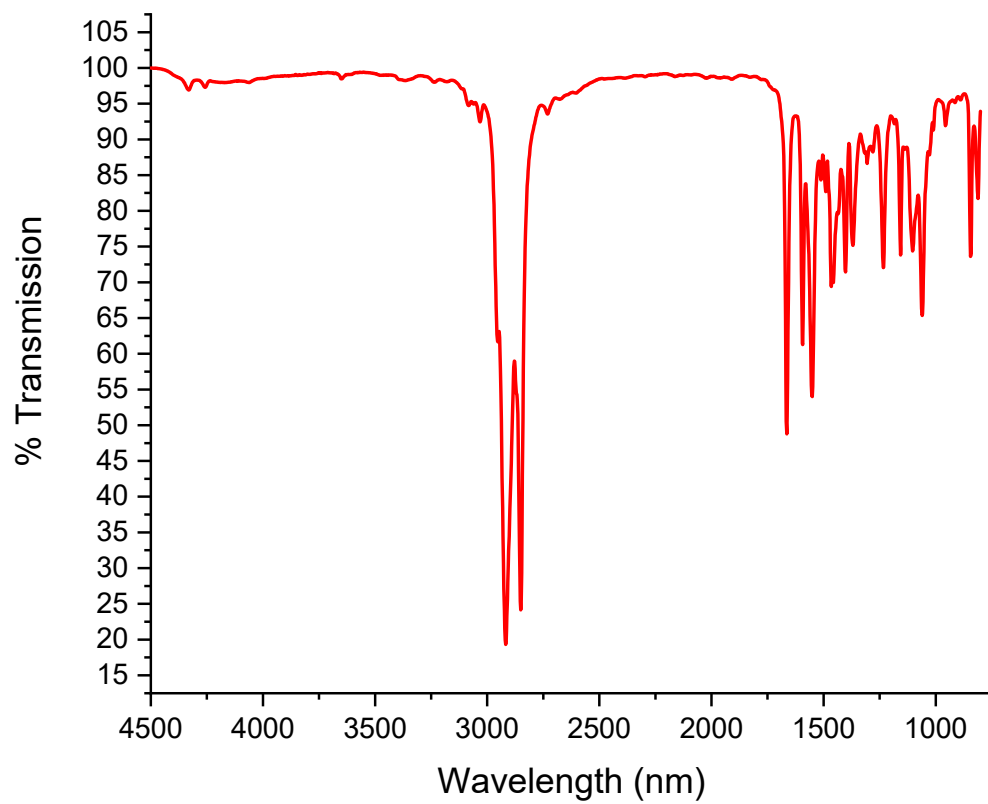


Figure S99. FT-IR spectrum of **11**.

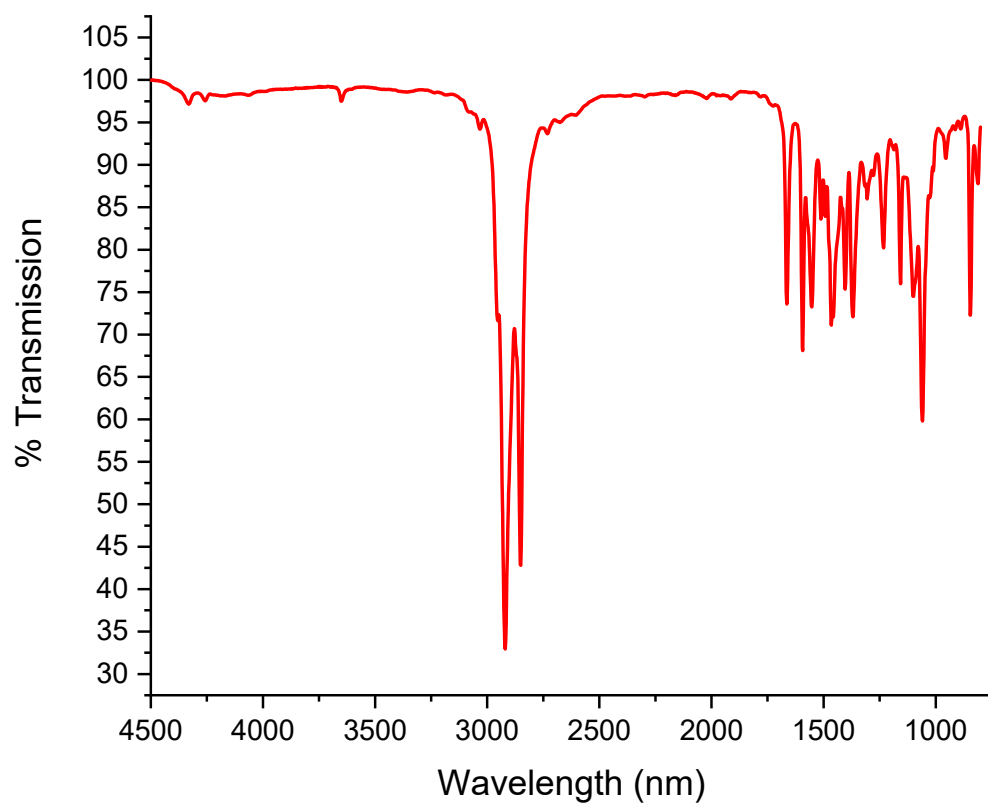


Figure S100. FT-IR spectrum of **12**.

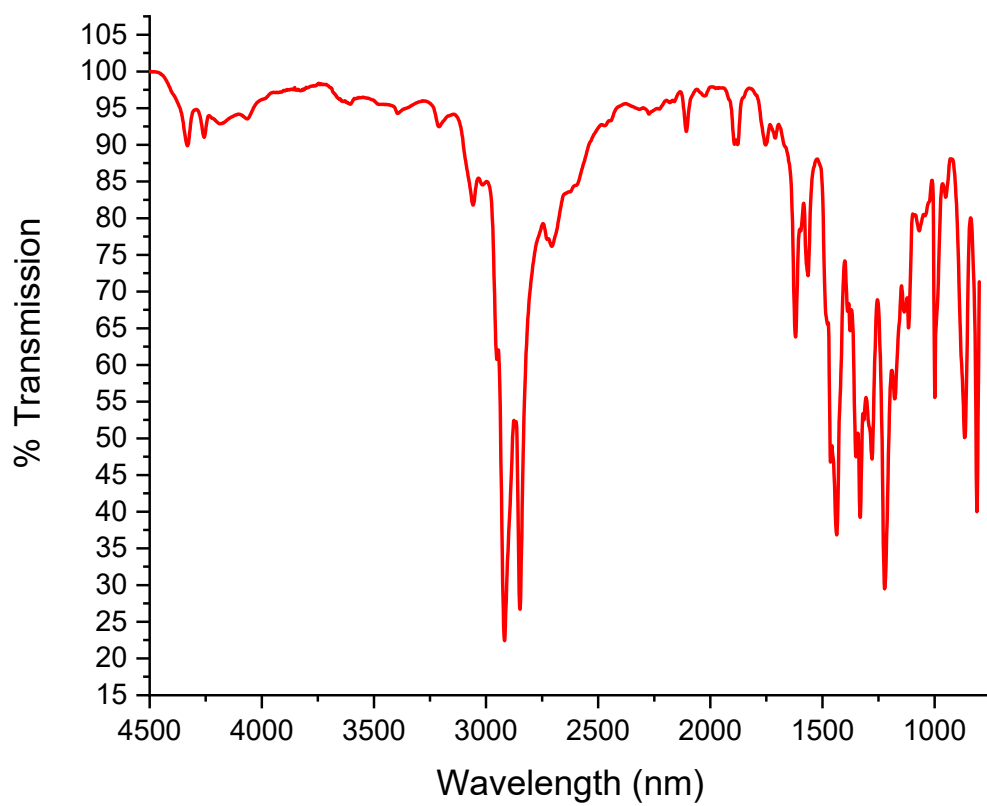


Figure S101. FT-IR spectrum of **13**.

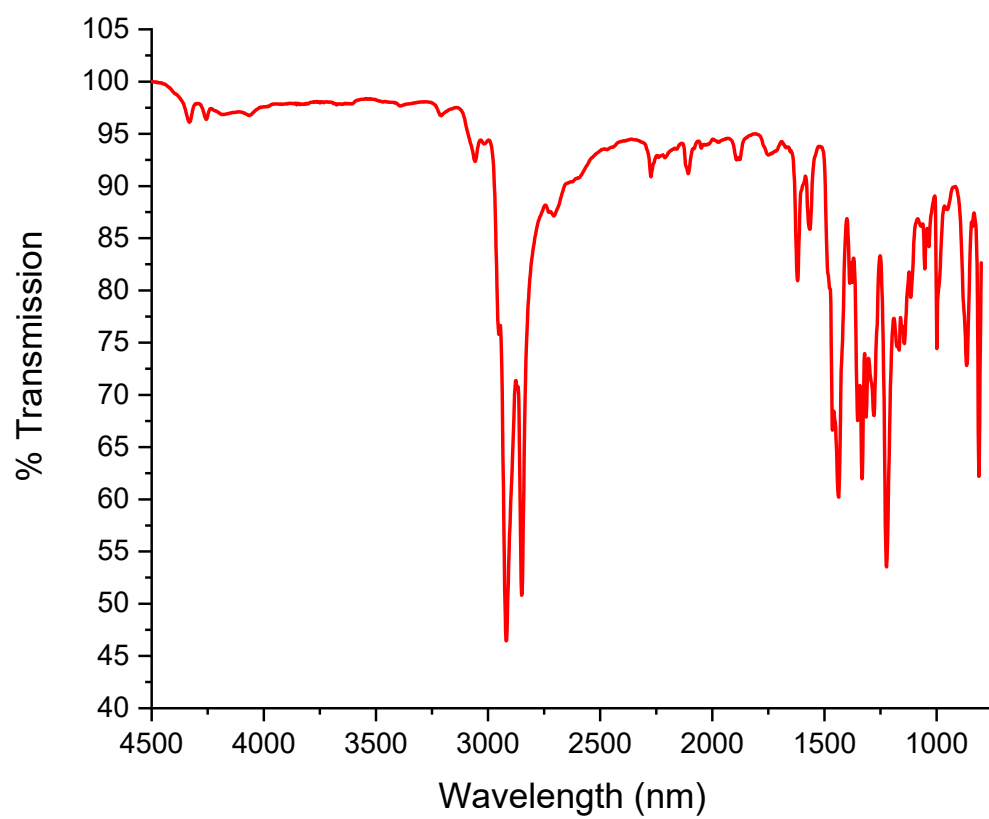


Figure S102. FT-IR spectrum of **14**.

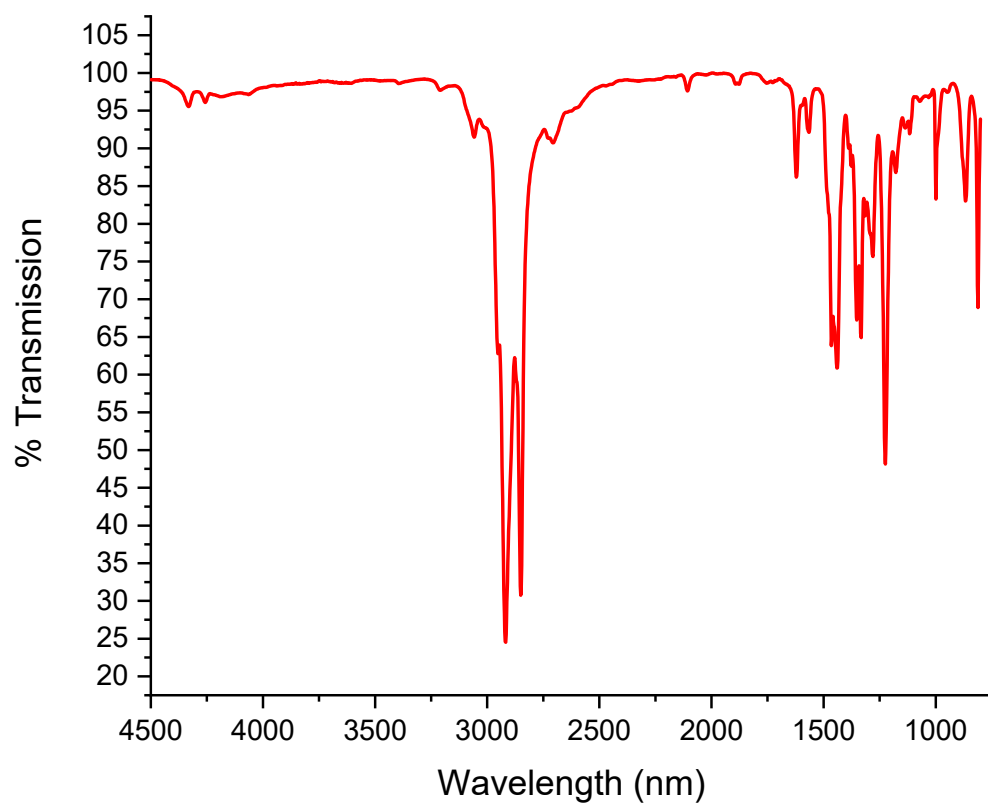


Figure S103. FT-IR spectrum of **15**.

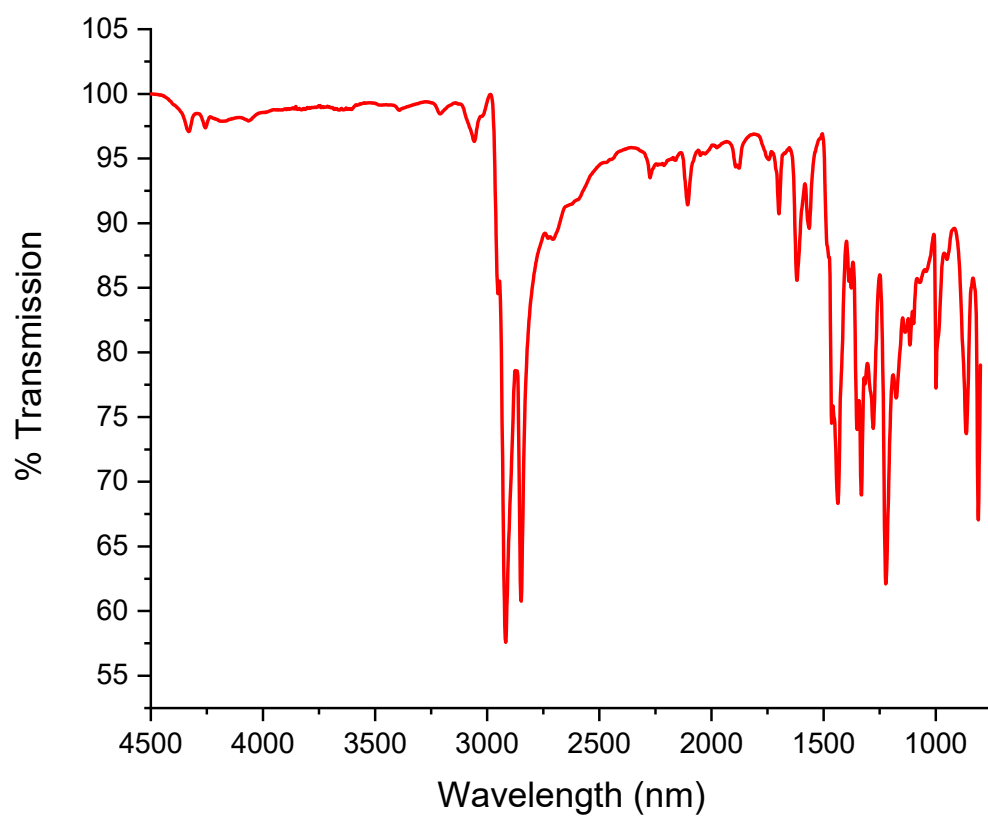


Figure S104. FT-IR spectrum of **16**.

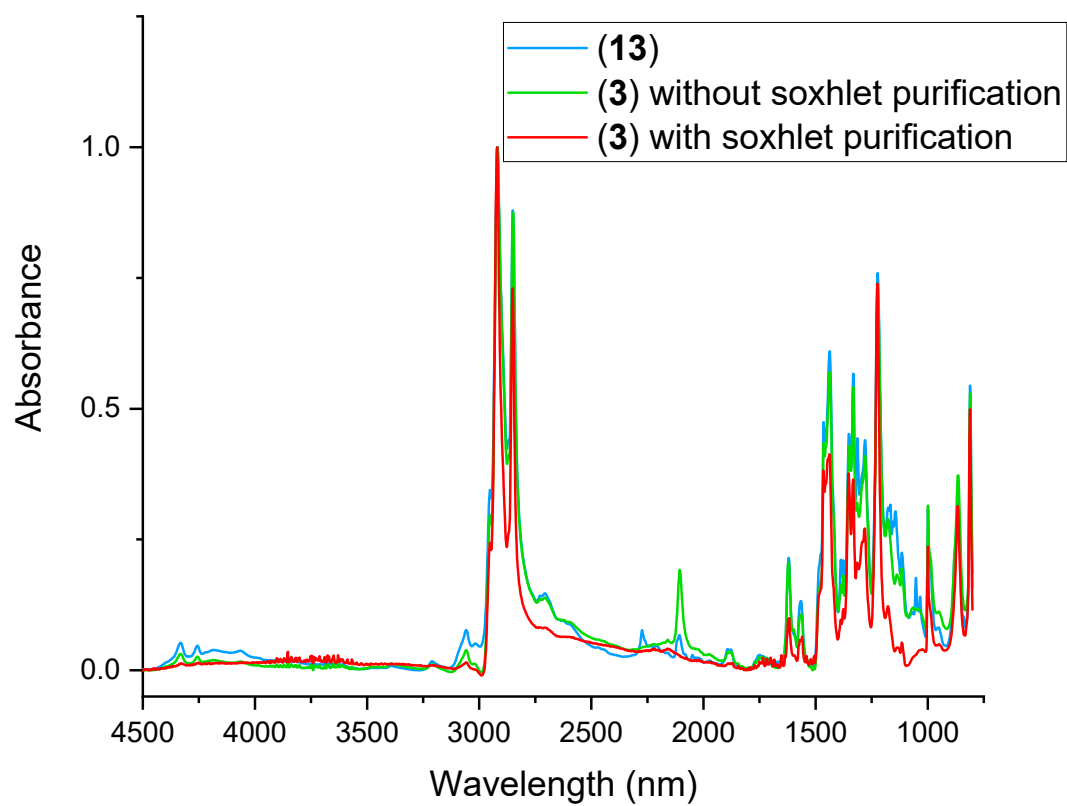


Figure S105. Normalized FT-IR spectrum of **3** (soxhlet purified), **3** (without soxhlet purification) and **13**.

14. High Temperature Gel Permeation Chromotography (HT-GPC) Data

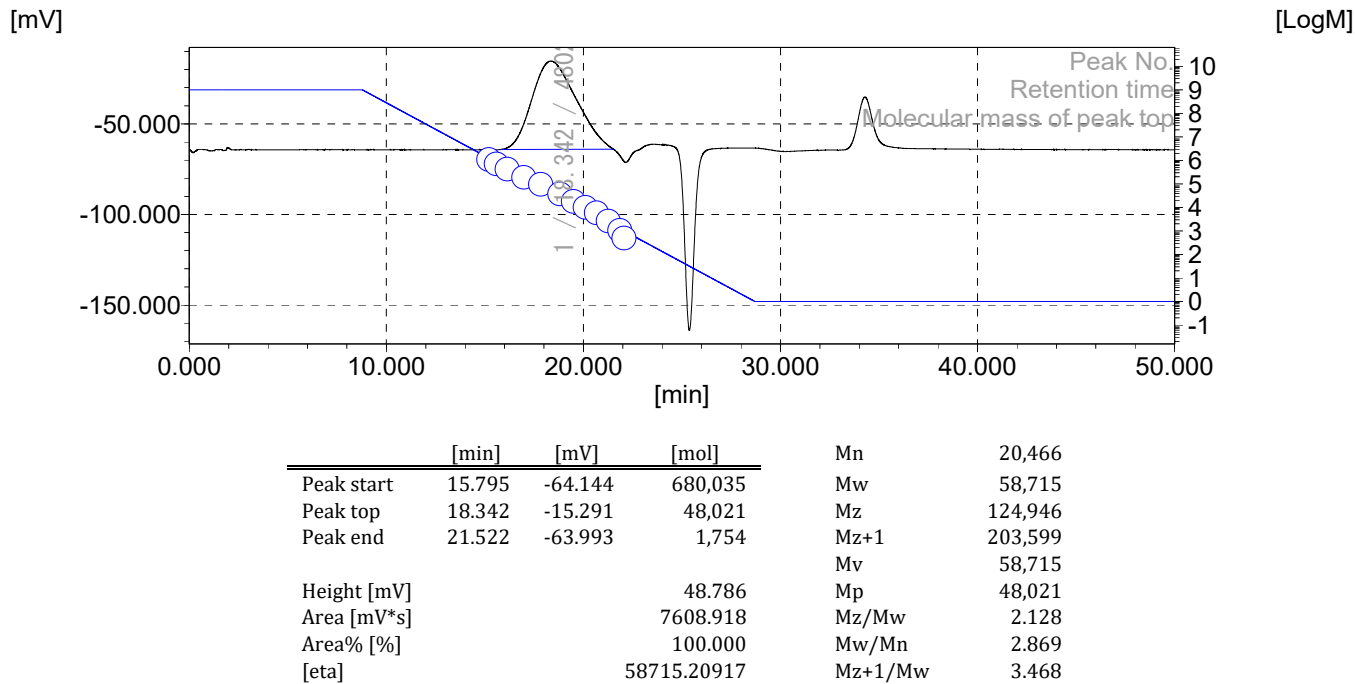


Figure S106. HT-GPC data for optimization of 3 (entry 1).

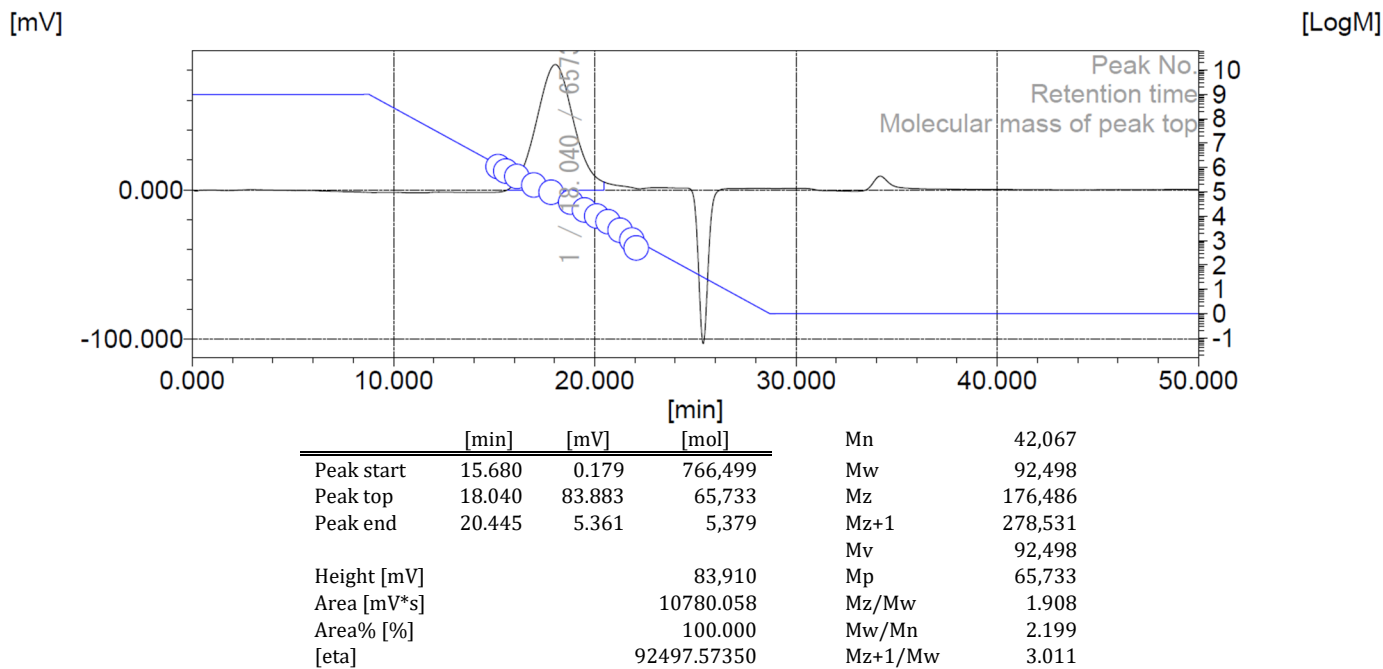


Figure S107. HT-GPC data for optimization of 3 (entry 2).

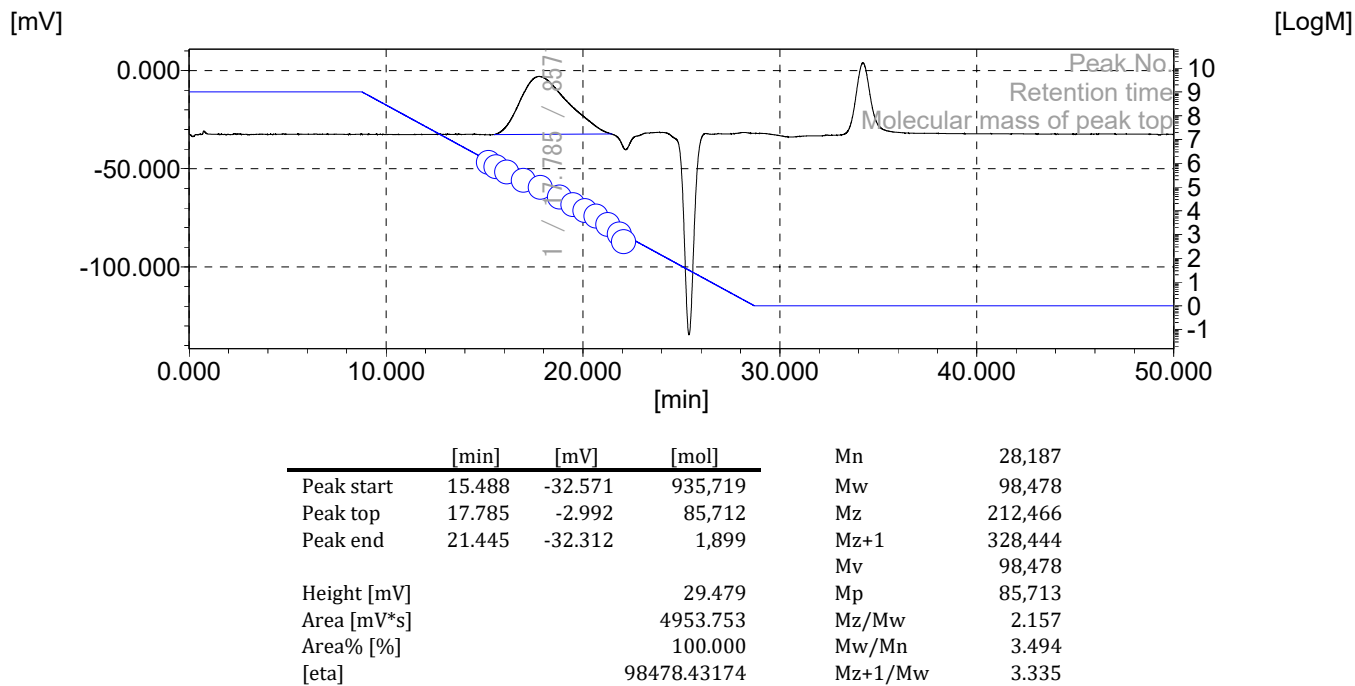


Figure S108. HT-GPC data for optimization of 3 (entry 4).

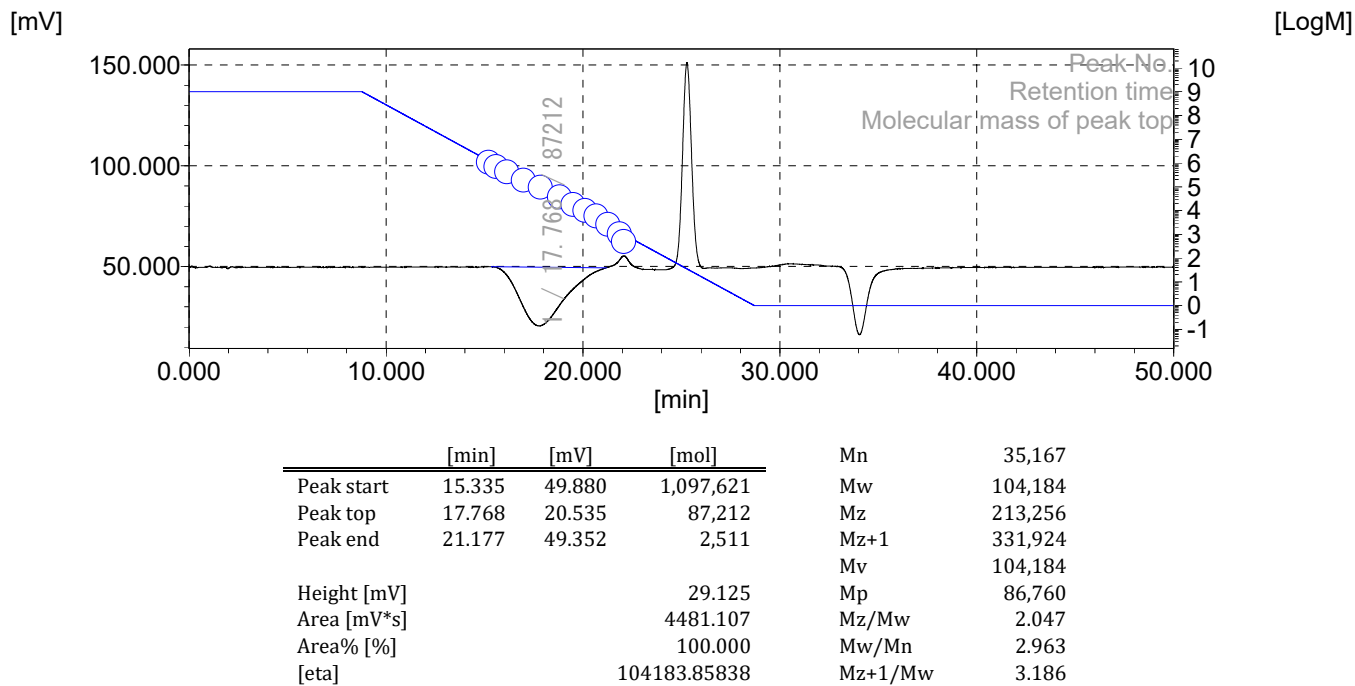


Figure S109. HT-GPC data for optimization of 3 (entry 6).

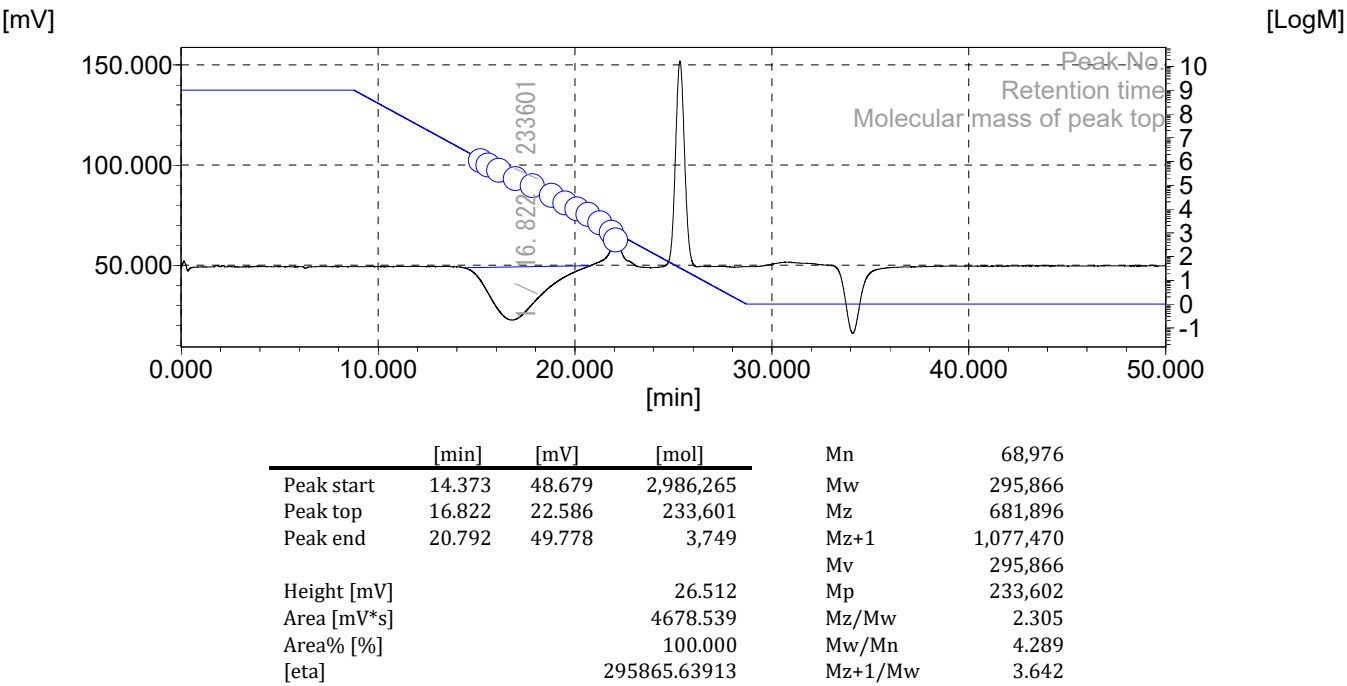


Figure S110. HT-GPC data for optimization of 3 (entry 7).

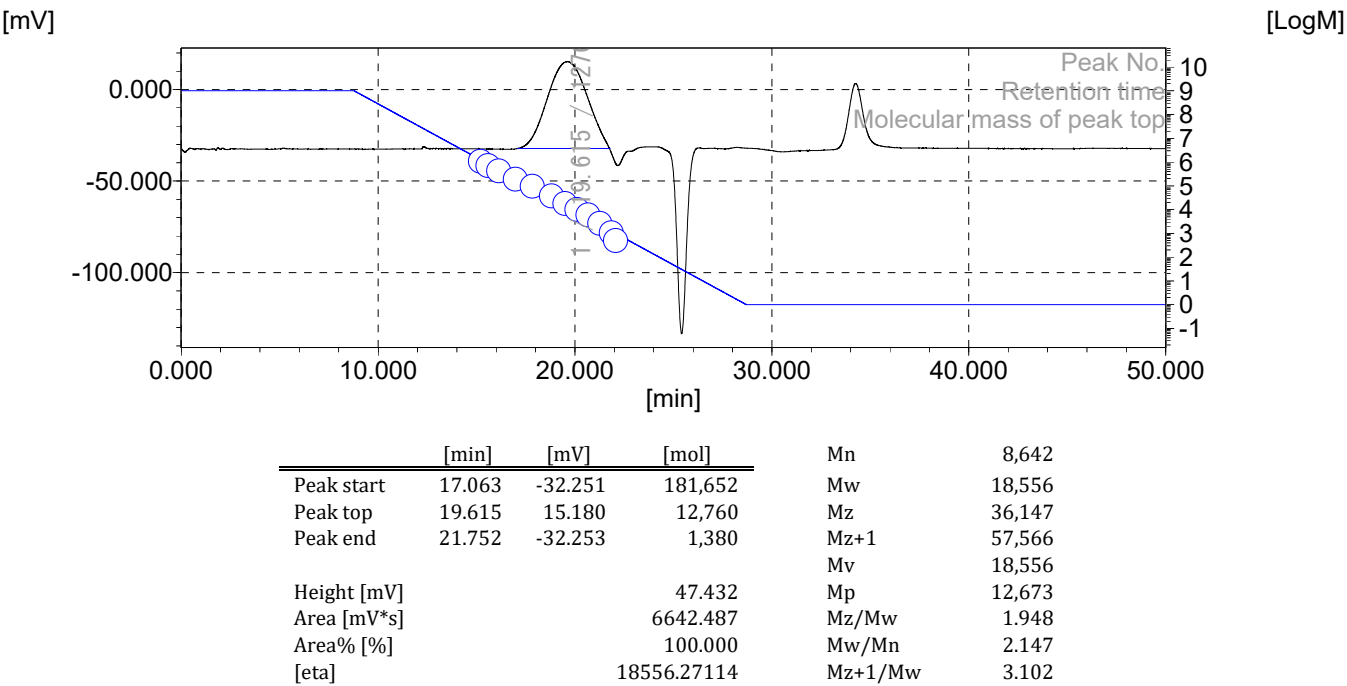


Figure S111. HT-GPC data for optimization of 3 (entry 8).

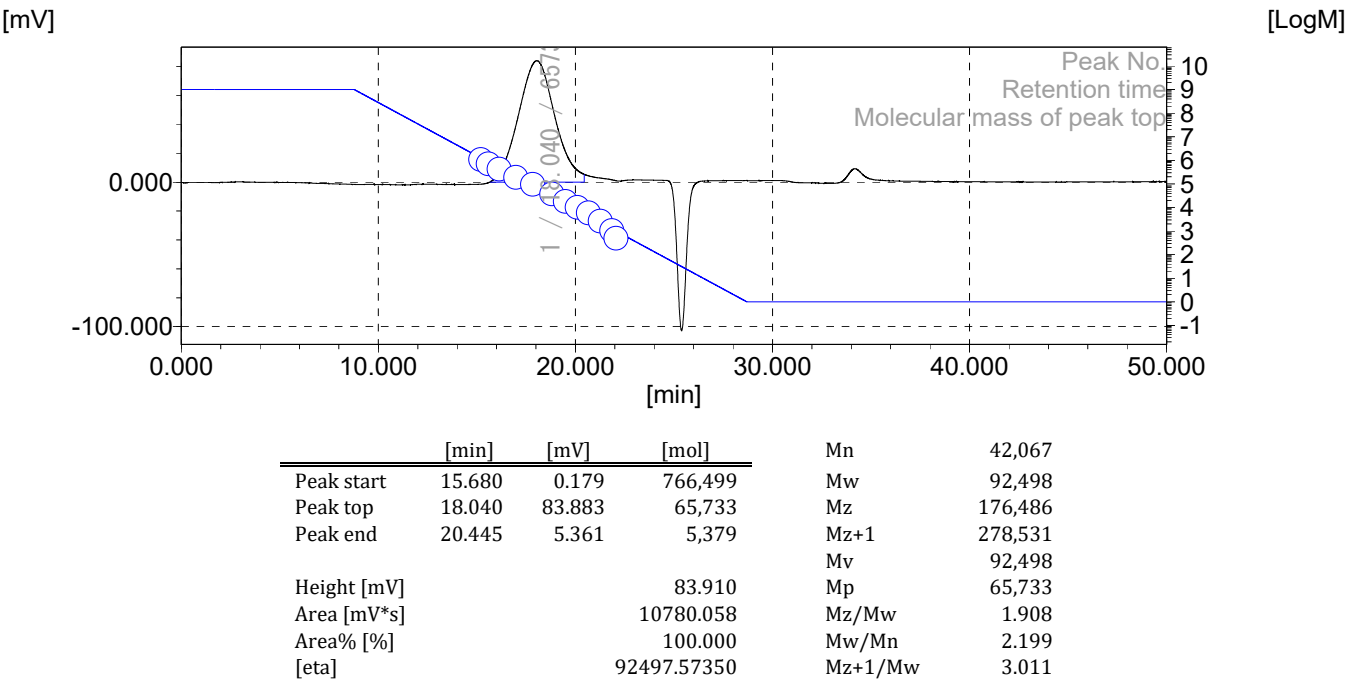


Figure S112. HT-GPC data of 3.

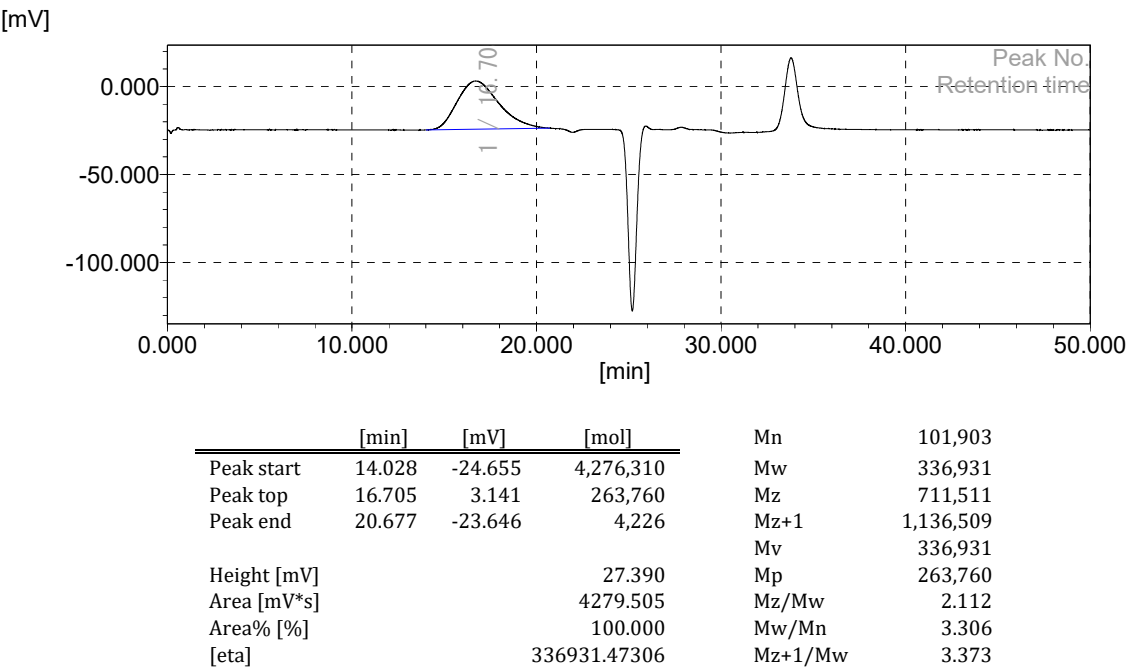


Figure S113. HT-GPC data of 6.

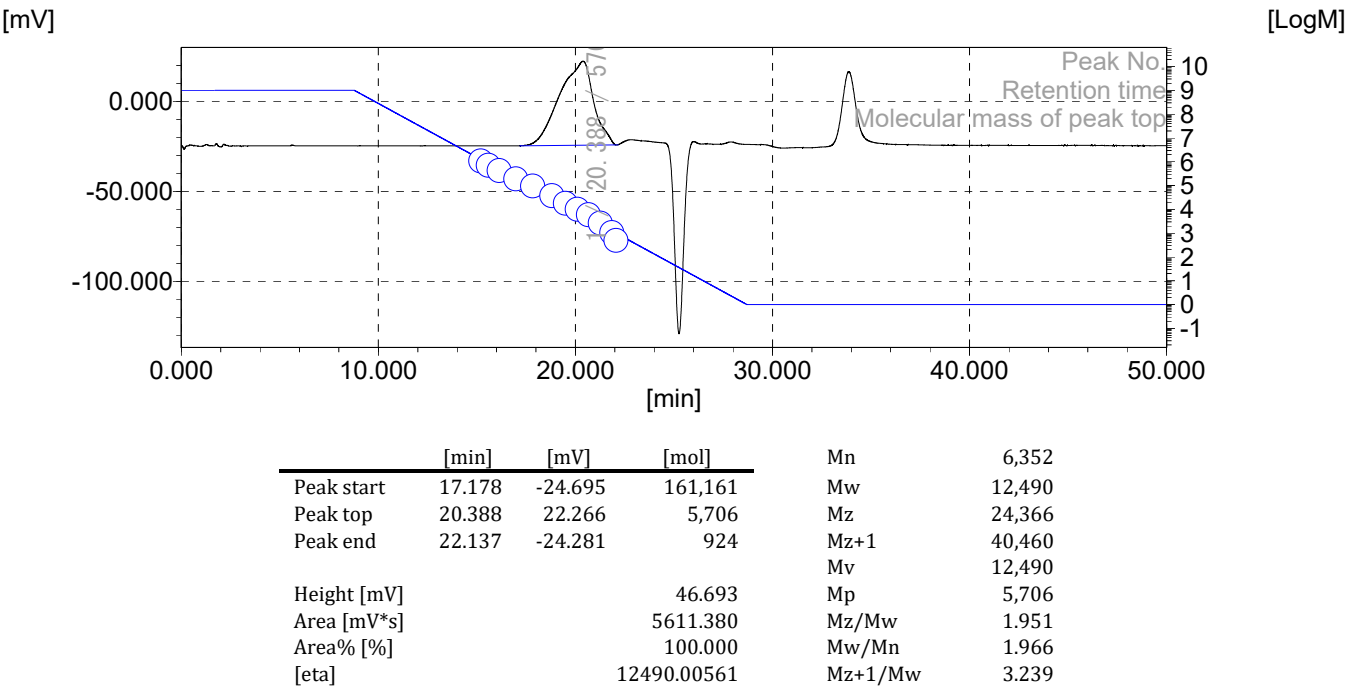


Figure S114. HT-GPC data of **7**.

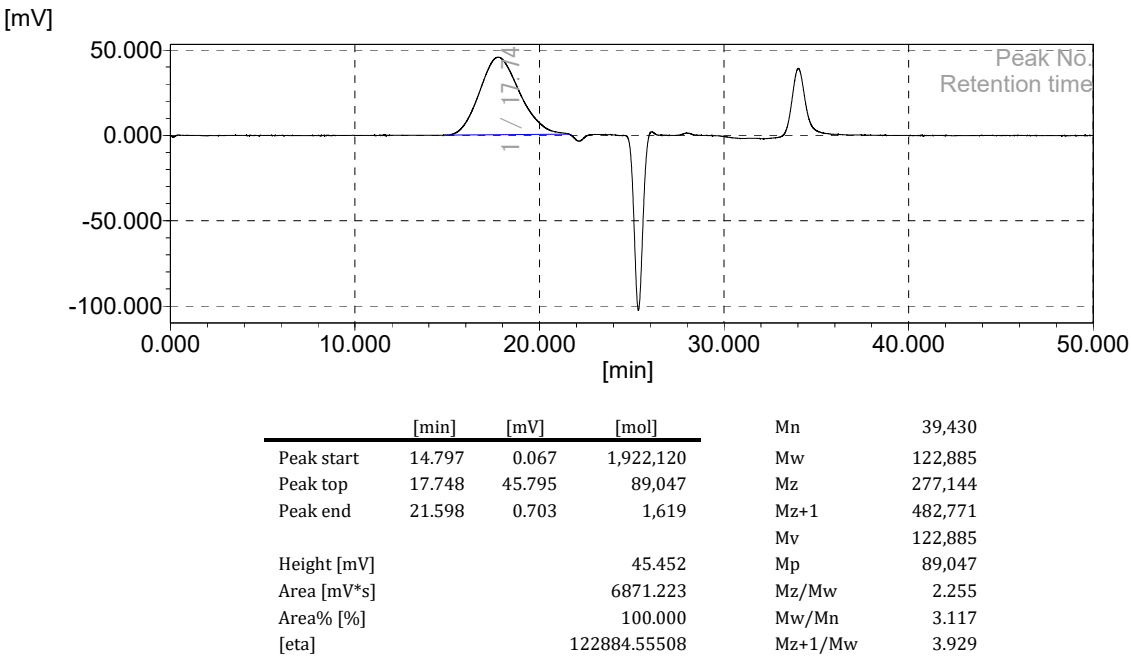


Figure S115. HT-GPC data of **8**.

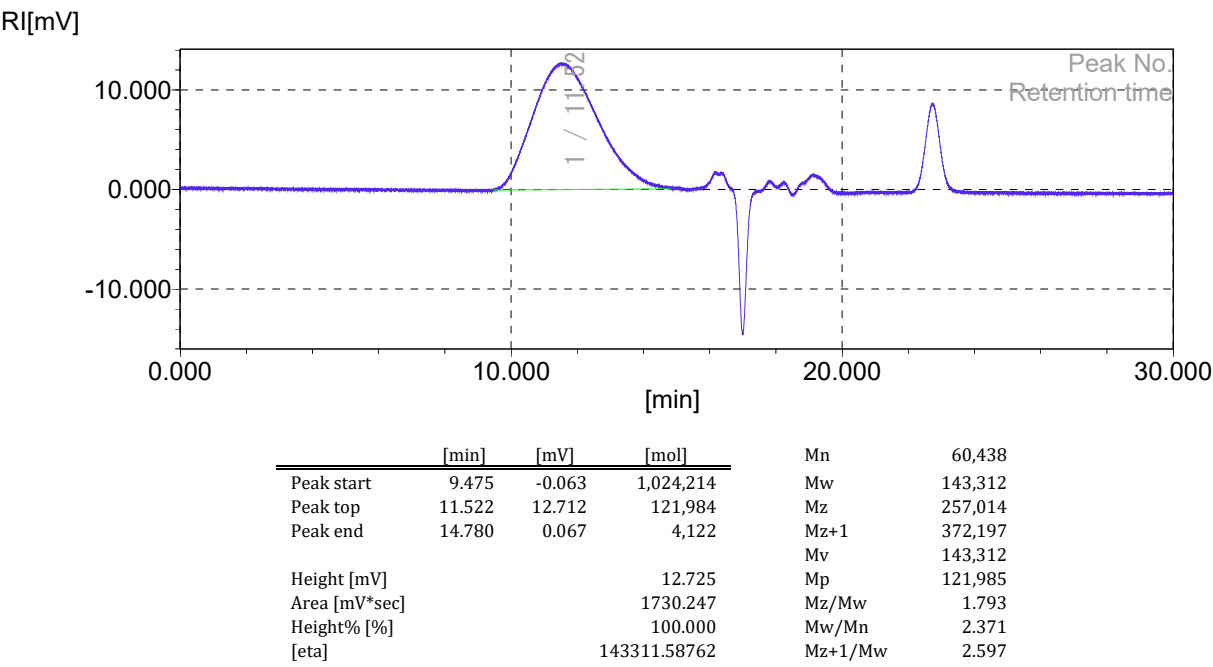


Figure S116. HT-GPC data of 9.

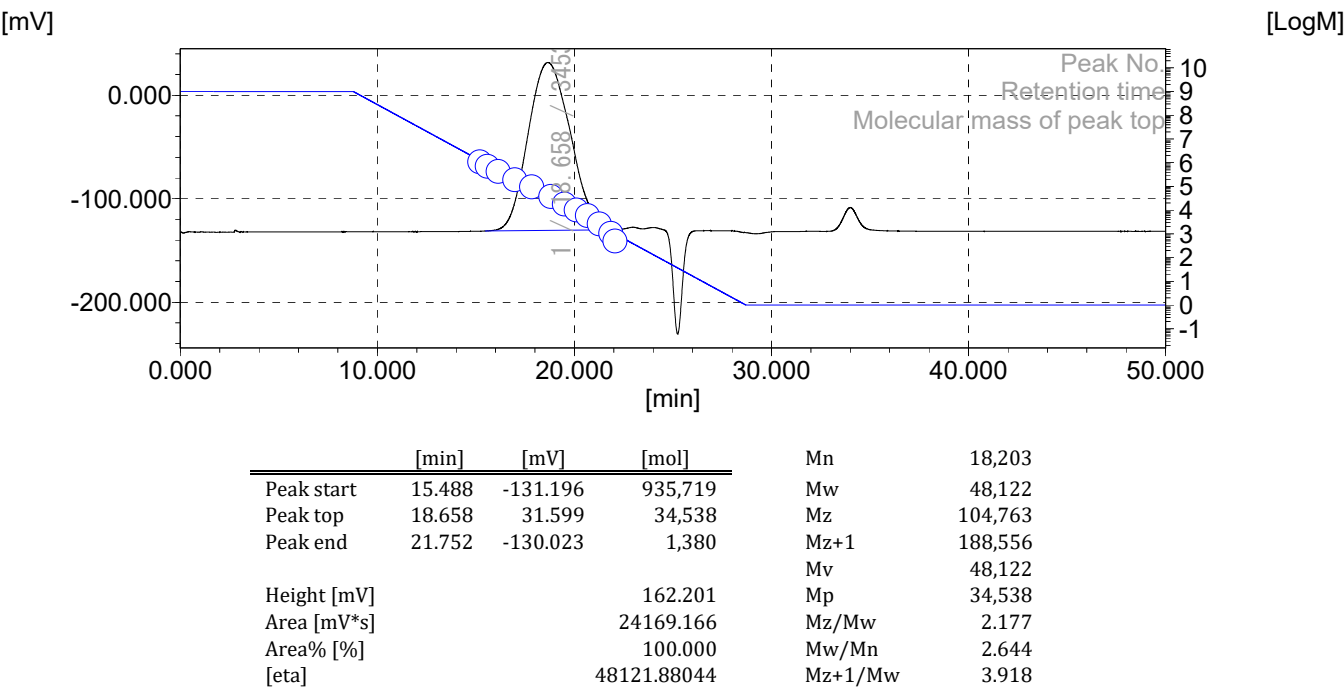
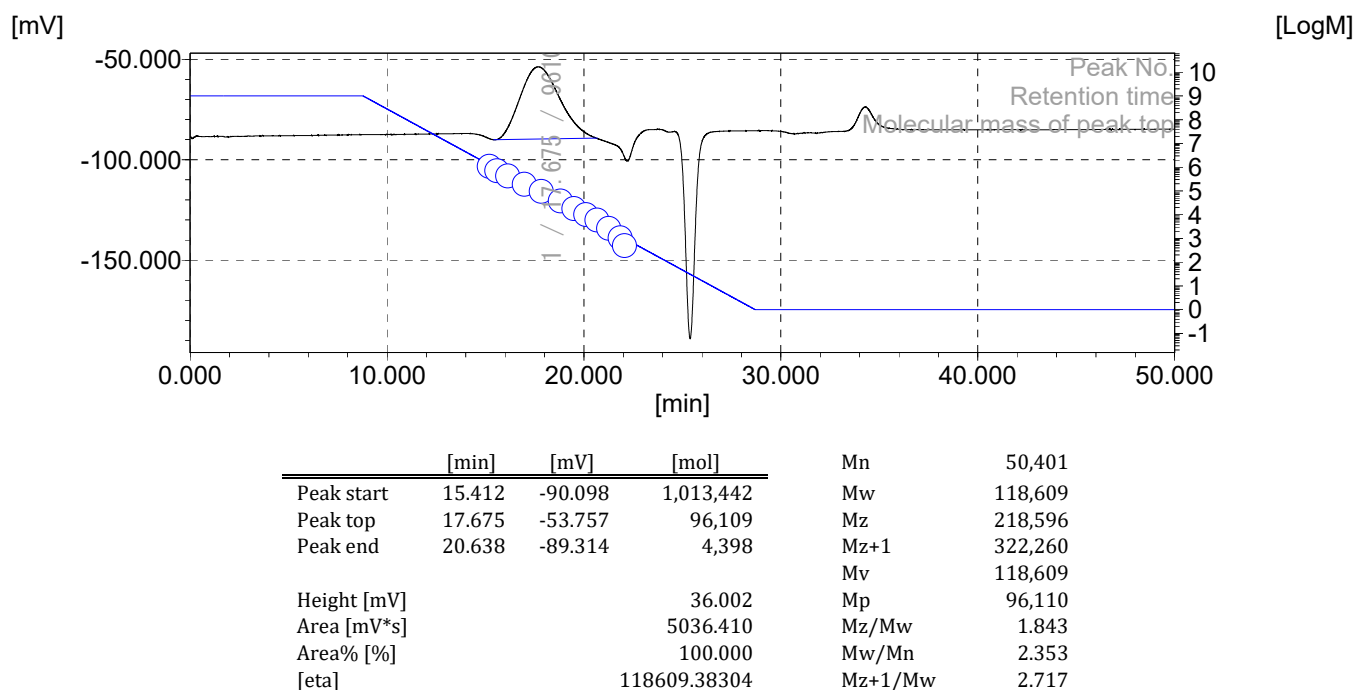
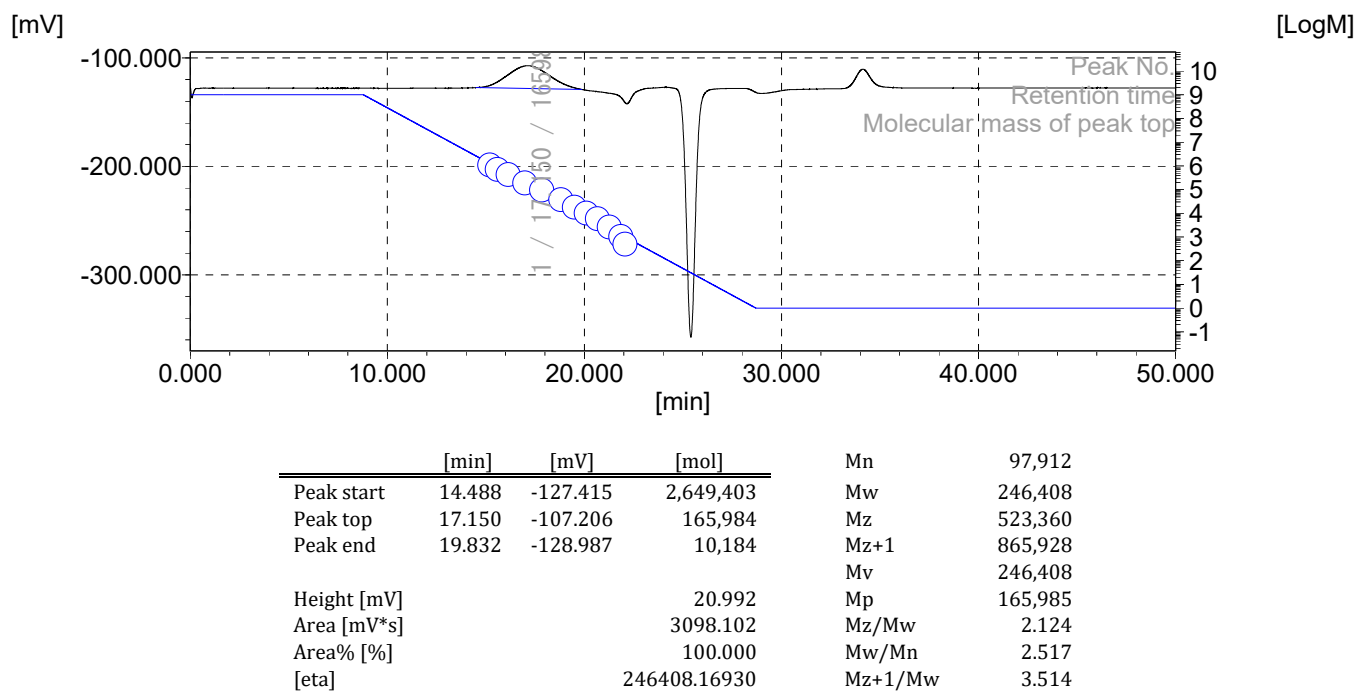
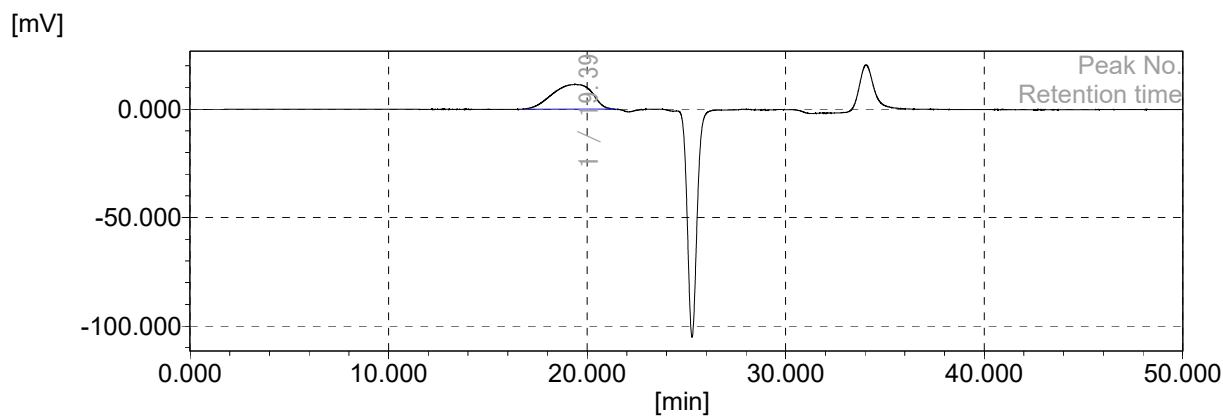
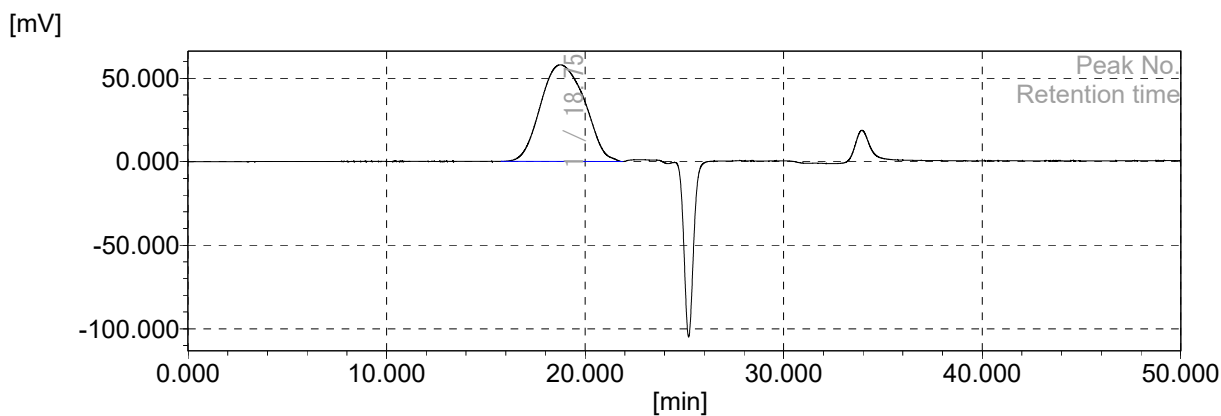


Figure S117. HT-GPC data of 10.

Figure S118. HT-GPC data of **11**.Figure S119. HT-GPC data of **12**.



	[min]	[mV]	[mol]	Mn	14,103
Peak start	16.718	-0.055	260,125	Mw	28,468
Peak top	19.397	11.360	16,016	Mz	55,281
Peak end	21.368	0.024	2,057	Mz+1	87,673
				Mv	28,468
Height [mV]			11.369	Mp	16,017
Area [mV*s]			1586.423	Mz/Mw	1.942
Area% [%]			100.000	Mw/Mn	2.019
[eta]			28468.39072	Mz+1/Mw	3.080

Figure S120. HT-GPC data of **13**.

	[min]	[mV]	[mol]	Mn	16,459
Peak start	15.757	0.228	707,714	Mw	41,822
Peak top	18.758	57.990	31,124	Mz	89,640
Peak end	21.868	0.061	1,222	Mz+1	154,303
				Mv	41,822
Height [mV]			57.844	Mp	31,124
Area [mV*s]			8929.473	Mz/Mw	2.143
Area% [%]			100.000	Mw/Mn	2.541
[eta]			41822.39767	Mz+1/Mw	3.689

Figure S121. HT-GPC data of **14**.

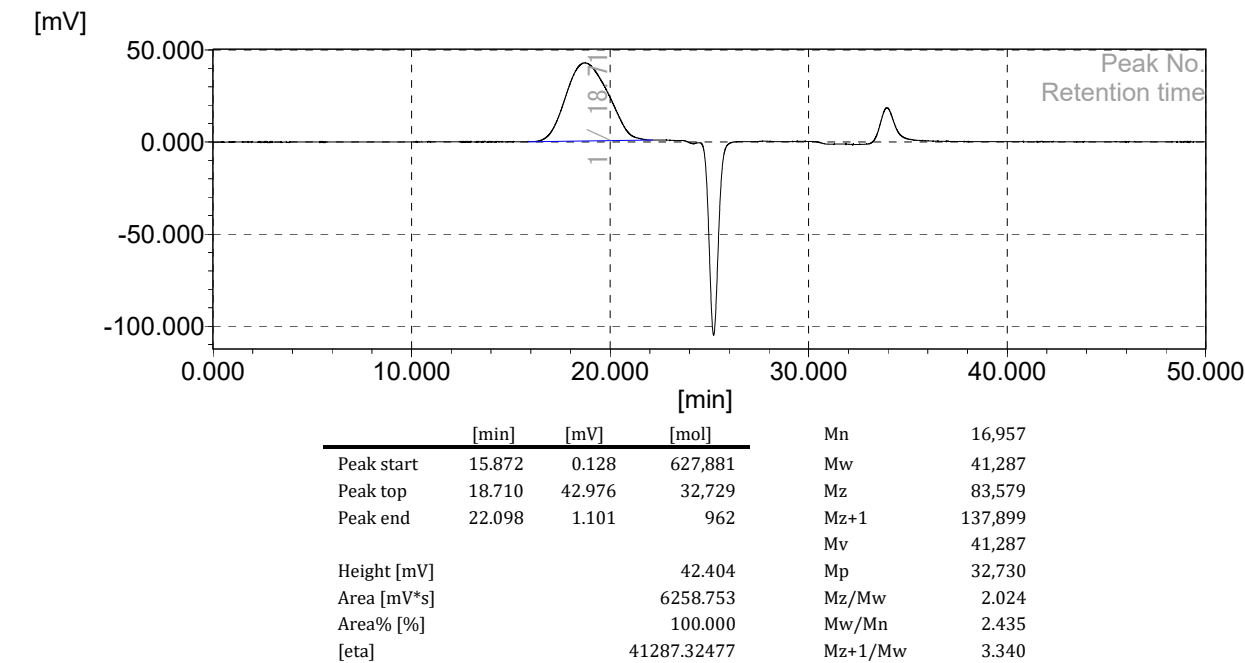


Figure S122. HT-GPC data of 15.

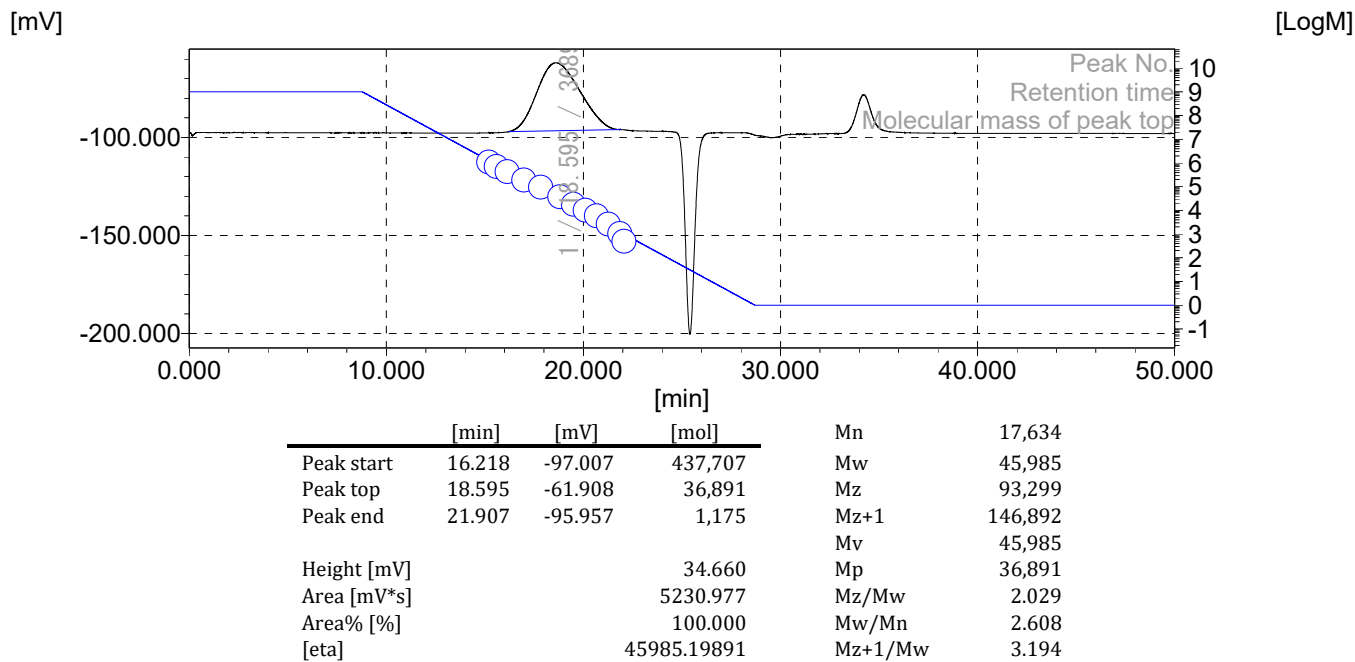
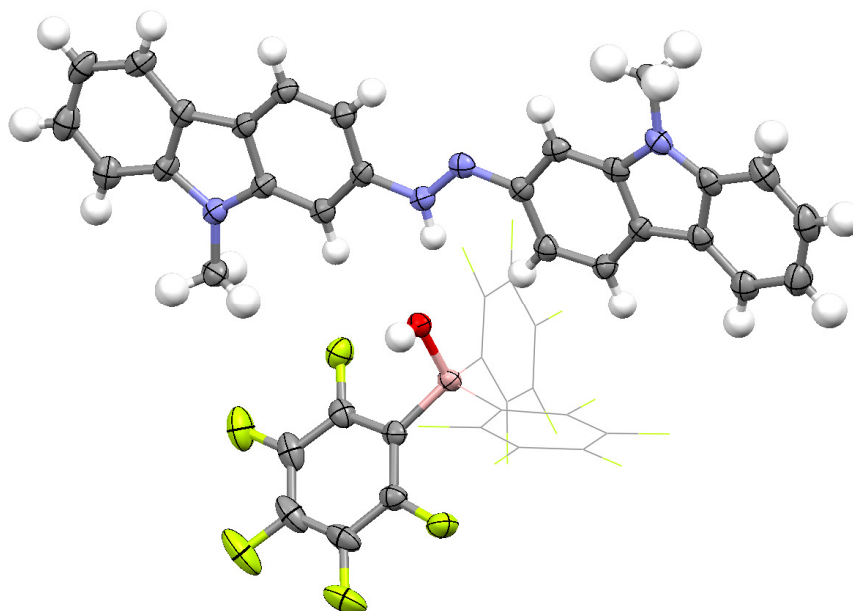


Figure S123. HT-GPC data of 16.

15. X-Ray Diffraction Data

AzoCarbazole B(C₆F₅)₃/H₂O adduct (17a)

Crystal data	
Chemical formula	2(C ₁₈ HBF ₁₅ O)·C ₂₆ H ₂₀ N ₄ ·2(C ₂₆ H ₂₁ N ₄)
<i>M</i> _r	2225.39
Crystal system, space group	Triclinic, <i>P</i> -1
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	15.0605 (16), 17.2367 (17), 20.238 (2)
α, β, γ (°)	67.095 (6), 88.512 (7), 88.113 (7)
<i>V</i> (Å ³)	4836.4 (9)
<i>Z</i>	2
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	1.16
Crystal size (mm)	0.19 × 0.14 × 0.05
Data collection	
Diffractometer	Bruker AXS D8 Quest diffractometer with PhotonIII_C14 charge-integrating and photon counting pixel array detector
Absorption correction	Multi-scan, TWINABS 2012/1: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D. (2015). <i>J. Appl. Cryst.</i> 48 3-10.
<i>T</i> _{min} , <i>T</i> _{max}	0.589, 0.754
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	70344, 19498, 16118
<i>R</i> _{int}	0.065

$(\sin \theta/\lambda)_{\max} (\text{\AA}^{-1})$	0.641
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.063, 0.173, 1.05
No. of reflections	19498
No. of parameters	1451
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}, \Delta\rho_{\min} (\text{e \AA}^{-3})$	0.49, -0.31

Structure Solution and Refinement. The crystals under investigation were multi-component with multiple domains. Most crystals screened did not diffract to sufficient resolution. The crystal chosen for data collection featured one dominant major domain with sufficient medium and high angle data for collection of acceptable resolution data, and several smaller domains. Transformation matrices identified using the program Cell_Now were ambiguous, suggesting that minor domains were not related to the major domain by a typical twin relationship. Analysis of data using only the major domain did however indicate presence of twinning, with apparent difference densities of one to two electrons per cubic Angstrom in positions incompatible with disorder, ill-defined ADPs, and higher than expected R values. Application of the Cell_Now suggested transformation matrices and integration of the data as two component did not result in reduction of these effects. The possibility of twinning was instead investigated using the program Rotax (Cooper et al., 2001) as embedded in WinGX (Farrugia, 2012), which identified the most likely type of twinning present to be a 180 degree rotation around the reciprocal $[1\ 0\ 0]$ reciprocal lattice direction, with a twin transformation matrix of $1\ -0.047\ -0.023, 0\ -1\ 0, 0\ 0\ -1$. Application of the approximate matrix $1\ 0\ 0, 0\ -1\ 0, 0\ 0\ -1$ using a TWIN command in Shelx resulted in some reduction of effects from twinning. The exact twinning matrix as obtained from Rotax was applied to the major component and the data were subsequently integrated using SAINT using both components and corrected for absorption using twinabs, resulting in the following statistics:

41682 data (13063 unique) involve domain 1 only, mean I/sigma 11.1
 41549 data (13057 unique) involve domain 2 only, mean I/sigma 7.9
 28815 data (11803 unique) involve 2 domains, mean I/sigma 18.2
 23 data (23 unique) involve 3 domains, mean I/sigma 23.2

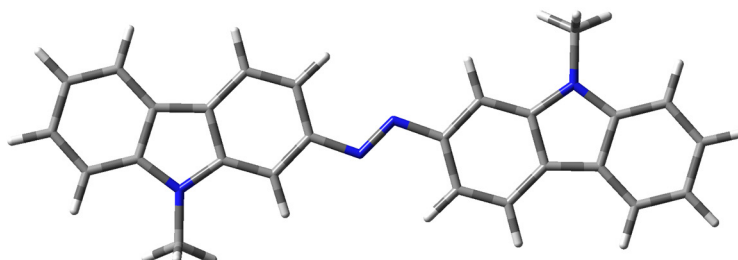
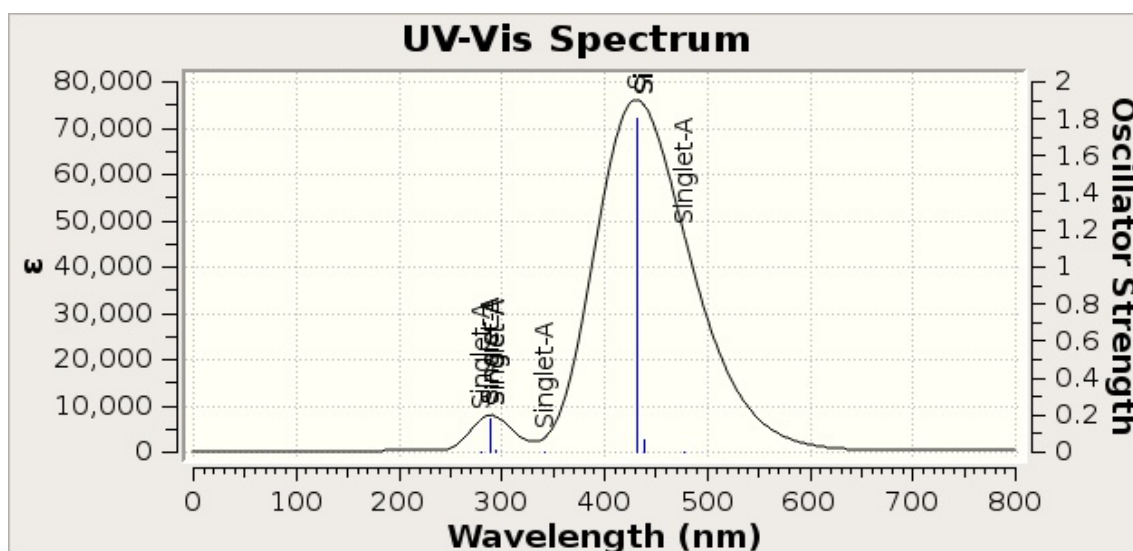
The exact twin matrix identified by the integration program was found to be:

1.00082 -0.03854 -0.01864
 0.02951 -0.99920 -0.00326
 0.02744 0.00358 -1.00161

The Rint value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Sheldrick, 2012)).

16. DFT Calculations and Optimized Structures

Computational Methods. Geometry optimizations were performed using the Gaussian16 software package.²⁰ All geometries were fully optimized at the B3LYP/6-31G(d,p) level of DFT. A polarizable continuum model (PCM) was used to apply solvent corrections for all compounds in C₆H₅Cl.



TD State	Wavelength (nm)	Oscillator Strength	ϵ
1	479.66	0.00080	2673
2	437.44	0.076	253888
3	436.62	0	0
4	433.17	1.8321	6120375
5	341.12	0	0
6	294.32	0	0
7	292.98	0.0090	30066
8	289.12	0.1796	599978
9	288.60	0	0

10	279.95	0	0
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Functional and Basis Set: B3LYP/6-31G(d,p)

Charge: 0

Multiplicity: 1

Imaginary Frequencies: 0

Sum of electronic and thermal Free Energies: -1221.527517 Hartrees

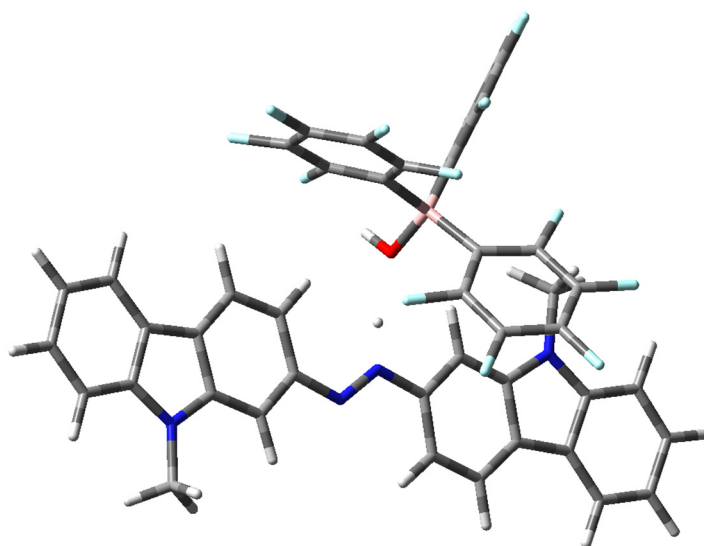
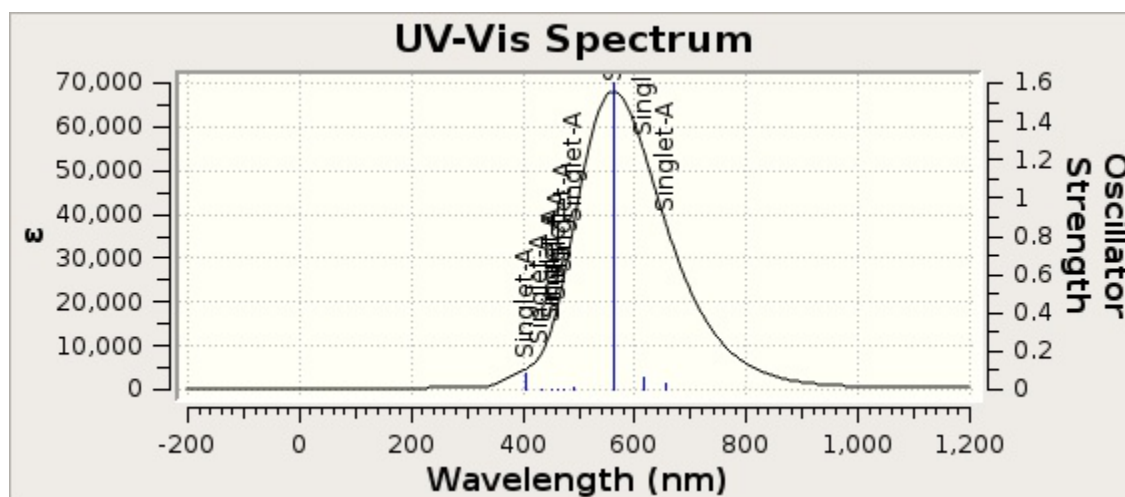
Cartesian Coordinates:

C	5.91622800	-0.78649700	0.01062200
C	4.47352500	-0.76159500	0.00173500
C	4.09130800	0.60849000	-0.02312300
C	2.74985200	0.98806200	-0.02282100
C	3.48023500	-1.75533800	0.01352600
C	1.77721500	-0.02054700	-0.01059900
C	2.14470600	-1.38921000	0.00672400
H	3.75872400	-2.80519100	0.03054100
H	1.35902400	-2.13435200	0.01766800
H	2.42845900	2.02348000	-0.02735800
N	0.44428900	0.45049200	-0.01176500
C	-2.14470600	1.38921000	0.00671300
C	-3.48023500	1.75533800	0.01351500
C	-1.77721500	0.02054700	-0.01059400
C	-4.47352500	0.76159500	0.00173900
H	-3.75872400	2.80519100	0.03051900
C	-2.74985300	-0.98806300	-0.02280200
C	-4.09130800	-0.60849000	-0.02310500
H	-2.42845900	-2.02348000	-0.02732800
C	-6.34436600	-0.57089800	-0.00966200

C	-5.91622800	0.78649700	0.01063000
C	-7.70250000	-0.90892000	0.00618300
C	-6.87055300	1.81299600	0.03502700
C	-8.62789000	0.13174800	0.03056600
H	-8.03081400	-1.94292800	0.00519900
C	-8.22114700	1.47958500	0.04397100
H	-6.55829500	2.85333400	0.04941400
H	-9.68780300	-0.10453900	0.04315300
H	-8.97126700	2.26398400	0.06430700
C	6.34436600	0.57089800	-0.00968700
C	7.70250000	0.90892000	0.00615100
C	6.87055300	-1.81299600	0.03502800
C	8.62789000	-0.13174700	0.03054300
H	8.03081400	1.94292800	0.00515400
C	8.22114700	-1.47958400	0.04396400
H	6.55829500	-2.85333400	0.04942700
H	9.68780300	0.10453900	0.04312400
H	8.97126800	-2.26398300	0.06430700
C	-5.25943000	-2.85003200	-0.02703200
H	-6.12475800	-3.20824600	-0.58854500
H	-4.36174800	-3.23854000	-0.51091400
H	-5.31081800	-3.24517200	0.99411300
C	5.25943000	2.85003100	-0.02707900
H	5.31082000	3.24518300	0.99406200
H	6.12475700	3.20823900	-0.58859900
H	4.36174700	3.23853500	-0.51096300
N	-5.23210800	-1.39973200	-0.04648900
N	5.23210800	1.39973200	-0.04652000

N -0.44428900 -0.45049200 -0.01175900

H -1.35902400 2.13435300 0.01764700



TD State	Wavelength (nm)	Oscillator Strength	ϵ
1	657.02	0.033	216835
2	614.90	0.061	396986
3	561.60	1.60	10453955
4	489.95	0.012	79266
5	472.62	0.00020	1310
6	461.18	0.0021	13756.93
7	452.21	0.00050	3275

8	450.62	0.0028	18343
9	432.02	0.00020	1310
10	406.70	0.082	537175

Functional and Basis Set: B3LYP/6-31G(d,p)

Charge: 0

Multiplicity: 1

Imaginary Frequencies: 0

Sum of electronic and thermal Free Energies: -3506.094310

Cartesian Coordinates:

C	-5.12884800	4.06127200	-0.56282600
C	-3.70408300	3.86734500	-0.57776100
C	-3.48828100	2.48756700	-0.86056800
C	-2.21257800	1.94287600	-0.93330700
C	-2.59637200	4.70865100	-0.37334300
C	-1.13408200	2.81362800	-0.70964800
C	-1.31519100	4.18958100	-0.43654000
H	-2.74186100	5.76239100	-0.15665100
H	-0.44650300	4.81327100	-0.27113400
H	-2.02827000	0.89818000	-1.15158400
N	0.14637200	2.23689100	-0.76967600
C	2.73375700	1.02955600	-1.10898100
C	4.04034900	0.59466500	-1.20038300
C	2.44913000	2.37775200	-0.74752700
C	5.09227800	1.48598800	-0.92311700
H	4.24695900	-0.43299400	-1.48115200
C	3.49483300	3.29443100	-0.48677800

C	4.80013300	2.83895800	-0.57256800
H	3.23489400	4.31123200	-0.21717600
C	7.04225200	2.63194500	-0.54960400
C	6.52111900	1.35608400	-0.90807100
C	8.41935700	2.84767000	-0.42702300
C	7.39773500	0.28763600	-1.15536400
C	9.26320100	1.77118300	-0.67983400
H	8.82259000	3.81241700	-0.13862800
C	8.76332300	0.50340600	-1.04072000
H	7.00970700	-0.69004400	-1.42461400
H	10.33627400	1.91134500	-0.59100900
H	9.45705700	-0.31023400	-1.22489200
C	-5.71383600	2.78939800	-0.83048400
C	-7.10300700	2.62204800	-0.86762300
C	-5.95460900	5.17464400	-0.34534900
C	-7.89483000	3.74367000	-0.64771100
H	-7.55477600	1.65384800	-1.05380900
C	-7.33183000	5.00966400	-0.39040800
H	-5.52084400	6.14917800	-0.14136300
H	-8.97532200	3.63859600	-0.67116600
H	-7.98491900	5.85993200	-0.22247700
C	6.11775600	4.90009500	0.05831700
H	7.03026200	5.33078400	-0.35947700
H	5.27280400	5.47851100	-0.32058500
H	6.14921600	4.99152300	1.15048300
C	-4.88108000	0.42592400	-1.23883600

H	-4.78176000	-0.13742000	-0.30496300
H	-5.86765400	0.24360200	-1.66645200
H	-4.13305500	0.06089800	-1.94604600
N	5.99272400	3.52045000	-0.36796900
N	-4.70780500	1.85477000	-1.02597000
N	1.19789700	2.94707900	-0.64714100
H	1.93166800	0.33383300	-1.31039500
H	0.15068100	1.17464100	-0.87811600
B	-0.45082100	-1.52344700	-0.03389400
C	0.99759500	-2.26513700	0.32224700
C	1.38255400	-2.72936400	1.58328700
C	1.97081500	-2.43688600	-0.66109600
C	2.62863400	-3.29183300	1.85728900
C	3.23674000	-2.96766800	-0.43378900
C	3.57263300	-3.40303800	0.84188700
C	-1.47854200	-2.64936900	-0.68664800
C	-2.20133300	-2.48176000	-1.86884000
C	-1.69572800	-3.88519700	-0.06760100
C	-3.05262500	-3.44175900	-2.41374200
C	-2.52989300	-4.87884800	-0.57190700
C	-3.21548200	-4.65744200	-1.76233500
C	-1.07871300	-0.72989600	1.27193500
C	-0.28725200	0.18819100	1.96846000
C	-2.39153600	-0.81055800	1.73668700
C	-0.72736300	0.94879200	3.04635600
C	-2.88337600	-0.06774300	2.81077500

C	-2.04351900	0.81440700	3.47818800
O	-0.19141700	-0.41860000	-1.03219800
H	-0.02352400	-0.79143200	-1.90499900
F	4.78578500	-3.91548600	1.08896300
F	2.93346600	-3.71020200	3.09460400
F	4.14835100	-3.01414000	-1.42724600
F	1.73609100	-2.03671100	-1.94655300
F	0.54427800	-2.63764900	2.63359700
F	0.99739400	0.39808400	1.58333900
F	0.09532500	1.81124000	3.66410800
F	-2.49674600	1.53887500	4.50898600
F	-4.16480700	-0.18944200	3.19107300
F	-3.30529400	-1.60774600	1.13116700
F	-1.09856500	-4.16120300	1.10953500
F	-2.68554700	-6.04010700	0.07993800
F	-4.02588700	-5.59678600	-2.26649400
F	-3.71645200	-3.19599700	-3.55563300
F	-2.13447500	-1.31756500	-2.58072300

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