

Supplementary Data for:

P(III)-Cyclic Oligomers *via* Catalytic Hydrophosphination

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General considerations

All manipulations of air- and/or water-sensitive compounds were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques or a Vacuum Atmospheres inert atmosphere glovebox. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were acquired on a Bruker Avance 300 MHz spectrometer or a Varian Mercury 300 MHz spectrometer. ^1H resonances were referenced internally to the residual protonated solvent resonances. ^{13}C resonances were referenced internally to the deuterated solvent resonances. ^{31}P resonances were referenced externally to H_3PO_4 . Mass spectra were recorded with a VG 70-250S mass spectrometer in positive ion electron impact (EI) mode. Calculated isotopic distribution for each ion matched with experimental values. Infrared spectra were recorded using a Perkin-Elmer Spectrum One FT-IR spectrometer at 25 °C, either as a nujol mull or deposited onto the NaCl plate from a CH_2Cl_2 or C_6D_6 solution. Elemental analyses were performed using a Perkin-Elmer 2400 C/H/N analyzer. Absorbance UV-vis/near-IR spectra were obtained for THF solutions of the analyte on a Perkin-Elmer Lambda 900 spectrometer. Matrix-assisted laser desorption/ionization – time-of-flight (MALDI-TOF) mass spectra were acquired using a Waters Micromass MALDI micro MX. Spectra were acquired using the following conditions: positive polarity mode, reflectron flight path, 12 kV flight tube voltage, 10 Hz laser firing rate, 10 shots per spectrum, pulse 1950 V, detector 2350 V. The instrument was calibrated using polyethyleneglycol (PEG). For polymer **7**, the matrix solution consisted of 6 mg α -cyano-4-hydroxycinnamic acid (CHCA) in 1 mL of a 6 : 3 : 1 mixture of CH_3CN : CH_3OH : H_2O plus one drop of CF_3COOH . The analyte solution consisted of 3 mg/mL polymer **7** in THF. The sample was prepared using the layer method,¹ by spotting 1 μL of matrix onto the sample plate followed by 1 μL of the analyte. For polymer **8**, the matrix solution consisted of 20 mg pyrene in 1 mL THF plus one drop of CF_3COOH . The analyte solution consisted of 1 mg/mL polymer **8** in THF. The two solutions were mixed in a 9 : 1 ratio of matrix : analyte, and 1.5 μL of the resultant solution was spotted onto the sample plate.¹ Polymer molecular weights were determined by gel permeation chromatography (GPC) using one of two instruments. Absolute and relative molecular weights were determined by triple detection GPC using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6x300 mm), HR2 x 2 and HR4, Waters 2410 differential refractometer (refractive index detector, $\lambda = 940$ nm), Wyatt tristar miniDAWN (laser light scattering detector, $\lambda = 690$ nm) and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL/min was used and samples were dissolved in THF (ca. 2 mg/mL), and prepared in air. Relative molecular weights were determined using a Waters liquid chromatograph equipped with a Waters 1515 HPLC pump, Waters Styragel columns (4.6x300 mm), HR 4E x 3, Waters 2414 differential refractometer (refractive index detector, $\lambda = 880$ nm). A flow rate of 1.0 mL/min was used and samples were dissolved in THF (ca. 2 mg/mL) and prepared in air. Polystyrene standards were purchased from Polymer Laboratories, with molecular weights varying between 580 and 283 300 g mol^{-1} .

Materials

Anhydrous solvents including toluene, pentane, hexanes, ether, tetrahydrofuran, and dichloromethane were purchased from Aldrich and purified using Grubbs' column systems manufactured by Innovative Technology. C_6D_6 and THF- d_8 were purchased from Cambridge Isotopes Laboratories, vacuum distilled from Na/benzophenone, and freeze-pump-thaw degassed (x 3). Diethylamine was purchased from Aldrich and degassed by sonication or sparging with N_2 prior to use. Hyflo Super Cel® (Celite) was purchased from Aldrich and dried for at least 12 h in a vacuum oven prior to use. 4 Å molecular sieves were purchased from Aldrich and dried at 100 °C under vacuum using a Schlenk line. Phenylacetylene was purchased from Aldrich, vacuum distilled from CaH_2 , and stored in the dark at -35 °C. nBuLi (1.6 M in hexanes) and tBuLi (1.7 M in pentane) were purchased from Aldrich. nBuLi was titrated prior to use to determine its concentration.² CuI , $CuCl$, $HCl_{(g)}$, $LiAlH_4$, $MgSO_4$ and $BrCH_2CH(CH_3)_2$ were purchased from Aldrich and used as received. *trans*- $Pd(PPh_3)_2Cl_2$ was purchased from Strem and used as received. 1-bromo-2,6-diisopropyl-4-iodobenzene,³ and $CIP(NEt_2)_2$ ⁴ were synthesized according to literature procedures.

Synthesis of compound 1

To a solution of 1-bromo-2,6-diisopropyl-4-iodobenzene (4.440 g, 12.10 mmol) in 100 mL $HNEt_2$ was added 2.5 mol % *trans*- $Pd(PPh_3)_2Cl_2$ (211 mg, 0.301 mmol) and 1 mol % CuI (24 mg, 0.13 mmol). The yellow mixture was stirred and 1.3 equiv. $HC\equiv CPh$ (1.602 g, 15.68 mmol) was added by syringe. The mixture was allowed to stir at room temperature overnight, the solvent was removed *in vacuo*, and the residue extracted with Et_2O . Filtration through celite followed by removal of Et_2O *in vacuo* resulted in a brown oil that crystallized upon standing.

Yield: 4.028 (97.6 %) 1H NMR (C_6D_6 , 25 °C, 300 MHz) δ : 7.58–7.54 (m, 2H, *o*- C_6H_5), 7.46 (s, 2H, C_6H_2), 7.02–6.99 (m, 3H, *m*- and *p*- C_6H_5), 3.50 (septet, 2H, $CH(CH_3)_2$, $^3J_{H-H} = 7$ Hz), 1.07 (d, 12H, $CH(CH_3)_2$, $^3J_{H-H} = 7$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6 , 25 °C, 75.5 MHz) δ : 148.6 (s, *ipso*-C), 131.9 (s, Ar), 128.8 (s, Ar), 128.6 (s, Ar), 127.4 (s, Ar), 123.8 (s, Ar), 123.3 (s, Ar), 90.2 (s, $C\equiv C$), 90.1 (s, $C\equiv C$), 33.9 (s, $CH(CH_3)_2$), 22.8 (s, $CH(CH_3)_2$). EI-MS (*m/z*): 342.1 and 340.1 (100 %, 99 %) $[M]^+$; 327.1 and 325.1 (48 %, 52 %) $[M]^+ - Me$. HRMS: $C_{20}H_{21}^{79}Br$ mass 340.0829, calc'd mass 340.0827, fit 0.6 ppm. FT-IR (25 °C, nujol mull): $\nu(C\equiv C)$ 2210 cm^{-1} (weak). Anal. Calc'd for $C_{20}H_{21}Br$: C, 70.39; H, 6.20. Found: C, 70.31; H, 6.17.

Synthesis of compound 2

A dark red solution of **1** (6.154 g, 18.03 mmol) in 300 mL THF was cooled to -78 °C, and 1.9 equiv. tBuLi (1.7 M in pentane, 20.2 mL, 34.34 mmol) was added via syringe over ca. 30 min to give a dark brown mixture. The mixture was stirred at -78 °C for 3 h, then the cold bath was removed and the dark purple mixture was stirred at room temperature for 1 h. $CuCl$ (2.142 g, 21.64 mmol, 1.2 equiv.) was added at room temperature, then the mixture was cooled again to -78 °C, whereupon $CIP(NEt_2)_2$ was added (3.80 g, 18.0 mmol) via syringe over ca. 15 min. The mixture was stirred overnight while warming to room temperature. All volatile material was removed *in vacuo* to give a green-brown residue, which was extracted with 100 mL toluene, filtered through celite, and evacuated once again. Addition of 50 mL toluene resulted in the formation of a beige precipitate, which was isolated and dried on a frit. An

additional crop was isolated from the filtrate by removing the toluene *in vacuo*, adding 20 mL pentane, and isolating the beige solid.

Yield: 7.895 g (76.3 %) ^1H NMR (C_6D_6 , 25 °C, 300 MHz) δ : 7.65–7.64 (m, 2H, C_6H_2), 7.60–7.57 (m, 2H, *o*- C_6H_5), 7.01–6.98 (m, 3H, *m*- and *p*- C_6H_5), 4.30–4.24 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.15–2.95 (m, 8H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 1.31 (d, 12H, $\text{CH}(\text{CH}_3)_2$, $^3\text{J}_{\text{H-H}} = 7$ Hz), 1.01 (t, 12H, $\text{N}(\text{CH}_2\text{CH}_3)_2$, $^3\text{J}_{\text{H-H}} = 7$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C, 121.5 MHz) δ : 88.9. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C, 75.5 MHz) δ : 153.3 (d, *ipso*-C, $^1\text{J}_{\text{P-C}} = 12$ Hz), 132.0 (s, Ar), 131.6 (s, Ar), 128.7 (s, Ar), 128.5 (s, Ar), 127.2 (s, Ar), 125.3 (s, Ar), 124.0 (s, Ar), 91.0 (s, $\text{C}\equiv\text{C}$), 90.4 (s, $\text{C}\equiv\text{C}$), 43.4 (d, $\text{P}(\text{N}(\text{CH}_2\text{CH}_3)_2)_2$, $^2\text{J}_{\text{P-C}} = 12$ Hz), 30.2 (s, $\text{CH}(\text{CH}_3)_2$), 28.4 (d, $\text{P}(\text{N}(\text{CH}_2\text{CH}_3)_2)_2$, $^3\text{J}_{\text{P-C}} = 13$ Hz), 25.8 (s, $\text{CH}(\text{CH}_3)_2$). EI-MS (*m/z*): 436.3 (7 %) $[\text{M}]^+ - \text{CuBr}$; 364.2 (100 %) $[\text{M}]^+ - \text{CuBr} - \text{NEt}_2$; 292.1 (28 %) $[\text{M}]^+ - \text{CuBr} - 2\text{NEt}_2$; 175.1 (37 %) $[\text{P}(\text{NEt}_2)_2]^+$. HRMS: $\text{C}_{28}\text{H}_{41}\text{N}_2\text{P}$ mass 436.3010, calc'd mass 436.3007, fit 0.7 ppm. FT-IR (25 °C, nujol mull): $\nu(\text{C}\equiv\text{C})$ 2209 cm^{-1} (weak). Anal. Calc'd for $\text{C}_{28}\text{H}_{41}\text{BrCuN}_2\text{P}$: C, 57.98; H, 7.12; N, 4.83. Found: C, 58.35; H, 7.08; N, 5.24.

Synthesis of compound 3

A yellow solution of **2** (9.161 g, 15.79 mmol) in 150 mL toluene was cooled in an ice-water bath, and $\text{HCl}_{(\text{g})}$ was bubbled through the solution for 15 to 20 min., during which time a fine white precipitate was generated. The yellow solution was filtered through a Schlenk frit containing celite, 75 mL toluene was added to the original flask, and the suspension was bubbled with $\text{HCl}_{(\text{g})}$ for a further 3 min. This solution was also filtered through the Schlenk frit, and the precipitate was washed with a further 50 mL toluene. All toluene extracts were combined and all volatiles were removed *in vacuo* to give a yellow solid.

Yield: 5.218 g (89.4 %) ^1H NMR (C_6D_6 , 25 °C, 300 MHz) δ : 7.56–7.52 (m, 4H, *o*- C_6H_5 and C_6H_2), 6.99–6.97 (m, 3H, *m*- and *p*- C_6H_5), 4.12–4.06 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 1.12 (d, 12H, $\text{CH}(\text{CH}_3)_2$, $^3\text{J}_{\text{H-H}} = 7$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C, 121.5 MHz) δ : 162.7. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C, 75.5 MHz, partial) δ : 155.1 (d, *ipso*-C, $^1\text{J}_{\text{P-C}} = 23$ Hz), 135.6 (s, Ar), 134.6 (s, Ar), 132.1 (s, Ar), 129.1 (s, Ar), 128.8 (s, Ar), 123.2 (s, Ar), 92.6 (s, $\text{C}\equiv\text{C}$), 89.6 (s, $\text{C}\equiv\text{C}$), 30.9 (d, $\text{CH}(\text{CH}_3)_2$, $^3\text{J}_{\text{P-C}} = 27$ Hz), 24.4 (s, $\text{CH}(\text{CH}_3)_2$). EI-MS (*m/z*): 362.1 (27 %) $[\text{M}]^+$; 327.1 (100 %) $[\text{M}]^+ - \text{Cl}$. HRMS: $\text{C}_{20}\text{H}_{21}\text{Cl}_2\text{P}$ mass 362.0753, calc'd mass 362.0758, fit -1.4 ppm. FT-IR (25 °C, nujol mull): $\nu(\text{C}\equiv\text{C})$ 2209 cm^{-1} (s). Anal. Calc'd for $\text{C}_{20}\text{H}_{21}\text{Cl}_2\text{P}$: C, 66.13; H, 5.83. Found: C, 66.32; H, 5.90.

Synthesis of compound 4

An orange solution of **3** (1.760 g, 4.845 mmol) in 20 mL Et_2O and 20 mL toluene was added dropwise via cannula over 30 min. to a -78 °C slurry of LiAlH_4 (1.014 g, 26.72 mmol, 5.5 equiv.) in 70 mL Et_2O . The mixture was stirred overnight while warming to room temperature. The brown mixture was cooled again in an ice-water bath, and 10 mL degassed water was added dropwise with much bubbling. The organic layer was transferred by cannula to a flask containing MgSO_4 . The aqueous layer was washed with two portions of 20 mL Et_2O and all organic portions were combined in the flask containing MgSO_4 . The yellow solution was then cannula transferred to a Schlenk frit and filtered. Upon removal of all volatiles *in vacuo*, a yellow residue was obtained. Crystals suitable for X-ray diffraction were obtained upon standing.

Yield: 1.003 g (70.3 %) ^1H NMR (C_6D_6 , 25 °C, 300 MHz) δ : 7.60–7.57 (m, 2H, *o*- C_6H_5), 7.54 (d, 2H, C_6H_2 , $^4\text{J}_{\text{P-H}} = 2$ Hz), 7.00–6.89 (m, 3H, *m*- and *p*- C_6H_5), 3.77 (d, 2H, PH_2 , $^1\text{J}_{\text{P-H}} = 206$ Hz), 3.23 (d of septets, 2H, $\text{CH}(\text{CH}_3)_2$, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^4\text{J}_{\text{P-H}} = 3$ Hz), 1.08 (d, 12H, $\text{CH}(\text{CH}_3)_2$, $^3\text{J}_{\text{H-H}} = 7$ Hz). ^{31}P NMR (C_6D_6 , 25 °C, 121.5 MHz) δ : -156.3 (t, $^1\text{J}_{\text{P-H}} = 207$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C, 75.5 MHz, partial) δ : 152.2 (d, *ipso*-C, $^1\text{J}_{\text{P-C}} = 9$ Hz), 152.3 (d, *ipso*-C, $^1\text{J}_{\text{P-C}} = 10$ Hz), 132.0 (s, Ar), 128.7 (s, Ar), 126.5 (s, Ar), 124.1 (s, Ar), 123.9 (s, Ar), 90.9 (s, $\text{C}\equiv\text{C}$), 90.3 (s, $\text{C}\equiv\text{C}$), 33.1 (d, $\text{CH}(\text{CH}_3)_2$, $^3\text{J}_{\text{P-C}} = 11$ Hz), 23.4 (s, $\text{CH}(\text{CH}_3)_2$). EI-MS (*m/z*): 294.2 (100 %) $[\text{M}]^+$; 251.1 (83 %) $[\text{M}]^+ - \text{CH}(\text{CH}_3)_2$. HRMS: $\text{C}_{20}\text{H}_{23}\text{P}$ mass 294.1542, calc'd mass 294.1537, fit 1.74 ppm. FT-IR (25 °C, nujol mull): $\nu(\text{C}\equiv\text{C})$ 2315 cm^{-1} (br). Anal. Calc'd for $\text{C}_{20}\text{H}_{23}\text{P}$: C, 81.60; H, 7.88. Found: C, 81.10; H, 8.12.

Synthesis of compound 5

Compound 4 (190 mg, 0.645 mmol) and 6 mL hexanes were placed in a 20 mL scintillation vial inside a brass plate designed to surround the bottom and walls of the vial, and the entire assembly was cooled to -35 °C. Freshly titrated $n\text{BuLi}$ in hexanes (0.41 mL of 1.578 mol/L, 0.647 mmol, 1.00 equiv.) was added to the yellow stirred solution to generate an orange solution that became opaque after ca. 5 min. The entire assembly was warmed to room temperature over 4 hours, then $\text{BrCH}_2\text{CH}(\text{CH}_3)_2$ was added dropwise (88 mg, 0.64 mmol, 1.0 equiv.), as well as 4 mL toluene, and the reaction mixture was stirred overnight. The orange-brown mixture was filtered through celite, and all volatiles were removed *in vacuo* to give a brown oil.

Yield: 179 mg (79.2 %). ^1H NMR (C_6D_6 , 25 °C, 300 MHz) δ : 7.62–7.57 (m, 4H, *o*- C_6H_5 and C_6H_2), 7.03–6.97 (m, 3H, *m*- and *p*- C_6H_5), 4.36 (ddd, 1H, PH , $^1\text{J}_{\text{P-H}} = 212$ Hz, $^3\text{J}_{\text{H-H}} = 9$ Hz, $^3\text{J}_{\text{H-H}} = 6$ Hz), 3.78–3.67 (m, 2H, $\text{ArCH}(\text{CH}_3)_2$), 1.86–1.76 (m, 1H, PCH_aH_b), 1.74–1.64 (m, 1H, $\text{PCH}_2\text{CH}(\text{CH}_3)_2$), 1.49–1.37 (m, 1H, PCH_aH_b), 1.20 (d, 6H, $\text{ArCH}(\text{CH}_3)_a(\text{CH}_3)_b$, $^3\text{J}_{\text{H-H}} = 7$ Hz), 1.13 (d, 6H, $\text{ArCH}(\text{CH}_3)_a(\text{CH}_3)_b$, $^3\text{J}_{\text{H-H}} = 7$ Hz), 0.97 (d, 3H, $\text{PCH}_2\text{CH}(\text{CH}_3)_a(\text{CH}_3)_b$, $^3\text{J}_{\text{H-H}} = 4$ Hz), 0.94 (d, 3H, $\text{PCH}_2\text{CH}(\text{CH}_3)_a(\text{CH}_3)_b$, $^3\text{J}_{\text{H-H}} = 4$ Hz). ^{31}P NMR (C_6D_6 , 25 °C, 121.5 MHz) δ : -99.0 (d, $^1\text{J}_{\text{P-H}} = 212$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C, 75.5 MHz) δ : 153.5 (d, *ipso*-C, $^1\text{J}_{\text{P-C}} = 11$ Hz), 133.9 (s, Ar), 133.6 (s, Ar), 132.0 (s, Ar), 128.7 (s, Ar), 126.9 (s, Ar), 124.6 (s, Ar), 124.1 (s, Ar), 90.9 (s, $\text{C}\equiv\text{C}$), 90.4 (s, $\text{C}\equiv\text{C}$), 34.2 (d, $\text{PCH}_2\text{CH}(\text{CH}_3)_2$, $^1\text{J}_{\text{P-C}} = 13$ Hz), 33.0 (d, $\text{ArCH}(\text{CH}_3)_2$, $^3\text{J}_{\text{P-C}} = 13$ Hz), 28.4 (d, $\text{PCH}_2\text{CH}(\text{CH}_3)_2$, $^2\text{J}_{\text{P-C}} = 12$ Hz), 24.7 (s, $\text{ArCH}(\text{CH}_3)_a(\text{CH}_3)_b$), 24.3 (s, $\text{ArCH}(\text{CH}_3)_a(\text{CH}_3)_b$), 23.94 (s, $\text{PCH}_2\text{CH}(\text{CH}_3)_a(\text{CH}_3)_b$), 23.86 (s, $\text{PCH}_2\text{CH}(\text{CH}_3)_a(\text{CH}_3)_b$). EI-MS (*m/z*): 350.2 (37 %) $[\text{M}]^+$; 293.1 (100 %) $[\text{M}]^+ - \text{CH}_2\text{CH}(\text{CH}_3)_2$. HRMS: $\text{C}_{24}\text{H}_{31}\text{P}$ mass 350.2164, calc'd mass 350.2163, fit 0.3 ppm. FT-IR (25 °C, nujol mull): $\nu(\text{C}\equiv\text{C})$ 2320 cm^{-1} (br). Suitable elemental analysis data could not be obtained.

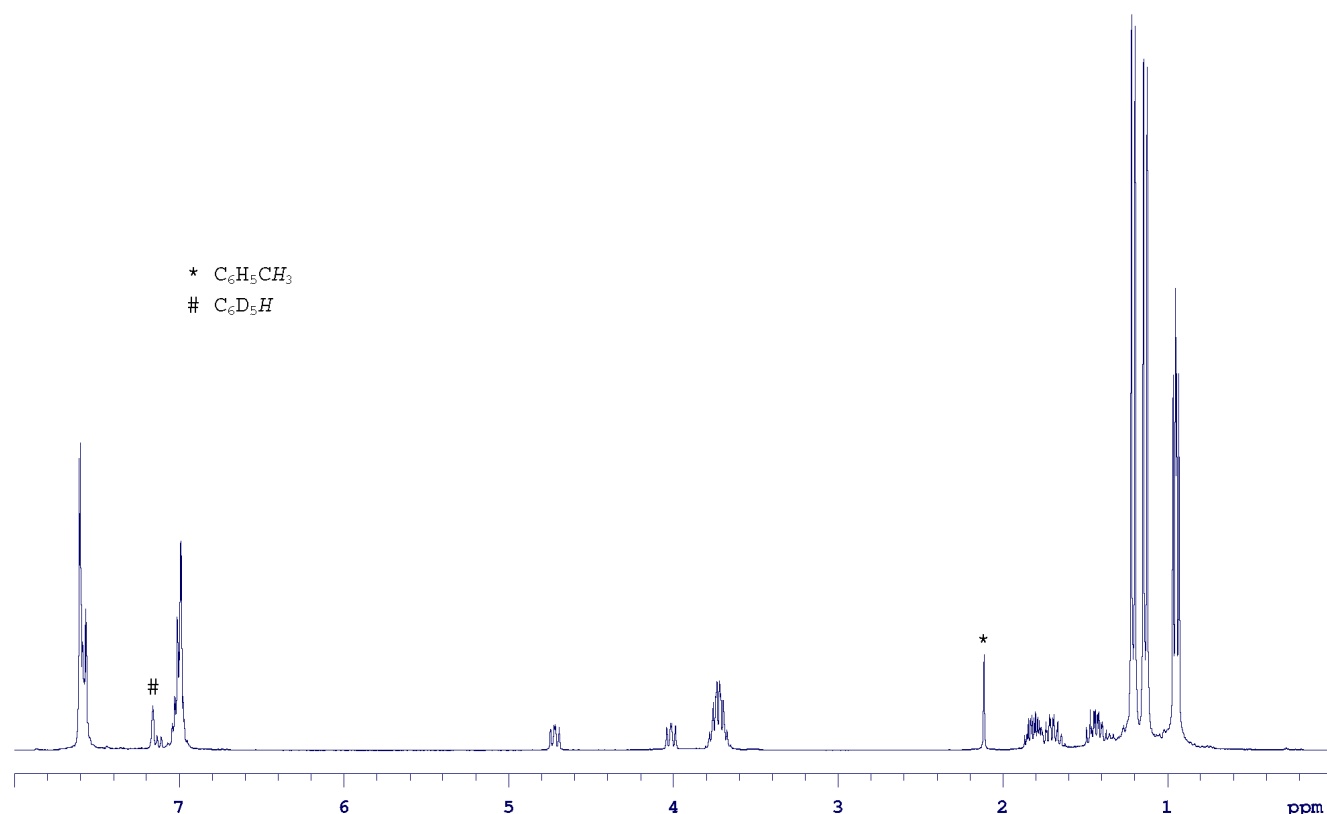


Figure A1. ^1H NMR spectrum for (**5**).

Synthesis of compound **6**

Compound **5** (0.999 g, 2.85 mmol) and 3 mL THF were placed in a 20 mL scintillation vial, to which freshly titrated n-BuLi in hexanes (0.365 mL of 1.578 mol/L, 0.576 mmol, 0.200 equiv.) was added with stirring. The resultant dark brown mixture was stirred overnight, then precipitated into a vortex of pentane. The brown supernatant was decanted to give a dark brown gummy residue, which was then dissolved in 2 mL THF and re-precipitated into hexanes. This step was repeated (3 or 4 precipitations total). The dark brown gummy residue was then dried under vacuum to give a dark brown solid.

Yield: 0.380 g (38.0 %). ^1H NMR (THF- d_8 , 25 °C, 300 MHz) δ : 7.7–5.9 (br, 7H, ArH), 4.1–3.6 (br, 2H, ArCH(CH $_3$) $_2$), 1.6–0.5 (br, 21H, PCH $_2$ CH(CH $_3$) $_2$ and ArCH(CH $_3$) $_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C $_6$ D $_6$, 25 °C, 121.5 MHz) δ : -20 (br). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C, 75.5 MHz, partial) δ : 156 (br, Ar), 148 (br, Ar), 143 (br, Ar), 130 (b, Ar), 129 (br, Ar), 126 (br, Ar), 37 (br, alkyl), 35.6 (s, alkyl), 33 (br, alkyl), 32.7 (s, alkyl), 30.1 (s, alkyl), 29 (br, alkyl), 25 (br, alkyl), 24.6 (s, alkyl), 19.1 (s, alkyl), 14.6 (s, alkyl), 10.4 (s, alkyl). FT-IR (25 °C, deposited from a C $_6$ D $_6$ solution): extremely weak peak at 2280 cm^{-1} . UV-vis/near-IR: $\lambda = 484$ nm. GPC (triple detection, versus polystyrene standards): M_n 3600 g mol^{-1} , M_w 9200 g mol^{-1} . GPC (refractive index detection, versus polystyrene standards): M_n 3300 g mol^{-1} , M_w 13800 g mol^{-1} . GPC (laser light scattering): M_n 21000 g mol^{-1} , M_w 25000 g mol^{-1} .

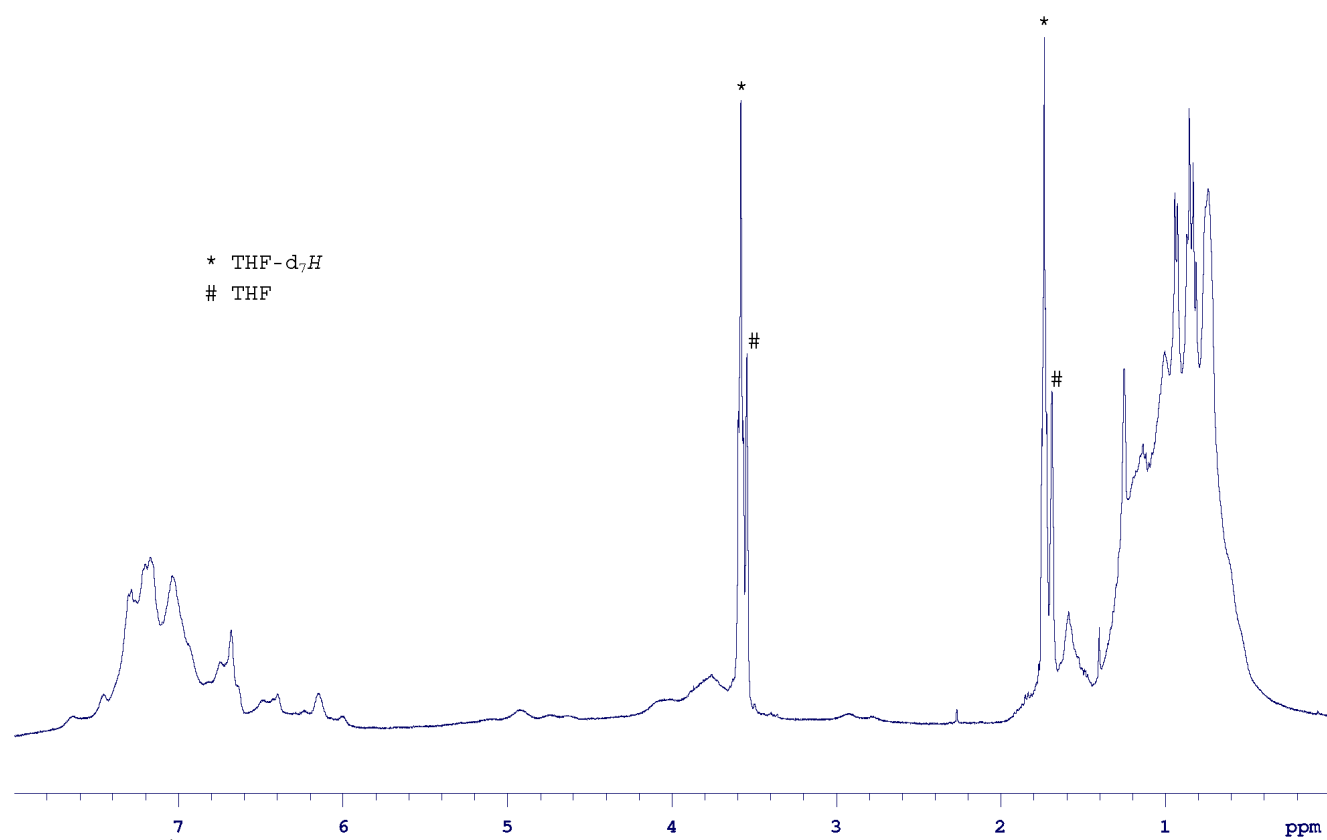


Figure A2. ^1H NMR spectrum for (6).

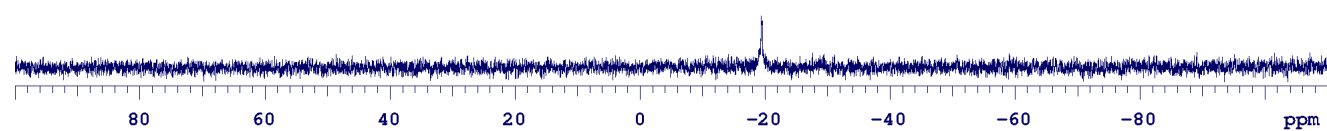


Figure A3. $^{31}\text{P}\{^1\text{H}\}$ spectrum for (6).

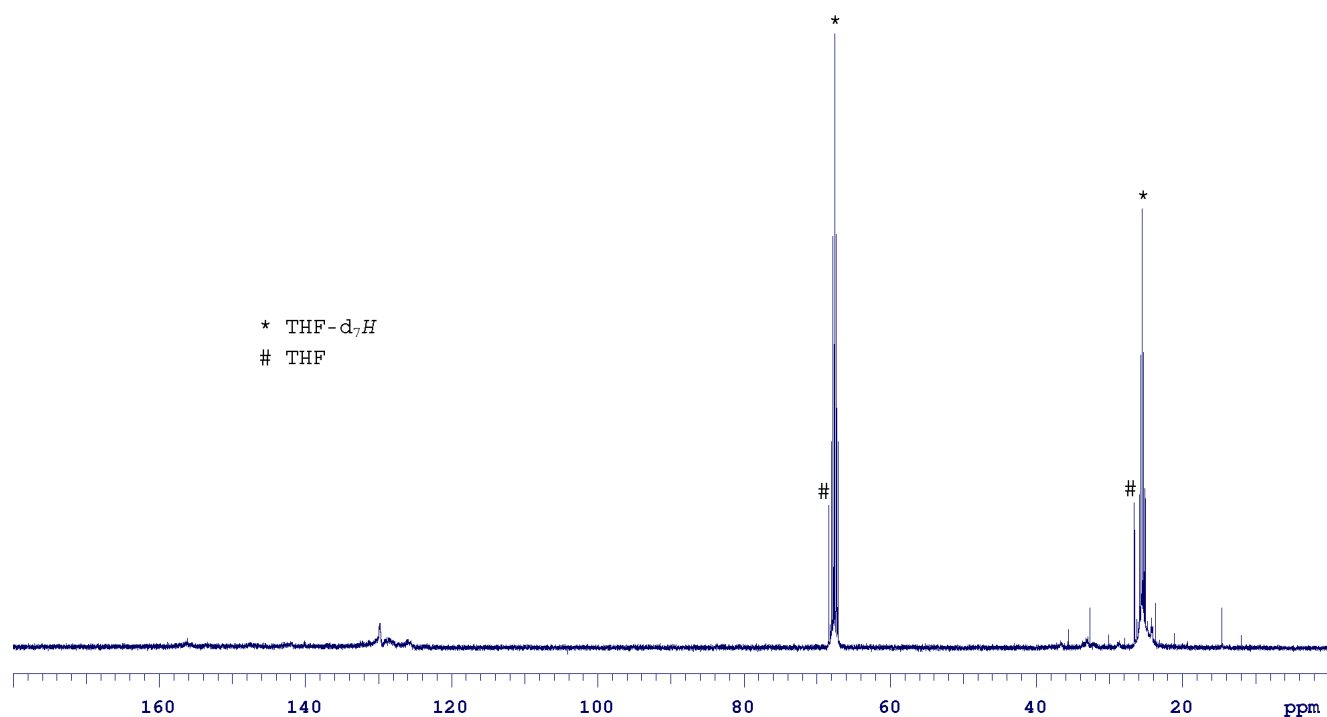


Figure A4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **(6)**.

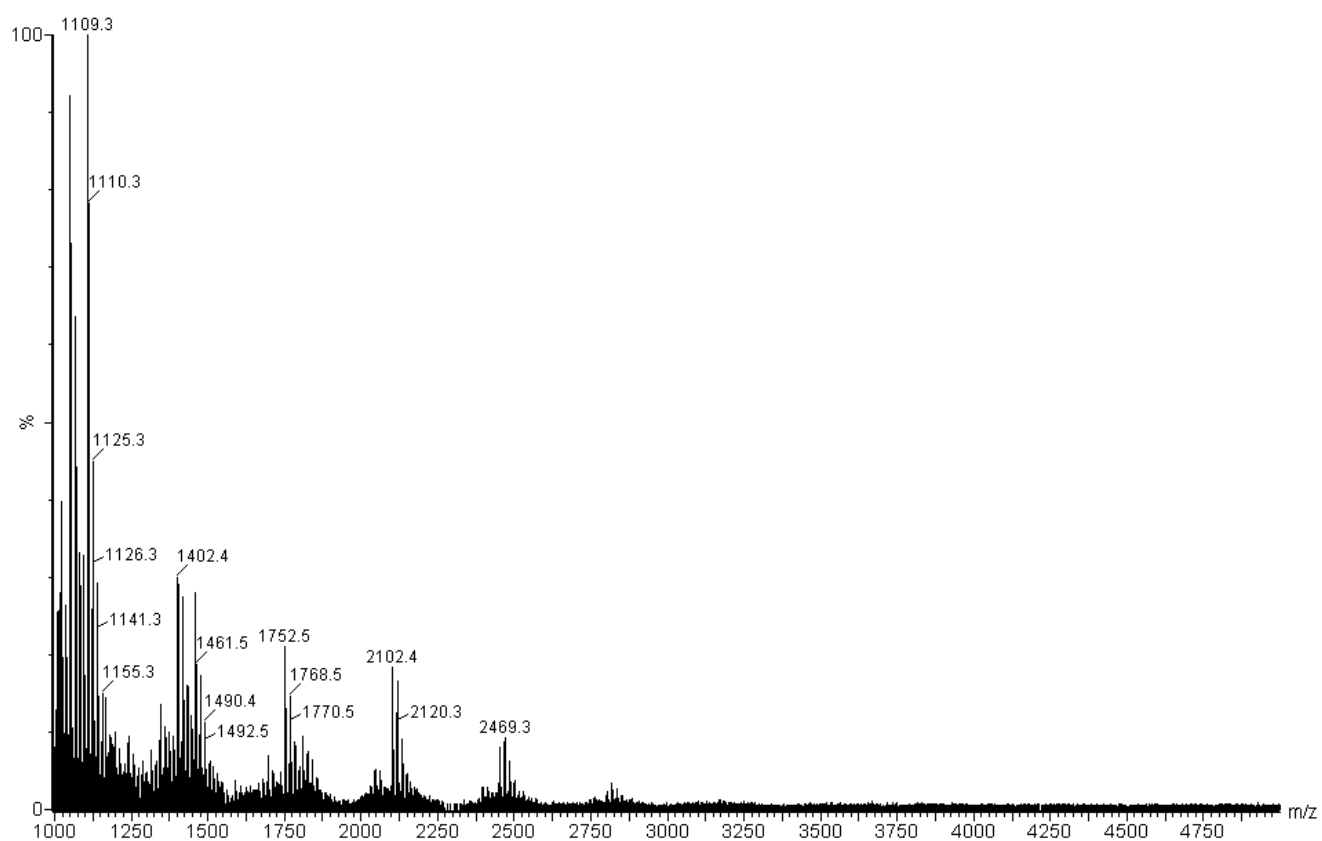


Figure A5. Matrix-Assisted Laser Desorption/Ionization – Time-of-Flight (MALDI-TOF) mass spectrum for **(6)**.

Synthesis of compound 7

Compound 6 (50 mg, 0.14 mmol) and 4 mL THF were placed in a 20 mL scintillation vial, to which elemental sulfur was added (6 mg, 0.19 mmol). The reaction was stirred overnight at room temperature. The brown solution was precipitated into a vortex of hexanes, and the resultant beige solid was isolated from the supernatant by decanting, and dried under vacuum.

Yield: 45 mg (82 %). ^1H NMR (THF- d_8 , 25 °C, 300 MHz) δ : 7.9–6.5 (br, 7H, ArH), 4.3–4.0 (br, 2H, ArCH(CH $_3$) $_2$), 2.3–0.3 (br, 21H, PCH $_2$ CH(CH $_3$) $_2$ and ArCH(CH $_3$) $_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C $_6$ D $_6$, 25 °C, 121.5 MHz) δ : 46.2 (br). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C, 75.5 MHz, partial) δ : 157 (br, Ar), 139 (br, Ar), 133 (br, Ar), 131 (b, Ar), 129 (br, Ar), 128 (br, Ar), 36 (s, alkyl), 33 (s, alkyl), 31 (br, alkyl), 30 (s, alkyl), 28 (s, alkyl), 24 (s, alkyl), 21 (s, alkyl), 14 (s, alkyl), 12 (s, alkyl). FT-IR (25 °C, deposited from a C $_6$ D $_6$ solution): extremely weak peak at 2279 cm^{-1} . UV-vis/near-IR: no peak was discerned for the light brown solution. GPC (refractive index detection, versus polystyrene standards): M_n 3000 g mol^{-1} , M_w 9600 g mol^{-1} .

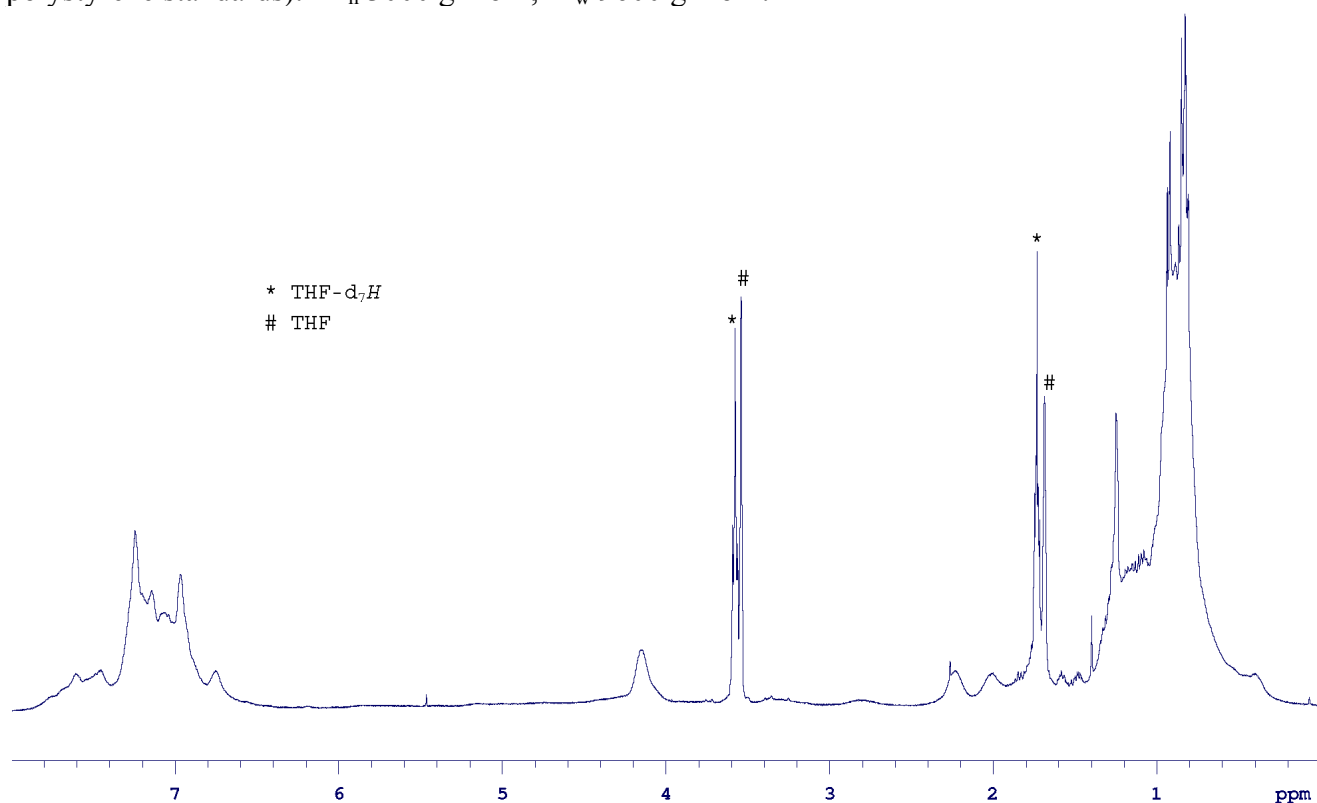


Figure A6. ^1H NMR spectrum for (7).

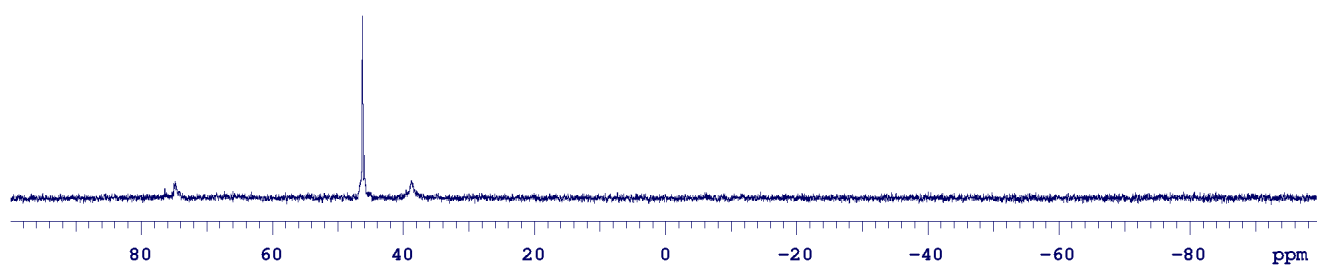


Figure A7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for (7).

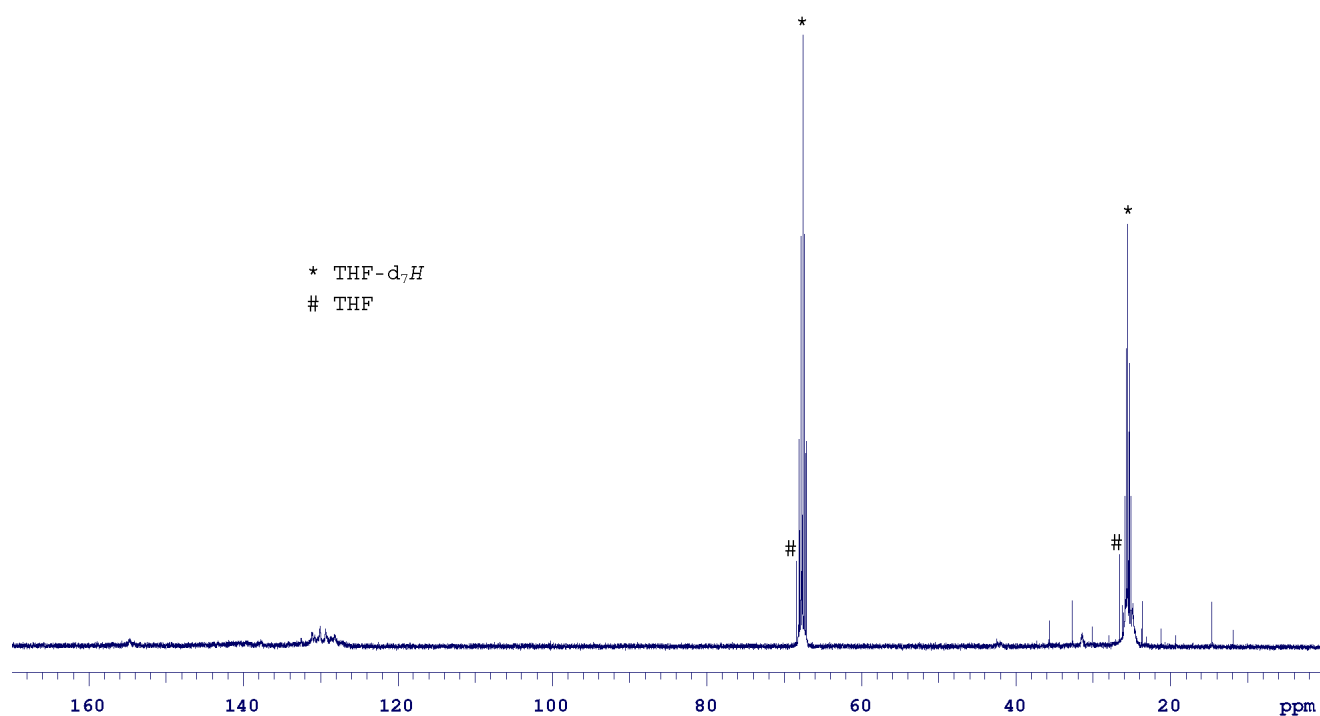


Figure A8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for (7).

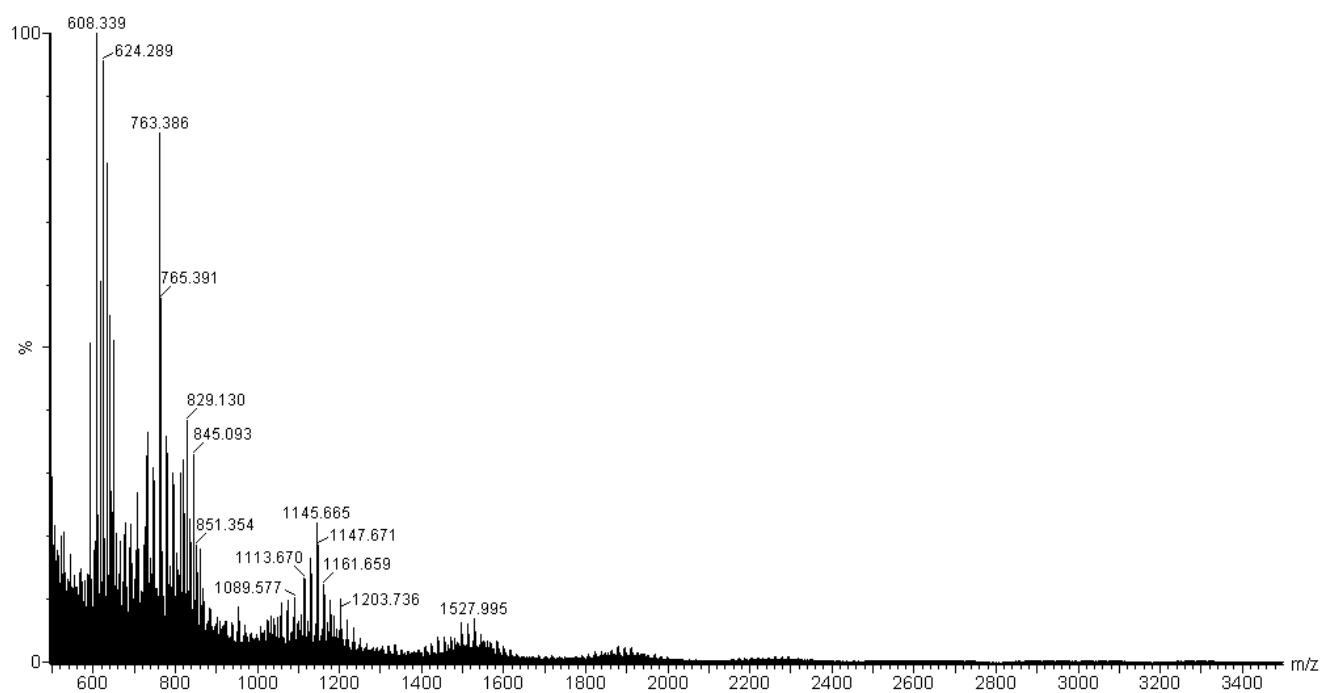


Figure A9. MALDI-TOF mass spectrum for (7).

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