

Bifunctional [c2]Daisy-Chains and Their Incorporation into Mechanically Interlocked Polymers

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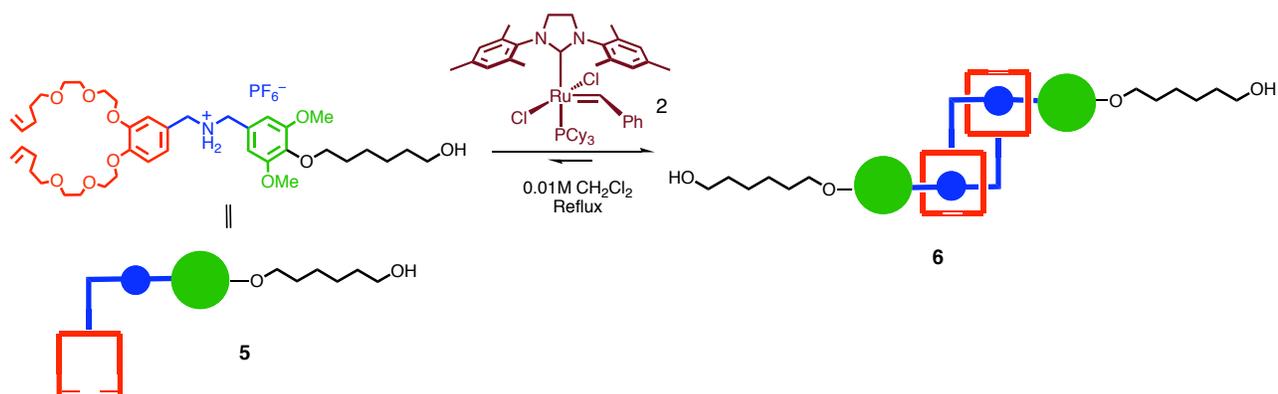
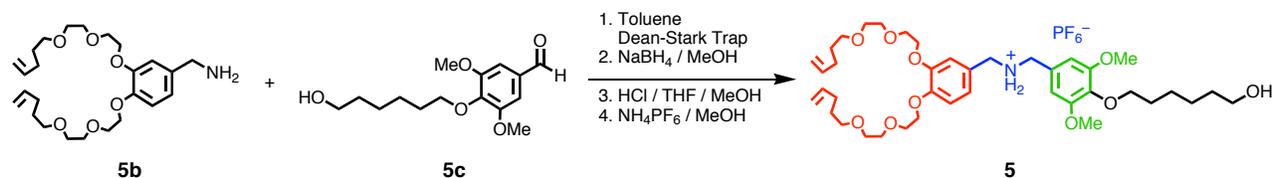
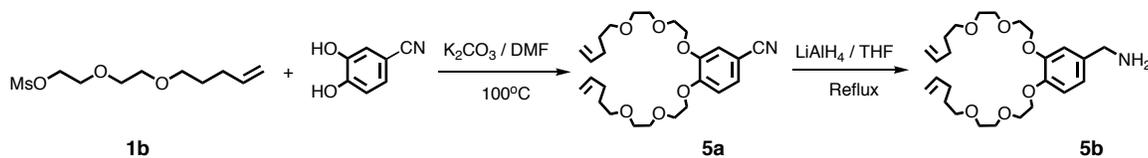
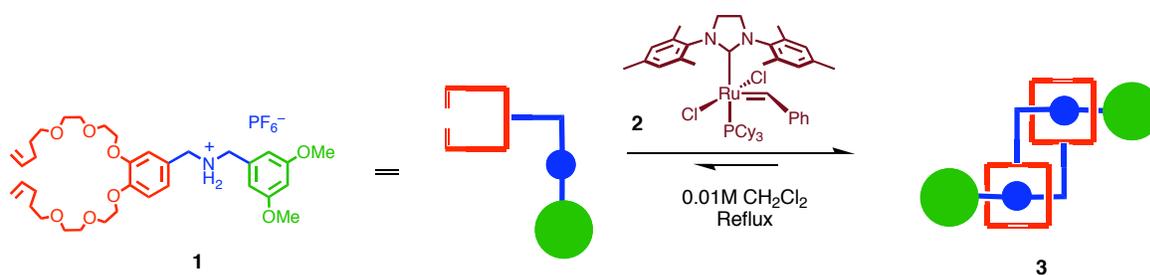
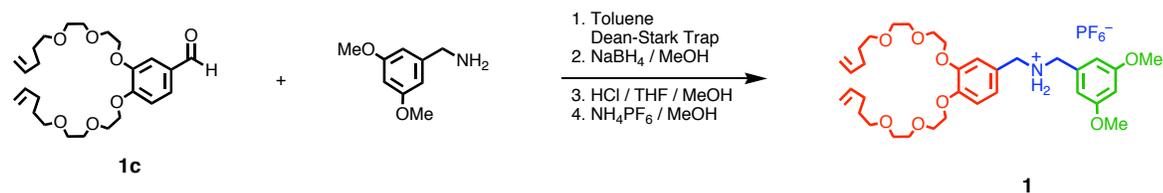
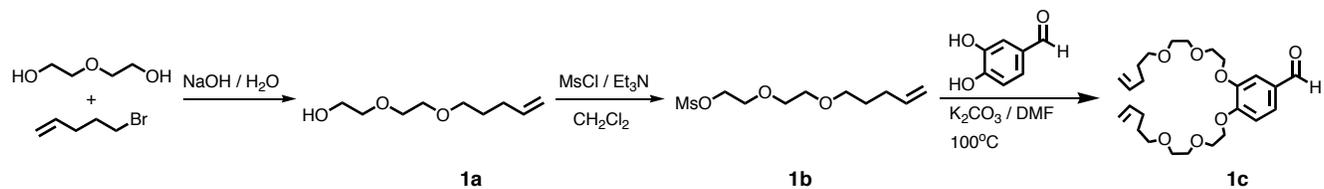
Supporting Information

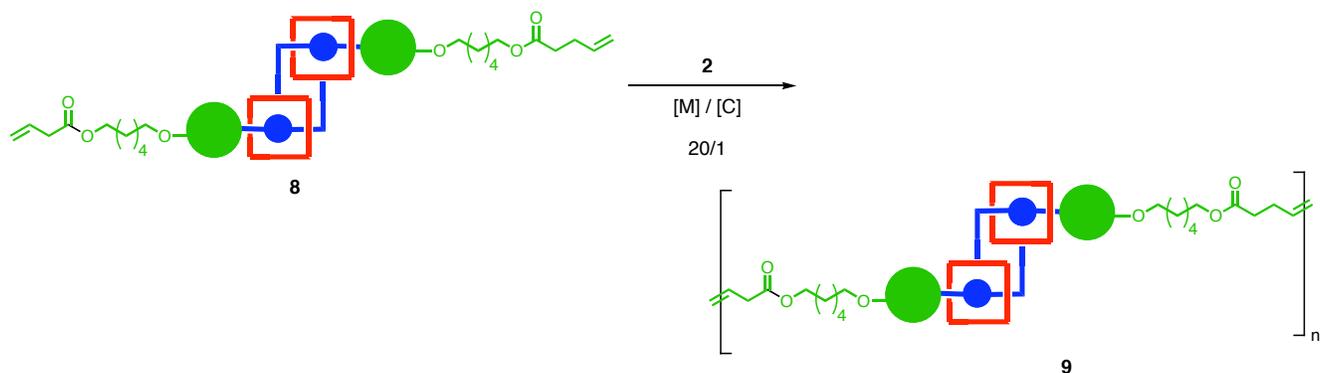
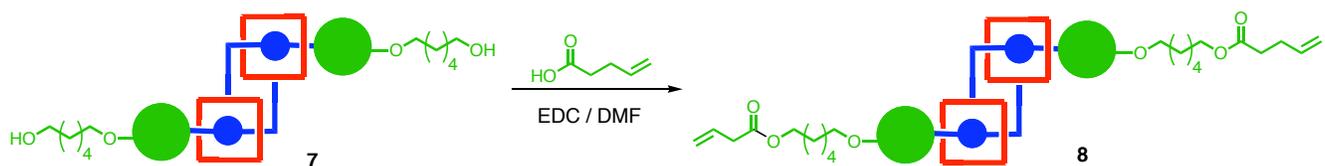
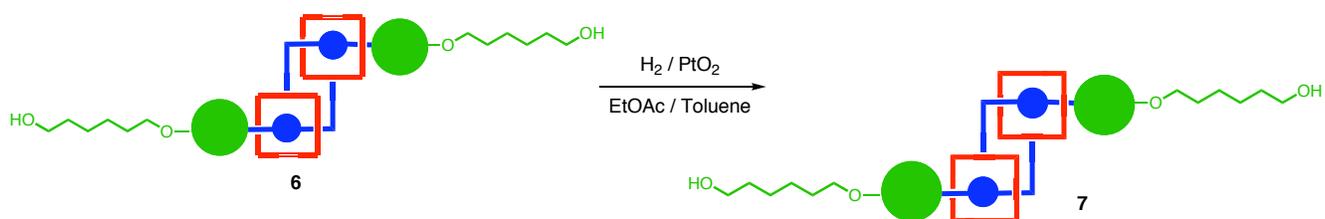
Experimental procedures and characterization data (^1H and ^{13}C NMR, HRMS) for all compounds and their precursors.

General Experimental Section. NMR spectra were recorded on an Oxford 300 MHz or 500 MHz NMR spectrometer running Varian VNMR software. Chemical shifts are reported in parts per million (ppm) with reference to internal solvent. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), and broad (br). High-resolution mass spectra (EI, MALDI and FAB) were provided by California Institute of Technology Mass Spectrometry Facility. Molecular mass calculations were performed with ChemDraw Ultra 9 (Cambridge Scientific). Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization was performed using UV and iodine stain. Flash column chromatography was performed using silica gel 60 (230-400 mesh)

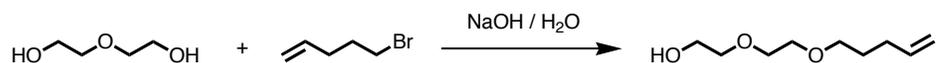
from EM Science. Grubbs 2nd Generation catalyst $(\text{H}_2\text{IMes})(\text{PCy}_3)(\text{Cl})_2\text{Ru}=\text{CHPh}$ (**2**) was obtained from Materia. All other chemicals were purchased from Aldrich or Acros Chemical Companies and used as obtained unless noted otherwise. Tetrahydrofuran and dichloromethane were purified and dried by passage through a solvent column.ⁱⁱ Anhydrous dimethyl formamide was purchased in Acros seal bottles from Acros and used as received. Reverse-phase high pressure liquid chromatography (HPLC) was conducted using Gemini 5 micron c-18 column under a steady ramp (10% MeCN in 0.1% aqueous trifluoroacetic acid to 100% MeCN) with UV detection at 254 nm using a Beckman System Gold detector. Gel permeation chromatography (GPC) was determined on an HPLC type system, using a Shimadzu LC-10AD pump, a rheodyne model 7125 injector with a 100 μL loop, PLgel 5 μm 10E3A size exclusion column and PLgel 5 μm guard column (purchased from polymer laboratories) connected in series with a Alltech on-line degassing system, a Wyatt Technology optilab DSP differential refractometer and a Wyatt Technology Dawn EOS multi angle laser light scattering (MALLS) detector. Astra V was used to analyze the raw MALLS and RI data. The eluent (DMF with 0.1M NH_4PF_6) was prepared using HPLC grade DMF (purchased from Fischer Scientific) and NH_4PF_6 (purchased from Aldrich), which was filtered through a 0.45 micron filter before use. The flow rate was set to 0.5 mL/min. Instrument normalization and calibration was performed using a 30K Polystyrene standard with a PDI = 1.06 (purchased from Pressure Chemical Company). No calibration standards were used in determination of molecular weights or polydispersities. The dn/dc values were obtained for each injection assuming 100% mass elution from the columns. These values were verified by measuring dn/dc independently using a Wyatt optilab differential refractometer.

Experimental Section

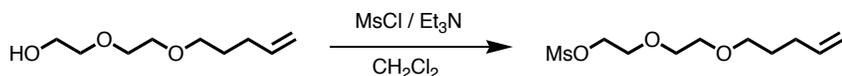




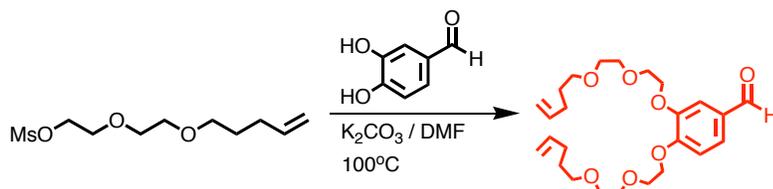
Experimental Procedures:



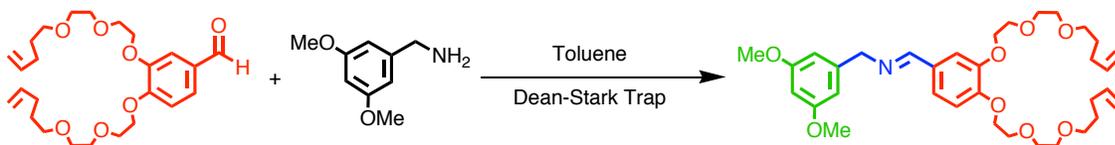
1a: A solution of diethylene glycol (320 ml, 3.35 moles), 5-bromo-1-pentene (50 g, 0.335 moles) and H_2O containing NaOH (67 g, 1.72 moles, in 67 ml H_2O) was heated at 80°C for 12 hours. The reaction mixture was diluted with water and washed with methylene chloride three times to give a crude product, which was purified by column chromatography (SiO_2 : hexanes/ethyl acetate 4:1) to yield the monoalkylated product as a colorless oil (36 g, 62% yield). Characterization for this compound has been reported previously (Badjic', J. D., Cantrill, S. J., Grubbs, R. H.; Guidry, E. N.; Orenes, R.; Stoddart, J. F. *Angew. Chem. Int. Ed.* **2004**, *43*, 3273-3278.).



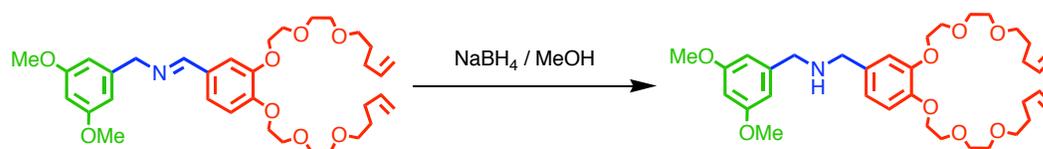
1b: The monoalkylated product **1a** (36 g, 0.207 moles) and triethylamine (43 ml, 0.306 moles) were dissolved in CH_2Cl_2 (500 ml, 0.4 M) and cooled to 0 °C. A solution of mesyl chloride (24.3 ml, 0.207 moles) in CH_2Cl_2 (50 ml) was added slowly. The reaction was gradually warmed to room temperature and stirred overnight. The reaction mixture was diluted with brine and washed with methylene chloride three times, to give a crude product, which was purified by column chromatography (SiO_2 : hexanes/ethyl acetate 2:1) to yield **1b** as a colorless oil (51 g, 98 % yield). ^1H NMR (300 MHz, CDCl_3): δ 5.70 (m, center, 1H), 4.95-4.83 (br m, 2H), 4.29-4.26 (m, 2H), 3.68-3.65 (m, 2H), 3.65-3.61 (m, 2H), 3.57-3.53 (m, 2H), 3.49-3.45 (m, 2H), 3.37 (t, $J = 10.2$ Hz, 2H), 2.99 (s, 3H), 2.04-1.96 (m, 2H), 1.56 (quint, $J = 6.6$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 138.10, 114.72, 70.55, 69.92, 69.45, 68.90, 52.57, 37.54, 30.11, 28.67. HRMS-FAB (m/z): $[\text{M} + \text{H}]$ calcd for $\text{C}_{10}\text{H}_{21}\text{O}_5\text{S}$, 253.1110; found, 253.1113.



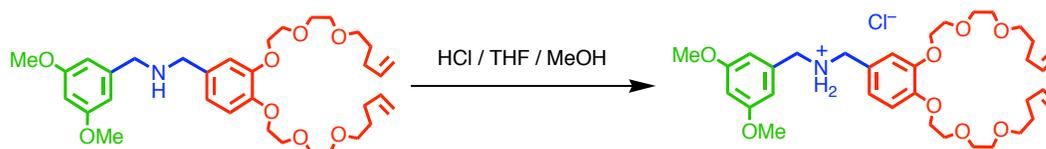
1c: Compound **1b** (37.1 g, 0.147 moles), 3,4-dihydroxybenzaldehyde (9.67 g, 0.0699 moles), and potassium carbonate (29 g, 0.210 moles) were suspended in anhydrous DMF (500 ml, 0.3 M). The reaction mixture was heated to 80 °C and stirred for 3 days. The reaction mixture was diluted with water and washed with ethyl acetate three times to give a crude product, which was purified by column chromatography (SiO_2 : hexanes/ethyl acetate 1:1) to yield the alkylated product as an orange oil (28 g, 91 % yield). ^1H NMR (300 MHz, CDCl_3): δ 9.83 (s, 1H), 7.45-7.42 (m, 2H), 7.00 (d, $J = 8.7$ Hz, 1H), 5.87-5.73 (m, 2H), 5.04-4.92 (m, 4H), 4.23 (quint, $J = 4.8$ Hz, 4H), 3.90 (q, $J = 5.4$ Hz, 4H), 3.75-3.72 (m, 4H), 3.61-3.58 (m, 4H), 3.47 (t, $J = 6.6$ Hz, 4H), 2.10 (q, $J = 7.8$ Hz, 4H), 1.67 (quint, $J = 6.9$ Hz, 4H). ^{13}C NMR (75 MHz, CDCl_3): δ 191.04, 154.51, 149.34, 138.41, 138.37, 130.39, 126.84, 114.91, 114.88, 112.65, 112.07, 71.18, 71.10, 70.92, 70.34, 69.71, 69.59, 68.90, 68.85, 30.38, 28.91. HRMS-FAB (m/z): $[\text{M} + \text{H}]$ calcd for $\text{C}_{25}\text{H}_{39}\text{O}_7$, 451.2696; found, 451.2713.



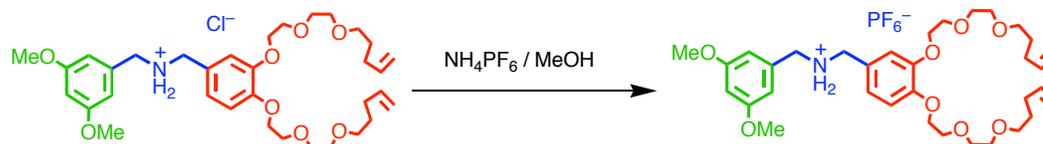
1: Compound **1c** (3 g, 6.66 mmol) and 3,5-dimethoxy benzylamine (1.11 g, 6.66 mmol) were dissolved in toluene (70 ml, 0.1 M). The reaction was heated under reflux for 12 hours using a Dean-Stark apparatus. The solvent was evaporated under reduced pressure to give the crude imine as an orange oil (3.99 g). This product was immediately used in the next step without purification.



The imine (3.99 g, 6.66 mmol) was dissolved in MeOH (67 ml, 0.1 M). After portion-wise addition of sodium borohydride (0.78 g, 19.98 mmol), the reaction mixture was stirred for 4 hours. The solvent was evaporated under reduced pressure and the crude residue was partitioned between CH₂Cl₂ (200 ml) and 2M NaOH solution (200 ml). The aqueous layer was further washed with CH₂Cl₂ (200 ml). The organic phases were combined and washed with NaCl (sat.) and dried over MgSO₄. Filtration, followed by evaporation gave the crude product, an orange oil (3.8 g) which was used in the next step without further purification.

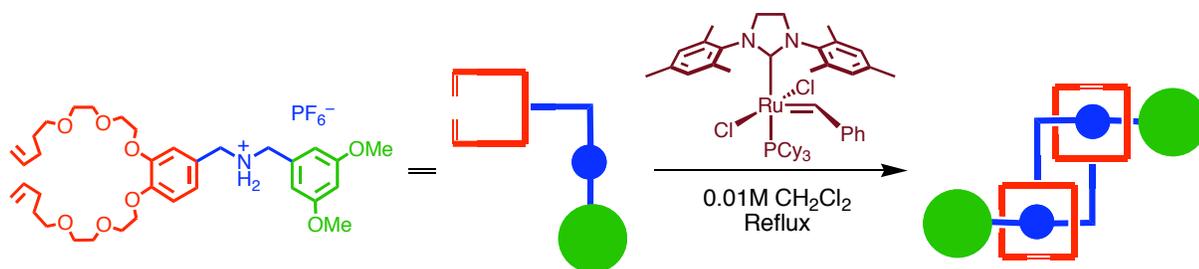


The amine (3.8 g, 6.33 mmol) was dissolved in a solution of 100 ml of THF, 20 ml of MeOH and 2 ml of 1M HCl. The reaction mixture was stirred for 1 hour. The THF and MeOH were removed under reduced pressure. The crude mixture was partitioned between water and CH₂Cl₂. The organic layer was extracted twice more with water. The organic layer was dried over magnesium sulfate, filtered and the solvent was removed under reduced pressure to yield an orange solid. The solid was purified by washing with cold ether (2X, 20 ml) to yield a white solid (3.74 g). The solid was used in the next step without any further purification.



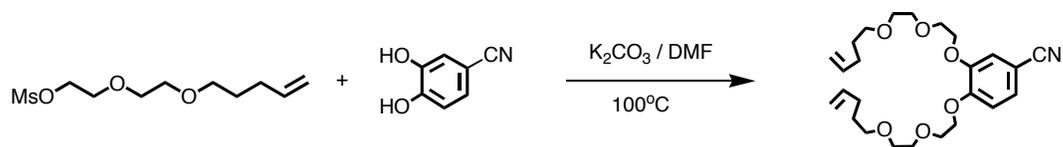
1-H·PF₆: The chloride salt (3.74 g, 5.88 mmol) and ammonium hexafluorophosphate (1.91 g, 11.76 mmol) were dissolved in MeOH (60 ml, 0.1 M). The reaction was stirred at room temperature for 4 hours. The solvent was removed under reduced pressure. The crude mixture was partitioned between CH₂Cl₂ and water. The organic layer was washed two times and dried over magnesium sulfate. The solvent was removed under reduced pressure to yield a sticky pale yellow solid (3.69 g, 84 % yield). ¹H NMR (300 MHz, CDCl₃): δ 7.59 (broad s, 2H), 6.93 (d, J = 7.8 Hz, 1H), 6.79-6.75 (m, 2H), 6.67 (m, 2H), 6.44 (s, 1H), 5.77-5.64 (m, 2H), 4.95-4.88 (m, 4H), 4.43 (m, 2H), 4.23 (m, 2H), 4.01 (s, 4H), 3.74 (s, 6H), 3.65-3.61 (m, 12H), 3.50-3.42 (m, 4H), 2.07-1.98 (m, 4H), 1.61 (hex, J = 6.9 Hz, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 161.48, 147.35, 146.64, 137.79, 137.72, 133.43, 123.76, 123.43, 115.30,

115.25, 114.86, 114.10, 113.14, 106.49, 100.76, 71.83, 71.59, 71.03, 70.94, 70.84, 70.16, 70.07, 69.79, 69.58, 68.83, 68.12, 55.61, 52.54, 52.31, 30.16, 28.70, 28.66 . HRMS-FAB (m/z): [M + e] calcd for C₃₄H₅₂NO₈, 602.3693; found, 602.3690.

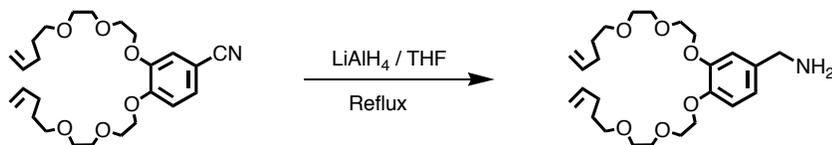


3-H·PF₆: Compound **1**-H·PF₆ (3 g, 4.02 mmoles) was dissolved in anhydrous, degassed CH₂Cl₂ (400 ml, 0.01M). The catalyst (H₂IMes)(PCy₃)(Cl)₂Ru=CHPh **2** (0.170 g, 0.201 mmoles) was added under a dry Ar atmosphere and the reaction was heated to 40 °C for 12 h. The reaction quenched by addition of ethyl vinyl ether. The reaction was stirred for an additional 30 minutes at 40°C. The reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure and the crude oil was purified by column chromatography (SiO₂: methylene chloride/methanol 100:1 gradient to 100:2) to yield the daisy chain dimer **3**-H·PF₆ as a pale brown foamy solid (2.74 g, 95 % yield). ¹H NMR (300 MHz, CDCl₃): δ 6.94-6.91 (m, 2H), 6.85-6.80 (m, 2H), 6.72-6.66 (m, 6H), 6.48-6.46 (m, 2H), 5.46-5.32 (m, 4H), 4.68-4.25 (broad m, 16H), 3.85-3.47 (m, 28H), 2.33-2.26 (m, 8H), 2.09-1.96 (m, 4H), 1.78-1.48 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 161.62, 146.94, 146.48, 133.91, 133.74, 131.23, 130.99, 129.95, 129.63, 123.80, 123.65, 113.71, 112.86, 112.62, 106.55, 106.46, 105.64, 100.48, 72.901, 72.45, 72.23, 72.09, 71.81, 71.35, 70.59, 70.13, 69.85, 69.59, 68.75, 68.53, 55.70, 52.69, 52.45, 52.17, 51.94, 30.64, 30.49, 29.04, 28.95, 28.66, 25.40, 25.30. HRMS-FAB (m/z): [M + e] calcd for C₆₄H₉₅N₂O₁₆, 1147.668; found, 1147.661.

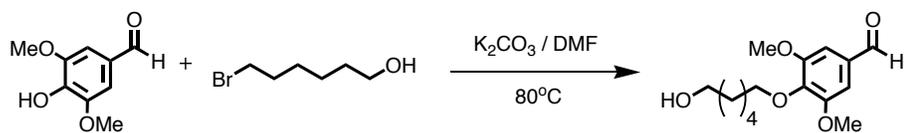
Crystals suitable for X-ray analysis were grown by slow evaporation from EtOAc. Crystallization lead to fractional separation of the mesoform, which remained dissolved in the mother liquor. The racemic modification produced crystals suitable for X-ray analysis. Crystals of **4**-H₂·2PF₆ diffract poorly and appear to be twinned. Data used for least-squares refinement was restricted to 2θ < 40° with data between 36-40° being extremely weak. Disorder is observed in the ring-closed portion of the molecules. Restraints were placed on temperature factors, bond distances and bond angles in this portion of the molecules. The structure has been deposited in the CCDC; number xxx. See the CIF file for complete details.



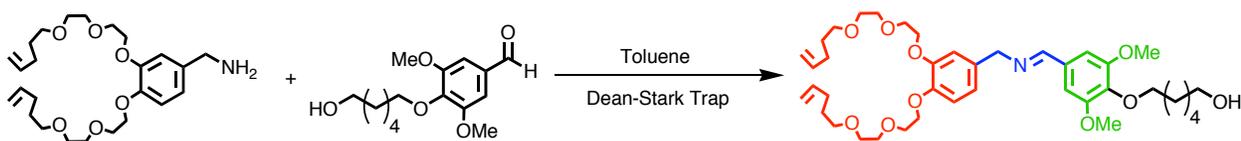
5a: Compound **1b** (51 g, 0.202 moles), 3,4-dihydroxybenzonitrile (13 g, 0.963 moles), and potassium carbonate (40 g, 0.289 moles) were suspended in anhydrous DMF (500 ml, 2 M). The reaction mixture was heated to 80 °C and stirred for 3 days. The reaction mixture was diluted with water and washed with ethyl acetate three times to give a crude product, which was purified by column chromatography (SiO₂: hexanes/ethyl acetate 3:1) to yield the alkylated product **5a** as an orange oil (23 g, 53 % yield). ¹H NMR (300 MHz, CDCl₃): δ 7.26-7.23 (m, 1H), 7.15-7.14 (m, 1H), 6.92 (d, J = 8.7 Hz, 1H), 5.87-5.73 (m, 2H), 5.04-4.93 (m, 4H), 4.22-4.15 (m, 4H), 3.88 (qt, J = 5.1 Hz, 4H), 3.71 (m, 4H), 3.59 (q, J = 3.3 Hz, 4H), 3.49-3.44 (m, 4H), 2.10 (qt, J = 7.2 Hz, 4H), 1.73-1.63 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 152.89, 148.86, 138.24, 138.19, 126.77, 119.17, 117.08, 114.76, 114.73, 113.49, 104.10, 70.98, 70.96, 70.79, 70.77, 70.18, 70.16, 69.56, 69.42, 69.15, 68.69, 30.21, 28.74. HRMS-FAB (m/z): [M + H] calcd for C₂₆H₄₀NO₆, 462.2856; found, 462.2857.



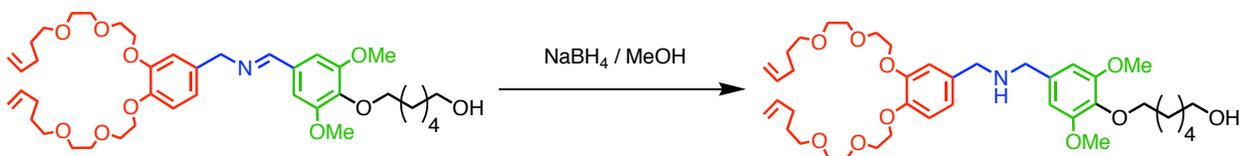
5b: The alkylated product **5a** (23 g, 0.0515 moles) was dissolved in anhydrous THF (250 ml, 0.2 M) and cooled to 0 °C, under an argon atmosphere. Lithium aluminum hydride (5.9 g, 0.155 moles) was added slowly, piecewise, to the reaction mixture. The reaction was warmed to 76 °C and refluxed under an argon atmosphere for 12 hours. The reaction was quenched by addition of 6 ml of H₂O, followed by addition of 6 ml of NaOH(aq) (15 %) followed by addition of 18 ml of H₂O. A large excess of celite was added and the mixture was filtered and then the solvent was removed under reduced pressure. The reaction mixture was diluted with methylene chloride and washed with water three times with water to yield compound **5b** as a yellow oil (18 g, 78 % yield). No further purification was necessary. ¹H NMR (300 MHz, CDCl₃): δ 6.89-6.80 (m, 3H), 5.87-5.73 (m, 2H), 5.04-4.92 (m, 4H), 4.19-4.13 (m, 4H), 3.85 (q, J = 5.4 Hz, 4H), 3.77 (s, 2H), 3.73-3.70 (m, 4H), 3.60-3.57 (m, 4H), 3.46 (t, 6.9 Hz, 4H), 2.10 (q, J = 6.9 Hz, 4H), 1.67 (quint, J = 6.9 Hz, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 149.20, 147.91, 138.40, 120.02, 115.18, 114.85, 114.00, 70.97, 70.87, 70.32, 69.93, 69.24, 69.04, 46.27, 30.37, 28.90.



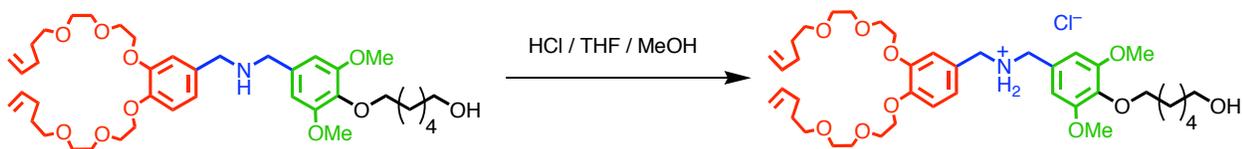
5c: Syringaldehyde (15 g, 0.0823 moles), 6-bromo-1-hexanol (17.9 g, 0.0989 moles), and potassium carbonate (34 g, 0.247 moles) were suspended in anhydrous DMF (0.2 M, 400 ml). The reaction mixture was heated to 80 °C and stirred for 2 days. The reaction mixture was diluted with water and washed with ethyl acetate three times to give a crude product, which was purified by column chromatography (SiO₂: hexanes/ethyl acetate 3:2) to yield the alkylated product **5c** as an orange oil (18.6 g, 80 % yield). ¹H NMR (300 MHz, CDCl₃): δ 9.85 (s, 1H), 7.11 (s, 2H), 4.06 (t, J = 6.6 Hz, 2H), 3.90 (s, 6H), 3.64 (t, J = 6.6 Hz, 4H), 1.77 (quint, 6.6 Hz, 4H), 1.63-1.36 (m, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 191.36, 154.03, 147.96, 143.11, 131.71, 106.88, 73.67, 62.99, 56.40, 32.84, 30.20, 25.71. HRMS-EI (m/z): [M + e] calcd for C₁₅H₂₂O₅, 282.1467; found, 282.1459.



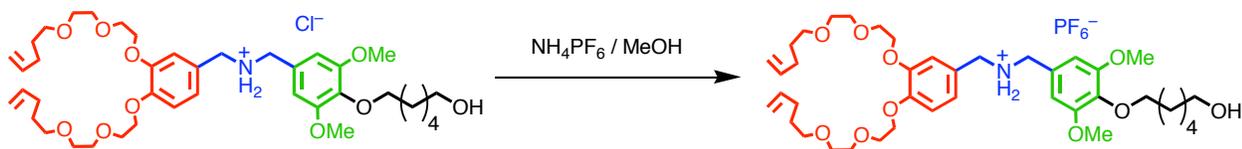
5: Compound **5b** (18 g, 0.0399 moles) and compound **5c** (11.25 g, 0.0399 moles) were dissolved in toluene (400 ml, 0.1 M). The reaction was heated under reflux for 12 hours using a Dean-Stark apparatus. The solvent was evaporated under reduced pressure to give the crude imine as an orange oil (28.5 g). This product was immediately used in the next step without purification.



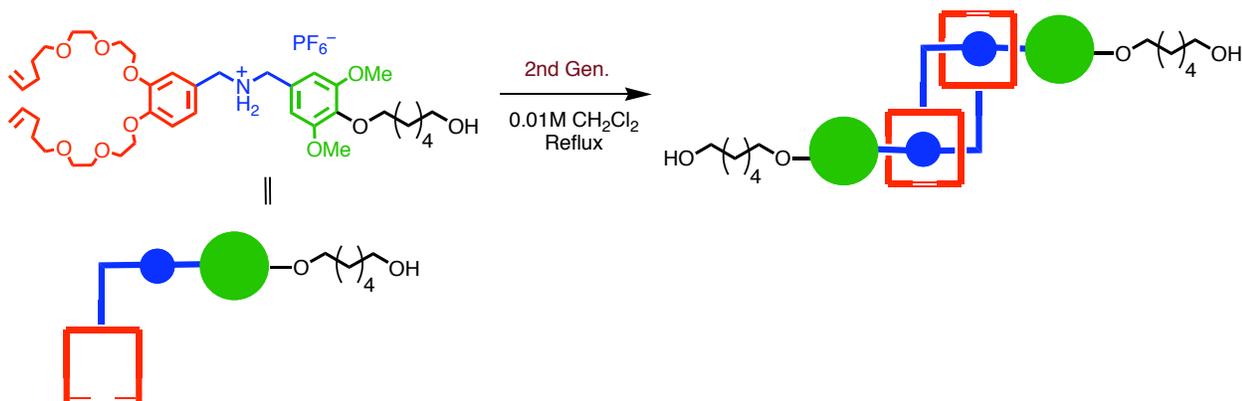
The imine (28.5 g, 0.0399 moles) was dissolved in MeOH (400 ml, 0.1 M). After portion-wise addition of sodium borohydride (4.5 g, 0.120 moles), the reaction mixture was stirred for 4 hours. The solvent was evaporated under reduced pressure and the crude residue was partitioned between CH₂Cl₂ (400 ml) and 2M NaOH solution (400 ml). The aqueous layer was further washed with CH₂Cl₂ (400 ml). The organic phases were combined and washed with NaCl (sat.) and dried over MgSO₄. Filtration, followed by evaporation gave the crude product, an orange oil (28.5 g) which was used in the next step without further purification.



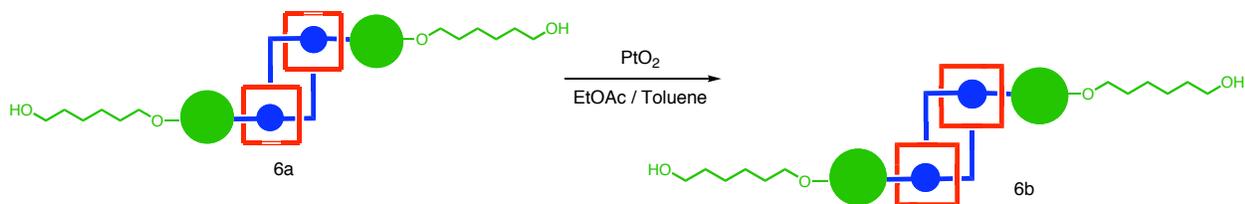
The amine (28.5 g, 0.399 moles) was dissolved in a solution of 200 ml of THF, 40 ml of MeOH and 5 ml of 1M HCl. The reaction mixture was stirred for 1 hour. The THF and MeOH were removed under reduced pressure. The crude mixture was partitioned between water and CH_2Cl_2 . The organic layer was extracted twice more with water. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure to yield an orange solid. The solid was purified by washing with cold ether (2X, 50 ml) to yield a white solid (27.3 g).



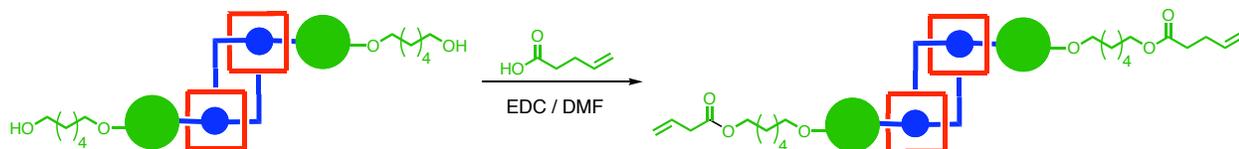
5-H·PF₆: The chloride salt (27.3 g, 0.0363 moles) and ammonium hexafluorophosphate (11.8 g, 0.0726 moles) were dissolved in MeOH (360 ml, 0.1 M). The reaction was stirred at room temperature for 4 hours. The solvent was removed under reduced pressure. The crude mixture was partitioned between CH_2Cl_2 and water. The organic layer was washed two times and dried over magnesium sulfate. The solvent was removed under reduced pressure to yield **5-H·PF₆** as a sticky pale yellow solid (26.6 g, 85 % yield). ¹H NMR (300 MHz, CDCl_3): δ 7.38 (broad s, 2H), 6.95 (d, $J = 8.1$ Hz, 1H), 6.83-6.73 (m, 4H), 5.77-5.64 (m, 2H), 4.95-4.88 (m, 4H), 4.37 (s, 2H), 4.24 (s, 2H), 4.02 (s, 4H), 3.87 (t, $J = 6.3$ Hz, 2H), 3.77 (s, 6H), 3.63-3.42 (m, 16H), 2.01 (m, 4H), 1.62 (quint, $J = 6.9$ Hz, 6H), 1.55-1.45 (m, 2H), 1.38-1.31 (m, 4H). ¹³C NMR (75 MHz, CDCl_3): δ 153.94, 147.49, 146.80, 137.79, 137.75, 126.43, 123.73, 123.65, 115.30, 115.26, 114.10, 113.08, 106.14, 73.45, 71.48, 71.20, 71.04, 70.97, 69.96, 69.91, 69.48, 69.36, 68.56, 68.00, 62.81, 65.38, 52.65, 52.40, 32.68, 30.14, 29.96, 28.63, 25.61, 25.53. HRMS-FAB (m/z): $[\text{M} + \text{H}]$ calcd for $\text{C}_{40}\text{H}_{64}\text{NO}_{10}$, 718.4530; found, 718.4505.



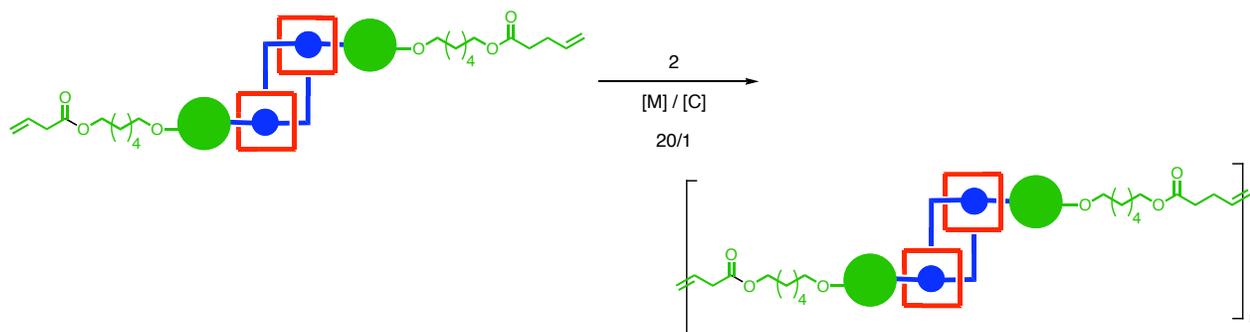
6-H₂·2PF₆: Compound **5-H·PF₆** (3 g, 0.00359 moles) was dissolved in anhydrous, degassed CH₂Cl₂ (360 ml, 0.01M). The catalyst (H₂IMes)(PCy₃)(Cl)₂Ru=CHPh **2** (0.147 g, 0.174 mmoles) was added under a dry Ar atmosphere and the reaction was heated to 40 °C for 12 h. The reaction quenched by addition of ethyl vinyl ether. The reaction was stirred for an additional 30 minutes at 40°C. The reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure and the crude oil was purified by column chromatography (SiO₂: methylene chloride/methanol 100:1 gradient to 100:2) to yield the product **6-H₂·2PF₆** as a pale brown foamy solid (2.84 g, 98 % yield). ¹H NMR (300 MHz, CDCl₃): δ 7.75 (br s, 4H), 6.99-6.75 (m, 10H), 5.44 (br m, 4H), 4.63-4.31 (br m, 12H), 4.00 (t, J = 6.9 Hz, 8H), 3.83 (s, 6H), 3.82 (s, 6H), 3.68-3.50 (br m, 36H), 2.32 (m, 2H), 2.12 (m, 8H), 1.79-1.35 (m, 24H). ¹³C NMR (75 MHz, CDCl₃): δ 153.94, 147.49, 146.80, 137.79, 137.75, 126.43, 123.73, 123.65, 115.30, 115.26, 114.10, 113.08, 73.62, 73.00, 72.69, 72.43, 72.29, 72.01, 71.58, 71.02, 70.50, 69.95, 68.63, 68.39, 63.05, 56.59, 52.69, 52.36, 32.83, 31.12, 30.18, 29.90, 29.78, 29.56, 27.95, 26.04, 25.77, 25.60. HRMS-FAB (m/z): [M + H + PF₆] calcd for C₇₆H₁₂₀N₂O₂₀F₆P, 1526.7346; found, 1525.8044.



7-H₂·2PF₆: Compound **6-H₂·2PF₆** (0.25g, 0.150 mmoles) was dissolved in ethyl acetate (0.001 M, 150 ml). PtO₂ (Adam's catalyst, 1.70 g, 0.0075 mmoles) was added and the reaction atmosphere was flushed with hydrogen for 5 minutes. An atmosphere of hydrogen was placed over the reaction using a balloon, and it was vigorously stirred a room temperature for 30 minutes. The reaction was filtered through a pad of celite and solvent removed under reduced pressure to yield **7-H₂·2PF₆** as a light brown sticky solid (0.24 g, 97 % yield). ¹H NMR (300 MHz, CDCl₃): δ 7.75 (br s, 4H), 7.01-6.77 (m, 10H), 4.63-4.33 (br m, 12H), 4.00 (t, J = 6.6 Hz, 8H), 3.83 (s, 12H), 3.74-3.50 (br m, 36H), 2.20 (m, 8H), 1.79-1.26 (br m, 24H), 0.882-0.83 (m, 8H). ¹³C NMR (75 MHz, CDCl₃): δ 154.23, 154.10, 146.92, 146.43, 138.07, 126.86, 123.90, 123.70, 113.82, 112.54, 105.643, 105.13, 73.68, 73.01, 72.71, 72.45, 72.28, 72.08, 71.53, 71.06, 70.53, 69.97, 68.64, 68.39, 63.05, 56.59, 52.69, 52.36, 32.83, 31.12, 30.18, 29.90, 29.78, 29.56, 27.95, 26.04, 25.77, 25.69, 22.89, 14.33, 1.22. HRMS-FAB (m/z): [M + H + PF₆] calcd for C₇₆H₁₂₄N₂O₂₀F₆P, 1529.8389; found, 1529.8329.



8-H₂·2PF₆: EDC (0.64g, 3.35 mmoles), 4-pentenoic acid (0.34g, 3.35 mmoles) and DMAP (0.02g, 0.16 mmoles) were dissolved in anhydrous DMF (9 ml, 0.1M) and stirred at room temperature for 30 minutes. The diol **7-H₂·2PF₆** (1.40g, 0.84 mmoles) was dissolved in anhydrous DMF (1ml) and added via syringe to the EDC mixture. The reaction was stirred under Ar for 24 hours. The reaction mixture was diluted with brine and ethyl acetate. The aqueous layer was extracted twice with brine. The organic layer was extracted twice with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude oil was purified by column chromatography (SiO₂: methylene chloride/methanol 100:1 gradient to 100:2) to yield the product **8-H₂·2PF₆** as a pale brown foamy solid (1.2 g, 80 % yield). ¹H NMR (300 MHz, CDCl₃): δ 7.74 (br s, 4H), 7.01-6.91 (m, 4H), 6.81-6.76 (m, 6H), 5.89-5.76 (m, 2H), 5.09-4.98 (m, 4H), 4.65-4.33 (m, 12H), 4.09 (t, J = 6.9 Hz, 8H), 3.98 (t, J = 6.6 Hz, 8H), 3.83 (s, 12H), 3.76 (br m, 36H), 2.45-2.34 (m, 8H), 1.83-1.39 (br m, 64H). ¹³C NMR (75 MHz, CDCl₃): δ 173.39, 173.37, 154.21, 154.08, 146.91, 146.42, 138.14, 136.92, 127.28, 126.89, 123.91, 123.67, 115.65, 113.85, 112.55, 105.09, 73.69, 73.04, 72.71, 72.45, 72.28, 71.55, 71.06, 70.52, 70.02, 68.67, 68.39, 64.61, 56.58, 52.71, 52.36, 37.77, 30.24, 29.94, 29.77, 29.10, 28.81, 27.94, 27.88, 25.91, 25.83, 25.76, 25.70. HRMS-FAB (m/z): [M + H + PF₆] calcd for C₈₆H₁₃₆N₂O₂₂F₆P, 1693.9227; found, 1693.9293.

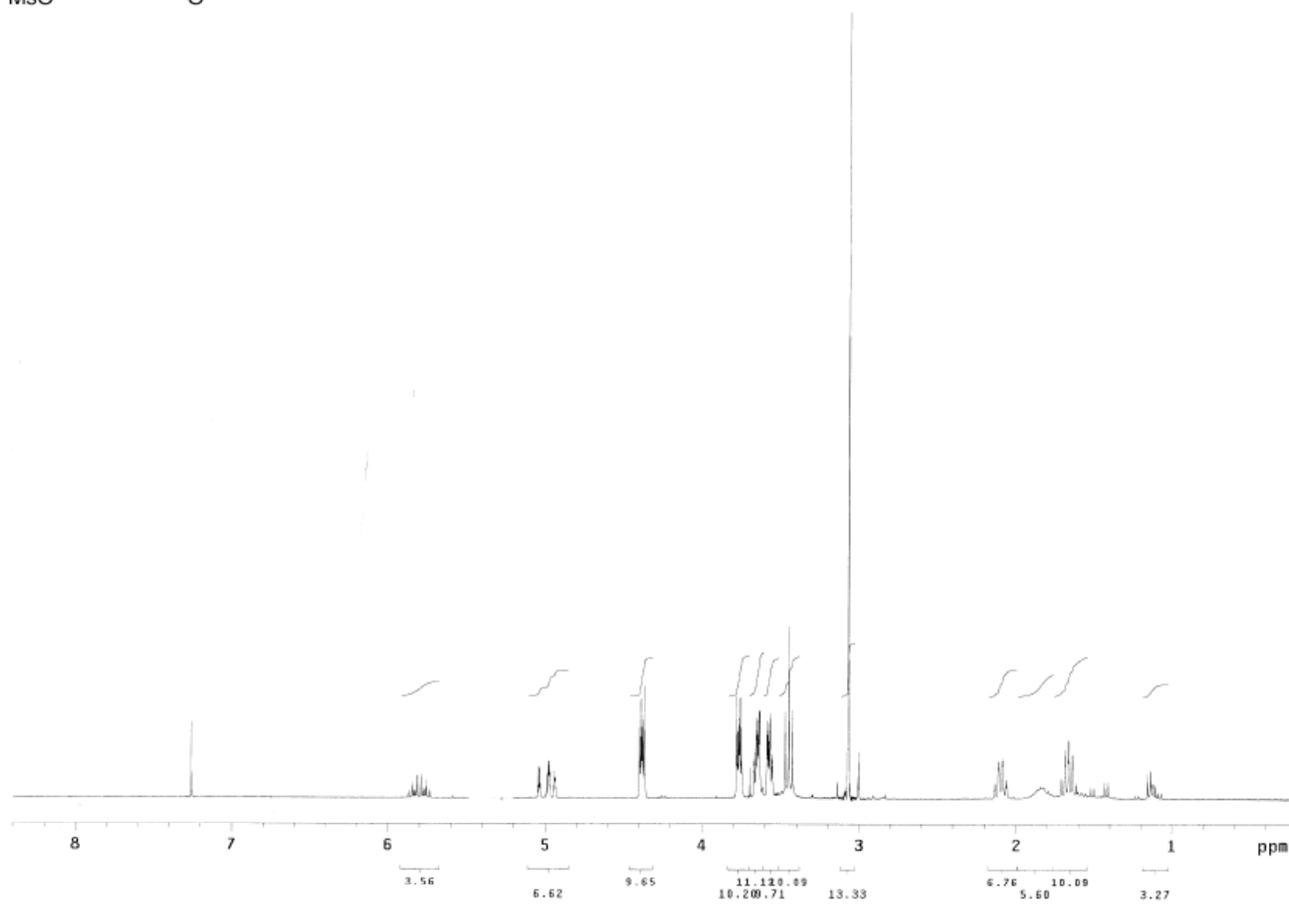
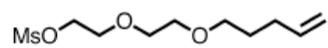


9-H_{2n}·2nPF₆: The diene (20.5 mg, 0.01 mmoles) was dissolved in 1ml of dry degassed CH₂Cl₂ and placed in a schlenk tube with a teflon stopper. Metathesis catalyst **2** (0.47 mg, 0.00005 mmoles) was added in 50 uL of CH₂Cl₂. The schlenk tube was heated to 40°C, with a continuous Ar purge until minimal solvent remained (approximately 25 uL- approximately 30 minutes). The teflon stopper was closed, and the heating continued for 24 hours. The polymerization was quenched by adding ethyl vinyl ether. The solvent was removed under reduced pressure. No further purification was performed. ¹H NMR (500 MHz, CDCl₃): δ 7.75 (br s, 4H), 6.99-6.79 (m, 10H), 5.58-5.31 (br m, 2H), 4.65-4.36 (br m, 12H), 4.14-3.50 (br m, 56H), 2.55-2.21 (br m, 8H), 1.94-1.86 (br m, 64H).

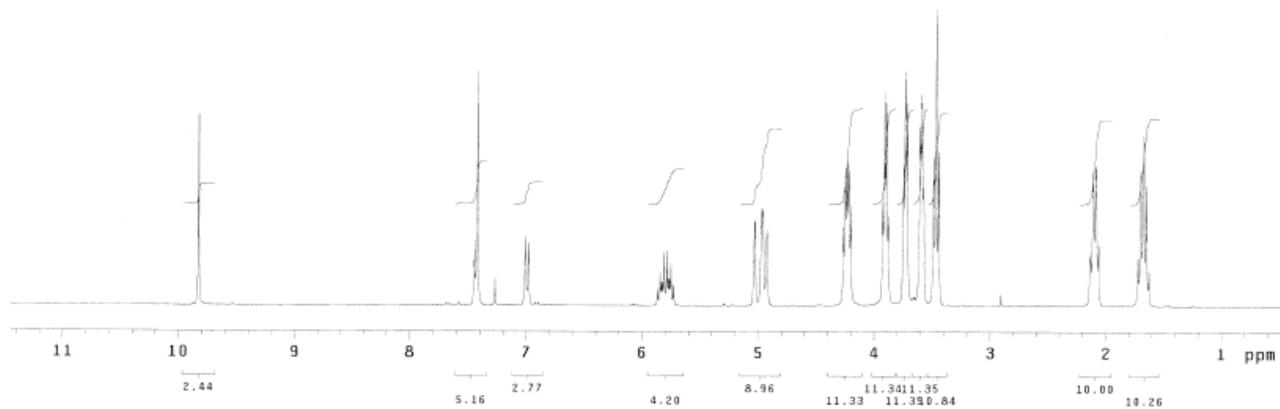
M_n was not able to be determined using GPC due to poor chromatography. Both solvent (THF, DCM, DMF, DMF with 0.1 M LiBr, DMF with 0.1 M NH₄PF₆) and column types (PLgel 5 um 10E3A size

exclusion column and PLgel 5um guard column - purchased from polymer laboratories and ViscoGEL I-Series columns, I-MBLMW-3078 and I-MBHMW-3078 - purchased from viscotek) were varied to try and improve chromatography, but with little success. To further confirm the polymerization results observed in the ^1H NMR and MALDI, HPLC was employed. HPLC was used to verify polymerization rather than olefin isomerization (which would have similar olefin region in the ^1H NMR). Diene **6** has an elution time of 46.876 minutes (steady ramp -10% MeCN in 0.1% aqueous trifluoroacetic acid to 100% MeCN). Polymer **7** was placed on the HPLC under identical ramp conditions. Diene **6** had completely disappeared and no new signals were observed over the course of the 90 minute run, indicating that the internal olefin protons observed in the ^1H NMR are due to ADMET polymerization rather than olefin isomerization.

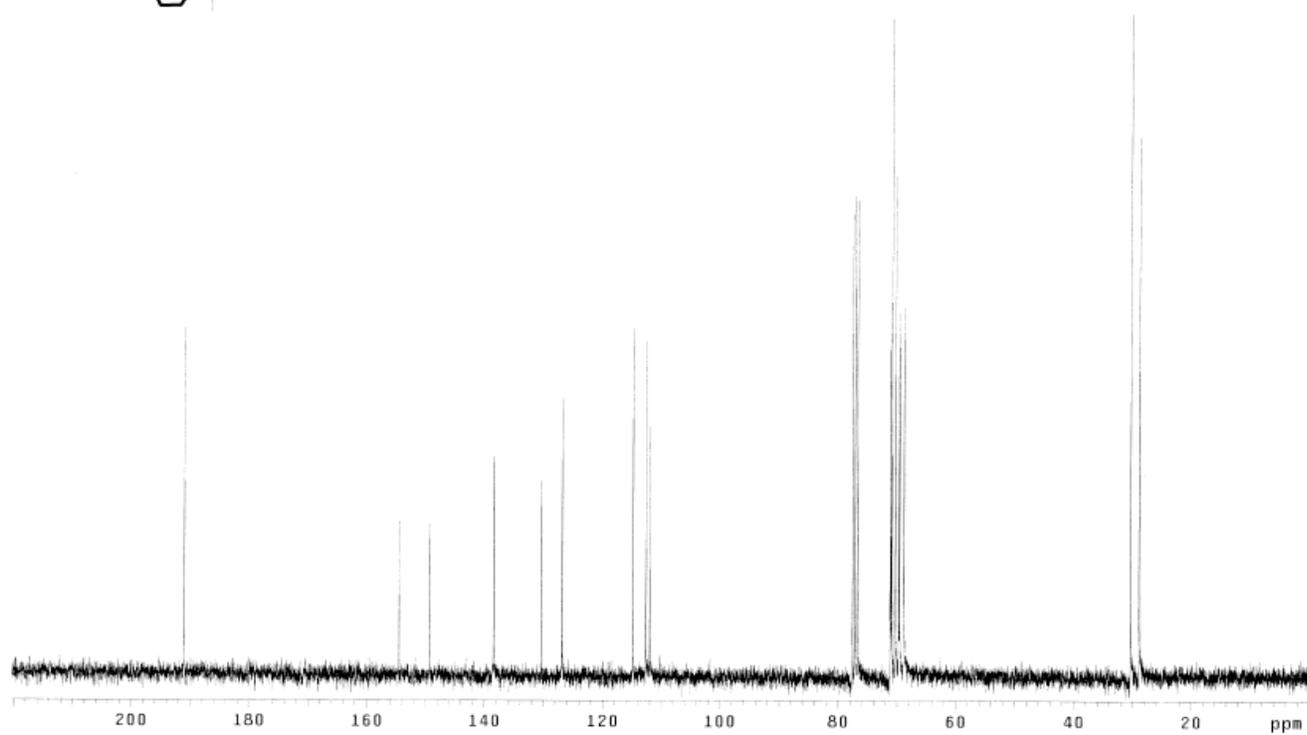
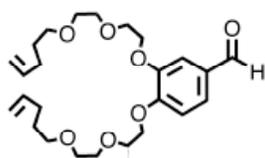
¹H NMR compound **1b**:



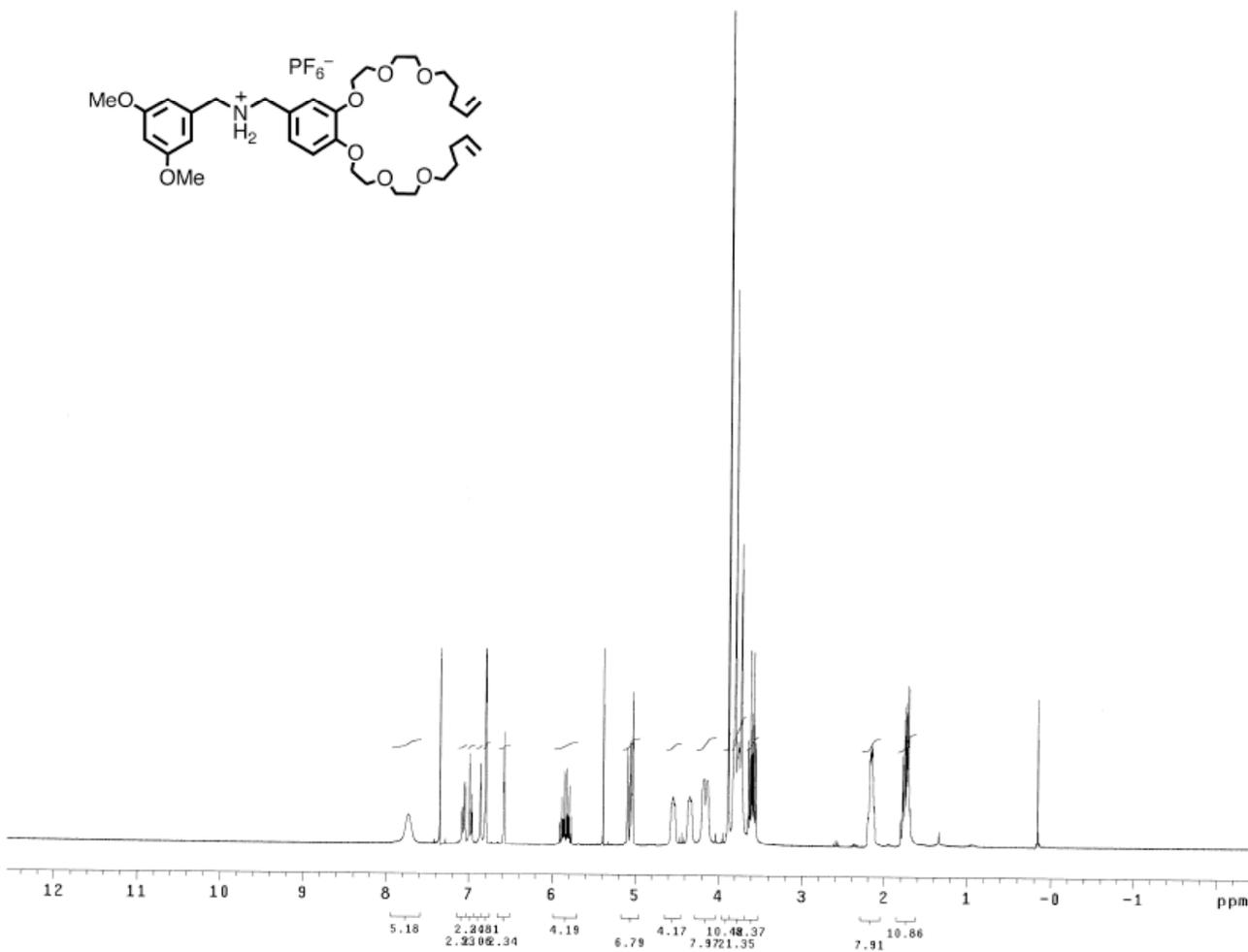
¹H NMR compound **1c**:



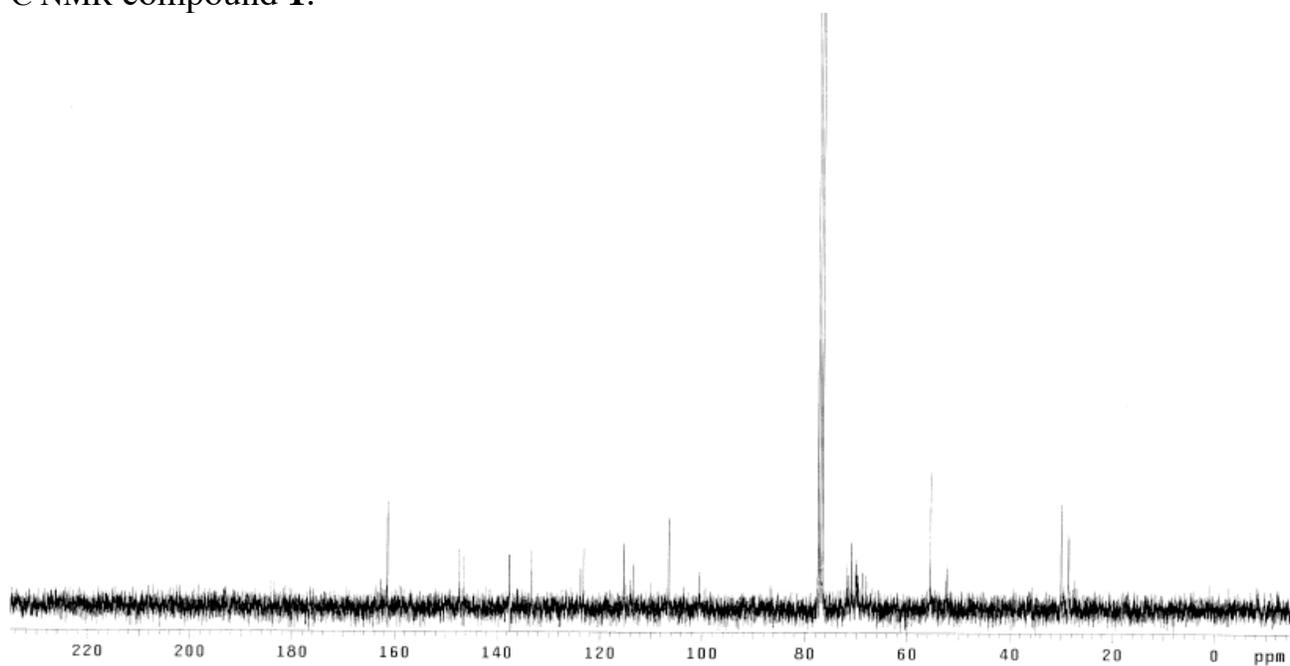
^{13}C NMR compound **1c**:



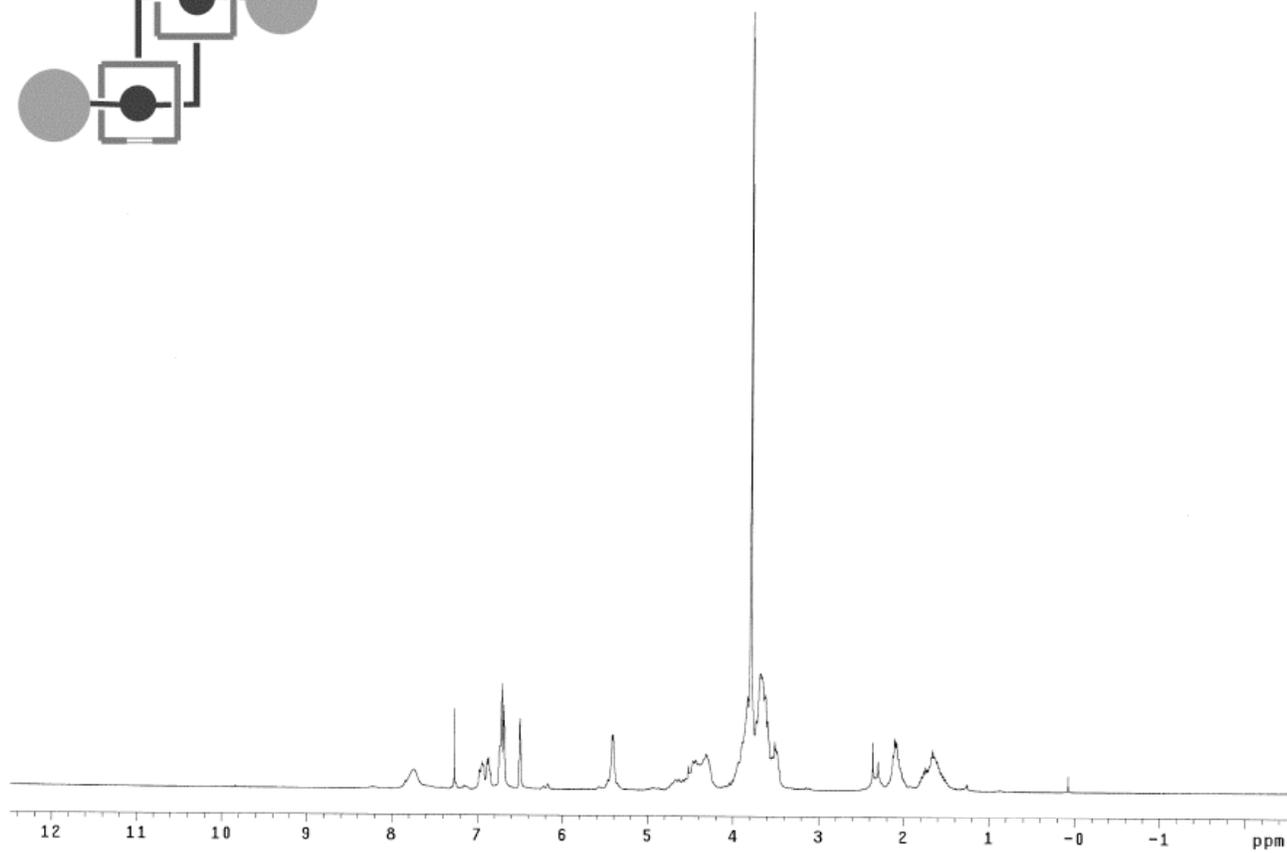
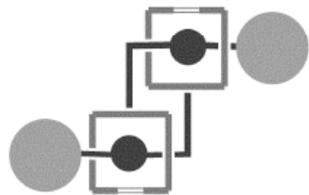
¹H NMR compound 1:



^{13}C NMR compound **1**:

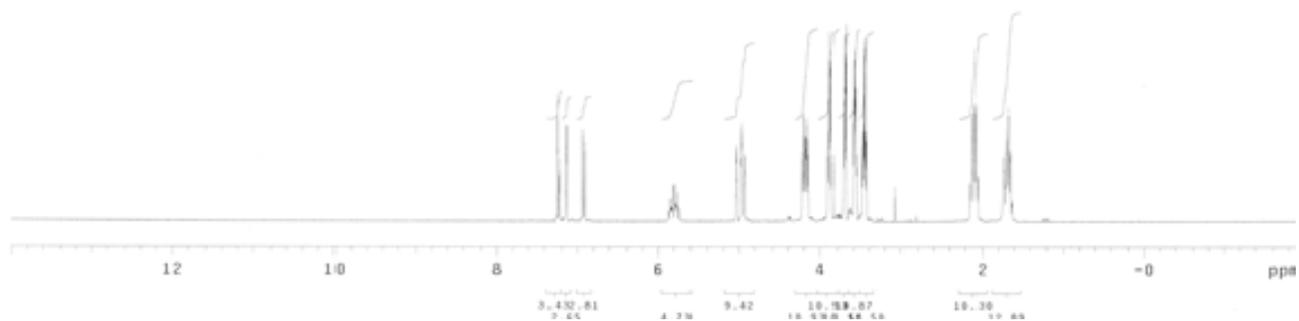
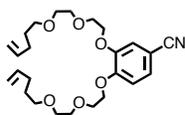


^1H NMR compound **3**:

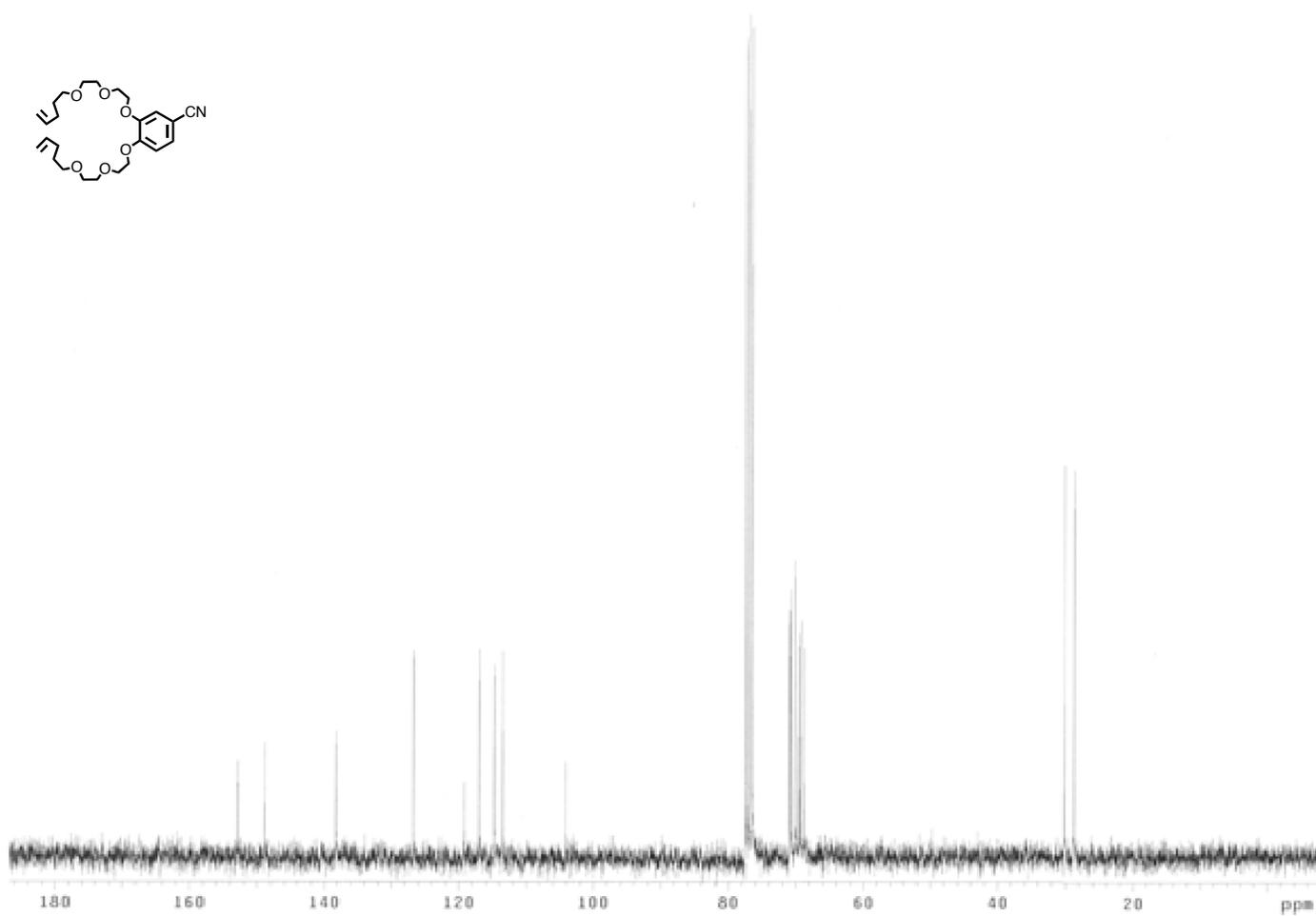
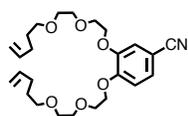


¹H NMR compound **5a**:

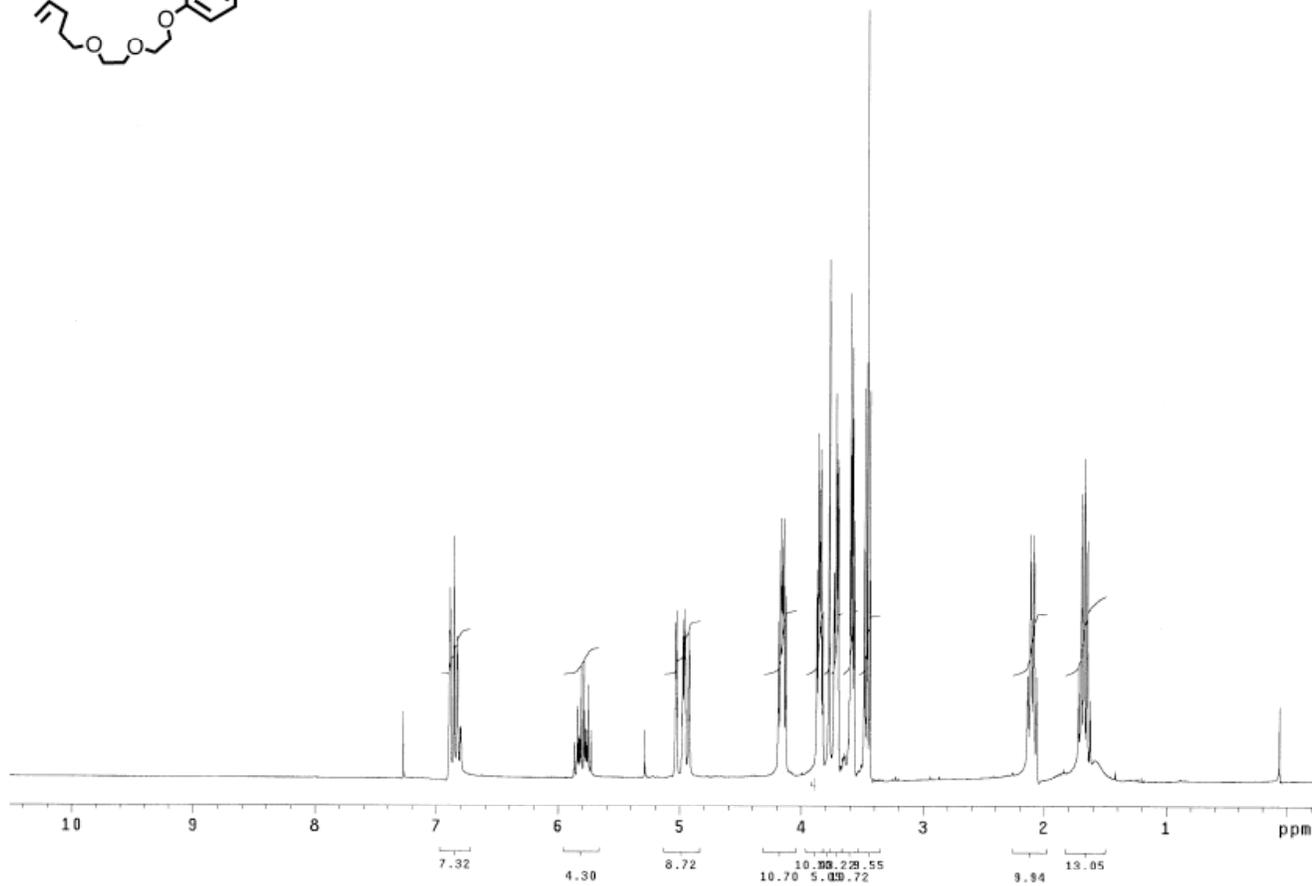
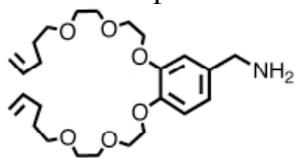
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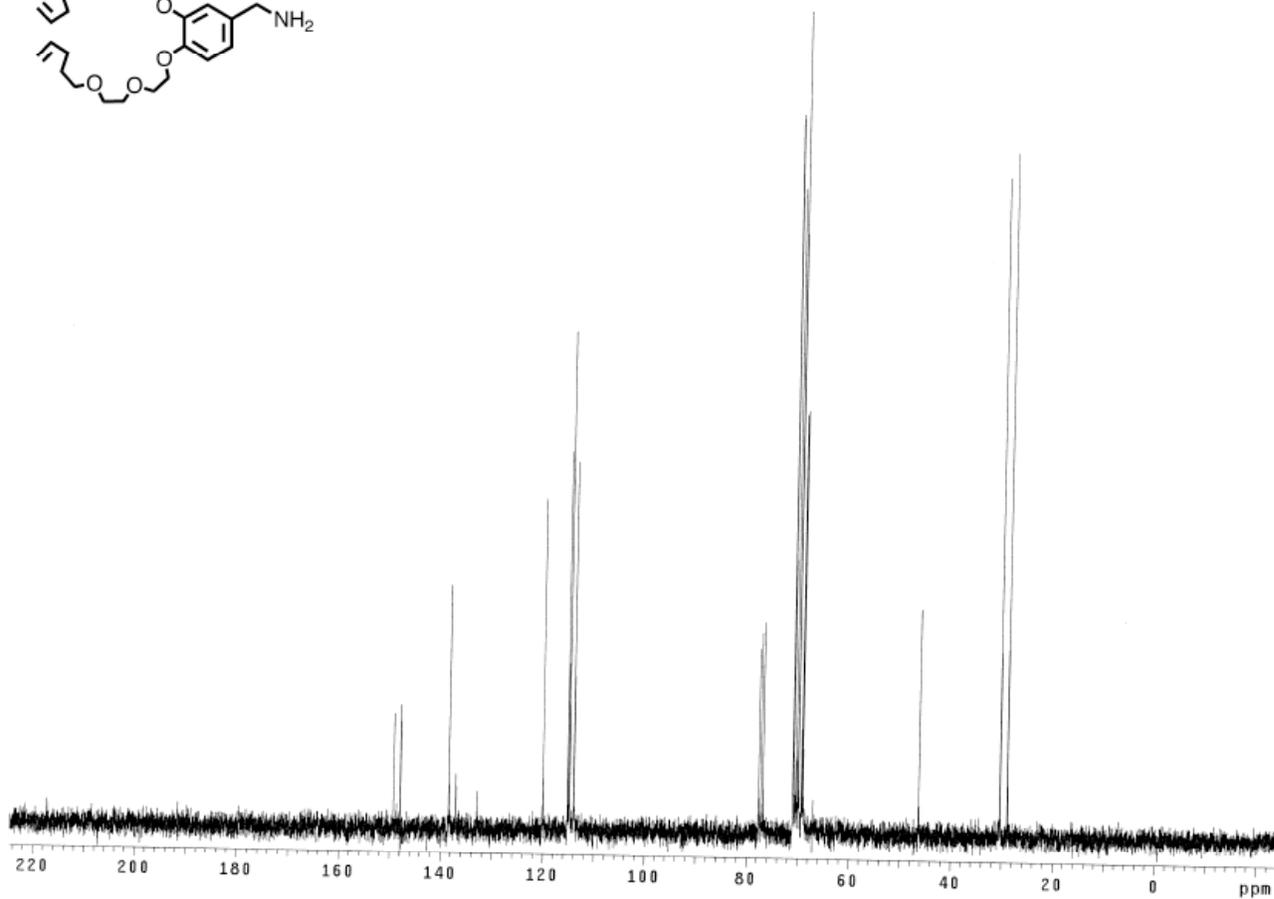
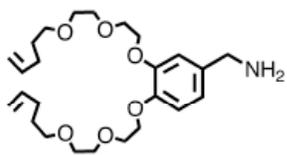
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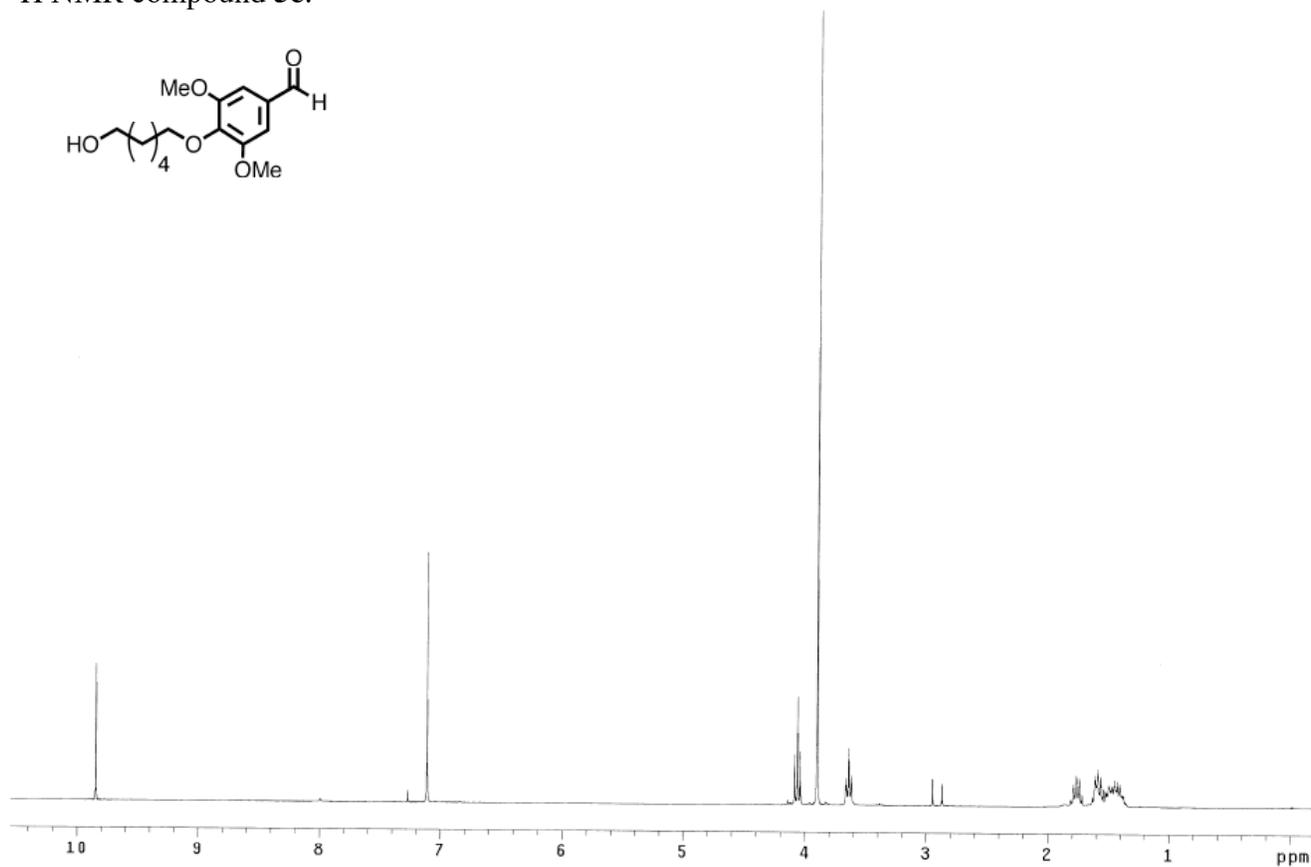
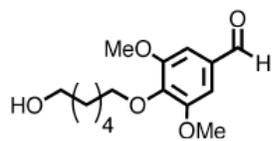
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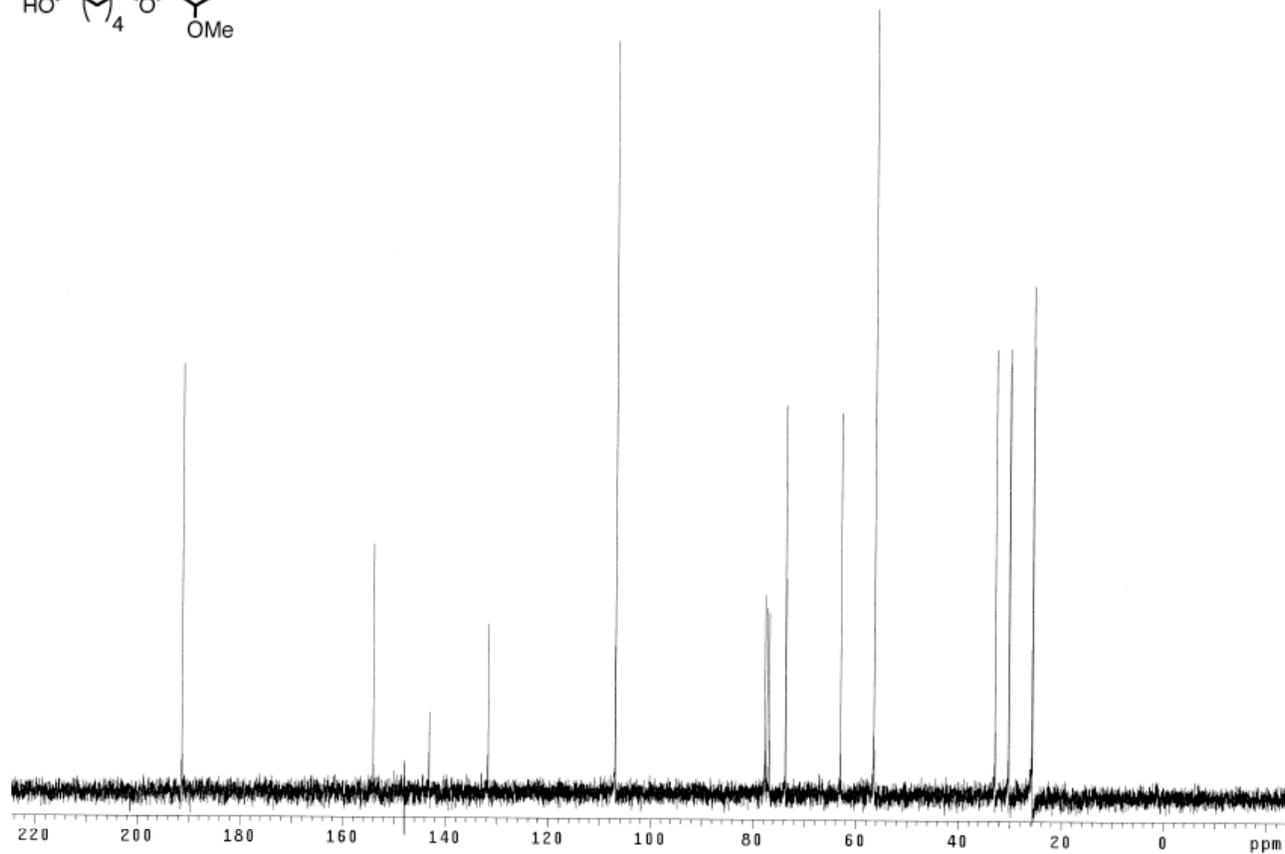
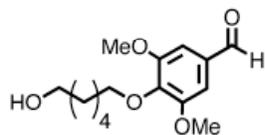
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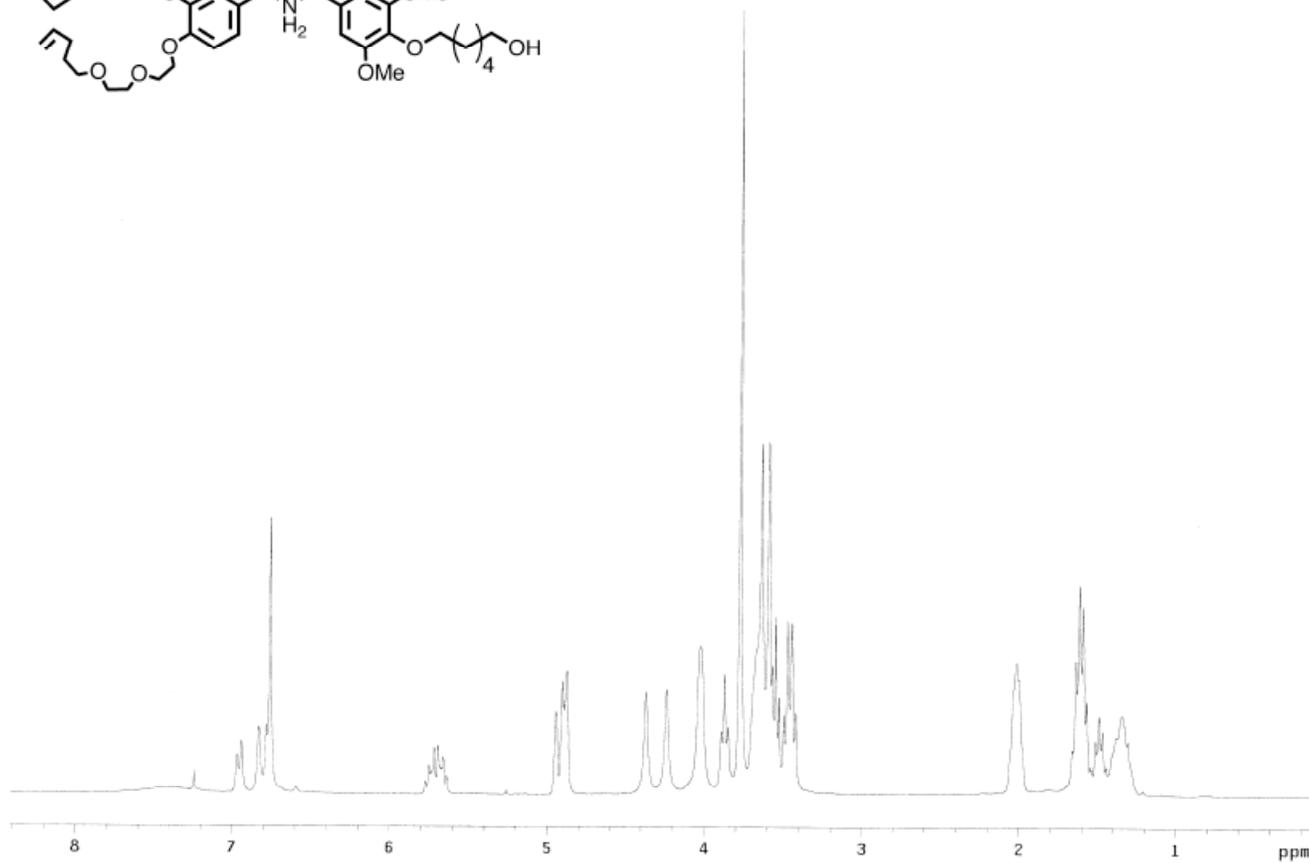
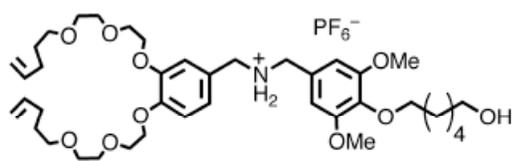
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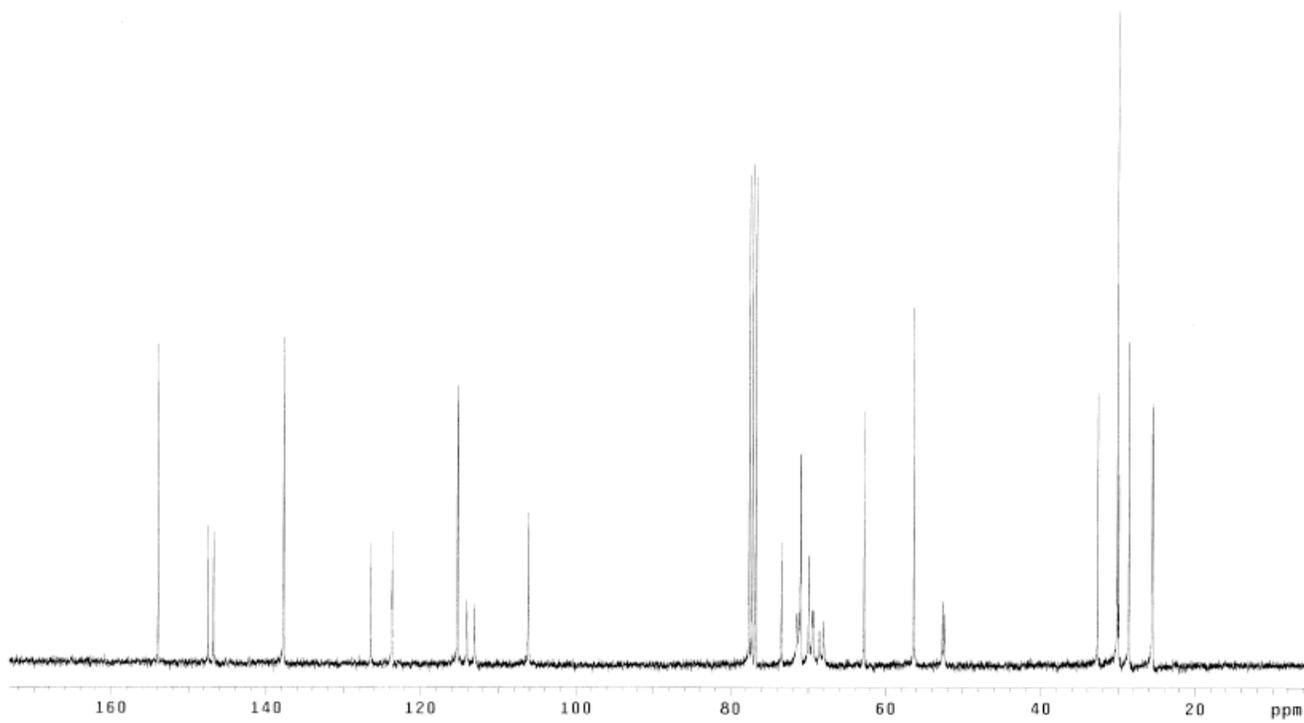
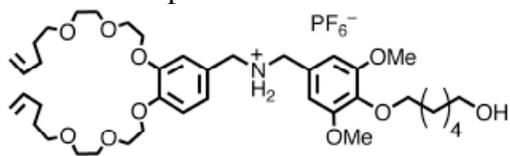
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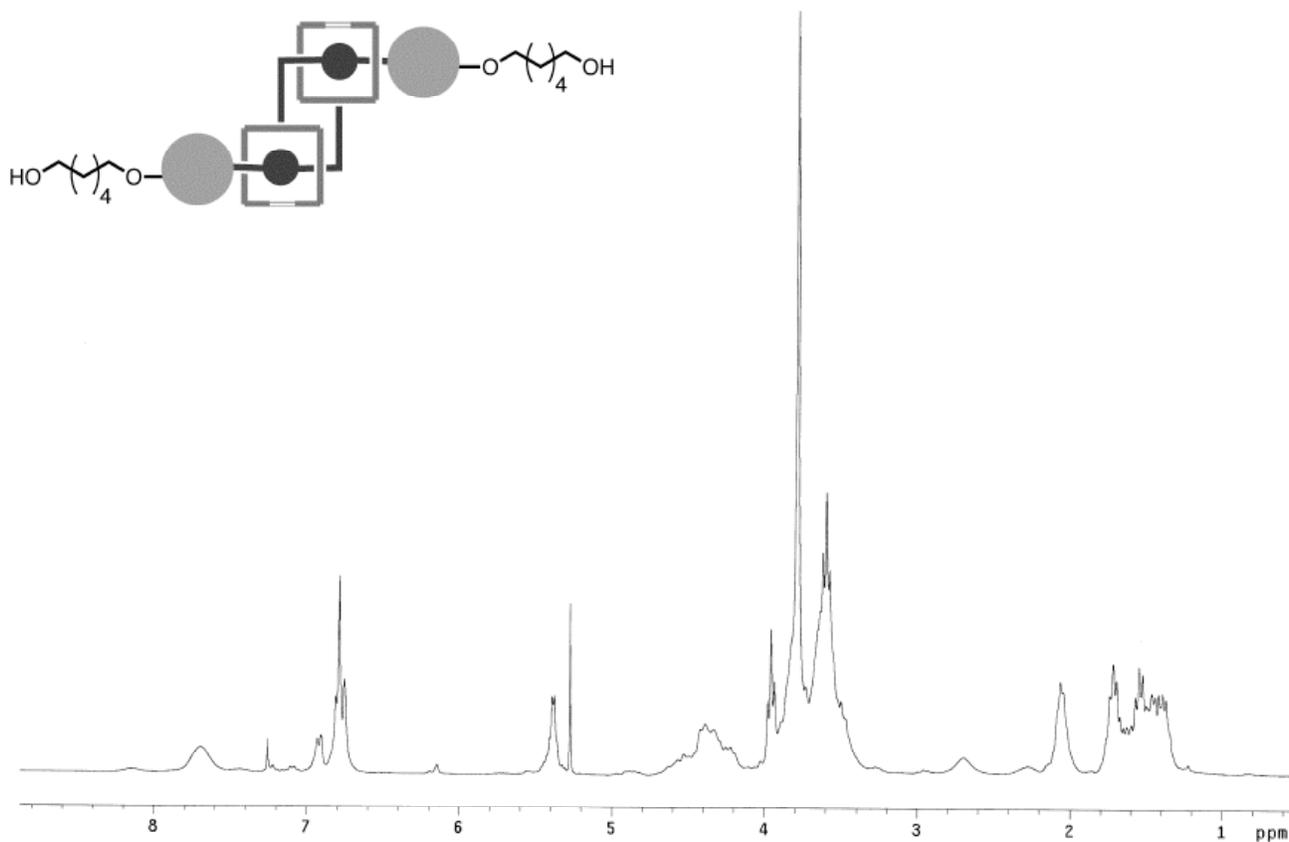
¹H NMR compound **5**:



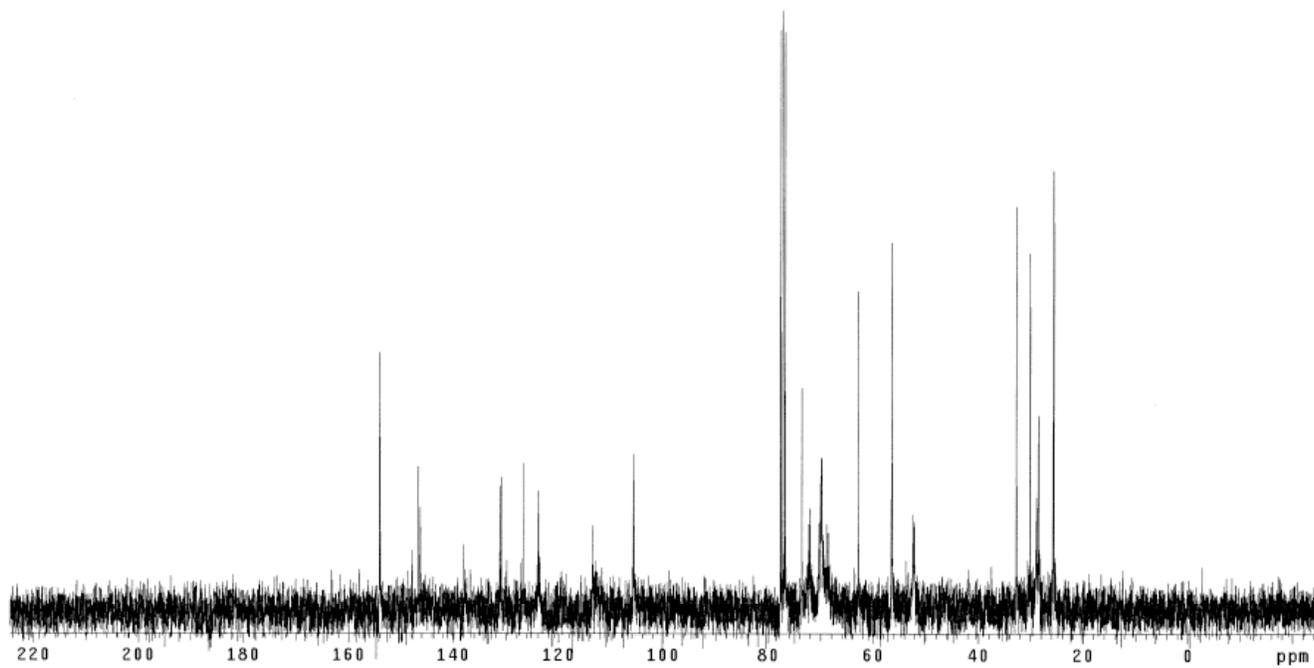
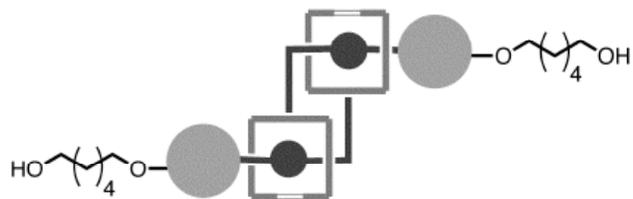
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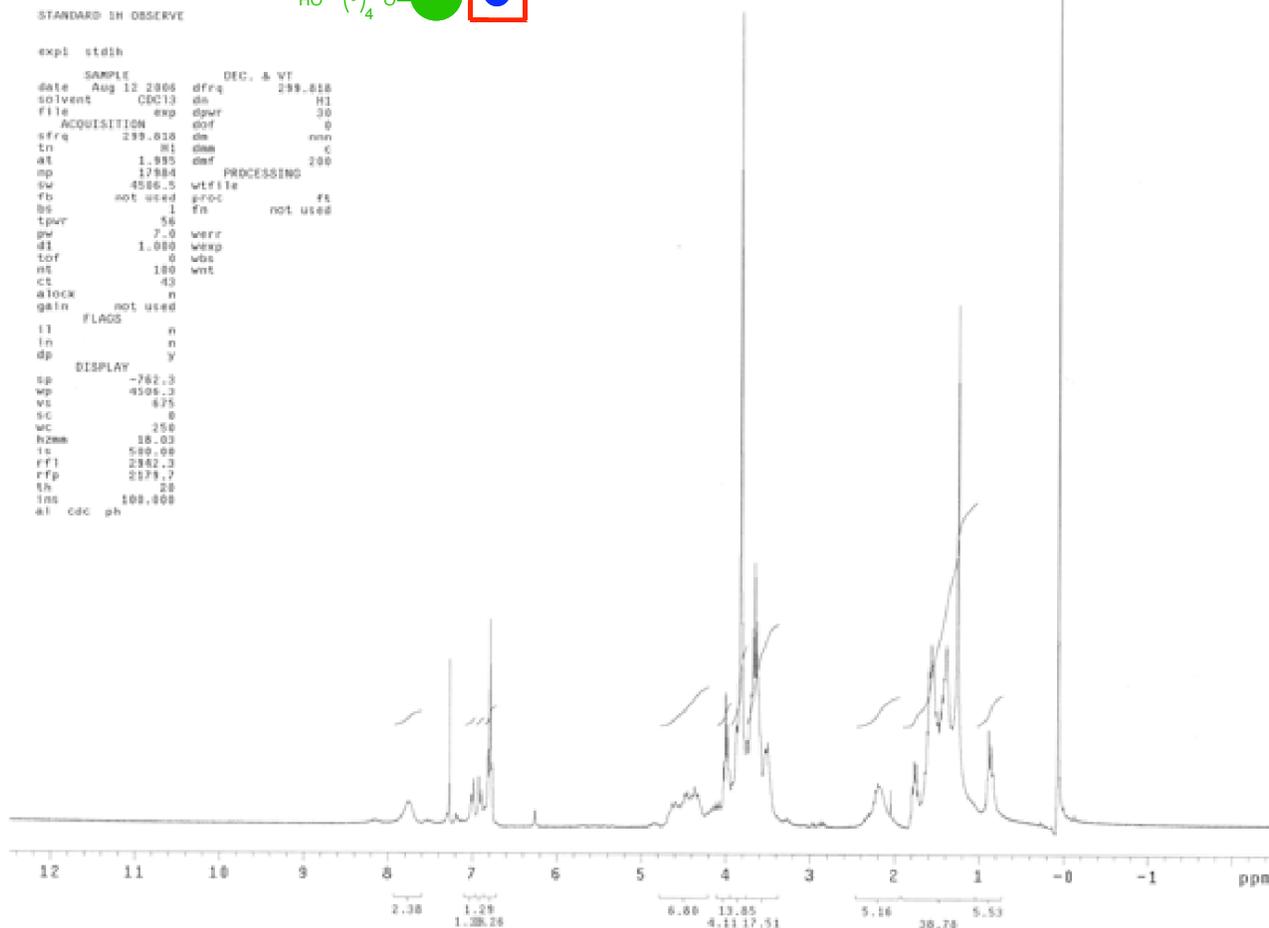
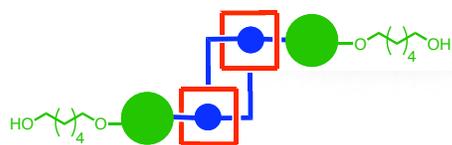
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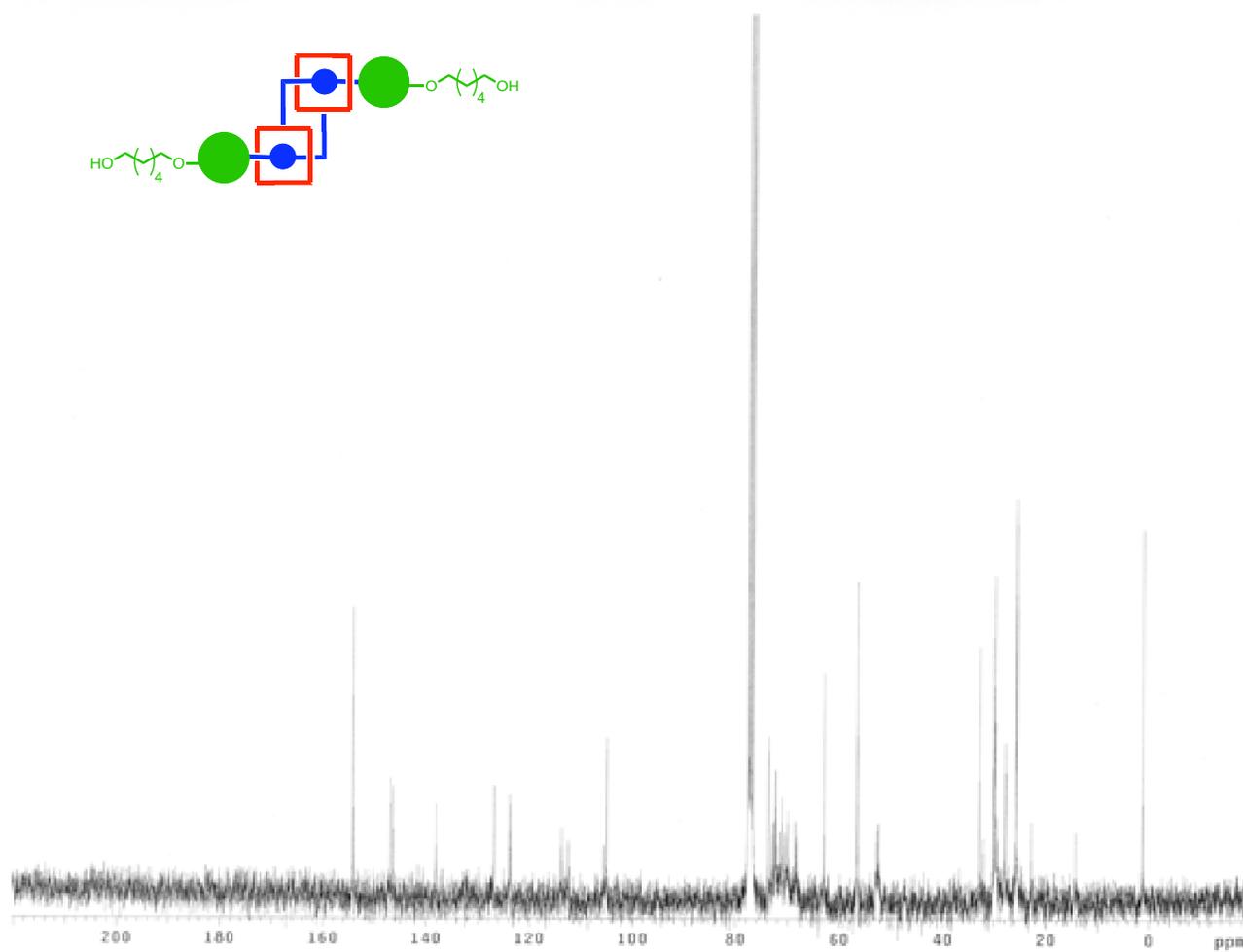
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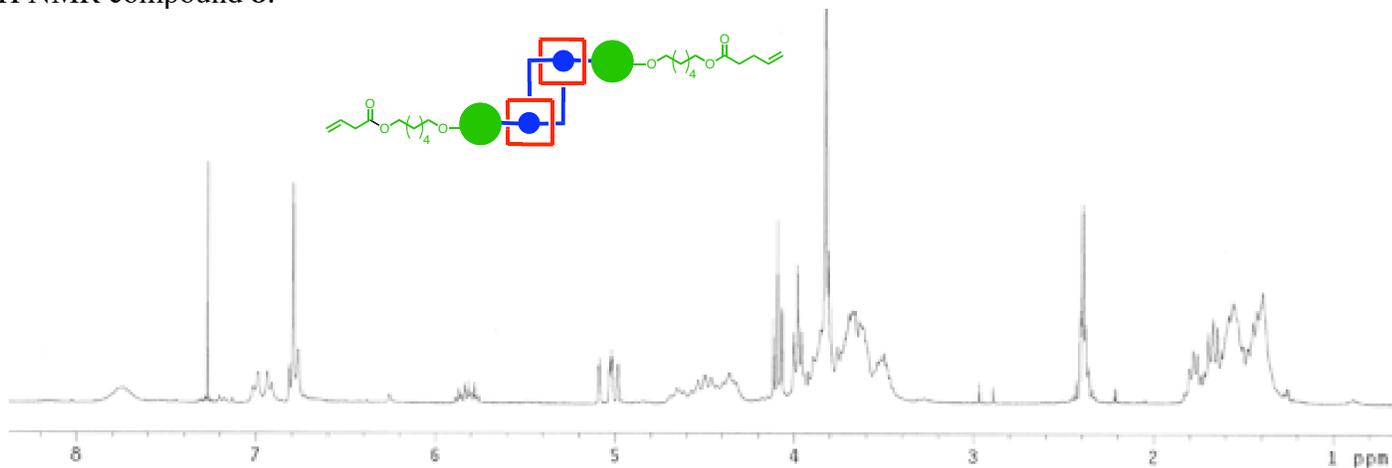
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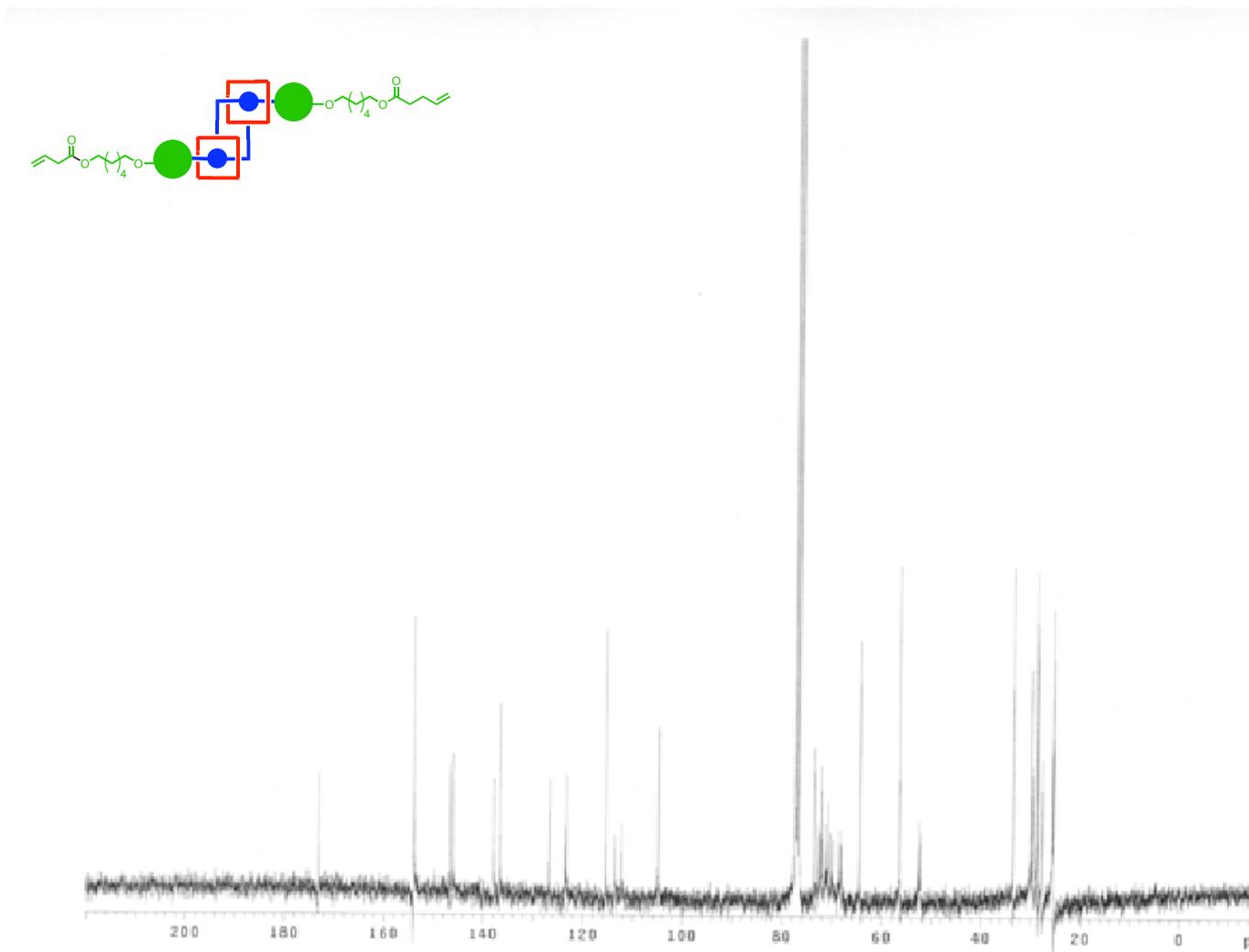
^{13}C NMR compound 7:



^1H NMR compound **8**:



^{13}C NMR compound **8**:

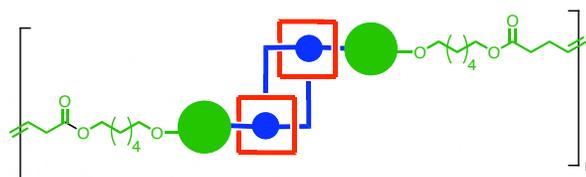


¹H NMR compound 9:

STANDARD PROTON PARAMETERS

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7

