Electronic Supporting Information

Homochiral Self-Sorting of BINOL Macrocycles

Scott W. Sisco and Jeffrey S. Moore

Department of Chemistry, University of Illinois at Urbana-Champaign

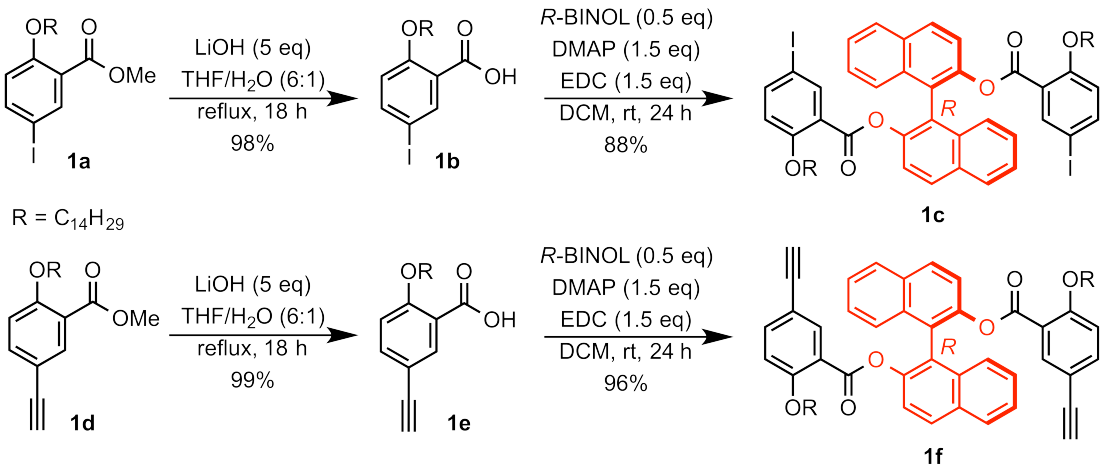
600 South Mathews Avenue, Urbana, Illinois 61801

General. All air or moisture-sensitive manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques or in an argon-filled glove box. Analytical thin-layer chromatography (TLC) was performed on Kieselgel F-254 precoated silica gel plates. Visualization was performed with UV light (254 nm). Flash chromatography was performed using 60 Å silica gel from Silicycle, Inc. Preparative TLC was performed using Kieselgel F-254 precoated silica gel plates (L x W: 20 cm x 20 cm, silica thickness: 1 mm) from Silicycle, Inc. All polymerization and metathesis reactions were prepared in an argon filled glove box and run under an inert atmosphere; the reaction vessels were 20 mL I-CHEM vials fitted with PTFE/Silicone septa purchased from VWR International. All glassware was oven-dried prior to use.

Materials. Unless otherwise stated, all starting materials and reagents were purchased from Sigma-Aldrich and used without further purification. Palladium tetrakis(triphenylphosphine) was purchased from Strem Chemicals, Inc., 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) was purchased from TCI America, and TMS-acetylene was purchased from GFS Chemicals, Inc. The following compounds were prepared according to literature procedures: trisamidomolybdenum (VI) propylidyne[1], (2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)*p*-toluenesulfonate (TgOTs)[2], compounds **1a**, **1d**, and **2a**[3]. Tetrahydrofuran (THF) and toluene was obtained from a Solvent Delivery System (SDS) equipped with activated neutral alumina columns under argon. Dichloromethane (DCM) was dried over 3Å MS and stored under nitrogen.

Characterization & Calculations. ^{1}H and ^{13}C NMR spectra were obtained on Varian Unity 500 MHz, Varian VXR 500 MHz, and Inova 500NB spectrometers. All spectra were recorded in $CDCl_3$. Chemical shifts are reported in δ (ppm) relative to the residual solvent peak ($CDCl_3$: 7.26 for ^{1}H, 77.2 for ^{13}C). Coupling constants (J) are expressed in hertz (Hz). Splitting patterns are designated as: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet), bs (broad singlet), bd (broad doublet), bm (broad multiplet). Low resolution ESI mass spectra were recorded on a Waters Quattro II spectrometer. High resolution ESI mass spectra were recorded on a Micromass Q-TOF Ultima spectrometer. High resolution MALDI mass spectra were recorded on a Bruker Daltonics UltrafleXtreme MALDI TOFTOF spectrometer. FD mass spectra were recorded on a Micromass 70-VSE spectrometer. Analytical gel permeation chromatography (GPC) analyses were performed on a system composed of a Waters 515 HPLC pump, a Thermoseparations Trace series AS100 autosampler, a series of three Waters HR Styragel columns (7.8’ 300 mm, HR3, HR4, and HR5), and a Viscotek TDA Model 300 triple detector array, in HPLC grade THF (flow rate = 1.0 mL/min) at 30°C. The GPC was calibrated using a series of monodisperse polystyrene standards. Molecular modeling, geometry optimization, and frequency calculations were completed using Spartan ‘10 Quantum Mechanics Program (Version 1.1.0; Wavefunction, Inc.) at the RHF level using the 3-21G* basis set.

Synthesis of *R*-P1



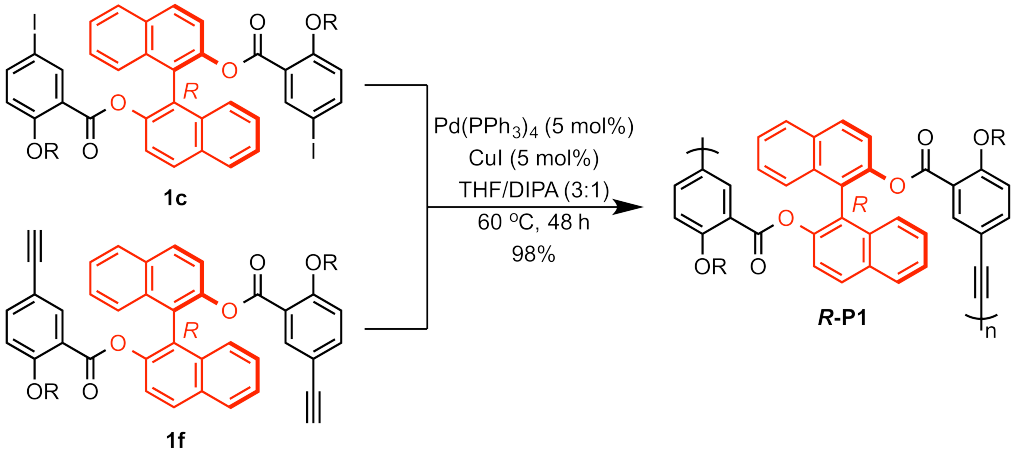
5-iodo-2-tetradecyloxybenzoic acid (1b). In a 200 mL round bottom flask equipped with a reflux condenser, methyl 5-iodo-2-tetradecyloxybenzoate **1a** (1.53 g, 3.22 mmol, 1 eq), LiOH (676 mg, 16.1 mmol, 5 eq), THF (55 mL), and H_2O (9 mL) were combined. The mixture was refluxed for 18 hours after which it was concentrated to remove THF. The residue was diluted with H_2O (20 mL) and acidified to pH = 1 with conc. HCl. The solid was extracted with DCM (4 x 50 mL) then dried over $MgSO_4$ and concentrated to obtain **1b** as a white solid (1.45 g, 3.16 mmol, 98%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 10.8 (s, 1H, CO_2H), 8.46 (d, J = 2.5 Hz, 1H, ArH), 7.81 (dd, J = 2.5, 9.0 Hz, 1H, ArH), 6.81 (d, J = 8.5 Hz, 1H, ArH), 4.22 (t, J = 6.5 Hz, 2H, OCH_2), 1.90 (m, 2H, CH_2), 1.47 (m, 2H, CH_2), 1.25 (bm, 20H, CH_2), 0.87 (t, J = 6.5 Hz, 3H, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.1, 157.5, 143.6, 142.3, 119.7, 115.0, 84.4, 70.80, 32.09, 29.85, 29.81, 29.77, 29.67, 29.58, 29.53, 29.34, 28.98, 25.96, 22.87, 14.31; LR-MS (ESI+): m/z (%): 478.2 (11), 462.2 (19), 461.2 (100), 443.1 (5); HR-MS (ESI+): Calc for $C_{21}H_{33}O_3I$ $(M+H)^+$ 461.1553, Found 461.1563.

(*R*)-[1,1'-binaphthalene]-2,2'-diyl(5-iodo-2-tetradecyloxybenzoate) (1c). In a 100 mL round bottom flask, 5-iodo-2-tetradecyloxybenzoic acid **1b** (920.5 mg, 2 mmol, 1 eq), (*R*)-(+)-1,1'-bi(2-naphthol) (286.5 mg, 1 mmol, 0.5 eq), 4-dimethylaminopyridine (DMAP) (366.5 mg, 3 mmol, 1.5 eq), and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (576 mg, 3 mmol, 1.5 eq) were dissolved in 20 mL DCM. The mixture was stirred at room temperature for 24 hours under N_2. After 24 hours, the mixture was diluted with DCM (20 mL) and washed with a saturated aqueous $NaHCO_3$ solution (50 mL). The organic layer was dried over $MgSO_4$ then concentrated to a light yellow oil. Purified by column chromatography [silica gel, hexane then ethyl acetate (AcOEt) /hexane 5:95] to obtain **1c** as a sticky colorless solid (1.03 g, 0.88 mmol, 88%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.07 (d, J = 9 Hz, 2H, ArH), 7.96 (d, J = 8 Hz, 2H, ArH), 7.63 (d, J = 9 Hz, 2H, ArH), 7.50 (dd, J = 2.5, 8.5 Hz, 2H, ArH), 7.46 (t, J = 7.0 Hz, 2H, ArH), 7.40 (d, J = 8.0 Hz, 2H, ArH), 7.32 (t, J = 7.0 Hz, 2H, ArH), 6.98 (d, J = 2.5 Hz, 2H, ArH), 6.52 (d, J = 9.0 Hz, 2H, ArH), 3.81 (m, 4H, OCH_2), 1.65 (m, 4H, CH_2), 1.25 (bm, 44H, CH_2), 0.89 (t, J = 7.0 Hz, 6H, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 162.2, 158.7, 147.0, 142.0, 139.7, 133.5, 131.7, 130.0, 128.4, 127.1, 126.2, 126.0, 123.8, 122.2, 121.6, 115.2, 81.35,

69.22, 32.11, 29.90, 19.88, 29.87, 29.73, 29.56, 29.48, 28.96, 25.94, 22.88, 14.32; LR-MS (ESI+): m/z (%): 1231.4 (23), 1230.4 (35), 1194.4 (52), 1193.4 (75), 1171.4 (100); HR-MS (ESI+): Calc for $C_{62}H_{76}O_6I_2$ $(M+H)^+$ 1171.3794, Found 1171.3810.

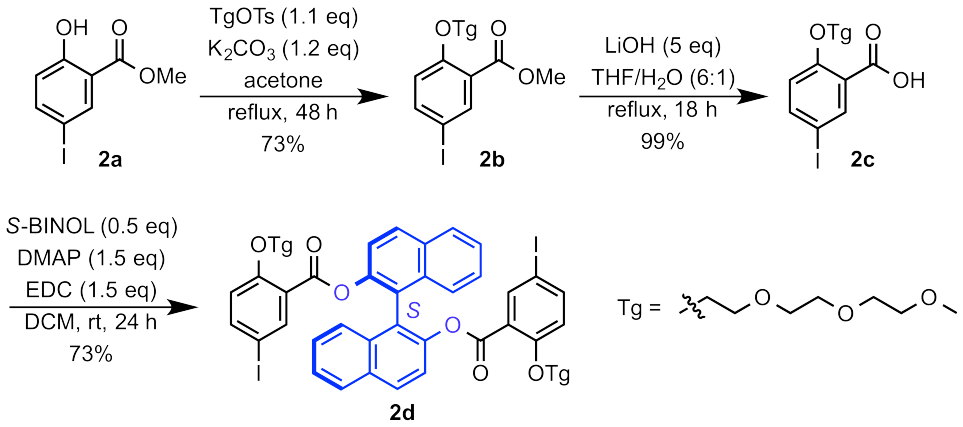
5-ethynyl-2-tetradecyloxybenzoic acid (1e). In a 200 mL round bottom flask equipped with a reflux condenser, methyl 5-ethynyl-2-tetradecyloxybenzoate **1d** (1.60 g, 4.29 mmol, 1 eq), LiOH (902.5 mg, 21.5 mmol, 5 eq), THF (72 mL), and H_2O (12 mL) were combined. The mixture was refluxed for 18 hours after which it was concentrated to remove THF. The residue was diluted with H_2O (20 mL) and acidified to pH = 1 with conc. HCl. The solid was extracted with DCM (4 x 50 mL) then dried over $MgSO_4$ and concentrated to obtain **1e** as a white solid (1.51 g, 4.23 mmol, 99%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 10.9 (s, 1H, CO_2H), 8.28 (d, J = 2 Hz, 1H, ArH), 7.62 (dd, J = 1.5 , 7.5 Hz, 1H, ArH), 6.98 (d, J = 9 Hz, 1H, ArH), 4.23 (t, J = 6.5 Hz, 1H, OCH_2), 3.05 (s, 1H, CCH), 1.90 (m, 2H, CH_2), 1.47 (m, 2H, CH_2), 1.24 (bm, 20H, CH_2), 0.86 (t, J = 6.5 Hz, 3H, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.9, 157.8, 138.4, 137.7, 118.0, 116.3, 112.9, 81.87, 77.69, 70.70, 32.07, 29.83, 29.79, 29.75, 29.66, 29.56, 29.50, 29.33, 28.97, 25.95, 22.84, 14.27; LR-MS (ESI+): m/z (%): 360.3 (19), 359.3 (76), 342.3 (23), 341.2 (100), 338.3 (29), 163.0 (59); HR-MS (ESI+): Calc for $C_{23}H_{34}O_3$ $(M+H)^+$ 359.2586, Found 359.2591.

(*R*)-[1,1'-binaphthalene]-2,2'-diyl(5-ethynyl-2-tetradecyloxybenzoate) (1f). In a 100 mL round bottom flask, 5-ethynyl-2-tetradecyloxybenzoic acid **1e** (592 mg, 1.65 mmol, 1 eq), (*R*)-(+)-1,1'-bi(2-naphthol) (236 mg, 0.825 mmol, 0.5 eq), DMAP (303 mg, 2.48 mmol, 1.5 eq), and EDC (475 mg, 2.48 mmol, 1.5 eq) were dissolved in 17 mL DCM. The mixture was stirred at room temperature for 24 hours under N_2. After 24 hours, the mixture was diluted with DCM (20 mL) and washed with a saturated aqueous $NaHCO_3$ solution (50 mL). The organic layer was dried over $MgSO_4$ then concentrated to a light yellow oil. Purified by column chromatography [silica gel, DCM/hexane 1:3 then DCM/hexane 1:1] to obtain **1f** as a sticky colorless solid (764 mg, 0.79 mmol, 96%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.02 (d, J = 8.5 Hz, 2H, ArH), 7.92 (d, J = 8.0 Hz, 2H, ArH), 7.60 (d, J = 9.0 Hz, 2H, ArH), 7.44 (t, J = 8.0 Hz, 2H, ArH), 7.40 (d, J = 9.0 Hz, 2H, ArH), 7.37 (dd, J = 2.0, 8.5 Hz, 2H, ArH), 7.31 (t, J = 7.5 Hz, 2H, ArH), 6.99 (d, J = 2.0 Hz, 2H, ArH), 6.70 (d, J = 9.0 Hz, 2H, ArH), 3.83 (m, 4H, OCH_2), 2.95 (s, 2H, CCH), 1.64 (m, 4H, CH_2), 1.25 (bm, 44H, CH_2), 0.89 (t, J = 7.0 Hz, 6H, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 163.0, 159.1, 147.1, 137.1, 135.6, 133.5, 131.7, 129.8, 128.2, 126.9, 126.3, 125.8, 123.9, 122.2, 119.7, 113.6, 112.8, 82.64, 76.28, 69.10, 32.10, 29.89, 29.88, 29.86, 29.84, 29.80, 29.72, 29.55, 29.47, 28.94, 25.92, 22.87, 14.31; LR-MS (ESI+): m/z (%): 1094.1 (29), 1093.1 (54), 991.6 (25), 990.6 (69), 989.6 (100), 967.6 (21); HR-MS (ESI+): Calc for $C_{66}H_{78}O_6$ $(M+H)^+$ 967.5881, Found 967.5877.



***R*-P1.** In a glovebox, a 20 mL vial was charged with *R*-diiodo monomer **1c** (849 mg, 0.725 mmol, 1 eq), *R*-diethynyl monomer **1f** (701 mg, 0.725 mmol, 1 eq), CuI (6.9 mg, 0.036 mmol, 0.05 eq), and $Pd(PPh_3)_4$ (41.6 mg, 0.036 mmol, 0.05 eq). The solids were dissolved in THF (3 mL) and diisopropylamine (DIPA) (1 mL). The vial was sealed with tape and heated at 60 °C for 48 hours. After 48 hours, the solvent was removed and the solid dissolved in minimal $CHCl_3$. This polymer solution was slowly added to rapidly stirring methanol (400 mL) to obtain ***R*-P1** as a yellow solid (1.44 g, 98%). GPC (THF): Mn = 25 kDa, Mw = 50 kDa, PDI = 2.0, Ret. Volume = 24-31 mL; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.97 (bm, 2H, ArH), 7.82 (bm, 2H, ArH), 7.44-7.30 (bm, 8H, ArH), 6.98 (bs, 2H, ArH), 6.71 (bm, 2H, ArH), 3.83-3.65 (bm, 4H, OCH_2), 1.62-1.58 (bm, 4H, CH_2), 1.25 (bm, 44H, CH_2), 0.88 (bm, 6H, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 163.3, 163.3, 158.9, 158.6, 147.3, 147.2, 136.5, 136.3, 135.7, 134.9, 133.7, 133.6, 131.7, 131.7, 129.8, 129.7, 128.3, 128.0, 126.9, 126.7, 126.2, 125.8, 125.6, 124.0, 123.9, 122.3, 122.1, 119.8, 119.6, 115.1, 115.1, 113.2, 112.9, 87.63, 87.37, 69.09, 48.70, 32.09, 29.89, 29.85, 29.82, 29.80, 29.77, 29.55, 29.53, 29.51, 29.00, 25.95, 22.85, 19.22, 14.29.

Synthesis of *S*-P2

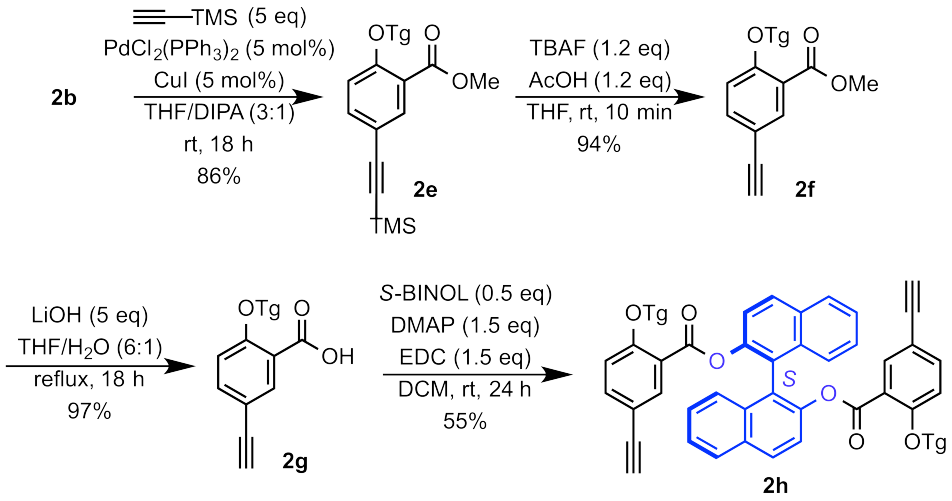


Methyl 5-iodo-2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoate (2b). In a 200 mL round bottom flask equipped with a reflux condenser, methyl 2-hydroxy-5-iodobenzoate **2a** (4.5 g, 16.2 mmol, 1 eq), (2-(2-(2-methoxyethoxy)ethoxy)ethoxy)*p*-toluenesulfonate (TgOTs) (5.67 g, 17.8 mmol, 1.1 eq), K_2CO_3 (2.68 g, 19.4 mmol, 1.2 eq), NaI (243 mg, 1.62 mmol, 0.1 eq) and acetone (80 mL) were combined. The mixture was refluxed for 48 hours under N_2, after which it was concentrated to remove acetone. The residue was diluted with DCM (50 mL) and washed with brine (40 mL). The organic layer was dried over $MgSO_4$ and then concentrated to obtain a light yellow oil. Purified by column chromatography [silica gel, gradient from 1:2 AcOEt/hexane to 3:1 AcOEt/hexane] to obtain **2b** as a pale yellow oil (5.01 g, 11.8 mmol, 73%) containing 10% unreacted TgOTs (382 mg, 1.2 mmol). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 2.5 Hz, 1H, ArH), 7.61 (dd, J = 2.5, 8.5 Hz, 1H, ArH), 6.70 (dd, J = 2.0, 9.0 Hz, 1H, ArH), 4.10 (t, J = 5.0 Hz, 2H, OCH_2), 3.81 (d, J = 5.0 Hz, 2H, OCH_2), 3.80 (s, 3H, OCH_3), 3.69 (t, J = 5.0 Hz, 2H, OCH_2), 3.58 (m, 4H, OCH_2), 3.47 (t, J = 4.5 Hz, 2H, OCH_2), 3.30 (s, 3H, OCH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 165.1, 158.2, 141.8, 139.9, 112.9, 116.2, 82.19, 71.91, 70.98, 70.72, 70.66, 70.51, 69.46, 69.22, 69.17, 68.65, 58.98, 52.10; LR-MS (ESI+): m/z (%): 448 (12), 447 (100), 425 (26), 393 (33), 147.1 (12), 103.1 (45); HR-MS (ESI+): Calc for $C_{15}H_{21}O_6I$ $(M+Na)^+$ 447.0269, Found 447.0281.

5-iodo-2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoic acid (2c). In a 200 mL round bottom flask equipped with a reflux condenser, methyl 5-iodo-2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoate **2b** (containing 10% unreacted TgOTs) (1.6 g, 3.77 mmol, 1 eq), LiOH (793 mg, 18.9 mmol, 5 eq), THF (64 mL), and H_2O (11 mL) were combined. The mixture was refluxed for 18 hours after which it was concentrated to remove THF. The residue was diluted with H_2O (20 mL) and acidified to pH = 1 with conc. HCl. The solid was extracted with DCM (4 x 50 mL) then dried over $MgSO_4$ and concentrated to obtain **2c** as a sticky colorless solid (1.53 g, 3.73 mmol, 99%) containing 7% unreacted TgOTs (83 mg, 0.27 mmol). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.33 (bs, 1H, CO_2H), 8.33 (d, J = 2.5 Hz, 1H, ArH), 7.74 (dd, J = 2.0, 8.5 Hz, 1H, ArH), 6.78 (d, J = 9.0 Hz, 1H, ArH), 4.30 (t, J = 4.5 Hz, 2H, OCH_2), 3.87 (t, J = 4.5 Hz, 2H, OCH_2), 3.69 (m, 2H, OCH_2), 3.63 (m, 2H, OCH_2), 3.60 (m, 2H, OCH_2), 3.50 (m, 2H, OCH_2), 3.33 (s, 3H, OCH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.4, 157.3, 143.1, 141.8, 121.0, 115.9, 84.57, 71.94, 70.83, 70.61, 70.58, 69.54, 68.63, 59.03; LR-MS (ESI+): m/z (%): 434 (12), 433 (100), 411 (15), 393 (21), 103.1 (19); HR-MS (ESI+): Calc for $C_{14}H_{19}O_6I$ $(M+Na)^+$ 433.0110, Found 433.0124.

(*S*)-[1,1'-binaphthalene]-2,2'-diyl(5-iodo-2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy) benzoate) (2d). In a 100 mL round bottom flask, **2c** (containing 7% unreacted TgOTs) (967 mg, 2.36 mmol, 1 eq), (*S*)-(-)-1,1'-bi(2-naphthol) (338 mg, 1.18 mmol, 0.5 eq), DMAP (432.5 mg, 3.54 mmol, 1.5 eq), and EDC (678 mg, 3.54 mmol, 1.5 eq) were dissolved in 23.5 mL DCM. The mixture was stirred at room temperature for 24 hours under N_2. After 24 hours, the mixture was diluted with DCM (20 mL) and washed with a saturated aqueous $NaHCO_3$ solution (50 mL). The organic layer was dried over MgSO4 then concentrated to a light yellow oil. Purified by column chromatography [silica gel, acetone/DCM 1:9, acetone/DCM 1:4, then acetone/DCM 1:2] to obtain **2d** as a sticky colorless solid (916 mg, 0.856 mmol, 73%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.06 (d, J = 9.0 Hz, 2H, ArH), 7.96 (d, J = 8.0 Hz, 2H,

ArH), 7.61 (d, J = 9.0 Hz, 2H, ArH), 7.52 (dd, J = 2.0, 8.5 Hz, 2H, ArH), 7.47 (t, J = 7.5 Hz, 2H, ArH), 7.38 (d, J = 8.0 Hz, 2H ArH), 7.32 (t, J = 7.5 Hz, 2H, ArH), 6.98 (d, J = 2.0 Hz, 2H, ArH), 6.60 (d, J = 9.0 Hz, 2H, ArH), 3.96 (m, 4H, OCH_2), 3.68 (t, J = 5.0 Hz, 4H OCH_2), 3.64 (m, 4H, OCH_2), 3.59 (m, 8H, OCH_2), 3.50 (m, 4H, OCH_2), 3.34 (s, 6H, OCH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 162.0, 158.7, 147.0, 142.2, 139.8, 133.5, 131.71, 130.0, 128.4, 127.1, 126.2, 126.0, 123.8, 122.2, 116.3, 82.18, 72.07, 71.08, 70.78, 70.64, 69.48, 69.30, 59.16; LR-MS (ESI+): m/z (%): 1095.1 (14), 1094.1 (51), 1093.1 (100), 1089.2 (30), 1088.2 (59), 1072.1 (23), 1071.1 (48); HR-MS (ESI+): Calc for $C_{48}H_{48}O_{12}I_2$ $(M+H)^+$ 1071.1323, Found 1071.1314.



Methyl 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-(trimethylsilyl)ethynylbenzoate (2e). In a 100 mL Schlenk flask, CuI (42.8 mg, 0.225 mmol, 0.05 eq) and $PdCl_2(PPh_3)_2$ (158 mg, 0.225 mmol, 0.05 eq) were added and then sealed with a septa. The flask was evacuated and refilled with N_2 three times. Next, a solution of methyl 5-iodo-2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoate **2b** (containing 10% unreacted TgOTs) (1.921 g, 4.87 mmol, 1 eq) in THF (18 mL) was added via syringe followed by DIPA (6 mL) and trimethylsilylacetylene (3.2 mL, 22.5 mmol, 5 eq). The mixture was stirred at room temperature for 18 hours after which it was filtered through a short pad of silica. The resulting solution was concentrated to a dark brown oil. Purified by column chromatography [silica gel, gradient from 1:4 AcOEt/hexane to 4:1 AcOEt/hexane] to obtain **2e** as a light brown oil (1.65 g, 4.18 mmol, 86%) containing 15% unreacted TgOTs (199 mg, 0.625 mmol). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.88 (d, J = 2.5 Hz, 1H, ArH), 7.50 (dd, J = 2.0, 8.5 Hz, 1H, ArH), 6.88 (d, J = 8.5 Hz, 1H, ArH), 4.17 (t, J = 5.0 Hz, 2H, OCH_2), 3.87 (t, J = 6.0 Hz, 2H, OCH_2), 3.84 (s, 3H, OCH_3), 3.74 (t, J = 4.5 Hz, 2H, OCH_2), 3.62 (m, 4H, OCH_2), 3.51 (t, J = 4.5 Hz, 2H, OCH_2), 3.34 (s, 3H, OCH_3), 0.21 (s, 9H, $SiCH_3$); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 165.9, 158.4, 136.8, 135.6, 120.8, 115.6, 113.6, 104.0, 93.69, 72.06, 71.15, 70.81, 70.65, 69.59, 69.33, 69.09, 59.11, 52.09, 0.075; LR-MS (ESI+): m/z (%): 417.2 (100), 395.2 (77), 364.2 (14), 363.2 (64), 103.1 (55); HR-MS (ESI+): Calc for $C_{20}H_{30}O_6Si$ $(M+H)^+$ 395.1890, Found 395.1877.

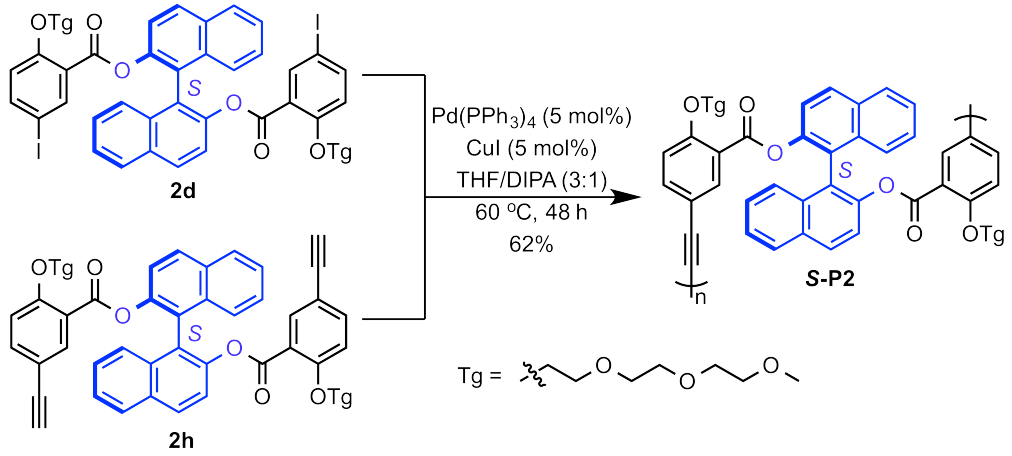
Methyl 5-ethynyl-2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoate (2f). In a 200 mL round bottom flask, **2e** (containing 15% TgOTs) (1.61 g, 4.07 mmol, 1 eq) was dissolved in THF (80 mL). Next, tetrabutylammonium fluoride (4.9 mL, 4.9 mmol, 1.2 eq) and acetic acid (0.28 mL, 4.85 mmol, 1.2 eq)

were added via syringe. After stirring for 10 minutes at room temperature, the solution was concentrated to a yellow oil. Purified by column chromatography [silica gel, 1:1 AcOEt/hexane, 3:1 AcOEt/hexane, then 6:1 AcOEt/hexane] to obtain **2f** as a light brown oil (1.23 g, 3.82 mmol, 94%) containing 15% unreacted TgOTs (182 mg, 0.57 mmol). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.84 (d, J = 2.5 Hz, 1H, ArH), 7.47 (dd, J = 2.0, 8.5 Hz, 1H, ArH), 6.87 (d, J = 9.0 Hz, 1H, ArH), 4.14 (t, J = 5.0 Hz, 2H, OCH_2), 3.83 (t, J = 4.5 Hz, 2H, OCH_2), 3.80 (s, 3H, OCH_3), 3.69 (t, J = 5.0 Hz, 2H, OCH_2), 3.58 (m, 4H, OCH_2), 3.47 (t, J = 4.5 Hz, 2H, OCH_2), 3.30 (s, 3H, OCH_3), 2.99 (s, 1H, CCH); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 165.7, 158.5, 136.8, 135.4, 120.8, 114.3, 113.6, 82.44, 76.82, 71.90, 71.00, 70.70, 70.66, 70.48, 69.43, 69.00, 58.94, 52.01; LR-MS (ESI+): m/z (%): 345.2 (37), 323.1 (61), 291.1 (65), 147.1 (20), 103.1 (100); HR-MS (ESI+): Calc for $C_{17}H_{22}O_6$ $(M+H)^+$ 323.1495, Found 323.1498.

5-ethynyl-2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoic acid (2g). In a 200 mL round bottom flask equipped with a reflux condenser, methyl 5-ethynyl-2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoate **2f** (containing 15% unreacted TgOTs) (993 mg, 3.08 mmol, 1 eq), LiOH (755 mg, 18 mmol, 5 eq), THF (62 mL), and H_2O (10 mL) were combined. The mixture was refluxed for 18 hours after which it was concentrated to remove THF. The residue was diluted with H_2O (40 mL) and acidified to pH = 1 with conc. HCl. The solid was extracted with DCM (4 x 50 mL) then dried over $MgSO_4$ and concentrated to obtain **2g** as a pale brown oil (926 mg, 3.0 mmol, 97%) containing 5% unreacted TgOTs (58 mg, 0.18 mmol). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.93 (bs, 1H, $CO2_H$), 8.19 (d, J = 2.0 Hz, 1H, ArH), 7.58 (dd, J = 2.0, 8.5 Hz, 1H, ArH), 6.96 (d, J = 8.5 Hz, 1H, ArH), 4.33 (t, J = 4.5 Hz, 2H, OCH_2), 3.89 (t, J = 5.0 Hz, 2H, OCH_2), 3.71 (m, 2H, OCH_2), 3.65 (m, 2H, OCH_2), 3.61 (m, 2H, OCH_2), 3.51 (m, 2H, OCH_2), 3.34 (s, 3H, OCH_3), 3.04 (s, 1H, CCH); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 165.2, 157.5, 137.8, 137.2, 119.7, 116.5, 113.7, 82.02, 77.62, 72.00, 70.91, 70.67, 70.64, 69.44, 68.74, 59.07; LR-MS (ESI+): m/z (%): 331.1 (78), 309.1 (32), 291.1 (52), 103.1 (100); HR-MS (ESI+): Calc for $C_{16}H_{20}O_6$ $(M+H)^+$ 309.1338, Found 309.1330.

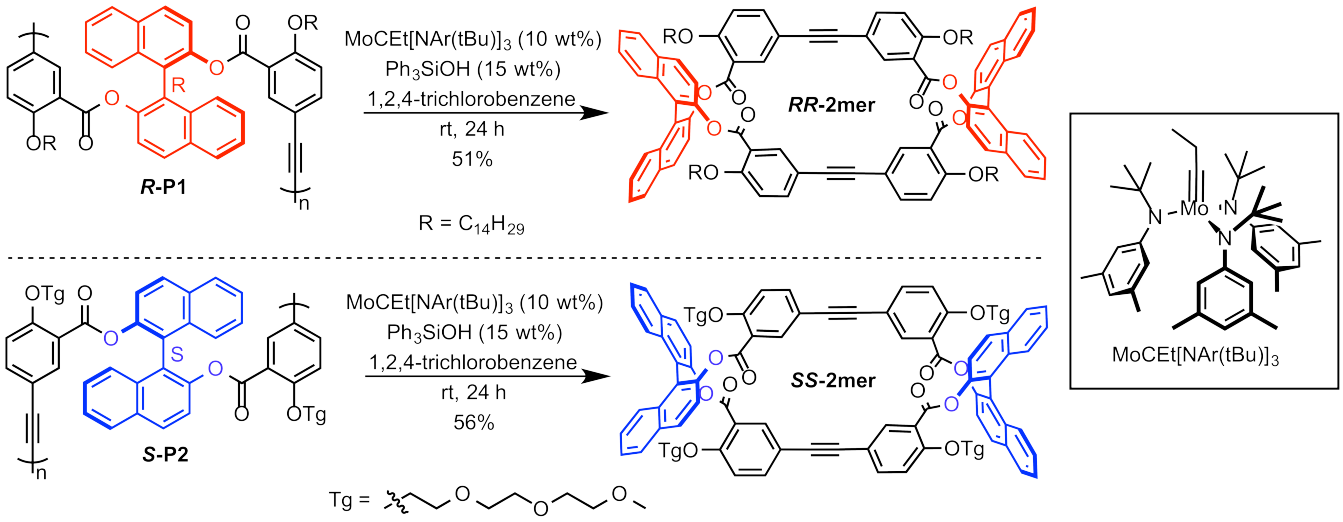
(*S*)-[1,1'-binaphthalene]-2,2'-diyl(5-ethynyl-2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy) benzoate) (2h). In a 100 mL round bottom flask, **2g** (containing 5% unreacted TgOTs) (890 mg, 2.89 mmol, 1 eq), (*S*)-(-)-1,1'-bi(2-naphthol) (413 mg, 1.44 mmol, 0.5 eq), DMAP (529 mg, 4.33 mmol, 1.5 eq), and EDC (830 mg, 4.33 mmol, 1.5 eq) were dissolved in 29 mL DCM. The mixture was stirred at room temperature for 24 hours under N_2. After 24 hours, the mixture was diluted with DCM (20 mL) and washed with a saturated aqueous $NaHCO_3$ solution (50 mL). The organic layer was dried over $MgSO_4$ then concentrated to a light yellow oil. Purified by column chromatography [silica gel, gradient from acetone/DCM 1:9 to acetone/DCM 1:2] to obtain **2h** as a sticky colorless solid (688 mg, 0.794 mmol, 55%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.01 (d, J = 9.0 Hz, 2H, ArH), 7.91 (d, J = 8.5 Hz, 2H, ArH), 7.58 (d, J = 9.0 Hz, 2H, ArH), 7.44 (t, J = 8.0 Hz, 2H, ArH), 7.38 (m, 4H, ArH), 7.31 (t, J = 7.5 Hz, 2H, ArH), 6.97 (d, J = 2.0 Hz, 2H, ArH), 6.76 (d, J = 9.0 Hz, 2H, ArH), 3.98 (m, 4H, OCH_2), 3.66 (t, J = 5.0 Hz, 4H, OCH_2), 3.62 (m, 4H, OCH_2), 3.57 (m, 8H, OCH_2), 3.49 (m, 4H, OCH_2), 3.34 (s, 6H, OCH_3), 2.98 (s, 2H, CCH); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 162.7, 158.9, 147.1, 137.1, 135.6, 133.5, 131.7, 129.8, 128.2, 127.0, 126.2, 125.9, 123.8, 122.1, 119.9, 114.3, 113.8, 82.44, 76.59, 72.03, 71.04, 70.73,

70.59, 69.39, 69.05, 59.09; LR-MS (ESI+): m/z (%): 891.2 (24), 890.1 (65), 889.1 (100), 867.2 (64), 780.1 (11), 779.1 (20); HR-MS (ESI+): Calc for $C_{52}H_{50}O_{12}$ $(M+H)^+$ 867.3358, Found 867.3381.



***S*-P2.** In a glovebox, a 20 mL vial was charged with *S*-diiodo monomer **2d** (428 mg, 0.4 mmol, 1 eq), *S*-diethynyl monomer **2h** (347 mg, 0.4 mmol, 1 eq), CuI (3.8 mg, 0.02 mmol, 0.05 eq), and $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol, 0.05 eq). The solids were dissolved in THF (3 mL) and DIPA (1 mL). The vial was sealed with tape and heated at 60 °C for 48 hours. After 48 hours, the solvent was removed and the solid dissolved in minimal $CHCl_3$. This polymer solution was slowly added to rapidly stirring methanol (400 mL) to obtain ***S*-P2** as a light yellow solid (463 mg, 62%). GPC (THF): Mn = 14 kDa, Mw = 32 kDa, PDI = 2.3, Ret. Volume = 25-33 mL; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.96 (bm, 2H, ArH), 7.82 (bd, 2H, ArH), 7.62 (bm, 2H, ArH), 7.42-7.30 (bm, 8H, ArH), 6.96 (bs, 2H, ArH), 6.81 (bm, 2H, ArH), 3.99 (bm, 4H, OCH_2), 3.64-3.47 (bm, 20H, OCH_2), 3.31 (s, 6H, OCH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ163.0, 158.5, 147.2, 136.4, 134.9, 133.5, 131.7, 129.8, 128.3, 127.0, 126.2, 125.9, 123.9, 122.2, 122.1, 120.1, 115.6, 113.9, 87.73, 87.43, 72.04, 72.02, 71.00, 70.97, 70.70, 70.58, 70.56, 69.42, 69.03, 59.07.

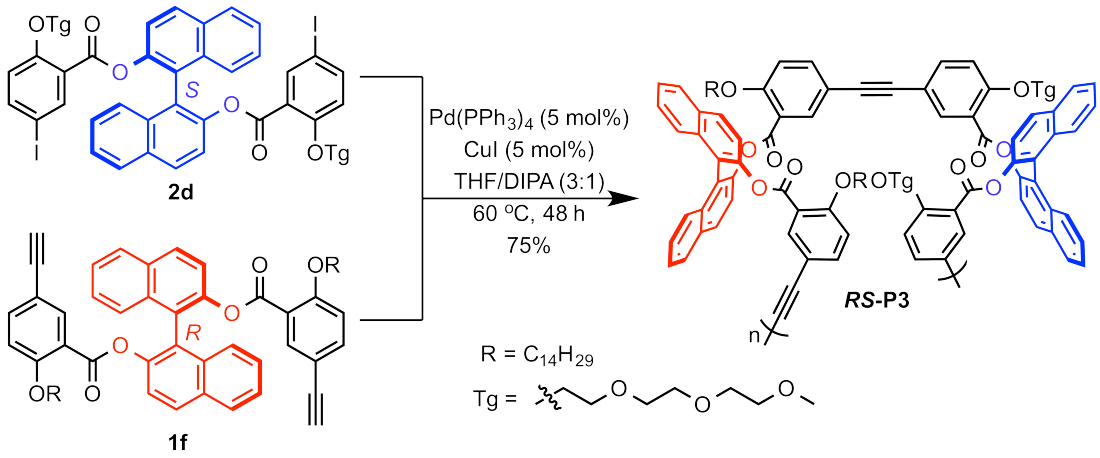
Synthesis of *RR*-2mer and *SS*-2mer



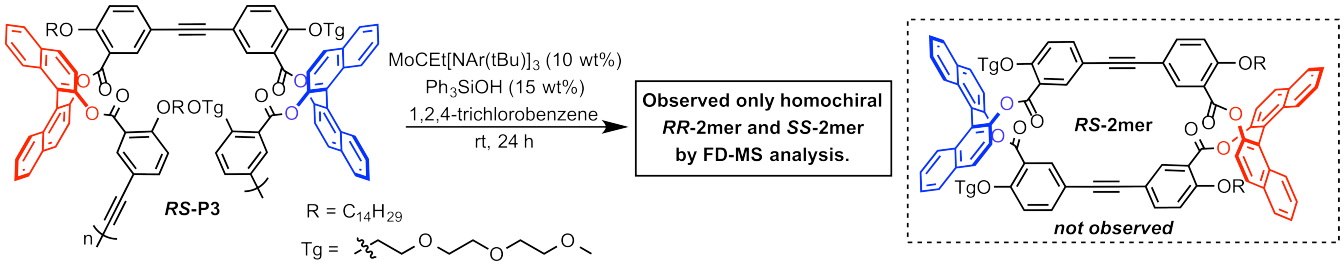
***RR*-2mer.** In a glove box, a solution of $MoCEt[NAr(tBu)]_3$ (8 mg, 0.012 mmol, 10 wt%) and Ph_3SiOH (12 mg, 0.0434 mmol, 15 wt%) in 1,2,4-trichlorobenzene (5 mL) in a 20 mL vial was stirred for 10 minutes. The catalyst solution was added to another 20 mL vial containing a solution of ***R*-P1** (80 mg) in 1,2,4-trichlorobenzene (3 mL). The vial was sealed with tape and stirred at room temperature for 24 hours. After which, the 1,2,4-trichlorobenzene was removed via vacuum distillation. The crude material was purified via preparative-TLC [silica gel, acetone/DCM 2:3] to obtain ***RR*-2mer** as a pale yellow solid (41 mg, 51%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.96 (d, J = 9.0 Hz, 4H, ArH), 7.88 (d, J = 8.0 Hz, 8H, ArH), 7.55 (d, J = 8.5 Hz, 4H, ArH), 7.39 (m, 8H, ArH), 7.30-7.26 (m, 8H, ArH), 6.61 (d, J = 8.5 Hz, 4H, ArH), 3.65 (m, 8H, OCH_2), 1.45 (bm, 8H, CH_2), 1.27 (bs, 88H, CH_2), 0.89 (t, J = 6.5 Hz, 12H, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 163.3, 158.9, 147.3, 136.6, 135.6, 133.8, 131.7, 129.7, 128.0, 126.7, 125.7, 125.4, 124.0, 122.1, 119.5, 115.1, 113.1, 87.63, 69.00, 32.11, 29.90, 29.88, 29.84, 29.72, 29.55, 29.49, 28.88, 25.88, 22.88, 14.31; HR-MS (MALDI): Calc for $C_{128}H_{152}O_{12}$ $(M)^+$ 1881.1278, Found 1881.1370.

***SS*-2mer.** In a glove box, a solution of $MoCEt[NAr(tBu)]_3$ (8 mg, 0.012 mmol, 10 wt%) and Ph_3SiOH (12 mg, 0.0434 mmol, 15 wt%) in 1,2,4-trichlorobenzene (5 mL) in a 20 mL vial was stirred for 10 minutes. The catalyst solution was added to another 20 mL vial containing a solution of ***S*-P2** (80 mg) in 1,2,4-trichlorobenzene (3 mL). The vial was sealed with tape and stirred at room temperature for 24 hours. After which, the 1,2,4-trichlorobenzene was removed via vacuum distillation. The crude material was purified via preparative-TLC [silica gel, MeOH/acetone/DCM 4:26:70] to obtain ***SS*-2mer** as a pale yellow solid (45 mg, 56%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.99 (d, J = 9.0 Hz, 4H, ArH), 7.95 (s, 4H, ArH), 7.89 (d, J = 8.0 Hz, 4H, ArH), 7.56 (d, J = 8.5 Hz, 4H, ArH), 7.43 (m, 8H, ArH), 7.28 (m, 8H, ArH), 6.63 (d, J = 9.0 Hz, 4H, ArH), 3.78 (m, 4H, OCH_2), 3.68 (m, 4H, OCH_2), 3.57-3.48 (bm, 32H, OCH_2), 3.42 (m, 8H, OCH_2), 3.33 (s, 12H, OCH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 163.0, 158.7, 147.3, 136.7, 135.7, 133.7, 131.7, 129.8, 128.1, 126.8, 126.7, 125.8, 123.9, 122.2, 119.5, 115.8, 114.1, 87.69, 72.02, 70.96, 70.70, 70.58, 69.23, 68.95, 59.14; LR-MS (ESI+): m/z (%): 1684.6 (21), 1683.6 (52), 1682.6 (100), 1681.6 (80), 842.8 (17), 842.3 (41), 841.3 (65); HR-MS (ESI+): Calc for $C_{100}H_{96}O_{24}$ $(M+H)^+$ 1681.6370, Found 1681.6371.

Synthesis of *RS*-P3 and Mixing Experiments



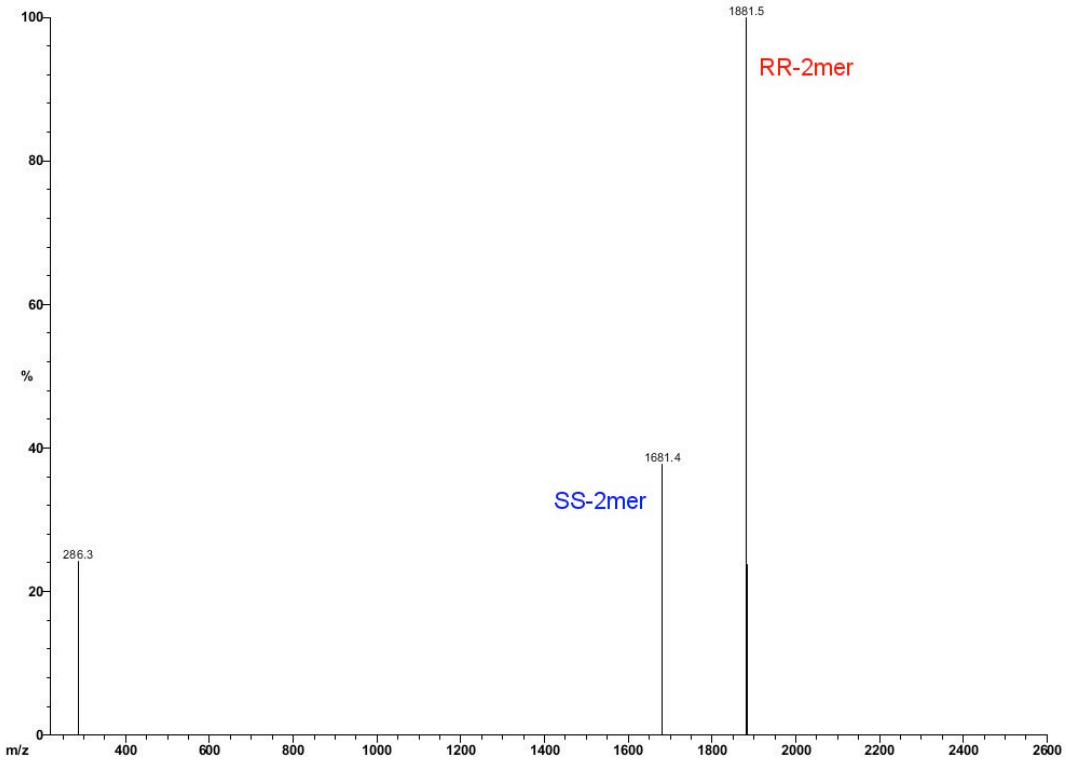
***RS*-P3.** In a glovebox, a 20 mL vial was charged with *S*-diiodo monomer **2d** (236 mg, 0.22 mmol, 1 eq), *R*-diethynyl monomer **1f** (213 mg, 0.22 mmol, 1 eq), CuI (2.1 mg, 0.011 mmol, 0.05 eq), and $Pd(PPh_3)_4$ (12.7 mg, 0.011 mmol, 0.05 eq). The solids were dissolved in THF (3 mL) and DIPA (1 mL). The vial was sealed with tape and heated at 60 °C for 48 hours. After 48 hours, the solvent was removed and the solid dissolved in minimal $CHCl_3$. This polymer solution was slowly added to rapidly stirring methanol (200 mL) to obtain ***RS*-P3** as a light yellow solid (295 mg, 75%). GPC (THF): Mn = 19 kDa, Mw = 39 kDa, PDI = 2.0, Ret. Volume = 24-33 mL; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.96 (bm, 2H, ArH), 7.83 (bd, 2H, ArH), 7.63 (bm, 2H, ArH), 7.45-7.38 (bm, 8H, ArH), 6.96 (bm, 2H, ArH), 6.83 (bm, 2H, ArH), 4.01 (bs, 2H, OCH_2), 3.85 (bs, 2H, OCH_2), 3.66-3.47 (bm, 10H, OCH_2), 3.32 (bs, 3H, OCH_3), 1.64 (bm, 2H, CH_2), 1.25 (bm, 22H, CH_2), 0.87 (bm, 3H, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.1, 164.0, 163.2, 163.0, 158.6, 158.6, 158.4, 158.4, 147.5, 147.2, 147.1, 136.4, 135.6, 135.5, 134.9, 133.9, 133.6, 133.5, 131.7, 131.7, 129.7, 129.6, 128.3, 128.0, 127.9, 127.0, 126.9, 126.2, 125.9, 124.1, 124.0, 123.9, 122.2, 120.3, 120.1, 120.0, 119.8, 115.7, 114.9, 114.6, 113.8, 113.3, 113.0, 87.58, 87.17, 72.05, 72.03, 72.00, 71.01, 70.98, 70.81, 70.71, 70.66, 70.63, 70.58, 69.40, 69.10, 68.98, 68.95, 68.86, 59.16, 59.11, 32.07, 29.87, 29.82, 29.78, 29.74, 29.71, 29.52, 29.48, 29.39, 28.97, 25.93, 22.84, 14.29.



***RS*-P3 Depolymerization**. In a glove box, a solution of $MoCEt[NAr(tBu)]_3$ (10 mg, 0.015 mmol, 10 wt%) and Ph_3SiOH (15 mg, 0.054 mmol, 15 wt%) in 1,2,4-trichlorobenzene (6 mL) in a 20 mL vial was stirred for 10 minutes. The catalyst solution was added to another 20 mL vial containing a solution of ***RS*-P3** (100 mg) in 1,2,4-trichlorobenzene (4 mL). The vial was sealed with tape and stirred at room

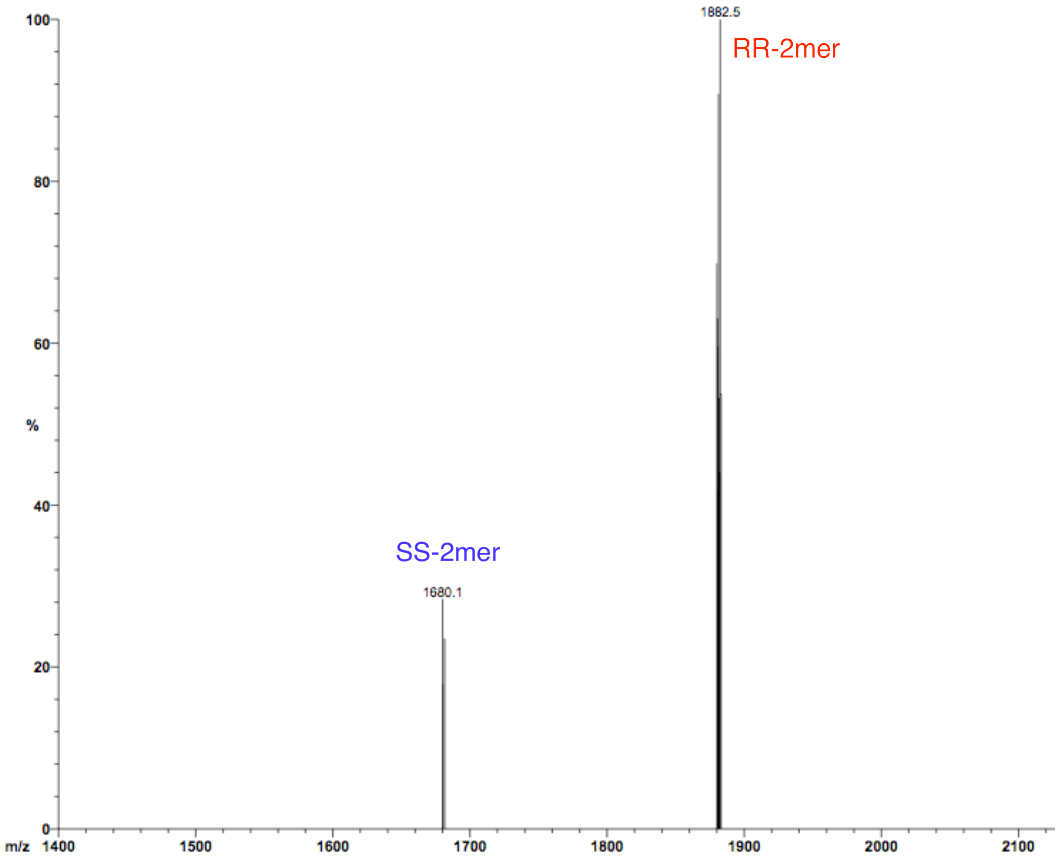
temperature for 24 hours. After which, the 1,2,4-trichlorobenzene was removed via vacuum distillation. The crude material was analyzed by FD-MS and GPC.

Figure S1. FD-MS Analysis of *RS*-P3 Depolymerization.



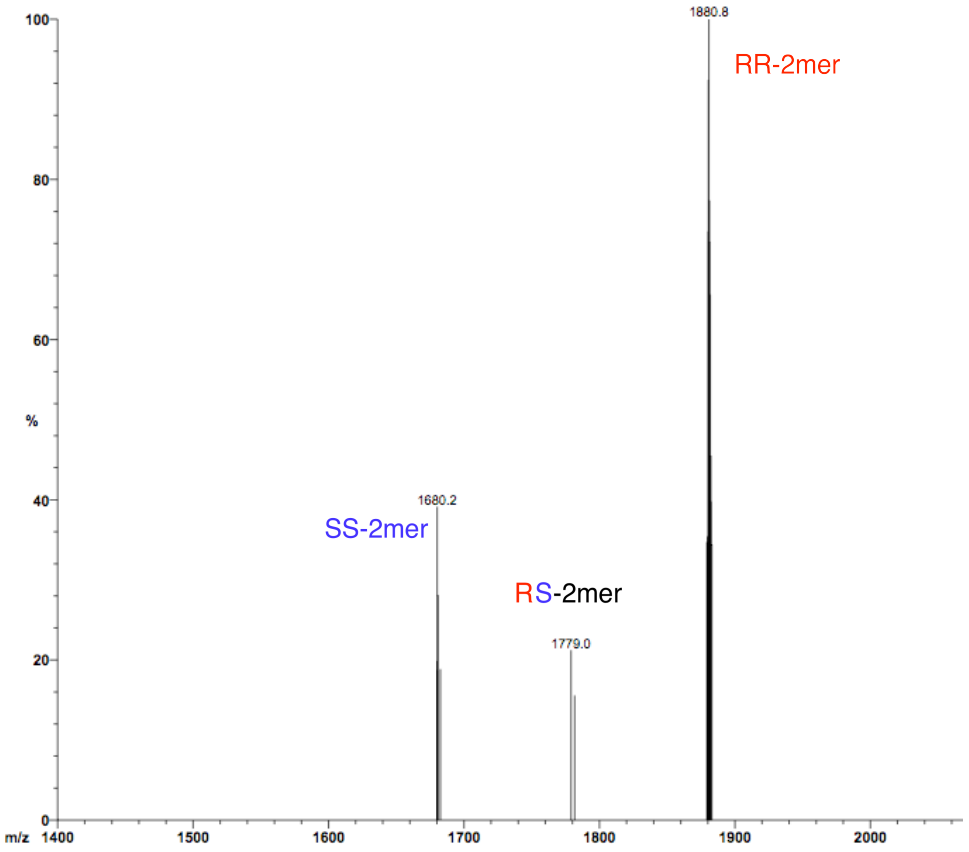
***RS*-P3 Depolymerization in Toluene**. In a glove box, a solution of $MoCEt[NAr(tBu)]_3$ (4 mg, 0.006 mmol, 10 wt%) and Ph_3SiOH (6 mg, 0.022 mmol, 15 wt%) in toluene (4 mL) in a 20 mL vial was stirred for 10 minutes. The catalyst solution was added to another 20 mL vial containing ***RS*-P3** (40 mg). The vial was sealed with tape and stirred at room temperature for 24 hours. After which, toluene was removed and the crude material was analyzed by FD-MS.

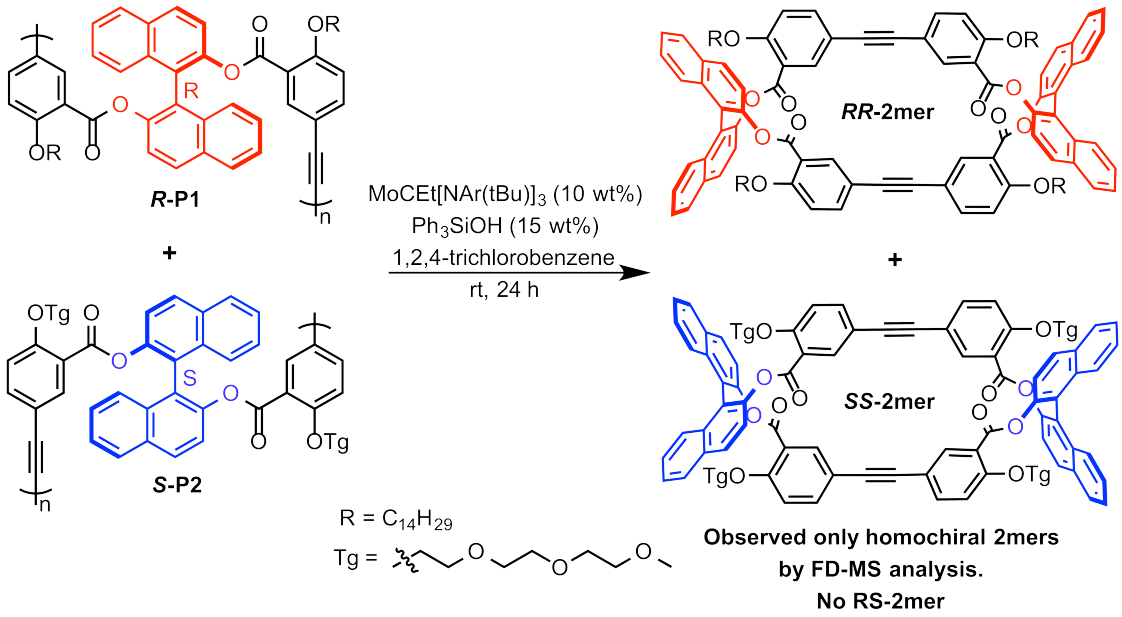
Figure S2. FD-MS Analysis of *RS*-P3 Depolymerization in Toluene.



Low Temperature *RS*-P3 Depolymerization in Toluene. In a glove box, a solution of $MoCEt[NAr(tBu)]_3$ (4 mg, 0.006 mmol, 10 wt%) and Ph_3SiOH (6 mg, 0.022 mmol, 15 wt%) in toluene (4 mL) in a 20 mL vial was stirred for 10 minutes. The catalyst solution was added to another 20 mL vial containing ***RS*-P3** (40 mg). The vial was sealed with tape and stirred at 5 °C for 24 hours in a cold room. After which, toluene was removed and the crude material was analyzed by FD-MS.

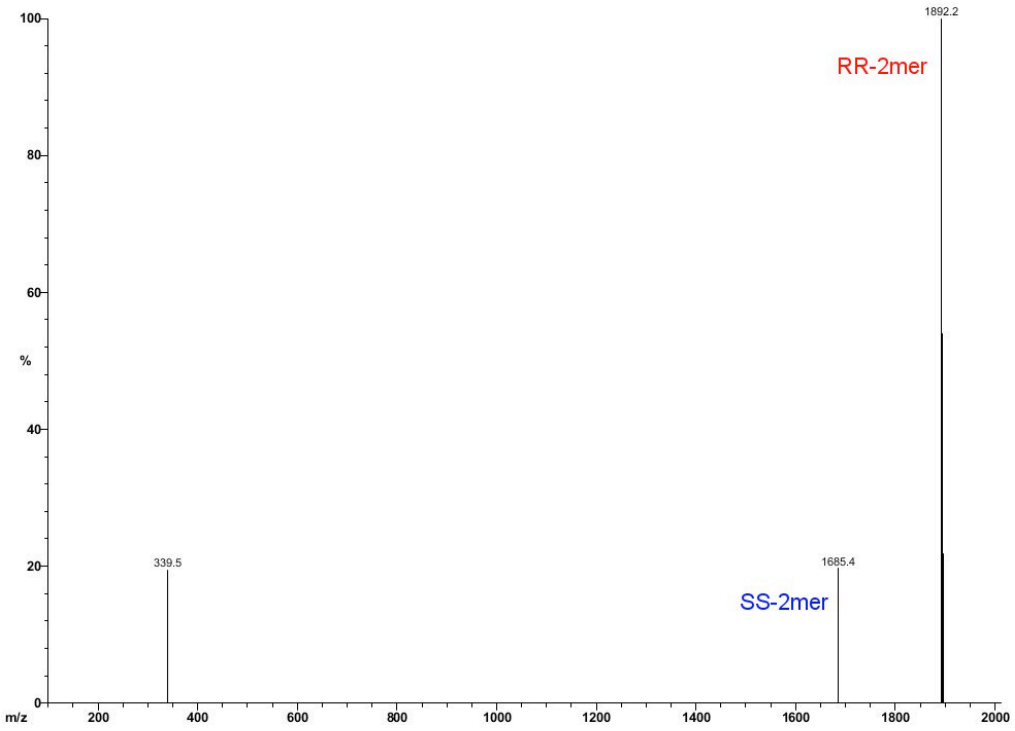
Figure S3. FD-MS Analysis of Low Temperature *RS*-P3 Depolymerization in Toluene.





Homochiral *R*-P1 + *S*-P2 Mixing Experiment. In a glove box, a solution of MoCEt[NAr(tBu)]$_3$ (8 mg, 0.012 mmol, 10 wt%) and Ph_3SiOH (12 mg, 0.0434 mmol, 15 wt%) in 1,2,4-trichlorobenzene (5 mL) in a 20 mL vial was stirred for 10 minutes. The catalyst solution was added to another 20 mL vial containing a solution of ***R*-P1** (40 mg) and ***S*-P2** (40 mg) in 1,2,4-trichlorobenzene (3 mL). The vial was sealed with tape and stirred at room temperature for 24 hours. After which, the 1,2,4-trichlorobenzene was removed via vacuum distillation. The crude material was analyzed by FD-MS and GPC analysis.

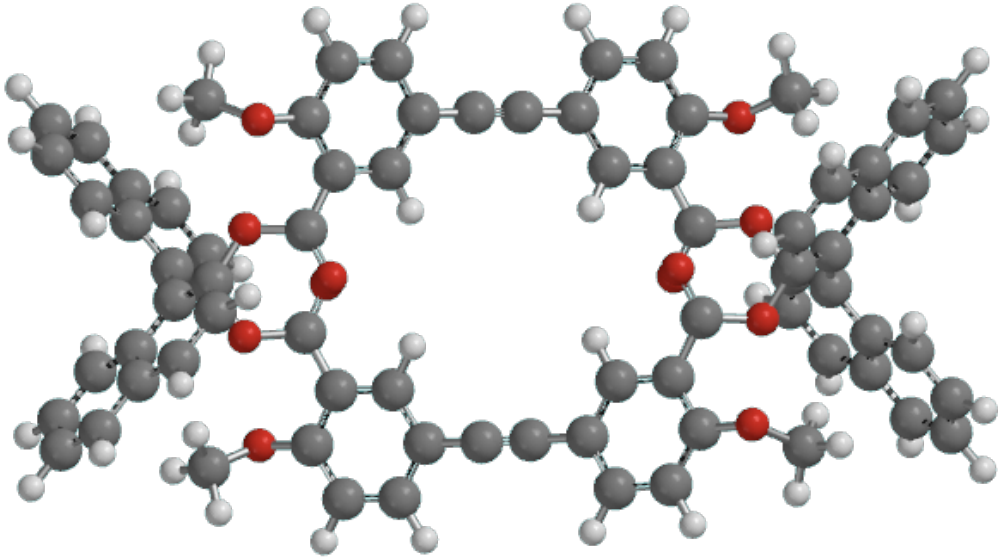
Figure S4. FD-MS Analysis of Crude Depolymerization of *R*-P1 + *S*-P2.

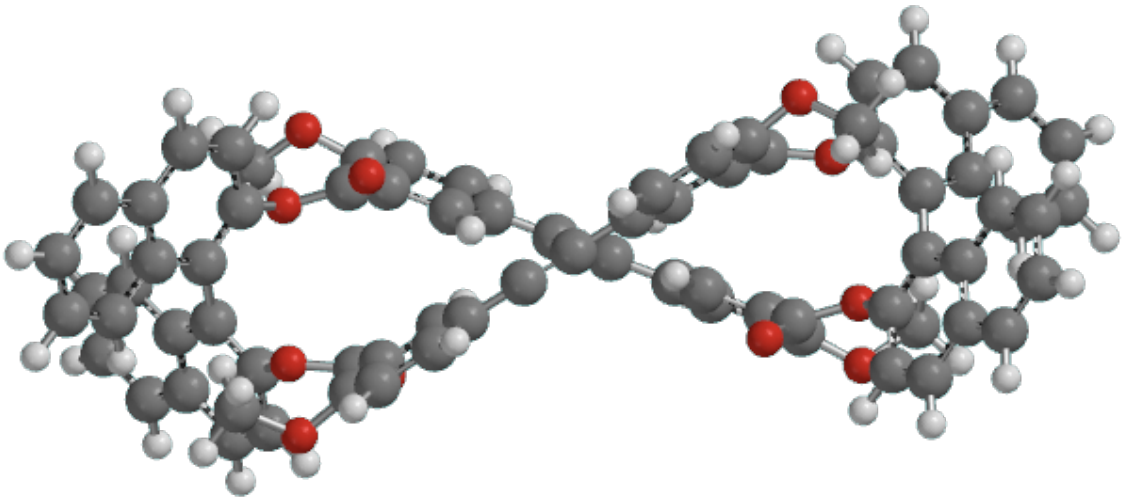


Optimized Macrocycle Structures

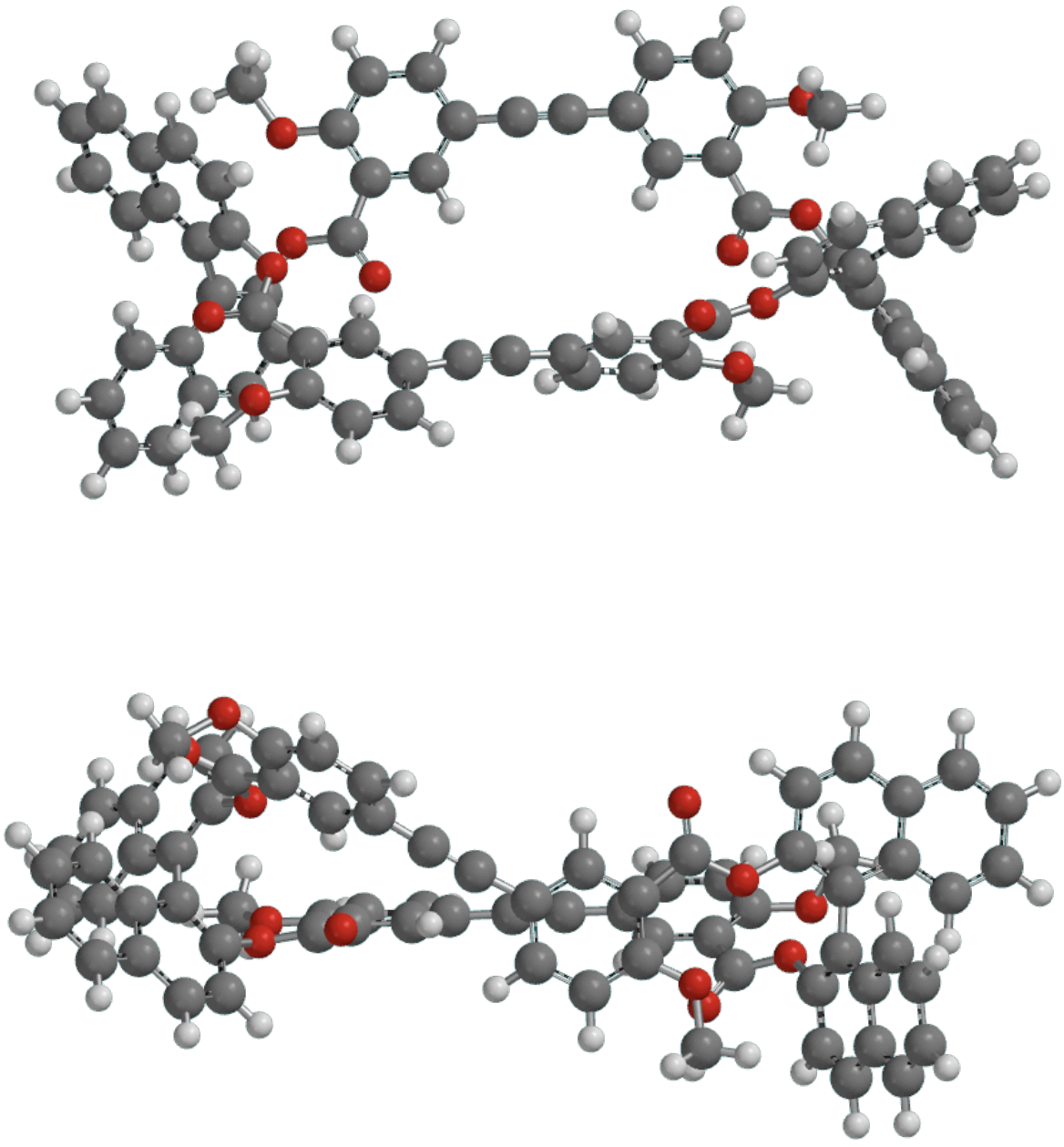
SS-2mer (methyl groups in place of triethylene glycol chains).

Note: ***RR*-2mer** is identical in three-dimensional structure except for the BINOL monomer having opposite chirality.



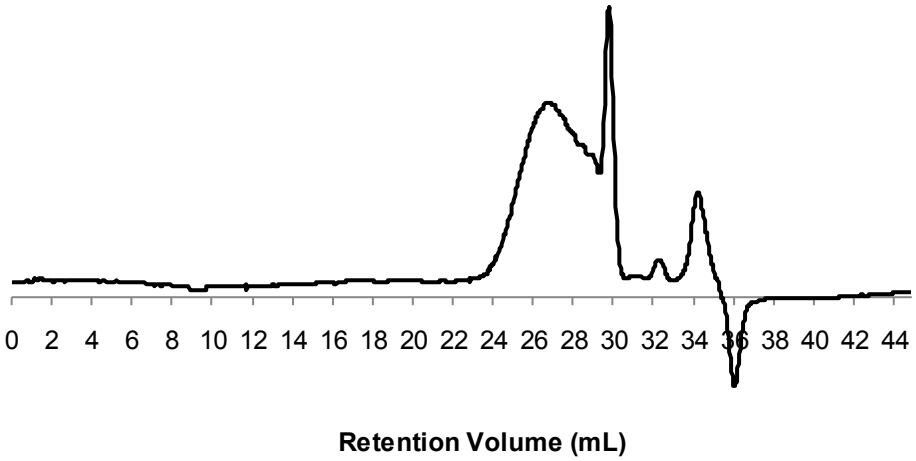


***RS*-2mer (methyl groups in place of triethylene glycol and tetradecyl chains).**

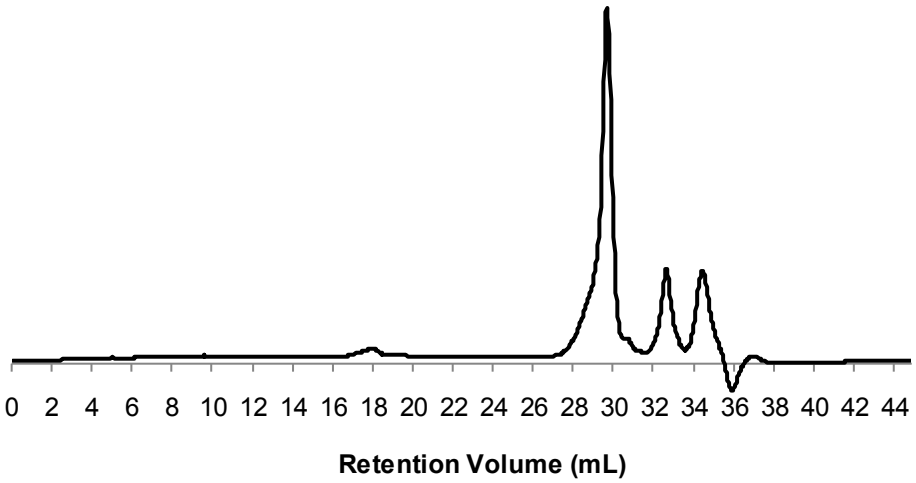


GPC Data for Polymers, Depolymerizations, and Macrocycles

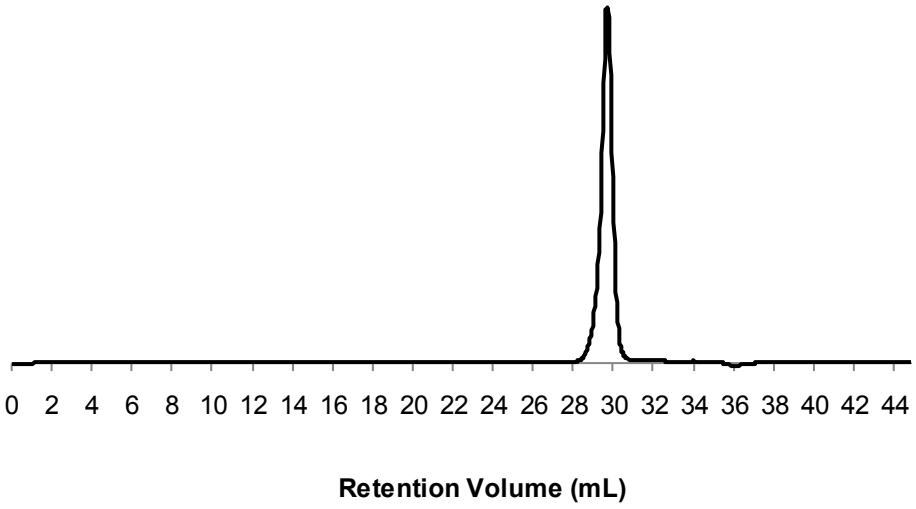
GPC trace of ***R*-P1**.



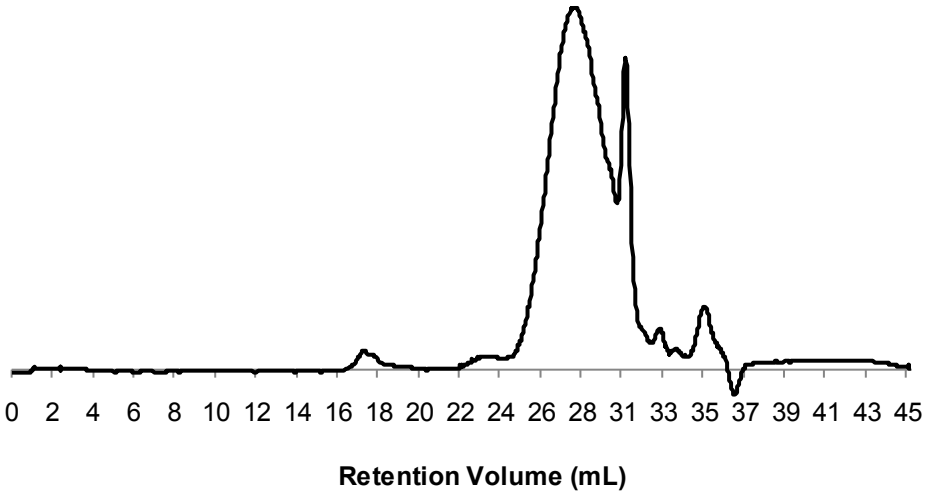
GPC trace of crude depolymerization of ***R*-P1**.



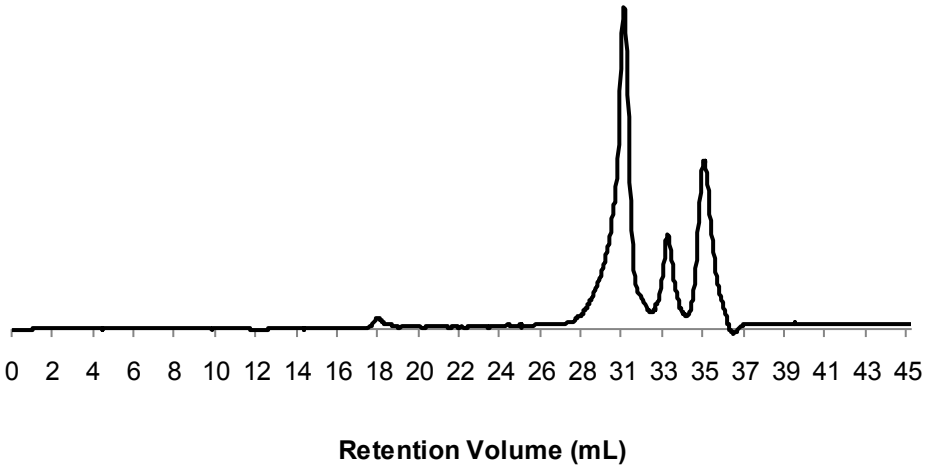
GPC trace of pure ***RR*-2mer**.



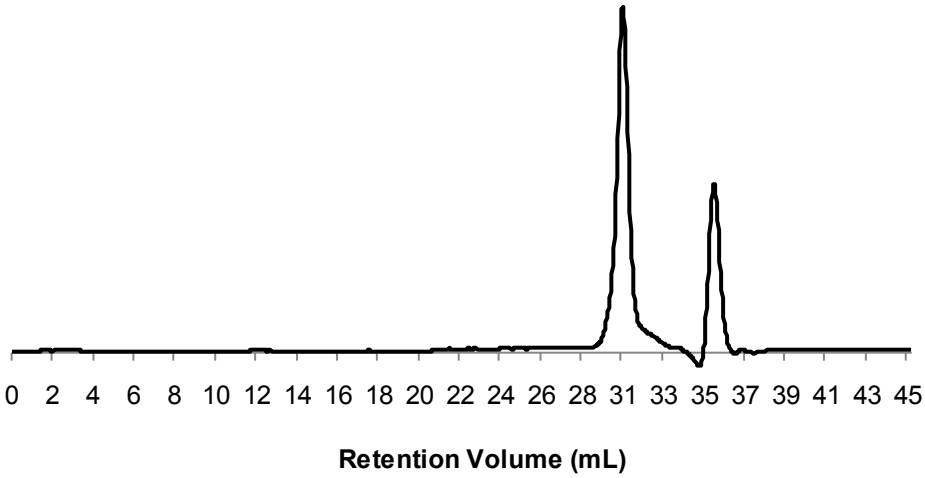
GPC trace of ***S*-P2**.



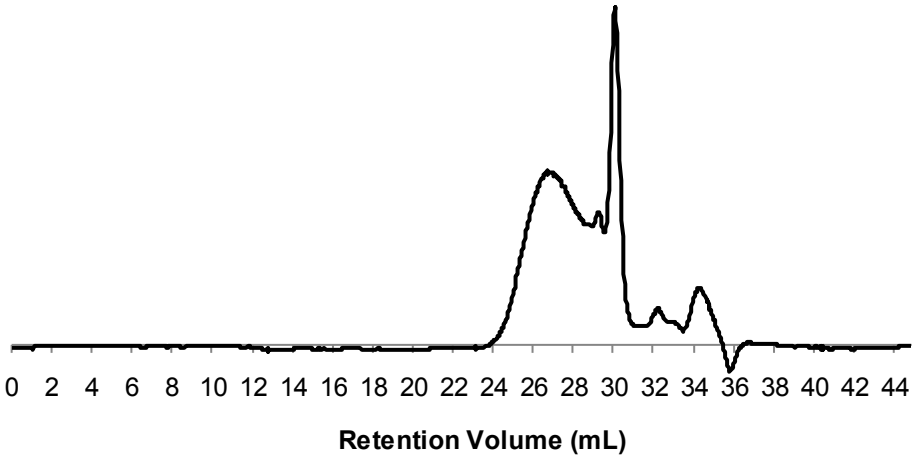
GPC trace of crude depolymerization of ***S*-P2**.



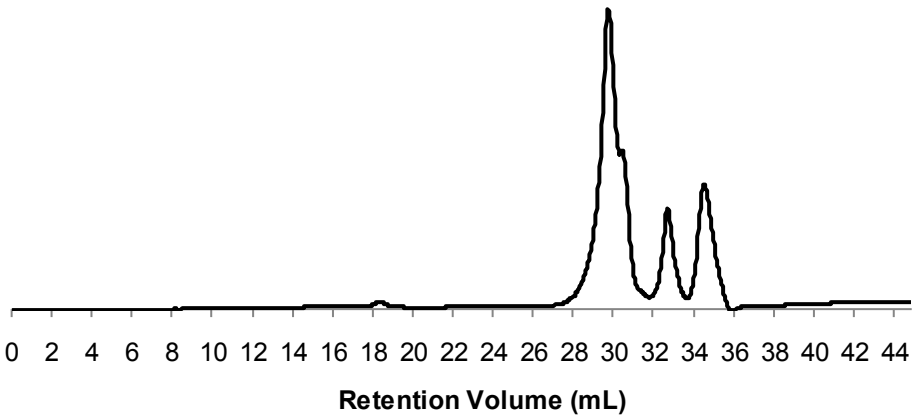
GPC trace of pure ***SS*-2mer**.



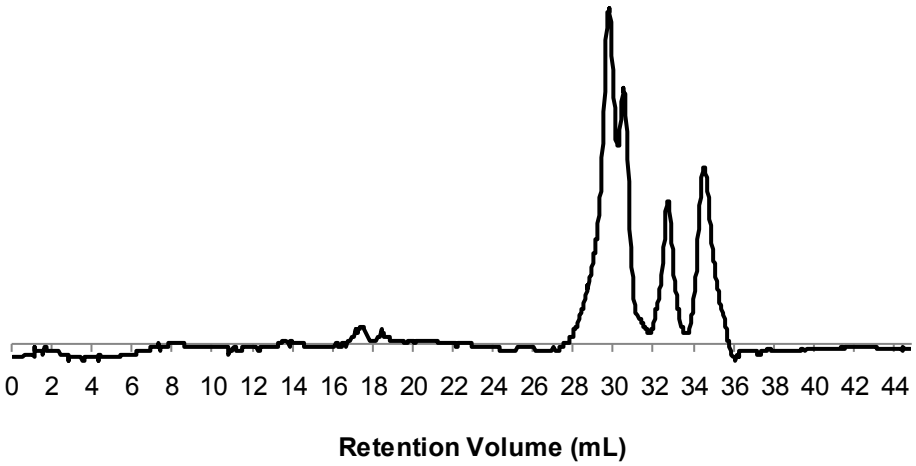
GPC trace of ***RS*-P3**.

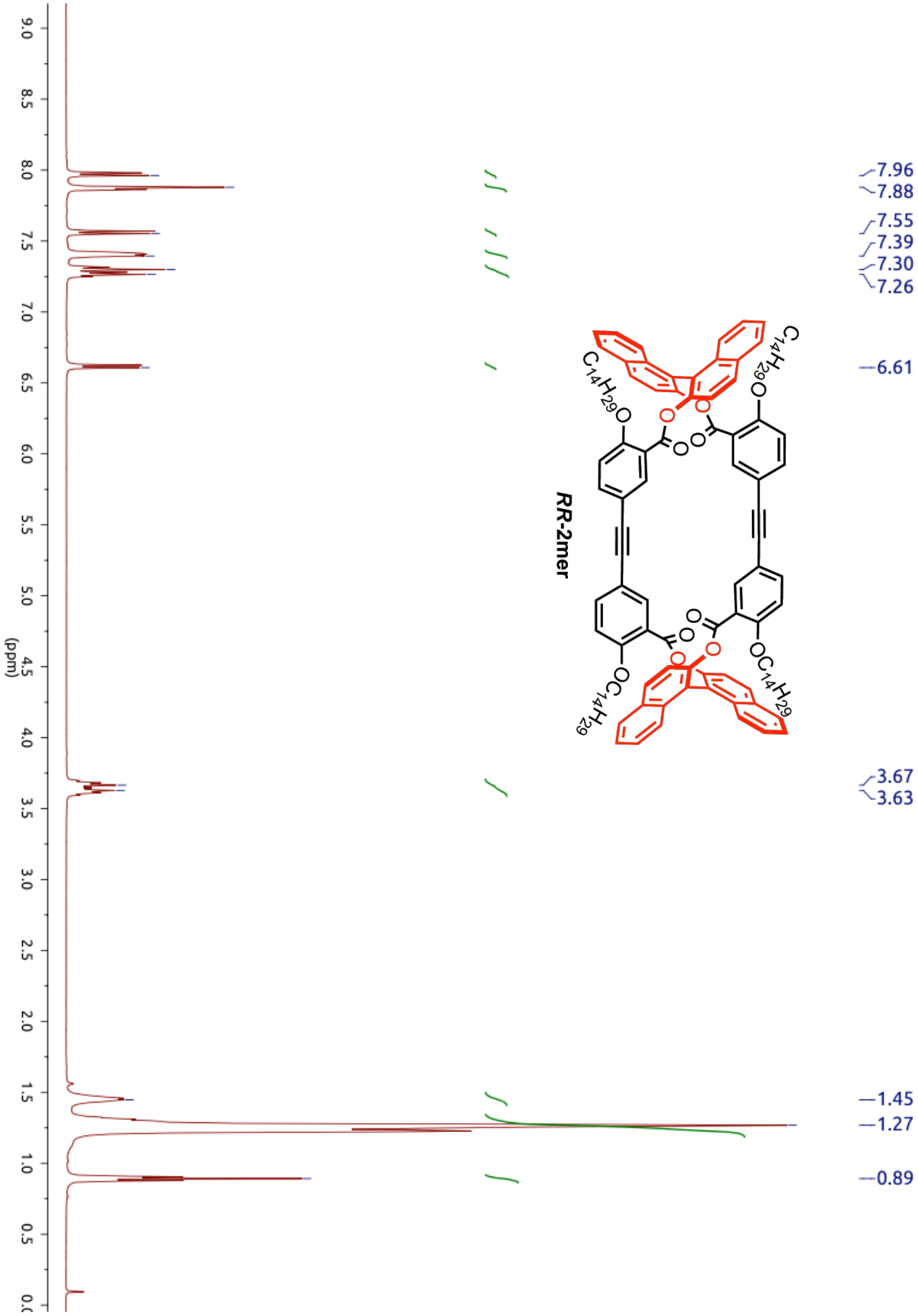


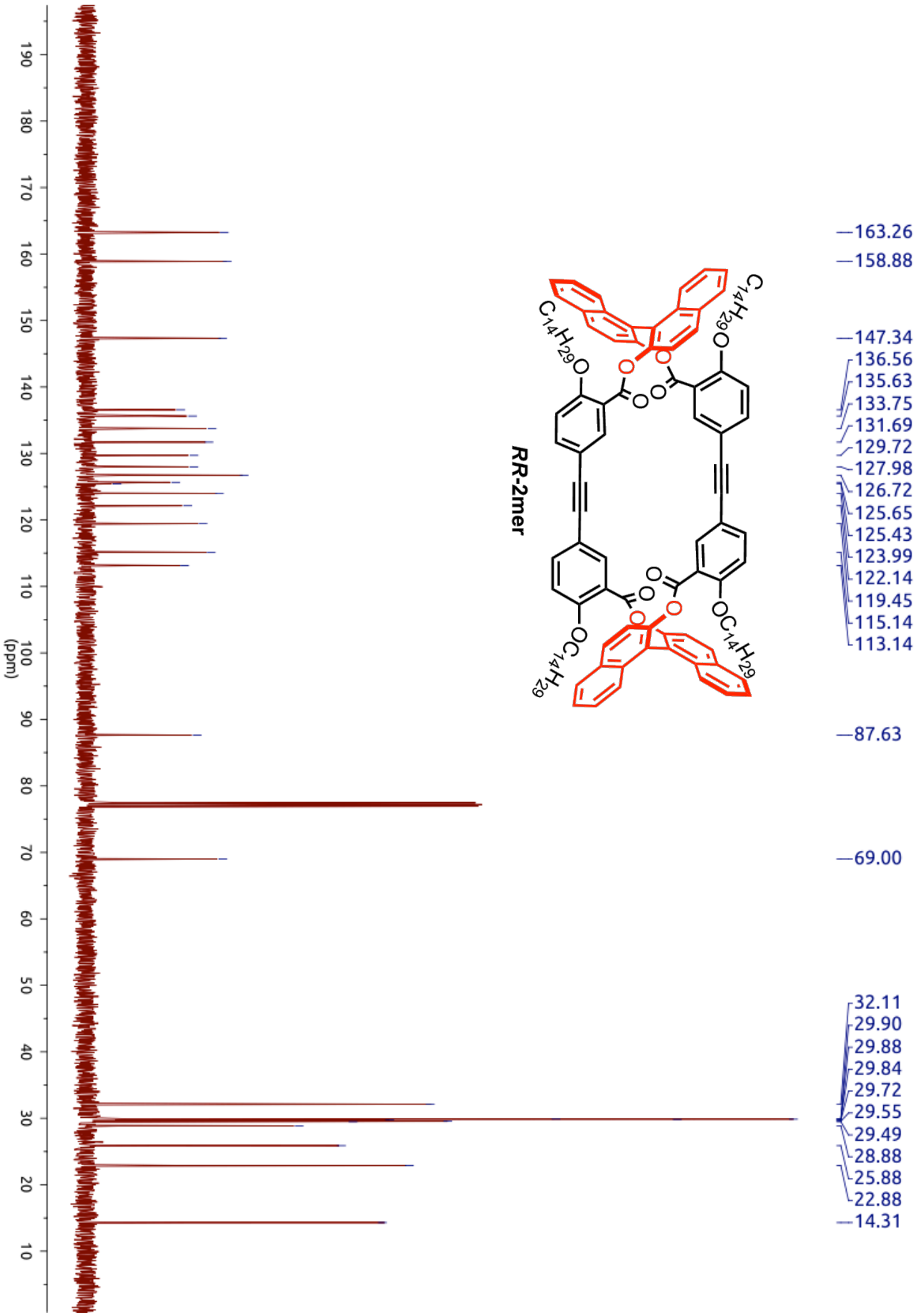
GPC trace of crude depolymerization of ***RS*-P3**.

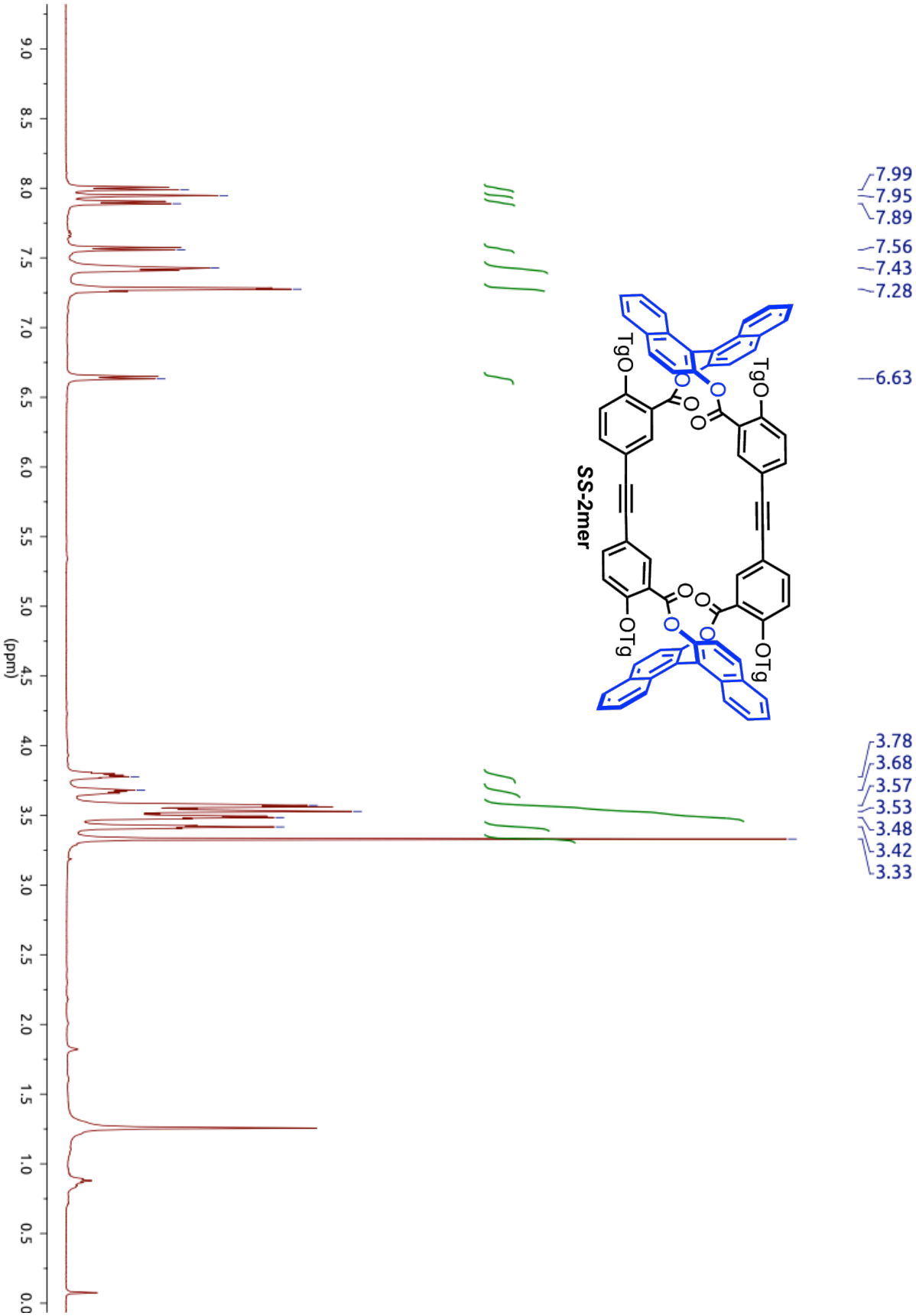


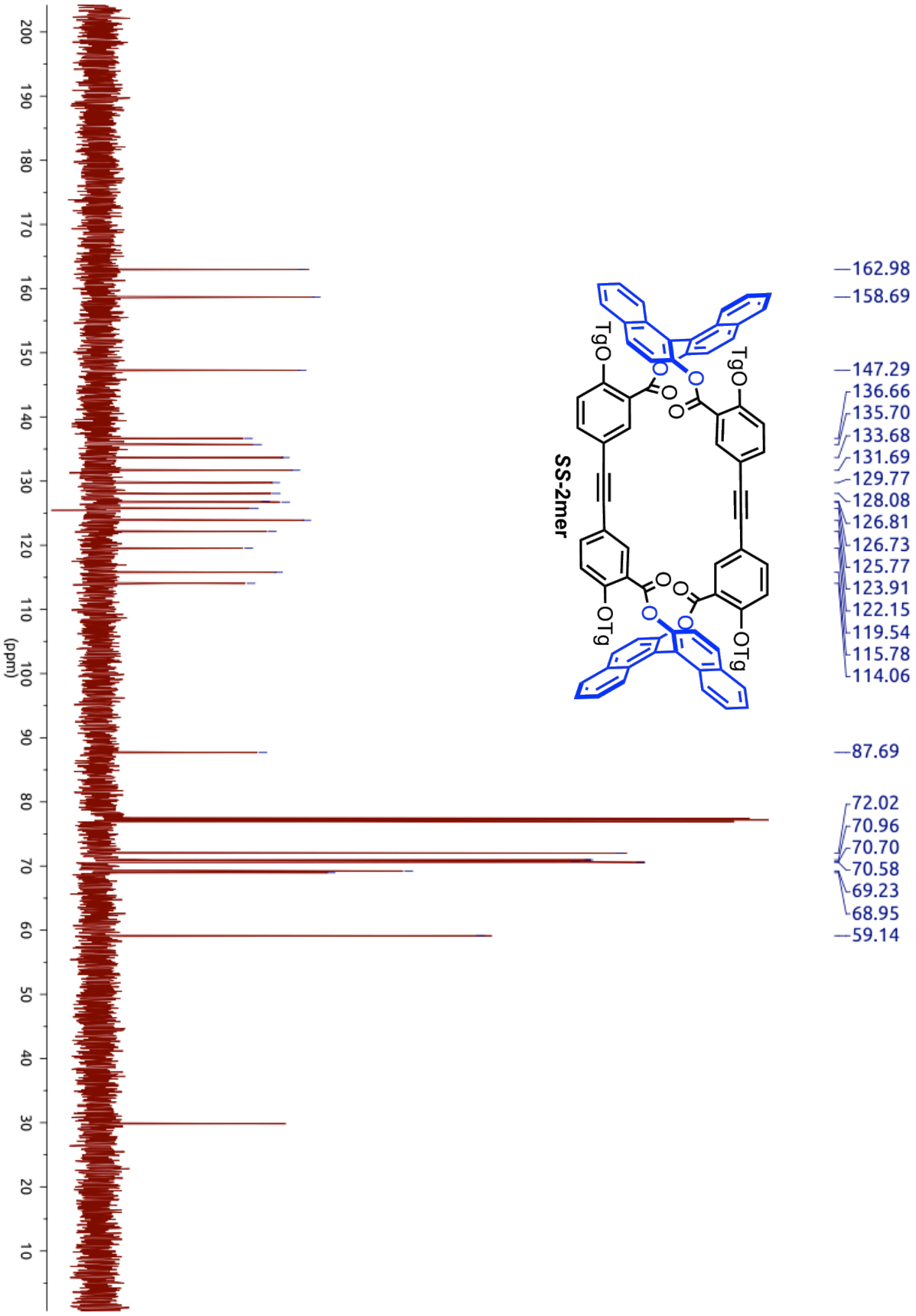
GPC trace of crude depolymerization of homochiral mixing ***R*-P1** + ***S*-P2**.

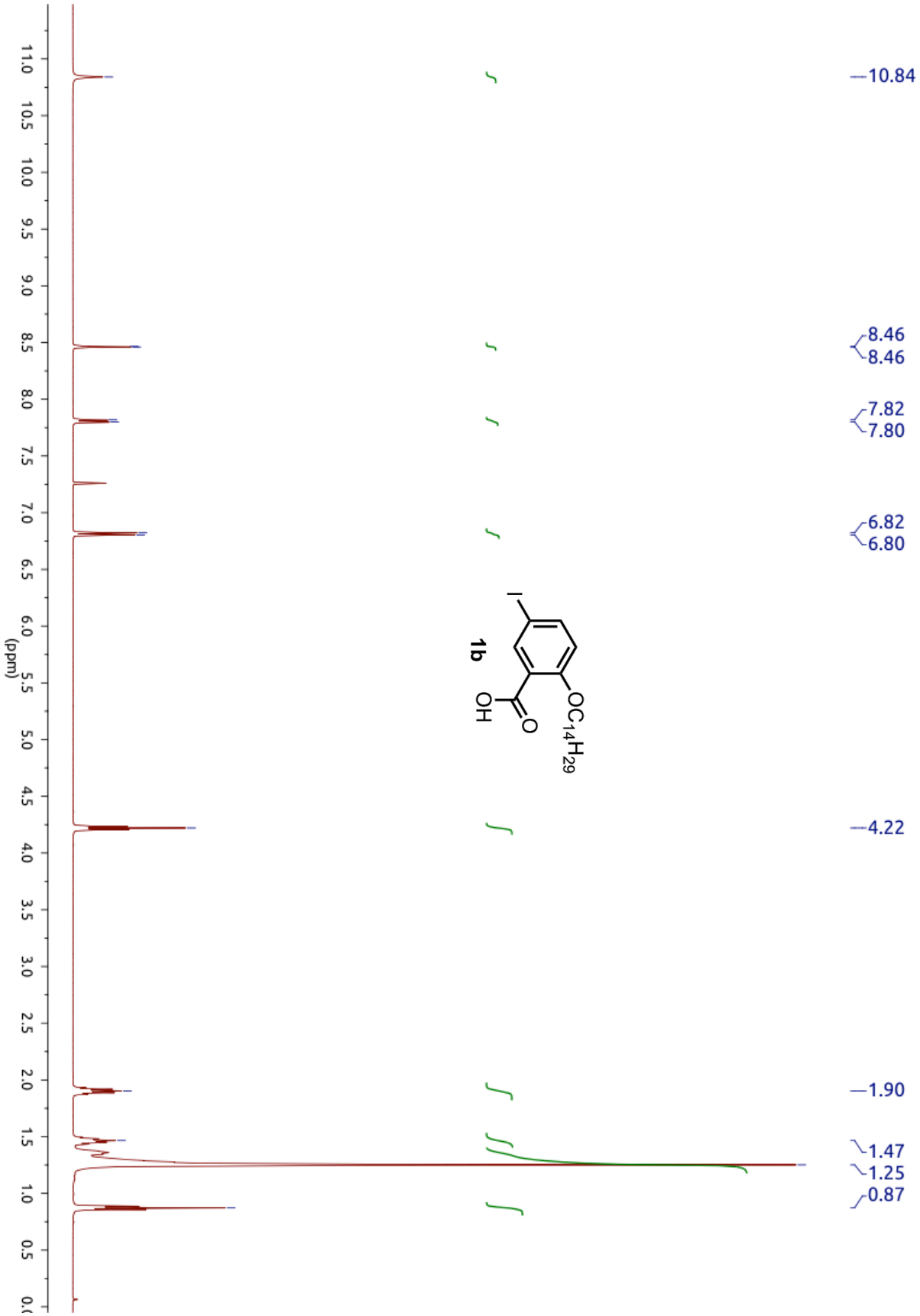


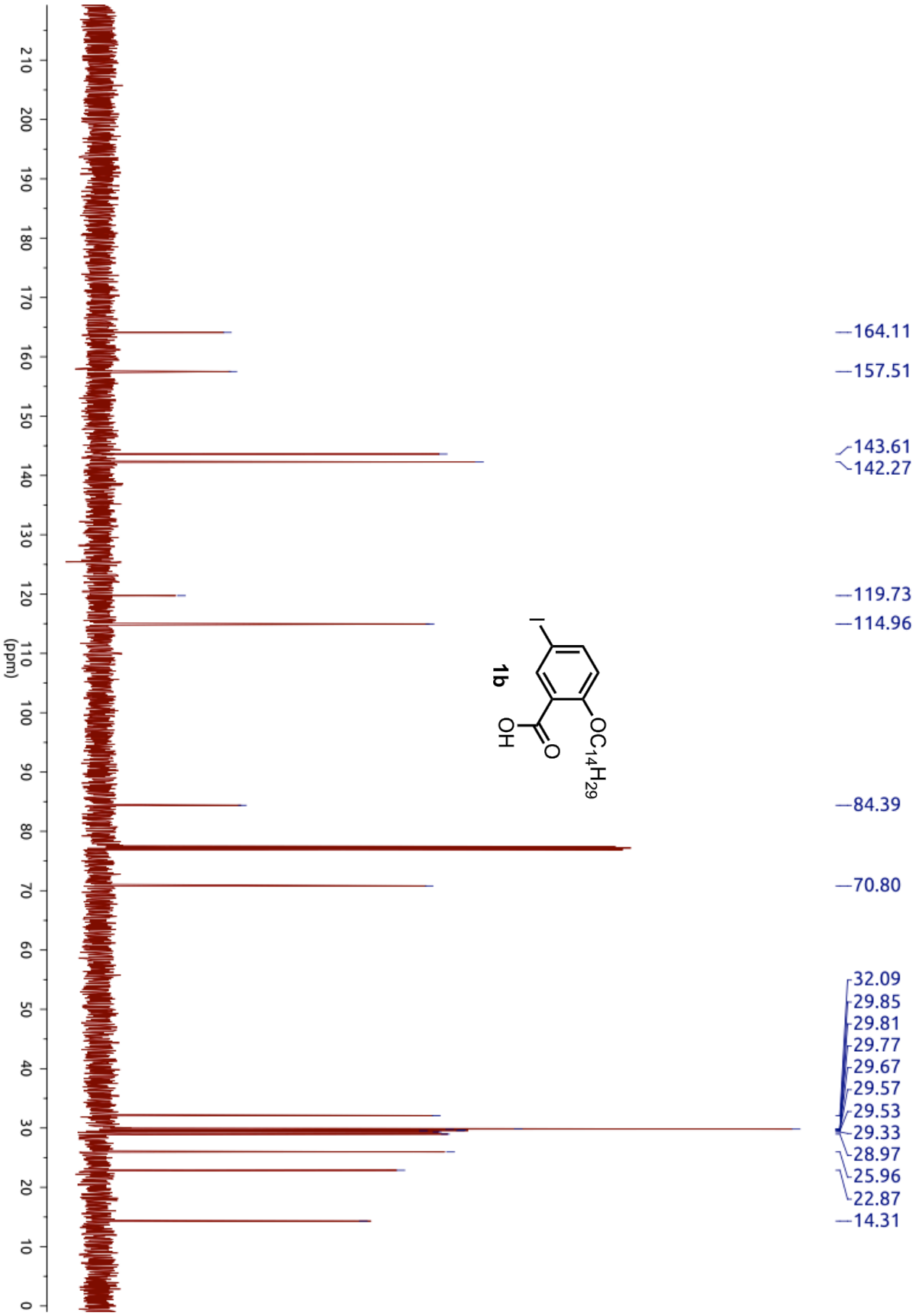

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)
7.96
7.88
7.55
7.39
7.30
7.26
6.61
3.67
3.63
1.45
1.27
0.89
RR-2mer
C14H29O
C14H29O
C14H29O
C14H29O

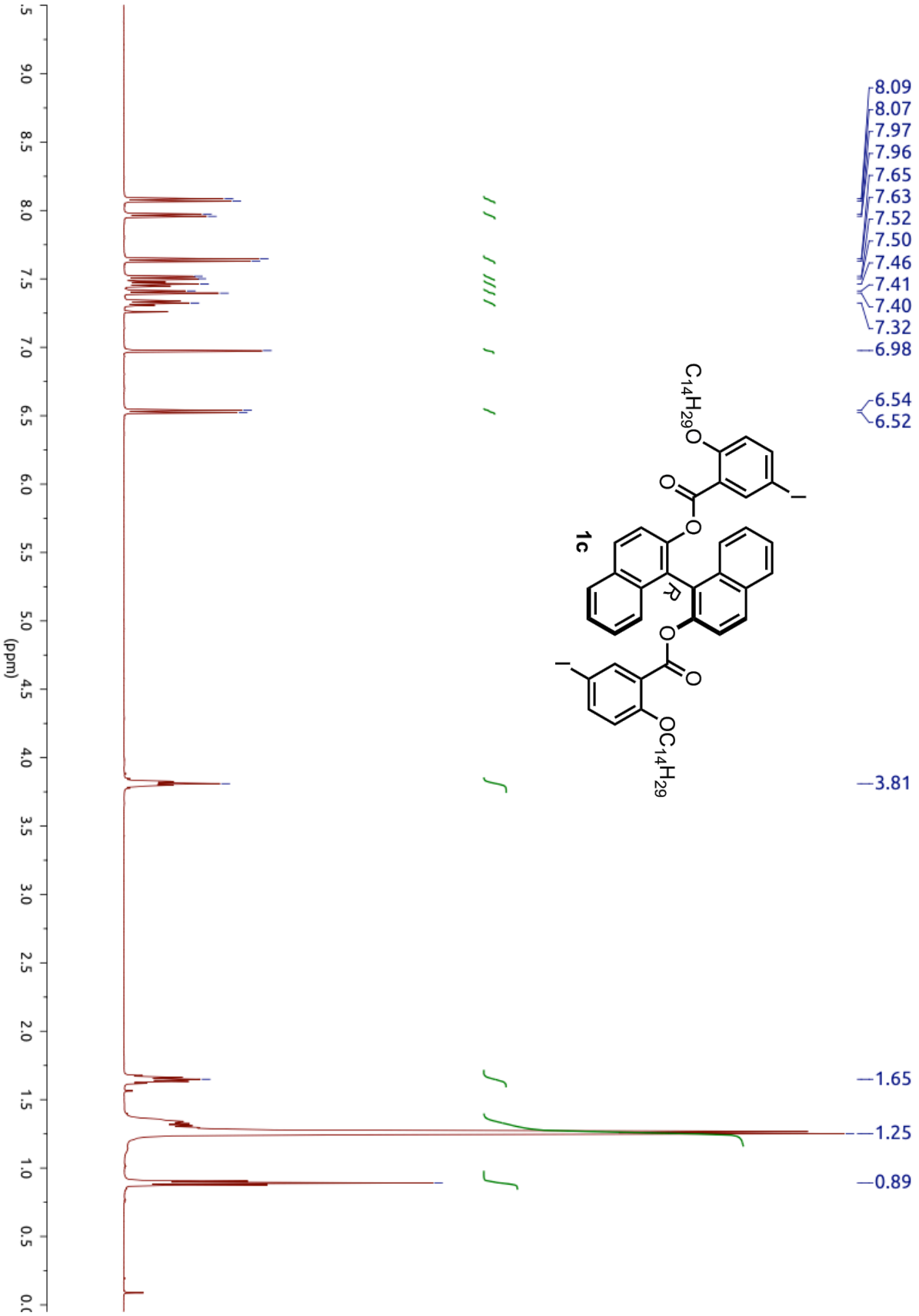


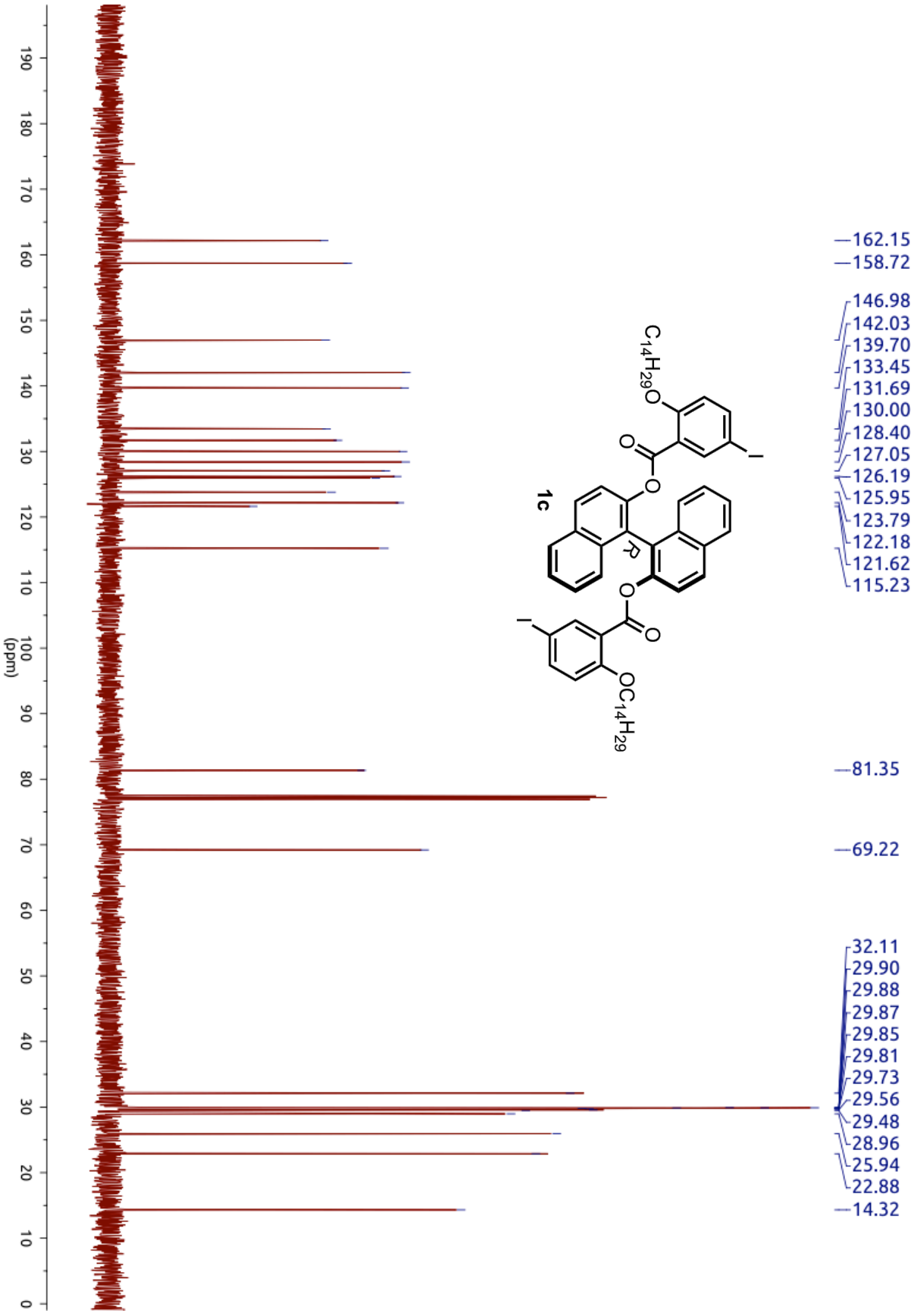

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)
7.99
7.95
7.89
7.56
7.43
7.28
6.63
3.78
3.68
3.57
3.53
3.48
3.42
3.33
TgO
TgO
OTg
OTg
SS-2mer

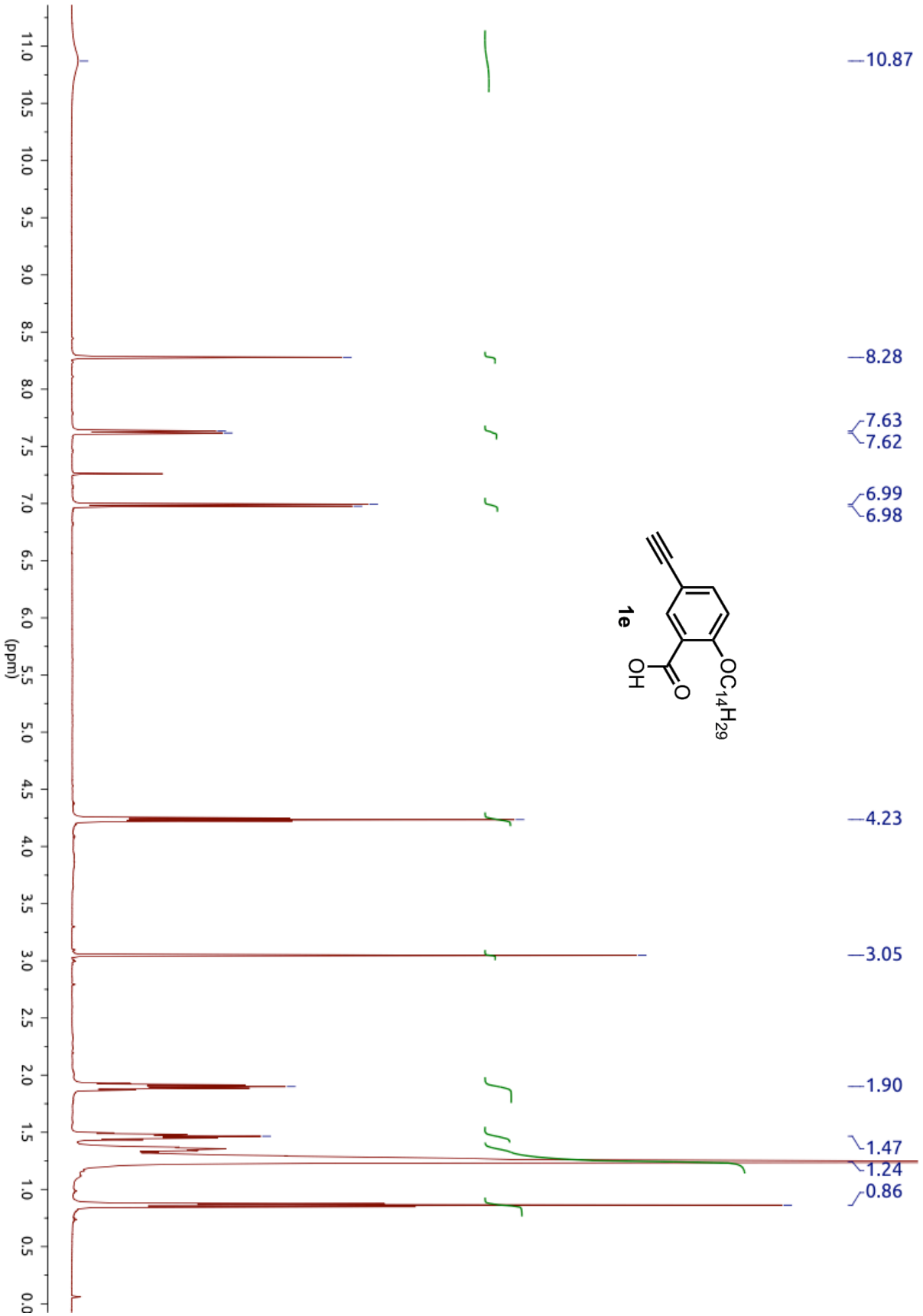


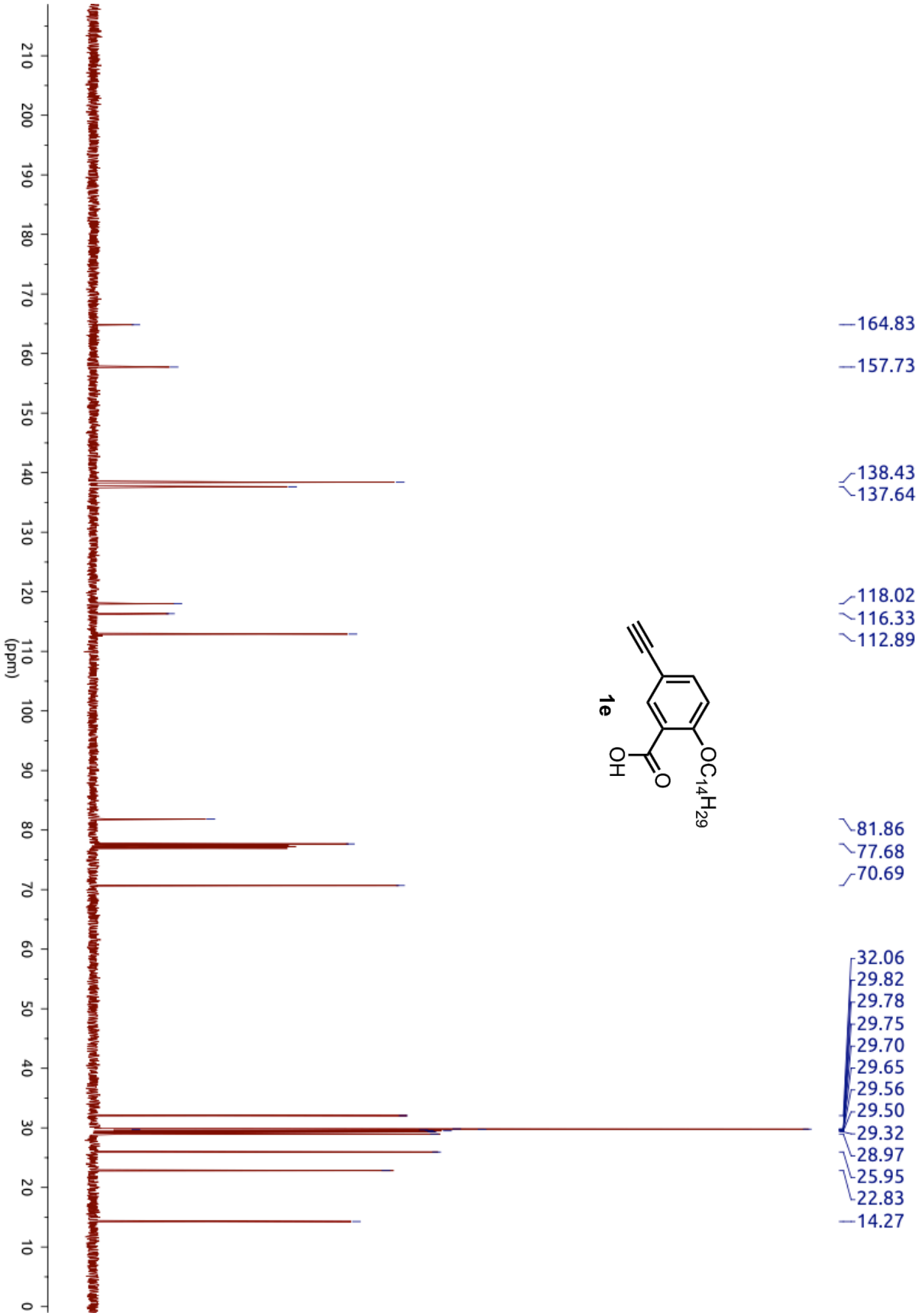


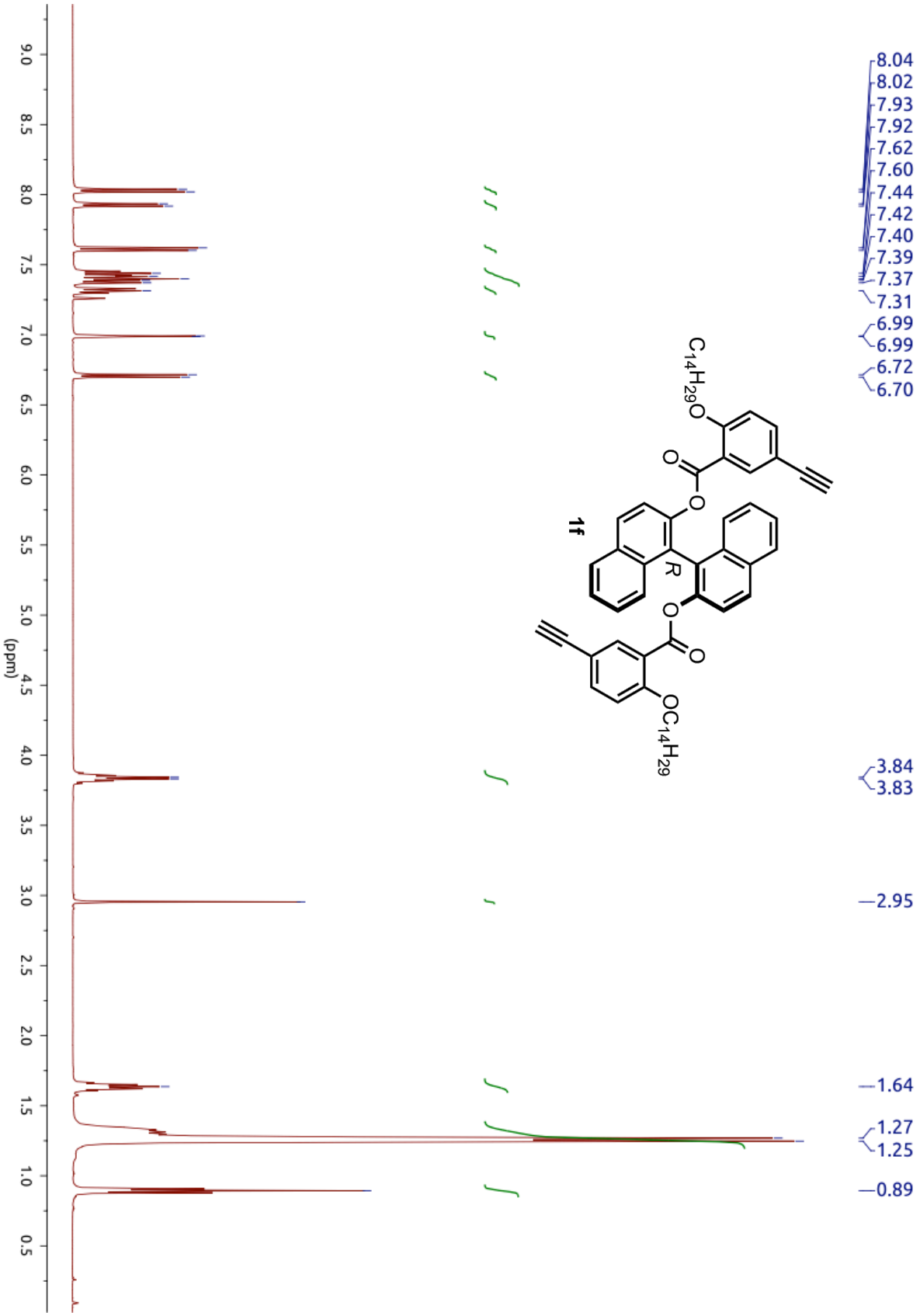


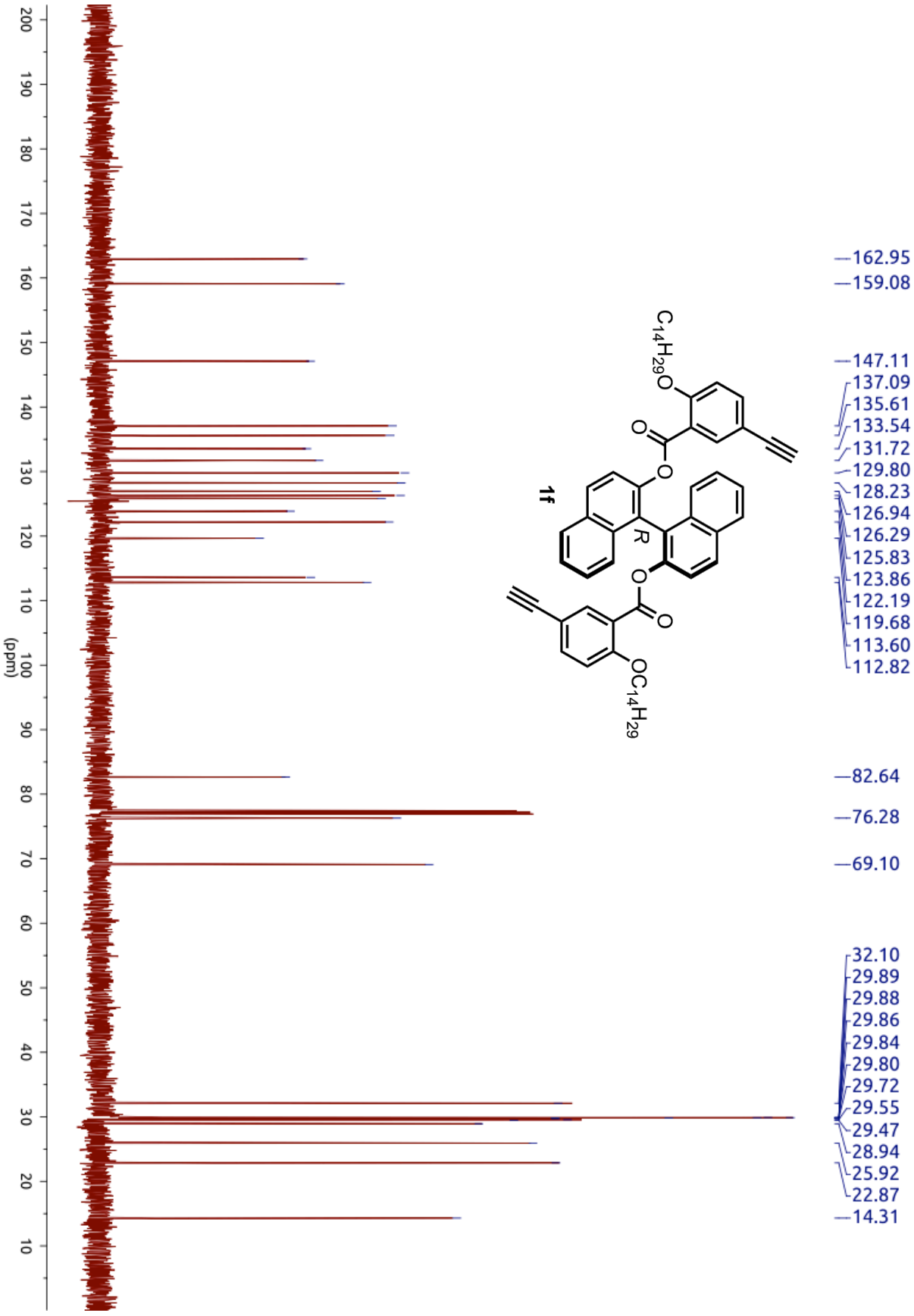


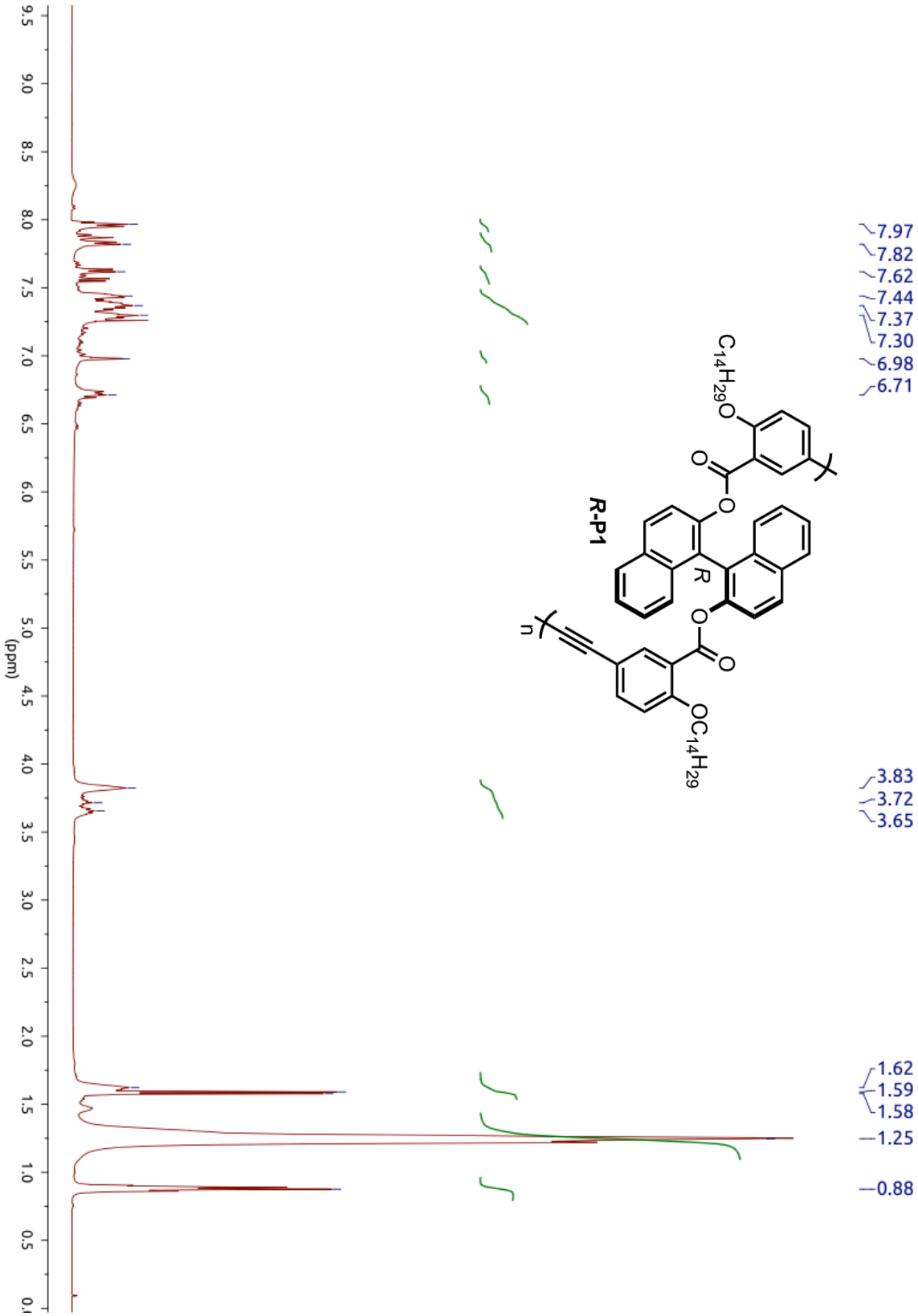


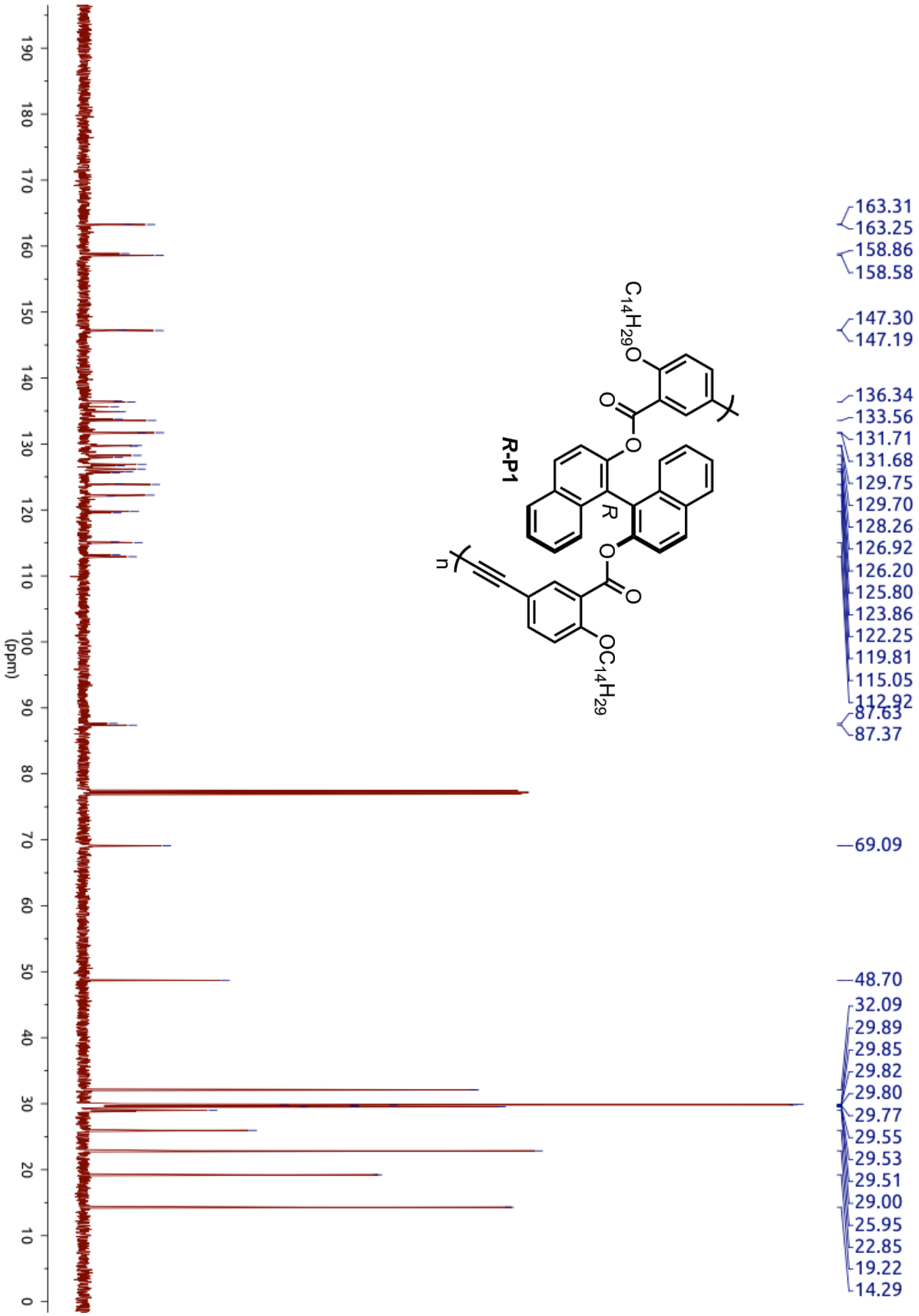


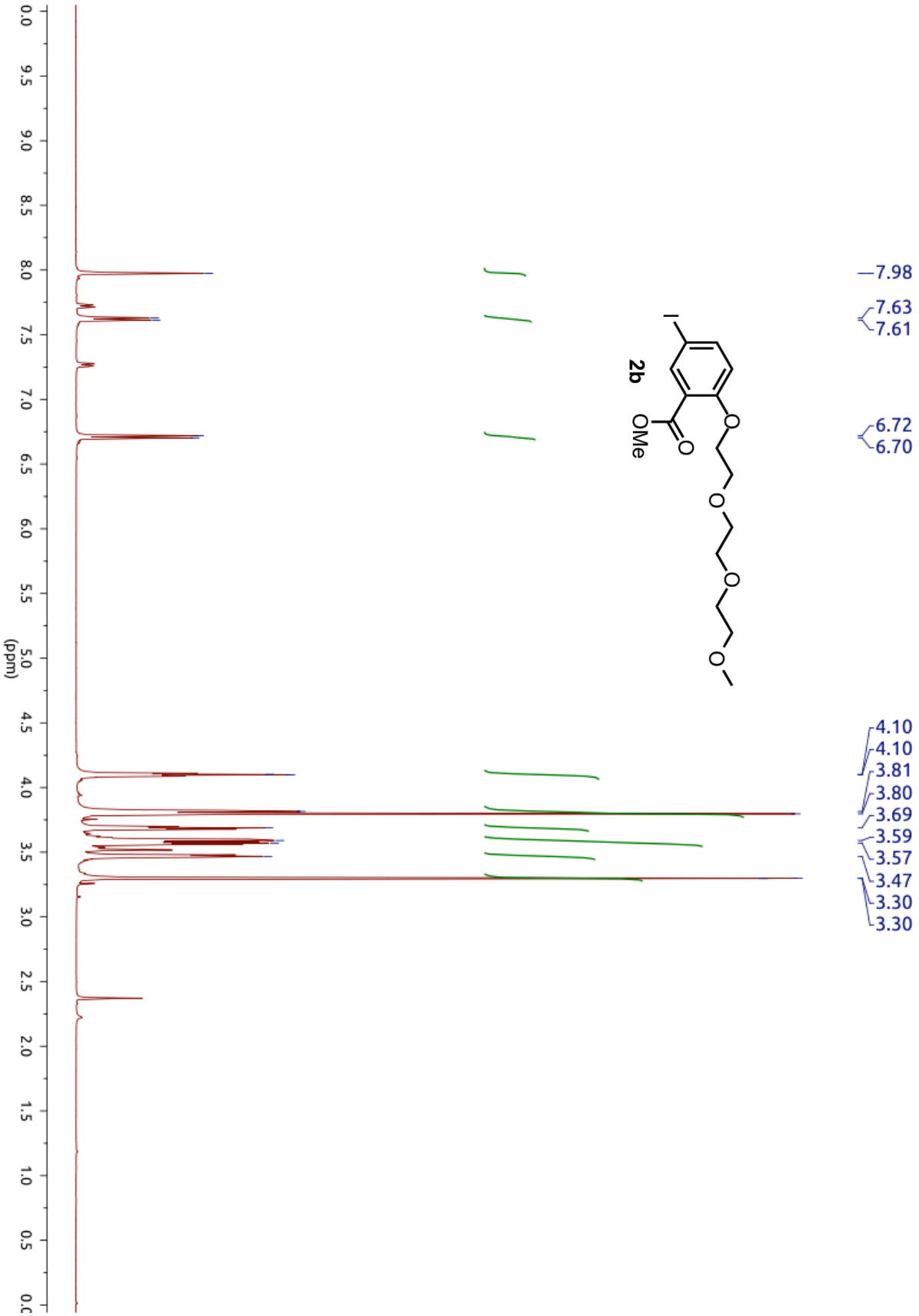


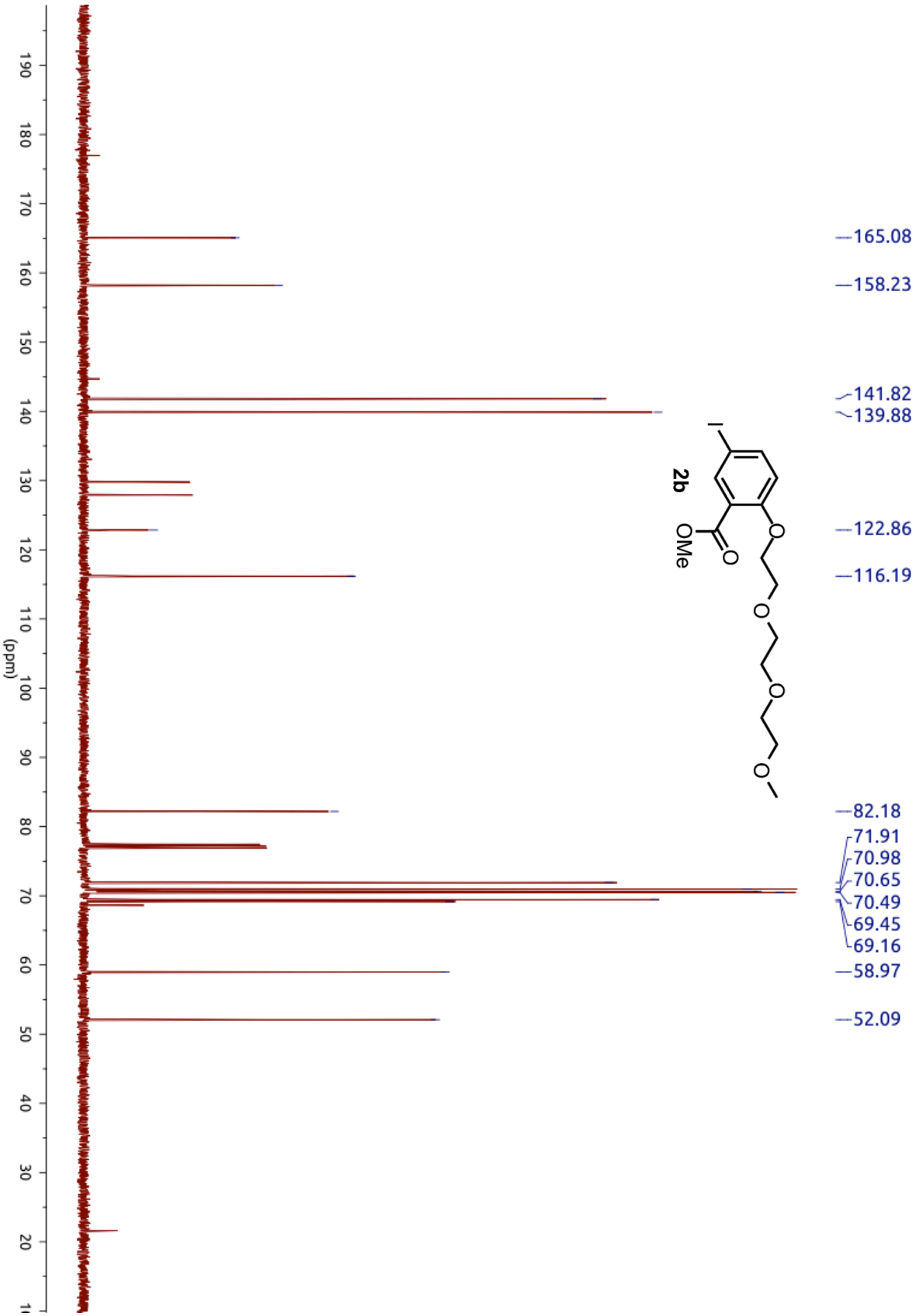


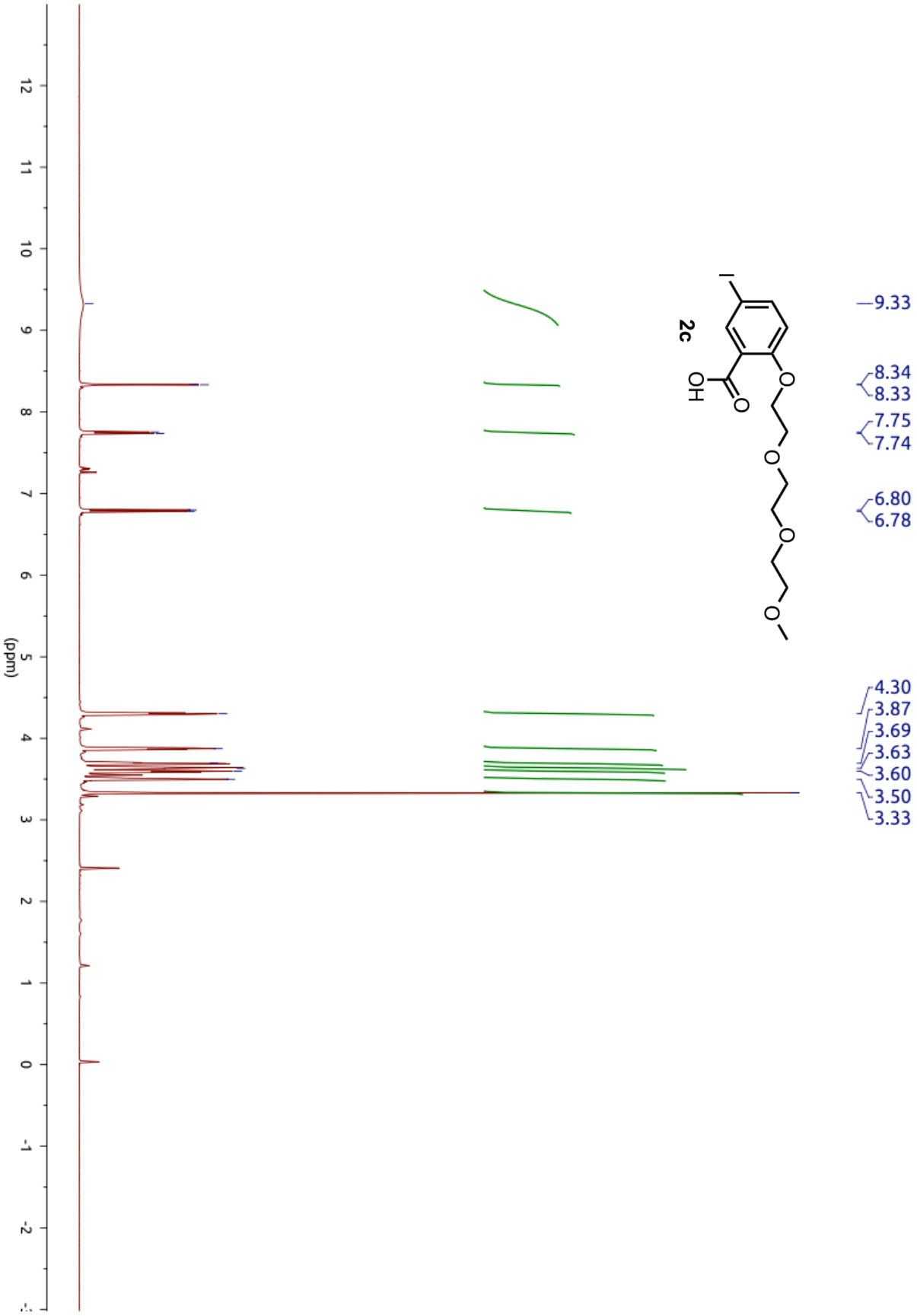


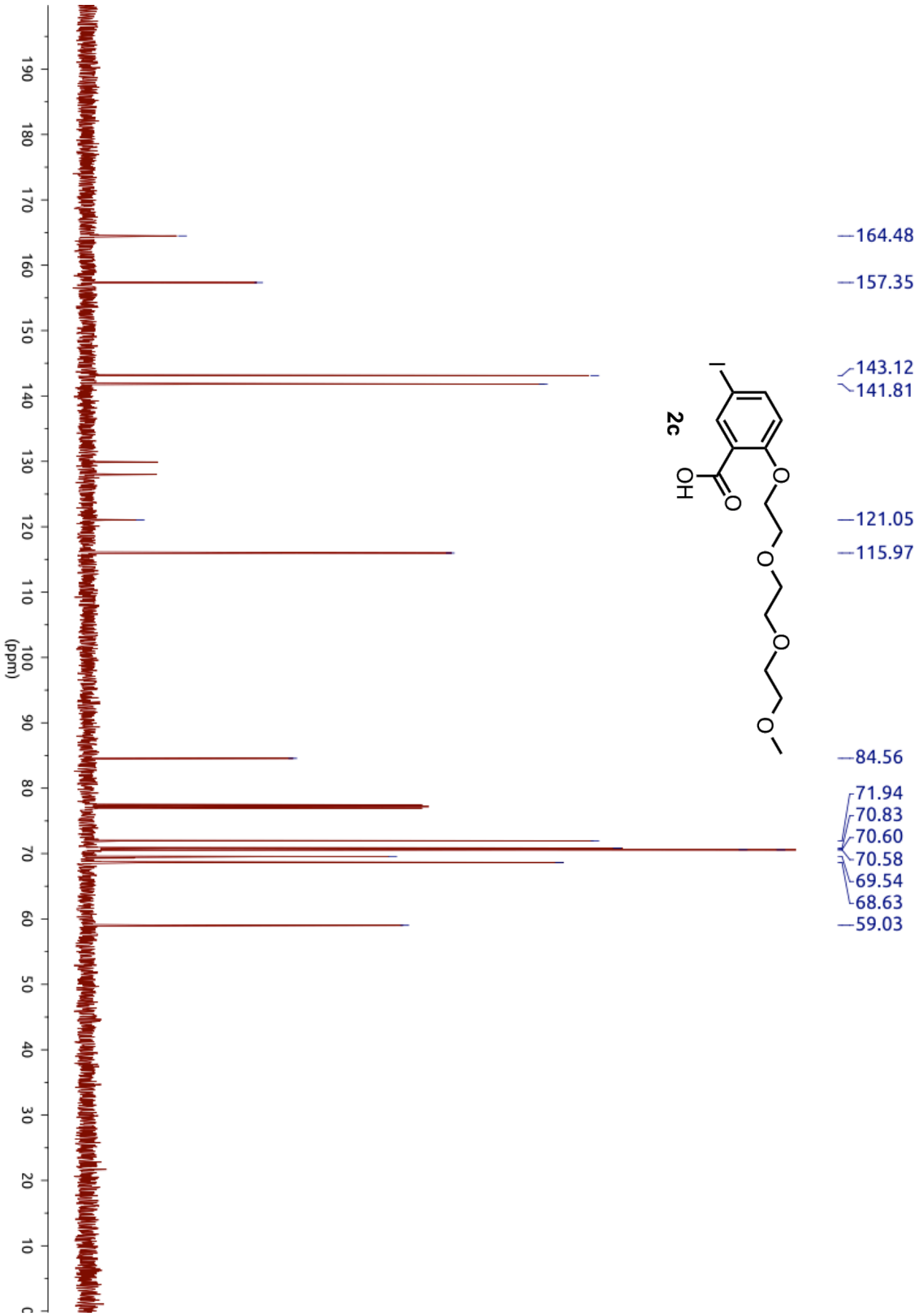


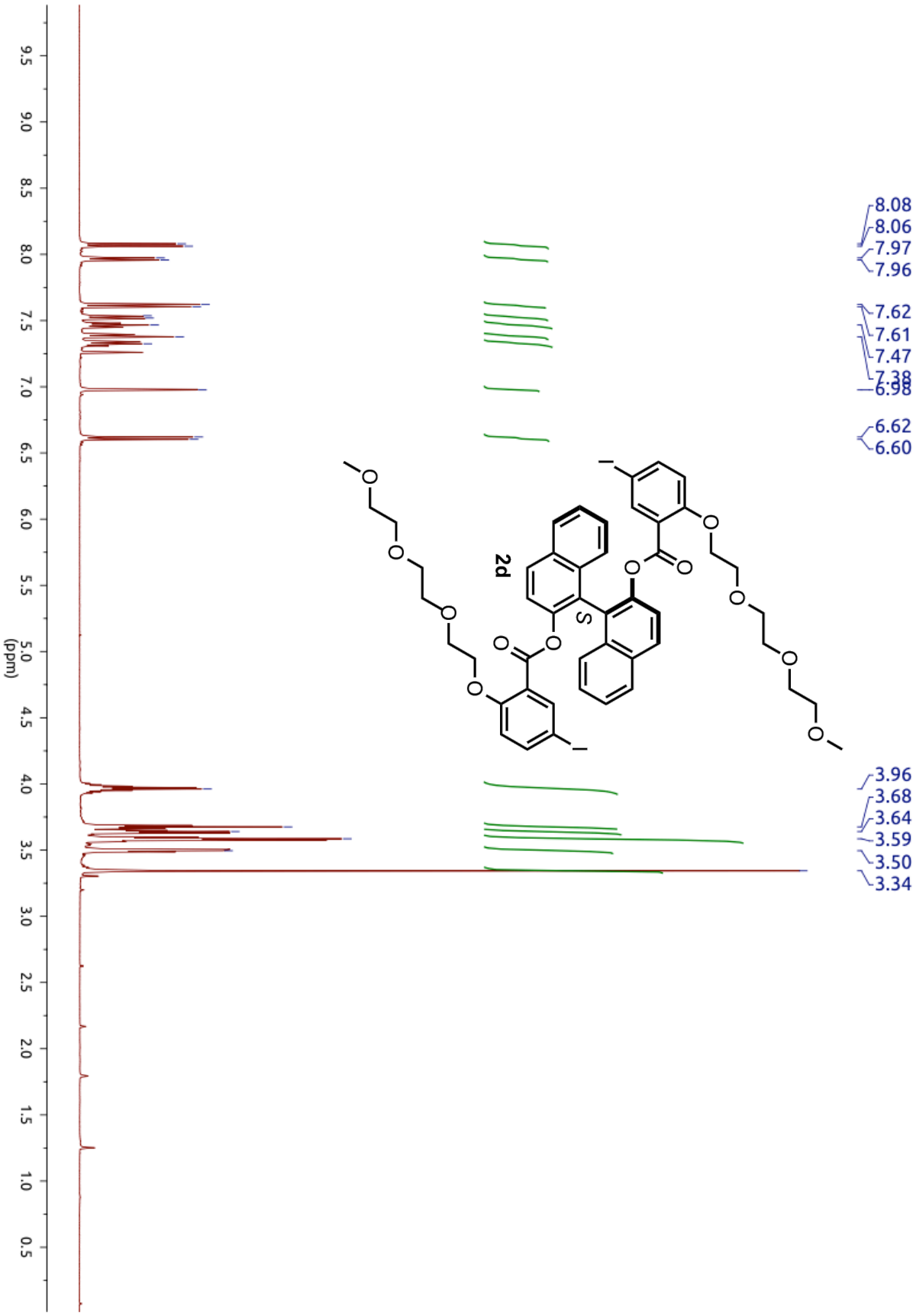


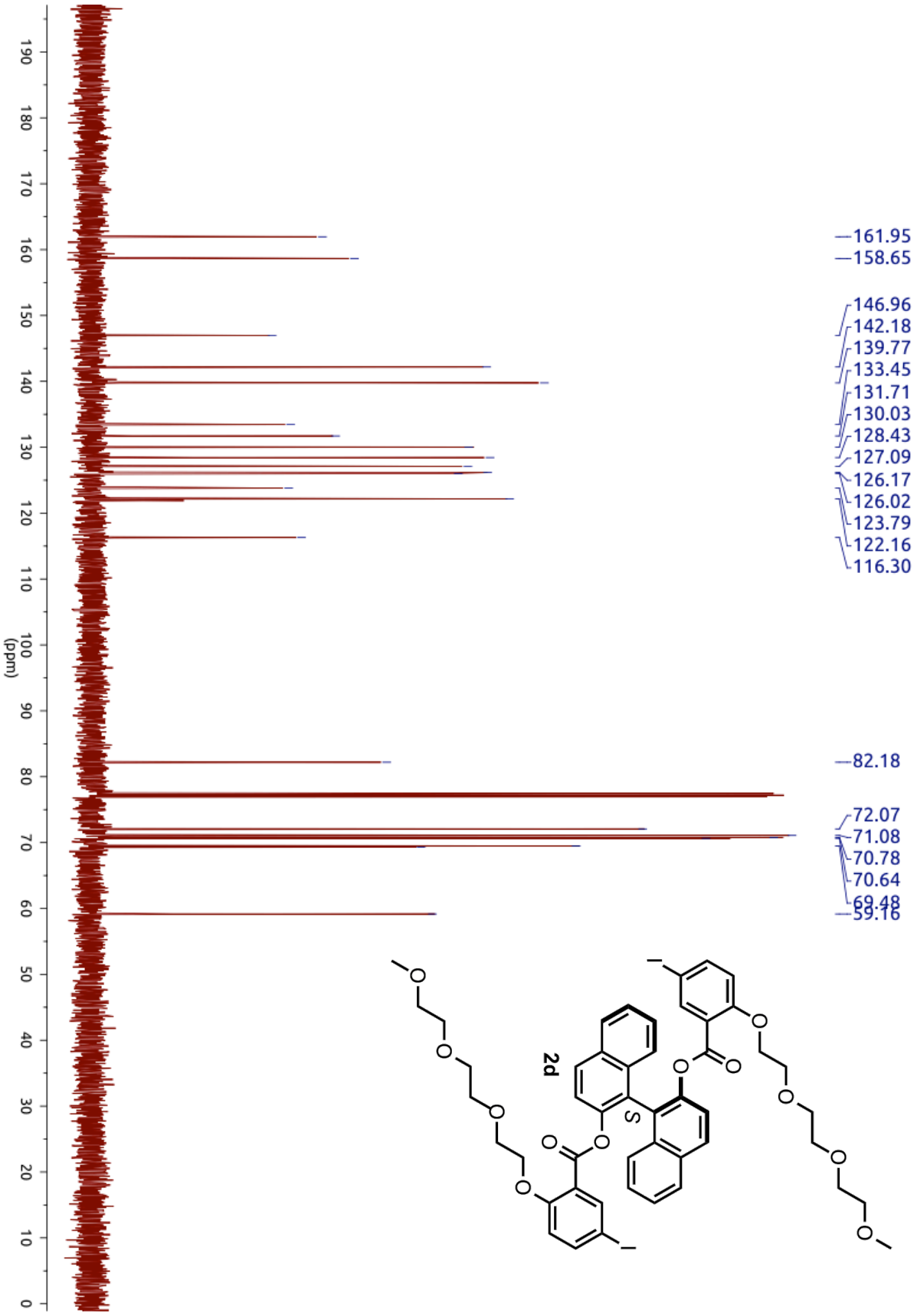


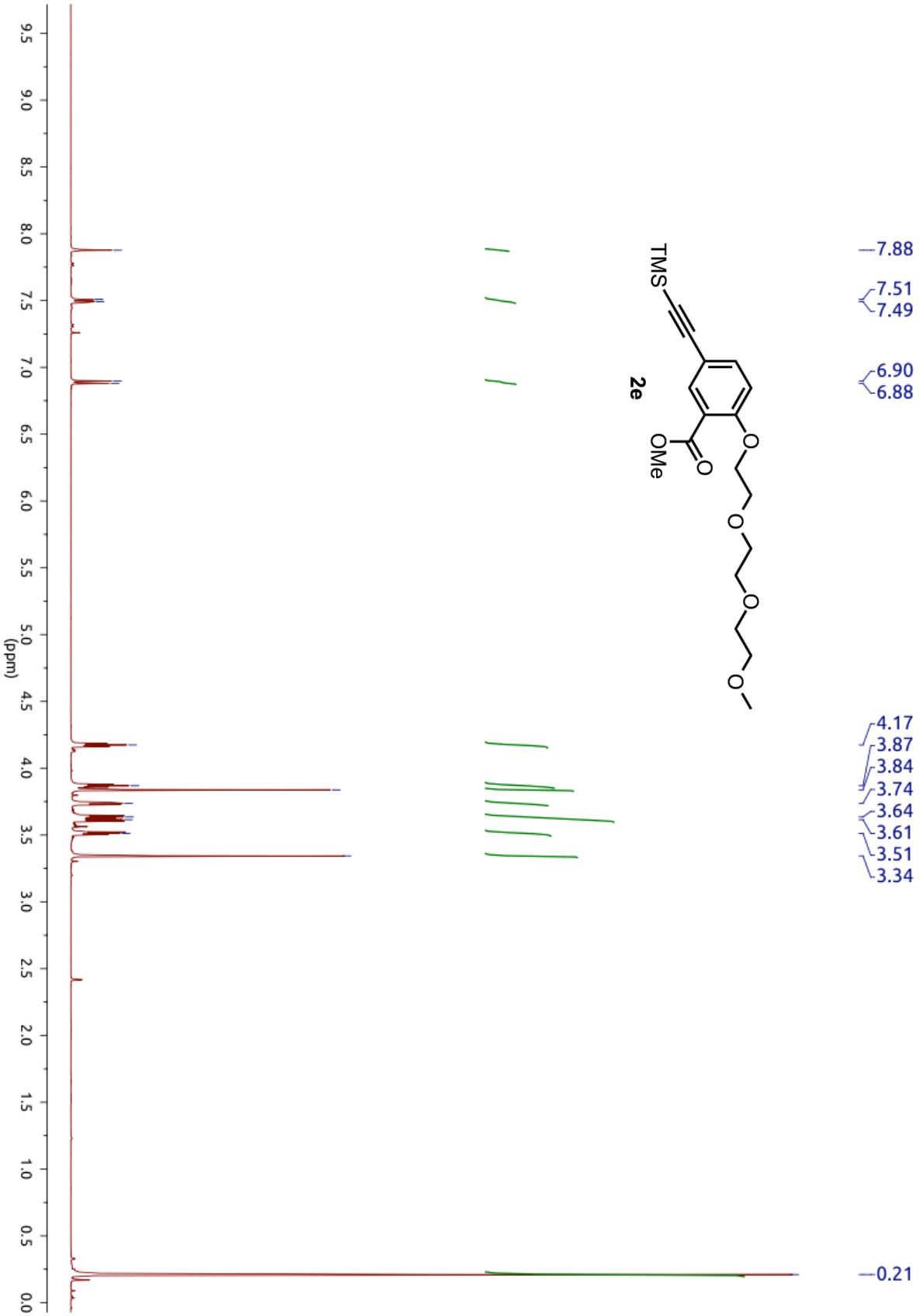


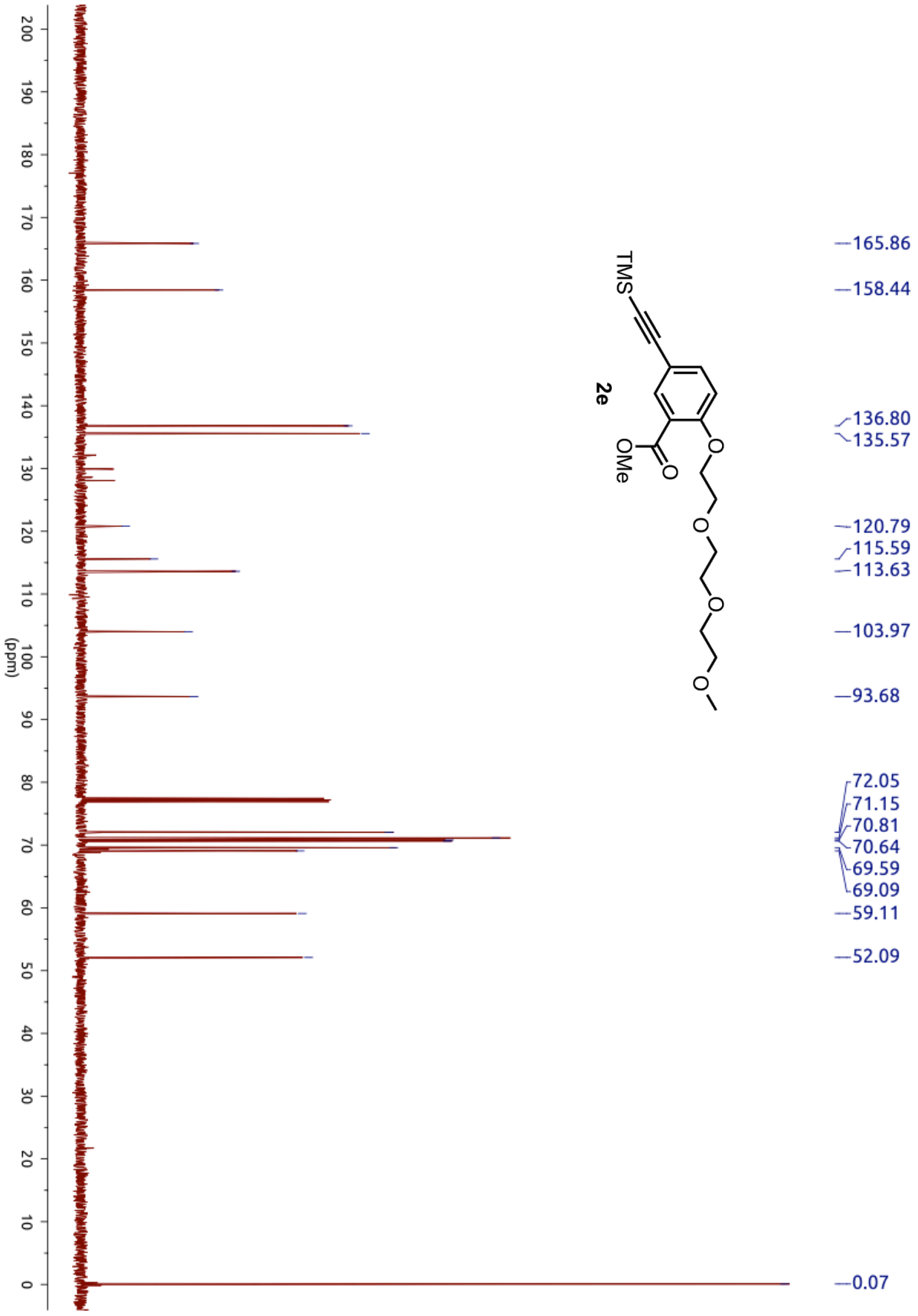


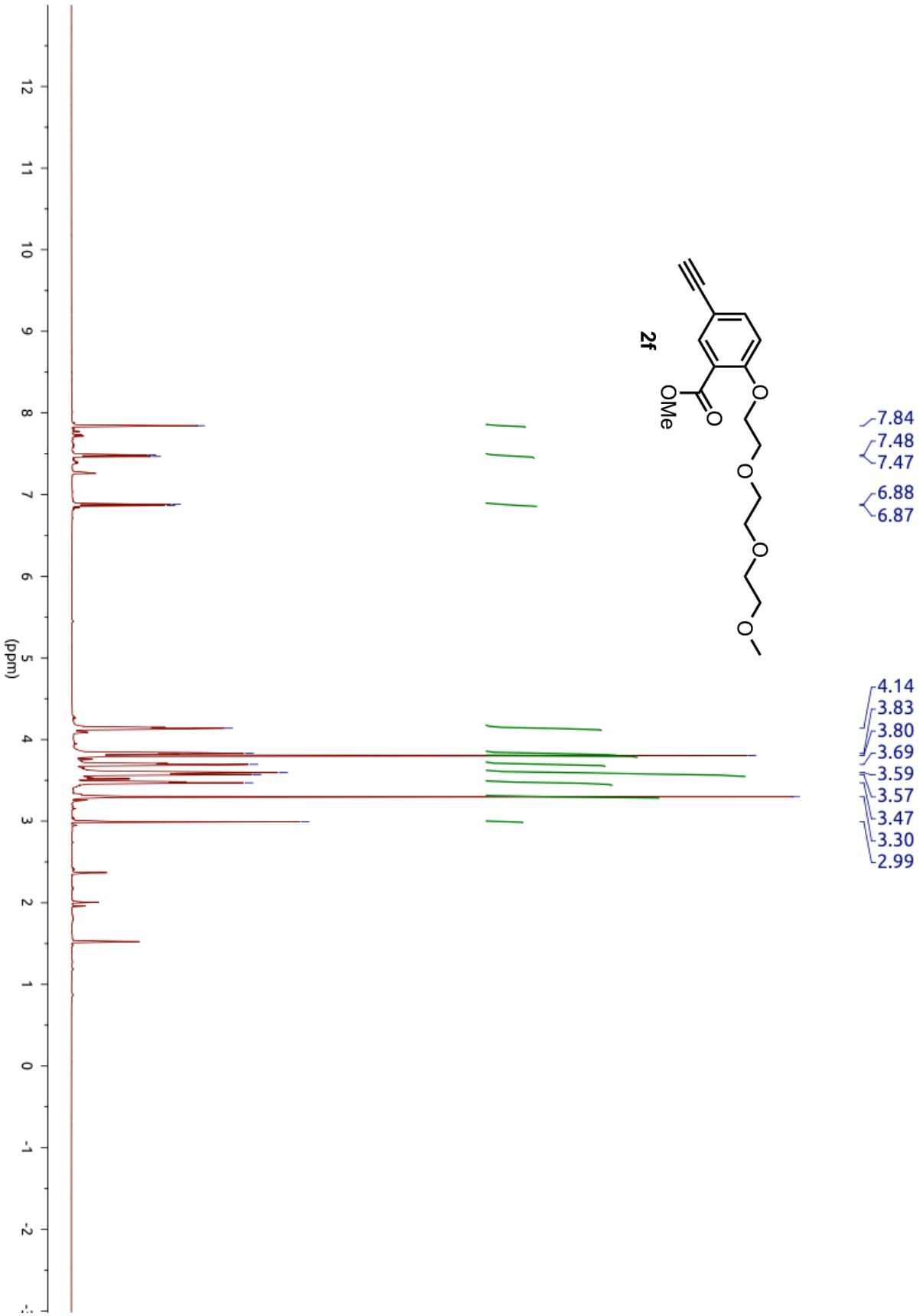


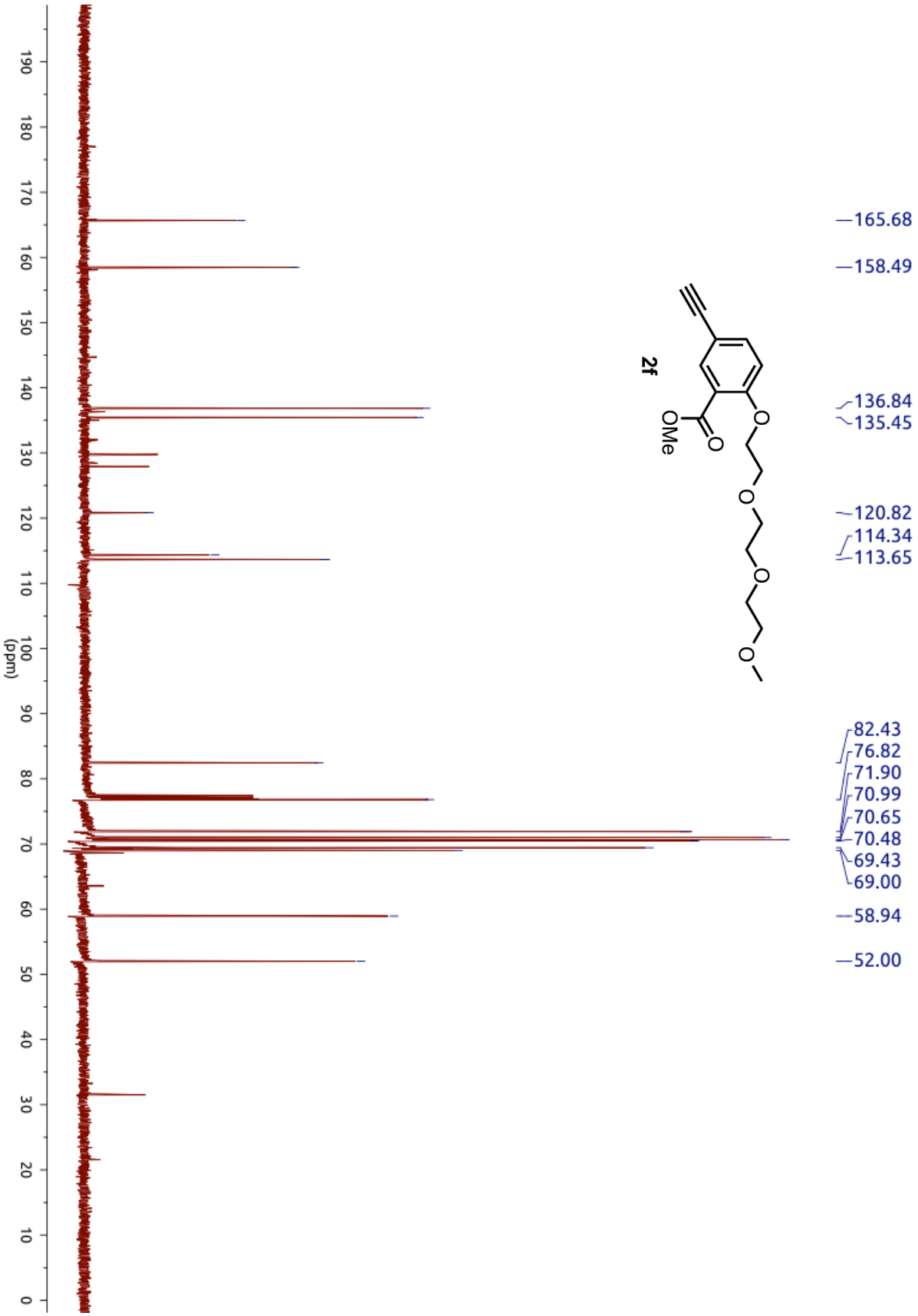


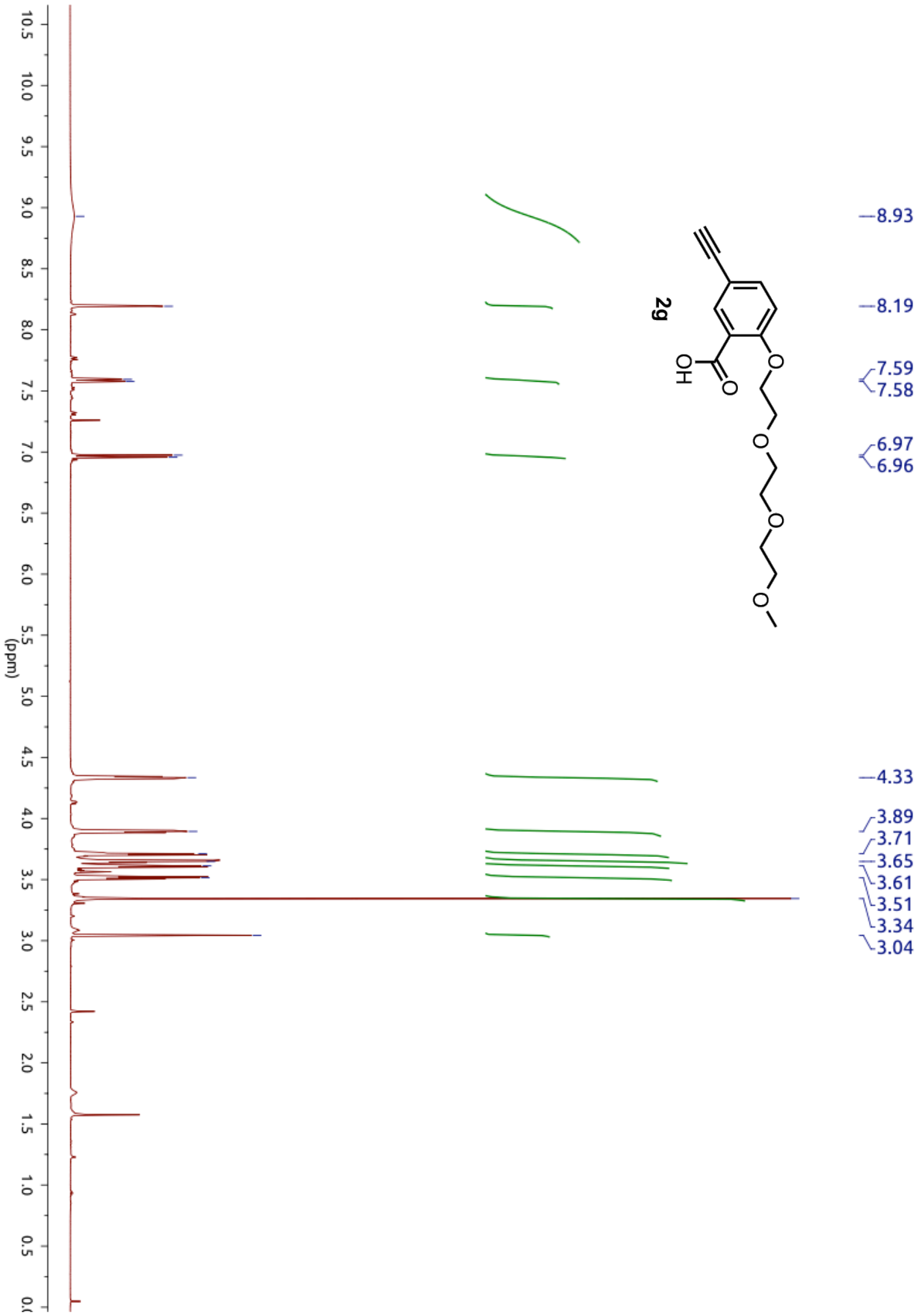

161.95
158.65
146.96
142.18
139.77
133.45
131.71
130.03
128.43
127.09
126.17
126.02
123.79
122.16
116.30
82.18
72.07
71.08
70.78
70.64
69.48
59.16
(ppm)
2d
S

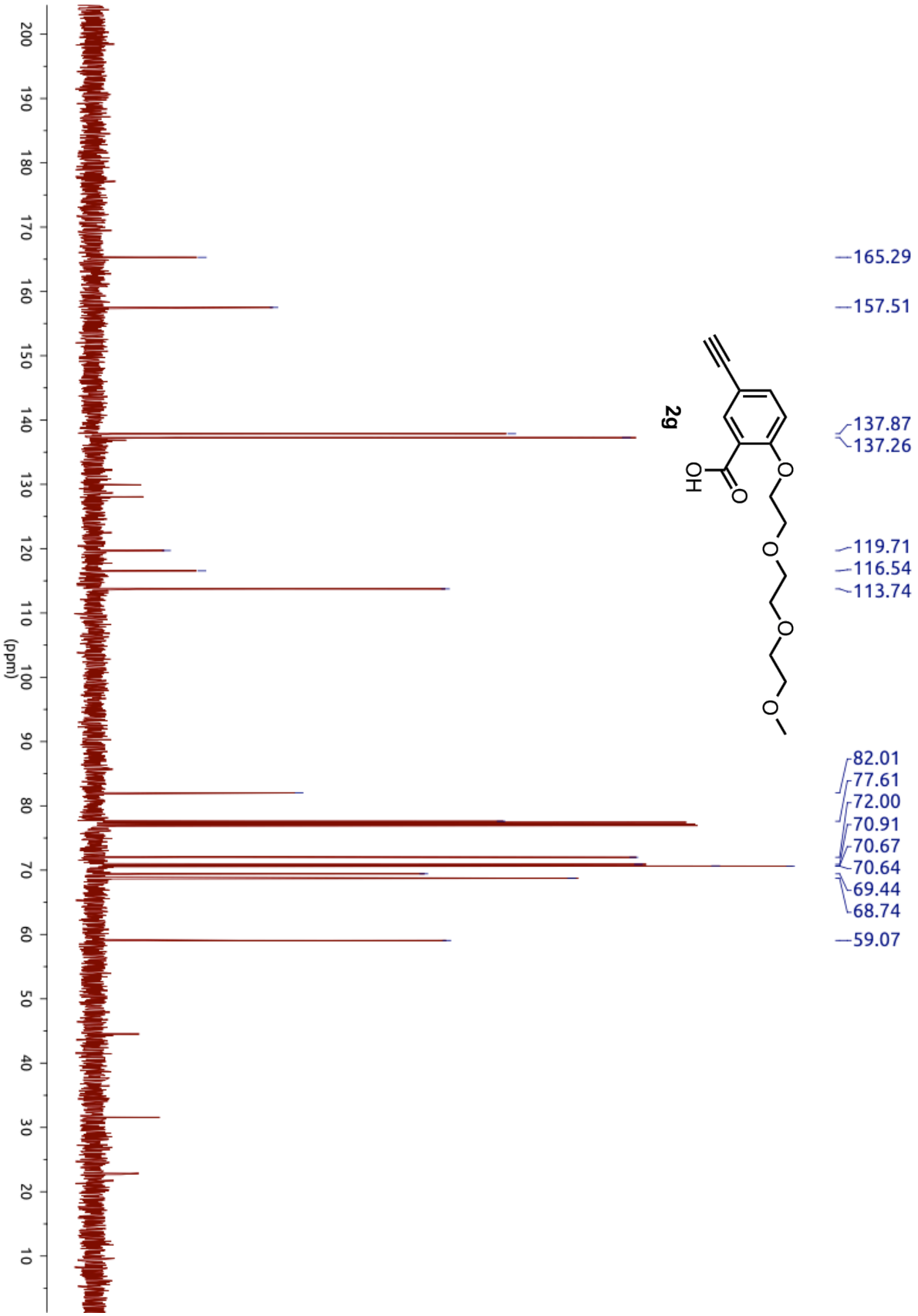


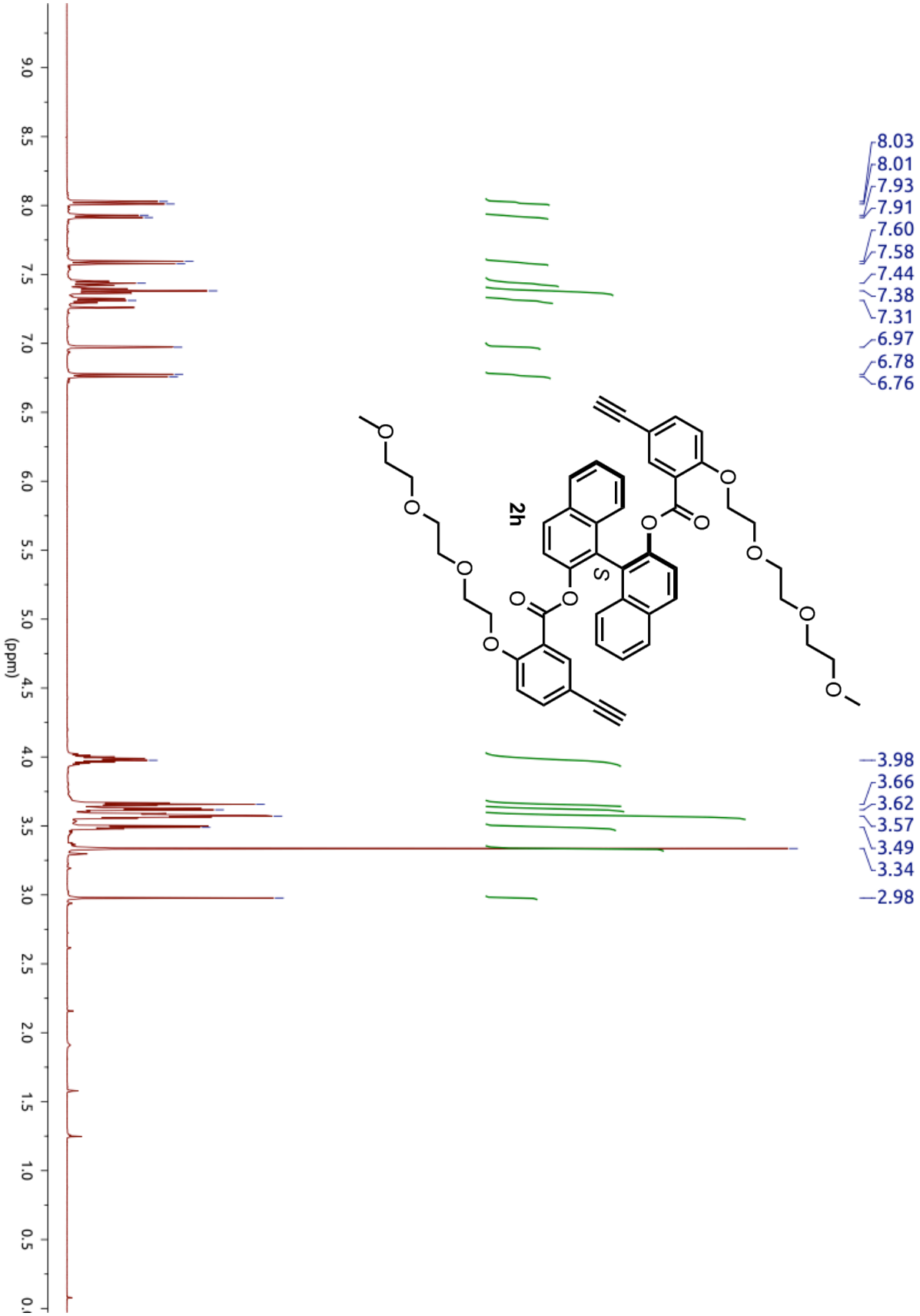


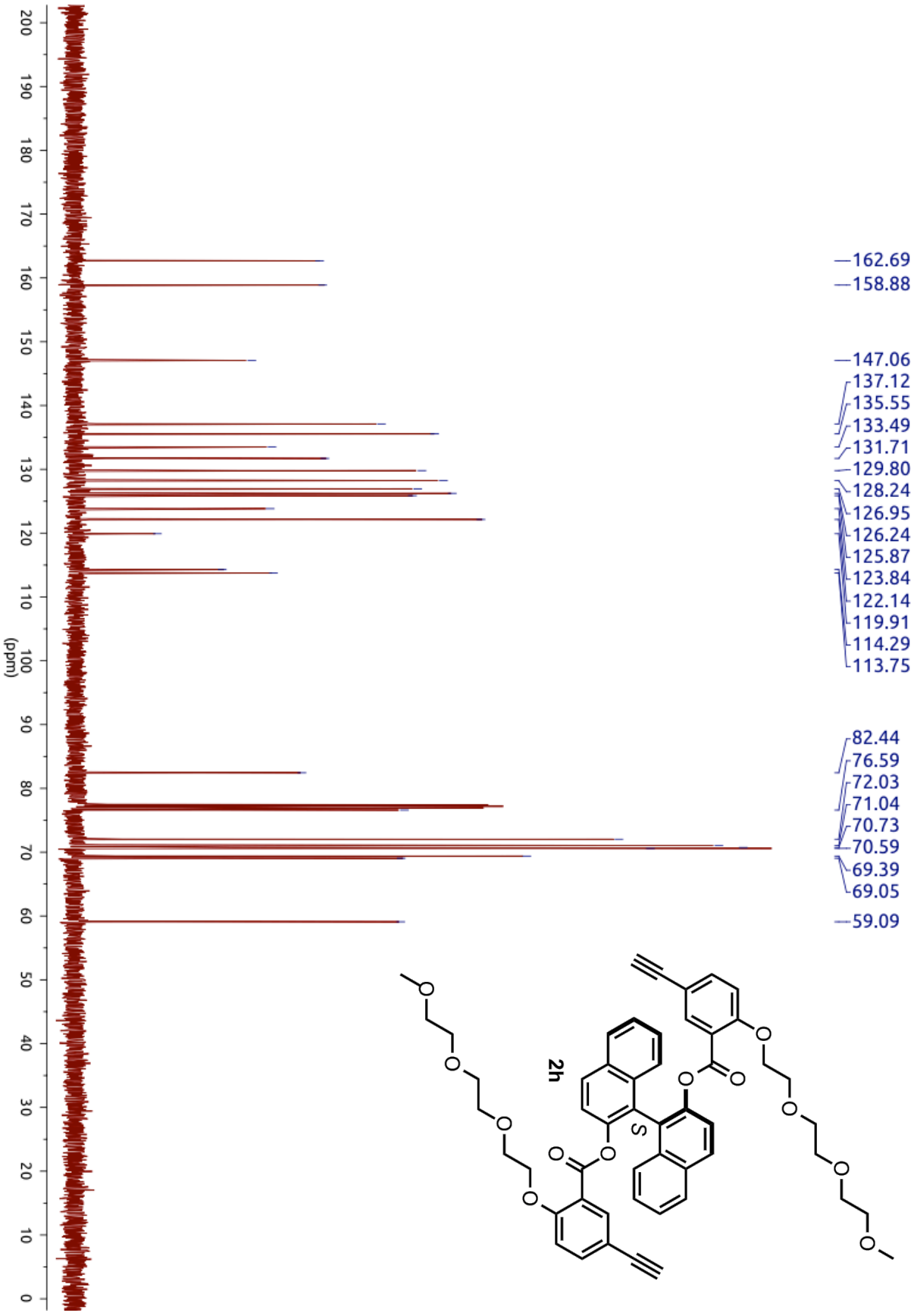


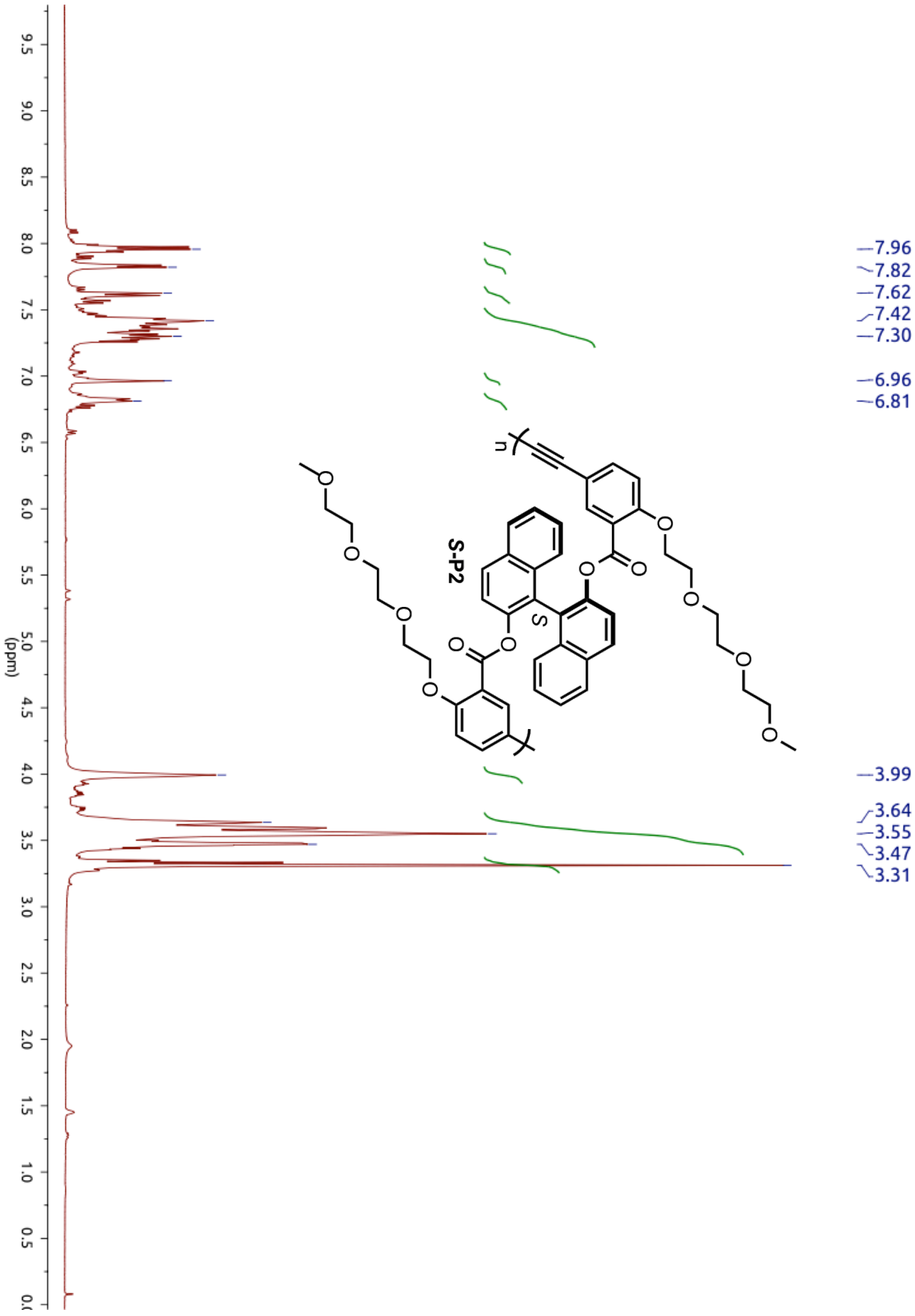


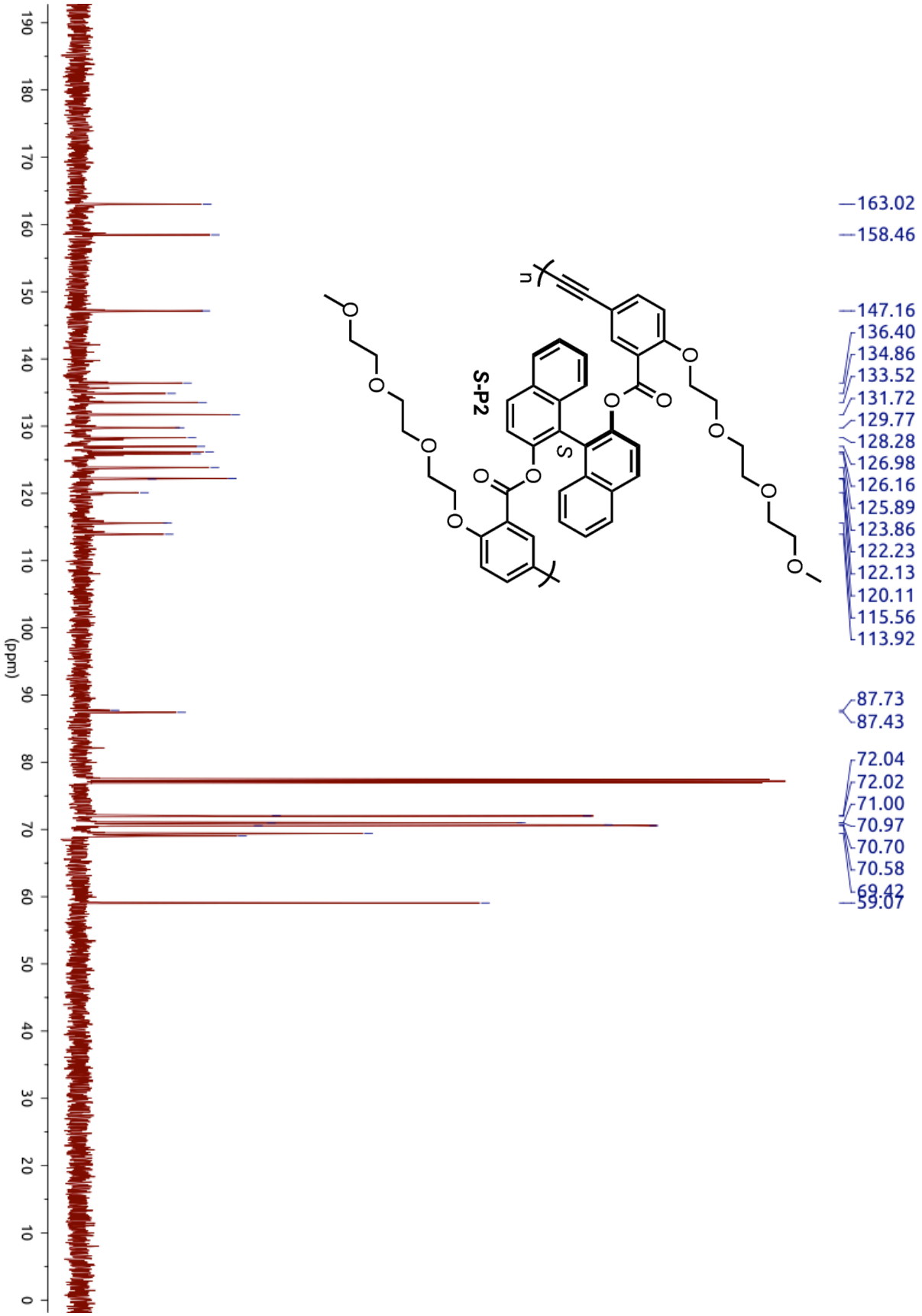


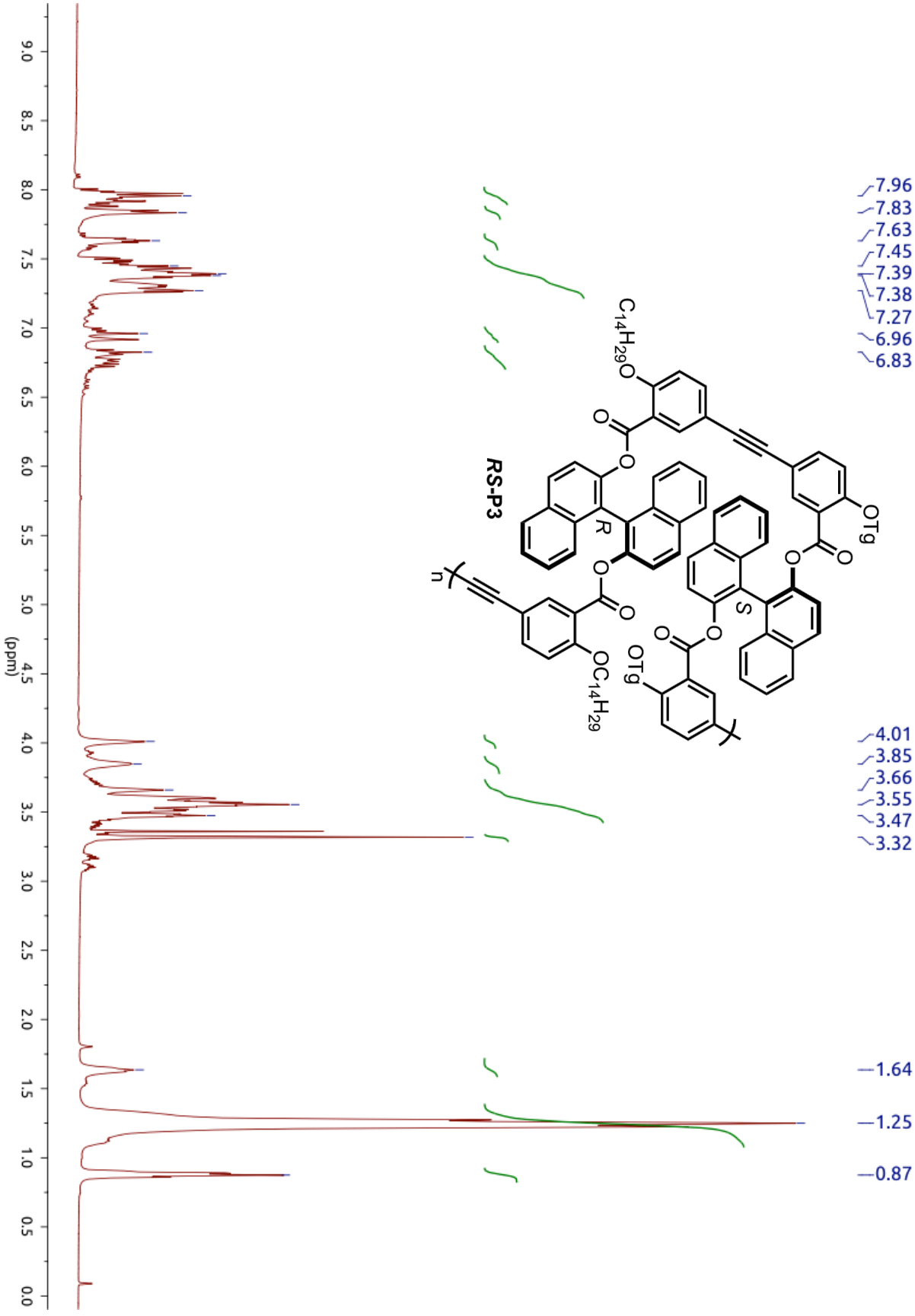


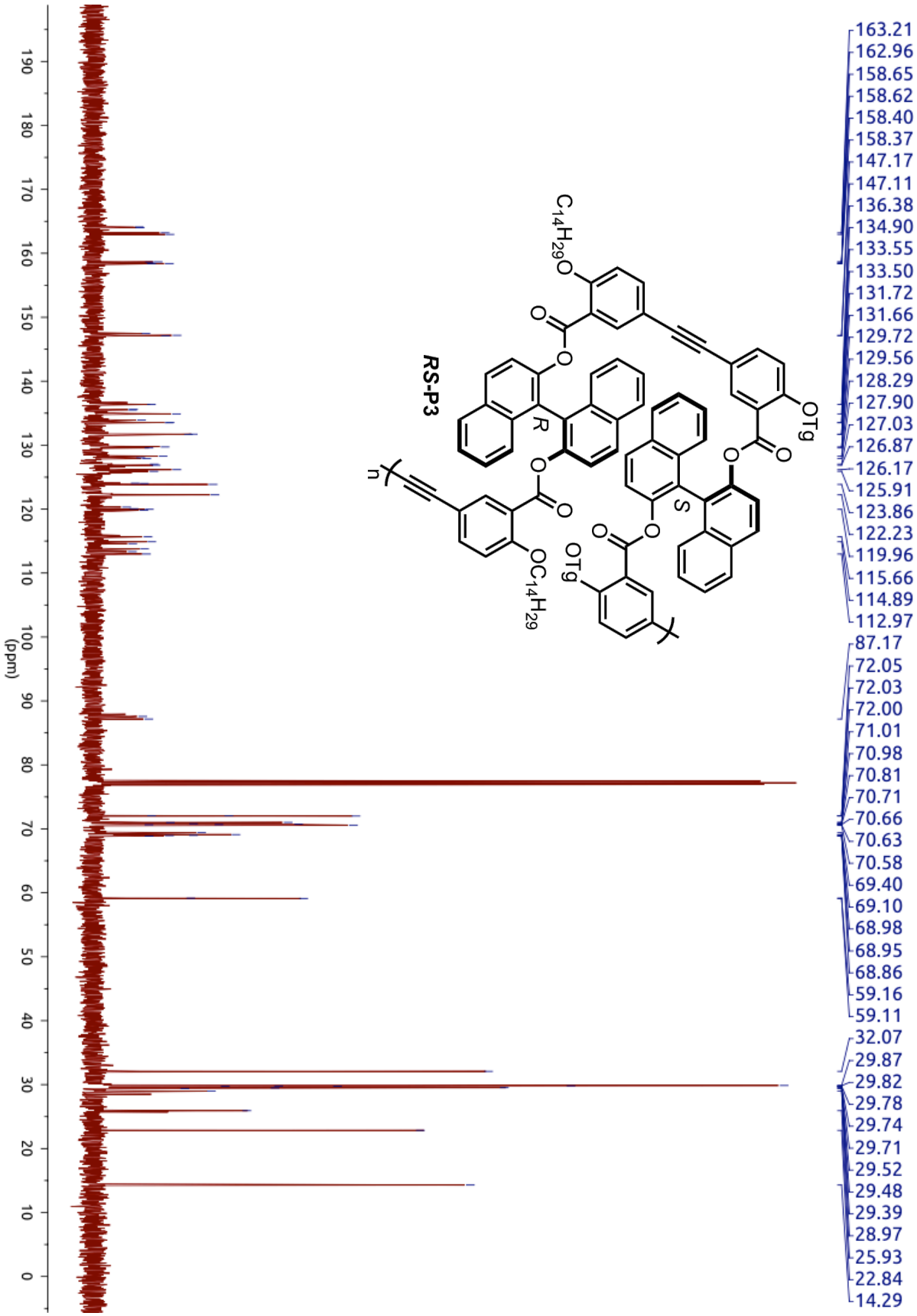












References

1. W. Zhang, J. S. Moore, *Org. Synth.* 2007, **84**, 163.
2. K. Susumu, M. J. Therien, *J. Am. Chem. Soc.* 2002, **124**, 8550.
3. S. W. Sisco, J. S. Moore, *J. Am. Chem. Soc.* 2012, **134**, 9114.