

Supporting Information For:
Furan-Containing Singlet Oxygen-Responsive Conjugated Polymers

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1. General Considerations

The following chemicals were purchased from commercial sources and used as received: *n*-butyllithium (Aldrich), furan (Aldrich), iodine (Aldrich), phenylboronic acid (Strem), 4-methoxyphenylboronic acid (Strem), 4-fluorophenylboronic acid (Strem), 4-(trifluoromethyl)phenylboronic acid (Alfa Aesar), 3,5-bis(trifluoromethyl)phenylboronic acid (Aldrich), PdCl₂(PPh₃)₂ (Strem), BBr₃ (Aldrich), 1-dodecanethiol (Aldrich), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (Aldrich), Pd(PPh₃)₄ (Strem), Aliquat 336 (Aldrich), K₂CO₃ (Fisher), NaOH (Aldrich), and KOH (Fisher). Tetrahydrofuran (THF), dichloromethane (DCM), diethylether (Et₂O), and toluene were dried on an Innovative Technologies PureSolv 400 solvent purifier. Dry dimethyl sulfoxide (DMSO) was purchased from Acros (AcroSeal). Dry 1-methyl-2-pyrrolidinone (NMP) was purchased from Sigma (Sure/Seal).

All synthetic manipulations were performed under standard air-free conditions under an atmosphere of argon gas with magnetic stirring unless otherwise mentioned. Flash chromatography was performed using silica gel (230-400 mesh) as the stationary phase. NMR spectra were acquired on a Bruker Avance III 500 or Bruker DPX-300 spectrometer. Chemical shifts are reported relative to residual protonated solvent (7.27 ppm for CHCl₃). High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility using a peak-matching protocol to determine the mass and error range of the molecular ion. Molecular weight distribution measurements of the polymers were conducted with a Shimadzu Gel Permeation Chromatography (GPC) system equipped with a Tosoh TSKgel GMHhr-M mixed-bed column and guard column using either UV or refractive index detectors. The column was calibrated with low polydispersity poly(styrene) standards (Tosoh, PSt Quick Kit) with THF as the mobile phase eluting at 0.75 mL/min. All reactants and solvents were purchased from commercial suppliers and used without further purification, unless otherwise noted.

2. Optical Experiments

All solution optical spectra were acquired of samples in quartz cuvettes (NSG Precision Cells). Electronic absorbance spectra were acquired with a Varian Cary-100 instrument in double-beam mode using a solvent-containing cuvette for background subtraction spectra. Fluorescence emission spectra were obtained by using a PTI Quantum Master 4 equipped with a 75 W Xe lamp. All fluorescence spectra are corrected for the output of the lamp and the dependence of detector response to the wavelength of emitted light. Fluorescence spectra were acquired using sample absorbances less than 0.1 OD. Fluorescence quantum yields were determined relative to either quinine sulfate in 0.1 N H₂SO₄ or Coumarin 6 in ethanol. Irradiation of the methylene blue photosensitizer to generate ¹O₂ was performed with either 1) 200W Hg/Xe lamp (Newport-Oriel) equipped with a condensing lens, recirculating water, shutter, and 515 nm and 590 nm high-pass filters, or 2) a 4.5 mW 635 nm laser diode (ThorLabs).

2a. Fluorescence response to singlet oxygen

A cuvette containing the test sample solution was irradiated for numerous timed intervals. Both the absorbance and fluorescence spectra were taken after each interval of irradiation. The

absorbance for both methylene blue and samples was approximately 0.1 OD. The excitation wavelengths used for the fluorescence spectra are summarized in the Table 1.

	PFa	PFb	PFc	PFd	PF-8a	PF-8c
λ_{ex}	380 nm	395 nm	390 nm	395 nm	380 nm	390 nm

Table S1. Excitation wavelengths chosen for fluorescence spectra.

2b. Kinetics

A stock solution of methylene blue was prepared in CH₂Cl₂ to give an absorbance of ~1.0 at its peak. 2-Phenyl-5-(4-methoxyphenyl)furan (**4a**), 2-(4-fluorophenyl)-5-(4-methoxyphenyl)furan (**4b**), 2-(4-trifluorophenyl)-5-(4-methoxyphenyl)furan (**4c**), or 2-(3,5-bis(trifluoromethyl)phenyl)-5-(4-methoxyphenyl)furan (**4d**) was dissolved in CH₂Cl₂ at a concentration of 0.005 M to give stock solutions. When 25 μ L of each stock solution was dissolved in 3.5 mL MB solution, the final concentration of the corresponding compound in the sample was 35.5 μ M. The solution was irradiated for numerous timed intervals, with acquisition of an absorbance spectrum after each interval until the spectra stopped changing between intervals of irradiation (all furan groups having reacted). This procedure was repeated several times for (**4a-4d**), 9,10-diphenylanthracene (DPA), and all conjugated polymers in CH₂Cl₂. The initial concentration of polymer was adjusted in a way that it contains the same concentration of furan moieties as the small molecule kinetics experiments. The wavelengths used for the analysis of kinetics were the peaks of the highest absorbance of small molecule furan pendants (**4a-4d**).

3. Detailed Synthetic Procedures

2-Iodofuran (1). A solution of *n*-Butyllithium (3.28 mL, 1.6 M in hexanes, 5.25 mmol, 1.0 eq) was added dropwise to a solution of furan (0.53 mL, 7.4 mmol, 1.4 eq) in dry Et₂O (5 mL) at -78 °C under argon and stirred vigorously at -78 °C for 30 minutes. The reaction mixture was then warmed to 0 °C and stirred for 1 hour. The solution was then warmed to room temperature and stirred for 90 minutes before being cooled again to -78 °C. Iodine (1.87 g, 7.35 mmol, 1.4 eq) in 10 mL of Et₂O was slowly added to this solution, which was warmed slowly to room temperature and stirred overnight. The reaction was stopped by adding Na₂S₂O₃ (15% aq). Organics were extracted twice with Et₂O, and the combined organic phases were washed with brine, dried over MgSO₄ and filtered. Removal of solvent *in vacuo* yielded 0.79 g of 2-iodofuran (77%) as a brown liquid pure by NMR¹ that was taken to the next step immediately without further purification.

2-Phenylfuran (2-H). Phenylboronic acid (245 mg, 2.0 mmol, 1.0 eq) was suspended in 8 mL of a DMF/water (3:1) mixture (which was deoxygenated by sparging with argon), followed by the addition of 2-iodofuran (662 mg, 3.4 mmol, 1.7 eq), PdCl₂(PPh₃)₂ (28 mg, 0.04 mmol, 0.02 eq), and K₂CO₃ (691 mg, 5.0 mmol, 2.5 eq) under argon atmosphere. The mixture was heated to 80 °C and stirred overnight. The mixture was then cooled to room temperature and water was added. Organics were extracted twice with Et₂O, and combined organic phases were washed with brine and dried over MgSO₄, filtered, and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes to yield **2-H**.² Yield: 197 mg (68%).

2-(4-fluorophenyl)furan (2-F). 4-fluorophenylboronic acid (848 mg, 6.1 mmol, 1.0 eq) was suspended in 24 mL of a DMF/water (3:1) mixture (which was deoxygenated by sparging with argon), followed by the addition of 2-iodofuran (2.0 g, 0.010 mol, 1.7 eq), PdCl₂(PPh₃)₂ (85 mg, 0.12 mmol, 0.02 eq), and K₂CO₃ (2.1 g, 15.3 mmol, 2.5 eq) under argon atmosphere. The mixture was heated to 80 °C and stirred overnight. The mixture was then cooled to room temperature and stopped by adding water. Organics were extracted twice with Et₂O, and combined organic phases were washed with brine and dried over MgSO₄, filtered, and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes to yield **2-F**.³ Yield: 546 mg (55%).

2-(4-Methoxyphenyl)furan (2-OMe). 4-Methoxyphenylboronic acid (309 mg, 2.03 mmol, 1.0 eq) was suspended in 8 mL of a DMF/water (3:1) mixture (which was deoxygenated by sparging with argon), followed by the addition of 2-iodofuran (670 mg, 3.45 mmol, 1.7 eq), PdCl₂(PPh₃)₂ (28.5 mg, 0.04 mmol, 0.02 eq), and K₂CO₃ (701 mg, 5.1 mmol, 2.5 eq) under argon atmosphere. The mixture was heated to 80 °C and stirred overnight. The mixture was then cooled to room temperature and stopped by adding water. Organics were extracted twice with Et₂O, and combined organic phases were washed with brine and dried over MgSO₄, filtered, and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and EtOAc (9.8:0.2, v/v) to yield **2-OMe**.⁵ Yield: 233 mg (66%).

2-Phenyl-5-iodofuran (3-H). A solution of *n*-butyllithium (0.52 mL, 1.6 M in hexanes, 0.83 mmol, 1.4 eq) was added dropwise to a solution of 2-phenylfuran (85 mg, 0.59 mmol, 1.0 eq) in dry THF (1 mL) at -78 °C under argon. The reaction mixture was then warmed to 0 °C and stirred for 10 minutes before being cooled again to -78 °C. Iodine (162 mg, 0.64 mmol, 1.1 eq) in 0.5 mL of THF was slowly added to this solution, which was warmed slowly to room temperature and stirred overnight. The reaction was stopped by adding Na₂S₂O₃ (15% aq). Organics were extracted twice with hexanes, and the combined organic phases were washed with brine, dried over MgSO₄, filtered, and concentrated using rotary evaporation. Compound **3-H** was taken to the next step immediately without further purification.

2-(4-fluorophenyl-5-iodofuran) (3-F). A solution of *n*-butyllithium (1.4 mL, 1.6 M in hexanes, 2.2 mmol, 1.4 eq) was added dropwise to a solution of 2-(4-fluorophenyl)furan (252 mg, 1.55 mmol, 1.0 eq) in dry THF (3.0 mL) at -78 °C under argon. The reaction mixture was then warmed to 0 °C and stirred for 20 minutes before being cooled again to -78 °C. Iodine (426 mg, 1.7 mmol, 1.1 eq) in 1.5 mL of THF was slowly added to this solution, which was warmed slowly to room temperature and stirred overnight. The reaction was stopped by adding Na₂S₂O₃ (15% aq). Organics were extracted twice with hexanes, and the combined organic phases were washed with brine, dried over MgSO₄, filtered, and concentrated using rotary evaporation. Compound **3-F** was taken to the next step immediately without further purification.

2-(4-methoxyphenyl-5-iodofuran) (3-OMe). A solution of *n*-butyllithium (1.75 mL, 1.6 M in hexanes, 2.8 mmol, 1.4 eq) was added dropwise to a solution of 2-(4-methoxyphenyl)furan (85 mg, 2.0 mmol, 1.0 eq) in dry THF (3.9 mL) at -78 °C under argon. The reaction mixture was then warmed to 0 °C and stirred for 20 minutes before being cooled again to -78 °C. Iodine (551 mg, 2.2 mmol, 1.1 eq) in 1.9 mL of THF was slowly added to this solution, which was warmed slowly to room temperature and stirred overnight. The reaction was stopped by adding Na₂S₂O₃ (15% aq). Organics were extracted twice with hexanes, and the combined organic phases were

washed with brine, dried over MgSO₄, filtered, and concentrated using rotary evaporation. Compound **3-OMe** was taken to the next steps immediately without further purification.

2-Phenyl-5-(4-methoxyphenyl)furan (4a). 4-methoxyphenylboronic acid (30 mg, 0.19 mmol, 1.0 eq) was suspended in 1.0 mL of a DMF/water (3:1) mixture (which was deoxygenated by sparging with argon), followed by the addition of **3-H** (90 mg, 0.33 mmol, 1.7 eq), PdCl₂(PPh₃)₂ (2.8 mg, 0.004 mmol, 0.02 eq), and K₂CO₃ (66 mg, 0.48 mmol, 2.5 eq) under an argon atmosphere. The mixture was heated to 80 °C and stirred overnight. The mixture was then cooled to room temperature and stopped by adding water. Organics were extracted twice with Et₂O, and combined organic phases were washed with brine and dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and EtOAc (8:1, v/v) to yield **4a**.² Yield: 42 mg (86%).

2-(4-fluorophenyl)-5-(4-methoxyphenyl)furan (4b). Compound (**3-F**) (99 mg, 0.34 mmol, 1.7 eq) and 4-methoxyphenyl boronic acid (31 mg, 0.2 mmol, 1.0 eq) were suspended in 1.2 mL of a DMF/water (3:1) mixture (which was deoxygenated by sparging with argon), followed by the addition of PdCl₂(PPh₃)₂ (3.0 mg, 4 μmol, 0.02 eq), and K₂CO₃ (70 mg, 0.5 mmol, 2.5 eq) under an argon atmosphere. The mixture was heated to 80 °C and stirred overnight. The mixture was then cooled to room temperature and stopped by adding water. Organics were extracted twice with Et₂O, and combined organic phases were washed with brine and dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and CH₂Cl₂ (5:1, v/v) to yield **4b**.⁴ Yield: 29 mg (54%).

2-(4-trifluorophenyl)-5-(4-methoxyphenyl)furan (4c). 4-trifluorophenylboronic acid (112 mg, 0.6 mmol, 1.0 eq) was suspended in 3.7 mL of a DMF/water (3:1) mixture (which was deoxygenated by sparging with argon), followed by the addition of **3-OMe** (301 mg, 1.0 mmol, 1.7 eq), PdCl₂(PPh₃)₂ (8.4 mg, 0.01 mmol, 0.02 eq), and K₂CO₃ (207 mg, 1.5 mmol, 2.5 eq) under an argon atmosphere. The mixture was heated to 80 °C and stirred overnight. The mixture was then cooled to room temperature and stopped by adding water. Organics were extracted twice with Et₂O, and combined organic phases were washed with brine and dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and EtOAc (9:1, v/v) to yield **4c**. Yield: 107 mg (56%). ¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, J=8 Hz, 2H), 7.70 (d, J=8.5 Hz, 2H), 7.65 (d, J=8 Hz, 2H), 6.97 (d, J=8.5 Hz, 2H), 6.84 (d, J=3.5 Hz, 1H), 6.64 (d, J=3.5 Hz, 1H), 3.87 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 159.5, 154.6, 151.2, 134, 128.6 (q, J=129 Hz), 125.7 (q, J=15 Hz), 125.4, 124.2 (q, J=1080 Hz), 123.5, 123.4, 114.3, 109.3, 105.9, 55.4. HRMS calcd for C₁₈H₁₃F₃O₂ (M+H)⁺, 319.0940, found, 319.0924.

2-(3,5-Bis(trifluoromethyl)phenyl)-5-(4-methoxyphenyl)furan (4d). Compound **3-OMe** (690 mg, 2.3 mmol, 1.7 eq) and 3,5-bis(trifluoromethyl)phenyl boronic acid (348 mg, 1.4 mmol, 1.0 eq) were suspended in 8.4 mL of a DMF/water (3:1) mixture (which was deoxygenated by sparging with argon), followed by the addition of PdCl₂(PPh₃)₂ (19 mg, 0.03 mmol, 0.02 eq), and K₂CO₃ (469 mg, 3.4 mmol, 2.5 eq) under an argon atmosphere. The mixture was heated to 80 °C and stirred overnight. The mixture was then cooled to room temperature and stopped by adding water. Organics were extracted twice with Et₂O, and combined organic phases were washed with brine and dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and EtOAc (9.5:0.5, v/v) to yield

4d. Yield: 400 mg (45%). ¹H NMR (500 MHz, CDCl₃): δ 8.09 (s, 2H), 7.72-7.70 (m, 3H), 6.99 (d, J=8.5 Hz, 2H), 6.91 (d, J=3.5 Hz, 1H), 6.66 (d, J=3 Hz, 1H), 3.88 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 159.8, 155.3, 149.6, 132.7, 132.2 (q, J=133 Hz), 125.6, 123.3 (q, J=1085 Hz), 123 (m, 2C), 119.9 (m, 1C), 114.3, 110.2, 106, 55.4. HRMS calcd for C₁₉H₁₂F₆O₂ (M+H)⁺, 387.0814, found, 387.0805.

2-Phenyl-5-(4-hydroxyphenyl)furan (5a). Compound **4a** (277 mg, 1.1 mmol, 1.0 eq) was suspended in 8.5 mL of dry DCM, followed by the addition of BBr₃ (2.77 mL, 1.0 M in DCM, 2.77 mmol, 2.5 eq) at -78 °C under argon and stirred for 4.5 hours. The reaction was stopped by pouring the reaction mixture onto ice. Organics were extracted twice with DCM, and combined organic phases were washed with brine, dried over MgSO₄, and filtered. Removal of solvent *in vacuo* yielded 165 mg of **5a** (63%) that was taken to the next step immediately without further purification. ¹H NMR (500 MHz, CDCl₃): δ 7.75-7.72 (m, 2H), 7.67-7.64 (m, 2H), 7.42-7.39 (m, 2H), 7.3-7.25 (m, 1H), 6.91-6.88 (m, 2H), 6.72 (d, J=3.5 Hz, 1H), 6.61 (d, J=3 Hz, 1H), 4.74 (s, 1H). ¹³C NMR: (125 MHz, CDCl₃) δ 155, 153.4, 152.8, 130.9, 128.7, 127.1, 125.4, 124.2, 123.6, 115.7, 107.2, 105.7. HRMS calcd for C₁₆H₁₂O₂ (M+H)⁺, 237.0910, found, 237.0903.

2-(4-fluorophenyl)-5-(4-hydroxyphenyl)furan (5b). Compound **4b** (19.4 mg, 0.07 mmol, 1.0 eq) was suspended in 0.7 mL of dry DCM, followed by the addition of BBr₃ (1.8 mL, 0.1M in DCM, 0.18 mmol, 2.5 eq) at -78 °C under argon and stirred overnight. The reaction was stopped by pouring the reaction mixture onto ice. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and EtOAc (3:1, v/v) to yield **5b**. Yield: 10 mg (58%). ¹H NMR (500 MHz, CDCl₃): δ 7.71-7.68 (m, 2H), 7.63 (d, J=8.5 Hz, 2H), 7.1 (t, J=9 Hz, 2H), 6.89 (d, J=9 Hz, 2H), 6.65 (d, J=3.5 Hz, 1H), 6.59 (d, J=3.5 Hz, 1H), 4.77 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 163, 161.1, 155.1, 153.4, 152, 127.3, 127.2, 125.4, 125.3, 125.2, 124.1, 115.8, 115.7, 115.6, 106.8, 105.7. HRMS calcd for C₁₆H₁₁FO₂ (M+H)⁺, 255.0816, found, 255.0819.

2-(4-trifluorophenyl)-5-(4-hydroxyphenyl)furan (5c). Compound **4c** (95.3 mg, 0.3 mmol, 1.0 eq) and NaOH (36 mg, 0.9 mmol, 3.0 eq) were dissolved in 0.3 mL of dry NMP, followed by the addition of 1-dodecanethiol (108 uL, 0.45 mmol, 1.5 eq) at room temperature under argon. The mixture was heated to 135 °C and stirred overnight. The mixture was then cooled to room temperature. The reaction was stopped by acidification with 1N HCl. Organics were extracted twice with EtOAc, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and EtOAc (3:1, v/v) to yield **5c**. Yield: 85 mg (93%). ¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, J= 8 Hz, 2H), 7.65 (t, J=8 Hz, 4H), 6.91 (d, J=8.5 Hz, 2H), 6.84 (d, J=3 Hz, 1H), 6.64 (d, J=3.5 Hz, 1H), 4.84 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 155.6, 154.6, 151.1, 134, 128.6 (q, J=129 Hz), 125.7 (m, 2C), 124.2 (q, J=1080 Hz), 123.6, 123.4, 115.8, 109.3, 105.9. HRMS calcd for C₁₇H₁₁F₃O₂ (M+H)⁺, 305.0784, found, 305.0778.

2-(3,5-Bis(trifluoromethyl)phenyl)-5-(4-hydroxyphenyl)furan (5d). Compound **4d** (30 mg, 0.08 mmol, 1.0 eq) was suspended in 1.1 mL of dry DCM, followed by the addition of BBr₃

(0.19 mL, 1.0 M in DCM, 0.19 mmol, 2.5 eq) at -78 °C under argon and stirred overnight. The reaction was stopped by pouring the reaction mixture onto ice. Organics were extracted twice with DCM, and combined organic phases were washed with brine, dried over MgSO₄, and filtered. Removal of solvent *in vacuo* yielded 27 mg of **5d** (93%) that was taken to the next step immediately without further purification. ¹H NMR (500 MHz, CDCl₃): δ 8.09 (s, 2H), 7.73 (s, 1H), 7.68 (d, J=8 Hz, 2H), 6.93-6.92 (m, 3H), 6.66 (d, J=3.5 Hz, 1H), 4.85 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 155.7, 155.2, 149.6, 132.2 (m, 2C), 125.9, 123.3 (q, J=1085.5 Hz), 123.3, 123 (m, 1C), 120 (m, 1C), 115.8, 110.2, 106.1. HRMS calcd for C₁₈H₁₀F₆O₂ (M+H)⁺, 373.0658, found, 373.0643.

2-(4-(4-bromobutoxy)phenyl)-5-phenylfuran (6a). Compound **5a** (159 mg, 0.67 mmol, 1.0 eq) and KOH (75 mg, 1.34 mmol, 2.0 eq) were dissolved in 2.5 mL of dry DMSO, followed by the addition of 1,4-dibromobutane (0.25 mL, 2.0 mmol, 3.0 eq) at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was chromatographed on silica gel column using stepwise gradient elution of hexanes, and then hexanes and EtOAc (5:1, v/v) to yield **6a**. Yield: 188 mg (75%).

¹H NMR (500 MHz, CDCl₃): δ 7.74 (d, J=8 Hz, 2H), 7.68 (d, J=8.5 Hz, 2H), 7.41 (t, J=7.5 Hz, 2H), 7.27-7.25 (m, 1H), 6.94 (d, J=8.5 Hz, 2H), 6.72 (d, J=3.5 Hz, 1H), 6.61 (d, J=3.5 Hz, 1H), 4.05 (t, J= 6 Hz, 2H), 3.52 (t, J=6.5 Hz, 2H), 2.11 (quintet, J= 7 Hz, 2H), 1.98 (quintet, J=6.5 Hz, 2H).

¹³C NMR (125 MHz, CDCl₃): δ 158.4, 153.5, 152.7, 130.9, 128.7, 127.1, 125.2, 124, 123.6, 114.8, 107.2, 105.7, 67, 33.4, 29.5, 27.9. HRMS calcd for C₂₀H₁₉BrO₂ (M+H)⁺, 371.0641, found, 371.0648.

2-(4-(4-bromobutoxy)phenyl)-5-(4-fluorophenyl)furan (6b). Compound **5b** (23 mg, 0.09 mmol, 1.0 eq) and KOH (10 mg, 0.18 mmol, 2.0 eq) were dissolved in 0.4 mL of dry DMSO, followed by the addition of 1,4-dibromobutane (54 uL, 0.45 mmol, 5.0 eq) at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was chromatographed on silica gel column using stepwise gradient elution of hexanes, and then hexanes and EtOAc (6:1, v/v) to yield **6b**. Yield: 26 mg (75%). ¹H NMR (500 MHz, CDCl₃): δ 7.71-7.68 (m, 2H), 7.67 (d, J=8.5 Hz, 2H), 7.11 (t, J=8.5 Hz, 2H), 6.94 (d, J=8.5 Hz, 2H), 6.65 (d, J=3 Hz, 1H), 6.60 (d, J=3 Hz, 1H), 4.05 (t, J=6 Hz, 2H), 3.52 (t, J=6.5 Hz, 2H), 2.13-2.08 (m, 2H), 2.01-1.96 (m, 2H).

¹³C NMR (125 MHz, CDCl₃): δ 163, 161, 158.4, 153.5, 151.9, 127.3, 127.3, 125.3, 125.2, 125.2, 123.9, 115.8, 115.6, 114.8, 106.8, 105.7, 67, 33.4, 29.5, 27.9. HRMS calcd for C₂₀H₁₈BrFO₂ (M+H)⁺, 389.0547, found, 389.0552.

2-(4-(4-bromobutoxy)phenyl)-5-(4-trifluorophenyl)furan (6c). Compound **5c** (65 mg, 0.2 mmol, 1.0 eq) and KOH (24 mg, 0.4 mmol, 2.0 eq) were dissolved in 1 mL of dry DMSO, followed by the addition of 1,4-dibromobutane (128 uL, 1.0 mmol, 5.0 eq) at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with

brine, dried over MgSO_4 , filtered and concentrated using rotary evaporation. The crude product was chromatographed on silica gel column using stepwise gradient elution of hexanes, and then hexanes and EtOAc (5:1, v/v) to yield **6c**. Yield: 64 mg (68%). ^1H NMR (500 MHz, CDCl_3): δ 7.81 (d, $J=8$ Hz, 2H), 7.69 (d, $J=8.5$ Hz, 2H), 7.64 (d, $J=8.5$ Hz, 2H), 6.95 (d, $J=8.5$ Hz, 2H), 6.84 (d, $J=3.5$ Hz, 1H), 6.64 (d, $J=3.5$ Hz, 1H), 4.06 (t, $J=6$ Hz, 2H), 3.52 (t, $J=6.5$ Hz, 2H), 2.14-2.08 (m, 2H), 2.01-1.96 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3): δ 158.8, 154.6, 151.2, 134, 128.6 (q, $J=129$ Hz), 125.7 (q, $J=15$ Hz), 125.5, 124.2 (q, $J=1080$ Hz), 123.5, 123.4, 114.8, 109.3, 105.9, 66.9, 32.4, 29.5, 27.9.

HRMS calcd for $\text{C}_{21}\text{H}_{18}\text{Br}_2\text{F}_3\text{O}_2$ ($\text{M}+\text{H}$) $^+$, 439.0515, found, 439.0513.

2-(4-(4-bromobutoxy)phenyl)-5-(3,5-Bis(trifluoromethyl)phenyl)furan (6d). Compound **5d** (27 mg, 0.07 mmol, 1.0 eq) and KOH (8.2 mg, 0.15 mmol, 2.0 eq) were dissolved in 0.3 mL of dry DMSO, followed by the addition of 1,4-dibromobutane (26 μL , 0.2 mmol, 3.0 eq) at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. Organics were extracted twice with CH_2Cl_2 , and combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated using rotary evaporation. The crude product was chromatographed on silica gel column using stepwise gradient elution of hexanes, and then hexanes and EtOAc (8:1, v/v) to yield **6d**. Yield: 30 mg (82%). ^1H NMR (500MHz, CDCl_3): δ 8.09 (s, 2H), 7.71-7.69 (m, 3H), 6.97 (d, $J=8.5$ Hz, 2H), 6.92 (d, $J=3$ Hz, 1H), 6.67 (d, $J=2.5$ Hz, 1H), 4.07 (t, $J=5$ Hz, 2H), 3.52 (t, $J=6.5$ Hz, 2H), 2.14-2.08 (m, 2H), 2.06-1.98 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 159, 155.3, 149.6, 132.7, 132.2 (q, $J=132.5$ Hz), 125.6, 123.3 (q, $J=1084$ Hz), 123 (m, 2C), 120 (m, 1C), 114.9, 110.2, 106, 67, 33.3, 29.5, 27.9. HRMS calcd for $\text{C}_{22}\text{H}_{17}\text{BrF}_6\text{O}_2$ ($\text{M}+\text{H}$) $^+$, 507.0389, found, 507.0388.

2-(4-(4-(2,5-diiodo-4-methoxyphenoxy)butoxy)phenyl)-5-phenylfuran (7a). Compound **6a** (22.7 mg, 0.06 mmol, 1.0 eq), KOH (7 mg, 0.12 mmol, 2.0 eq) and 2,5-diiodo-4-methoxyphenol (26.5 mg, 0.07 mmol, 1.2 eq) were dissolved in 0.4 mL of dry DMSO at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl.

Organics were extracted twice with CH_2Cl_2 , and combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated using rotary evaporation. The crude product was dissolved in CH_2Cl_2 and washed with 10% aq NaOH, dried over MgSO_4 , filtered and concentrated using rotary evaporation to yield **7a**. Yield: 35 mg (86%) ^1H NMR (500 MHz, CDCl_3): δ 7.74 (d, $J=8$ Hz, 2H), 7.68 (d, $J=9$ Hz, 2H), 7.41 (t, $J=8$ Hz, 2H), 7.27-7.25 (m, 1H), 7.22 (s, 1H), 7.20 (s, 1H), 6.96 (d, $J=9$ Hz, 2H), 6.73 (d, $J=3$ Hz, 1H), 6.61 (d, $J=3.5$ Hz, 1H), 4.12 (t, $J=6$ Hz, 2H), 4.05 (t, $J=5.5$ Hz, 2H), 3.83 (s, 3H), 2.06-2.03 (m, 4H).

^{13}C NMR (125 MHz, CDCl_3): δ 158.5, 153.5, 153.4, 152.8, 152.7, 131, 128.7, 127.1, 125.2, 123.9, 123.6, 123, 121.6, 114.8, 107.2, 105.6, 86.3, 85.5, 69.9, 67.6, 57.2, 26.1, 26. HRMS calcd for $\text{C}_{27}\text{H}_{24}\text{I}_2\text{O}_4$ ($\text{M}+\text{H}$) $^+$, 666.9837, found, 666.9859.

2-(4-(4-(2,5-diiodo-4-methoxyphenoxy)butoxy)phenyl)-5-(4-fluorophenyl)furan (7b).

Compound **6b** (27 mg, 0.07 mmol, 1.0 eq), KOH (8 mg, 0.14 mmol, 2.0 eq) and 2,5-diiodo-4-methoxyphenol (52 mg, 0.14 mmol, 2.0 eq) were dissolved in 0.4 mL of dry DMSO at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. Organics were extracted twice with CH_2Cl_2 , and combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated using rotary evaporation. The crude product was dissolved in CH_2Cl_2 and washed with 10% aq NaOH, dried over MgSO_4 , filtered and concentrated using rotary evaporation. The crude product was purified *via* flash

chromatography using hexanes and EtOAc (5:1, v/v) to yield **7b**. Yield: 36 mg (75%). ¹H NMR (500 MHz, CDCl₃): δ 7.71–7.68 (m, 2H), 7.66 (d, J=9 Hz, 2H), 7.21 (s, 1H), 7.20 (s, 1H), 7.10 (t, J=8.5 Hz, 2H), 6.96 (d, J=8.5 Hz, 2H), 6.65 (d, J=3.5 Hz, 1H), 6.59 (d, J=3 Hz, 1H), 4.12 (t, J=6 Hz, 2H), 4.04 (t, J=5.5 Hz, 2H), 3.83 (s, 1H), 2.08–2.03 (m, 4H). ¹³C NMR (125 MHz, CDCl₃): δ 163, 161, 158.5, 153.5, 153.4, 152.8, 151.9, 127.4, 127.3, 125.3, 125.2, 125.2, 123.7, 123, 121.6, 115.8, 115.6, 114.8, 106.8, 105.6, 86.3, 85.5, 69.9, 67.6, 57.2, 26.1, 26. HRMS calcd for C₂₄H₂₃FI₂O₄ (M+H)⁺, 684.9742, found, 684.9742.

2-(4-(4-(2,5-diiodo-4-methoxyphenoxy)butoxy)phenyl)-5-(4-trifluorophenyl)furan (7c).

Compound **6c** (56 mg, 0.13 mmol, 1.0 eq), KOH (14 mg, 0.26 mmol, 2.0 eq) and 2,5-diiodo-4-methoxyphenol (96 mg, 0.26 mmol, 2.0 eq) were dissolved in 0.8 mL of dry DMSO at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was dissolved in CH₂Cl₂ and washed with 10% aq NaOH to yield **7c**. Yield: 80 mg (86%). ¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, J=8 Hz, 2H), 7.69 (d, J=8.5 Hz, 2H), 7.65 (d, J=8 Hz, 2H), 7.22 (s, 1H), 7.20 (s, 1H), 6.97 (d, J=8.5 Hz, 1H), 6.84 (d, J=3 Hz, 1H), 6.64 (d, J=3 Hz, 1H), 4.13 (t, J=6 Hz, 2H), 4.05 (t, J=6 Hz, 2H), 3.83 (s, 3H), 2.08–2.05 (m, 4H). ¹³C NMR (125 MHz, CDCl₃): δ 158.9, 154.7, 153.4, 152.8, 151.1, 134, 128.6 (q, J=129 Hz), 125.7 (q, J=15 Hz), 125.4, 124.2 (q, J=1080 Hz), 123.4, 123.4, 123, 121.5, 114.9, 109.3, 105.9, 86.3, 85.5, 69.9, 67.6, 57.2, 26.1, 26. HRMS calcd for C₂₈H₂₃F₃I₂O₄ (M+H)⁺, 734.9711, found, 734.9698.

2-(4-(4-(2,5-diiodo-4-methoxyphenoxy)butoxy)phenyl)-5-(3,5-Bis(trifluoromethyl)furan

(7d). Compound **6d** (27 mg, 0.05 mmol, 1.0 eq), KOH (6 mg, 0.1 mmol, 2.0 eq) and 2,5-diiodo-4-methoxyphenol (40 mg, 0.2 mmol, 2.0 eq) were dissolved in 0.4 mL of dry DMSO at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was dissolved in CH₂Cl₂ and washed with 10% aq NaOH, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and EtOAc (6:1, v/v) to yield **7d**. Yield: 32 mg (75%). ¹H NMR (500 MHz, CDCl₃): δ 8.1 (s, 2H), 7.72–7.69 (m, 3H), 7.22 (s, 1H), 7.20 (s, 1H), 6.99 (d, J=8.5 Hz, 2H), 6.92 (d, J=3.5 Hz, 2H), 6.66 (d, J=3.5 Hz, 1H), 4.14 (t, J=5.5 Hz), 4.05 (t, J=5 Hz), 3.84 (s, 1H), 2.10–2.04 (m, 4H).

¹³C NMR (125 MHz, CDCl₃): δ 159.1, 155.4, 153.4, 152.8, 149.6, 132.7, 132.2 (q, J=133 Hz), 125.6, 123.3 (q, J=1084 Hz), 123 (m, 3C), 121.5, 119.9 (m, 1C), 115, 110.2, 106, 86.3, 85.5, 69.9, 67.6, 57.2, 26.1, 26. HRMS calcd for C₂₉H₂₂F₆I₂O₄ (M+H)⁺, 802.9584, found, 802.9586.

PFa. Equimolar amounts of two monomers: 9,9-dioctylfluorene-2,7-diboronic acid bis (1,3-propanediol) ester (25 mg, 40. μmol) and **7a** (30. mg, 40. μmol) were weighed into a Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was added less than 0.5 mg of Pd(PPh₃)₄. 1 mL of deoxygenated toluene, 1 mL of deoxygenated 2M aqueous potassium carbonate solution, and several drops of Aliquat 336 were added under a heavy argon flow. Deoxygenation of solvents was achieved by sparging with argon. The reaction mixture in the sealed tube was then stirred vigorously at 90 °C for 48 hours. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several milliliters deionized water. The polymer was then precipitated from the toluene solution into 15

mL of methanol and collected by centrifugation and decanting. The polymer was then dissolved in 2 mL of diethyl ether and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 15 mL of methanol and isolated by centrifugation and decanting. Yield: 30 mg (93%) M_n [g/mol]: 11800, M_w [g/mol]: 28800. ^1H NMR (500 MHz, CDCl_3): δ 7.84-7.61, 7.41-7.40, 7.27-7.24, 7.18-7.15, 6.88-6.84, 6.72-6.71, 6.58-6.56, 4.01, 3.99-3.96, 3.88-3.86, 2.1-1.94, 1.3-0.8.

PFb. Equimolar amounts of two monomers: 9,9-dioctylfluorene-2,7-diboronic acid bis (1,3-propanediol) ester (21.7 mg, 32.0 μmol) and **7b** (26.5 mg, 32.0 μmol) were weighed into a Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was added less than 0.5 mg of $\text{Pd}(\text{PPh}_3)_4$, 0.7 mL of deoxygenated toluene, 0.7 mL of deoxygenated 2M aqueous potassium carbonate solution, and several drops of Aliquat 336 were added under a heavy argon flow. Deoxygenation of solvents was achieved by sparging with argon. The reaction mixture in the sealed tube was then stirred vigorously at 90 $^\circ\text{C}$ for 48 hours. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several milliliters deionized water. The polymer was then precipitated from the toluene solution into 15 mL of methanol and collected by centrifugation and decanting. The polymer was then dissolved in 2 mL of toluene and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 15 mL of methanol and isolated by centrifugation and decanting. M_n [g/mol]: 8000, M_w [g/mol]: 12000. Yield: 23 mg (88%). ^1H NMR (500 MHz, CDCl_3): δ 7.83-7.6, 7.17-7.15, 7.10-7.07, 6.85, 6.63, 6.56, 4.09, 3.97-3.96, 3.86-3.83, 2.05-1.94, 1.28-0.8.

PFc. Equimolar amounts of two monomers: 9,9-dioctylfluorene-2,7-diboronic acid bis (1,3-propanediol) ester (23 mg, 41.0 μmol) and **7c** (30 mg, 40.0 μmol) were weighed into a Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was added less than 0.5 mg of $\text{Pd}(\text{PPh}_3)_4$, 1 mL of deoxygenated toluene, 1 mL of deoxygenated 2M aqueous potassium carbonate solution, and several drops of Aliquat 336 were added under a heavy argon flow. Deoxygenation of solvents was achieved by sparging with argon. The reaction mixture in the sealed tube was then stirred vigorously at 90 $^\circ\text{C}$ for 48 hours. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several milliliters deionized water. The polymer was then precipitated from the toluene solution into 15 mL of methanol and collected by centrifugation and decanting. The polymer was then dissolved in 2 mL of toluene and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 15 mL of methanol and isolated by centrifugation and decanting. M_n [g/mol]: 24500, M_w [g/mol]: 57000. Yield: 25 mg (70%). ^1H NMR (500 MHz, CDCl_3): δ 7.82-7.62, 7.17-7.15, 6.87-6.86, 6.82, 6.6-6.58, 4.1, 3.98, 3.86, 2.07-1.94, 1.4-0.8.

PFd. Equimolar amounts of two monomers: 9,9-dioctylfluorene-2,7-diboronic acid bis (1,3-propanediol) ester (14.1 mg, 25.0 μmol) and **7d** (20.2 mg, 25.0 μmol) were weighed into a Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was added less than 0.5 mg of $\text{Pd}(\text{PPh}_3)_4$, 0.6 mL of deoxygenated toluene, 0.6 mL of deoxygenated 2M aqueous potassium carbonate solution, and several drops of Aliquat 336 were added under a heavy argon flow. Deoxygenation of solvents was achieved by sparging with argon. The reaction mixture in the sealed tube was then stirred vigorously at 90 $^\circ\text{C}$ for 48 hours. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several milliliters deionized water. The polymer was then precipitated from the toluene solution into 15 mL of methanol and collected by centrifugation and decanting. The polymer was then

dissolved in 2 mL of toluene and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 15 mL of methanol and isolated by centrifugation and decanting. M_n [g/mol]: 10300, M_w [g/mol]: 17300. Yield: 17 mg (72%). ^1H NMR (500 MHz, CDCl_3): δ 8.09-8.07, 7.84, 7.72-7.7, 7.63-7.62, 7.18-7.15, 6.88, 6.62-6.6, 4.1, 3.99, 3.87, 2.06-1.9, 1.38-0.8.

5,5'-(4,4'-(4,4'-(2,5-diiodo-1,4-phenylene)bis(oxy)bis(butane-4,1-diyl))bis(oxy)bis(4,1-phenylene))bis(2-phenylfuran) (8a). Compound **6a** (95 mg, 0.26 mmol, 2.0 eq), KOH (29 mg, 0.5 mmol, 4.0 eq) and 1,4-diiodo-2,5-hydroquinone (47 mg, 0.13 mmol, 1.0 eq) were dissolved in 1.4 mL of dry DMSO at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. Organics were extracted twice with CH_2Cl_2 , and combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated using rotary evaporation. The crude product was dissolved in CH_2Cl_2 and washed with 10% aq NaOH, dried over MgSO_4 , filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and CH_2Cl_2 (2:1, v/v) to yield **8a**. Yield: 49 mg (40%). ^1H NMR (500 MHz, CDCl_3): δ 7.74 (d, $J=8$ Hz, 4H), 7.67 (d, $J=8.5$ Hz, 4H), 7.40 (t, $J=7.5$ Hz, 4H), 7.27-7.24 (m, 2H), 7.21 (s, 2H), 6.96 (d, $J=8$ Hz, 4H), 6.72 (m, 2H), 6.61 (d, $J=3.5$ Hz, 2H), 4.12 (t, $J=6$ Hz, 4H), 4.04 (t, $J=5$ Hz, 4H), 2.05 (m, 8H).

^{13}C NMR (125 MHz, CDCl_3): δ 158.5, 153.5, 152.8, 152.7, 131, 128.7, 127.1, 125.2, 123.9, 123.6, 122.8, 114.8, 107.2, 105.6, 86.3, 69.9, 67.6, 26.1, 26. HRMS calcd for $\text{C}_{46}\text{H}_{40}\text{I}_2\text{O}_6$ ($\text{M}+\text{NH}_4$) $^+$, 960.1253, found, 960.1275.

5,5'-(4,4'-(4,4'-(2,5-diiodo-1,4-phenylene)bis(oxy)bis(butane-4,1-diyl))bis(oxy)bis(4,1-phenylene))bis(2-(4-(trifluoromethyl)phenyl)furan) (8c). Compound **6c** (97 mg, 0.22 mmol, 2.0 eq), KOH (25 mg, 0.44 mmol, 4.0 eq) and 1,4-Diiodo-2,5-hydroquinone (40 mg, 0.11 mmol, 1.0 eq) were dissolved in 3.2 mL of dry DMSO at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. Organics were extracted twice with CH_2Cl_2 , and combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated using rotary evaporation. The crude product was dissolved in CH_2Cl_2 and washed with 10% aq NaOH, dried over MgSO_4 , filtered and concentrated using rotary evaporation. The crude product was recrystallized from hexanes and CH_2Cl_2 mixture to yield **8c**. Yield: 45 mg (38%). ^1H NMR (500 MHz, CDCl_3): δ 7.82 (d, $J=8$ Hz, 4H), 7.69 (d, $J=8.5$ Hz, 4H), 7.64 (t, $J=8.5$ Hz, 4H), 7.21 (s, 2H), 6.97 (d, $J=8.5$ Hz, 4H), 6.84 (d, $J=3$ Hz, 2H), 6.64 (d, $J=3$ Hz, 2H), 4.13 (t, $J=6$ Hz, 4H), 4.04 (t, $J=6$ Hz, 4H), 2.07-2.03 (m, 8H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.9, 154.7, 152.8, 151.1, 134.0, 128.6 (q, $J=130$ Hz), 125.7 (m, 1C), 125.4, 124.2 ($J=1080$ Hz), 123.4, 123.4, 122.8, 114.9, 109.3, 105.9, 86.3, 69.9, 67.6, 26.1, 26.0. HRMS calcd for $\text{C}_{48}\text{H}_{38}\text{F}_6\text{I}_2\text{O}_6$ ($\text{M}+\text{NH}_4$) $^+$, 1096.1000, found, 1096.1007.

PF-8a. Equimolar amounts of two monomers: 9,9-dioctylfluorene-2,7-diboronic acid bis (1,3-propanediol) ester (13.6 mg, 24.0 μmol) and **8a** (23 mg, 24.0 μmol) were weighed into a Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was added less than 0.5 mg of $\text{Pd}(\text{PPh}_3)_4$. 0.75 mL of deoxygenated toluene, 0.75 mL of deoxygenated 2M aqueous potassium carbonate solution, and several drops of Aliquat 336 were added under a heavy argon flow. Deoxygenation of solvents was achieved by sparging with argon. The reaction mixture in the sealed tube was then stirred vigorously at 90 $^\circ\text{C}$ for 48 hours. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several milliliters deionized water. The polymer was then precipitated from the toluene solution into 15

mL of methanol and collected by centrifugation and decanting. The polymer was then dissolved in 1 mL of toluene and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 15 mL of methanol and isolated by centrifugation and decanting. Yield: 12.5 mg (50%) M_n [g/mol]: 8285, M_w [g/mol]: 11500. ^1H NMR (500 MHz, CDCl_3): δ 7.84-7.61, 7.4-7.38, 7.25, 7.16, 6.84, 6.73-6.7, 6.6-6.55, 4.1, 3.94, 2.07-1.93, 1.28-0.79.

PF-8c. Equimolar amounts of two monomers: 9,9-dioctylfluorene-2,7-diboronic acid bis (1,3-propanediol) ester (13.5 mg, 24.0 μmol) and **8c** (26 mg, 24.0 μmol) were weighed into a Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was added less than 0.5 mg of $\text{Pd}(\text{PPh}_3)_4$. 0.6 mL of deoxygenated toluene, 0.6 mL of deoxygenated 2M aqueous potassium carbonate solution, and several drops of Aliquat 336 were added under a heavy argon flow. Deoxygenation of solvents was achieved by sparging with argon. The reaction mixture in the sealed tube was then stirred vigorously at 90 °C for 48 hours. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several milliliters deionized water. The polymer was then precipitated from the toluene solution into 15 mL of methanol and collected by centrifugation and decanting. The polymer was then dissolved in 1 mL of toluene and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 15 mL of methanol and isolated by centrifugation and decanting. M_n [g/mol]: 8200, M_w [g/mol]: 10000. Yield: 14.8 mg (51%). ^1H NMR (500 MHz, CDCl_3): δ 7.77-7.59, 7.16, 6.85-6.84, 6.8, 6.56, 4.08, 3.95, 2.05-1.93, 1.28-0.8.

PPEa: Equimolar amounts of two monomers: 1,4-Diethynyl-2,5-bis(octyloxy)benzene (15 mg, 39.0 μmol) and **7a** (26.7 mg, 24.0 μmol) were weighed into a Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was added less than 0.5 mg of $\text{Pd}(\text{PPh}_3)_4$ and CuI . 6 mL of deoxygenated toluene: diisopropylamine (4:1) solution was added under a heavy argon flow. Deoxygenation of solvents was achieved by sparging with argon. The reaction mixture in the sealed tube was then stirred vigorously at 65 °C overnight. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several milliliters deionized water. The polymer was then precipitated into 15 mL of methanol and collected by centrifugation and decanting. The polymer was then dissolved in 1 mL of toluene and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 15 mL of methanol and isolated by centrifugation and decanting. M_n [g/mol]: 12500, M_w [g/mol]: 35600. Yield: 24 mg (77%) ^1H NMR (500 MHz, CDCl_3): δ 7.77-7.69, 7.62, 7.42-7.37, 7.32-7.24, 7.09-7.05, 6.92-6.89, 6.7, 6.59, 4.14-4.00, 3.93-3.85, 2.09, 1.88-1.8, 1.6-1.47, 1.41-1.28, 0.88-0.86.

Supplemental Figures

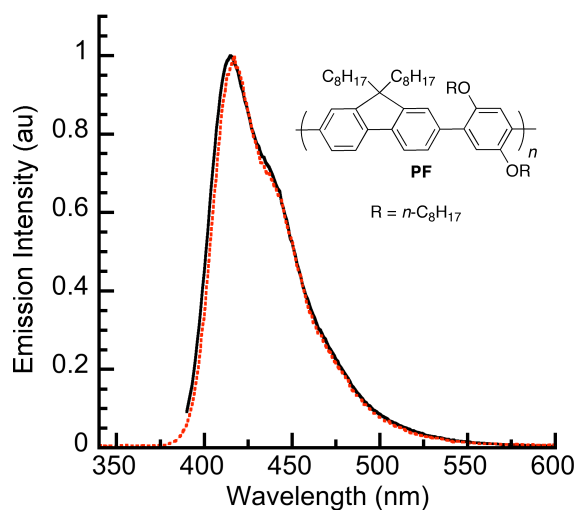


Figure S1. Normalized emission spectra of **PFa** (black solid line) and **PF** in CH_2Cl_2 .

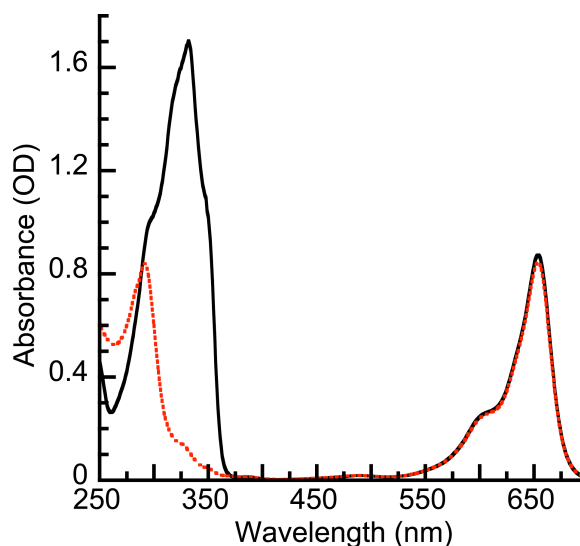


Figure S2. Full absorbance spectrum of diarylfuran **4a** in the presence of methylene blue (band at 650 nm) before (black solid line) and after (red dotted line) 45 seconds of exposure to $^1\text{O}_2$.

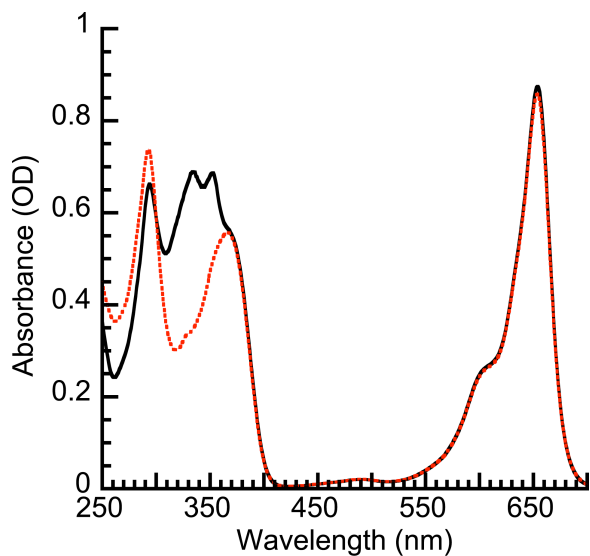


Figure S3. Full absorbance spectrum of polymer **PFa** in the presence of methylene blue (band at 650 nm) before (black solid line) and after (red dotted line) 35 seconds of exposure to $^1\text{O}_2$.

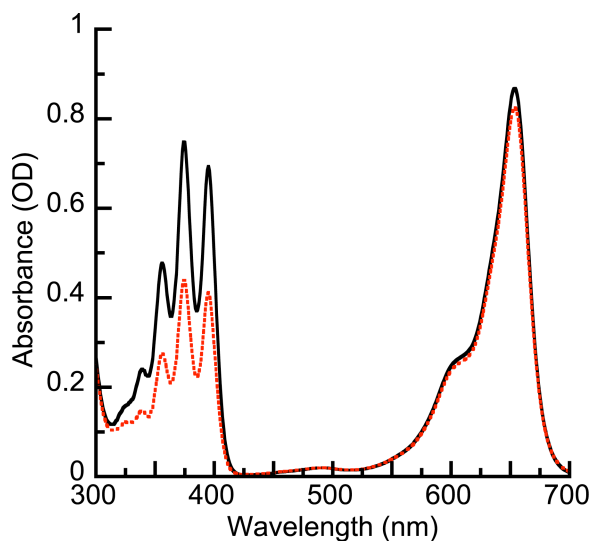


Figure S4. Full absorbance spectrum of 9,10-diphenylanthracene in the presence of methylene blue (band at 650 nm) before (black solid line) and after (red dotted line) 540 seconds of exposure to $^1\text{O}_2$.

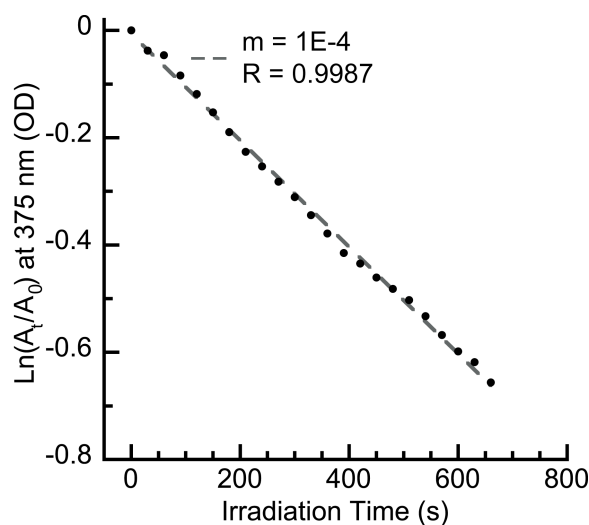


Figure S5. Pseudo-first order kinetic plot of 9,10-diphenylanthracene reacting with photogenerated $^1\text{O}_2$ under conditions identical to those in Figure 4c in the text of the main article.

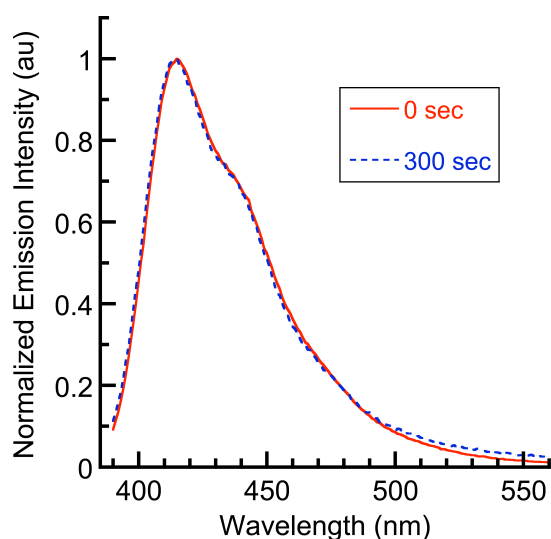


Figure S6. Overlaid, normalized emission spectra of PFa before and after reaction with $^1\text{O}_2$ for 300 seconds, during which time quantum yield of fluorescence decreased by ca. 5-fold.

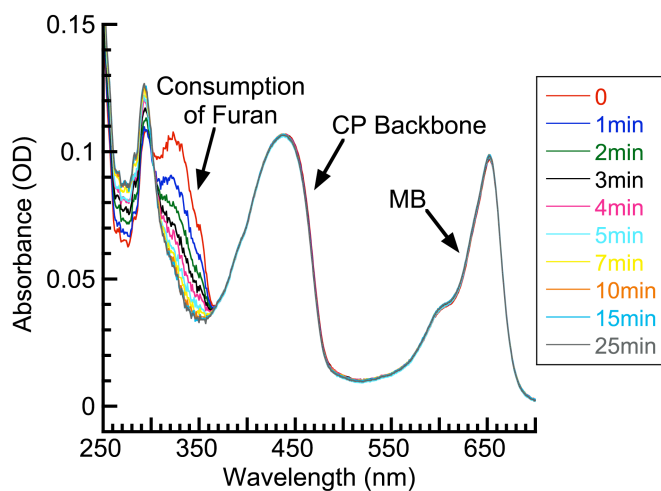


Figure S7. Absorbance spectra showing reaction of PPEa with photogenerated $^1\text{O}_2$ using methylene blue (MB) as a sensitizer. These spectra correspond to experiment in Figure 6b in the main article.

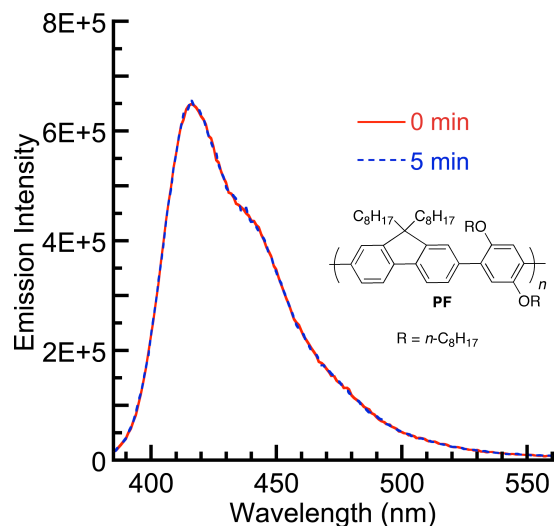


Figure S8. Emission spectra of PF, which contains furan pendants, before (*red solid line*) and after (*blue dashed line*) exposure to $^1\text{O}_2$ for 5 minutes under conditions identical to those described in main article.

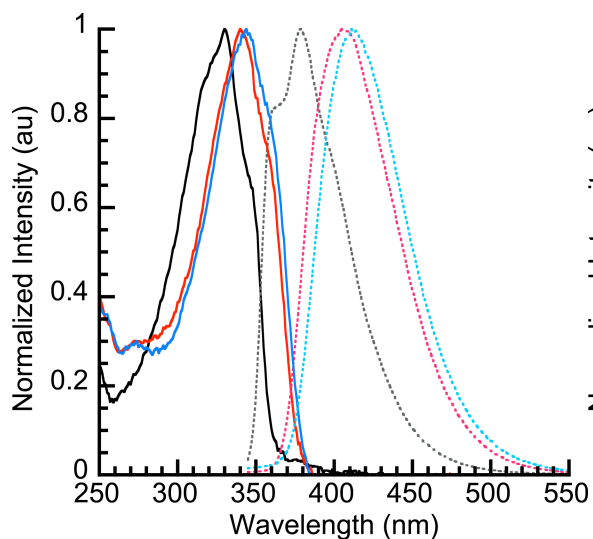


Figure S9. Normalized absorption (solid lines) and fluorescence (dotted lines) spectra of **4b** (black), **4c** (red), and **4d** (blue).

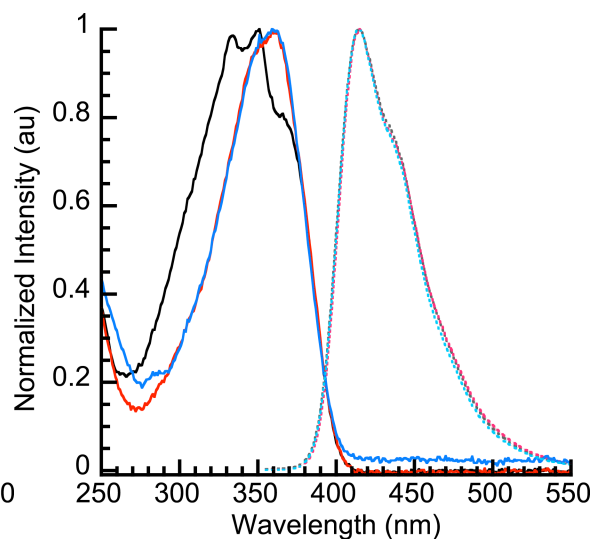


Figure S10. Normalized absorption (solid lines) and fluorescence (dotted lines) spectra of **PFb** (black), **PFc** (red), and **PFd** (blue).

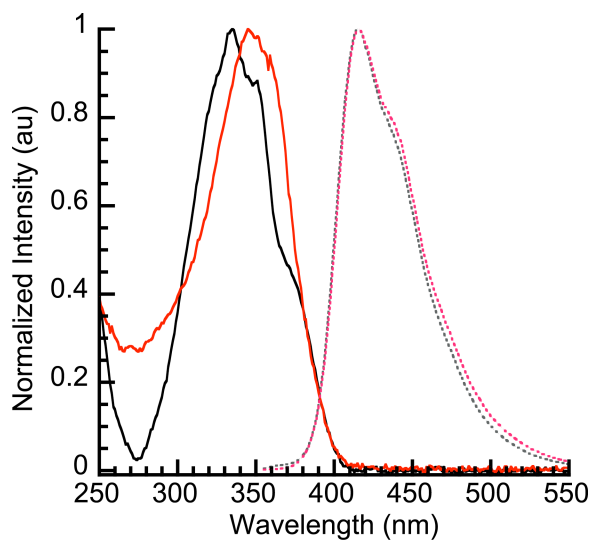


Figure S11. Normalized absorption (solid lines) and fluorescence (dotted lines) spectra of **PF-8a** (black) and **PF-8c** (red).

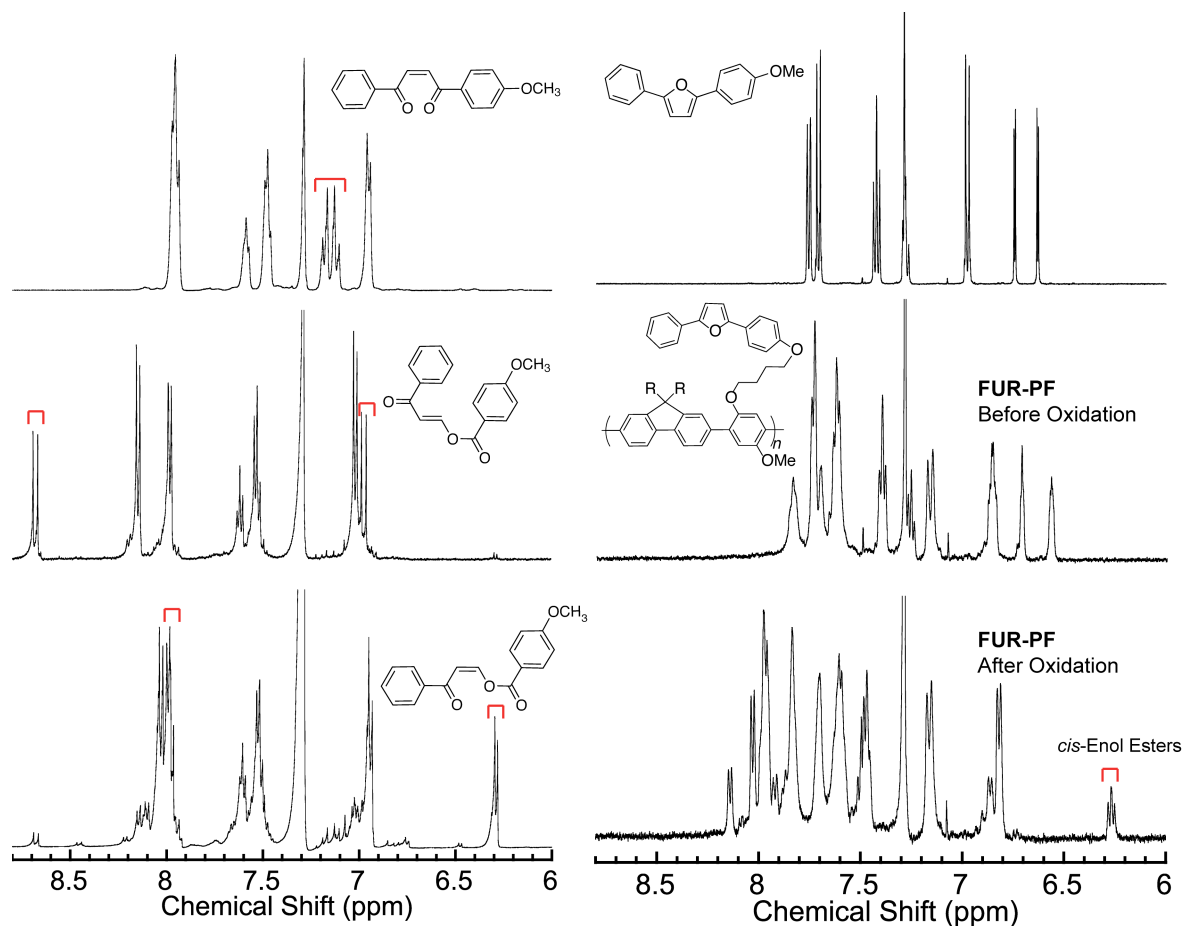
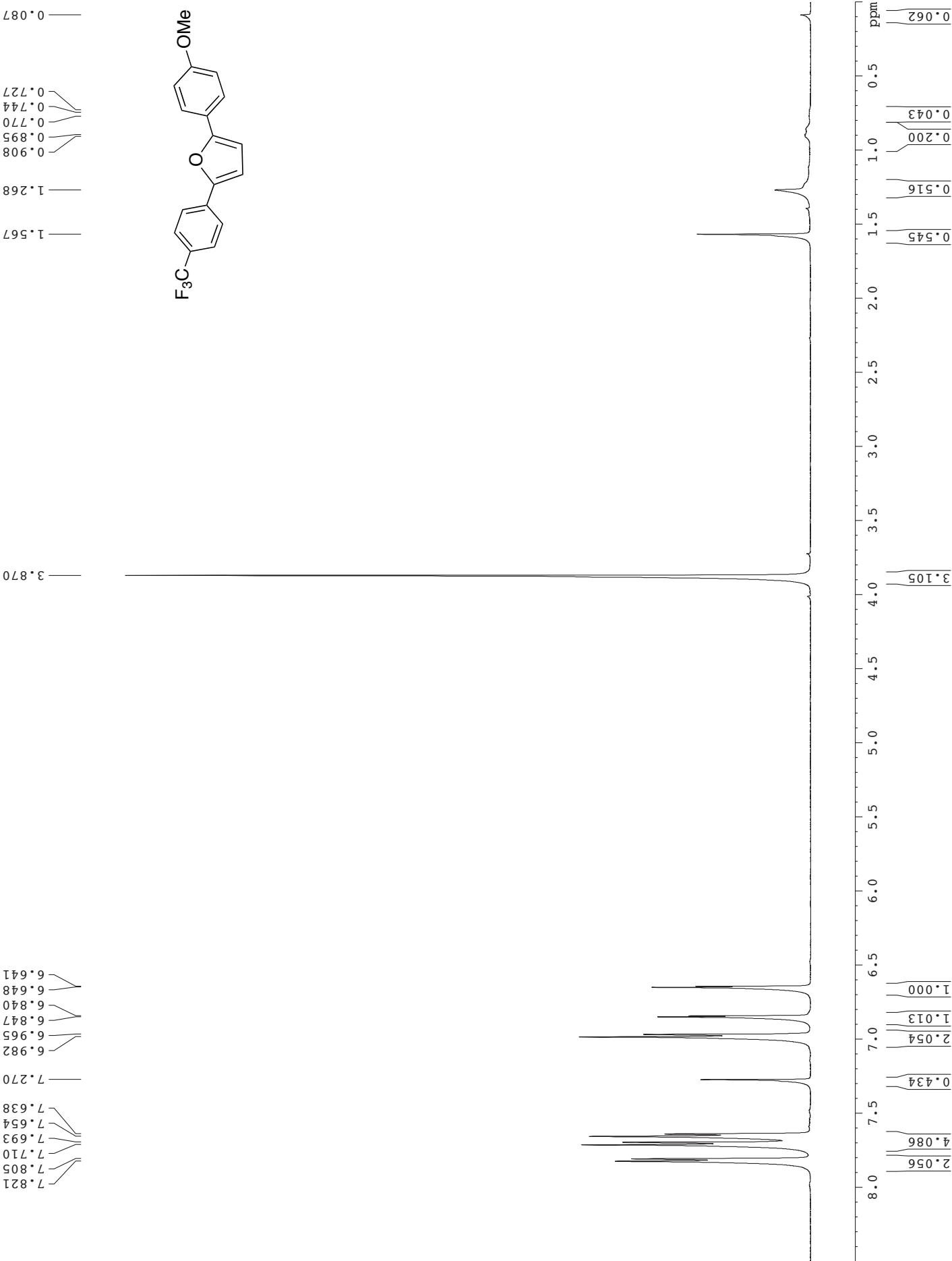
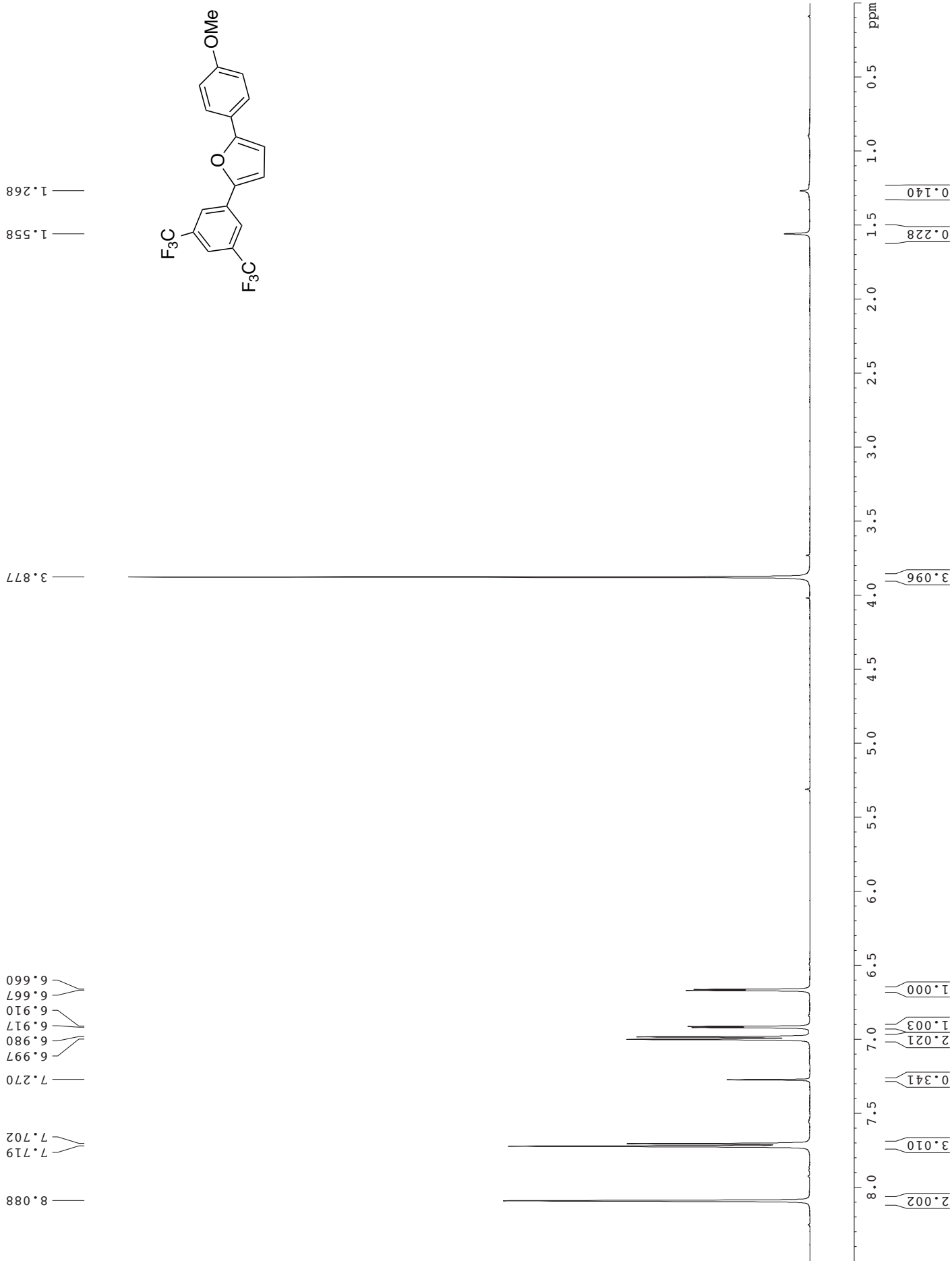


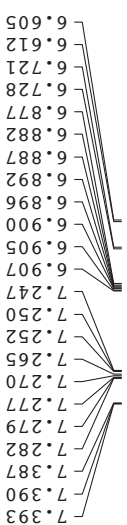
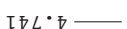
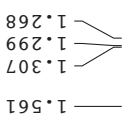
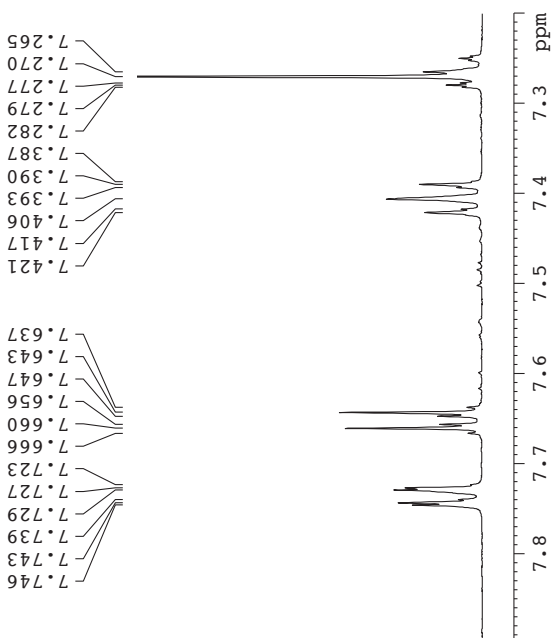
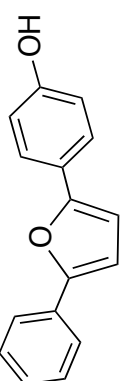
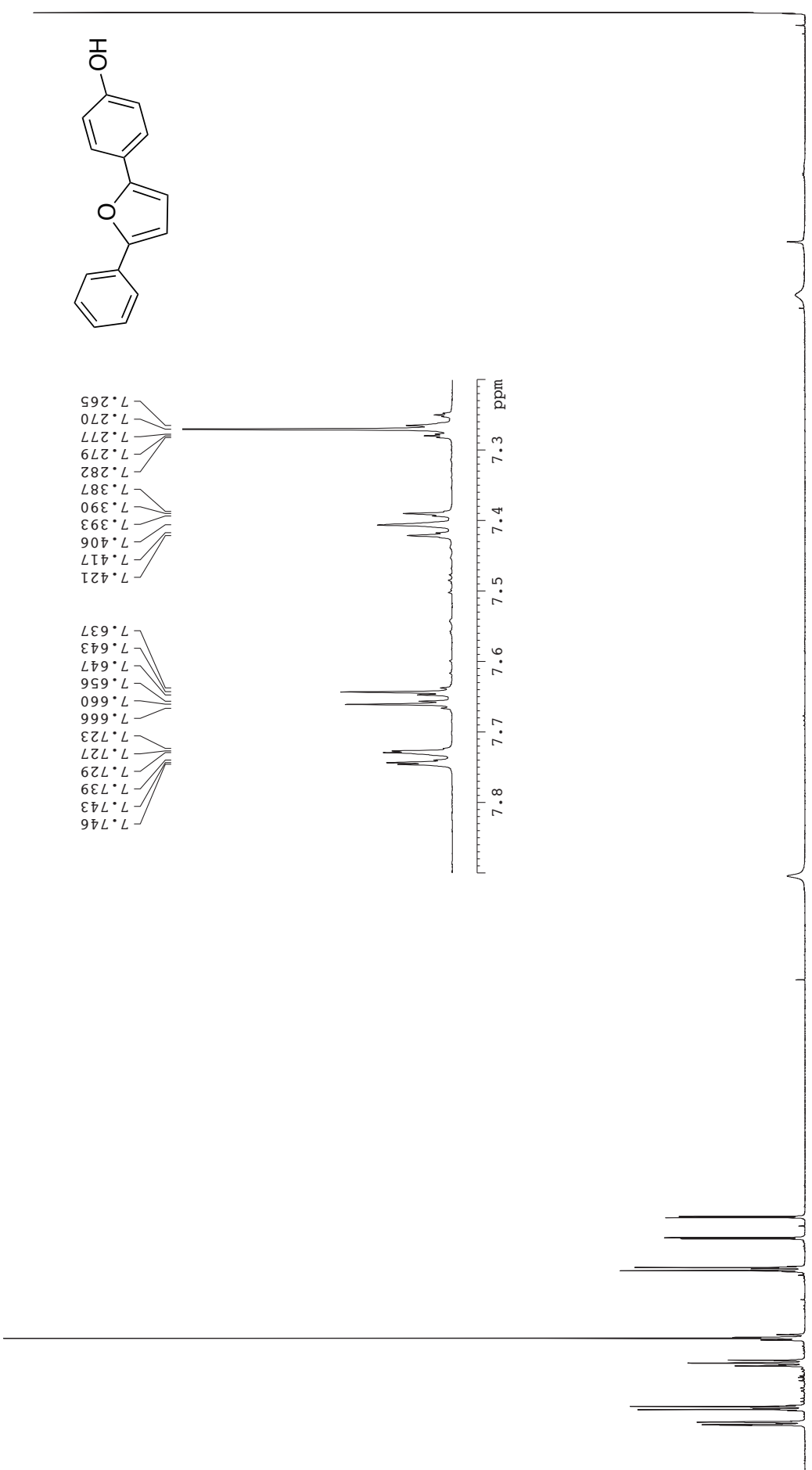
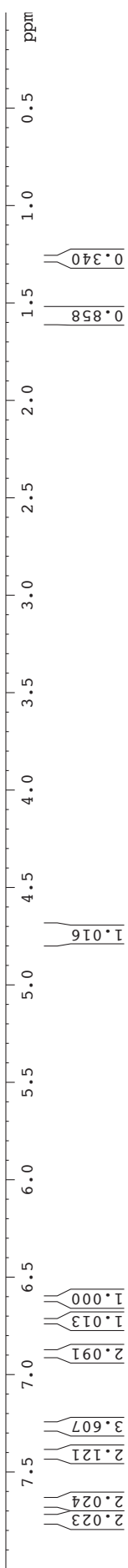
Figure S12. ^1H NMR spectra of the isolated $^1\text{O}_2$ -derived products of **4a** (left) and of **PFa** before and after exposure to $^1\text{O}_2$ for 15 minutes (right). Red brackets indicate resonances due to the vinylic protons.

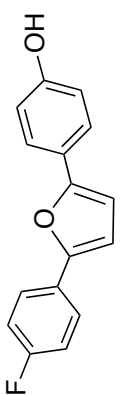
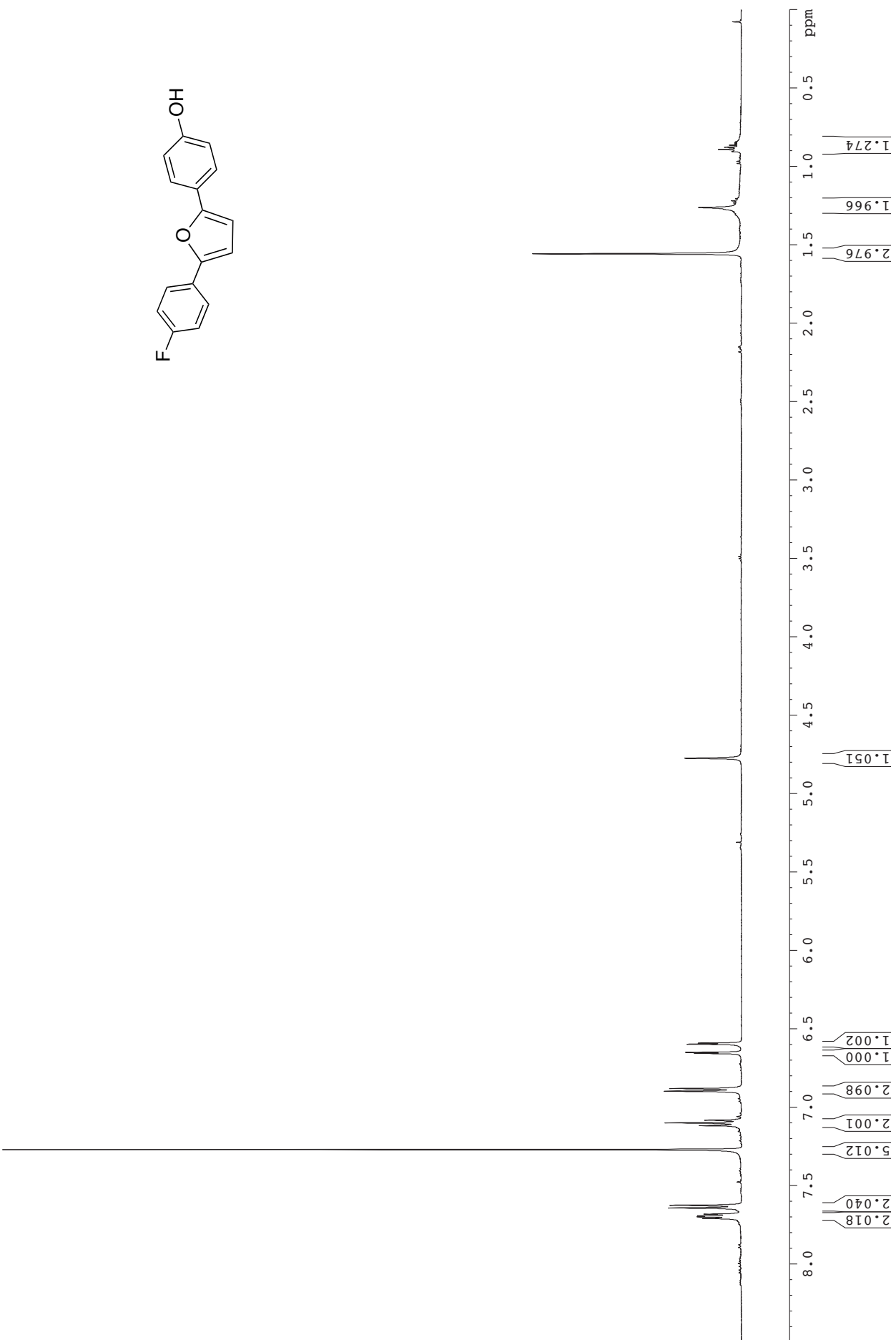
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4. Jiang, H.; Zeng, W.; Li, Y.; Wu, W.; Huang, L.; Fu, W. *J. Org. Chem.* **2012**, *77*, 5179–5183.
5. L'Helgoual'ch, J.; Bentabed-Ababsa, G.; Chevallier, F.; Yonehara, M.; Uchiyama, M.; Derdour, A.; Mongin, F. *Chem. Commun.* **2008**, 5375–5377.





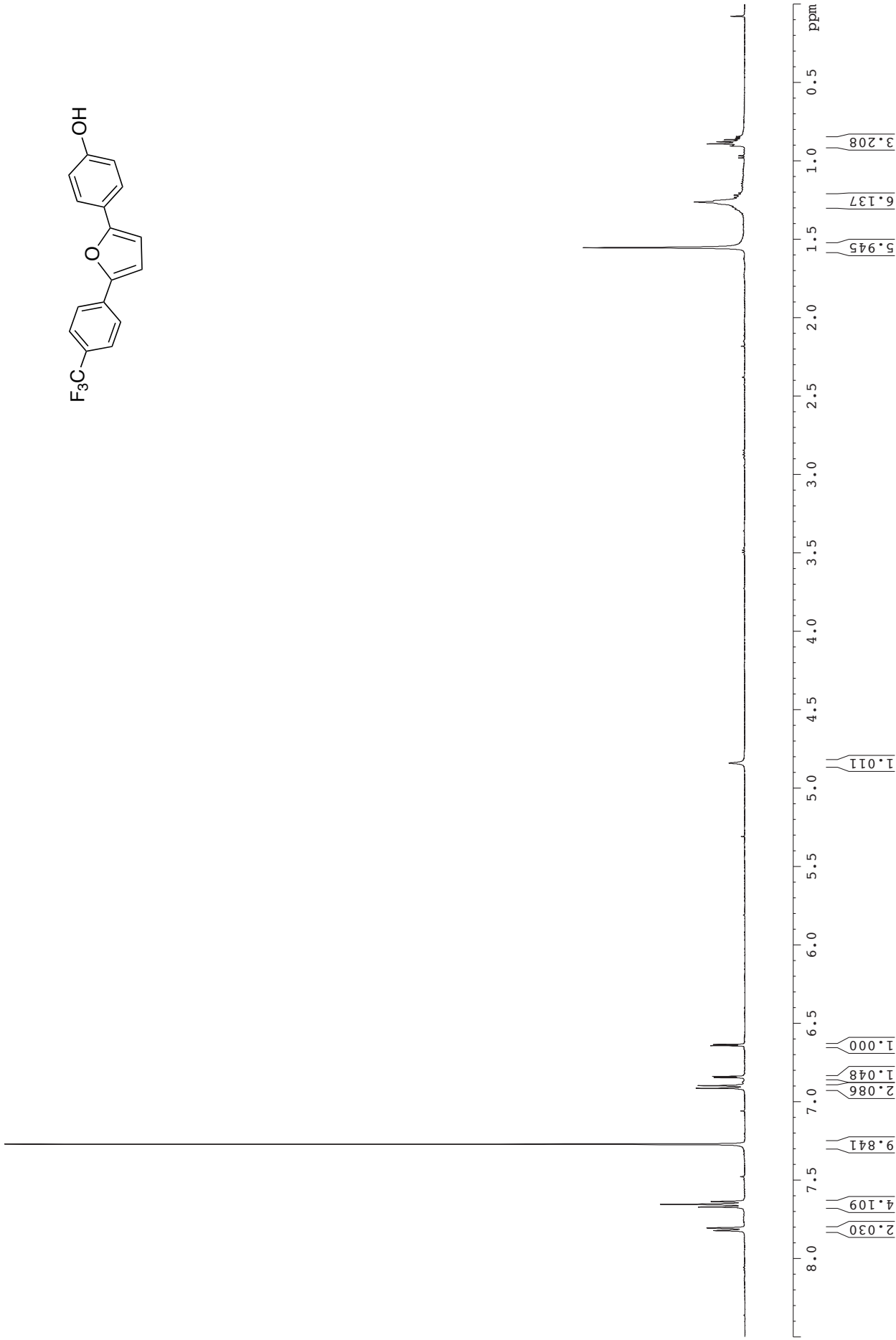


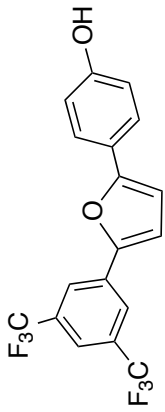
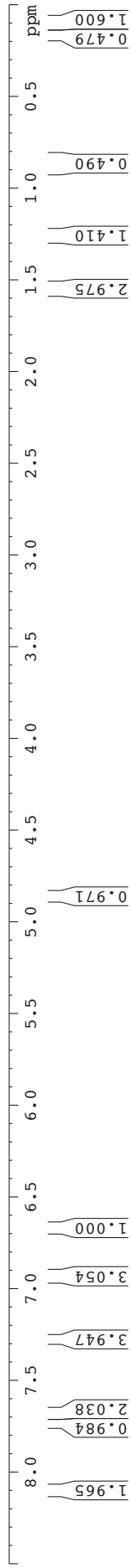


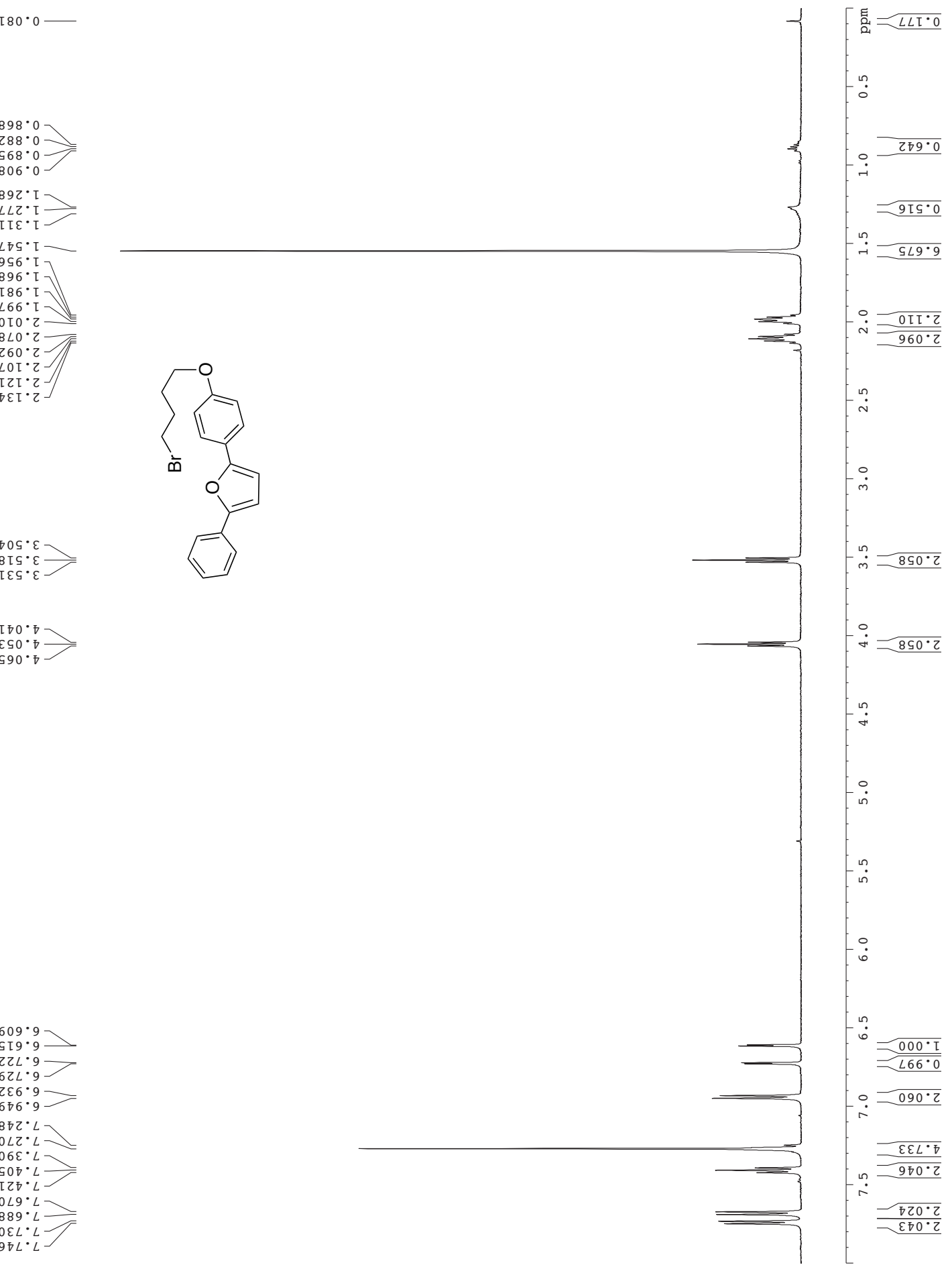
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0.866

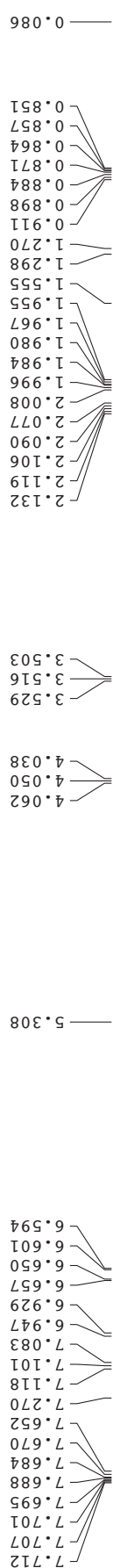
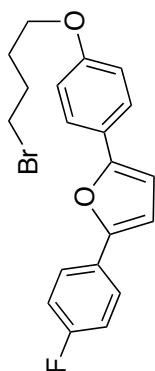
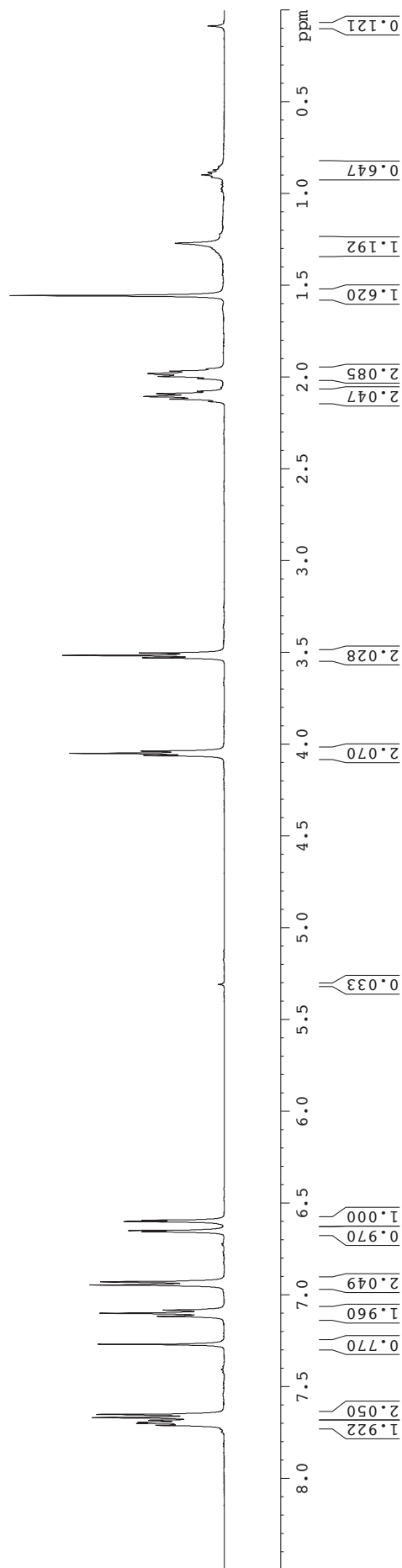
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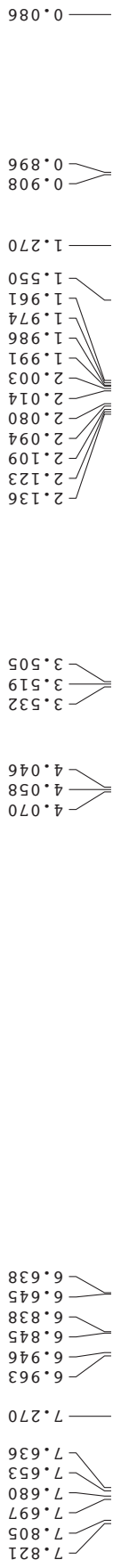
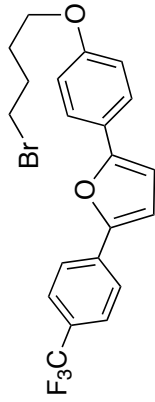
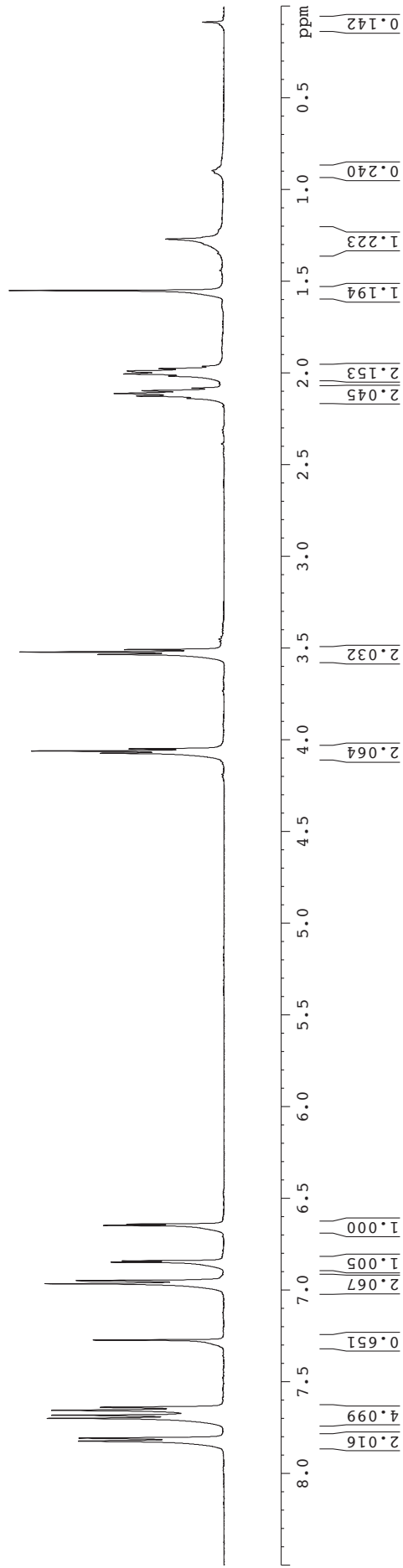
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6.650
6.598
6.591

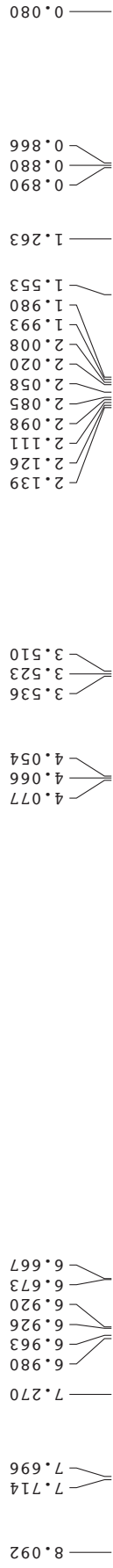
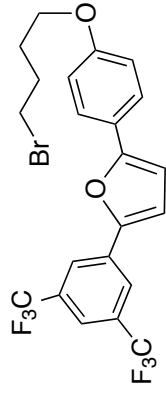
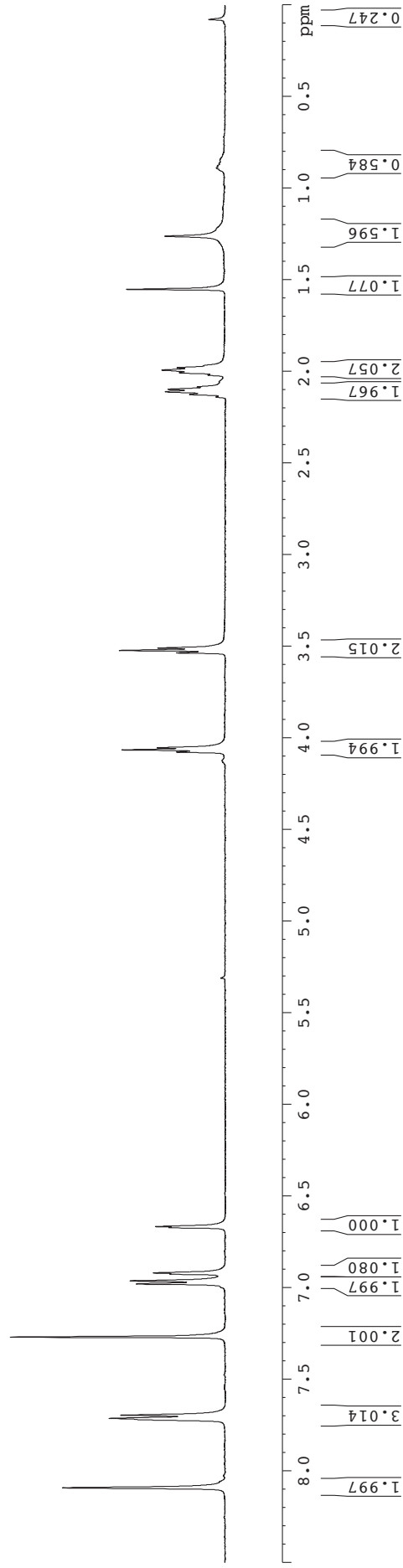


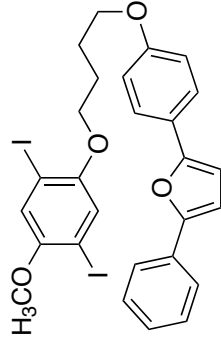
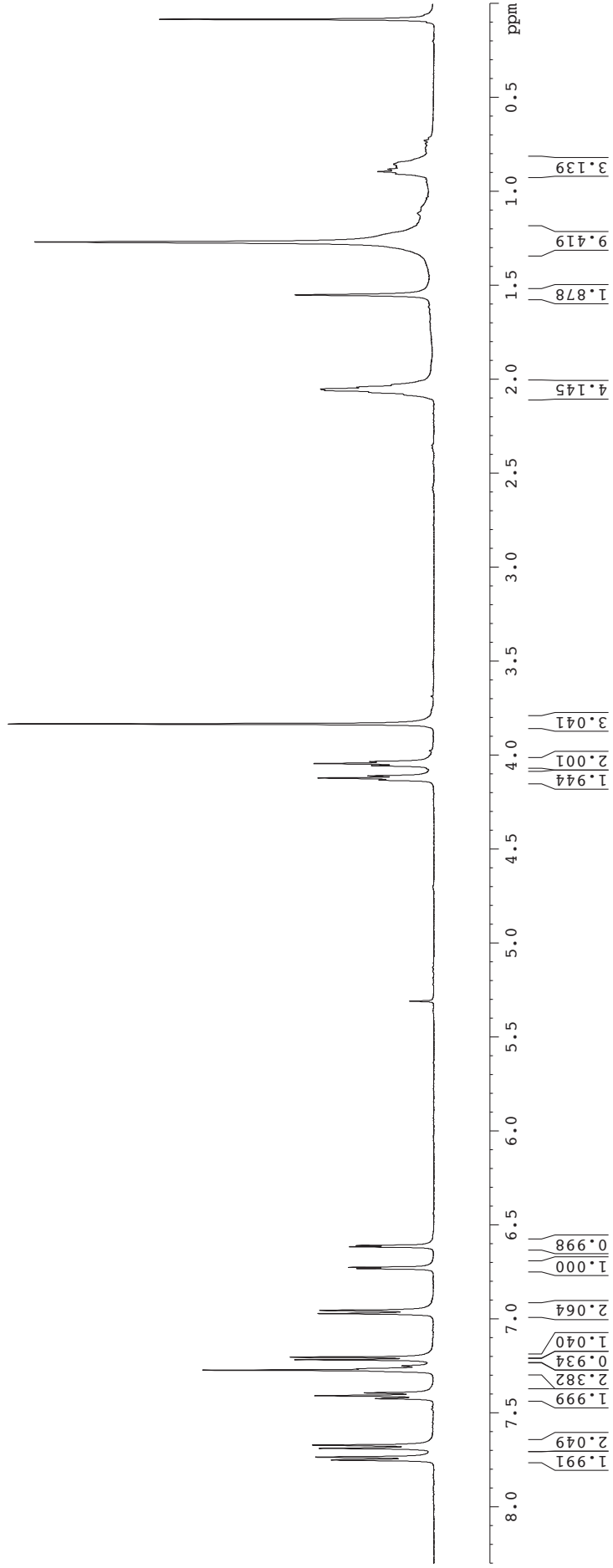








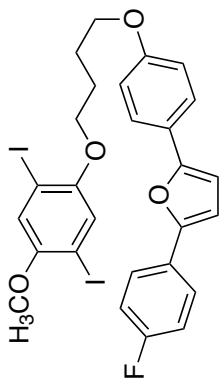
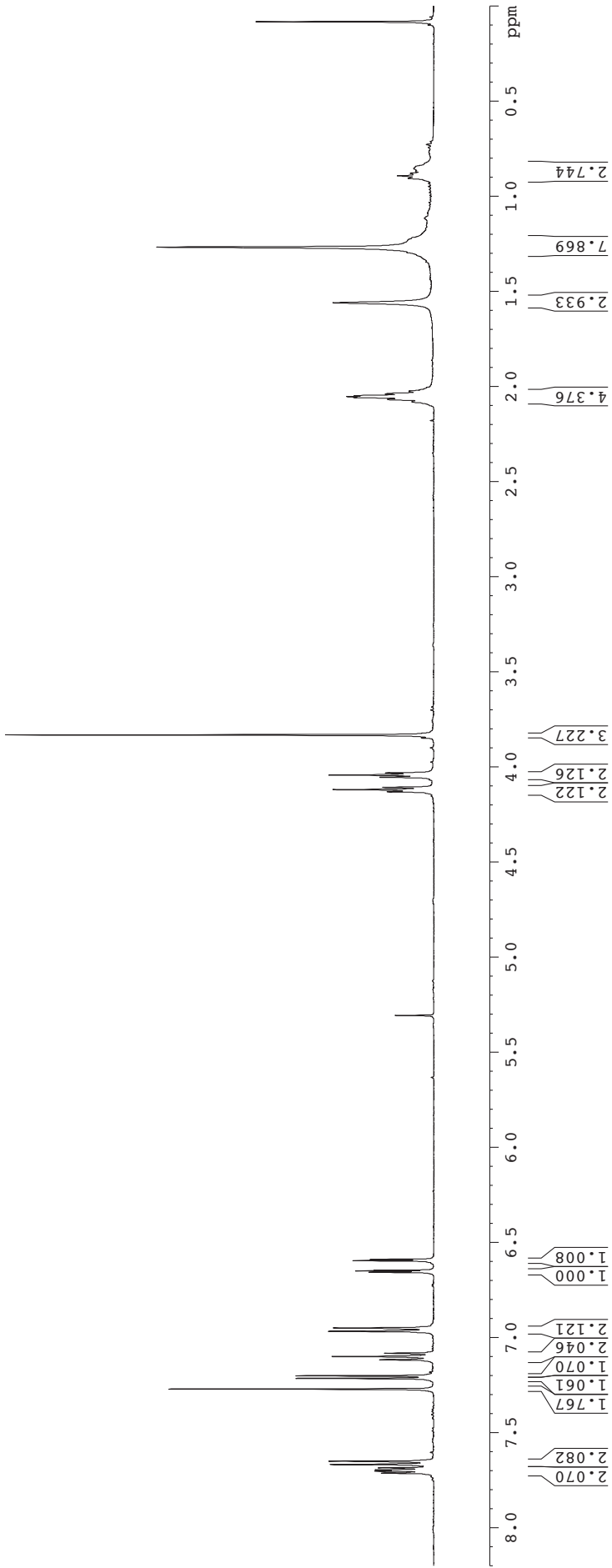


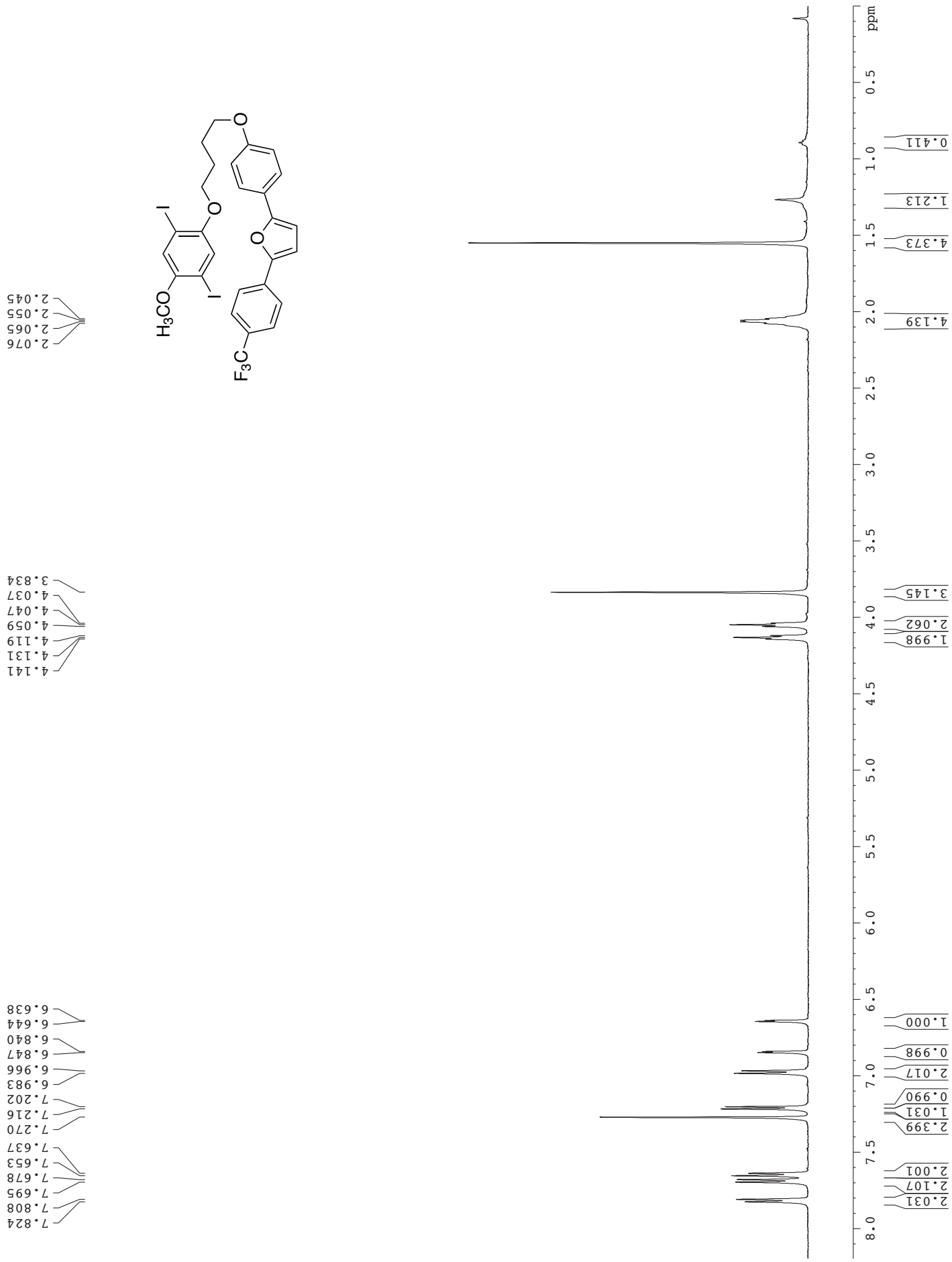


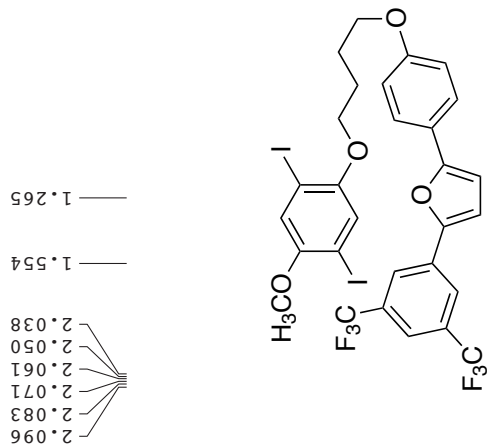
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4.056
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7.733
7.686
7.669
7.421
7.406
7.391
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6.723
6.614
6.607



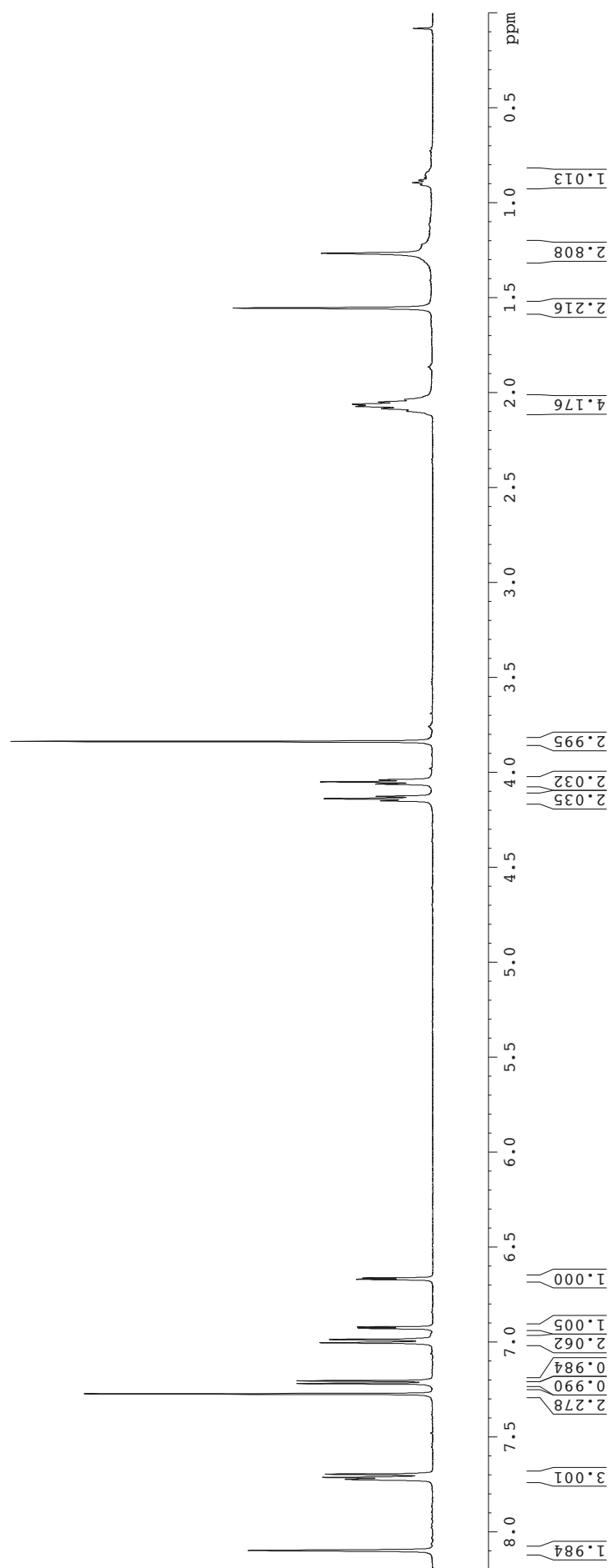


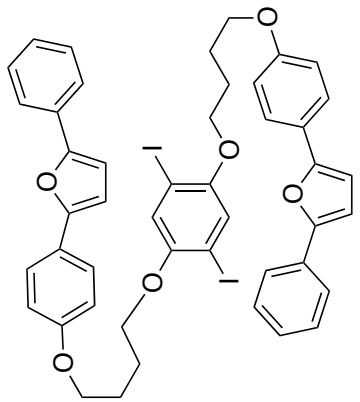
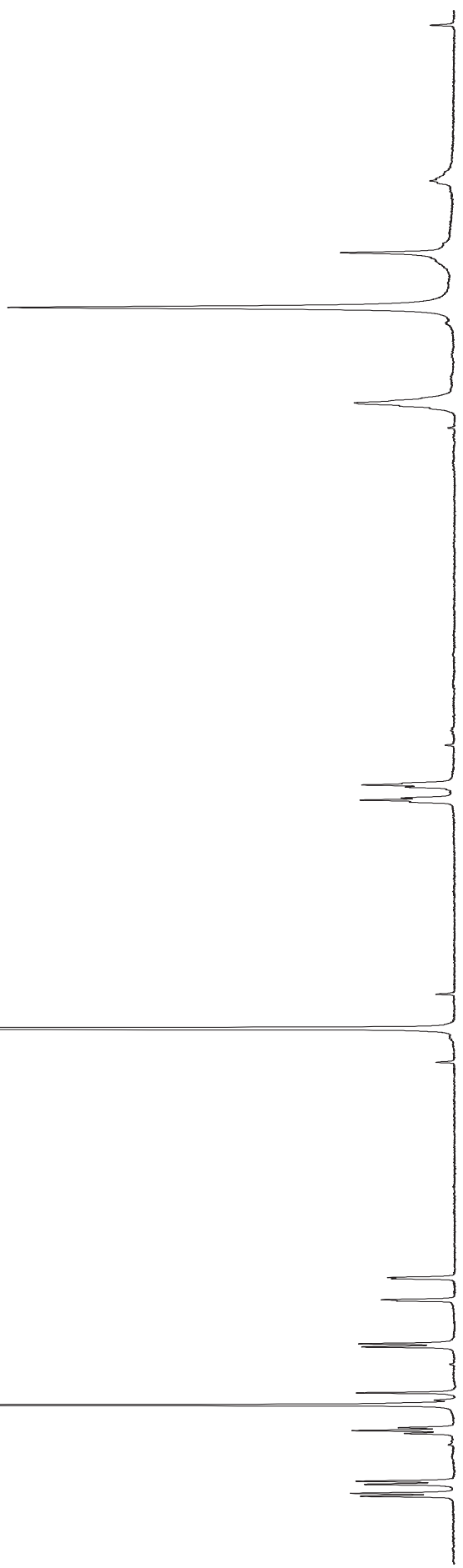
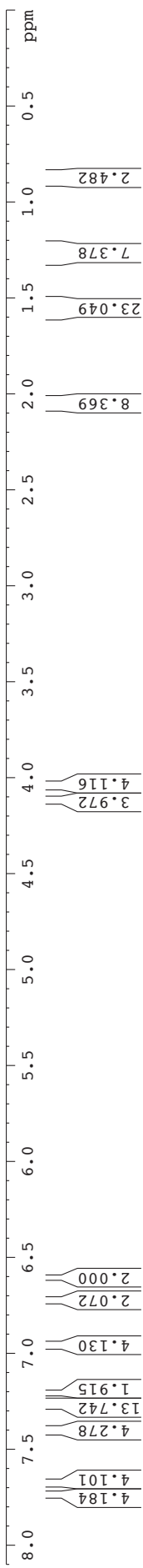


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 2.071
 2.083
 2.096

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 4.061
 4.126
 4.138
 4.149

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 6.669
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 8.095



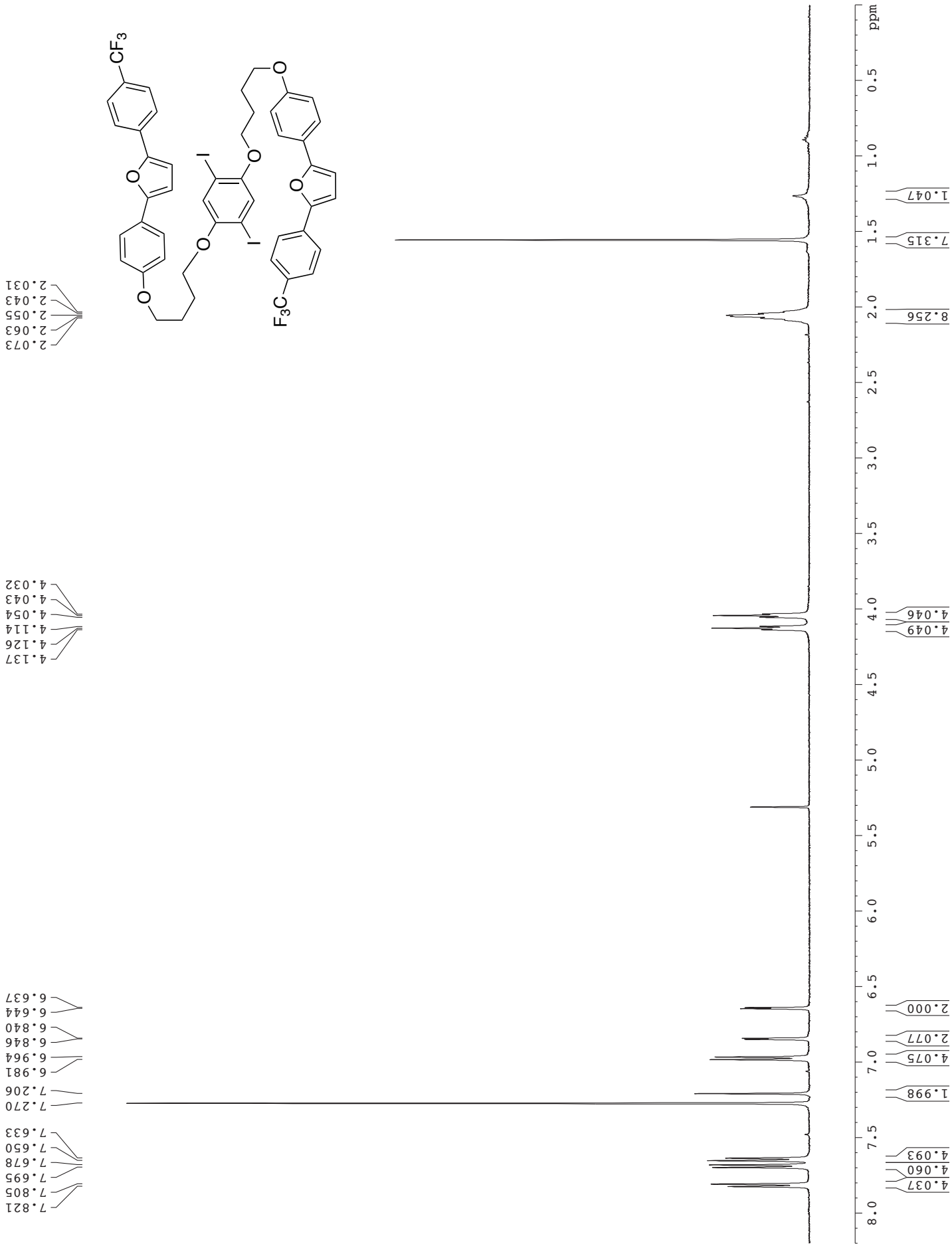


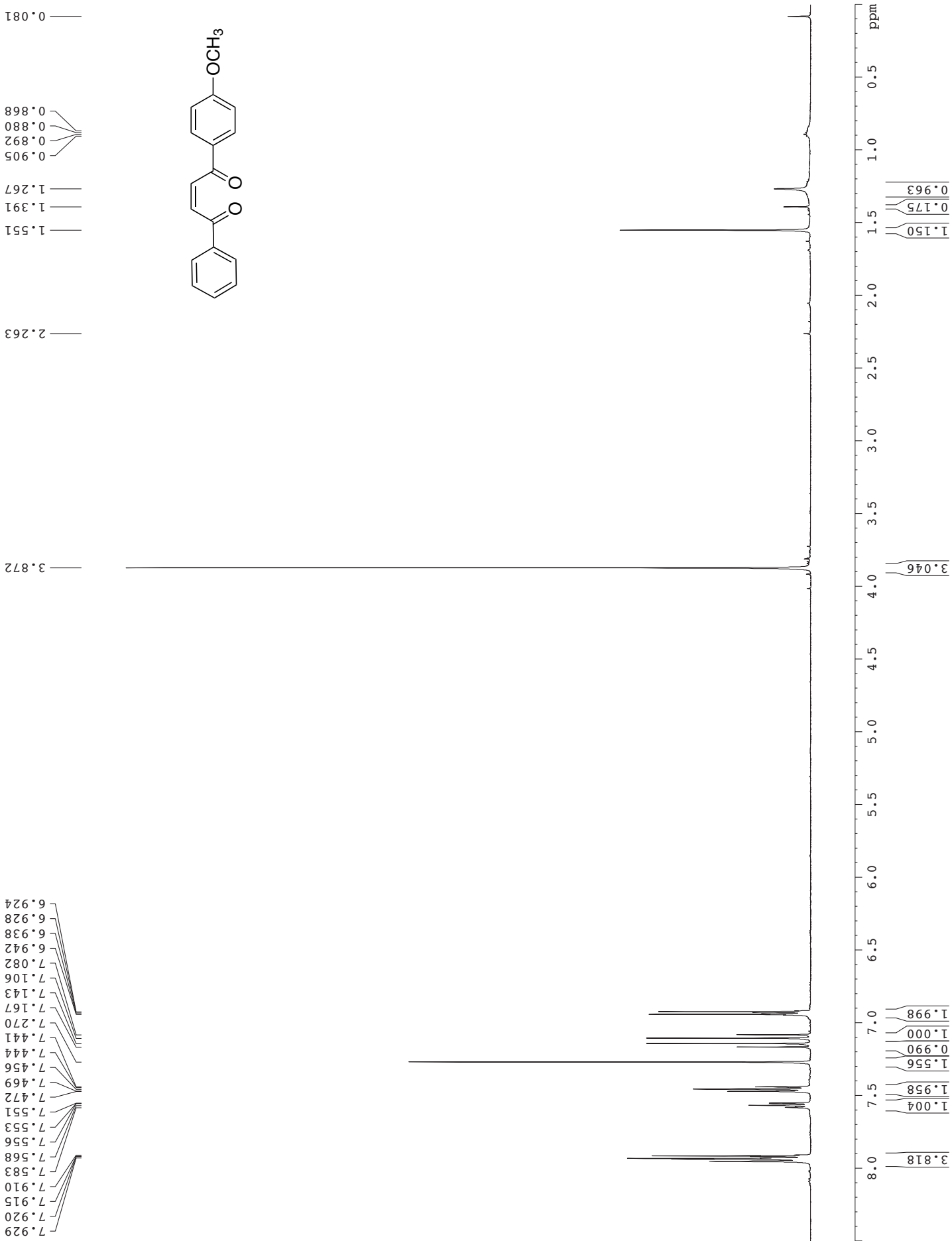
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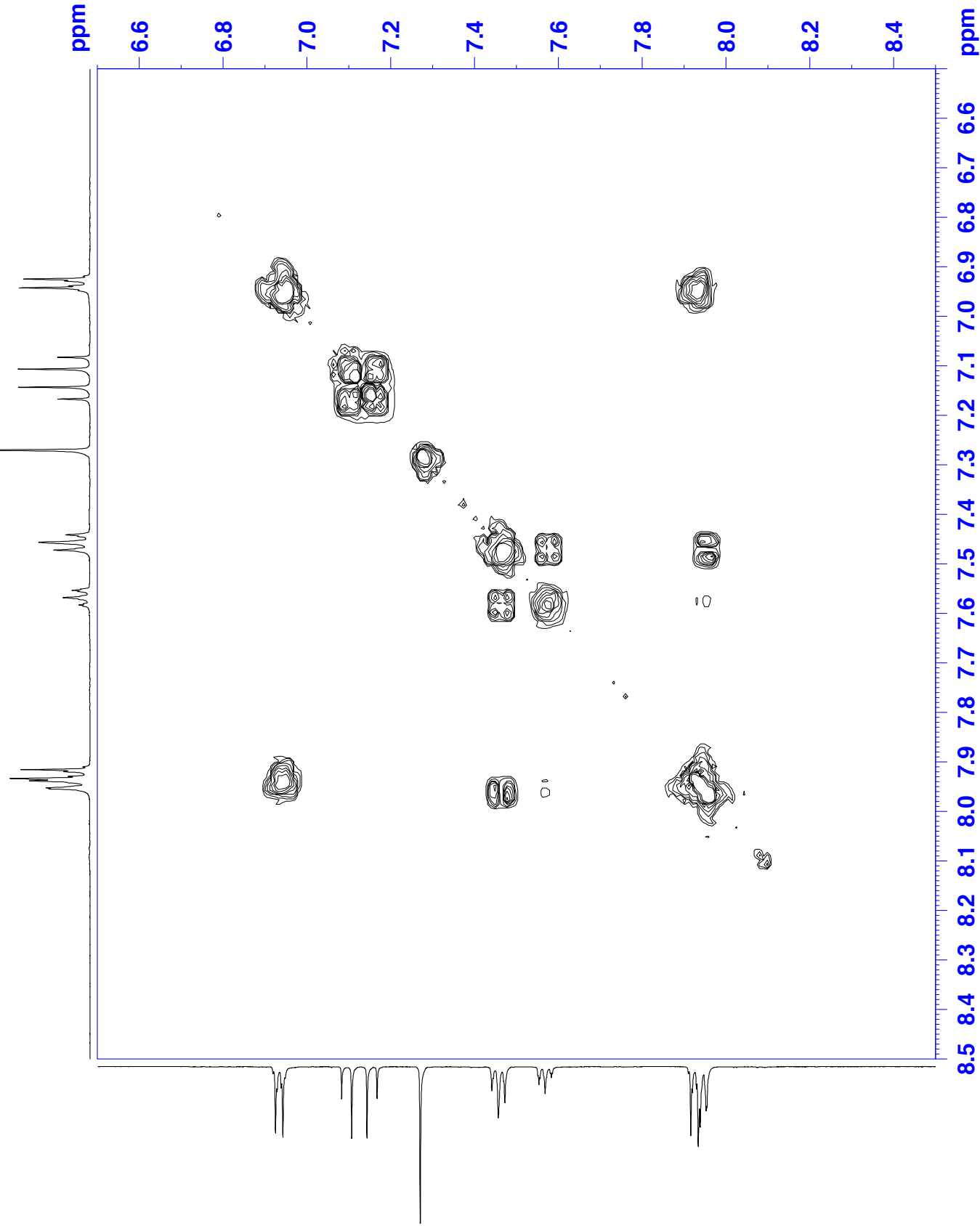
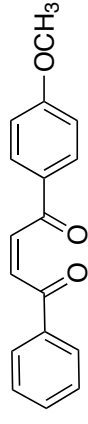
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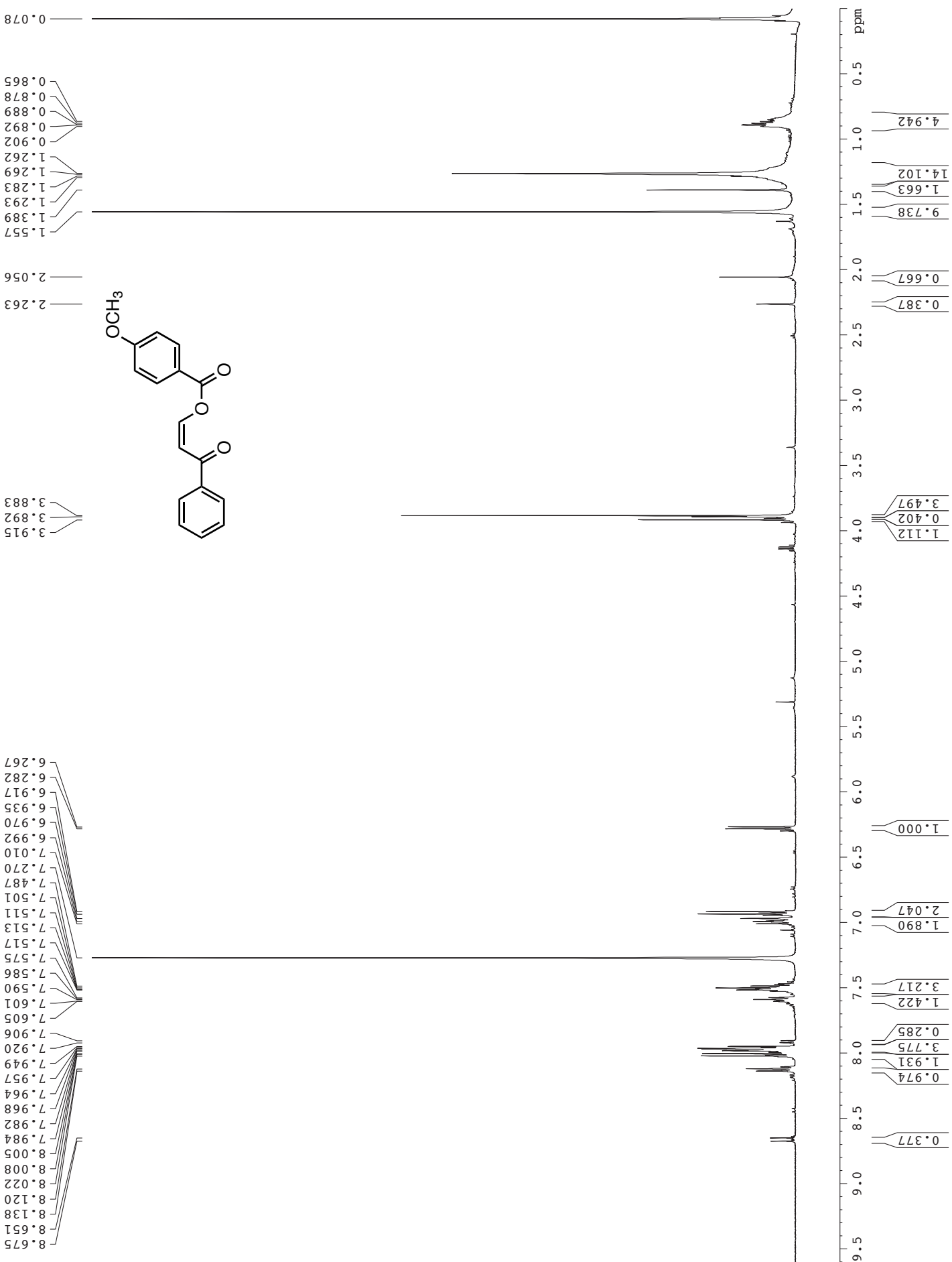
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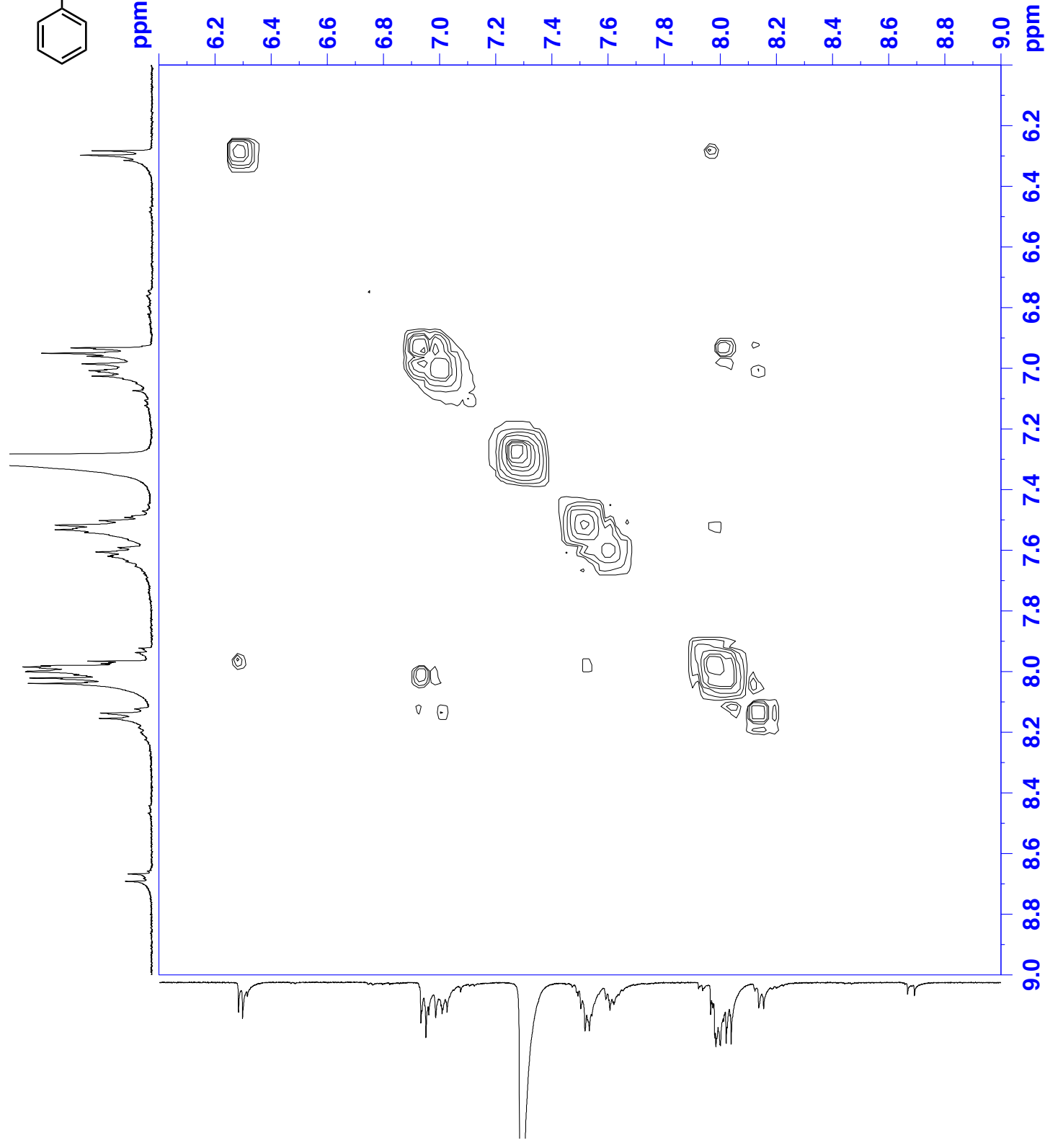
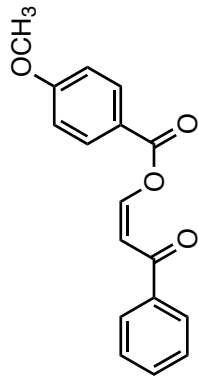
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6.720
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0.078

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1.442
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1.263
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0.865
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3.915

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8.650

