Electronic Supplementary Information For:

Crystal Engineering of Heterocyclic Arylene(ethynylene) Oligomers through Programmed Aromatic Stacking

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General Considerations

All reactants and solvents were purchased from commercial sources and used without further purification. All synthetic manipulations were performed using standard Schlenk techniques under an argon atmosphere, and were based on previously reported literature procedures. Flask column chromatography was performed using silica gel (230–400 mesh). NMR spectra were acquired on a Bruker Avance III 500 or a Bruker DPX-300 spectrometer. Mass spectrometry data are provided for compounds without associated crystal structures, and were acquired using an Agilent LC-MS TOF 6230 spectrometer in ESI positive mode. Stock solutions were prepared in DMSO, and water/acetonitrile was used as the mobile phase. See page S29 of this document for mass spectra and analysis.

UV/visible absorbance and fluorescence spectra were acquired for target compounds in dilute chloroform solution and thin films. UV/visible absorbance spectra were acquired using a Varian Cary-100 spectrophotometer, employing quartz cuvettes and glass microscope slides for solution and thin film measurements, respectively. Emission spectra were acquired using a PTI Quantum Master 4 equipped with a 75 W Xe lamp and a time-correlated single photon-counting module. For solution-state measurements, compound stock solutions were prepared at a concentration of 1 mg/mL. Solutions for analysis were prepared by diluting the stock solutions with chloroform to 0.3-0.4 optical densities; the exact concentrations are unknown. Quantum yields were measured for dilute chloroform solutions with a PTI Petite K-Sphere, using a cuvette with pure chloroform as a blank. Fluorescence lifetimes were determined using a 403 nm pulsed LED light source for time correlated single photon counting (TCSPC). Ludox (1 drop in 3 mL deionized water) was used to determine the instrument response function. Data was analyzed using FelixGX version 4 data analysis, with 1 to 4 exponential lifetime analysis. Decay curves were sampled from 70 – 5 % (at minimum) of the maximum signal. Due to incompatibility of the solution-state emission of ED-1 and ED-2 with the excitation pulse, lifetimes could not be determined. Thin film preparation was accomplished by drop-casting 1 mg/mL solutions of compound onto 1" x 1" glass slides. The exact volume of solution used is unknown; however, the volume used is estimated to be 0.1-0.2 mL. The solutions were evaporated under a watch glass over the course of one hour. Thin films were then annealed for ten minutes at 100 °C in order to alleviate solvent effects.

Preparation of Core Intermediates
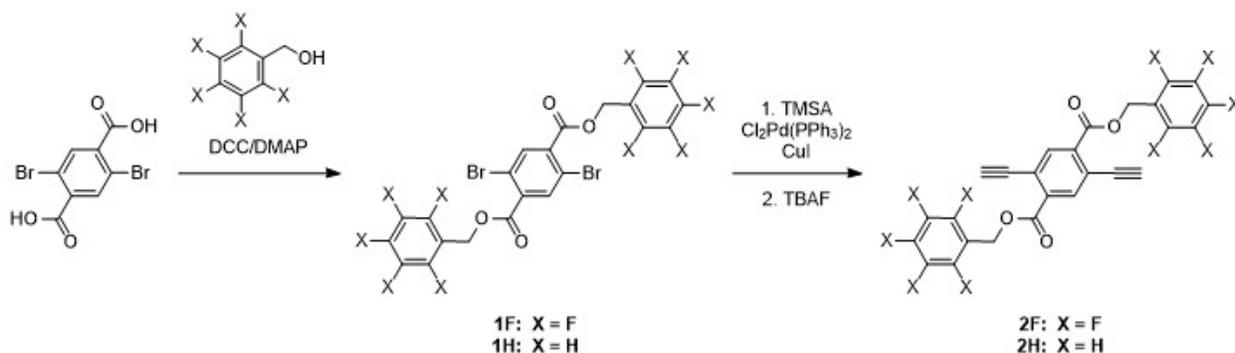
Scheme S 1: Synthesis of core intermediates **1** and **2**
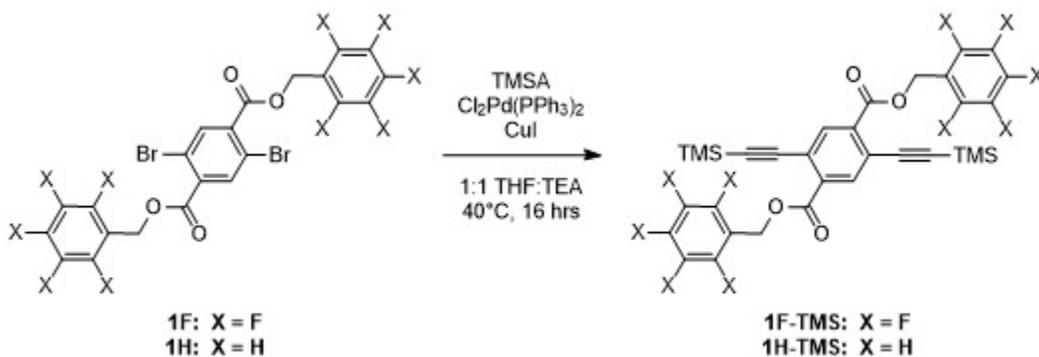
Preparation of 1F and 1H:
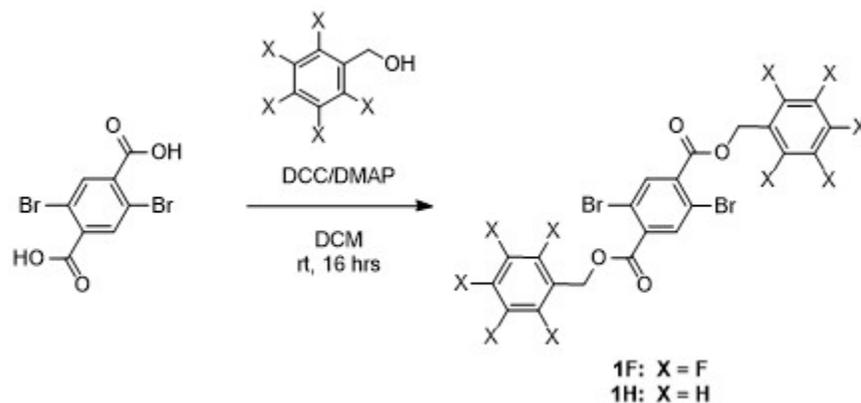
Scheme S 2: Preparation of **1F** and **1H**

A solution of either pentafluorobenzyl alcohol or benzyl alcohol (2.05 eq., 10.3 mmol) in dichloromethane (50 mL) was added to a flame-dried round bottom flask under argon containing 2,5-dibromoterephthalic acid (1 eq., 5.0 mmol), N,N'-dicyclohexylcarbodiimide (2.1 eq., 10.5 mmol), and 4-dimethylaminopyridine (0.2 eq., 1.0 mmol). The reaction mixture was stirred for 16 hours at room temperature, then filtered over a bed of Celite, and rinsed with diethyl ether. The resulting organic solution was washed with water and brine, dried over MgSO$_4$, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel, using 1:1 CH$_2$Cl$_2$:Hexanes as the eluent. Both **1F** and **1H** were recovered as white solids.

1F: 1.78 g recovered, 52% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.03 (s, 2H), 5.49 (s, 4H). ^{13}C (125 MHz, CDCl$_3$): δ 163.3, 145.8 (d, $J = 252$ Hz), 142.1 (d, $J = 252$ Hz), 137.6 (d, $J = 252$ Hz), 136.8, 134.9, 120.4, 108.5, 54.8.

1H: 1.24 g recovered, 49% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.06 (s, 2H), 7.49-7.39 (m, 10H), 5.41 (s, 4H). ^{13}C (125 MHz, CDCl$_3$): δ 164.0, 136.6, 135.6, 134.9, 128.8, 128.7, 128.6, 120.3, 68.0.
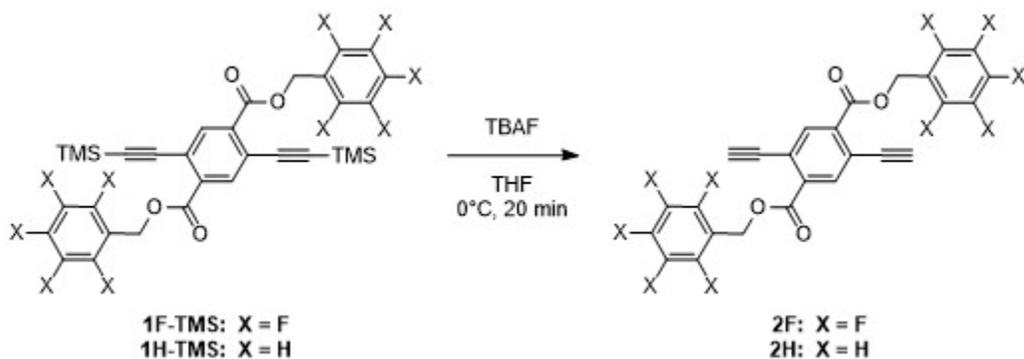
Preparation of 1F-TMS and 1H-TMS:

Scheme S 3: Preparation of **1F-TMS** and **1H-TMS**

40 mL of degassed 1:1 THF:triethylamine (v/v) were added to a Schlenk flask containing either **1F** or **1H** (1 eq., 2.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.05 eq,. 0.1 mmol), and copper (I) iodide (0.05 eq,. 0.1 mmol) under argon. Trimethylsilyl acetylene (TMSA, 2.2 eq., 4.4 mmol) was then added, and the reaction mixture was stirred for 16 hours at 40°C. The reaction mixture was cooled to room temperature and filtered over a pad of Celite. The pad was rinsed with CH_2Cl_2, and the combined organics were washed with water and brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Crude product was purified by flash column chromatography on silica gel. Both **1F-TMS** and **1H-TMS** were recovered as off-white solids.

1F-TMS: 2:1 Hexanes:CH_2Cl_2 used as eluent. 1.20 g recovered, 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (s, 2H), 5.48 (s, 4H), 0.27 (s, 18H). ^{13}C (125 MHz, $CDCl_3$): δ 164.0, 145.8 (d, $J = 252$ Hz), 142.1 (d, $J = 252$ Hz), 137.6 (d, $J = 252$ Hz), 136.4, 133.9, 123.1, 109.1, 104.0, 101.4, 54.2, -0.5.

1H-TMS: 3:2 CH_2Cl_2:Hexanes used as eluent. 0.73 g recovered, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (s, 2H), 7.49-7.36 (m, 10H), 5.42 (s, 4H), 0.24 (s, 18H). ^{13}C (125 MHz, $CDCl_3$): δ 164.9, 136.4, 135.6, 134.7, 128.6, 128.4, 128.3, 122.9, 103.2, 102.0, 67.3, -0.3.

Preparation of 2F and 2H:

**Scheme S 4:** Preparation of **2F** and **2H**

1F-TMS or **1H-TMS** (1 eq., 1.0 mmol) was dissolved in 30 mL of THF and cooled to 0°C in an ice-water bath. Tetrabutylammonium fluoride (TBAF, 2.1 equiv., 2.1 mmol) was added as a 1.0 M solution in THF, and the reaction mixture was stirred for 20 minutes. The reaction mixture was then poured into water, and the product was extracted with diethyl ether. The combined organics were washed with water and brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Crude product was purified by flash column chromatography on silica gel. Both **2F** and **2H** were recovered as white solids.

2F: 3:2 CH_2Cl_2:Hexanes used as eluent. 0.25 g recovered, 43% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.12 (s, 2H), 5.50 (s, 4H), 3.51 (s, 2H). ^{13}C (125 MHz, THF-d8): δ 163.2, 145.9 (d, J = 252 Hz), 141.8 (d, J = 252 Hz), 137.6 (d, J = 252 Hz), 136.1, 134.6, 122.6, 109.7, 86.2, 79.9, 53.9.

2H: 3:1 CH_2Cl_2:Hexanes used as eluent. 0.23 g recovered, 58% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.18 (s, 2H), 7.50-7.38 (m, 10H), 5.42 (s, 4H), 3.48 (s, 2H). ^{13}C (125 MHz, CDCl$_3$): δ 164.3, 136.7, 135.2, 135.0, 128.7, 128.6, 128.5, 122.7, 85.2, 80.7, 67.7.

Preparation of Flankers

Preparation of 3
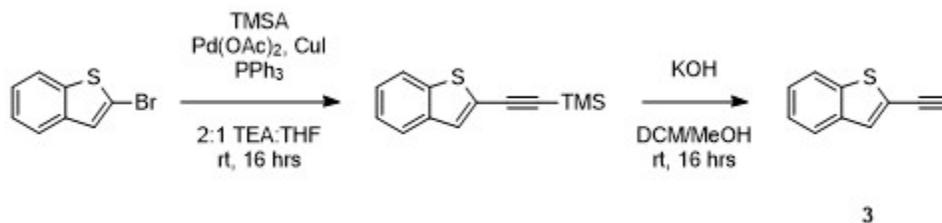
Scheme S 5: Preparation of **3**

Compound **3** was prepared according to a previously reported procedure.[1] Degassed 2:1 triethylamine:THF (v/v, 10 mL) was added to a Schlenk flask containing 2-bromobenzothiophene (1 eq., 2 mmol), palladium (II) acetate (0.003 eq., 0.006 mmol), copper (I) iodide (0.06 eq., 0.12 mmol), and triphenylphosphine (0.1 eq., 0.2 mmol) under argon. Trimethylsilyl acetylene (TMSA, 1.5 eq., 3 mmol) was then added, and the reaction mixture was stirred for 16 hours at room temperature. Solvents were removed in vacuo. Hexanes was then added, and the crude mixture was filtered through a pad of Celite. The filtrate was concentrated in vacuo, and the crude residue was dissolved in 2 mL of dichloromethane. KOH (5 mL of a 1 M solution) in methanol was added, and the reaction mixture was stirred for 16 hours at room temperature. Solvents were removed in vacuo. Water was then added, and the product was extracted with diethyl ether. The combined organics were then concentrated in vacuo, and crude product was purified by column chromatography on silica gel, using hexanes as eluent. Compound **3** was isolated as a clear oil in a 60% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.81-7.77 (m, 2H). 7.55 (s, 1H), 7.43-7.39 (m, 2H), 3.47 (s, 1H) in agreement with the literature.[1]
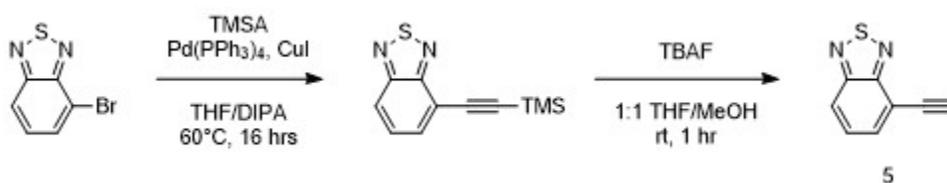
Preparation of 4
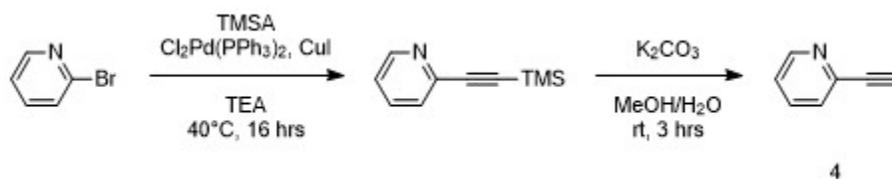
Scheme S 6: Preparation of **4**

Degassed triethylamine (10mL) were added to a Schlenk flask containing 2-bromopyridine (1 eq., 2 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.05 eq,. 0.1 mmol), and copper (I) iodide (0.05 eq,. 0.1 mmol) under argon. Trimethylsilyl acetylene (TMSA, 1.2 eq., 2.4 mmol) was then added, and the reaction mixture was stirred for 16 hours at 40°C. The reaction mixture was cooled to room temperature and filtered over a pad of Celite. The pad was rinsed with CH_2Cl_2, and the combined organics were washed with water and brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Crude product was purified by flash column chromatography on silica gel, using 10% ethyl acetate in hexanes as eluent. The TMS-protected product was then suspended in 10 mL of 1:1 water:methanol (v:v). Potassium carbonate (1 eq., 2 mmol) was then added, and the reaction mixture stirred at room temperature for 3 hours. The reaction mixture was poured into water, extracted with chloroform, washed with water and brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Crude product was purified by column chromatography on silica gel, using 25% ethyl acetate in hexanes as eluent. Compound **4** was isolated as a clear oil in a 60% yield. ¹H NMR (500 MHz, CDCl₃): δ 8.62 (d, 1H), 7.68 (t, 1H), 7.50 (d, 1H), 7.29 (d, 1H), 3.18 (s, 1H) in agreement with the literature.[2]
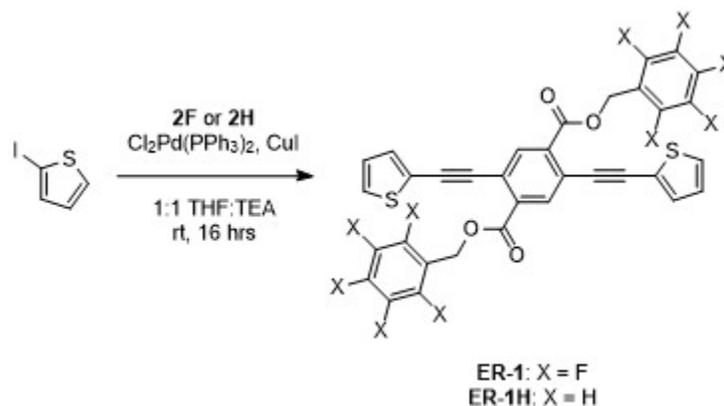

Preparation of 5

Scheme S 7: Preparation of **5**

Compound **5** was prepared according to a previously reported procedure.[3] Degassed THF (6.3 mL) were added to a Schlenk flask containing 4-bromo-1,2,3-benzothiadiazole (1 eq., 0.5 mmol), tetrakis(triphenylphosphine)palladium (0) (0.05 eq., 0.025 mmol), and copper (I) iodide (0.1 eq,. 0.05 mmol) under argon. Trimethylsilyl acetylene (TMSA, 2 eq., 1 mmol) and degassed diisopropylamine (0.3 mL) were then added, and the reaction mixture was stirred for 16 hours at 60°C. The reaction mixture was cooled to room temperature and filtered over a pad of celite. The pad was rinsed with CH_2Cl_2, and the combined organics were washed with water and brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Crude product was

purified by flash column chromatography on silica gel, using 60:40 hexanes: CH_2Cl_2 as eluent. The TMS-protected product was then suspended in 18 mL of 1:1 THF:methanol (v:v). Tetrabutylammonium fluoride (1 M in THF) was added, and the reaction mixture stirred at room temperature for 1 hour. The reaction mixture was poured into water, extracted with diethyl ether, washed with water and brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Crude product was purified by column chromatography on silica gel, using 1:1 hexanes CH_2Cl_2 as eluent. Compound **5** was isolated as a light brown solid in a 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, 1H), 7.83 (d, 1H), 7.60 (t, 1H) 3.61 (s, 1H) in agreement with the literature.[3]

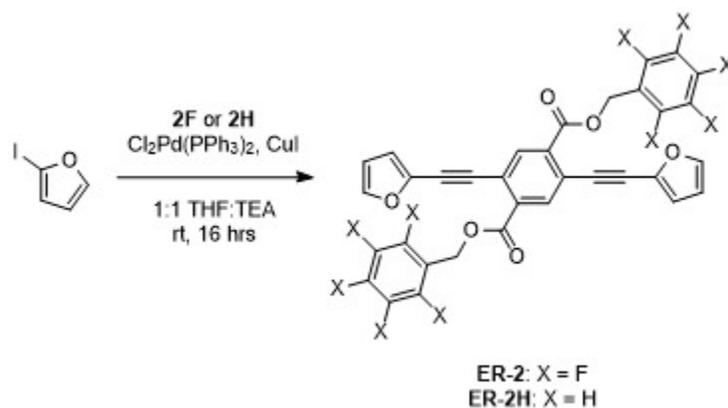**Preparation of ER-1 and ER-1H**

Scheme S 8: Preparation of **ER-1** and **ER-1H**

Degassed 1:1 THF:triethylamine (v/v, 4 mL) were added to a Schlenk flask containing either **2F** or **2H** (1 eq., .1 mmol), 2-iodothiophene (2.2 eq., 0.22 mmol) bis(triphenylphosphine)palladium(II) dichloride (0.05 eq,. 0.005 mmol), and copper (I) iodide (0.05 eq., 0.005 mmol) under argon. The reaction was stirred for 16 hours at room temperature. Solvents were then removed in vacuo, and crude product was purified by column chromatography on silica gel and recrystallization, the details of which are specified below.

ER-1: 1:1 CH_2Cl_2:hexanes used as eluent, recrystallized from $CHCl_3$/MeOH as a white powder in a 38% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (s, 2H), 7.29 (d, 2H) 7.06 (t, 2H) 5.51 (s, 4H). ^{13}C NMR (500 MHz, THF-*d*8): δ 161.4, 144.1 (d, $J = 252$ Hz), 139.8 (d, $J = 252$ Hz), 135.6 (d, $J = 252$ Hz), 133.7, 131.6, 130.9, 127.0, 125.3, 120.9, 120.4, 108.0, 88.5, 88.4, 52.2.

ER-1H: 2:1 CH_2Cl_2:hexanes used as eluent, recrystallized from $CHCl_3$/MeOH as yellow needles in a 54% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (s, 2H), 7.51 (d, 4H) 7.37 (m, 8H), 7.22 (d, 2H), 7.03 (t, 2H), 5.46 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.7, 135.9, 135.5, 133.8, 133.0, 128.7, 128.5, 128.4, 127.3, 122.8, 122.7, 91.4, 90.6, 67.6.
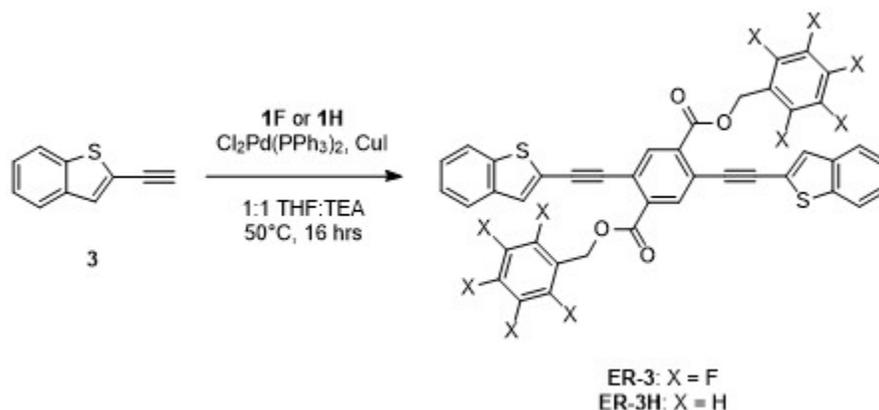
Preparation of ER-2 and ER-2H

Scheme S 9: Preparation of **ER-2** and **ER-2H**

Degassed 1:1 THF:triethylamine (v/v, 4 mL) were added to a Schlenk flask containing either **2F** or **2H** (1 eq., 0.1 mmol), 2-iodofuran (2.2 eq., 0.22 mmol) bis(triphenylphosphine)palladium(II) dichloride (0.05 eq,. 0.005 mmol), and copper (I) iodide (0.05 eq,. 0.005 mmol) under argon. The reaction was stirred for 16 hours at room temperature. Solvents were then removed in vacuo, and crude product was purified by column chromatography on silica gel and recrystallization, the details of which are specified below.

ER-2: 1:1 CH_2Cl_2:hexanes used as eluent, recrystallized from $CHCl_3$/MeOH as yellow needles in a 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (s, 2H), 7.47 (d, 2H), 6.74 (d, 2H), 6.48 (t, 2H), 5.52 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8, 145.8 (d, J = 252 Hz), 144.6, 142.0 (d, J = 252 Hz), 137.5 (d, J = 252 Hz). 136.5, 136.3, 132.8, 122.6, 117.1, 111.4, 108.8, 91.1, 87.4, 54.5. HRMS (TOF, EI): *m/z* calculated for $C_{34}H_{12}F_{10}O_6$ (M^+ + 1), 707.0474; found 707.0520.

ER-2H: 1:1 CH_2Cl_2:hexanes used as eluent, recrystallized from $CHCl_3$/MeOH as yellow needles in a 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (s, 2H), 7.52-7.37 (m, 12H), 6.64 (d, 2H), 6.45 (t, 2H), 5.45 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4, 144.5, 136.8, 135.9, 135.4, 133.7, 128.7, 128.6, 128.4, 122.5, 116.9, 111.3, 91.7, 87.2, 67.7,
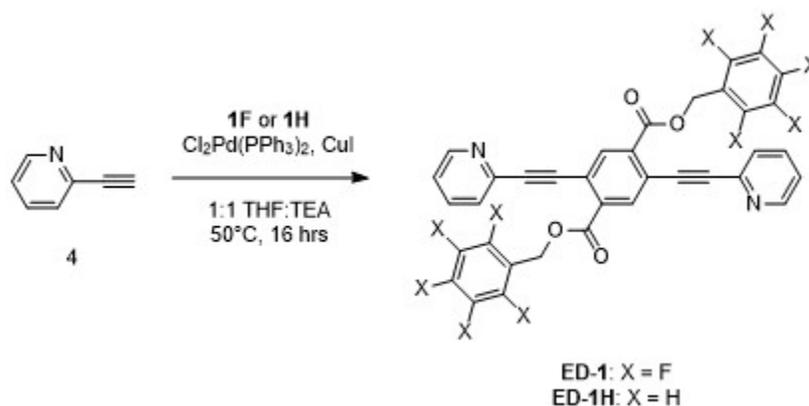
Preparation of ER-3 and ER-3H

Scheme S 10: Preparation of **ER-3** and **ER-3H**

Degassed 1:1 THF:triethylamine (v/v, 4 mL) were added to a Schlenk flask containing either **1F** or **1H** (1 eq., 0.1 mmol), compound **3** (2.2 eq., 0.22 mmol) bis(triphenylphosphine)palladium(II) dichloride (0.05 eq,. 0.005 mmol), and copper (I) iodide (0.05 eq., 0.005 mmol) under argon. The reaction was stirred for 16 hours at 50°C. Solvents were then removed in vacuo, and crude product was purified by column chromatography on silica gel and recrystallization, the details of which are specified below.

ER-3: 1:1 CH_2Cl_2:hexanes, then pure CH_2Cl_2used as eluent, recrystallized from $CHCl_3$/MeOH as a white powder in a 52% yield. ^{1}H NMR (500 MHz, THF-d8): δ 8.23 (s, 2H), 7.83 (dd, 4H), 7.58 (s, 2H), 7.40 (quint., 4H), 5.58 (s, 4H). ^{13}C NMR (125 MHz, THF-d8): δ 164.0, 141.6, 139.9, 136.6, 134.6, 130.7, 126.7, 125.6, 124.8, 123.5, 122.9, 122.7, 110.6, 92.8, 91.4, 55.0. Due to low solubility in all deuterated organic solvents, the aromatic sidechain fluorocarbons are not observable in the presented ^{13}C NMR spectrum. However, they are present in the associated crystal structure, and the presented ^{1}H NMR shows high purity.

ER-3H: CH_2Cl_2used as eluent, recrystallized from $CHCl_3$/MeOH as a yellow powder in a 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (s, 2H), 7.79 (dd, 4H), 7.54-7.28 (m, 16H), 5.50 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.6, 140.9, 139.0, 136.2, 135.4, 134.0, 130.0, 129.9, 128.7, 128.5, 125.8, 124.8, 124.1, 122.7, 122.5, 122.1, 92.9, 90.9, 67.8. HRMS (TOF, EI): species observed in mass spectrum is a molecular ion dimer plus a sodium cation; m/z calculated for $C_{42}H_{26}O_4S_2$ (($2xM^+$) + Na^+), 1339.2444; found 1339.2388.
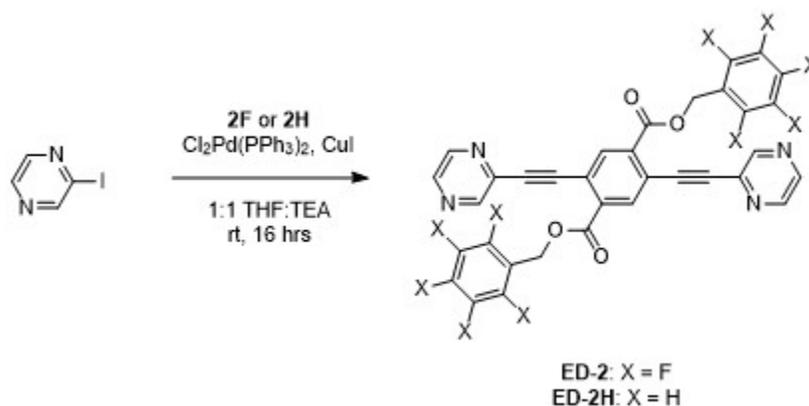
Preparation of ED-1 and ED-1H

Scheme S 11: Preparation of **ED-1** and **ED-1H**

Degassed 1:1 THF:triethylamine (v/v, 4 mL) were added to a Schlenk flask containing either **1F** or **1H** (1 eq., 0.1 mmol), compound **4** (2.2 eq., 0.22 mmol) bis(triphenylphosphine)palladium(II) dichloride (0.05 eq,. 0.005 mmol), and copper (I) iodide (0.05 eq,. 0.005 mmol) under argon. The reaction was stirred for 16 hours at 50°C. Solvents were then removed in vacuo, and crude product was purified by column chromatography on silica gel and recrystallization, the details of which are specified below.

ED-1: A gradient of 25% to 50% ethyl acetate in hexanes used as eluent, recrystallized from CHCl$_3$/MeOH as a pale orange solid in a 55% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.66 (s, 2H), 8.34 (s, 2H), 7.75 (t, 2H), 7.59 (s, 2H), 7.33 (s, 2H), 5.51 (s, 4H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 163.5, 148.9 (d, J = 252 Hz), 143.8 (d, J = 252 Hz), 139.5 (d, J = 252 Hz), 136.8, 136.2, 133.7, 127.5, 123.5, 123.2, 108.9, 96.3, 86.2, 54.4.

ED-1H: 40% ethyl acetate in hexanes used as eluent, obtained as an off-white solid in a 60% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.66 (d, 2H), 8.39 (s, 2H), 7.68 (t, 2H), 7.50-7.30 (m, 14H), 5.45 (s, 4H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 164.3, 150.1, 142.9, 136.6, 136.2, 135.3, 134.6, 128.6, 128.4, 127.7, 123.2, 122.9, 95.9, 86.8, 67.7. HRMS (TOF, EI): *m/z* calculated for C$_{36}$H$_{24}$N$_2$O$_4$ (M$^+$ + 1), 549.1736; found 549.1788.
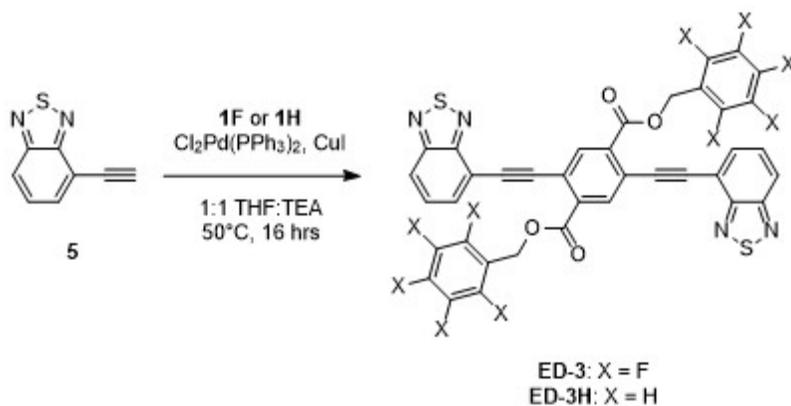
Preparation of ED-2 and ED-2H

Scheme S 12: Preparation of **ED-2** and **ED-2H**

Degassed 1:1 THF:triethylamine (v/v, 4 mL) were added to a Schlenk flask containing either **2F** or **2H** (1 eq., 0.1 mmol), 2-iodopyrazine (2.2 eq., 0.22 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.05 eq,. 0.005 mmol), and copper (I) iodide (0.05 eq,. 0.005 mmol) under argon. The reaction was stirred for 16 hours at room temperature. Solvents were then removed in vacuo, and crude product was purified by column chromatography on silica gel and recrystallization, the details of which are specified below.

ED-2: 2:1 hexanes:ethyl acetate used as eluent, recrystallized from $CHCl_3$/MeOH as a pale orange powder in a 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.83 (s, 2H), 8.63 (s, 2H), 8.59 (s, 2H), 8.37 (s, 2H), 5.54 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.2, 148.1, 145.9 (d, J = 252 Hz), 144.6, 143.6, 142.1 (d, J = 252 Hz), 139.6, 137.6 (d, J = 252 Hz), 136.9, 133.9, 123.0, 108.6, 93.6, 89.6, 54.6. HRMS (TOF, EI): m/z calculated for $C_{34}H_{12}F_{10}N_4O_4$ (M^+ + 1), 731.0699; found 731.0745.

ED-2H: 60:40 hexanes:ethyl acetate used as eluent, recrystallized from $CHCl_3$/MeOH as a pale orange powder in a 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.63 (s, 4H), 8.55 (s, 2H), 8.42 (s, 2H), 7.50 (d, 4H), 7.37 (m, 6H), 5.46 (4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.9, 148.1, 144.6, 143.3, 139.8, 136.8, 136.7, 135.0, 134.8, 128.8, 128.7, 122.8, 93.3, 90.3, 68.0.

Preparation of ED-3 and ED-3H

Scheme S 13: Preparation of **ED-3** and **ED-3H**

Degassed 1:1 THF:triethylamine (v/v, 6 mL) were added to a Schlenk flask containing either **2F** or **2H** (1 eq., 0.07 mmol), compound **5** (2.2 eq., 0.15 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.05 eq,. 0.003 mmol), and copper (I) iodide (0.05 eq,. 0.003 mmol) under argon. The reaction was stirred for 16 hours at 50°C. Solvents were then removed in vacuo, and crude product was purified by column chromatography on silica gel and recrystallization, the details of which are specified below.

ED-3: CH$_2$Cl$_2$ used as eluent, recrystallized from CHCl$_3$/MeOH as a bright yellow powder in a 76% yield. ^{1}H NMR (500 MHz, THF-d8): δ 8.33 (s, 2H), 8.11 (d, 2H), 7.83 (d, 2H), 7.68 (t, 2H), 5.60 (s, 4H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 163.9, 154.5, 154.2, 145.8 (d, J = 252 Hz), 141.7 (d, J = 252 Hz), 137.5 (d, J = 252 Hz), 136.7, 133.7, 133.2, 129.1, 123.3, 122.8, 116.3, 108.9, 93.0, 92.5, 54.5.

ED-3H: CH$_2$Cl$_2$ used as eluent, recrystallized from CHCl$_3$/MeOH as a bright yellow powder in a 93% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.47 (s, 2H), 8.05 (d, 2H), 7.68 (d, 2H), 7.59 (t, 2H), 7.46 (d, 4H), 7.25 (s, 6H), 5.49 (s, 4H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 164.7, 154.6, 154.4, 136.7, 135.3, 134.4, 133.3, 129.2, 128.6, 128.4, 128.3, 123.1, 122.5, 116.6, 93.2, 92.7, 67.8.

Figure S1: ^{1}H and ^{13}C NMR Spectra of **1F**
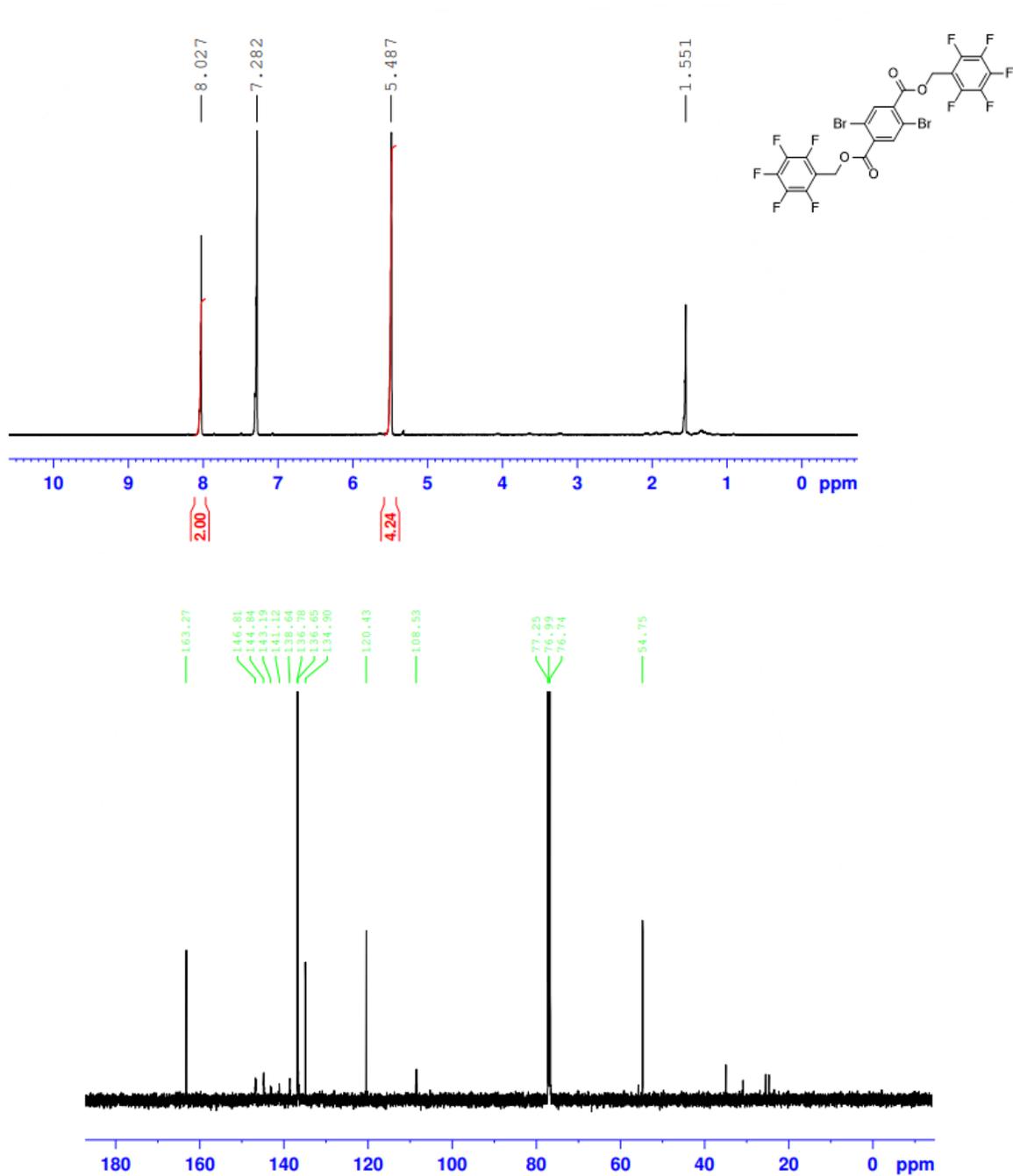
Figure S2: ^{1}H and ^{13}C NMR Spectra of **1H**
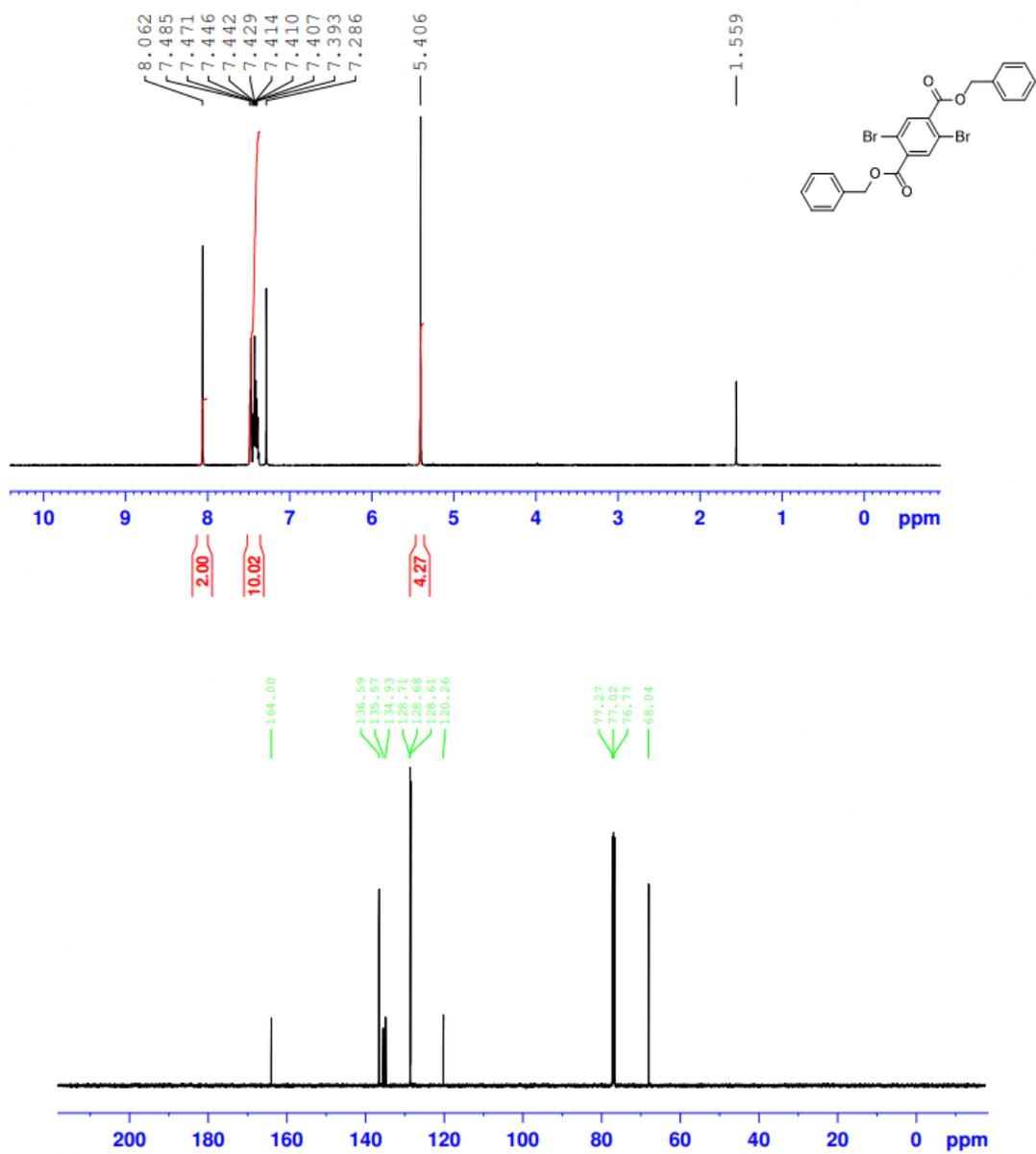
Figure S3: ^{1}H and ^{13}C NMR Spectra of **1F-TMS**
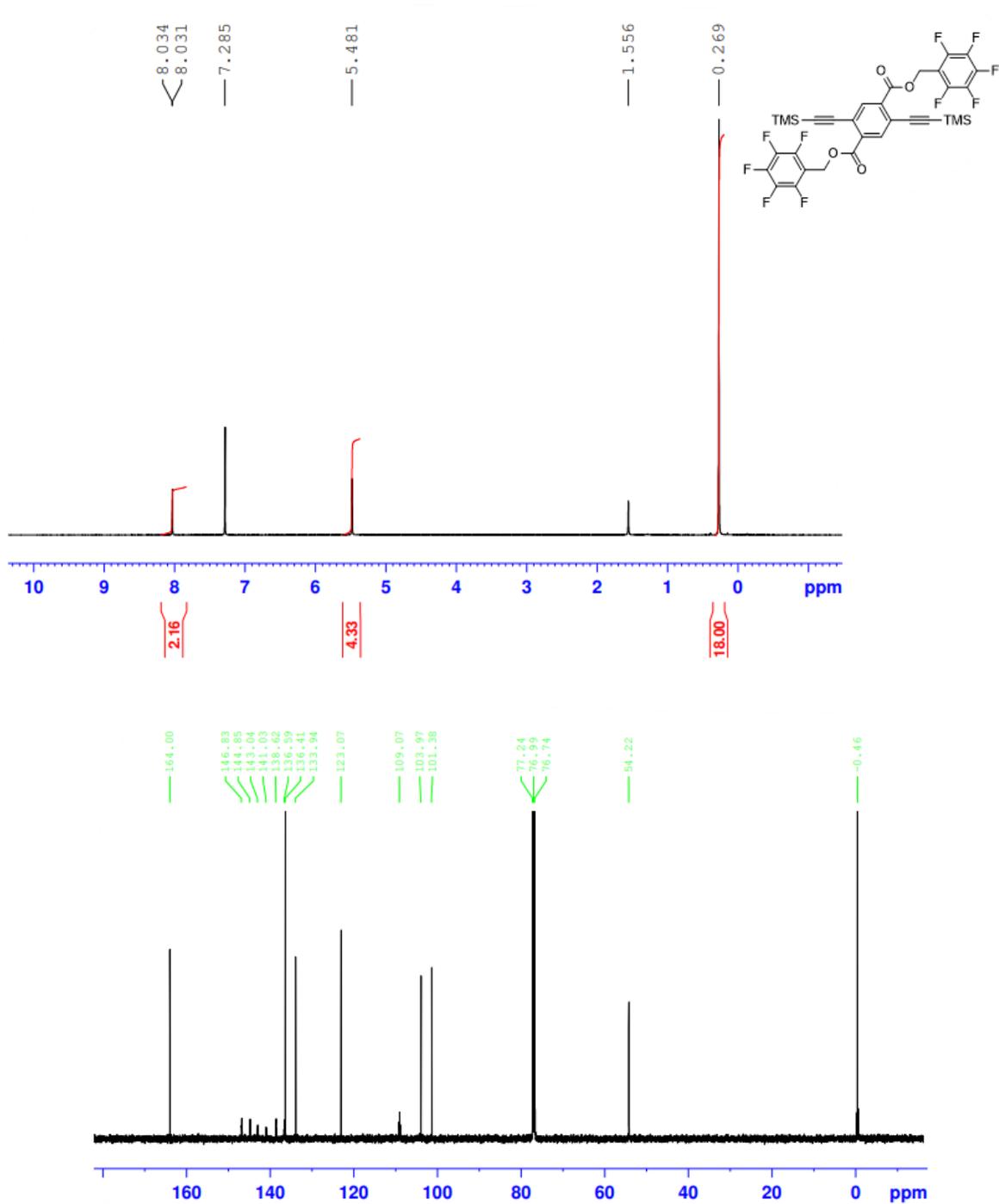
Figure S4: ^{1}H and ^{13}C NMR Spectra of **1H-TMS**
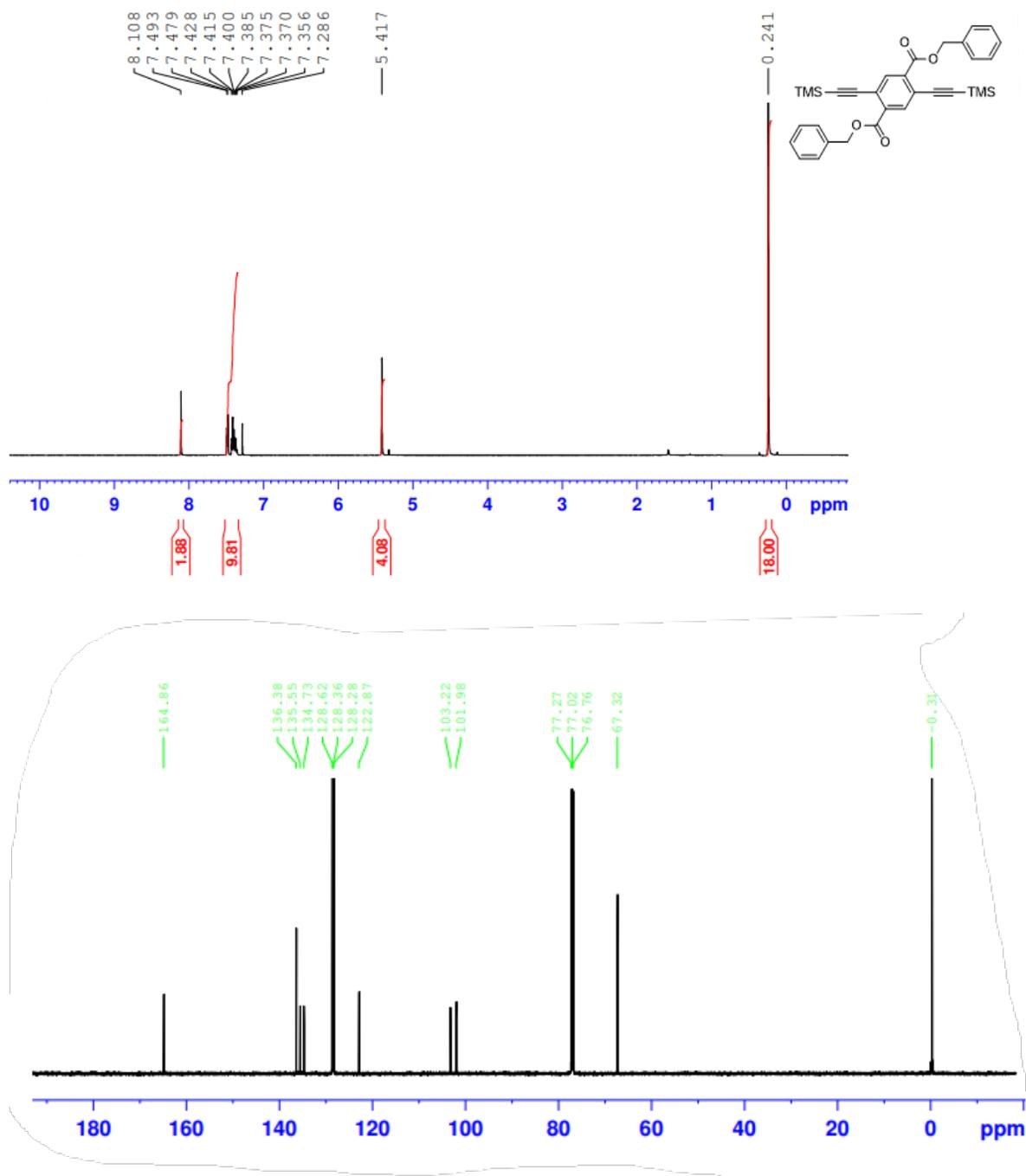
Figure S5: ^{1}H and ^{13}C NMR Spectra of **2F**
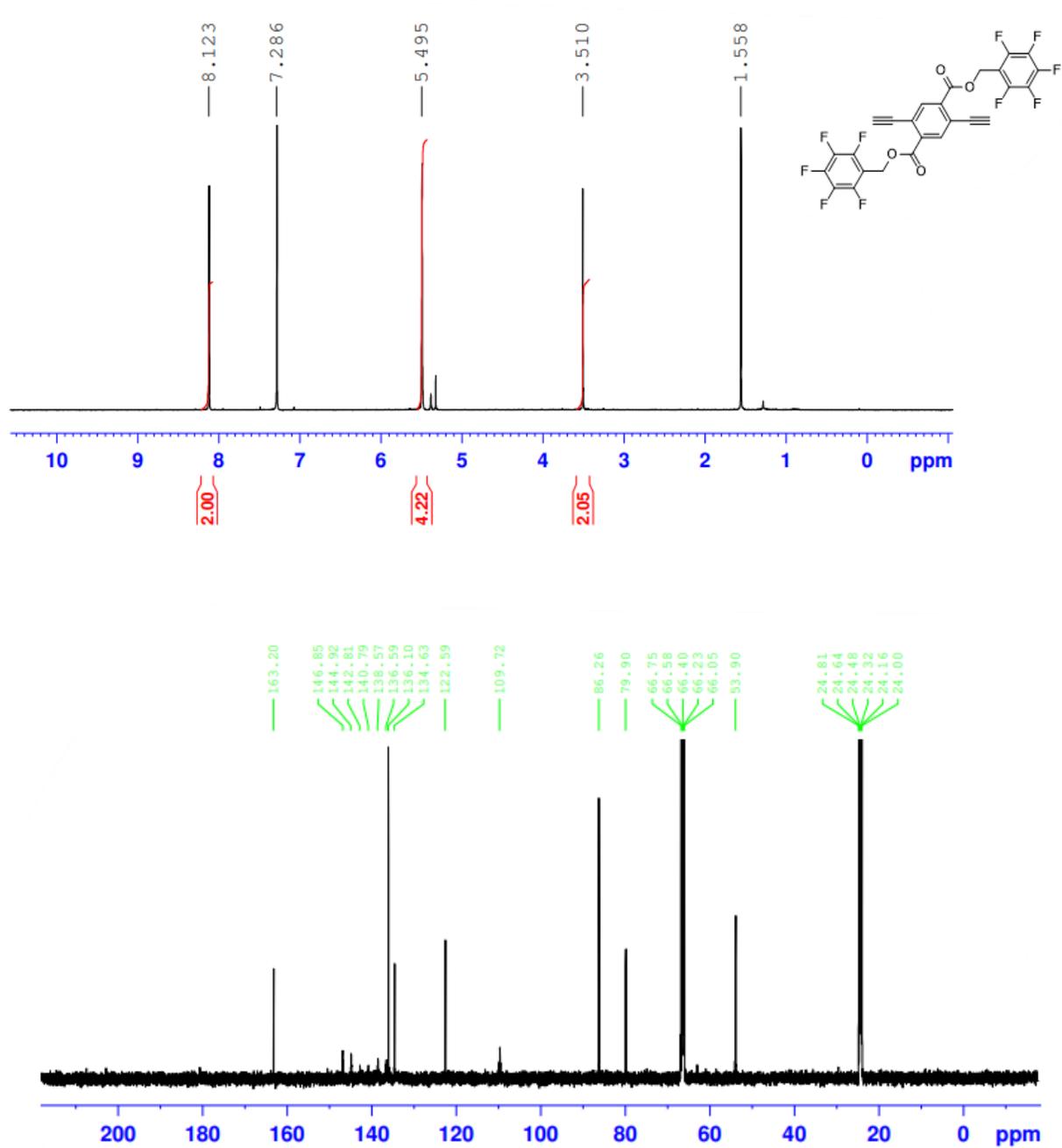
Figure S6: ^{1}H and ^{13}C NMR Spectra of **2H**
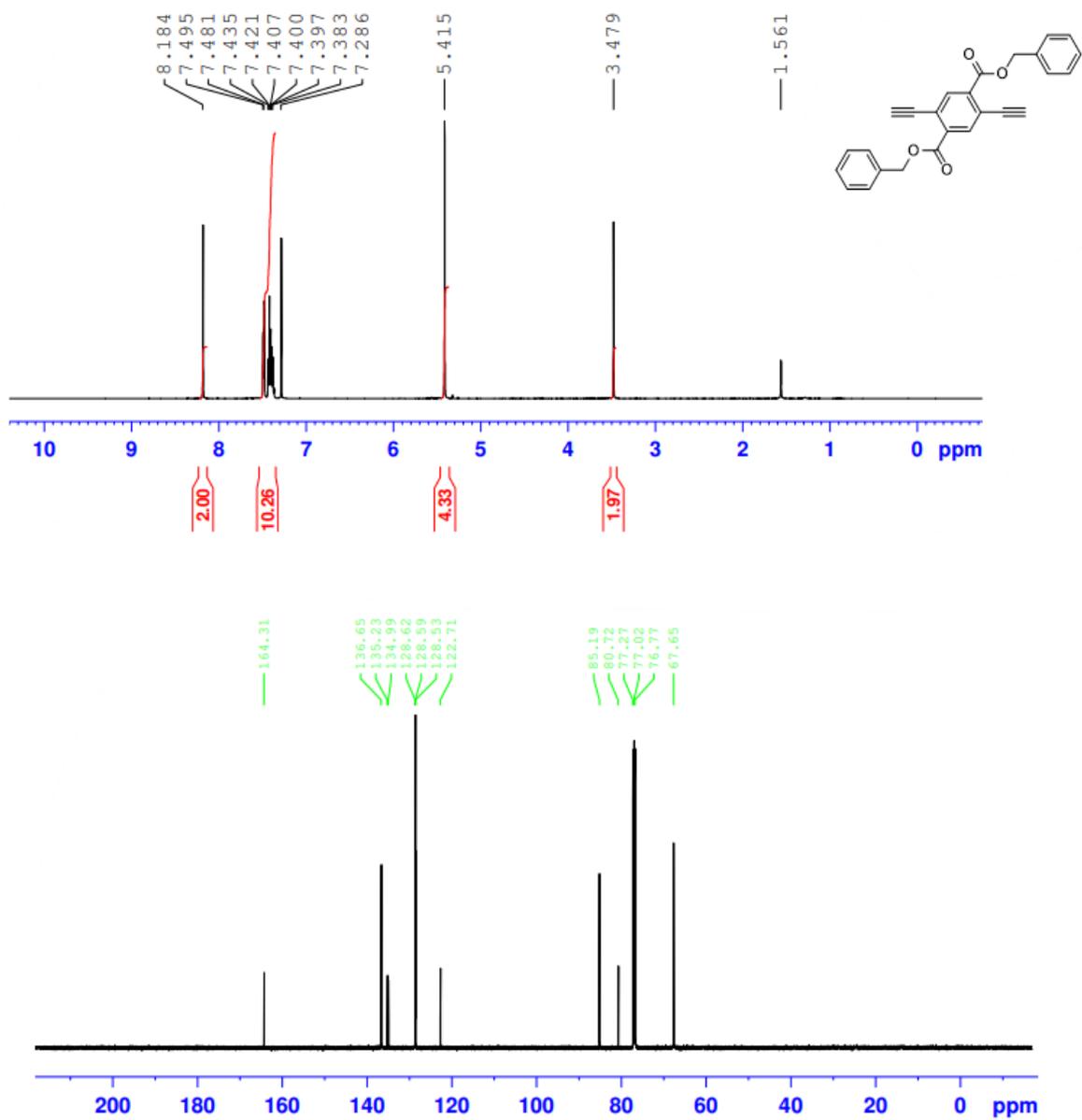
Figure S7: ^{1}H and ^{13}C NMR Spectra of **ER-1**
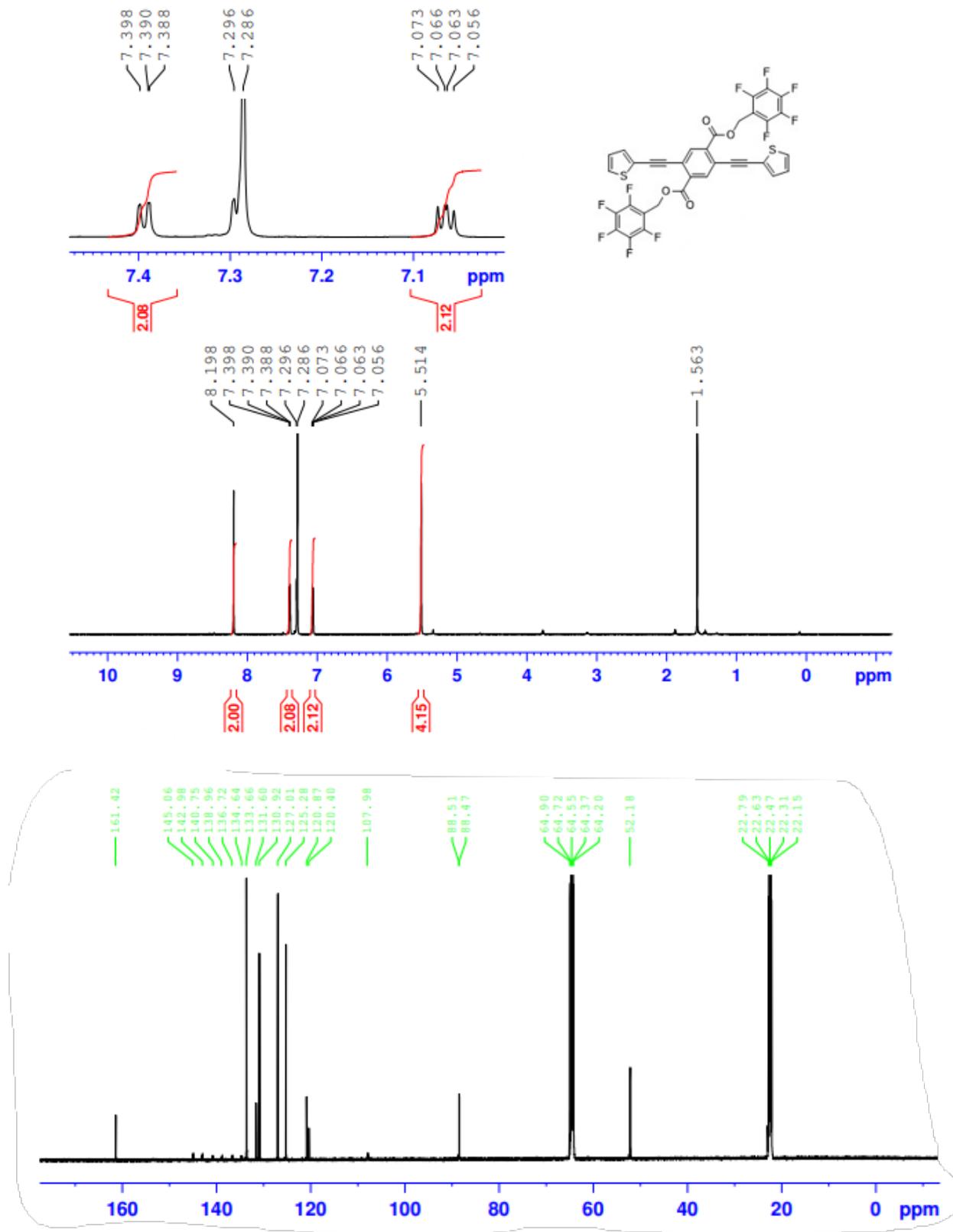
Figure S8: ^{1}H and ^{13}C NMR Spectra of **ER-1H**
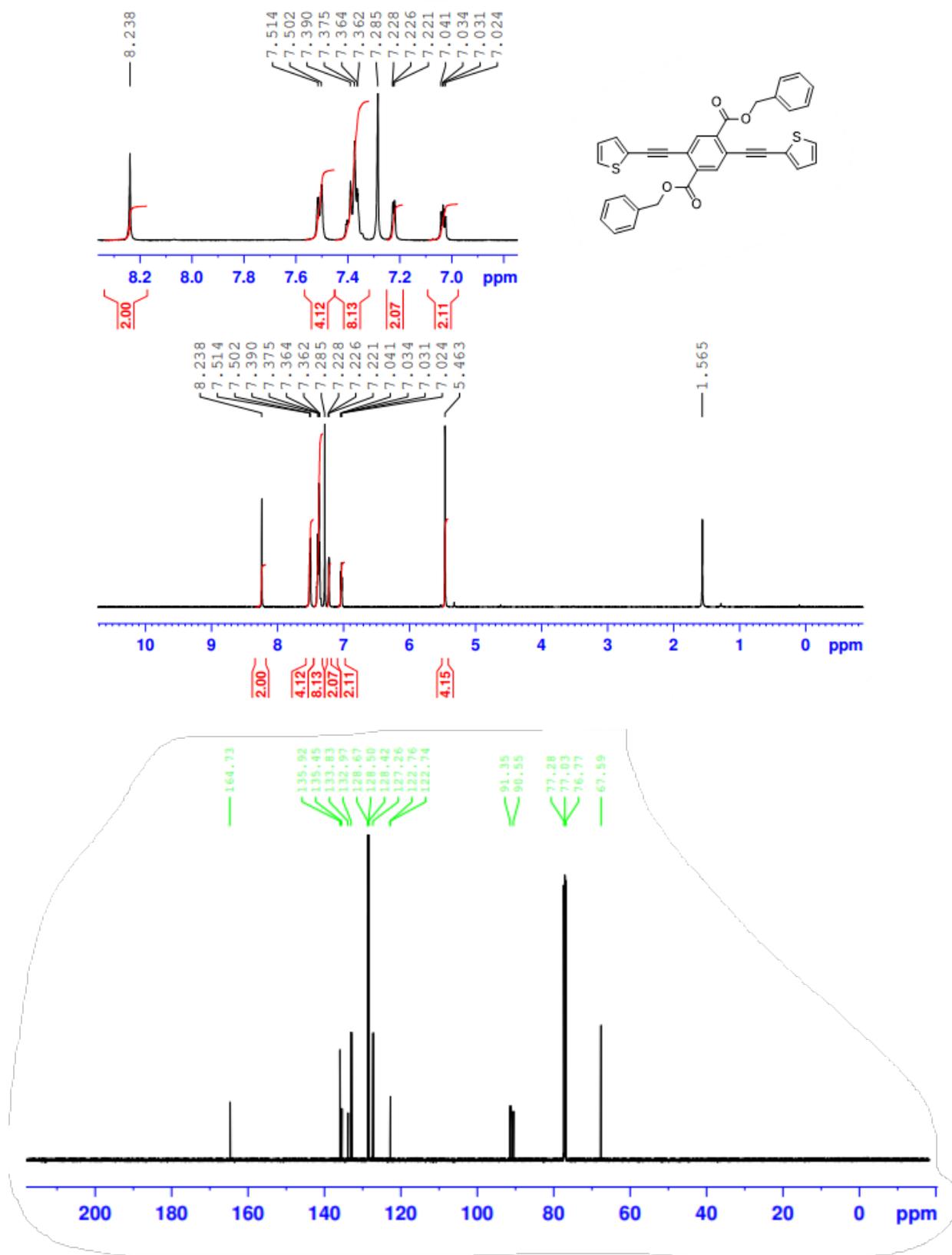
Figure S9: ^{1}H and ^{13}C NMR Spectra of **ER-2**
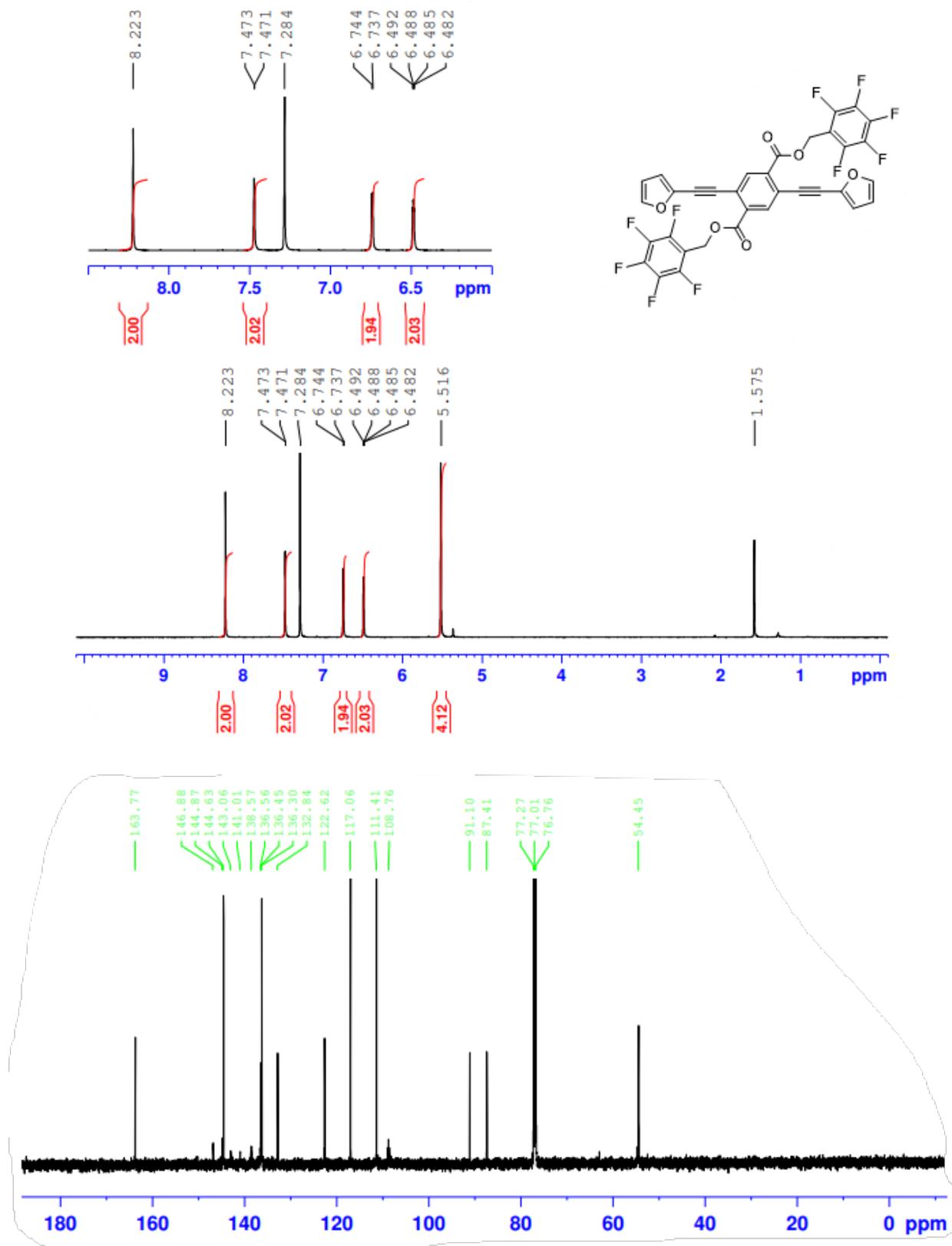
Figure S10: ^{1}H and ^{13}C NMR Spectra of **ER-2H**
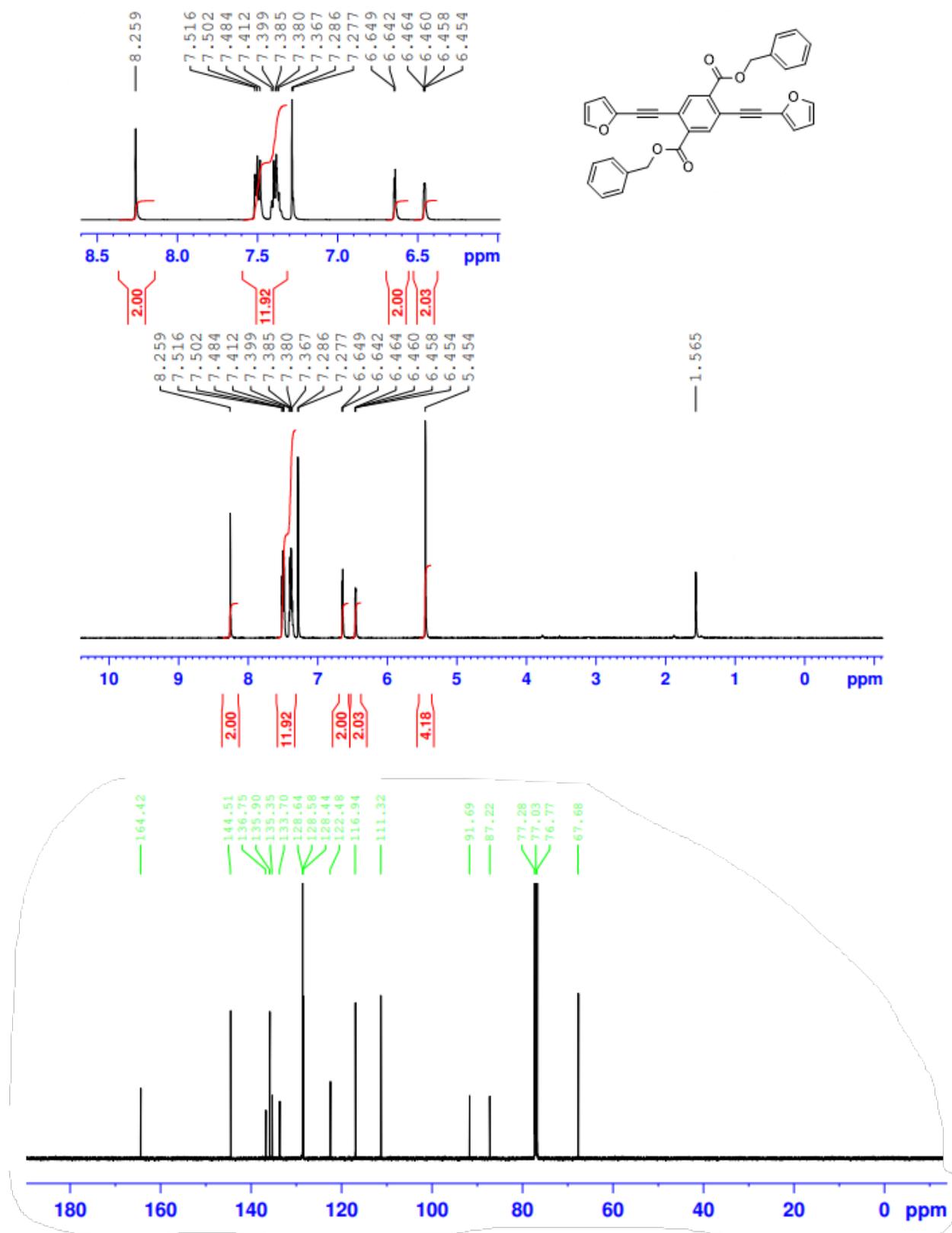
Figure S12: ^{1}H and ^{13}C NMR Spectra of **ER-3H**
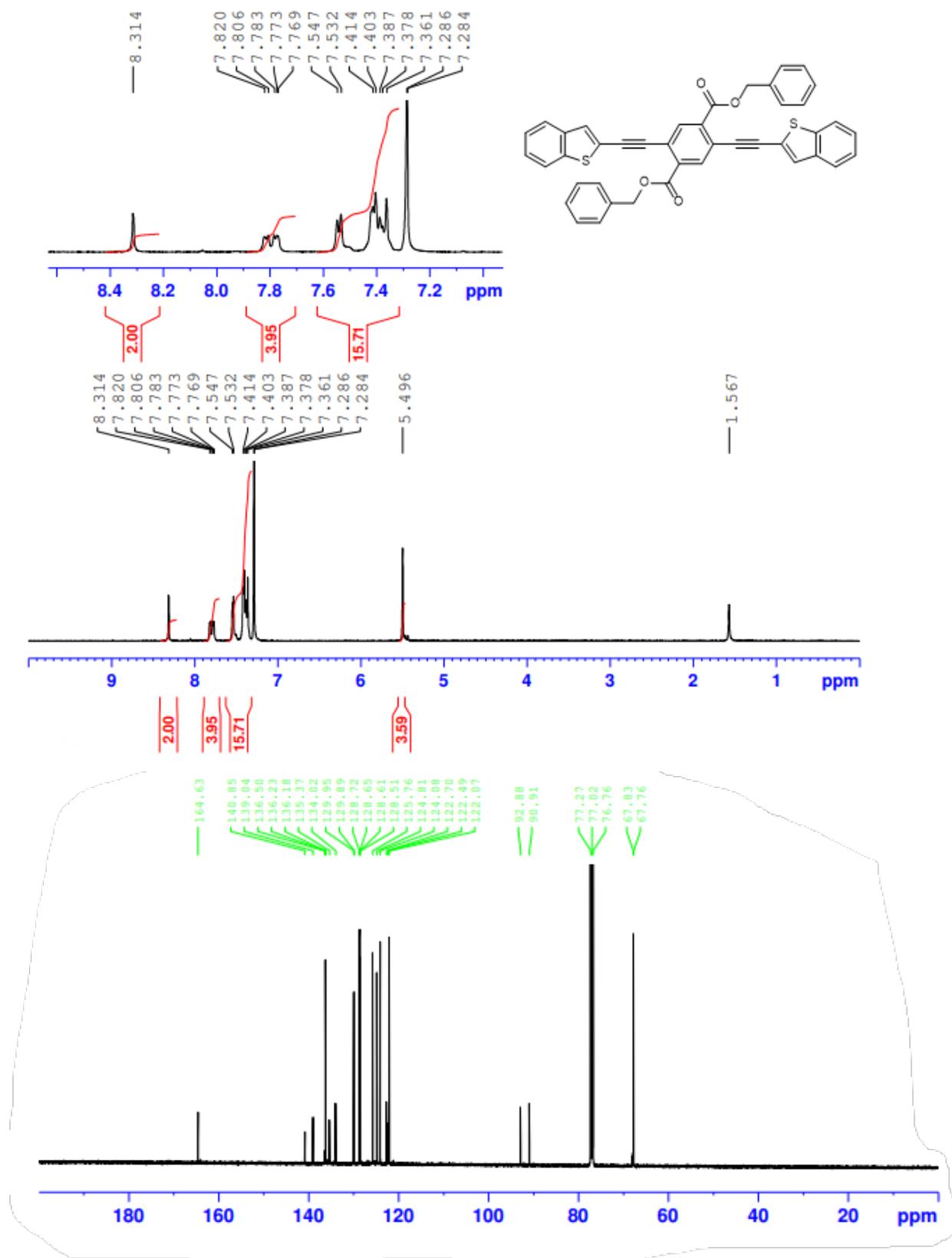
Figure S13: ^{1}H and ^{13}C NMR Spectra of **ED-1**
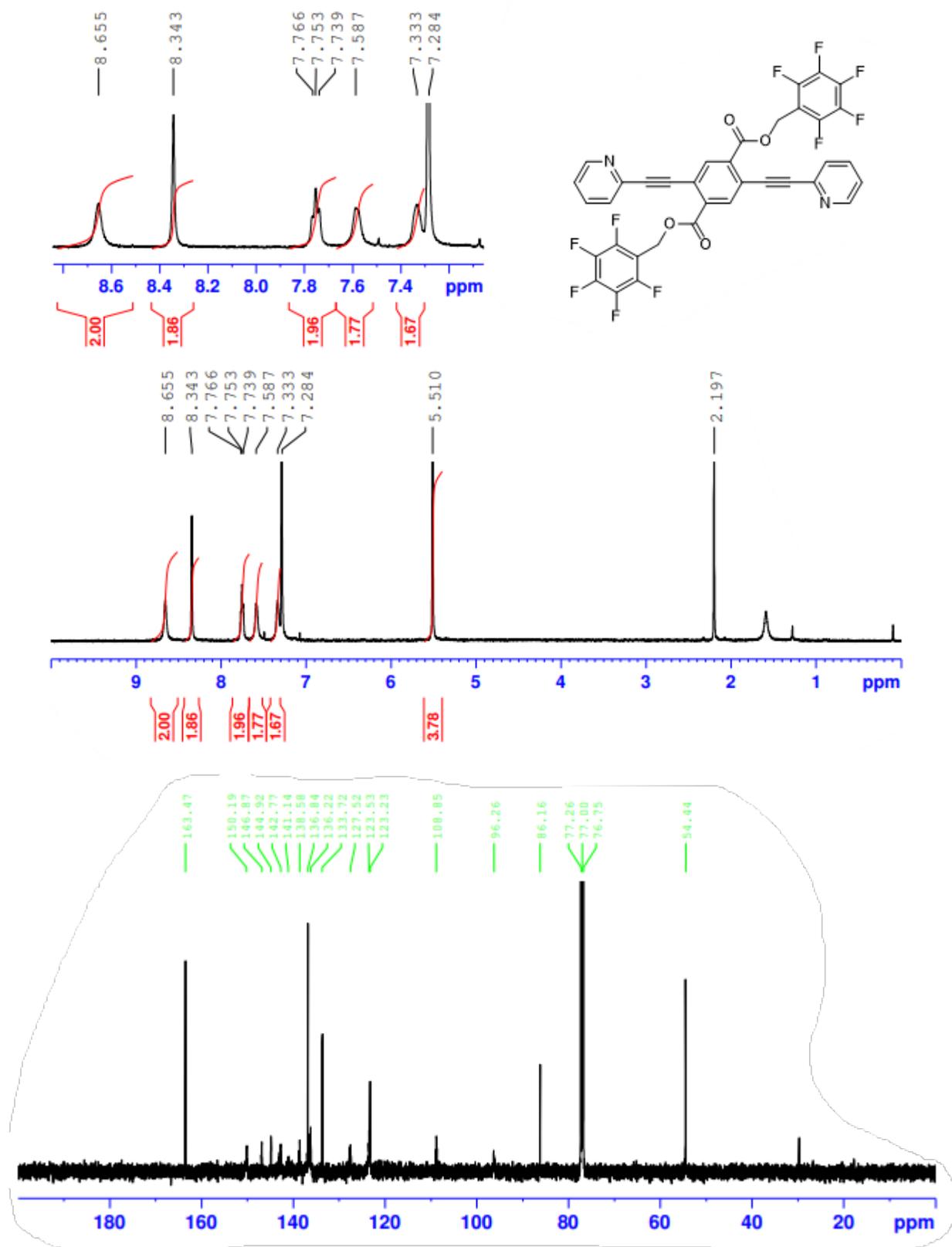
Figure S14: ^{1}H and ^{13}C NMR Spectra of **ED-1H**
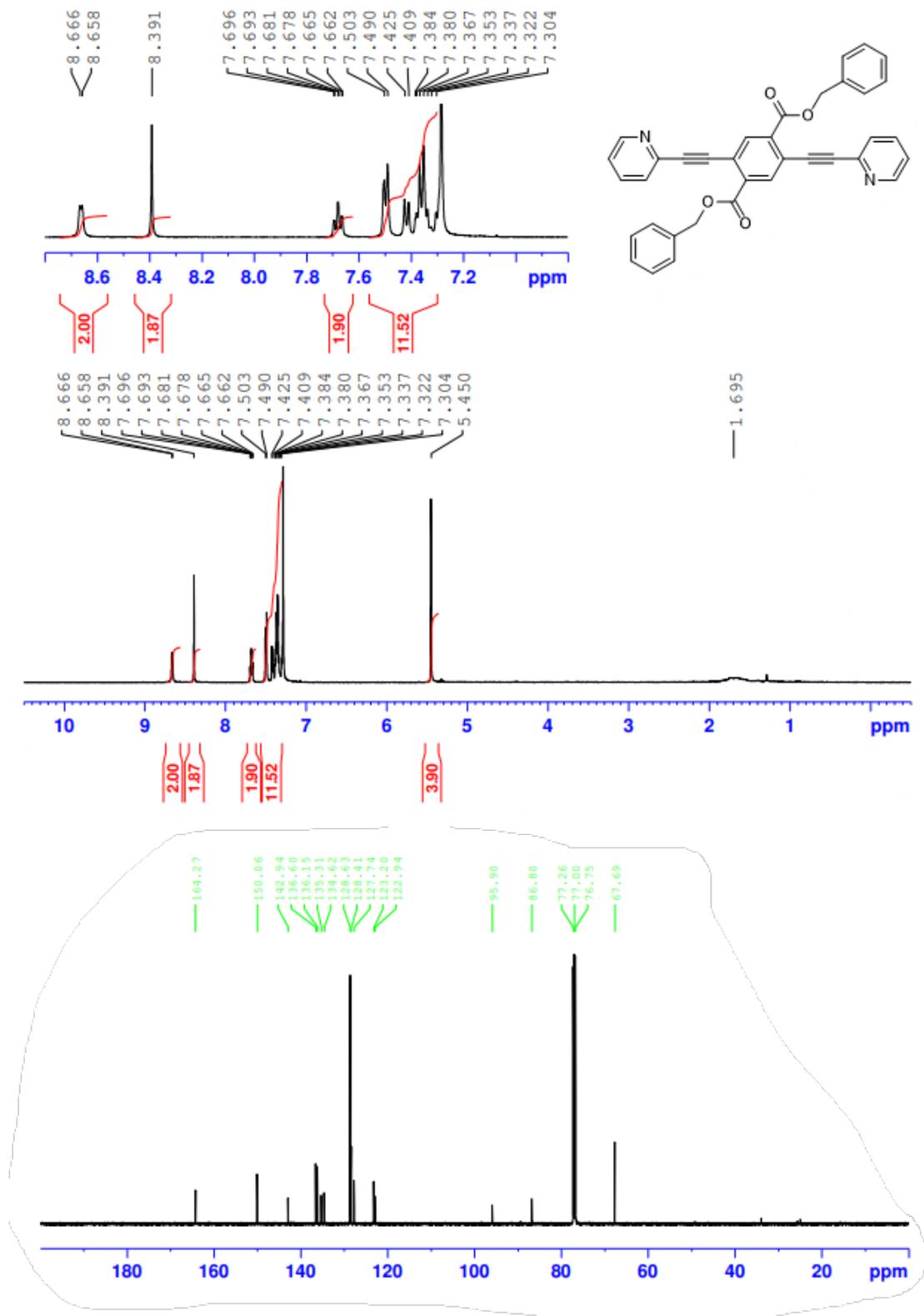
Figure S15: ^{1}H and ^{13}C NMR Spectra of **ED-2**
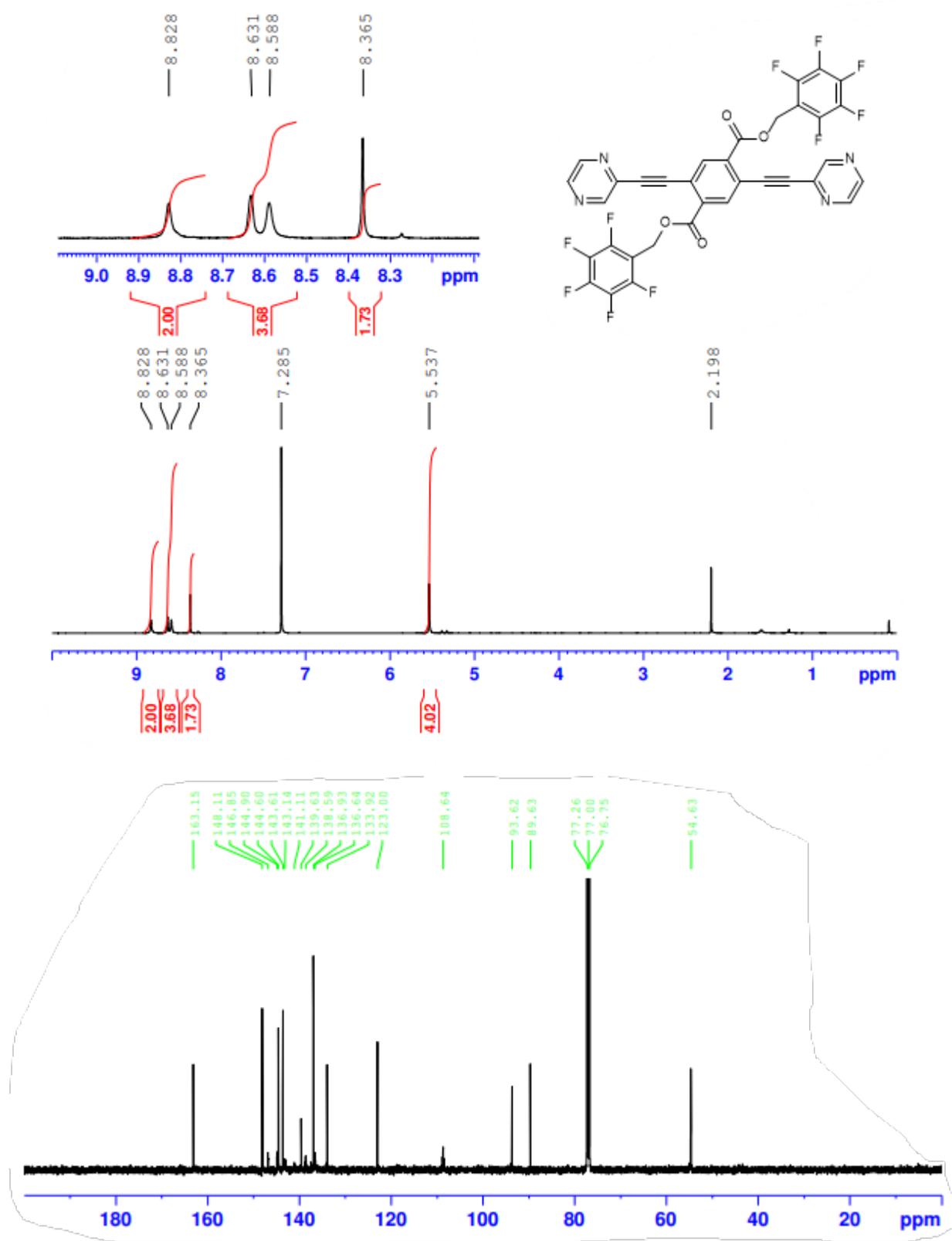
Figure S16: ^{1}H and ^{13}C NMR Spectra of **ED-2H**
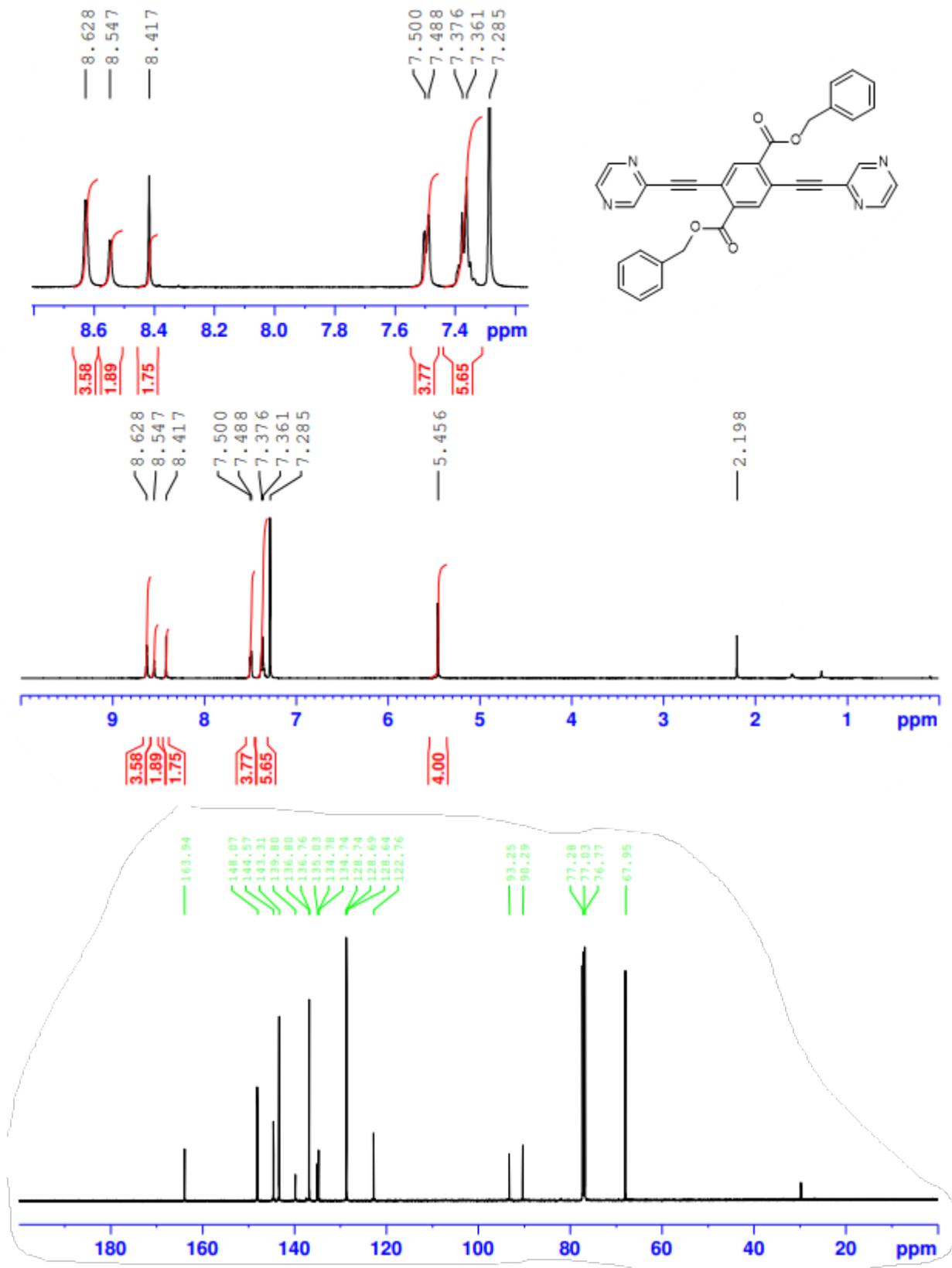
Figure S17: ^{1}H and ^{13}C NMR Spectra of **ED-3**
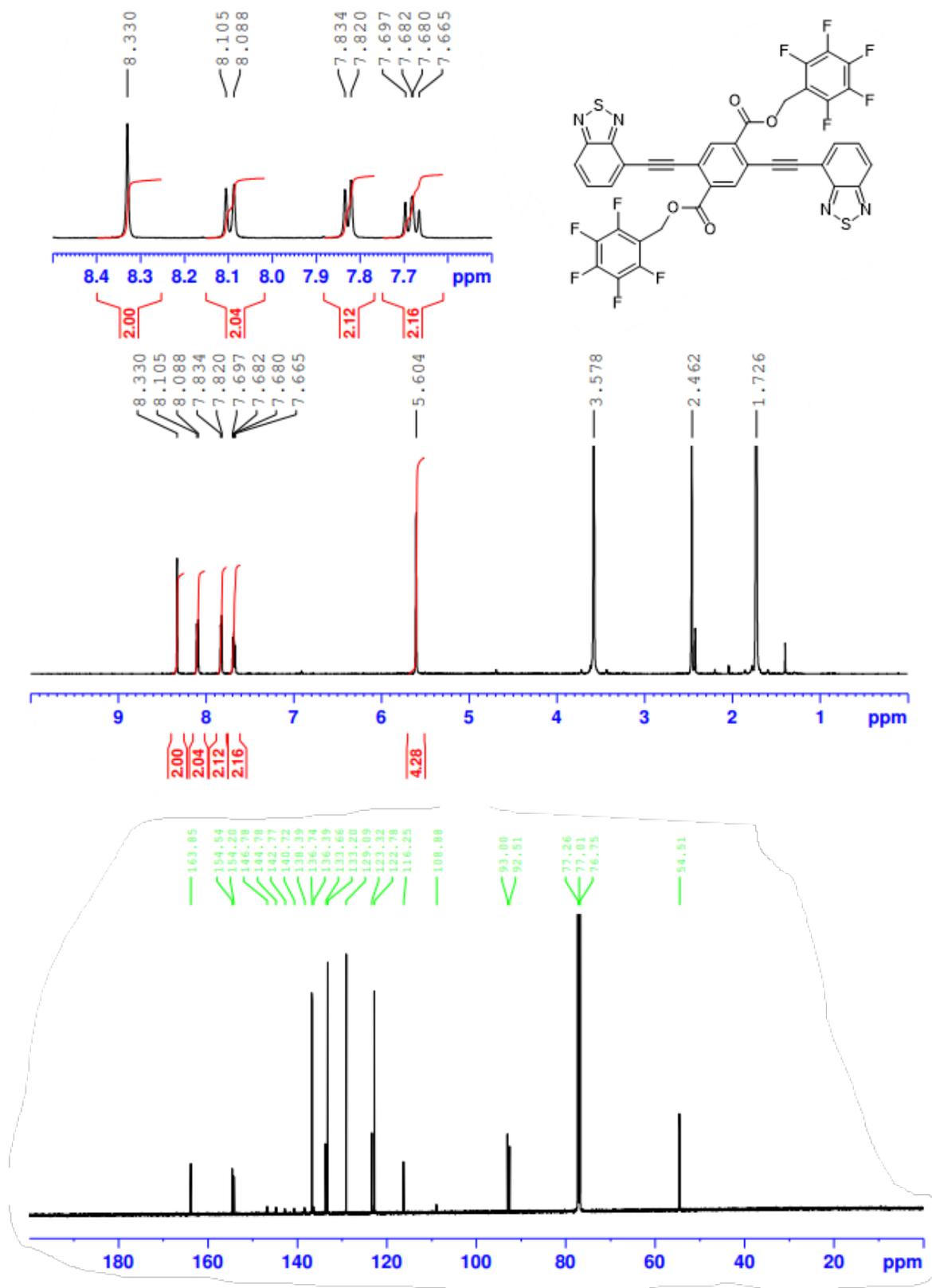
Figure S18: ^{1}H and ^{13}C NMR Spectra of **ED-3H**
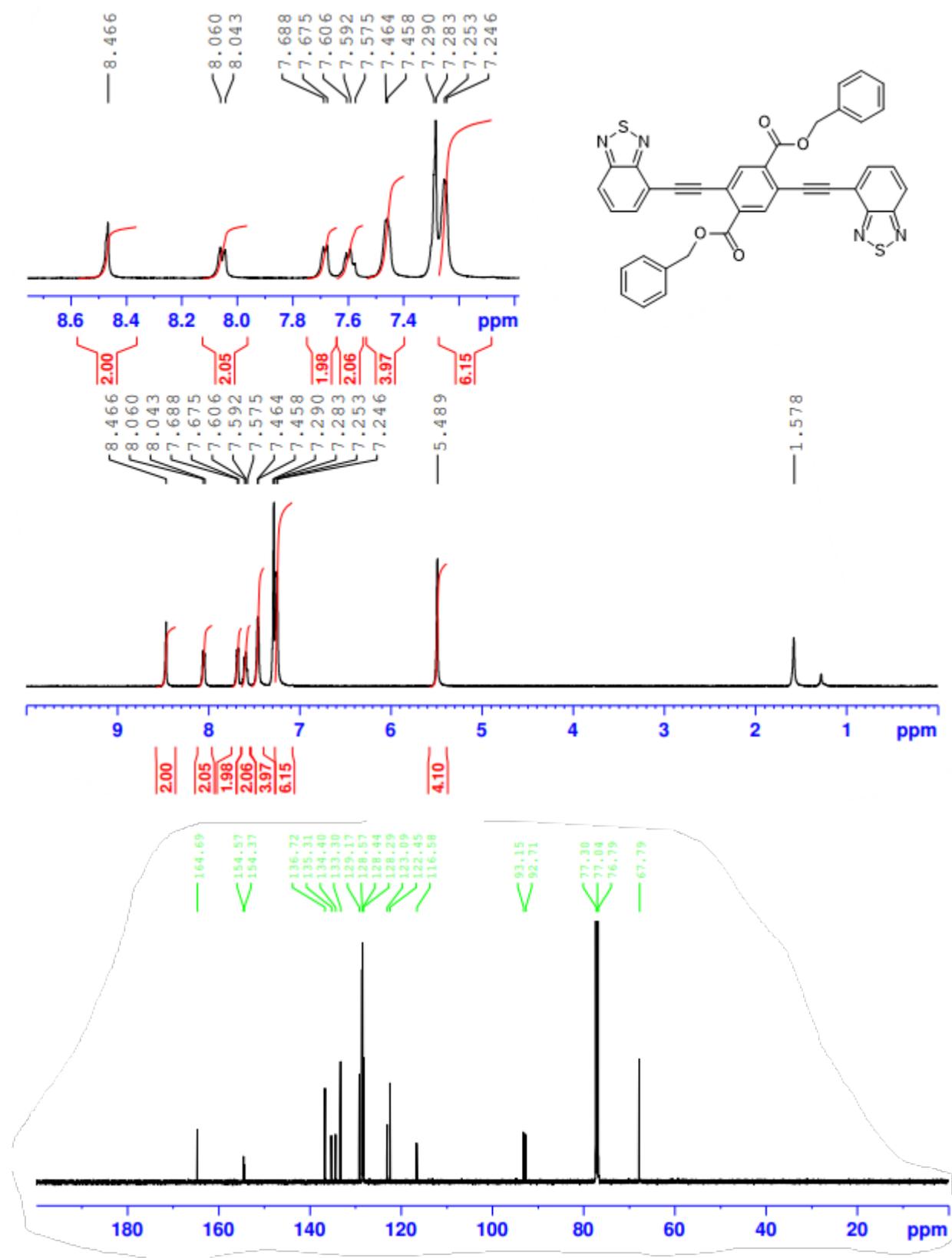
1. **ED-1H**
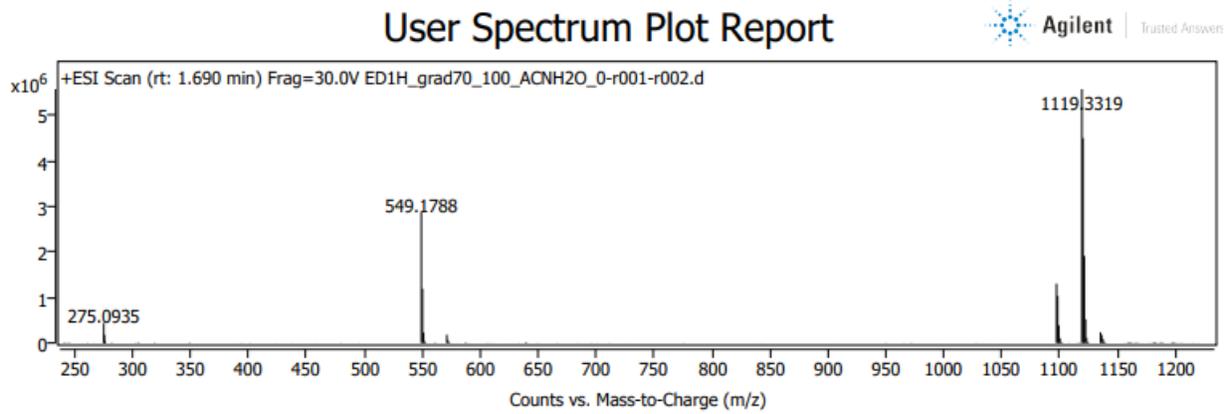
Figure S19: Mass spectrum of **ED-1H.** Species observed: M+1 (549.1788) and M Dimer + Na (1119.3319)

2. **ED-2**
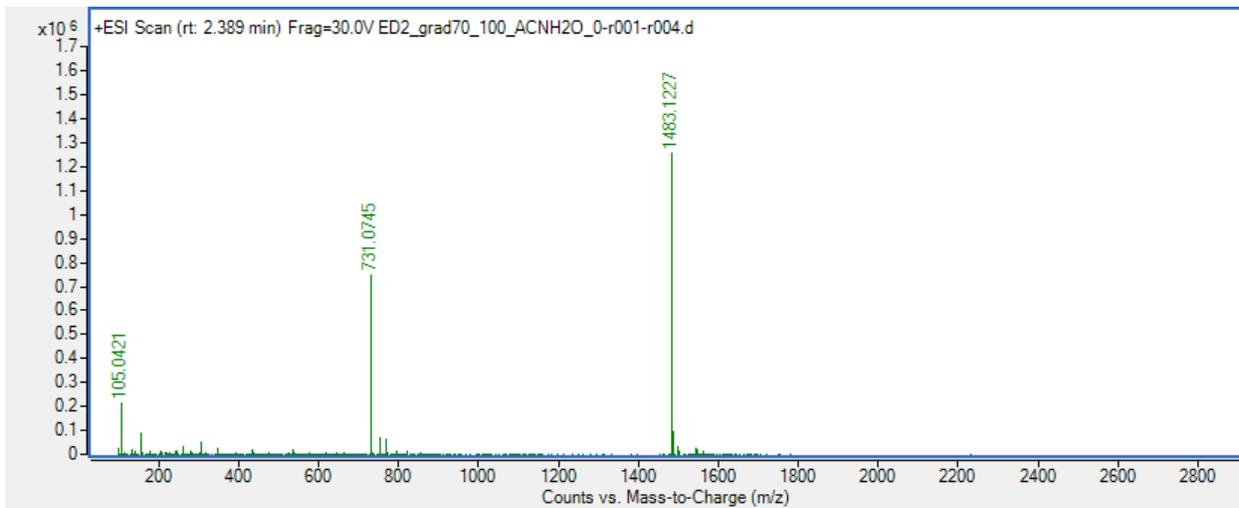
Figure S20: Mass spectrum of **ED-2.** Species observed: M+1 (731.0745) and M Dimer + Na (1438.1227)

3. ER-2
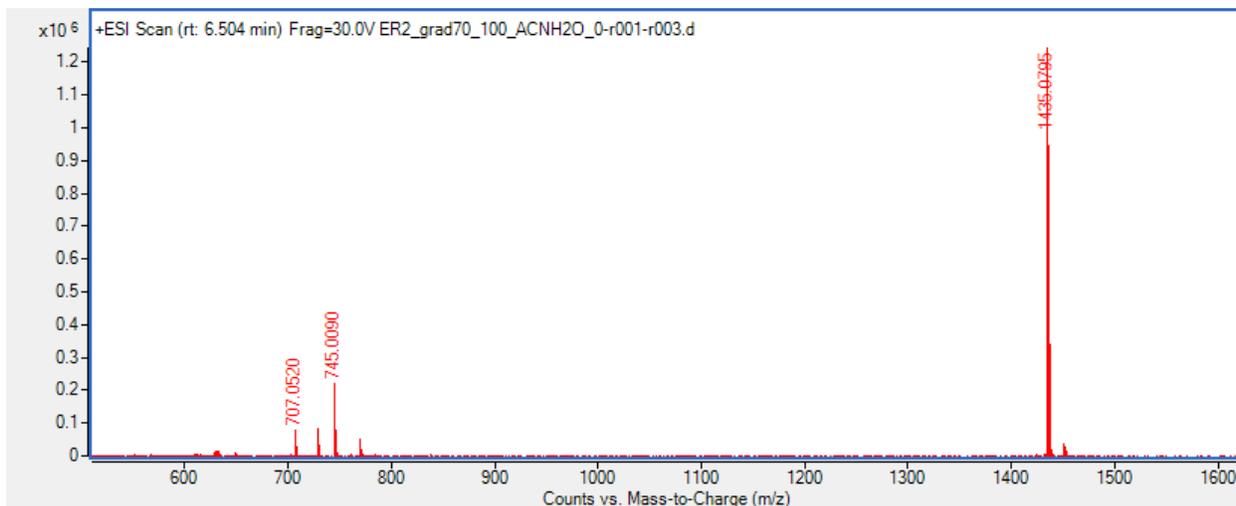
Figure S21: Mass spectrum of **ER-2.** Species observed: M+1 (707.0520), M + K (745.0090), M Dimer + Na (1435.0795)

4. ER-3H
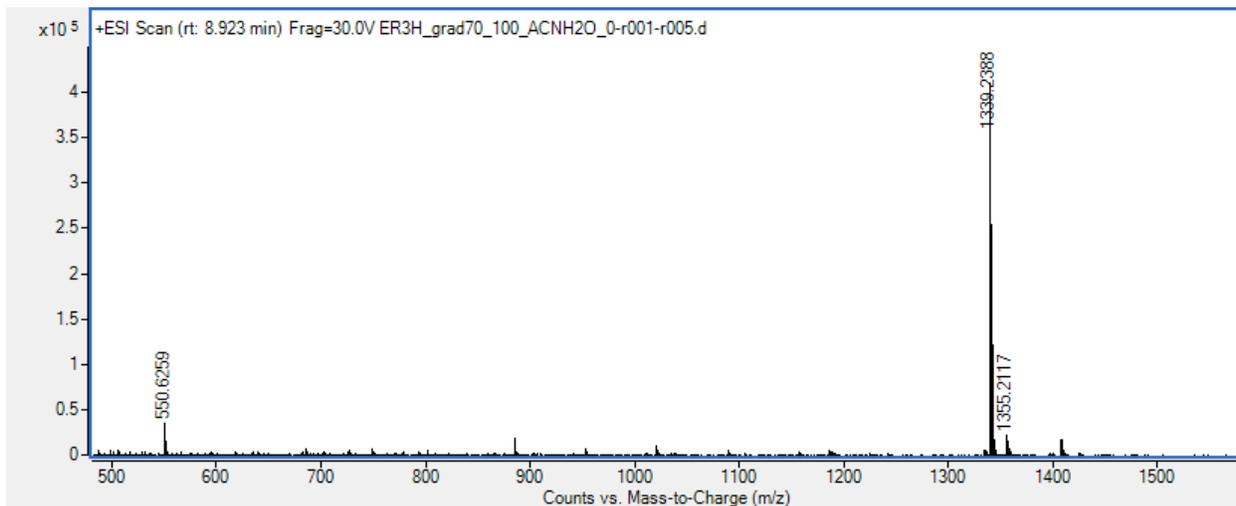
Figure S22: Mass spectrum of **ER-3H.** Species observed: M Dimer + Na (1339.2388) and M Dimer + K (1355.2117)

Figure S23: Optical Spectroscopy of **ER-1**. Absorbance (top left), excitation (top right), and emission spectra (bottom left) in dilute chloroform solution (solid blue line) and drop cast thin film (black dashed line). Solvatochromism spectra (bottom right) are given as well.
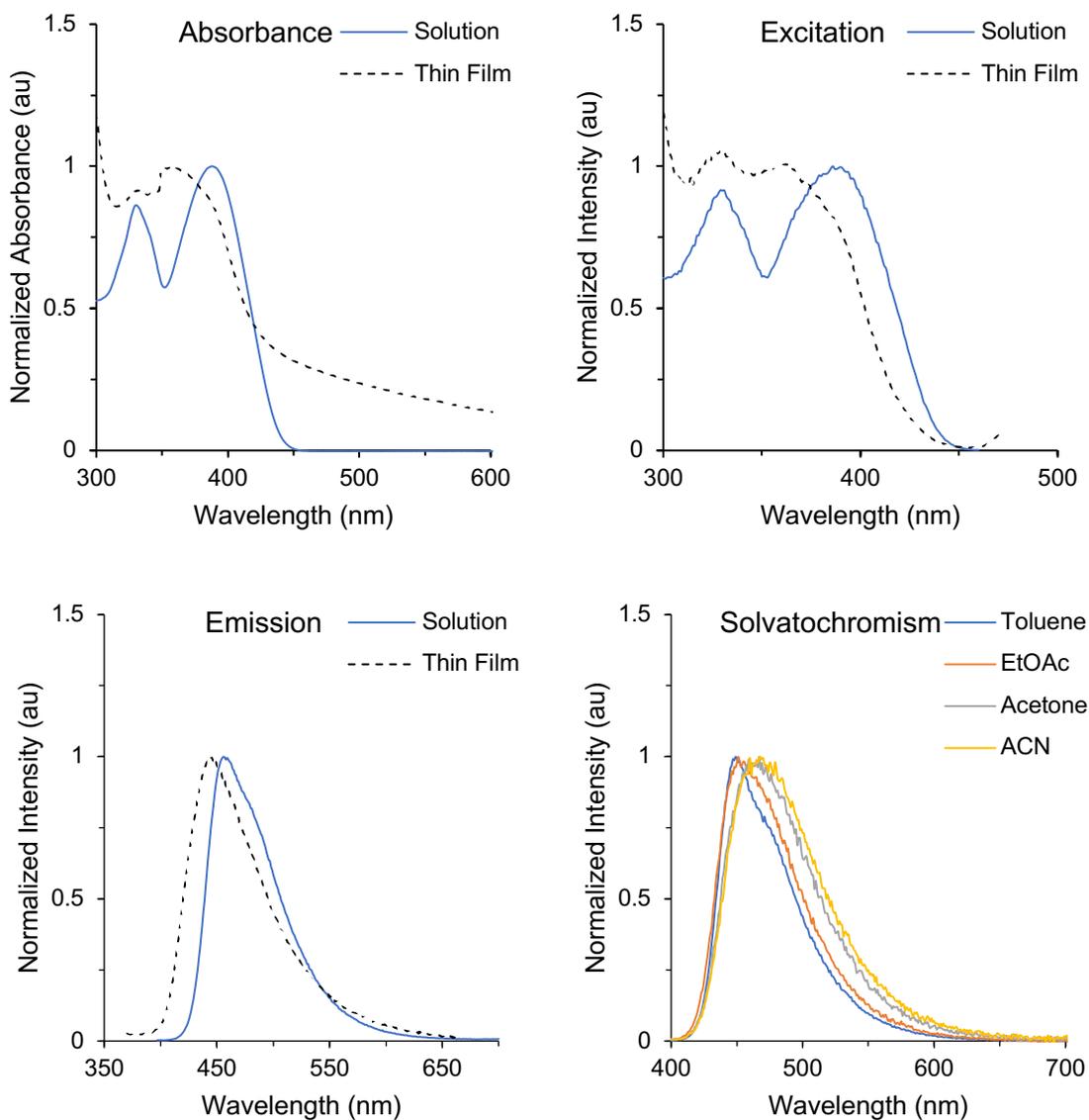
Figure S24: Optical Spectroscopy of **ER-1H**. Absorbance (top left), excitation (top right), and emission spectra (bottom left) in dilute chloroform solution (solid blue line) and drop cast thin film (black dashed line). Solvatochromism spectra (bottom right) are given as well.
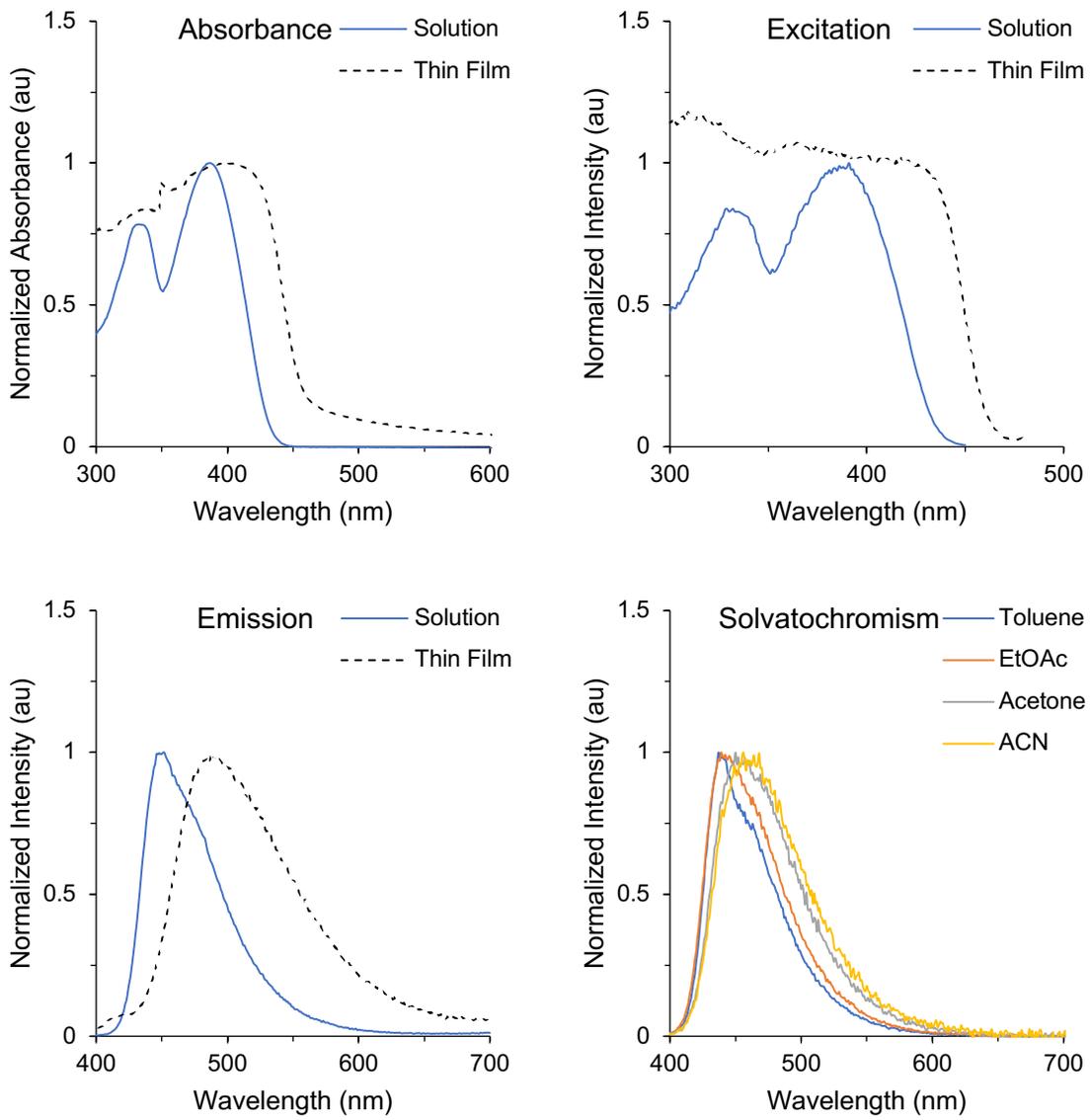
Figure S25: Optical Spectroscopy of **ER-2**. Absorbance (top left), excitation (top right), and emission spectra (bottom left) in dilute chloroform solution (solid blue line) and drop cast thin film (black dashed line). Solvatochromism spectra (bottom right) are given as well.
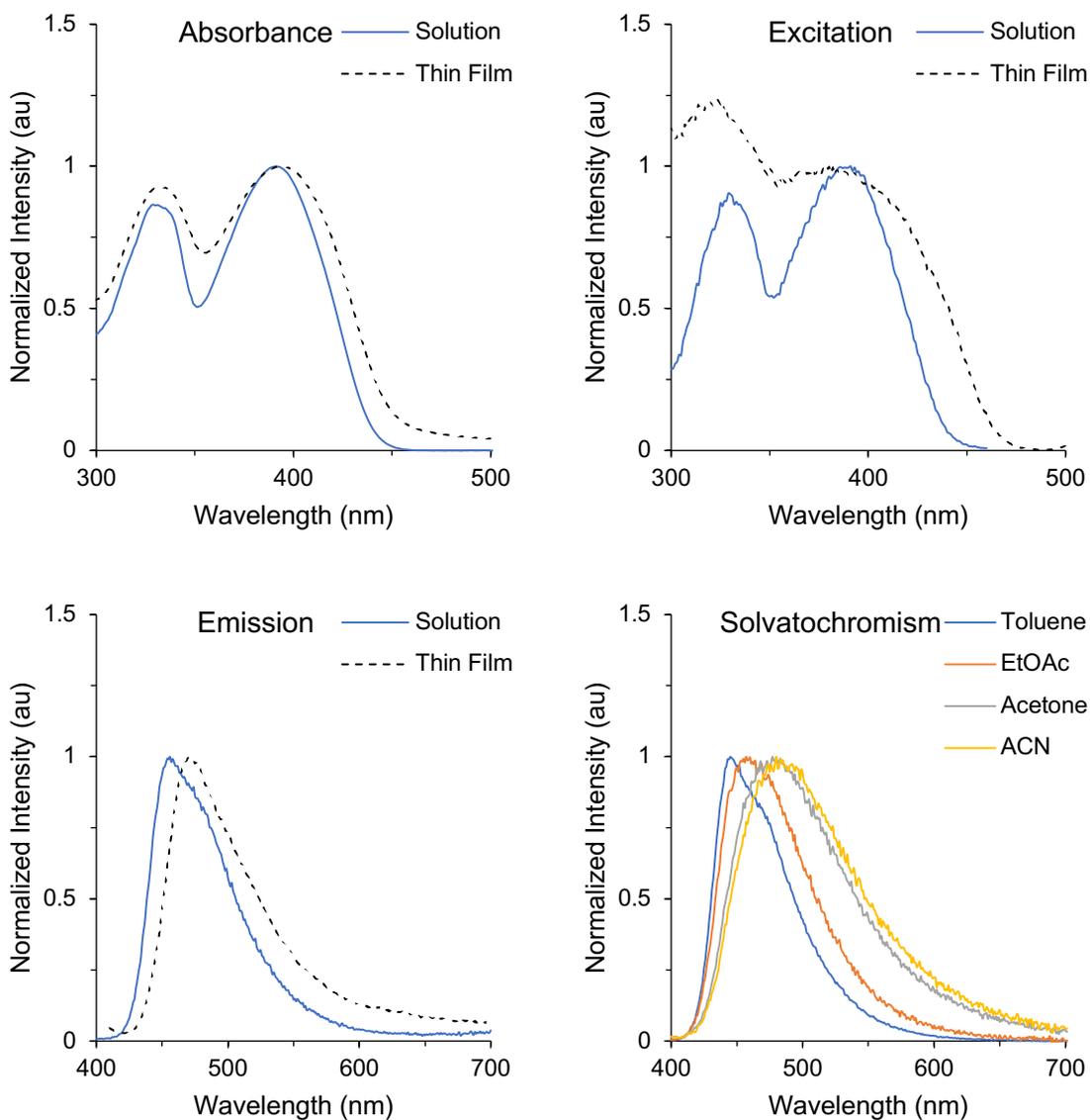
Figure S26: Optical Spectroscopy of **ER-2H**. Absorbance (top left), excitation (top right), and emission spectra (bottom left) in dilute chloroform solution (solid blue line) and drop cast thin film (black dashed line). Solvatochromism spectra (bottom right) are given as well.
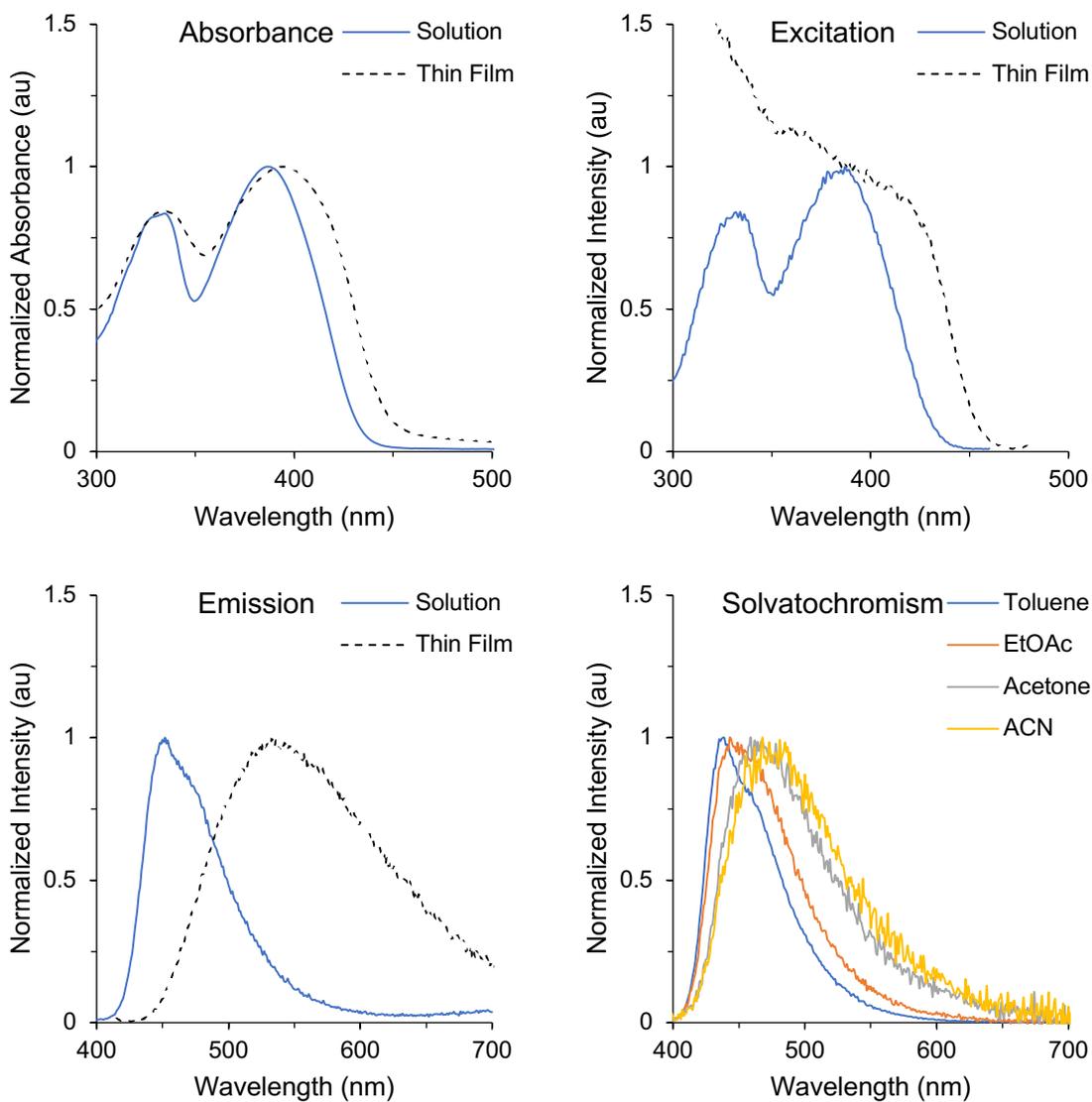
Figure S27: Optical Spectroscopy of **ER-3**. Absorbance (top left), excitation (top right), and emission spectra (bottom left) in dilute chloroform solution (solid blue line) and drop cast thin film (black dashed line). Solvatochromism spectra (bottom right) are given as well.
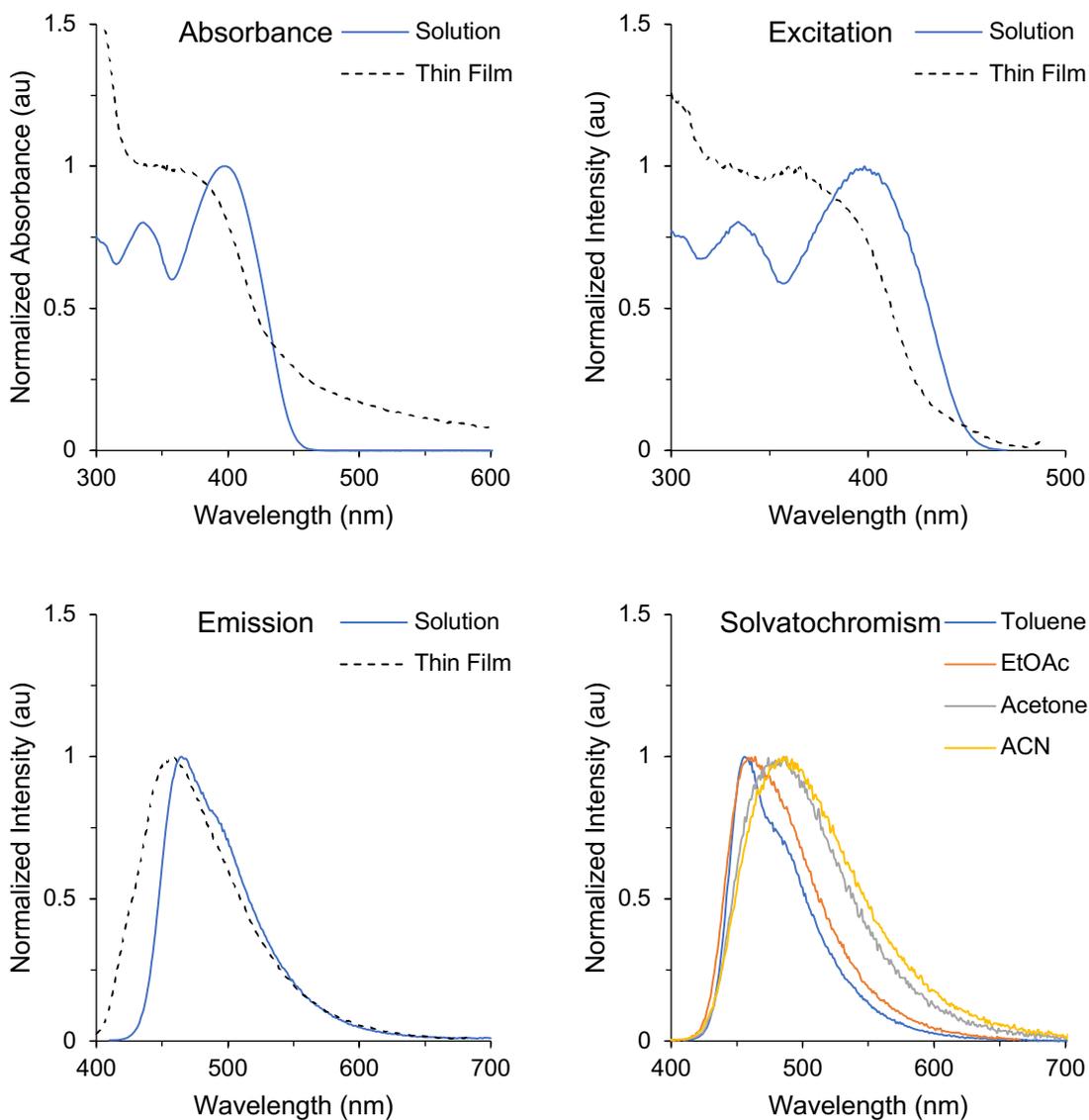
Figure S28: Optical Spectroscopy of **ER-3H**. Absorbance (top left), excitation (top right), and emission spectra (bottom left) in dilute chloroform solution (solid blue line) and drop cast thin film (black dashed line). Solvatochromism spectra (bottom right) are given as well.
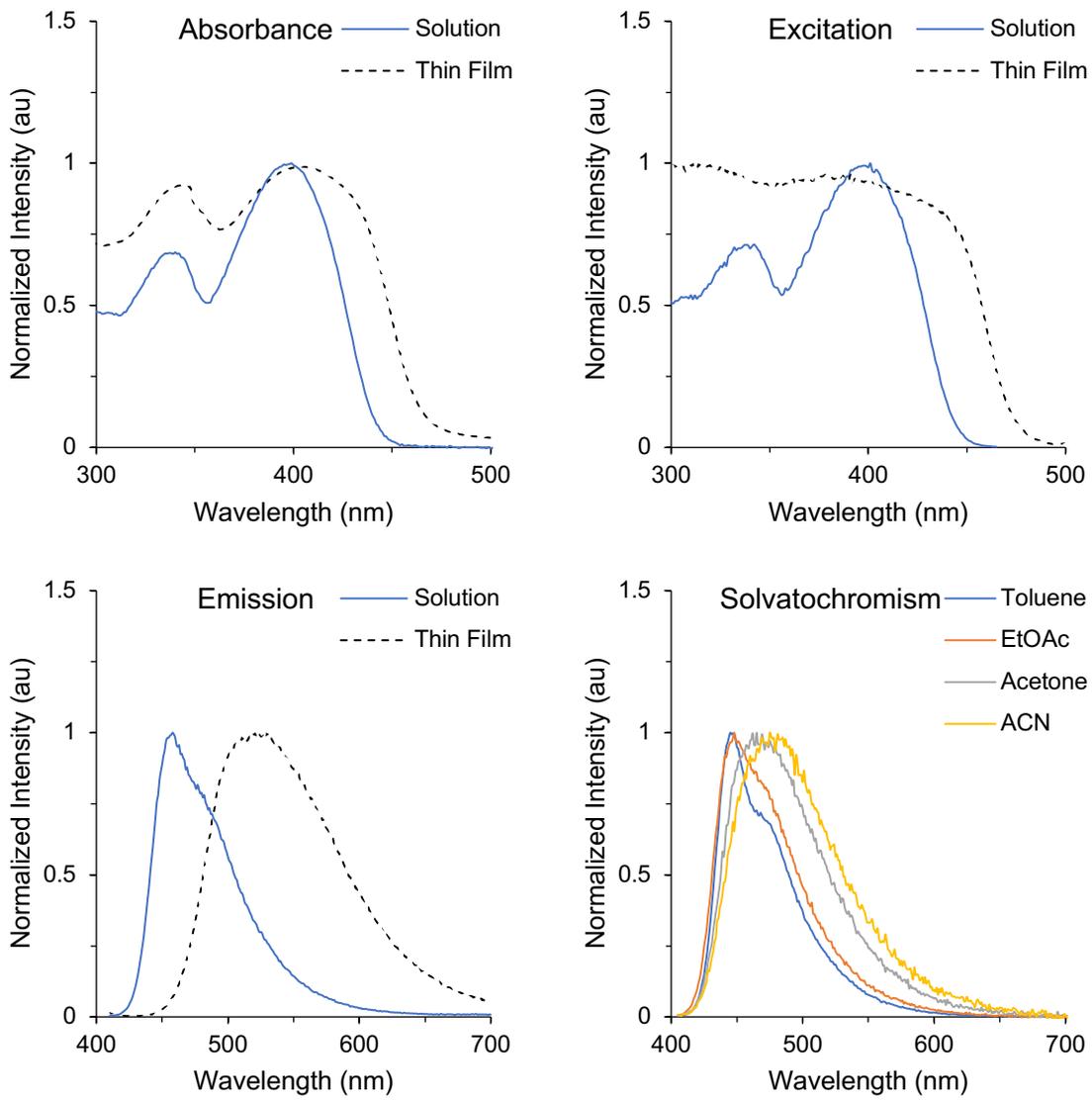
Figure S29: Optical Spectroscopy of **ED-1**. Absorbance (top left), excitation (top right), and emission spectra (bottom left) in dilute chloroform solution (solid blue line) and drop cast thin film (black dashed line). Solvatochromism spectra (bottom right) are given as well.
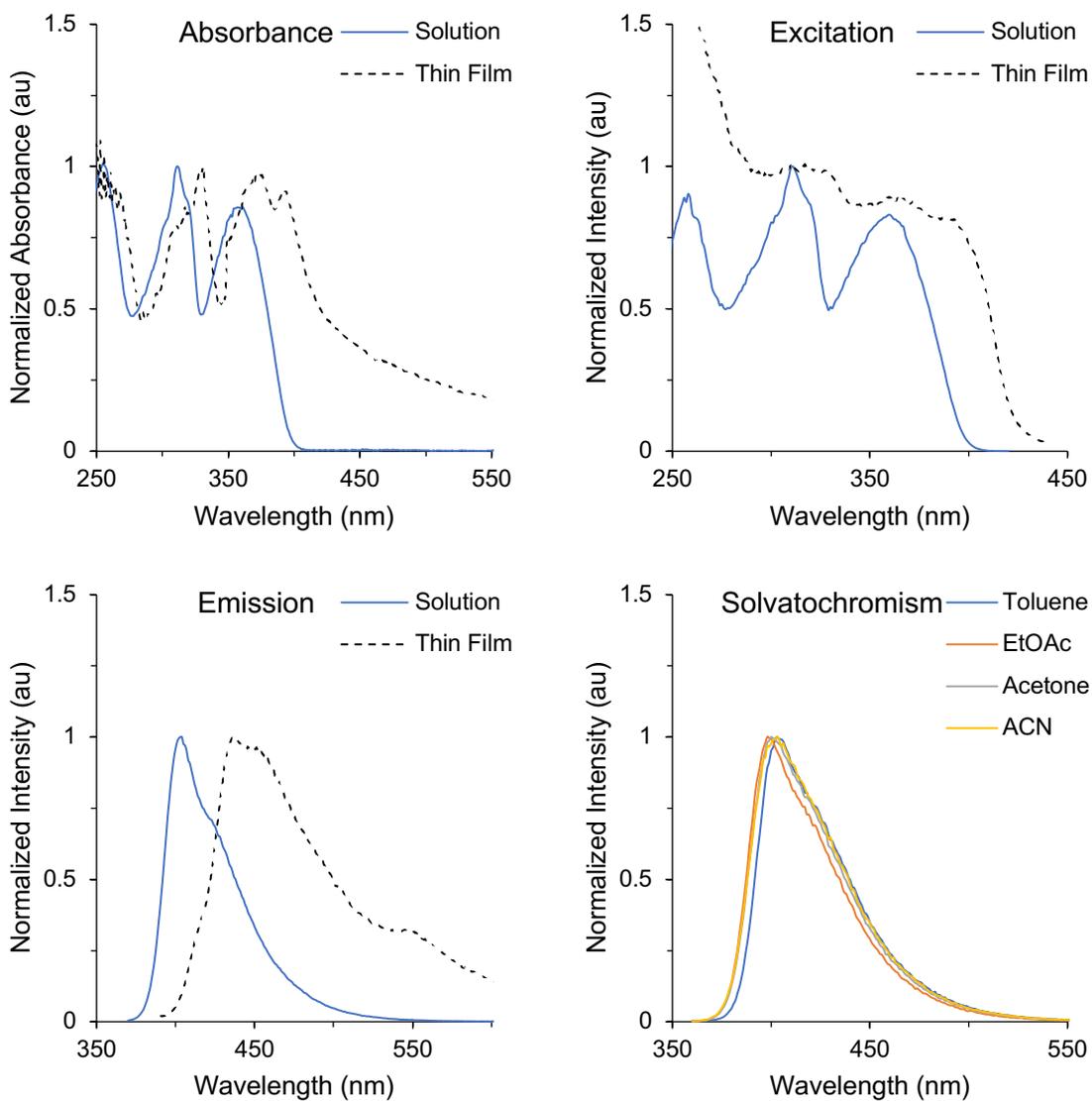
Figure S30: Optical Spectroscopy of **ED-1H**. Absorbance (top left), excitation (top right), and emission spectra (bottom left) in dilute chloroform solution (solid blue line) and drop cast thin film (black dashed line). Solvatochromism spectra (bottom right) are given as well.
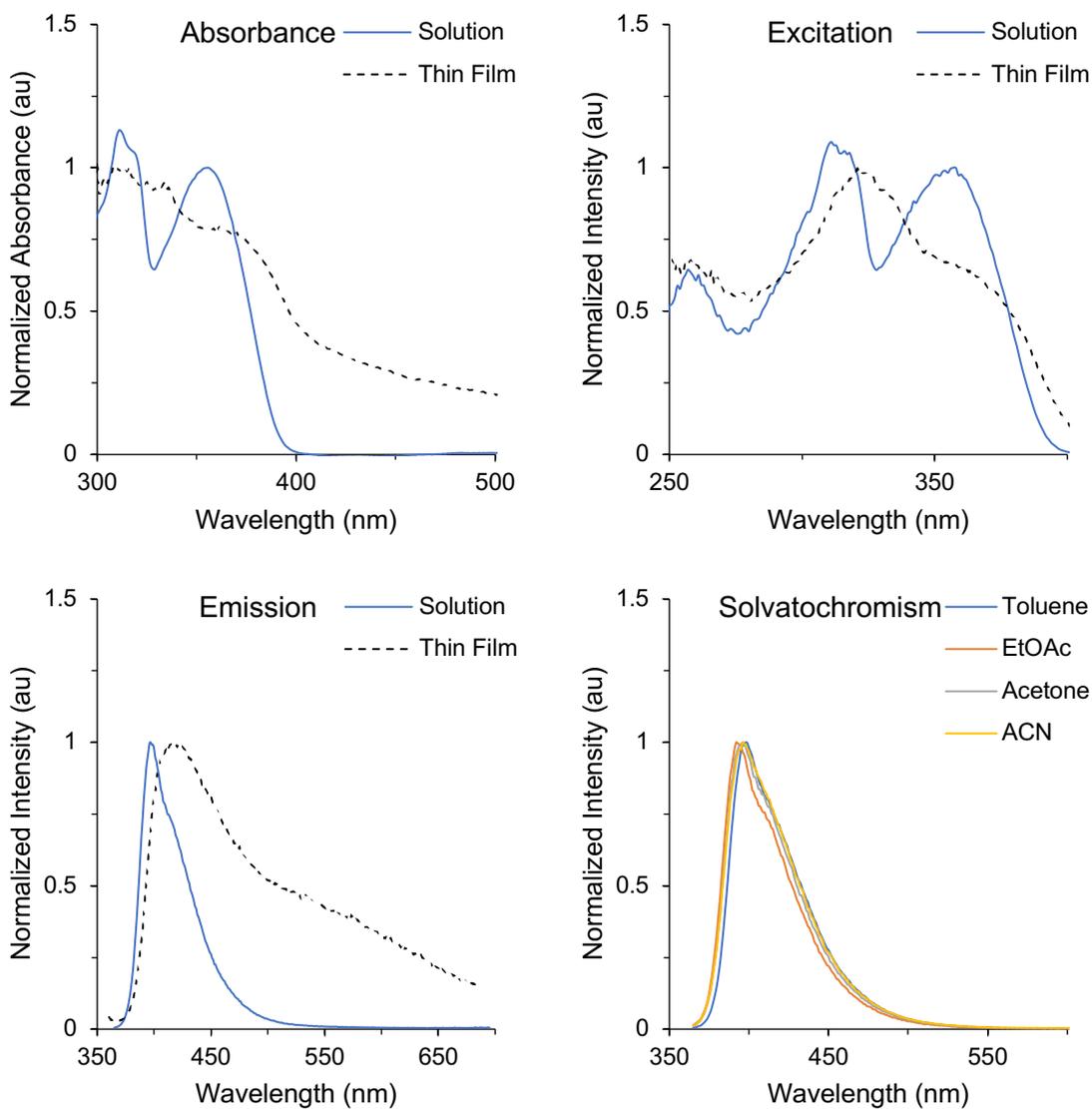
Figure S31: Optical Spectroscopy of **ED-2**. Absorbance (top left), excitation (top right), and emission spectra (bottom left) in dilute chloroform solution (solid blue line) and drop cast thin film (black dashed line). Solvatochromism spectra (bottom right) are given as well.
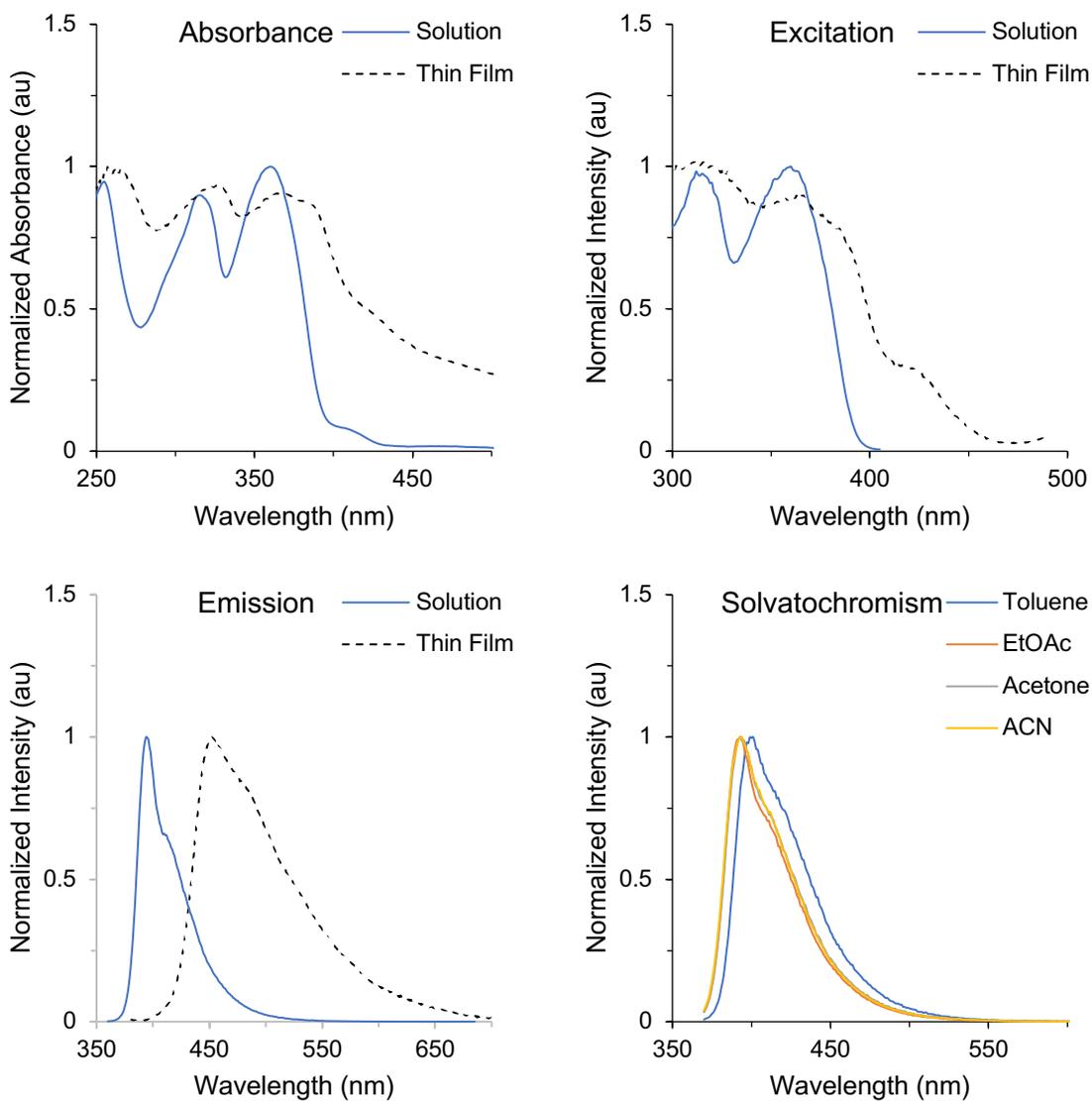
Figure S32: Optical Spectroscopy of **ED-2H**. Absorbance (top left), excitation (top right), and emission spectra (bottom left) in dilute chloroform solution (solid blue line) and drop cast thin film (black dashed line). Solvatochromism spectra (bottom right) are given as well.
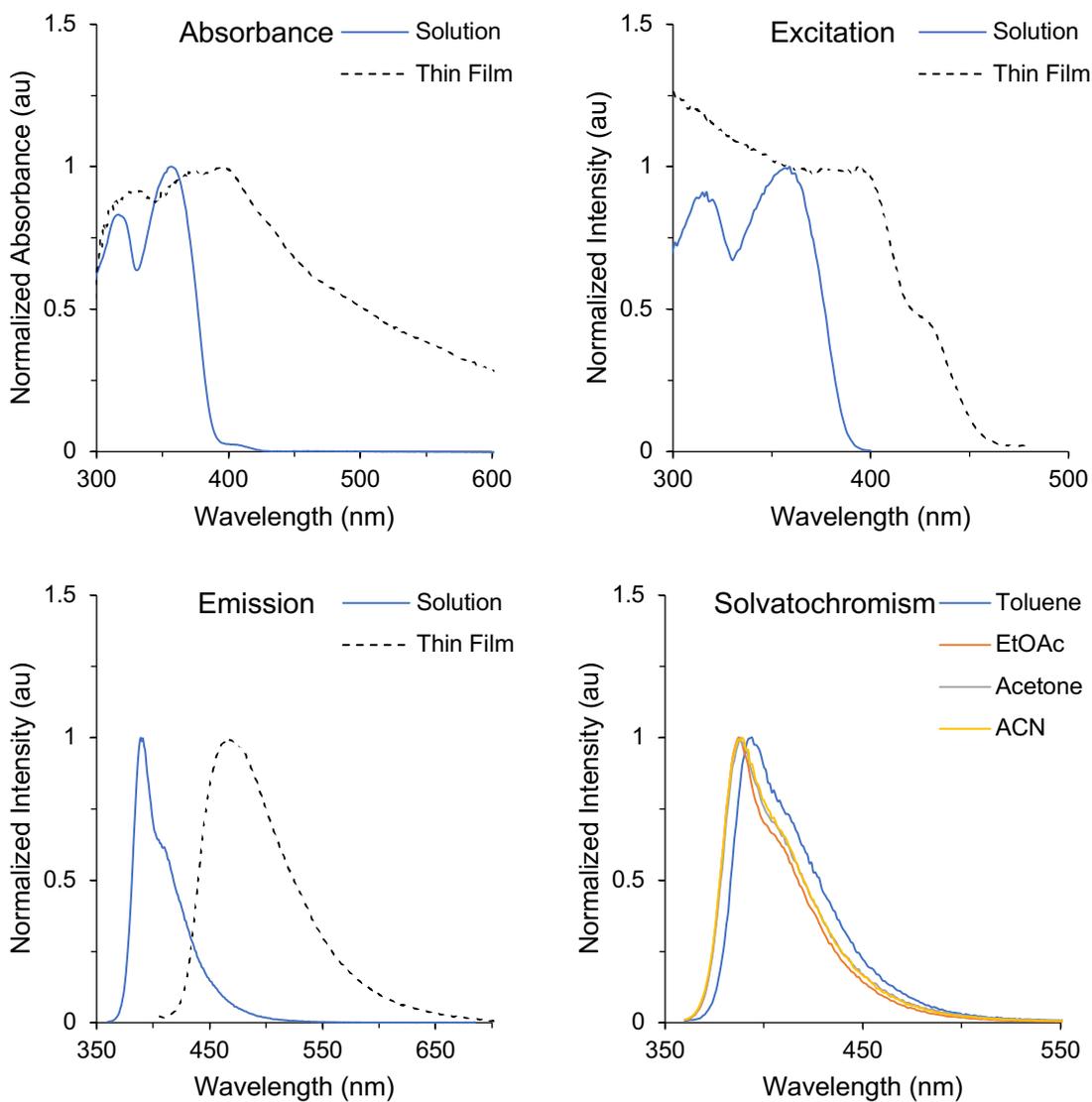
Figure S33: Optical Spectroscopy of **ED-3**. Absorbance (top left), excitation (top right), and emission spectra (bottom left) in dilute chloroform solution (solid blue line) and drop cast thin film (black dashed line). Solvatochromism spectra (bottom right) are given as well.
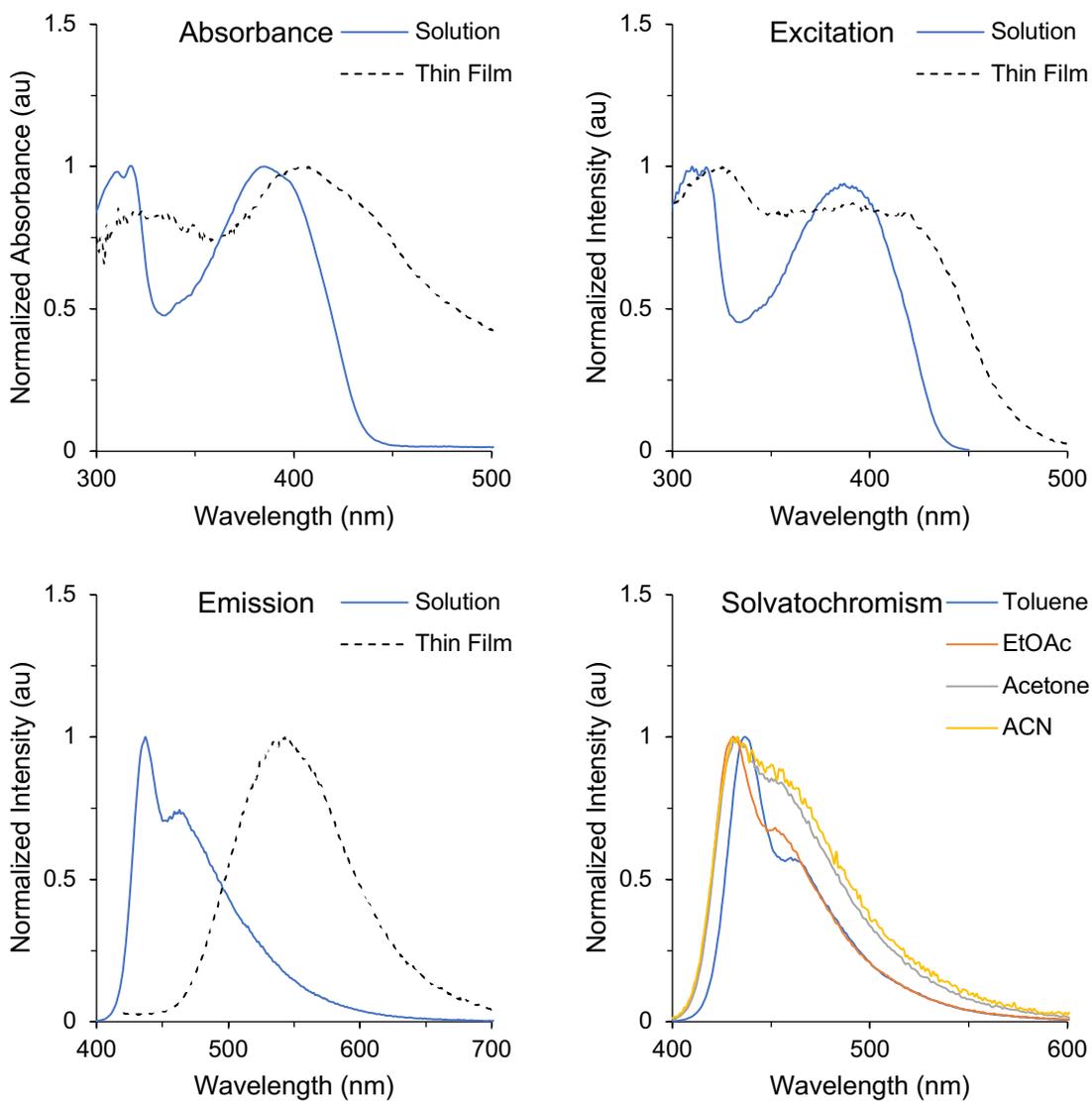
Figure S34: Optical Spectroscopy of **ED-3H**. Absorbance (top left), excitation (top right), and emission spectra (bottom left) in dilute chloroform solution (solid blue line) and drop cast thin film (black dashed line). Solvatochromism spectra (bottom right) are given as well.
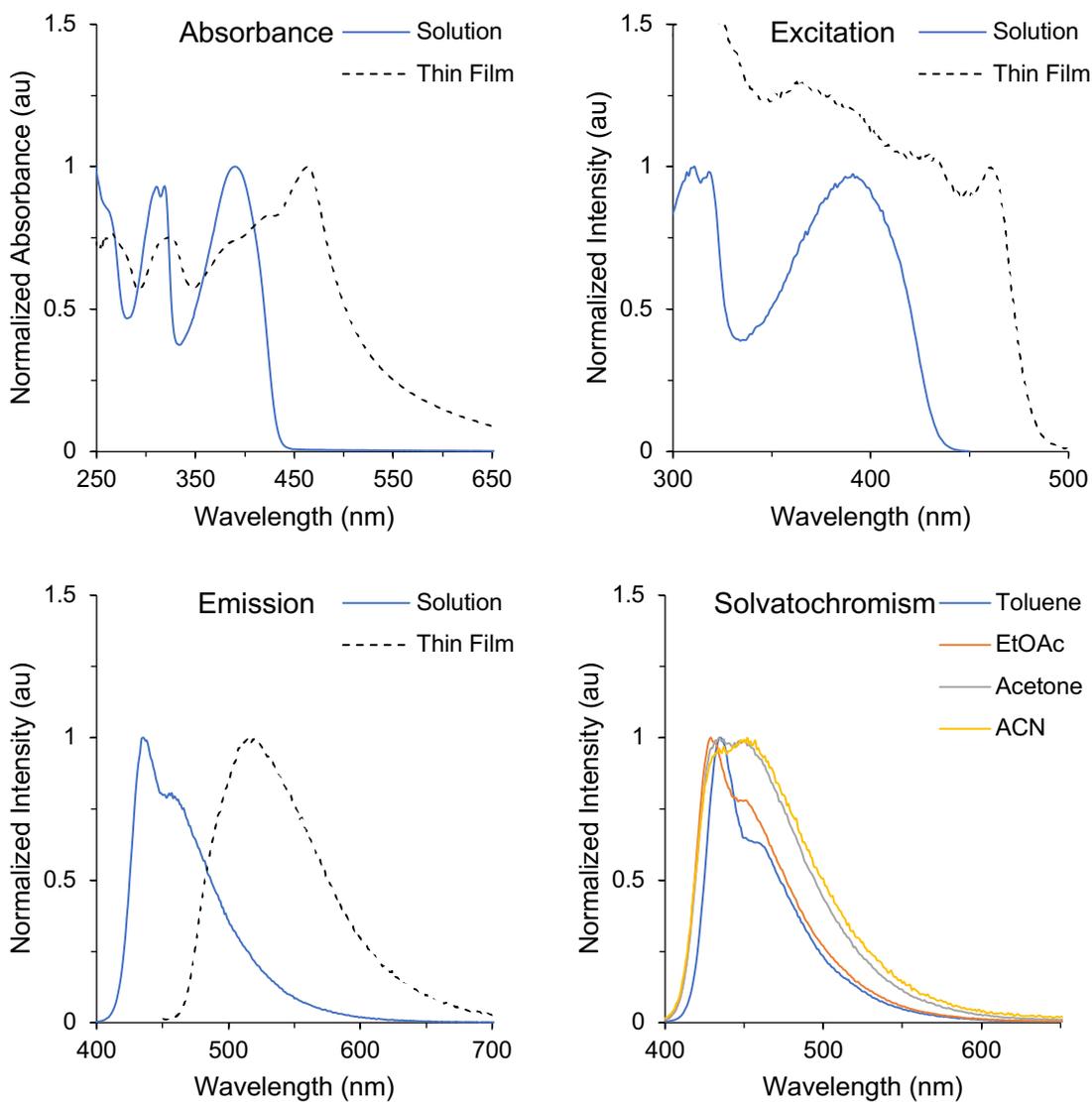
Figure S35: Mechanofluorochromism of fluorinated **ER** Oligomers
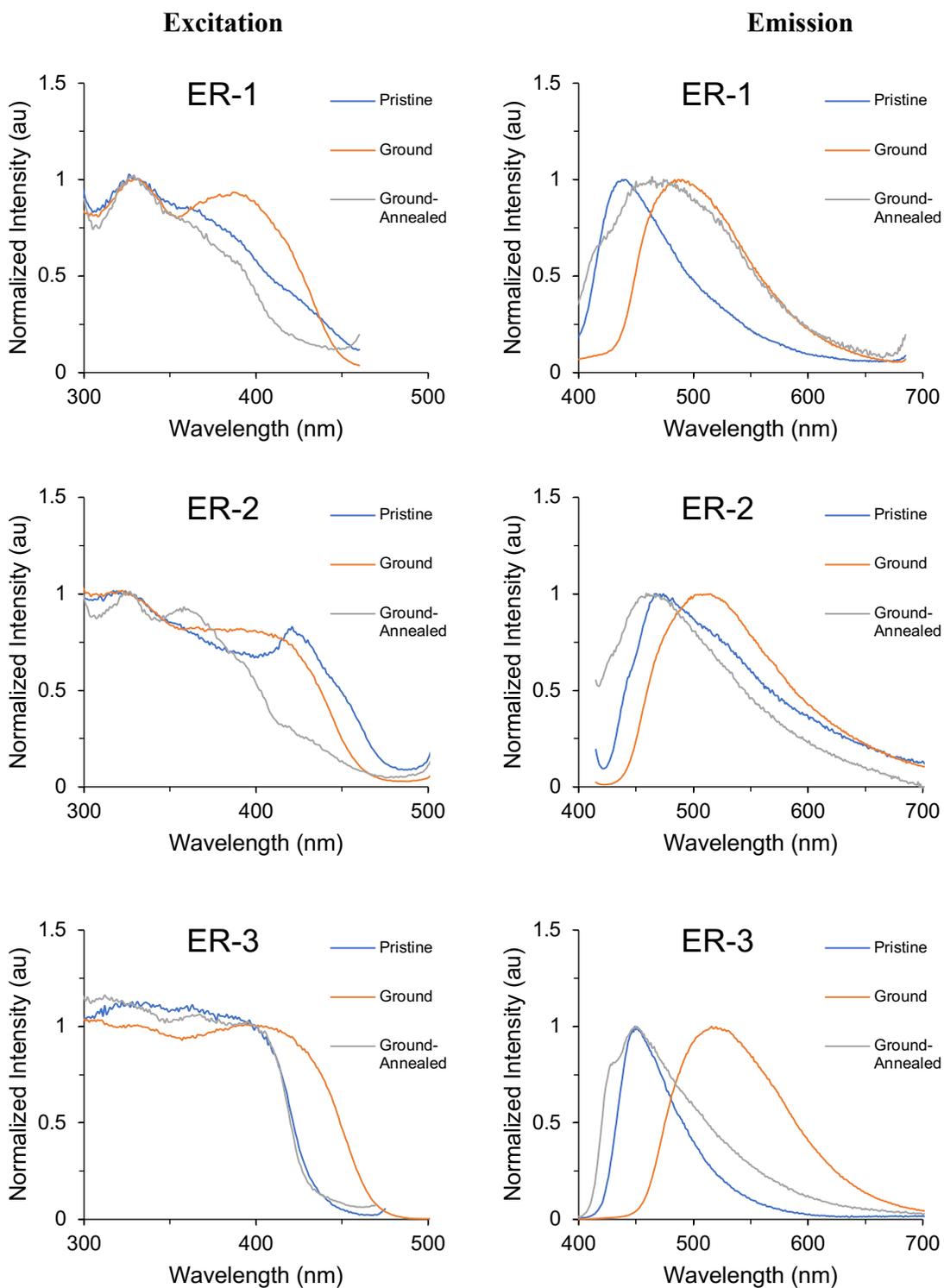
Figure S36. Mechanofluorochromism of fluorinated **ED** Oligomers
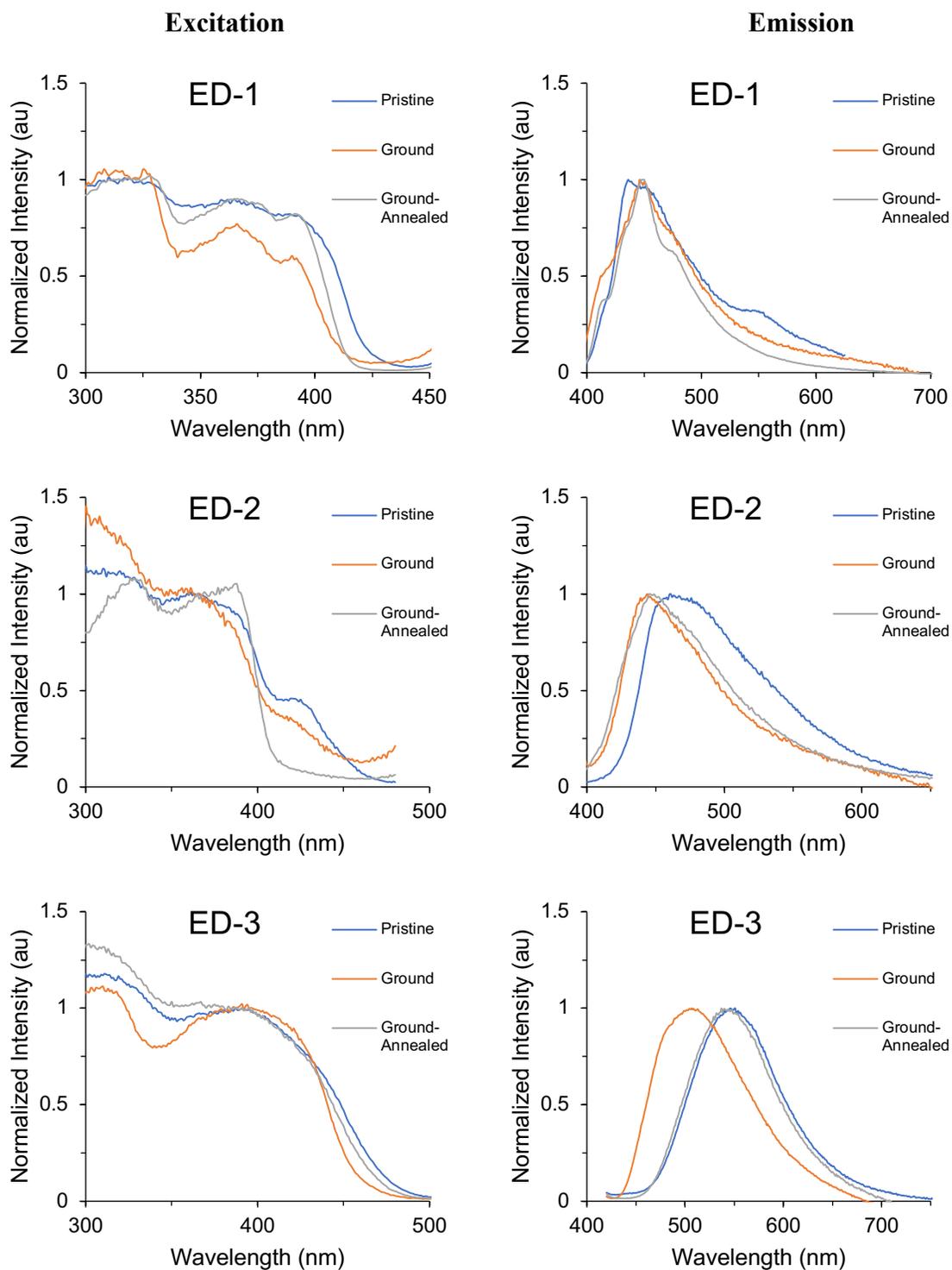
Figure S37: Mechanofluorochromism of **ER-1H** and **ED-1H**
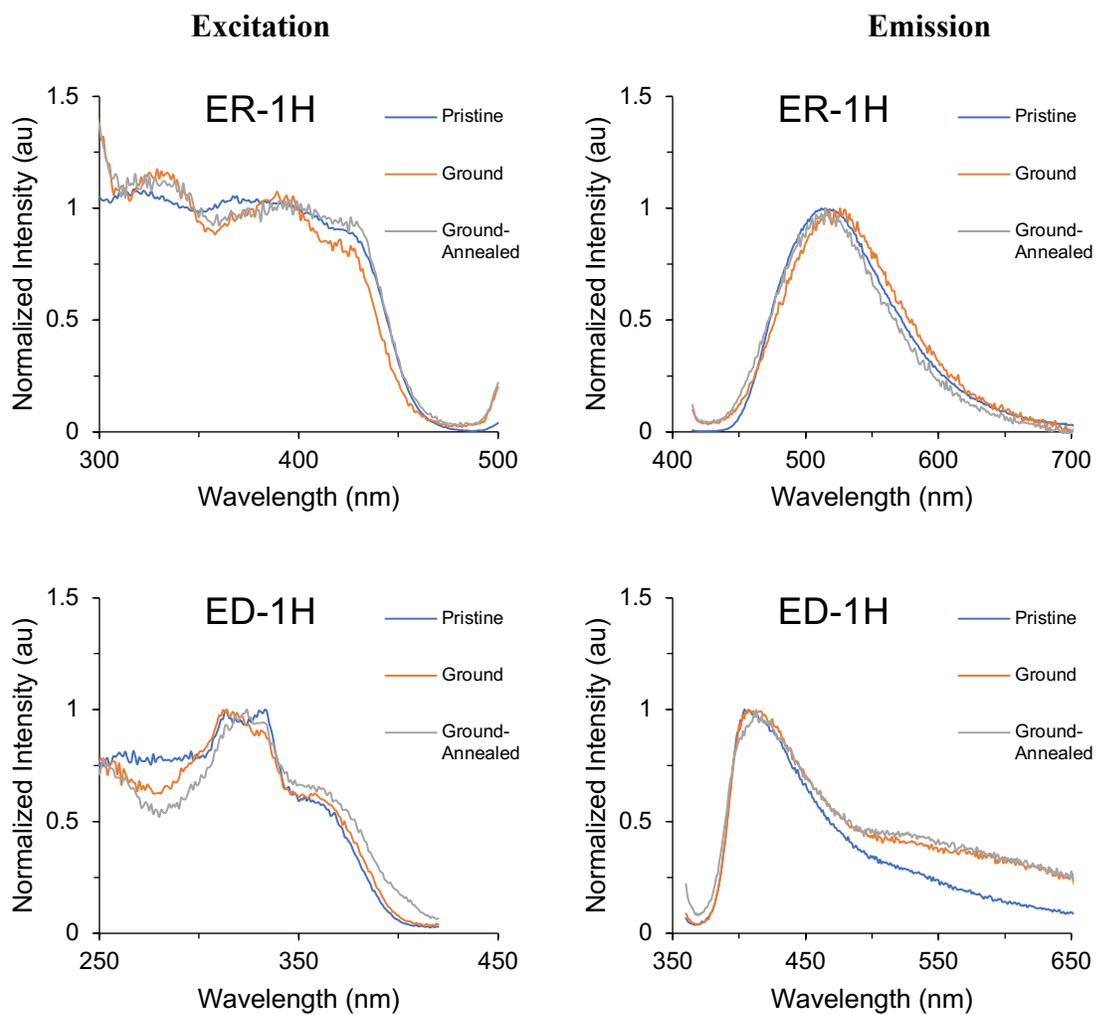
Figure S38: Reproducibility of drop-cast films, **ER-1** and **ED-2**.

Excitation

Emission
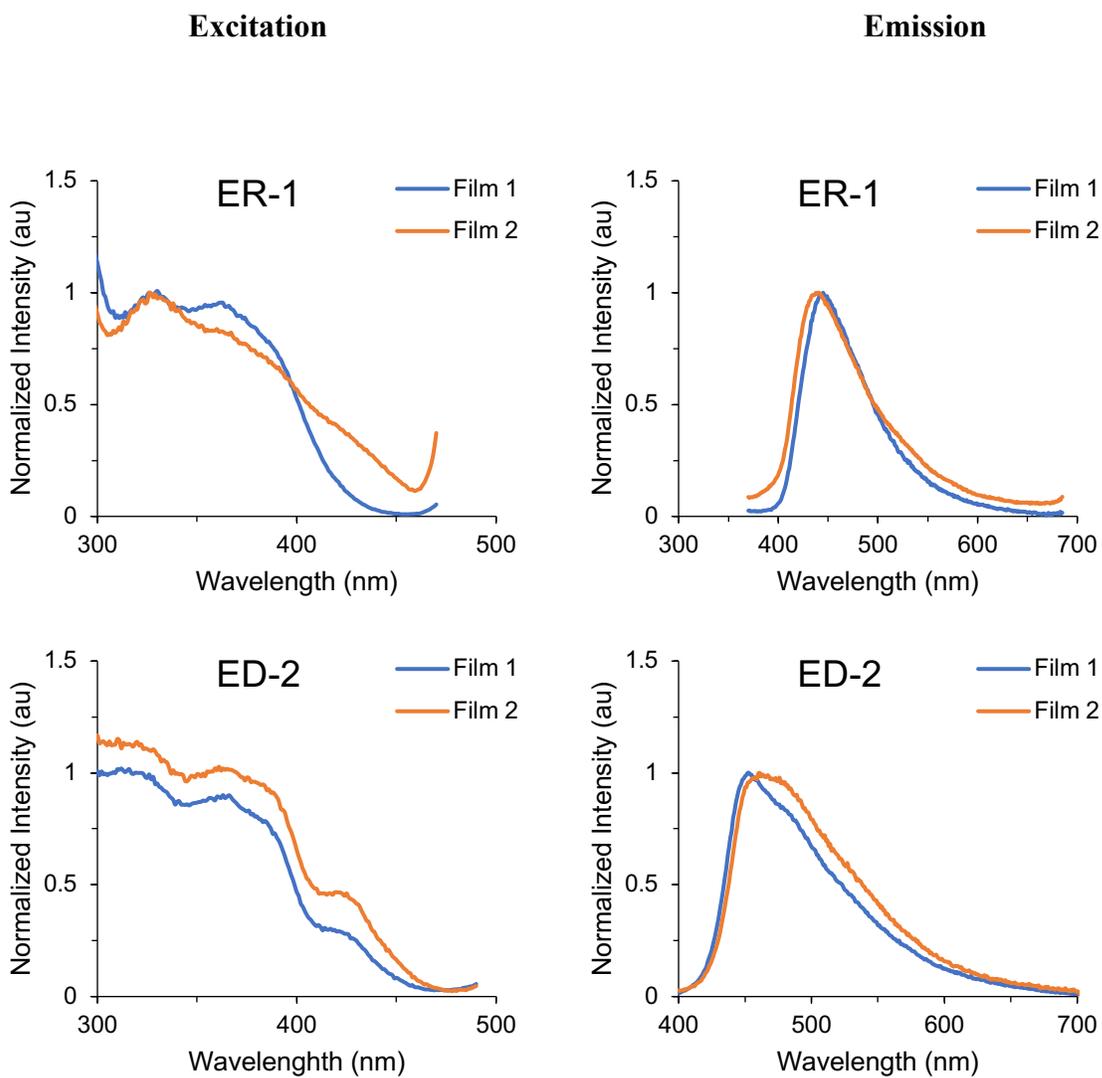
X-Ray Crystallography

Crystal growth for each compound was attempted using either a slow evaporation from chloroform or diffusion of hexanes into chloroform solution. Eight of the twelve crystals grown produced diffraction quality data. Low-temperature single crystal diffraction data were collected on a Bruker D8 Quest diffractometer coupled to a Photon CMOS detector with Mo Kα radiation ($\lambda = 0.71073$ Å) from a fine-focused sealed tube source for **ED-1** and **ER-1H**. Data were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex2 CCD detector with Mo Kα radiation ($\lambda = 0.71073$ Å), from an IμS micro-source for **ED-2H** and on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Photon 3 CPAD detector with Mo Kα radiation ($\lambda = 0.71073$ Å) or with Cu Kα radiation ($\lambda = 1.54184$ Å), from an IμS micro-source for **ED-3**, **ED-3H**, **ER-1**, **ER-2H,** and **ER-3** in collaboration with Peter Müller and the MIT X-Ray Diffraction Facility. For all structures, data were collected performing φ- and ω-scans. All structures were solved with dual-space methods using the program SHELXT[4] and refined against F^2 on all data with SHELXL[5] using established refinement techniques.[6]

The following compounds suffer from a similar disorder, in which the ethynyl flankers are flipped 180° about the conjugated backbone: **ED-3**, **ER-1**, **ER-1H**, **ER-2H**, and **ER-3**. The disorders were straightforward and routine. All disorders were refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid-bond restraints. In addition, since the specific nature of this ring-flip disorder leads to pairwise almost overlap of atoms, such atom pairs were constrained to exhibit identical anisotropic displacement parameters in the structures of .**ER-1H**, **ER-2H**, and **ER-3**. The disorder ratios were refined freely and converged at 0.782(3) for **ED-3**, at 0.601(4) for **ER-1**, at 0.655(2) for **ER-1H**, at 0.855(3) for **ER-2H,** and 0.0598(2) for **ER-3**.

The structure of **ED-3** was refined as a pseudo-merohedral twin. Even though the minor twin component is relatively small (the twin ratio converged at 0.04622(7)), introduction of the twin law (-1 0 0 0 -1 0 1 0 1) improved the structure significantly. The crystal of **ER-1** was a non-merohedral twin. Two independent orientation matrices for the unit cell were found using the program CELL_NOW[7], and data reduction taking into account the twinning was performed with SAINT[8]. The program TWINABS[9] was used to perform absorption correction and to set up the HKLF5 format file for structure refinement. The twin ratio was refined freely and converged at 0.2544(13).

Table S1. Crystal data and structure refinement for **ER-1**.

Identification code	er1
Empirical formula	$C_{34} H_{12} F_{10} O_4 S_2$
Formula weight	738.56
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 6.9881(11)$ Å $\qquad \alpha = 89.898(6)°$.
	$b = 7.0240(11)$ Å $\qquad \beta = 82.720(6)°$.
	$c = 15.623(3)$ Å $\qquad \gamma = 72.540(6)°$.
Volume	725.1(2) Å^3
Z	1
Density (calculated)	1.691 Mg/m^3
Absorption coefficient	0.291 mm^{-1}
$F(000)$	370
Crystal size	0.205 x 0.155 x 0.015 mm^3
Theta range for data collection	1.315 to 30.503°.
Index ranges	-9<=h<=9, -10<=k<=10, -21<=l<=22
Reflections collected	4346
Independent reflections	4346 [R_{int} = 0.0622]
Completeness to theta = 25.242°	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.746027 and 0.595286
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4346 / 209 / 264
Goodness-of-fit on F^2	1.081
Final R indices [I>2$\sigma(I)$]	$R1$ = 0.0558, $wR2$ = 0.1194
R indices (all data)	$R1$ = 0.0762, $wR2$ = 0.1297
Largest diff. peak and hole	0.321 and -0.275 e.Å^{-3}

Table S2. Crystal data and structure refinement for **ER-1H**.

Identification code	er1h
Empirical formula	$C_{34} H_{22} O_4 S_2$
Formula weight	558.63
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 15.1412(11) Å $\quad \alpha = 90°$.
	b = 4.8090(3) Å $\quad \beta = 105.317(3)°$.
	c = 18.5187(13) Å $\quad \gamma = 90°$.
Volume	1300.52(16) Å^3
Z	2
Density (calculated)	1.427 Mg/m^3
Absorption coefficient	0.246 mm^{-1}
$F(000)$	580
Crystal size	0.150 x 0.150 x 0.100 mm^3
Theta range for data collection	2.281 to 27.158°.
Index ranges	-19<=h<=19, -6<=k<=6, -23<=l<=23
Reflections collected	49570
Independent reflections	2880 [R_{int} = 0.0393]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2880 / 209 / 194
Goodness-of-fit on F^2	1.027
Final R indices [$I>2\sigma(I)$]	R1 = 0.0347, wR2 = 0.0838
R indices (all data)	R1 = 0.0412, wR2 = 0.0883
Largest diff. peak and hole	0.373 and -0.218 e.Å^{-3}

Table S3. Crystal data and structure refinement for **ER-2H**.

Identification code	er2h
Empirical formula	$C_{34} H_{22} O_6$
Formula weight	526.51
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 14.9173(3)$ Å $\alpha = 90°$.
	$b = 4.73320(10)$ Å $\beta = 105.1300(10)°$.
	$c = 18.6755(4)$ Å $\gamma = 90°$.
Volume	1272.90(5) Å^3
Z	2
Density (calculated)	1.374 Mg/m^3
Absorption coefficient	0.094 mm^{-1}
$F(000)$	548
Crystal size	0.250 x 0.200 x 0.110 mm^3
Theta range for data collection	1.563 to 32.688°.
Index ranges	$-22<=h<=22, -7<=k<=7, -28<=l<=28$
Reflections collected	47388
Independent reflections	4657 [$R_{int} = 0.0342$]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4657 / 237 / 194
Goodness-of-fit on F^2	1.047
Final R indices [$I>2\sigma(I)$]	$R1 = 0.0405, wR2 = 0.1089$
R indices (all data)	$R1 = 0.0470, wR2 = 0.1150$
Largest diff. peak and hole	0.416 and -0.308 e.Å^{-3}

Table S4. Crystal data and structure refinement for **ER-3**.

Identification code	wm72
Empirical formula	C42 H16 F10 O4 S2
Formula weight	838.67
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1

Unit cell dimensions
$a = 7.1753(8)$ Å $\alpha = 89.010(4)°$.
$b = 7.4190(8)$ Å $\beta = 79.454(4)°$.
$c = 16.0501(19)$ Å $\gamma = 84.755(4)°$.

Volume	836.45(16) Å^3
Z	1
Density (calculated)	1.665 Mg/m^3
Absorption coefficient	0.263 mm^{-1}
$F(000)$	422
Crystal size	0.345 x 0.305 x 0.175 mm^3
Theta range for data collection	1.290 to 32.577°.
Index ranges	-10<=h<=10, -11<=k<=11, -24<=l<=24
Reflections collected	81800
Independent reflections	6093 [$R_{int} = 0.0352$]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6093 / 436 / 287
Goodness-of-fit on F^2	1.135
Final R indices [$I>2\sigma(I)$]	$R1 = 0.0351$, $wR2 = 0.0972$
R indices (all data)	$R1 = 0.0372$, $wR2 = 0.0987$
Largest diff. peak and hole	0.580 and -0.337 e.Å^{-3}

Table S5. Crystal data and structure refinement for **ED-1**.

Identification code	ed1
Empirical formula	$C_{36} H_{14} F_{10} N_2 O_4$
Formula weight	728.49
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 5.8211(5)$ Å $\qquad \alpha = 87.599(3)°$.
	$b = 7.9754(7)$ Å $\qquad \beta = 88.956(3)°$.
	$c = 15.4547(13)$ Å $\qquad \gamma = 88.604(3)°$.
Volume	716.54(11) Å^3
Z	1
Density (calculated)	1.688 Mg/m^3
Absorption coefficient	0.154 mm^{-1}
$F(000)$	366
Crystal size	0.200 x 0.150 x 0.100 mm^3
Theta range for data collection	2.557 to 30.099°.
Index ranges	$-8 \le h \le 8, -11 \le k \le 11, -21 \le l \le 21$
Reflections collected	43653
Independent reflections	4206 [$R_{int} = 0.0294$]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4206 / 0 / 235
Goodness-of-fit on F^2	1.030
Final R indices [$I>2\sigma(I)$]	$R1 = 0.0547, wR2 = 0.1432$
R indices (all data)	$R1 = 0.0688, wR2 = 0.1565$
Largest diff. peak and hole	0.663 and -0.195 e.Å^{-3}

Table S6. Crystal data and structure refinement for **ED-2H**.

Identification code	ed2h
Empirical formula	$C_{34} H_{22} N_4 O_4$
Formula weight	550.55
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 15.266(5) Å α = 90°.
	b = 4.7151(14) Å β = 104.014(5)°.
	c = 18.595(6) Å γ = 90°.
Volume	1298.7(7) Å^3
Z	2
Density (calculated)	1.408 Mg/m^3
Absorption coefficient	0.094 mm^{-1}
F(000)	572
Crystal size	0.320 x 0.080 x 0.015 mm^3
Theta range for data collection	1.979 to 30.626°.
Index ranges	-21<=h<=21, -6<=k<=6, -26<=l<=26
Reflections collected	29535
Independent reflections	3985 [R_{int} = 0.0843]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3985 / 0 / 190
Goodness-of-fit on F^2	1.018
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0577, $wR2$ = 0.1356
R indices (all data)	$R1$ = 0.0996, $wR2$ = 0.1583
Largest diff. peak and hole	0.447 and -0.347 e.Å^{-3}

Table S7. Crystal data and structure refinement for **ED-3**.

Identification code	ed3
Empirical formula	$C_{38} H_{12} F_{10} N_4 O_4 S_2$
Formula weight	842.64
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 4.6076(2)$ Å $\qquad \alpha = 90°.$
	$b = 10.9493(4)$ Å $\qquad \beta = 93.834(3)°.$
	$c = 31.9883(13)$ Å $\qquad \gamma = 90°.$
Volume	1610.20(11) Å^3
Z	2
Density (calculated)	1.738 Mg/m^3
Absorption coefficient	2.515 mm^{-1}
$F(000)$	844
Crystal size	0.180 x 0.015 x 0.005 mm^3
Theta range for data collection	1.384 to 72.288°.
Index ranges	$-5<=h<=5, -13<=k<=13, -39<=l<=39$
Reflections collected	34679
Independent reflections	3276 [$R_{int} = 0.0725$]
Completeness to theta = 67.679°	99.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3276 / 496 / 354
Goodness-of-fit on F^2	1.124
Final R indices [$I>2\sigma(I)$]	$R1 = 0.0429, wR2 = 0.0818$
R indices (all data)	$R1 = 0.0561, wR2 = 0.0880$
Largest diff. peak and hole	0.327 and -0.324 e.Å^{-3}

Table S8. Crystal data and structure refinement for **ED-3H**.

Identification code	ed3h
Empirical formula	$C_{38} H_{22} N_4 O_4 S_2$
Formula weight	662.71
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 6.7871(2)$ Å $\alpha = 72.7900(10)°$.
	$b = 10.7706(3)$ Å $\beta = 82.5830(10)°$.
	$c = 11.4277(2)$ Å $\gamma = 72.8690(10)°$.
Volume	761.77(3) Å^3
Z	1
Density (calculated)	1.445 Mg/m^3
Absorption coefficient	0.226 mm^{-1}
$F(000)$	342
Crystal size	0.295 x 0.190 x 0.185 mm^3
Theta range for data collection	1.868 to 33.192°.
Index ranges	-10<=h<=10, -16<=k<=16, -17<=l<=17
Reflections collected	59196
Independent reflections	5837 [R_{int} = 0.0289]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5837 / 0 / 217
Goodness-of-fit on F^2	1.058
Final R indices [I>2$\sigma(I)$]	$R1$ = 0.0325, $wR2$ = 0.0896
R indices (all data)	$R1$ = 0.0356, $wR2$ = 0.0919
Largest diff. peak and hole	0.492 and -0.471 e.Å^{-3}
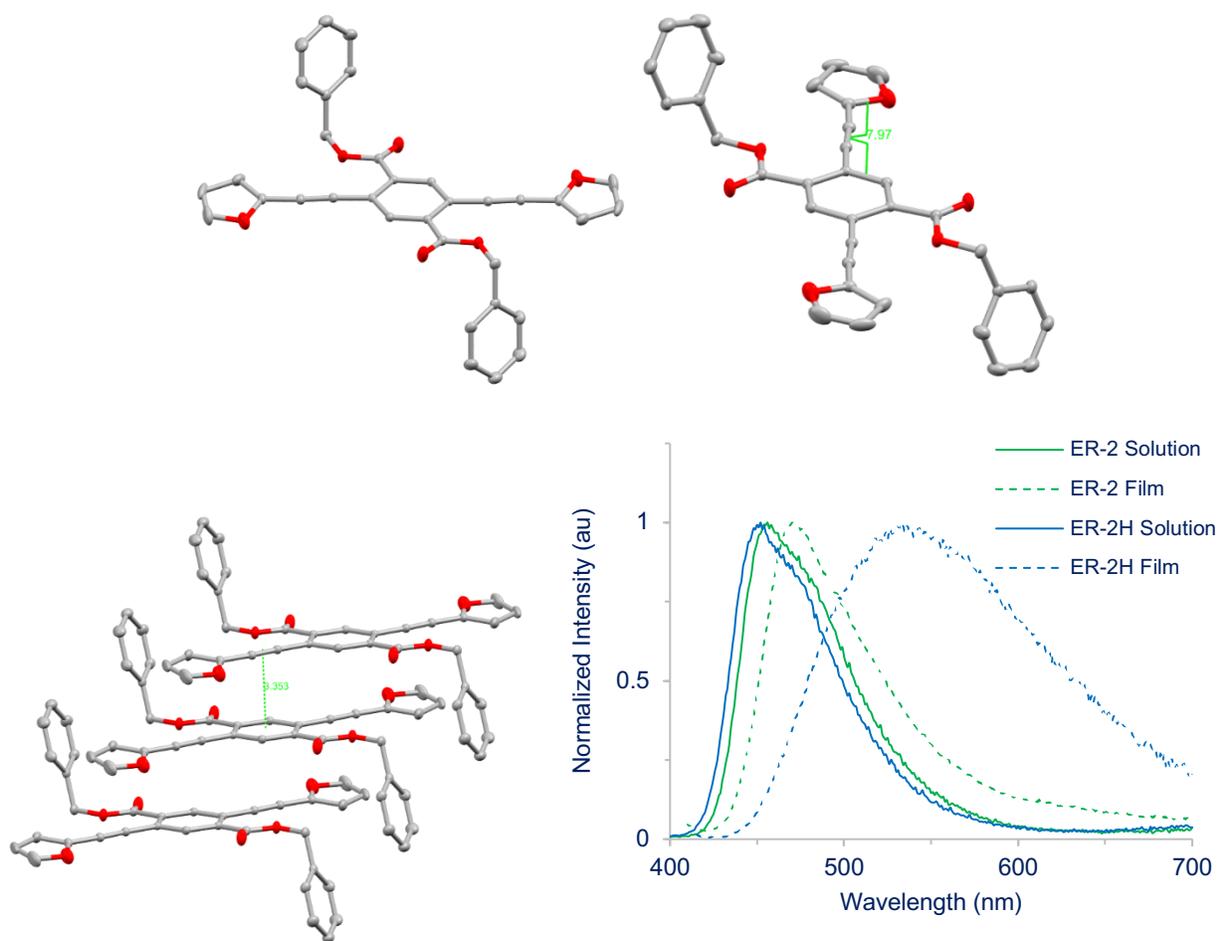
Figure S39: Images of the **ER-2H** crystal structure, showing tosional angles of 8° and interchromophore distances of 3.35Å. Ellipsoids are at 50% probability and hydrogen atoms have been imitted for clarity. The bottom right plot compares the optical spectra of **ER-2** (green) and **ER-2H** (blue) in solution (solid lines) and thin films (dashed lines). **ER-2** shows bathochromic shifting of 14 nm in the solid state, while **ER-2H** shows an 81nm shift. Based on this difference in bathochromic shifting, we infer that the backbone of **ER-2** is twisted and non-aggregated, similar to that of **ER-1** and **ER-3**.
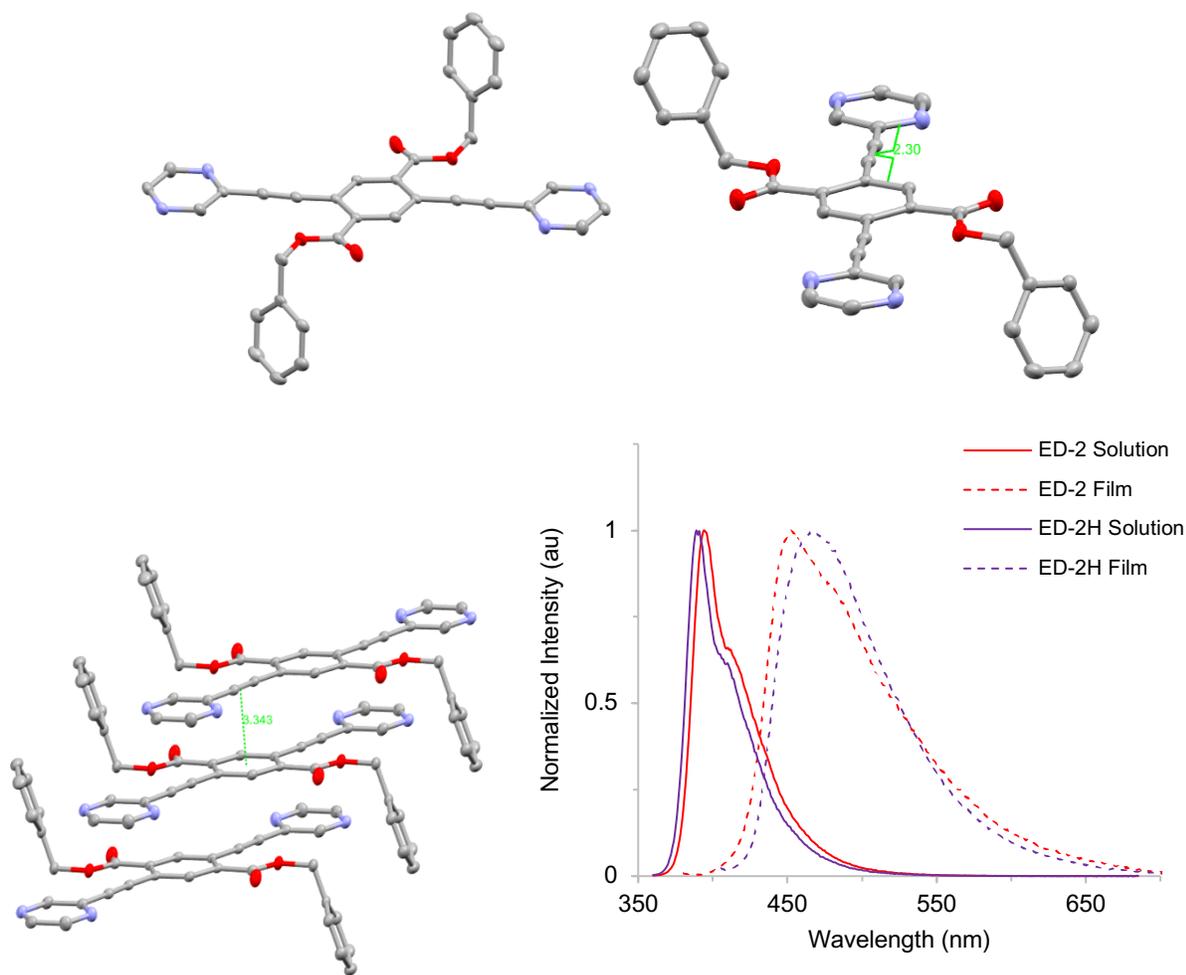
Figure S40: Images of the **ED-2H** crystal structure, showing tosional angles of 2° and interchromophore distances of 3.34Å. Ellipsoids are at 50% probability and hydrogen atoms have been imitted for clarity. The bottom right plot compares the optical spectra of **ED-2** (red) and **ED-2H** (purple) in solution (solid lines) and thin films (dashed lines). **ED-2** shows bathochromic shifting of 59 nm in the solid state, while **ED-2H** shows an 77nm shift. Based on this similarity in bathochromic shifting, as well as the position of the onset of emission in the solid-state, we infer that **ED-2** packs in a similar manner as **ED-2H** and **ED-1**.

Computational Details

Conformations were located using Crest[10] at the GFN2-xTB level of theory,[11] keeping all unique conformers based on a 0.125 Å RMSD cut-off and within a 10 kcal mol^{-1} energy window. These structures were then further optimized at the wB97X-D/def2SVP level of theory (in the gas phase). Solution-phase single point energies were carried out for unique conformations (based on a 0.4 Å RMSD cut-off) lying within 7 kcal/mol of the global minimum energy structure at the wB97X-D/def2TZVP level of theory. The 'open' conformations were built manually and then optimized at the wB97X-D/def2SVP level of theory, followed by wB97X-D/def2TZVP single points, since they were not identified automatically by Crest. All optimized structures were confirmed to be energy minima based on the absence of any imaginary harmonic vibrational frequencies. Energies and oscillator strengths for the ten lowest excited states were computed using TD-DFT for all unique conformations at the PCM-PBE0/def2TZVP level of theory. The simulated UV-vis spectra were then generated by either a Boltzmann weighting of all TD-DFT data for the different conformations (based on relative enthalpies at 298K) or for the single (presumed) conformation in the solid state using AaronTools.[12] Natural transition orbitals (NTO) were computed for selected systems based on these TD-DFT computations and plotted using ChimeraX with the SEQCROW plugin.[13]

Table S9. Absolute enthalpies [H(298K), in hartrees] and relative enethalpies (H$_{rel}$, in kcal/mol) for conformations of **ED-X** oligomers computed at the PCM-wb97X-D/def2TZVP//wb97XD/def2SVP level of theory. Corresponding optimized Cartesian coordinates for each conformer can be found in the accompanying XYZ files.

ED-1	H(298K)	H$_{rel}$	ED-2	H(298K)	H$_{rel}$	ED-3	H(298K)	H$_{rel}$
Cf02	-2788.648074	0.2	Cf11	-2820.735513	0.3	Cf02	-3769.552186	0.0
Cf9022	-2788.647973	0.3	Cf76	-2820.73551	0.3	Cf09	-3769.552065	0.1
Cf16	-2788.648203	0.2	Cf56	-2820.735617	0.2	Cf11	-3769.551632	0.3
Cf10	-2788.648076	0.2	Cf21	-2820.735911	0.0	Cf27	-3769.551767	0.3
Cf33	-2788.648459	0.0	Cf29	-2820.735918	0.0	Cf23	-3769.551385	0.5
Cf39	-2788.648167	0.2	Cf51	-2820.733092	1.8	Cf31	-3769.551073	0.7
Cf18	-2788.644659	2.4	Cf9036	-2820.732978	1.8	Cf37	-3769.549147	1.9
Cf01	-2788.644578	2.4	Cf12	-2820.733175	1.7	Cf58	-3769.548902	2.1
Cf15	-2788.644783	2.3	Cf09	-2820.733209	1.7	Cf71	-3769.548606	2.2
Cf9064	-2788.644817	2.3	Cf9000	-2820.730418	3.5	Cf75	-3769.548544	2.3
Cf9053	-2788.641303	4.5	Cf05	-2820.730561	3.4	Cf9015	-3769.545527	4.2
Cf30	-2788.641479	4.4	Cf9063	-2820.732007	2.5	Cf70	-3769.545706	4.1
Cf55	-2788.64514	2.1	Cf9054	-2820.731912	2.5	Cf81	-3769.545316	4.3
Cf9073	-2788.645253	2.0	Cf47	-2820.73221	2.3	Cf78	-3769.545228	4.4
Cf86	-2788.645401	1.9	Cf37	-2820.732131	2.4	Open	-3769.535246	10.6
Cf77	-2788.64539	1.9	Cf9017	-2820.732581	2.1			
Cf53	-2788.643648	3.0	Cf53	-2820.732518	2.1			
Cf52	-2788.643588	3.1	Cf77	-2820.732858	1.9			
Cf9000	-2788.643674	3.0	Cf52	-2820.732784	2.0			
Cf80	-2788.643868	2.9	Cf20	-2820.729488	4.0			
Cf69	-2788.643286	3.2	Cf31	-2820.729352	4.1			
Cf9012	-2788.643247	3.3	Cf72	-2820.729942	3.7			
Cf71	-2788.641758	4.2	Cf24	-2820.730166	3.6			
Cf82	-2788.641703	4.2	Cf22	-2820.730045	3.7			
Cf9007	-2788.641495	4.4	Cf84	-2820.729994	3.7			
Cf70	-2788.641477	4.4	Cf9048	-2820.730099	3.7			
Cf60	-2788.640377	5.1	Cf9022	-2820.72756	5.2			
Cf9008	-2788.641542	4.3	Cf86	-2820.72755	5.3			
Cf9016	-2788.641538	4.3	Cf9037	-2820.730413	3.5			
Cf9057	-2788.642428	3.8	Cf9027	-2820.730494	3.4			
Cf9004	-2788.638297	6.4	Cf9046	-2820.730344	3.5			
Cf88	-2788.638225	6.4	Cf9052	-2820.730459	3.4			
Cf9088	-2788.641804	4.2	Cf9026	-2820.730561	3.4			
Cf9077	-2788.6418	4.2	Cf9020	-2820.727618	5.2			
Cf9093	-2788.641807	4.2	Cf88	-2820.727912	5.0			
Cf9089	-2788.641895	4.1	Cf82	-2820.727822	5.1			
Open	-2788.635823	7.9	Cf9013	-2820.728169	4.9			
			Cf9045	-2820.728151	4.9			
			Cf64	-2820.728269	4.8			
			Cf70	-2820.728307	4.8			

				Open	-2820.725243	6.7			

Table S10. Absolute enthalpies [H(298K), in hartrees] and relative enethalpies (H$_{rel}$, in kcal/mol) for conformations of **ER-X** oligomers computed at the PCM-wb97X-D/def2TZVP//wb97XD/def2SVP level of theory. Corresponding optimized Cartesian coordinates for each conformer can be found in the accompanying XYZ files.

ER-1	H(298K)	H$_{rel}$	ER-2	H(298K)	H$_{rel}$	ER-3	H(298K)	H$_{rel}$
Cf17	-3398.163856	0.0	Cf36	-2752.182462	0.1	Cf07	-3705.356875	0.8
Cf11	-3398.163851	0.0	Cf39	-2752.182302	0.2	Cf46	-3705.357407	0.4
Cf06	-3398.163426	0.3	Cf07	-2752.182515	0.1	Cf21	-3705.357947	0.1
Cf05	-3398.162962	0.6	Cf15	-2752.182418	0.1	Cf12	-3705.35812	0.0
Cf19	-3398.163472	0.2	Cf22	-2752.182522	0.1	Cf10	-3705.357507	0.4
Cf00	-3398.162915	0.6	Cf29	-2752.182618	0.0	Cf05	-3705.357023	0.7
Cf35	-3398.161227	1.6	Cf73	-2752.179724	1.8	Cf63	-3705.3556	1.6
Cf31	-3398.16082	1.9	Cf25	-2752.179668	1.9	Cf41	-3705.354982	2.0
Cf67	-3398.16109	1.7	Cf9029	-2752.179876	1.7	Cf53	-3705.355089	1.9
Cf30	-3398.160787	1.9	Cf64	-2752.179813	1.8	Cf71	-3705.355551	1.6
Cf41	-3398.161134	1.7	Cf30	-2752.178818	2.4	Cf52	-3705.355244	1.8
Cf24	-3398.160589	2.1	Cf18	-2752.178872	2.4	Cf9045	-3705.354591	2.2
Cf77	-3398.16092	1.8	Cf43	-2752.178941	2.3	Cf9007	-3705.354768	2.1
Cf26	-3398.160517	2.1	Cf42	-2752.178952	2.3	Cf55	-3705.355214	1.8
Cf59	-3398.159148	3.0	Cf71	-2752.177896	3.0	Cf85	-3705.350436	4.8
Cf9002	-3398.158344	3.5	Cf9011	-2752.177956	2.9	Cf9034	-3705.351112	4.4
Cf60	-3398.158417	3.4	Cf76	-2752.177858	3.0	Cf67	-3705.350431	4.8
Cf56	-3398.15796	3.7	Cf82	-2752.177834	3.0	Cf9037	-3705.351153	4.4
Cf65	-3398.157957	3.7	Cf80	-2752.178042	2.9	Cf9028	-3705.350015	5.1
Cf9034	-3398.158148	3.6	Cf9042	-2752.177974	2.9	Cf9036	-3705.350068	5.1
Cf9031	-3398.15804	3.6	Cf9053	-2752.177932	2.9	Open	-3705.343635	9.1
Cf9028	-3398.157569	3.9	Cf9039	-2752.177968	2.9			
Cf9025	-3398.157679	3.9	Cf63	-2752.177997	2.9			
Cf9006	-3398.157848	3.8	Cf59	-2752.177704	3.1			
Cf9000	-3398.15738	4.1	Cf9019	-2752.177844	3.0			
Cf9072	-3398.158216	3.5	Cf9030	-2752.177964	2.9			
Cf61	-3398.158296	3.5	Cf9052	-2752.177026	3.5			
Cf9069	-3398.157773	3.8	Cf9065	-2752.177152	3.4			
Cf79	-3398.158334	3.5	Open	-2752.173611	5.7			
Cf9079	-3398.157755	3.8						
Open	-3398.152621	7.1						

Table S11. Absolute enthalpies [H(298K), in hartrees] and relative enethalpies (H_{rel}, in kcal/mol) for conformations of **ED-XH** oligomers computed at the PCM-wb97X-D/def2TZVP//wb97XD/def2SVP level of theory. Corresponding optimized Cartesian coordinates for each conformer can be found in the accompanying XYZ files.

ED-1H	H(298K)	H_{rel}	ED-2H	H(298K)	H_{rel}	ED-3H	H(298K)	H_{rel}
Cf15	-1796.088188	0.0	Cf15	-1828.177936	0.0	Cf17	-2776.994331	0.0
Cf00	-1796.088096	0.1	Cf00	-1828.178008	0.0	Cf04	-2776.994338	0.0
Cf9011	-1796.085535	1.7	Cf20	-1828.177608	0.3	Cf08	-2776.993009	0.8
Cf76	-1796.085403	1.7	Cf24	-1828.177196	0.5	Cf09	-2776.992884	0.9
Cf78	-1796.082812	3.4	Cf31	-1828.17745	0.4	Cf22	-2776.992579	1.1
Cf10	-1796.087217	0.6	Cf10	-1828.177436	0.4	Cf25	-2776.992447	1.2
Cf07	-1796.087072	0.7	Cf09	-1828.176965	0.7	Cf18	-2776.991717	1.6
Cf09	-1796.086997	0.7	Cf43	-1828.174977	1.9	Cf28	-2776.991439	1.8
Cf42	-1796.084463	2.3	Cf37	-1828.174852	2.0	Cf33	-2776.991047	2.1
Cf64	-1796.084418	2.4	Cf12	-1828.176607	0.9	Cf37	-2776.990716	2.3
Cf72	-1796.084303	2.4	Cf27	-1828.176929	0.7	Cf61	-2776.990738	2.3
Cf22	-1796.086327	1.2	Cf28	-1828.176912	0.7	Cf39	-2776.988442	3.7
Cf29	-1796.086267	1.2	Cf22	-1828.176899	0.7	Cf59	-2776.988227	3.8
Cf16	-1796.086156	1.3	Cf42	-1828.174392	2.3	Cf33	-2776.991047	2.1
Cf13	-1796.086219	1.2	Cf56	-1828.17427	2.3	Cf37	-2776.990716	2.3
Cf27	-1796.085848	1.5	Cf33	-1828.176216	1.1	Cf61	-2776.990738	2.3
Cf25	-1796.08593	1.4	Cf63	-1828.174488	2.2	Cf39	-2776.988442	3.7
Cf35	-1796.085763	1.5	Cf19	-1828.17607	1.2	Cf59	-2776.988227	3.8
Cf77	-1796.083459	3.0	Cf68	-1828.174308	2.3	Open	-2776.980585	8.6
Cf33	-1796.085049	2.0	Cf88	-1828.171948	3.8			
Cf45	-1796.085202	1.9	Cf9006	-1828.171952	3.8			
Cf68	-1796.085064	2.0	Cf36	-1828.175522	1.6			
Cf54	-1796.084926	2.0	Cf46	-1828.175286	1.7			
Cf52	-1796.084252	2.5	Cf39	-1828.175485	1.6			
Cf62	-1796.084271	2.5	Cf71	-1828.173014	3.1			
Cf81	-1796.083569	2.9	Cf82	-1828.172946	3.2			
Cf88	-1796.083404	3.0	Cf50	-1828.174237	2.4			
Cf9012	-1796.083887	2.7	Cf45	-1828.174102	2.5			
Cf83	-1796.08387	2.7	Cf66	-1828.173314	2.9			
Cf9047	-1796.08088	4.6	Cf78	-1828.173107	3.1			
Cf9044	-1796.080471	4.8	Cf75	-1828.172516	3.4			
Cf9006	-1796.082323	3.7	Cf9009	-1828.172619	3.4			
Cf9015	-1796.083106	3.2	Cf86	-1828.173344	2.9			
Cf9016	-1796.082492	3.6	Cf9002	-1828.172459	3.5			
Cf9018	-1796.083163	3.2	Cf9011	-1828.17247	3.5			
Cf9007	-1796.082678	3.5	Cf79	-1828.172883	3.2			
Cf9022	-1796.082703	3.4	Cf9025	-1828.172586	3.4			
Cf9026	-1796.082144	3.8	Cf85	-1828.172515	3.4			
Cf9035	-1796.082113	3.8	Cf9008	-1828.172733	3.3			
Cf9030	-1796.082606	3.5	Cf9012	-1828.172803	3.3			

Cf9013	-1796.081265	4.3	Cf9021	-1828.171494	4.1
Cf9019	-1796.081657	4.1	Cf9010	-1828.171418	4.1
Cf9034	-1796.081685	4.1	Cf9013	-1828.172432	3.5
Cf9037	-1796.082016	3.9	Cf9020	-1828.172442	3.5
Cf9038	-1796.0816	4.1	Cf9022	-1828.172328	3.6
Cf9012	-1796.083887	2.7	Cf78	-1828.173107	3.1
Cf83	-1796.08387	2.7	Cf75	-1828.172516	3.4
Cf9047	-1796.08088	4.6	Cf9009	-1828.172619	3.4
Cf9044	-1796.080471	4.8	Cf86	-1828.173344	2.9
Cf9006	-1796.082323	3.7	Cf9002	-1828.172459	3.5
Cf9015	-1796.083106	3.2	Cf9011	-1828.17247	3.5
Cf9016	-1796.082492	3.6	Cf79	-1828.172883	3.2
Cf9018	-1796.083163	3.2	Cf9025	-1828.172586	3.4
Cf9007	-1796.082678	3.5	Cf85	-1828.172515	3.4
Cf9022	-1796.082703	3.4	Cf9008	-1828.172733	3.3
Cf9026	-1796.082144	3.8	Cf9012	-1828.172803	3.3
Cf9035	-1796.082113	3.8	Cf9021	-1828.171494	4.1
Cf9030	-1796.082606	3.5	Cf9010	-1828.171418	4.1
Cf9013	-1796.081265	4.3	Cf9013	-1828.172432	3.5
Cf9019	-1796.081657	4.1	Cf9020	-1828.172442	3.5
Cf9034	-1796.081685	4.1	Cf9022	-1828.172328	3.6
Cf9037	-1796.082016	3.9	Open	-1828.167686	6.5
Cf9038	-1796.0816	4.1			
Open	-1796.078178	6.3			

Table S12. Absolute enthalpies [H(298K), in hartrees] and relative enethalpies (H_{rel}, in kcal/mol) for conformations of **ER-XH** oligomers computed at the PCM-wb97X-D/def2TZVP//wb97XD/def2SVP level of theory. Corresponding optimized Cartesian coordinates for each conformer can be found in the accompanying XYZ files.

ER-1H	H(298K)	H_{rel}	ER-2H	H(298K)	H_{rel}	ER-3H	H(298K)	H_{rel}
Cf57	-2405.603425	0.0	Cf11	-1759.623736	0.1	Cf10	-2712.797134	0.0
Cf21	-2405.602708	0.4	Cf15	-1759.623889	0.0	Cf09	-2712.797213	0.0
Cf03	-2405.60288	0.3	Cf07	-1759.622794	0.7	Cf13	-2712.796265	0.6
Cf17	-2405.602446	0.6	Cf10	-1759.62282	0.7	Cf05	-2712.796215	0.6
Cf10	-2405.60244	0.6	Cf40	-1759.621257	1.7	Cf06	-2712.796301	0.6
Cf20	-2405.602349	0.7	Cf46	-1759.621332	1.6	Cf87	-2712.795363	1.2
Cf11	-2405.60225	0.7	Cf01	-1759.621836	1.3	Cf15	-2712.795267	1.2
Cf9006	-2405.601908	1.0	Cf00	-1759.621865	1.3	Cf27	-2712.79539	1.1
Cf16	-2405.602116	0.8	Cf22	-1759.620401	2.2	Cf47	-2712.795459	1.1
Cf07	-2405.601673	1.1	Cf43	-1759.620318	2.2	Cf33	-2712.795268	1.2
Cf01	-2405.601455	1.2	Cf39	-1759.621918	1.2	Cf29	-2712.795091	1.3
Cf66	-2405.601887	1.0	Cf52	-1759.618811	3.2	Cf24	-2712.794496	1.7
Cf23	-2405.601265	1.4	Cf54	-1759.618877	3.1	Cf23	-2712.794199	1.9
Cf29	-2405.600919	1.6	Cf56	-1759.619444	2.8	Cf21	-2712.794315	1.8
Cf30	-2405.601361	1.3	Cf23	-1759.620796	1.9	Cf43	-2712.792967	2.7
Cf50	-2405.600247	2.0	Cf32	-1759.621465	1.5	Cf48	-2712.792905	2.7
Cf49	-2405.600349	1.9	Cf85	-1759.619912	2.5	Cf45	-2712.793567	2.3
Cf40	-2405.600706	1.7	Cf88	-1759.619852	2.5	Cf36	-2712.793732	2.2
Cf44	-2405.599345	2.6	Cf49	-1759.620369	2.2	Cf52	-2712.792143	3.2
Cf45	-2405.599499	2.5	Cf38	-1759.620195	2.3	Cf41	-2712.792213	3.1
Cf31	-2405.600231	2.0	Cf51	-1759.618878	3.1	Cf30	-2712.793719	2.2
Cf37	-2405.601281	1.3	Cf74	-1759.618848	3.2	Cf31	-2712.792838	2.7
Cf48	-2405.601206	1.4	Cf50	-1759.61951	2.7	Cf32	-2712.792795	2.8
Cf41	-2405.600175	2.0	Cf89	-1759.619638	2.7	Cf64	-2712.793026	2.6
Cf26	-2405.600069	2.1	Cf80	-1759.619518	2.7	Cf56	-2712.792261	3.1
Cf43	-2405.601028	1.5	Cf66	-1759.6187	3.3	Cf53	-2712.792166	3.2
Cf47	-2405.600535	1.8	Cf9013	-1759.619959	2.5	Cf60	-2712.791444	3.6
Cf85	-2405.598974	2.8	Cf9005	-1759.617245	4.2	Cf66	-2712.791308	3.7
Cf59	-2405.599095	2.7	Cf9006	-1759.617157	4.2	Cf88	-2712.791535	3.6
Cf62	-2405.599117	2.7	Cf83	-1759.618061	3.7	Cf80	-2712.791457	3.6
Cf35	-2405.600038	2.1	Cf9000	-1759.620423	2.2	Cf75	-2712.790886	4.0
Cf72	-2405.599737	2.3	Cf87	-1759.618673	3.3	Cf77	-2712.790656	4.1
Cf61	-2405.598566	3.0	Cf79	-1759.618587	3.3	Cf73	-2712.790974	3.9
Cf58	-2405.599121	2.7	Cf45	-1759.620257	2.3	Cf57	-2712.791361	3.7
Cf51	-2405.599609	2.4	Cf78	-1759.618754	3.2	Cf69	-2712.791443	3.6
Cf71	-2405.598195	3.3	Cf70	-1759.618685	3.3	Cf83	-2712.790789	4.0
Cf79	-2405.598195	3.3	Cf73	-1759.618772	3.2	Cf70	-2712.790802	4.0
Cf70	-2405.598161	3.3	Cf82	-1759.618841	3.2	Cf63	-2712.791602	3.5
Cf64	-2405.598051	3.4	Cf64	-1759.619487	2.8	Cf82	-2712.792491	3.0
Cf56	-2405.59874	2.9	Cf9017	-1759.619744	2.6	Cf81	-2712.791468	3.6

Cf60	-2405.598262	3.2	Cf9018	-1759.61691	4.4	Cf30	-2712.793719	2.2
Cf76	-2405.598238	3.3	Cf9011	-1759.617327	4.1	Cf31	-2712.792838	2.7
Cf81	-2405.59905	2.7	Cf9015	-1759.617306	4.1	Cf32	-2712.792795	2.8
Cf9004	-2405.597449	3.7	Cf9010	-1759.618547	3.4	Cf64	-2712.793026	2.6
Cf9001	-2405.59843	3.1	Cf60	-1759.618832	3.2	Cf56	-2712.792261	3.1
Cf9008	-2405.598745	2.9	Cf9003	-1759.617717	3.9	Cf53	-2712.792166	3.2
Cf84	-2405.598155	3.3	Cf9004	-1759.617477	4.0	Cf60	-2712.791444	3.6
Cf87	-2405.597991	3.4	Cf51	-1759.618878	3.1	Cf66	-2712.791308	3.7
Cf9018	-2405.595938	4.7	Cf74	-1759.618848	3.2	Cf88	-2712.791535	3.6
Cf67	-2405.59838	3.2	Cf50	-1759.61951	2.7	Cf80	-2712.791457	3.6
Cf9011	-2405.597164	3.9	Cf89	-1759.619638	2.7	Cf75	-2712.790886	4.0
Cf9014	-2405.596831	4.1	Cf80	-1759.619518	2.7	Cf77	-2712.790656	4.1
Cf58	-2405.599121	2.7	Cf66	-1759.6187	3.3	Cf73	-2712.790974	3.9
Cf51	-2405.599609	2.4	Cf9013	-1759.619959	2.5	Cf57	-2712.791361	3.7
Cf71	-2405.598195	3.3	Cf9005	-1759.617245	4.2	Cf69	-2712.791443	3.6
Cf79	-2405.598195	3.3	Cf9006	-1759.617157	4.2	Cf83	-2712.790789	4.0
Cf70	-2405.598161	3.3	Cf83	-1759.618061	3.7	Cf70	-2712.790802	4.0
Cf64	-2405.598051	3.4	Cf9000	-1759.620423	2.2	Cf63	-2712.791602	3.5
Cf56	-2405.59874	2.9	Cf87	-1759.618673	3.3	Cf82	-2712.792491	3.0
Cf60	-2405.598262	3.2	Cf79	-1759.618587	3.3	Cf81	-2712.791468	3.6
Cf76	-2405.598238	3.3	Cf45	-1759.620257	2.3	Open	-2712.786587	6.7
Cf81	-2405.59905	2.7	Cf78	-1759.618754	3.2			
Cf9004	-2405.597449	3.7	Cf70	-1759.618685	3.3			
Cf9001	-2405.59843	3.1	Cf73	-1759.618772	3.2			
Cf9008	-2405.598745	2.9	Cf82	-1759.618841	3.2			
Cf84	-2405.598155	3.3	Cf64	-1759.619487	2.8			
Cf87	-2405.597991	3.4	Cf9017	-1759.619744	2.6			
Cf9018	-2405.595938	4.7	Cf9018	-1759.61691	4.4			
Cf67	-2405.59838	3.2	Cf9011	-1759.617327	4.1			
Cf9011	-2405.597164	3.9	Cf9015	-1759.617306	4.1			
Cf9014	-2405.596831	4.1	Cf9010	-1759.618547	3.4			
Open	-2405.594935	5.3	Cf60	-1759.618832	3.2			
			Cf9003	-1759.617717	3.9			
			Cf9004	-1759.617477	4.0			
			Open	-1759.615681	5.2			

References

1. D. J. M. Blanchard, T. Z. Cservenyi and R. A. Manderville, *Chem. Commun.*, 2015, **51**, 16829.
2. D. Wang, X. Chen, H. Yang, D. Zhong, B. Liu, X. Yang, L. Yue, G. Zhou, M. Ma and Z. Wu, *Dalt. Trans.*, 2020, **49**, 15633.
3. K. T. Chan, G. S. M. Tong, W. P. To, C. Yang, L. Du, D. L. Phillips and C. M. Che, *Chem. Sci.*, 2017, **8**, 2352.
4. Sheldrick, G. M., *Acta Cryst.* **2015**, *A71*, 3-8.
5. Sheldrick, G. M., *Acta Cryst.* **2015**, *C71*, 3-8.
6. Müller, P., *Crystallography Reviews* **2009**, *15*, 57-83.
7. Sheldrick, G. M (**2008**). CELL_NOW, University of Göttingen, Germany.
8. Bruker (**2020**). SAINT, Bruker-AXS Inc., Madison, Wisconsin, USA.
9. Sheldrick, G. M (**2008**). TWINABS, University of Göttingen, Germany.
10. P. Pracht, F. Bohle and S. Grimme, *Phys Chem Chem Phys*, 2020, **22**, 7169-7192.
11. C. Bannwarth, S. Ehlert and S. Grimme, *Journal of Chemical Theory and Computation*, 2019, **15**, 1652-1671.
12. V. M. Ingman, A. J. Schaefer, L. R. Andreola and S. E. Wheeler, *WIREs Computational Molecular Science*, 2020, **11**, e1510.
13. A. J. Schaefer, V. M. Ingman and S. E. Wheeler, *J Comput Chem*, 2021, **42**, 1750-1754.