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Directed Polymorphism and Mechanofluorochromism of Conjugated Materials through Weak Non-Covalent Control

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ELECTRONIC SUPPLEMENTAL INFORMATION

Contents

1. Experimental methods

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. Melting points were measured on an SRS Digimelt MPA 160, and were recorded in triplicate to ensure melting point convergence, or by differential scanning calorimetry (DSC). All reactants and solvents were purchased from commercial suppliers and used without further purification, unless otherwise noted. UV/Visible absorbance spectra were acquired with a Varian Cary-100 spectrophotometer in double-beam mode using a solvent-containing cuvette for background subtraction spectra when acquiring solution spectra, or a clean glass slide when acquiring spectra of thin films. Fluorescence emission spectra were obtained by using a PTI Quantum Master 4 equipped with a 75 W Xe lamp and time-correlated single photon counting (TCSPC) module. All fluorescence spectra are corrected for the output of the lamp and the dependence of detector response to the wavelength of emitted light. Absorbance and fluorescence spectra of solutions were acquired using sample absorbances less than 0.1 to minimize inner filter effects.

Relative quantum yields were determined relative to quinine sulfate in 0.05 M sulfuric acid using the value $\varphi_f = 0.51$ reported by Tønnesen and Velapoldi[1] for all compounds in dilute chloroform solution. Fluorescence lifetimes were determined using a 403 nm pulsed LED light source for time correlated single photon counting (TCSPC) monitoring at 418 nm. Ludox (diluted in 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. Absorbance and fluorescence spectra of solutions were recorded in chloroform unless otherwise noted. Absorbance and fluorescence spectra of solids were recorded from films of materials that had been drop-cast from solutions in chloroform onto glass slides (1 mg / mL), which were evaporated slowly under a watch glass unless otherwise noted. Film samples were ground by rubbing with a spatula until the mechanofluorochromic shift was observed by fluorescence. Films were annealed on a Torrey-Pines hot plate for 15 minute cycles at specified temperatures.

Single crystal fluorescence spectroscopy (emission and excitation) probed samples from the same crystallization trial and demonstrating visually indistinguishable fluorescence as the crystal chosen for X-ray diffraction. Low-temperature single crystal diffraction data were collected on a Bruker D8 Quest diffractometer coupled to a Photon CMOS detector with Mo Kα radiation (λ = 0.71073 Å) from a fine-focused sealed tube performing φ and ω scans to a minimum of 86.5% data completeness to Theta = 25° and to 99.3% at a minimum Theta value of 22°. While data completeness for structures **CO2-1C** and **CO2-2A** achieves at least 99.6% to Theta = 25°, issues in data quality and absence of high resolution reflections for structures of propyl and butyl chain derivatives **CO2-3A**, **CO2-3B**, and **CO2-4A** lead to complications in completeness either in data completeness or sampled Theta values (see validation response forms in cif files). The structures were solved by direct methods using SHELXS-97[2] and refined against F^2 on all data by full-matrix least squares with SHELXL-2014[3,4] following established refinement strategies.[5] All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

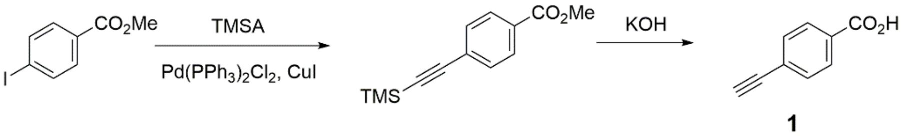
Differential scanning calorimetry (DSC) was performed on a TA Discovery DSC 250 equipped with a finned-air cooling system (FACS). Scans were recorded in TZero pans sealed with TZero lids at a rate of 10 °C/min. Pristine powder samples (1-3 mg) were loaded into pans. For ground powder experiments, 1-3 mg powders were ground upon glass slides with a spatula, then collected from the surface of the glass by scraping with a second, clean glass slide and loaded into pans. Thermograms were recorded within 5 minutes of initial grinding.

Time-Dependent Density Functional Theory (TD-DFT) calculations were carried out with the B3LYP functional using the Tamm-Dancoff approximation for the first 40 excited states at the 6-31G(d,p) level of theory using atomic coordinates derived from crystal structures. All DFT calculations were carried out using the Gaussian 09 software package.[6]

Single crystals in crystal-to-crystal studies were heated on a Torrey-Pines Echotherm HP60 Programmable hotplate at specified heating rates and temperatures. Fluorescence images and videos were recorded on a AmScope MA1000 10MP digital microscope camera with UV exposure from a handheld UV lamp (λ = 280 nm). Software settings for image capture were as follows: Exposure = 6, Gain = 6, Gamma = 0, default contrast, default saturation, color enhancement applied, no color balance modification. For visual clarity, photographs were edited in Adobe Photoshop using the following corrections with Brightness/Contrast and Vibrance tools: Brightness = +50, Contrast = +100, Vibrance = +0, Saturation = +80.

WAXS scans were carried out at Brookhaven National Laboratory NSLS-II on the Life Science X-ray Scattering beamline 16-ID using a wavelength of 0.9178 Å. Single crystals, for which representative samples were structurally confirmed by SCXRD and thermally treated prior to measurement, were mounted on clear adhesive tape and rastered over the beam, recording 11 scans per sample to minimize missing reflections due to preferred orientations. For a set of variable-temperature measurements, selected crystals all originated from a single recrystallization batch confirmed by SCXRD. Similarly prepared crystal samples were separately measured by PXRD at University of Connecticut (UConn) on a D2 Phaser instrument using line-source Cu-Kα radiation λ = 1.54184 Å, recording from 5 - 40° 2θ using a step size of 0.2° and integration time of 0.5 s for samples mounted on a Si wafer to minimize background. For these PXRD measurements, samples were measured at room temperature, then heated through the transition temperature and measured again. For consistency, all plots of X-ray scattering data are presented with 2-Theta values adjusted for Cu radiation λ = 1.54184 Å.

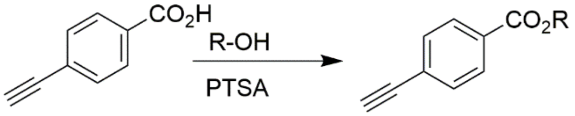
2. Synthesis



1

Intermediate 4-ethynylbenzoic acid **1** was synthesized according to previously reported methods through Sonogashira coupling of commercially available methyl 4-iodobenzoate with trimethylsilylacetylene, followed by deprotection of the methyl ester and TMS group with excess 2 M potassium hydroxide in methanol.[7]

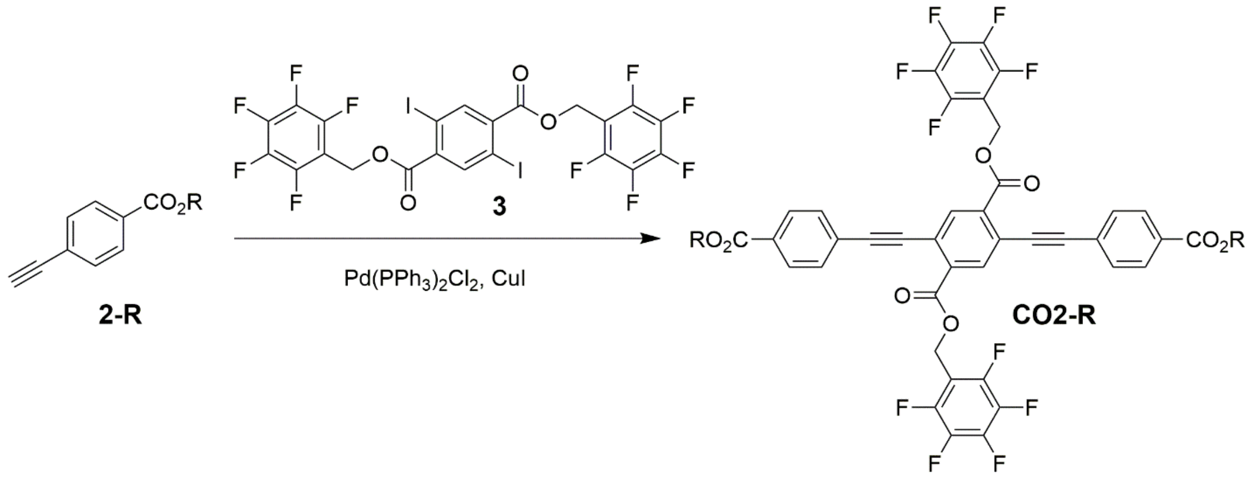
General Esterification Procedure (2-R)



1 **2-R**

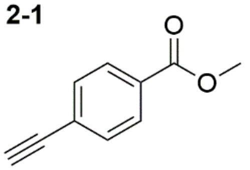
For compounds **2-2** through **2-8**, 4-ethynylbenzoic acid **1** (1 eq) and para-toluenesulfonic acid (0.5 eq) were added to a round bottom flask equipped with condenser and stirred neat in excess R-OH at elevated temperature for 24 – 48 h. Upon reaction completion as indicated by TLC, the mixture was cooled to room temperature and excess R-OH was removed by distillation or evaporation *in vacuo*. The resulting residue was dissolved in dichloromethane, washed with aqueous sodium bicarbonate, water, and brine. The combined organic layers were dried over magnesium sulfate, filtered, and evaporated *in vacuo*. The resulting oil was purified by flash chromatography (dichloromethane:hexanes) to give the product **2-R** as a colorless oil.

General Sonogashira Procedure (CO2-R)



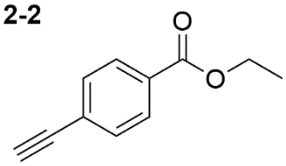
2,5-diiodoterephthalate intermediate **3** (1 eq, synthesized according to previously reported methods),[8] Cl$_2$Pd(PPh$_3$)$_2$ (5-10 mol%), and CuI (5-10 mol%) were added to a round bottom flask equipped with condenser and the atmosphere was evacuated and replaced with argon. The solids were dissolved in argon-sparged 1:1 (vol/vol) THF:NEt$_3$ and stirred at room temperature. In an air-free flask, **2-R** (2 eq) was dissolved in a minimum volume of 1:1 (vol/vol) argon-sparged THF:NEt$_3$ and transferred via syringe to the reaction mixture. The mixture was stirred at 60 °C for a minimum of 16 h. Upon reaction completion as indicated by a single fluorescent blue spot in TLC, the mixture was cooled to room temperature, filtered over a plug of Celite, and evaporated *in vacuo*. The resulting solid was purified by flash chromatography (dichloromethane:hexanes) followed by recrystallization to give the final product as a colorless crystalline solid with violet, blue, and/or green fluorescence.

2-1



Synthesis of this compound is previously reported.[7]

2-2

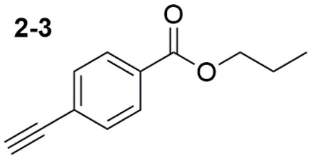


Compound **2-2** was synthesized according to the General Esterification Procedure using 145 mg **1** (0.992 mmol) and 211 mg PTSA (1.11 mmol, 1.1 eq) in 20 mL ethanol. The mixture was stirred 48 h at 60 °C and excess ethanol was removed by evaporation in vacuo upon reaction completion. After aqueous workup, the resulting oil was purified by flash chromatography (1:3 dichloromethane:hexanes) giving 122 mg oil in 69% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 3.25 (s, 1H), 1.42 (t, J = 7.1 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.0, 132.0, 129.4, 126.6, 82.9, 90.0, 61.2, 14.3 in agreement with the literature.[9]

2-3

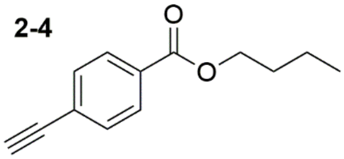


Compound **2-3** was synthesized according to the General Esterification Procedure using 125 mg **1** (0.855 mmol) and 64 mg PTSA (0.33 mmol, 0.4 eq) in 8 mL 1-propanol. The mixture was stirred 41 h at 95 °C and excess 1-propanol was removed by evaporation. After aqueous workup, the resulting oil was purified by flash chromatography (1:3 dichloromethane:hexanes) giving 128 mg oil in 80% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 4.31 (t, J = 6.7 Hz, 2 H), 3.25 (s, 1H), 1.82 (sextet, J = 7.1 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.0, 132.1, 130.5, 129.4, 126.6, 82.9, 79.9, 66.8, 22.1, 10.5.

2-4

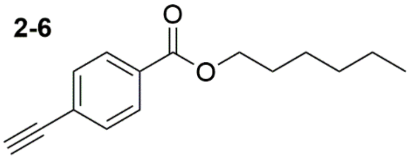


Compound **2-4** was synthesized according to the General Esterification Procedure using 156 mg **1** (1.07 mmol) and 106 mg PTSA (0.557 mmol, 0.5 eq) in 30 mL 1-butanol. The mixture was stirred 66 h at 80 °C and excess 1-butanol was removed by evaporation . After aqueous workup, the resulting oil was purified by flash chromatography (1:3 dichloromethane:hexanes) giving 118 mg oil in 55% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2 H), 4.35 (t, J = 6.6 Hz, 2H), 3.25 (s, 1H), 1.77 (quintet, 7.1 Hz, 2H), 1.50 (sextet, J = 7.7 Hz, 2H), 1.00 (t, J = 7.4 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.0, 132.0, 130.5, 129.4, 126.6, 82.9, 80.0, 65.1, 30.7, 19.3, 13.7 in agreement with the literature.[7]

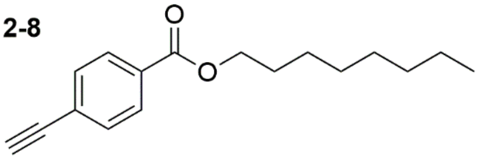
2-6



Compound **2-6** was synthesized according to the General Esterification Procedure using 91 mg **1** (0.25 mmol) and 47 mg PTSA (0.24 mmol, 0.4 eq) in 10 mL 1-hexanol. The mixture was stirred 22 h at 115 °C and excess 1-hexanol was removed by distillation upon reaction completion. After aqueous workup, the resulting oil was purified by flash chromatography (1:4 dichloromethane:hexanes) giving 98 mg oil in 68% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.97 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 4.29 (t, J = 6.6 Hz, 2H), 3.21 (s, 1H), 1.29 (m, 6H), 0.88 (t, J = 6.5 Hz, 3H) in agreement with the literature.[10]

2-8

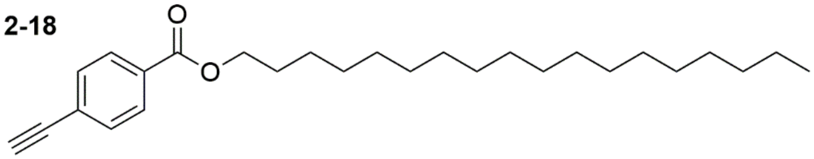


Compound **2-8** was synthesized according to the General Esterification Procedure using 166 mg **1** (1.14 mmol) and 89 mg PTSA (0.47 mmol, 0.4 eq) in 35 mL 1-octanol. The mixture was stirred 42 h at 90 °C and excess 1-octanol was removed by distillation upon reaction completion. After aqueous workup, the resulting oil was purified by flash chromatography (1:3 dichloromethane:hexanes, then gradient to 1:2 dichloromethane:hexanes) giving 74 mg oil in 25% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.91 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 4.24 (t, J = 7.2 Hz, 2H), 3.15 (s, 1H), 1.68 quintet, J = 7.3 Hz, 2H), 1.35 (quintet, J = 7.2 Hz, 2H), 1.21 (m, 8H), 0.81 (t, J = 7.2 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.0, 132.0, 130.6, 129.4 126.6, 82.9, 79.9, 65.4, 31.8, 29.2, 29.1, 28.7, 26.0, 22.6, 14.1

2-18

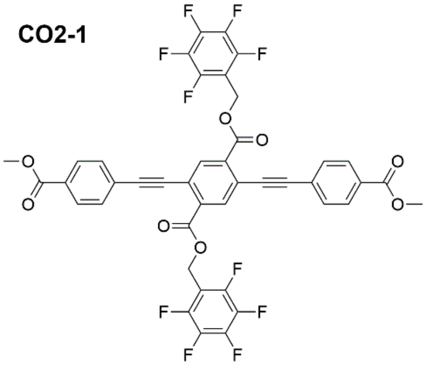


The procedure for **2-18** was adapted from the literature.[11] 105 mg compound **1** (0.718 mmol), 198 mg (0.960 mmol, 1.3 eq) N,N'-dicyclohexylcarbodiimide, 12 mg (0.098 mmol, 0.1 eq) 4-dimethylaminopyridine, and 250 mg (0.924 mmol, 1.3 eq) 1-octadecanol were added to an oven-dried 50 mL round bottom flask with condenser. The solids were dissolved in 15 mL anhydrous dichloromethane and stirred 24 h at room temperature. Upon reaction completion, the mixture was filtered over Celite to remove insoluble solids, and dried *in vacuo*. The resulting oil was purified by flash chromatography (1:4 EtOAc:Hexanes) giving 254 mg orange oil in 64% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 4.34 (t, J = 6.7 Hz, 2H), 3.25 (s, 1H), 1.78 (quintet, J = 7.1 Hz, 2H), 1.46 (quintet, J = 7.2 Hz, 2H), 1.41-1.22 (broad m, 28 H), 0.91 (t, J = 7.0 Hz, 3H)

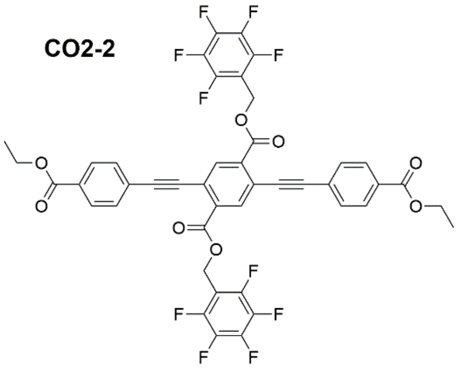
^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.0, 132.0, 130.6, 129.4, 126.6, 82.9, 79.9, 65.4, 34.9, 21.9, 29.7, 29.6, 20.5, 29.4, 29.3, 28.7, 26.0, 25.5, 22.7, 14.1 (unresolved peaks in alkyl region)

CO2-1



Synthesis of this molecule has been previously reported.[8]

CO2-2



Compound **CO2-2** was synthesized according to the General Sonogashira Procedure using 100 mg **3** (0.13 mmol), 58 mg (0.33 mmol, 2.6 eq) **2-2**, 4 mg (0.006 mmol, 4 mol%) $Cl_2Pd(PPh_3)_2$, 2 mg (0.01

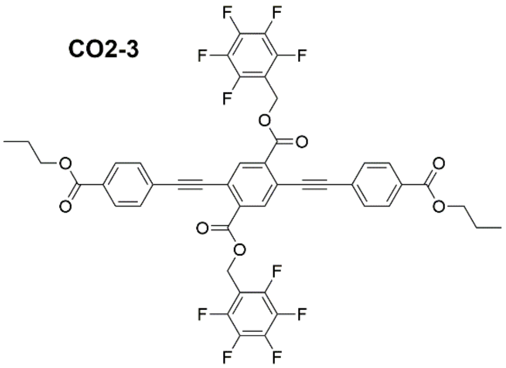
mmol, 10 mol%) CuI dissolved in 12 mL argon-sparged 1:1 (vol/vol) THF:NEt_3. The mixture was stirred 24 h at 60 °C, and after work-up was purified by flash chromatography (1:3 dichloromethane:hexanes with 1% NEt_3, then gradient to dichloromethane) followed by recrystallization from chloroform/hexanes to give 95 mg crystalline solid in 85% yield (melting point = 185 – 186 °C). HRMS (ESI TOF) calculated for $C_{44}H_{24}F_{10}O_8$ $[M+H]^+$: 871.1390 found $[M+H]^+$: 871.1390

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.23 (s, 2H), 8.07 (d, J = 8.5 Hz, 4H), 7.56 (d, J = 8.5 Hz, 4H), 5.52 (s, 4H), 4.44 (q, J = 7 Hz, 4H), 1.44 (t, J = 7.5 Hz, 6H)

^{19}F NMR (470 MHz, $CDCl_3$) δ: -141.4 (q, J = 10 Hz), -151.5 (t, J = 21 Hz), -161.0 (dt, J_1 = 21 Hz, J_2 = 7 Hz)

^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.9, 163.8, 145.7 (d, J = 256 Hz), 142.0 (d, J = 233 Hz), 137.5 (d, J = 264 Hz), 136.4, 135.2, 134.5, 133.5, 130.8, 126.8, 123.2, 108.8 (t, J = 15 Hz), 96.6, 89.2, 61.3, 54.5, 14.3

CO2-3



Compound **CO2-3** was synthesized according to the General Sonogashira Procedure using 180 mg **3** (0.23 mmol), 128 mg (0.68 mmol, 2.9 eq) **2-3**, 5 mg (0.007 mmol, 3 mol%) $Cl_2Pd(PPh_3)_2$, 6 mg (0.03 mmol, 10 mol%) CuI dissolved in 15 mL argon-sparged 1:1 (vol/vol) THF:NEt_3. The mixture was stirred 17 h at 60 °C, then purified over a plug of silica gel eluting with dichloromethane. The eluent was evaporated, and the resulting solid was recrystallized from chloroform/methanol to give 197 mg crystalline solid in 95% yield (melting point = 158 – 159 °C).

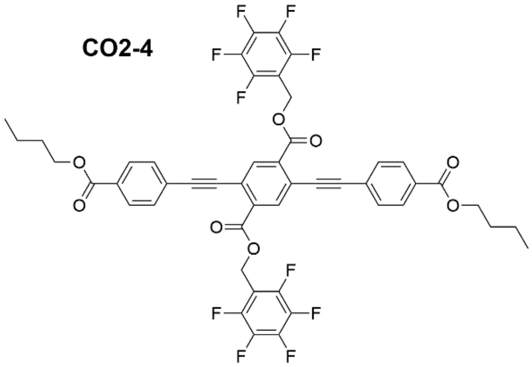
HRMS (ESI TOF) calculated for $C_{46}H_{28}F_{10}O_8$ $[M+H]^+$: 898.1624 found $[M+H]^+$: 898.1613.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.23 (s, 2H), 8.07 (d, J = 8.5 Hz, 4H), 7.56 (d, J = 8.5 Hz, 4H), 5.52 (s, 4H), 4.34 (t, J = 6.5 Hz, 4H), 1.84 (sextet, J = 7Hz, 4H), 1.08 (t, J = 7.5 Hz, 6H)

^{19}F NMR (470 MHz, $CDCl_3$) δ: -141.4 (q, J = 10 Hz), -151.5 (t, J = 21 Hz), -161.0 (dt, J_1 = 21 Hz, J_2 = 7 Hz)

^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.9, 163.8, 145.7 (d, J = 252 Hz), 141.9 (d, J = 257 Hz), 137.5 (d, J = 252 Hz), 136.4, 133.5, 131.4, 130.76, 129.5, 126.7, 123.2, 108.7 (t, J = 17 Hz), 96.6, 89.2, 66.8, 54.5, 22.1, 10.5

CO2-4



Compound **CO2-4** was synthesized according to the General Sonogashira Procedure using 89 mg **3** (0.11 mmol), 99 mg (0.49 mmol, 4.2 eq) **2-4**, 24 mg (0.034 mmol, 30 mol%) $Cl_2Pd(PPh_3)_2$, 7 mg (0.04 mmol, 30 mol%) CuI dissolved in 12 mL argon-sparged 1:1 (vol/vol) THF:NEt_3. The mixture was stirred 20 h at 60 °C, and after work-up was purified by flash chromatography (1:2 dichloromethane:hexanes with 1% NEt_3, then gradient to dichloromethane) followed by recrystallization from chloroform/methanol to give 32 mg crystalline solid in 30% yield (melting point = 148 – 149 °C).

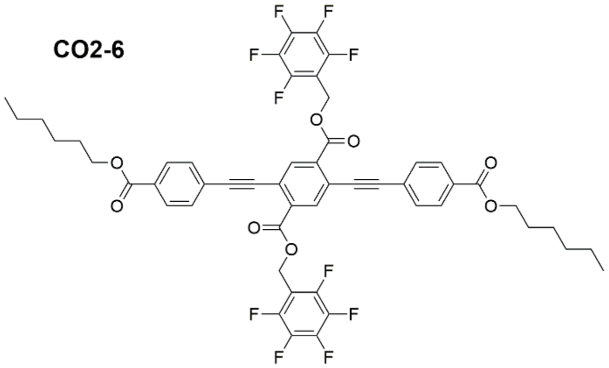
HRMS (ESI TOF) calculated for $C_{48}H_{32}F_{10}O_8$ [M^+]: 926.1937 found [M^+]: 926.1927

^1H NMR (500 MHz, $CDCl_3$) δ: 8.24 (s, 2H), 8.06 (d, 4H, J = 8.8 Hz), 7.56 (d, 4H, J = 8.6 Hz), 5.52 (s, 4H, CH2), 4.38 (t, 4H, J = 6.5), 1.81 (sextet, 4H, J = 6.5Hz), 1.53 (sextet, 4H, J = 7.5 Hz), 1.03 (t, J = 7.4 Hz, 6H)

^{19}F NMR (470 MHz, $CDCl_3$) δ: -141.4 (q, J = 10 Hz), -151.5 (t, J = 21 Hz), -161.0 (dt, J_1 = 21 Hz, J_2 = 8 Hz)

^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.9, 163.8, 145.8 (d, J=255 Hz), 141.9 (d, J = 257 Hz), 137.6 (d, J = 264 Hz), 136.4, 133.5, 131.4, 130.8, 129.5, 126.8, 123.2, 108.7 (t, J = 18 Hz), 96.6, 89.2, 65.2, 54.5, 30.8, 19.3, 13.8

CO2-6



Compound **CO2-6** was synthesized according to the General Sonogashira Procedure using 123 mg **3** (0.16 mmol), 85 mg (0.37 mmol, 2.3 eq) **2-6**, 3 mg (0.004 mmol, 3 mol%) $Cl_2Pd(PPh_3)_2$, 4 mg (0.02 mmol, 10 mol%) CuI dissolved in 15 mL argon-sparged 1:1 (vol/vol) THF:NEt_3. The mixture was stirred 16 h at 60 °C, and after work-up was purified over a plug of silica gel, eluting with dichloromethane. The eluent was evaporated *in vacuo*, and the resulting solid was recrystallized from chloroform/methanol to give 44 mg crystalline solid in 28% yield (melting point = 128 – 130 °C).

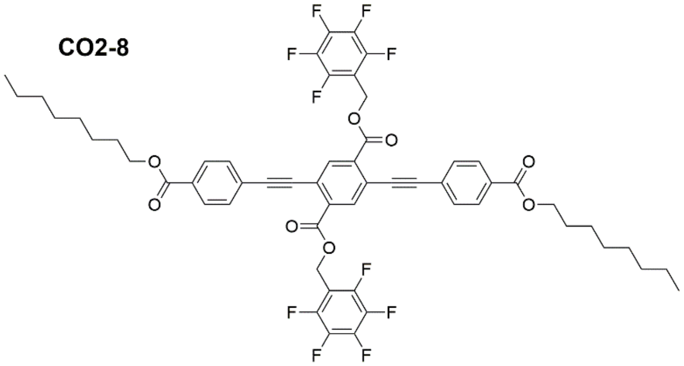
HRMS (ESI TOF) calculated for $C_{52}H_{40}F_{10}O_8$ [M^+]: 982.2564, found [M^+]: 982.2531

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.24 (s, 2H), 8.07 (d, J = 8.5 Hz, 4H), 7.56 (d, J = 8.5 Hz, 4H), 5.52 (s, 4H), 4.37 (t, J = 6.7 Hz, 4H), 1.82 (quintet, J = 7.1 Hz, 4H), 1.48 (quintet, J = 7.5, 4H), 1.38 (m, 8H), 0.95 (t, J = 7.1 Hz, 6H)

^{19}F NMR (470 MHz, $CDCl_3$) δ: -141.4 (q, J = 10 Hz), -151.5 (t, J = 21 Hz), -161.0 (dt, J_1 = 21 Hz, J_2 = 7 Hz)

^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.9, 163.8, 145.7 (d, J = 256 Hz), 141.9 (d, J = 257 Hz), 137.6 (d, J = 257 Hz), 136.4, 133.5, 131.4, 130.8, 129.5, 126.8, 123.2, 108.8 (t, J = 18 Hz) 96.6, 89.2, 65.5, 54.5, 21.5, 28.7, 25.7, 22.6, 14.0

CO2-8



Compound **CO2-8** was synthesized according to the General Sonogashira Procedure using 128 mg **3** (0.17 mmol), 128 mg (0.50 mmol, 3.0 eq) **2-8**, 5 mg (0.007 mmol, 4 mol%) $Cl_2Pd(PPh_3)_2$, and 4 mg (0.02 mmol, 10 mol%) CuI dissolved in 12 mL argon-sparged 1:1 (vol/vol) THF:NEt_3. The mixture was stirred 18 h at 60 °C, and after work-up was purified by flash chromatography (1:1 dichloromethane:hexanes with 1% NEt_3, then gradient to 3:1 dichloromethane:hexanes) followed by recrystallization from chloroform/methanol to give 73 mg crystalline solid in 43% yield (melting point = 123 – 124 °C).

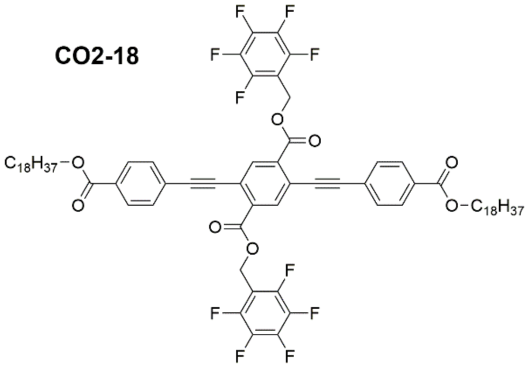
HRMS (ESI TOF) calculated for $C_{56}H_{48}F_{10}O_8$ [M^+]: 1038.3190 found [M^+]: 1038.3173

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.29 (s, 2H), 8.06 (d, J = 8.5 Hz, 4H), 7.56 (d, J = 8.6 Hz, 4H), 5.52 (s, 4H), 4.37 (t, J = 6.7 Hz, 4H), 1.81 (q, J = 7.2 Hz, 4H), 1.48 (q, J = 7.7 Hz, 4H), 1.41-1.28 (broad m, 16H), 0.92 (t, J = 6.5 Hz, 6H)

^{19}F NMR (470 MHz, $CDCl_3$) δ: -141.4 (q, J = 10 Hz), -151.5 (t, J = 21 Hz), -161.0 (dt, J_1 = 21 Hz, J_2 = 7 Hz)

^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.9, 163.8, 145.8 (d, J=255 Hz), 137.5 (d, J = 263 Hz), 138.5, 136.4, 131.4, 130.8, 129.5, 126.8, 132.2, 108.8 (t, J = 18 Hz), 96.6, 89.2, 65.5, 54.5, 31.8, 29.3, 28.7, 26.0, 22.7, 14.1

CO2-18



Compound **CO2-18** was synthesized according to the General Sonogashira Procedure using 98 mg **3** (0.126 mmol), 227 mg (0.569 mmol, 4.5 eq) **2-18**, 3 mg (0.004 mmol, 3 mol%) $Pd(PPh_3)_2Cl_2$, 3 mg (0.02 mmol, 10 mol%) CuI dissolved in 12 mL argon-sparged 1:1 (vol/vol) $THF:NEt_3$. The mixture was stirred 20 h at 60 °C, and after work-up was purified by FCC (1:6 EtOAc:Hexanes) followed by recrystallization from chloroform/methanol to give 128 mg crystalline solid in 77% yield [melting point = 106 °C (dec.)].

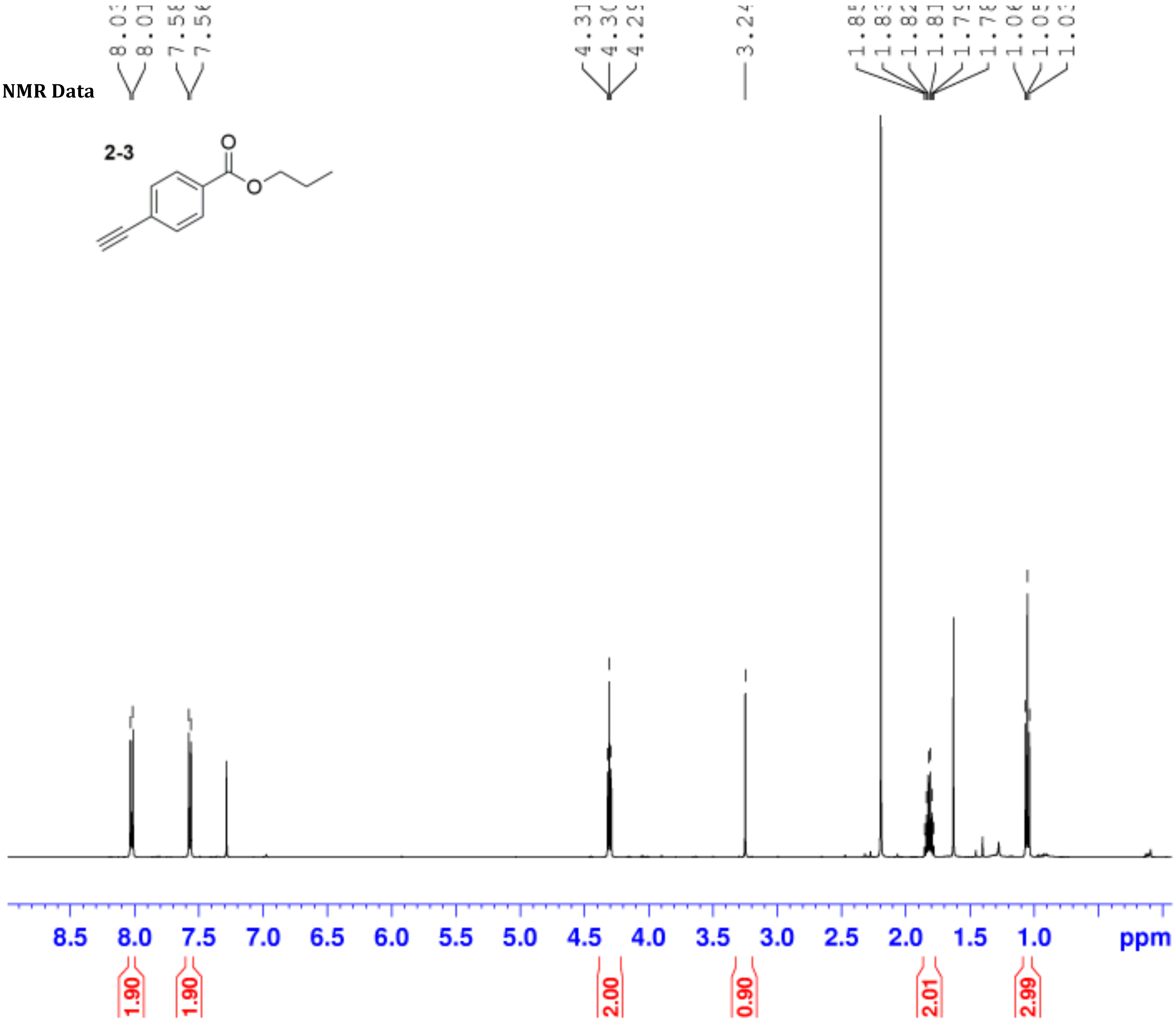
HRMS (ESI QTOF) calculated for $C_{76}H_{88}F_{10}O_8$ $[M+H]^+$: 1319.6398 found $[M+H]^+$: 1319.6460

^1H NMR (500 MHz, $CDCl_3$) δ: 8.23 (s, 2H), 8.06 (d, J = 8.3 Hz, 4H), 7.56 (d, J = 8.3 Hz, 4H), 5.52 (s, 4H), 4.37 (t, J = 6.5 Hz, 4H), 1.82 (quintet, J = 7.1 Hz, 4H), 1.47 (quintet, J = 7.2 Hz, 4H), 1.35-1.25 (broad m, 56 H), 0.90 (t, J = 6.9 Hz, 6H)

^{19}F NMR (470 MHz, $CDCl_3$) δ: -141.4 (q, J = 10 Hz), -151.5 (t, J = 21 Hz), -161.0 (dt, J_1 = 21Hz, J_2 = 7 Hz)

^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.9, 163.8, 136.4, 133.5, 131.4, 130.8, 129.5, 126.8, 123.2, 96.6, 89.2, 65.5, 54.5, 21.9, 29.7 (3 peaks), 29.6 (2 peaks), 29.4, 29.3, 28.7, 26.0, 22.7, 14.1 unresolved peaks, overlapping in alkyl region.

NMR Data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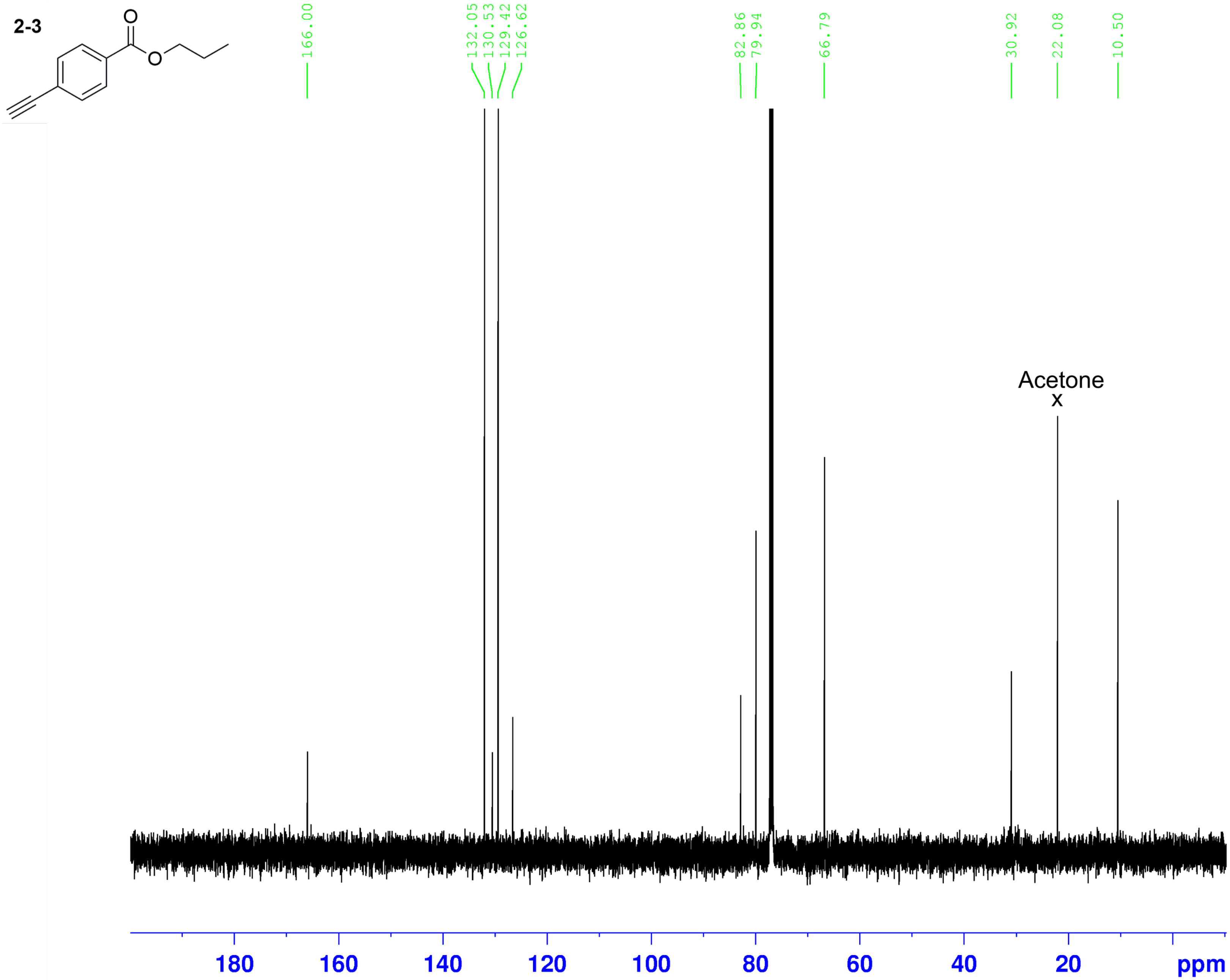
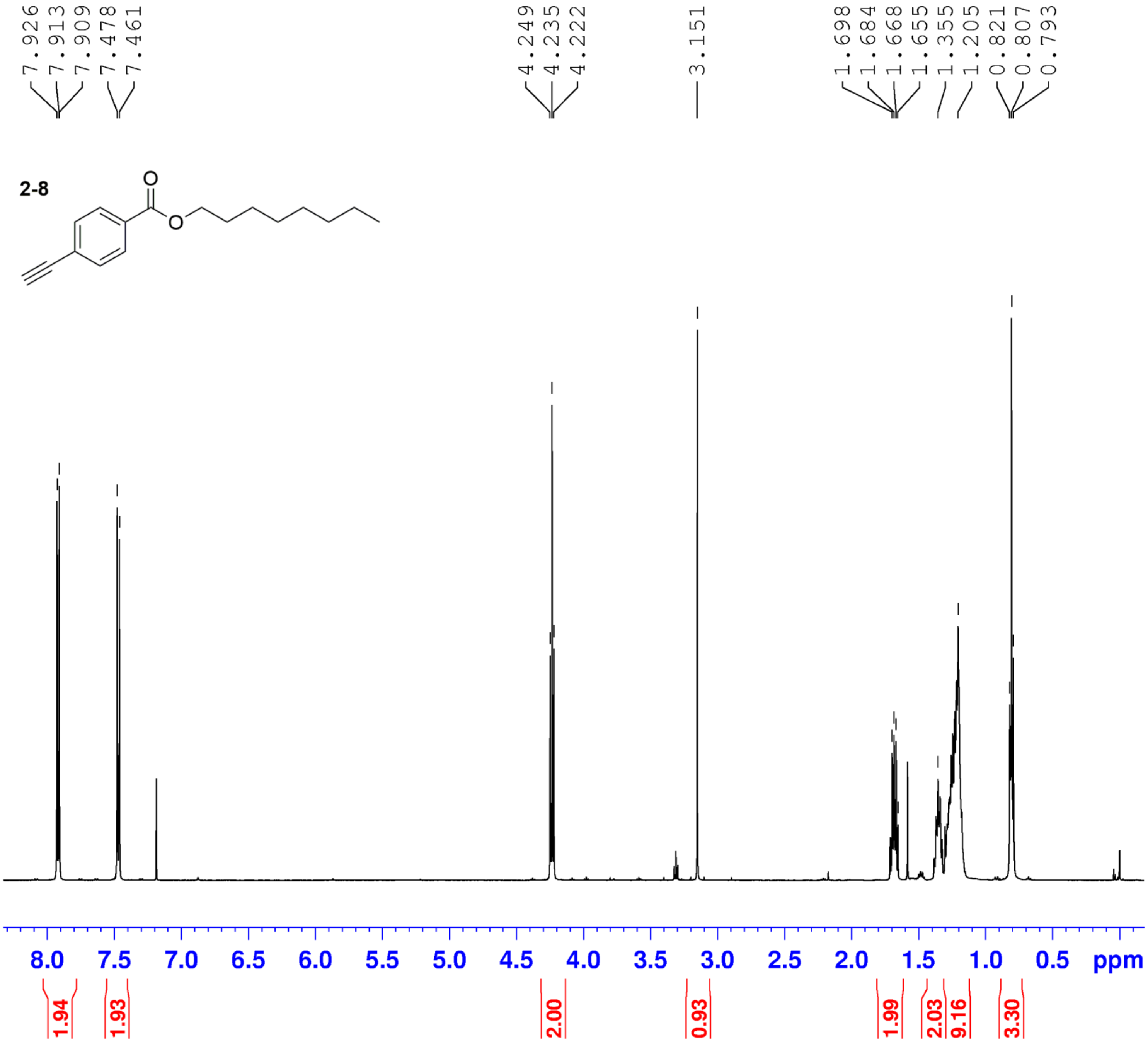
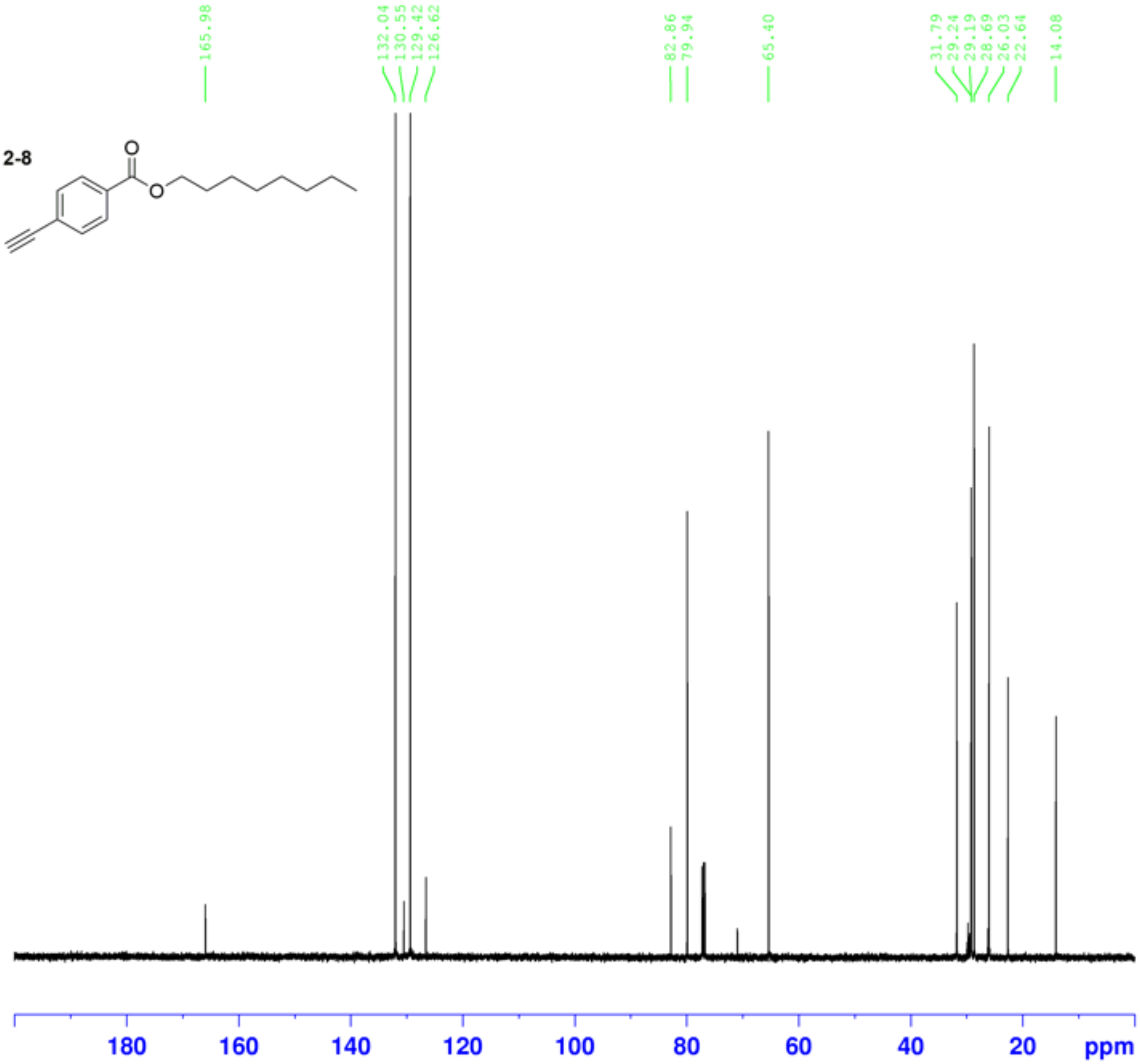
8.01
7.58
7.5
4.31
4.3
4.2
3.2
1.8
1.8
1.8
1.81
1.7
1.78
1.0
1.0
1.0
2-3
O
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.90
1.90
2.00
0.90
2.01
2.99

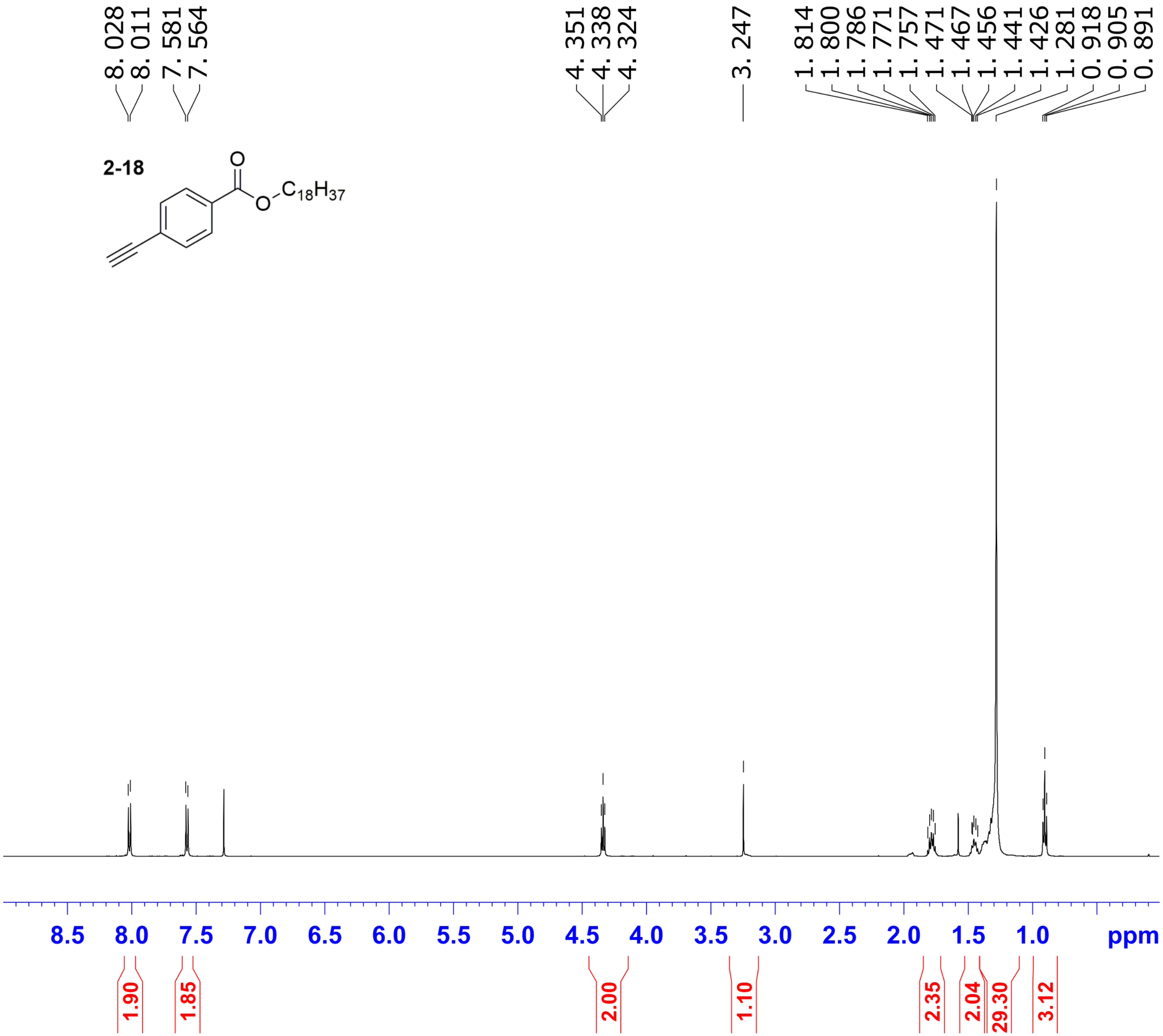
2-3


O
O
166.00
132.05
130.53
129.42
126.62
82.86
79.94
66.79
30.92
22.08
10.50
Acetone
x
180
160
140
120
100
80
60
40
20
ppm


2-8
O
O
7.926
7.913
7.909
7.478
7.461
4.249
4.235
4.222
3.151
1.698
1.684
1.668
1.655
1.355
1.205
0.821
0.807
0.793
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.94
1.93
2.00
0.93
1.99
2.03
9.16
3.30

2-8


165.98
132.04
130.55
129.42
126.62
82.86
79.94
65.40
31.79
29.24
29.19
28.69
26.03
22.64
14.08
O
O
180
160
140
120
100
80
60
40
20
ppm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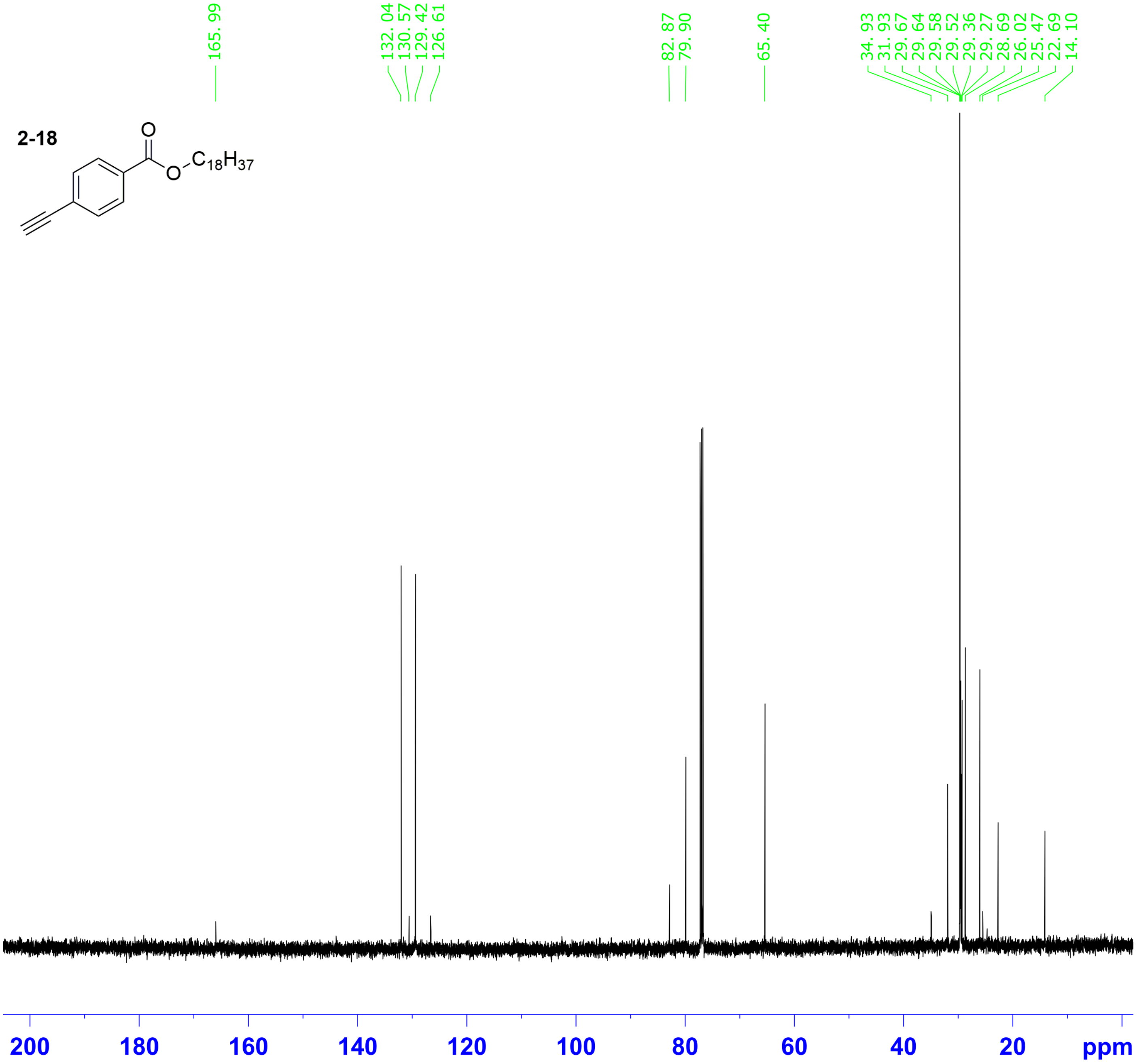
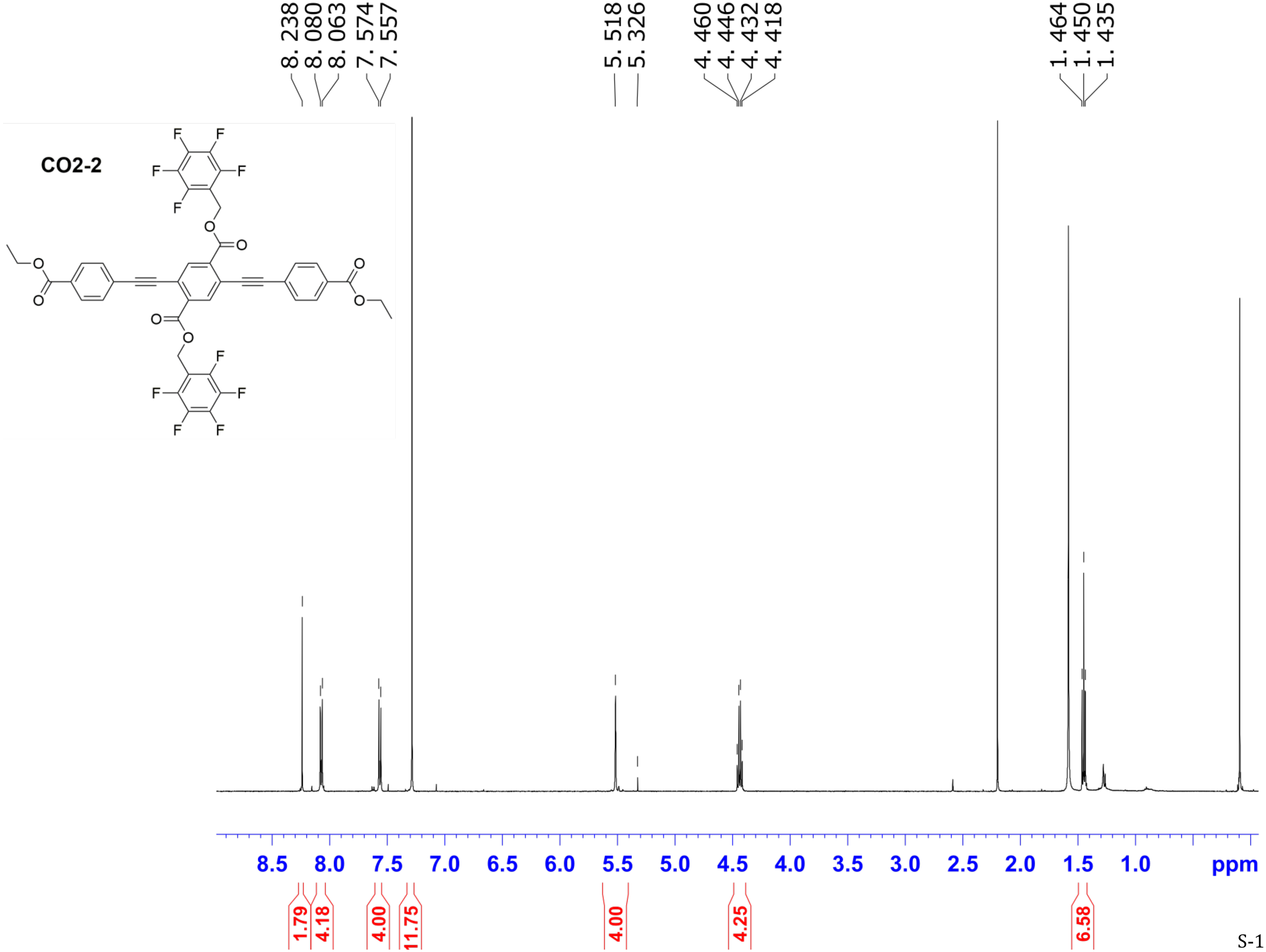
8.011
7.581
7.564
4.351
4.338
4.324
3.247
1.814
1.800
1.786
1.771
1.757
1.471
1.467
1.456
1.441
1.426
1.281
0.918
0.905
0.891
2-18
O
O
$C_{18}H_{37}$
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.90
1.85
2.00
1.10
2.35
2.04
29.30
3.12

2-18

O
O
C18H37



165.99
132.04
130.57
129.42
126.61
82.87
79.90
65.40
34.93
31.93
29.67
29.64
29.58
29.52
29.36
29.27
28.69
26.02
25.47
22.69
14.10
200
180
160
140
120
100
80
60
40
20
ppm



CO2-2

8.238
8.080
8.063
7.574
7.557
5.518
5.326
4.460
4.446
4.432
4.418
1.464
1.450
1.435
F
F
F
F
F
O
O
O
O
O
O
O
O
F
F
F
F
F
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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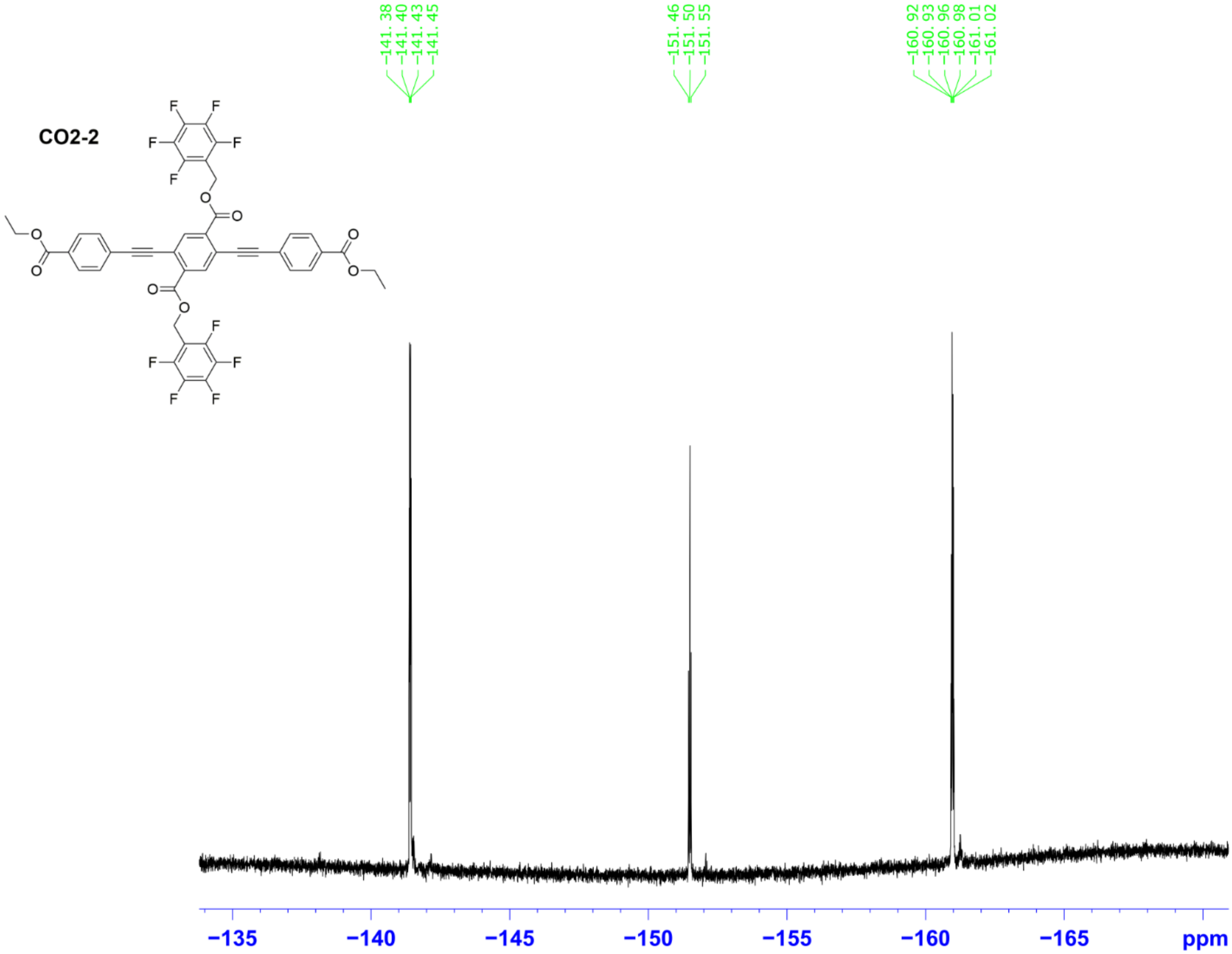
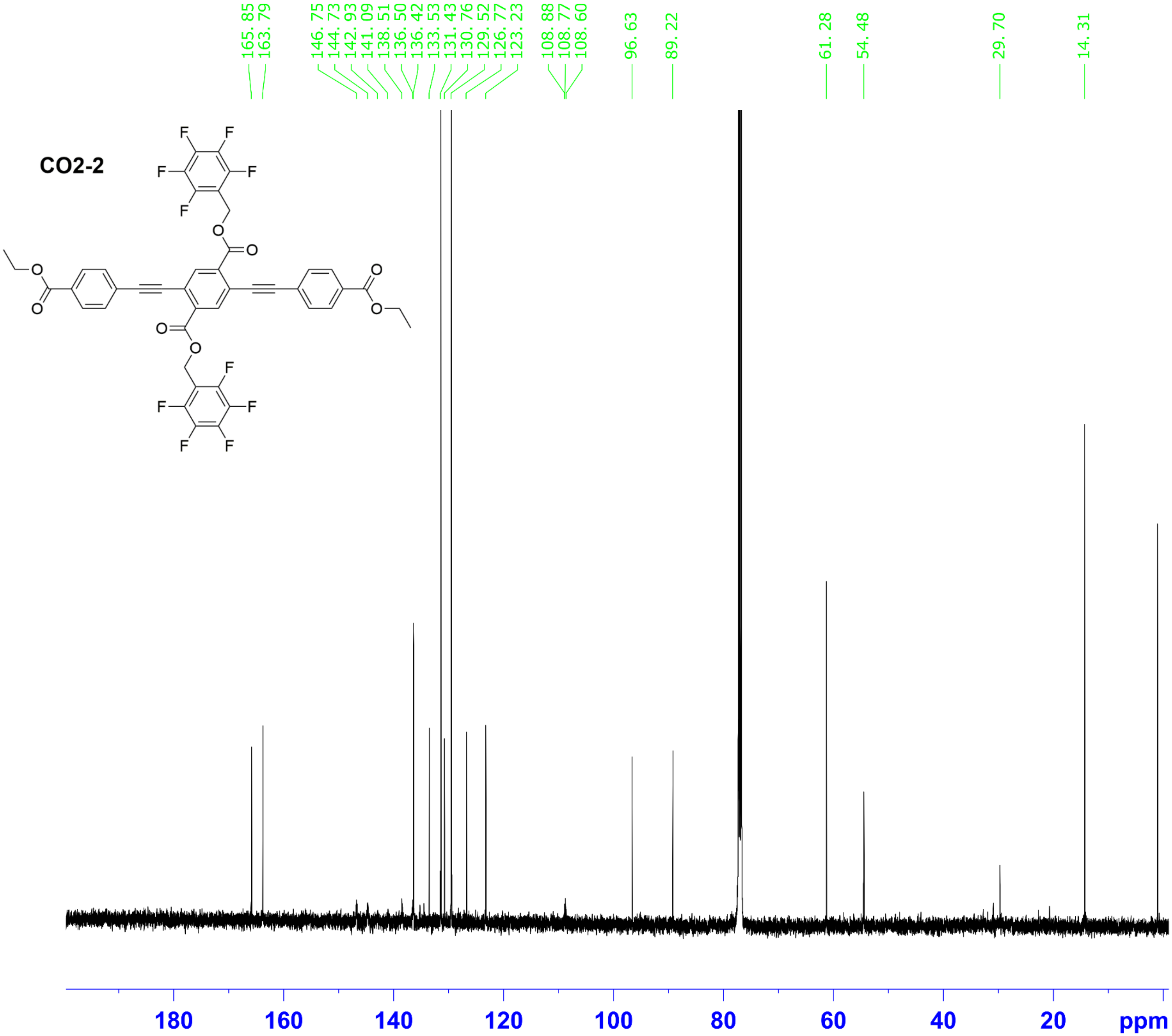
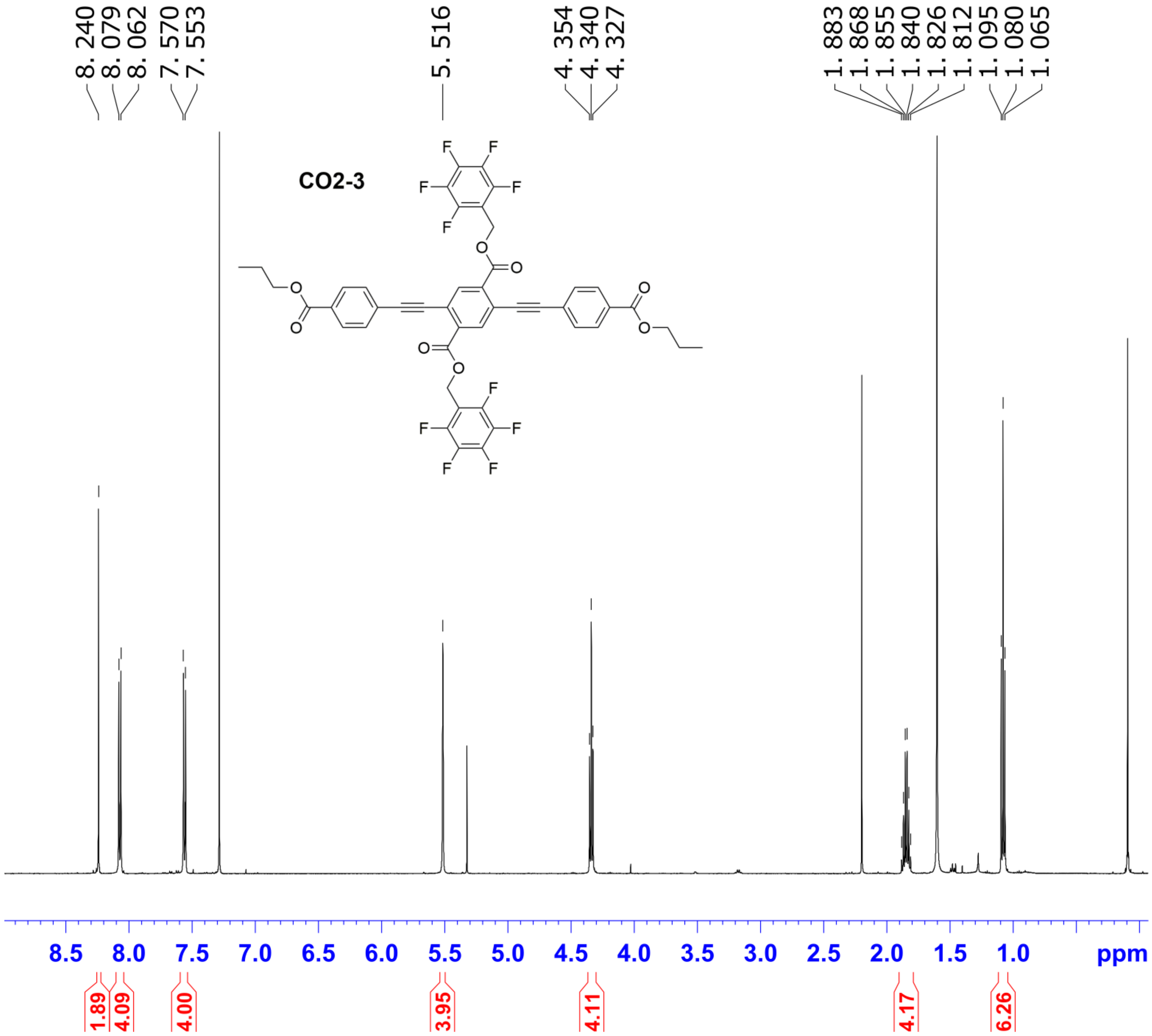
4.18
4.00
11.75
4.00
4.25
6.58

CO2-2

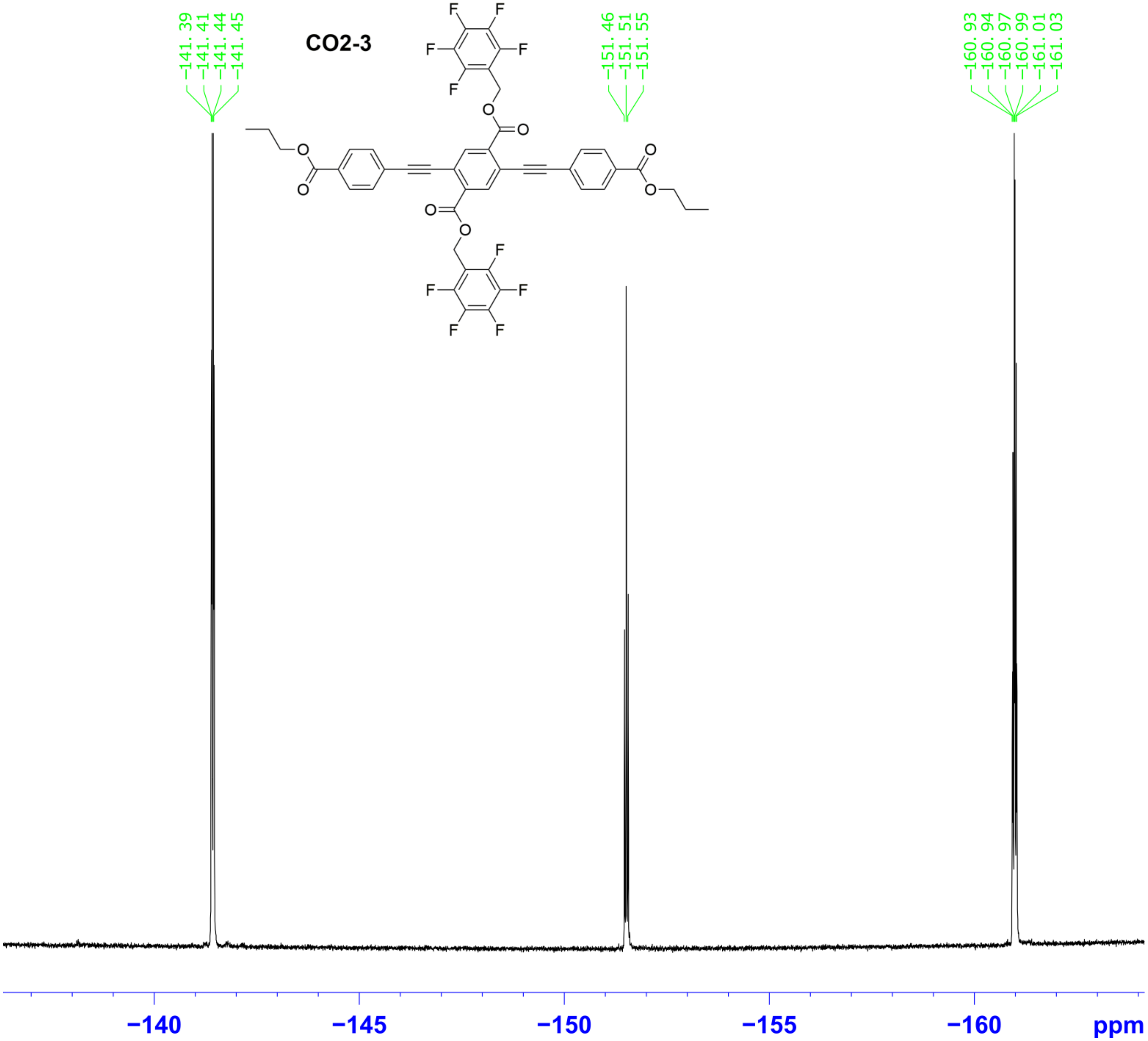


-141.38
-141.40
-141.43
-141.45
-151.46
-151.50
-151.55
-160.92
-160.93
-160.96
-160.98
-161.01
-161.02
F
O
-135
-140
-145
-150
-155
-160
-165
ppm


CO2-2
165.85
163.79
146.75
144.73
142.93
141.09
138.51
136.50
136.42
133.53
131.43
130.76
129.52
126.77
123.23
108.88
108.77
108.60
96.63
89.22
61.28
54.48
29.70
14.31
180
160
140
120
100
80
60
40
20
ppm
F
O

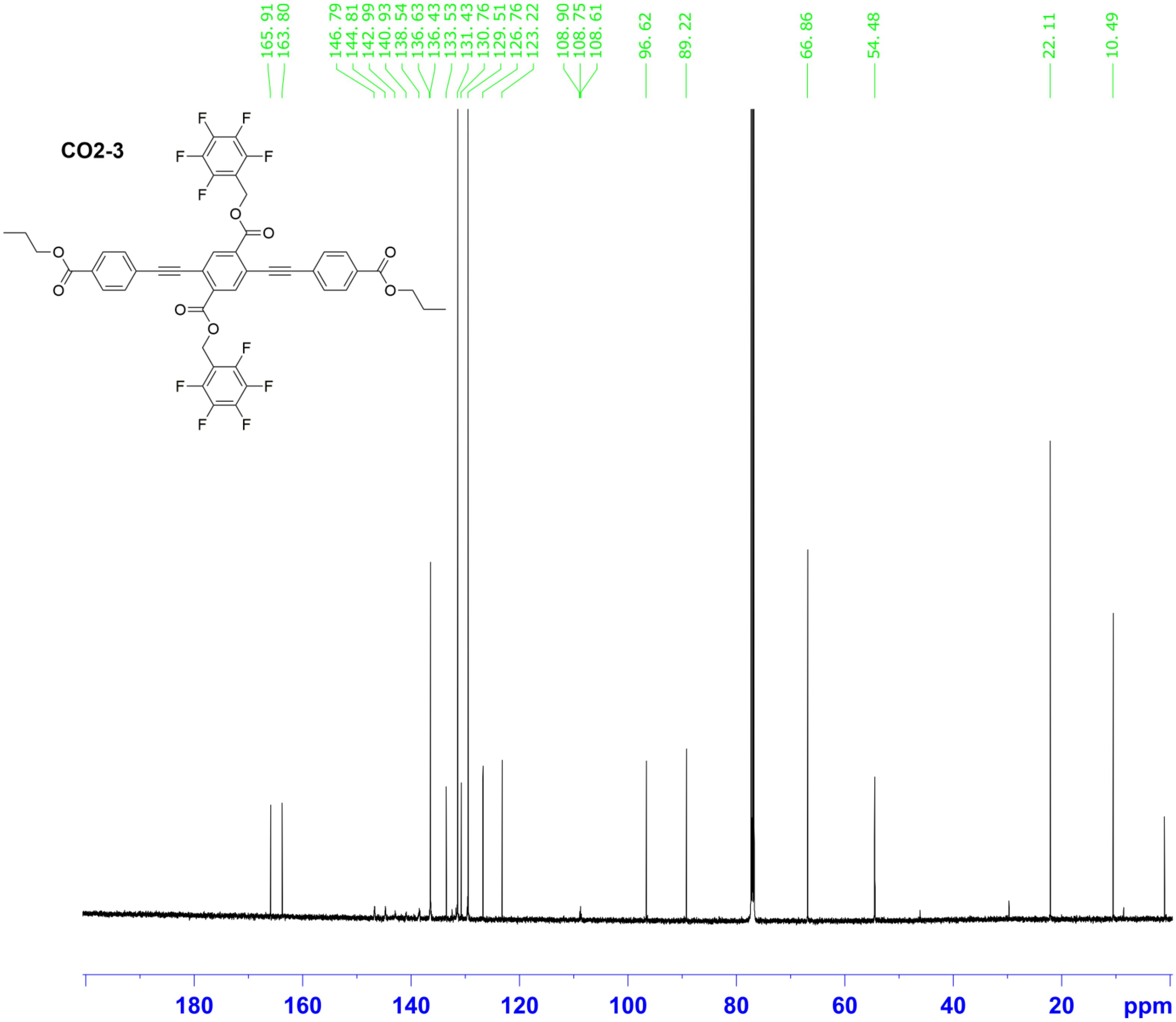

8.240
8.079
8.062
7.570
7.553
5.516
4.354
4.340
4.327
1.883
1.868
1.855
1.840
1.826
1.812
1.095
1.080
1.065
CO2-3
F
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.89
4.09
4.00
3.95
4.11
4.17
6.26

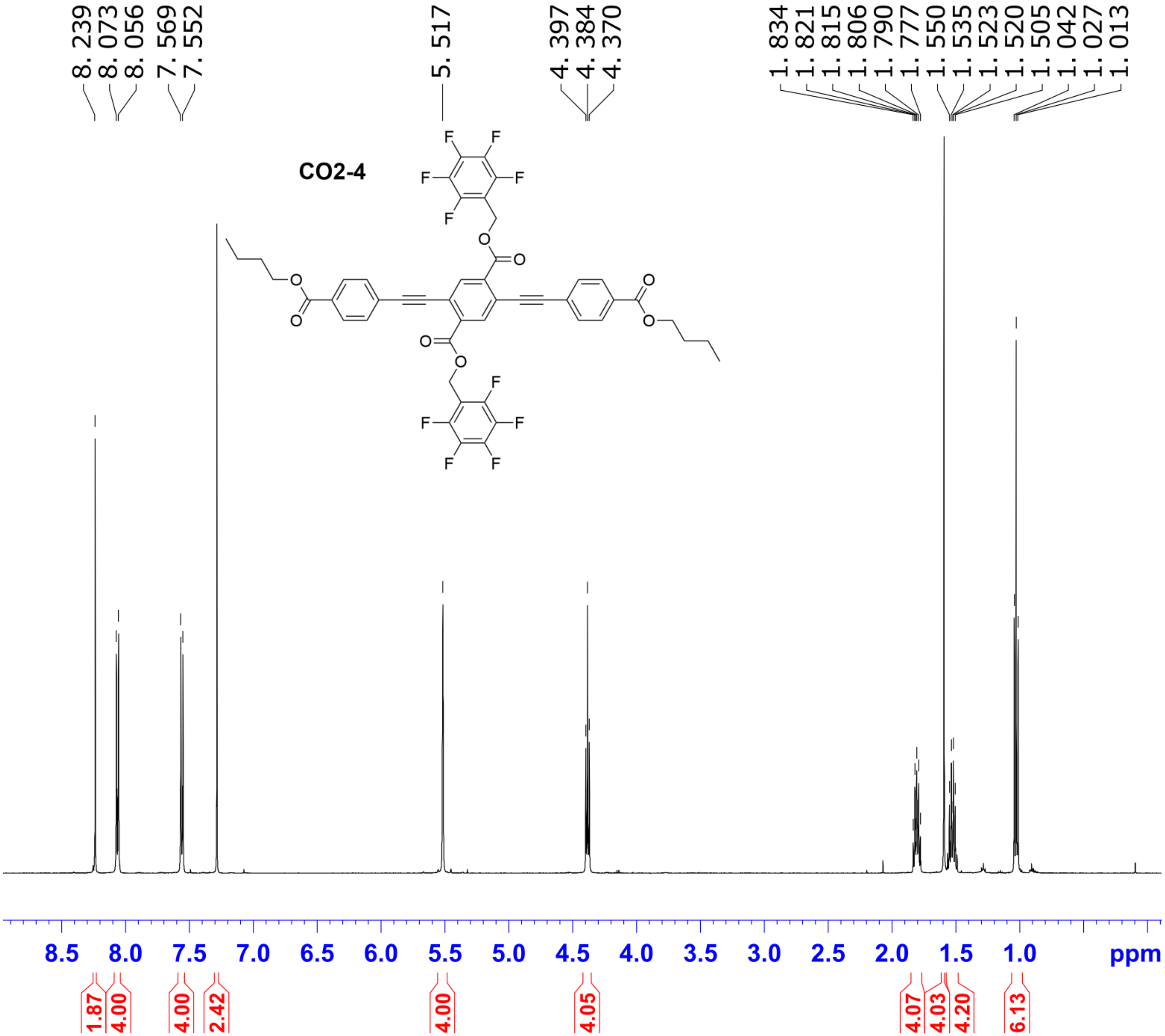
CO2-3



-141.39
-141.41
-141.44
-141.45
-151.46
-151.51
-151.55
-160.93
-160.94
-160.97
-160.99
-161.01
-161.03
F
O
−140
−145
−150
−155
−160
ppm

CO2-3


165.91
163.80
146.79
144.81
142.99
140.93
138.54
136.63
136.43
133.53
131.43
130.76
129.51
126.76
123.22
108.90
108.75
108.61
96.62
89.22
66.86
54.48
22.11
10.49
F
O
180
160
140
120
100
80
60
40
20
ppm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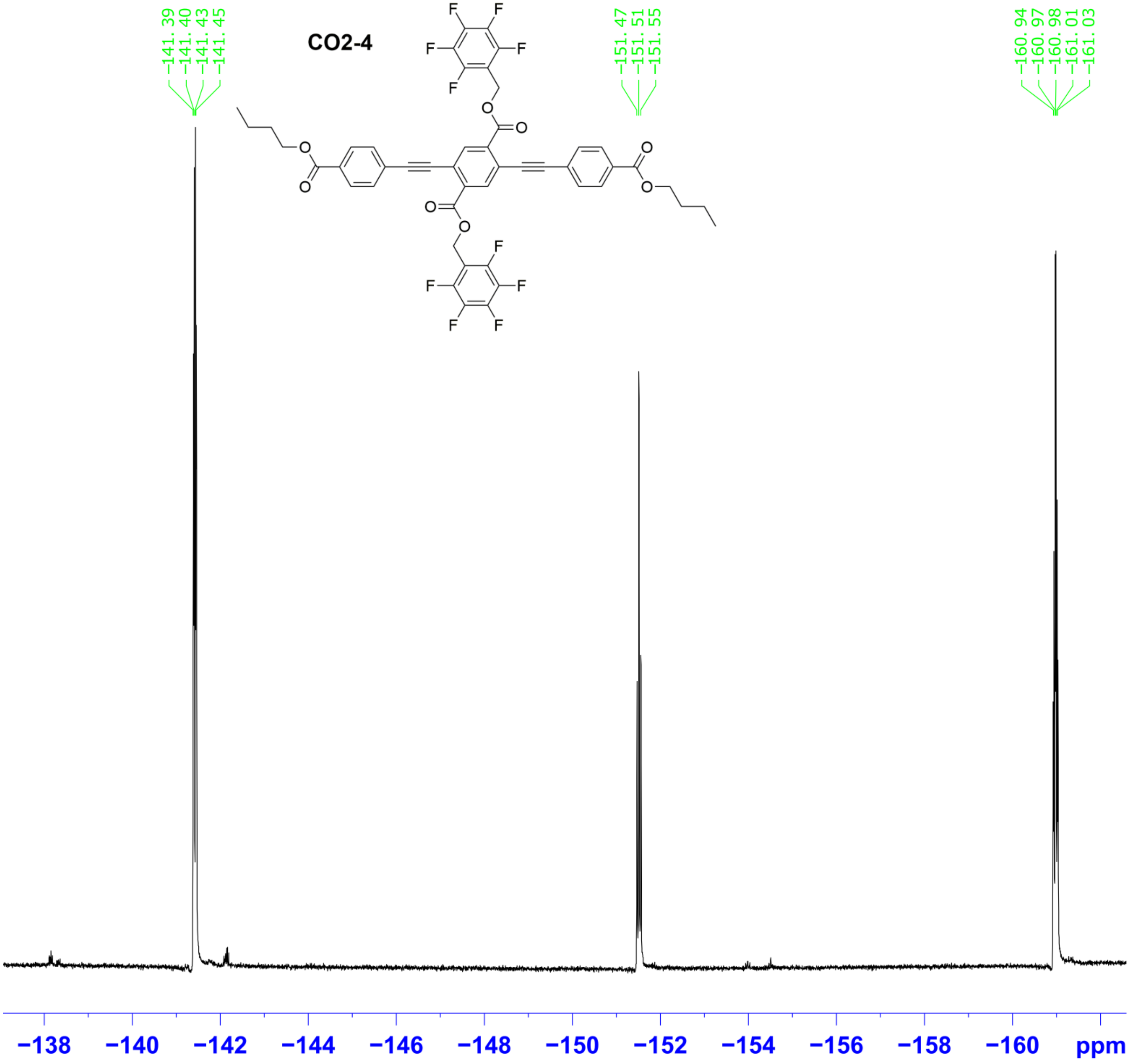
8.073
8.056
7.569
7.552
5.517
4.397
4.384
4.370
1.834
1.821
1.815
1.806
1.790
1.777
1.550
1.535
1.523
1.520
1.505
1.042
1.027
1.013
CO2-4
F
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.87
4.00
4.00
2.42
4.00
4.05
4.07
4.03
4.20
6.13


CO2-4
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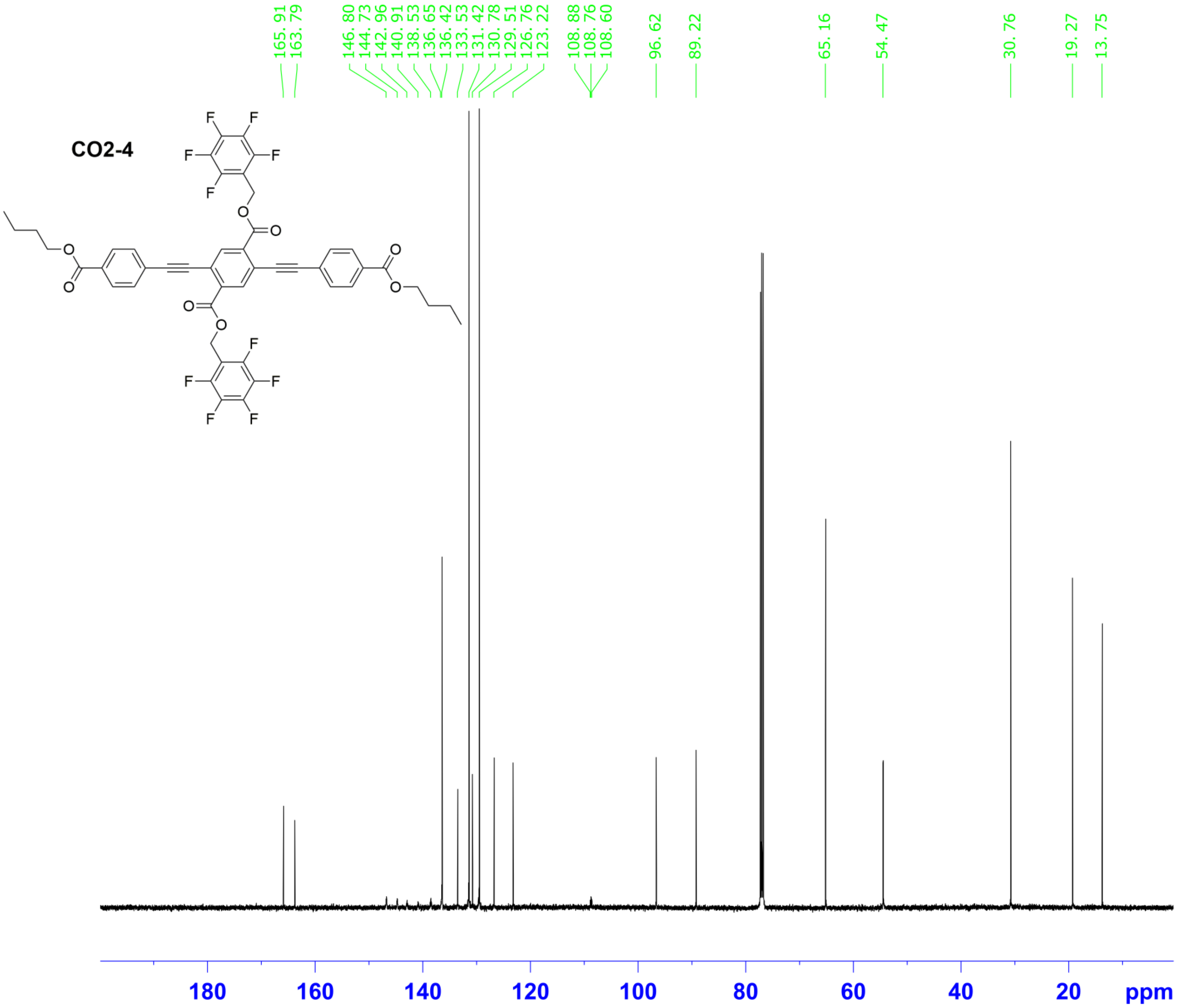
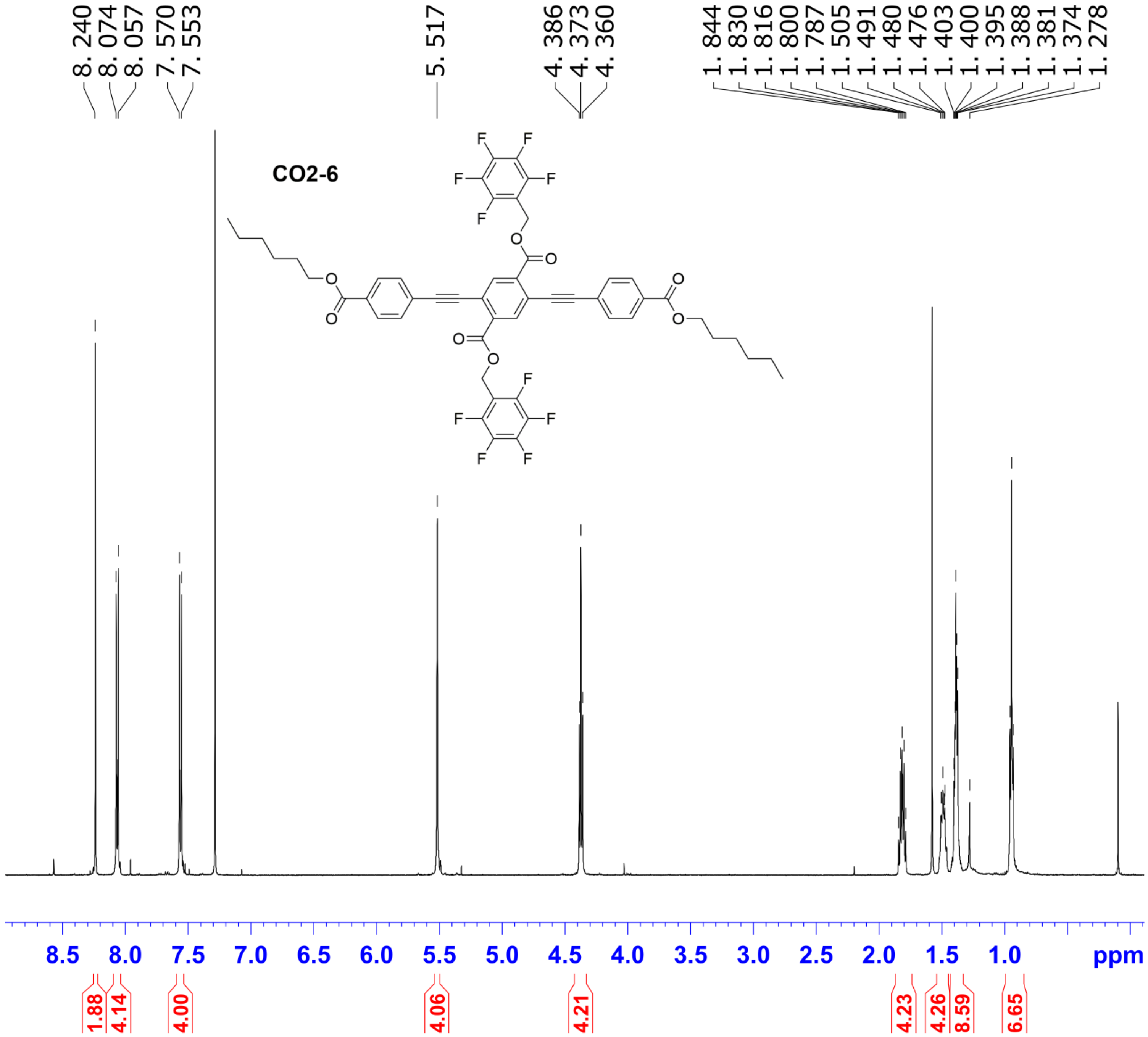
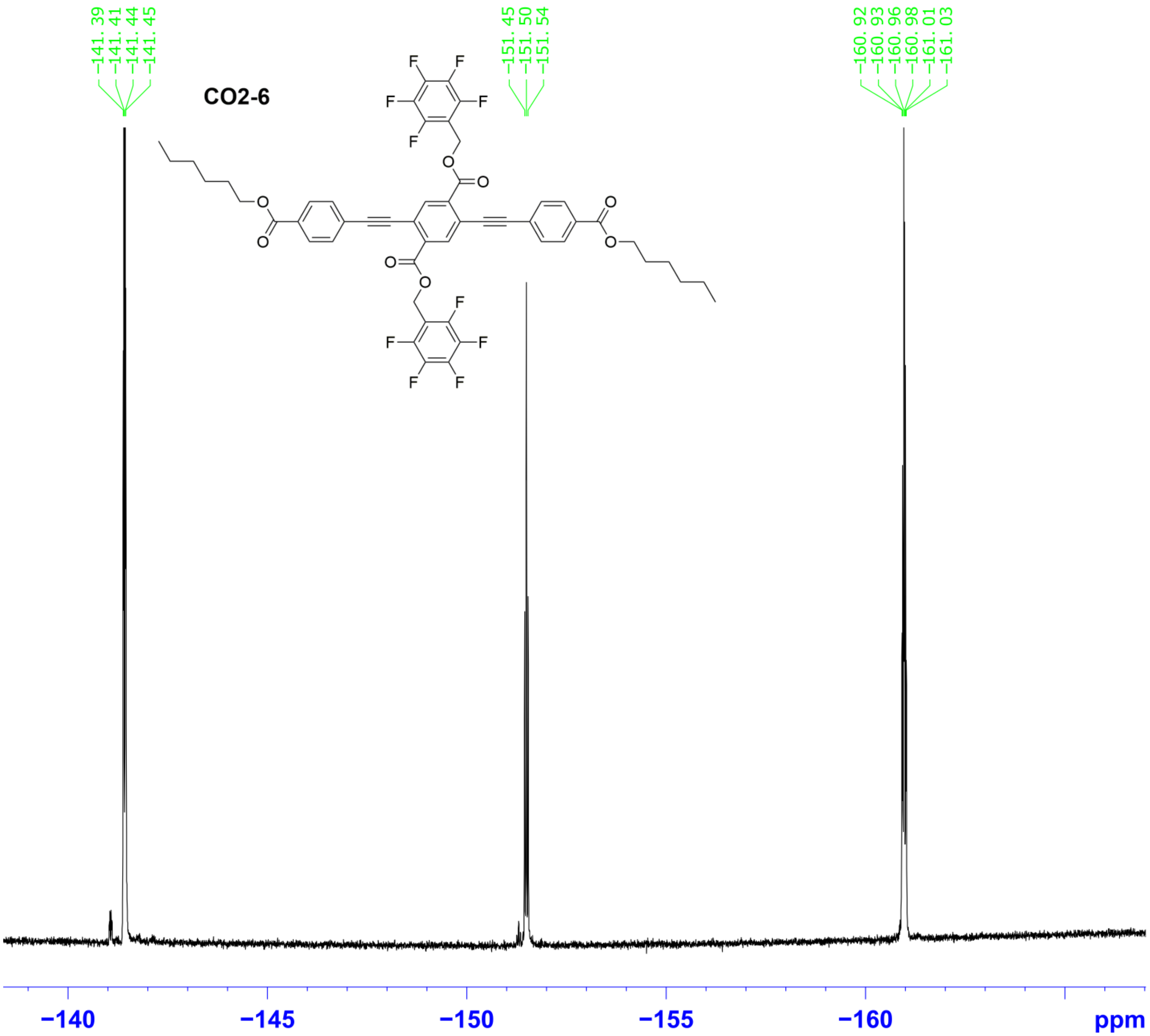
-141.43
-141.45
-151.47
-151.51
-151.55
-160.94
-160.97
-160.98
-161.01
-161.03
F
O
-138
-140
-142
-144
-146
-148
-150
-152
-154
-156
-158
-160
ppm

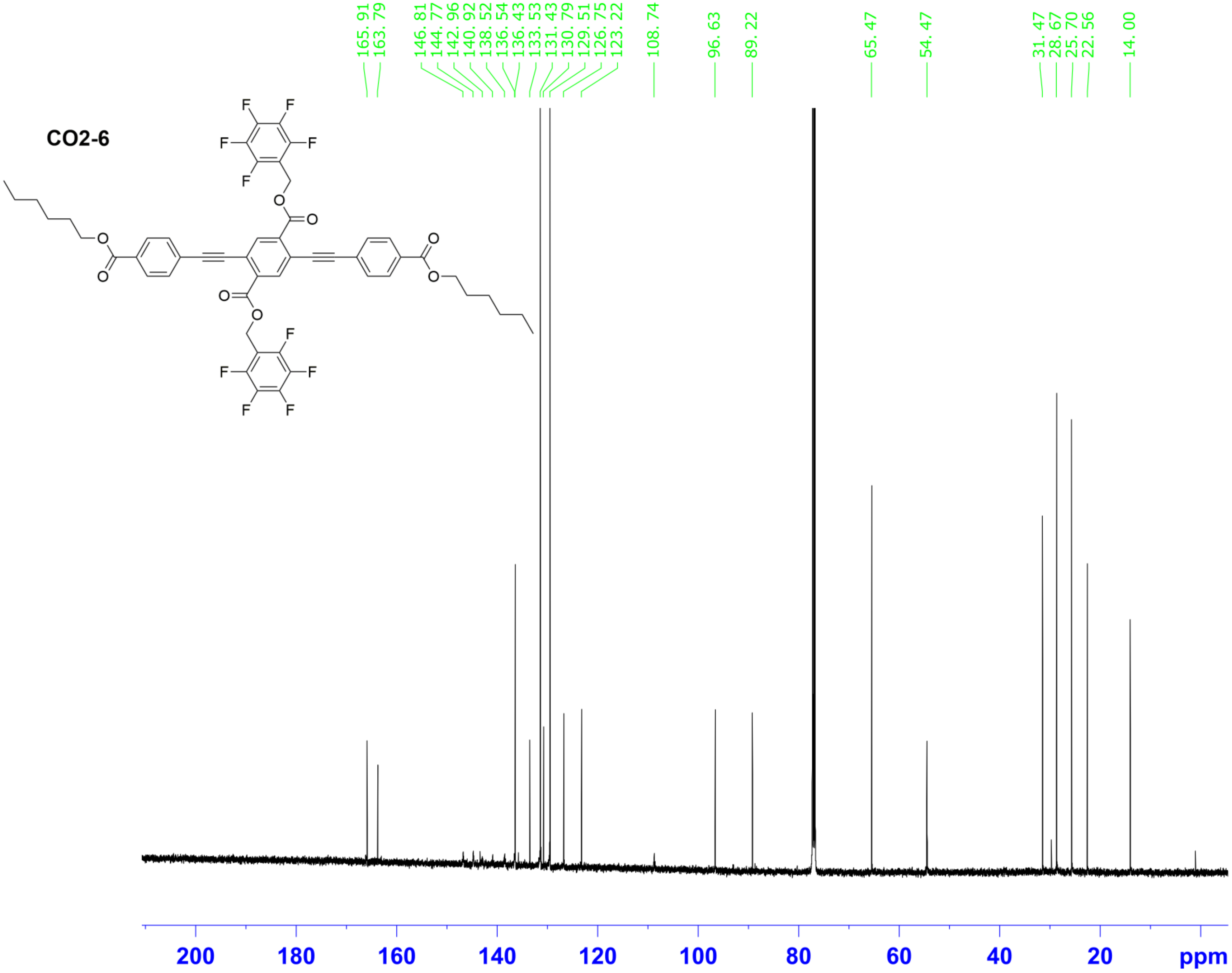
CO2-4

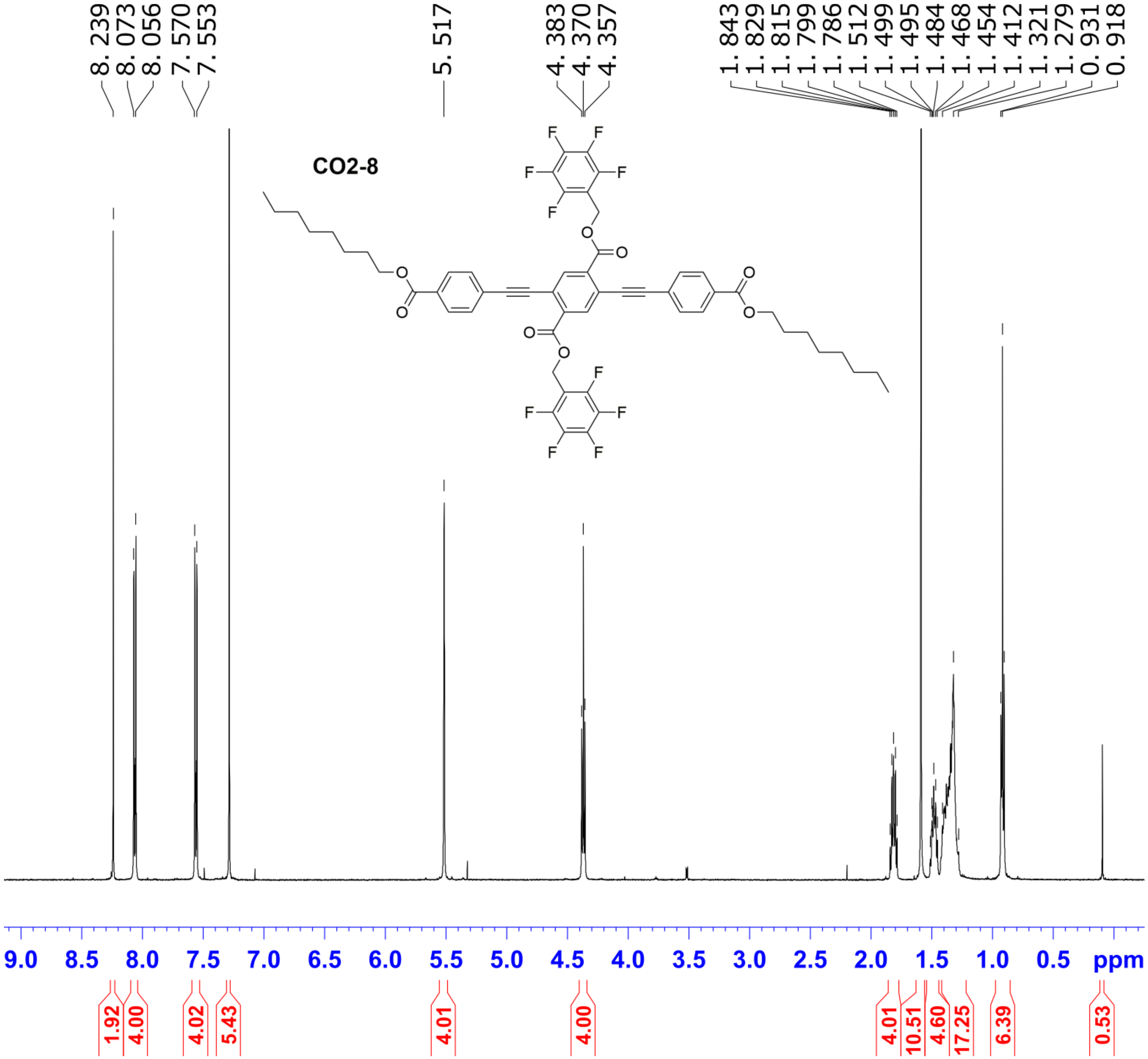

165.91
163.79
146.80
144.73
142.96
140.91
138.53
136.65
136.42
133.53
131.42
130.78
129.51
126.76
123.22
108.88
108.76
108.60
96.62
89.22
65.16
54.47
30.76
19.27
13.75
F
F
F
F
F
O
O
O
O
O
O
O
O
F
F
F
F
F
180
160
140
120
100
80
60
40
20
ppm



CO2-6
8.240
8.074
8.057
7.570
7.553
5.517
4.386
4.373
4.360
1.844
1.830
1.816
1.800
1.787
1.505
1.491
1.480
1.476
1.403
1.400
1.395
1.388
1.381
1.374
1.278
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.88
4.14
4.00
4.06
4.21
4.23
4.26
8.59
6.65

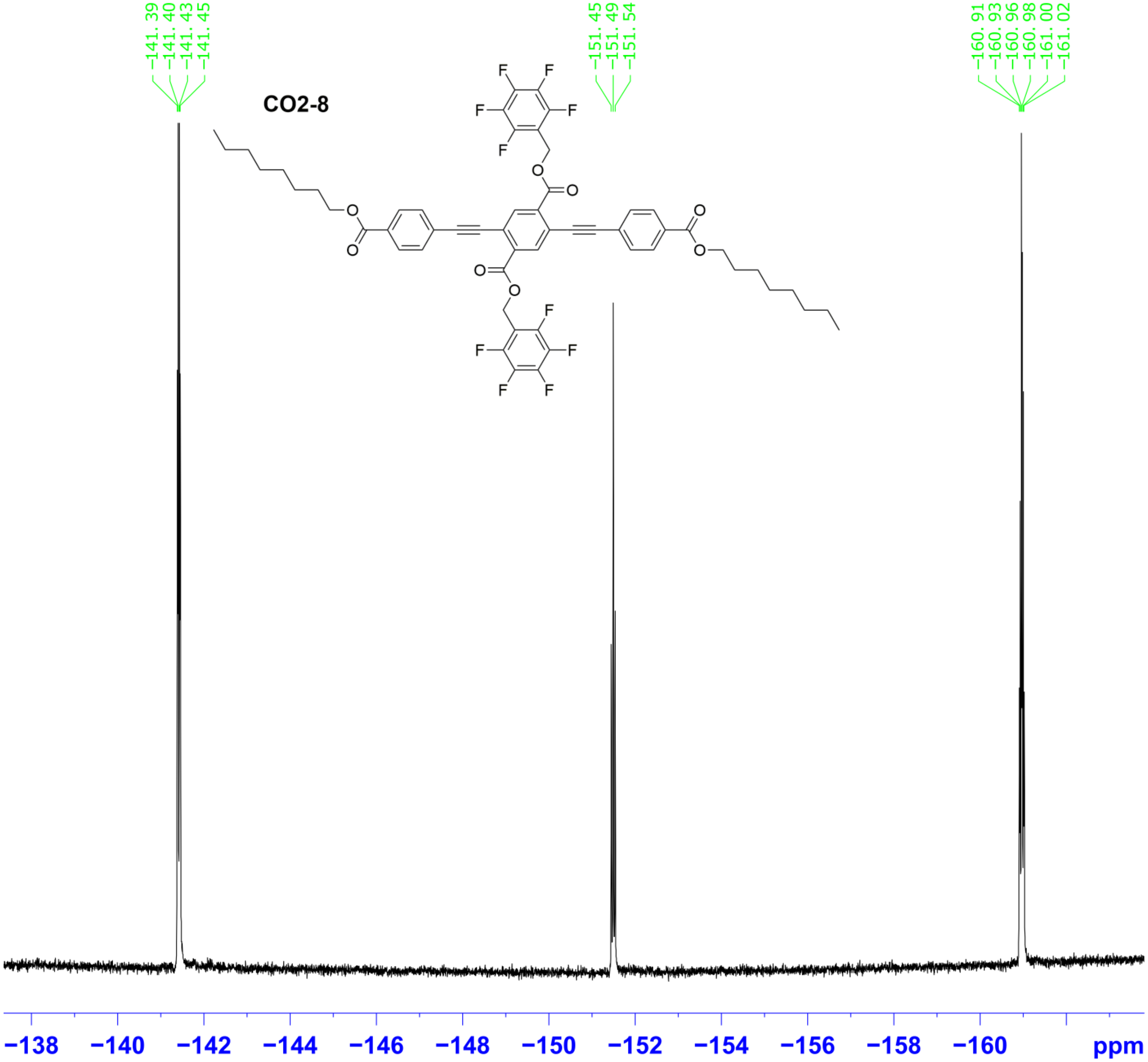

-141.39
-141.41
-141.44
-141.45
CO2-6
-151.45
-151.50
-151.54
-160.92
-160.93
-160.96
-160.98
-161.01
-161.03
F
O
−140
−145
−150
−155
−160
ppm


CO2-6
165.91
163.79
146.81
144.77
142.96
140.92
138.52
136.54
136.43
133.53
131.43
130.79
129.51
126.75
123.22
108.74
96.63
89.22
65.47
54.47
31.47
28.67
25.70
22.56
14.00
F
O
200
180
160
140
120
100
80
60
40
20
ppm

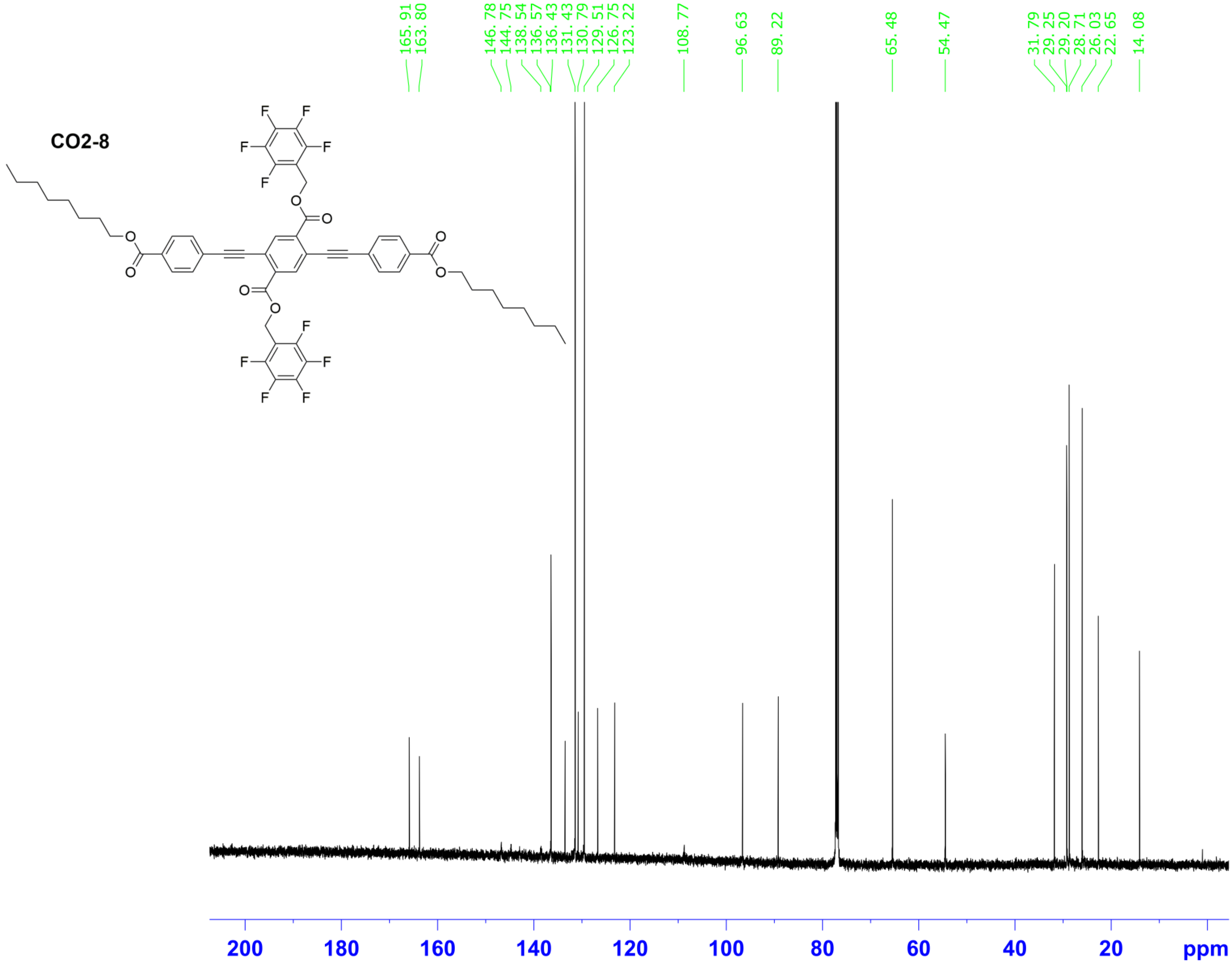


CO2-8

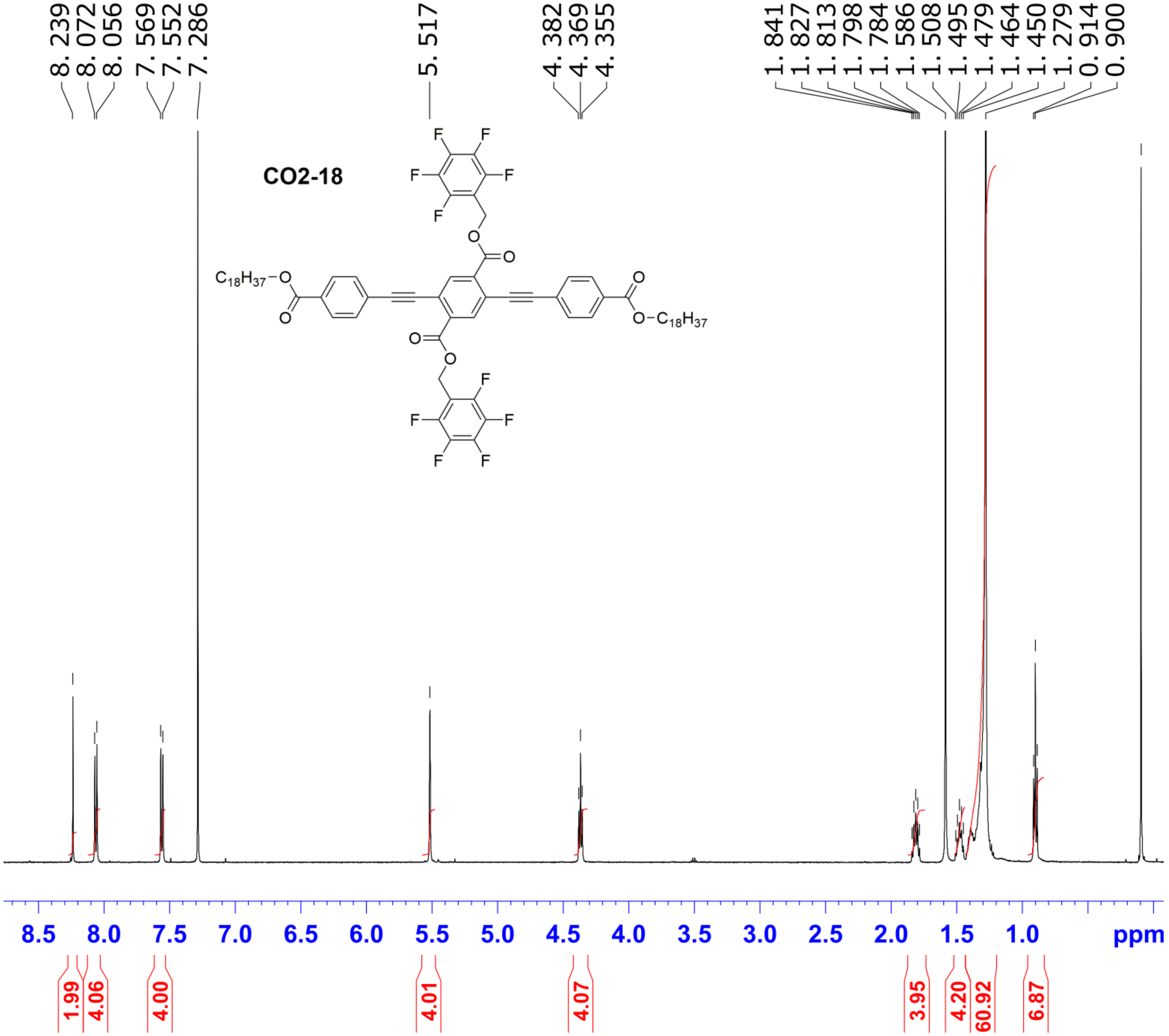
8.239
8.073
8.056
7.570
7.553
5.517
4.383
4.370
4.357
1.843
1.829
1.815
1.799
1.786
1.512
1.499
1.495
1.484
1.468
1.454
1.412
1.321
1.279
0.931
0.918
F
O
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.92
4.00
4.02
5.43
4.01
4.00
4.01
10.51
4.60
17.25
6.39
0.53

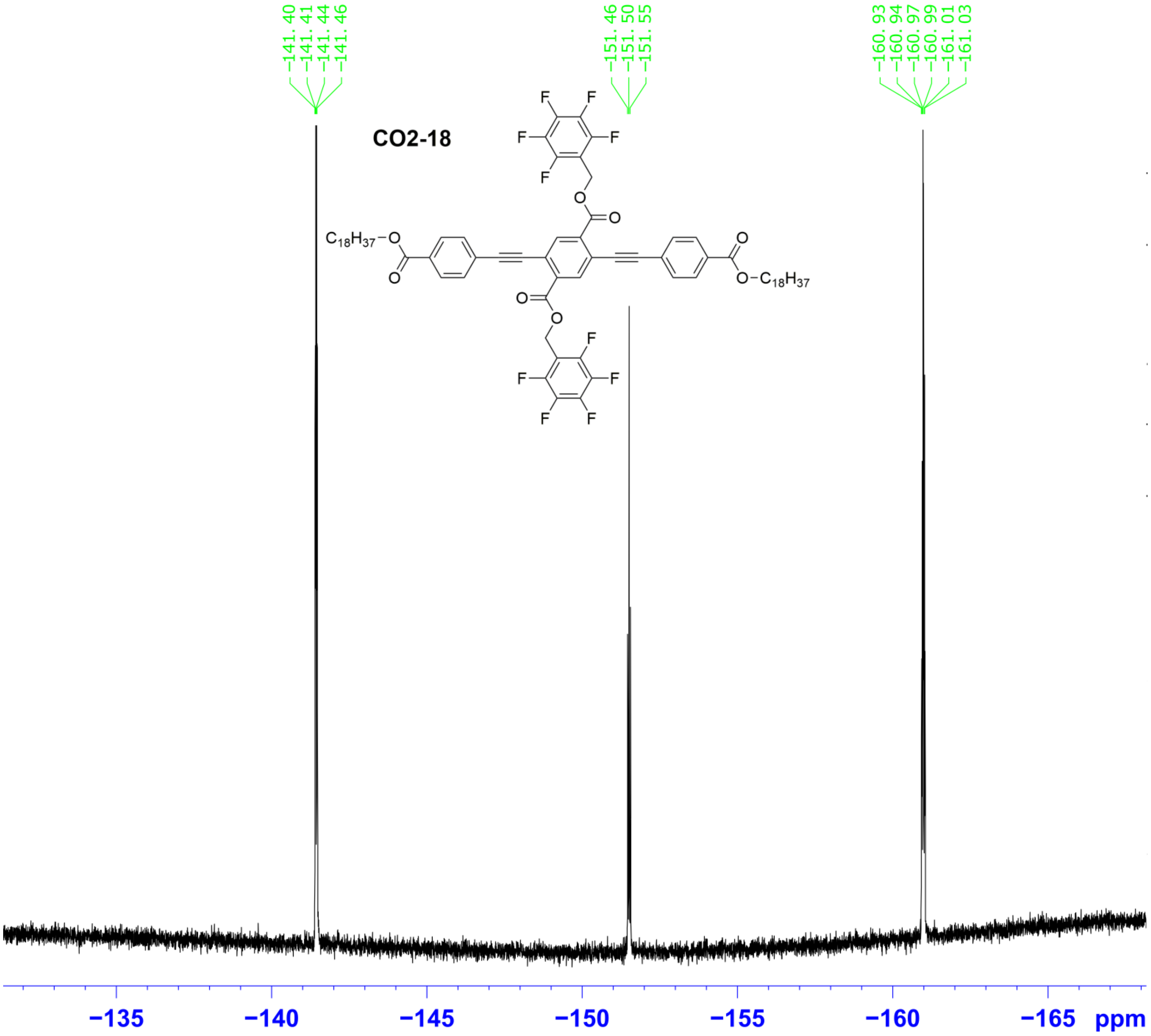

-141.39
-141.40
-141.43
-141.45
-151.45
-151.49
-151.54
-160.91
-160.93
-160.96
-160.98
-161.00
-161.02
CO2-8
F
O
-138
-140
-142
-144
-146
-148
-150
-152
-154
-156
-158
-160
ppm

CO2-8

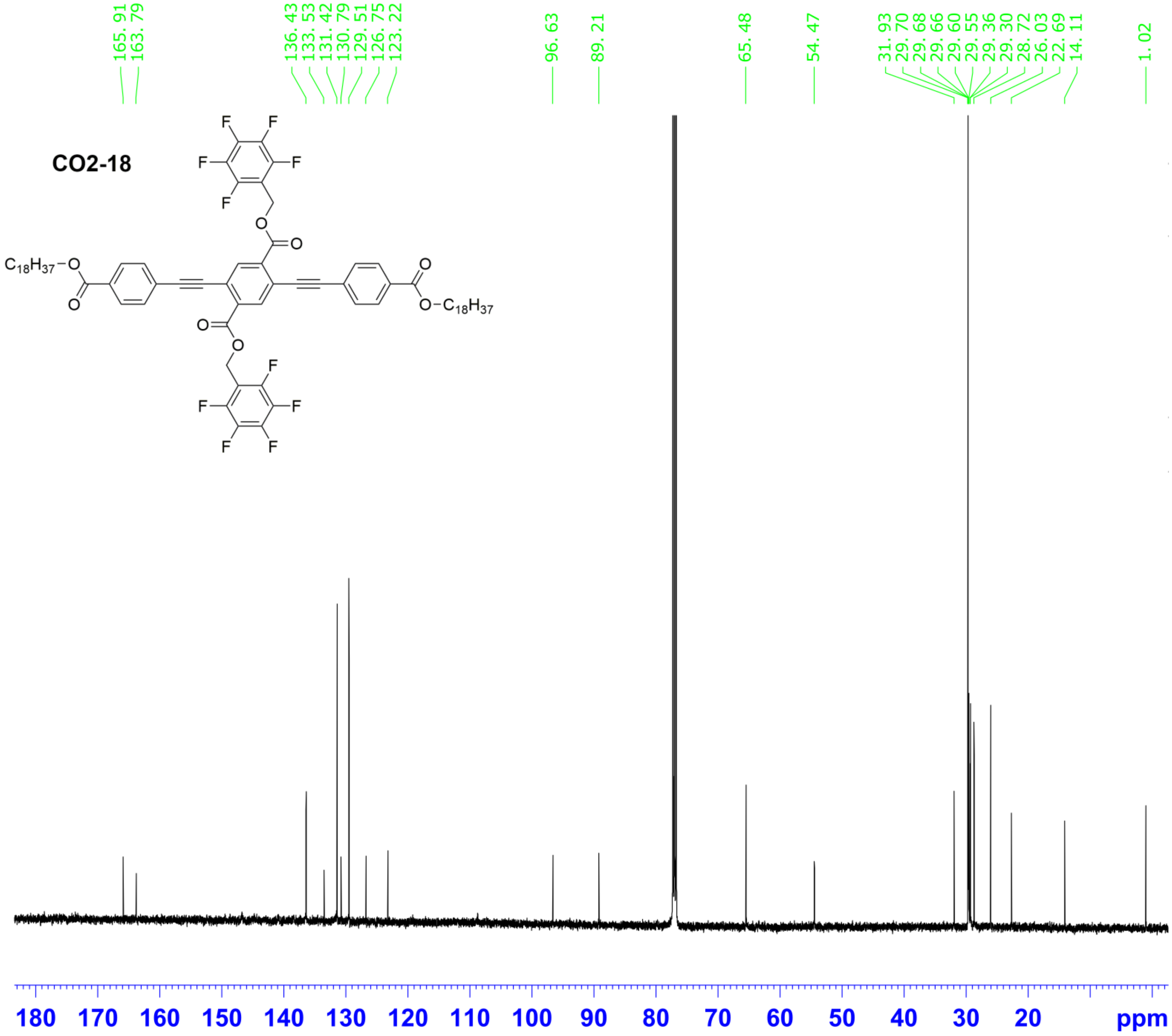


165. 91
163. 80
146. 78
144. 75
138. 54
136. 57
136. 43
131. 43
130. 79
129. 51
126. 75
123. 22
108. 77
96. 63
89. 22
65. 48
54. 47
31. 79
29. 25
29. 20
28. 71
26. 03
22. 65
14. 08
F
F
F
F
F
O
O
O
O
O
O
O
O
F
F
F
F
F
200
180
160
140
120
100
80
60
40
20
ppm


8.239
8.072
8.056
7.569
7.552
7.286
5.517
4.382
4.369
4.355
1.841
1.827
1.813
1.798
1.784
1.586
1.508
1.495
1.479
1.464
1.450
1.279
0.914
0.900
CO2-18
$C_{18}H_{37}$
F
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.99
4.06
4.00
4.01
4.07
3.95
4.20
60.92
6.87


CO2-18

-141.40
-141.41
-141.44
-141.46
-151.46
-151.50
-151.55
-160.93
-160.94
-160.97
-160.99
-161.01
-161.03
F
O
C18H37−O
O−C18H37
-135
-140
-145
-150
-155
-160
-165
ppm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136.43
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129.51
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54.47
31.93
29.70
29.68
29.66
29.60
29.55
29.36
29.30
28.72
26.03
22.69
14.11
1.02
F
O
C18H37−O
O−C18H37
180
170
160
150
140
130
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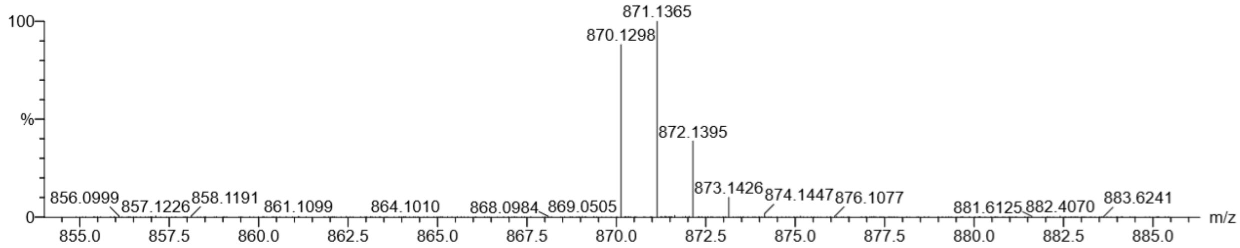
110
100
90
80
70
60
50
40
30
20
ppm

CO2-18

HRMS

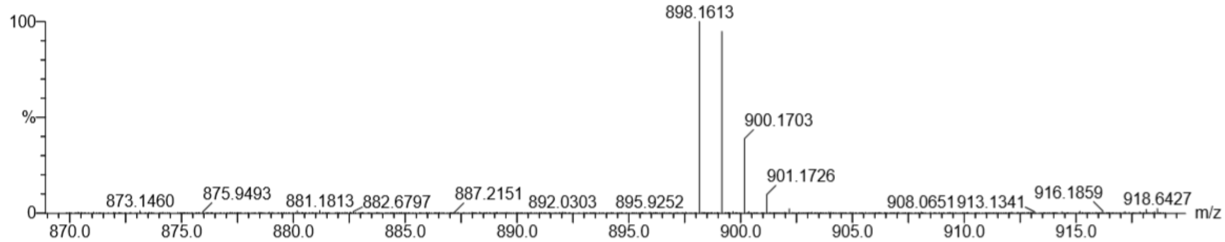
CO2-2



```
Minimum:                            -1.5
Maximum:               50.0    5.0   50.0

Mass       Calc. Mass  mDa     PPM     DBE     i-FIT   Norm    Conf(%) Formula
871.1365   871.1390    -2.5    -2.9    27.5    348.7   n/a     n/a     C44 H25 O8 F10
```

CO2-3



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Minimum:                            -1.5
Maximum:               50.0    5.0   50.0

Mass       Calc. Mass  mDa     PPM     DBE     i-FIT   Norm    Conf(%) Formula
898.1613   898.1624    -1.1    -1.2    28.0    384.5   n/a     n/a     C46 H28 O8 F10
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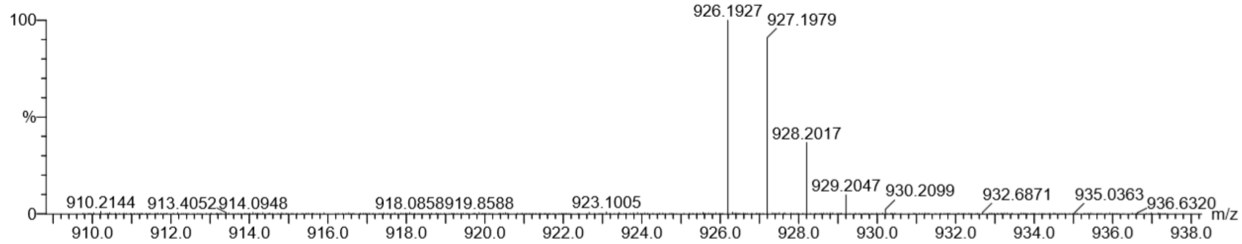
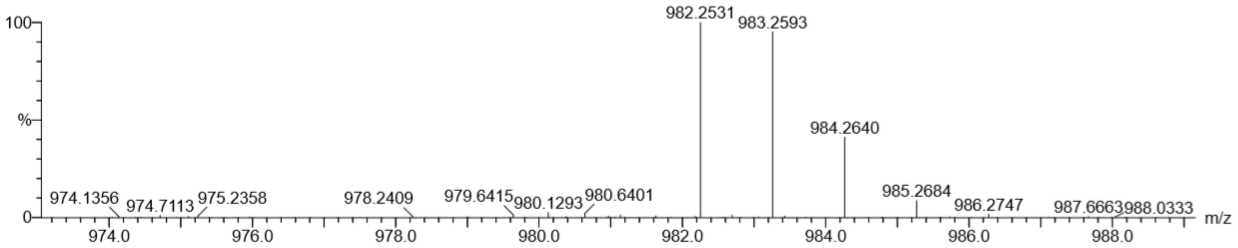
CO2-4



```
Minimum:                            -1.5
Maximum:               50.0    5.0   50.0

Mass       Calc. Mass  mDa     PPM     DBE     i-FIT   Norm    Conf(%) Formula
926.1927   926.1937    -1.0    -1.1    28.0    410.7   n/a     n/a     C48 H32 O8 F10
```

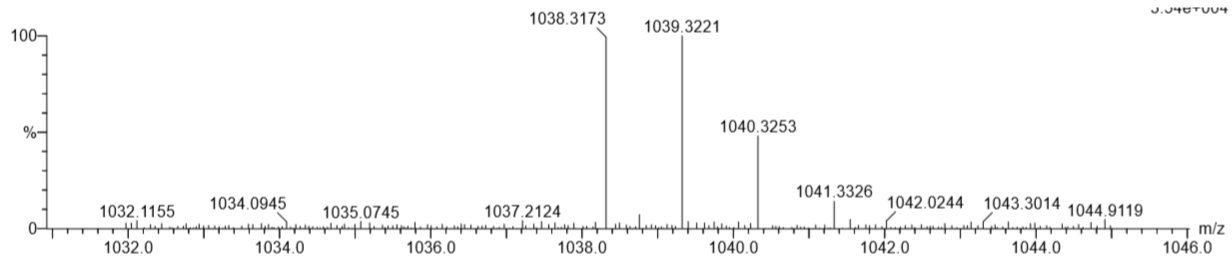
CO2-6



```
Minimum:                          -1.5
Maximum:                50.0   5.0   50.0

Mass       Calc. Mass  mDa    PPM    DBE    i-FIT   Norm    Conf(%) Formula
982.2531   982.2564    -3.3   -3.4   28.0   84.3    n/a     n/a     C52 H40 O8 F10
```

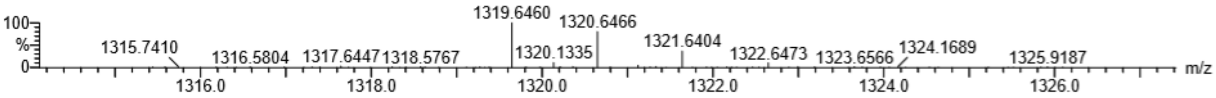
CO2-8



```
Minimum:                          -1.5
Maximum:                50.0   5.0   50.0

Mass       Calc. Mass  mDa    PPM    DBE    i-FIT   Norm    Conf(%) Formula
1038.3173  1038.3190   -1.7   -1.6   28.0   462.0   n/a     n/a     C56 H48 O8 F10
```

CO2-18



```
Minimum:                              -1.5
Maximum:                5.0      5.0      100.0

Mass       Calc. Mass   mDa      PPM      DBE      i-FIT      Formula

1319.6460  1319.6468    -0.8     -0.6     37.5     4.4        C85  H86  F10  Na
           1319.6492    -3.2     -2.4     40.5     6.0        C87  H85  F10
           1319.6398    6.2      4.7      27.5     0.6        C76  H89  O8   F10
```

5. Photophysical Properties in Solution and Spectra of Single Crystals

Table S1. Photophysical properties of **CO2-1** in various solvents.

Solvent	Abs λ_{max} (nm)	Em λ_{max} (nm)	ϕ_f
DMF	360	416	0.36
ACN	356	413	0.40
EtOAc	359	411	0.40
DCM	364	415	0.41
THF	362	413	0.45
Toluene	370	417	0.53
Hexane	361	409	0.50

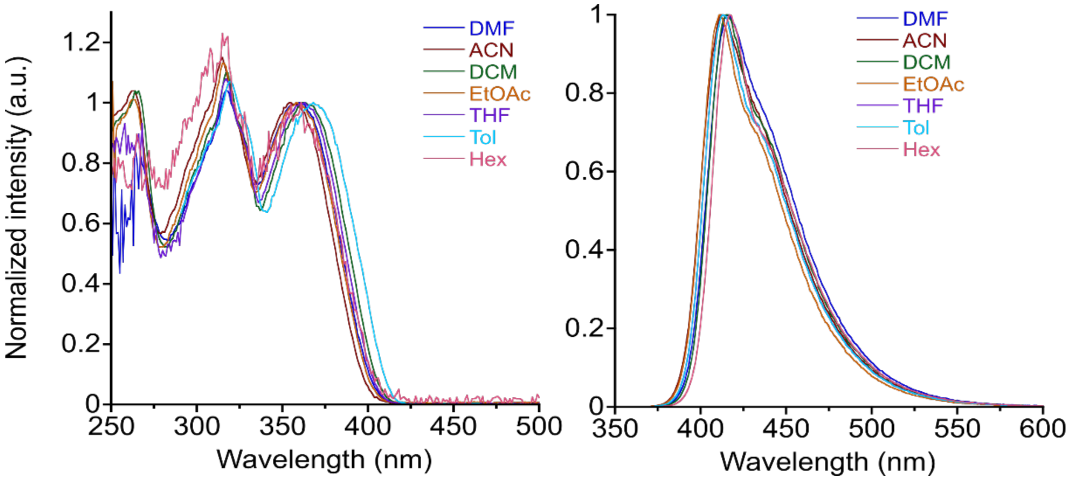


Figure S1. Absorbance (left) and emission spectra (right) of **CO2-1** in various solvents. λ_{ex} = 330 nm.

6. Photophysical and Material Properties of Polymorphs

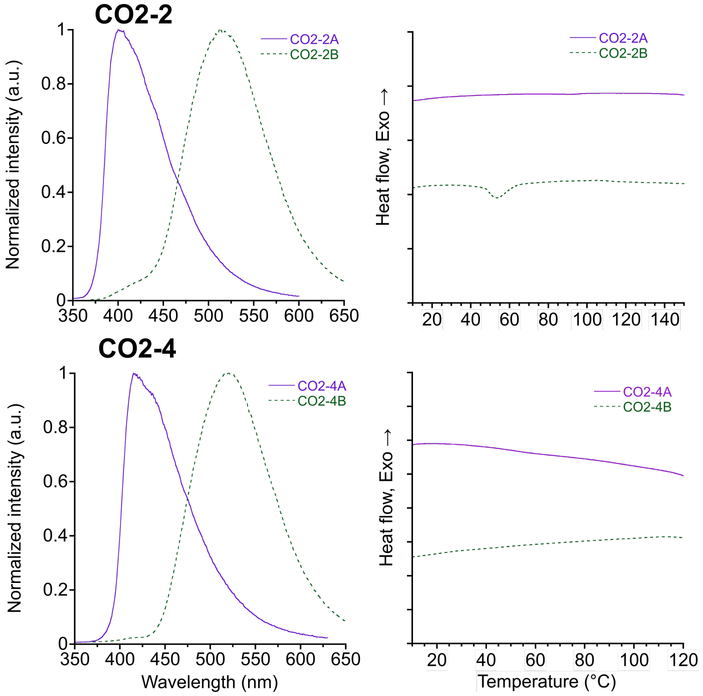


Figure S2. Emission Spectra (left) and DSC thermograms (right) for polymorphs of **CO2-2** and **CO2-4** obtained by recrystallization. λ_{ex} = 330 nm for **A** phases, 350 nm for **B** phases.

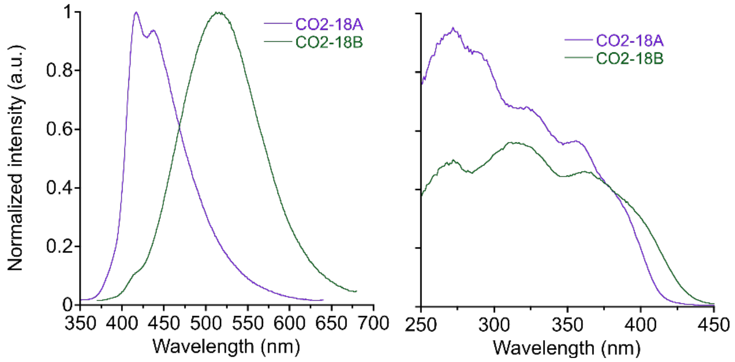


Figure S3. Emission (left) and excitation spectra (right) of violet and green emitting domains in a **CO2-18** drop-cast film. λ_{ex} = 330 nm for **A** phases, 350 nm for **B** phase.

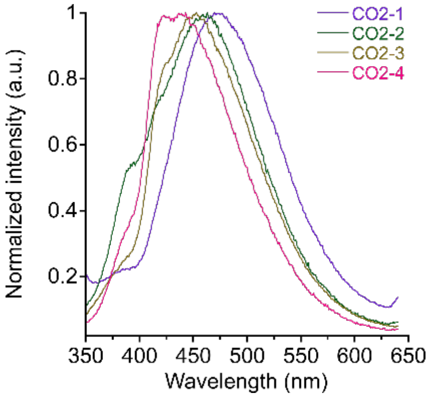


Figure S4. Emission spectra of spin-coated films. λ_{ex} = 330 nm.

7. Crystallographic Data and Additional Perspectives

Table S2. Structural parameters from violet emitting crystals

Structure	Space group	Z	Cell Vol. (Å^3)	Density (g/cm^3)	Torsions (°)	ArF-ArH Centroids (Å)
CO2-1A	P21/c	2	1767.9	1.583	67-71	3.78
CO2-2A	P1-	2	1859.8	1.555	69-76	3.98
CO2-3A	P1-	4	3920.9	1.522	67-77	4.07 - 4.10
CO2-4A	P21/c	4	4086	1.402	43-61	6.09 - 6.22

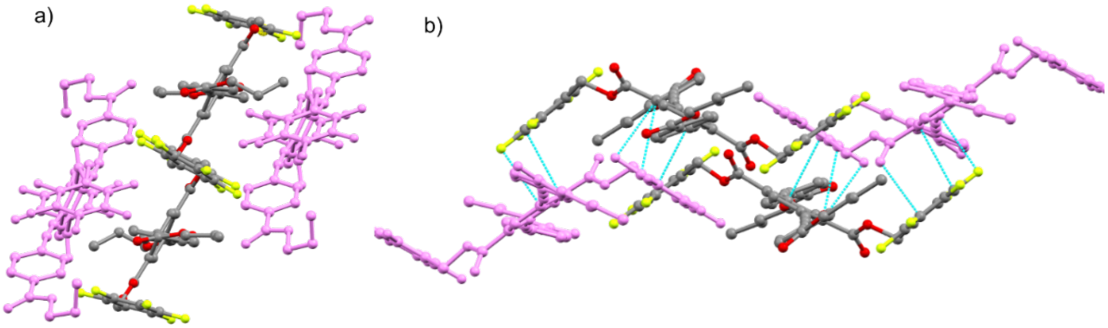


Figure S5. A) Herringbone packing of **CO2-3A** with PEs viewed end-on down the long molecular axis. b) Diagonal intermolecular ArF-ArH stacking of four **CO2-4** molecules, viewed end-on down the long molecular axis. Short contacts highlighted between ArF rings and terephthalates. Interacting molecules are colored by element and magenta and hydrogens omitted for clarity.

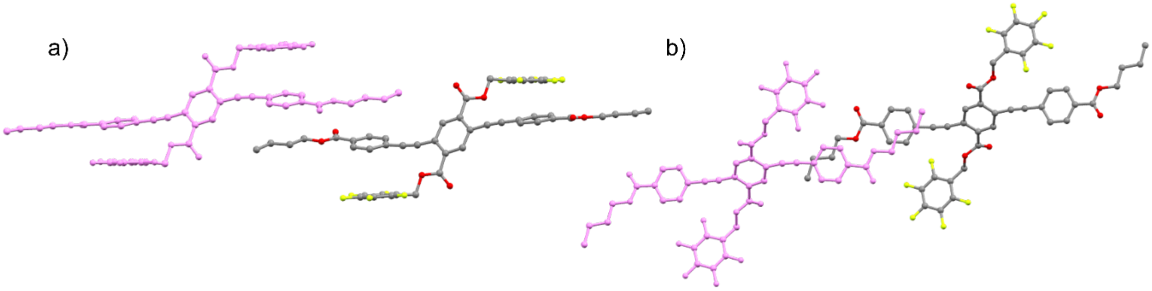


Figure S6. Additional perspectives of **CO2-4A**, showing butyl chains of a neighboring PE (magenta) occupying region of space that is normally occupied by ArF rings during intramolecular ArF-ArH cofacial stacking, viewed a) parallel to plane of ArF pendants b) perpendicular to plane of ArH arenes. Hydrogens omitted for clarity.

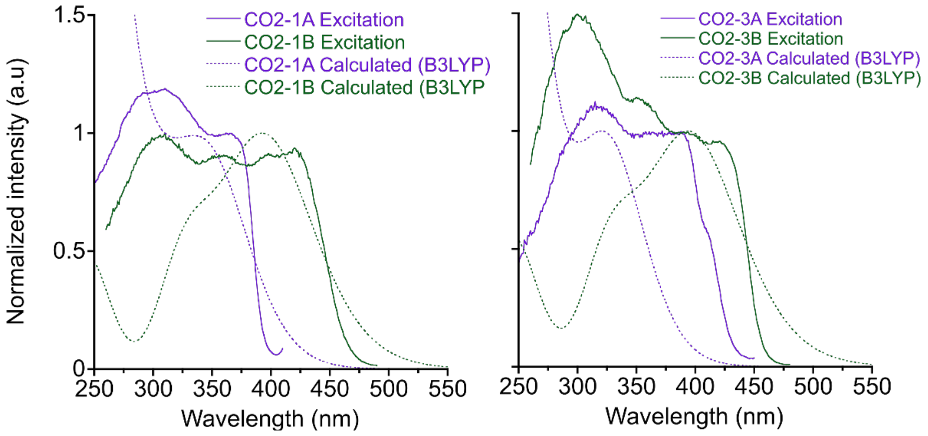


Figure S7. Excitation spectra of polymorphs yielding twisted and planar crystal structures for **CO2-1** and **CO2-3** with corresponding simulated UV-Vis spectra from TD-DFT calculations (B3LYP/6-31G(d,p))

8. X-Ray Scattering Data

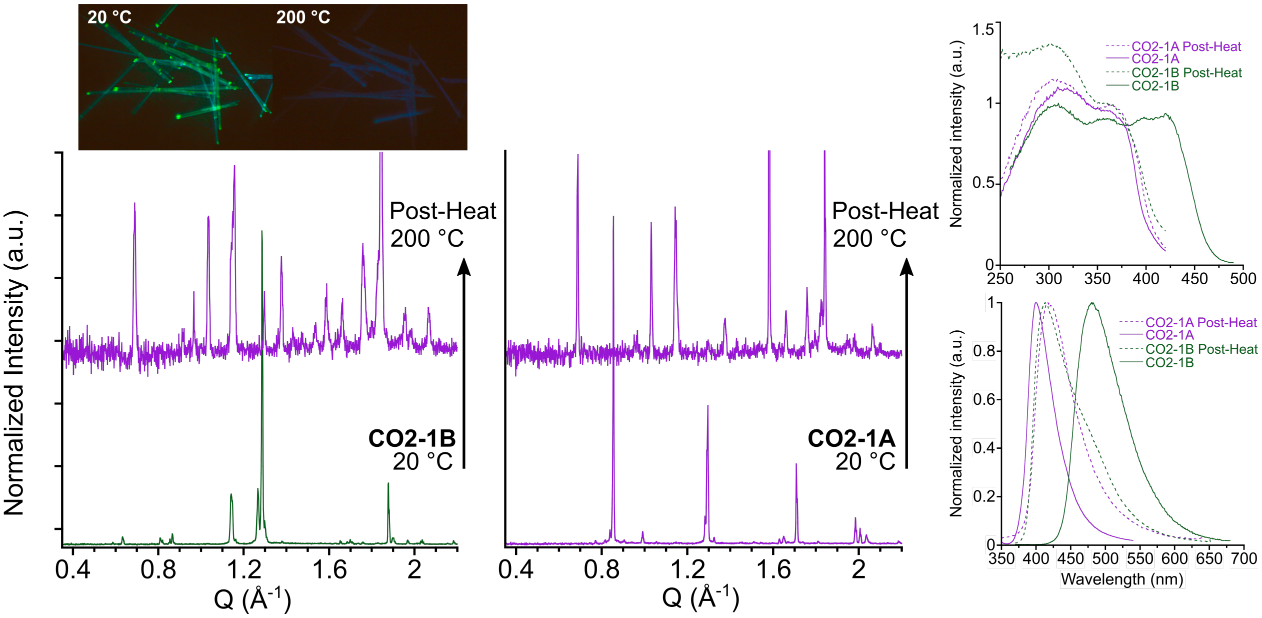


Figure S8. Crystal-to-crystal transitions of **CO2-1** polymorphs. (Left) PXRD (λ = 1.54184) shows patterns of green and violet emitting polymorphs at room temperature and after heating to 200 °C, with accompanying photos of green emissive **CO2-1B** before and after heating. Corresponding excitation and emission spectra (top and bottom right, respectively) of the polymorphs before and after heating transformation to violet fluorescence after heating. λ_{ex} = 330

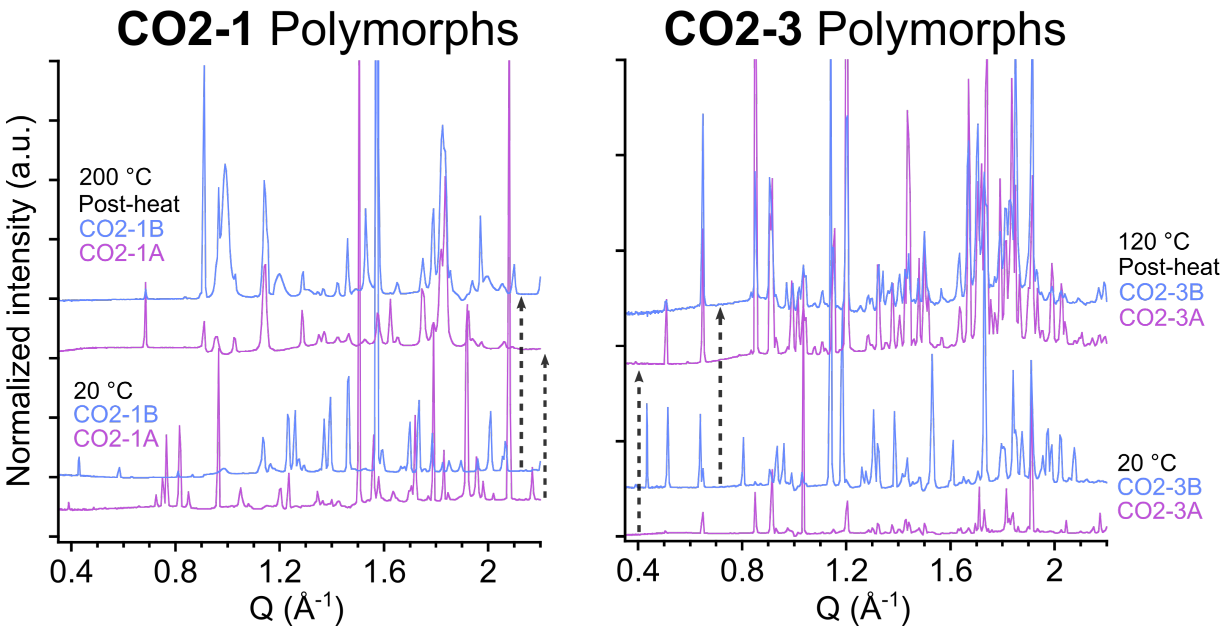


Figure S9. WAXS data from synchrotron radiation of **CO2-1** and **CO2-3** crystal-to-crystal transitions corresponding to Figure 6 and 7 PXRD Data. λ = 0.9178 Å. (Left) Patterns of **CO2-1A** and **CO2-1B** crystal samples before and after heating from room temperature to 200 °C, after which the patterns converge on a violet fluorescent phase. (Right) Patterns of **CO2-3A** and **CO2-3B** crystal samples before and after heating from room temperature to 120 °C, after which the patterns converge on a violet fluorescent phase closely corresponding to the room temperature **CO2-3A** pattern.

9. MFC Response of **CO2-R** Compounds

*Table S3. Mechanofluorochromism Data of **CO2-R** drop-cast films*

	Annealed Films		Ground Films		Optical Shift (nm)	
PE	Abs λ_{max} (nm)	Em λ_{max} (nm)	Abs λ_{max} (nm)	Em λ_{max} (nm)	Abs λ_{max} (nm)	Em λ_{max} (nm)
CO2-1	350	405	371	485	21	80
CO2-2	349	414	353	450	4	36
CO2-3	346	414	356	457	10	43
CO2-4	355	412	347	440	-8	28
CO2-6	354	414	354	419	0	5
CO2-8	355	408	354	422	-1	14
CO2-18	355	410	356	472	1	62

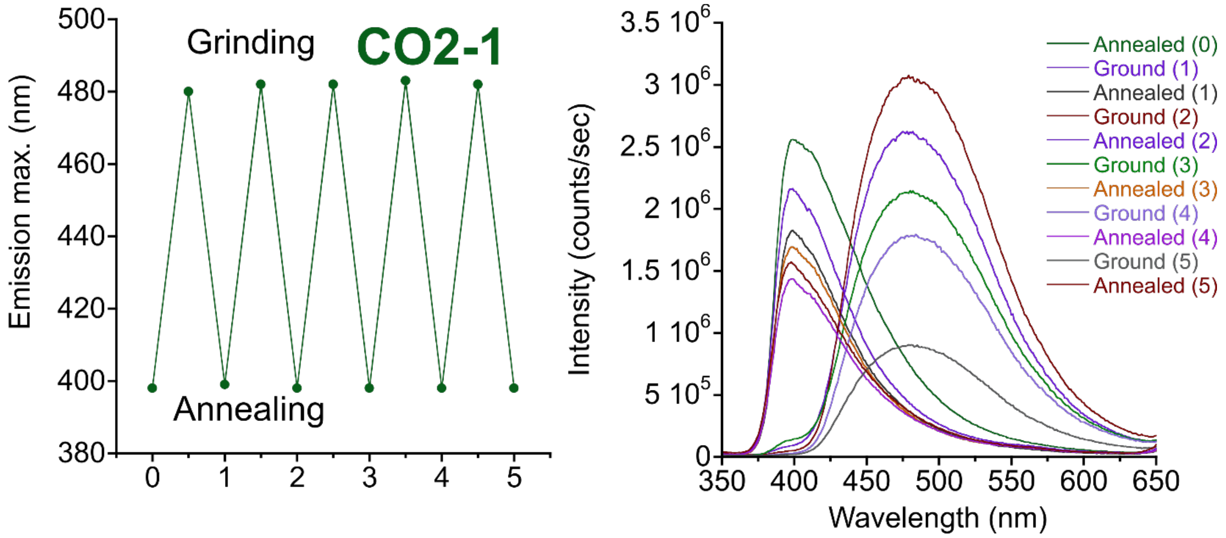


Figure S10. Reversibility of MFC response in **CO2-1**. (Left) Emission maxima of a **CO2-1** film over five grinding and annealing steps (180 °C for 5 minutes) taken from (right) emission spectra over the five steps. $\lambda_{ex} = 330$ nm.

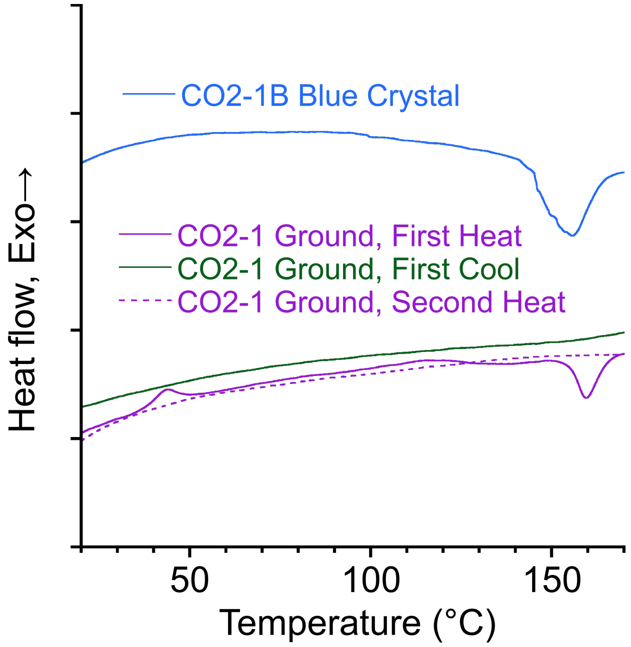


Figure S11. DSC thermogram of **CO2-1** ground powder, showing an irreversible exothermic peak in the first heat from 40 – 50 °C. Thermogram of **CO2-1B** crystals, first heat, is provided for comparison.

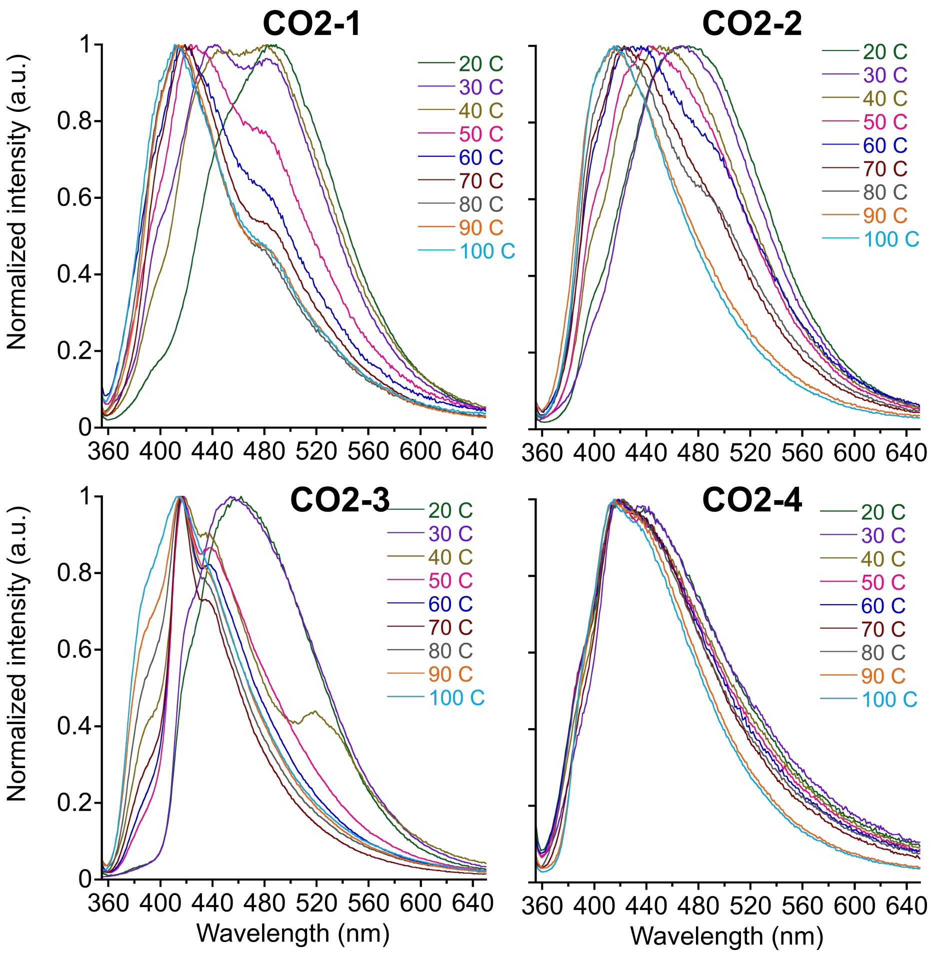


Figure S12. Thermal recovery of **CO2-1** - **CO2-4** ground films: Normalized emission spectra of **CO2-R** films after grinding, heated at 10 °C increments to 100 °C. $\lambda_{ex} = 330$ nm.

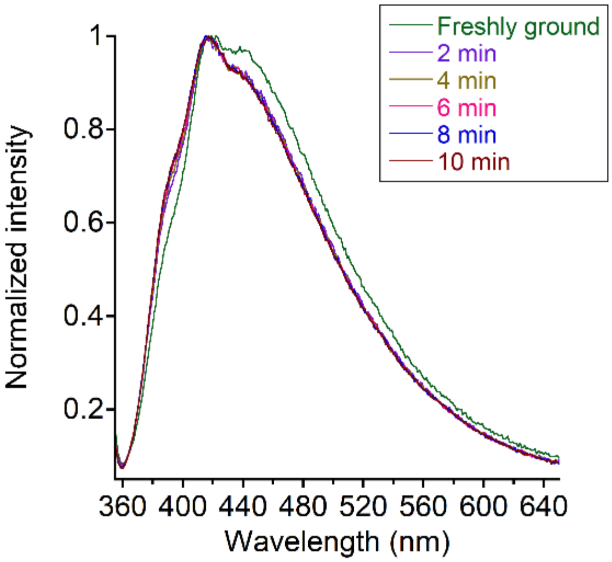


Figure S13. Emission spectra showing thermal recovery of a **CO2-4** ground film at room temperature. Thermal recovery at room temperature is rapid enough that emission spectra after grinding is representative of violet emission; fluorsence converts from green to violet within seconds after grinding, after which point fluorescence spectra show minimal changes as original emission is fully recovered within minutes. $\lambda_{ex} = 330$ nm.

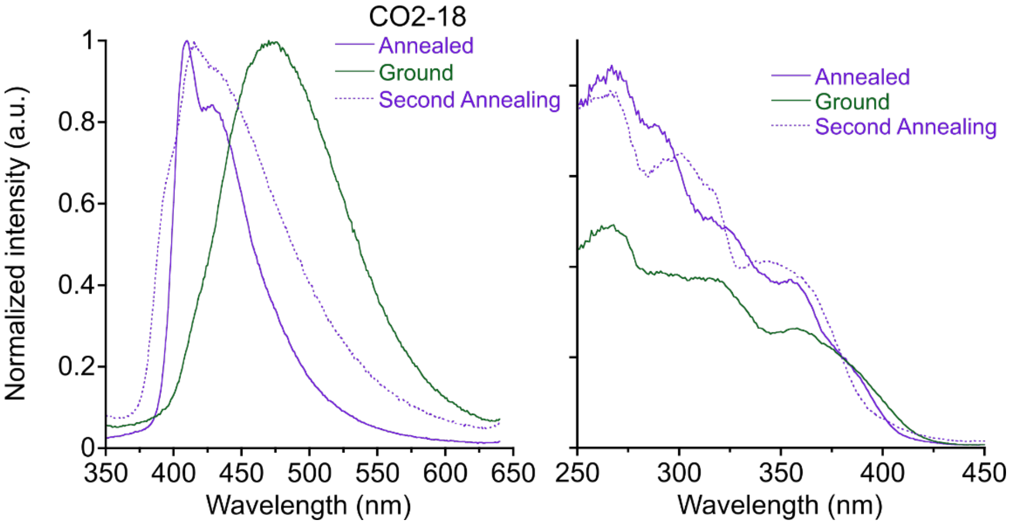


Figure S14. MFC Response of a **CO2-18** drop-cast film in (left) emission spectra and (right) excitation spectra. λ_{ex} = 330 nm for emission spectra of annealed films, 350 nm for spectra of ground film.

10. Crystallography tables

Table 1. Crystal data and structure refinement for **CO2-1C**.

Identification code	SS190115_0m_a	
Empirical formula	C44 H22 Cl6 F10 O8	
Formula weight	1081.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.5910(6) Å	α= 90°.
	b = 5.8584(2) Å	β= 101.6230(10)°.
	c = 26.0228(11) Å	γ = 90°.
Volume	2178.81(15) $Å^3$	
Z	2	
Density (calculated)	1.648 Mg/m^3	
Absorption coefficient	0.492 mm^{-1}	
F(000)	1084	
Crystal size	0.5 x 0.2 x 0.2 mm^3	
Theta range for data collection	2.850 to 25.357°.	
Index ranges	-17<=h<=17, -6<=k<=7, -31<=l<=31	
Reflections collected	39436	
Independent reflections	3980 [R(int) = 0.0826]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3980 / 0 / 308	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.0952	
R indices (all data)	R1 = 0.0711, wR2 = 0.1066	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.455 and -0.976 e.$Å^{-3}$	

Table 2. Crystal data and structure refinement for **CO2-2A**

Identification code	SS170710_0m_a	
Empirical formula	C44 H24 F10 O4	
Formula weight	806.63	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.5972(8) Å	α= 100.489(2)°.
	b = 13.9199(14) Å	β= 91.139(2)°.
	c = 18.3585(19) Å	γ = 102.556(2)°.
Volume	1859.8(3) $Å^3$	
Z	2	
Density (calculated)	1.440 Mg/m^3	
Absorption coefficient	0.125 mm^{-1}	
F(000)	820	
Crystal size	0.300 x 0.200 x 0.100 mm^3	
Theta range for data collection	1.130 to 26.628°.	
Index ranges	-9<=h<=9, -17<=k<=17, -23<=l<=23	
Reflections collected	31077	
Independent reflections	7770 [R(int) = 0.0343]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7770 / 0 / 561	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.1206	
R indices (all data)	R1 = 0.0606, wR2 = 0.1347	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.720 and -0.769 e.$Å^{-3}$	

Table 3. Crystal data and structure refinement for **CO2-3A**

Identification code	SS170815_0m_a	
Empirical formula	$C_{46} H_{28} F_{10} O_8$	
Formula weight	898.68	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.7988(16) Å	α= 97.224(3)°.
	b = 15.4277(18) Å	β= 97.656(2)°.
	c = 19.196(2) Å	γ = 101.419(2)°.
Volume	3920.9(8) $Å^3$	
Z	4	
Density (calculated)	1.522 Mg/m^3	
Absorption coefficient	0.135 mm^{-1}	
F(000)	1832	
Crystal size	0.150 x 0.150 x 0.030 mm^3	
Theta range for data collection	1.084 to 21.860°.	
Index ranges	-14<=h<=14, -16<=k<=16, -20<=l<=20	
Reflections collected	41215	
Independent reflections	9377 [R(int) = 0.0374]	
Completeness to theta = 21.860°	99.3 %	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9377 / 0 / 1157	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.1174	
R indices (all data)	R1 = 0.0596, wR2 = 0.1356	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.807 and -0.545 e.$Å^{-3}$	

Table 4. Crystal data and structure refinement for **CO2-3B**

Identification code	SS170830_0m_a_06_	
Empirical formula	$C_{46} H_{28} F_{10} O_8$	
Formula weight	898.68	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 5.1931(13) Å	α= 90°.
	b = 13.104(3) Å	β= 93.665(5)°.
	c = 28.245(7) Å	γ = 90°.
Volume	1918.1(8) $Å^3$	
Z	2	
Density (calculated)	1.556 Mg/m^3	
Absorption coefficient	0.138 mm^{-1}	
F(000)	916	
Crystal size	0.500 x 0.050 x 0.050 mm^3	
Theta range for data collection	1.445 to 22.768°.	
Index ranges	-5<=h<=5, -14<=k<=14, -30<=l<=30	
Reflections collected	19201	
Independent reflections	2596 [R(int) = 0.0639]	
Completeness to theta = 22.768°	99.8 %	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2596 / 0 / 290	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0651, wR2 = 0.1702	
R indices (all data)	R1 = 0.0888, wR2 = 0.2108	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.673 and -0.361 e.$Å^{-3}$	

Table 5. Crystal data and structure refinement for **CO2-4A**

Identification code	SS170523_0ma_a	
Empirical formula	C48 H32 F10 O4	
Formula weight	862.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 22.23(3) Å	α= 90°.
	b = 7.883(9) Å	β= 94.09(5)°.
	c = 23.37(3) Å	γ = 90°.
Volume	4086(9) $Å^3$	
Z	4	
Density (calculated)	1.402 Mg/m^3	
Absorption coefficient	0.119 mm^{-1}	
F(000)	1768	
Crystal size	0.200 x 0.100 x 0.020 mm^3	
Theta range for data collection	2.728 to 24.982°.	
Index ranges	-26<=h<=26, -8<=k<=8, -25<=l<=25	
Reflections collected	51711	
Independent reflections	6223 [R(int) = 0.0347]	
Completeness to theta = 24.982°	86.5 %	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6223 / 0 / 597	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0310, wR2 = 0.0782	
R indices (all data)	R1 = 0.0395, wR2 = 0.0837	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.242 and -0.183 e.$Å^{-3}$	

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