Electronic Supplementary Material (ESI) for Materials Advances.

Fluorinated Triphenylene Discotic Liquid Crystals Prepared via Sequential Photocyclodehydrofluorination and Aromatic Nucleophilic Substitution Reactions Synthesis, Structural and Transport Properties

Zhe Li[1*], Mitchell Powers[2], Sonya Adas[1], Kayla Ivey[1], Scott Bunge[1], Brett Ellman[2], Robert J. Twieg[1]

[1]Department of Chemistry & Biochemistry, Kent State University, Kent, OH, 44242

[2]Department of Physics, Kent State University, Kent, OH, 44242
*Presently at Advenchen Laboratories, LLC., 887 Patriot Dr A, Moorpark, CA 93021

E-mail:

zli10@kent.edu, mpower16@kent.edu, sadas@kent.edu, kivey@kent.edu, sbunge@kent.edu, bellman@kent.edu,
rtwieg@kent.edu

Contents

Contents ii

Introduction 1

Synthesis 2

Procedures for S_NAr model reactions 2

Procedures for the synthesis of fluorinated triphenylene discotic liquid crystals 5

NMR Spectra for 1,2,3,4-tetrafluorotriphenylene 17

DSC Analysis of Mesogenic Compounds 50

X-ray Study of Selected Mesogens 60

Time of Flight Hole Mobility 71

X-ray Crystallography Data for 1,4-Difluoro-2,3-dimethoxytriphenylene 74

1. Introduction

The chemical reagents used in this research were purchased from major chemical vendors including Sigma Aldrich, Fischer Scientific, Acros Organic, Alfa Aesar, TCI America, Matrix Scientific, Oakwood Chemical and Combi-Blocks.

A Mettler Toledo FP82HT Hot Stage controlled by a Mettler Toledo FP90 Central Processor (Mettler Toledo, P.O. Box 71, USA-Hightstown, NJ) was used to determine melting points. Phase changes were observed using a Nikon Eclipse E600 POL microscope.

A Bruker 400 NMR was used for NMR data acquisition (Frequency: 400 MHz for 1H-NMR; 100 MHz for 13C-NMR and 376 MHz for 19F-NMR) and the plots were generated by TOPSPIN 2 software.

X-ray crystallography samples were prepared by mounting each crystal onto a thin glass fiber from a pool of Fluorolube™ and immediately placing it under a liquid N_2 cooled N_2 stream, on a Bruker AXS diffractometer. The radiation used was graphite monochromatized Mo Kα radiation (λ = 0.7107 Å). The lattice parameters were optimized from a least-squares calculation on carefully centered reflections. Lattice determination, data collection, structure refinement, scaling, and data reduction were carried out using APEX2 version 2014.11-0 software package. The structure was solved using direct methods and this procedure yielded a number of the C atoms. Subsequent Fourier synthesis yielded the remaining atom positions. The hydrogen atoms were fixed in positions of ideal geometry and refined within the XSHELL software. These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 or 1.5 times the equivalent isotropic U of the C atoms to which they were bonded. The final refinement of each compound included anisotropic thermal parameters on all non-hydrogen atoms.

For the photocyclization reactions, the Rayonet photochemical reactor can be fitted with up to 16 × 254 nm lamps or 16 × 300 nm lamps. Solutions of the materials were charged in quartz tubes (approximately 40 cm × 25 mm with a 24/40 ST joint) for irradiation.

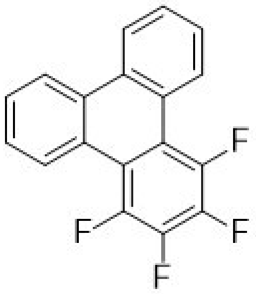
For liquid crystal samples, differential scanning calorimetry (DSC) analysis was run on a Model 2920 DSC (TA Instruments Inc., New Castle, DE, USA) to determine their phase transition temperatures. Results of the DSC analysis were verified by polarized microscopy. Experimental data was exported and analyzed using Thermal Advantage software (Version 1.1A, TA Instruments Inc., New Castle, DE, USA).

Mobility data was obtained using the time of flight (TOF) technique, using a Continuum Surelite pulsed Nd:YAG laser in conjunction with a harmonic generator and Raman shifter to illuminate a sample with an appropriate wavelength of light to photogenerate charge. Further details of the optical setup and analysis methods are provided further in this text.

Synthesis

Procedures for S_NAr model reactions

1,2,3,4-tetrafluorotriphenylene



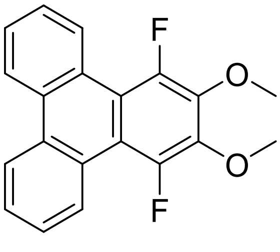
Chemical Formula: $C_{18}H_8F_4$
Molecular Weight: 300.25

In a quartz vessel, 2-(pentafluorophenyl)biphenyl (0.486 g, 1.5 mmol) was dissolved in acetonitrile (80 mL). The solution was degassed with nitrogen and irradiated for 12 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps. After chromatography (eluent: hexanes: DCM = 10:1), a pale tan powder (0.423 g, 1.4 mmol, 94 % yield) was obtained as the desired product.

M.P.: 197.0 – 203.5 °C (Lit.: 197.0 – 203.5 °C).
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.92 (d, *J* = 8.0 Hz, 2H), 8.63 (d, *J* = 8.0 Hz, 2H), 7.72 – 7.63 (m, 4H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 146.27 (d, *J* = 247 Hz), 139.60 (d, *J* = 243 Hz), 130.56, 128.58, 127.97, 127.71, 126.09, 123.33, 116.51.
^{19}F-NMR (376 MHz, $CDCl_3$) δ: -138.03 (d, *J* = 13.7 Hz, 2F), -157.48 (d, *J* = 13.7 Hz, 2F).
GCMS (m/z): 301.02.

Reference: Z. Li, R. J. Twieg, *Chem. Eur. J.* 2015, **21,** 15534.

1,4-Difluoro-2,3-dimethoxytriphenylene

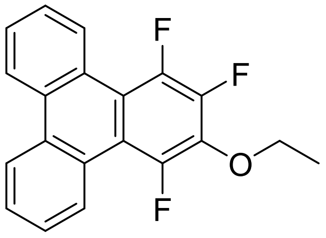


Chemical Formula: $C_{20}H_{14}F_2O_2$
Molecular Weight: 324.33

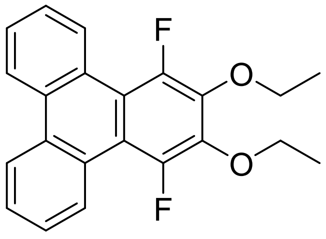
A 100 mL round bottom flask was charged with 1,2,3,4-tetrafluorotriphenylene (0.603 g, 2.0 mmol), methanol (25 mL), toluene (25 mL) and *t*-BuOK (1.798 g, 16.0 mmol, 8 eq). The mixture was heated in an oil bath to give a clear solution that was refluxed for 3 hours. After this time TLC showed that no 1,2,3,4-tetrafluorotriphenylene starting material remained and the mixture was cooled down to room temperature. Silica gel (approximately 2 g) was added and the remaining solvent was removed by rotary evaporation. The brown powder obtained was placed at the top of a silica gel column and eluted (hexanes). Fractions containing the product were combined and concentrated to give white fibrous crystals (0.398 g, 0.12 mmol, 60 % yield) as final product.

M.P.: 127.0 – 128.5 °C
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.99 – 8.96 (m, 2H), 8.63 – 8.60 (m, 2H), 7.68 - 7.61 (m, 4H), 4.13 (m, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 151.00 (dd, J_1 = 248 Hz, J_2 = 4 Hz), 140.93 (dd, J_2 = 13.5 Hz, J_2 = 7.8 Hz), 130.24, 127.84 (t, J = 19.7 Hz), 127.84 (d, J = 31.3 Hz), 127.59 (d, J = 11.1 Hz), 126.83, 123.11, 116.12 (t, J = 5.5 Hz), 62.24.
^{19}F-NMR (376 MHz, $CDCl_3$) δ: -132.77 (s).

2-ethoxy-1,3,4-trifluorotriphenylene and 2,3-diethoxy-1,4-difluorotriphenylene



Chemical Formula: $C_{20}H_{13}F_3O$
Molecular Weight: 326.32



Chemical Formula: $C_{22}H_{18}F_2O_2$
Molecular Weight: 352.38

A 100 mL round bottom flask was charged with 1,2,3,4-tetrafluorotriphenylene (0.601 g, 2.0 mmol), ethanol (25 mL), toluene (25 mL) and *t*-BuOK (1.804 g, 16.0 mmol, 8 eq). The mixture was heated in a 90 °C oil bath to give a clear solution and refluxed overnight (approximately 12 hours). After this time, TLC showed that no starting material remained and only the mono-substituted product was formed. A Dean-Stark apparatus was utilized to remove approximately half the amount of solvent and the remaining solution was refluxed for another 5 hours. After this time TLC showed that a new product with higher polarity had formed. The reaction was cooled to room temperature, silica gel (approximately 2 g) was added and the remaining solvent was removed by rotary evaporation. The brown powder obtained was placed at the top of a silica gel column and eluted (hexanes). Fractions containing the product were combined and concentrated to give white fibrous crystals (0.218 g, 6.7 mmol, 33 % yield) as the first product 2-ethoxy-1,3,4-trifluorotriphenylene and colorless needle like crystals (0.386 g, 1.1 mmol, 55% yield) 2,3-diethoxy-1,4-difluorotriphenylene as the second product.

The mono-substituted 2-ethoxy-1,3,4-trifluorotriphenylene can be efficiently converted to di-substituted 2,3-diethoxy-1,4-difluorotriphenylene when a Dean-Stark apparatus was applied to remove the excess amount of low boiling point solvents.

A 100 mL round bottom flask was charged with 2-ethoxy-1,3,4-trifluorotriphenylene (0.328 g, 1.0 mmol), ethanol (15 mL), toluene (25 mL) and *t*-BuOK (1.119 g, 10.0 mmol). The mixture was refluxed in a 90°C oil bath for half an hour, then a Dean-Stark apparatus was utilized to remove the ethanol and the remaining solution was refluxed at 110 °C for another 12 hours. After this time, TLC showed that the starting material 1,2,3,4-tetrafluorotriphenylene was nearly consumed and the mixture was cooled to room temperature. Silica gel (approximately 2 g) was added and the remaining solvent was removed by rotary evaporation. The brown powder obtained was placed at the top of a silica gel column and eluted (Eluent: hexanes). Fractions containing the product were combined together and concentrated to give white crystals (0.275 g, 0.78 mmol, 78 % yield) as final product.

2-ethoxy-1,3,4-trifluorotriphenylene.

M.P.: 114.0 – 115.5 °C

^{1}H-NMR (400 MHz, $CDCl_3$): 8.94 – 8.89 (m, 2H), 8.60 – 8.57 (m, 2H), 7.67 - 7.59 (m, 4H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.50 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): 150.78 (d, *J* = 249 Hz), 146.28 (d, *J* = 250 Hz), 143.96 (d, *J* = 247 Hz), 130.27 (d, *J* = 10.2 Hz), 128.07, 128.01, 127.00, 127.97, 127.82, 127.76, 127.73, 127.70, 127.68, 127.65, 127.53, 126.46, 123.16 (d, *J* = 1.1Hz), 115.94 (d, *J* = 25.4 Hz), 71.09, 15.56.

^{19}F-NMR (376 MHz, $CDCl_3$): -130.99 - -131.04 (m), -140.08 - -140.17 (m), -152.12 (dd, J_1 = 18.8 Hz, J_2 = 7.1 Hz).

2,3-diethoxy-1,4-difluorotriphenylene.

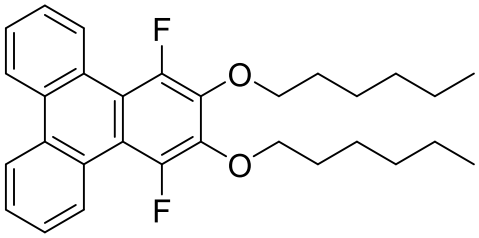
M.P.: 96.0 – 102.0 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.99 – 8.96 (m, 2H), 8.62 – 8.59 (m, 2H), 7.66 - 7.59 (m, 4H), 4.34 (q, *J* = 7.2 Hz, 4H), 1.49 (t, *J* = 7.2 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ: 151.35 (dd, J_1 = 248 Hz, J_2 = 4 Hz), 140.28 (dd, J_1 = 13.5 Hz, J_2 = 7.5 Hz), 130.25, 127.88 (t, *J* = 19.8 Hz), 127.88 (d, *J* = 30.5 Hz), 127.56 (d, *J* = 6.2 Hz), 126.98, 123.12, 116.05 (t, *J* = 5.8 Hz), 70.59, 15.70.

^{19}F-NMR (376 MHz, $CDCl_3$) δ: -132.24 (s).

1,4-Difluoro-2,3-dihexyloxytriphenylene



Chemical Formula: $C_{30}H_{34}F_2O_2$
Molecular Weight: 464.60

A 100 mL round bottom flask was charged with 1,2,3,4-tetrafluorotriphenylene (0.301 g, 1.0 mmol), 1-hexanol (0.809 g, 8.0 mmol), *p*-xylene (10 mL) and *t*-BuOK (0.901 g, 8.0 mmol). The resulting mixture was refluxed for 24 hours and TLC showed that the starting material 1,2,3,4-tetrafluorotriphenylene was consumed.

The mixture was cooled to room temperature, the solvent and excess hexanol was removed by Kugelrohr distillation. The residue was dissolved in ethyl acetate (~ 10 mL) and silica gel (approximately 2 g) was added. After removing the solvent by rotary evaporation, the brown powder obtained was placed at the top of a silica gel column and eluted (Eluent: hexanes). Fractions containing the product were combined together and concentrated to give sticky yellow oil, which was cooled to give waxy yellow crystals (0.112 g, 0.24 mmol, 24 % yield) as final product.

The recrystallization of the waxy solid was attempted in various solvents but ended in failure.

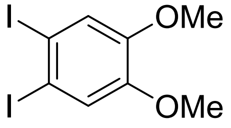
M.P.: 46.0 – 49.0 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.99 – 8.97 (m, 2H), 8.62 – 8.60 (m, 2H), 7.66 - 7.60 (m, 4H), 4.25 (q, *J* = 6.6 Hz, 4H), 1.90 – 1.82 (m, 4H), 1.590 -1.51 (m, 4H), 1.40 – 1.36 (m, 8H), 0.93 (q, *J* = 7.0 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ: 151.33 (dd, J_1 = 248 Hz, J_2 = 4 Hz), 140.61 (dd, J_1 = 13.5 Hz, J_2 = 7.7 Hz), 130.24, 127.90 (d, J = 30.5 Hz), 127.90 (t, J = 19.7 Hz), 127.54 (d, J = 3.4 Hz), 123.12, 122.98, 115.99 (t, J = 5.3 Hz), 75.19, 31.65, 30.23, 25.59, 22.66, 14.07.
^{19}F-NMR (376 MHz, $CDCl_3$) δ: -132.24 (s).

Procedures for the synthesis of fluorinated triphenylene discotic liquid crystals

1,2-diiodo-4,5-dimethoxybenzene (Compound 2)



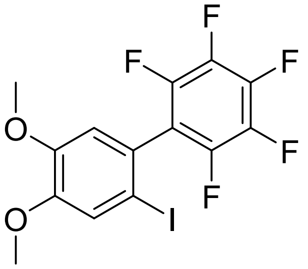
Molecular Weight: 389.96

In a 100 mL flask, periodic acid (4.560 g, 20.0 mmol) was dissolved in methanol (30 mL). Iodine (10.356 g, 40.8 mmol) was then added and the mixture obtained was stirred for 15 min under room temperature. Veratrol (6.944 g, 50.3 mmol) was added and the mixture was gently refluxed at 70 °C for 4 hours. During this time, a white precipitate formed. The mixture was then cooled to room temperature and poured into a solution of Na_2SO_3 (20 g in 200 mL water). The white solid formed was isolated via suction filtration, washed with cold methanol (20 mL) and air-dried, giving white powder (17.296 g, 44.4 mmol, 89 % yield) as the desired product.

M.P.: 132.0 – 133.0 °C (Lit: 133 °C).
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.24 (s, 2H), 3.84 (d, J = 0.4 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 149.55, 121.58, 96.05, 56.15.

Reference: Lacour, J.; Monchaud, D.; Bernardinelli, G.; Favarger, F., *Org. Lett.* **2001**, *3* (9), 1407-1410.

2,3,4,5,6-pentafluoro-2'-iodo-4',5'-dimethoxy-1,1'-biphenyl (Compound 3)

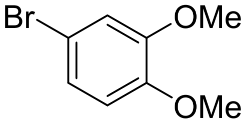


Molecular Weight: 430.11

A 100 mL flask equipped with magnetic stirbar was flushed thoroughly with nitrogen and charged with potassium pentafluorobenzoate (5.002 g, 20.0 mmol), CuI (0.765 g, 4.0 mmol), 4,5-diiodoveratrol (7.809 g, 20.0 mmol) and diglyme (20 mL). The mixture was stirred at 145 °C and TLC was used to follow the reaction progress. After six hours, TLC indicated some 4,5-diiodoveratrol still persisted so more potassium pentafluorobenzoate (2.511 g, 10.0 mmol) was added and the reaction was complete in two additional hours. The resulting mixture was cooled and diluted with ethyl acetate (100 mL). After gravity filtration the filtrate was washed with water (150 mL x 5) thoroughly to remove diglyme residue. The organic phase was dried over with anhydrous $MgSO_4$ and mixed with silica gel (~ 10g). After the removal of solvent, the yellow powder obtained was placed at the top of a silica column and eluted (eluent: hexanes). Fractions containing the desired product were combined and concentrated.After removal of the solvent by rotary evaporation, a colorless oil was obtained which crystallized on standing (4.725 g, 11.0 mmol, 55 % yield). However, this product is not pure, which contains small amount di-substituted product might mixed with the final product (cannot be isolated) which caused a board melting point of the product.

M.P.: 88 – 93 °C.
^{1}H-NMR (400 MHz, CDCl$_3$) δ: 7.19 (s, 1H), 6.76 (s, 1H), 3.96 (s, 3H), 3.89 (s, 3H).
^{13}C-NMR (100 MHz, CDCl$_3$) δ: 150.58, 148.54, 144.30 (d, J = 250.1 Hz), 141.10 (d, J = 253.0 Hz), 136.63 (d, J = 251.9 Hz), 119.45, 115.65, 114.83, 114.07, 56.26, 56.21.
^{19}F-NMR (376 MHz, CDCl$_3$) δ: 139.57 (dd, J_1 = 23.5 Hz, J_2 = 8.1 Hz, 2F), -154.78 (t, J = 20.9 Hz, 1F), -161.83 – -161.98 (m, 2F).

4-Bromoveratol (Compound 4)



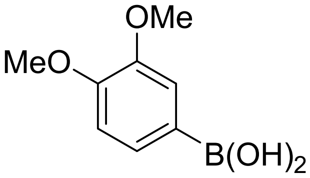
Molecular Weight: 217.06

A 250 mL flask was charged with CHCl$_3$ (50 mL), veratrol (6.902 g, 50.0 mmol), NBS (8.975 g, 50.4 mmol) and silica gel (~ 5 g). The mixture obtained was stirred at room temperature overnight (~ 12 h). After that, the solid was filtered and the filtrate was washed with Na$_2$SO$_3$ solution (10 g in 100 mL water, 50 mL x 2). The organic phase was dried over anhydrous MgSO$_4$, the drying agent was removed by filtration and the solvent was removed via rotary evaporation. The crude product obtained was purified by Kugelrohr distillation (1 millibar, 110 °C), giving a colorless oil (9.971 g, 45.9 mmol, 92 % yield) as the desired product.

^{1}H-NMR (400 MHz, CDCl$_3$) δ: 7.01 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.96 (d, J = 2.4 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H).
^{13}C-NMR (100 MHz, CDCl$_3$) δ: 149.68, 148.26, 123.32, 114.69, 112.64, 112.44, 56.01, 55.95.

Reference: Konishi, Hisatoshi; Aritomi, Katsutomo; Okano, Tamon; Kiji, Jitsuo *Bull. Chem. Soc. Jpn.,* 1989, vol. 62, # 2 p. 591 – 593

3,4-dimethoxyphenylboronic acid (Compound 5)



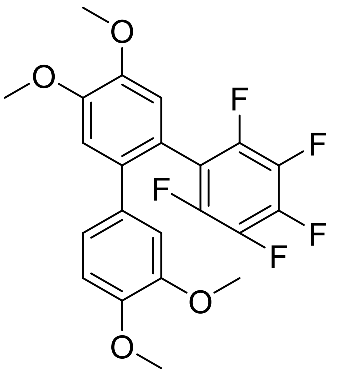
Molecular Weight: 181.98

An oven dried 250 mL flask equipped with magnetic stir bar was charged with 4-bromoveratrol (8.683 g, 40.0 mmol) and freshly distilled anhydrous THF (40 mL). The resulting solution was cooled to -78 °C under a nitrogen atmosphere and *n*-BuLi solution (32 mL, 1.6 M in hexane, 51.2 mmol) was added dropwise. After being stirred for approximately 1 hour, B(O-*i*-Pr)$_3$ (11.316 g, 60.2 mmol) was added to the previous solution to give a pale-yellow suspension. The mixture obtained was stirred overnight (~ 12h) and the temperature was permitted to rise to room temperature. It was then treated with hydrochloric acid (1M, 100 mL) to form two layers. The aqueous phase was extracted with diethyl ether (100 mL x 3) and organic phases were combined. After drying with anhydrous $MgSO_4$, the solution was concentrated to give yellow sticky oil. Hexanes (~ 10 mL) were added to precipitate the final product (3.713 g, 20.4 mmol, 51 % yield) as a white solid.

M.P.: 247.0 – 250.5 °C.
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.86 (s, 2H), 7.38 (s, 1H), 7.38 (d, *J* = 6.8 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 150.58, 147.89, 127.65, 125.73, 117.16, 110.87, 55.31, 55.25.

Reference: Rosen, Brad M.; Wilson, Daniela A.; Wilson, Christopher J.; Peterca, Mihai; Won, Betty C.; Huang, Chenghong; Lipski, Linda R.; Zeng, Xiangbing; Ungar, Goran; Heiney, Paul A.; Percec, Virgil. *J. Am. Chem. Soc.,* 2009, 131, 17500 – 17521.

2,3,4,5,6-pentafluoro-3'',4',4'',5'-tetramethoxy-1,1':2',1''-terphenyl (Compound 6)

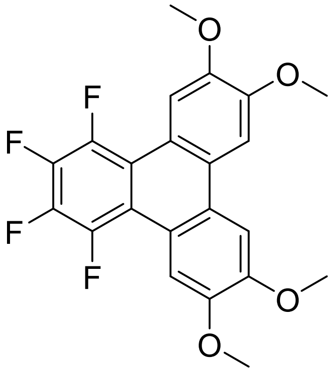


Molecular Weight: 440.37

A nitrogen flushed 50 mL flask with magnetic stir bar was charged with 3,4-dimethoxyphenylboronic acid (0.882 g, 4.85 mmol), 2,3,4,5,6-pentafluoro-2'-iodo-4',5'-dimethoxy-1,1'-biphenyl (1.491 g, 3.5 mmol), potassium carbonate (0.675 g, 4.89 mmol), toluene (20 mL) and ethanol (5 mL). The resulting mixture was heated to a gentle reflux and tetrakis(triphenylphosphine)palladium (0) (40.812 mg, 0.035 mmol, 1%) was added. After being refluxed for 12 hours, TLC indicated that a new compound was formed, and the mixture was cooled to room temperature. The solid was filtered off with gravity filtration and the filtrate was mixed with silica gel (~ 5g). The volatile solvent was removed by rotary evaporation and the adsorbed material was placed at the top of a silica gel column to elute (eluent: hexane: EtOAc = 10:1). Fractions containing the desired product were combined and condensed, affording white crystals (1.319 g, 3.0 mmol, 86 % yield) as desired product. The compound was sufficiently pure for subsequent reactions.

M.P.: 152.0 – 154.5 °C.
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.97 (s, 1H), 6.78 (s, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.70 – 6.65 (m, 2H), 3.96 (s, 3H), 3.92 (s, 3H), 3.87 (s, 3H), 3.76 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 149.77, 148.34, 148.26, 148.14, 144.29 (d, *J* = 243.8 Hz), 140.37 (d, *J* = 252.2 Hz), 137.34 (d, *J* = 249.6 Hz), 135.89, 133.03, 120.91, 116.56, 115.97, 113.55, 113.14, 111.87, 110.79, 56.17, 56.02, 55.79, 55.76.
^{19}F-NMR (376 MHz, $CDCl_3$) δ: -140.54 (dd, J_1 = 23.7 Hz, J_2 = 8.3 Hz, 2F), -156.11 (t, *J* = 20.7 Hz, 1F), -163.07 – -163.21 (m, 2F).

1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (Compound 7)

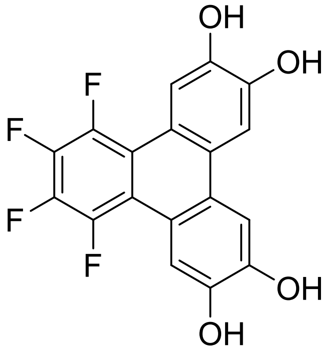


Molecular Weight: 420.36

In a quartz vessel, 2,3,4,5,6-pentafluoro-3'',4',4'',5'-tetramethoxy-1,1':2',1''-terphenyl (0.444 g, 1.0 mmol) was dissolved in acetonitrile (100 mL). The solution was degassed with nitrogen and irradiated for 2 hours in a Rayonette photochemical reactor equipped with 16 x 254 nm ultraviolet lamps. After that time, TLC indicated the starting material was completely consumed and white needle-like crystals precipitated out of the solution. About half of the solvent was removed by rotary evaporation and the remaining slurry was cooled in ice bath. The suspended solid was isolated by suction filtration and air dried, giving gray crystals (0.357 g, 0.85 mmol, 85 % yield as product) as desired product.

Phase behavior (°C): K 197.6 Col_h 310.3 I 307.5 Col_h 181.7 K
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.23 (dd, J_1 = 4.0 Hz, J_2 = 2.4 Hz, 2H),7.63 (s, 2H), 4.11 (s, 6H), 4.04 (s, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 149.68, 148.56, 145.37 (d, J = 249.1 Hz), 138.49 (d, J = 250.1 Hz), 124.80, 119.41, 115.19, 108.77 (d, J = 31.4 Hz), 103.61, 55.84, 55.80.
^{19}F-NMR (376 MHz, $CDCl_3$) δ: -139.84 – -139.89 (m, 2F), -159.36 (d, J = 16.2 Hz, 2F).

9,10,11,12-tetrafluorotriphenylene-2,3,6,7-tetraol (Compound 8)



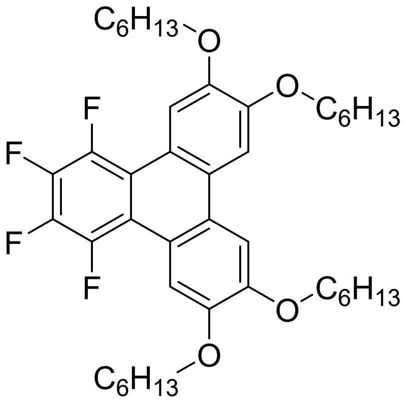
Molecular Weight: 364.25

A 100 mL round bottom flask equipped with magnetic stirbar was charged with 1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (0.631 g, 1.5 mmol) and dichloromethane (50 mL). The resulting solution was chilled in an ice bath and a solution of BBr_3 (2.230 g, 9.0 mmol, 6 eq) in dichloromethane (10 mL) was added dropwise. After the addition is completed, the mixture obtained was stirred overnight and the temperature was allowed to reach room temperature. Water (50 mL) was added followed by ether (50 mL) and then the organic phase was isolated and dried with anhydrous $MgSO_4$. After the removal of drying agent via gravity filtration, the solvent was removed under reduced pressure to give tan solid (0.537.g, 1.47 mmol, 98 %) as desired product.

This compound was used as crude in the next step without any further purifications.

M.P.: > 375 °C.
^{1}H-NMR (400 MHz, DMSO) δ: 9.78 – 9.78 (br, 4H), 8.23 (s, 2H), 7.76 (s, 2H).
^{13}C-NMR (100 MHz, DMSO) δ: 147.51, 145.60, 144.64 (d, *J* = 242.5 Hz), 137.47 (d, *J* = 244.8 Hz), 124.16, 117.09, 114.82, 112.61 (t, *J* = 14.7 Hz), 107.94.
^{19}F-NMR (376 MHz, DMSO) δ: -139.89 (d, *J* = 16.5 Hz, 2F), -160.39 (d, *J* = 17.3 Hz, 2F).

1,2,3,4-tetrafluoro-6,7,10,11-tetrakis(hexyloxy)triphenylene (Compound 9b)

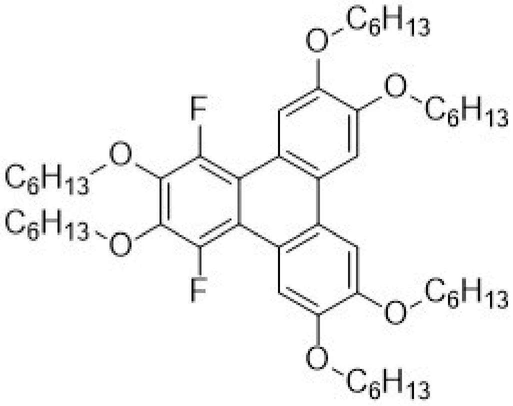


Molecular Weight: 700.90

A 100 mL flask equipped with magnetic stirbar was charged with 9,10,11,12-tetrafluorotriphenylene-2,3,6,7-tetraol (0.365 g, 1.0 mmol), 1-iodohexane (1.701 g, 8.0 mmol) potassium carbonate (2.223 g, 16 mmol) and anhydrous DMF (5 mL). The mixture was heated at 100 °C for 24 hours and TLC indicated a single new product was formed and the starting material tetraol was completely consumed. The mixture was then cooled to room temperature and diluted with water to a total volume of 100 mL and stirred for 2 hours. The solid was filtered and air-dried, giving a gray powder (0.607 g, 0.87 mmol, 87 % yield) as product.

Phase behavior (°C): K 97.7 Col$_h$ 183.0 I 180.3 Col$_h$ 58.0 K
^{1}H-NMR (400 MHz, CDCl$_3$) δ: 7.72 (s, 2H), 7.26 (s, 2H), 4.23 (t, *J* = 6.4 Hz, 4H), 4.15 (t, *J* = 6.4 Hz, 4H), 1.95 – 1.90 (m, 8H), 1.63 – 1.56 (m, 8H), 1.42 – 1.38 (m, 16H), 0.96 – 0.92 (m, 12H).
^{13}C-NMR (100 MHz, CDCl$_3$) δ: 149.78, 148.72, 145.42 (d, *J* = 248.8 Hz), 138.43 (d, *J* = 241.5 Hz), 125.01, 119.51, 115.41, 110.83 (t, *J* = 15.5 Hz), 106.25, 69.38, 69.05, 31.69, 31.67, 29.31, 29.22, 25.84, 25.80, 22.67, 14.06.
^{19}F-NMR (376 MHz, CDCl$_3$) δ: -140.41 (d, *J* = 11.6 Hz, 2F), -160.20 (d, *J* = 16.2 Hz, 2F).

1,4-difluoro-2,3,6,7,10,11-hexakis(hexyloxy)triphenylene (Compound 10b)

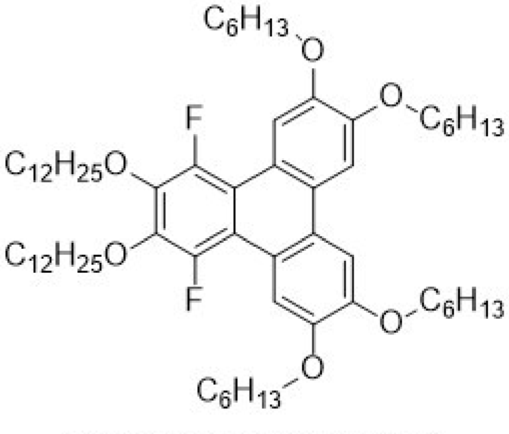


Molecular Weight: 865.24

A 100 mL round bottom flask with magnetic stir bar was placed with 1,2,3,4-tetrafluoro-6,7,10,11-tetrakis(hexyloxy)triphenylene (0.423 g, 0.6 mmol), 1-hexanol (10 mL) and *t*-BuOK (0.551 g, 4.8 mmol). The mixture was heated up to achieve a gentle reflux and after 2 days, it was cooled to room temperature and diluted with diethyl ether to a total volume of 100 mL followed by water washing (100 mL x 3). The organic phase was then dried over with anhydrous MgSO$_4$ and mixed with silica gel (~2 g). After the removal of solvent, the yellow powder obtained was placed at the top of a silica column and eluted (eluent: hexanes:EtOAc = 20:1). Fractions containing the product were combined and concentrated to give sticky oil, which became waxy solid (0.306 g, 58 % yield) after cooling.

Phase behavior (^{o}C): (T<-150) Col$_h$ 116.5 I 113.5 CoI$_h$ (T<-150)
^{1}H-NMR (400 MHz, CDCl$_3$) δ: 8.51 – 8.47 (m, 2H), 7.83 – 7.80 (m, 2H), 4.29 – 4.17 (m, 12H), 2.00 – 1.85 (m, 12H), 1.65 – 1.54 (m, 12H), 1.47 – 1.39 (m, 24 H), 0.99 – 0.89 (m, 18H).
^{13}C-NMR (100 MHz, CDCl$_3$) δ: 150.72 (d, *J* = 245.7 Hz), 149.19, 148.58, 139.49 (d, *J* = 7.5 Hz), 124.88, 120.71, 115.97, 111.74, 106.83, 75.13, 69.11, 69.09, 31.83, 31.67, 30.52, 30.22, 29.39, 29.26, 25.92, 22.71, 22.66, 14.09, 14.04.
^{19}F-NMR (376 MHz, CDCl$_3$) δ: -133.47 - -133.56 (m, 2F).

2,3-bis(dodecyloxy)-1,4-difluoro-6,7,10,11-tetrakis(hexyloxy)triphenylene (Compound 10c-i)



Molecular Weight: 1033.56

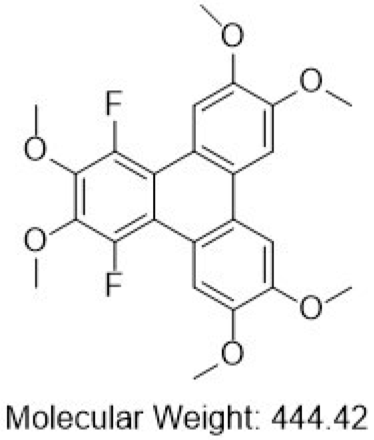
This compound was prepared by using the same methodology in the synthesis of compound 1,4-difluoro-2,3,6,7,10,11-hexakis(hexyloxy)triphenylene.

A 100 mL flask with magnetic stir bar was charged with 1,2,3,4-tetrafluoro-6,7,10,11-tetrakis(hexyloxy)triphenylene (0.301 g, 0.43 mmol), potassium *t*-butoxide (0.391 g, 3.5 mmol, 8 eq) and 1-decanol (10 mL). The mixture was heated up to 110 °C to make all the solid dissolved.

After being heated for 4 days, the mixture was cooled and the solvent was removed by rotary evaporation and the excess amount of alcohol was removed by Kugelrohr distillation (125 °C, 0.35 millibar). The solid was then dissolved again in diethyl ether (10 mL) and mixed with silica gel (~ 2 g). After the removal of solvent, the resulting tan powder was placed on the top of silica gel column and eluted (eluent: hexanes: EtOAc = 50:1), giving sticky solid (0.360 g, 0.35 mmol, 81 %) as final product.

Phase behavior (°C): K 39.6 $\mathrm{Col_h}$ 42.4 I 35.1 $\mathrm{Col_h}$ 12.8 K
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.47 (t, *J* = 2.8 Hz, 2H), 7.81 (s, 2H), 4.24 (t, *J* = 6.8 Hz, 2H), 4.22 (t, *J* = 6.8 Hz, 2H), 4.19 (t, *J* = 6.8 Hz, 2H), 1.96 – 1.82 (m, 12H), 1.61 – 1.50 (m, 12H), 1.41 – 1.27 (m, 48H), 0.93 (t, *J* = 6.4 Hz, 3H), 0.93 (t, *J* = 6.4 Hz, 2H), 0.88 (t, *J* = 6.4 Hz, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 150.77 (dd, J_1 = 246.0 Hz, J_2 = 3.1 Hz), 149.18, 148.57, 139.44 (dd, J_1 = 13.3 Hz, J_2 = 7.6 Hz), 124.87, 120.71, 115.50 (t, *J* = 5.5 Hz), 111.51 (t, *J* = 15.8 Hz), 106.78, 75.14, 69.53, 69.09, 31.95, 31.68, 30.28, 29.73, 29.68, 29.51, 29.39, 29.35, 29.26, 25.95, 25.83, 22.71, 22.67, 14.13, 14.06.
^{19}F-NMR (376 MHz, $CDCl_3$) δ: -134.08 (s, 2F).

1,4-difluoro-2,3,6,7,10,11-hexamethoxytriphenylene (Compound 11)

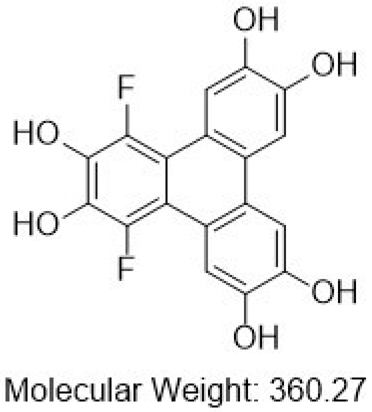


A 100 mL flask was charged with 1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (0.846 g, 2.0 mmol), potassium *t*-butoxide (2.258 g, 20 mmol, 10 eq) and methanol (10 mL)/toluene (40 mL)/THF (10 mL) as solvents. The mixture was heated up to slowly dissolve the solid.

The obtained mixture was gently refluxed for 2 days and after the mixture was cooled .The solvent was removed by rotary evaporation. The remaining solid was stirred with water (50 mL) for 2 hours. The mixture was then filtered and the solid was air-dried (tan powder, 0.723 g, 1.6 mmol, 80 % yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.44 – 8.42 (m, 2H), 7.72 (s, 2H), 4.13 (s, 6H), 4.12 (s, 6H), 4.07 (s, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 150.44 (d, *J* = 246.5 Hz), 148.73 (d, *J* = 78.6 Hz), 139.95, 124.70, 120.41, 115.45, 109.24, 109.24 (d, *J* = 32.2 Hz), 103.81, 62.28, 55.86, 55.83.
^{19}F-NMR (376 MHz, $CDCl_3$) δ: -134.50 (t, *J* = 3.38 Hz, 2F).

1,4-difluorotriphenylene-2,3,6,7,10,11-hexaol (Compound 12)

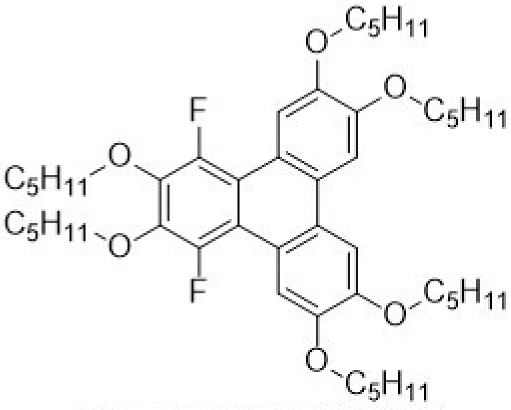


A 100 mL flask equipped with magnetic stirbar was charged with 1,4-difluoro-2,3,6,7,10,11-hexamethoxytriphenylene (0.222 g, 0.5 mmol), pyridine hydrochloride (3.452 g, 30 mmol). The mixture was heated up to approximately 170 °C and pyridine hydrochloride solid melted. The resulting mixture was heated while stirring for 4 hours and then it was cooled to room temperature.

The black solid was dispensed in water (20 mL)with sonication . This mixture was extracted with ethyl acetate (50 mL x 5). Organic phases were combined and dried over with anhydrous $MgSO_4$. After the drying agent was filtered, the filtrate was concentrated to dryness, giving a black reside (0.196 g) as desired product.

This product was not characterized and it was used directly in the next step without further purification.

1,4-difluoro-2,3,6,7,10,11-hexakis(pentyloxy)triphenylene (Compound 10a)



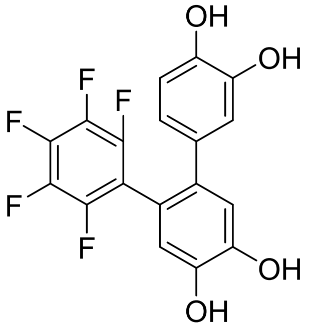
This compound was prepared by using the same methodology in the synthesis of compound 1,4-difluoro-2,3,6,7,10,11-hexakis(hexyloxy)triphenylene.

A 100 mL flask equipped with magnetic stirbar was charged with 1,4-difluorotriphenylene-2,3,6,7,10,11-hexaol (crude, 0.195 g, 0.54 mmol), 1-iodopentane (1.290 g, 6.5 mmol, 12 eq) , potassium carbonate (1.799 g, 13 mmol, 24 eq) and anhydrous DMF (10 mL). The mixture was heated at 100 °C for 24 hours and TLC indicated a new product was formed. The mixture was then cooled to room temperature and diluted with EtOAc to a total of 100 mL and washed with water (100 mL x 5) to remove DMF. The organic phase was dried over with anhydrous $MgSO_4$ and mixed with silica gel (2 g) after the removal of drying agent.

After the removal of solvent, the yellow powder obtained was placed at the top of a silica column and eluted (eluent: hexanes). Fractions containing the pure product were combined and concentrated to give light yellow solid (0.167.g, 0.21 mmol, 39 %) as final product.

Phase behavior (°C): K -12.4 Col_h 142.1 I 139.1 Col_h -40.6 K
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.48 – 8.46 (m, 2H), 7.81 (s, 2H), 4.26 – 4.18 (m, 12H), 2.00 – 1.84 (m, 12H), 1.60 – 1.42 (m, 24 H), 0.99 – 0.95 (m, 18H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 150.77 (d, *J* = 245.9 Hz), 149.17, 148.54, 139.50 (d, *J* = 7.5 Hz), 124.87, 120.69, 115.50, 111.49 (d, *J* = 15.8 Hz), 106.70, 75.13, 69.48, 69.08, 29.95, 29.05, 28.96, 28.34, 28.07, 22.57, 22.54, 14.10, 14.08.
^{19}F-NMR (376 MHz, $CDCl_3$) δ: -134.10 (d, *J* = 2.63 Hz, 2F).

2'',3'',4'',5'',6''-pentafluoro-[1,1':2',1''-terphenyl]-3,4,4',5'-tetraol (Compound 13)



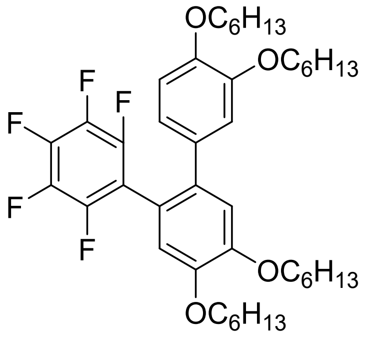
Molecular Weight: 384.26

A 250 mL flask with magnetic stir bar was charged with 2,3,4,5,6-pentafluoro-3'',4',4'',5'-tetramethoxy-1,1':2',1''-terphenyl (1.106 g, 2.5 mmol) which was dissolved in dichloromethane (50 mL). The resulting solution was chilled in an ice bath and a solution of BBr_3 (3.698 g, 15.0 mmol, 6 eq) in dichloromethane (15 mL) was added dropwise. The mixture obtained was stirred overnight and the temperature was allowed to reach room temperature. Water (100 mL) was added to form a cloudy mixture. Diethyl ether (50 mL) was added to make the mixture become clear. The organic phase was isolated and dried with anhydrous $MgSO_4$. After the removal of drying agent via filtration, the solvent was removed under reduced pressure to give gray crystals (1.131 g) as crude product.

The yield of the crude product obtained was higher than the theoretical yield, which was used directly in the next step.

M.P.: 59.0 – 65.0 °C.
^{1}H-NMR (400 MHz, DMSO) δ: 6.82 (s, H), 6.73 (s, H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.41 (d, *J* = 2.0 Hz, 1H), 6.29 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H).
^{13}C-NMR (100 MHz, DMSO) δ: 146.59, 144.588, 144.20, 144.14, 143.76 (d, *J* = 240.4 Hz), 139.26 (d, *J* = 248.7 Hz), 136.76 (d, *J* = 250.7 Hz), 133.88, 131.25, 119.06, 117.91, 116.90, 116.31 (t, *J* = 19.5 Hz), 115.52, 115.40, 113.73.
^{19}F-NMR (376 MHz, DMSO) δ: -140.85 (dd, J_1 = 25.6 Hz, J_2 = 7.5 Hz, 2F), -157.49 (t, *J* = 22.2 Hz, 1F), -163.29 – -163.44 (m, 2F).

2,3,4,5,6-pentafluoro-3'',4',4'',5'-tetrakis(hexyloxy)-1,1':2',1''-terphenyl (Compound 14)



Molecular Weight: 720.91

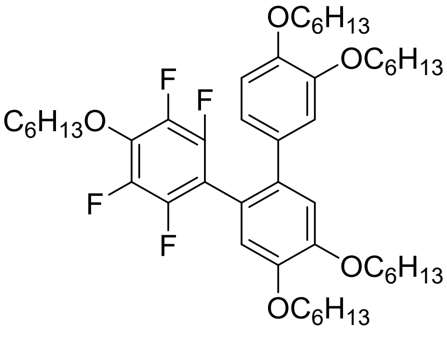
A 50 mL flask with magnetic stir bar was charged with crude 2'',3'',4'',5'',6''-pentafluoro-[1,1':2',1''-terphenyl]-3,4,4',5'-tetraol (0.969 g, 2.5 mmol), 1-iodohexane (3.196 g, 15.0 mmol), potassium carbonate (2.868 g, 20.0 mmol) and DMF (10 mL). The obtained mixture was stirred at 100 °C under nitrogen for 24 hours and then cooled to room temperature. The mixture was diluted with diethyl ether to a total volume of 100 mL and washed with water (3 x 100 mL). The organic phase was separated and dried over anhydrous $MgSO_4$. Drying agent was removed by filtration and silica gel (~ 2 g) was added. After the removal of solvent, the powder obtained was placed on a silica gel column to elute (Eluent: hexanes). The fractions containing the product were combined and concentrated to dryness, giving a colorless sticky oil (1.198 g, 1.7 mmol, 68 % yield) as desired product.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.97 (s, H), 6.80 (s, H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.67 – 6.64 (m, 2H), 4.07 (t, *J* = 6.6 Hz, 2H), 4.02 (t, *J* = 6.6 Hz, 2H), 3.96 (t, *J* = 6.6 Hz, 2H), 3.84 (t, *J* = 6.6 Hz, 2H), 1.89 – 1.71 (m, 8H), 1.53 – 1.44 (m, 8H), 1.37 – 1.33 (m, 16H), 0.92 – 0.90 (m, 12H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ: 150.07, 148.43, 148.35, 148.08, 144.08 (d, *J* = 243.8 Hz), 140.23 (d, *J* = 251.4 Hz), 137.27 (d, *J* = 253.4 Hz), 136.05, 133.26, 121.10, 116.40, 116.28, 116.13, 115.10, 114.60, 113.16, 69.56, 69.23, 69.12, 69.06, 31.62, 31.58, 31.53, 31.42, 29.29, 29.25, 29.16, 25.72, 25.64, 22.76, 22.60, 13.92, 13.89.

^{19}F-NMR (376 MHz, $CDCl_3$) δ: -140.03 – -140.13 (m, 2F), -156.29 (t, *J* = 20.9 Hz, 1F), -162.92 – -163.07 (m, 2F).

2,3,5,6-tetrafluoro-3'',4,4',4'',5'-pentakis(hexyloxy)-1,1':2',1''-terphenyl (Compound 15)



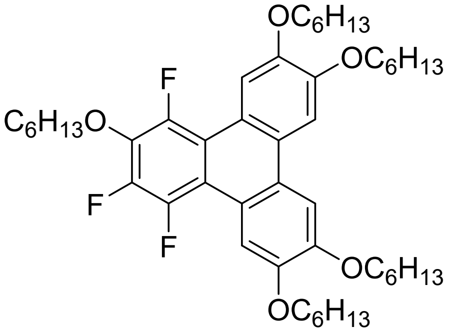
Molecular Weight: 803.08

A 50 mL flask with magnetic stir bar was charged with 2,3,4,5,6-pentafluoro-3'',4',4'',5'-tetrakis(hexyloxy)-1,1':2',1''-terphenyl (0.901 g, 1.25 mmol), 1-hexanol (10 mL) and *t*-BuOK (0.282 g, 2.5 mmol). The mixture was heated up to approximately 100 °C to make all the solids dissolve and after 24 hours TLC indicated the starting material was consumed. The mixture was cooled to room temperature and diluted with diethyl ether to a total volume of 100 mL followed washing with water (3 x 100 mL). The organic phase was dried over anhydrous $MgSO_4$ and the drying agent was then removed by gravity filtration. After the removal of solvent, the excess 1-hexanol present was removed by

Kugelrohr distillation (75 °C, 0.8 millibar). The remaining residue was dissolved in ethyl acetate (~ 50 mL) and mixed with silica gel (~ 2g). The yellow powder obtained after removing the solvent and was placed at the top of a silica column (eluent: hexane). Fractions containing the product were combined and concentrated to give sticky oil as desired product (0.700 g, 0.87 mmol, 70 % yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.95 (s, 1 H), 6.79 (s, 1 H), 6.75 (d, J = 8.0 Hz, 1H), 6.67 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 6.63 (d, J = 2.0 Hz, 1H), 4.16 (t, J = 6.6 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 4.02 (t, J = 6.6 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 3.80 (t, J = 6.6 Hz, 2H), 1.88 – 1.69 (m, 10H), 1.51 – 1.40 (m, 10H), 1.36 – 1.32 (m, 20H), 0.92 – 0.88 (m, 15H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 149.75, 148.30, 148.19, 147.91, 144.41 (d, J = 242.4 Hz), 141.06 (dd, J_1 = 245.4 Hz, J_2 = 15.3 Hz), 135.93, 133.58, 121.10, 117.37, 116.42, 115.13, 114.57, 114.48, 113.24, 75.29, 69.58, 69.23, 69.20, 69.17, 31.64, 31.60, 31.57, 31.46, 29.88, 29.40, 29.31, 29.26, 29.25, 29.18, 25.75, 25.73, 25.72, 25.67, 25.23, 22.64, 22.57, 14.03, 14.00.
^{19}F-NMR (376 MHz, $CDCl_3$) δ: -142.20 (dd, J_1 = 22.9 Hz, J_2 = 8.3 Hz, 2F), -158.08 (dd, J_1 = 22.9 Hz, J_2 = 8.3 Hz, 2F).

1,2,4-trifluoro-3,6,7,10,11-pentakis(hexyloxy)triphenylene (Compound 16b)

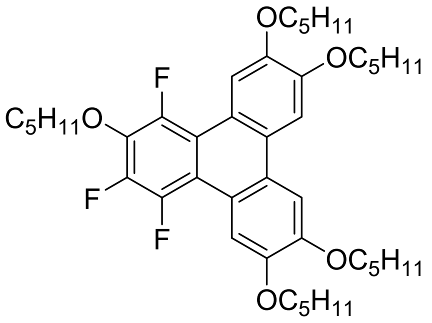


Molecular Weight: 783.07

In a quartz vessel, 2,3,5,6-tetrafluoro-3'',4,4',4'',5'-pentakis(hexyloxy)-1,1':2',1''-terphenyl (0.680 g, 0.85 mmol) was dissolved in acetonitrile (100 mL). The solution was degassed with nitrogen and irradiated for 8 hours in a Rayonette photochemical reactor equipped with 16 x 254nm ultraviolet lamps. After this time, the solvent was removed to give a brown residue (0.673 g) as crude product. The solid was dissolved again in ethyl acetate (~ 5 mL) and mixed with silica gel (~ 2 g). After concentration to dryness, the tan powder obtained was placed on the top of silica gel column and eluted (eluent: hexanes). Fractions containing the product were combined and concentrated, giving a sticky solid (0.368 g, 0.47 mmol, 55 % yield). A portion of the product was further recrystallized out of methanol and propanol to yield a less sticky solid as the final product.

Phase behavior (°C): G -12.7 K' 25.5 K 34.7 Col$_h$ 160.8 I 158.1 Col$_h$ -18.5 G
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.41 (d, J = 6.0 Hz, 1H), 8.38 (d, J = 6.0 Hz, 1H), 7.77 (d, J = 2.4 Hz, 2H), 4.29 (d, J = 6.6 Hz, 2H), 4.23 (d, J = 6.6 Hz, 2H), 4.18 (d, J = 6.6 Hz, 2H), 4.17 (d, J = 6.6 Hz, 2H), 1.96 – 1.85 (m, 10H), 1.60 – 1.54 (m, 10H), 1.41 – 1.36 (m, 20H), 0.95 – 0.92 (m, 15H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 151.40, 149.47, 149.43, 148.94, 148.65, 145.66 (dd, J_1 = 247.0 Hz, J_2 = 11.7 Hz), 143.18 (dd, J_1 = 245.2 Hz, J_2 = 6.3 Hz), 143.01 (dd, J_1 = 245.4 Hz, J_2 = 6.3 Hz), 134.61 (d, J = 12.2 Hz), 134.43 (d, J = 9.6 Hz), 124.99, 124.88, 120.15, 115.43, 115.16, 111.40 (d, J = 30.8 Hz), 111.0 (d, J = 29.7 Hz), 106.57 (d, J = 4.0 Hz), 75.56, 69.46, 69.08, 69.05, 31.69, 31.67, 31.57, 30.08, 29.34, 29.26, 29.23, 25.84, 25.82, 25.39, 22.67, 22.62, 14.06.
^{19}F-NMR (376 MHz, $CDCl_3$) δ: -132.42 – -132.49 (m, 1F), -141.40 – -141.50 (m, 1F), -153.68 (dd, J_1 = 18.8 Hz, J_2 = 5.6 Hz, 1F).

1,2,4-trifluoro-3,6,7,10,11-pentakis(pentyloxy)triphenylene (Compound 16a)



Molecular Weight: 712.94

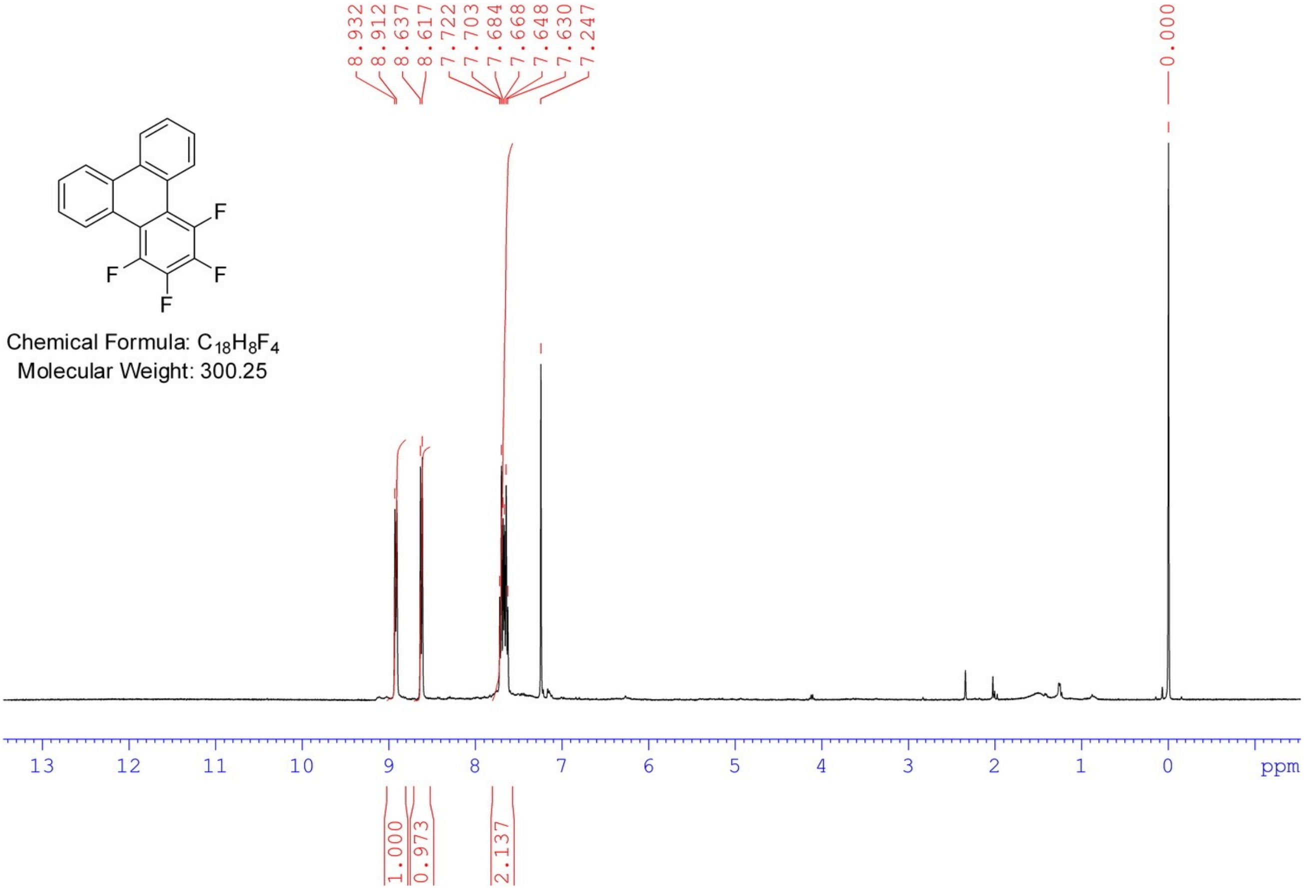
This compound was prepared by using the same methodology as for the synthesis of 1,2,4-trifluoro-3,6,7,10,11-pentakis(hexyloxy)triphenylene.

Beginning with 2'',3'',4'',5'',6''-pentafluoro-[1,1':2',1''-terphenyl]-3,4,4',5'-tetraol, 1-iodopentane was used with Na_2CO_3 in DMF to install four pentyloxy groups on the nonfluorinated rings. Next, 1-pentanol was used with *t*-BuOK to perform the S_NAr reaction and install one pentyloxy group on the *para-* position of the pentafluorinated ring. Finally, the PCDHF reaction was performed to give 1,2,4-trifluoro-3,6,7,10,11-pentakis(pentyloxy)triphenylene as the final product.

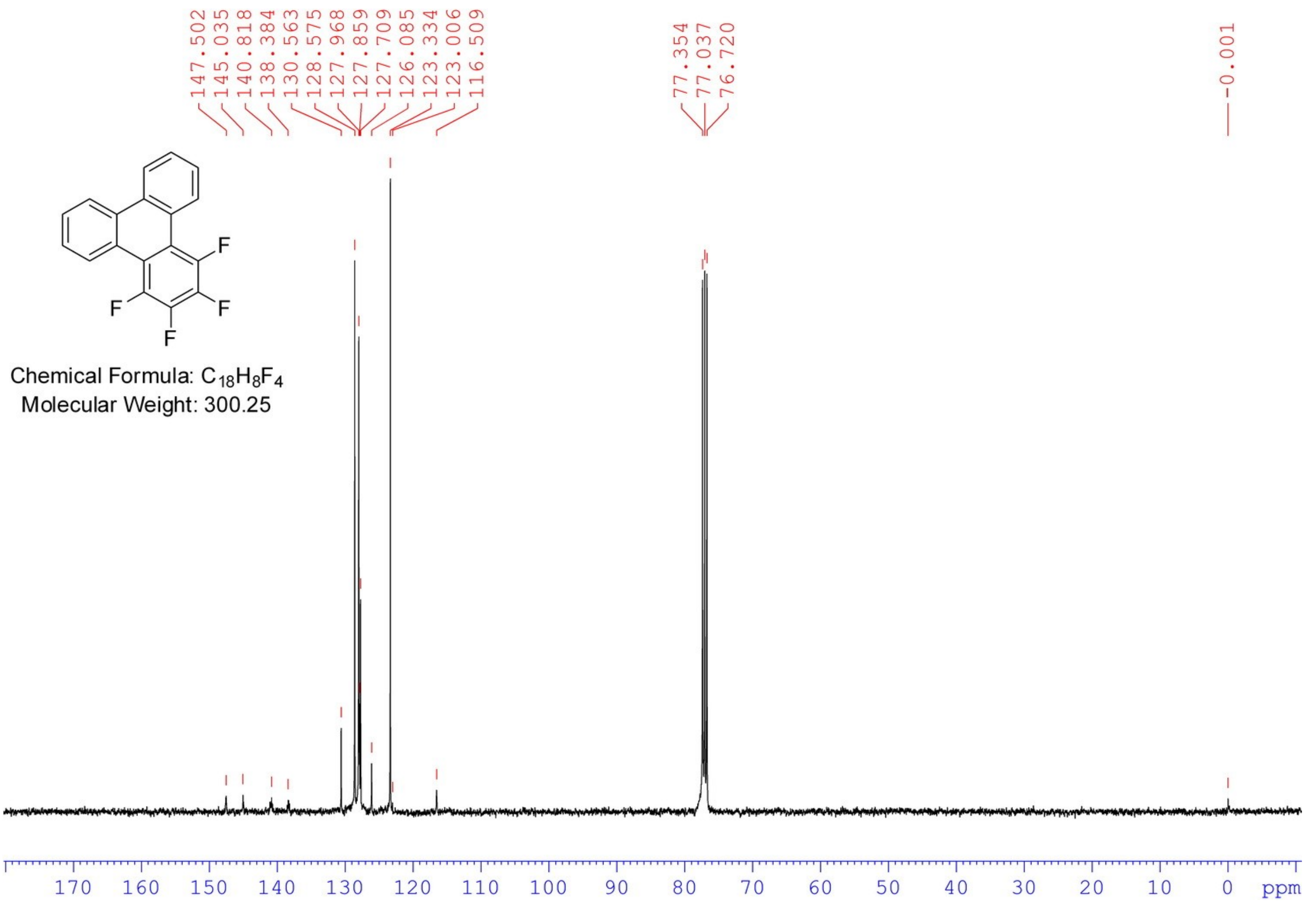
Phase behavior (°C): K 7.7 Col_h 171.5 I 168.9 Col_h -23.6 K
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.39 (d, *J* = 6.0 Hz, 1H), 8.35 (d, *J* = 6.0 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 2H), 4.28 (d, *J* = 6.6 Hz, 2H), 4.23 (d, *J* = 6.6 Hz, 2H), 4.23 (d, *J* = 6.6 Hz, 2H), 4.18 (d, *J* = 6.6 Hz, 2H), 4.16 (d, *J* = 6.6 Hz, 2H), 1.98 – 1.91 (m, 10H), 1.59 – 1.42 (m, 20H), 1.00 – 0.95 (m, 15H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 151.38, 149.42, 149.15, 148.92, 148.60, 145.62 (d, *J* = 238.0 Hz), 143.15 (d, *J* = 240.0 Hz), 143.06 (d, *J* = 238.0 Hz), 134.67, 124.96, 124.85, 120.10, 115.41, 115.12, 115.07, 111.35 (d, *J* = 31.4 Hz), 110.93 (d, *J* = 29.6 Hz), 106.68, 106.45 (d, *J* = 4.2 Hz), 75.55, 75.53, 69.39, 69.06, 69.02, 29.82, 29.06, 28.99, 28.96, 28.38, 28.36, 28.31, 27.88, 22.59, 22.56, 22.47, 14.13, 14.11.
^{19}F-NMR (376 MHz, $CDCl_3$) δ: -132.45 – -132.49 (m, 1F), -141.42 – -141.52 (m, 1F), -153.66 (dd, J_1 = 19.2 Hz, J_2 = 6.0 Hz, 1F).

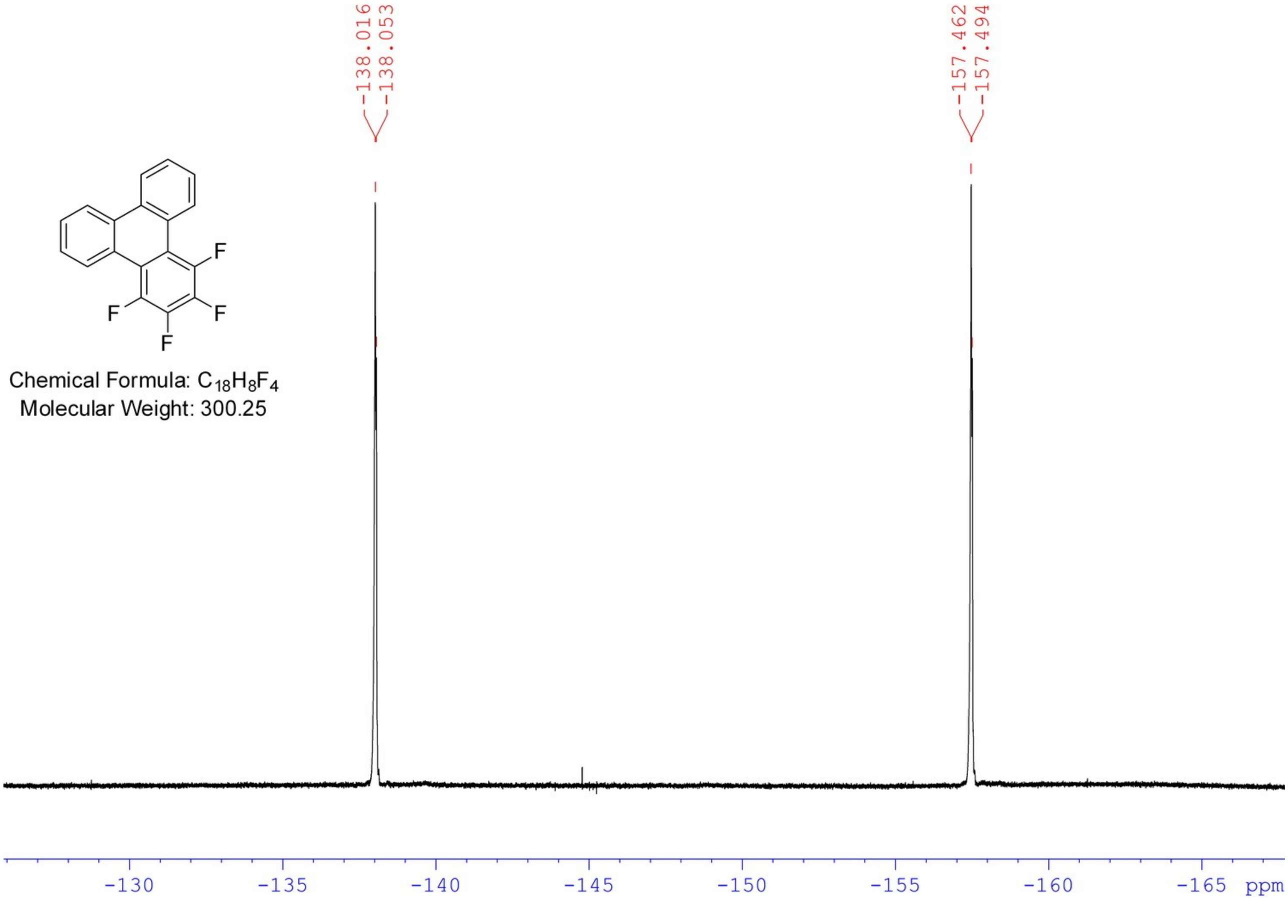
NMR Spectra

1,2,3,4-tetrafluorotriphenylene

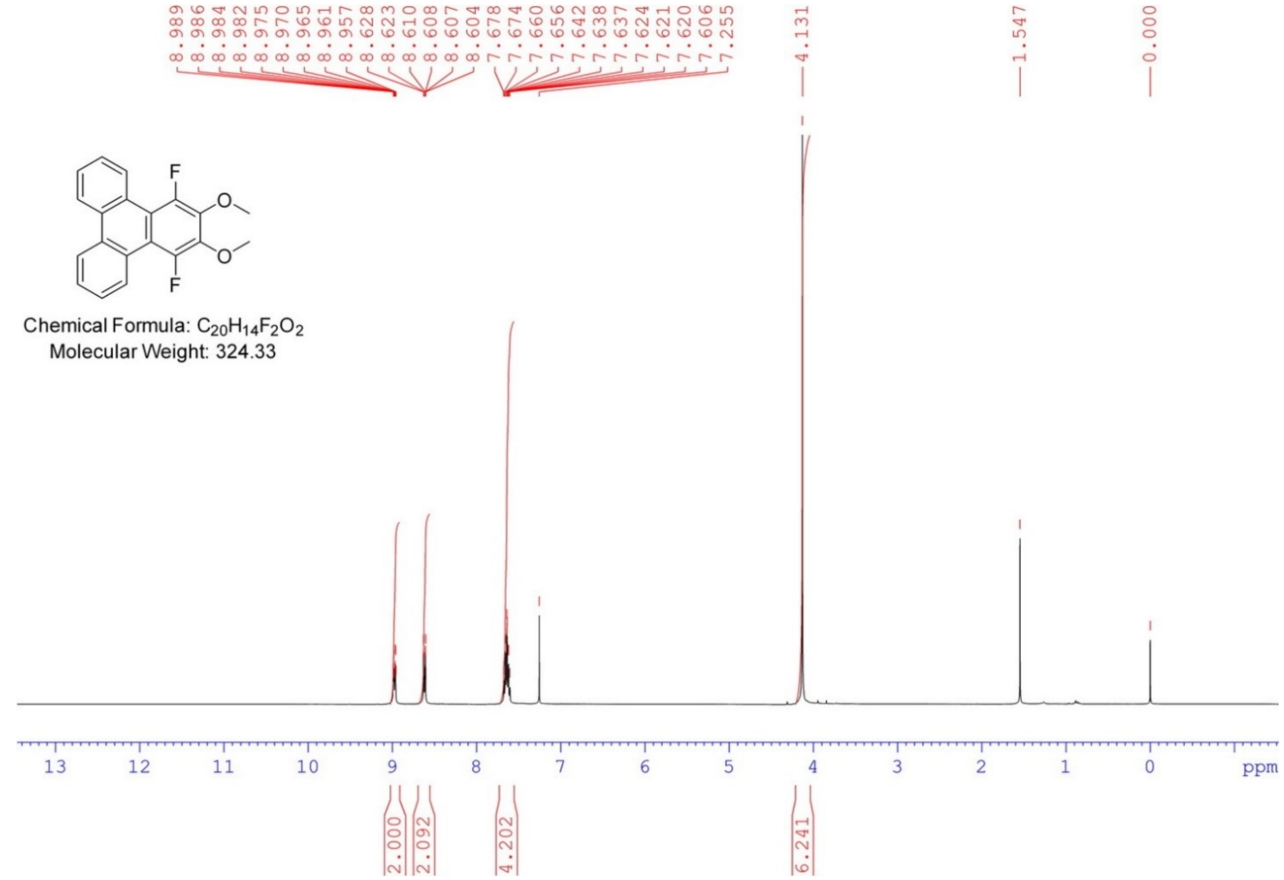


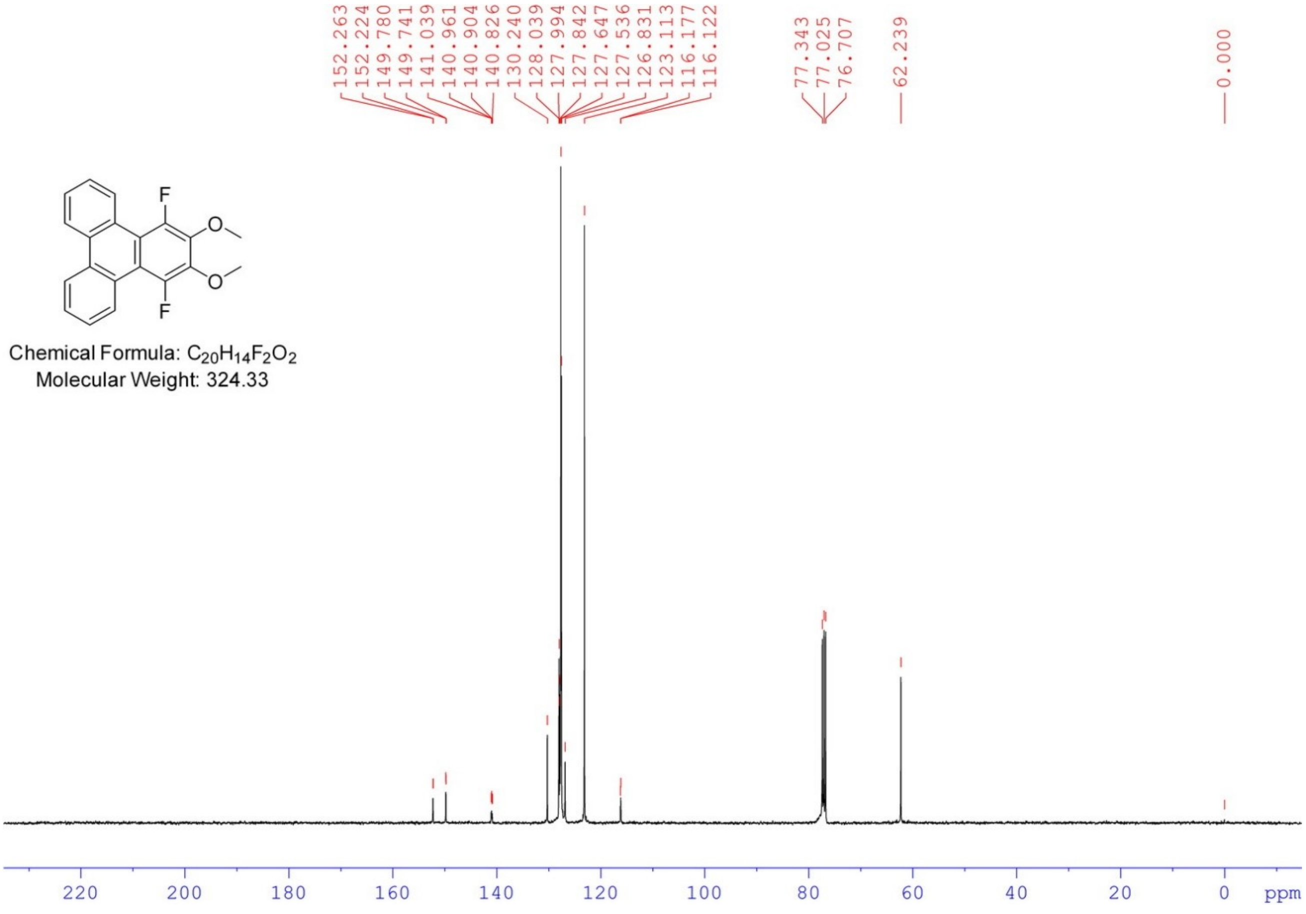
Chemical Formula: $C_{18}H_8F_4$
Molecular Weight: 300.25

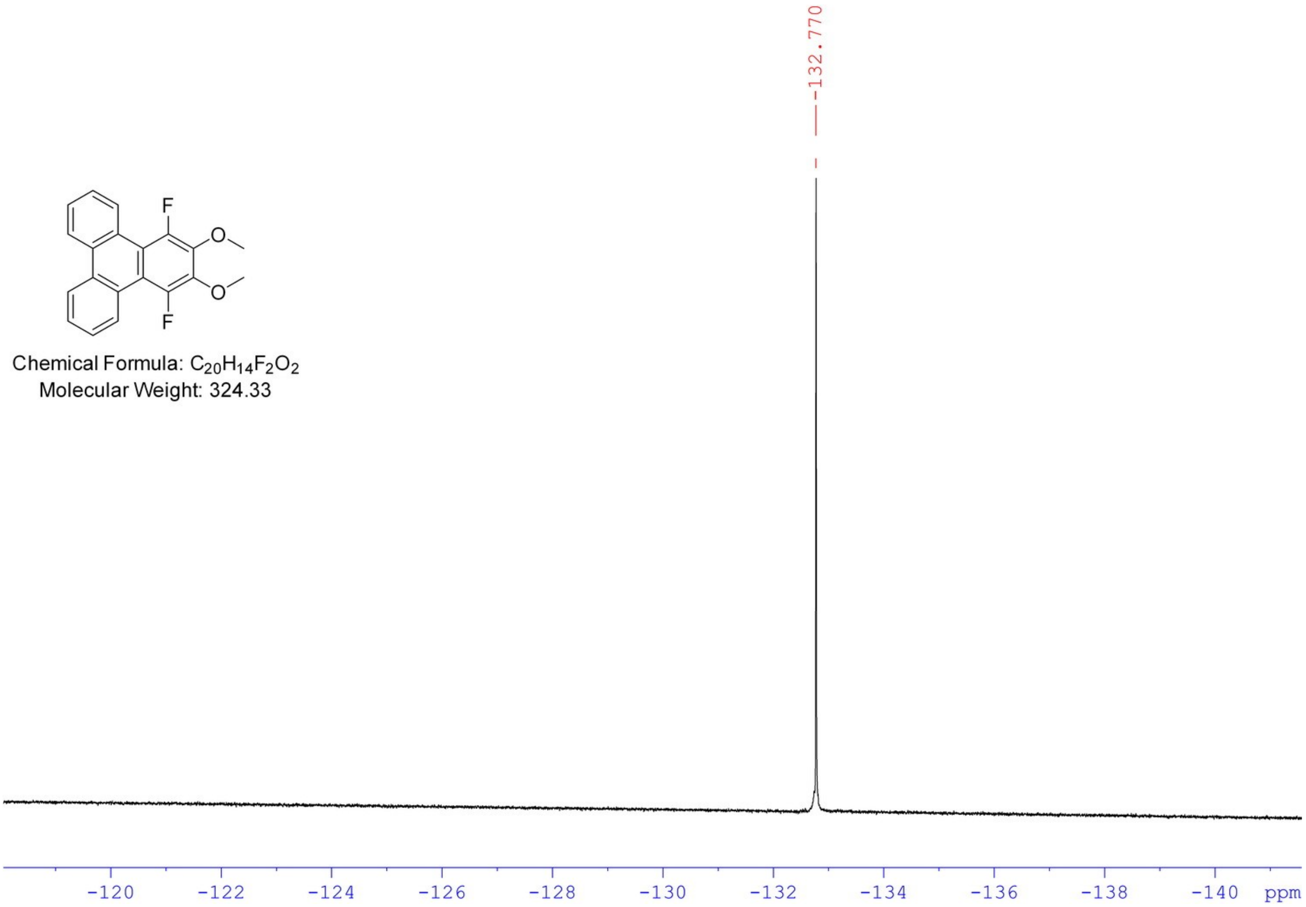

147.502
145.035
140.818
138.384
130.563
128.575
127.968
127.859
127.709
126.085
123.334
123.006
116.509
77.354
77.037
76.720
-0.001
F
F
F
F
Chemical Formula: $C_{18}H_8F_4$
Molecular Weight: 300.25
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-138.016
-138.053
-157.462
-157.494
F
F
F
F
Chemical Formula: $C_{18}H_8F_4$
Molecular Weight: 300.25
-130
-135
-140
-145
-150
-155
-160
-165
ppm

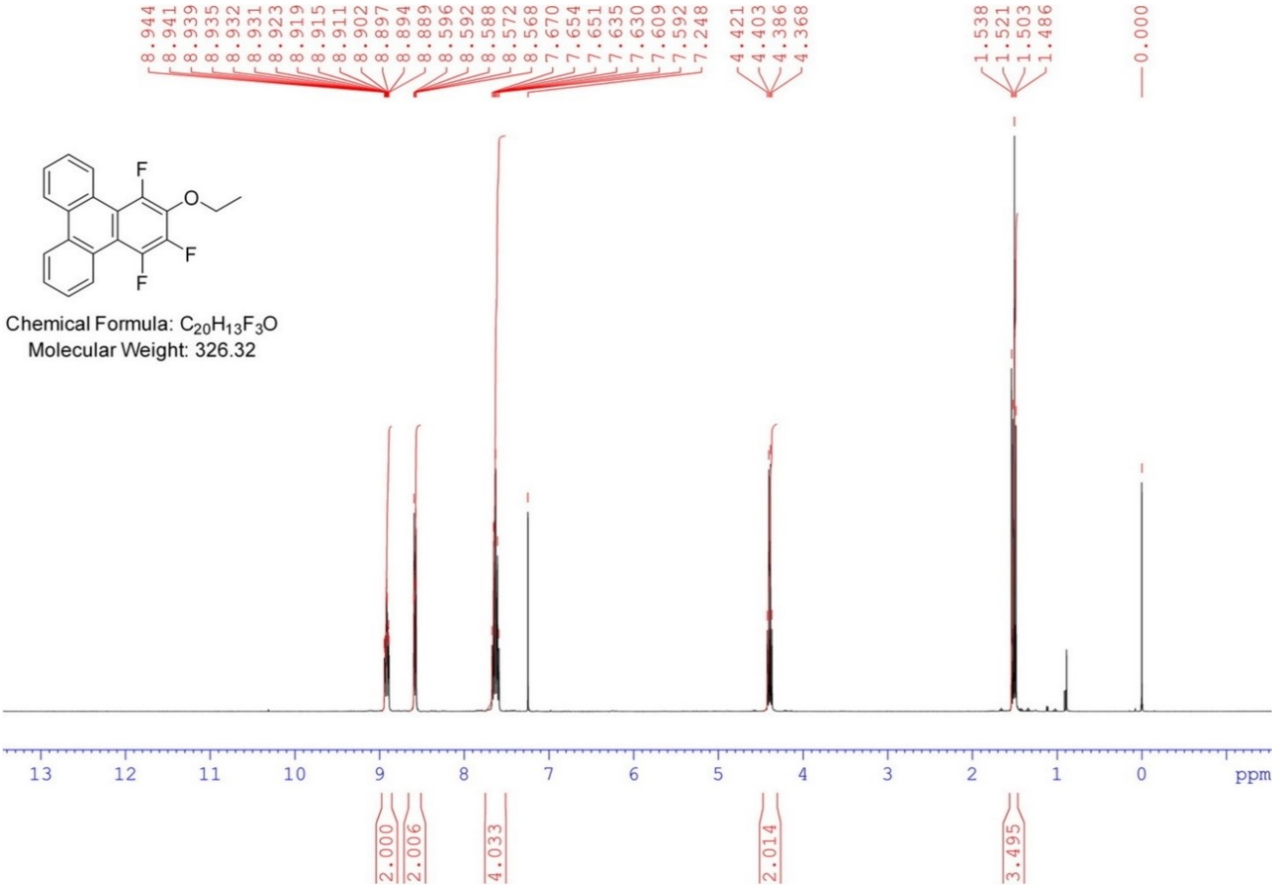
1,4-difluoro-2,3-dimethoxytriphenylene

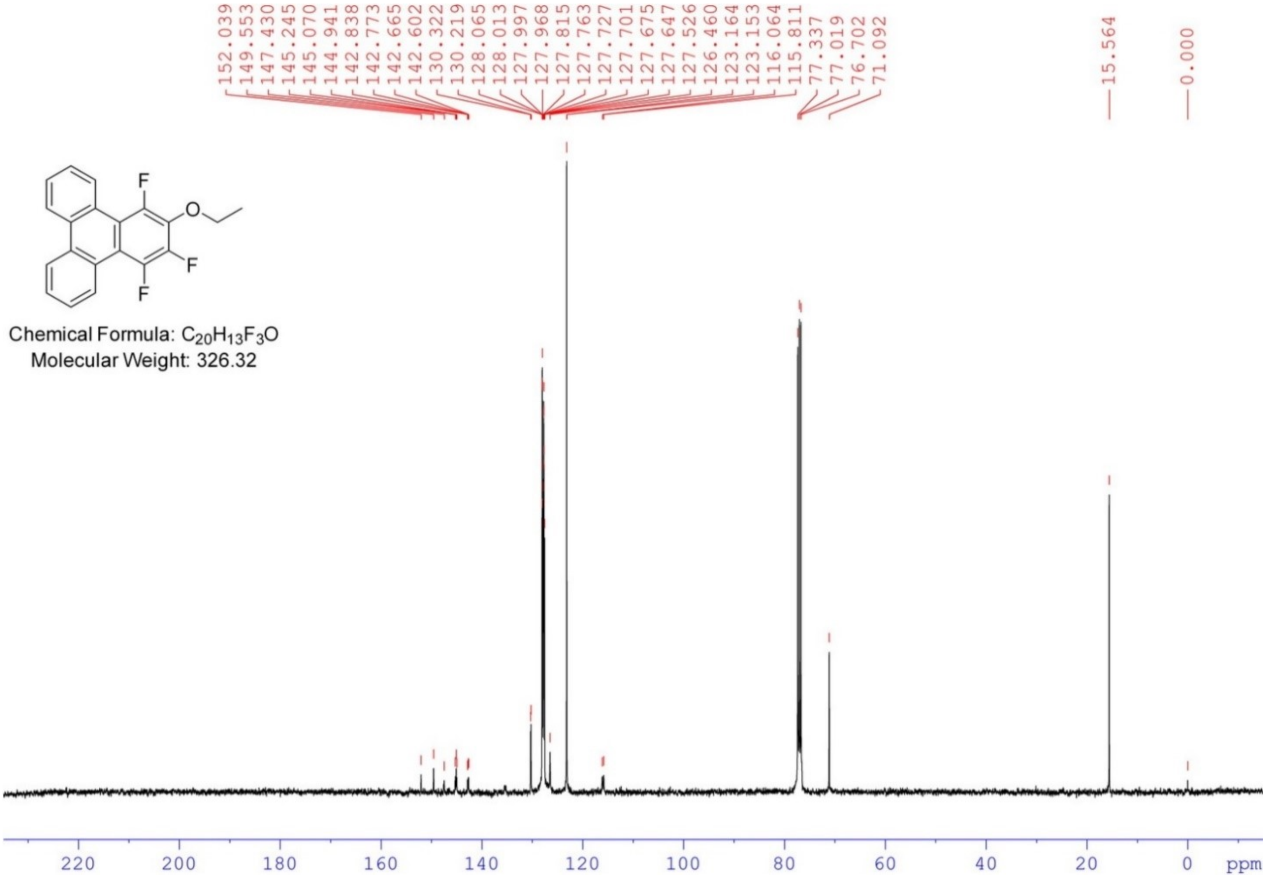


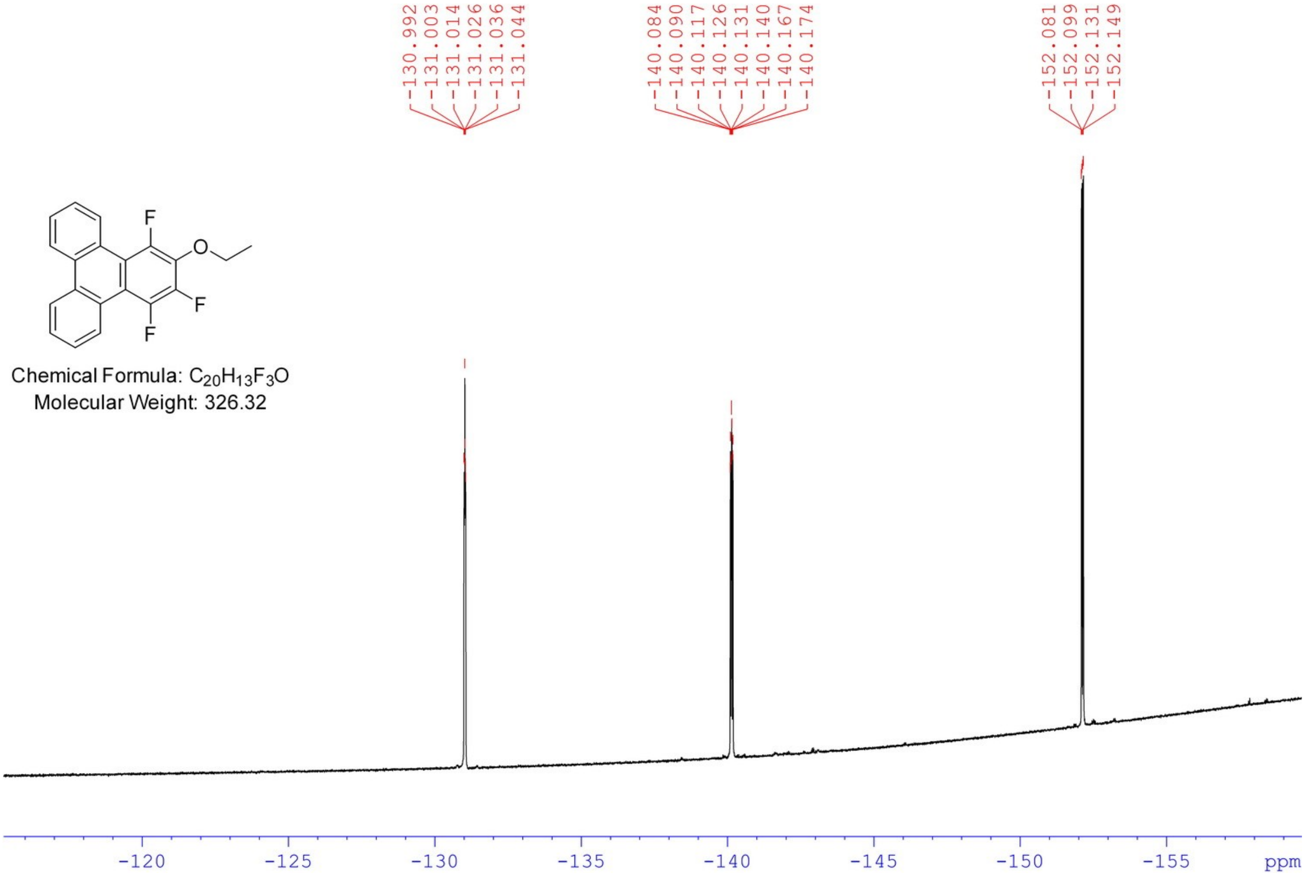




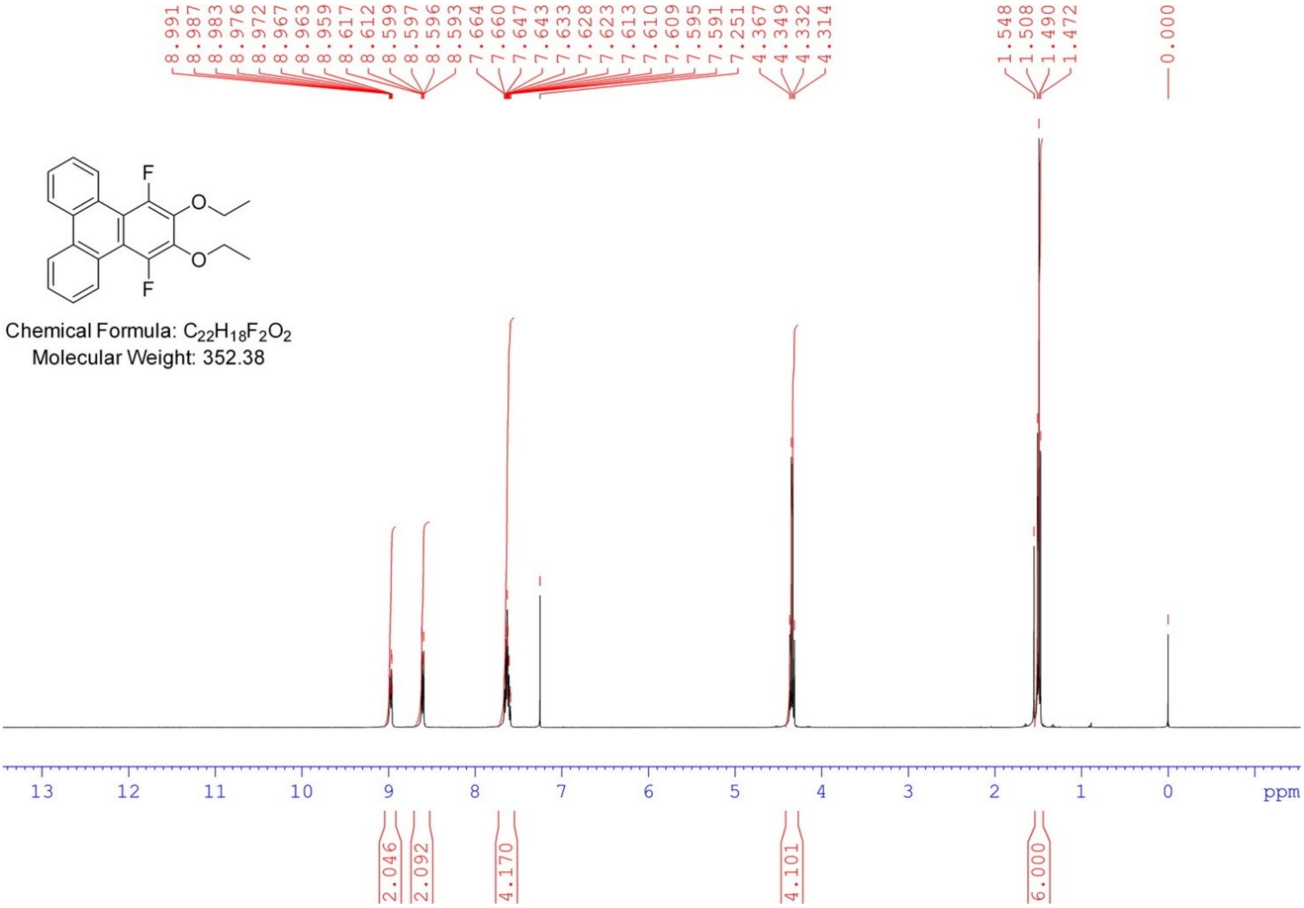
2-ethoxy-1,3,4-trifluorotriphenylene



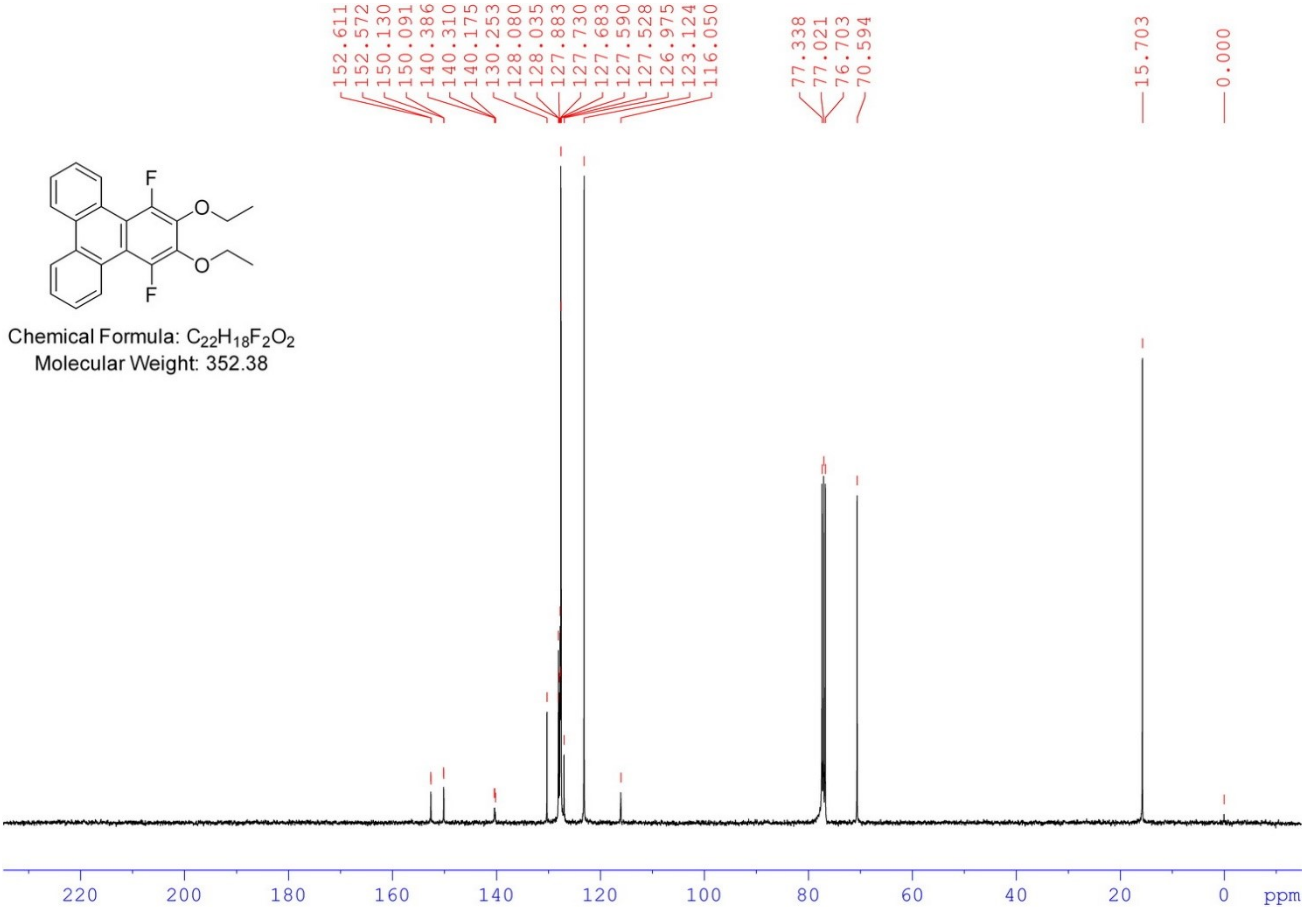




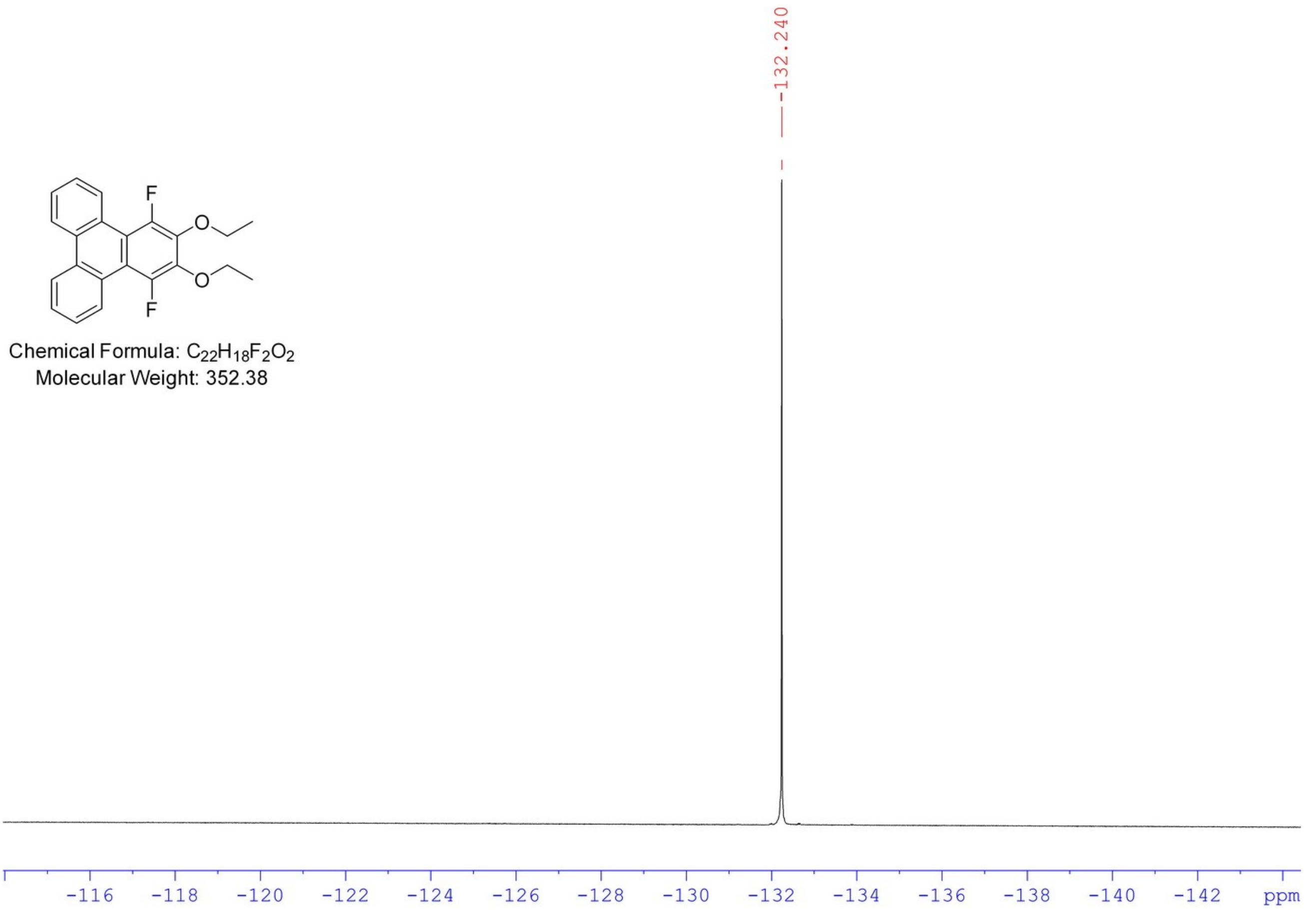
2,3-diethoxy-1,4-difluorotriphenylene



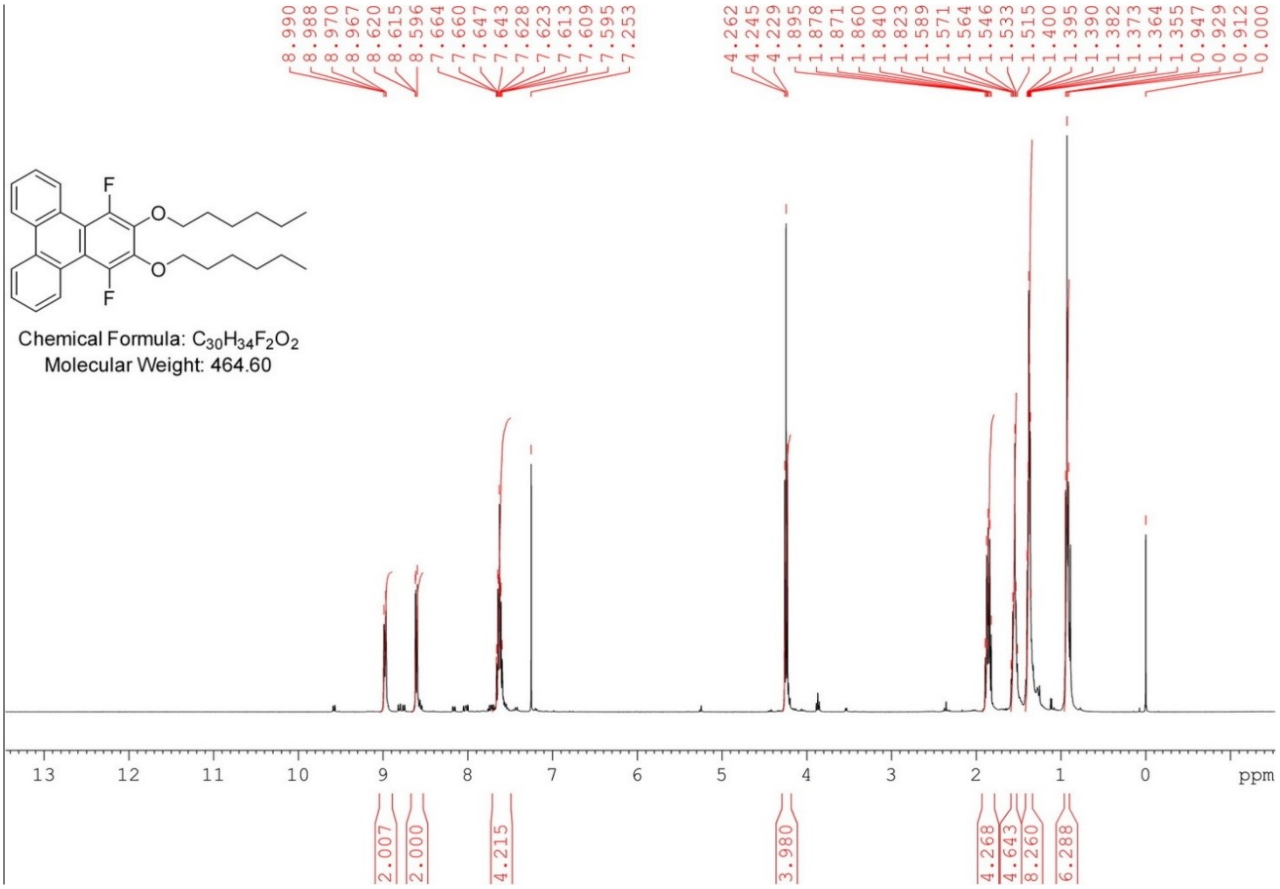
Chemical Formula: $C_{22}H_{18}F_2O_2$
Molecular Weight: 352.38

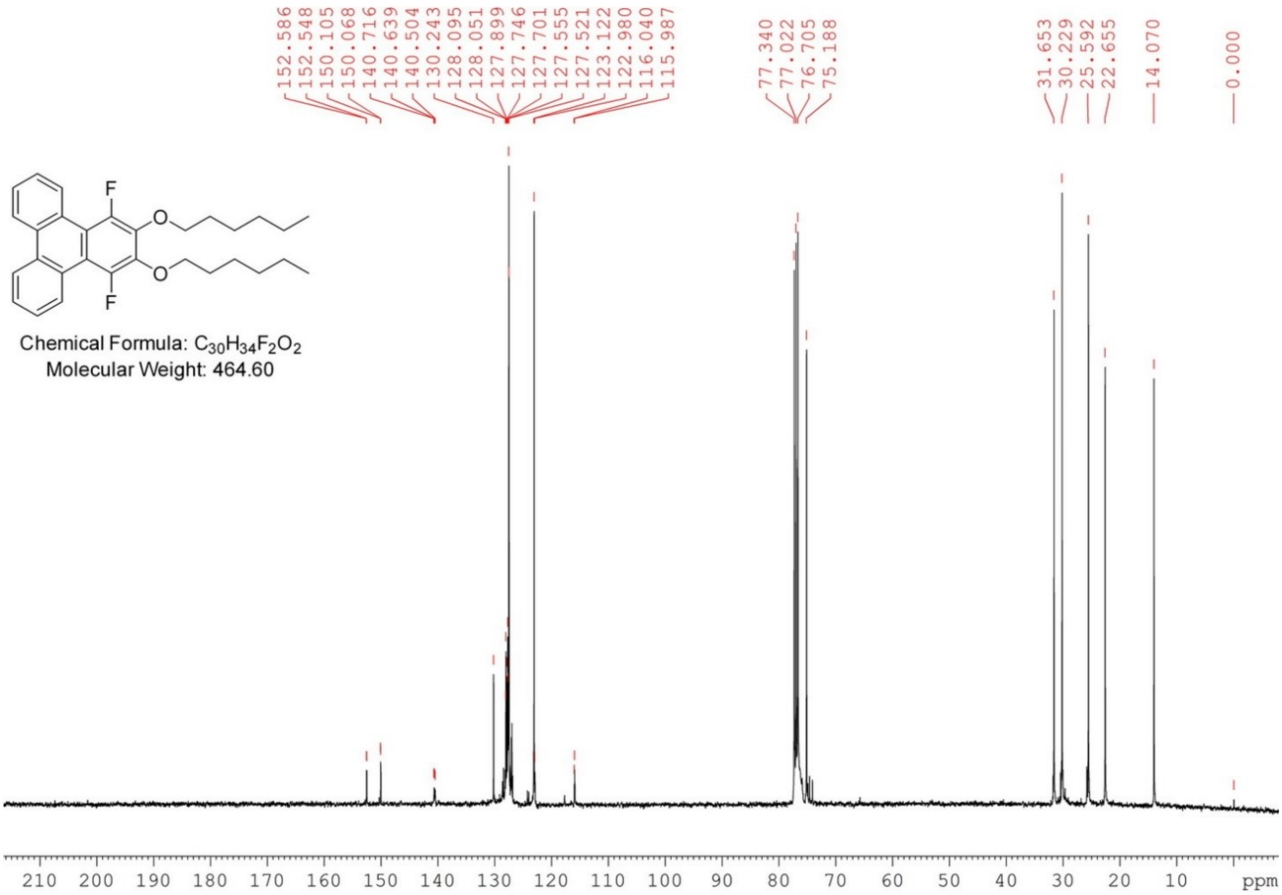


Chemical Formula: $C_{22}H_{18}F_2O_2$
Molecular Weight: 352.38

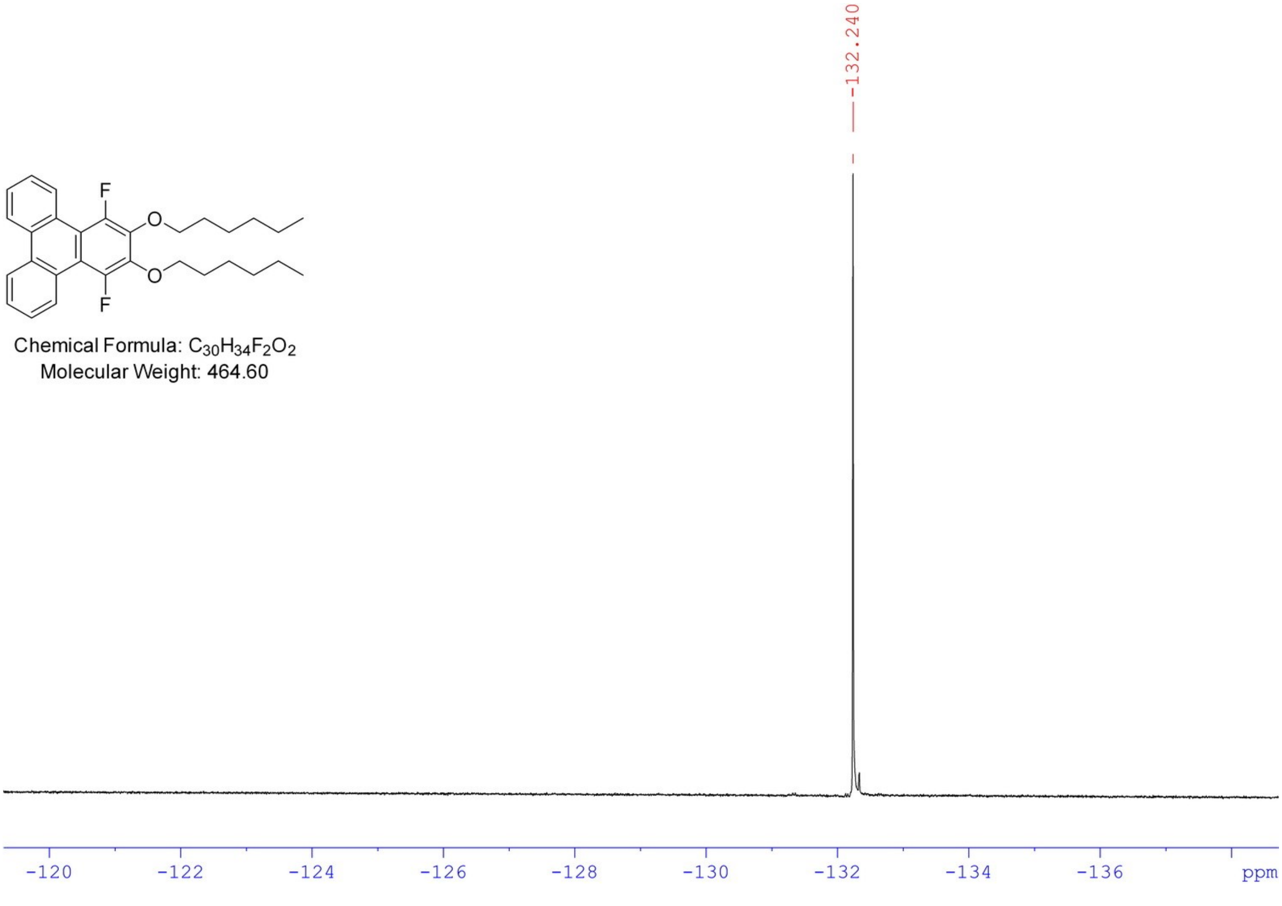


1,4-difluoro-2,3-dihexyloxytriphenylene



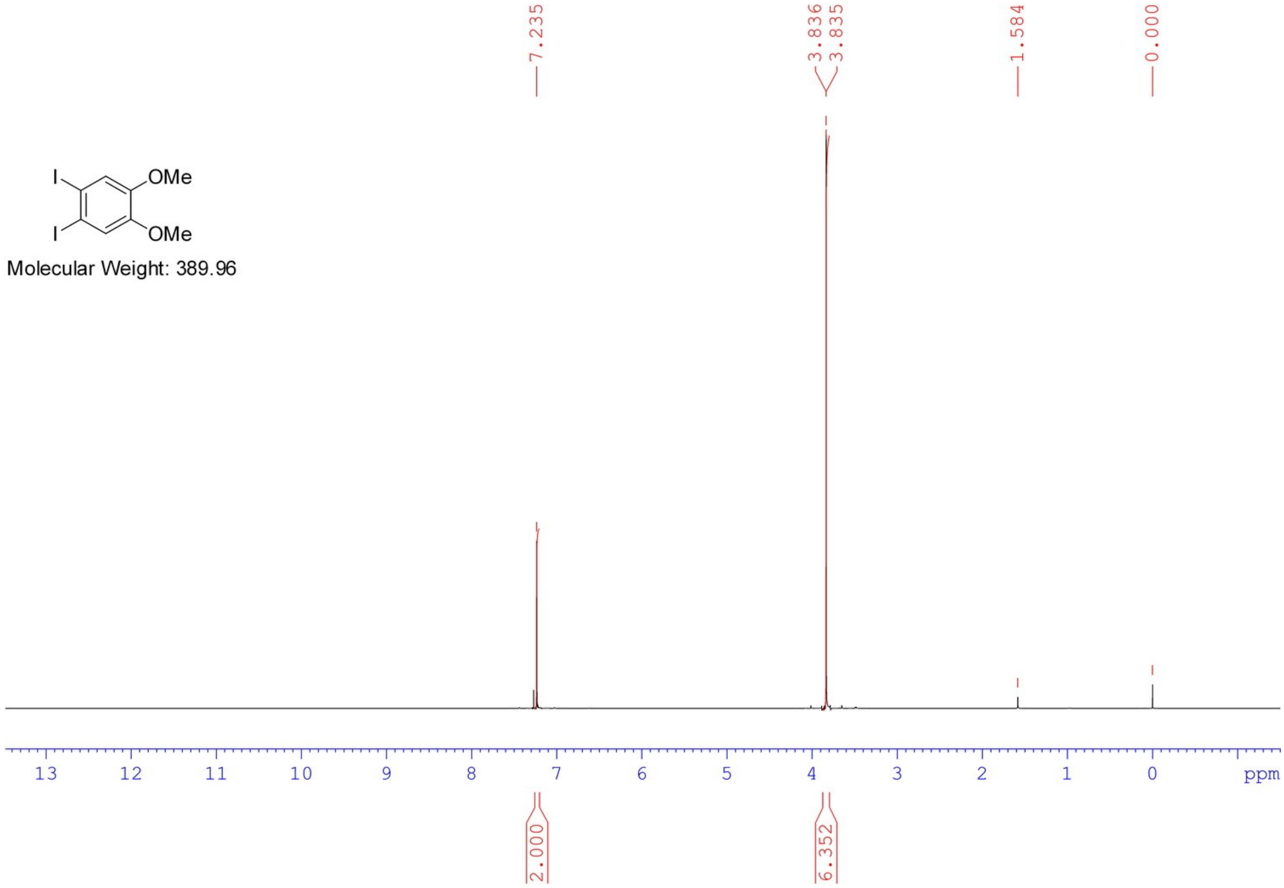


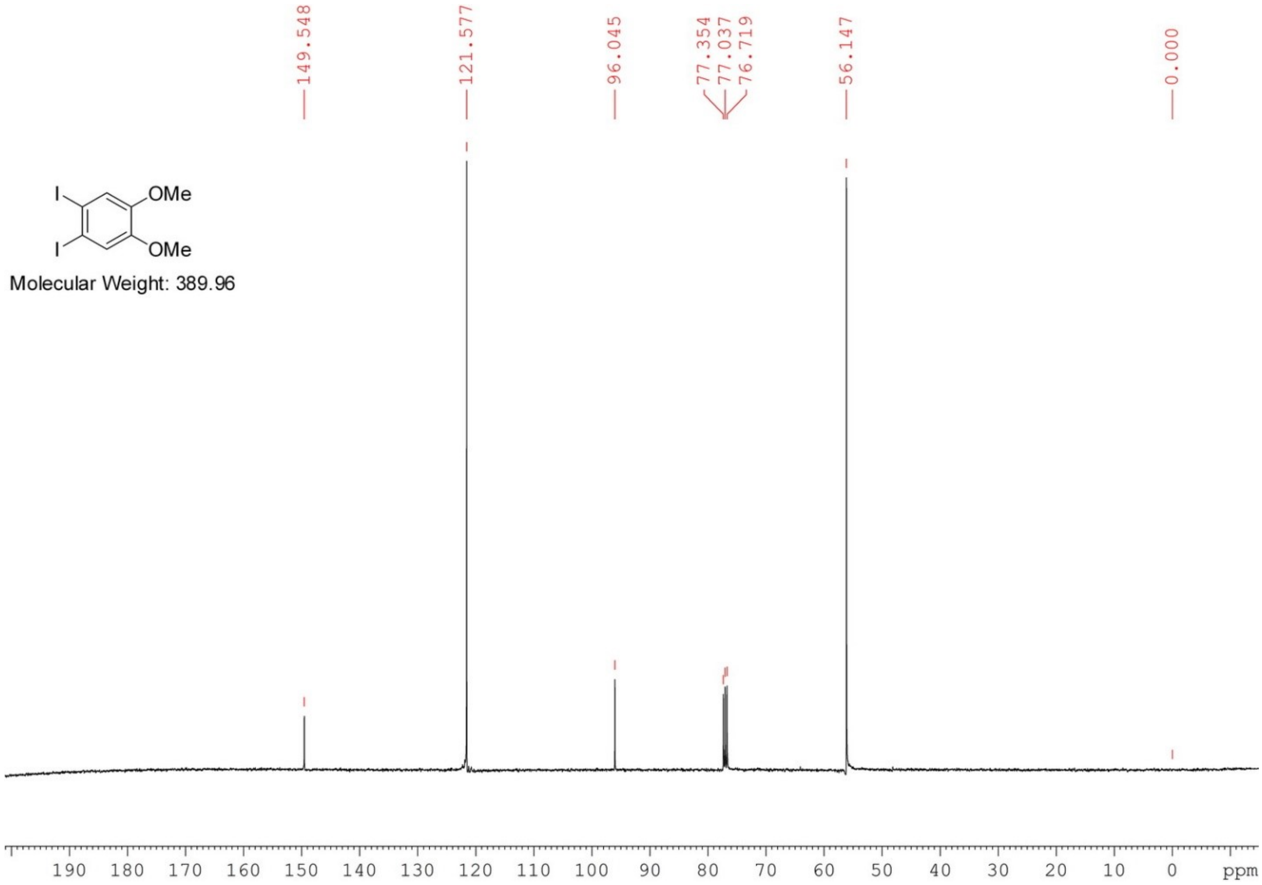
Chemical Formula: $C_{30}H_{34}F_2O_2$
Molecular Weight: 464.60



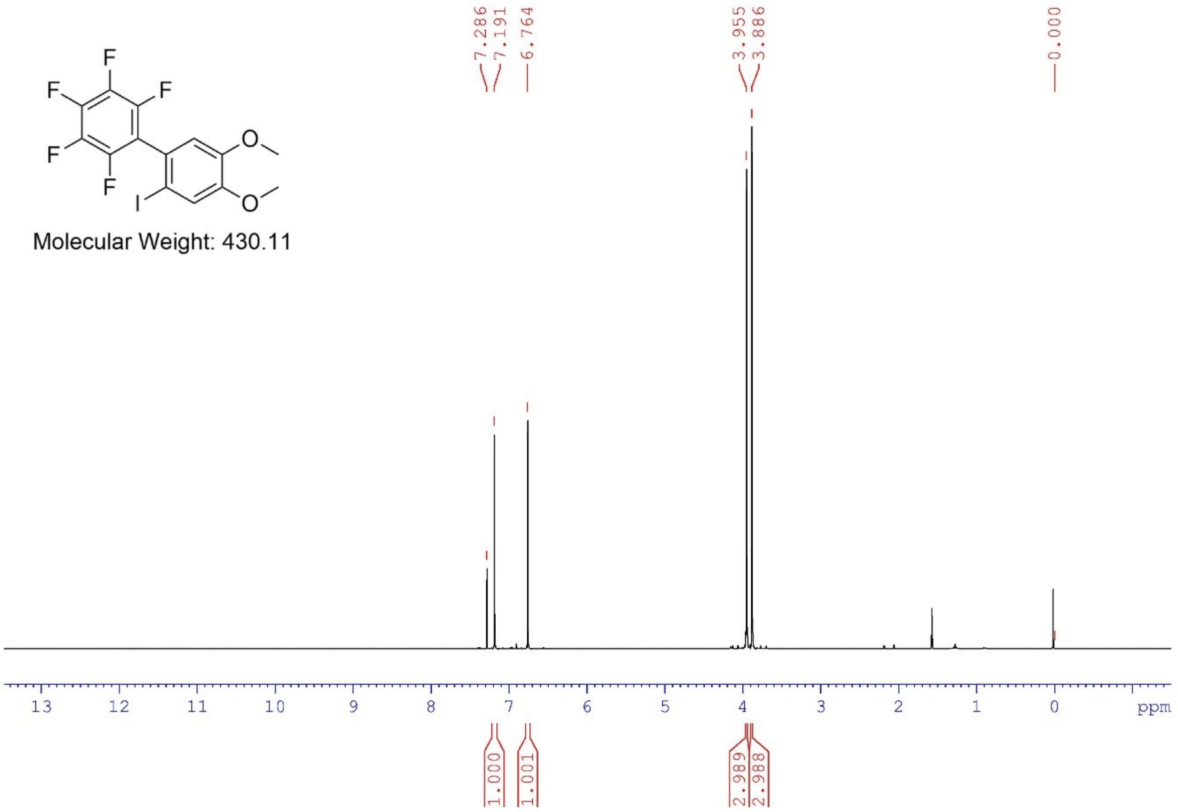
Chemical Formula: $C_{30}H_{34}F_2O_2$
Molecular Weight: 464.60

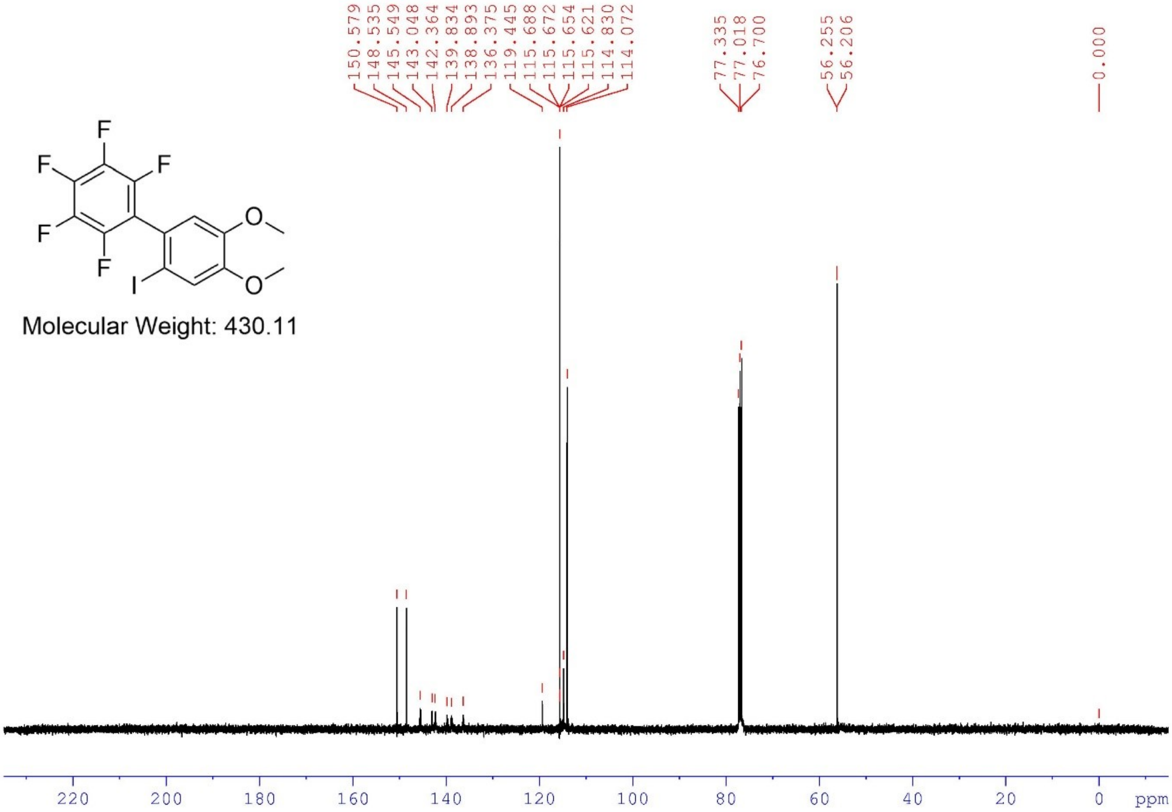
1,2-diiodo-4,5-dimethoxybenzene (Compound 2)

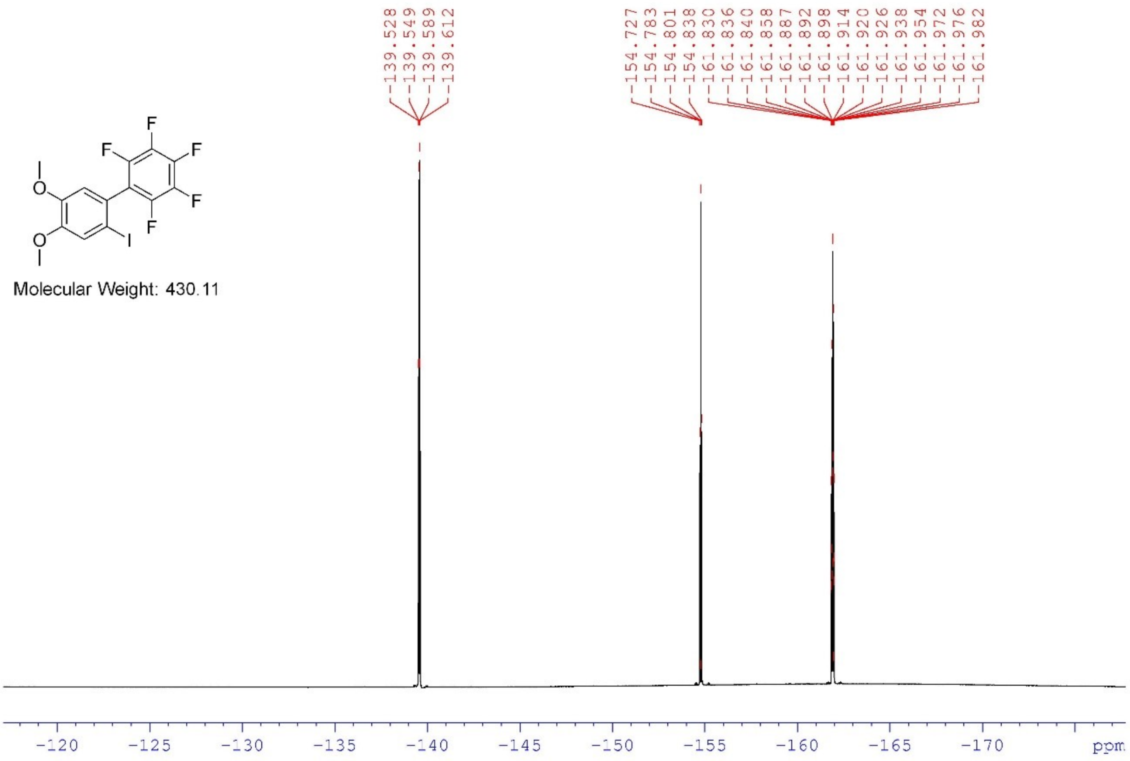




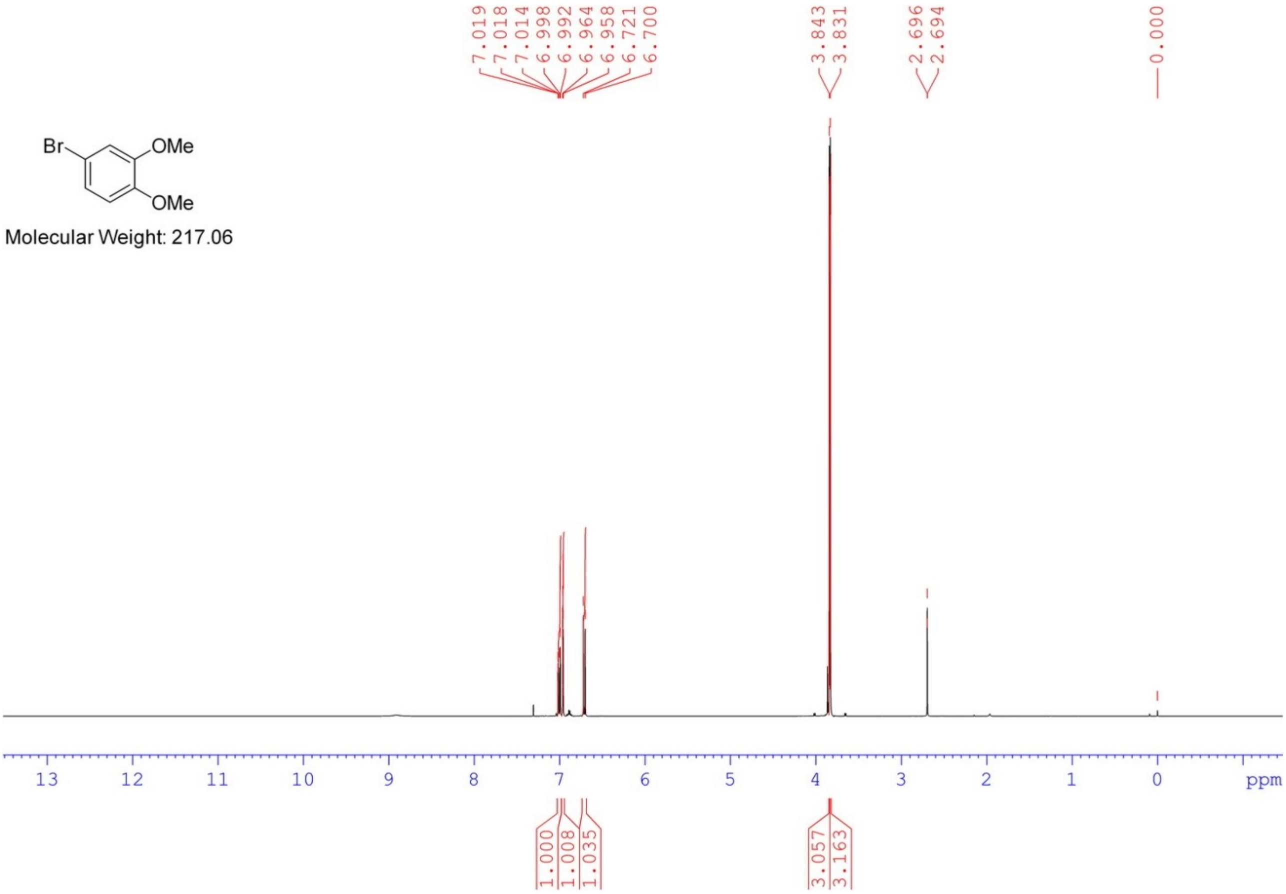
2,3,4,5,6-pentafluoro-2'-iodo-4',5'-dimethoxy-1,1'-biphenyl (Compound 3)

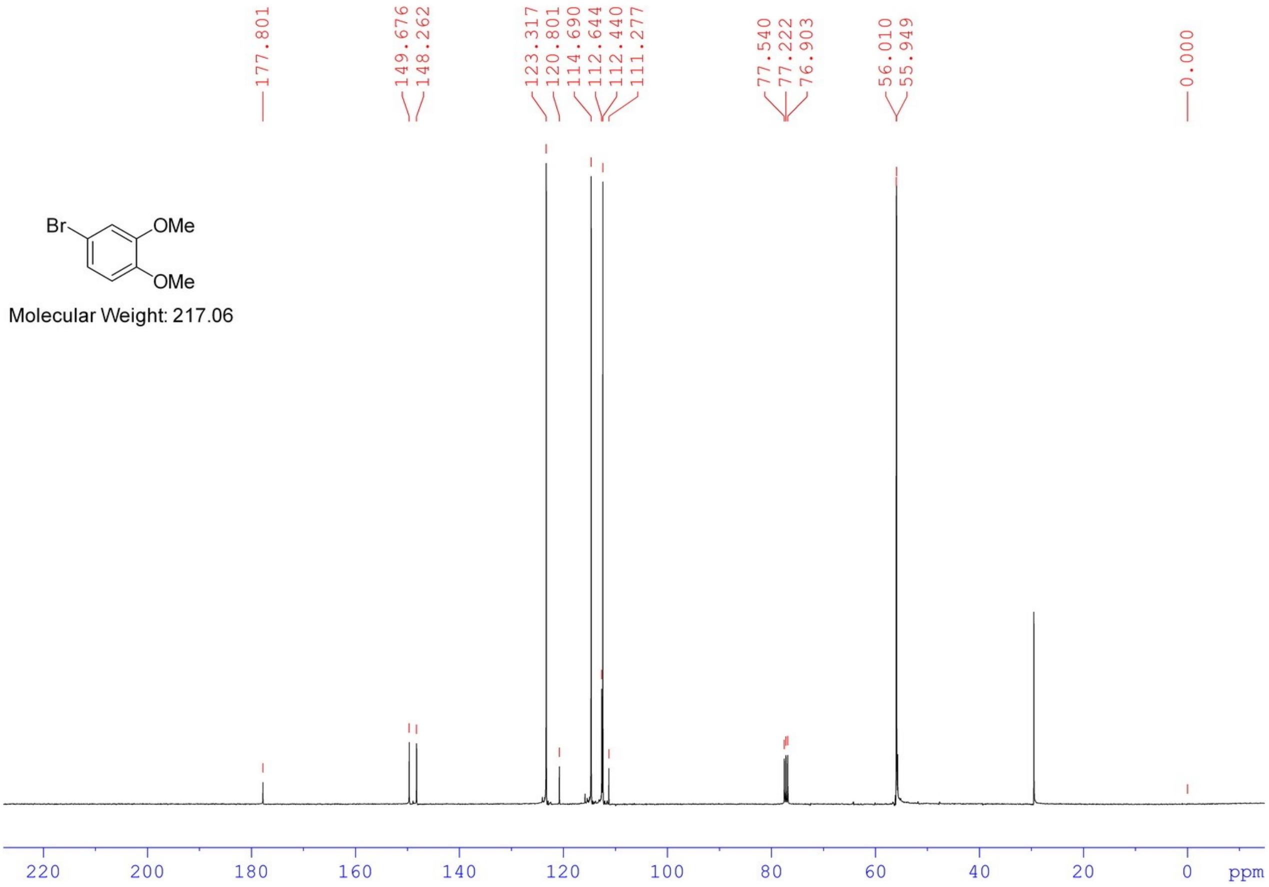



150.579
148.535
145.549
143.048
142.364
139.834
138.893
136.375
119.445
115.688
115.672
115.654
115.621
114.830
114.072
77.335
77.018
76.700
56.255
56.206
0.000
F
F
F
F
F
O
O
I
Molecular Weight: 430.11
220
200
180
160
140
120
100
80
60
40
20
0
ppm

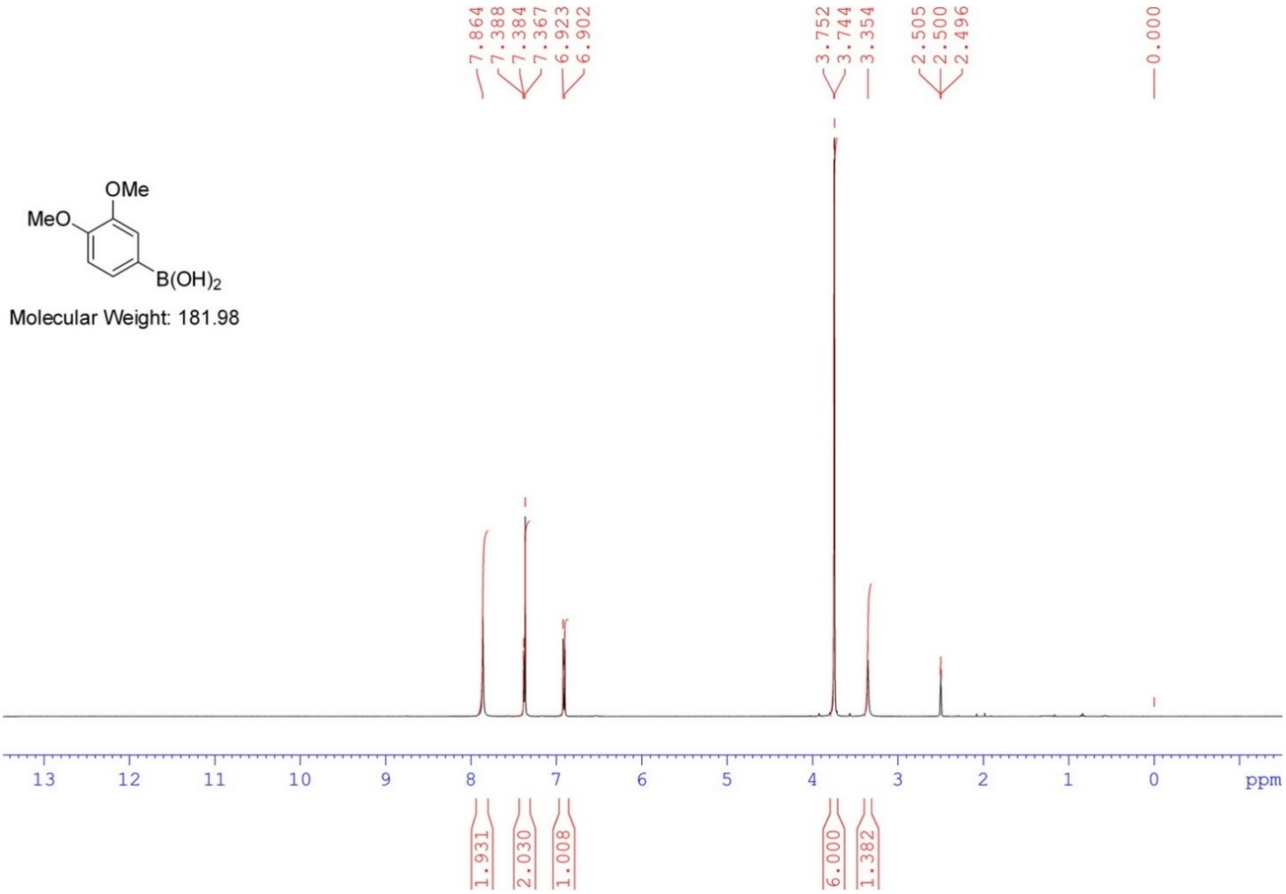


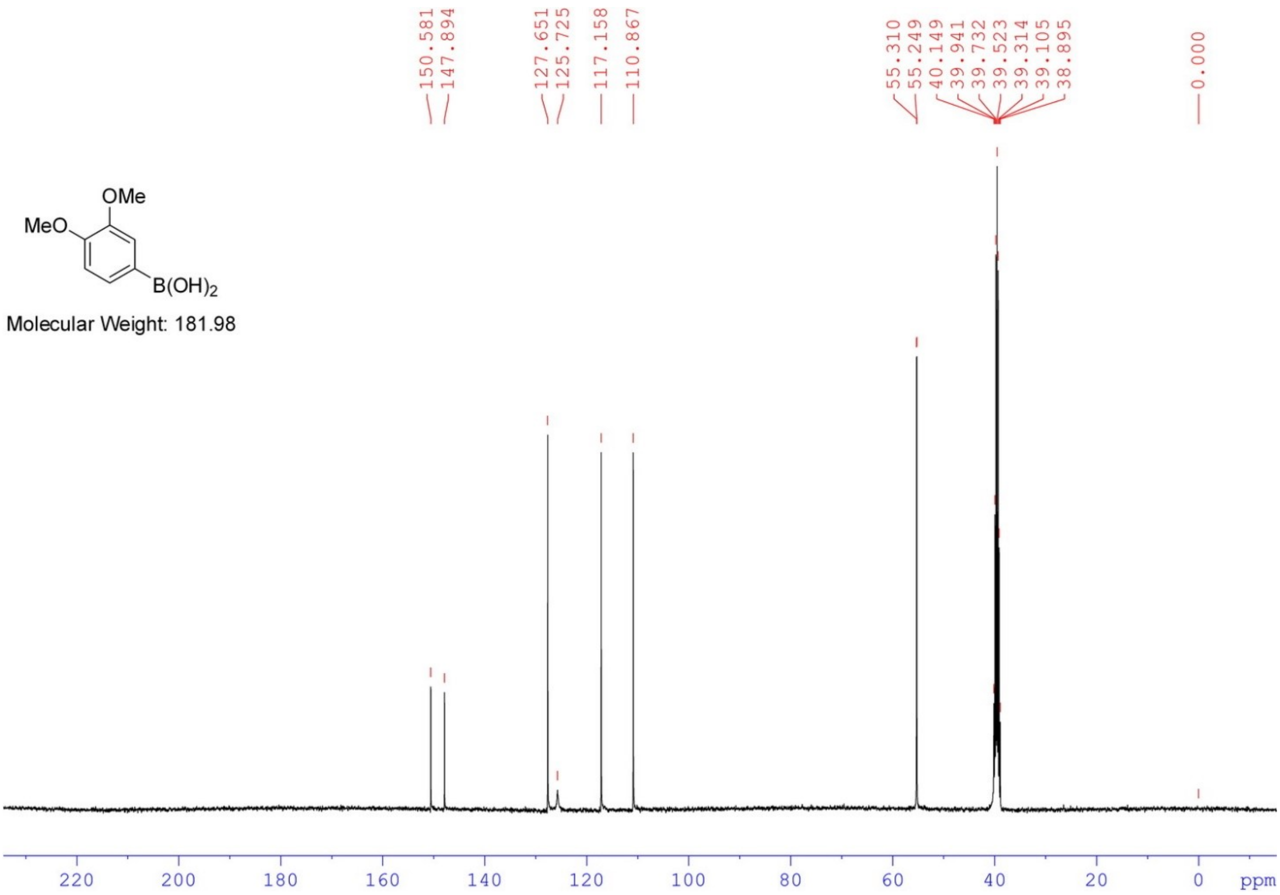
4-bromoveratol (Compound 4)



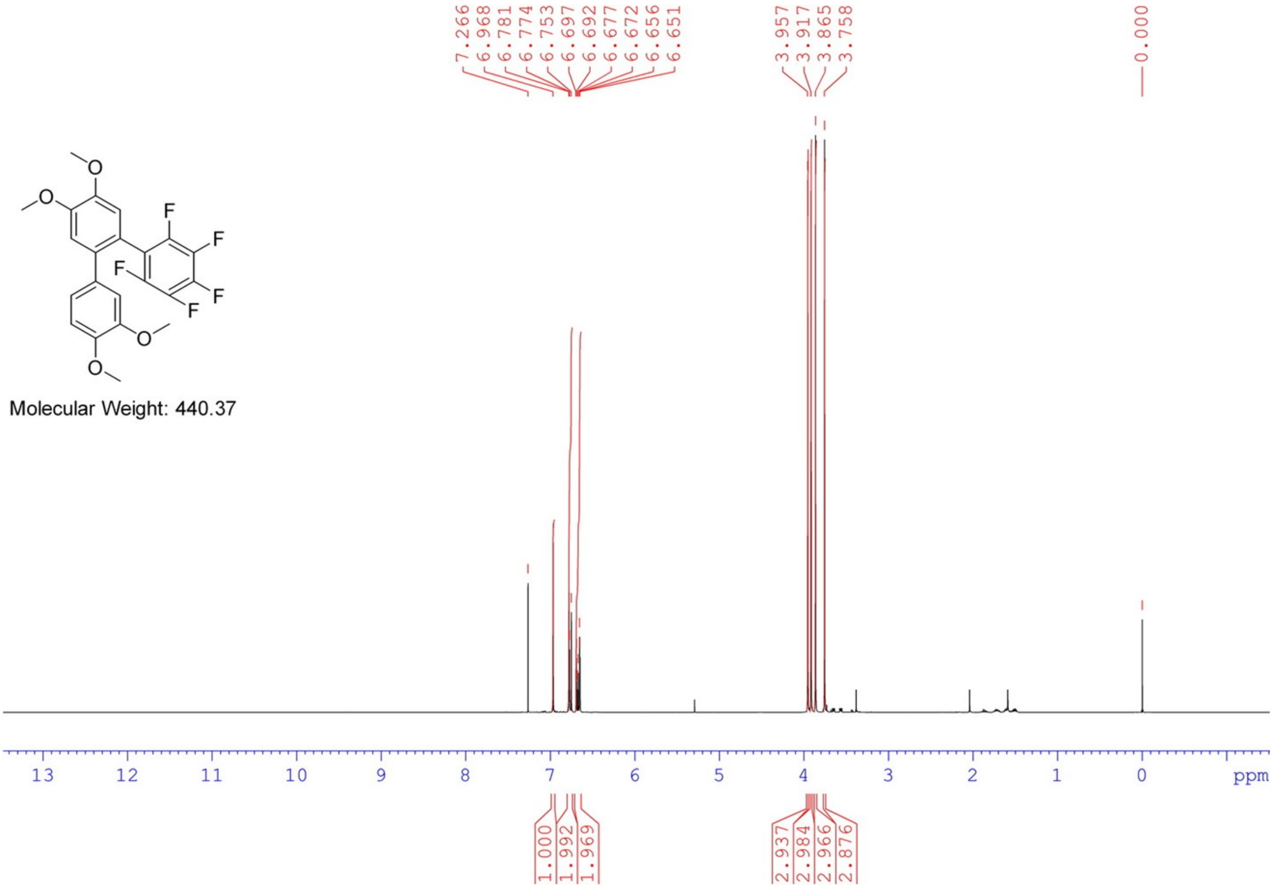


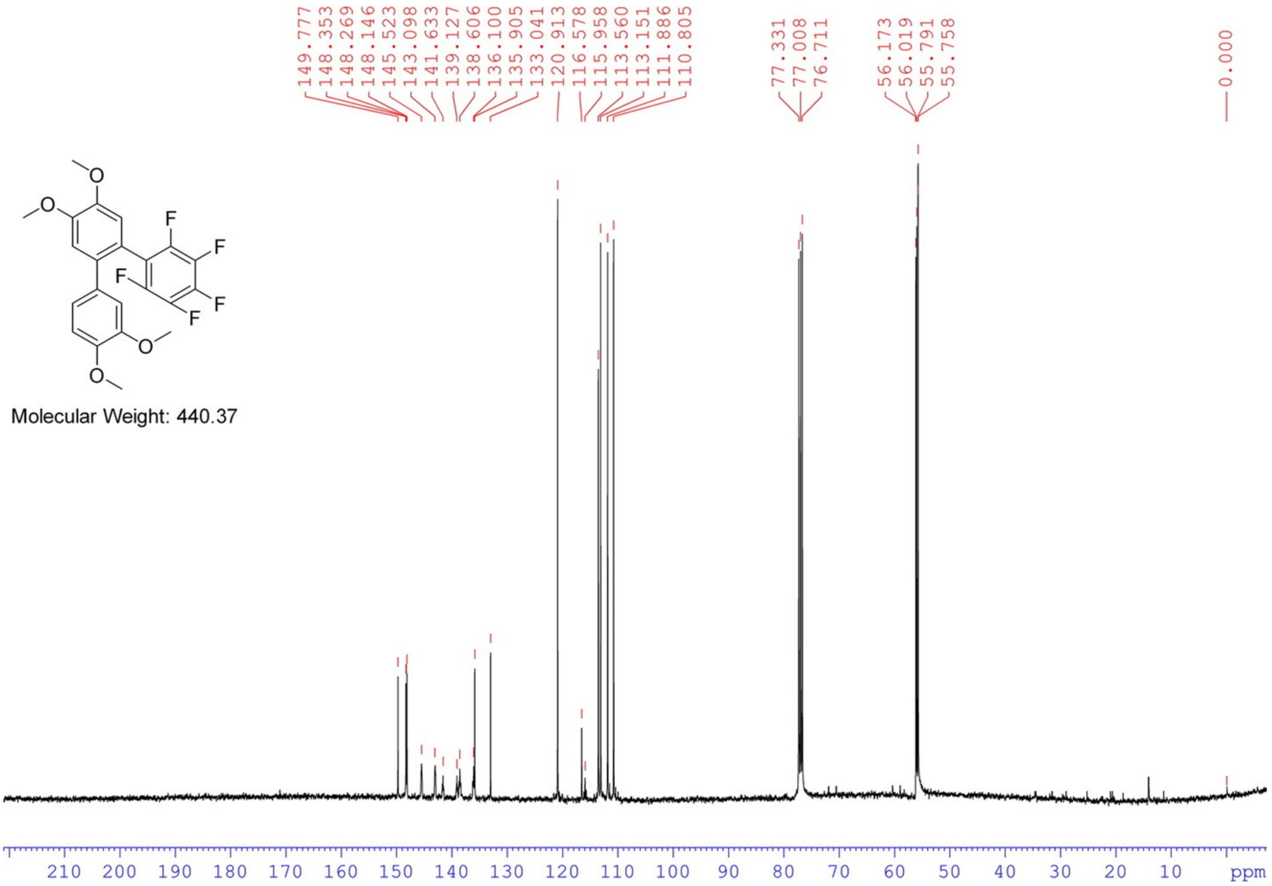
3,4-dimethoxyphenylboronic acid (Compound 5)

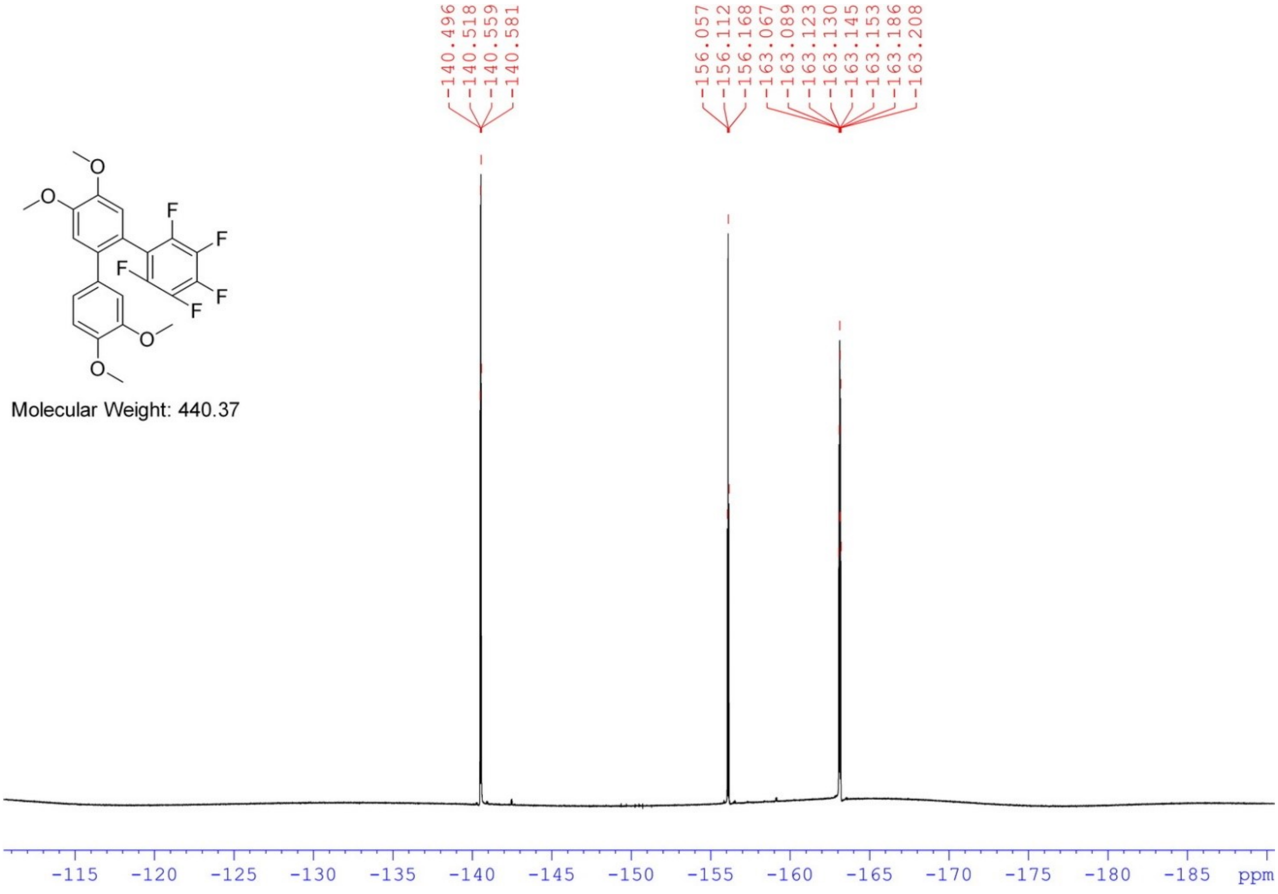




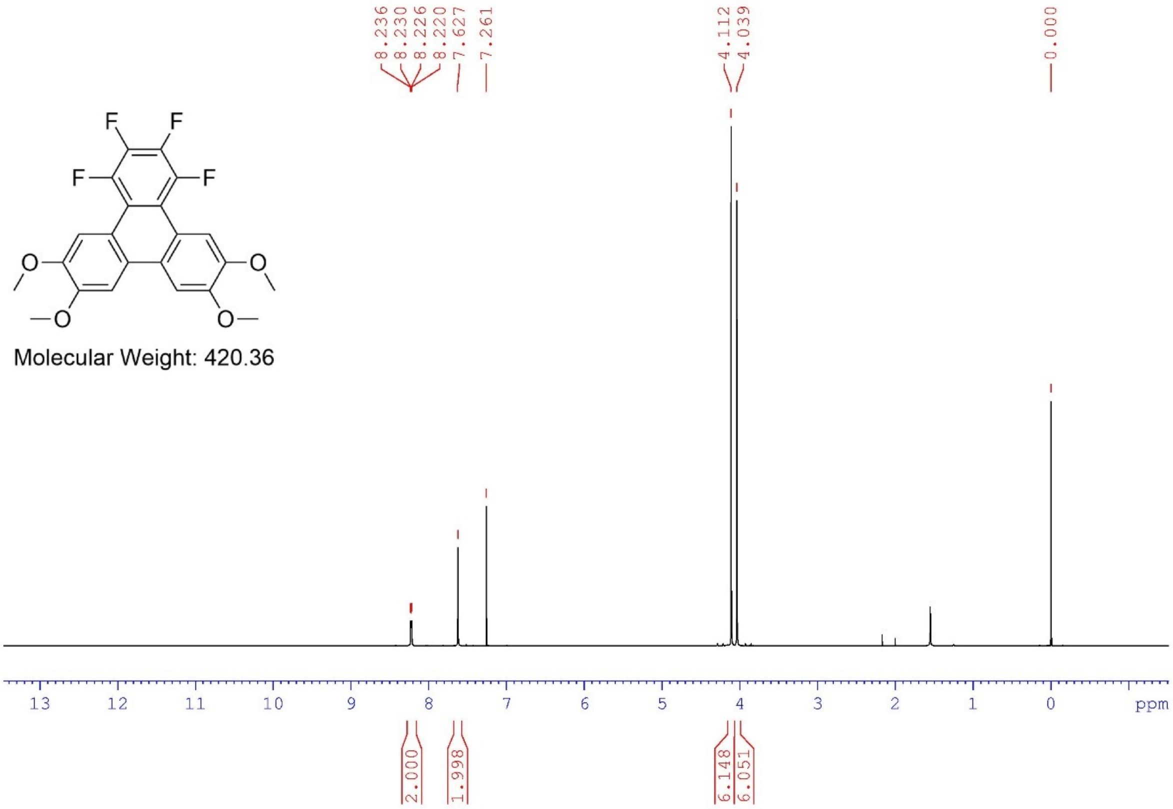
2,3,4,5,6-pentafluoro-3'',4',4'',5'-tetramethoxy-1,1':2',1''-terphenyl (Compound 6)

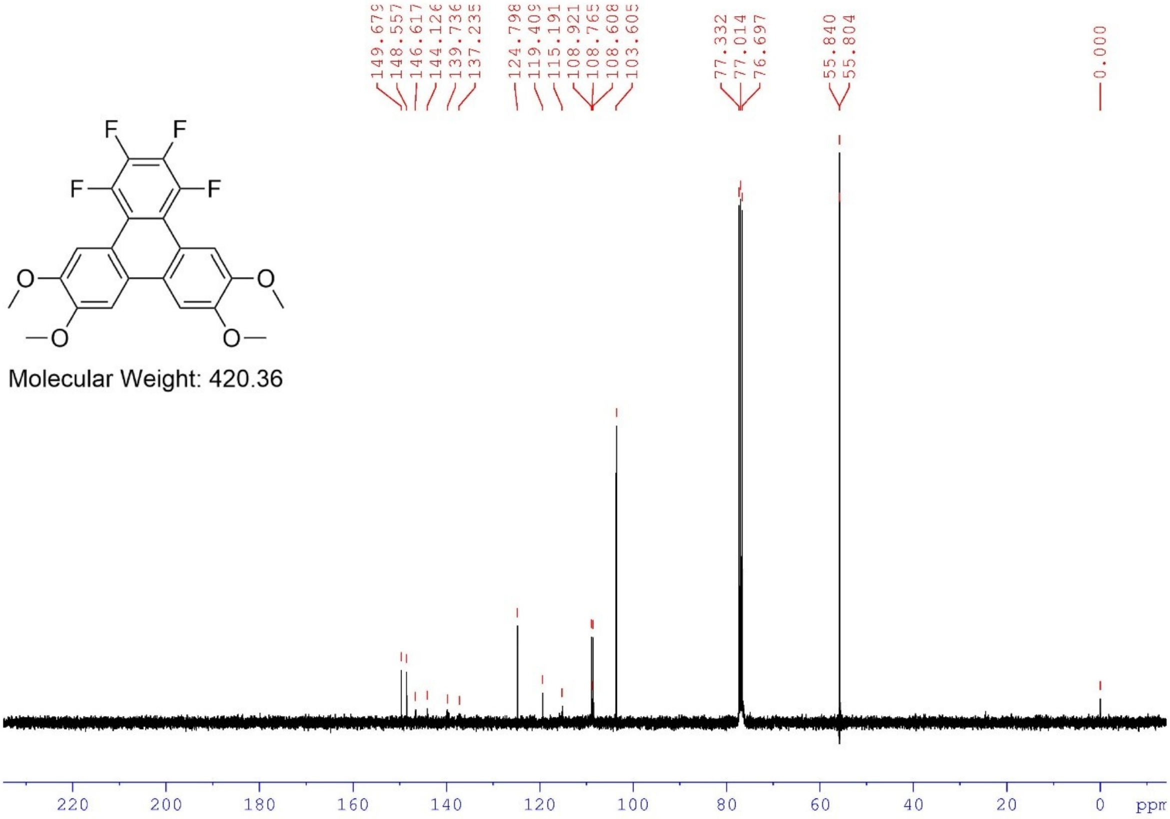


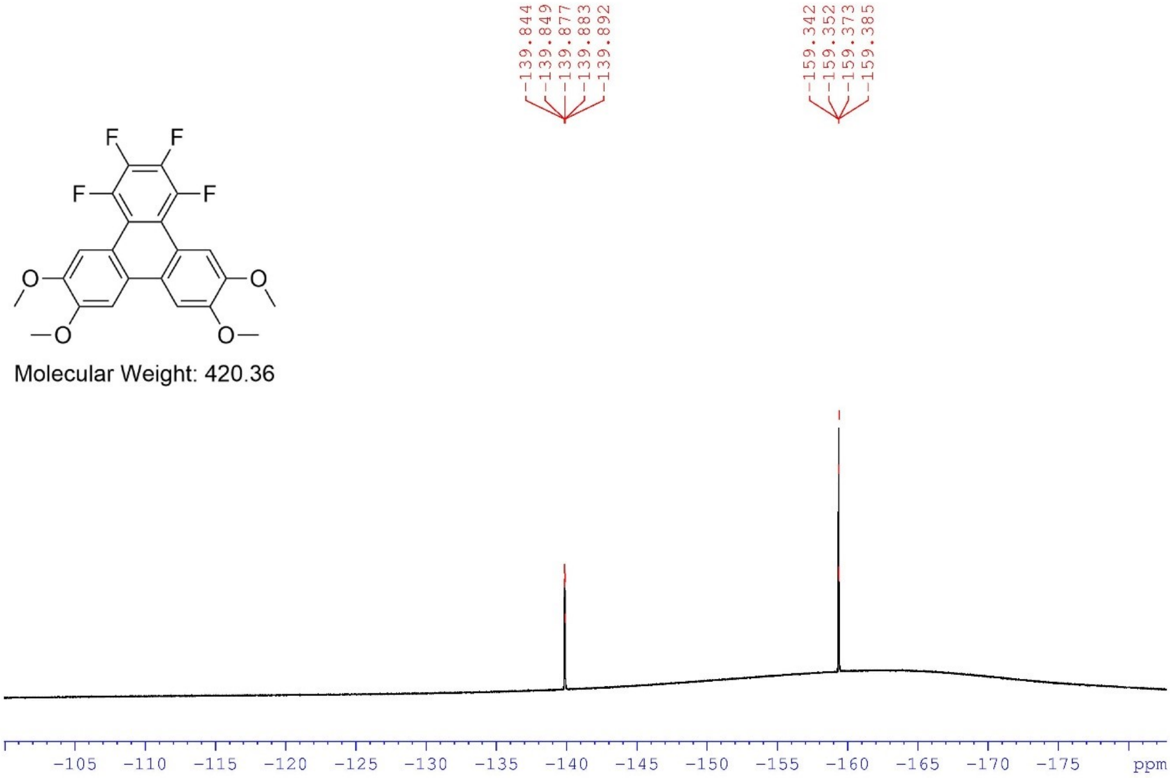

149.777
148.353
148.269
148.146
145.523
143.098
141.633
139.127
138.606
136.100
135.905
133.041
120.913
116.578
115.958
113.560
113.151
111.886
110.805
77.331
77.008
76.711
56.173
56.019
55.791
55.758
0.000
F
F
F
F
O
O
O
O
Molecular Weight: 440.37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


-140.496
-140.518
-140.559
-140.581
-156.057
-156.112
-156.168
-163.067
-163.089
-163.123
-163.130
-163.145
-163.153
-163.186
-163.208
F
F
F
F
O
O
O
O
Molecular Weight: 440.37
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
ppm

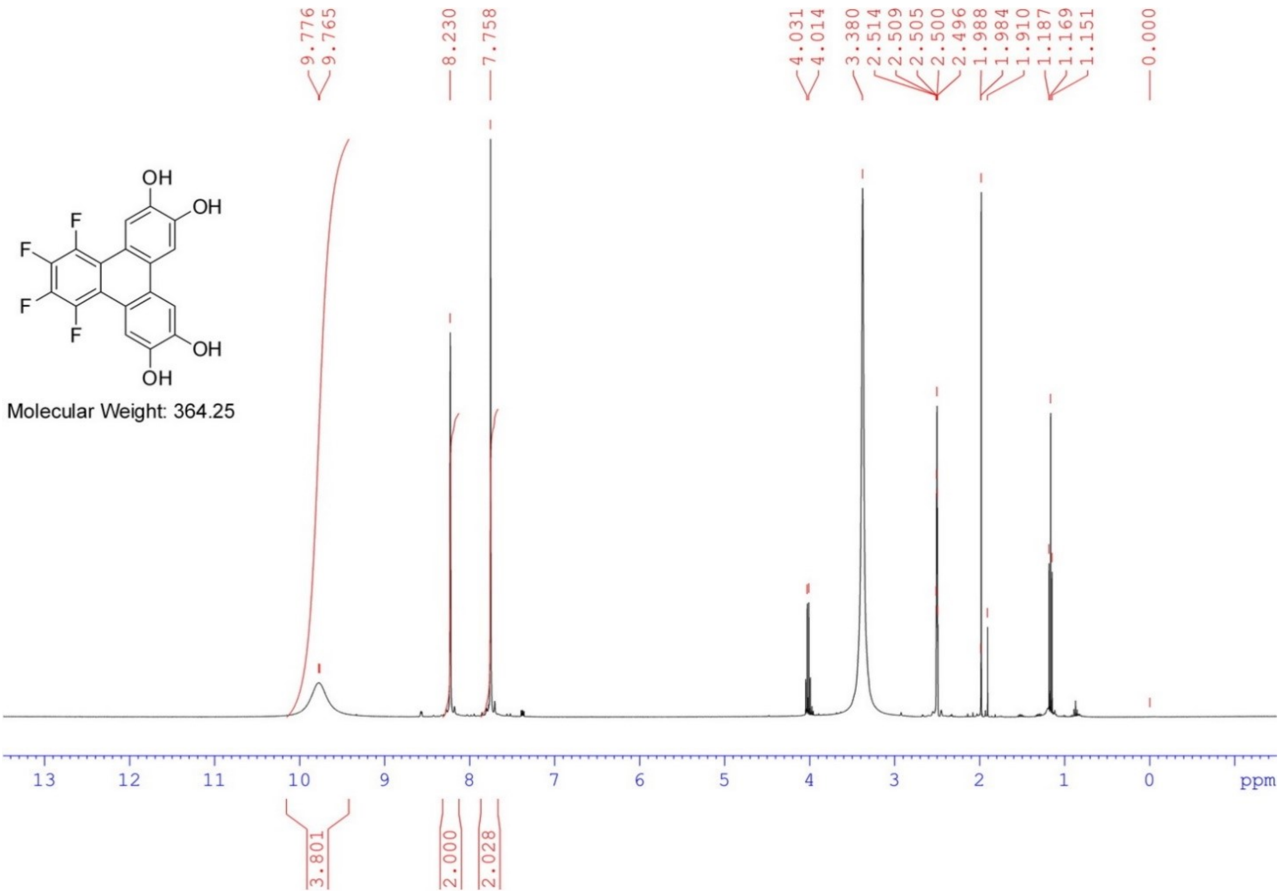
1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (Compound 7)

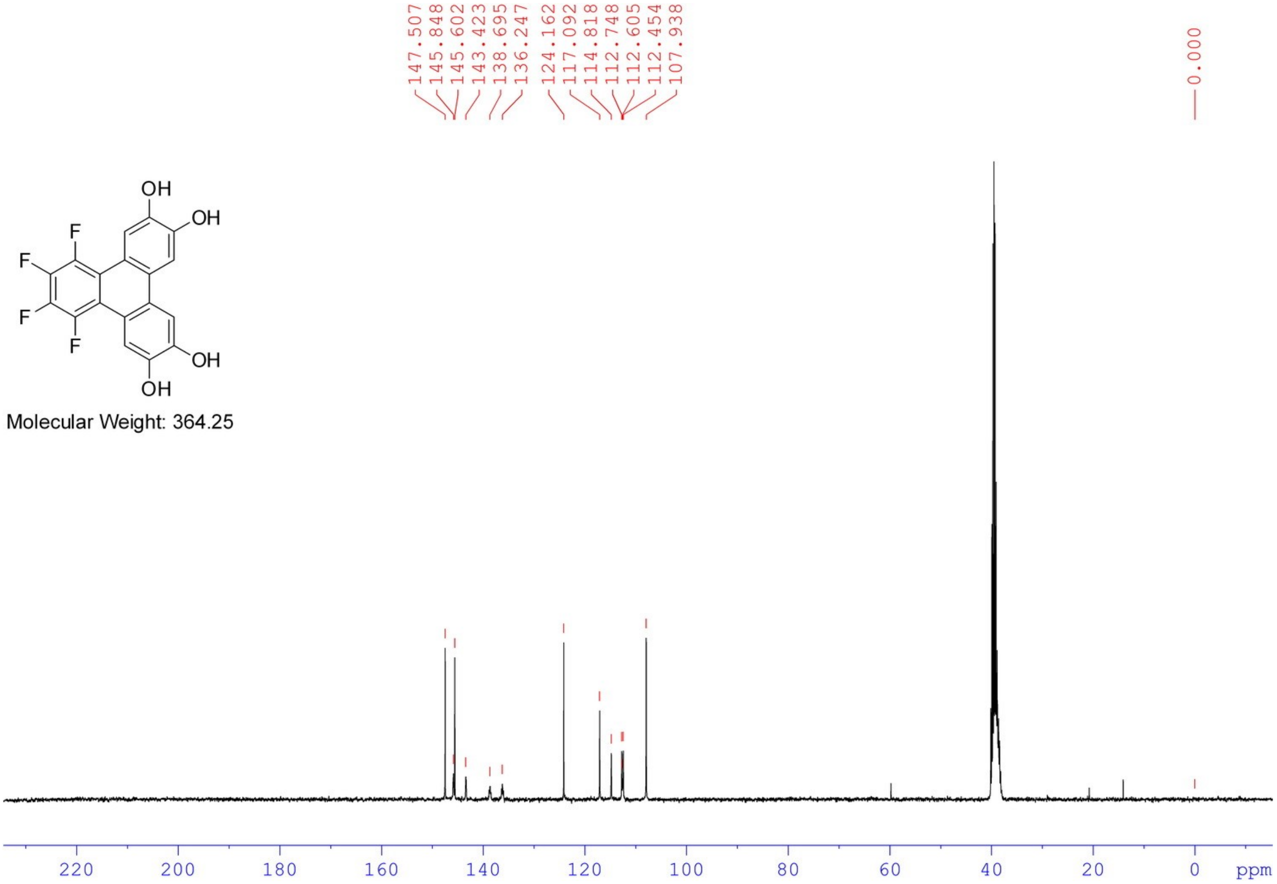


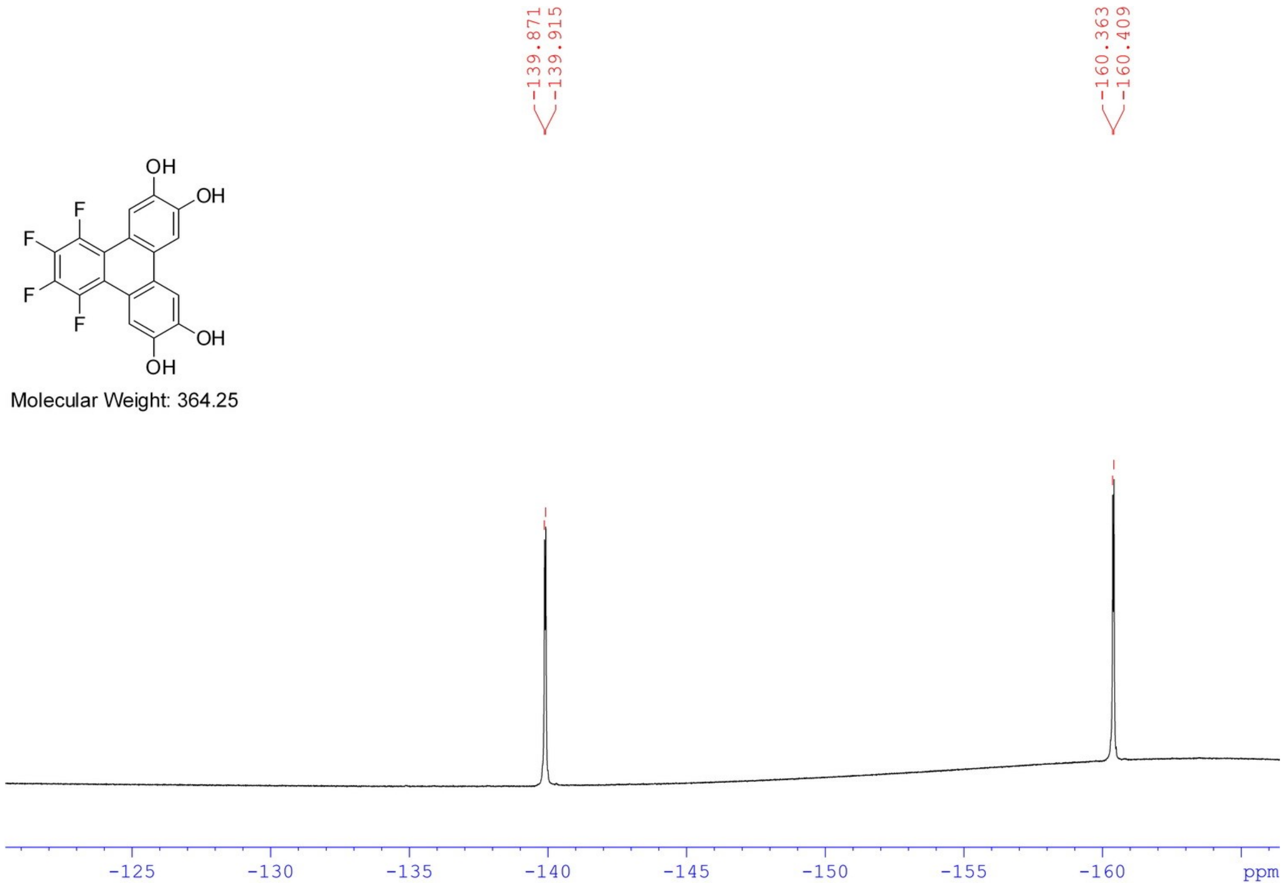

149.679
148.557
146.617
144.126
139.736
137.235
124.798
119.409
115.191
108.921
108.765
108.608
103.605
77.332
77.014
76.697
55.840
55.804
0.000
F
F
F
F
O
O
O
O
Molecular Weight: 420.36
220
200
180
160
140
120
100
80
60
40
20
0
ppm



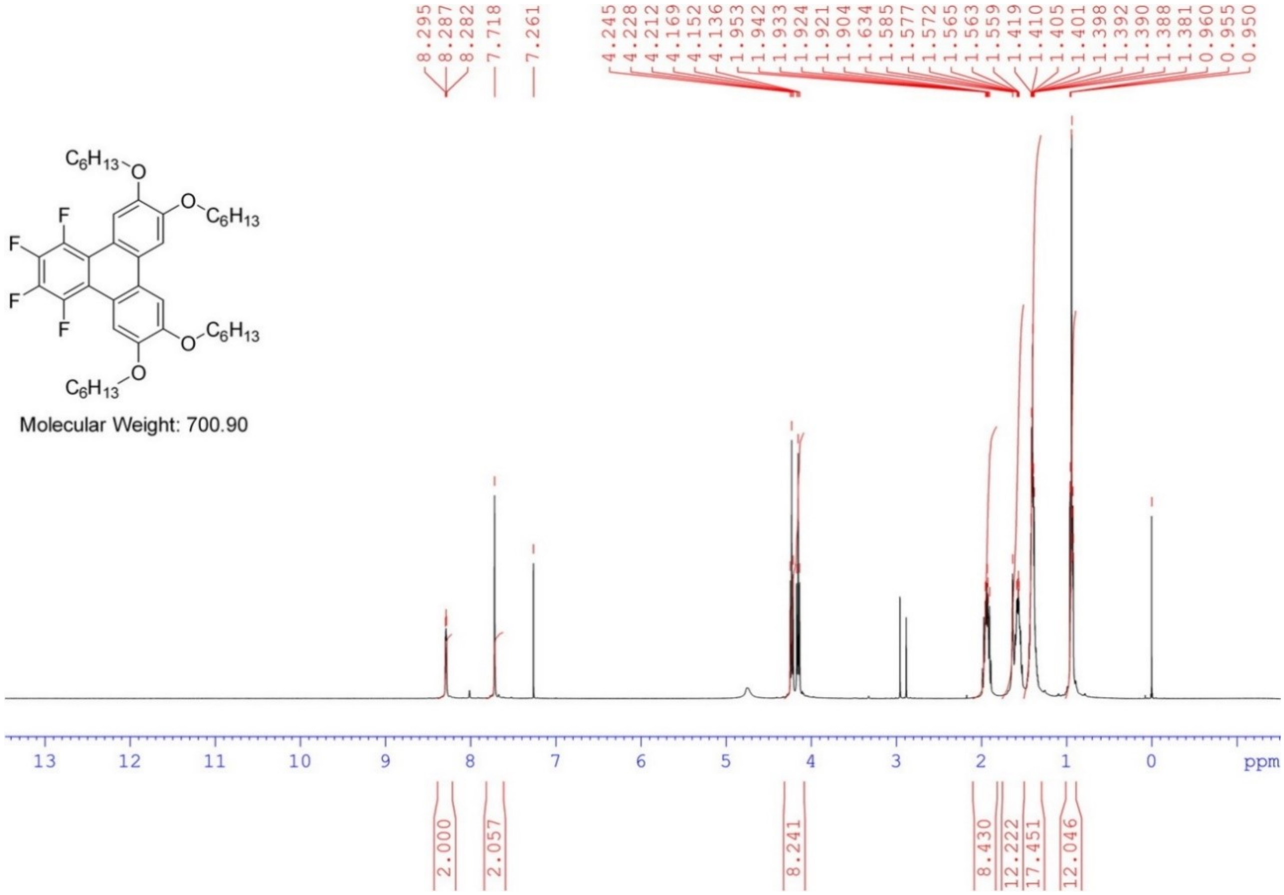
NMR Spectra for 9,10,11,12-tetrafluorotriphenylene-2,3,6,7-tetraol (Compound 8)

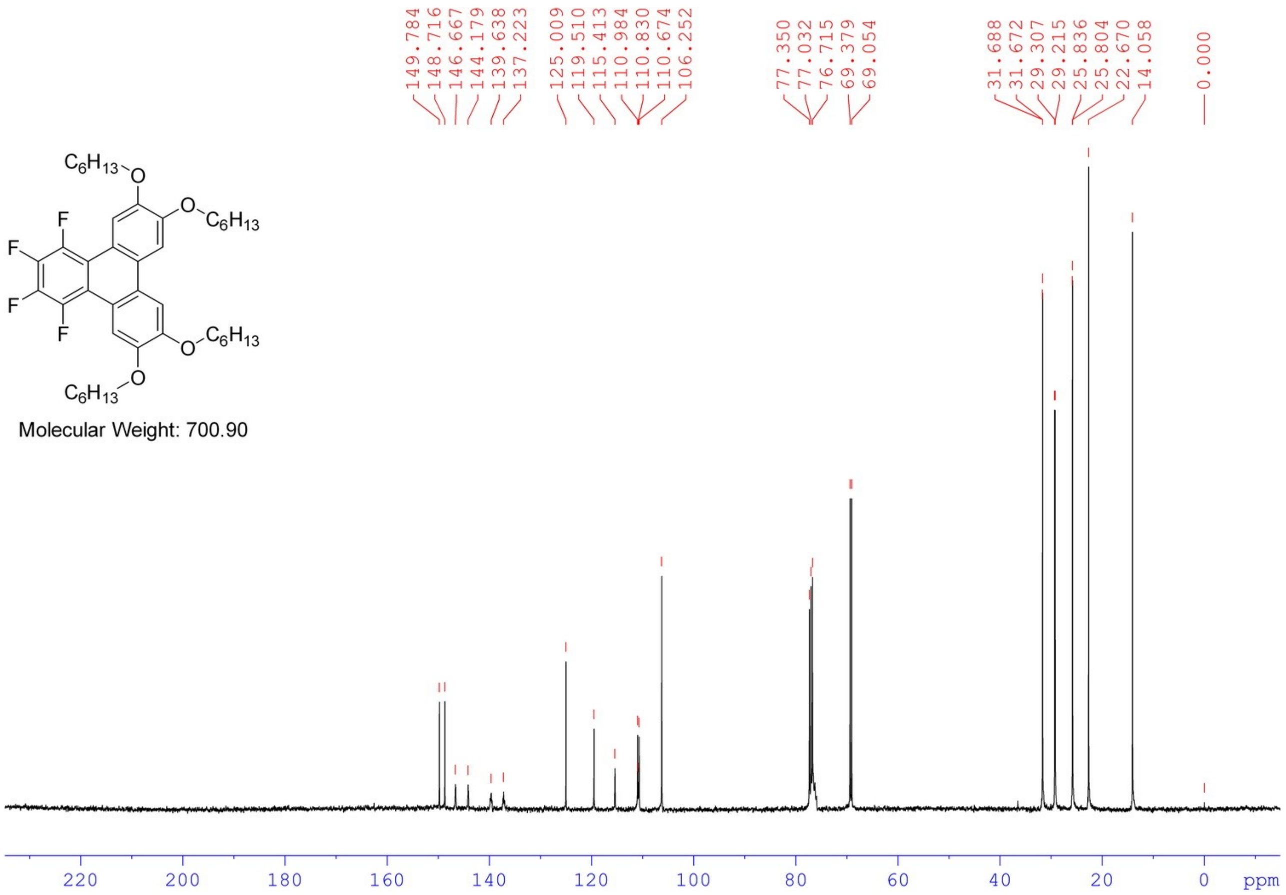

9.776
9.765
8.230
7.758
4.031
4.014
3.380
2.514
2.509
2.505
2.500
2.496
1.988
1.984
1.910
1.187
1.169
1.151
0.000
OH
OH
F
F
F
F
OH
OH
Molecular Weight: 364.25
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.801
2.000
2.028

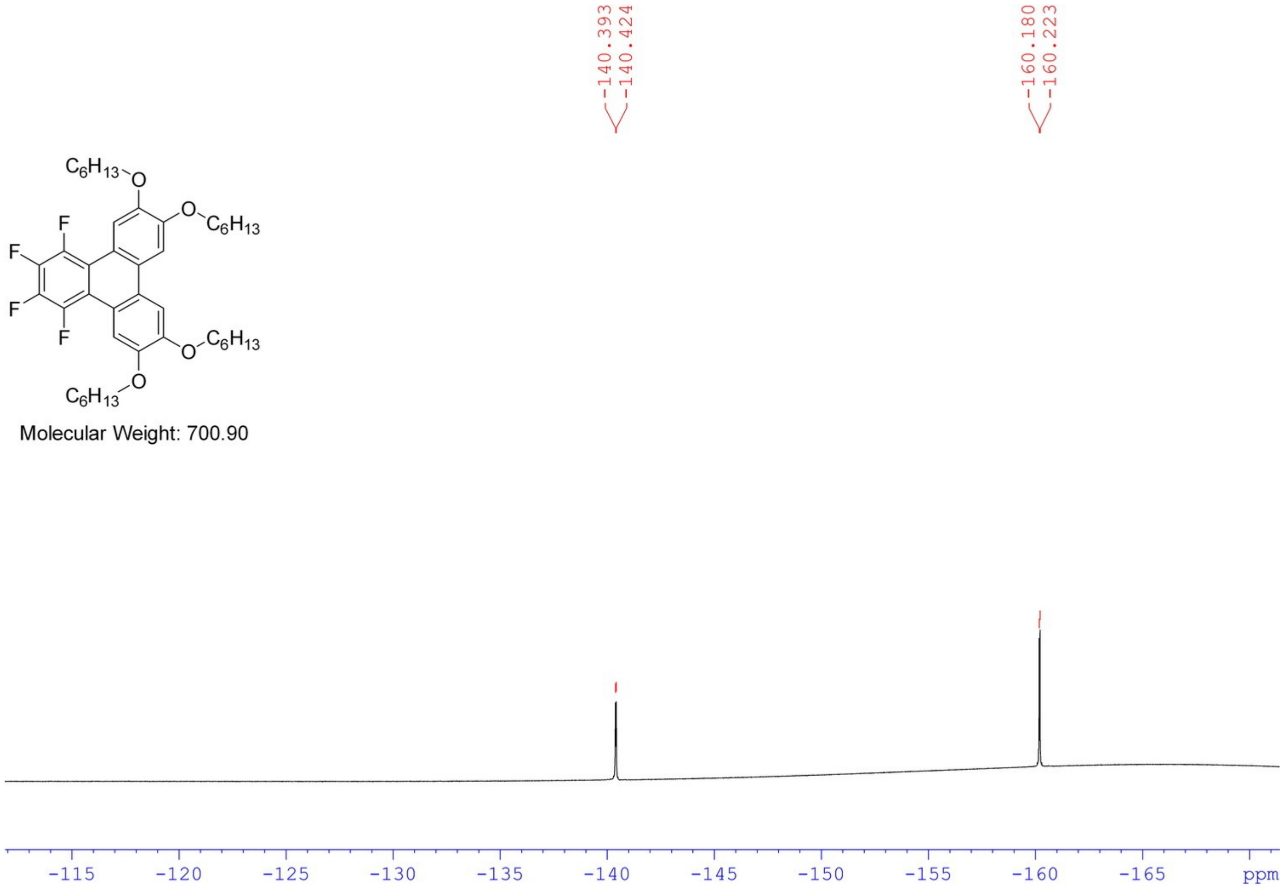

147.507
145.848
145.602
143.423
138.695
136.247
124.162
117.092
114.818
112.748
112.605
112.454
107.938
0.000
OH
OH
F
F
F
F
OH
OH
Molecular Weight: 364.25
220
200
180
160
140
120
100
80
60
40
20
0
ppm



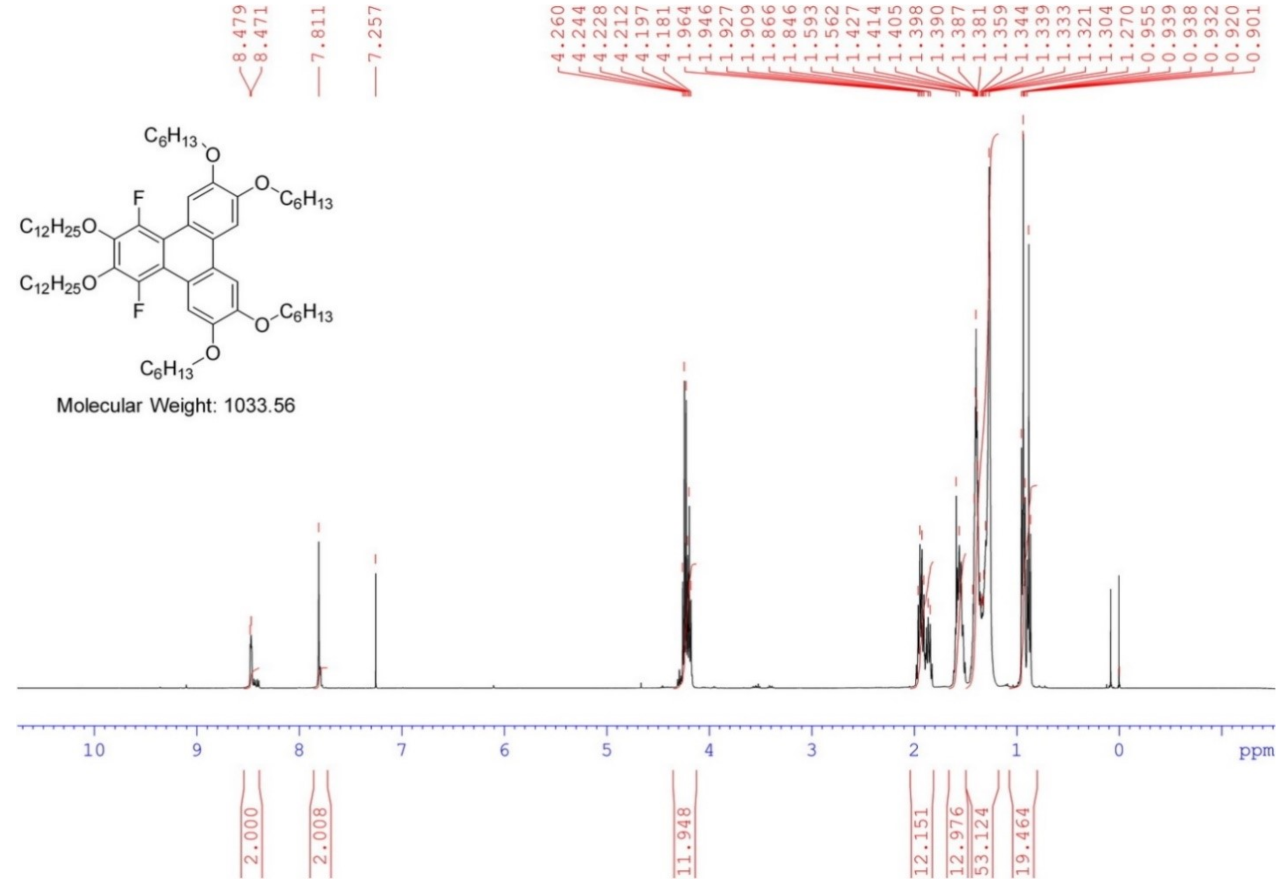
1,2,3,4-tetrafluoro-6,7,10,11-tetrakis(hexyloxy)triphenylene (Compound 9)

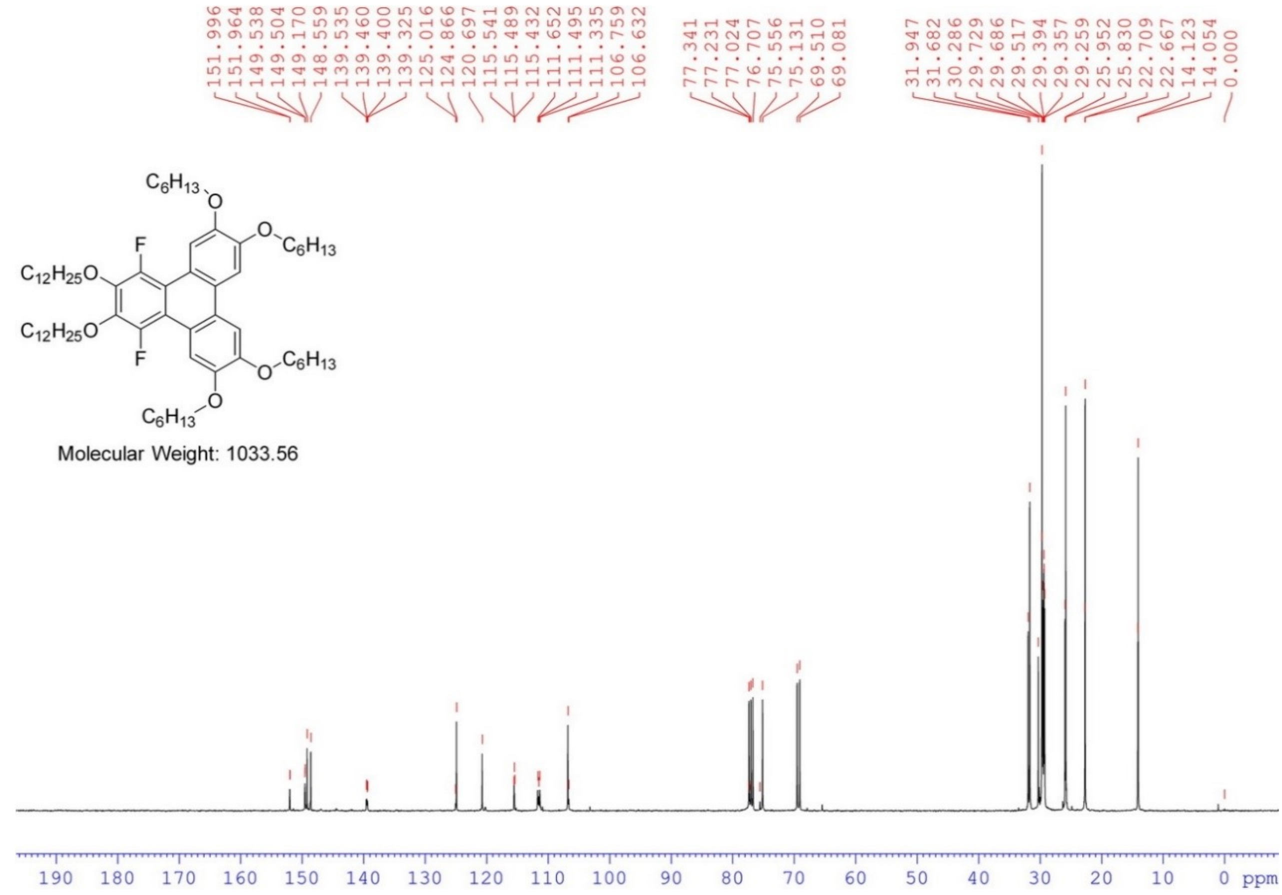


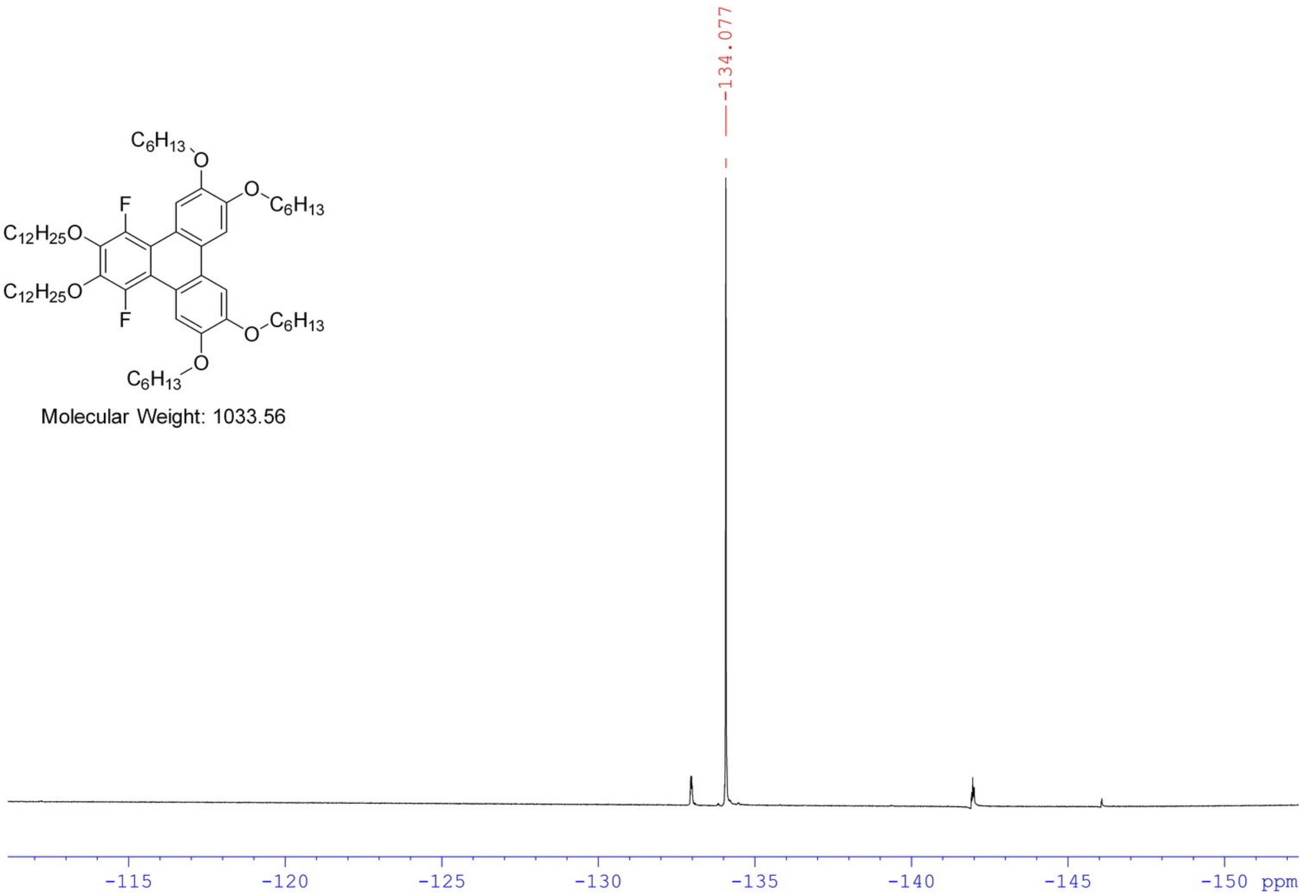

149.784
148.716
146.667
144.179
139.638
137.223
125.009
119.510
115.413
110.984
110.830
110.674
106.252
77.350
77.032
76.715
69.379
69.054
31.688
31.672
29.307
29.215
25.836
25.804
22.670
14.058
0.000
C_6H_{13}
O
C_6H_{13}
F
F
F
F
C_6H_{13}
C_6H_{13}
Molecular Weight: 700.90
220
200
180
160
140
120
100
80
60
40
20
0
ppm


-140.393
-140.424
-160.180
-160.223
C_6H_{13}
O
C_6H_{13}
F
F
F
F
C_6H_{13}
C_6H_{13}
Molecular Weight: 700.90
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
ppm

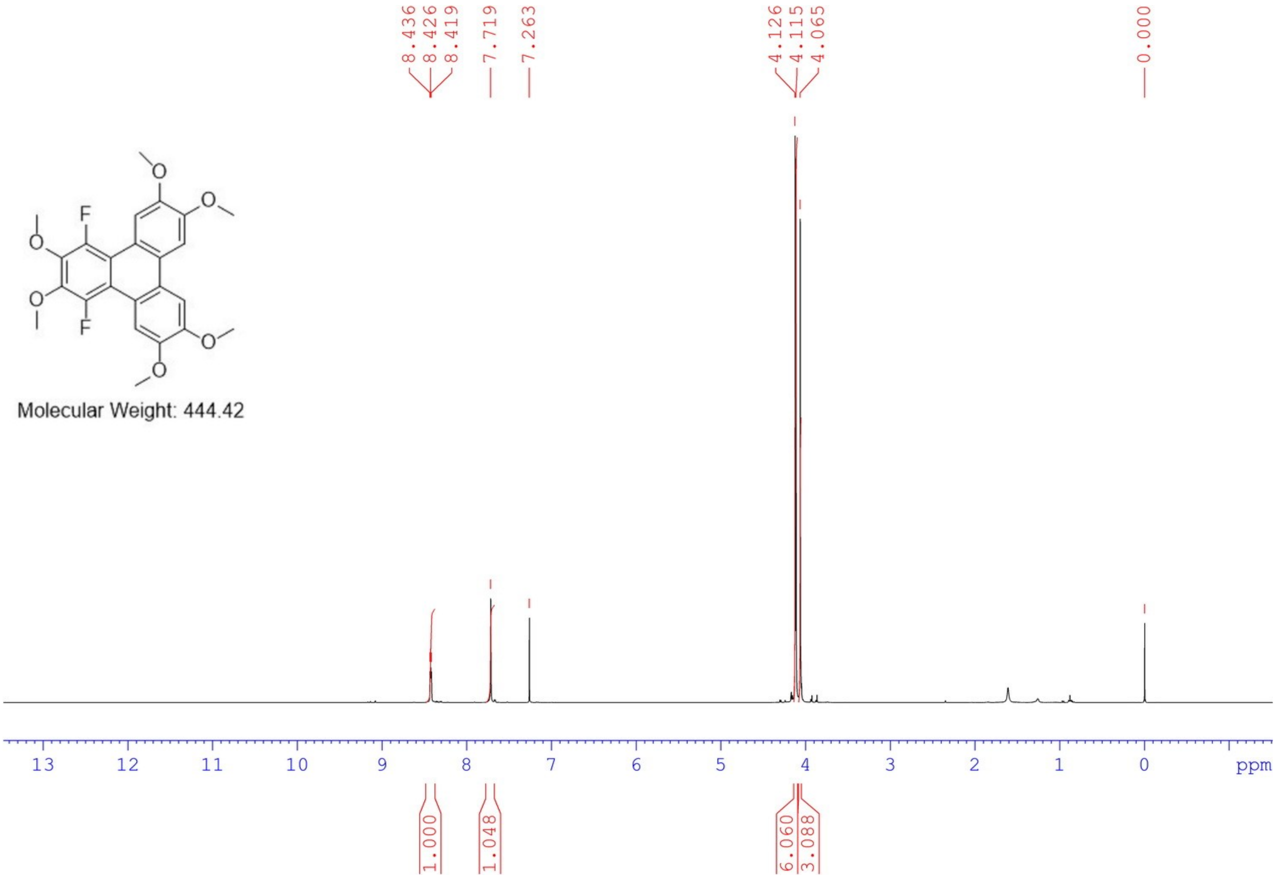
2,3-bis(dodecyloxy)-1,4-difluoro-6,7,10,11-tetrakis(hexyloxy)triphenylene (Compound 10)

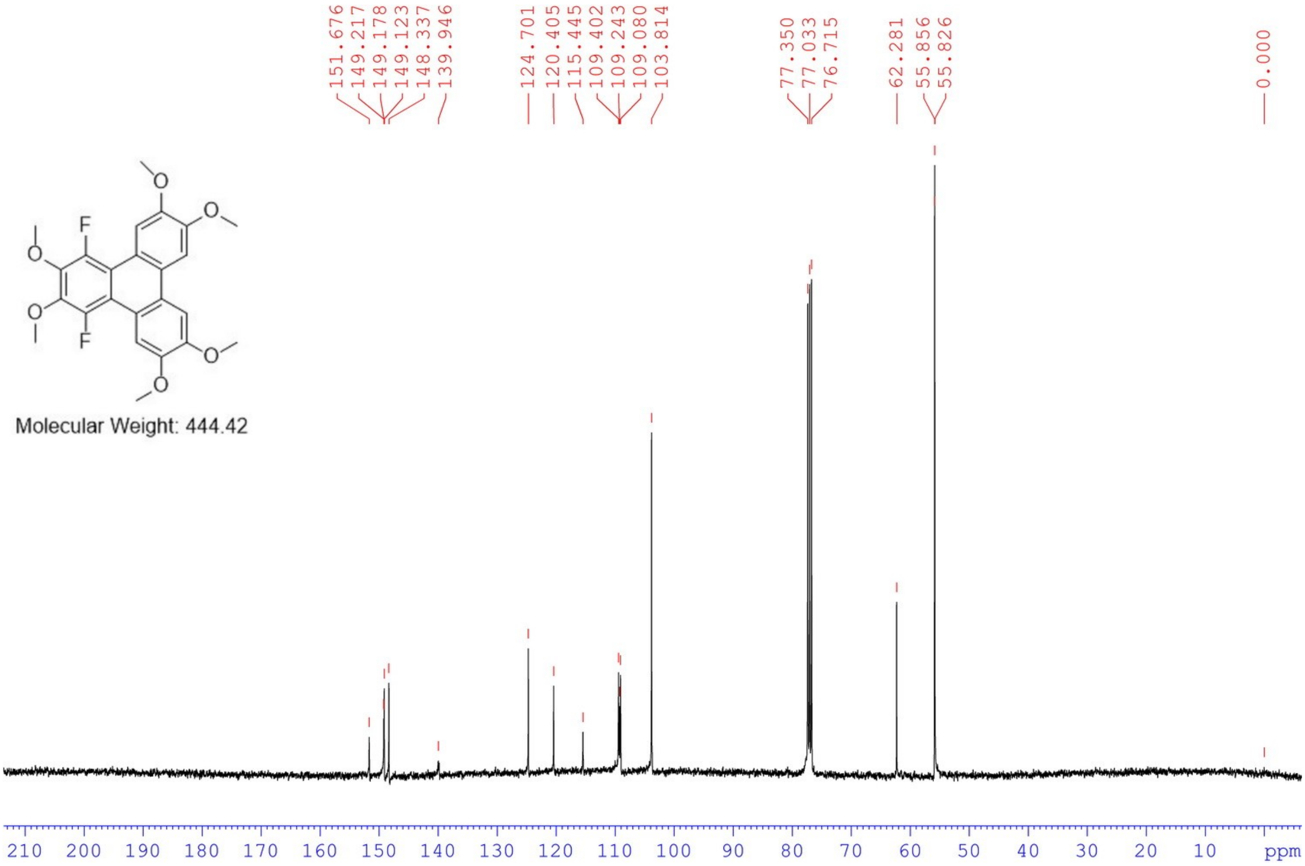


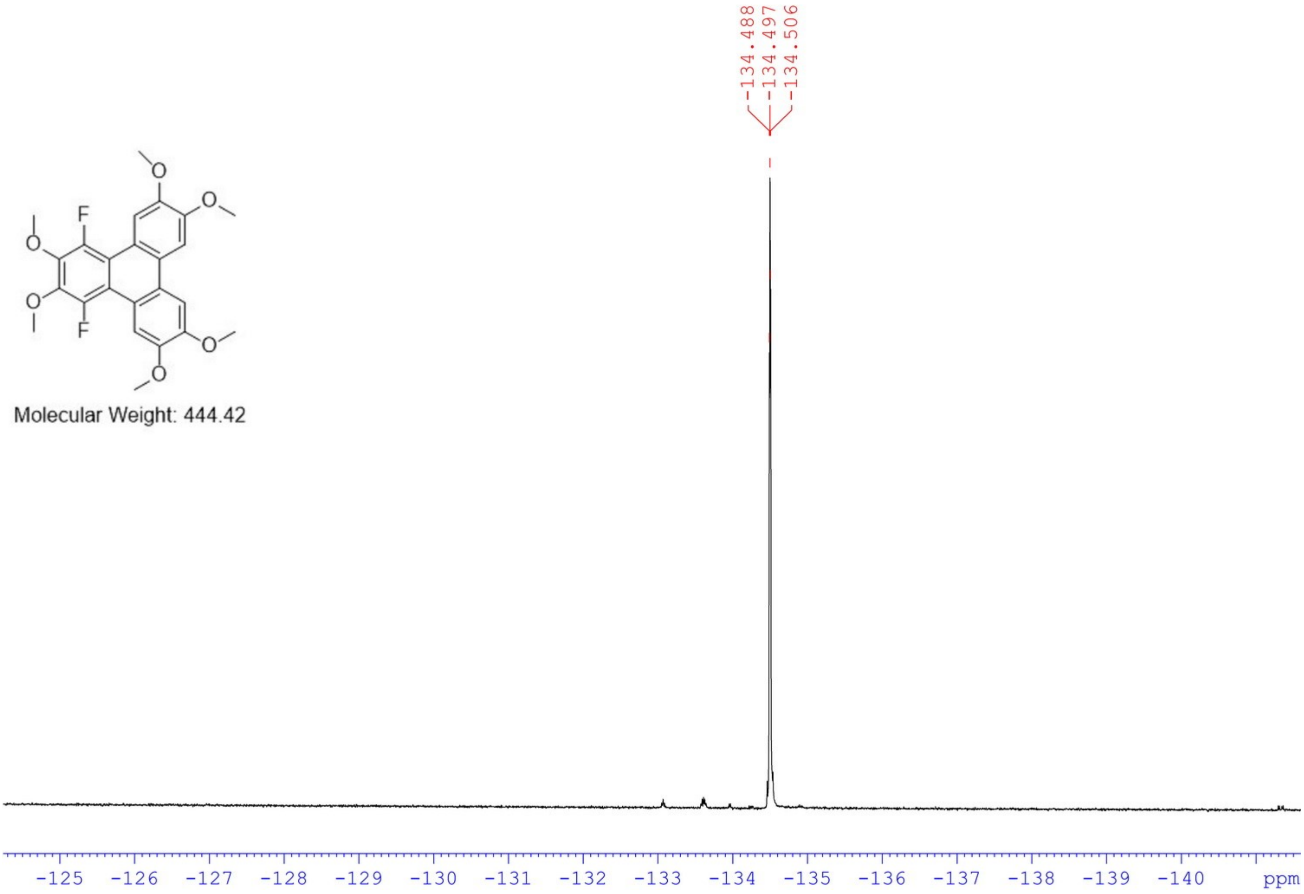




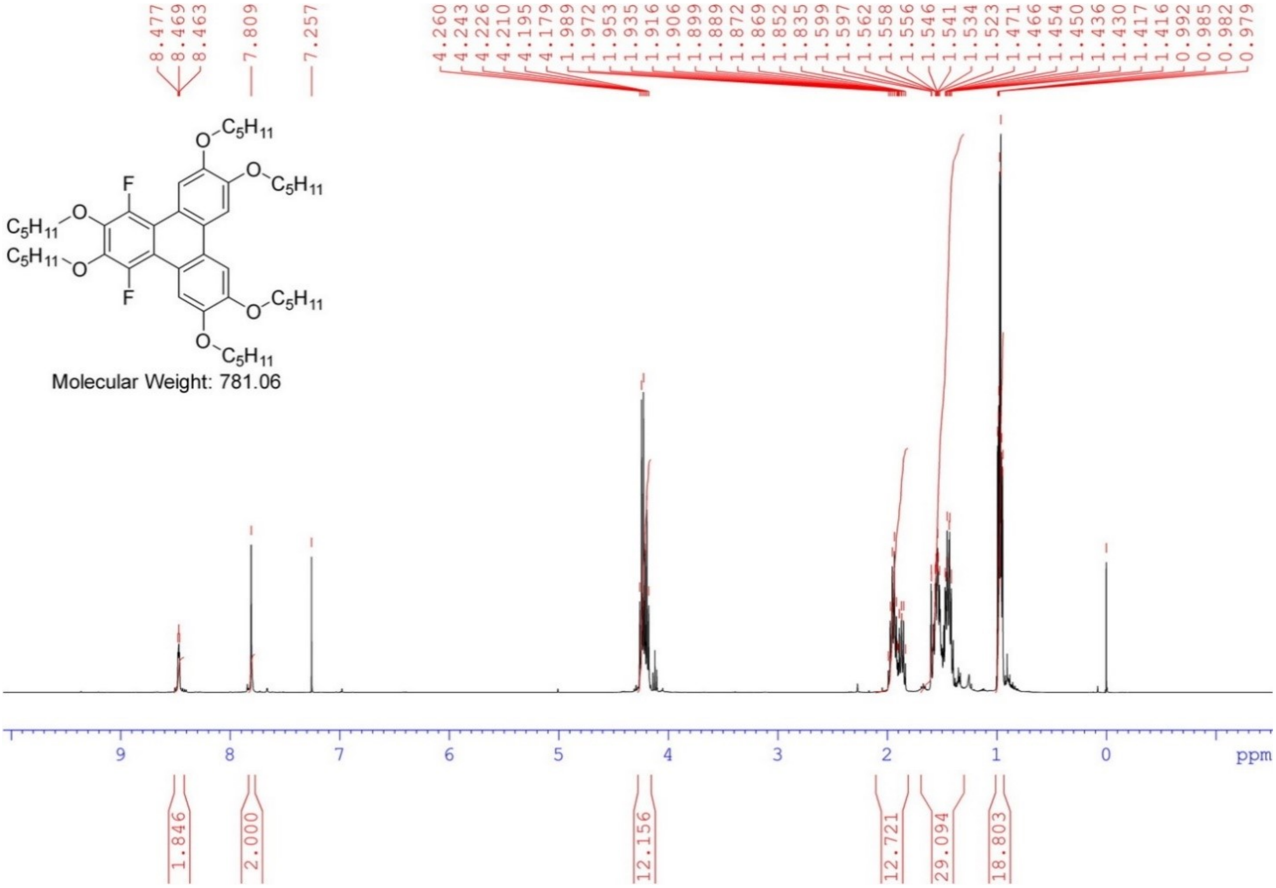
1,4-difluoro-2,3,6,7,10,11-hexamethoxytriphenylene (Compound 11)

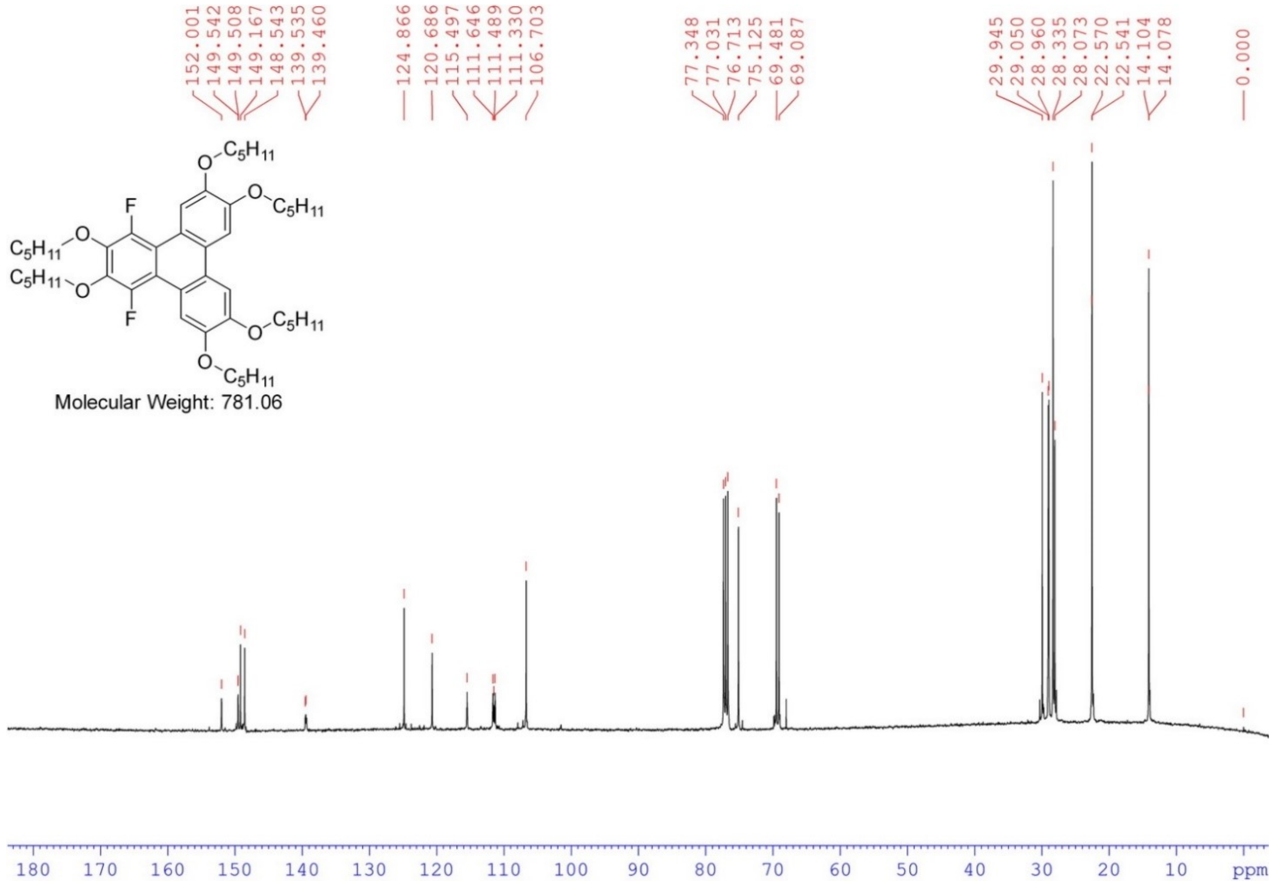


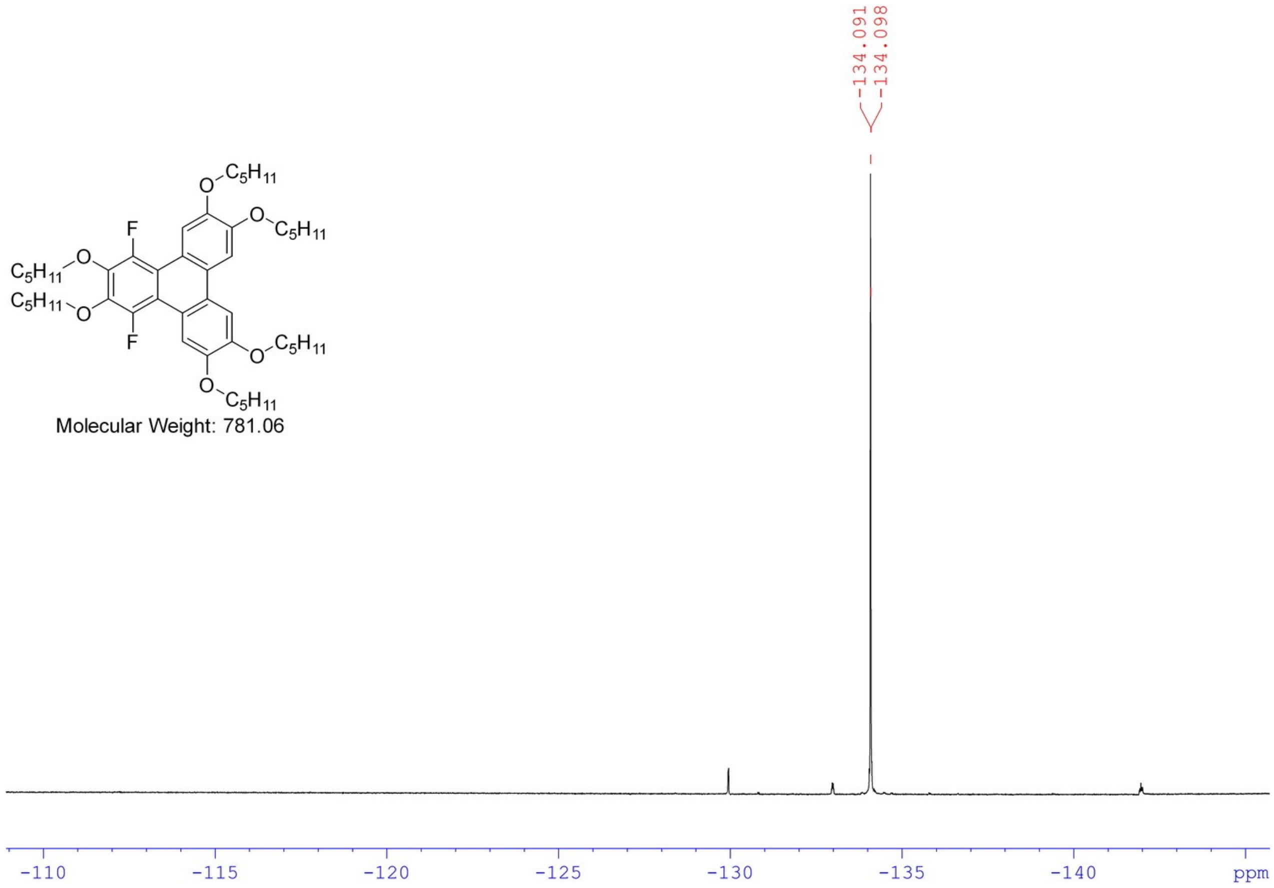

151.676
149.217
149.178
149.123
148.337
139.946
124.701
120.405
115.445
109.402
109.243
109.080
103.814
77.350
77.033
76.715
62.281
55.856
55.826
0.000
F
F
O
Molecular Weight: 444.42
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


-134.488
-134.497
-134.506
F
F
O
Molecular Weight: 444.42
-125 -126 -127 -128 -129 -130 -131 -132 -133 -134 -135 -136 -137 -138 -139 -140 ppm

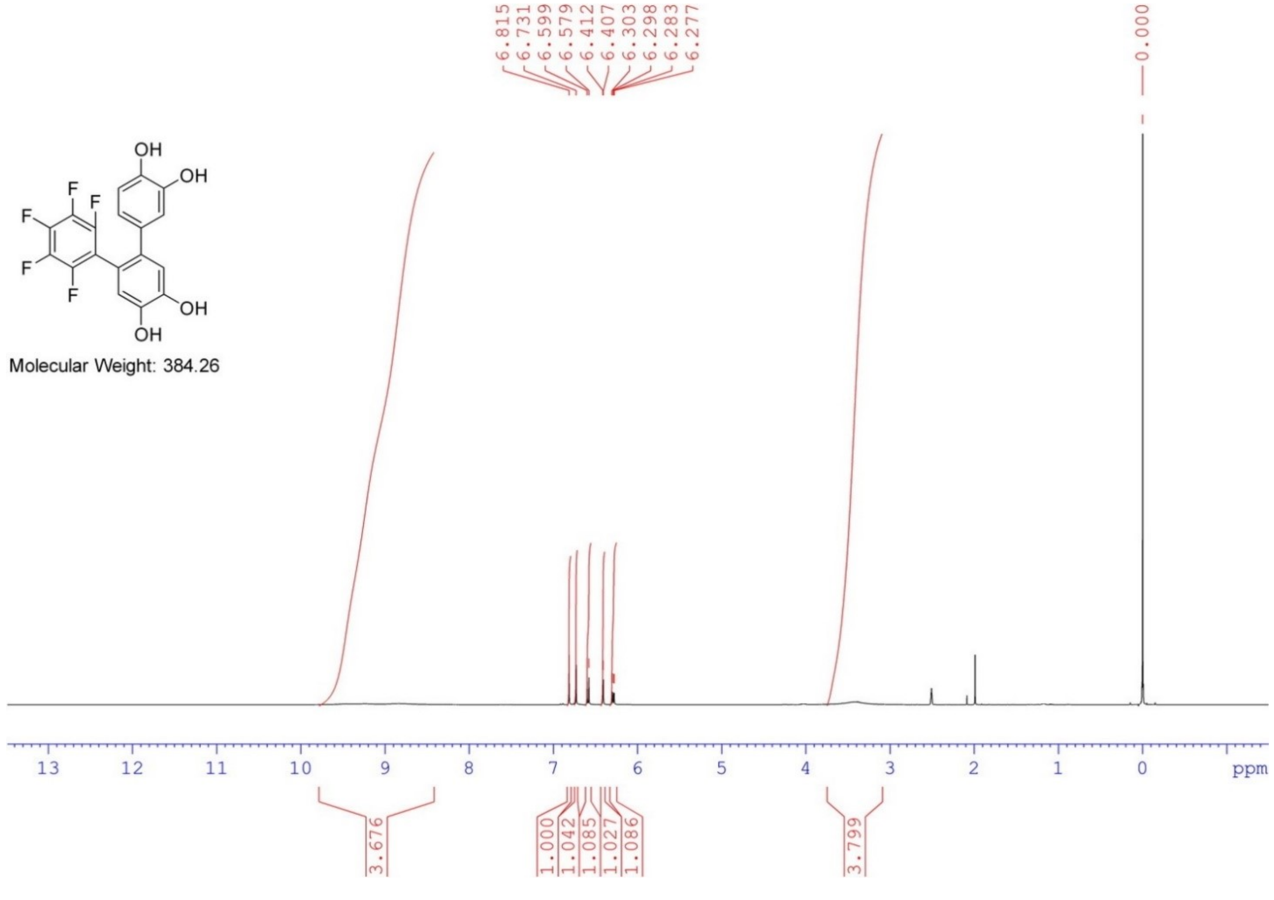
1,4-difluoro-2,3,6,7,10,11-hexakis(pentyloxy)triphenylene (Compound 10)

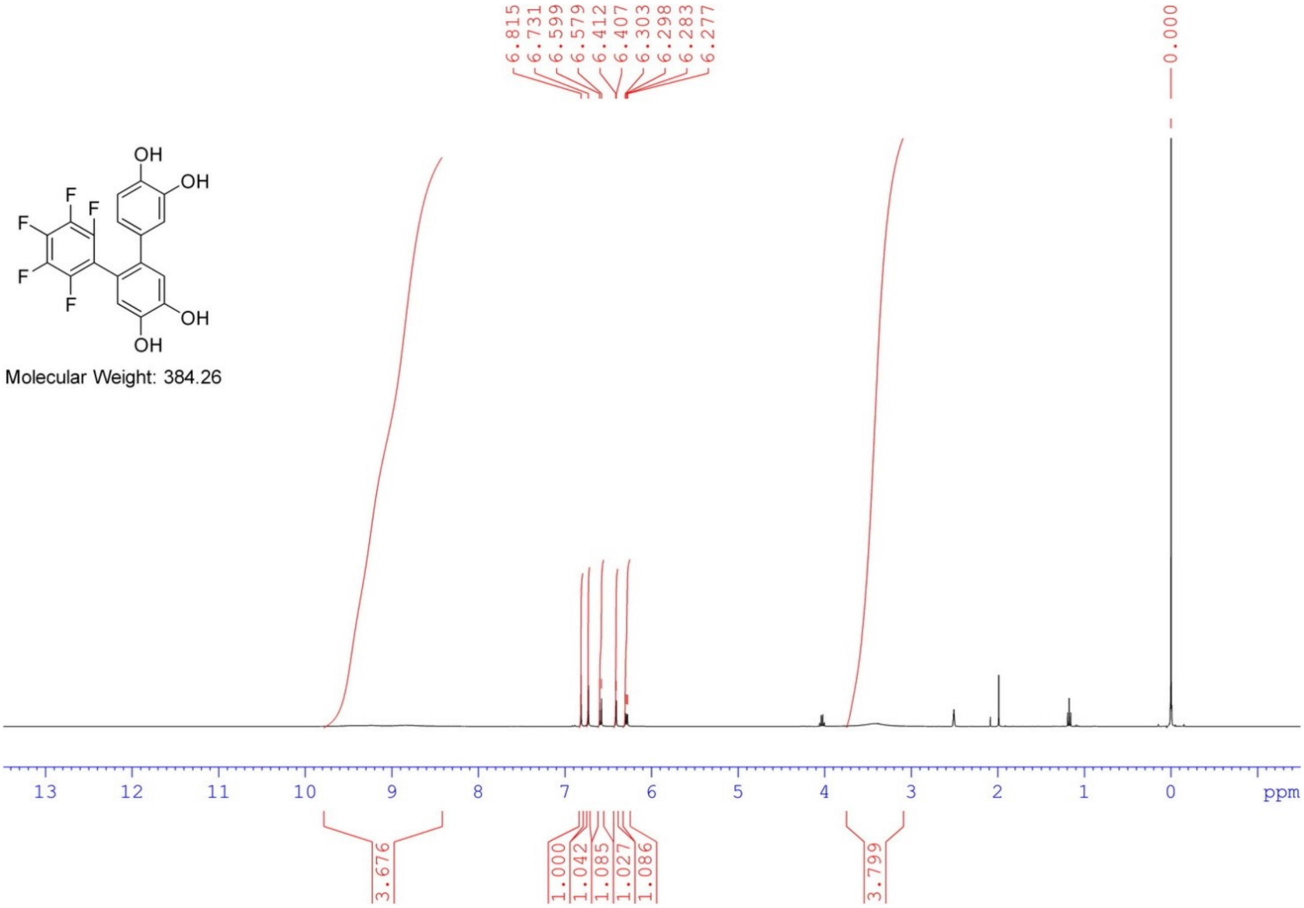


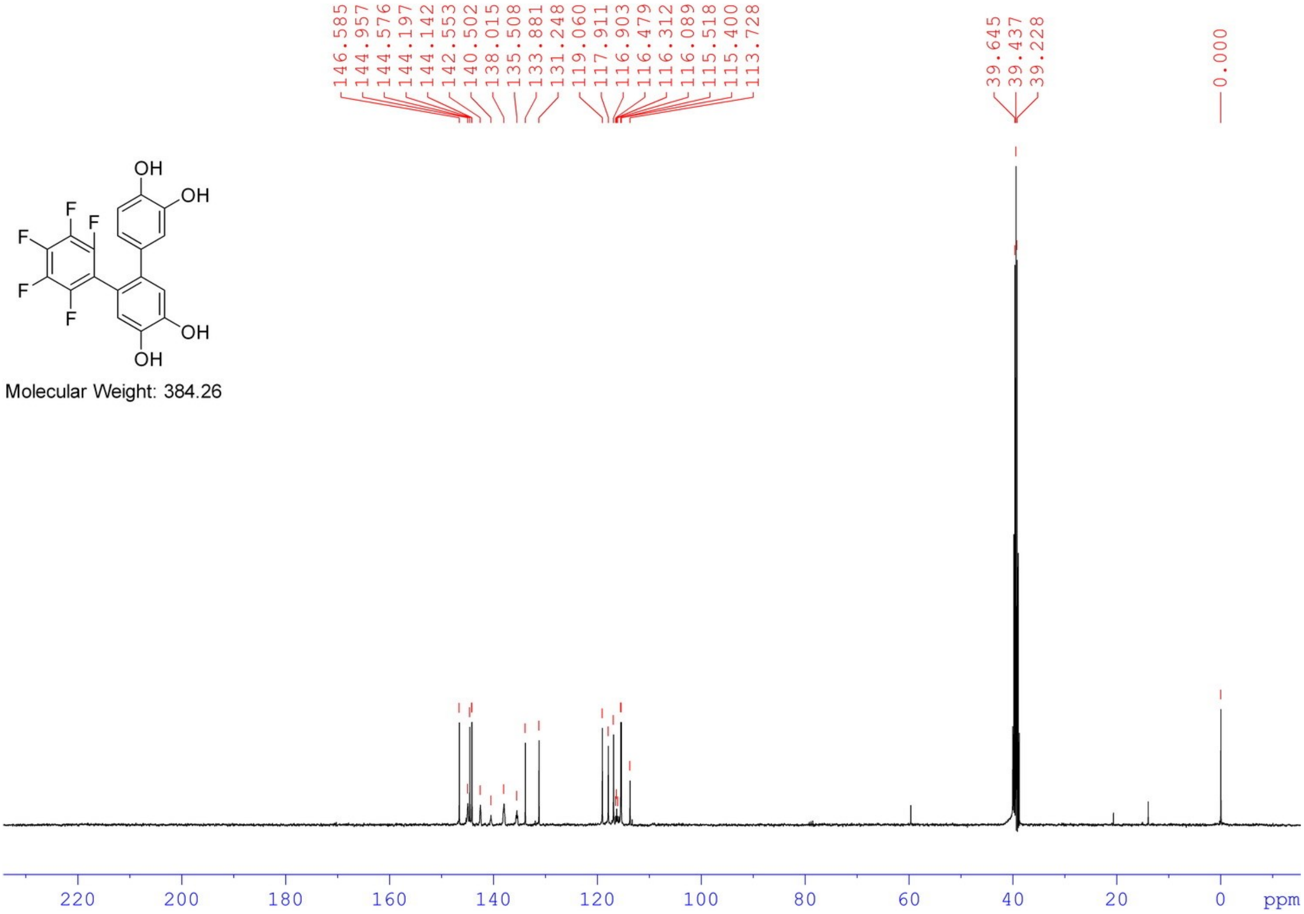




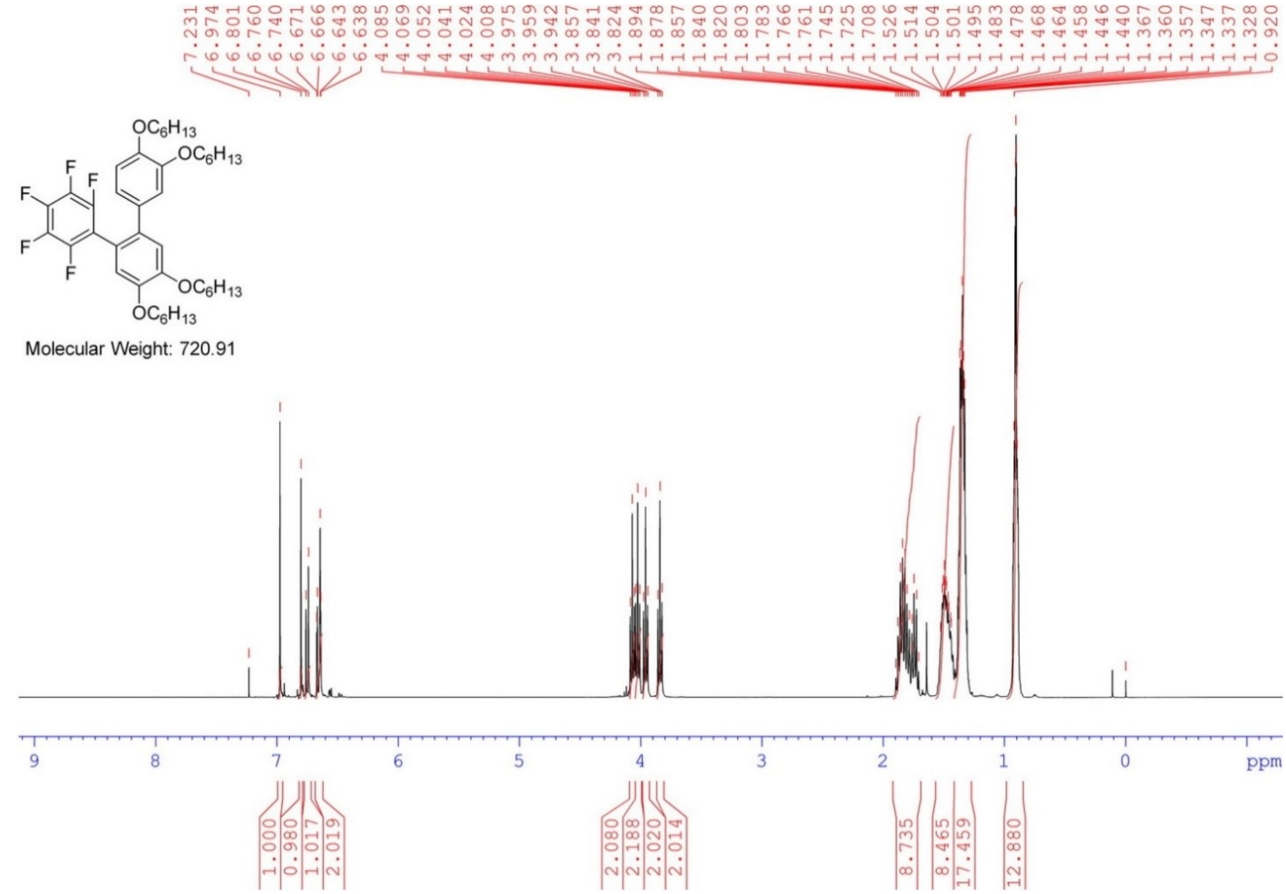
2'',3'',4'',5'',6''-pentafluoro-[1,1':2',1''-terphenyl]-3,4,4',5'-tetraol (Compound 13)

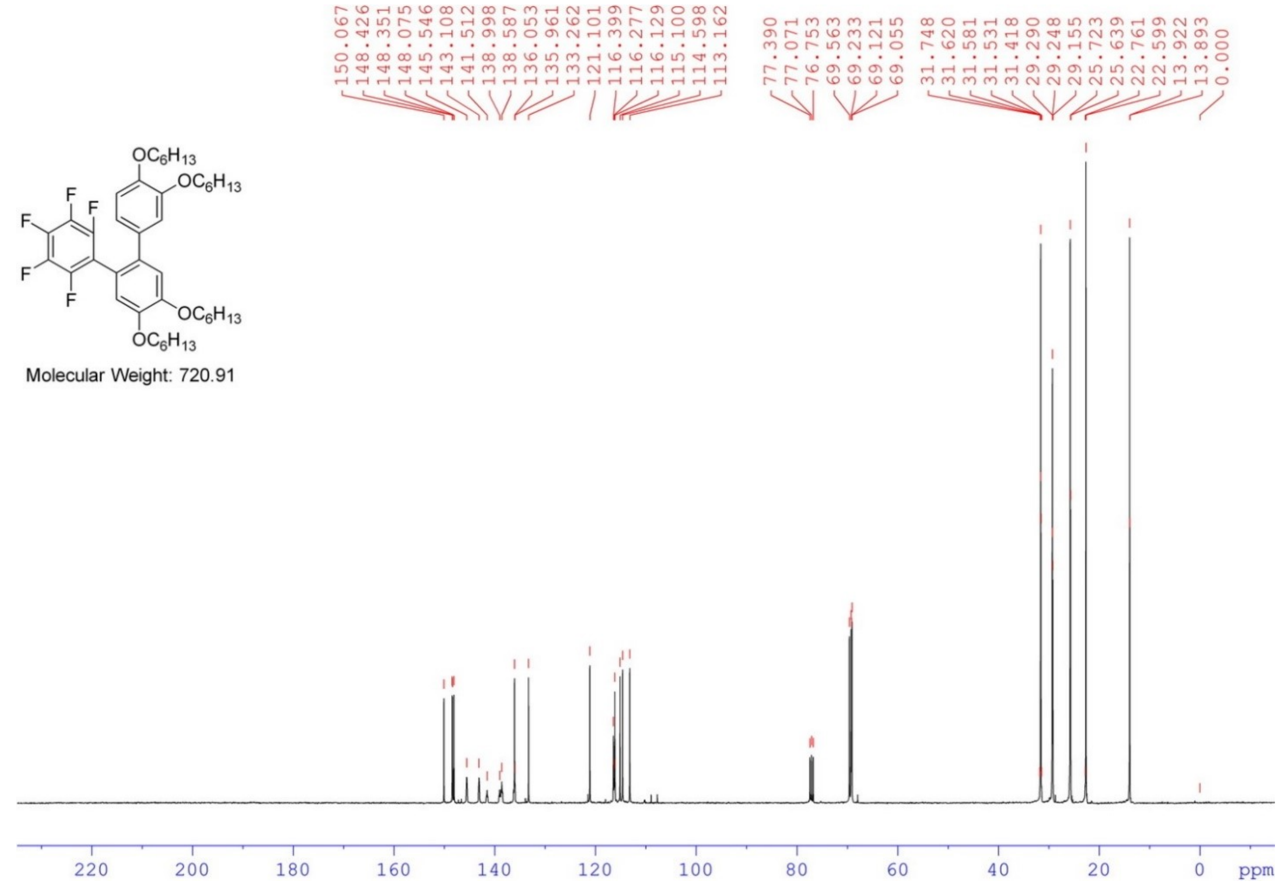


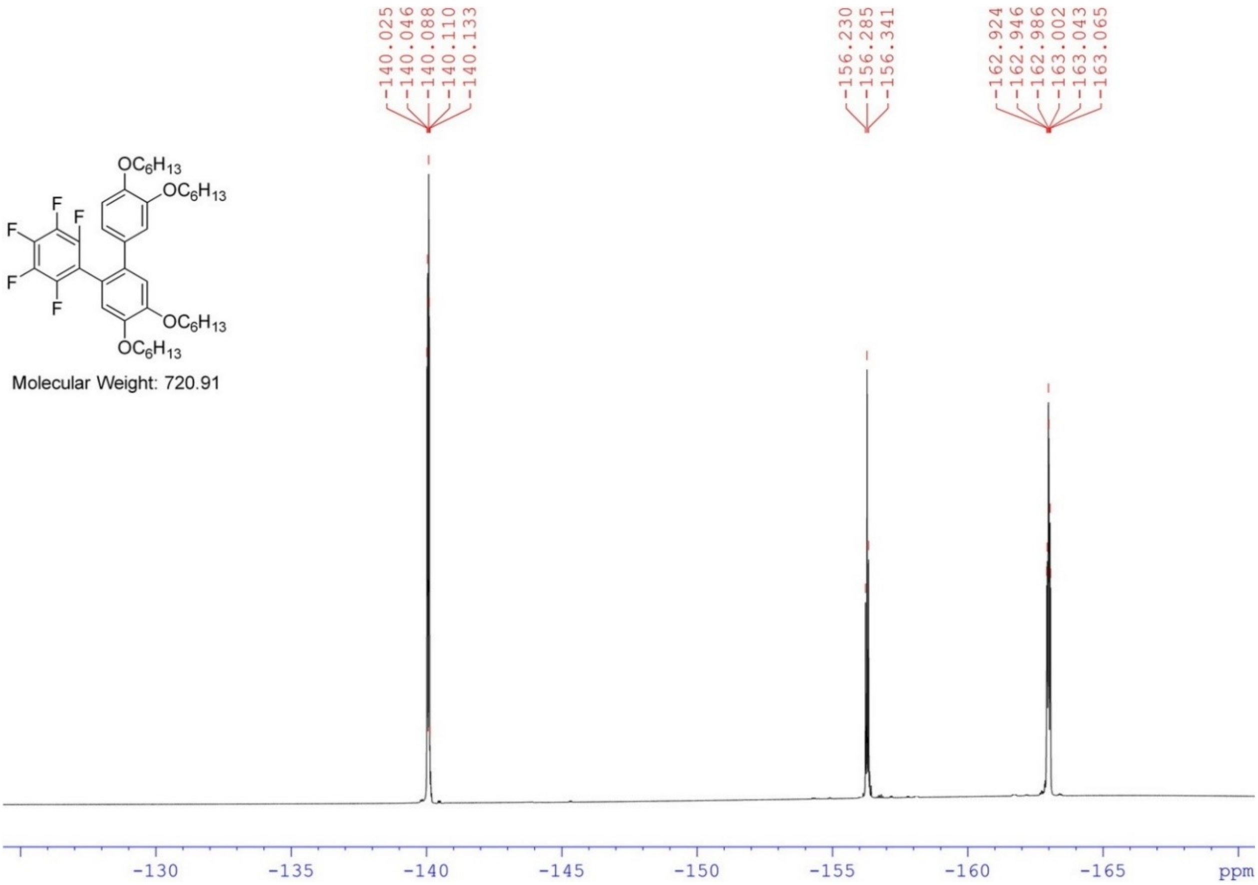

6.815
6.731
6.599
6.579
6.412
6.407
6.303
6.298
6.283
6.277
0.000
OH
OH
F
F
F
F
F
OH
OH
Molecular Weight: 384.26
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.676
1.000
1.042
1.085
1.027
1.086
3.799


146.585
144.957
144.576
144.197
144.142
142.553
140.502
138.015
135.508
133.881
131.248
119.060
117.911
116.903
116.479
116.312
116.089
115.518
115.400
113.728
39.645
39.437
39.228
0.000
OH
OH
F
F
F
F
F
OH
OH
Molecular Weight: 384.26
220
200
180
160
140
120
100
80
60
40
20
0
ppm

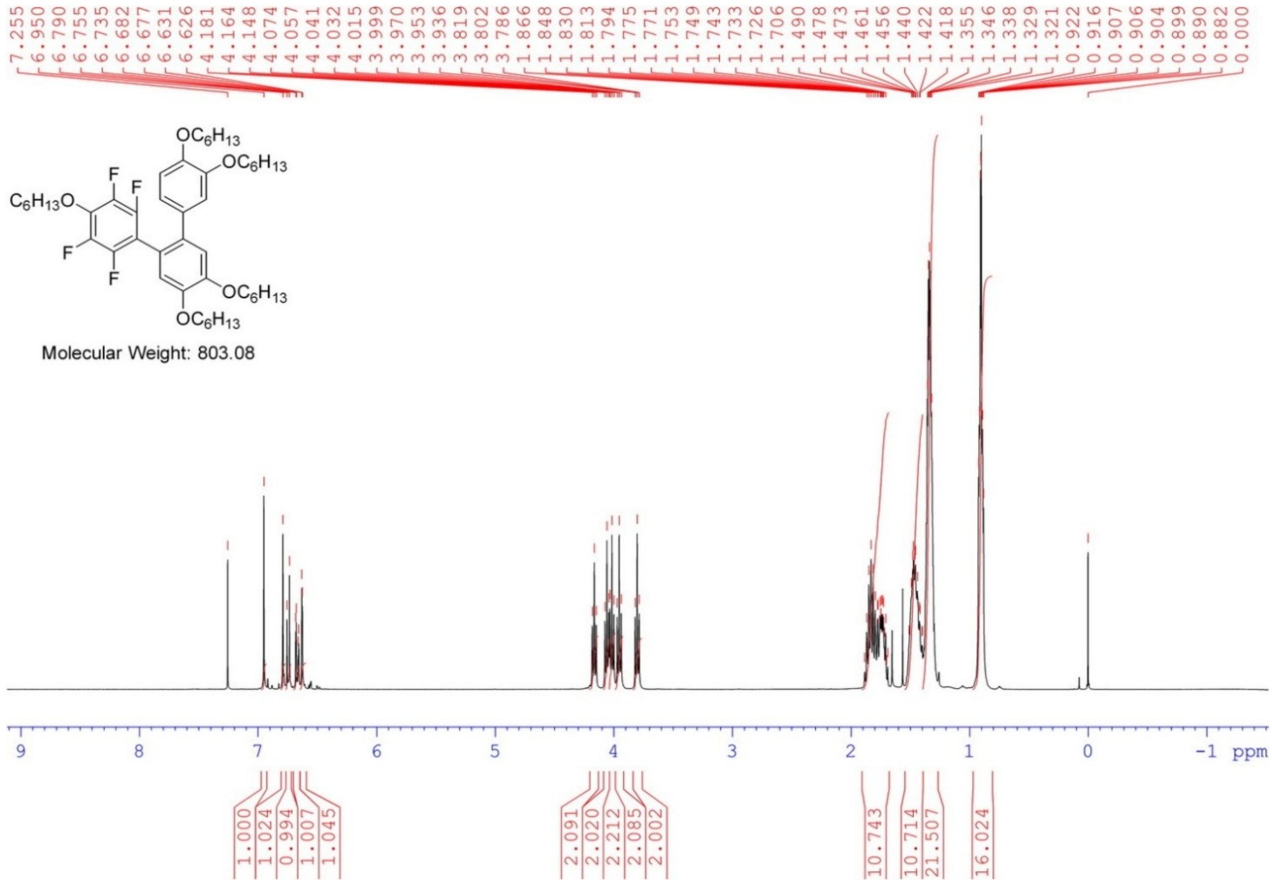
NMR Spectra for 2,3,4,5,6-pentafluoro-3'',4',4'',5'-tetrakis(hexyloxy)-1,1':2',1''-terphenyl (Compound 14)

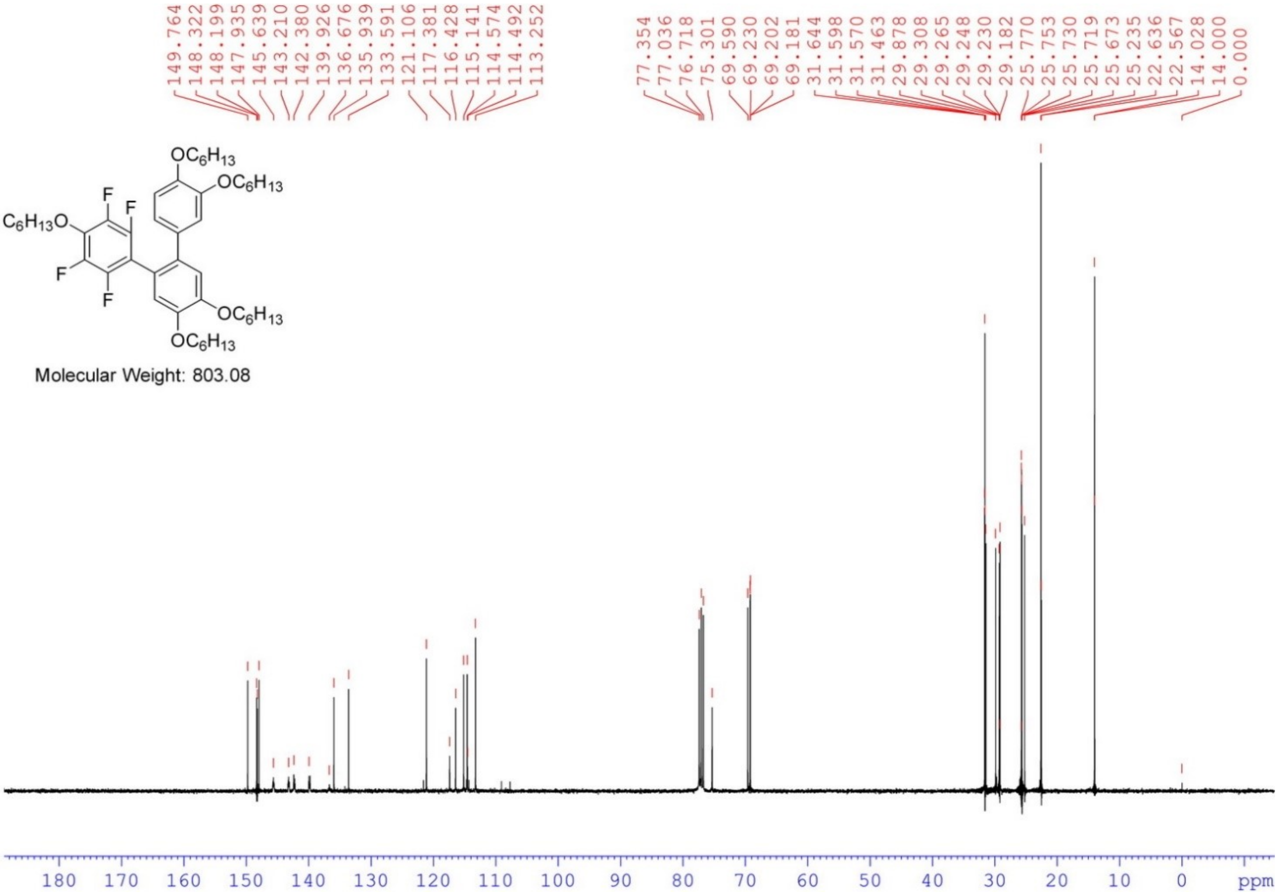


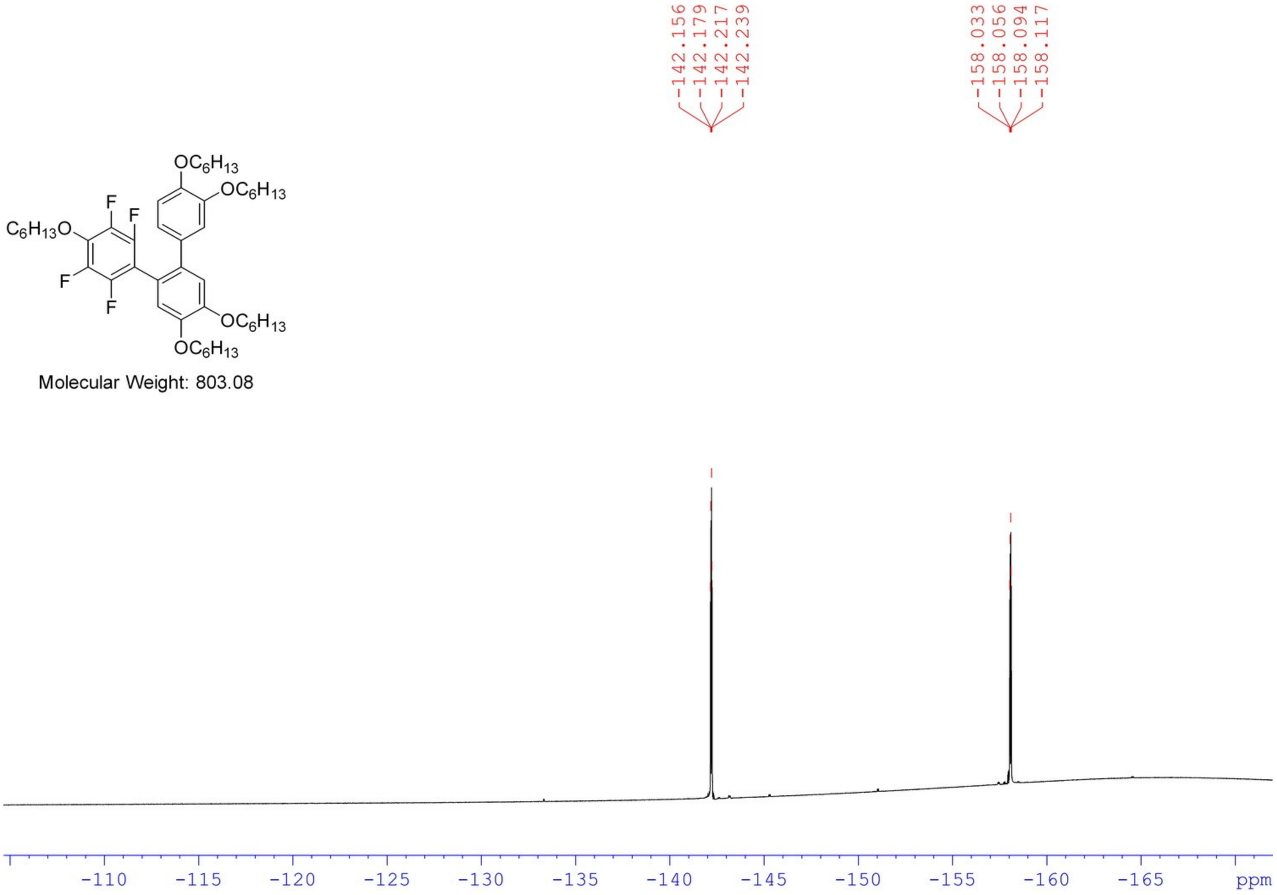




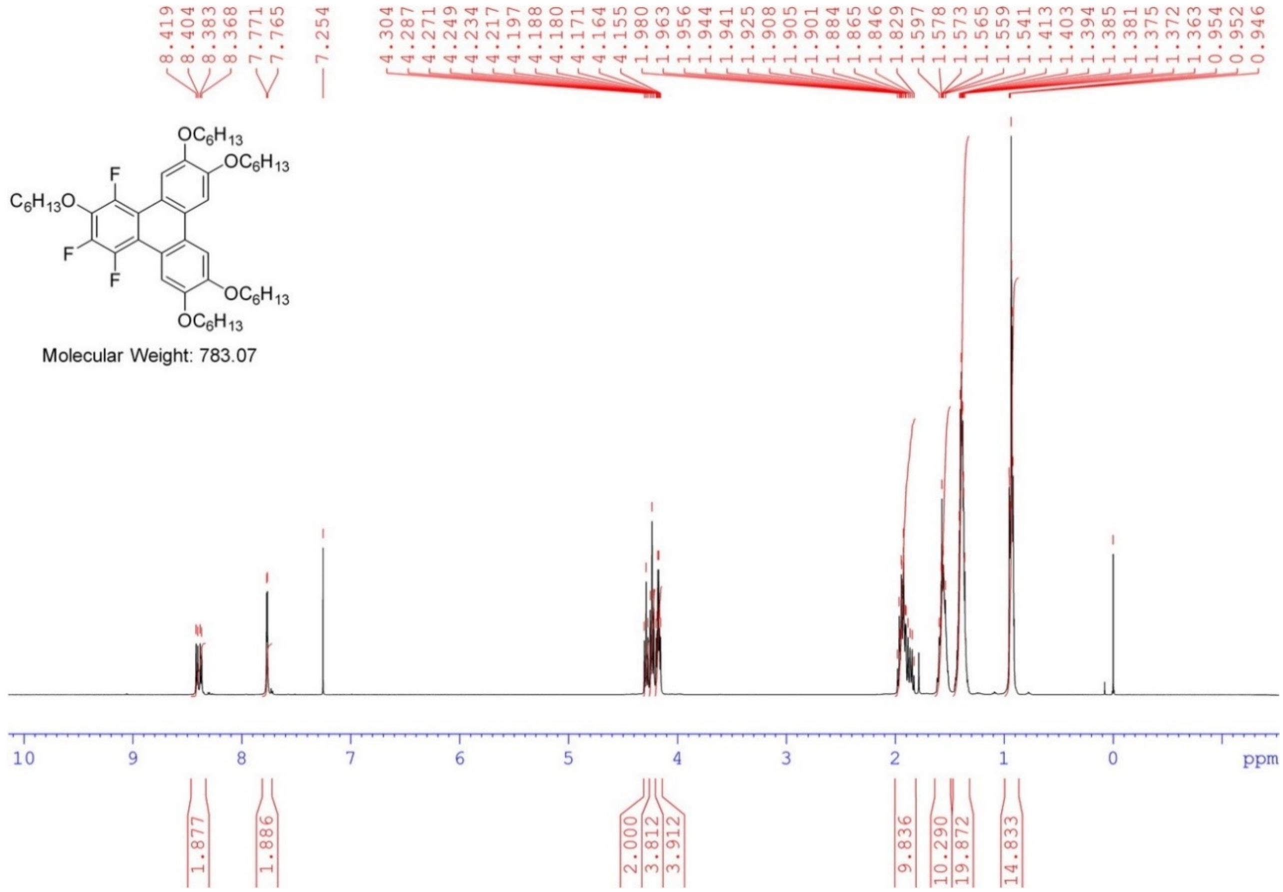
2,3,5,6-tetrafluoro-3'',4,4',4'',5'-pentakis(hexyloxy)-1,1':2',1''-terphenyl (Compound 15)

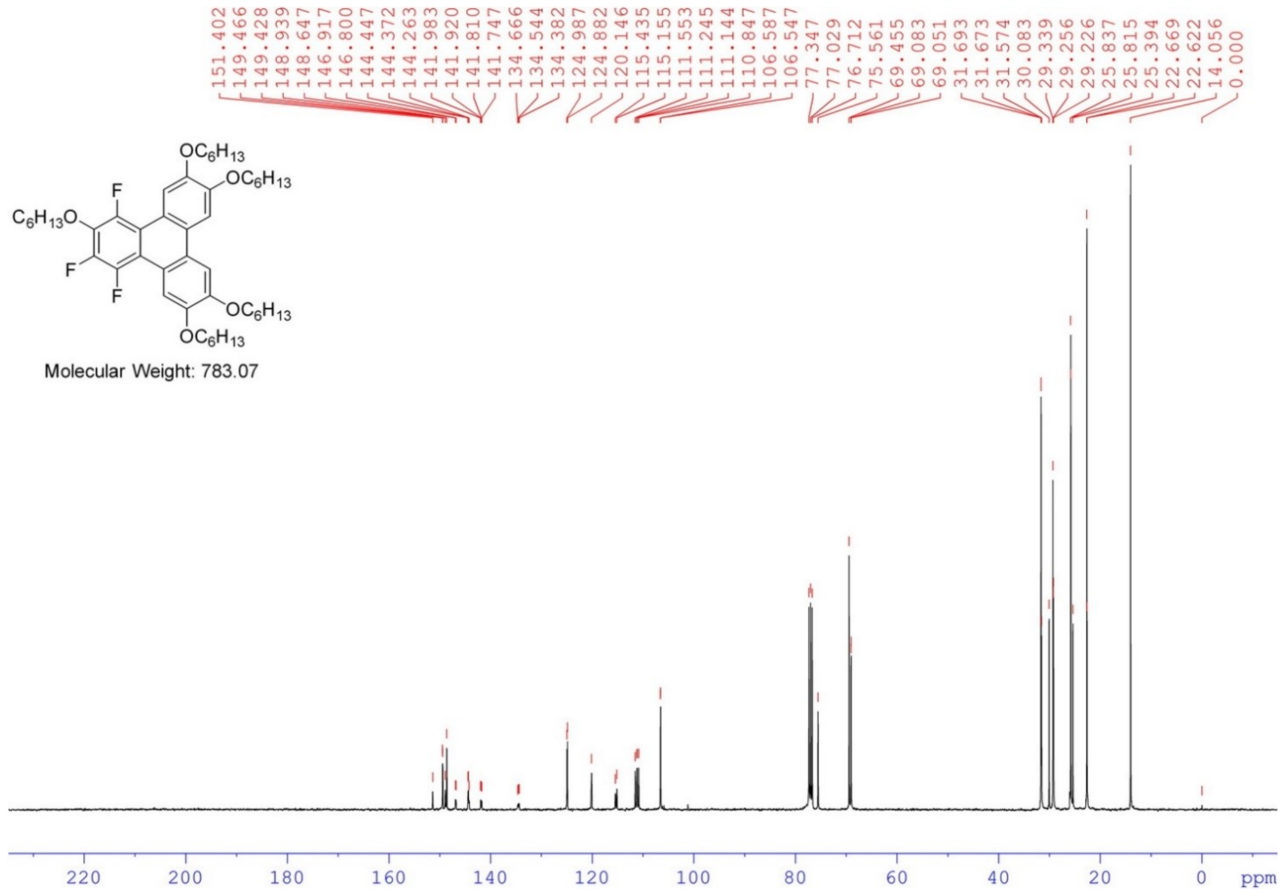


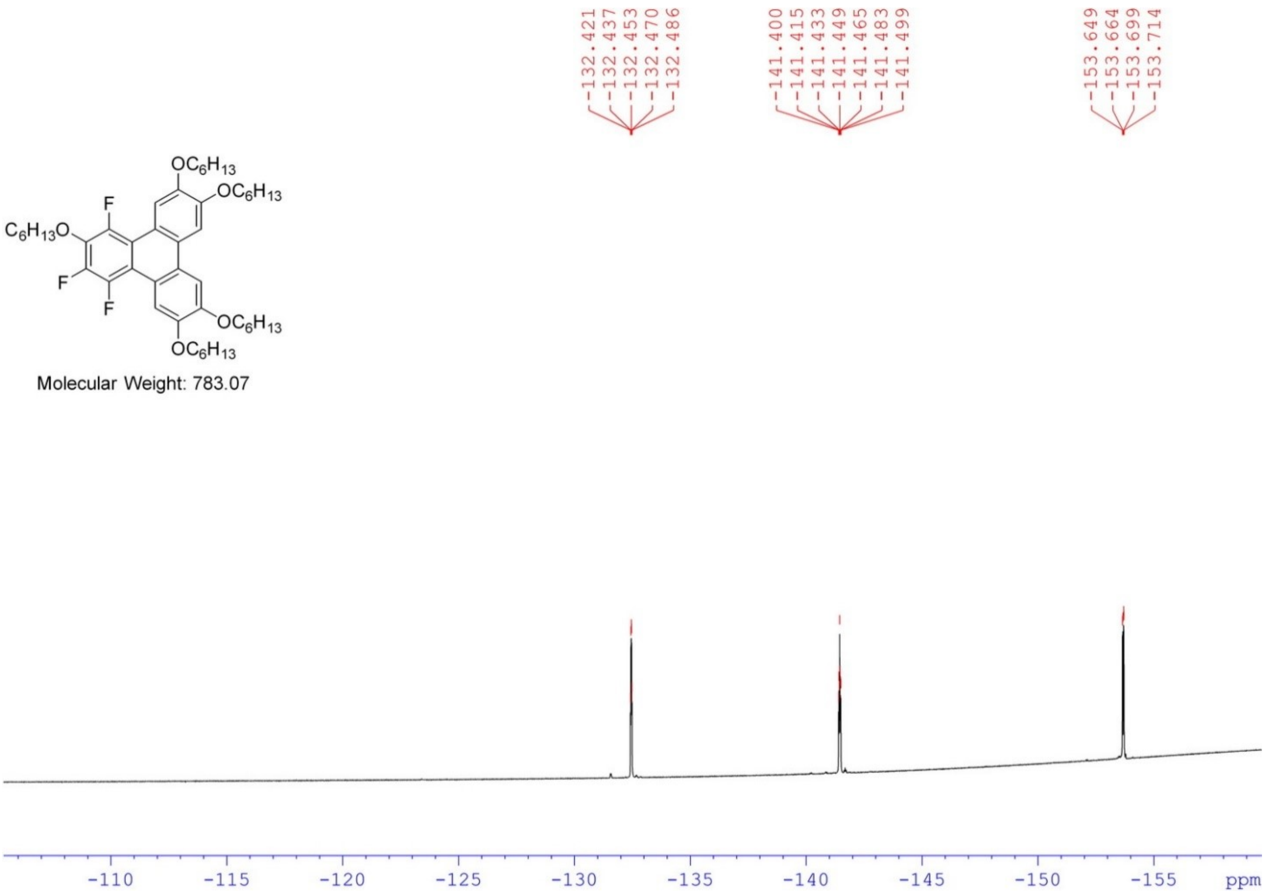

149.764
148.322
148.199
147.935
145.639
143.210
142.380
139.926
136.676
135.939
133.591
121.106
117.381
116.428
115.141
114.574
114.492
113.252
77.354
77.036
76.718
75.301
69.590
69.230
69.202
69.181
31.644
31.598
31.570
31.463
29.878
29.308
29.265
29.248
29.230
29.182
25.770
25.753
25.730
25.719
25.673
25.235
22.636
22.567
14.028
14.000
0.000
OC6H13
OC6H13
C6H13O
F
F
F
F
OC6H13
OC6H13
Molecular Weight: 803.08
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-142.156
-142.179
-142.217
-142.239
-158.033
-158.056
-158.094
-158.117
OC6H13
OC6H13
C6H13O
F
F
F
F
OC6H13
OC6H13
Molecular Weight: 803.08
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
ppm

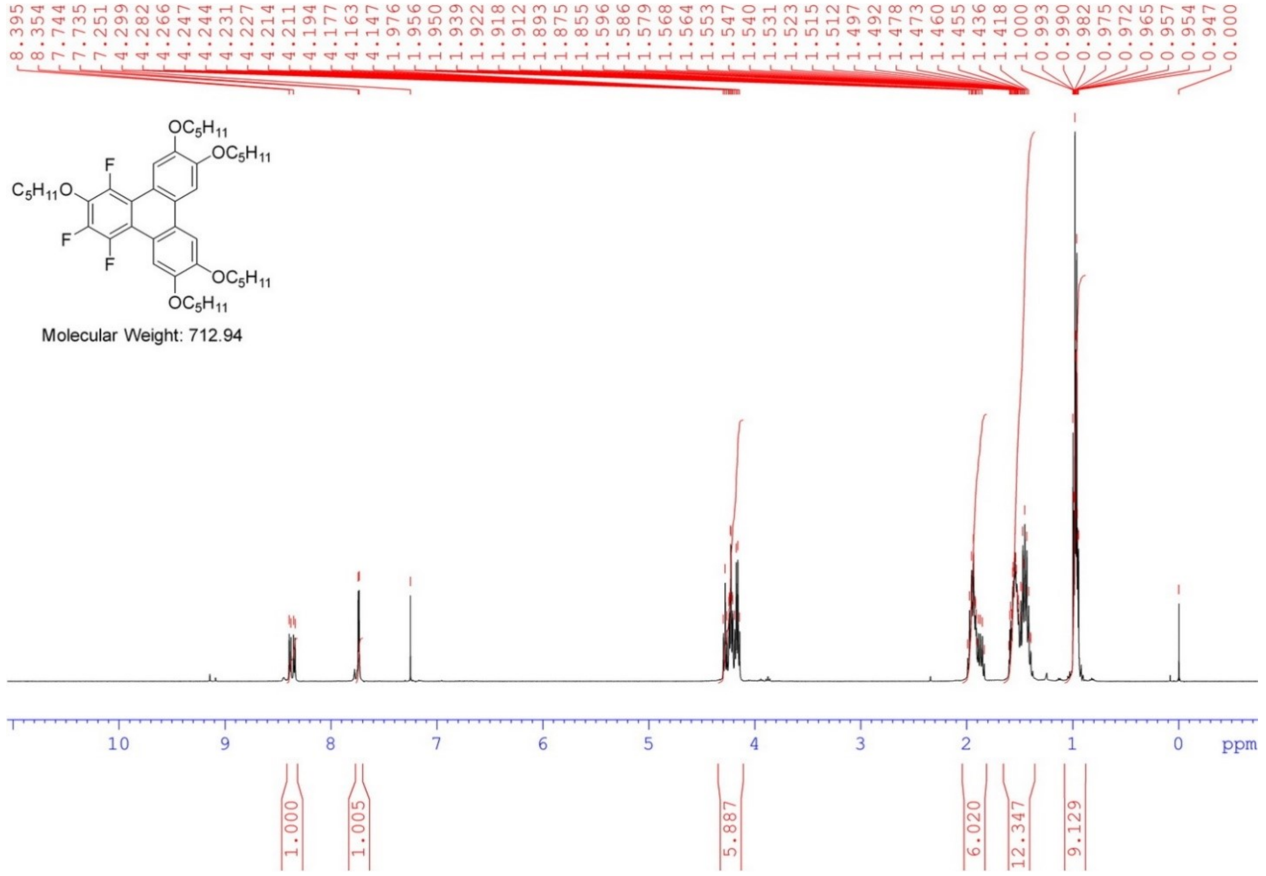
1,2,4-trifluoro-3,6,7,10,11-pentakis(hexyloxy)triphenylene (Compound 16)

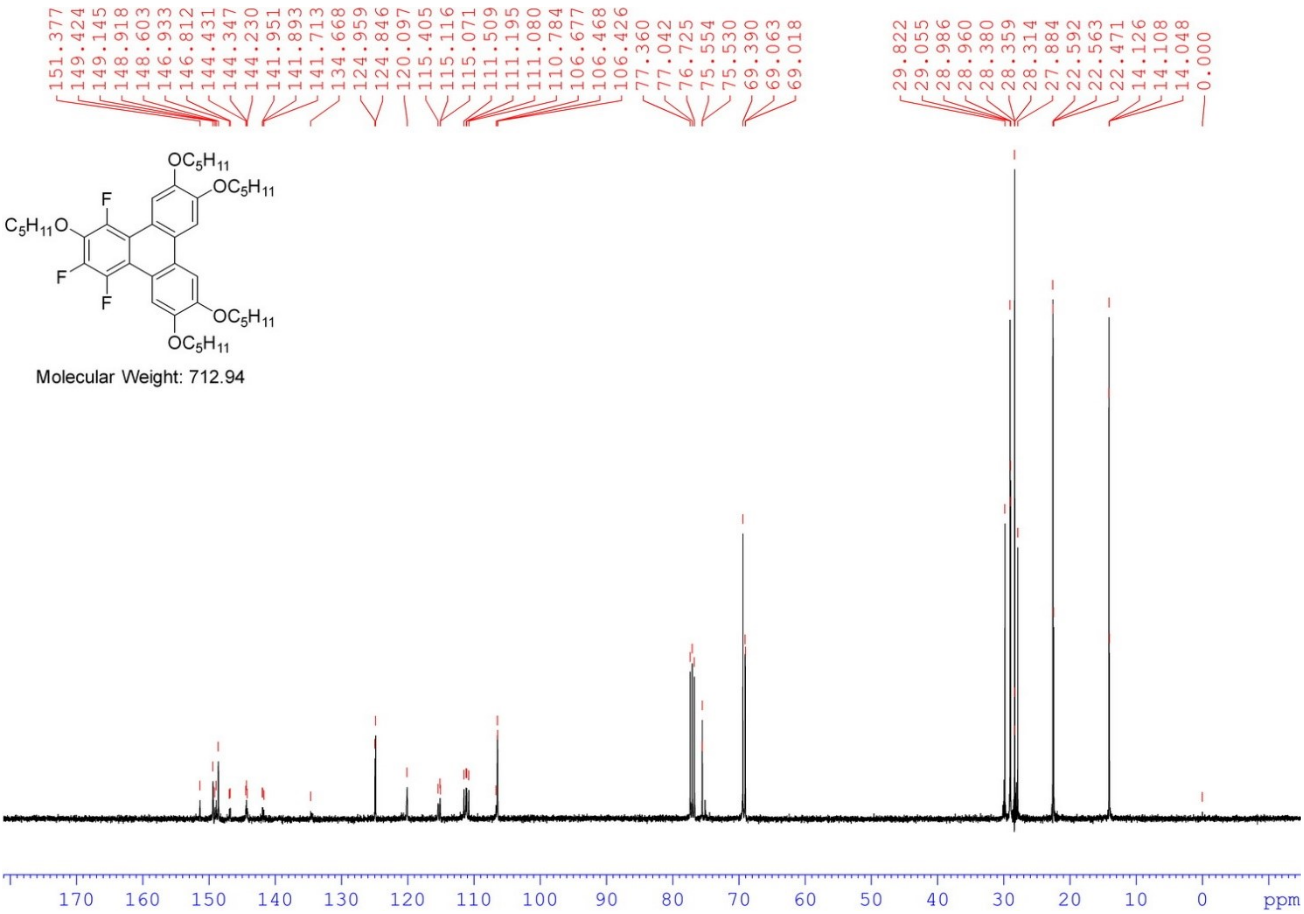


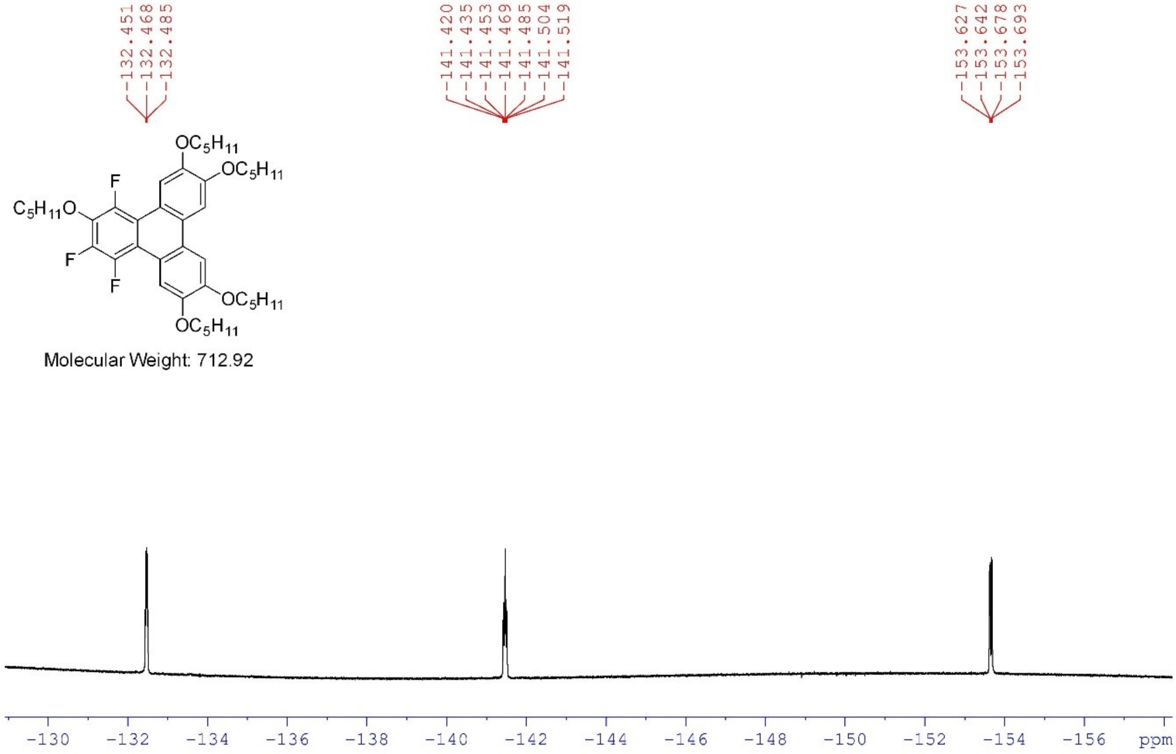




1,2,4-trifluoro-3,6,7,10,11-pentakis(pentyloxy)triphenylene (Compound 16)



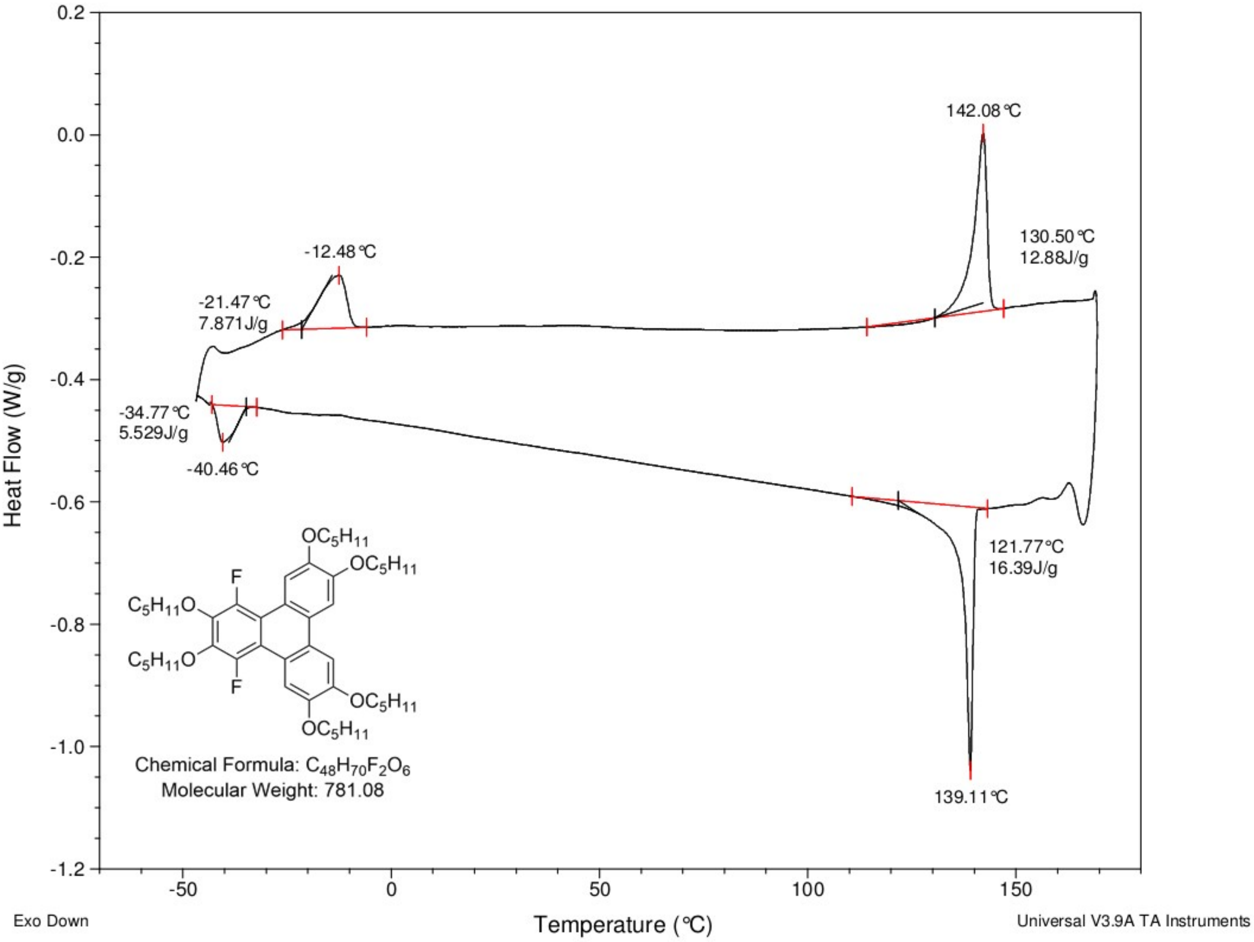

151.377
149.424
149.145
148.918
148.603
146.933
146.812
144.431
144.347
144.230
141.951
141.893
141.713
134.668
124.959
124.846
120.097
115.405
115.116
115.071
111.509
111.195
111.080
110.784
110.677
106.468
106.426
77.360
77.042
76.725
75.554
75.530
69.390
69.063
69.018
29.822
29.055
28.986
28.960
28.380
28.359
28.314
27.884
22.592
22.563
22.471
14.126
14.108
14.048
0.000
OC5H11
OC5H11
C5H11O
F
F
F
OC5H11
OC5H11
Molecular Weight: 712.94
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-132.451
-132.468
-132.485
-141.420
-141.435
-141.453
-141.469
-141.485
-141.504
-141.519
-153.627
-153.642
-153.678
-153.693
OC5H11
OC5H11
C5H11O
F
F
F
OC5H11
OC5H11
Molecular Weight: 712.92
-130
-132
-134
-136
-138
-140
-142
-144
-146
-148
-150
-152
-154
-156
ppm

3. DSC Analysis of Mesogenic Compounds

DSC analysis was performed on a model 2920 DSC (TA Instruments Inc., New Castle, DE, USA). Data was collected on the second cycle, after heating into the isotropic phase and cooling once. The scan rate of this data collection cycle was 5° K/min unless otherwise noted. In all cases, a small amount (not less than 2.0 mg) was sealed inside an aluminum sample pan (Thermal Support). Phase sequences were subsequently confirmed by polarized microscopy, with special attention paid to any unusual features of the DSC curves. DSC curves are provided along with the mass of each sample, and the phase sequence (in degrees C) and parenthetical enthalpies (in J/g).

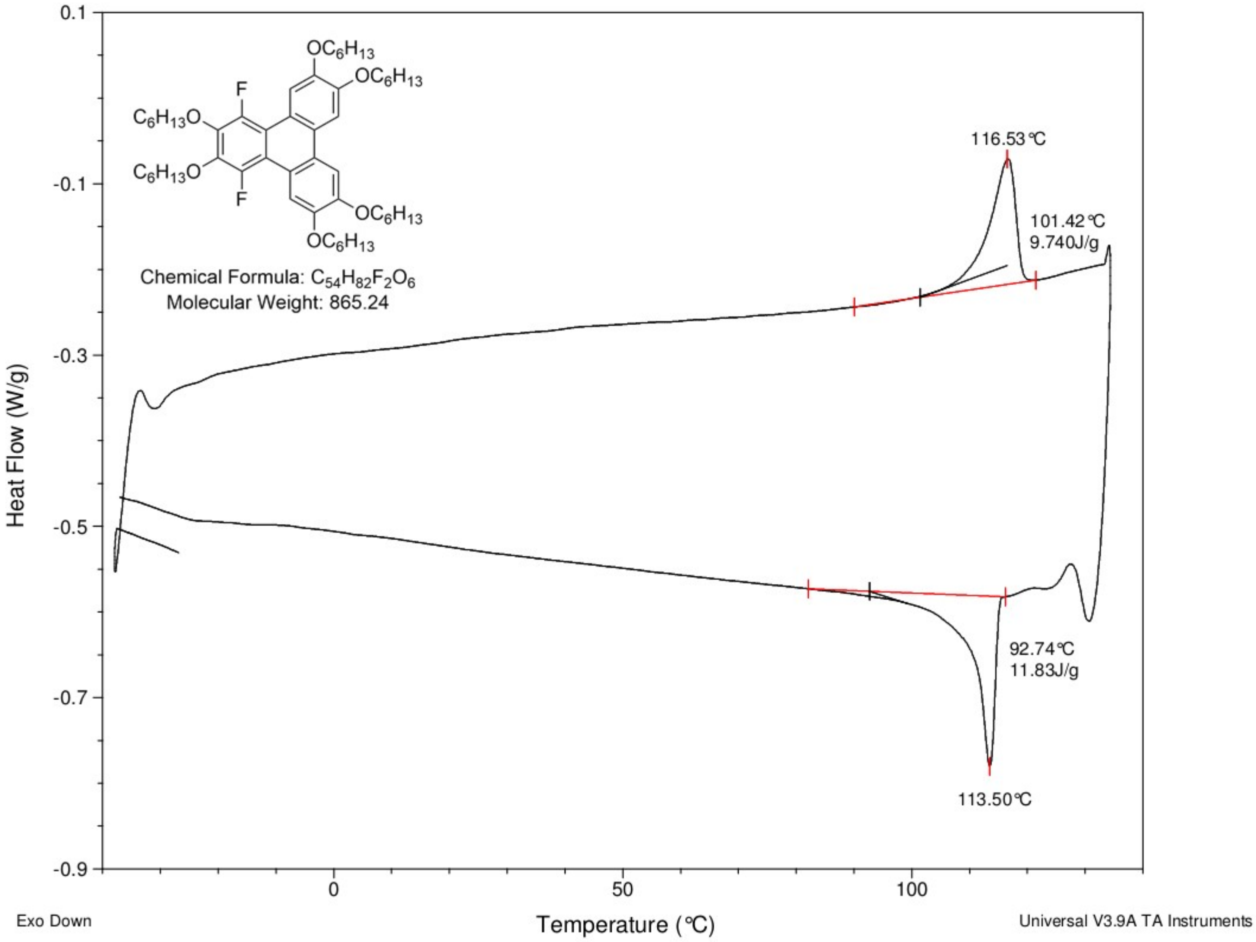
1,4-difluoro-2,3,6,7,10,11-hexakis(pentyloxy)triphenylene (Compound 10a)



mass: 2.354mg

Phase sequence: K -12.48 (7.87) Col$_h$ 142.1 (12.9) I 139.1 (16.4) Col$_h$ -40.46 (5.53) K

1,4-difluoro-2,3,6,7,10,11-hexakis(hexyloxy)triphenylene (Compound 10b)



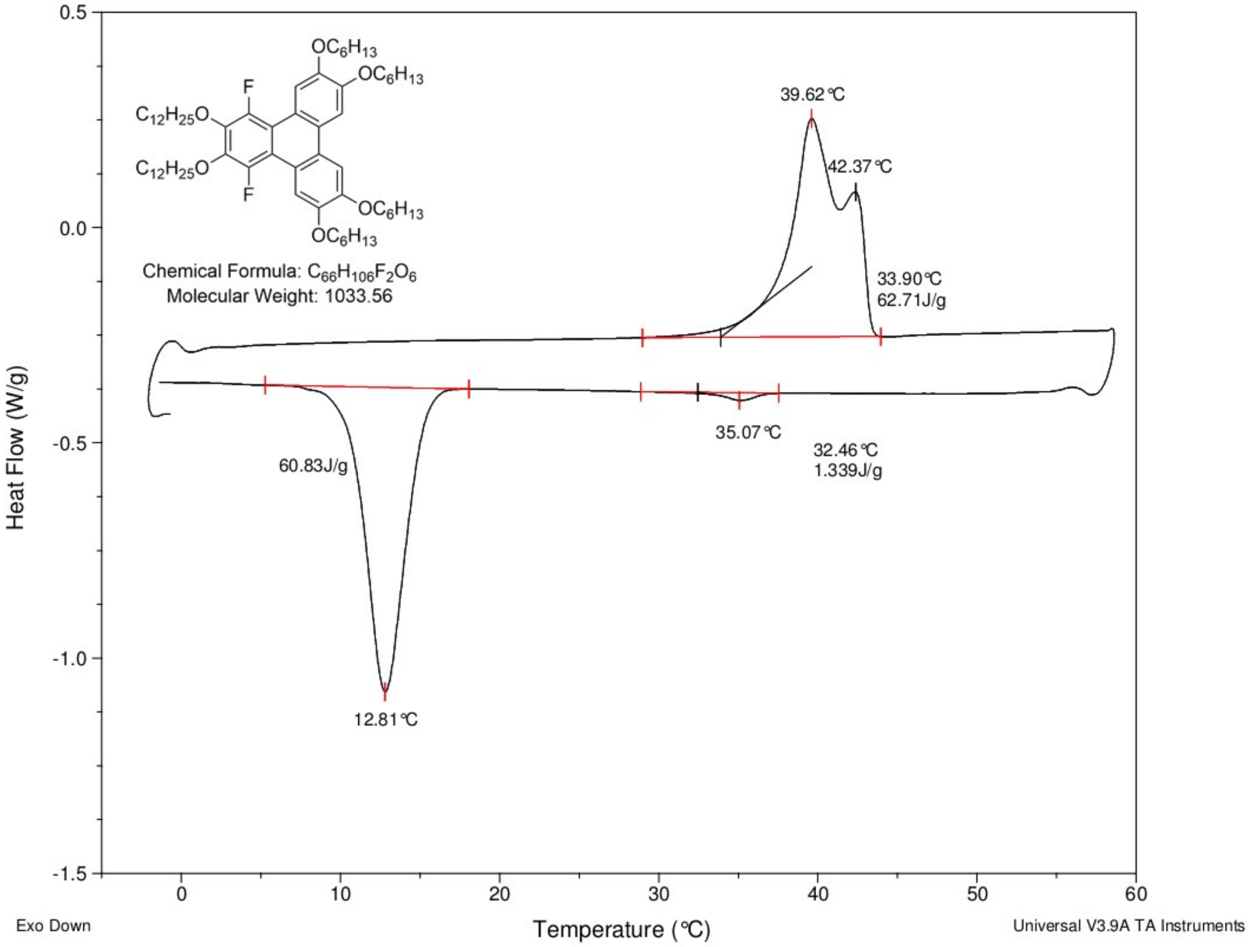
mass: 2.200 mg

Phase sequence: (T< -150) Col$_h$ 116.5 (9.74) I 113.5 (11.8) Col$_h$ (T< -150)

The small exothermic feature on cooling near -20^{o}C has not been observed to correspond to any transition in the material and does not have a corresponding endothermic peak on heating.

The transmission of polarized 632nm light from a HeNe laser was measured while cooling the sample well below room temperature. There was no effect on the polarization state of transmitted light down to -150^{o}C.

2,3-bis(dodecyloxy)-1,4-difluoro-6,7,10,11-tetrakis(hexyloxy)triphenylene (Compound 10c-i)

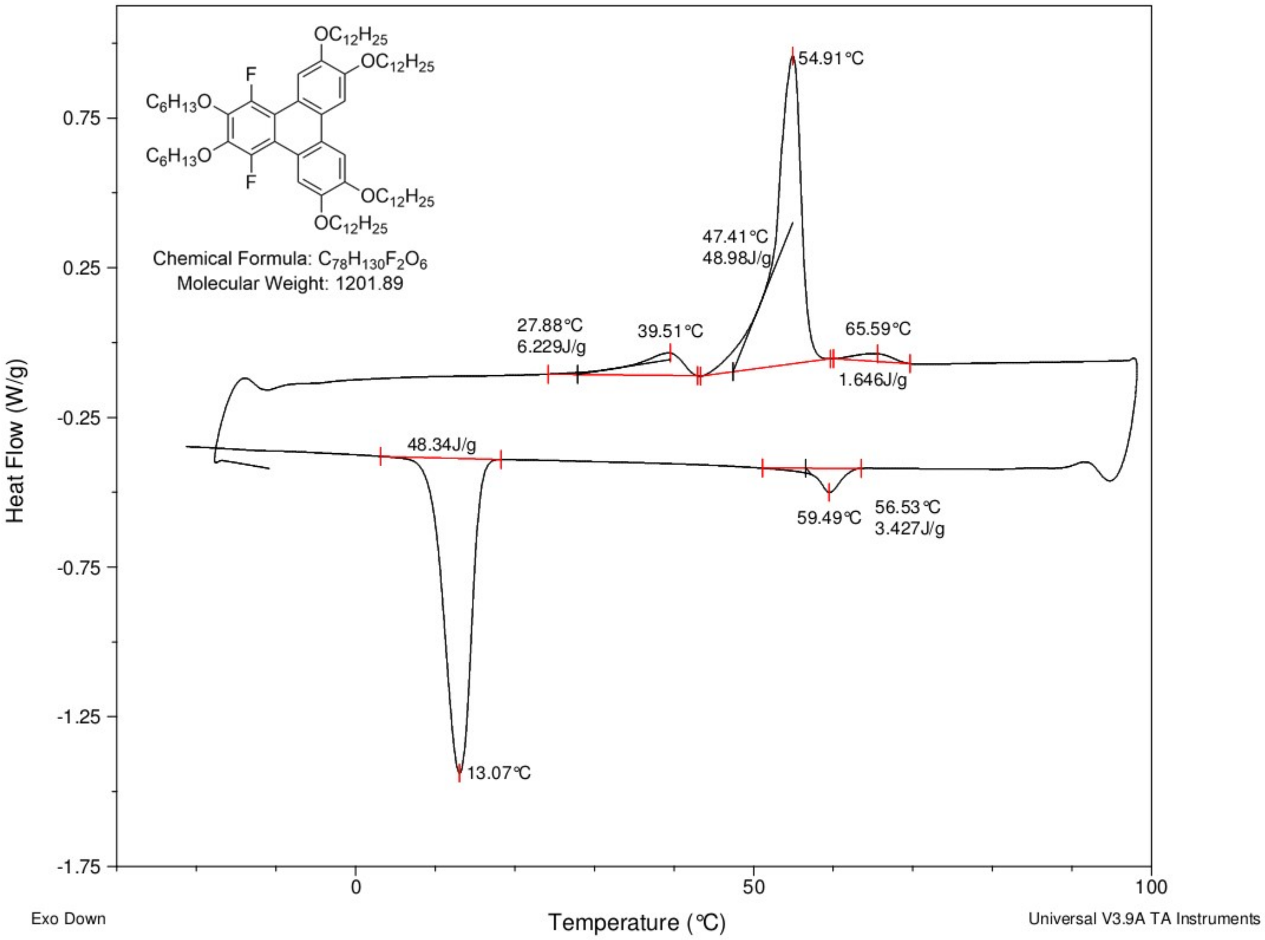


mass: 2.513 mg

Phase Sequence: K 39.62 Col_h 42.37 (62.7) I 35.1 (1.34) Col_h 12.81 (60.8) K

While a mesophase is clearly present on cooling, it is difficult to isolate a stable mesophase on heating. The double peak present here is interpreted as a two-step melting process with some material melting into a mesophase before the bulk melts fully into the isotropic (the double peak represents both K-D-I and K-I transitions).

2,3-bis(hexyloxy)-1,4-difluoro-6,7,10,11-tetrakis(dodecyloxy)triphenylene (Compound 10c-ii)

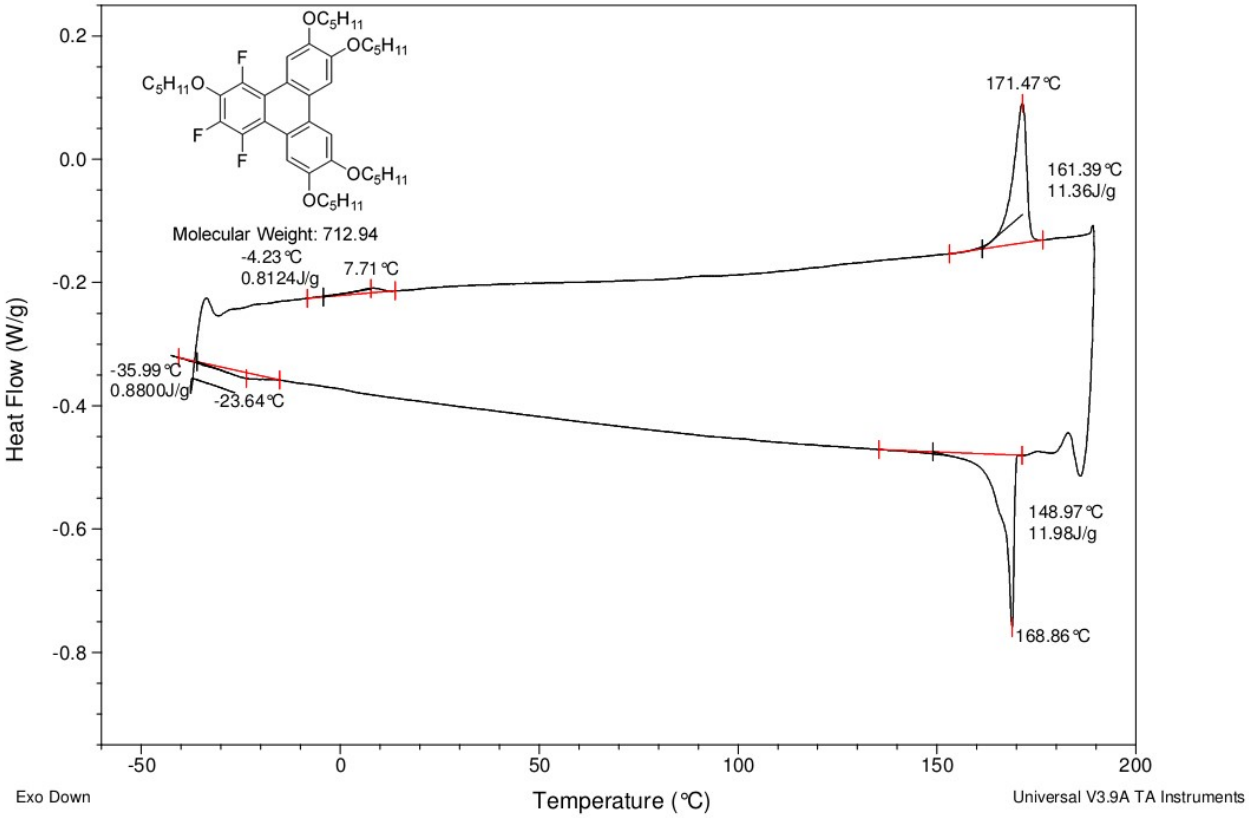


mass: 4.331 mg

Phase Sequence:

K 27.88 (6.23) K’ 54.91 (49.0) Col$_h$ 65.59 (1.65) I 59.49 (3.43) Col$_h$ 13.07 (48.3) K

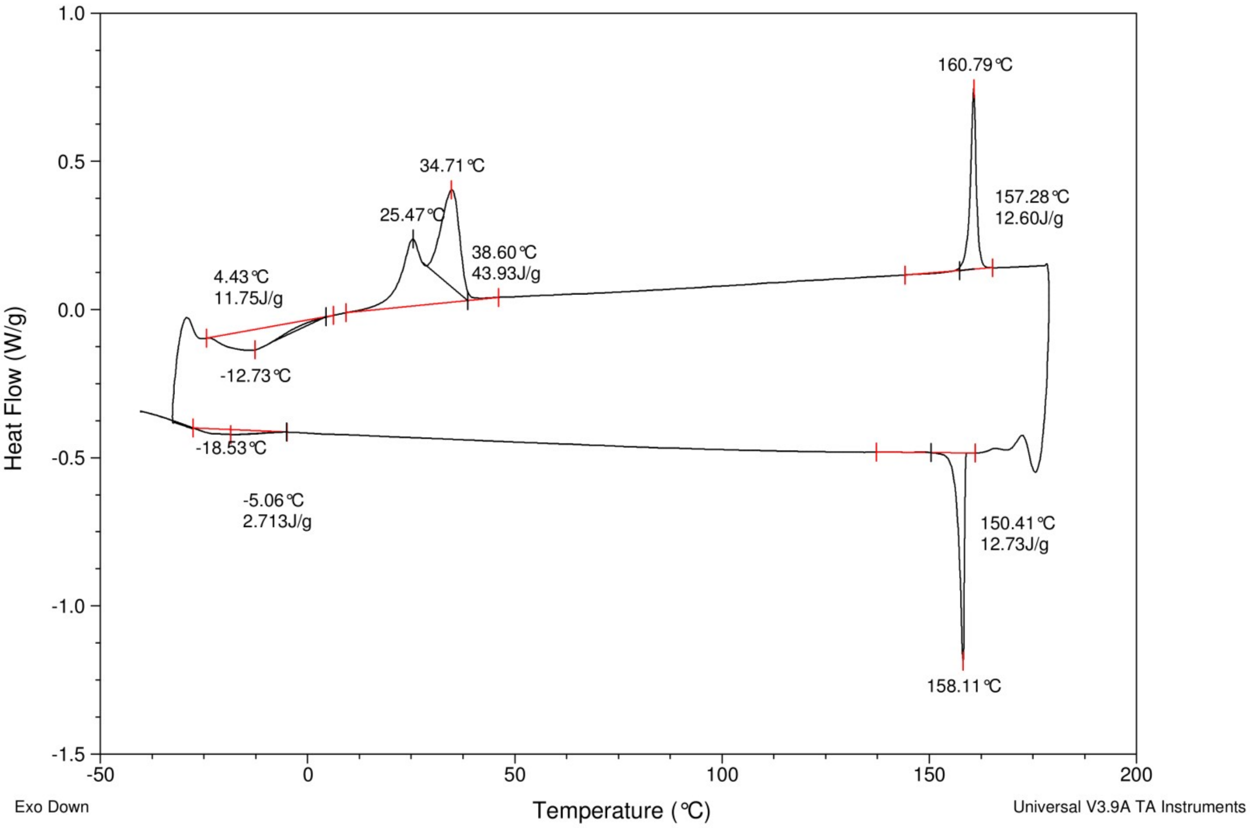
1,2,4-trifluoro-3,6,7,10,11-pentakis(pentyloxy)triphenylene (Compound 16a)



mass: 3.250 mg

Phase sequence: K 7.71 (0.812) Col_h 171.47 (11.4) I 168.9 (12.0) Col_h -23.64 (0.880) K

1,2,4-trifluoro-3,6,7,10,11-pentakis(hexyloxy)triphenylene (Compound 16b)



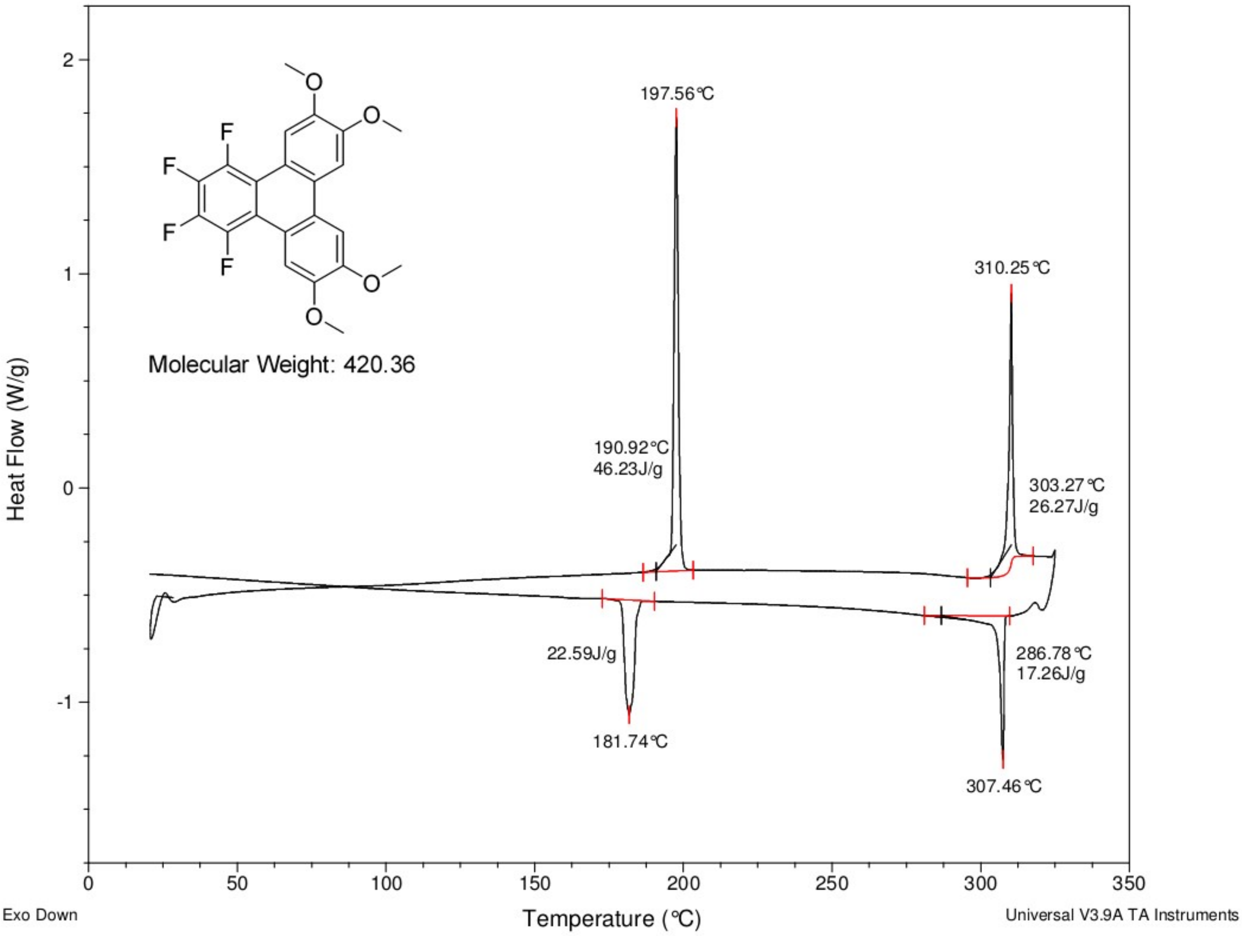
mass: 3.789 mg

The phase sequence of this material is dependent on the scan rate. The exothermic peaks shown here near -18^{o}C on cooling and -12^{o}C on heating correspond to the same crystallization process, which is kinetically hindered at low temperature. We expect that the low temperature state is a non-equilibrium glass state, which undergoes multiple solid-solid transitions before becoming a liquid crystal above 35^{o}C. We are unable to separate the enthalpies of the transitions at 25 and 35^{o}C, and they are reported here together. It is of some note that we observe this behavior in this material, but not in 3F-PAT5.

Phase Sequence (3 K/m):

G -12.7 (-11.8) K’ 25.47 K 34.7 (43.9) Col$_h$ 160.8 (12.6) I 158.1 (12.7) Col$_h$ -18.5 (2.7) G

1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (Compound 7)

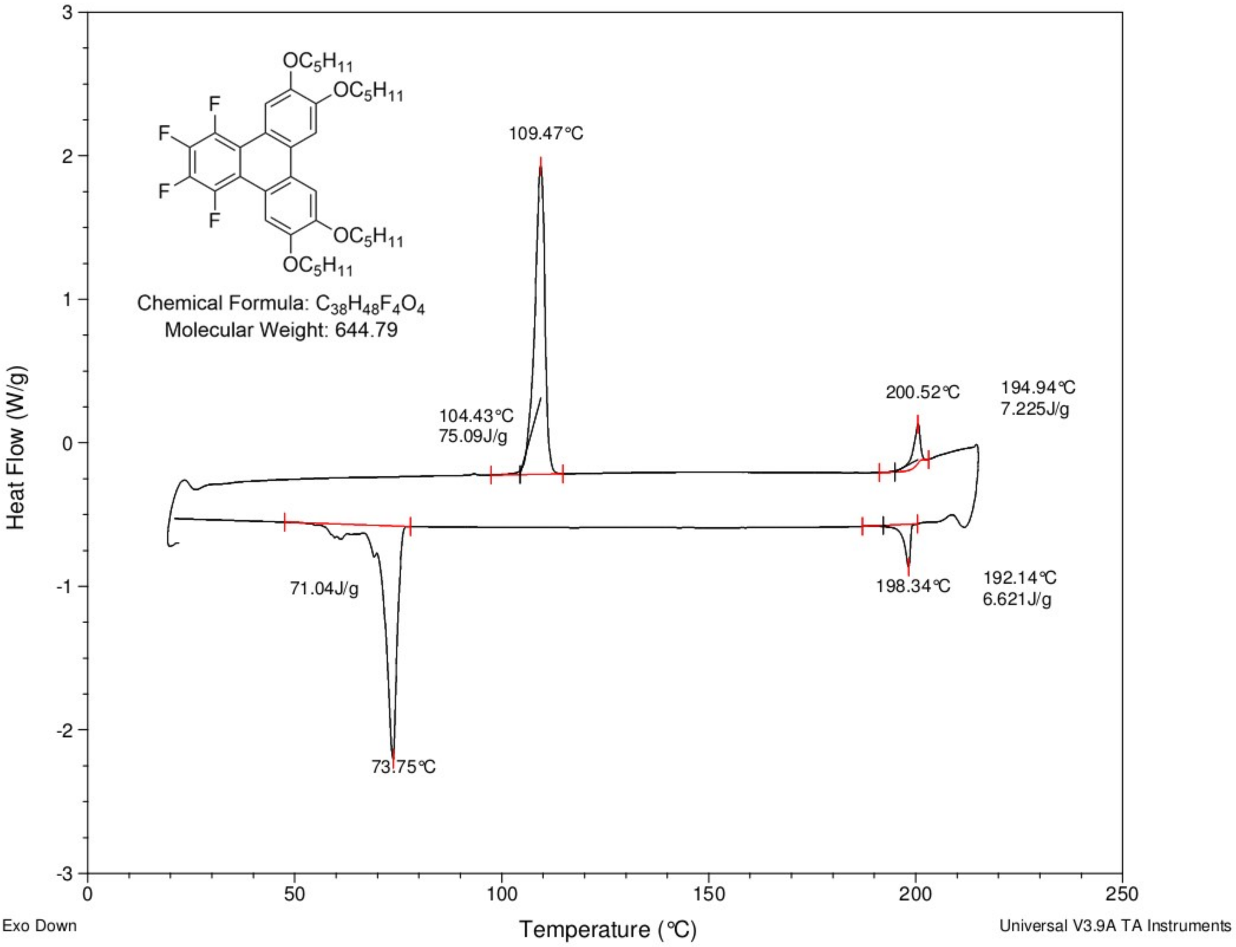


mass: 2.239 mg

Phase Sequence: K 197.6 (46.2) Col$_h$ 310.3 (26.3) I 307.5 (286.8) Col$_h$ 181.7 (22.6) K

The low molecular mass of this short-tailed compound, coupled with its high clearing transition temperature, makes it remarkably volatile. Care is taken to seal the DSC cell to prevent material from evaporating, but some of material loss is still expected. This likely contributes to the significant difference in enthalpy at the otherwise reversible isotropic transition.

1,2,3,4-tetrafluoro-6,7,10,11-tetrakis(pentyloxy)triphenylene (Compound 9a)

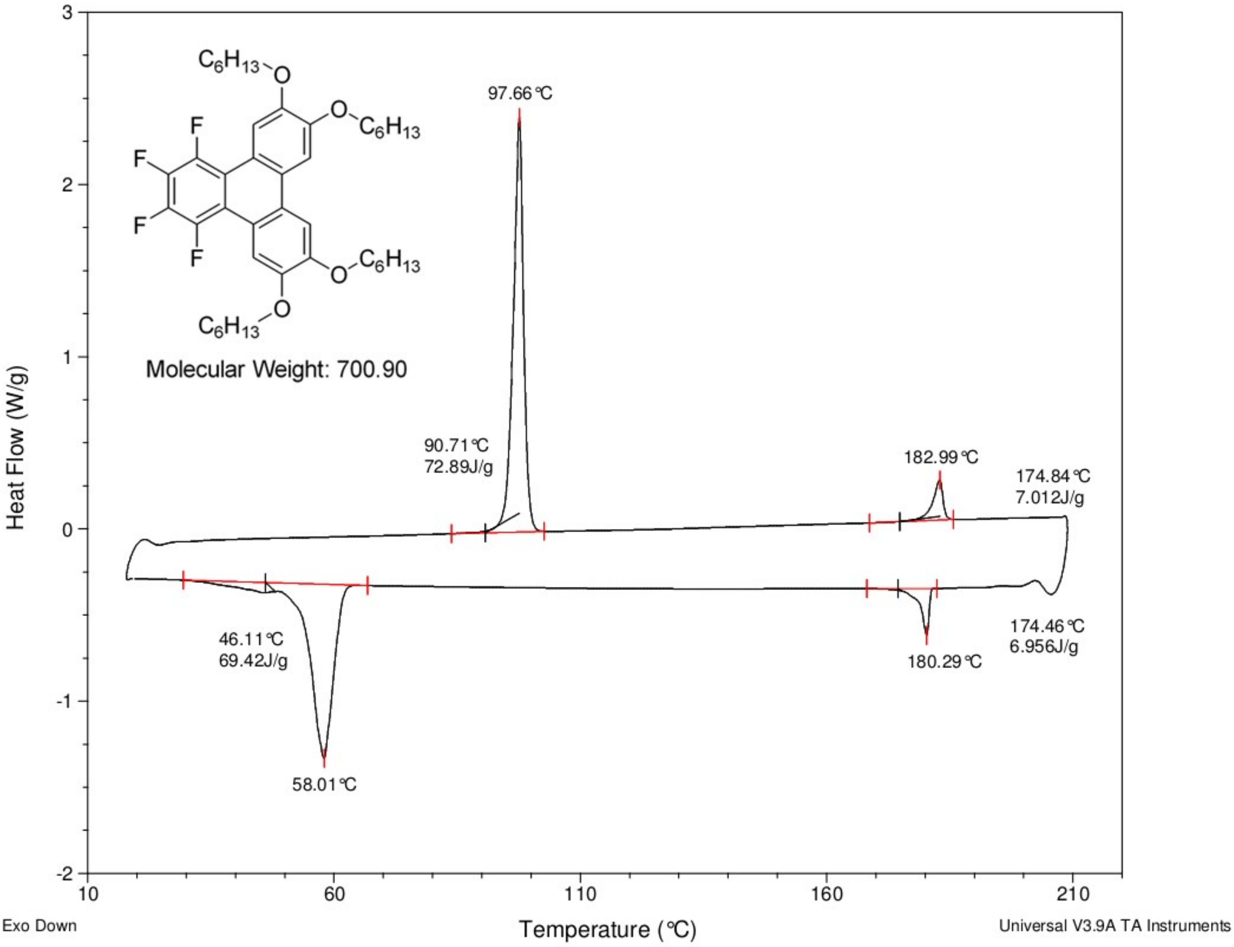


mass: 2.269 mg

Phase Sequence: K 109.5 (75.1) Col$_h$ 200.5 (7.23) I 198.3 (6.62) Col$_h$ 73.75 (71.0) K

The features following the 73^{o}C transition on cooling are expected to be the result of material in different areas of the pan freezing separately.

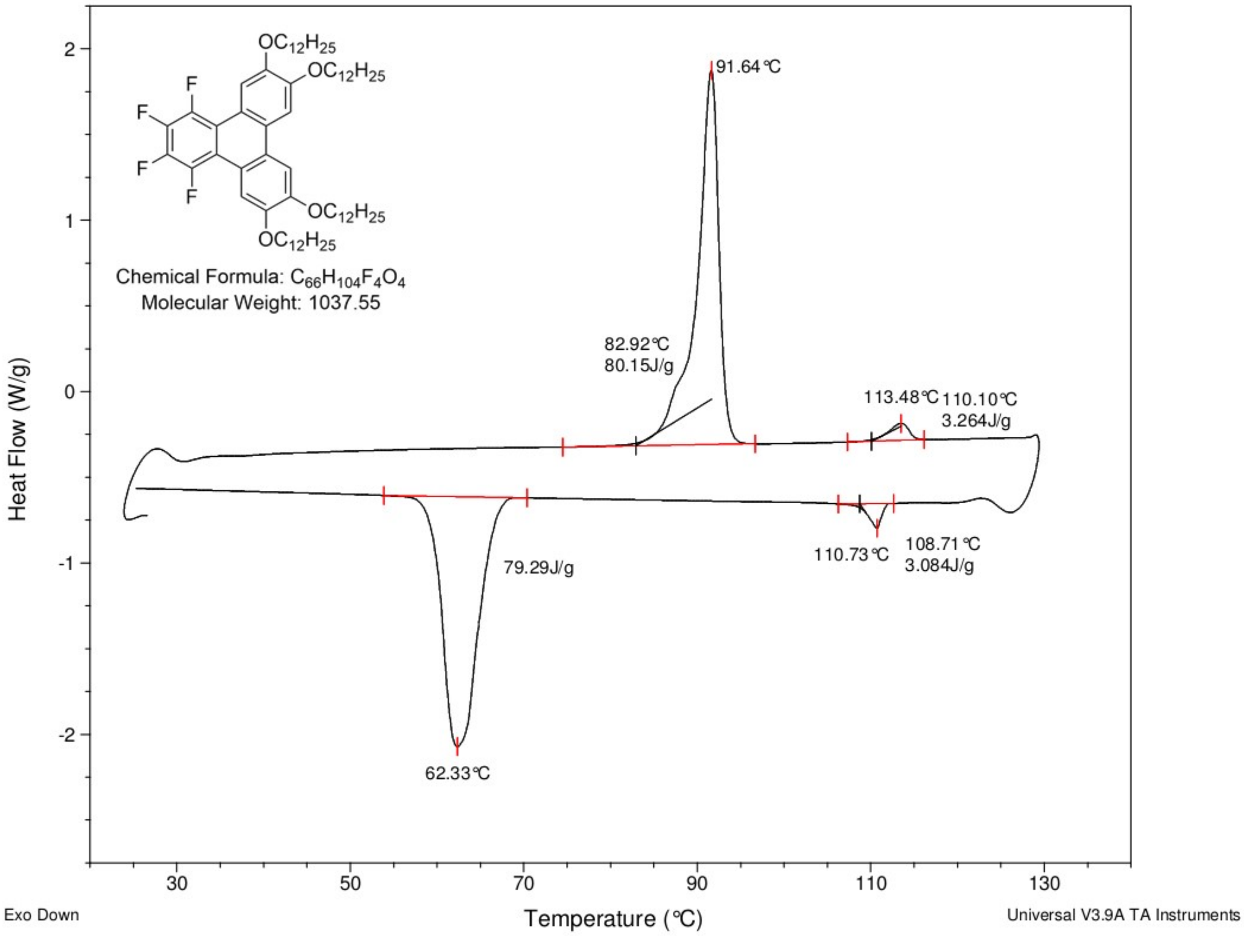
1,2,3,4-tetrafluoro-6,7,10,11-tetrakis(hexyloxy)triphenylene (Compound 9b)



mass: 5.038 mg

Phase Sequence: K 97.66 (72.9) Col_h 183.0 (7.01) I 180.3 (6.96) Col_h 58.01 (69.4) K

1,2,3,4-tetrafluoro-6,7,10,11-tetrakis(dodecyloxy)triphenylene (Compound 9c)



mass: 2.310 mg

Phase Sequence: K 91.64 (80.2) Col 113.5 (3.26) I 110.7 (3.08) Col 62.33 (72.29) K

The shoulder on 91°C transition is expected to be the result of some pre-melting behavior attributed to the long -$OC_{12}H_{25}$ tails as this feature is not seen in the shorter tailed 4F-TATn compounds.

4. X-ray Study of Selected Mesogens

To aide in the mesophase identification of our compounds, temperature dependent small angle x-ray scattering (SAXS) scans were taken of a representative subset of our compounds. The compounds studied are 2F-HAT(6/12), 2F-HAT(12/6), 3F-PAT5, 4F-TAT1, 4F-TAT5, and 4F-TAT6. 2F-HAT6 has previously been identified as Col_h and based on the roughly hexagonal symmetry that can be observed during the isotropic to columnar transition of 2F-HAT5, we are confident in identifying it as Col_h as well.

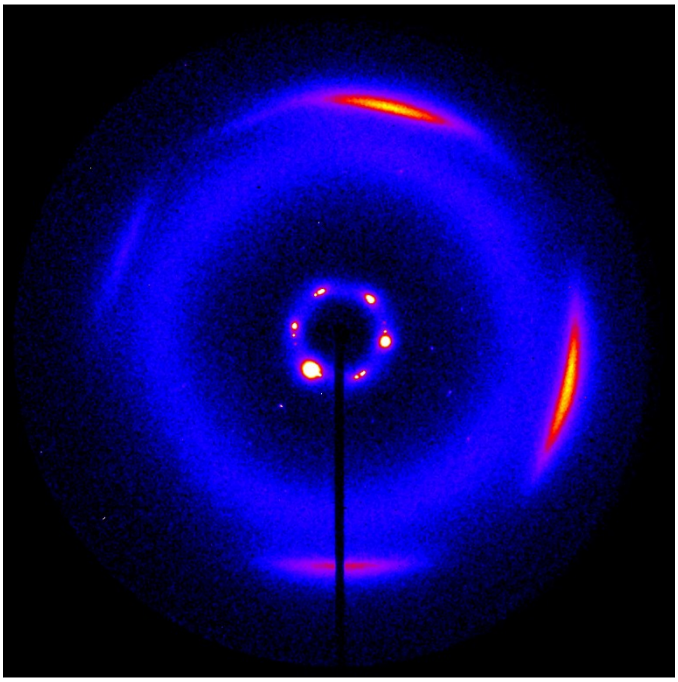
The SAXS experiment was carried out using a Rigaku Screen Machine using a 35W microfocus sealed Copper tube and a Mercury 3 CCD detector with a 1024 x 1024 array of 73.2 μm pixels. Samples were prepared by filling a 1mm diameter quartz capillary and heated using a Linkam HST420 hot stage. Separate capillaries of the same type were used for the sample measurements, the background scan of an empty capillary, and calibration scans using silver behenate. Calibrating using silver behenate is sufficient that we have sub 0.1Å precision in our d-spacing identification. A pair of magnets situated in our hot stage help to align the samples. Large monodomains can be obtained, but often we probe poorly oriented polycrystalline domains.

To identify the Col_h mesophase, we require the presence of a strong reflection and weak secondary reflection corresponding to d_{100} and d_{110} with a ratio of $1:\sqrt{3}$. If this second peak is not observed, we also accept a single strong peak at low angle corresponding to d_{100} along with a clearly hexagonal symmetry observed via polarized microscopy during the isotropic to columnar transition.

For each studied compound, a 2D-SAXS pattern is provided, along with a 1D-SAXS profile and a table of d-spacings. Any additional notes, such as the temperature of the scan and any unusual features are noted. With the exception of 4F-TAT1, all compounds were observed while isotropic and in their mesophase. In samples with easily reached freezing points, the solid phase was also observed. We do not attempt to identify their crystal structures from this study, but are able confirm their phase sequences.

1,4-difluoro-2,3,6,7,10,11-hexakis(pentyloxy)triphenylene (Compound 10a)

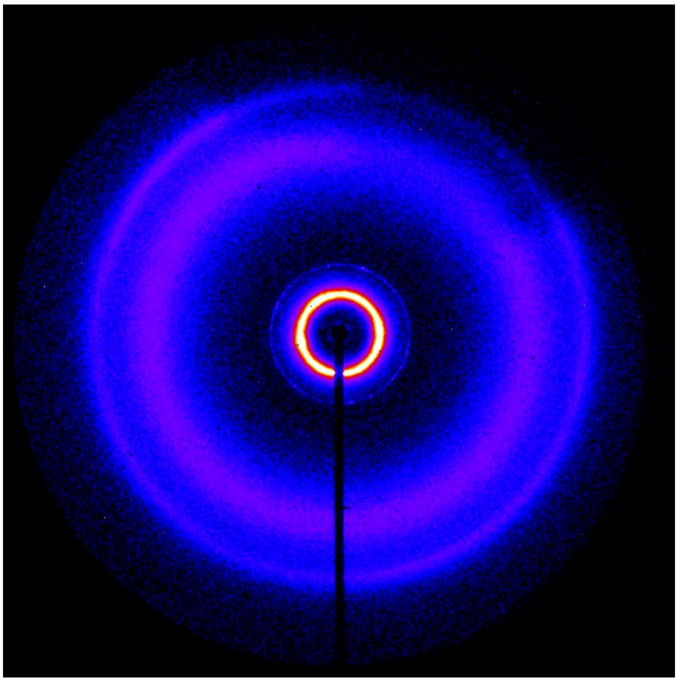
Scan shown at 30°C, on cooling. Multiple peaks at wide angle, and splitting of small angle peaks, is likely a result of probing multiple domains.



T=30°C	Measured (Å)	Calculated (Å)
d_{100}	22.9	
d_{110}	13.2	13.2
d_{200}	11.5	22.9
d_{001}	3.5	

2,3-bis(dodecyloxy)-1,4-difluoro-6,7,10,11-tetrakis(hexyloxy)triphenylene (Compound 10c-i)

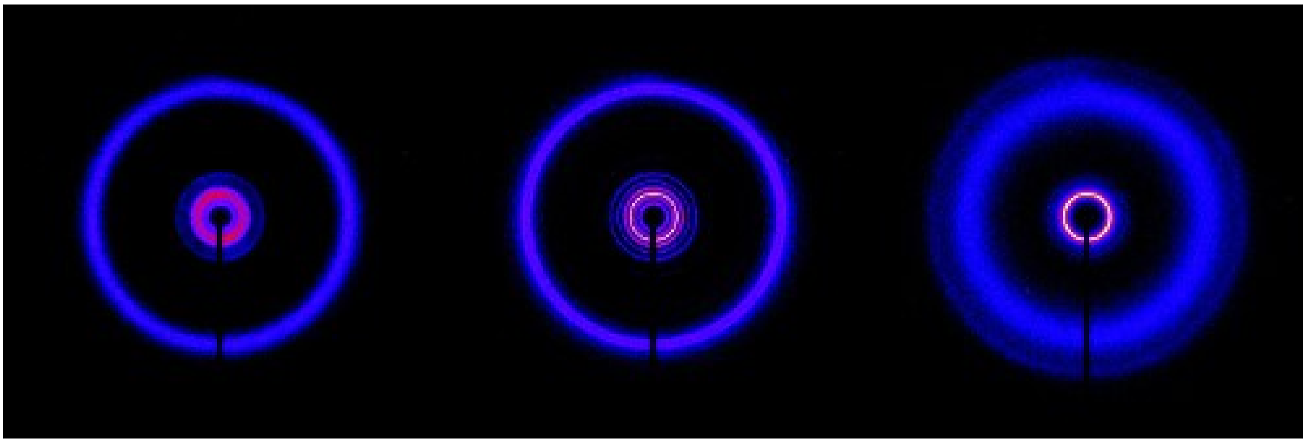
SAXS pattern collected at 25°C on cooling.



T=25°C	Measured (Å)	Calculated (Å)
d_{100}	20.1	
d_{110}	11.6	11.6
d_{001}	3.5	

2,3-bis(hexyloxy)-1,4-difluoro-6,7,10,11-tetrakis(dodecyloxy)triphenylene (Compound 10c-ii)

Scans shown were collected on heating in order to clearly document the phase sequence. Values for the mesophase are in agreement with measurements taken on cooling. The similar structure between the low temperature state and the mesophase, along with DSC and CPM measurements, suggests that this is a glassy phase resulting from an incomplete crystallization, which fully develops on heating.

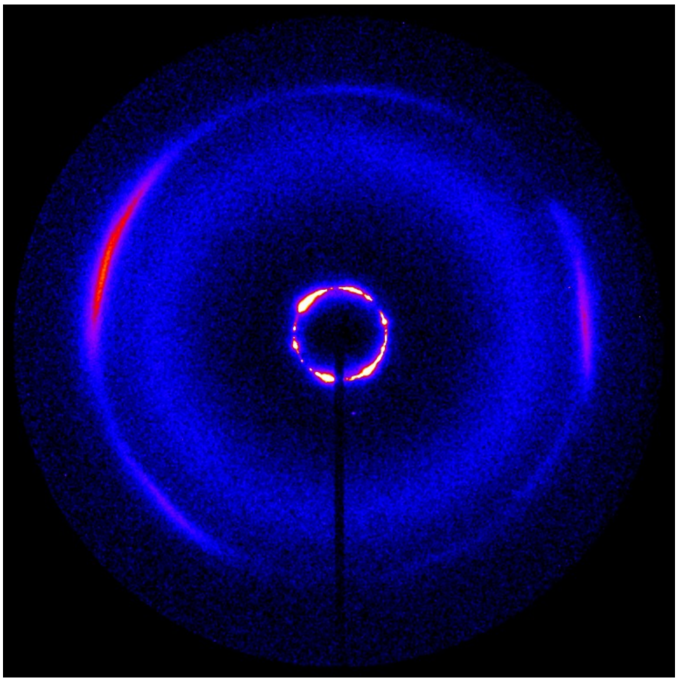


(Left to right) SAXS patterns collected on heating at 35, 47 and 57°C showing the low temperature glassy state, crystalline, and liquid crystalline states. The glassy state is reached by cooling the mesophase and bypassing crystallization until the structure of the mesophase is frozen in.

T=30°C	Measured (Å)	Calculated (Å)
d_{100}	22.9	
d_{110}	13.2	13.2
d_{200}	11.5	22.9
d_{001}	3.5	

1,2,4-trifluoro-3,6,7,10,11-pentakis(hexyloxy)triphenylene (Compound 16a)

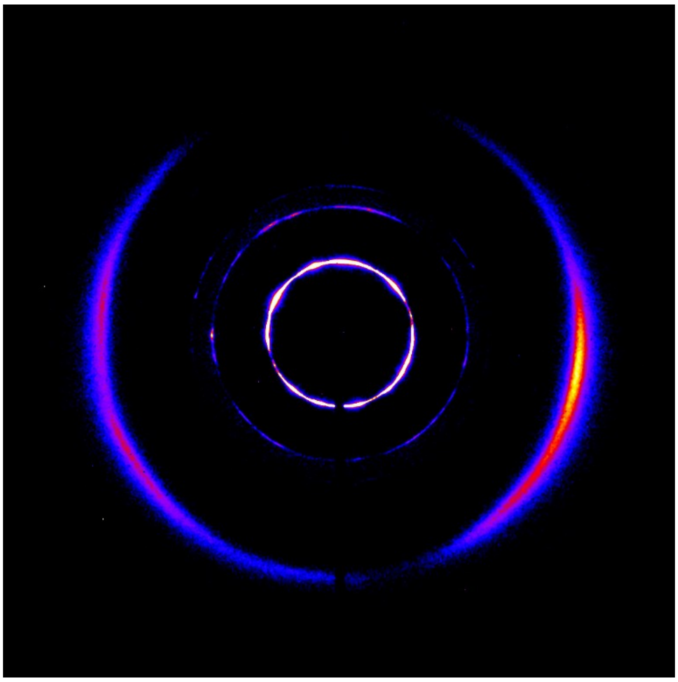
SAXS pattern collected at 50°C on cooling.



T=50°C	Measured (Å)	Calculated (Å)
d_{100}	17.3	
d_{110}	10.0	10.0
d_{001}	3.5	

1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (Compound 7)

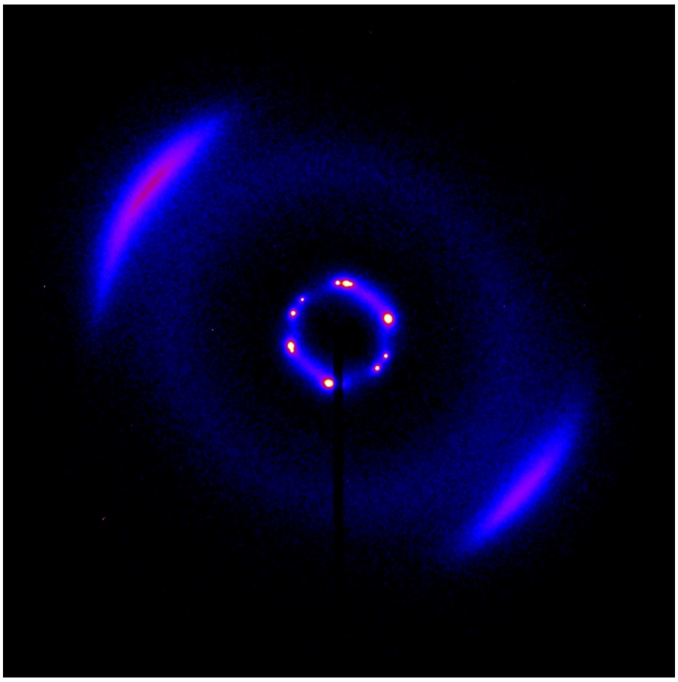
SAXS pattern collected at 220°C on heating. While most other data presented here is taken on cooling, this was collected on heating to avoid damaging the sample and equipment. The sample was melted outside the hot stage via heat gun, and then measured on subsequent heating in the hot stage.



T=220°C	Measured (Å)	Calculated (Å)
d_{100}	11.0	
d_{110}	6.4	6.4
d_{200}	5.5	5.5
d_{001}	3.6	

1,2,3,4-tetrafluoro-6,7,10,11-tetrakis(pentyloxy)triphenylene (Compound 9a)

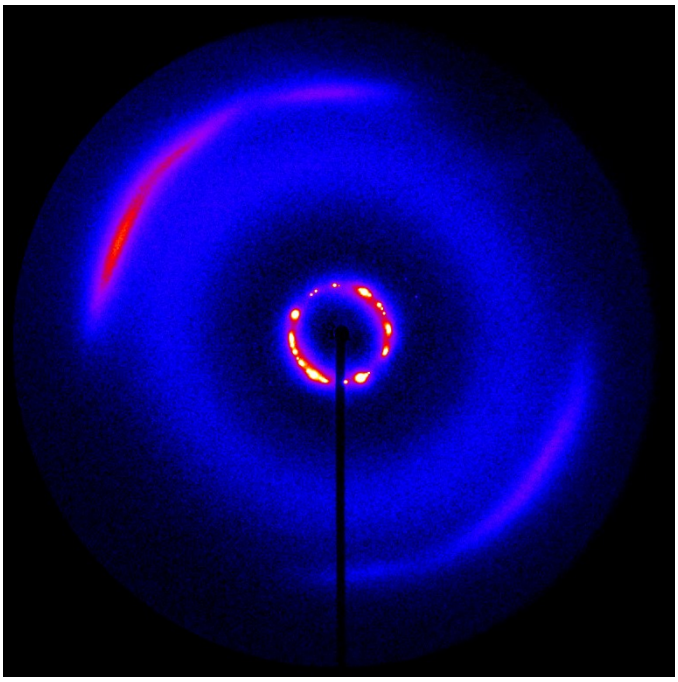
SAXS pattern collected at 190°C on cooling.



190°C	Measured (Å)
d_{100}	15.8
d_{001}	3.5

1,2,3,4-tetrafluoro-6,7,10,11-tetrakis(hexyloxy)triphenylene (Compound 9b)

SAXS pattern collected at 180°C on cooling. Sample is poorly aligned, and we are likely probing multiple domains, resulting in irregular orientation of peaks at wide and small angle.



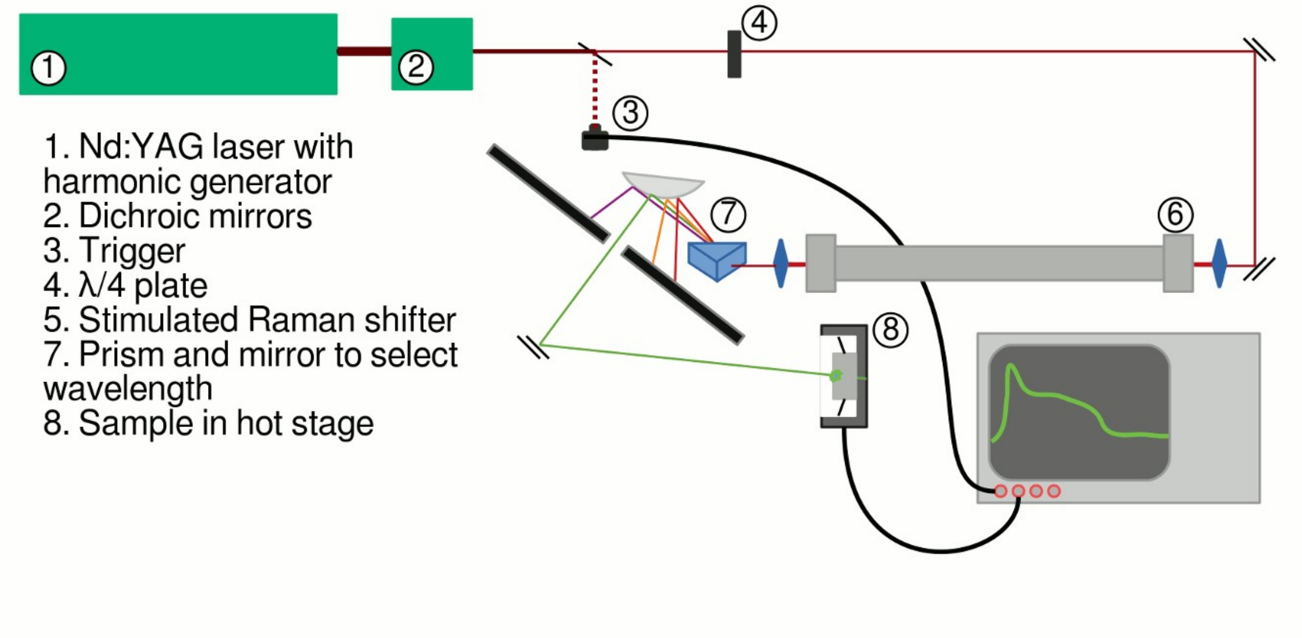
180°C	Measured (Å)
d_{100}	16.8
d_{001}	3.6

5. Time of Flight Hole Mobility

Mobility measurements were carried out using the time of flight technique, using the optical layout shown below. A Continuum Surelite SL-II Nd:YAG laser, combined with a harmonic generator and a stimulated Raman shifter, was used to generate a pulse of light with a wavelength sufficient to photogenerate charge in the studied compounds. The sample cells themselves were two ITO coated electrodes, held parallel in a small clamp and separated by a spacer (either 20.2 micron silica spheres, or two strips of 25.4 micron Kapton film). The parallel orientation was evident based on diffraction fringes visible in the empty cell. The cell was then filled by capillary action above the material's isotropic temperature. No special alignment techniques were used other than slow cooling. The clamps holding the cells were designed to fit nicely into our hot stage (Instec HCS402) or into a cryostat if the mesophase range extended below room temperature (temperature controlled in both cases by an LS331 controller). Cryostat mounts were made to be compatible with the hot stage, so that samples can be moved freely between the two.

The potential used to drive the photogenerated charges was produced using either a DS345 signal generator, or a Stanford Research Systems PS325 high voltage source. The potential from the DS345 was further amplified with a gain of approximately 39.5.

The determination of the time of flight itself is a non-trivial process. Our determination of the time of flight was carried out using a prototype time of flight measurement algorithm designed to rapidly extract the time of flight from a large number of photocurrents. All time of flights are determined from a linear-linear plot of the photocurrent, and data is not reported from voltage and temperature settings from which it was impossible to extract a linear time of flight, even if a time of flight was still detectable on a log-log representation. The "transit plateau" and "down slope" regions were estimated, and a line of best fit was determined for these regions, their intercept being the time of flight. All results were checked against values determined by manually selecting these regions, and they were found to be in good agreement. The error bars that are reported with the mobility measurements includes uncertainties resulting from the lines of best fit used to find the time of flight. The signal used for determining the time of flight was filtered using an analog low-pass filter to remove radio interference and a digital Bessel filter to remove additional noise. The digitally



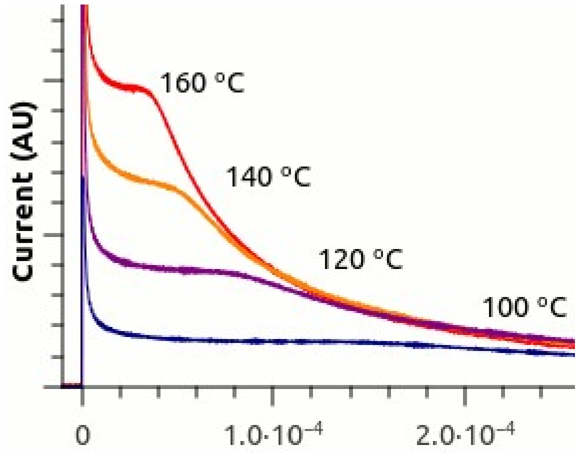
Optical layout for the time of flight measurements. In addition to what is shown, a neutral density filter and/or borosilicate microscope slides were used as a beam attenuator when necessary, to avoid space charge effects and sample degradation.

filtered signal was compared directly with the unfiltered signal to check that the time of flight was appropriate and not heavily influenced by the filtering process.

A multistep process was used to fit the mobility data to the model. First, at each temperature, the zero-field mobility was determined by extrapolating a line of best fit of the log of the mobility with respect to the root of the applied field, to zero. The temperature dependence of the zero-field mobility, and the Poole-Frenkel coefficient (the slope of line of best fit), was used to test for the influence of polarons. The zero-field mobility was fitted to a model with, and without, a Boltzmann activated polaron energy. In all cases, the model without a polaron contribution resulted in a better fit, and so we expect that polaronic effects are limited.

4F-TAT5 (Compound 9a)

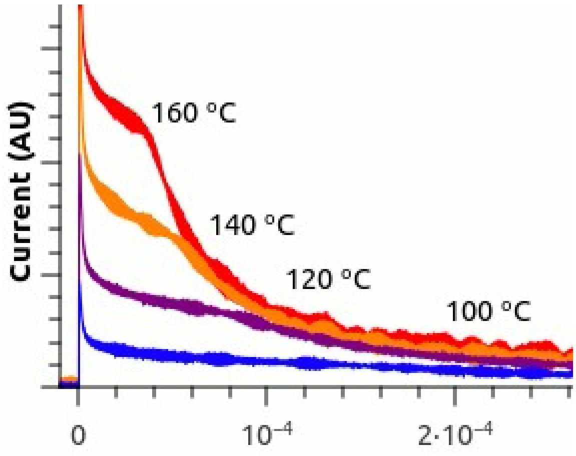
Temperatures (Celsius): 100, 120, 140, 160, 190
20.2um silica spacers
μ_o = 0.0471 +/- 0.0024 cm^2/Vs
σ = 82.7 +/- 0.02 meV
Σ = 1.60 +/- 0.15
c = 1.81e-3 +/- .022e-3 $(cm/V)^{1/2}$



Representative photo-currents from 4F-TAT5, all taken with the same applied voltage (98V). Shown without digital filtering.

4F-TAT6 (Compound 9b)

Temperatures (Celsius): 100, 120, 140, 160
20.2 um silica spacers
μ_o 0.0652 +/- 0.0033 cm^2/Vs
σ = 89.70 +/- 0.024 meV
Σ = 1.5 +/ 0.154
c = 0.00319 +/- .000323 $(cm/V)^{1/2}$



Representative photo-currents from 4F-TAT5, all taken with the same applied voltage (98V). Shown without digital filtering.

3F-PAT6 (Compound 16b)

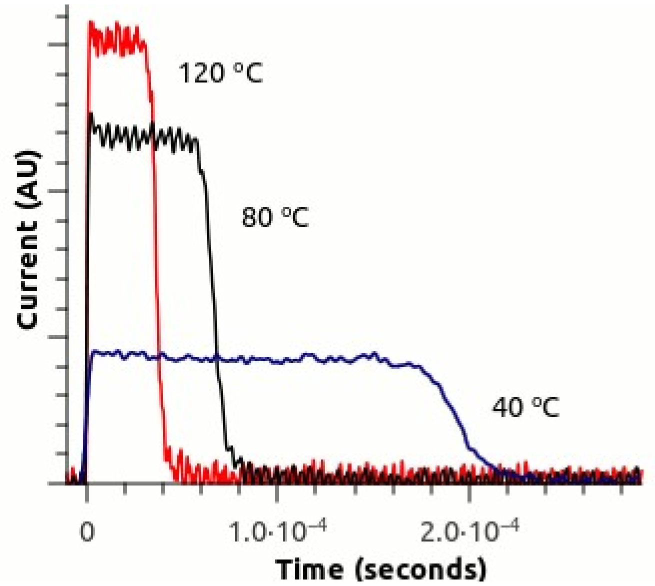
Temperatures (Celsius): 120, 100, 80, 70, 40, 23, 14, 5, 0, -5

μ_o = 0.0877 +/- 0.0049 cm^2/Vs

σ = 74.20 +/- 0.018 meV

Σ = 1.78 +/- 0.11

c = 0.0023 +/- 0.000094 $(cm/V)^{1/2}$



Representative photocurrents from 3F-PAT6, all taken with the same applied voltage (98V). Shown with digital filtering.

2F-HAT5 (Compound 10a)

Temperatures (Celsius): 135, 105, 75, 45, 30, 20, 10, 0, -10

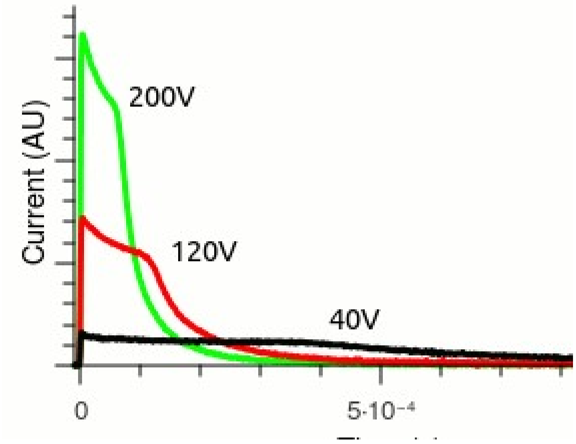
25.4um kapton spacers

μ_o = 0.0214 +/- 0.00367 cm^2/Vs

σ = 61.1 +/- 1.21 meV

Σ = 1.76 +/- 0.11

c = 0.00405 +/- 0.000481 $(cm/V)^{1/2}$



Representative photo-currents from 2F-HAT5, all taken at the same temperature (30^{o}C). Shown without digital filtering.

6. X-ray Crystallography Data for 1,4-Difluoro-2,3-dimethoxytriphenylene

A colorless crystalline block (0.12 x 0.07 x 0.05 mm) ($C_{20}H_{14}F_2O_2$, M_w = 324.31 gmol^{-1}) was found to belong to the monoclinic space group $P2_1/c$ with a = 9.680(3) Å, b = 3.9219(10) Å, c = 37.508(10) Å, β = 91.613(8)°, V = 1423.4(7) Å^3, Z = 4, ρ_{calcd} = 1.513 g.cm^{-3}, and μ = 0.114 mm^{-1}. A total of 5570 reflections (2451 independent) were measured over the 2Θ range 1.086° to 25.723° at 100(2) °K using a Bruker AXS diffractometer upgraded with an APEX II CCD detector and Mo(Kα) λ= 0.71073 Å) radiation. Refinement converged with R_1 = 0.0658, wR_2 = 0.1491 ($I > 2\sigma(I)$), R_1 = 0.1540 and wR_2 = 0.2046 (all data). CCDC reference number 1456337.

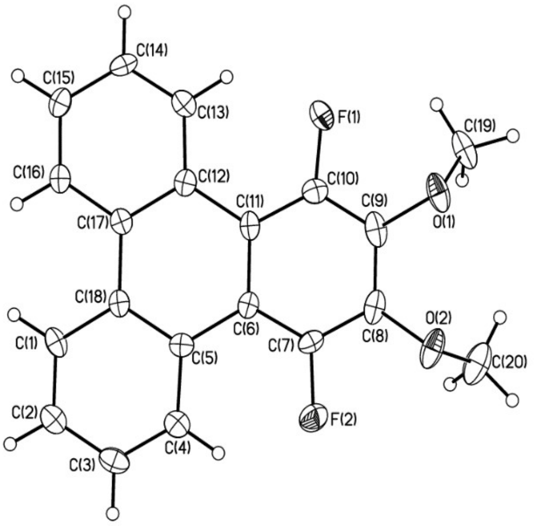


Table 1. Crystal data and structure refinement for 1,4-Difluoro-2,3-dimethoxytriphenylene.

Identification code	1,4-Difluoro-2,3-dimethoxytriphenylene
Empirical formula	$C_{20}H_{14}F_2O_2$
Formula weight	324.31
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 9.680(3) Å alpha = 90 deg. b = 3.9219(10) Å beta = 91.613(8) deg. c = 37.508(10) Å gamma = 90 deg.

Volume	1423.4(7) Å ^3
Z, Calculated density	4, 1.513 Mg/m^3
Absorption coefficient	0.114 mm^-1
F(000)	672
Crystal size	0.120 x 0.070 x 0.050 mm
Theta range for data collection	1.086 to 25.723 deg.
Limiting indices	-6<=h<=11, -4<=k<=4, -40<=l<=45
Reflections collected / unique	5570 / 2451 [R(int) = 0.0730]
Completeness to theta = 25.242	92.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.994 and 0.746
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2451 / 0 / 219
Goodness-of-fit on F^2	0.904
Final R indices [I>2sigma(I)]	R1 = 0.0658, wR2 = 0.1491
R indices (all data)	R1 = 0.1540, wR2 = 0.2046
Extinction coefficient	n/a
Largest diff. peak and hole	0.270 and -0.283 e. Å ^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^2 x 10^3) for 1,4-Difluoro-2,3-dimethoxytriphenylene. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
F(1)	9524(2)	-1513(7)	1273(1)	30(1)
F(2)	4407(2)	-1669(7)	658(1)	31(1)
O(1)	9128(3)	-4242(8)	628(1)	31(1)
O(2)	6469(3)	-4376(8)	320(1)	32(1)
C(1)	3709(4)	4499(11)	1872(1)	20(1)
C(2)	2429(5)	4815(12)	1706(1)	24(1)
C(3)	2229(5)	3705(11)	1358(1)	25(1)
C(4)	3313(4)	2239(12)	1179(1)	23(1)
C(5)	4640(4)	1826(11)	1343(1)	18(1)
C(6)	5813(4)	257(11)	1158(1)	17(1)
C(7)	5670(4)	-1338(11)	825(1)	20(1)
C(8)	6740(5)	-2735(11)	638(1)	21(1)
C(9)	8052(5)	-2643(11)	799(1)	23(1)
C(10)	8221(4)	-1233(12)	1132(1)	21(1)
C(11)	7151(4)	286(11)	1322(1)	17(1)
C(12)	7376(4)	1811(11)	1680(1)	17(1)
C(13)	8707(4)	2176(11)	1849(1)	22(1)
C(14)	8882(5)	3476(12)	2184(1)	24(1)
C(15)	7739(5)	4509(12)	2374(1)	23(1)
C(16)	6454(4)	4293(12)	2215(1)	20(1)
C(17)	6221(4)	3001(11)	1867(1)	16(1)
C(18)	4843(4)	3076(11)	1696(1)	16(1)
C(19)	10249(5)	-2061(12)	527(1)	34(1)
C(20)	6776(6)	-2469(13)	12(1)	40(2)

Table 3. Bond lengths [Å] and angles [deg] for 1,4-Difluoro-2,3-dimethoxytriphenylene.

F(1)-C(10)	1.359(5)
F(2)-C(7)	1.365(5)
O(1)-C(9)	1.387(5)
O(1)-C(19)	1.441(5)
O(2)-C(8)	1.375(5)
O(2)-C(20)	1.414(5)
C(1)-C(2)	1.376(6)
C(1)-C(18)	1.412(6)
C(1)-H(1)	0.9500
C(2)-C(3)	1.386(6)
C(2)-H(2)	0.9500
C(3)-C(4)	1.385(6)
C(3)-H(3)	0.9500
C(4)-C(5)	1.418(6)
C(4)-H(4)	0.9500
C(5)-C(18)	1.420(6)
C(5)-C(6)	1.482(6)
C(6)-C(7)	1.397(6)
C(6)-C(11)	1.419(6)
C(7)-C(8)	1.382(6)
C(8)-C(9)	1.390(6)
C(9)-C(10)	1.372(6)
C(10)-C(11)	1.408(6)
C(11)-C(12)	1.480(6)
C(12)-C(17)	1.416(6)
C(12)-C(13)	1.426(6)
C(13)-C(14)	1.363(6)
C(13)-H(13)	0.9500
C(14)-C(15)	1.394(6)
C(14)-H(14)	0.9500
C(15)-C(16)	1.367(6)
C(15)-H(15)	0.9500
C(16)-C(17)	1.413(6)
C(16)-H(16)	0.9500
C(17)-C(18)	1.464(6)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800

C(20)-H(20C)	0.9800

C(9)-O(1)-C(19)	115.7(3)
C(8)-O(2)-C(20)	114.9(4)
C(2)-C(1)-C(18)	121.9(4)
C(2)-C(1)-H(1)	119.1
C(18)-C(1)-H(1)	119.1
C(1)-C(2)-C(3)	119.8(4)
C(1)-C(2)-H(2)	120.1
C(3)-C(2)-H(2)	120.1
C(4)-C(3)-C(2)	119.9(4)
C(4)-C(3)-H(3)	120.1
C(2)-C(3)-H(3)	120.1
C(3)-C(4)-C(5)	121.9(4)
C(3)-C(4)-H(4)	119.1
C(5)-C(4)-H(4)	119.1
C(4)-C(5)-C(18)	117.7(4)
C(4)-C(5)-C(6)	122.8(4)
C(18)-C(5)-C(6)	119.5(4)
C(7)-C(6)-C(11)	117.3(4)
C(7)-C(6)-C(5)	123.1(4)
C(11)-C(6)-C(5)	119.6(4)
F(2)-C(7)-C(8)	113.7(4)
F(2)-C(7)-C(6)	121.2(4)
C(8)-C(7)-C(6)	125.1(4)
O(2)-C(8)-C(7)	120.0(4)
O(2)-C(8)-C(9)	122.6(4)
C(7)-C(8)-C(9)	117.2(4)
C(10)-C(9)-O(1)	122.0(4)
C(10)-C(9)-C(8)	119.3(4)
O(1)-C(9)-C(8)	118.5(4)
F(1)-C(10)-C(9)	114.2(4)
F(1)-C(10)-C(11)	121.5(4)
C(9)-C(10)-C(11)	124.3(4)
C(10)-C(11)-C(6)	116.8(4)
C(10)-C(11)-C(12)	122.7(4)
C(6)-C(11)-C(12)	120.5(4)
C(17)-C(12)-C(13)	117.6(4)
C(17)-C(12)-C(11)	119.0(4)
C(13)-C(12)-C(11)	123.4(4)
C(14)-C(13)-C(12)	122.2(4)
C(14)-C(13)-H(13)	118.9
C(12)-C(13)-H(13)	118.9
C(13)-C(14)-C(15)	120.1(4)

C(13)-C(14)-H(14)	119.9
C(15)-C(14)-H(14)	119.9
C(16)-C(15)-C(14)	118.9(4)
C(16)-C(15)-H(15)	120.5
C(14)-C(15)-H(15)	120.5
C(15)-C(16)-C(17)	123.1(4)
C(15)-C(16)-H(16)	118.5
C(17)-C(16)-H(16)	118.5
C(16)-C(17)-C(12)	117.9(4)
C(16)-C(17)-C(18)	121.2(4)
C(12)-C(17)-C(18)	120.7(4)
C(1)-C(18)-C(5)	118.8(4)
C(1)-C(18)-C(17)	120.9(4)
C(5)-C(18)-C(17)	120.2(4)
O(1)-C(19)-H(19A)	109.5
O(1)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
O(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(2)-C(20)-H(20A)	109.5
O(2)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(2)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å ^2 x 10^3) for 1,4-Difluoro-2,3-dimethoxytriphenylene. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
F(1)	25(2)	33(2)	32(2)	-6(1)	4(1)	9(1)
F(2)	30(2)	33(2)	29(2)	-6(1)	-4(1)	-5(1)
O(1)	37(2)	15(2)	41(2)	-4(2)	19(2)	2(2)
O(2)	57(2)	20(2)	20(2)	-4(2)	6(2)	-9(2)
C(1)	23(2)	10(3)	27(3)	2(2)	8(2)	4(2)
C(2)	22(3)	18(3)	32(3)	1(2)	5(2)	0(2)
C(3)	19(2)	21(3)	36(3)	5(2)	0(2)	-1(2)
C(4)	24(3)	19(3)	25(3)	3(2)	1(2)	1(2)
C(5)	19(2)	14(3)	20(3)	5(2)	0(2)	-2(2)
C(6)	24(2)	10(3)	16(3)	2(2)	2(2)	1(2)
C(7)	24(2)	15(3)	20(3)	1(2)	-6(2)	-1(2)
C(8)	39(3)	7(3)	18(3)	0(2)	6(2)	-4(2)
C(9)	34(3)	6(3)	30(3)	0(2)	12(2)	3(2)
C(10)	23(3)	16(3)	24(3)	2(2)	-2(2)	1(2)
C(11)	24(2)	10(3)	16(3)	4(2)	8(2)	-2(2)
C(12)	23(2)	12(3)	16(3)	6(2)	4(2)	-3(2)
C(13)	20(2)	18(3)	28(3)	0(2)	4(2)	-1(2)
C(14)	23(2)	28(3)	21(3)	0(2)	-8(2)	0(2)
C(15)	30(3)	20(3)	19(3)	-3(2)	1(2)	-2(2)
C(16)	25(3)	15(3)	18(3)	1(2)	5(2)	0(2)
C(17)	20(2)	8(3)	20(3)	3(2)	4(2)	-2(2)
C(18)	22(2)	11(3)	17(3)	5(2)	5(2)	0(2)
C(19)	32(3)	31(3)	42(3)	1(3)	19(2)	7(3)
C(20)	68(4)	33(3)	21(3)	2(3)	2(3)	-4(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 1,4-Difluoro-2,3-dimethoxytriphenylene.

	x	y	z	U(eq)
H(1)	3833	5260	2111	24
H(2)	1684	5792	1830	29
H(3)	1350	3950	1241	30
H(4)	3163	1489	941	27
H(13)	9499	1489	1723	26
H(14)	9784	3678	2288	29
H(15)	7851	5349	2611	28
H(16)	5682	5048	2345	23
H(19A)	9875	-16	409	52
H(19B)	10843	-3287	363	52
H(19C)	10792	-1396	740	52
H(20A)	6353	-206	27	61
H(20B)	6409	-3652	-201	61
H(20C)	7780	-2228	-4	61