

Supporting Information

Synthesis

2,3,4,5,6-pentafluoro-2'-iodo-4',5'-dimethoxy-1,1'-biphenyl (14)

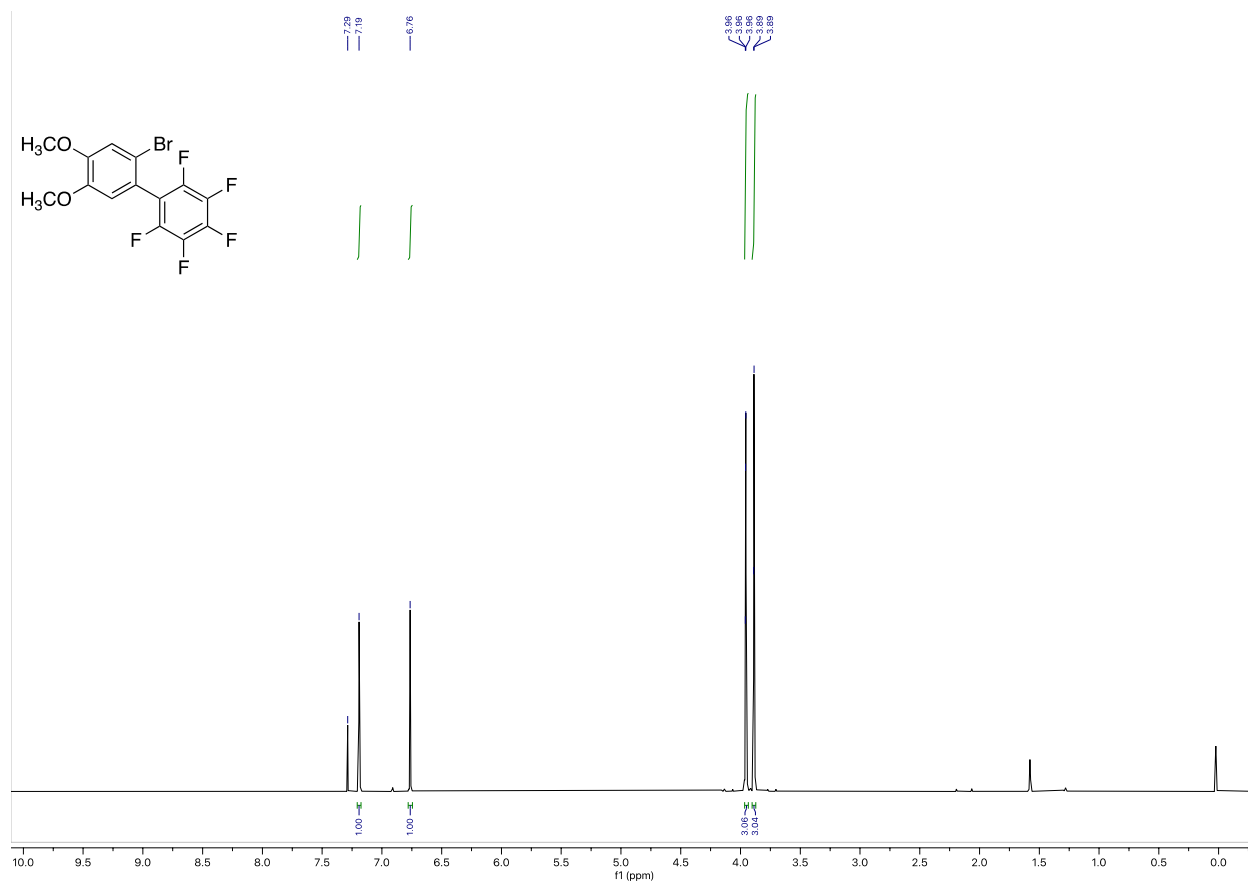
In a 200 ml round bottom flask was placed potassium pentafluorobenzoate (7.5 g, 30.0 mmol), 1-bromo-2-iodo-4,5-dimethoxybenzene (6.84 g, 20.0 mmol), CuI (1.14 g, 30 mol%) and dry diglyme (35.0 ml). The mixture was refluxed at 160 °C for five hours and monitored by TLC to observe complete transformation of the starting material to a new product which was confirmed by GCMS. The reaction mixture was cooled to room temperature and ethyl acetate was added to bring the volume up to 200 ml. The mixture was vacuum filtered through a sintered glass funnel and the filtrate was washed with water and brine. The organic extract was dried over anhydrous magnesium sulfate and vacuum filtered. Some silica gel was added to the filtrate and solvent was removed under reduced pressure and the silica powder thus obtained was placed at the top of a column and eluted with a mixture of ethyl acetate and hexanes (10% EtOAc in hexane). Fractions containing the desired product were combined and concentrated to obtain a viscous colorless liquid product which crystallized on long standing. Yield – 6.25 g (82 %)

GCMS- m/z 381

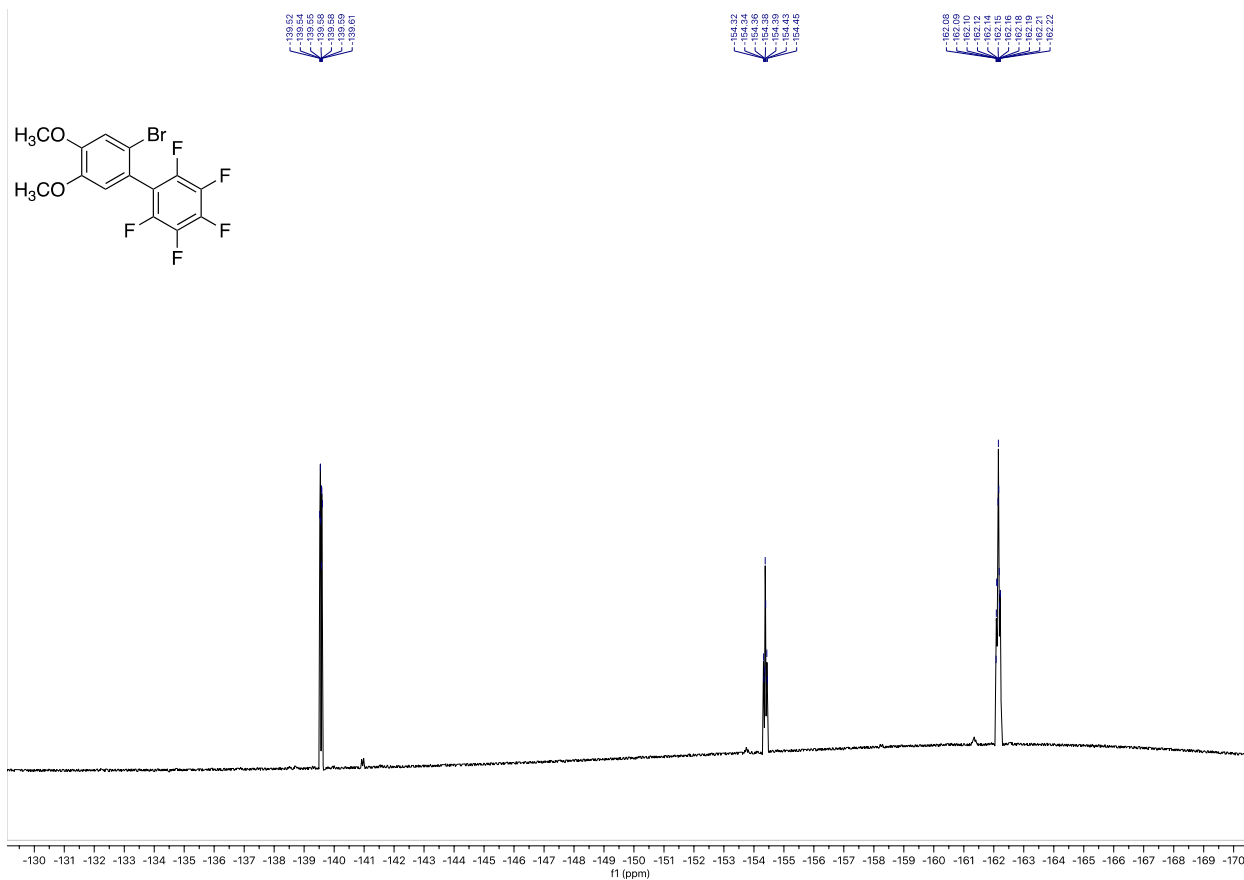
¹⁹F NMR (376 MHz, CDCl₃) δ -137.89 – -140.86 (m, 2F), -154.39 (td, *J* = 21.2, 7.0 Hz, 1F), -162.16 (tdd, *J* = 21.2, 8.9, 4.8 Hz, 2F).

¹H NMR (400 MHz, CDCl₃) δ 7.19 (s, 1H), 6.76 (s, 1H), 3.96 (d, *J* = 0.8 Hz, 3H), 3.89 (d, *J* = 1.0 Hz, 3H).

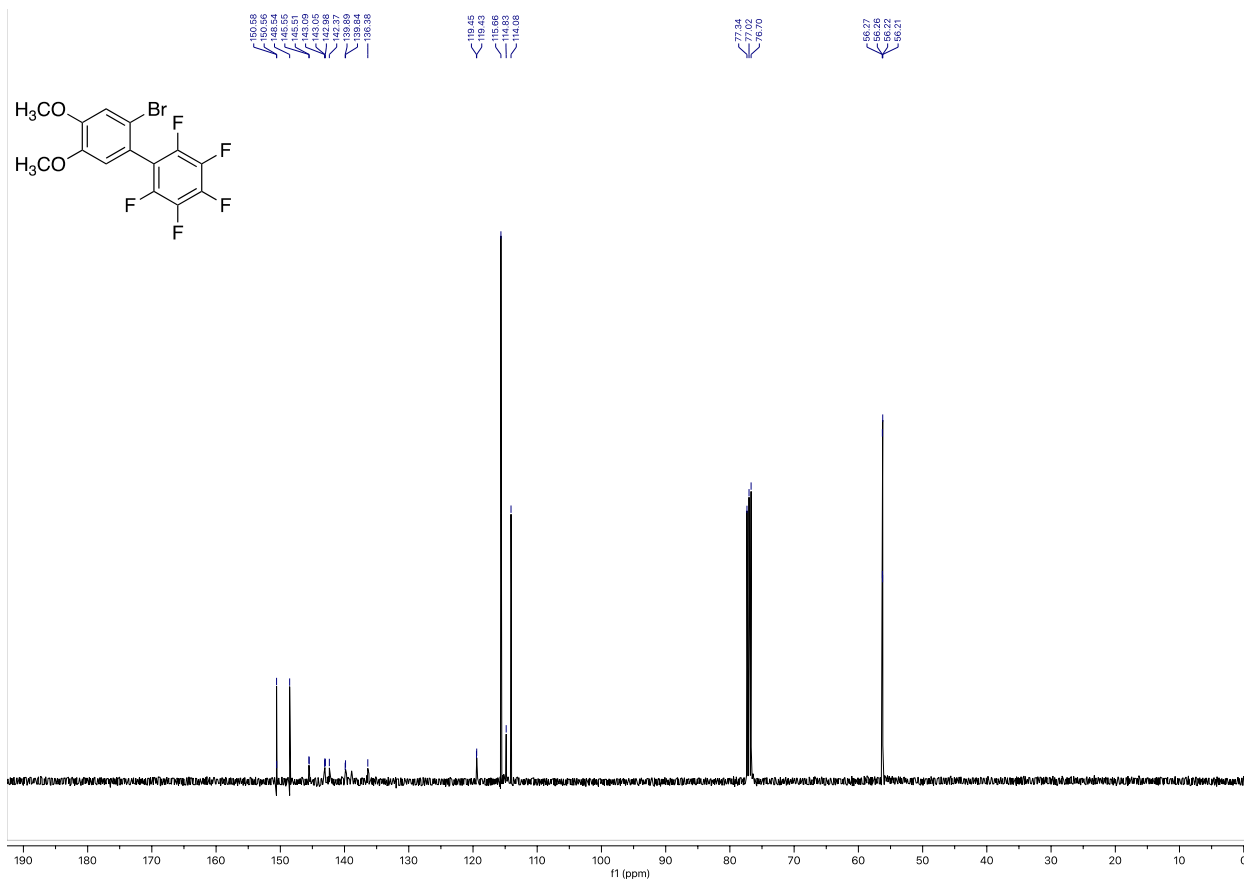
¹³C NMR (101 MHz, CDCl₃) δ 150.58, 148.54, 145.55, 145.51, 143.09, 143.05, 142.37, 139.84, 136.38, 119.45, 119.43, 115.69, 115.66, 114.84, 114.08, 56.27, 56.26, 56.21.



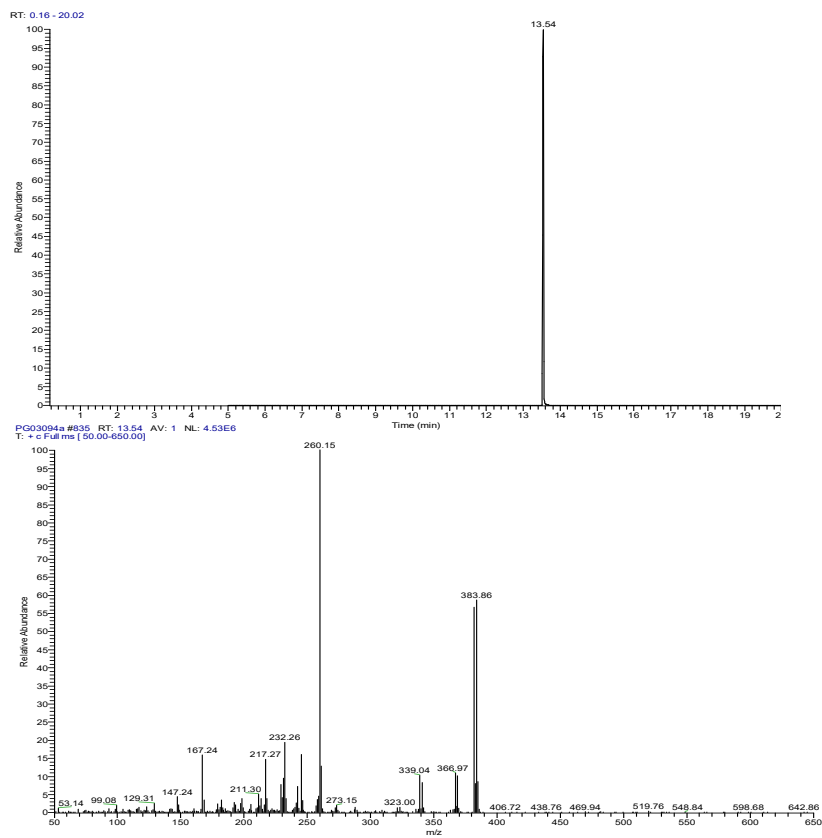
Spectrum 1a: ¹H- NMR of 2,3,4,5,6-pentafluoro-2'-iodo-4',5'-dimethoxy-1,1'-biphenyl (**14**)



Spectrum 1b: ¹⁹F-NMR of 2,3,4,5,6-pentafluoro-2'-iodo-4',5'-dimethoxy-1,1'-biphenyl (**14**)



Spectrum 1c: ¹³C-NMR of 2,3,4,5,6-pentafluoro-2'-iodo-4',5'-dimethoxy-1,1'-biphenyl (14)



Spectrum 1d: GCMS spectra of 2,3,4,5,6-pentafluoro-2'-iodo-4',5'-dimethoxy-1,1'-biphenyl (**14**)

2,3,4,5,6-pentafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl (15**)**

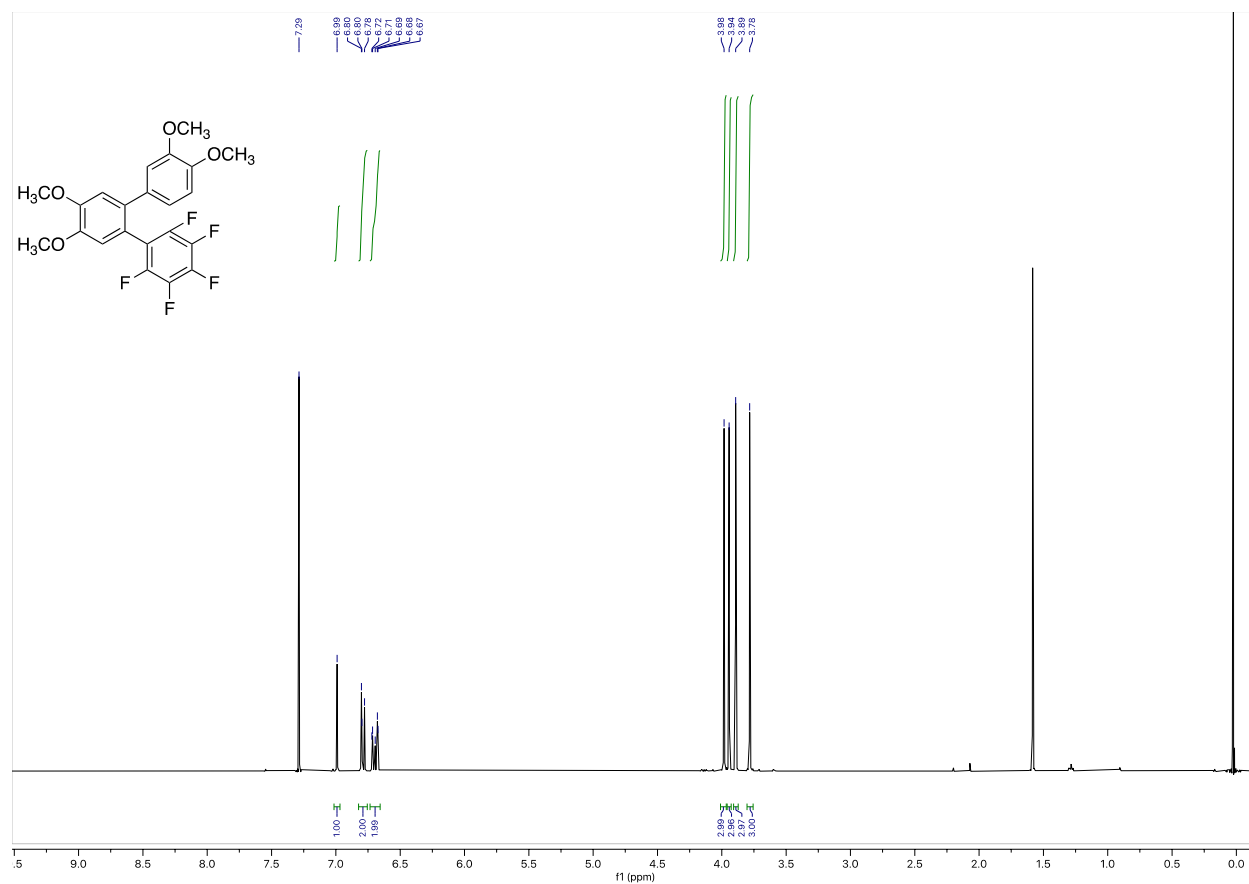
In a 200 ml round bottom flask was placed 2,3,4,5,6-pentafluoro-2'-bromo-4',5'-dimethoxy-1,1'-biphenyl (3.82 g, 10.0 mmol), 3,4-dimethoxyphenylboronic acid (2.73 g, 15.0 mmol), dioxane (30.0 ml) and water (10.0 ml). The mixture was stirred while potassium carbonate (2.12 g, 15.0 mmol) was added, and the mixture was heated in an oil bath under a nitrogen atmosphere. At 70°C, PdCl₂(PPh₃)₂ (0.15 g, 2.0 mol%) was added and the temperature was gradually raised up to 95°C. The reaction was complete after four hours as indicated by the new spot in TLC. After cooling to room temperature ice water was added dropwise with stirring to fill the flask. The black solid crude product was vacuum filtered, then dissolved in ethyl acetate and some silica gel and Montmorillonite clay was added and the mixture was concentrated by rotary evaporation. This material was placed at the top of a column packed with silica made up with ethyl acetate and hexanes (10% EtOAc in hexanes) and then eluted with the same solvent. Fractions containing pure product were combined and concentrated to a get cream colored solid product. Yield – 3.17 g (72 %)

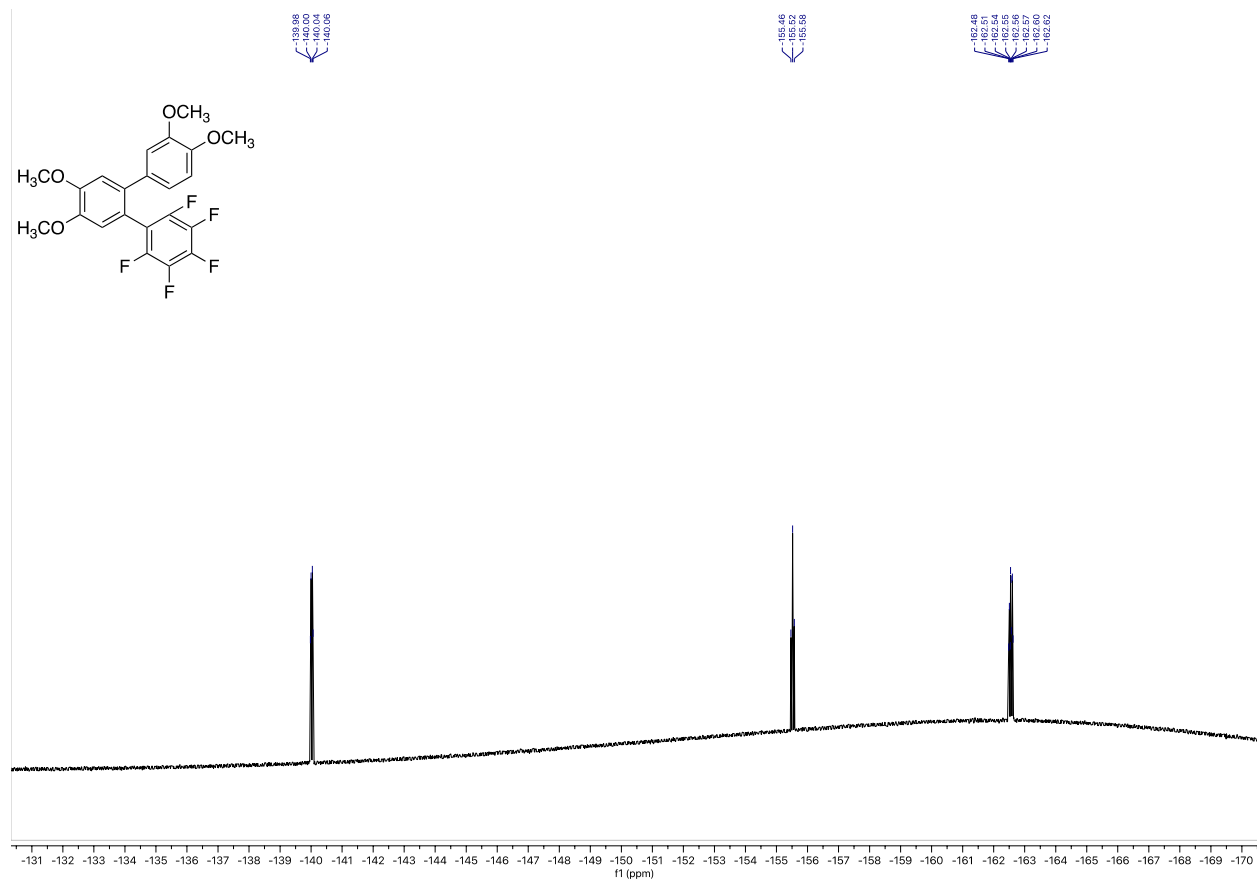
GCMS- m/z 440

^{19}F NMR (376 MHz, CDCl_3) δ -138.94 – -140.87 (m, 2F), -155.52 (t, $J = 21.0$ Hz, 1F), -162.55 (ddd, $J = 23.7, 20.8, 8.3$ Hz, 2F).

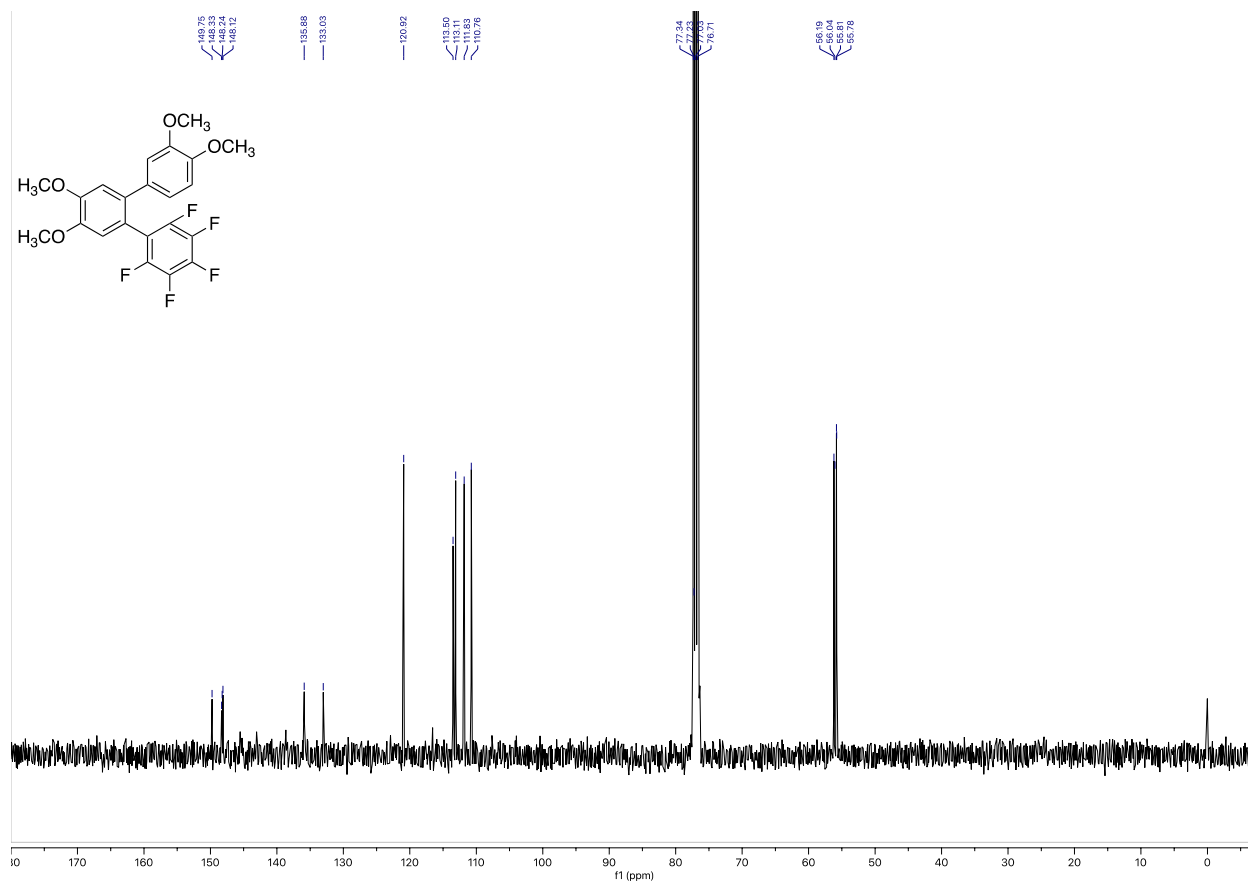
^1H NMR (400 MHz, CDCl_3) δ 6.99 (s, 1H), 6.82 – 6.75 (m, 2H), 6.74 – 6.65 (m, 2H), 3.98 (s, 3H), 3.94 (s, 3H), 3.89 (s, 3H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 149.75, 148.33, 148.24, 148.12, 135.88, 133.03, 120.92, 113.50, 113.11, 111.83, 110.76, 56.19, 56.04, 55.81, 55.78.

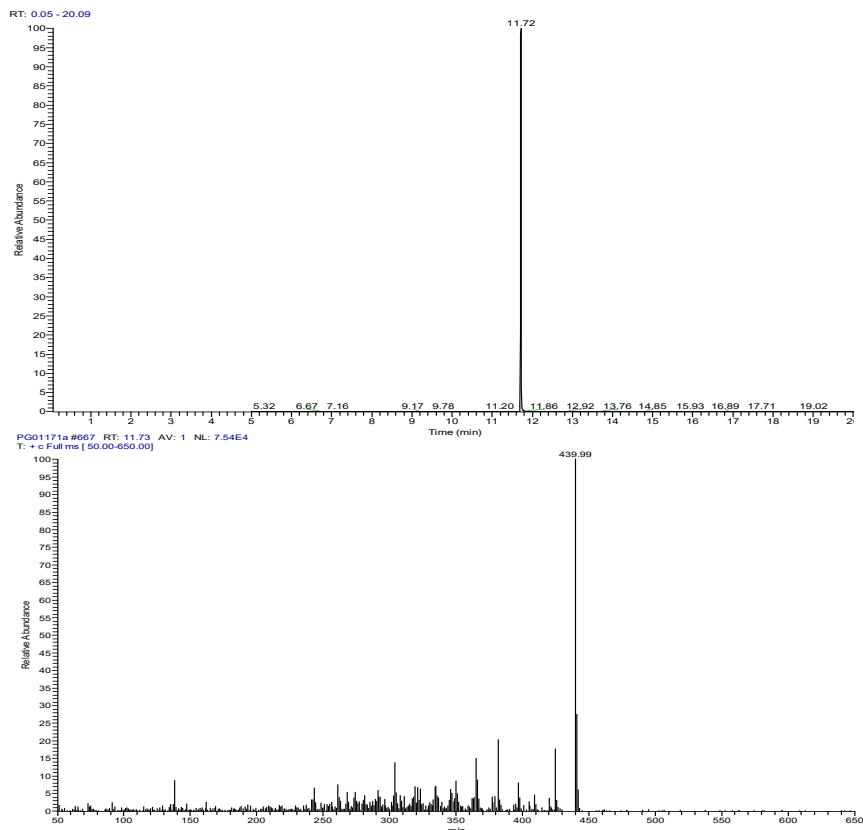




Spectrum 2b: ¹⁹F-NMR of 2,3,4,5,6-pentafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl (**15**)



Spectrum 2c: ¹³C-NMR of 2,3,4,5,6-pentafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl (15)



Spectrum 2d: GCMS spectra of 2,3,4,5,6-pentafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl (**15**)

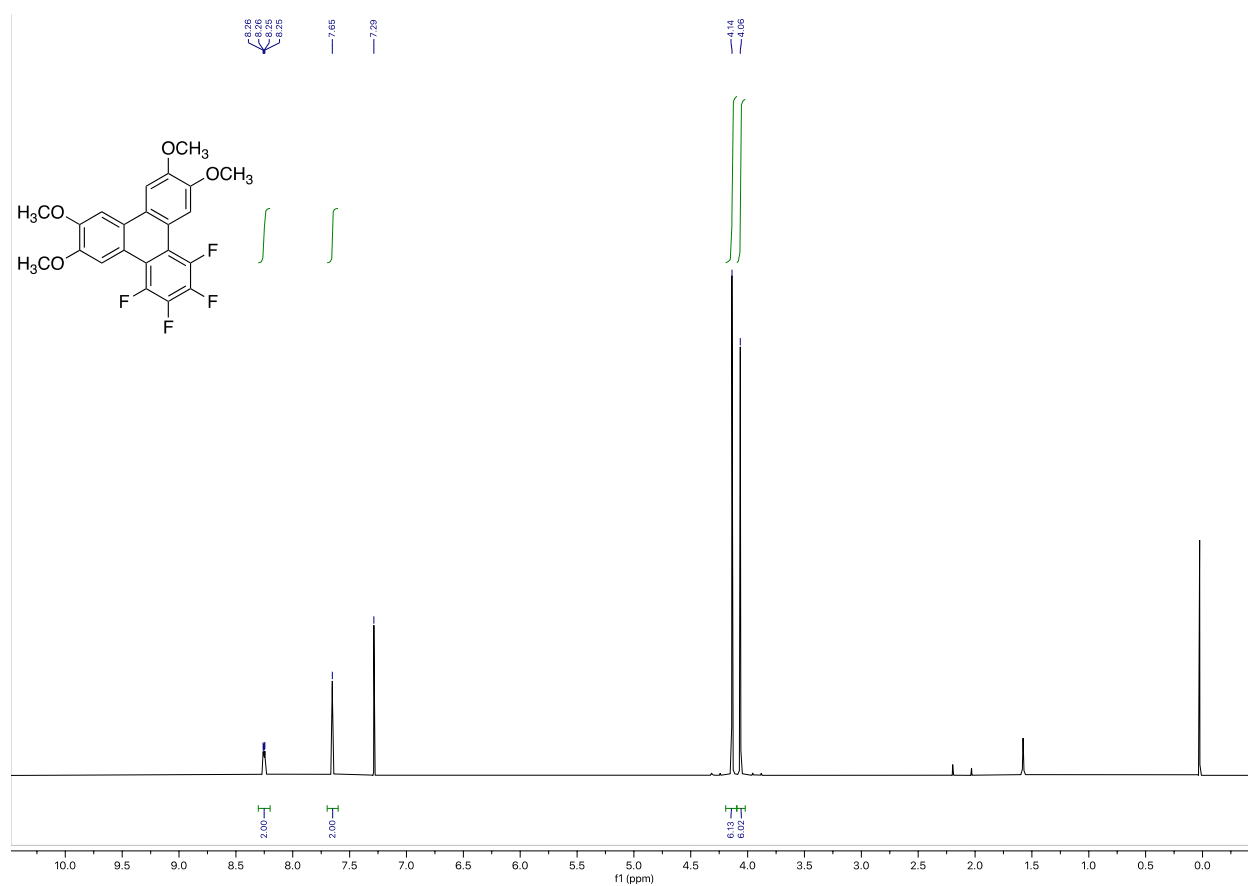
1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (1)

In a (100 cm x 10 cm) quartz tube was placed 2,3,4,5,6-pentafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl (0.57 g, 1.31 mmol) and acetonitrile (60 ml). The mixture was irradiated with 16x254 nm lamps for twelve hours in a Rayonet. The solution turned from colorless to dark brown and some white crystalline precipitate appeared at the bottom of the tube. The photoreaction was monitored by GCMS which indicated the complete transformation of the starting material and so the reaction was terminated after a total of twenty hours. The precipitate was vacuum filtered and washed with acetonitrile. The filtrate was concentrated and redissolved in ethyl acetate and adsorbed on some silica gel. The yellow silica gel powder was placed at the top of a column and eluted with a mixture of ethyl acetate and hexanes (10% EtOAc in hexanes). The fractions containing the product were combined and concentrated to get a solid white product which was combined with the previously filtered off product. Yield – 0.40 g (73 %)

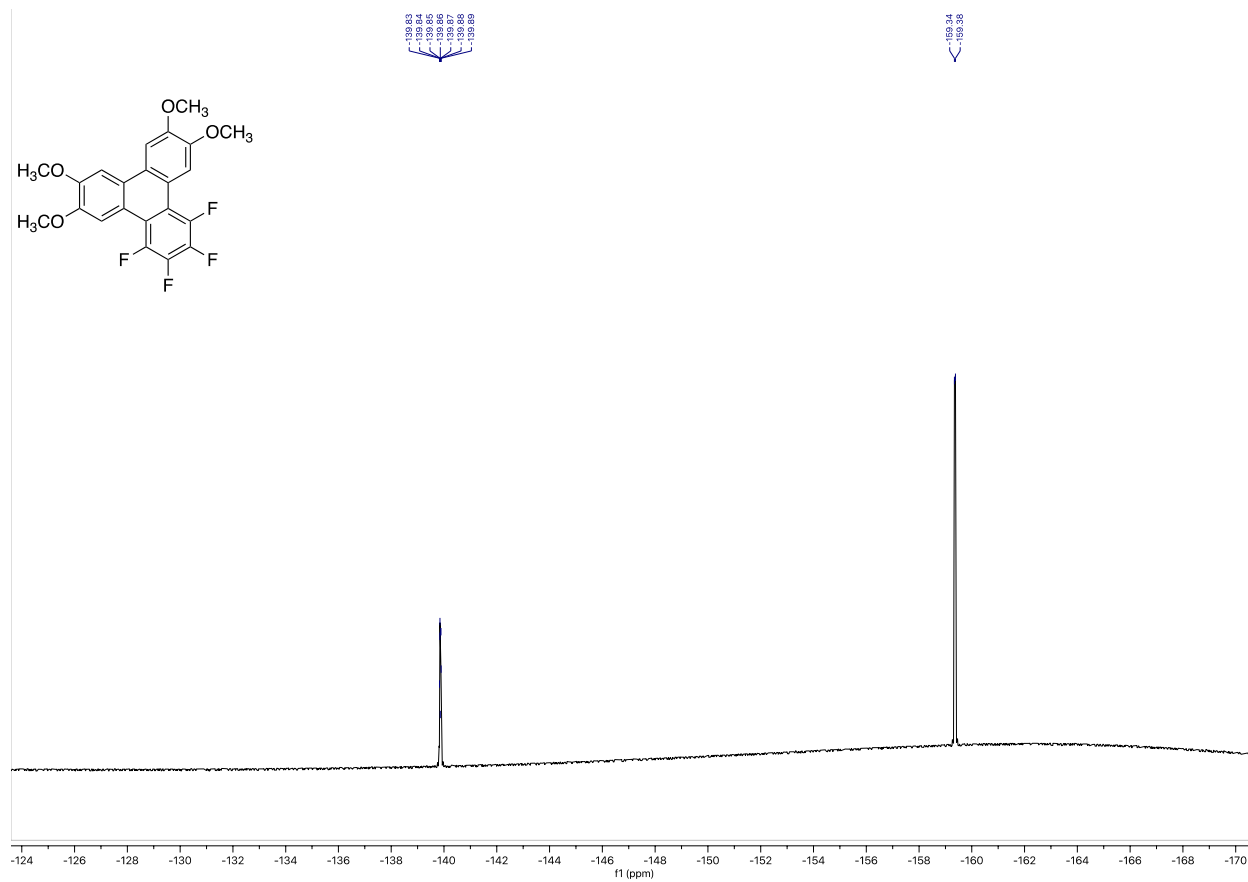
^{19}F NMR (376 MHz, CDCl_3) δ -139.74 – -139.94 (m, 2F), -159.30 – -159.43 (m, 2F).

^1H NMR (400 MHz, CDCl_3) δ 8.25 (dd, J = 4.1, 2.3 Hz, 2H), 7.65 (s, 2H), 4.14 (s, 6H), 4.06 (s, 6H).

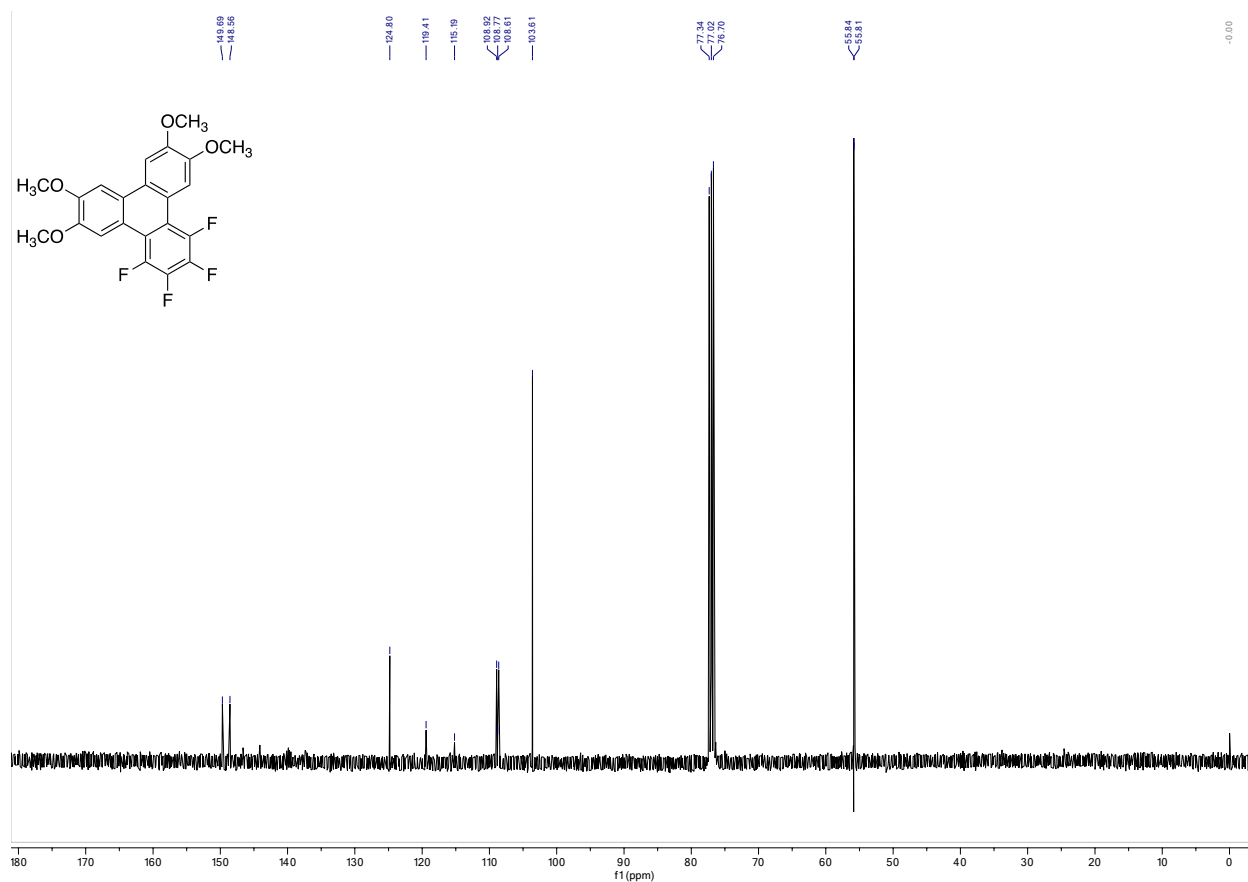
^{13}C NMR (101 MHz, CDCl_3) δ 149.68, 148.56, 124.80, 119.41, 115.19, 108.92, 108.77, 108.61, 103.61, 55.84, 55.81.



Spectrum 3a: ¹H-NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (**1**)



Spectrum 3b: ^{19}F -NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (1)



Spectrum 3c: ¹³C-NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (1)

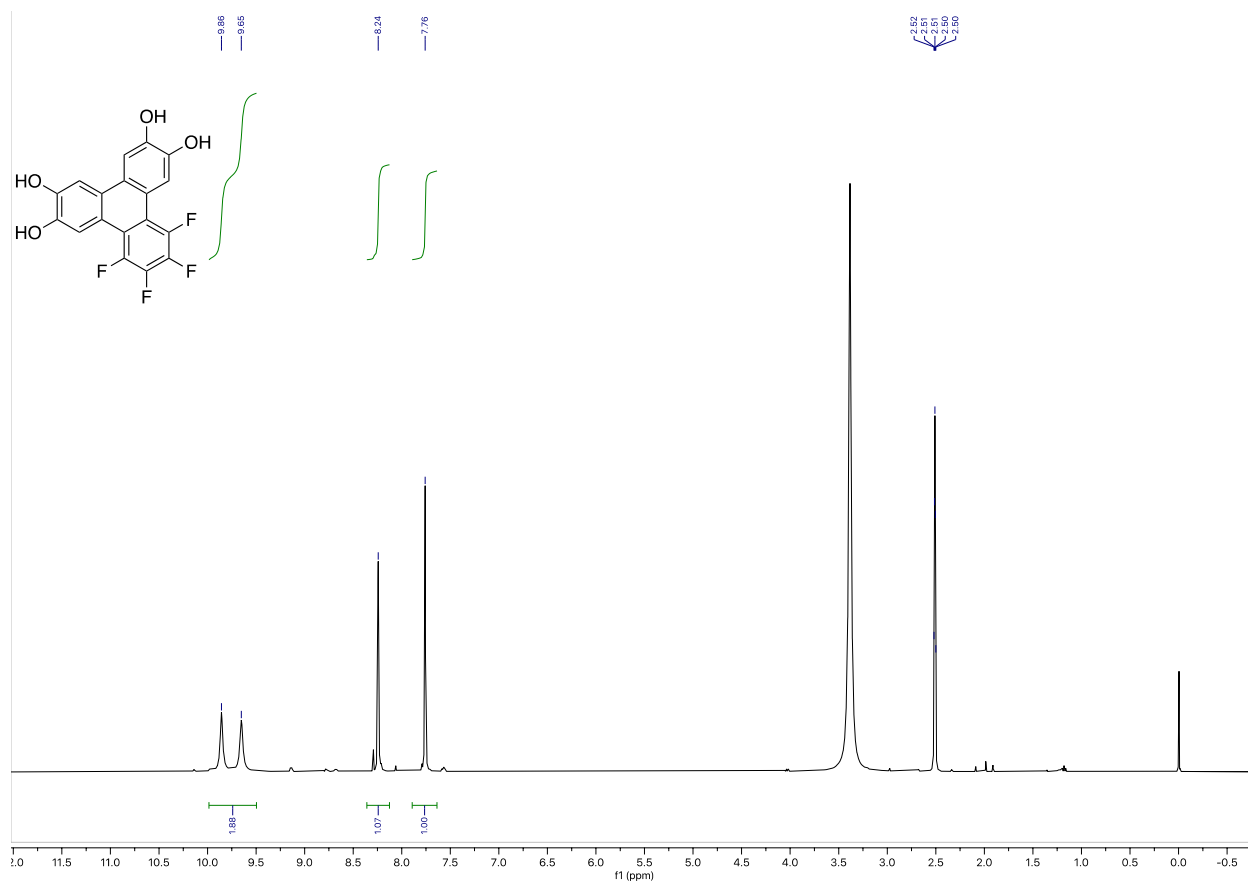
1,2,3,4-tetrafluoro-6,7,10,11-tetrahydroxytriphenylene (16)

In a 100 ml round bottom flask was placed 1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (0.83 g, 2.0 mmol) and pyridine hydrochloride (9.21 g, 80.00 mmol) under nitrogen. The mixture was heated at 170°C and the resulting liquid was stirred at the same temperature for five hours. The reaction was stopped and left the mixture to cool down to room temperature. Aqueous 10% HCl (150 ml) was added to the black precipitate with stirring and the mixture was vacuum filtered to give a muddy brown colored residue as product. This crude product was used without any further purification in the subsequent step. Yield – (quantitative)

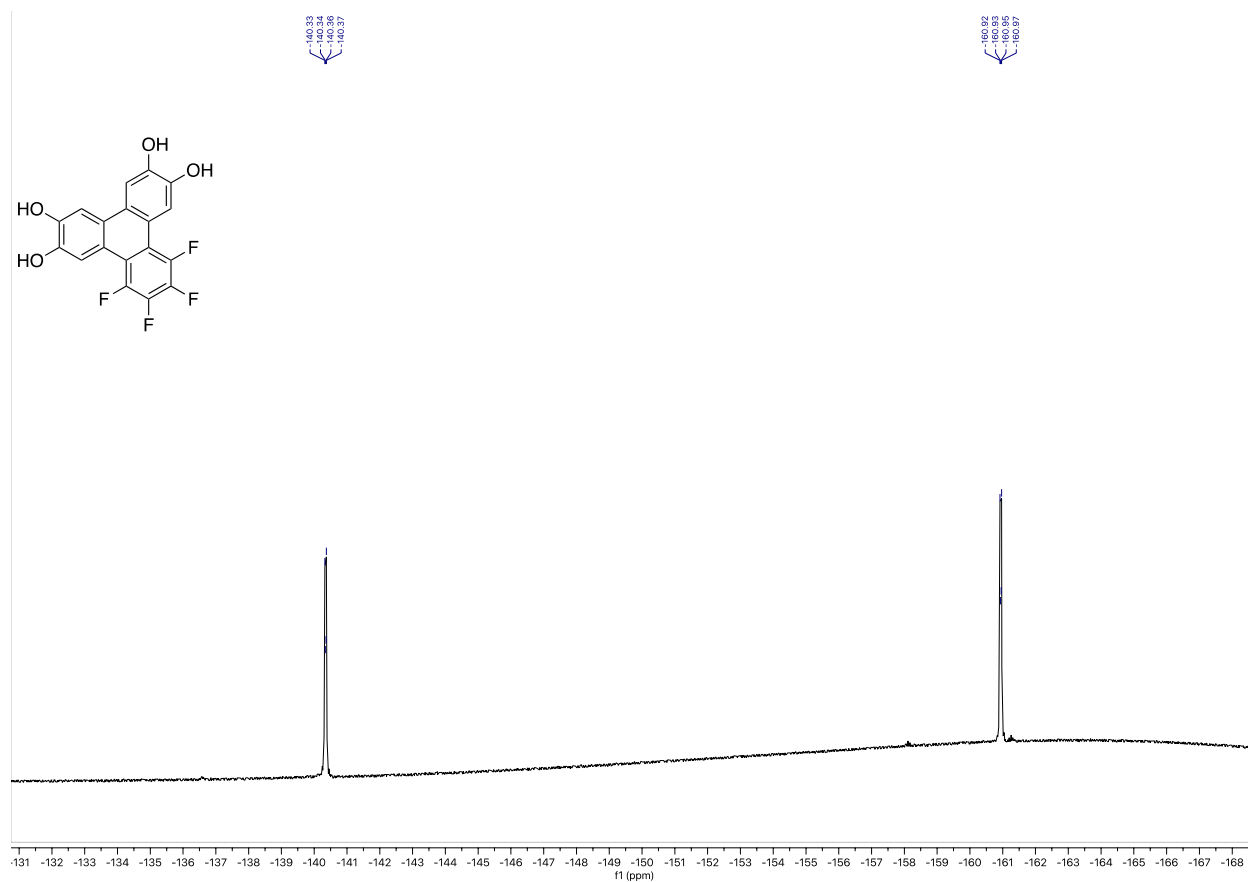
¹H NMR (400 MHz, DMSO) δ 9.86 (s, 2H), 9.65 (s, 2H), 8.24 (s, 2H), 7.76 (s, 2H).

¹⁹F NMR (376 MHz, DMSO) δ -140.20 – -140.49 (m, 2F), -160.79 – -161.09 (m, 2F).

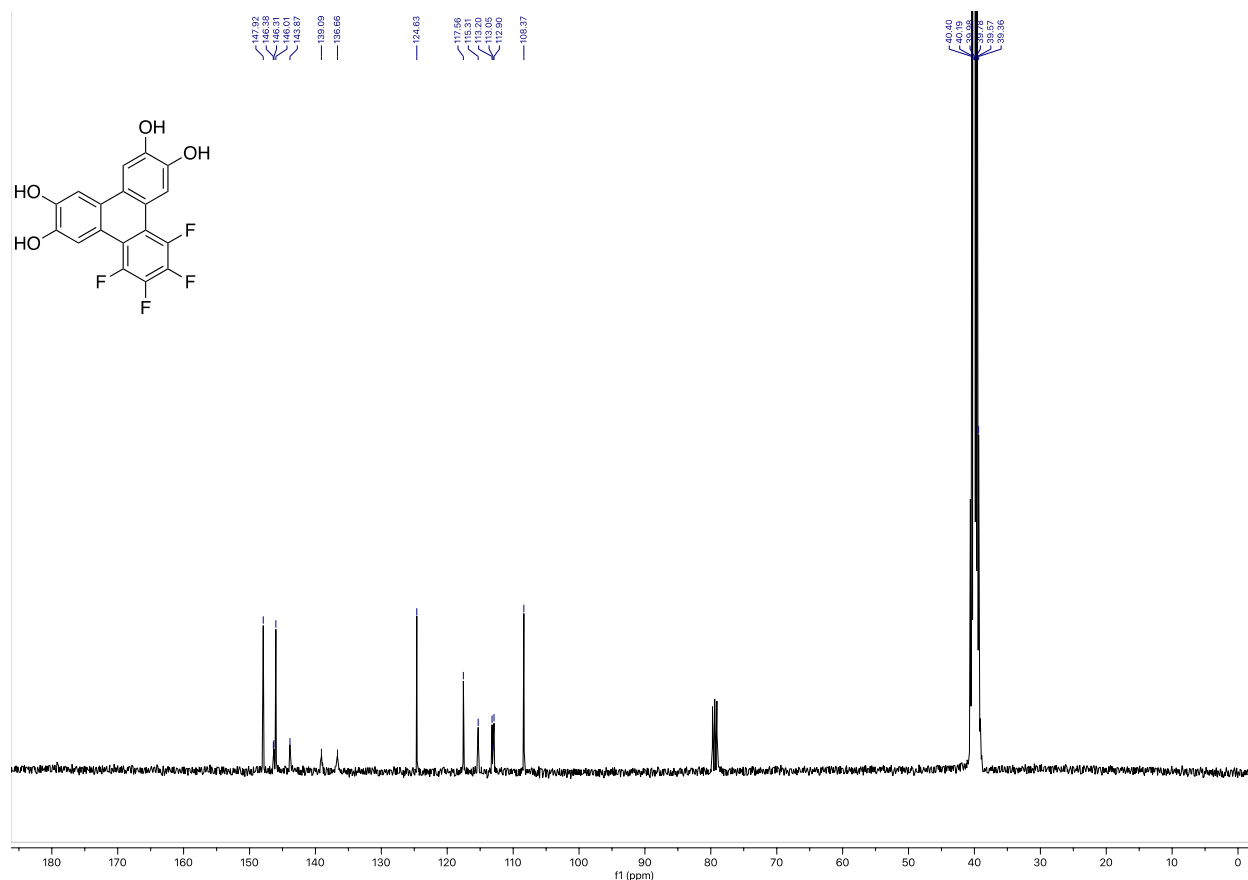
¹³C NMR (101 MHz, DMSO) δ 147.92, 146.38, 146.30, 146.01, 143.88, 139.10, 136.65, 124.63, 117.56, 115.31, 113.20, 112.90, 108.37.



Spectrum 4a: ¹H-NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetrahydroxytriphenylene (**16**)



Spectrum 4b: ^{19}F -NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetrahydroxytriphenylene (**16**)



Spectrum 4c: ¹³C-NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetrahydroxytriphenylene (**16**)

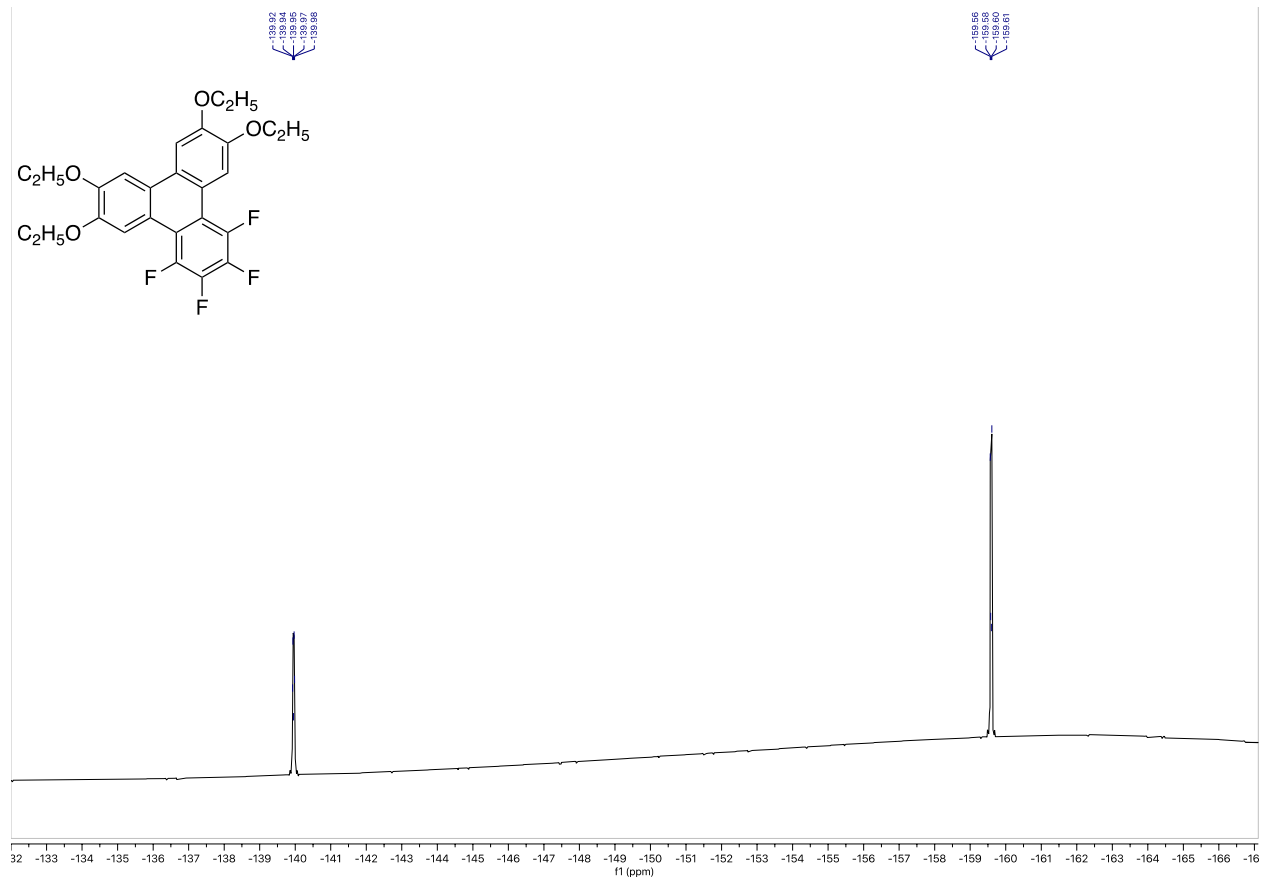
1,2,3,4-tetrafluoro-6,7,10,11-tetraethoxytriphenylene (**2**)

In a 100-ml round bottom flask was placed 1,2,3,4-tetrafluoro-6,7,10,11-tetrahydroxytriphenylene (0.18 g, 0.5 mmol), iodoethane (0.63 g, 4.0 mmol), potassium carbonate (1.12 g, 8.0 mmol) and anhydrous DMF (5 ml). The mixture was heated at 80°C for twenty hours and TLC showed complete transformation of the starting material to a new product. The reaction mixture was cooled to room temperature and water was added to make the volume up to 100 ml and stirred for two hours. The brown precipitate was collected by vacuum filtration, dissolved in THF and the mixture was adsorbed on silica and placed at the top of a column made up with a mixture of ethyl acetate and hexane (10% EtOAc in hexanes) and eluted with the same solvent. Fractions containing pure product were combined and concentrated to provide a white powder which was recrystallized from 1-propanol to obtain the pure crystalline product. Yield – 0.18 g (78 %)

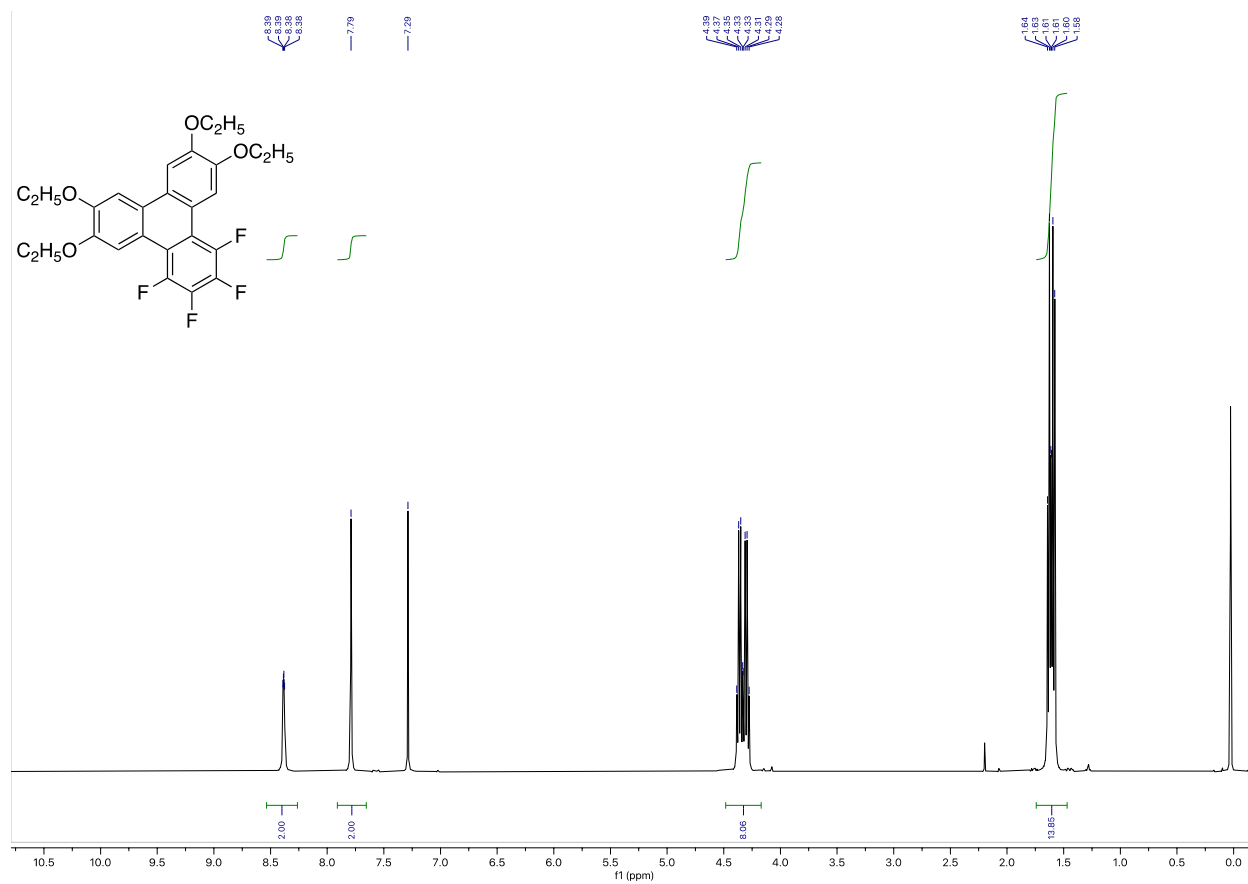
¹⁹F NMR (376 MHz, CDCl₃) δ -139.04 – -141.70 (m, 2F), -158.12 – -161.31 (m, 2F).

¹H NMR (400 MHz, CDCl₃) δ 8.38 (dd, *J* = 3.7, 2.1 Hz, 2H), 7.79 (s, 2H), 4.33 (dq, *J* = 22.6, 7.0 Hz, 8H), 1.61 (dt, *J* = 11.7, 6.9 Hz, 12H).

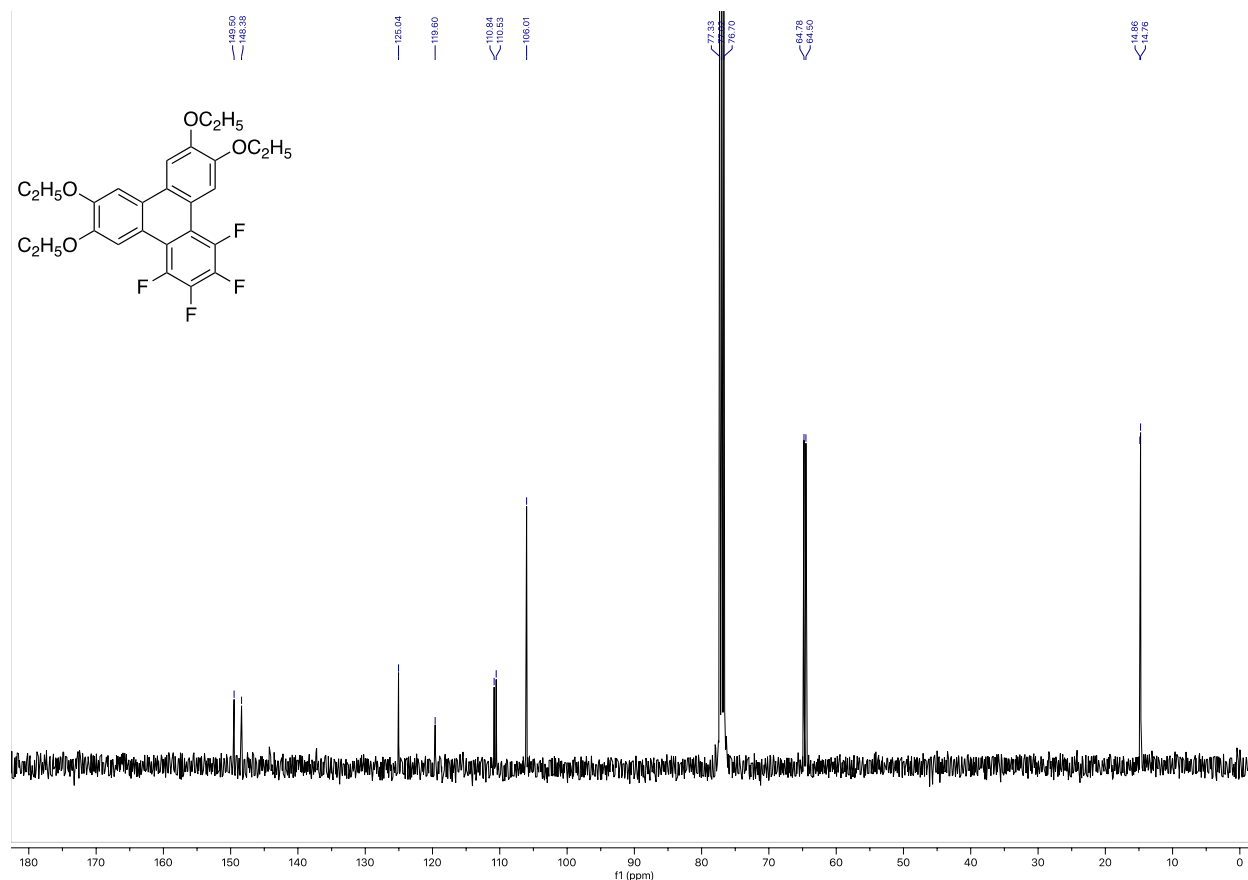
¹³C NMR (101 MHz, CDCl₃) δ 149.50, 148.38, 125.04, 119.60, 110.84, 110.53, 106.01, 64.78, 64.50, 14.86, 14.76.



Spectrum 5a: ^{19}F -NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetraethoxytriphenylene (2)



Spectrum 5b: ¹H-NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetraethoxytriphenylene (**2**)



Spectrum 5C: ¹³C-NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetraethoxytriphenylene (**2**)

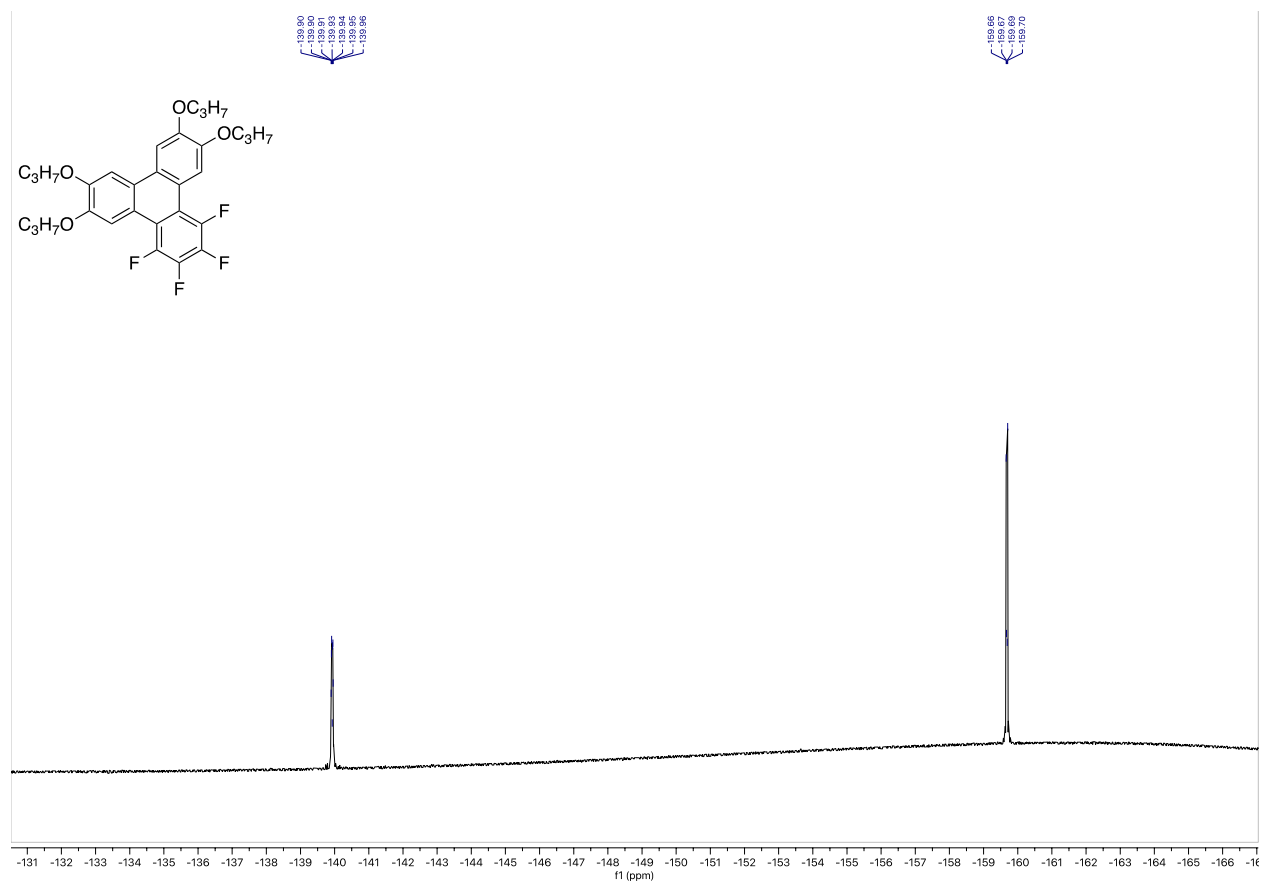
1,2,3,4-tetrafluoro-6,7,10,11-tetrapropoxytriphenylene (3)

In a 100-ml round bottom flask was placed 1,2,3,4-tetrafluoro-6,7,10,11-tetrahydroxytriphenylene (0.27 g, 0.75 mmol), 1-iodopropane (1.03 g, 6.0 mmol), potassium carbonate (1.70 g, 12.0 mmol) and anhydrous DMF (6.0 ml). The mixture was heated at 100°C for twenty hours when TLC showed complete transformation of the starting material to a new product. The reaction mixture was cooled to room temperature, water was added to bring the volume up to 100 ml and stirred for two hours. The brown precipitate was collected by vacuum filtration and after drying it was recrystallized from 1-propanol to provide the pure crystalline product. Yield – 0.34 g (87 %)

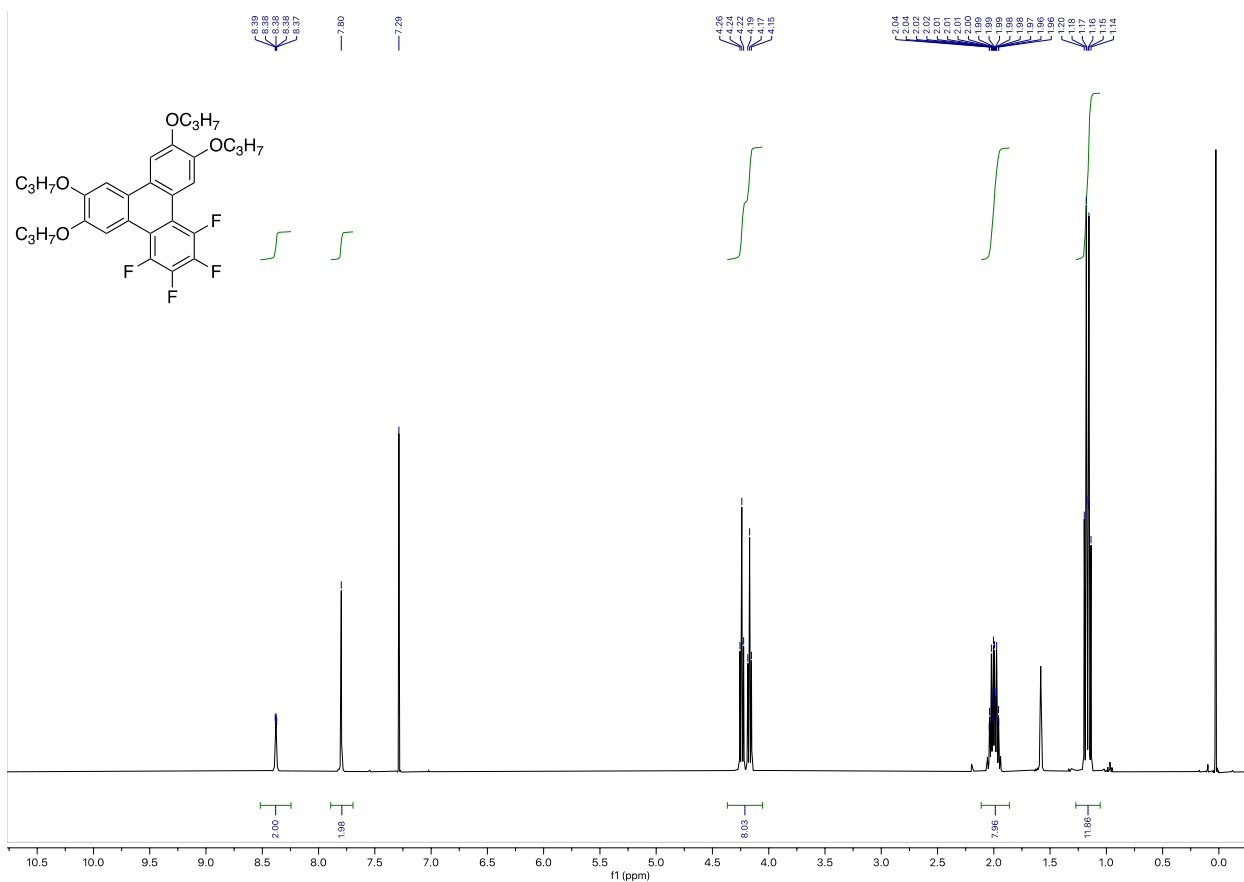
¹⁹F NMR (376 MHz, CDCl₃) δ -139.76 – -140.05 (m), -159.61 – -159.75 (m).

¹H NMR (400 MHz, CDCl₃) δ 8.42 – 8.35 (m, 2H), 7.80 (s, 2H), 4.20 (dt, *J* = 27.8, 6.6 Hz, 8H), 2.08 – 1.92 (m, 8H), 1.17 (dt, *J* = 9.5, 7.4 Hz, 12H).

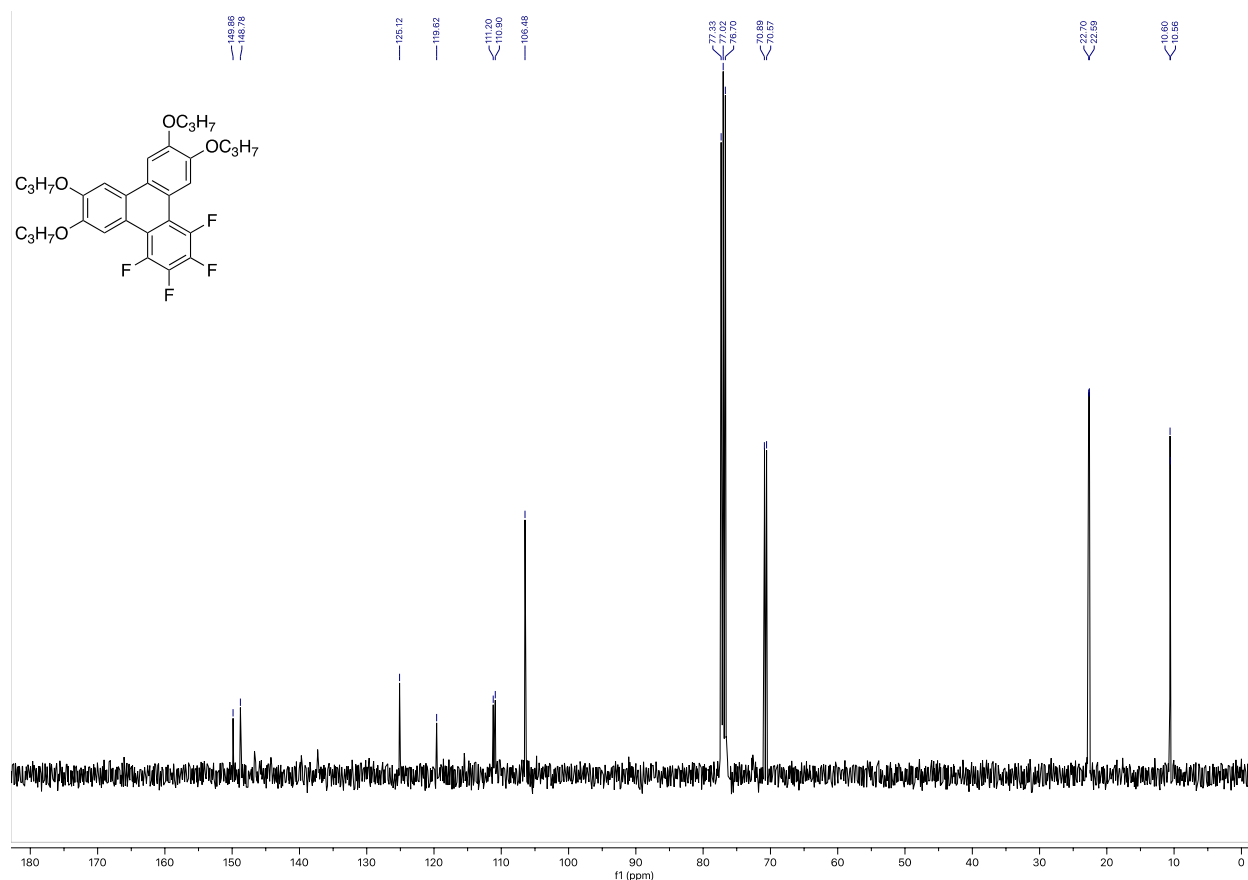
¹³C NMR (101 MHz, CDCl₃) δ 149.86, 148.78, 125.12, 119.62, 111.20, 110.90, 106.48, 70.89, 70.57, 22.70, 22.59, 10.60, 10.56.



Spectrum 6a: ^{19}F -NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetrapropoxytriphenylene (**3**)



Spectrum 6b: ¹H-NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetrapropoxytriphenylene (**3**)



Spectrum 6c: ^{13}C -NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetrapropoxytriphenylene (**3**)

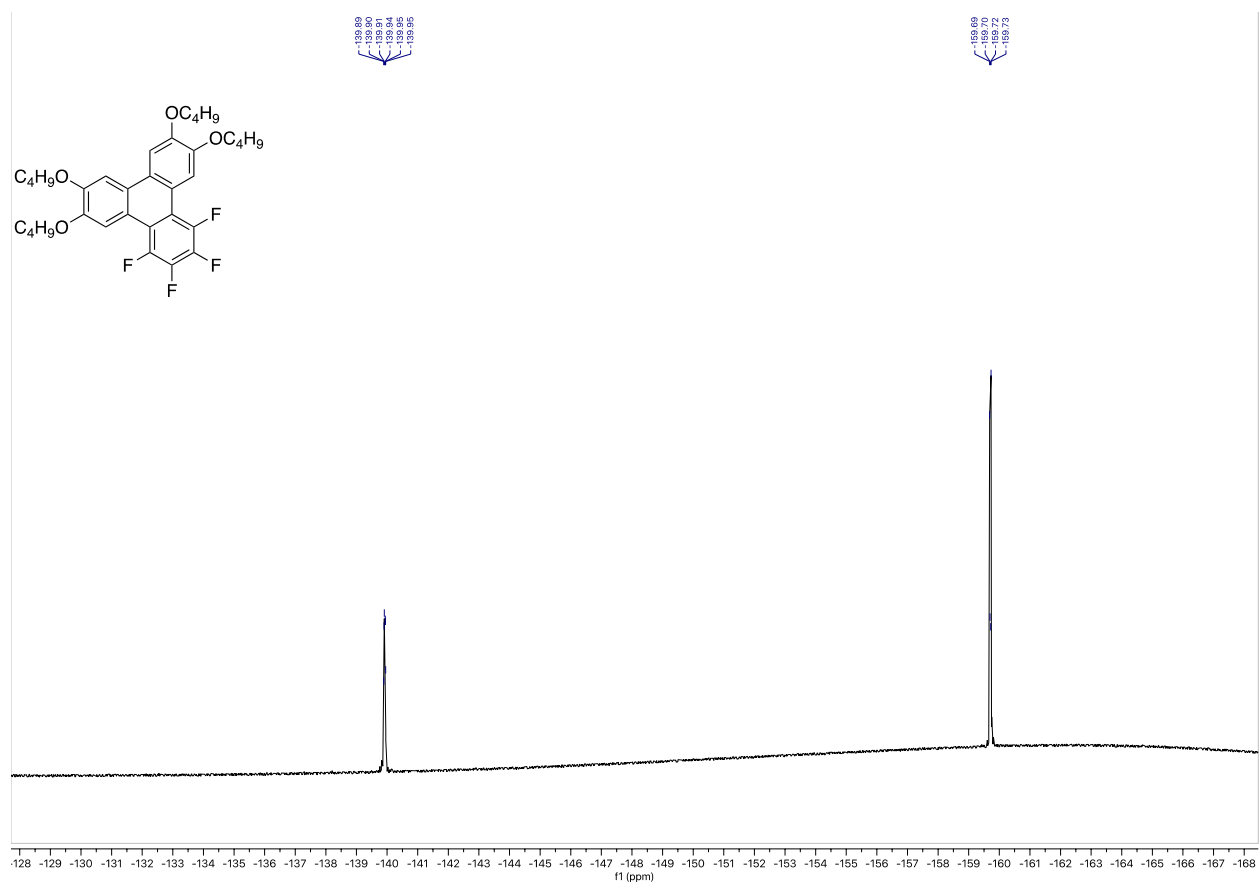
1,2,3,4-tetrafluoro-6,7,10,11-tetrabutoxytriphenylene (4)

In a 100-ml round bottom flask was placed 1,2,3,4-tetrafluoro-6,7,10,11-tetrahydroxytriphenylene (0.27 g, 0.75 mmol), 1-iodobutane (1.10 g, 6.0 mmol), potassium carbonate (1.70 g, 12.0 mmol) and anhydrous DMF (6.0 ml). The mixture was heated at 100°C for twenty hours when TLC showed complete transformation of the starting material to give a new product. The reaction mixture was allowed to cool to room temperature and water was added to bring the volume up to 100 ml and stirred for two hours. The brown precipitate was collected by vacuum filtration and after drying it was recrystallized from 1-propanol to provide the pure crystalline product. Yield – 0.36 g (84 %)

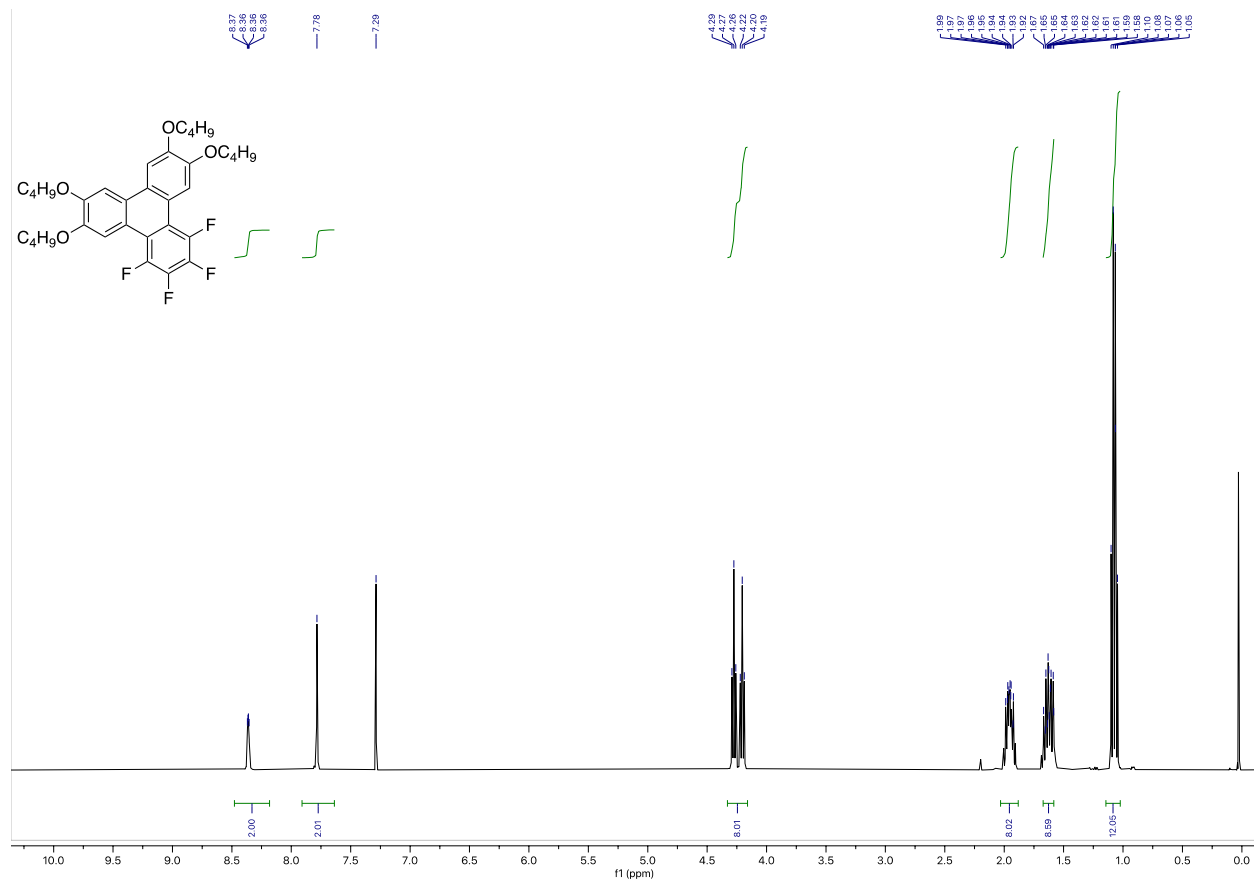
^{19}F NMR (376 MHz, CDCl_3) δ -139.84 – -140.05 (m, 2F), -159.64 – -159.78 (m, 2F).

^1H NMR (400 MHz, CDCl_3) δ 8.36 (dd, $J = 3.5, 2.0$ Hz, 2H), 7.78 (s, 2H), 4.24 (dt, $J = 28.3, 6.6$ Hz, 8H), 2.03 – 1.88 (m, 8H), 1.71 – 1.55 (m, 8H), 1.07 (q, $J = 7.3$ Hz, 12H).

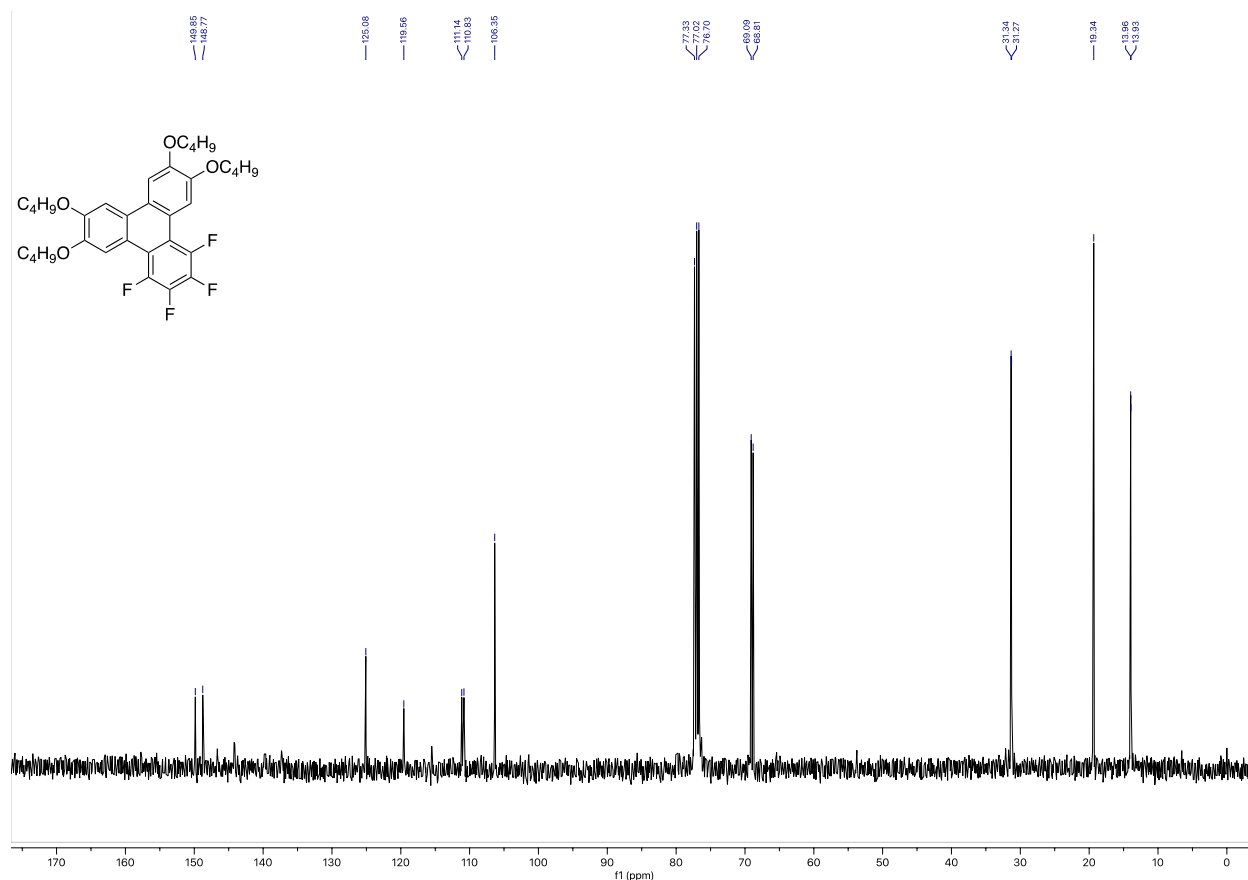
^{13}C NMR (101 MHz, CDCl_3) δ 149.85, 148.77, 125.08, 119.56, 111.14, 110.83, 106.35, 69.09, 68.81, 31.34, 31.27, 19.34, 13.96, 13.93.



Spectrum 7a: ^{19}F -NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetrabutoxytriphenylene (**4**)



Spectrum 7b: ¹H-NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetrabutoxytriphenylene (**4**)



Spectrum 7c: ¹³C-NMR of 1,2,3,4-tetrafluoro-6,7,10,11-tetrabutoxytriphenylene (**4**)

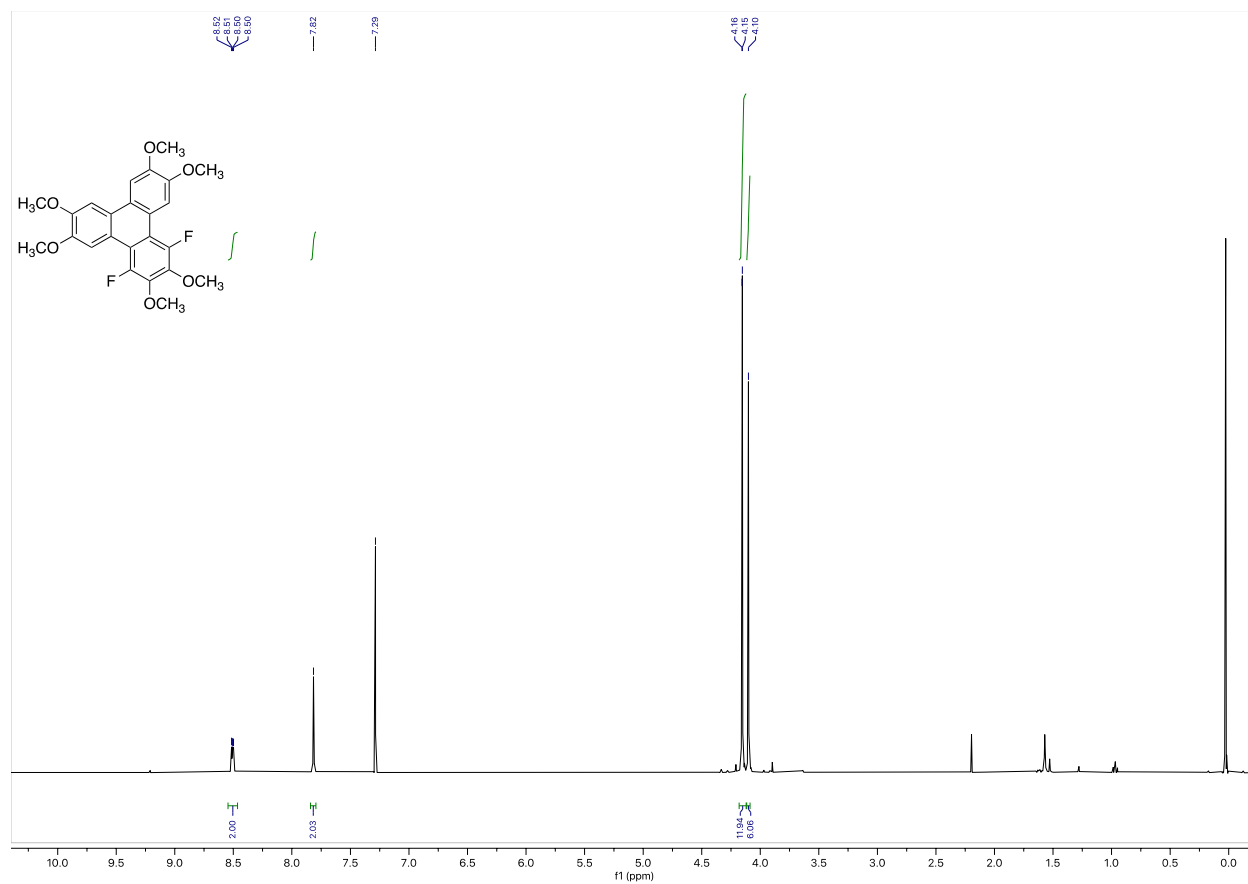
1,4-difluoro-2,3,6,7,10,11-hexamethoxytriphenylene (**7**)

In a 200 ml round bottom flask was placed 1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene (0.21 g, 0.5 mmol), methanol (6 ml), *t*-BuOK (0.66 g, 6.0 mmol) and THF (20 ml). The mixture was stirred and heated up to 65°C and refluxed for two days. The reaction was monitored by TLC, but it never showed any new spot other than the reactant spot, however the reaction was terminated by cooling to room temperature followed by dropwise addition of 10 % HCl (100 ml). The tan colored precipitate was vacuum filtered, washed with water and dried. It was then recrystallized from 1-propanol to get white crystals. Yield – 0.15 g (68 %)

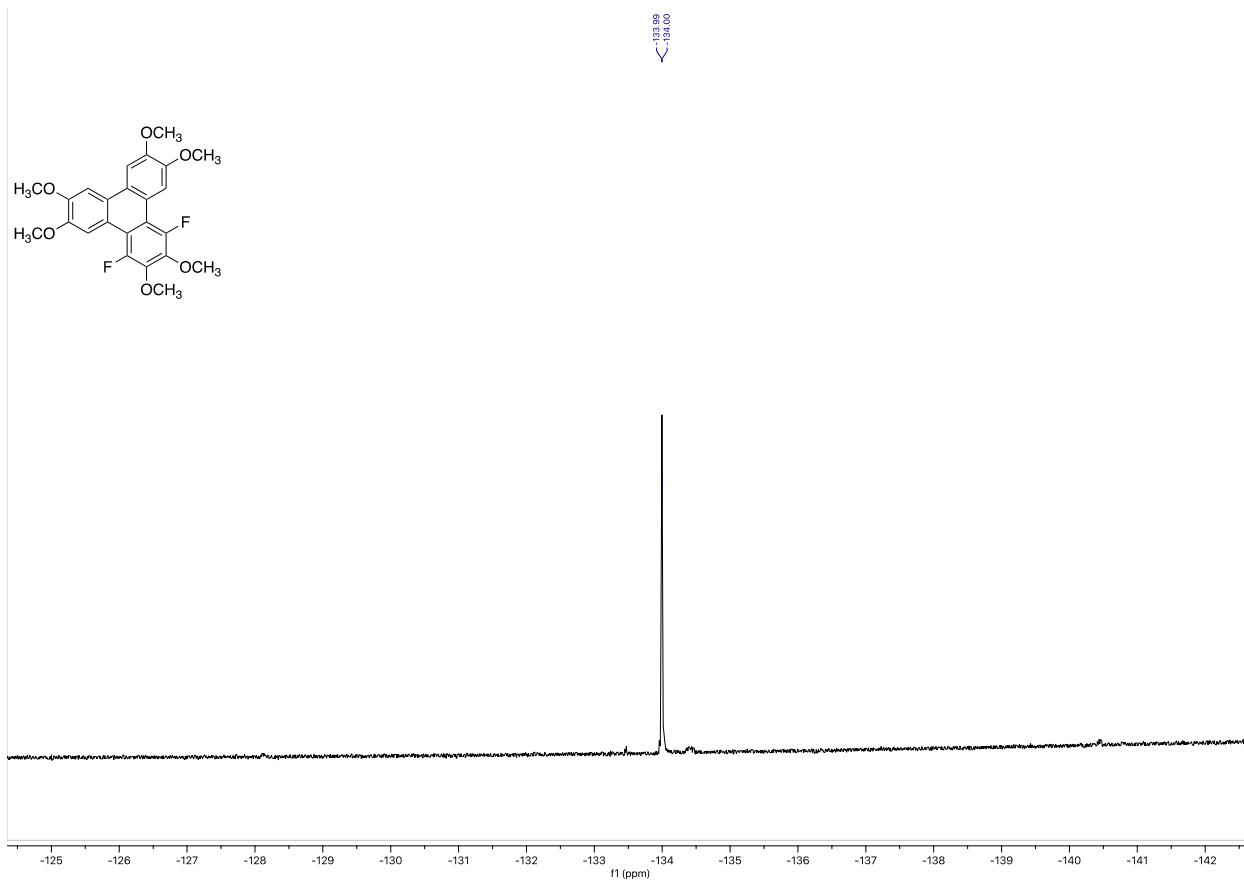
¹⁹F NMR (376 MHz, CDCl₃) δ -132.41 – -135.11 (m, 2F).

¹H NMR (400 MHz, CDCl₃) δ 8.51 (dd, *J* = 4.2, 2.6 Hz, 2H), 7.82 (s, 2H), 4.15 (d, *J* = 1.2 Hz, 12H), 4.10 (s, 6H).

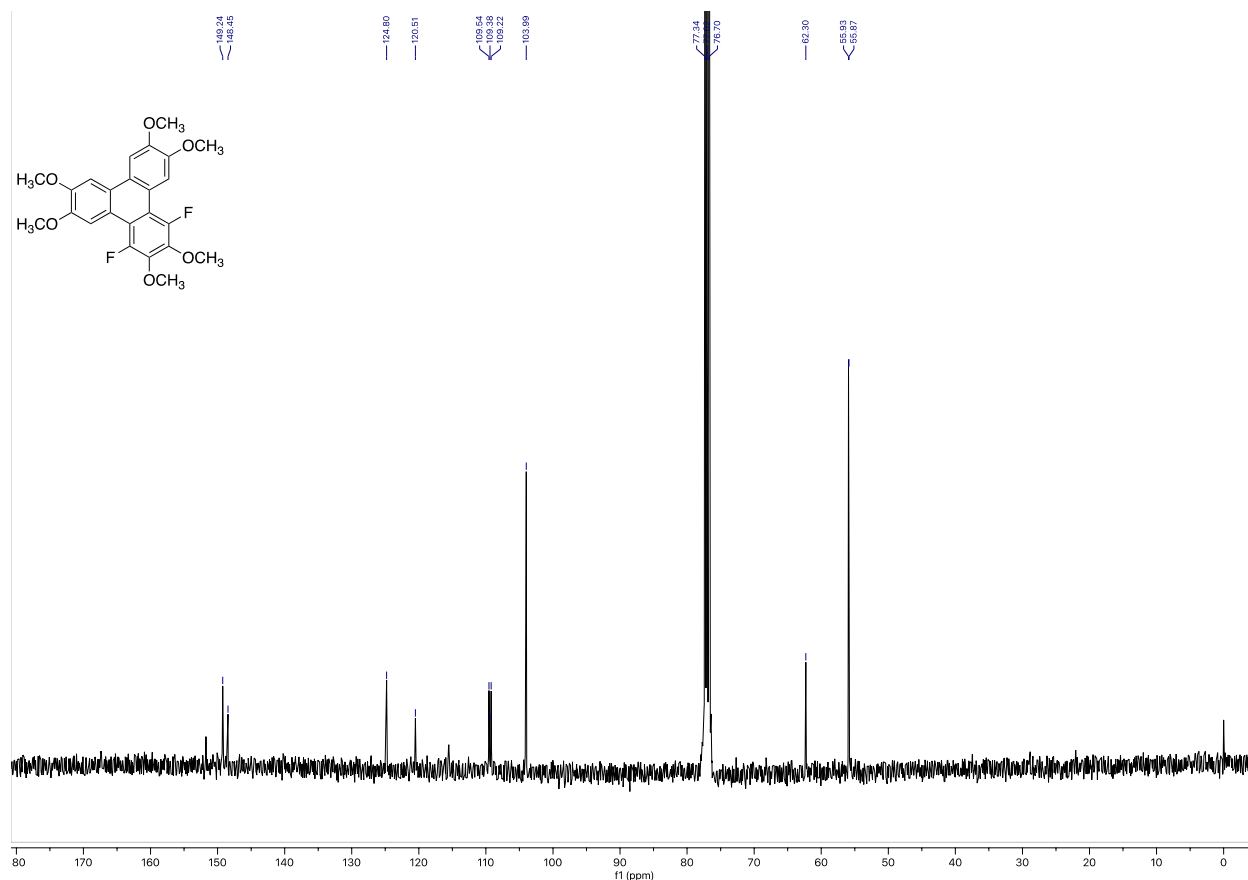
¹³C NMR (101 MHz, CDCl₃) δ 149.25, 148.45, 124.80, 120.51, 109.54, 109.38, 109.22, 103.99, 62.30, 55.93, 55.87.



Spectrum 8a: ¹H-NMR of 1,4-difluoro-2,3,6,7,10,11-hexamethoxytriphenylene (7)



Spectrum 8b: ^{19}F -NMR of 1,4-difluoro-2,3,6,7,10,11-hexamethoxytriphenylene (7)



Spectrum 8c: ¹³C - NMR of 1,4-difluoro-2,3,6,7,10,11-hexamethoxytriphenylene (**7**)

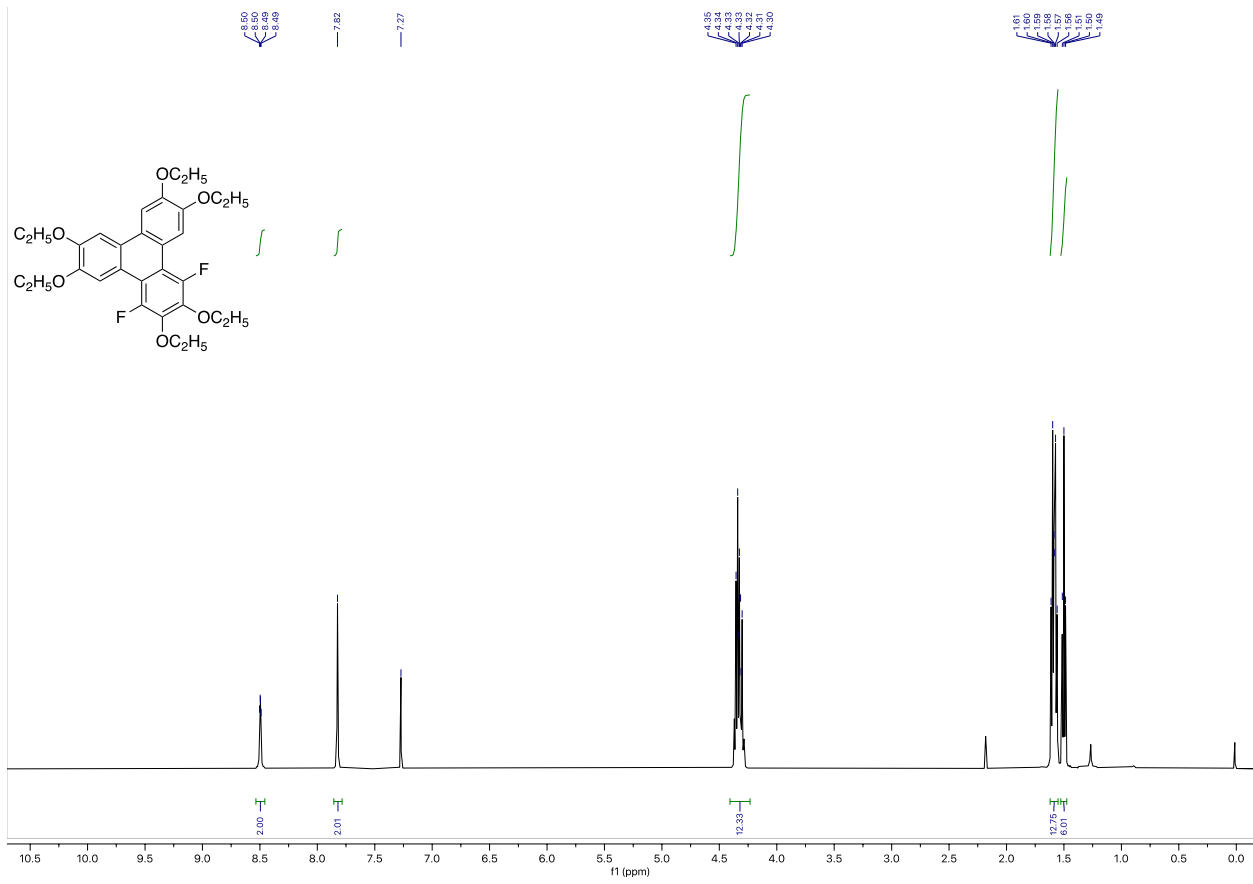
1,4-difluoro-2,3,6,7,10,11-hexaethoxytriphenylene (**8**)

In a 200 ml round bottom flask was placed 1,2,3,4-tetrafluoro-6,7,10,11-tetraethoxytriphenylene (0.11 g, 0.25 mmol), ethanol (8 ml), *t*-BuOK (0.33 g, 6.0 mmol), cyclohexane (15 ml) and THF (5 ml) under nitrogen atmosphere. The mixture was stirred, and temperature was raised and boiled for two days. The reaction it was monitored by TLC, but it never showed any new spot other than the reactant spot, however the reaction was terminated by cooling to room temperature and dropwise addition of 10% HCl (50 ml). The mixture was extracted with ethyl acetate, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to a residue which was found to be the desired product. The product was recrystallized from methanol. Yield- 0.08 g (67 %)

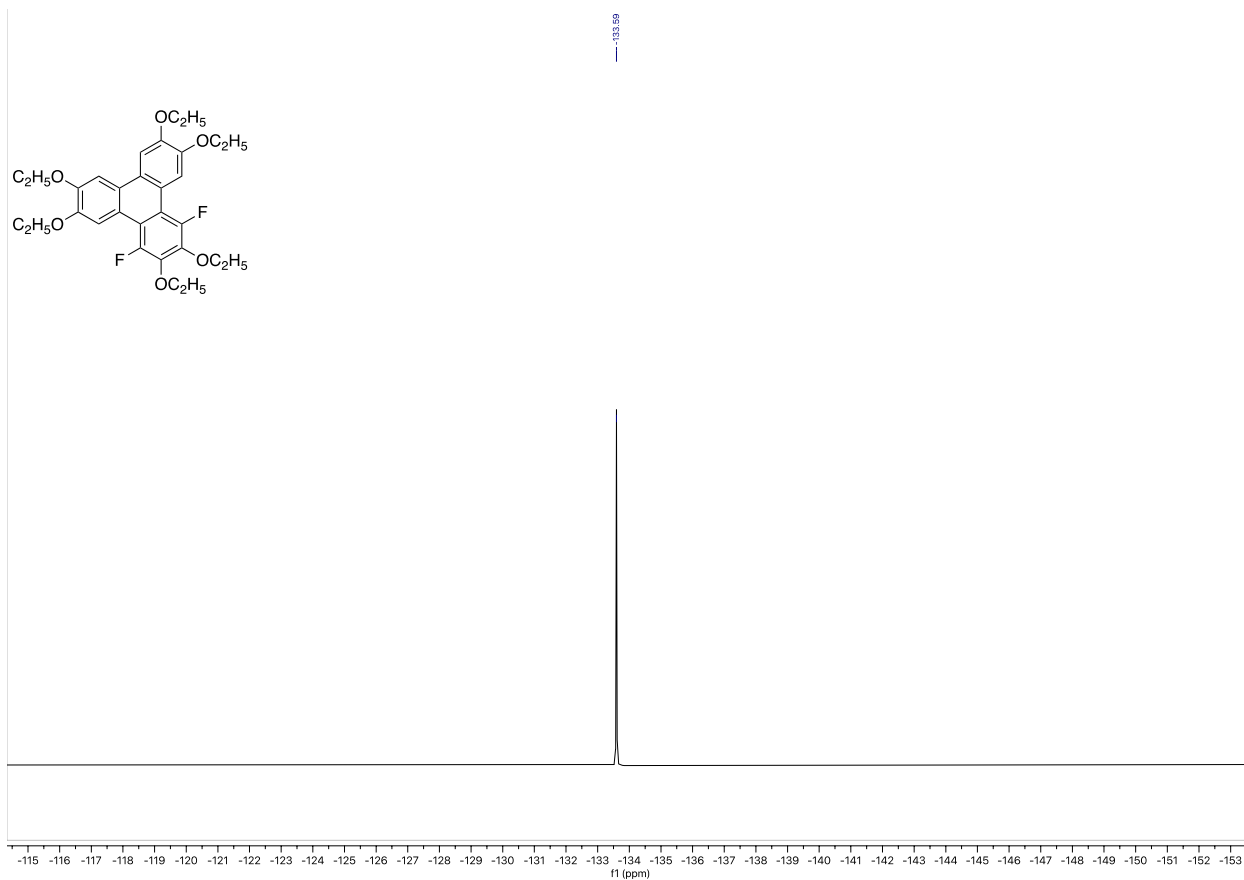
¹⁹F NMR (470 MHz, CDCl₃) δ -133.59 (m, 2F).

¹H NMR (500 MHz, CDCl₃) δ 8.50 (dd, *J* = 4.0, 2.3 Hz, 2H), 7.82 (s, 2H), 4.33 (dt, *J* = 12.2, 7.1 Hz, 12H), 1.59 (dt, *J* = 12.2, 7.0 Hz, 12H), 1.50 (t, *J* = 7.1 Hz, 6H).

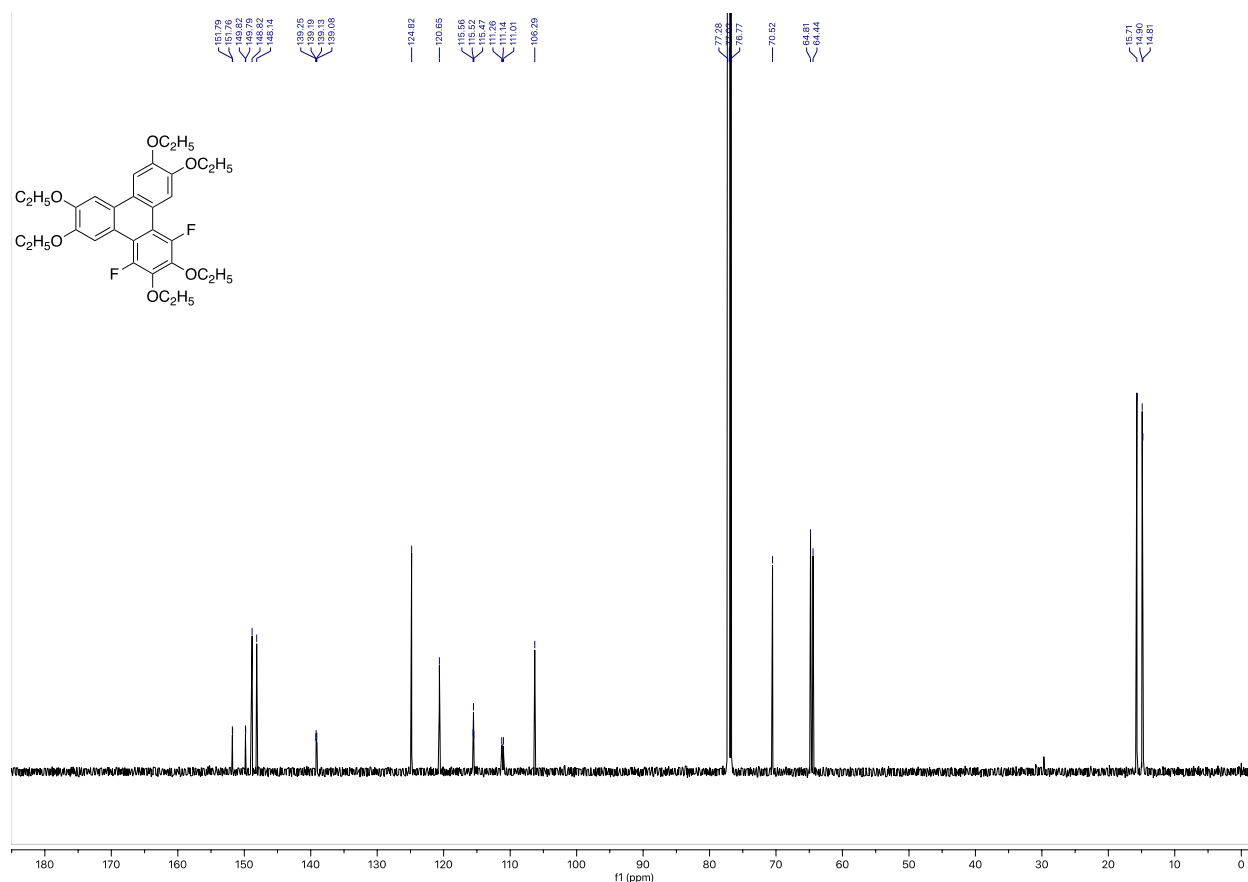
¹³C NMR (126 MHz, CDCl₃) δ 151.79, 151.76, 149.82, 149.79, 148.82, 148.14, 139.25, 139.19, 139.13, 139.08, 124.82, 120.65, 115.56, 115.52, 115.47, 111.26, 111.01, 106.29, 70.52, 64.81, 64.44, 15.71, 14.90, 14.81.



Spectrum 9a: ¹H - NMR of 1,4-difluoro-2,3,6,7,10,11-hexaethoxytriphenylene (**8**)



Spectrum 9b: ^{19}F - NMR of 1,4-difluoro-2,3,6,7,10,11-hexaethoxytriphenylene (**8**)



Spectrum 9c: ^{13}C - NMR of 1,4-difluoro-2,3,6,7,10,11-hexaethoxytriphenylene (**8**)

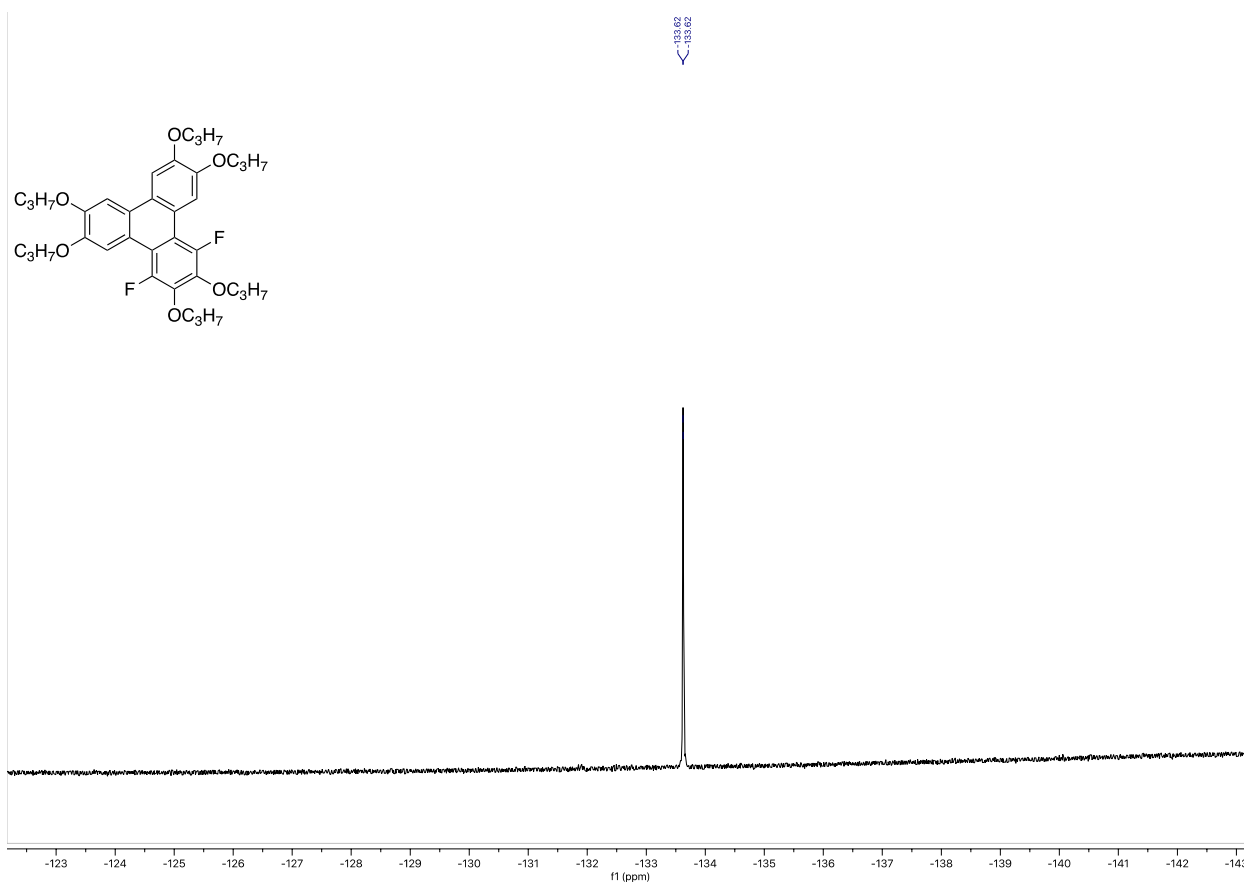
1,4-difluoro-2,3,6,7,10,11-hexapropoxytriphenylene (**9**)

In a 200 ml round bottom flask was placed 1,2,3,4-tetrafluoro-6,7,10,11-tetrapropoxytriphenylene (0.13 g, 0.25 mmol), 1-propanol (8 ml), *t*-BuOK (0.33 g, 6.0 mmol) and dioxane (20 ml). The mixture was stirred, and the mixture was boiled for two days. The reaction it was monitored by TLC, but it never showed any new spot other than the reactant spot, however the reaction was terminated by cooling to room temperature followed by dropwise addition of 10% HCl (50 ml). The mixture was extracted with ethyl acetate and dried over anhydrous magnesium sulfate then concentrated under reduced pressure to get a brown residue. The product was recrystallized from methanol. Yield – 0.09 g (64 %)

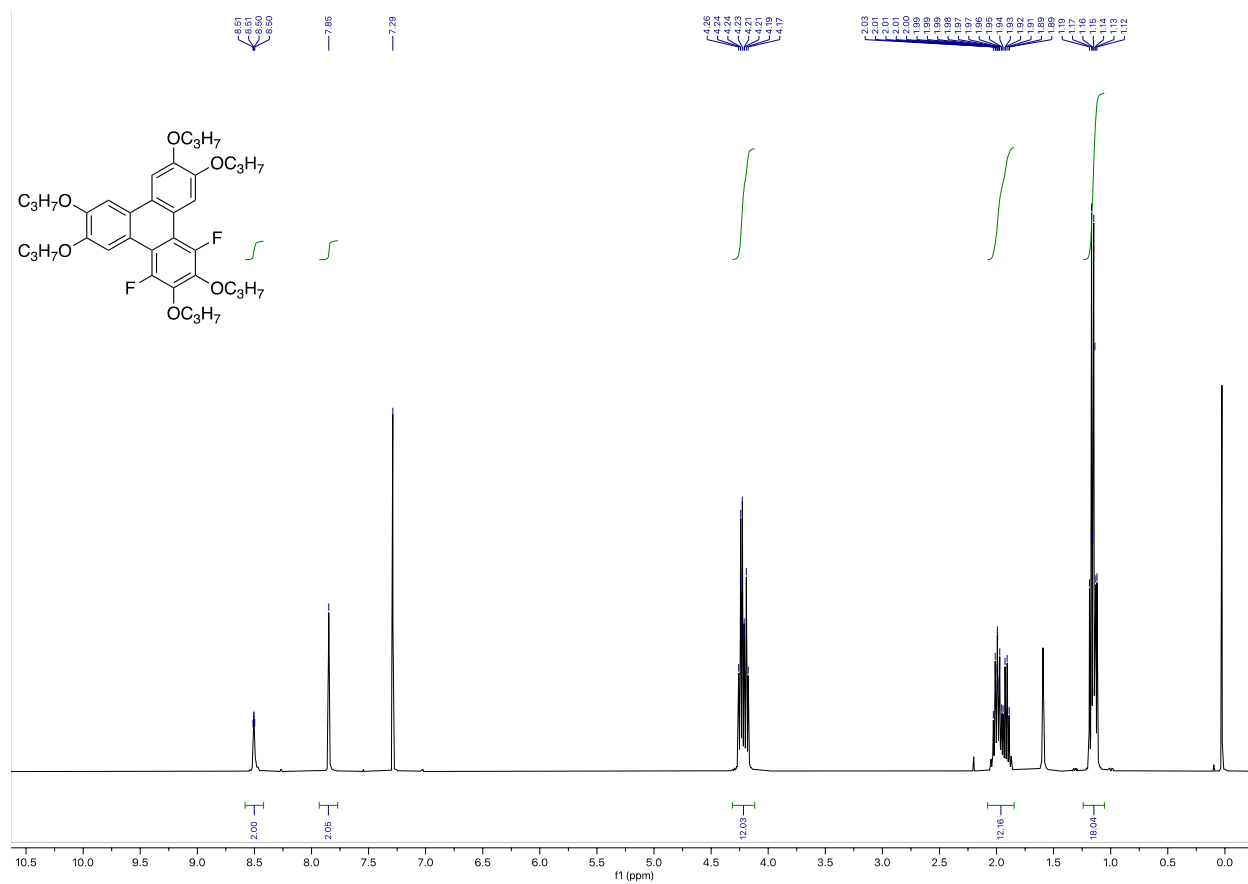
^{19}F NMR (376 MHz, CDCl_3) δ -133.62 (d, 2F).

^1H NMR (400 MHz, CDCl_3) δ 8.50 (dd, J = 3.8, 2.3 Hz, 2H), 7.85 (s, 2H), 4.30 – 4.15 (m, 12H), 2.07 – 1.85 (m, 12H), 1.23 – 1.10 (m, 18H).

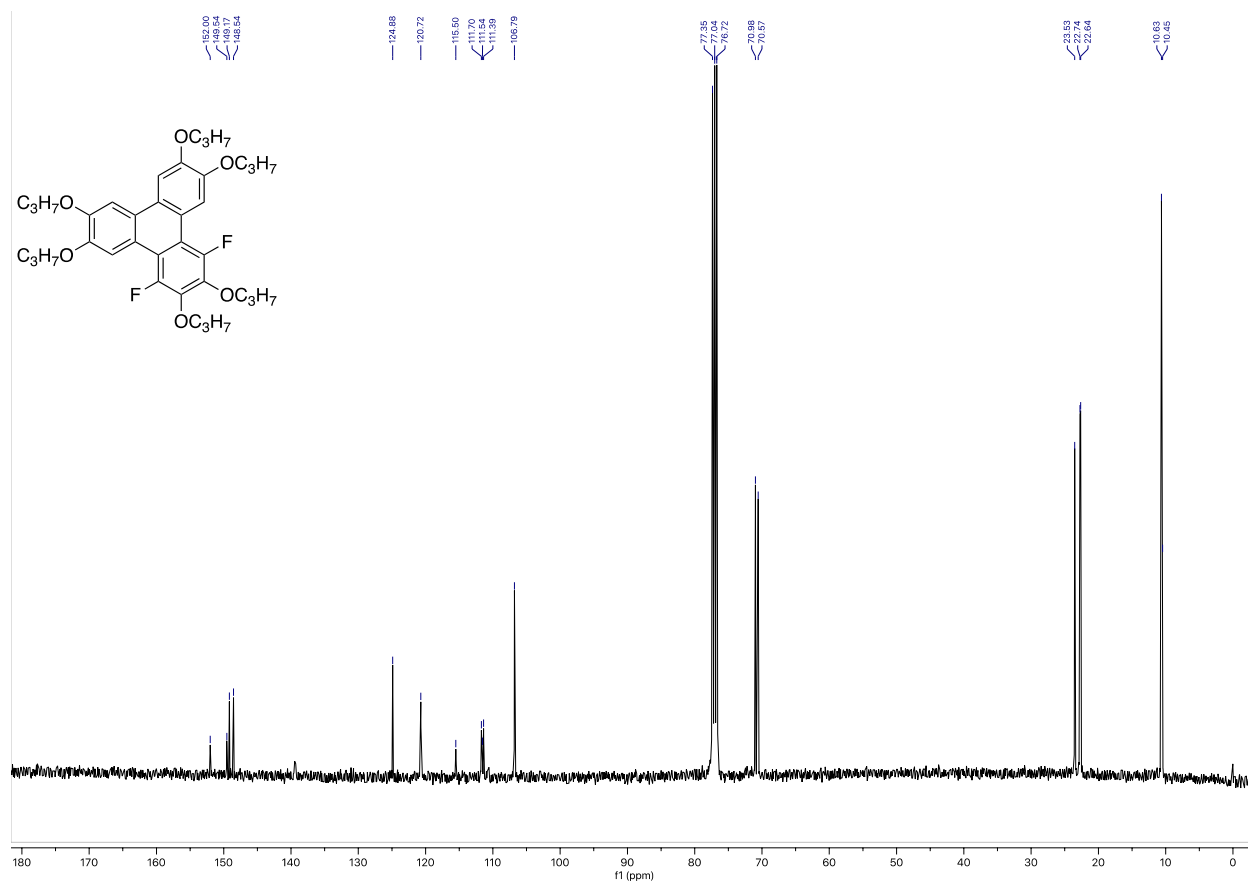
^{13}C NMR (101 MHz, CDCl_3) δ 124.88, 120.72, 115.50, 111.70, 111.54, 111.39, 106.79, 70.98, 70.57, 23.53, 22.74, 22.64.



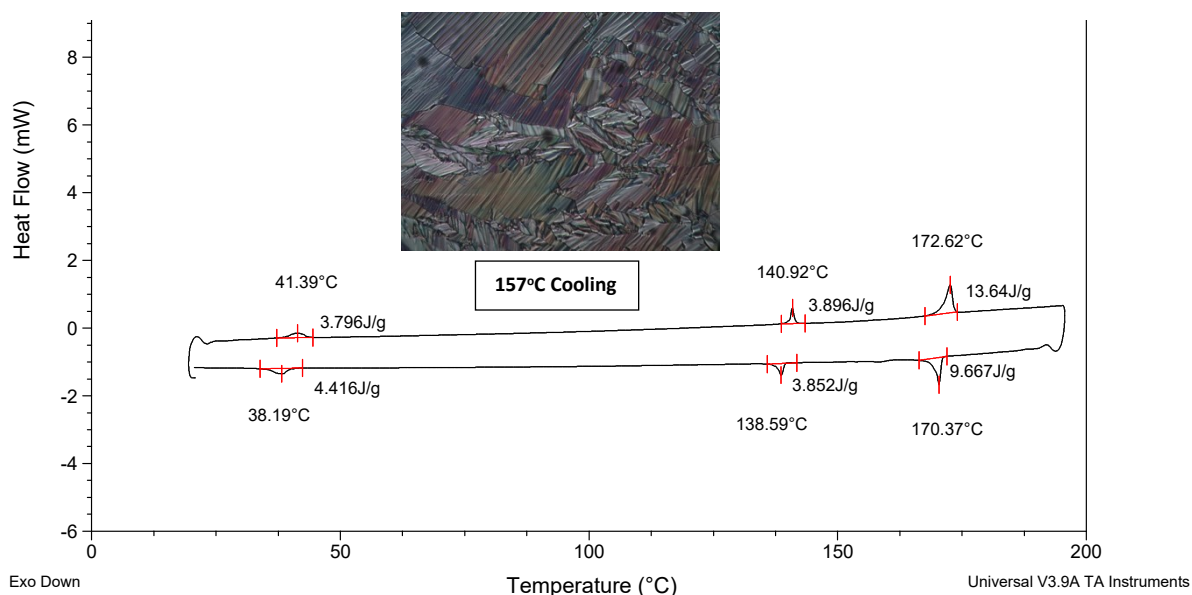
Spectrum 10a: ^{19}F - NMR of 1,4-difluoro-2,3,6,7,10,11-hexapropoxytriphenylene (9)



Spectrum 10b: ¹H - NMR of 1,4-difluoro-2,3,6,7,10,11-hexapropoxytriphenylene (9)



Spectrum 10c: ¹³C - NMR of 1,4-difluoro-2,3,6,7,10,11-hexapropoxytriphenylene (9)



Thermogram 1: A DSC scan (2nd cycle) of 1,4-difluoro-2,3,6,7,10,11-hexapropoxytriphenylene and a POM image of the compound while cooling down from isotropic liquid at 157°C (9)

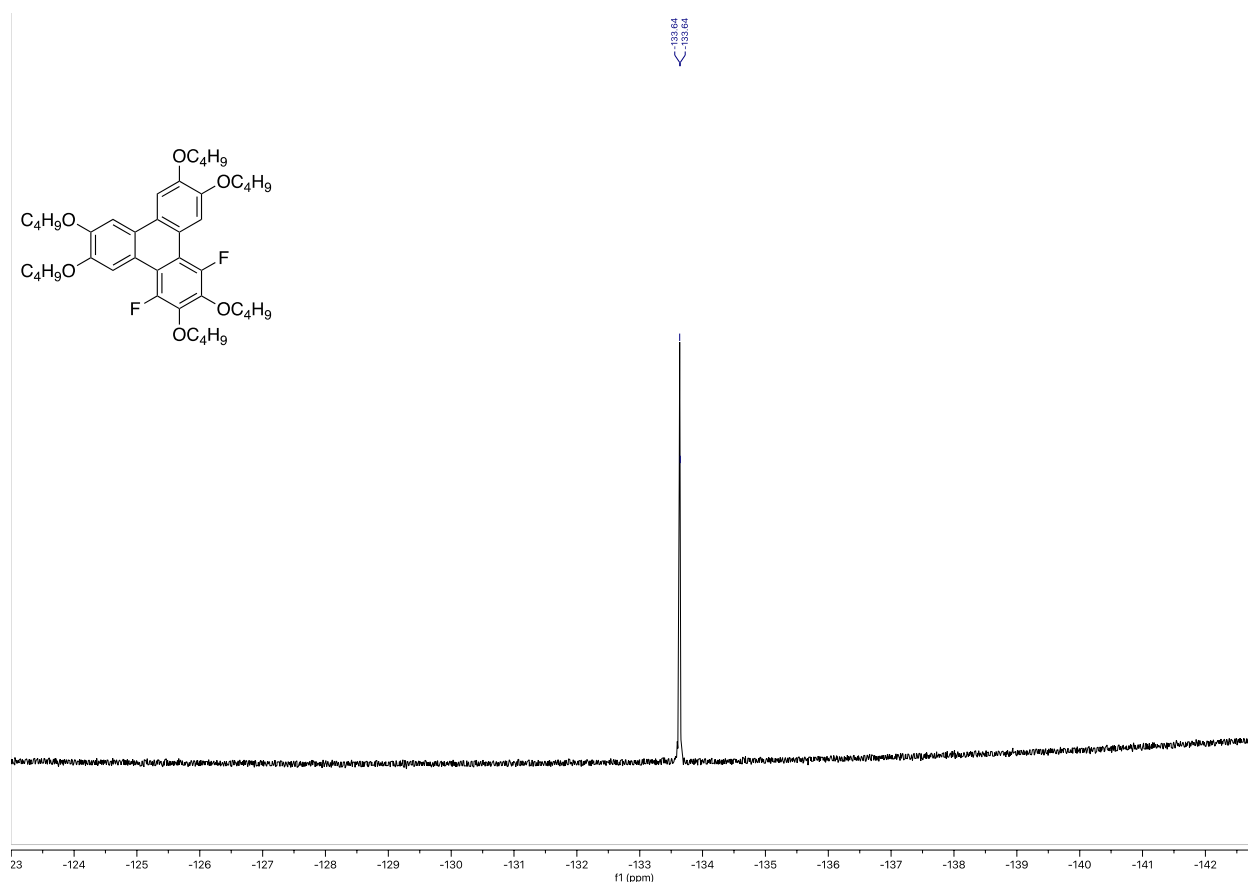
1,4-difluoro-2,3,6,7,10,11-hexabutoxytriphenylene (10)

In a 200 ml round bottom flask was placed 1,2,3,4-tetrafluoro-6,7,10,11-tetrabutoxytriphenylene (0.13 g, 0.25 mmol), 1-butanol (8 ml), *t*-BuOK (0.35 g, 6.0 mmol) and toluene (20 ml). The mixture was stirred and boiled for two days. The reaction it was monitored by TLC, but it never showed any new spot other than the reactant spot, however the reaction was terminated by cooling to room temperature followed by dropwise addition of 10% HCl (50 ml). The mixture was extracted with ethyl acetate, dried over anhydrous magnesium sulfate, filtered and then concentrated under reduced pressure to provide brown sticky residue which was recrystallized from methanol to obtain the pure product. Yield- 0.10 g (67 %)

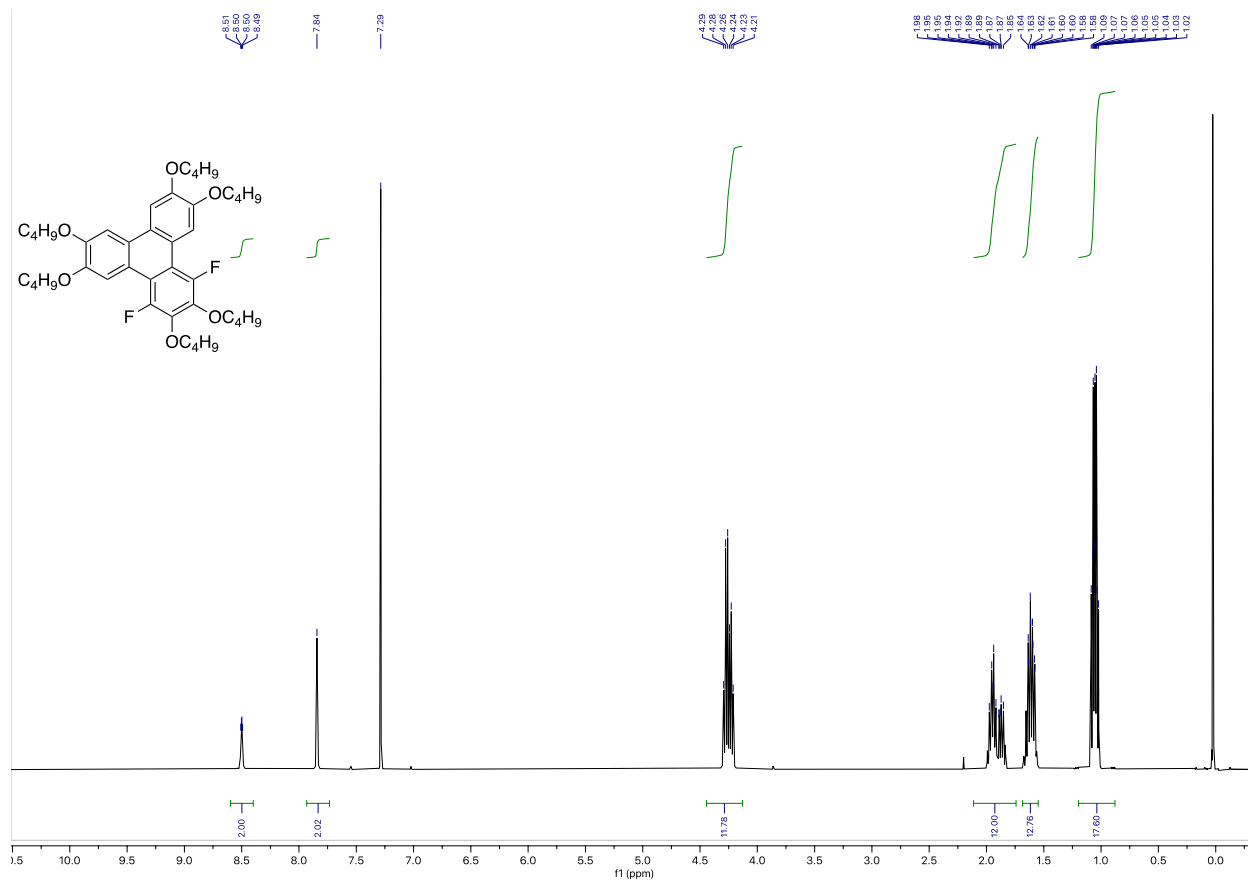
^{19}F NMR (376 MHz, CDCl_3) δ -133.64 (d, $J = 3.2$ Hz).

^1H NMR (400 MHz, CDCl_3) δ 8.50 (dd, $J = 3.8, 2.3$ Hz, 2H), 7.84 (s, 2H), 4.25 (dq, $J = 12.8, 6.7$ Hz, 12H), 2.01 – 1.81 (m, 12H), 1.72 – 1.54 (m, 12H), 1.11 – 1.00 (m, 18H).

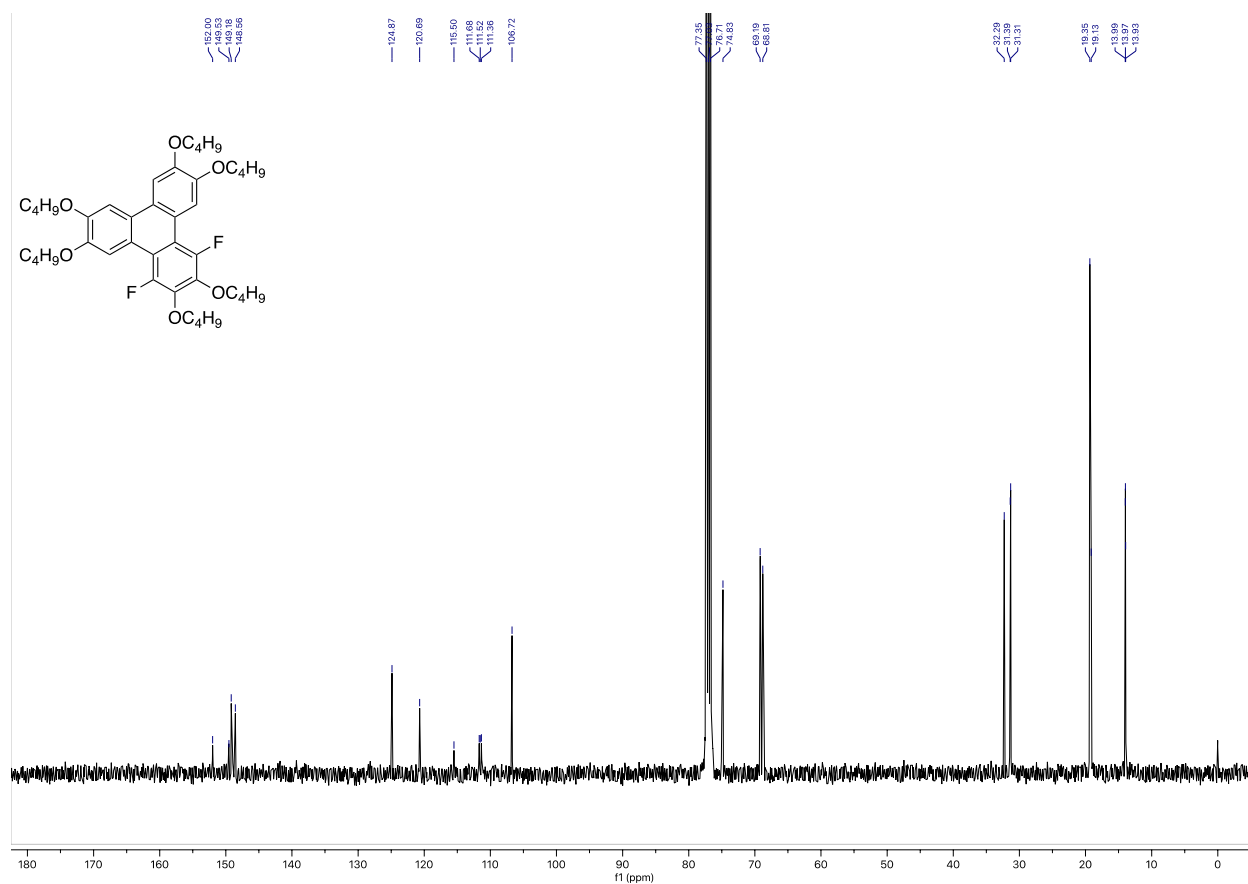
^{13}C NMR (101 MHz, CDCl_3) δ 152.00, 149.53, 149.18, 148.56, 124.87, 120.69, 115.50, 111.68, 111.52, 111.36, 106.72, 74.83, 69.19, 68.81, 32.29, 31.39, 31.31, 19.35, 19.13, 13.99, 13.97, 13.93.



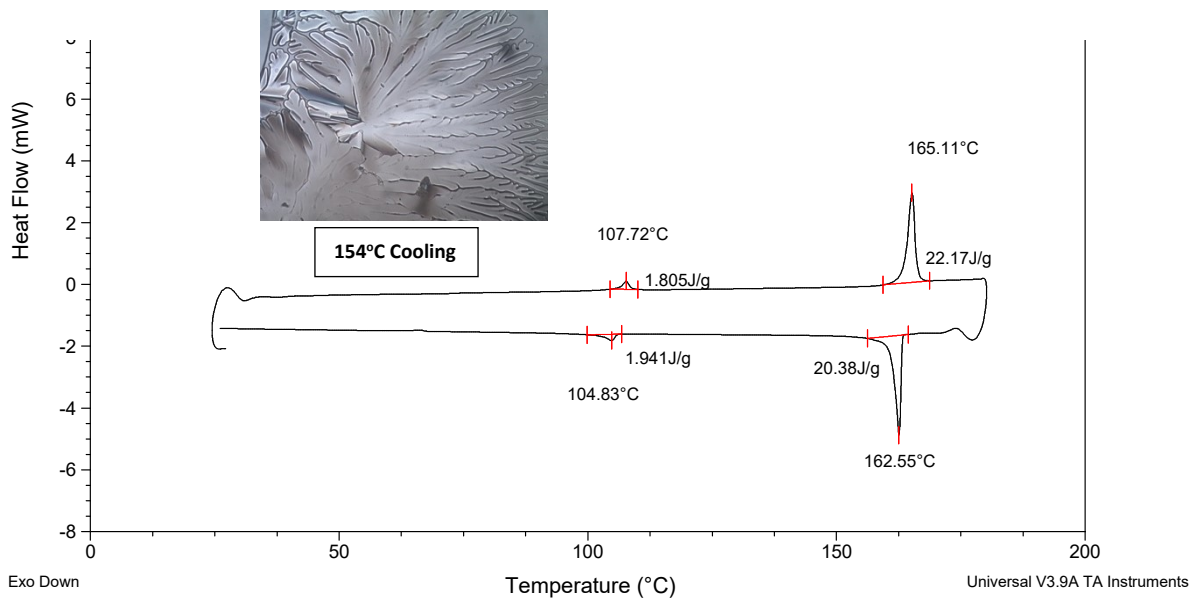
Spectrum 11a: ^{19}F - NMR of 1,4-difluoro-2,3,6,7,10,11-hexabutoxytriphenylene (10)



Spectrum 11b: ^1H - NMR of 1,4-difluoro-2,3,6,7,10,11-hexabutoxytriphenylene (**10**)



Spectrum 11c: ^{13}C - NMR of 1,4-difluoro-2,3,6,7,10,11-hexabutoxytriphenylene (**10**)



Thermogram 2: A DSC scan (2nd cycle) of 1,4-difluoro-2,3,6,7,10,11-hexabutoxytriphenylene and a POM image of the compound while cooling down from isotropic liquid at 154°C (**10**)