Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Spontaneous Mirror Symmetry Breaking and Chiral Segregation in an Achiral Ferronematic Compound DIO

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Synthesis of DIO

Reagents

2-propylpropane-1,3-diol, 3,5-difluorobenzaldehyde, 5-bromo-1,2,3-trifluorobenzene, 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane), 4-bromo-3-fluorophenol, [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (1:1), 1,2-dimethoxyetane, N,N'-dicyclohexylcarbodiimide, 4-(dimethylamino)pyridine, 1,4-dioxane, potassium acetate, caesium carbonate, p-toluenesulfonic acid monohydrate, butylated hydroxytoluene and all solvents were used as purchased from Sigma Aldrich, Fisher Scientific or Fluorochem.

Thin Layer Chromatography

Reactions were monitored using thin layer chromatography, and the different solvent mixture system, using Sigma Aldrich TLC Silica gel 60 $F_{254,}$ 25 Aluminium sheets 20×20 cm. UV-vis light was used to observe the TLC.

Column Chromatography

Column chromatography was carried out using silicagel 60A 35-70 micron particle size, purchased from Fluorochem, and the solvent using all purchase from Fisher Scientific.

Structure characterisation

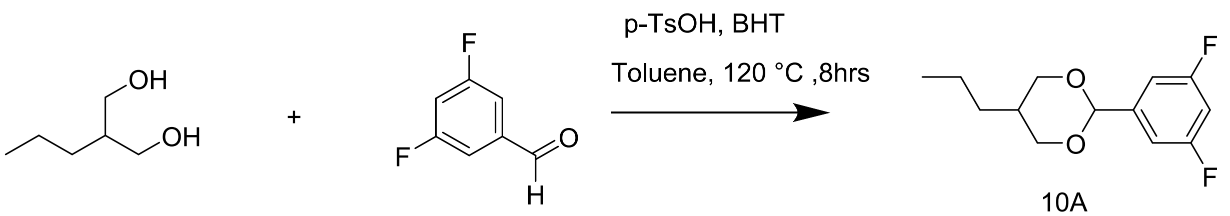
The NMR results were obtained from a 400 MHz ASC64 JEOL RESONANCE NMR spectrometer.

Purity Analysis

The purity of the final product was measured by high-resolution mass spectrometry using ***mass spectroscopy by Mr Dean Moore at University of Hull.

The synthesis of the material DIO (2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoate) follows broadly the synthetic procedures described in the literature. [1,2]

2-(3,5-difluorophenyl)-5-propyl-1,3-dioxane



10A

Scheme 1 Synthesis of 2-(3,5-difluorophenyl)-5-propyl-1,3-dioxane

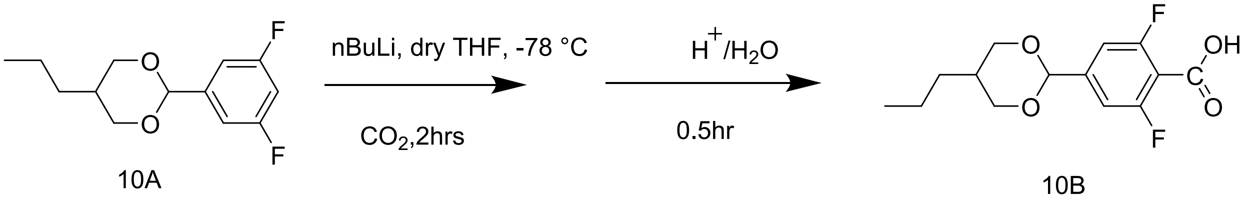
2-propylpropane-1,3-diol (3.80 g, 32 mmol), 3,5-difluorobenzaldehyde (3.80 g, 26.8 mmol), butylated hydroxytoluene (0.0888 g, 0.40 mmol), p-toluenesulfonic acid monohydrate (0.255 g, 1.34 mmol) were added to 180 mL toluene in a 250 mL flask and reflux at 140℃ overnight. Toluene was removed by vacuum. This was followed by extraction with DCM and the organic layer was gathered and dried over $MgSO_4$. The organic solvent was removed by rotary evaporation. The crude was purified by flash column chromatograph using a 1:50 mixture of hexane: DCM as eluent. It was used for further reactions without further purification.

Yield 5.81 g, 89.3%

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.11 – 6.95 (2H, m), 6.77 (1H, tt, *J* = 8.9, 2.4 Hz), 5.36 (1H, s), 4.23 (2H, dd, *J* = 11.8, 4.6 Hz), 3.51 (2H, t, *J* = 11.5 Hz), 2.22 – 2.05 (1H, m), 1.33 (2H, ddd, *J* = 20.1, 10.2, 5.1 Hz), 1.14 – 1.01 (2H, m), 0.94 (3H, dt, *J* = 11.8, 7.3 Hz).

Data consistent with reported values.

2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoic acid



Scheme 2 synthesis of 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoic acid

A 250 mL three-neck flask was loaded with **10 A** (0.456 g, 1.88 mmol) and dry THF 100 mL, then the mixture was supplied with nitrogen under -78 °C for 10 minutes. n-BuLi (2.5 M hexane solution, 0.9 mL, 2.25 mmol) was injected to the mixture dropwise over 10 min. After stirring 1 hour, an excess amount of dry ice was added into the solution under nitrogen atmosphere and stirred for 2 hours. After that the reaction mixture was quenched by 0.5 N diluted HCl solution. This was followed by extraction with ethyl acetate for three times. The combined organic layers were dried over $MgSO_4$. The solvent was removed through rotary evaporation and the crude product was purified with flash column chromatograph using ethyl acetate: methanol= 2:1. The acid was used without further purification.

Yield 0.24 g, 45%

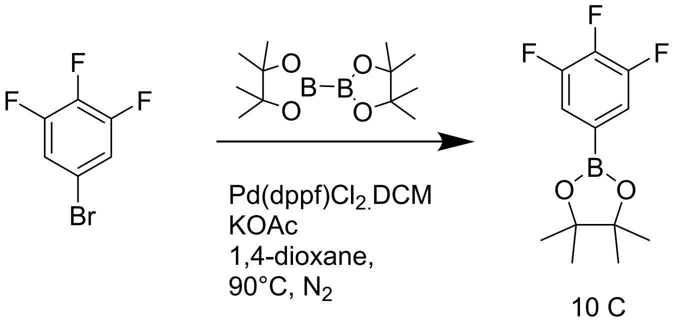
^{1}HNMR (400 MHz, $CDCl_3$): δ 7.14 (2H, t, J = 11.2 Hz), 5.37 (1H, s), 4.24 (2H, dd, J = 11.8, 4.6 Hz), 3.52 (2H, t, J = 11.5 Hz), 2.24 – 2.01 (1H, m), 1.46 – 1.23 (2H, m), 1.21 – 1.02 (2H, m), 0.94 (3H, dt, J = 11.5, 7.4 Hz).

^{13}CNMR (101MHz, $CDCl_3$) : δ166.91, 162.46, 159.89, 145.21, 110.41, 110.14, 98.94, 72.6, 33.93,30.26,19.59,14.26

^{19}F-NMR (377 MHz, $CDCl_3$): δ -107.8

Data consistent with reported values.

4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane



Scheme 3 Synthesis of 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane

5-bromo-1,2,3-trifluorobenzene (30 g, 0.142 mol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (30.1 g, 0.118 mol) and potassium acetate (35.9 g, 0.366 mol) were added to a 500 mL in a three neck round bottom flask, and then were dissolved in 1,4-dioxane (300 mL) and nitrogen was bubbled through the solution for 30 minutes. $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (5.36 g, 5.9 mmol) was added in one portion and the reaction was heated to reflux under a nitrogen atmosphere for 2 days. After cooling to ambient temperature, the reaction mixture was filtered through celite, and the filtrate was concentrated in vacuo. The residue was purified through flash column chromatograph using pure hexane and after the starting material washed out, the solvent mixture ethyl acetate: hexane= 1:1 was used to eluate the pure compound. The pure compound is a colourless oil.

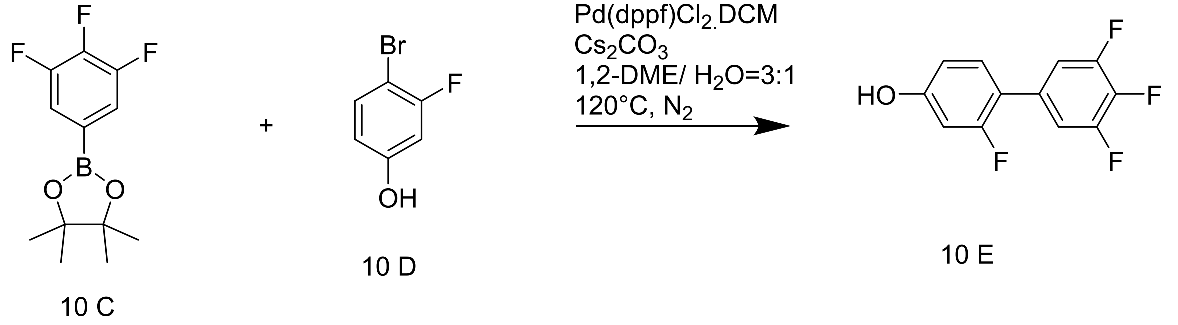
Yield 22.8 g, 74.8 %

^{1}HNMR (400 MHz, $CDCl_3$): δ 7.41 – 7.31 (2H, m), 1.30 (12H, d, *J* = 14.3 Hz).

^{13}CNMR (101 MHz, $CDCl_3$): δ 152.43, 149.93, 143.30, 140.76, 118.45, 84.73, 24.85

^{19}FNMR (377 MHz, $CDCl_3$): δ -135.64, -156.90

2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-ol



Scheme 4 Synthesis of 2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-ol

4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane **10 C** (5.92 g, 22.9 mmol), 4-bromo-3-fluorophenol **10 D** (3.37 g, 17.7 mmol) and caesium carbonate (1.6 g, 1.77 mmol) were dissolved in a mixture of 1,2-dimethoxyethane (75 mL) and water (25 mL) in a 250 mL three neck round bottom flask. Nitrogen gas was bubbled through the solution for 15 minutes, Pd(dppf)Cl2.CH$_2$Cl2 (1.6 g, 1.77 mmol) was added in one portion and the reaction was heated to reflux under a nitrogen atmosphere for 1 day. After cooling to ambient temperature, the solvent was removed and the reaction mixture was then extracted by ethyl acetate in brine. This was followed by filtration through celite and the solvent was removed under vacuum through rotary evaporation. The residue was purified through flash column chromatograph using the solvent mixture ethyl acetate: hexane= 1: 6. Further purification using recrystallization in hexane produced a white solid.

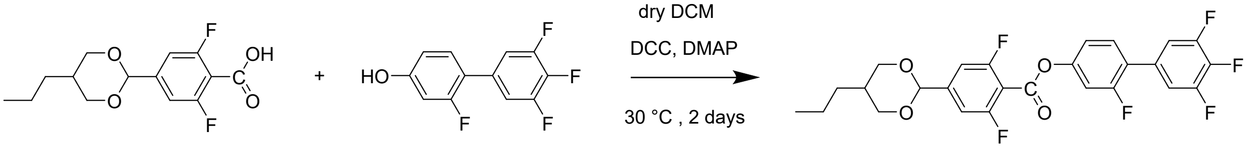
Yield 3.12 g, 92.4 %

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.22 (1H, d, *J* = 8.5 Hz), 7.16 – 7.08 (2H, m), 6.73 – 6.64 (3H, m).

^{13}C-NMR (101 MHz, CDCl$_3$): δ 161.44, 158.96, 157.17, 152.47, 149.99, 140.39, 137.89, 131.63, 130.97, 118.98, 113.03, 112.84, 112.09, 104.22, 103.96

^{19}F-NMR (377 MHz, CDCl$_3$): δ -115.28, -134.65, -162.36

2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoate



10B

10 E

10F

Scheme 5 Synthesis of 2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoate

2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-ol (0.93g, 3.84 mmol), 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoic acid (1.1 g, 3.84 mmol) were dissolved in dry DCM in a 250 mL three neck round bottom flask. Nitrogen gas was bubbled through the solution for 15 minutes, before N,N’-

dicyclohexylcarbodiimide (0.872 g, 4.22 mmol) and 4-(dimethylamino)pyridine (0.047 g, 0.384 mmol) were added. The mixture was heated to 30 ℃ and left stirring for 2 days. After that the mixture was passed through a filter to remove the solid dicyclohexylurea salt. DCM was removed by rotary evaporatorion under vacuum. The residue was purified through flash column chromatograph using solvent mixture ethyl acetate: hexane= 1:8. Followed by recrystallization with hexane for twice. The pure compound crystallized as a white solid.

Yield 1.49 g, 76 %

m/z: $[M+Na]^+$ Calculated mass for $C_{26}H_{20}F_6O_4Na$: 533.1163. Found: 533.1161.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 11.8, 5.5 Hz), 7.18 (ddd, *J* = 8.5, 8.0, 5.5 Hz), 5.42 (s), 4.27 (dd, *J* = 11.8, 4.6 Hz), 3.56 (t, *J* = 11.5 Hz), 2.27 – 2.04 (m), 1.44 – 1.29 (m), 1.20 – 1.05 (m), 0.95 (t, *J* = 7.3 Hz).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 162.24, 160.66, 159.73, 159.34, 152.53, 151.10, 150.99, 149.91, 145.79, 140.33, 138.31, 130.71, 124.37, 118.21, 113.40, 110.82, 110.56, 110.48, 110.24, 109.43, 98.84, 72.64, 33.98, 30.29, 19.61, 14.25

^{19}F-NMR (377 MHz, $CDCl_3$): δ -108.33, -114.25, -134.05, -161.02

Proton-Fluorine-Carbon: δ 160.99,159.37, 151.25, 151.03, 145.70, 140.95, 138.50, 130.90, 130.72, 124.37, 118.23, 113.29, 110.72, 110.38, 109.48, 98.86, 72.66, 33.96, 30.27, 19.58, 14.25

Detailed calorimetric data have been reported in [3].

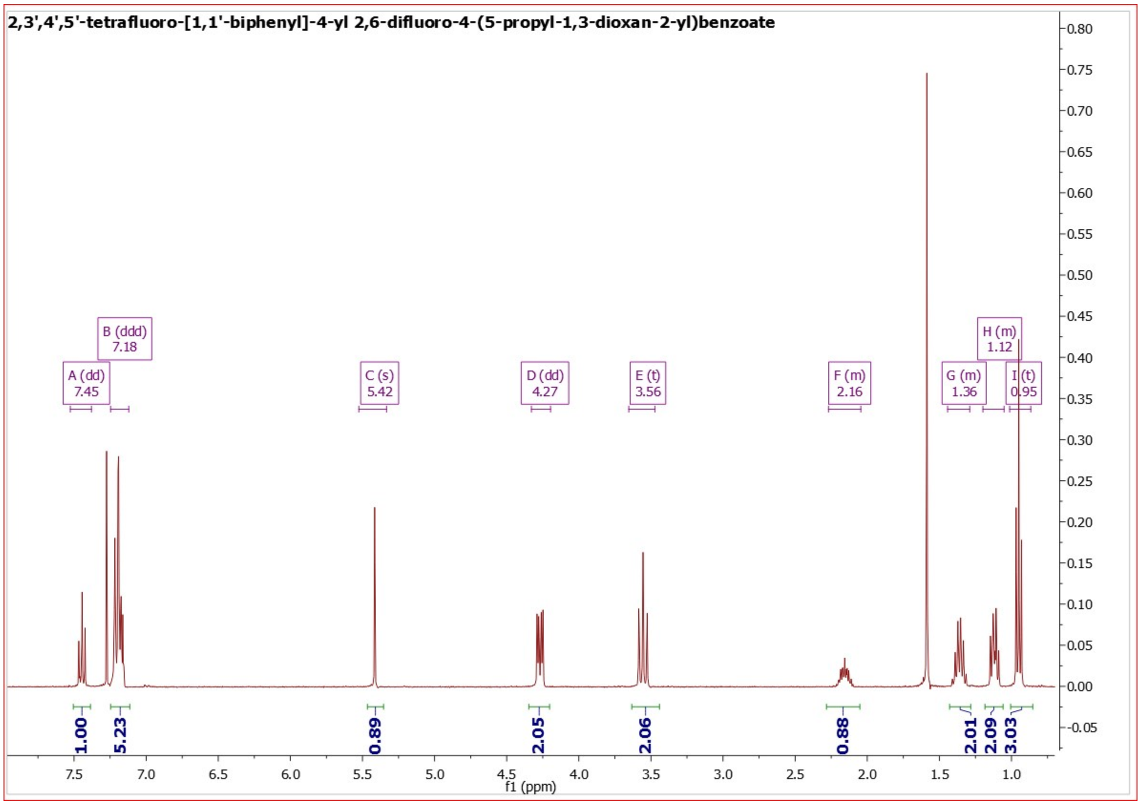


Figure 1. ^{1}HNMR spectrum of 2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoate

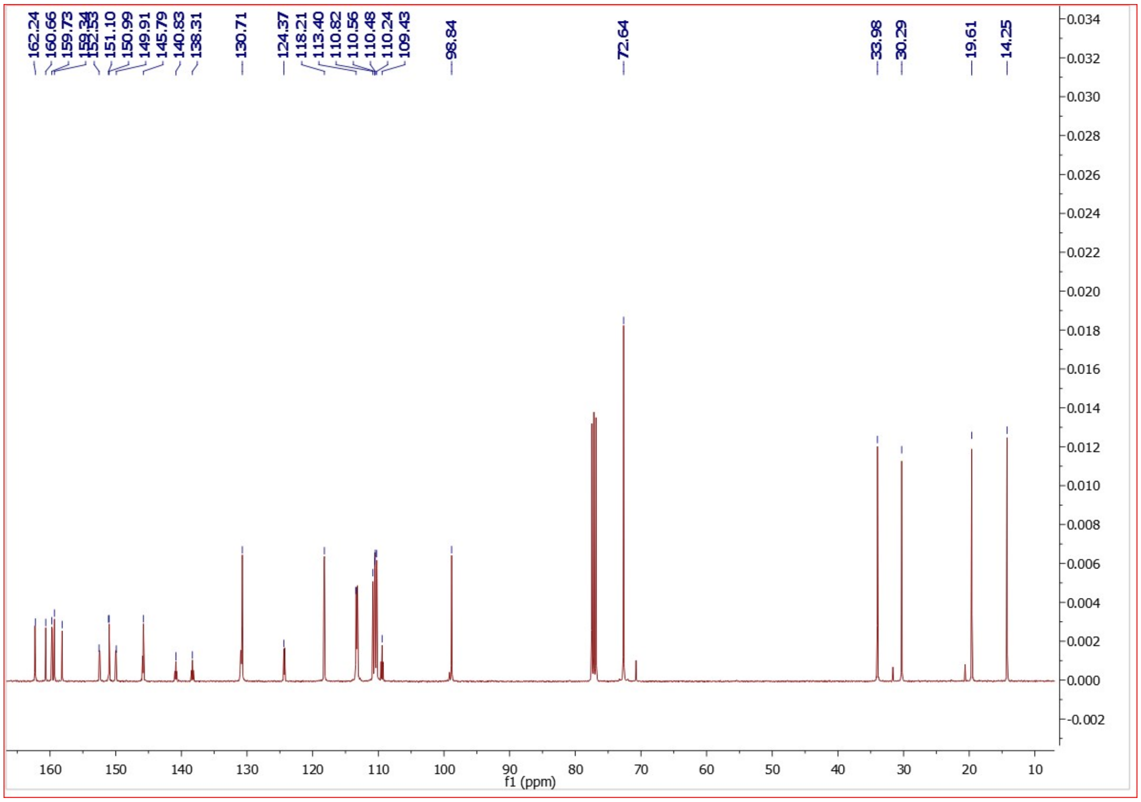


Figure 2. ^{13}CNMR spectrum of 2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoate

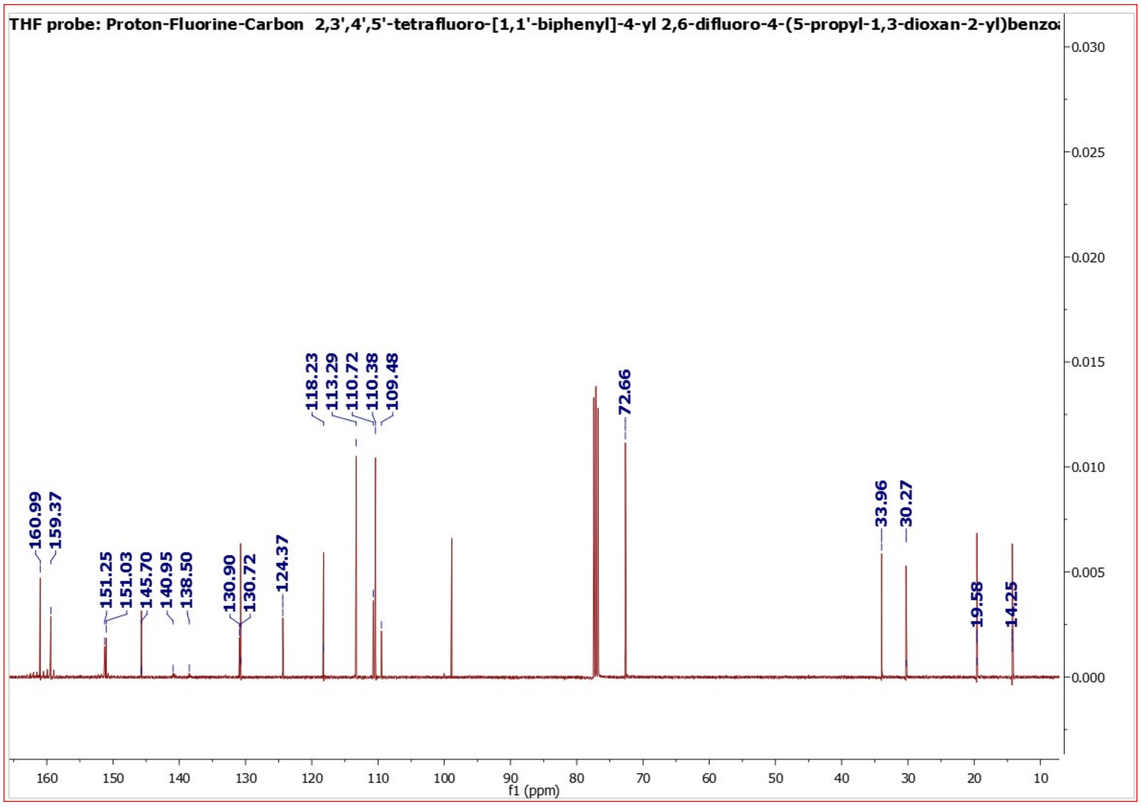


Figure 3. Proton-Fluorine-Carbon decoupled NMR spectrum of 2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoate

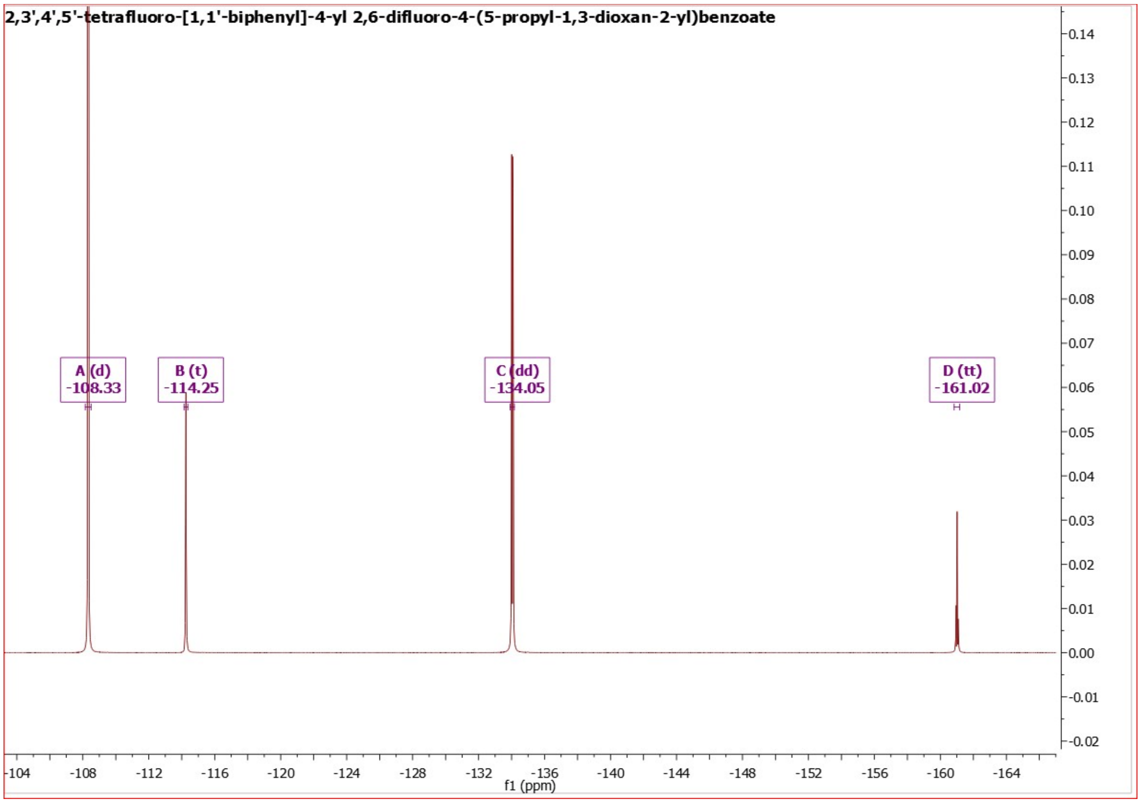


Figure 4. ^{19}FNMR spectrum of 2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoate

References

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[3] J. Thoen, G. Cordoyiannis, W. Jiang, G. H. Mehl, C. Glorieux, *Phase transitions study of the liquid crystal DIO with a ferroelectric nematic, a nematic and an intermediate phase and of mixtures with the ferroelectric nematic compound RM734 by adiabatic scanning calorimetry*, Phys. Rev. E, 2023, **107**, 014701; DOI: 10.1103/PhysRevE.107.014701