Supplementary Information

Colossal permittivity and Superparaelectricity in phenyl pyrimidine based liquid crystals

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1 Synthesis of Compounds

1.1 Scheme of Synthesis for WJ16 and WJ18

2-propylpropane-1,3-diol, 3,5-difluorobenzaldehyde, 5-bromo-1,2,3-trifluorobenzene, n-butyllithium 1.6M in hexanes, dry ice, 2-bromopyrimidin-5-ol, (bromomethyl)benzene, 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), , N,N'-dicyclohexylcarbodiimide, 4-(dimethylamino) pyridine, hydrogen, potassium acetate, caesium carbonate, p-toluenesulfonic acid monohydrate, butylated hydroxytoluene and all solvents were used as purchased from Sigma Aldrich, Fisher Scientific or Fluorochem.

Chemical Analysis

The samples were tested on a Bruker maxis, a Hybrid Quadrupole / Atmospheric Pressure Ionization orthogonal accelerated Time-Of-Flight mass spectrometer.

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

Elemental Analysis was collected from a FISONS Instruments EA 1108 CHN and using software Eager Xperience for processing the data.

Analysis was performed using an Agilent 1290 Infinity II HPLC system (Agilent, Santa Clara, CA, United States), with a diode array detector. Chromatographic separations were performed using an Agilent InfinityLab Poroshell 120 EC-C18 (2.1 x 50 mm, 1.9 um) at a column temperature of 40 ºC. The mobile phase used was 0.1 % TFA in water (95 %) and 0.1 % TFA in acetonitrile (5%) and the gradient running to 5 % water over 5 minutes and held at 95% acetonitrile for 2 minutes at a flow rate of 0.5 mL/min. The DAD recorded the chromatogram at a wavelength of 254 nm. Dr J. William, Analytical Services, University of Leeds is very gratefully acknowledged.

Simulations

The dipole moments of all compounds were calculated by Gaussian View 09, with the molecular parameters of energy-minimized conformations calculated using the OPT+FRE in B3LYP/ 6-31G(D, P) level of DFT. Empirical dispersion, GD3BJ.

Column Chromatography

Column chromatography was carried out using silica gel 60A 35–70-micron particle size, purchased from Fluorochem and the solvents used were all purchased from Fisher Scientific.

Recent reports [R1, R2] highlight the issue of stereoisomers relevant for the LC properties of 2,5-di-substituted 1,3-dioxanes compounds. The 2,5-di-substituted 1,3-dioxanes occur in principle in two conformations; eq-trans (trans C3) and ax-trans (cis C3), typically the less favoured isomer. The diastereomeric ratio of the isomers can affect LC phase properties. For DIO it was reported [S1, S2] that the ax-trans (cis C3) variant of DIO is non-mesogenic and that it has also a detrimental effect on the strong dipole-dipole interactions between the eq-trans

(trans C3) variant. The ax-trans isomer is characterized in the ^{1}H-NMR spectra by an additional small singlet next to singlet peak of eq-trans (trans C3) in the vicinity of ~5.4 ppm. The relevant regions of the spectra have been magnified [S13,S30,S34].

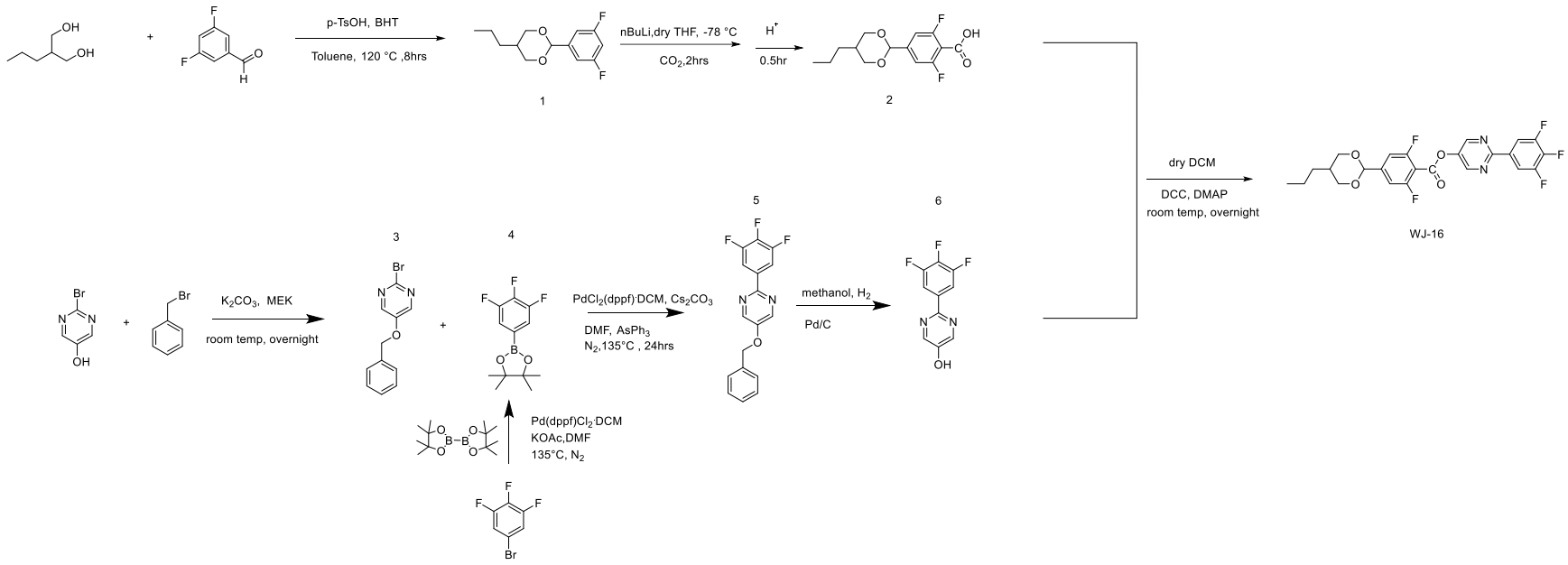
For 2-(3,4,5-trifluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate (**WJ-16**), a magnification of the area of the spectrum in the vicinity of the singlet peak at 5.41 ppm indicates that there is very limited evidence for a signal of the ax-trans (cis C3) diastereomer based on the sensitivity of the NMR spectrometer (1-2%). [S13]

For 2-(4-cyano-3,5-difluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate (**WJ-18**), a magnification of the area of the spectrum in the vicinity of the singlet peak at 5.41 ppm indicates that there is a very small signal at ~5.45 ppm indictive of ~1% ax-trans (cis of the ax-trans (cis C3) diastereomer, based on the sensitivity of NMR spectrometer. [S30]

For 2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoate (DIO) ,), a magnification of the area of the spectrum in the vicinity of the singlet peak at 5.41 ppm indicates that there is no indication for a signal of ax-trans (cis C3) diastereomer, based on the sensitivity of NMR spectrometer. [S34]

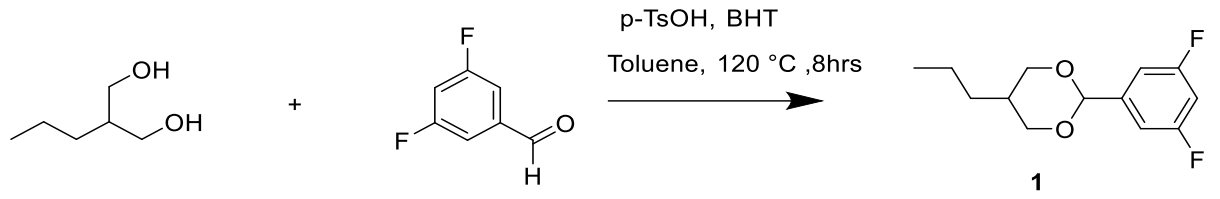
Reagents

2-propylpropane-1,3-diol, 3,5-difluorobenzaldehyde, 5-bromo-1,2,3-trifluorobenzene, n-butyllithium 1.6M in hexanes, dry ice, 2-bromopyrimidin-5-ol, (bromomethyl)benzene, 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), , N,N'-dicyclohexylcarbodiimide, 4-(dimethylamino) pyridine, hydrogen, potassium acetate, caesium carbonate, p-toluenesulfonic acid monohydrate, butylated hydroxytoluene and all solvents were used as purchased from Sigma Aldrich, Fisher Scientific or Fluorochem.



Scheme S1. Synthesis scheme for synthesis of 2-(3,4,5-trifluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate **WJ-16**

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



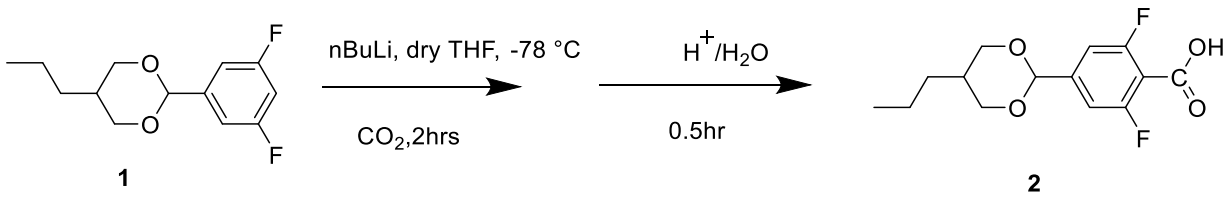
Scheme S2. Synthesis of 2-(3,5-difluorophenyl)-5-propyl-1,3-dioxane

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 refluxed 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 [R3].

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



Scheme S3. synthesis of 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoic acid

A 250 mL three-neck flask was loaded with **1** (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}H-NMR (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).

Proton-Fluorine-Carbon decoupled ^{13}CNMR: δ 166.74, 161.15, 145.14, 110.25, 109.82, 98.93, 72.58, 33.92, 30.23, 19.56, 14.22

^{19}F-NMR (376 MHz, $CDCl_3$): δ -107.8 (2F, d, d=9.3 Hz, Ar-F).

Data consistent with reported values [R3].

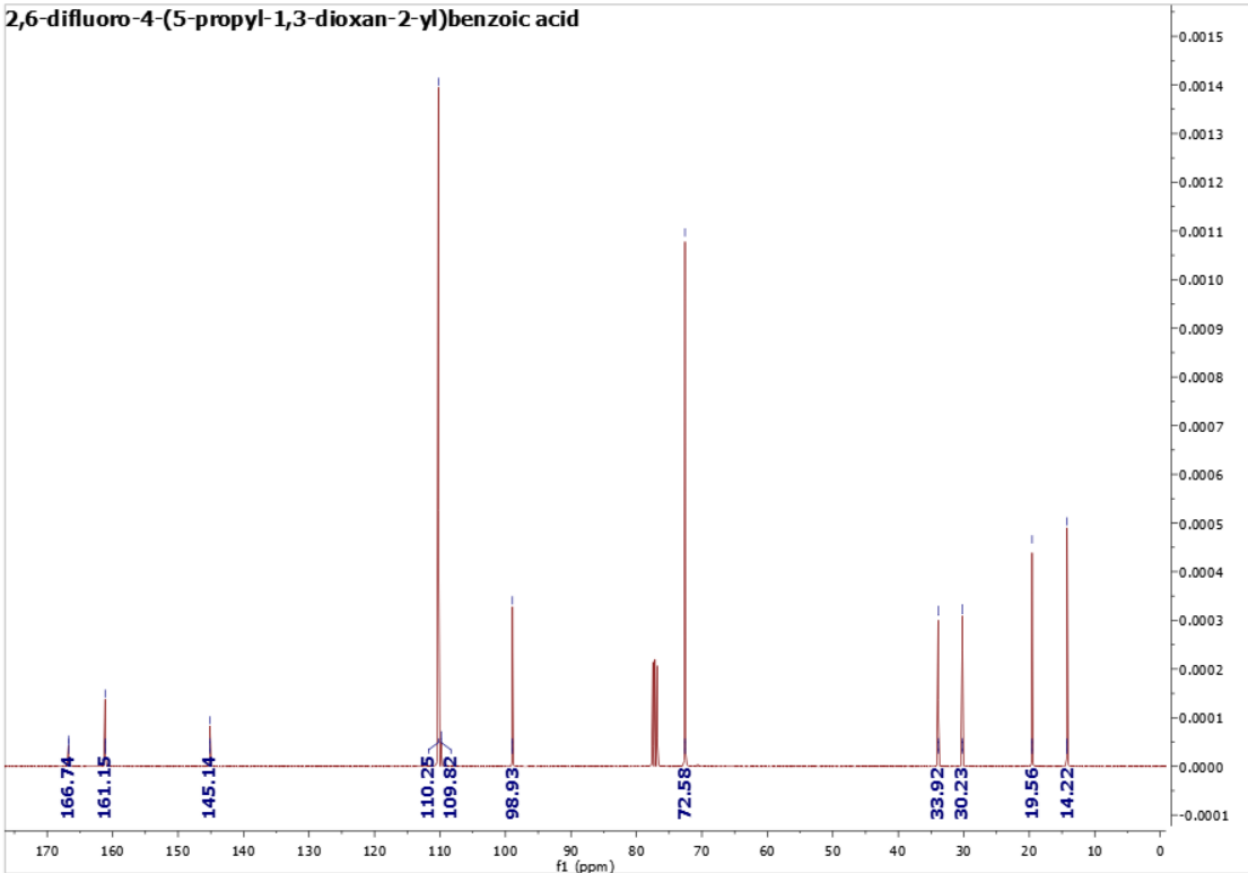
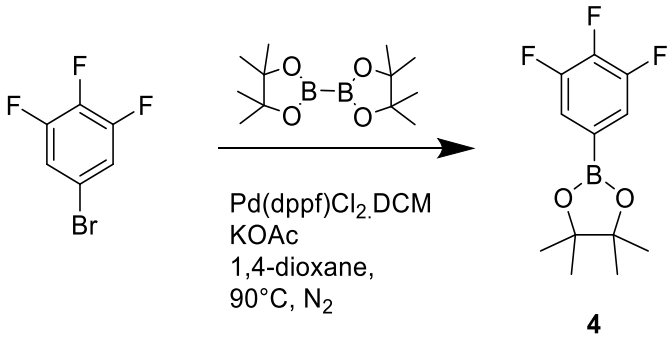


Figure S1. Proton-Fluorine-Carbon decoupled NMR spectrum of 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoic acid.

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



Scheme S4. 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 10 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 solvent was removed by vacuum and the related crude was extracted by chloroform. The solvent of organic layer was dried with magnesium sulphate and then passed through filter, 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 elute the pure compound. The pure compound is a colourless oil. **Yield 22.8 g, 74.8 %**

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

^{13}C-NMR (101 MHz, $CDCl_3$): δ 151.23 (dd, J_{C-F} = 249.6 Hz, 8Hz), 142.18 (dt, J_{C-F} = 254.9 Hz, 15Hz), 118.47 (dd, J_{C-F} = 14.2 Hz), 84.73 (s), 24.85 (s).

^{19}F-NMR (376 MHz, $CDCl_3$): δ -135.64 (2F, dd, J = 19.8, 7.8 Hz, Ar-F), -156.90 (1F, tt, J= 18.8 HZ, 7.5 HZ, Ar-F)

Data consistent with reported values [R4]

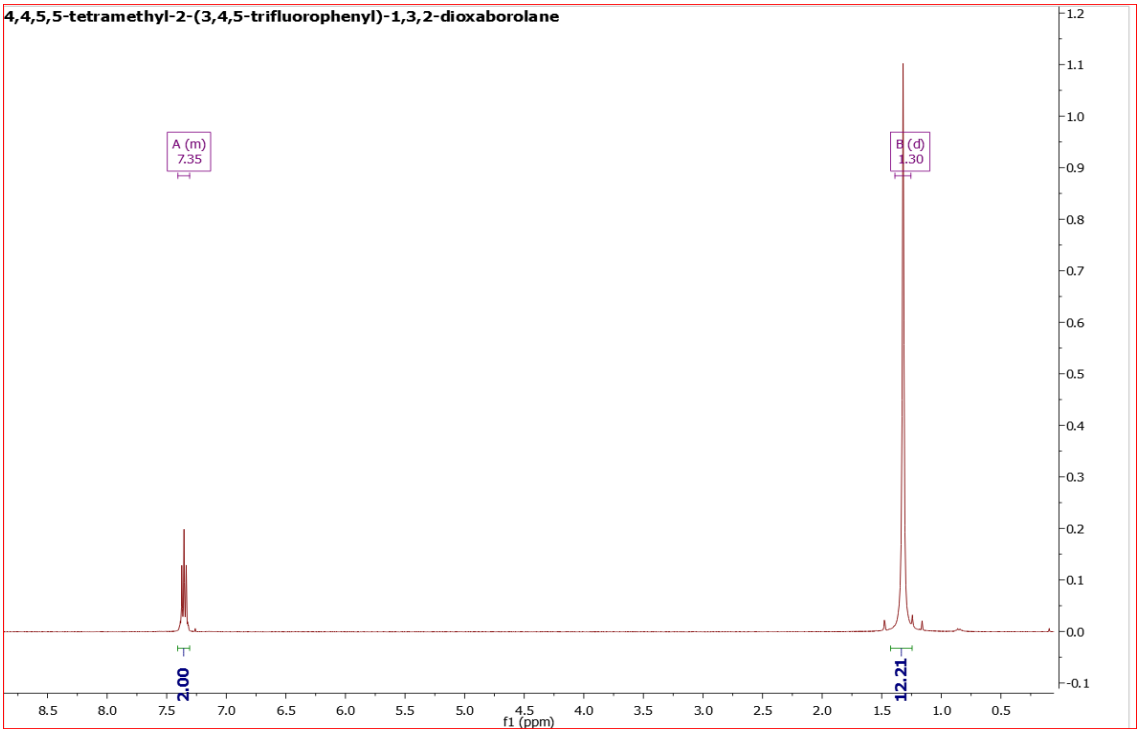


Figure S2. ^{1}H NMR of 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane

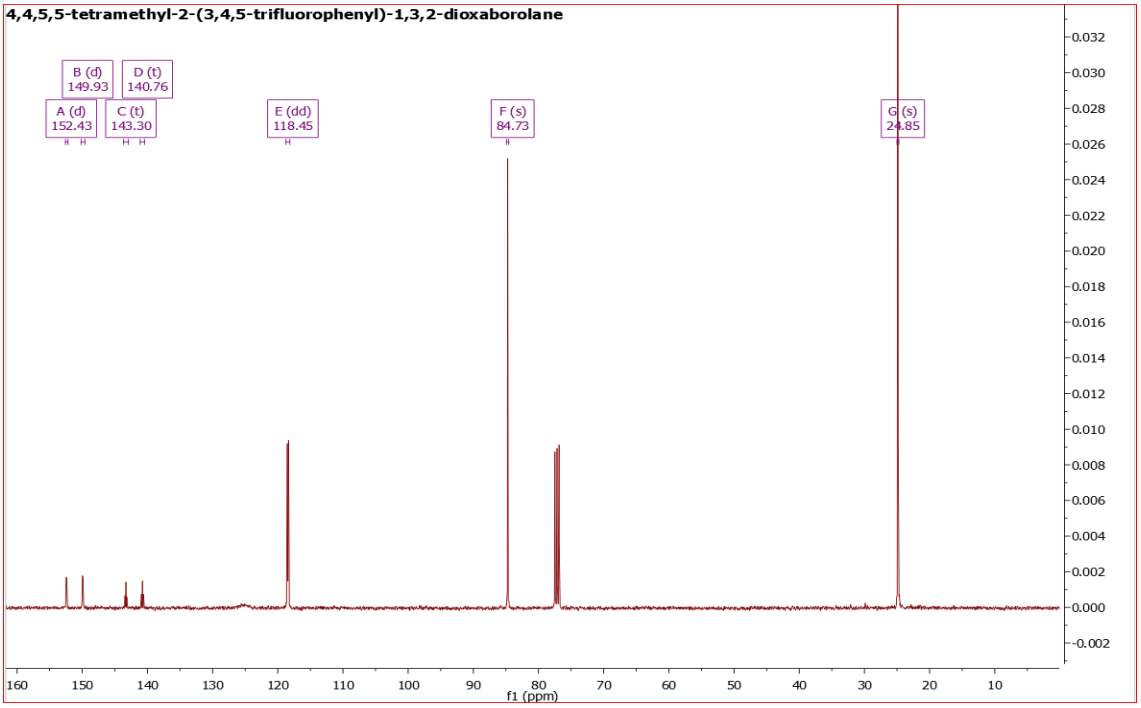


Figure S3. ^{13}C-NMR of 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane

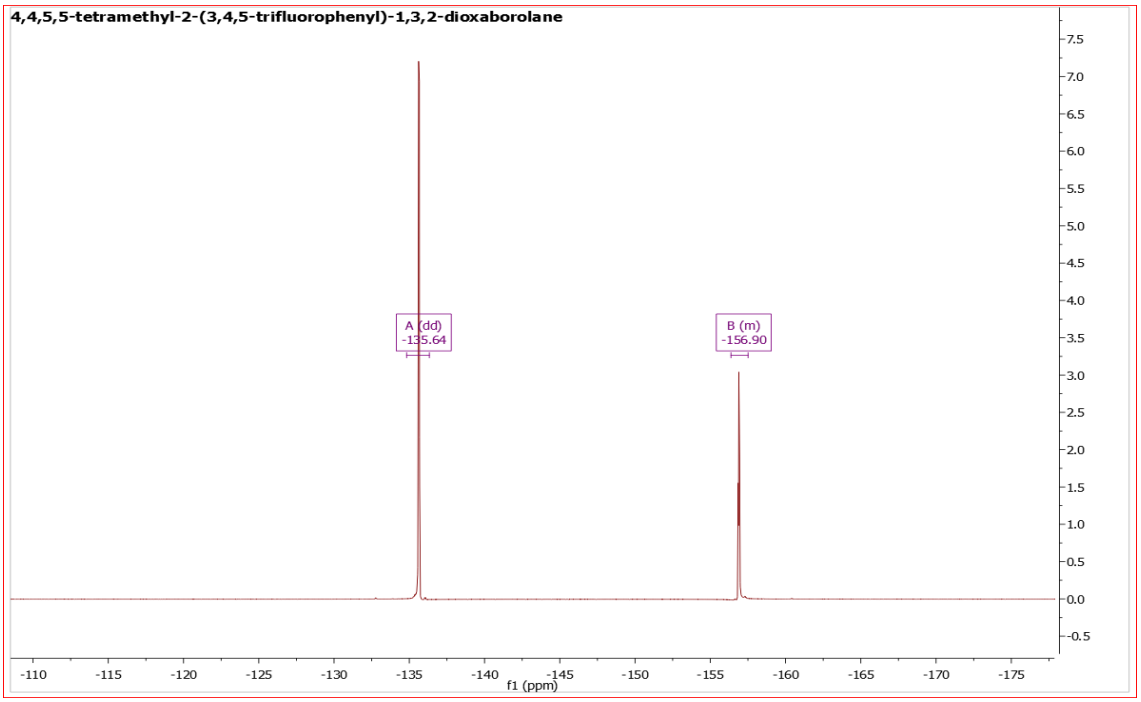
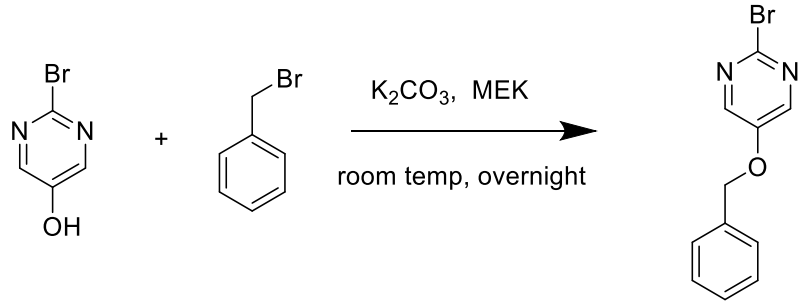


Figure S4. ^{19}F-NMR of 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane

5-(benzyloxy)-2-bromopyrimidine



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Scheme S5. Synthesis of 5-(benzyloxy)-2-bromopyrimidine

2-bromopyrimidin-5-ol (1 equiv, 2.54 g) was dissolved in 2-butanone (150 mL) and anhydrous potassium carbonate (1.5 equiv, 3 g) was added under nitrogen atmosphere. The benzyl bromide (1.21 equiv, 3 g) was introduced into the reaction flask and the mixture was stirred overnight. Water (100 mL) was added to quench the reaction, followed by extraction with chloroform. The

organic layer was dried over magnesium sulphate, and after suction filtration, the filtrate was concentrated in vacuo, which left an orange solid as crude. The crude was purified through flash column chromatograph using mixture of ethyl acetate and petrol ether 40-60 ° C (1:7), that produced a white solid eventually. The product was used for the next step reaction without further purification. **Yield 3.43 g, 89.2 %**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s), 7.46 – 7.33 (m), 5.13 (s).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.34, 146.62, 142.78, 134.62, 128.86, 128.78, 127.59, 71.06

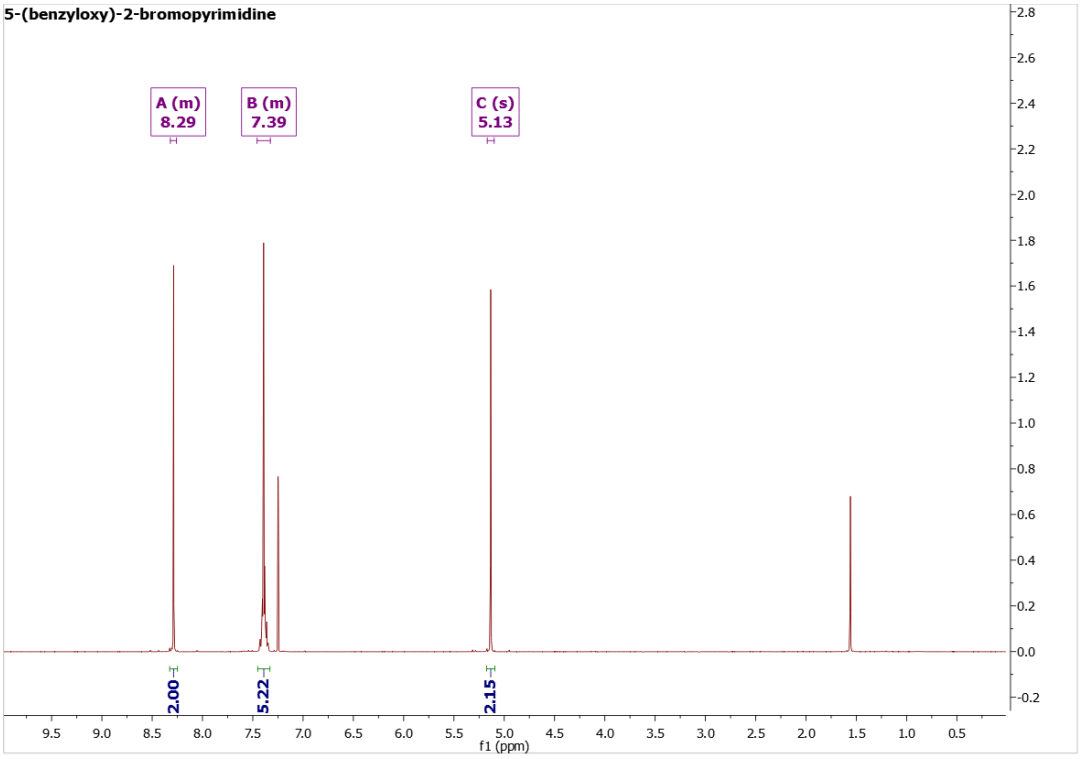


Figure S5. ^{1}H-NMR of 5-(benzyloxy)-2-bromopyrimidine

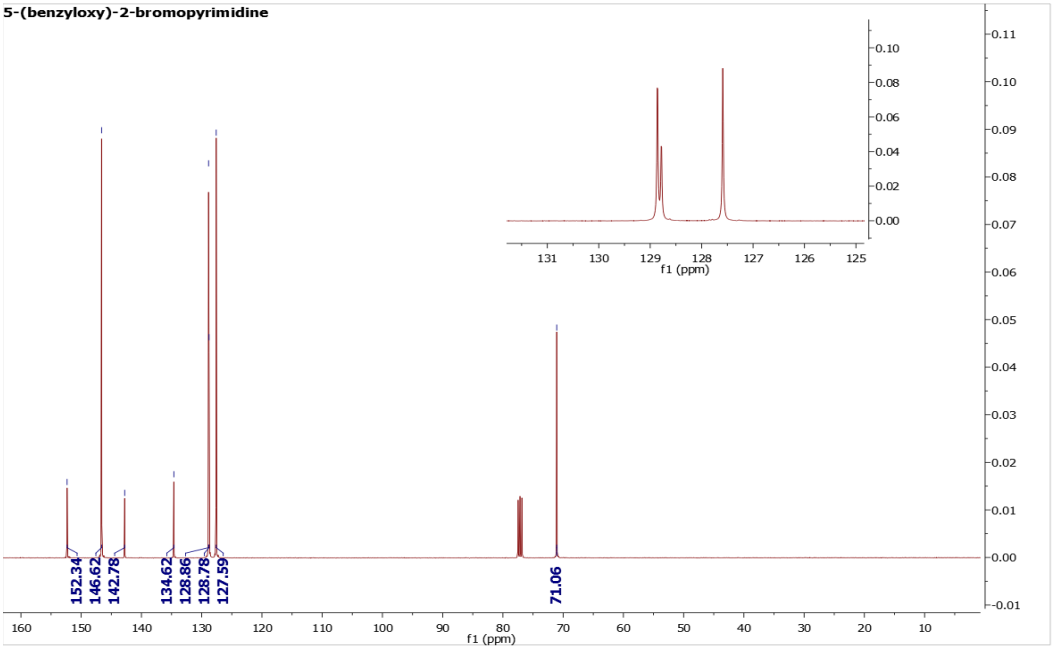
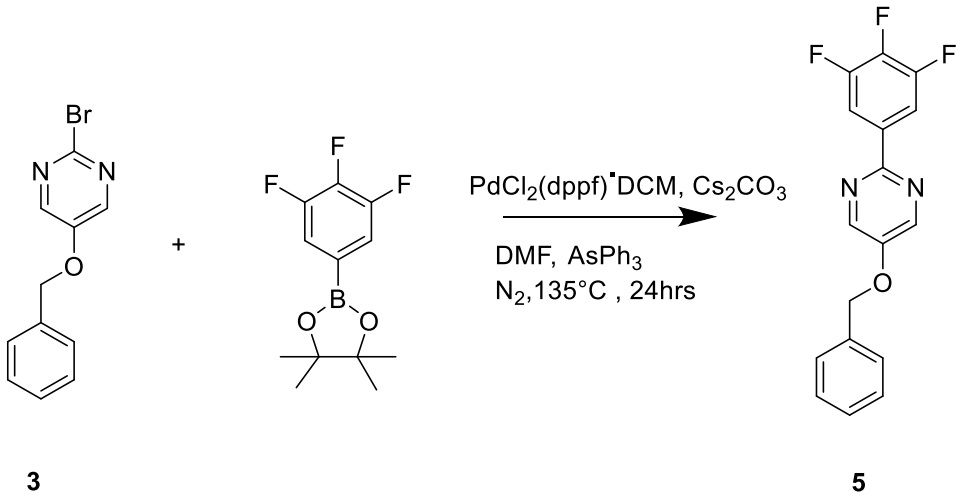


Figure S6. ^{13}C-NMR of 5-(benzyloxy)-2-bromopyrimidine

5-(benzyloxy)-2-(3,4,5-trifluorophenyl) pyrimidine



3 **5**

Scheme S6. Synthesis of 5-(benzyloxy)-2-(3,4,5-trifluorophenyl)pyrimidine

5-(benzyloxy)-2-bromopyrimidine **3** (0.76 g, 2.86 mmol), 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane (0.812 g, 3.146 mmol) and potassium carbonate (1.19 g, 8.58 mmol) were dissolved in dimethylformamide/H_2O= 12/1 v/v (150 mL) and nitrogen gas was

bubbled through the solution for 15 minutes. $Pd(dppf)Cl_2.CH_2Cl_2$ (0.13 g, 5 mol%) and triphenylarsine (0.13 g, 0.43 mmol) were added in one portion and the reaction was heated to 140 °C under a nitrogen atmosphere for 2 days. After cooling to ambient temperature, the solvent was removed by vacuum, the crude was extracted with chloroform and dried over by magnesium sulphate, and the filtrate was concentrated in vacuo. The product was isolated by flash column chromatograph using mixture of ethyl acetate and petrol ether 40-60 ° C (1:5). The product was isolated as an off white solid. **Yield: 0.73 g, 88.5 %**

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.49 (s), 8.08 – 7.92 (m), 7.51 – 7.33 (m), 5.21 (s).

Proton-Fluorine-Carbon decoupled ^{13}CNMR: δ 154.93, 151.8, 151.46, 144.37, 141.06, 135.20, 133.63, 129.04, 128.88, 127.74, 111.73, 71.03

^{19}F-NMR (376 MHz, $CDCl_3$): δ -134.15 (2F, dd, J = 18.8 Hz, 9 Hz, Ar-F), -158.83 (1F, tt, J= 7.5 Hz, 18.8 Hz, Ar-F)

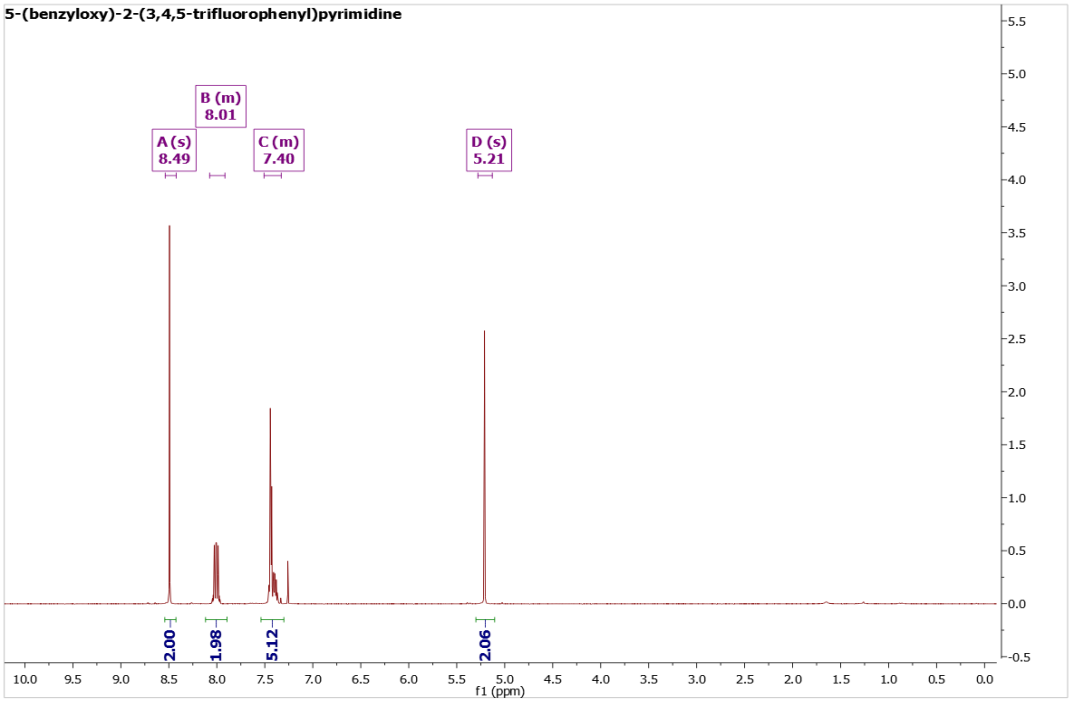


Figure S7. ^{1}H-NMR of 5-(benzyloxy)-2-(3,4,5-trifluorophenyl) pyrimidine

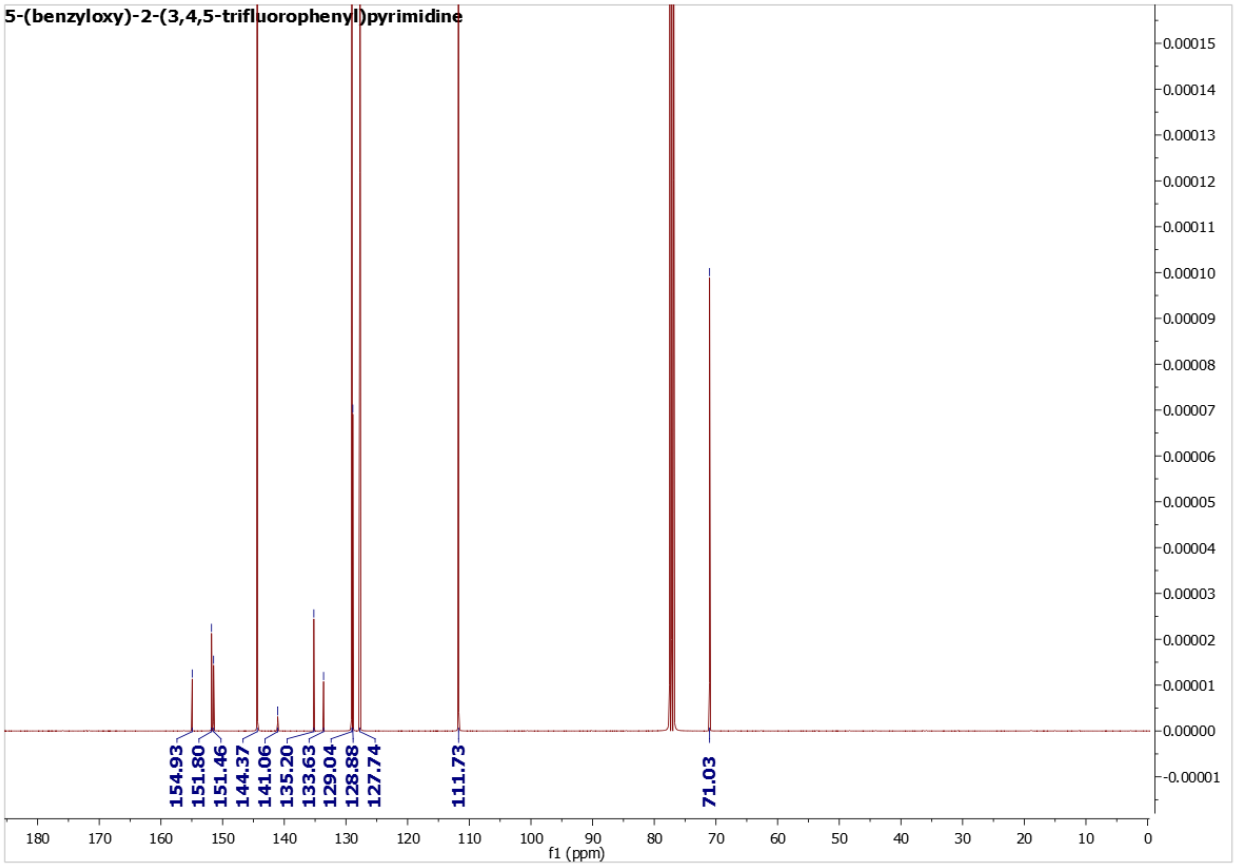


Figure S8. Proton-Fluorine-Carbon decoupled NMR spectrum of 5-(benzyloxy)-2-(3,4,5-trifluorophenyl) pyrimidine

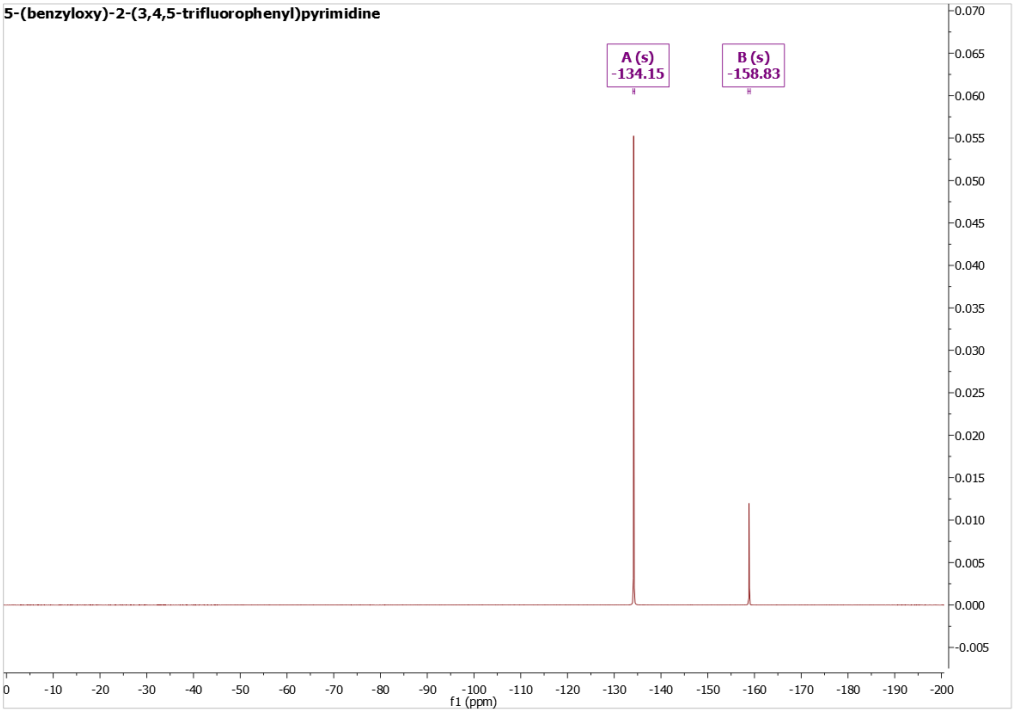
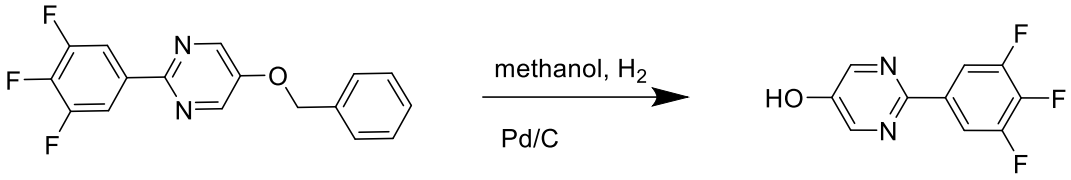


Figure S9. ^{19}F-NMR of 5-(benzyloxy)-2-(3,4,5-trifluorophenyl) pyrimidine

2-(3,4,5-trifluorophenyl) pyrimidin-5-ol



5 **6**

Scheme S7: Synthesis of 2-(3,4,5-trifluorophenyl) pyrimidin-5-ol

To a pre-dried pressure bottle, 5-(benzyloxy)-2-(3,4,5-trifluorophenyl) pyrimidine (0.55 g, 1.74 mmol) **5** was dissolved in methanol (100 mL) and added with stirring until totally dissolve. Then 10% Pd/C catalyst (0.19 g, 1.74 mmol) was added. The pressure bottle was replaced with hydrogen gas for three times. It was left under hydrogen atmosphere at room temperature for 3 days at 2psi. Hydrogen was pumped out of the bottle. The mixture was passed through celite and washed with

methanol and the solvent was removed by vacuum. The product was isolated by flash column chromatograph using a mixture of ethyl acetate and petrol ether 40-60 ° C (1:5). The product was isolated as a white solid without further recrystallization. **Yield: 0.35 g, 89 %**

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.44 (s), 8.08 – 7.92 (m), 5.56 (s).

^{13}C-NMR (101 MHz, C_2D_6OS): δ 151.79, 151.32, 149.3 (dd, J_{C-F} = 10 Hz, 3Hz), 144.68, 139.8 (dt , J_{C-F} = 252Hz, 16.2Hz), 134.20 (td, J_{C-F} = 8Hz, 4 Hz), 110.85 (dd, J_{C-F} = 6Hz, 17.1 Hz)

^{19}F-NMR (376 MHz, $CDCl_3$): δ -134.1 (2F, dd, J = 20.9, 9.2 Hz, Ar-F), -158.71 (1F, tt, J= 22.6 Hz, 7.5 Hz, Ar-F).

High resolution mass: C10H6F3N2O experimental value 227.0427, theoretical value 227.0427.

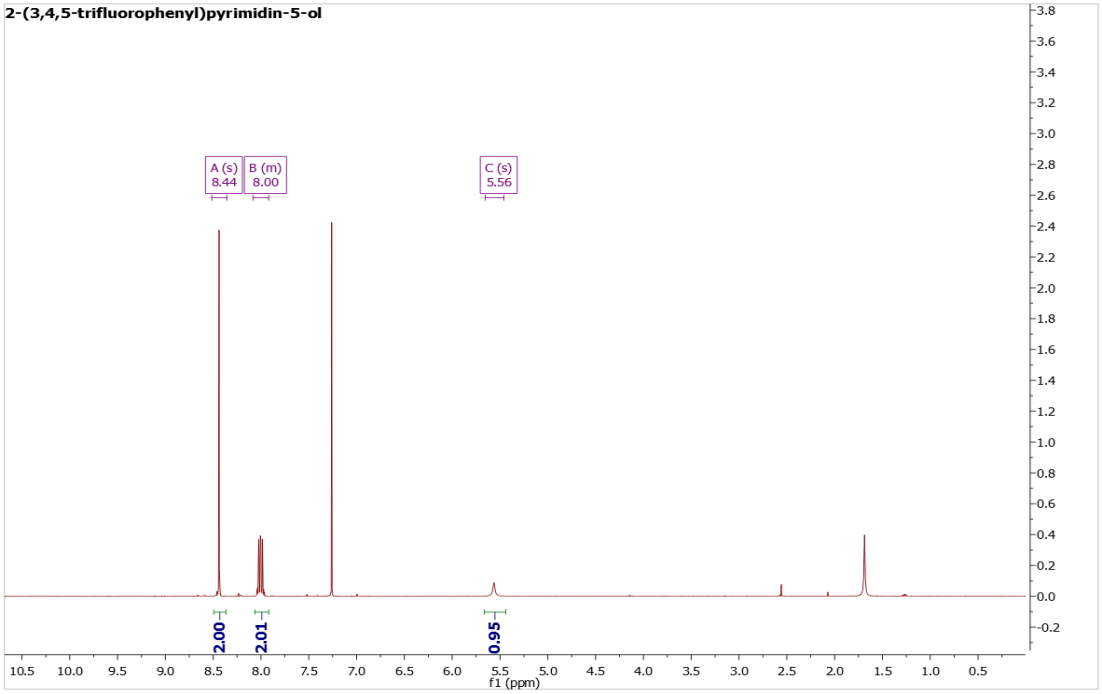


Figure S10. ^{1}H-NMR of 2-(3,4,5-trifluorophenyl) pyrimidin-5-ol

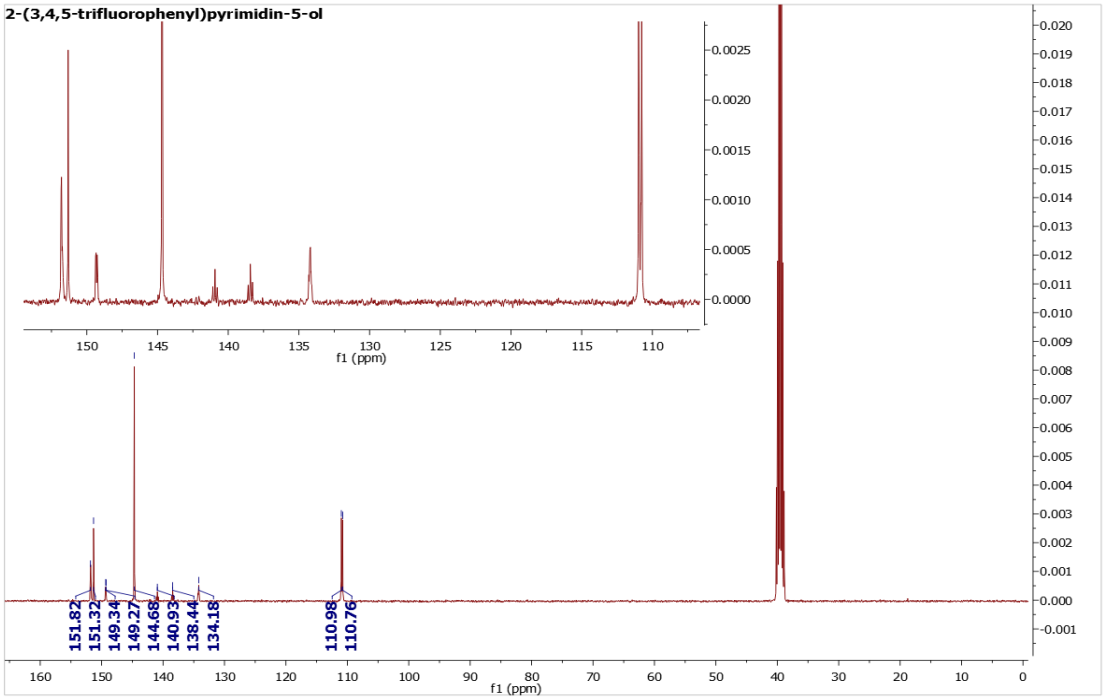


Figure S11. ^{13}C-NMR of 5-(benzyloxy)-2-(3,4,5-trifluorophenyl) pyrimidine

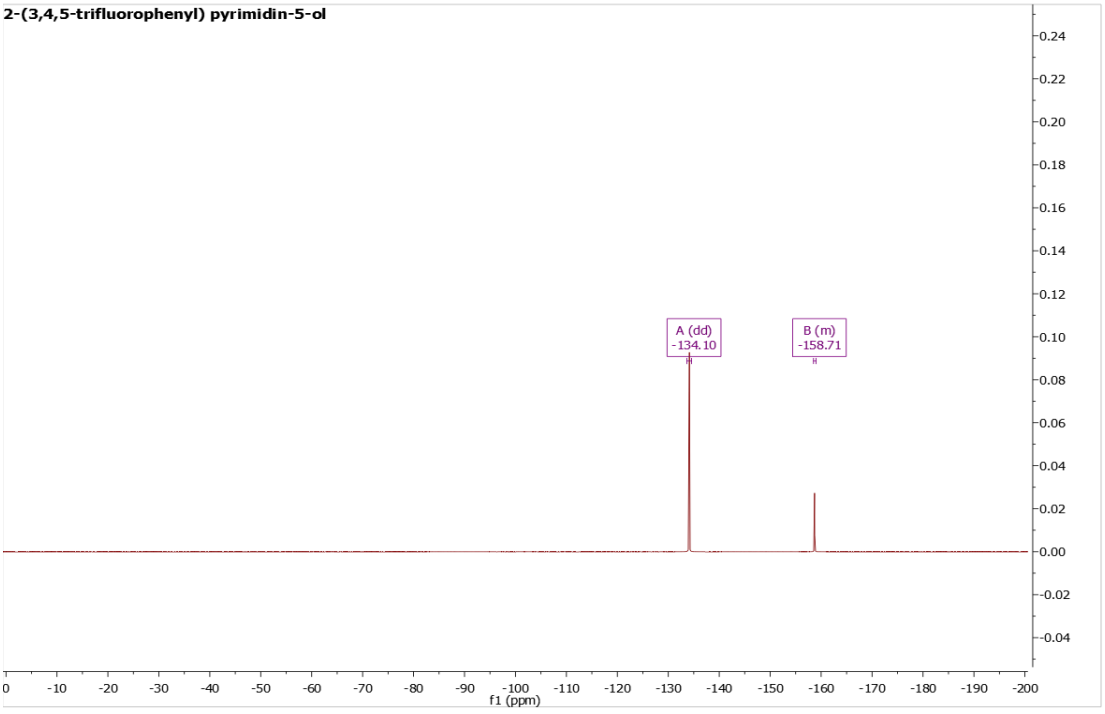
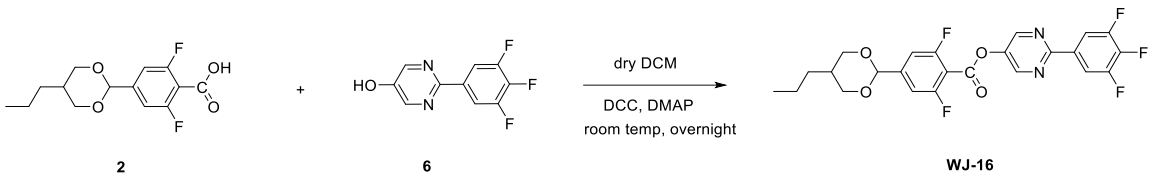


Figure S12. ^{19}F-NMR of 2-(3,4,5-trifluorophenyl) pyrimidin-5-ol

2-(3,4,5-trifluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate



2 6 WJ-16

Scheme S8. Synthesis of 2-(3,4,5-trifluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate.

A dried three neck flask and cooled kept in an ice bath at 0 °C, 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoic acid **2** (0.17 g, 0.59 mmol), 2-(3,4,5-trifluorophenyl) pyrimidin-5-ol **6** (0.13 g , 0.58 mmol), and 4-dimethylaminopyridine (9.3mg , 7.63×10^{-2} mmol) were added. All solids were solubilised with anhydrous dichloromethane (50 mL) and stirred for 10 min before N,N'-dicyclohexylcarbodiimide (0.16 g , 0.76 mmol) was added to the flask. The temperature of the reaction mixture was increased to room temperature and the reaction was left overnight. The crude was passed through celite and washed with chloroform; filtrate was collected. The solvent was removed under vacuum and was further purified by flash column chromatograph using mixture of ethyl acetate and petrol ether 40-60 °C (1:5). White solid was obtained, and further purified by recrystallization from hexane. **Yield: 0.15 g, 52.8 %**

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 2H), 8.17 – 8.08 (m, 2H), 7.22 (d, J = 9.4 Hz, 2H), 5.41 (s, 1H), 4.26 (dd, J = 11.8, 4.6 Hz, 2H), 3.55 (t, J = 11.5 Hz, 2H), 2.21 – 2.07 (m, 1H), 1.42 – 1.28 (m, 2H), 1.15 – 1.06 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ161.29 (dd, J_{C-F} = 260.6 Hz, 5Hz),159.29,158.85,151.54 (dd, J_{C-F} = 250.5 Hz, 10.1Hz, 4Hz),150.59,146.54 (t, J_{C-F} = 10.1Hz),144.68,141.76(dt, J_{C-F} = 256.5 Hz, 16.2Hz), 133.04 (t, J_{C-F} = 8Hz),112.65(dd, J_{C-F} = 17.2Hz, 6Hz),110.63(dd, J_{C-F} = 23.2Hz, 3Hz),108.48(t, J_{C-F} =16.2 Hz),98.80,72.74,34.03,30.34,19.67,14.33

^{19}F-NMR (376 MHz, $CDCl_3$): δ -107.29 (2F, d, J = 10.7 Hz, Ar-F), -133.71 (2F, dd, J = 21.6, 9.4 Hz, Ar-F), -157.14 (1F, tt, J= 18.8 HZ, 7.4 HZ, Ar-F)

DEPT (101 MHz, $CDCl_3$):

-CH_2: δ 72.68 (s), 30.28 (s), 19.61 (s)

-CH_3 & CH: δ 150.53 (s), 112.59 (dd, J = 23.2, 6.1 Hz), 110.57 (dd, J = 23.6, 3.2 Hz), 98.74 (s), 33.97 (s), 14.27 (s)

High resolution mass: C24H19F5N2O4Na m/z 517.1158, err -0.1 ppm.

Elemental Analysis: Theoretical: C 58.30%, H 3.87%, N 5.67%; Experimental: C 58.37%, H 3.82%, N 5.70%

HPLC measurements : Chromatographic separations were performed using an Agilent InfinityLab Poroshell 120 EC-C18 (2.1 x 50 mm, 1.9 um) at a column temperature of 40ºC. The mobile phase used was 0.1 % TFA in water (95 %) and 0.1 % TFA in acetonitrile (5%) and the gradient running to 5 % water over 5 minutes and held at 95% acetonitrile for 2 minutes at a flow rate of 0.5 mL/min. The DAD recorded the chromatogram at a wavelength of 254 nm.

Purification result 99%.

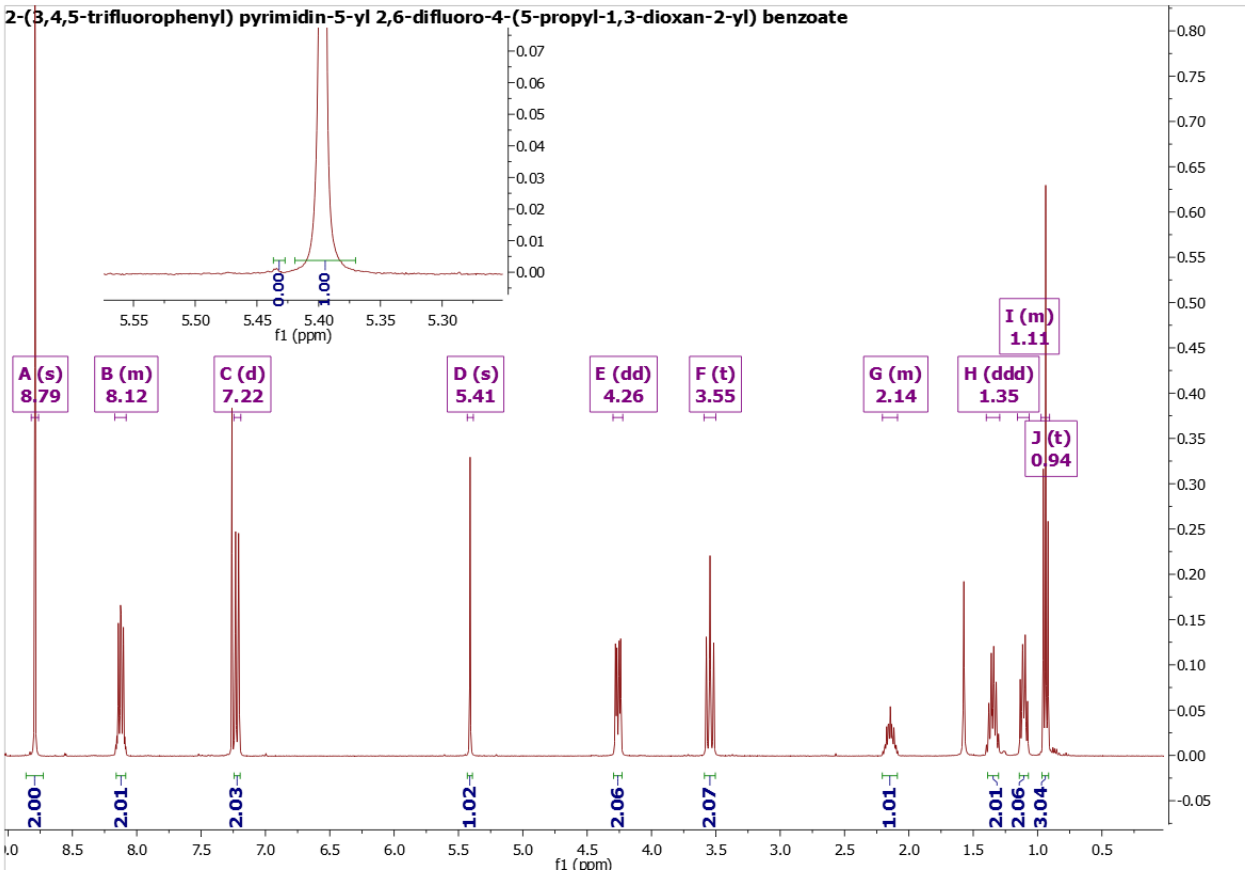


Figure S13. ^{1}H-NMR of 2-(3,4,5-trifluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate.

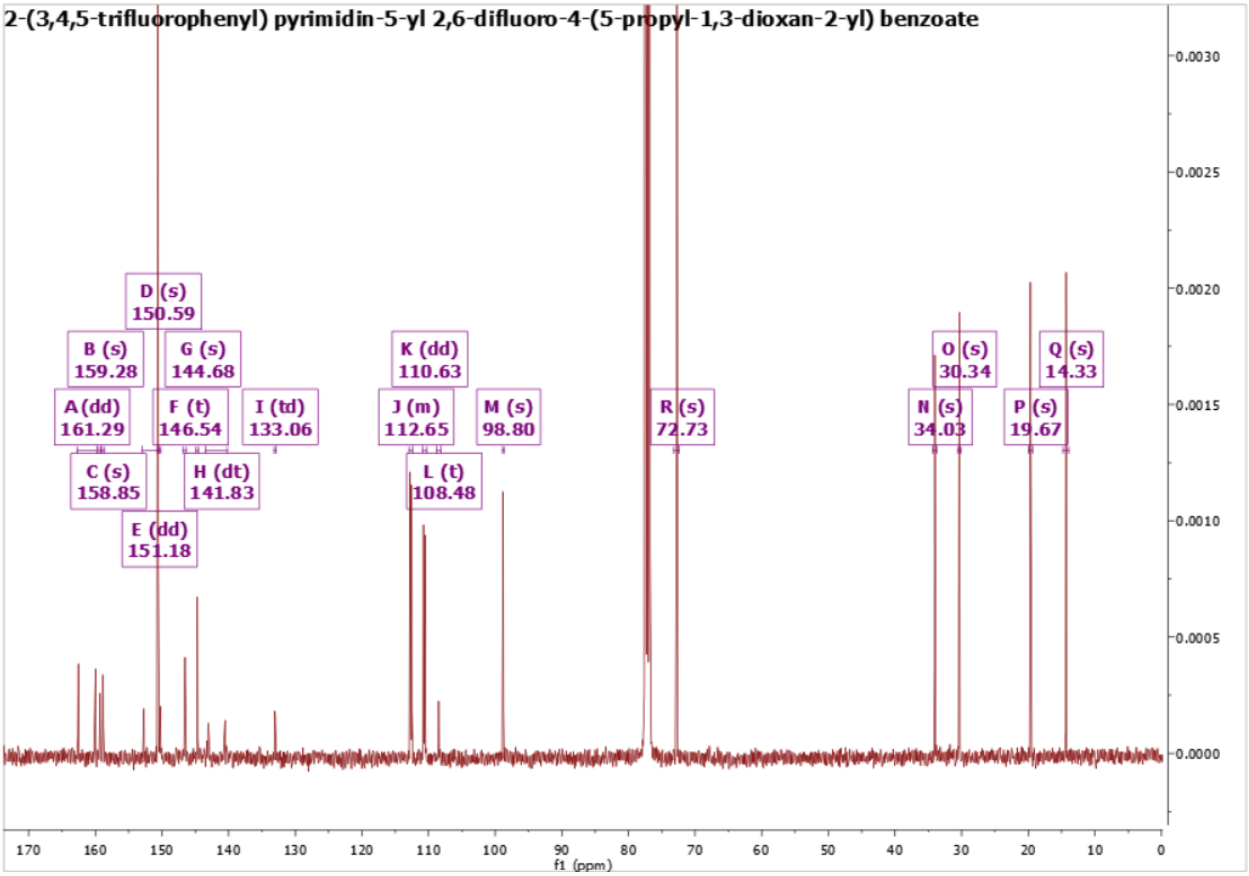


Figure S14. ^{13}C-NMR of 2-(3,4,5-trifluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate

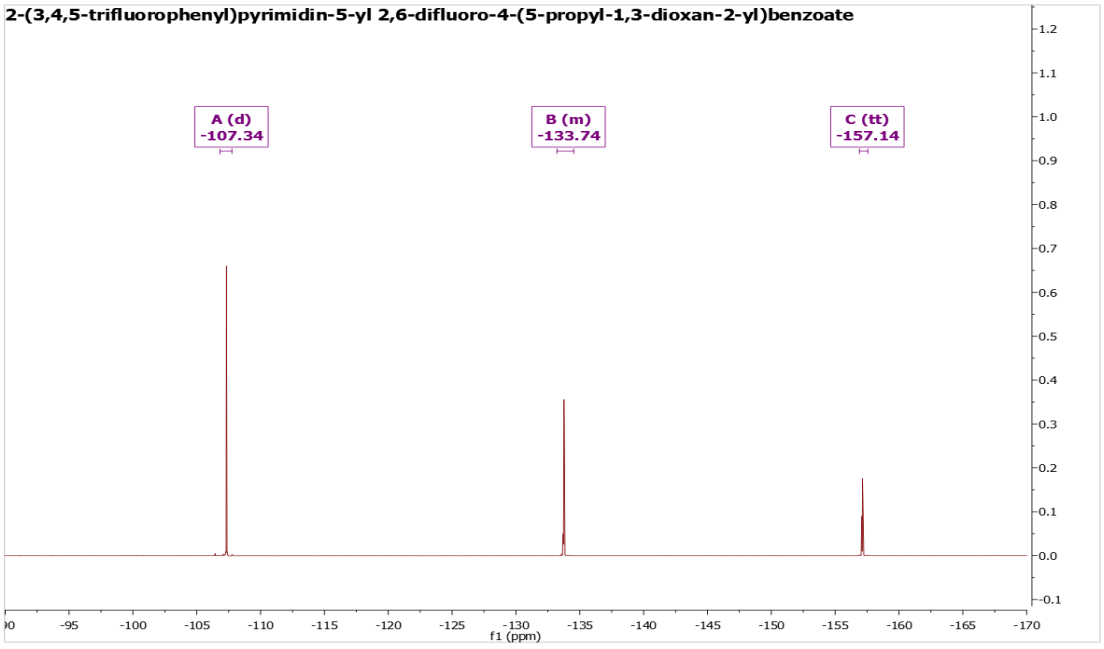


Figure S15. ^{19}F-NMR of 2-(3,4,5-trifluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate

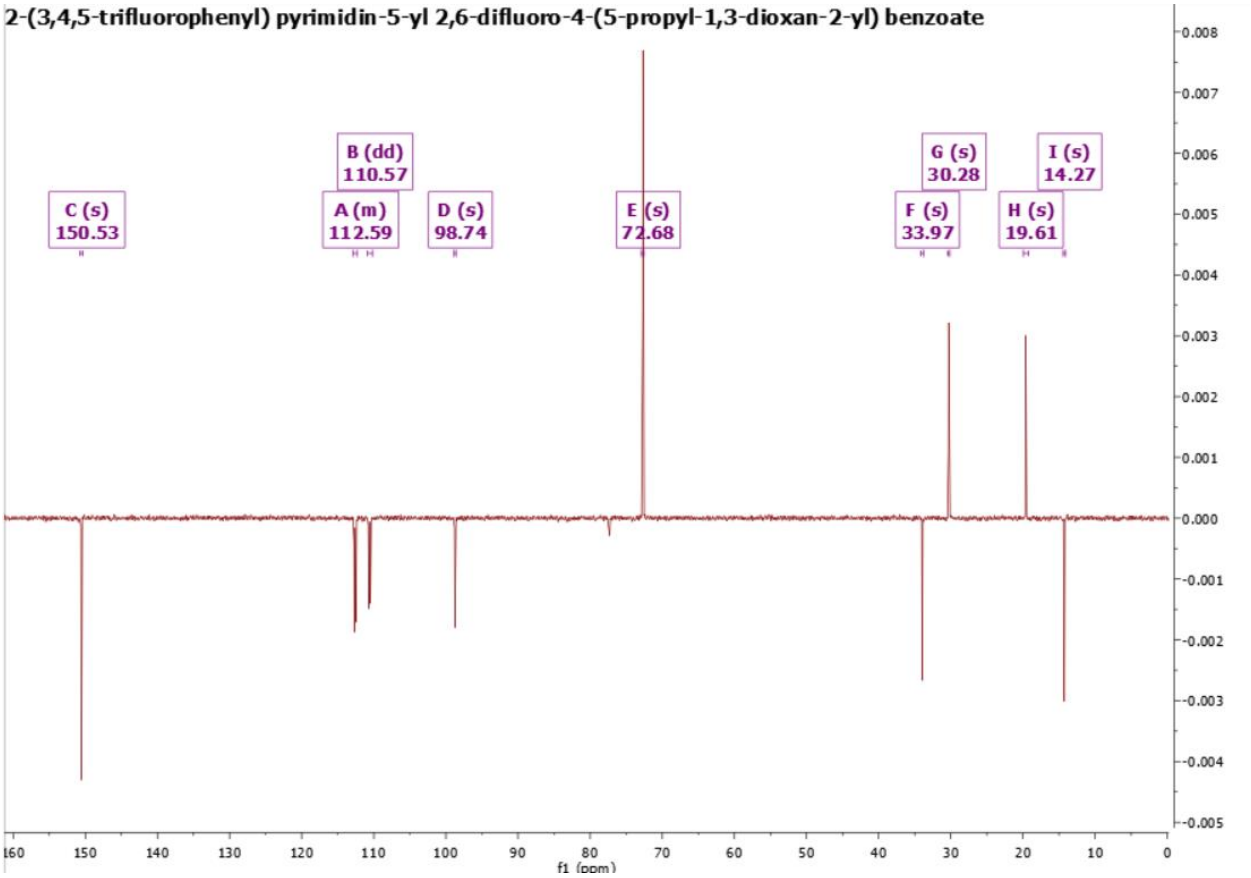


Figure S16. DEPT spectrum of 2-(3,4,5-trifluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate

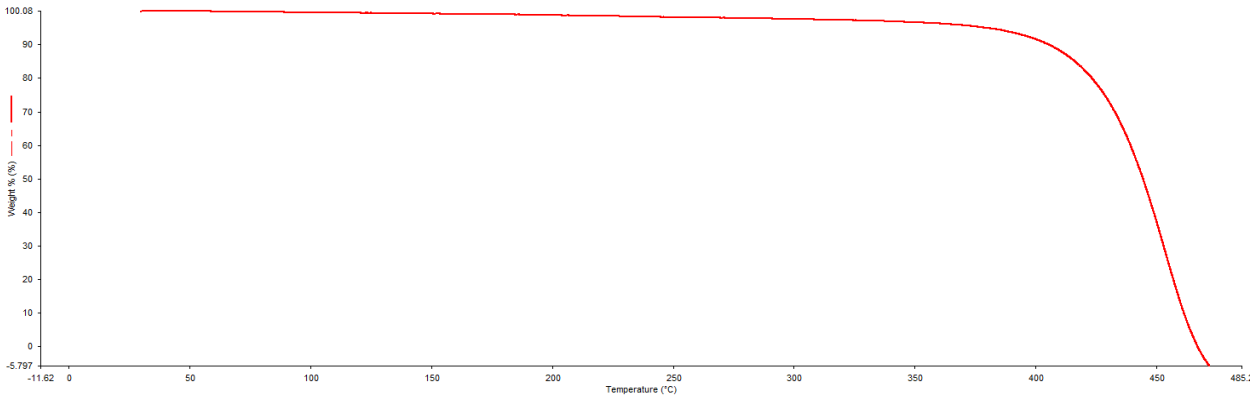
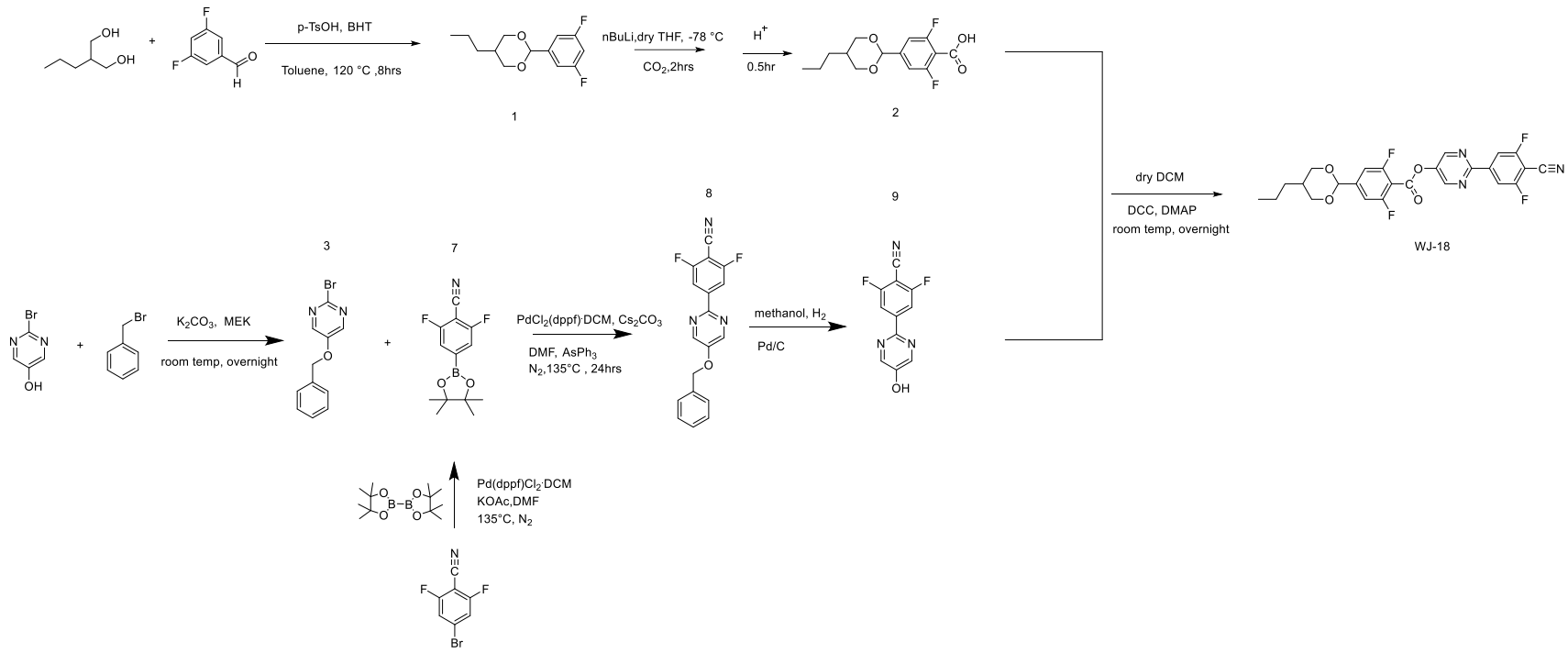


Figure S17. TGA (Thermogravimetric Analyzer) results for 2-(3,4,5-trifluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate **WJ-16.**

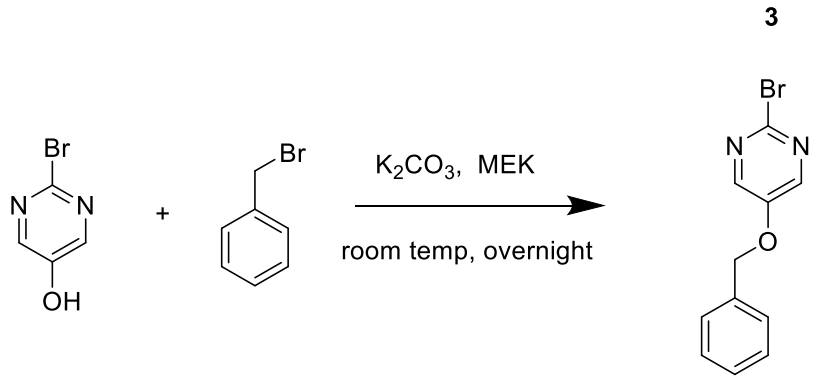


Scheme S9. Synthesis of 2-(4-cyano-3,5-difluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate **WJ-18**

Scheme S8 for WJ18 and its characterization using NMR

The first three steps involved in the synthesis of **WJ18** are exactly the same as for **WJ16**. The scheme from step 4 is shown as S9 and the induvial steps as shown below.

5-(benzyloxy)-2-bromopyrimidine



Scheme S10: Synthesis of 5-(benzyloxy)-2-bromopyrimidine

2-bromopyrimidin-5-ol (1 equiv, 2.54 g) was dissolved in 2-butanone (150 mL) and anhydrous potassium carbonate (1.5 equiv, 3 g) was added under nitrogen atmosphere. The benzyl bromide (1.21 equiv, 3 g) was introduced into the reaction flask and the mixture was stirred under reflux overnight. Water (100 mL) was added to quench the reaction, followed by extraction with chloroform. The organic layer was dried over magnesium sulphate, and after suction filtration, the filtrate was concentrated in vacuo, which left an orange solid as crude. The crude was purified through flash column chromatograph using mixture of ethyl acetate and petrol ether 40-60 ℃ (1:7), that produced a white solid eventually. The product was used for the next step reaction without further purification. **Yield 3.43 g, 89.2 %**

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.29 (s), 7.46 – 7.33 (m), 5.13 (s).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 152.34, 146.62, 142.78, 134.62, 128.86, 128.78, 127.59, 71.06

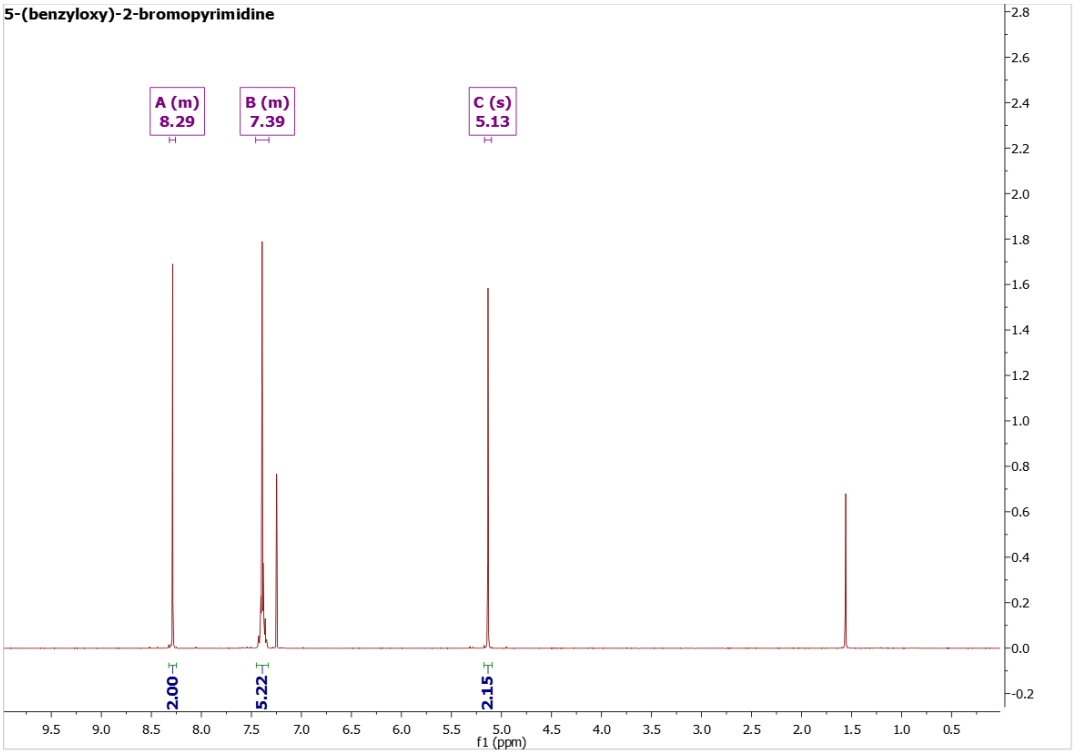


Figure S18. ^{1}H-NMR of 5-(benzyloxy)-2-bromopyrimidine

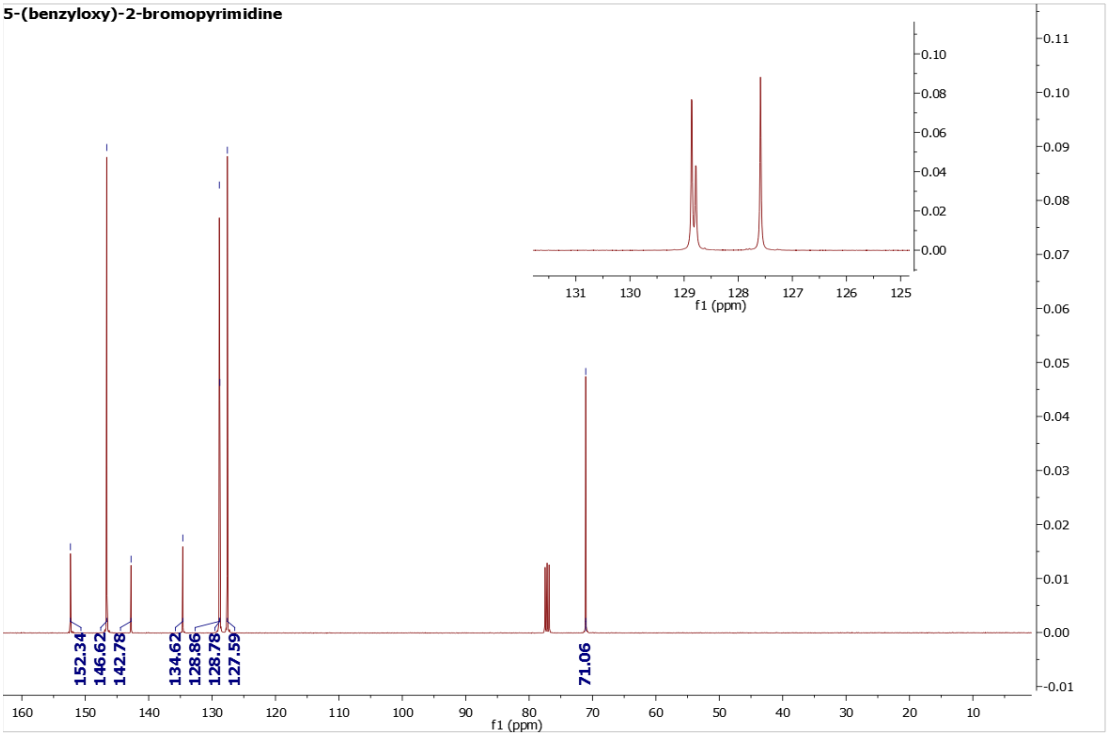
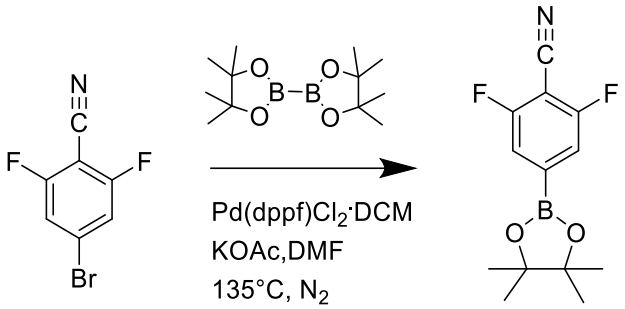


Figure S19. ^{13}C-NMR of 5-(benzyloxy)-2-bromopyrimidine

2,6-difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzonitrile



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Scheme 11: Synthesis of 2,6-difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzonitrile

4-bromo-2,6-difluorobenzonitrile (15 g, 0.069 mol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (20.97 g, 0.083 mol) and potassium acetate (20.93 g, 0.213 mol) were added to a 250 mL in a three neck round bottom flask, and then were dissolved in dimethylformamide (200 mL) and nitrogen was bubbled through the solution for 5 mins. $Pd(dppf)Cl_2.CH_2Cl_2$ (3.13 g, 0.0034 mol) 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 solvent was removed through vacuum. The reaction mixture was extracted by chloroform, the organic layer was dried magnesium sulphate and passed through filter, and the filtrate was concentrated in vacuo. The crude was passed through short silica gel pad and washed with chloroform, and then used for the next step directly.

Yield: 15.33 g, 84 %

^{1}HNMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 7.6 Hz), 1.36 (s, J = 15.2 Hz).

Proton-Fluorine-Carbon decoupled ^{13}CNMR: δ 166.74, 161.15, 145.14, 110.25, 109.82, 98.93, 72.58,33.92,30.23,19.56, 14.22

^{19}FNMR (376 MHz, $CDCl_3$): δ -104.70 (2F, d, J = 8.3 Hz, Ar-F).

Data consistent with reported values [R5].

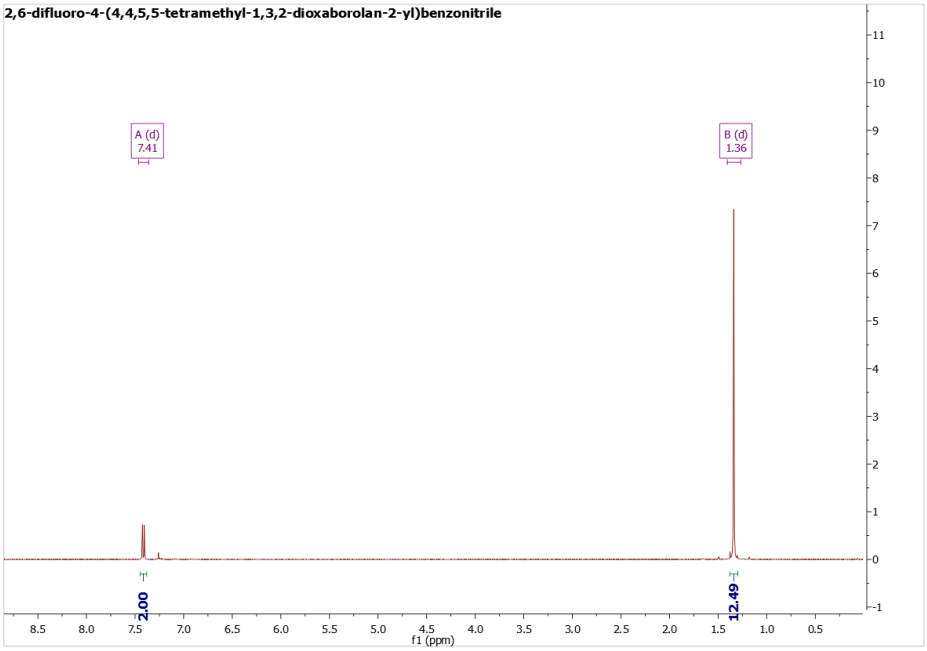


Figure S20. [1]HNMR of 2,6-difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzonitrile

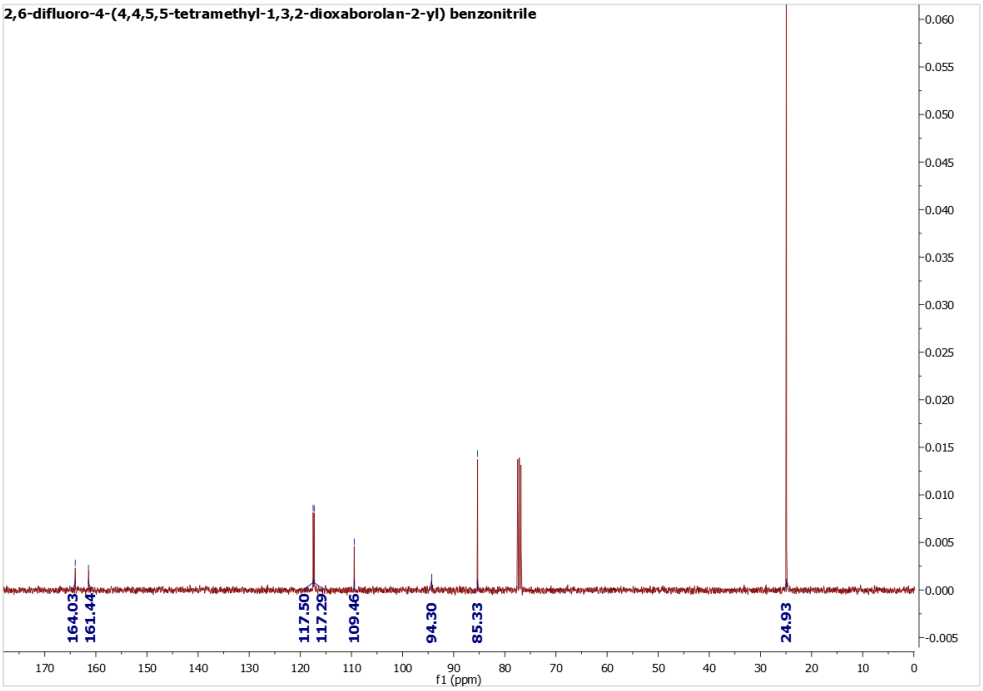


Figure S21. [13]CNMR of 2,6-difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzonitrile

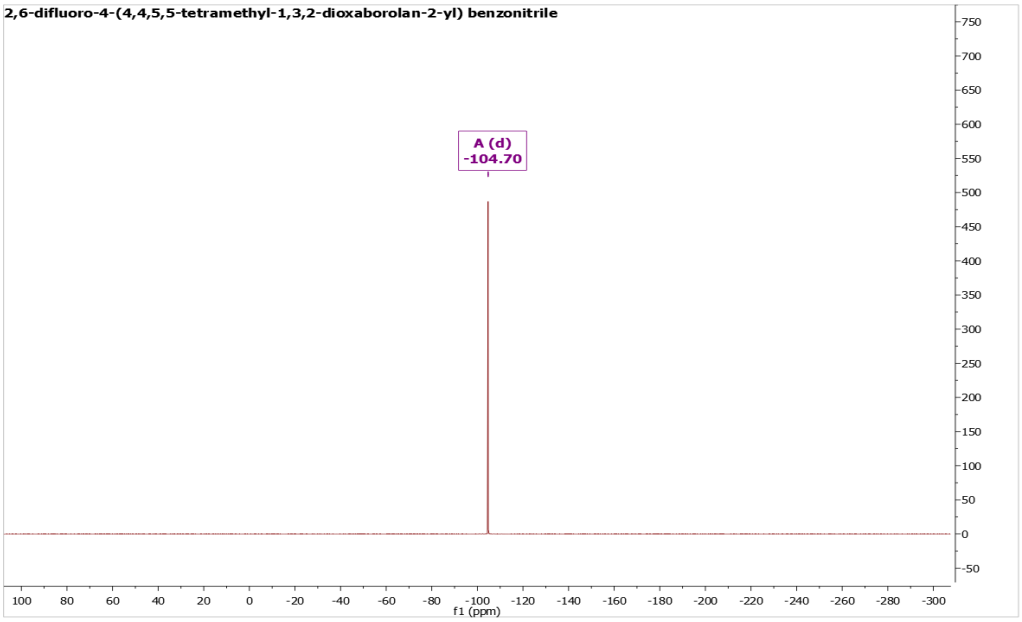
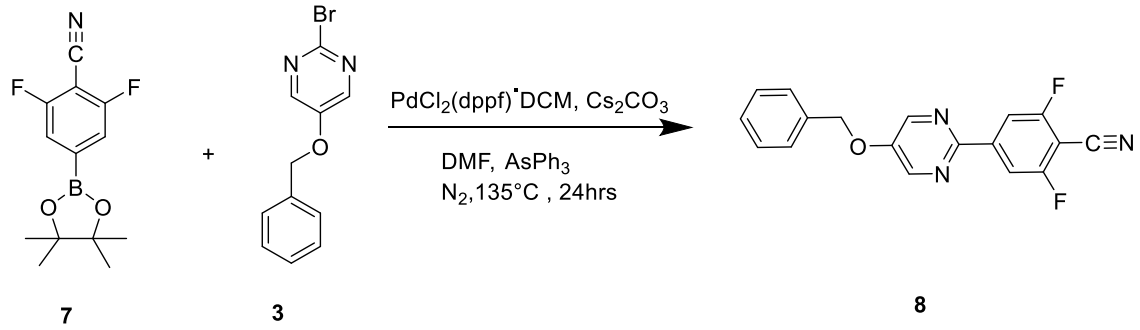


Figure S22. ^{19}FNMR of 2,6-difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzonitrile

4-(5-(benzyloxy) pyrimidin-2-yl)-2,6-difluorobenzonitrile



7 3 8

Scheme 12: Synthesis of 4-(5-(benzyloxy) pyrimidin-2-yl)-2,6-difluorobenzonitrile

5-(benzyloxy)-2-bromopyrimidine **3** (0.85 g, 3.2 mmol), 2,6-difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzonitrile **7** (0.93 g, 3.51 mmol) and potassium carbonate (1.32 g, 9.6 mmol) were dissolved in dimethylformamide /H_2O= 12/1 v/v (150 mL) and nitrogen gas was bubbled through the solution for 15 minutes. Pd(dppf)Cl_2.CH_2Cl_2 (0.15 g, 5 mol%) and triphenylarsine (0.15 g, 0.48 mmol) were added in one portion and the reaction heated to 140 ℃ under a nitrogen atmosphere for 2 days. After cooling to ambient temperature, the solvent was removed by vacuum, the crude was extracted with chloroform and dried over by magnesium sulphate, and the filtrate was concentrated in vacuo. The product was isolated by flash column

chromatograph using mixture of diethyl ether and petrol ether 40-60 ℃ (1:1). The product was isolated as yellow solid. **Yield: 0.47g, 45.6 %**

^{1}HNMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 0.8 Hz), 8.07 (d, J = 9.5 Hz), 7.52 – 7.31 (m), 5.25 (s).

^{13}CNMR (101 MHz, CDCl3): δ 163.33 (dd, JC-F = 259.6, 4.6 Hz), 153.55 (t, JC-F = 3.1 Hz), 152.44 (s), 145.33 (t, JC-F = 9.8 Hz), 144.32 (s), 134.86 (s), 128.99 (s), 128.90 (s), 127.70 (s), 110.73 (dd, J = 21.8, 3.0 Hz), 109.56 (s), 92.50 (t, J = 19.7 Hz), 71.03 (s).

DEPT (101 MHz, CDCl3):

-CH_2: δ 71.09 (s).

-CH_3& CH: δ 144.38 (s), 129.05 (s), 128.96 (s), 127.76 (s), 110.79 (dd, J = 21.8, 3.0 Hz)

^{19}FNMR (376 MHz, CDCl3): δ -103.68 (2F, d, J = 11.1 Hz, Ar-F).

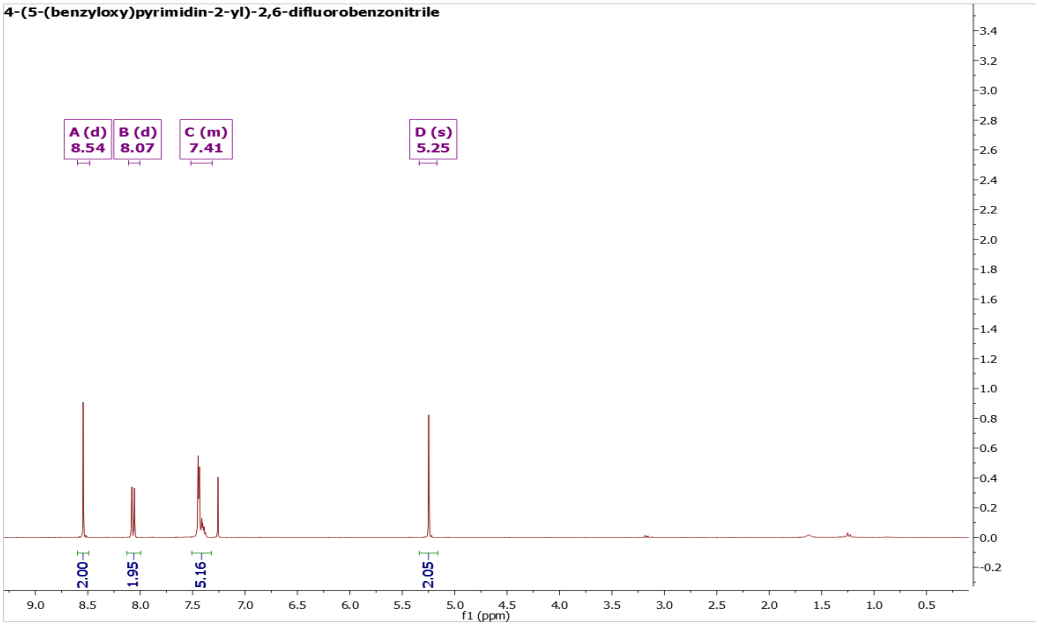


Figure S23. ^{1}HNMR of 4-(5-(benzyloxy) pyrimidin-2-yl)-2,6-difluorobenzonitrile

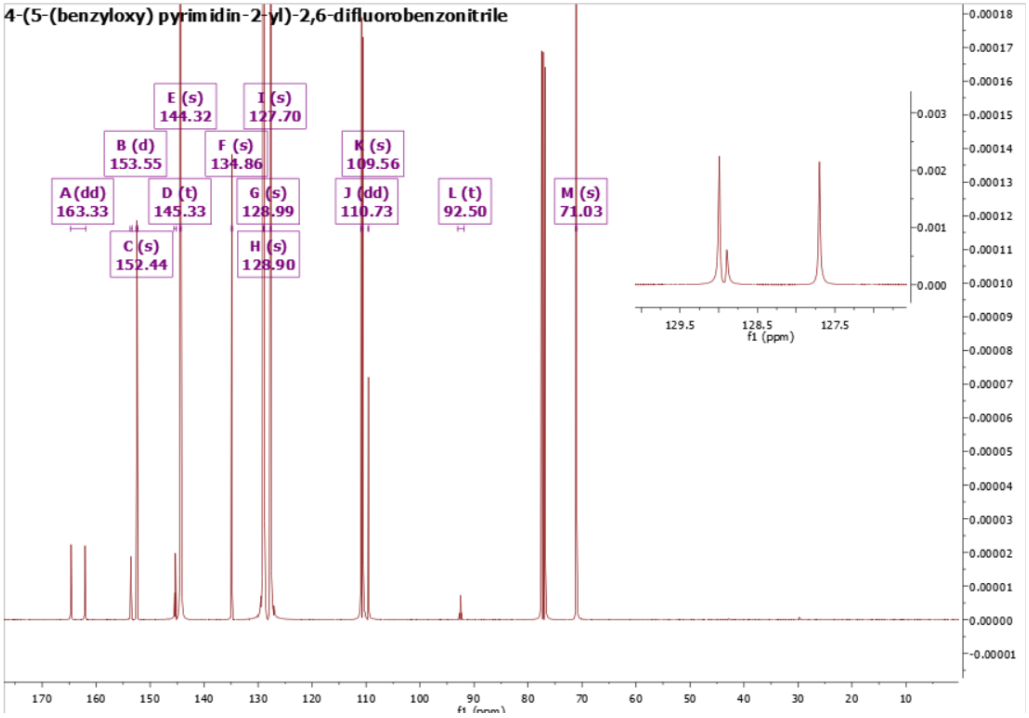


Figure S24. ^{13}C-NMR of 4-(5-(benzyloxy) pyrimidin-2-yl)-2,6-difluorobenzonitrile

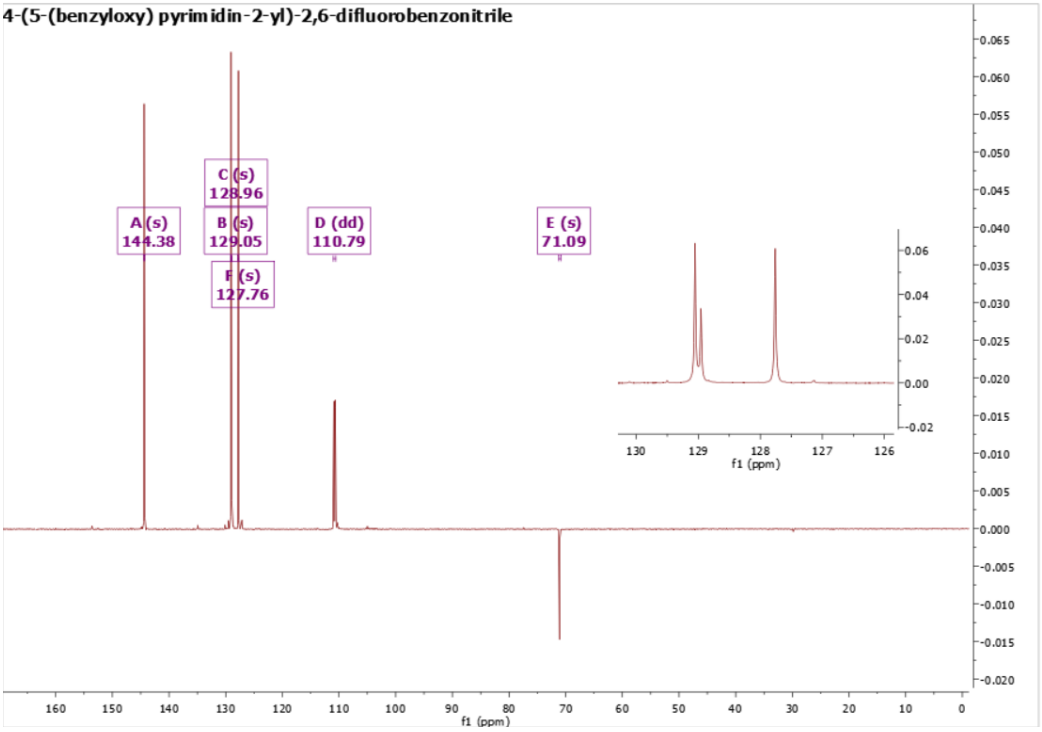


Figure S25. DEPT spectrum of 4-(5-(benzyloxy) pyrimidin-2-yl)-2,6-difluorobenzonitrile

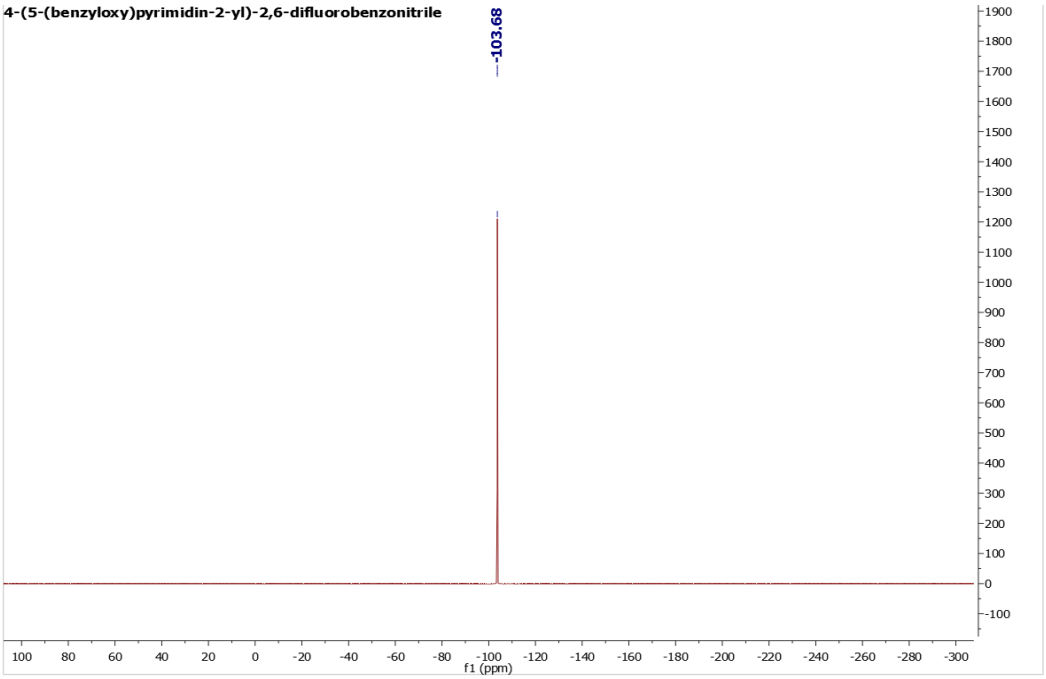
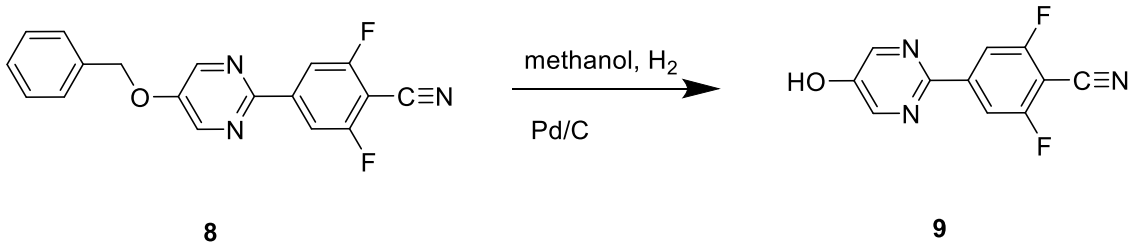


Figure S26. ^{19}F-NMR spectrum of 4-(5-(benzyloxy) pyrimidin-2-yl)-2,6-difluorobenzonitrile

2,6-difluoro-4-(5-hydroxypyrimidin-2-yl) benzonitrile



8 **9**

Scheme 13: Synthesis of 2,6-difluoro-4-(5-hydroxypyrimidin-2-yl) benzonitrile

To a pre-dried pressure bottle, 4-(5-(benzyloxy) pyrimidin-2-yl)-2,6-difluorobenzonitrile (0.75 g, 2.32 mmol) was dissolved in methanol (100 mL) and added with stirring until totally dissolve. Then 10% Pd/C catalyst (0.25 g, 2.32 mmol) was added. The pressure bottle was replaced with hydrogen gas for three times. And then was left under hydrogen atmosphere at room temperature for 3 days at 2psi. Hydrogen was pumped out of the bottle. The mixture was passed through celite and washed with methanol, And the solvent was removed by vacuum. The compound was used directly without further purification. **Yield: 0.3 g, 55.5 %**

High resolution mass: C11H5F2N3NaO m/z 256.0296, err -1.4 ppm.

^{1}HNMR (400 MHz, DMSO): δ 8.53 (s), 8.09 (q, J = 1.5 Hz).

^{13}CNMR (101 MHz, DMSO): δ 162.4 (dd, J_{C-F} = 258.6Hz,5Hz), 151.79, 150.85 (t, J_{C-F} =3Hz), 145.52 (t, J_{C-F} = 10.1Hz), 144.51, 109.70(dd, 21.2Hz, 3Hz), 109.08, 90.9 (t, J_{C-F} = 20.2 Hz)
^{19}FNMR (376 MHz, DMSO): δ -104.86 (2F, d, J = 9.3 Hz, Ar-F).

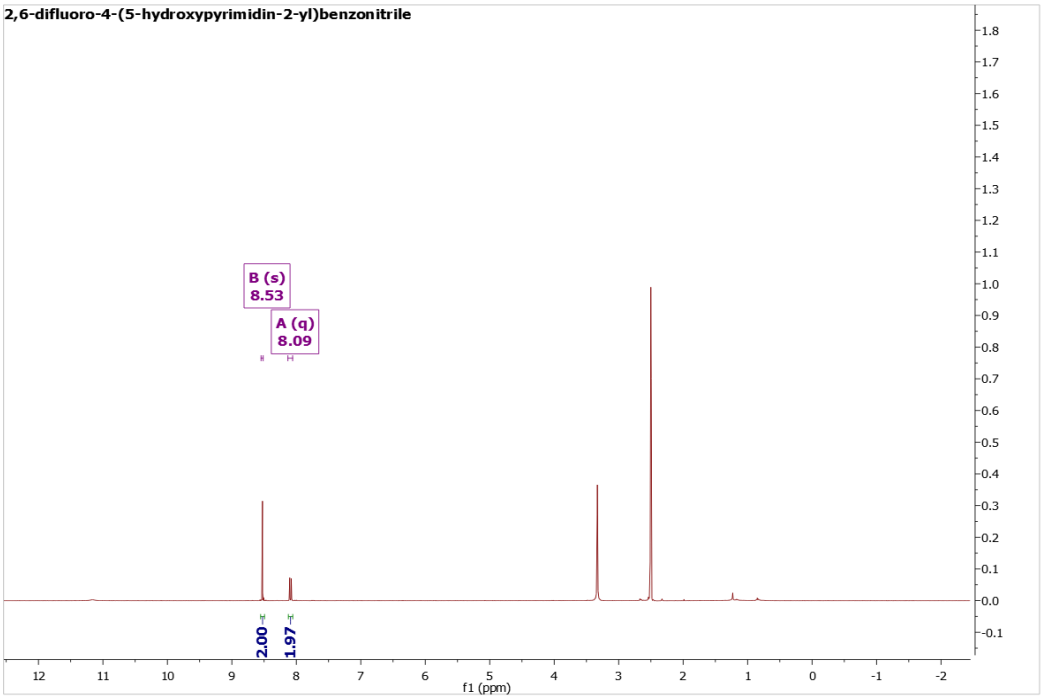


Figure S27. ^{1}HNMR of 2,6-difluoro-4-(5-hydroxypyrimidin-2-yl) benzonitrile

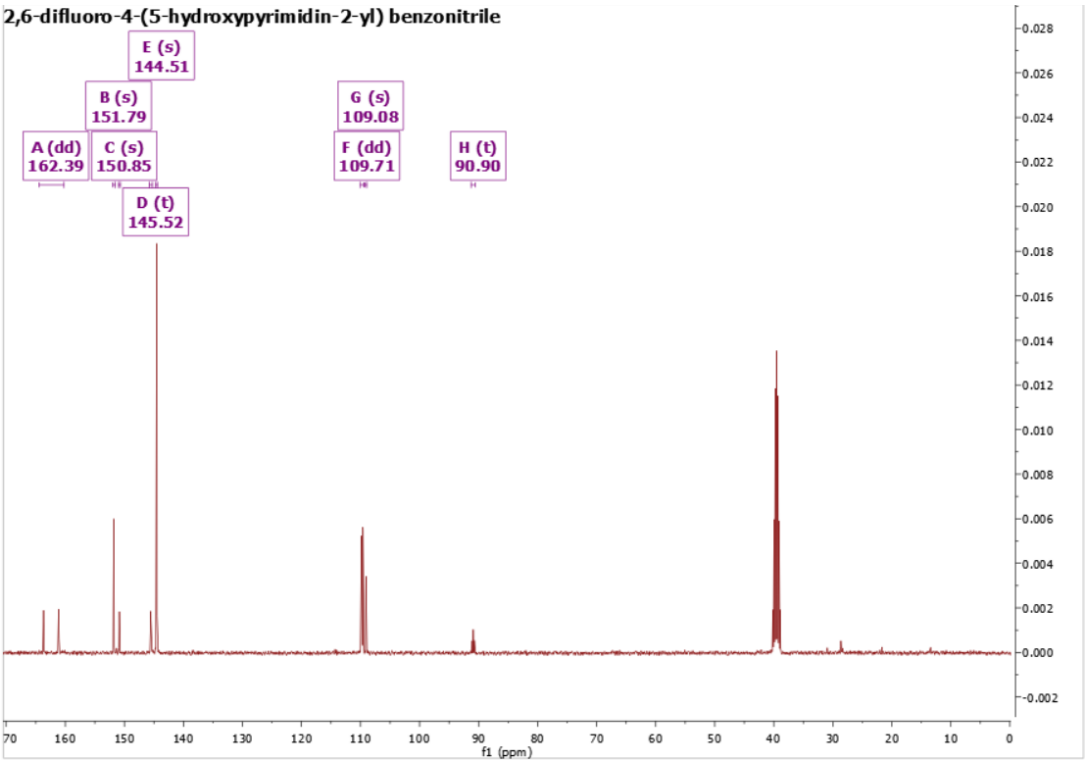


Figure S28. ^{13}CNMR of 2,6-difluoro-4-(5-hydroxypyrimidin-2-yl) benzonitrile

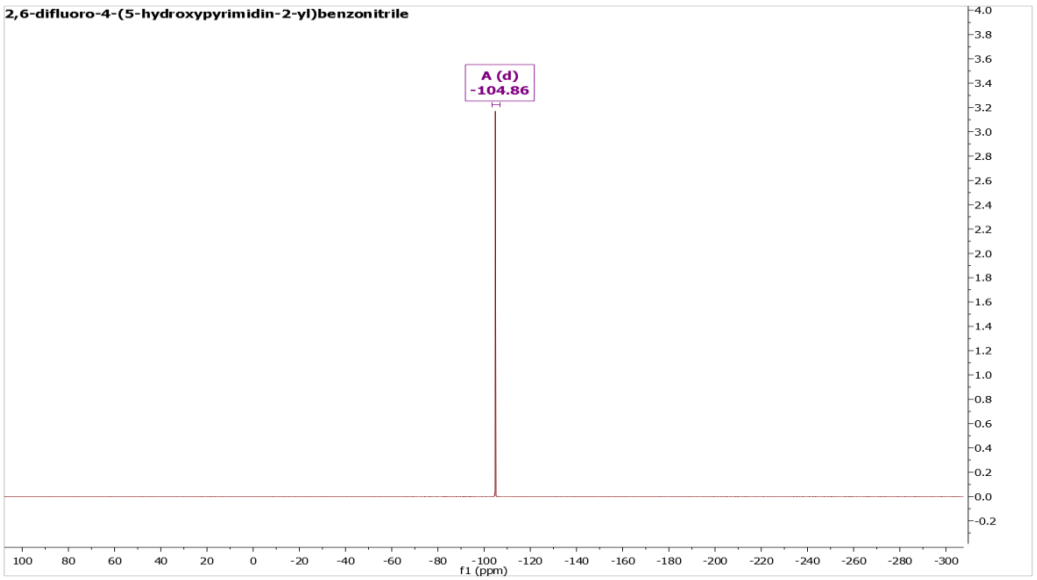
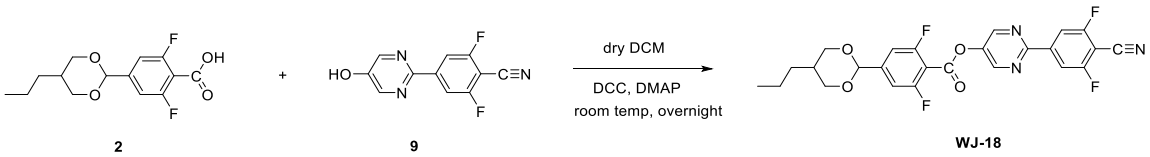


Figure S29. ^{19}FNMR of 2,6-difluoro-4-(5-hydroxypyrimidin-2-yl) benzonitrile

2-(4-cyano-3,5-difluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate



2 9 WJ-18

Scheme 14: Synthesis of 2-(4-cyano-3,5-difluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate

Prepared a dried three neck flask and kept it into the ice bath at 0 °C, 2,6-difluoro-4-(5-hydroxypyrimidin-2-yl) benzonitrile **9** (0.48 g, 2.06 mmol), 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoic acid **2** (0.59 g, 2.06 mmol), and 4-dimethylaminopyridine (0.033 g, 0.273 mmol) were added. All solids were solubilised with anhydrous dichloromethane (100 mL) and stirred for 10 min before N, N'-dicyclohexylcarbodiimide (0.56 g, 2.73 mmol) was added to the flask. The temperature of the reaction mixture was increased to room temperature and the reaction was left overnight. The crude was passed through celite and washed with chloroform; filtrate was collected. The solvent was removed under vacuum and was further purified by flash column chromatograph using mixture of diethyl ether and petrol ether 40-60 °C (1:4). White solid was obtained, and further purified by recrystallization from hexane. **Yield: 0.55 g, 53.3 %**
High resolution mass: C25H20F4N3O4 m/z 502.1384, err 0.5 ppm.

^{1}HNMR (400 MHz, $CDCl_3$): δ 8.86 (s), 8.22 – 8.14 (d), 7.23 (d, J = 9.4 Hz), 5.41 (s), 4.26 (dd, J = 11.8, 4.6 Hz), 3.55 (t, J = 11.5 Hz), 2.21 – 2.05 (m), 1.43 – 1.28 (m), 1.16 – 1.05 (m), 0.94 (t, J = 7.3 Hz).

^{13}CNMR (101 MHz, $CDCl_3$): δ 163.48 (dd, J_{C-F} = 224.2 Hz, 5Hz), 161.26 (dd, J_{C-F} = 224.2 Hz, 5Hz), 158.7, 158.2, 150.8, 146.8 (t, J_{C-F} =10.1 Hz), 145.3, 144.6 (t, J_{C-F} =9 Hz), 111.7 (dd, J_{C-F} = 21.9 Hz, 3Hz), 110.68 (dd, J_{C-F} = 23.6 Hz, 3.2Hz), 109.43, 108.2 (t, J_{C-F} =16.2 Hz), 98.7, 93.86 (t, J_{C-F} =20 Hz), 72.7, 34.0, 30.3, 19.7, 14.3

DEPT (101 MHz, $CDCl_3$):

-CH_2: δ 72.68 (s), 30.28 (s), 19.61 (s)

-CH_3 & CH: δ 150.76 (s), 111.70 (dd, J = 21.8, 3.2 Hz), 110.63 (dd, J = 23.5, 3.2 Hz), 98.70 (s), 33.97 (s), 14.28 (s).

^{19}FNMR (376 MHz, $CDCl_3$): δ -103.02 (2F, d, J = 8.5 Hz, Ar-F), -107.11 (2F, d, J = 9.0 Hz, Ar-F)

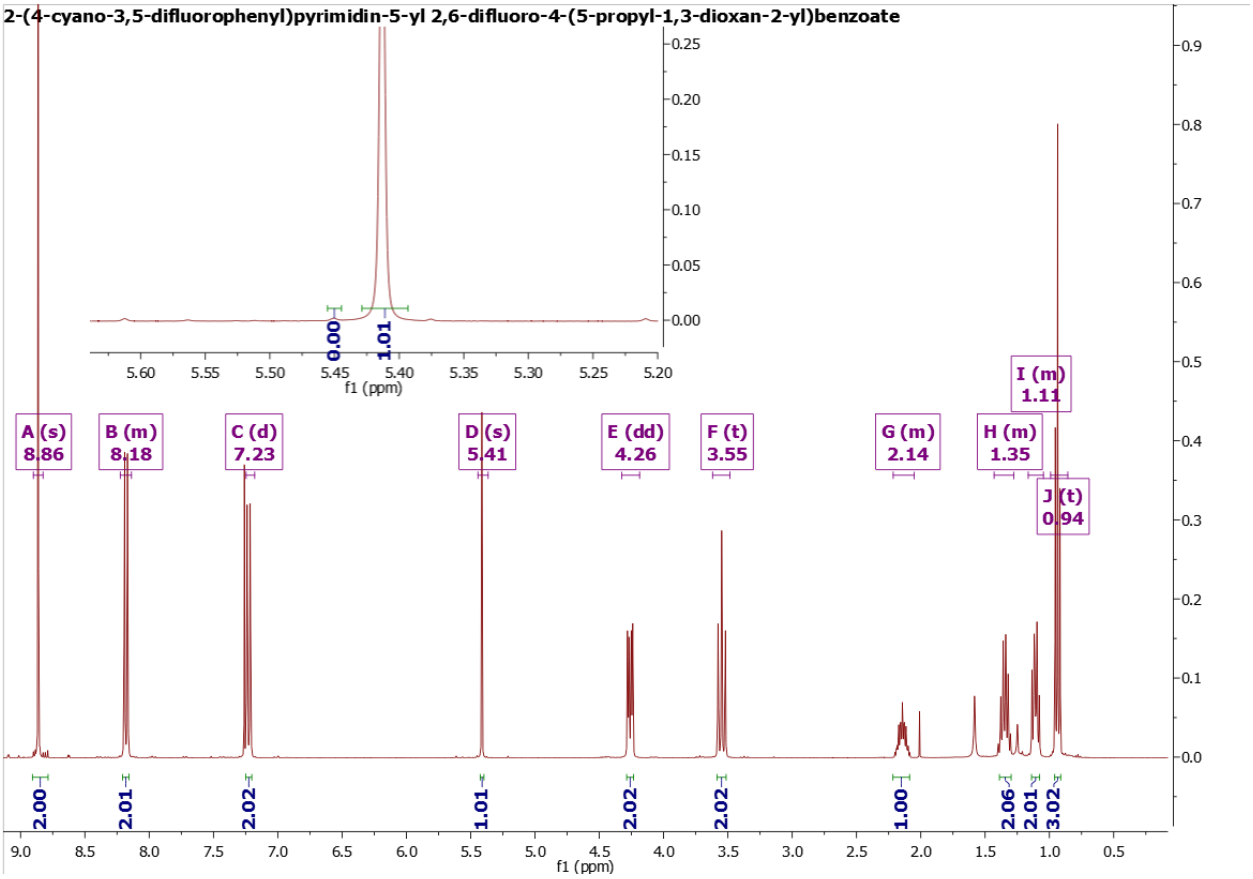


Figure S30. [1]HNMR spectrum of 2-(4-cyano-3,5-difluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate.

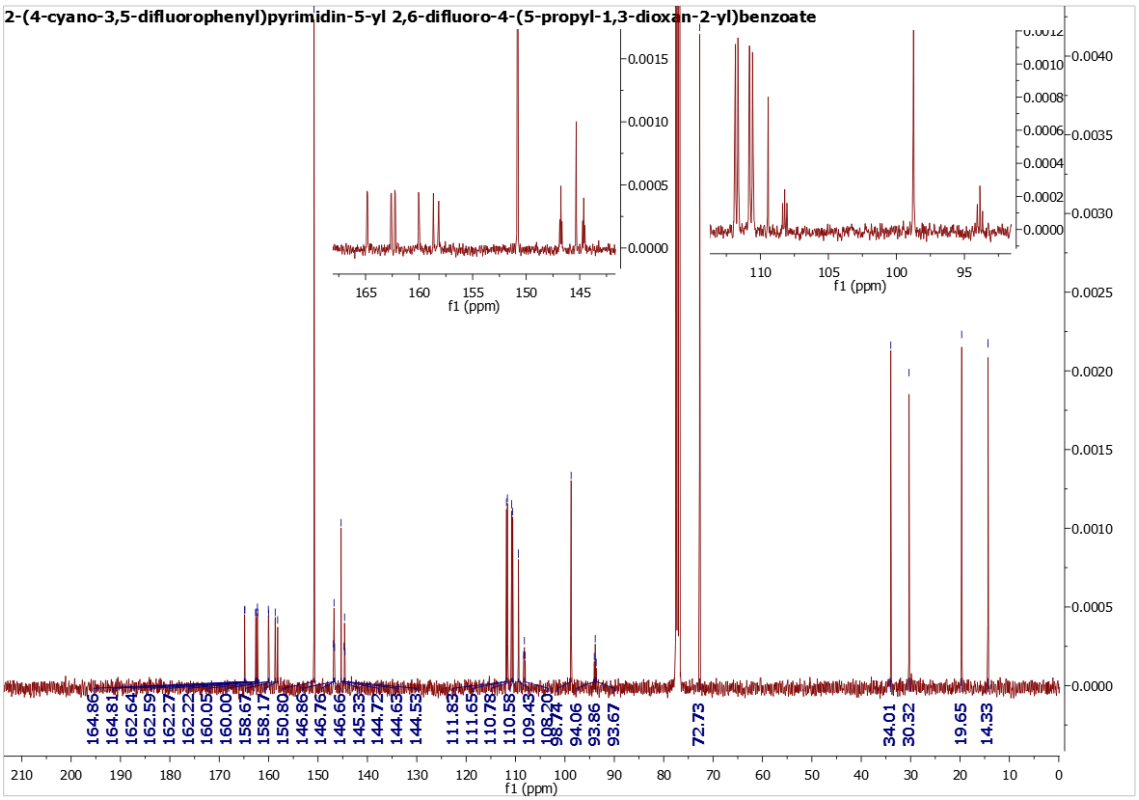


Figure S31. ^{13}C-NMR spectrum of 2-(4-cyano-3,5-difluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate.

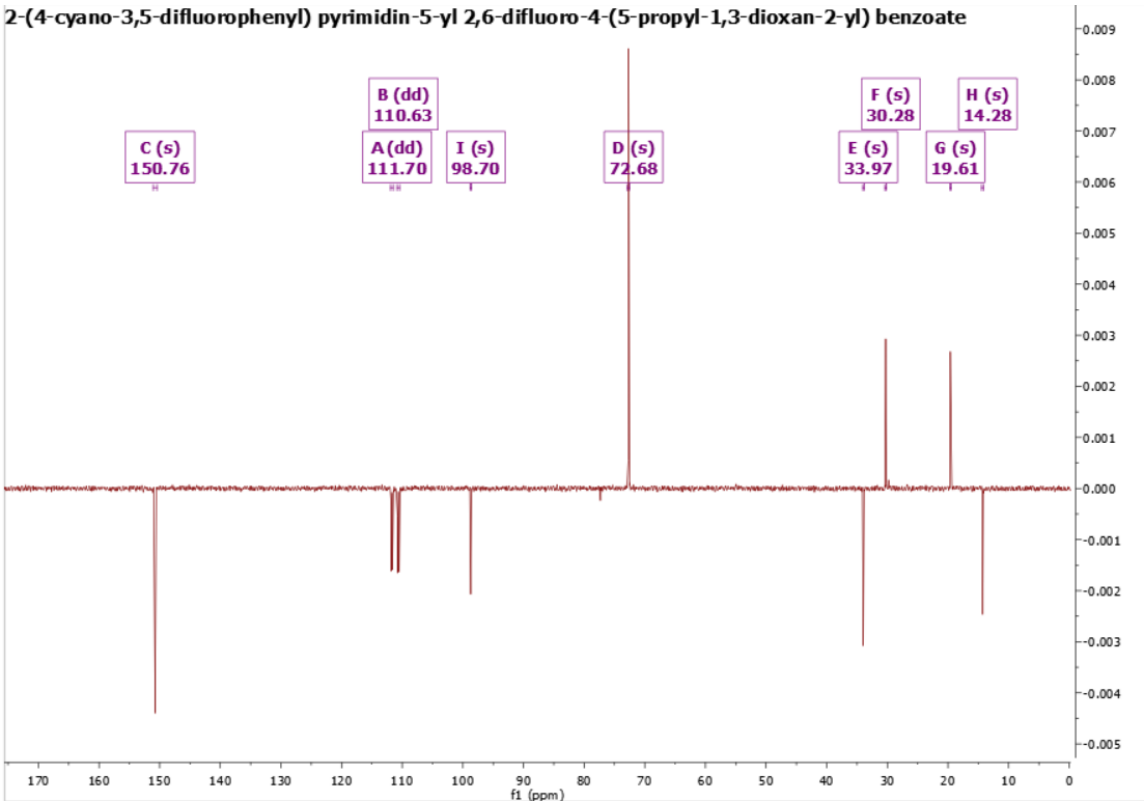


Figure S32. DEPT spectrum of 2-(4-cyano-3,5-difluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate.

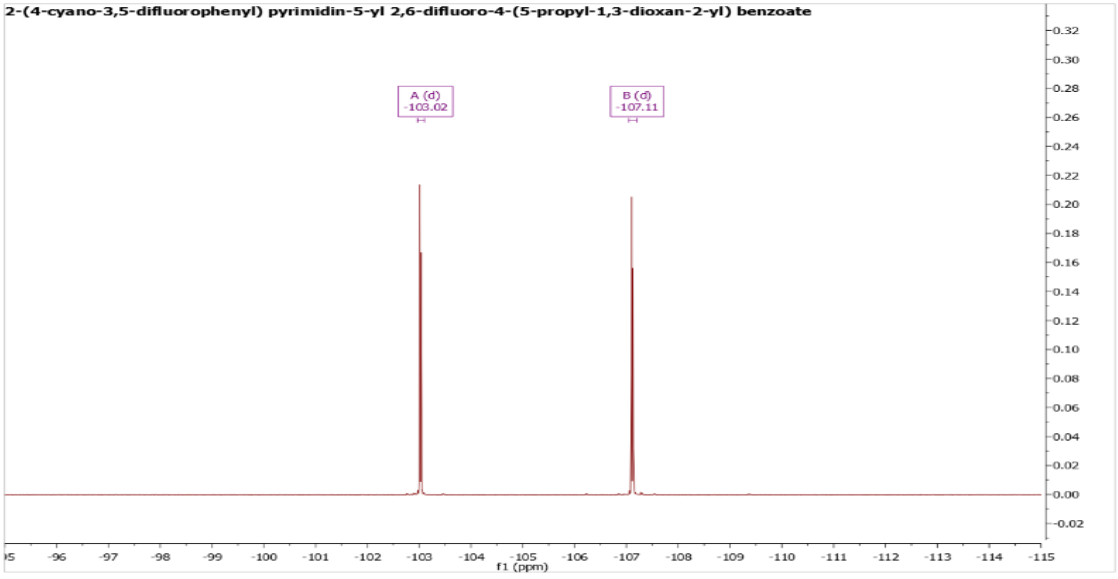
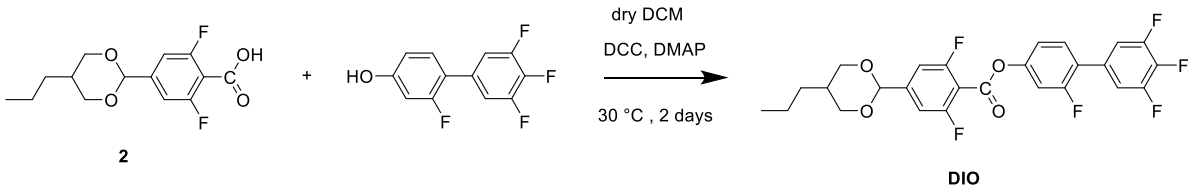


Figure S33. ^{19}FNMR of 2-(4-cyano-3,5-diflurophenyl) pyrimidin-5-yl 2,6-difluro-4-(5-propyl-1,3-dioxan-2-yl) benzoate.

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



Scheme 15: Synthesis of 2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate **DIO**.

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 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 evaporation under vacuum. The residue was purified through flash column chromatograph using solvent mixture ethyl acetate: hexane= 1:8, Rf=0.43. Followed by recrystallization with hexane for twice. The pure compound crystallized as a white solid.

Yield: 1.49 g, 76 %

DSC: Iso 174 N 83 SmZ_A 69 N_F 34 Cr [R6]

High resolution mass: $C_{26}H_{20}F_6O_4Na$, m/z: 533.1161, err: 0.2 ppm

^{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).

^{19}F-NMR (376 MHz, $CDCl_3$): δ -108.32 (d, J = 9.5 Hz, Ar-F), -114.25 (t, J = 9.0 Hz, Ar-F), -134.05 (dd, J = 20.2, 8.6 Hz, Ar-F), -161.01 (ttt, J = 18.8, 3.8 Hz, Ar-F).

Proton-Fluorine-Carbon decoupled ^{13}CNMR: 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 the published paper [R7].

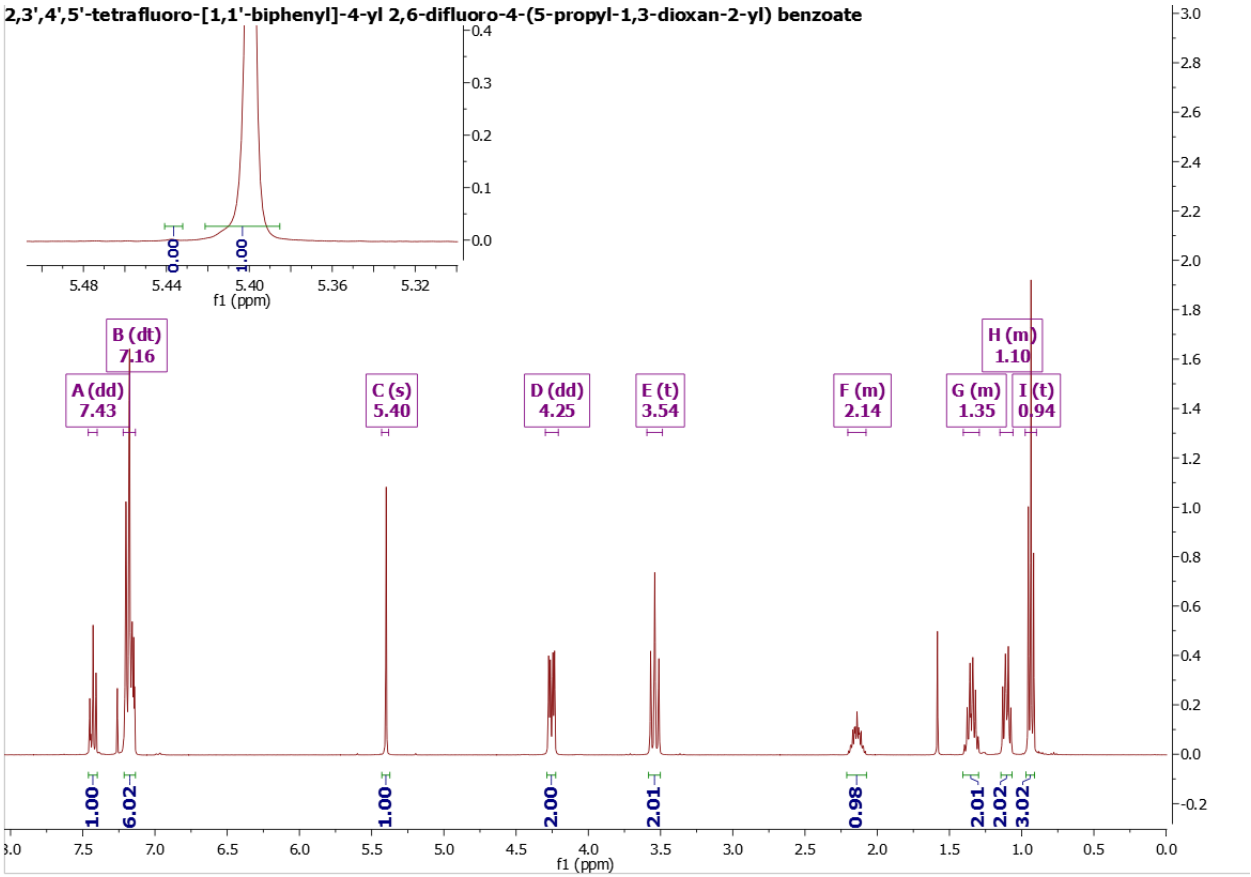


Figure S34 ^{1}HNMR spectrum of 2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate.

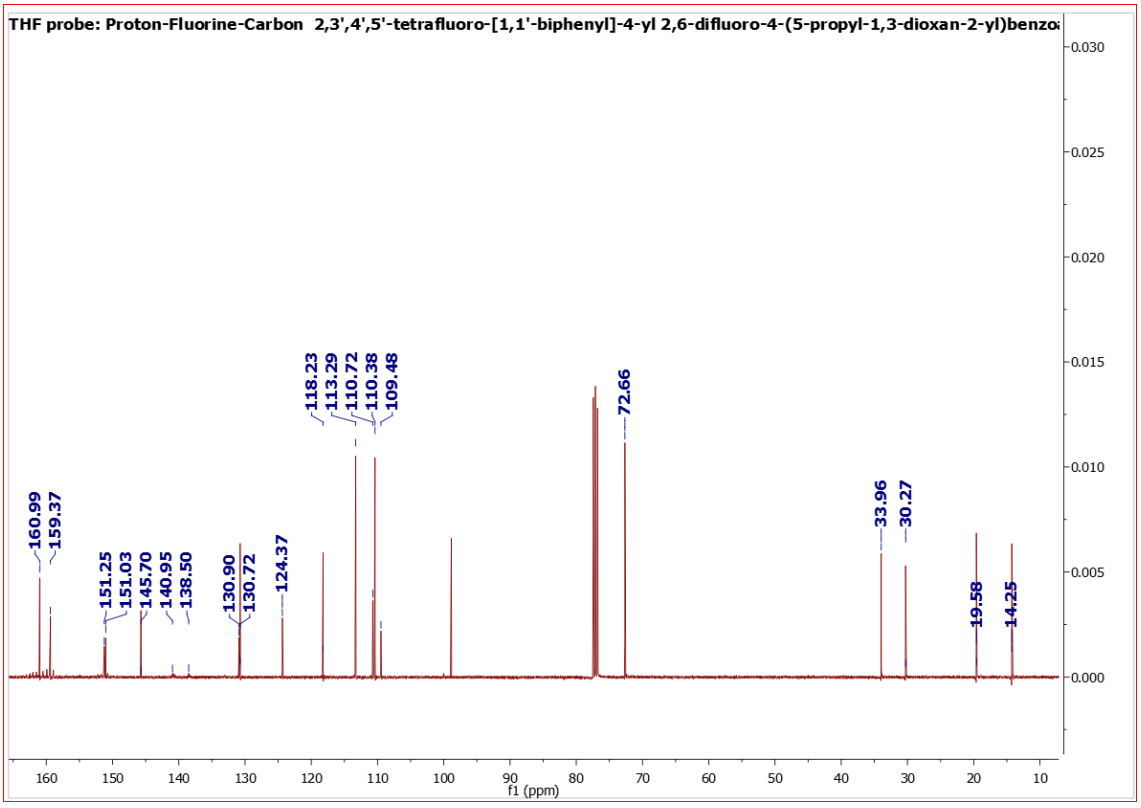


Figure S35. Proton-Fluorine-Carbon decoupled NMR spectrum of 2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate.

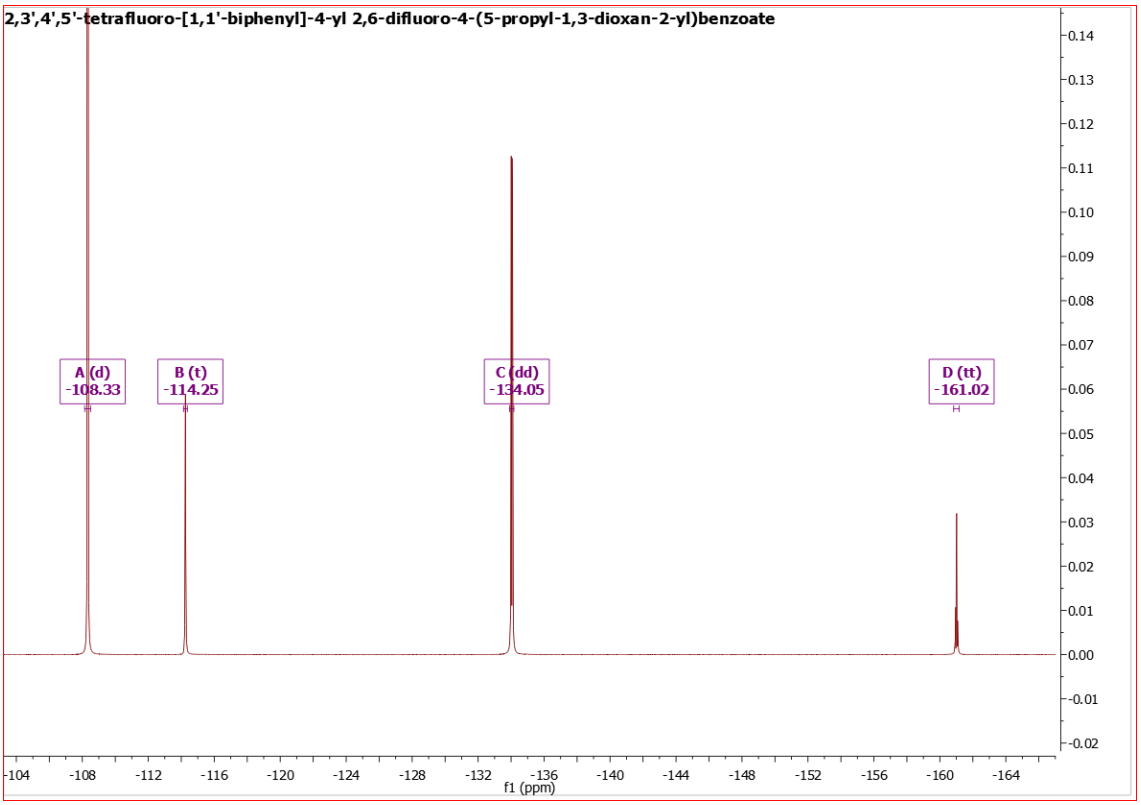


Figure S36. ^{19}F-NMR spectrum of 2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate.

2. Differential Scanning Calorimetry (DSC)

DSC were measured by Perkin Elmer Differential Scanning Calorimeter DSC 4000. An aluminum reference pan has been used to load the reference and sample, the calibration material is standard indium. DSC results were normally quoted by the average values for the onset of the second heating and cooling curve, the heating rate, if not mentioned specifically, was at 10 ˚C/min.

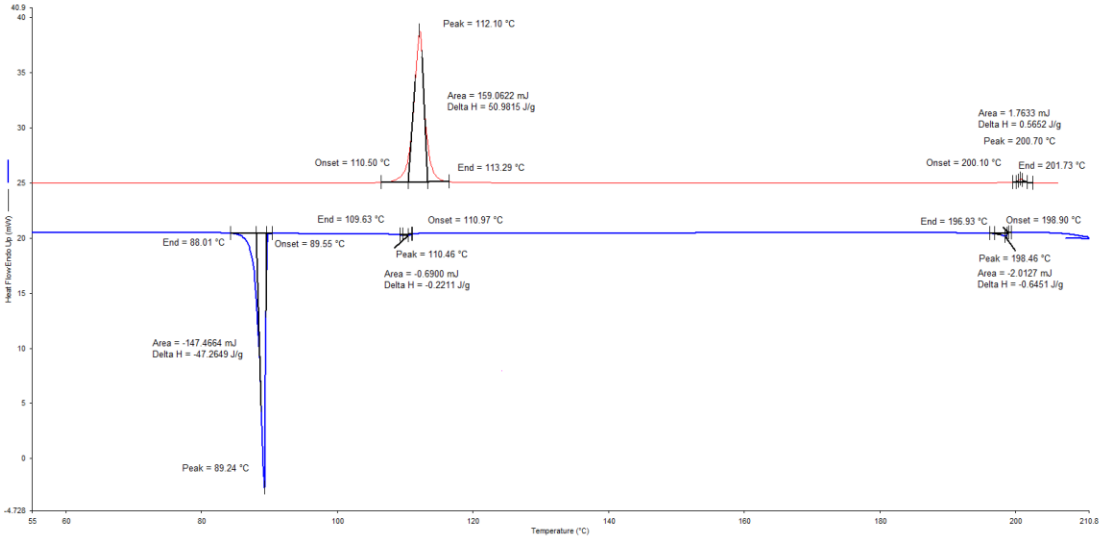


Figure S37. DSC curve for 2-(3,4,5-trifluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate **WJ-16,** rate 10 ˚C/ min. (blue curve for cooling, red curve for heating)

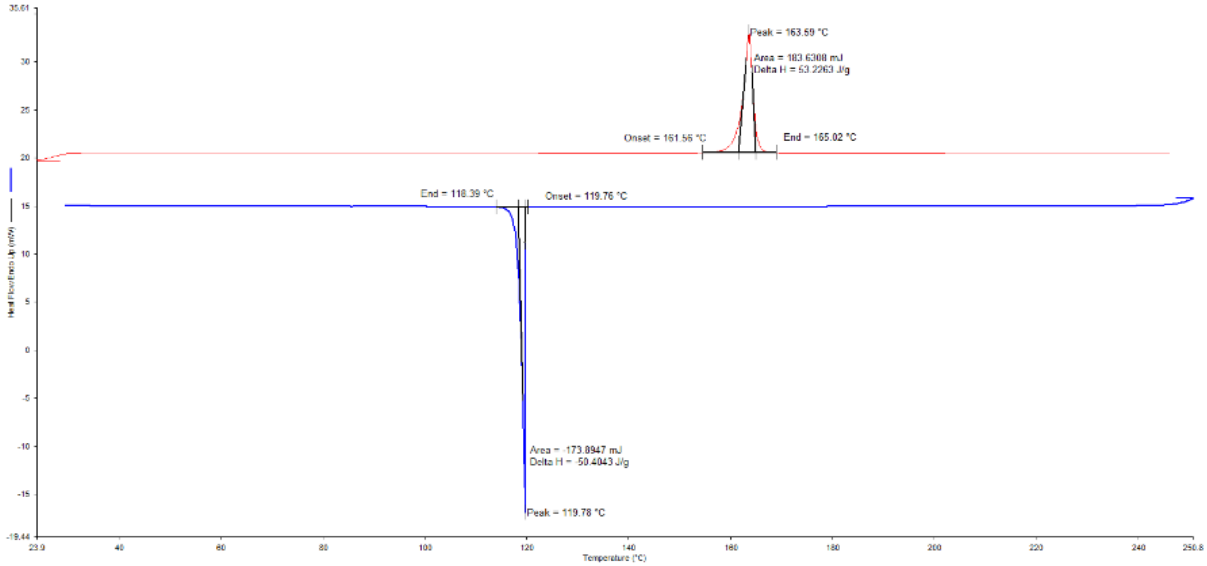


Figure S38. DSC second curve for 2-(4-cyano-3,5-difluorophenyl) pyrimidin-5-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate **WJ-18**, temperature range 30-250 ℃ rate 10 ℃/ min. (blue curve for cooling, red curve for heating), sample decomposes at 238 ℃.

3. POM

Textures

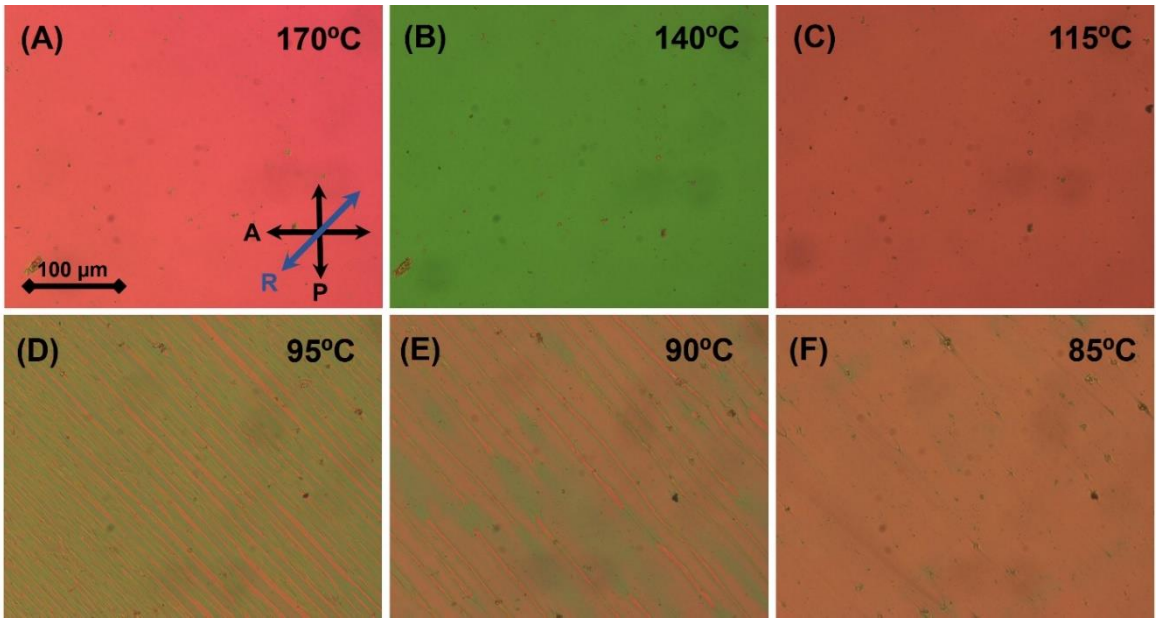


Figure S39: POM textures of WJ-16 filled 15 µm thick planar cell (A-F) under different temperatures. Here, A and P refers to the analyzer and polarizer while R refers to the rubbing direction in planar cells. The scale bar denotes 100 µm.

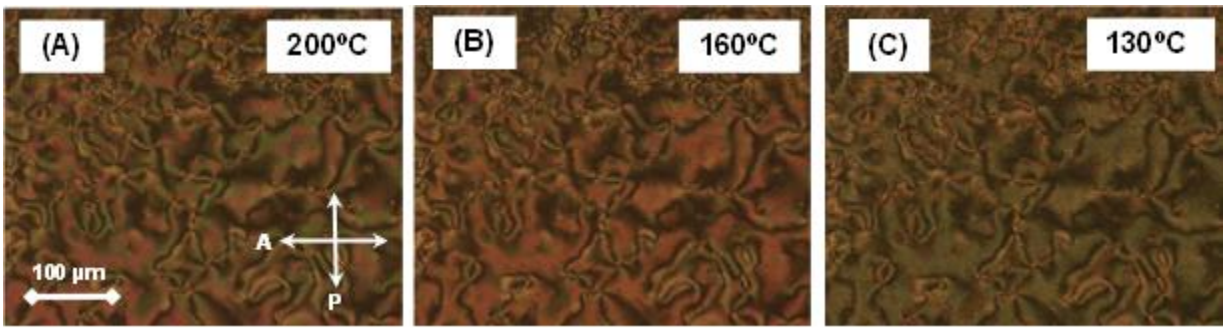
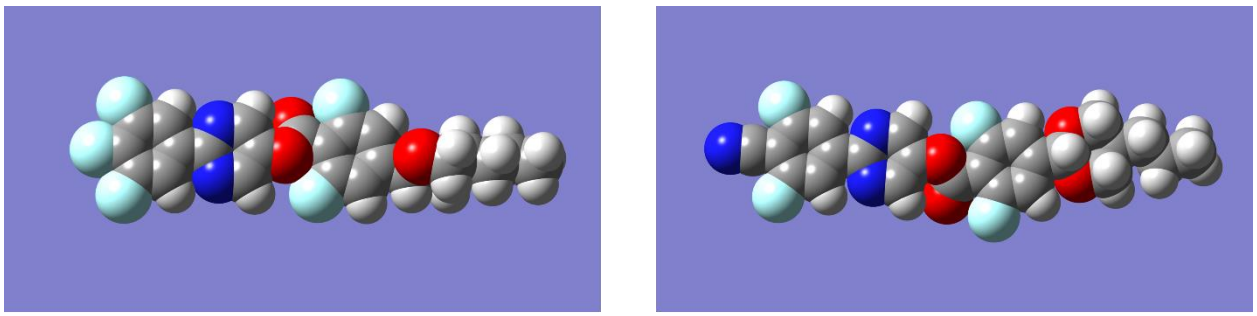


Figure S40: POM textures of WJ-18 filled 9 µm thick uncoated cell (A-C) under different temperatures. WJ-18 shows quasi-planar (Q-P) Schlieren texture in uncoated cell. Here, A and P refers to the analyzer and polarizer while R 45 deg to P/A refers to the rubbing direction in planar cells. The scale bar denotes 100 µm.

4. DFT calculations of the dipole moments



(A) **(B)**

Figure S41: Modelling calculated by (B3LYP-GD3BJ/ 6-31G (D, P) level of DFT) using Guassin View. (A) space modelling of compound **WJ-16**, dipole moment ~10.4 D (B) filling space modelling of compound **WJ-18**, dipole moment ~14.8 D.

5. XRD Results

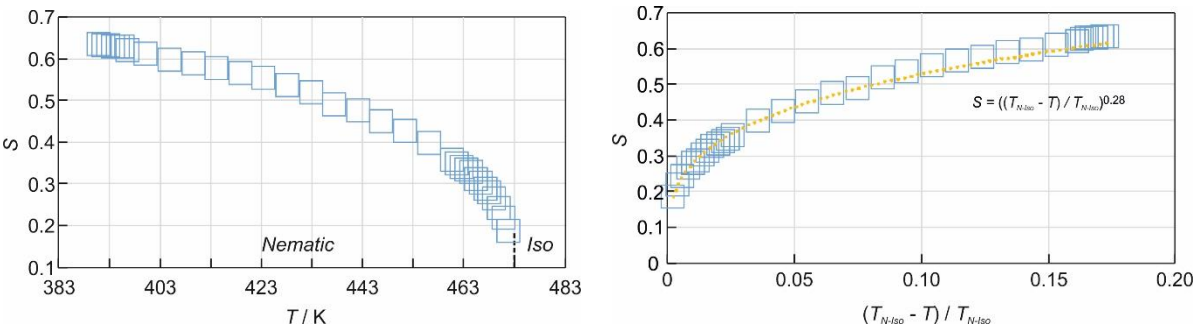


Figure S42: Measurement of the nematic order parameter *S* of WJ-16, based on WAXS studies of samples aligned by external magnetic field, showing that $S = (\frac{T_{\mathrm{N-Iso}} - T}{T_{\mathrm{N-Iso}}})^{0.28}$. The nematic order parameters are retrieved by fitting the WAXS intensity curve as a function of azimuthal angle following the established procedure [R8].

To get an understanding on the molecular correlation length ($\xi_{\parallel}$) in the longitudinal direction in the N phase, the *SAXS* peak retrieved along the external magnetic field direction are normalised (**Figure S43A**). On heating, the width of *SAXS* peaks are expanding as towards *Iso* phase. The full width at half maximum (FWHM) is then calculated and plotted as a function of temperature

(**Figure S43B**). The longitudinal correlation length can then be calculated using $\xi_{\parallel} = \frac{2}{FWHM}$ (**Figure S43C**).[R9] On heating, $\xi_{\parallel}$ in the N phase just above the SmA-N transition is around 210 Å, 9 times the molecular length of WJ16. $\xi_{\parallel}$ decreases with increasing temperature, faster at the lower temperature region and then slowly to a value of about single extended molecular length (~ 23.3 Å) near the N-Iso phase transition.

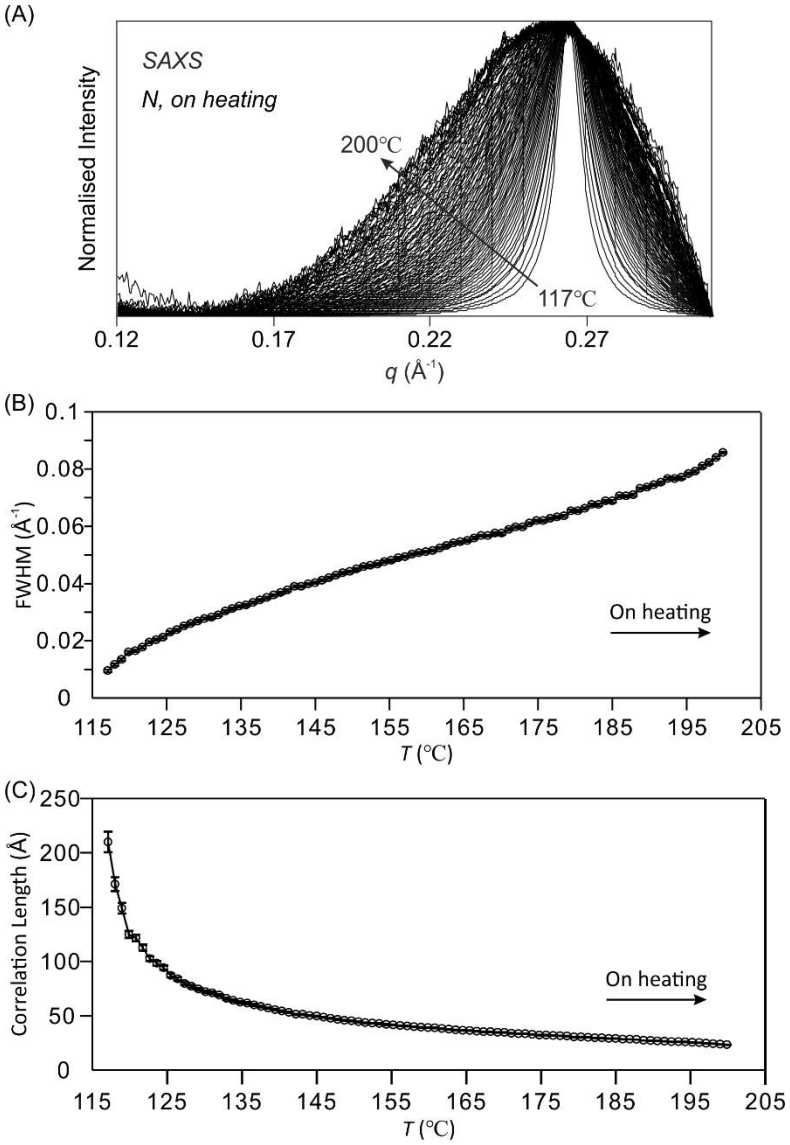


Figure S43: Longitudinal correlation length of the molecules in the N phase formed in WJ16 compound. (A) Normalised *SAXS* diffractograms, retrieved along the external magnetic field direction. The data was recorded for the N phase range during heating from SmA to Iso phase. (B)

A full width at half maximum (FWHM) of the *SAXS* peak plotted as a function of temperature, based on the data in (A), with error bar displayed. (C) The longitudinal correlation length calculated based on the FWHM collected in (B), with the error bar to show the increasing effect of the *SAXS* resolution-limit on the data precision while towards the SmA phase.

Similarly, the lateral correlation length ($\xi_{\perp}$) in the N phase can be retrieved from the *WAXS* peak in the direction perpendicular to the external magnetic field. Normalised WAXS spectra are shown in **Figure S44A**. On heating from SmA to N phase, a small step-wise increase in the FWHM is observed (**Figure S44B**), i.e., a decrease of the lateral correlation length at the transition (**Figure S44C**). The lateral correlation length remains virtually constant in the N phase.

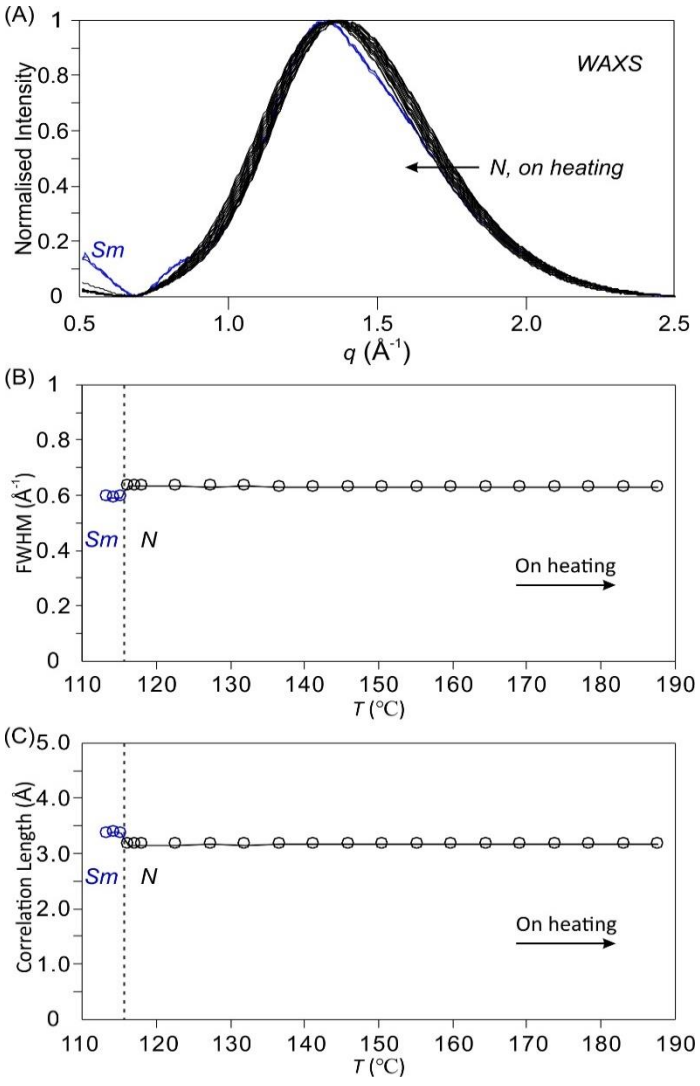


Figure S44: Lateral correlation length of the molecules in the N phase formed in WJ16 compound. (A) Normalised *WAXS* peaks, retrieved perpendicular to the external magnetic field direction. The data was recorded for the N phase range on heating from SmA to Iso phase. (B) A FWHM of the *WAXS* peak plotted as a function of temperature, based on the data in (A). (C) The lateral correlation length calculated based on the FWHM collected in (B).

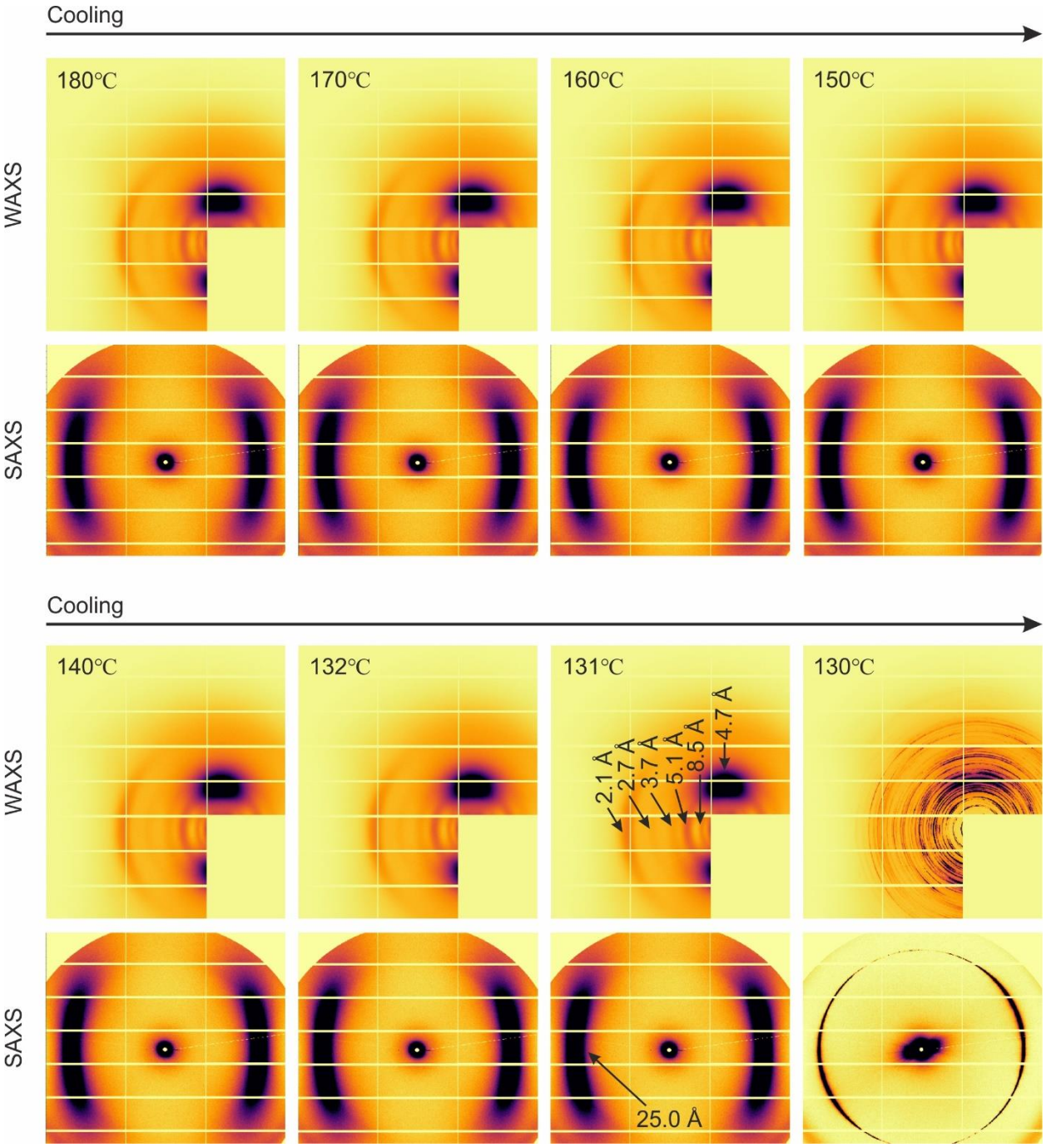


Figure S45: Simultaneous SAXS/WAXS patterns of WJ-18, recorded on cooling from 180°C (nematic) to 130°C, where sample crystallises, at a rate of 2°C/min. The 1st SAXS peak has d-spacing of ~25.0Å, almost exactly the same as the length of the WJ-18 molecule. The wide-angle scattering in the vertical direction centres around 4.7 Å, suggesting a slightly larger side-way distance between parallel molecules, compared to that of WJ-16 (~4.5Å).

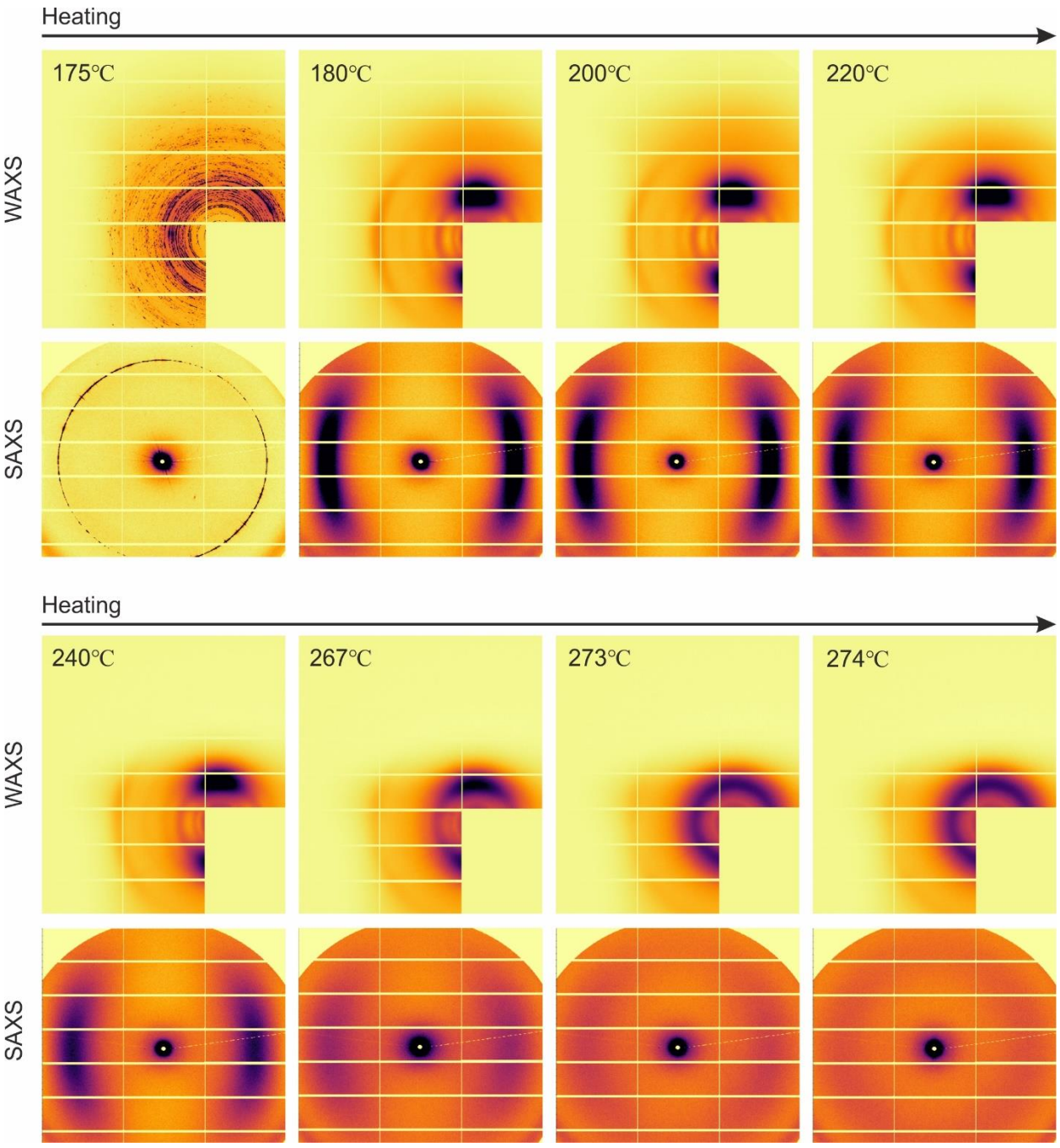


Figure S46: Simultaneous SAXS/WAXS patterns of WJ-18 compound, recorded on heating from crystal (175°C), to nematic (180°C to 267°C), and isotropic (above 273°C). The heating rate used was 2°C/min.

References

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[R2] Nishikawa, H.; *et al.* "Nano-clustering mediates phase transitions in a diastereomerically-stabilized ferroelectric nematic system." Communications Materials, 2022: **3**, 89.

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[R9] Li, Y.X.; *et al.* A case of antiferrochirality in a liquid crystal phase of counter-rotating staircases, Nat. Commun. 2022, **13**, 384.