Supplementary Information (SI) for Soft Matter.

Supporting Information for

Helical vs. non-helical nematic and lamellar proper ferroelectric liquid crystal phases

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1. Experimental
2. Organic synthesis and analytical data
3. Crystallographic data
4. Additional results

1. Experimental:

Synthesis progress and purity of synthesized compounds were determined using SHIMADZU GCMS-QP2010S (Shimadzu, Kyoto, Japan) series gas chromatograph equipped with quadrupole mass analyser MS(EI) and by thin layer chromatography (silica gel 60 with fluorescent indicator on aluminum, Macherey-Nagel, Germany). Proton (1H) and carbon (13C) nuclear magnetic resonance (NMR) spectra in CDCl3 were collected using a Bruker, model Avance III spectrometer (Bruker, Billerica, MA, USA). High-resolution mass spectroscopy was performed using a Thermo Scientific Orbitrap Exploris 120 mass spectrometer (Thermo-Fisher Scientific, Waltham, MA, USA).

Phase transition temperatures and the associated enthalpy changes were measured by differential scanning calorimetry using a differential scanning calorimeter DSC 204 F1 Phoenix instrument (Netzsch, Selb, Germany). Measurements were performed under a nitrogen atmosphere with a heating/cooling rate of 10 K min^{-1}, unless otherwise specified.

Observations of optical textures of liquid crystalline phases was carried out by polarised-light optical microscopy using a Zeiss AxioImager.A2m microscope equipped with a Linkam heating stage.

Optical birefringence was measured with a setup based on a photoelastic modulator (PEM-90, Hinds) working at a modulation frequency f = 50 kHz; as a light source a halogen lamp (Hamamatsu LC8) equipped with narrow bandpass filters was used. The transmitted light intensity was monitored with a photodiode (FLC Electronics PIN-20) and the signal was deconvoluted with a lock-in amplifier (EG&G 7265) into 1f and 2f components to yield a retardation induced by the sample. Knowing the sample thickness, the retardation was recalculated into optical birefringence. Samples were prepared in 1.6-μm-thick cells with planar anchoring. The alignment quality was checked prior to measurement by inspection under the polarised-light optical microscope.

Single crystal X-ray diffraction: For each homologue a suitable single crystal was mounted on a nylon loop and subjected to single-crystal diffraction experiment on a SuperNova diffractometer, equipped with CuKα (λ = 1.54184Å) radiation source and HyPix detector. The crystals were kept at cryogenic temperatures (Table S1). For each homologue x-ray data reduction was conducted using CrysalisPro from Rigaku Oxford Diffraction[1]. All of the structures were solved and refined using Olex2[2]. For homologue n=1 and n=2 the structure was solved with the SHELXT[3] structure solution program using Intrinsic Phasing while for n=3 the structure was solved with the SHELXS using Direct Methods and for n=4 the structure was solved with the SHELXD. All structures were refined with the SHELXL[4] refinement package using Least Squares minimisation. H-atoms were visible in the Fourier maps in all instances, but have been refined in riding approximation (AFIX). For structure visualization Mercury software was used[5,6].

X-ray diffraction measurements of samples in liquid crystalline phases were carried out using a Bruker D8 GADDS system, equipped with micro-focus-type X-ray source with Cu anode and dedicated optics and VANTEC2000 area detector. Small angle diffraction experiments were performed on a Bruker Nanostar system (IµS microfocus source with copper target, MRI heating stage, Vantec 2000 area detector).

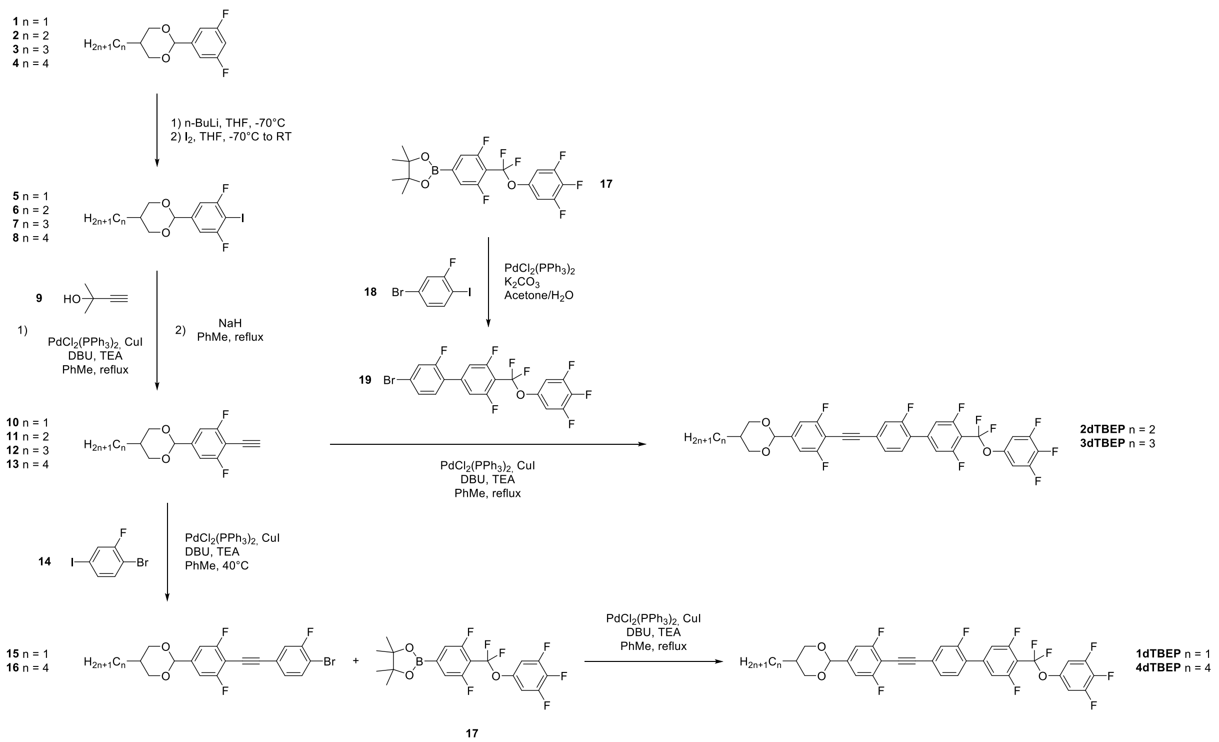
The complex dielectric permittivity, ε*, was measured using a Solartron 1260 impedance analyser, in the 1 Hz −10 MHz frequency range, and a probe voltage of 50 mV. The material was placed in a 3-10 µm glass cell with gold or ITO electrodes.

To determine the helical pitch length in N_{TBF} phase a diffraction of laser light on material placed in a glass cell was monitored, in this geometry the helical structure acts as the polarization grating due to the periodic change of refractive index.

Spontaneous polarization, P_s, was determined from integration of switching current flow through a resistor (1K-10K Ohm) connected in series with the cell under testing. A triangular-wave voltage of frequency 1 to 10 Hz was applied. A Siglent SDG2042X arbitrary waveform generator, FLC A200 amplifier and Siglent SDS2000X Plus oscilloscope were used.

The SHG activity has been tested with setup based on a solid-state laser EKSPLA NL202, with 9 ns pulses at a 10 Hz repetition rate and max. 2 mJ pulse energy at λ=1064 nm. The infra-red beam incident onto a cells with planar anchoring resulted in generation of green light.

2. Organic Synthesis:



*2-(3,5-difluoro-4-iodophenyl)-5-methyl-1,3-dioxane (**5**)*

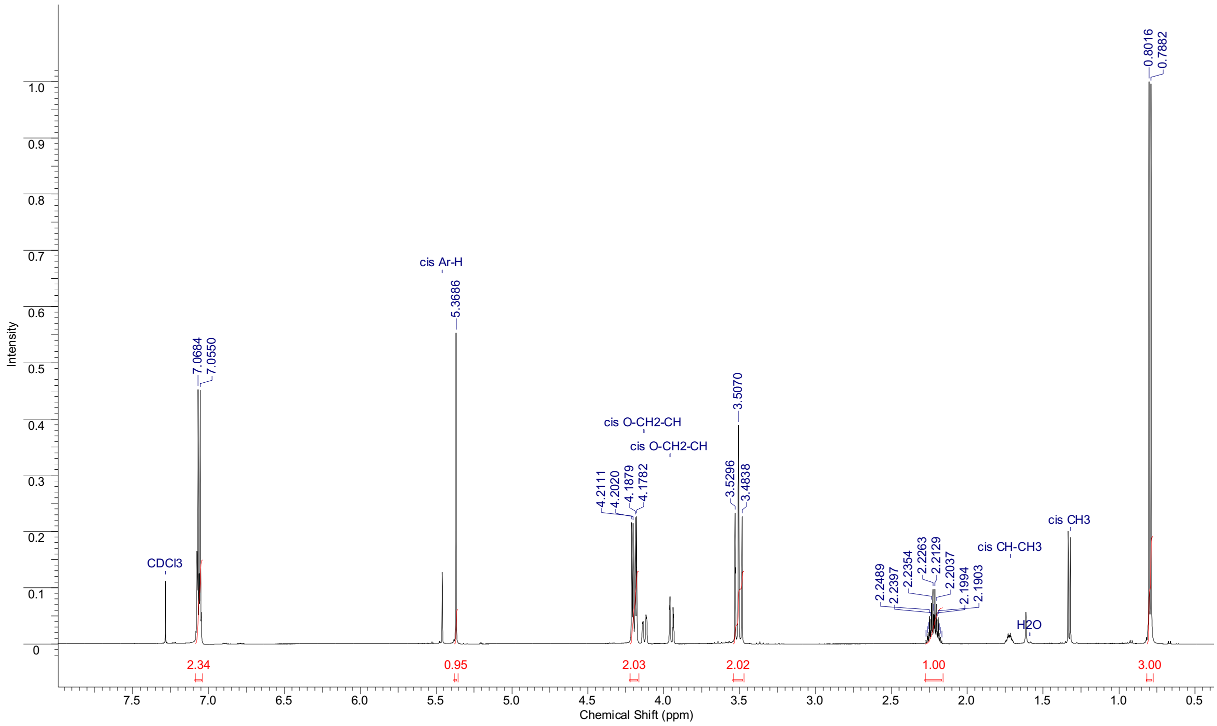
To a stirred solution of 2-(3,5-difluorophenyl)-5-methyl-1,3-dioxane (**1**, 40 g, 0.187 mol) in THF (500 mL) at –78 °C, a solution of *n*-butyllithium in hexanes (0.215 mol, 2.5 M) was added dropwise. The mixture was stirred at –78 °C for 2 h. Then, a solution of I_2 (54.57 g, 0.215 mol) in THF was added dropwise, and the mixture was allowed to warm to room temperature. THF was removed under reduced pressure using a rotary evaporator. The residue was washed with a saturated aqueous solution of Na_2SO_3 and extracted with DCM. The phases were separated, and the organic layer was dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The crude product was used without further purification.

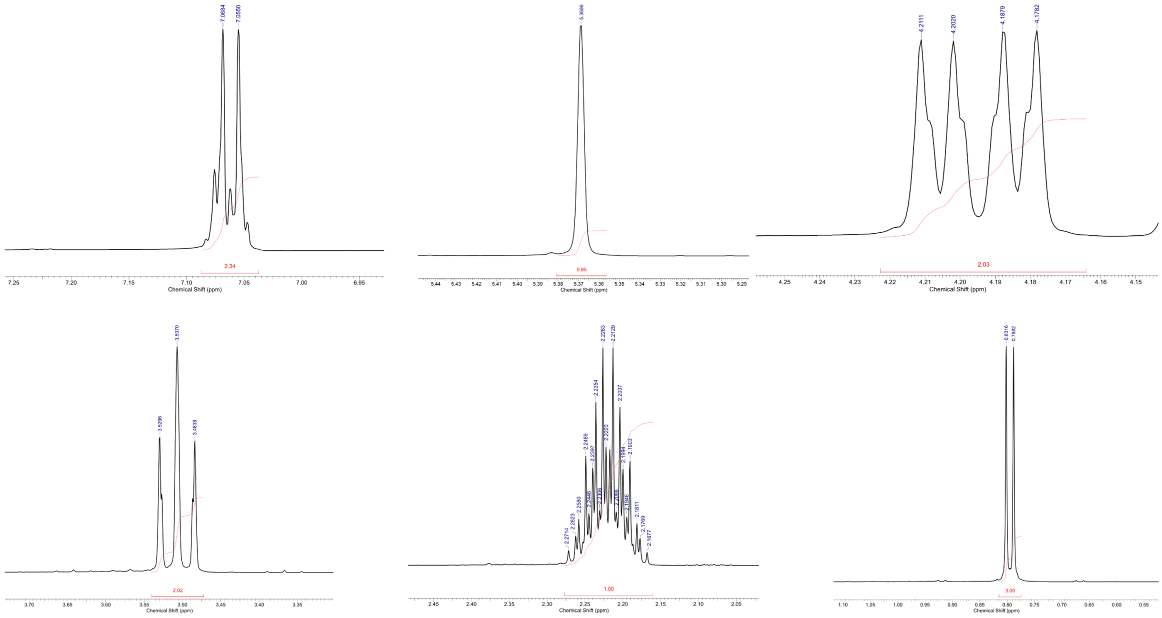
Yield: 59.55 g (93.6%)

Purity (GCMS): 97.6% (77.5% of trans isomer)

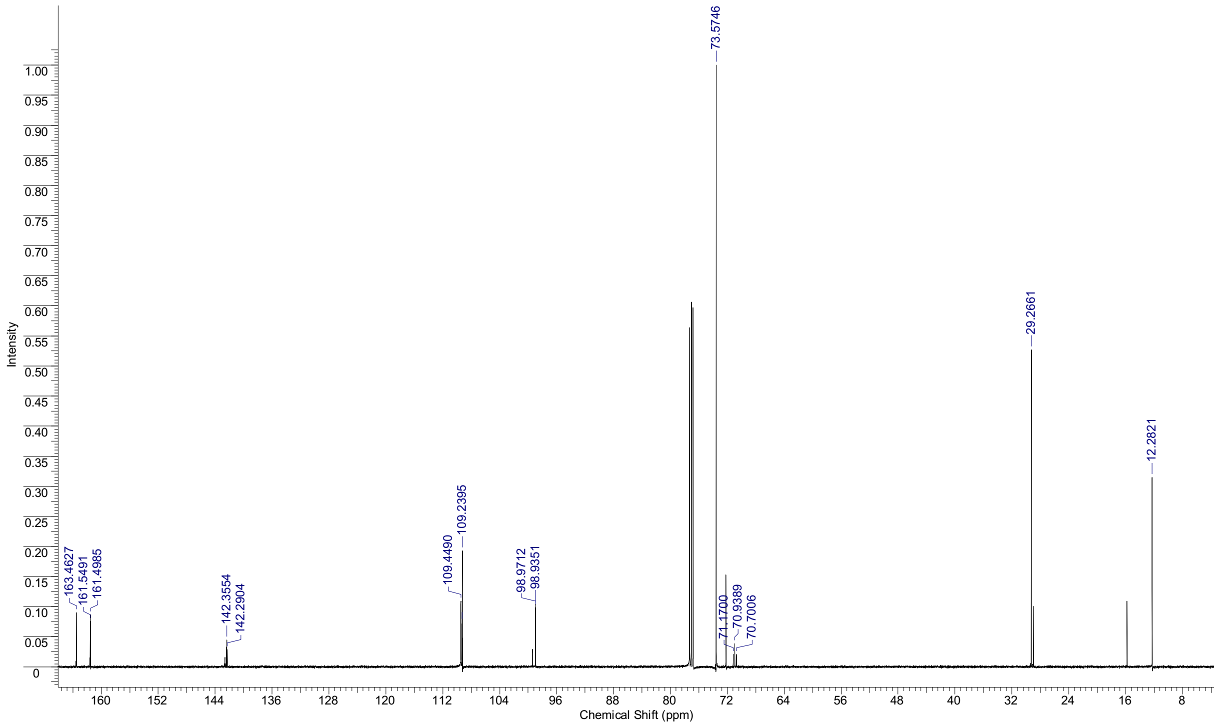
MS (EI) m/z: 340; 321; 285; 267; 239; 213; 194; 159; 141

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.06 (d, *J*=6.71 Hz, 2 H, overlapping aromatic proton signals of cis isomer); 5.37 (s, 1 H); 4.19 (dd, *J*=11.75, 4.73 Hz, 2 H); 3.51 (t, *J*=11.44 Hz, 2 H); 2.22 (m, 1 H); 0.79 (d, *J*=6.71 Hz, 3 H)





^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.50 (dd, *J*=245, 6.36 Hz); 142.36 (t, *J*=9.09 Hz); 109.33 (m); 98.95 (t, *J*=2.27 Hz); 73.57; 70.94 (t, *J*=29.52 Hz); 29.27; 12.28



*2-(3,5-difluoro-4-iodophenyl)-5-ethyl-1,3-dioxane (**6**)*

The synthesis was carried out in the same manner as in **5**.

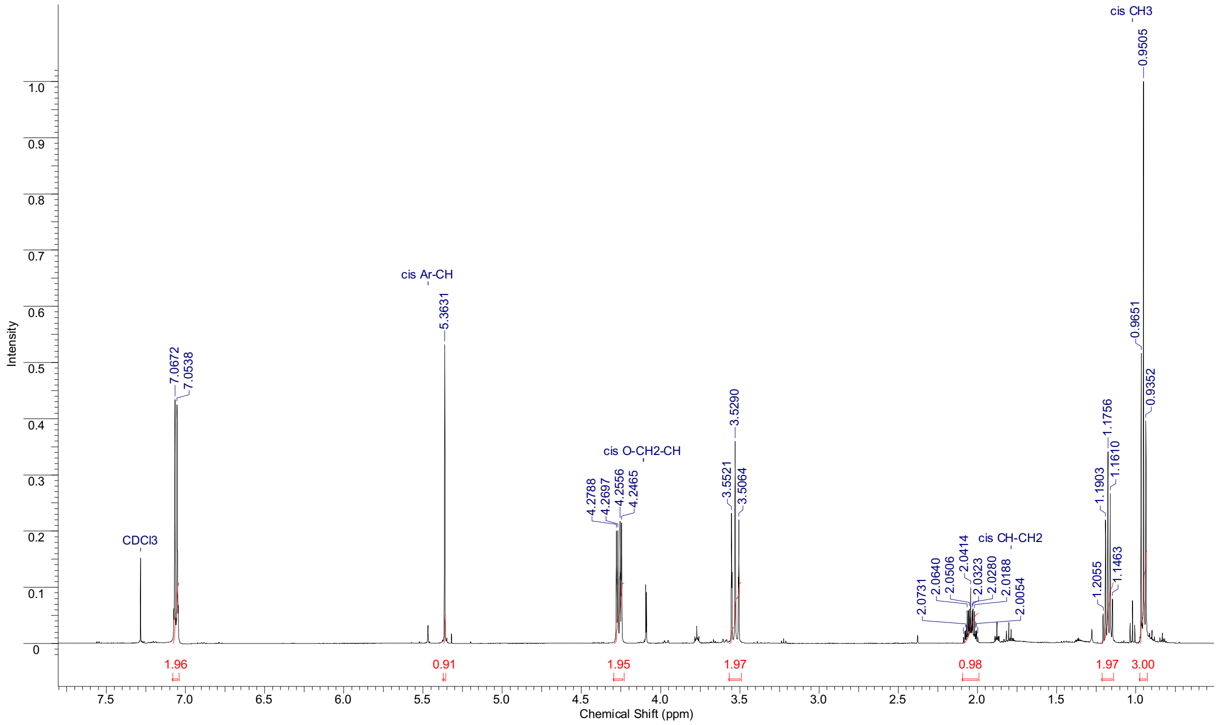
Quantities used: 2-(3,5-difluorophenyl)-5-ethyl-1,3-dioxane (**2**, 47.98g, 0.210mol), n-butyllithium (0.242mol, 2.5M), I_2 (61.42g, 0.242mol).

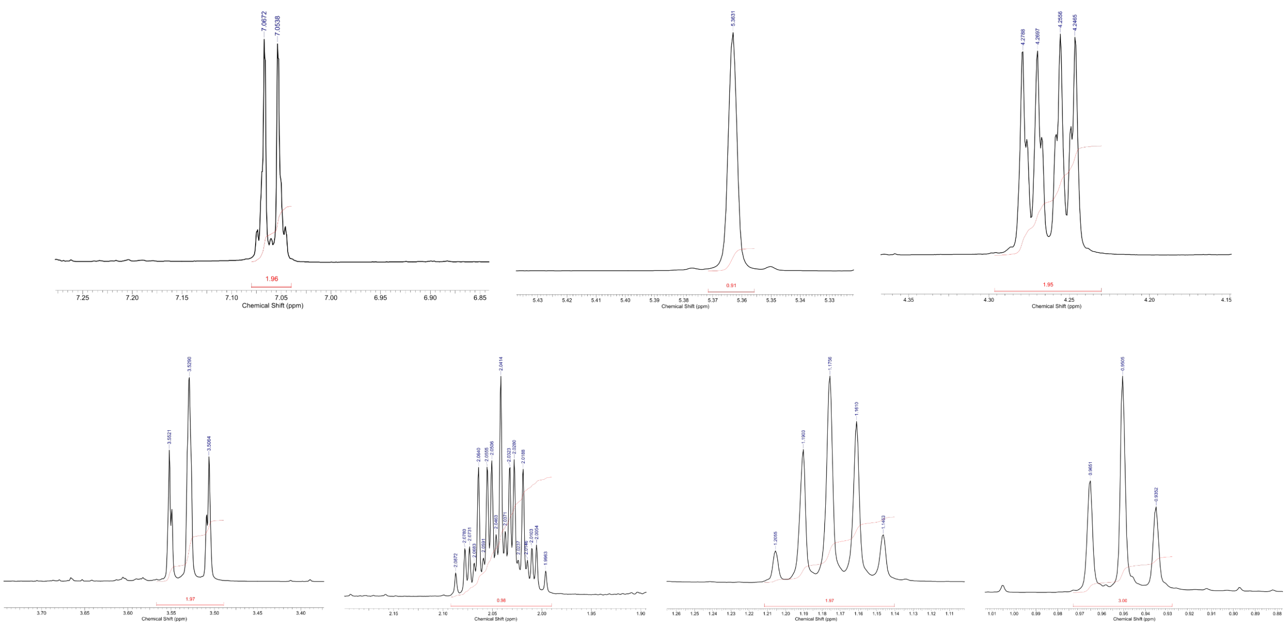
Yield: 66.65g (89.6%)

Purity (GCMS): 96.0% (73.0% of trans isomer)

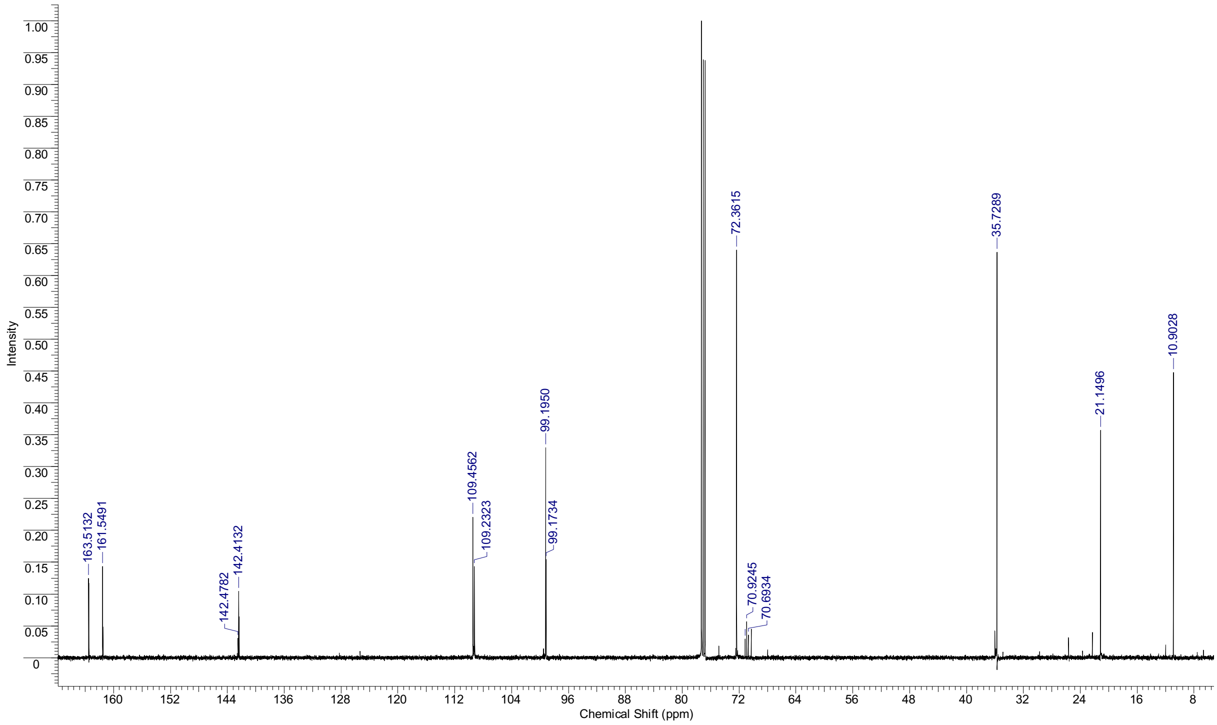
MS (EI) m/z: 354; 335; 267; 240; 208; 159; 141

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.06 (d, *J*=6.71 Hz, 2 H); 5.36 (s, 1 H); 4.26 (dd, *J*=11.60, 4.58 Hz, 2 H); 3.53 (t, *J*=11.44 Hz, 2 H); 2.04 (m, 1 H); 1.18 (m, 2 H); 0.95 (t, *J*=7.48 Hz, 3 H)





^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.51 (dd, *J*=247.05, 6.36 Hz); 142.41 (t, *J*=8.63 Hz); 109.34 (m); 99.20 (t, *J*=2.27 Hz); 72.36; 70.93 (t, *J*=29.52 Hz); 35.73; 21.15; 10.90



*2-(3,5-difluoro-4-iodophenyl)-5-propyl-1,3-dioxane (**7**)*

The synthesis was carried out in the same manner as in **5**.

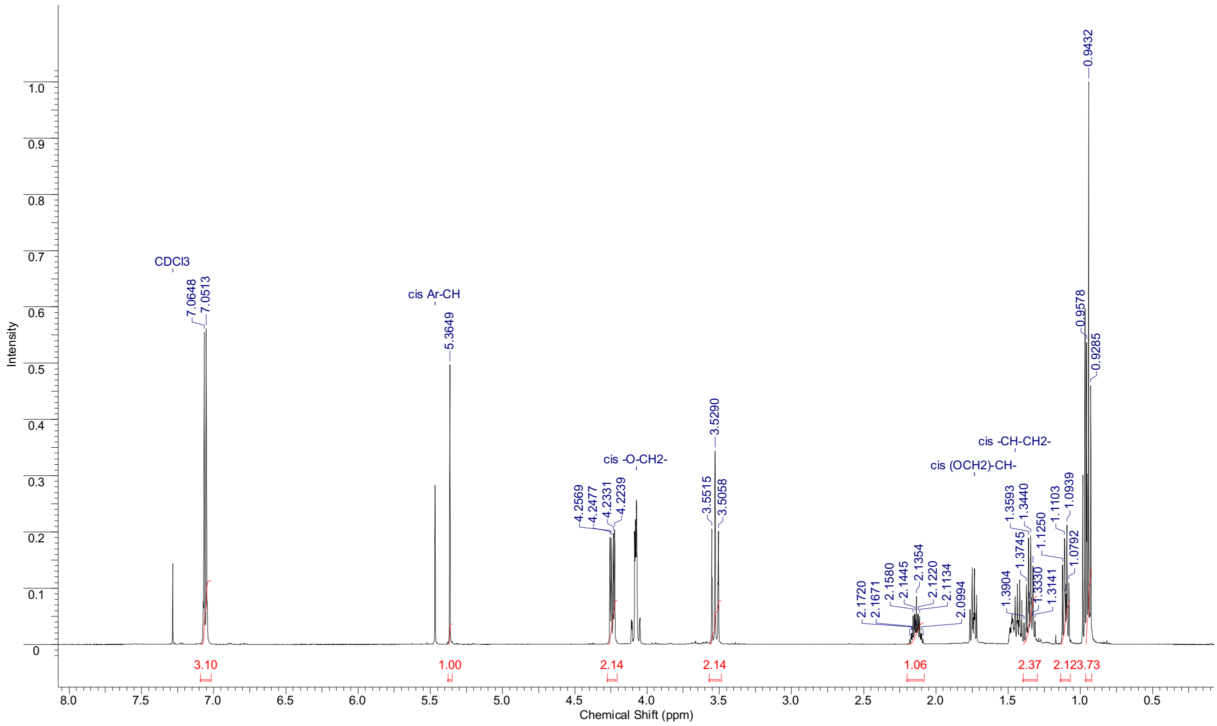
Quantities used: 2-(3,5-difluorophenyl)-5-propyl-1,3-dioxane (**3**, 66.21g, 0.273mol), n-butyllithium (0.314mol, 2.5M), I_2 (79.7g, 0.314mol).

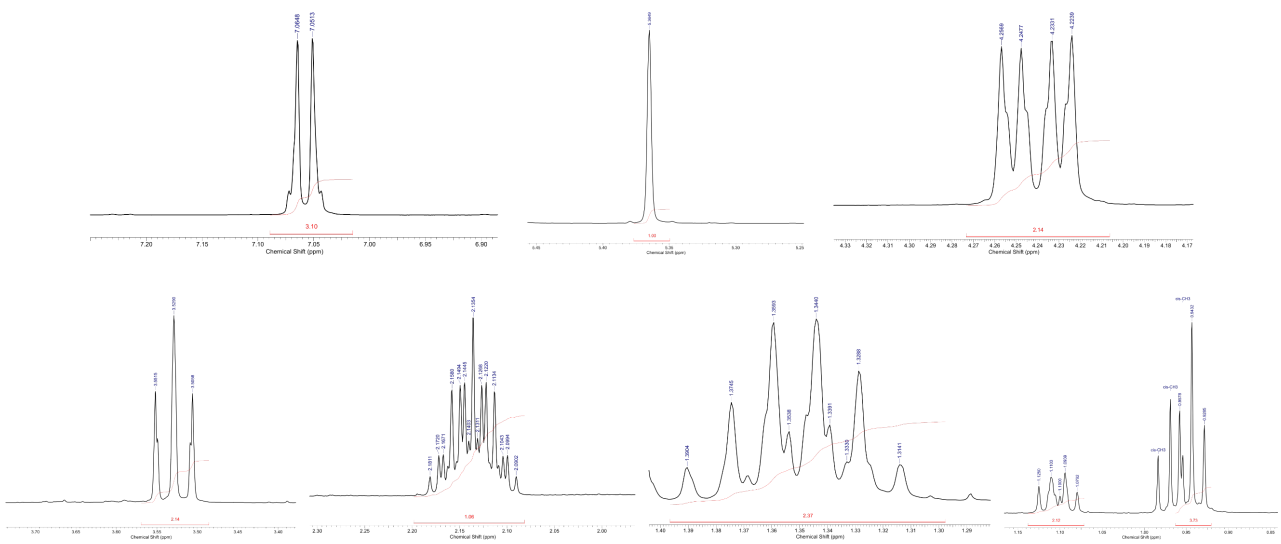
Yield: 100g (99.5%)

Purity (GCMS): 98.1% (76% of trans isomer)

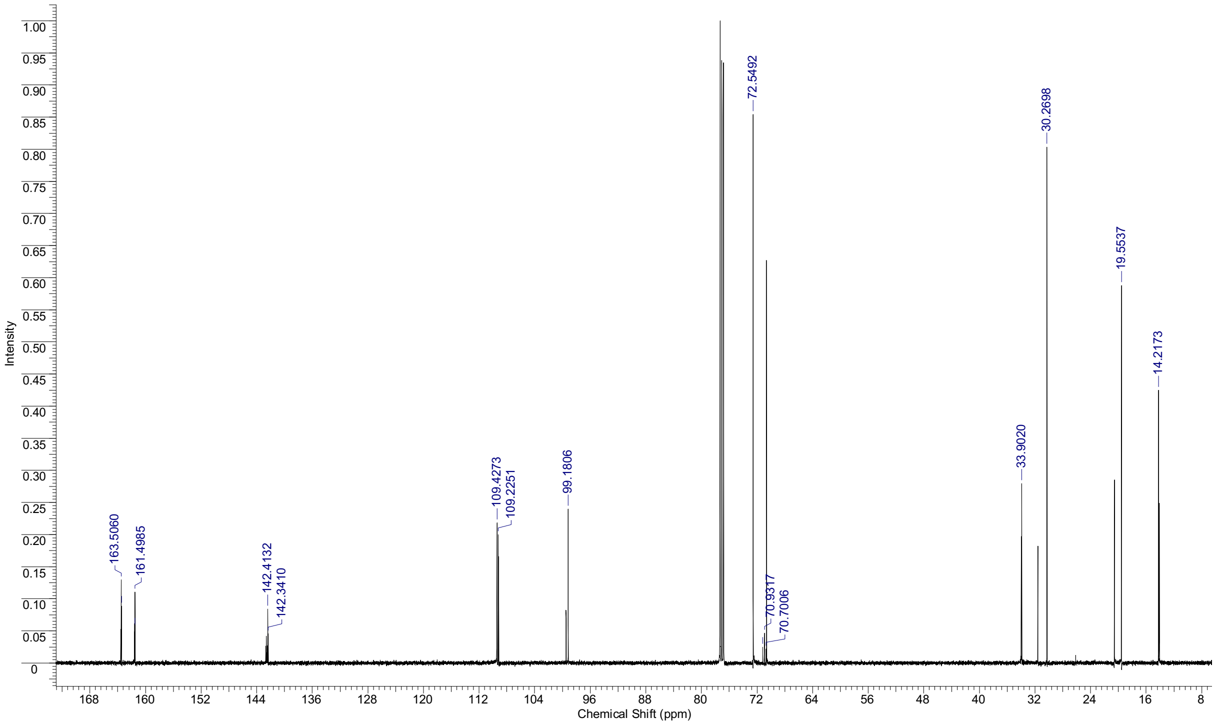
MS (EI) m/z: 368; 267; 240; 211; 180; 141

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.06 (d, *J*=6.71 Hz, 2 H, overlapping aromatic proton signals of cis isomer); 5.36 (s, 1 H); 4.24 (dd, *J*=11.90, 4.58 Hz, 2 H); 3.53 (t, *J*=11.44 Hz, 2 H); 2.14 (m, 1 H); 1.35 (m, 2 H); 1.10 (m, 2 H); 0.94 (t, *J*=7.32 Hz, 3 H)





^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.50 (dd, *J*=245.53, 5.45 Hz), 142.41 (t, *J*=9.08 Hz); 109.28 (m); 99.18 (t, *J*=2.27 Hz); 72.55; 70.93 (t, *J*=29.52 Hz); 33.90; 30.27; 19.55; 14.22



*2-(3,5-difluoro-4-iodophenyl)-5-butyl-1,3-dioxane (**8**)*

The synthesis was carried out in the same manner as in **5**.

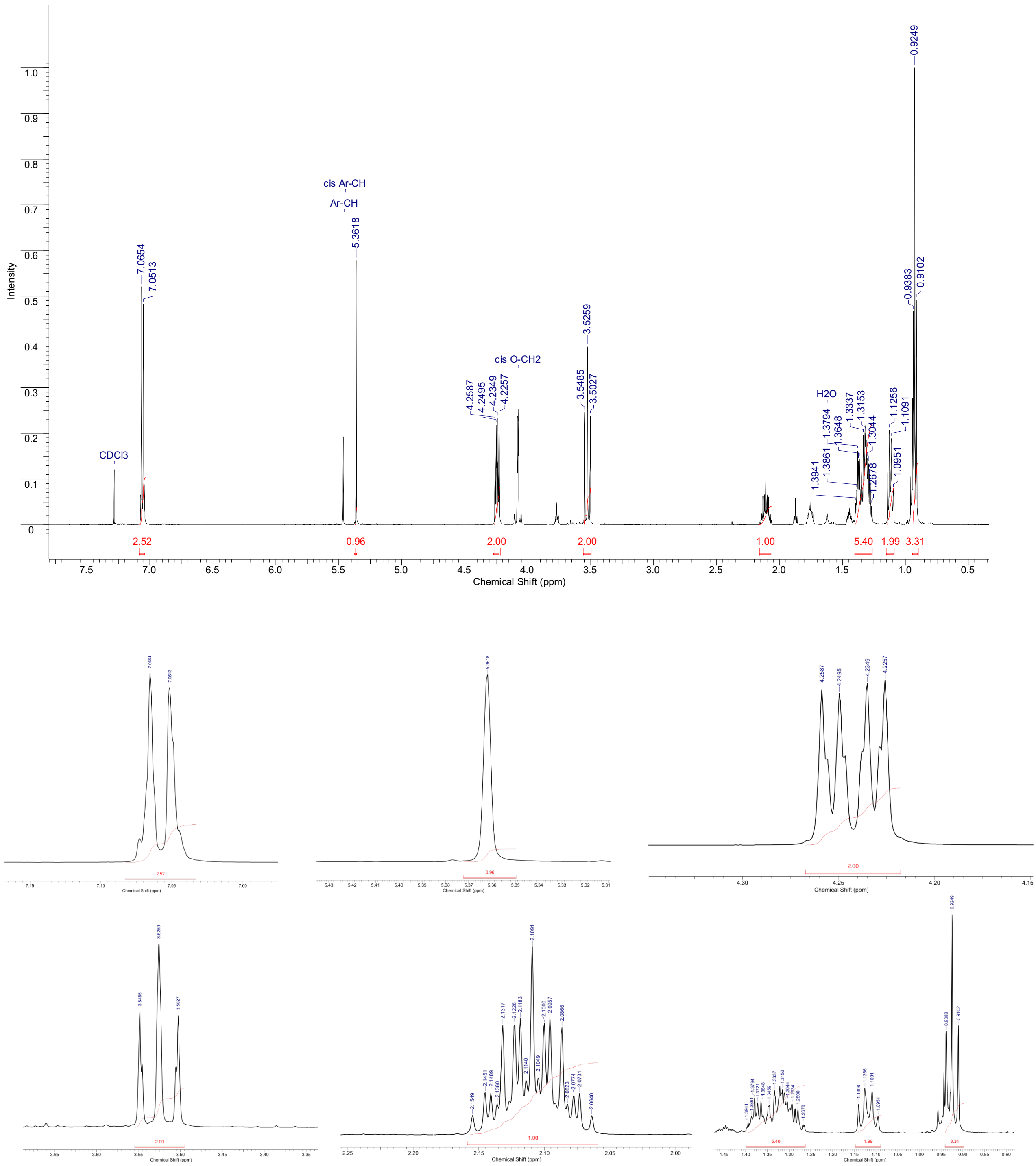
Quantities used: 2-(3,5-difluorophenyl)-5-butyl-1,3-dioxane (**4**, 43.76g, 0.171mol), n-butyllithium (0.197mol, 2.5M), I_2 (50.0g, 0.197mol).

Yield: 61g (93.3%)

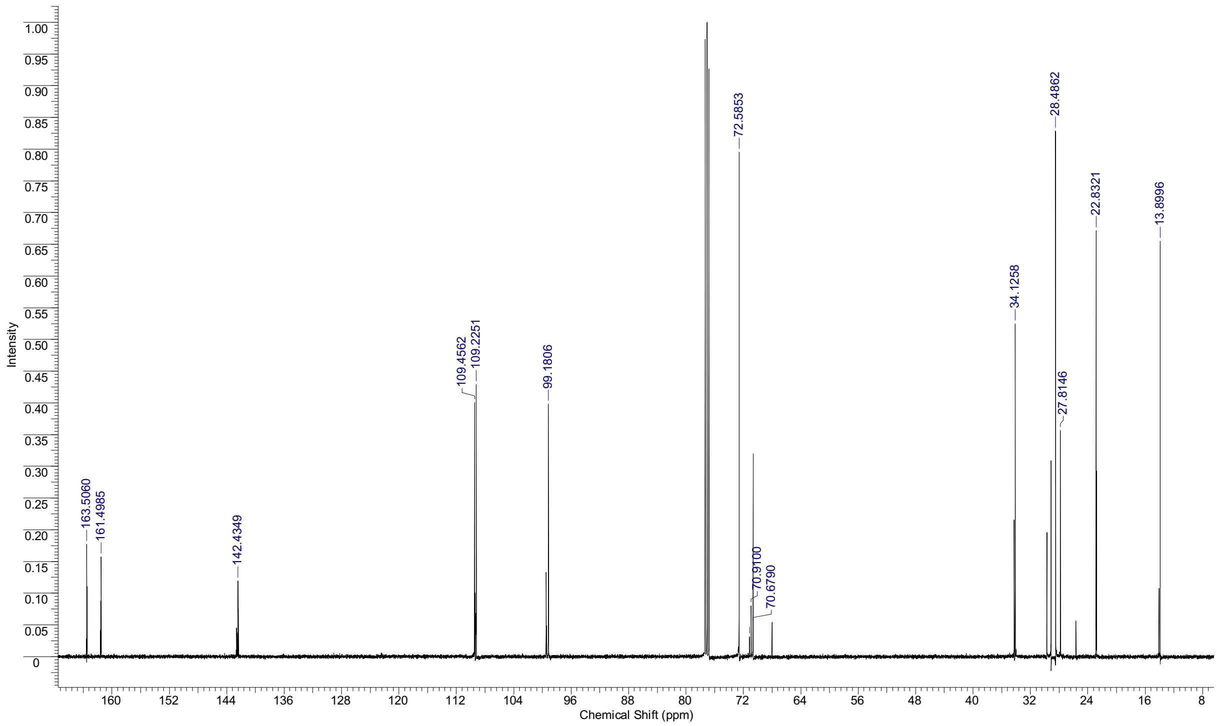
Purity (GCMS): 98.7% (77% of trans isomer)

MS (EI) m/z: 382; 363; 267; 240; 221; 159; 141

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.06 (d, *J*=7.02 Hz, 2 H, overlapping aromatic proton signals of cis isomer); 5.36 (s, 1 H); 4.24 (dd, *J*=11.90, 4.58 Hz, 2 H); 3.53 (t, *J*=11.44 Hz, 2 H); 2.11 (m, 1 H); 1.33 (m, 4 H, overlapping terminal alkyl chain CH2 proton signals of cis isomer); 1.12 (m, 2 H); 0.92 (t, *J*=7.02 Hz, 3 H, overlapping CH3 signals of cis isomer)



^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.50 (dd, *J*=245.53, 5.45 Hz); 142.43 (t, *J*=8.63 Hz); 109.32 (m); 99.18 (t, *J*=2.73 Hz); 72.59; 70.91 (t, *J*=29.52 Hz); 34.13; 28.49; 27.81; 22.83; 13.90



*2-(4-ethynyl-3,5-difluorophenyl)-5-methyl-1,3-dioxane (**10**)*

To a stirred solution of 2-(3,5-difluoro-4-iodophenyl)-5-methyl-1,3-dioxane **5** (40g, 0.118mol) in toluene (150mL) DBU (40.42g, 0.266mol) and triethylamine (17.91g, 0.177mol) were added and the mixture was refluxed for 15 minutes under N_2 atmosphere. Then it was cooled and $PdCl_2(PPh_3)_2$ (0.3%mol) and CuI (0.1%mol) were added. Then to a boiling mixture 2-methylbut-3-yn-2-ol (**9**, 14.9g, 0.177mol) was added dropwise and the reaction mixture was refluxed for 48h. Later it was washed with H_2O and diluted HCl and extracted with toluene. The phases were separated, and the organic layer was dried over $MgSO_4$. The solvent was evaporated under reduced pressure.

Crude product was dissolved in toluene (150mL) and NaH (ca 10%mol) was added. The reaction flask was equipped with Vigreux column and distilling head. As the mixture was refluxed, acetone (byproduct) was collected. The mixture was refluxed until the boiling point of a distillate reached ca 110-111°C (bp of toluene – indicating that no more acetone is formed and the reaction is completed). Then it was cooled, washed with diluted HCl and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography with hexane/DCM mixture (2/1 v/v) as mobile phase.

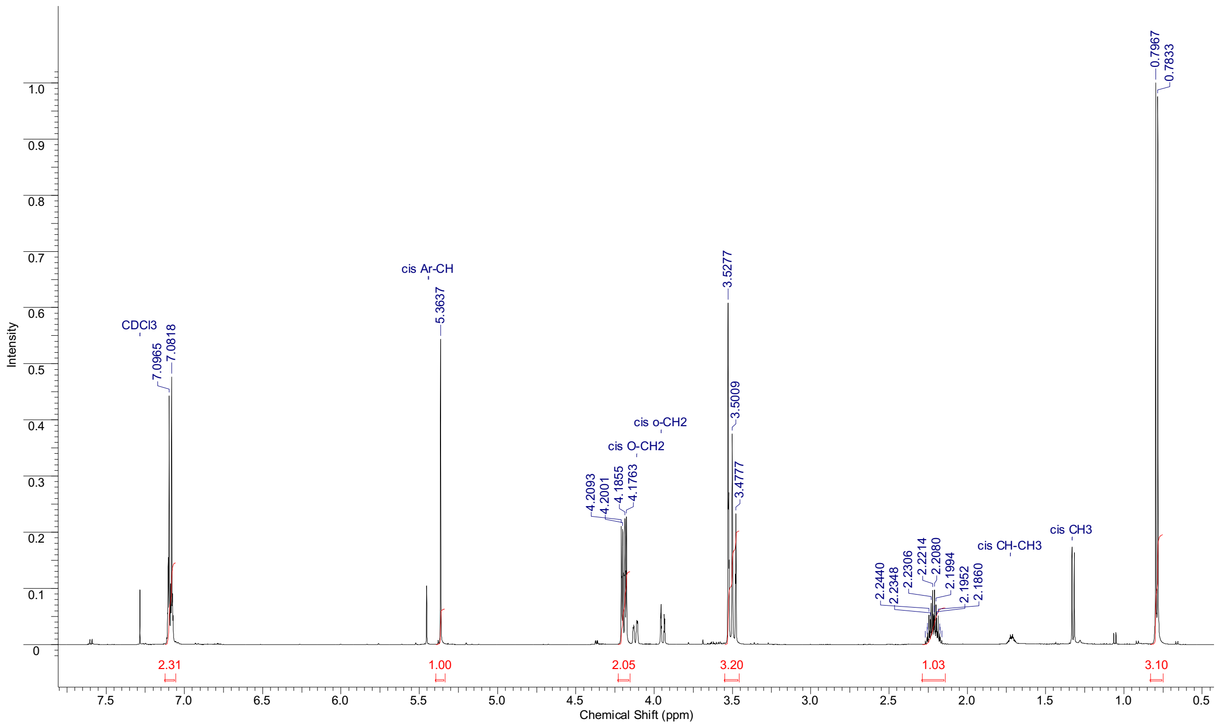
Yield: 17,21g (61.2%)

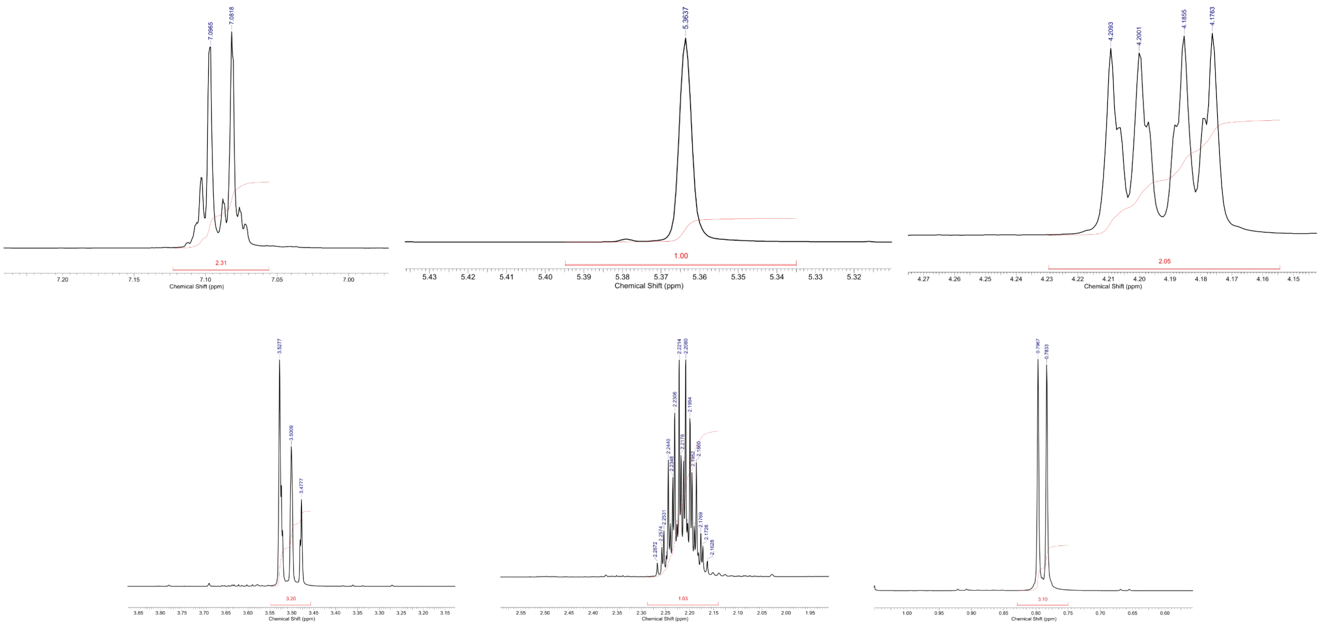
Purity (GCMS): 98.8% (81.1% of trans isomer)

R_F (n-hexane/DCM - 2/1): 0.25

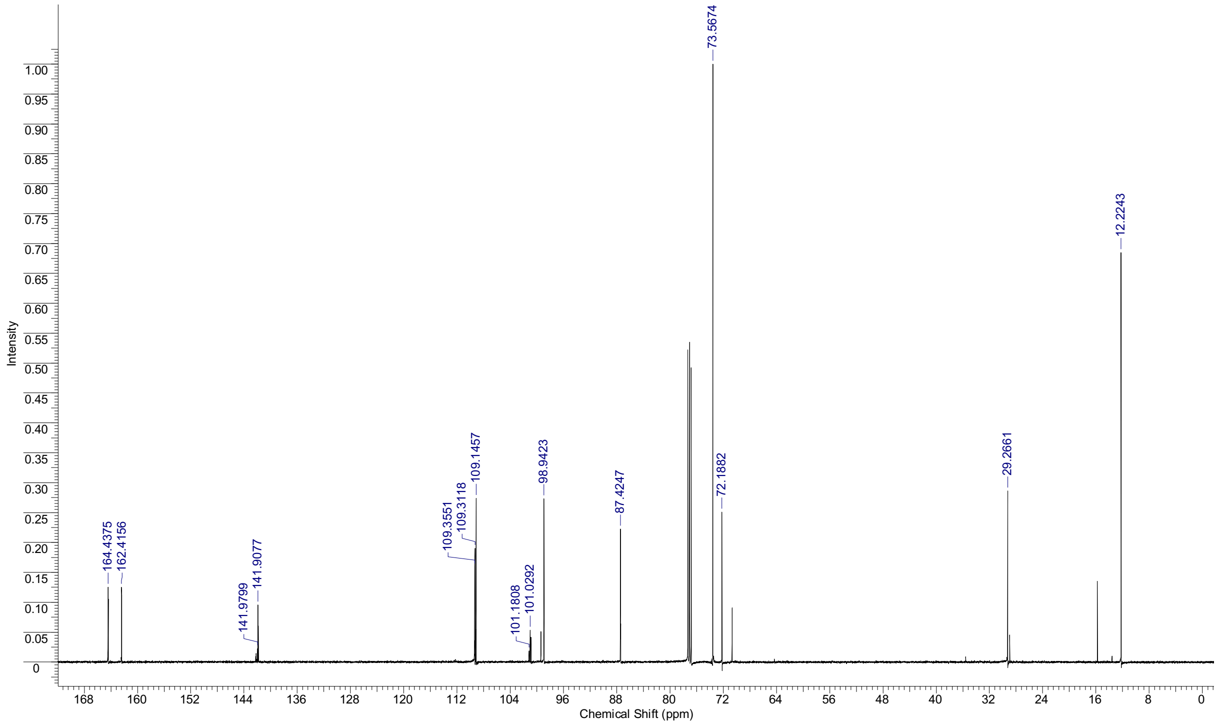
MS (EI) m/z: 238; 219; 183; 165; 151, 138; 119

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.09 (d, *J*=7.32 Hz, 2 H); 5.36 (s, 1 H); 4.19 (dd, *J*=11.90, 4.58 Hz, 2 H); 3.50 (m, 3 H, overlapping -O-CH_2-C and CCH protons), 2.22 (m, 1 H); 0.79 (d, *J*=6.71 Hz, 3 H)





^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.40 (dd, *J*=254.32, 5.45 Hz); 141.91 (t, *J*=9.08 Hz); 109.23 (m); 101.03 (t, *J*=19.53 Hz); 98.94 (t, *J*=2.73 Hz); 87.42 (t, *J*=2.73 Hz); 73.57; 72.19; 29.27; 12.22



*2-(4-ethynyl-3,5-difluorophenyl)-5-ethyl-1,3-dioxane (**11**)*

The synthesis was carried out in the same manner as in **10**.

Quantities used: 2-(3,5-difluoro-4-iodophenyl)-5-ethyl-1,3-dioxane (**6**, 40g, 0.113 mol), 2-methylbut-3-yn-2-ol (**9**, 14.3g, 0.170mol), DBU (38.82g, 0.255mol), triethylamine (17.2g, 0.170mol)

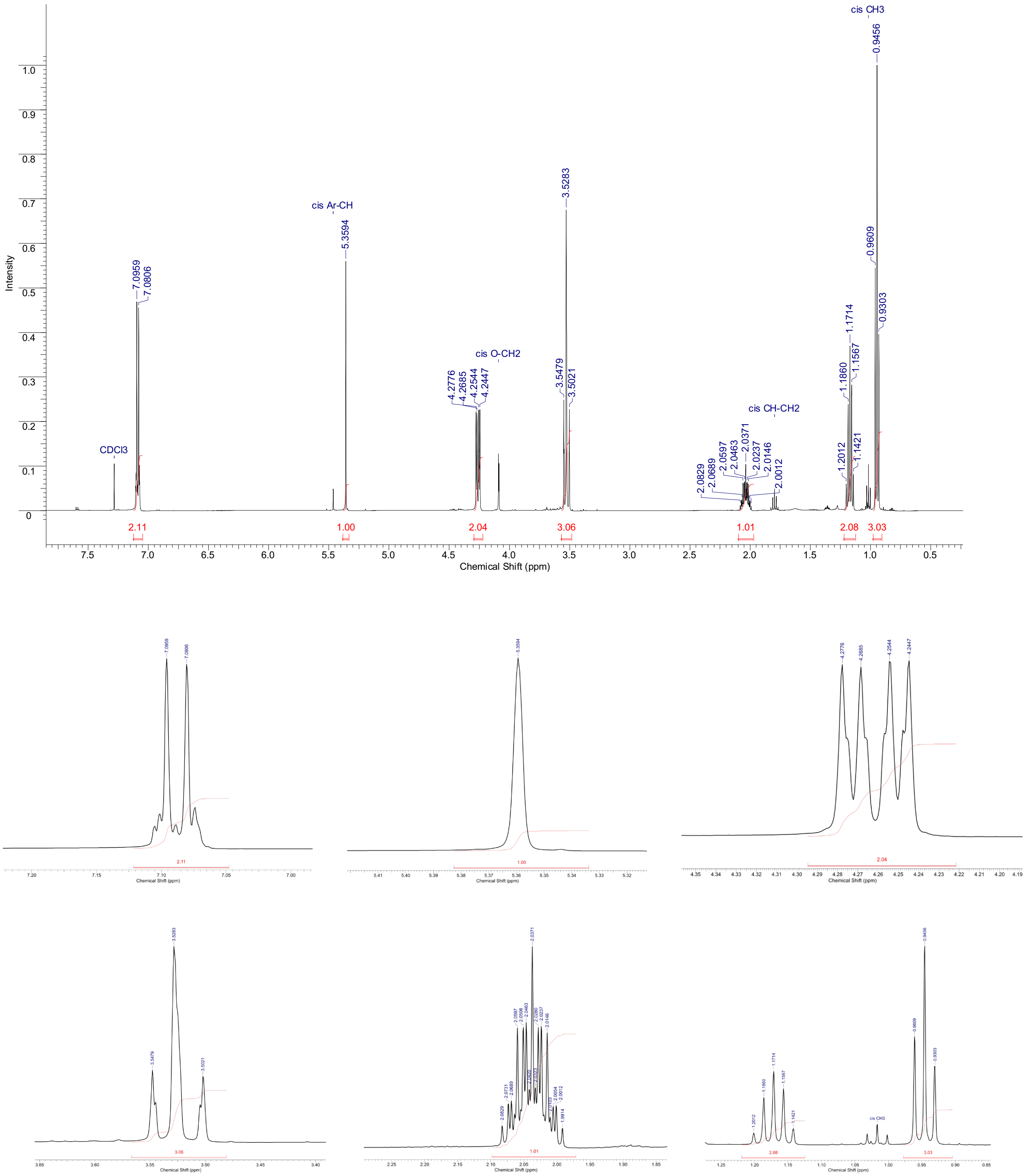
Yield: 14.32g (50.2%)

Purity (GCMS): 98.9% (90.2% of trans isomer)

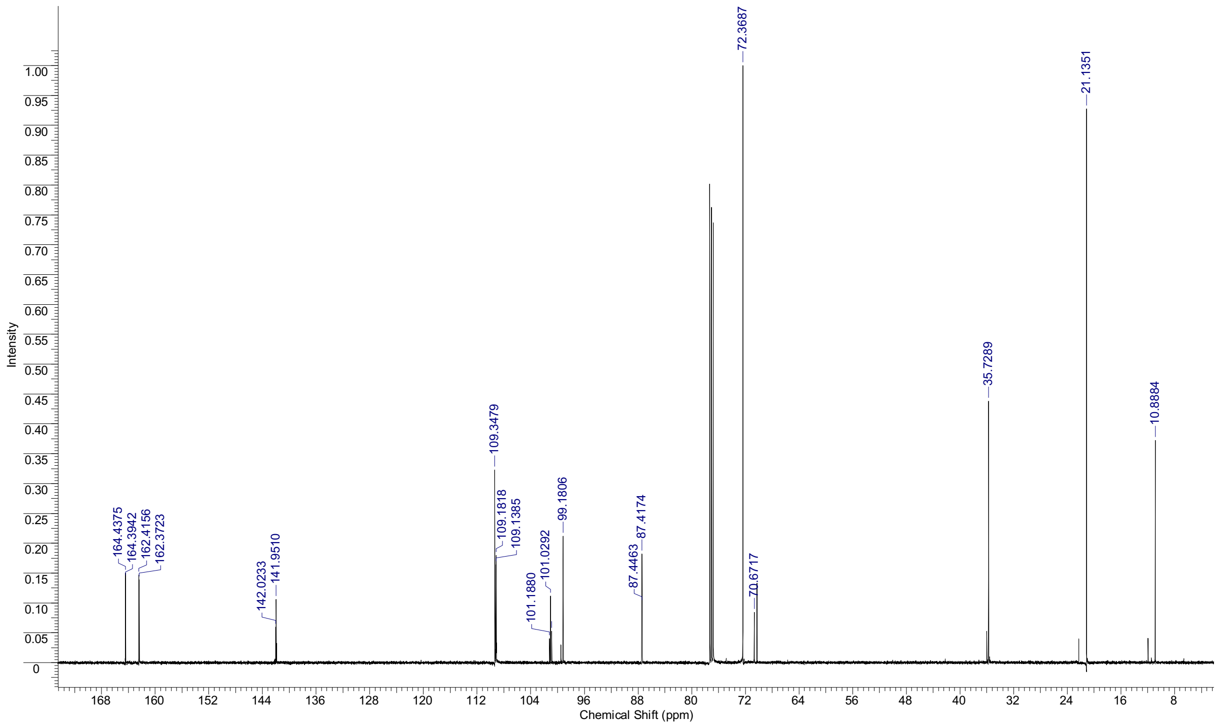
R_F (n-hexane/DCM - 2/1): 0.25

MS (EI) m/z: 252; 223; 207; 183; 165; 151; 138; 119

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.09 (d, *J*=7.63 Hz, 2 H); 5.36 (s, 1 H); 4.26 (dd, *J*=11.75, 4.73 Hz, 2 H); 3.53 (m, 3 H, overlapping -O-CH_2-C and CCH protons); 2.04 (m, 1 H); 1.17 (m, 2 H); 0.95 (t, *J*=7.63 Hz, 3 H)



^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.40 (dd, *J*=254.32, 5.45 Hz); 141.95 (t, *J*=9.08 Hz); 109.24 (m); 101.03 (t, *J*=19.98 Hz); 99.18 (t, *J*=2.73 Hz); 87.42 (t, *J*=3.18 Hz); 72.37; 70.67; 35.73; 21.14; 10.89



*2-(4-ethynyl-3,5-difluorophenyl)-5-propyl-1,3-dioxane (**12**)*

The synthesis was carried out in the same manner as in **10**.

Quantities used: 2-(3,5-difluoro-4-iodophenyl)-5-propyl-1,3-dioxane (**7**, 43g, 0.117 mol), 2-methylbut-3-yn-2-ol (**9**, 14.81g, 0.176mol), DBU (40,19g, 0.264mol), triethylamine (17.81g, 0.176mol)

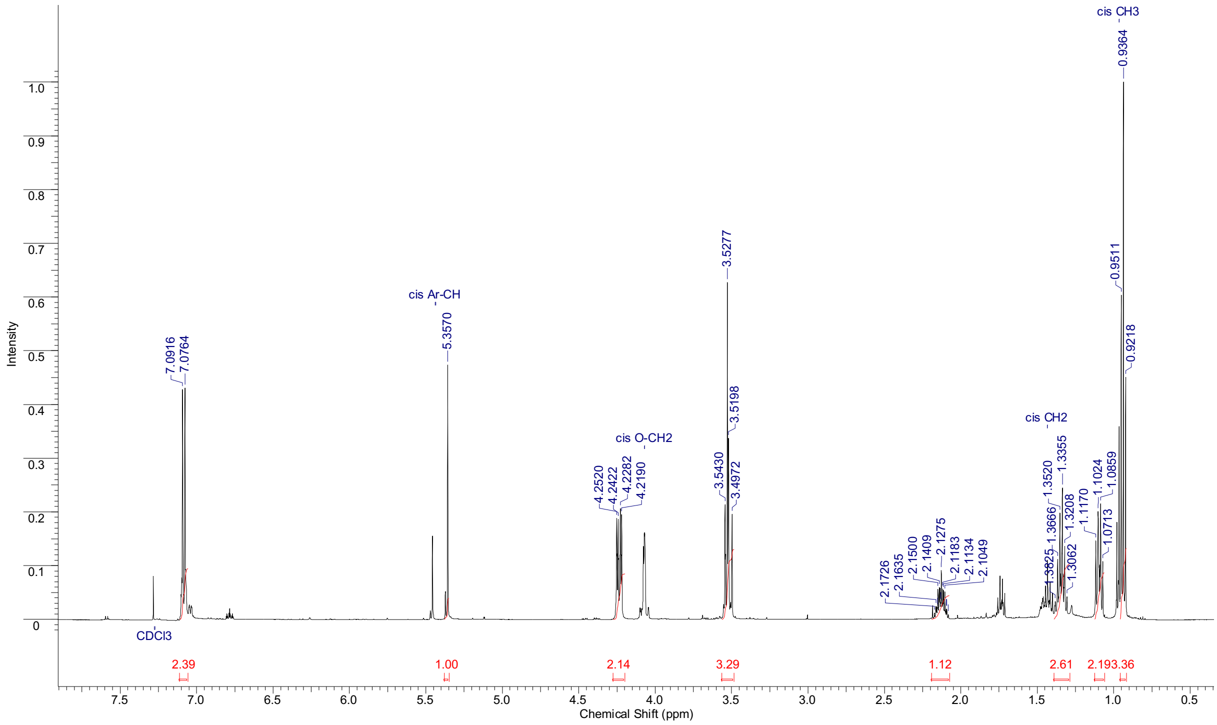
Yield: 22g (70.6%)

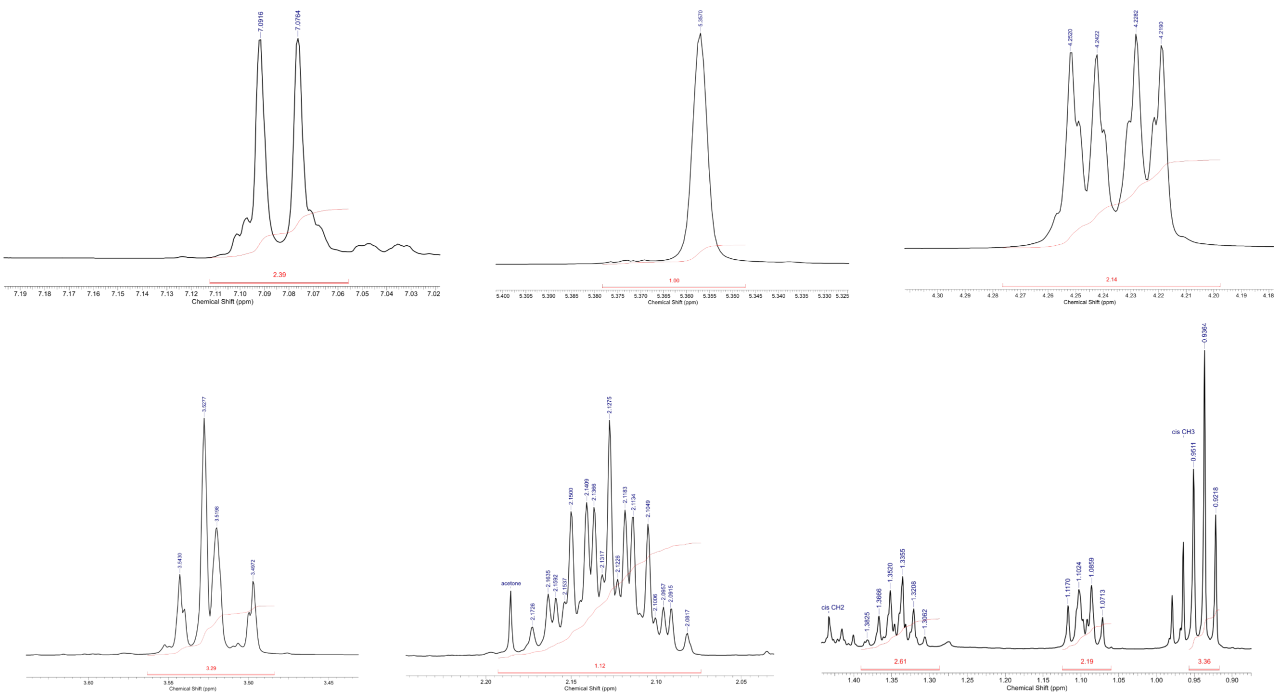
Purity (GCMS): 91.2% (71.8% of trans isomer)

R_F (n-hexane/DCM - 2/1): 0.25

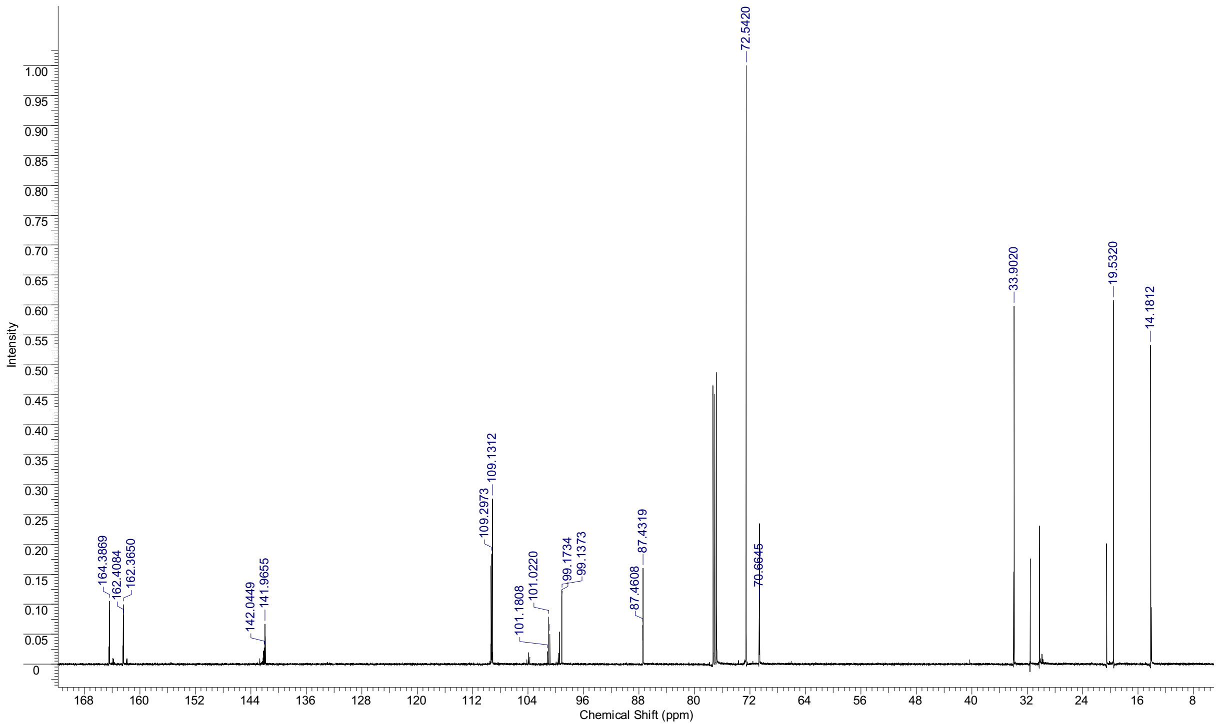
MS (EI) m/z: 266; 247; 223; 207; 179; 165; 151; 138; 119

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.08 (d, *J*=7.63 Hz, 2 H); 5.36 (s, 1 H); 4.24 (dd, *J*=11.75, 4.73 Hz, 2 H); 3.52 (m, 3 H, overlapping -O-CH_2-C and CCH protons); 2.13 (m, 1 H); 1.34 (m, 2 H, overlapping terminal alkyl chain CH2 proton signals of cis isomer); 1.09 (m, 2 H); 0.94 (t, *J*=7.32 Hz, 3 H, overlapping CH3 proton signals of cis isomer)





^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.40 (dd, *J*=254.32, 5.45 Hz); 141.97 (t, *J*=9.54 Hz); 109.24 (m); 101.02 (t, *J*=19.98 Hz); 99.16 (t, *J*=2.73 Hz); 87.43 (t, *J*=3.18 Hz); 72.54; 70.66; 33.90; 19.53; 14.18



*2-(4-ethynyl-3,5-difluorophenyl)-5-butyl-1,3-dioxane (**13**)*

The synthesis was carried out in the same manner as in **10**.

Quantities used: 2-(3,5-difluoro-4-iodophenyl)-5-butyl-1,3-dioxane (**8**, 40g, 0.105 mol), 2-methylbut-3-yn-2-ol (**9**, 13.29g, 0.158mol), DBU (36.09g, 0.237mol), triethylamine (16g, 0.158mol)

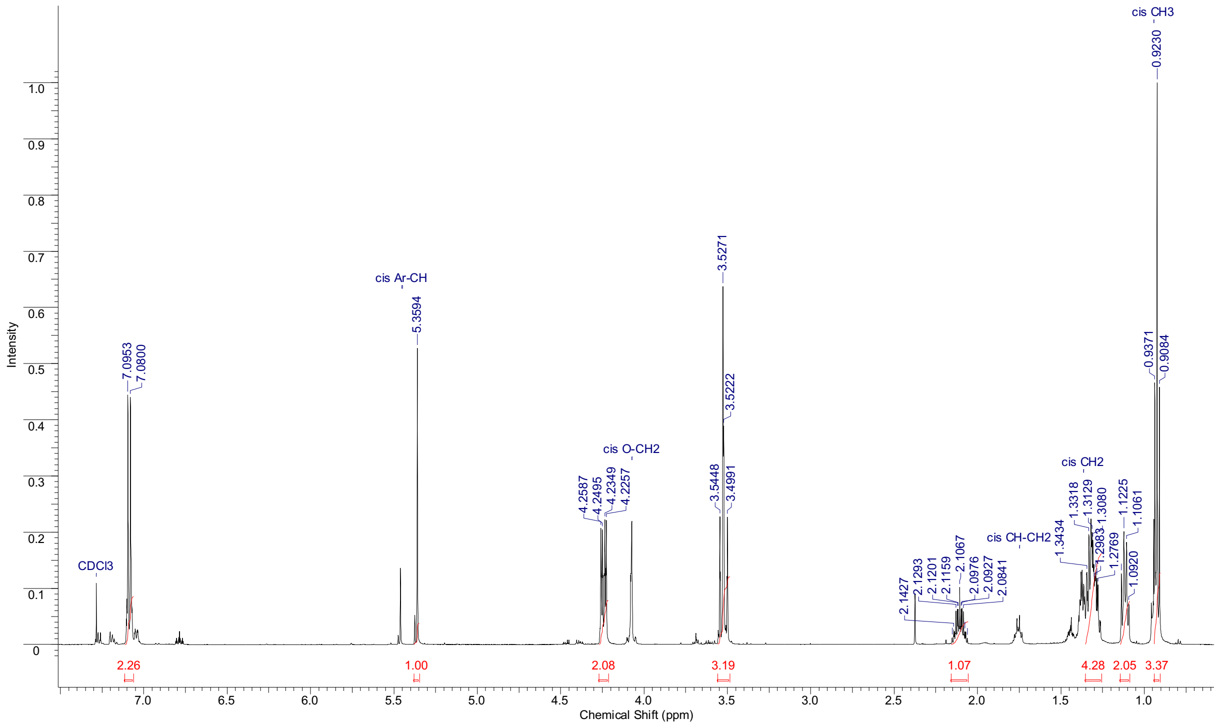
Yield: 21.76g (73.9%)

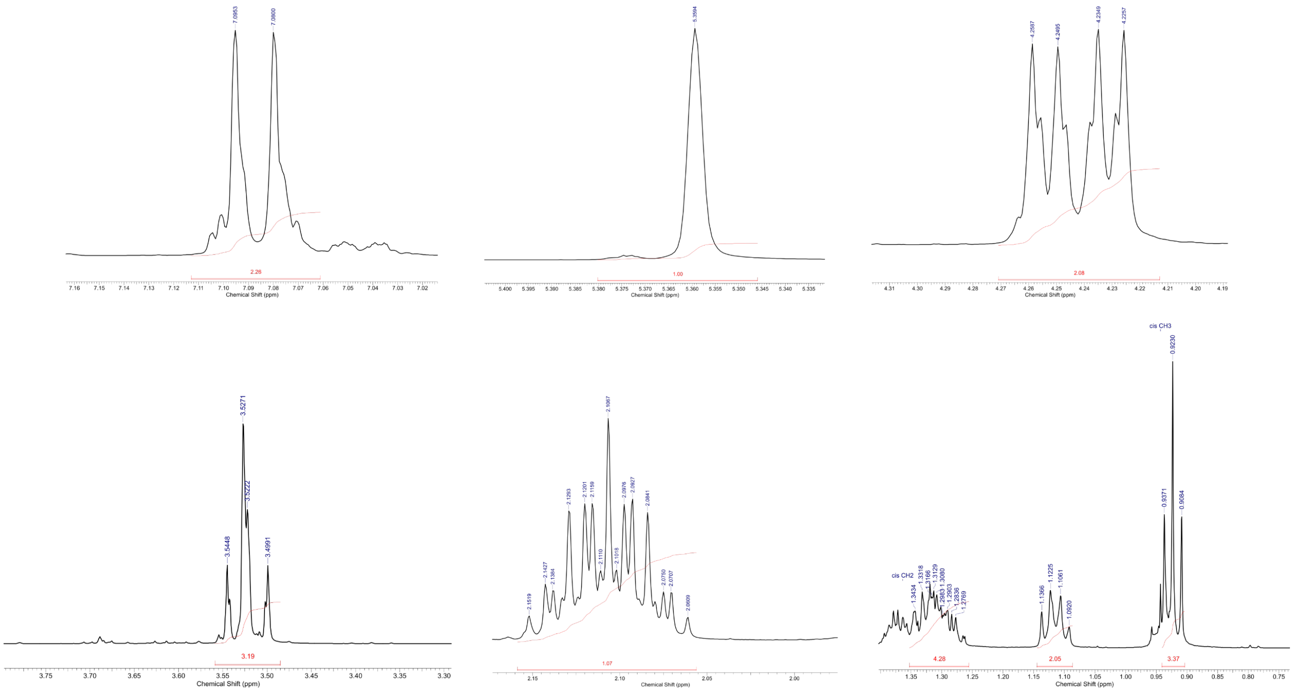
Purity (GCMS): 93% (72.6% of trans isomer)

R_F (n-hexane/DCM - 2/1): 0.25

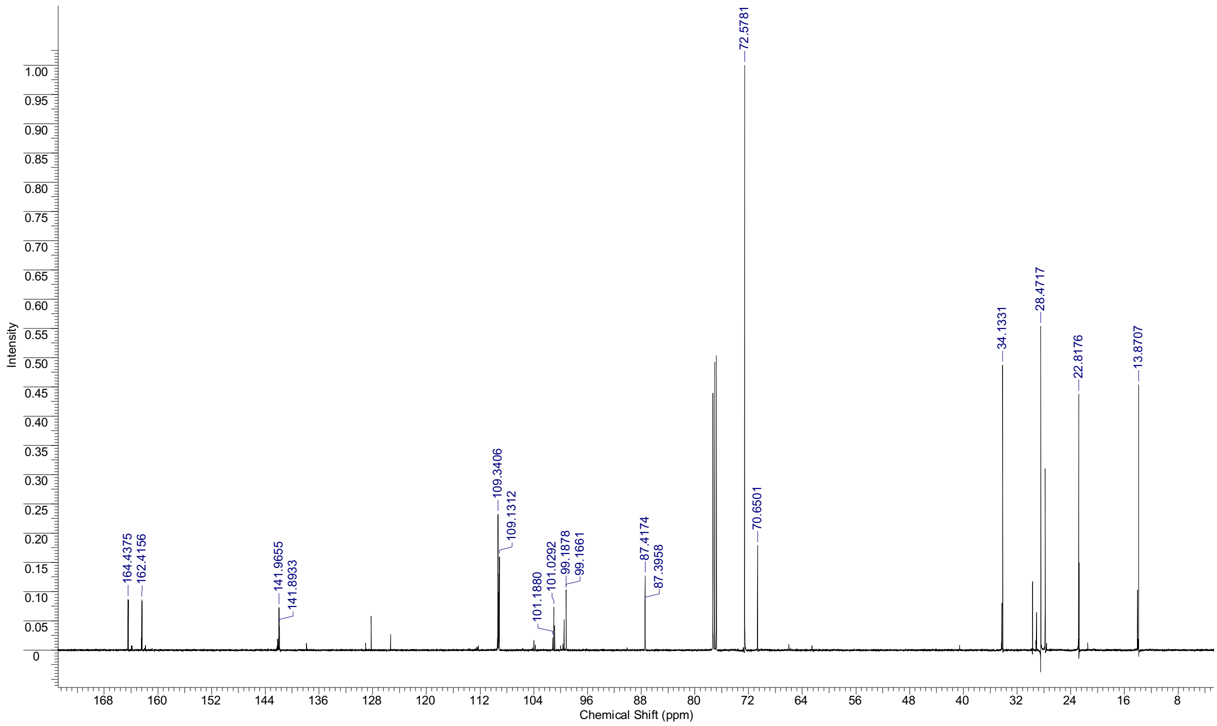
MS (EI) m/z: 280; 261; 223; 207; 194; 179; 165; 151; 138; 119

[1]**H NMR** (500 MHz, $CDCl_3$) δ: 7.09 (d, *J*=7.63 Hz, 2 H); 5.36 (s, 1 H); 4.24 (dd, *J*=11.90, 4.58 Hz, 2 H); 3.52 (m, 3 H); 2.11 (m, 1 H); 1.30 (m, 4 H); 1.11 (m, 2 H); 0.92 (t, *J*=7.17 Hz, 3 H)





^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.40 (dd, *J*=254.32, 5.45 Hz); 141.97 (t, *J*=9.08 Hz); 109.24 (m); 101.03 (t, *J*=19.98 Hz); 99.17 (t, *J*=2.73 Hz); 87.42 (t, *J*=3.18 Hz); 72.58; 70.65; 34.13; 28.47; 22.82; 13.87



*2-(4-((4-bromo-3-fluorophenyl)ethynyl)-3,5-difluorophenyl)-5-methyl-1,3-dioxane (**15**)*

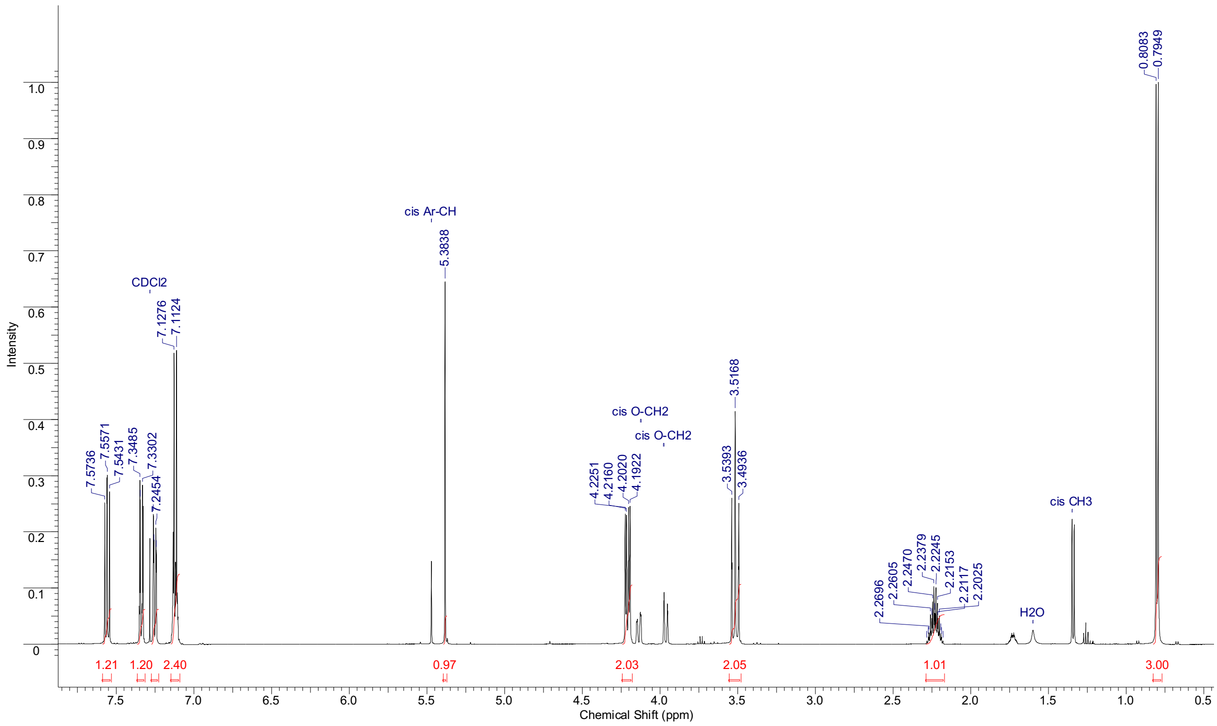
To a stirred solution of 1-bromo-2-fluoro-4-iodobenzene (**14**, 3.46g, 0.0115mol) in toluene (50mL) DBU (2.88g, 0.0189mol) and triethylamine (1.27g, 0.0126mol) were added and the mixture was refluxed for 15 minutes under N_2 atmosphere. Then it was cooled to room temperature and $PdCl_2(PPh_3)_2$ (0.3%mol) and CuI (0.1%mol) were added. The mixture was heated to 40°C and 2-(4-ethynyl-3,5-difluorophenyl)-5-methyl-1,3-dioxane (**10**, 3g, 0.0126mol) dissolved in toluene was added dropwise. The mixture was stirred at 40°C for 3h. Later it was washed with H_2O and diluted HCl and extracted with toluene. The phases were separated, and the organic layer was dried over $MgSO_4$. The solvent was evaporated under reduced pressure. Crude product was then recrystallized from ethanol.

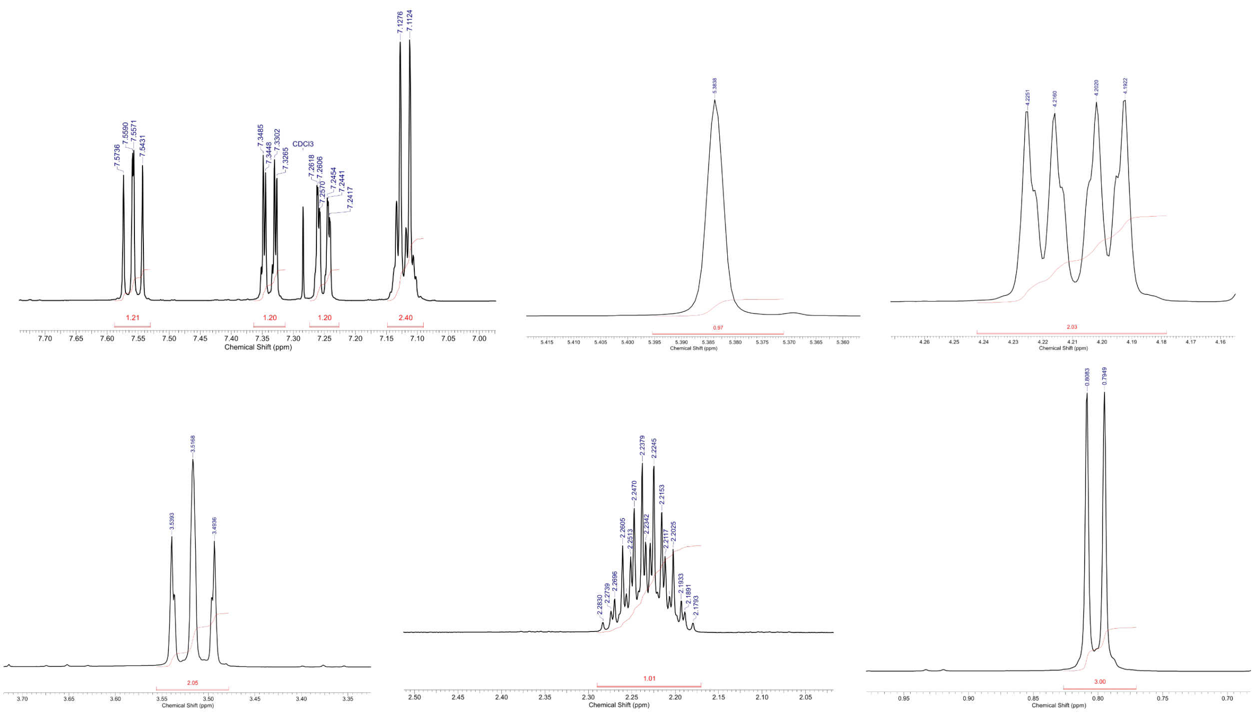
Yield: 4.4g (93%)

Purity (GCMS): 99.8% (85% of trans isomer)

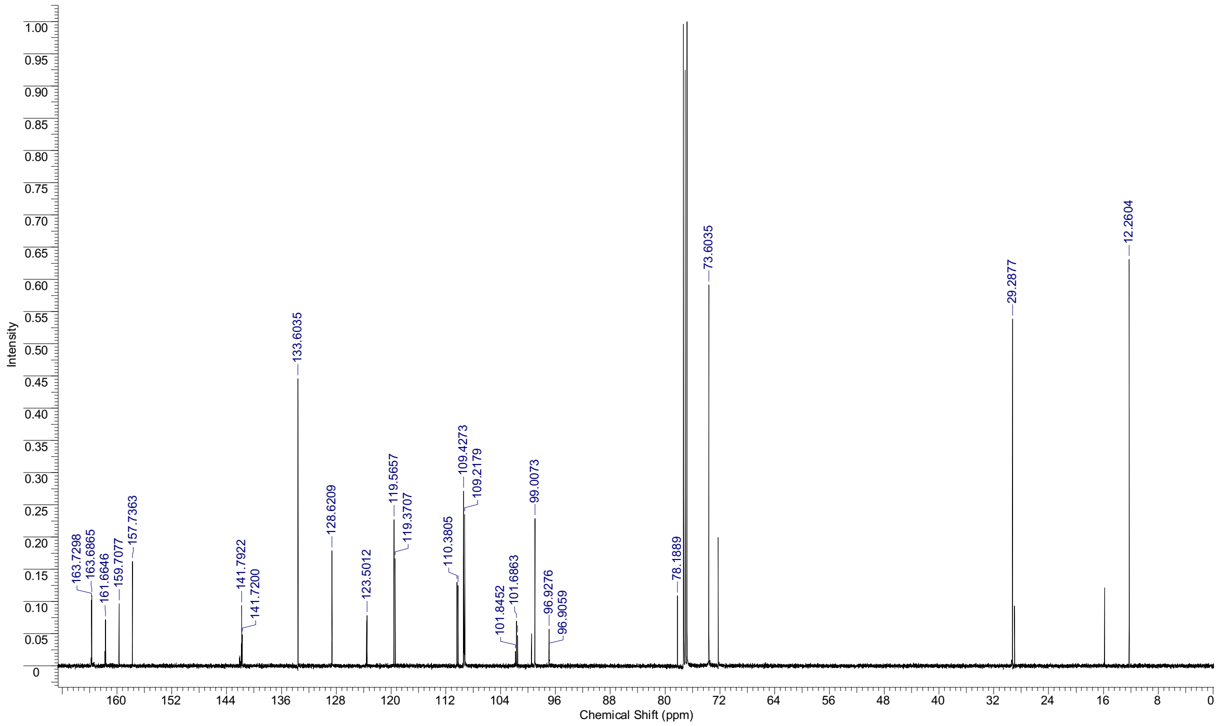
MS (EI) m/z: 410; 393; 356; 338; 310; 259; 230; 210; 191; 162; 141

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56 (m, 1 H); 7.34 (dd, *J*=9.16, 1.83 Hz, 1 H); 7.25 (m, 1 H); 7.12 (d, *J*=7.63 Hz, 2 H); 5.38 (s, 1 H); 4.21 (dd, *J*=11.75, 4.73 Hz, 2 H); 3.52 (t, *J*=11.44 Hz, 2 H); 2.23 (m, 1 H); 0.80 (d, *J*=6.71 Hz, 3 H)





^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.70 (dd, *J*=252.74, 5.45 Hz); 158.72 (d, *J*=247.96 Hz); 141.79 (t, *J*=9.08 Hz); 133.60; 128.64 (d, *J*=3.64 Hz); 123.54 (d, *J*=9.08 Hz); 119.47 (d, *J*=24.52 Hz); 110.30 (d, *J*=20.89 Hz); 109.32 (m); 101.69 (t, *J*=19.98 Hz); 99.00 (t, *J*=2.27 Hz); 96.94 (m); 78.19; 73.60; 29.29; 12.26



*2-(4-((4-bromo-3-fluorophenyl)ethynyl)-3,5-difluorophenyl)-5-butyl-1,3-dioxane (**16**)*

The synthesis was carried out in the same manner as in **15**.

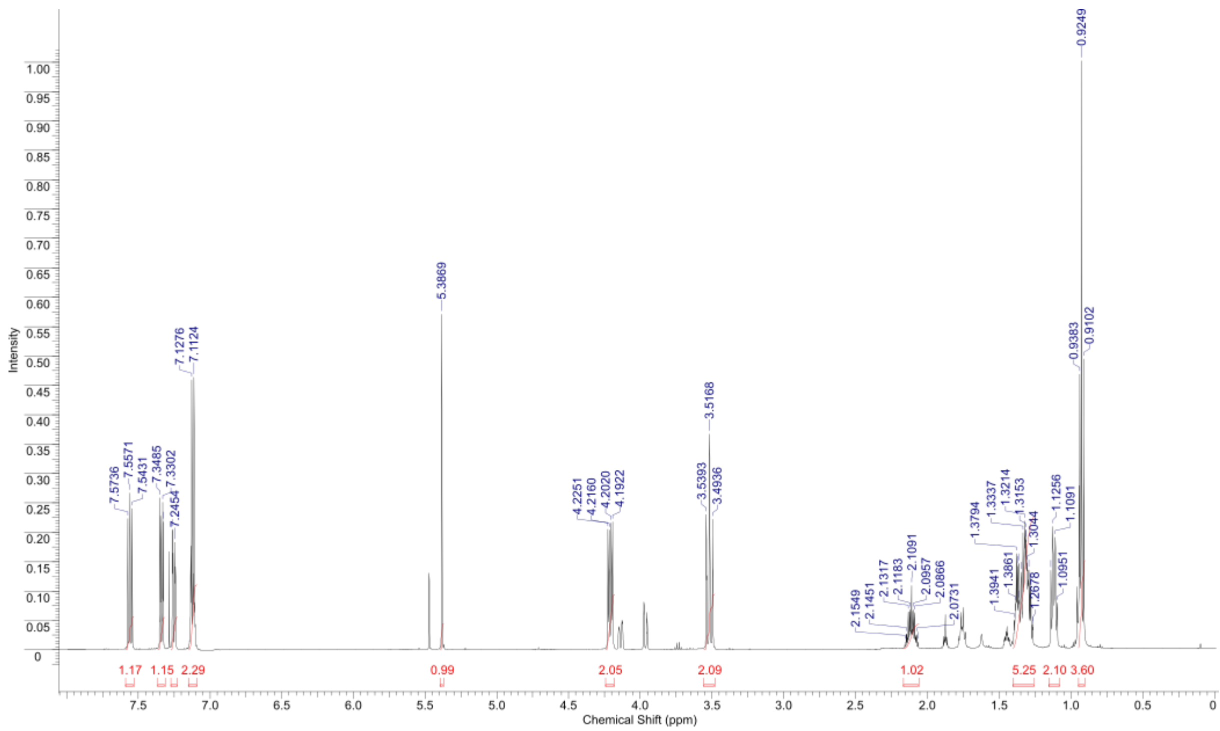
Quantities used: 1-bromo-2-fluoro-4-iodobenzene (**14**, 2.93g, 0.00973mol), 2-(4-ethynyl-3,5-difluorophenyl)-5-butyl-1,3-dioxane (**13**, 3g, 0.0107mol), DBU (2.45g, 0.0161mol), triethylamine (1.08g, 0.0107mol)

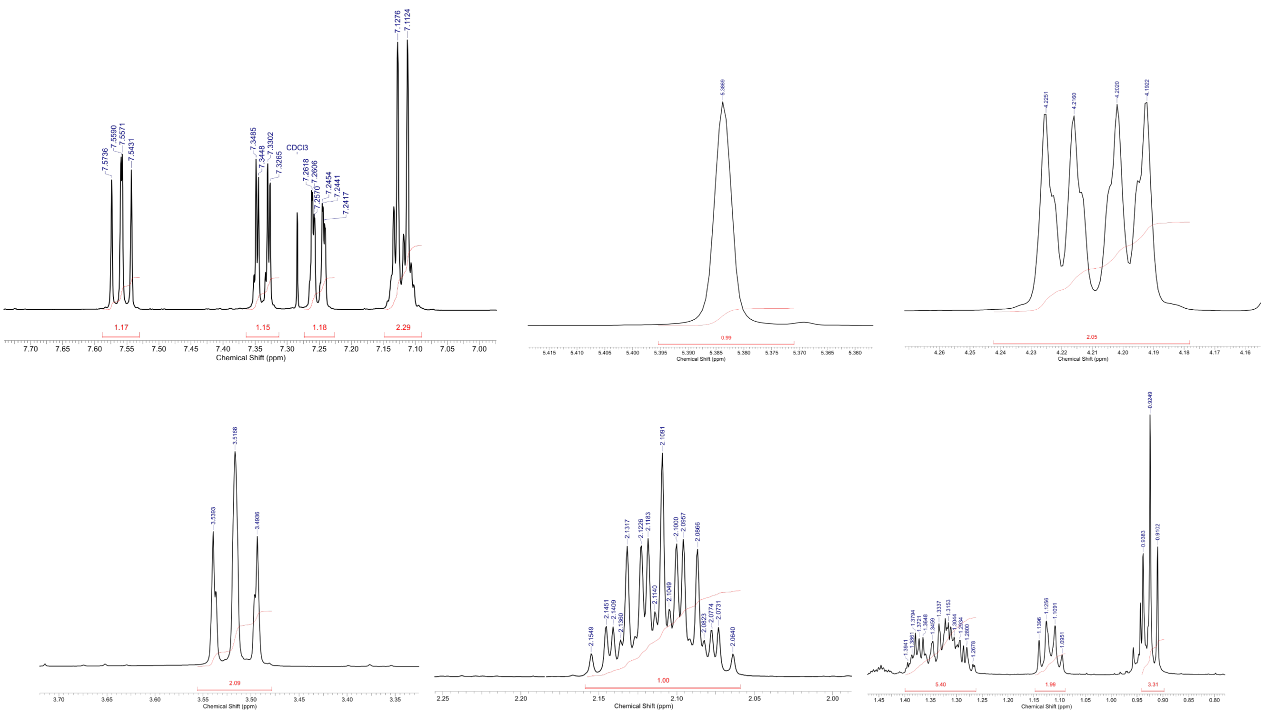
Yield: 2.92g (66.4%)

Purity (GCMS): 98.8% (86.8% of trans isomer)

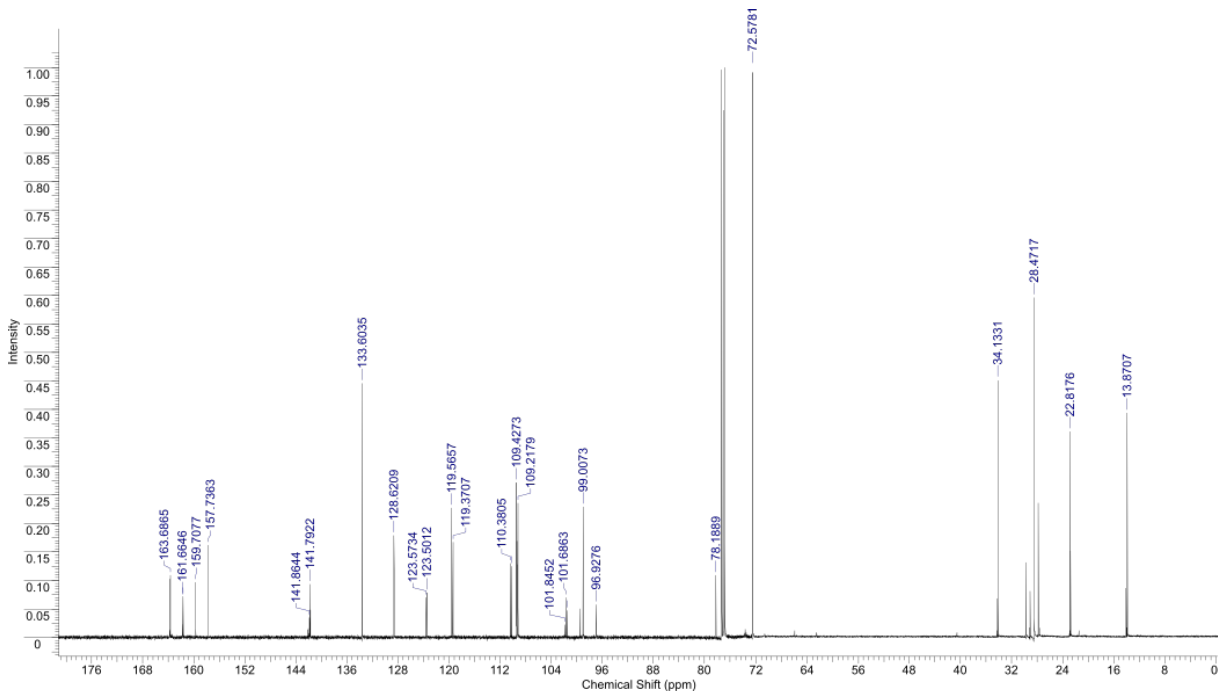
MS (EI) m/z: 452; 397; 373; 356; 338; 312; 277; 259; 230; 211; 191; 162; 141

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56 (m, 1 H); 7.33 (dd, *J*=9.10, 1.86 Hz, 1 H); 7.25 (m, 1 H); 7.11 (d, *J*=7.63 Hz, 2 H); 5.39 (s, 1 H); 4.21 (dd, *J*=11.76, 4.72 Hz, 2 H); 3.52 (t, *J*=11.42 Hz, 2 H); 2.11 (m, 1 H); 1.34 (m, 4 H, overlapping terminal alkyl chain CH2 proton signals of cis isomer); 1.11 (m, 2 H); 0.93 (t, *J*=7.05 Hz, 3 H, overlapping CH3 proton signals of cis isomer)





^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.70 (dd, *J*=252.74, 5.45 Hz); 158.72 (d, *J*=247.96 Hz); 141.79 (t, *J*=9.08 Hz); 133.60; 128.64 (d, *J*=3.64 Hz); 123.54 (d, *J*=9.08 Hz); 119.47 (d, *J*=24.52 Hz); 110.30 (d, *J*=20.89 Hz); 109.32 (m); 101.69 (t, *J*=19.98 Hz); 99.00 (t, *J*=2.27 Hz); 96.94 (m); 78.19; 72.58; 34.13; 28.47; 22.82; 13.87



*4-bromo-4'-(difluoro(3,4,5-trifluorophenoxy)methyl)-2,3',5'-trifluoro-1,1'-biphenyl (**19**)*

The mixture of 4-bromo-2-fluoro-1-iodobenzene (**18**, 8g, 0.0266mol) and $PdCl_2(PPh_3)_2$ (186.8mg, 1%mol) in acetone (160mL) was stirred at room temperature under N_2 atmosphere for 30 minutes. Then 2-(4-(difluoro(3,4,5-trifluorophenoxy)methyl)-3,5-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**17**, 11.6g, 0.0266mol), K_2CO_3 (12.88g, 0.0932mol) and water (40mL) were added and the mixture was refluxed for 2h. Acetone was removed under reduced pressure using a rotary evaporator. The residue was washed with diluted HCl and extracted with DCM. Organic phase was dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The residual 4-bromo-2-fluoro-1-iodobenzene (**18**) was removed by short path vacuum distillation and the product was then purified by column chromatography using hexane as the mobile phase.

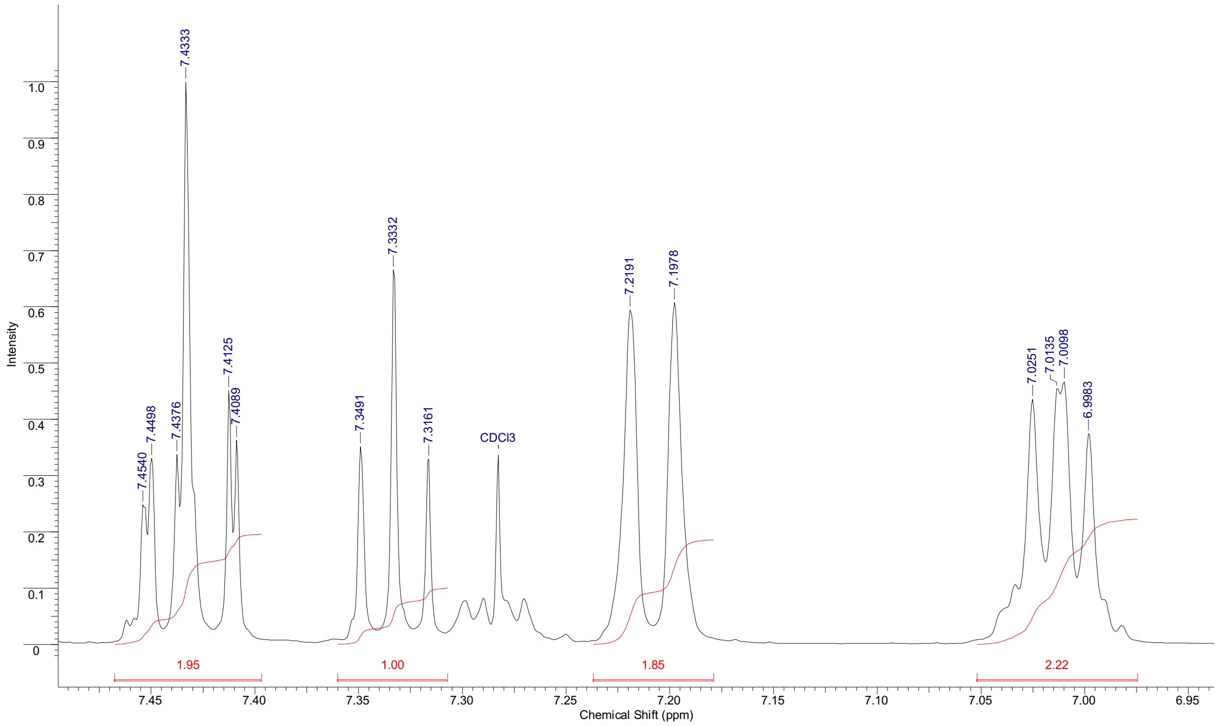
Yield: 5.46g (42.5%)

Purity (GCMS): 89%

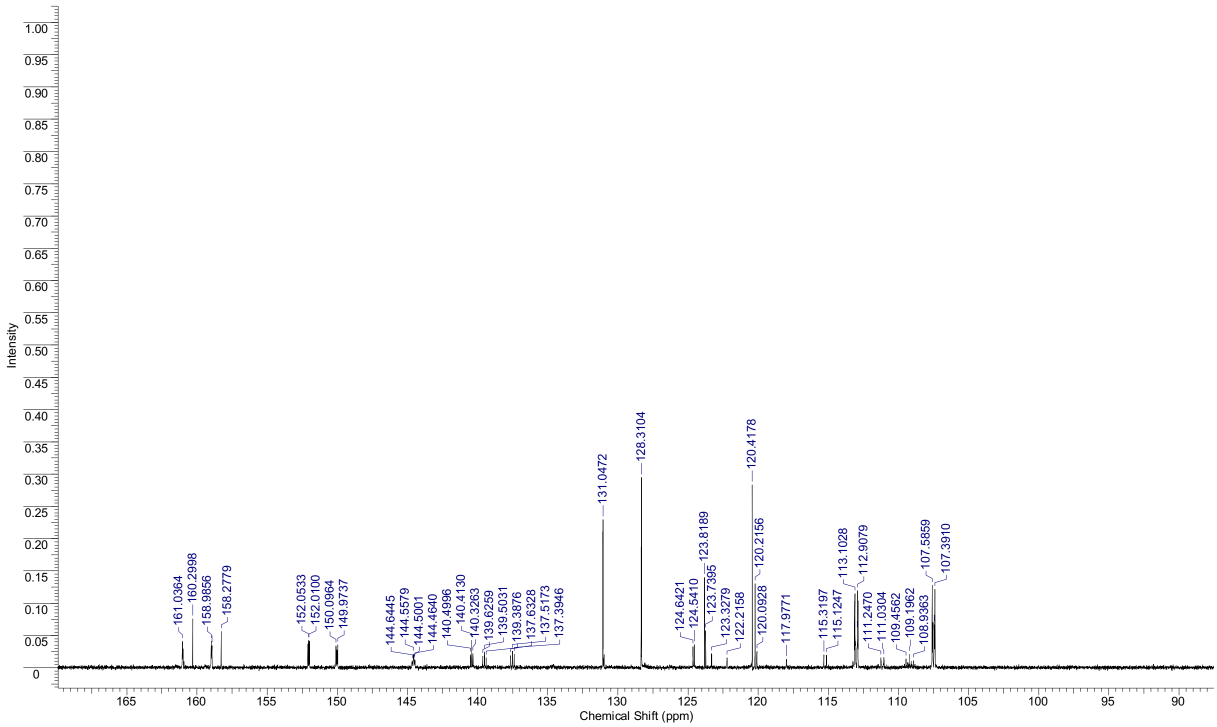
R_F (n-hexane): 0.33

MS (EI) m/z: 482; 463; 445; 417; 403; 384; 363; 335; 315; 296; 269; 255; 237; 223; 206; 186; 167; 141; 119

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.43 (m, 2 H); 7.33 (t, *J*=8.24 Hz, 1 H); 7.21 (d, *J*=10.68 Hz, 2 H); 7.01 (dd, *J*=7.63, 5.80 Hz, 2 H);



^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.99 (dd, *J*=257.95, 6.36 Hz); 159.29 (d, *J*=254.32 Hz)151.03 (ddd, *J*=250.69, 10.90, 5.45 Hz); 144.57 (m); 140.41 (t, *J*=10.90 Hz); 138.51 (dt, *J*=249.78, 15.44 Hz); 131.06 (d, *J*=3.63 Hz, 1 C); 128.32 (m); 124.60 (m); 123.78 (d, *J*=9.99 Hz); 123.31 (d, *J*=3.63 Hz); 120.32 (d, *J*=25.43 Hz); 120.09 (t, *J*=266.13 Hz); 115.22 (d, *J*=24.52 Hz); 113.01 (m); 111.14 (d, *J*=27.25 Hz); 109.20 (t, *J*=32.70 Hz); 107.49 (m);



*2-(4-((4'-(difluoro(3,4,5-trifluorophenoxy)methyl)-2,3',5'-trifluoro-[1,1'-biphenyl]-4-yl)ethynyl)-3,5-difluorophenyl)-5-methyl-1,3-dioxane (**1dTBEP**)*

A stirred solution of 2-(4-((4-bromo-3-fluorophenyl)ethynyl)-3,5-difluorophenyl)-5-methyl-1,3-dioxane (**15**, 2.5g, 0.00608mol), 2-(4-(difluoro(3,4,5-trifluorophenoxy)methyl)-3,5-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**17**, 2.92g, 0.00669mol) K_2CO_3 (3.24g, 0.0234mol) in acetone (60mL) and water (12mL) was refluxed under N_2 atmosphere for 30 minutes. Then it was cooled and $Pd(OAc)_2$ (0.1%mol) was added. The reaction mixture was refluxed for 2h. Later it was washed with H_2O and diluted HCl and extracted with DCM. The phases were separated, and the organic layer was dried over $MgSO_4$. The solvent was evaporated under reduced pressure. Crude product was recrystallized three times from ethanol/acetone mixture to give white crystals.

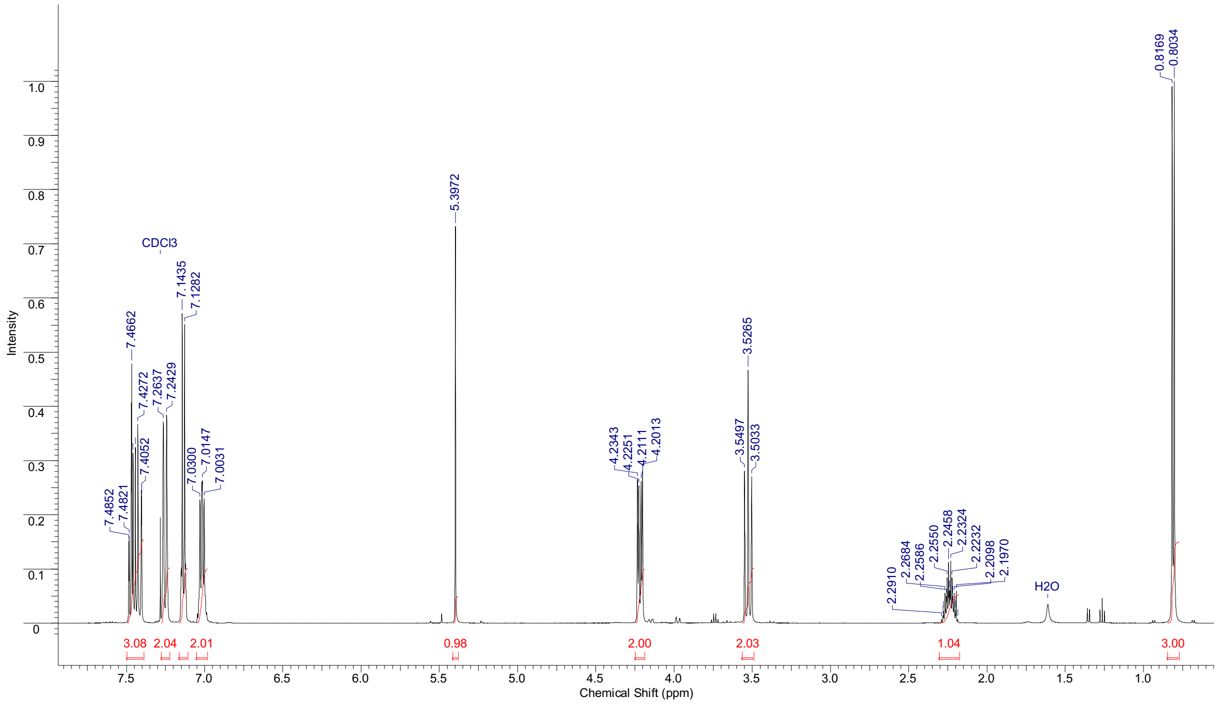
Yield: 2.1g (54.0%)

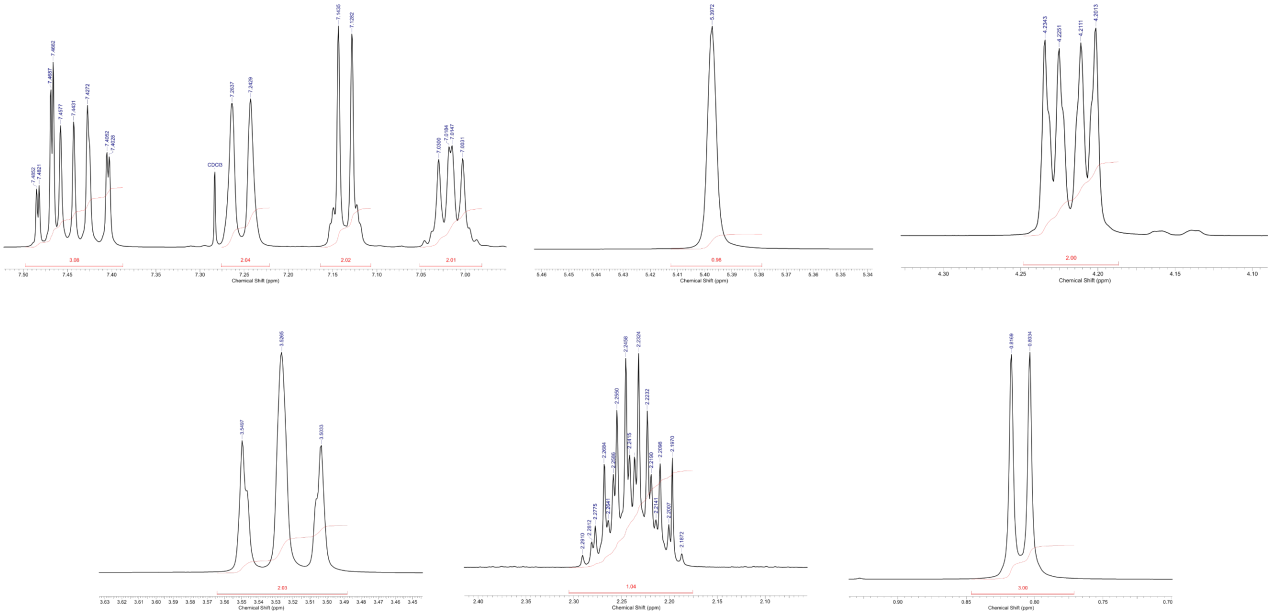
Purity (GCMS): >99.9% (99.3% of trans isomer)

MS (EI) m/z: 640; 609; 567; 493; 463; 421; 393; 353; 322; 291; 246; 210; 171; 147; 119

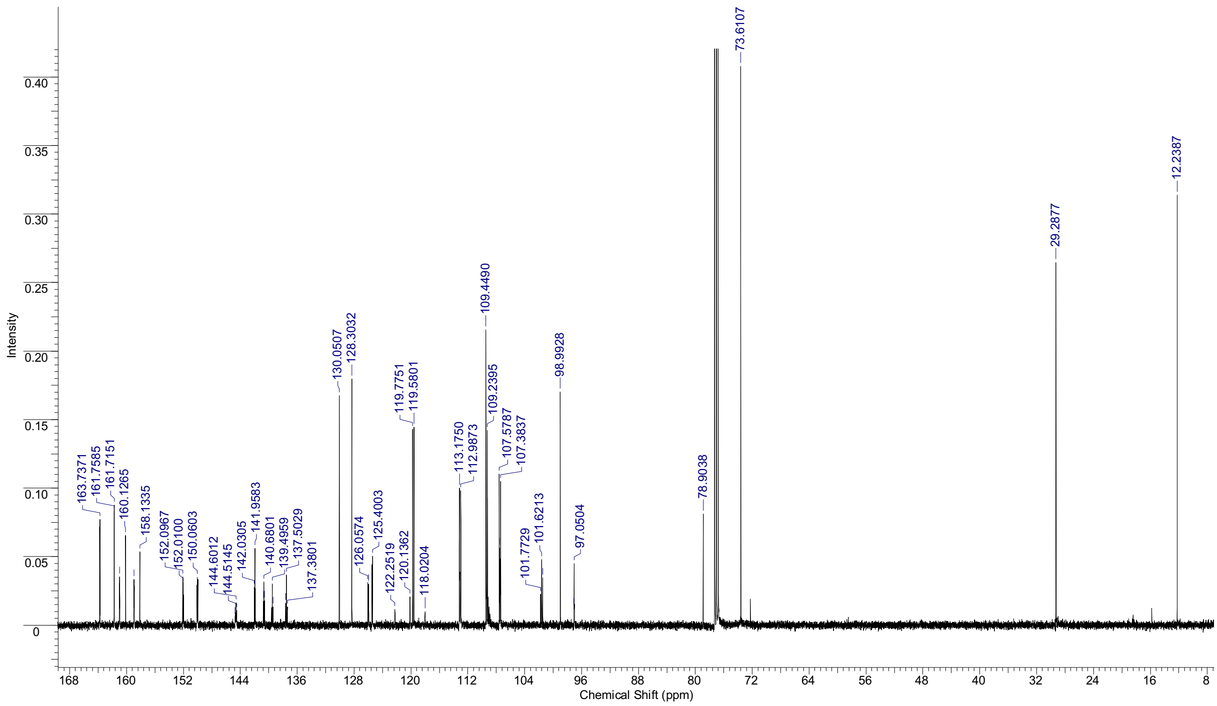
HRMS (HESI) m/z: calculated for $C_{32}H_{19}F_{10}O_3^+$ ($[M+H]^+$) 641.1169, found 641.1171

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 (m, 3 H); 7.25 (d, *J*=10.38 Hz, 2 H); 7.14 (d, *J*=7.63 Hz, 2 H); 7.02 (dd, *J*=7.63, 5.80 Hz, 2 H); 5.40 (s, 1 H); 4.22 (dd, *J*=11.75, 4.73 Hz, 2 H); 3.53 (t, *J*=11.60 Hz, 2 H); 2.24 (m, 1 H); 0.81 (d, *J*=6.71 Hz, 3 H)

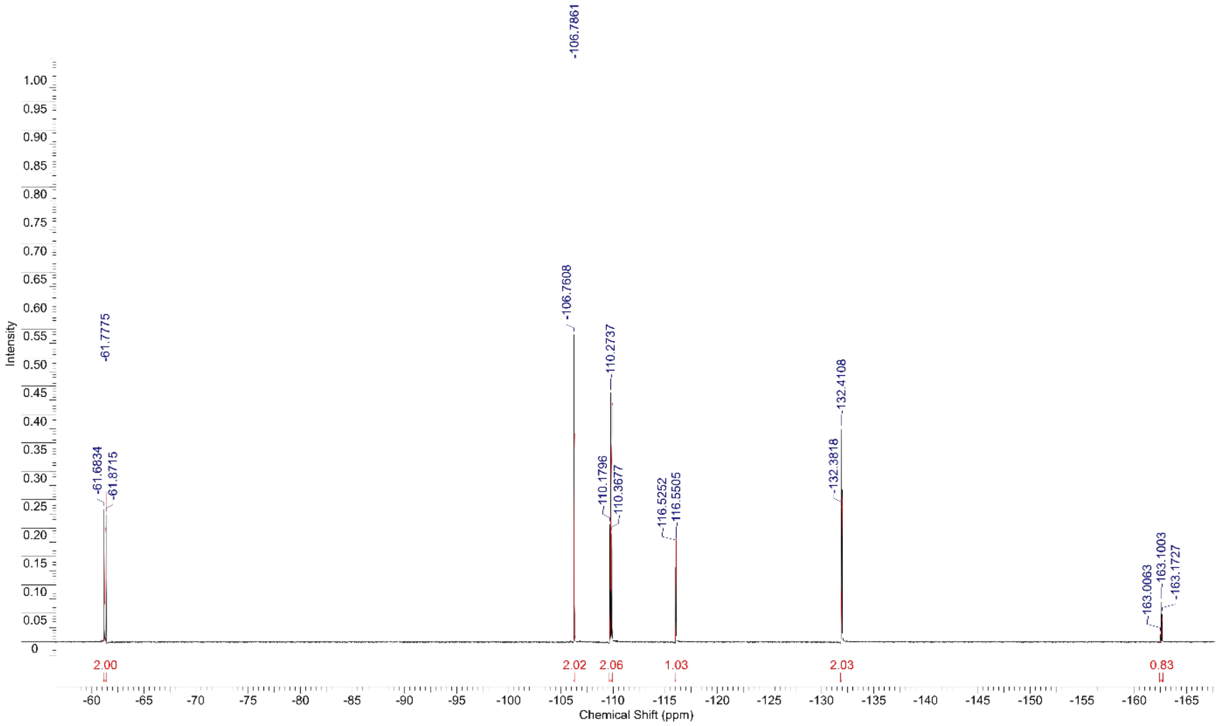




^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.75 (dd, *J*=254.32, 5.45 Hz); 159.96 (d, *J*=257.50, 5.90 Hz); 159.13, (d, *J*=250.69 Hz); 151.04 (ddd, *J*=250.69, 10.90, 5.45 Hz); 144.62 (m); 141.96 (t, *J*=9.08 Hz); 140.68 (t, *J*=10.90 Hz); 138.50 (dt, *J*=250.69, 15.44 Hz); 130.06 (d, *J*=2.73 Hz); 128.32 (d, *J*=3.63 Hz); 126.01 (d, *J*=12.72 Hz); 125.44 (d, *J*=9.99 Hz, 1 C); 120.14 (t, *J*=266.13 Hz); 119.68 (d, *J*=24.52 Hz); 113.08 (m); 109.34 (m); 107.48 (m); 101.62 (t, *J*=19.53 Hz); 98.99; 97.04 (m); 78.90; 73.61; 29.29; 12.24



^{19}F NMR (282 MHz, $CDCl_3$) δ: -61.78 (t, J=26.57 Hz, 2 F); -106.77 (d, J=7.15 Hz, 2 F); -110.29 (td, J=26.31, 9.71 Hz, 2 F); -116.52 (dd, J=11.24, 7.15 Hz, 1 F); -132.43 (dd, J=20.91, 8.18 Hz,2 F); -163.10 (tt, J=20.44, 5.13 Hz, 1 F)



*2-(4-((4'-(difluoro(3,4,5-trifluorophenoxy)methyl)-2,3',5'-trifluoro-[1,1'-biphenyl]-4-yl)ethynyl)-3,5-difluorophenyl)-5-ethyl-1,3-dioxane (**2dTBEP**)*

A stirred solution of 4-bromo-4'-(difluoro(3,4,5-trifluorophenoxy)methyl)-2,3',5'-trifluoro-1,1'-biphenyl (**19**, 2.16g, 0.00447mol), DBU (1.12g, 0.00738mol) and triethylamine (0.5g, 0.00492mol) was refluxed under N_2 atmosphere for 30 minutes. Then it was cooled to room temperature and $PdCl_2(PPh_3)_2$ (0.3%mol) and CuI (0.1%mol) were added. The mixture was heated to reflux and the solution 2-(4-ethynyl-3,5-difluorophenyl)-5-ethyl-1,3-dioxane (**11**, 1.24g, 0.00492mol) in toluene was added dropwise. The reaction mixture was refluxed for 2h. Later it was washed with H_2O and diluted HCl and extracted with toluene. The phases were separated, and the organic layer was dried over $MgSO_4$. The solvent was evaporated under reduced pressure. Crude product was recrystallized three times from ethanol/acetone mixture to give white crystals.

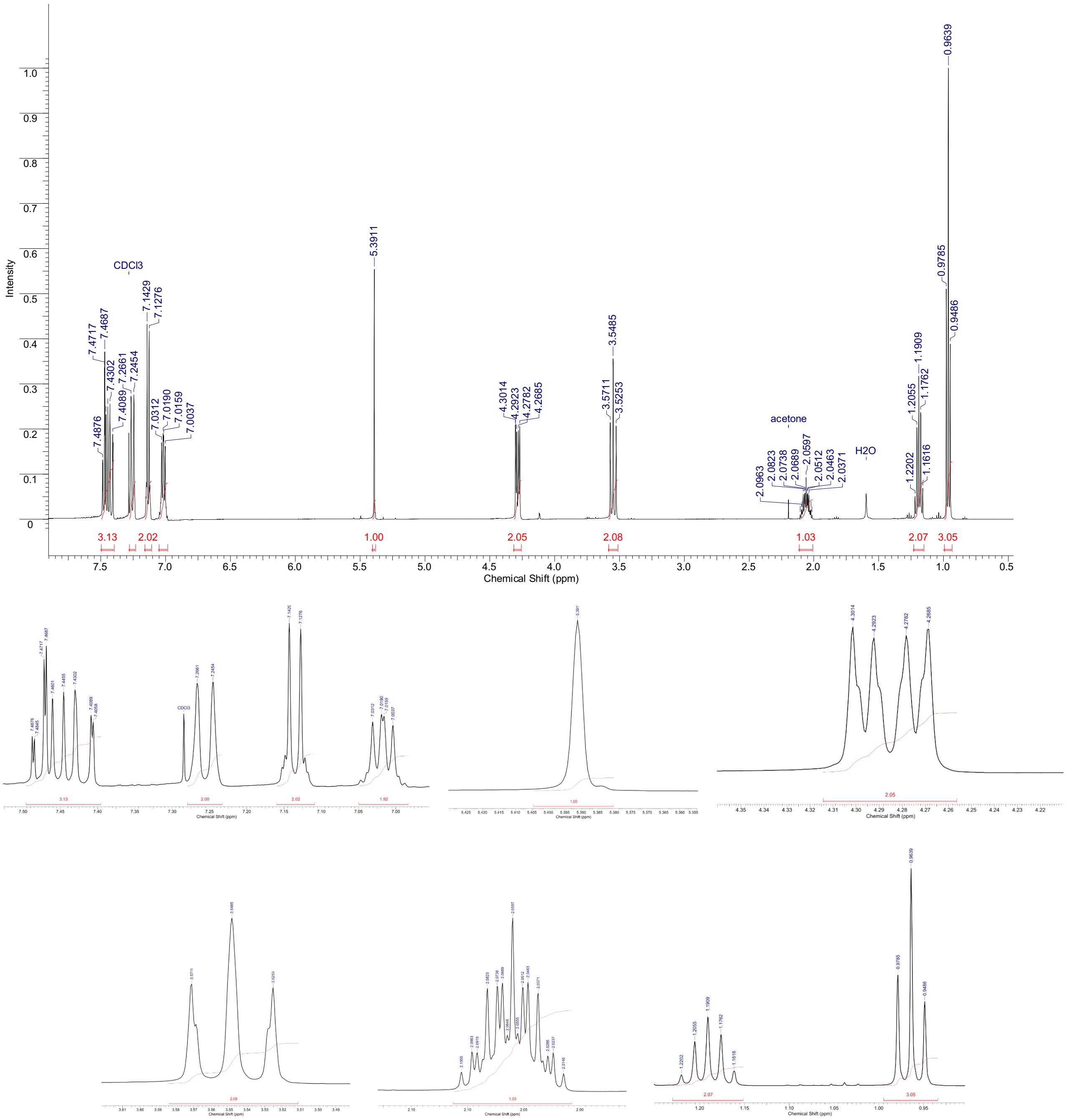
Yield: 1.85g (63.1%)

Purity (GCMS): 99.5% (99.0% of trans isomer)

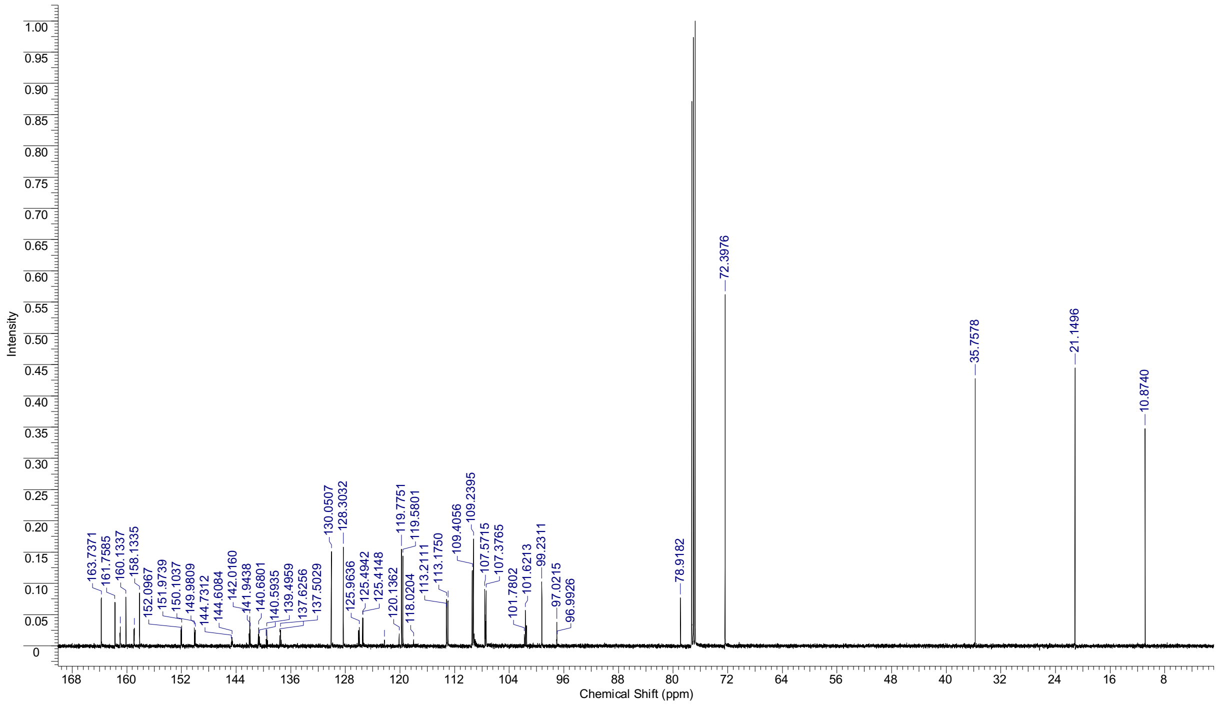
MS (EI) m/z: 654; 603; 567; 541; 507; 477; 421; 393; 353; 322; 281; 254; 210; 171; 147; 119

HRMS (HESI) m/z: calculated for $C_{33}H_{21}F_{10}O_3^+$ ($[M+H]^+$) 655.1326, found 655.1343

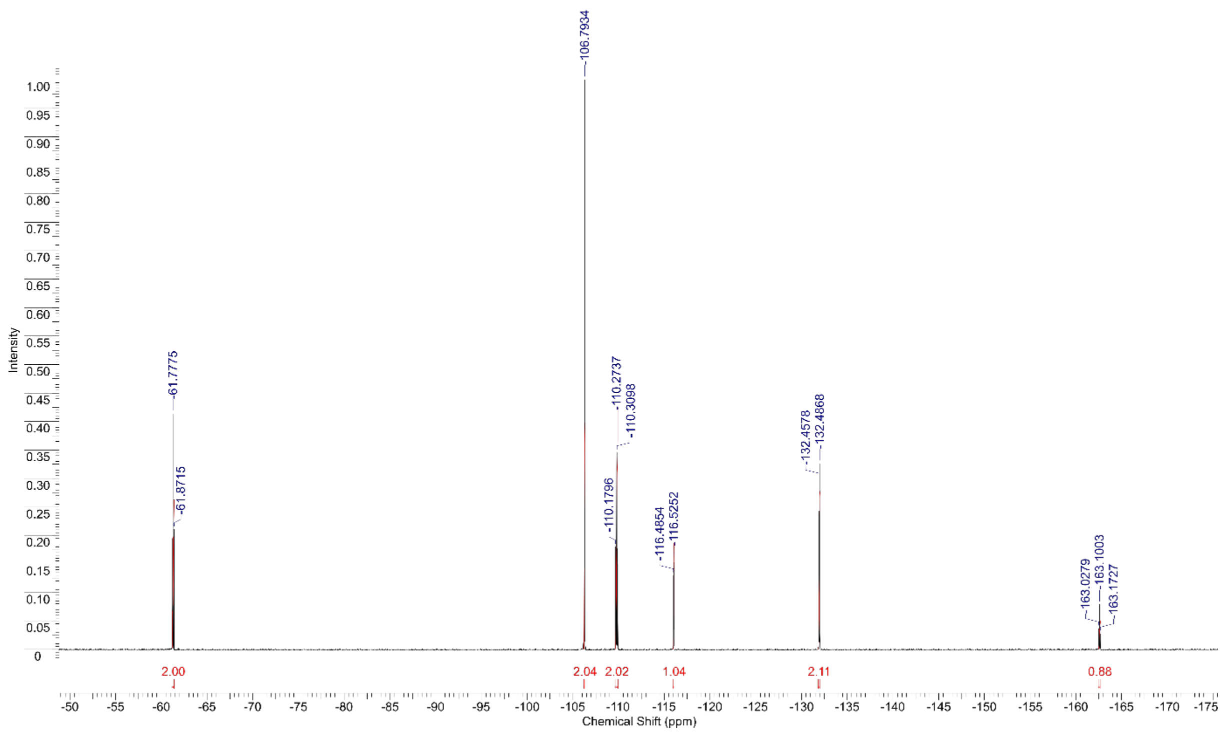
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 (m, 3 H); 7.26 (d, *J*=10.38 Hz, 2 H); 7.14 (d, *J*=7.63 Hz, 2 H); 7.02 (dd, *J*=7.63, 6.10 Hz, 2 H); 5.39 (s, 1 H); 4.29 (dd, *J*=11.75, 4.73 Hz, 2 H); 3.55 (t, *J*=11.44 Hz, 2 H); 2.06 (m, 1 H); 1.19 (m, 2 H); 0.96 (t, *J*=7.48 Hz, 3 H)



^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.75 (dd, *J*=254.32, 5.45 Hz); 159.94 (dd, *J*=257.95, 6.36 Hz); 159.13 (d, *J*=251.60 Hz) 151.04 (ddd, *J*=250.69, 10.90, 5.45 Hz); 144.62 (m); 142.02 (t, *J*=9.08 Hz); 140.68 (t, *J*=11.35 Hz); 138.50 (dt, *J*=250.69, 14.99 Hz); 130.06 (d, *J*=2.73 Hz); 128.32 (d, *J*=3.63 Hz); 126.01 (d, *J*=12.72 Hz); 125.45 (d, *J*=9.99 Hz); 120.14 (t, *J*=266.13 Hz); 119.68 (d, *J*=24.52 Hz); 113.08 (dd, *J*=27.70, 4.09 Hz); 109.34 (m); 107.48 (m); 101.62 (t, *J*=19.98 Hz, 1 C); 99.23 (m); 97.03 (m); 78.92; 72.40; 35.76; 21.15; 10.87



^{19}F NMR (282 MHz, $CDCl_3$) δ: -61.78 (t, *J*=26.57 Hz, 2 F); -106.78 (d, *J*=8.17 Hz, 2 F); -110.29 (td, *J*=26.57, 10.22 Hz, 2 F); -116.52 (dd, *J*=11.24, 7.15 Hz, 1 F); -132.44 (dd, *J*=20.95, 7.66 Hz, 2 F); -163.10 (tt, J=20.44, 5.13 Hz, 1 F)



*2-(4-((4'-(difluoro(3,4,5-trifluorophenoxy)methyl)-2,3',5'-trifluoro-[1,1'-biphenyl]-4-yl)ethynyl)-3,5-difluorophenyl)-5-propyl-1,3-dioxane (**3dTBEP**)*

The synthesis was carried out in the same manner as in **2dTBEP**.

Quantities used: 4-bromo-4'-(difluoro(3,4,5-trifluorophenoxy)methyl)-2,3',5'-trifluoro-1,1'-biphenyl (**19**, 3,3g, 0.00683mol), 2-(4-ethynyl-3,5-difluorophenyl)-5-propyl-1,3-dioxane (**12**, 2g, 0.00751mol), DBU (1.72g, 0.0113mol), triethylamine (0.76g, 0.00751mol)

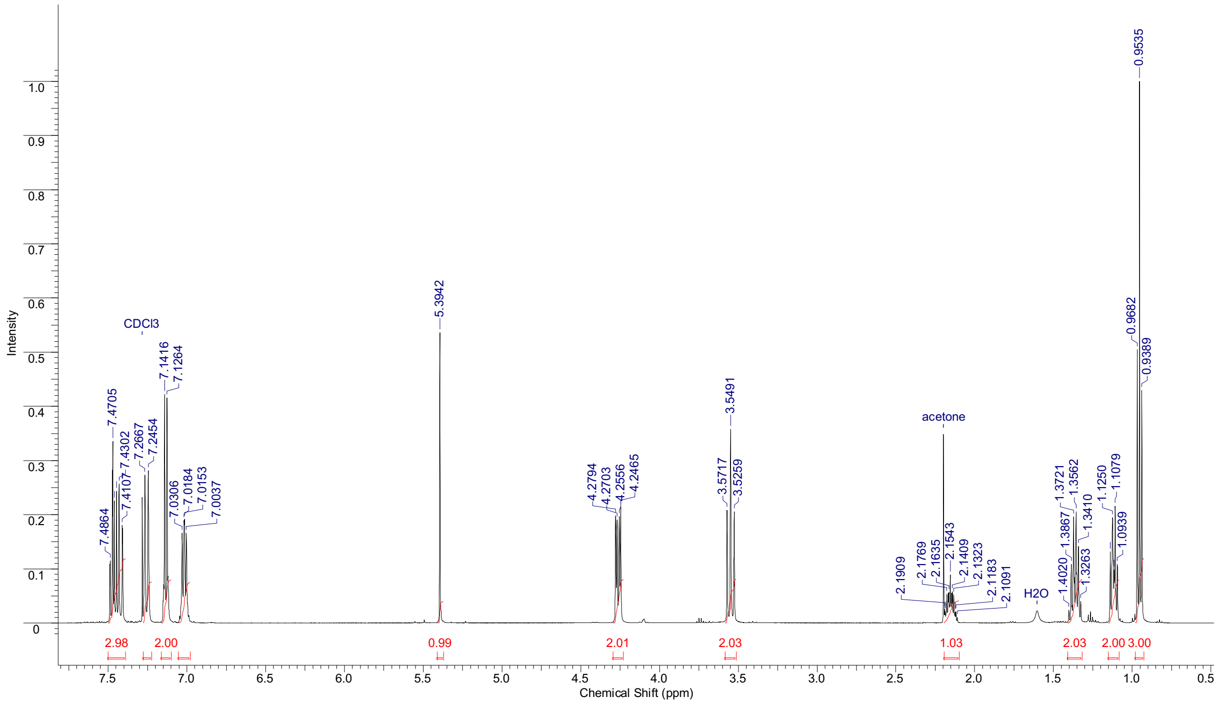
Yield: 2.75g (60.2%)

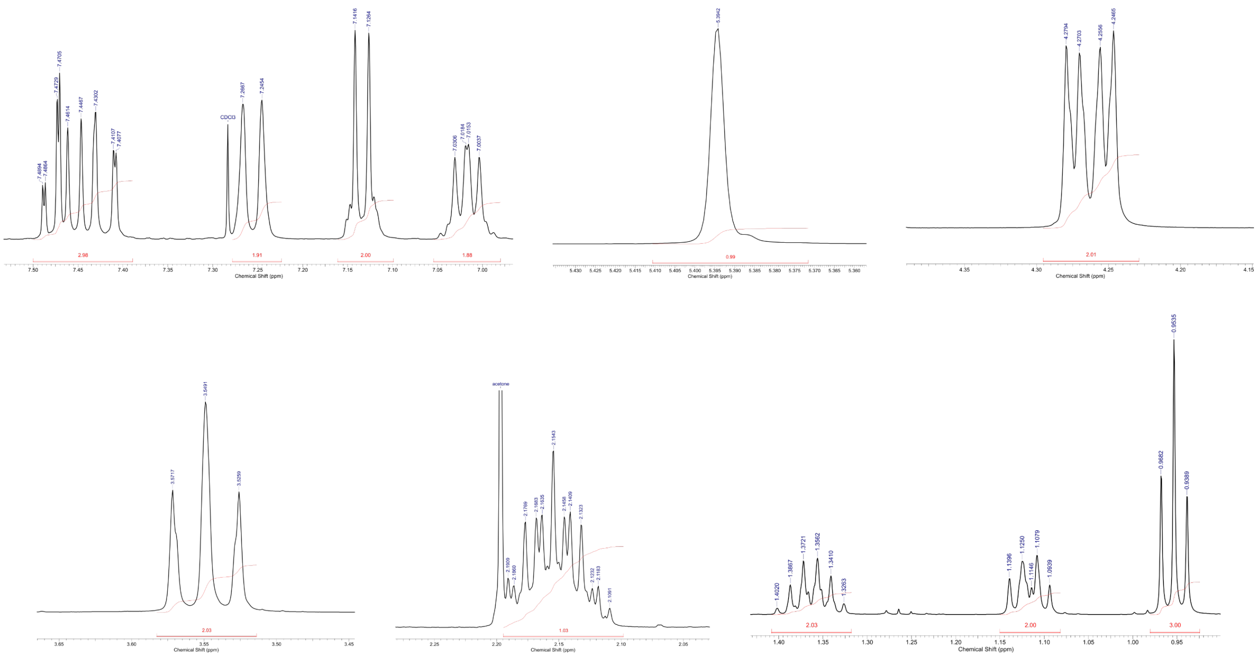
Purity (GCMS): >99.9% (99.1% of trans isomer)

MS (EI) m/z: 668; 644; 609; 567; 521; 479; 452; 421; 393; 353; 322; 281; 254; 210; 171; 147; 119

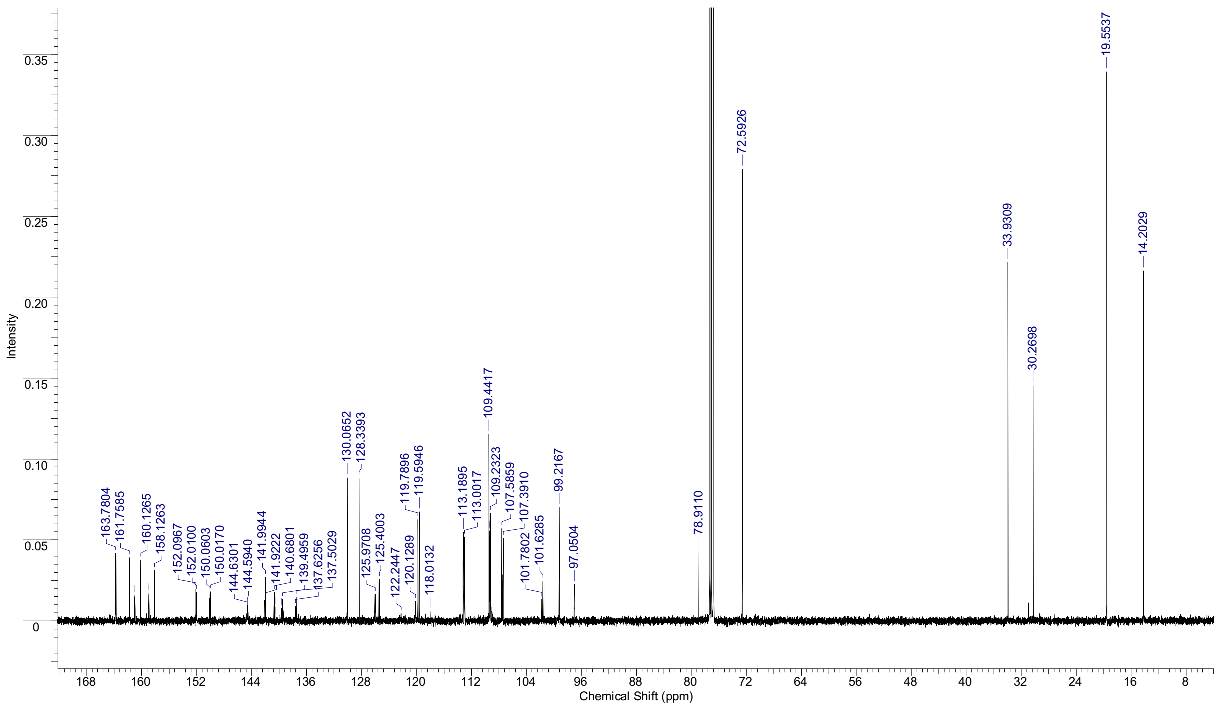
HRMS (HESI) m/z: calculated for $C_{34}H_{23}F_{10}O_3^+$ ($[M+H]^+$) 669.1482, found 669.1475

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 (m, 3 H); 7.26 (d, *J*=10.68 Hz, 2 H); 7.13 (d, *J*=7.63 Hz, 2 H); 7.02 (dd, *J*=7.48, 5.95 Hz, 2 H); 5.39 (s, 1 H); 4.26 (dd, *J*=11.90, 4.58 Hz, 2 H); 3.55 (t, *J*=11.44 Hz, 2 H); 2.15 (m, 1 H); 1.36 (m, 2 H); 1.12 (m, 2 H); 0.95 (t, *J*=7.32 Hz, 3 H)

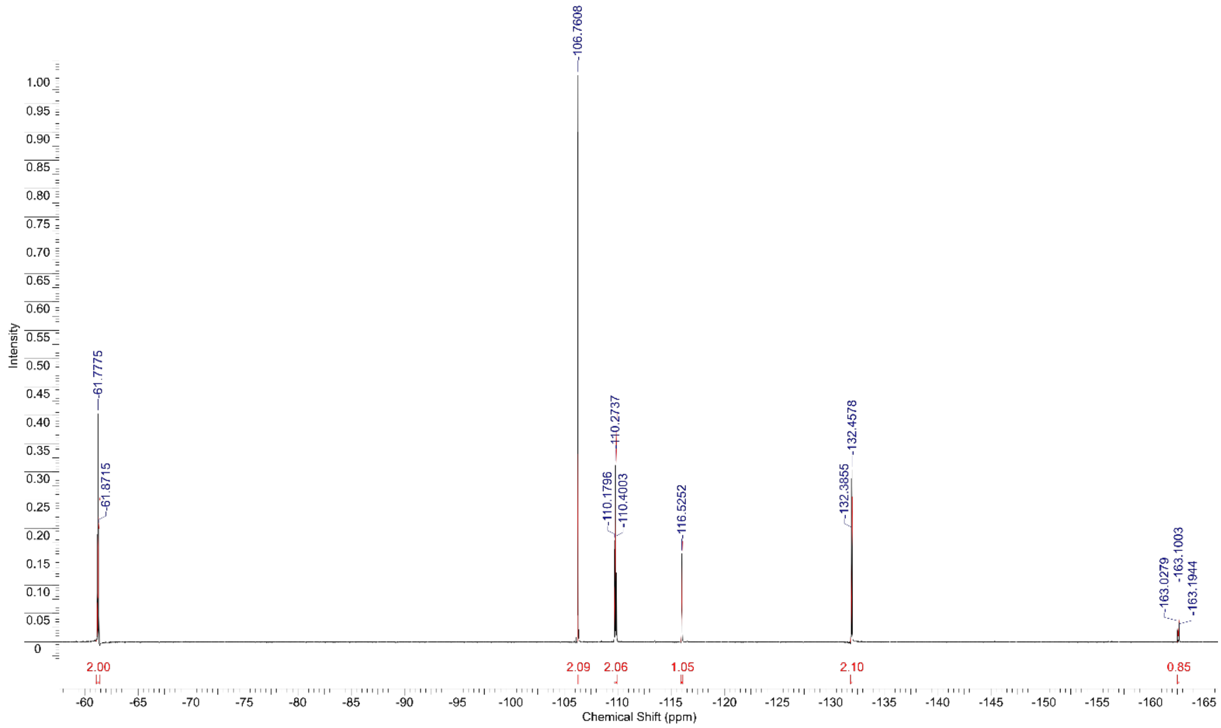




^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.75 (dd, *J*=254.32, 5.45 Hz); 159.96 (dd, *J*=257.95, 5.45 Hz); 159.13 (d, *J*=250.69 Hz); 151.04 (ddd, *J*=250.69, 10.90, 5.45 Hz); 144.61 (m); 141.99 (t, *J*=9.08 Hz); 140.68 (t, *J*=11.35 Hz); 138.50 (dt, *J*=250.69, 14.99 Hz); 130.08 (d, *J*=2.72 Hz); 128.32 (d, *J*=3.63 Hz); 126.02 (d, *J*=12.72 Hz); 125.44 (d, *J*=9.99 Hz); 120.13 (t, *J*=266.13 Hz); 119.69 (d, *J*=24.52 Hz); 113.09 (m); 109.34 (m); 107.49 (m); 101.63 (t, *J*=19.53 Hz); 99.22 (t, *J*=2.27 Hz); 97.04 (m); 78.91; 72.59; 33.93; 30.27; 19.55; 14.20



^{19}F NMR (282 MHz, $CDCl_3$) δ: -61.78 (t, *J*=26.06 Hz, 2 F); -106.78 (d, *J*=8.17 Hz, 2 F); -110.29 (dt, *J*=26.31, 9.71 Hz, 2 F); -116.52 (dd, *J*=11.24, 7.15 Hz, 1 F); -132.44 (dd, *J*=20.91, 7.66 Hz, 2 F); -163.10 (tt, J=20.44, 5.13 Hz, 1 F)



*2-(4-((4'-(difluoro(3,4,5-trifluorophenoxy)methyl)-2,3',5'-trifluoro-[1,1'-biphenyl]-4-yl)ethynyl)-3,5-difluorophenyl)-5-butyl-1,3-dioxane (**4dTBEP**)*

The synthesis was carried out in the same manner as in **1dTBEP**.

Quantities used: 2-(4-((4-bromo-3-fluorophenyl)ethynyl)-3,5-difluorophenyl)-5-butyl-1,3-dioxane (**16**, 2.92g, 0.00644mol), 2-(4-(difluoro(3,4,5-trifluorophenoxy)methyl)-3,5-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**17**, 3.09g, 0.00708mol), K_2CO_3 (3.43g, 0.0248mol)

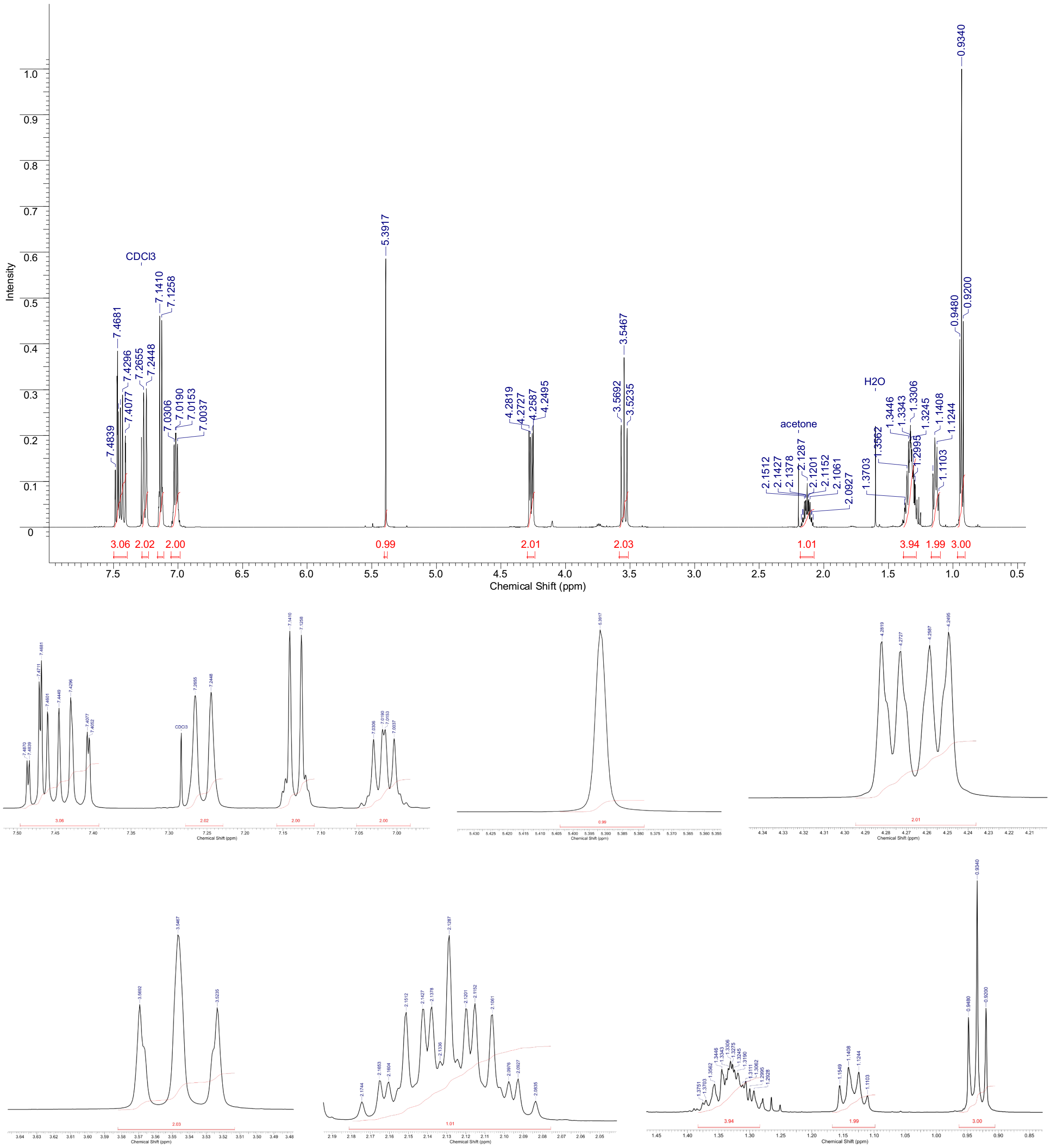
Yield: 2.27g (51.6%)

Purity (GCMS): 99.0% (98.5% of trans isomer)

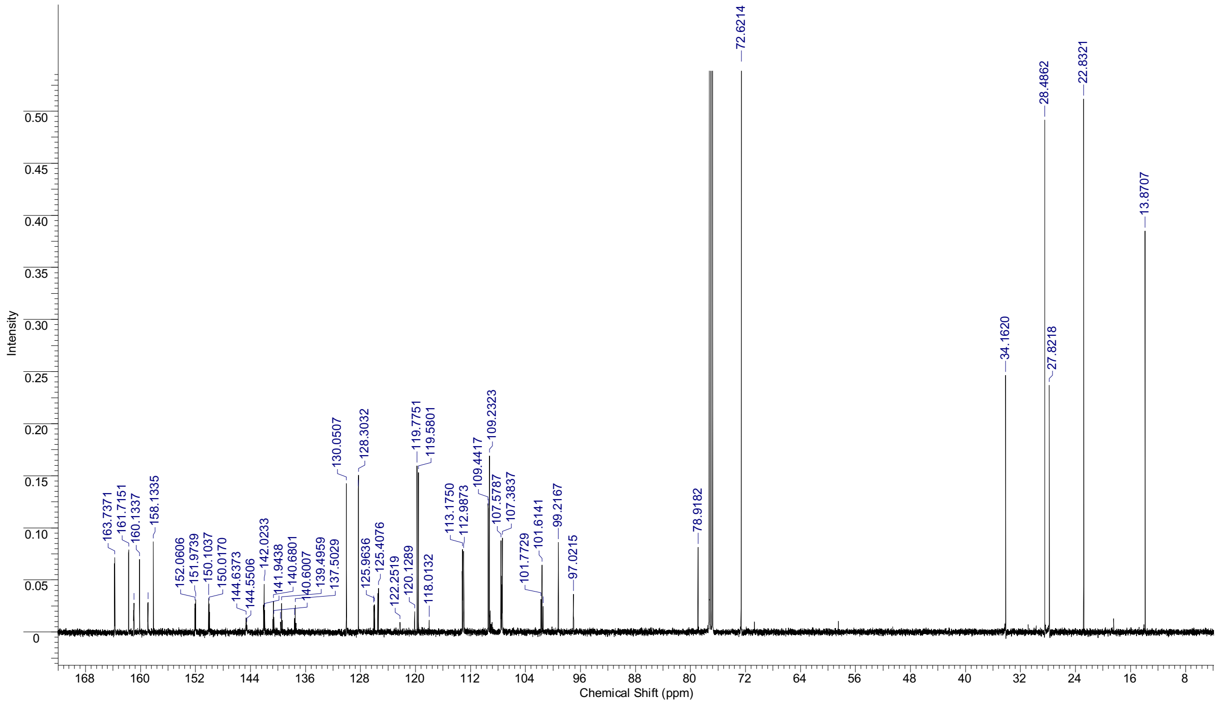
MS (EI) m/z: 682; 651; 626; 567; 535; 477; 452; 421; 393; 353; 322; 291; 267; 210; 171; 147; 119

HRMS (HESI) m/z: calculated for $C_{35}H_{25}F_{10}O_3^+$ ([M+H]$^+$) 683.1639, found 683.1627

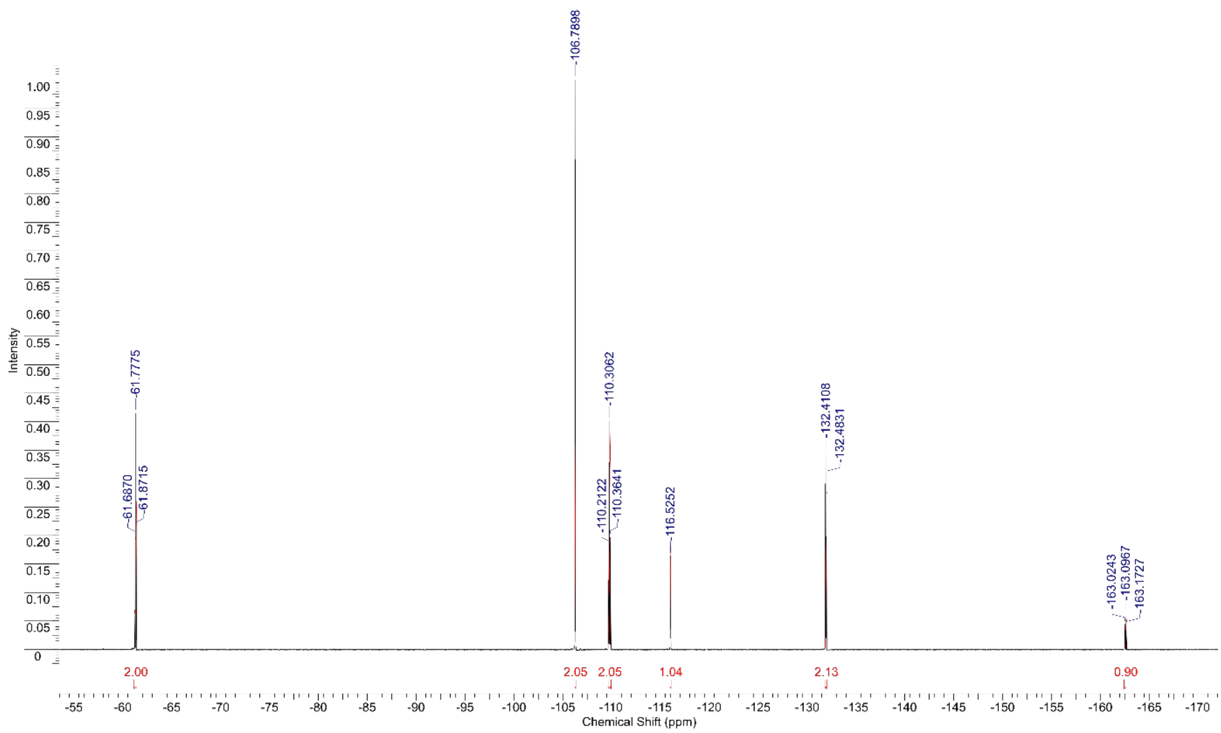
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 (m, 3 H); 7.26 (d, *J*=10.38 Hz, 2 H); 7.13 (d, *J*=7.63 Hz, 2 H); 7.02 (dd, *J*=7.63, 5.80 Hz, 2 H); 5.39 (s, 1 H); 4.27 (dd, *J*=11.60, 4.58 Hz, 2 H); 3.55 (t, *J*=11.44 Hz, 2 H); 2.13 (m, 1 H); 1.33 (m, 4 H); 1.13 (m, 2 H); 0.93 (t, *J*=7.02 Hz, 3 H)

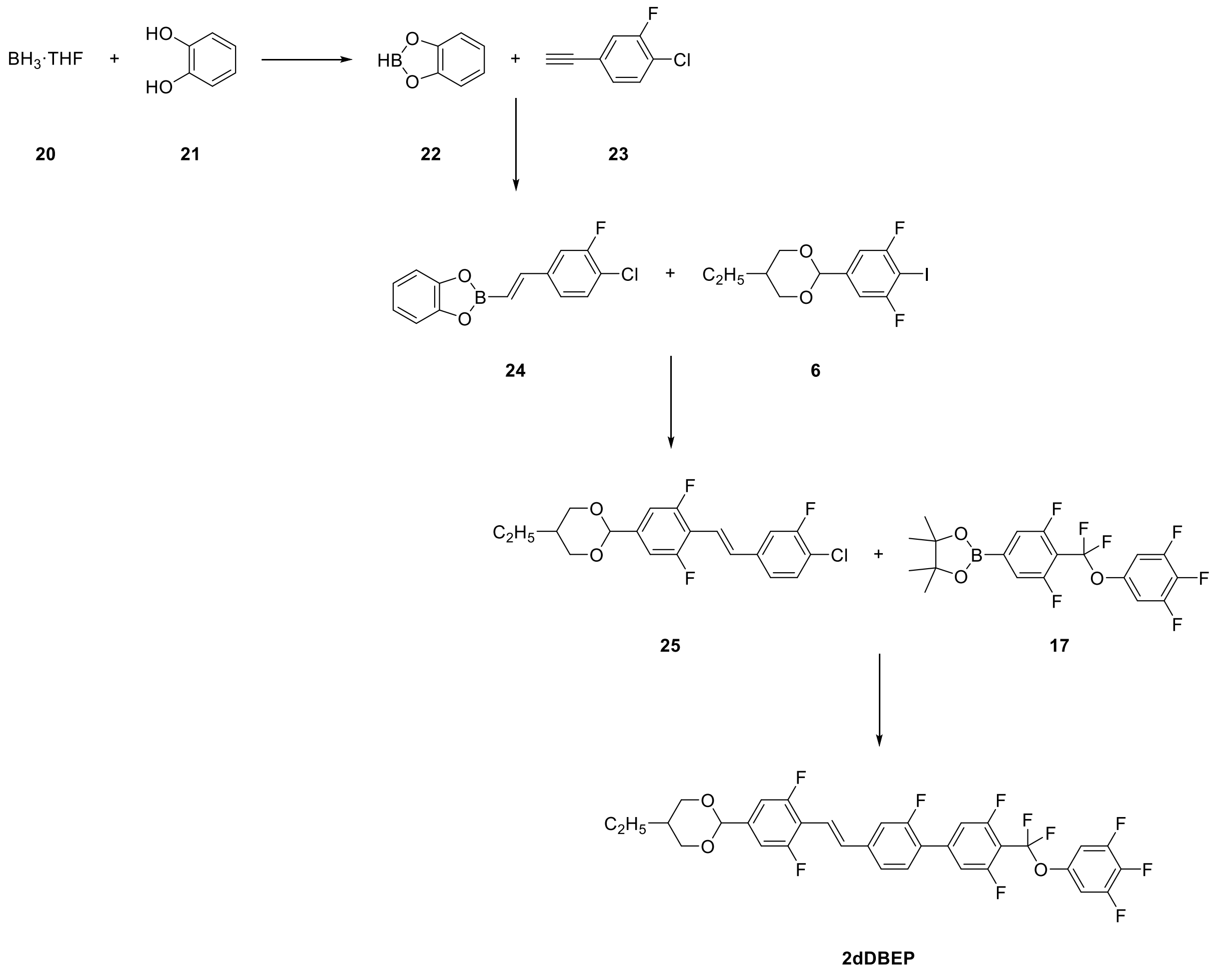


^{13}**C NMR** (125 MHz, $CDCl_3$) δ: 162.75 (dd, *J*=254.32, 5.45 Hz); 159.96 (dd, *J*=257.95, 6.36 Hz); 159.13 (d, *J*=251.60 Hz); 151.04 (ddd, *J*=251.37, 10.67, 5.00 Hz); 144.62 (m); 142.02 (t, *J*=9.54 Hz); 140.68 (t, *J*=10.45 Hz); 138.50 (dt, *J*=250.69, 15.44 Hz); 130.06 (d, *J*=2.73 Hz); 128.32 (d, *J*=3.63 Hz); 126.01 (d, *J*=12.72 Hz); 125.45 (d, *J*=9.99 Hz); 120.13 (t, *J*=266.13 Hz); 119.68 (d, *J*=24.52 Hz); 113.08 (dd, *J*=27.70, 4.09 Hz); 109.34 (m); 107.48 (m); 101.61 (t, *J*=19.98 Hz); 99.22 (m); 97.03 (q, *J*=2.73 Hz); 78.92; 72.62; 34.16; 28.49; 27.82; 22.83; 13.87



^{19}**F NMR** (282 MHz, $CDCl_3$) δ: -61.78 (t, *J*=26.06 Hz, 2 F); -106.78 (d, *J*=8.17 Hz, 2 F); -110.29 (td, *J*=26.57, 10.22 Hz, 2 F); -116.52 (dd, *J*=11.24, 7.15 Hz, 1 F); -132.43 (dd, *J*=20.91, 8.17 Hz, 2 F); -163.10 (tt, *J*=20.82, 5.13, 1 F)





*(E)-2-(4-(4-chloro-3-fluorostyryl)-3,5-difluorophenyl)-5-ethyl-1,3-dioxane (**25**)*

To a stirred solution of catechol (**21**, 2.2g, 0.02mol) in anhydrous THF (20mL) at 0°C, the BH_3·THF complex (**20**, 20mL, 0.02mol) was added dropwise. The mixture was stirred at 0°C for 30 minutes and for additional 1h at room temperature until cessation of gas release was observed.

To a resulting catecholborane (**22**) the solution of 1-chloro-4-ethynyl-2-fluorobenzene (**23**, 3.09g, 0.02mol) in THF (10mL) was added in one portion. THF was then removed from the mixture by short path distillation and the neat mixture of **22** and **23** was stirred at 100°C for 1h.

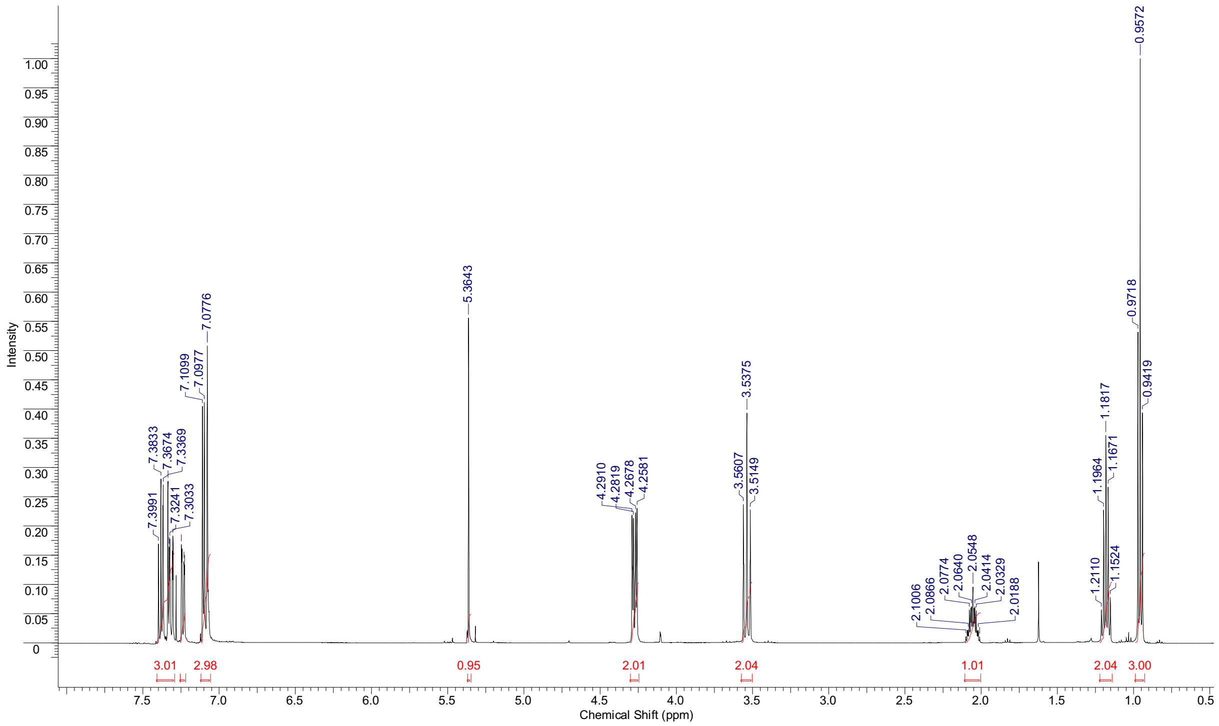
To a resulting (E)-2-(4-chloro-3-fluorostyryl)benzo[d][1,3,2]dioxaborole (**24**) 2-(3,5-difluoro-4-iodophenyl)-5-ethyl-1,3-dioxane (**6**, 3.54g, 0.01mol), $K_3PO_4 \cdot 3H_2O$ (18.64g, 0.07mol), $Pd(OAc)_2$ (0.1%mol) and anhydrous THF (30mL) were added and the mixture was refluxed for 2h. Later it was washed with H_2O and diluted HCl and extracted with DCM. The phases were separated, and the organic layer was dried over $MgSO_4$. The solvent was evaporated under reduced pressure. Crude product was recrystallized from ethanol.

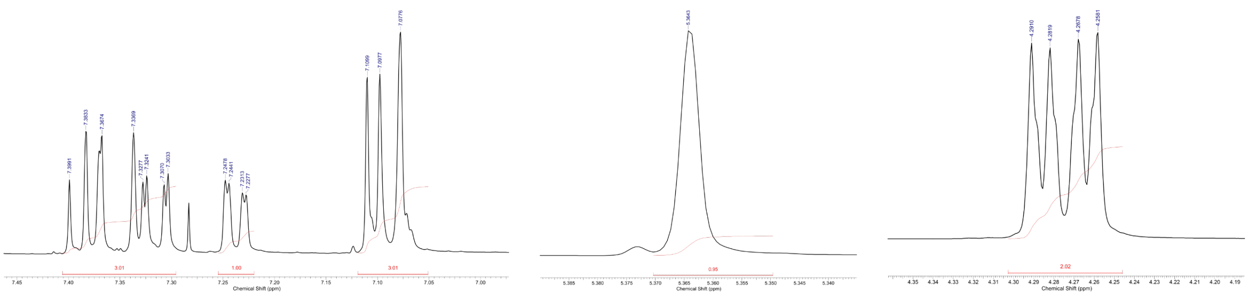
Yield: 1.3g (34.0%)

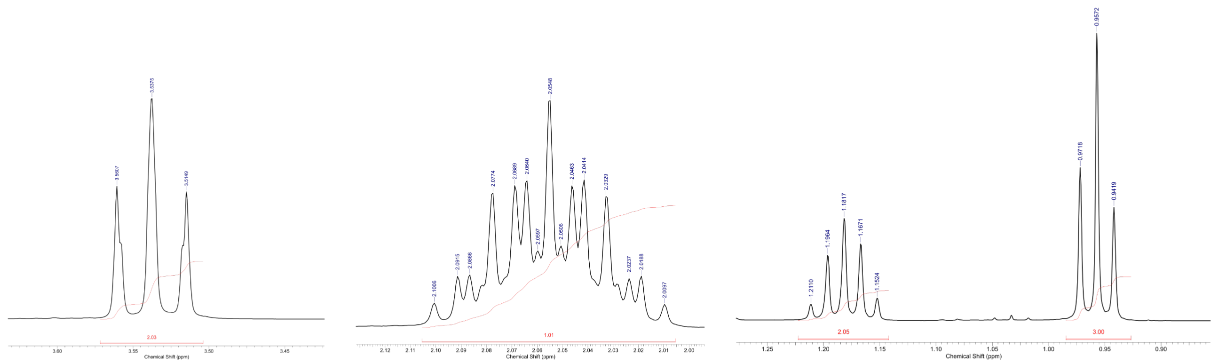
Purity (GCMS): >99.9% (93.8% of trans 1,3-dioxane unit and E isomer of vinyl unit)

MS (EI) m/z: 382; 347; 323; 296; 268; 232; 193; 154; 130

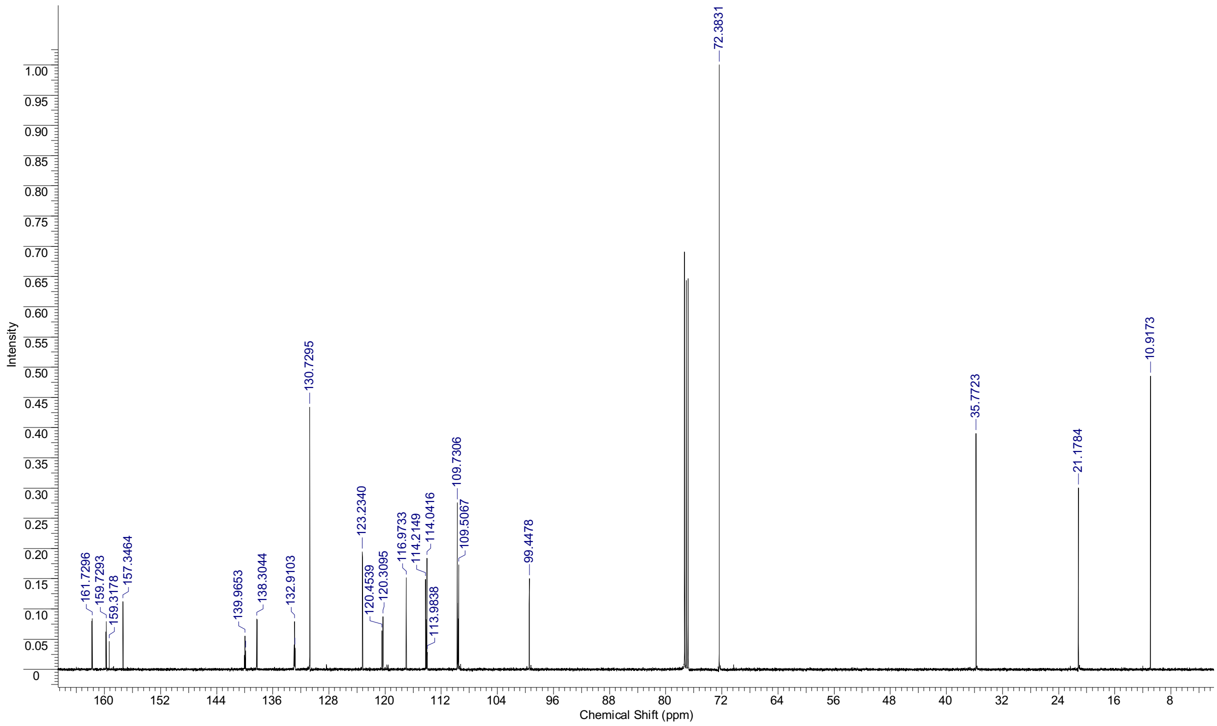
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34 (m, 3 H); 7.24 (dd, *J*=8.24, 1.83 Hz, 1 H); 7.10 (m, 3 H); 5.36 (s, 1 H); 4.27 (dd, *J*=11.75, 4.73 Hz, 2 H); 3.54 (t, *J*=11.44 Hz, 2 H); 2.06 (m, 1 H); 1.18 (m, 2 H); 0.96 (t, *J*=7.48 Hz, 3 H)







^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.76 (dd, *J*=252.05, 7.72 Hz); 158.33 (d, *J*=247.97 Hz); 139.97 (t, *J*=9.99 Hz); 138.28 (d, *J*=6.36 Hz); 132.90 (m); 130.73; 123.22 (d, *J*=3.63 Hz); 120.38 (d, *J*=18.17 Hz); 116.97; 114.21; 114.10; 114.04; 113.98; 109.62 (m); 99.45 (t, *J*=2.27 Hz); 72.38; 35.77; 21.18; 10.92



*(E)-2-(4-(2-(4'-(difluoro(3,4,5-trifluorophenoxy)methyl)-2,3',5'-trifluoro-[1,1'-biphenyl]-4-yl)vinyl)-3,5-difluorophenyl)-5-ethyl-1,3-dioxane (**2dDBEP**)*

A stirred solution of (E)-2-(4-(4-chloro-3-fluorostyryl)-3,5-difluorophenyl)-5-ethyl-1,3-dioxane (**25**, 1.3g, 0.0034mol), 2-(4-(difluoro(3,4,5-trifluorophenoxy)methyl)-3,5-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**17**, 1.63g, 0.00374mol), $K_3PO_4 \cdot 3H_2O$ (3.49g, 0.0131mol) in anhydrous THF (30mL) was refluxed under N_2 atmosphere for 30 minutes. Then it was cooled and $Pd(OAc)_2$ (0.1%mol) and SPhos (0.1%mol) was added. The reaction mixture was refluxed for 2h. Later it was washed with H_2O and diluted HCl and extracted with DCM. The phases were separated, and the organic layer was dried over $MgSO_4$. The solvent was evaporated under reduced pressure. Crude product was recrystallized three times for ethanol/acetone mixture.

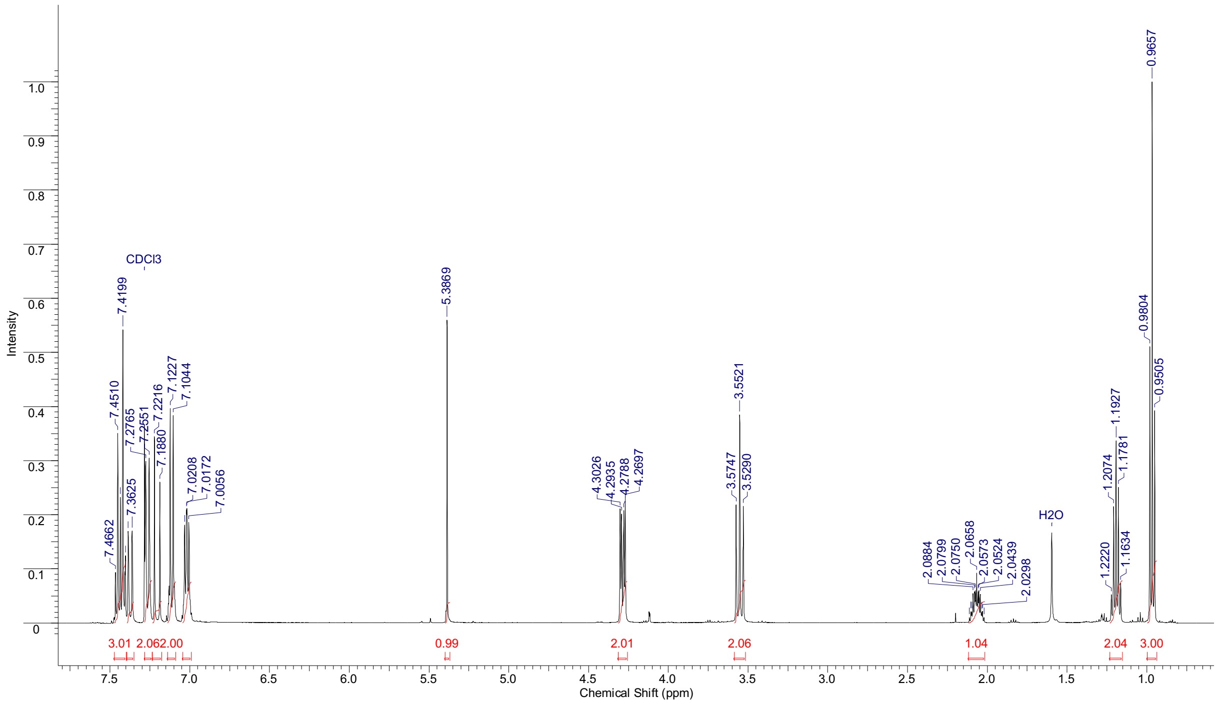
Yield: 0.85g (38.1%)

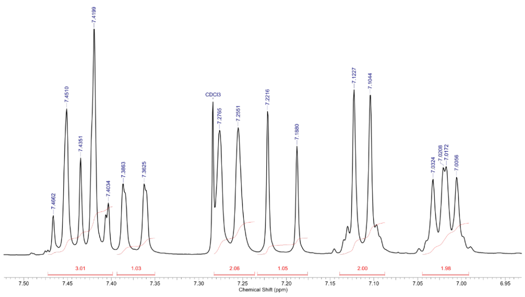
Purity (GC-MS): >99.9% (96.5% of trans 1,3-dioxane unit and E isomer of vinyl unit)

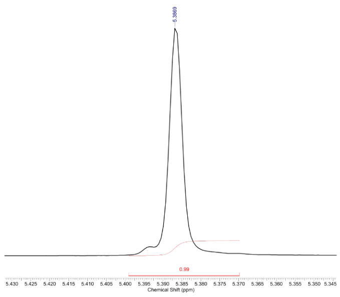
MS (EI) m/z: 656; 631; 605; 569; 543; 509; 479; 423; 395; 355; 324; 281; 255; 211; 188; 147; 119

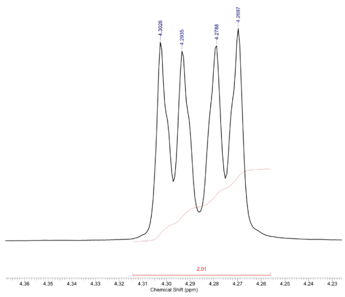
HRMS (HESI) m/z: calculated for $C_{33}H_{23}F_{10}O_3^+$ ($[M+H]^+$) 657.1482, found 657.1470

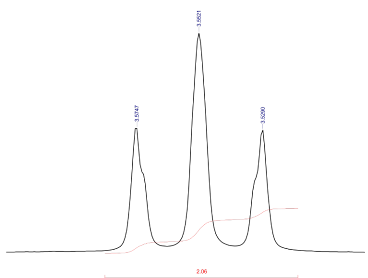
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.43 (m, 3 H); 7.37 (d, *J*=11.90 Hz, 1 H); 7.27 (d, *J*=10.68 Hz, 2 H); 7.20 (d, *J*=16.79 Hz, 1 H); 7.11 (d, *J*=9.16 Hz, 2 H); 7.02 (dd, *J*=7.63, 5.80 Hz, 2 H); 5.39 (s, 1 H); 4.29 (dd, *J*=11.90, 4.58 Hz, 2 H); 3.55 (t, *J*=11.44 Hz, 2 H); 2.07 (m, 1 H); 1.19 (m, 2 H); 0.97 (t, *J*=7.48 Hz, 3 H)

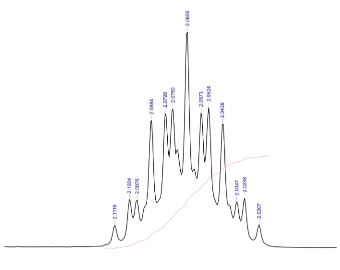

Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
CDCl3
7.4662
7.4510
7.4199
7.3625
7.2765
7.2551
7.2216
7.1880
7.1227
7.1044
7.0208
7.0172
7.0056
5.3869
4.3026
4.2935
4.2788
4.2697
3.5747
3.5521
3.5290
2.0884
2.0799
2.0750
2.0658
2.0573
2.0524
2.0439
2.0298
H2O
1.2220
1.2074
1.1927
1.1781
1.1634
0.9804
0.9657
0.9505
3.01
2.06
2.00
0.99
2.01
2.06
1.04
2.04
3.00
Chemical Shift (ppm)

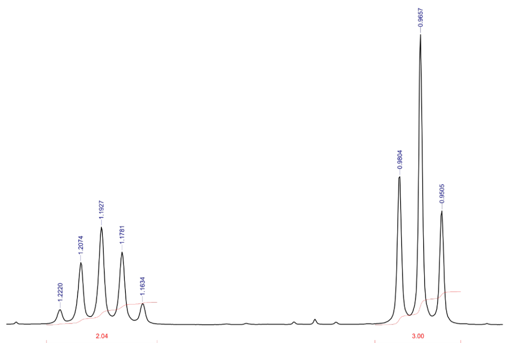




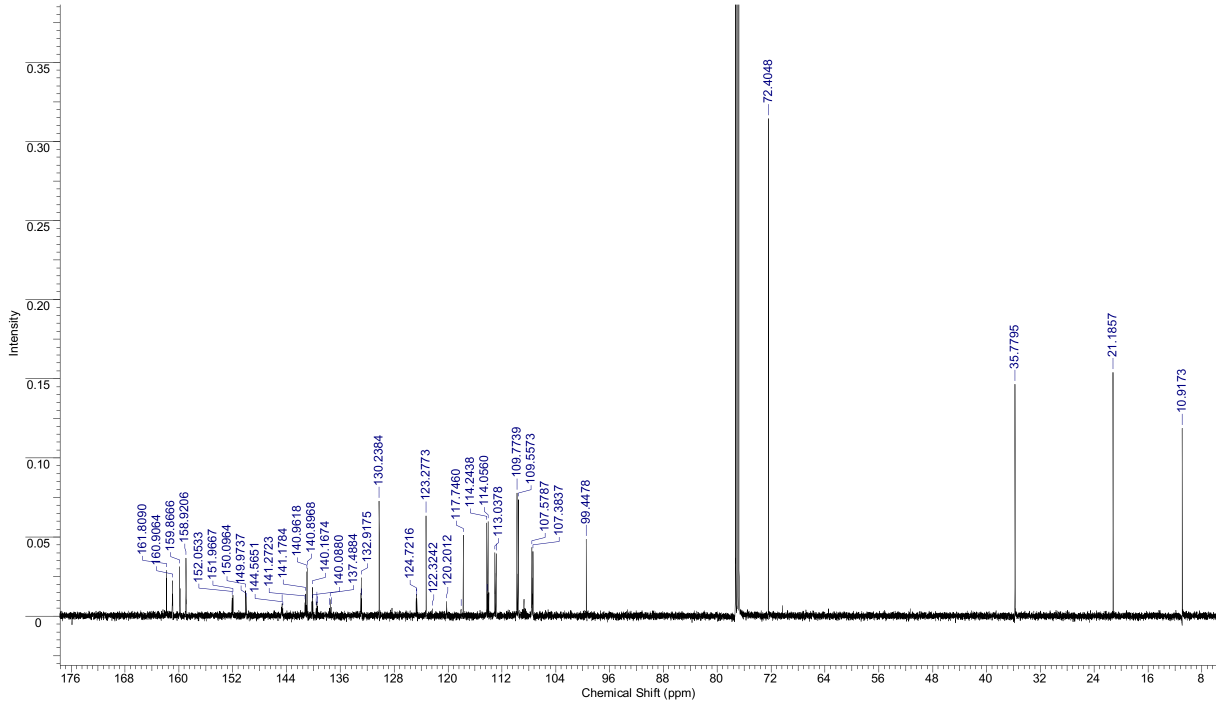




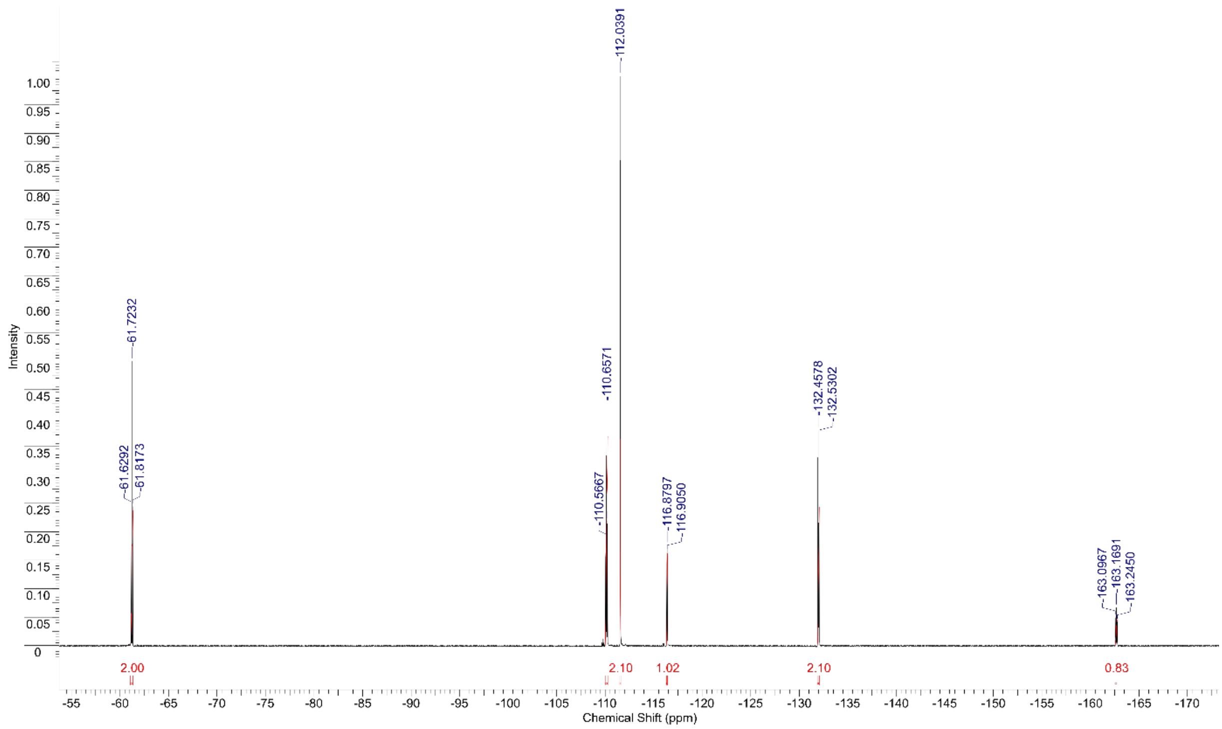




^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.94 (m, overlapping s and d of C-F); 160.84 (dd, *J*=252.50, 8.17 Hz); 158.92 (m, overlapping s and d of C-F); 151.03 (ddd, *J*=250.69, 10.90, 5.45 Hz); 144.66 (m); 141.18 (t, *J*=9.99 Hz); 140.93 (d, *J*=8.17 Hz); 140.17 (t, *J*=9.99 Hz); 138.48 (t, *J*=249.78, 14.99 Hz); 132.91 (m); 130.23 (d, *J*=2.72 Hz); 124.68 (m); 123.27 (d, *J*=2.72 Hz); 120.20 (t, *J*=267.04 Hz); 117.75; 114.24; 114.19; 114.06; 113.95; 112.94 (m); 109.67 (m); 107.48 (m); 99.45 (t, *J*=2.27 Hz); 72.40; 35.78; 21.19; 10.92



^{19}F NMR (282 MHz, $CDCl_3$) δ: -61.72 (t, *J*=26.57 Hz, 2 F); -110.64 (td, *J*=26.06, 10.22 Hz, 2 F); -112.06 (d, *J*=10.22 Hz, 2 F); -116.87 (dd, *J*=12.26, 7.15 Hz, 1 F); -132.48 (dd, *J*=20.91, 8.17 Hz, 2 F); -163.17 (tt, *J*=20.82, 5.13, 1 F)

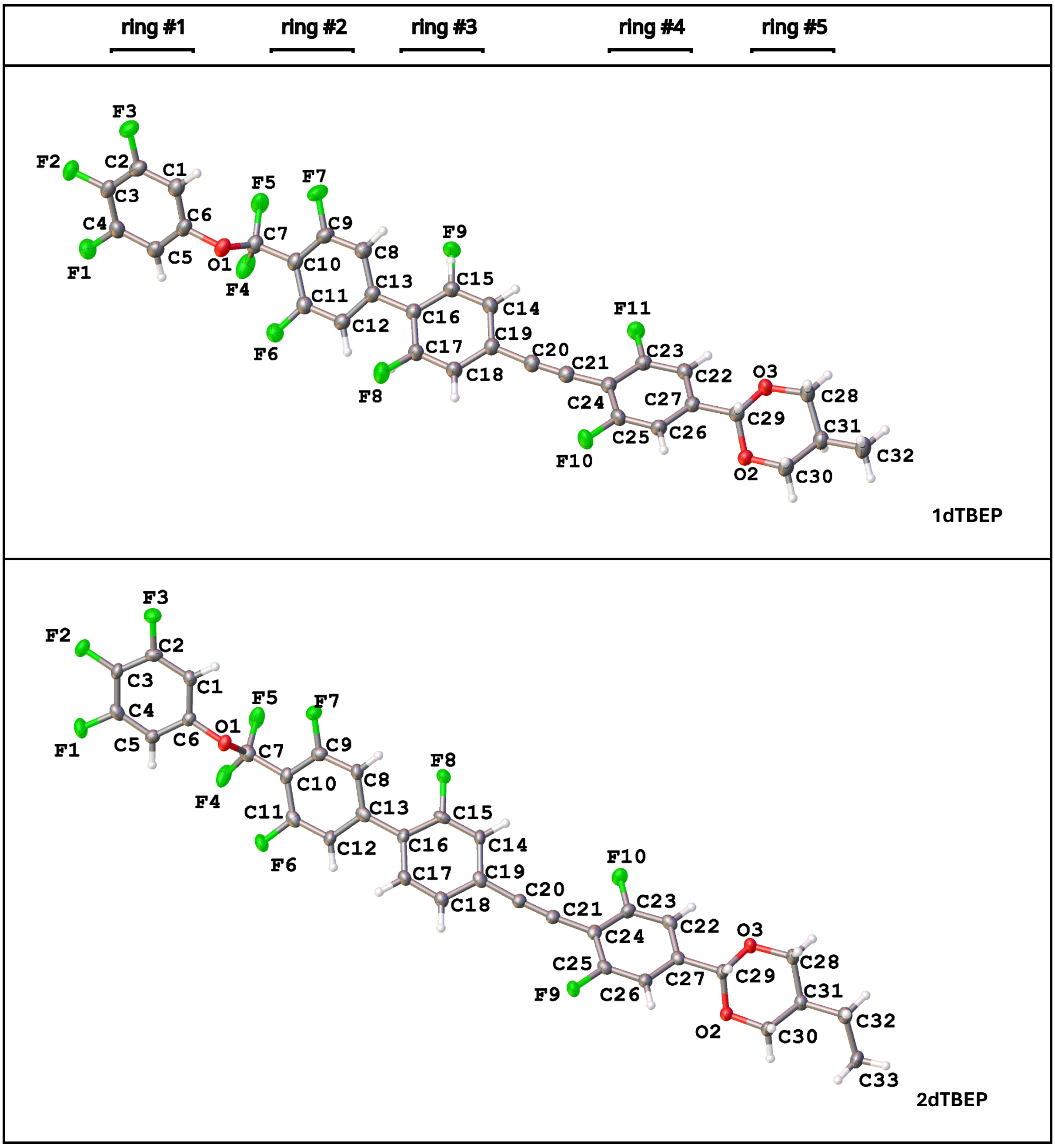


3. Crystallographic data

Table S1. Crystal data and structure refinement statistics.

Compound	1dTBEP	2dTBEP	3dTBEP	4dTBEP
CCDC #	2517654	2517656	2517655	2517653
Formula	$C_{32}H_{18}F_{10}O_3$	$C_{33}H_{20}F_{10}O_3$	$C_{34}H_{22}F_{10}O_3$	$C_{32}H_{18}F_{10}O_3$
Formula weight	640.46	654.49	668.51	640.46
Temperature/K	125.00(10)	100.15	100.00(10)	125.00(10)
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	P-1	P21	P-1	P-1
a/Å	9.7365(4)	10.0779(2)	10.2066(3)	9.7365(4)
b/Å	10.0238(3)	15.6905(3)	11.0223(3)	10.0238(3)
c/Å	14.1978(4)	17.9427(3)	12.7763(4)	14.1978(4)
α/°	81.899(3)	90	87.237(2)	81.899(3)
β/°	86.722(3)	104.416(2)	85.078(2)	86.722(3)
γ/°	74.851(3)	90	79.927(2)	74.851(3)
Volume/Å^3	1323.86(8)	2747.90(9)	1409.15(7)	1323.86(8)
Z	2	4	2	2
ρcalc / g/cm^3	1.607	1.582	1.576	1.607
μ/mm^{-1}	1.327	1.291	1.272	1.327
F(000)	648.0	1328.0	680.0	648.0
Crystal size/mm^3	0.36 × 0.06 × 0.03	0.13 × 0.05 × 0.02	0.2 × 0.09 × 0.06	0.36 × 0.06 × 0.03
2Θ range /°	6.29 to 155.888	5.086 to 147.84	8.826 to 145.192	6.29 to 155.888
Reflections collected	25075	29812	23998	25075
Independent reflections	5567 Rint = 0.0491 Rsigma = 0.0391	10908 Rint = 0.0386 Rsigma = 0.0475	5079 Rint = 0.0364 Rsigma = 0.0288	5567 Rint = 0.0491 Rsigma = 0.0391
Data/restraints/parameters	5567/0/483	10908/1/832	5079/0/434	5567/0/483
GooF on F^2	1.025	1.029	1.048	1.025
Final R indexes [I>=2σ (I)]	R1 = 0.0439 wR2 = 0.1159	R1 = 0.0460 wR2 = 0.1114	R1 = 0.0360 wR2 = 0.0954	R1 = 0.0439 wR2 = 0.1159
Final R indexes [all data]	R1 = 0.0558 wR2 = 0.1251	R1 = 0.0594 wR2 = 0.1180	R1 = 0.0444 wR2 = 0.1013	R1 = 0.0558 wR2 = 0.1251
Largest diff. peak/hole / e Å^{-3}	0.27/-0.23	0.41/-0.27	0.26/-0.20	0.27/-0.23
Hooft par.	---	0.30(14)	---	---
F / H disorder in ring III	F9 and H17 occ.: 93% F8 and H15 occ.: 7%	none	F9 and H17 occ.: 80% F8 and H15 occ.: 20%	F9 and H17 occ.: 60% F8 and H15 occ.: 40%

Figure S1 shows how the homologues differ in terms of the molecular shape. Homologue n=1 and n=2 exhibit a smaller bend between rings C1-C6 and C8-C13 then homologues n=3 and n=4 (Table S3) which affects their crystal packing. In particular, the fluorine atoms F4 and F5 adopt different positions in the shorter homologues compared to the longer ones, as indicated by the selected torsion angles in Table S2.



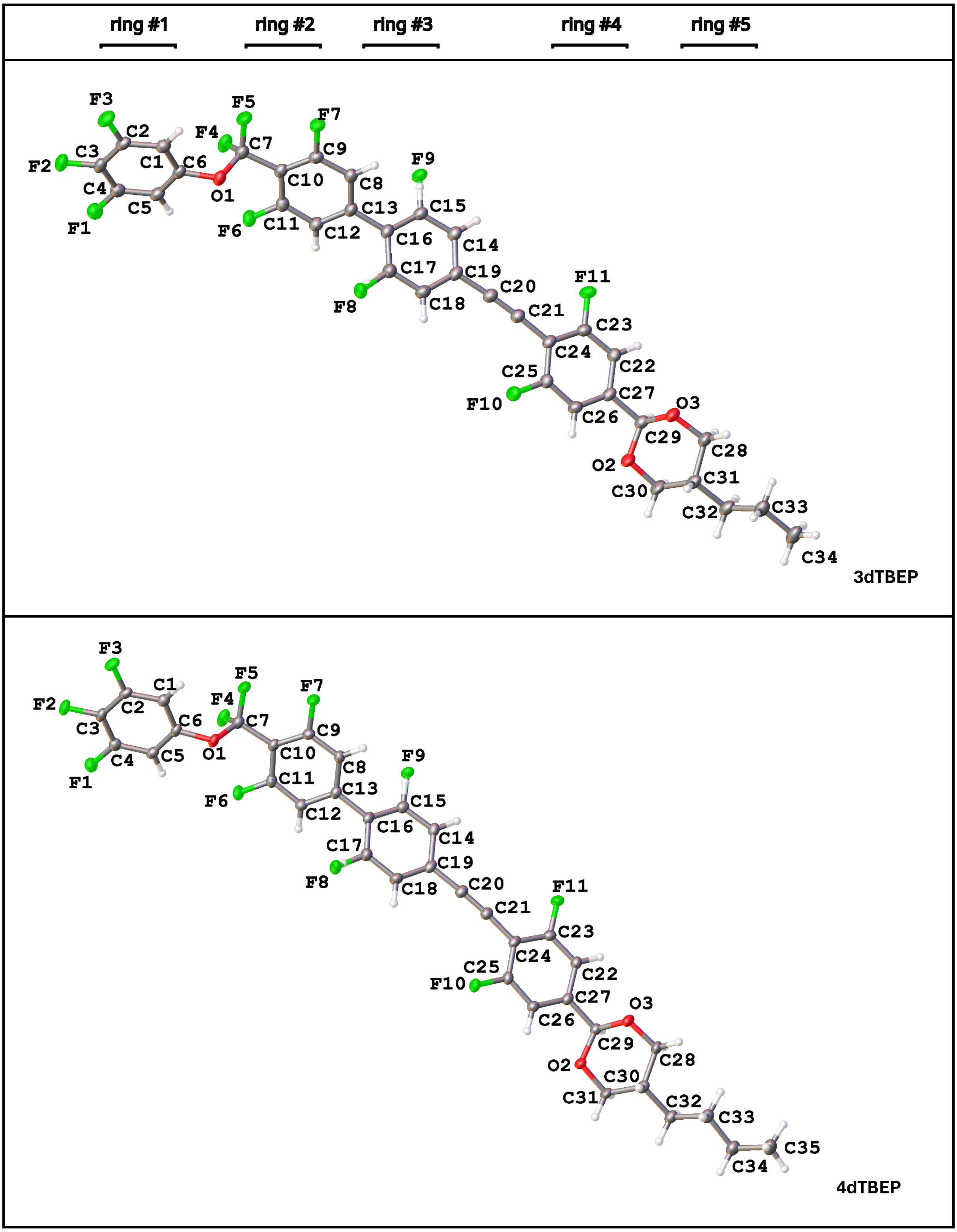


Fig. S1: ORTEP-like representations of all four homologues in order from n=1, with atom numbering schemes. H atom numbers are the same as those of the closest covalently bound C atom. Anisotropic atomic displacement parameters represented at 50% probability level. For homologue n=2 only one molecule, labelled from C1 to C33, has been shown. The second molecule, related by non-crystallographic center of symmetry, has been labeled from C34 to C67 (respective fluorine atoms have also been labeled from F1 to F11 and from F12 to F23 for the molecule not shown). Labels on top of the table indicate the numbering of the rings in the mesogenic core. For ring #5, which adopts a 'chair' conformation, the atoms used to calculate the mean plane were as follows: C28-C31 and O2-O3.

Table S2: Comparison of torsion angles for atoms F5 C7 C10 C9 for all four homologues.

Homologue	Torsion angles for atoms F5-C7-C10-C9
1dTBEP	25.4(3)
2dTBEP	47.5(6)
3dTBEP	5.2(2)
4dTBEP	5.5(2)

The torsion angle for homologue n=2 is the largest which could be due to the fact that this is the only structure solved with two molecules related by non-crystallographic symmetry in the asymmetric unit and due to strong interactions between them. The triple bond C20-C21 is bent in opposite directions with respect to ring #3 (Fig. S2) for the shorter vs. the longer homologues.

Table S3 summarizes the geometry of molecules *n*dTBEP with respect to the relative orientation of the ring systems. The most interesting data have been highlighted:

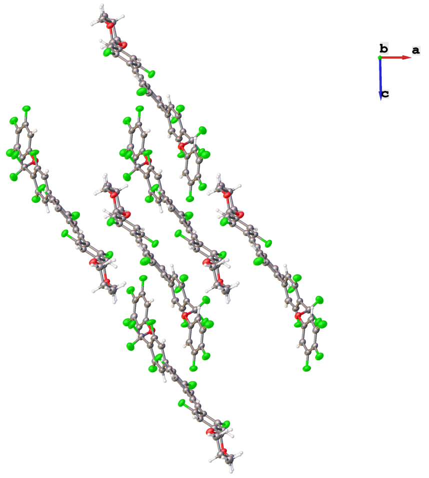
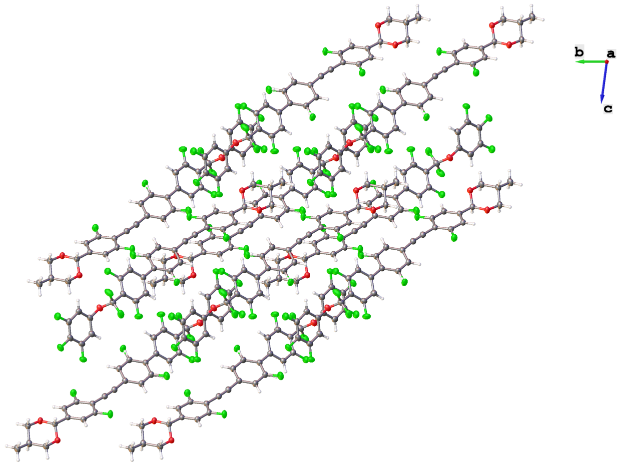
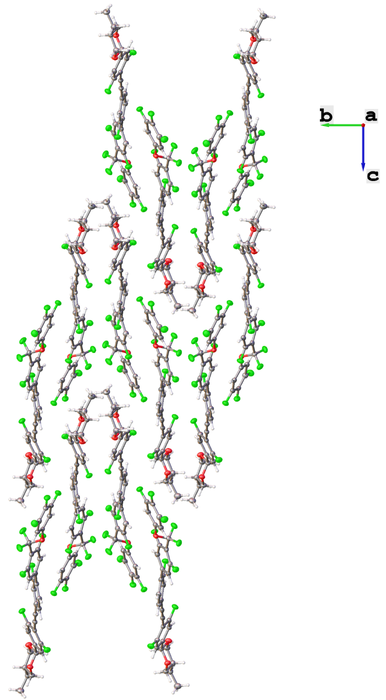
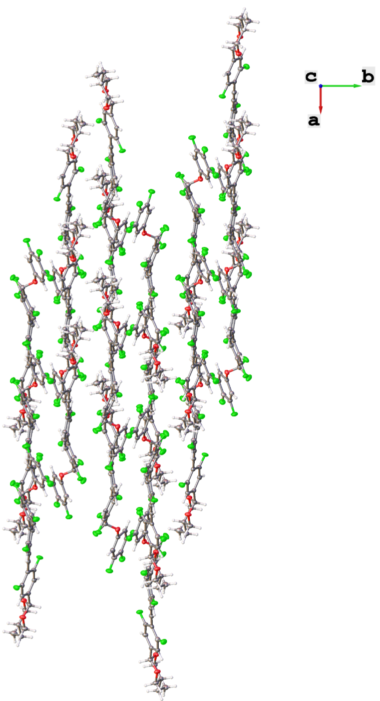
Table S3: Data on relative geometry of aromatic rings presented in Figure 2 for all four homologues.

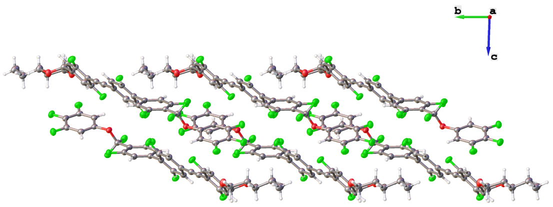
Plane	Homologue (n)	Distance between centroids [A]	Angle between ring plane and normals [º]	Twist angle [º]
#1-#2	1	6.358(2)	**17.93(11)**	**16.92(11)**
	2(1) (C1-C33)	6.353(3)	**169.90(15)**	**176.46(17)**
	2(2) (C34-C66)	6.362(3)	**10.33(15)**	**3.83(17)**
	3	6.257(9)	14.65(6)	12.43(6)
	4	6.263(8)	16.41(5)	13.56(5)
#2-#3	1	4.318(14)	34.72(2)	34.54(2)
	2(1) (C1-C33)	4.319(3)	144.58(17)	145.31(17)
	2(2) (C34-C66)	4.315(3)	35.16(17)	34.37(17)
	3	4.301(9)	50.88(6)	50.87(6)
	4	4.309(8)	47.63(5)	47.62(5)
#3-#4	1	6.866(2)	**17.53(11)**	**17.21(11)**

	2(1) (C1-C33)	6.863(3)	**18.38(17)**	**17.46(17)**
	2(2) (C34-C66)	6.870(3)	19.06(16)	18.33(16)
	3	6.884(9)	**5.21(5)**	**0.90(6)**
	4	6.881(9)	**7.38(5)**	**0.18(5)**
#4-#5	1	4.158(14)	28.33(17)	26.35(18)
	2(1) (C1-C33)	4.161(3)	29.25(16)	26.31(17)
	2(2) (C34-C66)	4.158(3)	28.81(16)	25.97(17)
	3	4.153(8)	**44.05(6)**	**41.74(6)**
	4	4.156(8)	**35.15(5)**	**32.59(5)**

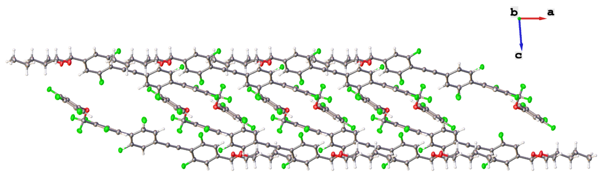
For planes #1 and #2 we see a significant difference in the twist and normal to normal angles for homologues n=1 and n=2. This could be a result of the fact that homologue n=2 crystallized with two independent molecules unlike n=1 which could have influenced the positioning of the rings through structural and π-π interactions. For the #3-#4 plane angles we observe a big difference between homologues n =1,2 and n= 3,4. These structural differences could be influencing the emerging of smectic phases in longer homologues (perhaps a smaller twist angle between the II and III ring is better for forming layers such as in smectics). There is also a big, observable difference between twist and normal to normal angles for planes #4-#5 for homologues n=3 and n=4, which could influence phase transition temperatures.

All 4 molecules are almost fully stretched, as illustrated by the maximal distances between the furthest non-H atoms, which increase with the lengthening of the terminal aliphatic chain: 27.2482(9)Å for n=1, 28.989(3) [or 28.998(3)] Å for n=2, 29.2032(12) Å for n=3 and 30.7432(10) for n=4. The length for an average C-C bond for an alkyl chain is 1.530 A (as given in Crystallographic Tables[7]) so we would expect the difference in length between homologue n=1 and n=4 to be about 3.6 Å, taking into account the 'zig-zag' geometry of an aliphatic chain. The crystallographic data shows a difference of about 3.49 Å, which is within a reasonable error margin.

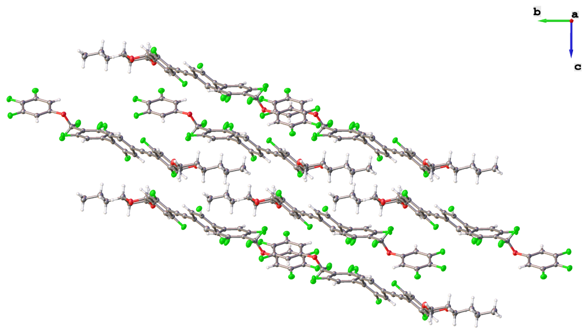
Figure S3: Views of the molecule packing in crystal structures for each homologue along selected crystallographic directions.	
	
Homologue n=1, view along [010]	Homologue n=1, view along [100]
	
Homologue n=2, view along [100]	Homologue n=2, view along [001]



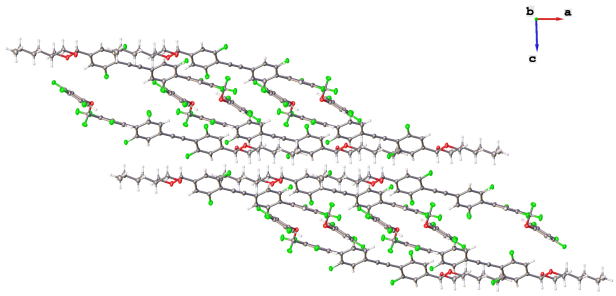
Homologue n=3, view along [100]



Homologue n=3, view along [010]



Homologue n=4, view along [100]



Homologue n=4, view along [010]

Figure S3 summarizes crystal packing for the homologues n=1 to n=4 in selected crystallographic directions. There are no distinct layers formed in homologues n=1,2, which is consistent with the fact, that these homologues predominantly form nematic, non-layered liquid crystalline phases. Conversely, we can see a formation of layers as the alkyl chains get longer for homologues n=3 and n=4, with layer boundaries constituted by the longer stretched aliphatic chains. Molecules within layers are tilted at about 60 degrees with respect to the normal of the layer (which coincides with [001] crystallographic directions). Importantly, each layer contains antiparallelly oriented molecules, cancelling the effects of their dipole moments. There are no strong hydrogen bonds for any of the homologue structures. However, there are interesting π-π stacking interactions to consider, as summarized in Table S7. There are no intermolecular π-π interactions in the crystal structure of homologue n=4.

Table S4: π-π interactions for each homologue. In order to easily distinguish between plane to plane interaction between molecules each molecule has been given a corresponding letter from A to D.

Homologue	Planes	Transformation	Angle	Centroid-centroid distance	Shift distance
1	IA - IIB (IIA-IB)	1-X, 2-Y, 2-Z	17.93	3.827	0.584
	IVC - IVA	-X, -Y, 1-Z	0.00	3.693	1.365
2	IA - IIB (IC-IID)	+X, +Y, +Z	10.54	3.657	1.365
	IVB-IVC	-2+X, +Y, 1+Z	0.96	3.882	0.813
	IB - IIA (IIC-ID)	+X, +Y, +Z	10.18	3.659	0.795

3	IVA - IVB	3-X, -Y, 2-Z	0.00	3.813	1.740
4	-	-	-	-	-

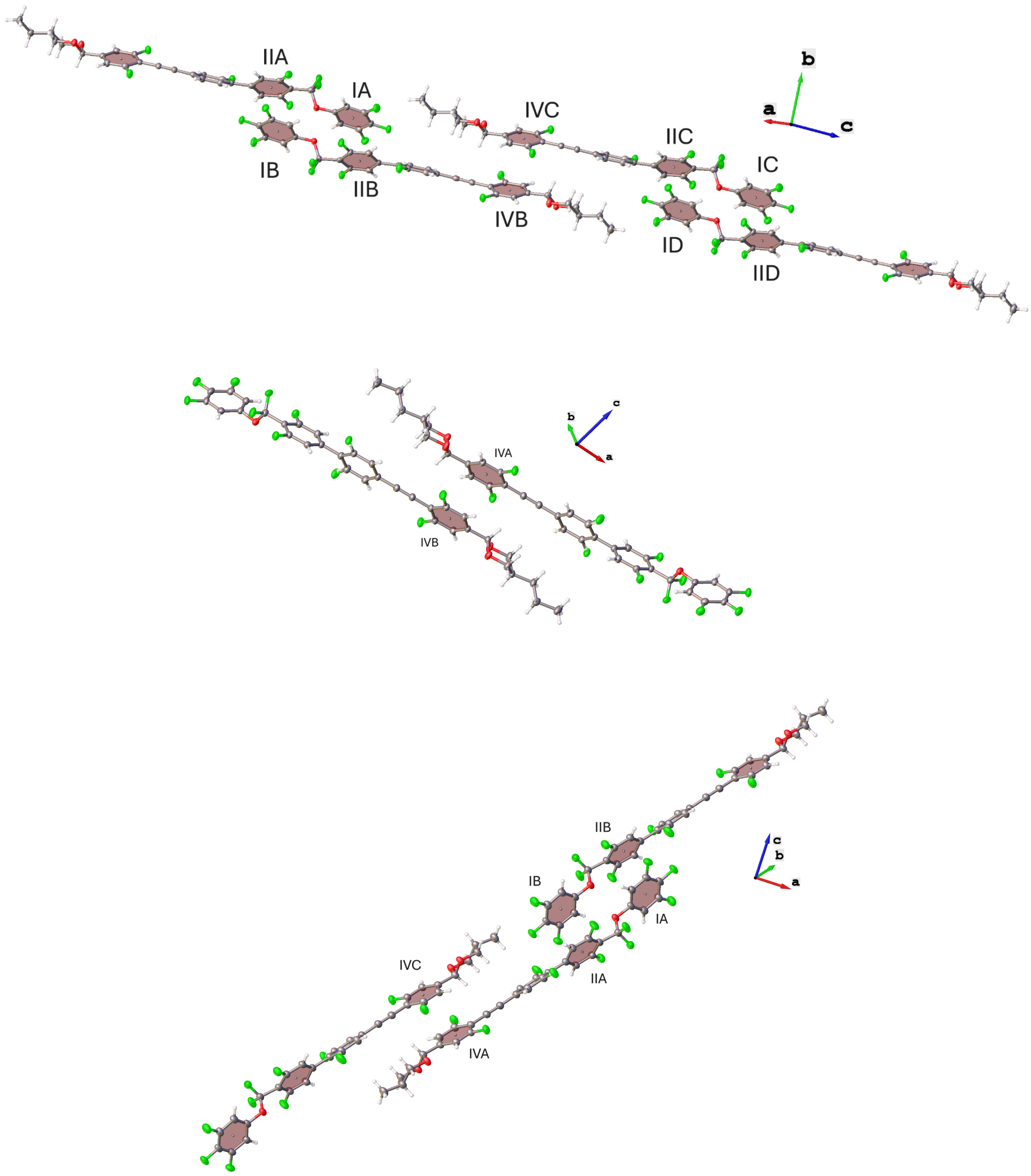
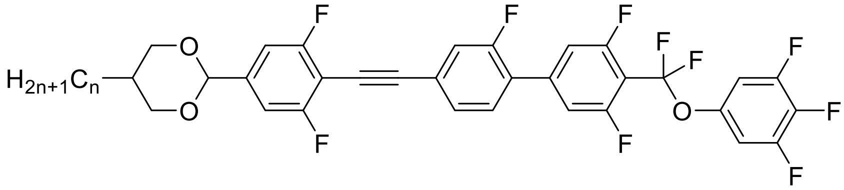


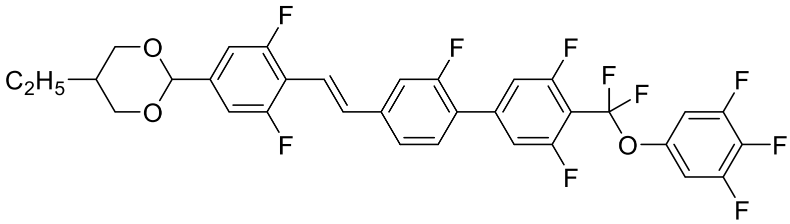
Fig. S4: Illustrations of π-π interactions in homologues n=1, n=2 and n=3 (top to bottom). As the aliphatic chain gets longer but remains aligned with the main molecule axis, it blocks the ability to form π-π interactions between rings I and II. Mean planes calculated from the ring carbon atoms with ring numbers, represented for homologue n=2.

4. Additional results

Table S5. Phase transition temperatures (in °C) and associated thermal effects (in kJ mol^{-1}) of studied compounds – the ndTBEP series and 2dDBEP.



Acronym	n	Phase sequence
1dTBEP	1	Cr 125.2 [25.56] N_{TBF} 138.2[a] N_F 196.2 [0.22] N 254.1 [0.92] Iso
2dTBEP	2	Cr 114.5 [25.91] N_{TBF} 144.7[0.067] N_F 164.3 [0.039] N_X 169.5[a] N 262.7 [0.75] Iso
3dTBEP	3	Cr 103.0 [14.19] SmC_P^H 120.4[a] SmC_F 128.1[a] SmA_F 149.9 [0.031] SmA 151.7 [0.018] N 272.2 [0.99] Iso
4dTBEP	4	Cr 108.5 [25.83] SmC_F 121.7[a] SmA_F 143.1 [0.026] SmA_{AF} 145.9 [0.013] SmA 179.2 [0.059] N 263.8 [0.84] Iso



Acronym	Phase sequence
2dDBEP	Cr1 131.3 [6.67] Cr2 142.3 [15.96] $SmA_{AF\text{-}mod}$ 154[a] SmA 200.0 [0.11] N 267.6 [0.96] Iso

[a] from microscopic observations

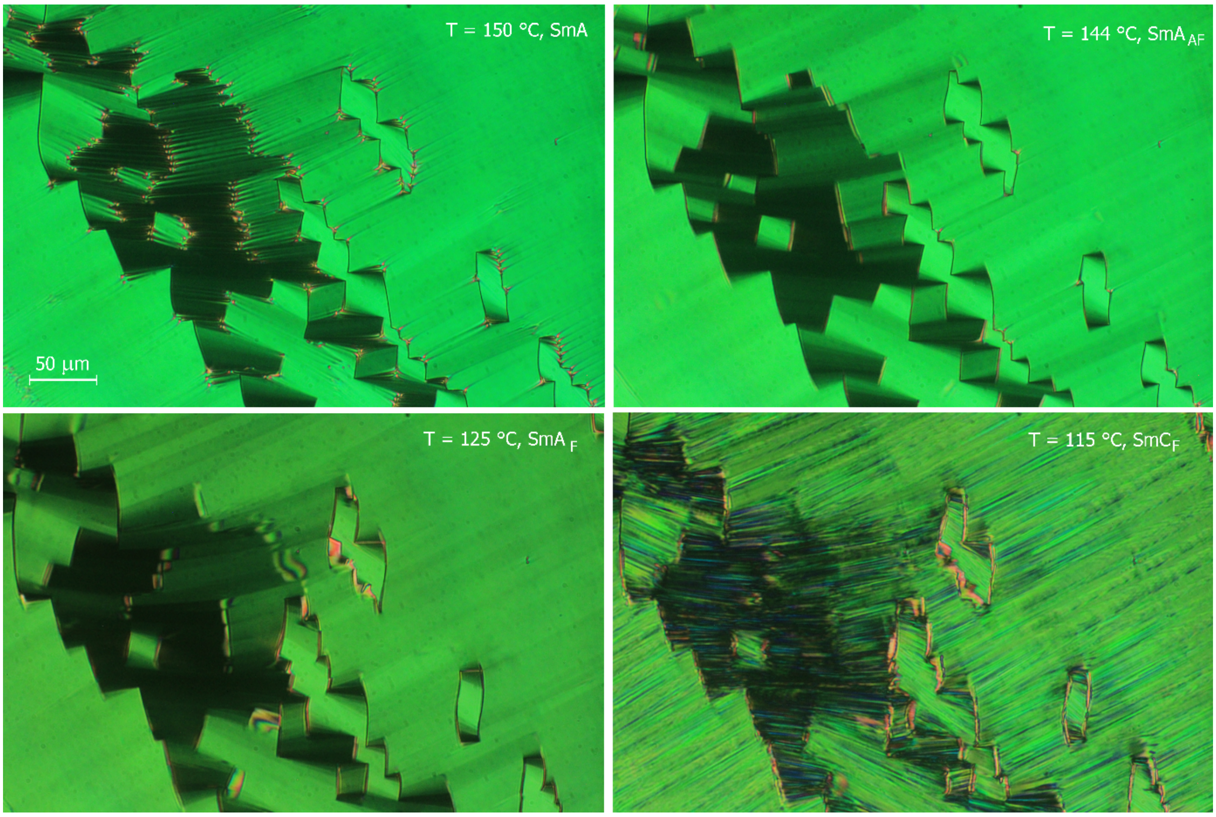


Figure S5. Optical textures of smectic phases formed by 4dTBEP taken in 5-µm-thick cell placed between crossed polarizers.

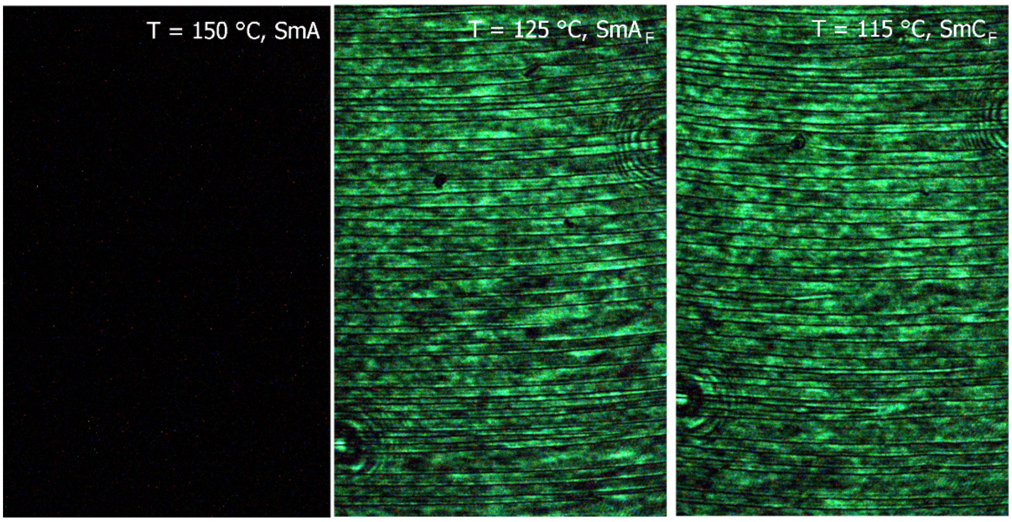


Figure S6. SHG microscopy images taken in smectic phases formed by 4dTBEP compound. Irradiation od the sample with IR light (λ=1064 nm) resulted in emission of green light in case of phases with polar order and thus non-centrosymmetric structure.

Bibliography:

1. Rigaku Oxford Diffraction, *CrysAlisPro* software system (version 1.171.38.46), Rigaku Oxford Diffraction, Oxford, UK, 2019.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, Journal of Applied Crystallography, 2009, 42, 339–341, DOI: 10.1107/S0021889808042726
3. G. M. Sheldrick, Acta Crystallographica Section A: Foundations and Advances, 2015, 71, 3–8, DOI: 10.1107/S2053273314026370.
4. G. M. Sheldrick, Acta Crystallographica Section C: Structural Chemistry, 2015, 71, 3–8, DOI: 10.1107/S2053229614024218.
5. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *Mercury* software, Cambridge Crystallographic Data Centre, Cambridge, UK, 2006.
6. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, Journal of Applied Crystallography, 2008, 41, 466–470, DOI: 10.1107/S0021889807067908
7. F. H. Allen, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor E. Prince, in *International Tables for Crystallography, Volume C: Mathematical, Physical and Chemical Tables*, ed. E. Prince, International Union of Crystallography, Chester, 3rd edn., 2006, vol. C, ch. 9.5, pp. 790-811