Supporting Information

Deuterated Liquid Crystals – design and synthesis of deuterium labelled 4,4″-dialkyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyls using batch and continuous flow systems

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1. Analytical Instrumentation

The purity of synthesised compounds was confirmed by gas chromatography (GC-MS(EI), Agilent 6890 N equipped with a flame ionisation detector GC-FID, a mass selective detector GC-MS(EI) Agilent MSD 5973N) and thin layer chromatography (TLC, aluminium plated, silica gel coated (0.2 mm) with fluorescent indicator 254 nm, Fluka). Nuclear magnetic resonance (NMR) was used to confirm the molecular structures and isotopic purity. All ^{1}H and ^{13}C NMR spectra were recorded on a JNM-ECX500 (JEOL Ltd., Tokyo, Japan) (500 MHz for ^{1}H NMR and 126 MHz for ^{13}C NMR) in $CDCl_3$ as a solvent and TMS as an internal standard (Kanto Chemical Co., Tokyo, Japan). Chemical shifts (δ) are reported in ppm relative to the TMS peak. Phase transition temperatures and enthalpy data were determined by polarizing optical microscopy (POM, OLYMPUS BX51 polarizing microscope (Shinjuku, Tokyo, Japan) equipped with a Linkam hot stage THMS-600 (Linkam Scientific Instruments Ltd., Tadworth, UK) and by differential scanning calorimetry (calorimeter SETARAM DSC 141 (KEP Technologies Group's DNA, Montauban, France), during heating and cooling cycles, the scanning rate was 2 K/min on both heating and cooling cycles under a flow of nitrogen gas.

Photostability was tested on the example of three isotopologues from 2T3 series (non-deuterated molecule 2T3 H, deuterated molecules 2T3-d_4 **72** and 2T3-d_9 **35** using the Asahi LAX-C100 UV lamp (Xe) (Asahi Spectra, Tokyo, Japan). The samples were placed in an aluminium pan on the heating stage and irradiated in the air atmosphere at 77 °C in the nematic phase. The distance between the lamp and the sample was 1 cm, the UV irradiance at the sample position was 80 mW/cm^2 at λ=365nm. UV light intensity was measured using a Digital UV Intensity Meter UIT-201 equipped with a Photodetector UVD-365PD (Ushio Inc., Tokyo, Japan). For each sample the irradiation process was carried out separately (5, 15, 30 and 60 min). The total doses after the given irradiation time were 24 J/cm^2 (5 min), 72 J/cm^2 (15 min), 144 J/cm^2 (30 min) and 288 J/cm^2 (60 min). After the irradiation time, the sample was placed

in the Shimadzu DSC 60 instrument at a rate of 2 K/min under a flow of nitrogen gas (50 mL/min) and phase transition temperatures were detected.

Comparative fragmentation tests of chemical stability were carried out on the example of two molecules (deuterated 2T3-d_9 **35** and non-deuterated analogue 2T3 H) using an Agilent Technologies GC-MS/MS gas chromatograph equipped with Agilent Technologies 7000D GC-MS Triple Quad tandem mass spectrometer MS/MS(EI). The analyses were performed using MRM mode for equimolar samples.

Photodegradation products were detected for symmetric deuterated (**24**; acronym 6T6-d_8) and non-deuterated (6T6 H) molecules. The samples were placed in an aluminium pan on the heating stage and irradiated in the air atmosphere at 110 °C in the nematic phase and irradiated for 5, 15, 30 and 120 minutes, using the OmniCure S2000 UV lamp (Hg) (Excelitas Canada Inc., Mississauga, Canada). The distance between the lamp and the sample was 1 cm, the UV irradiance at the sample position was 374 mW/cm^2 in the range ~300-600 nm. For each sample, the irradiation process was performed separately. Total doses after the irradiation time were 67 J/cm^2 (5 min), 337 J/cm^2 (15 min) 673 J/cm^2 (30 min) and 2693 J/cm^2 (120 min). After UV exposure, the samples were dissolved in the mixture of CH_2Cl_2-THF, and chromatograms were recorded using GC-MS/FID. After the MS spectra analysis, photodegradation products were proposed.

2. Synthetic protocols

2.1. General synthetic procedures

I - General procedure for deuteration in a flow continuous reactor H-Cube Pro (ThalesNano, Budapest, Hungary; heavy water D_2O 99.88 Atom-%D, Armar AG, Dottingen, Switzerland): The substrate dissolved in a suitable solvent was placed in the conical flask. Reaction parameters: catalyst Pd/C(10%), cartridge length 7 cm, flow rate 1 mL/min, temperature 40 °C,

pressure 40 bar. After completion of the reaction, the reaction mixture was concentrated on a rotary evaporator, and the crude product was crystallised or purified as described in the detailed preparation.

II - General procedure for deuteration in a batch reactor (Berghof, Germany): The substrate, catalyst Pd/C(10%) and anhydrous THF were placed in the teflon reactor vessel. The reactor was charged with deuterium gas (Deuter 2.7 Linde (to a pressure of 50 bar) and then the reaction vessel was washed. The operation was repeated. Next, the reactor was refilled with deuterium and the reaction was carried out at the room temperature. When the reaction was finished, the pressure in the reactor was slowly reduced and the vessel was washed twice with an inert gas – argon, and then the reactor was opened. In order to remove catalyst from the reaction mixture, it was filtered through a cylindrical sintered filter funnel. Further purification was performed as described in the detailed preparation.

III - General procedure for the Suzuki-Miyaura reaction: In a four-neck round bottom flask equipped with a mechanical stirrer, a reflux condenser and a thermometer were placed aryl halide, boronic acid (or ester of boronic acid), base and solvents. The mixture was stirred under nitrogen at reflux for 15 min and then, cooled down to 40 ºC. The catalyst $Pd(OAc)_2$ (2% mol) was added and the reaction was heated to reflux again. Reaction progress was monitored by gas chromatography (GC-MS/FID). After completion of the reaction, the mixture was cooled down to room temperature and a 10% solution of hydrochloric acid was added to pH ~ 6. The mixture was extracted with dichloromethane. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. Further purification was performed as described in detail.

IV - General procedure for carrying out the carbonyl protection reaction: In three-neck round-bottom flask equipped with a magnetic stirrer, heating mantle, reflux condenser, temperature probe, Vigreux column, azeotropic condenser and tube with $CaCl_2$, the appropriate aryl-

aliphatic ketone, ethane-1,2-diol (1.1 eq.), anhydrous toluene and *p*TsOH(cat.) were placed. The reaction was carried out under reflux and the water formed was collected. After completion of the reaction, the reaction mixture was extracted with water into toluene. The organic phase was dried with anhydrous $MgSO_4$ and concentrated on a rotary evaporator followed by distillation under reduced pressure.

V – General Ortho-Lithiation-Metalation procedure: In a four-necked round-bottom flask equipped with a mechanical stirrer, a reflux condenser and temperature probe and dropping funnel, the appropriate substrate and anhydrous THF were placed. The mixture was cooled down to −78 °C under nitrogen atmosphere and *n*-BuLi solution (2.5 M in hexane) or *s*-BuLi solution (1.4 in cyclohexane) was added dropwise, keeping the temperature below -70 °C. The mixture was stirred for 2 hours at −78°C. Next, a solution of iodine in THF was added dropwise at −78 °C. After 15 min, the reaction was allowed to reach room temperature and aqueous Na_2SO_3 was added. The mixture was extracted with hexane. The organic layer was washed three times with water, dried over anhydrous $MgSO_4$ and concentrated on a rotary evaporator. The crude product was usually used for the next reaction steps without further purification.

VI – General procedure for the synthesis of arylboronic acids by boronation of Grignard compounds: In a four-neck round-bottom flask equipped with a mechanical stirrer, reflux condenser with a double water jacket, temperature probe and dropping funnel, the magnesium flakes and anhydrous THF were placed under an atmosphere of N_2. A solution of aryl bromide in THF was placed in the dropping funnel and a small amount of was added dropwise to initiate the reaction. If the initiation of the reaction was difficult, a few drops of ethylene bromide or iodine crystal were added, or the mixture was heated with an air heater. After the appearance of a slight turbidity and characteristic bubbles indicating the initiation of the reaction, the remaining amount of aryl bromide was added dropwise, keeping the reaction under gentle boiling throughout. The reaction was carried out under reflux until the magnesium was

completely consumed (usually 5 hours). Then, the reaction was cooled to -78 °C and tripropyl borate was added dropwise keeping the temperature below -70 °C. 15 Min after completion of dropwise addition, the temperature was raised to room temperature and 10% HCl solution was added to pH ~ 6. The reaction mixture was then transferred to a single neck round bottom flask and the THF was concentrated on a rotary evaporator. The precipitated solid was filtered on a Buchner funnel, washed with hexane and filtered off again. Boronic acids cannot be analysed by the GC-MS/FID technique, therefore they were derivatized to cyclic esters for GC-MS/FID analyses were then performed. Derivatization was carried out with 1,3-propanediol in toluene by heating the reaction tube for 5 min at 110 °C (Figure S1).

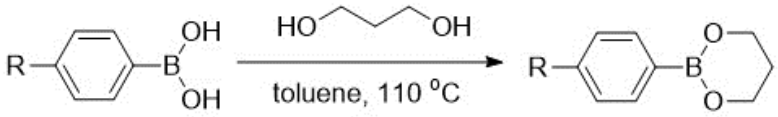


Figure S1. Formation of cyclic boronic esters from arylboronic acids.

2.2. Synthetic procedures for LCs.

4'-(2-^{2}H)Ethynyl-2,3-difluoro-[1,1']biphenyl 2: Obtained in part according to general procedure **V** from 4'-ethynyl-2,3-difluoro-[1,1']biphenyl **1** (6.5 g; 30.0 mmol), *n*-BuLi (15.8 mL; 39.0 mmol) and anhydrous THF (100 mL). After 1 hour the mixture was heated to 0 °C and the solution of D_2O (2.7 mL; 0.2 mol) in THF (10 mL) was added dropwise. Next, the mixture was heated to room temperature. The mixture was filtrated under vacuum through a filter plate with SiO_2 layer, washed with THF and concentrated on a rotary evaporator. The crude product was used to the next stage. Colourless oil. Yield 99% (6.4 g; 29.8 mmol). MS(EI) m/z: 215 (M^+); 95; 108; 94.

4'-(1,1,2,2,2-^{2}H$_5$)Ethyl-2,3-difluoro-[1,1']biphenyl 3: Prepared according to general procedure **II** from 4'-(2-^{2}H)ethynyl-2,3-difluoro-[1,1']biphenyl **2** (6.4 g; 29.8 mmol) and Pd/C (10%) (0.3 g). The crude product was distilled under reduced pressure using Kugelrohr (95 °C;

0.4 mmHg). Colourless oil. Yield 81% (5.4 g; 24.2 mmol). MS(EI) m/z: 223 (M^+); 205; 185; 171; 152.

4'-(1,1,2,2,2-$^2H_5$)Ethyl-2,3-difluoro-4-iodo-[1,1']biphenyl 5: Prepared according to general procedure **V** from 4'-(1,1,2,2,2-$^2H_5$)ethyl-2,3-difluoro-[1,1']biphenyl **3** (4.5 g; 20.0 mmol), *n*-BuLi (9.7 mL; 24.0 mmol), I_2 (6.15 g; 24.0 mmol). The crude product was transported to the next step without further purification. Yellow oil. Yield 78% (6.5 g; 18.6 mmol). MS(EI) m/z: 349 (M^+); 331; 203; 165; 127.

4-(1,1,2,2,2-$^2H_5$)Ethyl-2′,3′-difluoro-4″-(pent-1-yn-1-yl)-[1,1′:4′,1″]terphenyl 9 (2TA3-*d*$_5$): Obtained according to general procedure **III** from 4'-(1,1,2,2,2-$^2H_5$)ethyl-2,3-difluoro-4-iodo-[1,1']biphenyl **5** (6.0 g; 17.2 mmol), [4-(pent-1-yn-1-yl)phenyl]boronic acid **8a** (3.4 g; 18.0 mmol), K_2CO_3 (5.9 g; 43.0 mmol). The reaction mixture was stirred at 55 °C for 5 h. The crude product was purified on chromatography column (SiO_2/hexane), concentrated and crystalised from the mixture of EtOH-acetone. White solid. Yield 77% (4.8 g; 13.2 mmol). MS(EI) *m/z*: 365 (M^+); 350; 336; 318; 301; 166.

4-(1,1,2,2,2-$^2H_5$)Ethyl-2′,3′-difluoro-4″-(hex-1-yn-1-yl)-[1,1′:4′,1″]terphenyl 10 (2TA4-*d*$_5$): Obtained according to general procedure **III** from 4'-(1,1,2,2,2-$^2H_5$)ethyl-2,3-difluoro-4-iodo-[1,1']biphenyl **5** (3.5 g; 10.0 mmol), [4-(hex-1-yn-1-yl)phenyl]boronic acid **8b** (2.1 g; 10.5 mmol), K_2CO_3 (3.5 g; 25.0 mmol). The reaction mixture was stirred at 55 °C for 5 h. The crude product was purified on chromatography column (SiO_2/hexane), concentrated and crystalised from EtOH. White solid. Yield 67% (2.6 g; 6.7 mmol). MS(EI) *m/z*: 379 (M^+); 364; 350; 336; 318; 301; 281; 236; 173, 159.

2′,3′-Difluoro-4-(1,1,2,2-$^2H_4$)pentyl-4″-(1,1,2,2-$^2H_4$)propyl-[1,1′:4′,1″]terphenyl 18 (3T5-*d*$_8$): Obtained according to procedure **I** from 2′,3′-difluoro-4-(pent-1-yn-1-yl)-4″-(prop-1-yn-1-yl)-[1,1′:4′,1″]terphenyl **11** (1.6 g; 4.3 mmol). Solvents MeOH (30 mL), THF (45 mL),

concentration of the reaction solution c = 0.57 mol/dm^3. The crude product was crystalised from EtOH. White solid. Yield 81% (1.4 g; 3.5 mmol). MS(EI) *m*/*z*: 386 (M^+); 355; 327; 296; 274; 259; 203; 148. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.86-1.00 (m, 6H); 1.31-1.41 (m, 4H); 1.58-1.70 (m, 0,18H); 2.59-2.68 (m, 0.32H); 7.21-7.25 (m, 2H); 7.25-7.31 (m, 4H); 7.47-7.53 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 13.7; 14.2; 22.6; 31.4; 124.7; 128.8; 129.6; 132.1 (d); 142.9; 143.1; 147.3; 147.4; 149.8; 149.9; deuterium content (%D): 92% (-**CD_2**-CD_2-CH_3; -**CD_2**-CD_2-C_3H_7); 95% (-CD_2-**CD_2**-CH_3; -CD_2-**CD_2**-C_3H_7).

2′,3′-Difluoro-4-(1,1,2,2-$^2H_4$)hexyl-4″-(1,1,2,2-$^2H_4$)propyl-[1,1′:4′,1″]terphenyl 19 (3T6-*d*$_8$): Obtained according to procedure **I** from 2′,3′-difluoro-4-(hex-1-yn-1-yl)-4″-(prop-1-yn-1-yl)-[1,1′:4′,1″]terphenyl **12** (1.5 g; 4.3 mmol). Solvents MeOH (30 mL), THF (15 mL), concentration of the reaction solution c = 0.096 mol/dm^3. The crude product was crystalised from EtOH. White solid. Yield 81% (1.4 g; 3.4 mmol). MS(EI) *m*/*z*: 400 (M^+); 369; 327; 296; 274; 203; 148. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.86-0.92 (m, 6H); 1.21-1.37 (m, 6H); 1.59-1.69 (m, 0.21H); 2.56-2.64 (m, 0,15H); 2.66-2.69 (m, 0.12H); 7.22-7.25 (m, 2H); 7.25-7.32 (m, 4H); 7.35-7.47 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 11.4; 14.1; 22.6; 23.2; 31.8; 124.6 (dd); 126.9; 127.0; 127.6; 127.8; 130.4; 133.8; 139.2; 142.9; 143.7; 149.5; 150.2; deuterium content (%D): 93% (-**CD_2**-CD_2-CH_3); 94% (-**CD_2**-CD_2-C_4H_9); 95% (-CD_2-**CD_2**-CH_3; -CD_2-**CD_2**-C_4H_9).

4-(1,1,2,2-$^2H_4$)Butyl-2′,3′-difluoro-4″-(1,1,2,2-$^2H_4$)pentyl-[1,1′:4′,1″]terphenyl 20 (4T5-*d*$_8$): Obtained according to procedure **I** from 4-(but-1-yn-1-yl)-2′,3′-difluoro-4″-(pent-1-yn-1-yl)-[1,1′:4′,1″]terphenyl **13** (2.2 g; 5.7 mmol). Solvents MeOH (40 mL), THF (45 mL), concentration of the reaction solution c = 0.067 mol/dm^3. The crude product was crystalised from EtOH. White solid. Yield 81% (1.9 g; 4.8 mmol). MS(EI) *m*/*z*: 400 (M^+); 341; 296; 273; 203. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.83-0.92 (m, 6H); 1.20-1.33 (m, 4H); 1.59-1.70 (m, 0.23H); 2.56-2.64 (m, 0.24H); 2.65-2.69 (m, 0.12H); 7.21-7.25 (m, 2H); 7.25-7.36 (m, 4H);

7.47-7.53 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 13.7; 14.0; 22.6; 23.2; 31.3; 124.3 (dd); 126.9; 126.8; 127.6; 127.6; 127.7; 130.4; 133.2; 133.9; 139.2; 140.3; 142.9; 143.7; 149.5; 150.2; deuterium content (%D): 85% (-**CD$_2$**-CD_2-C_2H_5); 88% (-**CD$_2$**-CD_2-C_3H_7); 94% (-CD_2-**CD$_2$**-C_2H_5; -CD_2-**CD$_2$**-C_3H_7).

4-(1,1,2,2-$^2H_4$)Butyl-2′,3′-difluoro-4″-(1,1,2,2-$^2H_4$)-hexyl-[1,1′:4′,1″]terphenyl 21 (4T6-*d$_8$*): Obtained according to procedure **I** from 4-(but-1-yn-1-yl)-2′,3′-difluoro-4″-(hex-1-yn-1-yl)-[1,1′:4′,1″]terphenyl **14** (1.0 g; 2.6 mmol). Solvents MeOH (20 mL), THF (30 mL), concentration of the reaction solution c = 0.052 mol/dm^3. The crude product was crystalised from EtOH. White solid. Yield 63% (0.7 g; 1.6 mmol). MS(EI) *m*/*z*: 414 (M^+); 369; 341; 296; 274; 203. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.83-0.94 (m, 6H); 1.21-1.41 (m, 8H); 1.58-1.69 (m, 0.23H); 2.60-2. 67 (m, 0.37H); 7.19-7.36 (m, 2H); 7.38-7.53 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 13.7; 14.0; 22.6; 23.2; 29.3; 31.8; 124.3 (dd); 126.5; 126.8; 127.7; 127.8; 127.7; 130.2; 133.0; 134.0; 139.2; 140.3; 143.0; 143.7; 149.5; 150.2; deuterium content (%D): 91% (-**CD$_2$**-CD_2-C_2H_5; -**CD$_2$**-CD_2-C_4H_9); 94% (-CD_2-**CD$_2$**-C_2H_5; -CD_2-**CD$_2$**-C_4H_9).

2′,3′-Difluoro-4,4″-di(1,1,2,2-$^2H_4$)pentyl-[1,1′:4′,1″]terphenyl 22 (5T5-*d$_8$*): Obtained according to procedure **I** from 2′,3′-difluoro-4,4″-di(pent-1-yn-1-yl)-[1,1′:4′,1″]terphenyl **15** (4.6 g; 11.6 mmol). Solvents MeOH (50 mL), THF (40 mL), concentration of the reaction solution c = 0.12 mol/dm^3. Flow rate 1.5 mL/min, pressure 30 bar. The crude product was crystalised from EtOH. White solid. Yield 83% (4.0 g; 9.7 mmol). MS(EI) *m*/*z*: 414 (M^+); 355; 296; 277; 203; 148. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.85-0.98 (m, 6H); 1.28-1.42 (m, 8H); 1.58-1.69 (m, 0.8H); 2.60-2.67 (m, 1H); 7.19-7.31 (m, 6H); 7.45-7.53 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 14.1; 22.6; 31.4; 124.6; 124.6; 124.7; 128.8; 128.8; 129.5; 132.1; 138.8; 143.1; 147.2; 147.4; 149.8; 149.9; deuterium content (%D): 75% (-**CD$_2$**-CD_2-C_3H_7); 80% (-CD_2-**CD$_2$**-C_3H_7).

2′,3′-Difluoro-4-(1,1,2,2-$^2H_4$)hexyl-4″-(1,1,2,2-$^2H_4$)pentyl-[1,1′:4′,1″]terphenyl 23 (5T6-*d*$_8$): Obtained according to procedure **I** from 2′,3′-difluoro-4-(hex-1-yn-1-yl)-4″-(pent-1-yn-1-yl)-[1,1′:4′,1″]terphenyl **16** (3.7 g; 9.0 mmol). Solvents MeOH (70 mL), THF (35 mL), concentration of the reaction solution c = 0.085 mol/dm^3. The crude product was crystalised from EtOH. White solid. Yield 83% (3.1 g; 7.5 mmol). MS(EI) *m*/*z*: 428 (M^+); 355; 296; 273; 203. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.83-0.96 (m, 6H); 1.20-1.37 (m, 10H); 1.59-1.69 (m, 0.22H); 2.56-2.64 (m, 0.4H); 2.66-2.69 (m, 0.3H); 7.21-7.25 (m, 2H); 7.25-7.52 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 14.1; 22.6; 22.6; 22.7; 28.9; 31.3; 31.8; 124.4 (dd); 126.5; 126.9; 127.6; 127.7; 130.4; 133.8; 139.2; 142.9; 143.7; 149.5; 150.2; deuterium content (%D): 80% (-**CD$_2$**-CD_2-C_3H_7); 85% (-**CD$_2$**-CD_2-C_4H_9); 94% (-CD_2-**CD$_2$**-C_3H_7; -CD_2-**CD$_2$**-C_4H_9).

2′,3′-Difluoro-4,4″-di(1,1,2,2-$^2H_4$)hexyl-[1,1′:4′,1″]terphenyl 24 (6T6-*d*$_8$): Obtained according to procedure **I** from 2′,3′-difluoro-4,4″-di(hex-1-yn-1-yl)-[1,1′:4′,1″]terphenyl **17** (2.5 g; 5.7 mmol). Solvents MeOH (35 mL), THF (30 mL), concentration of the reaction solution c = 0.088 mol/dm^3. The crude product was crystalised from EtOH. White solid. Yield 87% (2.2 g; 5.0 mmol). MS(EI) *m*/*z*: 442 (M^+); 369; 296; 273; 203. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.90 (t, 6H); 1.26-1.34 (m, 12 H); 1.58-1.67 (m, 0.28H); 2.60-2.67 (m, 0.36H); 7.20-7.34 (m, 6H); 7.45-7.56 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 14.2; 22.7; 28.9; 31.8; 124.7; 128.7; 128.8; 129.6; 132.1; 143.1; 147.5; 147.7; 149.5; 149.7; 149.9; deuterium content (%D): 91%(-**CD$_2$**-CD_2-C_4H_9); 93%(-CD_2-**CD$_2$**-C_4H_9).

4-(1,1,2,2,2-$^2H_5$)Ethyl-2′,3′-difluoro-4″-(1,1,2,2-$^2H_4$)pentyl-[1,1′:4′,1″]terphenyl 25 (2T5-*d*$_9$): Obtained according to procedure **I** from 4-(1,1,2,2,2-$^2H_5$)ethyl-2′,3′-difluoro-4″-(pent-1-yn-1-yl)-[1,1′:4′,1″]terphenyl **9** (4.6 g; 12.6 mmol). Solvents MeOH (30 mL), THF (50 mL), concentration of the reaction solution c = 0.16 mol/dm^3. Flow rate 1.5 mL/min, pressure 30 bar. The crude product was crystalised from EtOH. White solid. Yield 72% (3.4 g; 9.0 mmol). MS(EI) *m*/*z*: 373 (M^+); 314; 296; 279; 203; 148. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.83-

0.92 (m, 3H); 1.18-1.25 (m, 4H); 1.27-1.29 (m, 0.14H); 1.64-1.71 (m, 0.21H); 2.60-2.64 (m, 0.31H); 2.65-2.68 (m, 0.12H); 7.18-7.36 (m, 6H); 7.47-7.53 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 14.0; 22.6; 31.3; 124.3 (dd); 126.9; 127.0; 127.6; 127.7; 128.1; 130.2; 130.4; 134.8; 139.2; 139.5; 142.9; 143.7; 149.5; 150.1; deuterium content (%D): 95% (-CD_2-**CD_3**); 95% (-**CD_2**-CD_3); 89% (-CD_2-**CD_2**-C_3H_7); 86% (-**CD_2**-CD_2-C_3H_7).

4-(1,1,2,2,2-$^2H_5$)Ethyl-2′,3′-difluoro-4″-(1,1,2,2-$^2H_4$)hexyl-[1,1′:4′,1″]terphenyl 26 (2T6-*d_9*): Obtained according to procedure **I** from 4-(1,1,2,2,2-$^2H_5$)ethyl-2′,3′-difluoro-4″-(hex-1-yn-1-yl)-[1,1′:4′,1″]terphenyl **10** (2.4 g; 6.3 mmol). Solvents MeOH (40 mL), THF (25 mL), concentration of the reaction solution c = 0,1 mol/dm^3. Flow rate 2.0 mL/min, pressure 30 bar. The crude product was crystalised from EtOH. White solid. Yield 92% (2.1 g; 5.5 mmol). MS(EI) *m*/*z*: 387 (M^+); 314; 279; 203; 148. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.83-0.92 (m, 3H); 1.22-1.26 (m, 0.13H); 1.28-1.38 (m, 6H); 1.63-1.68 (m, 0.17H); 2.62-2.71 (m, 0.45H); 7.18-7.25 (m, 2H); 7.25-7.36 (m, 4H); 7.47-7.53 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 14.0; 22.6; 29.3; 31.8; 124.4 (dd); 126.5; 127.0; 127.7; 127.8; 128.1; 128.2; 130.2; 130.4; 134.0; 139.3; 139.5; 143.0; 143.7; 149.5; 150.2; deuterium content (%D): 95% (-CD_2-**CD_3**); 89% (-**CD_2**-CD_3; -**CD_2**-CD_2-C_4H_9); 91% (-CD_2-**CD_2**-C_4H_9).

1-Chloro-4-(1,1,2,2-$^2H_4$)propylbenzene 27: Obtained according to procedure **II** from 1-chloro-4-(prop-1-yn-1-yl)benzene (9.5 g; 63.0 mmol), Pd/C (10%) (0.3 g) and THF (30 mL). The crude product was distilled under reduced pressure (95 °C; 11.0 mmHg). Yield 99.8% (9.9 g; 62.8 mmol). MS(EI) *m*/*z*: 158 (M^+); 127; 91.

4-(1,1,2,2-$^2H_4$)Butyl-1-chlorobenzene 28: Obtained according to procedure **II** from 4-(but-1-yn-1-yl)-1-chlorobenzene (25.0 g; 0.2 mol), Pd/C (10%) (0.5 g) and THF (30 mL). The crude product was distilled under reduced pressure using Kugelrohr (130 °C; 40.0 mmHg). Yield 93% (24.2 g; 0.1 mol). MS(EI) *m*/*z*: 172 (M^+); 127; 106; 93.

2,3-Difluoro-4′-(1,1,2,2-$^2H_4$)propyl-[1,1′]biphenyl 30: Obtained according to procedure **III** from 1-chloro-4-(1,1,2,2-$^2H_4$)propylbenzene **27** (3.0 g; 18.9 mmol), 2-(2,3-difluorophenyl)-1,3,2-dioksaborinane **29** (4.1 g; 21.0 mmol), $K_3PO_4x3H_2O$ (17.6 g; 66.0 mmol), THF (250 mL). After 30 min of degassing the reaction at 66 °C, it was cooled to 40 ° C and ligand S-Phos (0.16 g) and catalyst $Pd(OAc)_2$ (0.13 g) were added. The reaction was then stirred at 59 °C for 6 days. The crude product was purified on chromatography column (SiO_2/CH_2Cl_2), concentrated and distilled under reduced pressure (112 °C; 1.3 mmHg). Yield 59% (2.7 g; 11.2 mmol). MS(EI) *m*/*z*: 236 (M^+); 205; 185.

4′-(1,1,2,2-$^2H_4$)Butyl-2,3-difluoro-[1,1′]biphenyl 31: Obtained according to procedure **III** from 4-(1,1,2,2-$^2H_4$)butyl-1-chlorobenzene **28** (8.0 g; 46.5 mmol), 2-(2,3-difluorofenylo)-1,3,2-dioksaborinane **29** (10.1 g; 51.0 mmol), $K_3PO_4x3H_2O$ (43.3 g; 0.2 mol), THF (250 mL). After 30 min of degassing the reaction at 66 °C, it was cooled to 40 °C and ligand cataCxium (0.16 g) and catalyst $Pd(OAc)_2$ (0.1 g) were added The reaction was then stirred at 59 °C for 2 days. The crude product was purified on chromatography column (SiO_2/CH_2Cl_2), concentrated and distilled under reduced pressure (100 °C; 1.0 mmHg). Yield 67% (3.6 g; 14,4 mmol). MS(EI) *m*/*z*: 250 (M^+); 205; 185.

2,3-Difluoro-4-iodo-4′-(1,1,2,2-$^2H_4$)propyl-[1,1′]biphenyl 32: Obtained according to procedure **V** from 2,3-difluoro-4′-(1,1,2,2-$^2H_4$)propyl-[1,1′]biphenyl **30** (2.7 g; 11.0 mmol), n-BuLi (5.4 mL; 13.0 mmol), I_2 (3.3 g; 13.0 mmol). The crude product was used for the next reaction steps without further purification. Yellow oil. Yield 88% (3.5 g; 9.7 mmol). MS(EI) *m*/*z*: 362 (M^+); 331, 203.

4′-(1,1,2,2-$^2H_4$)Butyl-2,3-difluoro-4-iodo-[1,1′]biphenyl 33: Obtained according to procedure **V** from 4′-(1,1,2,2-$^2H_4$)butyl-2,3-difluoro-[1,1′]biphenyl **31** (3.6 g, 14.0 mmol), n-BuLi (6.8 mL; 17.0 mmol), I_2 (4.3 g; 17.0 mmol). The crude product was used for the next

reaction steps without further purification. Yellow oil. Yield 94% (4.9 g; 13.2 mmol). MS(EI) *m*/*z*: 376 (M^+); 331, 203; 185; 127.

(4-(1,1,2,2-$^2H_4$)Propylphenyl)boronic acid 34: Obtained according to the modified procedure **VI** included in the description below. In a reaction flask Mg* (70 mL, c = 2,5 g/100 mL in THF, Sigma Aldrich), $BrCH_2CH_2Br$ (1.05 g, 10% mol), *i*PrMgCl•LiCl (9.3 mL, c = 1.2 M, 20% mol), THF (50 mL) were placed and heated at 65 °C for 1 h. Next, a solution of 1-chloro-4-(1,1,2,2-$^2H_4$)propylbenzene **27** (8.92 g; 56.0 mmol) in 50 mL THF was added dropwise and heating was continued for 5 h. At this time, the reaction mixture was cooled to -78 °C and $B(OPr)_3$ was added dropwise (13.5 cm^3; 61.6 mmol). The next step was as in procedure **VI**. White solid. Yield 81% (7.6 g; 45.6 mmol). MS(EI) for ester of boronic acid obtained according to Figure S1: *m*/*z*: 208 (M^+); 177; 163; 119; 105; 92.

4-(1,1,2,2,2-$^2H_5$)Ethyl-2′,3′-difluoro-4″-(1,1,2,2-$^2H_4$)propyl-[1,1′:4′,1″]terphenyl 35 (2T3-*d*$_9$): Obtained according to procedure **III** from 4′-(1,1,2,2,2-$^2H_5$)ethyl-2,3-difluoro-4-iodo-[1,1′]biphenyl **5** (3.0 g; 8.6 mmol), 4-(1,1,2,2-$^2H_4$)propylphenyl)boronic acid **34** (1.5 g; 9.0 mmol), K_2CO_3 (3.0 g; 25.0 mmol). The reaction was stirred at 59 °C for 2 h. The crude product was purified on chromatography column (SiO_2/hexane), concentrated and crystallized from the mixture of EtOH-acetone. White solid. Yield 68% (2.0 g; 5.8 mmol). MS(EI) *m*/*z*: 345 (M^+); 328; 314; 296; 279; 259; 203; 148. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.98 (s, 3H); 1.24-1.26 (m, 0.14H); 1.64-1.71 (m, 0.19H); 2.61-2.64 (m, 0.31H); 2.65-2.68 (m, 0.11H); 7.18-7.36 (m, 4H); 7.47-7.56 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 13.7; 124.7; 128.3; 128.7; 128.8; 128.8; 128.9; 129.6; 129.7; 132.1; 142.9; 144.4; 147.5; 147.7; 149.5; 149.6; deuterium content (%D): 95% (-CD_2-**CD_3**); 96% (-**CD_2**-CD_3); 90% (-CD_2-**CD_2**-CH_3); 84% (-**CD_2**-CD_2-CH_3).

2′,3′-Difluoro-4,4″-di(1,1,2,2-$^2H_4$)propyl-[1,1′:4′,1″]terphenyl 36 (3T3-*d*$_8$): Obtained according to procedure **III** from 2,3-difluoro-4-iodo-4′-(1,1,2,2-$^2H_4$)propyl-[1,1′]biphenyl **32**

(3.0 g; 8.2 mmol), (4-(1,1,2,2-$^{2}H_4$)propylphenyl)boronic acid **34** (1.5 g; 8.7 mmol), K_2CO_3 (2.8 g; 20.5 mmol). The reaction was stirred at 59 °C for 2 h. The crude product was purified on chromatography column (SiO_2/hexane), concentrated and crystallized from EtOH. White solid. Yield 54% (1.9 g; 5.2 mmol). MS(EI) *m*/*z*: 358 (M^+); 327; 296; 273; 259; 203; 148. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.90 (s, 6H); 1.59-1.69 (m, 0.65H); 2.59-2.67 (m, 0.94H); 7.18-7.31 (m, 6H); 7.46-7.53 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 11.4; 124.0; 124.8; 127.0; 127.8; 127.9; 130.2; 134.0; 139.3; 143.0; 143.7; 149.5; 150.1; deuterium content (%D): 77% (-**CD_2**-CD_2-CH_3); 84% (-CD_2-**CD_2**-CH_3).

4-(1,1,2,2-$^{2}H_4$)Butyl-2′,3′-difluoro-4″-(1,1,2,2-$^{2}H_4$)propyl-[1,1′:4′,1″]terphenyl 37 (3T4-*d_8*): Obtained according to procedure **III** from 4′-(1,1,2,2-$^{2}H_4$)butyl-2,3-difluoro-4-iodo-[1,1′]biphenyl **33** (3.4 g; 9.0 mmol), 4-(1,1,2,2-$^{2}H_4$)propylphenyl)boronic acid **34** (1.5 g; 9.4 mmol), K_2CO_3 (3.1 g; 22.5 mmol). The reaction was stirred at 59 °C for 2 h. The crude product was purified on chromatography column (SiO_2/hexane), concentrated and crystallized from EtOH. White solid. Yield 54% (1.8 g; 4.9 mmol). MS(EI) *m*/*z*: 372 (M^+); 241; 327; 296; 273; 203; 148. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.86-0.91 (m, 6H); 1.26-1.32 (m, 2H); 1.58-1.69 (m, 0.21H); 2.56-2.63 (m, 0.15H); 2.66-2.70 (m, 0.14H); 7.21-7.25 (m, 2H); 7.26-7.34 (m, 4H); 7.46-7.54 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 11.4; 13.7; 23.2; 124.4; 126.8; 127.0; 127.6; 127.7; 127.8; 130.3; 132.9; 134.0; 139.3; 140.3; 143.0; 143.6; 149.5; 150.2; deuterium content (%D): 92% (-**CD_2**-CD_2-CH_3); 93% (-**CD_2**-CD_2-C_2H_5); 94% (-CD_2-**CD_2**-CH_3; -CD_2-**CD_2**-C_2H_5).

1-(2′,3′-Difluoro-[1,1′]biphenyl-4-yl)etanone 42: Obtained according to procedure **III** from 1-(4-bromophenyl)ethenone **38** (10.0 g; 50.0 mmol), 2-(2,3-difluorophenyl)-1,3,2-dioksaborinane **29** (10.9 g; 55.0 mmol) and K_2CO_3 (20.7 g; 0.15 mol). Crystallized from EtOH. White solid. Yield 87% (10.1 g; 90.5 mmol). MS(EI) *m*/*z*: 232 (M^+); 217; 188; 169; 143; 94.

1-(2′,3′-Difluoro-[1,1′]biphenyl-4-yl)propan-1-one 43: Obtained according to procedure **III** from 1-(4-bromophenyl)propan-1-one **39** (20.0 g; 94.0 mmol), 2-(2,3-difluorophenyl)-1,3,2-dioksaborinane **29** (19.5 g; 0.1 mol) and K_2CO_3 (38.9 g; 0.3 mol). Crystallized from EtOH. White solid. Yield 84% (20.0 g; 81.3 mmol). MS(EI) *m*/*z*: 246 (M^+); 217; 188; 169; 143; 108; 94.

1-(2′,3′-Difluoro-[1,1′]biphenyl-4-yl)butan-1-one 44: Obtained according to procedure **III** from 1-(4-bromophenyl)butan-1-one **40** (20.0 g; 88.0 mmol), 2-(2,3-difluorophenyl)-1,3,2-dioksaborinane **29** (26.0 g; 0.13 mol) and K_2CO_3 (36.4 g, 0.26 mol). Crystallized from EtOH. White solid. Yield 83% (19.8 g; 76.2 mmol). MS(EI) *m*/*z*: 260 (M^+); 232; 217; 188; 169; 143; 94.

1-(2′,3′-Difluoro-[1,1′]biphenyl-4-yl)pentan-1-one 45: Obtained according to procedure **III** from 1-(4-bromophenyl)pentan-1-one **41** (30.0 g; 0.13 mol), 2-(2,3-difluorophenyl)-1,3,2-dioksaborinane **29** (26.0 g; 0.13 mol) and K_2CO_3 (51.8 g; 0.4 mol). Crystallized from EtOH. White solid. Yield 73% (24.8 g; 90.5 mmol). MS(EI) *m*/*z*: 274 (M^+); 245; 232; 217; 188; 169; 143; 94.

4′-(1,1-$^2H_2$)Ethyl-2,3-difluoro-[1,1′]biphenyl 46: Obtained according to procedure **I** from 1-(2′,3′-difluoro-[1,1′]biphenyl-4-yl)etanone **42** (10.0 g; 43.0 mmol). Solvents MeOH (150 mL), THF (140 mL), concentration of the reaction solution c = 0.15 mol/dm^3. Flow rate 1.5 mL/min, p = 30 bar, 50 °C. The crude product was distilled under reduced pressure using Kugelrohr (80 °C; 0.1 mmHg). Yield 97% (9.1 g; 41.6 mmol). MS(EI) *m*/*z*: 219 (M^+); 204; 184; 170; 151.

2,3-Difluoro-4′-(1,1-$^2H_2$)propyl-[1,1′]biphenyl 47: Obtained according to procedure **I** from 1-(2′,3′-difluoro-[1,1′]biphenyl-4-yl)propan-1-one **43** (9.6 g; 39.0 mmol). Solvents MeOH (190 mL), THF (140 mL), concentration of the reaction solution c = 0.11 mol/dm^3. Flow rate 1.0 mL/min, p = 30 bar, 50 °C. The crude product was distilled under reduced pressure using

Kugelrohr (88 °C; 0.1 mmHg). Yield 98% (8.9 g; 38.1 mmol). MS(EI) *m*/*z*: 233 (M^+); 204; 184; 170; 151.

4′-(1,1-$^2H_2$)Butyl-2,3-difluoro-[1,1′]biphenyl 48: Obtained according to procedure **I** from 1-(2′,3′-difluoro-[1,1′]biphenyl-4-yl)butan-1-one **44** (19.0 g; 70.0 mmol). Solvents MeOH (330 mL), THF (225 mL), concentration of the reaction solution c = 0.13 mol/dm^3. Flow rate 1.0 mL/min, p = 30 bar, 50 °C. The crude product was distilled under reduced pressure using Kugelrohr (103 °C; 0.1 mmHg). Yield 99% (17.2 g; 69.6 mmol). MS(EI) *m*/*z*: 247 (M^+); 204; 184; 151.

2,3-Difluoro-4′-(1,1-$^2H_2$)pentyl-[1,1′]biphenyl 49: Obtained according to procedure **II** from 1-(2′,3′-difluoro-[1,1′]biphenyl-4-yl)pentan-1-one **45** (15.5 g; 56.6 mmol). Solvent THF, p = 50 bar, 25 °C, concentration of the reaction solution c = 0.14 mol/dm^3. The reaction was carried out for 8 hours. The crude product was distilled under reduced pressure using Kugelrohr (140 °C; 0.5 mmHg). Yield 93% (13.8 g; 52.8 mmol). MS(EI) *m*/*z*: 262 (M^+); 217; 204; 184; 151.

4′-(1,1-$^2H_2$)Ethyl-2,3-difluoro-4-iodo-[1,1′]biphenyl 50: Obtained according to procedure **V** 4′-(1,1-$^2H_2$)ethyl-2,3-difluoro-[1,1′]biphenyl **46** (9.1 g; 41.6 mmol), n-BuLi (20.0 mL; 50.0 mmol), I_2 (12.7 g; 50.0 mmol). The crude product was used to the next stage. Yellow oil. Yield 96% (13.8 g; 40.0 mmol). MS(EI) *m*/*z*: 345 (M^+); 330; 202; 188; 158; 127.

2,3-Difluoro-4-iodo-4′-(1,1-$^2H_2$)propyl-[1,1′]biphenyl 51: Obtained according to procedure **V** from 2,3-difluoro-4′-(1,1-$^2H_2$)propyl-[1,1′]biphenyl **47** (8.9 g; 38.0 mmol), n-BuLi (18.3 mL; 45.0 mmol), I_2 (11.4 g; 45.0 mmol). The crude product was used to the next stage. Yellow oil. Yield 97% (13.3 g; 37.0 mmol). MS(EI) *m*/*z*: 359 (M^+); 330, 202; 184; 127.

4′-(1,1-$^2H_2$)Butyl-2,3-difluoro-4-iodo-[1,1′]biphenyl 52: Obtained according to procedure **V** from 4′-(1,1-$^2H_2$)butyl-2,3-difluoro-[1,1′]biphenyl **48** (17.6 g; 71.0 mmol), n-BuLi (34.2 cm^3;

85.6 mmol), I_2 (21.7 g; 85.6 mmol). The crude product was used to the next stage. Yellow oil. Yield 97% (25.8 g; 69.2 mmol). MS(EI) *m*/*z*: 373 (M^+); 330, 202; 184; 127.

2,3-Difluoro-4-iodo-4′-(1,1-$^2H_2$)pentyl-[1,1′]biphenyl 53: Obtained according to procedure **V** from 2,3-difluoro-4′-(1,1-$^2H_2$)pentyl-[1,1′]biphenyl **49** (13.8 g; 52.7 mmol), n-BuLi (23.2 mL; 85.6 mmol), I_2 (14.7 g; 58.0 mmol). The crude product was used to the next stage. Yellow oil. Yield 95% (19.4 g; 50.0 mmol). MS(EI) *m*/*z*: 388 (M^+); 330; 203; 184; 127.

1-(2′,3′-Difluoro-4″-(1,1-$^2H_2$)pentyl-[1,1′:4′,1″]terphenyl-4-yl)pentan-1-one 54

4CD$_2$TC=O4: Obtained according to procedure **III** from 2,3-difluoro-4-iodo-4′-(1,1-$^2H_2$)pentyl-[1,1′]biphenyl **53** (5.0 g; 13.0 mmol), (4-pentanoylphenyl)boronic acid **81** (3.2 g; 13.0 mmol), K_2CO_3 (4.5; 32.5 mmol). Crystallized from EtOH. White solid. Yield 63% (3.4 g; 8.2 mmol). MS(EI) *m*/*z*: 422 (M^+); 380; 365; 322; 279; 258; 244; 154.

1-(4″-(1,1-$^2H_2$)Butyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl-4-yl)pentan-1-one 55

3CD$_2$TC=O4: Obtained according to procedure **III** from 4′-(1,1-$^2H_2$)butyl-2,3-difluoro-4-iodo-[1,1′]biphenyl **52** (4.86 g; 13.0 mmol), (4-pentanoylphenyl)boronic acid **81** (3.1 g; 13.0 mmol), K_2CO_3 (4.5; 32.5 mmol). Crystallized from EtOH. White solid. Yield 63% (3.4 g; 8.2 mmol). MS(EI) *m*/*z*: 407 (M^+); 365; 350; 322; 279; 264; 244; 154.

1-(4″-(1,1-$^2H_2$)Butyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl-4-yl)butan-1-one 56

3CD$_2$TC=O3: Obtained according to procedure **III** from 4′-(1,1-$^2H_2$)butyl-2,3-difluoro-4-iodo-[1,1′]biphenyl **52** (8.0 g; 21.0 mmol), (4-butyrylphenyl)boronic acid **80** (6.2 g; 32.3 mmol), K_2CO_3 (7.3 g; 53.0 mmol). Crystallized from EtOH. White solid. Yield 67% (5.5 g; 14.0 mmol). MS(EI) *m*/*z*: 393 (M^+); 365, 350; 322; 279; 244; 154; 129.

1-(2′,3′-Difluoro-4″-(1,1-$^2H_2$)propyl-[1,1′:4′,1″]terphenyl-4-yl)pentan-1-one 57

2CD$_2$TC=O4: Obtained according to procedure **III** from 2,3-difluoro-4-iodo-4′-(1,1-$^2H_2$)propyl-[1,1′]biphenyl **51** (3.0 g; 8.3 mmol), (4-pentanoylphenyl)boronic acid **81** (2.0 g; 8.8

mmol), K_2CO_3 (2.9 g; 20.7 mmol). Crystallized from EtOH. White solid. Yield 70% (2.3 g; 5.8 mmol). MS(EI) *m/z*: 393 (M^+); 364; 351; 336; 322; 279; 264; 244; 154;129.

1-(2′,3′-Difluoro-4″-(1,1-$^2H_2$)propyl-[1,1′:4′,1″]terphenyl-4-yl)butan-1-one **58**

2CD$_2$TC=O3: Obtained according to procedure **III** from 2,3-difluoro-4-iodo-4′-(1,1-$^2H_2$)propyl-[1,1′]biphenyl **51** (3.0 g; 8.3 mmol), (4-butyrylphenyl)boronic acid **80** (2,4 g; 8,8 mmol), K_2CO_3 (2.9 g; 20.7 mmol). Crystallized from EtOH. White solid. Yield 67% (2.1 g; 5.6 mmol). MS(EI) *m/z*: 379 (M^+); 351; 336; 279; 264; 244; 154; 129.

1-(2′,3′-Difluoro-4″-(1,1-$^2H_2$)propyl-[1,1′:4′,1″]terphenyl-4-yl)propan-1-one **59**

2CD$_2$TC=O2: Obtained according to procedure **III** from 2,3-difluoro-4-iodo-4′-(1,1-$^2H_2$)propyl-[1,1′]biphenyl **51** (7.0 g; 19.4 mmol), (4-propionylphenyl)boronic acid **79** (4.5 g; 20.0 mmol), K_2CO_3 (6.7 g; 48.6 mmol). Crystallized from EtOH. White solid. Yield 64% (4.5 g; 12.3 mmol). MS(EI) *m/z*: 365 (M^+); 336; 279; 264; 244; 188; 154; 129.

1-(4″-(1,1-$^2H_2$)Ethyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl-4-yl)pentan-1-one **60**

1CD$_2$TC=O4: Obtained according to procedure **III** from 4′-(1,1-$^2H_2$)ethyl-2,3-difluoro-4-iodo-[1,1′]biphenyl **50** (4.5 g; 13.0 mmol), (4-pentanoylphenyl)boronic acid **81** (3.1 g; 13.7 mmol), K_2CO_3 (4.5 g; 32.2 mmol). Crystallized from EtOH. White solid. Yield 69% (3.4 g; 9.0 mmol). MS(EI) *m/z*: 379 (M^+); 337; 322; 278; 264; 244; 188; 169; 154; 139.

1-(4″-(1,1-$^2H_2$)Ethyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl-4-yl)butan-1-one **61**

1CD$_2$TC=O3: Obtained according to procedure **III** from 4′-(1,1-$^2H_2$)ethyl-2,3-difluoro-4-iodo-[1,1′]biphenyl **50** (3.0 g; 8.6 mmol), (4-butyrylphenyl)boronic acid **80** (2.5 g; 9.1 mmol), K_2CO_3 (3.0 g; 21.5 mmol). Crystallized from EtOH. White solid. Yield 70% (2.2 g; 6.0 mmol). MS(EI) *m/z*: 365 (M^+); 337; 322; 278; 264; 244; 188; 153; 139.

1-(4″-(1,1-$^2H_2$)Ethyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl-4-yl)propan-1-one **62**

1CD$_2$TC=O2: Obtained according to procedure **III** from 4′-(1,1-$^2H_2$)ethyl-2,3-difluoro-4-iodo-

[1,1′]biphenyl **50** (3.0 g; 8.6 mmol), 4-propionylphenyl)boronic acid **79** (2.0 g; 9.1 mmol), K_2CO_3 (3.0 g; 21.5 mmol). Crystallized from EtOH. White solid. Yield 74% (2.2 g; 6.4 mmol). MS(EI) *m*/*z*: 351 (M^+); 322; 293; 264; 244; 188; 154; 129.

1-(4″-(1,1-$^2H_2$)Ethyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl-4-yl)ethanone 63 1CD$_2$TC=O1: Obtained according to procedure **III** from 4′-(1,1-$^2H_2$)ethyl-2,3-difluoro-4-iodo-[1,1′]biphenyl **50** (3.0 g; 8.6 mmol), (4-acetylphenyl)boronic acid **78** (1.7 g; 9.1 mmol), K_2CO_3 (3.0 g; 21.5 mmol). Crystallized from EtOH. White solid. Yield 64% (1.9 g; 5.5 mmol). MS(EI) *m*/*z*: 337 (M^+); 322; 293; 264; 238; 188; 154; 129.

2′,3′-Difluoro-4,4″-di(1,1-$^2H_2$)pentyl-[1,1′:4′,1″]terphenyl 64 (5T5-*d*$_4$): Obtained according to procedure **II** from 1-(2′,3′-difluoro-4″-(1,1-$^2H_2$)pentyl-[1,1′:4′,1″]terphenyl-4-yl)pentan-1-one **54** (3.0 g; 7.1 mmol). Crystallized from EtOH. White solid. Yield 89% (2.6 g; 6.3 mmol). MS(EI) *m*/*z*: 410 (M^+); 352; 395; 273; 259; 202; 147. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.91 (t, 6H); 1.29-1.41 (m, 8H); 1.59-1.71 (m, 4H); 2.59-2.67 (m, 0.7H); 7.20-7.31 (m, 6H); 7.46-7.53 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 14.1; 22.7; 31.0; 31.1; 31.6; 124.7; 128.8; 128.8; 129.6; 132.1; 143.1; 147.3; 147.4; 149.8; 149.9; deuterium content (%D): 83% (-**CD$_2$**-C_4H_9).

4-(1,1-$^2H_2$)Butyl-2′,3′-difluoro-4″-(1,1-$^2H_2$)pentyl-[1,1′:4′,1″]terphenyl 65 (4T5-*d*$_4$): Obtained according to procedure **II** from 1-(4″-(1,1-$^2H_2$)butyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl-4-yl)pentan-1-one **55** (2.1 g; 5.2 mmol). Crystallized from EtOH. White solid. Yield 92% (1.9 g; 4.8 mmol). MS(EI) *m*/*z*: 395 (M^+); 352; 338; 309; 295; 273; 203; 148. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.84-0.92 (m, 6H); 1.24-1.35 (m, 6H); 1.49-1.52 (m, 2H); 1.55-1.81 (m, 2H); 2.56-2.64 (m, 1H); 2.65-2.70 (m, 0.23H); 7.21-7.25 (m, 2H); 7.25-7.36 (m, 4H); 7.47-7.54 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 13.7; 14.0; 14.2; 22.7; 22.8;

29.5; 31.7; 32.8; 34.7; 124.3; 126.7; 126.9; 127.6; 127.7; 128.0; 130.3; 133.8; 141.7; 142.4; 143.0; 143.7; 149.5; 150.2; deuterium content (%D): 50% (-**CD$_2$**-C$_3$H$_7$); 88% (-**CD$_2$**-C$_4$H$_9$).

2′,3′-Difluoro-4-(1,1-^{2}H$_2$)pentyl-4″-(1,1-^{2}H$_2$)propyl-[1,1′:4′,1″]terphenyl 66 (3T5-*d*$_4$): Obtained according to procedure **II** from 1-(2′,3′-difluoro-4″-(1,1-^{2}H$_2$)propyl-[1,1′:4′,1″]terphenyl-4-yl)pentan-1-one **57** (2.5 g; 6.4 mmol). Crystallized from EtOH. White solid. Yield 52% (1.3 g; 3.3 mmol). MS(EI) *m*/*z*: 382 (M^+); 352; 324; 308; 295; 273; 259; 203; 148. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.86-1.00 (m, 6H); 1.25-1.34 (m, 4H); 1.53-1.68 (m, 4H); 2.58-2.68 (m, 0.57H); 7.21-7.25 (m, 2H); 7.25-7.31 (m, 4H); 7.47-7.53 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 11.4; 13.7; 14.2; 22.6; 26.8; 23.2; 31.4; 34.3; 124.7; 128.8; 129.6; 132.1 (d); 142.9; 143.1; 147.3; 147.4; 149.8; 149.9; deuterium content (%D): 86% (-**CD$_2$**-C$_2$H$_5$; -**CD$_2$**-C$_4$H$_9$).

4-(1,1-^{2}H$_2$)Ethyl-2′,3′-difluoro-4″-(1,1-^{2}H$_2$)pentyl-[1,1′:4′,1″]terphenyl 67 (2T5-*d*$_4$): Obtained according to procedure **II** from 1-(4″-(1,1-^{2}H$_2$)ethyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl-4-yl)pentan-1-one **60** (1.7 g; 4.7 mmol). Crystallized from EtOH. White solid. Yield 74% (1.2 g; 3.5 mmol). MS(EI) *m*/*z*: 367 (M^+); 352; 310; 295; 279; 259; 202; 147. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.83-0.92 (m, 3H); 1.14-1.16 (m, 3H); 1.19-1.31 (m, 4H); 1.56-1.62 (m, 2H); 2.60-2.64 (m, 0.22H); 2.67-2.74 (m, 1H); 7.18-7.36 (m, 6H); 7.47-7.53 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 14.2; 14.9; 22.7; 23.7; 29.1; 30.5; 31.2; 124.3 (dd); 126.9; 127.0; 127.6; 127.7; 128.1; 130.2; 130.4; 134.8; 139.2; 139.5; 141.7; 142.9; 143.6; 149.5; 150.2; deuterium content (%D): 50% (-**CD$_2$**-CH$_3$); 89% (-**CD$_2$**-C$_4$H$_9$).

4,4″-Di(1,1-^{2}H$_2$)butyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl 68 (4T4-*d*$_4$): Obtained according to procedure **II** from 1-(4″-(1,1-^{2}H$_2$)butyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl-4-yl)butan-1-one **56** (4.0 g; 10.2 mmol). Crystallized from EtOH. White solid. Yield 84% (3.3 g; 8.5 mmol). MS(EI) *m*/*z*: 381 (M^+); 338; 321; 308; 295; 277; 259; 203; 147. ^{1}H NMR (500 MHz, $CDCl_3$) δ

(ppm) 0.83-0.92 (m, 6H); 1.20-1.33 (m, 4H); 1.53-1.67 (m; 4H); 2.61-2.69 (m, 0.56H); 7.21-7.25 (m, 2H); 7.25-7.36 (m, 4H); 7.47-7.53 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 13.7; 22.6; 31.5; 34.5; 124.3 (dd); 126.9; 126.8; 127.6; 127.6; 127.7; 130.4; 133.2; 133.9; 139.2; 140.3; 142.9; 143.7; 149.5; 150.2; deuterium content (%D): 86% (-**CD_2**-C_3H_7).

4-(1,1-$^2H_2$)Butyl-2′,3′-difluoro-4″-(1,1-$^2H_2$)propyl[1,1′:4′,1″]terphenyl 69 (3T4-*d_4*): Obtained according to procedure **II** from 1-(2′,3′-difluoro-4″-(1,1-$^2H_2$)propyl-[1,1′:4′,1″]terphenyl-4-yl)butan-1-one **58** (1.9 g; 5.0 mmol). Crystallized from EtOH. White solid. Yield 52% (1.5 g; 4.1 mmol). MS(EI) *m*/*z*: 367 (M^+); 338; 324; 295; 273; 259; 203; 148. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.86-0.91 (m, 6H); 1.25-1.35 (m, 2H); 1.49-1.58 (m, 2H); 1.56-1.79 (m, 2H); 2.56-2.64 (m, 1H); 2.66-2.70 (m, 0.15H); 7.21-7.25 (m, 2H); 7.26-7.34 (m, 4H); 7.46-7.54 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 11.4; 13.7; 23.2; 23.6; 31.2; 34.5; 36.8; 124.4; 126.8; 127.0; 127.6; 127.7; 127.8; 130.3; 132.9; 134.0; 139.3; 140.3; 143.0; 143.6; 149.5; 150.2; deuterium content (%D): 50% (-**CD_2**-C_2H_5); 92% (-**CD_2**-C_3H_7).

4-(1,1-$^2H_2$)Butyl-4″-(1,1-$^2H_2$)ethyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl 70 (2T4-*d_4*): Obtained according to procedure **II** from 1-(4″-(1,1-$^2H_2$)ethyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl-4-yl)butan-1-one **61** (1.2 g; 3.3 mmol). Crystallized from EtOH. White solid. Yield 61% (0.7 g; 2.0 mmol). MS(EI) *m*/*z*: 353 (M^+); 338; 310; 295; 279; 259; 203; 148. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.83-0.92 (m, 3H); 1.14-1.16 (m, 3H); 1.25-1.35 (m, 2H); 1.49-1.52 (m, 2H); 2.59-2.76 (m, 0.72H); 7.18-7.36 (m, 6H); 7.47-7.53 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 14.0; 14.9; 22.6; 29.1; 30.5; 32.8; 124.3 (dd); 126.9; 127.0; 127.6; 127.7; 128.1; 130.2; 130.4; 134.8; 139.2; 139.5; 142.9; 143.7; 149.5; 150.1; deuterium content (%D): 82% (-**CD_2**-CH_3; -**CD_2**-C_3H_7).

2′,3′-Difluoro-4,4″-di(1,1-$^2H_2$)propyl-[1,1′:4′,1″]terphenyl 71 (3T3-*d_4*): Obtained according to procedure **II** from 1-(2′,3′-difluoro-4″-(1,1-$^2H_2$)propyl-[1,1′:4′,1″]terphenyl-4-

yl)propan-1-one **59** (4.0 g; 11.0 mmol). Crystallized from EtOH. White solid. Yield 64% (2.5 g; 7.1 mmol). MS(EI) *m*/*z*: 354 (M^+); 337; 325; 308; 396; 273; 259; 203; 148. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.90 (s, 6H); 1.20-1.35 (m, 4H); 2.60-2.68 (m, 0.58H); 7.18-7.31 (m, 6H), 7.46-7.53 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 11.4; 23.1; 31.2; 124.0; 124.8; 127.0; 127.8; 127.9; 130.2; 134.0; 139.3; 143.0; 143.7; 149.5; 150.1; deuterium content (%D): 86% (-**CD_2**-C_2H_5).

4-(1,1-$^2H_2$)Ethyl-2′,3′-difluoro-4″-(1,1-$^2H_2$)propyl-[1,1′:4′,1″]terphenyl 72 (2T3-*d_4*): Obtained according to procedure **II** from 1-(4″-(1,1-$^2H_2$)ethyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl-4-yl)propan-1-one **62** (1.7 g; 4.7 mmol). Crystallized from EtOH. White solid. Yield 82% (1.3 g; 3.9 mmol). MS(EI) *m*/*z*: 339(M^+); 324; 310; 295; 279; 259; 202; 147. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.97 (t, 3H); 1.30 (t, 3H); 1.64-1,72 (m, 2H); 2.61-2.67 (m, 0.2H); 2.67-2.76 (m, 1H); 7.22-7.26 (m, 2H); 7.26-7.34 (m, 4H); 7.49-7.55 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 14.0; 15.5; 24.4; 28.4; 28.7; 124.7; 128.2; 128.8; 128.8; 128.9; 129.6; 132.1; 142.9; 144.9; 144.4; 147.5; 147.6; 149.6; deuterium content (%D): 90% (-**CD_2**-CH_2-CH_3); 50% (-**CD_2**-CH_3).

4,4″-Di(1,1-$^2H_2$)Ethyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl 73 (2T2-*d_4*): Obtained according to procedure **II** from 1-(4″-(1,1-$^2H_2$)ethyl-2′,3′-difluoro-[1,1′:4′,1″]terphenyl-4-yl)ethanone **63** (1.5 g; 4.5 mmol). Crystallized from EtOH. White solid. Yield 72% (1.1 g; 3.2 mmol). MS(EI) *m*/*z*: 325 (M^+); 310; 294; 258; 226; 202; 147. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.97 (t, 3H); 1.30 (t, 3H); 2.60-2.67 (m, 0.68H); 7.22-7.26 (m, 2H); 7.26-7.34 (m, 4H); 7.49-7.55 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 11.8; 14.9; 29.5; 124.7; 128.2; 128.8; 128.8; 128.9; 129.6; 132.1; 142.9; 144.9; 144.4; 147.5; 147.6; 149.6; deuterium content (%D): 83% (-**CD_2**-CH_3).

2-(4-Bromophenyl)-2-methyl-1,3-dioxolane 74: Obtained according to general procedure **IV** from 1-(4-bromophenyl)ethenone **38** (40.0 g; 0.2 mol), ethane-1,2-diol (13.7 g; 0.2 mol), *p*-

TsOH (3.0 g). The reaction was heated at 110 °C for 4 days. The crude product was distilled under reduced pressure (85 °C; 0.6 mmHg). Yield 58% (26.2 g; 0,1 mol). MS(EI) *m/z*: 227; 183; 155, 103; 87. The MS spectrum does not contain the molecular ion.

2-(4-Bromophenyl)-2-ethyl-1,3-dioxolane 75: Obtained according to general procedure **IV** from 1-(4-bromophenyl)propan-1-one **39** (19.3 g; 90.6 mmol), ethane-1,2-diol (6.7 g; 0.1 mol), *p*-TsOH (3.0 g). The reaction was heated at 110 °C for 2 days. The crude product was distilled under reduced pressure (111 °C; 1.5 mmHg). Yield 68% (15.8 g; 61.5 mmol). MS(EI) *m/z*: 227; 183; 155, 103; 87. The MS spectrum does not contain the molecular ion.

2-(4-Bromophenyl)-2-propyl-1,3-dioxolane 76: Obtained according to general procedure **IV** from 1-(4-bromophenyl)butan-1-one **40** (30.0 g; 0.1 mol), ethane-1,2-diol (9.0 g; 0.15 mol), *p*-TsOH (3.0 g). The reaction was heated at 110 °C for 2 days. The crude product was distilled under reduced pressure (99 °C; 0.6 mmHg). Yield 75% (26.5 g; 97.8 mmol). MS(EI) *m/z*: 227; 183; 155, 103; 87. The MS spectrum does not contain the molecular ion.

2-(4-Bromophenyl)-2-butyl-1,3-dioxolane 77: Obtained according to general procedure **IV** from 1-(4-bromophenyl)pentan-1-one **41** (30.0 g; 0.1 mol), ethane-1,2-diol (8.5 g; 0.1 mol), *p*-TsOH (3.0 g). The reaction was heated at 110 °C for 1 day. The crude product was distilled under reduced pressure (104 °C; 0.4 mmHg). Yield 67% (21.8 g; 87.2 mmol). MS(EI) *m/z*: 227; 183; 155, 103; 87. The MS spectrum does not contain the molecular ion.

(4-Acetylphenyl)boronic acid 78: Obtained according to general procedure **VI** from 2-(4-bromophenyl)-2-methyl-1,3-dioxolane **74** **(**26.2 g; 0.11 mol), Mg flakes (2.6 g; 0.11 mol), $B(OPr)_3$ (28.4 cm^3; 0.1 mol). White solid. Yield 70% (12.4 g; 75.5 mmol). MS(EI) for ester of boronic acid obtained according to Figure S1: *m/z*: 204 (M^+); 189; 161; 133; 103; 77.

(4-Propionylphenyl)boronic acid 79: Obtained according to general procedure **VI** from 2-(4-bromophenyl)-2-ethyl-1,3-dioxolane **75** (15.8 g; 61.0 mmol), Mg flakes (1.5 g; 61.0 mmol),

$B(OPr)_3$ (14.7 cm^3; 67.0 mmol). White solid. Yield 72% (7.9 g; 43.9 mmol). MS(EI) for ester of boronic acid obtained according to Figure S1: *m*/*z*: 218 (M^+); 189; 161; 133; 103; 77.

(4-Butyrylphenyl)boronic acid 80: Obtained according to general procedure **VI** from 2-(4-bromophenyl)-2-propyl-1,3-dioxolane **76 (**26.6 g; 98.0 mmol), Mg flakes (2.35 g; 98.0 mmol), $B(OPr)_3$ (25.8 cm^3; 0.1 mol). White solid. Yield 72% (13.8 g; 72.0 mmol). MS(EI) for ester of boronic acid obtained according to Figure S1: *m*/*z*: 232 (M^+); 189; 161; 133; 103; 77.

(4-Pentanoylphenyl)boronic acid 81: Obtained according to general procedure **VI** from 2-(4-bromophenyl)-2-butyl-1,3-dioxolane **77** (21.8 g; 76.0 mmol), Mg flakes (1.8 g; 76.0 mmol), $B(OPr)_3$ (18.3 cm^3; 84.0 mmol). White solid. Yield 75% (11.7 g; 57.0 mmol). MS(EI) for ester of boronic acid obtained according to Figure S1: *m*/*z*: 246 (M^+); 204; 189; 161; 133; 103; 115; 77.

2.3. Synthetic procedures for single-ring model molecules

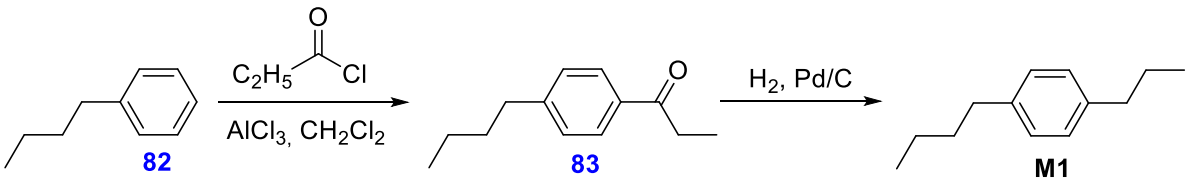


Figure S2. Synthesis of 1-butyl-4-propylbenzene **M1**.

1-(4-Butylphenyl)propan-1-one 83: In a four-neck round bottom flask equipped with a mechanical stirrer, a reflux condenser, dropping funnel, thermometer and a tube with an anhydrous $CaCl_2$ were placed anhydrous CH_2Cl_2 (250 cm^3) and $AlCl_3$ (13.1 g; 98.7 mmol). Then, propionyl chloride (9.6 g; 0.1 mol) was dropped, keeping the temperature ~30 °C. After solving $AlCl_3$, the butylbenzene **82** (12.6 g; 94.0 mmol) was dropped at 30 °C and the mixture was stirred at reflux for 6 h. Next day, the reaction mixture was poured into a beaker filled with ice. After the ice melted, the mixture was transferred into a separating funnel and organic phase

was separated. Organic layer was washed with water (3x50 cm^3), dried with $MgSO_4$ and concentrated on the rotary evaporator. Crude product was distilled under reduced pressure (73 °C; 0.1 mmHg). Yield 68% (12.1 g; 63.7 mmol). MS(EI) *m/z*: 190 (M^+).

1-Butyl-4-propylbenzene M1: Obtained according to modified procedure **II** from 1-(4-butylphenyl)propan-1-one **83** (5.0 g; 26.3 mmol), Pd/C (10%) (0.5 g), THF (30 cm^3). The reactor was charged with hydrogen gas (to a pressure of 50 bar) and then the reaction vessel was washed. The operation was repeated. Next, the reactor was refilled with hydrogen and the reaction was carried out at the room temperature. Then proceeded as in procedure II. Crude product was distilled under reduced pressure (100-102 °C; 5.0 mmHg). Yield 82% (3.8 g; 21.6 mmol). MS(EI) *m/z*: 176 (M^+); 147; 133; 117; 105; 91; 77.

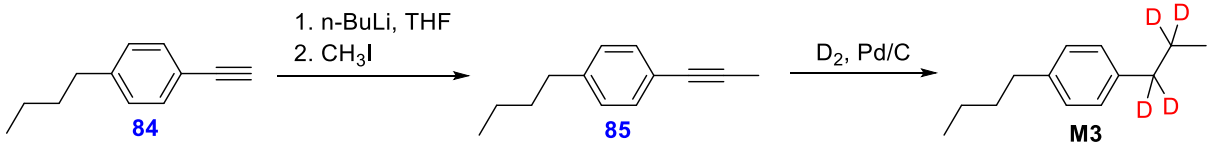


Figure S3. Synthesis of 1-butyl-4-(1,1,2,2-$^2H_4$)propylbenzene **M3**.

1-Butyl-4-(prop-1-yn-1-yl)benzene 85: Obtained in part according to general procedure **V** from 1-butyl-4-ethynylbenzene **84** (15.8 g; 0.1 mol) and n-BuLi (48 cm^3; 0.1 mol). After 1 h from the addition of n-BuLi, MeI (21.3 g; 0.2 mol) was added dropwise and then the reaction was carried out at 66 °C for 4 h. Then, the reaction mixture was cooled down to room temperature and extracted with hexane. Organic layer was dried with $MgSO_4$ and concentrated on rotary evaporator. Crude product was distilled under reduced pressure (90 °C; 3.0 mmHg). Yield 75% (13.9 g; 74.9 mmol). MS(EI) *m/z*: 172 (M^+); 129; 115.

1-Butyl-4-(1,1,2,2-$^2H_4$)propylbenzene M3: Obtained according to procedure **II** from 1-butyl-4-(prop-1-yn-1-yl)benzene **85** (12.8 g; 74.4 mmol), THF (30 cm^3) and Pd/C (10%) (0.5 g).

Crude product was distilled under reduced pressure (58 °C; 1.5 mmHg). Yield 93% (12.5 g; 69.4 mmol). MS(EI) *m/z*: 180 (M^+); 149; 137; 119; 106; 93; 79.

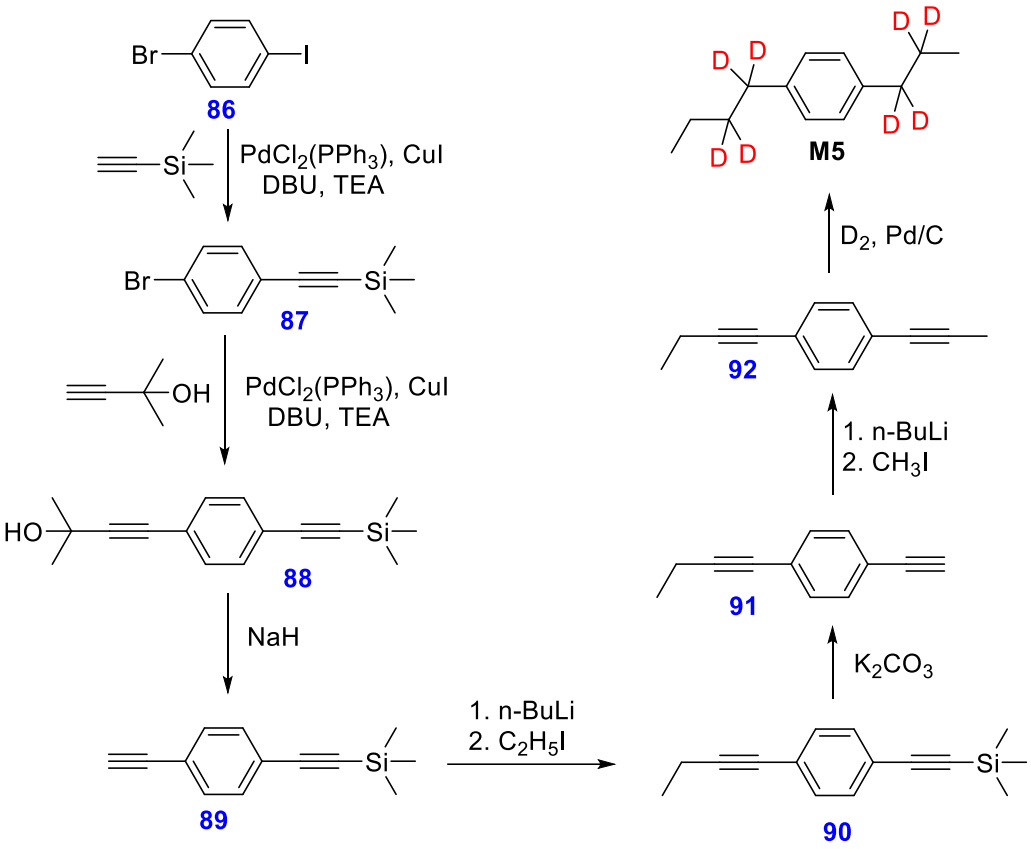


Figure S4. Synthesis of 1-(1,1,2,2-$^2H_4$)butyl-4-(1,1,2,2-$^2H_4$)propylbenzene **M5**.

((4-Bromophenyl)ethynyl)trimethylsilane 87: In a four-neck round bottom flask equipped with a mechanical stirrer, a reflux condenser, dropping funnel and thermometer a mixture of 1-bromo-4-iodobenzene **86** (25.0 g; 88.0 mmol), triethylamine (TEA) (8.9 g; 88.8 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (13.4 g; 88,8 mmol), toluene (350 cm^3), $PdCl_2(PPh_3)_2$ (3% mol) and CuI (1.5% mol) was stirred under nitrogen and heated at reflux for 15 min. Then, the reaction was cooled down to 40 °C and ethynyltrimethylsilane (9.5 g; 97.0 mmol) was added dropwise. Next, the reaction was stirred in 40 °C. The progress of the reaction was monitored by gas chromatography (GC-MS/FID). When the reaction was finished, water was added. Organic layer was washed with water, dried over $MgSO_4$, concentrated and purified on chromatography column (SiO_2/toluene). The crude product was distilled under reduced

pressure (100 °C; 2.0 mmHg). Yield 79% (17.5 g; 69.0 mmol). MS(EI) *m/z*: 254 (M^+); 237; 209; 143.

2-Methyl-4-(4-((trimethylsilyl)ethynyl)phenyl)but-3-yn-2-ol 88: Obtained as compound 101 from ((4-bromophenyl)ethynyl)trimethylsilane **87** (18.0 g; 71.0 mmol), 2-methyl-3-butyn-2-ol **19** (6.6 g; 78.1 mmol), TEA (7.2 g; 71.0 mmol), DBU (10.7 g; 71.0 mmol), toluene (350 cm^3), $PdCl_2(PPh_3)_2$ (3% mol), CuI (1.5% mol). The crude product was distilled under reduced pressure (98 °C; 0.2 mmHg). Yield 81% (14.8 g; 57.7 mmol). MS(EI) *m/z*: 256 (M^+); 241; 225; 183; 113.

((4-Ethynylphenyl)ethynyl)trimethylsilane 89: In a two-neck round bottom flask 2-methyl-4-(4-((trimethylsilyl)ethynyl)phenyl)but-3-yn-2-ol **88** (13.7 g; 53.5 mmol) and anhydrous toluene (250 cm^3) were placed. Next, catalytic amount of sodium hydride (10% mol) was added. The mixture was stirred under reflux while acetone was distilled off. When the reaction was completed, the mixture was extracted with water. Organic layer was dried with $MgSO_4$ and concentrated. The crude product was distilled under reduced pressure (61 °C; 1.0 mmHg). Yield 63% (6.7 g; 33.8 mmol). MS (EI) *m/z*: 198 (M^+); 183; 167; 153; 129.

((4-(But-1-yn-1-yl)phenyl)ethynyl)trimethylsilane 90: Obtained in part according to general procedure **V** from ((4-ethynylphenyl)ethynyl)trimethylsilane **89** (6.7 g; 33.8 mmol) and n-BuLi (16.2 cm^3; 40.6 mmol). After 1 h from the addition of n-BuLi, EtI (6.3 g; 40.6 mmol) was added dropwise and then the reaction was carried out at 66 °C for 2 h. Then, the reaction mixture was cooled down to room temperature and extracted with hexane. Organic layer was dried with $MgSO_4$ and concentrated on rotary evaporator. Crude product was distilled under reduced pressure (90 C; 0.4 mmHg). Yield 17% (1.3 g; 5.6 mmol). MS(EI) *m/z*: 226 (M^+); 211; 196; 180; 166; 152.

1-(But-1-yn-1-yl)-4-ethynylbenzene 91: In a round bottom flask were placed ((4-(but-1-yn-1-yl)phenyl)ethynyl)trimethylsilane (1.2 g; 5.3 mmol), K_2CO_3 (5% mol), methanol (25 cm^3) and acetone (25 cm^3). Reaction was stirred at room temperature for 1 h. Then, mixture was extracted with water into CH_2Cl_2, organic layer was dried with $MgSO_4$ and concentrated. Crude product was distilled under reduced pressure using Kugelrohr (104 °C; 10.0 mmHg). Yield 85% (0.7 g; 4.5 mmol). MS(EI) *m/z*: 154 (M^+), 139; 126; 115; 76; 63.

1-(But-1-yn-1-yl)-4-(prop-1-yn-1-yl)benzene 92: Obtained in part according to general procedure **V** from 1-(but-1-yn-1-yl)-4-ethynylbenzene **91** (0.7 g; 4.5 mmol) and n-BuLi (2.2 cm^3; 5.4 mmol). After 1 h from the addition of n-BuLi, MeI (1.3 g; 9.0 mmol) was added dropwise and then the reaction was carried out at 66 °C for 2 h. Then, the reaction mixture was cooled down to room temperature and extracted with hexane. Organic layer was dried with $MgSO_4$ and concentrated on rotary evaporator. Crude product was distilled under reduced pressure (84 °C; 1.0 mmHg). Yield 69% (0.5 g; 3.1 mmol). MS(EI) *m/z*: 168 (M^+); 152; 139; 128; 115; 82.

1-(1,1,2,2-$^2H_4$)Butyl-4-(1,1,2,2-$^2H_4$)propylbenzene M5: Obtained according to procedure **II** from 1-(but-1-yn-1-yl)-4-(prop-1-yn-1-yl)benzene **92** (0.7 g; 4.5 mmol), THF (30 cm^3) and Pd/C (10%) (0.1 g). Crude product was distilled under reduced pressure using Kugelrohr (67 °C; 1.0 mmHg). Yield 65% (0.5 g; 29.3 mmol). MS(EI) *m/z* 184 (M^+); 153; 139; 122; 108; 94; 80.

3. Phase transition temperatures and enthalpies

3.1. Liquid crystalline precursors of deuterated LCs

Table S1. Phase transition **temperatures T [°C]** and *enthalpies ΔH [kJ/mol]* of the investigated compounds **2TAn-*d*$_5$** measured by DSC method (onset point) with a heating rate at 2K/min. Cr – crystal phase; N – nematic; SmA – smectic A; Iso – isotropic liquid.

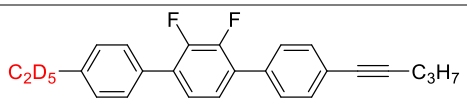
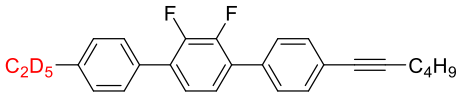
No Acronym	General structure	Transition temperature [°C] *Enthalpy (ΔH [kJ/mol])*
9 **2TA3-*d*$_5$**		Cr I **100.8** *(24.4)* Cr II **104.6** *(4.0)* N **154.7** *(0.4)* Iso
10 **2TA4-*d*$_5$**		Cr **81.6** *(24.9)* N **127.0** *(0.3)* Iso

Table S2. Phase transition **temperatures T [˚C]** and *enthalpies ΔH [kJ/mol]* of the investigated compounds **nCD$_2$TC=On** measured by DSC method (onset point) with a heating rate at 2K/min.

No Acronym	Transition temperature [°C] *Enthalpy (ΔH [kJ/mol])*
54 4CD$_2$TC=O4	Cr **86.6** *(21.4)* SmA **173.9** *(6.1)* Iso
55 3CD$_2$TC=O4	Cr **89.2** *(20.1)* SmA **167.7** *(6.0)* Iso
56 3CD$_2$TC=O3	Cr **108.2** *(23.9)* SmA **157.2** *(5.4)* Iso
57 2CD$_2$TC=O4	Cr **86.6** *(21.4)* SmA **167.1** *(3.5)* N **173.9** *(0.8)* Iso
58 2CD$_2$TC=O3	Cr **98.9** *(19.8)* SmA **154.9** *(3.3)* N **167.4** *(0.4)* Iso
59 2CD$_2$TC=O2	Cr I **63.5** *(8.7)* Cr II **110.6** *(14.1)* SmA **149.1** *(1.0)* N **197.0** *(0.5)* Iso
60 1CD$_2$TC=O4	Cr **112.9** *(23.8)* SmA **156.4** *(3.6)* N **165.3** *(0.4)* Iso
61 1CD$_2$TC=O3	Cr I **110.4** *(0.3)* Cr II **125.4** *(22.7)* SmA **149.5** *(4.6)* N **158.4** *(0.5)* Iso
62 1CD$_2$TC=O2	Cr **120.1** *(18.3)* SmA **145.1** *(2.3)* Iso
63 1CD$_2$TC=O1	Cr **144.5** *(20.3)* Iso

3.2 Deuterated LCs

Table S3. Phase transition **temperatures T [˚C]** and *enthalpies ΔH [kJ/mol]* of the investigated compounds **nTn-*d*$_x$** measured by the DSC method (onset point) with a heating rate at 2K/min.

No Acronym	Transition temperature [°C] *Enthalpy (ΔH [kJ/mol])*
24 6T6-*d*$_8$	Cr I **43.6** *(0.4)* Cr II **65.0** *(27.3)* N **103.2** *(0.6)* Iso
23	Cr **51.3** *(21.9)* N **108.4** *(1.0)* Iso

5T6-d_8	
21 4T6-d_8	Cr **36.4** *(22.8)* N **100.2** *(0.8)* Iso
19 3T6-d_8	Cr **37.6** *(21.3)* N **111.3** *(0.7)* Iso
26 2T6-d_9	Cr **52.1** *(27.5)* N **97.6** *(0.6)* Iso
22 5T5-d_8	Cr I **40.6** *(1.2)* Cr II **56.5** *(16.4)* N **115.9** *(0.8)* Iso
20 4T5-d_8	Cr **50.7** *(20.3)* N **109.5** *(0.8)* Iso
18 3T5-d_8	Cr **51.0** *(26.6)* N **121.9** *(0.9)* Iso
25 2T5-d_9	Cr **40.5** *(18.6)* N **108.7** *(0.7)* Iso
37 3T4-d_8	Cr **60.7** *(17.1)* N **113.1** *(0.5)* Iso
36 3T3-d_8	Cr **93.2** *(19.2)* N **128.4** *(0.7)* Iso
35 2T3-d_9	Cr **72.1** *(17.9)* N **113.2** *(0.5)* Iso

Table S4. Phase transition **temperatures T [˚C]** and *enthalpies ΔH [kJ/mol]* of the investigated compounds **nTn-*d*$_x$** measured by the DSC method (onset point) with a heating rate at 2K/min.

No **Acronym**	**Transition temperature [°C]** *Enthalpy (ΔH [kJ/mol])*
64 5T5-d_4	Cr I **37.6** *(6.2)* Cr II **59.6** *(19.6)* N **117.8** *(0.7)* Iso
65 4T5-d_4	Cr **50.2** *(20.4)* N **109.1** *(0.4)* Iso
66 3T5-d_4	Cr **50.5** *(25.9)* N **122.2** *(0.7)* Iso
67 2T5-d_4	Cr **40.4** *(18.2)* N **108.8** *(0.5)* Iso
68 4T4-d_4	Cr **66.6** *(22.3)* N **100.7** *(0.3)* Iso
69 3T4-d_4	Cr **60.4** *(19.0)* N **113.9** *(0.5)* Iso
70 2T4-d_4	Cr **54.2** *(18.3)* N **98.6** *(0.4)* Iso
71 3T3-d_4	Cr **94.5** *(22.9)* N **127.7** *(0.8)* Iso
72 2T3-d_4	Cr **72.3** *(16.2)* N **113.6** *(0.4)* Iso
73* 2T2-d_4	Cr **88.9** *(18.5)* (N) **94.4** *(0.4)* Iso

*For compounds **73** the monotropic nematic phase was observed.

4. ^{1}H NMR and ^{13}C NMR for 2T3 family

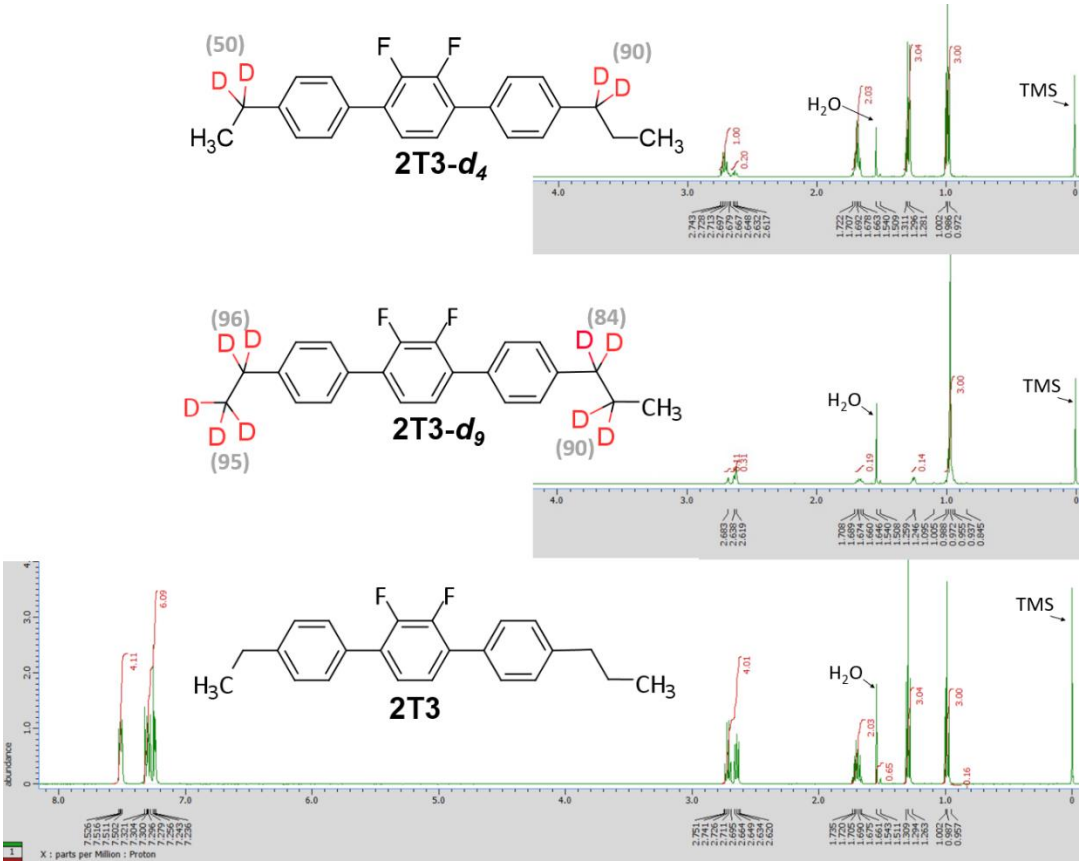


Figure S5. Comparison of ^{1}H NMR spectra for 2T3 isotopologues.

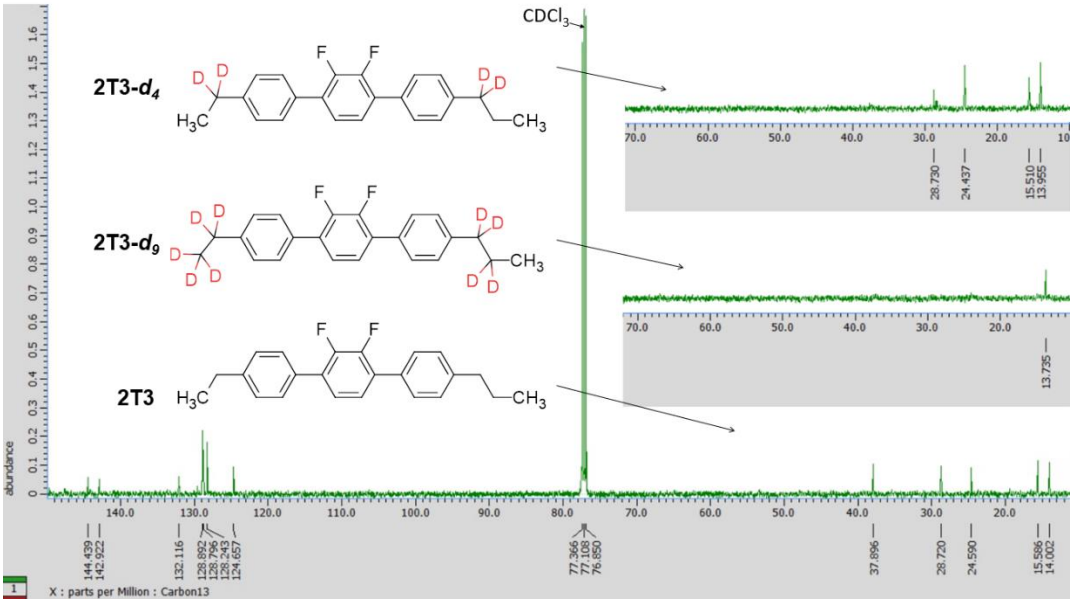


Figure S6. Comparison of ^{13}C NMR spectra for isotopologues from the 2T3 family in the range of 0-70 ppm (the area of occurrence of signals from carbon atoms of alkyl chains).

5. DSC analysis

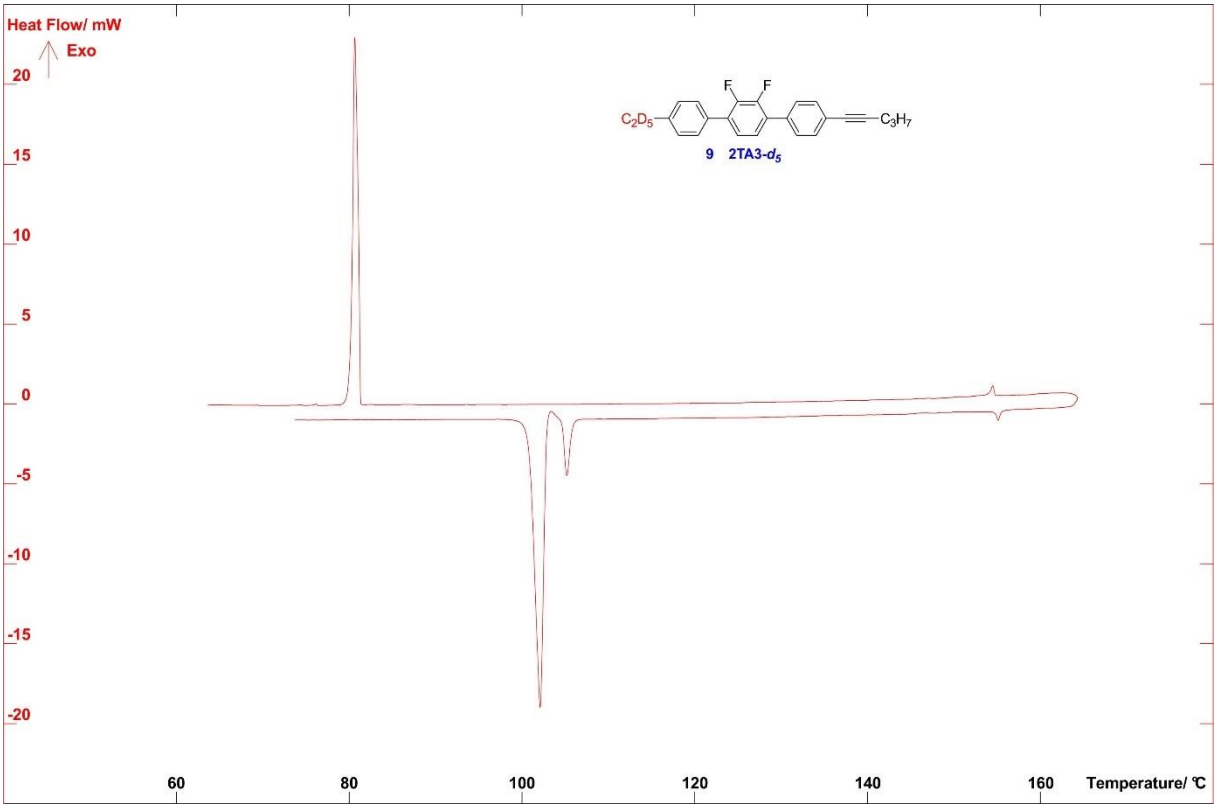


Figure S7. DSC trace of **9**.

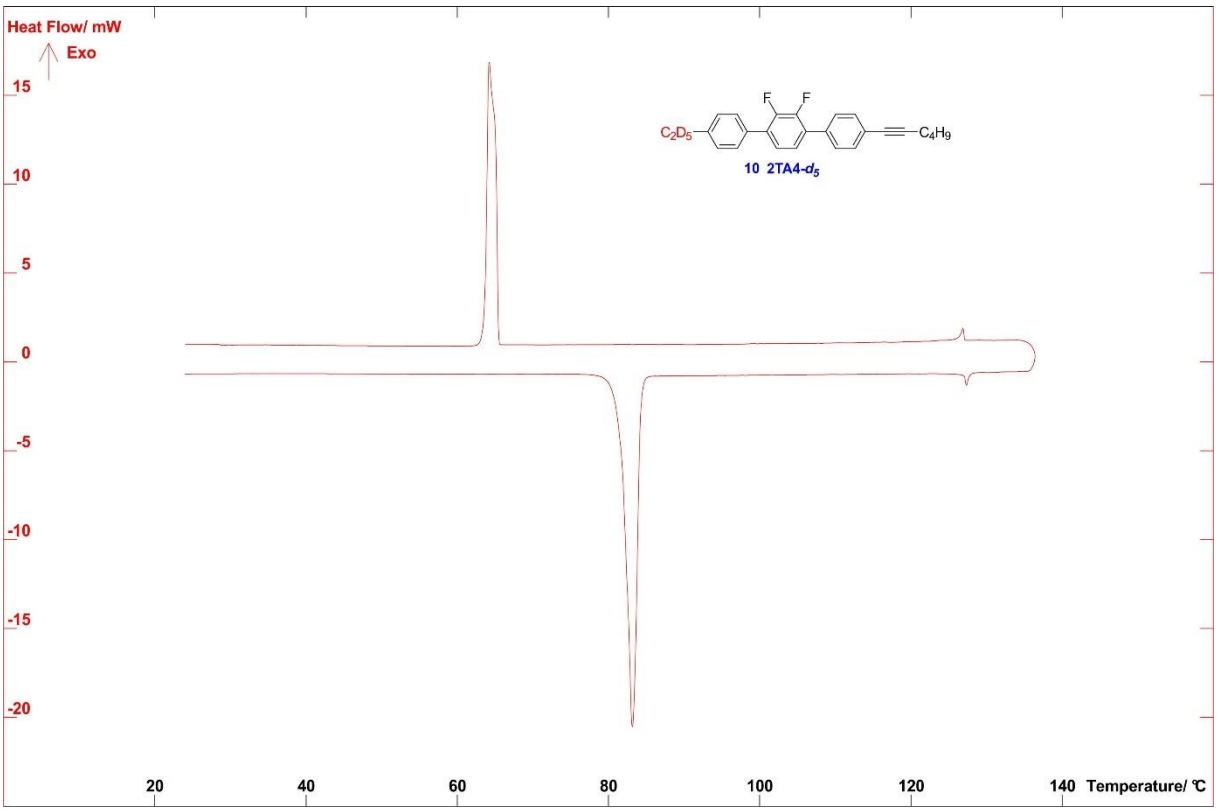


Figure S8. DSC trace of **10**.

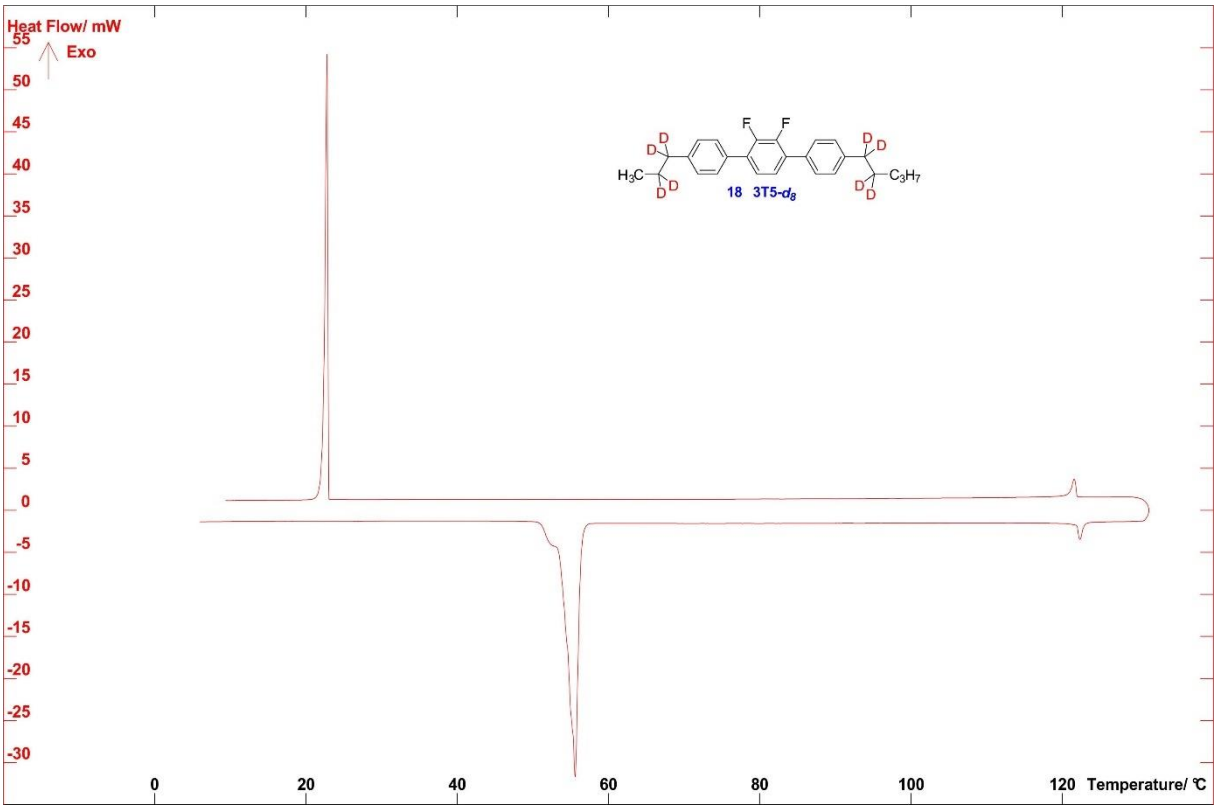


Figure S9. DSC trace of **18**.

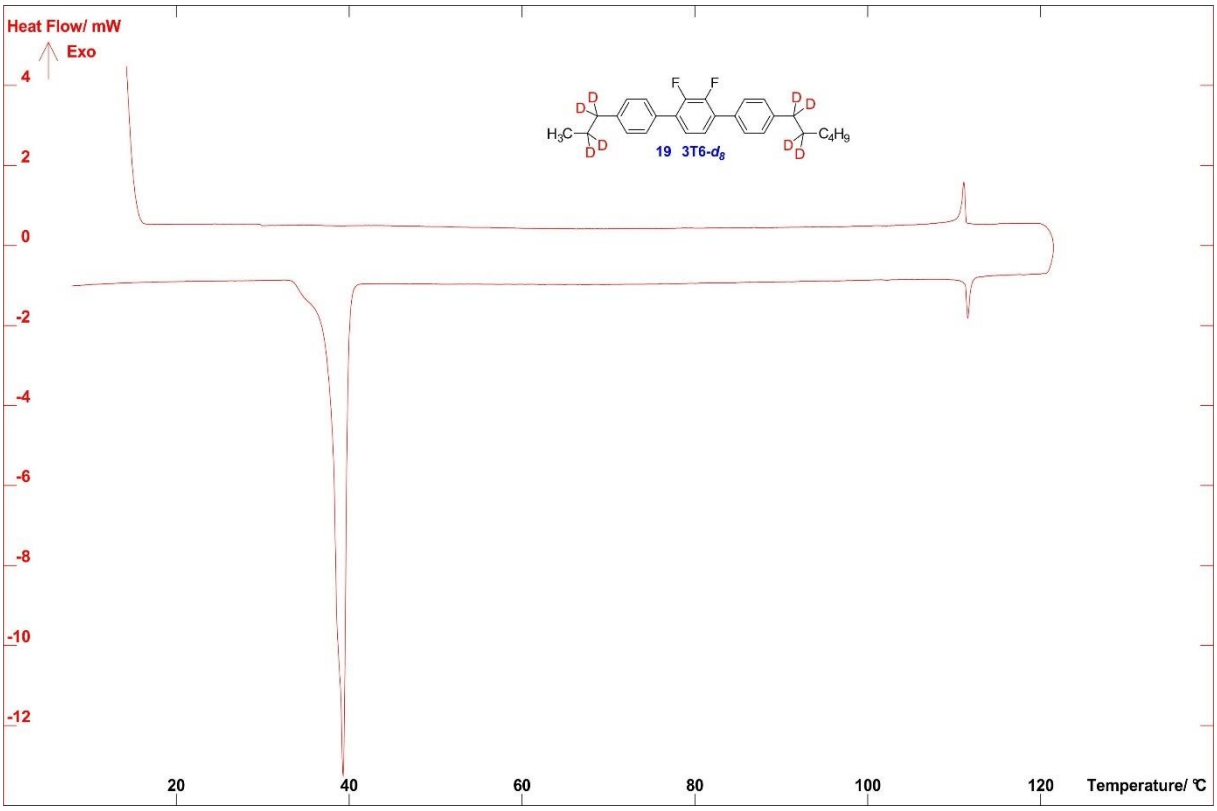


Figure S10. DSC trace of **19**.

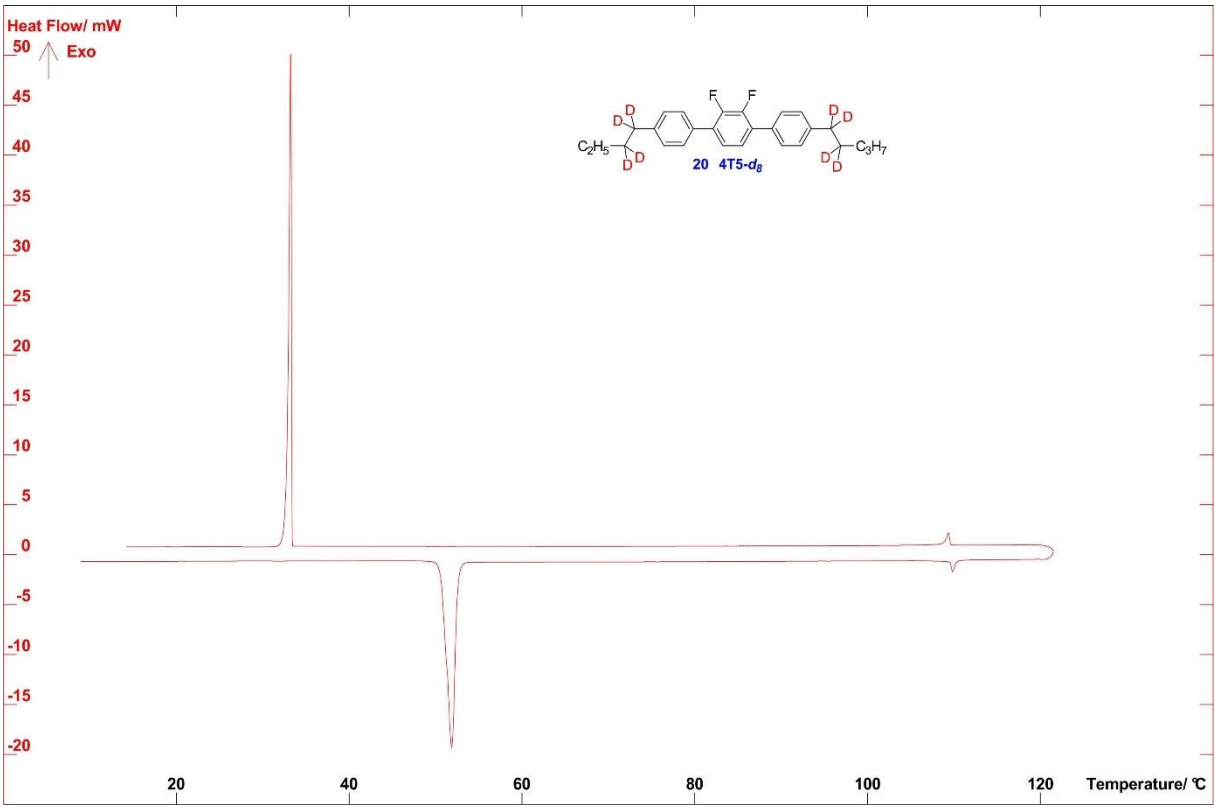


Figure S11. DSC trace of **20**.

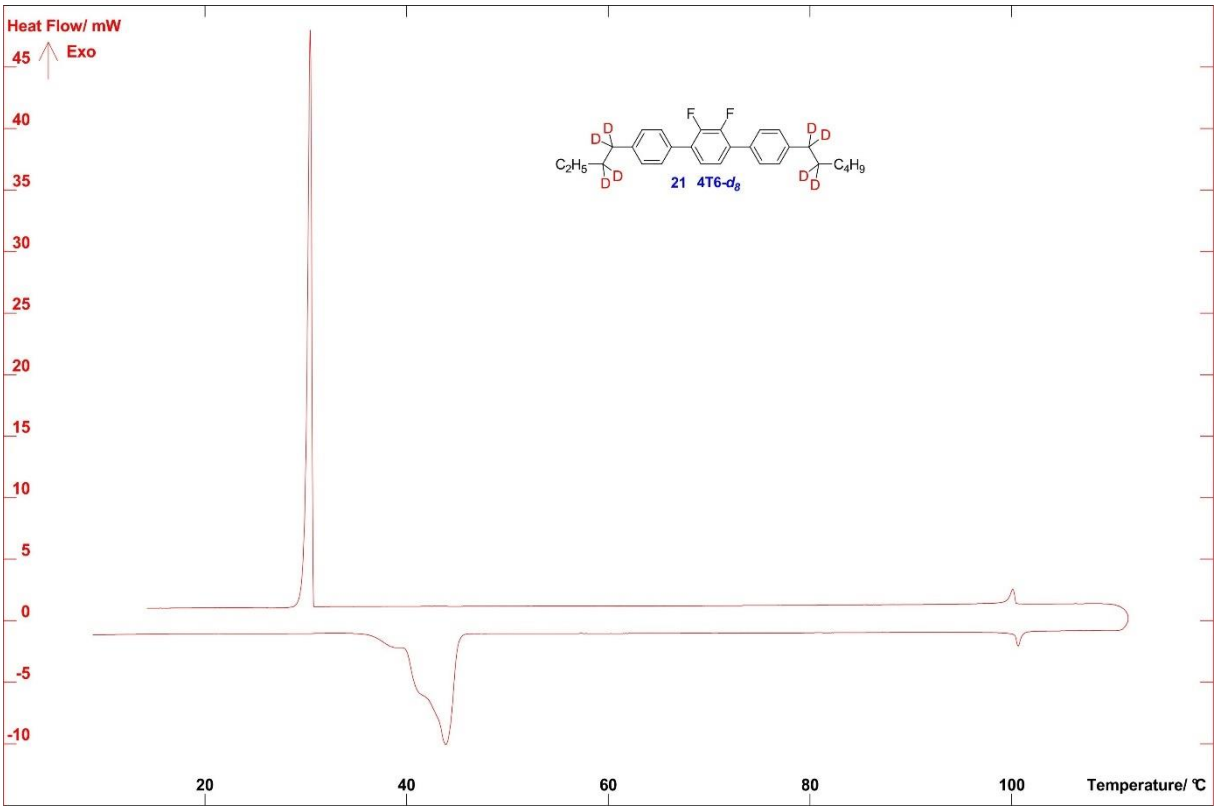


Figure S12. DSC trace of **21**.

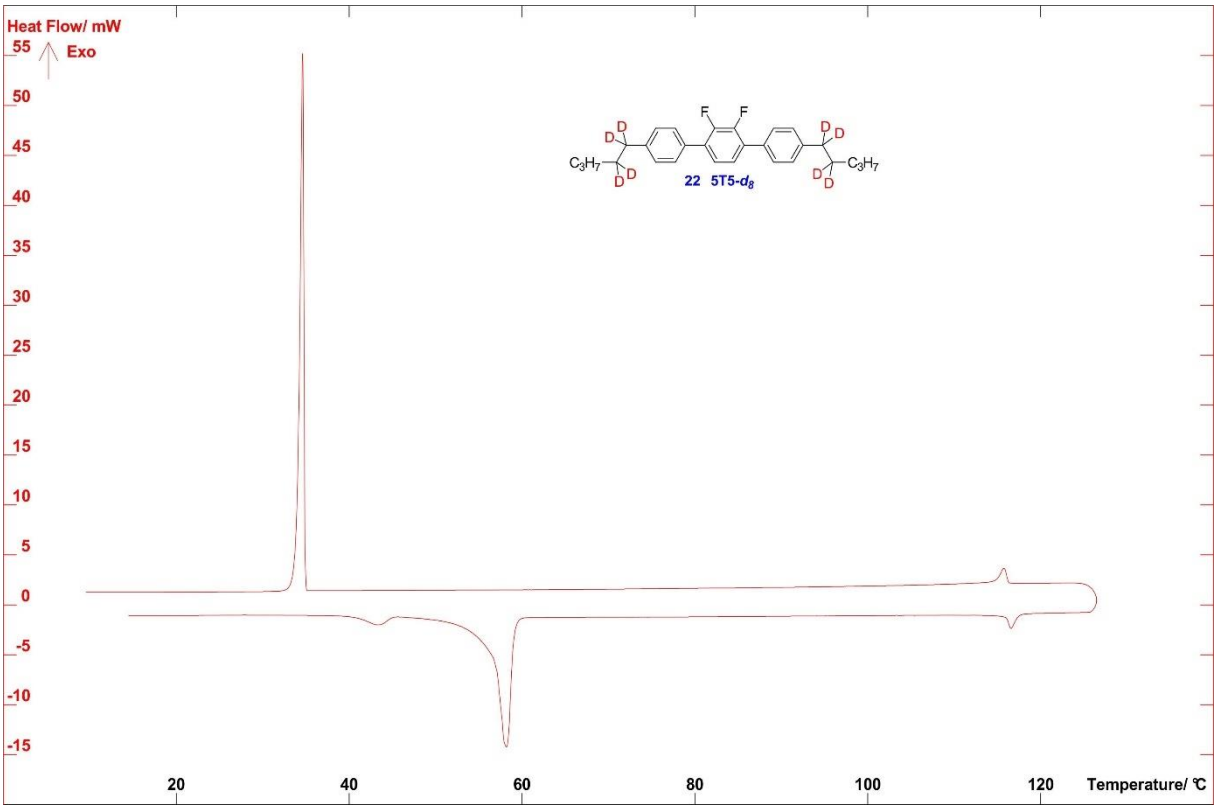


Figure S13. DSC trace of **22**.

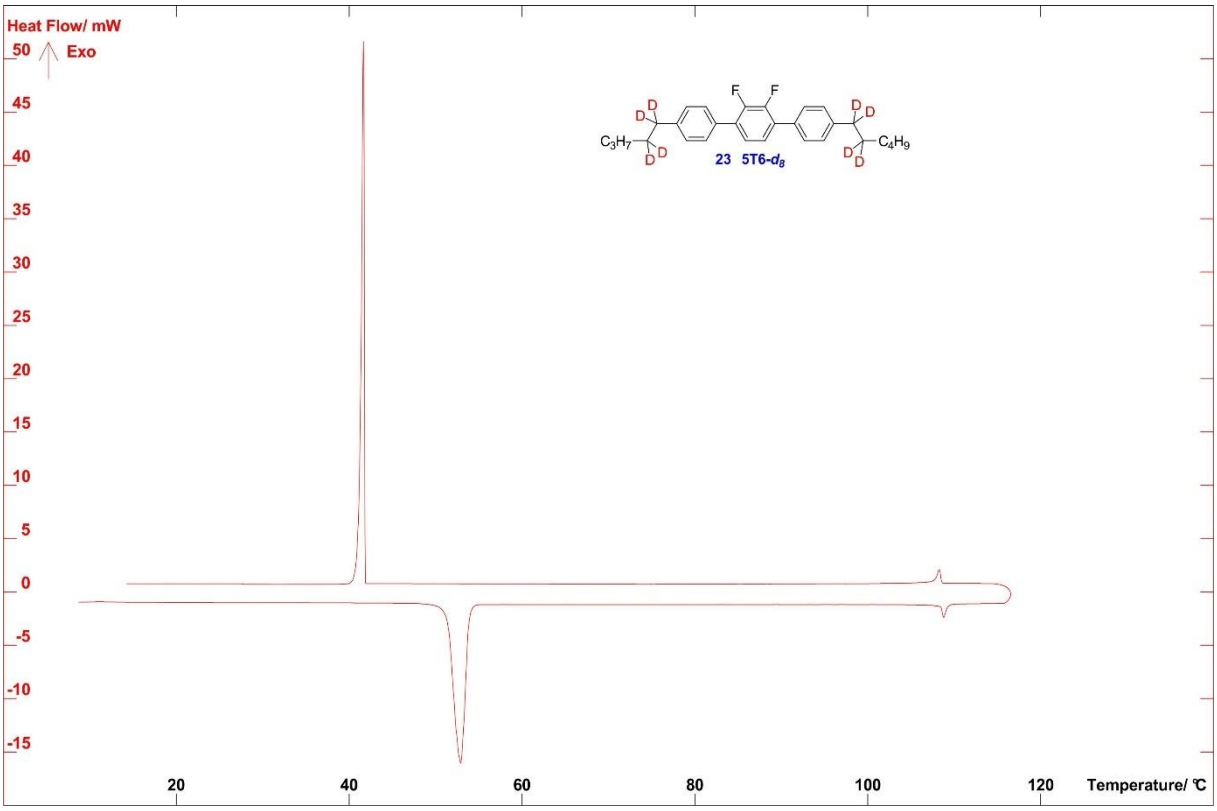


Figure S14. DSC trace of **23**.

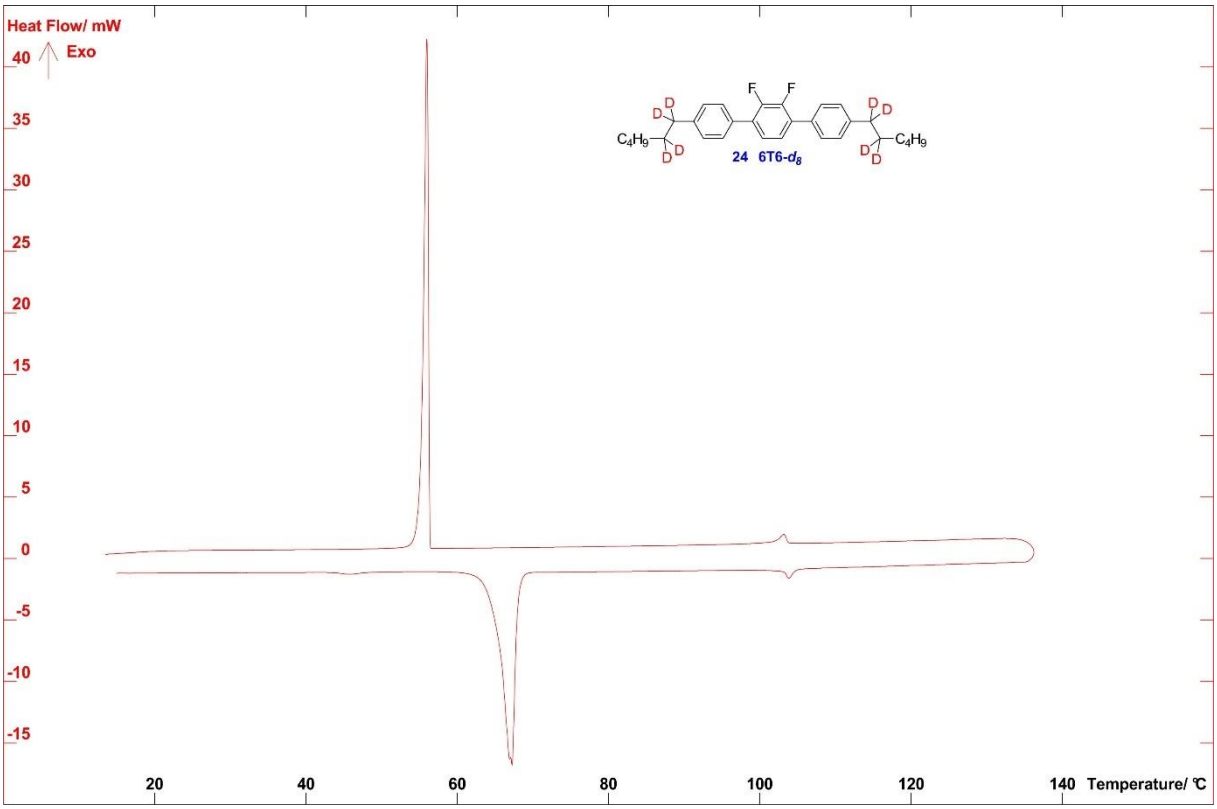


Figure S15. DSC trace of **24**.

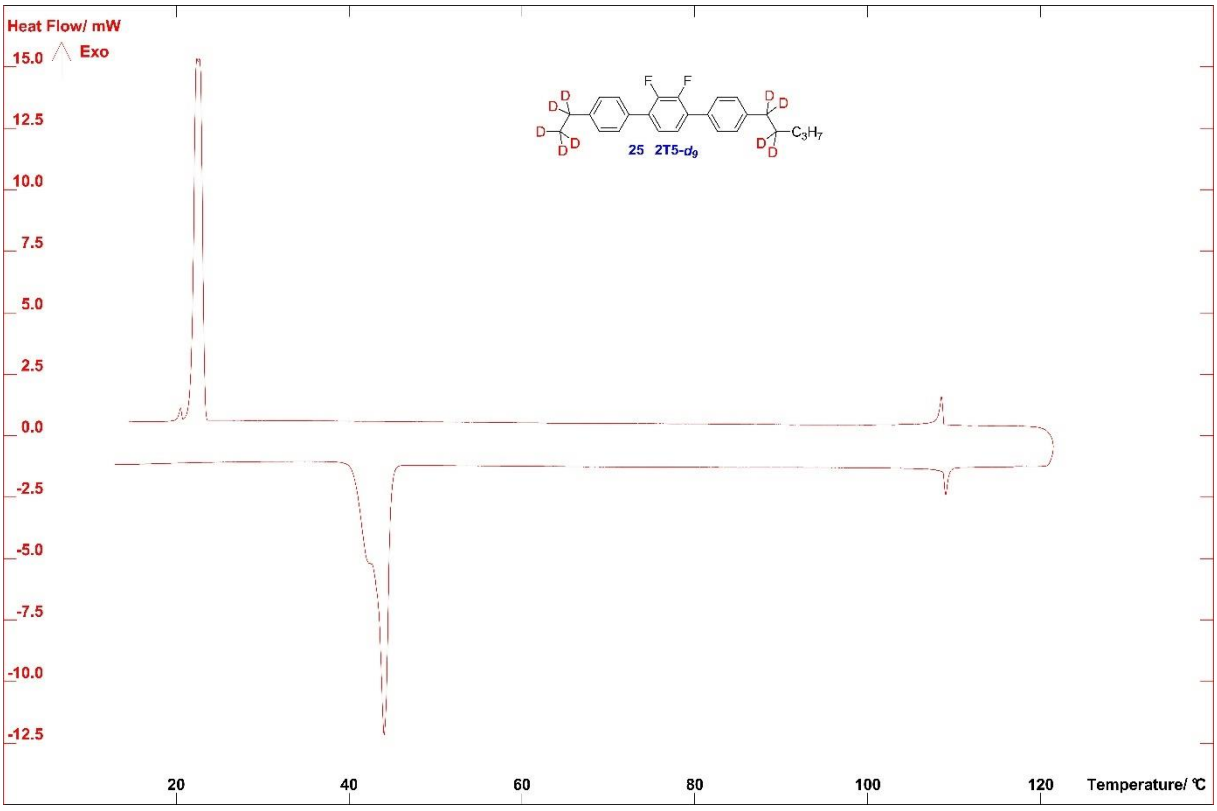


Figure S16. DSC trace of **25**.

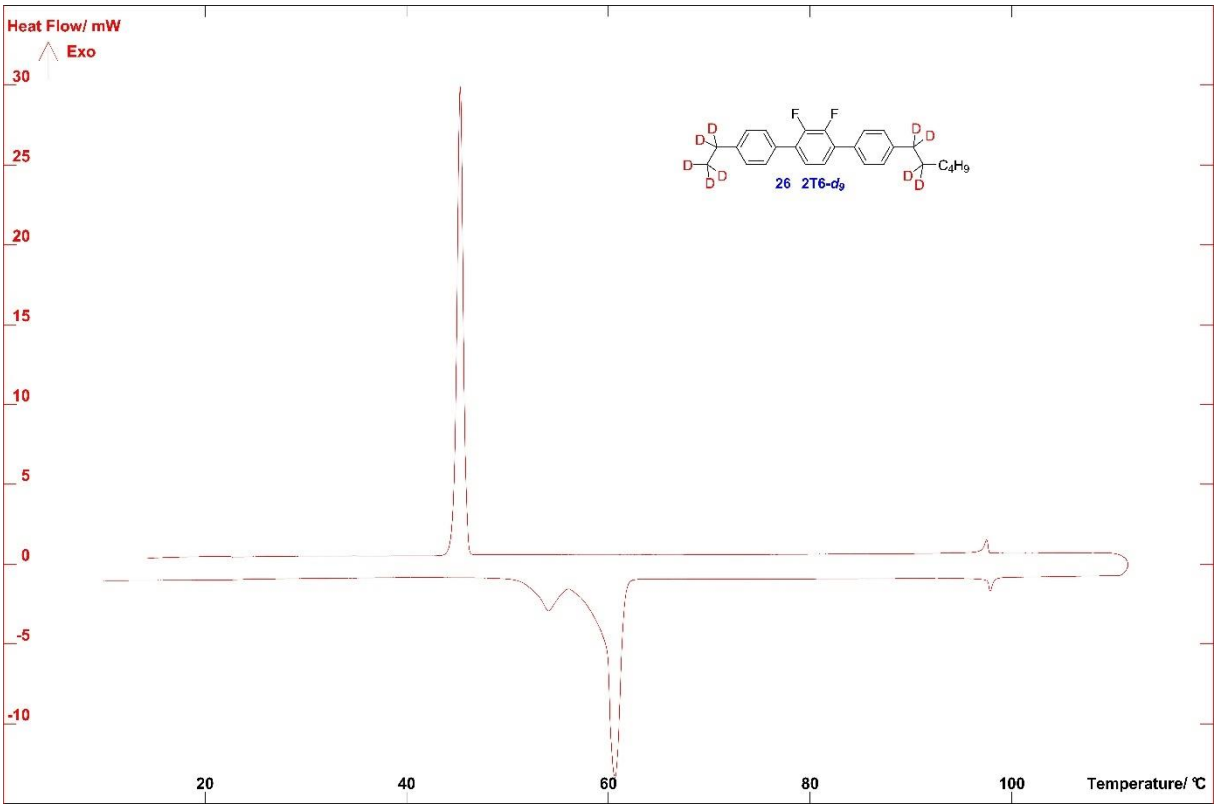


Figure S17. DSC trace of **26**.

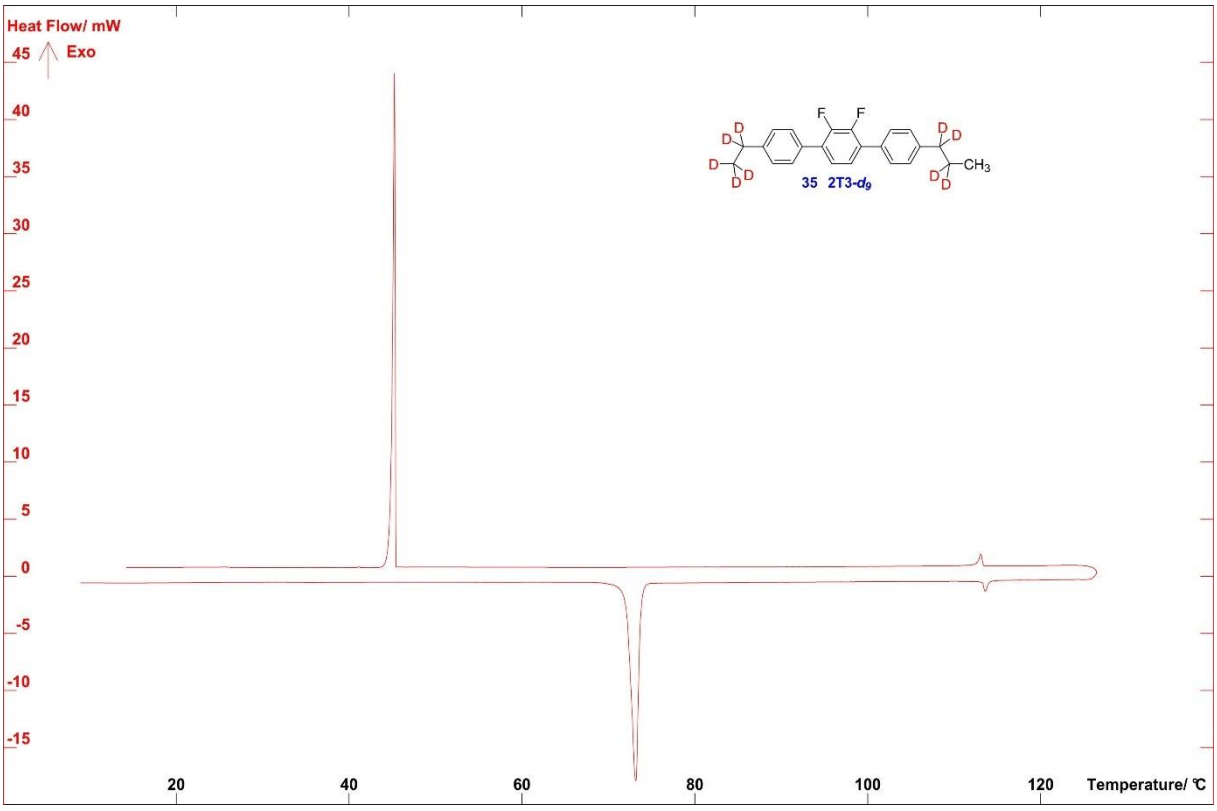


Figure S18. DSC trace of **35**.

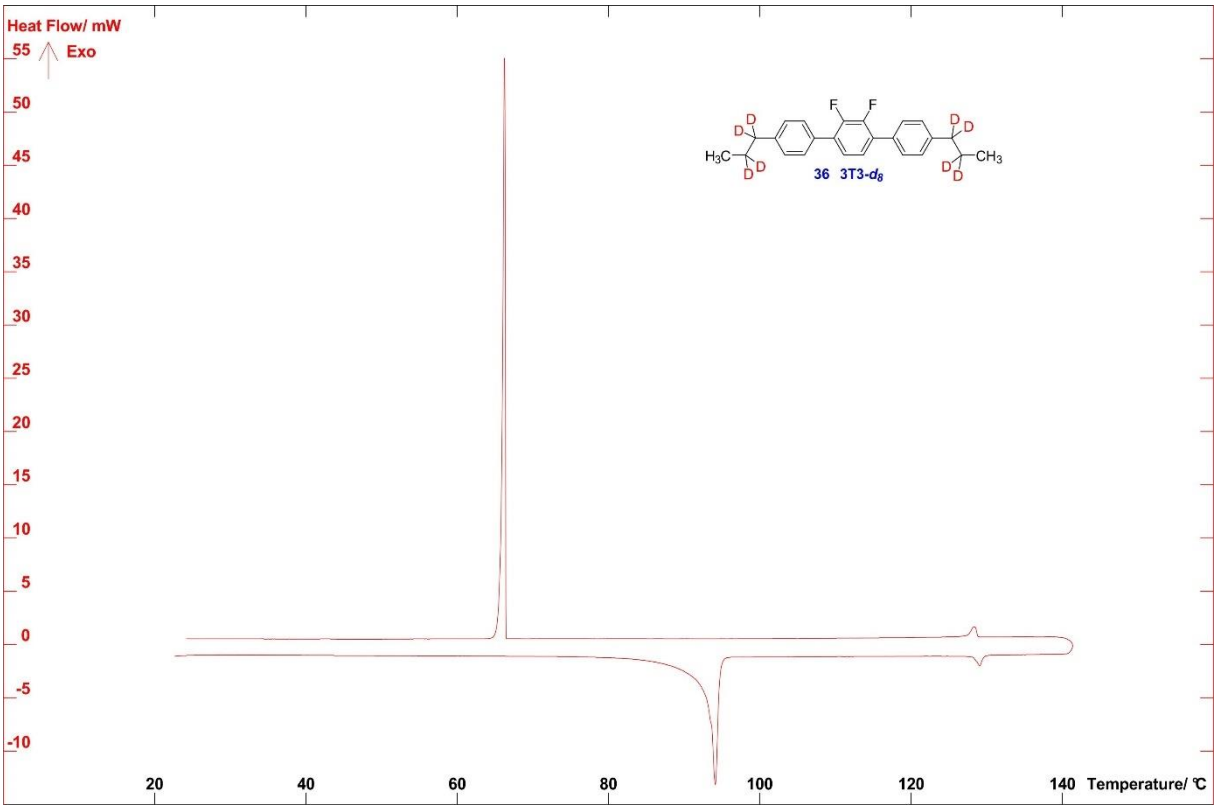


Figure S19. DSC trace of **36**.

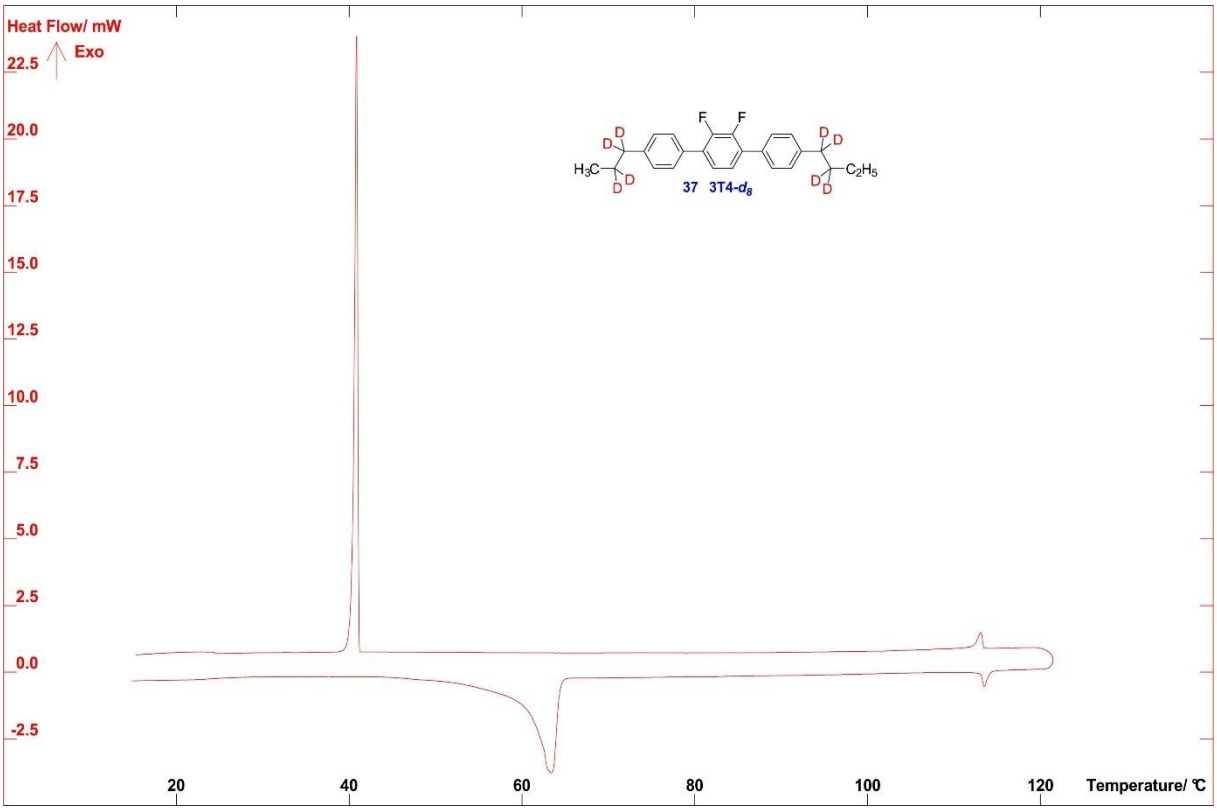


Figure S20. DSC trace of **37**.

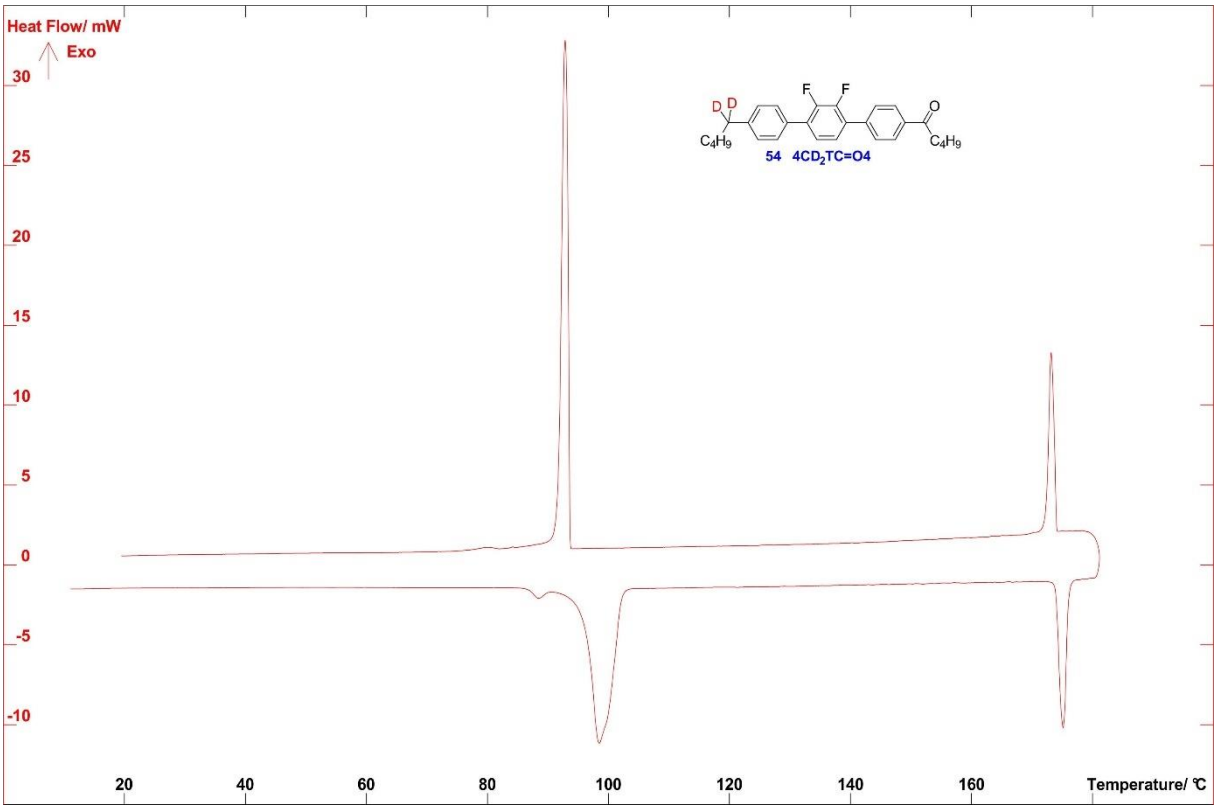


Figure S21. DSC trace of **54**.

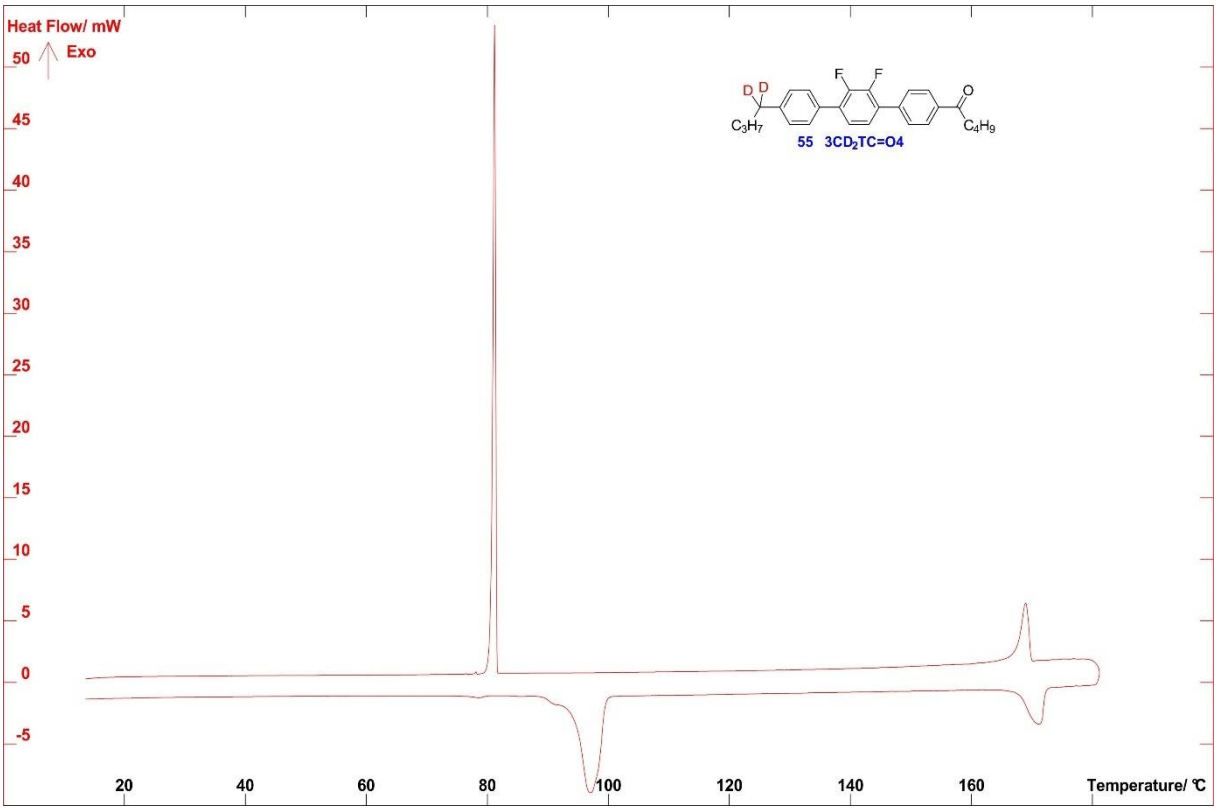


Figure S22. DSC trace of **55** .

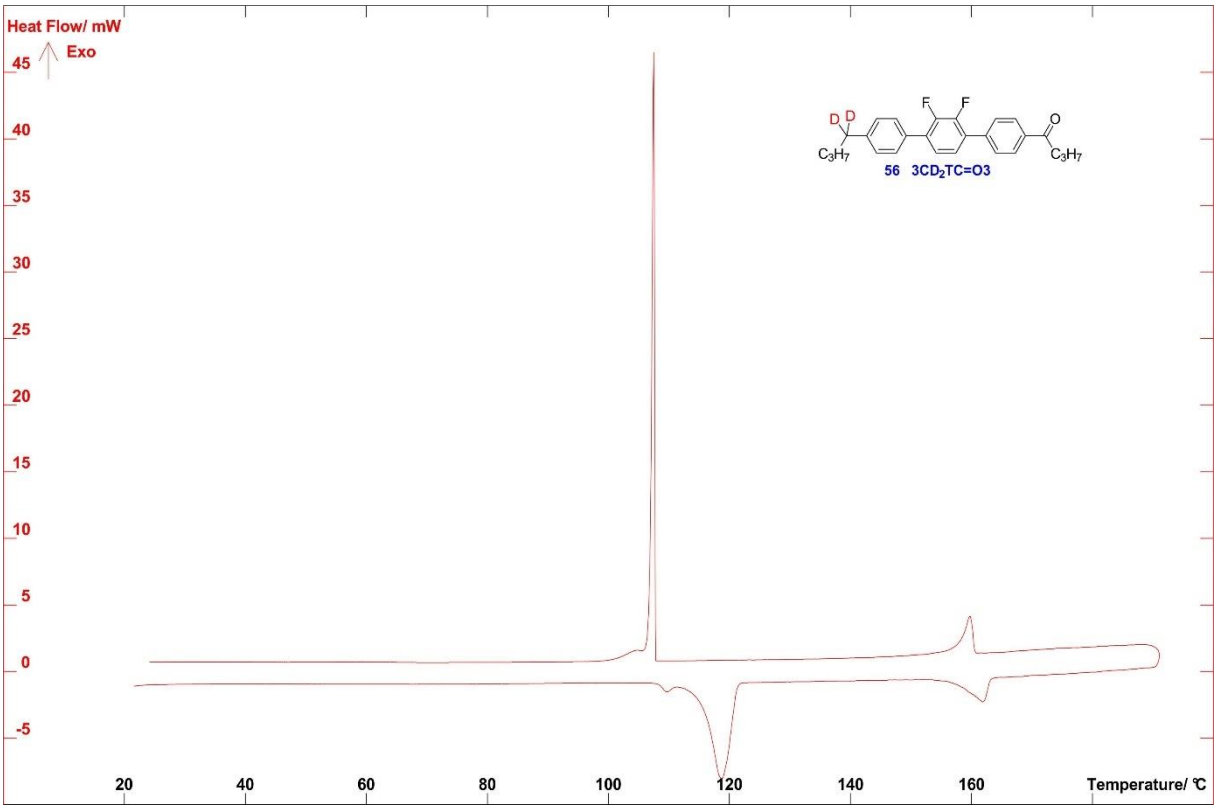


Figure S23. DSC trace of **56**.

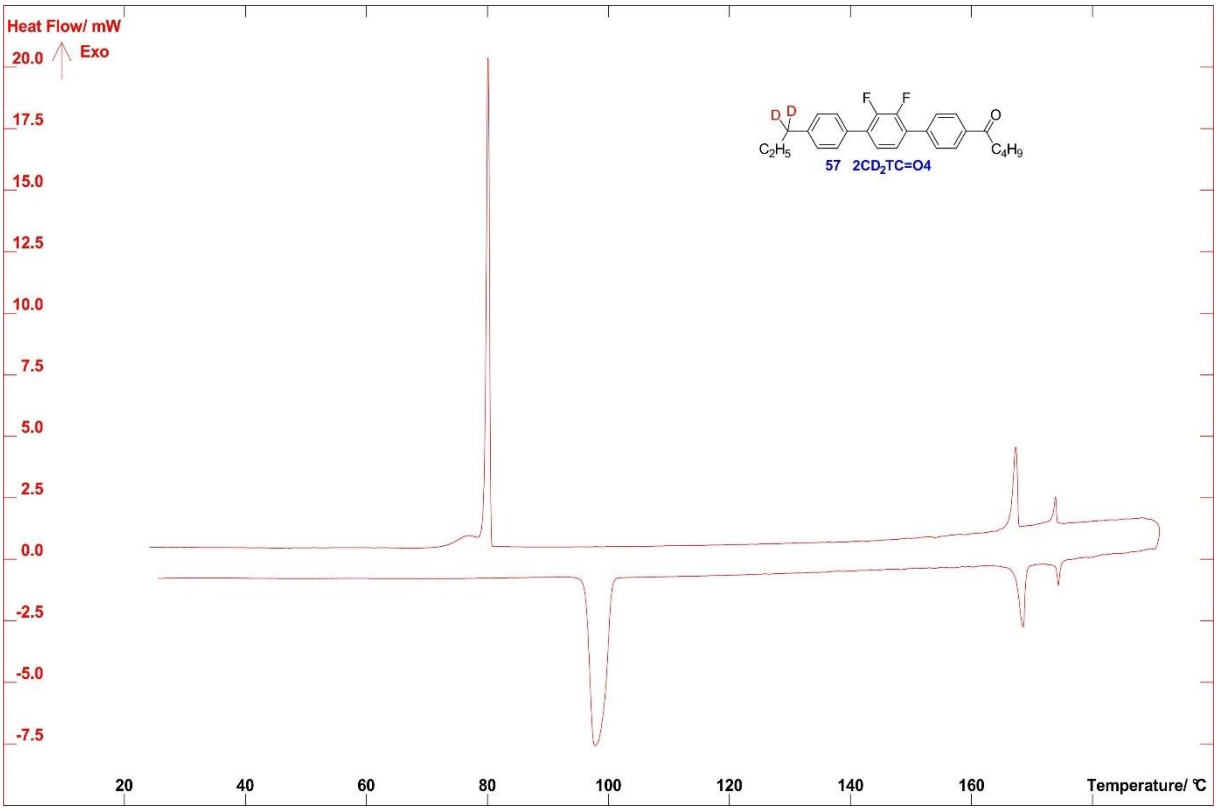


Figure S24. DSC trace of **57**.

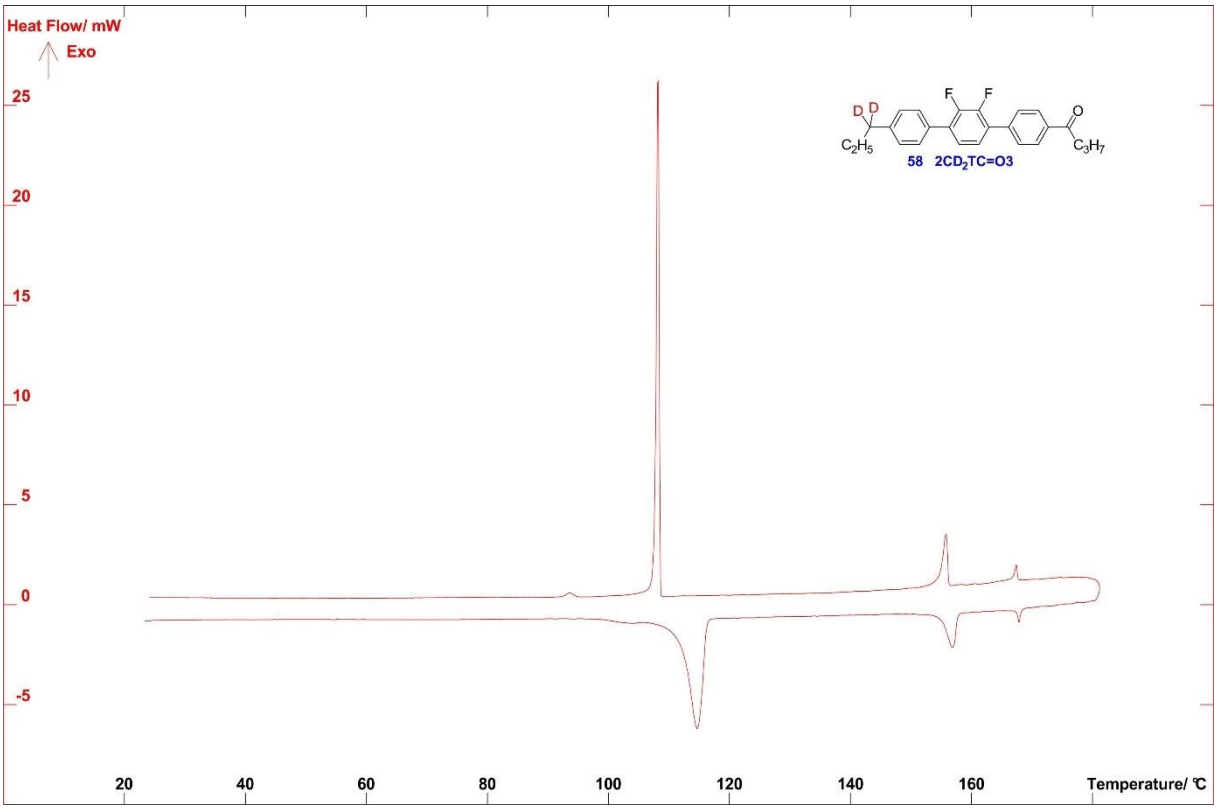


Figure S25. DSC trace of **58**.

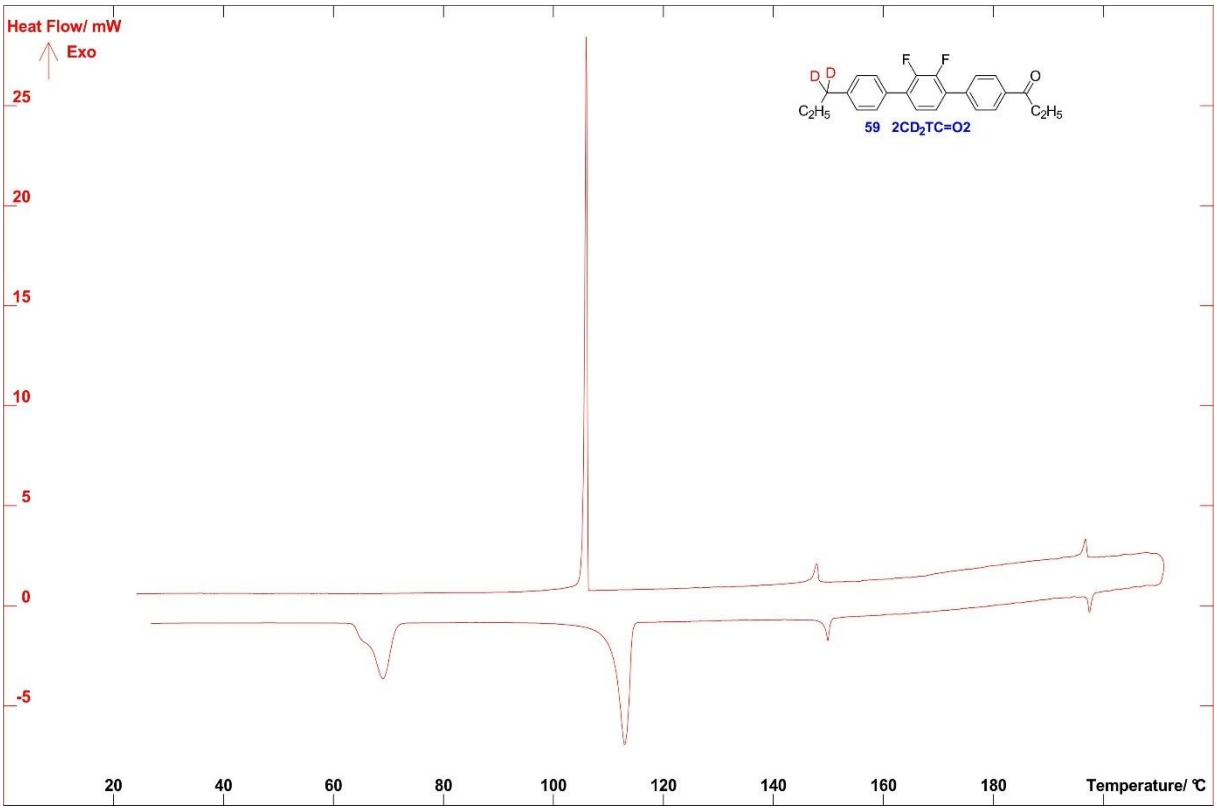


Figure S26. DSC trace of **59**.

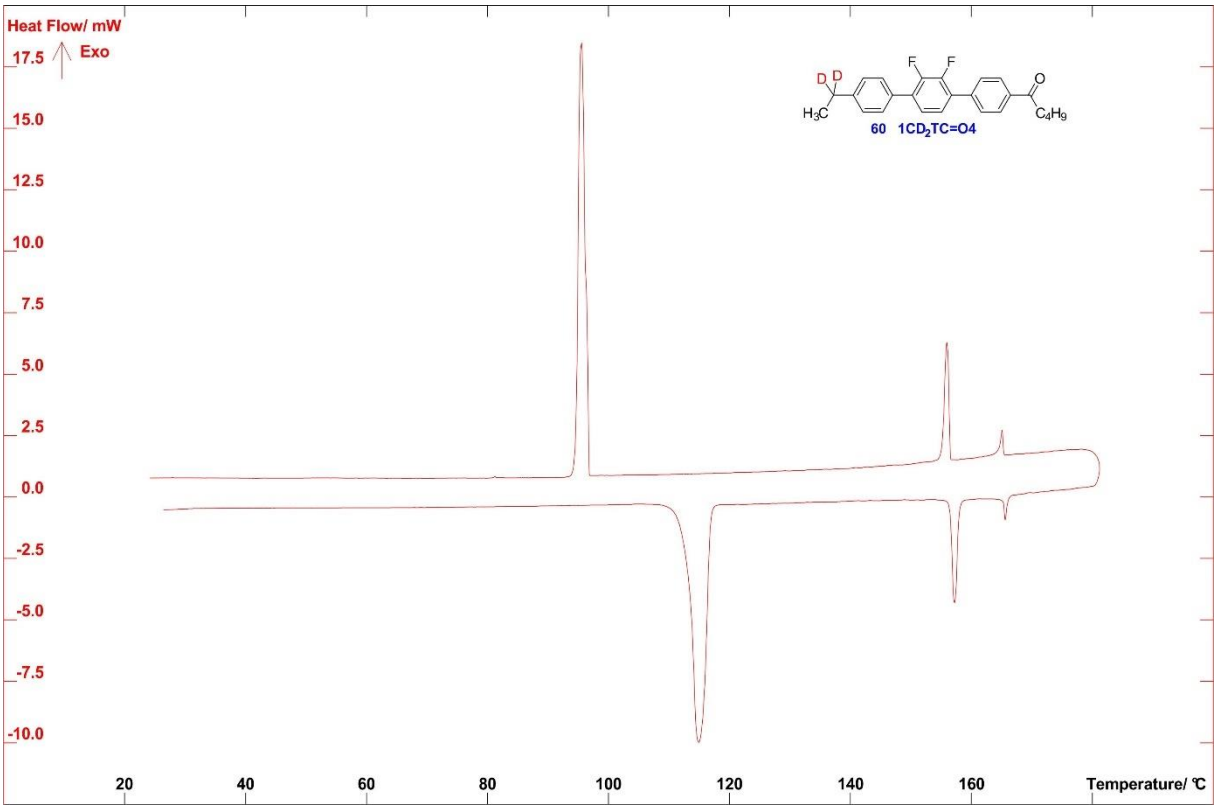


Figure S27. DSC trace of **60**.

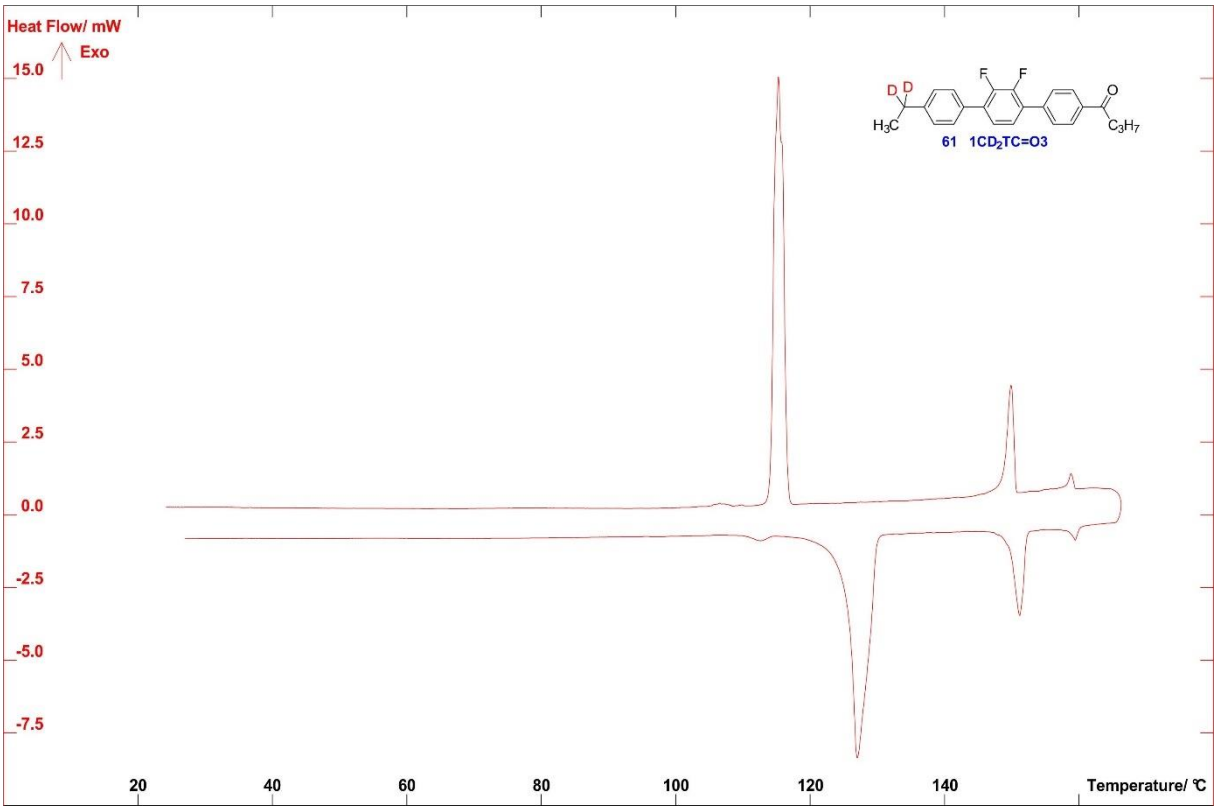


Figure S28. DSC trace of **61**.

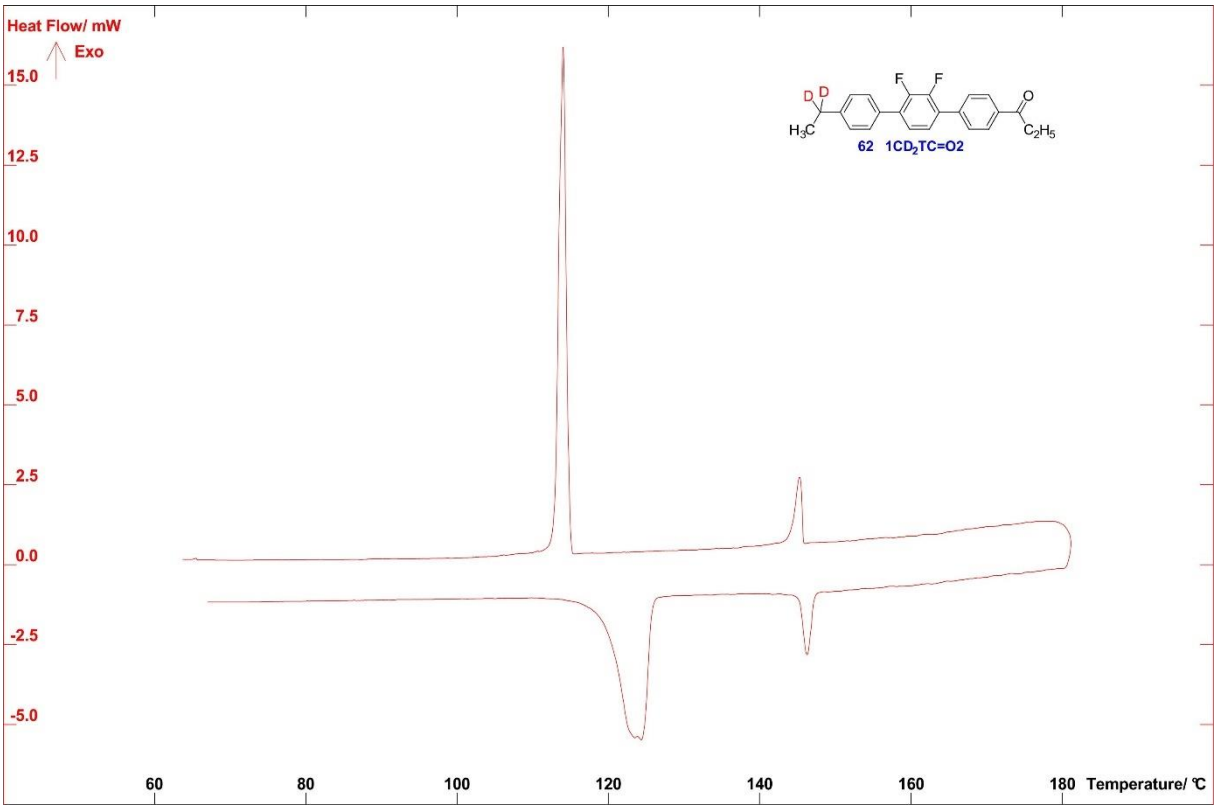


Figure S29. DSC trace of **62**.

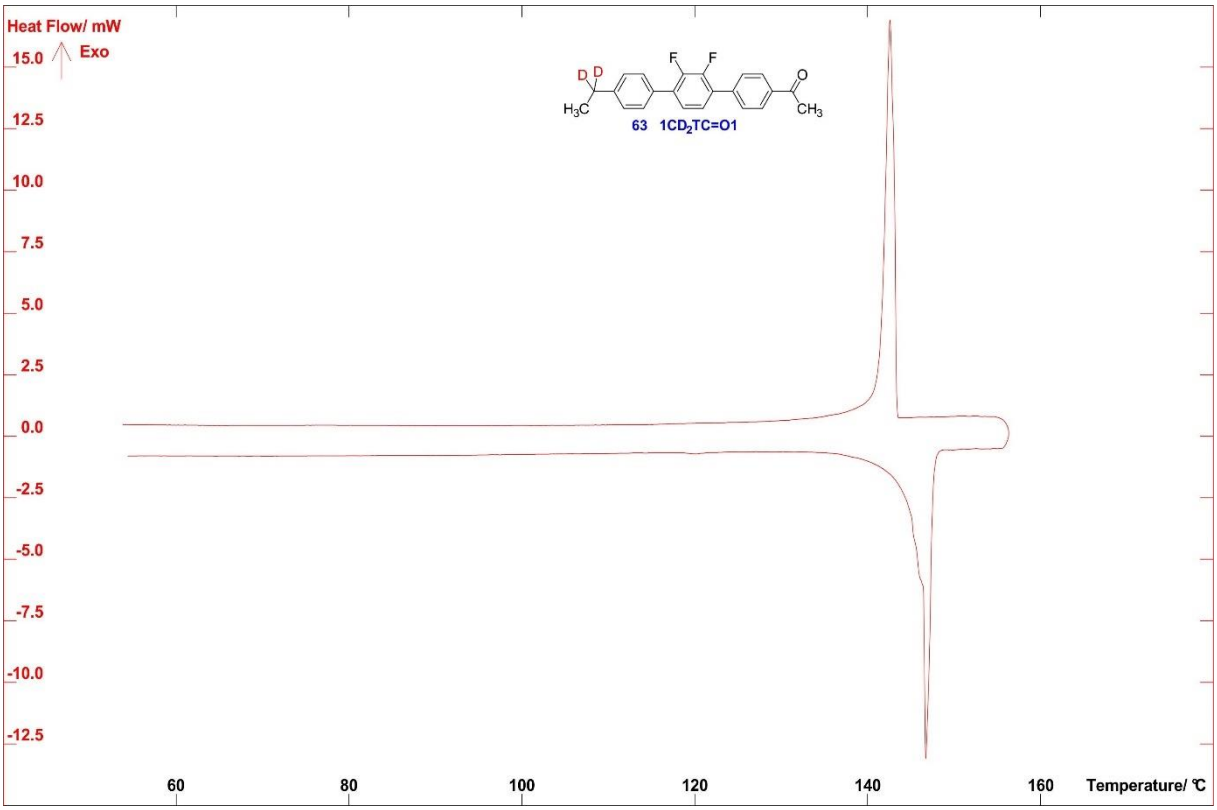


Figure S30. DSC trace of **63**.

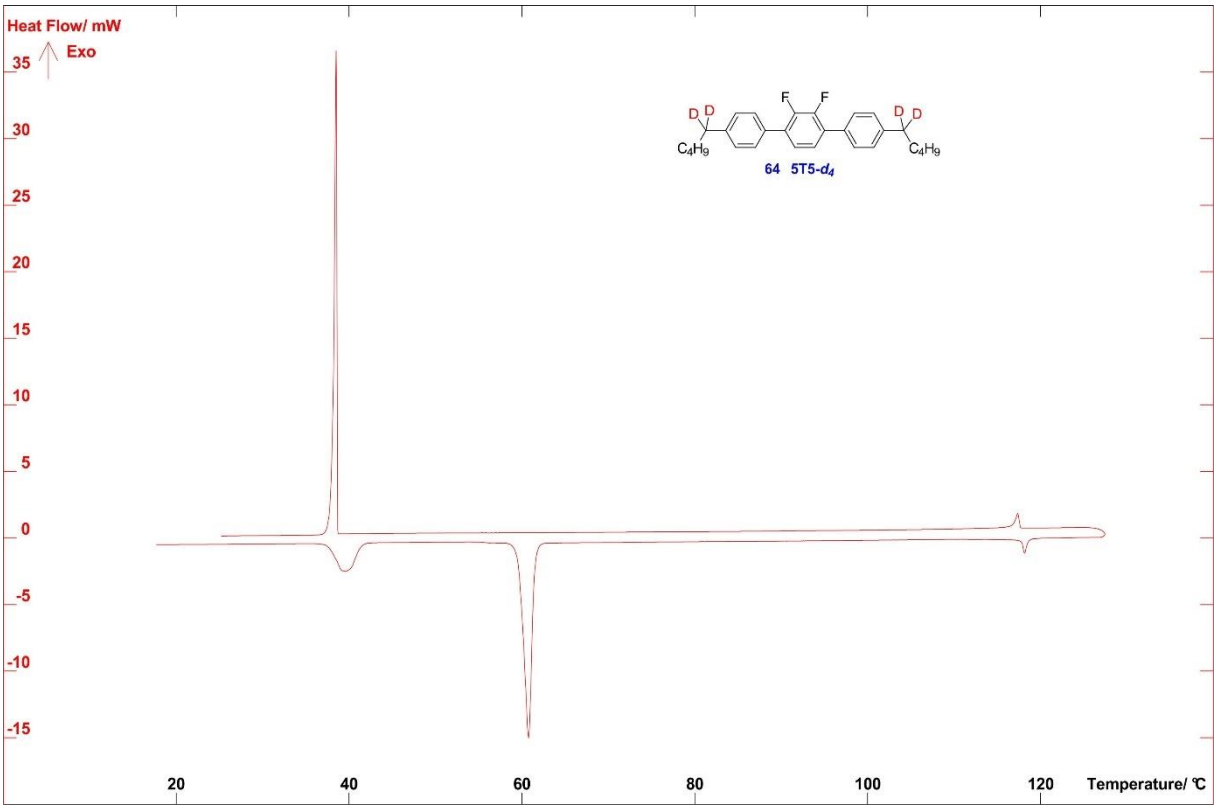


Figure S31. DSC trace of **64**.

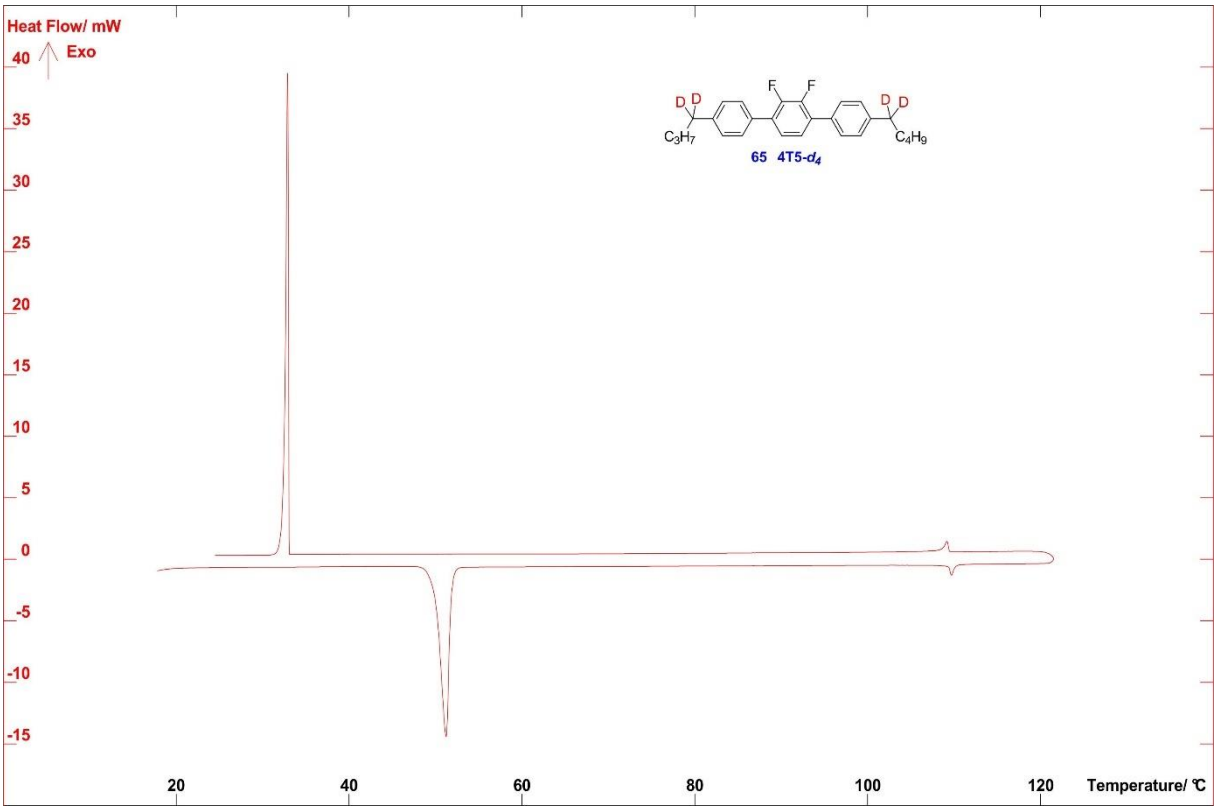


Figure S32. DSC trace of **65**.

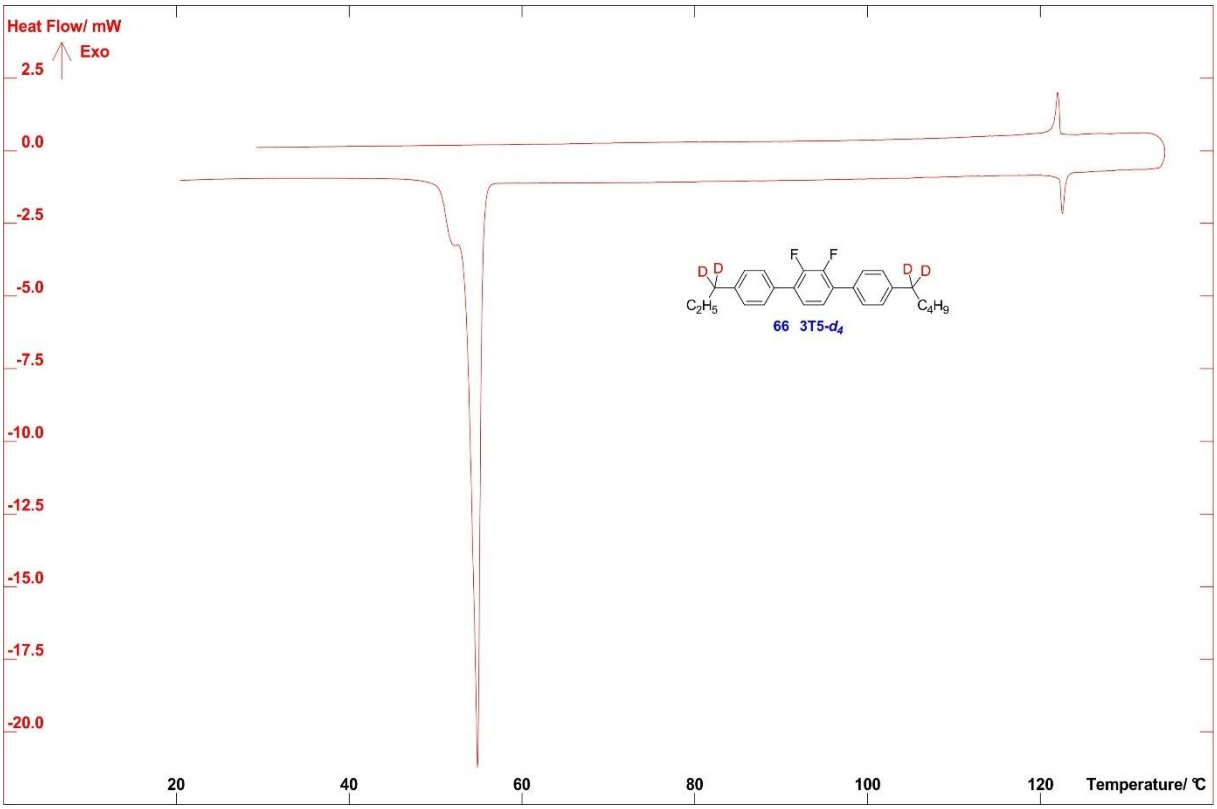


Figure S33. DSC trace of **66**.

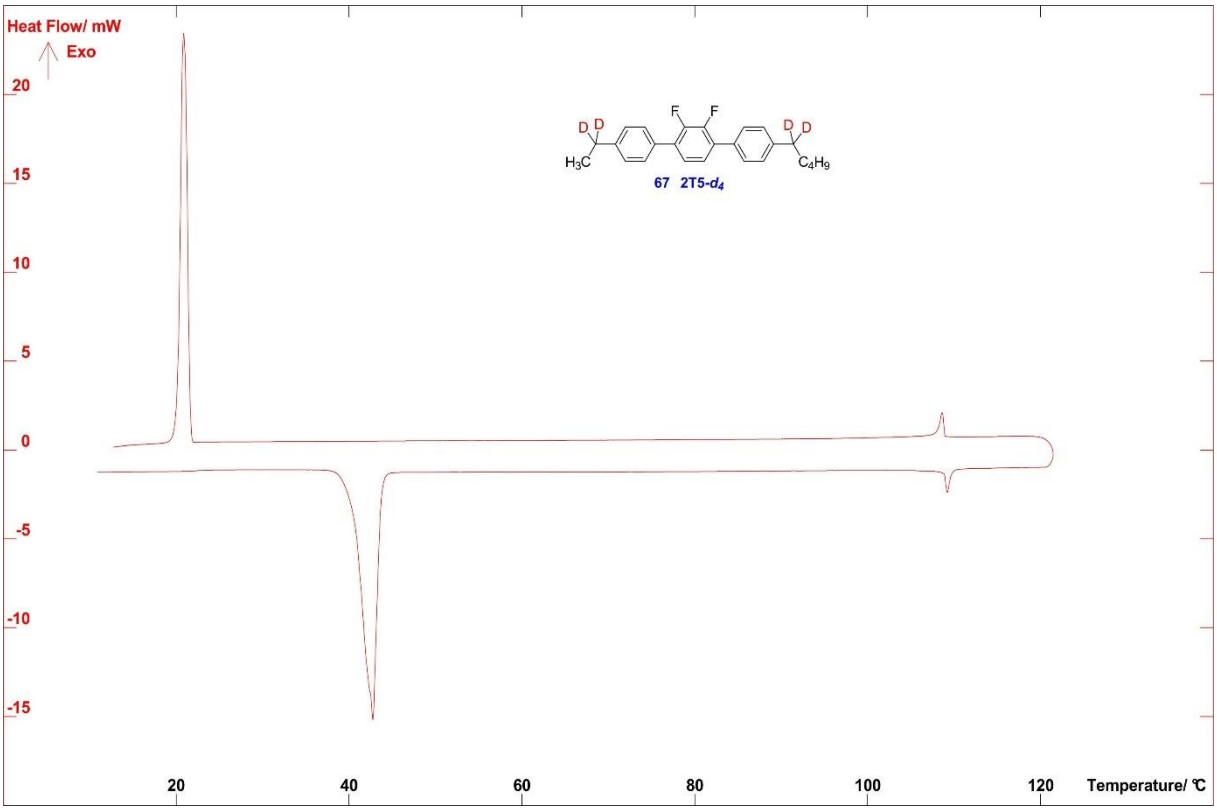


Figure S34. DSC trace of **67**.

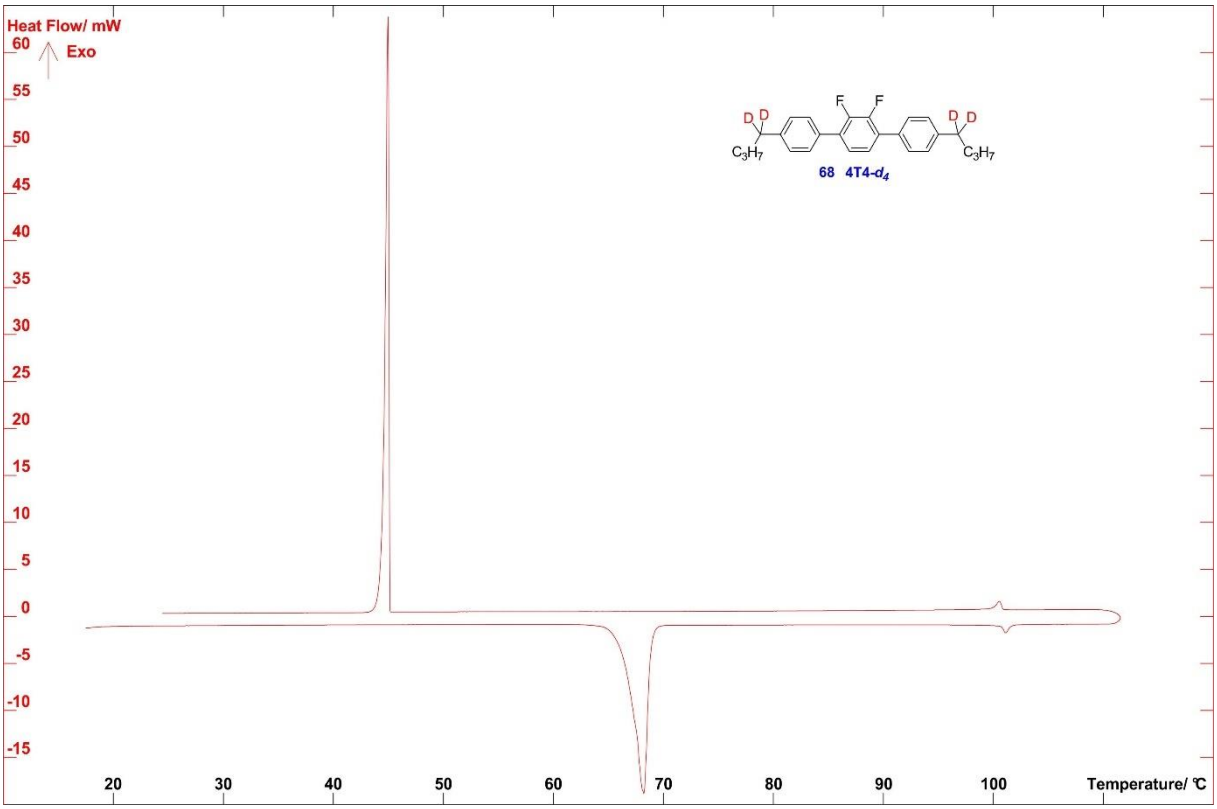


Figure S35. DSC trace of **68**.

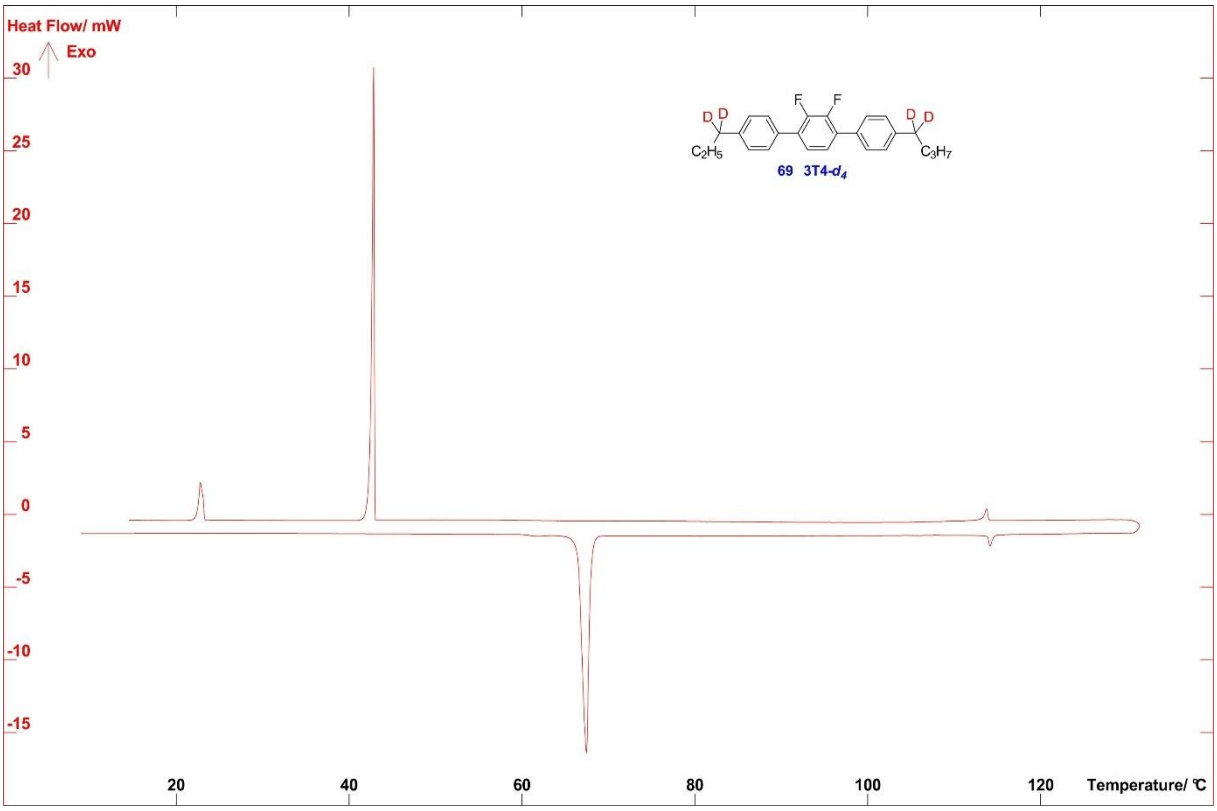


Figure S36. DSC trace of **69**.

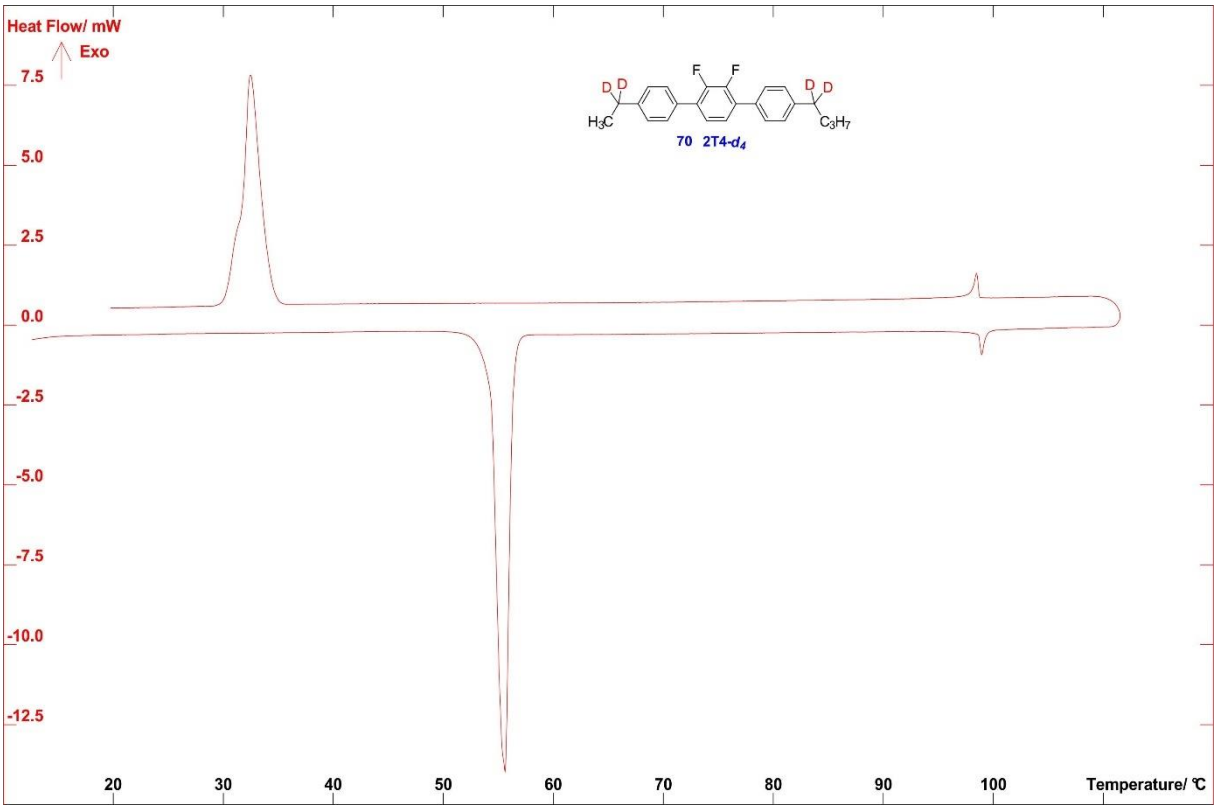


Figure S37. DSC trace of **70**.

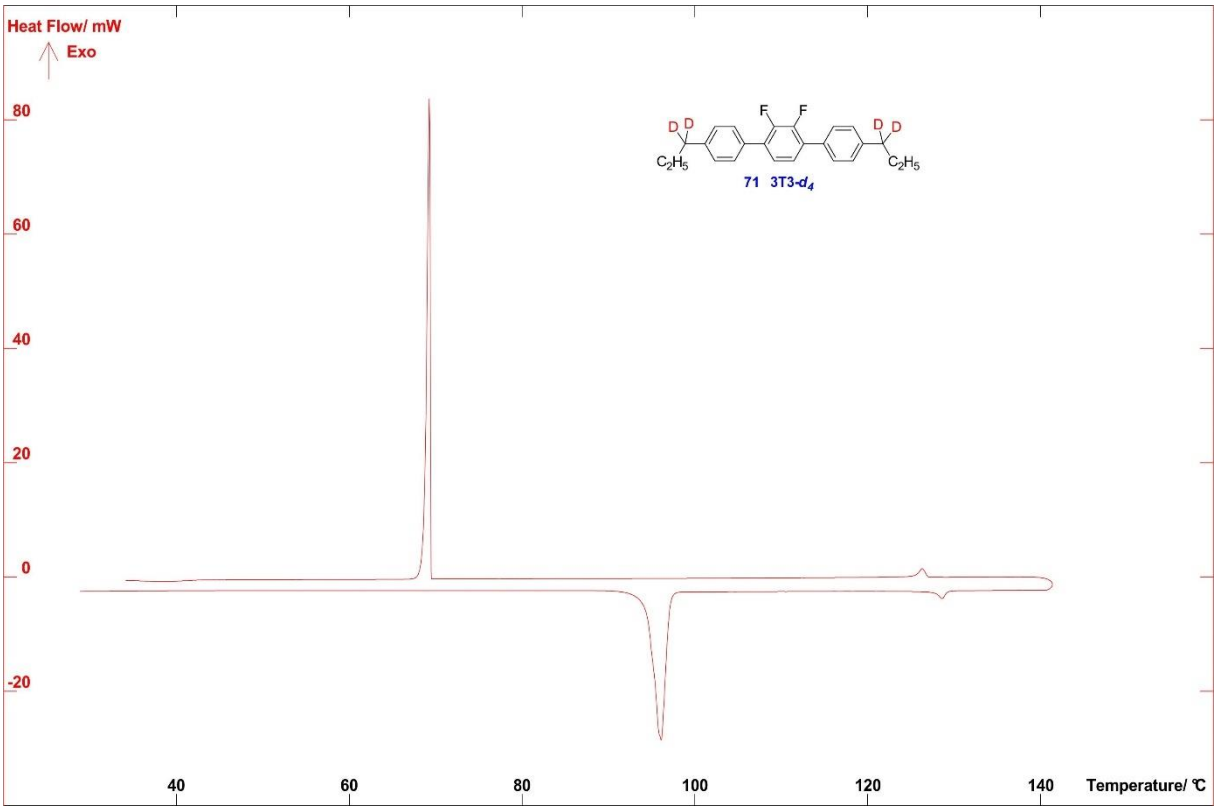


Figure S38. DSC trace of **71**.

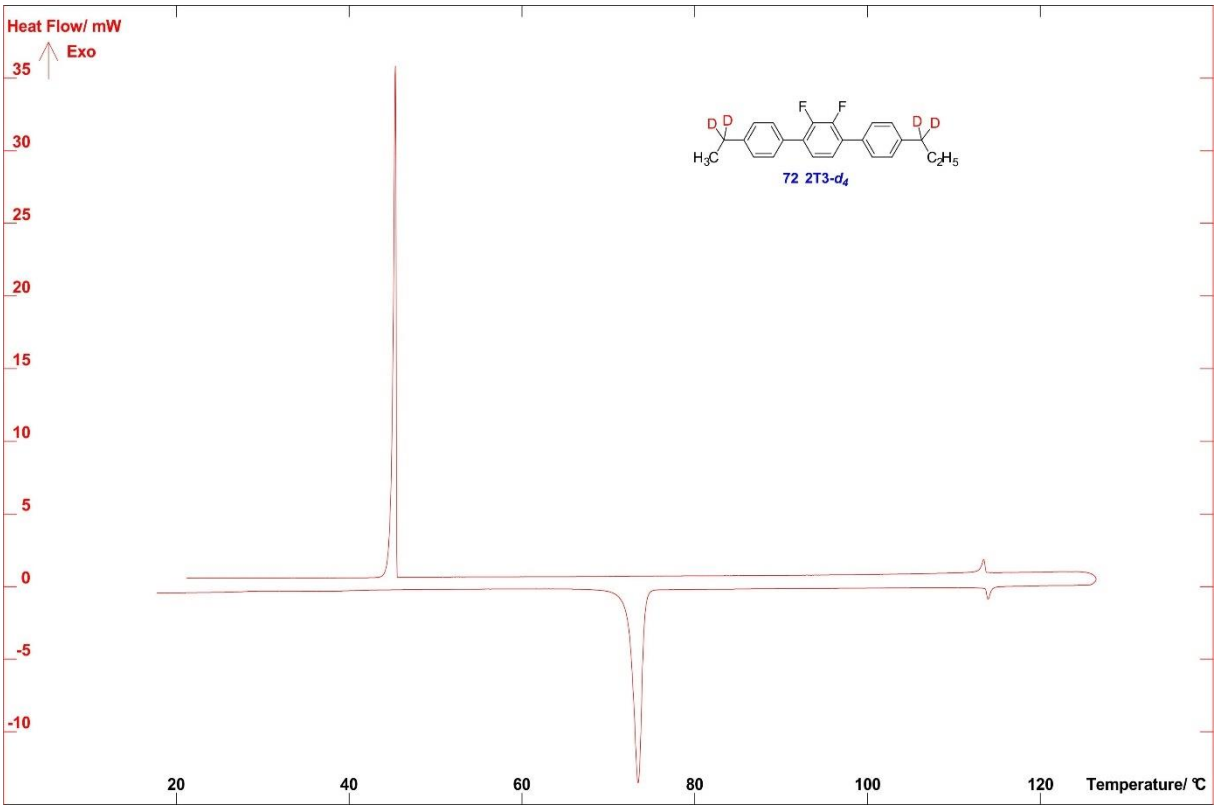


Figure S39. DSC trace of **72**.

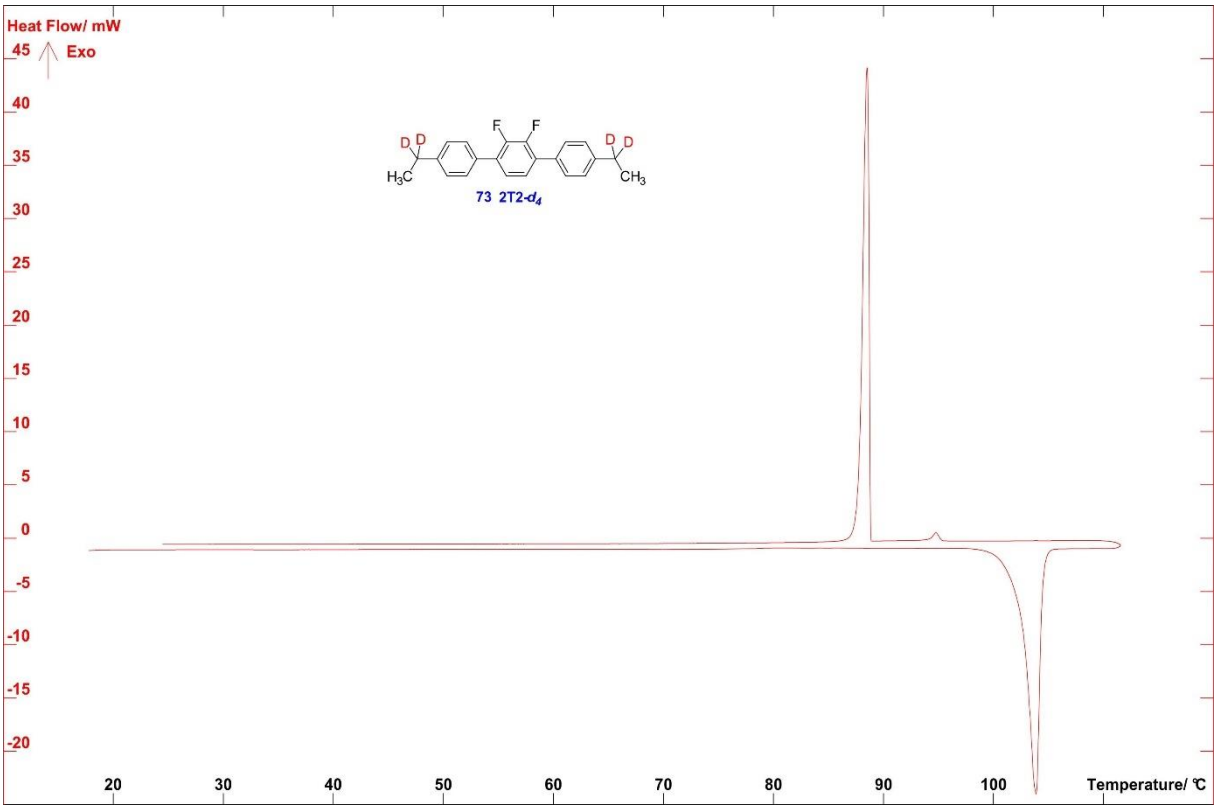


Figure S40. DSC trace of **73**.

6. Fragmentation paths and mass spectra for model compounds

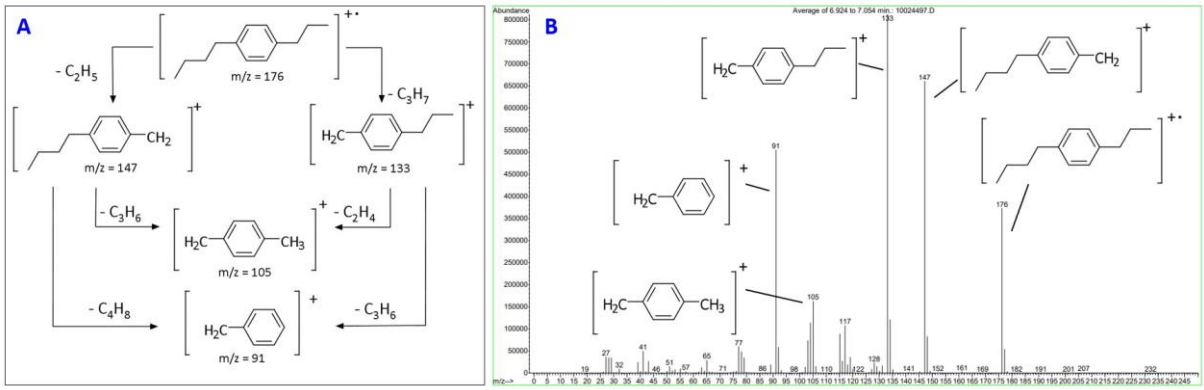


Figure S41. Fragmentation paths (A) and mass spectra (B) for **M1**.

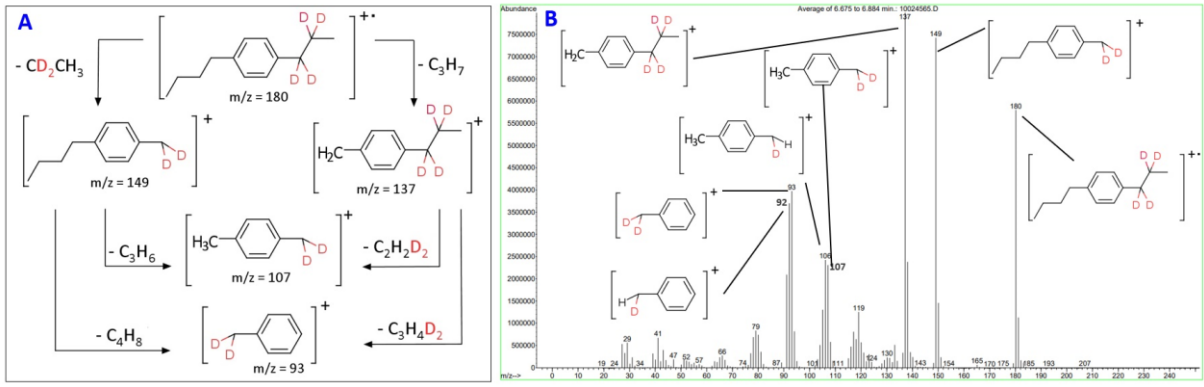


Figure S42. Fragmentation paths (A) and mass spectra (B) for **M3**.

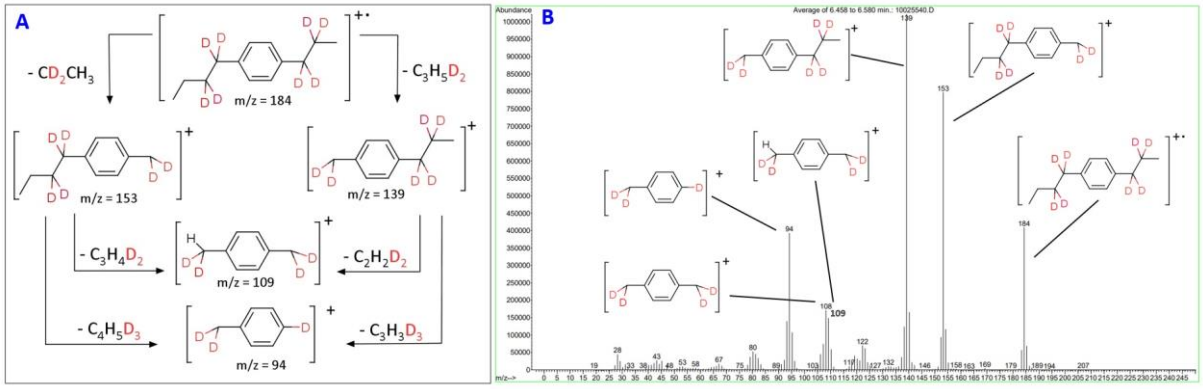


Figure S43. Fragmentation paths (A) and mass spectra (B) for **M5**.

7. Photodegradation - DSC analysis

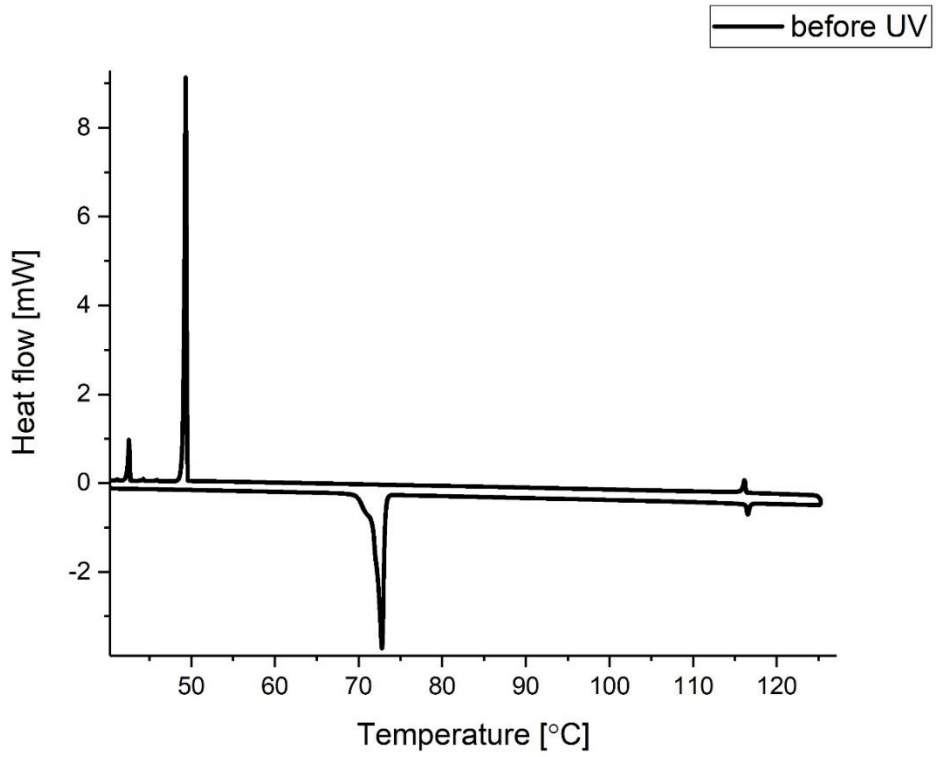


Figure S44. DSC trace of **2T3 H** before UV exposure.

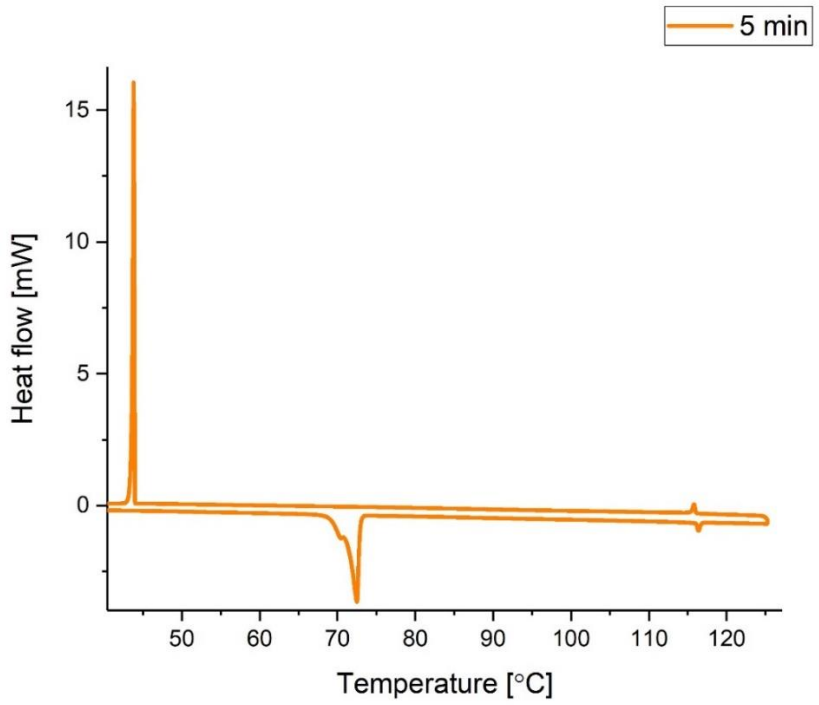


Figure S45. DSC trace of **2T3 H** after 5 min of UV exposure.

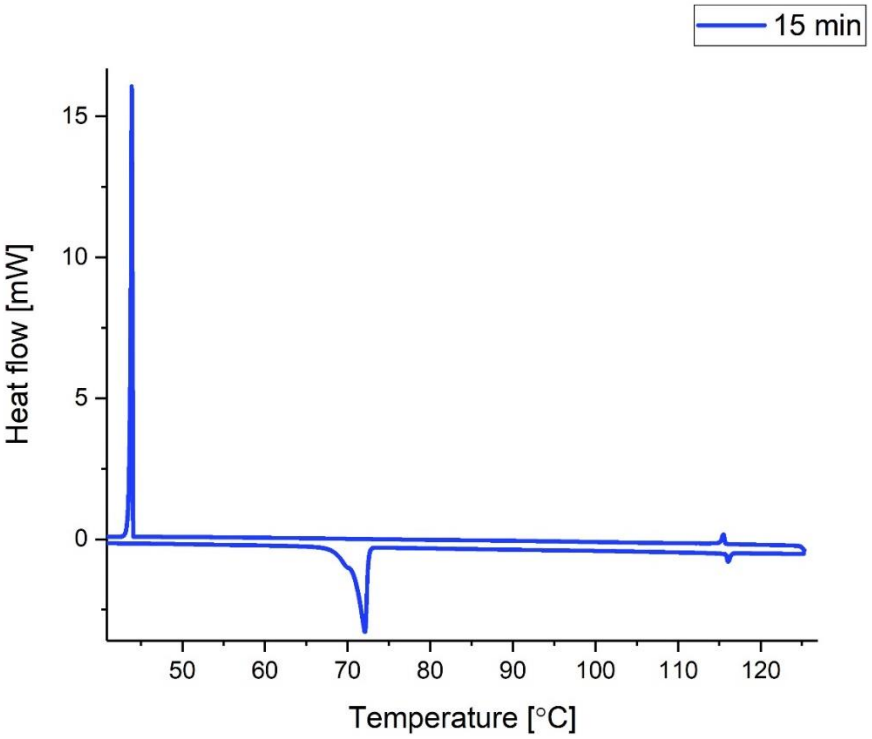


Figure S46. DSC trace of **2T3 H** after 15 min of UV exposure.

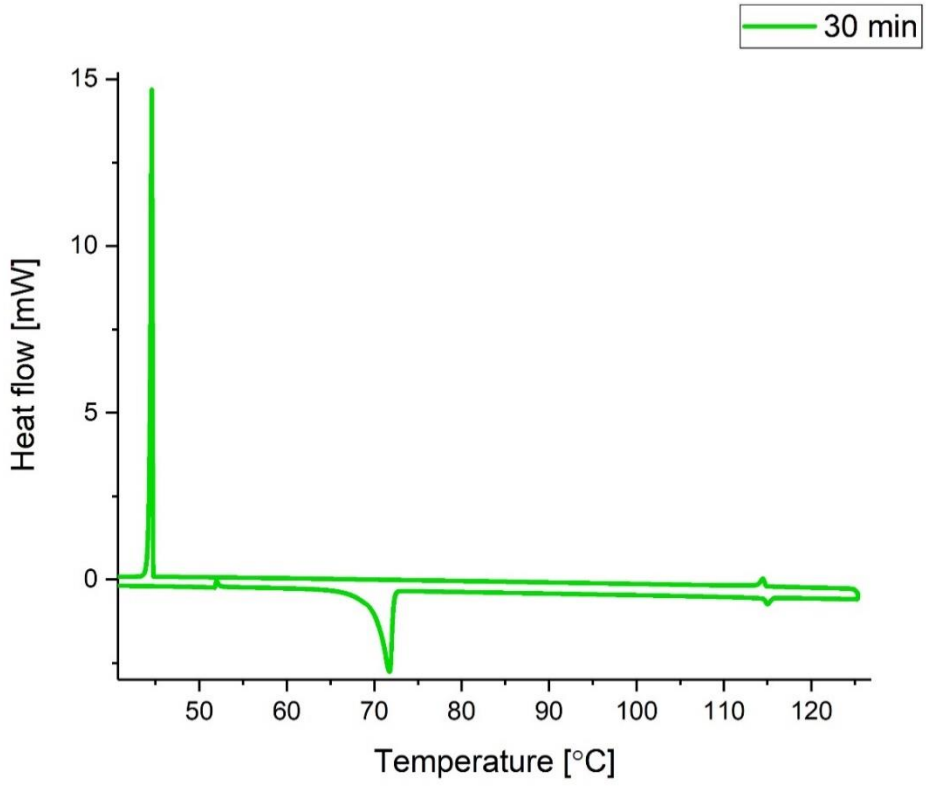


Figure S47. DSC trace of **2T3 H** after 30 min of UV exposure.

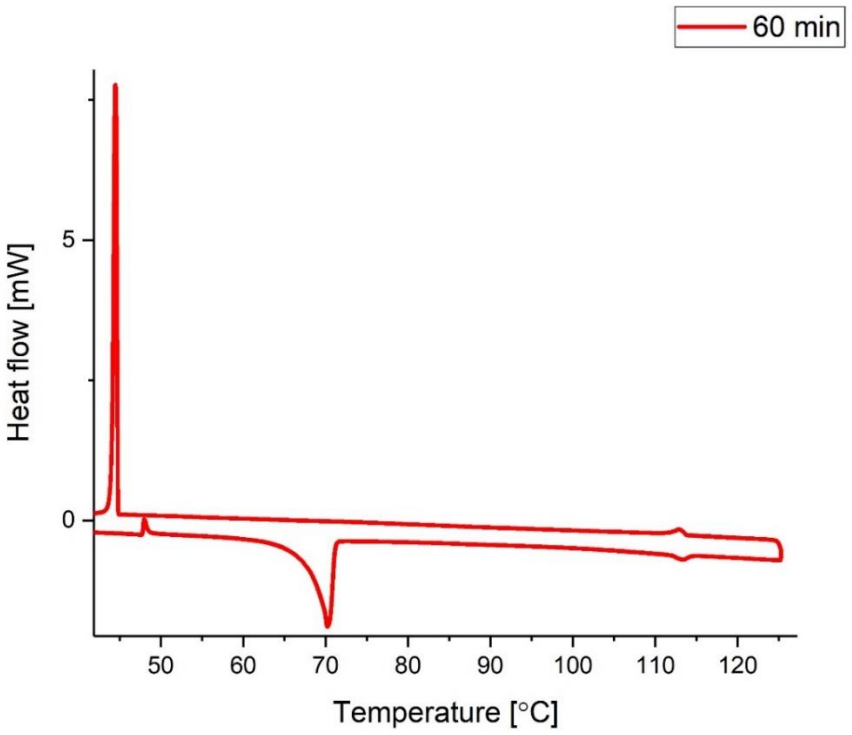


Figure S48. DSC trace of **2T3 H** after 60 min of UV exposure.

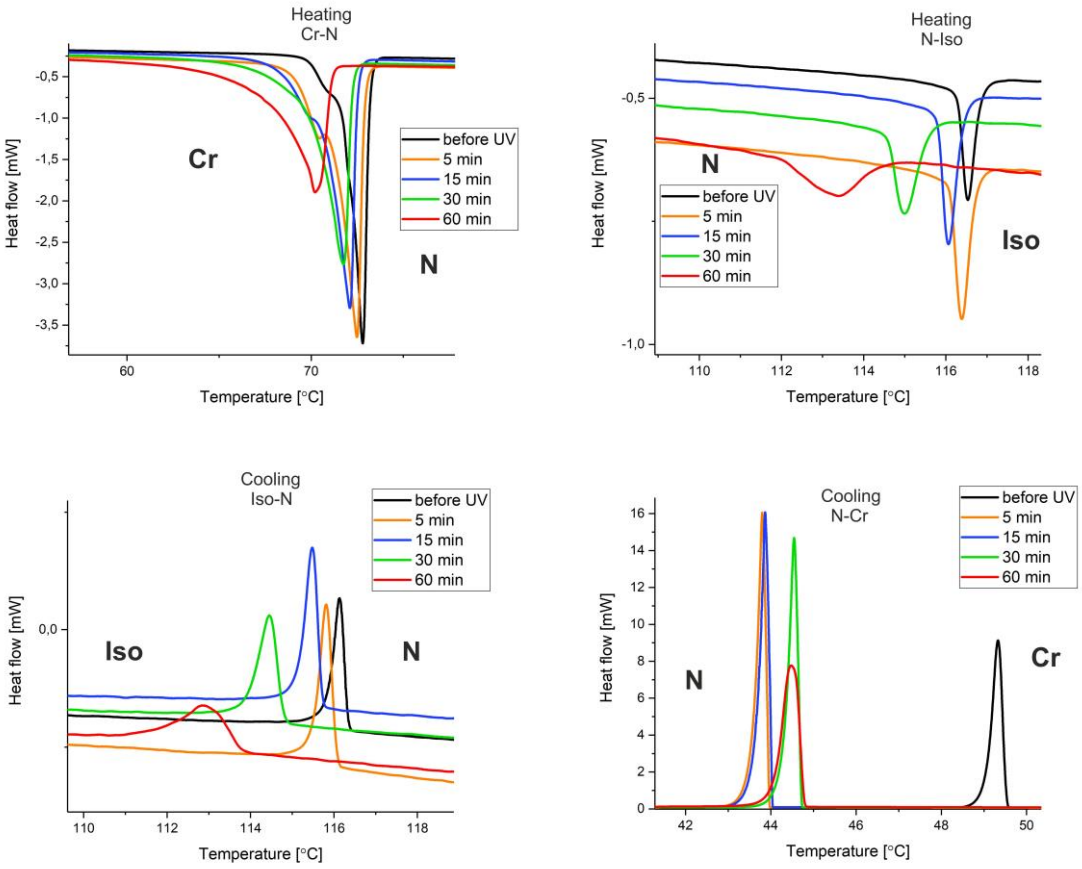


Figure S49. DSC trace of **2T3 H** before and after 5, 15, 30 and 60 min of UV exposure – comparison.

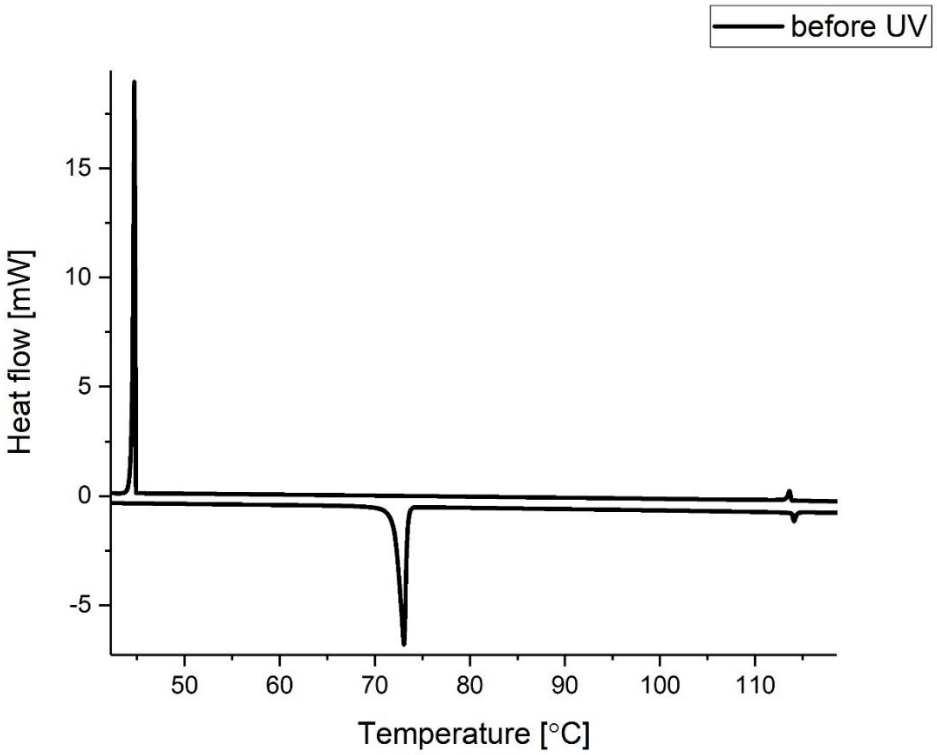


Figure S50. DSC trace of **2T3-*d*$_4$ 72** before UV exposure.

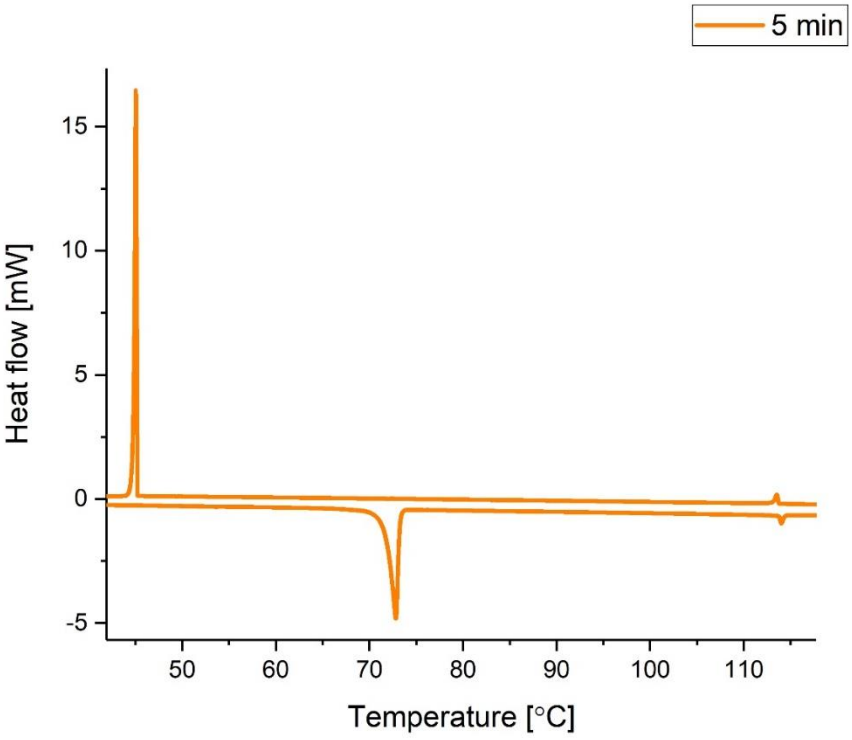


Figure S51. DSC trace of **2T3-*d*$_4$ 72** after 5 min of UV exposure.

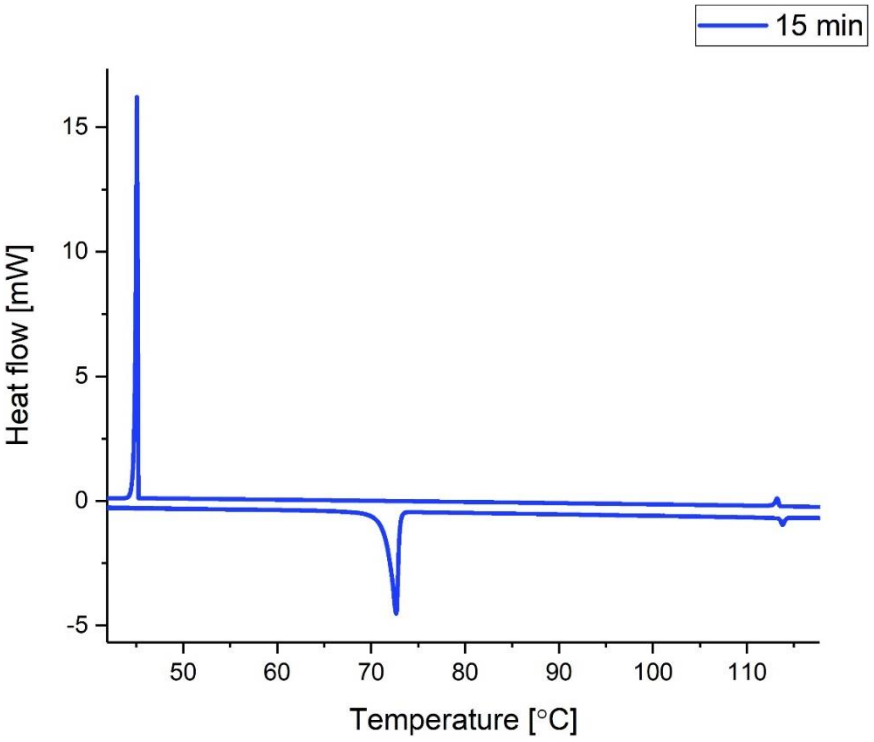


Figure S52. DSC trace of **2T3-*d*$_4$ 72** after 15 min of UV exposure.

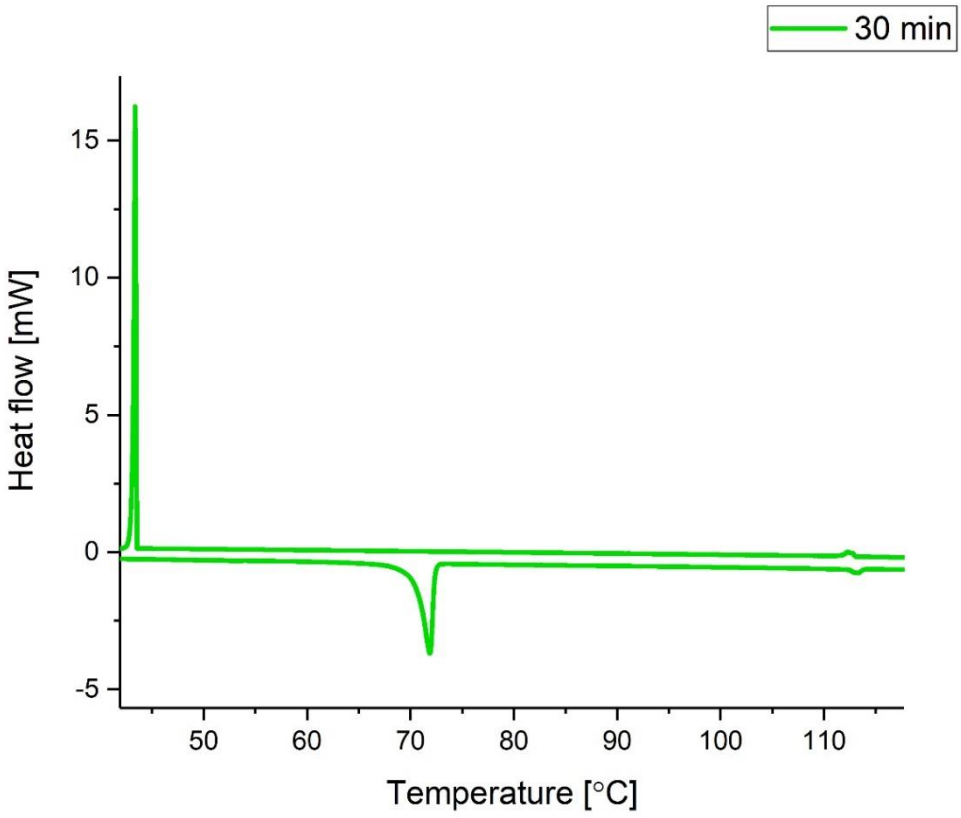


Figure S53. DSC trace of **2T3-*d*$_4$ 72** after 30 min of UV exposure.

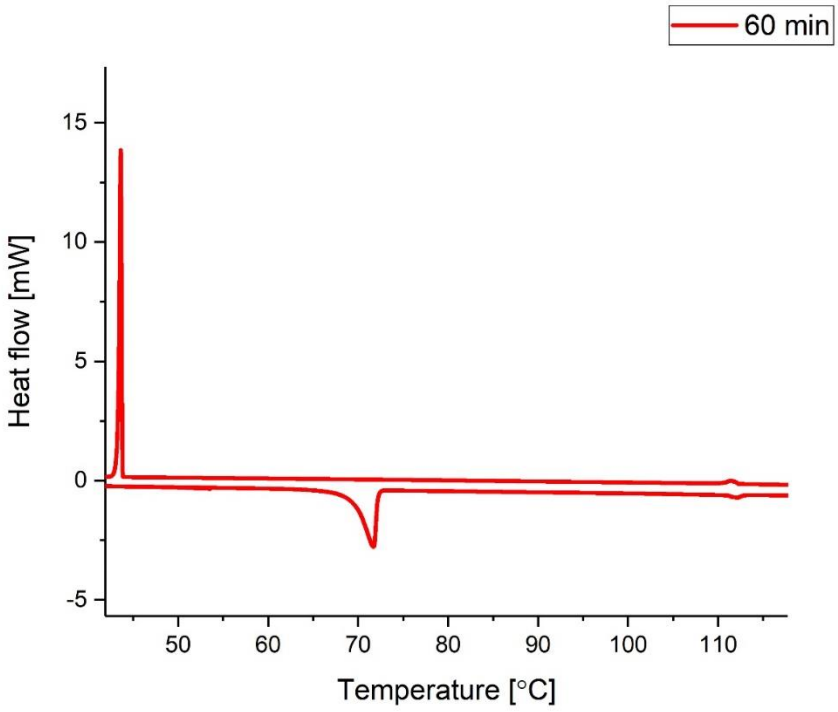


Figure S54. DSC trace of **2T3-*d*$_4$ 72** after 60 min of UV exposure.

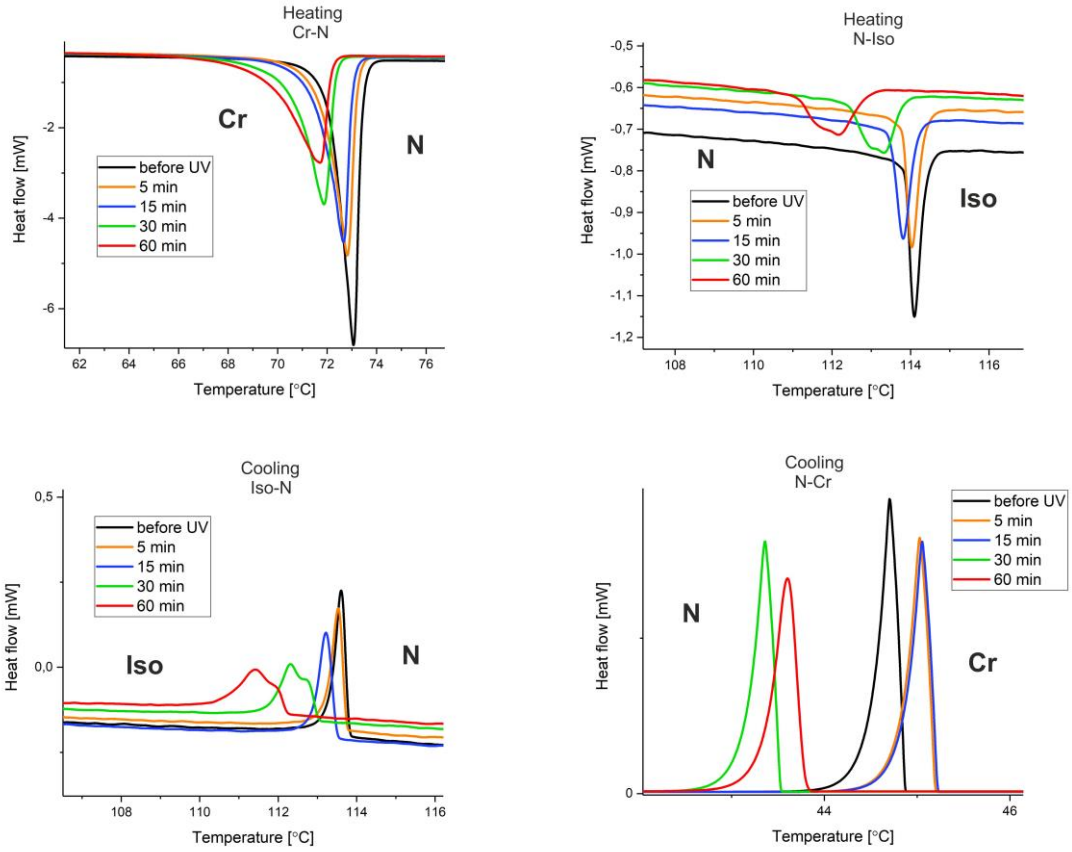


Figure S55. DSC trace of **2T3-*d*$_4$ 72** before and after 5, 15, 30 and 60 min of UV exposure – comparison.

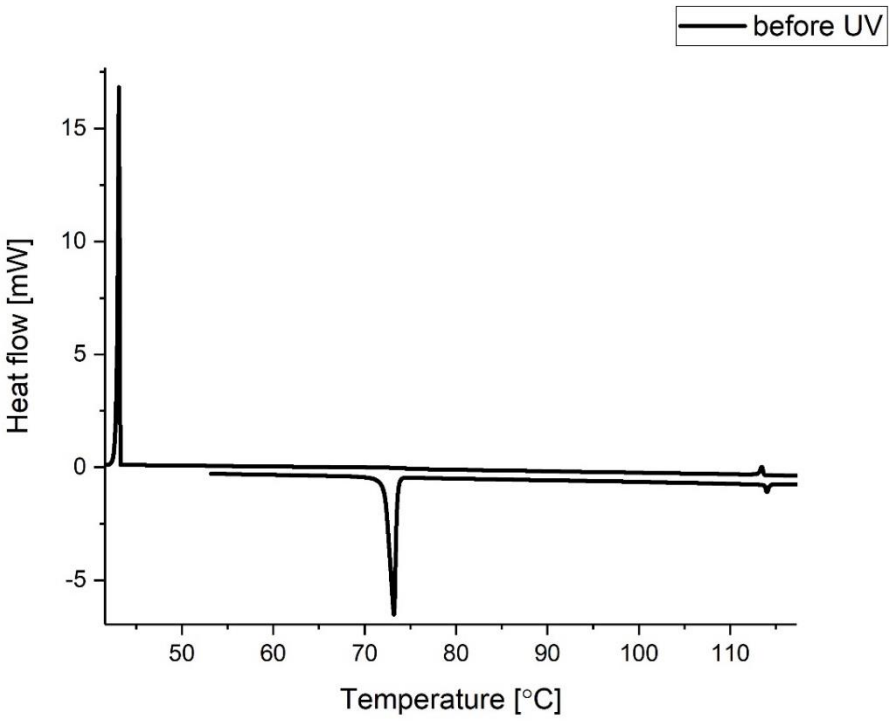


Figure S56. DSC trace of **2T3-*d*$_9$ 35** before UV exposure.

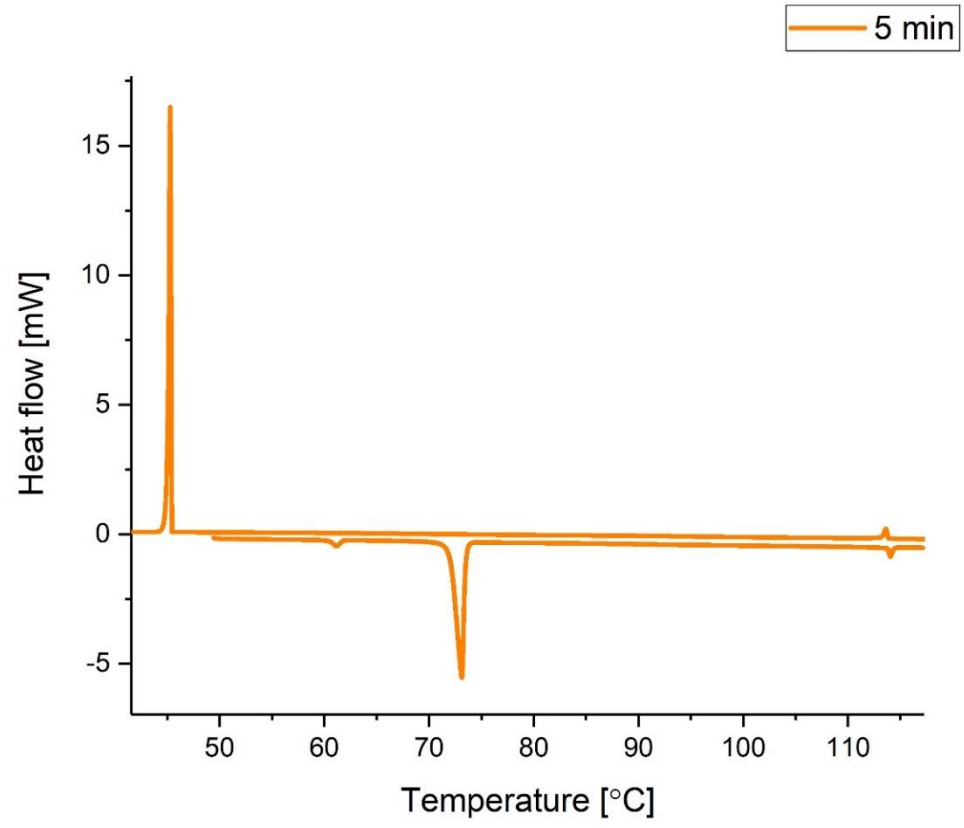


Figure S57. DSC trace of **2T3-*d9* 35** after 5 min of UV exposure.

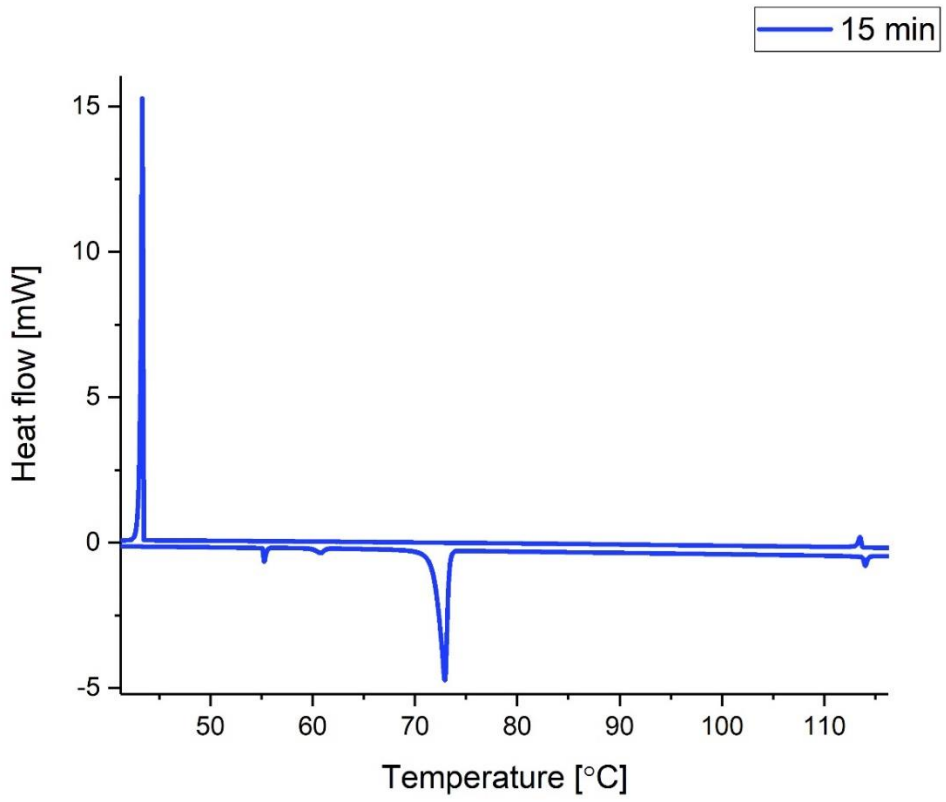


Figure S58. DSC trace of **2T3-d_9 35** after 15 min of UV exposure.

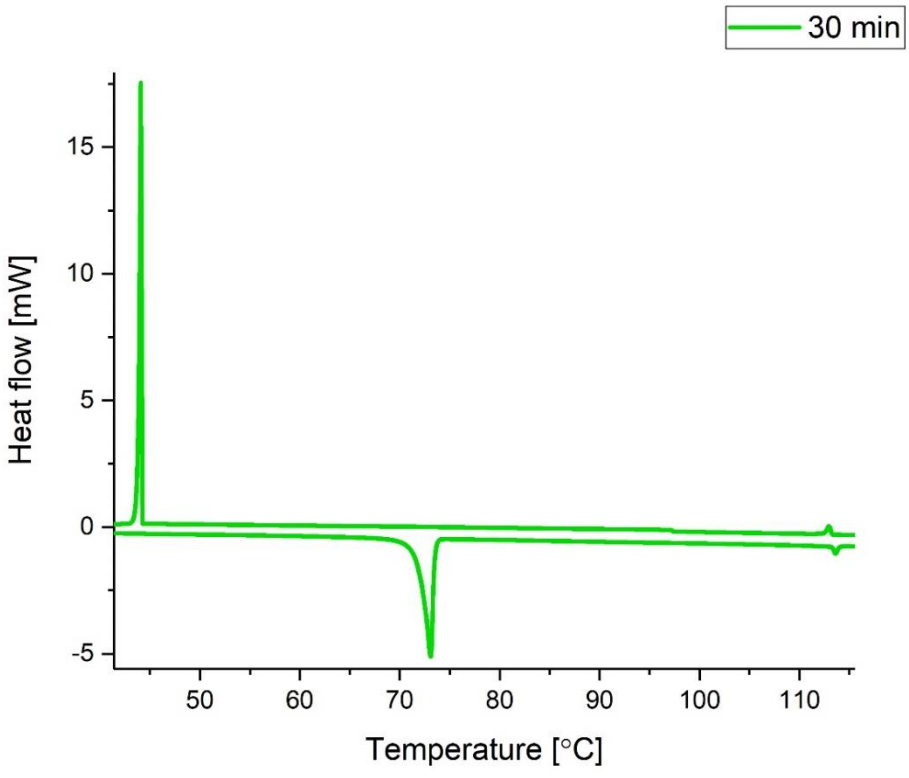


Figure S59. DSC trace of **2T3-d_9 35** after 30 min of UV exposure.

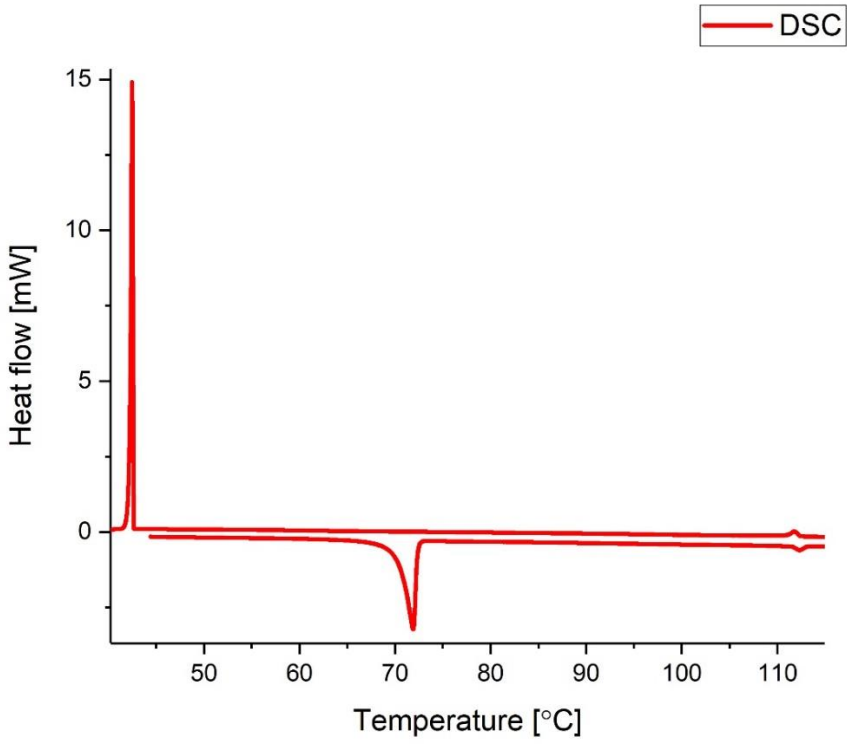


Figure S60. DSC trace of **2T3-*d*$_9$ 35** after 60 min of UV exposure.

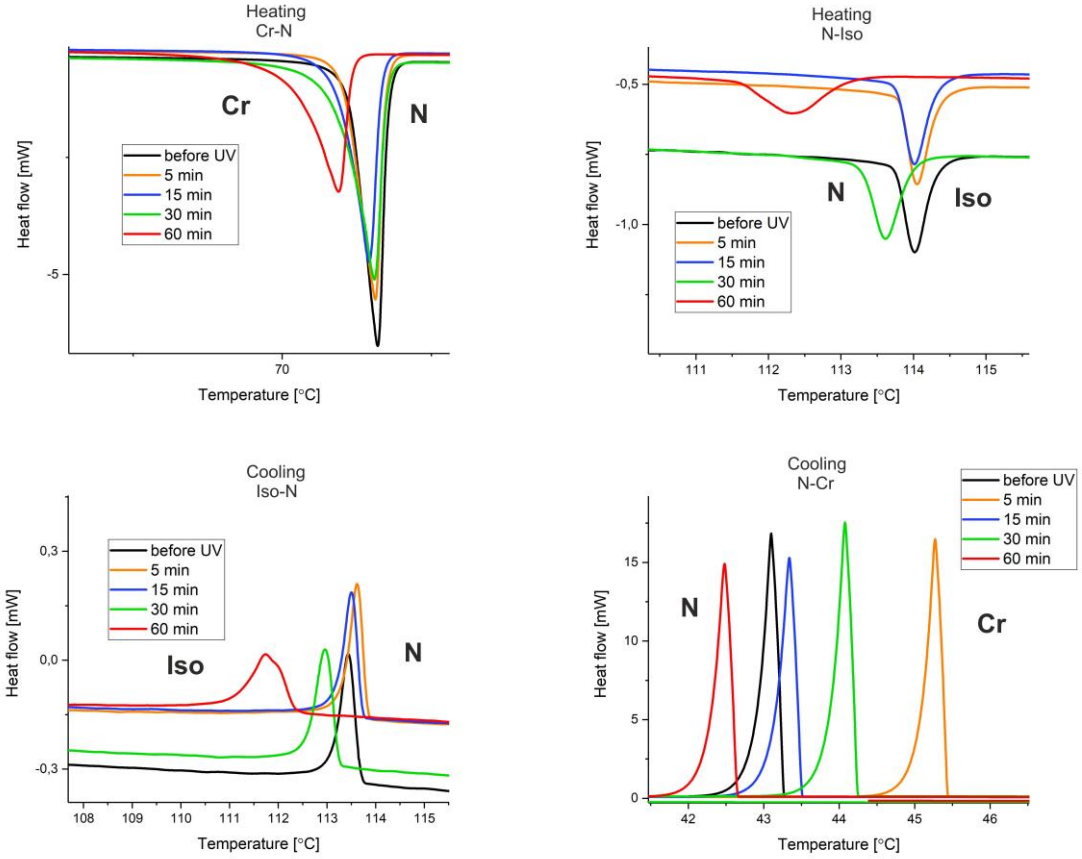


Figure S61. DSC trace of **2T3-*d*$_9$ 35** before and after 5, 15, 30 and 60 min of UV exposure – comparison.

8. GC-MS analysis and mass spectra for photodegradation products

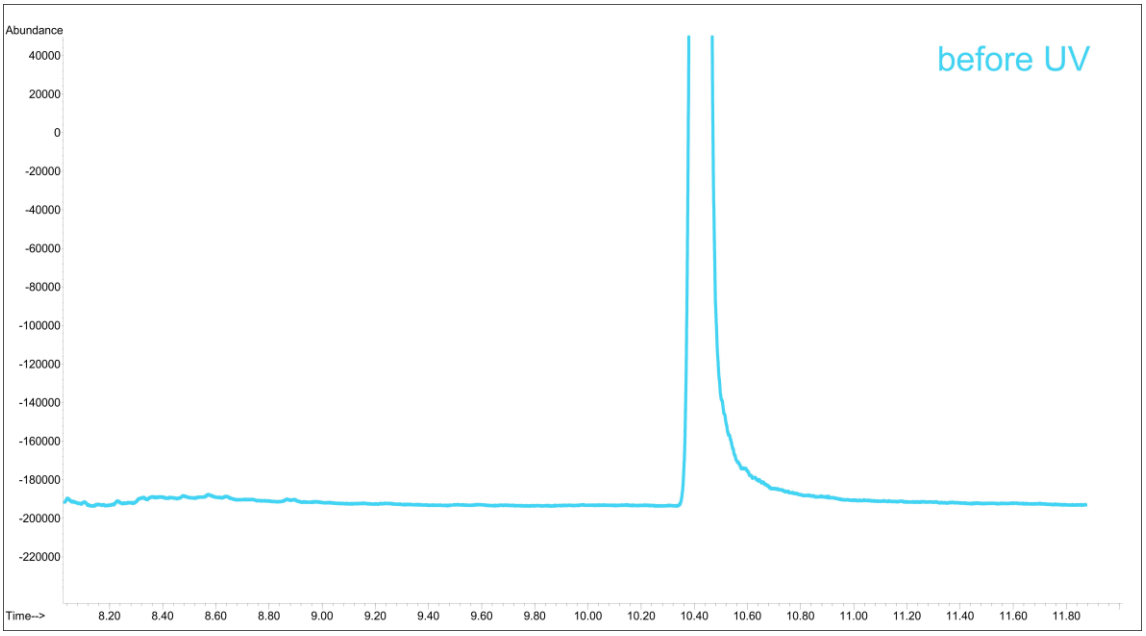


Figure S62. Chromatogram of the non-deuterated molecule 6T6 H before UV exposure.

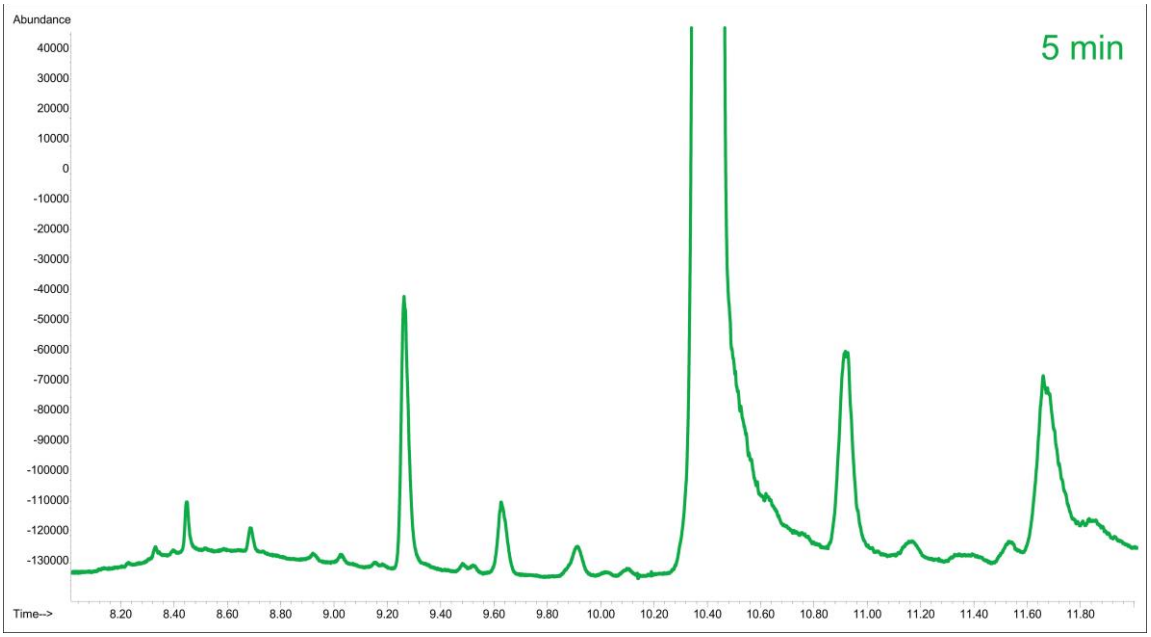


Figure S63. Chromatogram of the non-deuterated molecule 6T6 H after 5 min of UV exposure.

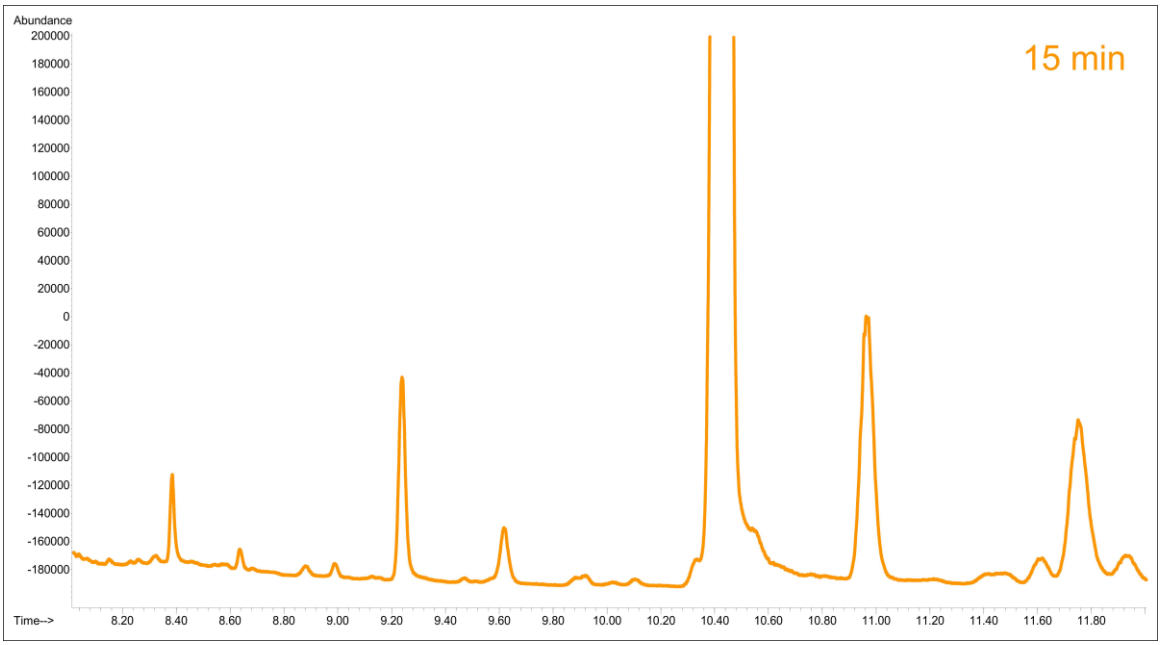


Figure S64. Chromatogram of the non-deuterated molecule 6T6 H after 15 min of UV exposure.

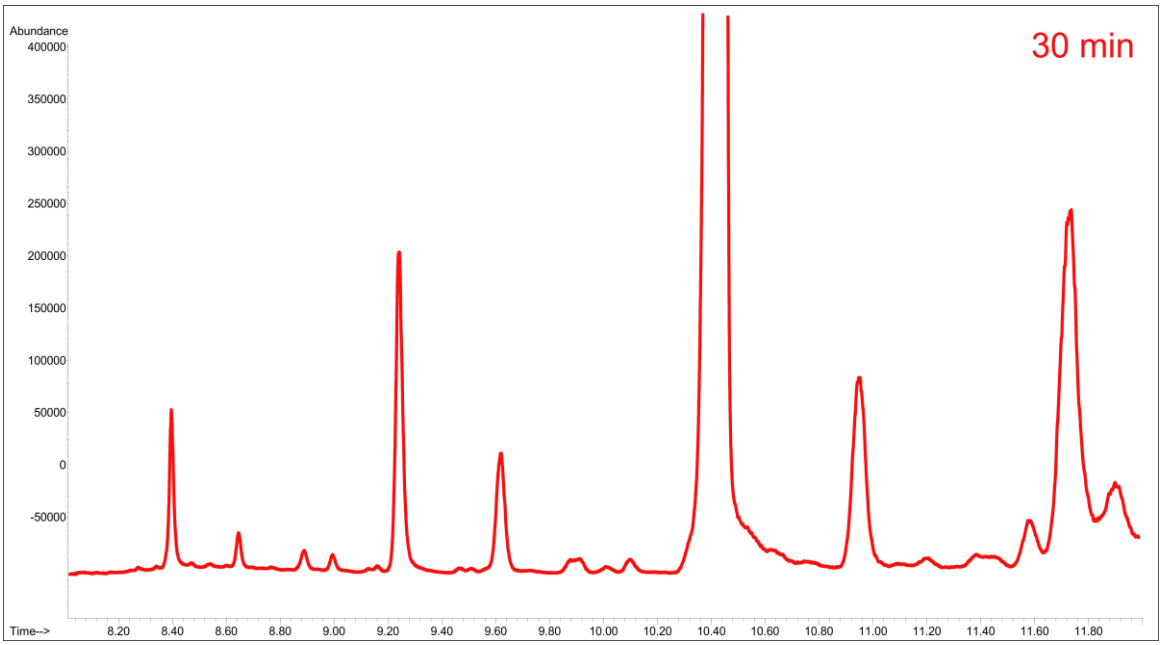


Figure S65. Chromatogram of the non-deuterated molecule 6T6 H after 30 min of UV exposure.

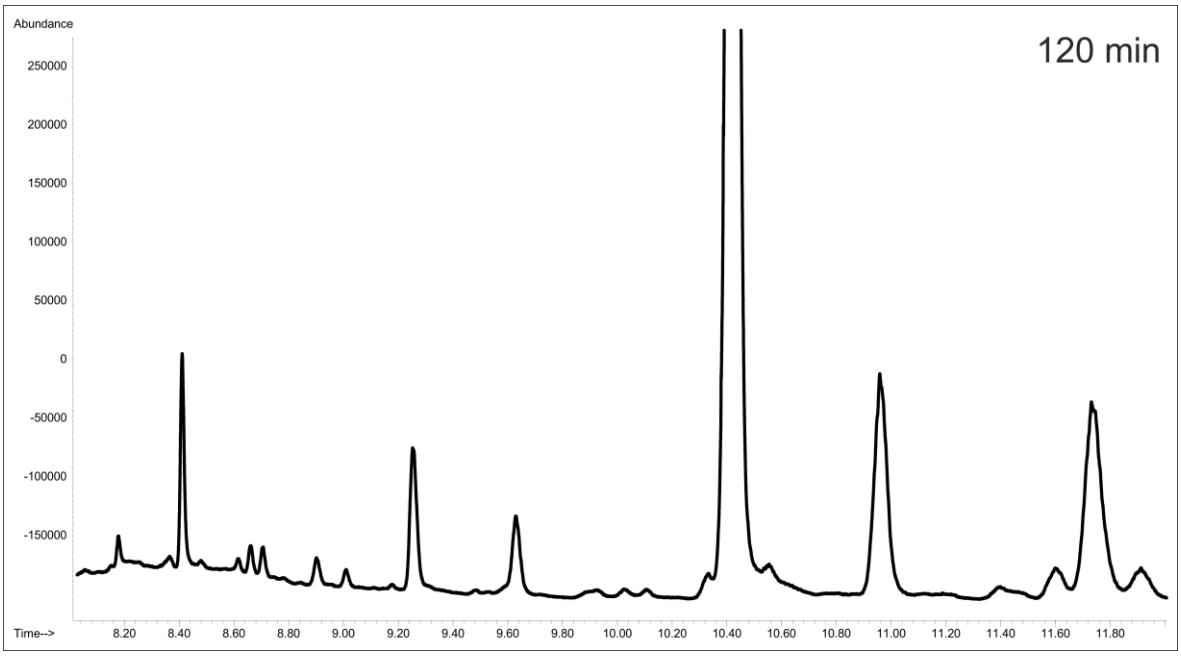


Figure S66. Chromatogram of the non-deuterated molecule 6T6 H after 120 min of UV exposure.

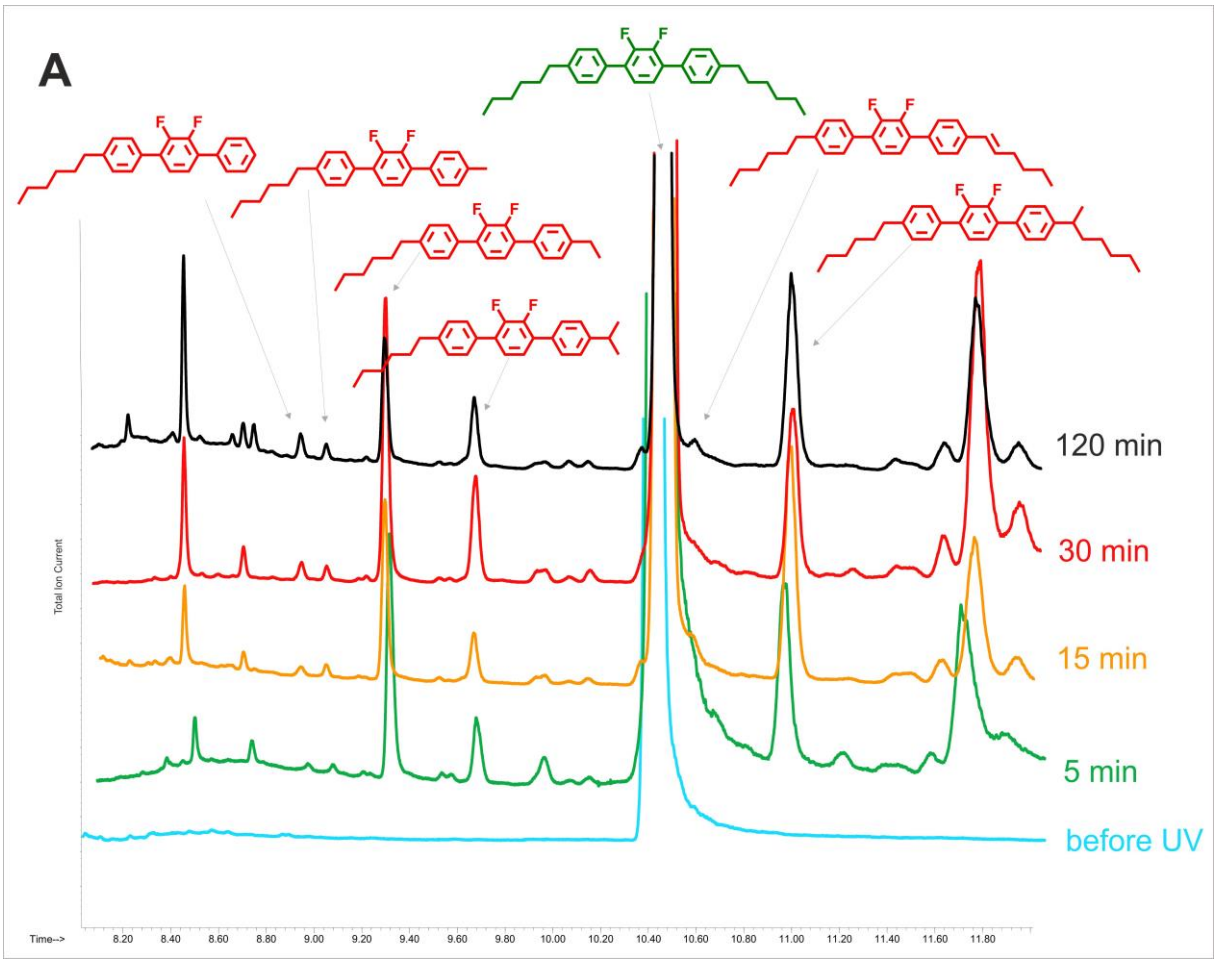


Figure S67. Chromatogram of the non-deuterated molecule 6T6 H obtained after 120 min exposure of UV radiation and proposed structures of photodegradation products after analysis of individual MS spectra.

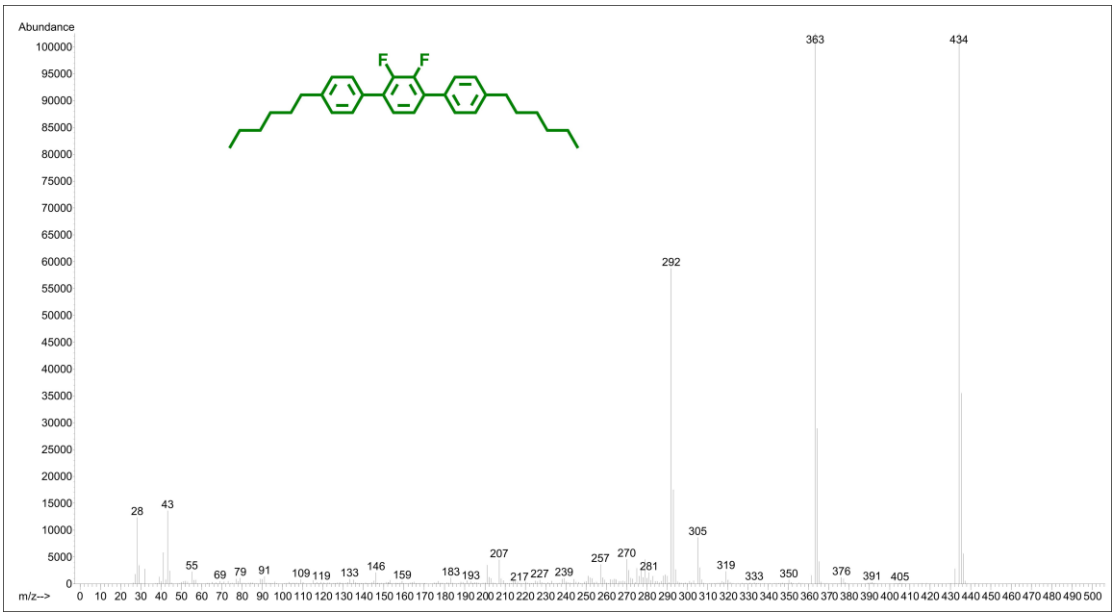


Figure S68. Mass spectra of the compound 6T6 H (m/z = 434).

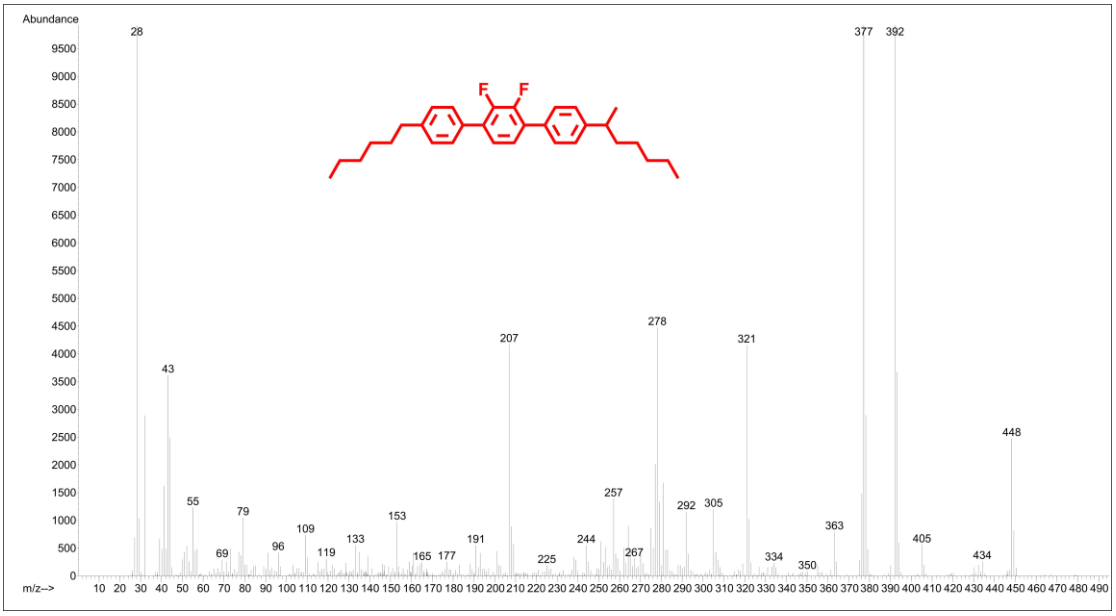


Figure S69. Mass spectra of the compound m/z = 448.

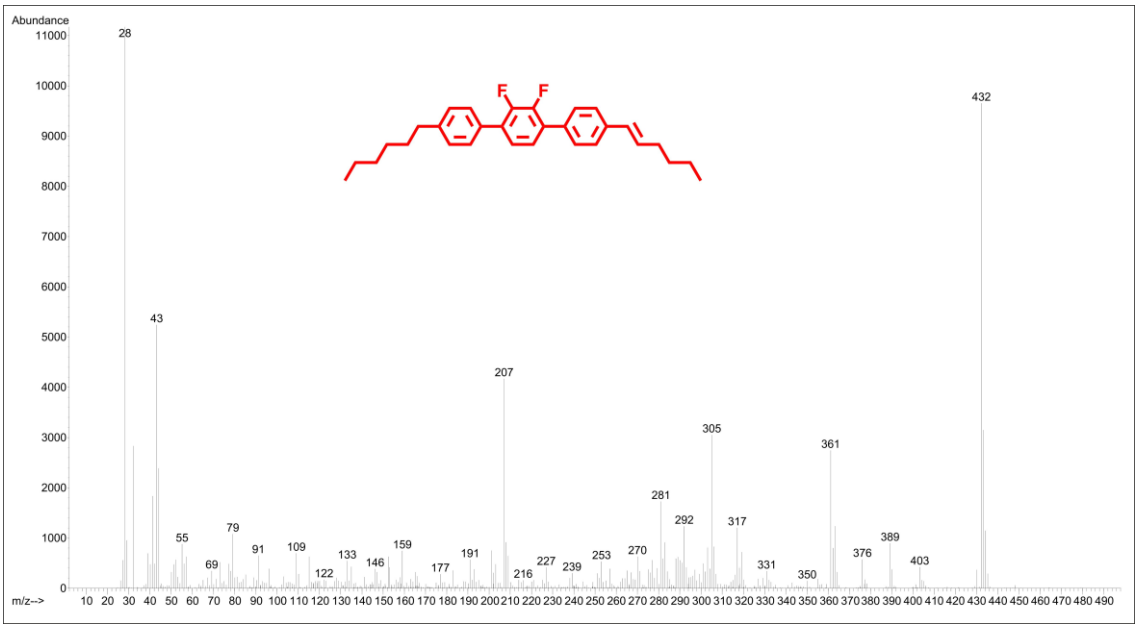


Figure S70. Mass spectra of the compound m/z = 432.

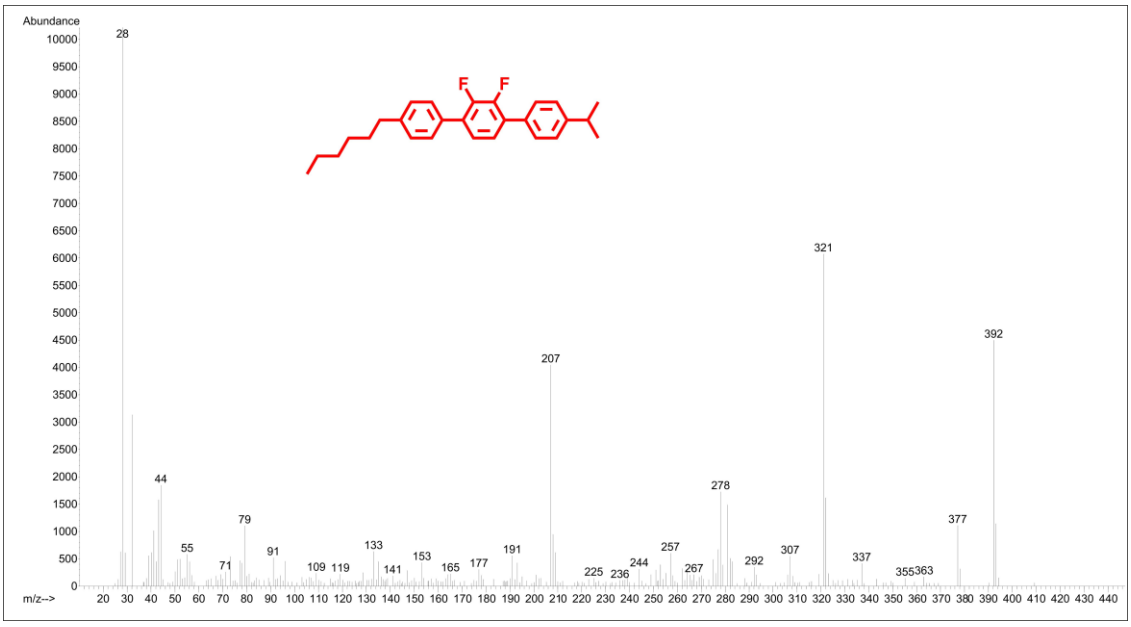


Figure S71. Mass spectra of the compound m/z = 392.

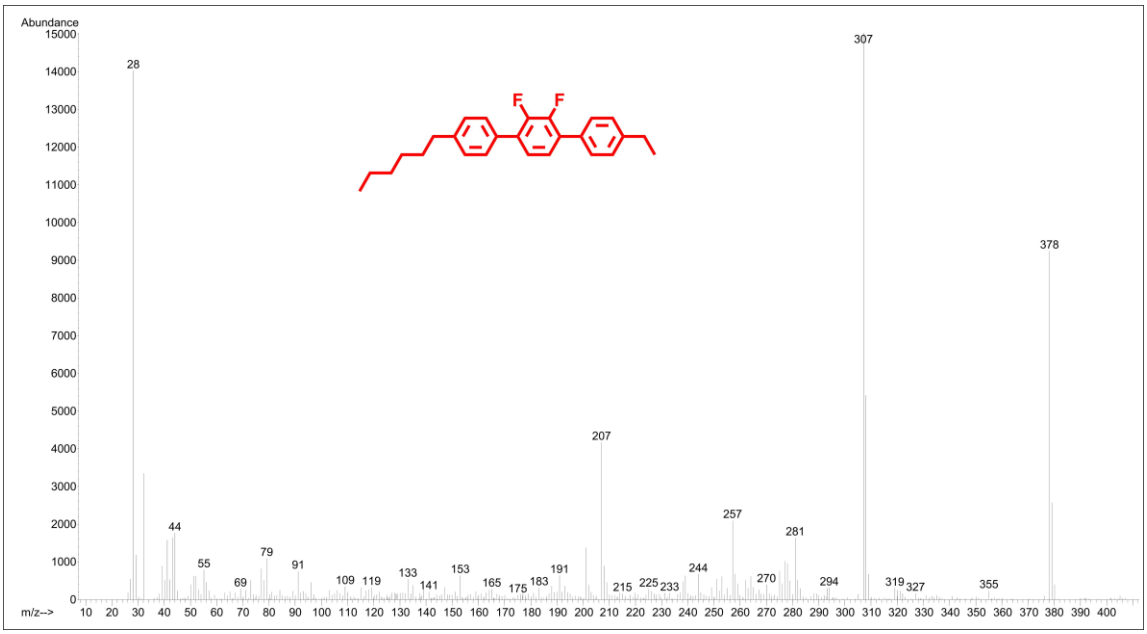


Figure S72. Mass spectra of the compound m/z = 378.

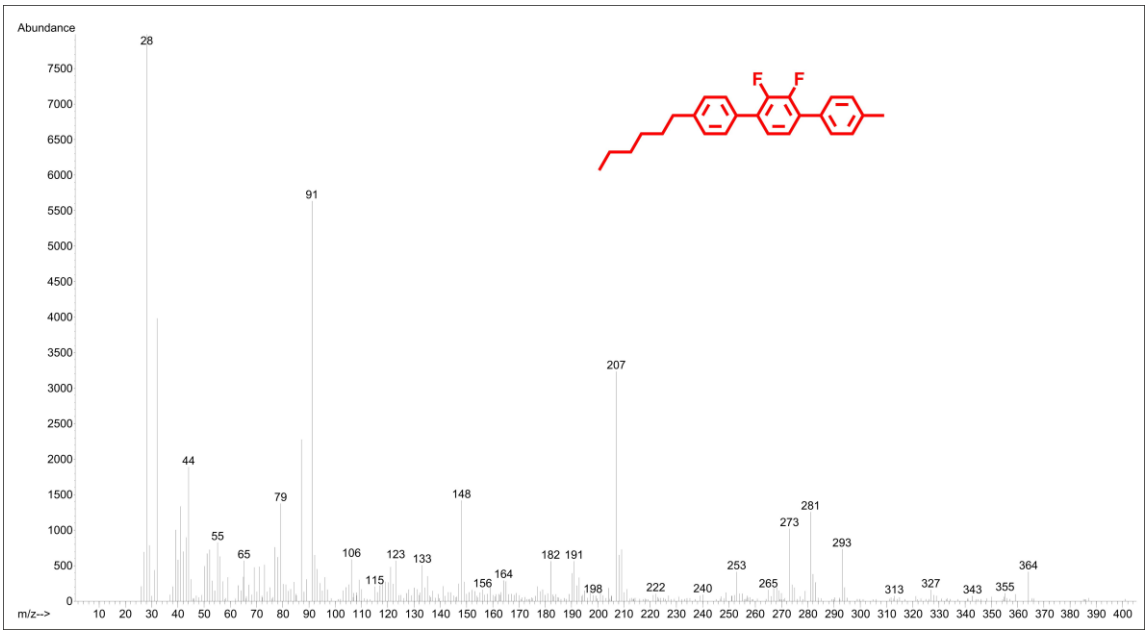


Figure S73. Mass spectra of the compound m/z = 364.

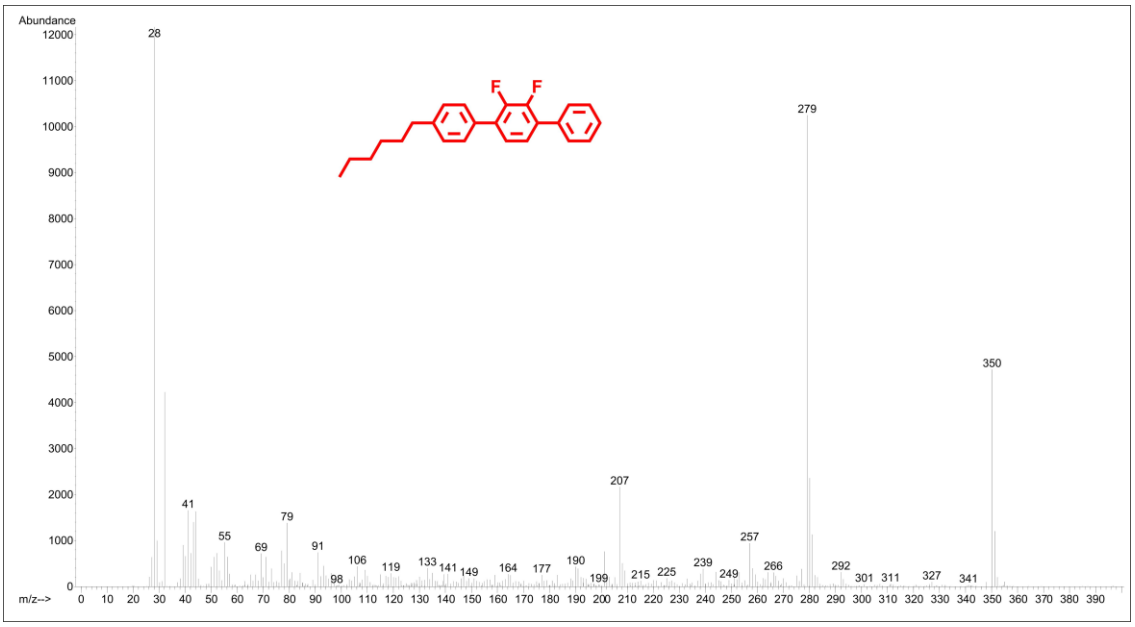


Figure S74. Mass spectra of the compound m/z = 350.

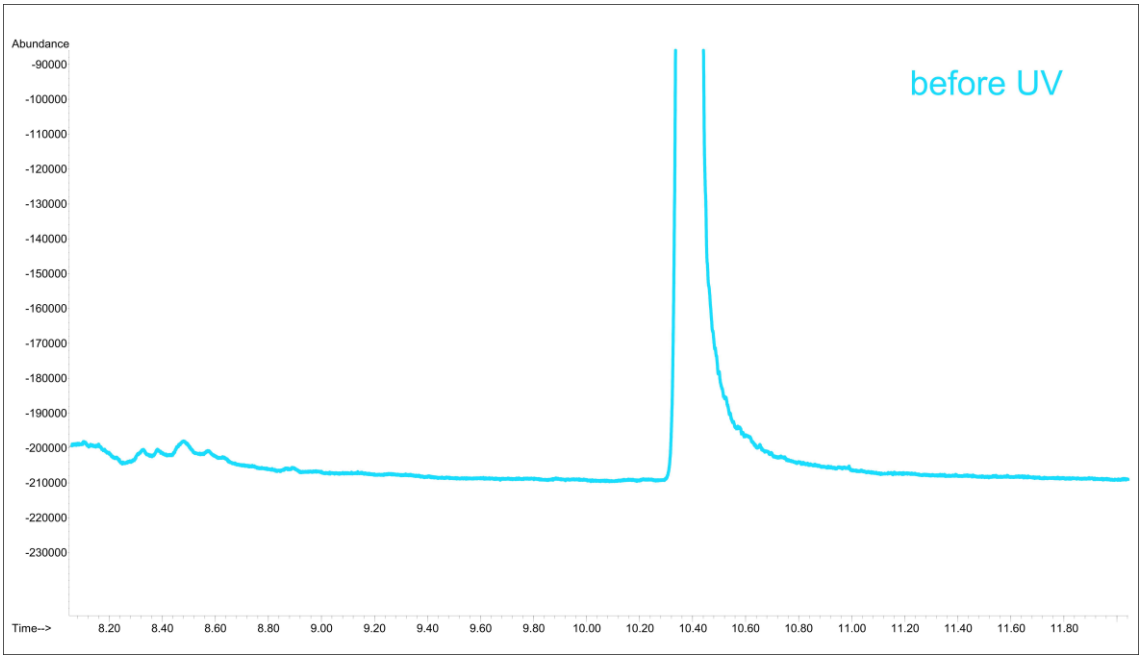


Figure S75. Chromatogram of the deuterated molecule 6T6-d_8 **24** before UV exposure.

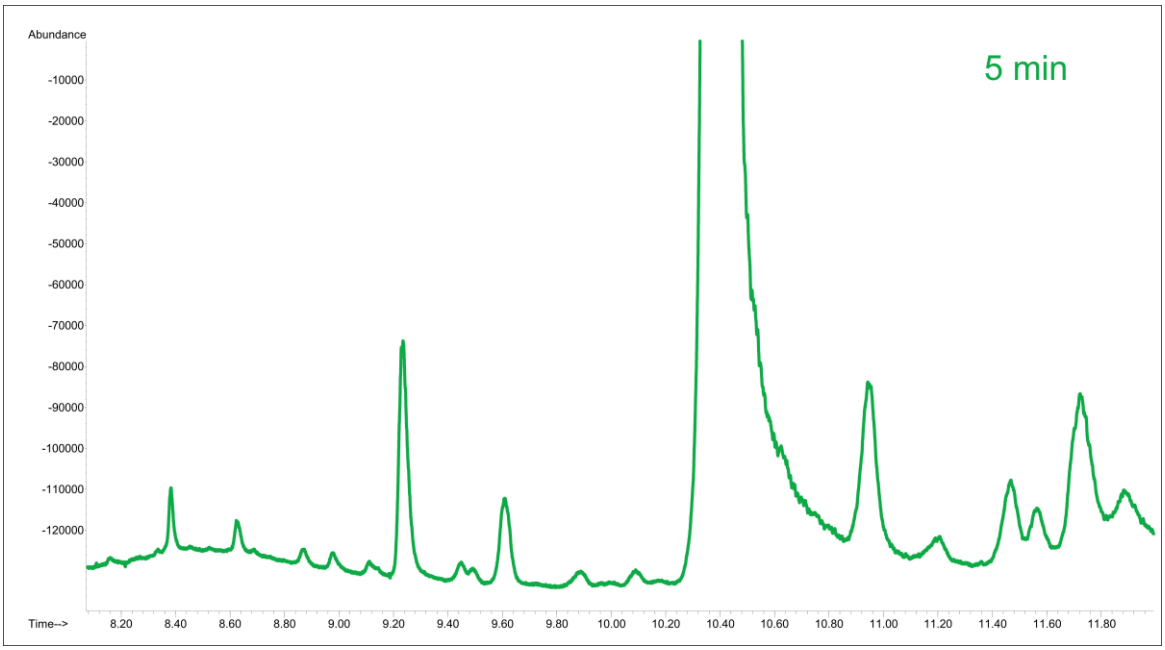


Figure S76. Chromatogram of the deuterated molecule 6T6-d_8 **24** after 5 min of UV exposure.

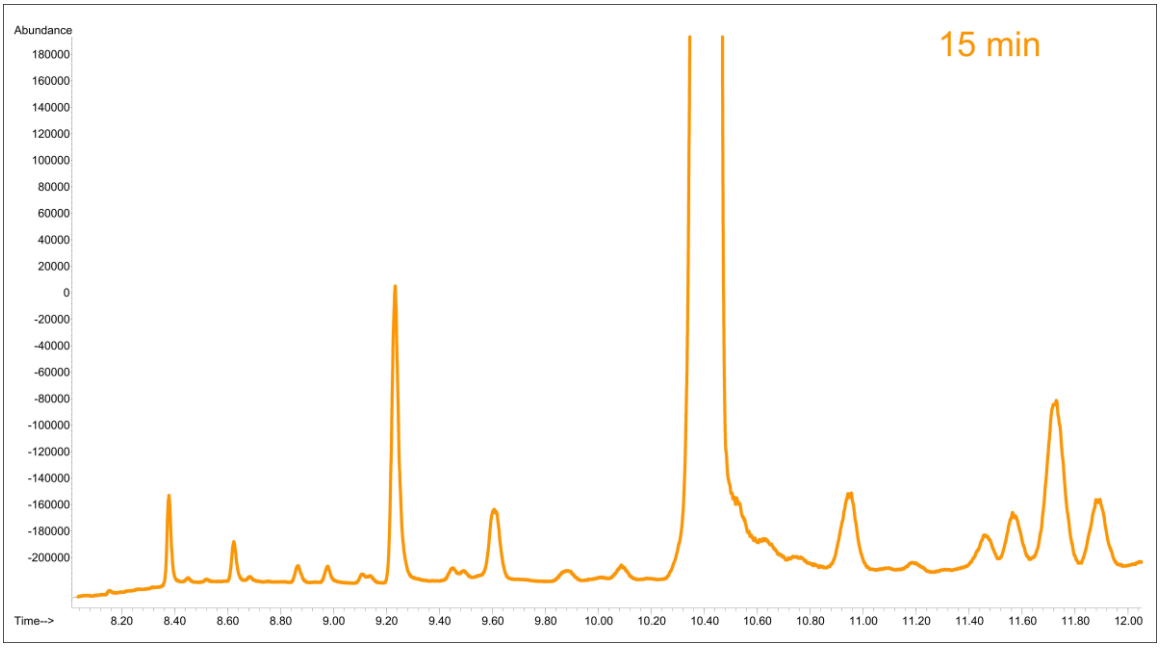


Figure S77. Chromatogram of the deuterated molecule 6T6-d_8 **24** after 15 min of UV exposure.

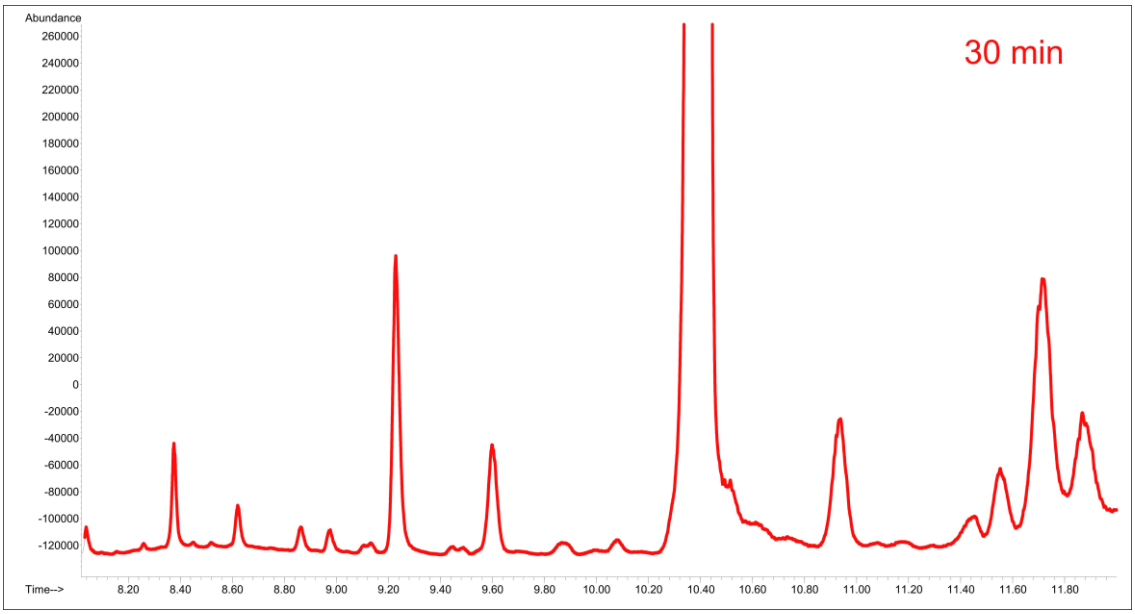


Figure S78. Chromatogram of the deuterated molecule 6T6-d_8 **24** after 30 min of UV exposure.

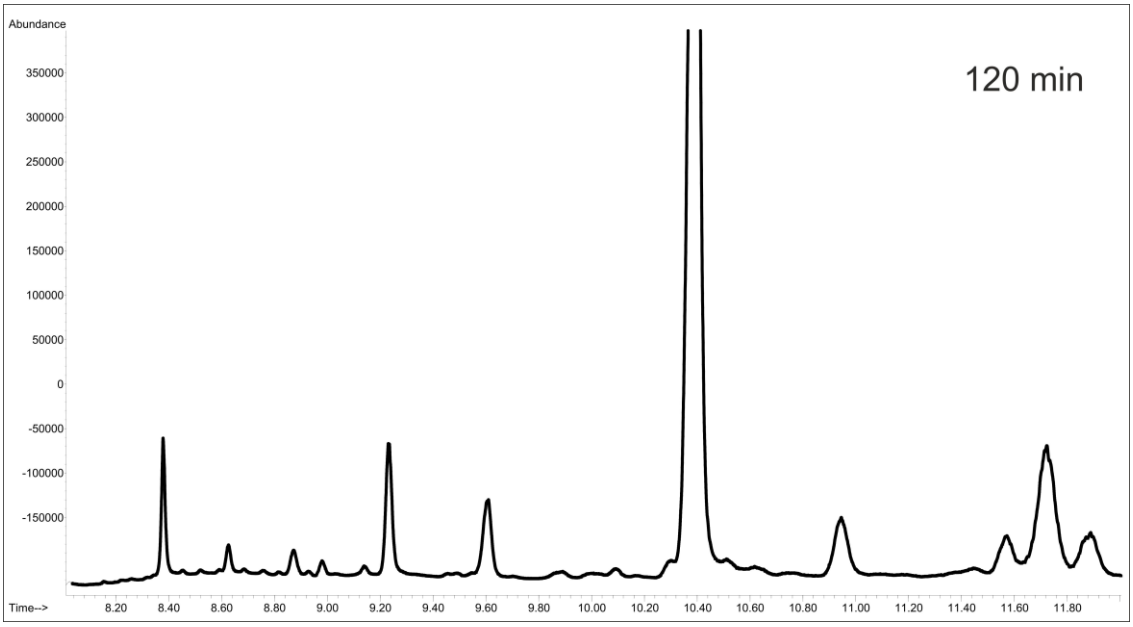


Figure S79. Chromatogram of the deuterated molecule 6T6-d_8 **24** after 120 min of UV exposure.

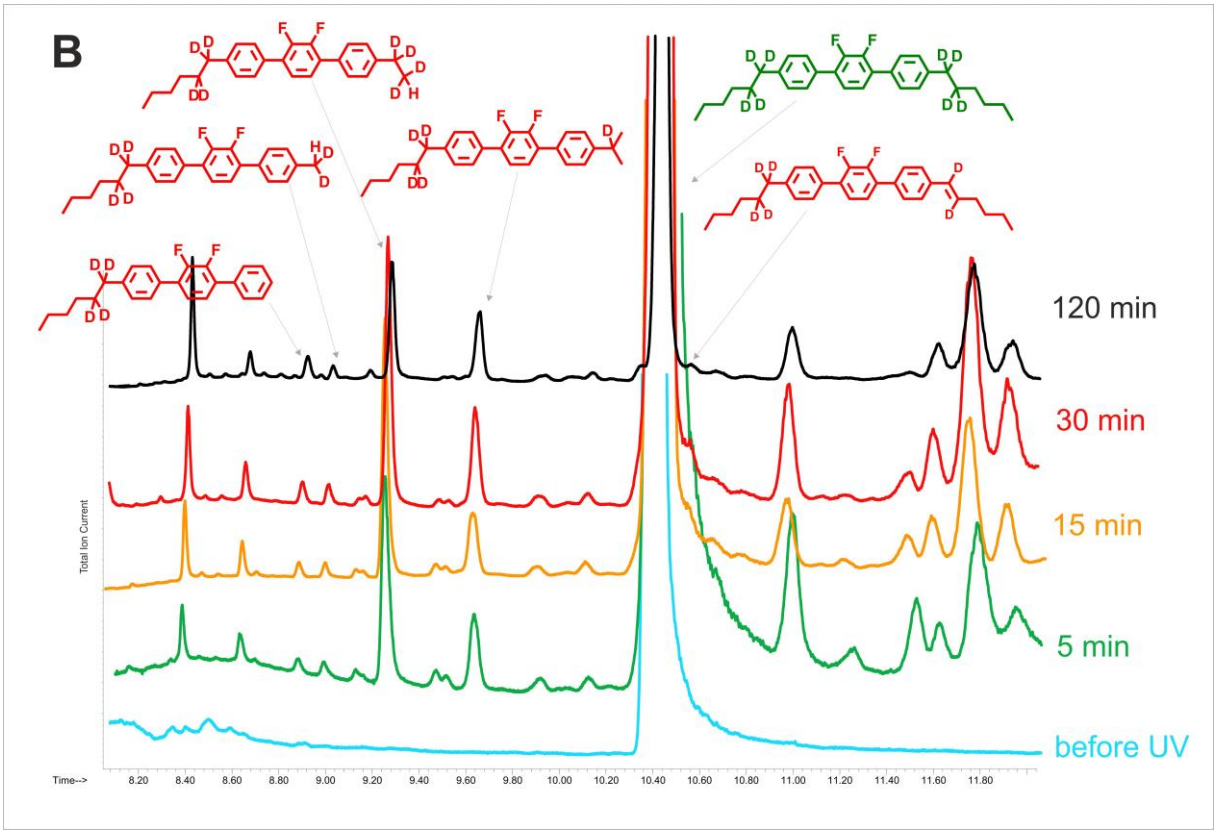


Figure S80. Chromatogram of 6T6-d_8 **24** obtained after 120 min exposure of UV radiation and proposed structures of photodegradation products after analysis of individual MS spectra.

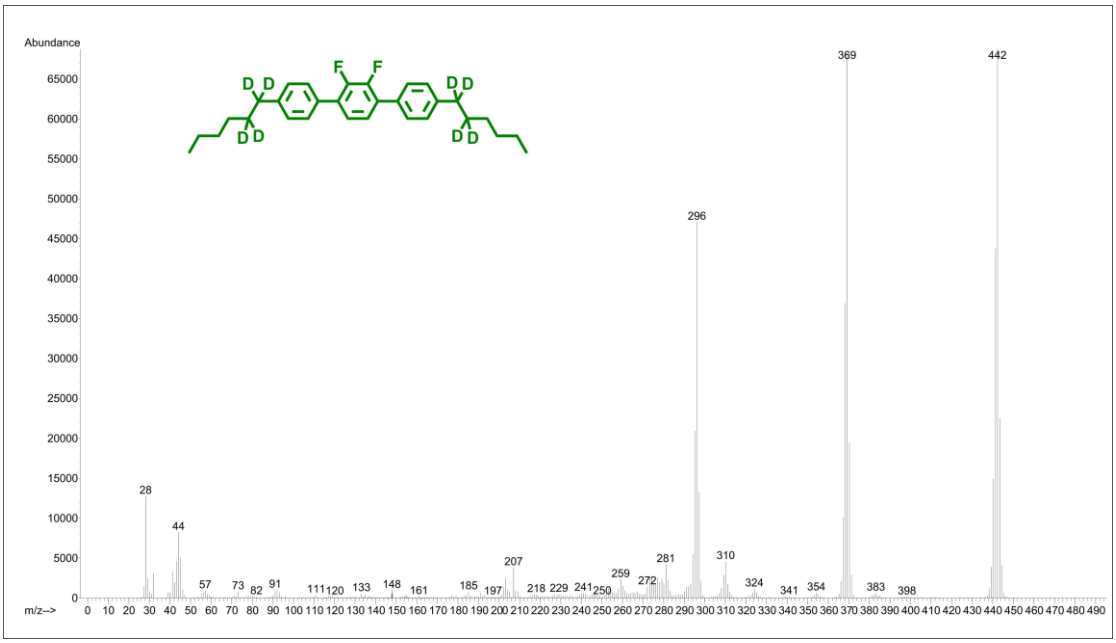


Figure S81. Mass spectra of the compound 6T6-d_8 **24** (m/z = 442).

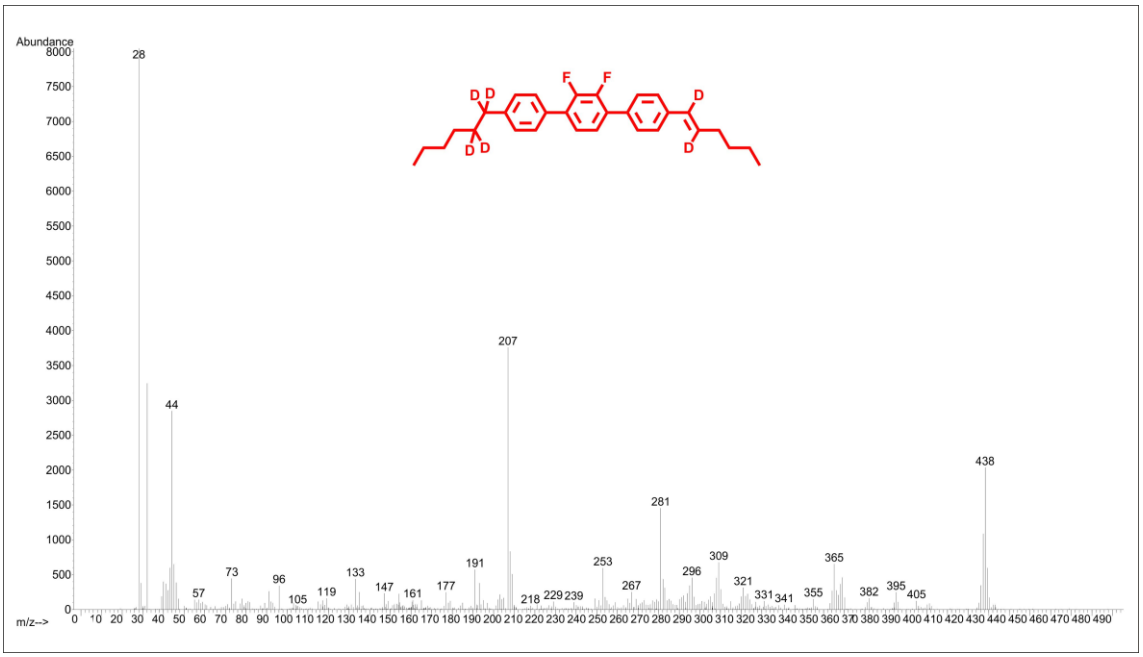


Figure S82. Mass spectra of the compound m/z = 438.

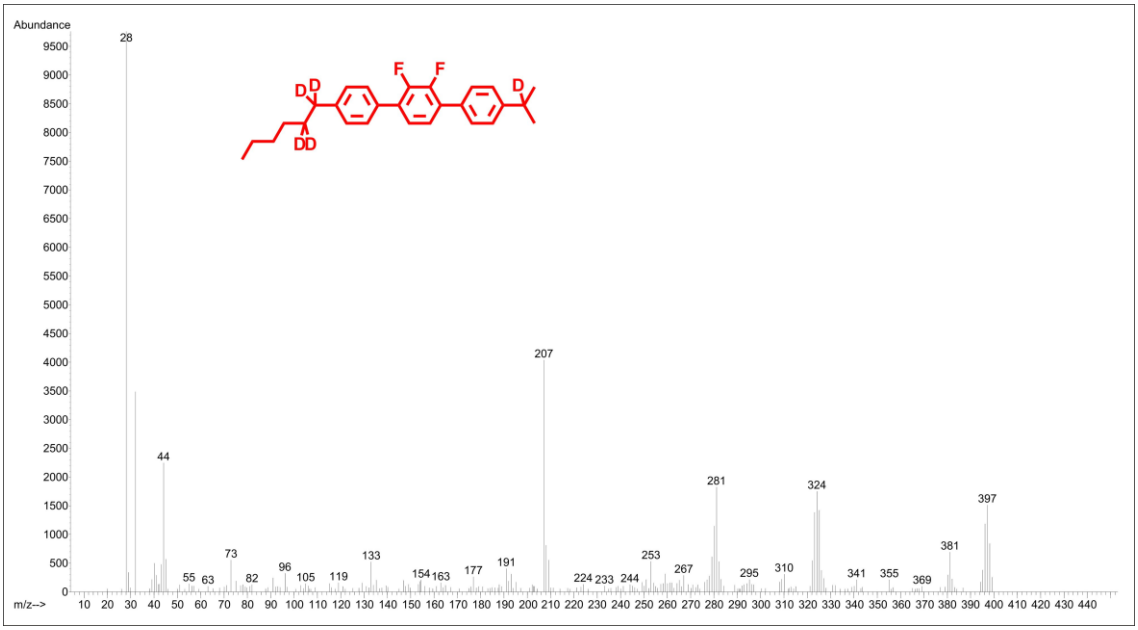


Figure S83. Mass spectra of the compound m/z = 397.

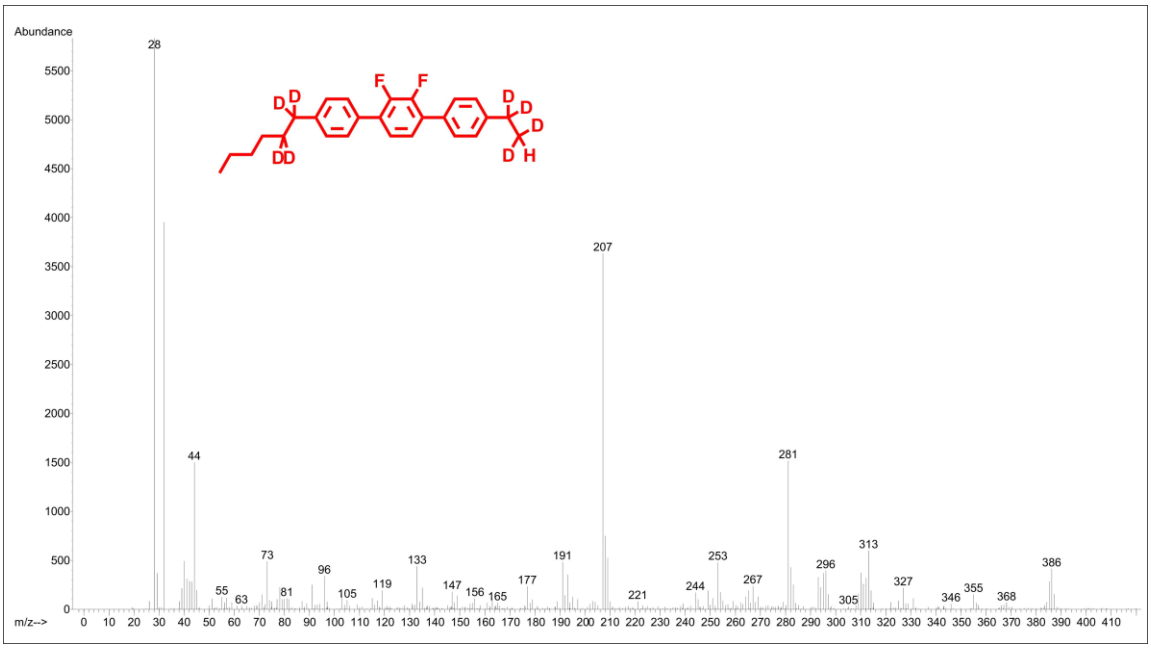


Figure S84. Mass spectra of the compound m/z = 386.

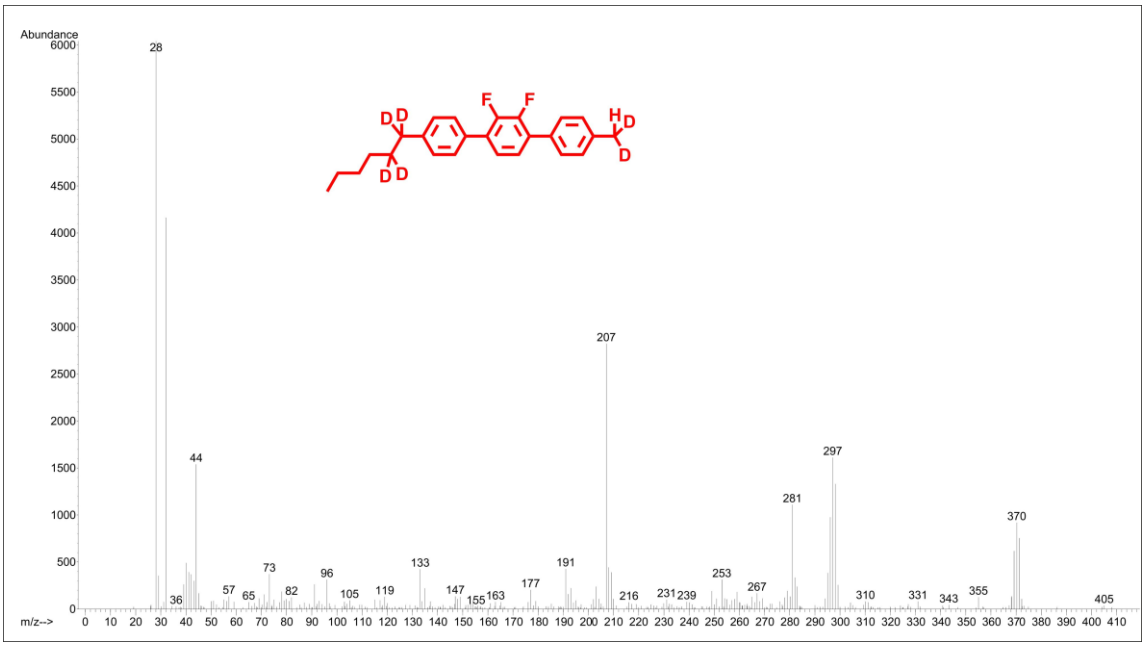


Figure S85. Mass spectra of the compound m/z = 370.

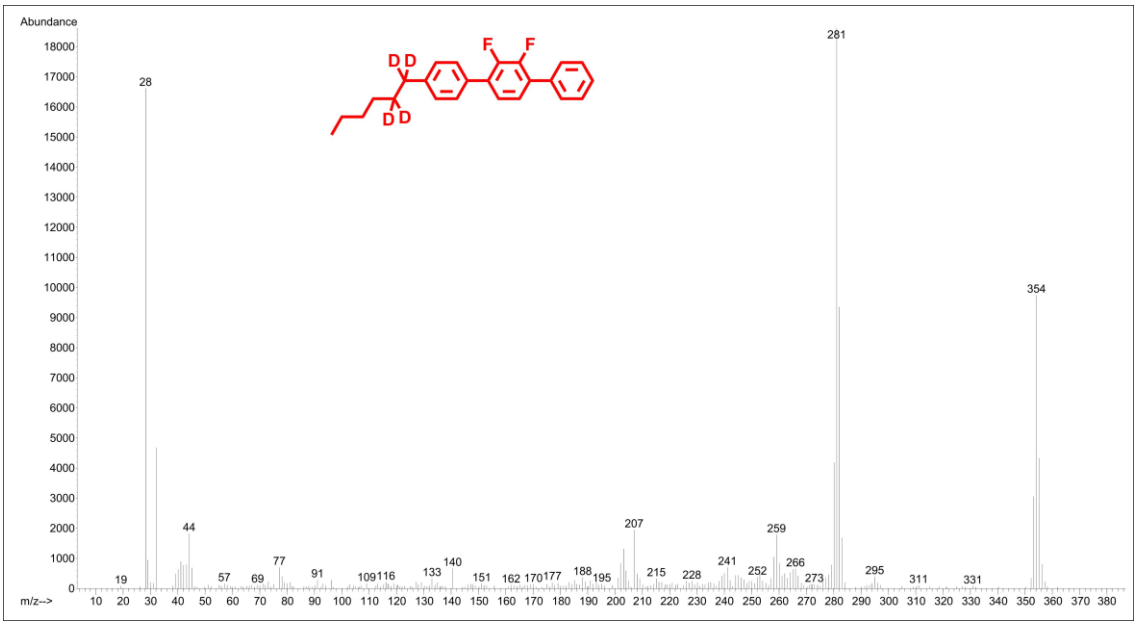


Figure S86. Mass spectra of the compound m/z = 354.