

Supporting information

Competition between mirror symmetry breaking and translation symmetry breaking in ferroelectric liquid crystals with increasing lateral substitution.

Grant J. Strachan,* Ewa Górecka, and Damian Pocięcha.

Faculty of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warsaw, Poland

*Author for correspondence: g.strachan@chem.uw.edu.pl

Experimental Methods	1
Additional data	2
Synthetic Procedures and Structural Characterisation	9

Experimental Methods

Transition temperatures and the associated enthalpy changes were measured by differential scanning calorimetry using a TA DSC Q200 instrument. 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 Axiolmager.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- μ m-thick cells with planar anchoring. The alignment quality was checked prior to measurement by inspection under the polarised-light optical microscope.

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 (μ S microfocus source with copper target, MRI heating stage, Vantec 2000 area detector).

AFM measurements were performed using a Bruker Dimension Icon Microscope working in tapping or scan assist mode and cantilevers with elastic constant of 0.4 N/m were applied.

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 5- or 10- μ m-thick glass cell with gold electrodes. Cells without polymer aligning layers were used, as the presence of the thin (~ 10 nm) polyimide layers at the cell surfaces acts as an additional high capacitance capacitor in a series circuit with the capacitor filled with the LC sample, which for materials with very high values of permittivity, may strongly affect the measured permittivity of the LC phases. Lack of a surfactant layer resulted in a random configuration of the director in the LC phases.

To determine the helical pitch length in N_{TBF} phase selective light reflection studies were carried out with the material placed on a glass substrate without a top cover. Light transmission/reflection was monitored with a fiber-coupled spectrometer (Filmetrics F20-UV) mounted onto the Zeiss Axio Imager A2m microscope.

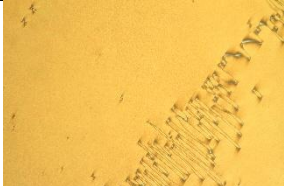
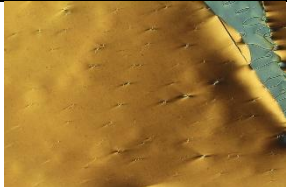
Additional data

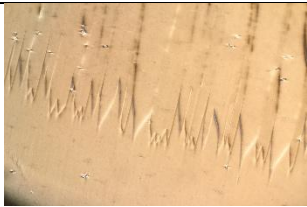
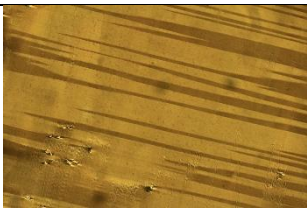
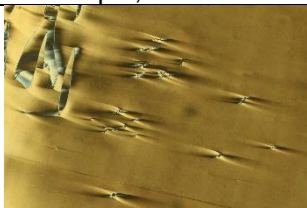
Table S1. The phase transition temperatures (in °C) of the compounds reported here.

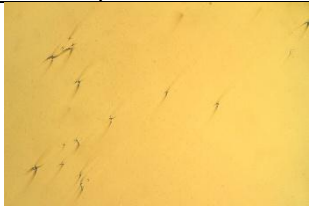
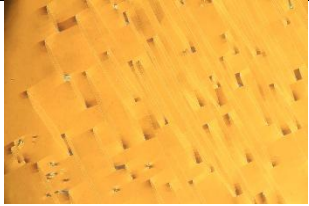
Compound	Melt	SmC _F	SmA _F	N _{TBF}	N _F	N _X	N	Iso
M-0-1 ^[1]	141	• 115	• 167		• 185		• 263	•
E-0-1	158	48 ^c	• 120		• 158		• 216	•
P-0-1	154	42 ^c		• 74 ^a	• 146		• 188	•
B-0-1	118				• 140	• 141	• 176	•
Q-0-1	124				• 129		• 164	•
M-1-1 ^[1]	139	• 108 ^b	• 130 ^a		• 191		• 253	•
E-1-1	132		• 95 ^d		• 178		• 221	•
P-1-1	130			• 55 ^d	• 163	• 165 ^c	• 190	•
B-1-1	117				• 152		• 174	•
Q-1-1	119				• 140		• 158	•
M-0-2 ^[1]	138	• 164 ^a	• 185		• 220		• 252	•
E-0-2	143	• 96 ^c	• 145 ^a		• 198		• 215	•
P-0-2	133	• 79 ^c		• 100 ^c	• 175		• 180	•
B-0-2	129	• 44 ^c		• 62 ^a	• 170		• 174	•
Q-0-2	112			• 42 ^a	• 158		• 160	•
M-1-2 ^[1]	141	• 143		• 151 ^a	• 224		• 247	•
E-1-2	145	• 100 ^c	• 115 ^c		• 201		• 210	•
P-1-2	115	• 55 ^c		• 71 ^a	• 183			•
B-1-2	102				• 173			•
Q-1-2	100				• 156			•

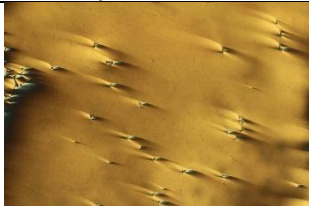
^a Taken from birefringence measurement. ^b Taken from SAXS. ^c Taken from POM. ^d Taken from dielectric spectroscopy.

Table S2. Representative POM textures in thin cells treated for planar alignment.

	SmC _F	SmA _F	N _{TBF}	N _F	N _x
E-0-1	 HG Cell, 1.8 μm, 37 °C	 HG Cell, 1.8 μm, 121 °C		 HG Cell, 1.8 μm, 132 °C	
P-0-1	 HG Cell, 1.7 μm, 42 °C		 HG Cell, 1.7 μm, 74 °C	 HG Cell, 1.7 μm, 132 °C	
B-0-1				 HG Cell, 1.8 μm, 120 °C	 HG Cell, 1.8 μm, 139 °C
Q-0-1				 HG Cell, 1.6 μm, 128 °C	

E-1-1		 HG Cell, 1.5 μm , 92°C		 HG Cell, 1.5 μm , 139 °C	
P-1-1	 HG 1.6 μm , 32 °C x50		 HG 1.6 μm , 54 °C	 HG 1.6 μm , 97 °C	 HG 1.6 μm , 165 °C ?
B-1-1				 HG 1.4 μm , 145 °C	
Q-1-1				 HG 1.6 μm , 141 °C	
E-0-2	 HG 1.6 μm , 90 °C	 HG 1.6 μm , 134 °C		 HG 1.6 μm , 158 °C	

P-0-2	 HG 1.8 μm , 66 °C		 HG 1.8 μm , 88 °C	 HG 1.8 μm , 105 °C	
B-0-2	 HG 1.8 μm , 42 °C + Cr		 HG 1.8 μm , 54 °C	 HG 1.8 μm , 120 °C	
Q-0-2			 HG 1.5 μm , 35 °C	 HG 1.5 μm , 136 °C	
E-1-2	 HG 1.5 μm , 90 °C	 HG 1.5 μm , 110 °C		 HG 1.6 μm , 150 °C	
P-1-2					

	HG 1.8 μm , 52 $^{\circ}\text{C}$ x50		HG 1.8 μm , 59 $^{\circ}\text{C}$ x50	HG 1.8 μm , 136 $^{\circ}\text{C}$	
B-1-2				 HG 1.7 μm , 84 $^{\circ}\text{C}$	
Q-1-2				 HG 1.6 μm , 116 $^{\circ}\text{C}$	

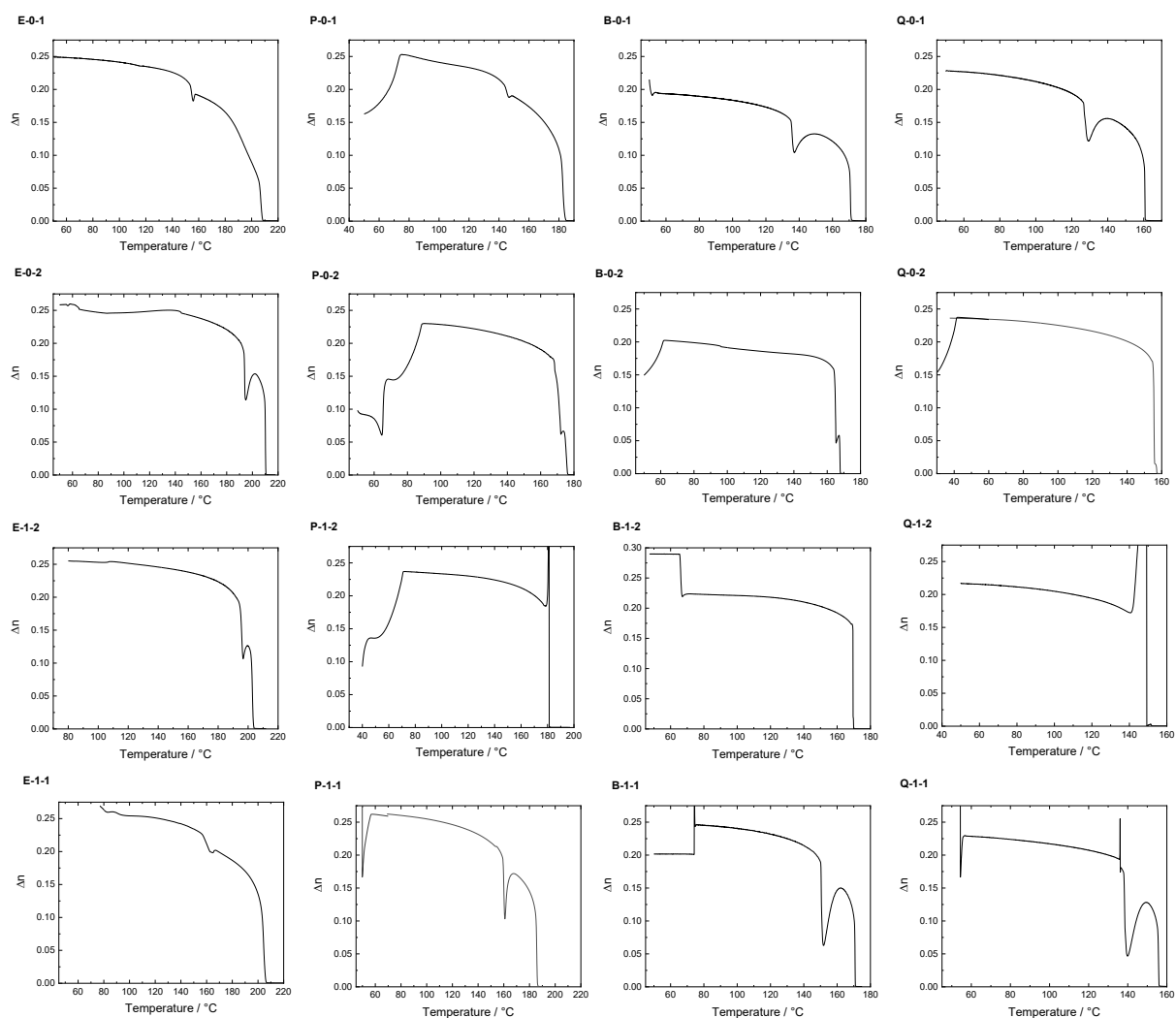


Figure S1. The temperature dependence of the optical birefringence measured with green light in thin cells treated for planar alignment.

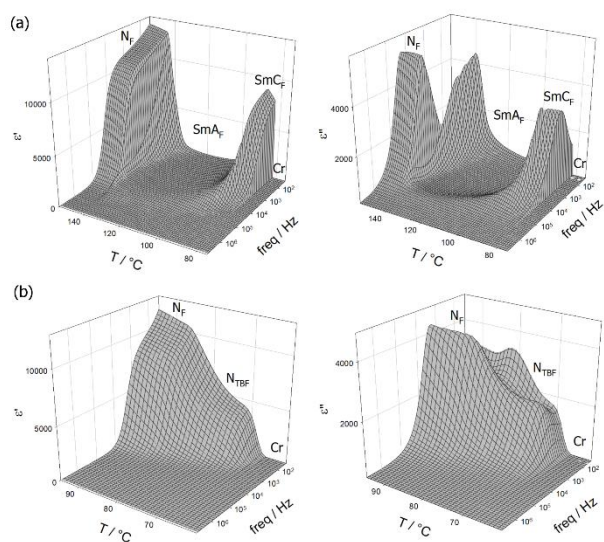


Figure S2. The real (ϵ') and imaginary (ϵ'') parts of apparent dielectric permittivity of (a) **E-0-2** and (b) **P-0-2** compounds, measured in 10- μm -thick cells with gold electrodes.

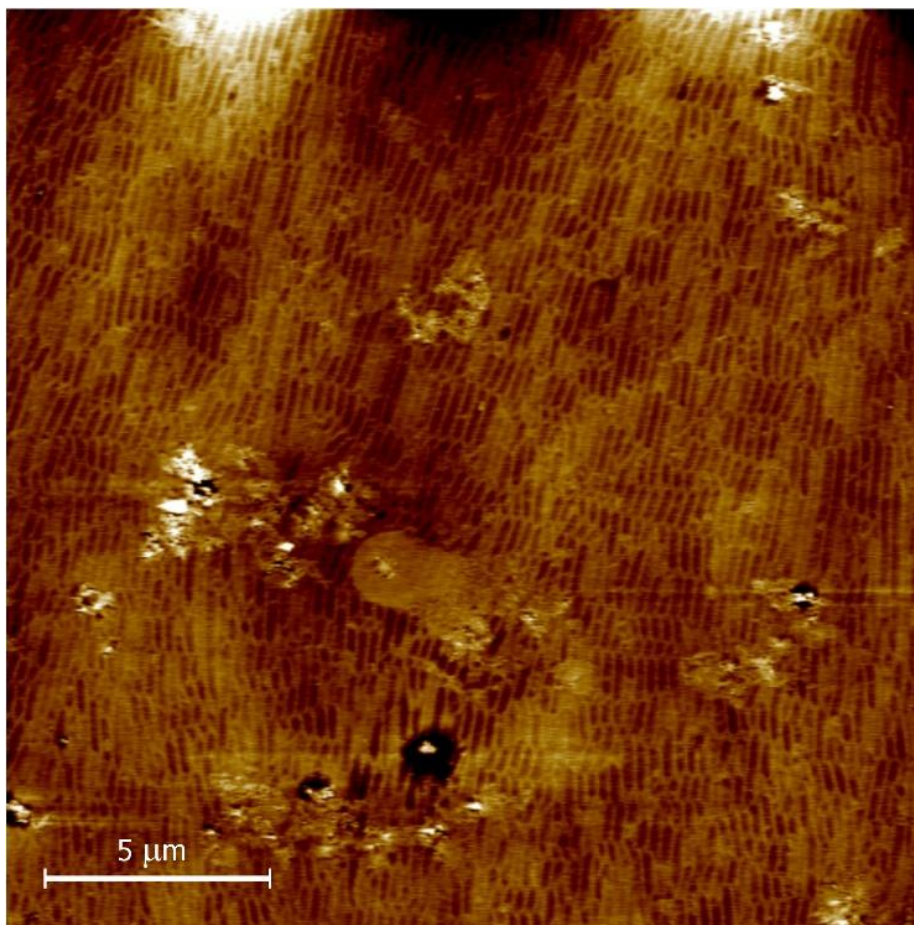
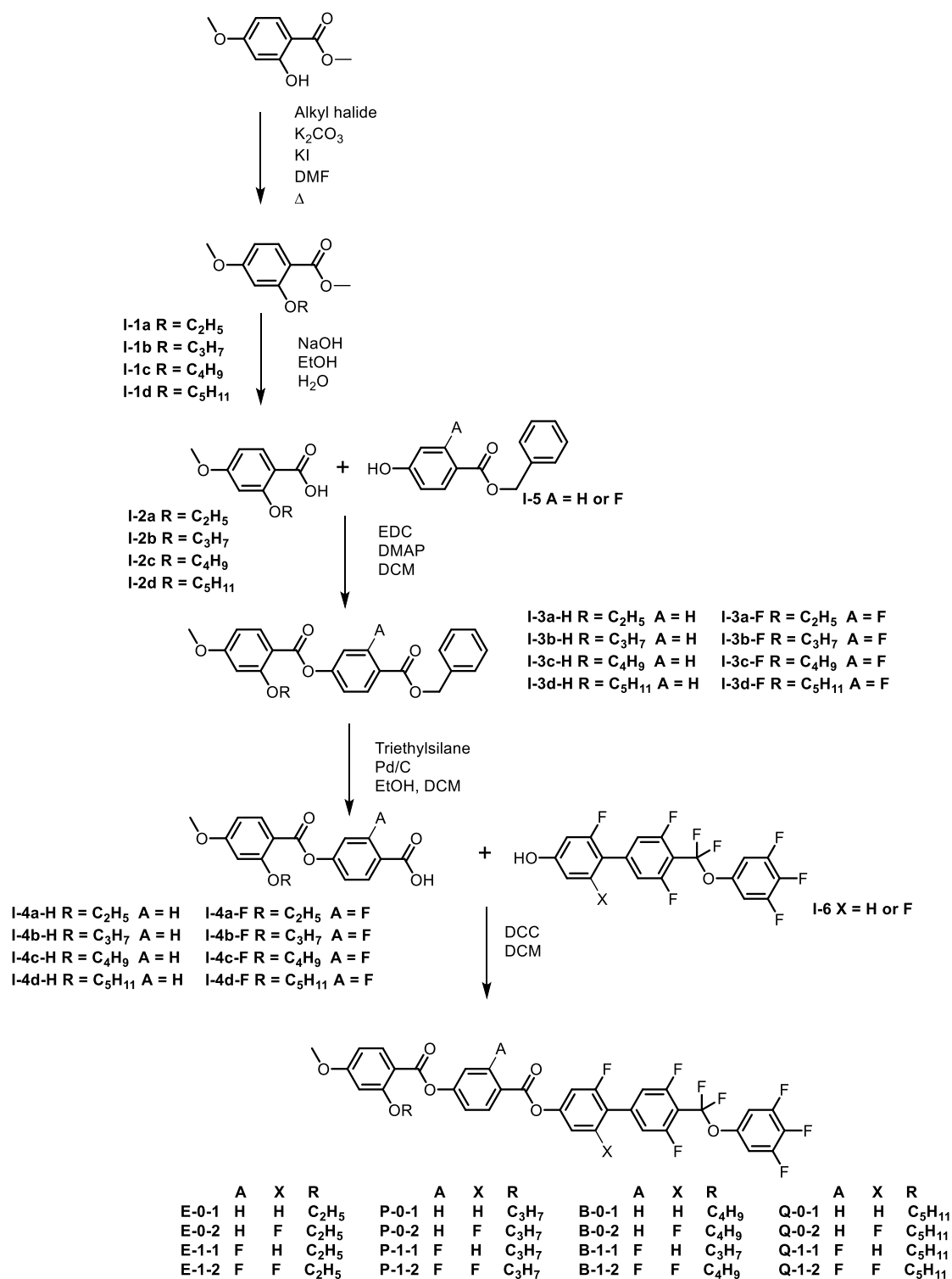


Figure S3. AFM image recorded for **P-1-1**.

Synthetic Procedures and Structural Characterisation

Unless otherwise stated, all materials were obtained from commercial sources and used without further purification. Reactions were monitored using thin layer chromatography (TLC) using aluminium-backed plates with a coating of Merck Kieselgel 60 F254 silica and an appropriate solvent system. Spots were visualised using UV light (254 nm). Flash column chromatography was carried out using silica grade 60 Å 40-63 micron. ^1H , ^{19}F , and ^{13}C NMR spectra were recorded on a 400 MHz Agilent NMR spectrometer using CDCl_3 as solvent and using residual non-deuterated trace solvents as reference. Chemical shifts (δ) are given in ppm relative to TMS ($\delta = 0.00$ ppm). Due to limited sample availability, solubility and the effect of ^{19}F coupling some ^{13}C multiplets are very weak, and spectra are reported as fingerprints for comparison. Mass spectroscopy was conducted on a Micromass LCT instrument.



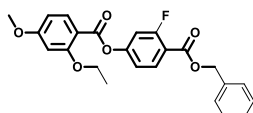
Scheme 1: Synthetic route to the new materials reported here.

The synthesis of intermediate compounds **I-1(a-d)**, **I-2(a-d)**, **I-3(a-d)-H** and **I-4(a-d)-H**, as well as the benzyl protected phenols **I-5** and the fluoroethers **I-6** has been reported previously. ^[1,2]

Esterification I-3x-F

The appropriate benzoic acid and EDC.HCl were dissolved in DCM and stirred for 10 minutes. Benzyl 2-fluoro-4-hydroxybenzoate and 4-dimethylaminopyridine (DMAP) were added and the reaction was left stirring at room temperature overnight. The reaction was washed 3x with water and the solvent removed *in vacuo*. The crude product was recrystallised from ethanol to yield the product as a white solid.

I-3a-F

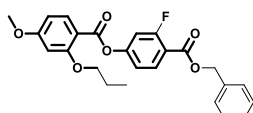


2-fluoro-4-hydroxybenzyl benzoate	245 mg,	1.0 mmol,	1 eq.
2-ethoxy-4-methoxybenzoic acid	217 mg,	1.1 mmol,	1.1 eq.
EDC.HCl	389 mg	2.0 mmol,	2 eq.
DMAP	15 mg,	0.1 mmol,	0.1 eq.
DCM	10 ml		

Recrystallised from ethanol, yield 138 mg.

¹H NMR (400 MHz, CDCl₃) δ = 8.02 (overlapping multiplets, 2H), 7.49 – 7.30 (m, 5H), 7.09 (d, J =9.8, 2H), 6.55 (dd, J =8.9, 2.2, 1H), 6.51 (d, J =2.2, 1H), 5.39 (s, 2H), 4.12 (q, J =7.1, 2H), 3.88 (s, 3H), 1.48 (t, J =7.1, 3H).

I-3b-F

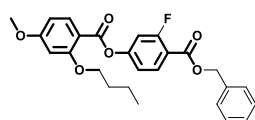


2-fluoro-4-hydroxybenzyl benzoate	246 mg,	1.0 mmol,	1 eq.
2-propoxy-4-methoxybenzoic acid	239 mg,	1.1 mmol,	1.1 eq.
EDC.HCl	387 mg	2.0 mmol,	2 eq.
DMAP	12 mg,	0.1 mmol,	0.1 eq.
DCM	10 ml		

Recrystallised from ethanol, yield 145 mg.

¹H NMR (400 MHz, CDCl₃) δ = 8.02 (overlapping multiplets, 2H), 7.49 – 7.32 (m, 5H), 7.08 (d, J =10.0, 2H), 6.54 (d, J =9.8, 1H), 6.50 (s, 1H), 5.39 (s, 2H), 4.07 – 3.97 (m, 2H), 3.88 (s, 3H), 1.87 (q, J =7.3, 2H), 1.06 (t, J =7.3, 3H).

I-3c-F

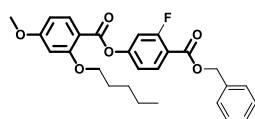


2-fluoro-4-hydroxybenzyl benzoate	999 mg,	4.0 mmol,	1 eq.
2-propoxy-4-methoxybenzoic acid	1.008 g,	4.5 mmol,	1.1 eq.
EDC.HCl	1.604 g,	8.4 mmol,	2.1 eq.
DMAP	53 mg,	0.4 mmol,	0.1 eq.
DCM	30 ml		

Recrystallised from ethanol, yield 954 mg

^1H NMR (400 MHz, CDCl_3) δ = 8.09 – 7.98 (m, 2H), 7.50 – 7.30 (m, 5H), 7.12 – 7.03 (m, 2H), 6.54 (dd, J =8.8, 2.3, 1H), 6.50 (d, J =2.3, 1H), 5.39 (s, 2H), 4.05 (t, J =6.4, 2H), 3.90 – 3.86 (m, 3H), 1.82 (dq, J =8.2, 6.4, 2H), 1.59 – 1.45 (m, 2H), 0.94 (t, J =7.4, 3H).

I-3d-F



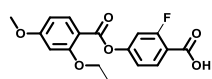
2-fluoro-4-hydroxybenzyl benzoate	335 mg,	1.4 mmol,	1 eq.
2-propoxy-4-methoxybenzoic acid	379 mg,	1.6 mmol,	1.1 eq.
EDC.HCl	569 mg,	3.0 mmol,	2.1 eq.
DMAP	18 mg,	0.4 mmol,	0.1 eq.
DCM	10 ml		

Recrystallised from ethanol, yield 148 mg

^1H NMR (400 MHz, CDCl_3) δ = 8.07 – 7.98 (m, 2H), 7.50 – 7.30 (m, 5H), 7.12 – 7.04 (m, 2H), 6.54 (dd, J =8.8, 2.3, 1H), 6.50 (d, J =2.3, 1H), 5.39 (s, 2H), 4.04 (t, J =6.5, 2H), 3.88 (s, 3H), 1.90 – 1.78 (m, 2H), 1.53 – 1.41 (m, 2H), 1.35 (h, J =7.2, 2H), 0.88 (t, J =7.2, 3H).

Deprotection I-4x

Under an argon atmosphere triethylsilane was added dropwise to a stirred solution of **I-3x** and 5 % Pd/C in a 1:1 mix of ethanol and DCM. The reaction was stirred for 5 minutes after addition was complete, then filtered through celite and the solvent removed *in vacuo*. The crude product was washed with hexane to yield the product as a white powder.

I-4a-F

I-3a-F 138 mg, 0.3 mmol

5% Pd/C 30 mg

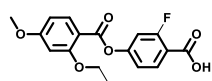
Triethylsilane 0.1 ml

DCM 3 ml

EtOH 3 ml

Recrystallised from ethanol, yield 103 mg.

^1H NMR (400 MHz, CDCl_3) δ = 8.13 – 8.05 (m, 1H), 8.04 (d, J =8.8, 1H), 7.15 (s, 1H), 7.12 (d, J =3.6, 1H), 6.58 – 6.49 (m, 2H), 4.13 (q, J =7.1, 2H), 3.89 (s, 3H), 1.49 (t, J =7.1, 3H).

I-4b-F

I-3b-F 160 mg, 0.36 mmol

5% Pd/C 40 mg

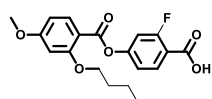
Triethylsilane 0.15 ml

DCM 3 ml

EtOH 3 ml

Crude product washed with hexane, yield 97 mg.

^1H NMR (400 MHz, CDCl_3) δ = 8.09 (t, J =8.5, 1H), 8.03 (d, J =8.8, 1H), 7.17 – 7.10 (m, 2H), 6.56 (dd, J =8.8, 2.3, 1H), 6.51 (d, J =2.3, 1H), 4.02 (t, J =6.4, 2H), 3.89 (s, 3H), 1.88 (h, J =7.0, 2H), 1.07 (t, J =7.4, 3H).

I-4c-F

I-3c-F 239 mg, 0.5 mmol

5% Pd/C 50 mg

Triethylsilane 0.25 ml

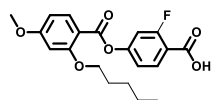
DCM 3 ml

EtOH 3 ml

Crude product washed with hexane, yield 159 mg.

^1H NMR (400 MHz, CDCl_3) δ = 8.08 (t, J =8.5, 1H), 8.02 (d, J =8.8, 1H), 7.15 – 7.07 (m, 2H), 6.54 (dd, J =8.8, 2.3, 1H), 6.50 (d, J =2.3, 1H), 4.05 (t, J =6.4, 2H), 3.88 (s, 3H), 1.88 – 1.77 (m, 2H), 1.57 – 1.47 (m, 2H), 0.95 (t, J =7.4, 3H).

I-4d-F



I-3d-F 210 mg, 0.45 mmol

5% Pd/C 50 mg

Triethylsilane 0.2 ml

DCM 3 ml

EtOH 3 ml

Crude product washed with hexane, yield 137 mg.

^1H NMR (400 MHz, CDCl_3) δ = 8.08 (t, J =8.5, 1H), 8.02 (d, J =8.8, 1H), 7.16 – 7.08 (m, 2H), 6.55 (d, J =9.5, 1H), 6.51 (s, 1H), 4.05 (t, J =6.6, 2H), 3.89 (s, 3H), 1.91 – 1.81 (m, 2H), 1.46 (q, J =7.7, 2H), 1.36 (q, J =7.3, 2H), 0.89 (t, J =7.2, 3H).

Esterification

Method A

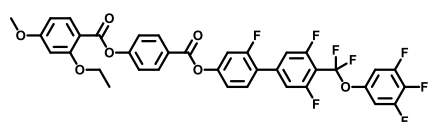
Intermediate acid **I-3x** and EDC.HCl were dissolved in 10 ml DCM and stirred for 5 minutes. The appropriate phenol and DMAP were added, and the mixture stirred overnight and monitored by TLC. The reaction mixture was washed 3 times with water and the organic layer dried over magnesium sulfate and removed *in vacuo*. The crude solid was dissolved in the minimum amount of chloroform and precipitated with hexane or ethanol.

Method B

Intermediate acid **I-4x** and DCC were dissolved in 10 ml DCM in an icebath and stirred for 30 minutes. The appropriate phenol was added, and the mixture stirred overnight and monitored by TLC. The reaction mixture was filtered and the solvent removed *in vacuo*. The crude solid was dissolved in the minimum amount of chloroform and precipitated with hexane or ethanol.

	Method	EDC.HCl	DMAP	DCC	Acid	Phenol	Antisolvent	Isolated Yield
E-0-1	A	67 mg, 0.3 mmol	3 mg, 0.02 mmol	-	76 mg, 0.2 mmol	93 mg, 0.2 mmol	Hexane	60 mg
E-0-2	B			55mg 0.3 mmol	100 mg, 0.3 mmol	104 mg, 0.2 mmol	Ethanol	52 mg
E-1-1	A	94 mg, 0.5 mmol	6 mg, 0.05 mmol	-	100 mg, 0.3 mmol	111 mg, 0.3 mmol	Ethanol	43 mg
E-1-2	B	-	-	31 mg, 0.2 mmol	60 mg, 0.2 mmol	59 mg, 0.1 mmol	Ethanol	19 mg
P-0-1	A	191 mg, 1 mmol	7 mg, 0.05 mmol	-	180 mg, 0.5 mmol	191 mg, 0.4 mmol	Ethanol	152 mg
P-0-2	B	-	-	38 mg, 0.2 mmol	79 mg, 0.2 mmol	80 mg, 0.2 mmol	Ethanol	12 mg
P-1-1	A	62 mg, 0.3 mmol	7 mg, 0.05 mmol	-	80 mg, 0.2 mmol	88 mg, 0.2 mmol	Ethanol	68 mg
P-1-2	B	-	-	71 mg, 0.3 mmol	159 mg, 0.5 mmol	150 mg, 0.3 mmol	Hexane	95 mg
B-0-1	A	46 mg, 0.2 mmol	2 mg, 0.02 mmol	-	46 mg, 0.1 mmol	57 mg, 0.1 mmol	Hexane	31 mg
B-0-2	B	-	-	68 mg, 0.3 mmol	99 mg, 0.3 mmol	92 mg 0.2 mmol	Ethanol	30 mg
B-1-1	A	69 mg, 0.3 mmol	8 mg, 0.06 mmol	-	76 mg, 0.2 mmol	80 mg, 0.2 mmol	Ethanol	73 mg
B-1-2	B	-	-	34 mg, 0.2 mmol	80 mg, 0.2 mmol	73 mg, 0.2 mmol	Ethanol	27 mg
Q-0-1	A	65 mg, 0.3 mmol	3 mg, 0.02 mmol	-	78 mg, 0.2 mmol	83 mg, 0.2 mmol	Hexane	44 mg
Q-0-2	B	-	-	43 mg, 0.2 mmol	80 mg, 0.2 mmol	68 mg, 0.2 mmol	Ethanol	85 mg
Q-1-1	A	48 mg, 0.2 mmol	3 mg, 0.02 mmol	-	62 mg, 0.2 mmol	69 mg, 0.2 mmol	Ethanol	47 mg
Q-1-2	B	-	-	28 mg, 0.1 mmol	68 mg, 0.2 mmol	60 mg, 0.1 mmol	Ethanol	33 mg

E-0-1



HRMS (ESI) m/z Calculated for $C_{36}H_{22}O_7F_8$:

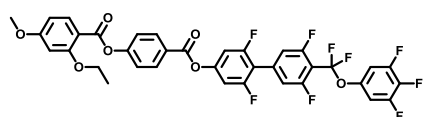
$[M+H]^+$ theoretical mass: 719.13105, found 719.13037, difference -0.952 ppm.

1H NMR (400 MHz, $CDCl_3$) δ = 8.26 (d, $J=8.6$, 2H), 8.08 (d, $J=8.9$, 1H), 7.50 (t, $J=8.6$, 1H), 7.39 (d, $J=8.6$, 2H), 7.27 – 7.14 (m, 4H), 7.04 – 6.96 (m, 2H), 6.57 (dd, $J=8.9$, 2.3, 1H), 6.53 (d, $J=2.3$, 1H), 4.15 (q, $J=7.0$, 2H), 3.89 (s, 3H), 1.50 (t, $J=7.0$, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -61.82 (t, $J=26.3$, 2F), -110.44 (td, $J=26.3$, 11.0, 2F), -113.87 (t, $J=9.8$, 1F), -132.45 (dd, $J=21.0$, 8.0, 2F), -163.10 (tt, $J=21.0$, 5.8, 1F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.22, 163.99, 163.08, 161.85, 161.24, 161.17, 160.80, 158.99, 158.93, 158.70, 158.64, 158.62, 158.61, 158.29, 155.92, 152.40, 152.29, 149.67, 144.53, 140.79, 139.71, 134.57, 131.87, 130.58, 130.54, 125.75, 122.44, 118.52, 118.48, 113.25, 113.23, 113.19, 113.01, 112.98, 112.96, 111.08, 110.83, 110.64, 107.60, 107.54, 107.41, 107.36, 104.99, 99.85, 64.64, 55.60, 14.66.

E-0-2



HRMS (ESI) m/z Calculated for $C_{36}H_{21}O_7F_9$:

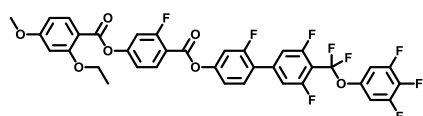
$[M+H]^+$ theoretical mass: 737.12163, found 737.12174, difference 0.145 ppm.

1H NMR (400 MHz, $CDCl_3$) δ = 8.25 (d, $J=8.7$, 2H), 8.08 (d, $J=8.7$, 1H), 7.40 (d, $J=8.7$, 2H), 7.18 (d, $J=10.7$, 2H), 7.01 (t, $J=7.7$, 4H), 6.58 (d, $J=8.7$, 1H), 6.53 (d, $J=2.0$, 1H), 4.20 – 4.10 (m, 2H), 3.90 (s, 3H), 1.54 – 1.46 (m, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -61.99 (t, $J=26.5$, 2F), -110.63 (td, $J=26.5$, 10.7, 2F), -112.06 (d, $J=8.8$, 2F), -132.43 (dd, $J=20.9$, 8.3, 2F), -163.06 (tt, $J=20.9$, 5.9, 1F).

^{13}C NMR (101 MHz, $cdcl_3$) δ 165.24, 163.60, 163.02, 161.87, 160.99, 160.92, 158.49, 158.41, 156.10, 134.58, 131.93, 125.34, 122.52, 114.88, 114.64, 110.59, 107.65, 107.41, 106.97, 106.68, 105.00, 99.85, 64.64, 55.60, 14.66.

E-1-1



HRMS (ESI) m/z Calculated for $C_{36}H_{21}O_7F_9$:

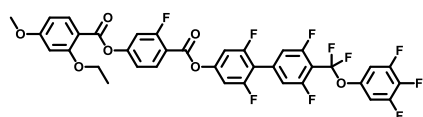
$[M+H]^+$ theoretical mass: 737.12163, found 737.12200, difference 0.498 ppm.

^1H NMR (400 MHz, CDCl_3) δ = 8.17 (t, J =8.3, 1H), 8.06 (d, J =8.8, 1H), 7.50 (t, J =8.5, 1H), 7.29 – 7.16 (m, 6H), 7.00 (t, J =7.0, 2H), 6.57 (d, J =8.8, 1H), 6.53 (d, J =2.5, 1H), 4.15 (q, J =7.1, 2H), 3.90 (s, 3H), 1.50 (t, J =7.1, 3H).

^{19}F NMR (376 MHz, CDCl_3) δ = -61.83 (t, J =26.2, 2F), -104.30 – -104.42 (m, 1F), -110.42 (td, J =26.2, 10.9, 2F), -113.82 (t, J =9.8, 1F), -132.44 (dd, J =20.7, 8.3, 2F), -163.10 (tt, J =20.7, 5.9, 1F).

^{13}C NMR (101 MHz, CDCl_3) δ 165.44, 164.23, 162.49, 161.98, 161.67, 161.63, 161.60, 161.23, 161.18, 160.77, 158.26, 156.84, 156.72, 152.32, 152.21, 152.02, 151.91, 149.77, 149.67, 140.93, 140.73, 140.63, 139.71, 137.31, 134.64, 133.35, 130.57, 130.53, 123.40, 120.14, 118.48, 118.45, 118.25, 118.21, 117.44, 114.25, 114.16, 113.23, 112.99, 111.69, 111.44, 111.06, 110.80, 110.11, 107.60, 107.53, 107.41, 107.36, 105.07, 99.80, 64.63, 55.62, 14.65.

E-1-2



HRMS (ESI) m/z Calculated for $\text{C}_{36}\text{H}_{20}\text{O}_7\text{F}_{10}$:

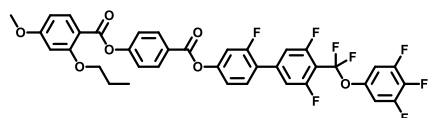
$[\text{M}+\text{H}]^+$ theoretical mass: 755.11221, found 755.11244, difference 0.303 ppm.

^1H NMR (400 MHz, CDCl_3) δ = 8.15 (t, J =8.2, 1H), 8.05 (d, J =8.8, 1H), 7.28 – 7.14 (m, 4H), 7.07 – 6.97 (m, 4H), 6.57 (dd, J =8.8, 2.3, 1H), 6.52 (d, J =2.7, 1H), 4.15 (q, J =7.0, 2H), 3.90 (s, 3H), 1.50 (t, J =7.0, 3H).

^{19}F NMR (376 MHz, CDCl_3) δ = -61.99 (t, J =26.4, 2F), -104.10 (dd, J =11.2, 8.1, 1F), -110.61 (td, J =26.4, 10.6, 2F), -111.99 (d, J =8.9, 2F), -132.44 (dd, J =20.7, 7.1, 2F), -163.06 (tt, J =20.7, 5.8, 1F).

^{13}C NMR (101 MHz, CDCl_3) δ 165.47, 164.26, 162.44, 162.00, 161.63, 161.27, 161.23, 160.97, 160.89, 158.47, 158.39, 157.04, 156.93, 152.32, 152.29, 152.23, 152.17, 151.80, 151.66, 151.52, 149.82, 149.77, 144.49, 139.87, 139.74, 134.65, 134.43, 134.36, 134.20, 133.37, 119.99, 118.32, 118.29, 114.88, 114.63, 113.86, 113.77, 113.02, 111.74, 111.49, 110.05, 107.64, 107.55, 107.47, 107.40, 106.95, 106.92, 106.87, 106.68, 106.66, 106.65, 105.08, 99.80, , 64.63, 55.62, 14.64.

P-0-1



HRMS (ESI) m/z Calculated for $\text{C}_{37}\text{H}_{24}\text{O}_7\text{F}_8$:

$[\text{M}+\text{H}]^+$ theoretical mass: 733.14670, found 733.14596, difference -1.016 ppm.

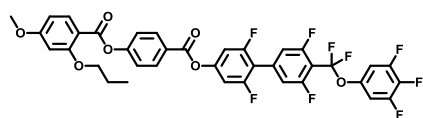
^1H NMR (400 MHz, CDCl_3) δ = 8.27 (d, J =8.0, 2H), 8.07 (d, J =8.7, 1H), 7.50 (t, J =8.6, 1H), 7.39 (d, J =8.0, 2H), 7.23 (d, J =10.8, 2H), 7.21 – 7.13 (m, 2H), 7.04 – 6.96 (m, 2H), 6.57 (d,

$J=8.7$, 1H), 6.53 (s, 1H), 4.03 (t, $J=6.4$, 2H), 3.89 (s, 3H), 1.89 (h, $J=7.1$, 2H), 1.08 (t, $J=7.4$, 3H).

^{19}F NMR (376 MHz, CDCl_3) δ = -61.82 (t, $J=26.3$, 2F), -110.44 (td, $J=26.3$, 10.9, 2F), -113.87 (t, $J=9.9$, 1F), -132.44 (dd, $J=20.7$, 8.3, 2F), -163.11 (tt, $J=20.7$, 5.8, 1F).

^{13}C NMR (101 MHz, CDCl_3) δ 165.22, 163.99, 163.24, 161.93, 161.24, 161.18, 160.80, 158.67, 158.59, 158.29, 155.96, 152.41, 152.30, 152.22, 152.16, 149.83, 149.77, 149.72, 149.67, 144.58, 140.79, 139.70, 137.22, 134.64, 131.90, 130.58, 130.54, 125.74, 123.27, 123.14, 122.79, 122.43, 120.13, 120.12, 118.52, 118.48, 117.45, 113.26, 113.22, 113.01, 112.98, 112.95, 111.08, 110.82, 110.62, 107.60, 107.54, 107.43, 107.36, 104.95, 99.67, 70.40, 55.59, 22.51, 10.62.

P-0-2



HRMS (ESI) m/z Calculated for $\text{C}_{37}\text{H}_{23}\text{O}_7\text{F}_9$:

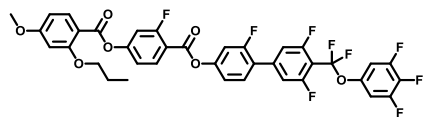
$[\text{M}+\text{H}]^+$ theoretical mass: 751.13728, found 751.13738, difference 0.129 ppm.

^1H NMR (400 MHz, CDCl_3) δ = 8.24 (d, $J=8.7$, 2H), 8.06 (d, $J=8.8$, 1H), 7.38 (d, $J=8.7$, 2H), 7.16 (d, $J=10.7$, 2H), 7.04 – 6.96 (m, 4H), 6.56 (dd, $J=8.8$, 2.3, 1H), 6.52 (d, $J=2.3$, 1H), 4.02 (t, $J=6.5$, 2H), 3.88 (s, 3H), 1.94 – 1.81 (m, 2H), 1.07 (t, $J=7.4$, 3H).

^{19}F NMR (376 MHz, CDCl_3) δ = -61.99 (t, $J=26.5$, 2F), -110.63 (td, $J=26.5$, 10.7, 2F), -112.06 (d, $J=8.7$, 2F), -132.43 (dd, $J=20.9$, 7.9, 2F), -163.06 (tt, $J=20.9$, 5.8, 1F).

^{13}C NMR (101 MHz, CDCl_3) δ 165.25, 163.60, 163.18, 161.95, 160.99, 160.91, 158.49, 158.41, 156.13, 134.65, 131.95, 125.34, 122.51, 114.87, 114.63, 110.56, 107.65, 107.41, 106.97, 106.94, 106.67, 104.96, 99.67, 70.40, 55.60, 22.51, 10.62.

P-1-1



HRMS (ESI) m/z Calculated for $\text{C}_{37}\text{H}_{23}\text{O}_7\text{F}_9$:

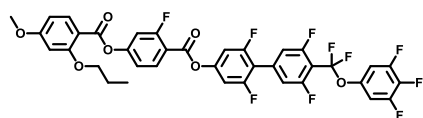
$[\text{M}+\text{H}]^+$ theoretical mass: 751.13728, found 751.13811, difference 1.101 ppm.

^1H NMR (400 MHz, CDCl_3) δ = 8.17 (t, $J=8.5$, 1H), 8.05 (d, $J=8.8$, 1H), 7.50 (t, $J=8.6$, 1H), 7.26 – 7.14 (m, 6H), 7.04 – 6.96 (m, 2H), 6.56 (dd, $J=8.5$, 2.3, 1H), 6.52 (d, $J=2.3$, 1H), 4.03 (t, $J=6.4$, 2H), 3.90 (s, 3H), 1.89 (h, $J=7.1$, 2H), 1.08 (t, $J=7.4$, 3H).

^{19}F NMR (376 MHz, CDCl_3) δ = -61.83 (t, $J=26.4$, 2F), -104.34 (dd, $J=11.3$, 8.2, 1F), -110.42 (td, $J=26.4$, 10.7, 2F), -113.82 (t, $J=9.8$, 1F), -132.36 – -132.53 (m, 2F), -163.10 (tt, $J=20.9$, 5.9, 1F).

^{13}C NMR (101 MHz, CDCl_3) δ 165.44, 164.24, 162.64, 162.07, 161.61, 160.77, 158.26, 156.86, 156.75, 152.27, 152.02, 151.76, 149.76, 149.67, 144.59, 140.74, 134.72, 133.39, 130.57, 130.54, 118.48, 118.44, 118.25, 114.26, 113.23, 112.99, 111.69, 111.44, 111.06, 110.80, 110.08, 107.60, 107.36, 105.04, 99.63, 70.40, 55.62, 22.49, 10.62.

P-1-2



HRMS (ESI) m/z Calculated for $\text{C}_{37}\text{H}_{22}\text{O}_7\text{F}_{10}$:

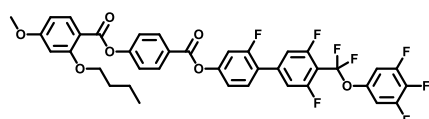
$[\text{M}+\text{H}]^+$ theoretical mass: 769.12786, found 769.12802, difference 0.207 ppm.

^1H NMR (400 MHz, CDCl_3) δ = 8.15 (t, $J=8.3$, 1H), 8.05 (d, $J=8.8$, 1H), 7.23 – 7.14 (m, 4H), 7.02 (p, $J=6.5$, 4H), 6.56 (dd, $J=8.8$, 2.0, 1H), 6.52 (d, $J=2.0$, 1H), 4.03 (d, $J=7.2$, 2H), 3.89 (s, 3H), 1.89 (h, $J=7.1$, 2H), 1.08 (t, $J=7.5$, 3H).

^{19}F NMR (376 MHz, CDCl_3) δ = -61.99 (t, $J=26.5$, 2F), -104.08 (dd, $J=11.3$, 8.0, 1F), -110.61 (td, $J=26.5$, 10.8, 2F), -111.99 (d, $J=8.8$, 2F), -132.44 (dd, $J=20.9$, 8.2, 2F), -163.06 (tt, $J=20.9$, 5.9, 1F).

^{13}C NMR (101 MHz, CDCl_3) δ 165.47, 164.27, 163.33, 162.58, 162.09, 161.65, 161.27, 161.23, 161.03, 160.97, 160.89, 158.47, 158.39, 157.08, 156.96, 152.34, 152.25, 152.21, 152.16, 151.66, 149.83, 149.78, 149.67, 139.71, 134.72, 134.46, 134.36, 134.30, 133.40, 127.18, 120.01, 118.32, 118.29, 114.88, 114.63, 113.86, 113.77, 111.74, 111.49, 110.02, 107.64, 107.57, 107.46, 107.41, 106.95, 106.92, 106.67, 106.65, 105.05, 99.62, 70.39, 55.62, 22.49, 10.62.

B-0-1



HRMS (ESI) m/z Calculated for $\text{C}_{38}\text{H}_{26}\text{O}_7\text{F}_8$:

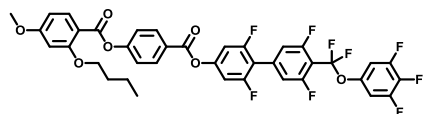
$[\text{M}+\text{H}]^+$ theoretical mass: 747.162350, found 747.16190, difference -0.609 ppm.

^1H NMR (400 MHz, CDCl_3) δ = 8.27 (d, $J=8.3$, 2H), 8.07 (d, $J=8.7$, 1H), 7.50 (t, $J=8.6$, 1H), 7.38 (d, $J=8.3$, 2H), 7.28 – 7.13 (m, 4H), 7.04 – 6.96 (m, 2H), 6.57 (d, $J=8.7$, 1H), 6.53 (s, 1H), 4.07 (t, $J=6.4$, 2H), 3.90 (s, 3H), 1.85 (p, $J=6.7$, 2H), 1.61 – 1.47 (m, 2H), 0.96 (t, $J=7.3$, 3H).

^{19}F NMR (376 MHz, CDCl_3) δ = -61.82 (t, $J=26.3$, 2F), -110.43 (td, $J=26.3$, 10.9, 2F), -113.86 (t, $J=9.8$, 1F), -132.44 (dq, $J=20.6$, 8.0, 2F), -163.10 (tt, $J=20.6$, 5.8, 1F).

^{13}C NMR (101 MHz, CDCl_3) δ 165.21, 163.99, 163.20, 161.94, 161.23, 161.18, 160.79, 158.68, 158.29, 158.00, 155.96, 152.30, 134.64, 131.89, 130.54, 125.74, 122.43, 118.48, 113.23, 112.99, 111.08, 110.83, 110.63, 107.60, 107.36, 104.91, 99.67, 68.59, 55.60, 31.13, 19.20, 13.80.

B-0-2



HRMS (ESI) m/z Calculated for $C_{38}H_{25}O_7F_9$:

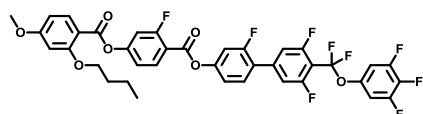
$[M+H]^+$ theoretical mass: 765.15293, found 765.15322, difference 0.375 ppm.

1H NMR (400 MHz, $CDCl_3$) δ = 8.25 (d, $J=8.3$, 2H), 8.07 (d, $J=8.7$, 1H), 7.39 (d, $J=8.3$, 2H), 7.18 (d, $J=10.7$, 2H), 7.01 (t, $J=7.6$, 4H), 6.57 (d, $J=9.0$, 1H), 6.53 (s, 1H), 4.07 (t, $J=6.5$, 2H), 3.90 (s, 3H), 1.84 (p, $J=6.9$, 2H), 1.62 – 1.47 (m, 2H), 0.96 (t, $J=7.4$, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -61.99 (t, $J=26.3$, 2F), -110.63 (td, $J=26.3$, 10.8, 2F), -112.05 (d, $J=8.9$, 2F), -132.43 (dd, $J=21.0$, 8.3, 2F), -163.06 (tt, $J=21.0$, 6.0, 1F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.24, 163.60, 163.15, 161.96, 161.00, 160.91, 158.49, 158.47, 158.37, 156.13, 152.20, 152.06, 149.77, 149.63, 134.65, 131.95, 125.33, 122.51, 114.88, 114.63, 110.56, 107.65, 107.41, 106.97, 106.68, 104.93, 99.66, 68.59, 55.60, 31.12, 19.20, 13.80.

B-1-1



HRMS (ESI) m/z Calculated for $C_{38}H_{25}O_7F_9$:

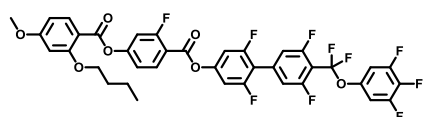
$[M+H]^+$ theoretical mass: 765.15293, found 765.15317, difference 0.310 ppm.

1H NMR (400 MHz, $CDCl_3$) δ = 8.23 (t, $J=8.4$, 1H), 8.11 (d, $J=8.8$, 1H), 7.56 (t, $J=8.5$, 1H), 7.34 – 7.21 (m, 6H), 7.06 (t, $J=7.0$, 2H), 6.62 (d, $J=8.8$, 1H), 6.59 (d, $J=2.2$, 1H), 4.13 (t, $J=6.4$, 2H), 3.96 (s, 3H), 1.91 (p, $J=6.7$, 2H), 1.67 – 1.54 (m, 2H), 1.03 (t, $J=7.4$, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -61.82 (t, $J=26.3$, 2F), -104.35 (dd, $J=11.4$, 8.1, 1F), -110.42 (td, $J=26.3$, 10.8, 2F), -113.82 (t, $J=9.9$, 1F), -132.45 (dd, $J=20.7$, 8.2, 2F), -163.11 (tt, $J=20.7$, 5.8, 1F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.44, 164.24, 162.60, 162.08, 161.63, 161.24, 160.77, 158.61, 156.87, 152.03, 151.92, 149.83, 144.57, 140.74, 139.95, 137.19, 134.71, 133.38, 130.57, 130.53, 123.40, 120.08, 118.48, 118.44, 118.23, 118.20, 117.37, 114.25, 114.16, 113.26, 113.23, 113.20, 113.01, 112.99, 112.95, 111.68, 111.43, 111.06, 110.80, 110.09, 107.60, 107.54, 107.42, 107.36, 105.01, 99.63, 68.59, 55.62, 31.11, 19.20, 13.79.

B-1-2



HRMS (ESI) m/z Calculated for $C_{38}H_{24}O_7F_{10}$:

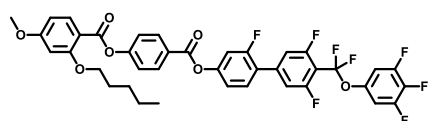
$[M+H]^+$ theoretical mass: 783.14351, found 783.14392, difference 0.522 ppm.

1H NMR (400 MHz, $CDCl_3$) δ = 8.14 (t, $J=9.0$, 1H), 8.04 (d, $J=8.8$, 1H), 7.22 – 7.13 (m, 4H), 7.07 – 6.96 (m, 4H), 6.56 (dd, $J=8.9$, 2.3, 1H), 6.52 (d, $J=2.3$, 1H), 4.06 (t, $J=6.4$, 2H), 3.89 (s, 3H), 1.90 – 1.78 (m, 2H), 1.60 – 1.47 (m, 2H), 0.96 (t, $J=7.4$, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -61.99 (t, $J=26.5$, 2F), -104.10 (t, $J=9.8$, 1F), -110.62 (td, $J=26.5$, 10.8, 2F), -111.99 (d, $J=8.9$, 2F), -132.44 (dd, $J=20.8$, 8.2, 2F), -163.07 (tt, $J=20.8$, 6.2, 1F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.46, 164.27, 162.64, 162.06, 161.64, 161.28, 161.24, 161.02, 160.90, 158.47, 158.37, 157.08, 156.96, 155.00, 152.25, 152.18, 134.73, 133.38, 118.31, 118.28, 114.91, 114.88, 114.66, 114.64, 113.86, 111.73, 111.48, 110.05, 107.65, 107.57, 107.45, 107.41, 106.95, 106.94, 106.68, 106.65, 105.03, 99.63, 68.93, 55.62, 28.77, 28.13, 22.37, 14.00.

Q-0-1



HRMS (ESI) m/z Calculated for $C_{39}H_{28}O_7F_8$:

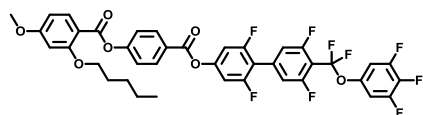
$[M+H]^+$ theoretical mass: 761.17800, found 761.17749, difference -0.677 ppm.

1H NMR (400 MHz, $CDCl_3$) δ = 8.27 (d, $J=8.3$, 2H), 8.07 (d, $J=8.8$, 1H), 7.50 (t, $J=8.5$, 1H), 7.38 (d, $J=8.3$, 2H), 7.28 – 7.14 (m, 4H), 7.00 (t, $J=7.0$, 2H), 6.57 (d, $J=8.7$, 1H), 6.53 (s, 1H), 4.06 (t, $J=6.6$, 2H), 3.89 (s, 3H), 1.86 (p, $J=6.9$, 2H), 1.53 – 1.43 (m, 2H), 1.36 (h, $J=7.5$, 2H), 0.89 (t, $J=7.3$, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -61.82 (t, $J=26.3$, 2F), -110.43 (td, $J=26.3$, 10.8, 2F), -113.87 (t, $J=10.0$, 1F), -132.44 (dd, $J=20.9$, 8.2, 2F), -163.10 (tt, $J=20.9$, 5.7, 1F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.21, 163.99, 163.28, 161.90, 160.79, 158.65, 158.29, 155.96, 152.30, 149.70, 134.65, 131.88, 130.54, 125.74, 122.43, 118.48, 113.23, 112.99, 111.08, 110.83, 110.65, 107.60, 107.37, 104.93, 99.68, 68.93, 55.60, 28.79, 28.13, 22.39, 14.00.

Q-0-2



HRMS (ESI) m/z Calculated for $C_{39}H_{27}O_7F_9$:

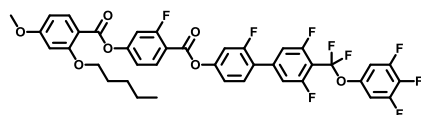
$[M+H]^+$ theoretical mass: 779.16858, found 779.16885, difference 0.343 ppm.

1H NMR (400 MHz, $CDCl_3$) δ = 8.25 (d, $J=7.8$, 2H), 8.06 (d, $J=8.7$, 1H), 7.39 (d, $J=7.8$, 2H), 7.18 (d, $J=10.7$, 2H), 7.05 – 6.97 (m, 4H), 6.57 (dd, $J=8.7$, 2.6, 1H), 6.52 (d, $J=2.6$, 1H), 4.06 (t, $J=6.6$, 2H), 3.89 (s, 3H), 1.86 (p, $J=7.2$, 2H), 1.49 (p, $J=7.4$, 2H), 1.37 (p, $J=7.5$, 2H), 0.89 (t, $J=6.9$, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -61.99 (t, $J=26.3$, 1F), -110.63 (dt, $J=26.3$, 10.8, 1F), -112.06 (d, $J=8.9$, 1F), -132.43 (dd, $J=20.9$, 8.3, 1F), -163.06 (tt, $J=20.9$, 5.9, 1F).

^{13}C NMR (101 MHz, $cdcl_3$) δ 165.24, 163.60, 163.23, 161.92, 160.98, 160.91, 158.49, 158.41, 156.13, 152.22, 152.06, 151.93, 149.86, 149.73, 142.53, 141.40, 139.73, 134.66, 134.43, 134.39, 131.94, 125.34, 122.51, 114.87, 114.63, 110.57, 107.65, 107.41, 106.97, 106.68, 104.94, 99.67, , 68.93, 55.60, 28.79, 28.13, 22.39, 14.00.

Q-1-1



HRMS (ESI) m/z Calculated for $C_{39}H_{27}O_7F_9$:

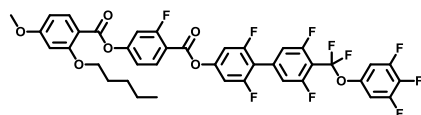
$[M+H]^+$ theoretical mass: 779.16858, found 779.16901, difference 0.548 ppm.

1H NMR (400 MHz, $CDCl_3$) δ = 8.17 (t, $J=8.3$, 1H), 8.04 (d, $J=8.7$, 1H), 7.50 (t, $J=8.5$, 1H), 7.28 – 7.14 (m, 6H), 7.00 (t, $J=7.1$, 2H), 6.56 (d, $J=8.7$, 1H), 6.52 (s, 1H), 4.06 (t, $J=6.4$, 2H), 3.89 (s, 3H), 1.87 (p, $J=6.9$, 2H), 1.53 – 1.43 (m, 2H), 1.43 – 1.30 (m, 2H), 0.90 (t, $J=7.4$, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -61.82 (t, $J=26.3$, 2F), -104.36 (dd, $J=11.4$, 8.1, 1F), -110.42 (td, $J=26.3$, 10.8, 2F), -113.82 (t, $J=9.8$, 1F), -132.44 (dd, $J=20.7$, 8.2, 2F), -163.10 (tt, $J=20.7$, 5.8, 1F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.43, 162.68, 162.04, 161.61, 134.72, 133.37, 130.57, 130.53, 118.48, 118.45, 118.20, 114.24, 114.15, 113.27, 113.23, 113.00, 112.99, 111.96, 111.68, 111.43, 111.06, 110.80, 110.12, 107.60, 107.52, 107.42, 107.36, 105.02, 99.64, 68.93, 55.62, 28.78, 28.13, 22.38, 14.00.

Q-1-2



HRMS (ESI) m/z Calculated for $C_{39}H_{26}O_7F_{10}$:

$[M+H]^+$ theoretical mass: 797.15916, found 797.15962, difference 0.575 ppm.

^1H NMR (400 MHz, CDCl_3) δ = 8.14 (t, J =8.8, 1H), 8.03 (d, J =8.8, 1H), 7.23 – 7.13 (m, 4H), 7.06 – 6.96 (m, 4H), 6.56 (dd, J =8.8, 2.3, 1H), 6.51 (d, J =2.3, 1H), 4.05 (t, J =6.5, 2H), 3.89 (s, 3H), 1.91 – 1.80 (m, 2H), 1.52 – 1.42 (m, 2H), 1.41 – 1.31 (m, 2H), 0.90 (t, J =7.2, 3H).

^{19}F NMR (376 MHz, CDCl_3) δ = -61.99 (t, J =26.5, 2F), -104.10 (t, J =9.8, 1F), -110.62 (td, J =26.5, 10.8, 2F), -111.99 (d, J =8.9, 2F), -132.44 (dd, J =20.8, 8.2, 2F), -163.07 (tt, J =20.8, 6.2, 1F).

^{13}C NMR (101 MHz, CDCl_3) δ 166.26, 165.46, 164.27, 162.64, 162.06, 161.64, 161.29, 161.24, 160.97, 160.87, 158.47, 158.40, 157.08, 134.73, 133.38, 118.31, 118.28, 114.88, 114.65, 111.73, 111.48, 110.05, 107.65, 107.58, 107.47, 107.41, 106.95, 106.92, 106.67, 106.65, 105.03, 99.63, 68.93, 55.62, 28.77, 28.13, 22.37, 14.00.

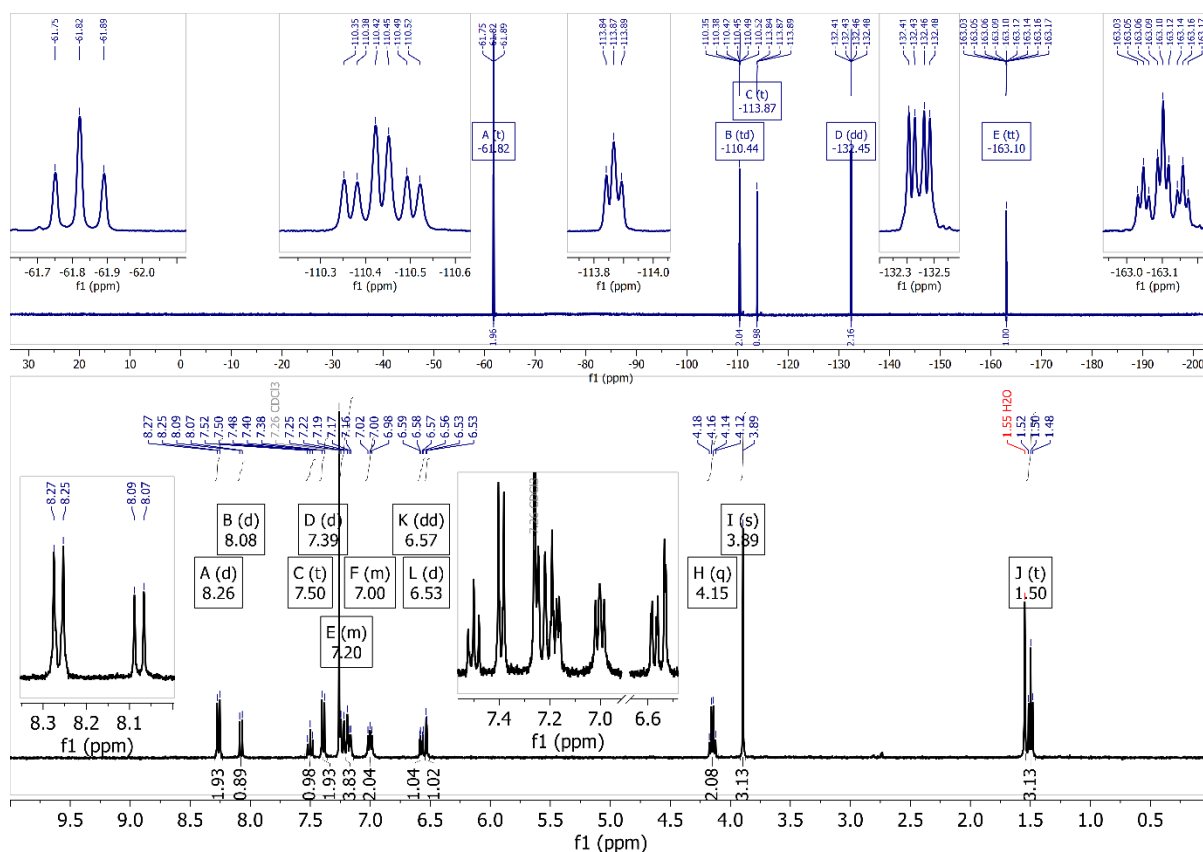


Figure S4. ¹⁹F and ¹H NMR spectra of **E-0-1** in CDCl₃.

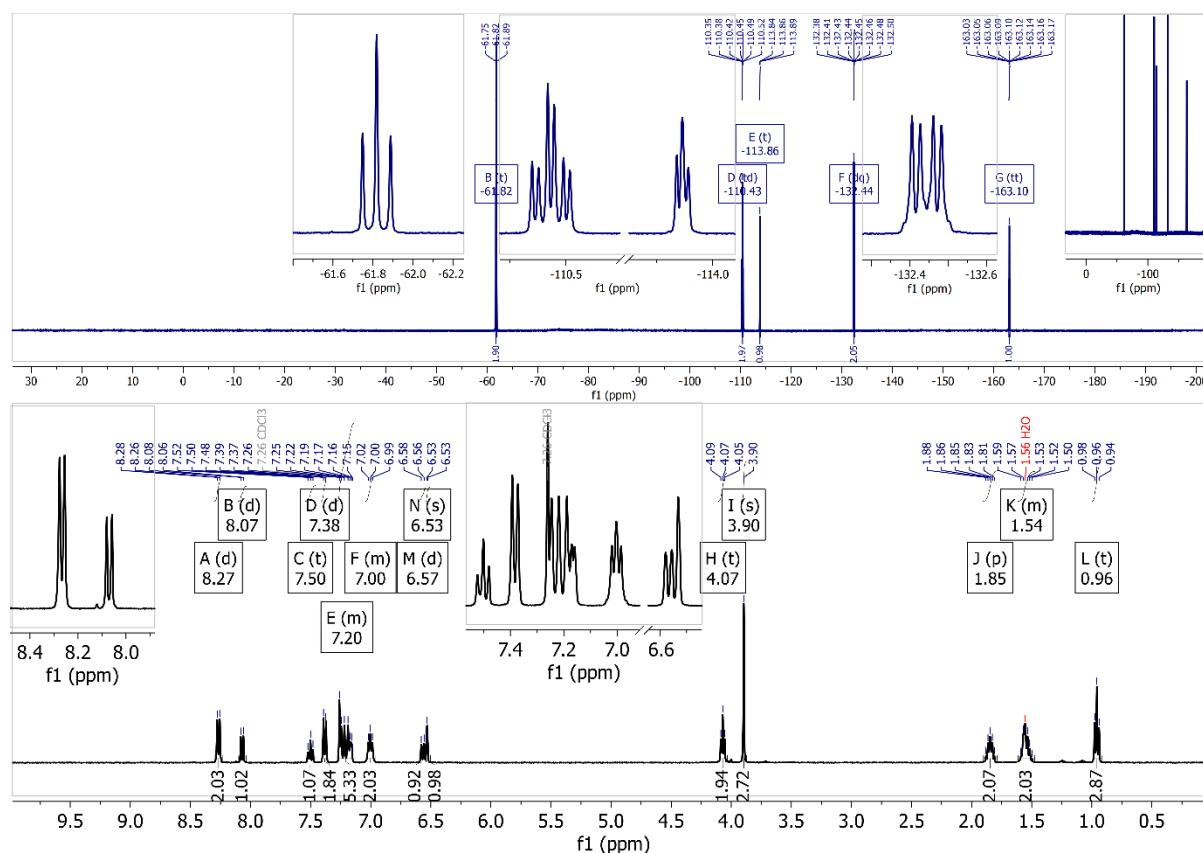


Figure S5. ¹⁹F and ¹H NMR spectra of **P-0-1** in CDCl₃.

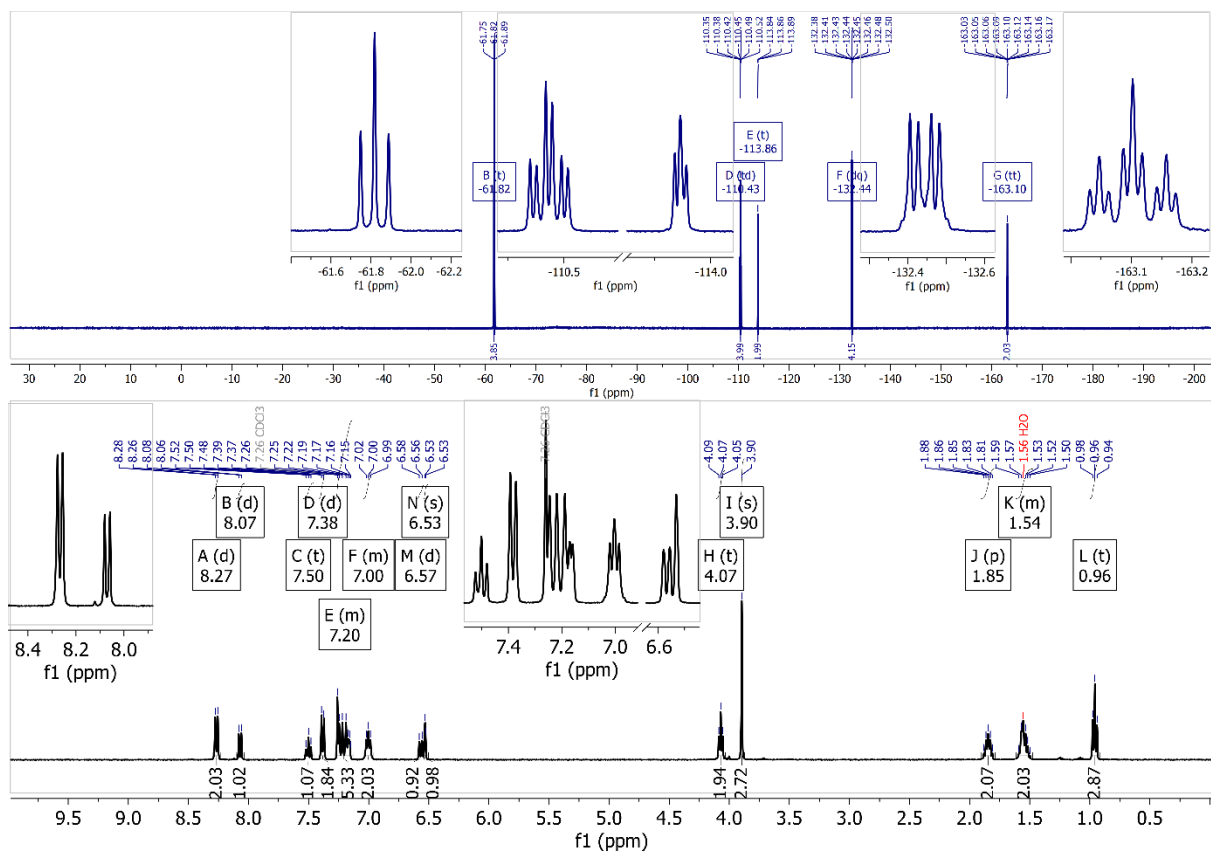


Figure S6. ^{19}F and ^1H NMR spectra of **B-0-1** in CDCl_3 .

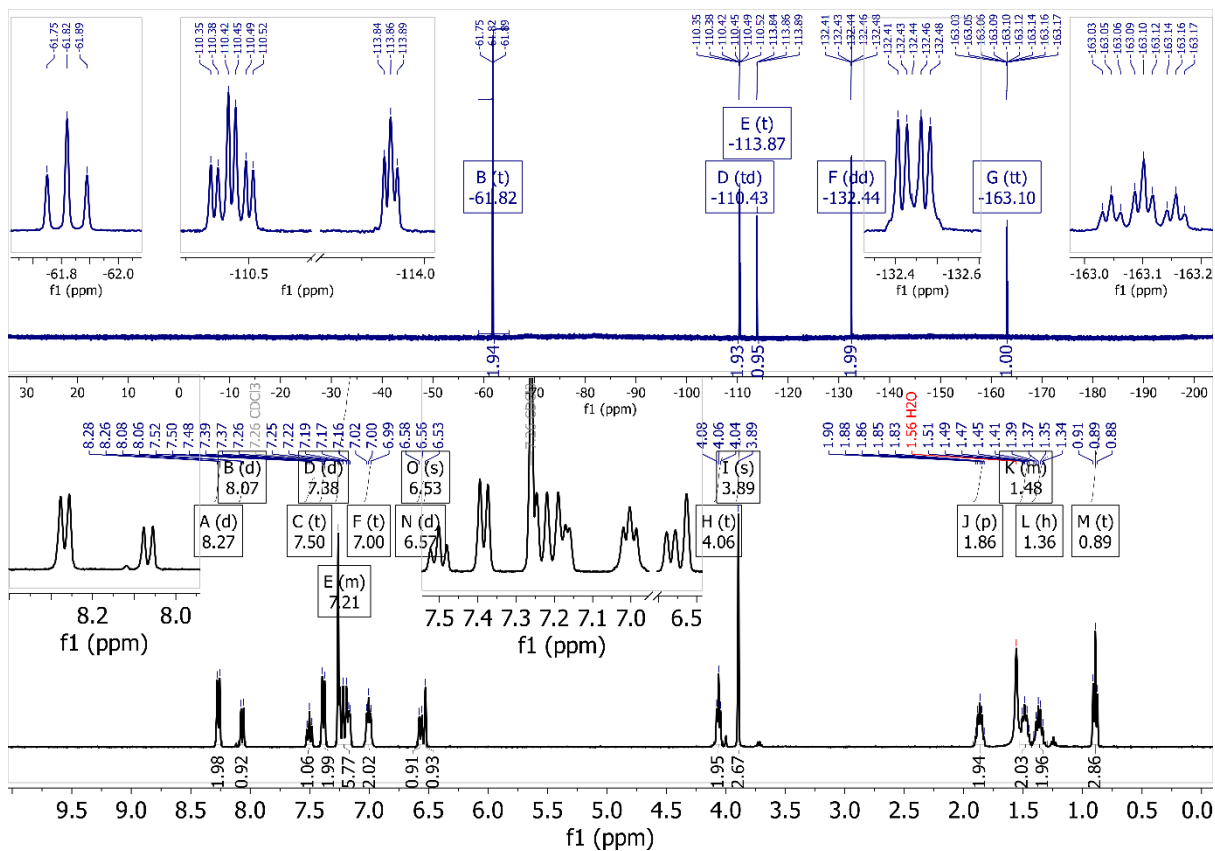


Figure S7. ^{19}F and ^1H NMR spectra of **Q-0-1** in CDCl_3 .

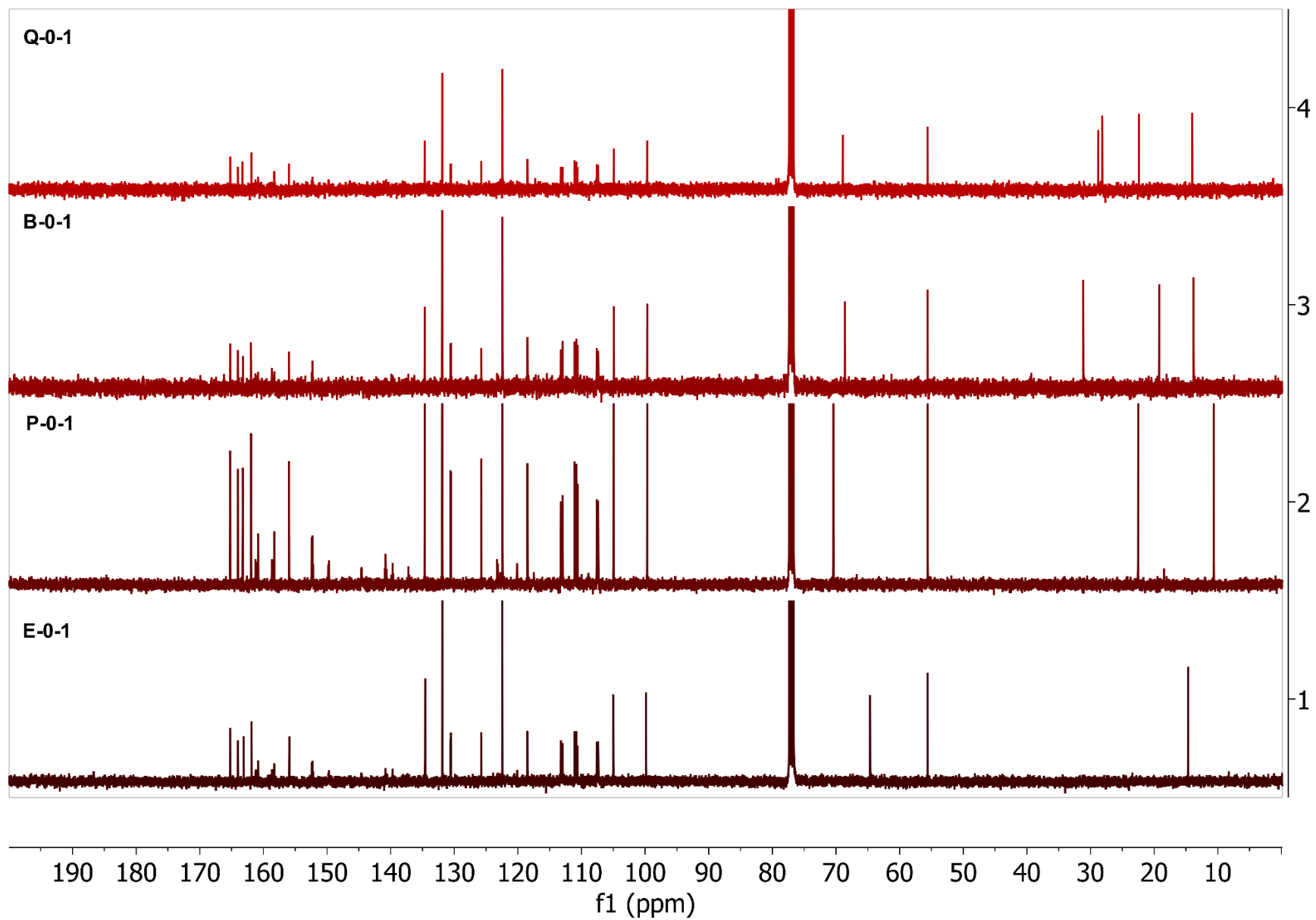


Figure S8. Stacked ^{13}C NMR spectra of **E-0-1**, **P-0-1**, **B-0-1** and **Q-0-1** in CDCl_3 .

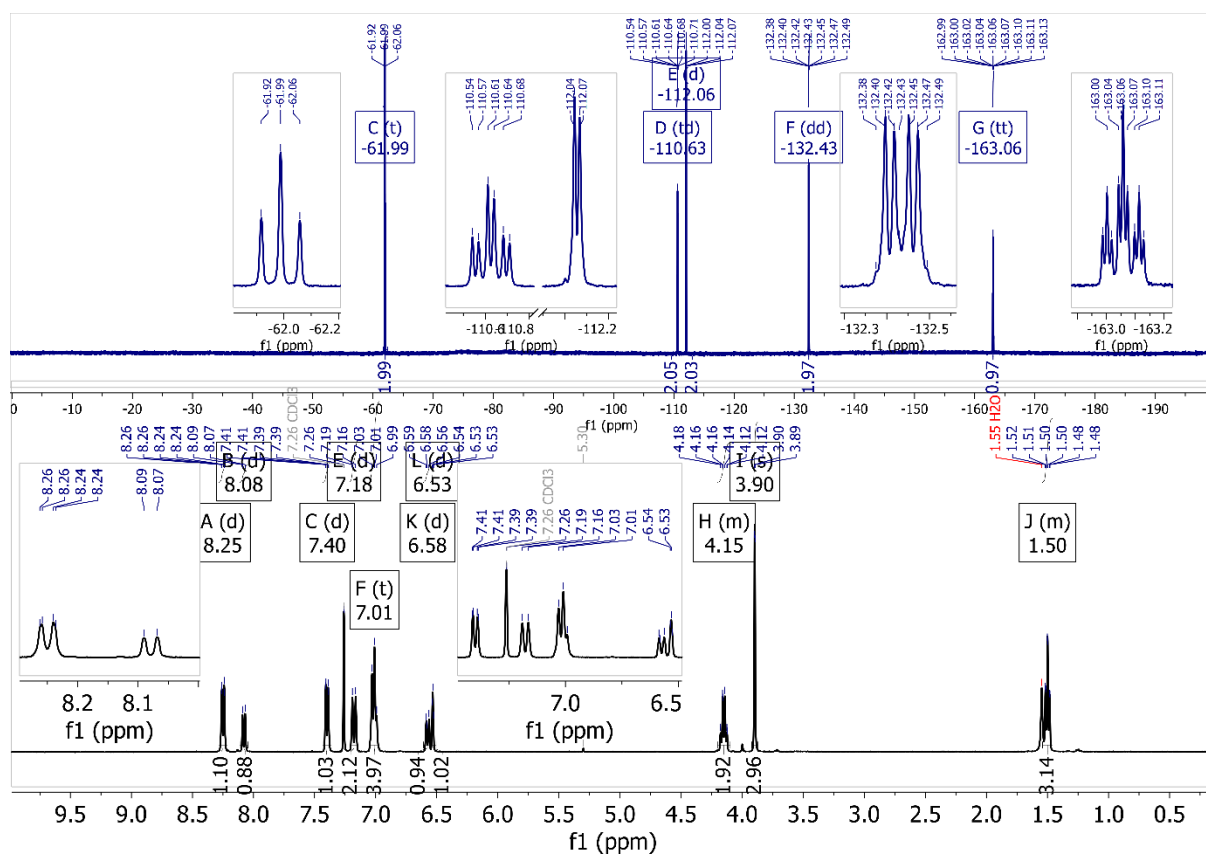


Figure S9. ¹⁹F and ¹H NMR spectra of **E-0-2** in CDCl₃.

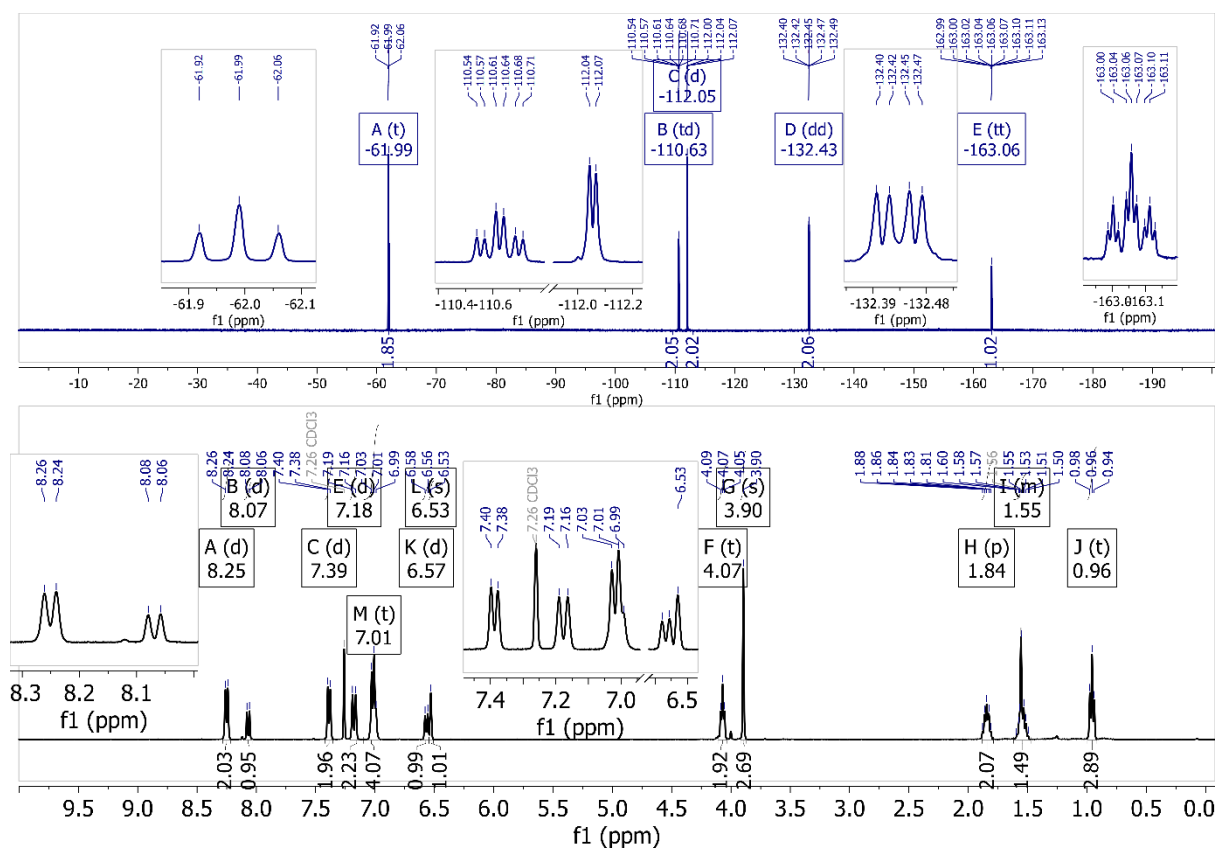


Figure S10. ¹⁹F and ¹H NMR spectra of **P-0-2** in CDCl₃.

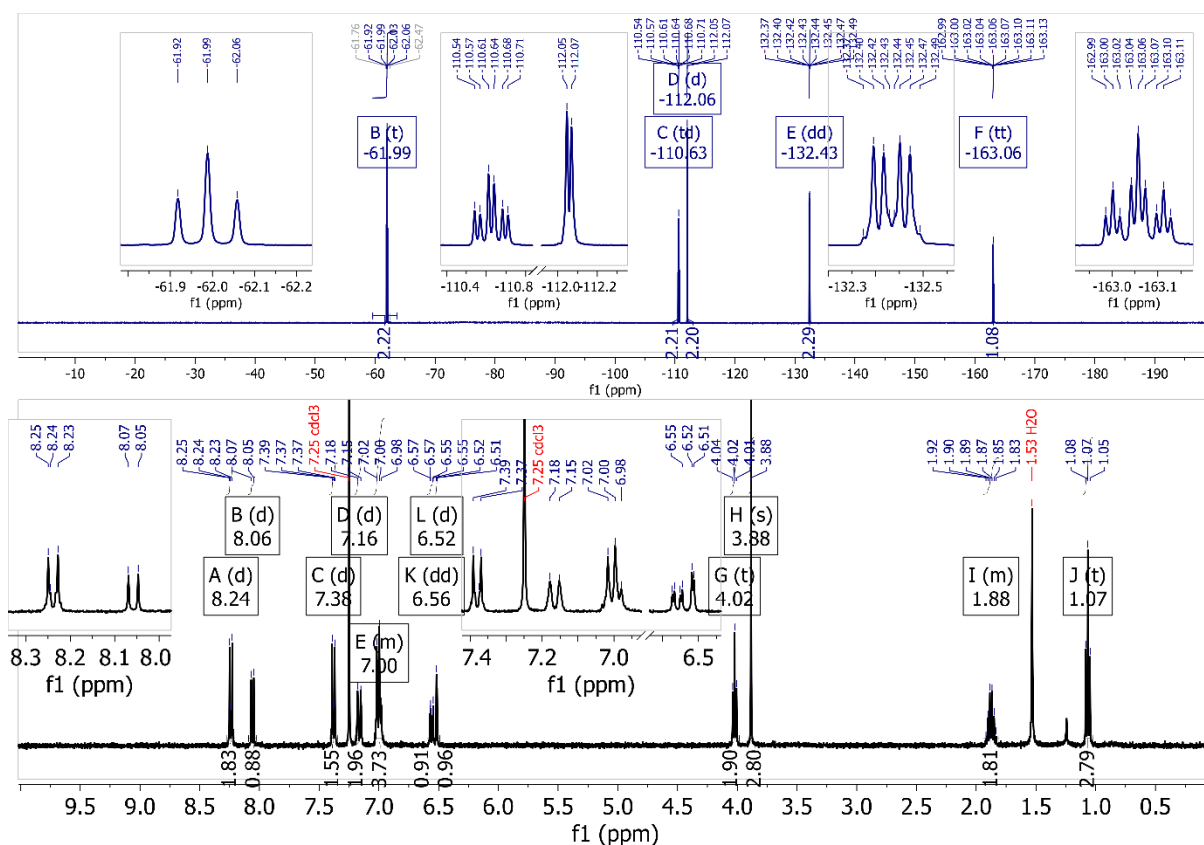


Figure S11. ^{19}F and ^1H NMR spectra of **P-0-2** in CDCl_3 .

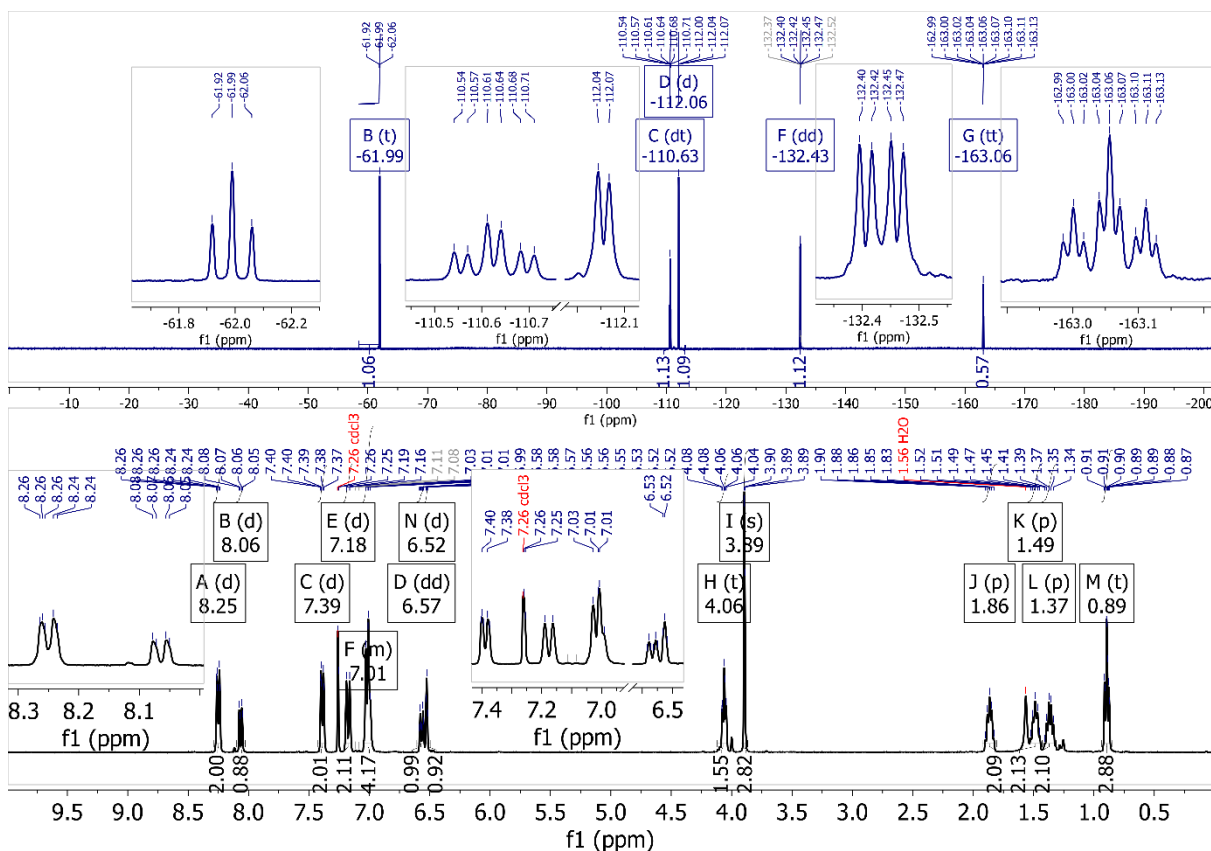


Figure S12. ^{19}F and ^1H NMR spectra of **Q-0-2** in CDCl_3 .

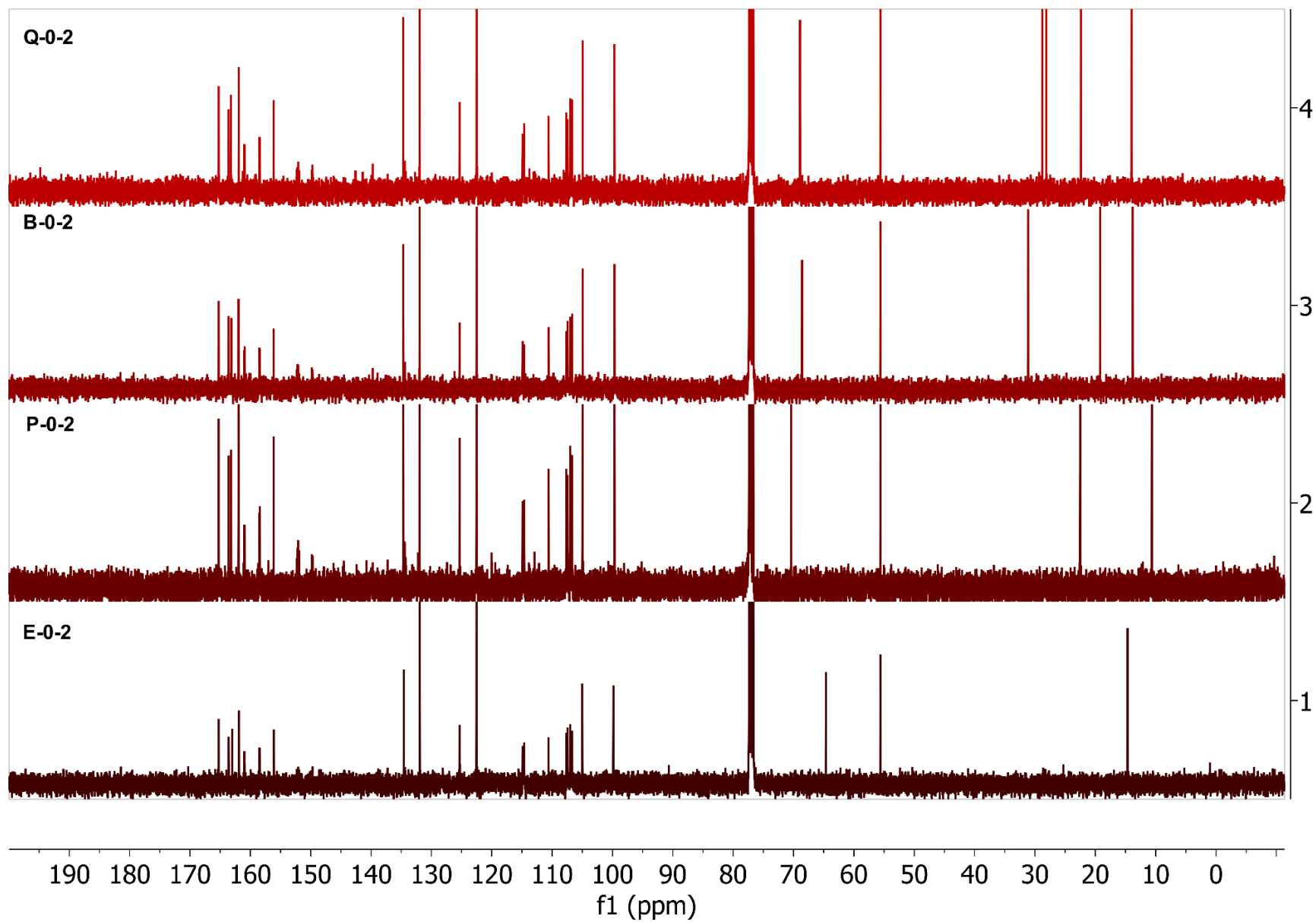


Figure S13. Stacked ^{13}C NMR spectra of **E-0-2**, **P-0-2**, **B-0-2** and **Q-0-2** in CDCl_3

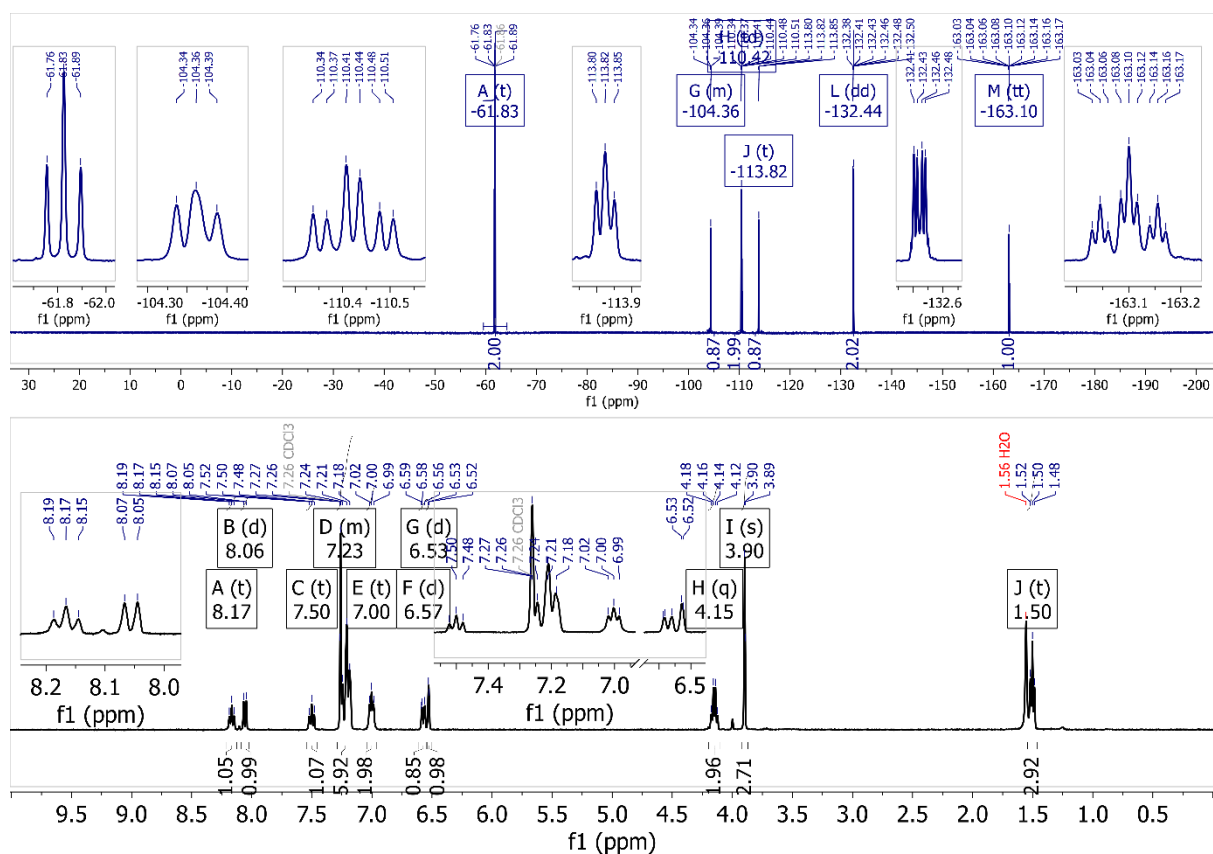


Figure S14. ^{19}F and ^1H NMR spectra of **E-1-1** in CDCl_3 .

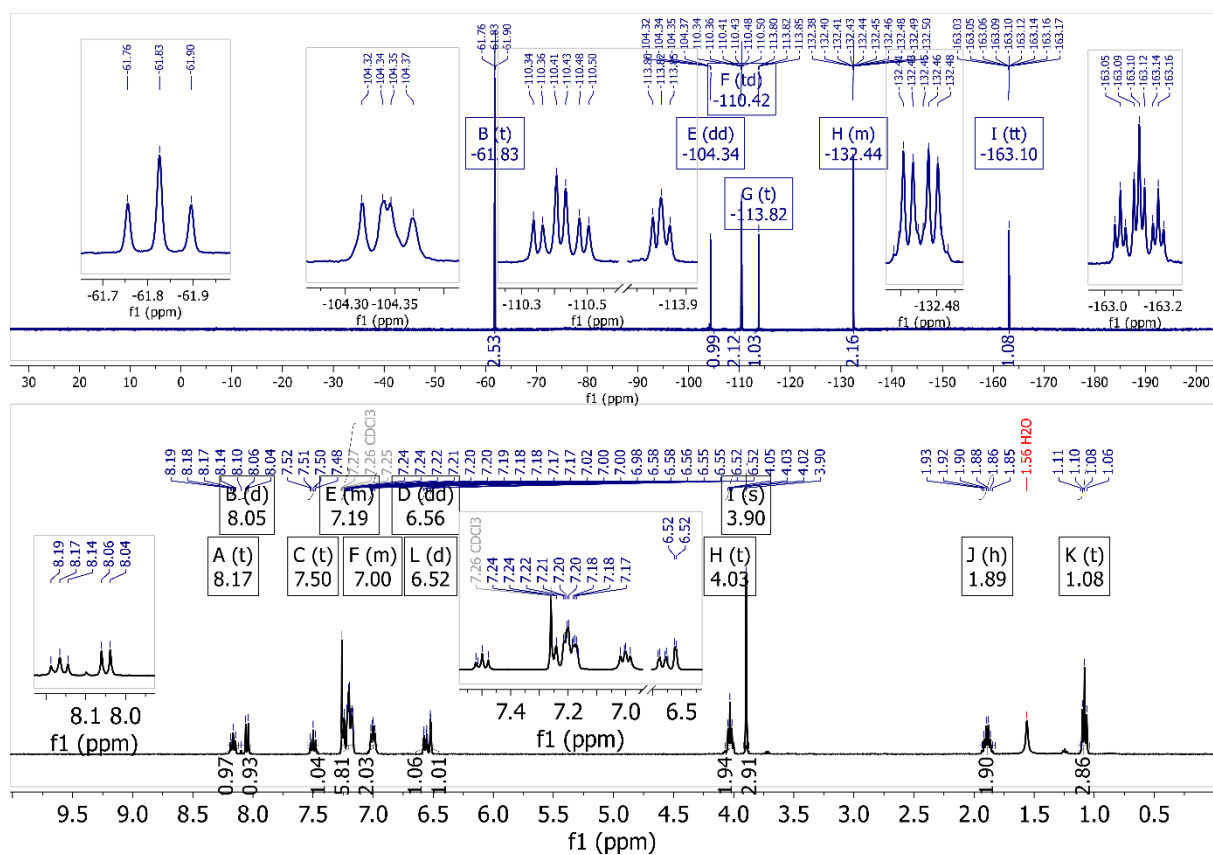


Figure S15. ^{19}F and ^1H NMR spectra of **P-1-1** in CDCl_3 .

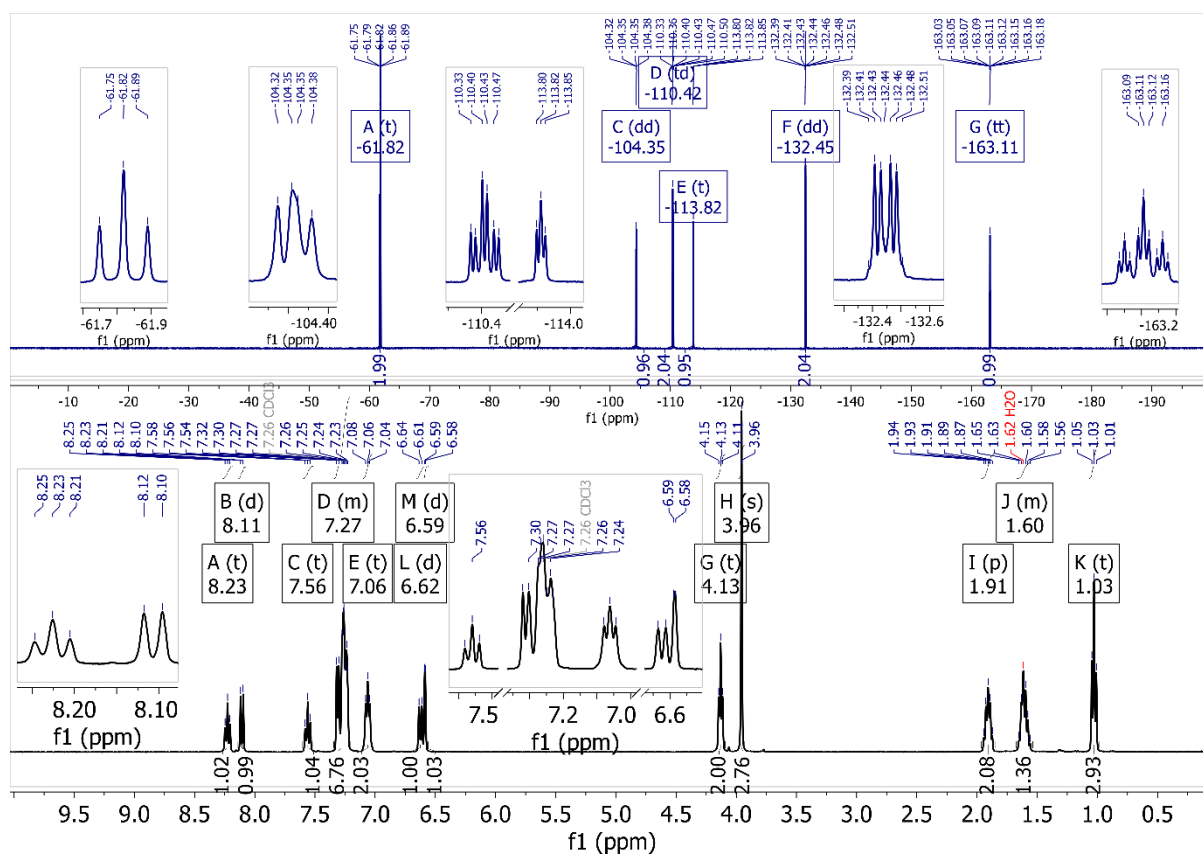


Figure S16. ^{19}F and ^1H NMR spectra of **B-1-1** in CDCl_3 .

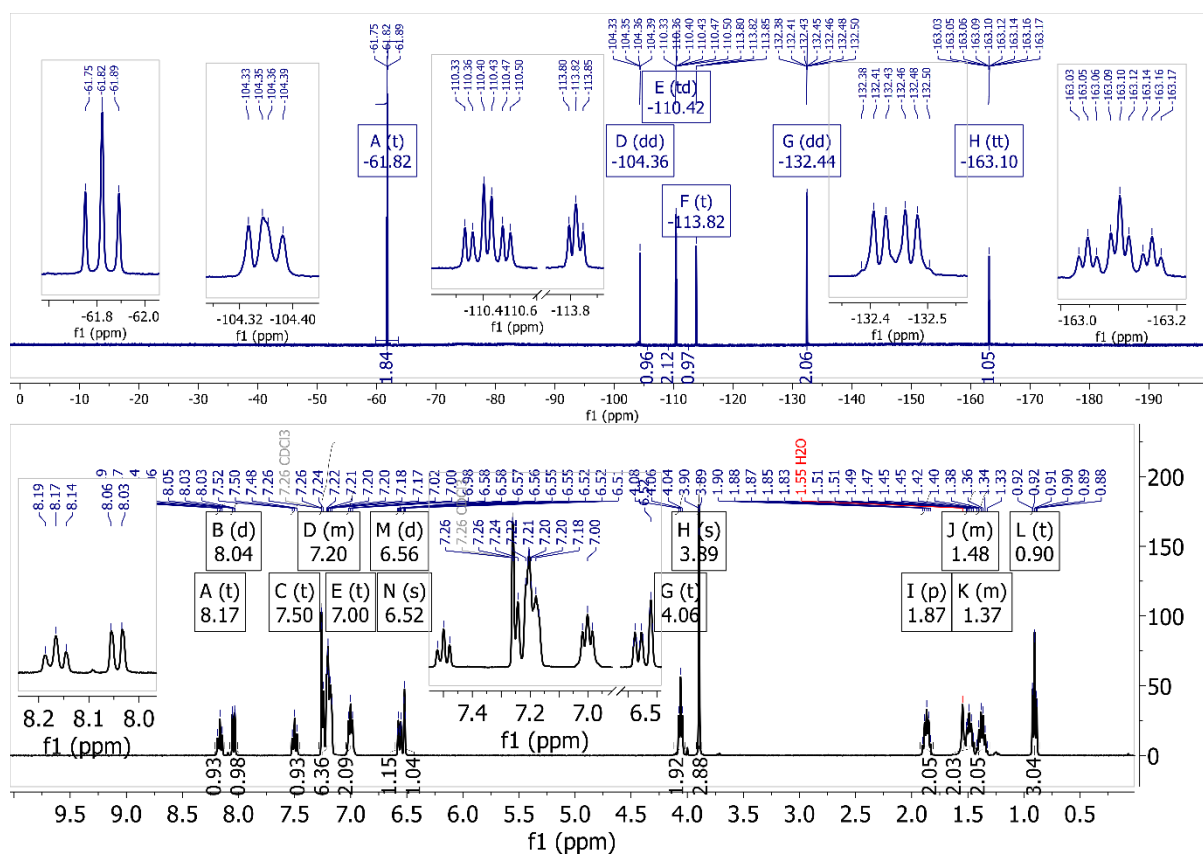


Figure S17. ^{19}F and ^1H NMR spectra of **Q-1-1** in CDCl_3 .

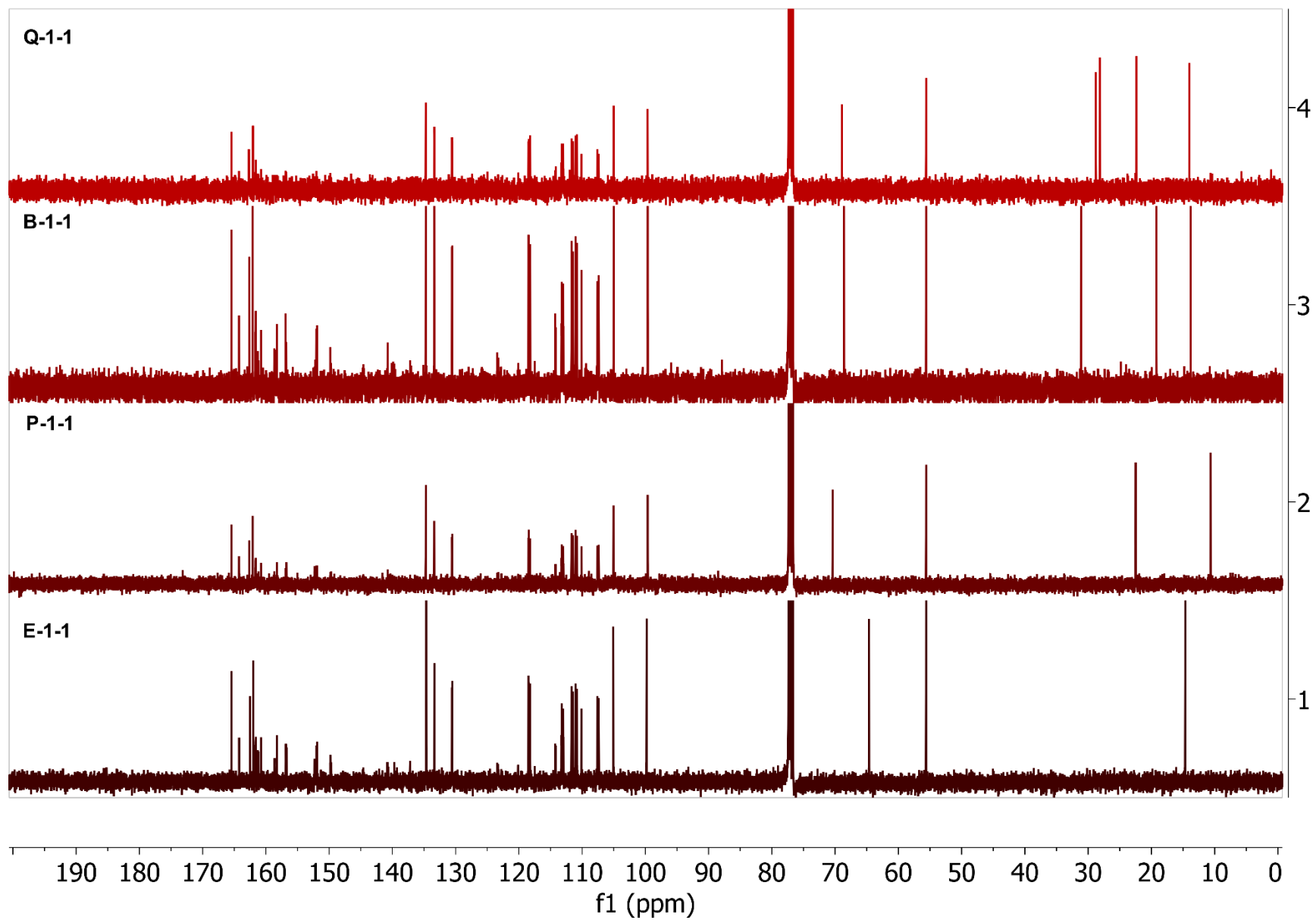


Figure S18. Stacked ^{13}C NMR spectra of **E-1-1**, **P-1-1**, **B-1-1** and **Q-1-1** in CDCl_3 .

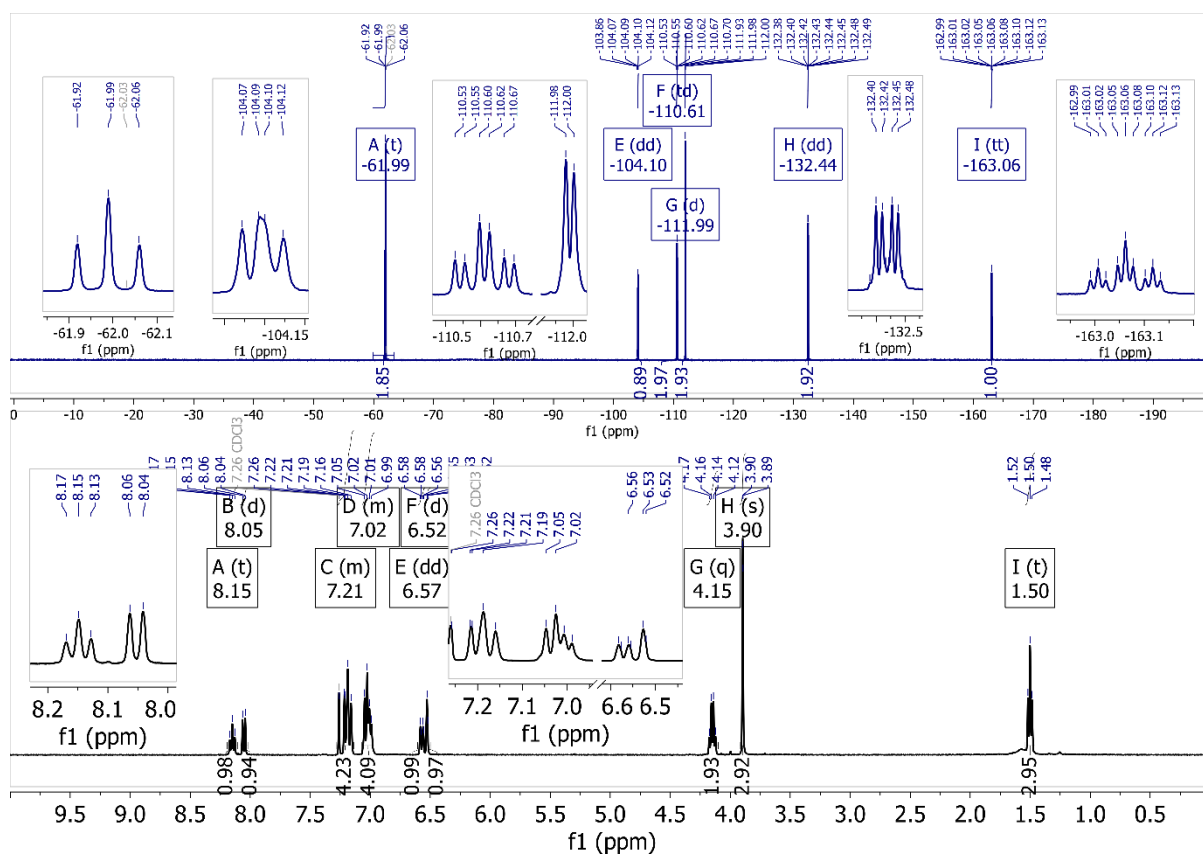


Figure S19. ¹⁹F and ¹H NMR spectra of **E-1-2** in CDCl₃.

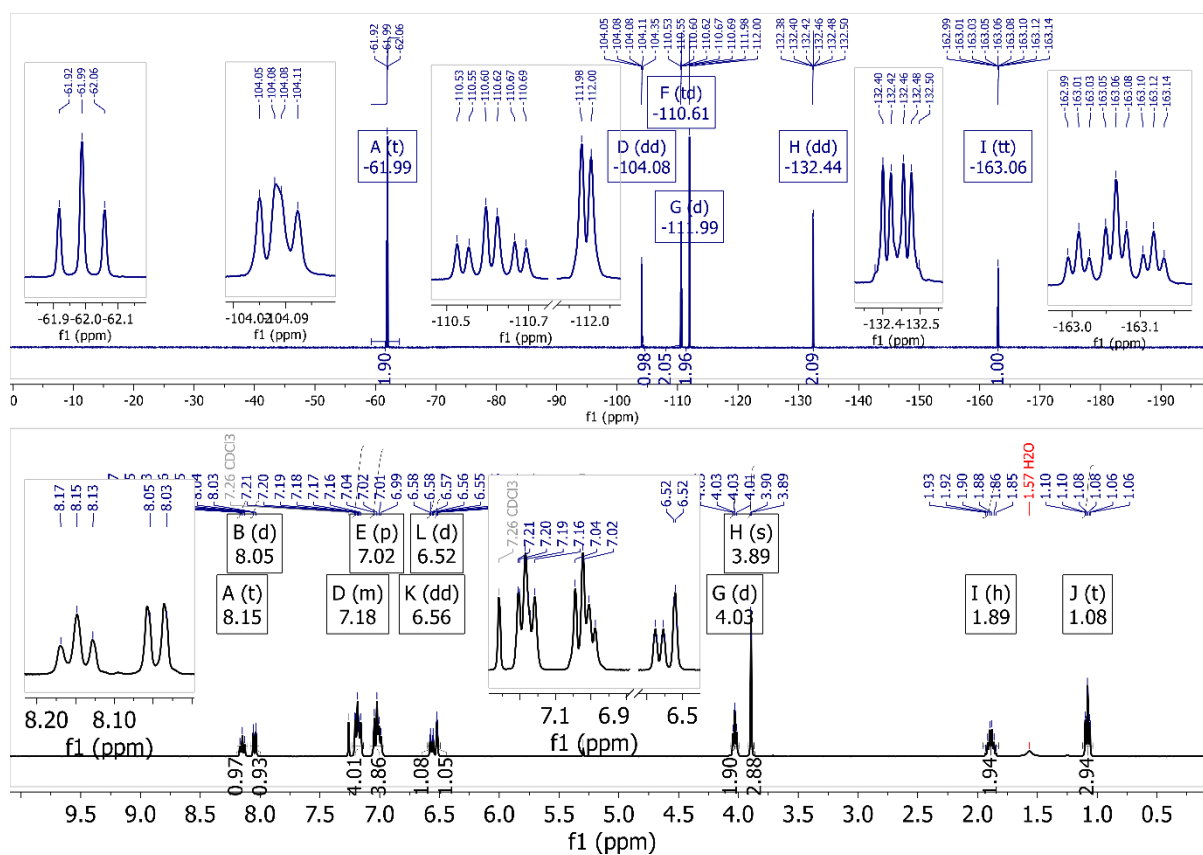


Figure S20. ¹⁹F and ¹H NMR spectra of **P-1-2** in CDCl₃.

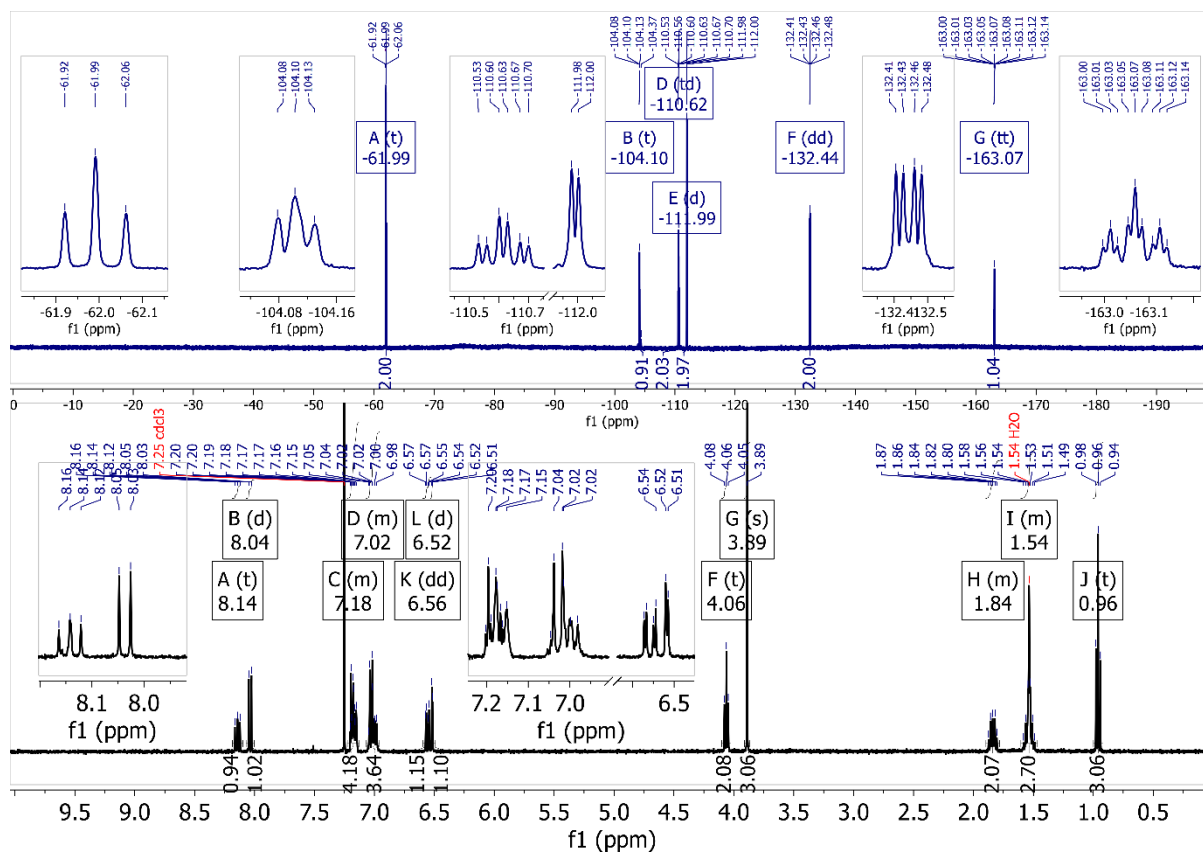


Figure S21. ^{19}F and ^1H NMR spectra of **B-1-2** in CDCl_3 .

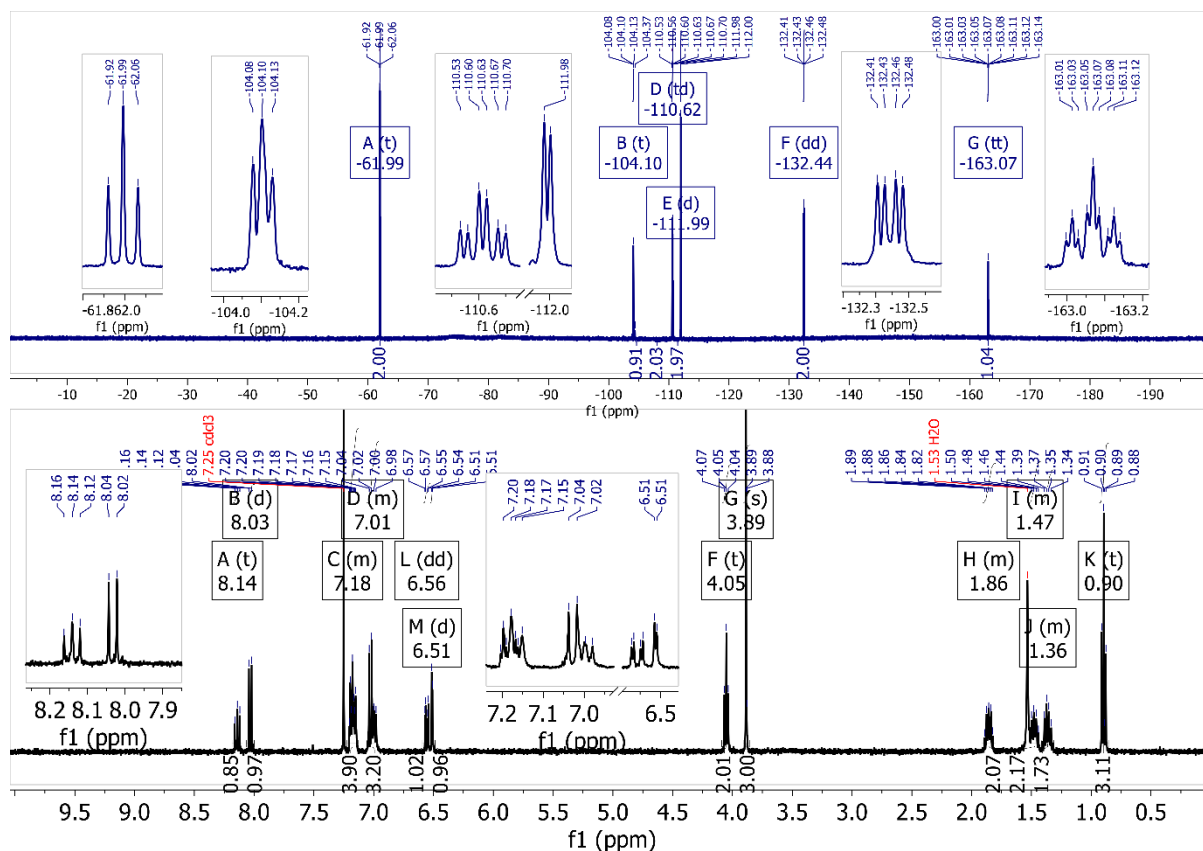


Figure S22. ^{19}F and ^1H NMR spectra of **Q-1-2** in CDCl_3 .

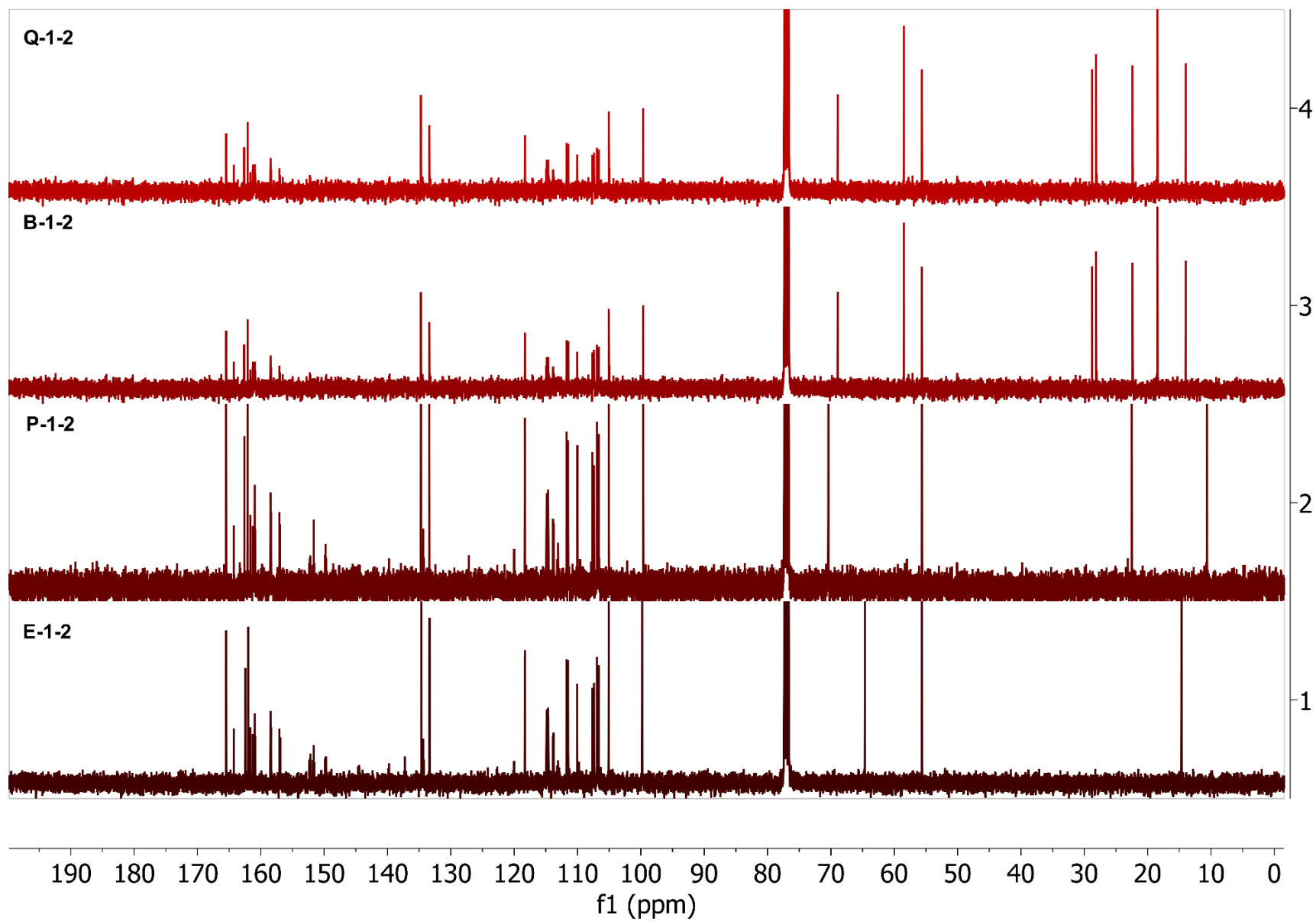


Figure S23. Stacked ^{13}C NMR spectra of **E-1-2**, **P-1-2**, **B-1-2** and **Q-1-2** in CDCl_3 . **B-1-2** and **Q-1-2** contain additional peaks from ethanol at 18 and 58 ppm.

References

- [1] G. J. Strachan, E. Górecka, J. Hobbs, D. Pocięcha, *J. Am. Chem. Soc.* **2025**, *147*, 6058–6066.
- [2] E. Cruickshank, A. Pearson, S. Brown, J. M. Storey, C. T. Imrie, R. Walker, *Liquid Crystals* **2023**, *50*, 1960–1967.