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Supporting Information

Tailoring liquid crystal honeycombs by head-group choice in bird-like bent-core mesogens

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Contents

S1. Experimental methods

DSC thermograms were recorded on a DSC 200 F3 Maia calorimeter (NETZSCH) with heating/cooling rates as specified.

Optical micrographs with crossed polarizers (**POM**) were recorded using an Olympus BX50 microscope equipped with a Mettler hot stage. Optical retardation was measured with a Berek compensator. A λ-plate was used to determine the direction of the optic axis.

Grazing incidence X-ray scattering (**GISAXS**) experiments were carried out on beamline BM28 (XMaS) at European Synchrotron Radiation Facility (ESRF), France and I16 at Diamond Light Source, U.K. The X-ray energy was 12.0 keV, and 2d diffractograms were collected using a MAR165 CCD camera (ESRF) and Pilatus 2M detector (Diamond). Thin film samples were prepared from melt on silicon substrate. *n*-Tetracontane was used to calibrate the sample-to-detector distance. **Powder SAXS and WAXS** experiments were done at station I22 of Diamond Light Source. Powder samples were prepared in 1 mm glass capillaries and held in a modified Linkam hot stage. Pilatus 2M detector at a distance of 2.2 m from the sample was used. The X-ray energy was 12.4 keV.

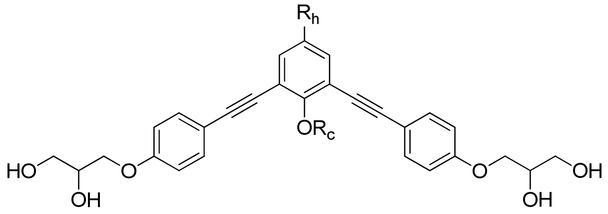
Electron density (ED) maps were calculated by inverse Fourier transformation using the standard procedure as described in International Tables for Crystallography. The structures *p*6*mm* and *p*2*gg* are centrosymmetric, thus the phase angle (ϕ) choices of the reflections are either 0 or π. However, this restriction does not apply to reflections (10) and (20) of the *p*3*m*1 phase and (11), (21), (22), (31) and (32) of the *p*31*m* phase. The selection of the maps is considered based on the physical and chemical information i.e. chemical structure, known electron densities of the molecular fragments, molecular models and simulation.

Samples of ca. 50 µm thickness for **Second Harmonic Generation (SHG)** measurements were prepared on the rough side of silicon wafer and examined using a Zeiss LSM 510 Meta upright laser-scanning confocal microscope (Oberkochen, Germany) with a 40X/0.75NA objective. Temperature was controlled by a Mettler hot stage. A Chameleon Ti: Sapphire femtosecond pulsed laser (Coherent, California, USA) tuned to 800 nm, was attached to the microscope and focused onto the sample resulting in a SHG signal detectable at 400 nm. In order to exclude possible surface effects, first the beam was focused at the bottom of the LC film in contact with the Si substrate, then at 10 µm and 20 µm height, respectively. The SHG ratio was calculated by dividing the intensities at 400 nm by the averaged background signals around the peak.

Molecular models were built using Materials Studio (Accelrys). Geometry optimization and molecular dynamic simulation were performed using the Forcite Plus module with Universal Force Field. The experimental value for *a*-parameter and the value for *c* from Table S7 were used. The convergence tolerances for geometry optimization were 1 cal/mol for energy and 0.5 kcal/mol/Å for force. Constant volume (NVT) annealing dynamics was performed through 30 cycles between 300 and 600 K with a total annealing time of 30 ps.

S2. DSC results

Table S1 Phase transition temperatures of the mesogenic compounds.



Compound R$_h$-F/H [a]	R$_c$	*a* (*a*$_{sub}$) (Å) [b]	*T* /°C [Δ*H*/kJ mol^{-1}] [c]
CO_2CH_3-F	$C_6H_{12}C_4F_9$	29.8	↑ Cr 55 Iso ↓ glass r.t. ↑ *p*3*m*1-reg 42 Iso [d]
Br-H	$CH_2CH(C_5H_{11})_2$	26.9	↑ Cr$_1$ 78.7[8.9] Cr$_2$ 118.8[40.1] Iso ↓ 91.9[1.9] *p*3*m*1-reg 32.2[8.6] Cr ↑ 113.7[33.3] Iso
$CONH_2$-F	$C_4H_8C_6F_{13}$	30.1	↑ Cr 91.5[1.2] *p*3*m*1-reg 213.5[15.2] Iso ↓ 209.2[13.2] *p*3*m*1-reg ↑ 212.5[13.3] Iso
CN-F	$C_6H_{12}C_4F_9$	51.7 (29.8)	↑ Cr$_1$ 63[5.8] Cr$_2$ 73.3[4.2] *p*31*m*-sup 83.4[0.2] Iso ↓ 77 (onset) *p*31*m*-sup ↑ 82.9[0.1] Iso
CN-H	$CH_2CH(C_5H_{11})_2$	24.5	↑ Cr 112[16.9] Iso ↓ 81.5[1.6] *p*6*mm*-ran ↑ 84.4[1.6] Iso
NO_2-F	$C_4H_8C_6F_{13}$	*a* 63.3 *b* 50.6 (29.2-31.7)	↑ Cr 85.7[0.7] *p2gg* 116.3[0.9] Iso ↓ 114[0.09] *p2gg* 109.9[1.5] ↑ *p2gg*-sup 117[2.0] Iso

[a] First part of compound name is the head group R$_h$, second part denotes the type of the attached chain. [b] Lattice parameter (subcell lattice parameter). For superlattice *p*31*m*, $a_{sub} = \frac{\sqrt{3}}{3}a$. For superlattice *p2gg*, *a*$_{sub}$ is in the range of $\frac{\sqrt{3}}{4}b$ and $\frac{1}{2}a$. [c] Peak DSC transition temperatures [and enthalpies] on 1st heating (↑), followed by cooling (↓) and 2nd heating (↑), all at 10 K min^{-1}. [d] Transition temperatures of CO_2CH_3-F are determined by XRD, SHG and POM. Phase abbreviations: Cr = crystal, *p*6*mm*-ran = hexagonal columnar phase with random orientation of the local 3-fold axis with 6-fold *p*6*mm* overall symmetry; *p*3*m*1-reg = columnar phase with trigonal symmetry and one column per unit cell; *p*31*m*-sup = trigonal superlattice with three columns per unit cell; *p2gg*-sup = rectangular superlattice with *p2gg* symmetry and four columns per cell; Iso = isotropic melt.

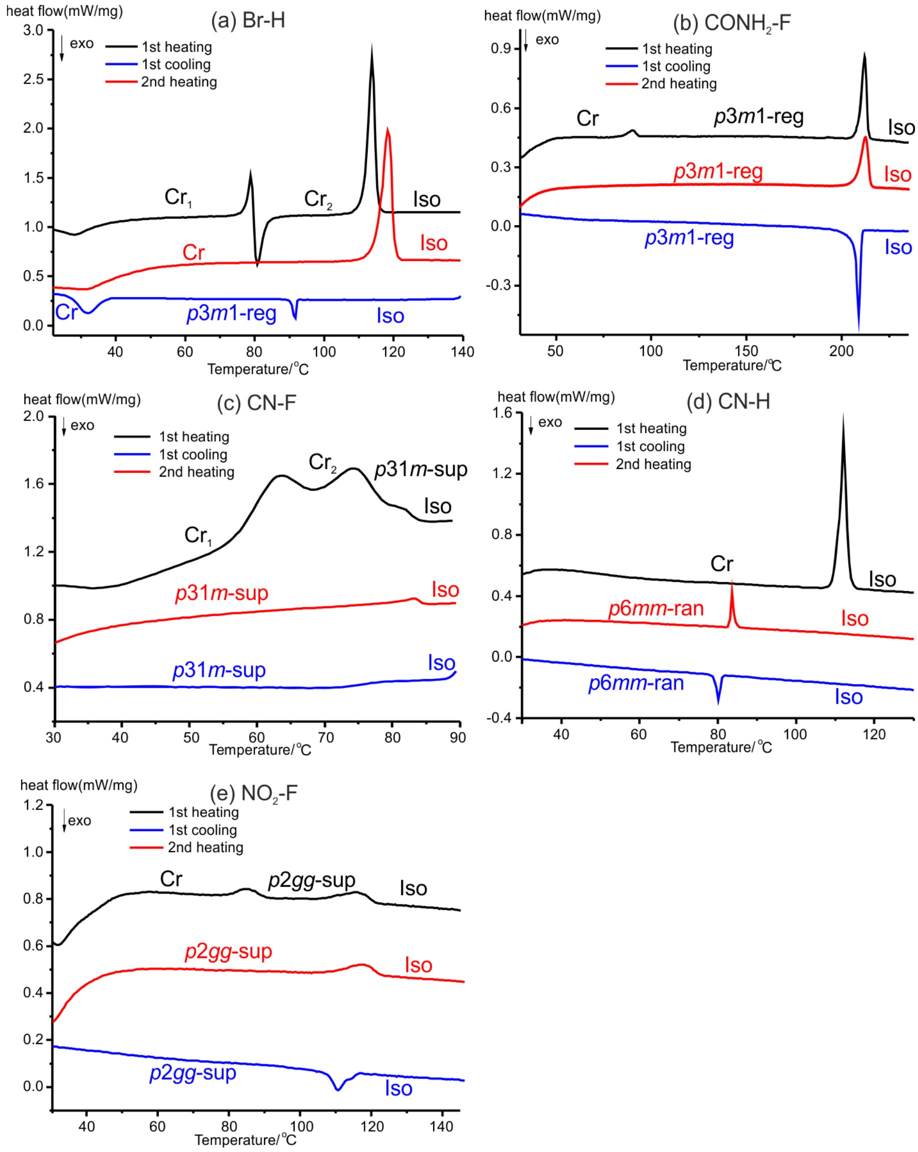


Figure S1 DSC thermograms of compounds (a) **Br-H** at heating and cooling scan rate of 10 K min^{-1}; (b) **CONH$_2$-F** at heating and cooling scan rate of 10 K min^{-1}; (c) **CN-F** at heating and cooling scan rate of 10 K min^{-1}; (d) **CN-H** at heating and cooling scan rate of 10 K min^{-1}; (e) **NO$_2$-F** at heating and cooling scan rate of 10 K min^{-1}.

S3. Additional POM images

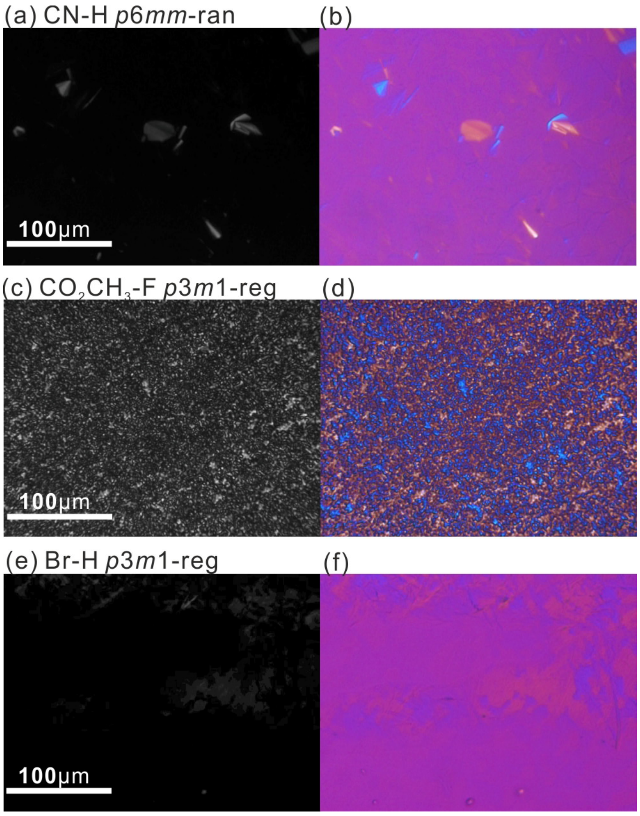


Figure S2 Polarized optical microscopy textures of (a, b) CN-H recorded at 70 °C (cooled from 100 °C), *p*6*mm*-ran = hexagonal columnar phase with *p*6*mm* symmetry and overall random packing; (c, d) CO$_2$CH$_3$-F recorded at 25 °C (cooled from 60 °C), *p*3*m*1-reg = the hexagonal columnar phase with three-fold symmetry and regular lattice; (e, f) Br-H recorded at 70 °C (cooled from 110 °C); (b, d and f) are recorded with a full-wave (λ) plate.

S4. Additional X-ray diffraction, SHG and molecular modelling/simulation results of individual compounds

S4.1. CO_2CH_3-F

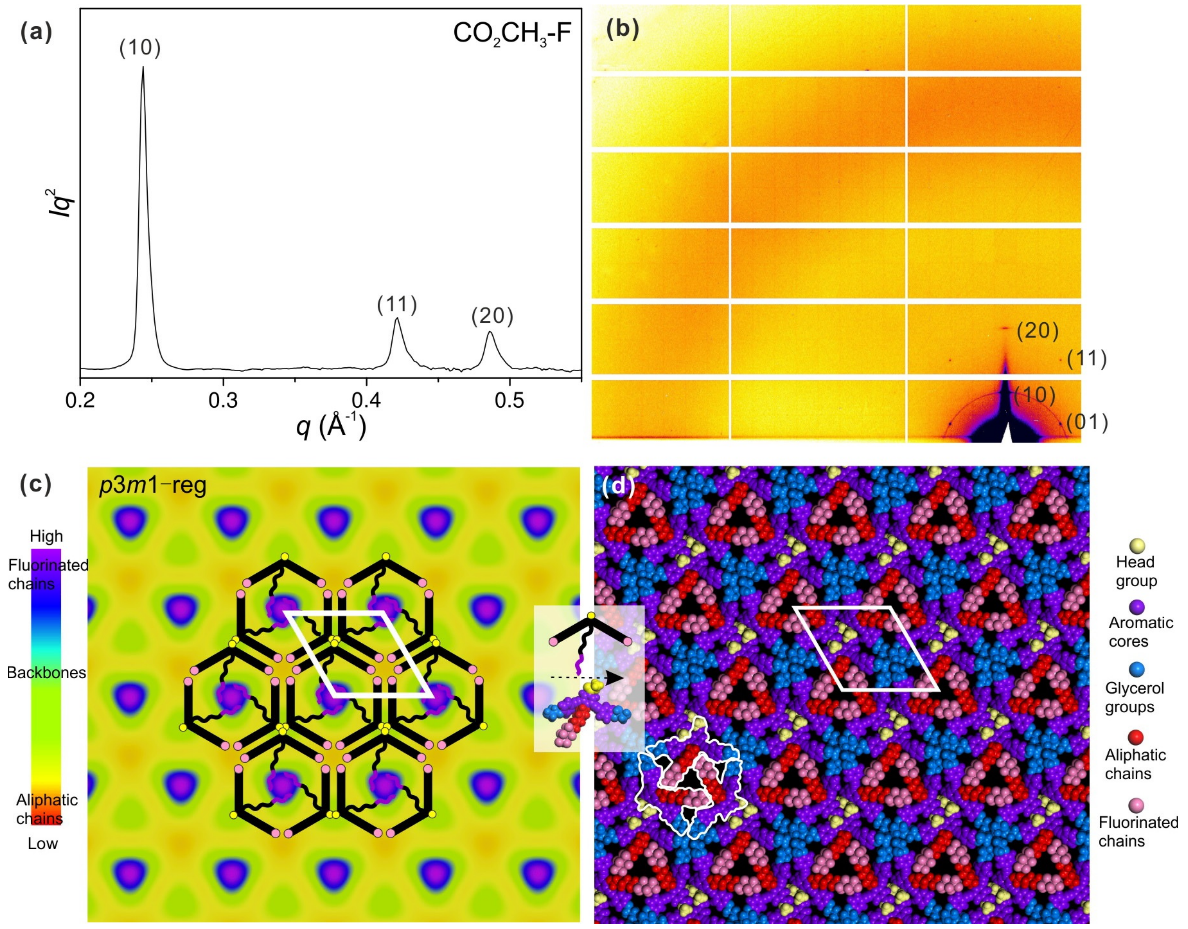


Figure S3 (a) Powder SAXS curve and (b) GIWAXS/GISAXS pattern of CO_2CH_3-F recorded at 23 °C (cooled from isotropic temperature and kept at room temperature for 12 h to form liquid crystal phase); (c) reconstructed ED map (ϕ(10) = 20°, ϕ(11) = 0° and ϕ(20) = 300°) with schematic model overlaid; (b) Geometry optimized molecular model.

Table S2 The indices, experimental, calculated *d*-spacings and relative integrated intensities of CO_2CH_3-F obtained from SAXS at 23 °C. All intensity values are Lorentz and multiplicity corrected.

(hk)	*d*-spacing (Å) experimental	*d*-spacing (Å) calculated	*Intensity*	*Phase* (°)
(10)	25.8	25.8	100.0	20
(11)	14.9	14.9	16.2	0
(20)	12.9	12.9	12.4	300
a = 29.8 Å				

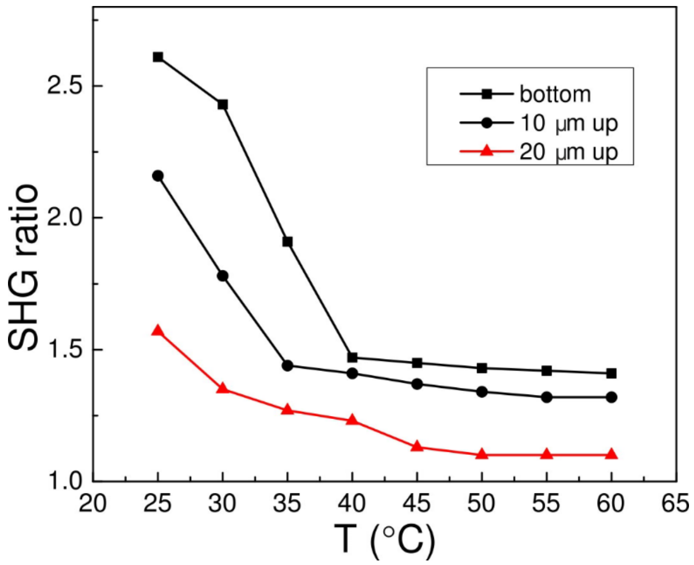


Figure S4 Temperature dependent intensity of the second harmonic (400 nm) vs. background for 800 nm excitation of CO_2CH_3-F, generated at different heights. (The sample was heated to 60 °C, cooled to room temperature and kept for 12 h to form LC phase. Next, it was heated and examined every 5 °C.)

S4.2. Br-H

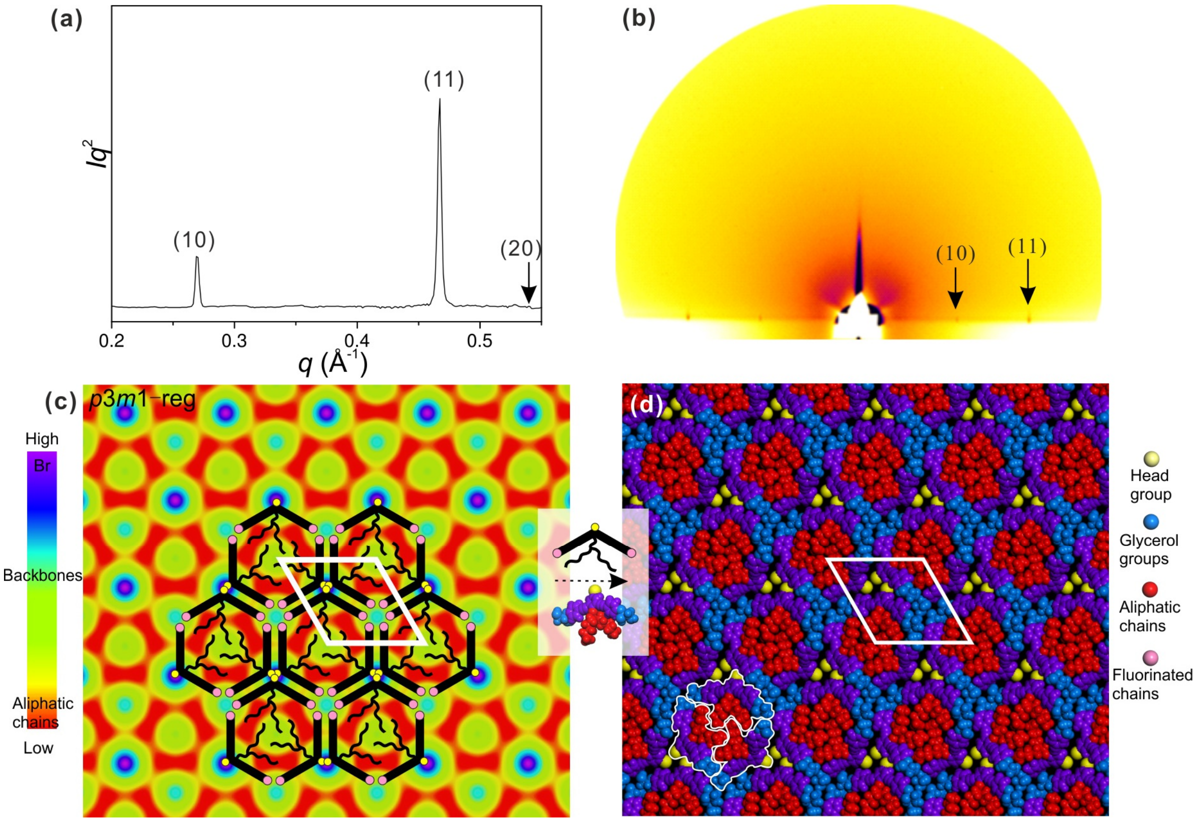


Figure S5 (a) Powder SAXS curve and (b) GISAXS diffraction pattern of Br-H recorded at 70 °C (cooled from 110 °C). The position of the arrow in (a) supposed to show (20), but the intensity of (20) is too weak to be observed; (c) reconstructed electron density map ($\phi_{(10)}$ = 20° and $\phi_{(11)}$ = 0°), with schematic molecules overlaid; (d) snapshot of dynamic simulation.

Table S3 The indices, experimental, calculated *d*-spacings and relative integrated intensities of Br-H obtained from SAXS at 70 °C (cooled from 110 °C). All intensity values are Lorentz and multiplicity corrected.

(hk)	*d*-spacing (Å) experimental	*d*-spacing (Å) calculated	*Intensity*	*Phase* (°)
(10)	23.3	23.3	26.3	20
(11)	13.5	13.5	100.0	0
a = 26.9 Å				

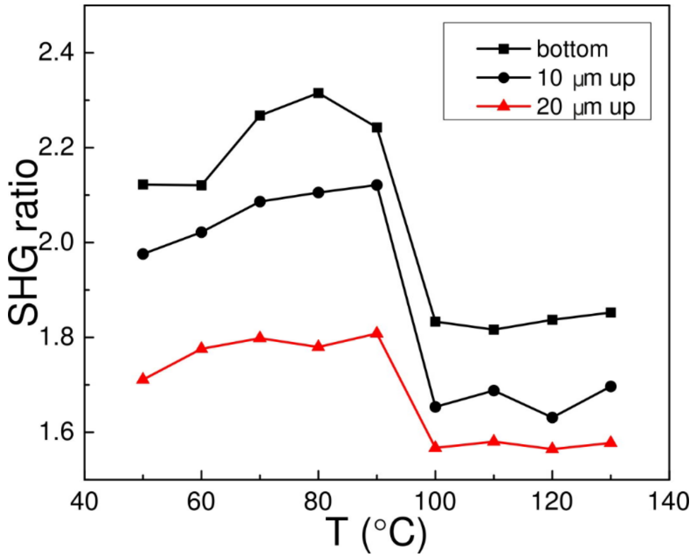


Figure S6 Temperature dependent intensity of the second harmonic (400 nm) vs. background for 800 nm excitation of Br-H, generated at different heights (cooled from 130 to 50 °C).

S4.3. CONH$_2$-F

Table S4 The indices, experimental, calculated *d*-spacings and relative integrated intensities of CONH$_2$-F obtained from SAXS at 130 °C (cooled from 230 °C). All intensity values are Lorentz and multiplicity corrected.

(hk)	*d*-spacing (Å) experimental	*d*-spacing (Å) calculated	*Intensity*	*Phase* (°)
(10)	26.1	26.1	100.0	20
(11)	15.1	15.1	50.8	0
(20)	13.1	13.1	8.45	140
a = 30.1 Å				

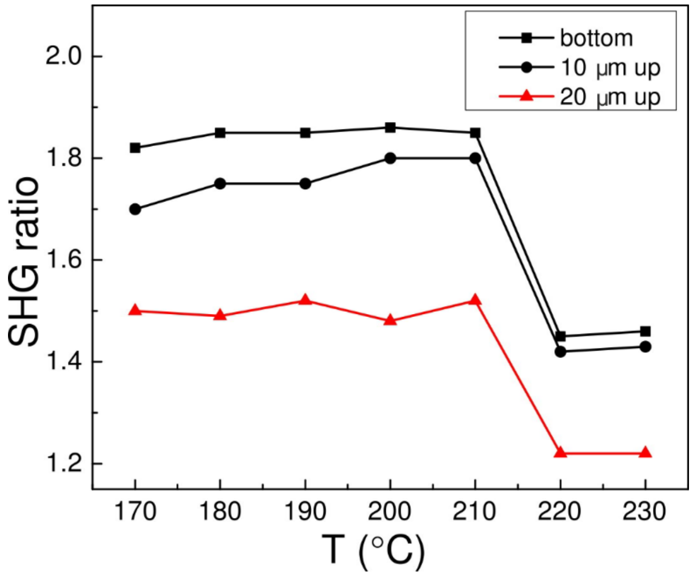


Figure S7 Temperature dependent intensity of the second harmonic (400 nm) vs. background for 800 nm excitation of $CONH_2$-F, generated at different heights (heated from 170 to 230 °C).

S4.4. CN-F

Table S5 The indices, experimental, calculated *d*-spacings, relative integrated intensities and phases of CN-F recorded at 70 °C (cooled from 90 °C) from SAXS. All intensities values are Lorentz and multiplicity corrected.

(*hk*)	*d*-spacing experimental (Å)	*d*-spacing calculated (Å)	*Intensity*	*Phase* (°)
(10)	44.9	44.8	0.2	0
(11)	25.9	25.9	90.8	20
(20)	22.4	22.4	0.1	0
(21)	16.9	16.9	13.7	240
(30)	14.9	14.9	46.6	0
(22)	12.9	12.9	3.6	20
(31)	12.4	12.4	6.5	220
(40)	11.2	11.2	1.0	180
(32)	10.2	10.3	100.0	60
a = 51.7 Å				

S4.5. CN-H

Table S6 The indices, experimental, calculated *d*-spacings and relative integrated intensities of CN-H obtained from SAXS at 70 °C (cooled from 100 °C). All intensity values are Lorentz and multiplicity corrected.

(hk)	*d*-spacing (Å) experimental	*d*-spacing (Å) calculated	*Intensity*	*Phase*
(10)	21.2	21.2	25.4	π
(11)	12.2	12.2	100.0	π
(20)	10.6	10.6	8.2	π
a = 24.5 Å				

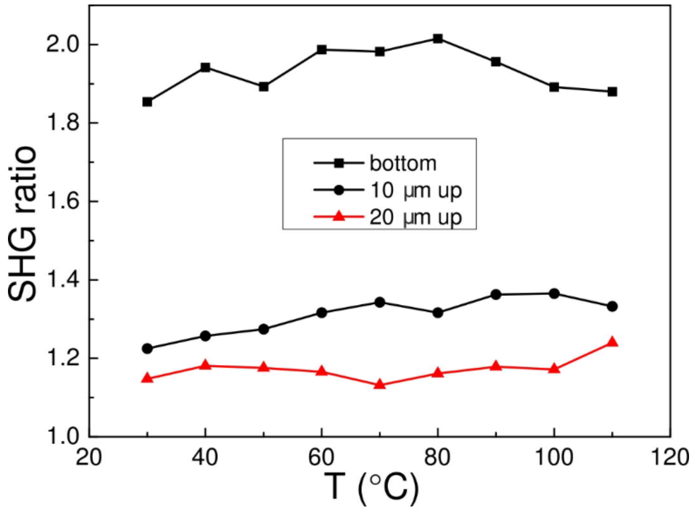


Figure S8 Temperature dependent intensity of the second harmonic (400 nm) vs. background for 800 nm excitation of CN-H, generated at different heights (cooling from 110 °C to 30 °C).

S4.6. NO_2-F

Table S7 The experimental, calculated d-spacings, intensities, phases and lattice parameters of the Col_{rec}/*p*2*gg* phase observed from SAXS at 100 °C. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	*d*-spacing (Å) experimental	*d*-spacing (Å) calculated	*Intensity*	*Phase*
(11)	39.5	39.5	1.9	0
(20)	31.6	31.7	11.6	0
(21)	26.9	26.8	86.6	0
(02)	25.2	25.3	100.0	π
(12)	23.4	23.5	0.6	π
(22)	19.8	19.8	2.0	0
(31)	19.5	19.5	0.8	π
(13)	16.3	16.3	1.2	0
(32)	16.2	16.2	1.2	0
(40)	15.8	15.8	5.1	-
(41)	15.1	15.1	0.5	-
(23)	14.9	14.9	11.1	-
a = 63.3 Å, b = 50.6 Å				

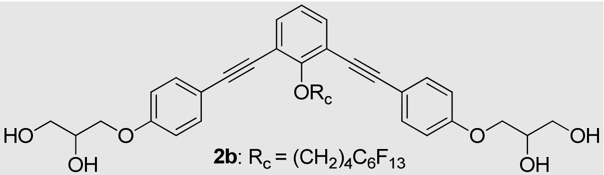
S5. Estimation of number of molecules per columnar stratum

Table S8 Estimation of number of molecules per column stratum

Sample	R_c	*Plane group*	*a* (Å)	*c* (Å)^a	V_{cell} (Å^3)^b	V_{mol} (Å^3)^c	n_{Cr}^{d}	n_{liq}^{e}	n_{ave}^{f}
CO_2CH_3-F	$C_6H_{12}C_4F_9$	*p*3*m*1-reg	29.8	4.3	3306.9	980.4	3.4	2.7	3.0
Br-H	$CH_2CH(C_5H_{11})_2$	*p*3*m*1-reg	26.9	5.0	3133.2	941.3	3.3	2.6	3.0
$CONH_2$-F	$C_4H_8C_6F_{13}$	*p*3*m*1-reg	30.1	4.2	3318.9	984.1	3.4	2.6	3.0
CN-F	$C_6H_{12}C_4F_9$	*p*31*m*-reg	51.7	4.1	9490.4	943.1	10.1	7.9	9.0
CN-H	$CH_2CH(C_5H_{11})_2$	*p*6*mm*-ran	24.5	6.0	3118.9	939.6	3.3	2.6	3.0
NO_2-F	$C_4H_8C_6F_{13}$	*p*2*gg*-*sup*	*a* 63.3 *b* 50.6	4.0	12940.0	961.0	13.5	10.5	12.0

a: Thickness of column stratum, or average spacing between molecules along column axis, *c*, is adjusted to obtain an integer value of n_{ave}.
b: Volume of the unit cell for hexagonal phase $V_{cell} = a^2*0.866*c$, and rectangular phase $V_{cell} = a*b*c$;
c: Volume of molecule (V_{mol}) = volume of a single molecule as calculated using the crystal volume increments[S1];
d: $n_{Cr} = V_{cell}/V_{mol}$;
e: $n_{liq} = 0.55/0.7*n_{Cr}$ (average packing coefficient in the crystal is k = 0.7, in isotropic liquid k = 0.55) [S2];
f: $n_{ave} = (n_{Cr} + n_{liq})/2$.

Table S9 Comparison of lattice parameters and column areas of honeycomb phases, including that of the previously reported anchor-shaped molecule 2b with R_h = H [S3].



2b: $R_c = (CH_2)_4C_6F_{13}$

Name	***Plane group***	***Lattice parameters* (Å)**	***Column area A* ($Å^2$)***
CN-H	*p*6*mm*-ran	24.5	519.8
Br-H	*p*3*m*1-reg	26.9	626.7
CO_2CH_3-F	*p*3*m*1-reg	29.8	769.1
CN-F	*p*31*m* -sup	51.7	771.6
$CONH_2$-F	*p*3*m*1-reg	30.1	784.6
NO_2-F	*p*2*gg*-sup	*a* = 63.3 *b* = 50.6	800.7
2b[S3]	*p*3*m*1-reg	28.8	718.3

*The column area of the regular lattices is calculated by $A = \frac{\sqrt{3}}{2}a^2$. For the superlattices *p*31*m* (CN-F) and *p*2*gg* (NO_2-F), there are 3 and 4 columns in each unit cell, respectively. The column area of *p*31*m*-sup is $\frac{\sqrt{3}}{6}a^2$ and that of *p*2*gg*-sup is $\frac{ab}{4}$.

S6. Electron densities of functional groups involved, non-bonded interaction energies and dipole moments of headgroups

Table S10 Electron densities of different functional groups involved [a].

Compound	Aromatic core (10^5 electron/$Å^3$)	glycerol groups (10^5 electron/$Å^3$)	head group (10^5 electron/$Å^3$)	Aliphatic chain 1 (10^5 electron/$Å^3$)	Fluorinated chain (10^5 electron/$Å^3$)
$CONH_2$-F	4.38	4.50	4.72 ($-CONH_2$)	3.69 ($-OC_4H_8$)	6.58 ($-C_6F_{13}$)
Br-H			10.60 (-Br)	3.35 ($-O-CH_2-(C_5H_{12})_2$)	-
CO_2CH_3-F			4.52 ($-COOCH_3$)	3.54 ($-OC_6H_{12}$)	6.60 ($-C_4F_9$)
CN-F			4.15 (-CN)	3.54 ($-OC_6H_{12}$)	6.60 ($-C_4F_9$)
CN-H			41.5 (-CN)	3.35 ($-O-CH_2-(C_5H_{12})_2$)	-
NO_2-F			6.39 ($-NO_2$)	3.69 ($-OC_4H_8$)	6.58 ($-C_6F_{13}$)

[a] Volume of relevant part of molecule is calculated using the method of crystal increments [S1].

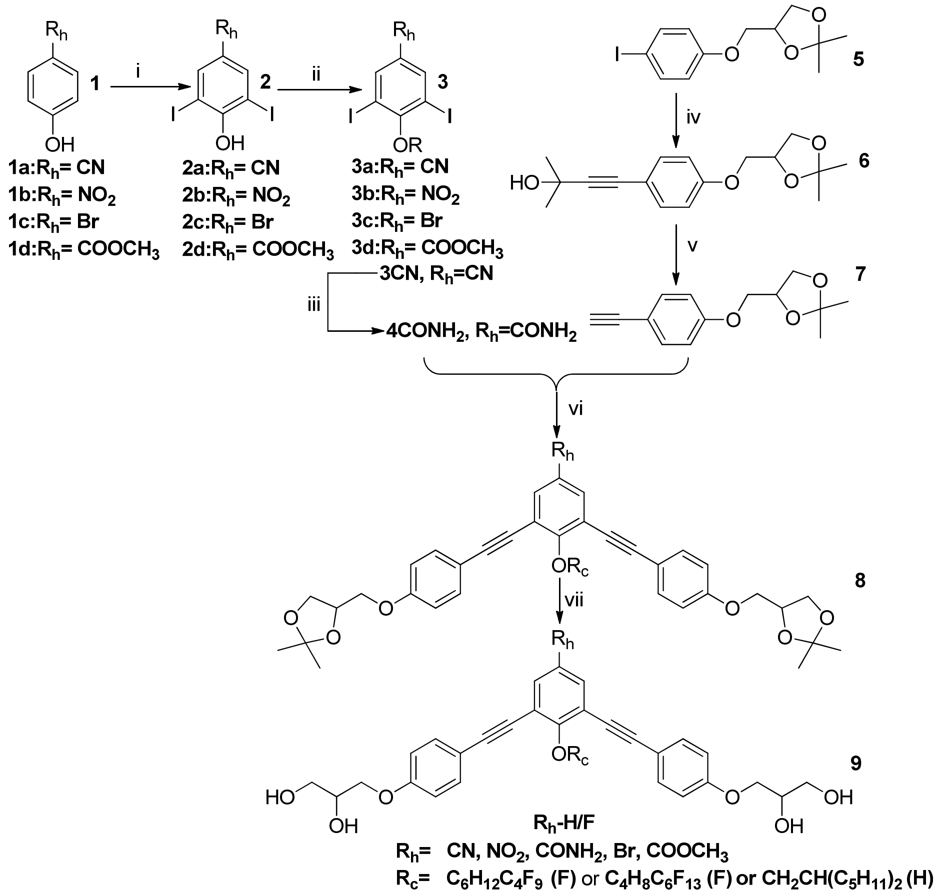
Table S11 Hydrogen bond enthalpies and dipole moments of glycerol and headgroups.

Functional Group	H-bond enthalpy between head group and C_{sp3}-OH (-kcal/mol)	Enthalpy of non-bonded interaction among headgroups (-kcal/mol)	Dipole moment of headgroup (D)
Glycerol	**4.8** (single intermolecular H-bond between glycerols)[S4]		-
Br	**0.7** (*n*-heptyl bromide with *n*-propanol [S5])	**1.0** (bromoform, dipolar) [S5]	**1.72** (bromobenzene [S6])
$CONH_2$	**4.5** (acetamide with isopropanol [S5])	**7.1** (formamide, H-bond) [S7]	-
CN	**3.1** (benzonitrile with water, similar to benzonitrile with alcohols [S8])	**3.1** (Benzonitrile, dipolar) [S8]	**4.48** (benzonitrile [S9])
NO_2	**2.8** (nitromethane with methanol [S10])	**3.1** (non-bonding between O_{nitro} and $\pi(N)_{nitro}$ [S11])	**4.22** (nitrobenzene[S12])
$COOCH_3$	2.3 (thienylacryloyl methyl ester with ethanol[S13]) 2.5 (5-methylthienylacryloyl methyl ester with ethanol[S13])	-	**1.75** (methyl acetate [S14])

S7. Synthesis and analytical data

General Remarks

Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140 °C). Commercially available chemicals were used as received. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker–DRX-500 spectrometer. Elemental analysis was performed using an Elementar VARIO EL elemental analyzer. HRMS were performed on LTQ Orbitrap XL. Column chromatography was performed with merck silica gel 60 (230-400 mesh).



Scheme 1 : Synthesis of bent shaped bola amphiphilies, reagents and conditions: (i) I_2, KI, ammonia, MeOH, 25 °C, 2 h, 52%; (ii) R-Br (R = $C_{14}H_{29}$ or $(CH_2)_nC_mF_{2m+1}$[S15]), K_2CO_3, CH_3CN, reflux, 20 h; (iii) Dihydrogenperoxide, sodium hydroxide inethanol, water, T= 60 °C[S16], 1 h; (iv) 2-methylbut-3-yn-2-ol, THF, Et_3N, $Pd(PPh_3)_4$, CuI, RT, 89%; (v) KOH, toluene, 100 °C, 15 h, 88%; (vi) THF, Et_3N, $Pd(PPh_3)_4$, CuI, RT, 64-88%; (vii) PPTS, CH_3OH, RT, 15 h, 77-87%.

General procedure for the synthesis of compounds 2 [16]

A solution of 4-X 15.0 mmol in 20 % ammonium hydroxide (12 mL) and methanol (6 mL) was stirred vigorously as a suspension of I_2 (30.0 mmol) and KI (60.0 mmol) in H_2O (15 mL) was added dropwise. The solution was stirred for 2 h at RT. The mixture was extracted with ethyl acetate (3×40 mL). The combined organic phase was washed with brine dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by recrystallization (Ethanol).

2a: 4-hydroxy-3,5-diiodobenzonitrile: Yield 66%, yellow crystal. ^1H NMR (400 MHz, $CDCl_3$), δ(ppm): 7.96 (s, 2 H, 2 Ar**H**), 6.23 (s, 1 H, O**H**).

2b: 2,6-diiodo-4-nitrophenol: Yield 51%, yellow crystal. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 8.59 (s, 2 H, 2 Ar**H**), 6.36 (s, 1 H, O**H**).

2c: 2,6-diiodo-4-bromophenol : Yield 61%, white crystal. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 7.87 (s, 2 H, 2 Ar**H**), 6.23 (s, 1 H, O**H**).

2d: Methyl-4-hydroxy-3,5-diiodobenzoate: Yield 59%, light yellow crystal. ^{1}HNMR (400 MHz, $CDCl_3$), δ(ppm): 8.36 (s, 2 H, 2Ar**H**), 6.13 (s, 1 H, O**H**), 3.89 (s, 3 H, $COOCH_3$).

General procedure for the synthesis of compounds 3

A mixture of 0.4 mmol **2**, 0.4 mmol corresponding bromoalkane, 3.6 mmol K_2CO_3 and 20 ml MeCN is stirred for 20 hours under reflux. Water is then added and the mixture is extracted three times with Et_2O. The combined organic phases are washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product is purified by column chromatography on silica gel (eluent: PE).

3a-H: 3,5-diiodo-4-(tetradecyloxy)benzonitrile: Yield 90%, colorless oil, 485.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 8.05 (s, 2 H, 2 Ar**H**), 3.89-3.87 (d, 2 H, J = 6.4 Hz, OCH_2), 2.04-2.00 (m, 1 H, C**H**), 1.59-1.54 (m, 2 H, CH_2), 1.47-1.38 (m, 4 H, 2 CH_2), 1.37-1.26 (m, 10 H, 5 CH_2), 0.92-0.89 (t, 6 H, J = 6.8 Hz, 2 CH_3).

3a-F: 3,5-diiodo-4-(7,7,8,8,9,9,10,10,10-nonafluorodeyloxy)benzonitrile: Yield: 84%, white solid, 565.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 8.05 (s, 2 H, 2 Ar**H**), 4.02 (t, ^3J(H,H) = 6.4 Hz, 2 H, $ArOCH_2$), 2.03 - 2.14 (m, 2 H, CH_2CF_2), 1.92- 1.99 (q, ^3J(H,H) = 7.0 Hz, 2 H, OCH_2CH_2), 1.60 - 1.72 (m, 4 H, 2 CH_2), 1.42 - 1.46 (m, 2 H, CH_2).

3b-F: 1,3-diiodo-5-nitro-2-(5,5,6,6,7,7,8,8,9,9,10,10,10-nonafluorodeyloxy)benzene: Yield: 68%, yellow solid, 520.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 8.65 (s, 2 H, 2 Ar**H**), 4.11-4.08 (t, 2 H, J = 6.4 Hz, OCH_2), 2.36-2.21 (m, 2 H, CH_2), 2.07-1.93 (m, 4 H, 2 CH_2).

3c-H: 1,3-diiodo-5-bromo-2-(tetradecyloxy)benzene: Yield 94%, colorless oil, 556.4 mg. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 7.88 (s, 2 H, 2 Ar**H**), 3.82-3.80 (d, 2 H, J = 6.0 Hz, OCH_2), 2.00-1.97 (t, 1 H, J = 6.6 Hz, C**H**), 1.58-1.52 (m, 2 H, CH_2), 1.42-1.38 (m, 4 H, 2 CH_2), 1.45-1.36 (m, 10 H, 5 CH_2), 0.92-0.89 (t, 6 H, J = 6.8 Hz, 2 CH_3).

3d-F: 3,5-diiodo-5-methyl-4-(7,7,8,8,9,9,10,10,10-nonafluoroyloxy)benzoate: Yield 83%, white solid, 589.1 mg. ^{1}H-NMR (400 MHz, $CDCl_3$), δ(ppm): 8.32 (s, 2 H, 2Ar**H**), 4.03-4.00 (t, 2 H, J = 6.4 Hz, OCH_2), 3.86 (s, 3 H, $COOCH_3$), 2.13-2.02 (m, 2 H, CH_2), 1.97-1.86 (m, 2 H, CH_2), 1.71-1.53 (m, 4 H, 2 CH_2), 1.52-1.42 (m, 2 H, CH_2).

General procedure for the synthesis of compounds 4 [S17]

A mixture of 3,5-diiodobenzonitrile **3** and 5.0 mmol NaOH was dissolved in 10 ml of ethanol solution, and then H_2O_2 was added for 15 drops, and refluxed at 78 °C for 4 h. After the reaction, ethyl acetate (3 × 30 mL) was added to the mixture, and the extracted organic layers were combined and washed with saturated brine (2 ×20 mL), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The crude product is purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1).

4-F: 3,5-diiodo-5-formamide-4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-10-deca-5,7,9-triyn-1-yloxy)benzamide: Yield 80%, white solid, 610.3 mg. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 8.21 (s, 2 H, 2 Ar**H**), 6.08-5.52 (m, 2 H, NH_2), 4.06-4.03 (t, 2 H, J = 6.4 Hz, OCH_2), 2.32-2.18 (m, 2 H, CH_2), 2.07-1.93 (m, 4 H, 2 CH_2).

General procedure for the synthesis of compounds 8 by Sonogashira coupling [S17]

The appropriate **3** or **4** (0.5 mmol) and 4-(4-ethynylphenoxymethyl)-2,2-dimethyl-1,3-dioxolane **7**[S3, 18] (1.2 mmol) were dissolved in a mixture of dry THF (7 mL) and dry triethylamine (5 mL) under a nitrogen atmosphere. Then a mixture of $Pd(PPh_3)_4$ (0.05 mmol), CuI (0.12 mmol) was added, and the solution was stirred for overnight at RT. Ethyl acetate (30 mL) was added into the mixture, and washed with water (3×10 mL) and brine (3×10 mL), the organic layer were separated and dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. The residue was purified by column chromatography (petroleum ether : ethyl acetate : chloroform = 10:1:1).

CN-H-4CH$_3$: Yield 75%, red-brown solid, 224.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 8.03 (s, 2 H, 2 Ar**H**), 7.49-7.45 (m, 4 H, 4 Ar**H**), 6.90-6.88 (d, J = 8.8 Hz, 4 H, 4 Ar**H**), 4.52-4.46 (m, 2 H, 2 OC**H**), 4.20-4.16 (m, 4 H, 2 $ArOC\mathbf{H}_2$), 4.09-4.05 (m, 2 H, $ArOC\mathbf{H}_2CH$), 3.98-3.95 (m, 2 H, $OC\mathbf{H}_2$), 3.93-3.89 (m, 2 H, $ArOC\mathbf{H}_2CH$), 1.83-1.80 (t, 1 H, J = 6.0 Hz, $ArOCH_2C\mathbf{H}$), 1.60-1.54 (m, 6 H, 3 $C\mathbf{H}_2$), 1.47 (s, 6 H, 2 $C\mathbf{H}_3$), 1.41 (s, 6 H, 2 $C\mathbf{H}_3$), 1.38-1.17 (m, 12 H, 6 $C\mathbf{H}_2$), 0.82-0.78 (t, J = 6.8 Hz, 6 H, 2 $C\mathbf{H}_3$).

CN-F-4CH$_3$: Yield 76%, red-brown solid, 267.9 mg. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 7.71 (s, 2 H, 2 Ar**H**), 7.48-7.46 (d, J = 8.8 Hz, 4 H, 4 Ar**H**), 6.94-6.92 (d, J = 8.8 Hz, 4 H, 4 Ar**H**), 4.53-4.48 (m, 2 H, OC**H**), 4.46-4.43 (t, J = 6.0 Hz, 2 H, $ArOC\mathbf{H}_2CH_2$), 4.22-4.17 (m, 2 H, $ArOC\mathbf{H}_2CH$), 4.11-4.06 (m, 2 H, $OC\mathbf{H}_2$), 4.01-3.94 (m, 2 H, $ArOC\mathbf{H}_2CH$), 3.93-3.91 (m, 2 H, $OC\mathbf{H}_2$), 2.00-1.96 (m, 2 H, $C\mathbf{H}_2CF_2$), 1.93-1.86 (m, 2 H, $OCH_2C\mathbf{H}_2$) 1.68-1.60 (m, 2 H, $C\mathbf{H}_2$), 1.57-1.50 (m, 2 H, $C\mathbf{H}_2$), 1.49 (s, 6 H, 2 $C\mathbf{H}_3$), 1.43 (s, 6 H, 2 $C\mathbf{H}_3$), 1.32-1.23 (m, 2 H, $C\mathbf{H}_2$).

NO$_2$-F-4CH$_3$: Yield 51%, brown-yellow solid, 198.5 mg. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 8.28 (s, 2 H, 2 Ar**H**), 7.48-7.44 (m, 4 H, 4 Ar**H**), 6.88-6.85 (d, J = 8.8 Hz, 4 H, 4 Ar**H**), 4.51-4.46 (m, 4 H, 2 $OC\mathbf{H_2}$**,** $ArOC\mathbf{H}_2CH_2$), 4.20-4.17 (m, 2 H, $ArOC\mathbf{H}_2CH$), 4.09-4.04 (m, 2 H, $OC\mathbf{H}_2$), 3.99-3.95 (m, 2 H, $ArOC\mathbf{H}_2CH$), 3.94-3.88 (m, 2 H, $OC\mathbf{H}_2$), 1.99-1.96 (m, 2 H, $C\mathbf{H}_2CF_2$), 1.94-1.89 (m, 2 H, $OCH_2C\mathbf{H}_2$), 1.75-1.64 (m, 2 H, $C\mathbf{H}_2$), 1.47 (s, 6 H, 2 $C\mathbf{H}_3$), 1.41 (s, 6 H, 2 $C\mathbf{H}_3$).

Br-H-4CH$_3$: Yield 79%, red-brown solid, 252.9 mg. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 7.53 (s, 2 H, 2 Ar**H**), 7.46-7.43 (m, 4 H, 4 Ar**H**), 6.90-6.88 (d, J = 8.8 Hz, 4 H, 4 Ar**H**), 4.52-4.46 (m, 2 H, 2 OC**H**), 4.20-4.16 (m, 4 H, 2 $ArOC\mathbf{H}_2$), 4.09-4.05 (m, 2 H, $ArOC\mathbf{H}_2CH$), 3.98-3.95 (m, 2 H, $OC\mathbf{H}_2$), 3.93-3.89 (m, 2 H, $ArOC\mathbf{H}_2CH$), 1.83-1.80 (t, 1 H, J = 6.0 Hz, $ArOCH_2C\mathbf{H}$), 1.60-1.54 (m, 6 H, 3 $C\mathbf{H}_2$), 1.47 (s, 6 H, 2 $C\mathbf{H}_3$), 1.41 (s, 6 H, 2 $C\mathbf{H}_3$), 1.38-1.17 (m, 12 H, 6 $C\mathbf{H}_2$), 0.82-0.78 (t, J = 6.8 Hz, 6 H, 2 $C\mathbf{H}_3$).

COOCH$_3$-F-4CH$_3$: Yield 82%, red-brown solid, 299.9 mg. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 8.10 (s, 2 H, 2 Ar**H**), 7.47-7.44 (d, J = 8.8 Hz, 4 H, 4 Ar**H**), 6.92-6.89 (d, J = 8.8 Hz, 4 H, 4 Ar**H**), 4.50-4.46 (m, 2 H, $OC\mathbf{H}_2$), 4.44-4.41(t, J = 6.0 Hz, 2 H, $ArOC\mathbf{H}_2CH_2$), 4.20-4.16 (m, 2 H, $ArOC\mathbf{H}_2CH$), 4.09-4.05 (m, 2 H, $OC\mathbf{H}_2$), 3.98-3.94 (m, 2 H, $ArOC\mathbf{H}_2CH$), 3.92-3.89 (m, 2 H, $OC\mathbf{H}_2$), 1.98-1.85 (m, 2H, $C\mathbf{H}_2CF_2$), 1.68-1.63 (m, 2 H, $OCH_2C\mathbf{H}_2$) , 1.62-1.49 (m, 6 **H** 3 $C\mathbf{H}_2$), 1.47 (s, 6 H, 2 $C\mathbf{H}_3$), 1.41 (s, 6 H, 2 $C\mathbf{H}_3$).

CONH$_2$-F-4CH$_3$: Yield 63%, red-brown solid, 244.8 mg. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 7.89 (s, 2 H, 2 Ar**H**), 7.46-7.44 (d, J = 8.8 Hz, 4 H, 4 Ar**H**), 6.91-6.89 (d, J = 8.8 Hz, 4 H, 4 Ar**H**), 4.52-4.46 (m, 2 H, OC**H**), 4.44-4.41(t, J = 6.0 Hz, 2 H, $ArOC\mathbf{H}_2CH_2$), 4.20-4.16 (m, 2 H, $ArOC\mathbf{H}_2CH$), 4.09-4.05 (m, 2 H, $OC\mathbf{H}_2$), 3.99-3.95 (m, 2 H, $ArOC\mathbf{H}_2CH$), 3.92-3.89 (m, 2 H, $OC\mathbf{H}_2$), 1.98-1.85 (m, 2 H, $C\mathbf{H}_2CF_2$), 1.68-1.63 (m, 2 H, $OCH_2C\mathbf{H}_2$), 1.62-1.49 (m, 2 H, $C\mathbf{H}_2$), 1.47 (s, 6 H, 2 $C\mathbf{H}_3$), 1.41 (s, 6 H, 2 $C\mathbf{H}_3$).

General procedure for the synthesis of compounds 9 [S3,18]

8 (0.5 mmol) was dissolved in CH_3OH (30 mL) and PPTS (120 mg) was added. The mixture was refluxed for 12 h, then cooled to RT, and extracted with chloroform (3×30 mL). The combined extracts were washed with aqueous saturated $NaHCO_3$ solution (3×30 mL) and H_2O (3×30 mL), dried over anhydrous Na_2SO_4, then the solvent was removed in vacuo. The residue was purified by column chromatography (petroleum ether : acetone = 3 : 2).

CN-H: Yeild 71%, white solid, 142.2 mg. ^1H NMR (400 MHz, $CDCl_3$), *δ*(ppm): 7.66 (s, 2 H, 2 Ar**H**), 7.47-7.44 (m, 4 H, 4 Ar**H**), 6.92-6.89 (t, *J* = 7.2 Hz, 4 H, 4 Ar**H**), 4.37-4.35 (d, 2 H, *J* = 5.2 Hz, ArOC$\mathbf{H}_2$CH$_2$), 4.15-4.12 (m, 2 H, 2 C**H**OH), 4.08-4.06 (t, 4 H, *J* = 3.2 Hz, 2 ArOC$\mathbf{H}_2$CH), 3.88-3.84 (m, 2 H, C$\mathbf{H}_2$OH), 3.78-3.74 (m, 2 H, C$\mathbf{H}_2$OH), 1.85-1.79 (m, 1 H, ArOCH$_2$C**H**), 1.62-1.53 (m, 2 H, C$\mathbf{H}_2$), 1.46-1.27 (m, 6 H, 3 C$\mathbf{H}_2$), 1.23-1.13 (m, 8 H, 4 C$\mathbf{H}_2$), 0.88-0.86 (t, 6 H, *J* = 6.3, 2 C$\mathbf{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$), *δ* (ppm): 163.97(1C), 158.94(2C), 136.39(2C), 133.17(4C), 118.59(2C), 117.66(1C), 115.26(2C), 114.66(4C), 106.76(1C), 95.62(2C), 82.86(2C), 70.24(4C), 69.19(4C), 63.51(4C), 39.36, 32.22, 31.09, 26.71, 22.62, 14.10(multi carbons in alkyl chain); elemental analysis calcd (%) for $C_{41}H_{49}NO_7$ (667.84): C 73.74, H 7.40, N 2.10; found: C 73.53, H 7.19, N 1.90. HRMS (ESI): m/z calcd for $C_{41}H_{49}NO_7Na$ $[M + Na]^+$ 690.34, found 690.34.

CN-F: Yeild 62%, white solid,149.0 mg. ^1H NMR (400 MHz, $CDCl_3$), *δ*(ppm): 7.70 (s, 2 H, 2 Ar**H**), 7.49-7.47 (d, 4 H, *J* = 8.4 Hz, 4 Ar**H**), 6.95-6.92 (d, 4 H, *J* = 8.8 Hz, 4 Ar**H**), 4.46-4.43 (t, 2 H, *J* = 6.0 Hz, ArOC$\mathbf{H}_2$CH$_2$), 4.16-4.13 (t, 2 H, *J* = 6.8 Hz, C**H**OH), 4.11-4.08 (t, 2 H, *J* = 5.4 Hz, ArOC$\mathbf{H}_2$CH), 3.90-3.86 (m, 2 H, C$\mathbf{H}_2$OH), 3.80-3.76 (m, 2 H, C$\mathbf{H}_2$OH), 2.20 (s, 4 H, 2 CH$_2$O**H**, 2 CHO**H**), 2.00-1.88 (m, 4 H, ArOCH$_2$C$\mathbf{H}_2$C$\mathbf{H}_2$), 1.67-1.63 (m, 2 H, C$\mathbf{H}_2$), 1.57-1.53 (m, 2 H, C$\mathbf{H}_2$), 1.47-1.42 (m, 2 H, C$\mathbf{H}_2$). ^{13}C NMR (100 MHz, $CDCl_3$), *δ* (ppm): 163.67(1C), 159.06(2C), 136.18(2C), 133.15(4C), 119.15(2C), 117.56(2C), 115.09(2C), 114.72(4C), 107.32(1C), 95.68(2C), 82.58(2C), 74.30(2C), 70.24 (2C), 69.16(2C), 63.48(2C), 30.87(1C), 30.65, 30.43, 30.26, 28.98, 25.98, 20.08(multi carbons in alkyl chain); elemental analysis calcd (%) for $C_{39}H_{36}F_9NO_7$ (801.70): C 58.43, H 4.53, N 1.75; found: C 58.21, H 4.37, N 1.53. HRMS (ESI): m/z calcd for $C_{39}H_{36}F_9NO_7Na$ $[M + Na]^+$ 824.22, found 824.22.

NO_2-F: Yield: 64%, yellow solid, 171.5 mg. ^1H NMR (400 MHz, $CDCl_3$), *δ*(ppm): 8.28 (s, 2 H,2 Ar**H**), 7.48-7.46 (d, 4 H, *J* = 8.4 Hz, 4 Ar**H**), 6.93-6.91 (d, 4 H, *J* = 8.4 Hz, 4 Ar**H**), 4.51 (s, 2 H, ArOC$\mathbf{H}_2$CH$_2$), 4.14 (s, 2 H, C$\mathbf{H}_2$OH), 4.08-4.07 (d, 2 H, *J* = 4.0 Hz, ArOC$\mathbf{H}_2$CH), 3.88-3.85 (m, 2 H, C$\mathbf{H}_2$OH), 3.78-3.75 (m, 2 H, C$\mathbf{H}_2$OH), 2.61 (s, 2 H, 2 CH$_2$O**H**), 2.14 (m, 2 H, C$\mathbf{H}_2$), 2.09 (s, 2 H, 2 CHO**H**), 2.02-1.97 (m, 4 H, 2 C$\mathbf{H}_2$). ^{13}C NMR (100 MHz, $CDCl_3$), *δ* (ppm): 164.42 (1C), 159.40(2C), 142.57 (2C), 132.86(2C), 127.53 (2C), 118.27(1C), 114.60(6C), 113.96(2C), 95.94(2C), 82.12(2C), 73.48(1C), 70.10(2C), 68.98(2C), 63.31(2C), 40.46, 40.25, 40.04, 39.83, 39.62, 39.42, 39.20, 30.36, 29.67, 29.40, 17.14(multi carbons in alkyl chain); elemental analysis calcd (%) for $C_{38}H_{32}F_{13}NO_9$ (893.65): C 51.07, H 3.61, N 1.57; found: C 49.82, H 3.42, N 1.39. HRMS (ESI): m/z calcd for $C_{38}H_{32}F_{13}NO_9Na$ $[M + Na]^+$ 916.18, found 916.18.

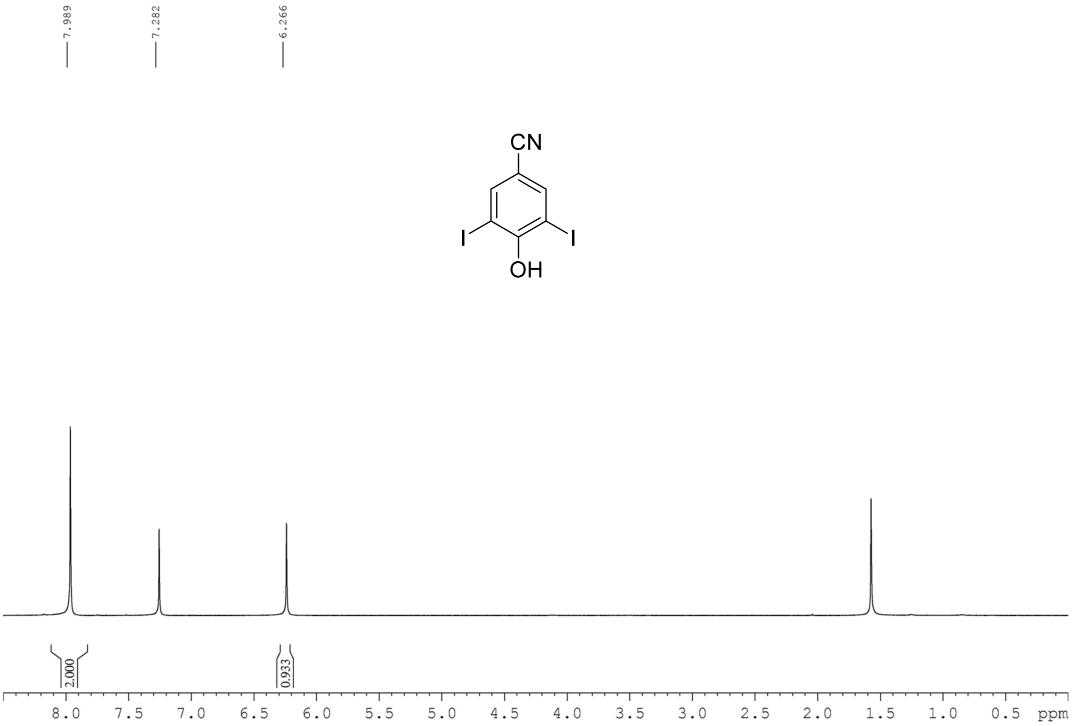
Br-H: Yeild 72%, white solid, 155.6 mg. ^1H NMR (400 MHz, $CDCl_3$), *δ*(ppm): 7.53 (s, 2 H, 2 Ar**H**), 7.47-7.43 (m, 4 H, 4 Ar**H**), 6.91-6.88 (m, 4 H, 4 Ar**H**), 4.22-4.19 (m, 2 H, ArOC$\mathbf{H}_2$CH$_2$), 4.17-4.12 (m, 2 H, C**H**OH), 4.11-4.06 (m, 4 H, 2 ArOC$\mathbf{H}_2$CH), 3.88-3.84 (m, 2 H, C$\mathbf{H}_2$OH), 3.78-3.74 (m, 2 H, C$\mathbf{H}_2$OH), 1.83-1.80 (t, 1 H, *J* = 6.0 Hz, ArOCH$_2$C**H**), 1.63-1.54 (m, 2 H, C$\mathbf{H}_2$), 1.42-1.28 (m, 6 H, 3 C$\mathbf{H}_2$), 1.24-1.15 (m, 8 H, 4 C$\mathbf{H}_2$), 0.88-0.86 (t, 6 H, *J* = 6.3, 2 C$\mathbf{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$), *δ* (ppm): 160.32(1C), 158.87(2C), 135.61(2C), 133.30(4C), 119.67(2C), 115.89(2C), 115.06(1C), 114.75(4C), 94.79(2C), 83.61(2C), 70.43(4C), 69.36(4C), 63.70(4C), 39.57, 32.42, 31.41, 26.96, 22.78, 14.25(multi carbons in alkyl chain); elemental analysis calcd (%) for $C_{40}H_{49}BrO_7$ (721.73) : C 66.57, H 6.84; found: C 66.34, H 6.64. HRMS (ESI): m/z calcd for $C_{40}H_{49}BrO_7Na$ $[M + Na]^+$ 743.26, found 743.26.

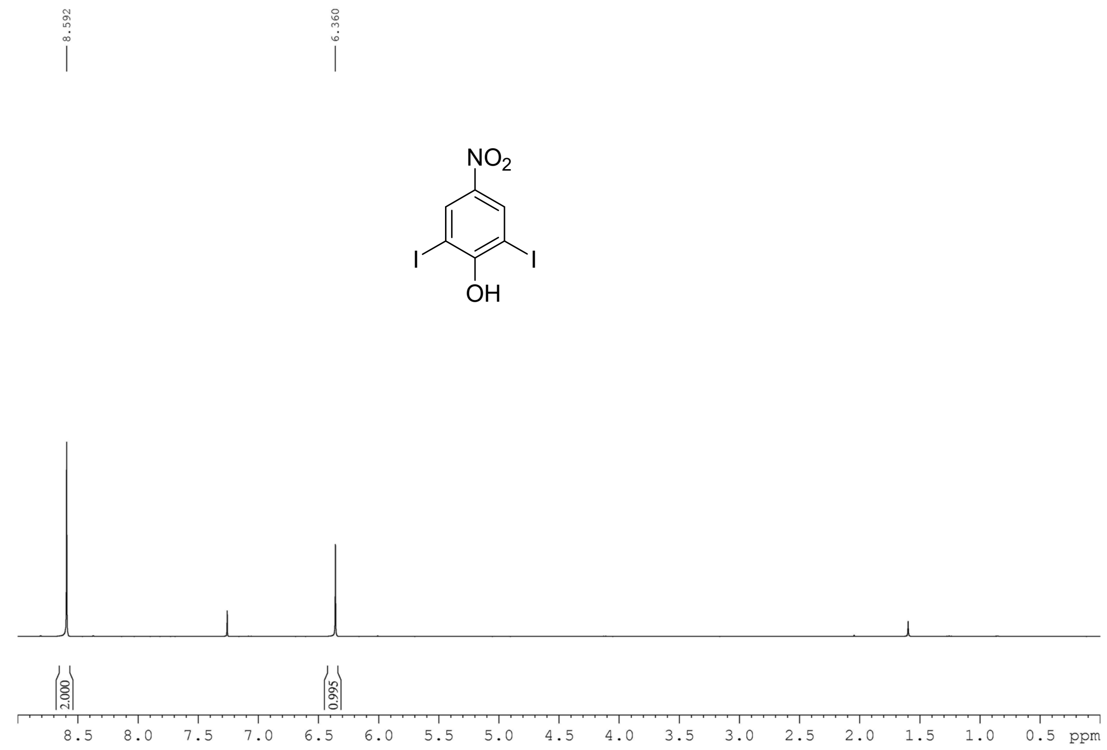
$COOCH_3$-F: Yield 74%, white solid, 185.2 mg. ^1H NMR (400 MHz, $CDCl_3$), *δ*(ppm): 8.09 (s, 2 H, 2 Ar**H**), 7.46-7.44 (d, 4 H, *J* = 8.8 Hz, 4 Ar**H**), 6.90-6.88 (d, 4 H, *J* = 8.8 Hz, 4 Ar**H**), 4.43-4.40 (t, 2 H, *J* = 6.0 Hz, ArOC$\mathbf{H}_2$CH$_2$), 4.14-4.11 (m, 2 H, ArOC$\mathbf{H}_2$CH), 4.07-4.02 (m, 4 H, ArOC**H**$_2$CH, C**H**$_2$OH), 3.91 (s, 3 H, COOC**H**$_3$), 3.87-3.83 (m, 2 H, C**H**$_2$OH), 3.76-3.73 (m, 2 H, C**H**$_2$OH), 2.89-2.61 (m, 4 H, 2 CH$_2$O**H**, 2 CHO**H**), 1.97-1.84 (m, 4 H, 2 C**H**$_2$), 1.67-1.60 (m, 2 H, C**H**$_2$), 1.54-1.48 (m, 2 H, C**H**$_2$), 1.44-1.37 (m, 2 H, C**H**$_2$). ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 165.81(1C), 164.07(1C), 158.91(2C), 134.64(2C), 133.19(4C), 125.38(1C), 117.93(2C), 115.84(2C), 114.80(4C), 94.37(2C), 83.92(2C), 74.19(2C), 70.46 (2C), 69.30(2C), 63.67(2C), 31.04, 30.82, 30.59, 30.44, 26.15, 20.23(multi carbons in alkyl chain); elemental analysis calcd (%) for $C_{40}H_{39}F_9O_9$ (834.73): C 57.56, H 4.71; found: C 57.32, H 4.46. HRMS (ESI): m/z calcd for $C_{40}H_{39}F_9O_9Na$ [M + Na]$^+$ 857.23, found 857.23.

CONH$_2$-F: Yield 57%, white solid, 148.4 mg. ^{1}H NMR (400 MHz, CDCl$_3$), δ(ppm): 7.87 (s, 2 H, 2 Ar**H**), 7.39-7.37 (d, 4 H, *J* = 8.4 Hz, 4 Ar**H**), 6.86-6.84 (d, 4 H, *J* = 8.8 Hz, 4 Ar**H**), 4.35-4.32 (t, 2 H, *J* = 6.0 Hz, ArOC**H**$_2$CH$_2$), 4.00-3.95 (m, 6 H, 3 C**H**$_2$), 3.73-3.69 (m, 2 H, C**H**$_2$), 3.66-3.62 (m, 2 H, C**H**$_2$), 1.99-1.90 (m, 2 H, C**H**$_2$), 1.85-1.80 (m, 2 H, C**H**$_2$), 1.62-1.55 (m, 2 H, C**H**$_2$), 1.53-1.45 (m, 2 H, C**H**$_2$), 1.41-1.37 (m, 2 H, C**H**$_2$). ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 168.78(1C), 162.91(1C), 159.05(2C), 132.82(6C), 132.26(2C), 128.30(1C), 117.87(2C), 115.10(2C), 114.55(6C), 94.34(2C), 83.45(2C), 74.03(1C), 70.23(2C), 68.90(2C), 63.19(2C), 30.71, 30.49, 30.27, 30.11, 28.83, 25.85, 19.93(multi carbons in alkyl chain); elemental analysis calcd (%) for $C_{39}H_{34}F_{13}NO_8$ (891.68): C 52.53, H 3.84, N 1.57; found: C 52.34, H 3.62, N 1.38. HRMS (ESI): m/z calcd for $C_{39}H_{34}F_{13}NO_8Na$ [M + Na]$^+$ 914.20, found 914.20.

S8. NMR spectra

^{1}H and ^{13}C NMR spectra for representive compounds

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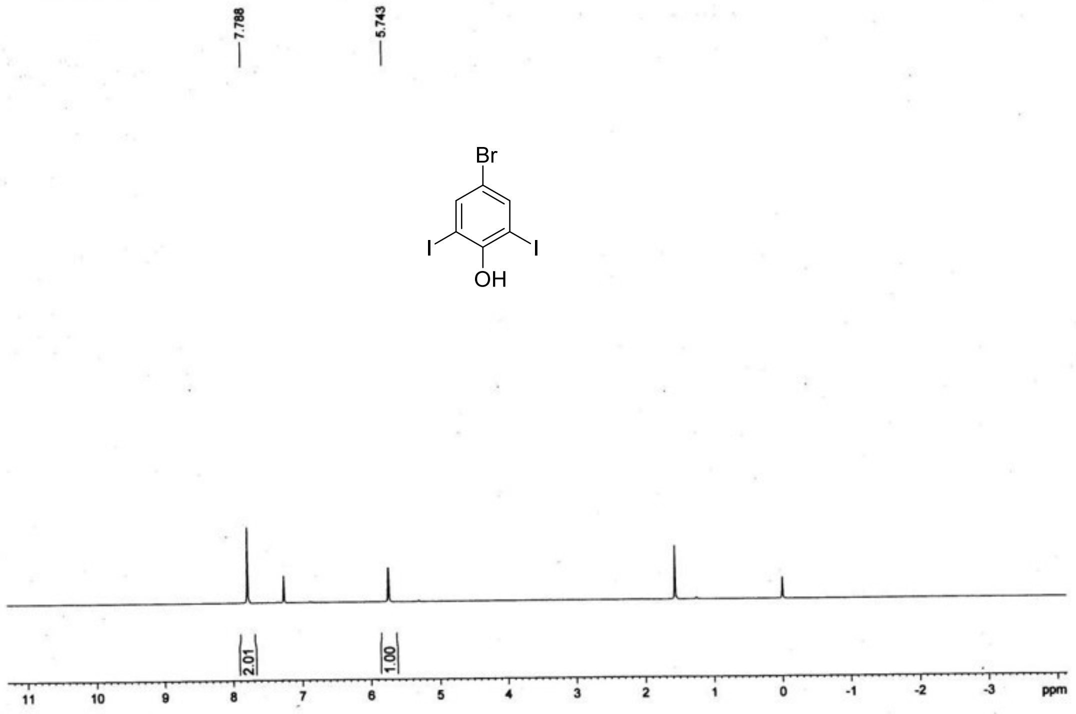
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11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm

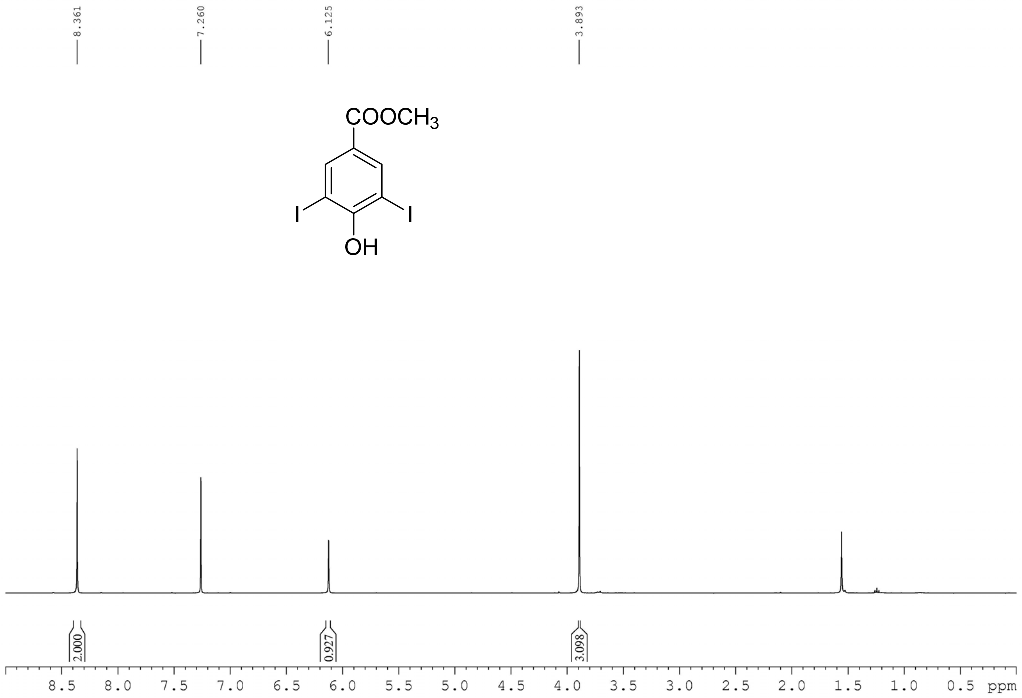
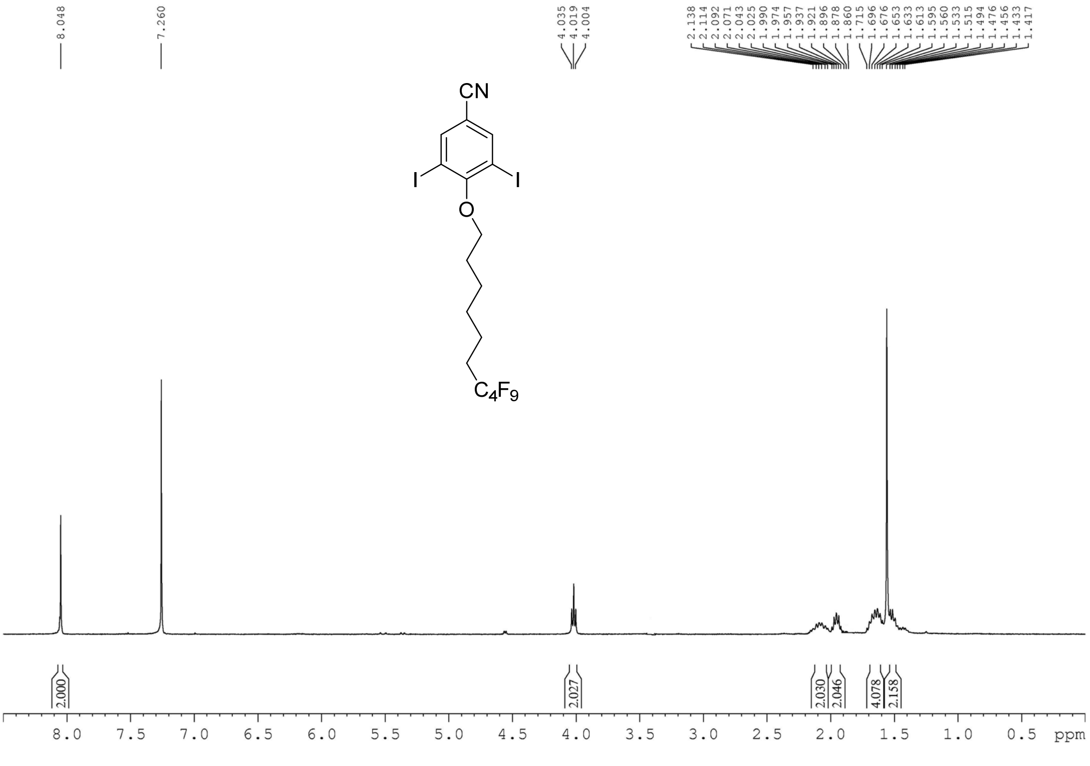
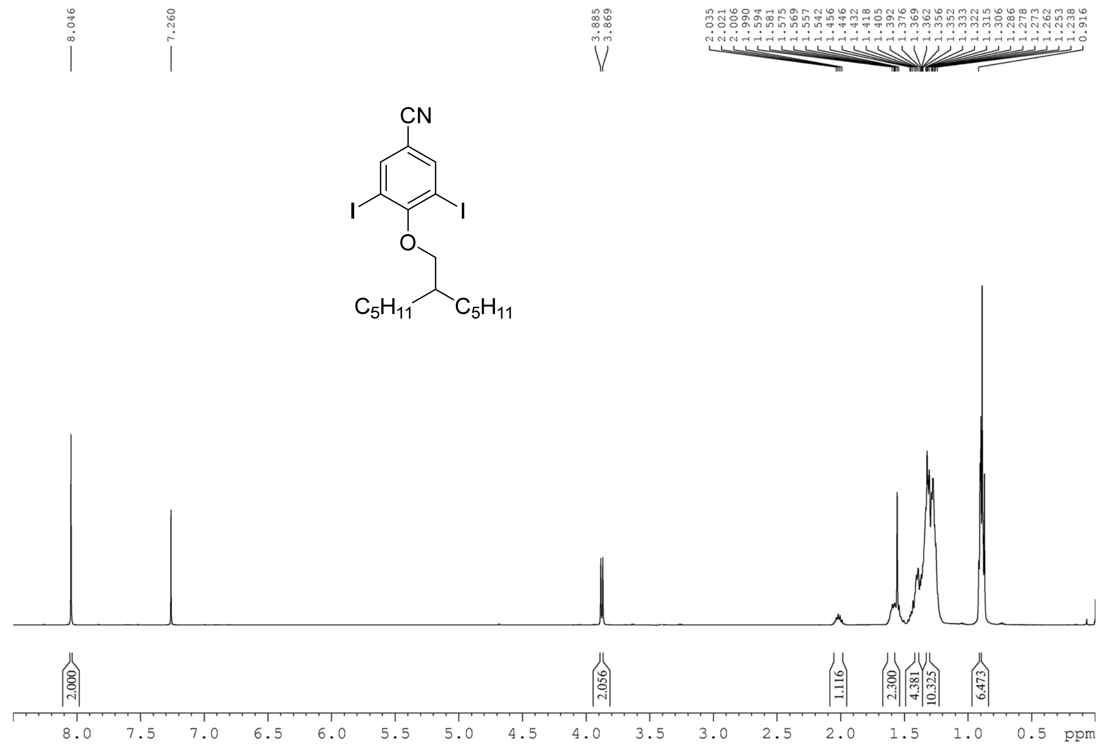
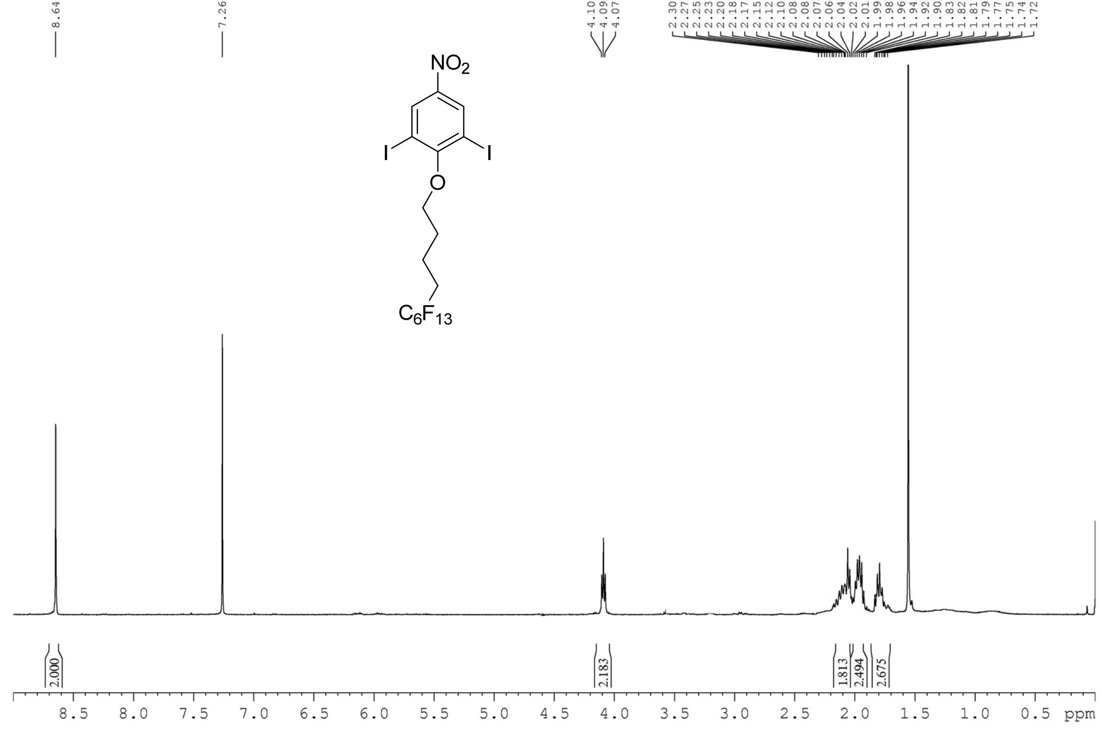
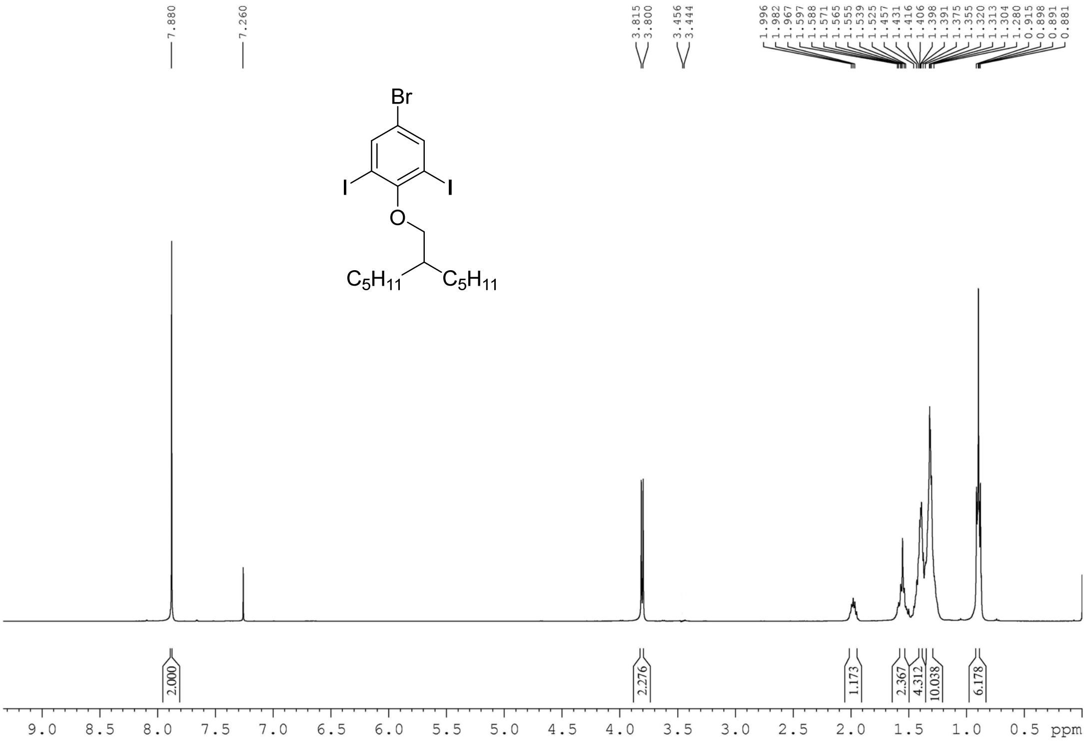


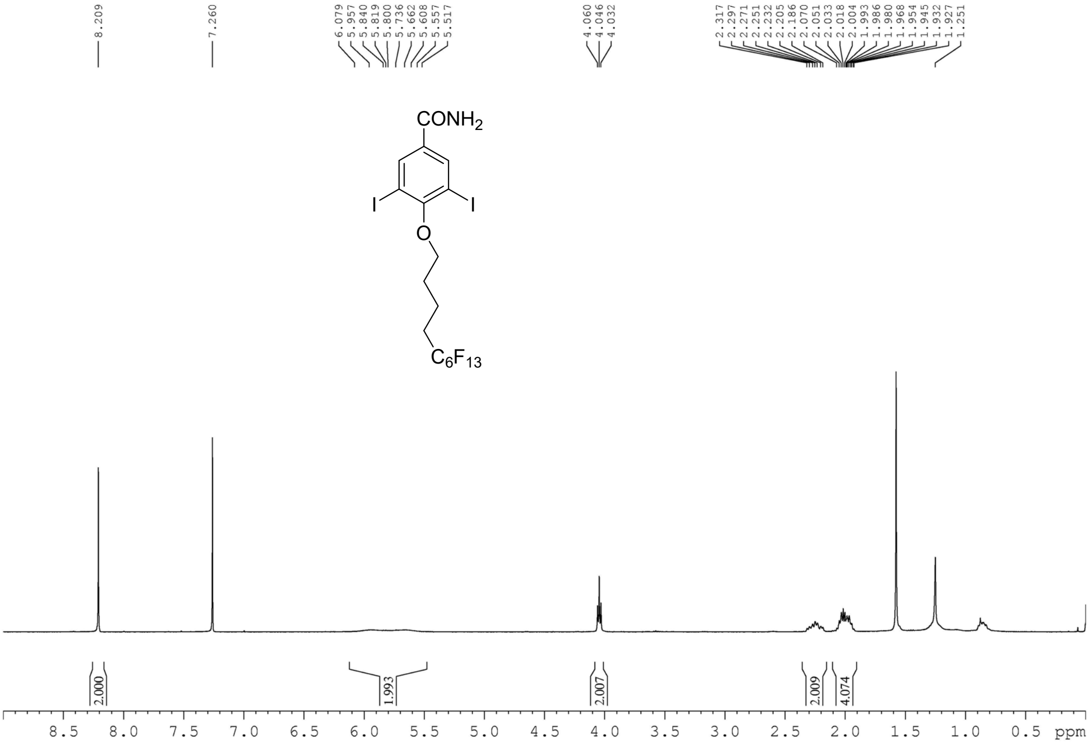
Figure S9 ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) spectra of compounds **4-R$_h$-2,6-diiodophenol** (R$_h$= CN, NO_2, Br, $COOCH_3$).




8.046
7.260
3.885
3.869
2.035
2.021
2.006
1.990
1.594
1.581
1.575
1.569
1.557
1.542
1.456
1.446
1.432
1.418
1.405
1.392
1.376
1.369
1.362
1.356
1.352
1.333
1.322
1.315
1.306
1.286
1.278
1.273
1.262
1.253
1.238
0.916
CN
I
I
O
C5H11
C5H11
2.000
2.056
1.116
2.300
4.381
10.325
6.473
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


8.646
7.260
4.106
4.092
4.077
2.301
2.275
2.253
2.233
2.208
2.188
2.175
2.155
2.129
2.108
2.088
2.083
2.078
2.060
2.043
2.029
2.014
1.996
1.980
1.963
1.943
1.927
1.902
1.834
1.821
1.813
1.795
1.773
1.757
1.748
1.727
NO2
I
I
O
C6F13
2.000
2.183
1.813
2.494
2.675
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


7.880
7.260
3.815
3.800
3.456
3.444
1.996
1.982
1.967
1.597
1.588
1.571
1.565
1.555
1.539
1.525
1.457
1.431
1.416
1.406
1.398
1.391
1.375
1.355
1.320
1.313
1.304
1.280
0.915
0.898
0.891
0.881
Br
I
I
O
C5H11
C5H11
2.000
2.276
1.173
2.367
4.312
10.038
6.178
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm


8.209
7.260
6.079
5.957
5.840
5.819
5.800
5.736
5.662
5.608
5.557
5.517
4.060
4.046
4.032
2.317
2.297
2.271
2.251
2.232
2.205
2.186
2.070
2.051
2.033
2.018
2.004
1.993
1.986
1.980
1.968
1.954
1.945
1.932
1.927
1.251
CONH2
I
I
O
C6F13
2.000
1.993
2.007
2.009
4.074
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm

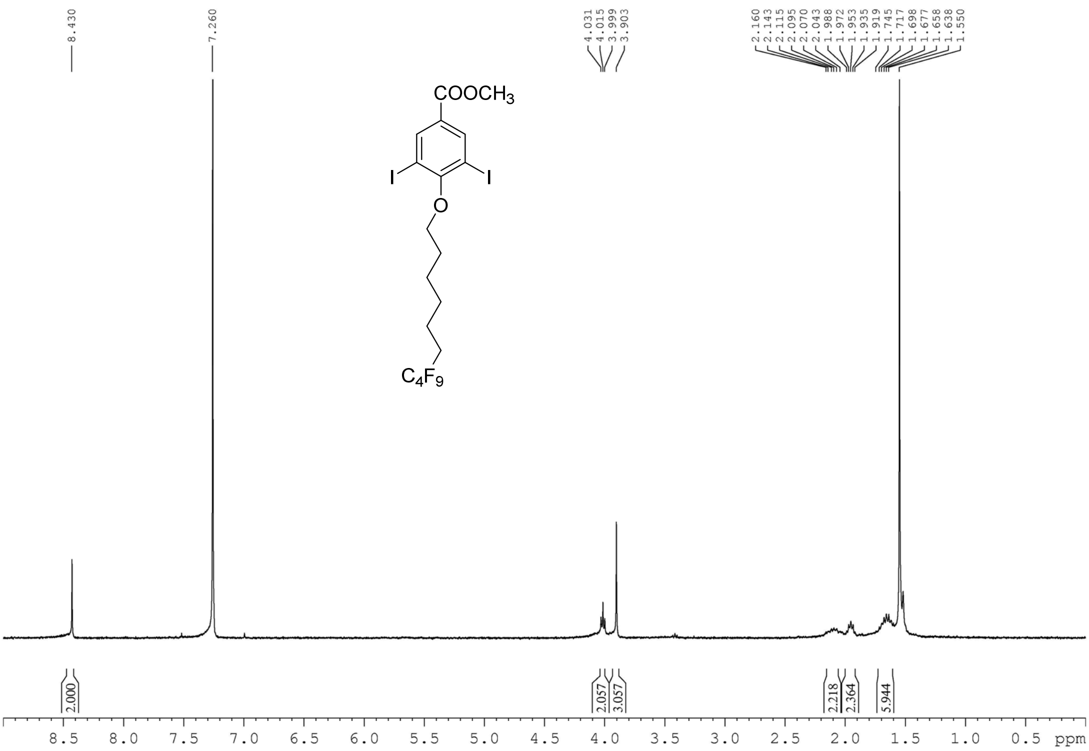
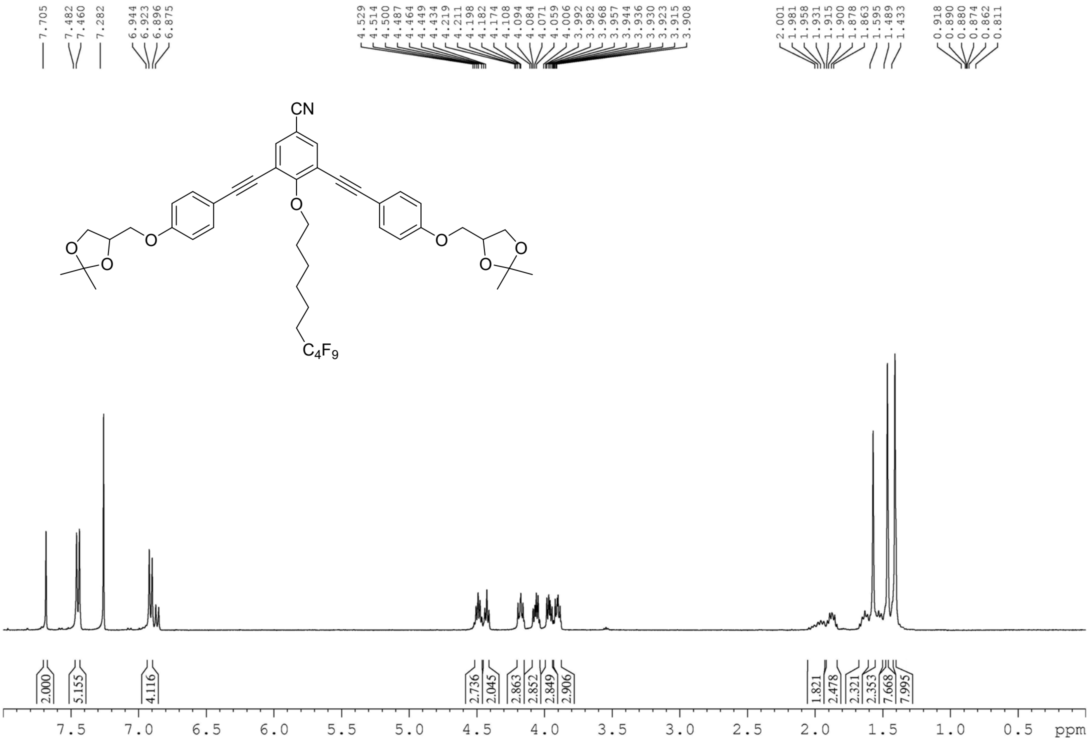
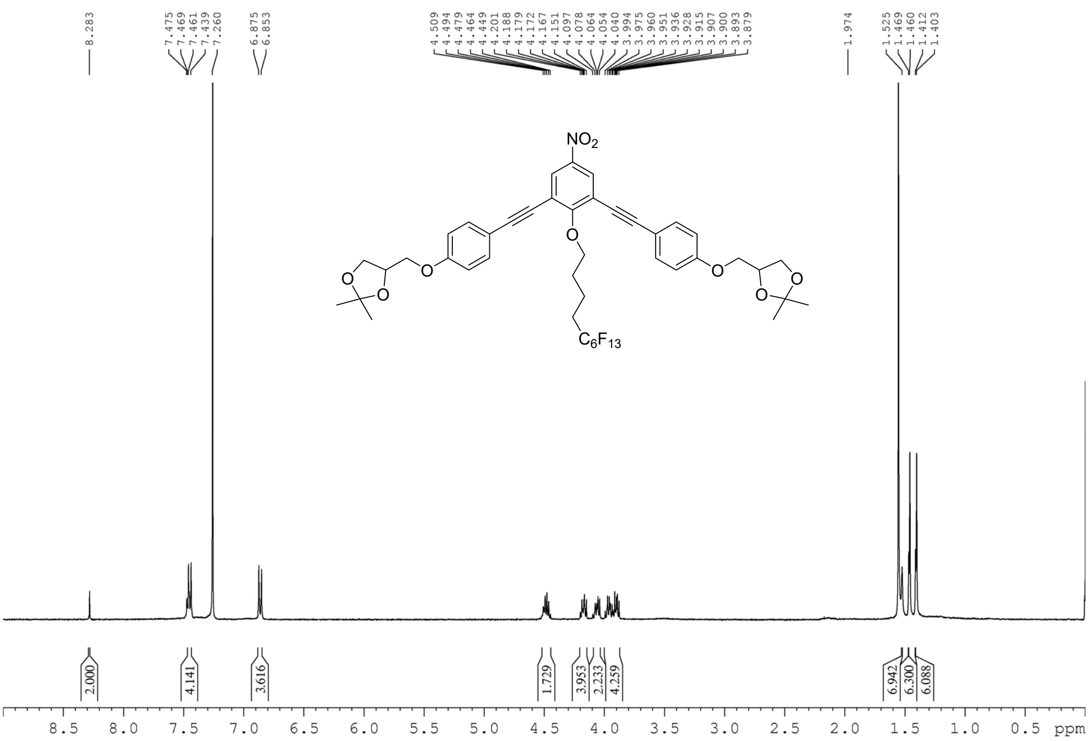
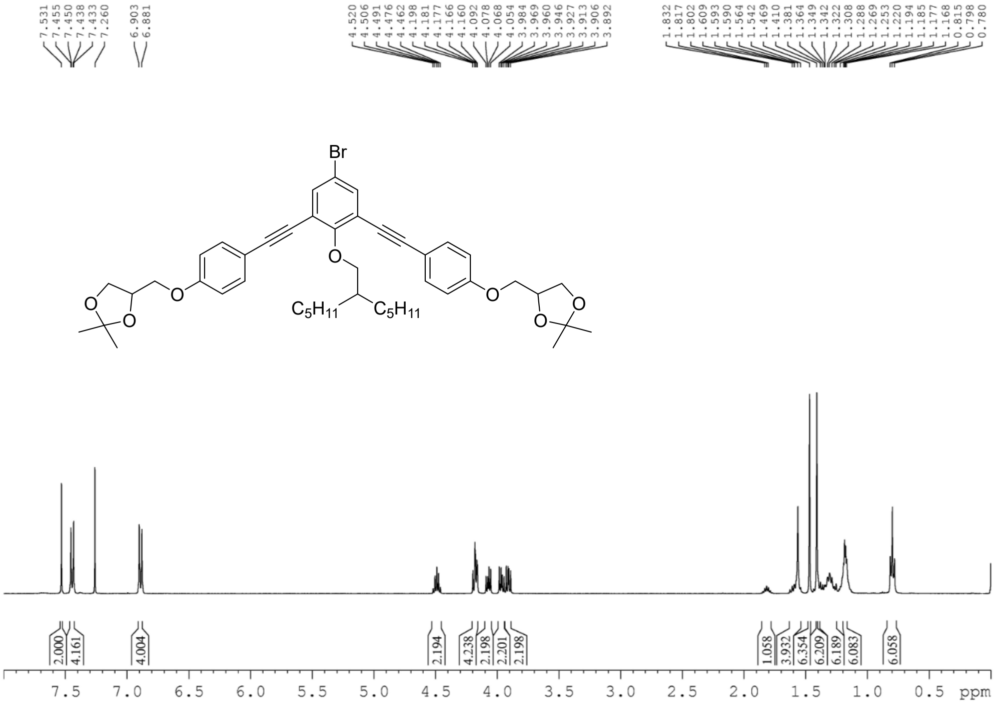


Figure S10 ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) spectra of compounds **3** and **4**.




8.283
7.475
7.469
7.461
7.439
7.260
6.875
6.853
4.509
4.494
4.479
4.464
4.449
4.201
4.188
4.179
4.172
4.167
4.151
4.097
4.078
4.064
4.054
4.040
3.994
3.975
3.960
3.951
3.936
3.928
3.915
3.907
3.900
3.893
3.879
1.974
1.525
1.469
1.460
1.412
1.403
NO2
O
O
O
O
O
O
O
C6F13
2.000
4.141
3.616
1.729
3.953
2.233
4.259
6.942
6.300
6.088
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


7.531
7.455
7.450
7.438
7.433
7.260
6.903
6.881
4.520
4.506
4.491
4.476
4.462
4.198
4.181
4.177
4.166
4.160
4.092
4.078
4.068
4.054
3.984
3.969
3.960
3.946
3.927
3.913
3.906
3.892
1.832
1.817
1.802
1.609
1.593
1.590
1.564
1.542
1.469
1.410
1.381
1.364
1.349
1.342
1.322
1.308
1.288
1.269
1.253
1.220
1.194
1.185
1.177
1.168
0.815
0.798
0.780
Br
O
O
O
O
O
O
O
C5H11
C5H11
2.000
4.161
4.004
2.194
4.238
2.198
2.201
2.198
1.058
3.932
6.354
6.209
6.189
6.083
6.058
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

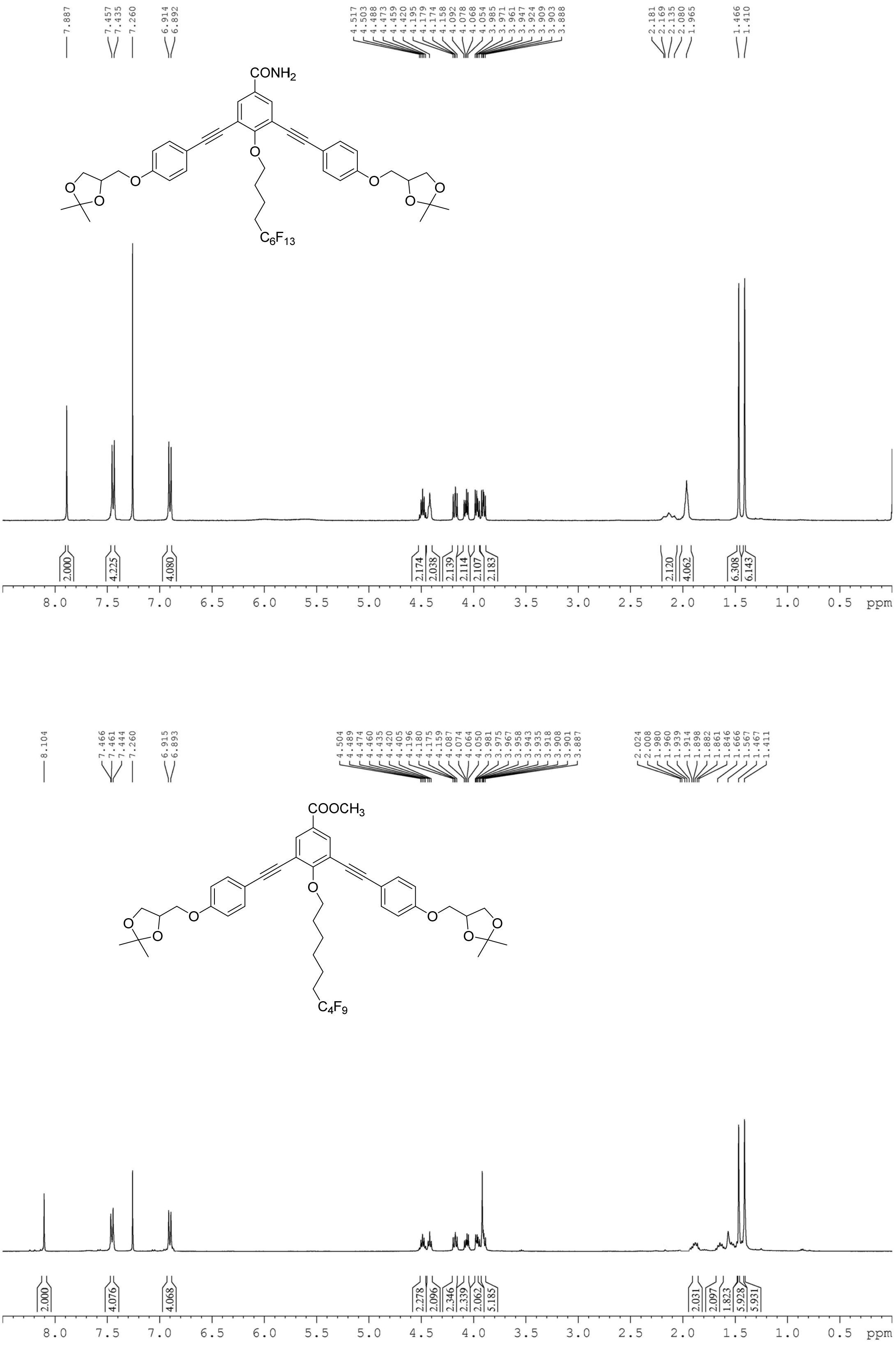
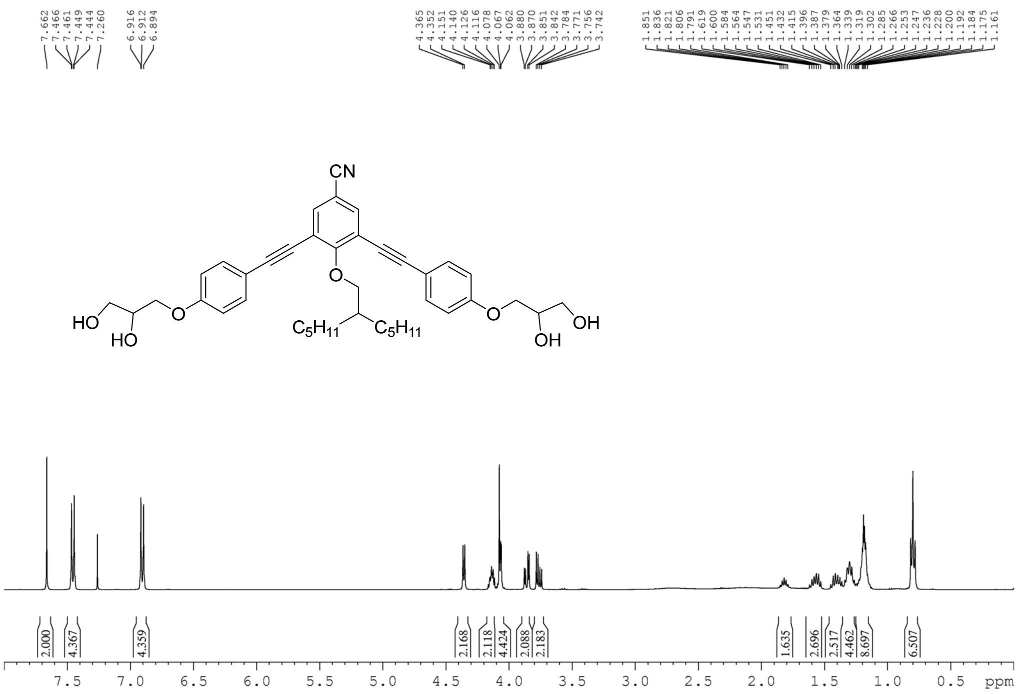
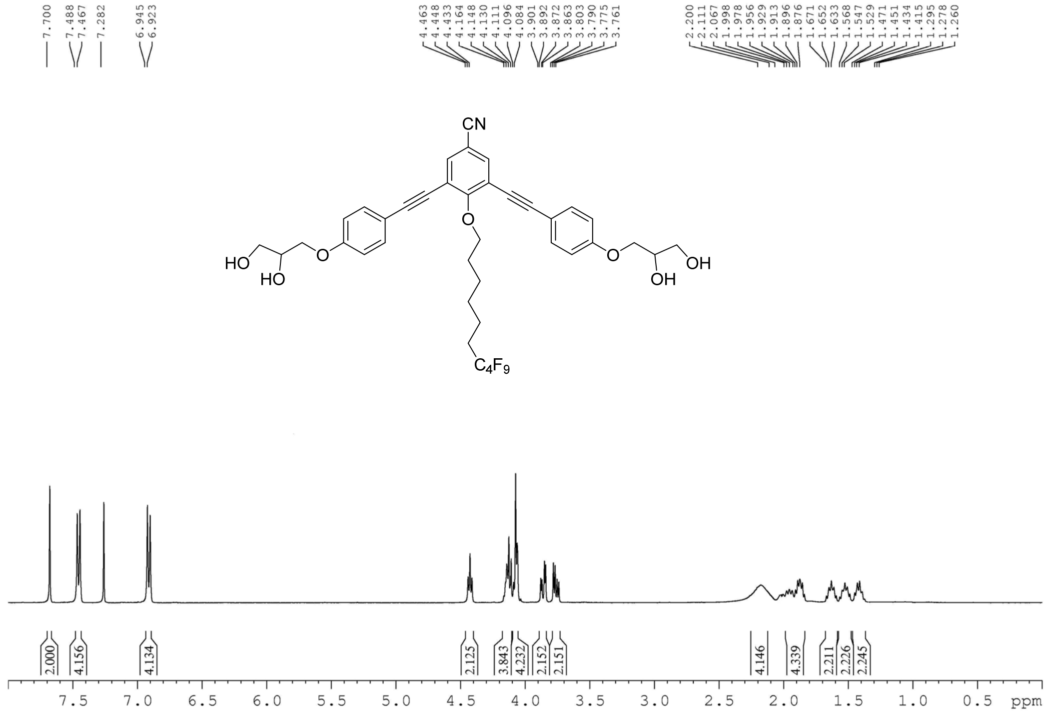


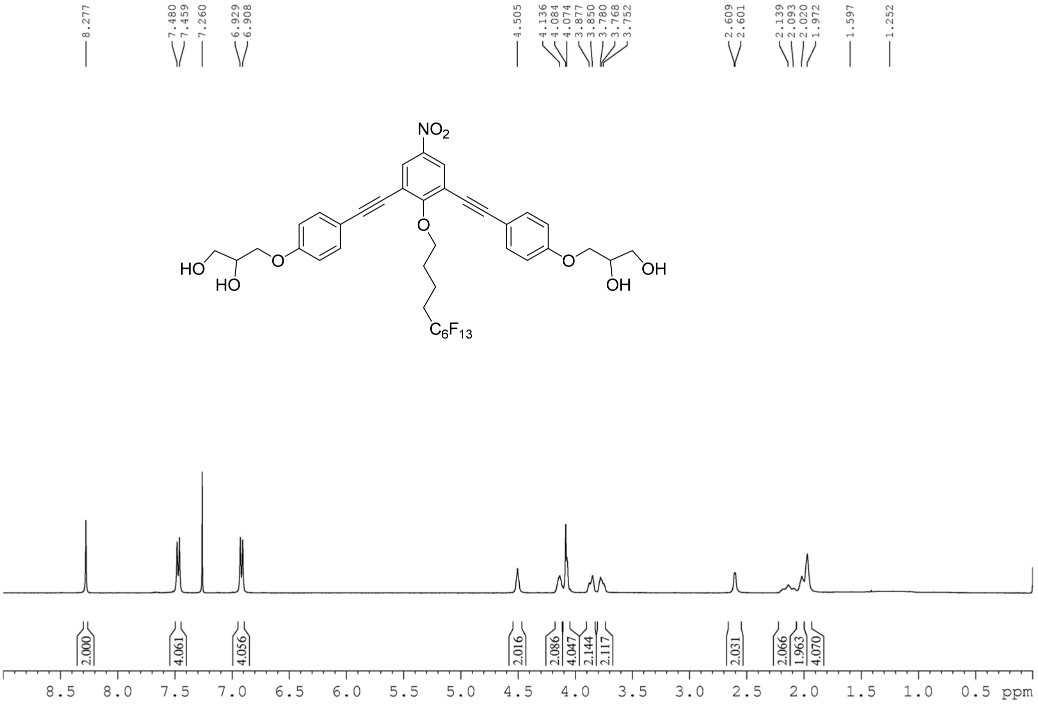
Figure S11 ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) spectra of compounds **8**

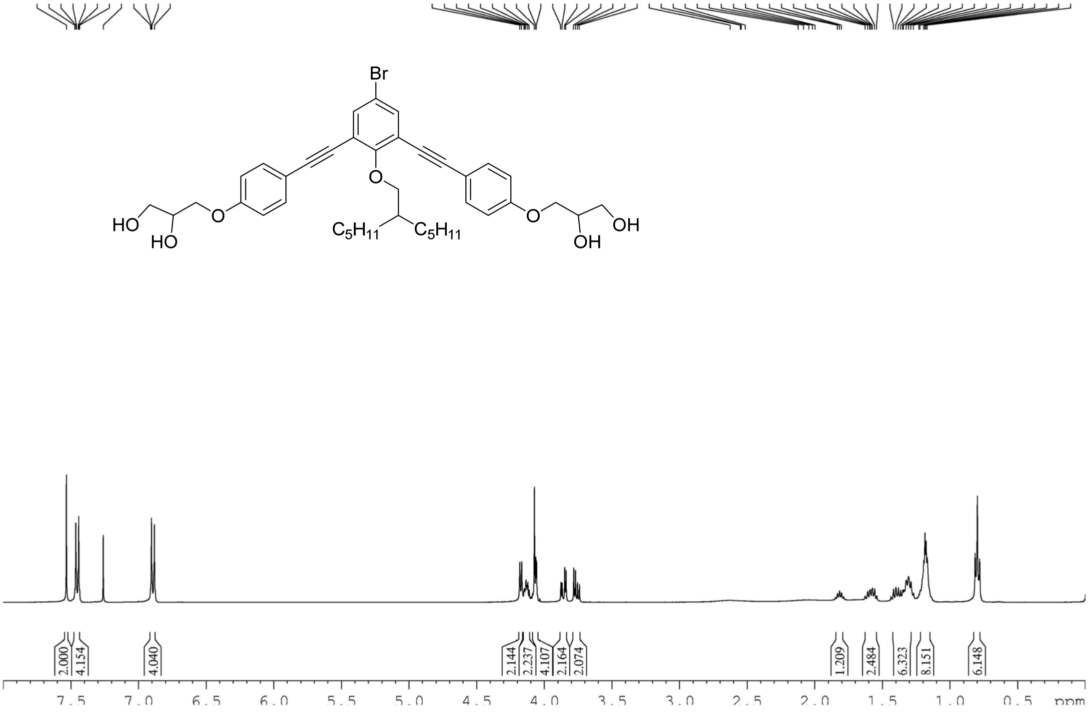


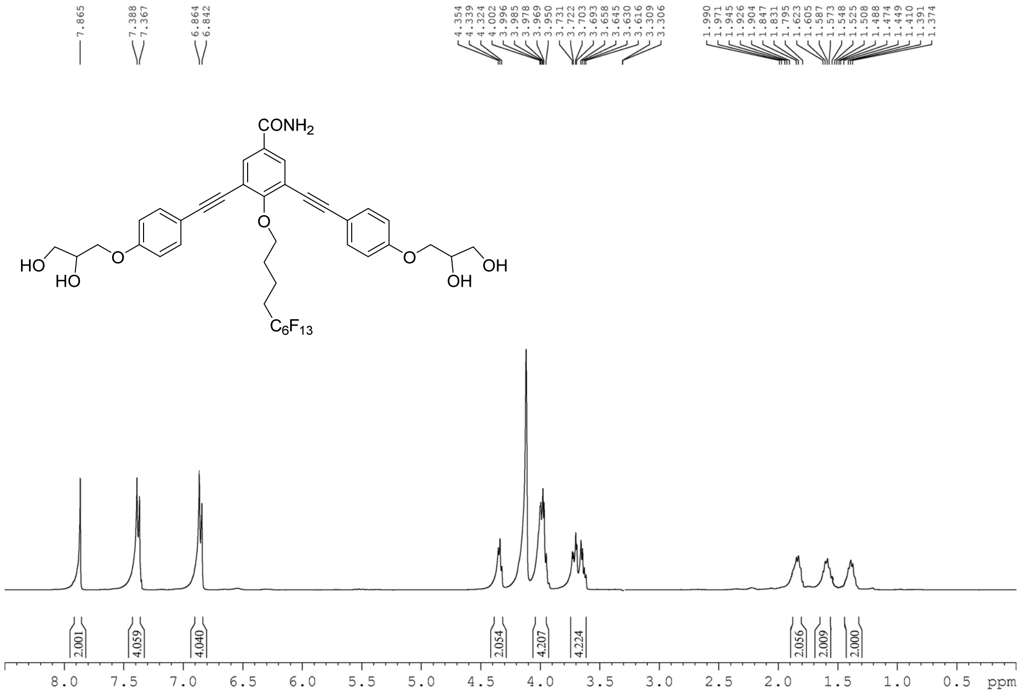
7.662
7.466
7.461
7.449
7.444
7.260
6.916
6.912
6.894
4.365
4.352
4.151
4.140
4.126
4.116
4.078
4.067
4.062
3.880
3.870
3.851
3.842
3.784
3.771
3.756
3.742
1.851
1.836
1.821
1.806
1.791
1.619
1.600
1.584
1.564
1.547
1.531
1.451
1.432
1.415
1.396
1.387
1.379
1.364
1.339
1.319
1.302
1.285
1.266
1.253
1.247
1.236
1.228
1.200
1.192
1.184
1.175
1.161
CN
O
HO
HO
O
O
OH
OH
C5H11
C5H11
2.000
4.367
4.359
2.168
2.118
4.424
2.088
2.183
1.635
2.696
2.517
4.462
8.697
6.507
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



7.700
7.488
7.467
7.282
6.945
6.923
4.463
4.448
4.433
4.164
4.148
4.130
4.111
4.096
4.084
3.901
3.892
3.872
3.863
3.803
3.790
3.775
3.761
2.200
2.111
2.067
1.998
1.978
1.956
1.929
1.913
1.896
1.876
1.671
1.652
1.633
1.568
1.547
1.529
1.471
1.451
1.434
1.415
1.295
1.278
1.260
CN
O
HO
HO
O
O
OH
OH
C4F9
2.000
4.156
4.134
2.125
3.843
4.232
2.152
2.151
4.146
4.339
2.211
2.226
2.245
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


8.277
7.480
7.459
7.260
6.929
6.908
4.505
4.136
4.084
4.074
3.877
3.850
3.780
3.768
3.752
2.609
2.601
2.139
2.093
2.020
1.972
1.597
1.252
NO2
O
HO
HO
O
O
OH
OH
C6F13
2.000
4.061
4.056
2.016
2.086
4.047
2.144
2.117
2.031
2.066
1.963
4.070
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


7.532
7.470
7.463
7.458
7.446
7.441
7.434
7.260
6.910
6.904
6.899
6.882
4.182
4.168
4.150
4.146
4.136
4.122
4.112
4.074
4.064
4.058
3.878
3.869
3.849
3.840
3.783
3.769
3.754
3.741
2.624
2.550
2.542
2.513
2.123
2.081
2.044
2.017
1.998
1.833
1.818
1.802
1.628
1.609
1.594
1.590
1.578
1.574
1.557
1.542
1.418
1.402
1.383
1.366
1.351
1.343
1.323
1.307
1.289
1.270
1.230
1.221
1.195
1.186
1.178
1.169
Br
O
HO
HO
O
O
OH
OH
C5H11
C5H11
2.000
4.154
4.040
2.144
2.237
4.107
2.164
2.074
1.209
2.484
6.323
8.151
6.148
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



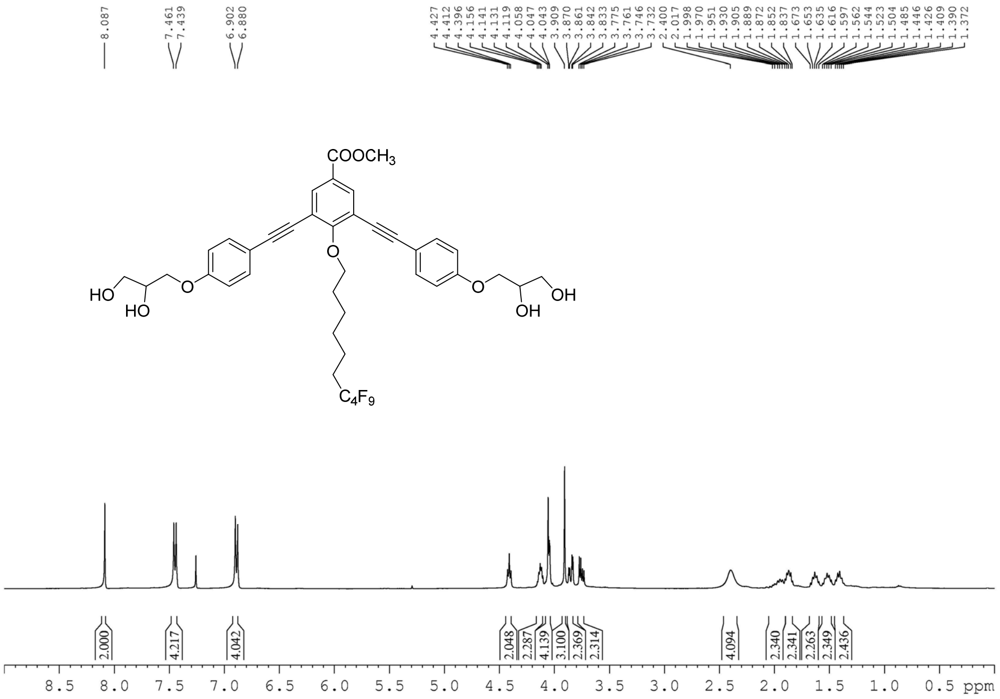
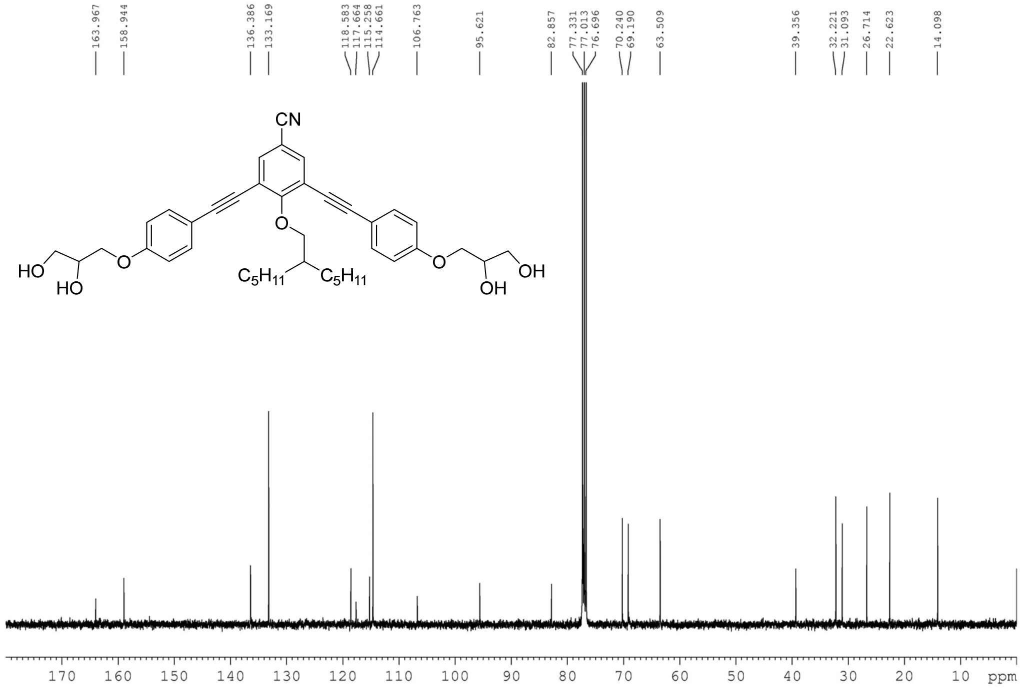
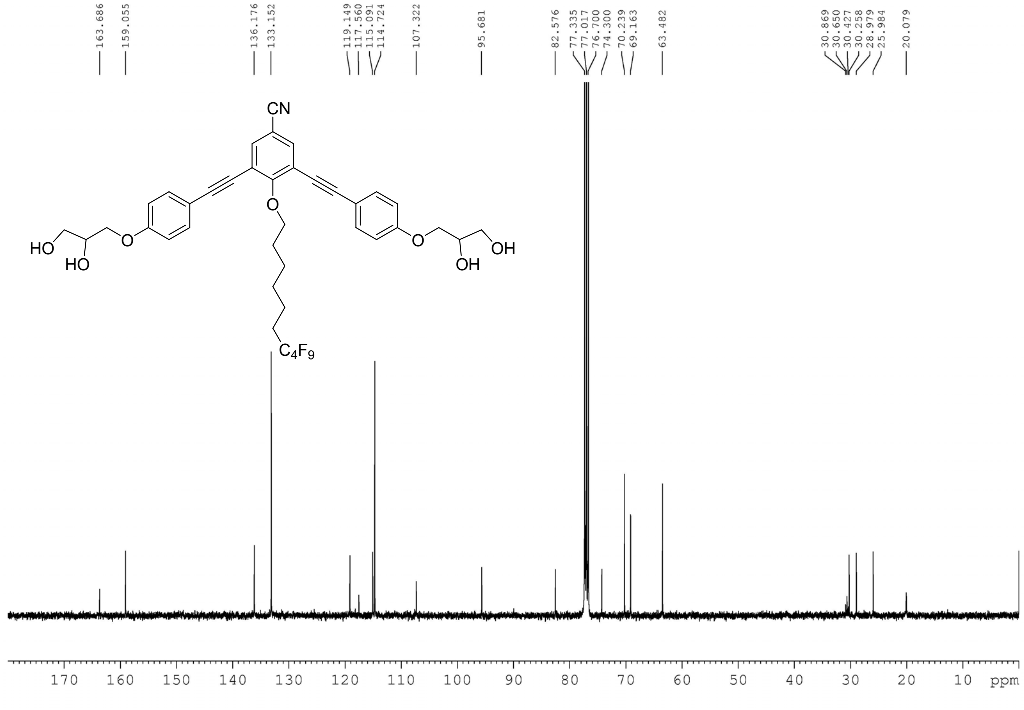
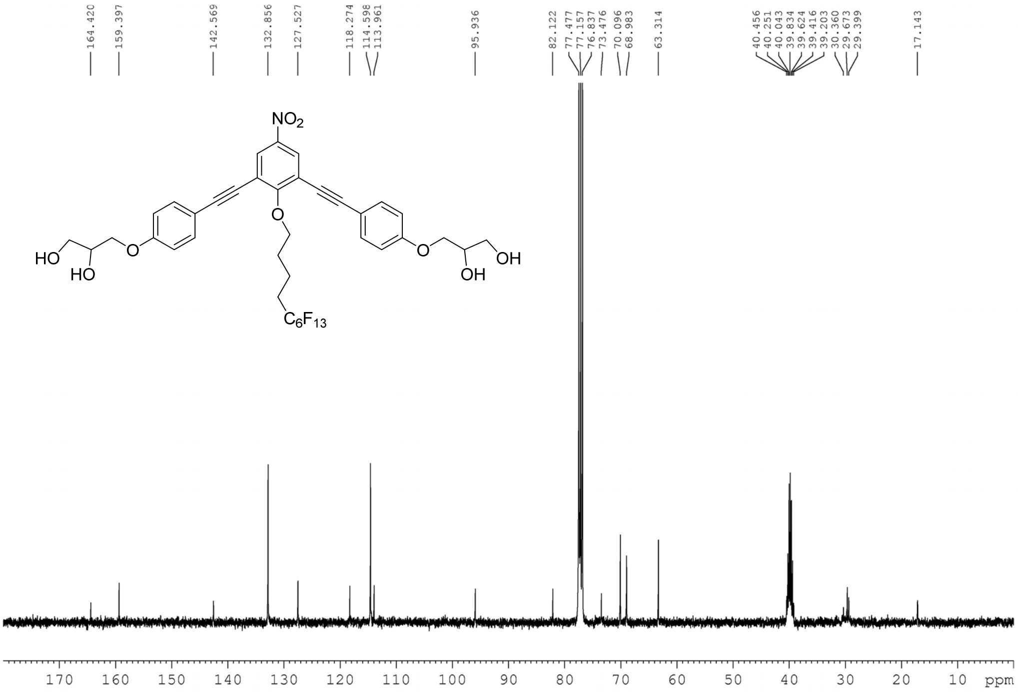
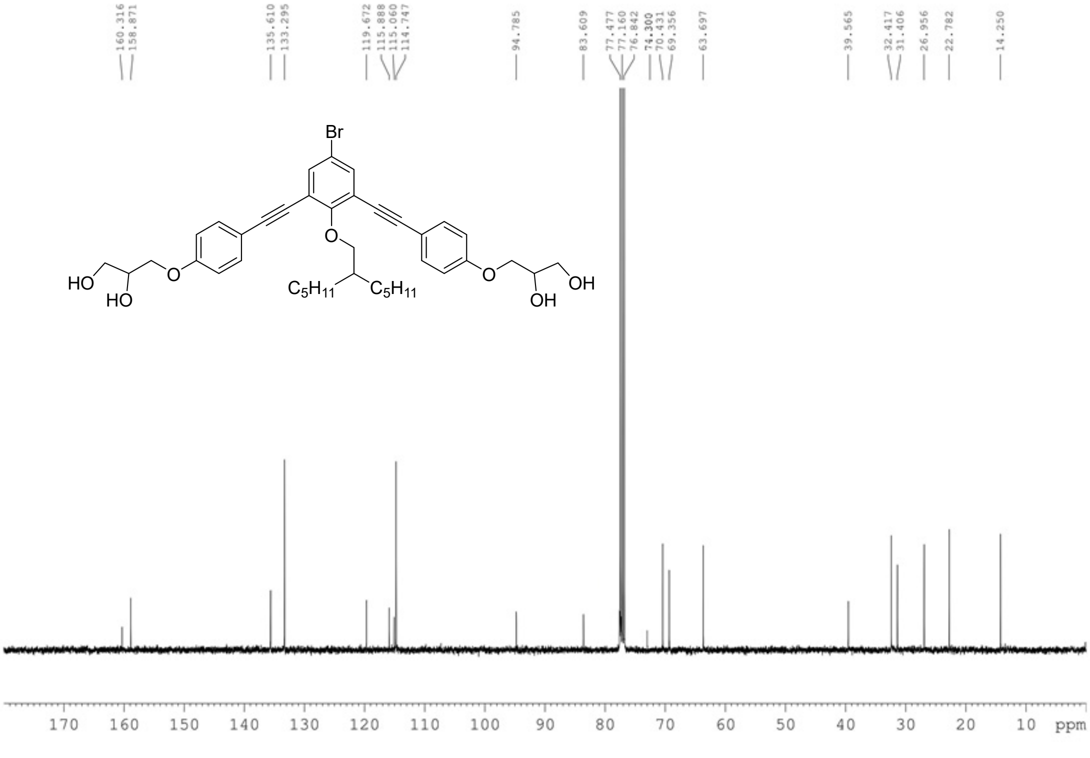


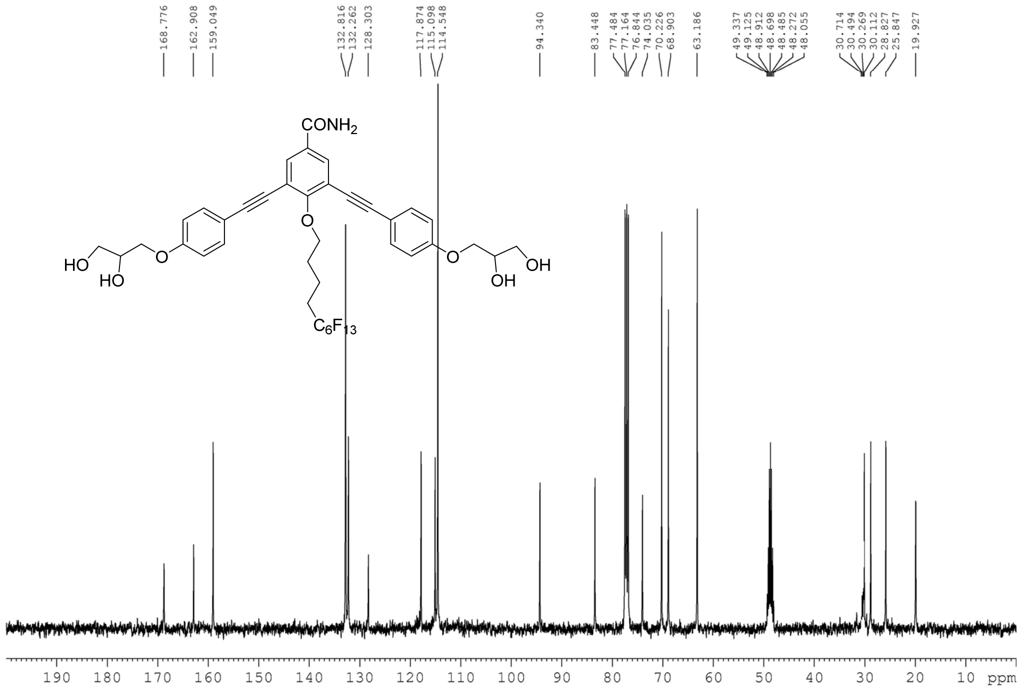
Figure S12 ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) spectra of compounds **Br-H**, **CN-H**, **CN-F**, **NO_2-F**, **$CONH_2$-F**, **$COOCH_3$-F.**


163.967
158.944
136.386
133.169
118.583
117.664
115.258
114.661
106.763
95.621
82.857
77.331
77.013
76.696
70.240
69.190
63.509
39.356
32.221
31.093
26.714
22.623
14.098
CN
HO
HO
O
O
C_5H_{11}
C_5H_{11}
O
OH
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


163.686
159.055
136.176
133.152
119.149
117.560
115.091
114.724
107.322
95.681
82.576
77.335
77.017
76.700
74.300
70.239
69.163
63.482
30.869
30.650
30.427
30.258
28.979
25.984
20.079
CN
HO
HO
O
O
C_4F_9
O
OH
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


164.420
159.397
142.569
132.856
127.527
118.274
114.598
113.961
95.936
82.122
77.477
77.157
76.837
73.476
70.096
68.983
63.314
40.456
40.251
40.043
39.834
39.624
39.416
39.203
30.360
29.673
29.399
17.143
NO2
O
HO
HO
O
O
OH
OH
C6F13
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


160.316
158.871
135.610
133.295
119.672
115.888
115.060
114.747
94.785
83.609
77.477
77.160
76.842
74.300
70.431
69.356
63.697
39.565
32.417
31.406
26.956
22.782
14.250
Br
O
HO
HO
O
O
OH
OH
C5H11
C5H11
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


168.776
162.908
159.049
132.816
132.262
128.303
117.874
115.098
114.548
94.340
83.448
77.484
77.164
76.844
74.035
70.226
68.903
63.186
49.337
49.125
48.912
48.698
48.485
48.272
48.055
30.714
30.494
30.269
30.112
28.827
25.847
19.927
CONH2
O
HO
HO
O
O
OH
OH
C6F13
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

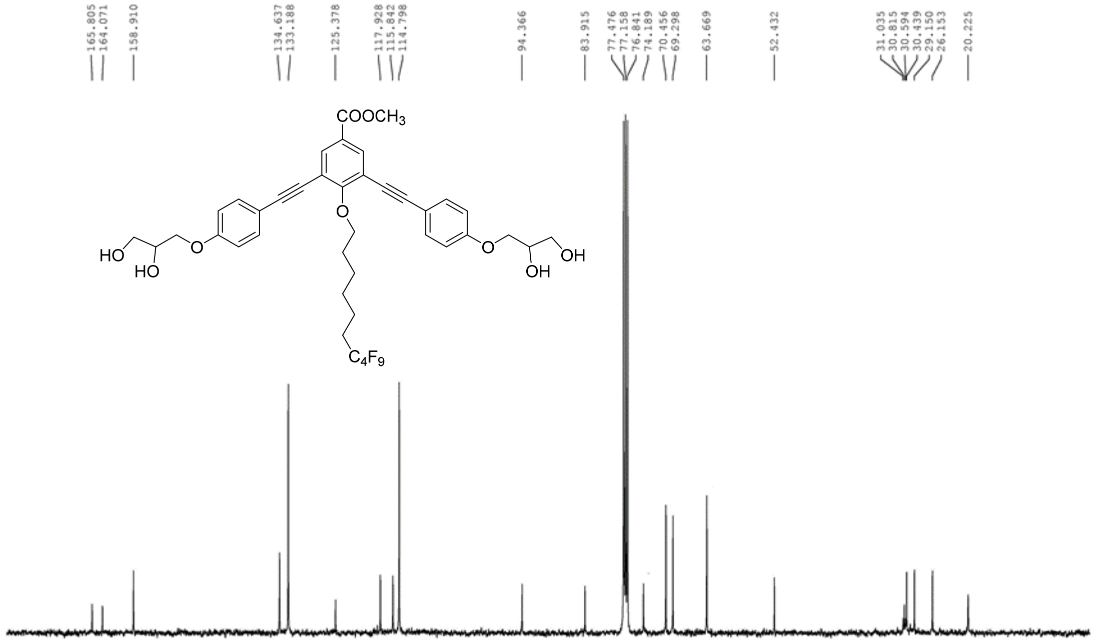
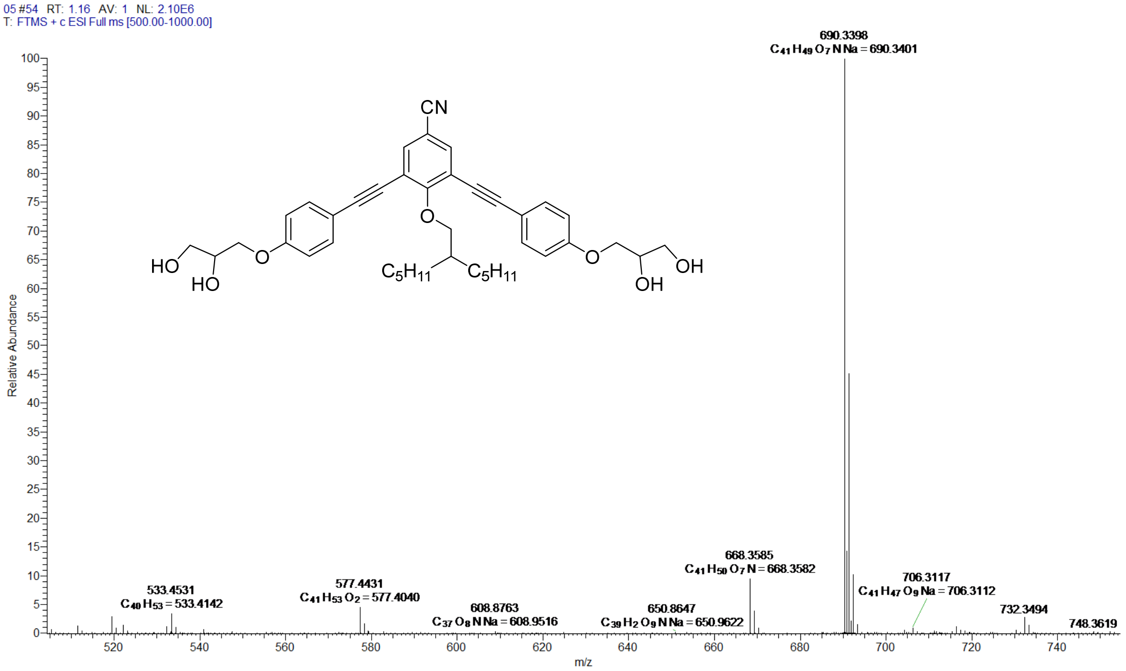
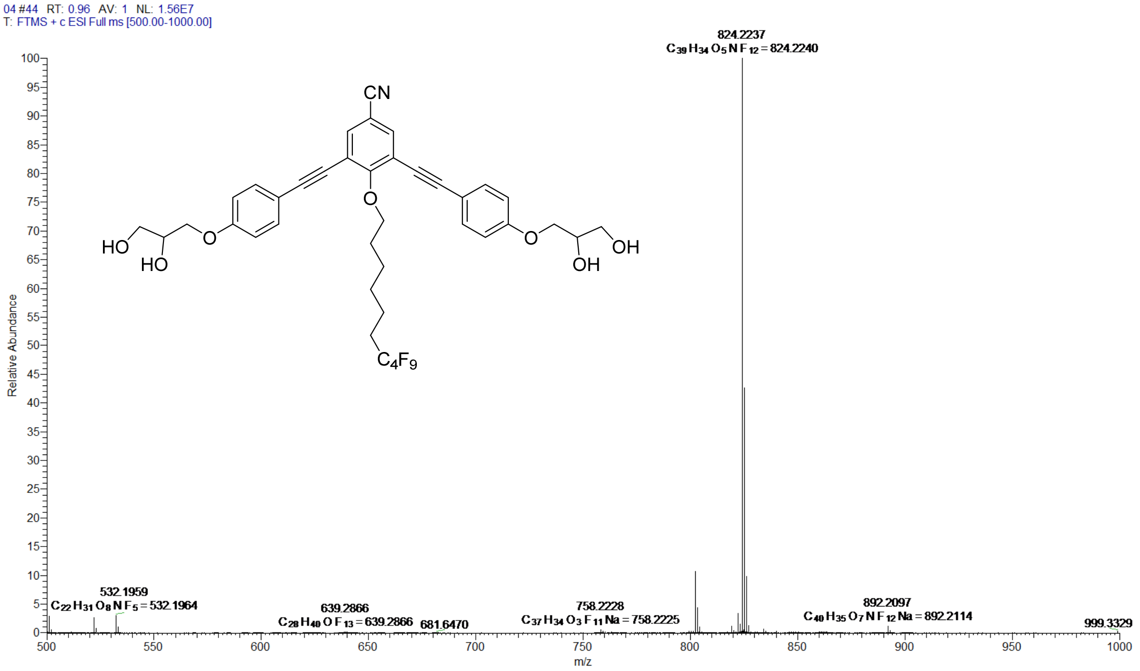
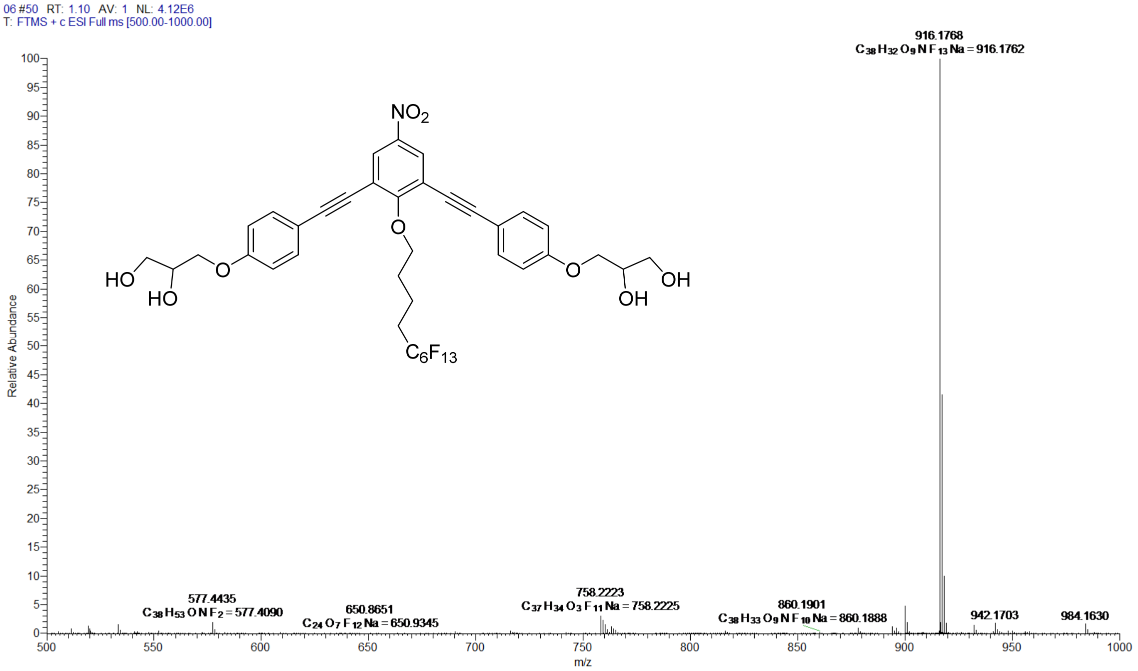

165.805
164.071
158.910
134.637
133.188
125.378
117.928
115.842
114.798
94.366
83.915
77.476
77.158
76.841
74.189
70.456
69.298
63.669
52.432
31.035
30.815
30.594
30.439
29.150
26.153
20.225
COOCH3
O
HO
HO
O
O
OH
OH
C4F9
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

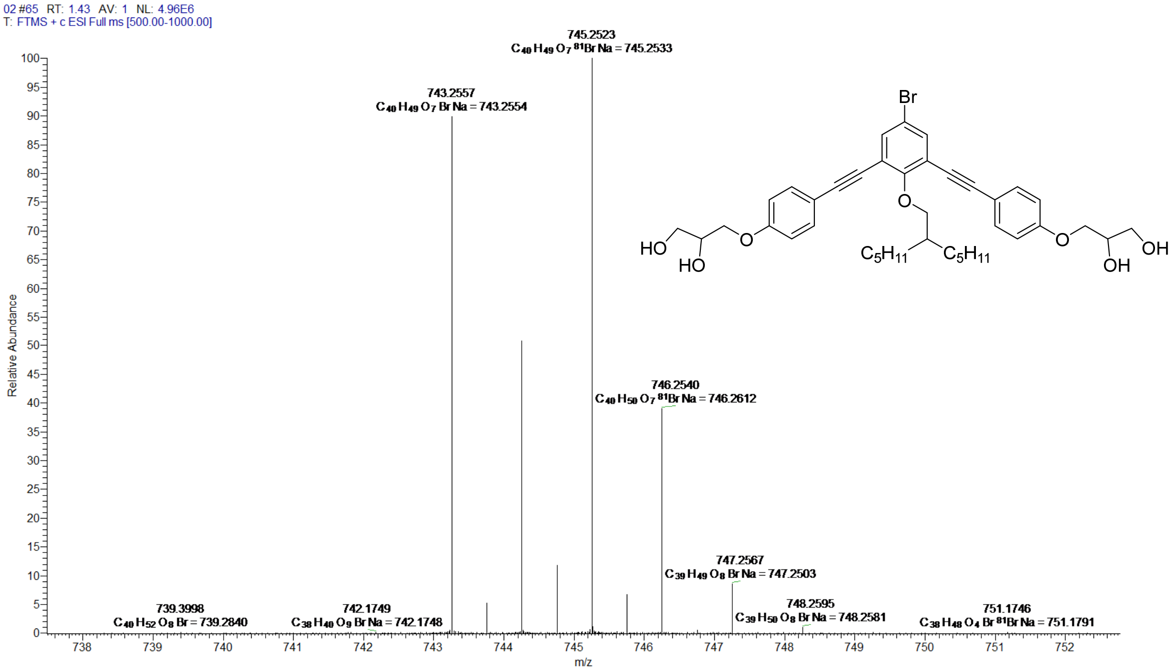
Figure S13 ^{13}C NMR ($CDCl_3$, 400 MHz, ppm) spectra of compounds **Br-H, CN-H, CN-F, NO_2-F, $CONH_2$-F, $COOCH_3$-F.**

HRMS (ESI) for representive final compounds 9






06 #50 RT: 1.10 AV: 1 NL: 4.12E6
T: FTMS + c ESI Full ms [500.00-1000.00]
916.1768
$C_{38}H_{32}O_9NF_{13}Na$ = 916.1762
577.4435
$C_{38}H_{53}ONF_2$ = 577.4090
650.8651
$C_{24}O_7F_{12}Na$ = 650.9345
758.2223
$C_{37}H_{34}O_3F_{11}Na$ = 758.2225
860.1901
$C_{38}H_{33}O_9NF_{10}Na$ = 860.1888
942.1703
984.1630
Relative Abundance
m/z
NO_2
HO
HO
O
O
O
OH
OH
C_6F_{13}


02 #65 RT: 1.43 AV: 1 NL: 4.96E6
T: FTMS + c ESI Full ms [500.00-1000.00]
745.2523
$C_{40}H_{49}O_7{}^{81}BrNa$ = 745.2533
743.2557
$C_{40}H_{49}O_7BrNa$ = 743.2554
746.2540
$C_{40}H_{50}O_7{}^{81}BrNa$ = 746.2612
747.2567
$C_{39}H_{49}O_8BrNa$ = 747.2503
748.2595
$C_{39}H_{50}O_8BrNa$ = 748.2581
739.3998
$C_{40}H_{52}O_8Br$ = 739.2840
742.1749
$C_{38}H_{40}O_9BrNa$ = 742.1748
751.1746
$C_{38}H_{48}O_4Br^{81}BrNa$ = 751.1791
Relative Abundance
m/z
Br
HO
HO
O
O
O
OH
OH
C_5H_{11}
C_5H_{11}

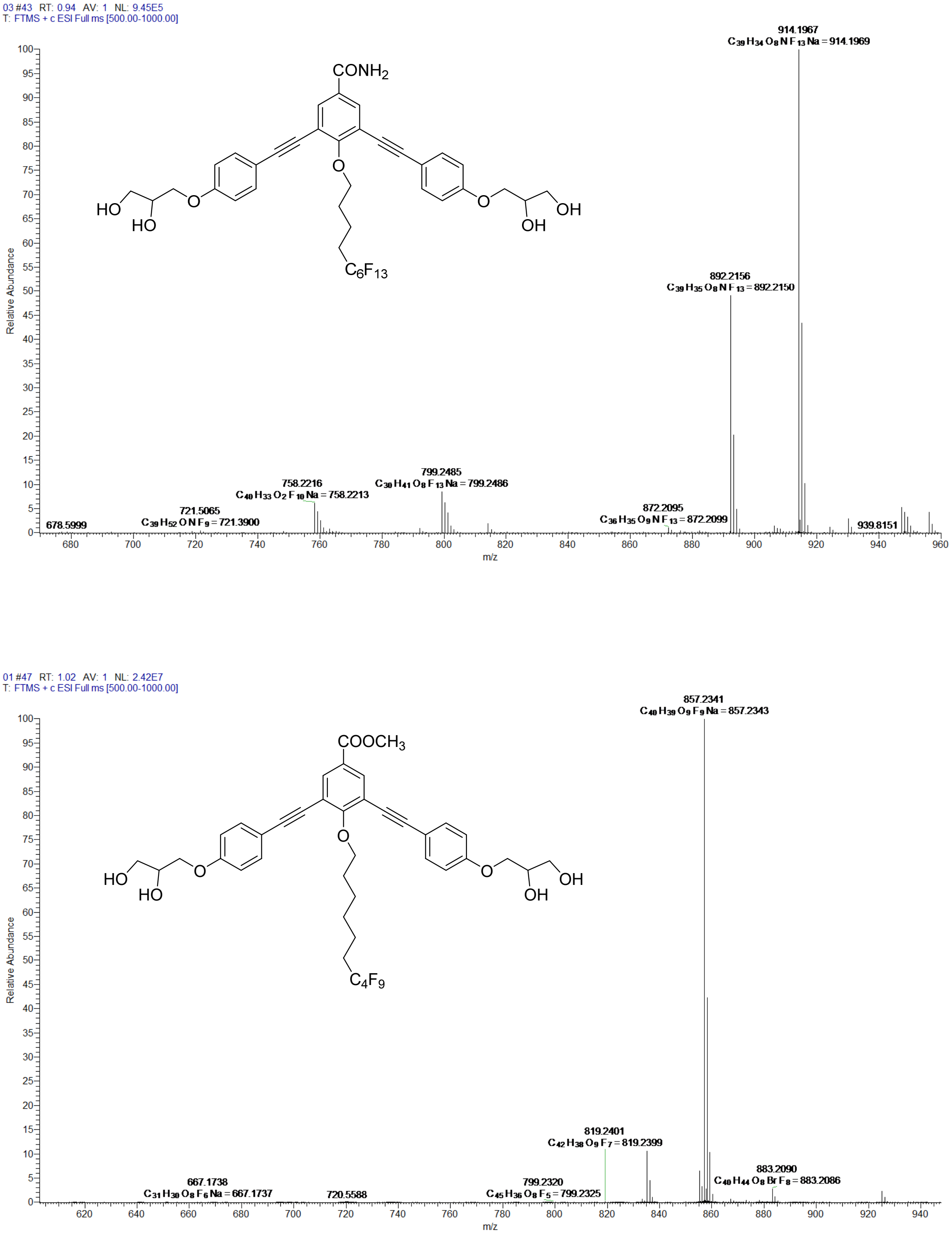


Figure S14 HRMS (ESI) results for the final compounds.

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