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Supporting Information

Crosslinkable Bis(diphenylamine)-Substituted Mixed Dihydroindeno[1,2-*b*]fluorenes for Solution-Processed Multilayer Organic Light-Emitting Diodes

Matthias Hempe, Johanna Paschek, Jürgen Schelter, Anne Umbach, Klaus Meerholz,* and Michael Reggelin*

1. Experimental details

Solvents and reagents: Tetrahydrofuran (THF) and toluene (PhMe) were distilled from sodium-benzophenone under argon atmosphere. Dichoromethane (DCM) was distilled from CaH under argon atmosphere. *N*-(4-Bromophenyl)-aniline **4a** was synthesized based on a literature procedure by Budén et al..[1] 4,4'-Dibromodiphenylamine **4b** was synthesized according to Ishow et al..[2] The starting material 6,6'-Bis(4-*tert*.-butylphenyl)-6,12-dihydroindeno[1,2-*b*]fluorene **6** was synthesized based on previous works.[3] Reagents were obtained from commercial sources and were used without further purification. Moisture and/or air sensitive experiments were conducted using flame-dried glassware under argon atmosphere.

NMR-Spectra: ^{1}H-NMR spectra were recorded on Bruker ARX 300 and DRX 500 spectrometers operating at 300 and 500 MHz, respectively at 300 K. ^{13}C-NMR spectra were recorded on the same instruments at 75 and 125 MHz. Chemical shifts (δ) in ^{1}H-NMR and ^{13}C-NMR spectra are reported in ppm and were referenced against the residual solvent signal as reported in the literature.[4] The fine structure of proton signals was specified as s (singulet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad).

Flash-chromatography was carried out on silica gel 60 (15-40 µm) by Merck at a pressure of 2-3 bar.

Mass spectra: EI-MS and HR-EI-MS were recorded on a double focusing mass spectrometer MAT 95. ESI-MS spectra were obtained using an Esquire LC spectrometer by Bruker-Franzen.

Elemental analysis were performed by the service of Technische Universität Darmstadt on a Vario El by Elementar.

Differential scanning calorimetry (DSC) was performed on a DSC1 by Mettler-Toledo.

Single-Crystal X-Ray analysis was performed by the service of Technische Universität Darmstadt on a four-circle-diffractometer Oxford XCALIBUR with a Sapphire CCD detector.

Cyclic voltammetry was performed using a potentiostat VMP2 (Princeton Applied Research). The measurements were performed under N_2 atmosphere in a 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) solution in DCM (abs.) using a glassy carbon working electrode, a platinum wire as counter electrode and a silver wire as quasi reference electrode. The potential scan rate was 20 mV/s. All compounds were measured in solution and ferrocene was added as internal standard.

Optical spectroscopy was recorded on a Specord S600 (UV/vis) by Analytik Jena AK and J&M TIDAS LSM / J&M TIDAS CCD UV/NIR (photoluminescence) using 10^{-6} M solutions of the compounds in THF (abs.).

OLED Fabrication

Film Deposition: The cleaned ITO coated substrates were ozone treated for 10 min in a custom-made ozonization chamber. Under clean-room conditions, the substrates were coated with a layer of PEDOT:PSS (Heraeus, Clevios P VP Al 4083), which was filtered prior to use with a 0.45 µm syringe PVDF-filter. After deposition, the films were heat-treated for 15 min at 150°C. The resulting layer thickness was ca. 30 nm.

Crosslinking of oxetane-functionalized organic materials was carried out in a nitrogen filled glove box equipped with active water, solvent, and oxygen removal system directly after spincoating of the organic material doped with varying concentration of the photoacid generator (PAG) 4-(octyloxy)phenyl)(phenyl)iodonium hexafluoroantimonate (OPPI). OPPI was added to the solution prior to spincoating. Subsequently to coating, the substrates were illuminated for 10 s with UV light (with a 6 W Phillips laboratory lamp) at 365 nm and cured on a hot plate for varying temperatures and duration (see Table S1). After cooling down to room temperature the crosslinked samples were rinsed three times with 100 µL toluene. Finally, the samples were post-cured at the chosen crosslinking temperature for 2 min. The film thickness was verified using a tactile DEKTAK® profilometer with a tip radius of 12.5 µm. All films (HTL and EML) were solution-processed under laminar flow in a dry nitrogen atmosphere using a Süss Microtec spin coater. Toluene (Merck, SeccoSolv, max. 0.005% H_2O) was used to dilute the organic materials.

Table S1. Spin-coating and crosslinking conditions.

Compound	Conc. [mg/mL]	OPPI [mol%]	RPM	Crosslinking time [min]	Crosslinking temp. [°C]	Thickness [nm]
OTPD	4	0.5	2000	2	110	10
OTPD	8	0.5	2000	2	110	30
QUPD	6	1	2000	2	110	20
QUPD	8	1	2000	2	110	30
0L-2G6	10	4	3000	5	150	30
4L6-2G6	4	2	2000	5	150	10
4L6-2G6	10	2	3000	5	150	30
F8BT	13	-	800	-	-	80

Electrode Evaporation: The devices were completed by cathode evaporation (3.5 nm CsF, 100 nm Al) through a shadow mask using a Leybold® Univex 450 high vacuum evaporation chamber at a base pressure of 10^{-6} mbar. For CsF evaporation rates between 0.2 and 0.5 $Å s^{-1}$ were typically used. For Al deposition the rate was regulated to 0.3 $Å s^{-1}$ until a layer thickness of 10 nm was reached, maintained below 1 $Å s^{-1}$ up to 30 nm, and afterwards gradually increased to 1 − 2 $Å s^{-1}$ until the desired layer thickness was achieved.

LIV Measurements: Current voltage characteristics were measured using a Keithley Model 2004 source meter. Luminance values were measured simultaneously with a calibrated photodiode. The applied bias voltage was varied in 0.2 to 0.25 V steps going from −2 to 9 V when characterizing OLEDs. The photodiode was calibrated with a luminance meter (Chroma Meter CS-100, Minolta).

Reference Materials

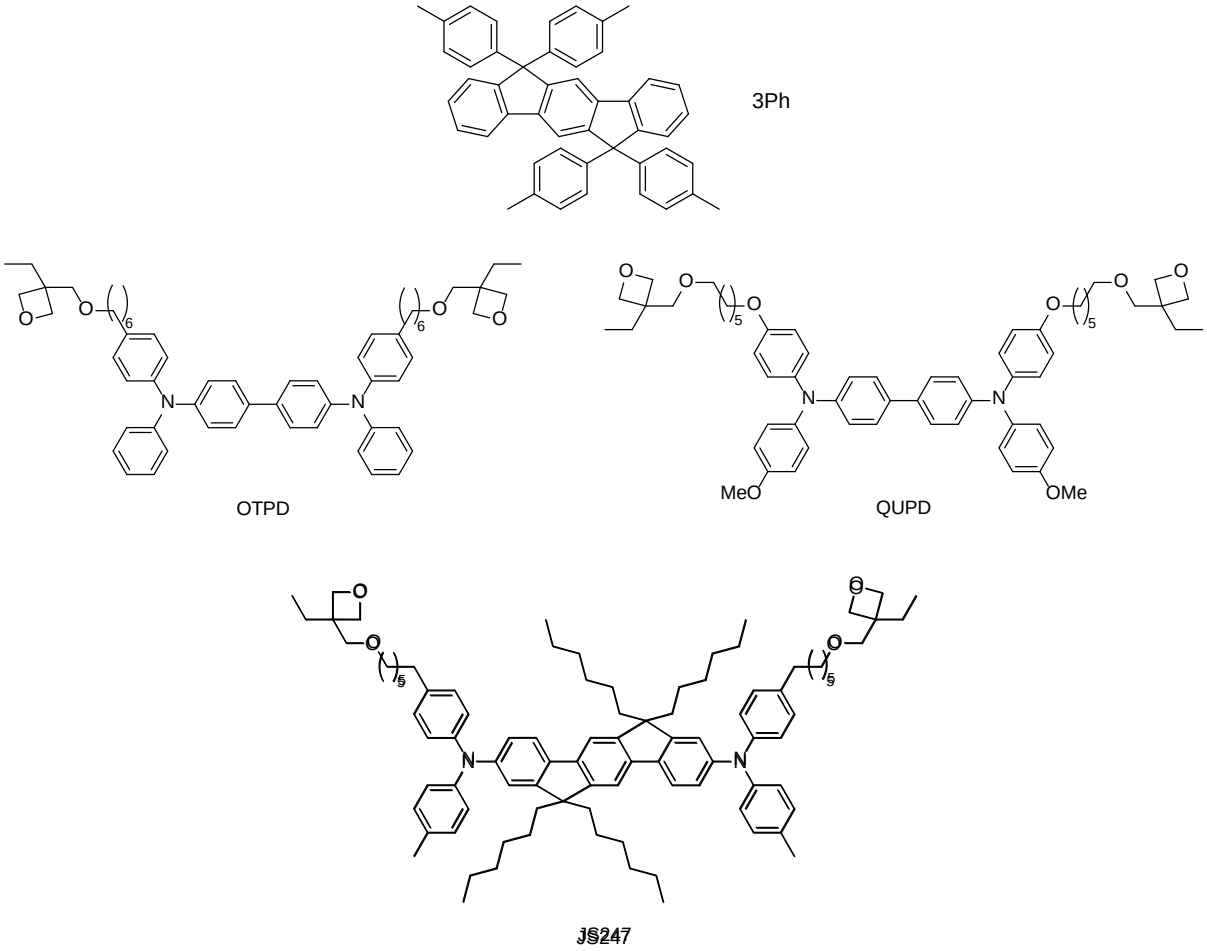
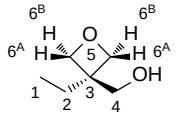


Figure S1. Molecular structures of the reference materials 3Ph,[5] OTPD and QUPD,[6] and JS247.

1.1. (3-Ethyloxetan-3-yl)methanol 1



According to a literature procedure[7], a mixture of 150.00 g (1.10 mol) 1,1,1-tris(hydroxyl-methyl)propane, 134.7 mL (1.00 eq., 1.10 mol) diethyl carbonate, 547.5 mg (0.01 eq., 9.76 mmol) potassium hydroxide and 12 mL of ethanol was refluxed at 110°C. After 1 h, the mixture was cooled and the reflux condenser was replaced by a distillation apparatus. The product was obtained by vacuum distillation (195°C, 23 mbar) as colorless liquid. Yield = 113 g (972.8 mmol, 89%). The analytical data are consistent with those reported in the literature.

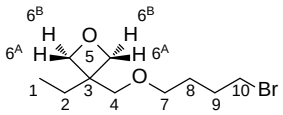
^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.876 (t, 1-H, 3 H), 1.702 (q, 2-H, 2 H), 2.655 (br., OH), 3.713 (s, 4-H, 2 H), 4.382 (m, 6_A-H or 6_B-H, 2 H), 4.438 (m, 6_A-H or 6_B-H, 2 H).

1.2. ω-Bromoalkyl-oxetanes 2

General procedure

Based on a literature procedure[8], a three-neck round bottom flask was charged with (3-ethyloxetan-3-yl)methanol, 3.1 eq. α,ω-dibromo-*n*-alkane and 0.02 eq. tetrabutylammonium bromide and *n*-hexane (100 mL/g (3-ethyloxetan-3-yl)methanol) **1**. Under vigorous stirring, a solution of potassium hydroxide in water (16 M, 18 eq.) was carefully added, using a dropping funnel. The resulting mixture was stirred over night at room temperature and was heated to reflux, afterwards. After 3 h, the mixture was allowed to cool to room temperature and water was added (100 mL/g (3-ethyloxetan-3-yl)methanol). The phases were separated and the aqueous phase was extracted with hexane (3x 100 mL/g). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. The resulting colorless liquid was purified by vacuum distillation to give rise to the desired product.

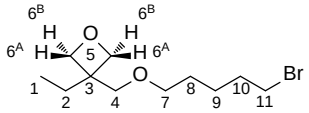
1.3. 3-(((4-Bromobutyl)oxy)methyl)-3-ethyloxetane 2a



According to the general procedure, 20.00 g (172.18 mmol) (3-ethyloxetan-3-yl)methanol **1** and 64.5 mL (3.1 eq., 533.75 mmol) 1,4-dibromo butane were used to obtain 31.3 g (124.45 mmol, 72%) **2a** as a colorless liquid. The analytical data are consistent with those reported in the literature.[8-9]

^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ (ppm) = 0.888 (t, 1-H, 3 H), 1.668-1.790 (m, 2-H, 8-H or 9-H, 4 H), 1.906-2.012 (m, 8-H or 9-H, 2 H), 3.446 (t, 7-H, 2 H), 3.498 (t, 10-H, 2 H), 3.528 (s, 4-H, 2 H), 4.376 (m, 6_A-H or 6_B-H, 2 H), 4.445 (m, 6_A-H or 6_B-H, 2 H).

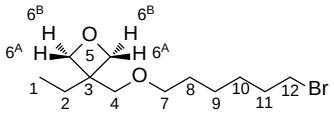
1.4. 3-(((5-Bromopentyl)oxy)methyl)-3-ethyloxetane 2b



According to the general procedure, 18.60 g (160.13 mmol) (3-ethyloxetan-3-yl)methanol **1** and 69.7 mL (3.1 eq., 496.39 mmol) 1,5-dibromo pentane were used to obtain 26.5 g (99.93 mmol, 62%) **2b** as a colorless liquid. The analytical data are consistent with those reported in the literature.[8-9]

^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ (ppm) = 0.876 (t, 1-H, 3 H), 1.505-1.604 (m, 8-H, 9-H, 4 H), 1.732 (q, 2-H, 2 H), 1.879 (m, 10-H, 2 H), 3.404 (t, 7-H, 2 H), 3.458 (t, 11-H, 2 H), 3.517 (s, 4-H, 2 H), 4.366 (m, 6_A-H or 6_B-H, 2 H), 4.436 (m, 6_A-H or 6_B-H, 2 H).

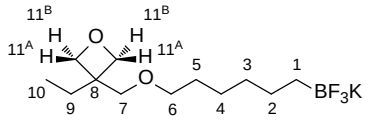
1.5. 3-(((6-Bromohexyl)oxy)methyl)-3-ethyloxetane 2c



According to the general procedure, 60.00 g (516.54 mmol) (3-ethyloxetan-3-yl)methanol **1** and 252.3 mL (3.1 eq., 1.60 mol) 1,6-dibromo hexane were used to obtain 125.6 g (449.9 mmol, 87%) **2c** as a colorless liquid. The analytical data are consistent with those reported in the literature.[8-9]

^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ (ppm) = 0.880 (t, 1-H, 3 H), 1.314-1.675 (m, 8-H, 9-H, 10-H, 6 H), 1.738 (q, 2-H, 2 H), 1.863 (m, 11-H, 2 H), 3.406 (t, 7-H, 2 H), 3.454 (t, 12-H, 2 H), 3.521 (s, 4-H, 2 H), 4.375 (m, 6_A-H or 6_B-H, 2 H), 4.442 (m, 6_A-H or 6_B-H, 2 H).

1.6. Potassium (6-((3-ethyloxetan-3-yl)methoxy)hexyltrifluoroborate 3



In a flame-dried flask equipped with a dropping funnel, 26.9 g of the bromoalkane **2c** (96.34 mmol) were dissolved in 150 mL of THF (abs.) under argon atmosphere and cooled to -78°C. At this temperature, a solution of 100 mL of *tert.*-butyllithium in heptane (2 M, 2.08 eq., 200 mmol) was added dropwise over the period of 1 h. The mixture was stirred for 3 h at -78°C and was then allowed to come to room temperature for another 30 min, after which it was cooled to -78°C again. The solution of metallated species was added dropwise to a solution of 24.49 mL (1.10 eq., 150.98 mmol) $B(O\textit{i}Pr)_3$ in 50 mL of THF (abs.) at -78°C and was allowed to warm to room temperature over night. The resulting suspension was cooled to 0°C and 24.83 g (3.30 eq., 317.93 mmol) of KHF_2 in 80 mL of H_2O was added. After 1 h of intensive stirring at room temperature, the mixture was cooled to 0°C again and 44.3 g (3.33 eq., 320.54 mmol) of K_2CO_3 was added. The organic phase was separated, and the solvent was evaporated *in vacuo*. The residue was thoroughly dried, suspended in hot acetone (3 x 100 mL) and filtered through

a pad of celite. The resulting solution was concentrated *in vacuo* and resuspended in hot *n*-hexane. The white solid was filtered and dried *in vacuo* to obtain 14.64 g of the compound **3** (50%).

^{1}H-NMR (DMSO-d_6, 500 MHz, 300 K) δ (ppm) = -0.060 (m, 1-H, 2 H), 0.832 (t, 10-H, 3 H), 1.067-1.359 (m, 2-H, 3-H, 4-H, 5-H, 8 H), 1.646 (q, 9-H, 2 H), 3.392 (t, 6-H, 2 H), 3.456 (s, 7-H, 2 H), 4.212 (m, 11_A-H or 11_B-H, 2 H), 4.295 (m, 11_A-H or 11_B-H, 2 H).

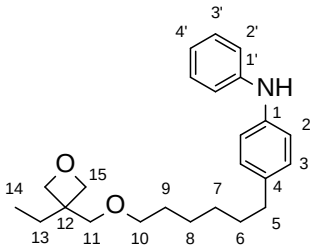
^{13}C-NMR (DMSO-d_6, 125 MHz, 300 K) δ (ppm) = 8.00 (10-C), 20.15 (br., 1-C), 25.60 (2-C), 25.93 (9-C), 26.36 (3-C or 4-C), 29.24 (5-C), 32.90 (3-C or 4-C), 42.76 (8-C), 70.88 (6-C), 72.72 (7-C), 77.14 (11-C).

^{19}F-NMR (DMSO-d_6, 470 MHz, 300 K) δ (ppm) = -136.9 (Alkyl-BF_3K).

^{11}B-NMR (DMSO-d_6, 160 MHz, 300 K) δ (ppm) = 4.89 (Alkyl-BF_3K).

ESI-MS (m/z): calc.: 306 ($C_{12}H_{23}BF_3O_2K$), found: 573 (2x[M-K^+]$^-$), 267 ([M-K^+]$^-$).

1.7. 4-(6-((3-Ethyloxetane-3-yl)methoxy)hexyl)-*N*-phenylaniline 5a



Based on a literature procedure,[10] a mixture of 1.30 g (5.24 mmol) 4-bromo-*N*-phenylaniline, 2.086 g (1.30 eq., 6.81 mmol) compound **3**, 72 mg (0.06 eq., 0.31 mmol) $Pd(OAc)_2$, 308.8 mg (0.12 eq., 0.63 mmol) RuPhos and 2.172 g (3.00 eq., 15.7 mmol) K_2CO_3 were dissolved in a mixture of 30 mL toluene and 3 mL of water. The resulting mixture was heated to 80°C for 20 h and was then allowed to cool to room temperature. The reaction mixture was filtered through a plug of silica, concentrated *in vacuo* and purified by flash chromatography (toluene/ethyl acetate, 4:1) afterwards. The product was isolated as brownish oil, which solidifies after a while. Yield = 1.096 g (2.98 mmol, 57%).

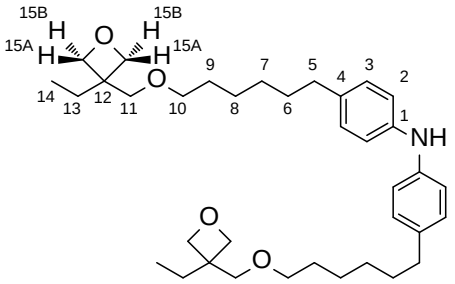
^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K δ) (ppm) = 1.128 (t, 14-H, 3 H), 1.618 (m, 7-H, 8-H, 4 H), 1.837 (m, 6-H, 9-H, 4 H), 1.983 (q, 13-H, 2 H), 2.800 (t, 5-H, 2 H), 3.691 (t, 10-H, 2 H), 3.762 (s, 11-H, 2 H), 4.621 (m, 15_A-H or 15_B-H, 2 H), 4.691 (m, 15_A-H or 15_B-H, 2 H), 5.892 (s(br.), N-H), 7.120 (t, 4'-H, 1 H), 7.253 (m, 2-H, 2'-H, 4 H), 7.322 (d, 3-H, 2 H), 7.478 (t, 3'-H, 2 H).

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 8.32 (14-C), 26.16 (7-C or 8-C), 26.94 (13-C), 29.23 (7-C or 8-C), 29.65 (6-C or 9-C), 31.72 (6-C or 9-C), 35.32 (5-C), 43.58 (12-C), 71.73 (10-C), 73.56 (11-C), 78.73 (15-C), 117.14 (2-C), 118.83 (2'-C), 120.45 (4'-C), 129.03 (3-C or 3'-C), 129.40 (3-C or 3'-C), 136.01 (4-C), 140.75 (1-C), 144.02 (1'-C).

EI-MS: m/z (%): 367 (55, [M]$^+$), 337 (5, [M-CH_2O]$^+$), 182 (100, [M-($C_{11}H_{21}O_2$)]$^+$).

HR-EI-MS ($C_{24}H_{33}NO_2$): calc.: 367.2511, found: 367.25234.

1.8. Bis(4-(6-((3-ethyloxetan-3-yl)methoxy)hexyl)phenyl)amine 5b



Based on a literature procedure,[10] a mixture of 115 mg (0.35 mmol) bis(4-bromophenyl)amine, 278 mg (2.56 eq., 0.91 mmol) compound **3**, 8.7 mg (0.11 eq., 0.04 mmol) $Pd(OAc)_2$, 38 mg (0.22 eq., 0.08 mmol) RuPhos and 291 mg (6.00 eq., 2.11 mmol) K_2CO_3 were dissolved in a mixture of 5 mL toluene and 0.5 mL of water. The resulting mixture was heated to 80°C for 72 h and was then allowed to cool to room temperature. The reaction mixture was filtered through a plug of silica, concentrated *in vacuo* and purified by flash chromatography (toluene/ethyl acetate, 4:1) afterwards. The product was isolated as red-brownish oil. Yield = 108 mg (0.19 mmol, 54%).

^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.908 (t, 14-H, 6 H), 1.343-1.458 (m, 7-H, 8-H, 8 H), 1.567- 1.673 (m, 6-H, 9-H, 8 H), 1.759 (q, 13-H, 4 H), 2.564 (t, 5-H, 4 H), 3.460 (t, 10-H, 4 H), 3.524 (s, 11-H, 4 H), 4.372-4.488 (m, 15_A-H, 15_B-H, 8 H), 5.950 (br., N-H), 6.970 (d, 2-H, 4 H), 7.057 (d, 3-H, 4 H).

$^3J_{2,3}$ = 8.3 Hz.

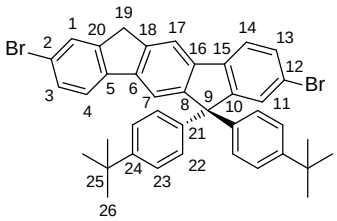
^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 8.00 (14-C), 25.86 (7-C or 8-C), 26.58 (13-C), 28.83 (7-C or 8-C), 29.29 (6-C or 9-C), 31.39 (6-C or 9-C), 34.93 (5-C), 43.18 (12-C), 71.32 (10-C), 73.22 (11-C), 78.17 (15-C), 117.40 (2-C), 128.81 (3-C), 134.43 (4-C), 141.29 (1-C).

EI-MS: m/z (%): 565 (100, $[M]^+$), 535 (45, $[M\text{-}CH_2O]^+$), 505 (15, $[M\text{-}2(CH_2O)]^+$), 380 (35, $[M\text{-}(C_{11}H_{21}O_2)]^+$).

HR-EI-MS ($C_{36}H_{55}NO_4$): calc.: 565.4126, found: 565.4122.

elemental analysis ($C_{36}H_{55}NO_4$) (%) calc.: C 76.42 H 9.80 N 2.48, found: C 76.51 H 9.817 N 2.209.

1.9. 4,10-Dibromo-6,6‘-di(4-*tert.*-butylphenyl)-6,12-dihydroindeno[1,2-*b*]fluorene 7



Based on a literature procedure,[11] a mixture of 10.00 g (19.28 mmol) of 6,6‘-di(4-*tert.*-butylphenyl)-6,12-dihydroindeno[1,2-*b*]fluorene[3] **6**, 64.3 g $CuBr_2/Al_2O_3$ ($CuBr_2 \cdot 2\ H_2O/Al_2O_3$, w/w, 1:2) and 175 mL CCl_4 was stirred at 77°C for 16 h. The mixture was cooled to room temperature and filtered through a plug of celite. The solvent was evaporated *in vacuo* and the residing pale solid was dispersed in 140 mL of acetonitrile. The suspension was heated to 82°C and mixed with 60 mL of toluene. After cooling to room

temperature, the precipitate was collected. The product was isolated as a white solid. Yield = 9.86 g (14.57 mmol, 76%).

Mp.: 326°C.

^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 1.294 (s, 26-H, 18 H), 3.846 (s, 19-H, 2 H), 7.176 (d, 22-H, 4 H), 7.275 (d, 23-H, 4 H), 7.349 (d, 13-H, 1 H), 7.389 (d, 14-H, 1 H), 7.488 (d, 3-H, 1 H), 7.563 (s, 11-H, 1 H), 7.594 (s, 1-H, 1 H), 7.625 (d, 4-H, 1 H), 7.682 (s, 7-H, 1 H), 7.817 (s, 17-H, 1 H).

$^3J_{3,4}$ = 8.1 Hz, $^4J_{11,13}$ = 1.6 Hz, $^3J_{13,14}$ = 8.1 Hz, $^3J_{22,23}$ = 8.5 Hz.

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm)= 31.49 (26-C), 34.54 (25-C), 36.67 (19-C), 64.79 (9-C), 116.81 (17-C), 117.90 (7-C), 120.54 (10-C), 121.28 (4-C or 14-C), 121.32 (4-C or C-14), 125.44 (23-C), 127.89 (22-C), 128.21 (1-C), 129.65 (11-C), 129.97 (13-C), 130.79 (3-C), 138.66 ($C_{quart.}$), 139.25 ($C_{quart.}$), 140.65 ($C_{quart.}$), 141.14 ($C_{quart.}$), 142.32 (21-C), 142.78 (18-C), 145.62 (12-C), 149.75 (24 C), 151.20 (8-C), 154.27 (2-C).

EI-MS: m/z (%): 676 [100, $[M]^+$), 661 [8, $[M\text{-}CH_3]^+$), 619 (7, $[M\text{-}C(CH_3)_3]^+$), 595 (27, $[M\text{-}Br]^+$), 516 (10, $[M\text{-}2Br]^+$), 429 (5, $[M\text{-}2Br\text{-}C(CH_3)_3\text{-}C_2H_6]^+$), 368 (7, $[M\text{-}2Br\text{-}C_{10}H_{13}\text{-}CH_3]^+$), 326 (10, $[M\text{-}2Br\text{-}C_{10}H_{13}\text{-}C(CH_3)_3]^+$), 251 (5, $[M\text{-}2Br\text{-}2(C_{10}H_{13})^+]$).

HR-EI-MS ($C_{40}H_{36}Br_2$) calc.: 674.1183, found: 674.12171.

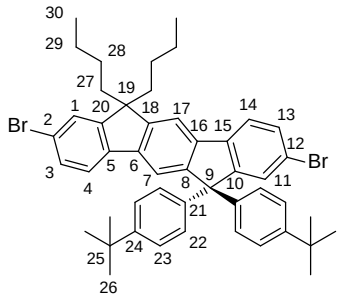
elemental analysis ($C_{40}H_{36}Br_2$) (%) calc.: C 71.01 H 5.36, found: C 69.85 H 5.24.

1.10. Synthesis of 4,10-Dibromo-12,12'-(dialkyl)-6,6'-di(4-*tert.*-butylphenyl) -6,12-dihydroindeno[1,2 *b*]fluorene 8

General procedure

In a flame-dried Schlenk flask, a 0.1 M solution of compound **7** in THF (abs.) was mixed with 18-crown-6 (2.2 eq.) under an argon atmosphere and cooled to 0°C. A 0.5 M solution of KO*t*Bu (3.0 eq.) in dry THF was added dropwise and the resulting mixture was stirred at room temperature for 2 h, after which it was cooled to 0°C again. After the addition of the haloalkane, the mixture was allowed to come to room temperature and stirred until the reaction was completed. The reaction mixture was filtered through a pad of silica and the solvent was evaporated *in vacuo.* The product was obtained by chromatography on silica using a mixture of toluene/ethyl acetate (9:1) as eluent.

1.11. 4,10-Dibromo-6,6‘-di(4-*tert.*-butylphenyl)-12,12‘-dibutyl-6,12-dihydroindeno[1,2-*b*]fluorene 8a



According to the general procedure, the reaction of 2.00 g (2.96 mmol) of compound **7** and 1.11 g (3.3 eq., 9.76 mmol) 4-iodobutane were used to obtain 2.03 g of compound **8a** (2.57 mmol, 87%) as a colorless solid.

Mp.: 308°C.

^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm)= 0.650-0.755 (m, 28-H, 30-H, 8 H), 1.089-1.187 (m, 29-H, 4 H), 1.302 (s, 26-H, 18 H), 2.004 (m, 27-H, 4 H), 7.139 (d, 22-H, 4 H), 7.266 (d, 23-H, 4 H), 7.404 (d, 3-H, 1 H), 7.462 (s, 1-H, 1 H), 7.470 (d, 4-H, 1 H), 7.485 (d, 13-H, 1 H), 7.550 (s, 11-H, 1 H), 7.639 (s, 17-H, 1 H), 7.645 (s, 7-H, 1 H), 7.656 (d, 14-H, 1 H).

$^3J_{22,23}$ = 8.6 Hz.

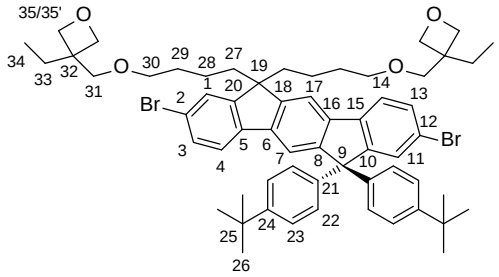
^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 13.97 (30-C), 23.20 (29-C), 26.18 (28-C), 31.51 (26-C), 34.55 (25-C), 40.42 (27-C), 55. 19 (19-C), 64.73 (9-C), 114.51 (17-C), 117.85 (7-C), 121.08 ($C_{quart.}$), 121.13 ($C_{quart.}$), 121.29 (4-C), 121.38 (14-C), 125.37 (23-C), 126.32 (1-C), 127.99 (22-C), 129.68 (11-C), 130.01 (3-C), 130.65 (13-C), 139.01 (16-C), 139.40 (15-C), 140.14 (5-C), 140.45 (6-C), 142.12 (21-C), 149.65 (24-C), 150.61 (18-C), 150.98 (10-C), 153.49 (20-C), 154.34 (8-C).

EI-MS: m/z (%): 788 (100, $[M]^+$), 731 (10, $[M\text{-}C_4H_9]^+$), 707 (8, $[M\text{-}Br]^+$).

HR-EI-MS ($C_{48}H_{52}Br_2$): calc.: 786.2430, found: 786.2422.

elemental analysis ($C_{48}H_{52}Br_2$) (%) calc.: C 73.09 H 6.65, found: C 72.78 H 6.671.

1.12. 4,10-Dibromo-6,6‘-di(4-*tert.*-butylphenyl)-12,12‘-di(3-ethyl(oxetane-3-methoxy)butyl)-6,12-dihydroindeno[1,2-*b*]fluorene 8b



According to the general procedure, the reaction of 15.00 g (22.17 mmol) of compound **7** and 16.55 g (2.97 eq., 65.87 mmol) of bromoalkane **2a** were used to obtain 14.618 g of compound **8b** (14.37 mmol, 65%) as a colorless solid.

Mp.: 98-101°C.

^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.712-0.818 (m, 28-H, 34-H, 10 H), 1.296 (s, 26-H, 18 H), 1.362-1.438 (m, 29-H, 4 H),1.386 (m, 30-H, 4 H), 1.593 (q, 34-H, 4 H), 2.032 (m, 27-H, 4 H), 3.265 (t, 30-H, 4 H), 3.387 (s, 31-H, 4 H), 4.254 – 4.338 (m, 35-H, 8 H), 7.118 (d, 22-H, 4 H), 7.258 (d, 23-H, 4 H), 7.404 (d, 3-H, 1 H), 7.441 (s, 1-H, 1 H), 7.474 (d, 4-H, 1 H), 7.483 (d, 13-H, 1 H), 7.538 (s, 11-H, 1 H), 7.624 (s, 17-H, 1 H), 7.634 (d, 14-H, 1 H), 7.638 (s, 7-H, 1 H).

$^4J_{1,3}$ = 1.7 Hz, $^3J_{3,4}$ = 8.1 Hz, $^3J_{11,13}$ = 1.7 Hz, $^3J_{22,23}$ = 8.6 Hz.

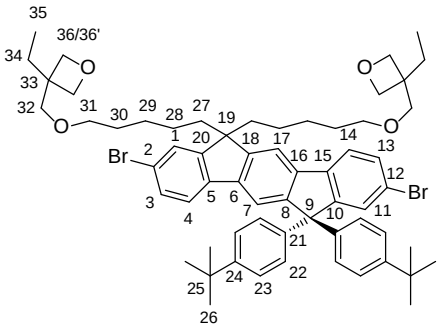
^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 8.30 (34-C), 20.64 (28-C), 26.83 (33-C), 29.79 (29-C), 31.49 (26-C), 34.56 (25-C), 40.35 (27-C), 43.47 (32-C), 55.21 (19-C), 64.74 (9-C), 71.06 (30 C), 73.41 (31-C), 78.70 (35-C), 114.42 (17-C), 117.93 (7-C), 121.18 ($C_{quart.}$), 121.26 ($C_{quart.}$), 121.36 (4-C), 121.40 (14-C), 125.37 (23-C), 126.23 (1-C), 127.98 (22-C), 129.73 (11-C), 130.19 (3-C), 130.68 (13-C), 139.16 (16-C), 139.27 (15-C), 140.19 (5-C), 140.44 (6-C), 142.39 (21-C), 149.70 (24-C), 150.15 (18-C), 151.15 (10-C), 153.02 (20-C), 154.29 (8-C).

EI-MS: m/z (%): 1014 (45, $[M]^+$), 986 (40, $[M\text{-}CH_2O]^+$), 956 (15, $[M\text{-}2(CH_2O)]^+$).

HR-EI-MS ($C_{60}H_{72}Br_2O_4$): calc.: 1014.3792, found: 1014.3808.

elemental analysis ($C_{60}H_{72}Br_2O_4$) (%) calc.: C 70.86 H 7.14, found: C 71.13 H 7.372.

1.13. 4,10-Dibromo-6,6‘-di(4-*tert.*-butylphenyl)-12,12‘-di(3-ethyl(oxetane-3-methoxy)pentyl)-6,12-dihydroindeno[1,2-*b*]fluorene 8c



According to the general procedure, the reaction of 15.00 g (22.17 mmol) of compound **7** and 17.57 g (2.99 eq., 66.24 mmol) bromoalkane **2b** were used to obtain 8.26 g of compound **8c** (7.90 mmol, 36%) as a colorless solid.

Mp.: 93-96°C.

^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.746 (m, 28-H, 4 H), 0.816 (t, 35-H, 6 H), 1.170 (m, 29-H, 4 H), 1.294 (s, 26-H, 18 H), 1.386 (m, 30-H, 4 H), 1.665 (q, 34-H, 4 H), 2.005 (m, 27-H, 4 H), 3.284 (t, 31-H, 4 H), 3.410 (s, 32-H, 4 H), 4.318 – 4.389 (m, 36-H, 8 H), 7.123 (d, 22-H, 4 H), 7.260 (d, 23-H, 4 H), 7.405 (d, 3-H, 1 H), 7.447 (s, 1-H, 1 H), 7.475 (d, 4-H, 1 H), 7.485 (d, 13-H, 1 H), 7.540 (s, 11-H, 1 H), 7.625 (s, 17-H, 1 H), 7.640 (s, 7-H, 1 H), 7.655 (d, 14-H, 1 H).

$^3J_{3,4}$ = 8.2 Hz, $^3J_{13,14}$ = 8.1 Hz, $^3J_{22,23}$ = 8.5 Hz.

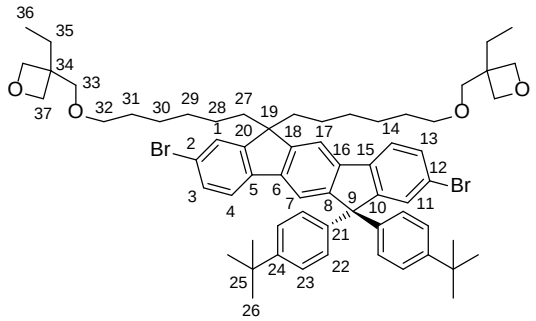
^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 7.31 (35-C), 22.78 (28-C), 25.58 (29-C), 25.87 (34-C), 28.32 (30-C), 30.49 (26-C), 33.55 (25-C), 39.55 (27-C), 42.50 (33-C), 51.17 (19-C), 63.71 (9-C), 70.52 (31 C), 72.52 (32-C), 77.66 (36-C), 113.45 (7-C or 17-C), 116.88 (7-C or 17-C), 120.11 (6-C or 16 C), 120.21 (6-C or 16-C), 120.39 (1-C), 124.36 (23-C), 125.22 (10-C), 126.96 (22-C), 128.67 (11-C), 129.09 (14-C), 129.67 (13-C), 138.08 (20-C), 138.28 (15-C), 139.13 (12-C), 139.41 (8-C), 141.40 (21-C), 148.63 (24-C), 149.32 (18-C), 150.00 (8-C), 152.16 (5-C), 153.25 (2-C).

EI-MS: m/z (%): 1044 (100, $[M]^+$), 1014 (35, $[M\text{-}CH_2O]^+$), 982 (15, $[M\text{-}2(CH_2O)]^+$), 897 (8, $[M\text{-}(CH_2O)\text{-}C_6H_{11}O_2]^+$),

HR-EI-MS ($C_{62}H_{76}Br_2O_4$): calc.: 1042.4105, found: 1042.4097.

elemental analysis ($C_{62}H_{76}Br_2O_4$) (%) calc.: C 71.25 H 7.33, found: C 71.17 H 7.438.

1.14. 4,10-Dibromo-6,6‘-di(4-*tert.*-butylphenyl)-12,12‘-di(3-ethyl(oxetane-3-methoxy)hexyl)-6,12-dihydroindeno[1,2-*b*]fluorene 8d



According to the general procedure, the reaction of 4.00 g (5.91 mmol) of compound **7** and 5.43 g (3.30 eq., 19.43 mmol) bromoalkane **2c** were used to obtain 4.47 g of compound **8d** (4.16 mmol, 70%) as a colorless solid.

Mp.: 95-99°C.

^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.734 (m, 28-H, 4 H), 0.853 (t, 36-H, 6 H), 1.154 (m, 29-H, 30-H, 8 H), 1.312 (s, 26-H, 18 H), 1.427 (m, 31-H, 4 H), 1.708 (q, 35-H, 4 H), 2.014 (m, 27-H, 4 H), 3.353 (t, 32-H, 4 H), 3.465 (s, 33-H, 4 H), 4.352 – 4.423 (m, 37-H, 8 H), 7.148 (d, 22-H, 4 H), 7.272 (d, 23-H, 4 H), 7.422 (d, 3-H, 1 H), 7.465 (s, 1-H, 1 H), 7.493 (d, 4-H, 1 H), 7.502 (d, 13-H, 1 H), 7.562 (s, 11-H, 1 H), 7.643 (s, 17-H, 1 H), 7.658 (s, 7-H, 1 H), 7.670 (d, 14 H, 1 H).

$^3J_{3,4}$ = 8.2 Hz, $^3J_{13,14}$ = 8.0 Hz, $^3J_{22,23}$ = 8.5 Hz.

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 8.36 (36-C), 23.92 (28-C), 25.89 (29-C or 30-C), 26.83 (35-C), 29.55 (31-C), 29.87 (29-C or 30-C), 31.50 (26-C), 34.49 (25-C), 40.48 (27-C), 43.49 (34-C), 55.18 (19-C), 64.70 (9-C), 71.62 (32-C), 73.52 (33-C), 78.69 (37-C), 114.41 (7-C or 17-C), 117.84 (7-C or 17-C), 121.06 (6-C or 16-C), 121.14 (6-C or 16-C), 121.31 (1-C), 125.32 (23-C), 126.21 (10-C), 127.94 (22-C), 129.63 (11-C), 130.04 (14-C), 130.62 (13-C), 139.02 (20-C), 139.31 (15-C), 140.09 (12-C), 140.41 (8-C), 142.38 (21-C), 149.60 (24-C), 150.43 (18-C), 150.98 (8-C), 153.28 (5-C), 154.27 (2-C).

EI-MS: m/z (%): 1072 (100, $[M]^+$), 1042 (35, $[M\text{-}C_2H_5]^+$), 1012 (7, $[M\text{-}2(C_2H_5)]^+$), 974 (9, $[M\text{-}C_6H_{11}O]^+$), 942 (3, $[M\text{-}C_6H_{11}O\text{-}C_2H_5]^+$), 874 (2, $[M\text{-}2(C_6H_{11}O)]^+$), 774 (2, $[M\text{-}C_6H_{11}O\text{-}C_{12}H_{23}O_2]^+$), 674 (5, $[M\text{-}2(C_{12}H_{23}O_2)]^+$), 593 (5, $[M\text{-}2(C_{12}H_{23}O_2)\text{-}Br^+]$).

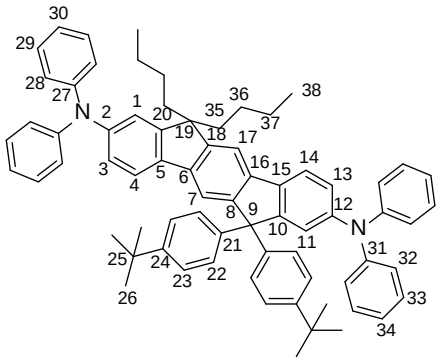
elemental analysis ($C_{64}H_{80}Br_2O_4$) (%) calc: C 71.63 H 7.51, found: C 71.58 H 7.52.

1.15. Synthesis of DPA-MIF derivatives 13

General procedure

In a flame-dried Schlenk flask, the dibromide **8** was dissolved in 24 mL/mmol of degassed toluene and mixed with 2.2 eq. of the diphenylamine compound **5**, 5-11 mol% $Pd(OAc)_2$, 20-44mol% P(*t*Bu)$_3$ (1 M solution in toluene) and 2.4-4.00 eq. NaO*t*Bu. The mixture was stirred for 10 minutes at room temperature and heated to 110°C afterwards. After completion of the reaction, the mixture was cooled to room temperature again and filtered through a pad of silica. The solvent was removed *in vacuo* and the remaining residue was purified by chromatography on silica (PhMe/EA, 20:1).

1.16. REF 9a



According to the general procedure, 600 mg (0.76 mmol) of compound **8a**, 290 mg (2.25 eq., 1.71 mmol) diphenylamine, 8.5 mg (0.05 eq., 0.04 mmol) $Pd(OAc)_2$, 175.4 mg (2.40 eq., 183 mmol) NaO*t*Bu and 0.152 mL (0.20 eq., 0.15 mmol) of a solution of P(*t*Bu)$_3$ in toluene (1 M) were used to obtain compound **9a** as an off-white solid. Yield = 573 mg (0.59 mmol, 78%).

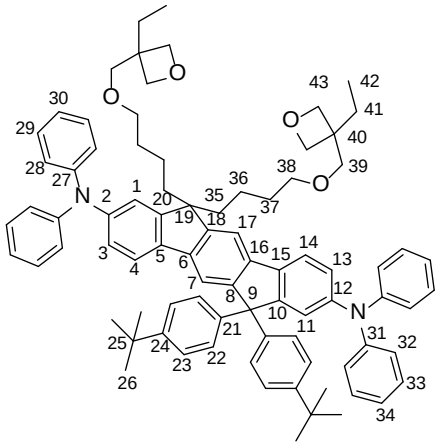
^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.681-0.815 (m, 36-H, 38-H, 10 H), 1.068-1.189 (m, 37-H, 4 H), 1.307 (s, 26-H, 18 H), 1.934 (m, 35-H, 4 H), 6.952-7.041 (m, 3-H, 13-H, 30-H, 34-H, 6 H), 7.062 (m, 28-H or 32-H, 4 H), 7.097-7.135 (m, 1-H, 28-H or 32-H, 5 H), 7.147 (d, 23-H, 4 H), 7.171-7.268 (m, 22-H, 29-H, 32-H, 12 H), 7.277 (s, 11-H, 1 H), 7.508 (d, 4-H, 1 H), 7.585 (s, 17-H, 1 H), 7.596 (s, 7-H, 1 H), 7.636 (d, 14-H, 1 H).

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 14.05 (38-C), 23.25 (37-C), 26.32 (36-C), 31.54 (26-C), 34.50 (25-C), 40.39 (35-C), 54.85 (19-C), 64.58 (9-C), 113.84 (17-C), 117.34 (7-C), 119.89 (1 C), 120.28 (4-C or 14-C), 120.38 (4-C or 14-C), 122.51 (30-C or 34-C), 122.59 (11-C), 122.67 (30-C or 34-C), 123.66 (13-C), 123.78 (28-C or 32-C), 123.89 (C-H), 124.03 (28-C or 32-C), 125.09 (22-C), 128.06 (23-C), 129.21 (29-C or 33-C), 129.25 (29-C or 33-C), 135.48 (15-C), 136.82 (5-C), 138.85 (16-C), 140.09 (6-C), 143.10 (21-C), 146.95 (2-C or 12-C), 147.03 (2-C or 12-C), 147.87 (27-C or 31-C), 148.16 (27-C or 31-C), 149.17 (24-C), 150.69 (8-C or 18-C), 150.74 (8-C or 18-C), 152.63 (20-C), 153.68 (10-C).

EI-MS: m/z (%): 964 (100, $[M]^+$), 864 (8, $[M\text{-}2(C_4H_9)^+]$).

HR-EI-MS ($C_{72}H_{72}N_2$): calc.: 964.5690, found: 964.5696.

1.17. 0L-2G4 9b



According to the general procedure, 500 mg (0.49 mmol) of compound **8b**, 193 mg (2.32 eq., 1.14 mmol) diphenylamine, 5.5 mg (0.05 eq., 0.02 mmol) $Pd(OAc)_2$, 113.4 mg (2.40 eq., 1.18 mmol) NaO*t*Bu and 0.098 mL (0.20 eq., 0.10 mmol) of a solution of P(*t*Bu)$_3$ in toluene (1 M) were used to obtain compound **9b** as an off-white solid. Yield = 498 mg (0.41 mmol, 84%).

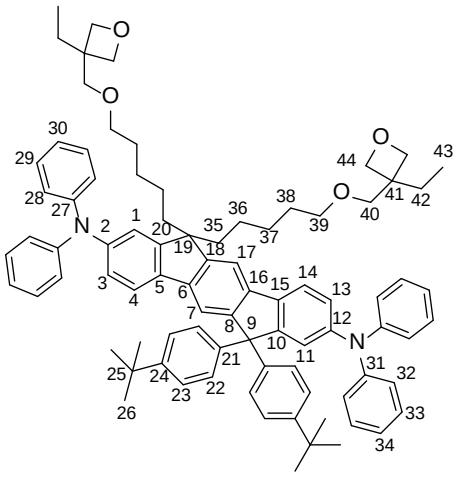
^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.770 (t, 42-H, 6 H), 0.810 (m, 36-H, 4 H), 1.299 (s, 26-H, 18 H), 1.387 (m, 37-H, 4 H), 1.631 (q, 41-H, 4 H), 1.853-2.051 (m, 35-H, 4 H), 3.260 (m, 38-H, 4 H), 3.417 (m, 39-H, 4 H), 4.286–4.372 (m, 43-H, 8 H), 6.958-7.032 (m, 3-H, 13-H, 30-H, 34-H, 6 H), 7.053 (m, 28-H or 32-H, 4 H), 7.076-7.113 (m, 1-H, 28-H or 32-H, 5 H), 7.125 (d, 23-H, 4 H), 7.168-7.246 (m, 22-H, 29-H, 32-H, 12 H), 7.256 (s, 11-H, 1 H), 7.486 (d, 4-H, 1 H), 7.558 (s, 17-H, 1 H), 7.583 (s, 7-H, 1 H), 7.606 (d, 14-H, 1 H).

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 8.29 (42-C), 20.88 (36-C), 26.81 (41-C), 30.00 (37-C), 31.52 (26-C), 34.49 (25-C), 40.43 (35-C), 43.50 (40 C), 54.82 (19-C), 64.55 (9-C), 71.57 (38-C), 73.51 (39-C), 78.70 (43_A-C or 43_B-C), 78.73 (44_A-C or 44_B-C), 113.73 (17-C), 117.37 (7-C), 119.53 (1-C), 120.34 (4-C or 14-C), 120.38 (4-C or 14-C), 122.46 (11-C), 122.62 (30-C or 34-C), 122.70 (30-C or 34-C), 123.55 (13-C), 123.87 (28-C or 32-C), 124.05 (28-C or 32-C), 125.07 (22-C), 128.05 (23-C), 129.22 (29-C or 33-C), 129.28 (29-C or 33-C), 135.28 (15-C), 136.72 (5-C), 138.95 (16-C), 140.10 (6-C), 143.07 (21-C), 147.06 (2-C or 12-C), 147.09 (2-C or 12-C), 147.83 (27-C or 31-C), 148.12 (27-C or 31-C), 149.20 (24-C), 150.19 (18-C), 150.84 (8-C), 152.12 (20-C), 153.62 (10-C).

EI-MS: m/z (%): 1192.7 (100, $[M]^+$), 1162.7 (40, $[M\text{-}2(CH_3)]^+$), 1132.6 (15, $[M\text{-}2(C_2H_4O)^+]$, 864 (10, $[M\text{-}2(C_{10}H_{19}O_2)]^+$).

HR-EI-MS ($C_{84}H_{92}N_2O_4$): calc.: 1192.7052, found: 1192.7069.

1.18. 0L-2G5 9c



According to the general procedure, 500 mg (0.48 mmol) of compound **8c**, 178 mg (2.20 eq., 1.05 mmol) diphenylamine, 5.3 mg (0.05 eq., 0.02 mmol) $Pd(OAc)_2$, 110.4 mg (2.40 eq., 1.15 mmol) Na*O*t*Bu and 0.096 mL (0.20 eq., 0.10 mmol) of a solution of P(*t*Bu)$_3$ in toluene (1 M) were used to obtain compound **9c** as an off-white solid. Yield = 344 mg (0.28 mmol, 59%).

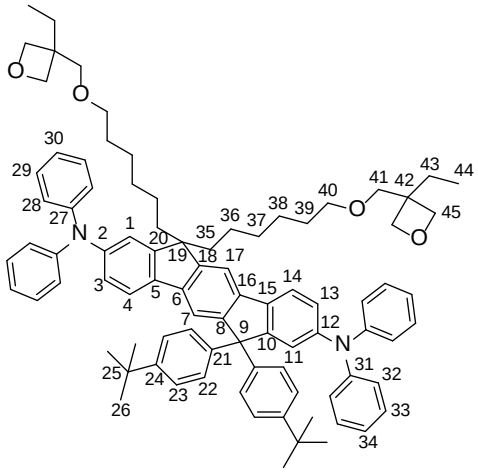
^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.720-0.818 (m, 36-H, 4 H), 0.843 (t, 43-H, 6 H), 1.104-1.211 (m, 37-H, 4 H), 1.300 (s, 26-H, 18 H), 1.405 (m, 38-H, 4 H), 1.692 (q, 42-H, 4 H), 1.856-2.005 (m, 35-H, 4 H), 3.319 (t, 39-H, 4 H), 3.447 (s, 40-H, 4 H), 4.321–4.418 (m, 44-H, 8 H), 6.959-7.031 (m, 3-H, 13-H, 30 H, 34-H, 6 H), 7.053 (m, 28-H or 32-H, 4 H), 7.088-7.121 (m, 1-H, 28-H or 32-H, 5 H), 7.132 (d, 23-H, 4 H), 7.168-7.258 (m, 22-H, 29-H, 32-H, 12 H), 7.266 (s, 11-H, 1 H), 7.497 (d, 4-H, 1 H), 7.566 (s, 17-H, 1 H), 7.586 (s, 7-H, 1 H), 7.621 (d, 14-H, 1 H).

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 8.34 (43-C), 23.94 (36-C), 26.61 (37-C), 26.88 (42 C), 29.66 (38-C), 31.52 (26-C), 34.48 (25-C), 40.57 (35-C), 43.55 (41-C), 54.78 (19-C), 64.56 (9-C), 71.68 (39-C), 73.57 (40-C), 78.69 (44-C), 113.72 (17-C), 117.36 (7-C), 119.63 (1-C), 120.36 (4-C/14-C), 122.50 (11-C), 122.58 (30-C or 34-C), 122.69 (30-C or 34-C), 123.58 (13-C), 123.82 (28-C or 32-C), 124.03 (28-C or 32-C), 125.07 (22-C), 128.05 (23-C), 129.21 (29-C or 33-C), 129.28 (29-C or 33-C), 135.33 (15-C), 136.74 (5-C), 138.92 (16-C), 140.05 (6-C), 143.07 (21-C), 147.01 (2-C or 12-C), 147.08 (2-C or 12-C), 147.84 (27-C or 31-C), 148.12 (27-C or 31-C), 149.19 (24-C), 150.48 (18-C), 150.78 (8-C), 152.34 (20-C), 153.66 (10-C).

EI-MS: m/z (%): 1220 (100, $[M]^+$), 1190 (45, $[M\text{-}2(CH_3)]^+$), 1023 (10, $[M\text{-}2(C_6H_{11}O)]^+$), 610 (50, $[M\text{-}2(C_{11}H_{21}O_2)\text{-}(C_{12}H_{10}N)\text{-}(C_4H_6)\text{-}(CH_3)]^+$).

elemental analysis ($C_{86}H_{96}N_2O_4$) (%) calc.: C 84.55 H 7.92 N 2.29, found: C 84.57 H 7.964 N 2.046.

1.19. 0L-2G6 9d



According to the general procedure, 500 mg (0.47 mmol) of compound **8d**, 183 mg (2.32 eq., 1.08 mmol) diphenylamine, 5.2 mg (0.05 eq., 0.02 mmol) $Pd(OAc)_2$, 107.5 mg (2.40 eq., 1.12 mmol) Na*O*t*Bu and 0.093 mL (0.20 eq., 0.09 mmol) of a solution of P(*t*Bu)$_3$ in toluene (1 M) were used to obtain compound **9d** as an off-white solid. Yield = 509 mg (0.41 mmol, 87%).

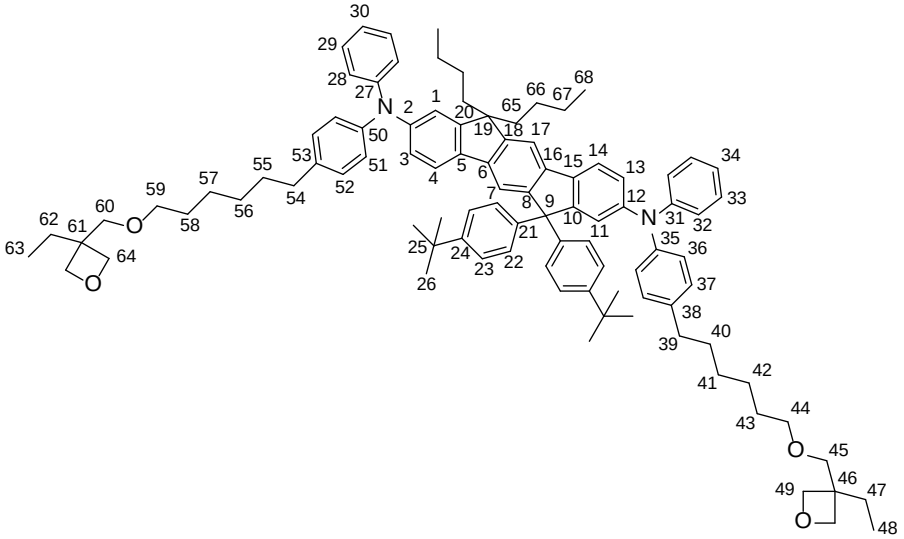
^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.721-0.807 (m, 36-H, 4 H), 0.855 (t, 44-H, 6 H), 1.056-1.203 (m, 37-H, 38-H, 8 H), 1.301 (s, 26-H, 18 H), 1.448 (m, 39-H, 4 H), 1.711 (q, 43-H, 4 H), 1.847-1.999 (m, 35-H, 4 H), 3.366 (t, 40-H, 4 H), 3.484 (s, 41-H, 4 H), 4.342–4.437 (m, 45-H, 8 H), 6.961-7.017 (m, 3-H, 30-H, 34-H, 5 H), 7.017 (d, 13-H, 1 H), 7.055 (m, 28-H or 32-H, 4 H), 7.087-7.117 (m, 28-H or 32-H, 4 H), 7.110 (s, 1-H, 1 H), 7.133 (d, 23-H, 4 H), 7.17-7.257 (m, 22-H, 29-H, 32-H, 12 H), 7.267 (s, 11-H, 1 H), 7.500 (d, 4-H, 1 H), 7.565 (s, 17-H, 1 H), 7.587 (s, 7-H, 1 H), 7.622 (d, 14-H, 1 H).

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 8.36 (44-C), 24.11 (36-C), 26.02 (37-C or 38-C), 26.88 (43 C), 29.66 (39-C), 30.05 (37-C or 38-C), 31.55 (26-C), 34.48 (25-C), 40.62 (35-C), 43.57 (42-C), 54.80 (19-C), 64.54 (9-C), 71.74 (40-C), 73.59 (41-C), 78.74 (45-C), 113.75 (17-C), 117.35 (7-C), 119.85 (4-C), 120.36 (14-C), 122.50 (30-C/34-C), 122.68 (11-C), 123.58 (13-C), 123.74 (28-C or 32-C), 124.02 (28-C or 32-C), 125.06 (22-C), 125.65 (1-C), 128.05 (23-C), 129.21 (29-C or 33-C), 129.26 (29-C or 33-C), 135.37 (15-C), 136.81 (5-C), 138.90 (16-C), 140.03 (6-C), 143.08 (21-C), 146.95 (2-C or 12-C), 147.06 (2-C or 12-C), 147.84 (27-C or 31-C), 148.15 (27-C or 31-C), 149.17 (24-C), 150.62 (18-C), 150.72 (8-C), 152.47 (20-C), 153.65 (10-C).

EI-MS: m/z (%): 1248 (100, $[M]^+$), 1218 (20, $[M\text{-}2(CH_3)]^+$), 624 (40, $[M\text{-}2(C_{12}H_{23}O_2)\text{-}(C_{12}H_{10}N)\text{-}(C_4H_9)]^+$).

elemental analysis ($C_{88}H_{100}N_2O_4$) (%) calc.: C 84.57 H 8.07 N 2.24, found: C 84.02 H 8.120 N 2.174.

1.20. 2L6-0G 9e



According to the general procedure, 390 mg (0.49 mmol) of compound **8a**, 400 mg (2.20 eq., 1.09 mmol) of the oxetane-functionalized diphenylamine **5a**, 12.4 mg (0.11 eq., 0.05 mmol) $Pd(OAc)_2$, 190 mg (4.00 eq., 1.98 mmol) NaO*t*Bu and 0.218 mL (0.44 eq., 0.22 mmol) of a solution of $P(tBu)_3$ in toluene (1 M) were used to obtain compound **9e** after chromatography on silica (PhMe/EA, 9:1) in form of an yellow oil. Yield = 482 mg (0.35 mmol, 72%).

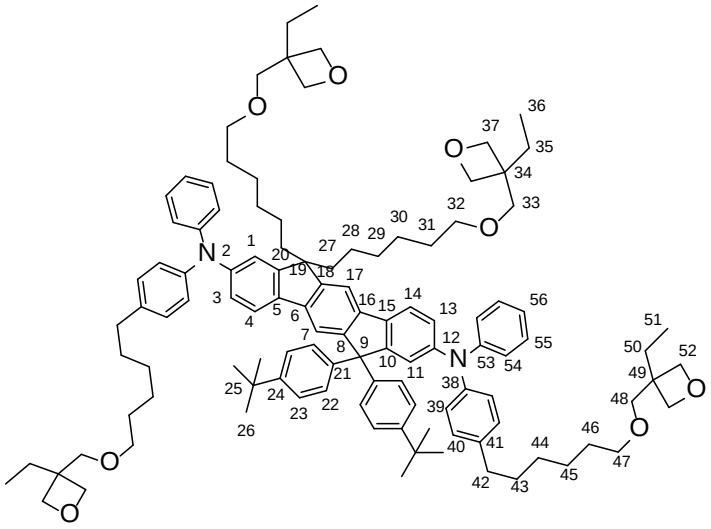
^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.671-0.810 (m, 66-H, 68-H, 10 H), 0.904 (t, 48-H, 63-H, 12 H), 1.063-1.167 (m, 67-H, 4 H), 1.302 (s, 26-H, 18 H), 1.355-1.454 (m, 41-H, 42-H, 56-H, 57-H, 16 H), 1.569-1.676 (m, 40-H, 43-H, 55-H, 58-H, 8 H), 1.764 (q, 47-H, 62-H, 4 H), 1.923 (m, 65-H, 4 H), 2.574 (m, 39-H, 54-H, 4 H), 3.473 (t, 44-H, 59-H, 4 H), 3.546 (s, 45-H, 60-H, 4 H), 4.375–4.483 (m, 49-H, 8 H), 6.917-6.990 (m, 36-H or 51-H, 30-H, 34-H, 3-H, 5 H), 6.990-7.116 (m, 13-H, 37-H, 52-H, 36-H or 51-H, 28-H, 32-H, 1-H,12 H), 7.140 (d, 22-H, 4 H), 7.162-7.244 (m, 23-H, 29-H, 33-H, 8 H), 7.256 (s, 11-H, 1 H), 7.485 (d, 4-H, 1 H), 7.567 (s, 17-H, 1 H), 7.579 (s, 7-H, 1 H), 7.615 (d, 14-H, 1 H).

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 8.35 (48-C or 63-C), 14.04 (68-C), 23.21 (67-C), 26.21 (66-C), 26.29 (CH_2), 26.93 (47-C, 62-C), 29.31 (CH_2), 29.36 (CH_2), 29.68 (CH_2), 31.52 (26-C), 31.60 (CH_2), 34.47 (25-C), 35.43 (CH_2), 35.46 (CH_2), 40.37 (65-C), 43.62 (46-C), 54.76 (19-C), 64.53 (9-C), 71.76 (44-C, 59-C), 73.62 (45-C, 60-C), 78.76 (49-C, 64-C), 113.76 (17-C), 117.25 (7-C), 119.62 (1-C), 120.16 (4-C), 120.26 (14-C), 122.04 (ArH), 122.18 (ArH), 122.33 (ArH), 123.44 (ArH), 123.59 (ArH), 124.18 (ArH), 124.43 (23-C), 125.03 (ArH), 128.07 (22-C), 129.15 (ArH), 135.18 ($C_{quart.}$), 136.52 ($C_{quart.}$), 137.35 ($C_{quart.}$), 137.50 ($C_{quart.}$), 138.81 ($C_{quart.}$), 140.04 ($C_{quart.}$), 143.15 (21-C), 147.10 ($C_{quart.}$), 147.19 ($C_{quart.}$), 148.34 ($C_{quart.}$), 149.10 (24-C), 150.59 ($C_{quart.}$), 150.69 ($C_{quart.}$), 152.53 (20-C), 153.78 (10-C).

EI-MS: m/z (%): 1361 (100, $[M]^+$), 1331 (20, $[M\text{-}2(CH_3)]^+$), 1262 (15, $[M\text{-}(C_6H_{11}O)^+]$.

HR-APCI ($C_{96}H_{117}N_2O_4$) (m/z): calc.: 1361.90079, found: 1361.90076.

1.21. 2L6-2G6 9f



According to the general procedure, 530 mg (0.4 mmol) of compound **8d**, 399 mg (2.20 eq., 1.09 mmol) of the oxetane-functionalized diphenylamine **5a**, 11.3 mg (0.11 eq., 0.05 mmol) $Pd(OAc)_2$, 190 mg (4.00 eq., 1.98 mmol) NaO*t*Bu and 0.198 mL (0.40 eq., 0.20 mmol) of a solution of P(*t*Bu)$_3$ in toluene (1 M) were used to obtain compound **9f** after chromatography on silica (PhMe/EA, 4:1) in form of an yellow oil. Yield = 550 mg (0.33 mmol, 68%).

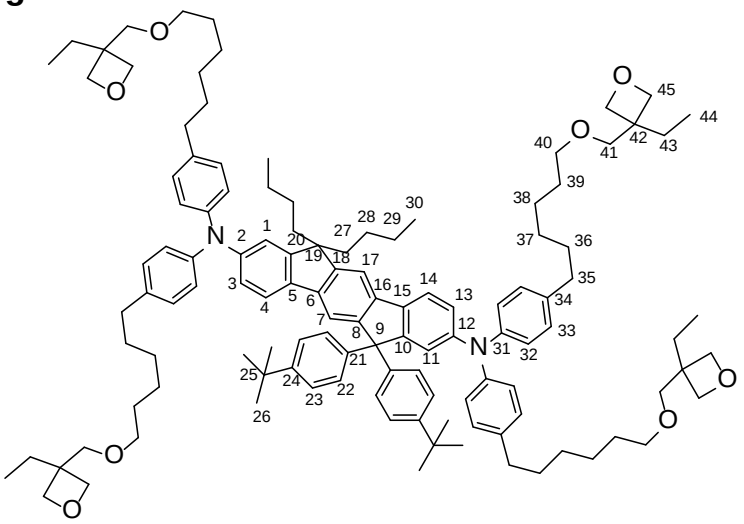
^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.875 (m, 4 H), 0.942 (t, 6 H), 0.989 (t, 6 H), 1.159-1.317 (m, 8 H), .1.372 (m, 2 H) 1.395 (s, 26-H, 18 H), 1.504 (m, 10 H), 1.713 (m, 8 H), 1.772-1.88 (m, 8 H), 2.024 (m, 27-H, 4 H), 2.666 (m, 42-H, 4 H), 3.459 (t, 4 H), 3.537-3.588 (m, 8 H), 3.629 (s, 4 H), 4.439 (m, 4 H), 4.476 (m, 4 H), 4.506 (m, 4 H), 4.557 (m, 4 H), 6.998-7.213 (m, 20 H), 7.217-7.276 (m, 6 H), 7.276-7.329 (m, 6 H), 7.355 (s, 11-H, 1 H), 7.577 (d, 4-H, 1 H), 7.6625 (s, 17-H, 1 H), 7.684 (s, 7-H, 1 H), 7.702 (d, 14-H, 1 H).

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 8.38 (CH_3), 21.37 (CH_3), 24.10 (CH_2), 26.02 (CH_2), 26.24 (CH_2), 26.90 (CH_2), 26.95 (CH_2), 29.35 (CH_2), 29.66 (CH_2), 29.69 (CH_2), 30.04 (CH_2), 31.55 (26-C), 31.62 (CH_2), 34.39 (25-C), 34.48 ($C_{quart.}$), 35.48 (42-C), 40.65 (27-C), 43.56 ($C_{quart.}$), 43.61 ($C_{quart.}$), 54.80 (19-C), 64.55 (9-C), 71.71 (CH_2), 71.74 (CH_2), 73.60 (CH_2), 73.62 (CH_2), 78.69 (37-C and 52-C), 113.70 (17-C), 117.29 (7-C), 119.53 (1-C), 120.29 (ArH), 122.10 (ArH), 122.26 (ArH), 123.28 (ArH), 123.51 (ArH), 123.70 (ArH), 124.18 (ArH), 124.46 (ArH), 125.05 (23-C), 128.10 (22-C), 128.38 ($C_{quart.}$), 129.13 (ArH), 129.19 (ArH), 135.10 ($C_{quart.}$), 136.05 ($C_{quart.}$), 136.52 (5-C), 137.34 ($C_{quart.}$), 137.51 ($C_{quart.}$), 138.91 ($C_{quart.}$), 140.06 ($C_{quart.}$), 143.17 (21-C), 145.46 ($C_{quart.}$), 145.75 ($C_{quart.}$), 147.15 ($C_{quart.}$), 147.26 ($C_{quart.}$), 148.00 ($C_{quart.}$), 148.36 ($C_{quart.}$), 149.10 (24-C), 150.59 ($C_{quart.}$), 150.68 ($C_{quart.}$), 151.69 ($C_{quart.}$), 152.39 (20-C), 153.59 (10-C).

ESI-MS ($C_{112}H_{144}N_2O_8$) (m/z): calc.: 1646.1, found: 1669 ($[M+Na]^+$), 1646 ($[M]^+$).

elemental analysis ($C_{112}H_{144}N_2O_8$) (%) calc: C 81.71 H 8.82 N 1.70, found: C 81.64 H 9.058 N 1.557.

1.22. 4L6-0G 9g



According to the general procedure, 260 mg (0.33 mmol) of compound **8a**, 410 mg (2.20 eq., 0.73 mmol) of the oxetane-functionalized diphenylamine **5b**, 8.3 mg (0.11 eq., 0.04 mmol) $Pd(OAc)_2$, 127 mg (4.00 eq., 1.32 mmol) NaO*t*Bu and 0.145 mL (0.44 eq., 0.15 mmol) of a solution of P(*t*Bu)$_3$ in toluene (1 M) were used to obtain compound **9g** after chromatography on silica (PhMe/EA, 4:1) in form of an yellow oil. Yield = 398 mg (0.23 mmol, 70%).

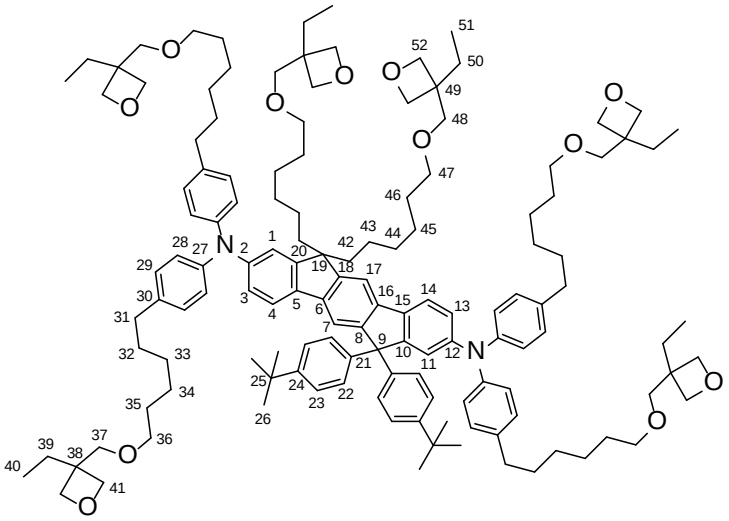
^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.701-0.813 (m, 30-H, 28-H, 10 H), 0.906 (t, 44-H, 12 H), 1.131 (m, 29-H, 4 H), 1.313 (s, 26-H, 18 H), 1.41 (m, 37-H, 38-H, 16 H), 1.627 (m, 36-H, 39-H, 16 H), 1.766 (q, 43-H, 8 H), 1.931 (m, 27-H, 4 H), 2.572 (m, 35-H, 8 H), 3.474 (t, 40-H, 8 H), 3.546 (s, 41-H, 8 H), 4.394 (m, 46_A-H or 46_B-H, 8 H), 4.471 (m, 46_A-H or 46_B-H, 8 H), 6.933-7.067 (m, 3-H, 13-H, 32-H, 33-H, 18 H), 7.098 (s, 1-H, 1 H), 7.153 (d, 22-H, 4 H), 7.213 (d, 23-H, 4 H), 7.245 (s, 11-H, 1 H), 7.473 (d, 4-H, 1 H), 7.571 (s, 17-H, 1 H), 7.583 (s, 7-H, 1 H), 7.602 (d, 14-H, 1 H).

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 8.31 (44-C), 14.00 (30-C), 23.16 (29-C), 26.16 (37-C or 38-C), 26.22 (28-C), 26.87 (43-C), 29.23 (CH_2), 29.28 (CH_2), 29.61 (CH_2), 31.54 (26-C), 34.40 (25-C), 35.37 (35-C), 40.31 (27-C), 43.54 (42-C), 54.66 (9-C), 64.45 (19-C), 71.68 (40-C), 73.55 (41-C), 78.64 (45-C), 113.63 (17-C), 117.12 (7-C), 119.26 (1-C), 120.01 (4-C), 120.11 (14-C), 122.02 (11-C), 122.92 (ArH), 123.65 (ArH), 123.87 (ArH), 124.95 (23-C), 125.58 (ArH), 128.04 (22-C), 128.31 ($C_{quart.}$), 128.98 (ArH), 129.05 (ArH), 134.80 ($C_{quart.}$), 135.95 ($C_{quart.}$), 136.14 ($C_{quart.}$), 136.80 ($C_{quart.}$), 136.93 ($C_{quart.}$), 138.75 (16-C), 139.98 (6-C), 143.18 (21-C), 145.59 ($C_{quart.}$), 145.91 ($C_{quart.}$), 147.26 (2-C or 12-C), 147.36 (2-C or 12-C), 148.96 (24-C), 150.47 (8-C or 18-C), 150.59 (8-C or 18-C), 152.38 (20-C), 153.44 (10-C).

ESI-MS ($C_{120}H_{160}N_2O_8$) (m/z): calc.: 1758.2, found: 1781 ($[M+Na]^+$), 1758 ([M]).

elemental analysis ($C_{120}H_{160}N_2O_8$) (%) calc.: C 81.96 H 9.17 N 1.59, found: C 81.61 H 9.357 N 1.414.

1.23. 4L6-2G6 9h



According to the general procedure, 350 mg (0.33 mmol) of compound **8d**, 406 mg (2.20 eq., 0.72 mmol) of the oxetane-functionalized diphenylamine **5b**, 8.2 mg (0.11 eq., 0.04 mmol) $Pd(OAc)_2$, 125 mg (4.00 eq., 1.30 mmol) NaO*t*Bu and 0.144 mL (0.44 eq., 0.14 mmol) of a solution of $P(tBu)_3$ in toluene (1 M) were used to obtain compound **9h** after chromatography on silica (PhMe/EA, 4:1) in form of an yellow oil. Yield = 436 mg (0.21 mmol, 65%).

^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.853 (t, 51-H, 6 H), 0.902 (t, 40-H, 12 H), 1.068-1.200 (m, 34-H, 44-H, 12 H), 1.303 (s, 26-H, 18 H), 1.366-1.479 (m, 33-H, 43-H, 45-H, 16 H), 1.567-1.674 (m, 32-H, 35-H, 46 H, 20 H), 1.709 (q, 50-H, 4 H), 1.758 (q, 39-H, 8 H), 2.564 (m, 31-H, 8 H), 3.366 (t, 42-H, 4 H), 3.445-3.495 (m, 36-H, 47-H, 12 H), 3.541 (s, 37-H, 48-H, 12 H), 4.349 (d, 52_A-H or 52_B-H, 4 H), 4.389 (d, 41_A-H or 41_B-H, 8 H), 4.412 (d, 52_A-H or 52_B-H, 4 H), 4.463 (d, 41_A-H or 41_B-H, 8 H), 6.941 (d, 28-H, 8 H), 6.986 (m, 13-H, 1 H), 7.000 (m, 3-H, 1 H), 7.036 (d, 29-H, 8 H), 7.069 (s, 1-H, 1 H), 7.126 (d, 22-H, 4 H), 7.200 (d, 23-H, 4 H), 7.223 (s, 11-H, 1 H), 7.455 (d, 14-H, 1 H), 7.537 (s, 17-H, 1 H), 7.559 (s, 7-H, 1 H), 7.584 (d, 4-H, 1 H).

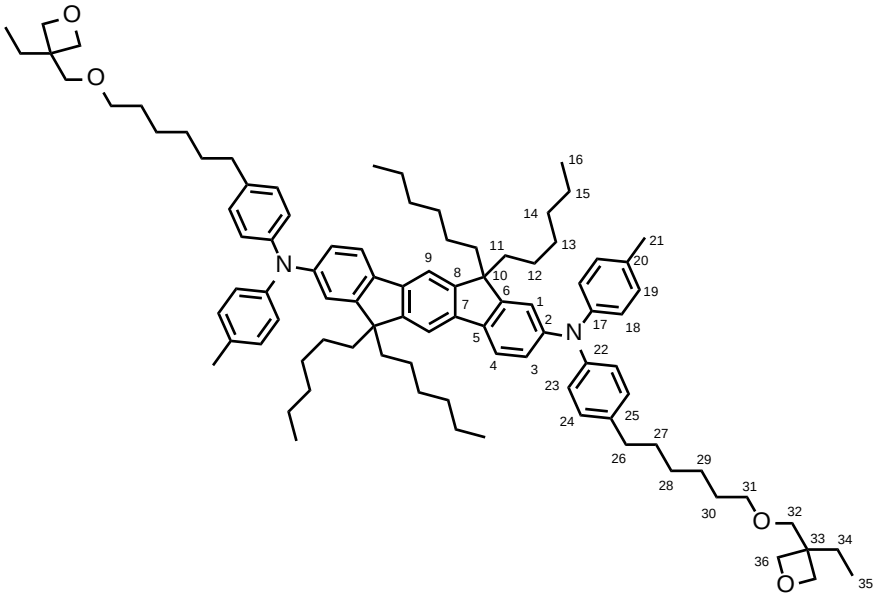
$^3J_{22,23}$ = 8.5 Hz, $^3J_{28,29}$ = 8.47 Hz.

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 8.33 (40-C, 51-C), 25.98 (43-C), 26.19 (35-C), 26.85 (50-C), 26.90 (39-C), 29.34 (34-C or 45-C), 29.64 (33-C), 29.80 (46-C), 30.33 (44-C), 31.50 (26-C), 31.58 (32-C), 34.43 (25-C), 35.42 (31-C), 43.54 (49-C), 43.58 (38-C), 54.73 (19-C), 64.47 (9-C), 71.72 (42-C, 36-C, 47-C), 73.57 (37-C, 48-C), 78.12 (41-C, 52-C), 113.58 (17-C), 117.16 (7-C), 119.07 (1-C), 119.24 (14-C), 120.09 (4-C), 121.99 (11-C), 122.89 (13-C), 123.72 (13-C), 123.93 (28-C), 124.98 (23-C), 128.05 (22-C), 129.02 (3-C or 29-C), 129.08 (3-C or 29-C), 134.73 (15-C), 136.11 (5-C), 137.02 (30-C), 138.80 (16-C), 139.99 (6-C), 143.19 (21-C), 145.92 (27-C), 147.19 (12-C), 147.29 (2-C), 149.03 (24-C), 150.46 (8-C or 18-C), 150.53 (8-C or 18-C), 152.26 (10-C), 153.45 (20-C).

HR-APCI ($C_{136}H_{188}N_2O_{12}$) (m/z): calc.: 2042.42351, found: 2043.43102.

elemental analysis ($C_{136}H_{188}N_2O_{12}$) (%) calc.: C 79.96 H 9.26 N 1.37, found: C 79.43 H 9.504 N 1.203.

1.24. Synthesis JS247



2,8-Dibromo-6,6,12,12-tetrahexyl-6,12-dihydroindeno[1,2-*b*]fluorene[12] (936 mg, 1.25 mmol), 4-(6-((3-ethyloxetan-3-yl)methoxy)hexyl)-*N*-*p*-tolylaniline[13] (1.00 g, 2.62 mmol) and sodium-*tert*-butylate (301 mg, 3.13 mmol) were dissolved in dry toluene (10 ml) and an argon atmosphere. After addition of tris(dibenzylideneacetone)dipalladium(0) (23 mg, 25 mmol) and tri-*tert*-butylphosphine (8.1 mg, 40 mmol) the reaction mixture was stirred overnight at 60°C. After completion, water was added and the product was extracted with *tert*-butylmethylether. The organic phase was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The product was first purified by column chromatography on silica with cyclohexane/ethyl acetate (4:1) as eluent, followed by further purification with recycling GPC and toluene as eluent. Yield = 370 mg (274 mmol, 22 %) of a yellow solid.

^{1}H-NMR (C_6D_6, 300 MHz, 300 K) δ (ppm) = 0.73 (m, 35-H, 6 H), 0.82 (m, 16-H, 12 H), 0.97 (m, 12-H, 8 H), 1.05 (m, 14-H, 8 H), 1.09 (m, 13-H, 8 H), 1.16 (m, 15-H, 8H), 1.28 (m, 29-H, 4 H), 1.30 (m, 28-H, 4 H), 1.51 (m, 30-H, 4 H), 1.56 (m, 27-H, 4 H), 1.64 (m, 34 H, 4 H), 1.86 (m, 11-H, 4 H), 1.94 (m, 11-H, 4 H), 2.13 (s, 21-H, 6 H), 2.50 (m, 26-H, m), 3.23 (m, 31-H, 4 H), 3.29 (s, 32-H, 4 H), 4.30 – 4.44 (m, 36-H, 8 H), 6.99 (m, 19-H, 4H), 7.08 (m, 24-H, 4 H), 7.23 (d, 3-H, 2 H), 7.27 (m, 18-H, 4 H), 7.32 (m, 23-H, 4 H), 7.43 (m, 1-H, 2 H), 7.54 (m, 4-H, 2 H), 7.67 (s, 9-H, 2 H).

^{13}C-NMR-APT (C_6D_6, 75 MHz, 300 K) δ (ppm) = 8.4 (35-C), 14.3 (16-C), 20.8 (21-C), 23.0 (15-C), 24.5 (12-C), 26.5 (29-C), 27.1 (34-C), 29.5 (28-C), 30.0 (30-C), 30.2 (13-C), 32.0 (14-C, 27-C), 35.7 (26-C), 40.9 (11-C), 43.6 (33-C), 55.1 (10-C), 71.7 (31-C), 73.8 (32-C), 78.2 (36-C), 113.6 (9-C), 119.2 (1-C), 120.7 (4-C), 123.4 (3-C), 124.4 (23-C), 124.7 (18-C), 129.6 (24-C), 130.3 (19 C), 132.3 (20-C), 136.9 (5-C), 137.2 (25-C), 140.6 (7-C), 146.5 (17-C), 146.8 (22-C), 147.9 (2-C), 150.7 (8-C), 153.0 (6-C).

HR-LIFDI-MS ($C_{94}H_{128}N_2O_4$) (m/z): calc.: 1348.98686, found: 1348.98712.

2. Cyclic Voltammetry

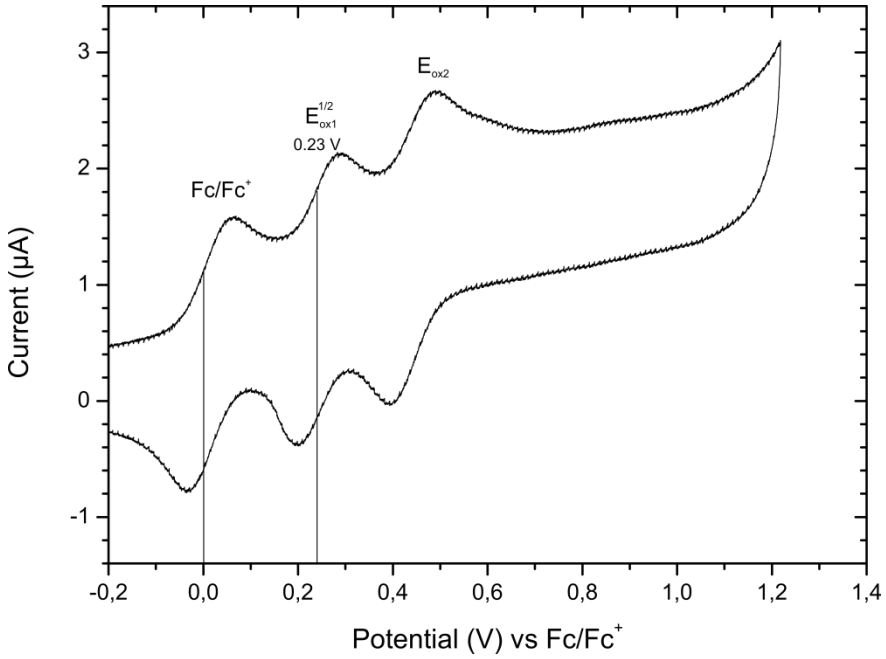


Figure S2. Cyclic voltammogram of REF **9a** in DCM (0.1 M Bu_4NPF_6), calibrated by the formal potential of ferrocene $FeCp_2/FeCp_2^+$.

3. OLED Devices

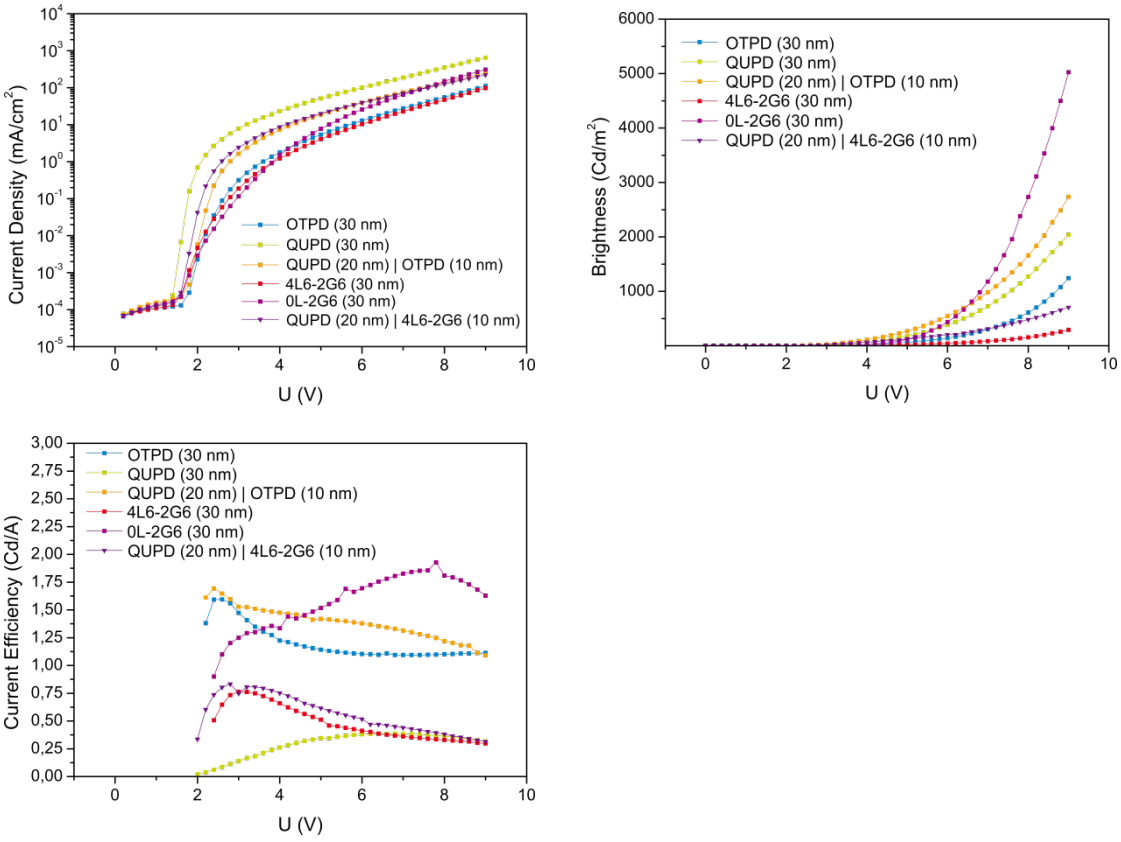


Figure S3. Performance data of crosslinked multilayer OLEDs of the general architecture ITO/PEDOT/HTL(30nm)/F8BT(80nm)/CsF/Al with various HTL configurations (given in the plots).

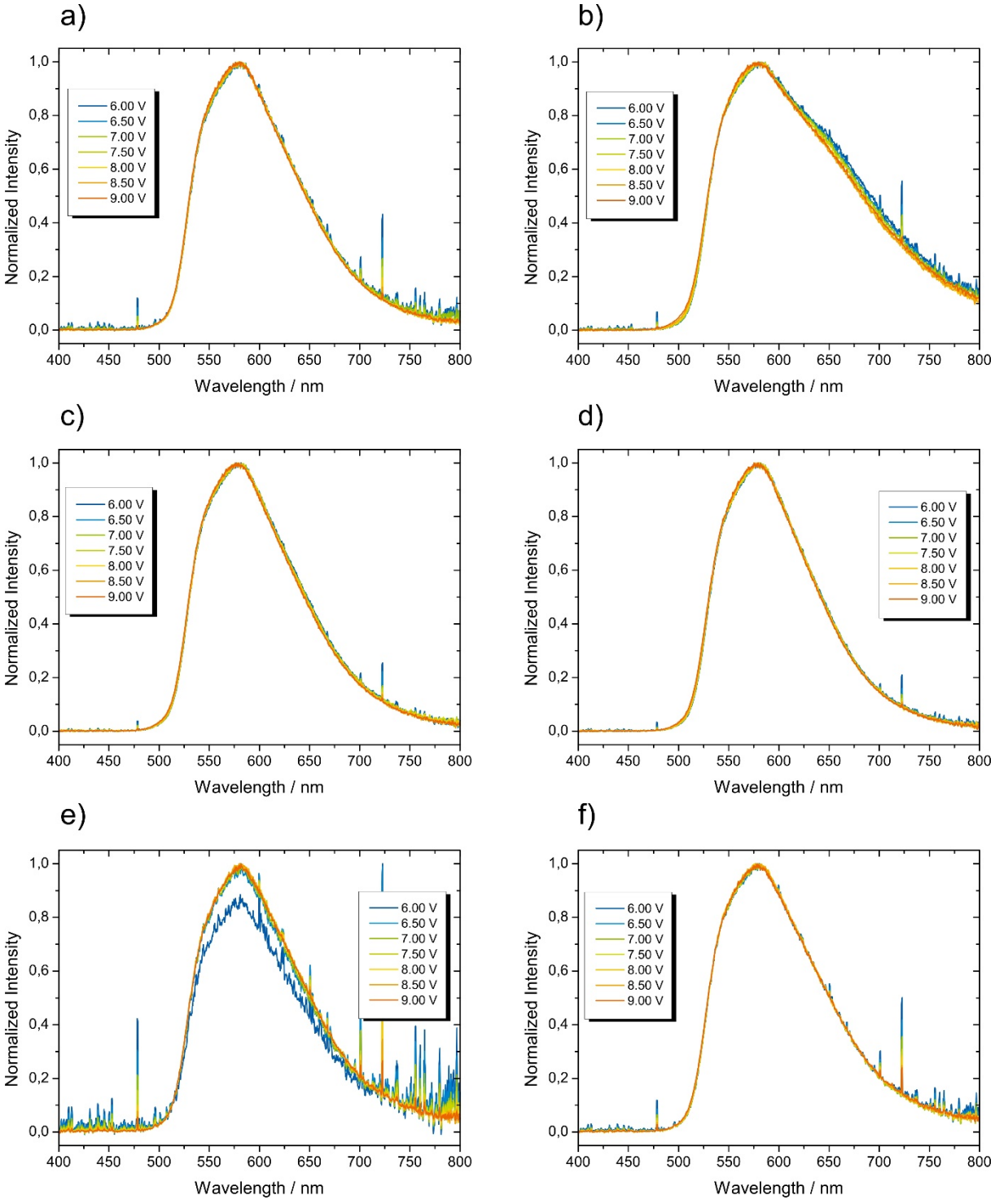


Figure S4. Electroluminescence spectra of crosslinked multi-layer OLED devices (ITO/PEDOT/HTL(30nm)/F8BT(80nm)/CsF/Al) with various crosslinked HTL configurations under various driving voltages: a) OTPD, b) QUPD, c) QUPD (20 nm)/OTPD (10 nm), d) 0L-2G6, e) 4L6-2G6, f) QUPD (20 nm)/4L6-2G6 (10 nm).

4. NMR spectra

4.1. (3-Ethyloxetane-3-yl)methanol 1

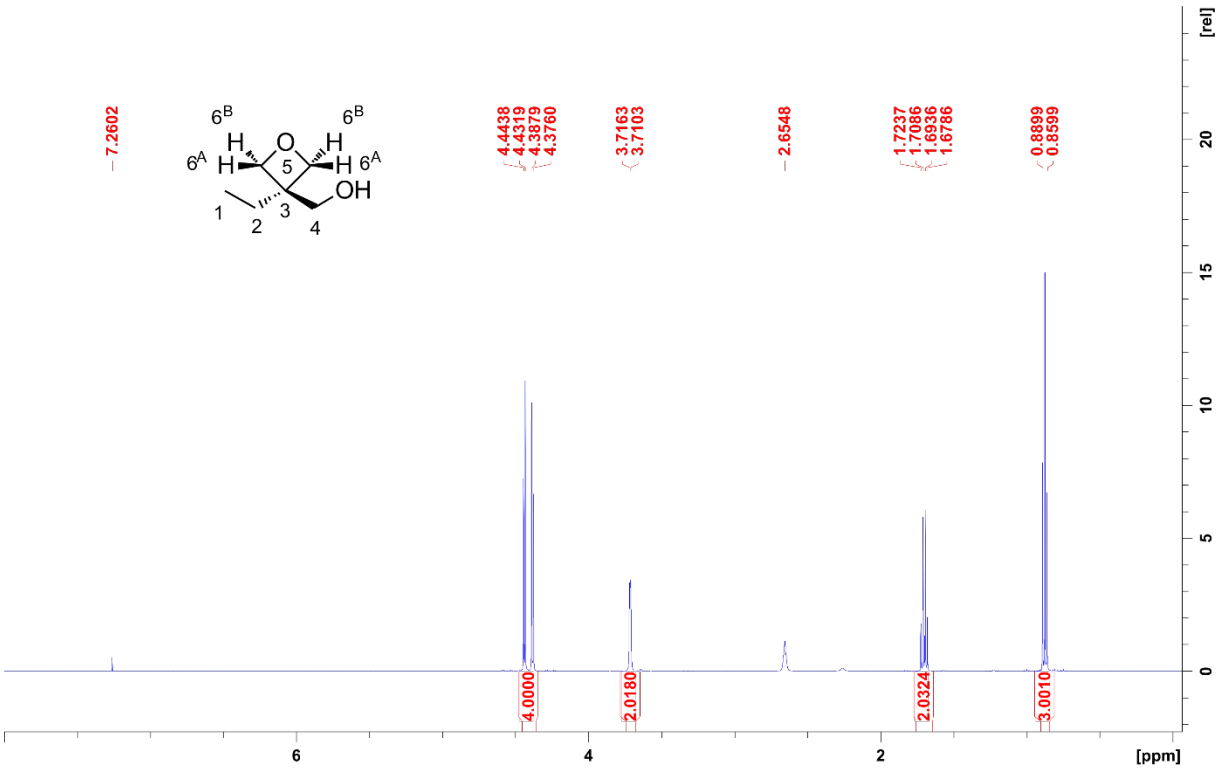


Figure S4. ^{1}H-NMR spectrum of (3-Ethyloxetane-3-yl)methanol **1** ($CDCl_3$, 500 MHz, 300 K).

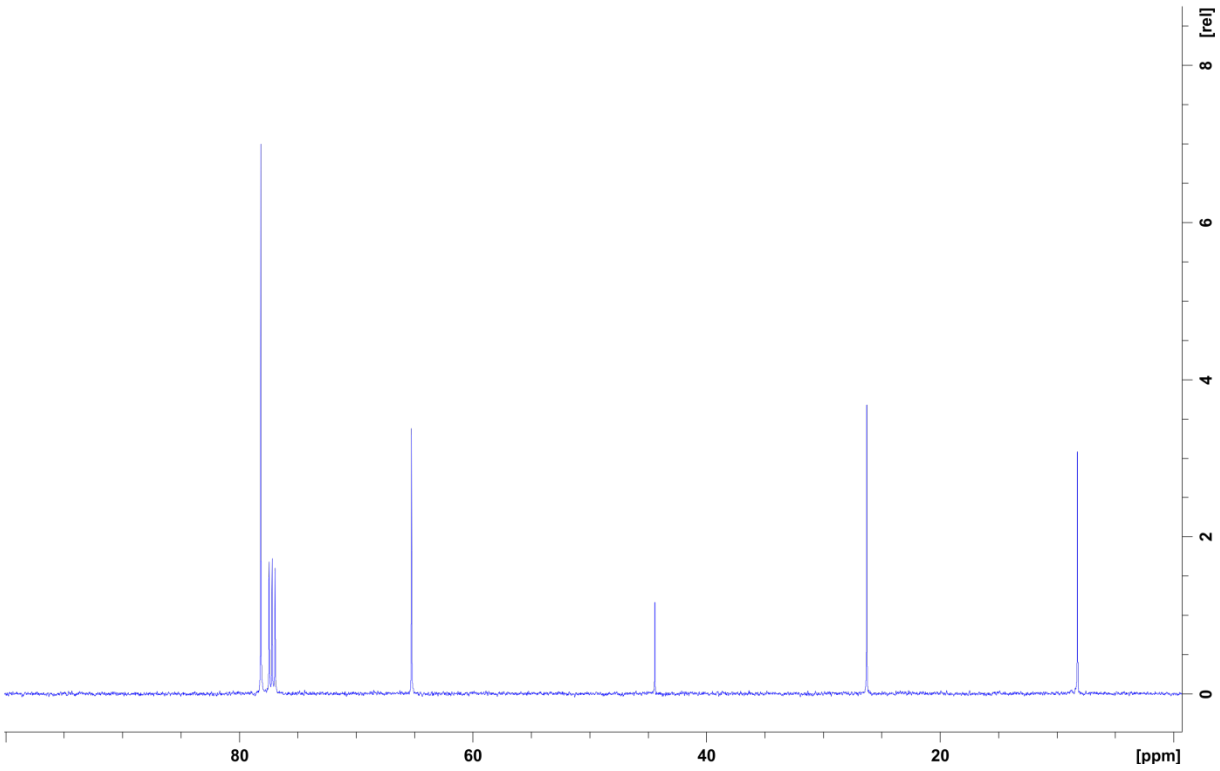


Figure S5. ^{13}C-NMR spectrum of (3-Ethyloxetane-3-yl)methanol **1** ($CDCl_3$, 125 MHz, 300 K).

4.2. 3-(((4-Bromobutyl)oxy)methyl)-3-ethyloxetane 2a

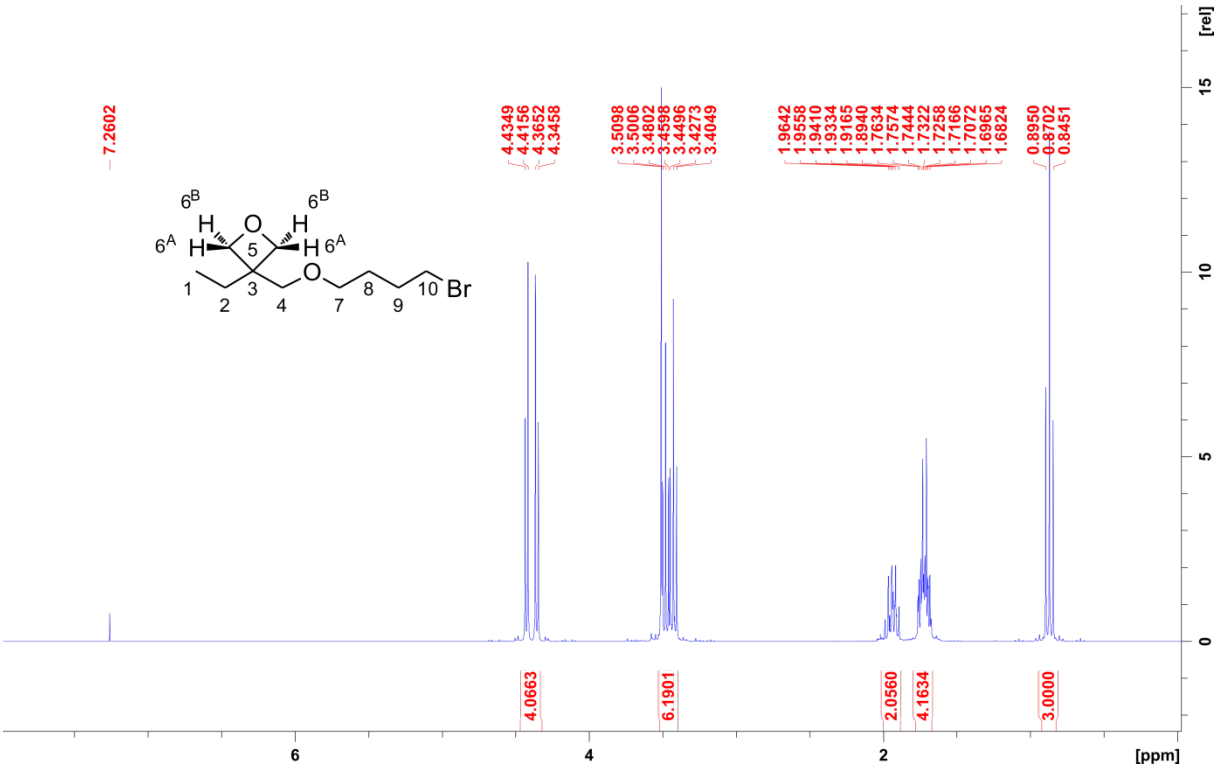


Figure S6. ^{1}H-NMR spectrum of 3-(((4-Bromobutyl)oxy)methyl)-3-ethyloxetane **2a** ($CDCl_3$, 300 MHz, 300 K).

4.3. 3-(((5-Bromopentyl)oxy)methyl)-3-ethyloxetane 2b

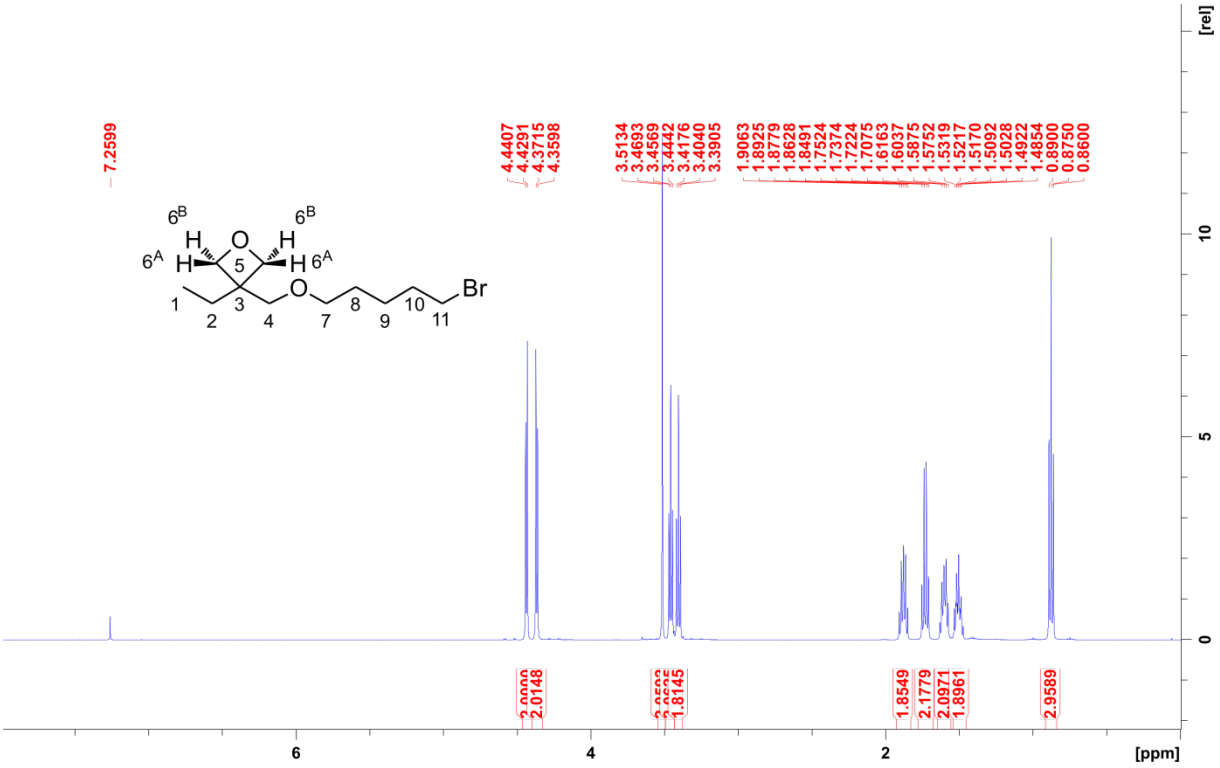


Figure S7. ^{1}H-NMR spectrum of 3-(((5-Bromopentyl)oxy)methyl)-3-ethyloxetane **2b** ($CDCl_3$, 500 MHz, 300 K).

4.4. 3-(((6-Bromohexyl)oxy)methyl)-3-ethyloxetane 2c

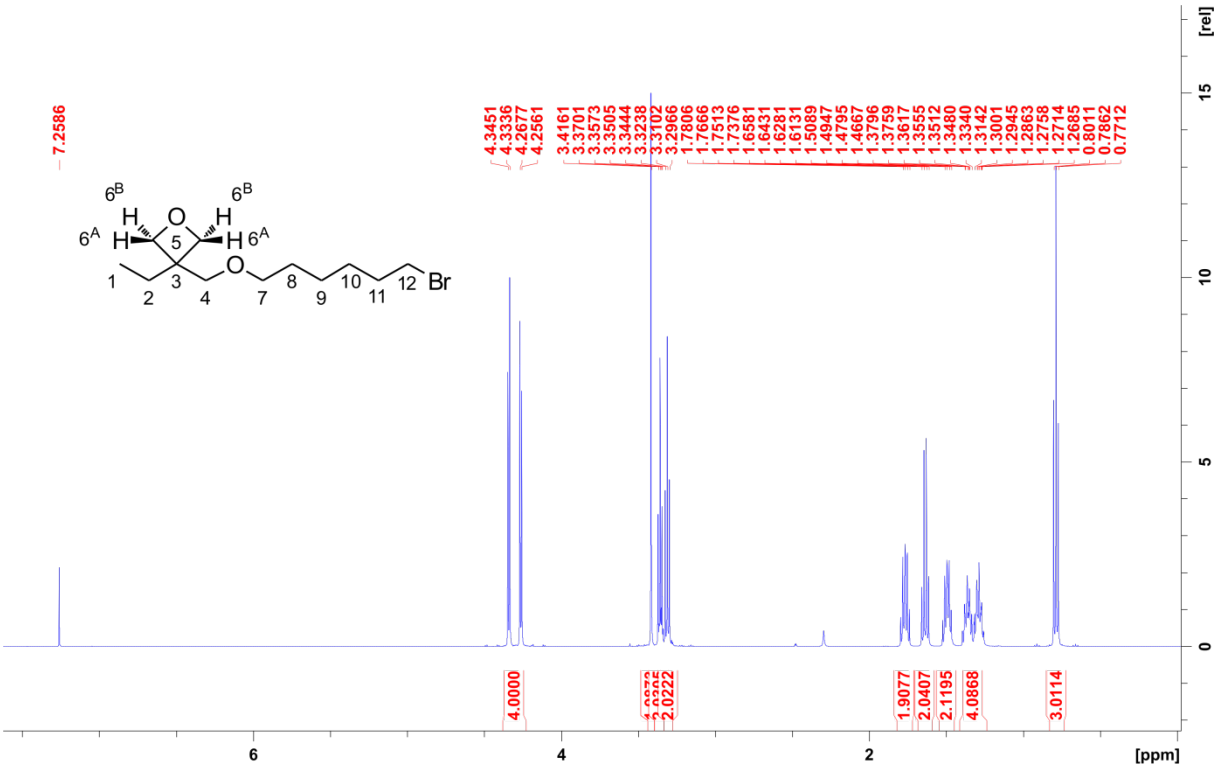


Figure S8. ^{1}H-NMR spectrum of 3-(((6-Bromohexyl)oxy)methyl)-3-ethyloxetane **2c** ($CDCl_3$, 500 MHz, 300 K).

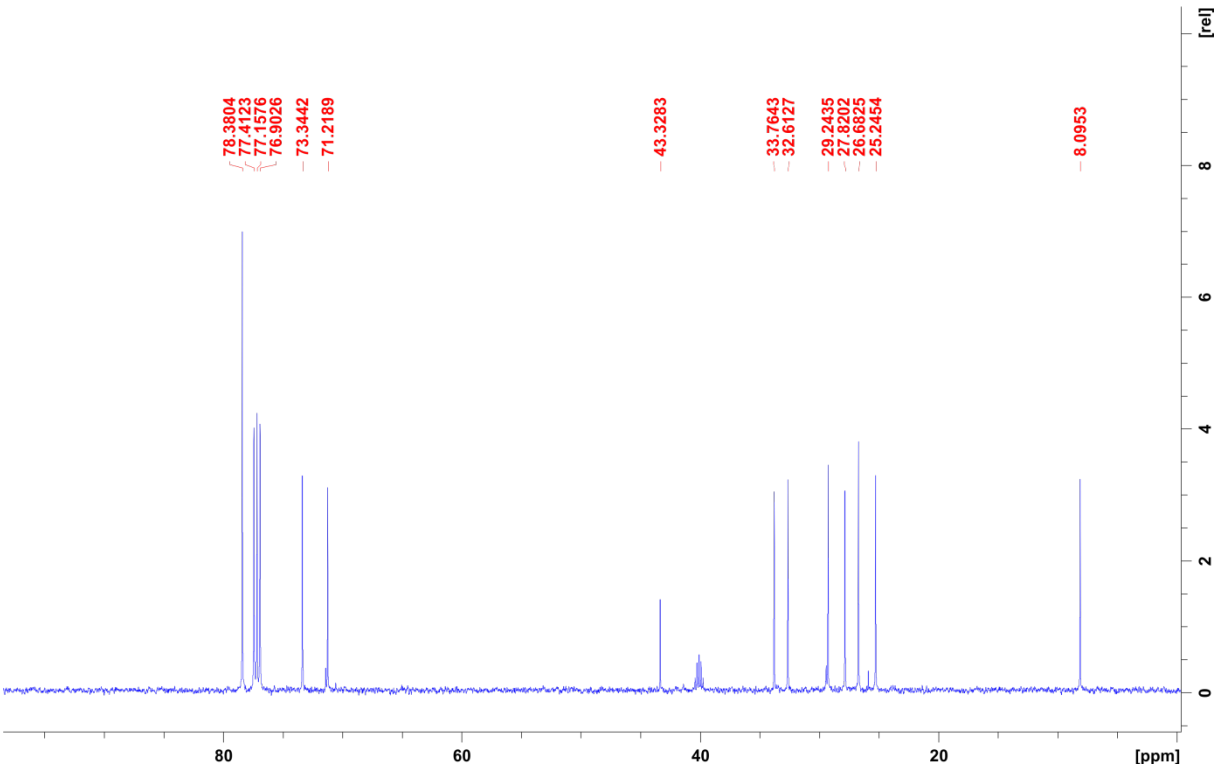


Figure S9. ^{13}C-NMR spectrum of 3-(((6-Bromohexyl)oxy)methyl)-3-ethyloxetane **2c** ($CDCl_3$, 125 MHz, 300 K).

4.5. Potassium (6-((3-ethyloxetane-3-yl)methoxy)hexyltrifluoroborate 3

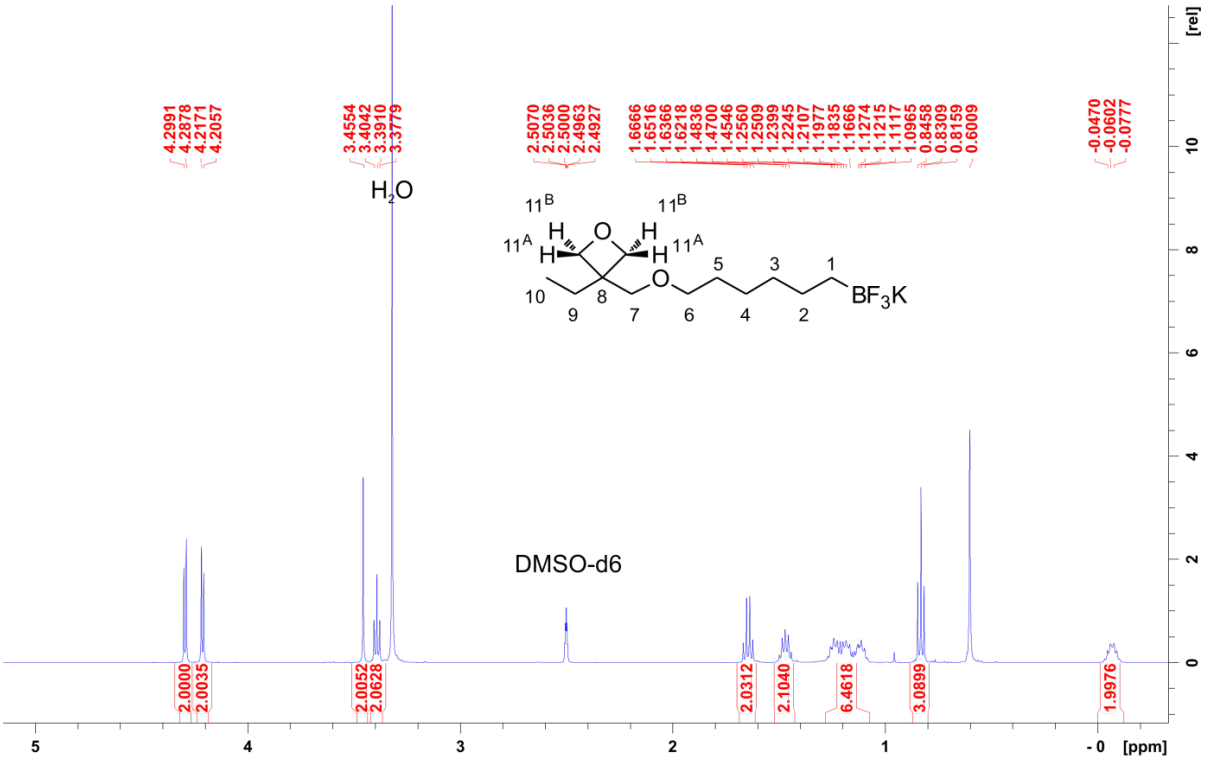


Figure S10. ^{1}H-NMR spectrum of potassium (6-((3-ethyloxetan-3-yl)methoxy)hexyltrifluoroborate **3** (DMSO-d_6, 500 MHz, 300 K).

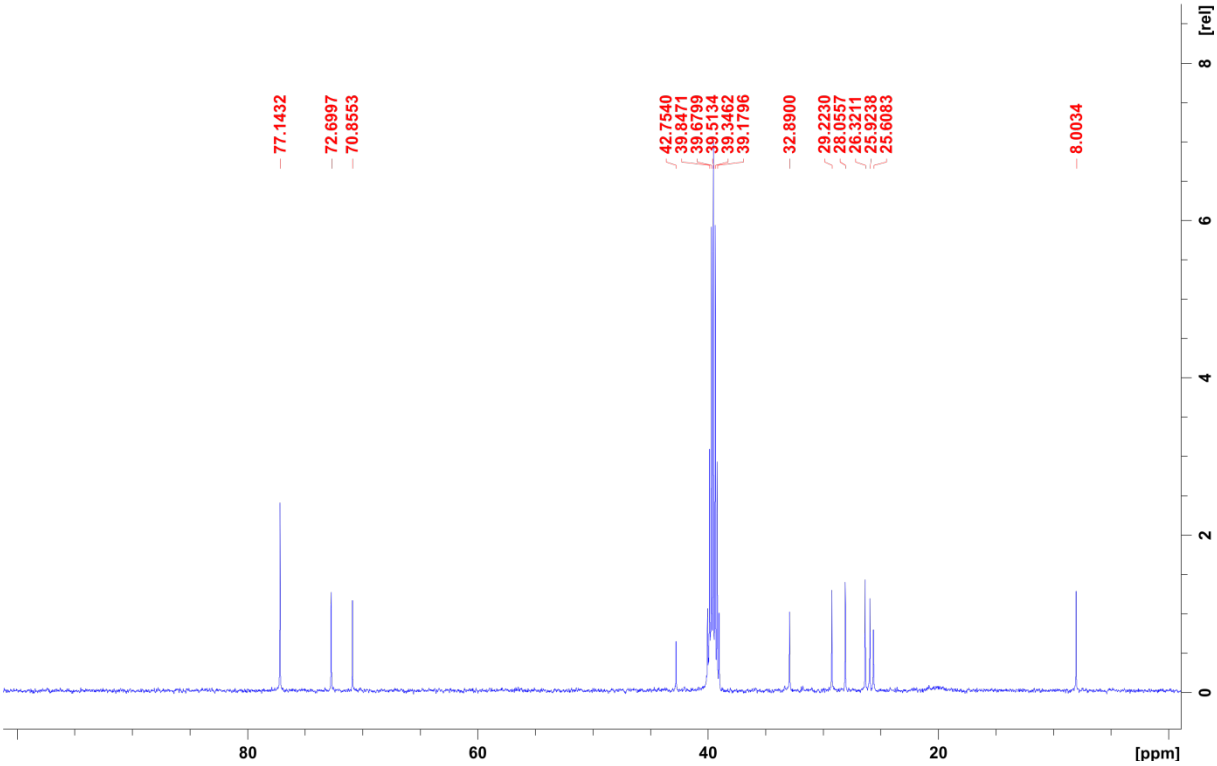


Figure S11. ^{13}C-NMR spectrum of potassium (6-((3-ethyloxetan-3-yl)methoxy)hexyltrifluoroborate **3** (DMSO-d_6, 125 MHz, 300 K).

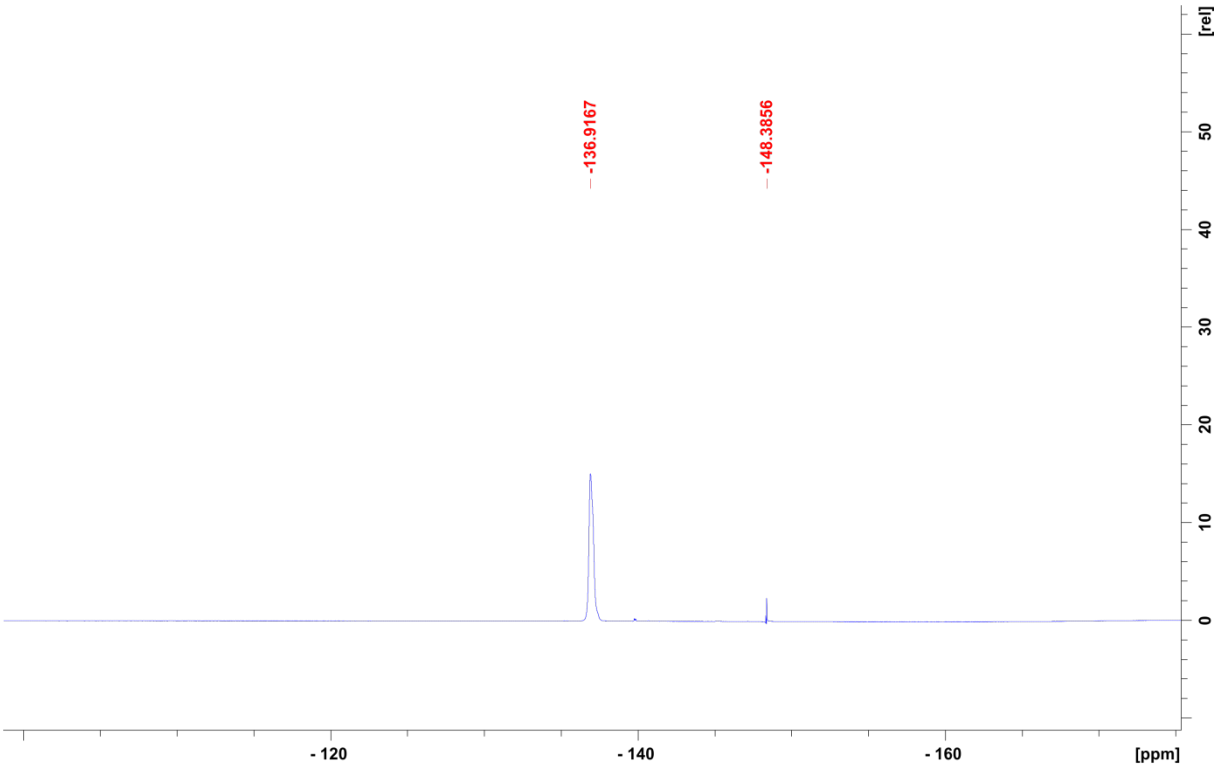


Figure S12. ^{19}F-NMR spectrum of potassium (6-((3-ethyloxetan-3-yl)methoxy)hexyltrifluoroborate **3** (DMSO-d_6, 470 MHz, 300 K).

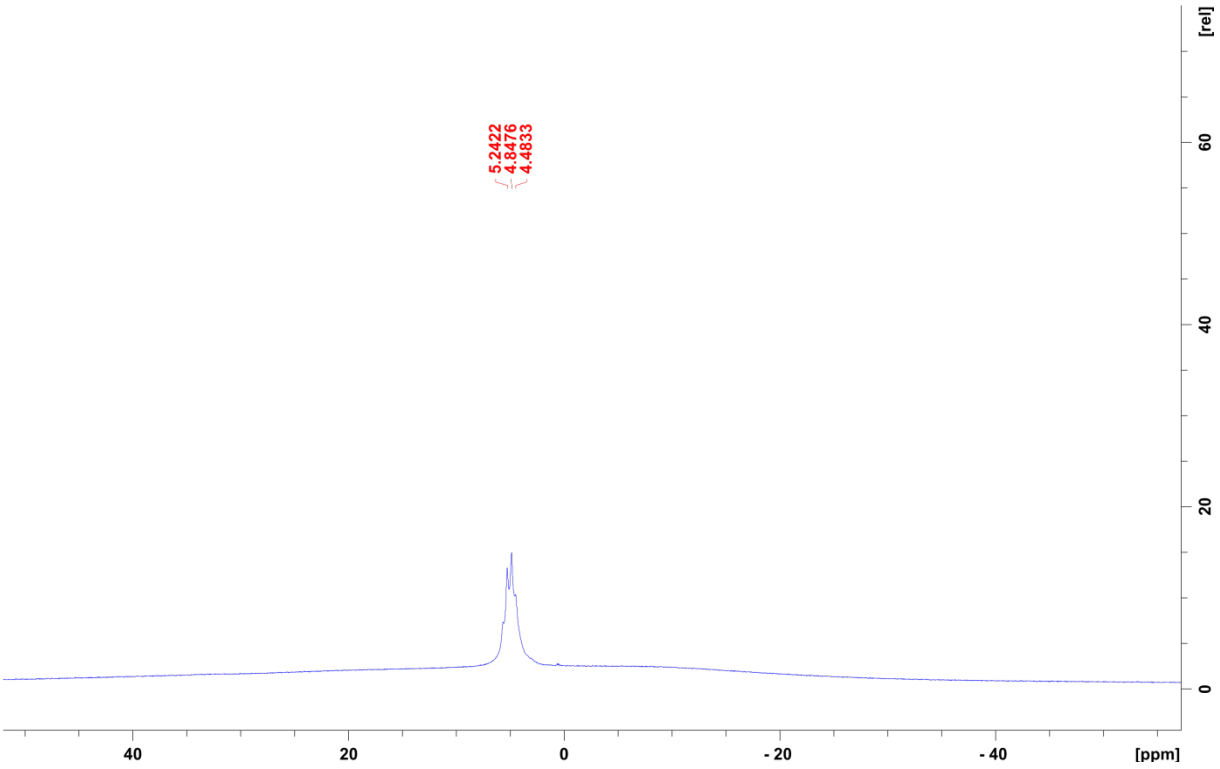


Figure S13. ^{11}B-NMR spectrum of potassium (6-((3-ethyloxetan-3-yl)methoxy)hexyltrifluoroborate **3** (DMSO-d_6, 160 MHz, 300 K).

4.6. 4-(6-((3-Ethyloxetane-3-yl)methoxy)hexyl)-*N*-phenylaniline 5a

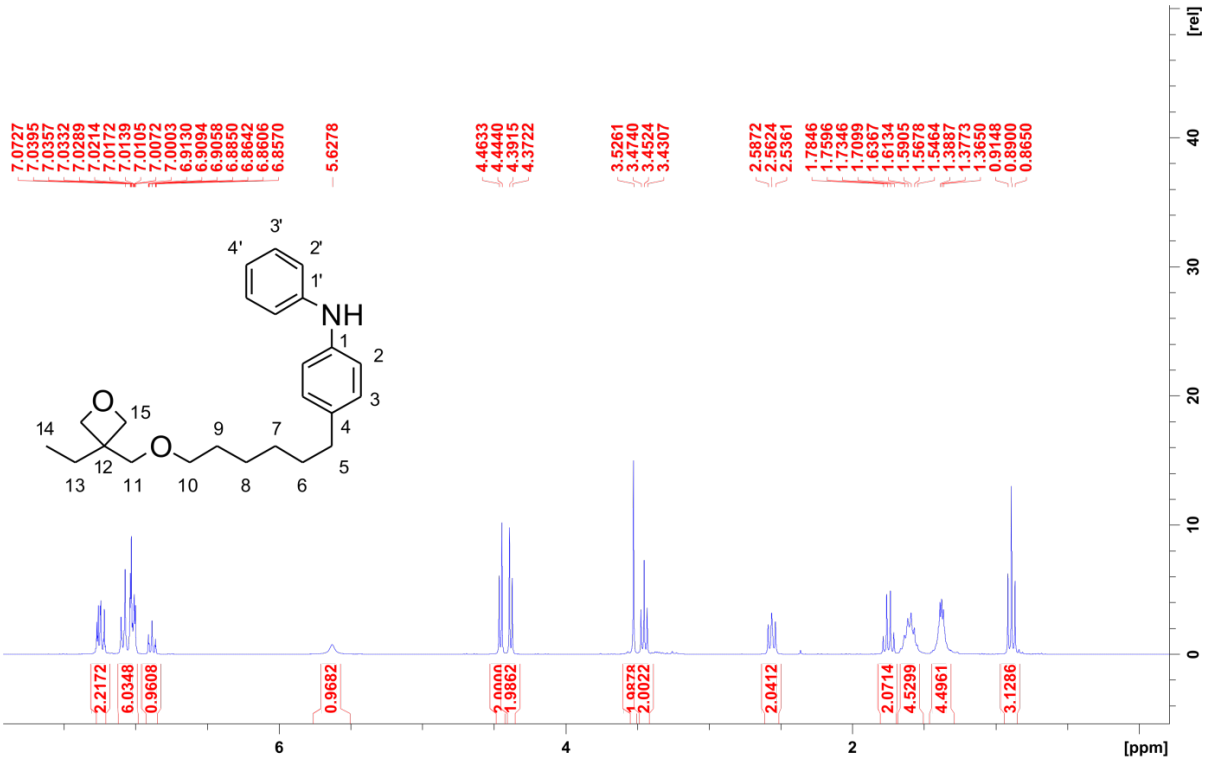


Figure S14. ^{1}H-NMR spectrum of 4-(6-((3-ethyloxetane-3-yl)methoxy)hexyl)-N-phenylaniline **5a** ($CDCl_3$, 300 MHz, 300 K).

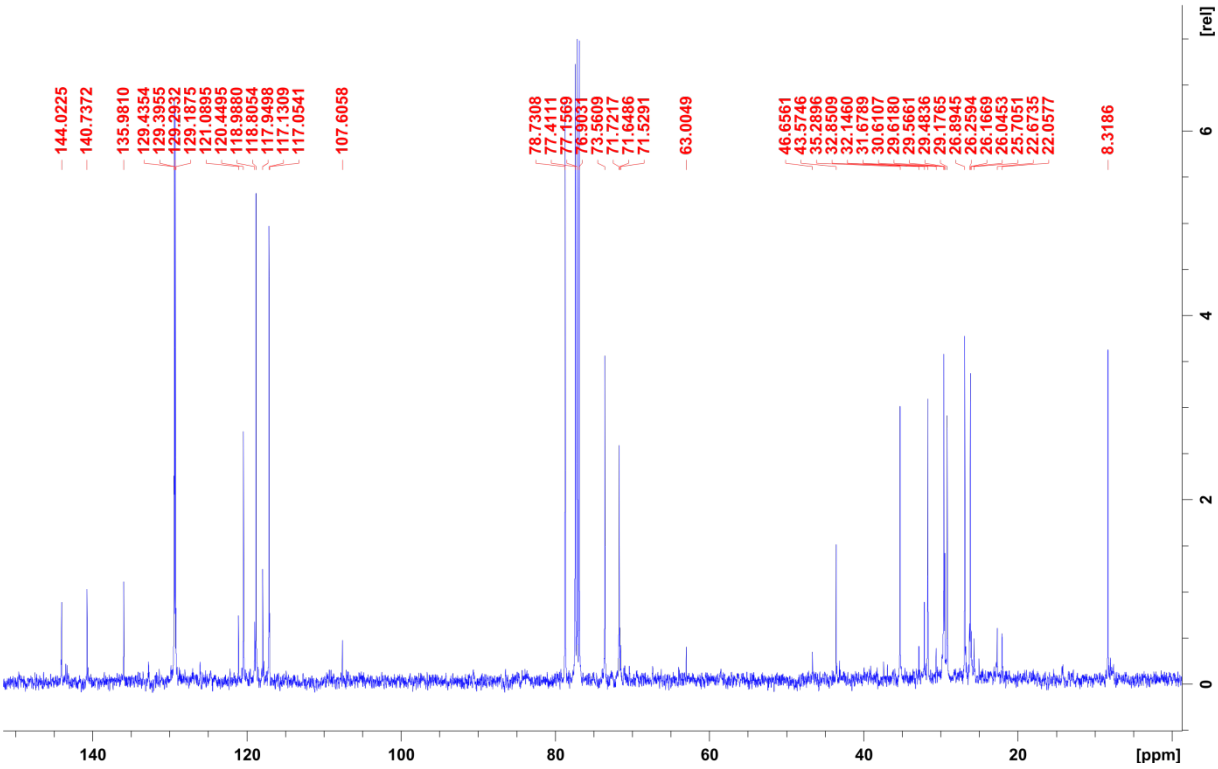


Figure S15. ^{13}C-NMR spectrum of 4-(6-((3-ethyloxetane-3-yl)methoxy)hexyl)-*N*-phenylaniline **5a** ($CDCl_3$, 125 MHz, 300 K).

4.7. Bis(4-(6-((3-ethyloxetan-3-yl)methoxy)hexyl)phenyl)amine 5b

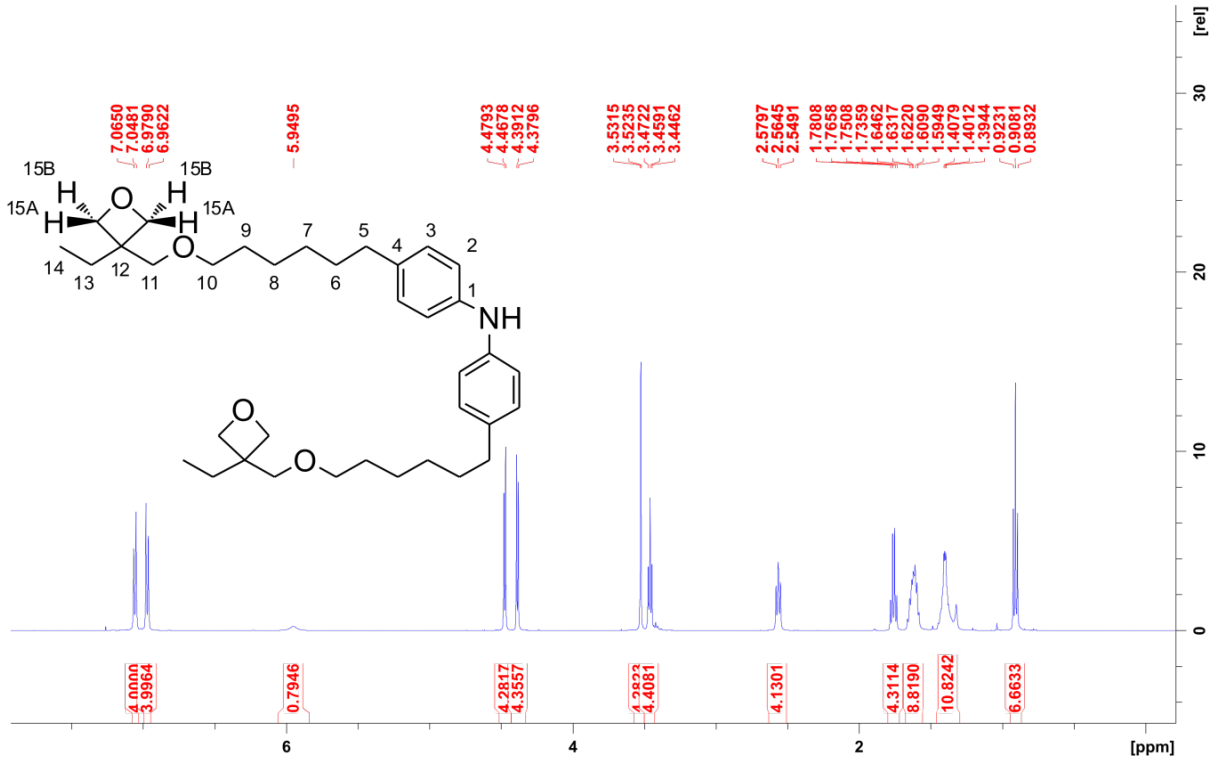


Figure S16. ^{1}H-NMR spectrum of bis(4-(6-((3-ethyloxetan-3-yl)methoxy)hexyl)phenyl)amine **5b** ($CDCl_3$, 500 MHz, 300 K).

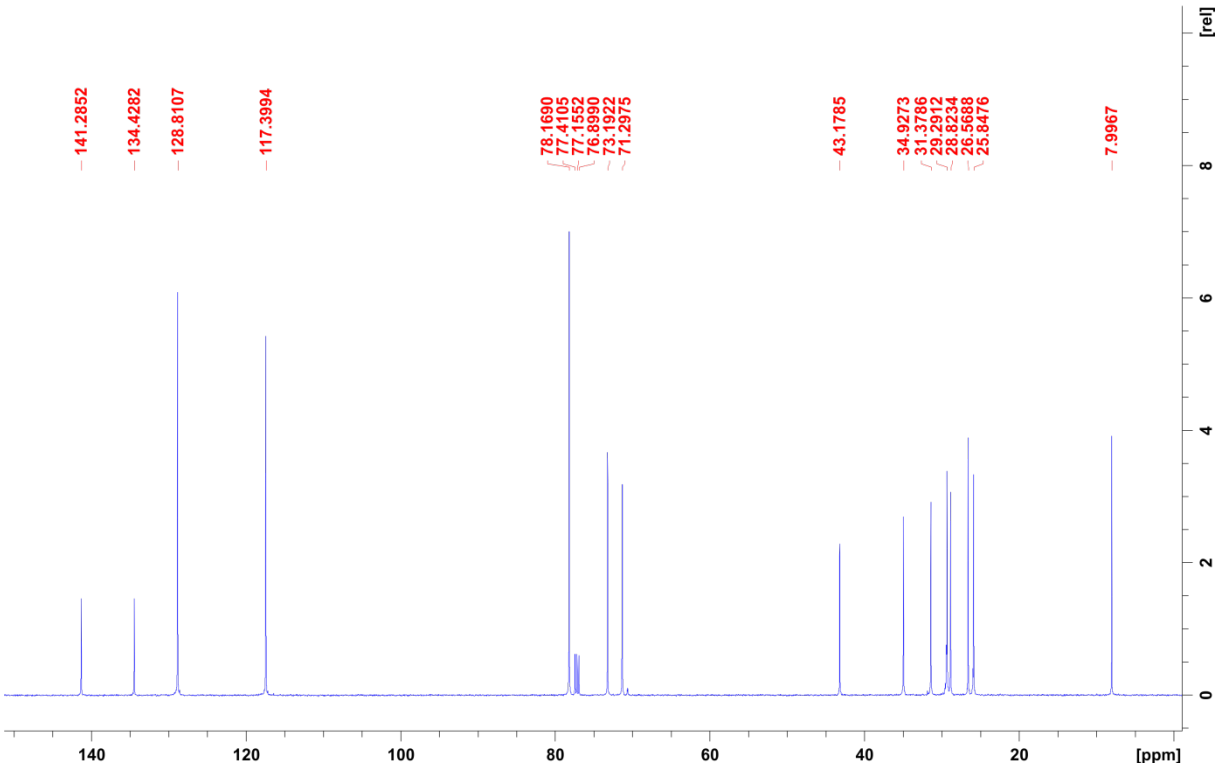


Figure S17. ^{13}C-NMR spectrum of bis(4-(6-((3-ethyloxetan-3-yl)methoxy)hexyl)phenyl)amine **5b** ($CDCl_3$, 125 MHz, 300 K).

4.8. 4,10-Dibromo-6,6‘-di(4-*tert.*-butylphenyl)-6,12-dihydroindeno[1,2-*b*]fluorene 7

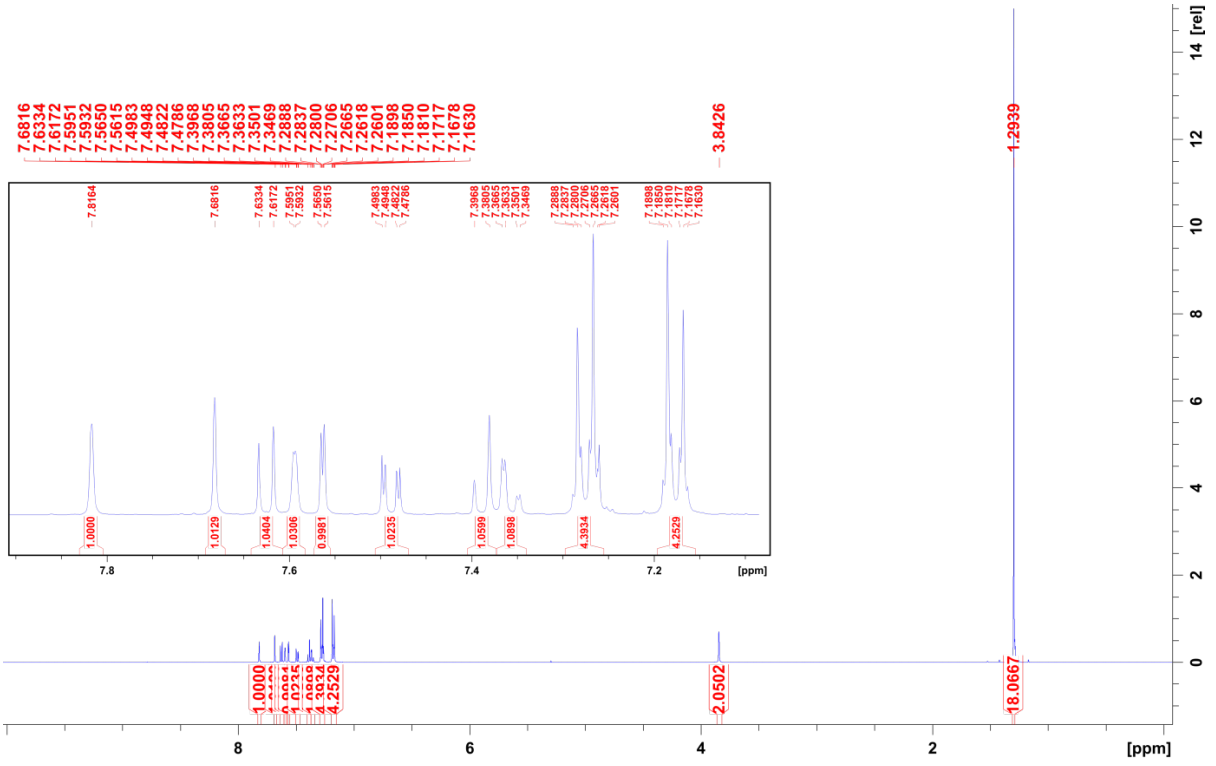


Figure S18. ^{1}H-NMR spectrum of 4,10-dibromo-6,6‘-di(4-*tert.*-butylphenyl)-6,12-dihydroindeno[1,2-*b*]fluorene **7** ($CDCl_3$, 500 MHz, 300 K).

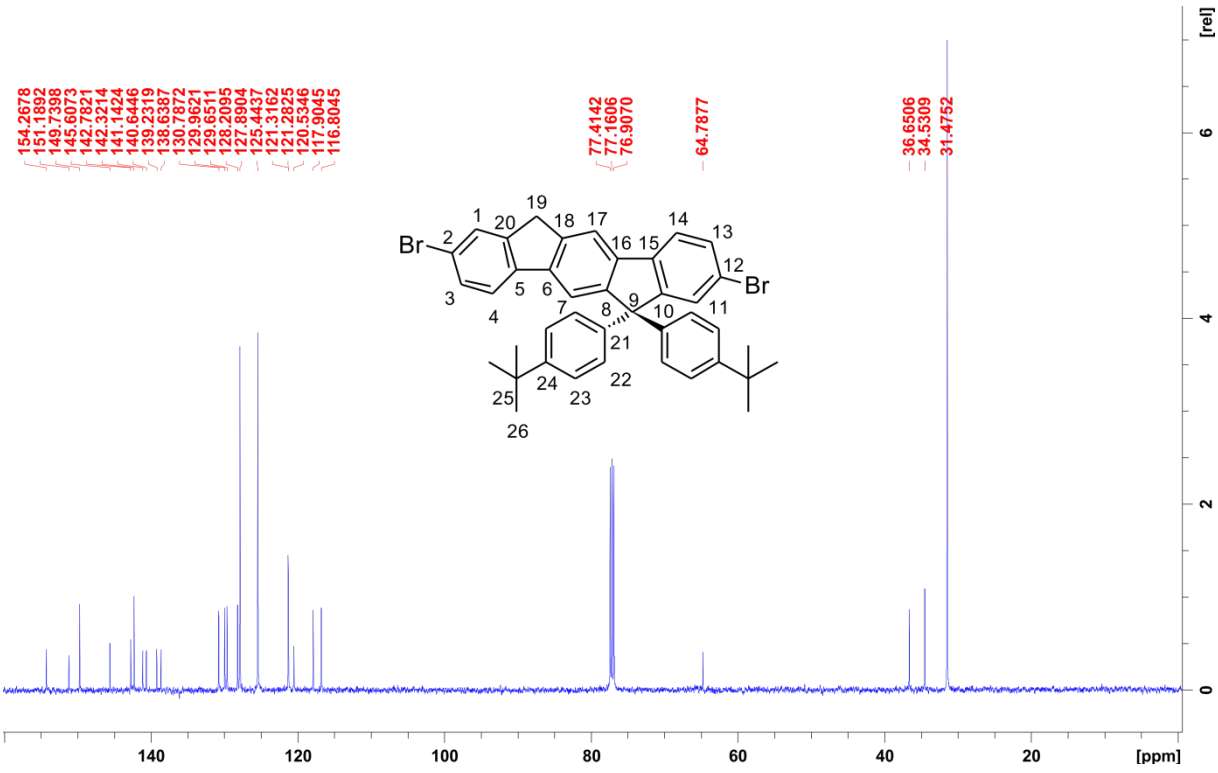


Figure S19. ^{13}C-NMR spectrum of 4,10-dibromo-6,6‘-di(4-*tert.*-butylphenyl)-6,12-dihydroindeno[1,2-*b*]fluorene **7** ($CDCl_3$, 125 MHz, 300 K).

4.9. 4,10-Dibromo-6,6‘-di(4-*tert.*-butylphenyl)-12,12‘-di-butyl-6,12-dihydroindeno[1,2-*b*]fluorene 8a

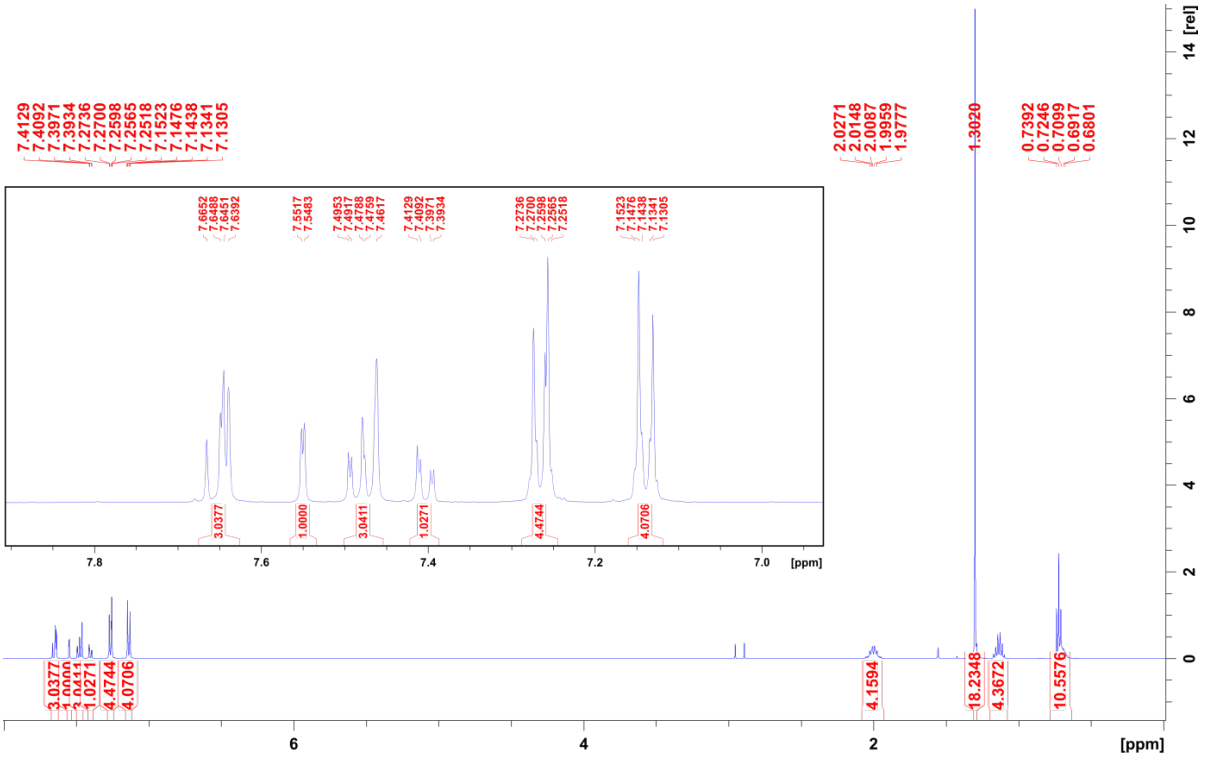


Figure S20. ^{1}H-NMR spectrum of 4,10-dibromo-6,6‘-di(4-*tert.*-butylphenyl)-12,12‘-di-butyl-6,12-dihydroindeno[1,2-*b*]fluorene **8a** ($CDCl_3$, 500 MHz, 300 K).

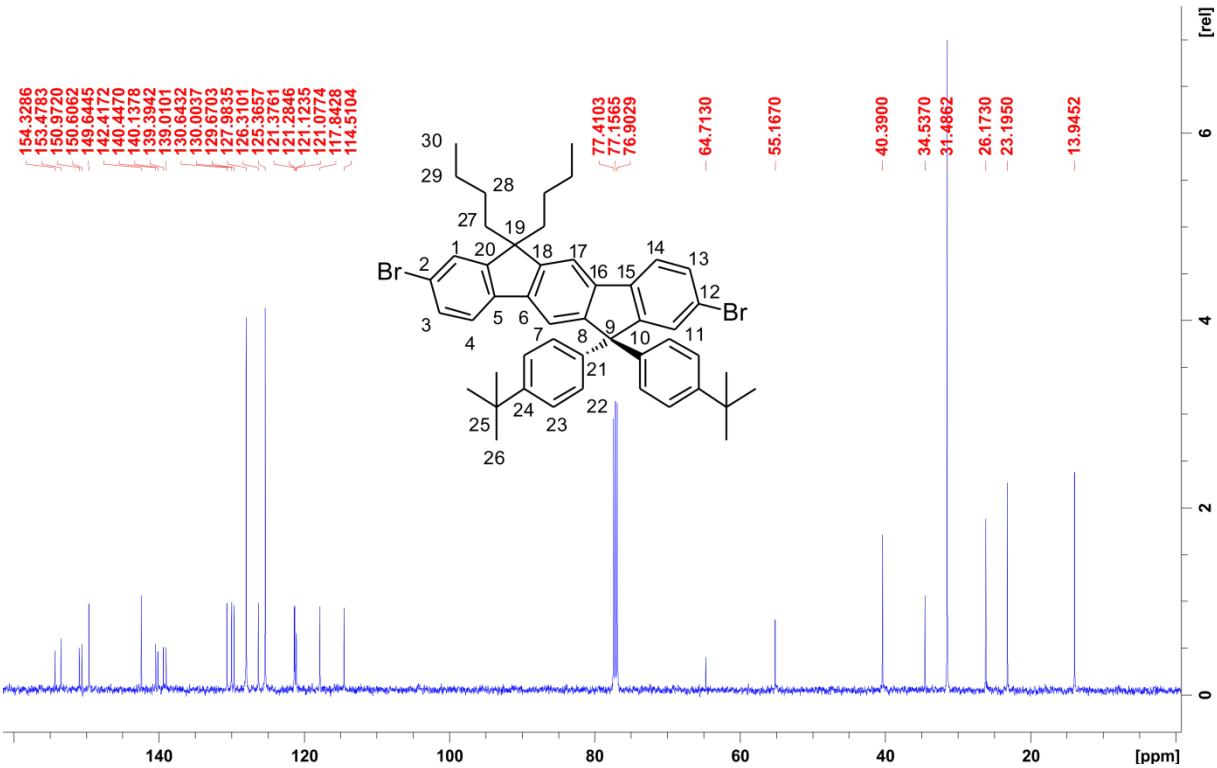


Figure S21. ^{13}C-NMR spectrum of 4,10-dibromo-6,6‘-di(4-*tert.*-butylphenyl)-12,12‘-di-butyl-6,12-dihydroindeno[1,2-*b*]fluorene **8a** ($CDCl_3$, 125 MHz, 300 K).

4.10. 4,10-Dibromo-6,6‘-di(4-*tert.*-butylphenyl)-12,12‘-di(3-ethyl(oxetane-3-methoxy)butyl)-6,12-dihydroindeno[1,2-*b*]fluorene 8b

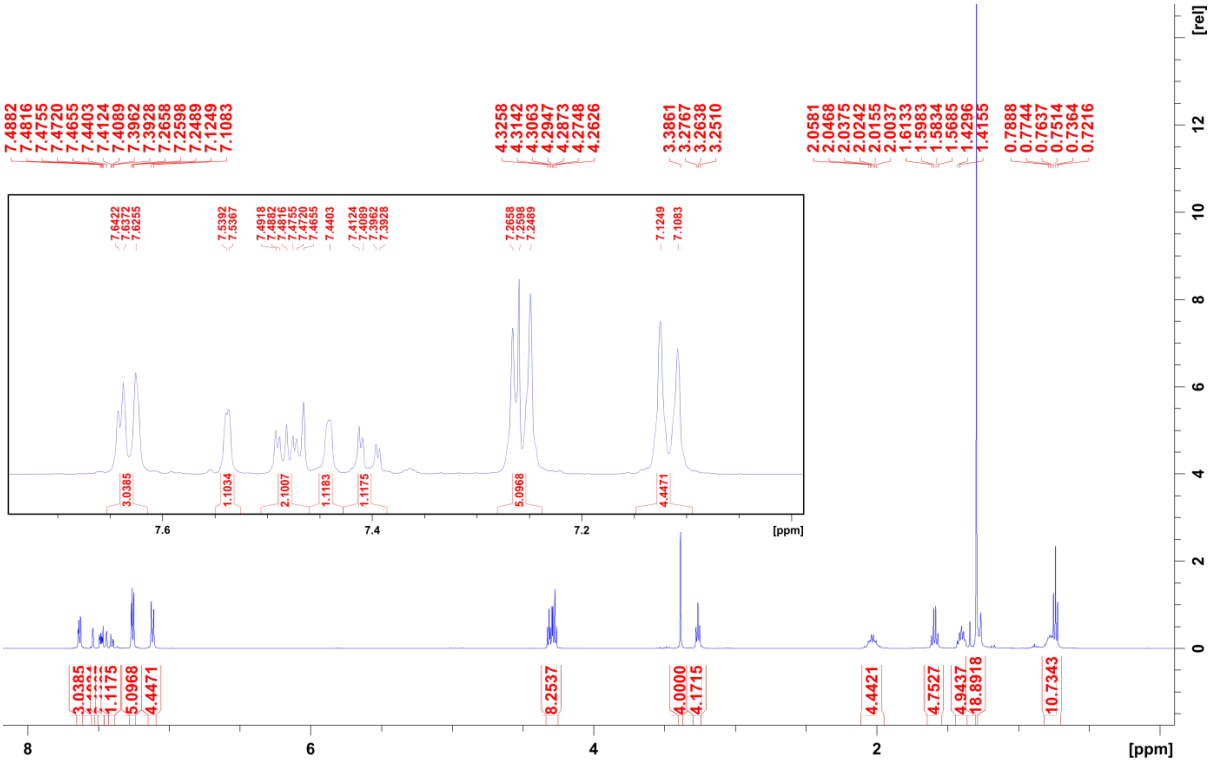


Figure S22. ^{1}H-NMR spectrum of 4,10-dibromo-6,6‘-di(4-*tert.*-butylphenyl)-12,12‘-di(3-ethyl(oxetane-3-methoxy)butyl)-6,12-dihydroindeno[1,2-*b*]fluorene **8b** ($CDCl_3$, 500 MHz, 300 K).

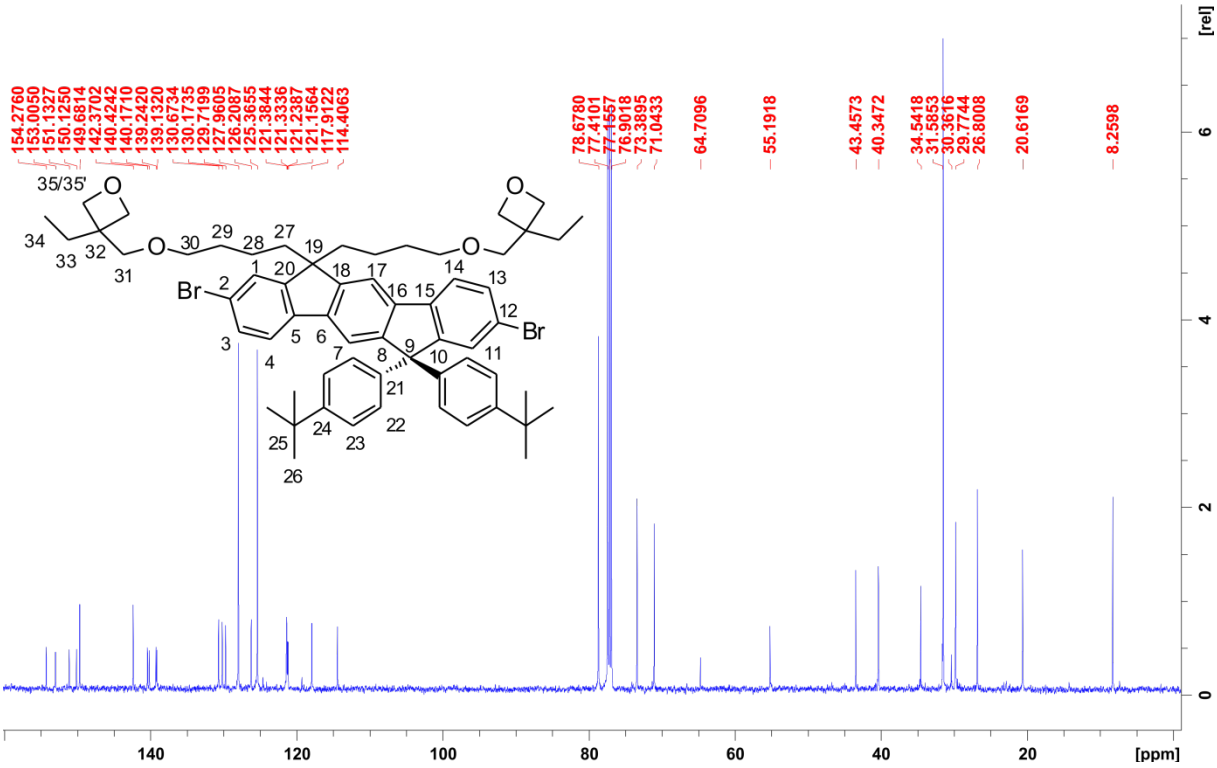


Figure S23. ^{13}C-NMR spectrum of 4,10-dibromo-6,6‘-di(4-*tert.*-butylphenyl)-12,12‘-di(3-ethyl(oxetane-3-methoxy)butyl)-6,12-dihydroindeno[1,2-*b*]fluorene **8b** ($CDCl_3$, 125 MHz, 300 K).

4.11. 4,10-Dibromo-6,6‘-di(4-*tert*.-butylphenyl)-12,12‘-di(3-ethyl(oxetane-3-methoxy)pentyl)-6,12-dihydroindeno[1,2-*b*]fluorene 8c

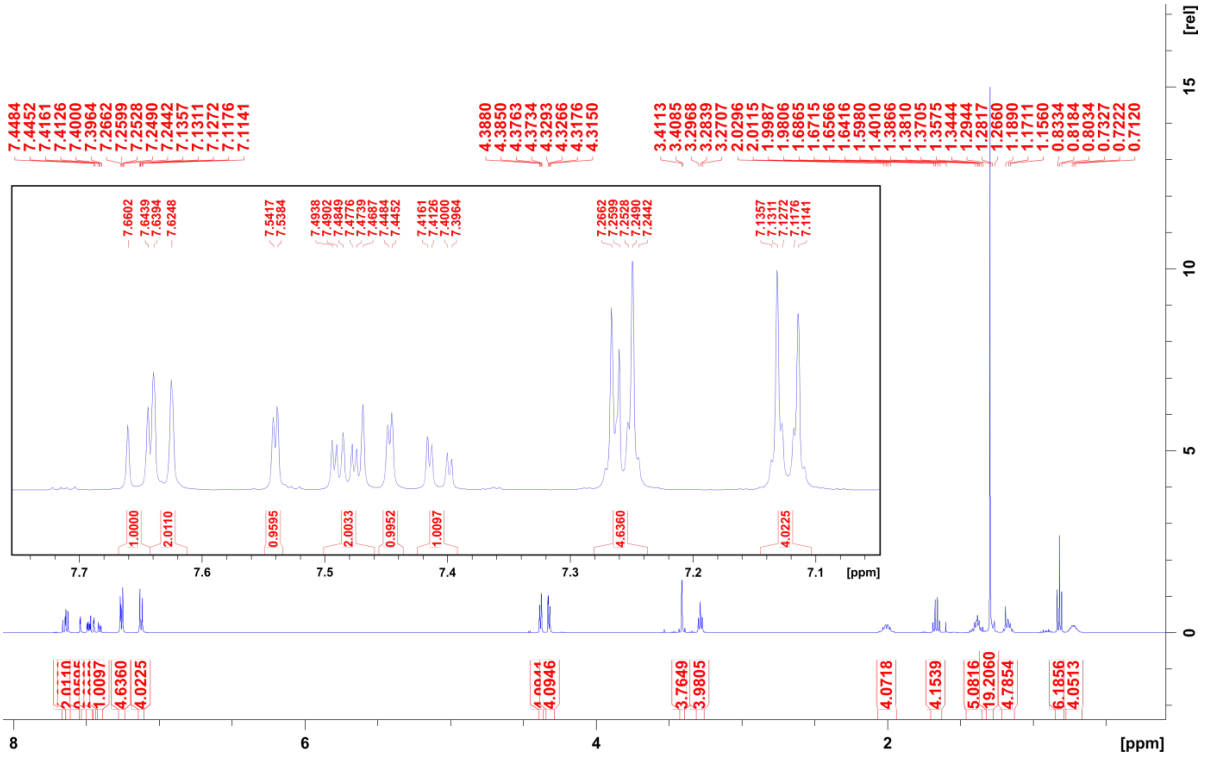


Figure S24. ^{1}H-NMR spectrum of 4,10-dibromo-6,6‘-di(4-*tert.*-butylphenyl)-12,12‘-di(3-ethyl(oxetane-3-methoxy)pentyl)-6,12-dihydroindeno[1,2-*b*]fluorene **8c** ($CDCl_3$, 500 MHz, 300 K).

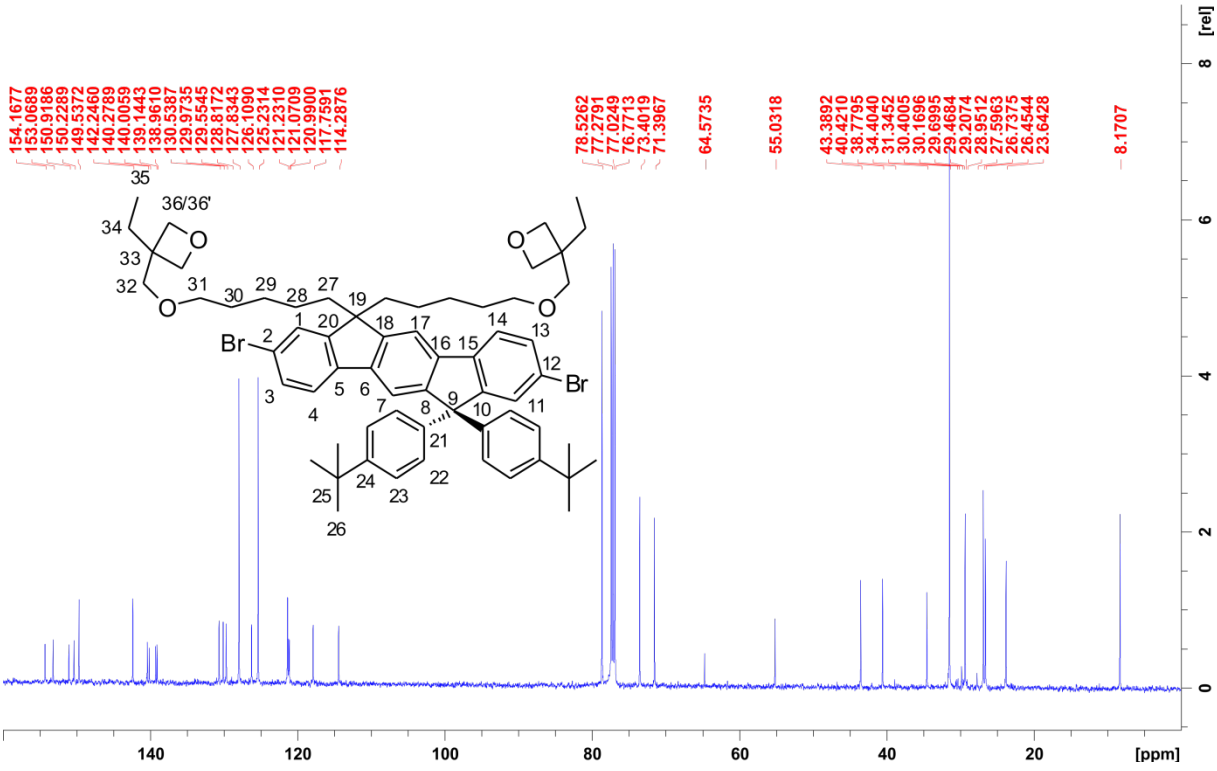


Figure S25. ^{13}C-NMR spectrum of 4,10-dibromo-6,6‘-di(4-*tert.*-butylphenyl)-12,12‘-di(3-ethyl(oxetane-3-methoxy)pentyl)-6,12-dihydroindeno[1,2-*b*]fluorene **8c** ($CDCl_3$, 125 MHz, 300 K).

4.12. 4,10-Dibromo-6,6‘-di(4-*tert.*-butylphenyl)-12,12‘-di(3-ethyl(oxetane-3-methoxy)hexyl)-6,12-dihydroindeno[1,2-*b*]fluorene 12d

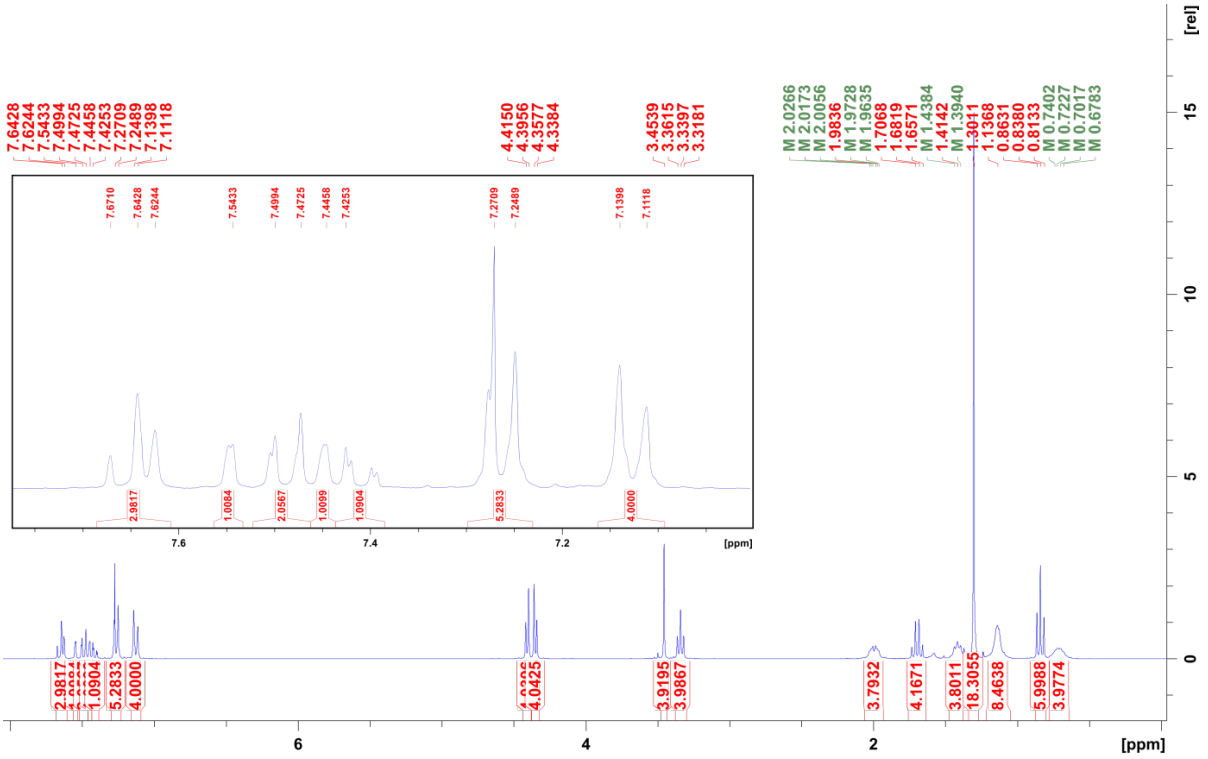


Figure S26. ^{1}H-NMR spectrum of 4,10-dibromo-6,6‘-di(4-tert.-butylphenyl)-12,12‘-di(3-ethyl(oxetane-3-methoxy)hexyl)-6,12-dihydroindeno[1,2-*b*]fluorene **8d** ($CDCl_3$, 300 MHz, 300 K).

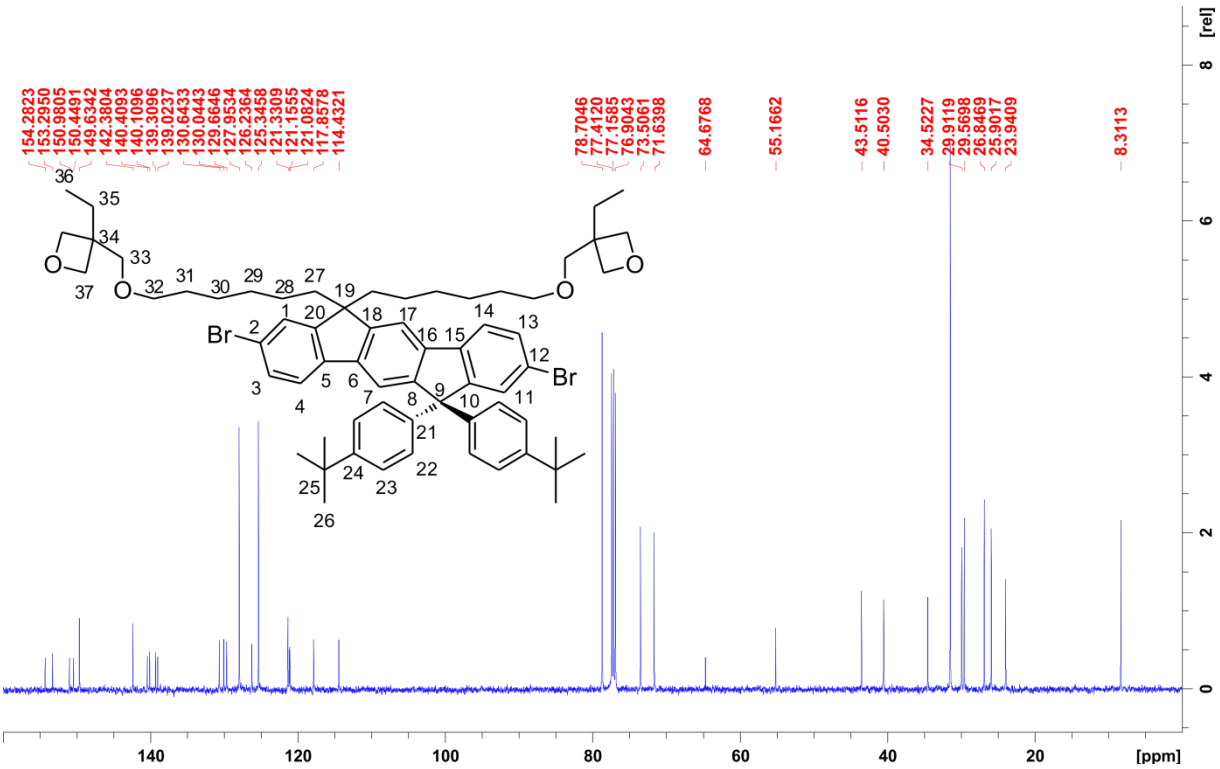


Figure S27. ^{1}H-NMR spectrum of 4,10-dibromo-6,6‘-di(4-tert.-butylphenyl)-12,12‘-di(3-ethyl(oxetane-3-methoxy)hexyl)-6,12-dihydroindeno[1,2-*b*]fluorene **8d** ($CDCl_3$, 125 MHz, 300 K).

4.13. REF 9a

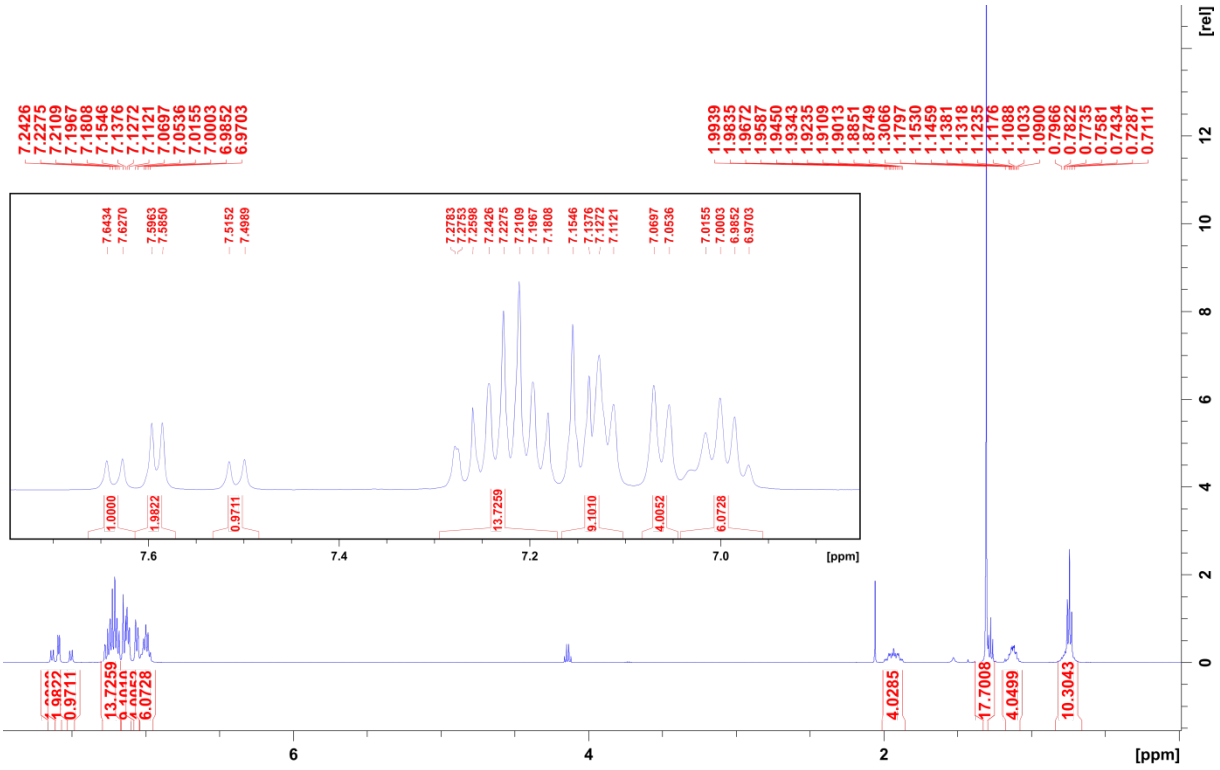


Figure S28. ^{1}H-NMR spectrum of REF **9a** ($CDCl_3$, 500 MHz, 300 K).

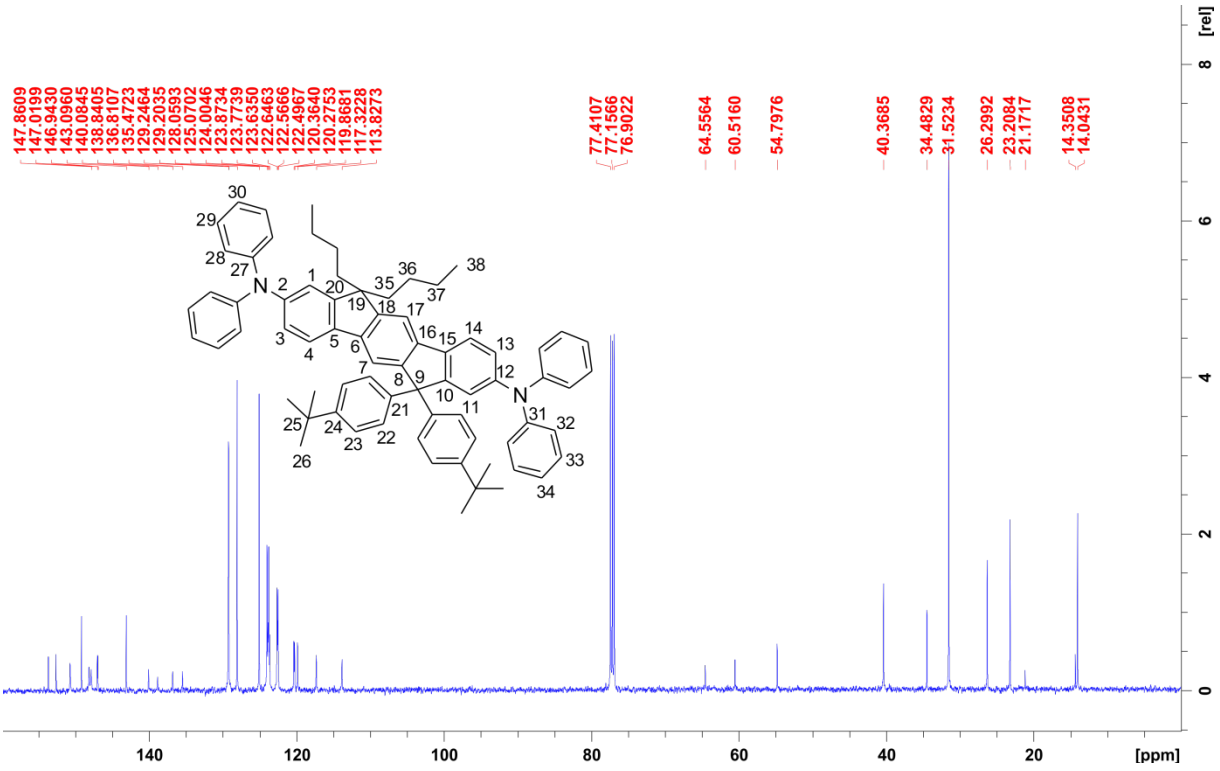


Figure S29. ^{13}C-NMR spectrum of REF **9a** ($CDCl_3$, 125 MHz, 300 K).

4.14. 0L-2G4 9b

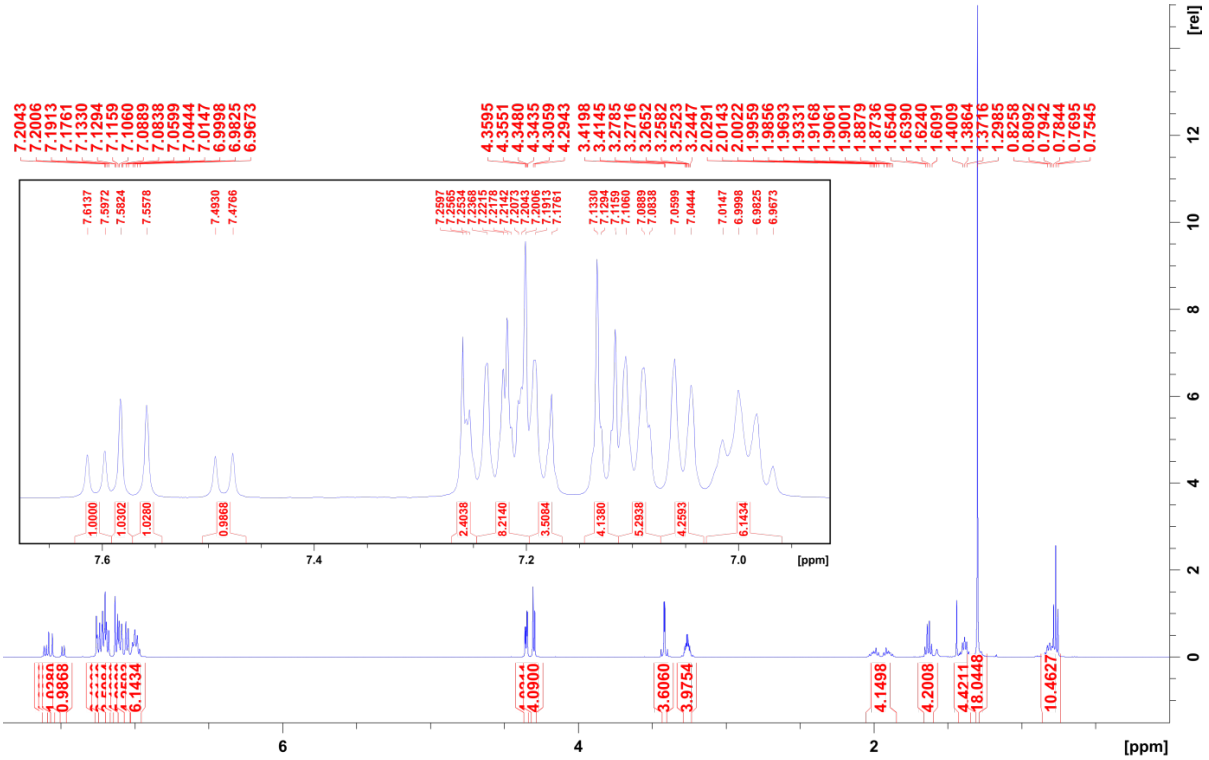


Figure S30. ^{1}H-NMR spectrum of 0L-2G4 **9b** ($CDCl_3$, 500 MHz, 300 K).

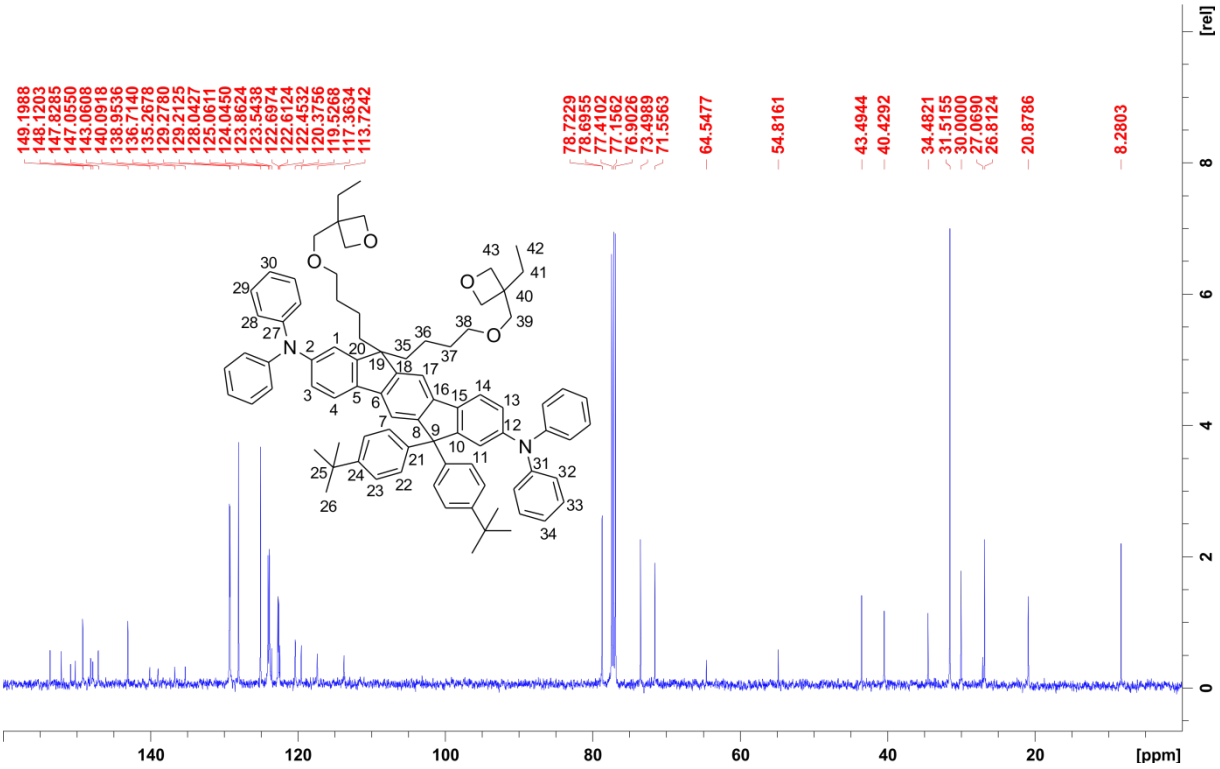


Figure S31. ^{13}C-NMR spectrum of 0L-2G4 **9b** ($CDCl_3$, 125 MHz, 300 K).

4.15. 0L-2G5 9c

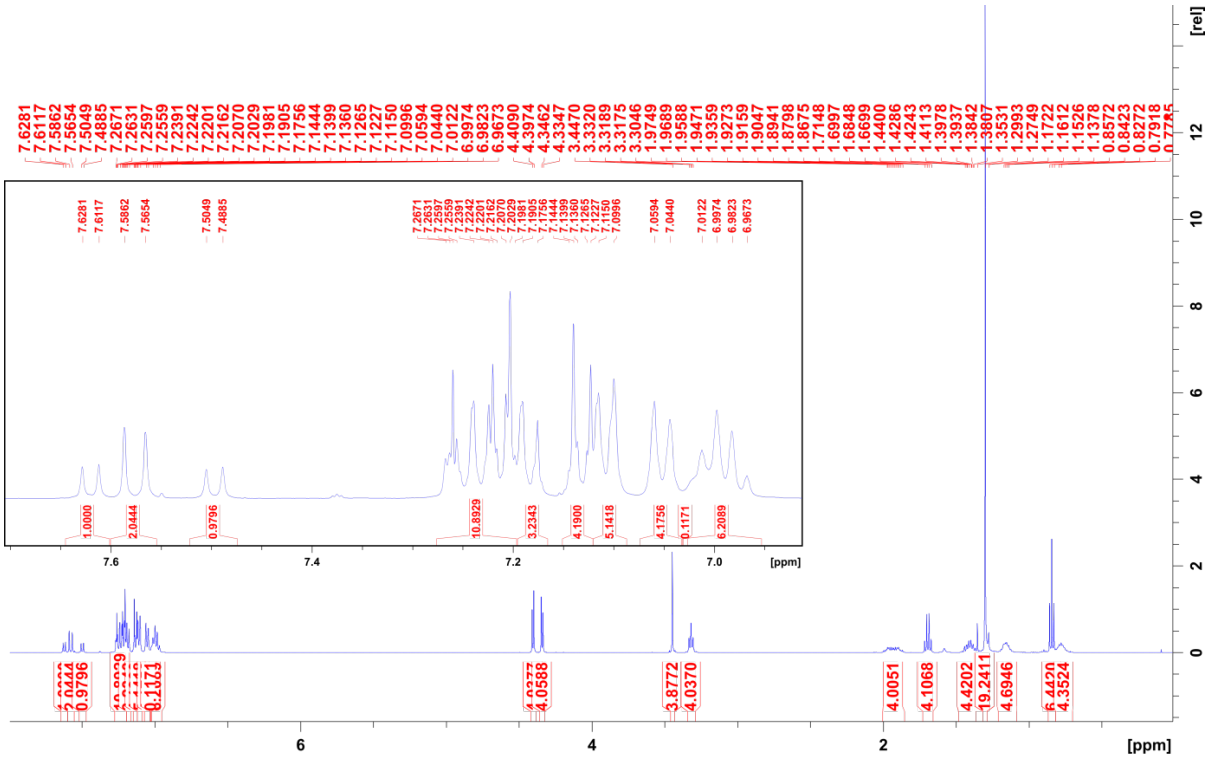


Figure S32. ^{1}H-NMR spectrum of 0L-2G5 **9c** ($CDCl_3$, 500 MHz, 300 K).

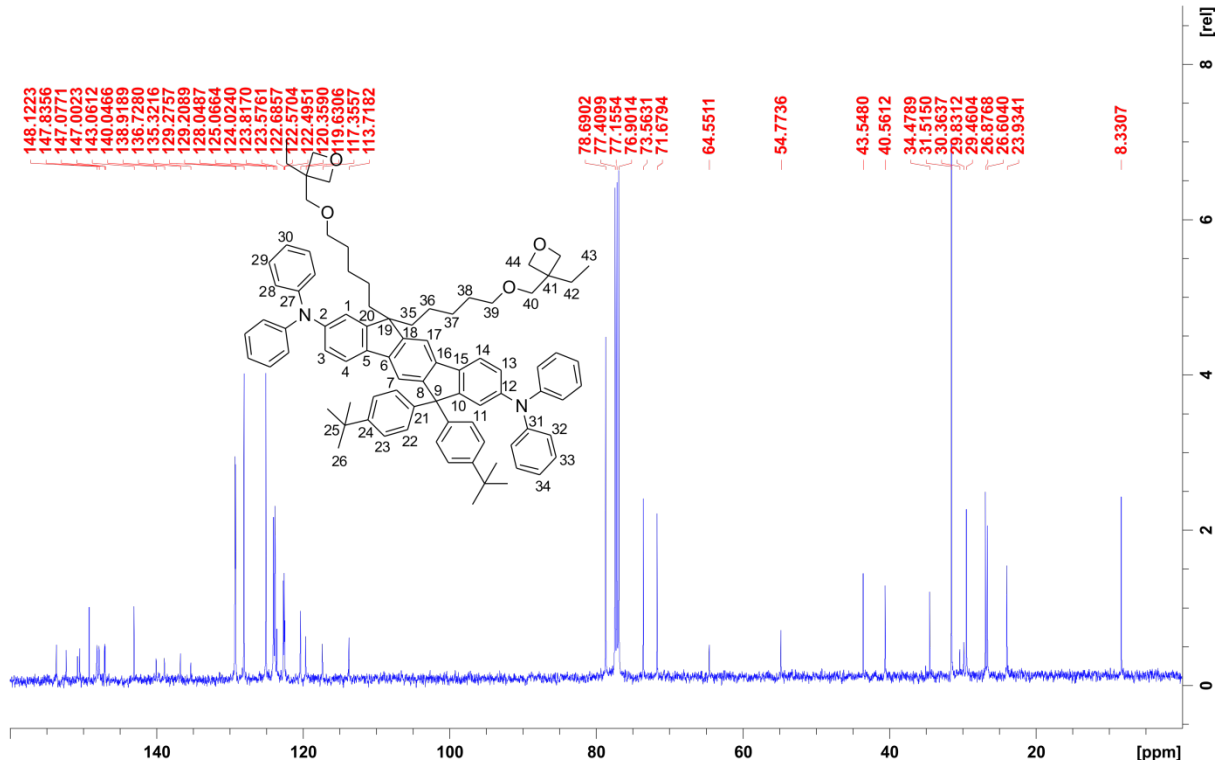


Figure S33. ^{13}C-NMR spectrum of 0L-2G5 **9c** ($CDCl_3$, 125 MHz, 300 K).

4.16. 0L-2G6 9d

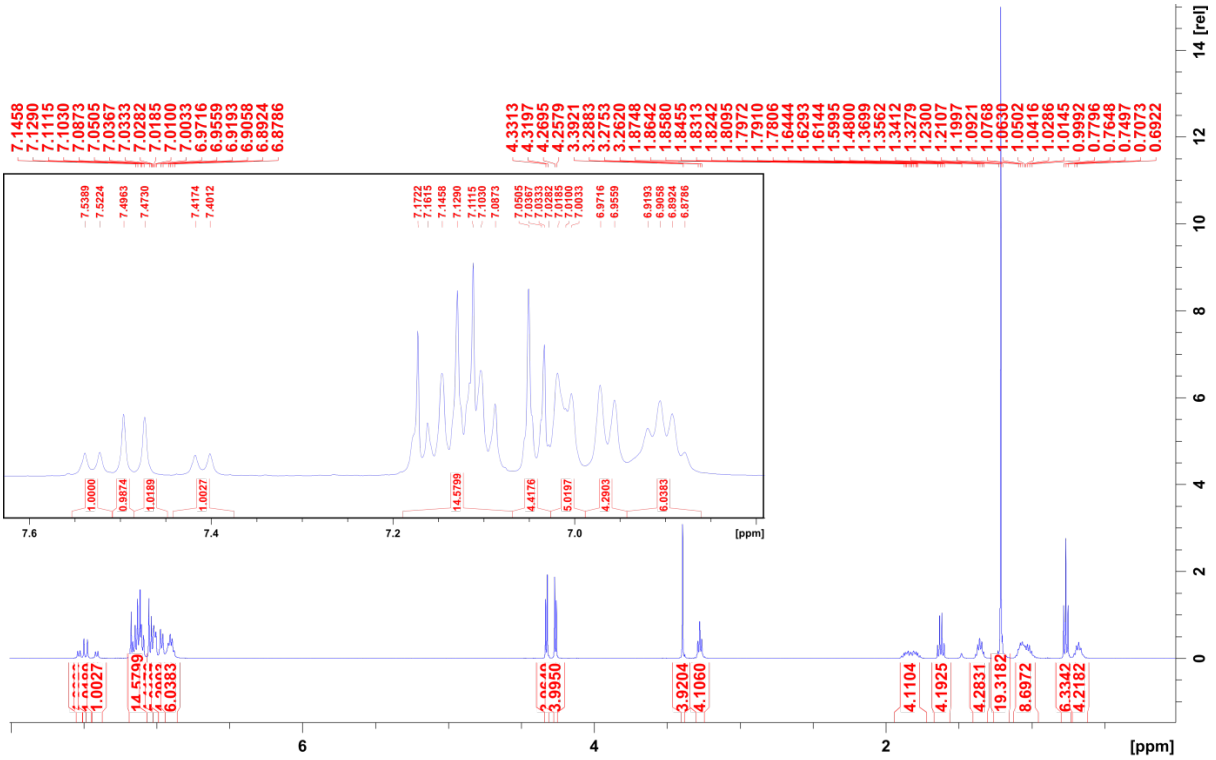


Figure S34. ^{1}H-NMR spectrum of 0L-2G6 **9d** ($CDCl_3$, 500 MHz, 300 K).

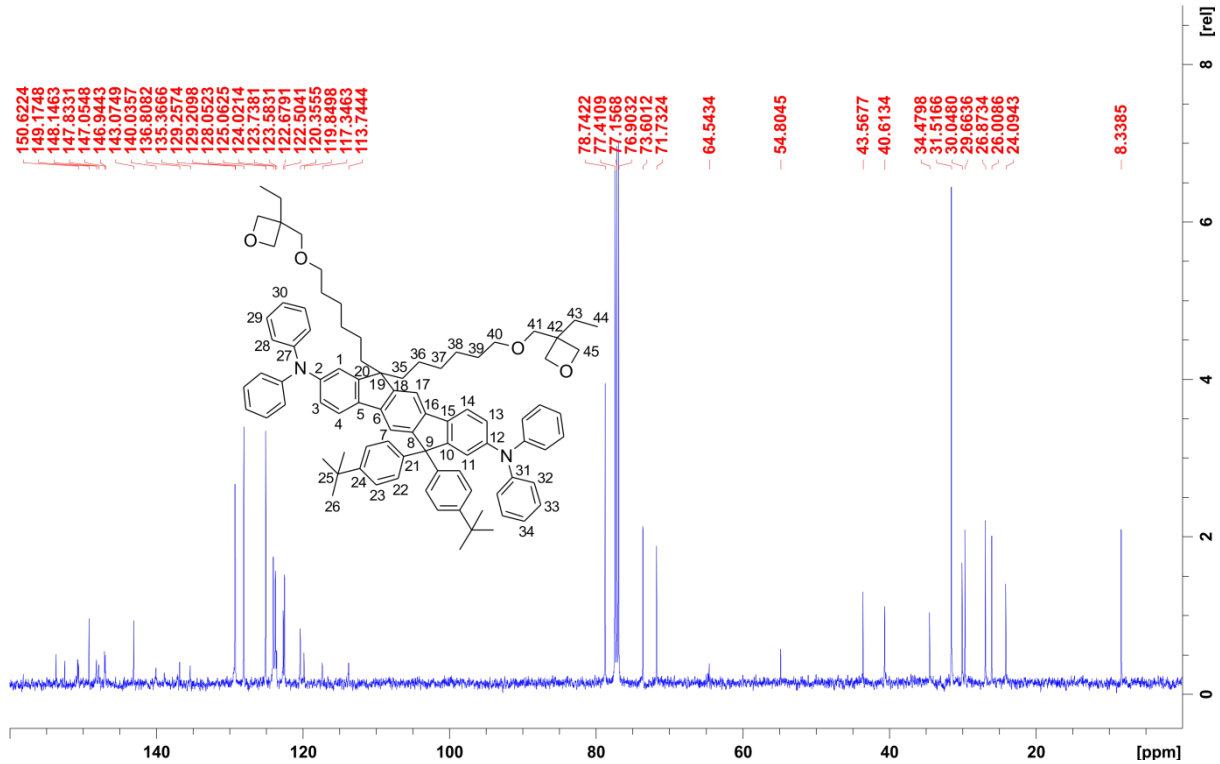


Figure S35. ^{13}C-NMR spectrum of 0L-2G6 **9d** ($CDCl_3$, 125 MHz, 300 K).

4.17. 2L6-0G 9e

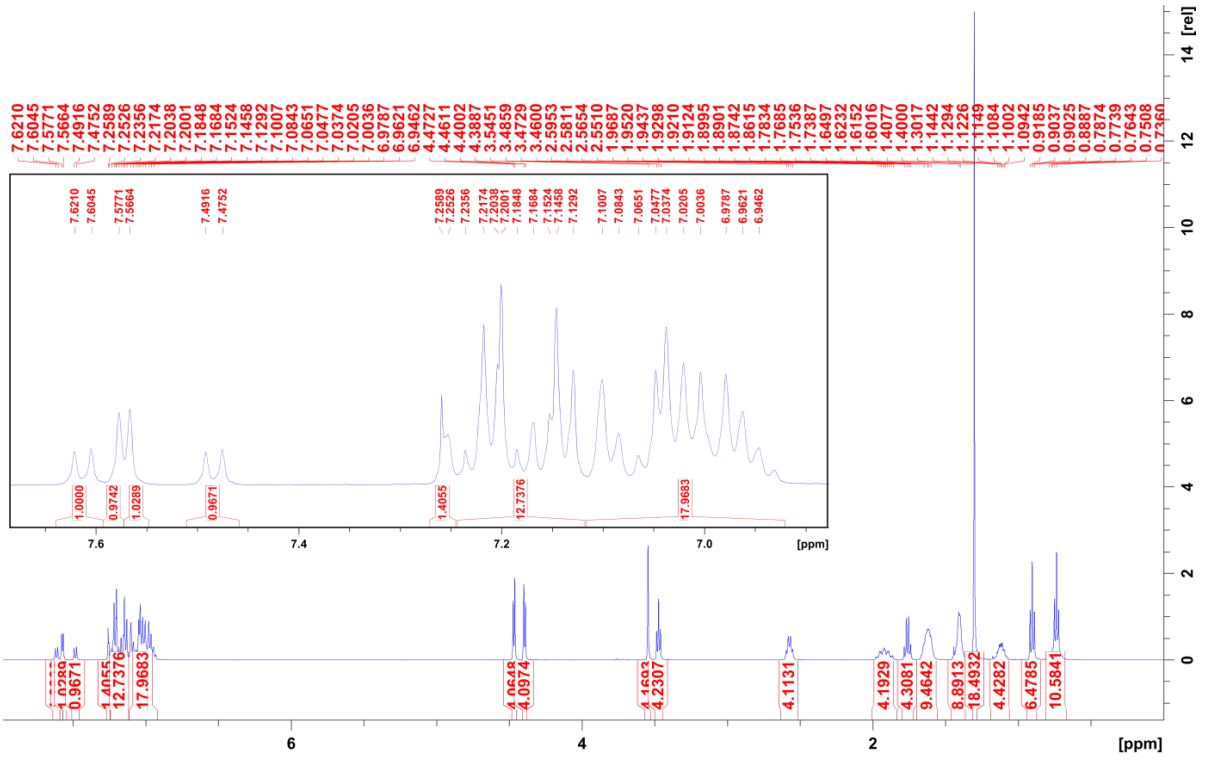


Figure S36. ^{1}H-NMR spectrum of 2L6-0G **9e** ($CDCl_3$, 500 MHz, 300 K).

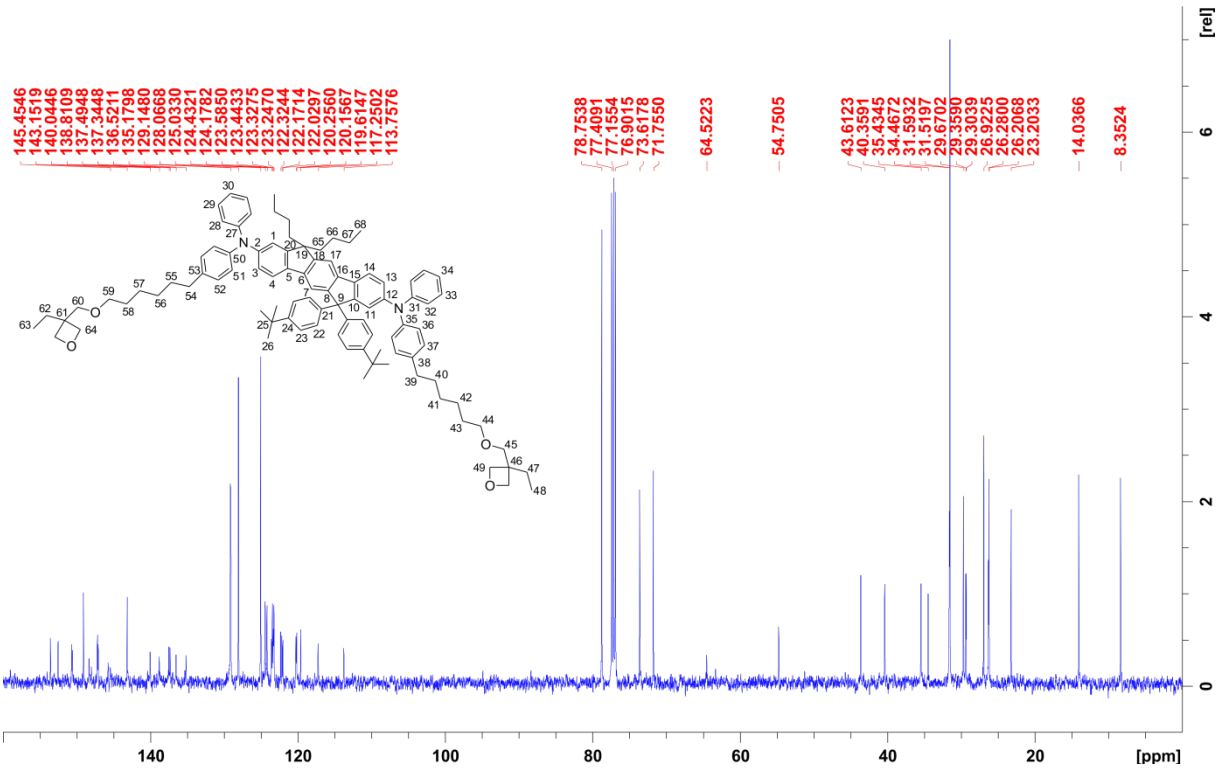


Figure S37. ^{13}C-NMR spectrum of 2L6-0G **9e** ($CDCl_3$, 125 MHz, 300 K).

4.18. 2L6-2G6 9f

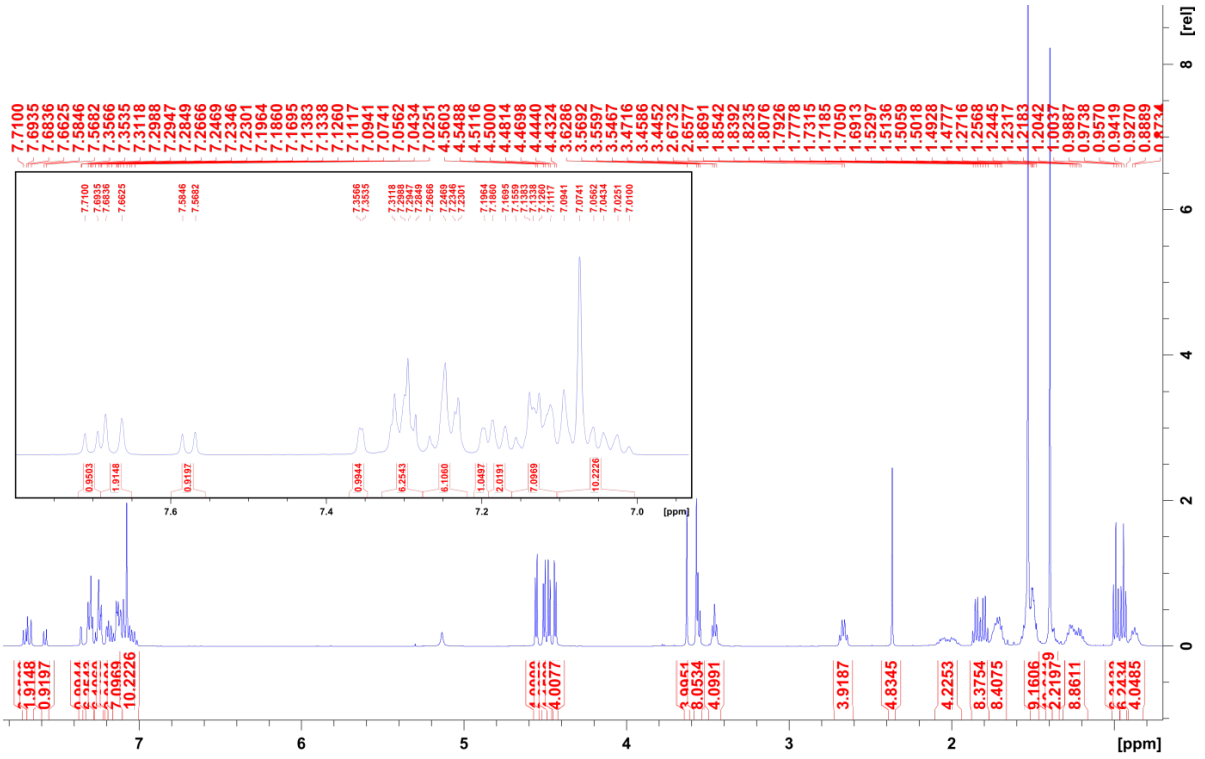


Figure S38. ^{1}H-NMR spectrum of 2L6-2G6 **9f** ($CDCl_3$, 500 MHz, 300 K).

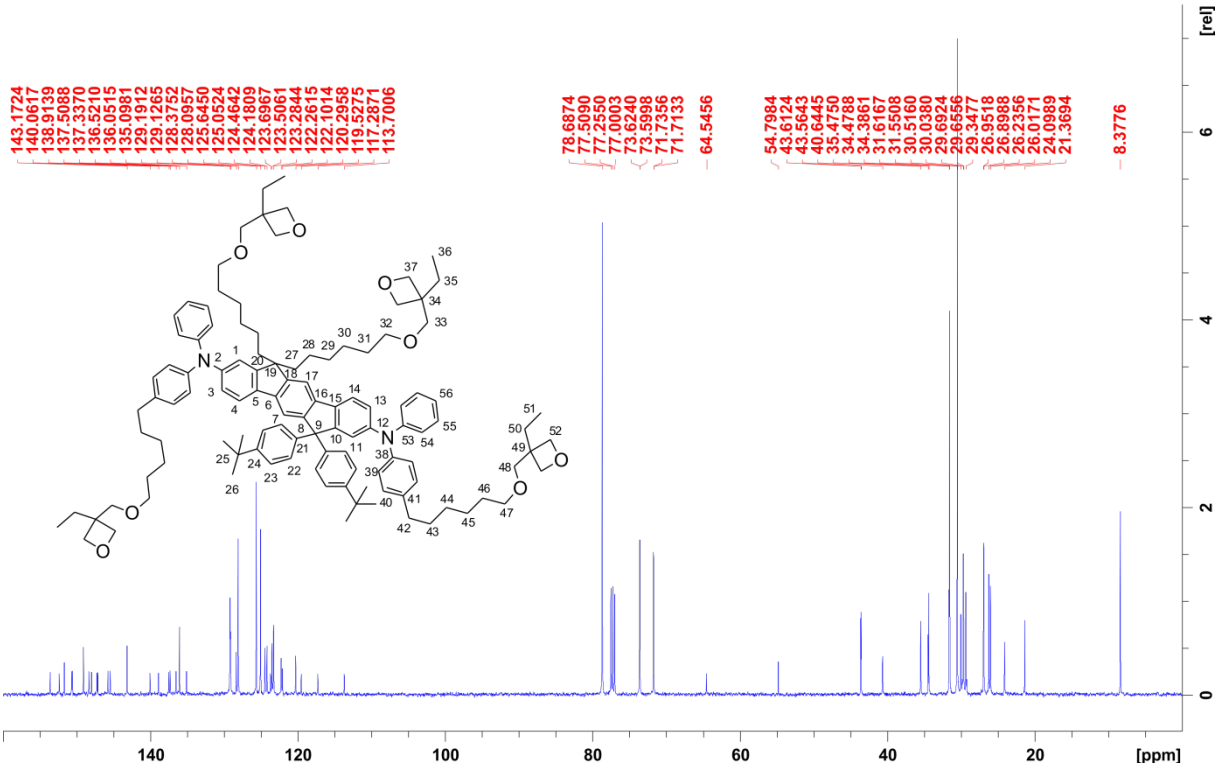


Figure S39. ^{13}C-NMR spectrum of 2L6-2G6 **9f** ($CDCl_3$, 125 MHz, 300 K).

4.19. 4L6-0G 9g

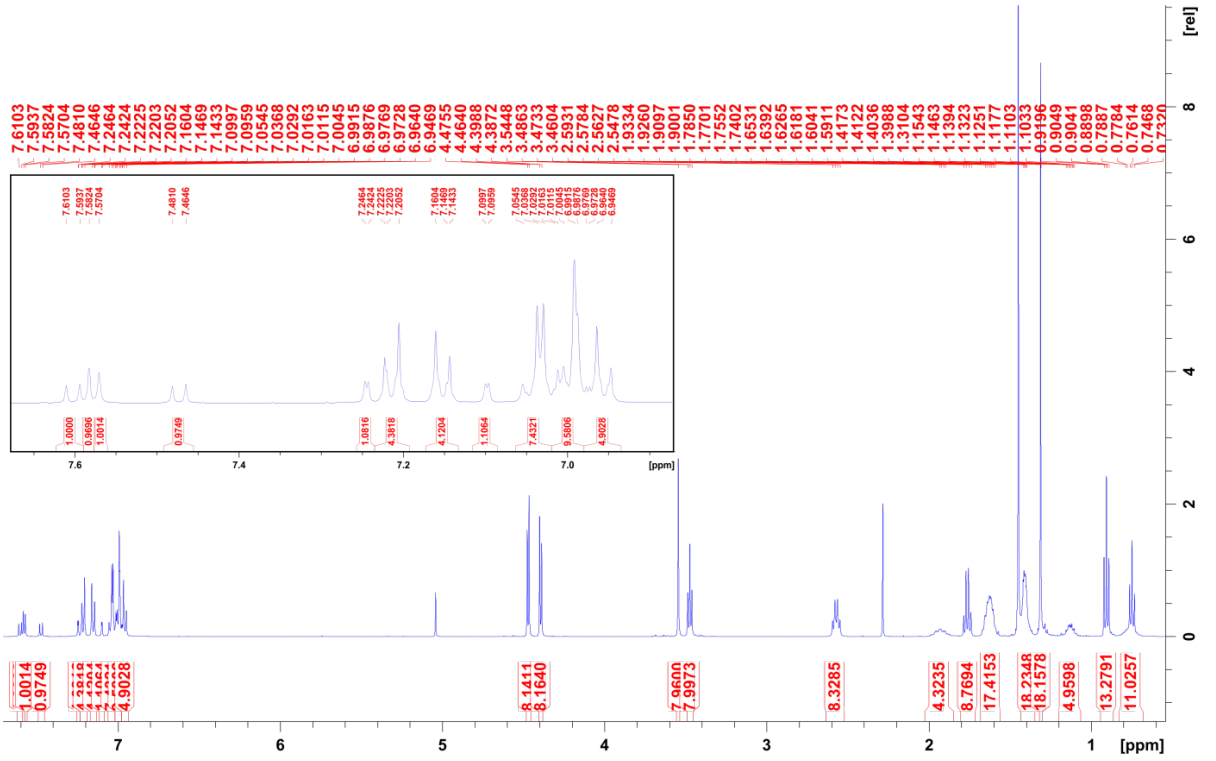


Figure S40. ^{1}H-NMR spectrum of 4L6-0G **9g** ($CDCl_3$, 500 MHz, 300 K).

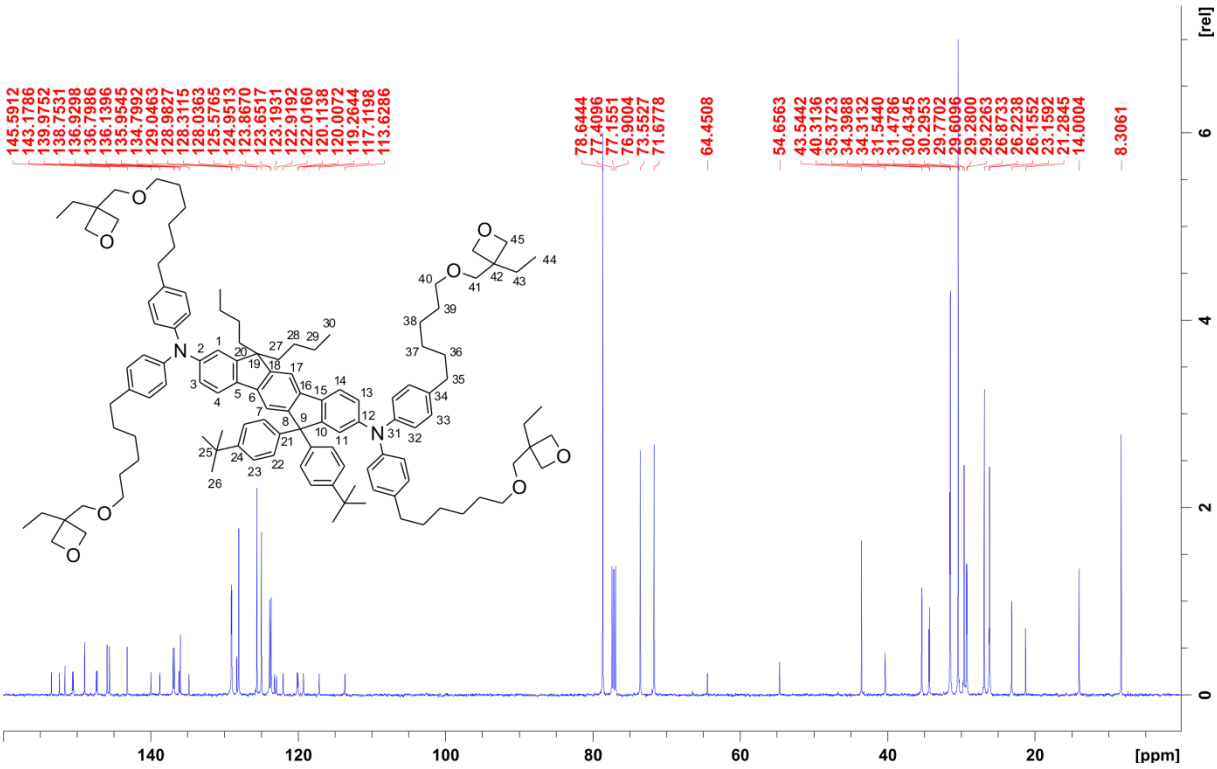


Figure S41. ^{13}C-NMR spectrum of 4L6-0G **9g** ($CDCl_3$, 125 MHz, 300 K).

4.20. 4L6-2G6 9h

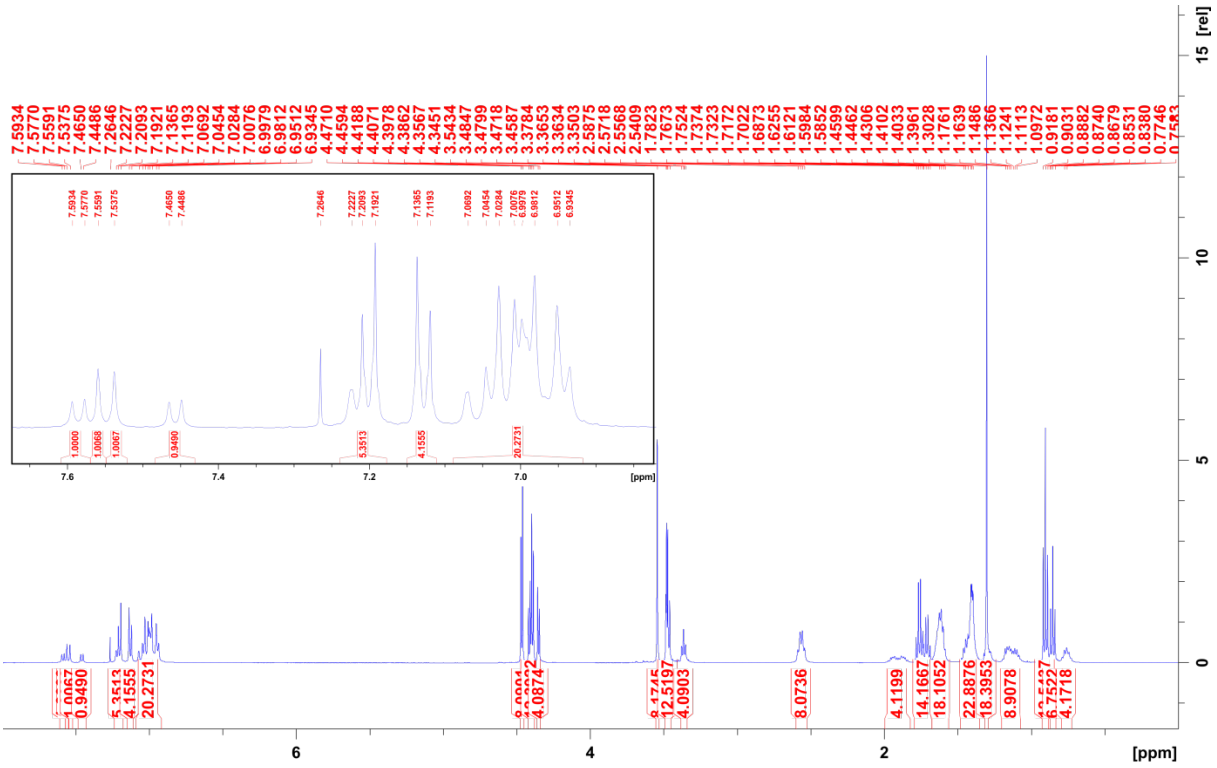


Figure S42. ^{1}H-NMR spectrum of 4L6-2G6 **9h** ($CDCl_3$, 500 MHz, 300 K).

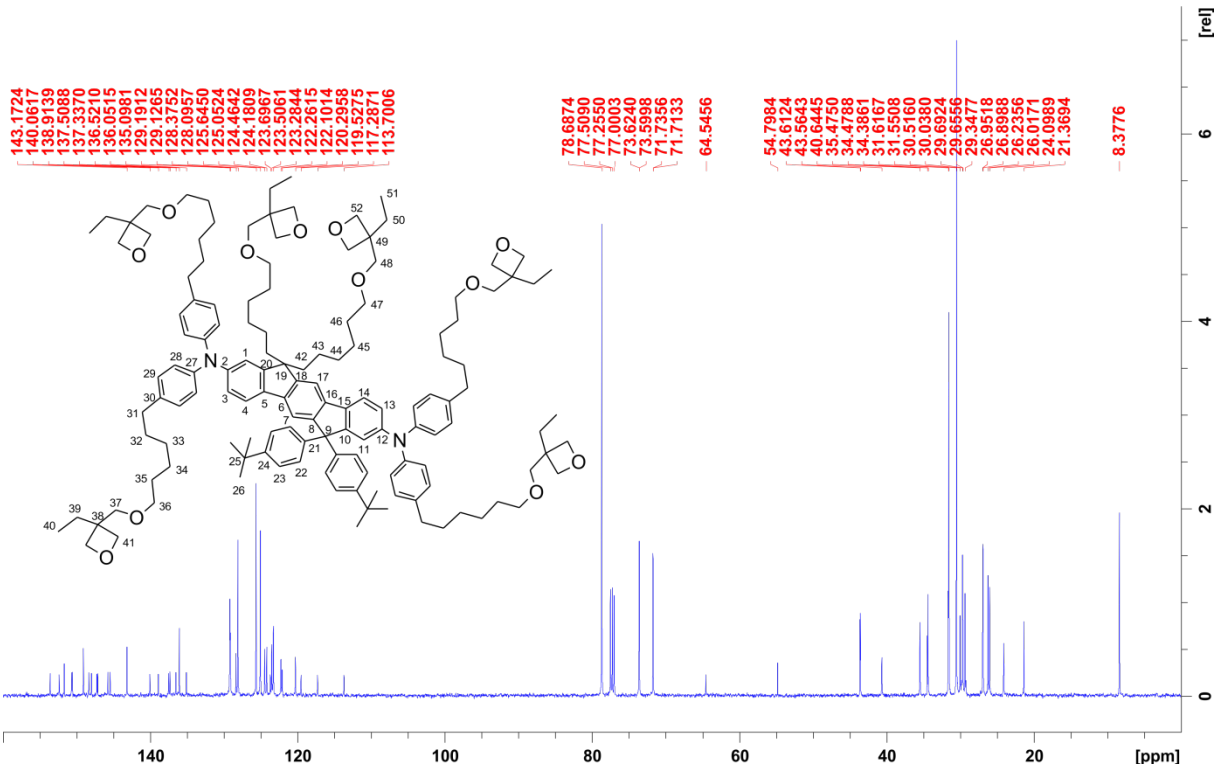


Figure S43. ^{13}C-NMR spectrum of 4L6-2G6 **9h** ($CDCl_3$, 125 MHz, 300 K).

4.21. JS247

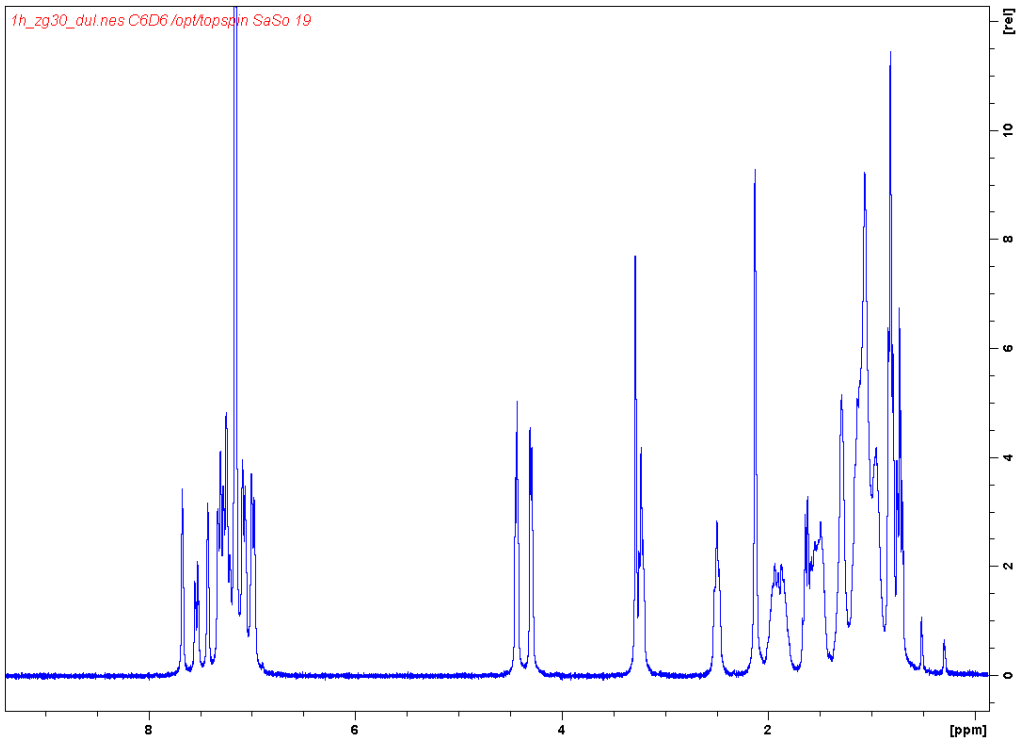


Figure S44. ^{1}H-NMR spectrum of **JS247** (C_6D_6, 300 MHz, 300 K)

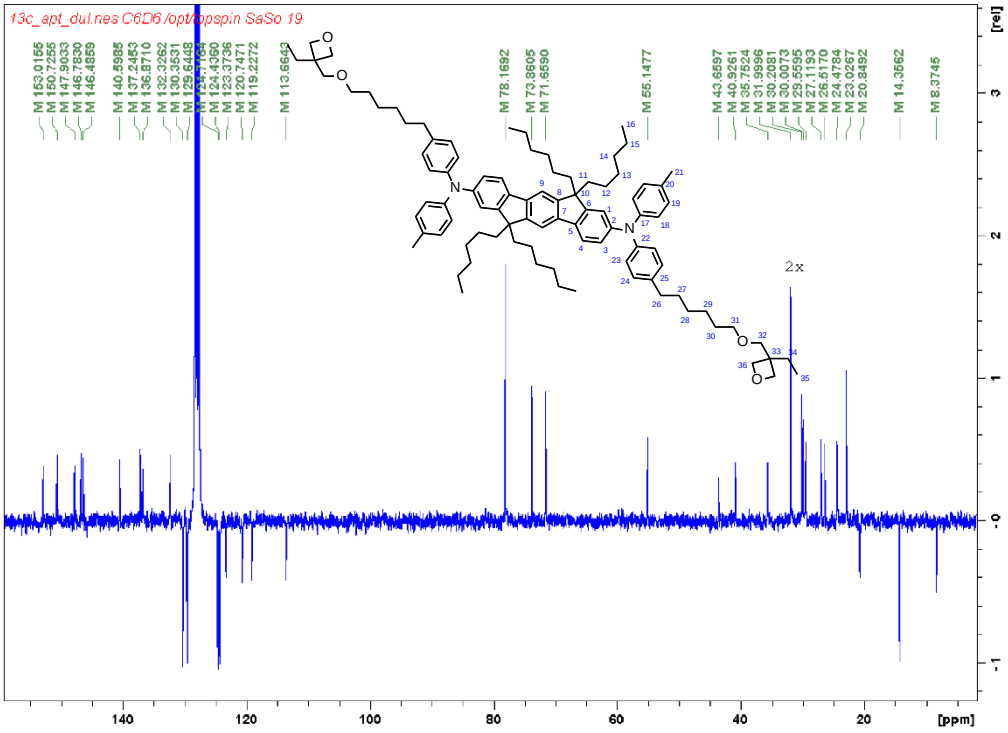


Figure S45. ^{13}C-NMR-APT spectrum of **JS247** (C_6D_6, 75 MHz, 300 K).

5. Thermal Gravimetric Analysis (TGA)

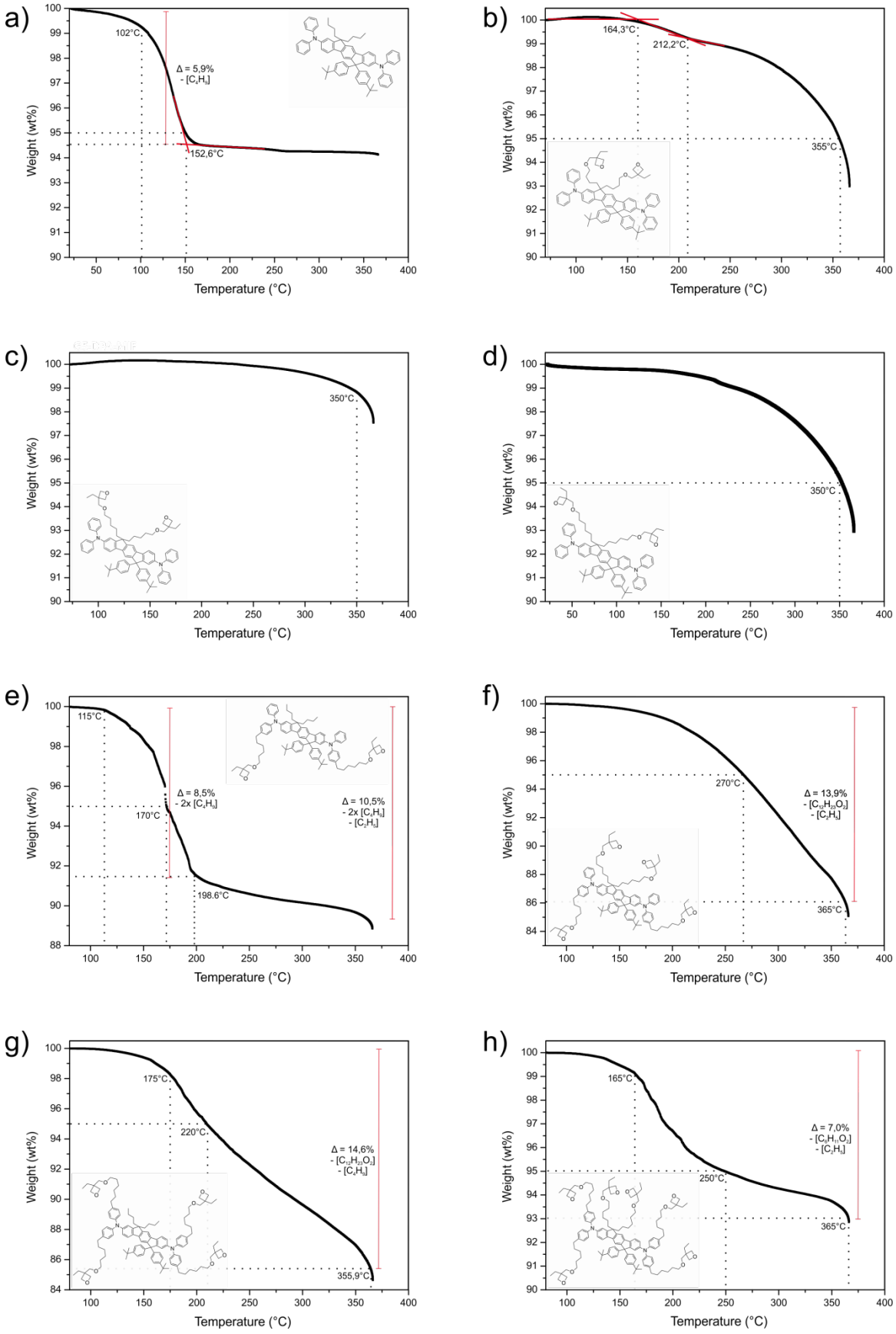


Figure S46. Thermogravimetric analysis of DPA-MIF derivatives (N_2 atmosphere, 10 K/min). a) REF **9a**, b) 0L-2G4 **9b**, c) 0L-2G5 **9c**, d) 0L-2G6 **9d**, e) 2L6-0G **9e**, f) 2L6-2G6 **9f**, g) 4L6-0G **9g**, h) 4L6-2G6 **9h**.

6. Crystallographic Data

6.1. 6,6‘-Bis(4-*tert.*-butylphenyl)-6,12-dihydroindeno[1,2-*b*]fluorene 6

Identification code	1282 (MAH-076)
Empirical formula	C40 H38
Formula weight	518.70
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.387(2) A alpha = 81.56(2) deg. b = 12.679(3) A beta = 85.64(2) deg. c = 15.339(3) A gamma = 71.53(2) deg.
Volume	1529.6(6) A^3
Z, Calculated density	2, 1.126 Mg/m^3
Absorption coefficient	0.063 mm^-1
F(000)	556
Crystal size	0.30 x 0.30 x 0.24 mm
Theta range for data collection	2.56 to 23.26 deg.
Limiting indices	-8<=h<=9, -13<=k<=14, -17<=l<=17
Reflections collected / unique	8241 / 4333 [R(int) = 0.0521]
Completeness to theta = 23.26 98.5 %	
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9850 and 0.9813
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4333 / 42 / 389
Goodness-of-fit on F^2	1.107
Final R indices [I>2sigma(I)]	R1 = 0.0990, wR2 = 0.1754
R indices (all data)	R1 = 0.1909, wR2 = 0.2138
Largest diff. peak and hole	0.292 and -0.211 e.A^-3

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1282. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	X	y	z	U(eq)
C(1)	1496(7)	402(5)	-781(4)	57(2)
C(2)	657(7)	475(6)	-1541(4)	74(2)
C(3)	-356(8)	1503(7)	-1905(4)	83(2)
C(4)	-554(7)	2462(6)	-1528(4)	78(2)
C(5)	249(7)	2393(5)	-748(4)	65(2)
C(6)	1271(6)	1358(5)	-375(4)	56(2)
C(7)	2214(6)	1040(5)	433(4)	51(1)
C(8)	2343(6)	1667(4)	1082(4)	53(1)
C(9)	3327(6)	1125(4)	1796(3)	47(1)
C(10)	3675(6)	1622(4)	2594(3)	50(1)
C(11)	4880(6)	577(5)	3085(4)	51(1)
C(12)	5661(7)	460(5)	3868(4)	65(2)
C(13)	6738(7)	-575(6)	4198(4)	71(2)
C(14)	7023(7)	-1485(6)	3761(4)	77(2)
C(15)	6250(7)	-1391(5)	2987(4)	67(2)
C(16)	5172(6)	-359(5)	2649(4)	51(1)
C(17)	4207(6)	-17(4)	1846(3)	49(1)
C(18)	4075(6)	-652(5)	1205(4)	57(2)
C(19)	3071(6)	-110(5)	500(4)	50(1)
C(20)	2667(7)	-607(5)	-262(4)	63(2)
C(21)	2118(6)	2026(4)	3195(3)	49(1)
C(22)	889(6)	1492(5)	3296(3)	60(2)
C(23)	-435(7)	1783(5)	3895(4)	66(2)
C(24)	-639(6)	2613(5)	4426(4)	61(2)
C(25)	592(7)	3146(5)	4322(4)	66(2)
C(26)	1942(6)	2843(5)	3729(4)	62(2)
C(27)	-2137(7)	2906(6)	5085(4)	75(2)
C(28)	-2195(9)	1816(7)	5665(5)	111(3)
C(29)	-3757(7)	3404(6)	4574(5)	108(3)
C(30)	-2013(8)	3736(7)	5669(5)	118(3)
C(31)	4501(6)	2537(4)	2270(3)	50(1)
C(32)	3566(7)	3615(5)	1970(4)	68(2)
C(33)	4297(7)	4440(5)	1678(4)	74(2)
C(34)	6045(7)	4222(5)	1676(4)	64(2)
C(35)	6953(7)	3141(5)	1954(4)	69(2)
C(36)	6227(6)	2314(5)	2248(4)	60(2)
C(37)	6865(9)	5150(6)	1416(5)	86(2)
C(38A)	5662(13)	6225(8)	940(8)	108(4)
C(39A)	7527(17)	5375(11)	2226(7)	129(4)
C(40A)	8277(12)	4764(8)	713(7)	97(4)
C(38B)	6620(40)	5590(30)	444(12)	116(5)
C(39B)	6180(30)	6064(18)	1948(16)	97(9)
C(40B)	8820(20)	4670(20)	1450(20)	96(5)

6.2. REF 9a

Identification code	1328 (MAH-274)	
Empirical formula	C72 H72 N2	
Formula weight	965.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.878(2) Å	α= 103.61(2)°.
	b = 13.339(2) Å	β= 105.51(2)°.
	c = 18.963(3) Å	γ = 104.26(2)°.
Volume	2879.6(9) $Å^3$	
Z	2	
Density (calculated)	1.113 Mg/m^3	
Absorption coefficient	0.063 mm^{-1}	
F(000)	1036	
Crystal size	0.200 x 0.080 x 0.040 mm^3	
Theta range for data collection	2.776 to 25.187°.	
Index ranges	-12<=h<=15, -15<=k<=15, -22<=l<=22	
Reflections collected	19321	
Independent reflections	10252 [R(int) = 0.1936]	
Completeness to theta = 25.242°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.997 and 0.987	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10252 / 85 / 667	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.1670, wR2 = 0.2720	
R indices (all data)	R1 = 0.4058, wR2 = 0.3637	
Largest diff. peak and hole	0.714 and -0.299 e.$Å^{-3}$	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1328. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7277(7)	536(7)	3019(5)	30(2)
C(2)	7142(7)	1347(7)	3691(5)	32(2)
C(3)	6360(7)	1127(8)	4064(5)	41(3)
C(4)	6304(7)	1973(8)	4634(5)	41(3)
C(5)	7073(8)	3024(8)	4829(5)	48(3)
C(6)	7861(7)	3242(8)	4459(5)	45(3)
C(7)	7877(7)	2400(7)	3888(5)	34(2)
C(8)	8582(7)	2382(7)	3388(5)	34(2)
C(9)	9449(7)	3245(7)	3363(5)	41(3)
C(10)	9971(7)	2989(8)	2824(5)	38(2)
C(11)	10903(7)	3764(7)	2667(5)	41(3)
C(12)	11024(7)	2984(8)	1985(5)	38(2)
C(13)	11698(7)	3255(7)	1564(5)	42(3)
C(14)	11668(8)	2426(8)	946(6)	46(3)
C(15)	11027(7)	1335(8)	807(5)	44(3)
C(16)	10355(7)	1078(8)	1235(5)	45(3)
C(17)	10335(7)	1915(8)	1824(5)	37(2)
C(18)	9659(7)	1910(7)	2326(5)	33(2)
C(19)	8808(7)	1075(7)	2365(5)	37(2)
C(20)	8253(7)	1315(7)	2891(5)	32(2)
C(21)	7617(7)	-364(7)	3281(5)	33(2)
C(22)	8745(8)	-229(7)	3651(5)	42(3)
C(23)	9057(8)	-1051(8)	3897(5)	48(3)
C(24)	8287(8)	-2058(8)	3773(5)	44(3)
C(25)	7150(8)	-2151(8)	3405(5)	44(3)
C(26)	6824(7)	-1336(7)	3173(5)	43(3)
C(27)	6225(7)	117(8)	2287(5)	40(3)
C(28)	5401(8)	592(8)	2172(6)	55(3)
C(29)	4458(8)	210(9)	1511(6)	69(4)
C(30)	4299(8)	-679(9)	908(6)	57(3)
C(31)	5125(9)	-1181(9)	999(6)	63(3)
C(32)	6065(8)	-771(8)	1674(6)	58(3)
C(33)	5869(8)	2189(8)	5819(6)	47(3)
C(34)	5512(7)	2990(8)	6191(6)	58(3)
C(35)	5900(9)	3345(9)	7019(6)	65(3)
C(36)	6642(11)	2967(11)	7426(8)	86(4)
C(37)	7021(12)	2221(12)	7048(8)	111(5)
C(38)	6638(11)	1842(10)	6254(7)	90(4)
C(39)	4306(8)	1318(7)	4559(6)	44(3)
C(40)	3531(8)	950(8)	4920(6)	61(3)
C(41)	2372(9)	516(9)	4498(7)	78(4)
C(42)	1973(9)	420(10)	3734(8)	81(4)
C(43)	2726(10)	737(9)	3377(7)	73(4)
C(44)	3883(9)	1182(8)	3771(6)	60(3)
C(45)	13420(10)	3469(10)	792(6)	64(3)
C(46)	14229(11)	3276(13)	1310(8)	118(5)
C(47)	15368(12)	4035(13)	1650(9)	124(5)
C(48)	15498(14)	4947(15)	1450(10)	136(6)
C(49)	14742(16)	5247(15)	967(10)	159(7)
C(50)	13629(12)	4391(13)	615(8)	115(5)
C(51)	11673(8)	2408(7)	-350(6)	44(3)
C(52)	12246(8)	2368(8)	-878(6)	63(3)

C(53)	11644(12)	2109(9)	-1659(6)	69(3)
C(54)	10527(12)	1869(9)	-1920(7)	70(3)
C(55)	9950(10)	1870(9)	-1416(8)	81(4)
C(56)	10506(9)	2138(8)	-619(6)	59(3)
C(57)	12030(8)	4259(8)	3364(6)	62(3)
C(58)	12509(10)	3437(9)	3635(6)	78(4)
C(59)	13780(10)	3946(10)	4138(7)	101(5)
C(60)	14548(11)	4044(13)	3655(10)	152(7)
C(61)	10524(9)	4696(8)	2442(6)	61(3)
C(62)	9397(10)	4341(10)	1800(7)	94(4)
C(63)	9092(15)	5159(14)	1357(11)	156(6)
C(64)	9700(20)	5190(20)	878(15)	297(14)
C(65)	8596(11)	-2967(10)	4012(8)	83(4)
C(66)	8137(16)	-3989(12)	3402(10)	203(7)
C(67)	8818(18)	-2816(15)	4808(9)	198(7)
C(68)	9818(15)	-2883(14)	4046(12)	198(8)
C(69)	3239(9)	-1122(12)	157(7)	82(4)
C(70)	2278(11)	-1748(14)	316(8)	162(7)
C(71)	3430(9)	-1770(12)	-533(7)	117(6)
C(72)	2925(13)	-138(16)	-32(8)	181(9)
N(1)	5481(6)	1780(6)	4997(4)	47(2)
N(2)	12286(6)	2662(6)	451(5)	55(2)

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