Supporting Information

Molecular Packing and Morphological Stability of Dihydroindeno[1,2-*b*]fluorenes in the Context of their Substitution Pattern

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1. General considerations

Solvents and reagents: Tetrahydrofuran (THF) was distilled from sodium-benzophenone under argon atmosphere. 2,5-dibromoterephthalic acid was synthesized according to Yao et al..[1] 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.[2] 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.

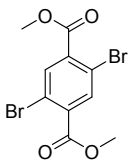
Elemental analysis were performed by the service of Technische Universität Darmstadt on a Vario El by Elementar.

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

2. Experimental procedures and characterization data

2.1. Synthesis of Dimethyl-2,5-dibromoterephthalate



A suspension of 10.12 g (31.24 mmol) 2,5-dibromoterephthalic acid in 100 mL methanol was cooled to 0°C. Carefully, 9.066 mL (4.00 eq., 124.97 mmol) thionyl chloride were added through a dropping funnel, resulting in a clear and colorless solution. The reaction mixture was heated to 68°C for 12 hours. The solvent was removed *in vacuo* and the remaining colorless solid was washed with H_2O. Afterwards, the solid was dissolved in ethyl acetate (100 mL), washed with a saturated, aqueous

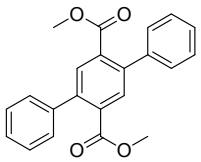
solution of $NaHCO_3$ and the organic layer was dried with Na_2SO_4. The solvent was removed *in vacuo*, resulting in 10.99 g (31.24 mmol, quant.) of the product in form of a colorless solid.

^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ (ppm) = 3.953 (s, H_6), 8.051 (s, H_2).

^{13}C-NMR ($CDCl_3$, 75 MHz, 300 K) δ (ppm) = 52.96 (CH_3), 120.19 ($C_{quart.}$), 135.43 (ArH), 136.63 ($C_{quart.}$), 164.54 ($C_{quart.}$).

EI-MS: *m/z*: 352 ($[M]^+$), 321 ($[M\text{-}CH_3O]^+$), 293 ($[M\text{-}C_2H_3O_2]^+$), 262 ($[M\text{-}C_2H_3O_2\text{-}CH_3O]^+$), 234 ($[M\text{-}2(C_2H_3O_2)]^+$), 155 ($[M\text{-}2(C_2H_3O_2)\text{-}^{79}Br]^+$), 76 $[M\text{-}2(C_2H_3O_2)\text{-}2(^{79}Br)]^+$).

2.2. Synthesis of Dimethyl-2,5-diphenylterephthalate (1)



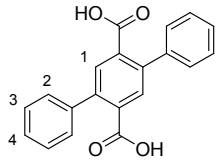
In modification of a literature procedure[3], a mixture of 8.00 g (22.73 mmol) dimethyl-2,5-dibromoterephthalate, 6.65 g (2.40 eq., 54.55 mmol) phenylboronic acid, 7.54 g (2.40 eq., 22.73 mmol) K_2CO_3, 260 mg (0.05 eq., 1.14 mmol) $Pd(OAc)_2$, 75 mL 2-methoxyethanol and 25 mL H_2O was purged with argon and stirred at room temperature for 3.5 hours. The resulting dark-brown suspension was extracted with DCM and washed with a saturated, aqueous solution of NaCl (200 mL). The combined organic layers were dried with magnesium sulfate and filtered through a pad of silica gel. The solvent was removed *in vacuo* and the remaining residue was purified by recrystallization from ethanol, resulting in 6.90 g (19.92 mmol, 88%) of the product in form of colorless needles.

The analytical data correlate with the data reported in the literature.[4]

^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ (ppm) = 3.67 (s, H_6), 7.35-7.48 (m, H_{10}), 7.84 (s, H_2).

EI-MS: *m/z* (%): 346 (15, $[M]^+$), 332 (5, $[M\text{-}(CH_3)]^+$), 315 (10, $[M\text{-}(CH_3O)]^+$).

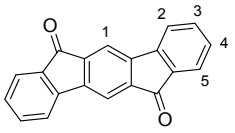
2.3. Synthesis of 2,5-Diphenylterephthalic acid (3)



In modification of a literature procedure[5], 6.74 g (19.46 mmol) dimethyl-2,5-diphenylterephthalate **(1)** were dissolved in 400 mL ethanol and mixed with a solution of 23.4 g (21.5 eq., 418.3 mmol) KOH in 200 mL water. The mixture was heated to 78°C for 12 hours and cooled to room temperature, afterwards. The ethanol was separated *in vacuo* and the remaining colorless suspension was neutralized using hydrochlorid acid. The mixture was extracted with ethyl acetate (4 x 500 mL) and the organic layer was dried with magnesium sulfate. The solvent was removed *in vacuo*, resulting in 5.88 g (18.49 mmol, 95%) of the product.
The analytical data match the data reported in the literature.[6]

^{1}H-NMR (DMSO-d_6, 300 MHz, 300 K) δ (ppm) = 7.36 – 7.50 (m, 2-H_4, 3-H_4, 4-H_2), 7.690 (s, 1-H_2).

2.4. Synthesis of Indeno[1,2-*b*]fluoren-6,12-dione (4)

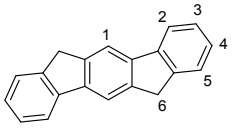


Following a literature procedure[7], 6.00 g (18.85 mmol) 2,5-diphenylterephthalic acid **(3)** are carefully dissolved in 300 mL sulfuric acid (conc.) and stirred for 2 hours at room temperature. The reaction mixture was carefully poured on ice water. The resulting purple-colored precipitate was separated and washed with water. The solid was suspended in a saturated solution of K_2CO_3 in water and was separated and dried afterwards, giving 4.79 g (16.96 mmol, 90%) of the desired compound.

The analytical data match the data reported in the literature.

^{1}H-NMR (THF-d_8, 300 MHz, 300 K) δ (ppm) = 7.368 (t, H_2), 7.588 (t, H_2), 7.639 (d, H_2), 7.791 (d, H_2), 7.951 (s, 1-H_2).

2.5. Synthesis of 6,12-Dihydroindeno[1,2-*b*]fluorene (5)

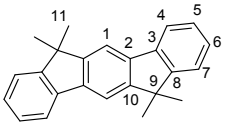


In modification of a literature procedure[7], 4.00 g (14.17 mmol) of the diketone **(4)** are suspended in 330 mL triethylene glycol and mixed with 19.7 g (24.80 eq., 351.41 mmol) KOH. Carefully, 26.5 mL (29.89 eq., 423.49 mmol) of a hydrazine monohydrate solution (80%) were added to the mixture and heated to 190°C for 64 hours. The reaction mixture was cooled to room temperature and poured into a mixture of 1 L ice water and 60 mL hydrochlorid acid (conc.). The precipitate was separated, dried and recrystallized from toluene (700 mL), resulting in 2.17 g (8.52 mmol, 60%) of the desired compound as colorless needles.

The analytical data match the data reported in the literature.

^{1}H-NMR (THF-d_8, 300 MHz, 300 K) δ (ppm) = 4.259 (s, 6-H_4), 7.574 (t, H_2), 7.662 (t, H_2), 7.862 (d, H_2), 8.199 (d, H_2), 8.366 (s, 1-H_2).

2.6. Synthesis of Methyl-IF (6a)



In modification of a literature procedure[8], 500 mg (1.97 mmol) of the dihydroindenofluorene **(5)** were suspended in 20 mL THF (abs.) under argon atmosphere and cooled to 0°C. At this temperature, 1.77 g (8.00 eq., 15.73 mmol) KO*t*Bu were added in portions and the resulting dark blue suspension was stirred for 2 hours at room temperature. Afterwards, the mixture was cooled to 0°C and was dropwise mixed with 0.983 mL (8.00 eq., 15.73 mmol) CH_3I. The reaction mixture was stirred for 48 hours at room temperature and subsequently filtered through silica gel. The solvent was separated *in vacuo*, resulting in 591 mg (1.90 mmol, 97%) of the product, which can be recrystallized from ethanol for further purification.

^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 1.569 (s, 11-H_{12}), 7.315 (t, 6-H_2), 7.362 (t, 5-H_2), 7.454 (d, 7-H_2), 7.756-7.799 (m, 1-H_2, 4-H_2).

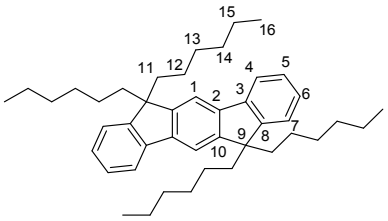
^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 27.57 (11-C), 46.70 (9-C), 114.26 (1-C), 119.84 (4-C), 122.72 (7-C), 127.09 (5-C, 6-C), 138.97 (2-C), 139.54 (3-C), 153.25 (10-C), 154.24 (8-C).

EI-MS: *m/z* (%): 310 (100, $[M]^+$), 295 (60, $[M\text{-}CH_3]^+$), 280 (40, $[M\text{-}C_2H_6]^+$), 265 (35, $[M\text{-}C_3H_9]^+$).

HR-EI-MS (*m/z*)($C_{24}H_{22}$): calc.: 310.1716
exp.: 310.1712

EA ($C_{24}H_{22}$) (%): calc.: C 92.86 H 7.14
exp.: C 92.64 H 7.149

2.7. Synthesis of Hexyl-IF (6c)



In modification of a literature procedure[8], 400 mg (1.57 mmol) of the dihydroindenofluorene **(5)** were suspended in 20 mL THF (abs.) under argon atmosphere and cooled to 0°C. At this temperature, 1.41 g (8.00 eq., 12.58 mmol) KO*t*Bu were added in portions and the resulting dark blue suspension was stirred for 2 hours at room temperature. Afterwards, the mixture was cooled to 0°C and was dropwise mixed with 1.76 mL (8.00 eq., 12.58 mmol) 1-bromohexane. The reaction mixture was stirred for 48 hours at room temperature and subsequently filtered through silica gel. The solvent was separated *in vacuo*, resulting in 720 mg (1.22 mmol, 78%) of the product, which can be recrystallized from ethanol for further purification.

^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.673 (m, 12-H_8), 0.746 (t, 16-H_{12}), 1.067 (m, 13-H_8, 14-H_8, 15-H_8), 2.033 (m, 11-H_8), 7.289 (m, 6-H_2), 7.348 (m, 5-H_2, 7-H_2), 7.629 (s, 1-H_2), 7.755 (m, 4-H_2).

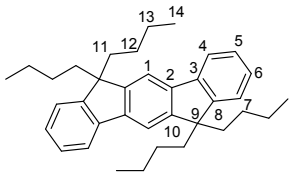
^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 14.10 (16-C), 22.66 (15-C), 23.87 (12-C), 29.86 (13-C or 14-C), 31.67 (13-C or 14-C), 40.84 (11-C), 54.86 (9-C), 114.00 (1-C), 119.49 (4-C), 122.99 (7-C), 126.76 (5-C+6-C), 140.72 (2-C), 141.68 (3-C), 150.12 (10-C), 151.28 (8-C).

EI-MS: *m/z* (%): 590 (100, $[M]^+$), 505 (85, $[M\text{-}C_6H_{13}]^+$), 421 (35, $[M\text{-}C_{12}H_{26}]^+$), 335 (5, $[M\text{-}C_{18}H_{39}]^+$).

HR-EI-MS (*m/z*)($C_{44}H_{62}$): calc.: 590.4846
exp.: 590.4833

EA ($C_{44}H_{62}$) (%): calc.: C 89.43 H 10.57
exp.: C 89.17 H 10.69

2.8. Synthesis of Butyl-IF (6b)



In a flame-dried Schlenk-flask, 20 mL of THF (abs.) are cooled to -78°C and mixed with 8.315 mL (8.00 eq., 20.79 mmol) of a 2.5 M solution of *n*-butyl lithium in *n*-hexane. At this temperature, a solution of 0.90 g (2.60 mmol) dimethyl-2,5-diphenyl-terephthalate **(1)** in 15 mL THF (abs.) was added and the resulting mixture was allowed to reach room temperature over 12 hours. A saturated, aqueous solution of NH_4Cl (20 mL) was added and the resulting yellow mixture was stirred for 30 minutes. The mixture was extracted with ethyl acetate and the organic phase was dried with Na_2SO_4. The solvent was removed *in vacuo*, resulting in 1.38 g of a yellow solid, which was used without further purification.

The solid was solved in 10 mL of DCM and a mixture of 2.49 mL (15.00 eq., 38.96 mmol) methanesulfonic acid and 3.79 g (15.00 eq., 38.96 mmol) poly phosphoric acid was added dropwise. The dark red reaction mixture was stirred at room temperature for 1 hour and mixed with 20 mL of ethanol afterwards. After 30 minutes, the mixture was heated to 80°C and stirred for 12 hours. After the reaction was completed, the mixture was neutralized using a saturated, aqueous solution of $NaHCO_3$. The aqueous phase was extracted with DCM. The organic phases were dried using $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (PE), resulting in 460 mg (0.96 mmol, 37%) of the desired compound in form of a colorless solid. The solid can be recrystallized from ethanol.

^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.691 (m, 12-H_8, 14-H_{12}), 1.116 (m, 13-H_8), 2.06 (m, 11-H_8), 7.313 (t, 6-H_2), 7.373 (m, 5-H_2, 7-H_2), 7.662 (s, 1-H_2), 7.782 (d, 4-H_2).

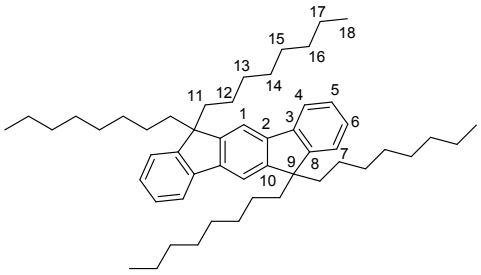
^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 13.98 (14-C), 23.26 (13-C), 26.18 (12-C), 40.65 (11-C), 54.78 (9-C), 114.06 (1-C), 119.50 (4-C), 123.03 (7-C), 126.80 (5-C+6-C), 140.71 (2-C), 141.65 (3-C), 150.14 (10-C). 151.29 (8-C).

EI-MS: *m/z* (%): 478 (100, $[M]^+$), 421 (50, $[M\text{-}C_4H_9]^+$), 364 (10, $[M\text{-}C_8H_{18}]^+$).

HR-EI-MS (*m/z*)($C_{36}H_{46}$): calc.: 478.3594
exp.: 478.3595

EA ($C_{36}H_{46}$) (%): calc.: C 90.32 H 9.68
exp.: C 89.89 H 10.12

2.9. Synthesis of Octyl-IF (6d)



In a flame-dried Schlenk-flask, 421 mg (10.00 eq., 17.32 mmol) magnesium turnings were mixed with 60 mL THF (abs.). Slowly, 2.435 mL (8.00 eq., 13.86 mmol) 1-bromooctane was added and the reaction mixture was heated to 80°C for 4 hours. In a separate flame-dried schlenk flask, 939 mg (2.20 eq., 3.81 mmol) cerium(III) chloride was suspended in 20 mL THF (abs.), mixed with 600 mg (1.73 mmol) dimethyl-2,5-diphenyl-terephthalat **(1)** and cooled to 0°C. At this temperature, the hot Grignard-solution was added dropwise and the reaction mixture was stirred at 80°C for 12 hours. The mixture was cooled to room temperature, 25 mL of a saturated aqueous solution of NH_4Cl was added and the mixture was subsequently extracted with DCM. The organic layer was dried with Na_2SO_4 and the solvent was removed *in vacuo*.

The remaining residue was solved in 10 mL DCM and the yellow solution was cooled to -20°C. Afterwards, a mixture of 1.66 mL (15.00 eq., 25.97 mmol) methanesulfonic acid and 2.52 g (15.00 eq., 25.97 mmol) poly phosphoric acid was carefully added and the mixture was stirred at room temperature for 12 hours. The mixture was diluted with 10 mL ethanol, neutralized using a saturated, aqueous solution of $NaHCO_3$ and was subsequently extracted with DCM. The organic layers were dried using $MgSO_4$. The solvent was removed *in vacuo* and the remaining brown oil was purified by column chromatography on silica gel (PE), resulting in 1.03 g (1.47 mmol, 85%) of the product in form of a solid, which can be recrystallized from ethanol.

^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.677 (m, 12-H_8), 0.802 (t, 18-H_{12}), 0.976-1.153 (m, 13-H_2, 14-H_2, 15-H_2, 16-H_2), 1.177 (m, 17-H_8), 2.029 (m, 11-H_8), 7.267-7.313 (m, 5-H_2), 7.319-7.370 (m, 7-H_2, 6-H_2), 7.629 (s, 1-H_2), 7.752 (m, 4-H_2).

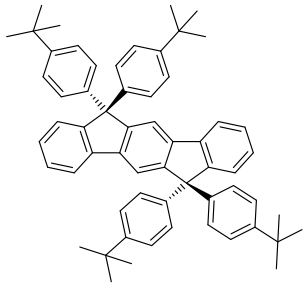
^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 14.28 (18-C), 22.82 (17-C), 24.00 (12-C), 29.44, 29.48, 30.28, 32.05, 40.90 (11-C), 54.96 (9-C), 114.11 (1-C), 119.60 (4-C), 119.60 (7-C), 123.10 (5-C), 126.86 (6-C), 140.81 (2-C or 10-C), 141.77 (3-C), 150.23 (2-C or 10-C), 151.38 (8-C).

EI-MS: *m/z* (%): 703 (100, $[M]^+$), 590 (35, $[M\text{-}C_8H_{17}]^+$), 476 (10, $[M\text{-}C_{16}H_{34}]^+$).

HR-EI-MS (*m/z*)($C_{52}H_{78}$): calc.: 702.6098
exp.: 702.6100

EA ($C_{52}H_{78}$) (%): calc.: C 88.82 H 11.18
exp.: C 88.40 H 11.25

2.10. Synthesis of tBuPh-IF (7a)



In a flame-dried Schlenk-flask, 2.06 mL (5.00 eq., 11.55 mmol) 1-bromo-4-*tert.*-butylbenzene were dissolved in 10 mL THF (abs.) and cooled to -78°C. At this temperature, 11.66 mL (10.10 eq., 23.33 mmol) of a 2.00 M solution of *tert.*-butyllithium in *n*-heptane were added dropwise and the resulting reaction mixture was stirred at -78°C for 2 hours. In a separate flame-dried Schlenk flask, 800 mg (2.31 mmol) dimethyl-2,5-diphenylterephthalat **(1)** were dissolved in 20 mL THF (abs.) and cooled to -78°C. The cooled solution was dropwise added to the solution of the metallated species and the resulting mixture was allowed to warm to room temperature over a time of 48 hours. At room temperature, 80 mL of a saturated, aqueous solution of NaCl were added and the resulting precipitate was isolated.

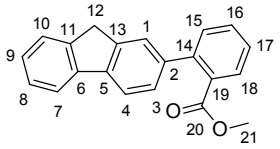
The isolated solid was dried *in vacuo* and mixed with 250 mL of glacial acetic acid. The mixture was heated to 118°C and was subsequently added 1 mL hydrochloric acid (conc.). The reaction mixture was stirred at 118°C for 48 hours and was cooled to room temperature. The resulting precipitate was isolated and washed with water. The solid was dried *in vacuo*, resulting in 1.45 g (1.85 mmol, 86%) of the product in form of a colorless solid, which can be recrystallized from chlorobenzene.

Because of its poor solubility, the compound was not characterized by NMR spectroscopy.

EI-MS: *m/z* (%): 783 (100, $[M]^+$), 725 (10, $[M\text{-}C_4H_9]^+$), 649 (12, $[M\text{-}C_{10}H_{13}]^+$).

HR-EI-MS (*m/z*)($C_{60}H_{62}$): calc.: 782.4846
exp.: 782.4823

2.11. Synthesis of 2-Fluorenyl methylbenzoate (10)



A suspension of 45.1 g (1.00 eq., 184 mmol) 2-bromofluorene **8**, 54.2 g (1.16 eq., 213.44 mmol) bis(pinacolato)diboron, 54.2 g (3.00 eq., 551.99 mmol) potassium acetate and 7.59 g (0.05 eq., 9.2 mmol) Pd(dppf)Cl2 • DCM in 2000 mL DMF (degassed) was heated to 80°C for 3 h under an argon atmosphere. After the mixture has come to room temperature, 27.06 mL (1.04 eq., 190.85 mmol) 2-bromo methylbenzoate **9** as well as a solution of 99.63 g (2.50 eq., 459.99 mmol) tripotassium phosphate in 460 mL water (degassed) have been added. The reaction was continued at 80°C for 4 h. After cooling, 500 mL of water and 800 mL DCM have been added. The mixture was filtered through a pad of celite and the organic phase was successively washed with 3x 500 mL water and 3x 500 mL brine. The organic layers were dried ($MgSO_4$), evaporated *in vacuo* and the residue was purified by column chromatography on silica gel (PE/DCM, 2:1 (v:v)). The title compound (43.52 g, 144.91 mmol, 79%) was obtained in form of colorless crystals of high purity by recrystallization through slow diffusion of *n*-hexane into a solution of **10** in ethyl acetate.

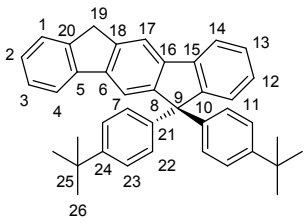
^{1}H-NMR (DMSO-d_6, 500 MHz, 300 K) δ (ppm) = 3.588 (s, 21-H, 3 H), 3.958 (s, 12-H, 2 H), 7.284 (d, 3-H, 1 H), 7.333 (t, 9-H, 1 H), 7.402 (t, 8-H, 1 H), 7.469 – 7.526 (m, 1/15/17-H, 3 H), 7.596 (d, 10-H, 1 H), 7.624 (t, 16-H, 1 H), 7.750 (d, 18-H, 1 H), 7.921 (m, 4/7-H, 2 H). $^3J_{3,4}$ = 7.9 Hz, $^3J_{9,10}$ = 7.5 Hz.

^{13}C-NMR (DMSO-d_6, 125 MHz, 300 K) δ (ppm) = 36.40 (12-C), 51.93 (21-C), 119.73/120.11 (4-C/7-C), 124.82 (1-C), 125.13 (10-C), 126.80 (8-C), 126.86 (9-C), 126.97 (3-C), 127.25 (15-C), 129.23 (18-C), 130.45 (17-C), 131.02 (14-C), 131.34 (16-C), 139.01 (2-C), 140.28 (5-C), 140.67 (6-C), 141.33 (14 C), 143.08 (13-C), 143.18 (11-C), 168.80 (20-C).

EI-MS: *m/z* (%): 300 (74, $[M]^+$]), 268 (100, $[M\text{-}OCH_3]^+$), 241 (10, $[M\text{-}CO_2CH_3]^+$), 135 (14, $[M\text{-}C_{13}H_9]^+$), 120 (32, $[M\text{-}C_{13}H_9\text{-}CH_3]^+$).

HR-EI-MS ($C_{21}H_{16}O_2$)	calc.: 300.115		
	exp.: 300.11118		
EA ($C_{21}H_{16}O_2$) (%)	calc.:	C 83.98	H 5.37
	exp.:	C 83.96	H 5.35

2.12. 6,6‘-Bis(4-tert-butylphenyl)-6,12-dihydroindeno[1,2-*b*]fluorene (12)



In a flame-dried 1 L-Schlenk flask, 31.78 mL (3 eq., 177.79 mmol) 1-bromo-4-*tert.*-butylbenzene **11** were solved in 300 mL of dry THF under an argon atmosphere and cooled to -78°C in an ethanol/dry ice bath. Over the period of 1 h, 188 mL (6.03 eq., 357.36 mmol, 1.9 M) of a solution of *tert.*-butyllithium in hexane was added dropwise. After 2.5 h, a solution of 17.80 g (1 eq., 59.26 mmol) 2-fluorenyl methylbenzoate **10** in 300 mL of dry THF was added dropwise over 1.5 h and the mixture was allowed to slowly warm to room temperature over 12 h. The reaction was quenched by the addition of 200 mL brine and the organic layer was successively washed with brine (3x 100 mL) and dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the residing yellow oil was held for 4 h at 90°C under high vacuum. The resulting crude product was used in the next step without further purification. Based on a literature procedure,[9] 34.72 g carbinol are dissolved in 3.75 L glacial acetic acid containing 10 mL conc. HCl and heated to 118°C for 2.5 h. The mixture was reduced to a volume of 700 mL by distillation and subsequently 300 mL water were added. After cooling to room temperature, the precipitate was collected by filtration, thoroughly washed with water and dried. The crude product was filtered through a pad of silica gel, using *n*-hexane as eluent. For further purification, the material obtained was digerated in petroleum ether (8 mL/mmol) and mixed with toluene (2 mL/mmol) under refluxing condition. The mixture was cooled to room temperature and the precipitated product was collected by filtration. This procedure was repeated for 3 times. The product was isolated as a white solid. Yield = 29.9 g (57.64 mmol, 97%).

^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 1.295 (s, 26-H, 18 H), 3.966 (s, 19-H, 2 H), 7.217 (d, 22-H, 4 H), 7.254 (d, 23-H, 4 H), 7.254 – 7.292 (m, 2-H, 12-H, 2 H), 7.337 (t, 3-H, 1 H), 7.370 (t, 13-H, 1 H), 7.457 (d, 11-H, 1 H), 7.532 (d, 1-H, 1 H), 7.731 (d, 4-H, 1 H), 7.792 (d, 14-H, 1 H), 7.813 (s, 7-H, 1 H), 7.927 (s, 17-H, 1 H).

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 31.52 (26-C), 34.49 (25-C), 37.07 (19-C), 64.68 (9-C), 116.74 (17-C), 117.96 (7-C), 119.91 (14-C), 120.01 (4-C), 125.11 (ArH), 125.20 (ArH), 126.46 (11 C), 126.66 (1-C), 126.81 (13-C), 127.45 (ArH), 127.99 (22-C), 139.44 (16-C), 140.42 (15-C), 141.79 (6-C), 141.92 (5-C), 142.99 (18-C), 143.19 (21-C), 143.77 (20-C), 149.29 (24-C), 151.18 (8-C), 152.35 (10-C).

EI-MS: m/z (%): 518 (100, $[M]^+$), 503 (12, $[M\text{-}CH_3]^+$), 461 (15, $[M\text{-}C(CH_3)_3]^+$), 431 (5, $[M\text{-}C(CH_3)_3\text{-}C_2H_6]^+$), 405 (4, $[M\text{-}2(C(CH_3)_3)]^+$), 386 (10, $[M\text{-}C_{10}H_{13}]^+$), 369 (11, $[M\text{-}C_{10}H_{13}\text{-}CH_3]^+$), 355 (17, $[M\text{-}C_{10}H_{13}\text{-}C_2H_6]^+$), 252 (7, $[M\text{-}2(C_{10}H_{13})^+]$).

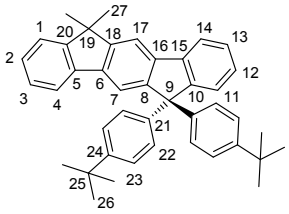
HR-EI-MS ($C_{40}H_{38}$)	calc.: 518.2973		
	exp.: 518.29454		
EA ($C_{40}H_{38}$) (%)	calc.:	C 92.62	H 7.38
	exp.:	C 92.29	H 7.32

2.13. Synthesis of alkylated, mixed substituted dihydroindenofluorenes (MIFs)

General procedure

In modification of a literature procedure[8] and in a flame-dried Schlenk-flask, the unsubstituted MIF precursor was dissolved in 10 mL/mmol THF (abs.) and the solution was cooled to 0°C. The solution was slowly mixed with 2.70 eq. KO*t*Bu and the resulting reaction mixture was stirred at room temperature for 2 hours. The mixture was cooled to 0°C, mixed with 3.00 eq. of the respective haloalkane and was stirred at room temperature for 24 hours. The reaction mixture was filtered through silica gel and the solvent was removed *in vacuo*. The resulting solid was purified by recrystallization.

2.13.1. Synthesis of Methyl-MIF (13a)



According to the general procedure, 1.00 g (1.93 mmol) of the MIF precursor **(8)** and 0.360 mL (3.00 eq., 5.78 mmol) CH_3I are used to obtain a red oil, which was purified by recrystallization form *n*Hex/PhMe, resulting in 1.00 g (1.83 mmol) of the product.

^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 1.332 (s, 26-H_{18}), 1.615 (s, 27-H_6), 7.247 (d, 22-H_4), 7.288 (d, 23-H_4), 7.289-7.358 (m, 2-H_1, 3-H_1, 12-H_1), 7.402 (t, 13-H_1), 7.455-7.499 (m, 1-H_1, 11-H_1), 7.698 (m, 4-H_1), 7.785 (s, 7-H_1), 7.829-7.860 (m, 17-H_1, 14-H_1).

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 27.59 (27-C), 31.51 (26-C), 34.49 (25-C), 46.69 (19-C), 64.65 (9-C), 114.29 (17-C), 118.05 (7-C), 119.88 (4-C or 14-C), 120.06 (4-C or 14-C), 122.68 (1-

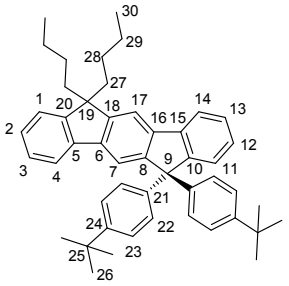
C) 125.16 (23-C), 126.49 (ArH), 127.01 (ArH) 127.15 (ArH), 127.36 (ArH), 127.40 (ArH), 128.06 (22-C), 139.32 ($C_{quart.}$), 139.49 ($C_{quart.}$), 139.86 ($C_{quart.}$), 140.49 ($C_{quart.}$), 143.25 (21-C), 149.27 (24-C), 151.21 (8-C), 152.34 (10-C), 153.48 (18-C), 154.15 (20-C).

EI-MS: *m/z* (%): 546 (100, $[M]^+$), 531 (15, $[M\text{-}CH_3]^+$), 398 (5, $[M\text{-}CH_3\text{-}C_{10}H_{13}]^+$).

HR-EI-MS (*m/z*)($C_{42}H_{42}$): calc.: 546.3281
exp.: 546.3282

EA ($C_{42}H_{42}$) (%): calc.: C 92.26 H 7.74
exp.: C 91.91 H 7.913

2.13.2. Synthesis of Butyl-MIF (13b)



According to the general procedure, 2.50 g (4.82 mmol) of the MIF precursor **(8)** and 1.645 mL (3.00 eq., 14.46 mmol) 1-iodobutane are used to obtain a yellow solid, which was purified by recrystallization from ethanol, resulting in 3.04 g (4.82 mmol, quant.) of the product.

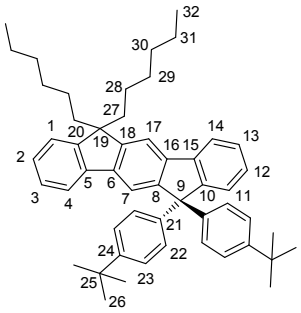
^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.640-0.802 (m, 30-H_6, 28-H_4), 1.128 (m, 29-H_4), 1.293 (s, 26-H_{18}), 2.042 (m, 27-H_4), 7.192 (d, 22-H_4), 7.249 (d, 23-H_4), 7.266-7.314 (m, 2-H_1, 4-H_1, 12-H_1), 7.332-7.389 (m, 1-H_1, 13-H_1), 7.449 (d, 11-H_1), 7.642 (m, 3-H_1), 7.706 (s, 17-H_1), 7.721 (s, 7-H_1), 7.810 (d, 14-H_1).

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 13.97 (30-C), 23.27 (29-C), 26.23 (28-C), 31.51 (26-C), 34.48 (25-C), 40.53 (27-C), 57.77 (19-C), 64.60 (9-C), 114.43 (17-C), 117.79 (7-C), 119.77 (3-C or 14-C), 119.90 (3-C or 14-C), 123.01 (1-C or 13-C), 125.13 (23-C), 126.52 (ArH), 126.77 (ArH), 126.91 (ArH), 127.26 (ArH), 127.36 (ArH), 128.08 (22-C), 139.69 (18-C), 140.58 ($C_{quart.}$), 141.11 ($C_{quart.}$), 141.32 ($C_{quart.}$), 143.01 (21-C), 149.21 (24-C), 150.69 ($C_{quart.}$), 150.89 ($C_{quart.}$), 151.26 (8-C), 152.35 (10-C).

EI-MS: *m/z* (%): 630 (100, $[M]^+$), 573 (40, $[M\text{-}C_4H_9]^+$), 440 (30, $[M\text{-}C_4H_9\text{-}C_{10}H_{13}]^+$).

HR-EI-MS (*m/z*)($C_{48}H_{54}$): calc.: 630.4220
exp.: 630.4215

2.13.3. Synthesis of Hexyl-MIF (13c)



According to the general procedure, 300 mg (0.58 mmol) of the MIF precursor **(8)** and 0.245 mL (3.00 eq., 1.74 mmol) 1-bromohexane are used to obtain an orange-colored solid, which was purified by recrystallization from DMF, resulting in 250 mg (0.36 mmol, 63%) of the product.

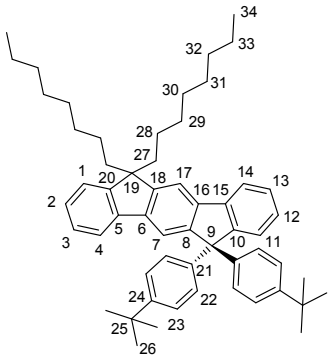
^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.728 (m, 28-H_4), 0.772 (t, 32-H_6), 1.03-1.172 (m, 29-H_4, 30-H_4, 31-H_4), 1.290 (s, 26-H_{18}), 2.027 (m, 27-H_4), 7.180 (d, 22-H_4), 7.239 (d, 23-H_4), 7.254-7.304 (m, 2-H_1, 3-H_1, 12-H_1), 7.311-7.379 (m, 1-H_1, 13-H_1), 7.441 (d, 11-H_1), 7.631 (m, 4-H_1), 7.692 (s, 17-H_1), 7.703 (s, 7-H_1), 7.801 (d, 14-H_1).

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 13.99 (32-C), 22.57 (28-C), 23.87 (31-C), 29.76 (CH_2), 31.36 (26-C), 31.51 (CH_2), 34.34 (25-C), 40.59 (27-C), 54.72 (9-C), 64.45 (19-C), 114.27 (17-C), 117.63 (7-C), 119.63 (4-C), 119.75 (14-C), 122.85 (1-C), 124.98 (23-C), 126.35 (11-C), 126.61 (2-C), 126.75 (3-C), 127.10 (ArH), 127.21 (ArH), 127.94 (22-C), 139.54 (16-C), 140.46 ($C_{quart.}$), 140.99 ($C_{quart.}$), 141.17 ($C_{quart.}$), 143.16 (21-C), 149.06 (24-C), 150.06 ($C_{quart.}$), 150.59 ($C_{quart.}$), 150.76 ($C_{quart.}$), 151.11 ($C_{quart.}$), 152.23 (10-C).

EI-MS: *m/z* (%): 687 (100, $[M]^+$), 601 (25, $[M\text{-}C_6H_{13}]^+$), 468 (20, $[M\text{-}C_6H_{13}\text{-}C_{10}H_{13}]^+$).

HR-EI-MS (*m/z*)($C_{52}H_{62}$): calc.: 686.4846
exp.: 686.4836

2.13.4. Synthesis of Octyl-MIF (13d)



According to the general procedure, 300 mg (0.58 mmol) of the MIF precursor **(8)** and 0.305 mL (3.00 eq., 1.74 mmol) 1-bromooctane are used to obtain an orange-colored solid, which was purified by recrystallization from DMF, resulting in 310 mg (0.42 mmol, 72%) of the product.

^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ (ppm) = 0.732 (m, 28-H_4), 0.814 (t, 34-H_6), 1.022-1.175 (m, 29-H_4, 30-H_4, 31-H_4, 32-H_4), 1.198 (m, 33-H_4), 1.291 (s, 26-H_{18}), 2.023 (m, 27-H_4), 7.181 (d, 22-H_4), 7.242 (d, 23-H_4), 7.256-7.303 (m, 2-H_1, 3-H_1, 12-H_1), 7.313-7.379 (m, 1-H_1, 13-H_1), 7.442 (d, 11-H_1), 7.631 (m, 4-H_1), 7.694 (s, 17-H_1), 7.706 (s, 7-H_1), 7.801 (d, 14-H_1).

^{13}C-NMR ($CDCl_3$, 125 MHz, 300 K) δ (ppm) = 14.20 (34-C), 22.73 (28-C), 24.03 (33-C), 29.36 (CH_2), 29.38 (CH_2), 30.23 (CH_2), 31.51 (26-C), 31.96 (CH_2), 34.49 (25-C), 40.72 (27-C), 54.87 (19-C), 64.59 (9-C), 114.42 (17-C), 117.78 (7-C), 119.78 (4-C), 119.90 (14-C), 123.00 (1-C), 125.13 (23-C), 126.50 (11-C), 126.76 (2-C), 126.90 (3-C), 127.24 (12-C), 127.34 (13-C), 128.09 (22-C), 139.69 ($C_{quart.}$), 140.60 (15-C), 141.13 (16-C), 141.33 (6-C), 143.32 (21), 149.20 (24-C), 150.73 ($C_{quart.}$), 150.89 ($C_{quart.}$), 151.26 (8-C), 152.38 (10-C).

EI-MS: *m/z* (%): 783 (100, $[M]^+$), 629 (30, $[M\text{-}C_8H_{17}]^+$), 496 (30, $[M\text{-}C_8H_{17}\text{-}C_{10}H_{13}]^+$).

HR-EI-MS (*m/z*)($C_{56}H_{70}$): calc.: 742.5472
exp.: 742.5450

EA ($C_{56}H_{70}$) (%): calc.: C 90.51 H 9.49
exp.: C 89.80 H 9.321

3. NMR Spectra

3.1. 2-Fluorenyl-methylbenzoate (10)

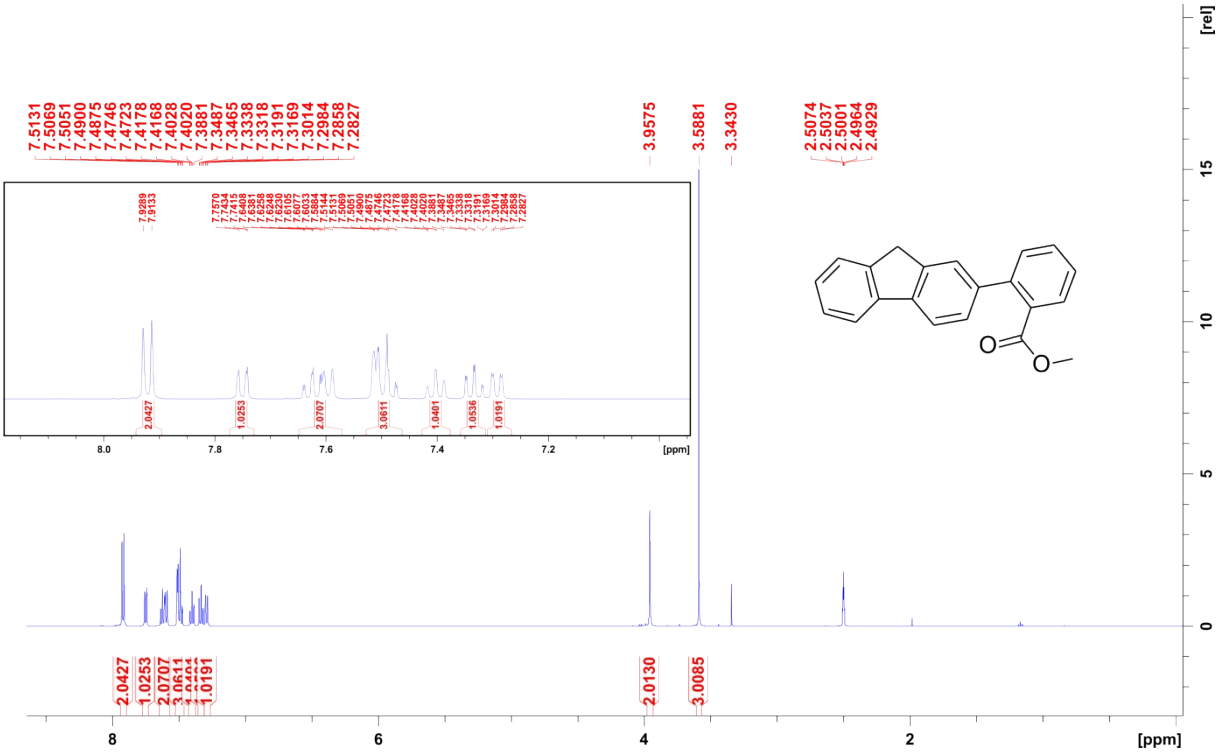


Figure S1. ^{1}H-NMR spectrum of 2-fluorenyl methylbenzoate 10 (DMSO-d$_6$, 500 MHz, 300 K).

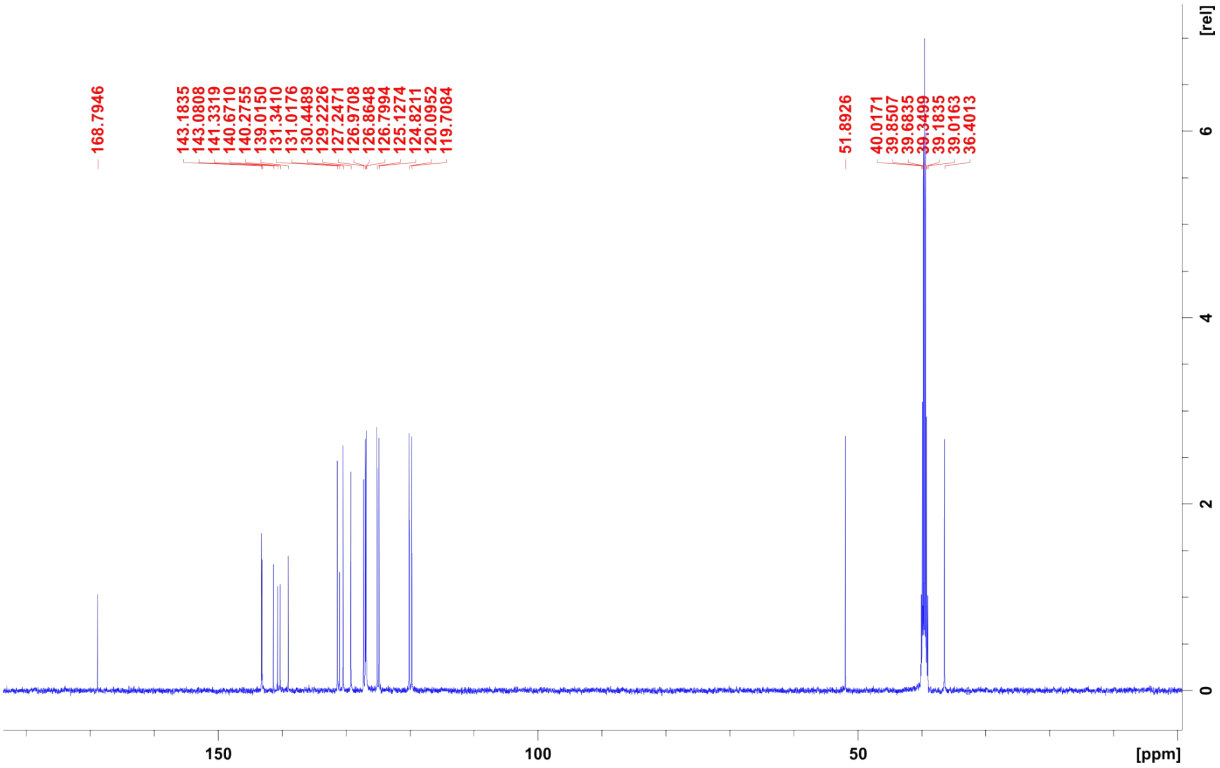


Figure S2. ^{13}C-NMR spectrum of 2-fluorenyl methylbenzoate 10 (DMSO-d$_6$, 125 MHz, 300 K).

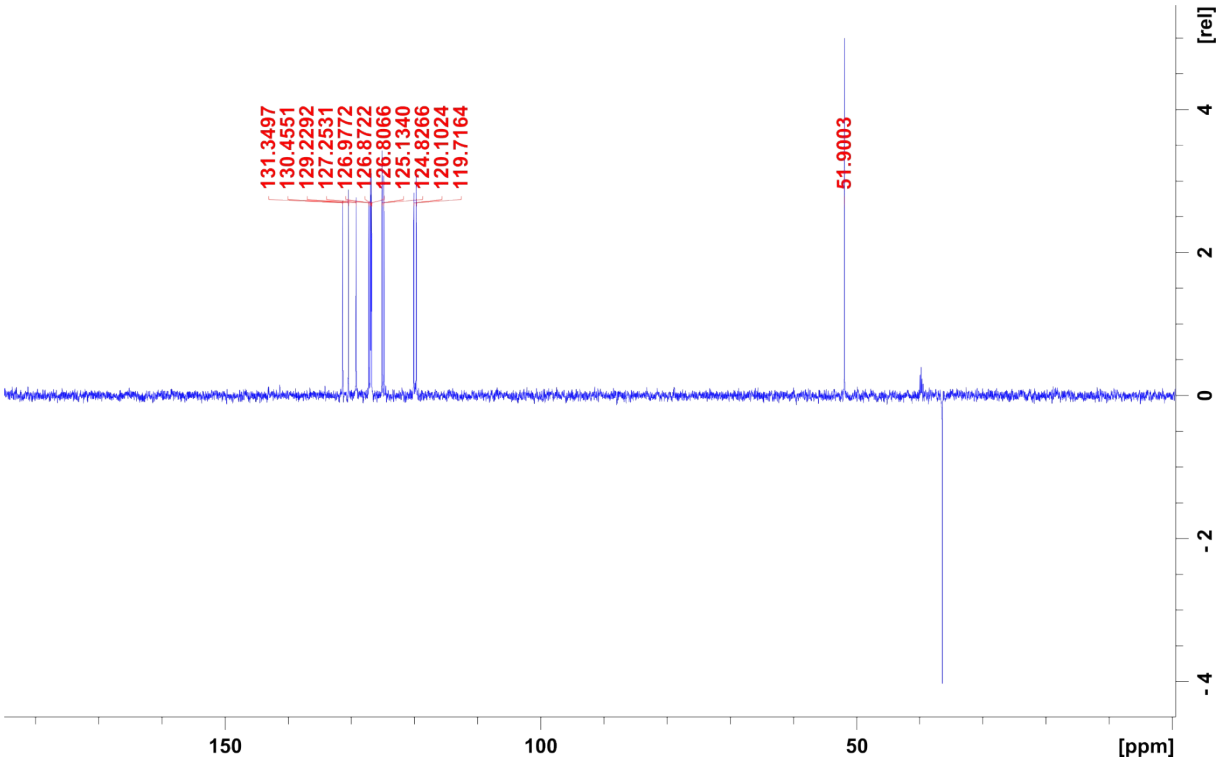


Figure S3. ^{13}C-DEPT-NMR spectrum of 2-fluorenyl methylbenzoate 10 (DMSO-d_6, 125 MHz, 300 K).

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

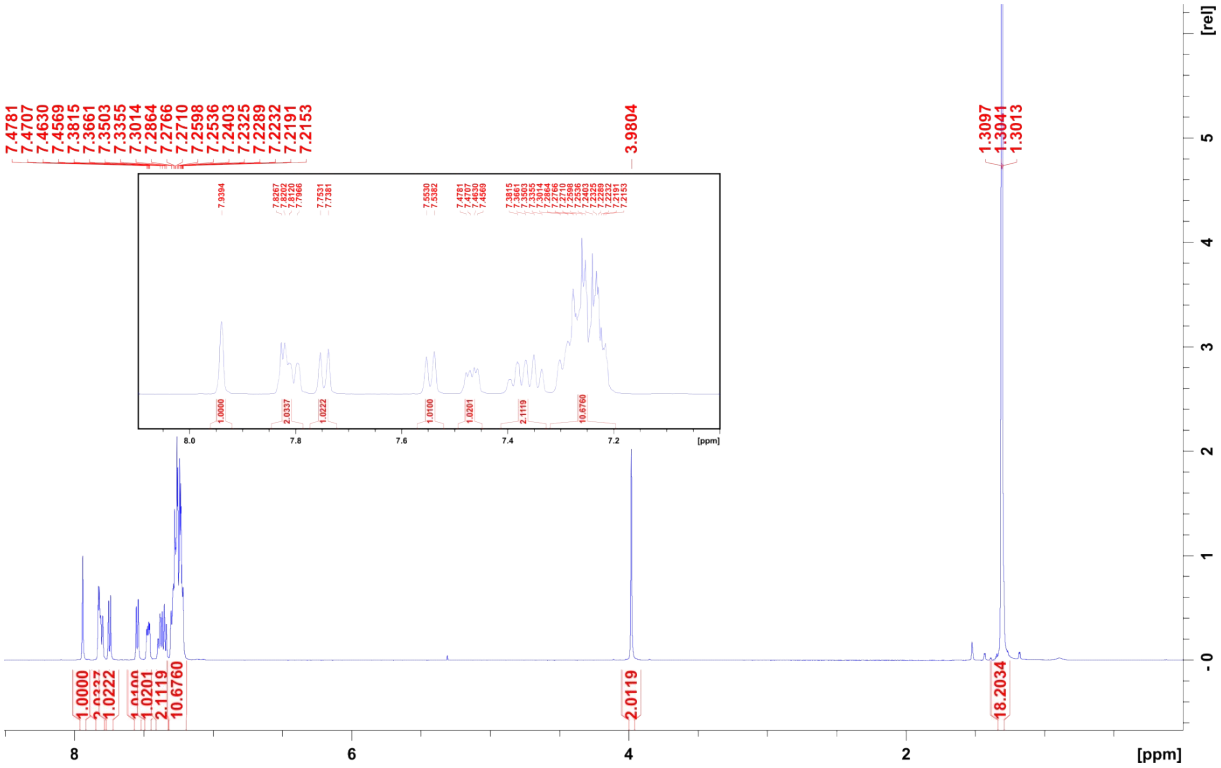


Figure S4. ^{1}H-NMR spectrum of 6,6‘-bis(4-*tert*.-butylphenyl)-6,12-dihydroindeno[1,2-*b*]fluorene 12 ($CDCl_3$, 500 MHz, 300 K).

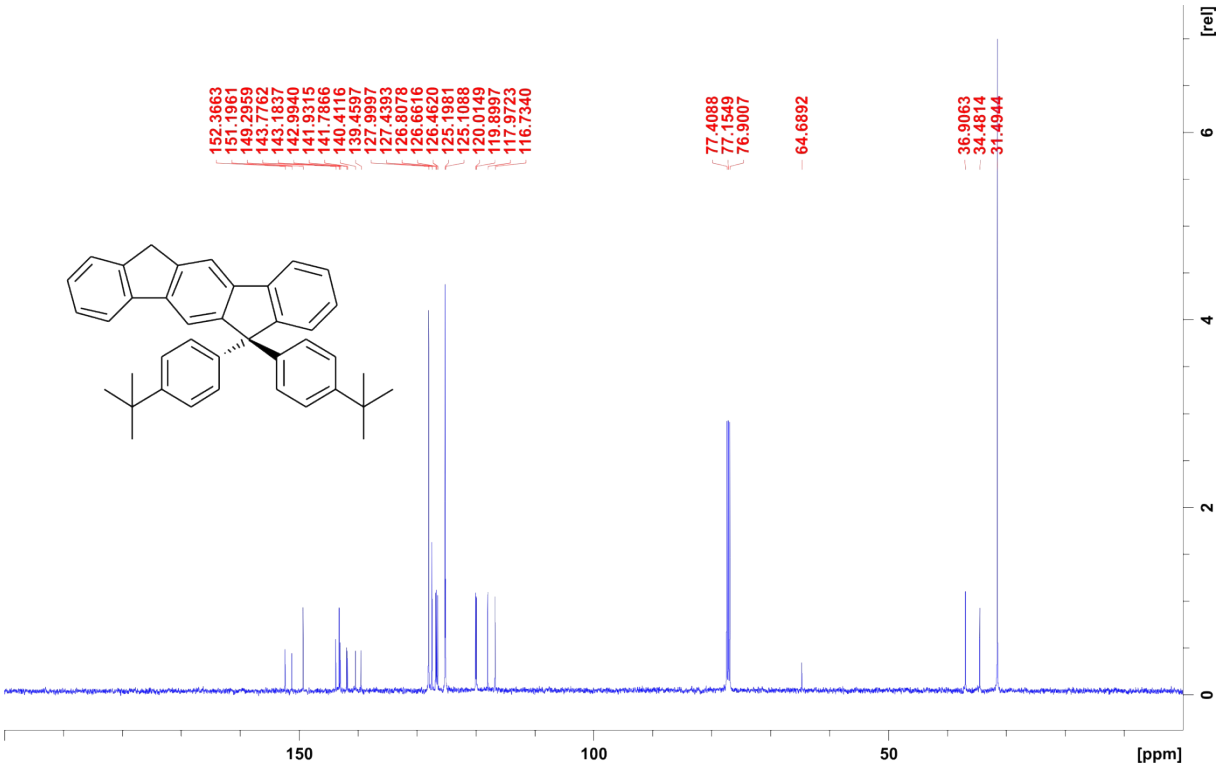


Figure S5. ^{13}C-NMR spectrum of 6,6‘-bis(4-*tert*.-butylphenyl)-6,12-dihydroindeno[1,2-*b*]fluorene 12 ($CDCl_3$, 125 MHz, 300 K).

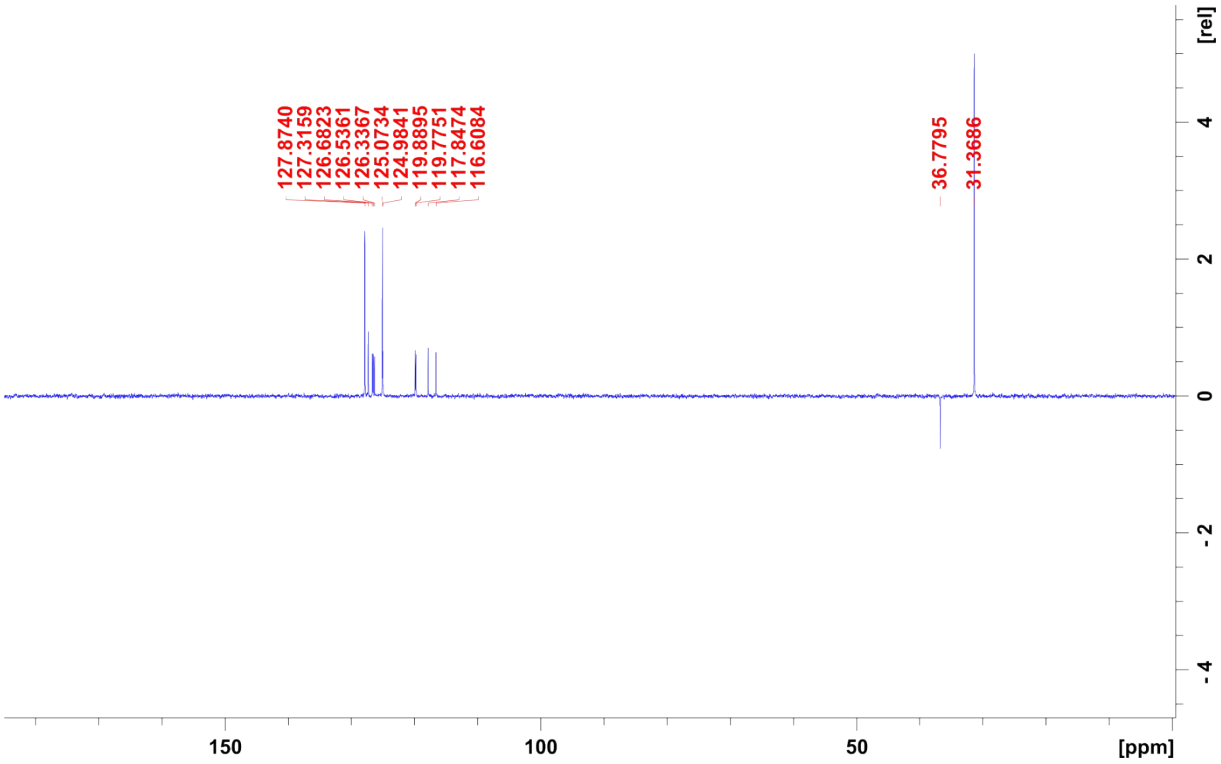


Figure S6. ^{13}C-DEPT-NMR spectrum of 6,6‘-bis(4-*tert*.-butylphenyl)-6,12-dihydroindeno[1,2-*b*]fluorene 12 ($CDCl_3$, 125 MHz, 300 K).

3.3. Methyl-MIF (13a)

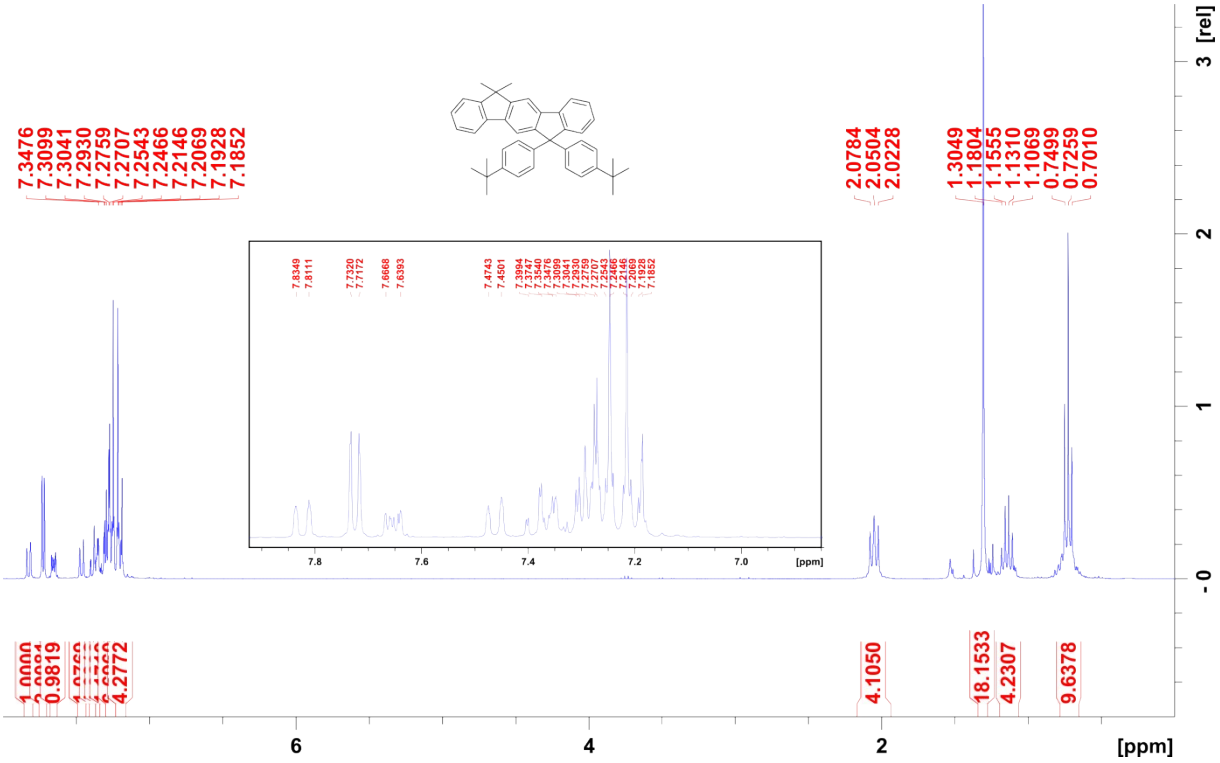


Figure S7. ^{1}H-NMR spectrum of Methyl-MIF 13a ($CDCl_3$, 500 MHz, 300 K).

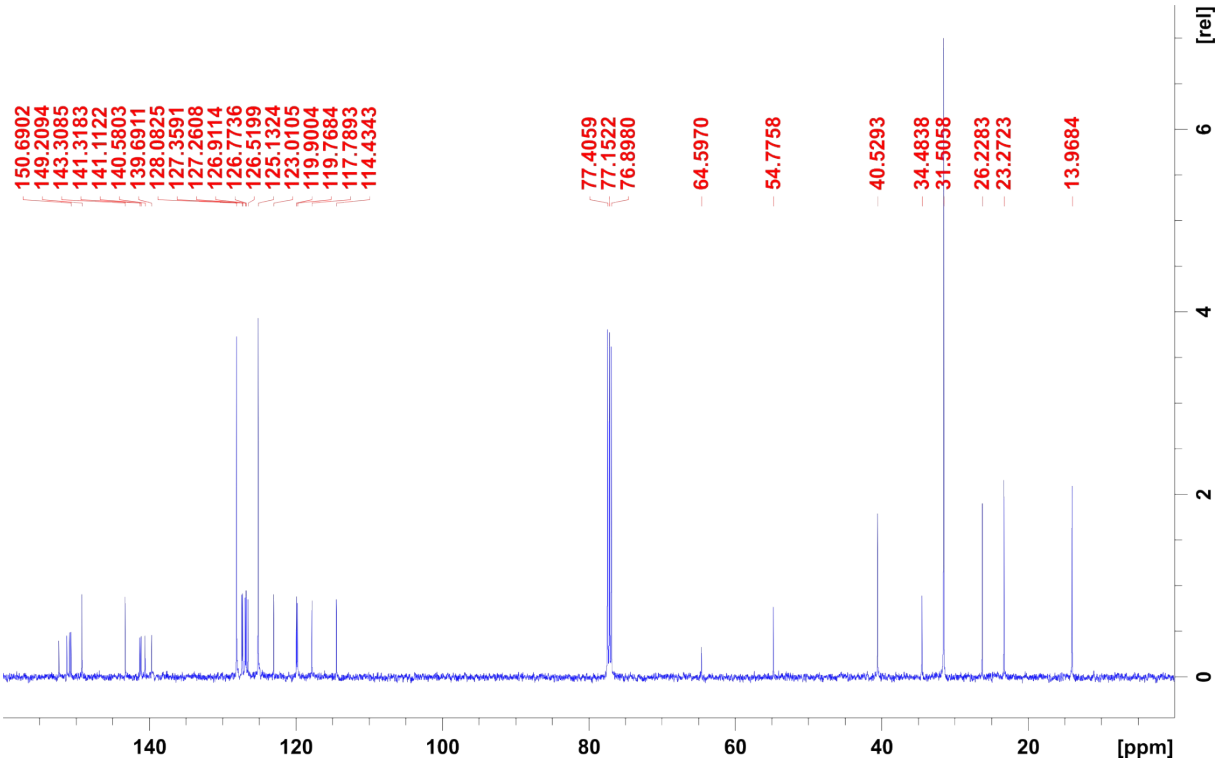


Figure S8. ^{13}C-NMR spectrum of Methyl-MIF 13a ($CDCl_3$, 125 MHz, 300 K).

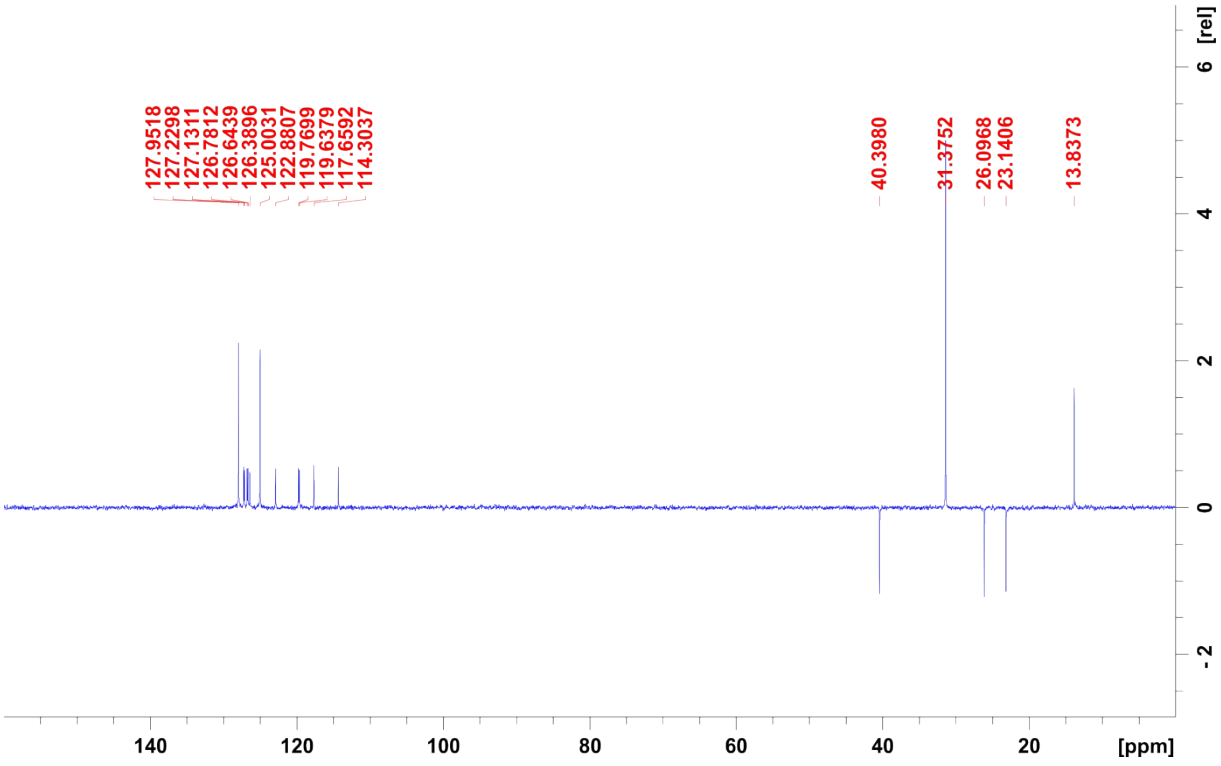


Figure S9. ^{13}C-DEPT-NMR spectrum of Methyl-MIF 13a ($CDCl_3$, 125 MHz, 300 K).

3.4. Butyl-MIF (13b)

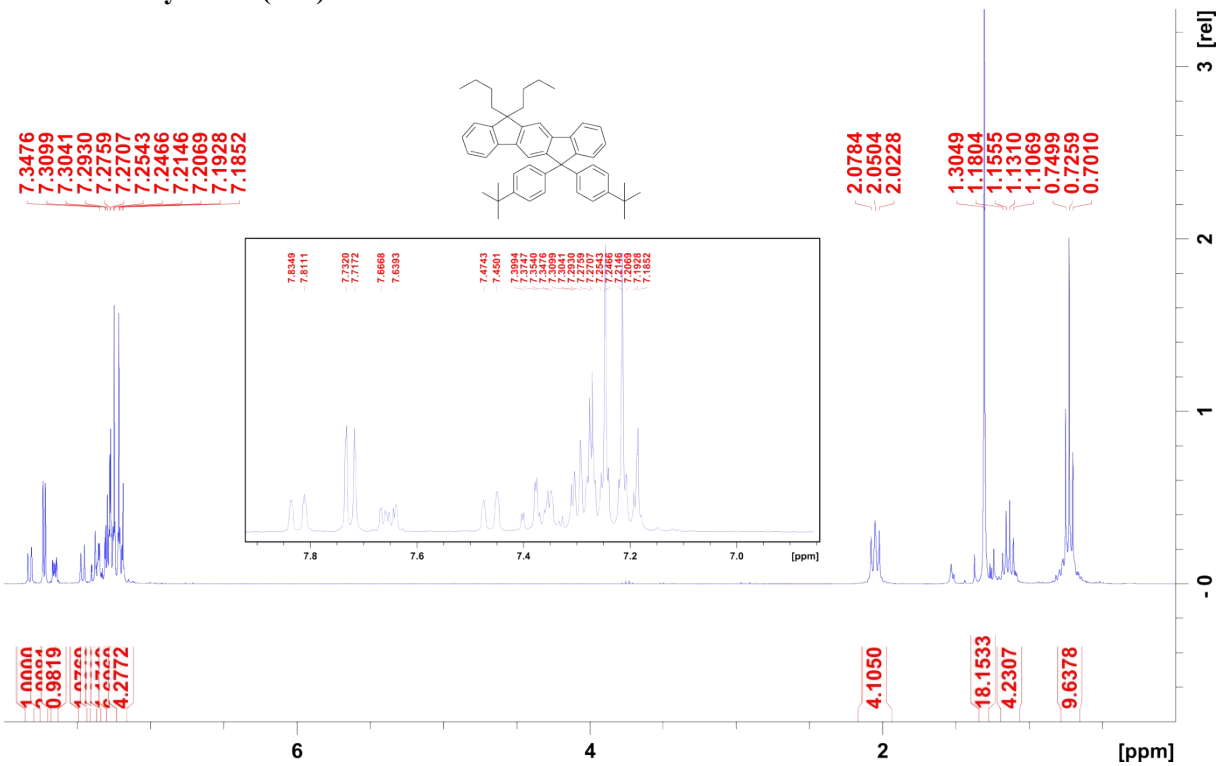


Figure S10. ^{1}H-NMR spectrum of Butyl-MIF 13b ($CDCl_3$, 500 MHz, 300 K).

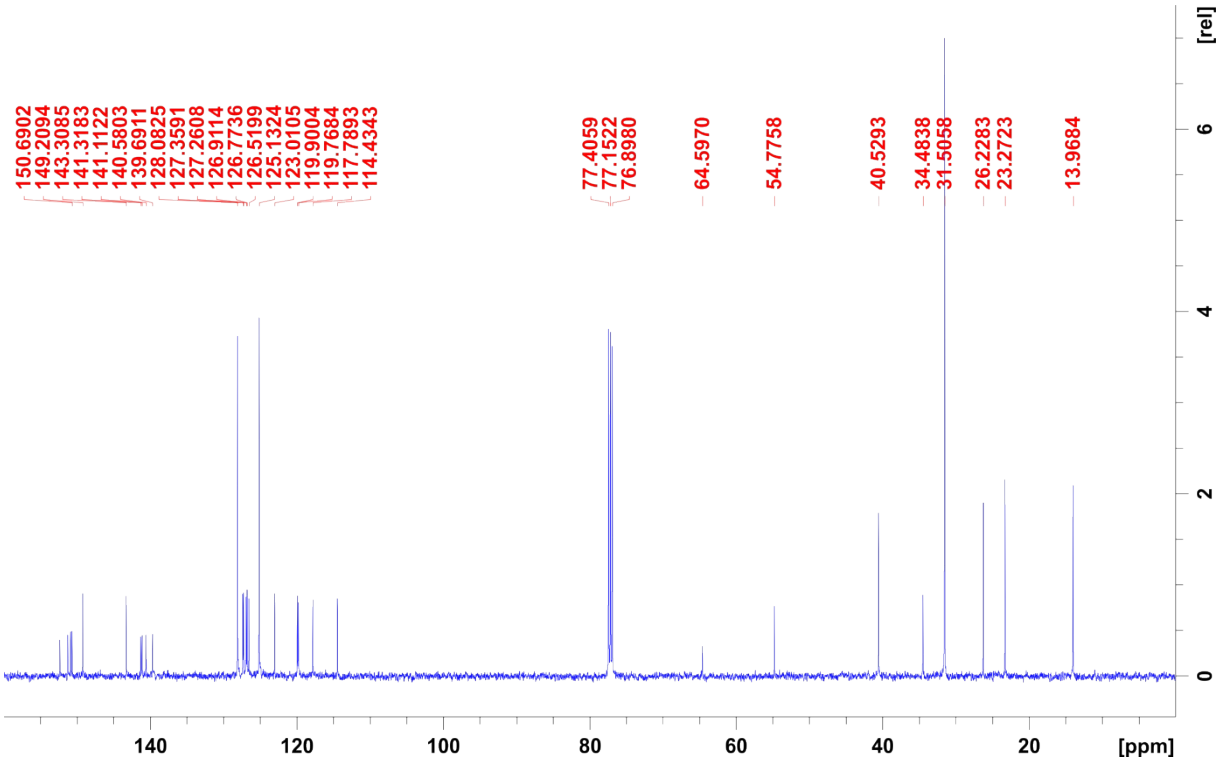


Figure S11. ^{13}C-NMR spectrum of Butyl-MIF 13b ($CDCl_3$, 125 MHz, 300 K).

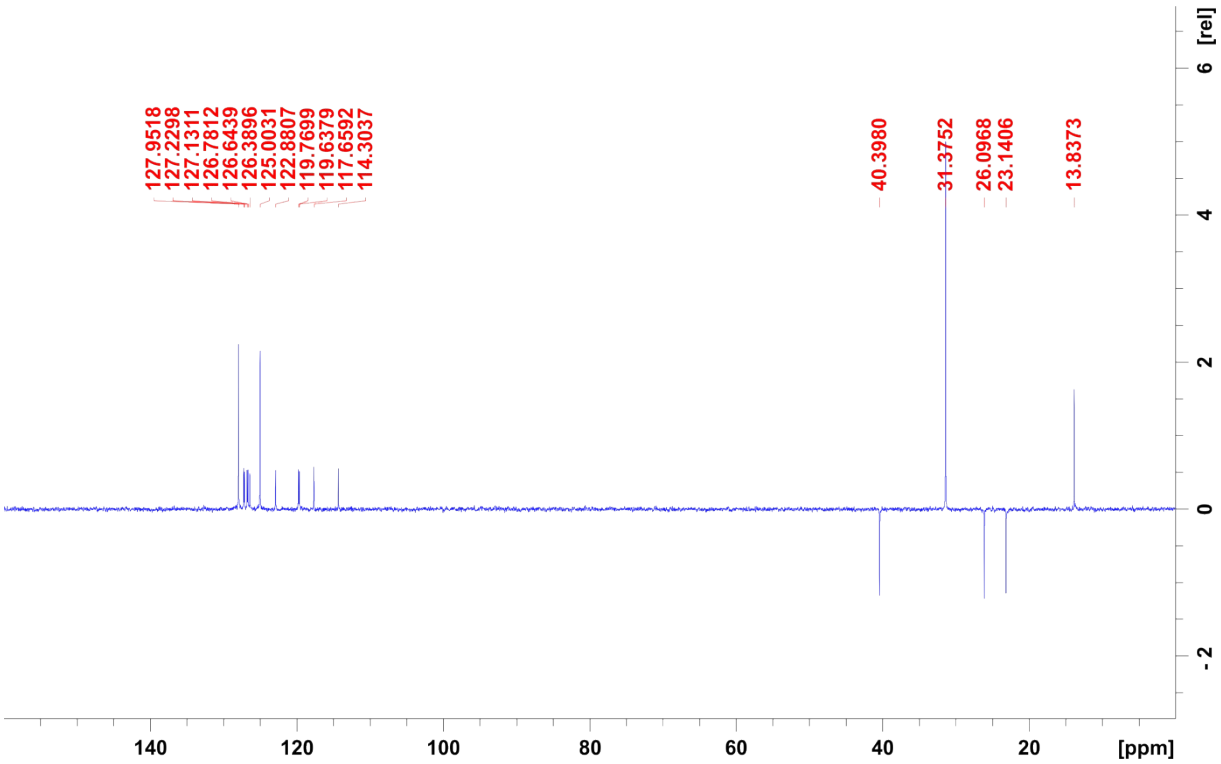


Figure S12. ^{13}C-DEPT-NMR spectrum of Butyl-MIF 13b ($CDCl_3$, 125 MHz, 300 K).

3.5. Hexyl-MIF (13c)

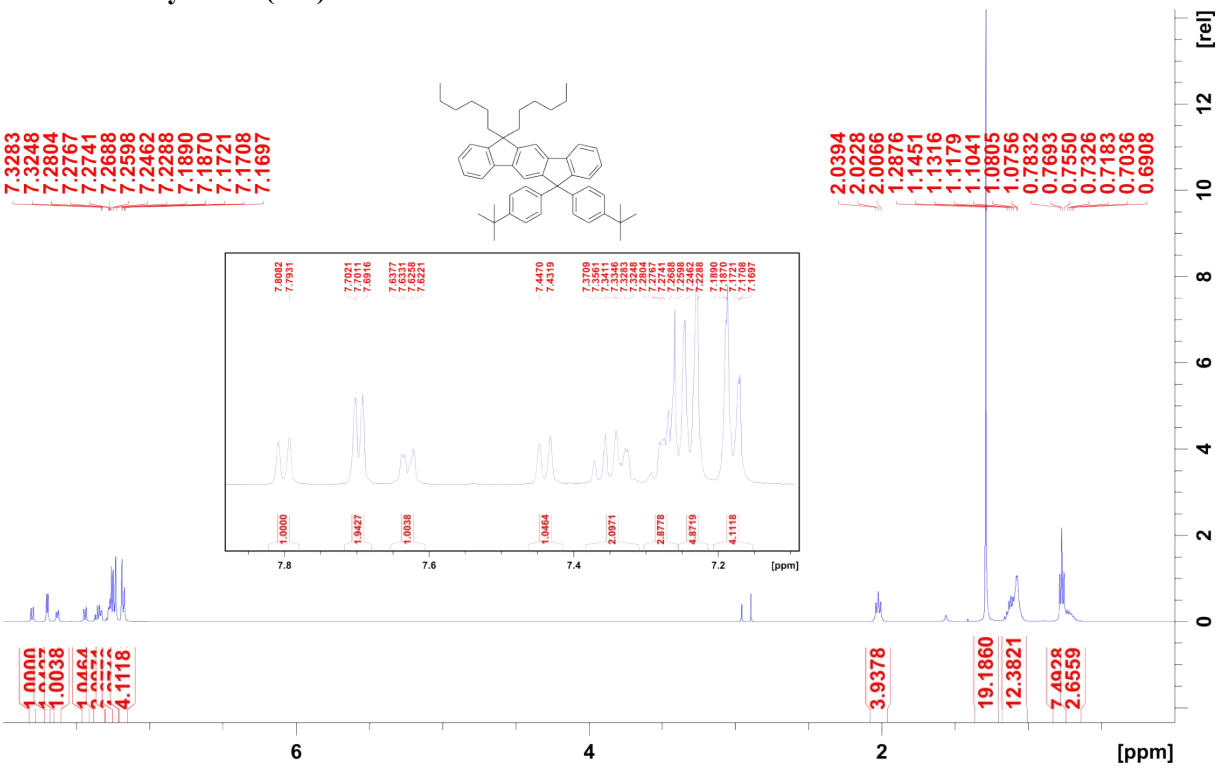


Figure S13. ^{1}H-NMR spectrum of Hexyl-MIF 13c ($CDCl_3$, 500 MHz, 300 K).

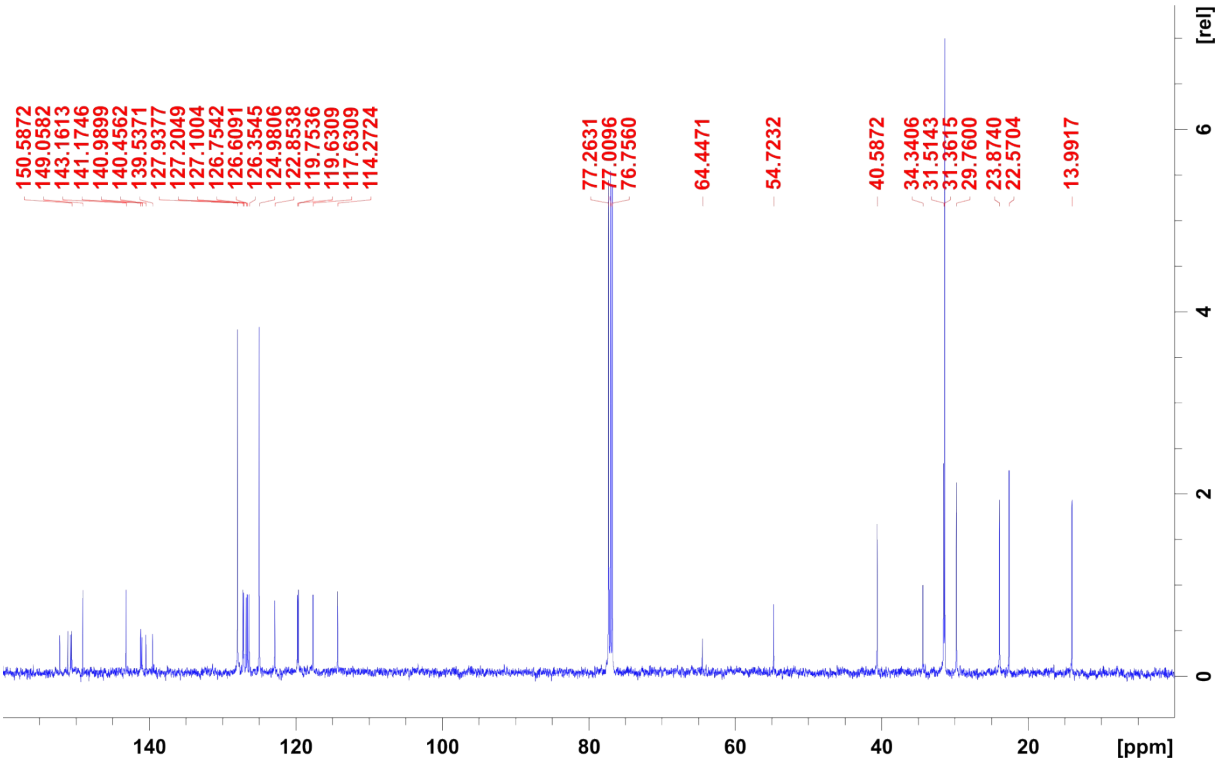


Figure S14. ^{13}C-NMR spectrum of Hexyl-MIF 13c ($CDCl_3$, 125 MHz, 300 K).

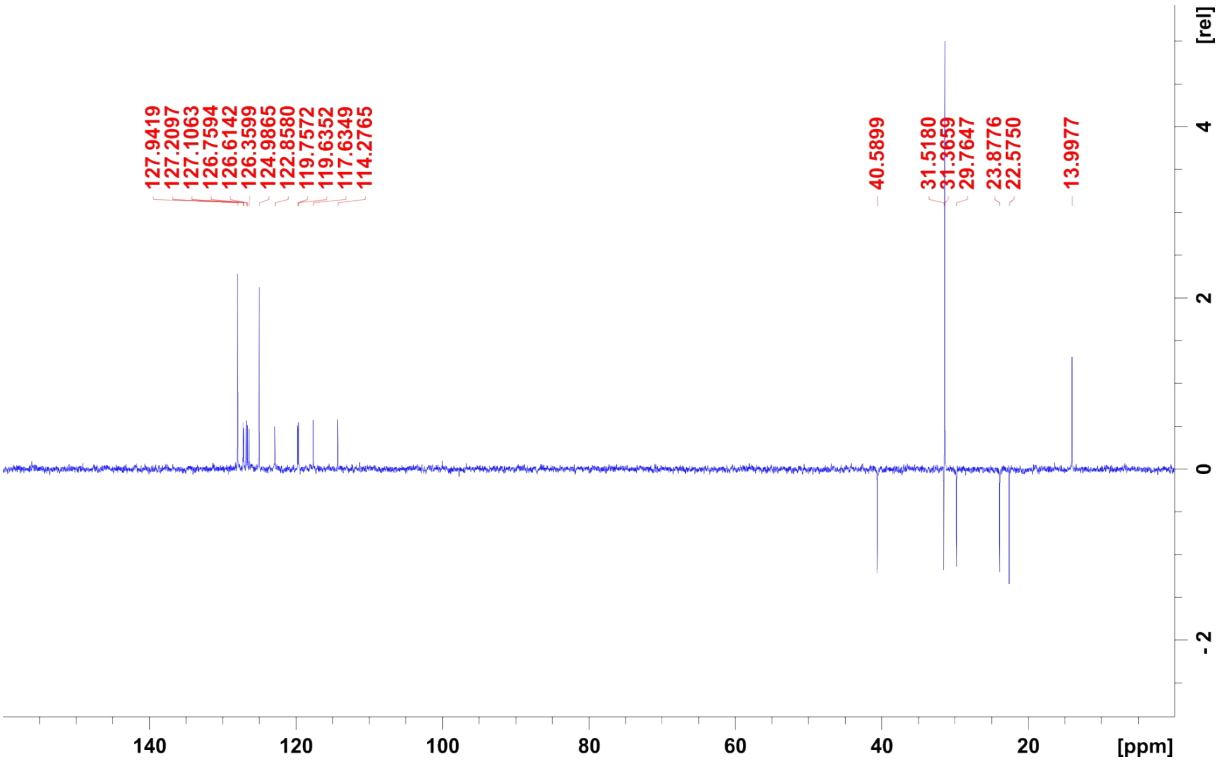


Figure S15. ^{13}C-DEPT-NMR spectrum of Hexyl-MIF 13c ($CDCl_3$, 125 MHz, 300 K).

3.6. Octyl-MIF (13d)

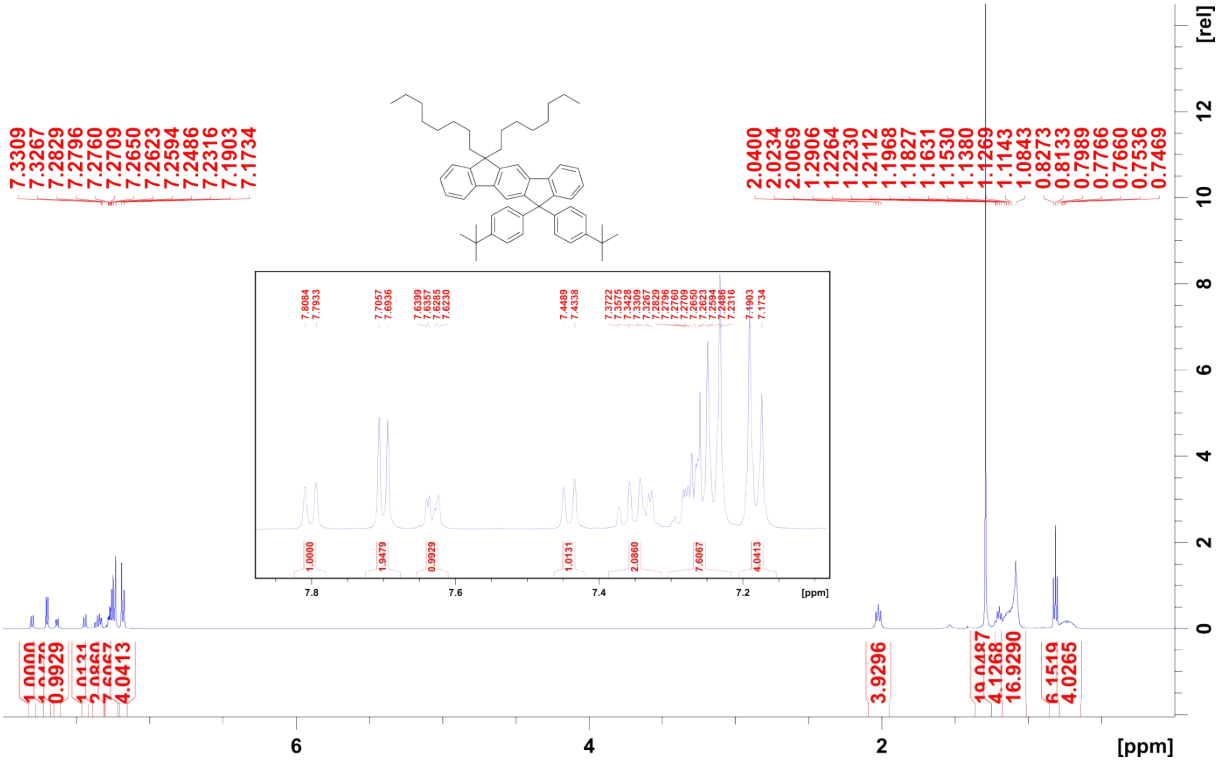


Figure S16. ^{1}H-NMR spectrum of Octyl-MIF 13d ($CDCl_3$, 500 MHz, 300 K).

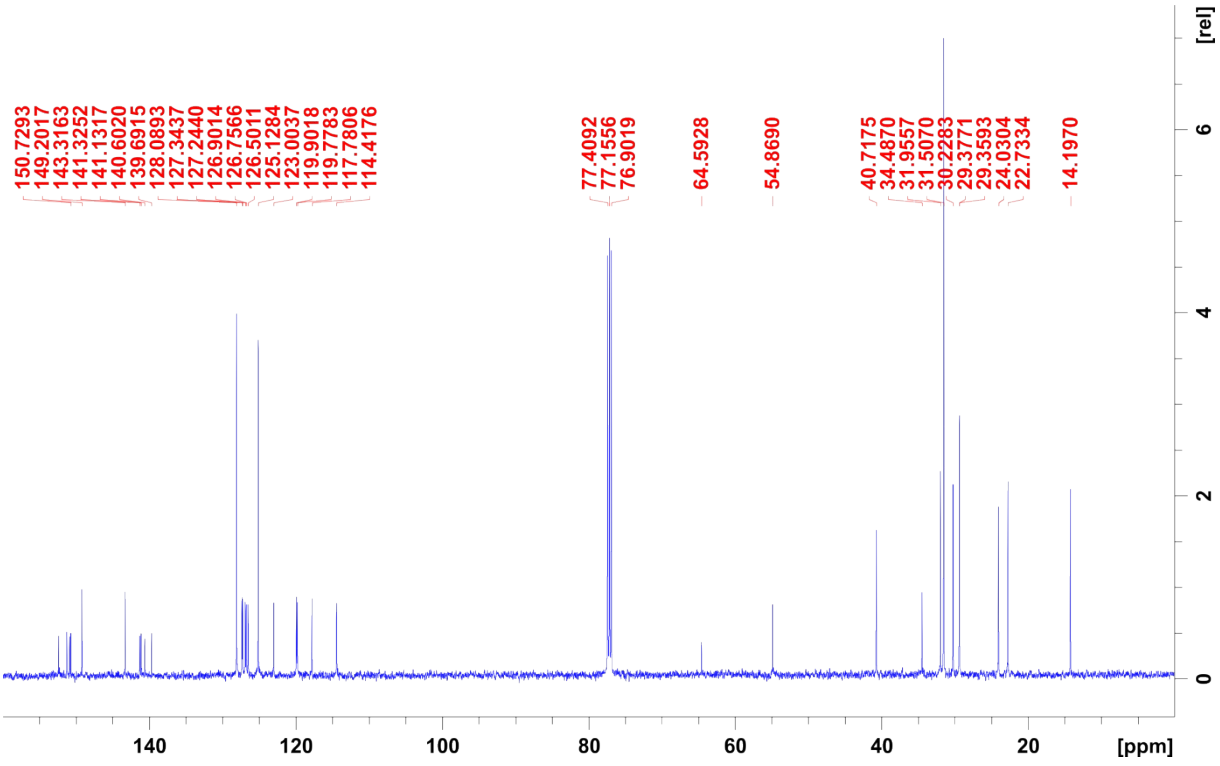


Figure S17. ^{13}C-NMR spectrum of Octyl-MIF 13d ($CDCl_3$, 125 MHz, 300 K).

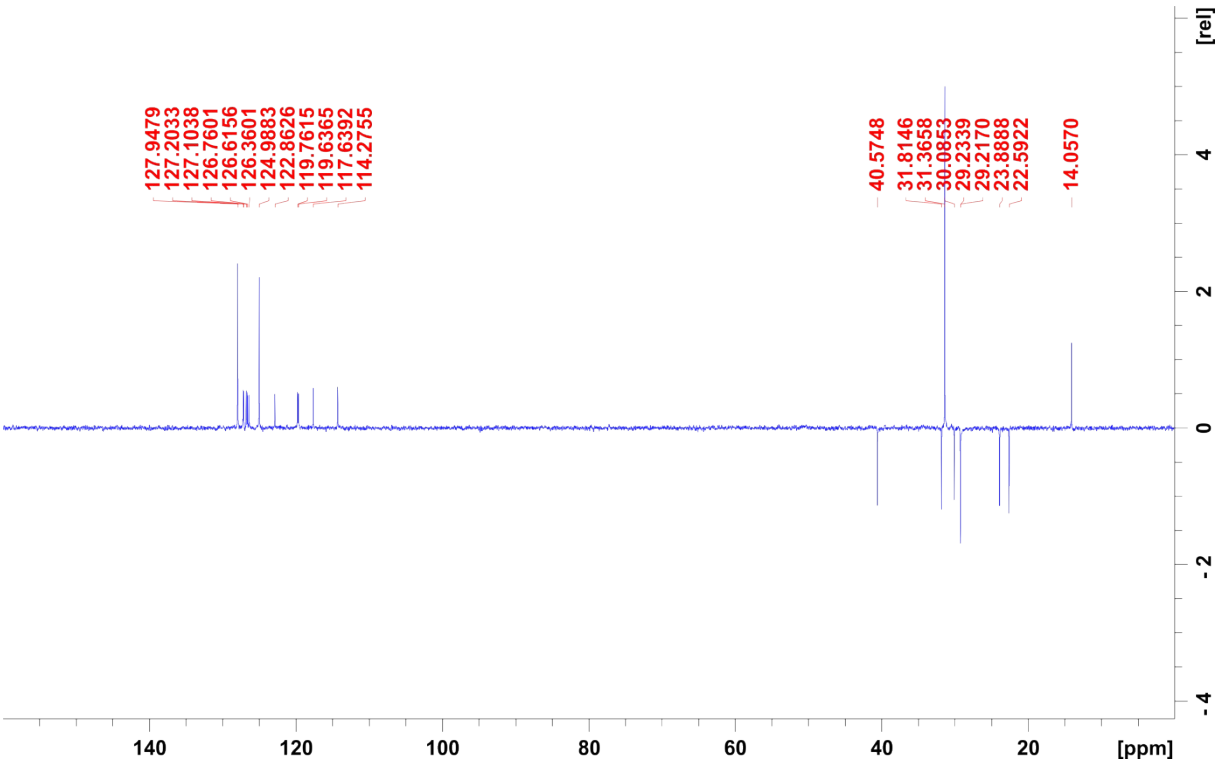


Figure S18. ^{13}C-DEPT-NMR spectrum of Octyl-MIF 13d ($CDCl_3$, 125 MHz, 300 K).

4. Additonal Crystallographic Data

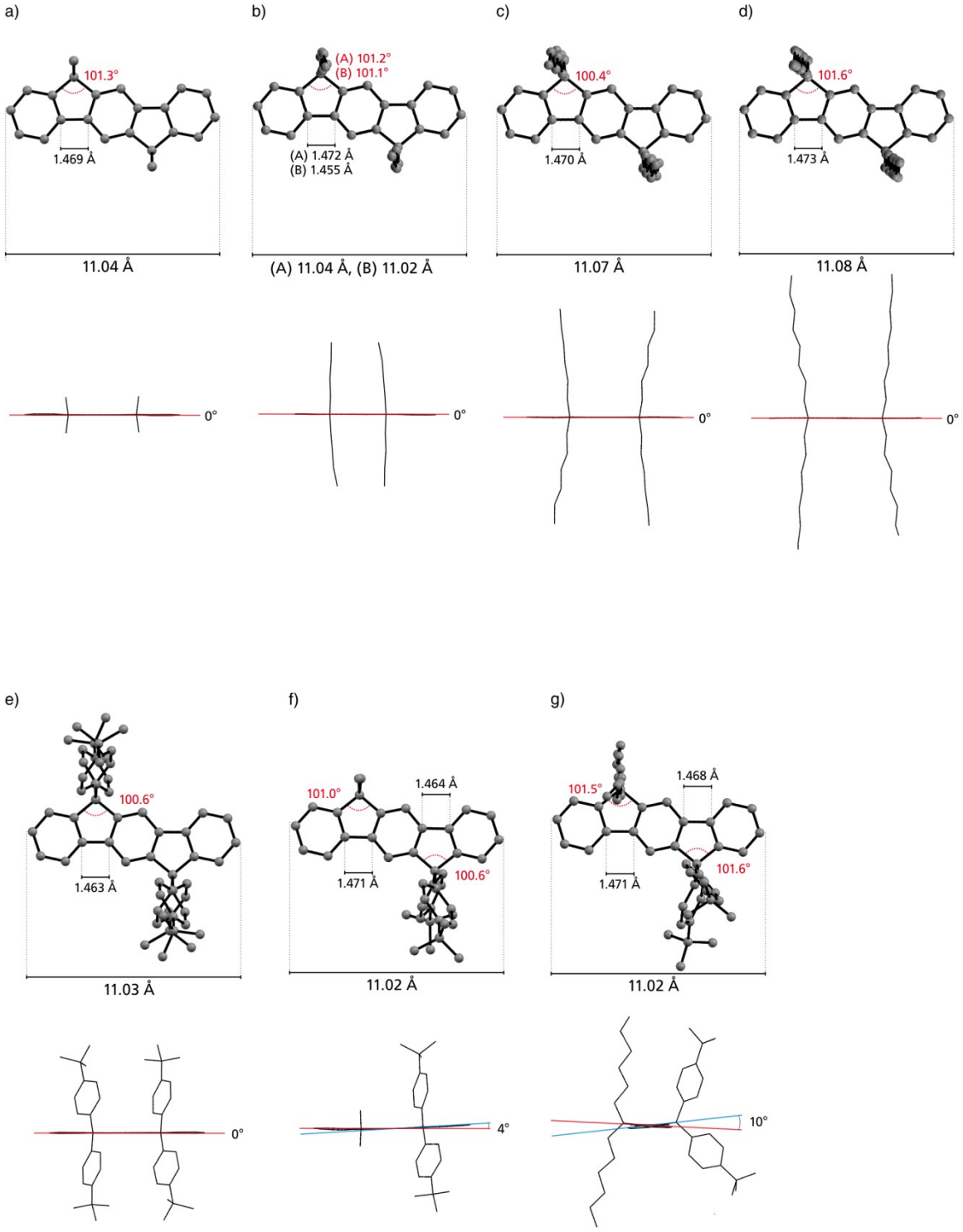


Figure S19. Molecular geometries obtained by single-crystal x-ray analysis. a) Methyl-IF (6a), b) Butyl-IF (6b), c) Hexyl-IF (6c), d) Octyl-IF (6d), e) tBuPh-IF (7a), f) Methyl-MIF (13a), g) Hexyl-MIF (13c)

5. References

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