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Supporting Information

The Liquid Crystal Click Procedure for Oligothiophene-Tethered Phthalocyanines – Self-Assembly, Alignment and Photo Current

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Content

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Supporting information for this article is given via a link at the end of the document.

1) Materials

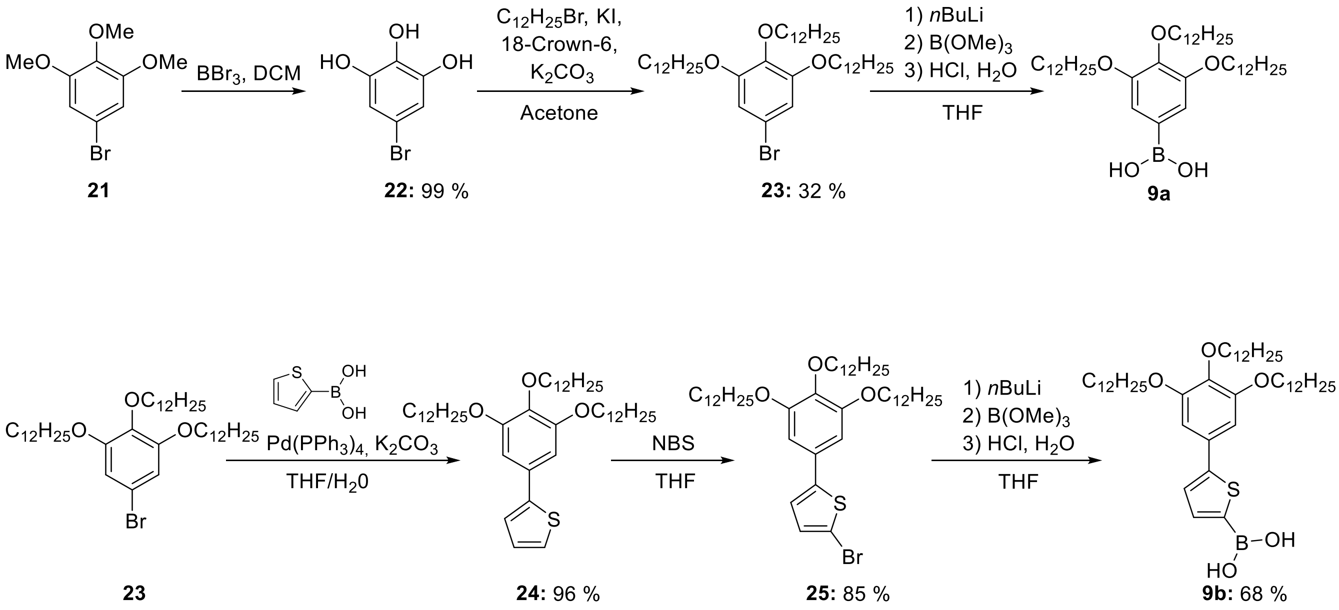
All commercial materials employed were used as received, without further purification.

2) Equipment

Preparative recycling gel permeation chromatography was performed with the liquid chromatograph *LC-20A* (Shimadzu). The column set (PSS *SDV* 50 Å, 20·600 mm; PSS *SDV* 500 Å, 20·600 mm) was eluted with HPLC-grade $CHCl_3$ at a flow rate of 4.0 $mL \cdot min^{-1}$. NMR spectra were recorded on a Bruker-Daltonics *Avance-400* spectrometer operating at 400 MHz (^1H) or 100 MHz (^{13}C) or on a Bruker-Daltonics *Ascend-600* operating at 600 MHz (^1H) or 151 MHz (^{13}C), with the residual solvent signal used as the internal standard. Mass spectra were recorded on a Bruker-Daltonics *autflex II* (MALDI), on a Bruker-Daltonics *ultrafleXtreme* (HRMS-MALDI) and on a Bruker-Daltonics *microTOF focus* (HRMS-ESI). Elemental analysis experiments were performed at the Institute of Inorganic Chemistry, University of Würzburg. The studies of optical textures of the mesophases were realized with a Nikon *Eclipse LV100Pol* optical polarizing microscope equipped with a Linkam *LTS420* heating stage and a Linkam *T95-HS* system controller. UV-Vis- absorption studies in solution and in thin film were performed with a JASCO *V-770*. Emission studies in solution were realized with an Edinburgh Instruments *FLS980*. The temperature dependent SAXS, MAXS and WAXS X-ray investigations were performed on a Bruker Nanostar (Detector Vantec2000, Microfocus copper anode X-ray tube Incoatec). The aligned fibers were transferred to Mark capillaries, which were sealed and glued into the metal sample holder. The XRS heating system was calibrated by liquid crystal standard compounds.

3) Synthesis

The synthesis of the core-precursor **6** as carried out according to reference [1]. The fullerene with spacer **20** was synthesized according to reference [2]. Compound **9a** (Scheme S1) has been prepared similar to literature procedures starting from bromine **21** [3], compound **25** has been prepared according to the literature.[4]



Scheme S1. Synthesis of the head group derivatives **9a** and **9b**.

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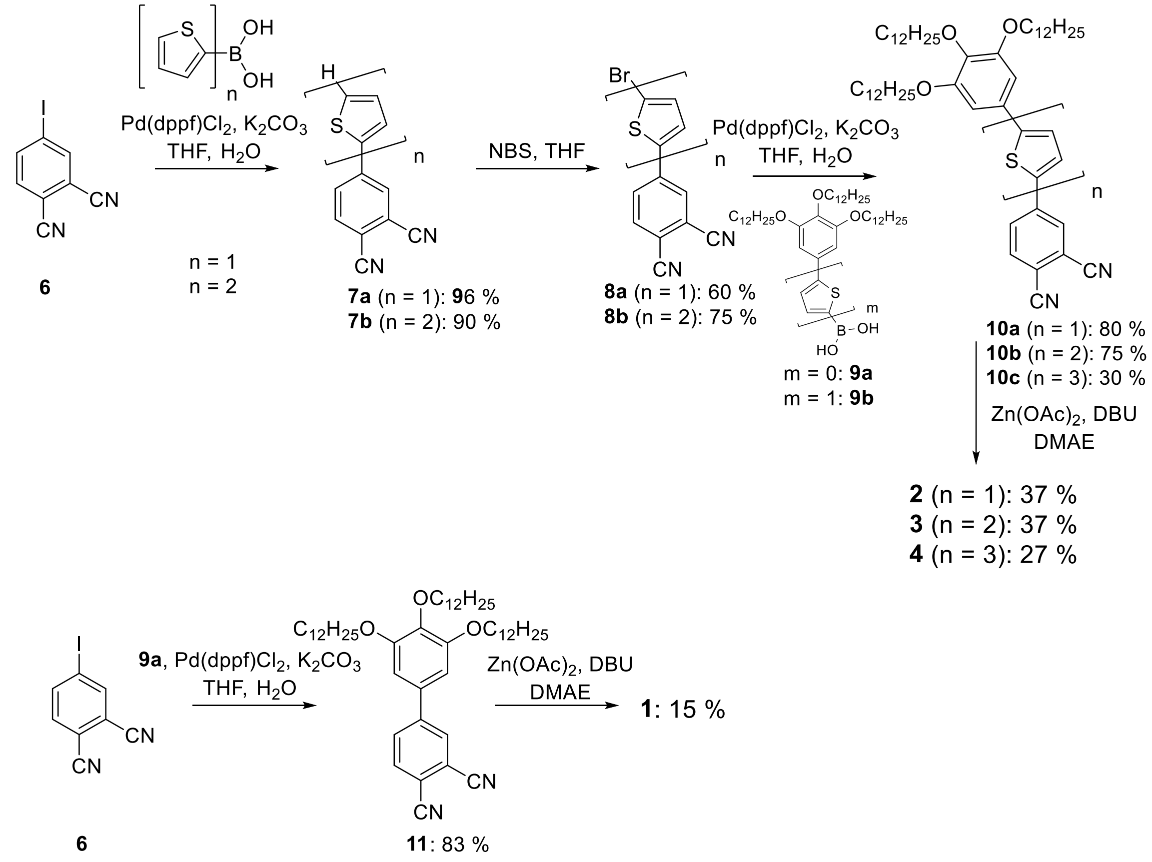
[1] M. Lehmann, M. Dechant, M. Holzapfel, A. Schmiedel, C. Lambert, *Angew. Chem. Int. Ed.* **2019**, *58*, 3610.

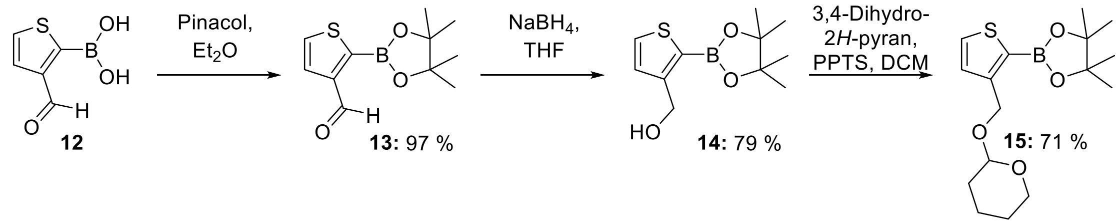
[2] M. Lehmann, M. Dechant, M. Hügel, N. Scheuring, T. Ghosh, *Chem. Eur. J.* **2019** , 25, 3352-3361.

[3] F. Lincker, P. Bourgun, P. Masson, P. Didier, L. Guidoni, J.-Y. Bigot, J.-F. Nicoud, B. Donnio, D. Guillon, *Organic Letters*, **2005**, *7*, 1505-1508.

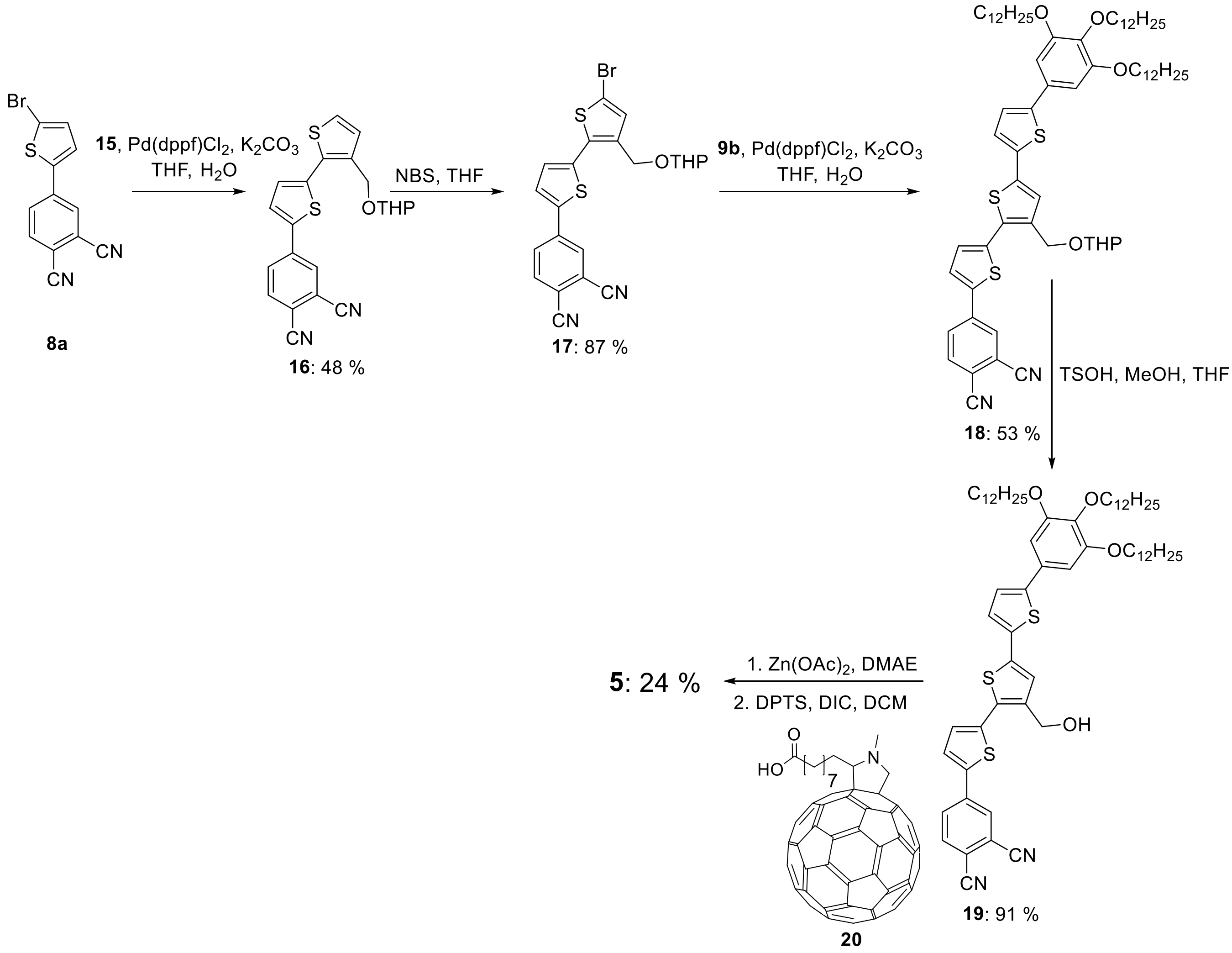
[4] T. Yasuda, T. Shimizu, F. Liu, G. Ungar,. T. Kato, *J. Am. Chem. Soc.* 2011, 133, 34, 13437-13444



Scheme S2. Synthesis of the phthalocyanines **1-4**.



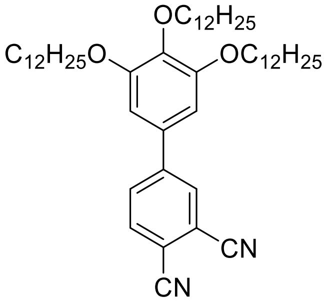
Scheme S3. Synthesis of the functionalized repeating unit **15**.



Scheme S2. Synthesis of phthalocyanine **5**.

Synthetic Procedures

3',4',5'-tris(dodecyloxy)-[1,1'-biphenyl]-3,4-dicarbonitrile (**11**)



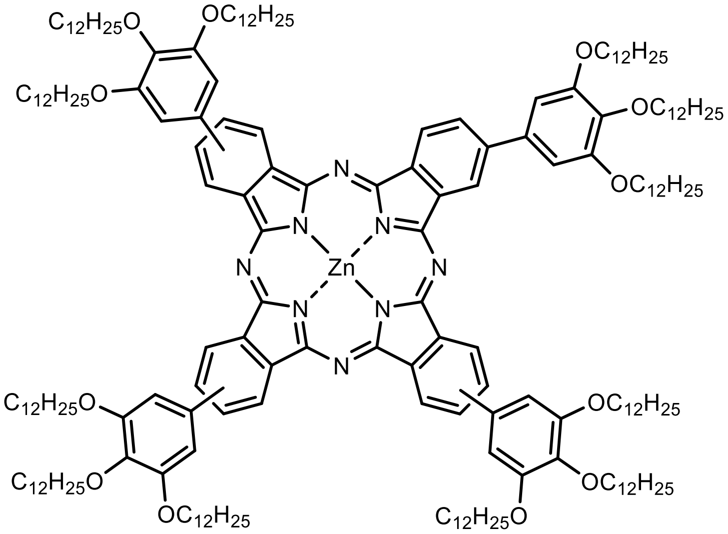
132 mg (518 µmol) compound **6** and 454 mg (673 µmol) of the boronic acid 2**5** were dissolvend in dry THF under nitrogen atmosphere. After degassing for 20 minutes, 19.0 mg (26.0 µmol) Pd(dppf)Cl_2 and 107 mg (777 µmol) K_2CO_3 dissolved in three mL dest. H_2O were added and the mixture was heated to 90 °C for 24 hours. After complete reaction, dest. H_2O was added and the aqueous phase was extracted with DCM. The combined organic phases were dried over Na2SO4, the solvent removed under reduced pressure and the crude product purified by column chromatography (silica, ethyl acetate : dichloromethane = 10 : 1 (*v*/*v*)) to yield 325 mg (429 µmol, 83 %) of a colorless solid.

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 0.88 (t, ^3J = 6.84 Hz, 6 H, C*H*$_3$), 0.88 (t, ^3J = 6.88 Hz, 3 H, C*H*$_3$), 1.27-1.35 (m, 48 H, C*H*$_2$), 1.46-1.51 (m, 6 H, C*H*$_2$), 1.73 (qui, ^3J = 7.1 Hz, 2 H, C*H*$_2$), 1.83 (qui, ^3J = 7.0 Hz, 4 H, $_2$C*H*$_2$), 3.98 (t, ^3J = 6.6 Hz, 2 H, C*H*$_2$), 4.03 (t, ^3J = 6.5 Hz, 4 H, C*H*$_2$), 6.76 (s, 1 H, aromat. H), 7.85 (dd, ^3J = 8.2 Hz, ^5J = 0.5 H, 1 H, aromat. H), 7.90 (dd, ^3J = 8.2 Hz, ^4J = 1.8 Hz, 1 H, aromat. H), 8.00 (dd, ^4J = 1.8 Hz, ^4J = 0.5 Hz, 1 H, aromat. H) ppm.

^{13}C NMR (100 MHz, CD_2Cl_2): δ = 14.3 (C_p), 26.5 29.7(7) 29.7(9), 29.9(8), 30.0(4), 30.0(6), 30.1(1), 30.1(4), 30.2. 30.7. 32.3. 69.7. 73.9 (C_s), 105.9 (C_t), 113.8, 116.1, 116.2,116.6 (C_q), 131.6, 132.2 (C_t), 132.4 (C_q), 134.2 (C_t), 139.9, 146.9, 154.3 (C_q) ppm.

MALDI-HRMS: m/z: calculated: 756.6163 $[M]^{\bullet+}$, found: 756.6147 $[M]^{\bullet+}$.

2(3),9(10),17(18),23(24)-Tetrakis-(5-(3,4,5-tris(dodecyloxy)phenyl))zinkphthalocyanine (**1**)



195 mg (258 µmol) **11**, 22.6 mg (103 µmol) $Zn(OAc)_2 \cdot 2H_2O$ and three drops of DBU were dissolved in DMAE under nitrogen atmosphere. The reaction was stirred at 130 °C for 24 hours. After complete reaction, the solvent was removed under removed pressure and the crude product purified by column chromatography (silica, ethyl acetate), by GPC and twice by recrystallization from a mixture of THF and methanol to 23.0 mg (9.37 µmol, 15 %) of a green solid.

^{1}H NMR (400.1 MHz, THF-d_8 + 2 drops of pyridine-d_5): δ = 0.84-0.92 (m, 36 H, CH_3), 1.26-1.46 (m, 192 H, CH_2), 1.57-1.64 (m, 24 H, CH_2), 1.84-1.87 (m, 8 H, CH_2), 1.95-1.99 (m, 16 H, CH_2), 4.09-4.14 (m, 8 H, CH_2), 4.24-4.29 (m, 16 H, CH_2), 7.27-7.32 (m, 8 H, aromat. H), 8.38 (bs, 4 H, aromat. H), 9.44-9.54 (m, 4 H, aromat. H), 9.62-9.70 (m, 4 H, aromat. H) ppm.

^{13}C NMR (151.0 MHz, THF-d_8 + 2 drops of pyridine-d_5): δ = 14.5 (C_p, CH_3), 23.6, 27.4, 30.3(8), 30.4(2), 30.6(0), 30.6(4), 30.7, 30.7(6), 30.8(4) 30.9, 31.6, 33.0, 32.9, 70.1, 73.8 (C_s), 107.8, 107.9, 121.9, 123.9, 129.4 (C_t), 138.0, 139.9, 140.4, 144.3, 154.8 (C_q) ppm.

Several quaternary and tertiary signals, especially of the phthalocyanine core and the arms of low intensity could not be identified certainly due to aggregation and the presence of four regioisomers. Moreover, only very broad signals could be obtained, for which reason, ^{13}C spectra are often omitted in the literature or only selected peaks are assigned.[5,6,7]

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[5] Garland et al. / *Tetrahedron* **2015,** *71,* 7310-7314

[6] M. Ince, F. Cardinali, J-H Yum, M. V. Martinez-Diaz, M. K. Nazeeruddin, M. Grätzel, T. Torres*, Chem. Eur. J.* **2012**, 18, 6343 – 6348.

[7] Z. Zhao, T. Nyokong and M. D. Maree, Dalton Trans., **2005** , 3732-3737.

UV-Vis (THF), λ max, (ε/10^4): 361 (10.31), 621 (5.59), 664 (7.56), 688 (34.38) nm.

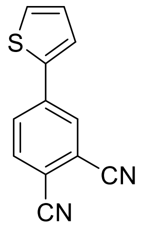
MALDI-HRMS, m/z: calculated: 3090.396 $[M]^{\bullet+}$, found: 3090.397 $[M]^{\bullet+}$.

FT-IR, $\tilde{\nu}$ [cm^{-1}]: 556.4, 667.3, 726.1, 747.3, 820.6, 873.6, 1012.5, 1043.3, 1105.0, 1241.9 (C-O), 1337.4, 1377.9, 1464.7, 1507.1, 1576.5 (aromat. C=C), 1667.2, 1713.4 (C=N), 2851.2, 2919.7 (C-H).

Elemental analysis (%) für $C_{200}H_{320}N_8O_{12}Zn$: calculated: C 77.64, H 10.42, N 3.62 found: C 76.00, H 10.18, N 3.49. [A]

Melting point: 249 °C.

4-(Thiophen-2-yl)phthalonitrile (**7a**)



1.00 g (3.93 mmol) **6** and 528 mg (4.13 mmol) thiophene-2-boronic acid were dissolved in dry THF under nitrogen atmosphere. After degassing for 20 minutes, 227 mg (200 µmol) $Pd(PPh_3)_4$ and 815 mg (5.90 mmol) K_2CO_3 dissolved in three mL dest. H_2O were added and the mixture was heated to 90 °C for 24 hours. After complete reaction, dest. H_2O was added and the aqueous phase was extracted with DCM. The combined organic phases were dried over Na2SO4, the solvent removed under reduced pressure and the crude product purified by column chromatography (silica, ethyl acetate : dichloromethane = 1 : 3 (*v*/*v*)) to yield 797 mg (3.79 mmol, 83 %) of a colorless solid.

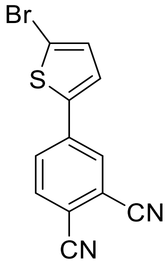
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.17-7.19 (m, 1 H, aromat. H), 7.49-7.51 (m, 2 H, aromat. H), 7.79 (dd, ^3J = 8.3 Hz, ^5J = 0.5 Hz, 1 H, aromat. H), 7.91 (dd, ^3J = 8.3 Hz, ^4J = 1.9 Hz; 1 H, aromat. H), 8.00 (dd, ^4J = 1.9 Hz, ^5J = 0.5 Hz;1 H, aromat. H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.4,115.4, 115.6, 116.9 (C_q), 126.7, 129.0, 129.2, 129.6, 130.2, 134.2 (C_t),139.7, 139.8 (C_q) ppm.

Elemental analysis (%) für $C1_2H_6N_2S$, calculated: C 68.55, H 2.88, N 13.32 S 15.25 found: C 68.49, H 2.78, N 13.46 15.32.

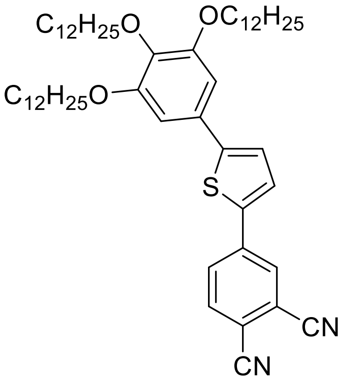
Melting point: 161.5 °C (160.6-162.4 °C)

4-(5-Bromthiophen-2-yl)phthalonitrile (**8a**)



797 mg (3.79 mmol) **7a** and 729 mg (4.10 mmol) NBS were dissolved in THF. After stirring at room temperature for three days, the solvent was removed under reduced pressure and the the crude product purified by column chromatography (silica, ethyl acetate : dichloromethane = 1 : 3 (*v*/*v*)) to yield 660 mg (2.27 mmol, 60 %) of a colorless solid.
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.17 (d, ^3J = 4.0 Hz, 1 H, aromat. H), 7.27 (d, ^3J = 4.0 Hz, 1 H, aromat. H), 7.82 (m, 2 H, aromat. H), 7.92-7.93 (m, 1 H, aromat. H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.8, 115.2, 115.4, 116.4, 117.0 (C_q), 126.9, 129.2, 129.8, 132.0, 134.4 (C_t),138.7, 141.0 (C_q) ppm.
ESI-HRMS, m/z: calculated: 310.9249 $[M]^+$, found: 310.9238 $[M]^+$.
Melting point: 180.9 °C

4-(5-(3,4,5-Tris(dodecyloxy)phenyl)thiophen-2-yl)phthalonitrile (**10a**)



410 mg (1.45 mmol) of the brominated compound **8a** and 454 mg (673 µmol) of the boronic acid 2**5** were dissolved in dry THF under nitrogen atmosphere. After degassing for 20 minutes, 84.0 mg (73.0 µmol) $Pd(PPh_3)_4$ and a solution of 300 mg (2.17 µmol) K_2CO_3 in three mL dest. H_2O were added and the mixture was heated to 90 °C for 24 hours. After complete reaction, dest. H_2O was added and the aqueous phase was extracted with DCM. The combined organic phases were dried over Na_2SO_4, the solvent removed under reduced pressure and the crude

product purified by column chromatography (silica, cyclohexane : dichloromethane = 10 : 1 (*v*/*v*)) to yield 1.06 g (1.25 µmol, 86 %) of a red solid.

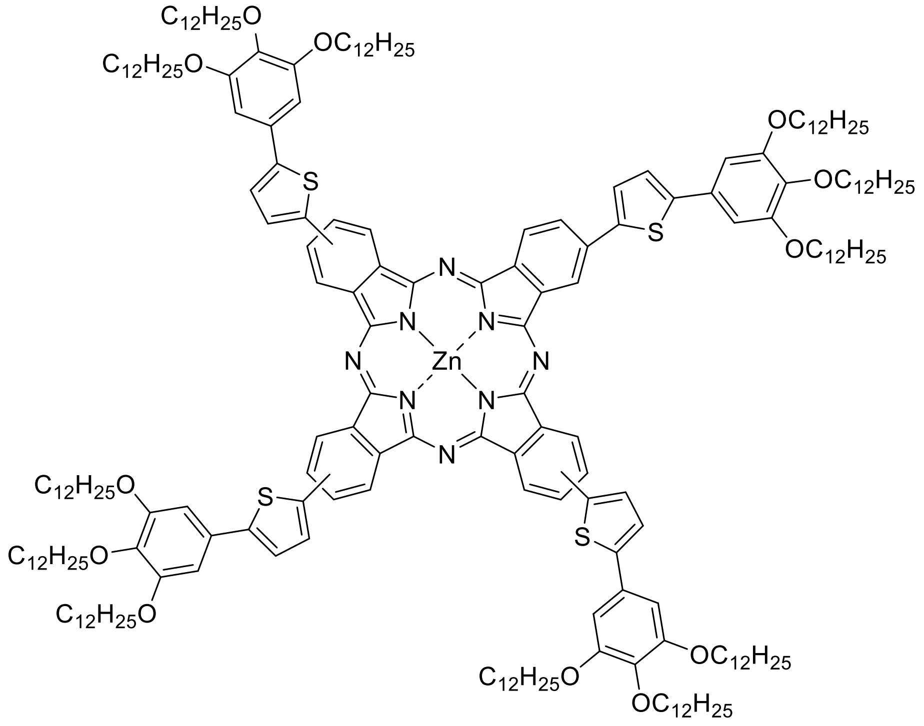
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.9 Hz, 9 H, CH_3), 1.26-1.38 (m, 48 H, CH_2), 1.46-1.53 (m, 6 H, CH_2), 1.76 (qui, ^3J = 7.1 Hz, 2 H, CH_2), 1.83 (qui, ^3J = 7.0 Hz, 4 H, CH_2), 3.99 (t, ^3J = 6.6 Hz, 2 H, CH_2), 4.03 (t, ^3J = 6.5 Hz, 4 H, CH_2), 6.80 (s, 2 H, aromat. H), 7.26 (d, ^3J = 3.9 Hz, aromat. H), 7.45 (d, ^3J = 3.9 Hz, aromat. H), 7.78 (dd, ^3J = 8.3 Hz; ^4J = 1.9 Hz 1 H, aromat. H), 7.89 (dd, ^3J = 8.3 Hz; ^4J = 1.9 Hz, 1 H, aromat. H), 7.99 (d, ^4J = 1.9 Hz; ^5J = 0.4 Hz, 1 H, aromat. H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3 (C_p, CH_3), 22.9, 26.3, 29.6, 29.7(5),29.8(0), 29.8(6), 29.8(9), 29.9(1), 29.5, 30.5, 32.0(8), 32.1(0), 69.5, 73.8 (C_s), 105.0 (C_t), 112.9, 115.4, 115.7, 116.9 (C_q), 124.5, 127.6 (C_t), 128.5 (C_q), 128.9, 129.7, 134.2 (C_t), 137.8, 139.3, 139.6 148.6 153.7 (C_q) ppm.

MALDI-MS, m/z (%): calculated: 838.60 ($[M]^{\bullet+}$, 100), found: 838.60 ($[M]^{\bullet+}$, 100).

ESI-HRMS, m/z: calculated: 838.6041 $[M]^{\bullet+}$, found: 838.6048 $[M]^{\bullet+}$.

2(3),9(10),17(18),23(24)-Tetrakis(5-(3,4,5-tris(dodecyloxy)phenyl)thiophen-2-yl)zinkphthalocyanine (**2**)



200 mg (230 µmol) **10a**, 41.8 mg (103 µmol) $Zn(OAc)_2 \cdot 2H_2O$ and three drops of DBU were dissolved in DMAE under nitrogen atmosphere. The reaction was stirred at 130 °C for 24 hours. After complete reaction, the solvent was removed under removed pressure and the

crude product purified by column chromatography (silica, ethyl acetate), by GPC and by recrystallization from a mixture of THF and methanol to yield 84.0 mg (22.0 µmol, 37 %) of a green solid.

^{1}H NMR (400.1 MHz, THF-d_8 + 2 drops of pyridine-d_5): δ = 0.90-0.96 (m, 36 H, CH_3), 1.30-1.47 (m, 192 H, CH_2), 1.61-1.70 (m, 24 H, CH_2), 1.84-1.99 (m, 24 H, CH_2), 4.12 (t, ^3J = 6.1 Hz, 8 H, CH_2), 4.17 (bs, 16 H, CH_2), 7.11-7.12 (m, 8 H, aromat. H), 7.52 (bs, 4 H, aromat. H), 7.86, 7.94 (bs, 4 H, aromat. H), 8.17-8.35 (m, 4 H, aromat. H), 8.82-9.43 (m, 8 H, aromat. H) ppm.

^{13}C NMR (100 MHz, THF-d_8): δ = 14.4 (C_p, CH_3), 23.5 (C_s), 27.2, 27.5, 30.3, 30.6, 30.6 (, 30.7, 30.9, 31.5, 32.8, 69.7, 73.7 (C_s), 105.0, 119.1, 123.2, 124.7, 126.1, 126.6 (C_t), 135.9, 137.0, 139.4, 143.9, 145.5, 152.8, 154.5 (C_q) ppm.

Several quaternary and tertiary signals, especially of the phthalocyanine core and the arms of low intensity could not be identified certainly due to aggregation and the presence of four regioisomers. Moreover, only very broad signals could be obtained, which could not always be assigned to individual atoms, for which reason, ^{13}C spectra are often omitted in the literature or only selected peaks are assigned.[5, 6, 7]

UV-Vis (THF): λ max, ($\varepsilon/10^4$): 356 (12.47), 639 (5.34), 676 (5.07), 710 (27.26) nm.

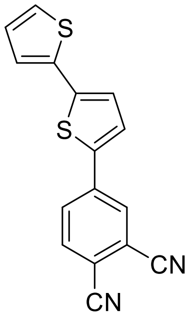
MALDI-HRMS, m/z: calculated: 3418.3471 $[M]^{\bullet+}$, found: 3418.3460 $[M]^{\bullet+}$.

FT-IR: $\tilde{\nu}$ [cm^{-1}]: 579.5, 666.3, 691.4, 720.3, 744.4, 763.7, 791.6, 823.5, 899.6, 1053.9, 1077.1, 1112.7, 1177.4, 1250.6 (C-O), 1327.8, 1349.0, 1377.9, 1427.1, 1465.6, 1540.9, 1578.5 (aromat. C=C), 1606.5, 1667.2 (C=N), 2850.3, 2918.7, 3066.3 (C-H).

Elemental analysis (%) for $C_{216}H_{328}N_8O_{12}S_4Zn$, calculated: C 75.80, H 9.66, N 3.27 S 3.75 found: C 75.08, H 9.77, N 3.55 S 3.55 [A]

Melting point: decomposition > 300 °C.

4-([2,2'-Bithiophen]-5-yl)phthalonitrile (**7b**)



1.19 g (7.16 mmol) 2,2-bithiophene were dissolved in dry THF under nitrogen atmosphere. At -78 °C, 3.01 ml (7.52 mmol) *n*BuLi were added and the reaction mixture was allowed to warm up to -20 °C. At -78 °C, 1.21 ml (1.12 g, 10.7 mmol) $B(OMe)_3$ were added and the reaction mixture was stirred for 24 hours. 1 m HCl and dest. water was added, the aqueous phase was extracted with DCM and the combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure to yield 1.37 g (6.51 mmol, 92 %) of the [2,2'-bithiophen]-5-ylboronic acid, which was directly used in the next step without further purification.

1.04 g (4.09 mmol) compound **6** and 1.37 g (6.51 mmol) of the [2,2'-bithiophen]-5-ylboronic acid were dissolved in dry THF under nitrogen atmosphere. After degassing for 20 minutes, 504 mg (436 µmol) $Pd(PPh_3)_4$ and a solution of 904 mg (6.54 µmol) K_2CO_3 in three mL dest. H_2O were added and the mixture was heated to 90 °C for 24 hours. After complete reaction, dest. H_2O was added and the aqueous phase was extracted with DCM. The combined organic phases were dried over Na_2SO_4, the solvent removed under reduced pressure and the crude product purified by column chromatography (silica, cyclohexane : ethyl acetate = 10 : 1 (*v*/*v*)) to yield 1.07 g (3.67µmol, 90 %) of a yellow solid.

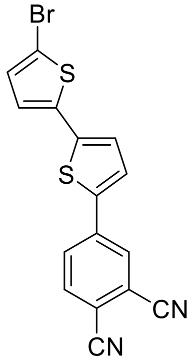
^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 7.08 (dd, ^3J = 3.6 Hz; ^3J = 5.1 Hz, 1 H, aromat. H), 7.25 (d, ^3J = 3.9 Hz, 1 H, aromat. H), 7.31 (dd, ^3J = 1.1 Hz; ^3J = 3.6 Hz, 1 H, aromat. H), 7.34 (dd, 3*J* = 1.1 Hz; ^3J = 5.1 Hz, 1 H, aromat. H), 7.45 (d, ^3J = 3.9 Hz, 1 H, aromat. H), 7.80 (dd, ^5J = 0.5 Hz; ^3J = 8.3 Hz, 1 H, aromat. H), 7.90 (dd, ^4J = 1.9 Hz; ^3J = 8.3 Hz, 1 H, aromat. H), 8.00 (dd, ^5J = 0.5 Hz; ^4J = 1.9 Hz, 1 H, aromat. H) ppm.

^{13}C NMR (100 MHz, CD_2Cl_2): δ = 113.4, 115.8, 116.1, 117.0 (C_q), 125.3, 125.6, 126.3, 127.9, 128.6, 129.3, 130.0, 134.5 (C_t), 136.5, 138.2, 139.4, 141.2 (C_q) ppm.

MALDI-HRMS, m/z: calculated: 292.0123 $[M]^{\bullet+}$, found: 292.0126 $[M]^{\bullet+}$.

Melting point: 229.9 °C

4-(5'-Bromo-[2,2'-Bithiophen]-5-yl)phthalonitrile (**8b**)



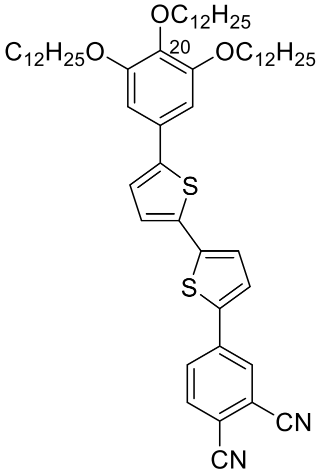
47.0 mg (161 µmol) **7b** and 31.0 mg (174 µmol) NBS were dissolved in THF. After stirring at room temperature for three days, the solvent was removed under reduced pressure and the the crude product purified by column chromatography (silica, ethyl acetate : cyclohexane = 1 : 1 (*v*/*v*)) to yield 45.0 mg (121 µmol, 75 %) of an orange solid.

^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.01 (d, ^3J = 3.9 Hz, 1 H, aromat. H), 7.02 (d, ^3J = 3.8 Hz, 1 H, aromat. H), 7.16 (d, ^3J = 3.9 Hz, 1 H, aromat. H), 7.40 (d, ^3J = 3.9 Hz, 1 H, H-10), 7.79 (dd, ^3J = 8.3 Hz; ^5J = 0.5 Hz, 1 H, aromat. H), 7.86 (dd, ^3J = 8.3 Hz; ^4J = 1.0 Hz, 1 H, aromat. H), 7.96 (dd, ^4J = 1.8 Hz; ^5J = 0.4 Hz, 1 H, aromat. H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.9, 113.4, 115.3, 115.5, 117.0 (C_q), 125.2, 125.5 (C_t), 127.5 (C_q), 129.1, 129.8, 131.2, 134.3 (C_t), 137.6, 138.2, 139.1, 139.9 (C_q) ppm.

MALDI-HRMS, m/z: calculated: 369.9229 $[M]^{\bullet+}$, found: 369.9246 $[M]^{\bullet+}$.

4-(5'-(3,4,5-Tris(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl) phthalonitrile (**10b**)

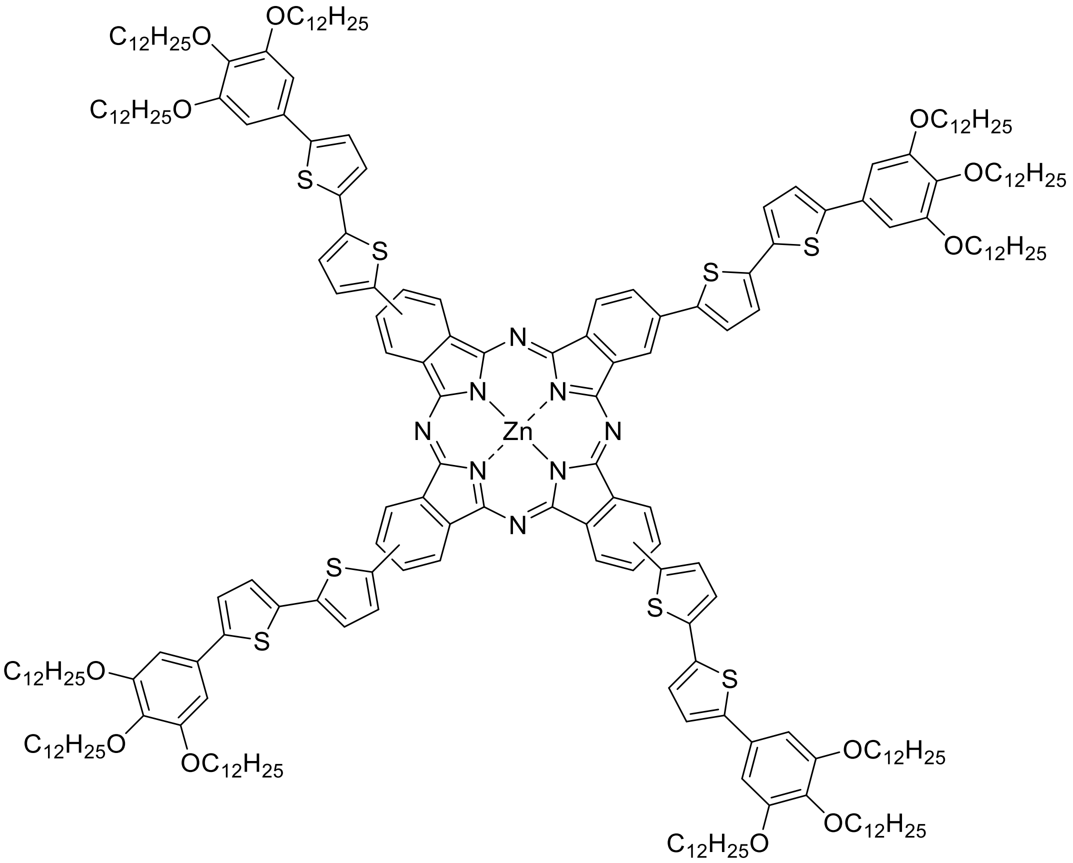


284 mg (760 µmol) of the brominated compound **8b** and 720 mg (1.07 µmol) of the boronic acid **25** were dissolved in dry THF under nitrogen atmosphere. After degassing for 20 minutes, 44.0 mg (38.1 µmol) $Pd(PPh_3)_4$ and a solution of 158 mg (1.14 µmol) K_2CO_3 in three mL dest. H_2O were added and the mixture was heated to 90 °C for 24 hours. After complete reaction, dest. H_2O was added and the aqueous phase was extracted with DCM. The combined organic phases were dried over Na_2SO_4, the solvent removed under reduced pressure and the crude product purified by column chromatography (silica, cyclohexane : ethyl acetate = 10 : 1 (*v*/*v*)) to yield 524 mg (569 µmol, 75 %) of a red solid.

^1H NMR (400.1 MHz, CD_2Cl_2): δ = 0.88 (t, ^3J = 6.88 Hz, 9 H, CH_3), 1.27-1.32 (m, 48 H, CH_2), 1.48 (q, ^3J = 7.1 Hz, 6 H, CH_2), 1.72 (q, ^3J = 7.1 Hz, 2 H, CH_2), 1.83 (q, ^3J = 7.0 Hz, 4 H, CH_2), 3.94 (t, ^3J = 6.6 Hz, 2 H, CH_2), 4.03 (t, ^3J = 6.5 Hz, 4 H, CH_2), 6.79 (s, 2 H, aromat. H), 7.21 (d, ^3J = 3.7 Hz, 1 H, aromat. H), 7.25 (d, ^3J = 3.9 Hz, 1 H, aromat. H), 7.26 (d, ^3J = 3.8 Hz, 1 H, aromat. H), 7.46 (d, ^3J = 3.9 Hz, 1 H, aromat. H), 7.80 (dd, ^3J = 8.3 Hz; ^5J = 0.5 Hz, 1 H, aromat. H), 7.89 (dd, ^3J = 8.3 Hz; ^4J = 1.8 Hz, 1 H, aromat. H), 8.01 (dd, ^4J = 1.9 Hz; ^5J = 0.5 Hz, 1 H, aromat. H) ppm.

^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ = 14.3 (C$_p$), 23.1, 26.5, 29.7(8), 29.8(1), 30.0, 30.0(6), 30.0(7), 30.1(2), 30.1(4), 30.2, 30.7, 32.2, 69.5, 73.8 (C$_s$), 104.6 (C$_t$), 113.3, 115.8, 116.1, 117.0 (C$_q$), 124.1,125.2, 126.1, 128.0 (C$_t$), 129.1 (C$_q$),129.3, 130.0, 134.5 (C$_t$), 135.1, 138.0, 138.7 139.4, 141.2, 145.5, 153.9 ppm.
MALDI-MS, m/z (%): calculated: 920.59 ([M]$^{•+}$, 100), calculated: 920.51 ([M]$^{•+}$, 100).
MALDI-HRMS, m/z: calculated: 920.5918 [M]$^{•+}$, found: 920.5905 [M]$^{•+}$.

(2(3),9(10),17(18),23(24)-tetrakis(5'-(3,4,5)-tris-(dodecyloxy)-phenyl)[2,2'-bithiophen]-5-yl)-zinkphthalocyanine (**3**)



405 mg (440 µmol) **10a**, 38.5 mg (176 µmol) Zn(OAc)$_2$·2H$_2$O and three drops of DBU were dissolved in DMAE under nitrogen atmosphere. The reaction was stirred at 130 °C for 24 hours. After complete reaction, the solvent was removed under removed pressure and the crude product purified by column chromatography (silica, ethyl acetate), by GPC and twice by recrystallization from a mixture of THF and methanol to yield 77.0 mg (21.1 µmol, 37 %) of a green solid.

^{1}H NMR (400.1 MHz, THF-d$_8$): δ = 0.87-0.95 (m, 36 H, CH_3), 1.35-1.50 (m, 192 H, CH_2), 1.55-1.64 (m, 24 H, CH_2), 1.77-1.90 (m, 24 H, CH_2), 3.99-4.06 (m, 24 H, CH_2), 6.89 (bs, 8 H, H-aromat. H), 7.26, 7.36 (bs, 8 H, aromat. H), 7.42, 7.47 (bs, 4 H, aromat. H), 7.86, 7.93 (bs, 4 H, H-8/9/12/13), 8.17 (m, 4 H, aromat. H), 8.86-9.26 (m, 8 H, aromat. H) ppm.

^{13}C NMR (151.0 MHz, THF-d_8): δ = 13.6 (C_p), 22.7, 26.3(6), 26.4(1), 29.5, 29.7, 29.8, 29.8, 30.0, 30.6, 32.0, 68.8, 72.9 (C_s), 104.0, 118.2, 118.7, 122.6, 123.5, 124.5(0), 124.6, 125.2, 125.3, 125.8 (C_t), 129.1, 134.7, 136.2, 137.7, 137.8, 138.5, 143.2, 143.4, 143.5, 151.8, 152.0, 153.7 (C_q) ppm.

Several quaternary and tertiary signals, especially of the phthalocyanine core and the arms of low intensity could not be identified certainly due to aggregation and the presence of four regioisomers. Moreover, only very broad signals could be obtained, which could not always be assigned to individual atoms, for which reason, ^{13}C spectra are often omitted in the literature or only selected peaks are assigned.[5, 6, 7]

UV-Vis (THF), λ max, ($\varepsilon/10^4$): 380 (14.49), 654 (6.04), 714 (17.47) nm.

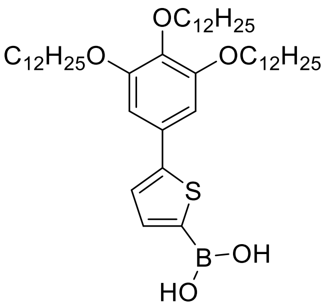
MALDI-HRMS, m/z: calculated: 3746.2979 $[M]^{\bullet+}$, found: 3746.3047 $[M]^{\bullet+}$.

FT-IR, $\tilde{\nu}$ [cm^{-1}]: 579.5, 666.3, 691.4, 720.3, 744.4, 763.7, 791.6, 823.5, 899.6, 1053.9, 1077.1, 1112.7, 1177.4, 1250.6 (C-O), 1327.8, 1349.0, 1377.9, 1427.1, 1465.6, 1540.9, 1578.5 (aromat. C=C), 1606.5, 1667.2 (C=N), 2850.3, 2918.7, 3066.3 (C-H).

Elemental analysis (%) for $C_{232}H_{336}N_8O_{12}S_8Zn$ calculated: C 74.29, H 9.03, N 2.99, S 6.84 found: C 73.83, H 9.17, N 3.06, S 6.56. [A]

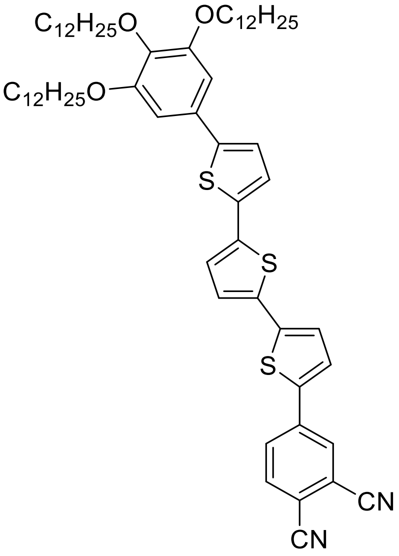
Melting point: decomposition > 300 °C.

(5-(3,4,5-Tris(dodecyloxy)phenyl)thiophen-2-yl)boronic acid (**9b**)



1.50 g (1.89 mmol) of the brominated compound **25** were dissolved under nitrogen atmosphere in dry THF. At -78 °C, 1.51 mL (234 mg, 3.79 mmol) of a 2.5 M *n*BuLi solution in hexane were add, and the mixture was allowed to warm up to -20 °C. At -78 °C, 844 µL (787 mg, 7.57 mmol) $B(OMe)_3$ were added and the mixture was stirred for 24 hours at room temperature. After complete reaction, 1 M HCl was added and the aqueous phase was extracted with DCM. The combined organic phases were dried over Na_2SO_4 and the solvent removed under reduced pressure to yield 975 mg (1.29 mmol, 68 %) of a green oil, which was used in the next reaction without further purification.

4-(5''-(3,4,5-Tris(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)phthalonitrile (**10c**)



389 mg (1.05 mmol) of the brominated compound **8b** and 1.19 g (1.57 mmol) of the boronic acid **9b** were dissolved in dry THF under nitrogen atmosphere. After degassing for 20 minutes, 38.4 mg (52.5 µmol) Pd(dppf)Cl_2 and a solution of 290 mg (2.10 mmol) K_2CO_3 in three mL dest. H_2O were added and the mixture was heated to 90 °C for 24 hours. After complete reaction, dest. H_2O was added and the aqueous phase was extracted with DCM. The combined organic phases were dried over Na_2SO_4, the solvent removed under reduced pressure and the crude product purified by column chromatography (silica, cyclohexane : ethyl acetate = 10 : 1 (*v*/*v*)) to yield 315 mg (313 µmol, 30 %) of a red solid.

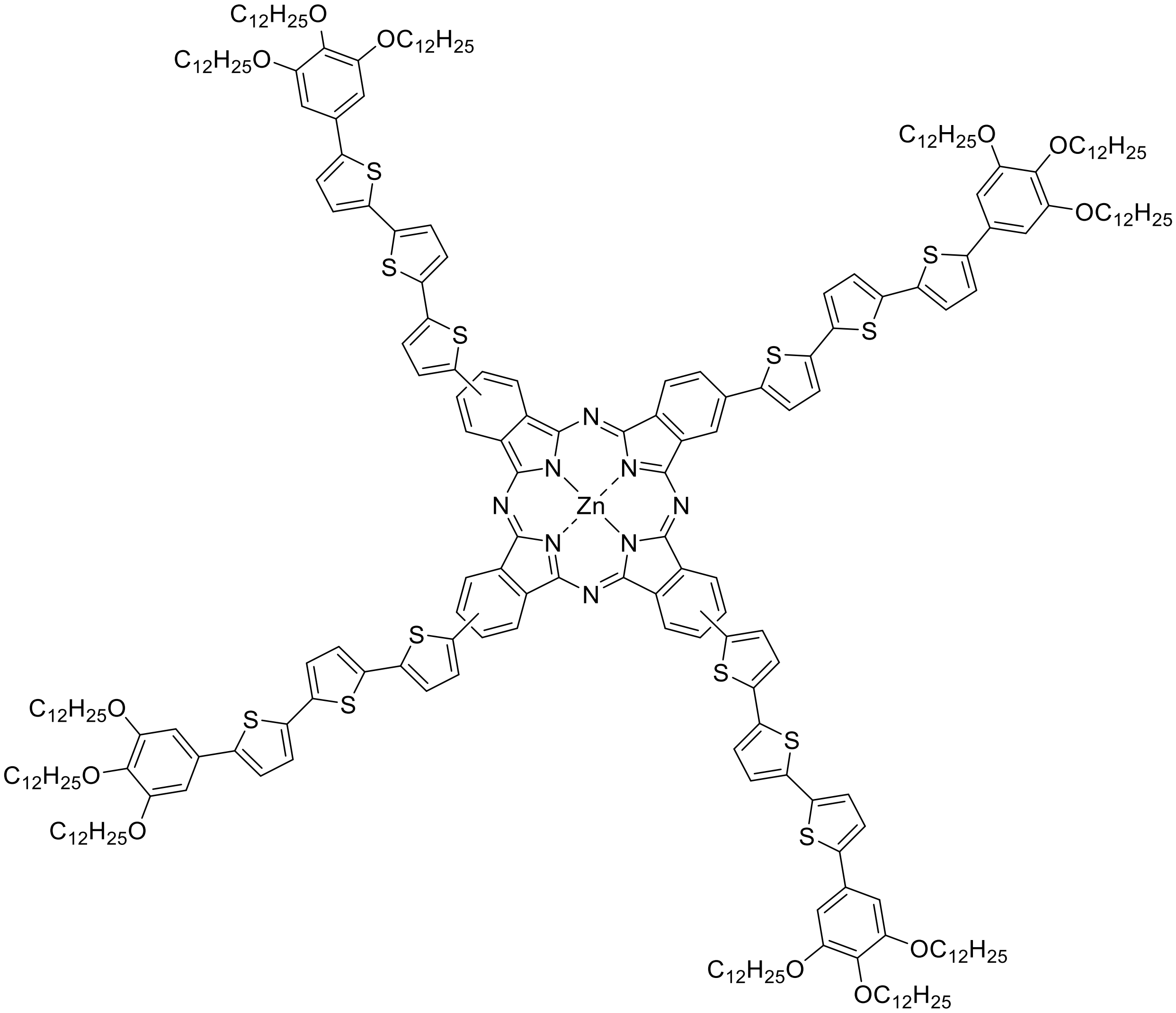
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.9 Hz, 6 H, CH_3), 0.88 (t, ^3J = 6.9 Hz, 3 H, CH_3) 1.27-1.39 (m, 48 H, CH_2), 1.46-1.53 (m, 6 H, CH_2), 1.73-1.78 (m, 2 H, CH_2), 1.83 (qui, ^3J = 7.0 Hz, 4 H, CH_2), 3.98 (t, ^3J = 6.6 Hz, 2 H, CH_2), 4.03 (t, ^3J = 6.5 Hz, 4 H, CH_2), 6.77 (s, 2 H, aromat. H), 7.11 (d, ^3J = 3.8 Hz, 1 H, aromat. H), 7.14 (d, ^3J = 3.8 Hz, 1 H, aromat. H), 7.15 (d, ^3J = 3.8 Hz, 1 H, aromat. H), 7.17 (d, ^3J = 3.8 Hz, 1 H, aromat. H), 7.19 (d, ^3J = 3.9 Hz, aromat. H), 7.41 (d, ^3J = 3.9 Hz, 1 H, aromat. H), 7.76 (dd, ^3J = 8.3 Hz, ^5J = 0.4 Hz, 1 H, aromat. H), 7.84 (dd, ^3J = 8.3 Hz, ^4J = 1.9 Hz; 1 H, aromat. H), 7.94 (d, ^4J = 1.9 Hz, ^5J = 0.4 Hz, 1 H, aromat. H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3 (C_p), 22.8, 26.2(5), 26.2(8), 29.5(2), 29.5(4), 29.6, 29.7(8), 29.8(0), 29.8(2), 29.8(5), 29.8(6), 29.8(9), 29.9(1), 30.5, 32.0(7), 32.0(9), 69.4, 73.7 (C_s),104.8 (C_t), 113.0, 115.3,115.6, 116.9 (C_q), 123.7, 124.3, 125.1, 125.1, 127.6, 128.9 (C_t), 129.1 (C_q), 129.6, 134.2 (C_t), 134.6, 135.4, 137.7, 138.1, 138.6, 139.1, 140.8 144.5, 153.6 (C_q) ppm.

MALDI-MS, m/z (%): calculated: 1002.58 ($[M]^{\bullet+}$, 100), found 1002.56 ($[M]^{\bullet+}$, 100).

ESI-HRMS, m/z: calculated: 1002.5795 $[M]^{\bullet+}$, found: 1002.5796 $[M]^{\bullet+}$.

2(3),9(10),17(18),23(24)--tetrakis(5''-(3,4,5)tris(dodecyloxy)-phenyl)-[2,2':5',2''-terthiophen]-5-yl)zinkphthalocyanine (**4**)



132 mg (132 µmol) **10c**, 23.1 mg (106 µmol) $Zn(OAc)_2 \cdot 2H_2O$ and three drops of DBU were dissolved in DMAE under nitrogen atmosphere. The reaction was stirred at 130 °C for 24 hours. After complete reaction, the solvent was removed under removed pressure and the crude product purified by column chromatography (silica, ethyl acetate), by GPC and twice by recrystallization from a mixture of THF and methanol to yield 84.0 mg (22.0 µmol, 37 %) of a green solid.

^{1}H NMR (400.1 MHz, $C_2D_2Cl_4$, 373 K): δ = 0.89 (bs, 36 H, $\mathrm{C}H_3$), 130 (bs, 192 H, $\mathrm{C}H_2$), 1.50 (bs, 24 H, $\mathrm{C}H_2$), 1.79 (bs, 24 H, $\mathrm{C}H_2$), 4.00 (bs, 24 H, $\mathrm{C}H_2$), 6.77 (bs, 8 H, aromat. H), 7.08 (bs, 24 H, aromat. H), 7.83 (bs, 4 H, aromat. H), 8.80 (bs, 8 H, aromat. H) ppm.

^{13}C NMR (151.0 MHz, CD_2Cl_2): δ = 14.3 (C_p), 23.2, 26.7, 29.9, 30.0, 30.3, 31.0, 32.4, 69.4, 73.8 (C_s), 104.2, 118.8, 120.0 (C_t), 124.0, 124.5, 125.2, 126.9, 129.0, 129.3, 133.1, 135.4, 135.6, 137.4, 138.4, 139.8, 140.5, 144.1 (C_t/C_q), 153.4, 153.6 (C_q, C-22) ppm.

Several quaternary and tertiary signals of low intensity, especially of the phthalocyanine core and the arms, could not be identified. This is attributed to aggregation and the presence of four regioisomers. Moreover, only very broad signals could be obtained, which could not always be assigned to individual atoms. For this reason, ^{13}C spectra are often omitted in the literature or only selected peaks are assigned.[5, 6, 7]

MALDI-MS, m/z (%): calculated: 4076.26 ($[M+2]^{\bullet+}$, 72), found: 4076.65 ($[M+2]^{\bullet+}$, 100).

MALDI-HRMS, m/z: calculated: 4074.2488 $[M]^{\bullet+}$, found: 4074.2443 $[M]^{\bullet+}$.

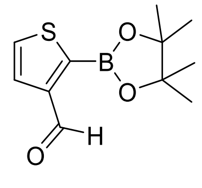
UV-Vis (THF), λ max, ($\varepsilon/10^4$): 418 (15.43), 658 (3.58), 717 (6.71) nm.

FT-IR, $\tilde{\nu}$ [cm^{-1}]: 721.2, 749.2, 785.9, 821.5, 1113.7, 1235.2, 1259.3, 1275.7, 1345.1, 1378.9, 1426.1, 1463.7, 1517.7, 1577.5 (aromat. C=C), 2850.3, 2918.7, 3064.3 (C-H).

Elemental analysis (%) for $C_{248}H_{344}N_8O_{12}S_{12}Zn$ calculated: C 73.01, H 8.50, N 2.75, S 9.43 found: C 72.37, H 8.38, N 2.69, S 8.90. [A]

Melting point: decomposition > 350 °C.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-3-carbaldehyde (**13**)

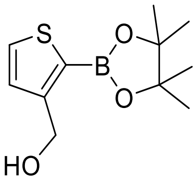


832 mg (5.33 mmol) of the aldehyde **12** and 694 mg (5.87 mmol) pinacol were dissolved in diethylether and stirred for 24 hours at room temperature. The solvent was removed under reduced pressure, the crude product dissolved in DCM and filtered to yield 1.23 g (5.17 mmol, 97 %) of a yellow oil.

^{1}H NMR (400.1 MHz, Aceton-d$_6$): δ = 1.40 (s, 12 H, $\mathrm{C}H_3$), 7.62 (dd, ^{3}J = 4.9 Hz; ^{5}J = 0.4 Hz, 1 H, aromat. H), 7.86 (dd, ^{3}J = 4.9 Hz; ^{4}J = 0.9 Hz, 1 H, aromat. H), 10.38 (dd, ^{4}J = 0.9 Hz; ^{5}J = 0.4 Hz, 1 H, $\mathrm{C}H\mathrm{O}$) ppm.

The data is in agreement with the literature.

(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-3-yl)-methanol (**14**)



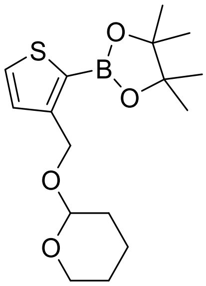
2.39 g (10.0 mmol) **13** were dissolved in dry THF unter nitrogen atmosphere. At 0 °C, 418 mg (11.0 mmol) NaBH4 were added and the reaction was stirred at room temperature for 24 hours. Dest. H_2O was added, the aqueous phase was extracted, the combined organic layers dried over Na_2SO_4, and the solvent removed under reduced pressure, to yield 1.91 g (7.96 mmol, 79 %) of a beige solid, which was used in the next step without further purification.

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 1.35 (s, 12 H, C*H*$_3$), 3.18 (m, 1 H, O*H*), 4.73 (m, 2 H, C*H*$_2$), 7.14 (d, ^3J = 4.7 Hz, 1 H, aromat. H), 7.56 (d, ^3J = 4.7 Hz, 1 H, aromat. H) ppm.

^{13}C NMR (100 MHz, CD_2Cl_2): δ = 24.9 (C_p), 60.4 (C_s), 84.9 (C_q), 130.1, 132.4 (C_t), 154.1 (C_q) ppm.

The signal of the carbon next to the boron atom could not be detected in the ^{13}C NMR spectrum, due to strong broadening of the signal.

4,4,5,5-Tetramethyl-2-(3-(((tetrahydro-2*H*-pyran-2-yl)oxy)methyl)-thiophen-2-yl)-1,3,2-dioxaborolane (**15**)



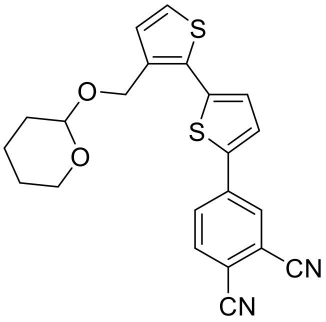
1.91 g (7.96 mmol) of the alcohol **14,** 200 mg (796 µmol) PPTS, and 1.44 mL (15.9 mmol) 3,4-dihydro-*2H*-pyran were dissolved in dry DCM under nitrogen atmosphere and stirred for 24 hours at room temperature. Saturated $NaHCO_3$ solution and dest. H_2O was added and the aqueous phase extracted with DCM. The combined organic layers were dried over Na_2SO_4 and the solvent removed under reduced pressure, to yield 1.84 g (5.67 mmol, 71 %) of a colorless solid, which was used in the next step without further purification.

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ =1.33 (s, 12 H, C*H*$_3$), 1.48-1.60 (m, 6 H, C*H*$_2$), 3.44-3.54 (m, 1 H, C*H*$_2$), 3.89-3.94 (m, 1 H, C*H*$_2$), 4.71 (d, ^2J = 12.0 Hz, 1 H, C*H*$_2$), 4.72 (t, ^3J = 3.4 Hz, 1 H, C*H*), 4.90 (d, ^3J = 12.0 Hz, 1 H, CH_2), 7.26 (d, ^3J = 4.8 Hz, 1 H, aromat. H), 7.55 (d, ^3J = 4.7 Hz, 1 H, aromat. H) ppm.

^{13}C NMR (100 MHz, Aceton-d$_6$): δ =20.0 (C_s), 25.1 (C_p), 26.3, 31.4, 62.1, 64.6 (C_s), 84.6 (C_q), 98.7, 130.8, 132.7 (C_t), 150.3 (C_q) ppm.

The signal of the carbon next to the boron atom could not be detected in the ^{13}C NMR spectrum, due to strong broadening of the signal.

4-(3'-(((tetrahydro-2H-pyran-2-yl)oxy)methyl)-[2,2'-bithiophen]-5-yl)phthalonitrile (**16**)



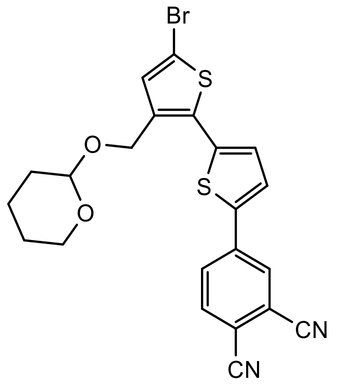
184 mg (635 µmol) of the brominated compound **8a** and 411 mg (1.27 mmol) of the pinacol **15** were dissolved in dry THF under nitrogen atmosphere. After degassing for 20 minutes, 35.0 mg (52.5 µmol) Pd(dppf)Cl_2 and a solution of 133 mg (906 µmol) K_2CO_3 in three mL dest. H_2O were added and the mixture was heated to 90 °C for 24 hours. After complete reaction, dest. H_2O was added and the aqueous phase was extracted with DCM. The combined organic phases were dried over Na_2SO_4, the solvent removed under reduced pressure and the crude product purified by column chromatography (silica, cyclohexane : ethyl acetate = 4 : 1 (*v*/*v*)) to yield 124 mg (305 µmol, 48 %) of a yellow solid.

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 1.54-1.88 (m, 6 H, CH_2), 3.48-3.54 (m, 1 H, CH_2), 3.83-3.87 (m, 1 H, CH_2), 4.61 (d, ^2J = 12.0 Hz, 1 H, CH_2), 4.73 (t, ^3J = 3.5 Hz, 1 H, C*H*), 4.82 (d, ^2J = 12.0 Hz, 1 H, CH_2), 7.18 (d, ^3J = 5.2 Hz, 1 H, aromat. H), 7.29 (d, ^3J = 3.92 Hz, 1 H, aromat. H), 7.31 (d, ^3J = 5.16 Hz, 1 H, aromat. H), 7.50 (d, ^3J = 3.9 Hz, 1 H, aromat. H), 7.81 (dd, ^3J = 8.3 Hz, ^5J = 0.5 Hz, 1 H, aromat. H), 7.91 (dd, ^3J = 8.3 Hz, ^4J = 1.9 Hz 1 H, aromat. H), 8.02 (dd, ^4J = 1.9 Hz, ^5J = 0.5 Hz, 1 H, aromat. H) ppm.

^{13}C NMR (100 MHz, CD_2Cl_2): δ = 19.8, 25.9, 31.0, 62.6, 63.0 (C_s), 98.5 (C_t), 113.5, 115.8, 116.1, 117.0 (C_q), 125.4, 127.7, 128.3, 129.5, 130.1, 131.1 (C_t), 133.1 (C_q), 134.5 (C_t), 137.0, 139.3, 139.4, 139.8 (C_q) ppm.

MALDI-HRMS, m/z: calculated: 406.0804 $[M]^{\bullet+}$, found: 406.0798 $[M]^{\bullet+}$.

4-(5'-Bromo-3'-(((tetrahydro-2H-pyran-2-yl)oxy)methyl)-[2,2'-bithiophen]-5-yl)phthalonitrile (**17**)



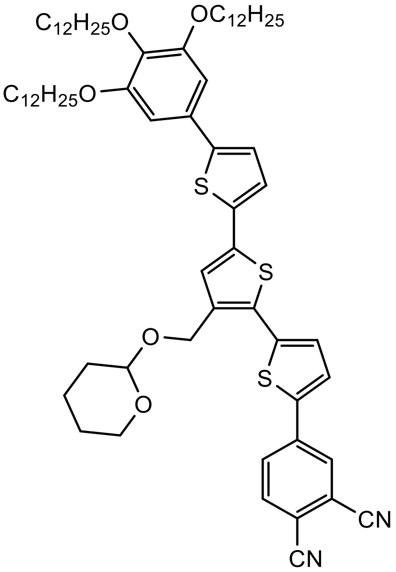
500 mg (1.23 mmol) of the protected compound **16** and 241 mg (1.35 mmol) NBS were dissolved in THF. After stirring at room temperature for three days, saturated $NaHCO_3$ solution and dest. H_2O were added and the aqueous phase extracted with DCM. The combined organic layers were dried over Na_2SO_4, the solvent was removed under reduced pressure and the crude product purified by column chromatography (silica, ethyl acetate : cyclohexane = 1 : 5 (*v*/*v*)) to yield 522 mg (1.08 mmol, 75 %) of an orange solid.

^{1}H NMR (400.1 MHz, THF-d_8): δ = 1.49-1.93 (m, 6 H, CH_2), 3.45-3.50 (m, 1 H, CH_2), 3.79-3.85 (m, 1 H, CH_2), 4.56 (d, ^3J = 12.4 Hz, 1 H, CH_2), 4.72 (t, ^3J = 3.3 Hz, 1 H, C*H*), 4.76 (d, ^3J = 12.4 Hz, 1 H, CH_2), 7.22 (s, 1 H, aromat. H), 7.31 (d, ^3J = 3.9 Hz, 1 H, aromat. H), 7.72 (d, ^3J = 3.9 Hz, 1 H, aromat. H), 7.95 (d, ^3J = 8.3 Hz 1 H, aromat. H), 8.06 (dd, ^3J = 8.3 Hz, ^4J = 1.9 Hz, 1 H, aromat. H), 8.31 (d, ^3J = 1.7 Hz, 1 H, aromat. H).

^{13}C NMR (100 MHz, THF-d_8): δ = 19.9, 26.3, 31.2, 62.2, 62.9, 98.5 (C_s), 111.9, 114.2 (C_q), 115.9, 116.1, 117.4 (C_q), 128.5, 129.1, 129.9, 130.6, 134.1 (C_t), 134.5, 137.7, 138.5, 139.3, 141.2 (C_q) ppm.

MALDI-HRMS, m/z: calculated: 483.9909 $[M]^{\bullet+}$, found: 483.9920 $[M]^{\bullet+}$.

4-(3'-(((Tetrahydro-2H-pyran-2-yl)oxy)methyl)-5''-(3,4,5-tris(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)phthalonitril (**18**)



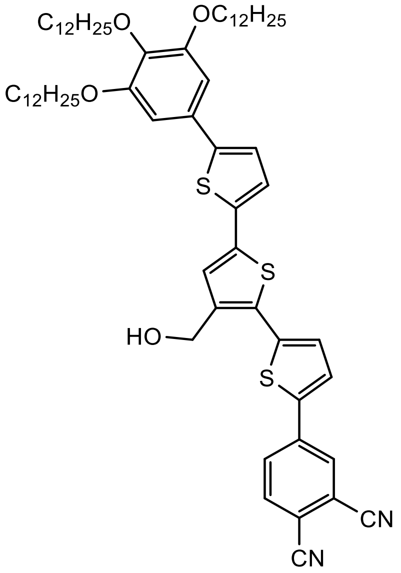
166 mg (340 µmol) of the brominated compound **17** and 566 mg (748 mmol) of the boronic acid **9b** were dissolved in dry THF under nitrogen atmosphere. After degassing for 20 minutes, 12.5 mg (17.0 µmol) Pd(dppf)Cl_2 and a solution of 93.9 mg (679 µmol) K_2CO_3 in three mL dest. H_2O were added and the mixture was heated to 90 °C for 24 hours. After complete reaction, dest. H_2O was added and the aqueous phase was extracted with DCM. The combined organic phases were dried over Na_2SO_4, the solvent removed under reduced pressure and the crude product purified by column chromatography (silica, cyclohexane : ethyl acetate = 5 : 1 (*v*/*v*)) to yield 202 mg (181 µmol, 53 %) of a red solid.

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 0.86-0.89 (m, 9 H, CH_3), 1.24-1.38 (m, 48 H, CH_2), 1.45-1.53 (m, 6 H, CH_2), 1.67-1.88 (m, 12 H, CH_2), 3.52-3.57 (m, 1 H, CH_2), 3.87-3.92 (m, 1 H, CH_2), 3.95 (t, ^{3}J = 6.6 Hz, 2 H, CH_2), 4.03 (t, ^{3}J = 6.6 Hz, 6 H, CH_2), 4.61 (d, ^{2}J = 12.2 Hz, 1 H, CH_2), 4.78 (m, 1 H, C*H*), 4.82 (d, ^{2}J = 12.2 Hz, 1 H, CH_2), 6.79 (s, 2 H, aromat. H), 7.19 (d, ^{3}J = 3.8 Hz, 1 H, aromat. H), 7.20 (d, ^{3}J = 3.8 Hz, 1 H, aromat. H), 7.27 (s, 1 H, aromat. H), 7.32 (d, ^{3}J = 4.0 Hz, 1 H, aromat. H), 7.51 (d, ^{3}J = 4.0 Hz, 1 H, aromat. H), 7.82 (dd, ^{3}J = 8.3 Hz, ^{5}J = 0.5 Hz, 1 H, aromat. H), 7.92 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.9 Hz 1 H, aromat. H), 8.03 (dd, ^{4}J = 1.9 Hz, ^{5}J = 0.5 Hz, 1 H, aromat. H) ppm.

^{13}C NMR (100 MHz, CD_2Cl_2): δ = 14.3 (C_p), 19.8, 23.1, 25.9, 26.5, 29.7(8), 29.8(2), 30.0, 30.0(5), 30.1(2), 30.2, 31.0, 32.3, 25.9, 26.5, 31.0, 29.8, 30.7, 62.6 63.1, 69.5, 73.9 (C_s), 98.5 104.5 (C_t), 113.5, 115.8, 116.1, 117.0 (C_q), 124.0, 125.5, 127.0, 127.8, 128.2 (C_t), 129.3 (C_q), 129.5, 130.1 (C_t), 131.4 (C_q), 134.5 (C_t), 135.5, 136.9, 137.9, 138.6, 139.0, 139.3, 139.8, 144.7, 153.9 (C_q) ppm.

MALDI-HRMS, m/z: calculated: 1116.6476 $[M]^{\bullet+}$, found: 1116.6478 $[M]^{\bullet+}$.

4-(3'-(hydroxymethyl)-5''-(3,4,5-tris(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)phthalonitril (**19**)



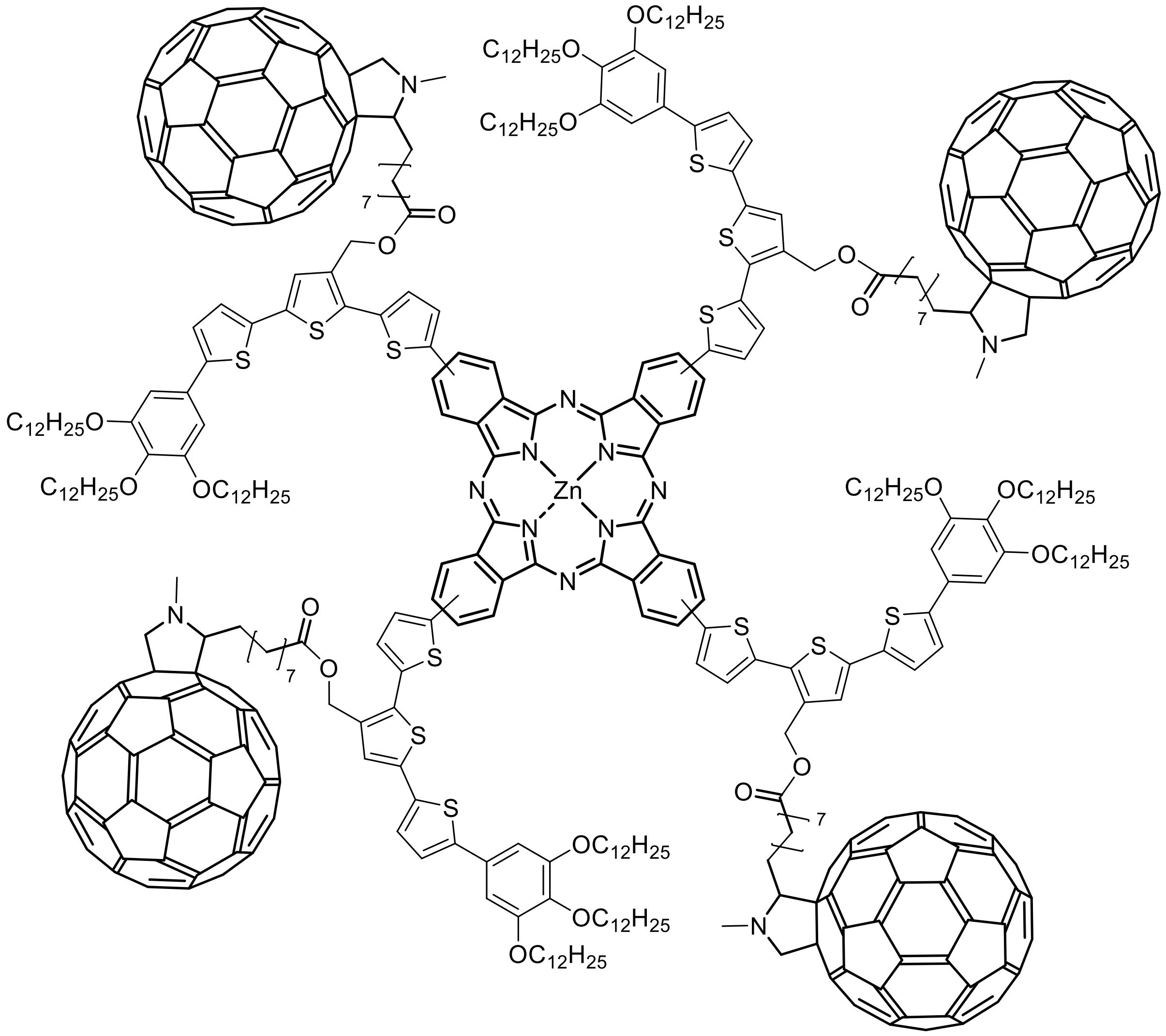
95.0 mg (85.0 µmol) of the protected compound **18** and 8.08 mg (42.5 µmol) *p*-TsOH were dissolved in a mixture of THF and methanol. After stirring at room temperature for twelve hours, saturated $NaHCO_3$ solution and dest. H_2O were added and the aqueous phase extracted with DCM. The combined organic layers were dried over Na_2SO_4, the solvent removed under reduced pressure, and the crude product purified by column chromatography (silica, cyclohexane : ethyl acetate = 3 : 1 (*v*/*v*)) to yield 80.0 mg (77.4 µmol, 91 %) of a red solid.

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 0.88 (t, ^3J = 6.9 Hz, 6 H, CH_3), 0.88 (t, ^3J = 6.9 Hz, 3 H, CH_3), 1.27-1.38 (m, 48 H, CH_2), 1.40-1.52 (m, 6 H, CH_2), 1.72 (qui, ^3J = 7.1 Hz, 2 H, CH_2), 1.82 (qui, ^3J = 7.0 Hz, 4 H, CH_2), 1.94 (t, ^3J = 5.6 Hz, 2 H, OH), 3.95 (t, ^3J = 6.6 Hz, 2 H, CH_2), 4.02 (t, ^3J = 6.5 Hz, 4 H, CH_2), 4.79 (d, ^3J = 5.0 Hz, 2 H, CH_2), 6.79 (s, 2 H, aromat. H), 7.18 (d, ^3J = 3.8 Hz, 1 H, aromat. H), 7.19 (d, ^3J = 3.8 Hz, 1 H, aromat. H), 7.28 (s, 1 H, aromat. H), 7.31 (d, ^3J = 3.9 Hz, 1 H, aromat. H), 7.51 (d, ^3J = 3.9 Hz, 1 H, aromat. H), 7.82 (dd, ^3J = 8.3 Hz, ^5J = 0.5 Hz, 1 H, aromat. H), 7.92 (dd, ^3J = 8.3 Hz, ^4J = 1.9 Hz, 1 H, aromat. H), 8.04 (dd, ^4J = 1.9 Hz, ^5J = 0.5 Hz, 1 H, aromat. H) ppm.

^{13}C NMR (100 MHz, CD_2Cl_2): δ = 14.3 (C_p), 23.1, 26.5, 29.8, 29.8, 30.0, 30.0(6), 30.1(0), 30.1(2), 30.1(5), 30.1(6), 30.7, 32.3, 59.4, 69.5, 73.9 (C_s), 104.5 (C_t), 113.5, 115.8 (C_q, C-2), 116.0, 117.0 (C_q), 124.0, 125.5, 126.3, 128.1, 128.8 (C_t), 129.3 (C_q), 129.5, 130.1 (C_t), 130.9 (C_q),134.5 (C_t), 135.4, 137.1, 138.6, 138.8, 139.2, 139.7, 140.3, 144.8, 153.9 (C_q) ppm.

ESI-HRMS, m/z: calculated: 1055.57984 $[M+Na]^+$, found: 1055.58025 $[M+Na]^+$.

Zinkphthalocyanine **5**



167 mg (161 µmol) **19**, 14.2 mg (64.7 µmol) Zn(OAc)$_2$·2H$_2$O were dissolved in DMAE under nitrogen atmosphere. The reaction was stirred at 130 °C for 24 hours. After complete reaction, the solvent was removed under removed pressure and the crude product purified by column chromatography (silica, DCM : THF = 10 : 1 (*v*/*v*)) and by GPC to yield 110 mg (26.1 µmol, 65 %) of a brown solid, which was used in the next step without purification.

MALDI-HRMS, m/z: calculated: 4194.2911 [M+4]$^{\bullet+}$, found: 4194.2911 [M+4]$^{\bullet+}$.

UV-Vis (THF), λ max, ($\varepsilon/10^4$): 413 (12.40), 646 (1.68), 715 (3.32) nm.

FT-IR, $\tilde{\nu}$ [cm^{-1}]: 505.3, 518.8, 535.2, 545.8, 559.3, 575.6, 592.0, 633.5, 648.0, 663.4, 680.7, 720.3, 747.3, 764.6, 791.6, 821.5, 891.6, 1070.3, 1112.7 (C-O), 1240.0, 1341.3, 1377.9, 1426.1, 1462.7, 1520.6, 1577.5 (aromat. C=C), 1652.7, 1667.2 (C=N), 2850.3, 2918.7 (C-H). 3372.9 (-OH).

50.0 mg (11.9 µmol) of this compound, 55.6 mg (59.5 µmol) of the fullerene with spacer **20**, 35.1 mg (119 µmol) DPTS and 41.0 µL (33.1 mg, 262 µmol) DIC were dissolved in dry DCM under nitrogen atmosphere and the reaction mixture was stirred for 30 days at room temperature. The solvent was removed under reduced pressure and the crude product purified by column chromatography (silica, DCM : THF = 1 : 1 (*v*/*v*)), subjected twice to preparative recycling GPC and precipitated two times from a mixture of THF and MeOH to yield 32.0 mg (4.45 µmol, 37 %) of a brown-green solid.

^{1}H NMR (400.1 MHz, $C_2D_2Cl_4$, 398 K): δ = 0.88 (bs, 36 H, CH_3), 1.32-1.90 (m, 288 H, $\mathrm{C}H_2$), 2.01-2.17 (bs, 8 H, $\mathrm{C}H_2$), 2.35 (bs, 8 H, $\mathrm{C}H_2$), 2.03-2.35 (bs, 24 H, $\mathrm{C}H_2$), 2.57 (bs, 12 H, $\mathrm{NC}H_3$), 3.69 (bs, 4 H, $\mathrm{NC}H_2/\mathrm{NC}H$), 4.02 (bs, 28 H, $\mathrm{OC}H_2/\mathrm{NC}H_2/\mathrm{NC}H$), 4.79 (bs, 4 H, $\mathrm{NC}H_2/\mathrm{NC}H$), 5.19 (bs, 8 H, $\mathrm{ArC}H_2$), 6.79 (bs, 8 H, aromat. H), 7.11 (bs, 20 H, aromat. H), 7.44 (bs, 4 H, aromat. H) 7.96 (bs, 8 H, aromat. H) ppm.

Due to the size of the molecule, aggregation, the presence of regioisomers and four additional C_{60}-units, only very broad peaks could be obtained, which could only slightly be improved by high-temperature measurement. Anyway, all relevant protons of the fullerene spacer and of the aromatic region could be identified. The broad signal ppm at 3.71 ppm with an integration of four protons can be attributed to the C*H* group within the pyrrolidine ring and confirms the successful and complete coupling of the four fullerene building block which is further supported by the mass spectra.

^{13}C NMR (151 MHz, THF-d_8): δ = 14.6 (C_p), 23.7, 27.3, 30.5, 30.8, 33.0 (C_s), 38.0 (C_p), 70.0, 73.8 (C_s), 105.4 (C_t), 125.9, 129.7, 135.8, 139.8, 140.7, 142.9, 143.5, 146.2, 146.9, 148.0 154.6, 158.4 (bs, $C_{t/q}$), 173.3 (C_q, *C*OO) ppm.

Several quaternary and ternary signals, especially of the phthalocyanine core, the fullerene-unit and the arms of low intensity could not be identified certainly, although a long time measurement at a 600-MHz-NMR-spectrometer with a highly sensitive cryoprobe was performed. Anyway, the very broad signals between 157.8-133.6 ppm and the signal of the ester at 172.4 ppm show the presence of the fullerene spacers attached to the phthalocyanine star mesogen.

MALDI-HRMS, m/z (most abundant peak): calculated: 7862.95567 $[M+8]^{\bullet-}$, found: 7862.93547 $[M+8]^{\bullet-}$.

UV-Vis (THF), λ max, ($\varepsilon/10^4$): 257 (38.96), 328 (17.01), 405 (13.22), 671 (2.37), 725 (3.69) nm.

FT-IR, $\tilde{\nu}$ [cm^{-1}]: 524.5, 792.6, 1109.8, 1239.0 (C-O-C), 1341.3, 1427.1, 1459.9, 1574.7, 1735.6 (C=O), 2850.3, 2919.7 (C-H).

Elemental analysis (%) for $C_{540}H_{436}N_{12}O_{20}S_{12}Zn$ calculated: : C 82.48, H 5.59, N 2.14, S 4.89 found: C 77.80, H 5.76, N 2.39, S 4.72. [A]

Melting point: decomposition > 300 °C

[A]

The elemental analysis of compounds **1-5** show satisfying results regarding the values of H and N. However, the values for C are too low for the two target molecules. This is a well-known problem, that lots of phthalocyanines show lower values for C due to incomplete combustion.[8, 9, 10]

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[8] Y. Takagi, K. Ohta, S. Shimosugi, T. Fujii, E. Itoh, *J. Mater. Chem.*, **2012**, 22, 14418– 14425.

[9] Z. Zao, T. Nyokong, M. D. Maree, *Dalton Trans.* **2005**, 3732–3737.

[10] T. Kamei, T. Kato, E. Itoh, K. Ohta, *J. Porphyrins Phthalocyanines* **2012**; *16*: 1261–1275.

4) NMR spectra of 1-5

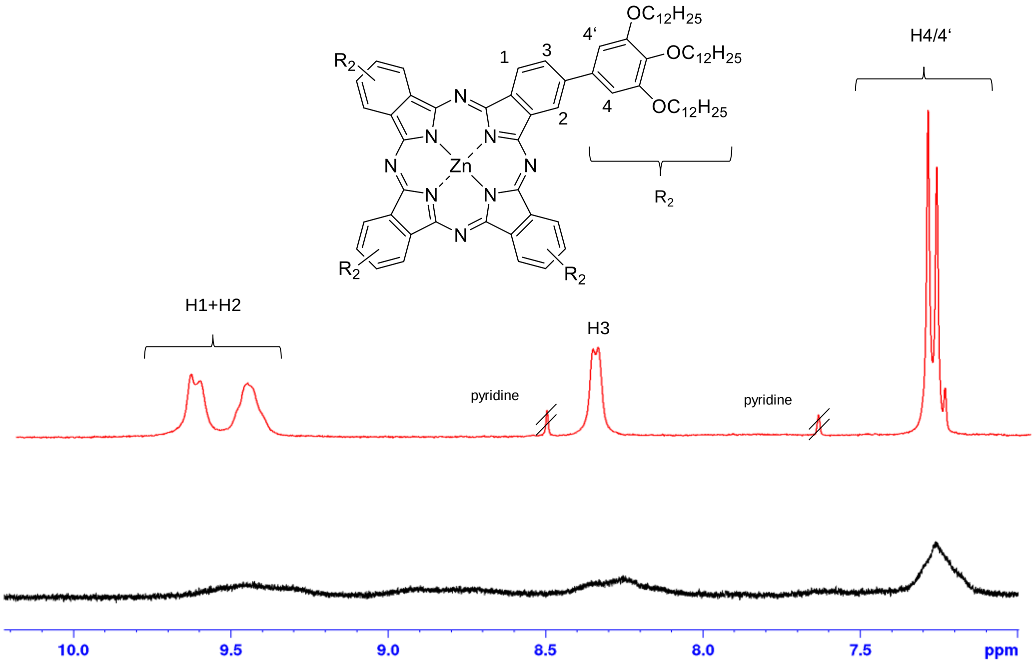

Figure S1. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of **1** between 7.0 ppm and 10.2 ppm without (black) and with two drops of pyiridine-*d*$_5$.

The best resolution of the aromatic region of compound **1** could be achieved in THF-*d*$_8$ with two drops of pyiridine-*d*$_5$ (Figure S1, red curve), whereas the same sample without pyridine-*d*$_5$ only gave very broad signals (black). The positions and integrals of the signals attributed to aromatic hydrogens are in agreement with the structure. Especially in the aromatic region, phthalocyanines show very broad peaks, due to aggregation and the mixture of different regioisomers, what complicates evaluation of the spectra.[11,12,13] The assignment of the hydrogen signals to the aromatic and olefinic protons of **1** is supported by 2D-NMR spectroscopy.

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[11] M. Sommerauer, C. Rager, M, Hanack, *J. Am. Chem. Soc.* **1996,** *118,* 10085-10093.

[12] B. Görlach, M. Drachtler, T. Glaser, K. Albert, M. Hanack, *Chem. Eur. J.* **2001**, *7*, No. 11, 2459-2465.

[13] M. Ince, F. Cardinali, J-H Yum, M. V. Martinez-Diaz, M. K. Nazeeruddin, M. Grätzel, T. Torres*, Chem. Eur. J.* **2012**, 18, 6343 – 6348.

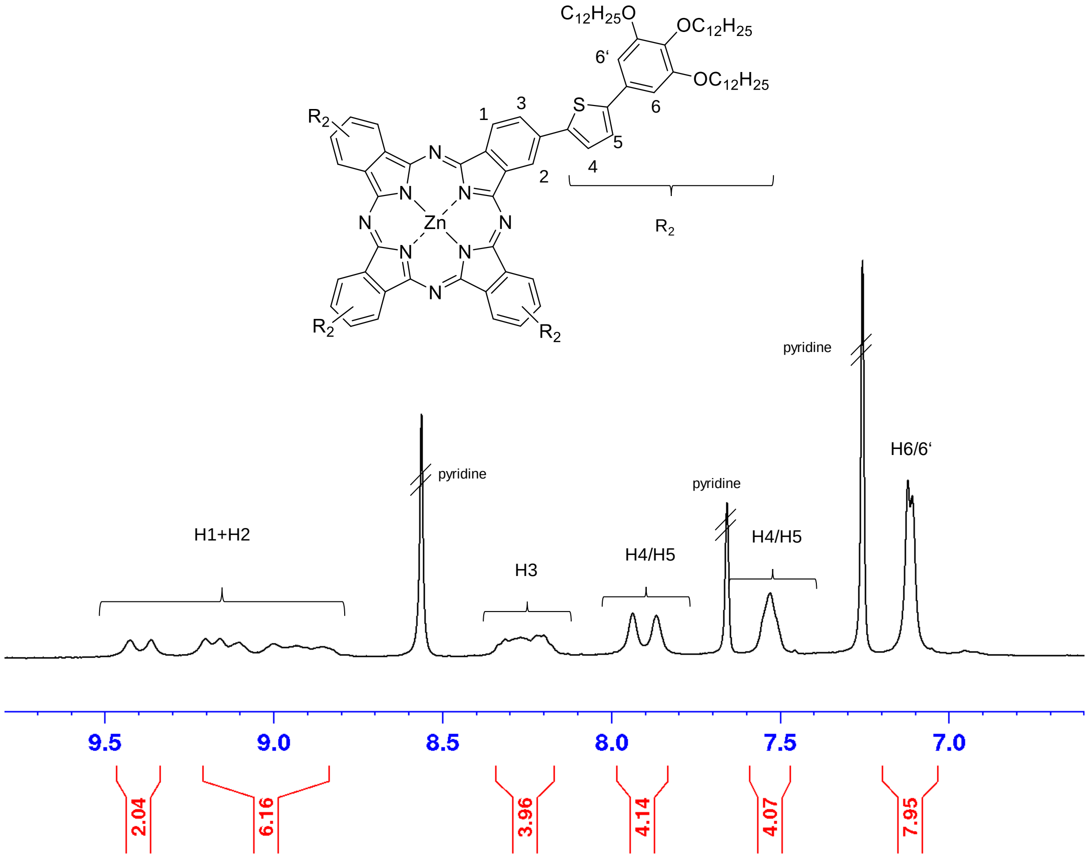

Figure S2. ^{1}H NMR spectrum (THF-d_8 with four drops of pyiridine-d_5, 400 MHz) of **2** between 6.5 ppm and 9.8 ppm.

The best resolution of the aromatic region of compound **2** could be achieved in THF-d_8 with four drops of pyiridine-d_5 (Figure S2) whereas the same sample without pyridine-d_5 only gave very broad signals. The positions and integrals of the signals attributed to the aromatic hydrogens are in agreement with the structure.

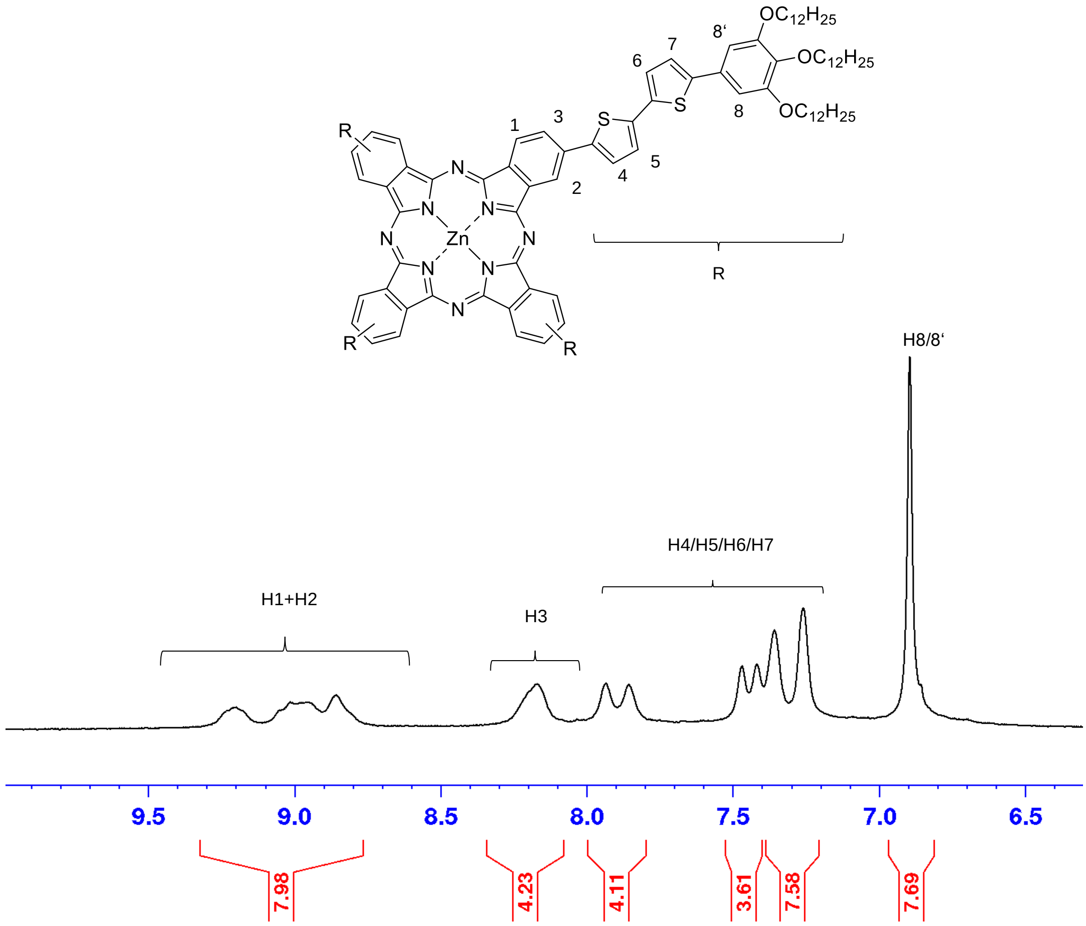

Figure S3. ${}^{1}H$ NMR spectrum (THF-d_8, 400 MHz) of **3** between 6.3 ppm and 10.0 ppm.

The ${}^{1}H$ NMR spectrum of compound **3** in THF-d_8 gives nicely resolved signals, although the peaks are still broad. Anyway, the positions and integrals of the signals attributed to the aromatic hydrogens are in agreement with the structure.

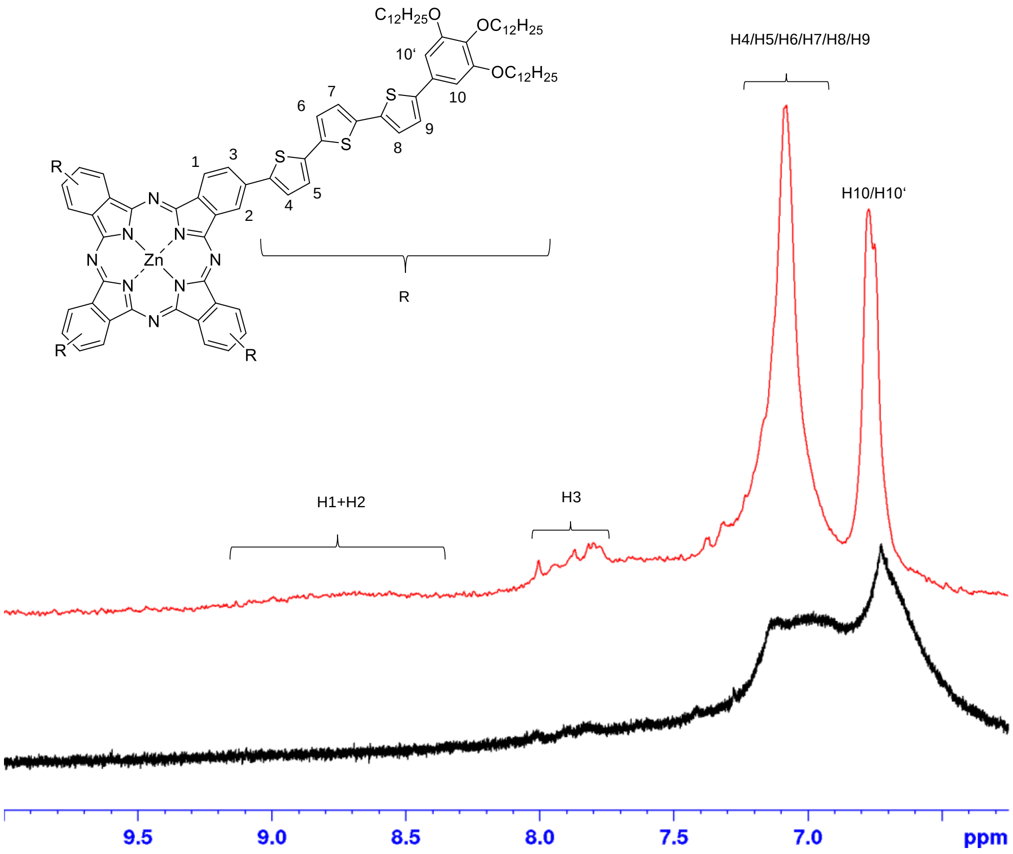

Figure S4. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 400 MHz) of **4** between 6.3 ppm and 10.0 ppm (black, 295 K, red 378 K).

The ^{1}H NMR spectrum of **4** in $C_2D_2Cl_4$ at room temperature (Figure S4, black) only shows very peaks, especially in the aromatic region. Measurement of a high-temperature ^{1}H NMR spectrum at 378 K (Figure S4, red) reveals the signals of the aromatic protons, especially of the phthalocyanine core, much better.

The assignment of the hydrogen signals to the aromatic protons of **1**-**4** are supported by 2D-NMR spectroscopy.

Compound **5** gave even broader signals due to the additional four bulky fullerene units, what makes the evaluation of the spectra more challenging.[14,15] The resolution of the spectrum could slightly by improved by the measurement of a high temperature ^{1}H NMR spectrum.[16]

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[14] A. Escosura, M. V. Martínez-Díaz, D. Guldi, T Torres, *Journal of the American Chemical Society* **2006** *128* (12), 4112-4118.

[15] Y. Geerts, O. Debever, C. Amato, S. Sergeye, B*eilstein J. Org. Chem.* **2009,** *5,* No. 49.

[16].M. Lehmann, M. Dechant, M. Holzapfel, A. Schmiedel, C. Lambert, *Angew. Chem. Int. Ed*., **2019**, *58*, 3610–3615.

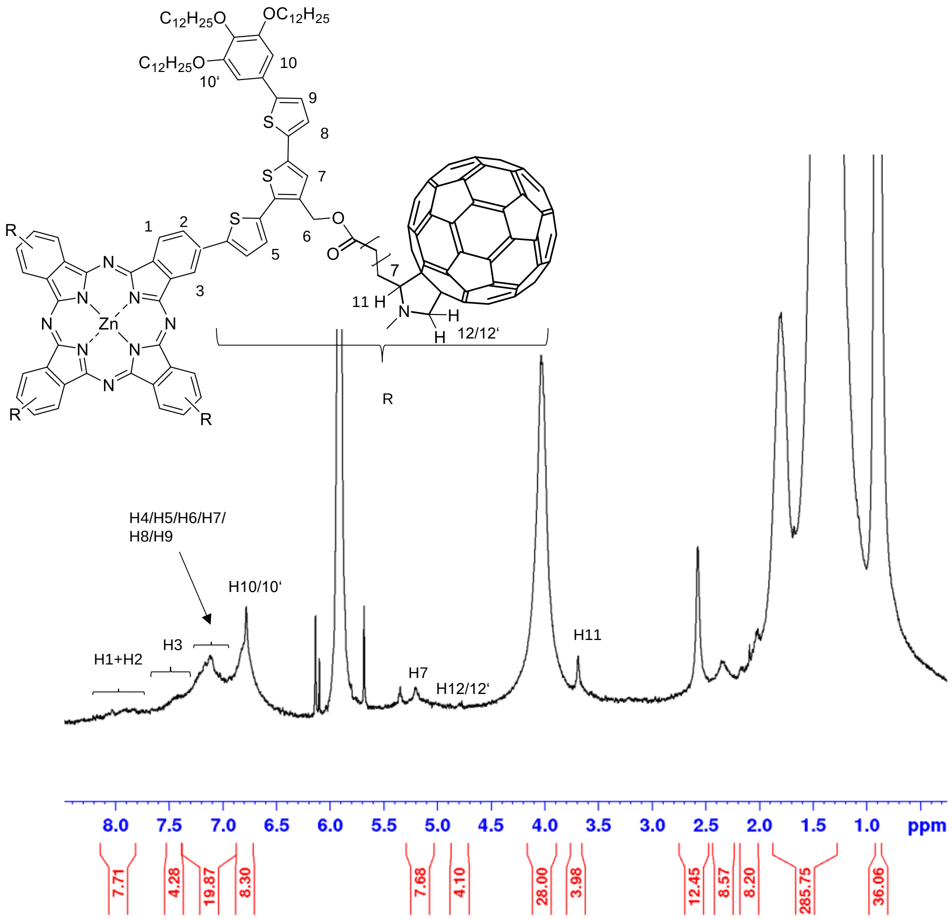

Figure S5. ^1H NMR spectrum ($C_2D_2Cl_4$, 400 MHz, 398 K) of **5** between 0.7 ppm and 8.5 ppm.

Figure S5 shows the high temperature ^1H NMR spectrum of molecule **5** at 398 K. The positions and integrals of the signals attributed to aromatic hydrogens and of the fullerene spacers are in agreement with the structure. All relevant protons of the fullerene spacer could be identified when they were compared to the spectrum of fullerene **21** (see Figure S6).

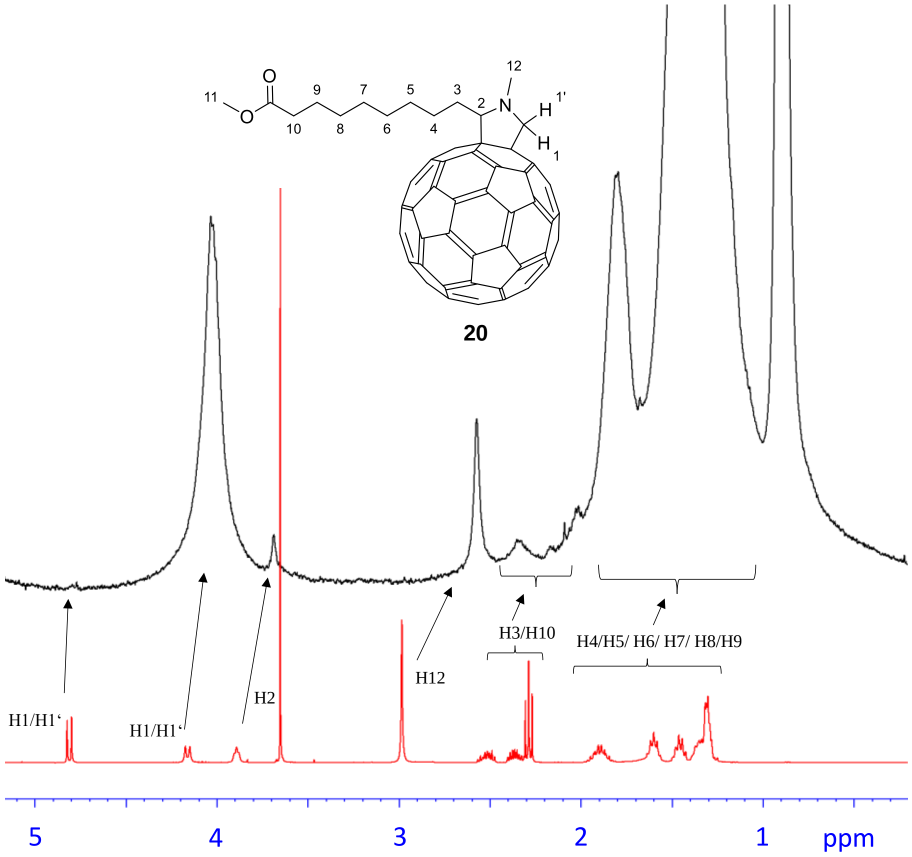

Figure S6. ^{1}H NMR spectrum of **5** (black, $C_2D_2Cl_4$, 400 MHz, 398 K) between 0.3 ppm and 5.2 ppm in comparison with the methyl ester of the fullerene **20** (black, $CDCl_3$, room temperature) The large signal at 3.63 ppm in the red spectrum belongs to the methyl group of the ester **20** and is therefore not present in **5**.

Figure S6 shows a comparison of the ^{1}H NMR spectra of the fullerene spacer **20** (red) and the target molecule **5** (black). One of the proton H1/H1' is superimposed by the signals of the dodecyloxy chains. However, spectra in Figures S5 and S6 are clearly consistent with the molecular structure and confirm the complete coupling with four fullerene building blocks, which is further supported by the mass spectra (Figure S8).

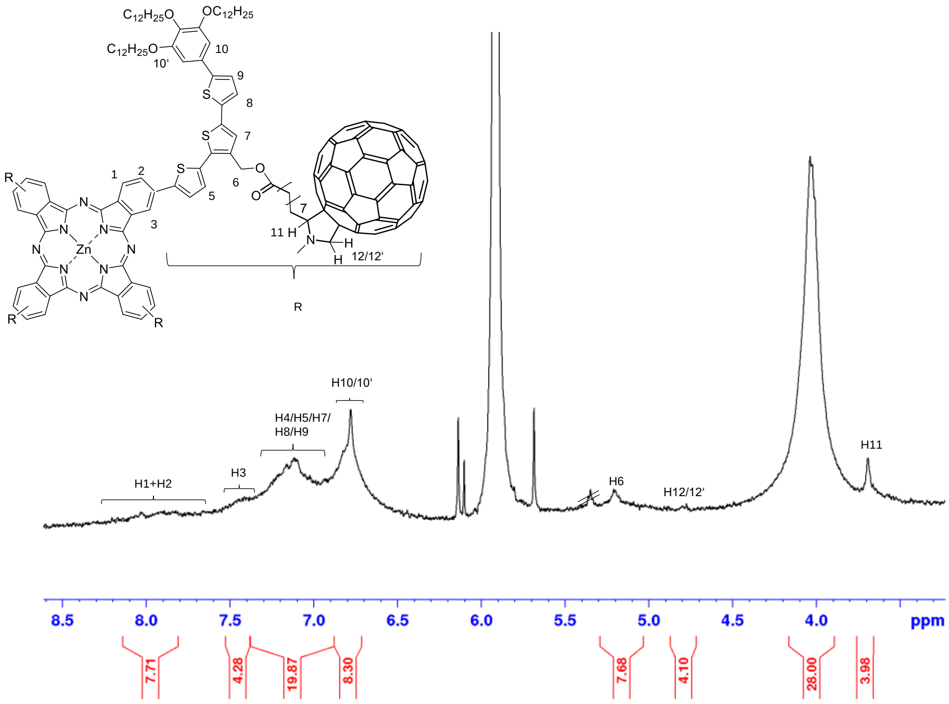

Figure S7: ^{1}H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of **5** at 398 K between 3.3 ppm and 8.6 ppm.

Figure S7 highlights the aromatic region of compound **5**. It confirms the presence of all aromatic protons and is in good agreement with the molecular structure. The broad signal at 4.72 ppm with an integration of four protons can be attributed to half of the diastereotopic protons of the CH$_2$ group, and the signal at 3.71 ppm can be attributed to the C*H* group belonging to the pyrrolidine ring (see Figure S7).

The presence of four spacers containing fullerenes was unambiguously confirmed, as Figures S5, S6 and S7 are in good agreement with the molecular structure. Moreover, the successful synthesis is further supported by the FT-IR spectroscopy and mass spectrometry (Figure S8 and Figure S11).

5) Mass spectra of target compounds

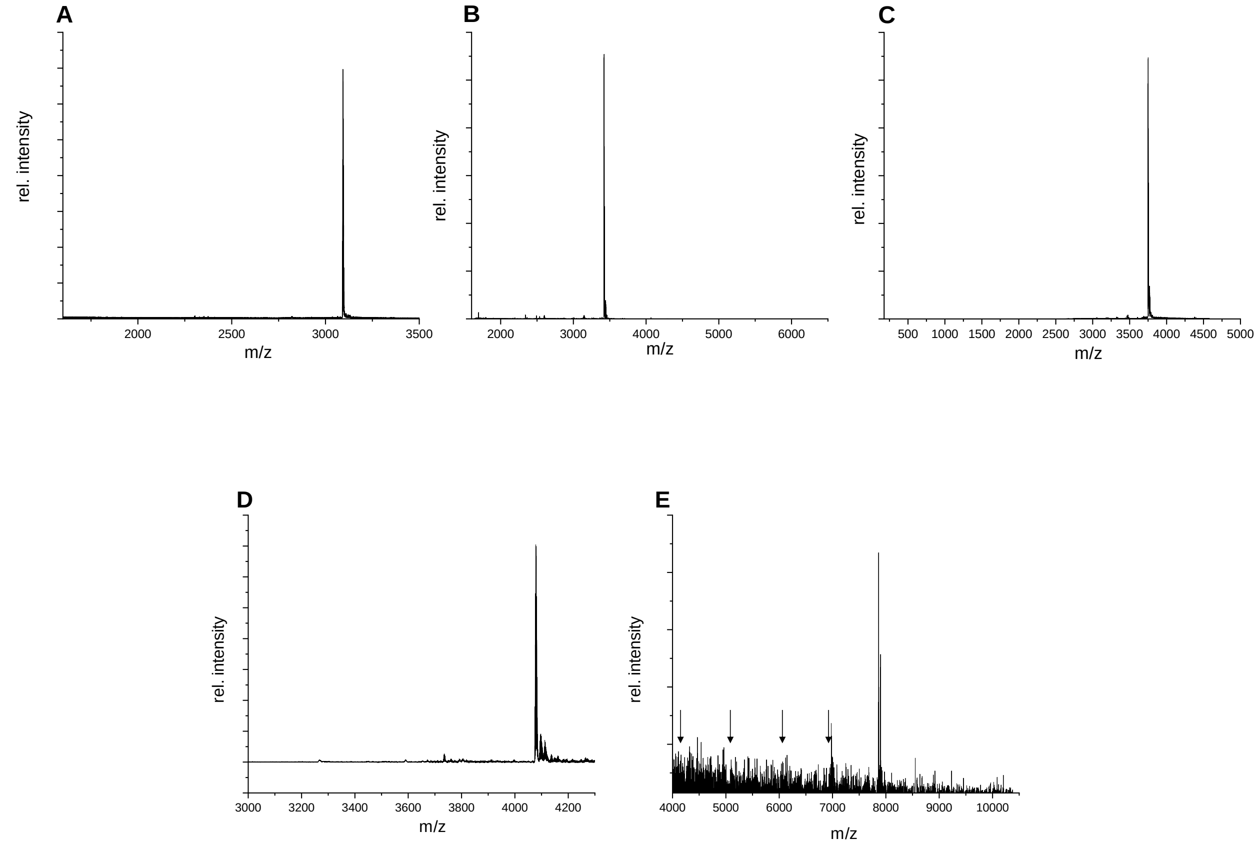

Figure S8. MALDI-MS spectra of compounds **1** (A), **2** (B), **3** (C), **4** (D) (positive) and **5** (E) (negative). The spectra of **5** (E) clearly shows that four fullerene building blocks are bound to the phthalocyanine since no additional signal at 6947, 6032, 5116 and 4200 m/z (highlighted with arrows) appears, which would be expected for phthalocyanines with only 3, 2, 1 and 0 fullerene unit. The additional signal in spectrum E belongs to the decomposed target compound due to the very high laser power, whereas the complete fourfold coupling is further supported by the absence of any OH-group in the FT-IR spectrum (Figure S11).

6) DSC measurement of 1-4

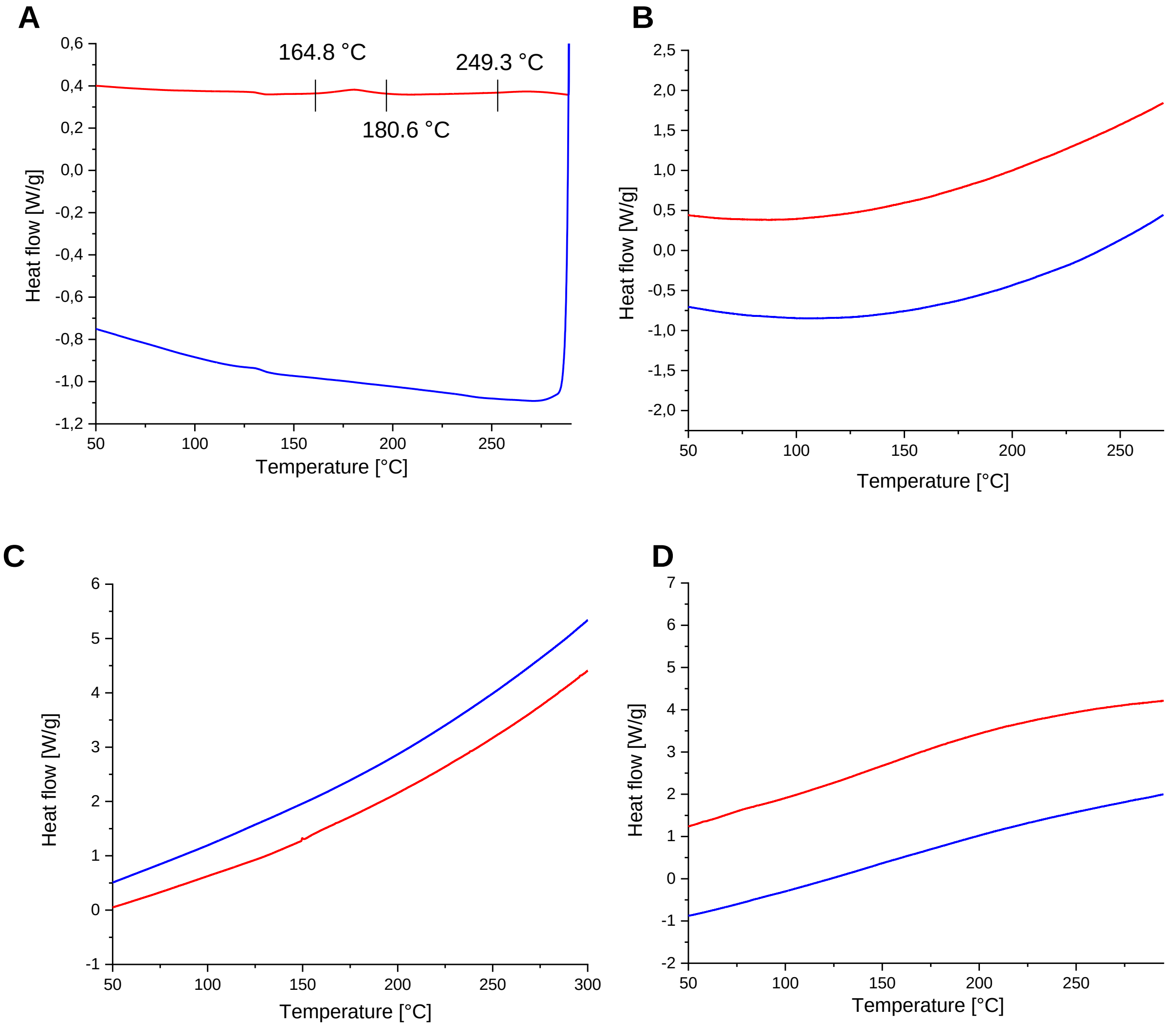

Figure S9: DSC heating (red) and cooling (blue) cycles of **1** (A), **2** (B), **3** (C) and **4** (D).

DSC trace of **1** shows a first transition at 164.8 °C from the Col$_{ort}$ into the Col$_r$ phase and a clearing temperature beginning at 249 °C. DSC measurements of **2**-**4** do not show any phase transition between 50 °C and 300 °C.

7) GPC elugrams of 1-5

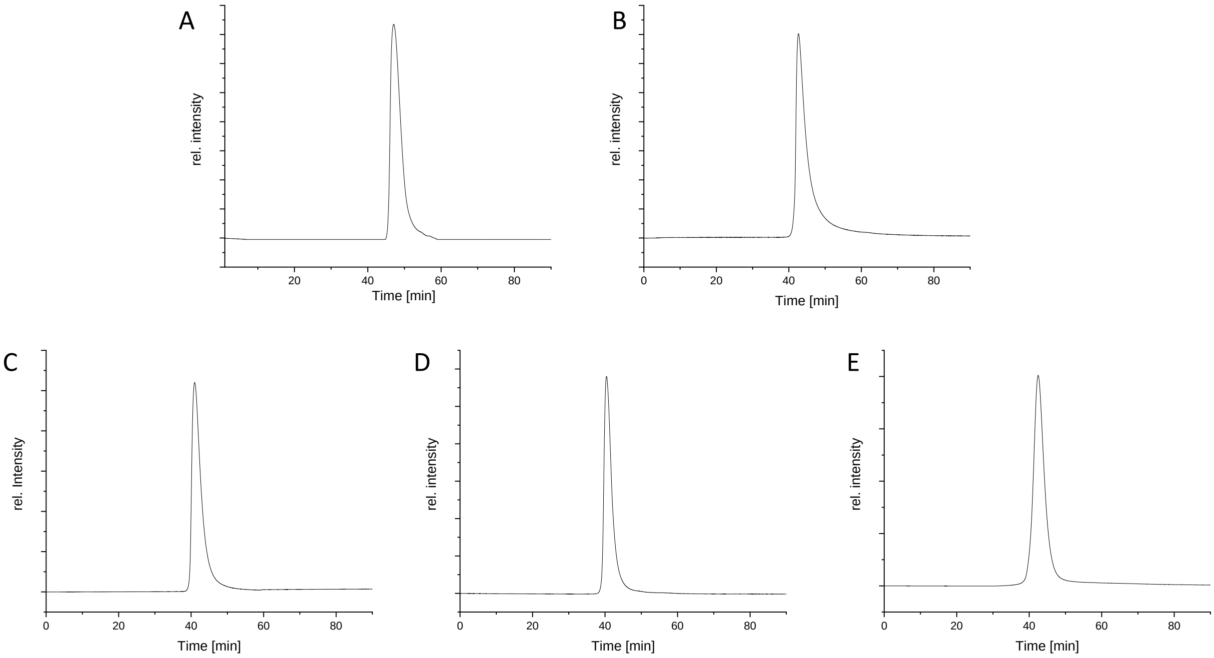

Figure S10: GPC elugrams of **1** (A), **2** (B), **3** (C), **4** (D), **5** (E).

The GPC elugrams of the pure compounds all show just a single peak, proving the purity of all compounds.

8) FT-IR spectrum of compound 5

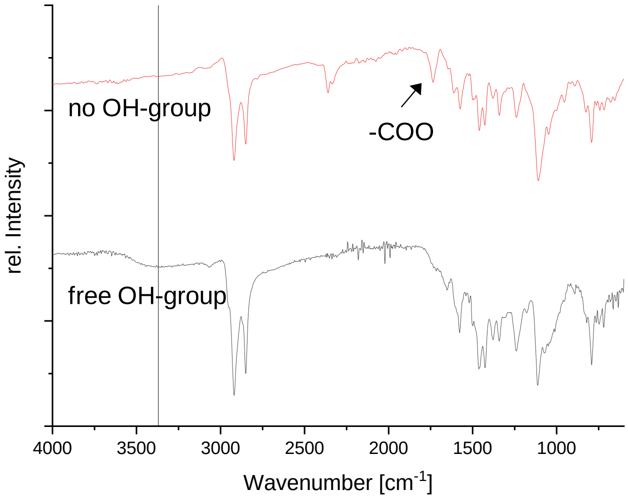

Figure S11: Comparison of the compound with free hydroxyl groups (black) and the target molecule **5** with no free hydroxyl groups (red).

The IR-spectrum of compound proves the successful fourfold coupling with the fullerene spacers in compound **5** due to the absence of any free OH-group at 3370 cm^{-1} (visualized by solid line).

9) Fluorescence spectra of the oligothiophene arm derivatives

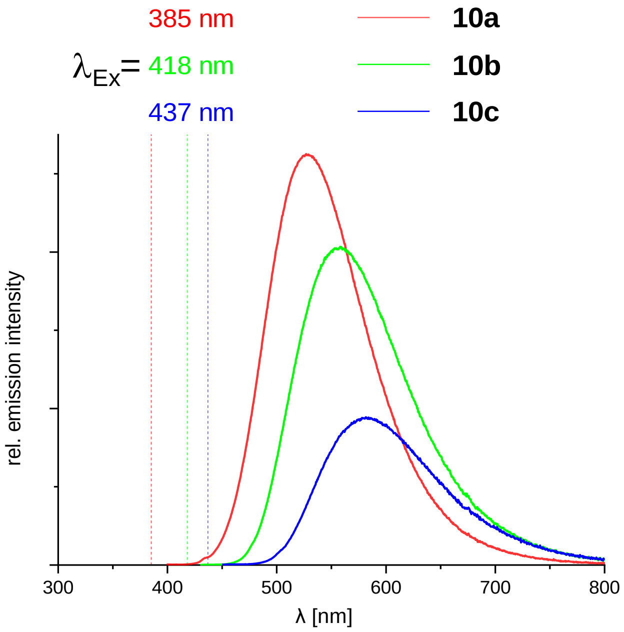

Figure S12: Concentration corrected emission spectra of the thiophene-arms **10a** (red, c=8.9*10^{-07} mol/l), **10b** (green, c=7.9*10^{-07} mol/l), **10c** (blue, c=6.9*10^{-07} mol/l) in THF. Dotted Lines indicate excitation wavelengths (λ_{Ex}).

Figure S12 shows the concentration corrected emission wavelength of compounds **10a-c**, showing a decrease of intensity with increasing numbers of thiophenes.

10) Density measurements by the buoyancy method at 23 °C

The density measurements of compounds **2**, **3** **4** and the mixture of **4** and **5** were carried out in mixtures of deionized water and aqueous calcium chloride (40 °wt%) solution. Before dissolving, the calcium chloride was dried at 140 °C under reduced pressure (1 × 10^{-3} mbar). All solvents were degassed by ultra sonication.

The samples were heated to 170 °C and extruded into a thin solid fiber under reduced pressure to avoid inclusion of air. The fiber was cut in small pieces. These samples were put in a vial containing deionized water. Aqueous calcium chloride (40 wt%) solution was added in small portions until the sample started floating. The mixture was allowed to equilibrate between additions. The weight percentage of calcium chloride was determined and the density was calculated according to reference.[17]

Note that this method relies on samples which are free from air inclusions, which cannot be completely guaranteed with the present procedure. For materials with much lower clearing temperatures and high thermal stability in the isotropic liquid, the samples can be prepared by keeping them a long time in the isotropic liquid under vacuum, which is supposed the eliminate all air bubbles.[18] However in the present case this is not possible since the star-compounds do not melt. Therefore, the present density can be only a minimum value for the molecules.

The following table gives an overview over the experimental densities obtained from the buoyancy method (ρ_{exp}) and from the XRS (ρ_{Xray}), whereas the maximal error of the XRS density was also calculated by propagation of error.

Table S1: Experimental and XRS densities.

Compound	ρ_{exp} [g·cm^{-3}]	ρ_{Xray} [g·cm^{-3}]	error of ρ_{Xray} [g·cm^{-3}]	number of molecules / *h*
1	1.08	1.16	0.06	2
2	1.02	0.95	0.08	1
3	1.03	0.78	0.05	1
3	1.03	1.22	0.08	2
4	1.066	1.07	0.05	2
4+**5** (1:1)	1.185	1.14	0.04	1

For compounds **2**, **4** and the 1 : 1 mixture of **4** and **5** the experimental density and the X-ray density are in agreement with each other and the model considering the maximal error of the XRS density calculated on the basis of propagation of error progression, whereas the assumed error of the *a* parameter amounts to 1.1 Å and of the *c*-Parameter to 0.1 Å . Compound **3** is obviously an intermediate case. The X-ray density for a single mesogen **3,** in 3.38 Å is much too low, even when adding the maximum error of the XRS experiment. Considering a dimer of mesogens in a columnar unit with *h* = 4.34 Å, the density is too high. Consequently, compound might realize a mixture of the two models, for which die dimer stacking is interrupted by defects of coplanar stacked mesogens.

Figure S13 shows the different monomers, whereas the intrinsic free space increases from mesogen **2** to **4** (left to right).

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[17] S. Mao, Z. Duan, J. Chem. Thermodyn **2008**, *40*, 1046-1063.

[18] M. Lehmann, M. Jahr, B. Donnio, R. Graf, S. Gemming, I. Popov, *Chem. Eur. J.* **2008**, *14*, 3562-3576.

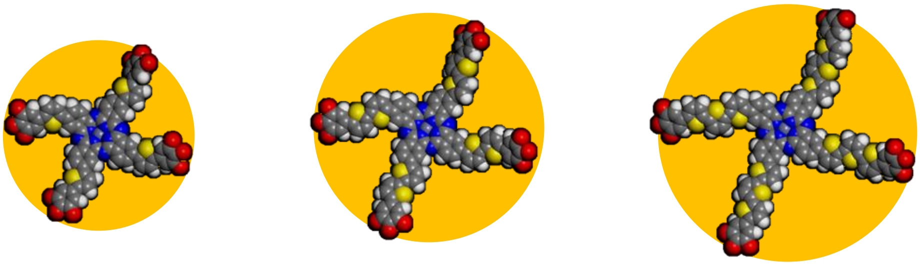


Figure S13: Monomers of compounds **2** (left), **3** (middle) and **4** (right) from top with intrinsic free space (orange).

Inspection of single molecules reveal that the intrinsic free space increase from compound **1** to **4** (see Figure S13, compound 1 with practically no free space is not shown). When the molecules simply stack on top of each other the free space of mesogens **1** and **2** is rather efficiently filled, whereas there is too much free space in case of molecule **4** (Figure S14). Consequently, compound **4** forms dimers, in which already some cavities are filled (see Figure S16). The residual cavities can be filled by nanosegregated chains of other dimers along the column. For compound **3**, the self-organization along the column is not completely clear, but density considerations and the remaining free space, which is more or less in the middle between **2** and **4** (Figure S13, middle) point to a mixture of dimers and monomers along the column.

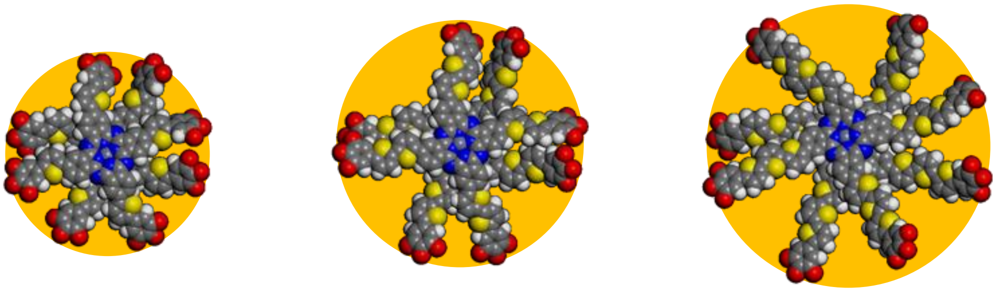


Figure S14: Co-planar stacked dimers of compounds **2** (left), **3** (middle) and **4** (right) from the top, whereas residual free space is marked with orange.

The side view of the co-planar stacked molecules (Figure S15) confirms, that mesogen **2** is more or less a flat compact disk, whereas the size of the cavities increases from **3** to **4**.

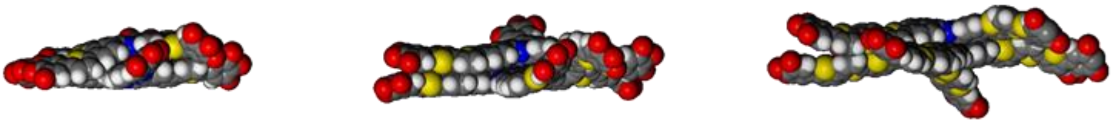


Figure S15: Co-planar stacked mesogens of compounds **2** (left), **3** (middle) and **4** (right) from the side.

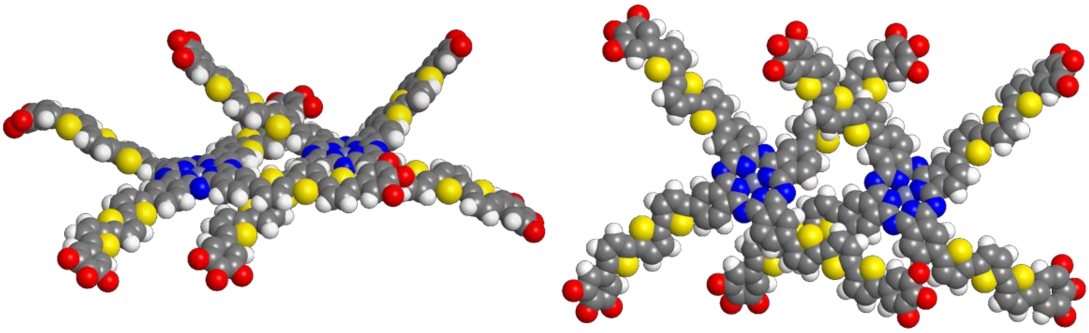


Figure S16: Propeller shaped dimer of compounds **4** from the side (left) and top (right).

11) Modelling of the LC phases of 2, 4 and the mixture of 4 and 5

General

The LC phases were modelled with the program Accelrys *Materials Studio 4.4*. For all structures the major regioisomer has been chosen to create the assembly. After the set-up of the unit cells the geometry optimization was first performed using the module “Forcite Plus (2017R2)” with the force field “COMPASSII” with the atom based summation method. Finally, the Ewald summation method has been applied, until the non-covalent interactions (electrostatic and van der Waals interactions) were large and negative.

*Mesophase of star mesogen **2***

The parameters for the columnar stratum determined by XRS are *a* = 45.38 Å, *h* = 3.35 Å. Since the modelling with a single molecule in the cell would produce a coplanar stacking with a core region which would not be nanosegregated or filled by aromatic units, we arbitrarily enlarged the unit cell to c = 33.5 Å. Here, ten molecules stack in the column with a density of 0.95 gcm^{-3}. The mesogens were rotated by values between 10° and 30° to each other along the column. This guaranteed the minimisation of steric interaction and the absence of an AB structure or helical stacking within this unit cell. For both structures there is no evidence in XRS. Geometry optimisation affords van der Waals interactions of -1535 kcal/mol (135 kcal/mol corresponding to a single mesogen) and electrostatic interactions of 7030 kcal/mol (703 kcal/mol corresponding to a mesogen). The latter consist mainly of the interaction between Zn^{2+} and the nitrogens.

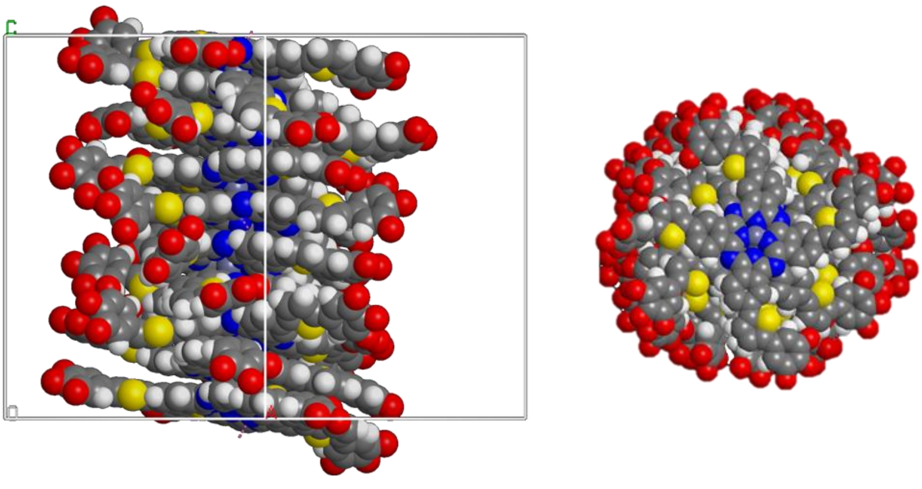


Figure S17: Geometry optimized model of the Col$_h$-phase of **2**. Left: side view, right: top view.

*Mesophase of star mesogen **4***

XRS results show that two mesogens pack in a columnar stratum of *a* = 61.23 Å and *h* = 3.9 Å at a density of δ = 1.07 g/cm^{-3}. Two disc-shaped cores cannot be placed in a cell with only 3.9 Å height, since this means that the molecules would be only 1.95 Å apart, which is much smaller than the typical van der Waals distance of aromatic systems (π-π distance approx. 3.3-3.7 Å). Therefore, the dimer model has been applied, in which two mesogens form a propeller-shaped dimer and consequently fill the free space of almost three of the four pockets between the arms of the star mesogen. This dimer is than arranged in a double helix by rotation of the next neighbour by 36 °, which is necessary to avoid steric congestions. The unit cell, containing a full helical pitch with 10 dimers, possesses a *c* parameter of 39 Å. The geometry optimisation affords a cell with large negative non-bonding interactions: Van der Waals -3244 kcal/mol (-162 kcal/mol/mesogen), electrostatic -13742 kcal/mol (-688 kcal/mol/mesogen). The structure further explains the almost missing signal for π-π interactions.

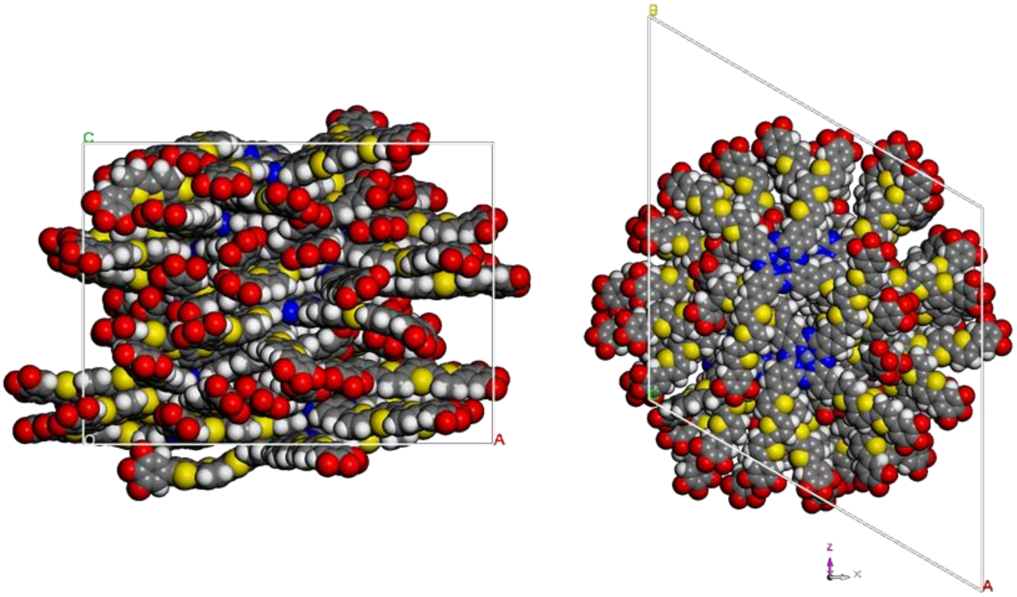


Figure S18: Geometry optimized model of the Col$_h$-phase of **4**. Left: side view, right: top view.

*Mesophase of the 1 : 1 mixture of **4** and **5***

XRS and density measurements reveal that in a hexagonal phase with a columnar stratum of *a* = 54.7 Å and *h = 3.3* Å a dimer consisting of one molecule **4** and one molecules **5** pack at a density of 1.16 g/cm^{-3}. As there are no meridional reflections, the quadruple helix has to be pretty much disordered, so just a small piece of the helix with *c* = 46.2 Å was modeled, whereas the dimers were rotated by 13 ° due to geometric reasons.

The final model has been geometry optimised to give finally a large negative non-bonding energy with -2788 kcal/mol (van der Waals, 199 kcal/mol corresponding to one mesogen) and -9559 kcal/mol (electrostatic, 683 kcal/mol corresponding to one mesogen). These are typical values demonstrating the high stability of the assembly.

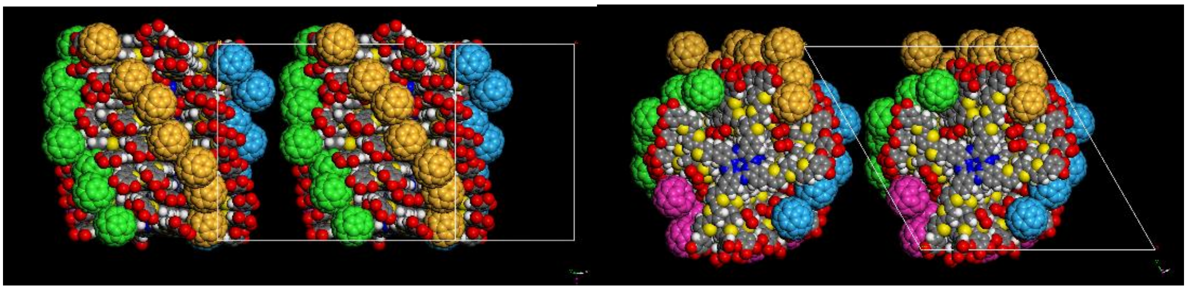


Figure S19: Geometry optimized model of the Col$_h$-phase of the 1 : 1 mixture of **4** and **5**. Left: side view, right: top view.

12) Fiber extrusion

The aligned fibers were produced by a home-made mini extruder with a pinhole of 0.7 mm in diameter. The mini extruder was loaded with 5-10 mg of the material, in a chamber with a diameter of 2 mm. The extruder was heated to 50 °C (**1**), 120 °C (**2**), 150 °C (**3**), 170 °C (**4**) and to 180 °C (mixtures **4**+**5**) and the material was extruded through the pinhole to a fiber of approx. 0.7 mm in diameter. These fibers were used for XRS and density investigations.

13) X-ray scattering pattern of the Col$_{ort}$-Phase of 1 and of the Col$_{rec}$-phase of 2

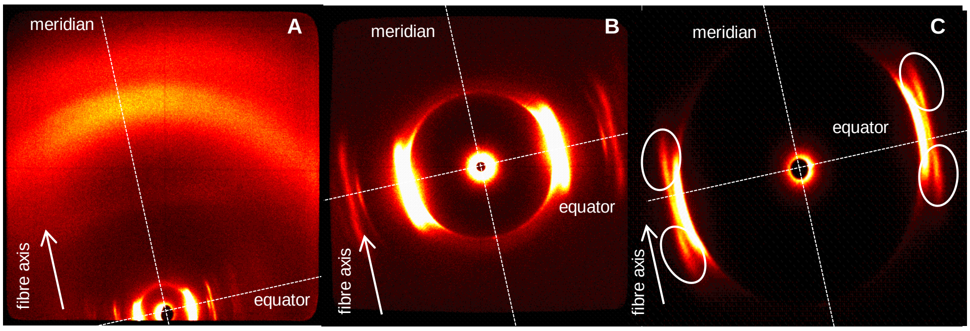


Figure S20: (A) WAXS pattern of the Col$_{ort}$-phase of **1** after cooling to room temperature. (B) SAXS pattern of the body centered Col$_{ort}$-phase of **1** after cooling to room temperature, and magnified view of the 100 and 101 reflection, whereas the meridional reflections are circled with white ellipses(C). Due to the huge amount of signals very close to the equator, this phase could not be fully evaluated.

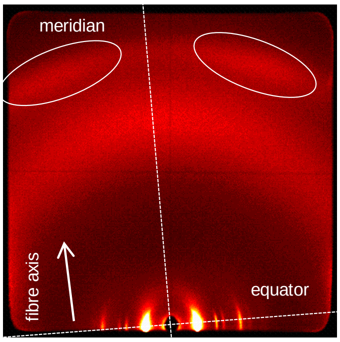


Figure S21: WAXS pattern of the Col$_{rec}$-phase of **2** at 220 °C. The splitted signals along (white ellipses) indicate the tilt angle of 23 °.

14) Results of the XRS-measurements

Table S2: Comparison of the cell-parameters of the Col phases of **1-4** and the mixture of **4** and **5** at 25 °C with the Core diameter.

Compound	*a*, *b* [Å]	Columnar diameter [Å] (25 °C)	Core diameter [Å]
1	66.0, 39.2	39.2	23.5
2	45.4	45.4	30.6
3	52.2	52.2	37.4
4	61.2	61.2	44.4
Mixture 4 + 5	54.7		

Table S3: Overview over cell parameters and Miller indices of **1**-**4**.

1: 25 °C, Cell parameter: *a* = 66.0 Å *b* = 39.2 Å, tilt angle = 27 °					
Miller Indices			d_{exp} [Å]	d_{theo} [°]	Correlation length [units]
h	k	l			
1	1	0	33.2	33.7	18
3	1	0	19.3	19.2	
2	2	0	16.7	16.9	
1	3	0	12.7	12.8	
3	3	0	11.2	11.2	
2	4	0	9.4	9.4	
Chain-distance			4.5		
π-π–distance			3.3		7

2: 220 °C, Cell parameter: *a* = 42.5 Å, *b* = 76.6 Å, tilt angle = 23 °					
Miller Indices			d_{exp} [Å]	d_{theo} [°]	Correlation length [units]
h	k	l			
1	1	0	37.2	37.2	12
3	1	0	21.5	21.4	
2	2	0	18.6	18.6	
Chain-distance			4.7		
π-π–distance			3.5		8

2: 25 °C, Cell parameter: *a* = *b* = 45.4 Å					
Miller Indices			d_{exp} [Å]	d_{theo} [°]	Correlation length [units]
h	k	l			
1	0	0	39.3	39.3	10

1	1	0	22.6	22.7	
2	0	0	19.4	19.5	
2	1	0	14.8	14.89	
Chain-distance			4.3		
π-π–distance			3.4		10

3: 220 °C, Cell parameter: *a* = *b* = 50.1 Å					
Miller Indices			d_{exp} [Å]	d_{theo} [°]	Correlation length [units]
h	k	l			
1	0	0	43.4	43.4	10
1	1	0	25.0	25.1	
2	0	0	21.6	21.7	
2	1	0	16.4	16.4	
3	0	0	14.5	14.5	
Chain-distance			4.3		
π-π–distance			3.4		10

3: 25 °C, Cell parameter: *a* = *b* = 52.2 Å					
Miller Indices			d_{exp} [Å]	d_{theo} [°]	Correlation length [units]
h	k	l			
1	0	0	45.2	45.2	8
1	1	0	26.1	26.1	
2	0	0	-	-	
2	1	0	17.1	17.1	
Chain-distance			4.2		
π-π–distance			3.4		10

4: 250 °C, Cell parameter: *a* = *b* = 59.4 Å

Miller Indices			d_{exp} [Å]	d_{theo} [°]	Correlation length [units]
h	k	l			
1	0	0	51.4	51.4	9
1	1	0	29.57	29.57	
2	0	0	-	-	
2	1	0	19.32	19.42	
Chain-distance			4.45		
π-π–distance			3.43		5

4: 25 °C, Cell parameter: *a* = *b* = 61.2 Å					
Miller Indices			d_{exp} [Å]	d_{theo} [°]	Correlation length [units]
H	k	l			
1	0	0	53.0	53.0	8
1	1	0	30.5	30.6	
2	0	0	-	-	
2	1	0	19.9	20.0	
Chain-distance			4.3		
π-π–distance			3.4		5

1:1 Mixture 4+5: 220°C, Cell parameter: *a* = *b* = 56.6 Å					
Miller Indices			d_{exp} [Å]	d_{theo} [°]	Correlation length [units]
h	k	l			
1	0	0	49.0	49.0	9
1	1	0	-	-	
2	0	0	25.6	25.5	
2	1	0	18.5	18.5	
Chain-distance			4.6		

π-π–distance			3.4		10

1:1 Mixture 4+5: 25 °C, Cell parameter: *a* = *b* = 54.7 Å					
Miller Indices			d_{exp} [Å]	d_{theo} [°]	Correlation length [units]
h	k	l			
1	0	0	47.4	47.4	9
1	1	0	27.4	27.4	
2	0	0	23.7	23.7	
2	1	0	18.0	17.90	
Chain-distance			4.5		
π-π–distance			3.3		10

15) Bar Coating of thin films

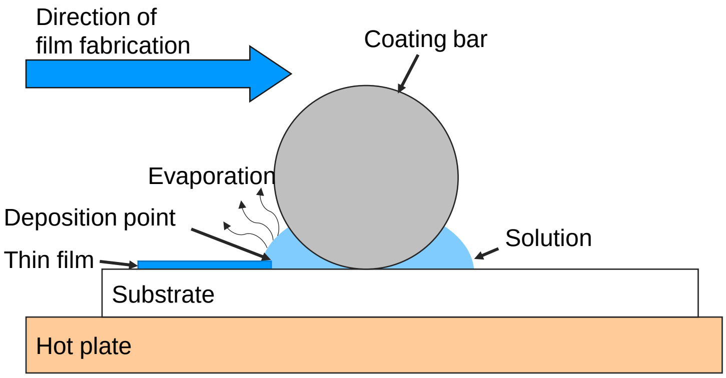


Figure S22: Schematic diagram of the bar coating process.

16) Vacuum deposition of Ag films

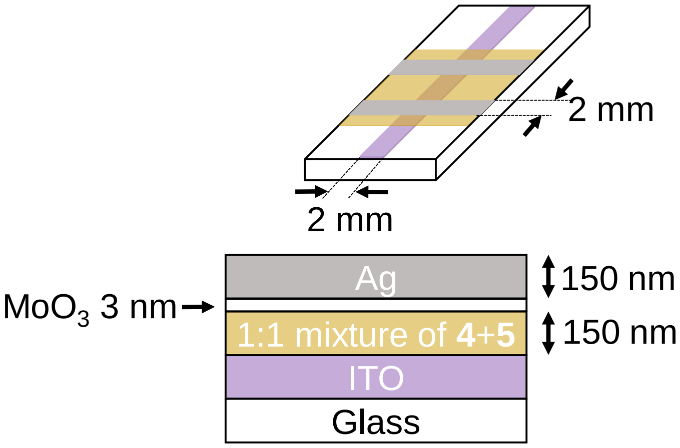
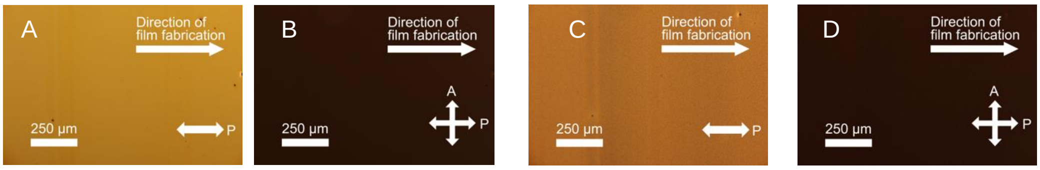


Figure S23: Schematic device structure for *J*-*V*-characteristics.

17) Orientation tests and I-V-characteristics

The 1:1 mixture of **4** and **5** was bar-coated onto an ITO-coated glass substrate, then a thin silver film (150 nm) was deposited onto the top. The POM pictures with crossed polarizers in reflection mode and *J*-*V* characteristics were taken under different conditions (Figure S23: without pre-annealing, post-annealing at 200 °C, Figure S24: pre-annealing at 220 °C for 5 minutes and post annealing at 200 °C, Figure S25: pre-annealing at 280 °C for 5 minutes and post annealing at 200 °C).

Without any pre-annealing, there is almost no difference of the *J*-*V* characteristics between dark and irradiated conditions. Moreover, also the POM reveals that there is no birefringence (B, D) as shown in Figure S23.



Before post-annealing After 36 h post-annealing at 200 °C

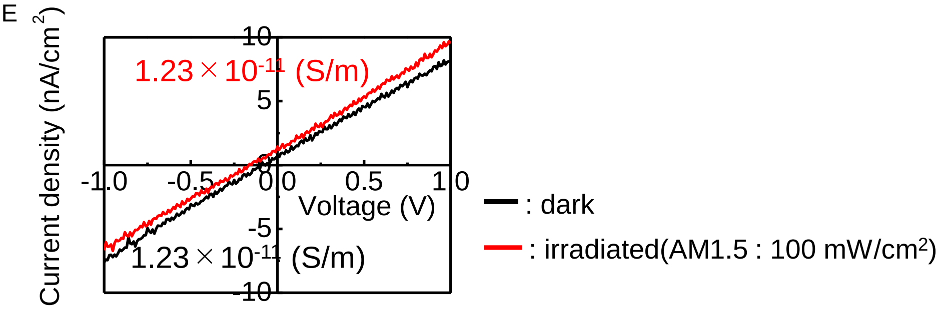


Figure S24: A-D: POM images of the 1:1 mixture of **4** and **5** before post-annealing process (A, B) and after 36 h post-annealing at 200 °C (C, D), without (A, C) and with (B, D) crossed polarizers. E: *J-V* characteristics under dark and irradiated conditions after post-annealing for 24 h.

The *J-V* characteristics in Figure S24 show no difference under dark and irradiated conditions, indicating that the pre-annealing should be carried out at higher temperatures.

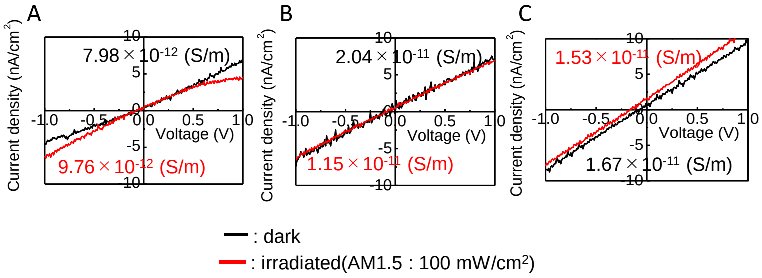
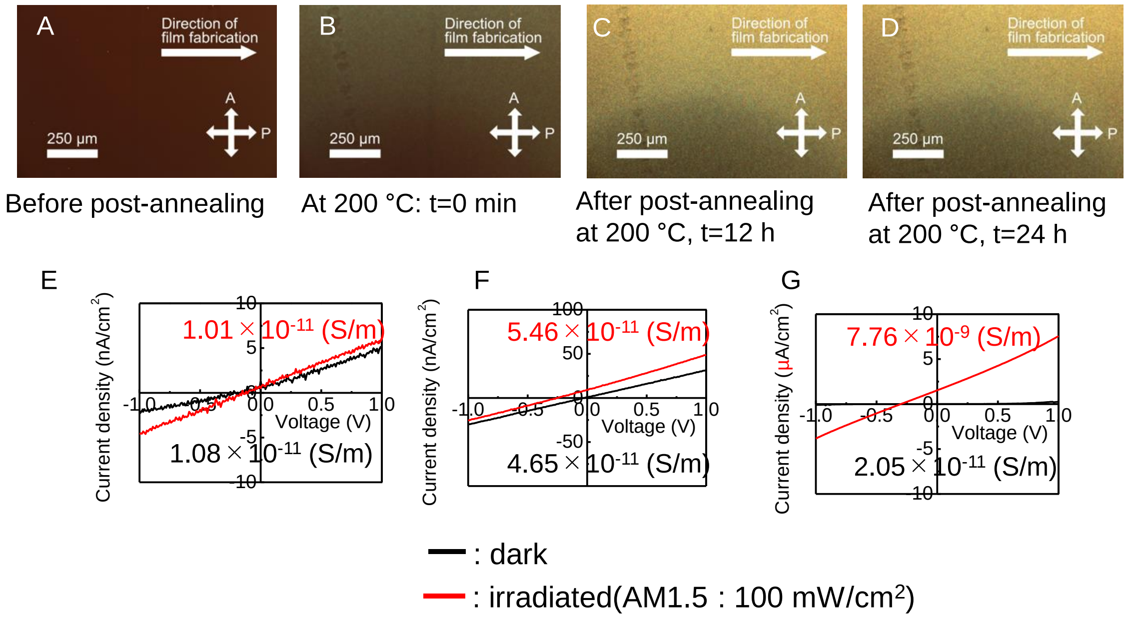


Figure S25: *J-V* characteristics of the 1:1 mixture of **4** and **5** before post-annealing (A) and after annealing for 12 h (B) and 24 h (C).

After the pre-annealing process at 280 °C for 5 minutes, there is no significant difference of the *J-V* characteristics between the dark and irradiated conditions. After post-annealing at 200 °C for 24 h (G), the irradiated *J-V* characteristics is about 300 times higher than the dark one, pointing to a partial reorientation of the sample. However, no complete homeotropic alignment was obtained.



Before post-annealing

At 200 °C: t=0 min

After post-annealing at 200 °C, t=12 h

After post-annealing at 200 °C, t=24 h

Figure S26: A-D: POM pictures of the 1:1 mixture of **4** and **5** before post-annealing process (A) directly after heating to 200 °C (B) and after 12 h (C) and 24 h (D) post-annealing at 200 °C with crossed polarizers in reflection mode. E-G: *J*-*V* characteristics before post-annealing (E) and after annealing for 12 h (F) and 24 h (G).

18) HOMO.LUMO levels of 4, 5 and the mixture

Table S4: HOMO, LUMO and Gap energies of **4**, **5** and the 1 : 1 mixture.

	HOMO [eV]	**LUMO [eV]**	**Gap [eV]**
4	5.20	3.63	1.57
5	5.38	3.80	1.58
Mixture before annealing	5.31	3.74	1.57
Mixture after annealing	5.27	3.73	1.54

19) Photoelectron yield spectroscopy

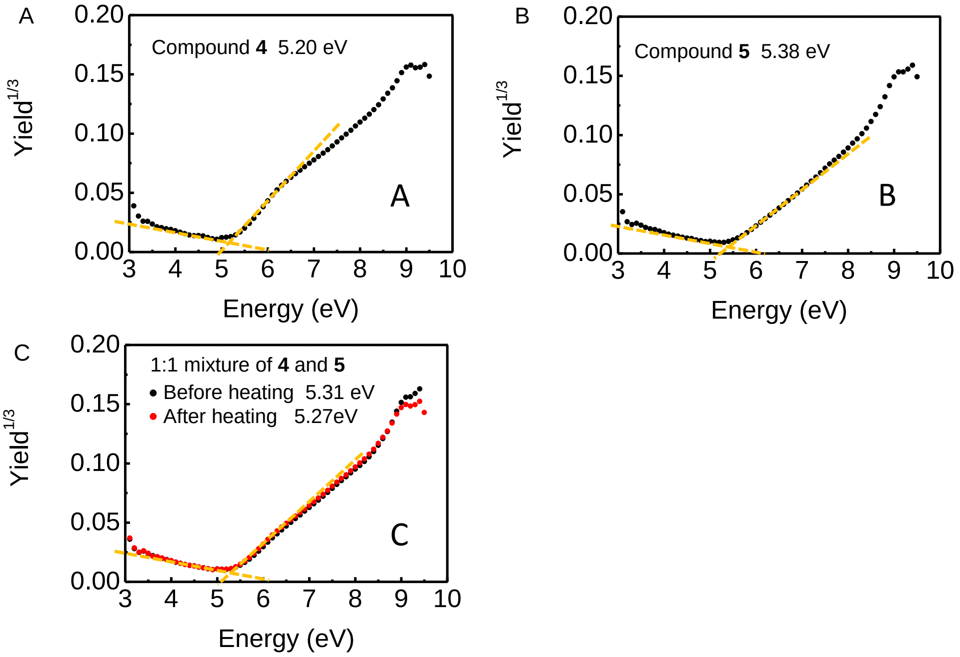
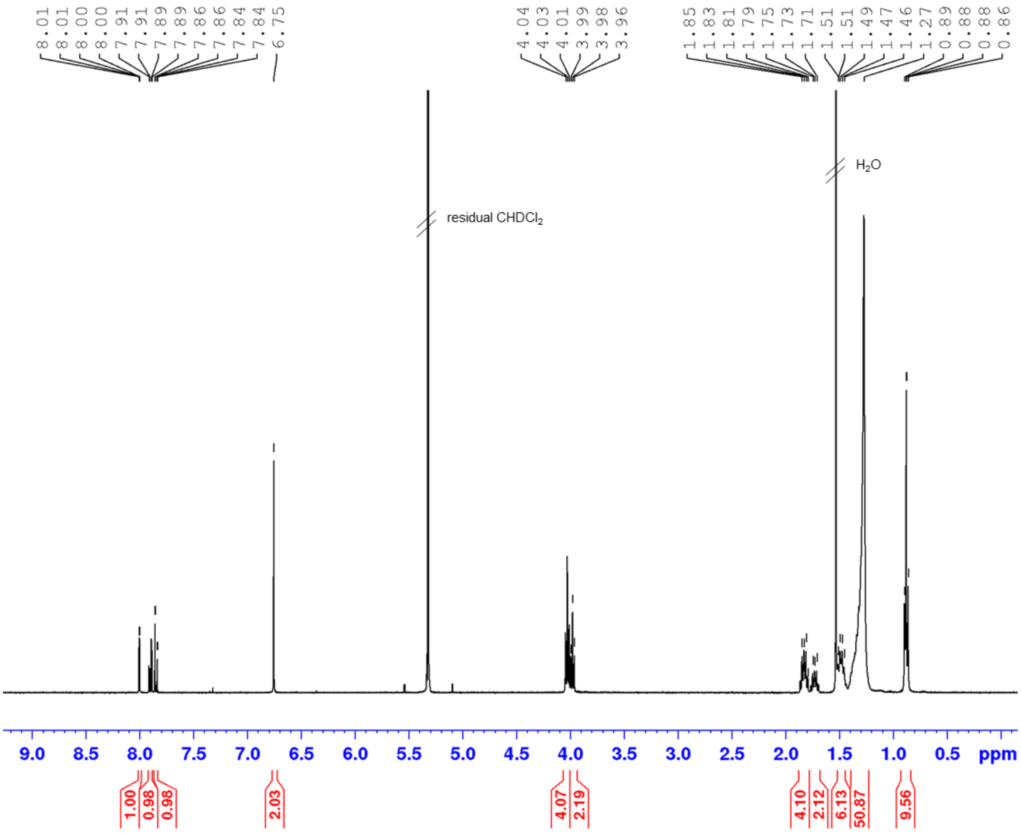


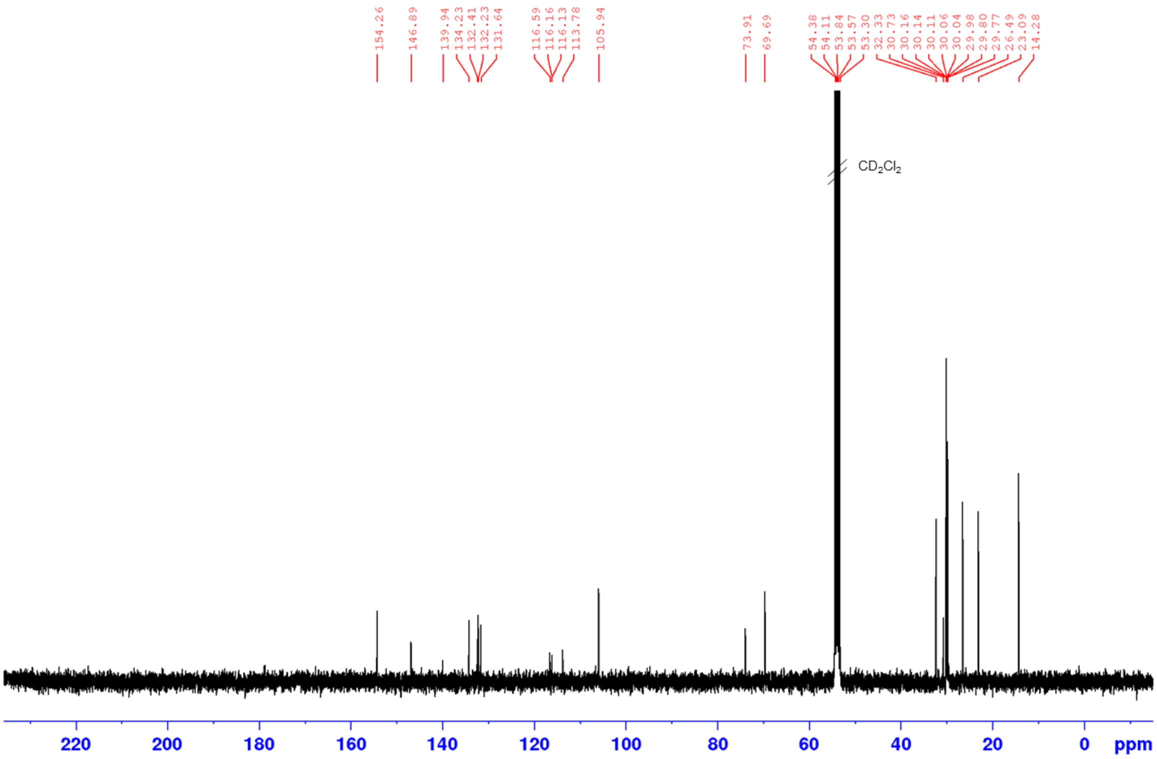
Figure S27: A-B: Photoelectron spectra of thin films of **4** and **5** without annealing process. C: Photoelectron spectra of thin films of 1:1 mixture of **4** and **5** before and after annealing at 220 °C for 5 minutes. The HOMO levels of these compounds were determined from the energies at the cross points of dashed lines.

20) NMR Spectra

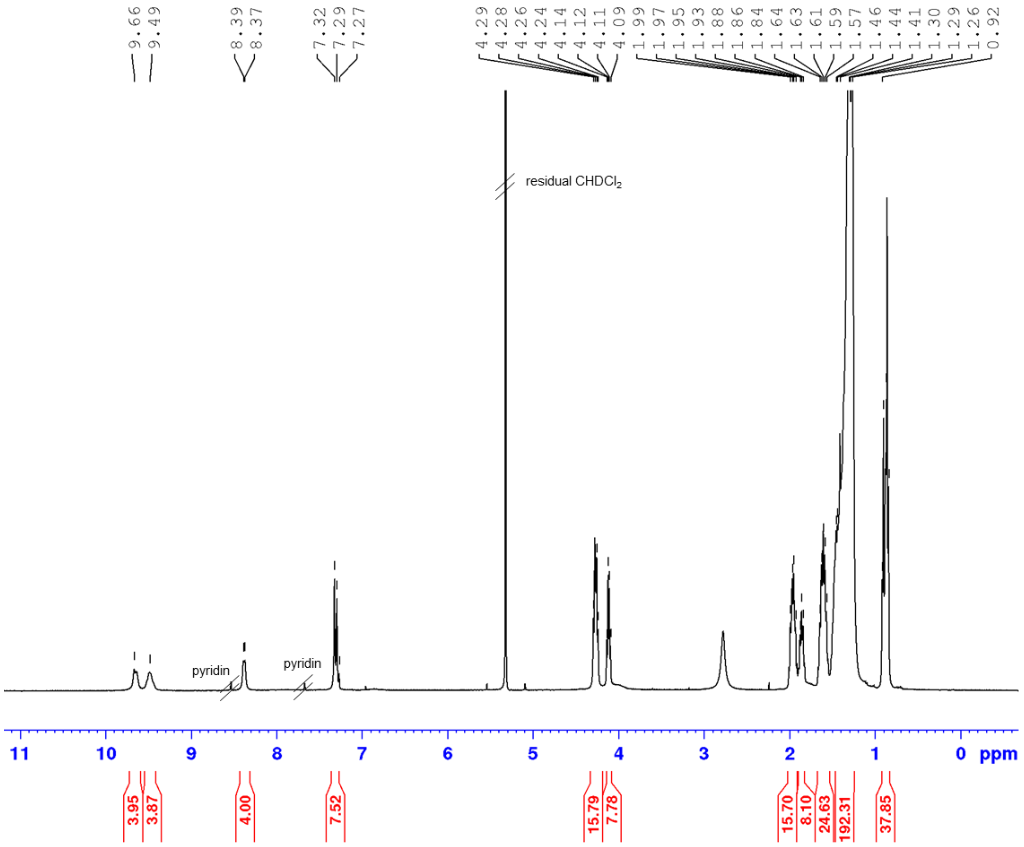
^{1}H NMR (400 MHz) spectrum of **11** in CD_2Cl_2



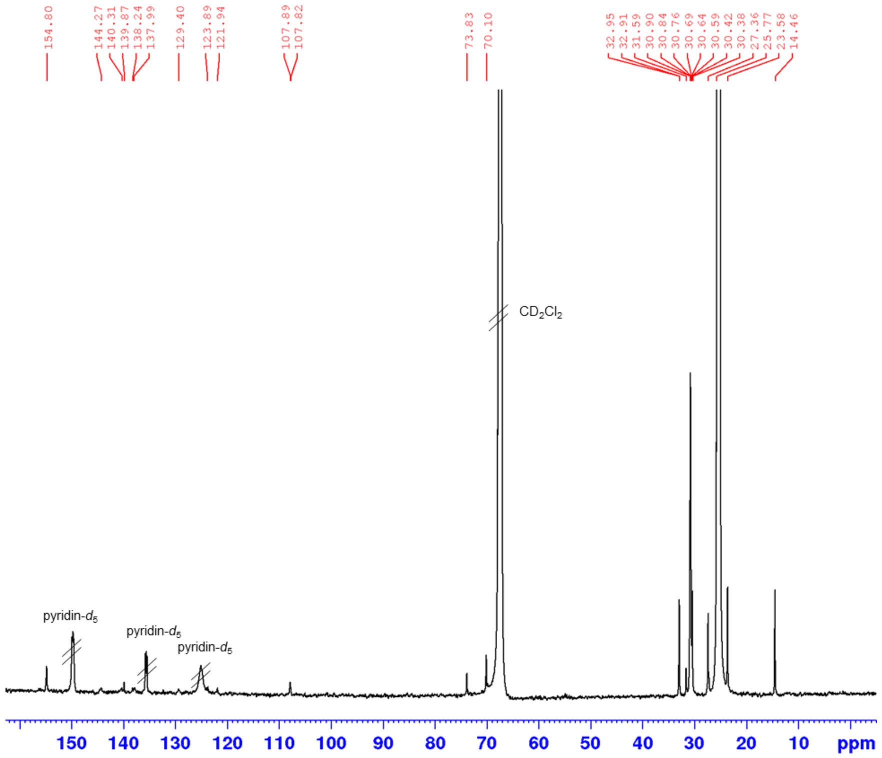
^{13}C NMR (100 MHz) spectrum of **11** in CD_2Cl_2



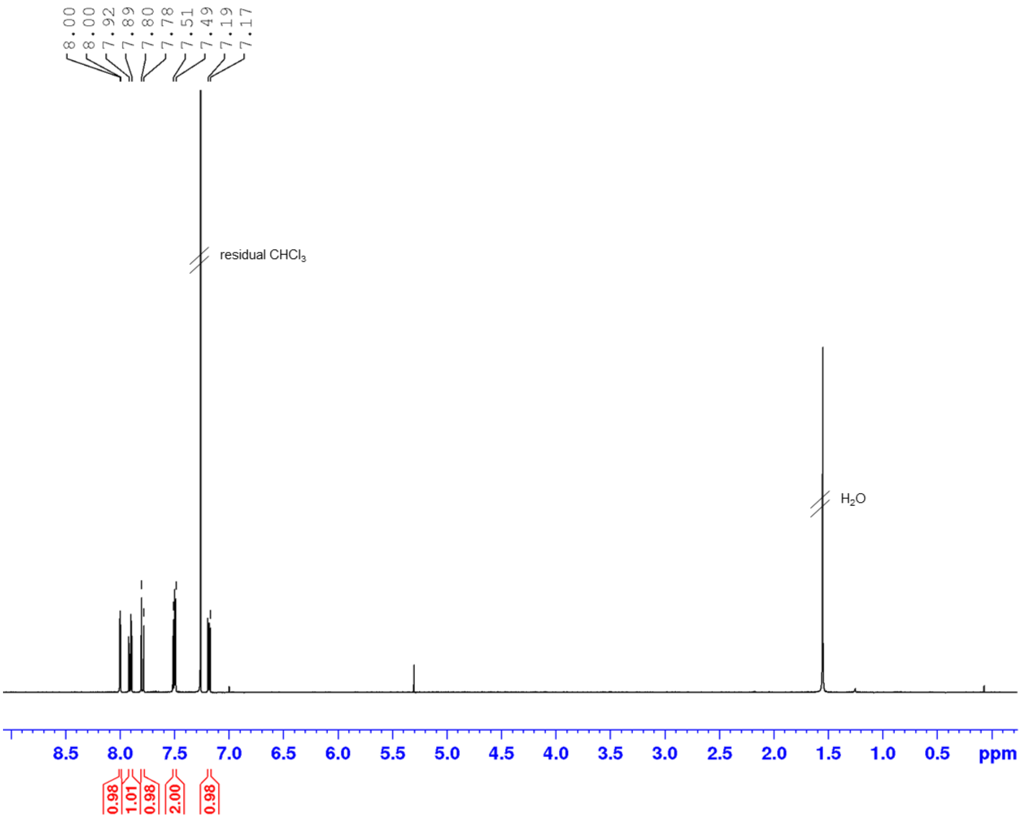
^{1}H NMR (400 MHz) spectrum of **1** in THF-d_8 + 2 drops of pyridine-d_5



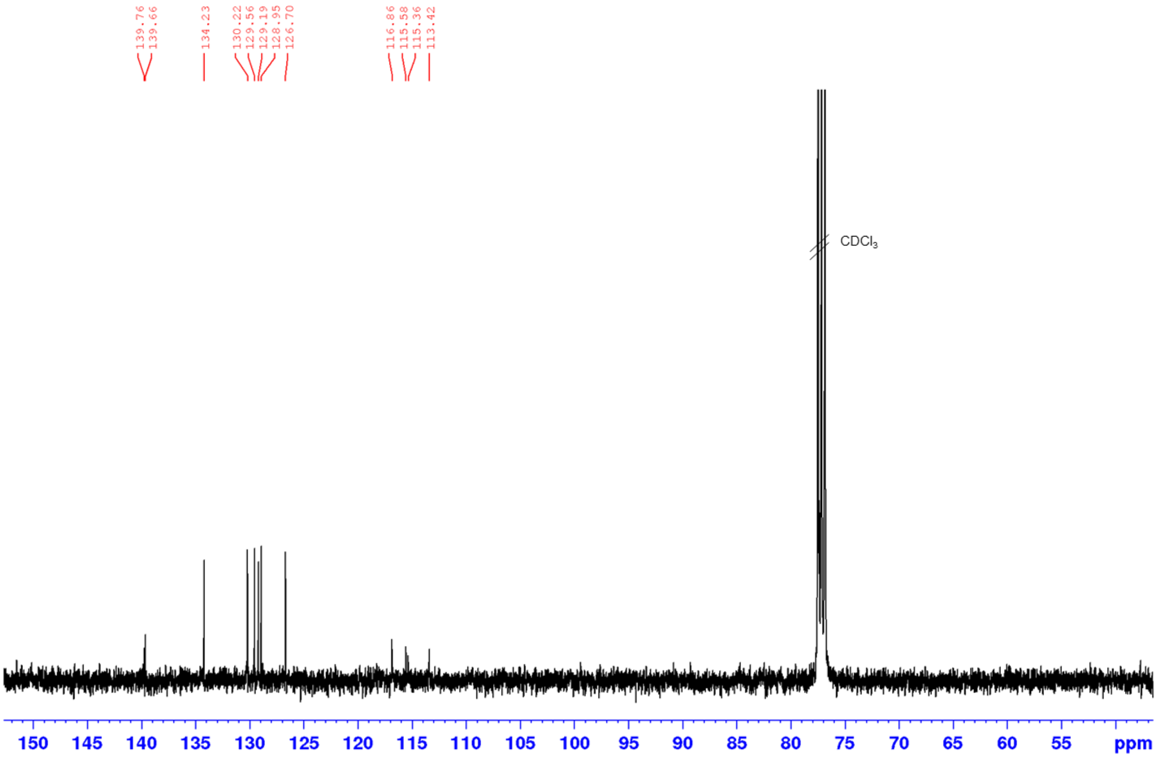
^{13}C NMR (151 MHz) spectrum of **1** in THF-d_8 + 2 drops of pyridine-d_5



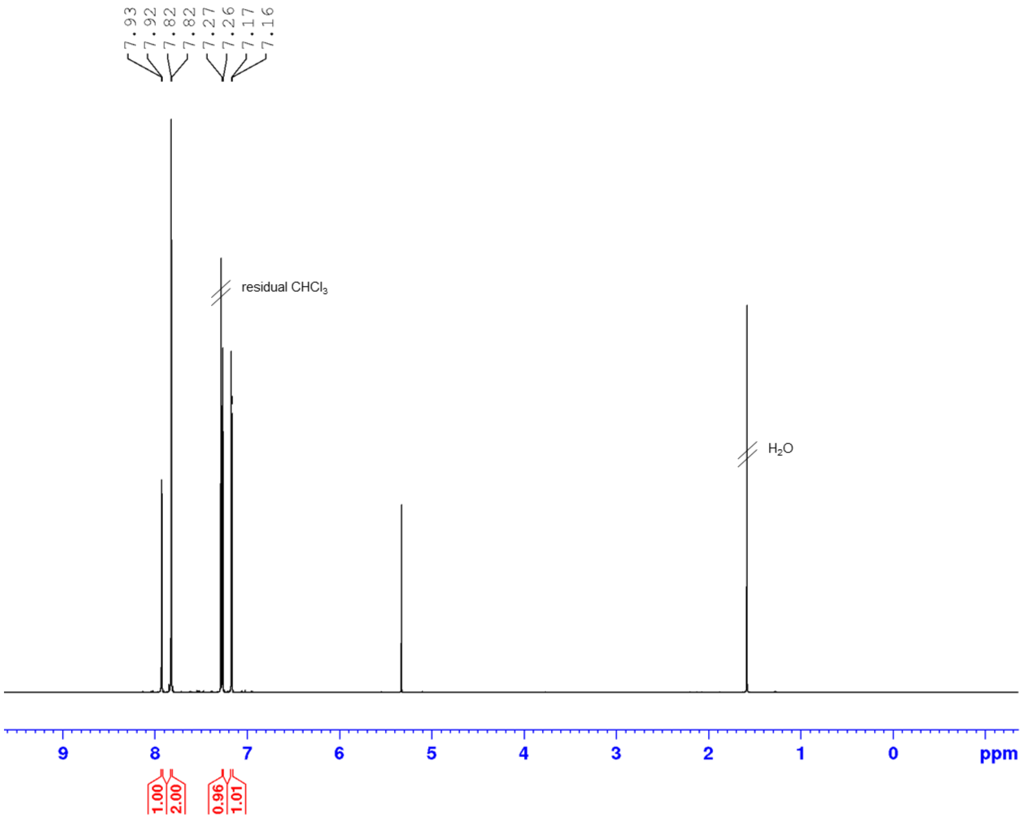
^{1}H NMR (400 MHz) spectrum of **7a** in $CDCl_3$



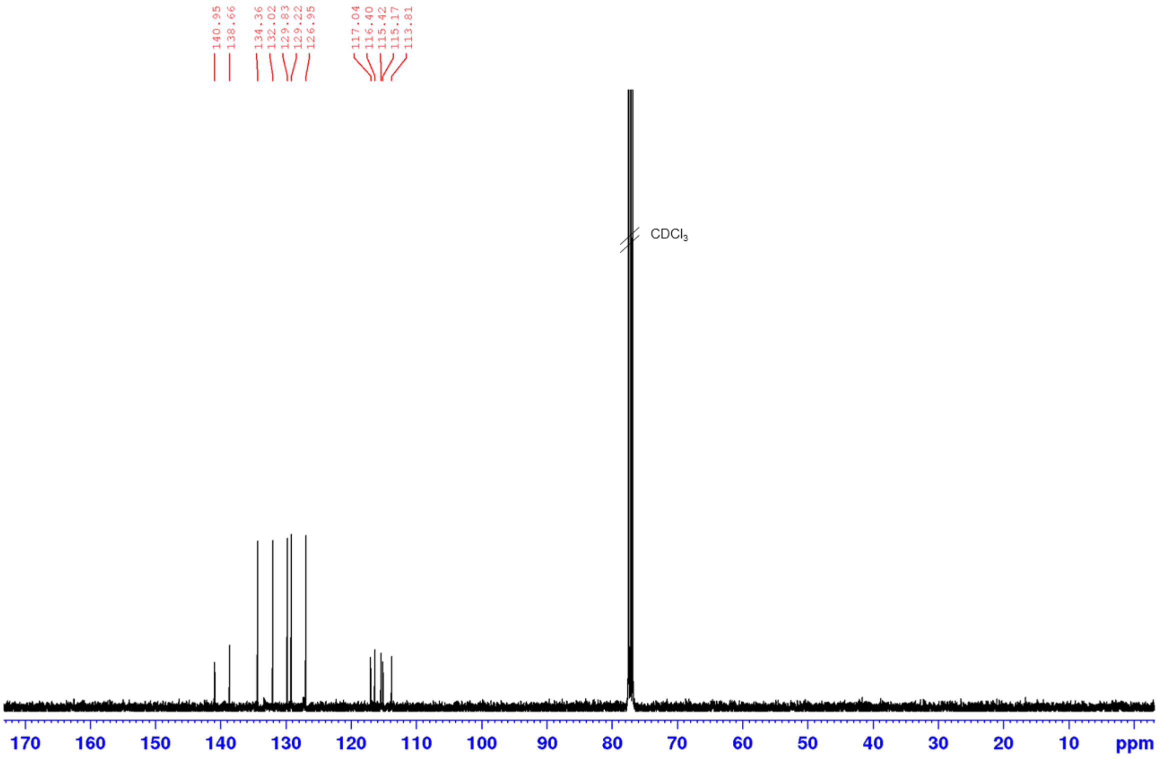
^{13}C NMR (100 MHz) spectrum of **7a** in $CDCl_3$



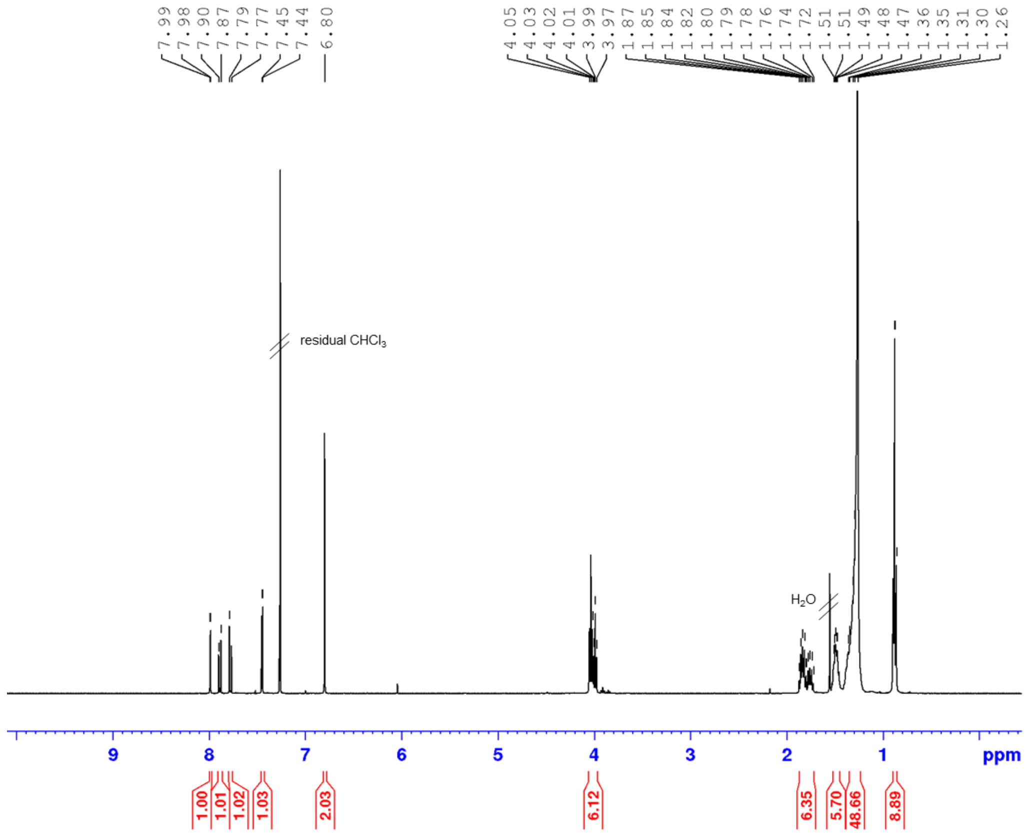
^{1}H NMR (400 MHz) spectrum of **8a** in $CDCl_3$



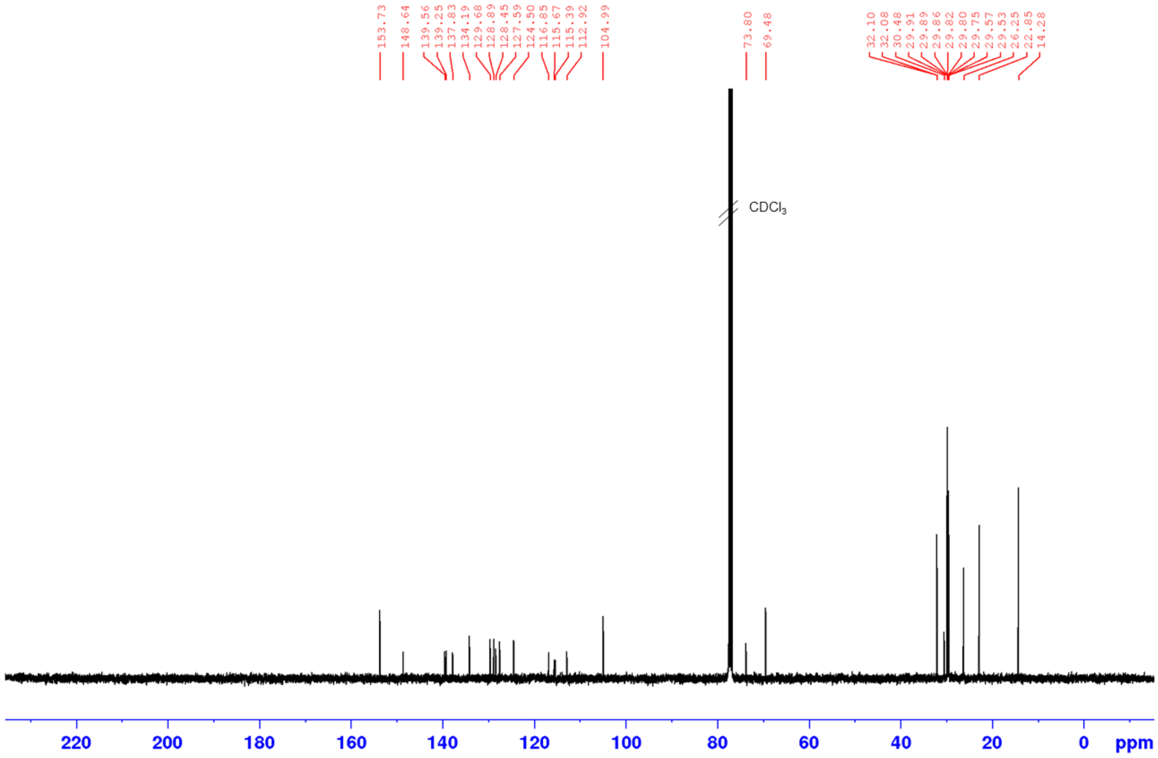
^{13}C NMR (100 MHz) spectrum of **8a** in $CDCl_3$



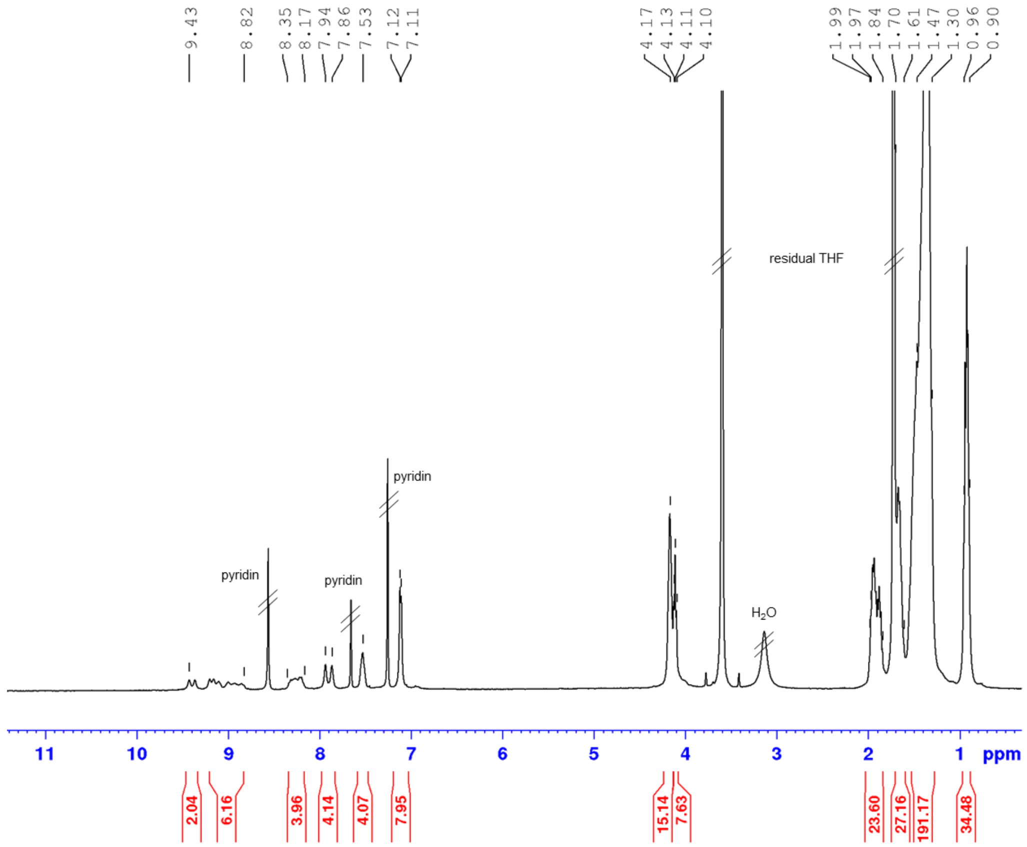
^{1}H NMR (400 MHz) spectrum of **10a** in $CDCl_3$



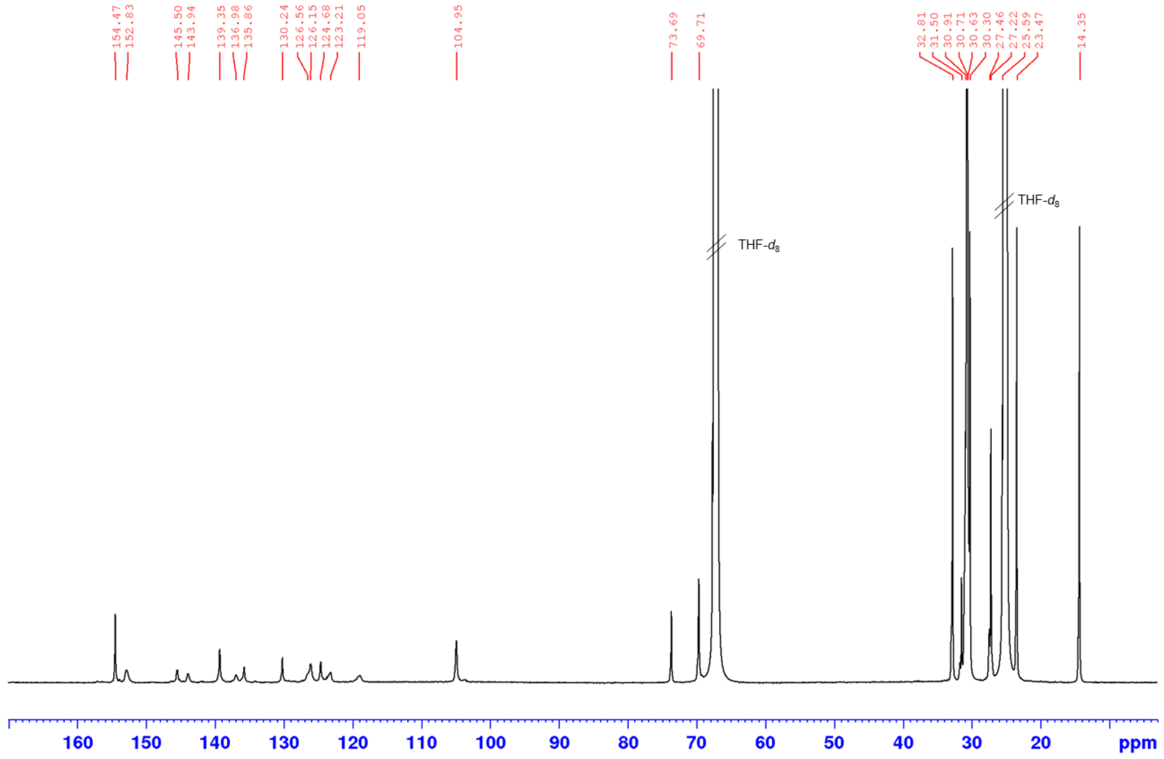
^{13}C NMR (100 MHz) spectrum of **10a** in $CDCl_3$



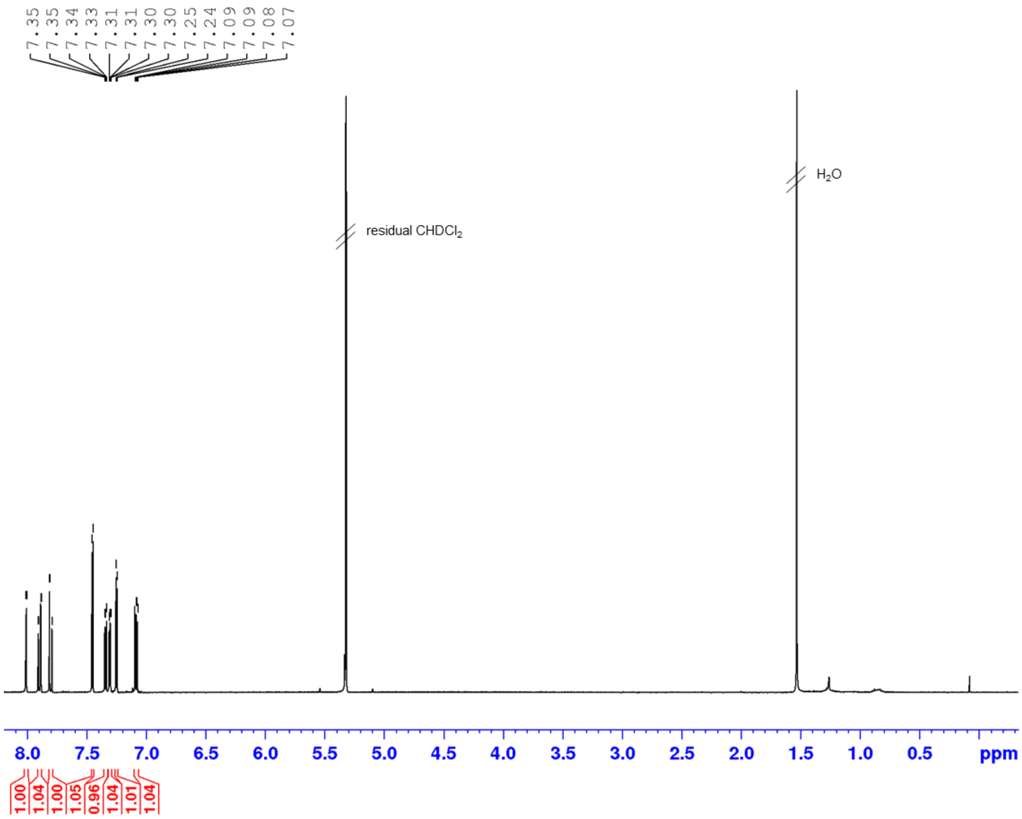
^{1}H NMR (400 MHz) spectrum of **2** in THF-d_8 + 2 drops of pyridine-d_5



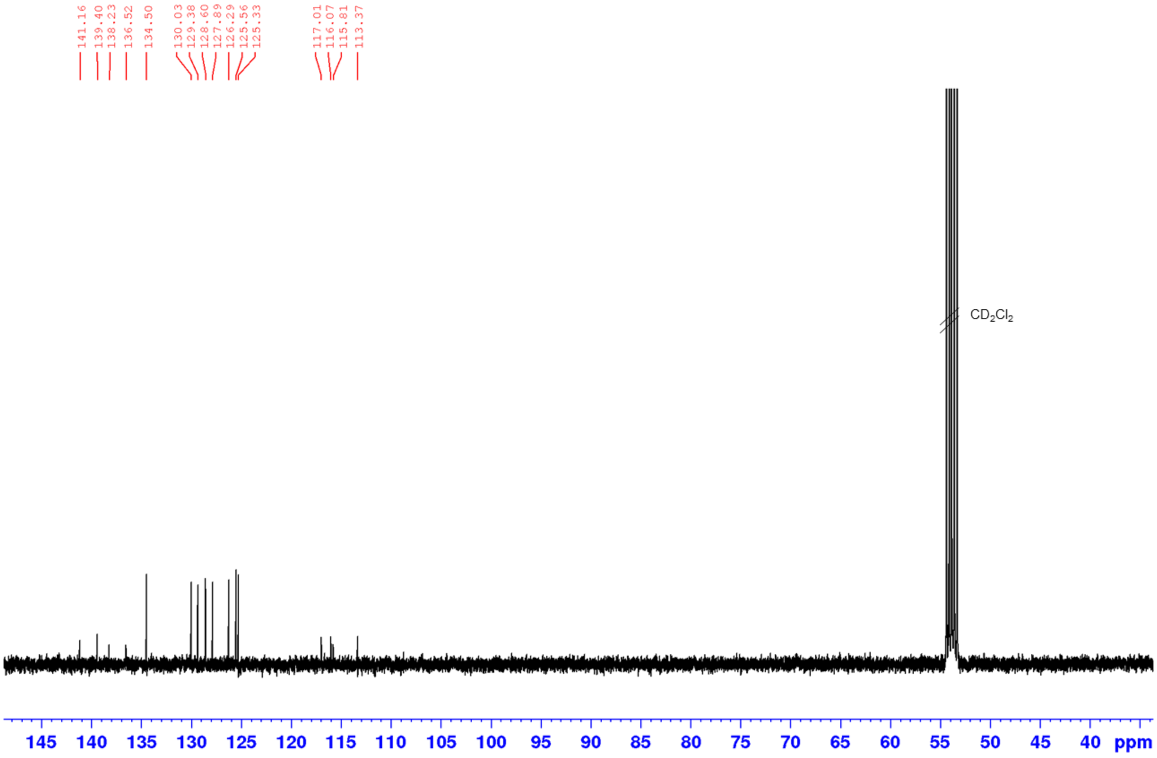
^{13}C NMR (100 MHz) spectrum of **2** in THF-d_8 + 2 drops of pyridine-d_5



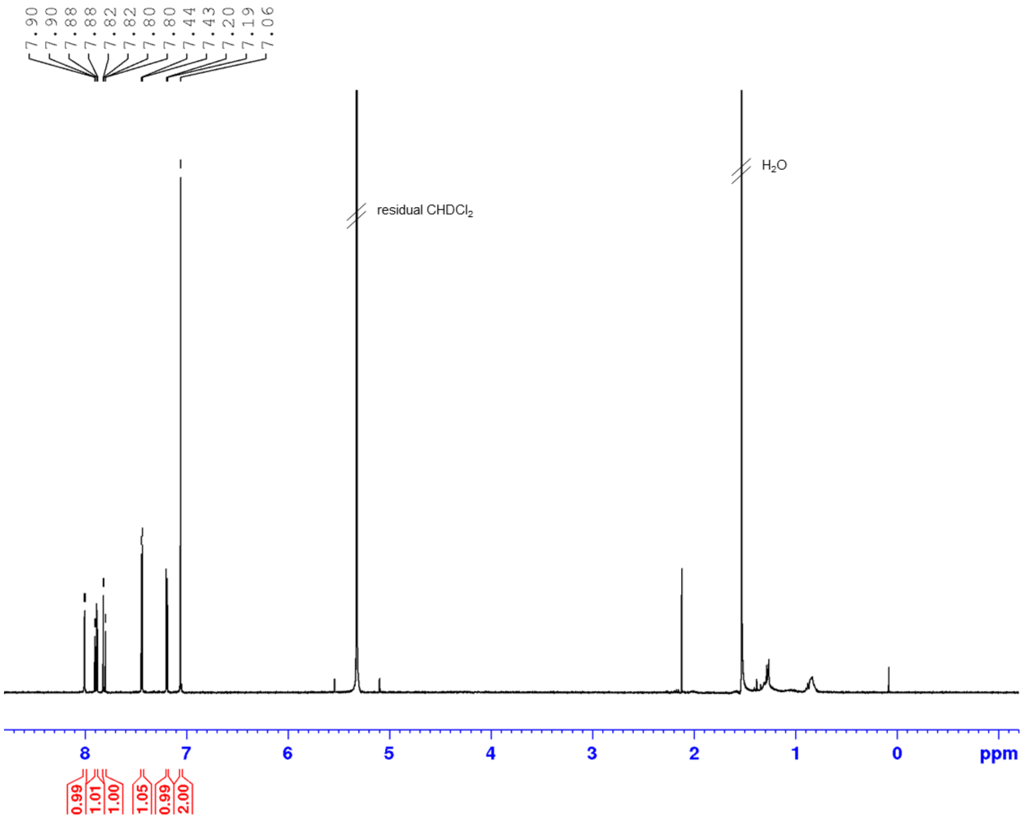
^1H NMR (400 MHz) spectrum of **7b** in CD_2Cl_2



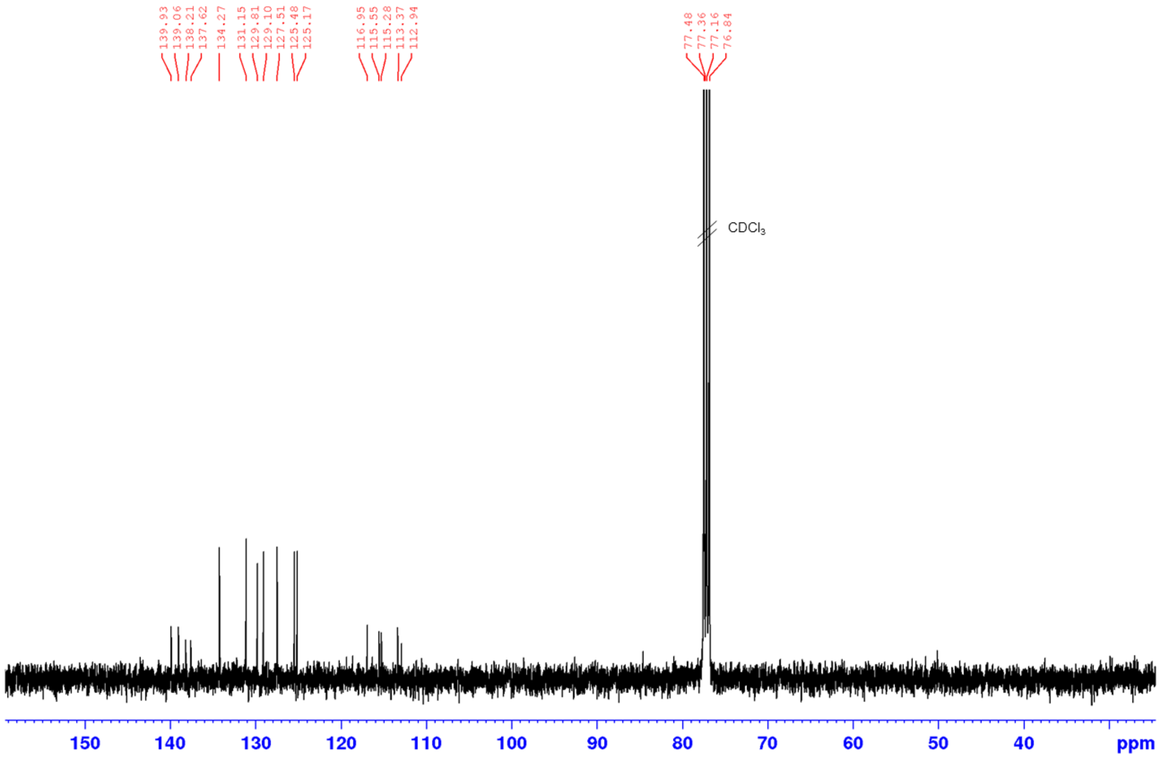
^{13}C NMR (100 MHz) spectrum of **7b** in CD_2Cl_2



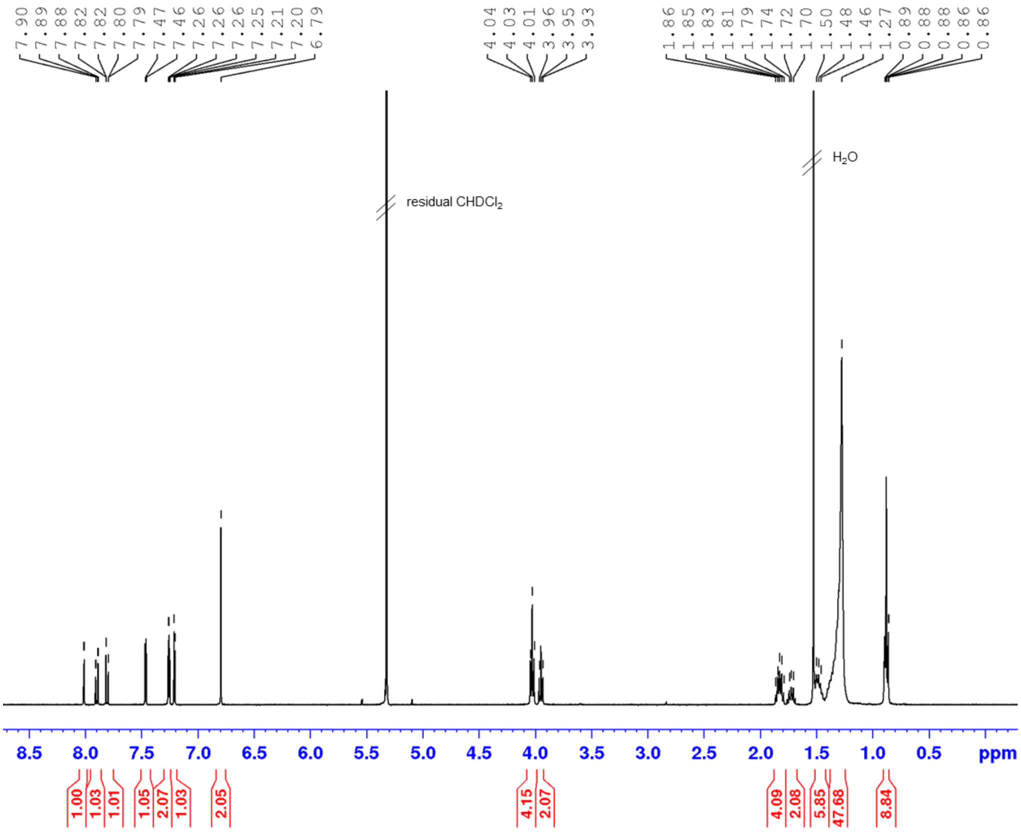
^{1}H NMR (400 MHz) spectrum of **8b** in $CDCl_3$



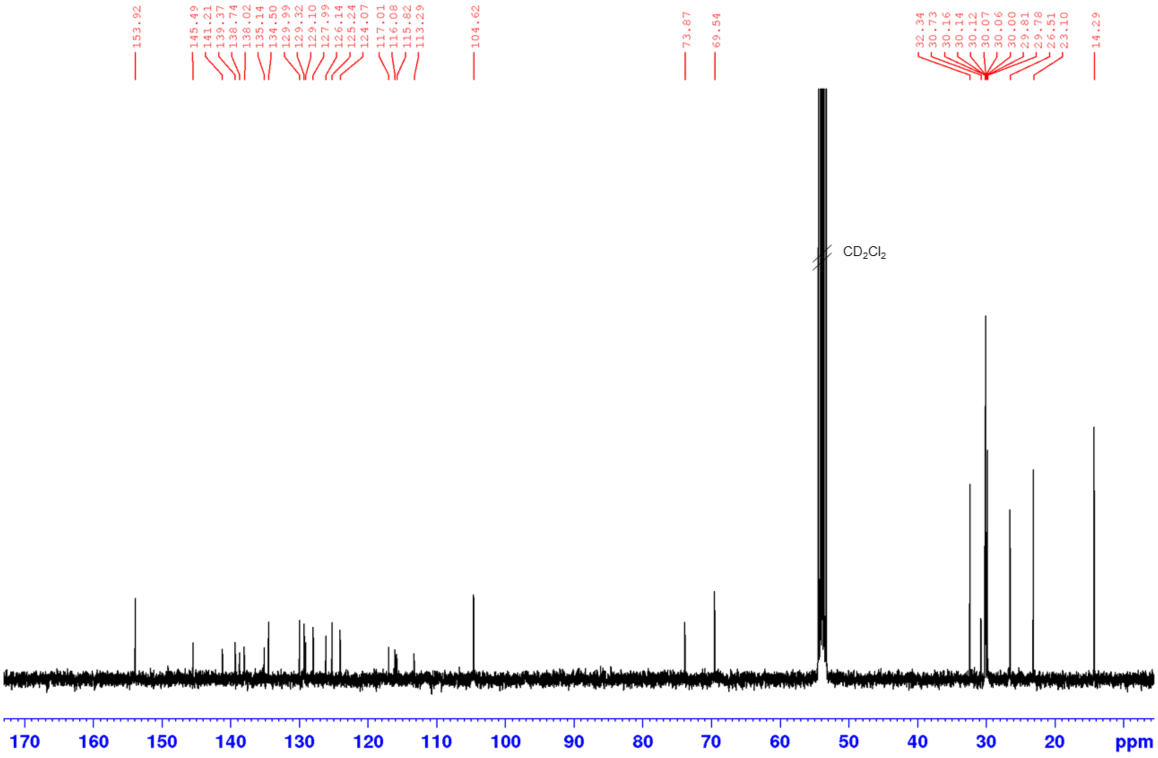
^{13}C NMR (100 MHz) spectrum of **8b** in $CDCl_3$



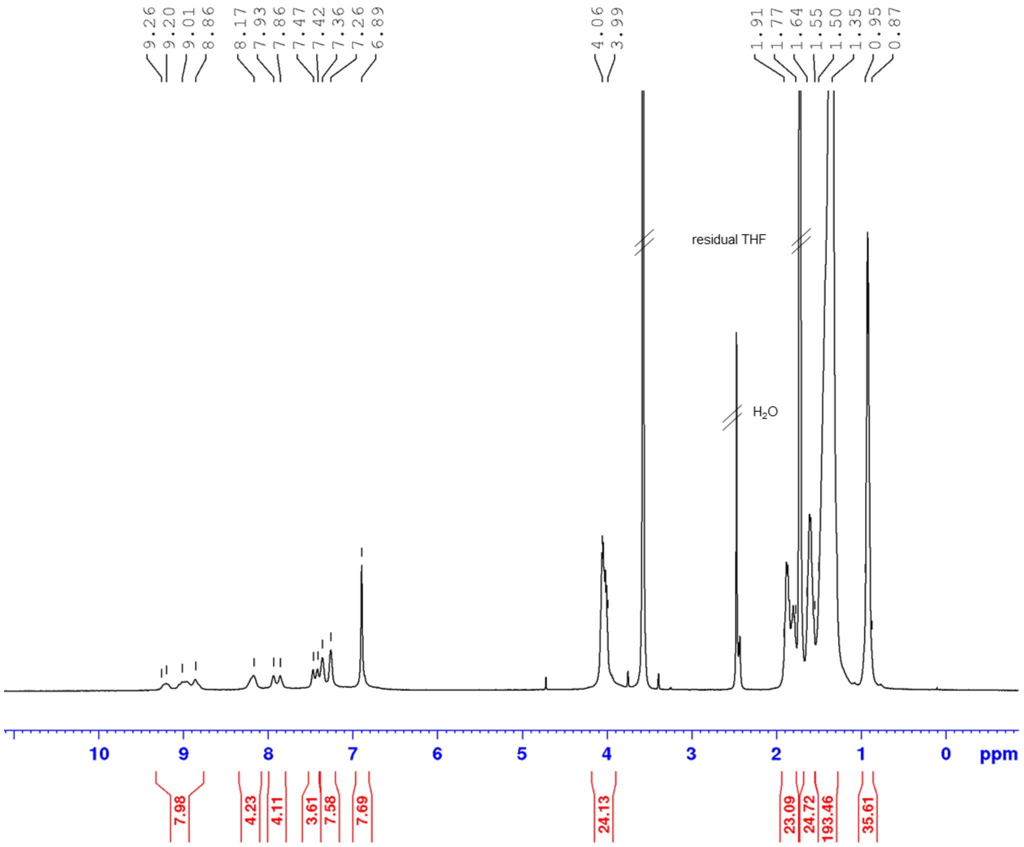
^{1}H NMR (400 MHz) spectrum of **10b** in CD_2Cl_2



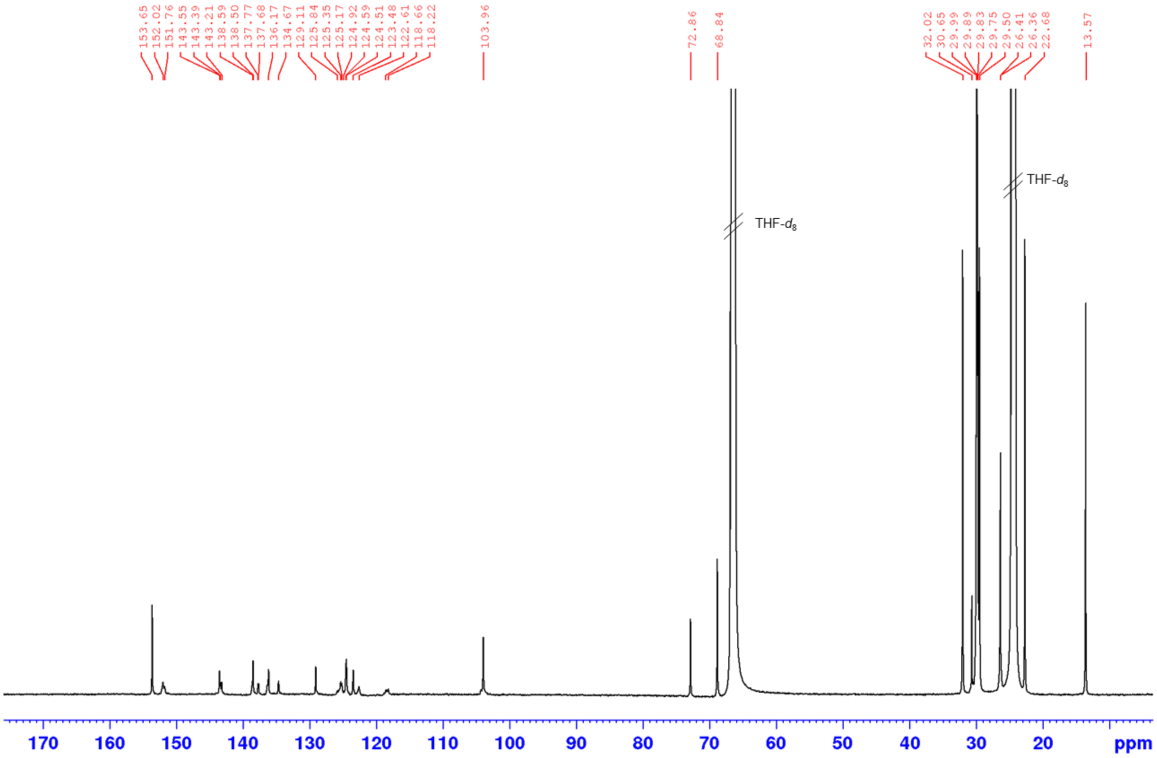
^{13}C NMR (100 MHz) spectrum of **10b** in CD_2Cl_2



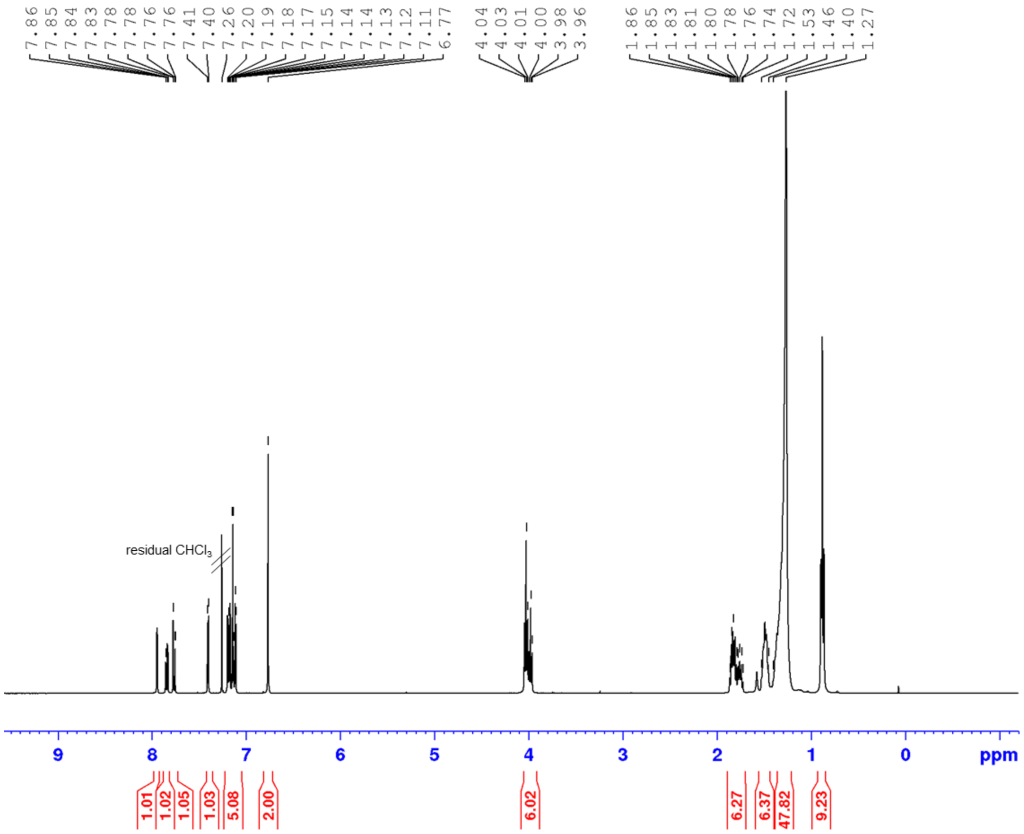
^{1}H NMR (400 MHz) spectrum of **3** in THF-d_8



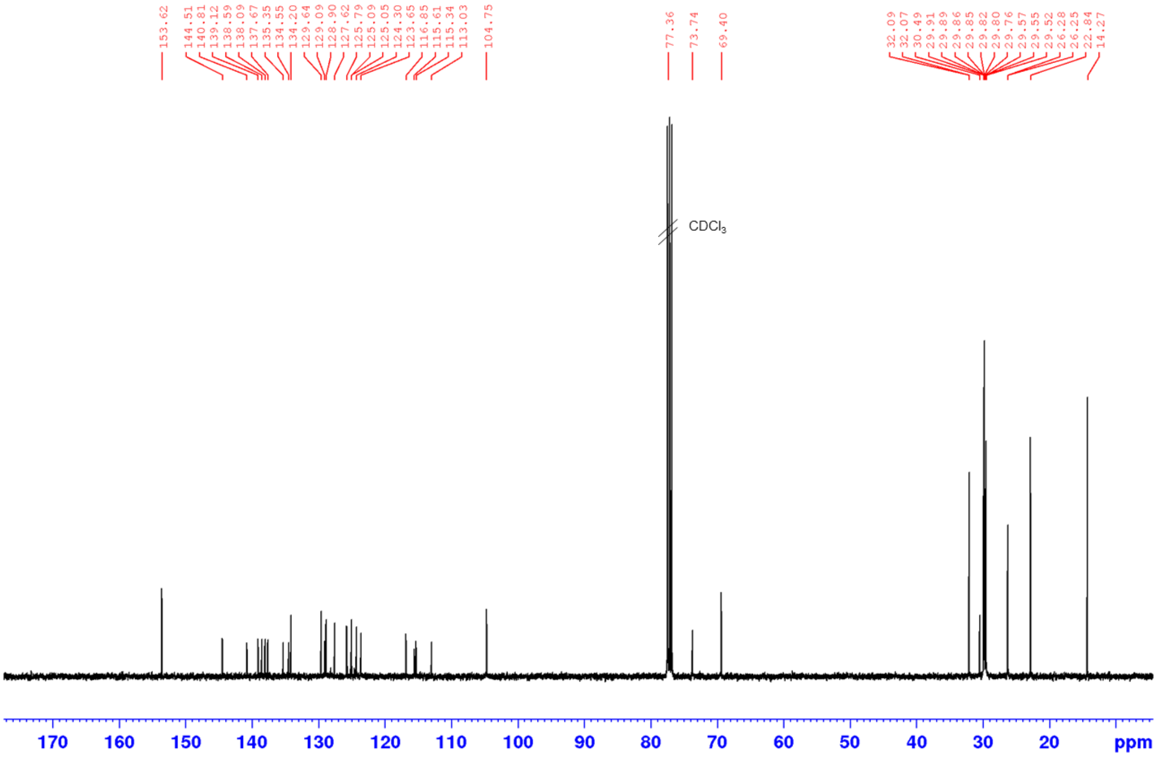
^{13}C NMR (151 MHz) spectrum of **3** in THF-d_8



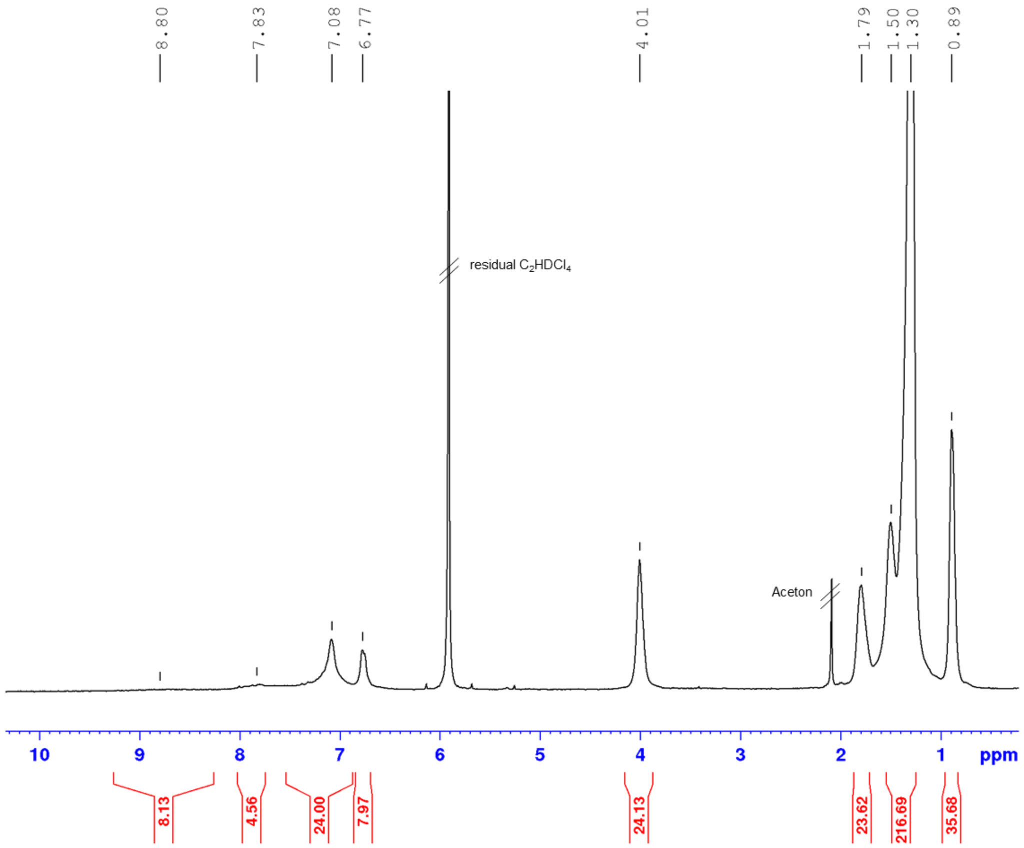
^{1}H NMR (400 MHz) spectrum of **10c** in $CDCl_3$



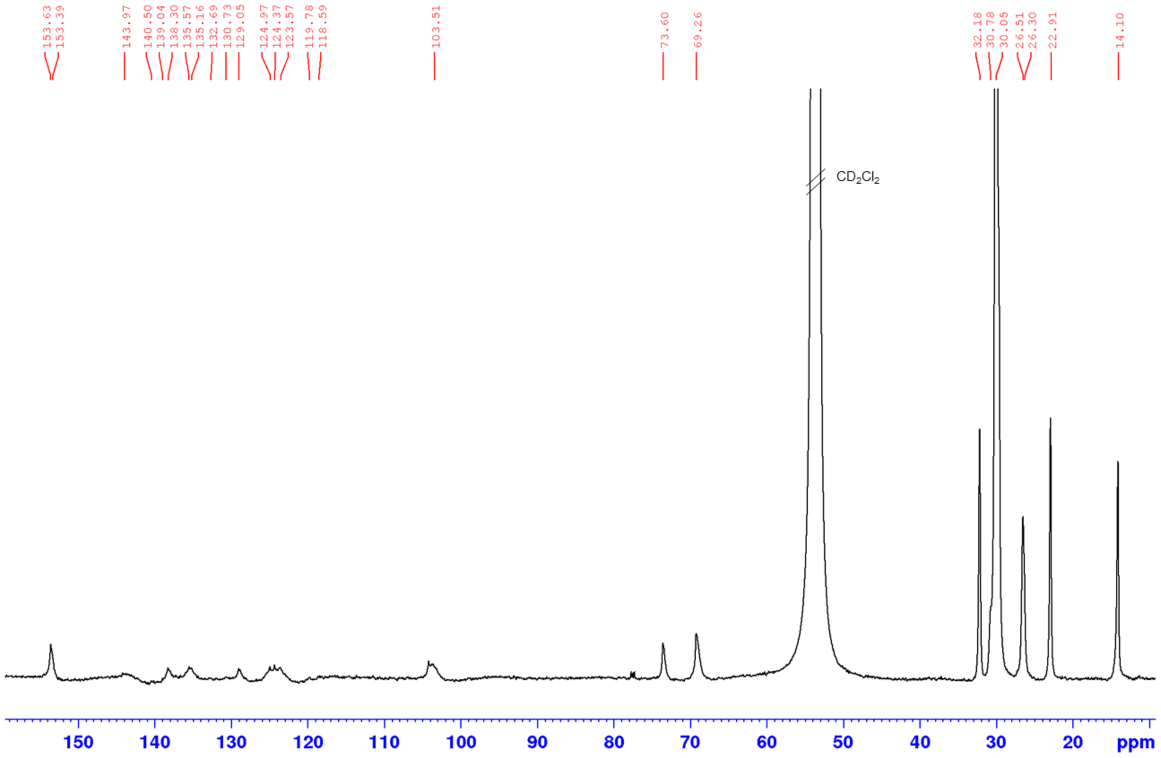
^{13}C NMR (100 MHz) spectrum of **10c** in $CDCl_3$



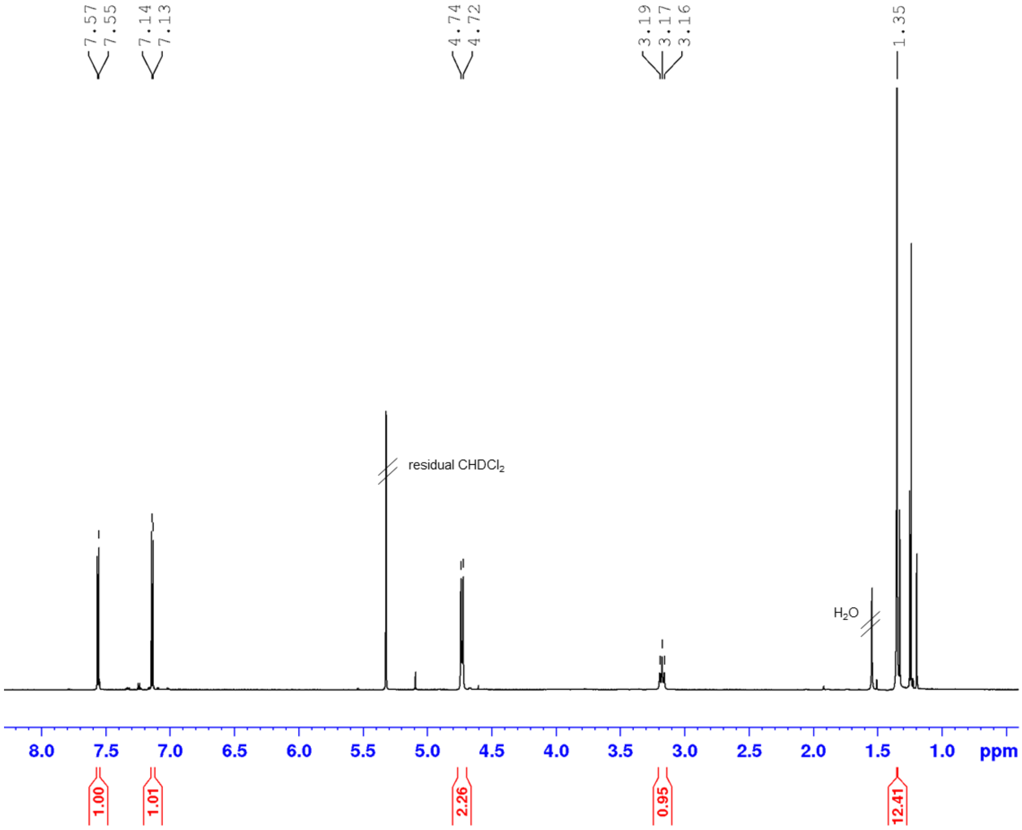
^{1}H NMR (400 MHz, 373 K) spectrum of **4** in $C_2D_2Cl_4$



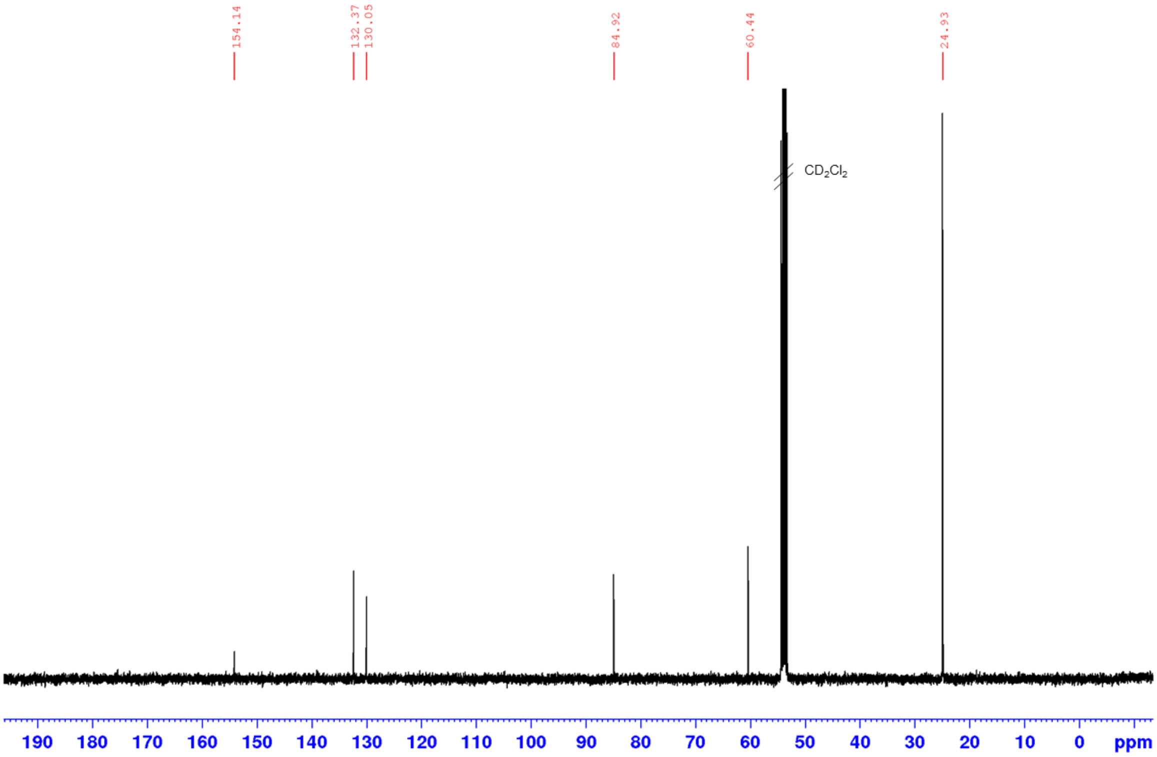
^{13}C NMR (151 MHz) spectrum of **4** in CD_2Cl_2



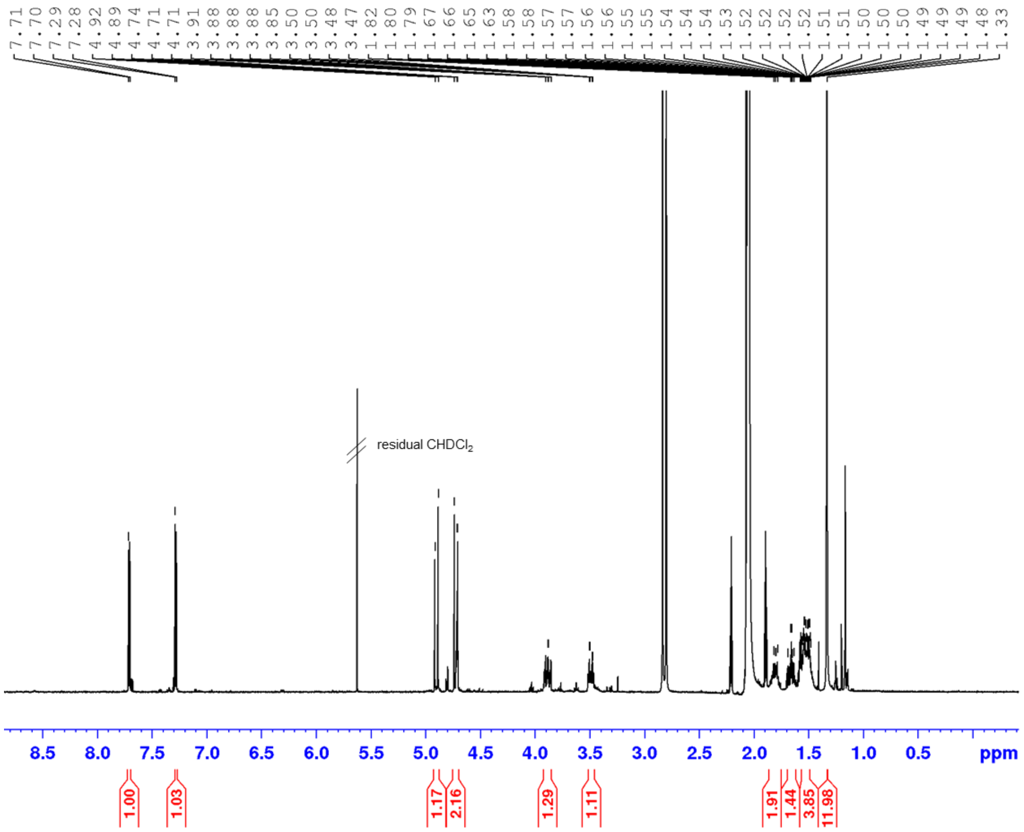
^{1}H NMR (400 MHz) spectrum of **14** in CD_2Cl_2



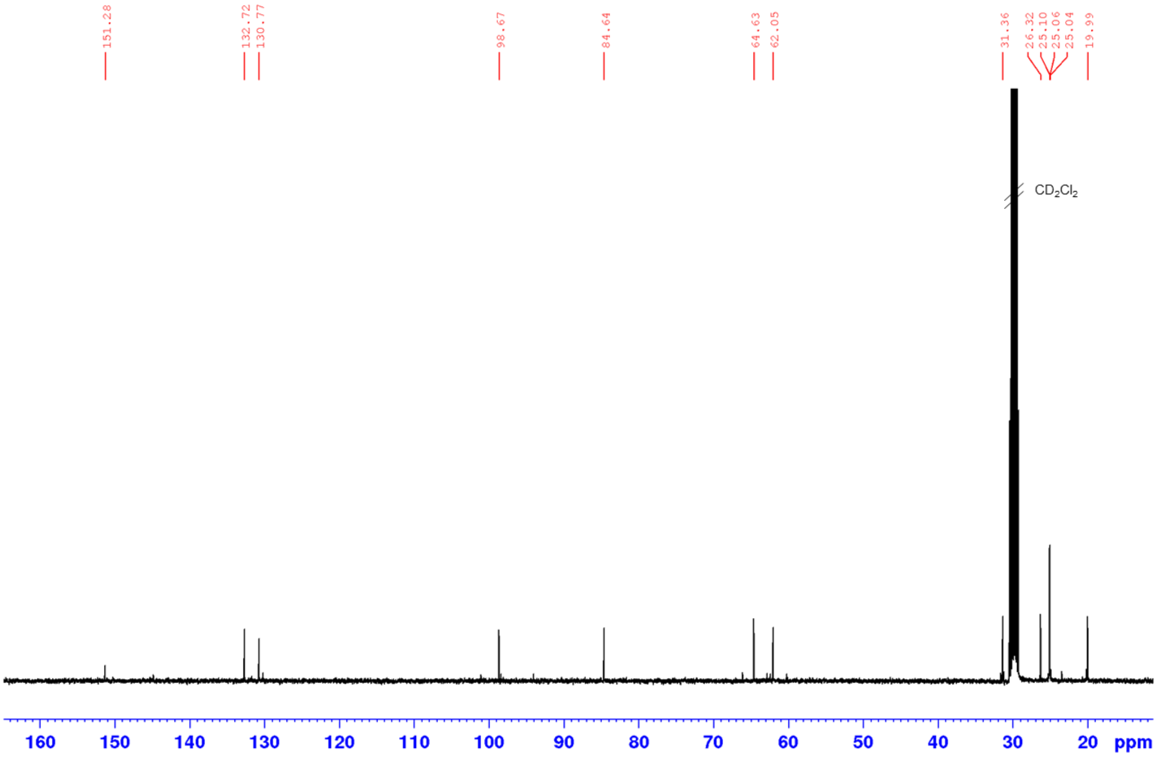
^{13}C NMR (100 MHz) spectrum of **14** in CD_2Cl_2



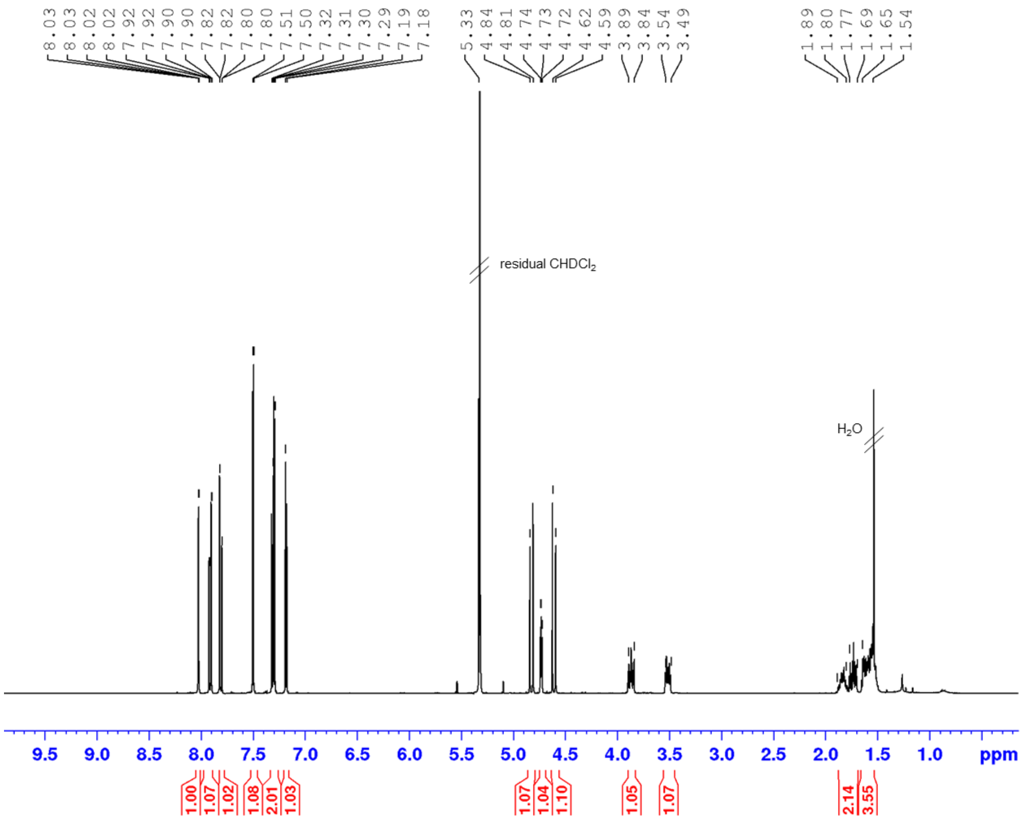
^{1}H NMR (400 MHz) spectrum of **15** in CD_2Cl_2



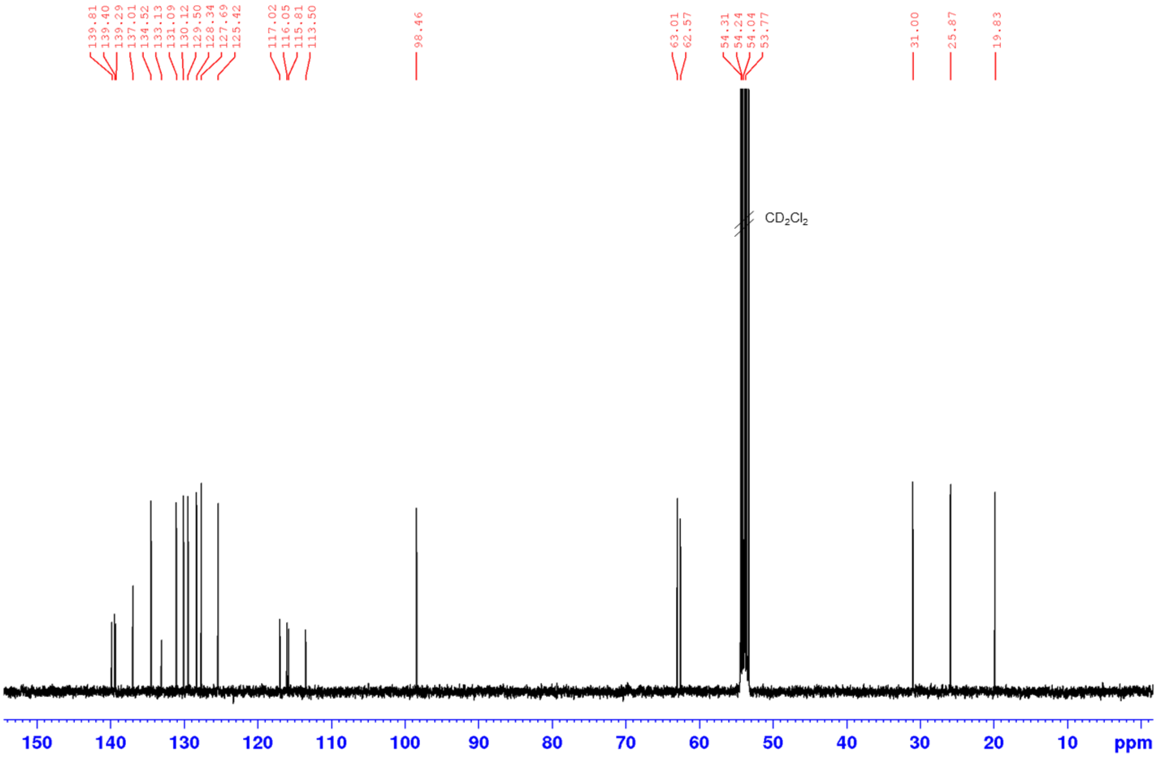
^{13}C NMR (100 MHz) spectrum of **15** in CD_2Cl_2



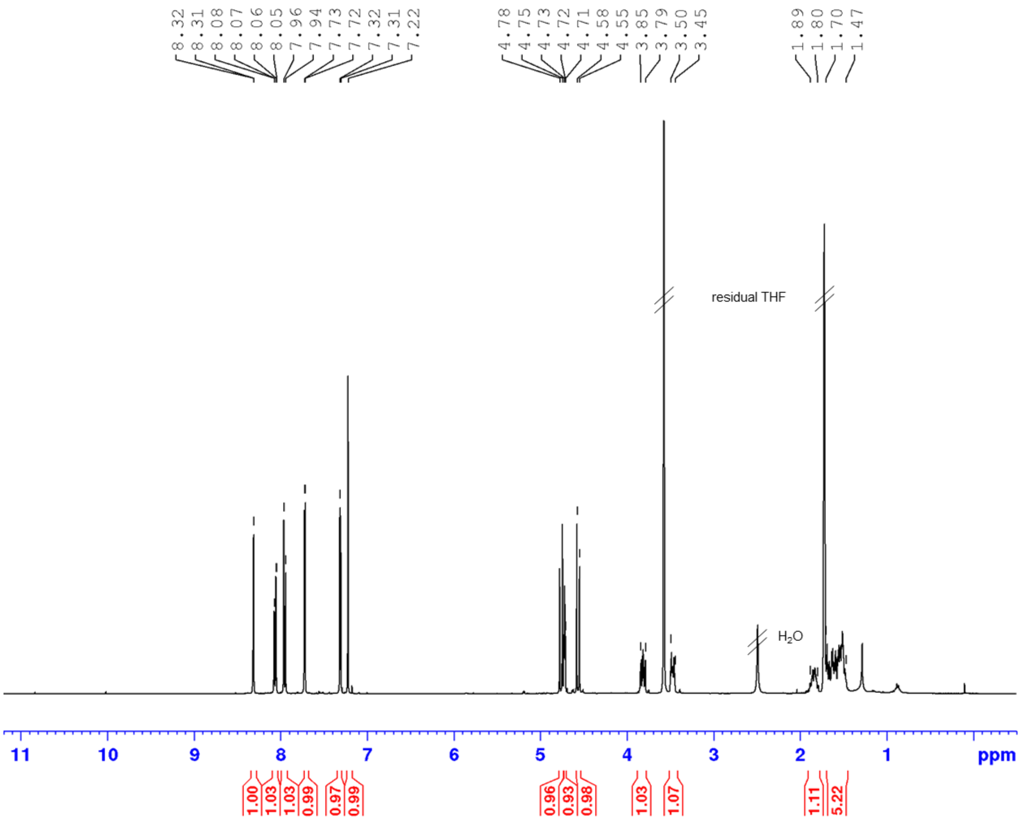
^{1}H NMR (400 MHz) spectrum of **16** in CD_2Cl_2



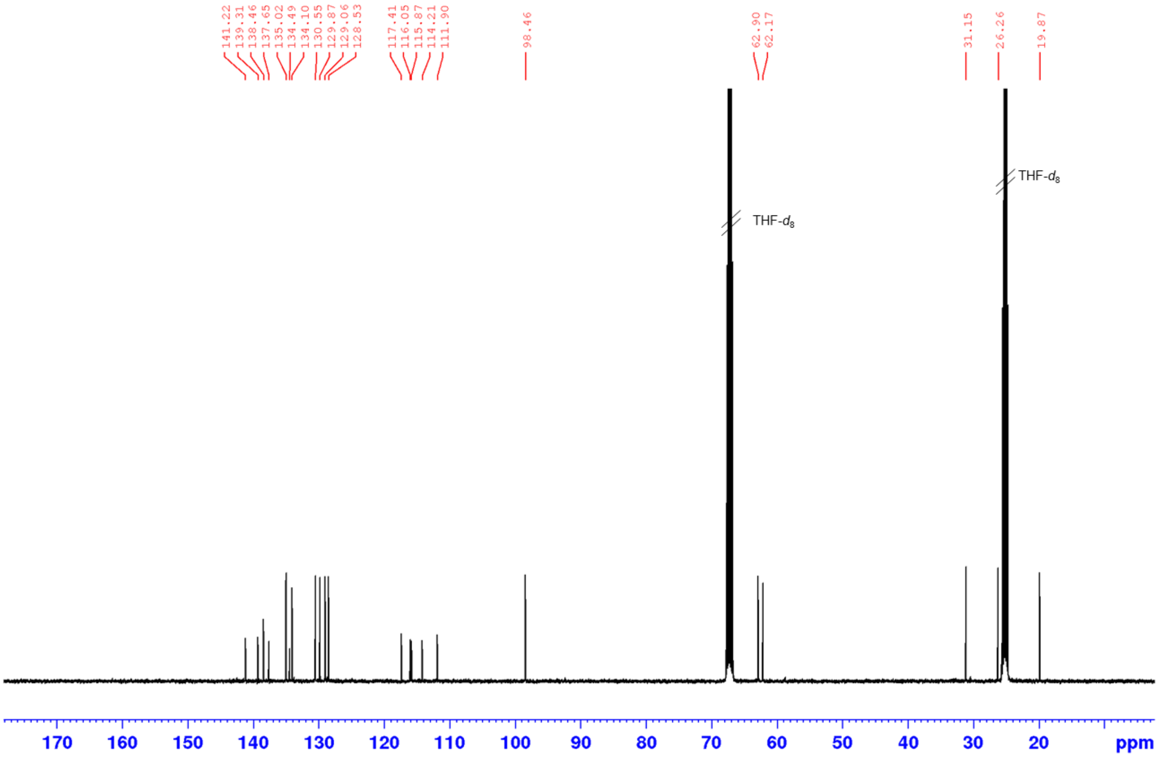
^{13}C NMR (100 MHz) spectrum of **16** in CD_2Cl_2



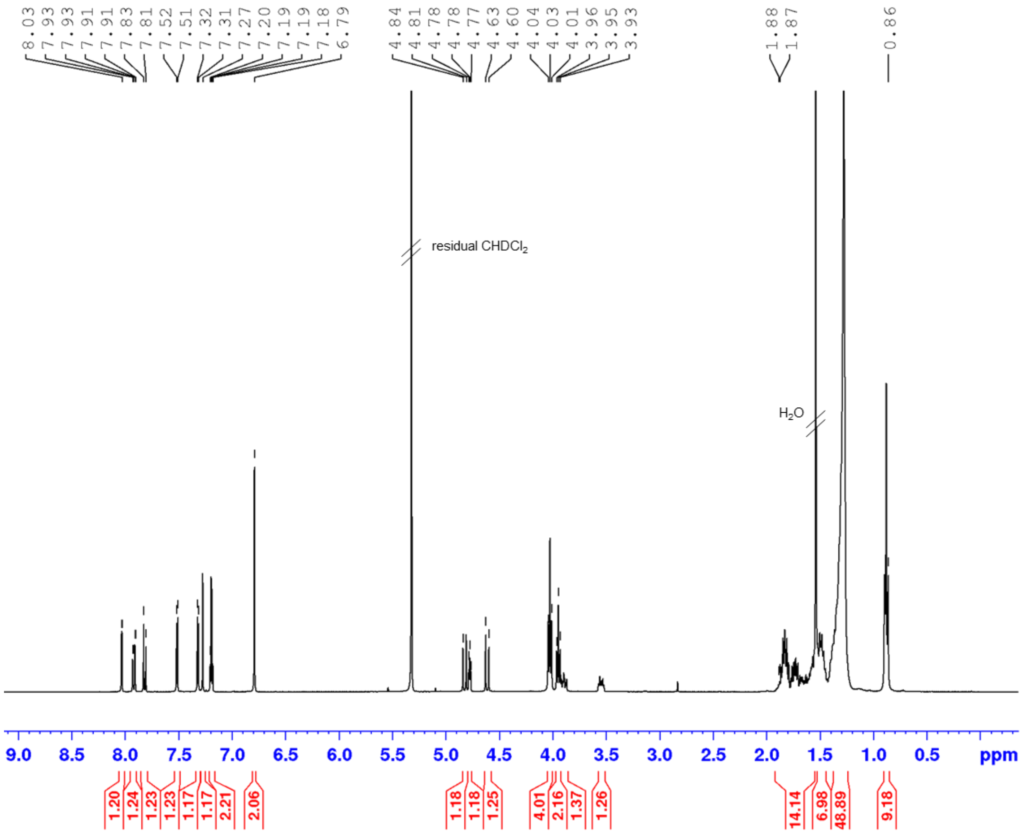
^{1}H NMR (400 MHz) spectrum of **17** in THF-d_8



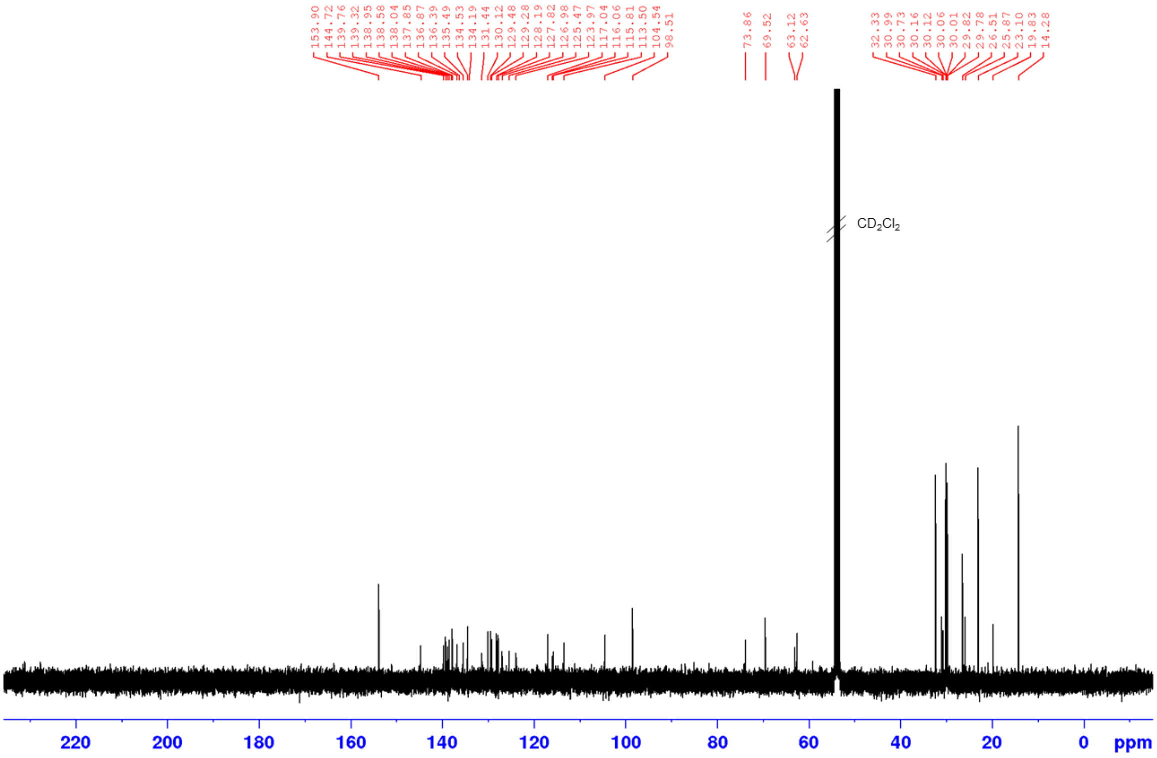
^{13}C NMR (100 MHz) spectrum of **17** in THF-d_8



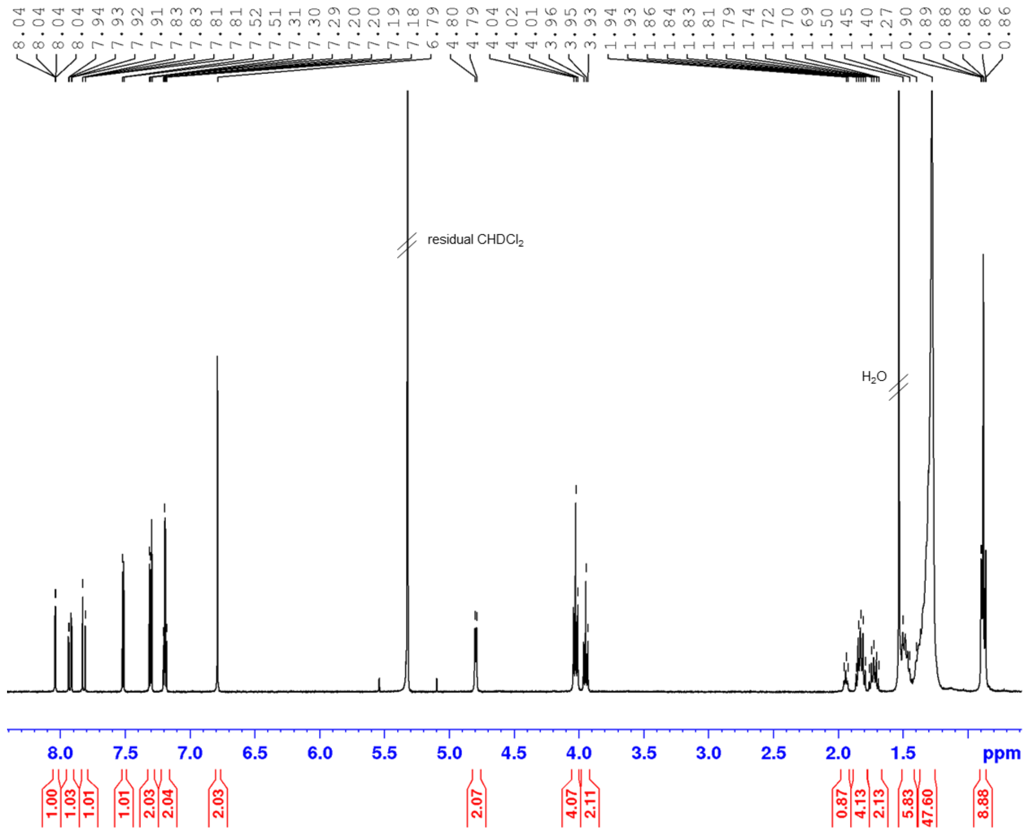
^{1}H NMR (400 MHz) spectrum of **18** in CD_2Cl_2



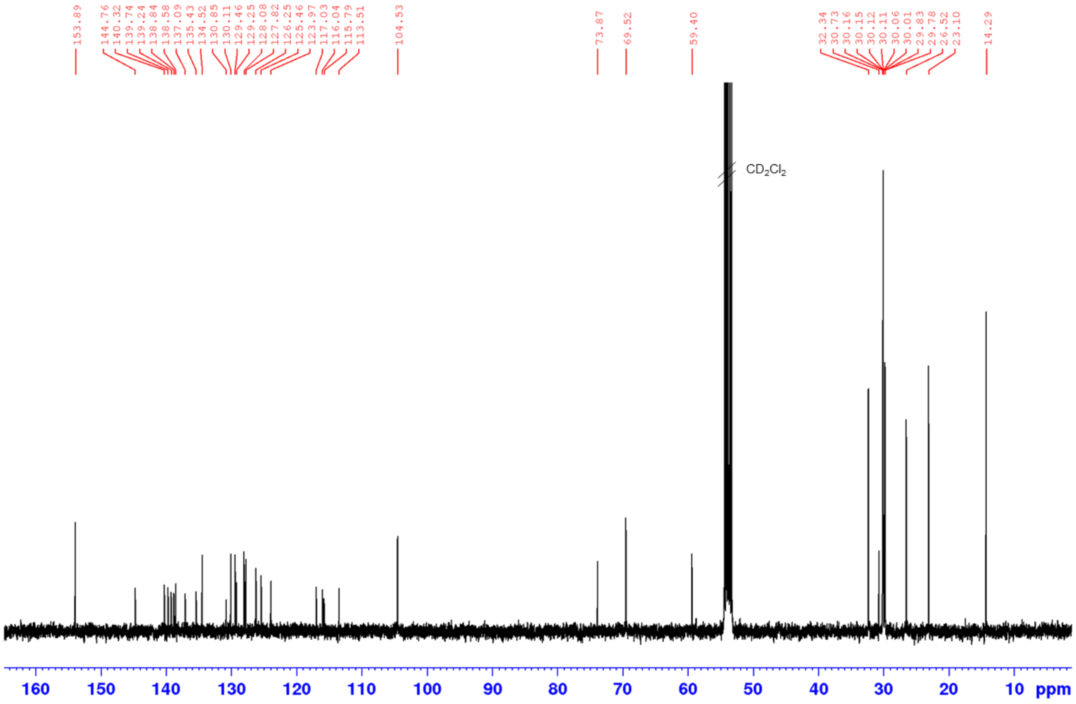
^{13}C NMR (100 MHz) spectrum of **18** in CD_2Cl_2



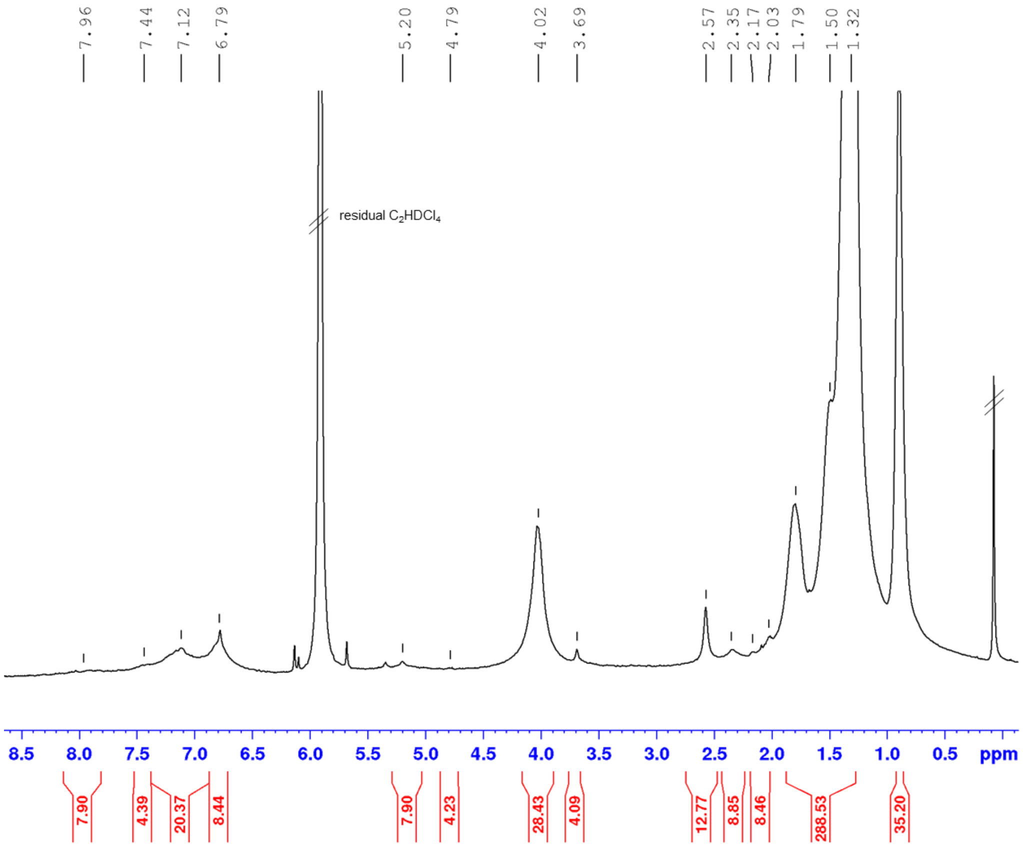
^1H NMR (400 MHz) spectrum of **19** in CD_2Cl_2



^{13}C NMR (100 MHz) spectrum of **19** in CD_2Cl_2



^{1}H NMR (400 MHz, 398 K) spectrum of **5** in $C_2D_2Cl_4$



^{13}C NMR (151 MHz) spectrum of **5** in THF-d_8