Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# Supporting Information

## Condensation of Pyrylium Salts with Mixed Anhydrides: Arylethers, Arylamines and Sterically Congested Aromatics

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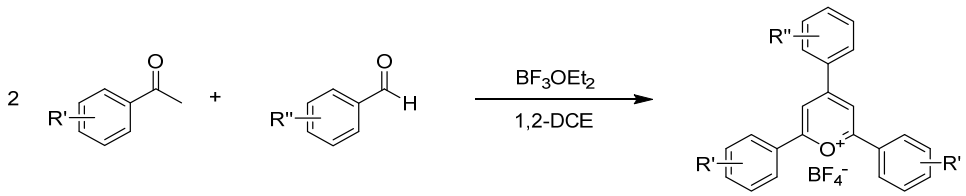
# 1. General Information

Commercially available chemicals were used without further purification. All air-sensitive reactions were carried out using standard Schlenk techniques under argon. All used solvents were either dried or purified inside a *M-Braun* MB-SPS-800 solvent purification system and used after degasification. All workup and chromatography solvents were either used in "p.a." quality or purified by distillation (dichloromethane, cyclohexane, ethylacetate). $^{1}H$ and $^{13}C$-NMR spectra were recorded on a *Bruker* Avance I 400 MHz, *Bruker* Avance I 500 MHz, *Bruker* Avance III HD 500 MHz Prodigy or a Bruker Avance III HD 700 MHz Cryo (400, 500 and 700 MHz for $^{1}H$ and 76, 126 and 176 MHz for $^{13}C$). Chemical shifts are given in parts per million (ppm) and calibrated by using the residual of the used deuterated solvent as internal reference [$^{1}H$-NMR/$^{13}C$-NMR: Acetone (2.05 ppm/29.84 ppm), $CDCl_3$ (7.26 ppm/77.16 ppm) $CD_2Cl_2$ (5.32 ppm/54.00 ppm), DMSO (2.50 ppm/39.52 ppm), THF (1.73 ppm/25.37 ppm)]. All NMR spectra were recorded at r.t. unless otherwise described. Mass spectra were measured on a *Thermo Finnigan* MAT 95 XL (EI-MS), a *Bruker* Daltonik micrOTOF-Q (ESI-MS), and a *Bruker* Daltonik ultrafleXtreme TOF/TOF (MALDI-MS; matrix material: DCTB, no salt added). m/z peaks smaller than 10 % (compared to basis peak) are not reported. Thin layer chromatography was conducted on silica gel coated aluminium plates (*Macherey-Nagel*, Alugram SIL G/UV 254, 0.25 mm coating with fluorescence indicator). Silica gel Kieselgel 60 (*Merck*, 0.040-0.063 mm) was used as the sationary phase for column chromatography. $R_f$ values were measured on silica plates using UV light as visualizing agent. Analytical gel permeation chromatography (GPC) was performed in THF at 35 °C on an *Agilent Technologies* system at a flow rate of 1 ml/min using an IsoPump G1310A, ALS G1329A autosampler, PSS columns (set of 4 columns 8 mm x 300 mm, polystyrene, porosity $10^2$, $10^3$, $10^5$ and $10^6$ Å, with precolumn, *Polymer Standards Service GmbH*), a VWD G1314B and a RID G1362A detector. Calibration was done with polystyrene standards by *Polymer Standard Service GmbH*. Recycling gel permeation chromatography (recGPC) was performed in THF at 35 °C on a *Shimadzu* system at a flow rate of 5 ml/min using a LC-20 AD pump, DGU-20 A3 degasser, SIL-20 A HAT autosampler, CTO-20 A oven, FRC-10 A fraction collector, FCV-20 AH2 switching valve, *PSS* columns (set of 3 columns 20 mm x 300 mm, polystyrene, preparative *PSS* SDV linear S with precolumn 20 mm x 50 mm, preparative *PSS* SDV) and a SPD-20A UV-detector ($\lambda_1$ = 254 nm and $\lambda_2$ = 366 nm). UV/Vis spectra were recorded on a *Perkin Elmer* Lambda 18 spectrometer, fluorescence spectra were measured on a *Perkin Elmer* LS-50 B luminescence spectrometer. For both methods 10 mm quartz cuvettes by *Hellma Analytics* were used.

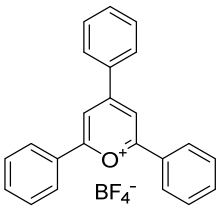
# 2. Synthesis of pyrylium salts

## 2.1 General procedure




Substituted pyrylium salts **1a – 1f** were synthesized by boron trifluoride-etherate mediated condensation between an acetophenone and benzaldehyde derivative.[1] Correspondingly substituted benzaldehyde (1.0 eq) and acetophenone (2.0 eq) were dissolved in 1,2-dichloroethane (approx. 1.5 ml/mmol benzaldehyde). $BF_3 \cdot OEt_2$ (5.0 eq) was dropped into the mixture at room temperature and it was refluxed for 3 h. After cooling to room temperature, the mixture was dropped into diethyl ether, resulting in precipitation of the product. The crude product was filtered of, recrystallized from acetone and dried in vacuum to obtain the pyrylium salt as a colored solid.

## 2.2 Pyrylium salts 1a – 1f




**1a**
Chemical Formula: $C_{23}H_{17}BF_4O$
Molecular Weight: 396,19

**1a) Yield** = 40 % (as a yellow solid) **$^1$H-NMR** (500 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 9.17 (s, 2H), 8.61 (d, $^3J_{HH}$ = 8.0 Hz, 6H), 7.88 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 7.83 - 7.77 (m, 6H). **$^{13}$C-NMR** (126 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 170.0, 165.1, 135.2, 135.0, 132.5, 130.0, 129.9, 129.8, 129.1, 128.8, 115.2. **MS (ESI+)**: *m/z* calculated for $C_{23}H_{17}O^+$: 309.1274 u, found: 309.128 u.

Analytical data in accordance with the literature.[2]

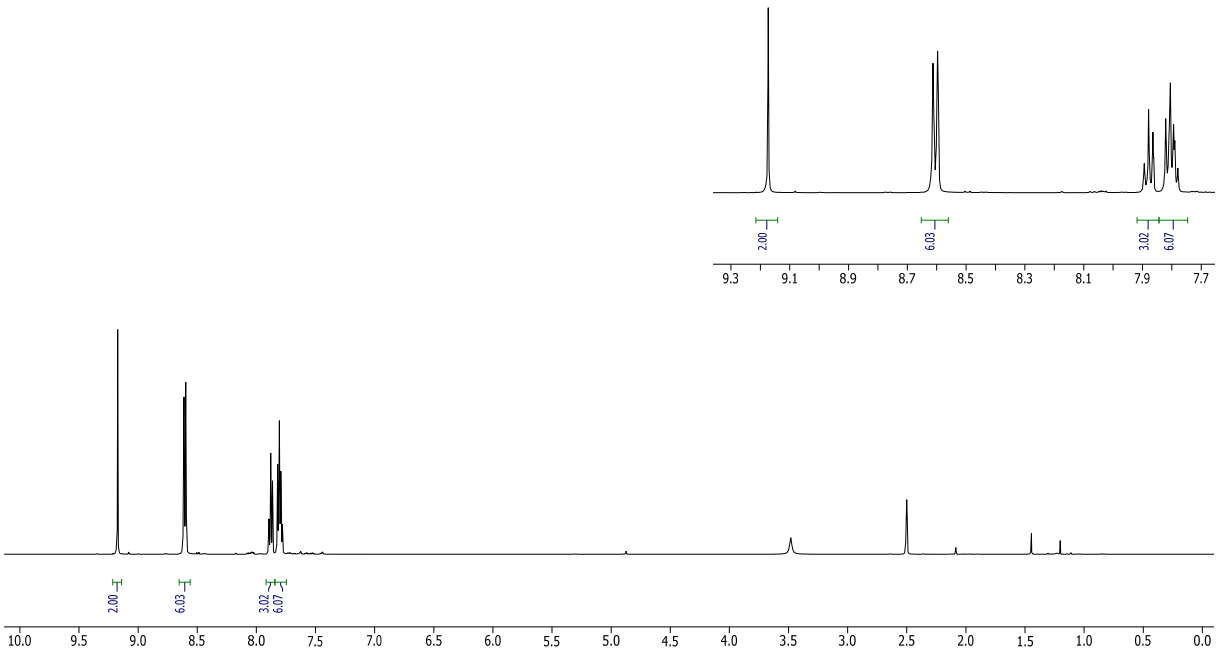



**Figure S1.** $^{1}$H-NMR spectrum of **1a** (500 MHz, DMSO-$d_6$, r.t.).

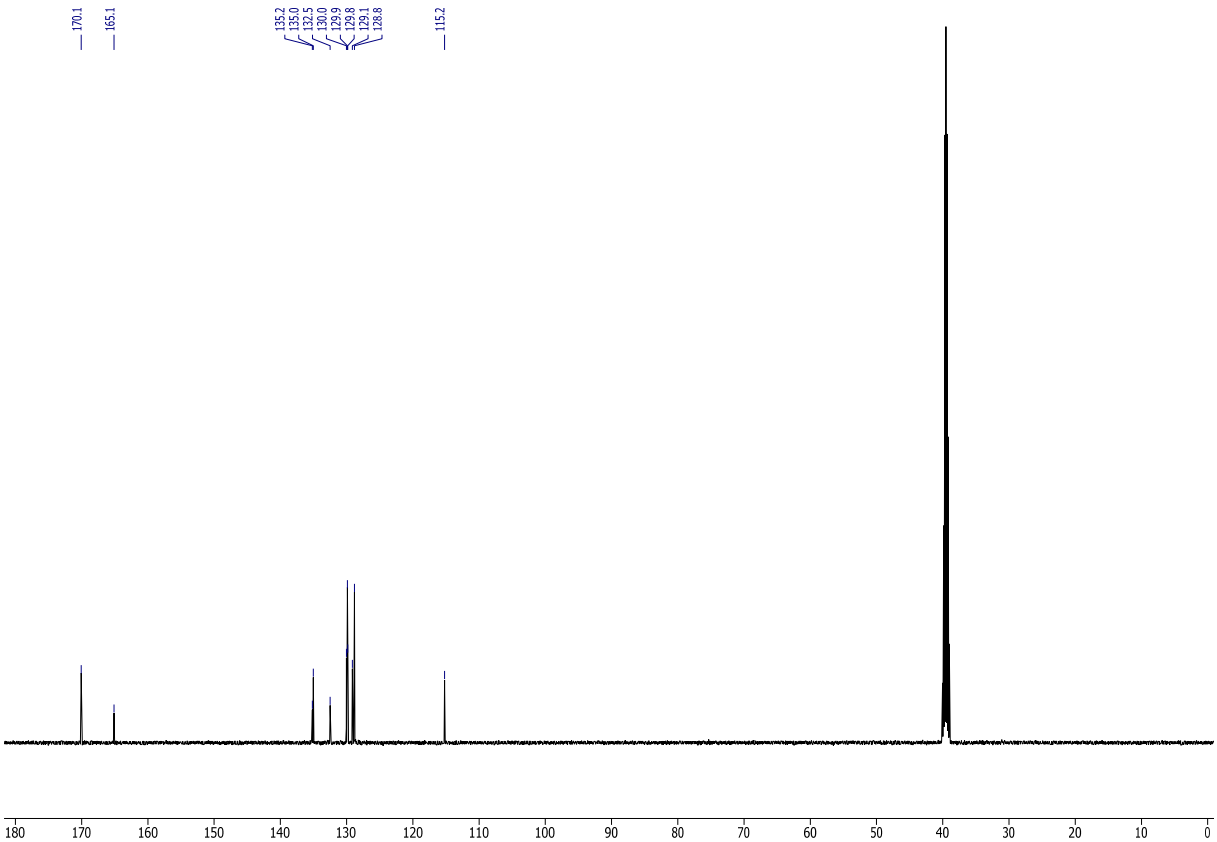
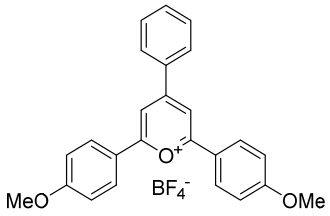



**Figure S2.** $^{13}$C-NMR spectrum of **1a** (126 MHz, DMSO-$d_6$, r.t.).




**1b**
Chemical Formula: $C_{25}H_{21}BF_4O_3$
Molecular Weight: 456,24

**1b) Yield** = 32 % (as a red solid) **$^1$H-NMR** (500 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 8.88 (s, 2H), 8.53 (d, $^3J_{HH}$ = 9.0 Hz, 4H), 8.50 (d, $^3J_{HH}$ = 7.6 Hz, 2H), 7.83 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.75 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.3 Hz, 2H) 7.30 (d, $^3J_{HH}$ = 9.0 Hz, 4H) 3.96 (s, 6H). **$^{13}$C-NMR** (126 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 168.9, 164.8, 163.2, 134.5, 132.8, 131.0, 129.7, 129.6, 121.4, 115.5, 112.7, 56.1. **MS (ESI+)**: *m/z* calculated for $C_{25}H_{21}O_3^+$: 369.1485 u, found: 369.148 u.

Analytical data in accordance with the literature.[3]

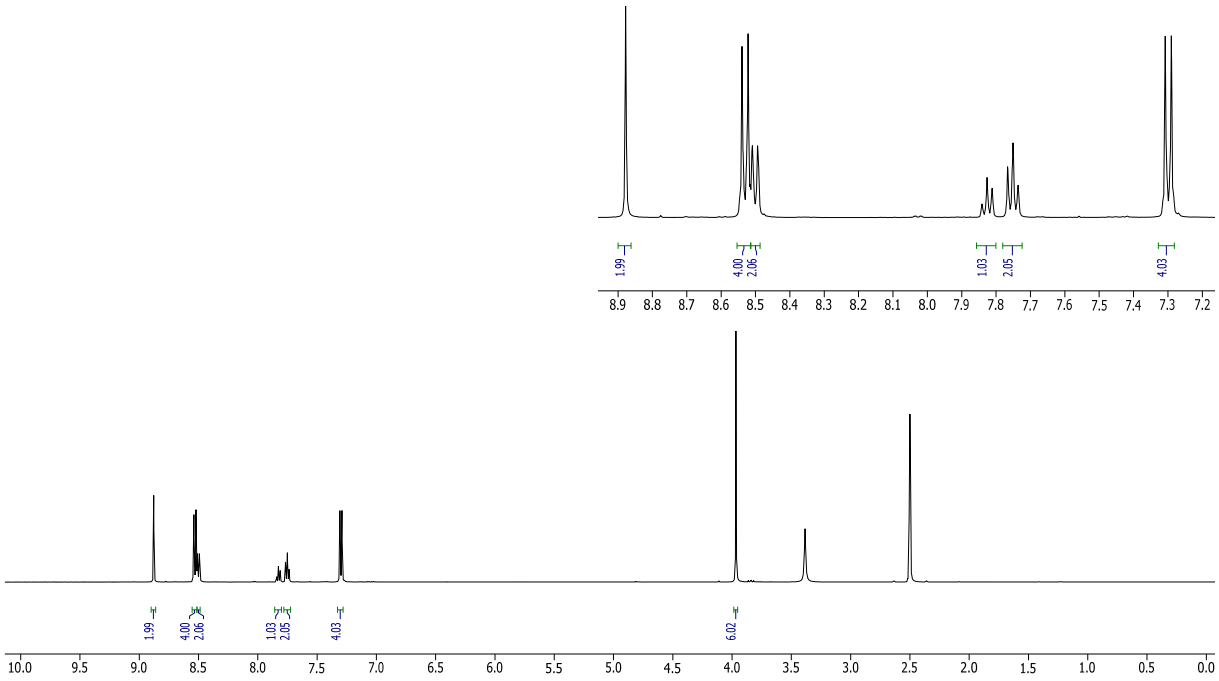



**Figure S3.** $^1$H-NMR spectrum of **1b** (500 MHz, DMSO-$d_6$, r.t.).

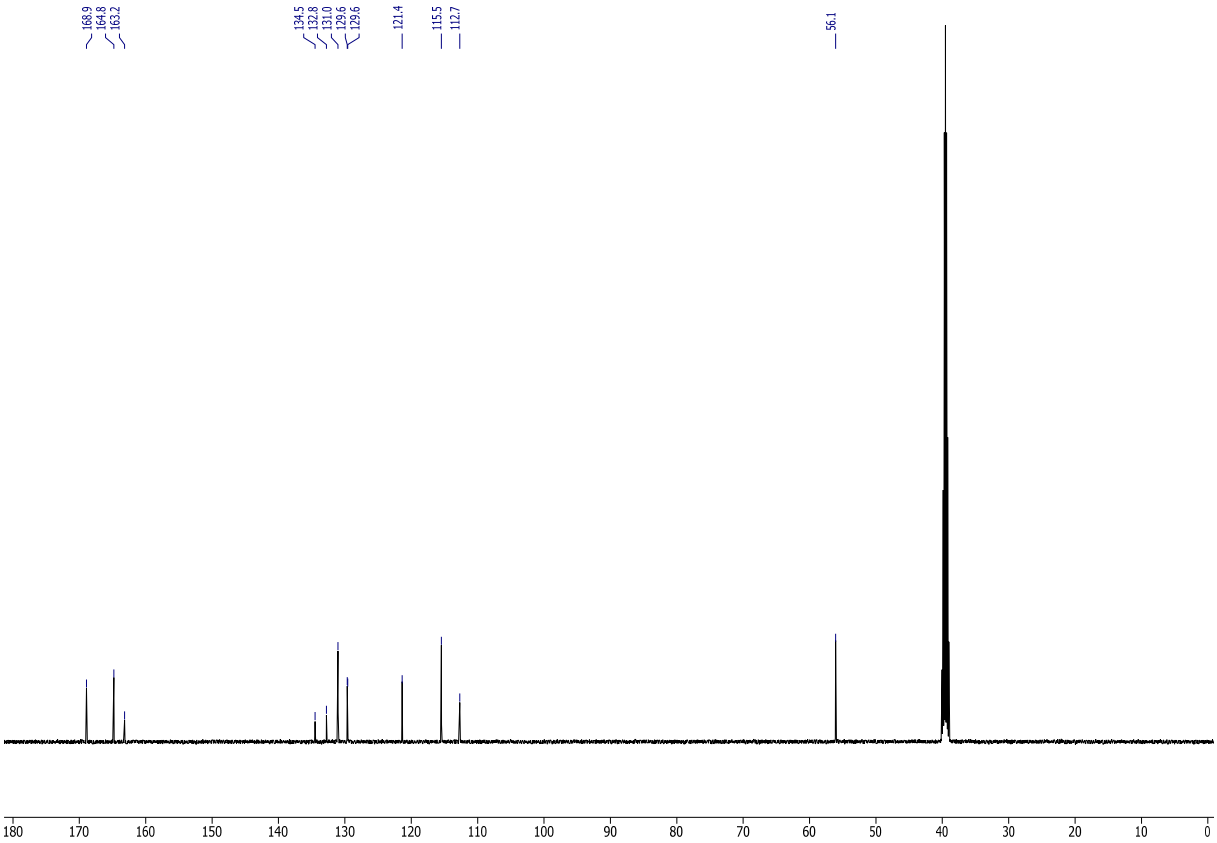
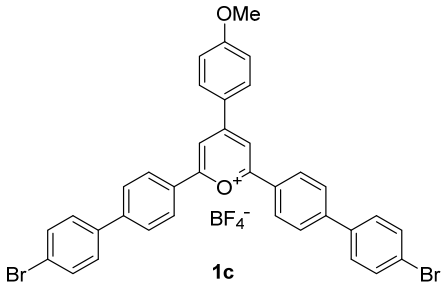



**Figure S4.** $^{13}$C-NMR spectrum of **1b** (126 MHz, DMSO-$d_6$, r.t.).




**1c**

Chemical Formula: $C_{36}H_{25}BBr_2F_4O_2$

Molecular Weight: 736,21

**1c) Yield** = 28 % (as a red solid) **$^1$H-NMR** (500 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 9.09 (s, 2H), 8.73 (d, $^3J_{HH}$ = 9.1 Hz, 2H), 8.64 (d, $^3J_{HH}$ = 8.7 Hz, 4H), 8.10 (d, $^3J_{HH}$ = 8.7 Hz, 4H), 7.86 (d, $^3J_{HH}$ = 8.6 Hz, 4H), 7.77 (d, $^3J_{HH}$ = 8.6 Hz, 4H), 7.33 (d, $^3J_{HH}$ = 9.1 Hz, 2H), 4.01 (s, 2H). **$^{13}$C-NMR** (126 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 168.2, 165.9, 163.1, 144.4, 137.3, 133.1, 132.1, 129.2, 129.2, 128.4, 127.7, 124.4, 122.7, 115.6, 113.2, 56.3. **MS (ESI+)**: *m/z* calculated for $C_{36}H_{25}Br_2O_2^+$: 647.0216 u, found: 647.017 u.

Analytical data in accordance with the literature.[4]

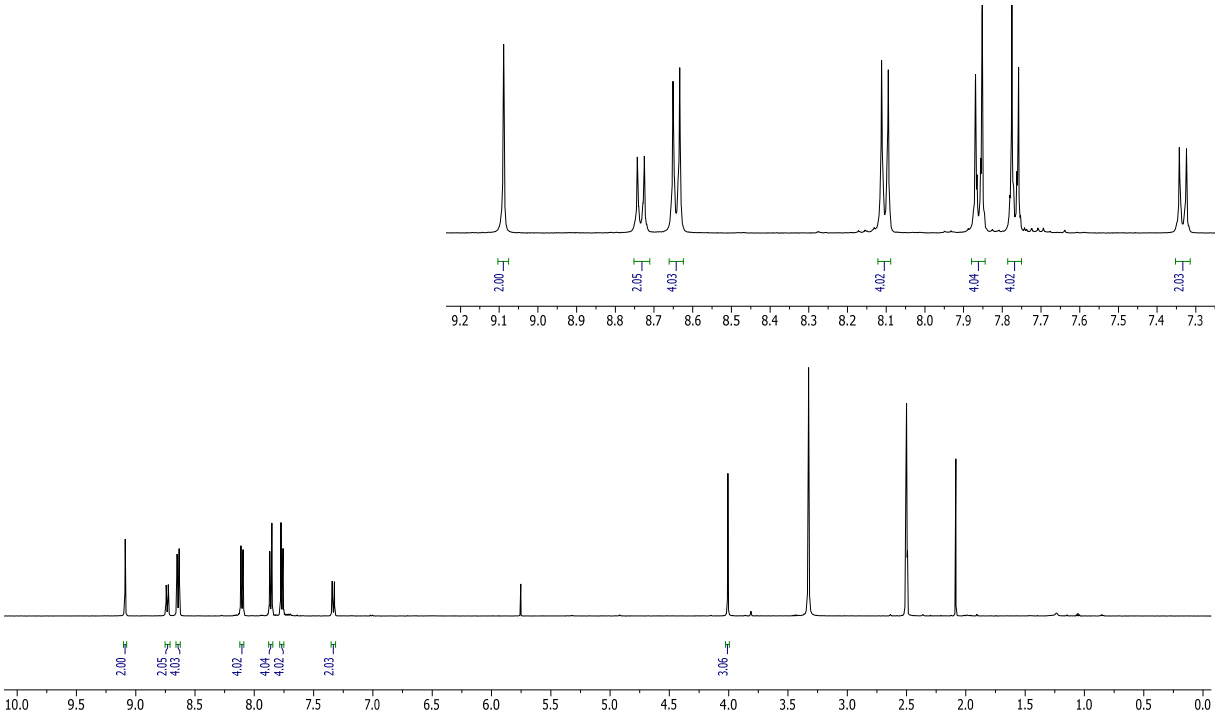



**Figure S5.** $^{1}$H-NMR spectrum of **1c** (500 MHz, DMSO-$d_6$, r.t.).

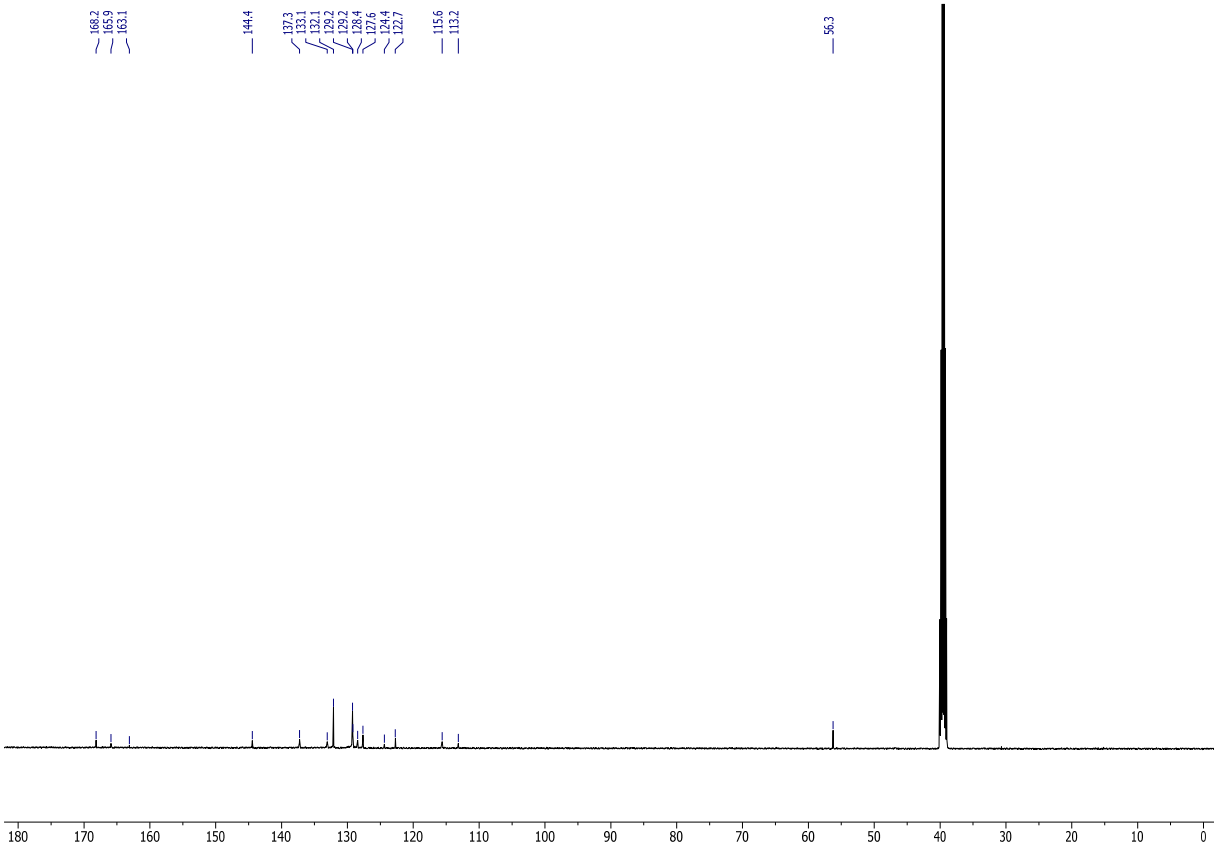
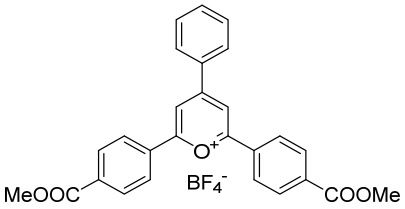



**Figure S6.** $^{13}$C-NMR spectrum of **1c** (126 MHz, DMSO-$d_6$, r.t.).




**1d**

Chemical Formula: $C_{27}H_{21}BF_4O_5$
Molecular Weight: 512,26

**1d) Yield** = 38 % (as a yellow solid) **$^1$H-NMR** (500 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 9.34 (s, 2H), 8.74 (d, $^3J_{HH}$ = 8.6 Hz, 4H) 8.65 (d, $^3J_{HH}$ = 7.6 Hz, 2H), 8.30 (d, $^3J_{HH}$ = 8.6 Hz, 4H), 7.91 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.82 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.4 Hz, 2H), 3.96 (s, 6H). **$^{13}$C-NMR** (126 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 169.2, 165.9, 165.2, 135.7, 134.6, 132.9, 132.2, 130.4, 130.1, 129.9, 129.3, 116.9, 52.8. **MS (ESI+)**: *m/z* calculated for $C_{27}H_{21}O_5^+$: 425.1384 u, found: 425.138 u.

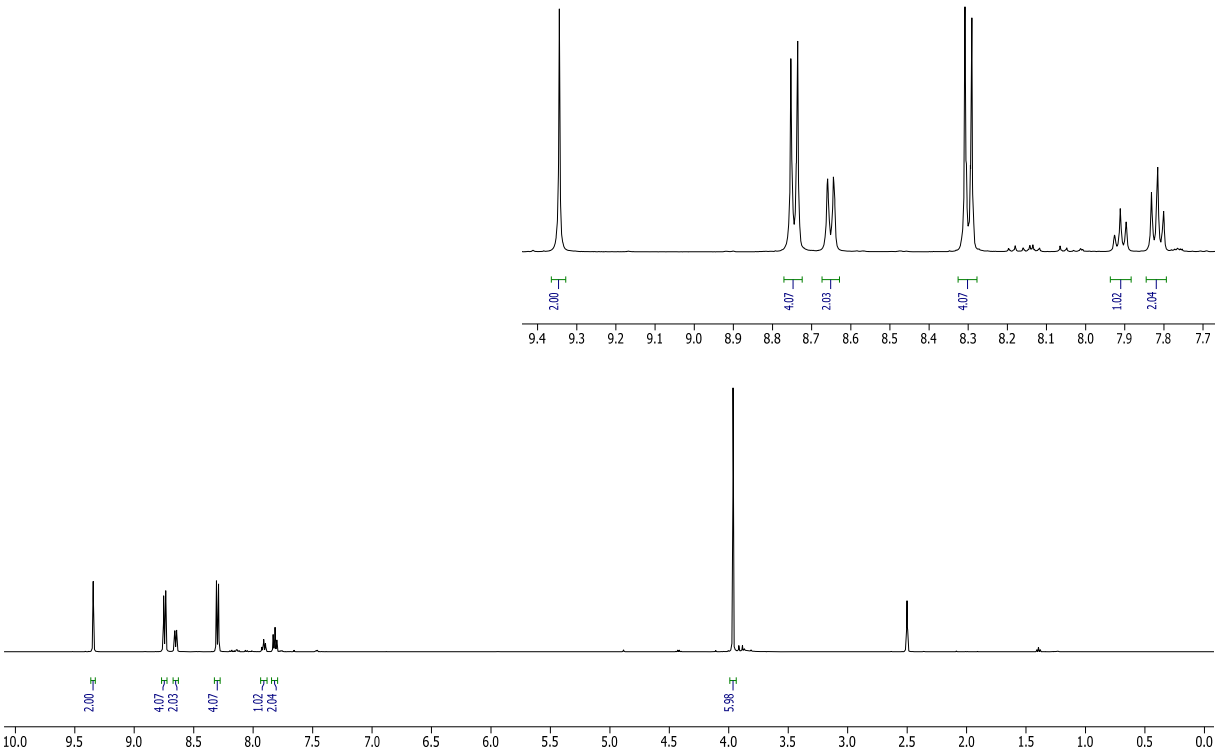



**Figure S7.** $^1$H-NMR spectrum of **1d** (500 MHz, DMSO-$d_6$, r.t.).

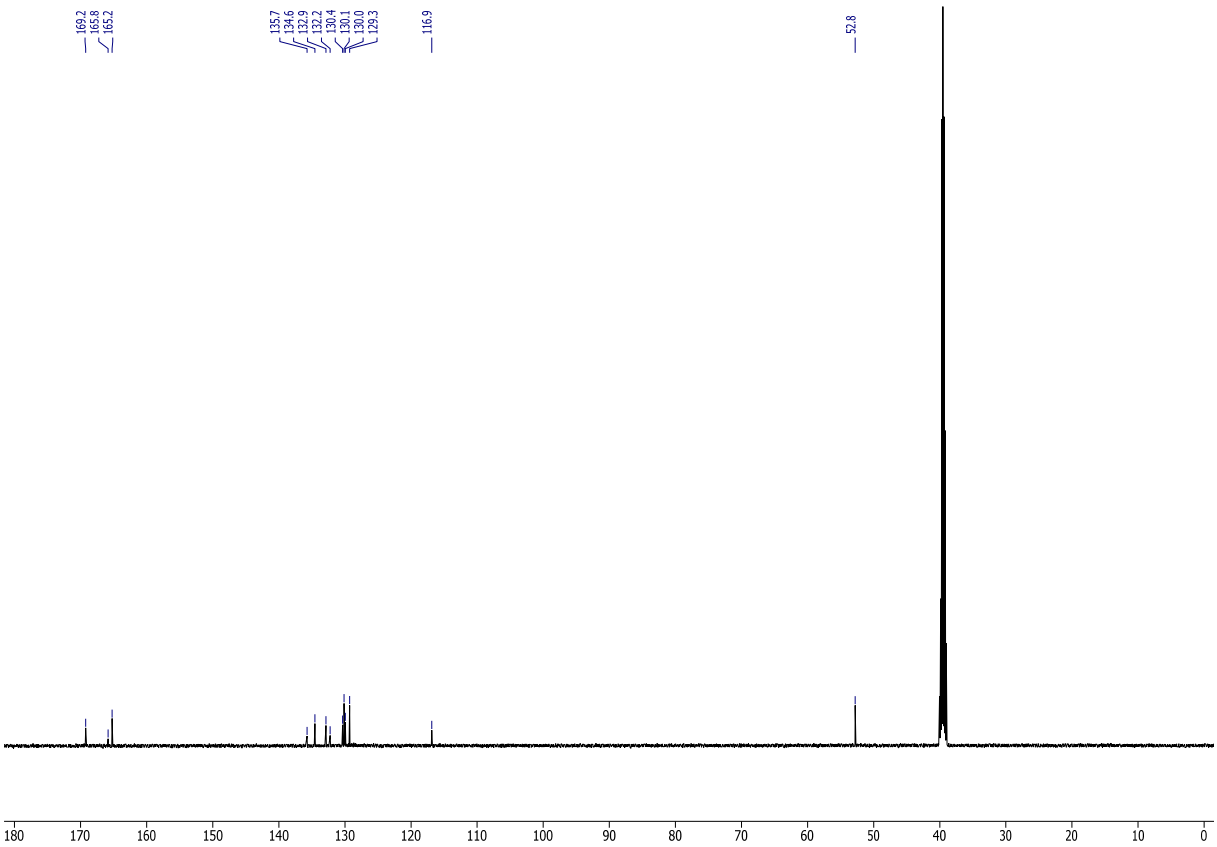
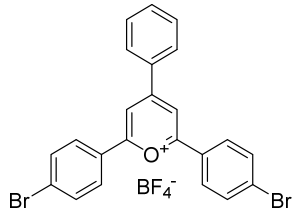



**Figure S8.** $^{13}$C-NMR spectrum of **1d** (126 MHz, DMSO-$d_6$, r.t.).




**1e**
Chemical Formula: $C_{23}H_{15}BBr_2F_4O$
Molecular Weight: 553,98

**1e) Yield** = 29 % (as a yellow solid) **$^1$H-NMR** (500 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 9.20 (s, 2H), 8.60 (d, $^3J_{HH}$ = 7.4 Hz, 2H) 8.52 (d, $^3J_{HH}$ = 8.7 Hz, 4H), 8.02 (d, $^3J_{HH}$ = 8.7 Hz, 4H), 7.88 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.79 (t, $^3J_{HH}$ = 7.4 Hz, 2H). **$^{13}$C-NMR** (126 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 169.3, 165.3, 135.4, 132.9, 132.3, 130.6, 130.1, 129.9, 129.6, 128.3, 115.6. **MS (ESI+)**: *m/z* calculated for $C_{23}H_{15}Br_2O^+$: 464.9484 u, found: 464.945 u.

Analytical data in accordance with the literature.[5]

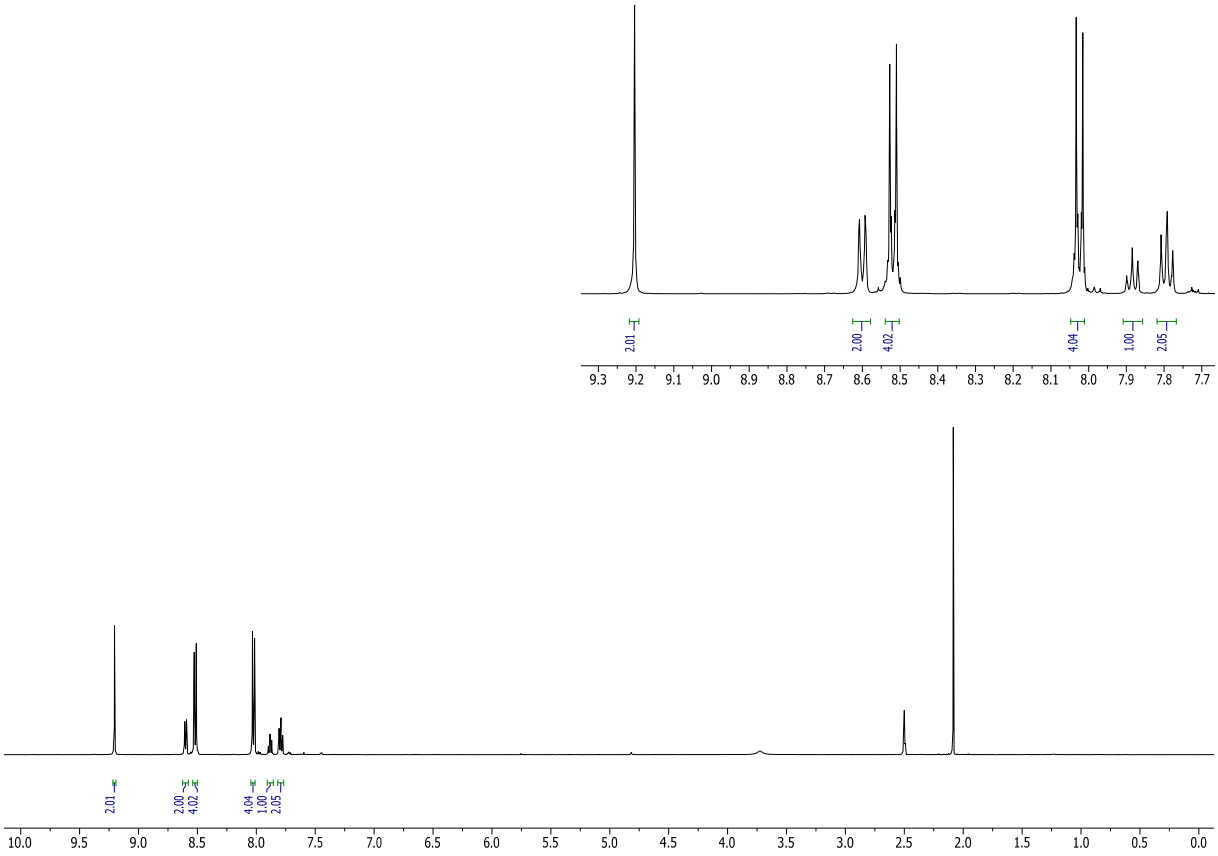



**Figure S9.** $^{1}$H-NMR spectrum of **1e** (500 MHz, DMSO-$d_6$, r.t.).

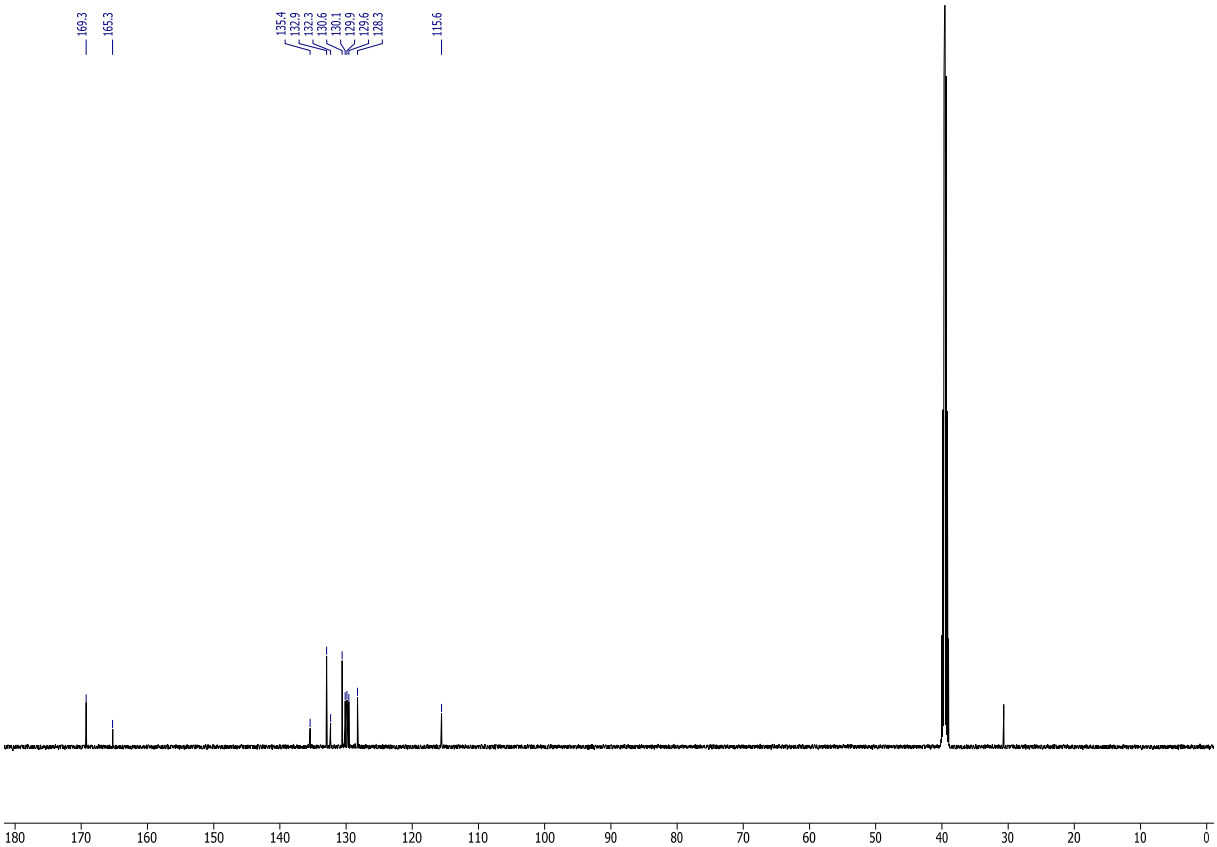
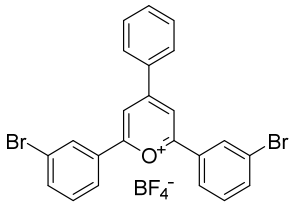



**Figure S10.** $^{13}$C-NMR spectrum of **1e** (126 MHz, DMSO-$d_6$, r.t.).




**1f**
Chemical Formula: $C_{23}H_{15}BBr_2F_4O$
Molecular Weight: 553,98

**1f) Yield** = 25 % (as a yellow solid) **$^{1}$H-NMR** (500 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 9.27 (s, 2H), 8.86 (t, $^{4}J_{HH}$ = 1.2 Hz, 2H) 8.65 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H), 8.54 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.2 Hz, 2H), 8.08 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HH}$ = 1.2 Hz, 2H), 7.91 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H), 7.85 – 7.75 (m, 4H). **$^{13}$C-NMR** (126 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 169.3, 166.2, 138.0, 136.2, 132.7, 132.4, 131.7, 131.7, 130.9, 130.4, 128.2, 123.5, 116.8. **MS (ESI+)**: *m/z* calculated for $C_{23}H_{15}Br_2O^+$: 464.9484 u, found: 464.946 u.

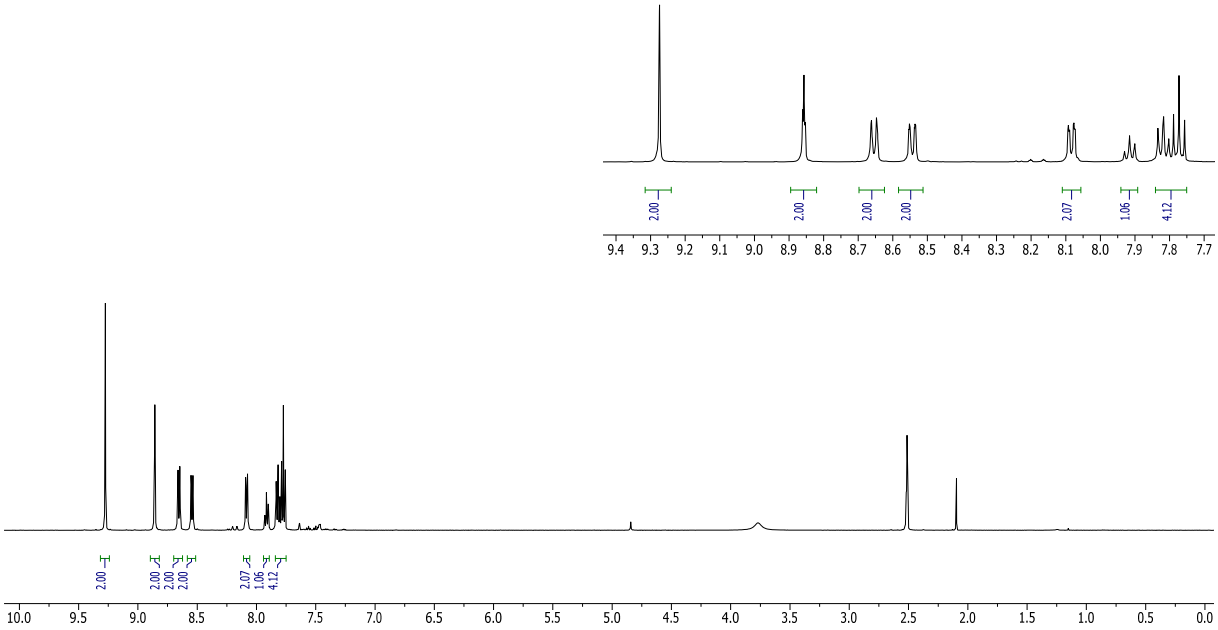



**Figure S11.** $^{1}$H-NMR spectrum of **1f** (500 MHz, DMSO-$d_6$, r.t.).

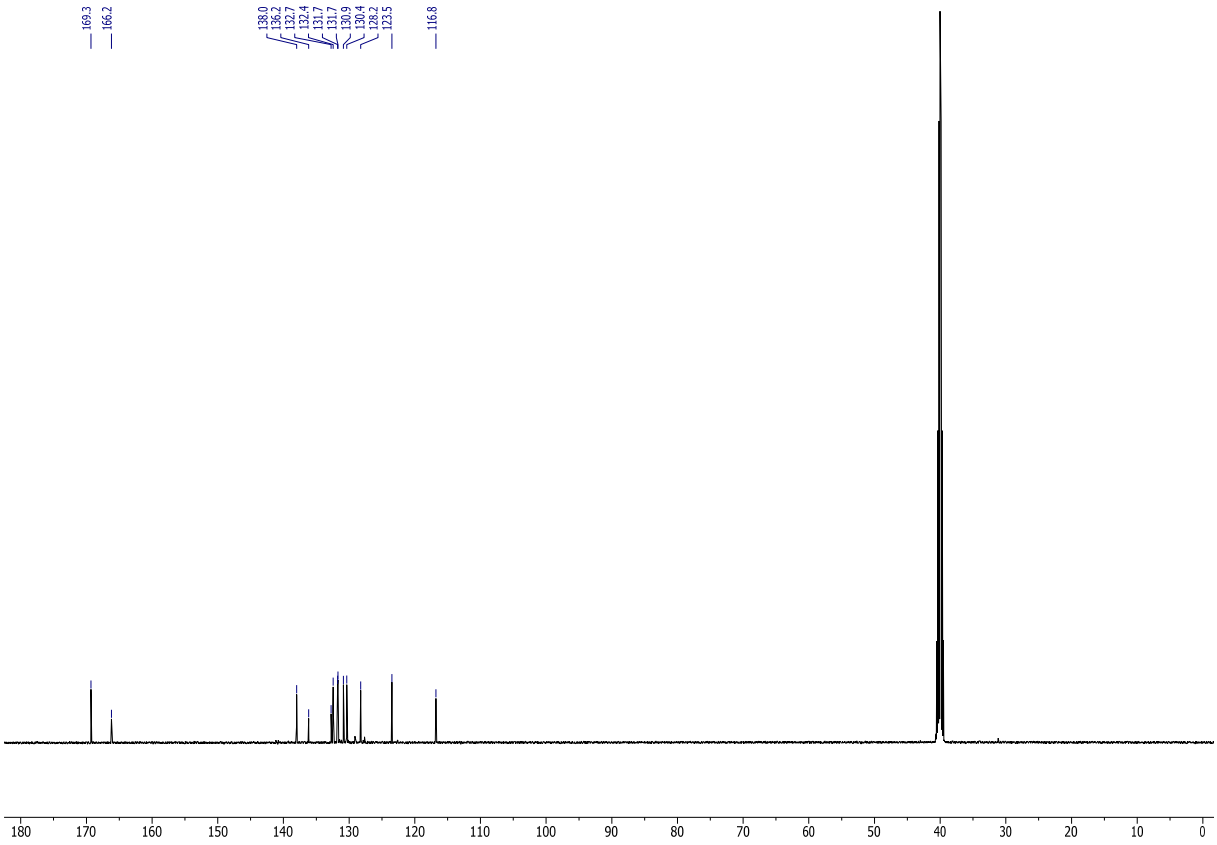
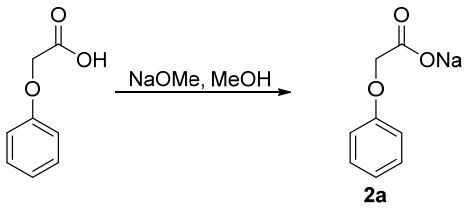



**Figure S12.** $^{13}$C-NMR spectrum of **1f** (126 MHz, DMSO-$d_6$, r.t.).

# 3. Synthesis of sodium salts

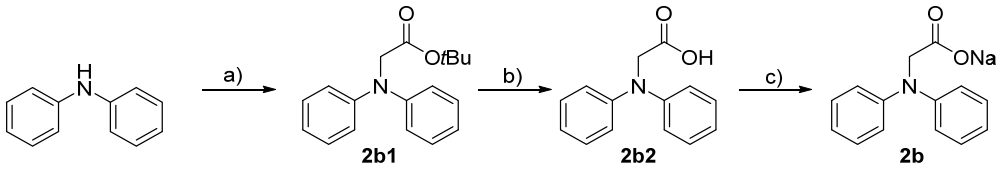
## 3.1 Synthesis of sodium phenoxyacetate (2a)



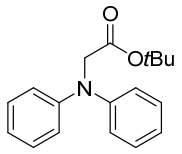

**2a**

A sodium methoxide solution (25% in methanol, 8.93 ml, 39.0 mmol, 1.0 eq.) was added slowly to a mixture of 2-phenoxyacetic acid (5.00 g, 39.0 mmol, 1.0 eq.) in methanol (100 ml) and stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the product was isolated as a colourless solid (5.85 g, 39.0 mmol, quantitative) and used without further purification.

## 3.2 Synthesis of sodium diphenylglycinate (2b)




**Scheme S1:** a) *tert*-Butyl 2-bromoacetate, NaH, DMF, 60 °C, 36 h, 27 %; b) DCM, TFA, RT, 16 h, 83 %; c) NaOMe, MeOH, 40 °C, 3 h, quant.




**2b1**
Chemical Formula: $C_{18}H_{21}NO_2$
Molecular Weight: 283,37

a) Synthesis of *tert*-butyl diphenylglycinate (**2b1**): A mixture of diphenylamine (22.3 g, 131.6 mmol, 1.0 eq.) and NaH (60% dispersion in mineral oil, 5.27 g, 131.6 mmol, 1.1 eq.) in dimethyformamide (300 ml) was stirred under argon at 60 °C for 18 h. After cooling to 0 °C, *tert*-butyl 2-bromoacetate (30.8 g, 157.9 mmol, 1.2 eq.) was added slowly to the mixture and stirred at 60 °C for 18 h. After cooling to room temperature, the reaction was quenched by the addition of $H_2O$. The solvent was evaporated, and the crude product was dissolved in DCM. The organic phase was washed with $H_2O$, saturated $NaHCO_3$, brine and dried over $Na_2SO_4$. The solvent was removed under reduced pressure, and the crude product is purified by column chromatography ($SiO_2$, eluent CH:DCM, 2:1, $R_f$ = 0.22). The product was isolated as a colourless solid (10.0 g, 35.3 mmol, 27%).

**$^1$H-NMR** (500 MHz, Acetone-$d_6$, r.t.): δ [ppm] = 7.27 (dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 7.4 Hz, 4H), 7.02 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.1 Hz, 4H), 7.49 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.1 Hz, 2H), 4.39 (s, 2H), 1.42 (s, 9H). **$^{13}$C-NMR** (126 MHz, Acetone-$d_6$, r.t.): δ [ppm] = 170.5, 148.6, 130.0, 122.4, 121.4, 81.6, 55.4, 28.2. **MS (EI, 70 eV)**, *m/z* (%): 283.1 (15) $[M]^{+\cdot}$, 227.0 (25) $[M\text{-}C_4H_8]^{+\cdot}$, 182.0 (100) $[M\text{-}CHO_2\cdot]^+$.

Analytical data in accordance with the literature.[6]

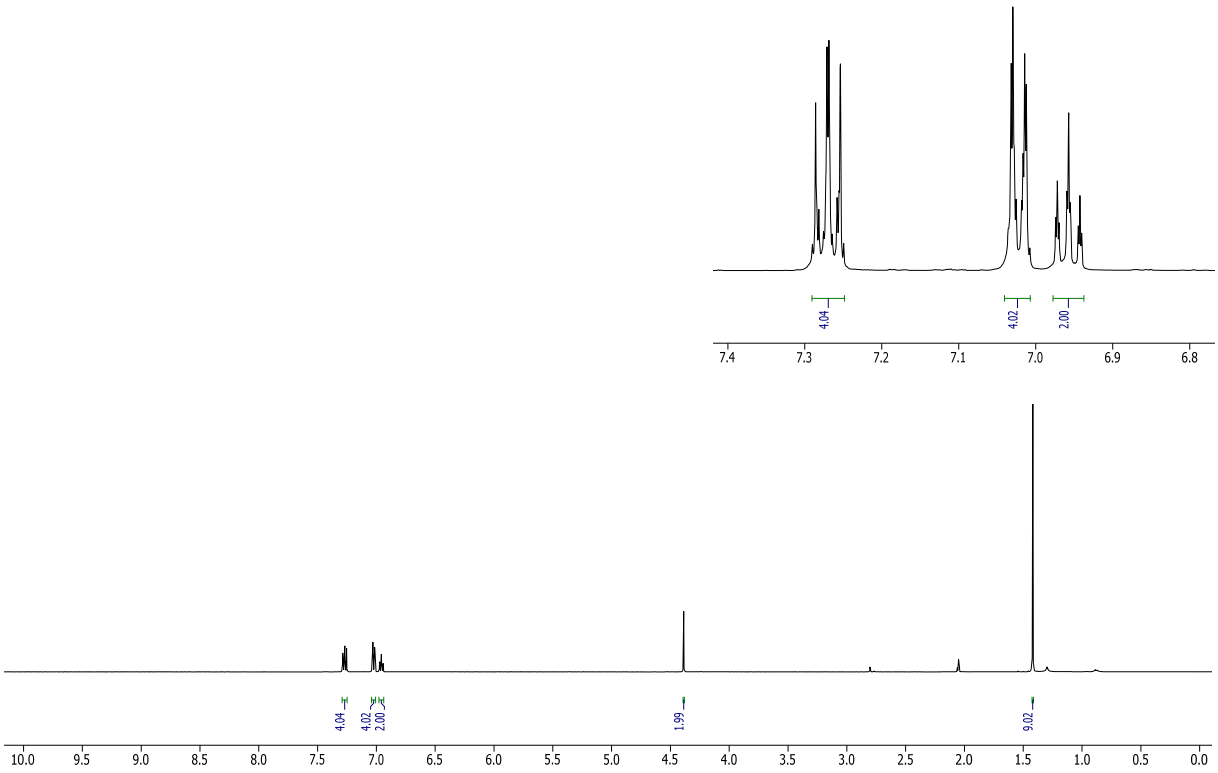



**Figure S13.** $^{1}$H-NMR spectrum of **2b1** (500 MHz, Acetone-$d_6$, r.t.).

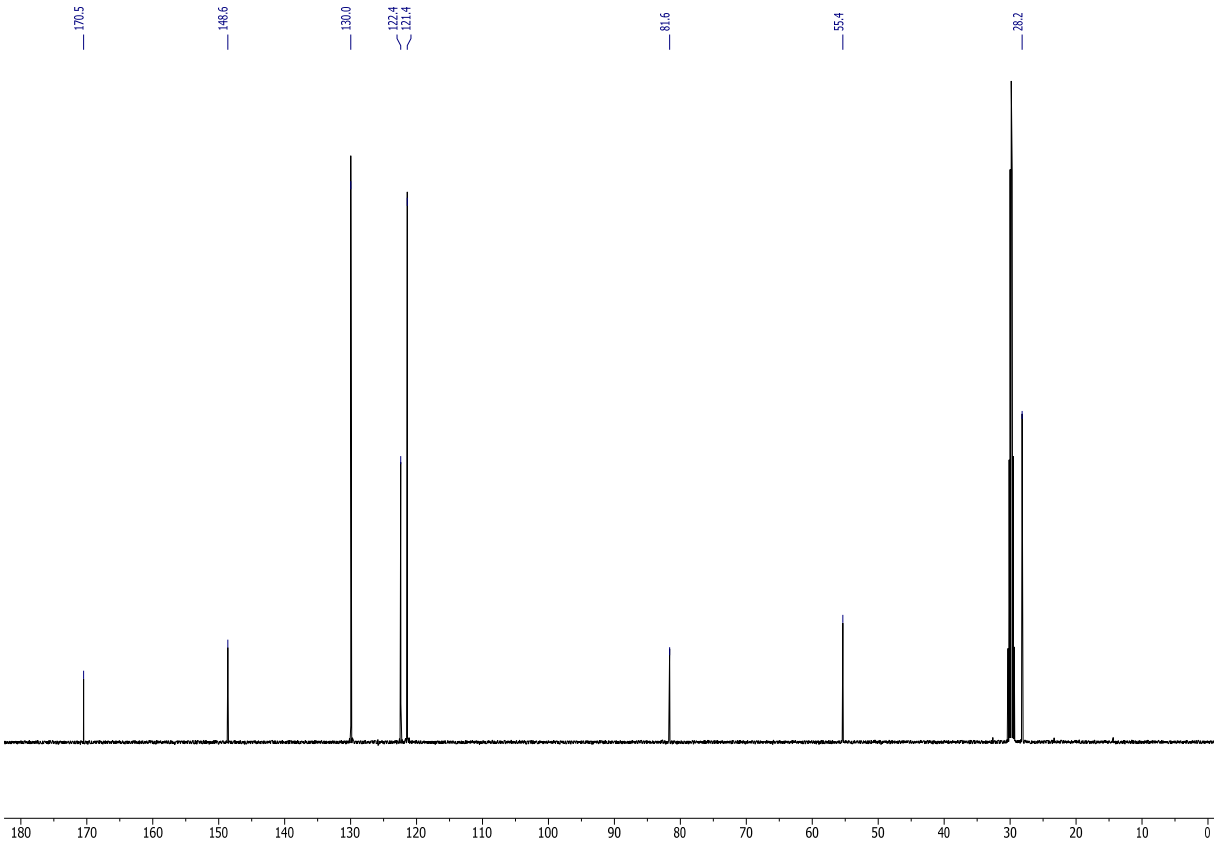
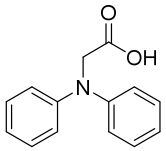



**Figure S14.** $^{13}$C-NMR spectrum of **2b1** (126 MHz, Acetone-$d_6$, r.t.).

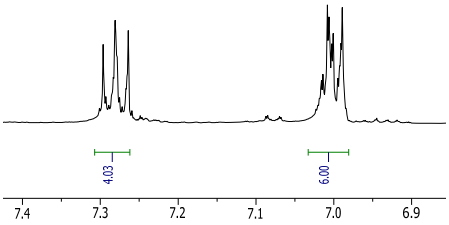


**2b2**
Chemical Formula: $C_{14}H_{13}NO_2$
Molecular Weight: 227,26

b) Synthesis of *N,N*-diphenylglycine (**2b2**): Trifluoroacetic acid (40.3 g, 353 mmol, 10.0 eq.) was added slowly at room temperature to a solution of tert-butyl diphenylglycinate (10.0 g, 35.3 mmol, 1.0 eq.) in DCM (150 ml). The mixture was stirred at room temperatur for 16 h. Subsequently, the mixture was made alkaline with 2 M NaOH and the phases were seperated. The organic phase was three times extracted with NaOH (2 M, 100 ml). The combined aqueous phases were washed three times with DCM (150 ml) and then acidified with concentrated HCl resulting in precipitation of the product. The product was dissolved in DCM, and the organic phase was washed with $H_2O$ and brine. The solution was dried over $Na_2SO_4$, and the solvent was removed under reduced pressure. The product was isolated as a colourless solid (6.66 g, 29.3 mmol, 83%).

**$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 7.28 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 7.4 Hz, 4H), 7.03 - 6.98 (m, 6H), 4.39 (s, 2H). **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 176.5, 147.8, 129.9, 122.7, 121.1. **MS (EI, 70 eV)**, *m/z* (%): 227.0 (40) $[M]^{+\cdot}$, 182.0 (100) $[M\text{-}CHO_2\cdot]^+$, 77.0 (30) $[C_6H_5\cdot]$.

Analytical data in accordance with the literature.[6]



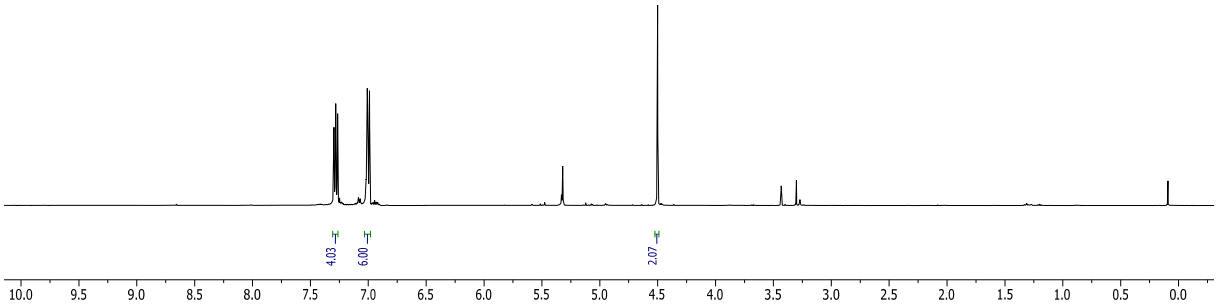



**Figure S15.** $^{1}$H-NMR spectrum **2b2** (500 MHz, $CD_2Cl_2$, r.t.).

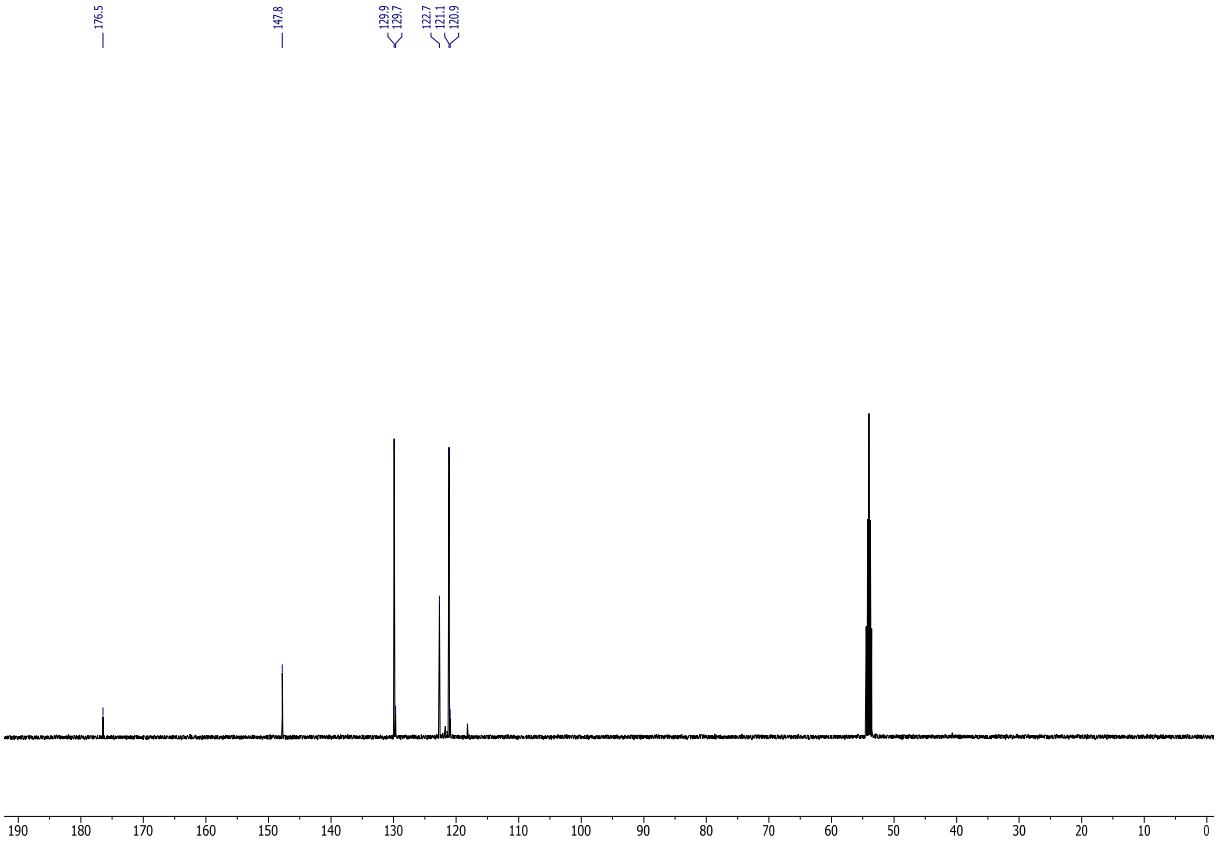
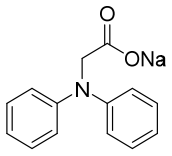


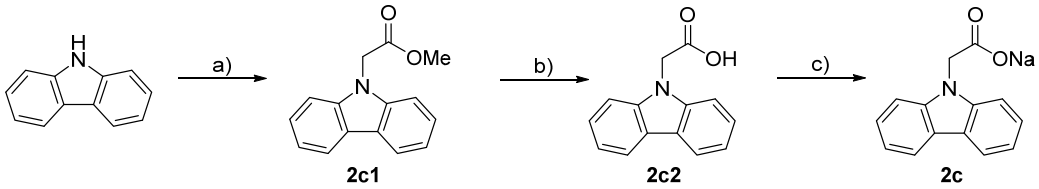

**Figure S16.** $^{13}$C-NMR spectrum of **2b2** (126 MHz, $CD_2Cl_2$, r.t.).



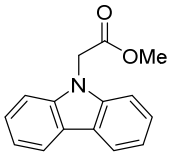

**2b**
Chemical Formula: $C_{14}H_{12}NNaO_2$
Molecular Weight: 249,24

c) Synthesis of sodium *N,N*-diphenylglycinate (**2b**): A sodium methoxide solution (25% in methanol, 2.01 ml, 8.78 mmol, 1.0 eq.) was added slowly to a mixture of diphenylglycine (2.00 g, 8.87 mmol, 1.0 eq.) in methanol (100 ml), and it was stirred at 40 °C for 3 h. The solvent was removed under reduced pressure, and the product was isolated as a colourless solid (2.19 g, 8.78 mmol, quantitative), and used without further purification.

## 3.3 Synthesis of sodium 2-(9*H*-carbazol-9-yl)acetate (2c):




**Scheme S2:** a) Methyl bromoacetate, $K_2CO_3$, MeCN, reflux, 17 h, 71 %; b) THF, $H_2O$, NaOH, r.t., 3 h, 97 %; c) NaOMe, MeOH, r.t., 16 h, quant.




**2c1**
Chemical Formula: $C_{15}H_{13}NO_2$
Molecular Weight: 239,27

a) Synthesis of methyl 2-(9*H*-carbazol-9-yl)acetate (**2c1**): A mixture of 9*H*-carbazole (3.63 g, 21.7 mmol, 1.0 eq.), $K_2CO_3$ (18.0 g, 130 mmol, 6.00 eq.) and methyl bromoacetate (6.65 g, 43.5 mmol, 2.00 eq.) in MeCN (200 ml) was stirred under relfux for 17 h. After cooling to room temperature, the residue was filtered off and washed with MeCN. The organic phase was washed with $H_2O$, saturated $NaHCO_3$, brine, and dried over $Na_2SO_4$. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography ($SiO_2$, eluent EE:CH, 1:4, $R_f$ = 0.43). The product was isolated as a colourless solid (3.68 g, 15.4 mmol, 71%).

**$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 8.12 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.0 Hz, 2H), 7.49 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz, 2H), 7.36 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.2 Hz, 2H), 7.29 (ddd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.0 Hz, 2H), 5.04 (s, 2H), 3.74 (s, 3H). **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 169.5, 141.1, 126.5, 123.6, 120.9, 120.2, 109.0, 53.0, 45.0. **MS (EI, 70 eV)**, *m/z* (%): 239.1 (35) $[M]^{+\cdot}$, 180.1 (100) $[M\text{-}CHO_2\cdot]^+$.

Analytical data in accordance with the literature.[7]

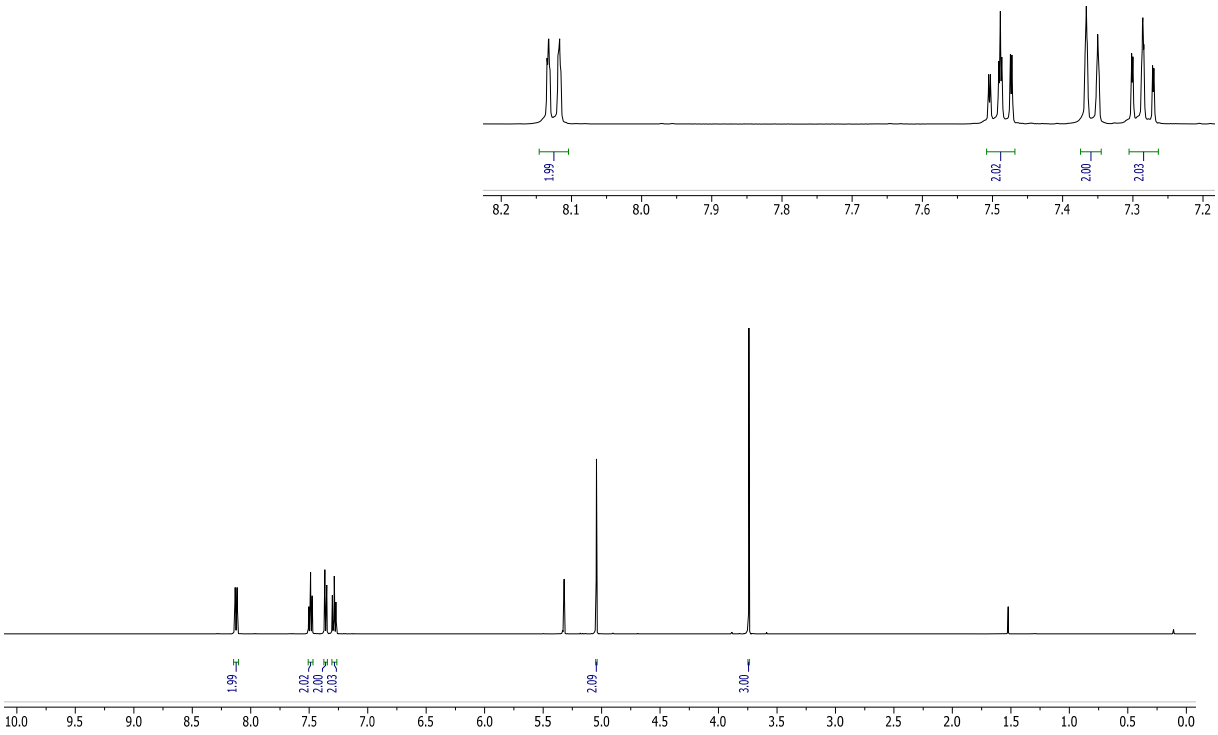



**Figure S17.** $^{1}$H-NMR spectrum of **2c1** (500 MHz, $CD_2Cl_2$, r.t.).

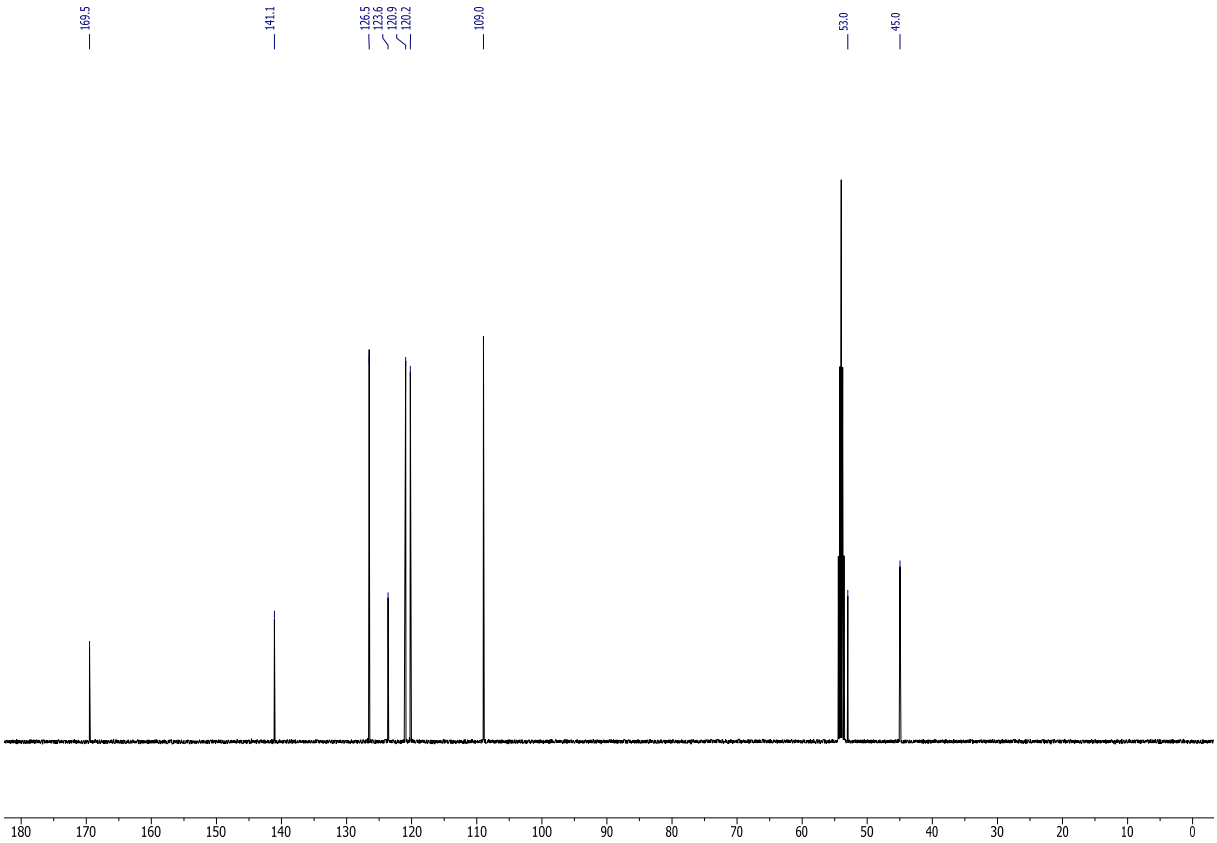
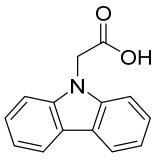


**Figure S18.** $^{13}$C-NMR spectrum of **2c1** (126 MHz, $CD_2Cl_2$, r.t.).



**2c2**
Chemical Formula: $C_{14}H_{11}NO_2$
Molecular Weight: 225,25

b) Synthesis of 2-(9*H*-carbazol-9-yl)acetic acid (**2c2**): A solution of NaOH in $H_2O$ (0.62 g in 20 ml, 30.4 mmol, 2.0 eq.) was added slowly at room temperature to a mixture of methyl 2-(9*H*-carbazol-9-yl)acetate (3.68 g, 15.4 mmol, 1.0 eq.) in MeOH (125 ml). The mixture was stirred at room temperatur for 3 h. Diethyl ether (100 ml) was added to the solution, and the phases were seperated. The organic phase was three times extracted with NaOH (2 M, 50 ml). The combined aqueous phases were washed three times with DCM (100 ml), and then acidified with concentrated HCl. The product precipitated, was dissolved in DCM, and the organic phase was washed with $H_2O$ and brine. The solution was dried over $Na_2SO_4$, and the solvent was removed under reduced pressure. The product was isolated as a colourless solid (3.36 g, 14.9 mmol, 97%).

**$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 8.11 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.0 Hz, $^4J_{HH}$ = 1.0 Hz, 2H), 7.48 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.0 Hz, 2H), 7.35 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.0 Hz, 2H), 7.29 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.0 Hz, 2H), 5.07 (s, 2H). **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 169.5, 141.1, 126.5, 123.6, 120.9, 120.2, 109.0, 53.0, 45.0. **MS (EI, 70 eV)**, *m/z* (%): 225.1 (35) $[M]^{+\cdot}$, 180.1 (100) $[M\text{-}CHO_2\cdot]^+$, 167.0 (15) $[M\text{-}C_3H_5O_2\cdot]^+$.

Analytical data in accordance with the literature.[7]

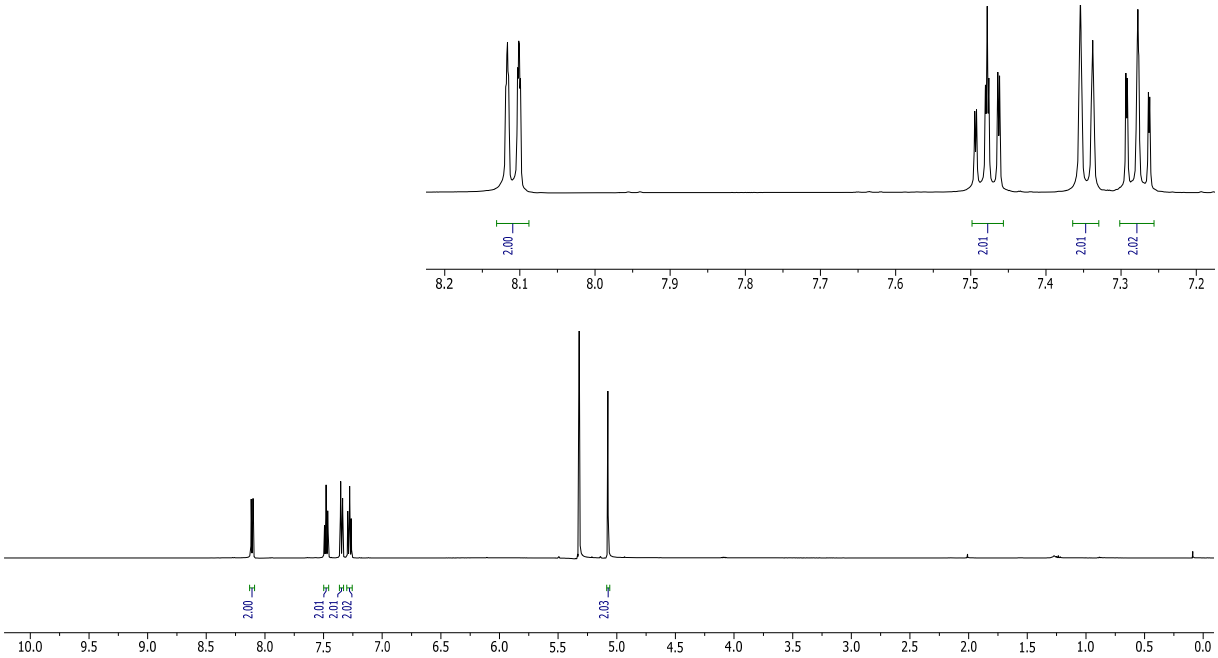



**Figure S19.** $^{1}$H-NMR spectrum of **2c2** (500 MHz, $CD_2Cl_2$, r.t.).

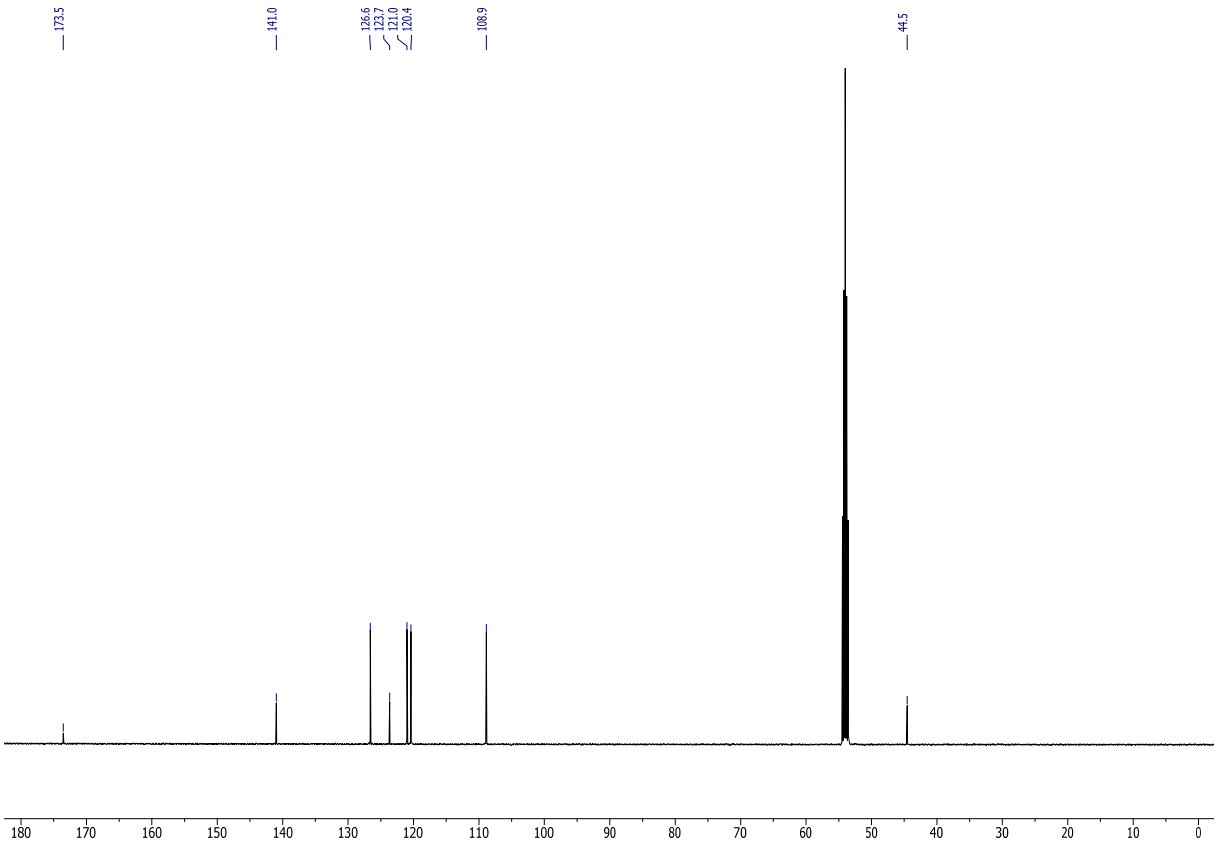
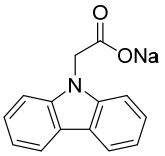



**Figure S20.** $^{13}$C-NMR spectrum of **2c2** (126 MHz, $CD_2Cl_2$, r.t.).




**2c**
Chemical Formula: $C_{14}H_{10}NNaO_2$
Molecular Weight: 247,23

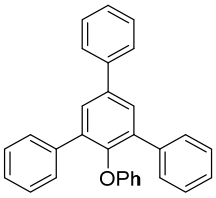
c) Synthesis of sodium 2-(9*H*-carbazol-9-yl)acetate (**2c**): A sodium methoxide solution (25% in methanol, 3.41 ml, 14.9 mmol, 1.0 eq.) was added slowly to a mixture of 2-(9*H*-carbazol-9-yl)acetic acid (3.36 g, 14.9 mmol, 1.0 eq.) in methanol (150 ml), and it was stirred at room temperature for 16 h. The solvent was removed under reduced pressure, and the product was isolated as a colourless solid (3.68 g, 14.9 mmol, quantitative), and used without further purification.

# 4. Synthesis of products 3, 4 and 5

## 4.1 General procedure

A mixture of **1(a-f)** (0.5 mmol), **2(a-c)** (0.5 mmol) and 1.50 g 4-trifluoromethylbenzoic anhydride was stirred at 160 °C for 4 h. Subliming anhydride was melted back to the reaction mixture using a heat gun. After cooling to room temperature, the residue was dissolved in dichloromethane, and filtered over a short column of silica gel with dichloromethane as eluent. The final purification was carried out by column chromatography using dichloromethane-cyclohexane or ethyl acetate-cyclohexane, and subsequent precipitation from dichloromethane by the addition of petroleum ether. The product was obtained as a colorless solid.

## 4.2 Diphenylethers (3a – 3d)




**3a**
Chemical Formula: $C_{30}H_{22}O$
Molecular Weight: 398,51

**3a) Yield** = 38 % $R_f$ = 0.33 (CH:DCM = 10:1) **$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 7.72 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.71 (s, 2H), 7.57 (d, $^3J_{HH}$ = 8.4 Hz, 4H), 7.49 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.39 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 7.33 (t, $^3J_{HH}$ = 7.6 Hz, 4H), 7.26 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 2.3 Hz, 2H), 6.99 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 6.73 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.1 Hz, 1H), 6.57 (d, $^3J_{HH}$ = 8.0 Hz, 2H). **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 158.5, 148.7, 140.7, 139.2, 138.5, 137.4, 129.9, 129.8, 129.5, 129.4, 128.6, 128.1, 127.9, 127.6, 121.6, 116.0. **MS (HRMS)**: *m/z* calculated for $C_{30}H_{22}O$: 398.1671 u, found: 398.1665 u.

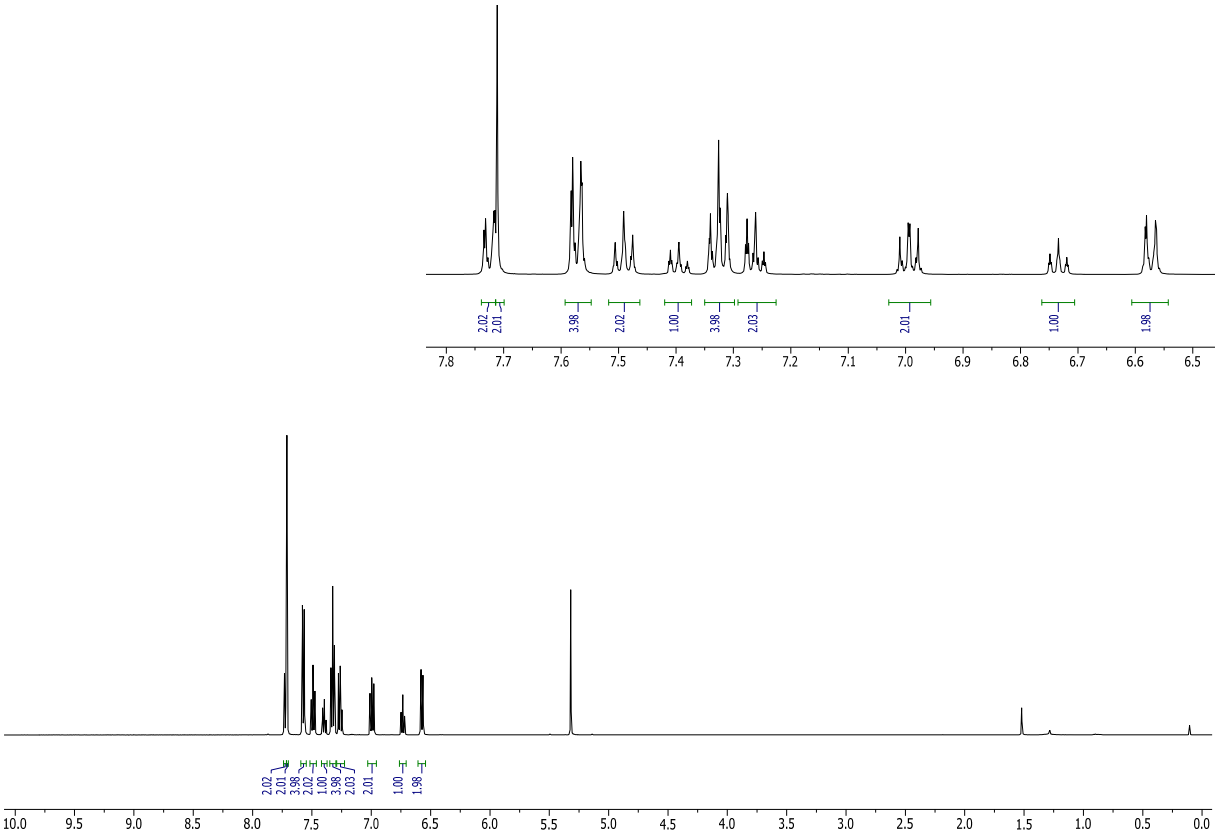


**Figure S21.** $^{1}$H-NMR spectrum of **3a** (500 MHz, $CD_2Cl_2$, r.t.).

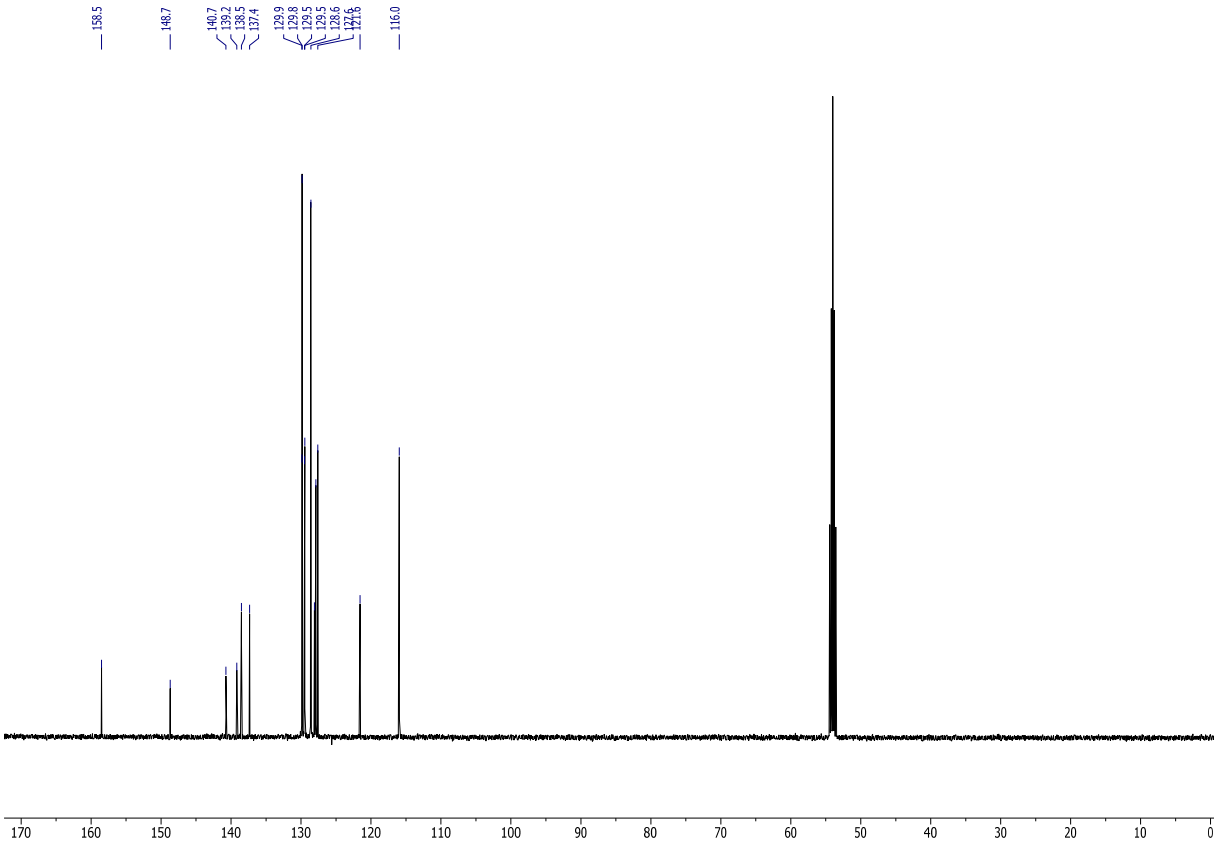
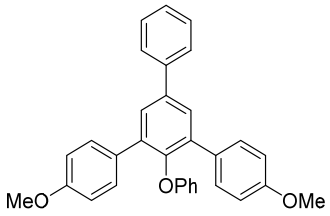


**Figure S22.** $^{13}$C-NMR spectrum of **3a** (126 MHz, $CD_2Cl_2$, r.t.).




**3b**
Chemical Formula: $C_{32}H_{26}O_3$
Molecular Weight: 458,56

**3b) Yield** = 60 % $R_f$ = 0.27 (CH:DCM = 2:1) **$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 7.75 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.68 (s, 2H), 7.53 - 7.45 (m, 6H), 7.42 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.05 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 6.89 (d, $^3J_{HH}$ = 8.8 Hz, 4H), 6.79 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 6.61 (d, $^3J_{HH}$ = 7.7 Hz, 2H), 3.81 (s, 6H). **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 159.6, 158.5, 148.6, 140.9, 139.1, 137.0, 130.9, 130.8, 129.5, 129.4, 129.2, 128.0, 127.6, 121.5, 115.9, 114.0, 55.7. **MS (HRMS)**: *m/z* calculated for $C_{32}H_{26}O_3$: 458.1882, found: 458.1878.

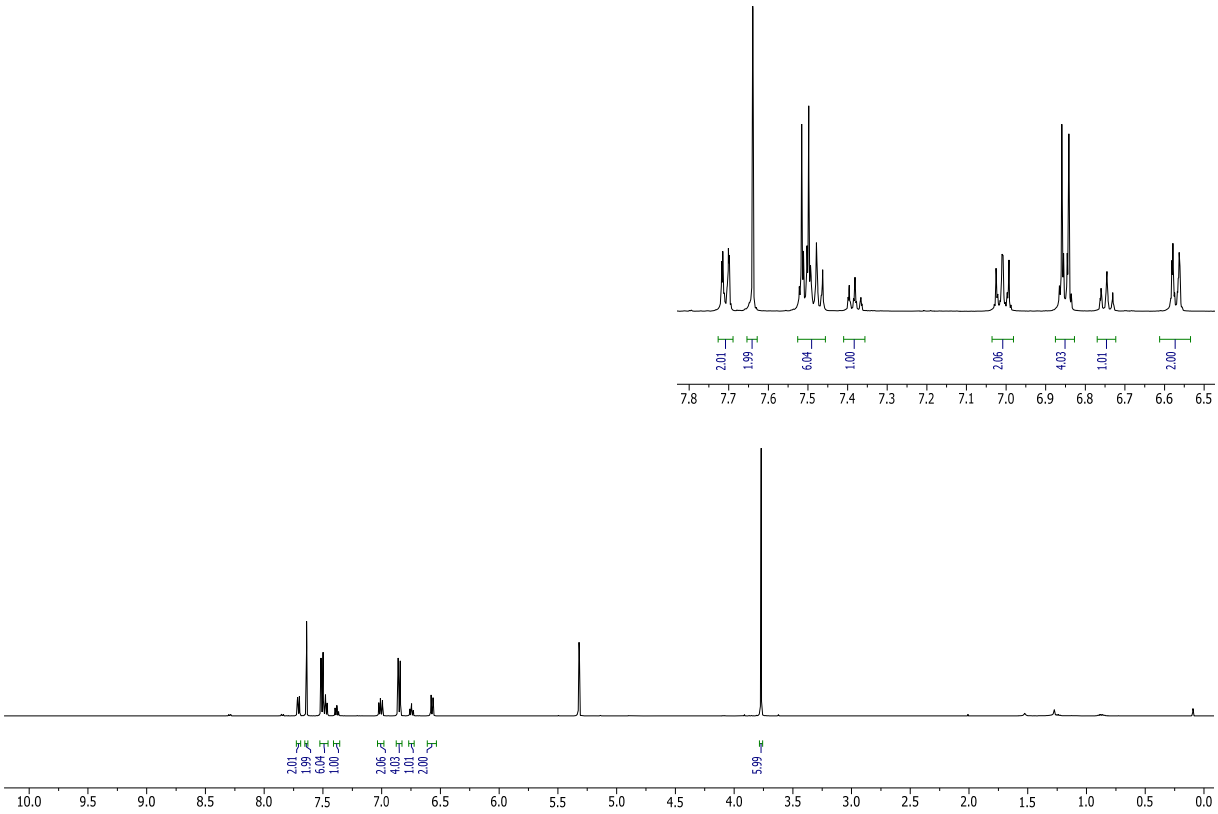



**Figure S23.** $^1$H-NMR spectrum of **3b** (500 MHz, $CD_2Cl_2$, r.t.).

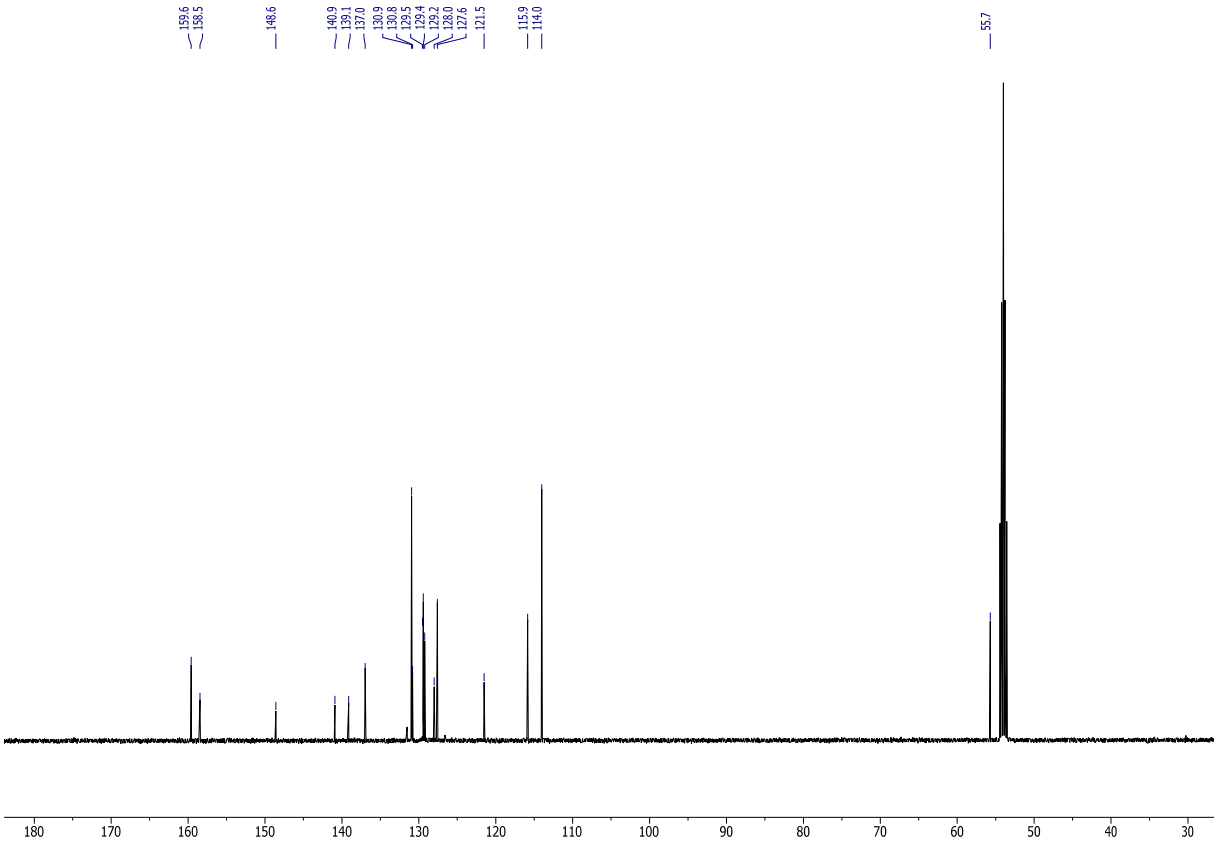
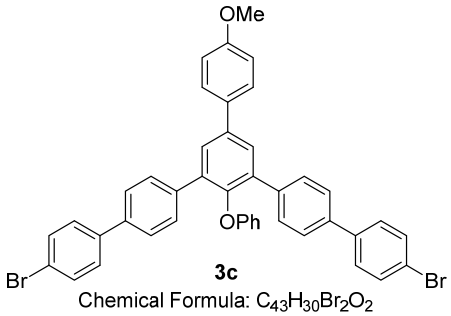



**Figure S24.** $^{13}$C-NMR spectrum of **3b** (126 MHz, $CD_2Cl_2$, r.t.).




**3c**
Chemical Formula: $C_{43}H_{30}Br_2O_2$
Molecular Weight: 738,52

**3c) Yield** = 35 % $R_f$ = 0.44 (CH:DCM = 2:1) **$^1$H-NMR** (400 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 7.73 (s, 2H), 7.68 (m, 6H), 7.55 (m, 8H), 7.47 (d, $^3J_{HH}$ = 8.6 Hz, 4H), 7.03 (m, 4H), 6.75 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 6.64 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 3.87 (s, 3H). **$^{13}$C-NMR** (100 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 160.1, 158.6, 148.3, 140.0, 139.2, 139.0, 138.0, 136.8, 133.0, 132.4, 130.4, 129.6, 129.4, 129.1, 128.6, 127.0, 122.0, 121.7, 116.0, 114.9, 55.9. **MS (MALDI-pos, DCTB)**: *m/z* calculated for $C_{43}H_{30}Br_2O_2$: 736.0613 u, found: 736.058 u.

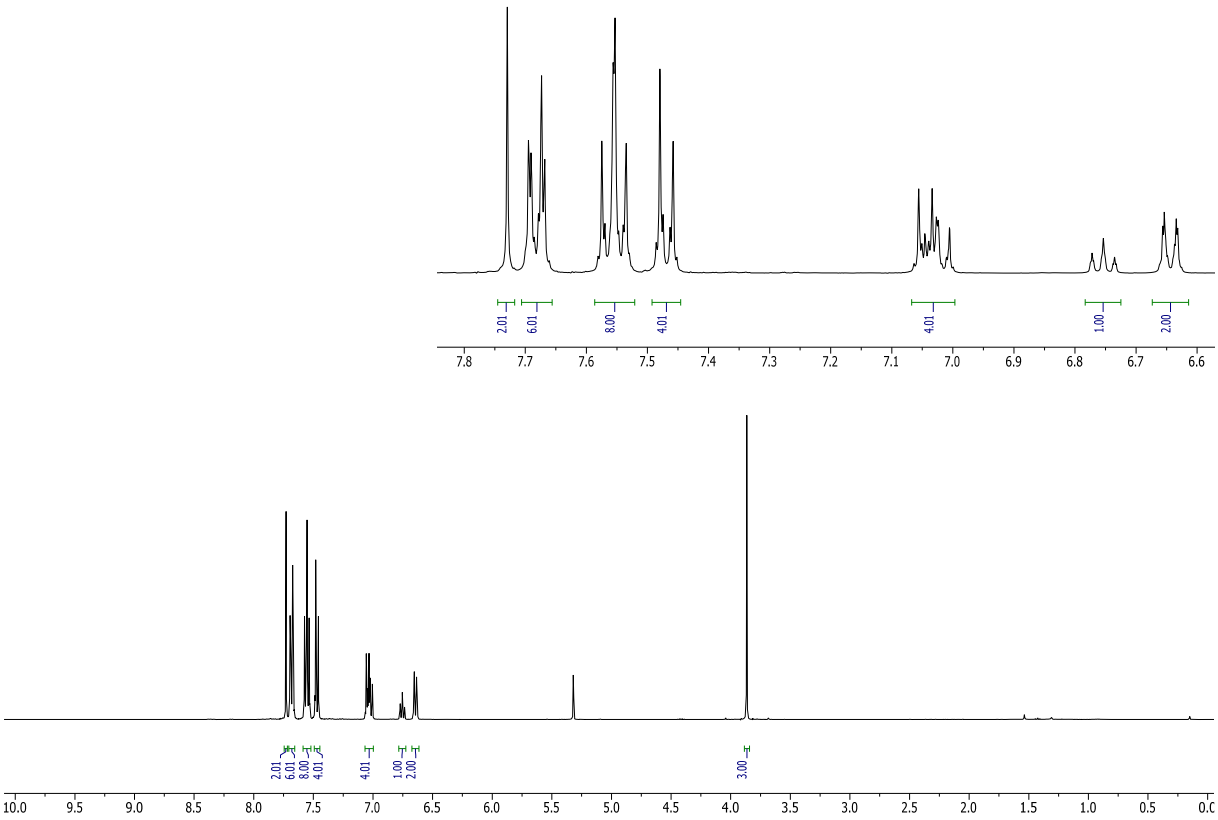



**Figure S25.** $^{1}$H-NMR spectrum of **3c** (500 MHz, $CD_2Cl_2$, r.t.).

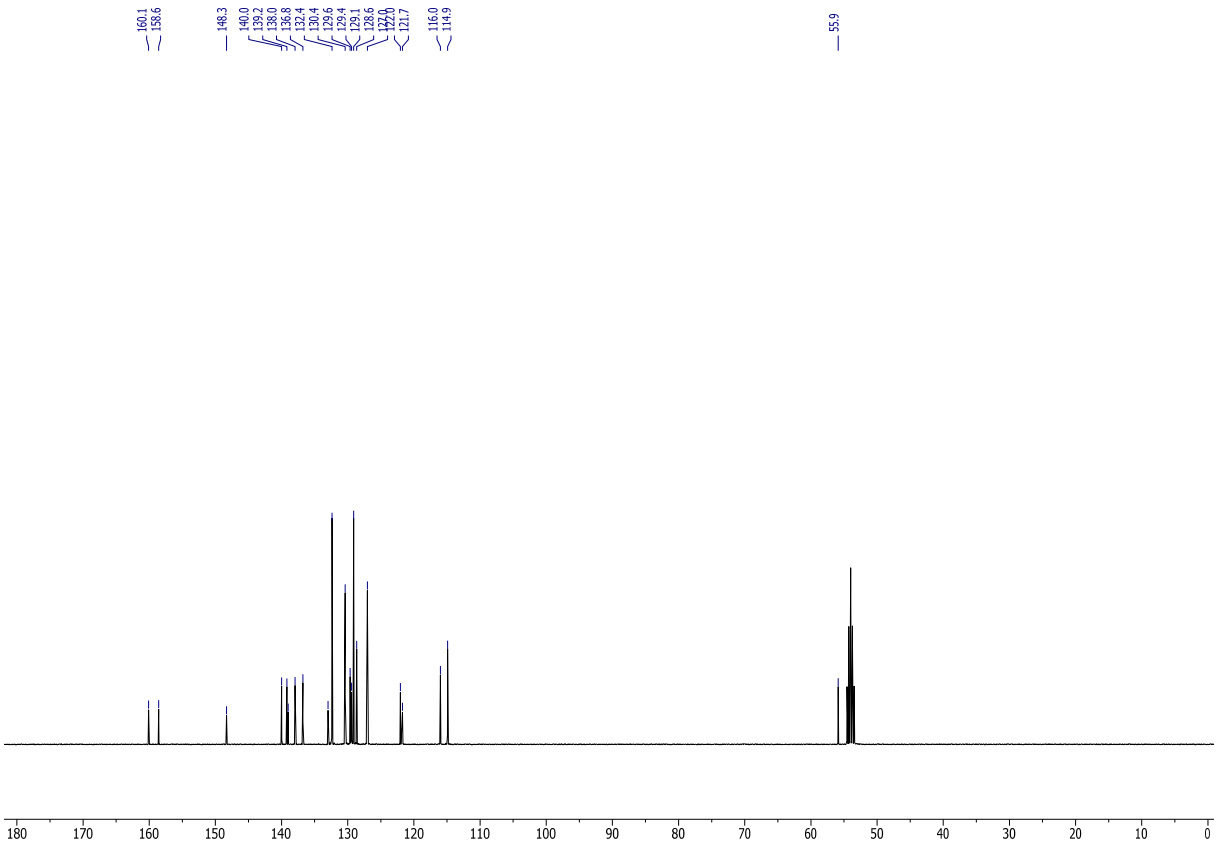
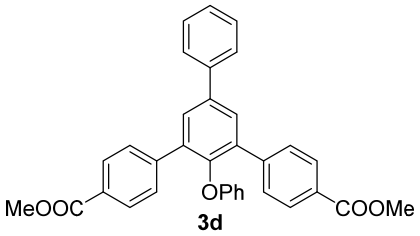



**Figure S26.** $^{13}$C-NMR spectrum of **3c** (126 MHz, $CD_2Cl_2$, r.t.).




**3d**

Chemical Formula: $C_{34}H_{26}O_5$
Molecular Weight: 514,58

**3d) Yield** = 34 % $R_f$ = 0.22 (CH:EE = 8:1) **$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 7.97 (d, $^3J_{HH}$ = 8.3 Hz, 4H), 7.75 (s, 2H), 7.72 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 7.66 (d, $^3J_{HH}$ = 8.3 Hz, 4H), 7.50 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.41 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 6.98 (t, $^3J_{HH}$ = 7.9 Hz, 2H), 6.73 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 6.55 (d, $^3J_{HH}$ = 7.9 Hz, 2H), 3.87 (s, 6H). **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 167.2, 158.2, 148.7, 142.9, 140.3, 139.5, 136.5, 130.4, 129.9, 129.8, 129.7, 129.5, 128.3, 127.6, 121.9, 115.9, 52.5 **MS (HRMS)**: *m/z* calculated for $C_{34}H_{26}O_5$: 514.1780 u, found: 514.1775 u.

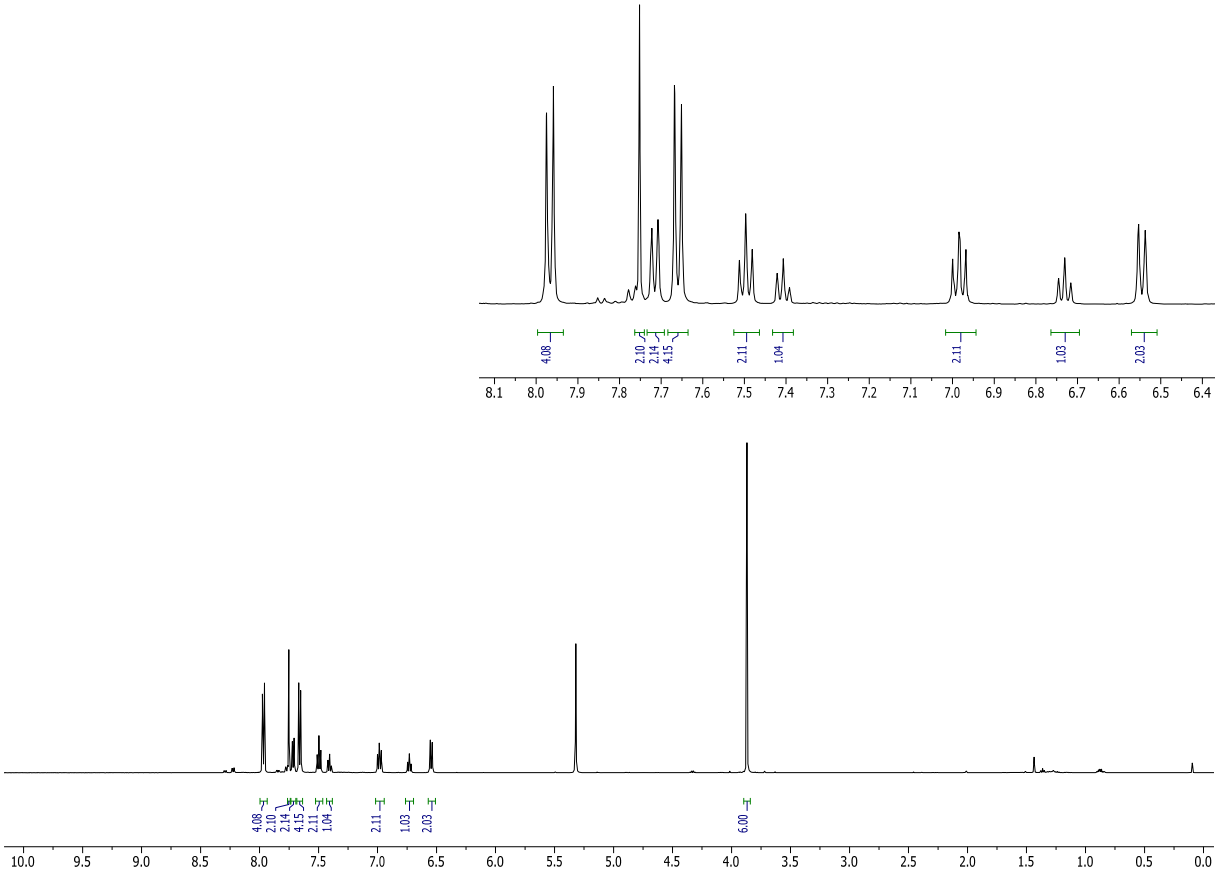



**Figure S27.** $^1$H-NMR spectrum of **3d** (500 MHz, $CD_2Cl_2$, r.t.).

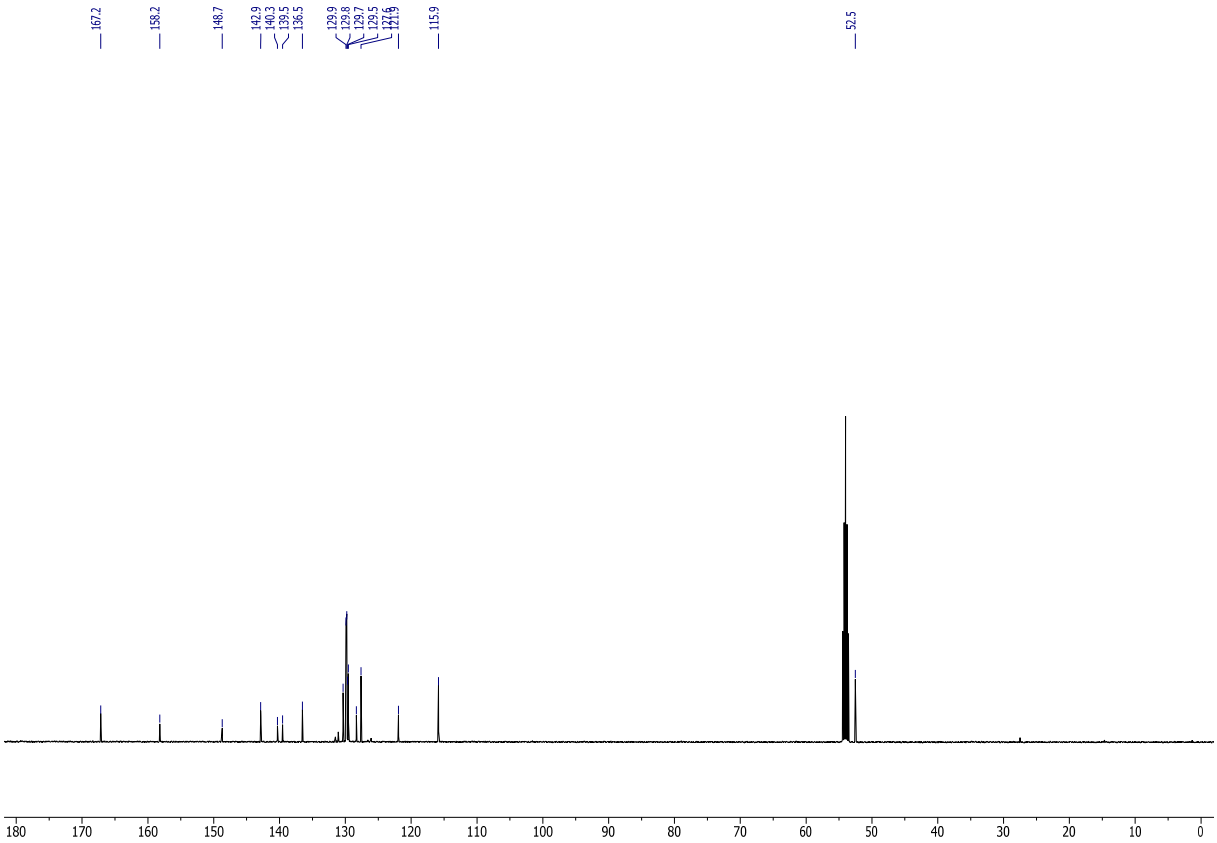
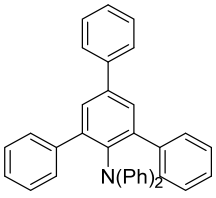



**Figure S28.** $^{13}$C-NMR spectrum of **3d** (126 MHz, $CD_2Cl_2$, r.t.).

## 4.3 Triphenylamines (4a – 4d)




**4a**
Chemical Formula: $C_{36}H_{27}N$
Molecular Weight: 473,62

**4a) Yield** = 16 % $R_f$ = 0.34 (CH:DCM = 10:1) **$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 7.72 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 7.64 (s, 2H), 7.47 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.4 Hz, 2H), 7.37 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.27-7.23 (m, 4H), 7.13-7.07 (m, 6H), 6.92 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 7.3 Hz, 4H), 6.80 (d, $^3J_{HH}$ = 7.8 Hz, 4H), 6.67 (t, $^3J_{HH}$ = 7.3 Hz, 2H). **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 147.3, 143.0, 141.2, 140.7, 140.6, 139.7, 130.6, 129.4, 129.1, 128.8, 128.2, 128.0, 127.5, 127.2, 121.5, 121.1. **MS (HRMS)**: *m/z* calculated for $C_{36}H_{27}N$: 473.2143 u, found: 473.2137 u.

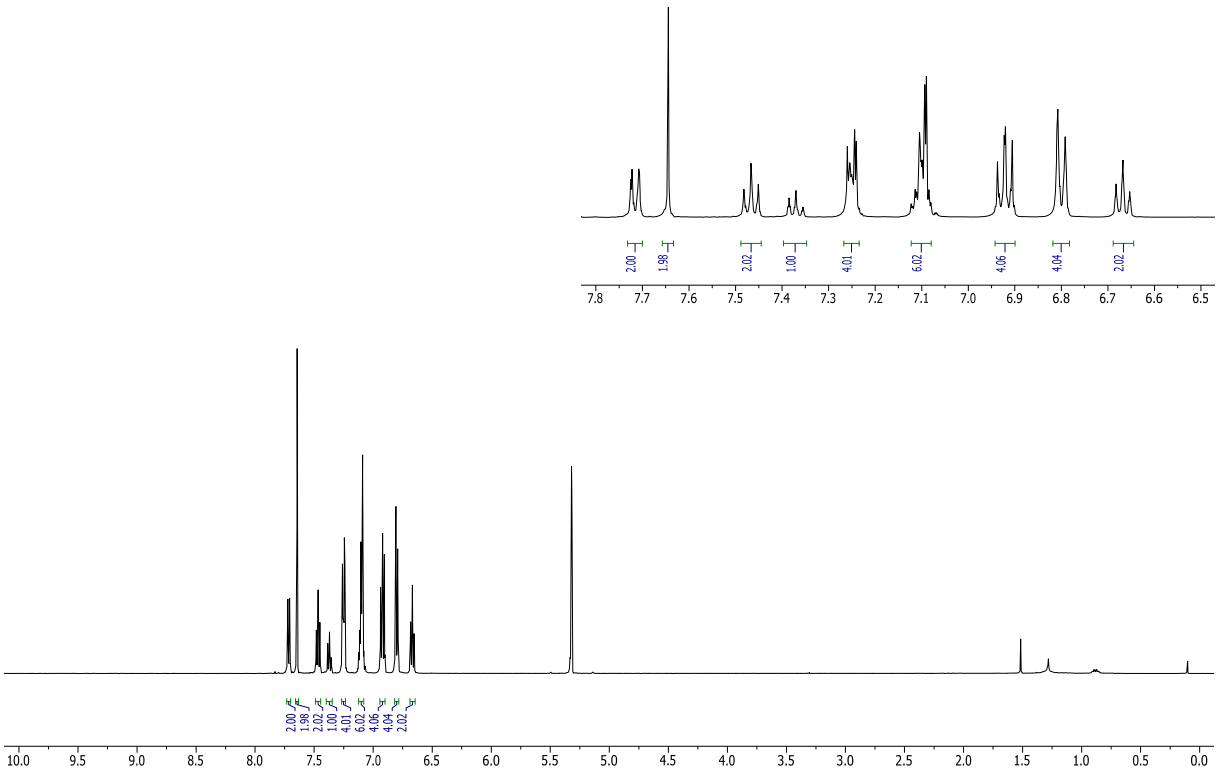


**Figure S29.** $^{1}$H-NMR spectrum of **4a** (500 MHz, $CD_2Cl_2$, r.t.).

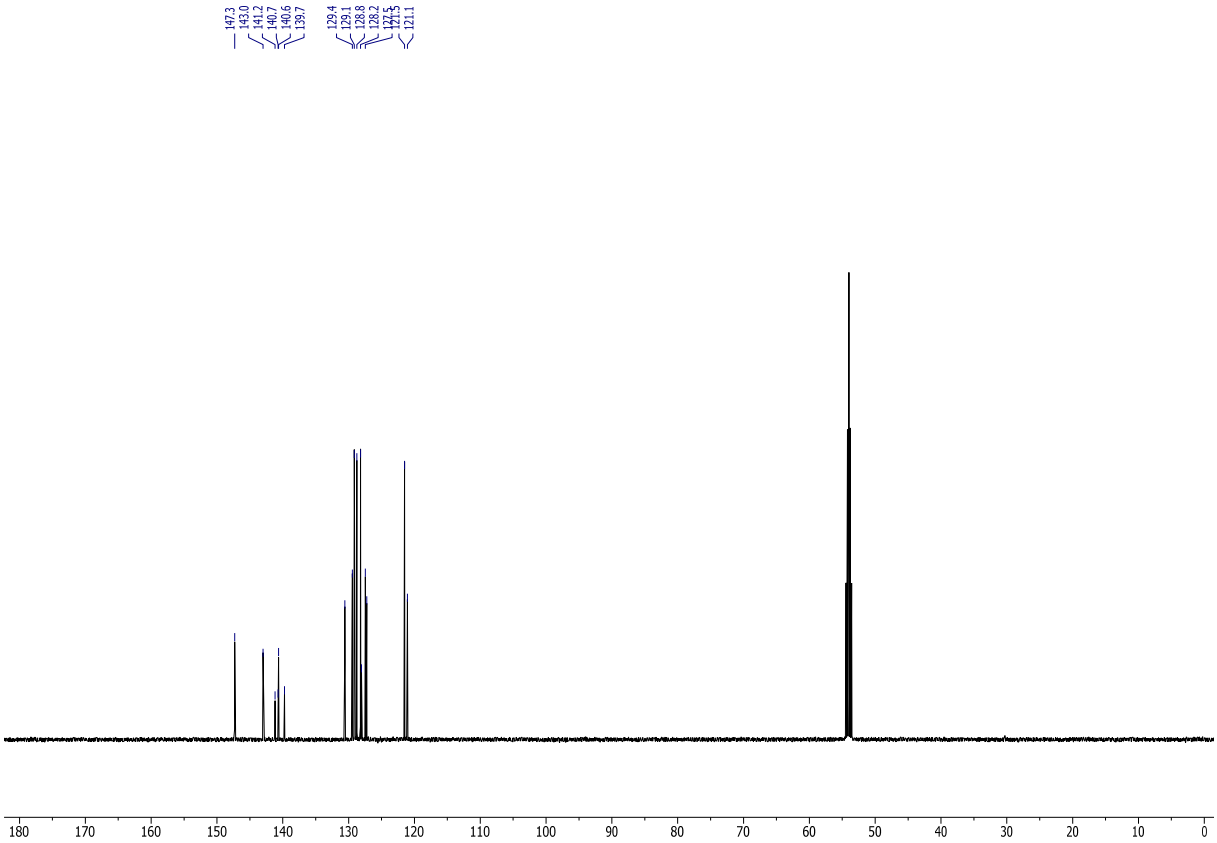
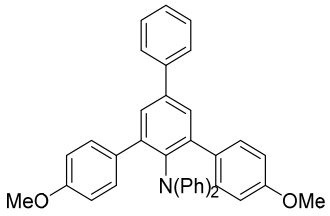


**Figure S30.** $^{13}$C-NMR spectrum of **4a** (126 MHz, $CD_2Cl_2$, r.t.).




**4b**
Chemical Formula: $C_{38}H_{31}NO_2$
Molecular Weight: 533,67

**4b) Yield** = 26 % $R_f$ = 0.22 (Cy:DCM = 3:1) **$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 7.70 (d, $^3J_{HH}$ = 7.7 Hz, 2H), 7.59 (s, 2H), 7.45 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.4 Hz, 2H), 7.36 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.16 (d, $^3J_{HH}$ = 8.7 Hz, 4H), 6.95 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 7.3 Hz, 4H), 6.81 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 6.69 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 6.63 (d, $^3J_{HH}$ = 8.7 Hz, 4H). **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 159.2, 147.3, 142.7, 141.2, 140.8, 139.7, 133.1, 130.2, 129.4, 128.8, 128.0, 127.4, 121.3, 121.0, 113.7, 55.7. **MS (HRMS)**: *m/z* calculated for $C_{38}H_{31}NO_2$: 533.2355 u, found: 533.2351 u.

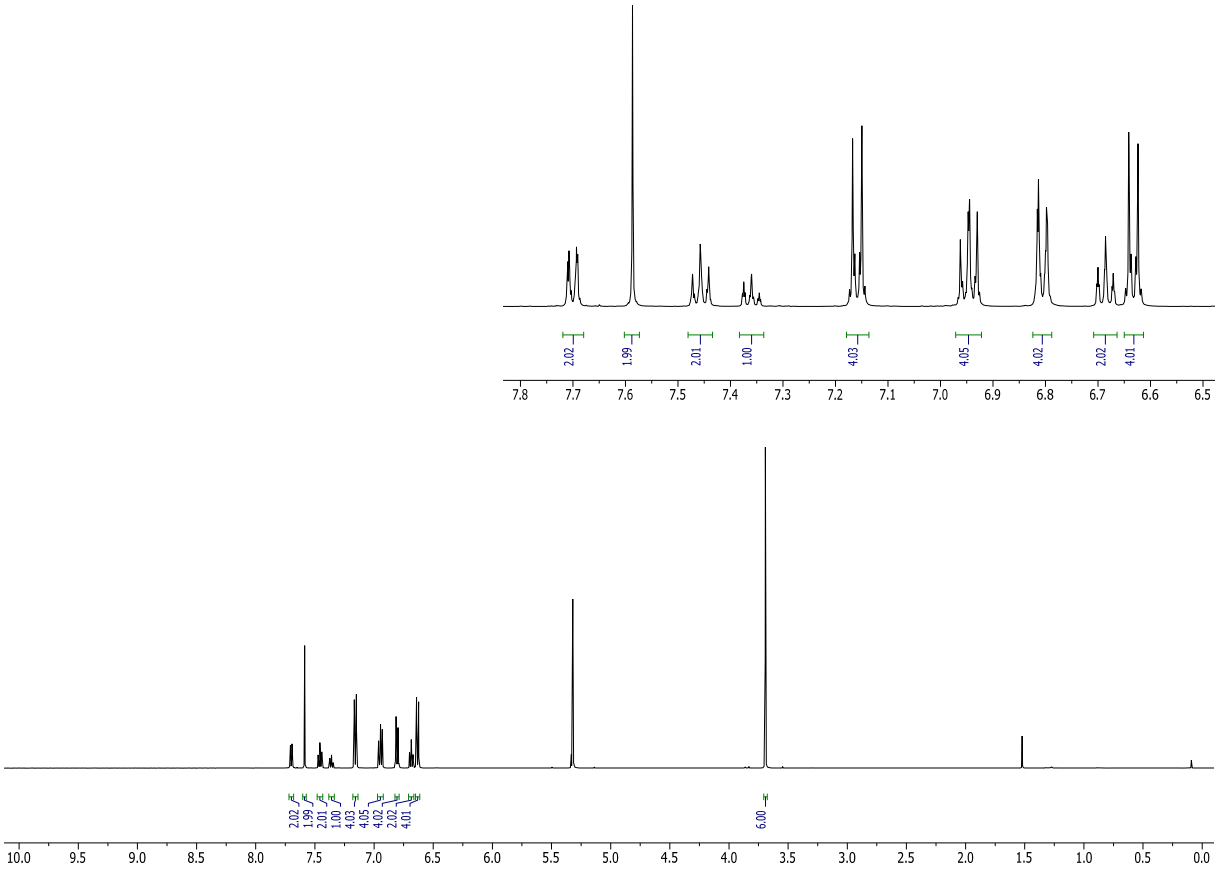



**Figure S31.** $^1$H-NMR spectrum of **4b** (500 MHz, $CD_2Cl_2$, r.t.).

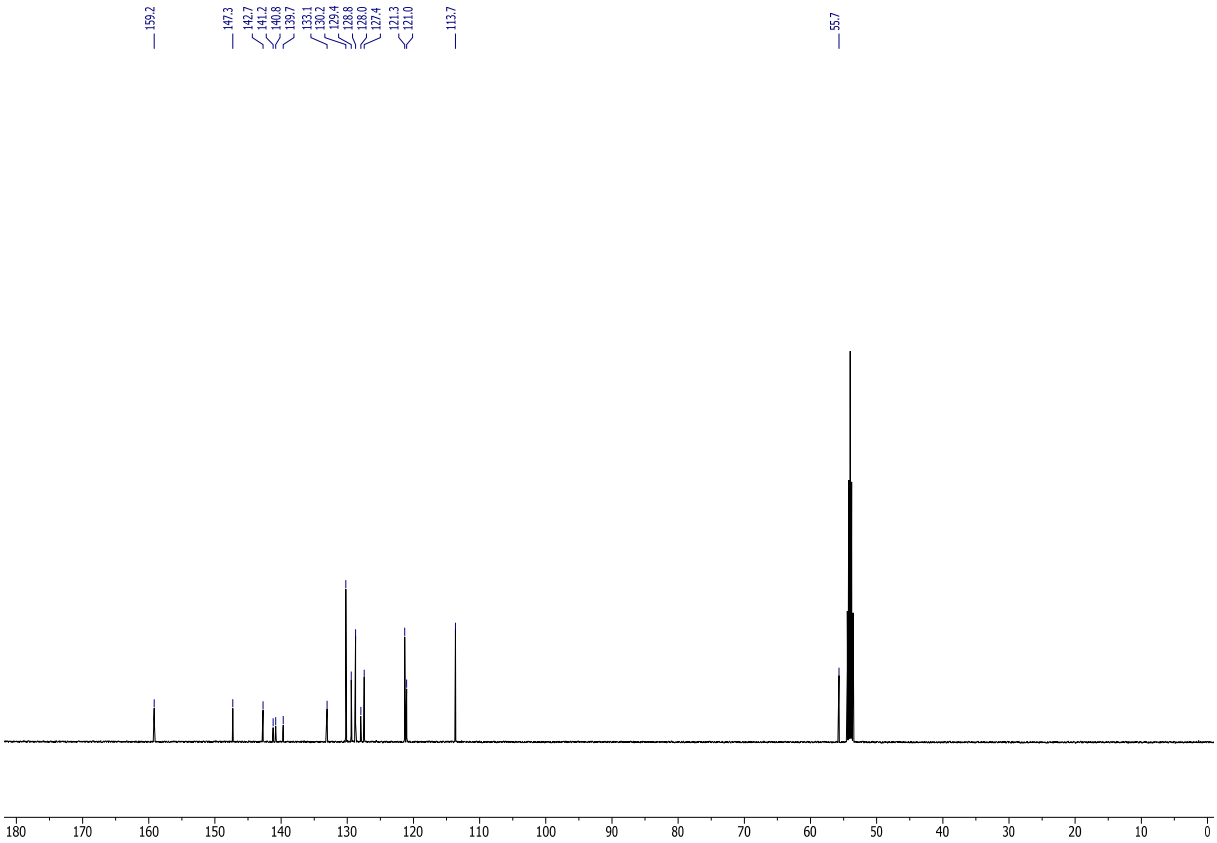
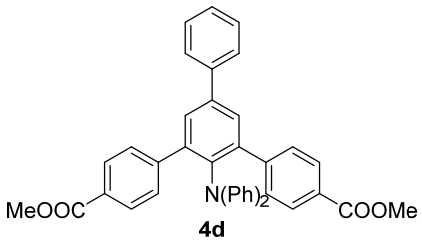



**Figure S32.** $^{13}$C-NMR spectrum of **4b** (126 MHz, $CD_2Cl_2$, r.t.).




**4d**

Chemical Formula: $C_{40}H_{31}NO_4$
Molecular Weight: 589,69

**4d) Yield** = 10 % $R_f$ = 0.35 (Cy:EE = 7:1) **$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 7.74 (d, $^3J_{HH}$ = 8.7 Hz, 4H), 7.70 (d, $^3J_{HH}$ = 7.6 Hz, 2H), 7.66 (s, 2H), 7.47 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.39 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.32 (d, $^3J_{HH}$ = 8.7 Hz, 4H), 6.93 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.2 Hz, 4H), 6.79 (d, $^3J_{HH}$ = 7.7 Hz, 4H), 6.68 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 3.84 (s, 6H). **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 167.2, 147.0, 145.2, 142.0, 141.3, 140.3, 140.0, 131.0, 129.5, 129.4, 129.2, 129.1, 129.0, 128.3, 127.5, 121.5, 52.4. **MS (HRMS)**: *m/z* calculated for $C_{40}H_{31}NO_4$: 589.2253, found: 589.2242 u.

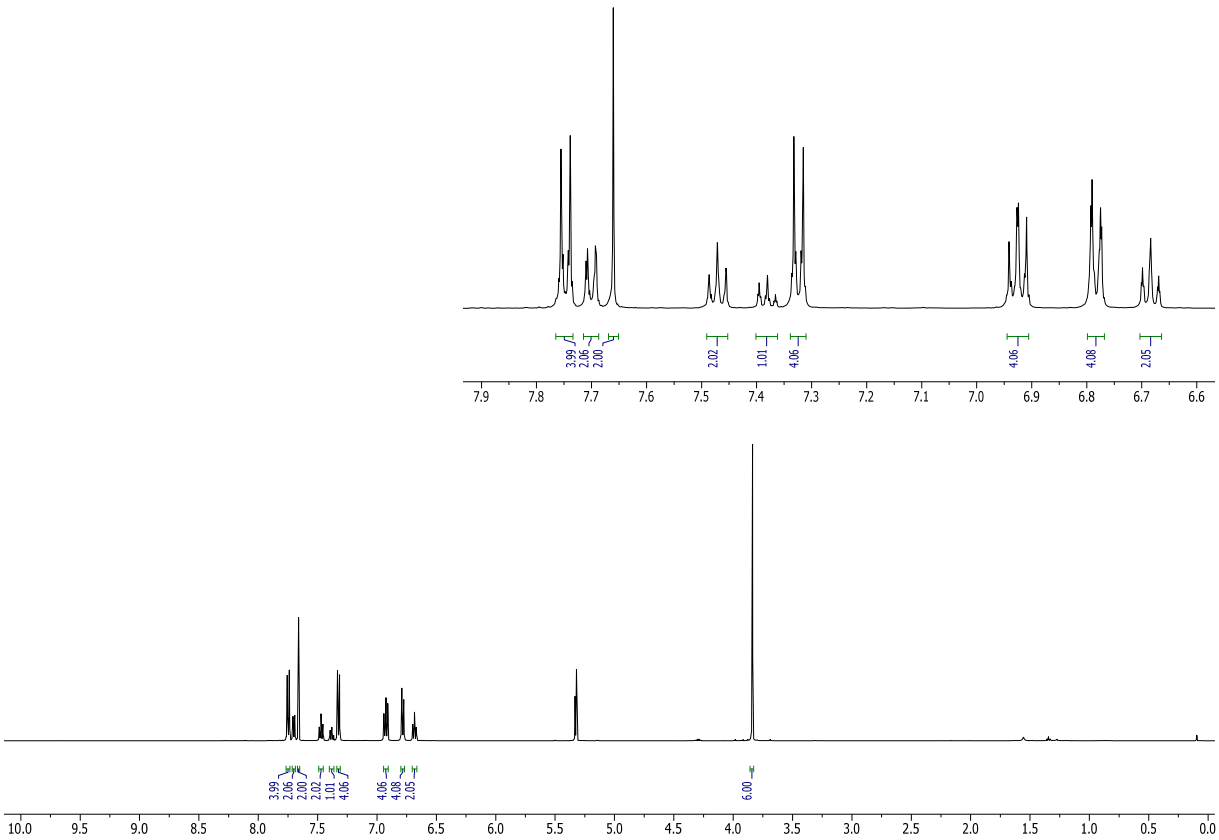



**Figure S33.** $^{1}$H-NMR spectrum of **4d** (500 MHz, $CD_2Cl_2$, r.t.).

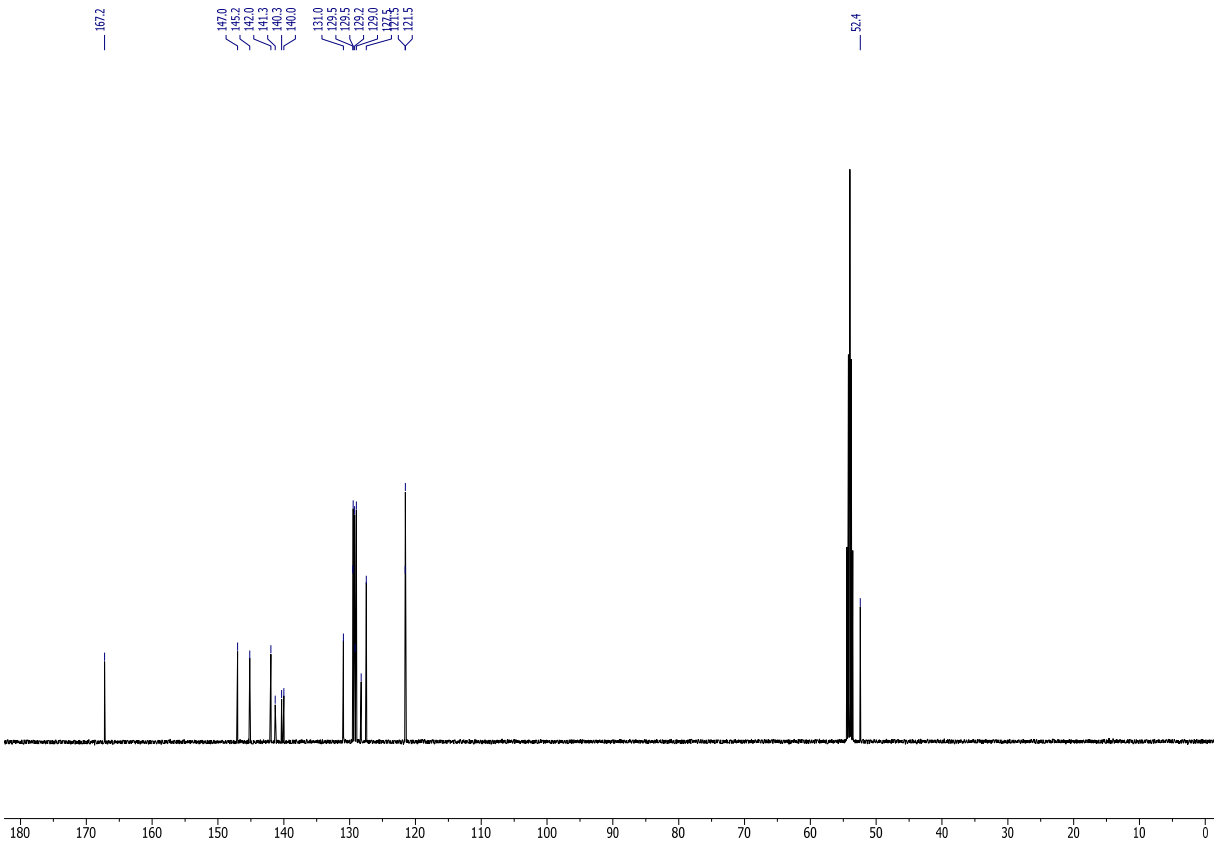
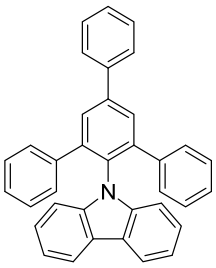



**Figure S34.** $^{13}$C-NMR spectrum of **4d** (126 MHz, $CD_2Cl_2$, r.t.).

## 4.4 Phenylcarbazoles (5a – 5f)



**5a**
Chemical Formula: $C_{36}H_{25}N$
Molecular Weight: 471,60

**5a) Yield** = 38 % $R_f$ = 0.33 (Cy:DCM = 10:1) **$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 7.92 (dt, $^3J_{HH}$ = 7.8 Hz, 2H), 7.85 (s, 2H), 7.80 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.8 Hz, 2H), 7.53 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 7.44 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.8 Hz, 2H), 7.21 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.0 Hz, 2H), 7.09 (td, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.0 Hz, 2H), 7.05 – 6.92 (m, 12H). **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 143.7, 142.4, 141.7, 140.5, 139.6, 130.0, 129.6, 128.5, 128.4, 128.3, 127.8, 127.7, 126.0, 123.2, 120.4, 119.7, 110.7. **MS (HRMS)**: *m/z* calculated for $C_{36}H_{27}N$: 471.1987 u, found: 471.1984 u

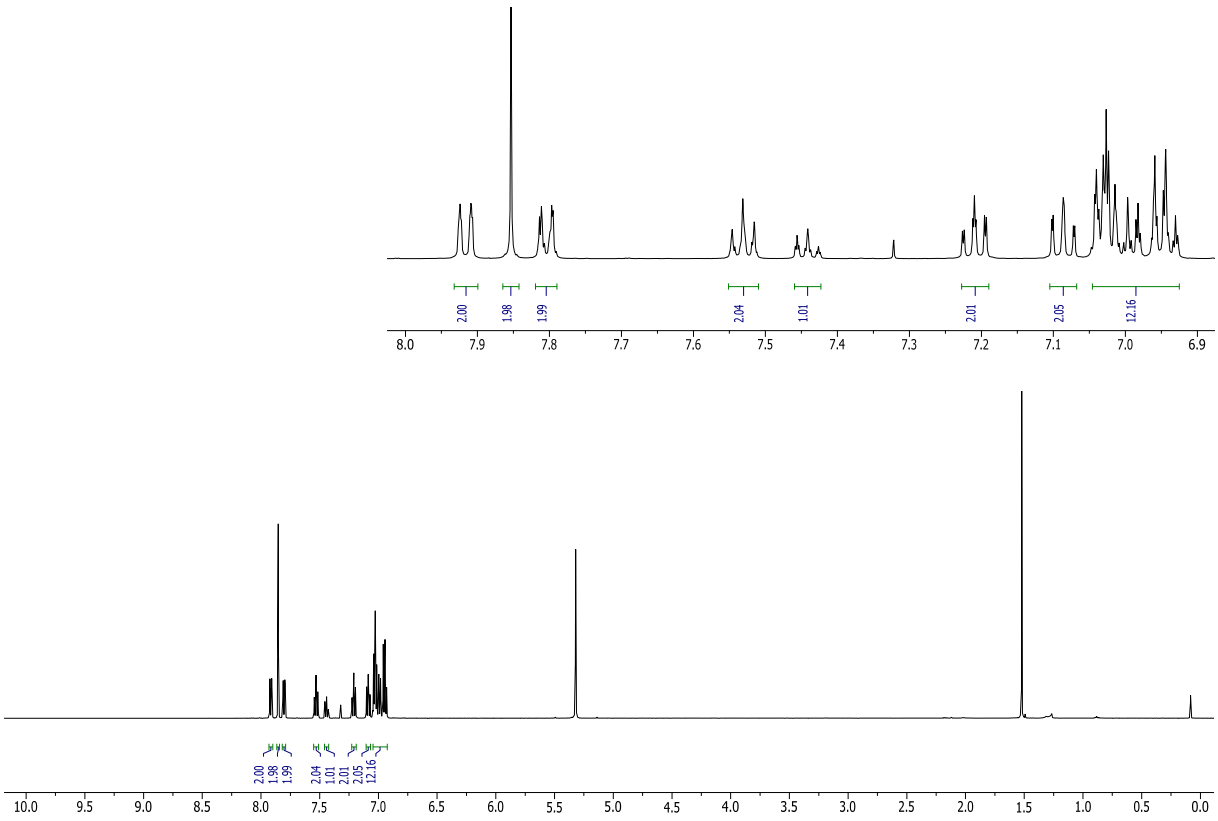



**Figure S35.** $^1$H-NMR spectrum of **5a** (500 MHz, $CD_2Cl_2$, r.t.).

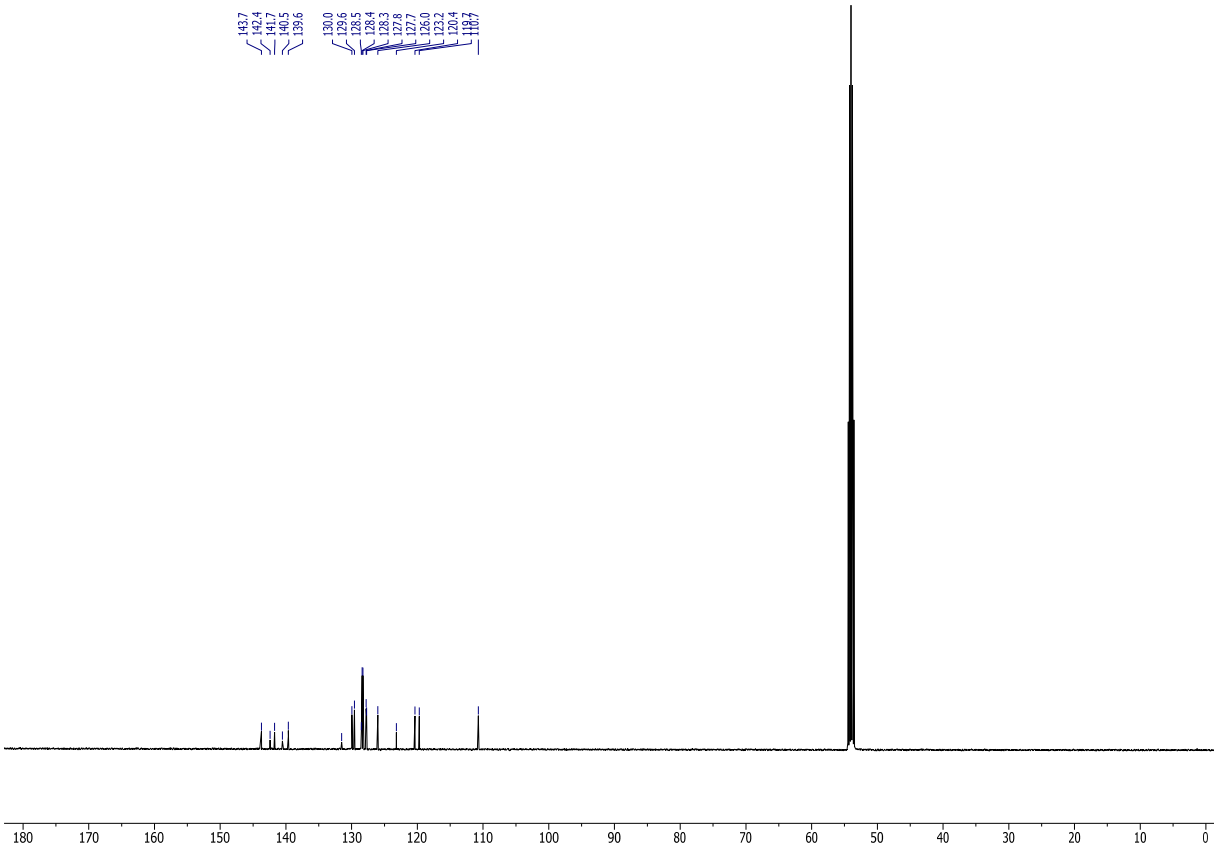
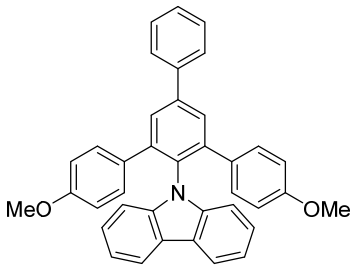



**Figure S36.** $^{13}$C-NMR spectrum of **5a** (126 MHz, $CD_2Cl_2$, r.t.).




**5b**
Chemical Formula: $C_{38}H_{29}NO_2$
Molecular Weight: 531,66

**5b) Yield** = 43 % $R_f$ = 0.44 (Cy:DCM = 1:1) **$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 7.95 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 0.9 Hz, 2H), 7.82 - 7.76 (m, 4H), 7.52 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 7.44 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.22 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 0.9 Hz, 2H), 7.11 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 0.9 Hz, 2H), 7.01 (dt, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 0.9 Hz, 2H), 6.93 (d, $^3J_{HH}$ = 8.8 Hz, 4H), 6.47 (d, $^3J_{HH}$ = 8.8 Hz, 4H), 3.85 (s, 6H); **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 159.4, 143.4, 141.7, 132.0, 129.6, 129.5, 129.5, 128.4, 127.8, 126.1, 123.3, 120.4, 119.7, 113.7, 110.7, 55.5; **MS (HRMS)**: *m/z* calculated for $C_{38}H_{29}NO_2$: 531.2198 u, found: 531.2196 u.

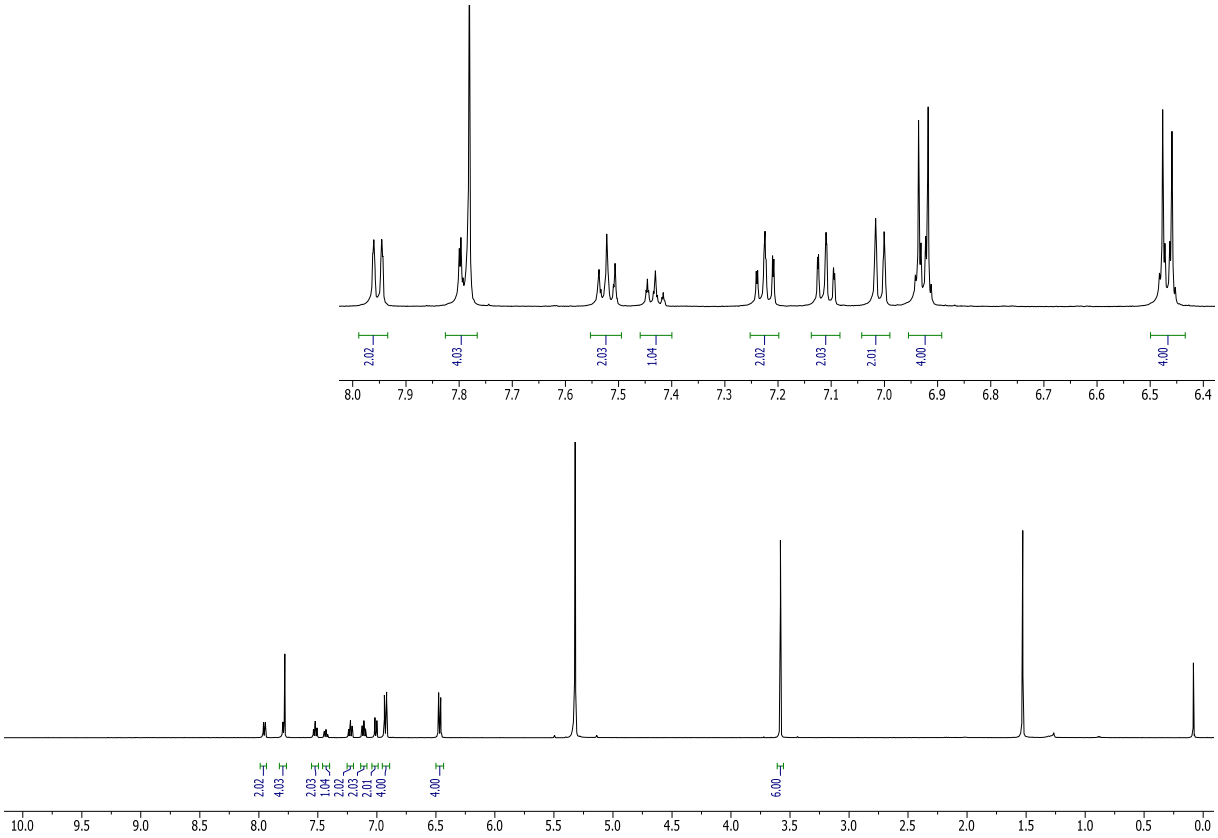



**Figure S37.** $^{1}$H-NMR spectrum of **5b** (500 MHz, $CD_2Cl_2$, r.t.).

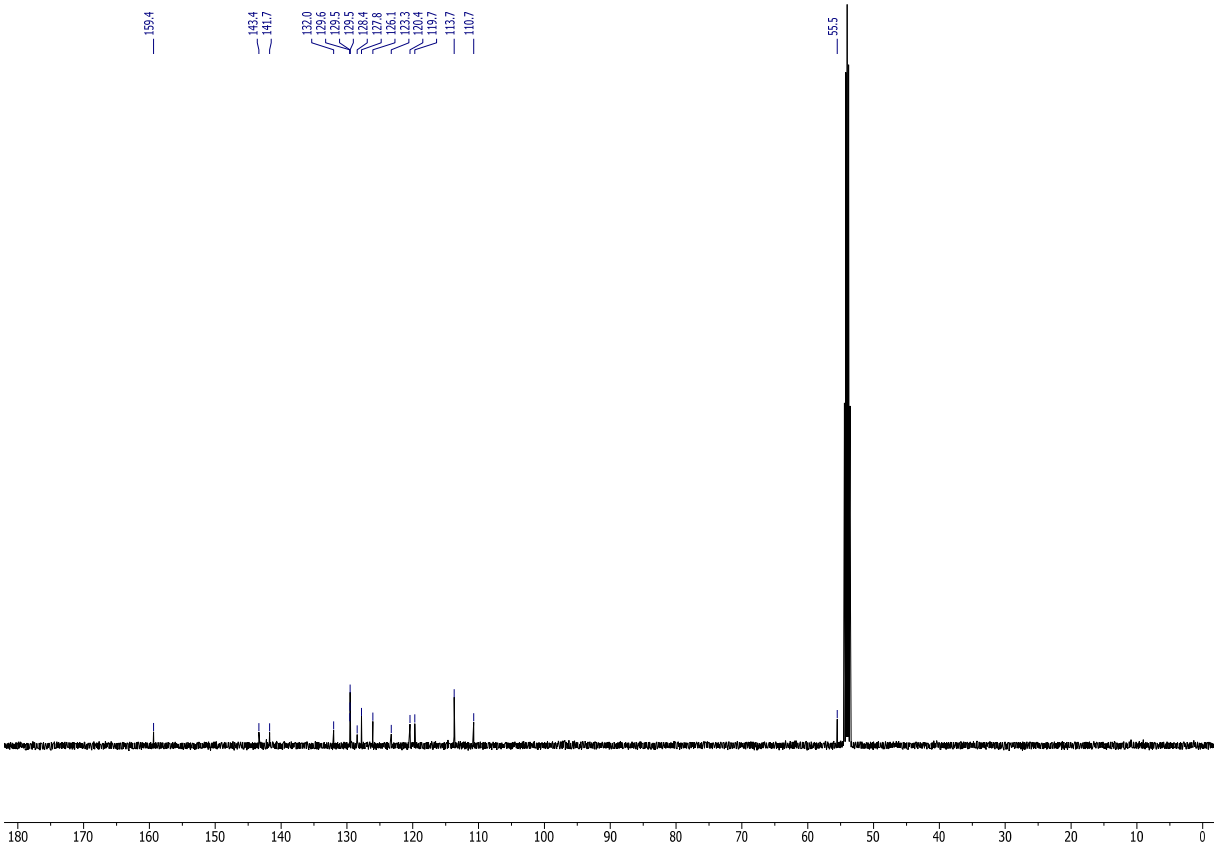
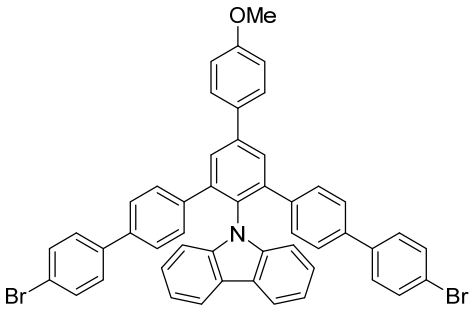



**Figure S38.** $^{13}$C-NMR spectrum of **5b** (126 MHz, $CD_2Cl_2$, r.t.).




**5c**
Chemical Formula: $C_{49}H_{33}Br_2NO$
Molecular Weight: 811,62

**5c) Yield** = 21 % $R_f$ = 0.52 (Cy:DCM = 1:1) **$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 7.93 (d, $^3J_{HH}$ = 7.7 Hz, 2H), 7.85 (s, 2H), 7.75 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 7.45 (d, $^3J_{HH}$ = 8.6 Hz, 4H), 7.29 – 7.21 (m, 6H), 7.17 (d, $^3J_{HH}$ = 8.5 Hz, 4H), 7.12 – 7.05 (m, 10H), 3.88 (s, 3H). **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 160.5, 143.2, 142.1, 141.9, 139.6, 139.1, 138.9, 132.3, 129.5, 129.0, 128.9, 128.9, 126.7, 126.2, 120.5, 119.9, 115.0, 110.7, 56.0. **MS (MALDI-pos, DCTB)**: *m/z* calculated for $C_{49}H_{33}Br_2NO$: 809.0929 u, found: 809.0920 u.

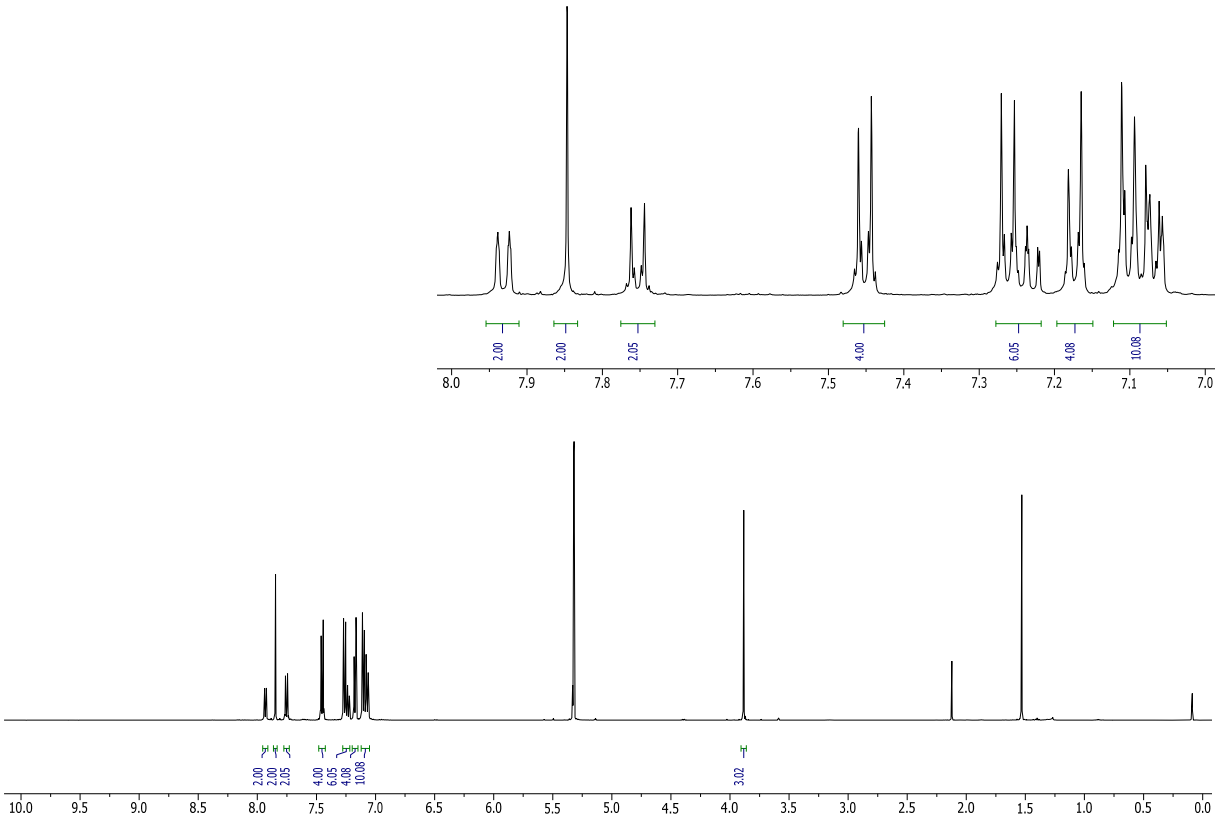



**Figure S39.** $^1$H-NMR spectrum of **5c** (500 MHz, $CD_2Cl_2$, r.t.).

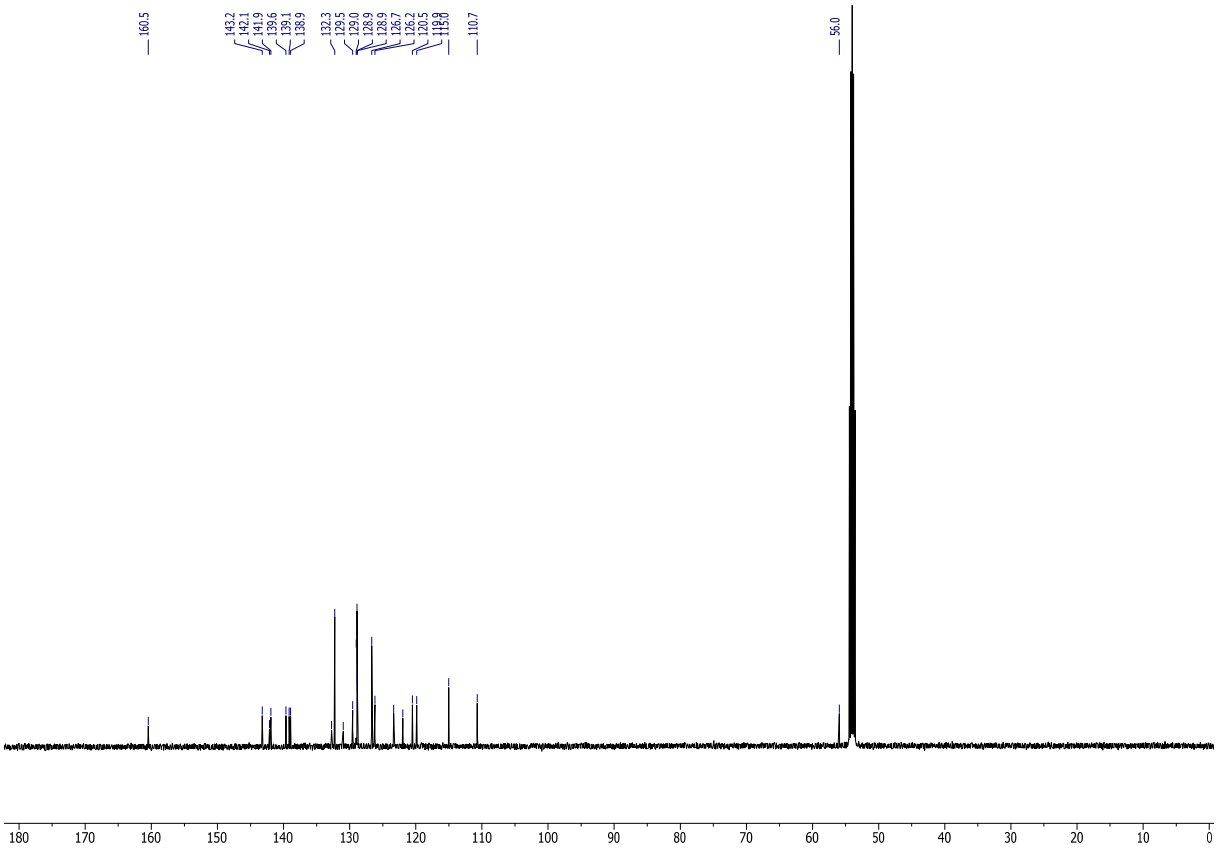
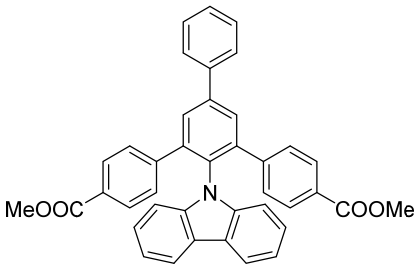



**Figure S40.** $^{13}$C-NMR spectrum of **5c** (126 MHz, $CD_2Cl_2$, r.t.).




**5d**
Chemical Formula: $C_{40}H_{29}NO_4$
Molecular Weight: 587,68

**5d) Yield** = 17 % $R_f$ = 0.35 (Cy:EE = 7:1) **$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 7.93 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.0 Hz , 2H), 7.90 (s, 2H), 7.81 – 7.78 (m, 2H), 7.59 (d, $^3J_{HH}$ = 8.7 Hz, 4H), 7.57 – 7.52 (m, 2H), 7.47 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 2.0 Hz), 7.22 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.0 Hz, 2H), 7.13 – 7.09 (m, 6H), 6.99 (dt, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.0 Hz, 2H), 3.75 (s, 6H). **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 166.9, 144.0, 142.8, 142.8, 141.5, 140.1, 131.6, 130.4, 129.7, 129.5, 128.8, 128.5, 127.8, 126.3, 123.3, 120.6, 120.1, 110.4, 52.4. **MS (HRMS)**: *m/z* calculated for $C_{40}H_{29}NO_4$: 587.2097 u, found: 587.2089 u.

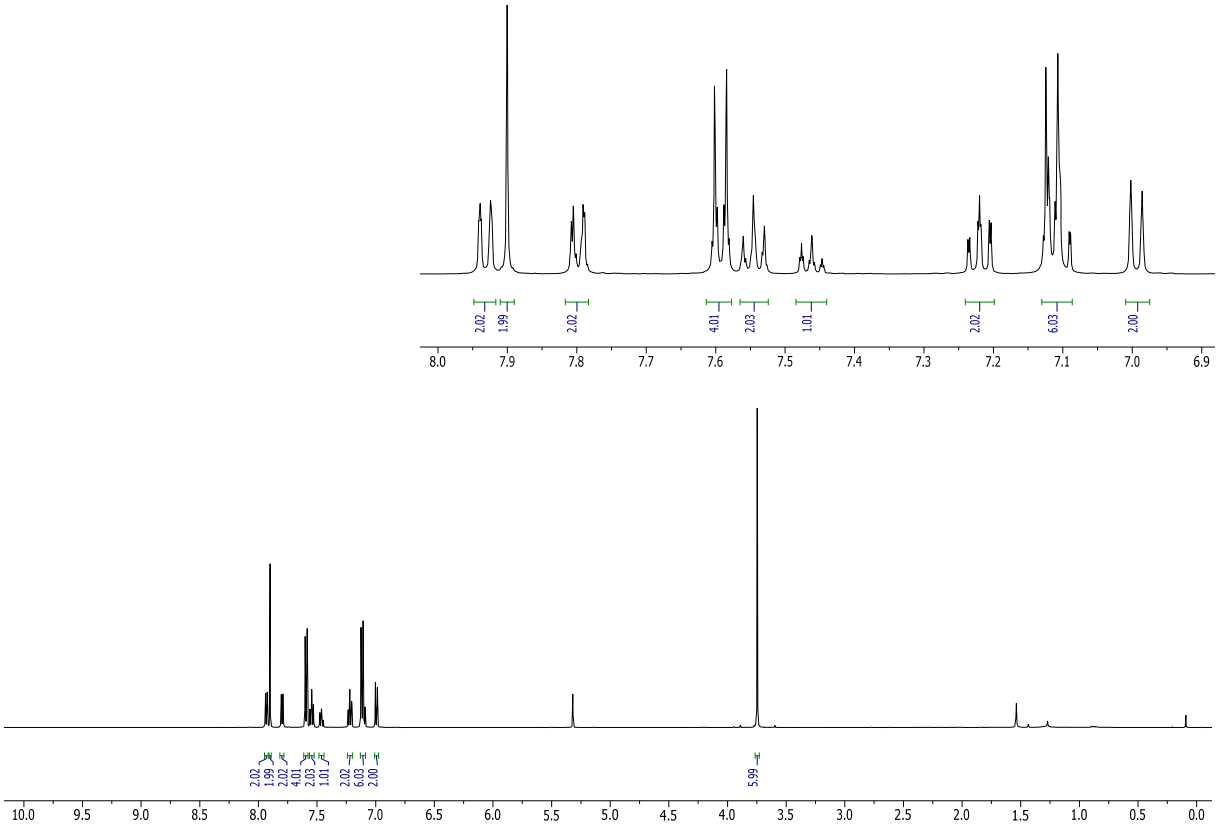



**Figure S41.** $^{1}$H-NMR spectrum of **5d** (500 MHz, $CD_2Cl_2$, r.t.).

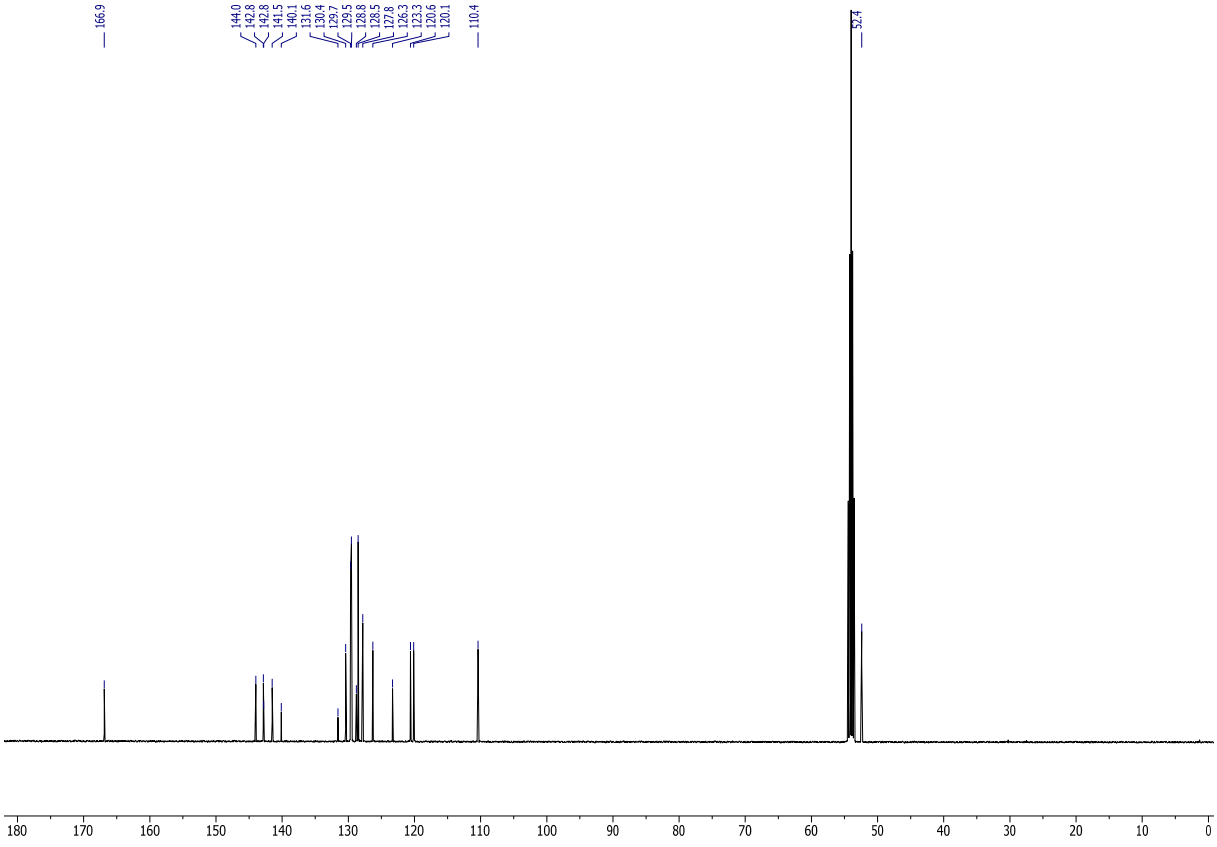
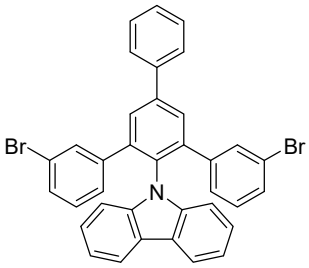



**Figure S42.** $^{13}$C-NMR spectrum of **5d** (126 MHz, $CD_2Cl_2$, r.t.).




**5e**
Chemical Formula: $C_{36}H_{23}Br_2N$
Molecular Weight: 629,40

**5e**) **Yield** = 43 % $R_f$ = 0.66 (Cy:DCM = 2:1) **$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 7.96 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.86 (s, 2H), 7.80 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.2 Hz, 2H), 7.55 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.46 (t, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.9 Hz, 1H), 7.30 – 7.24 (m, 4H), 7.14 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.0 Hz, 4H), 6.99 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 6.89 (ddd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz, $^4J_{HH}$ = 1.0 Hz, 2H), 6.78 (t, $^3J_{HH}$ = 7.8 Hz, 2H). **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 142.8, 142.4, 141.7, 141.3, 140.1, 131.6, 130.8, 130.2, 129.9, 129.7, 127.8, 127.0, 126.3, 122.2, 120.6, 120.1, 110.4. **MS (MALDI-pos, DCTB)**: *m/z* calculated for $C_{36}H_{23}Br_2N$: 627.0197 u, found: 627.0210 u.

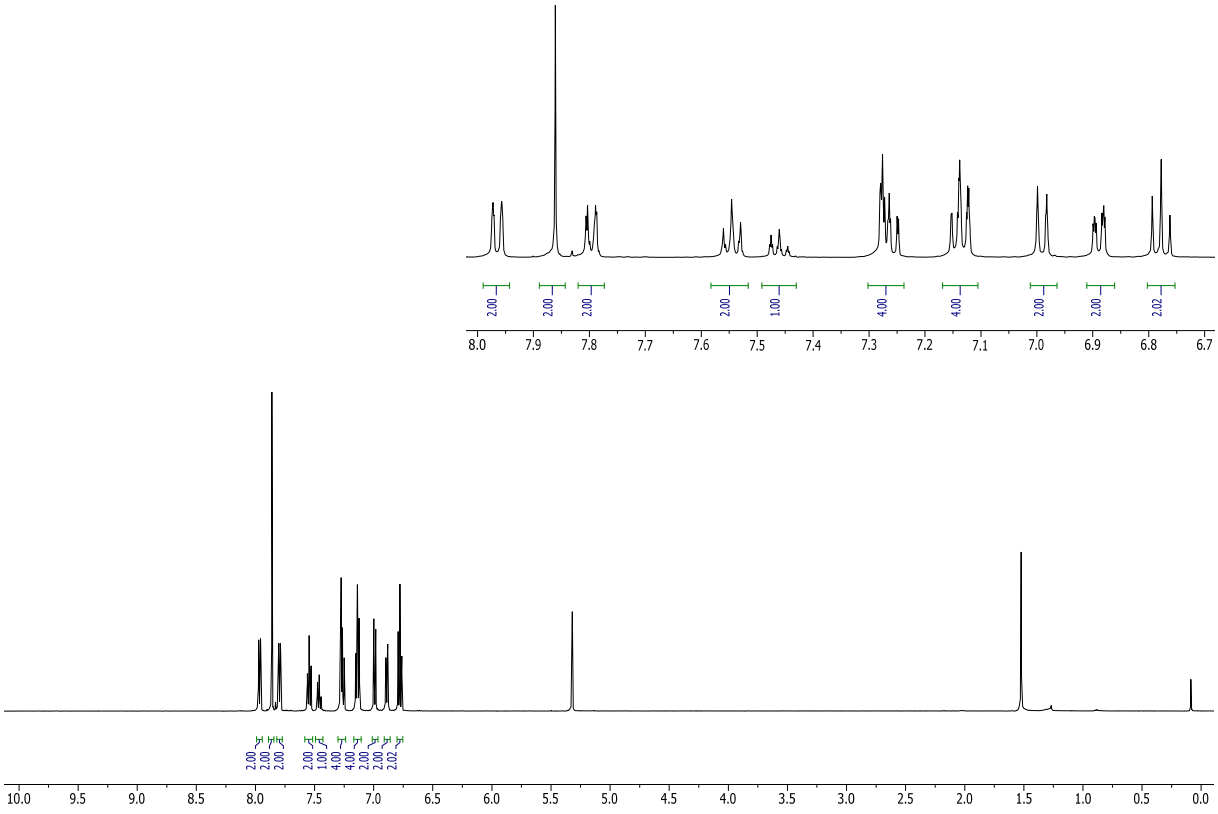


**Figure S43.** $^1$H-NMR spectrum of **5e** (500 MHz, $CD_2Cl_2$, r.t.).

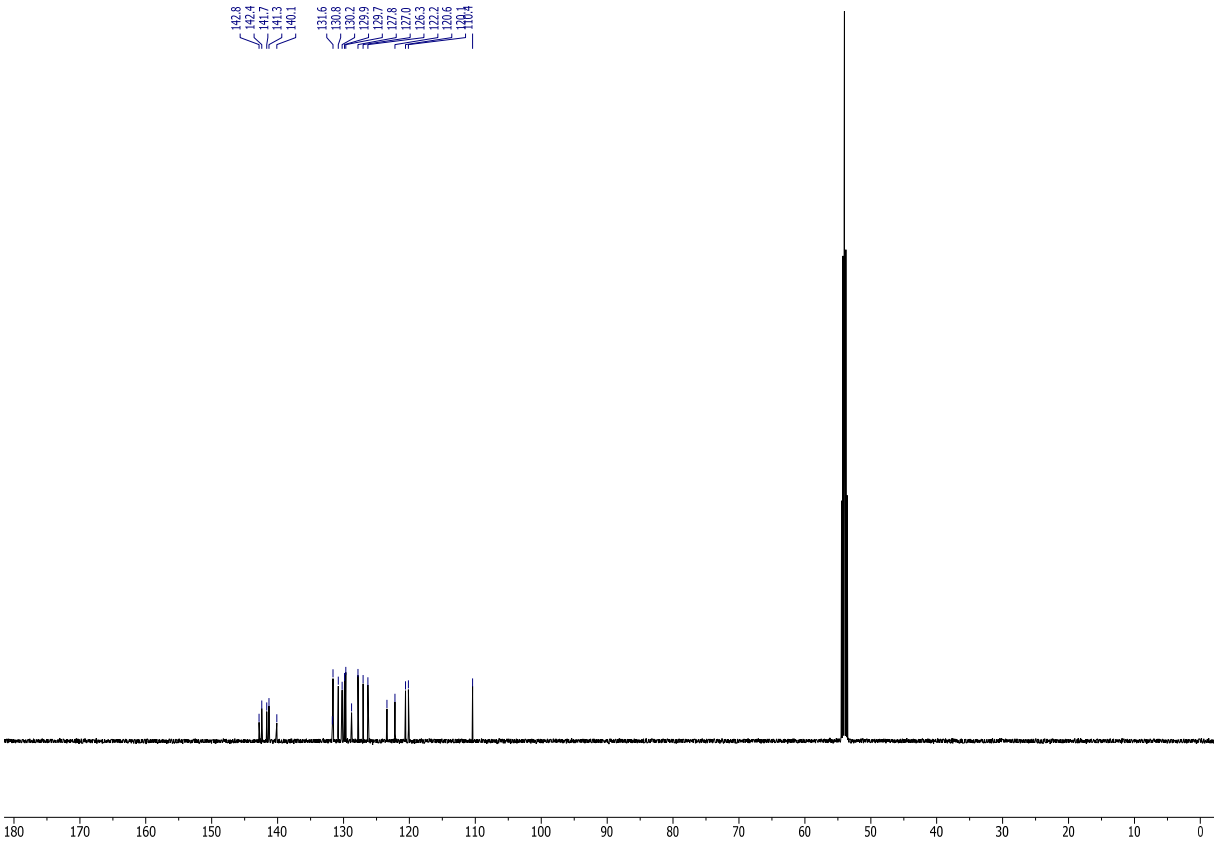
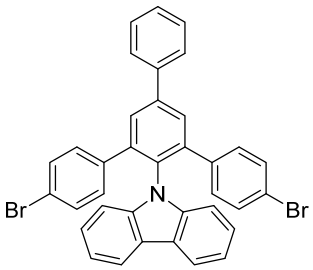



**Figure S44.** $^{13}$C-NMR spectrum of **5e** (126 MHz, $CD_2Cl_2$, r.t.).




**5f**
Chemical Formula: $C_{36}H_{23}Br_2N$
Molecular Weight: 629,40

**5f**) **Yield** = 22 % $R_f$ = 0.66 (Cy:DCM = 2:1) **$^1$H-NMR** (500 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 7.96 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 7.82 (s, 2H), 7.78 (d, $^3J_{HH}$ = 7.2 Hz, 2H), 7.54 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 7.45 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.24 (t, $^3J_{HH}$ = 8.1 Hz, 2H), 7.14 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.08 (d, $^3J_{HH}$ = 8.6 Hz, 4H), 6.98 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 6.90 (d, $^3J_{HH}$ = 8.6 Hz, 4H). **$^{13}$C-NMR** (126 MHz, $CD_2Cl_2$, r.t.): δ [ppm] = 142.7, 142.7, 141.5, 140.2, 138.4, 131.5, 130.1, 130.1, 129.6, 128.7, 127.8, 126.3, 123.3, 122.0, 120.7, 120.1, 110.4. **MS (MALDI-pos, DCTB)**: *m/z* calculated for $C_{36}H_{23}Br_2N$: 627.0197 u, found: 627.0222 u.

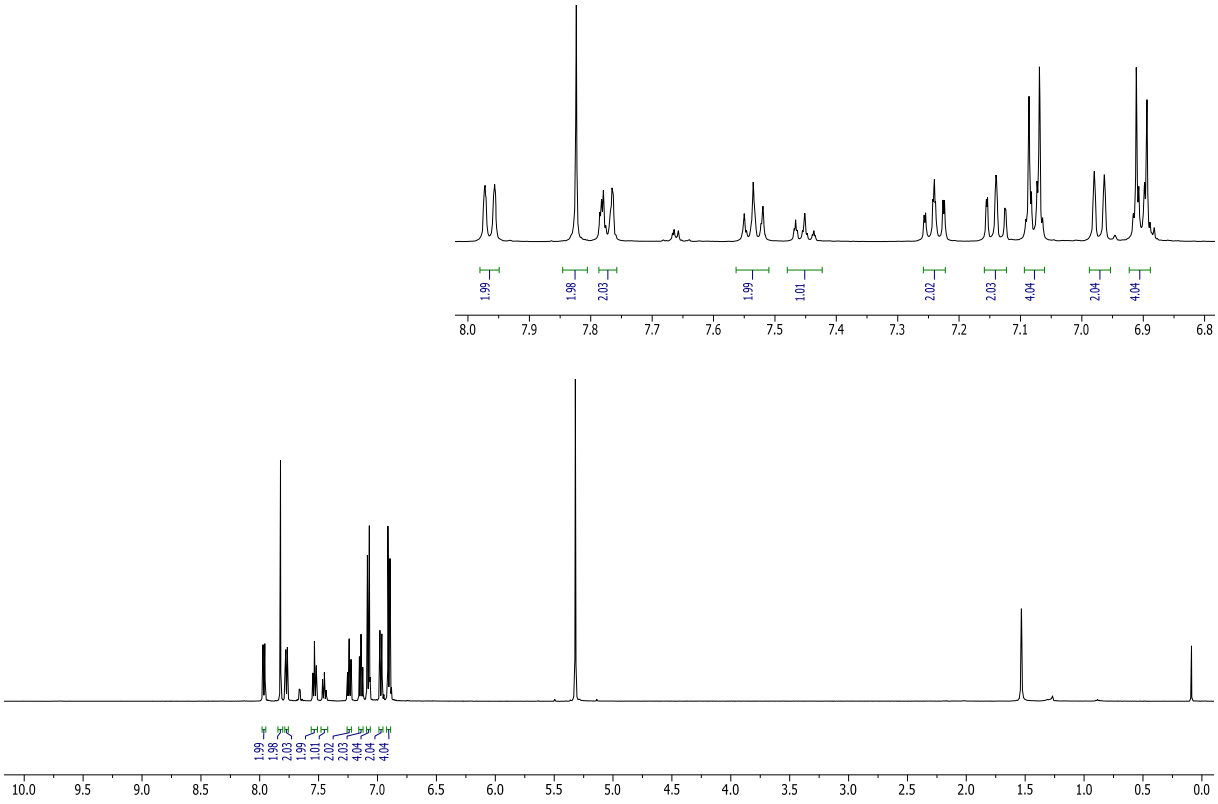



**Figure S45.** $^{1}$H-NMR spectrum of **5f** (500 MHz, $CD_2Cl_2$, r.t.).

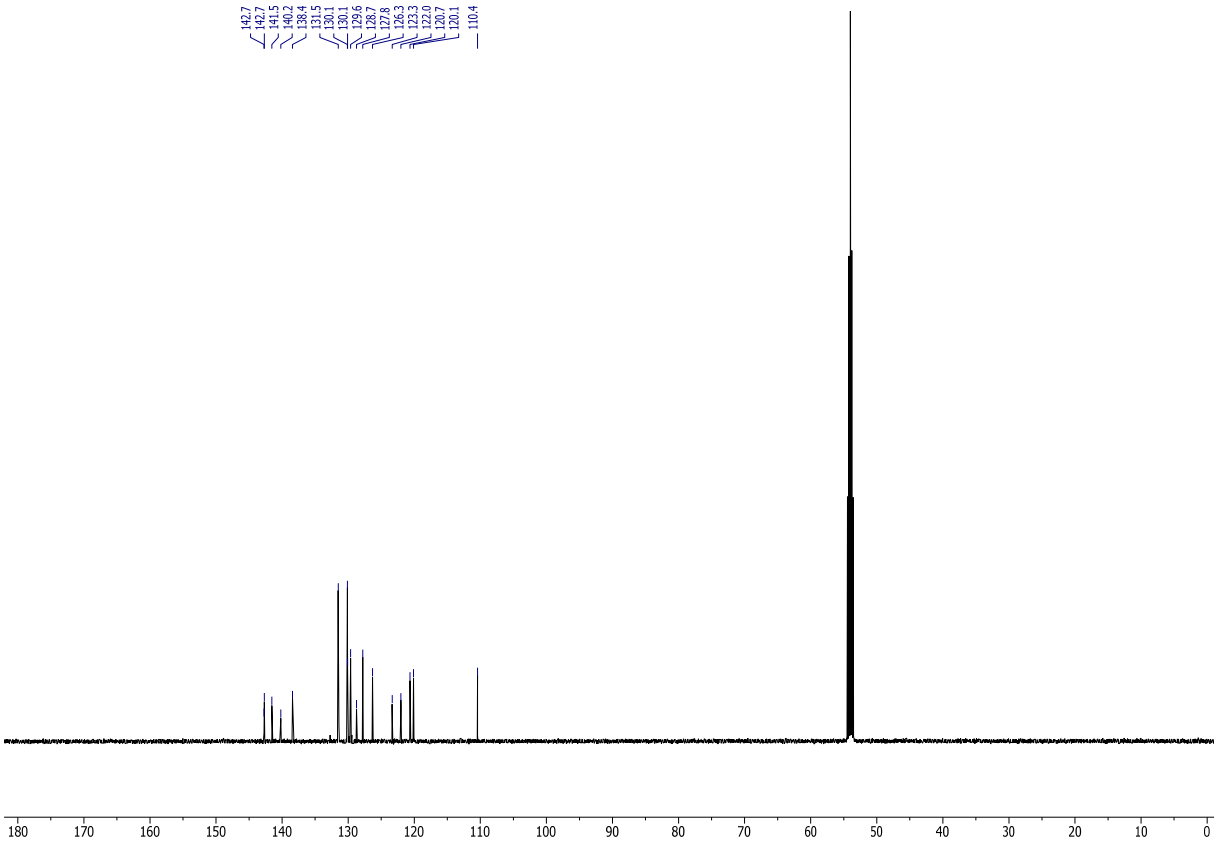
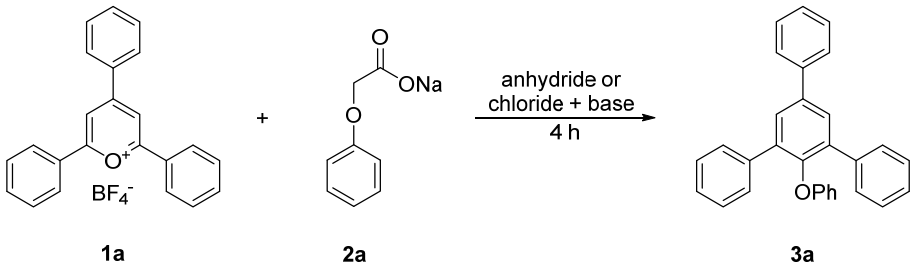



**Figure S46.** $^{13}$C-NMR spectrum of **5f** (126 MHz, $CD_2Cl_2$, r.t.).

# 5. Screening of acid anhydrides and chlorides

The screening was performed on the basis of the condensation between the unsubsituted pyrylium salt **1a** and sodium phenoxyacetate **2a** with the same batch size and reaction time to the product **3a**. In the case of the chlorides, a base was also added to deprotonate the *in situ* formed mixed anhydride. In all cases, sodium *tert*-butoxide was used as a non-nucleophilic base.




**1a** **2a** **3a**

**Scheme S3**: Screening reaction of different anhydrides and chlorides.

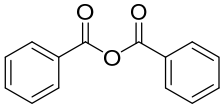
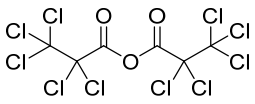
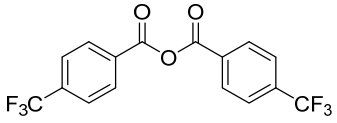
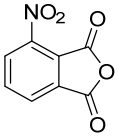
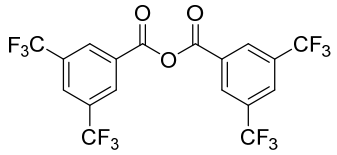
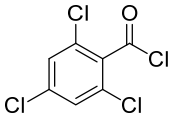
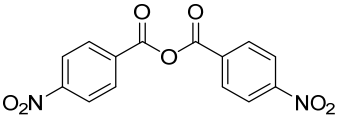
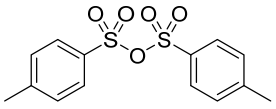
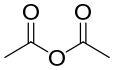
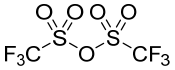
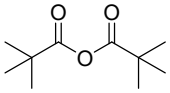
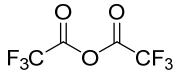
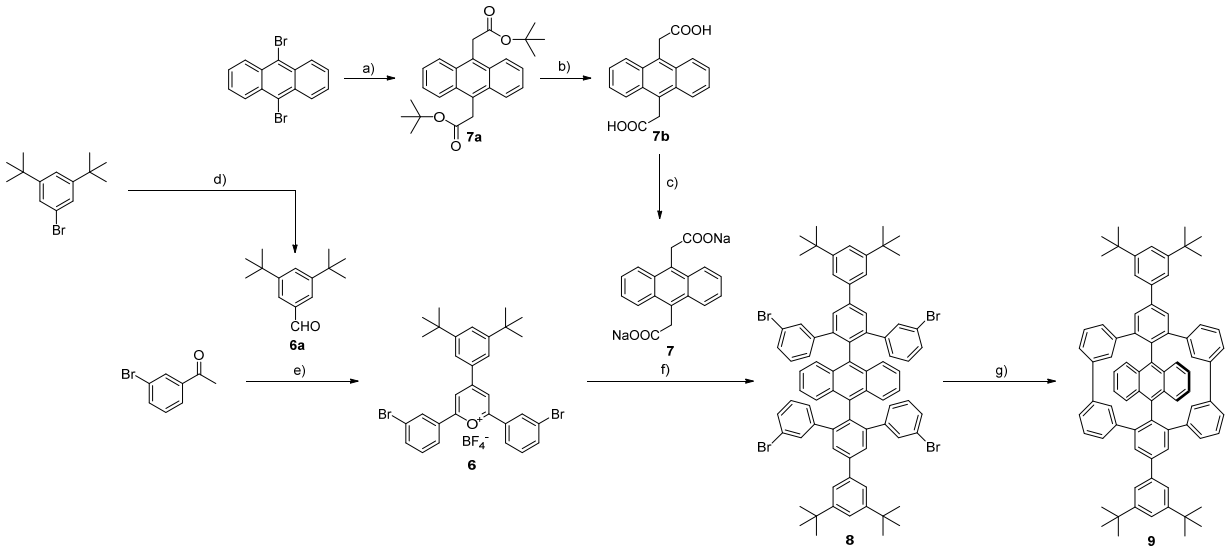
| Used anhydride or chloride | Yield (%) | Used anhydride or chloride | Yield (%) |
|---|---|---|---|
|  | 28 |  | - |
|  | 38 |  | - |
|  | 38 |  | 10 |
|  | 14 |  | - |
|  | 21 |  | - |
|  | 24 |  | - |
|  | - | | |

**Table S1**: Yields of product **3a** with different anhydrides and chlorides.

Various substituted carboxylic acid anhydrides and chlorides, as well as sulfonic acid anhydrides and chlorides were used for the screening. The product could not be obtained from any of the sulfonic acid derivatives. The perfluorinated carboxylic acid anhydrides are not able to dissolve the pyrylium salt, hence no reaction is occurred. The benzoic acid anhydrides proved to be the most suitable. These were then used with various electron-withdrawing substituents, from which both, the (4-trifluoromethyl)benzoic anhydride and 3,5-bistrifluoromethylbenzoic anhydride, gave the best yields. Therefore, for all condensations described here, the (4-trifluoromethyl)benzoic anhydride was used.

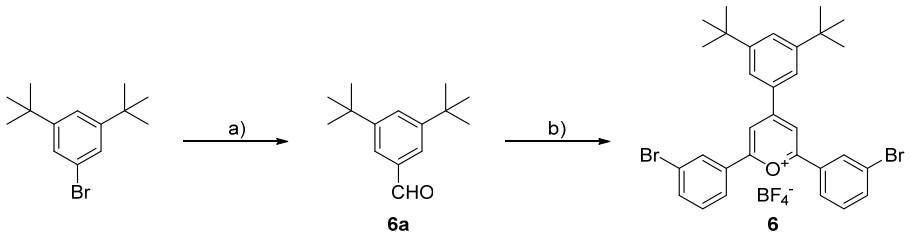
# 6. Synthesis of 9

## 6.1 Synthetic strategy



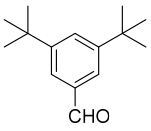

**Scheme S4:** a) 1. *tert*-Butyl bromoacetate, Zn*, THF, r.t., 1 h; 2. $AnBr_2$, $Pd(dba)_2$, $P(t\text{-}Bu)_3$, 80 °C, 19 h, 77 %; b) $F_3CCOOH$, DCM, r.t., 19 h, 82 %; c) NaOMe, MeOH, r.t., 1.5 h, quant.; **d)** 1. *n*BuLi (2.5 M in hexane), THF, -78 °C, 30 min; 2. DMF, -78 °C to r.t., 17 h, 3. $H_2O$, r.t., 30 min, 99 %; **e)** $BF_3$*$OEt_2$, DCE, 80 °C, 2 h, 34 %; **f)** benzoic anhydride, 160 °C, 4 h, 2 % or 4-(trifluoromethyl)benzoic anhydride, 160 °C, 4 h, 13 %; **g)** $Ni(COD)_2$, bipy, THF/COD, 120°C, 20 min, 21 %.

## 6.2 Synthesis of pyrylium salt 6




**6a** **6**

**Scheme S5:** a) 1. *n*BuLi (2.5 M in hexane), THF, -78 °C, 30 min; 2. DMF, -78 °C to r.t., 17 h; 3. $H_2O$, r.t., 30 min, 99 %; b) *m*-bromoacetophenone, $BF_3$*$OEt_2$, $C_2H_4Cl_2$, reflux, 3 h, 34 %.




**6a**
Chemical Formula: $C_{15}H_{22}O$
Molecular Weight: 218,34

Synthesis of 3,5-di-*tert*-butylbenzaldehyde (**6a**): 3,5-di-*tert*-butylbromobenzene (15.3 g, 56.8 mmol, 1.00 eq) was dissolved in dry THF (125 mL). The solution was cooled down to -78 °C and *n*BuLi (25.0 mL, 62.5 mmol, 1.10 eq, 2.5 M in hexane) was slowly added. The solution was stirred for 30 minutes and then DMF (4.80 mL, 62.5 mmol, 1.10 eq) was added. The reaction mixture was allowed to warm up to room temperature, and stirred overnight. Water was added, and the reaction mixture was stirred for another 30 minutes. The aqueous layer was separated and extracted three times with $Et_2O$. The combined organic layers were washed with dilute hydrochloric acid, water and brine, and dried over $Na_2SO_4$. The solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography ($SiO_2$, eluent: CH:DCM, 1:2, $R_f$ = 0.56). The product was obtained as a colorless solid (12.3 g, 56.2 mmol, 99 %).

**$^1$H-NMR** (500 MHz, $CDCl_3$, r.t.): δ [ppm] = 10.01 (s, 1H), 7.73 (d, $^4J_{HH}$ = 1.9 Hz, 2H), 7.71 (t, $^4J_{HH}$ = 1.9 Hz, 1H) 1.37 (s, 18H). **$^{13}$C-NMR** (126 MHz, $CDCl_3$, r.t.): δ [ppm] = 193.4, 152.0, 136.3, 129.1, 124.3, 35.1, 31.5. **MS (EI, 70 eV)**, *m/z* (%): 218.1 (15) $[M]^{+\cdot}$, 203.1 (100) $[M\text{-}CH_3\cdot]^+$.

Analytical data in accordance with the literature.[8]

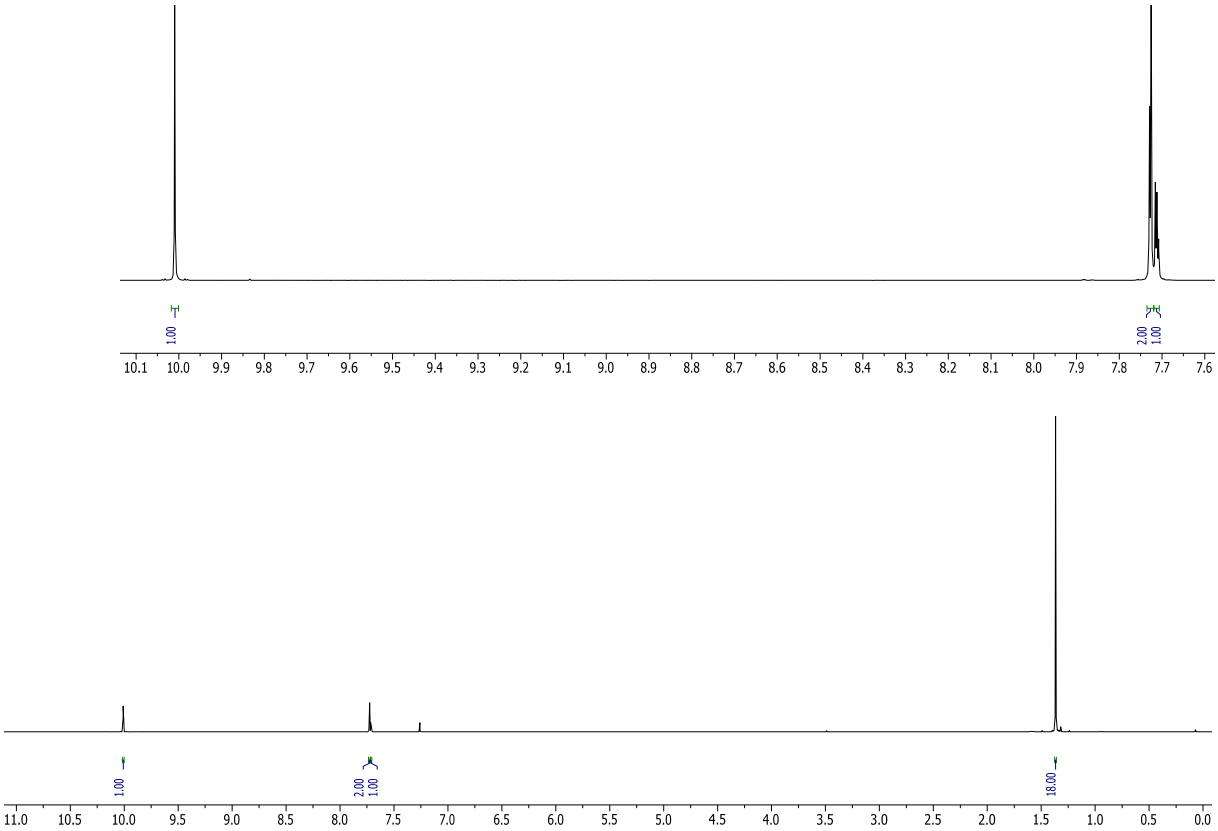



**Figure S47.** $^{1}$H-NMR spectrum of **6a** (500 MHz, $CDCl_3$, r.t.).

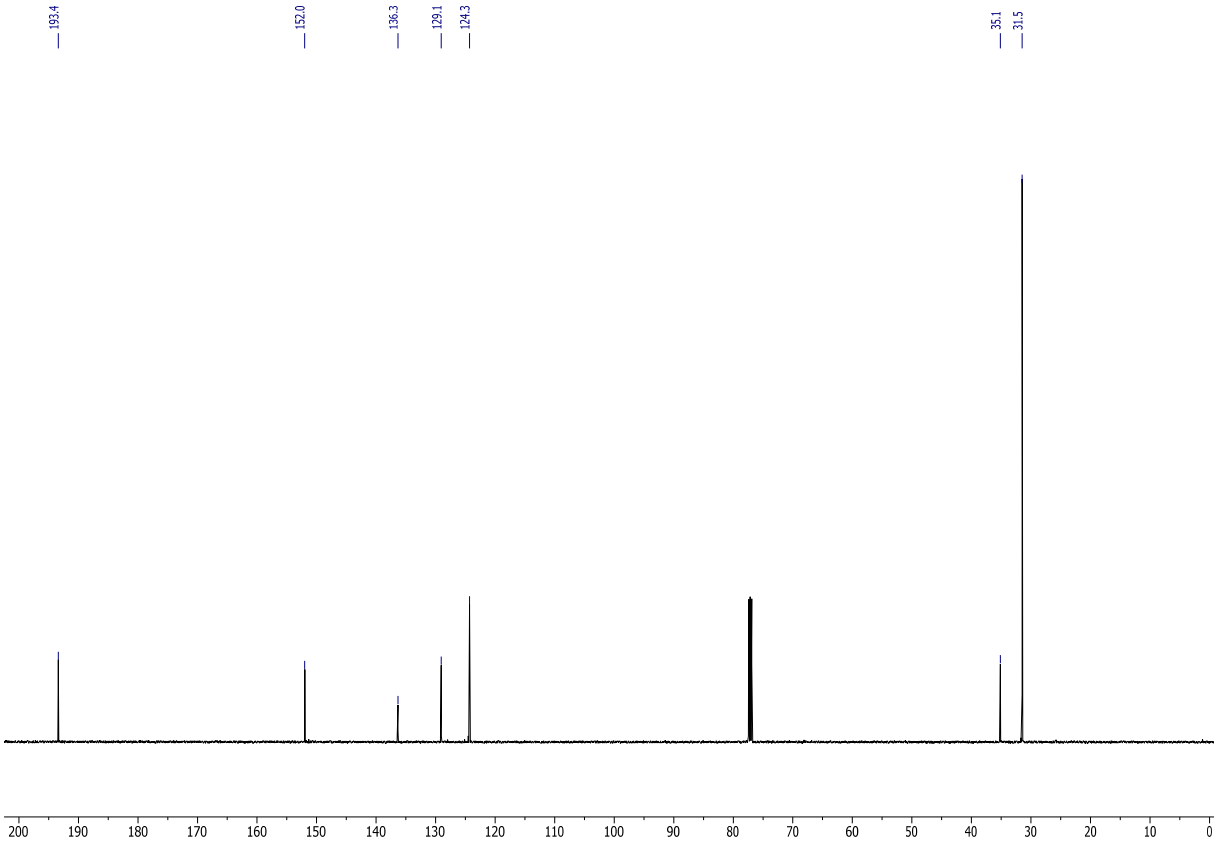
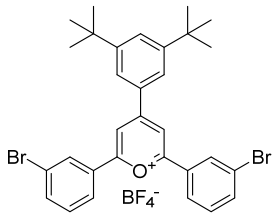



**Figure S48.** $^{13}$C-NMR spectrum of **6a** (126 MHz, $CDCl_3$, r.t.).




**6**
Chemical Formula: $C_{31}H_{31}BBr_2F_4O$
Molecular Weight: 666,20

Synthesis of pyrylium salt **6**: 3,5-di-*tert*-butylbenzaldehyde (11.4 g, 52.3 mmol, 1.00 eq) was dissolved in 1,2-dichloroethane (20 mL) and *m*-bromoacetophenone (15.2 mL, 115 mmol, 2.20 eq) was added. Then, $BF_3$*$OEt_2$ (33.1 mL, 261 mmol, 5.00 eq) was slowly added at room temperature. The reaction mixture was stirred at 130 °C for 3 h. After cooling down to room temperature, the solution was poured into $Et_2O$ (600 mL). A yellow solid precipitated, which was filtered off, washed with $Et_2O$, recrystallized from acetone, and dried under vacuum. The product was obtained as a yellow solid (11.8 g, 17.8 mmol, 34 %).

**$^1$H-NMR** (500 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 9.14 (s, 2H), 8.72 (t, $^4J_{HH}$ = 1.9 Hz, 2H), 8.52 (ddd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.9 Hz, $^4J_{HH}$ = 0.9 Hz, 2H), 8.18 (d, $^4J_{HH}$ = 1.9 Hz, 2H), 8.08 (ddd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.9 Hz, $^4J_{HH}$ = 0.9 Hz, 2H), 7.88 (t, $^4J_{HH}$ = 1.7 Hz, 1H), 7.78 (t, $^3J_{HH}$ = 8.0 Hz, 2H), 1.45 (s, 18H). **$^{13}$C-NMR** (126 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 168.6, 167.2, 152.5, 137.4, 132.8, 131.9, 131.4, 131.3, 129.2, 128.1, 124.5, 122.9, 117.3, 35.2, 31.1. **MS (ESI+)**: *m/z* calculated for $C_{31}H_{31}Br_2O^+$: 577.0736 u, found: 577.070 u.

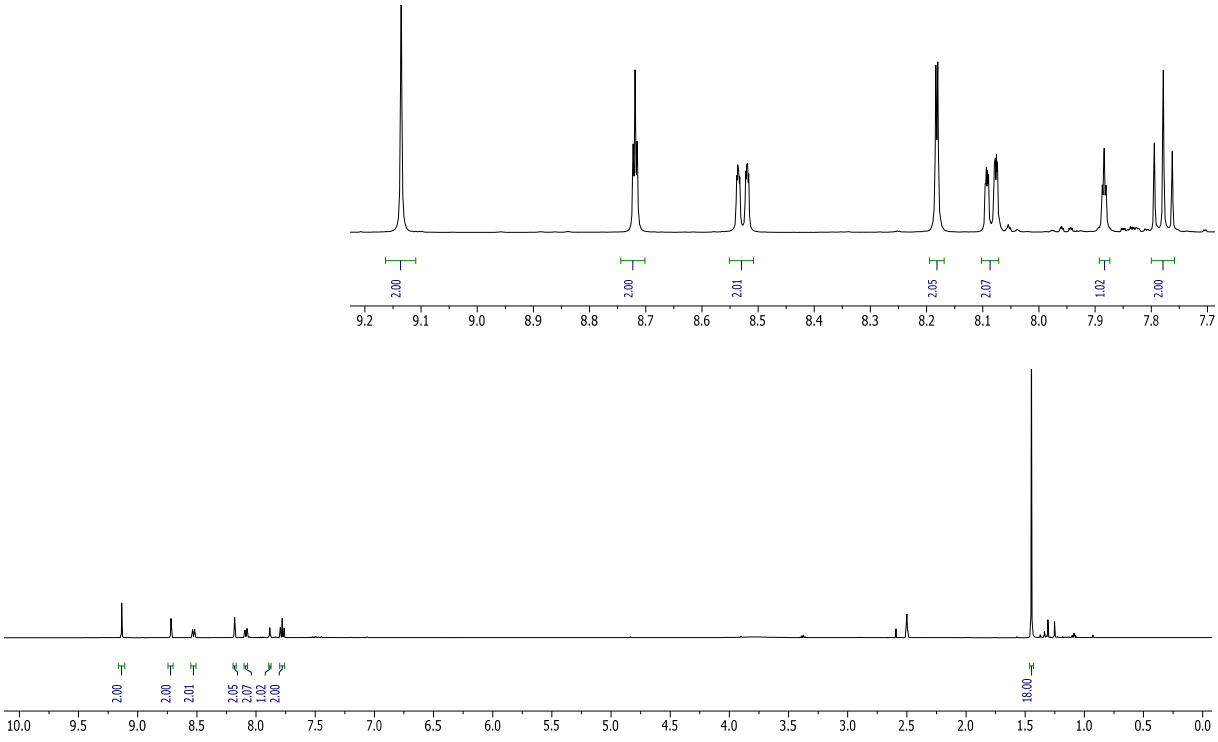



**Figure S49.** $^1$H-NMR spectrum of **6** (500 MHz, DMSO-$d_6$, r.t.).

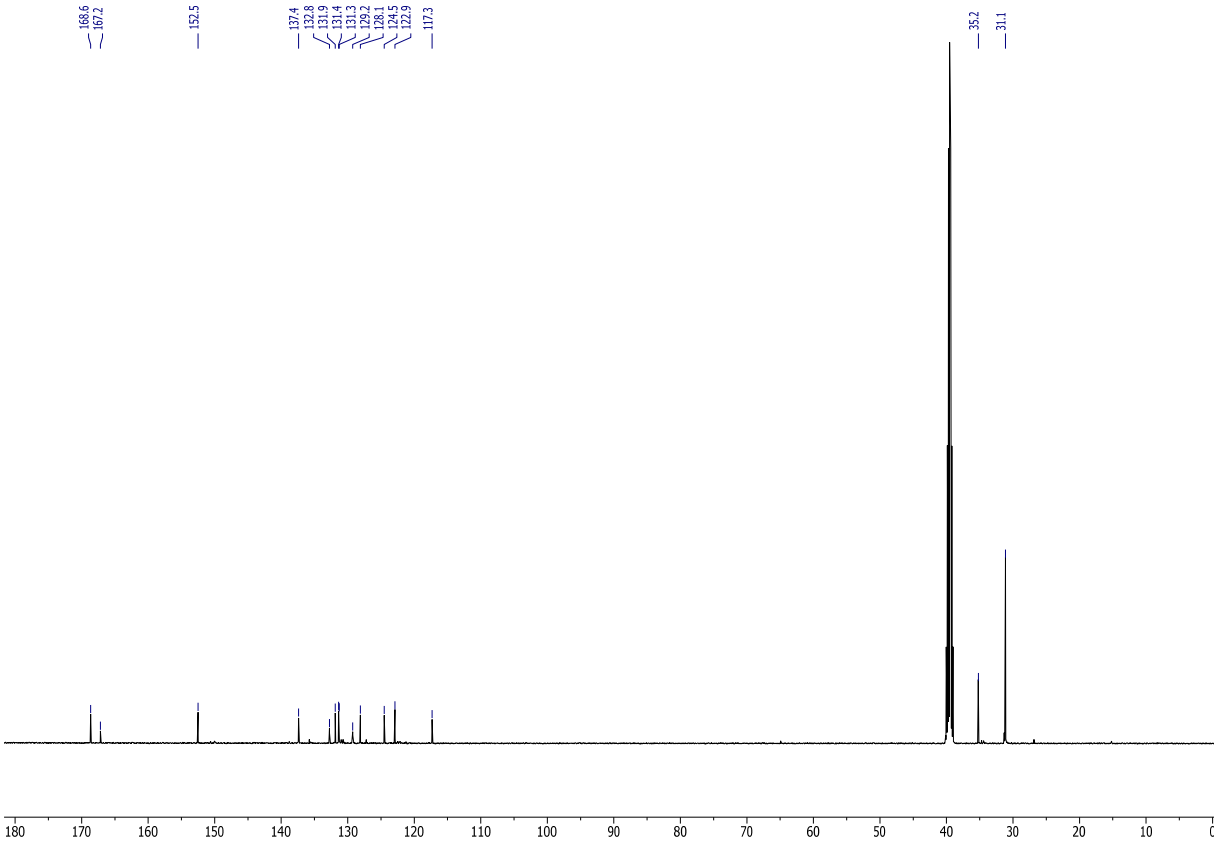
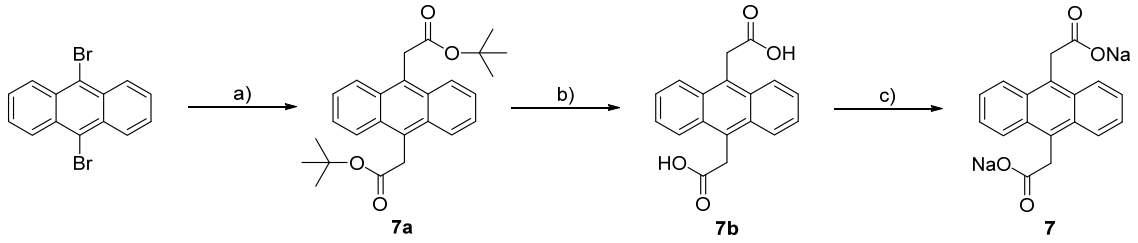
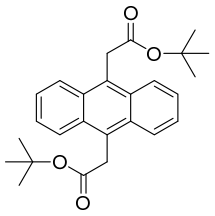



**Figure S50.** $^{13}$C-NMR spectrum of **6** (126 MHz, DMSO-$d_6$, r.t.).

# 6.3 Synthesis of anthracene sodium salt 7




**Scheme 6:** a) 1. *tert*-Butyl bromoacetate, Zn*, THF, r.t., 1 h; 2. $AnBr_2$, $Pd(dba)_2$, $P(t\text{-}Bu)_3$, 80 °C, 19 h, 77 %; b) $F_3CCOOH$, DCM, r.t., 19 h, 82 %; c) NaOMe, MeOH, r.t., 1.5 h, quant.



**7a**
Chemical Formula: $C_{26}H_{30}O_4$
Molecular Weight: 406,52

Synthesis of *tert*-butyl 2,2‘-(anthracene-9,10-diyl)diacetate (**7a**): Activated zinc powder (4.67 g, 71.4 mmol, 2.40 eq) was suspended in dry THF (150 mL). The zinc powder was activated prior by treatment with 2M hydrochloric acid for 30 minutes, filtering the powder off, washing it with acetone, and drying it under vacuum overnight. *tert*-Butylbromoacetate (10.6 mL, 71.4 mmol, 2.40 eq) was added, and the suspension was then stirred at room temperature for one hour. A white solid was formed and the temperature of the mixture strongly increased. Then, 9,10-dibromoanthracene (10.0 g, 29.8 mmol, 1.00 eq), tri-*tert*-butylphosphine (514 mg, 0.89 mmol, 0.03 eq) and $Pd(dba)_2$ (301 mg, 1.49 mmol, 0.05 eq) were added to the reaction mixture. The solution was stirred at 80 °C overnight. After cooling to room temperature, water and $Et_2O$ were added to the solution. The aqueous layer was separated from the organic phase, and extracted three times with $Et_2O$. The combined organic layers were washed with an aqueous solution of EDTA, water and brine, and were dried over $Na_2SO_4$. The solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography ($SiO_2$, eluent: Cy:DCM, 1:2, $R_f$ = 0.42). The product was obtained as a pale yellow solid (9.26 g, 22.8 mmol, 77 %).

**$^1$H-NMR** (500 MHz, $CDCl_3$, r.t.): δ [ppm] = 8.36 (dd, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 3.2 Hz, 4H), 7.55 (dd, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 3.2 Hz, 4H), 4.57 (s, 4H) 1.40 (s, 18H). **$^{13}$C-NMR** (126 MHz, $CDCl_3$, r.t.): δ [ppm] = 170.7, 130.6, 127.4, 125.6, 125.4, 81.3, 35.8, 28.2. **MS (EI, 70 eV)**, *m/z* (%): 406.2 (30) $[M]^{+\cdot}$, 350.1 (20) $[M\text{-}C_4H_8]^{+\cdot}$, 294.1 (75) $[M\text{-}2C_4H_8]^{+\cdot}$, 249.1 (100) $[M\text{-}2C_4H_8\text{-}CHO_2\cdot]^{+}$, 204.1 (90) $[C_{16}H_{12}]^{+\cdot}$, 202.0 (60) $[C_{16}H_{12}\text{-}H_2]^{+\cdot}$, 191.0 (22) $[C_{16}H_{12}\text{-}CH_3\cdot]^{+}$, 57.1 (75) $[C_4H_9]^{+}$.

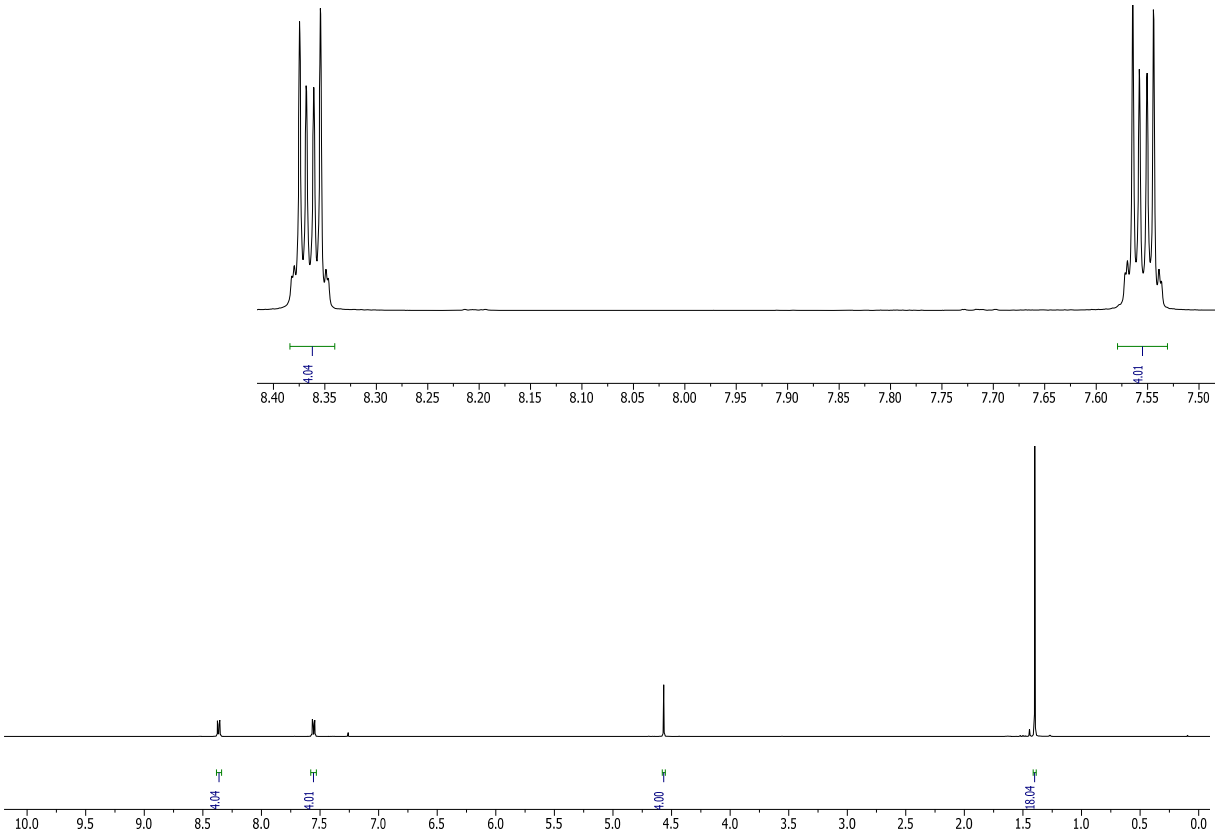



**Figure S51.** $^{1}$H-NMR spectrum of **7a** (500 MHz, $CDCl_3$, r.t.).

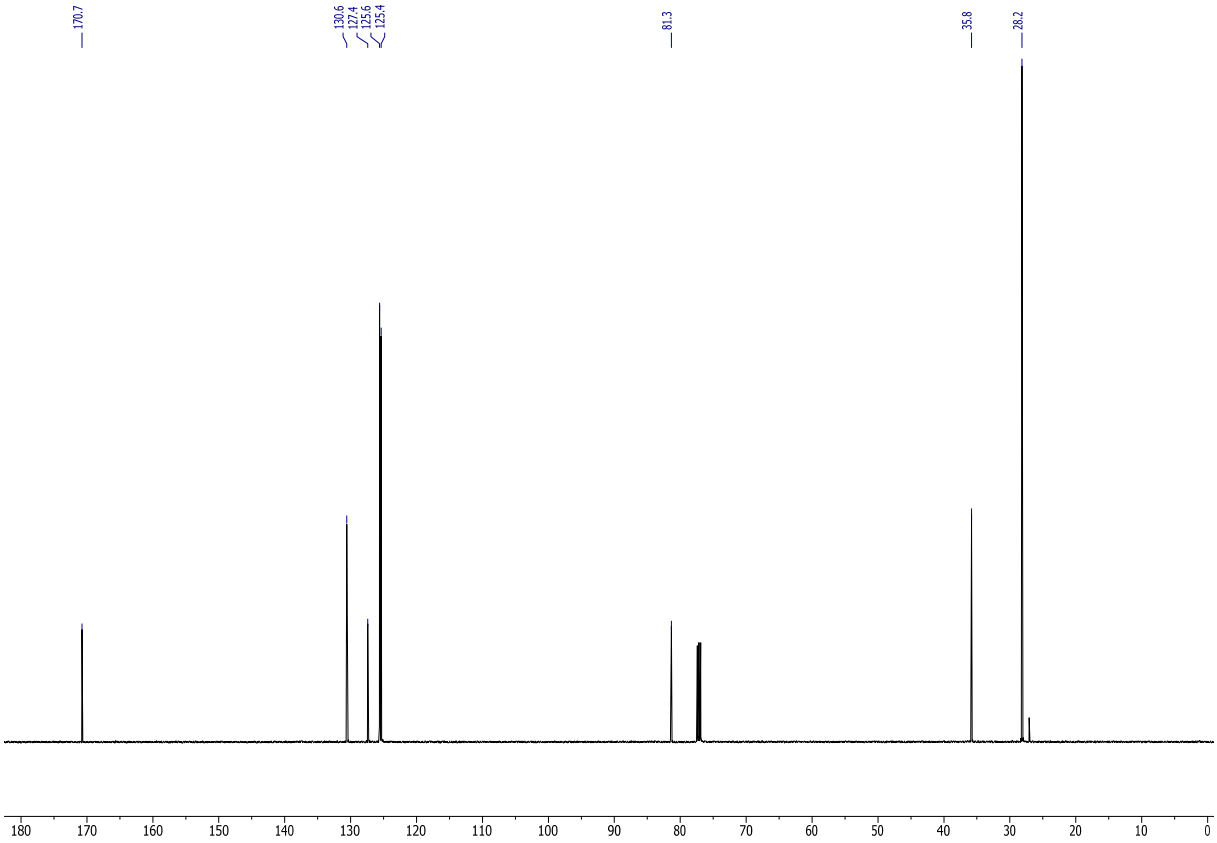
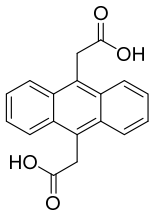



**Figure S52.** $^{13}$C-NMR spectrum of **7a** (126 MHz, $CDCl_3$, r.t.).



**7b**
Chemical Formula: $C_{18}H_{14}O_4$
Molecular Weight: 294,31

Synthesis of 2,2‘-(anthracene-9,10-diyl)diacetic acid (**7b**): *tert*-Butyl 2,2‘-(anthracene-9,10-diyl)diacetate (9.26 g, 22.8 mmol, 1.00 eq) was dissolved in DCM (80 mL). The solution was treated with trifluoroacetic acid (28.1 mL, 364 mmol, 16.0 eq) at room temperature. Already after a few minutes of stirring a white solid precipitated from the solution. The reaction mixture was stirred at room temperature overnight. The precipitate was dissolved by addition of an aqueous 20% NaOH-solution. The aqueous layer was washed with DCM. The combined organic layers were extracted three times with aqueous NaOH-solution. Concentrated hydrochloric acid was subsequently added to the combined aqueous layers, until a pale yellow solid precipitated. The solid was filtered off, washed with water, and dried under vacuum. The product was obtained as a pale yellow solid (5.46 g, 18.6 mmol, 82 %).

**$^1$H-NMR** (500 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 12.50 (s, 2H), 8.35 (dd, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 3.2 Hz, 4H), 7.59 (dd, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 3.2 Hz, 4H), 4.65 (s, 4H). **$^{13}$C-NMR** (126 MHz, DMSO-$d_6$, r.t.): δ [ppm] = 172.7, 129.9, 127.6, 125.6, 125.3, 33.7. **MS (EI, 70 eV)**, *m/z* (%): 294.0 (100) $[M]^{+\cdot}$, 249.0 (75) $[M\text{-}CHO_2\cdot]^+$, 205.0 (55) $[C_{16}H_{12}]^{+\cdot}$, 191.0 (20) $[C_{16}H_{12}\text{-}CH_3\cdot]^+$.

Analytical data in accordance with the literature.[9]

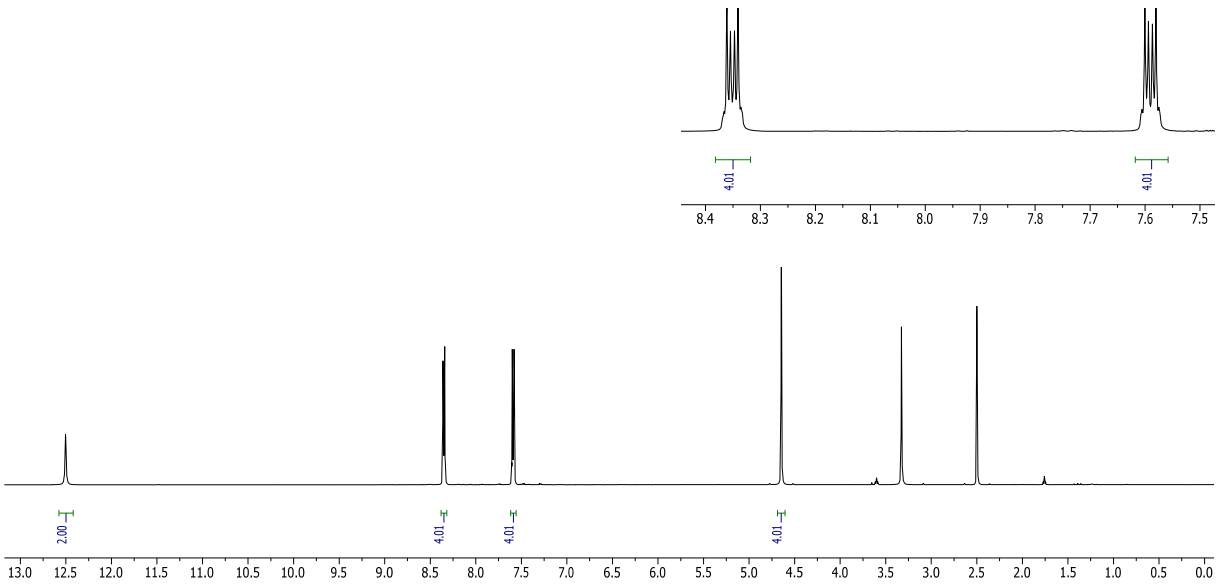



**Figure S53.** $^1$H-NMR spectrum of **7b** (500 MHz, DMSO-$d_6$, r.t.).

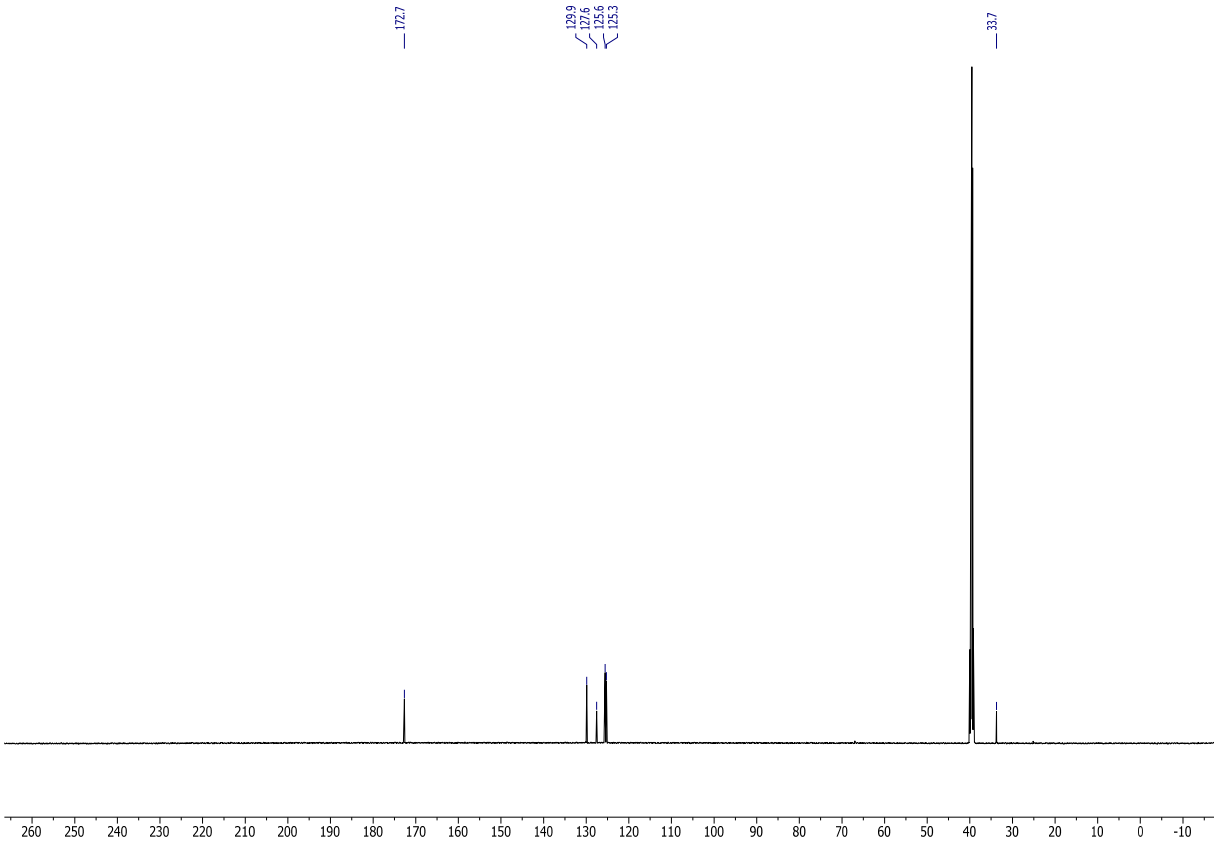
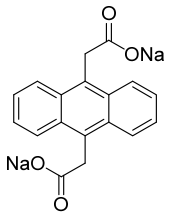


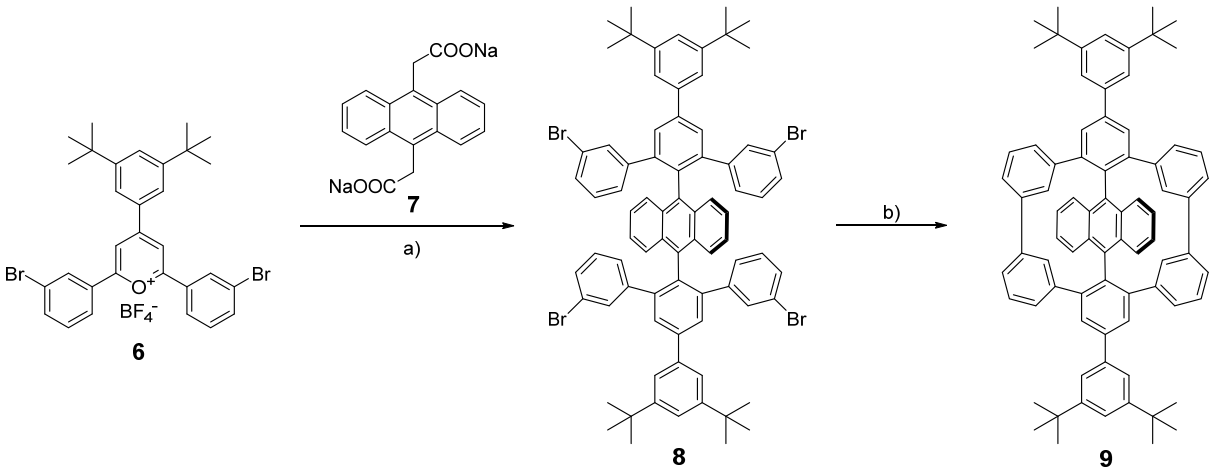

**Figure S54.** $^{13}$C-NMR spectrum of **7b** (126 MHz, DMSO-$d_6$, r.t.).




**7**
Chemical Formula: $C_{18}H_{12}Na_2O_4$
Molecular Weight: 338,27

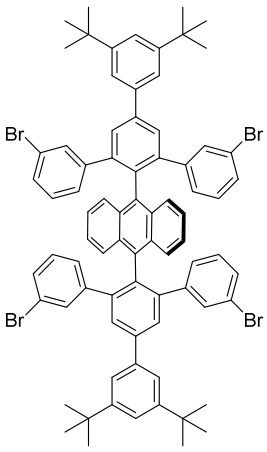
Synthesis of sodium anthracene salt **7**: A sodium methoxide solution (25% in methanol, 4.26 ml, 18.6 mmol, 1.0 eq.) was added slowly to a mixture 2,2‘-(anthracene-9,10-diyl)diacetic acid (5.46 g, 18.6 mmol, 1.0 eq.) in methanol (150 ml), and it was stirred at room temperature for 16 h. The solvent was removed under reduced pressure, and the product was isolated as a colourless solid (6.29 g, 18.6 mmol, quantitative) and used without further purification.

## 6.4 Synthesis of 8 and 9




**Scheme S7:** a) Benzoic anhydride, 160 °C, 4 h, 2 % or a) 4-(trifluormethyl)benzoic anhydride, 160 °C, 4 h, 13 %; b) $Ni(COD)_2$, pipy, THF/COD, 120 °C, 20 min, 21 %.

## 8




**8**
Chemical Formula: $C_{78}H_{70}Br_4$
Molecular Weight: 1327,03

**6** (1.00, 1.50 mmol, 2.54 eq), **7** (200 mg, 0.59 mmol, 1.00 eq) and 4-trifluorobenzoic anhydride (1.50 g, 4.14 mmol, 7.00 eq) were mixed. The flask was evacuated and flushed with argon three times. Under argon atmosphere, the reaction mixture was heated to 160 °C and stirred at this temperature for 4 h. Subliming anhydride was melted back to the reaction mixture using a heat gun. After cooling to room temperature, DCM was added, and the mixture was filtered through a short silica column (eluent: DCM). The solvent was removed under reduced pressure, and the crude product was obtained as a brown oil. The crude product was purified by flash column chromatography ($SiO_2$, eluent: Cy:DCM, 10:1, $R_f$ = 0.54). The product **8** was obtained as a white solid (106 mg, 0.08 mmol, 13 %).

**$^{1}$H-NMR** (700 MHz, THF-$d_8$, r.t.): δ [ppm] = 7.64 (s, 4H), 7.61 (dd, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 3.3 Hz, 4H), 7.59 (d, $^{4}J_{HH}$ = 1.8 Hz, 4H), 7.52 (t, $^{4}J_{HH}$ = 1.8 Hz, 2H), 7.34 (t, $^{4}J_{HH}$ = 2.0 Hz, 4H), 7.30 (dd, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 3.3 Hz, 4H), 7.09 (ddd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 2.0 Hz, $^{4}J_{HH}$ = 1.1 Hz, 4H), 6.45 (dt, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.1 Hz, 4H), 6.41 (t, $^{3}J_{HH}$ = 7.9 Hz, 4H), 1.40 (s, 36H). **$^{13}$C-NMR** (176 MHz, THF-$d_8$, r.t.): δ [ppm] = 152.1, 144.5, 144.0, 143.6, 140.8, 134.7, 134.5, 132.4, 131.2, 130.6, 129.8, 129.7, 127.8, 127.3, 126.0, 122.7, 122.6, 122.0, 35.7, 31.9. **MS (MALDI-pos, DCTB)**: *m/z* calculated for $C_{78}H_{70}Br_4$: 1322.2211 u, found: 1322.0 u.

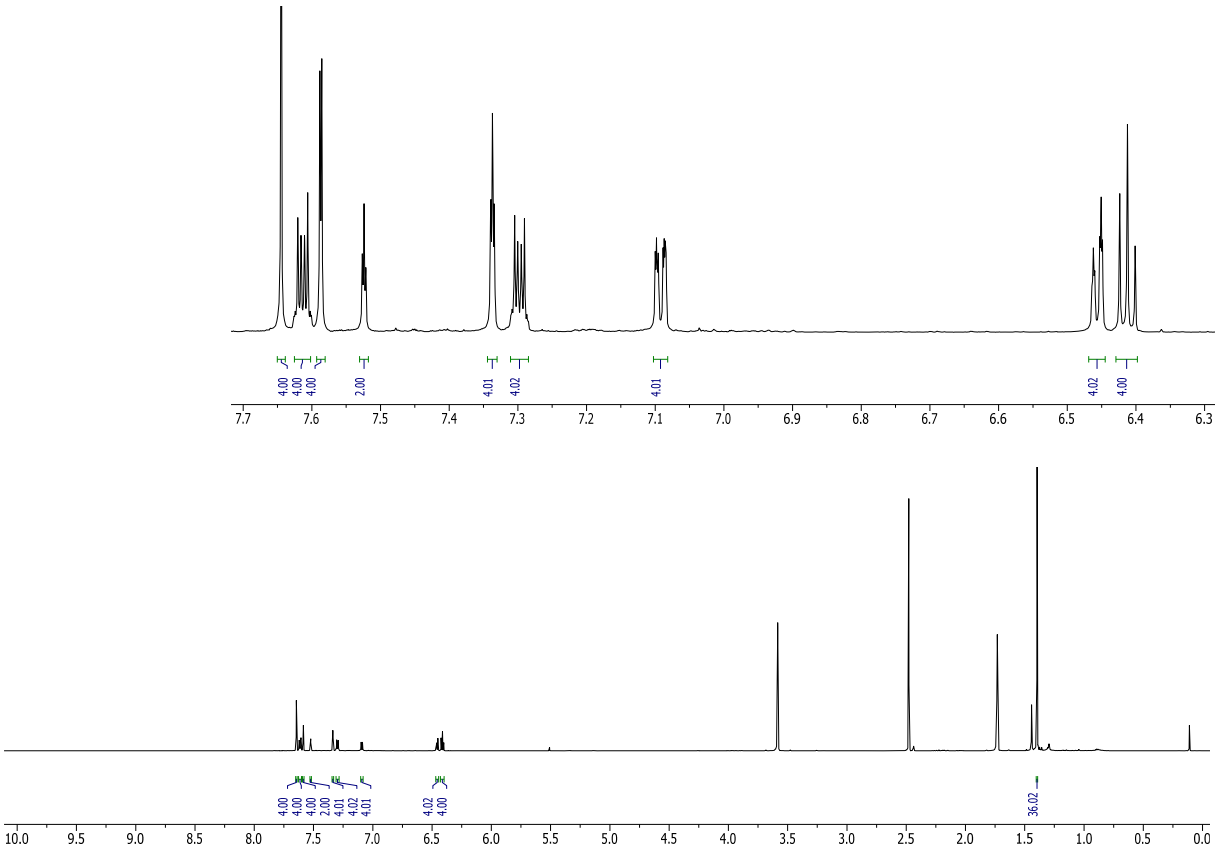



**Figure S55.** $^{1}$H-NMR spectrum of **8** (700 MHz, THF-$d_8$, r.t.).

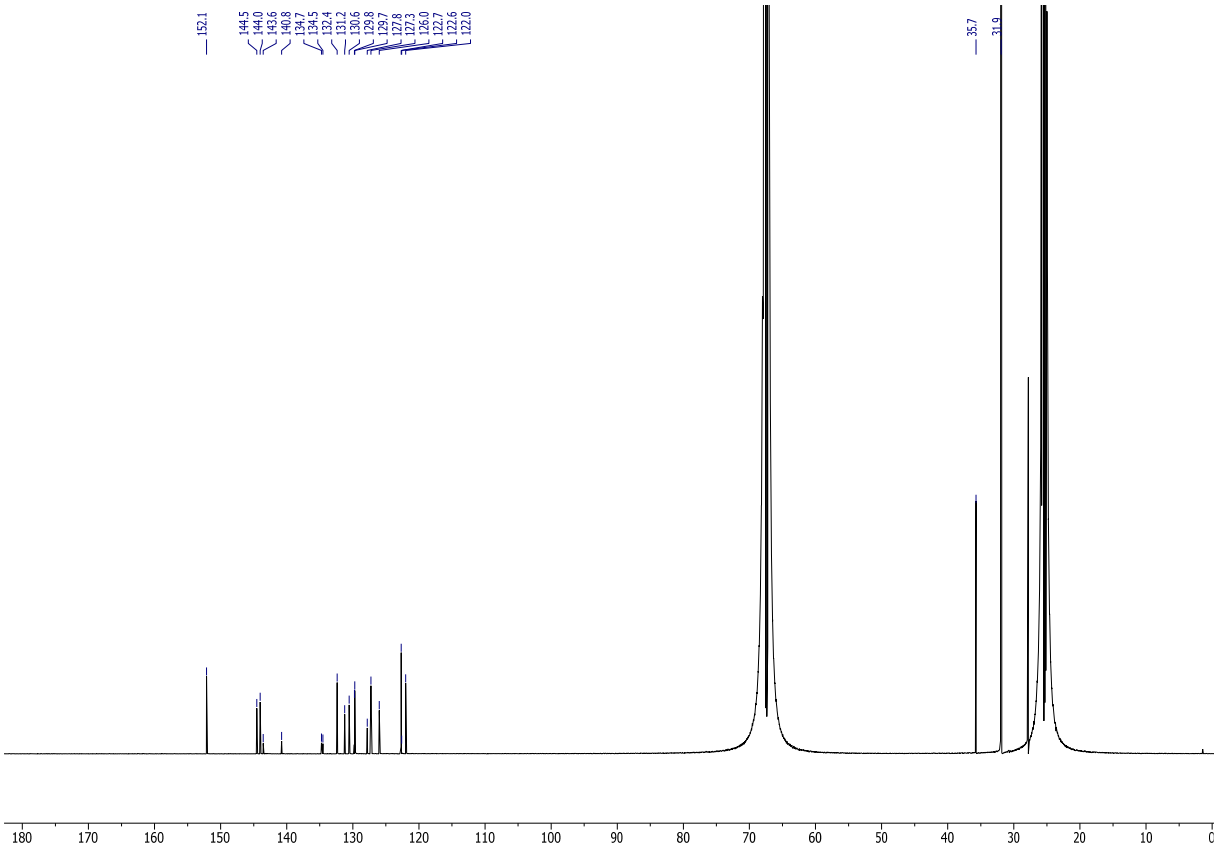
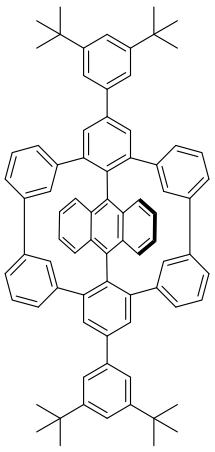



**Figure S56.** $^{13}$C-NMR spectrum of **8** (176 MHz, THF-$d_8$, r.t.).

# 9

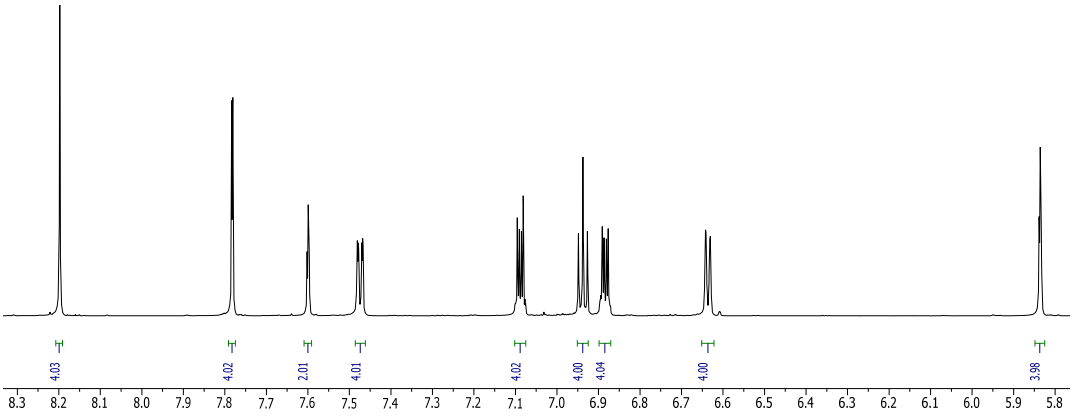


**9**
Chemical Formula: $C_{78}H_{70}$
Molecular Weight: 1007,42

Under argon atmosphere, **8** (10.0 mg, 7.54 µmol, 1.00 eq), $Ni(COD)_2$ (10.0 mg, 36.4 µmol, 4.83 eq) and bipy (5.0 mg, 32.0 µmol, 4.25 eq) were weighed a microwave vessel. To these solids, 8.0 ml of a solvent mixture of THF/COD (32:1) was added and the vessel was

immediately wrapped in tin foil to protect the reaction mixture from the exposure to light. The reaction mixture was stirred at 300 W and 120°C in the microwave for 20 minutes, during which a dark, flaky solid was formed. The solvent was removed under reduced pressure to give a greenish black oil. This oil was filtered through a short silica column (eluent: DCM). The solvent was again removed under reduced pressure and a yellow oil remained. By solving in DCM and reprecipitating in MeOH a yellow solid was obtained, which was then purified by recGPC. The product **9** was obtained as a light yellow solid (1.60 mg, 1.59 µmol, 21 %).

**$^{1}$H-NMR** (700 MHz, THF-$d_8$, r.t.): δ [ppm] = 8.20 (s, 4H), 7.78 (d, $^{4}J_{HH}$ = 1.8 Hz, 4H), 7.60 (t, $^{4}J_{HH}$ = 1.8 Hz, 2H), 7.47 (ddd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 2.0 Hz, $^{4}J_{HH}$ = 0.9 Hz, 4H), 7.09 (dd, $^{3}J_{HH}$ = 6.7 Hz, $^{4}J_{HH}$ = 3.2 Hz, 4H), 6.94 (t, $^{3}J_{HH}$ = 7.8 Hz, 4H), 6.88 (dd, $^{3}J_{HH}$ = 6.7 Hz, $^{4}J_{HH}$ = 3.2 Hz, 4H), 6.64 (ddd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 2.0 Hz, $^{4}J_{HH}$ = 0.9 Hz, 4H), 7.47 (t, $^{4}J_{HH}$ = 2.0 Hz, 4H), 1.49 (s, 36H). **$^{13}$C-NMR** (176 MHz, THF-$d_8$, r.t.): δ [ppm] = 152.3, 145.4, 143.9, 142.3, 141.4, 139.5, 138.9, 138.4, 135.4, 131.2, 129.3, 127.3, 127.0, 126.8, 126.7, 125.6, 123.0, 122.6, 35.9, 32.1. **MS (MALDI-pos, DCTB)**: *m/z* calculated for $C_{78}H_{70}$: 1006.5478 u, found: 1006.5489 u.



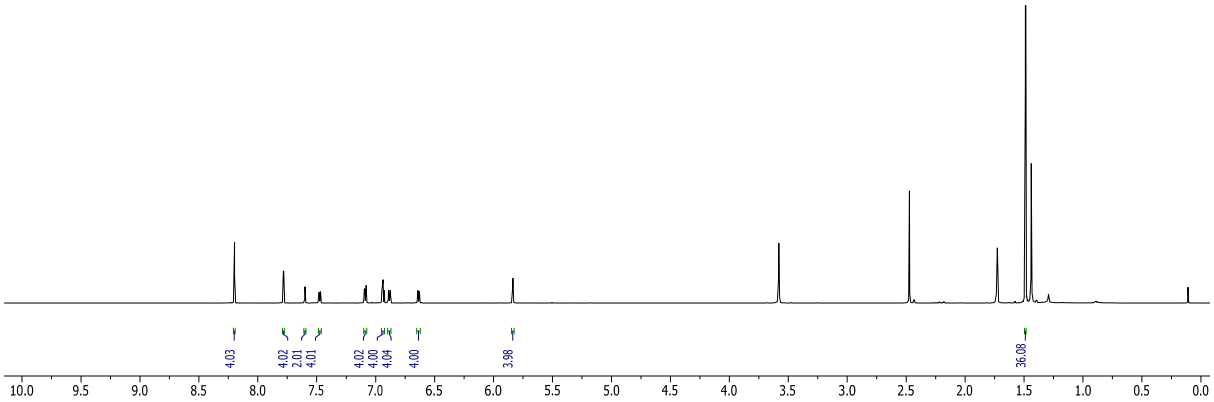



**Figure S57.** $^{1}$H-NMR spectrum of **9** (700 MHz, THF-$d_8$, r.t.).

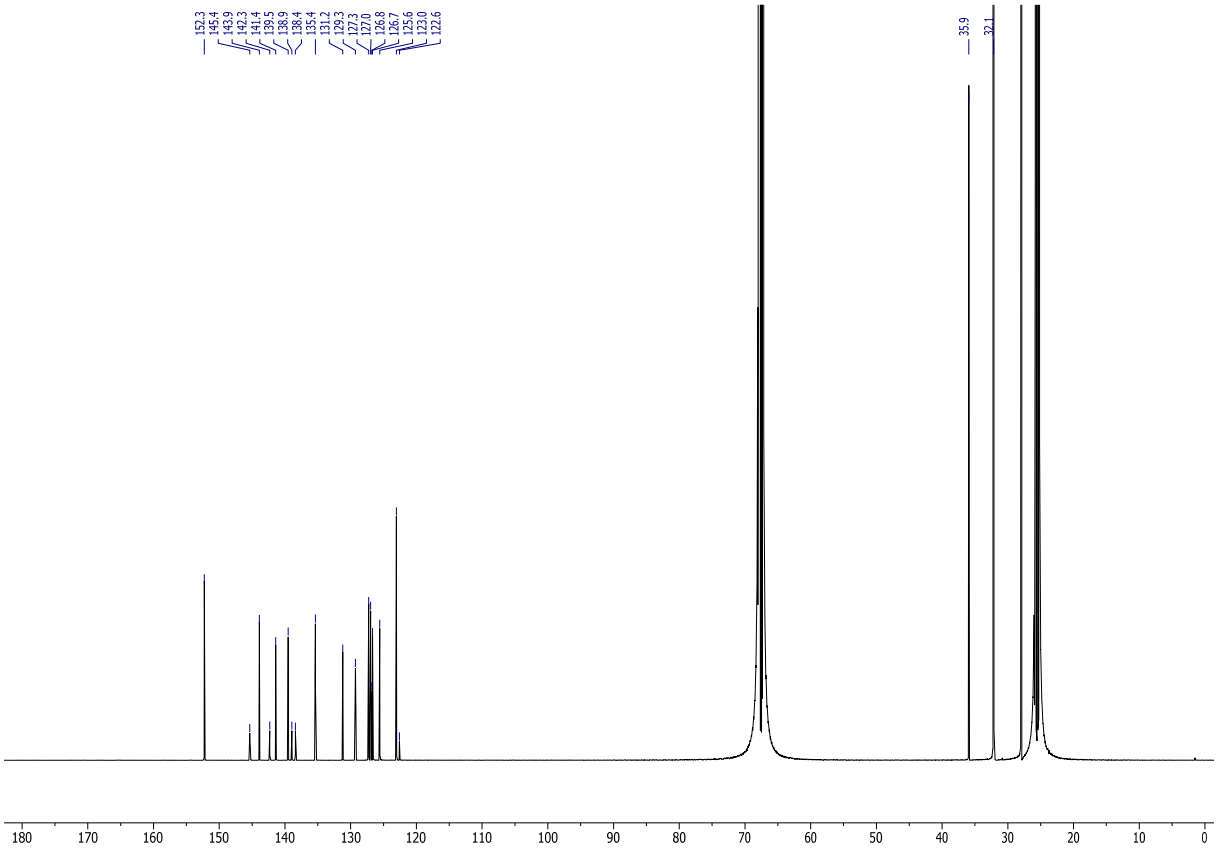



**Figure S58.** $^{13}$C-NMR spectrum of **9** (176 MHz, THF-$d_8$, r.t.).

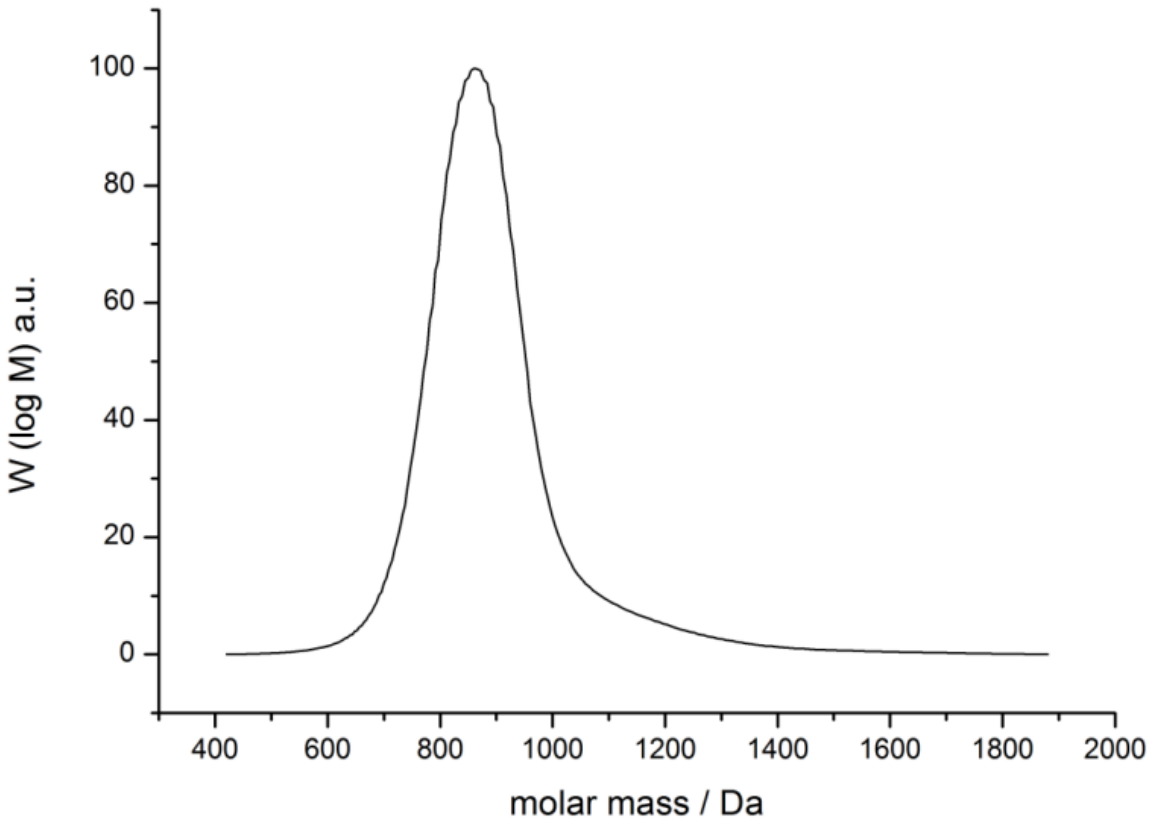



**Figure S59.** Molar mass distribution of **9** (relative to polystyrene).

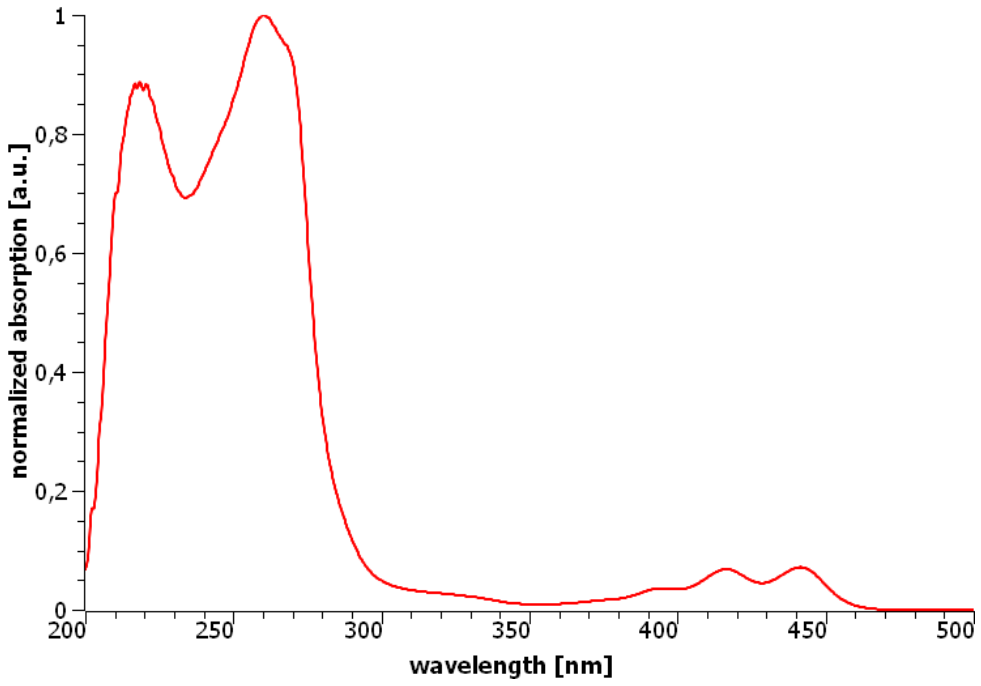



**Figure S60.** Normalized UV/Vis absorption spectrum of **9** in oxygen saturated *n*-octane (1 x $10^{-5}$ M).

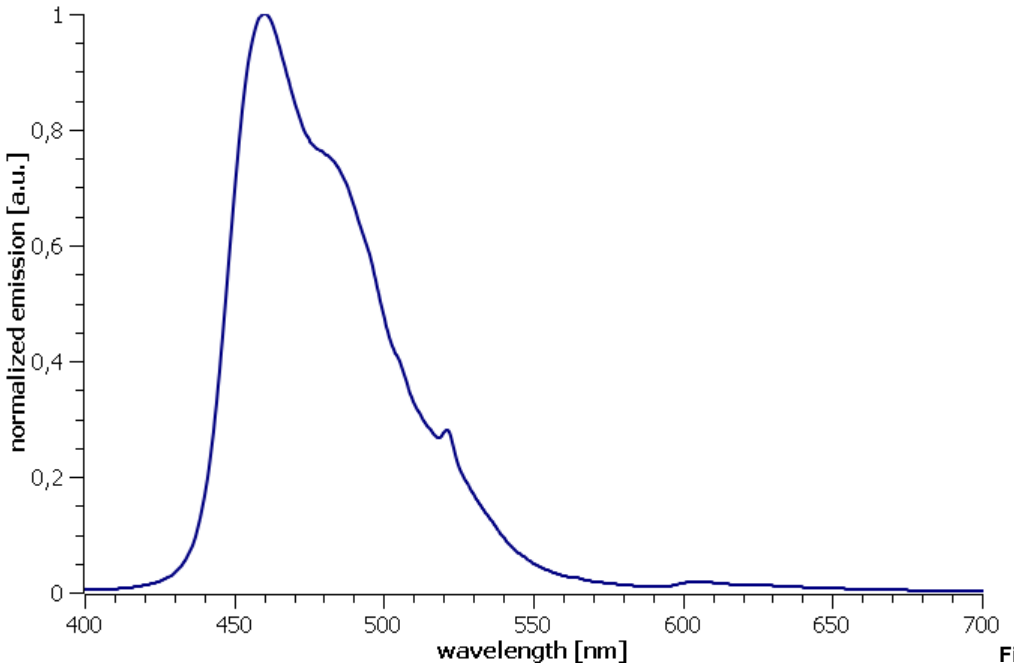



**Figure S61.** Normalized fluorescence spectrum of **9** in oxygen saturated *n*-octane (1 x $10^{-5}$ M).

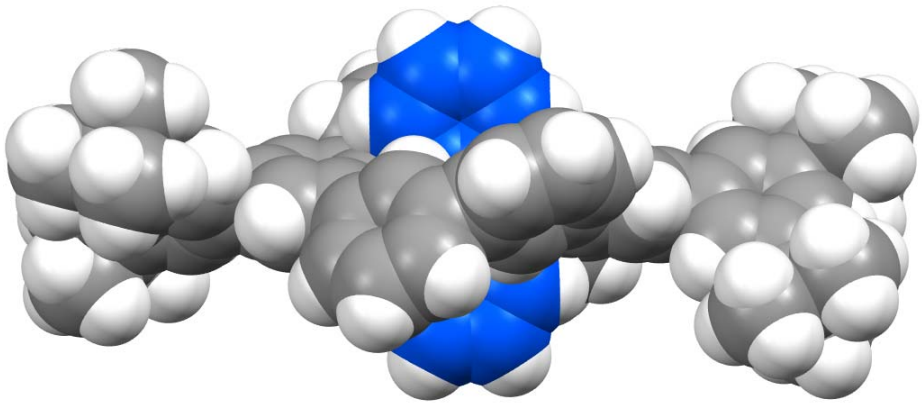


**Figure S62.** Space-filling model showing how the macrocycle (gray) protects the anthracene center (blue) of **9** (the disordered atoms were manually cleaned up for clarity).

# 7. Photochemical degradation

## 7.1 Reaction conditions

In order to observe maximum change in fluorescence and absorption, as solvent with high oxygen solubility *n*-octane was chosen. Prior to the measurement, the *n*-octane solution was saturated with oxygen.

## 7.2 Anthracene

100 mL of *n*-octane were saturated with oxygen and 0.2 mL of a fresh 5 x $10^{-3}$ M solution of anthracene in octane was added, so that a concentration of 1 x $10^{-5}$ M was achieved in the reaction flask. The solution was irradiated with UV-light (366 nm).

The UV/Vis spectrum (**Figure S62**) shows the considerable decline of UV absorbance, which is especially apparent at the absorption maximum at 252.4 nm. After 240 minutes, absorbance had already decreased by 50 %. The sample retrieved after 23.3 hours barely showed UV absorption anymore, with the absorbance being less than 10 % of the original value.

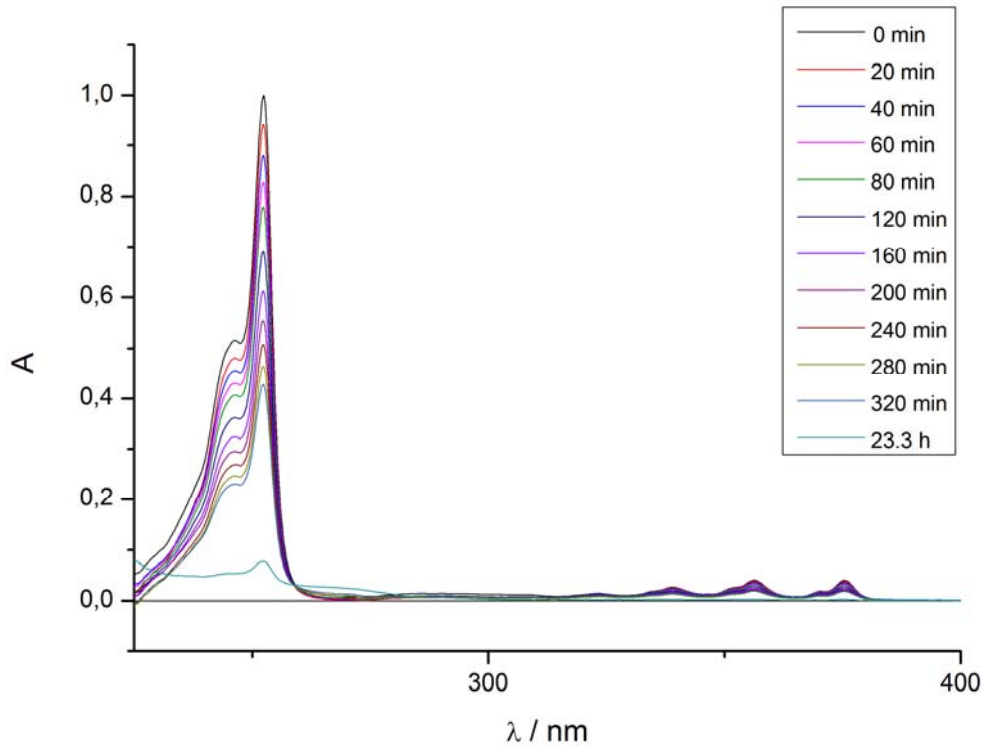



**Figure S63:** UV/Vis absorption spectrum of anthracene in oxygen-saturated *n*-octane over time upon irradiation with 366 nm.

## 7.3 9,10-Diphenylanthracene

100 mL of *n*-octane were saturated with oxygen and 0.6 mL of a fresh 1.7 x $10^{-3}$ M solution of 9,10-diphenylanthracene in octane were added, so that a concentration of 1 x $10^{-5}$ M was achieved in the reaction flask. The solution was irradiated with UV-light (366 nm).
The UV/Vis spectrum (**Figure S63**) shows a considerable decline of UV absorbance, which is especially apparent at the absorption maximum at 258.8 nm. The absorbance had decreased by 50% after 6 hours. The absorbance of the sample retrieved after 27.5 hours was approximately only 10 % of the original value.

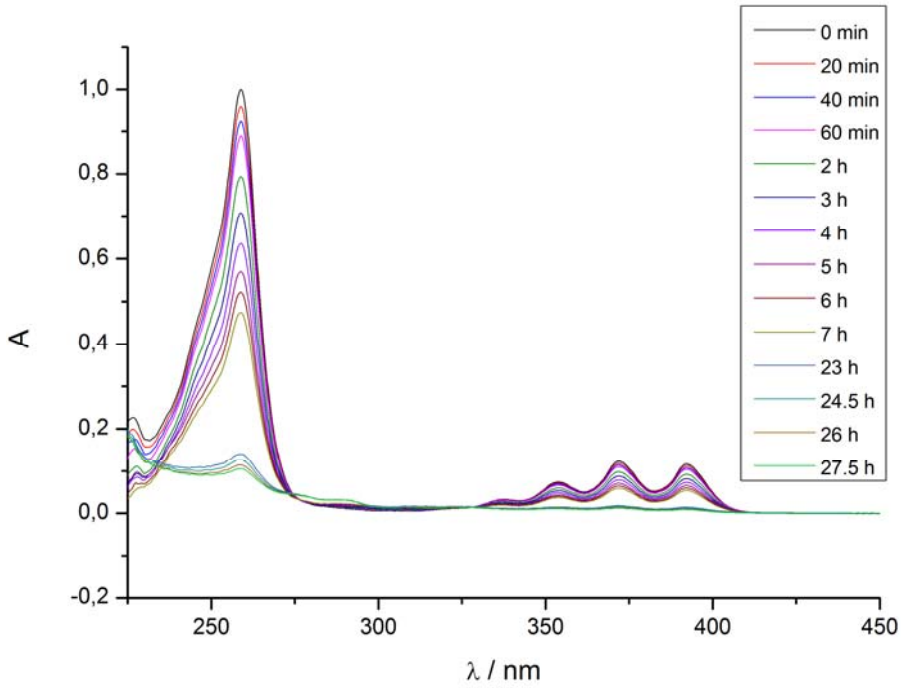



**Figure S64:** UV/Vis absorption spectrum of DPA in oxygen-saturated *n*-octane over time upon irradiation with 366 nm.

## 7.4 9

100 mL of *n*-octane were saturated with oxygen and 1.01 mg of the *meta*-bicyclophane **9** were added to achieve a concentration of 1 x $10^{-5}$ M. The solution was irradiated with UV-light (366 nm). After 22.5 hours, the solution was again saturated with oxygen. The last sample was retrieved after 95.3 hours.

The UV/Vis spectrum (**Figure S64**) showed no strong decline of absorbance. Even after 95.3 hours the absorbance had decreased by merely 5 %. The constant absorption of the

*m*-bicyclophane **9** gives good evidence that photodegradation reactions of the anthracene core are successfully suppressed.

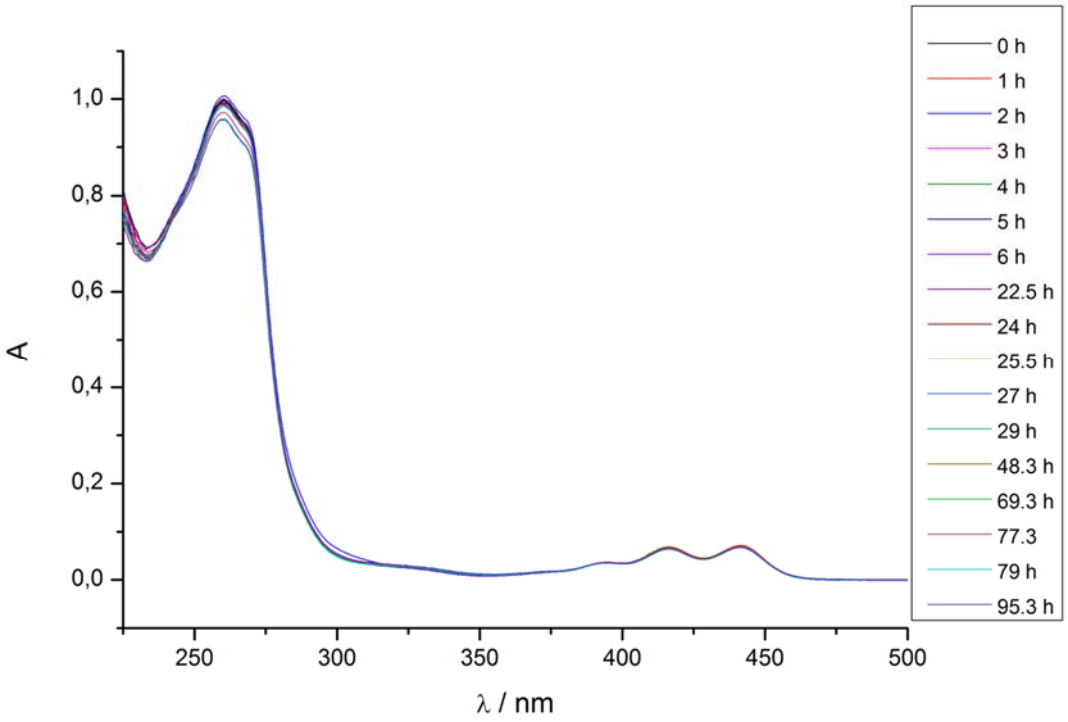



**Figure S65:** UV/Vis absorption spectrum of *m*-bicyclophane **9** in oxygen-saturated *n*-octane over time upon irradiation with 366 nm.

## 7.5 Comparison

The different experiments successfully demonstrated the different stabilities of the investigated anthracene derivatives against photobleaching. The direct comparison of the UV absorbances as a function of time clearly illustrates the high stability of **9** (**Figure S66**).

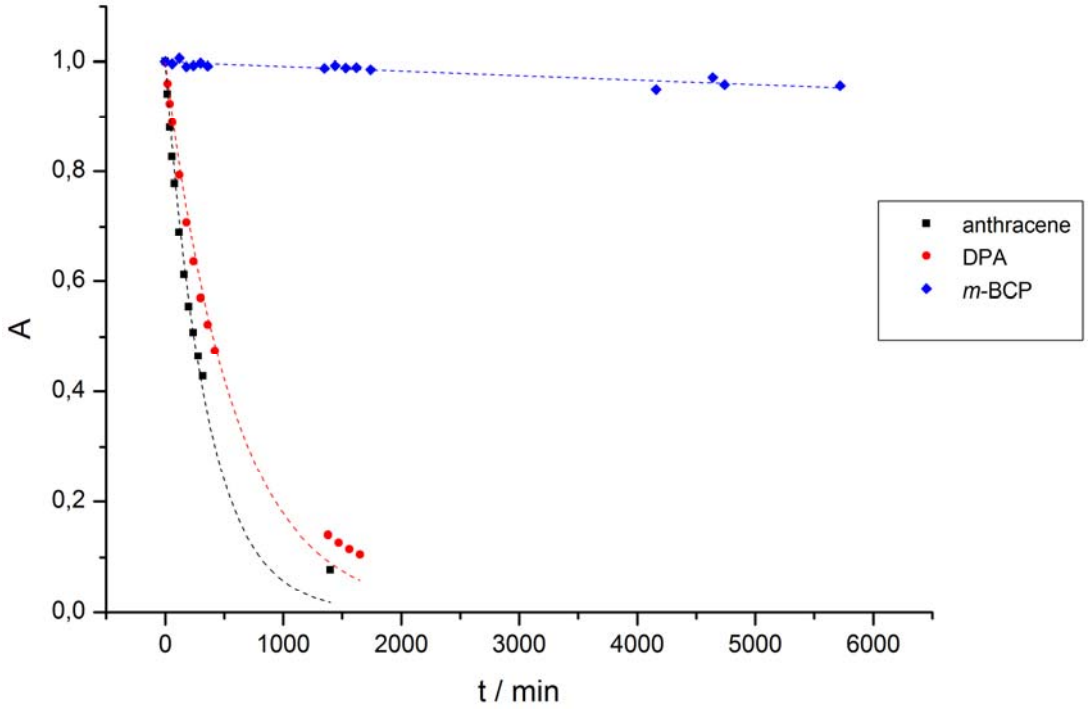



**Figure S66:** Comparison of the UV/Vis absorbances of anthracene, DPA and **9** upon irradiation with 366 nm as a function of time and the exponential fit.

Anthracene is the least stable of the three compounds with a half-life of approximately 4 h under the given reaction conditions. Under the same conditions, DPA has a half-life time of about 6 h. However, the degradation rates of anthracene and DPA are still in the same order of magnitude.

The *meta*-connected bicyclophane **9** is much more stable than both anthracene and DPA against photodegradation. The compound remained stable over the course of five days and the UV absorbance decreased only a few percent. The rate constants of degradation, obtained by an exponential fit of the time dependent absorbance indicate that **9** is about 350 times more stable against photo degradation than anthracene and 200 times more stable than DPA

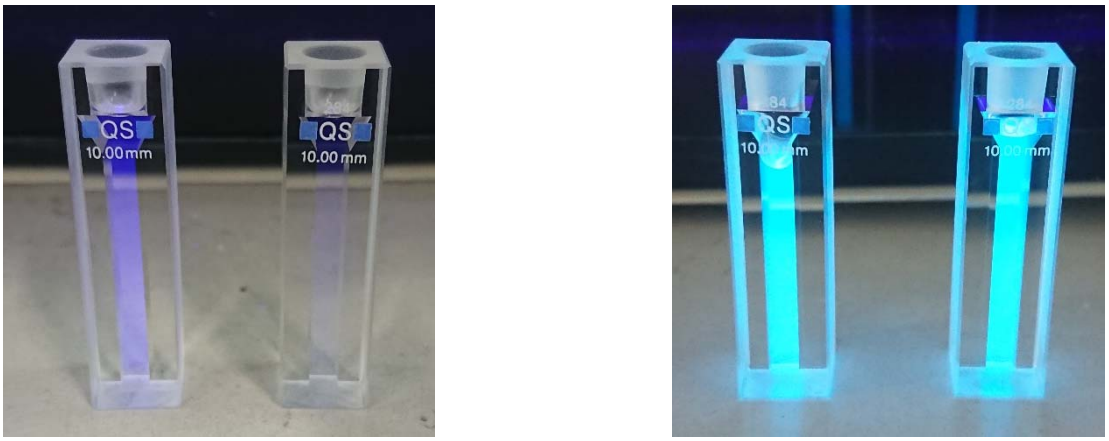



**Figure S67: Left:** Comparison of fluorescence of a freshly prepared solution of anthracene in octane (1 x $10^{-5}$ M) (left) vs the sample after 23.3 h (right); **Right:** Comparison of fluorescence of a freshly prepared solution of **9** in octane (1 x $10^{-5}$ M) (left) vs the sample after 95.3 h (right).

# 8. References

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