7. EXPERIMENTAL SECTION

7.1 General

All chemicals were purchased from Acros, Aldrich, Fluka, Janssen, and Lancaster and used without further purification. Diethylether and tetrahydrofuran were distilled from sodium/ benzophenone ketyl or potassium/benzophenone ketyl; in the cross-coupling reactions toluene was used in p.a. quality. The solvents used in the column chromatography were distilled prior to use. Experiments under a protective atmosphere were carried out with nitrogen in a purity of 4.0 and 5.0, purchased from Linde or Messer Griesheim. All reactions with moisture sensitive reagents (e. g., lithiations and hydroborations) were performed in dried glassware. Therefore the apparatus was evacuated (~15 mbar), heated with an electric dryer (~500 °C), and flushed with nitrogen. After cooling this procedure was repeated. All palladium-catalyzed cross-coupling reactions were carried out under oxygen-free conditions. For this a stream of nitrogen was run through the stirred mixture (15-30 min). Whenever a recrystallization step was performed from a mixture of two solvents, the so-called cold method was applied.[248] Several compounds were prepared according to literature procedures and gave satisfactory NMR and MS data: **2**,[136] **5**,[249] **9**,[144] **22**,[121a,b] **38**,[170,172,173] **41**,[179] **44g**,[250] **44k**,[251] **44l**,[252] **44m**,[253] **44n**,[254] **55**,[207] **56**,[205] **108**,[121a,b] triphenylmethylphosphonium iodide,[145] and (4-cyanobenzyl)-triphenylphosphonium bromide.[255] Pd(PPh$_3$)$_4$ was prepared according to Ref. 256, stored in a glove box (O$_2$: < 2.0 ppm, H$_2$O: < 0.3 ppm) and used without further characterization. Compounds **98**[257] and **101**[170,238] were prepared by other group members. Compounds **39**,[168,176] **53**,[203] and **58**[210] are included in the experimental section because of the lack of experimental and/or spectroscopical data in the literature. Compounds **3**,[138] **10**,[145] **18**,[152] **45a**,[222,258] **45h**,[112] **45i**,[111a] and **82**[259] were prepared differently than in the referenced literature procedures and therefore are described in full detail. The compounds' names were generated with AutoNom

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Engine 4.0 (Beilstein Institute 1998).

7.2 Chromatography

TLC:

All reactions were monitored on silica gel alumina sheets (Merck, ”Kieselgel 60”, F_{254}). For detection UV-light of the wavelengths λ = 254 nm or λ = 366 nm was used. Some of the compounds were spotted by putting the TLC plate either into a solution of 0.5 ml anisaldehyde (*p*-methoxy benzaldehyde), 50 ml glacial acetic acid, and 1 ml conz. sulfuric acid and heating it up to ~100 °C (for boranes, alcohols and ethers), or into an aqueous solution of potassium permanganate (0.5 %; for olefins).

Column chromatography:

For column chromatography variable amounts of silica gel (”Kieselgel 60”, 230-500 mesh ASTM, Merck) was used. Usually the raw product was pre-absorbed onto small amounts of silica gel prior to put it into the column. For all chromatographed compounds the R_f value is given with respect of the eluent in the TLC.

HPLC:

Reversed-Phase: *Analytical*: Knaur Eurosphere® 7µm C_{18}, 4·120 mm, UV-detection at 335 nm (for pyrene derivatives) or 254 nm.

Preparative: Machery-Nagel, Nucleosil® 5µm C_{18}, 32·250 mm, UV-detection at 335 nm (for pyrene derivatives) or 254 nm.

Silica gel: *Analytical*: Knaur Eurosphere® 7µm C_{18}, 4·120 mm, UV-detection at 335 nm (for pyrene derivatives) or 254 nm.

Preparative: Knaur Eurosphere® 5µm C_{18}, 32·250 mm, UV-detection at 335 nm (for pyrene derivatives) or 254 nm.

GPC (SEC):

Analytical: Waters Styragel HR 1 or HR 3 columns, Waters 2487 UV/VIS detector at 254 nm.
Preparative: Polymer Laboratories Gel, Waters 484 and Knaur UV photometer detector at 254 nm. Tetrahydrofuran served as the mobile phase, the UV detection was performed vs. polystyrene (calibration) and toluene as the standard.

Sometimes problems occurred in preparative separations: The purified samples contained various amounts of aliphatic and olefinic compounds that were detected in the ^{1}H NMR spectra. Typical chemical shifts were: ^{1}H: 1.60-2.05 (m), 3.88 (m), 5.50, 5.58, 5.65 (all dd, ^3J

= 6 Hz, ^{4}J = 1 Hz) ppm. It was presumed that these impurities stem from the eluent used (tetrahydrofuran), although it was distilled in an rotary evaporator prior to use. FAB mass analysis showed an (cyclic?) oligomeric THF-9-mer with one tetrahydrofuran end-group and eight ring-opened moieties that were partially dehydrogenated. In order to remove the impurities the samples were solved in tetrahydrofuran (as little as possible), some aqueous 1M NaOH was added, and the mixture was treated in an ultrasonic bath for an hour. Then a large amount of methanol was added and the precipitate was centrifugated off. Finally the resulting solid was lyophilized from benzene.

7.3 Analysis

Melting point:

Büchi SMP 510, uncorrected values.

NMR spectroscopy:

Bruker WH 270, Bruker AB 250, Bruker AC 500. The signal of the not-deuterated solvent served as internal standard (^{1}H: $CDCl_3$: 7.24 ppm , [D_6]-DMSO: 2.49 ppm, [D_3]-acetonitrile: 1.93 ppm; ^{13}C: $CDCl_3$: 77.00, [D_6]-DMSO: 39.70 ppm, [D_3]-acetonitrile: 117.70 ppm). The deuterated solvents were purchased from Merck and Deutero GmbH. All spectra were recorded at 20 °C. A couple of pyrene derivatives did not show all aromatic carbon signals in the routine ^{13}C NMR experiments which may be due to insufficient resolution or isochromism.

Mass spectrometry:

Perkin-Elmer Varian Type MAT 771 and CH6 (EI), Type CH5DF (FAB), or Bruker Reflex (MALDI-TOF) respectively. Given are the kind of ionization (EI, FAB, MALDI-TOF), the potential of ionization (70 or 80 eV) and the temperature of the ion source (EI) or the matrix material (FAB and MALDI-TOF). MALDI-TOF: UV-Laser (337 nm), delayed extraction source, reflector mode. The high resolution mass spec were obtained according to the peak match method (MAT 771).

Infrared spectroscopy:

Nicolet 5SXC (FTIR Interferometer). All solids were investigated in potassium bromide and the oils as films between potassium bromide plates. Only characteristic bands of important functional groups are given.

Elemental analysis:

Perkin-Elmer EA 240. In most cases a deviation of up to 0.4 % from the calculated carbon value was accepted.

Differential Scanning Calorimetry:

Netsch DSC 200. -60 to 250 °C, 10 K/min heating rate, under air.

Thermal Gravimetric Analysis:

Netsch TGA 209. 20 to 600 °C, 10 K/min heating rate. N_2 as protective atmosphere.

Absorbtion and emission specroscopy (in collaboration):

Methylcyclohexane, acetonitrile, and tetrahydrofuran of spectrophotometric grade were used as solvents for the spectroscopic measurements. For the fluorescence measurements, the pyrenyl derivatives were purified by preparative HPLC to ensure purities of > 99.5 %. UV-absorption spectra were measured on a ATI UNICAM UV series spectrometer UV-02113, and the fluorescence spectra were recorded on a AMINCO-Bowman series 2 spectrofluorimeter. They are corrected for instrumental sensitivity. A solution of quinine bisulfate in 0.1 N H_2SO_4 ($\Phi_f = 0.52$)[260] was applied as standard for the measurement of the fluorescence quantum yields. Fluorescence decay times of aerated solutions were determined with the time-correlated single-photon counting (SPC) technique[261] using an equipment described elsewhere.[262] An argon ion laser-pumped Ti:sapphire laser was used as excitation source. In section 7.4 the absorption maxima λ_{max} are given with respect to the extinction coefficient ε ($l \cdot mol^{-1} \cdot cm^{-1}$). Several photophysical data are summarized in table 2 in section 4.3.2. Transient absorption measurements used an excimer-pumped laser (XeCl). The laser power was 150 mJ/pulse with a pulse duration of 12 ns. The intensity of excitation was 10^{21} photons$\cdot cm^2 \cdot s^{-1}$. Details of the equipment for ESA measurements are published.[263]

X-ray analysis (in collaboration):

Suitable crystals of two compounds were measured on a Bruker AXS SMART CCD diffractometer [$Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator]. The structures were solved by direct methods and full-matrix least squares refinement against F^2. Details are given in section 7.5.

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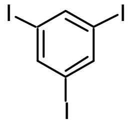
7.4 Syntheses

7.4.1 Compounds of Chapter 4.2.1

1,3,5-Triiodo-benzene (3)

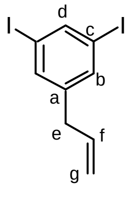


To a solution of 1,3,5-tris(trimethylsilanyl)-benzene **2** (66.0 g, 224.0 mmol) in 1 l dichloromethane a solution of iodomonochloride (122.4 g, 754.0 mmol, 3.4 eq.) in 400 ml dichloromethane was added at room temperature within 3 h. Cooling with a water bath was necessary. Product precipitated, and the suspension was stirred overnight. After removal of excess iodomonochloride with aqeous sodium pyrosulfite solution, the layers were separated and the aqeous one was washed with dichloromethane. The combined organic layers were dried over $MgSO_4$ and filtered. Some solvent was evaporated and the precipitated product was sucked off. This procedure was repeated for three times to yield 91.67 g (90 %) of **3** as colorless crystals.

The product was stored under exclusion of light to avoid brownish discoloring.

– **M.p.** 181 °C (Lit. 180 °C,[264] 183 °C[138]). – **^{1}H NMR** (270 MHz, $CDCl_3$): $\delta = 7.98$ (s, 3H). – **^{13}C NMR** (63 MHz, $CDCl_3$): $\delta = 95.21, 144.42$. – **MS** (EI, 80 eV, 50 °C): *m/z* (rel. Int.) = 456 (100) $[M]^+$, 329 (20) $[M\text{-}I]^+$. – **$C_6H_3I_3$ (455.80)**: calcd. C 15.81, H 0.66; found C 15.98, H 0.60.

1-Allyl-3,5-diiodo-benzene (4)



To a suspension of 1,3,5-triiodobenzene **3** (84.40 g, 185.17 mmol) in toluene (1000 ml) a 1.6 M solution of *n*-butyllithium in hexane (116.00 ml, 185.60 mmol, 1.00 eq.) was added within 60 min at room temperature. After 3 d allyl bromide (25.00 ml, 303.56 mmol, 1.64 eq.) was added all at once and the mixture was stirred for additional one day with a mechanical stirrer. 500 ml water were added, the phases separated, and the aqueous one was extracted with toluene twice. The combined organic layers were dried over $MgSO_4$, and evaporation of the

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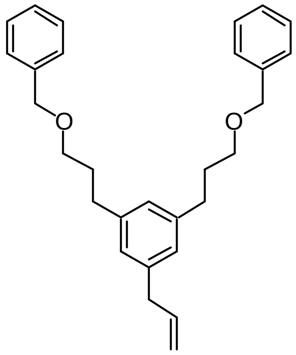
[264] C. Willgerodt, E. Arnold, *Chem. Ber.* **1901**, *34*, 3343-3354.

filtrate gave 70 g of a brownish oil. Distillation (75 °C, $8\cdot10^{-3}$ mbar, vigreux column) gave 58.73 g (86 %) of the desired 1-allyl-3,5-diiodo-benzene **4** as a colorless, mobile liquid. Long, colorless needles were obtained by recrystallization from ethanol at –22 °C, but these crystals were not stable at room temperature (22 °C).

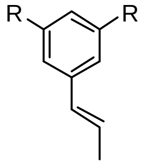
1,3-diiodo-benzene was identified as a side product (^{1}H NMR).

– **B.p.** 75 °C/ $8\cdot10^{-3}$ mbar. – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.25 (d, ^3J = 6.5 Hz, 2H, *H-e*), 5.03-5.14 (m, 2H, *H-g*), 5.86 (m, 1H, *H-f*), 7.49 (d, ^4J = 1.3 Hz, 2H, *H-b*), 7.87 (d, ^4J = 1.3 Hz, 1H, *H-d*). – **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 39.08 (*C-e*), 94.91 (*C-c*), 117.22 (*C-g*), 135.57 (*C-f*), 136.87 (*C-b*), 142.72 (*C-d*), 144.11 (*C-a*). – **MS** (70 eV, 25 °C): *m/z* (rel. Int.) = 370 (100) $[M]^+$, 243 (6), 116 (80). – **$C_9H_8I_2$ (369.97)**: calcd. C 29.22, H 2.18; found C 28.92, H 1.69.

1-Allyl-3,5-bis-(3-benzyloxy-propyl)-benzene (6)

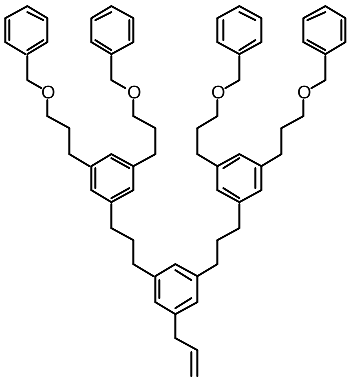


Allylbenzylether **5** (7.57 g, 51.08 mmol, 2.07 eq.) and 9-BBN (6.27 g, 51.38 mmol, 2.08 eq.) were suspended in toluene (100 ml) and stirred for one day at room temperature. After addition of aqueous sodium hydroxide (1 M, 60 ml) and 1-allyl-3,5-diiodo-benzene **4** (9.12 g, 24.65 mmol) the suspension was degassed. The catalyst precursor $Pd(PPh_3)_4$ (1.07 g, $9.3\cdot10^{-4}$ mol, 1.8 mol-% per coupling) was added and the suspension was stirred under gentle reflux for 16 h. Usual extractive work-up with toluene and purification by column chromatography through silica gel (hexane:ethyl acetate = 20:1) yielded 7.11 g (70 %) of **6** as a colorless oil. – **R_f** = 0.52 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 1.96 (m, 4H), 2.71 (t, 4H), 3.37 (d, 2H), 3.53 (t, 4H), 4.58 (s, 4H), 5.06-5.17 (m, 2H, CH=CH_2), 6.00 (m, 1H, *CH*=CH_2), 6.89 (s, 3H), 7.27-7.44 (m, 10H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 31.35, 32.01, 40.12, 69.53, 72.81, 115.54, 126.17, 126.38, 127.42, 127.55, 128.26, 137.54, 138.52, 139.90, 142.03. – **MS** (EI, 80 eV, 170 °C): *m/z* (rel. Int.) = 414 (2) $[M]^+$, 91 (100) $[C_7H_7]^+$. – **$C_{29}H_{34}O_2$ (414.58)**: calcd. C 84.02, H 8.27; found C 83.69, H 7.98.



The product was accompanied by varying amounts of the styrene derivative **7**, identified by the signals in the ^{1}H NMR spectra: 1.88 (d, 3H), 6.21 (m, 1H), 6.38 (d, ^3J = 15 Hz, 1H).

1-Allyl-3,5-bis-{3-[3,5-bis-(3-benzyloxy-propyl)-phenyl]-propyl}-benzene (8)



Procedure as described for **6**:

6: 9.83 g, 23.71 mmol, 2.04 eq.; 9-BBN: 3.01 g, 24.67 mmol, 2.12 eq.; toluene: 100 ml; aqueous sodium hydroxide (1 M, 70 ml); 1-allyl-3,5-diiodo-benzene **4**: 4.30 g, 11.62 mmol; Pd(PPh$_3$)$_4$: 0.29 g, 0.25 mmol, 1.08 mol-% per coupling; yield: 3.08 g (28 %) of **8** as a colorless oil.

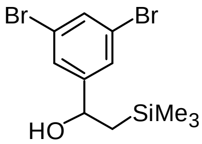
– **R$_f$** = 0.27 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (500 MHz, CDCl$_3$): δ = 1.96 (m, 12H), 2.64 (m, 8H), 2.71 (t, 8H), 3.40 (d, 2H), 3.53 (t, 8H), 4.55 (s, 8H), 5.06-5.17 (m, 2H, CH=*CH$_2$*), 6.02 (m, 1H, *CH*=CH$_2$), 6.88 (s, 9H), 7.32-7.39 (m, 20H). – **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 31.39, 31.53, 32.24, 33.07, 35.51, 69.56, 72.81, 115.54, 126.08, 126.32, 127.58, 127.78, 128.11, 128.29, 128.96, 137.64, 138.51, 139.82, 141.86, 142.27, 142.38. – **MS** (EI, 80 eV, 300 °C): *m/z* (rel. Int.) = 946 (12) [*M*]$^+$, 855 (100) [*M-C$_7$H$_7$*]$^+$. – **HRMS**: *m/z* calcd. for **$C_{67}H_{78}O_4$** 946.590012; found 946.59167.

The product was accompanied by varying amounts of the corresponding styrene derivative, see analysis of **6**.

7.4.2 Compounds of Chapter 4.2.2

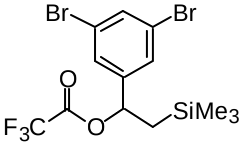
1,3-Dibromo-5-vinyl-benzene (10)

To a suspension of magnesia (1.70 g, 69.93 mmol, 1.01 eq.) in diethylether (10 ml) a solution of chloromethyl trimethyl silane (9.70 ml, 69.51 mmol) in 20 ml diethylether was added dropwise. Within one minute the reaction started, indicated by a vigorous reflux of the solvent. The mixture was then stirred at room temperature until the magnesia had disappeared (1 h). In a dropping funnel 3,5-dibromobenzaldehyde **9** (16.50 g, 62.52 mmol, 0.89 eq.) was solved in diethylether (150 ml), and the solution was added over a period of 30 min. After stirring another four hours 25 ml of hydrochloric acid (5 %) were added, followed by an usual extractive work-up that yielded 21.01 g (96 %) of **1-(3,5-dibromphenyl)-2-trimethylsilanyl-ethanol** (**11**) as an clear colorless oil.



– **R$_f$** = 0.28 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (270 MHz, CDCl$_3$): δ = -0.03 (s, 9H), 1.09 (m, 2H), 2.07 (s, br, 1H), 4.73 (t, ^3J = 7.5 Hz, 1H), 7.39 (s, 2H), 7.51 (s, 1H). – **^{13}C NMR** (63 MHz, CDCl$_3$): δ = -1.02, 28.58, 71.61, 122.89, 127.54, 132.78, 150.82. – **$C_{11}H_{15}Br_2SiO$ (351.13)**

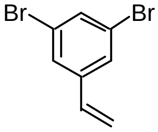
To an ice-cooled solution of **11** (13.80 g, 39.30 mmol) in diethylether (50 ml) were added pyridine (6.50 ml, 80.45 mmol, 2.13 eq.) and trifluoroacetic acid anhydride (9.00 ml, 64.71 mmol, 1.65 eq.). The reaction mixture was stirred overnight at room temperature and aqueous NaOH (3 M, 50 ml) and hexane (100 ml) were added. The phases were separated, and the aqueous one was extracted with hexane twice. The combined organic layers were dried over MgSO$_4$, and evaporation of the filtrate gave 16.30 g (93 %) of **trifluoracetic acid [1-(3,5-dibromphenyl)-2-trimethylsilanyl-ethyl] ester** (**12**) as a colorless oil. The compound was found to be unstable on silica gel. The attempt to obtain EI mass spec failed. The mass of styrene **10** was the highest observed signal.



– **R$_f$** = 0.59 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (270 MHz, CDCl$_3$): δ = -0.05 (s, 9H), 1.32 (dd, ^3J = 7.5 Hz, 1H), 1.47 (dd, ^3J = 7.5 Hz, 1H), 5.86 (t, ^3J = 7.5 Hz, 1H), 7.44 (s, 2H), 7.64 (s, 1H). – **$C_{13}H_{15}Br_2F_3O_2Si$ (448.14)**.

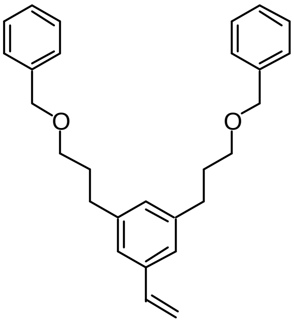
Ester **12** was solved in ethanol (250 ml) and stirred until it has disappeared in the TLC.

Extractive work-up gave the styrene **10** in a yield of 99 % (9.40 g). The product polymerized spontaneously when no stabilizing agent was added.



– **^{1}H NMR** (270 MHz, $CDCl_3$): δ = 5.36 (d, ^3J = 12 Hz, 1H), 5.77 (d, ^3J = 17 Hz, 1H), 6.58 (dd, ^3J = 12 Hz, ^3J = 17 Hz, 1H), 7.47(s, 2H), 7.55 (s, 1H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 116.78, 123.05, 127.82, 132.93, 134.21, 140.96. – **$C_8H_6Br_2$ (261.94)**.

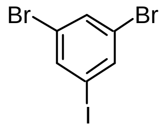
1,3-Bis-(3-benzyloxy-propyl)-5-vinyl-benzene (13)



As described for **6**:
5: 8.16 g, 55.06 mmol, 2.83 eq.; 9-BBN (0.5 M solution in tetrahydrofuran): 110.0 ml, 55.0 mmol, 2.82 eq.; aqueous sodium hydroxide (3 M, 50 ml); 1,3-dibromo-5-vinyl-benzene **10**: 5.10 g, 19.47 mmol; $Pd(PPh_3)_4$: 0.80 g, 0.69 mmol, 1.8 mol-% per coupling; yield after chromatographic separation through silica gel: 2.50 g (36 %) of **13** as a clear colorless oil that has shown great propensity to polymerize spontaneously when no stabilsator was added.
– **R_f** = 0.28 (hexane:ethyl acetate = 10:1). – **^{1}H NMR** (270 MHz, $CDCl_3$): δ = 1.97 (m, 4H), 2.73 (t, 4H), 3.53 (t, 4H), 4.55 (s, 4H), 5.24 (d, ^3J = 12 Hz, 1H), 5.75 (d, ^3J = 17 Hz, 1H), 6.81 (dd, ^3J = 12 Hz, ^3J = 17 Hz, 1H), 6.95 (s, 1H), 7.11 (s, 2H), 7.29-7.43 (m, 10H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 31.37, 32.27, 69.55, 72.90, 113.39, 123.39, 127.48, 127.60, 128.34, 137.05, 137.56, 138.61, 142.21. – **$C_{28}H_{32}O_2$ (400.55)**

7.4.3 Compounds of Chapter 4.2.3

1,3-Dibromo-5-iodo-benzene (18)

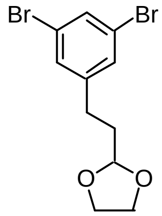


To a solution of 1,3,5-tribromobenzene **17** (13.43 g, 42.66 mmol) in diethylether (300 ml) *n*-butyl lithium (27.00 ml of a 1.6 M solution in hexane, 43.20 mmol, 1.01 eq.) was added within 30 min at -78 °C. After an additional hour solid 1,2-diiodo ethane (12.15 g, 43.11 mmol, 1.01 eq.) was added all at once, and the mixture was allowed to warm up to room temperature. 100 ml water were added, followed by usual extractive work-up. Recrystallization from diethylether gave 14.20 g (92 %) of the desired 1,3-dibromo-5-iodo-benzene **18** as colorless crystals.

The product was stored under exclusion of light to avoid brownish discoloring.

– **M.p.** 121 °C (Lit.: 122.5-123.5 °C)[152]. – ^{1}**H NMR** (270 MHz, $CDCl_3$): δ = 7.62 (s, ^{4}J = 1.7 Hz, 1H), 7.77 (s, ^{4}J = 1.7 Hz, 2H). – ^{13}**C NMR** (63 MHz, $CDCl_3$): δ = 94.43, 123.34, 133.60, 138.46. – **MS** (EI, 80 eV, 60 °C): *m/z* (rel. Int.) = 362 (100) $[C_6H_3{}^{79}Br^{81}BrI]^+$. – $\mathbf{C_6H_3Br_2I}$ **(361.80)**: calcd. C 19.92, H 0.84; found C 19.82, H 0.89.

2-[2-(1,3-Dibromo-phenyl)-ethyl]-[1,3]dioxolane (20a)

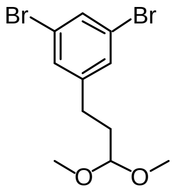


Procedure as described for **20b**:

2-Vinyl-[1,3]-dioxolane **19a**: 1.00 ml, 10.00 mmol; 9-BBN (0.5 M solution in tetrahydrofuran): 20.00 ml, 10.00 mmol; 1,3-dibromo-5-iodo-benzene **18**: 3.60 g, 9.95 mmol; additional tetrahydrofuran: 30 ml; aqueous sodium hydroxide (1 M): 25 ml; $Pd(PPh_3)_4$: 0.25 g, 0.22 mmol, 2.2 mol-%. Isolated yield: 1.84 g (55 %) of **20a** as a colorless oil.

– ^{1}**H NMR** (250 MHz, $CDCl_3$): δ = 1.92 (m, 2H), 2.67 (dd, 2H), 3.90 (m, 4H), 4.84 (t, 1H), 7.26 (s, 2H), 7.45 (s, 1H). – ^{13}**C NMR** (63 MHz, $CDCl_3$): δ = 29.31, 34.87, 64.95, 103.19, 122.73, 130.24, 131.52, 145.59. – **MS** (EI, 80 eV, 100 °C): *m/z* (rel. Int.) = 336 (66) $[C_{11}H_{12}{}^{79}Br^{81}BrO_2]^+$, 250 (26) $[H_2CCH(OCH_2)_2]^+$, 73 (100) $[HC(OCH_2)_2]^+$. – **HRMS**: *m/z* calcd. for $\mathbf{C_{11}H_{12}Br_2O_2}$ 335.918356; found 335.91635.

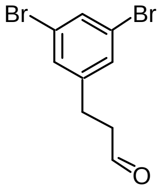
1,3-Dibromo-5-(3,3-dimethoxy-propyl)-benzene (20b)



3,3-Dimethoxy-propene **19b** (10.20 ml, 88.59 mmol) was added to a 0.5 M solution of 9-BBN in tetrahydrofuran (200.00 ml, 100.00 mmol, 1.13 eq.) at 0 °C, and the solution was stirred for 20 h at ambient temperature. After addition of 1,3-dibromo-5-iodo-benzene **18** (32.08 g, 88.67 mmol, 1.00 eq.), the catalyst precursor $Pd(PPh_3)_4$ (1.00 g, $8.65 \cdot 10^{-4}$ mol, 0.98 mol-%), aqueous sodium hydroxide (3 M, 85 ml) and additional tetrahydrofuran (50 ml) the suspension was stirred under reflux for 20 h. The reaction mixture was cooled with ice-water, and aqueous hydrogen peroxide (30 %, 35 ml) was added carefully. Extractive work-up with diethylether and column chromatography on silica gel (hexane, then hexane:ethyl acetate = 15:1) gave 20.36 g (68 %) of **20b** as a colorless oil.

– **R_f** = 0.23 (hexane:ethyl acetate = 10:1). – **^{1}H NMR** (270 MHz, $CDCl_3$): δ = 1.85 (m, 2H), 2.59 (dd, ^3J = 7.5 Hz, 2H), 3.33 (s, 6H), 4.39 (t, ^3J = 6.0 Hz, 1H), 7.25 (s, 2H), 7.48 (s, 1H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 30.17, 33.58, 52.80, 103.26, 122.76, 130.25, 131.56, 145.58. – **MS** (EI, 80 eV, 40 °C): *m/z* (rel. Int.) = 338 (7) $[C_{11}H_{14}{}^{79}Br^{81}BrO_2]^+$, 75 (100) $[HC(OCH_3)_2]^+$. – **HRMS**: *m/z* calcd. for **$C_{11}H_{14}Br_2O_2$** calcd. 335.97605; found 335.93298.

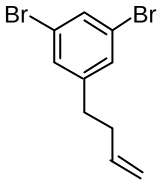
3-(3,5-Dibromo-phenyl)-propionaldehyde (21)



1,3-Dibromo-5-(3,3-dimethoxy-propyl)-benzene **20b** (9.42 g, 27.86 mmol) was solved in acetonitrile (120 ml) and water (13 ml). After addition of 2,3-dichloro-5,6-dicyano-quinone (0.63 g, 2.78 mmol, 0.1 eq.) the dark red suspension was stirred at room temperature for 18 h. A small amount of silica gel was added, and the solvent was evaporated. The residue was prepurified by a short column chromatography through celite (hexane:ethyl acetate = 10:1) to give 7.30 g (90 %) of **21** as a colorless oil.

– **R_f** = 0.20 (hexane:ethyl acetate = 6:1) – **^{1}H NMR** (270 MHz, $CDCl_3$): δ = 2.78 (m, 4H), 7.24 (s, 2H), 7.44 (s, 1H), 9.74 (s, 1H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 27.13, 44.38, 122.80, 130.10, 131.81, 144.30, 199.98. – **$C_9H_8Br_2O$ (291.97)**.

1-But-3-enyl-3,5-dibromo-benzene (15)



(a) Wittig procedure:

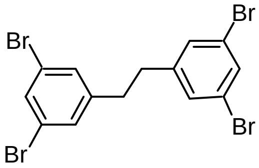
To a suspension of triphenylmethylphosphoniumiodide (9.34 g, 23.11 mmol) in tetrahydrofuran 14.30 ml of a 1.6 M solution of *n*-butyllithium in hexane (22.88 mmol, 0.99 eq.) were added at 0 °C within 5 min, and the orange solution was stirred for additional 45 min. 3-(3,5-Dibromo-phenyl)-propionaldehyde **21** (6.10 g, 20.89 mmol, 0.90 eq.) was solved in 20 ml tetrahydrofuran, and the solution was added dropwise. The mixture was stirred at room temperature for 2 h. The solution was decanted, the residue was washed with diethylether (3x), the combined organic layers were dried over $MgSO_4$. Purification by column chromatography on silica gel (hexane) gave 3.84 g (63 %) of **15** as a colorless liquid.

(b) Wurtz-Fittig-analogous procedure:

To a refluxing suspension of 3,5-dibromo-benzylbromide **14** (14.92 g, 45.37 mmol) in 50 ml diethylether 100 ml of a 1 M solution of allylmagnesiumbromide (100 mmol, 2.20 eq.) in diethylether was added within 15 min. The temperature was maintained for four additional hours. To the ice-cooled solution 50 ml of 5% hydrochloric acid was added carefully. The layers were separated, the aqueous one was extracted with diethylether (3x), the combined organic layers were dried over $MgSO_4$, filtered and evaporated. The resulting brownish oil was distilled (65 °C, $1{\cdot}10^{-2}$ mbar) to give 11.95 g (91 %) of **15** as a colorless liquid.

– **R_f** = 0.58 (hexane) – **^{1}H NMR** (270 MHz, $CDCl_3$): δ = 2.33 (q, 2H), 2.64 (t, 2H), 5.02 (m, 2H), 5.78 (m, 1H), 7.25 (s, 2H), 7.47 (s, 1H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 34.63, 34.79, 115.70, 122.67, 130.27, 131.48, 136.84, 145.65. – **MS** (EI, 80 eV, 40 °C): *m/z* (rel. Int.) = 290 (30) $[C_{10}H_{10}{}^{79}Br^{81}Br]^+$, 249 (100) $[M\text{-}C_3H_5]^+$. – **$C_{10}H_{10}Br_2$ (289.99)**: calcd. C 41.42, H 3.48; found C 41.41, H 3.07.

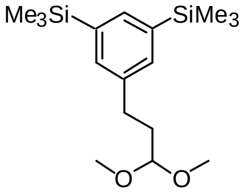
1,2-Bis-(3,5-dibromophenyl)-ethane (16)



This compound was isolated from a reaction mixture of **15**, inverse to procedure (b) when **14** was first reacted with magnesia. It was recrystallized from dichloromethane/diethylether and obtained as colorless crystals.

– **M.p.** 167 °C. – **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 2.84 (s, 4H), 7.22 (s, 4H), 7.52 (s, 2H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 36.67, 122.96, 130.30, 132.08, 144.50. – **MS** (EI, 80 eV, 160 °C): *m/z* (rel. Int.) = 498 (32) [$C_{14}H_{10}{}^{79}Br_2{}^{81}Br_2$]$^+$, 249 (100) [*M/2*]$^+$ or [*M*]$^{++}$ – **$C_{14}H_{10}Br_4$ (497.85)**: calcd. C 33.78, H 2.02; found C 33.95, H 1.83.

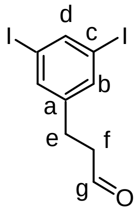
1,3-Bis-trimethylsilanyl-5-(3,3-dimethoxy-propyl)-benzene (23)



3,3-Dimethoxy-propene **19b** (17.0 ml, 147.7 mmol) was added to a solution of 9-BBN (18.1 g, 148.6 mmol, 1.0 eq.) in tetrahydrofuran (200 ml) at 0 °C, and the solution was stirred for 14 h at ambient temperature. After addition of 1-bromo-3,5-bis(trimethylsilanyl)-benzene **22** (41.9 g, 139.0 mmol, 0.94 eq.), the catalyst precursor $Pd(PPh_3)_4$ (1.60 g, 1.39 mmol, 1.0 mol-%), and aqueous sodium hydroxide (3 M, 100 ml) the suspension was stirred under reflux for 15 h. The reaction mixture was cooled with ice-water, and aqueous hydrogen peroxide (30 %, 60 ml) was added carefully. The solution was decanted, the residue was washed with diethylether (3x), the combined organic layers were washed with brine and dried over $MgSO_4$, and evaporation of the filtrate gave 60 g of a brownish oil. Column chromatography on silica gel (hexane, then hexane:ethyl acetate = 20:1) gave 36.6 g (76 %) of **23** as a colorless oil.

– **R_f** = 0.26 (hexane:ethyl acetate = 10:1) – **^{1}H NMR** (270 MHz, $CDCl_3$): δ = 0.27 (s, 18H), 1.95 (m, 2H), 2.68 (m, 2H), 3.46 (s, 6H), 4.42 (t, ^3J = 6.0 Hz, 1H), 7.35 (s, 2H), 7.51 (s, 1H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = -1.06, 31.15, 34.47, 52.80, 104.03, 133.99, 135.77, 139.54, 139.82. – **MS** (EI, 80 eV, 130 °C): *m/z* (rel. Int.) = 324 (2) [*M*]$^+$, 323 (7) [*M-H*]$^+$, 291 (4) [*M-HOCH$_3$*]$^+$, 276 (17) [*M-CH$_3$-HOCH$_3$*]$^+$, 73 (100) [*TMS*]$^+$. – **HRMS**: *m/z* calcd. for **$C_{11}H_{12}Br_2O_2$** 324.194087; found 324.19732. – **$C_{11}H_{12}Br_2O_2$ (324.60)**: calcd. C 62.90, H 9.94; found 62.46, H 9.95.

3-(3,5-Diiodo-phenyl)-propionaldehyde (26)

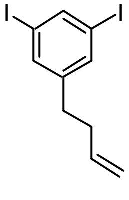


To a solution of 1,3-bis-trimethylsilanyl-5-(3,3-dimethoxy-propyl)-benzene **23** (30.8 g, 94.9 mmol) in 250 ml dichloromethane at 78 °C was added a solution of iodomonochloride (42.9 g, 264.4 mmol, 2.7 eq.) in 50 ml dichloromethane within 2 h. After additional 30 min of stirring, an aqueous saturated solution of $Na_2S_2O_5$ was added and the layers were separated. The aqueous one was washed with dichloromethane twice and the combined organic layers were dried ($MgSO_4$), filtered and the solvent removed. The residue was chromographed through a short column of silica gel (hexane:ethyl acetate = 20:1) and precipitated from dichloromethane/methanol to yield 9.2 g (25 %) of **26** as a pale yellow solid.

The raw reaction mixture also contained large amounts of the corresponding diiodoacetal **25**. To achieve a higher yield of **26** the mixture was reacted with DDQ as described for **21**. The isolated overall yield was increased to 74 % of **26**. It was found that aldehyde **26** was not stable on silica gel, therefore considerable loss occurred. The mass spec indicated the formation of the corresponding acid. The α-chloro derivative **27** was obtained when the desilylation step was performed at >0 °C (see text).

– **M.p.** 65-66 °C. – $\mathbf{R_f}$ = 0.23 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.74 (m, 2H), 2.80 (m, 2H), 7.48 (s, 2H, *H-b*), 7.86 (s, 1H, *H-d*), 9.77 (s, 1H, *H-g*). – **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 26.09 (*C-e*), 44.62 (*C-f*), 94.86 (*C-c*), 136.67 (*C-b*), 142.96 (*C-d*), 144.58 (*C-a*), 200.31 (*C-g*). – **MS** (EI, 80 eV, 90 °C): *m/z* (%) = 386 (100) $[M]^+$. – **$C_9H_8I_2O$ (385.97)**: calcd. C 28.01, H 2.09; found C 27.99, H 2.05.

1-But-3-enyl-3,5-diiodo-benzene (28)



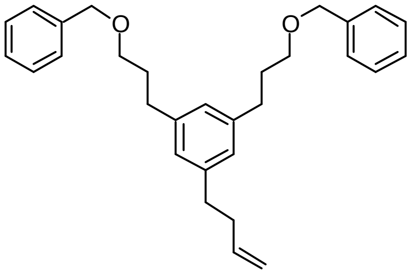
As desribed for **15**, procedure (a):

Triphenylmethylphosphoniumiodide: 0.70 g (1.73 mmol), tetrahydrofuran: 20 ml, *n*-butyl-lithium: 1.05 ml (1.6 M solution in hexane, 1.68 mmol, 1.14 eq.), 3-(3,5-diiodo-phenyl)-propionaldehyde **26**: 0.57 g (1.48 mmol), in 10 ml tetrahydrofuran, column chromatography on silica gel (hexane) gave 0.53 g (62 %) of **28** as a liquid.

– **R$_f$** = 0.70 (hexane:ethyl acetate = 6:1) – **^{1}H NMR** (270 MHz, CDCl$_3$): δ = 2.32 (m, 2H), 2.57 (t, 2H), 5.01 (m, 2H), 5.78 (m, 1H), 7.50 (s, 2H), 7.86 (s, 1H). – **^{13}C NMR** (63 MHz, CDCl$_3$): δ = 34.36, 34.85, 94.76, 115.68, 136.79, 136.89, 142.51, 145.96. – **MS** (EI, 80 eV, 40 °C): *m/z* (rel. Int.) = 384 (66) $[M]^+$, 343 (100) $[M\text{-}C_3H_5]^+$. – **$C_{10}H_{10}I_2$ (384.00)**: calcd. C 31.28, H 2.62; found C 31.52, H 2.48.

7.4.4 Compounds of Chapter 4.2.4

1-But-3-enyl-3,5-bis-(3-benzyloxy-propyl)-benzene (29)

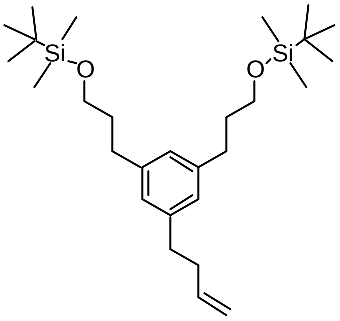


Procedure as described for **6**:

Allylbenzylether **5**: 1.51 g, 10.19 mmol, 3.08 eq.; 9-BBN (0.5 M solution in tetrahydrofuran): 20.0 ml, 10.0 mmol, 3.7 eq.; aqueous sodium hydroxide (1 M, 20 ml); 1-but-3-enyl-3,5-dibromo-benzene **15**: 0.78 g, 2.69 mmol; $Pd(PPh_3)_4$: 0.23 g, 0.11 mmol, 2.04 mol-% per coupling; 5 d reflux; yield: 1.10 g (95 %) of **29** as a colorless oil.

– **R_f** = 0.34 (hexane:ethyl acetate = 10:1). – **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 1.84 (m, 4H, $CH_2\mathit{CH_2}CH_2O$), 2.26 (m, 2H, $CH_2\mathit{CH_2}CH$), 2.59 (m, 6H, Ph-$\mathit{CH_2}$), 3.37 (t, ^{3}J = 7 Hz, 4H, $CH_2CH_2\mathit{CH_2}O$), 4.39 (s, 2H, Ph$\mathit{CH_2}$O), 4.86-4.98 (m, 2H, CH=$\mathit{CH_2}$), 5.77 (m, 1H, CH=CH_2), 6.92 (s, 3H), 7.32-7.44 (m, 10H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 31.33, 32.27, 35.27, 35.47, 69.45, 72.81, 114.75, 125.76, 125.88, 127.53, 128.16, 128.57, 138.04, 138.55, 141.86, 141.86. – **MS** (EI, 80 eV, 130 °C): *m/z* (rel. Int.) = 428 (2) $[M]^+$, 337 (100) $[M\text{-}C_7H_7]^+$. – **HRMS**: *m/z* calcd. for **$C_{30}H_{36}O_2$ (428.61)** 428.27153; found 428.27158.

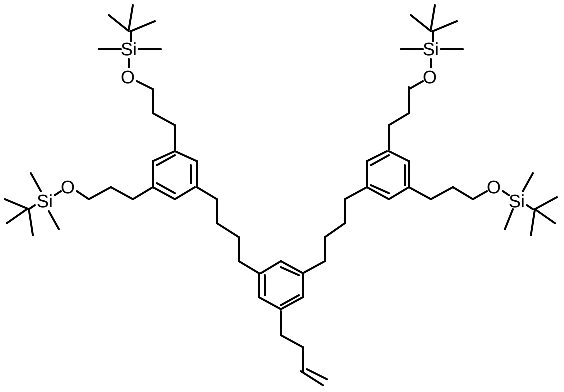
1-But-3-enyl-3,5-bis-[3-(*tert*-butyl-dimethyl-silanoxy)-propyl]-benzene (31)



Allyloxy-dimethyl-*tert*-butyl-silane **30** (11.00 ml, 51.76 mmol, 3.01 eq.) was added to a solution of 9-BBN (6.31 g, 51.71 mmol, 3.01 eq.) in tetrahydrofuran (60.00 ml) at 0 °C, and the solution was stirred for 20 h at ambient temperature. After addition of aqueous sodium hydroxide (1 M, 150 ml), 1-but-3-enyl-3,5-dibromo-benzene **15** (4.99 g, 17.21 mmol), the catalyst precursor $Pd(PPh_3)_4$ (0.44 g, $3.8\cdot10^{-4}$ mol, 1.1 mol-% per coupling), and additional tetrahydrofuran (100 ml) the suspension was stirred under reflux for 17 h. Extractive work-up with diethylether and column chromatography on silica gel (hexane:ethyl acetate = 20:1) gave 8.27 g (80 %) of **31** as a colorless liquid.

– $\mathbf{R_f}$ = 0.64 (hexane:ethyl acetate = 20:1). – $\mathbf{^1H}$ **NMR** (250 MHz, $CDCl_3$): δ = 0.08 (s, 12H, Si(CH_3)$_2$), 0.94 (s, 18H, ^{t}*Bu*), 1.86 (m, 4H, CH_2*CH_2*CH_2O), 2.36 (m, 2H, CH_2*CH_2*CH), 2.66 (m, 6H, Ph-*CH_2*), 3.66 (t, ^3J = 7.0 Hz, 4H, CH_2CH_2*CH_2*O), 4.98-5.11 (m, 2H, CH=*CH_2*), 5.89 (m, 1H, *CH*=CH_2), 6.87 (s, 3H). – $\mathbf{^{13}C}$ **NMR** (63 MHz, $CDCl_3$): δ = -5.26, 18.35, 25.99, 32.03, 34.49, 35.41, 35.62, 62.48, 114.69, 126.03, 126.24, 138.31, 141.75, 142.14. – **MS** (EI, 80 eV, 60 °C): *m/z* (rel. Int.) = 476 (<1) $[M]^+$, 460 (1) $[M\text{-}CH_4]^+$, 446 (1) $[M\text{-}2CH_3]^+$, 418 (33) $[M+H\text{-}^tBu]^+$, 346 (61) $[M+H\text{-}OSi(CH_3)_2{}^tBu]^+$, 75 (100) $[OSi(CH_3)_2]^+$. – $\mathbf{C_{28}H_{52}O_2Si_2}$ **(476.88)**: calcd. C 70.52, H 10.99; found C 70.74, H 10.75.

1-But-3-enyl-3,5-bis-(3-{3,5-bis-[3-(*tert*-butyl-dimethyl-silanoxy)-propyl]-phenyl}-propyl)-benzene (32)



Procedure as described for **31**:

31: 3.10 g (6.50 mmol, 3.09 eq.); 9-BBN (0.5 M solution in tetrahydrofuran): 13.00 ml (6.50 mmol, 3.09 eq.); aqueous sodium hydroxide (1 M): 25 ml); 1-but-3-enyl-3,5-diiodo-benzene **28**: 0.81 g (2.10 mmol); Pd(PPh_3)$_4$: 0.15 g ($1.3\cdot10^{-4}$ mol, 3.09 mol-% per coupling); additional tetrahydrofuran: 20 ml; yield: 1.71 g (75 %) of **32** as a colorless liquid.

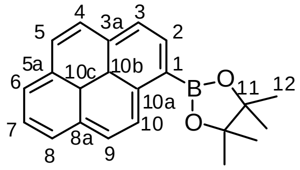
– $\mathbf{R_f}$ = 0.38 (hexane:ethyl acetate = 20:1). – $\mathbf{^1H}$ **NMR** (250 MHz, $CDCl_3$): δ = 0.01 (s, 24H, Si(CH_3)$_2$), 0.96 (s, 36H, ^{t}*Bu*), 1.70 (m, 8H, CH_2*CH_2CH_2*CH_2), 1.86 (m, 8H, CH_2*CH_2*CH_2O), 2.40 (m, 2H, CH_2*CH_2*CH), 2.63-2.70 (m, 18H, Ph-*CH_2*), 3.68 (t, ^3J = 7.0 Hz, 8H, CH_2CH_2*CH_2*O), 5.00-5.10 (m, 2H, CH=*CH_2*), 5.91 (m, 1H, *CH*=CH_2), 6.87-6.88 (m, 9H). – $\mathbf{^{13}C}$ **NMR** (63 MHz, $CDCl_3$): δ = -5.27, 18.33, 25.98, 26.19, 31.34, 32.03, 34.47, 35.38, 35.61, 35.81, 62.48, 114.70, 125.75, 125.91, 126.02, 126.68, 138.28, 141.67, 142.07, 142.53. – **MS** (EI, 80 eV, 200 °C): *m/z* (rel. Int.) = 1085 (1) $[M]^+$, 1070 (8) $[M\text{-}CH_3]^+$, 1028 (100) $[M\text{-}^tBu]^+$. – $\mathbf{C_{66}H_{116}O_4Si_4}$ **(1085.97)**: calcd. C 73.00, H 10.77; found C 72.97, H 10.69.

7.4.5 Compounds of Chapter 4.3.1

1-Bromopyrene (38)

Several literature procedures were performed (see text).[170,172,173] They all gave mixtures of pyrene, 1-bromopyrene, the three dibromopyrenes, and tribromopyrene which were purified by repeated recrystallisation from dichloromethane/methanol. The composition was determined by analytical reversed phase HPLC with methanol/ tetrahydrofuran 9:1 as eluent. Typical retention times were: pyrene 1.82 min, 1-bromopyrene 2.47 min, 1,8-dibromopyrene 3.47 min, 1,6-dibromopyrene 3.72 min, 1,3-dibromopyrene 4.12 min, and tribromopyrene 6.70 min. For the lithiation step (see **40**) only suitable fractions with amounts of di- and tribromopyrenes smaller than 3 % were used.

4,4,5,5-Tetramethyl-2-pyren-1-yl-1,3,2-dioxaborolane (40)

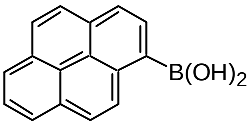


To a solution of 1.07 g 1-bromopyrene **38** (3.81 mmol) in 50 ml tetrahydrofuran at –78°C *n*-butyllithium (2.6 ml of a 1.6 M solution in hexane, 4.16 mmol, 1.09 eq.) was added dropwise. After stirring for 30 min at this temperature, triisopropyl borate (1.75 ml, 7.58 mmol, 2.00 eq.) was added and the solution was allowed to warm up to room temperature within 30 min. 50 ml of hydrochloric acid (5 %) were added, the layers were separated and the aqueous one was extracted with diethyl ether (3x). 2,3-dimethyl-2,3-butanediol (pinacole) (1.46 g, 12.35 mmol, 3.24 eq.) was added to the combined organic phases, and the solution was stirred at 40 °C for 45 min until completion of the reaction as detected by the disappearance of the free boronic acid in the TLC. After removal of the solvent under vacuo, the remaining dark oil was chromatographed on silica gel (hexane:ethyl acetate = 20:1). Precipitation from dichloromethane/methanol gave 1.06 g (85 %) of **40** as a yellowish solid.

– **M.p.** 123 °C. – **R_f** = 0.24 (hexane:ethyl acetate = 20:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.55 (s, 12H, *H-12*), 8.04 (t, ^3J = 7.6 Hz, 1H, *H-7*), 8.09 (d, ^3J = 8.8 Hz, 1H, *H-4*), 8.13 (d, ^3J = 8.8 Hz, 1H, *H-5*), 8.21 (d, ^3J = 7.6 Hz, 1H, *H-6*), 8.23 (d, ^3J = 9.0 Hz, 1H, *H-9*), 8.24 (d, ^3J = 7.6 Hz, 1H, *H-3*), 8.26 (d, ^3J = 7.6 Hz, 1H, *H-8*), 8.67 (d, ^3J = 7.6 Hz, 1H, *H-2*), 9.21 (d, ^3J = 9.0 Hz, 1H, *H-10*). – **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 24.98 (*C-12*), 83.80 (*C-11*), 124.03 (*C-3*), 124.31 (C-*10b*), 124.51 (C-*10c*), 125.14 (C-*6*), 125.29 (C-*8*), 125.63 (C-*7*), 127.40 (C-*4*), 127.74 (*C-9*), 127.95 (*C-10*), 128.47 (*C-5*), 130.67 (*C-8a*), 131.01 (*C-5a*), 133.38 (*C-3a*), 133.82 (*C-2*), 136.38 (*C-10a*). – **MS** (70 eV, 135 °C): *m/z* (%) = 328 (100) [*M*]$^+$, 313 (1), 270

(5), 255 (13), 228 (56), 202 (7). – **IR** (KBr): $\tilde{n}$ = 3046 (w), 2970 (m), 2926 (w), 1347, 1355, 1371, 1378, 1388 (s, *Ar-B(OR)₂*) cm^{-1}. – **$C_{22}H_{21}BO_2$ (328.21)**: calcd. C 80.51, H 6.45; found C 80.42, H 6.31.

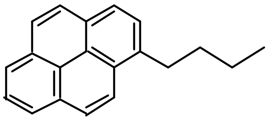
Pyren-1-yl-boronic acid (39)



This compound was obtained by chromatographic separation (hexane:ethyl acetate = 20:1, then ethanol) of the raw product after extractive work-up as described for **40**, and subsequent precipitation from ethanol.

– **M.p.** >265 °C. – **^{1}H NMR** (250 MHz, d_6-DMSO): δ = 8.04 (t, ^3J = 7.5 Hz, 1H, *H-7*), 8.14-8.30 (m, 6H), 8.35 (d, ^3J = 7.5 Hz, 1H, *H-2*), 8.66 (s, 2H, *B(O$\underline{H}$)₂*), 8.79 (d, ^3J = 9.0 Hz, 1H, *H-10*). – **^{13}C NMR** (63 MHz, d_6-DMSO): δ = 123.1, 123.7, 124.1 (br), 125.0 (br), 126.0 (br), 126.9 (br), 127.6 (br), 128.6 (br), 130.5, 130.9, 131.5, 131.9 (br), 132.6 (br), 134.1. – **MS** (70 eV, 40 °C): *m/z* (%) = 246 (33) [*M*]$^+$, 228 (21) [*M-H_2O*]$^+$, 202 (18) [*M-B(OH)₂*]$^+$. – **HRMS**: *m/z* calcd. for **$C_{16}H_{11}BO_2$** 246.08521; found 246.08921.

1-Butylpyrene



1-Butylpyrene was isolated as a side-product in the synthesis of 4,4,5,5-tetramethyl-2-pyren-1-yl-1,3,2-dioxaborolane **40**, when the lithiatation was performed in diethylether at room temperature.

– **M.p.** 63 °C (65 °C)[265]. – **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 1.01 (t, ^3J = 8 Hz, 3H), 1.56 (tq, ^3J = 8 Hz, 2H), 1.84 (tt, ^3J = 8 Hz, 2H), 3.34 (t, ^3J = 8 Hz, 2H), 7.87 (d, ^3J = 8 Hz, 1H), 7.95-8.20 (m, 7H), 8.29 (d, ^3J = 8 Hz, 1H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 14.14, 22.94, 33.32, 34.09, 123.52, 124.62, 124.78, 124.94, 125.73, 125.83, 126.47, 127.07, 127.37, 127.55, 128.62, 129.70, 130.97, 131.14, 131.48, 137.27. – **MS** (70 eV, 100 °C): *m/z* (rel. Int.) = 258 (25) [*M*]$^+$, 215 (100) [*M-C_3H_7*]$^+$, 202 (19) [*Pyrene*]$^+$. – **HRMS**: *m/z* calcd. for **$C_{20}H_{18}$** 258.140851; found 258.14422.

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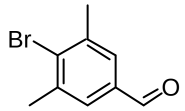
[265] C. Eaborn, Z. Lasocki, J. A. Sperry, *J. Organomet. Chem.* **1972**, *35*, 245-252.

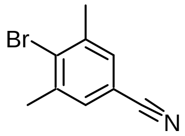
4-Bromo-3,5-dimethyl-benzaldehyde (42)



2,5-Dibromoxylene **41** (1.90 g, 7.20 mmol) in 20 ml diethylether was treated with *n*-butyllithium (4.5 ml of a 1.6 M solution in hexane, 1.0 eq.) at –78 °C. After stirring for 45 min, *N*,*N*-dimethylformamide (1.7 ml, 22.0 mmol, 3.06 eq.) was added and the solution was allowed to warm up to room temperature. The mixture was acidified with 5 % hydrochloric acid and extracted with diethylether. The obtained residue after usual work-up was chromatographed on silica gel (hexane:ethyl acetate = 10:1) and crystallized from diethylether to give 1.21 g (79 %) of **42** as colorless crystals.

– **M.p.** 67 °C. – **R_f** = 0.49 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 2.46 (s, 6H), 7.54 (s, 2H), 9.91 (s, 1H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 23.83, 128.81, 132.51, 134.76, 139.52, 191.61. – **MS** (EI, 80 eV, 30 °C): *m/z* (%) = 214 (80) $[C_9H_9{}^{81}BrO]^+$, 212 (78) $[C_9H_9{}^{79}BrO]^+$, 211 (100) $[C_9H_8{}^{79}BrO]^+$. – **IR** (KBr): $\tilde{n}$ = 1684 (*CO*, vs) cm^{-1}. – **C_9H_9BrO (213.07)**: calcd. C 50.73, H 4.26; found C 50.51, H 4.35.

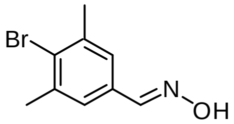
4-Bromo-3,5-dimethyl-benzonitrile (44e)



(I) From benzaldehyde 42: Aldehyde **42** (1.05 g, 4.93 mmol) was dissolved in a mixture of hydroxylamine hydrochloride (0.37 g, 5.33 mmol, 1.08 eq.) and pyridine (0.81 ml, 10.02 mmol, 2.03 eq.). After a few minutes 5 ml of toluene were added, and the solution was heated under reflux in a water trap for 2 h. The reaction mixture was extracted with toluene (3x), the combined organic phases were dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexane:ethyl acetate = 10:1). Yield: 39 % of **44e**. The main product was 4-bromo-3,5-dimethyl-benzaldehyde oxime **43** (see below).

– **M.p.** 144 °C. – **R_f** = 0.48 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 2.43 (s, 6H), 7.32 (s, 2H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 3.74, 110.60, 118.30, 130.99, 133.08, 139.92. – **MS** (EI, 80 eV, 40 °C): *m/z* (%) = 211 (99) $[C_9H_8{}^{81}BrN]^+$, 209 (100) $[C_9H_8{}^{79}BrN]^+$. – **IR** (KBr): $\tilde{n}$ = 2222 (*CN*, m) cm^{-1}. – **C_9H_8BrN (210.07)**: calcd. C 51.46, H 3.84, N 6.67; found C 51.11, H 3.68, N 6.59.

4-Bromo-3,5-dimethyl-benzaldehyde oxime (43)



The aldoxime **43** was isolated as the main product in the synthesis of **44e** according to route **I** in a 56 % yield.

– **R_f** = 0.20 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 2.41 (s, 6H), 7.26 (s, 2H), 8.04 (s, 1H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 23.80, 126.49, 129.48, 130.28, 138.90, 149.74. – **MS** (EI, 80 eV, 50 °C): *m/z* (%) = 229 (98) $[C_9H_{10}{}^{81}BrNO]^+$, 227 (100) $[C_9H_{10}{}^{79}BrNO]^+$. – **$C_9H_{10}BrNO$** (228.09)

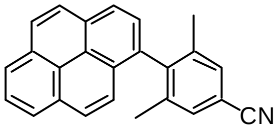
4-Bromo-3,5-dimethyl-benzonitrile (44e)

(II) From benzaldehyde oxime 43

Aldoxime **43** (0.40 g, 1.76 mmol) was supended in a mixture of carbondisulfide (0.75 ml), aqueous sodium hydroxide (3 M, 1 ml), toluene (3 ml), and tetra-*n*-butylammonium hydrogensulphate (0.14 g, 0.41 mmol). This mixture was stirred for 20 h at room temperature. After extractive work-up with toluene the residue was chromatographed on silica gel (hexane:ethyl acetate = 10:1) The product was precipitated from dichloromethane/methanol to give 0.30 g (75 %) of the benzonitrile **44e** as colorless crystals.

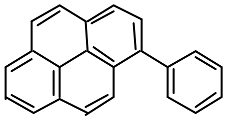
Typical procedure for the Suzuki cross-coupling of ***40*** *and* ***44a-n*** *and* ***98****. The isolated yields of phenylpyrenes* ***45a-n*** *are summarized in table 1 in chapter 4.3.1.*

3,5-Dimethyl-4-pyren-1-yl-benzonitrile (45e)



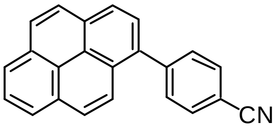
After degassing of a mixture of **40** (0.36 g, 1.10 mmol), **44e** (0.23 g, 1.09 mmol), toluene (20 ml), and aqueous sodium hydroxide (1 M, 10 ml), the catalyst precursor $Pd(PPh_3)_4$ (25.4 mg, 2 mol-%) was added, and the mixture was stirred under reflux for 20 h. The layers were separated, the aqueous layer was extracted with toluene (3x), the combined organic layers were dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexane:ethyl acetate = 20:1) to give 0.10 g (28 %) of **45e**. – **M.p.** 217-218 °C. – **R_f** = 0.23 (hexane:ethyl acetate = 20:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.92 (s, 6H), 7.45 (d, ^3J = 9.0 Hz, 1H), 7.53 (s, 1H), 7.71 (d, ^3J = 7.5 Hz, 1H), 7.98 (d, ^3J = 9.0 Hz, 1H), 8.03 (d, ^3J = 7.5 Hz, 1H), 8.13 (s, 1H), 8.18 (d, ^3J = 7.5 Hz, 1H), 8.23 (d, ^3J = 7.5 Hz, 1H), 8.27 (d, ^3J = 7.5 Hz, 1H). – **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 20.48, 111.22, 119.27, 123.81, 124.72, 124.89, 125.09, 125.27, 125.47, 126.04, 126.21, 127.30, 127.66, 128.05, 128.24, 130.84, 130.89, 131.23, 133.97, 138.75, 145.37. – **MS** (EI, 80 eV, 120°C): *m/z* (%) = 331 (100) [*M*]$^+$, 314 (37), 301 (11), 202 (4). – **UV/VIS** (Acetonitrile): λ_{max} = 342 nm. – **$C_{25}H_{17}N$ (331.41):** calcd. C 90.60, H 5.17, N 4.23; found C 90.19, H 5.18, N 4.27.

1-Phenyl-pyrene (45a)



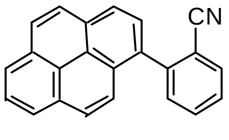
– **M.p.** 93 °C (83 °C)[258]. – **R_f** = 0.26 (hexane). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.51-7.72 (m, 5H), 7.99-8.27 (m, 9H). – **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 124.61, 124.78, 124.84, 124.89, 125.06, 125.23, 125.96, 127.21, 127.38, 127.42, 127.57, 128.34, 128.42, 130.52, 130.57, 130.91, 131.42, 137.68, 141.15. – **MS** (70 eV, 110 °C): *m/z* (%) = 278 (100) [*M*]$^+$. – **$C_{22}H_{14}$ (278.35)**: calcd. C 94.93, H 5.07; found C 94.48, H 5.02.

4-Pyren-1-yl-benzonitrile (45b)



– **M.p.** 153 °C. – **R_f** = 0.10 (hexane:ethyl acetate = 20:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.68 (d, ^3J = 8.5 Hz, 2H), 7.81 (d, ^3J = 8.5 Hz, 2H), 7.88 (d, ^3J = 7.8 Hz, 1H), 7.99-8.23 (m, 8H). – **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 110.89, 118.90, 124.09, 124.62, 125.54, 126.18, 127.04, 127.17, 127.96, 128.12, 130.66, 131.13, 131.27, 132.04, 135.15, 145.90. – **MS** (70 eV, 315 °C): *m/z* (%) = 303 (100) [*M*]$^+$, 276 (4), 138 (6). – **IR** (KBr): $\tilde{n}$ = 2224 (*CN*, m) cm^{-1}. – **UV/VIS** (Acetonitrile): λ_{max} = 344 nm (31500). – **$C_{23}H_{13}N$ (303.36)**: calcd. C 91.06, H 4.32, N 4.62; found C 91.11, H 4.59, N 4.53.

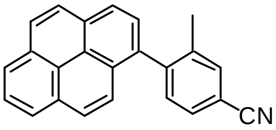
2-Pyren-1-yl-benzonitrile (45c)



– **M.p.** 176 °C. – **R_f** = 0.10 (hexane:ethyl acetate = 20:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.55 (t, ^3J = 7.5 Hz, 1H), 7.63 (d, ^3J = 7.5 Hz, 1H), 7.72 (t, ^3J = 7.5 Hz, 1H), 7.81 (d, ^3J = 10 Hz, 1H), 7.89 (d, ^3J = 7.5Hz, 1H), 7.97 (m, 3H), 8.12 (s, 2H), 8.18 (d, ^3J = 7.5Hz, 1H), 8.22

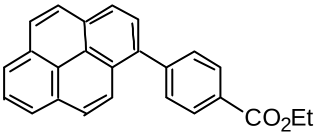
(d, ^3J = 7.5 Hz, 1H), 8.26 (d, ^3J = 8.0 Hz, 1H). – **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 113.75, 118.24, 124.19, 124.55, 124.59, 124.77, 125.31, 125.59, 126.16, 127.29, 127.36, 127.88, 128.08, 128.21, 128.80, 130.72, 131.26, 131.58, 131.96, 132.32, 132.98, 133.22, 144.83. – **MS** (70 eV, 120 °C): *m/z* (%) = 303 (100) [*M*]$^+$, 276 (6), 138 (7). – **IR** (KBr): $\tilde{n}$ = 2218 (*CN*, m) cm^{-1}. – **UV/VIS** (Acetonitrile): λ_{max} = 342 nm (19200). – **HRMS**: *m/z* calcd. for **$C_{23}H_{13}N$** 303.10480; found 303.10623.

3-Methyl-4-pyren-1-yl-benzonitrile (45d)



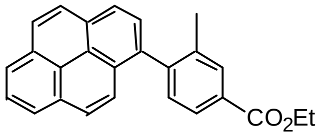
– **M.p.** 176 °C. – **R_f** = 0.10 (hexane:ethyl acetate = 20:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.06 (s, 3H), 7.45 (d, ^3J = 7.5 Hz, 1H), 7.57 (d, ^3J = 10.0 Hz, 1H), 7.64 (d, ^3J = 8.5 Hz, 1H), 7.68 (s, 1H), 7.79 (d, ^3J = 7.5 Hz, 1H), 8.02 (dd, ^3J = 8.5 Hz, 2H), 8.12 (s, 2H), 8.18 (d, ^3J = 7.5 Hz, 1H), 8.23 (d, ^3J = 8.5 Hz, 2H). – **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 20.08, 111.45, 119.09, 124.38, 124.58, 124.63, 125.28, 125.53, 126.23, 126.51, 127.27,1 27.80, 128.09, 128.36, 129.39, 130.75, 131.02, 131.27, 131.48, 133.44, 134.88, 138.62, 145.79. – **MS** (EI, 80 eV, 160 °C): *m/z* (%) = 317 (100) [*M*]$^+$. – **IR** (KBr): $\tilde{n}$ = 2230 (*CN*, s) cm^{-1}. – **UV/VIS** (Acetonitrile): λ_{max} = 342 nm (39800). – **$C_{24}H_{15}N$ (317.38)**: calcd. C 90.82, H 4.76, N 4.41; found C 90.77, H 4.86, N 4.23.

4-Pyren-1-yl-benzoic acid ethyl ester (45f)



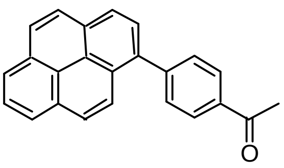
– **M.p.** 129 °C. – **R_f** = 0.44 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.37 (t, 3H), 4.39 (q, 4H), 7.57 (d, ^3J = 8.0 Hz, 2H), 7.80-8.17 (m, 11H). – **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 14.41, 61.06, 124.65, 124.78, 124.92, 125.04, 125.83, 126.13, 127.31, 127.34, 127.75, 127.85, 128.35, 129.33, 129.79, 130.58, 130.88, 130.90, 131.43, 136.48, 145.90, 166.59. – **MS** (EI, 80 eV, 180 °C): *m/z* (%) = 350 (100) [*M*]$^+$, 322 (16), 305 (4), 276 (28), 202 (7), 138 (8). – **IR** (KBr): $\tilde{n}$ = 1719 (*CO*, vs) cm^{-1}. – **UV/VIS** (Acetonitrile): λ_{max} = 342 nm (31200). – **HRMS**: *m/z* calcd. for **$C_{25}H_{18}O$** 350.13068; found 350.12470.

3-Methyl-4-pyren-1-yl-benzoic acid ethyl ester (45g)



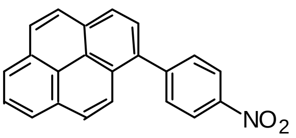
– **M.p.** 131 °C. – **R_f** = 0.45 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (500 MHz, CDCl$_3$): δ = 1.48 (t, 3H), 2.12 (s, 3H), 4.48 (q, 2H), 7.46 (d, ^3J = 7.5 Hz, 1H), 7.66 (d, ^3J = 10.0 Hz, 1H), 7.84 (d, ^3J = 7.5 Hz, 1H), 7.96-8.24 (m, 9H). – **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 14.39, 20.18, 60.98, 124.50, 124.61, 124.67, 124.83, 125.05, 125.26, 126.74, 126.81, 127.30, 127.49, 127.72, 128.50, 129.73, 130.82, 131.03, 131.28, 136.07, 137.33, 145.47, 166.75. – **MS** (EI, 80 eV, 180 °C): *m/z* (%) = 364 (100) [*M*]$^+$, 336 (7), 319 (5), 276 (15), 138 (11). – **IR** (KBr): $\tilde{n}$ = 1706 (*CO*, vs) cm^{-1}. – **UV/VIS** (Acetonitrile): λ_{max} = 342 nm (37900). – **$C_{26}H_{20}O_2$ (364.44)**: calcd. C 85.69, H 5.53; found C 85.44, H 5.58.

1-(4-Pyren-1-yl-phenyl)-ethanone (45h)



– **M.p.** 184-85 °C. – ***R_f*** = 0.22 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (500 MHz, CDCl$_3$): δ = 2.69 (s, 3H), 7.64 (d, ^3J = 8.2 Hz, 2H), 7.91 (d, ^3J = 7.9 Hz, 1H), 7.97-8.21 (m, 10H). – **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 26.62, 124.58, 124.80, 124.98, 125.31, 126.06, 127.17, 127.23, 127.70, 127.81, 128.19, 128.32, 130.69, 130.92, 131.31, 135.73, 136.12, 146.06, 197.74. – **MS** (70 eV, 315 °C): *m/z* (%) = 320 (100) [*M*]$^+$, 305 (6), 276 (51), 138 (13). – **IR** (KBr): $\tilde{n}$ = 1681 (*CO*, vs) cm^{-1}. – **UV/VIS** (Acetonitrile): λ_{max} = 343 nm (33200). – **HRMS**: *m/z* calcd. for **$C_{24}H_{16}O$** 320.120115; found 320.12341.

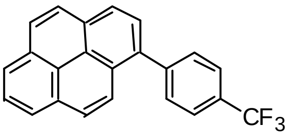
1-(4-Nitro-phenyl)-pyrene (45i)



– **M.p.** 206-207 °C. – **R_f** = 0.36 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (270 MHz, CDCl$_3$): δ = 7.77 (d, ^3J = 8.8 Hz, 2H), 7.93 (d, ^3J = 7.9 Hz, 1H), 8.00-8.25 (m, 8H), 8.39 (d, ^3J = 8.8 Hz, 2H). – **^{13}C NMR** (63 MHz, CDCl$_3$): δ = 123.59, 124.10, 124.69, 124.86, 125.30, 125.68, 126.29, 127.11, 127.24, 128.14, 128.19, 128.39, 130.72, 131.32, 134.80, 147.02, 148.05. – **MS** (EI, 80 eV, 250 °C): *m/z* (%) = 323 (100) [*M*]$^+$, 276 (46), 138 (12). – **IR** (KBr): $\tilde{n}$ = 1539

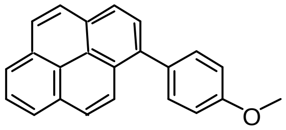
(*N*=*O* [ν_{as}], vs), 1342 (*N*=*O* [ν_s], vs) cm^{-1}. – **UV/VIS** (Acetonitrile): λ_{max} = 340 nm (18400). – **$C_{22}H_{13}NO$ (323.34)**: calcd. C 81.72, H 4.03, N 4.33; found C 81.66, H 4.14, N 4.19.

1-(4-Trifluoromethyl-phenyl)-pyrene (45j)



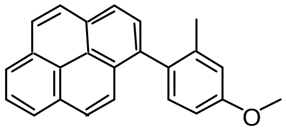
– **M.p.** 133 °C. – **R_f** = 0.54 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (250 MHz, CDCl$_3$): δ = 7.72 (d, ^3J = 8 Hz, 2H), 7.83 (d, ^3J = 8 Hz, 2H), 7.93 (d, ^3J = 8 Hz, 1H), 7.97-8.07 (m, 3H), 8.09 (s, 2H), 8.13-8.23 (m, 3H). – **^{13}C NMR** (63 MHz, CDCl$_3$): δ = 122.34, 124.56, 124.69, 124.92, 125.13, 125.37, 125.46, 126.18, 126.67, 127.32, 127.84, 127.99, 128.35, 129.16, 129.68, 130.89, 131.07, 131.43, 135.89, 144.93. – **MS** (EI, 80 eV, 120 °C): *m/z* (%) = 346 (100) [M^+], 276 (57), 138 (22). – **IR** (KBr): $\tilde{n}$ = 1615 (m), 1327 (vs, br) cm^{-1}. – **UV/VIS** (Acetonitrile): λ_{max} = 342 nm (30300). – **$C_{23}H_{13}F_3$ (346.35)**: calcd. C 79.76, H 3.78; found C 79.55, H 3.88.

1-(4-Methoxy-phenyl)-pyrene (45k)



– **M.p.** 160 °C. – **R_f** = 0.51 (hexane:ethyl acetate = 3:1). – **^{1}H NMR** (270 MHz, CDCl$_3$): δ = 3.92 (s, 3H), 7.09 (d, ^3J = 8.3 Hz, 2H), 7.56 (d, ^3J = 8.3 Hz, 2H), 7.94-8.21 (m, 9H). – **^{13}C NMR** (63 MHz, CDCl$_3$): δ = 55.42, 113.89, 124.63, 124.72, 124.99, 125.38, 125.96, 127.25, 127.32, 127.44, 127.48, 127.68, 128.63, 130.39, 131.04, 131.03, 131.04, 133.60, 137.51, 159.05. – **MS** (70 eV, 150 °C): *m/z* (%) = 308 (100) [M]$^+$, 293 (19), 263 (24). – **UV/VIS** (Acetonitrile): λ_{max} = 342 nm (21100). – **HRMS**: *m/z* calcd. for **$C_{23}H_{16}O$** 308.120115; found 308.12432.

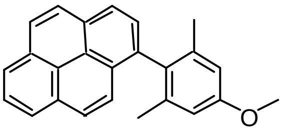
1-(4-Methoxy-2-methyl-phenyl)-pyrene (45l)



– **M.p.** 131 °C. – **R_f** = 0.53 (hexane:ethyl acetate = 3:1). – **^{1}H NMR** (500 MHz, CDCl$_3$): δ = 2.03 (s, 3H), 3.92 (s, 3H), 6.91 (d, ^3J = 7.5 Hz, 1H), 6.95 (s, 1H), 7.27 (d, ^3J = 7.5 Hz, 1H), 7.74 (d, ^3J = 9.0 Hz, 1H), 7.86 (d, ^3J = 7.5 Hz, 1H), 7.98 (m, 2H), 8.09 (s, 2H), 8.14 (d, ^3J =

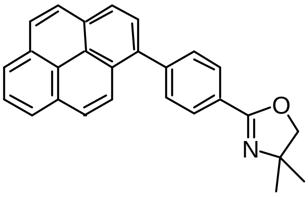
7.5 Hz, 1H), 8.19 (t, ^{3}J = 7.5 Hz, 2H). – **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 20.56, 55.31, 110.93, 115.39, 124.48, 124.75, 124.85, 125.01, 125.49, 125.94, 127.19, 127.32, 127.43, 127.79, 129.32, 130.41, 131.00, 131.43, 131.70, 133.11, 137.10, 138.37, 159.10. – **MS** (EI, 80 eV, 150 °C): *m/z* (%) = 317 (100) [*M*]$^+$. – **UV/VIS** (Acetonitrile): λ_{max} = 342 nm (36500). – **HRMS**: *m/z* calcd. for **$C_{24}H_{18}O$** 322.135765; found 322.13369.

1-(4-Methoxy-2,6-dimethyl-phenyl)-pyrene (45m)



– **M.p.** 139 °C. – **R_f** = 0.54 (hexane:ethyl acetate = 3:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.46 (s, 6H), 3.39 (s, 3H), 7.32 (s, 2H), 7.95-8.06 (m, 3H), 8.08 (s, 2H), 8.14-8.22 (m, 3H), 8.27 (d, ^{3}J = 10.0 Hz, 1H). – **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 16.24, 59.79, 124.53, 124.66, 124.89, 124.93, 125.45, 125.88, 127.18, 127.23, 127.38, 127.54, 128.46, 130.31, 130.70, 130.96, 131.45, 136.62, 137.60, 156.36. – **MS** (70 eV, 180 °C): *m/z* (%) = 336 (100) [*M*]$^+$, 321 (23), 306 (15), 276 (10), 138 (7). – **UV/VIS** (Acetonitrile): λ_{max} = 344 nm (27800). – **HRMS**: *m/z* calcd. for **$C_{25}H_{20}O$** 336.15141; found 336.151140.

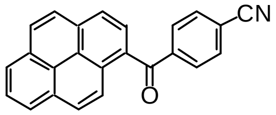
2-(4-Pyren-1-yl-phenyl)-4,4-dimethyl-2-oxazoline (45n)



– **M.p.** 139 °C. – **R_f** = 0.09 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.47 (s, 6H), 4.18 (s, 2H), 7.68 (d, ^{3}J = 7.5 Hz, 2H), 7.93 (d, ^{3}J = 8.0 Hz, 1H), 7.95-8.00 (m, 2H), 8.03 (s, 2H), 8.09-8.21 (m, 6H). – **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 28.35, 67.54, 79.06, 124.50, 124.62, 124.69, 124.73, 124.81, 125.11, 125.91, 126.75, 127.19, 127.46, 127.59, 128.18, 130.42, 130.48, 130.66, 130.69, 131.23, 136.50, 144.08, 161.93. – **MS** (70 eV, 175 °C): *m/z* (%) = 375 (100) [*M*]$^+$. – **IR** (KBr): $\tilde{n}$ = 1644 (*Ph-C=N-R*, s) cm^{-1}. – **UV/VIS** (Acetonitrile): λ_{max} = 343 nm (29500). – **$C_{27}H_{21}NO$ (375.46)**: calcd. C 86.37, H 5.64, N 3.73; found C 86.15, H 5.90, N 3.64.

7.4.6 Compounds of Chapter 4.4

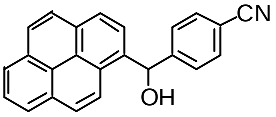
4-(1-Pyren-1-yl-methanoyl)-benzonitrile (50)



Pyrene **35** (7.05 g, 34.86 mmol) and 4-cyanobenzoyl chloride **49** (5.86 g, 35.41 mmol, 1.02 eq.) were dissolved in carbondisulfide (50 ml) and the mixture was cooled to 0°C. After the addition of $AlCl_3$ (6.80 g, 51.00 mmol, 1.46 eq.) in portions, the mixture was heated under reflux overnight, then poured into ice-water (50 g) and stirred until the color of the organic phase turned from black to yellow. The phases were separated, the aqueous one was extracted with toluene (3x), the combined organic phases were dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (dichloromethane) and precipitated from dichloromethane/methanol. Yield: 8.34 g (71 %) of **50** as bright yellow crystals.

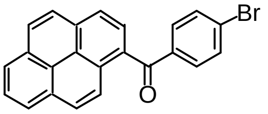
– **M.p.** 171 °C. – **R_f** = 0.21 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (270 MHz, $CDCl_3$): δ = 7.71 (d, ^3J = 8.0 Hz, 2H), 7.91 (d, ^3J = 8.0 Hz, 2H), 7.96-8.25 (m, 8H), 8.39 (d, ^3J = 9.5 Hz, 1H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 116.07, 117.93, 123.68, 124.19, 124.25, 124.78, 126.24, 126.45, 126.57, 127.03, 127.31, 129.45, 129.69, 130.04, 130.47, 130.65, 131.03, 131.11, 132.18, 133.69, 142.19, 196.52. – **MS** (EI, 80 eV, 150 °C): *m/z* (%) = 331 (100) $[M]^+$. – **IR** (KBr): $\tilde{n}$ = 2229 (*CN*, m) cm^{-1}. – **UV/VIS** (Acetonitrile): λ_{max} = 325, 337, 370, 391 nm. – **$C_{24}H_{13}NO$ (331.37)**: calcd. C 86.99, H 3.95, N 4.23; found C 86.86, H 4.02, N 4.00.
50 shows strong solvatochromism: $\lambda_{max,em}$ (MCH) = 464 nm; $\lambda_{max,em}$ (ACN) = 575 nm.

As the sole product of the reduction of **50** with sodium borohydride/ aluminiumchloride in tetrahydrofuran **4-(1-pyren-1-yl-hydroxy-methyl)-benzonitrile** (**51**) was obtained.



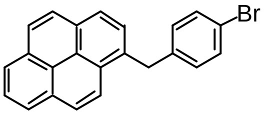
– **M.p.** 133 °C. – **R_f** = 0.16 (hexane:ethyl acetate = 3:1). – **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 3.39 (s, 1H, *OH*), 6.60 (s, 1H), 7.37 (d, ^3J = 8.3 Hz, 2H), 7.42 (d, ^3J = 8.3 Hz, 2H), 7.87 (d, ^3J = 7.8 Hz, 1H), 7.95-8.03 (m, 4H), 8.06 (d, ^3J = 7.8 Hz, 1H), 8.10-8.16 (m, 3H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 72.61, 110.70, 118.76, 122.47, 124.49, 124.83, 124.89, 125.02, 125.33, 125.59, 126.13, 127.02, 127.18, 127.78, 128.00, 128.09, 130.33, 131.10, 131.18, 132.00, 135.28, 148.69. – **MS** (EI, 80 eV, 60 °C): *m/z* (%) = 333 (100) $[M]^+$. – **IR** (KBr): $\tilde{n}$ = 2230 (*CN*, s) cm^{-1}. – **HRMS**: *m/z* calcd. for **$C_{24}H_{15}NO$** 333.11536; found 333.11734.

1-(4-Bromobenzoyl)-pyrene (53)[203]



– **M.p.** 173 °C (dichloromethane), [Lit.: 174-175 °C (acetic acid)]. – **R_f** = 0.25 (hexane:ethyl acetate = 10:1). – **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 7.59 (d, ^3J = 8.5 Hz, 2H), 7.74 (d, ^3J = 8.5 Hz, 2H), 8.02 (d, ^3J = 7.8 Hz, 1H), 8.06-8.25 (m, 7H), 8.31 (d, ^3J = 9.3 Hz, 1H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 123.77, 124.32, 124.49, 124.77, 126.03, 126.19, 126.46, 126.86, 127.13, 128.39, 129.05, 129.30, 129.73, 130.58, 131.11, 131.77, 131.99, 132.35, 133.23, 137.50, 197.26. – **MS** (EI, 80 eV, 150 °C): *m/z* (%) = 386 (100) $[C_{23}H_{13}{}^{81}BrO]^+$, 384 (94) $[C_{23}H_{13}{}^{79}BrO]^+$. – **IR** (KBr): $\tilde{n}$ = 1651 (*CO*, vs) cm^{-1}. – **$C_{23}H_{13}BrO$ (385.26)**: calcd. C 71.71, H 3.40; found C 71.59, H 3.35.

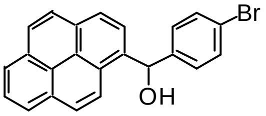
1-(4-Bromobenzyl)-pyrene (54)



Ketone **53** (10.5 g, 27.25 mmol) and sodium borohydride (5.12 g, 135.3 mmol, 4.97 eq.) were dissolved in tetrahydrofuran (200 ml) and aluminium chloride was added with caution at room temperature. The mixture was heated under reflux for 90 min and poured into ice-water (200 g). The reaction mixture was extracted with dichloromethane (2x), the combined organic phases were dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexane:ethyl acetate = 20:1), and the product was recrystallized from dichloromethane/methanol to give 7.60 g (75 %) of **54** as colorless crystals.

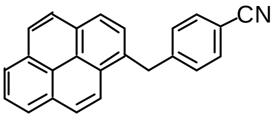
– **M.p.** 140 °C. – **R_f** = 0.37 (hexane:ethyl acetate = 10:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 4.63 (s, 2H), 7.05 (d, ^3J = 8.1 Hz, 2H), 7.37 (d, ^3J = 8.1 Hz, 2H), 7.81 (d, ^3J = 7.8 Hz, 1H), 7.97-8.19 (m, 8H). – **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 38.57, 119.15, 123.37, 124.71, 124.82, 124.93, 125.06, 125.09, 125.89, 126.95, 127.37, 128.05, 128.95, 130.27, 130.68, 131.24, 131.45, 133.55, 140.07. – **MS** (70 eV, 120 °C): *m/z* (%) = 372 (100) $[C_{23}H_{15}{}^{81}Br]^+$, 370 (98) $[C_{23}H_{15}{}^{79}Br]^+$. – **$C_{23}H_{15}Br$ (371.27)**: calcd. C 74.41, H 4.07; found C 74.27, H 4.01.

As a side product the incompletely reduced **1-(4-bromophenyl)-1-pyren-1-yl-methanol** was obtained.



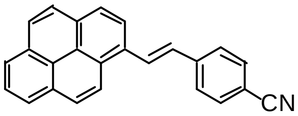
– **M.p.** 156 °C. – **R_f** = 0.31 (hexane:ethyl acetate = 3:1). – **^{1}H NMR** (250 MHz, d_6-DMSO): δ = 6.45 (d, 1H, *OH*), 6.75 (d, ^3J = 4.5 Hz, 1H), 7.40 (d, ^3J = 8.2 Hz, 2H), 7.47 (d, ^3J = 8.2 Hz, 1H), 8.02 (t, ^3J = 7.6 Hz, 1H), 8.11-8.33 (m, 7H). – **^{13}C NMR** (63 MHz, d_6-DMSO): δ = 71.78, 120.71, 124.09, 124.59, 124.80, 125.63, 125.81, 126.01, 126.27, 126.98, 127.76, 127.82, 128.06, 128.68, 129.68, 129.57, 130.71, 131.41, 131.72, 138.62, 145.04, 145.08. – **MS** (EI, 80 eV, 60 °C): *m/z* (%) = 388 (31) [$C_{23}H_{15}{}^{81}BrO$]$^+$, 386 (30) [$C_{23}H_{15}{}^{79}BrO$]$^+$, 203 (100) [*pyrene+H*]$^+$. – **IR** (KBr): $\tilde{n}$ = 3260 (s, br), 3041, 2922, 1588 (m), 1484 (s) cm^{-1}. – **HRMS**: *m/z* calcd. for **$C_{23}H_{15}BrO$** 386.03063; found 386.03265.

4-(Pyren-1-yl-methyl)-benzonitrile (47)



Bromoarene **54** (3.77 g, 10.15 mmol) and copper(I) cyanide (4.65 g, 51.92 mmol, 5.12 eq.) were suspended in 5 ml DMF, and the mixture was heated to 160 °C over night. The solvent was distilled off, the residue was chromatographed on silica gel (CH_2Cl_2) and the eluate precipitated from dichloromethane/methanol to give 3.22 g (80 %) of **47** as a colorless solid. – **M.p.** 141 °C. – **R_f** = 0.21 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 4.62 (s, 2H), 7.13 (d, ^3J = 8.1 Hz, 2H), 7.39 (d, ^3J = 8.1 Hz, 2H), 7.72 (d, ^3J = 7.5 Hz, 1H), 7.88-7.98 (m, 5H), 8.02 (m, 3H). – **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 39.23, 118.96, 123.11, 124.68, 124.92, 125.11, 126.05, 127.23, 127.34, 127.86, 128.14, 128.24, 129.01, 129.23, 130.54, 131.24, 132.19, 132.29, 132.36, 146.74. – **MS** (70 eV, 180 °C): *m/z* (%) = 317 (100) [*M*]$^+$, 215 (20). – **IR** (KBr): $\tilde{n}$ = 2224 (*CN*, vs) cm^{-1}. – **UV/VIS** (Acetonitrile): λ_{max} = 344 nm (46700). – **$C_{24}H_{15}N$ (317.38)**: calcd. C 90.82, H 4.76, N 4.41; found C 90.44, H 4.56, N 4.14.

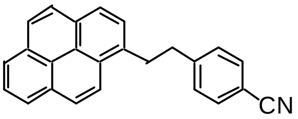
4-(2-Pyren-1-yl-vinyl)-benzonitrile (58)



Potassium *tert*-butoxide (16.5 g, 147.0 mmol, 1.05 eq.) was added to a stirred slurry of (4-cyanobenzyl)-triphenylphosphonium bromide (64.0 g, 140.0 mmol, 1.36 eq.) in dry tetrahydrofuran (250 ml). After stirring the resultant solution for 30 min at ambient temperature, pyrene carbaldehyde **55** (23.9 g, 103.4 mmol) was added at once. The mixture was stirred for 2 h at that temperature and then refluxed over night. After addition of a molar excess of water the organic solvent was removed under reduced pressure and the resultant aqueous mixture was extracted three times with dichloromethane. The combined organic layers were dried, filtered and the solvent evaporated. Column chromatography through silica gel (hexane:ethyl acetate = 20:1 to 5:1) gave (E/Z)-**58** (31.5 g, 92 %) as a pale yellow solid. The (E)-Isomer was separated by recrystallization from dichloromethane/methanol: – **M.p.** 189 °C. – **R_f** = 0.20 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.23 (d, ^3J = 16 Hz, 1H), 7.62 (s (!), 4H), 7.99-8.08 (m, 3H), 8.11-8.15 (m, 2H), 8.18-8.20 (m, 3H), 8.25 (d, ^3J = 8.0 Hz, 1H), 8.40 (d, ^3J = 9.6 Hz, 1H). – **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 110.54, 119.07, 122.53, 123.61, 124.77, 124.97, 125.10, 125.35, 125.67, 126.16, 126.89, 127.36, 127.81, 128.01, 128.71, 129.13, 129.41, 130.51, 130.76, 131.41, 131.47, 132.46, 141.99. – **MS** (EI, 80 eV, 180°C): *m/z* (%) = 329 (100) [*M*]$^+$. – **IR** (KBr): $\tilde{n}$ = 2215 (*CN*, s) cm^{-1}. – **UV/VIS** (Acetonitrile): λ_{max} = 380 nm. – **HRMS**: *m/z* calcd. for **$C_{25}H_{15}N$** 329.12045; found 329.12423.

The (E/Z)-mixture of **58** showed additional signals for the (Z)-isomer in the **^{1}H NMR** spectrum: 6.88 (d, ^3J = 12 Hz, 1H), 7.09 (d, ^3J = 8 Hz, 2H), 7.28 (d, ^3J = 8 Hz, 2H), 7.47 (d, ^3J = 12 Hz, 1H), 7.74 (d, ^3J = 8 Hz, 1H).

4-(2-Pyren-1-yl-ethyl)-benzonitrile (57)



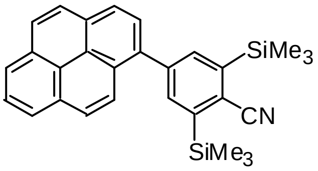
A mixture of 26.01 g (78.96 mmol) 4-(2-pyren-1-yl-vinyl)-benzonitrile **58**, 19.27 g (792.68 mmol, 10.04 eq.) magnesia and 3.25 g Pd/C (10%) in 1500 ml *n*-propanol was heated to reflux for 24 h. The mixture was filtered through celite and eluted with tetrahydrofuran. The solvent was removed, and the residue was purified by column chromatography on silica gel (dichloromethane) to give 25.10 g (96 %) of **57** as pale yellow crystals.

– **M.p.** 126 °C. – **R_f** = 0.22 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.16 (t, 2H), 3.59 (t, 2H), 7.19 (d, ^3J = 8.0 Hz, 2H), 7.51 (d, ^3J = 8.0 Hz, 2H), 7.67 (d, ^3J = 8.0 Hz, 1H), 7.98-8.06 (m, 4H), 8.10 (d, ^3J = 9.0 Hz, 1H), 8.17-8.20 (m, 3H). – **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 34.86, 37.89, 109.79, 119.07, 122.75, 124.72, 124.86, 124.99, 125.07, 125.91, 126.83, 127.22, 127.42, 127.52, 128.46, 129.27, 130.03, 130.71, 131.30, 132.12, 134.48, 147.10. – **MS** (EI, 80 eV, 120 °C): *m/z* (%) = 331 (13) [*M*]$^+$, 215 (100) [*M*-

CH_2PhCN]$^+$. – **IR** (KBr): $\tilde{n}$ = 2224 (*CN*, m) cm^{-1}. – **UV/VIS** (Acetonitrile): λ_{max} = 344 nm. – **$C_{25}H_{17}N$ (331.41)**: calcd. C 90.60, H 5.17, N 4.23; found C 90.49, H 5.20, N 4.09.

7.4.7 Compounds of Chapter 4.5.1

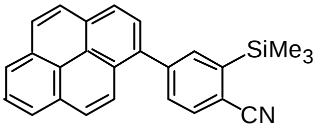
2,6-Bis(trimethylsilanyl)-4-(pyren-1-yl)-benzonitrile (62)



A solution of *n*-butyl lithium (12.5 ml of a 1.6 M solution in hexane, 20.0 mmol, 3.03 eq.) and 2,2,6,6-tetramethyl piperidine (3.40 ml, 20.15 mmol, 3.03 eq.) in tetrahydrofuran (40 ml) was cooled to –78 °C. Trimethylsilanyl chloride (5.0 ml, 40.06 mmol, 6.08 eq.) and 5 min later a solution of 4-(pyren-1-yl)-benzonitrile **45b** (2.00 g, 6.59 mmol) in 40 ml tetrahydrofuran were added slowly (1h). After stirring for additional 1.5 h brine (20 ml) were added, and the reaction mixture was allowed to warm up to room temperature. Extractive work-up with diethylether and column chromatography on silica gel (hexane:ethyl acetate = 20:1) gave 2.50 g (82 %) of the bis(trimethylsilanyl)- and 0.22 g (7 %) of the mono(trimethylsilanyl)-compound (**62** and **61**) as pale yellow crystals.

– **M.p.** 212 °C. – **R$_f$** = 0.56 (hexane:ethyl acetate = 10:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.62 (s, 18H), 7.97 (s, 2H), 8.04 (d, ^3J = 7.5 Hz, 1H), 8.07 (d, ^3J = 7.5 Hz, 1H), 8.13 (s, 2H), 8.17 (dd, 2H), 8.24 (dd, 2H), 8.29 (d, ^3J = 7.8 Hz, 1H). – **^{13}C NMR** (126 MHz, $CDCl_3$): δ = -1.15, 120.74, 124.33, 124.68, 124.87, 125.06, 125.44, 126.14, 127.22, 127.25, 127.83, 128.05, 128.32, 130.74, 131.02, 131.32, 136.35, 136.88, 143.13, 145.47. – **MS** (70 eV, 160 °C): *m/z* (rel. Int.) = 447 (100) [*M*]$^+$. – **IR** (KBr): $\tilde{n}$ = 2211 (*CN*, m) cm^{-1}. – **HRMS**: *m/z* calcd. for **$C_{29}H_{29}NSi_2$** 447.18385; found 44718643.

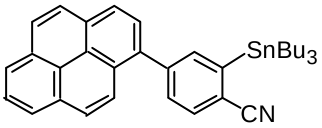
Trimethyl-(2-cyano-5-pyren-1-yl-phenyl)-silane (61)



Obtained as a minor product in the synthesis of **62** (see above).

– **M.p.** 135 °C. – **R$_f$** = 0.34 (hexane:ethyl acetate = 10:1). – **^{1}H NMR** (270 MHz, $CDCl_3$): δ = 0.52 (s, 9H), 7.68 (d, 1H), 7.85-8.27 (m, 11H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = -1.25, 115.94, 120.05, 124.31, 124.69, 124.94, 125.17, 125.54, 126.22, 127.19, 127.27, 127.97, 128.13, 128.32, 130.82, 131.19, 131.42, 133.44, 135.87, 136.68, 144.68, 145.02. – **MS** (70 eV, 160 °C): *m/z* (rel. Int.) = 375 (100) [*M*]$^+$. – **IR** (KBr): $\tilde{n}$ = 2214 (*CN*, m) cm^{-1}. – **HRMS**: *m/z* calcd. for **$C_{26}H_{21}NSi$** 375.144328; found 375.14734.

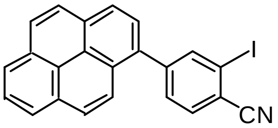
Tri-*n*-butyl-(2-cyano-5-pyren-1-yl-phenyl)-stannane (64)



4-(Pyren-1-yl)-benzonitrile **45b** (1.79 g, 5.90 mmol) and tri-*n*-butytin chloride (8.0 ml, 29.5 mmol, 5.0 eq.) in tetrahydrofuran (30 ml) were cooled to –78 °C, and a solution of *n*-butyl lithium (12.0 ml of a 1.6 M solution in hexane, 19.2 mmol, 3.3 eq.) and 2,2,6,6-tetramethyl piperidine (3.0 ml, 17.8 mmol, 3.0 eq.) in tetrahydrofuran (20 ml) were added within 15 min. The solution was stirred for additional 4 h when brine (20 ml) was added, and the reaction mixture was allowed to warm up to room temperature. After extractive work-up with diethylether an excess of tri-*n*-butytin chloride was removed by distillation in vacuo (80 °C, $2·10^{-2}$ mbar). Chromatographic separation on silica gel (hexane:ethyl acetate = 20:1) and recrystallization from dichloromethane/methanol yielded 1.16 g (33 %) of the monotin compound **64** as pale yellow amorphous solid.

– **M.p.** 67 °C. – **R$_f$** = 0.33 (hexane:ethyl acetate = 20:1). – **^{1}H NMR** (270 MHz, $CDCl_3$): δ = 0.93 (s, 9H), 1.34 (m, 12H), 1.64 (m, 6H), 7.59 (dd, ^3J = 8.1 Hz, ^3J = 1.7 Hz, 1H), 7.69 (d, ^3J = 8.1 Hz, 1H), 7.80 (d, ^3J = 7.5 Hz, 1H), 7.92-8.21 (m, 9H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 10.26, 13.64, 27.22, 29.04, 119.20, 120.76, 124.48, 124.72, 125.15, 125.50, 126.22, 127.23, 127.31, 127.93, 128.02, 128.36, 130.50, 130.88, 131.17, 131.46, 132.82, 136.16, 139.10, 144.36, 148.46. – **MS** (70 eV, 205 °C): *m/z* (rel. Int.) = 593 (23) [*M*]$^+$, 536 (100) [$M\text{-}C_4H_9$]$^+$, 480 (13) [$M\text{-}2C_4H_9$]$^+$, 422 (96) [$M\text{-}3C_4H_9$]$^+$, 301 (39) [$M\text{-}Sn(C_4H_9)_3$]$^+$. – **IR** (KBr): $\tilde{n}$ = 3039 (w), 2955, 2918, 2870, 2850 (m), 2214 (*CN*, m), 1579 (m) cm^{-1}. – **HRMS**: *m/z* calcd. for **$C_{35}H_{39}NSn$** 593.21045; found 593.21454.

2-Iodo-4-(pyren-1-yl)-benzonitrile (63)



(a) Via *ortho*-lithiation:

To a stirred solution of 4-(pyren-1-yl)-benzonitrile **45b** (9.5 g, 31.3 mmol) in 125 ml tetrahydrofuran –78 °C were added dropwise a solution of *n*-butyl lithium (20.0 ml of a 1.6 M solution in hexane, 32.0 mmol, 1.02 eq.) and 2,2,6,6-tetramethyl piperidine (6.0 ml, 35.6 mmol, 1.14 eq.) in tetrahydrofuran (40 ml). After stirring for an additional hour iodine (12.9

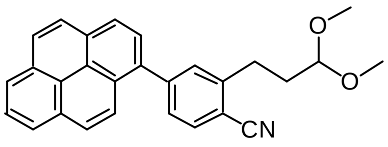
g, 50.8 mmol, 1.6 eq.) was added all at once, and the resulting solution was allowed to warm up to room temperature and was stirred overnight. The organic solution was washed with aqueous saturated solution of $Na_2S_2O_5$ and dried over $MgSO_4$. The solvent was removed by evaporation. The resulting solid was prepurified by column chromatography on silica gel (hexane:ethyl acetate = 20:1), and the product fraction was recrystallized from dichloromethane/methanol to yield 5.15 g (38 %) of **63** as a pale yellow amorphous solid. Large amounts of the unaffected educt were reisolated [R_f = 0.22 (hexane:ethyl acetate = 10:1)].

(b) Via iodo-de-stannylation:

A solution of **64** (2.65, 4.47 mmol) and iodine (2.00 g, 7.88 mmol, 1.76 eq.) in dichloromethane (50 ml) was stirred for 16 h at room temperature when an aqueous saturated solution of potassium fluoride (10 ml) was added. After 30 min an aqueous saturated solution of $Na_2S_2O_5$ was added, and the mixture was extracted with dichloromethane and chromographed through silica gel (hexane:ethyl acetate = 20:1) to give **63** (1.70 g, 89 %) as a pale yellow solid.

– **M.p.** 168 °C. – **R_f** = 0.16 (hexane:ethyl acetate = 10:1). – **^{1}H NMR** (270 MHz, $CDCl_3$): δ = 7.64 (dd, ^3J = 8.0 Hz, ^3J = 2.0 Hz, 1H), 7.76 (d, ^3J = 8.0 Hz, 1H), 7.86 (d, ^3J = 7.7 Hz, 1H), 7.98-8.26 (m, 9H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 98.35, 119.08, 119.39, 123.70, 124.51, 124.61, 124.74, 125.35, 125.74, 126.29, 126.90, 127.13, 128.04, 128.21, 128.47, 130.39, 130.61, 131.25, 131.46, 133.52, 133.77, 141.12, 147.08. – **MS** (70 eV, 160 °C): *m/z* (rel. Int.) = 429 (100) [*M*]$^+$, 301 (45) [*M-HI*]$^+$. – **IR** (KBr): $\tilde{n}$ = 2224 (*CN*, m) cm^{-1}. – **HRMS**: *m/z* calcd. for **$C_{23}H_{12}IN$** 426.985801; found 426.98822.

2-(3,3-Dimethoxy-propyl)-4-(pyren-1-yl)-benzonitrile (65)

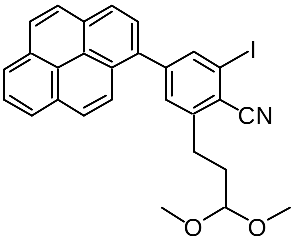


Procedure as decribed for **20b**:

3,3-Dimethoxy-propene **19b**: 1.80 ml, 15.63 mmol; 9-BBN (0.5 M solution in tetrahydrofuran): 32.0 ml, 16.0 mmol; aqueous sodium hydroxide 15 ml (3 M); additional tetrahydrofuran: 35 ml; 2-iodo-4-(pyren-1-yl)-benzonitrile **63**: 5.10 g, 11.88 mmol; $Pd(PPh_3)_4$: 0.27 g, 0.23 mmol, 1.97 mol-% per coupling; yield: 3.95 g (82 %) of **65** as a clear yellowish oil.

– **R_f** = 0.31 (hexane:ethyl acetate = 3:1). – **^{1}H NMR** (270 MHz, $CDCl_3$): δ = 2.09 (m, 2H), 3.02 (m, 2H), 3.36 (s, 6H), 4.49 (t, ^3J = 5.5 Hz, 1H), 7.47 (d, ^3J = 7.5 Hz, 1H), 7.59 (s, 1H), 7.74 (d, ^3J = 7.5 Hz, 1H), 7.85 (d, ^3J = 7.5 Hz, 1H), 7.96-8.37 (m, 8H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 29.65, 33.36, 52.79, 103.47, 110.97, 117.97, 124.15, 124.55, 124.76, 125.06, 125.43, 126.09, 126.97, 127.12, 127.83, 128.01, 128.68, 130.64, 131.07, 131.25, 131.55, 132.65, 135.34, 145.69, 145.92. – **MS** (EI, 80 eV, 165 °C): *m/z* (rel. Int.) = 405 (12) [*M*]$^+$, 75 (100) [$CH(OCH_3)_2$]$^+$. – **IR** (KBr): $\tilde{n}$ = 2222 (*CN*, vs) cm^{-1}. – **HRMS**: *m/z* calcd. for **$C_{28}H_{23}NO_2$** 405.17288; found 405.17633.

2-(3,3-Dimethoxy-propyl)-6-iodo-4-(pyren-1-yl)-benzonitrile (66)

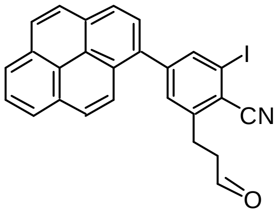


Procedure as described for **63** (procedure a):

2-(3,3-Dimethoxy-propyl)-4-(pyren-1-yl)-benzonitrile **65**: 2.41 g, 5.94 mmol; *n*-butyl lithium (1.6 M solution in hexane): 6.90 ml, 11.04 mmol, 1.86 eq.; 2,2,6,6-tetramethyl pyrrolidine: 2.05 ml, 12.05 mmol, 2.03 eq.; tetrahydrofuran: 70 ml; iodine: 4.56 g, 17.97 mmol, 3.02 eq.; column chromatography on silica gel (hexane:ethyl acetate = 5:1); recrystallization from dieethylether; yield: 1.80 g (57 %) of **66** as a pale yellow solid.

– **M.p.** 109-110 °C. – **R_f** = 0.33 (hexane:ethyl acetate = 3:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.05 (m, 2H), 3.03 (m, 2H), 3.35 (s, 6H), 4.46 (t, ^3J = 5.6 Hz, 1H), 7.54 (s, 1H), 7.84 (d, ^3J = 8.0 Hz, 1H), 7.96-8.12 (m, 6H), 8.15-8.23 (m, 3H). – **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 30.73, 33.18, 52.89, 99.29, 103.28, 118.62, 118.90, 123.85, 124.51, 124.62, 124.74, 125.34, 125.71, 126.29, 126.93, 127.17, 128.06, 128.17, 128.44, 130.61, 131.08, 131.24, 131.38, 133.81, 138.89, 146.89, 148.20. – **MS** (EI, 80 eV, 180 °C): *m/z* (rel. Int.) = 531 (19) [*M*]$^+$, 314 (9), 75 (100) [$CH(OCH_3)_2$]$^+$. – **IR** (KBr): $\tilde{n}$ = 2220 (*CN*, st) cm^{-1}. – **$C_{28}H_{22}INO_2$ (531.38):** calcd. C 63.29, H 4.17, N 2.64; found C 63.31, H 4.23, N 2.45.

3-(2-Cyano-3-iodo-5-pyren-1-yl-phenyl)-propionaldehyde (67)

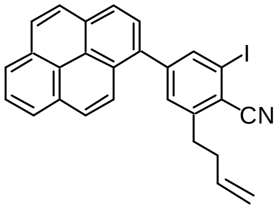


As described for **21**:

66: 1.70 g, 3.20 mmol; 2,3-Dichloro-5,6-dicyano-quinone: 76 mg, 0.34 mmol, 0.11 eq.; acetonitrile: 200 ml; water: 20 ml; dichloromethane: 100 ml (for dissolving the educt); 18 h at room temperature; short column chromatography on silica gel (hexane:ethyl acetate = 5:1); yield: 1.38 g (89 %) of **67** as a clear yellowish oil. Recrystallization from diethylether gave a yellow solid.

– **M.p.** 120-121 °C. – **R$_f$** = 0.19 (hexane:ethyl acetate = 3:1). – **^{1}H NMR** (500 MHz, CDCl$_3$): δ = 2.88 (t, ^3J = 7.0 Hz, 2H), 3.20 (t, ^3J = 7.0 Hz, 2H), 7.52 (s, 1H), 7.78 (d, ^3J = 8.0 Hz, 1H), 7.92-8.21 (m, 9H), 9.76 (s, 1H). – **^{13}C NMR** (125 MHz, CDCl$_3$): δ = 27.69, 43.57, 99.28, 118.77, 123.71, 124.42, 124.57, 124.66, 125.29, 125.67, 126.24, 126.88, 127.08, 127.97, 128.14, 128.42, 130.54, 131.16, 131.27, 131.36, 133.48, 139.11, 146.72, 146.88, 199.42. – **MS** (EI, 80 eV, 180 °C): *m/z* (rel. Int.) = 485 (100) [M]$^+$. – **C$_{26}$H$_{16}$INO (485.32):** calcd. C 64.55, H 3.32, N 2.89; found C 63.93, H 3.12, N 2.78.

2-(But-3-enyl)-6-iodo-4-(pyren-1-yl)-benzonitrile (59)

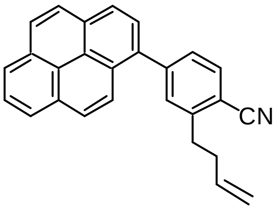


As desribed for **15**, procedure a:

Triphenylmethylphosphoniumiodide: 1.75 g, 4.33 mmol, 2.00 eq.; tetrahydrofuran: 100 ml, *n*-butyllithium (1.6 M solution in hexane): 2.65 ml, 4.24 mmol, 1.96 eq.; **67**: 1.05 g, 2.16 mmol in 10 ml tetrahydrofuran; column chromatography on silica gel (hexane:ethyl acetate = 10:1) gave 0.73 g (70 %) of olefin **59** as slightly yellow crystals.

– **M.p.** 104 °C. – **R$_f$** = 0.37 (hexane:ethyl acetate = 10:1). – **^{1}H NMR** (500 MHz, CDCl$_3$): δ = 2.54 (m, 2H), 3.09 (t, ^3J = 7.6 Hz, 2H), 5.09 (m, 2H), 5.87 (m, 1 H), 7.52 (s, ^4J = 1.4 Hz, 1H), 7.87 (d, ^3J = 7.9 Hz, 1H), 8.02-8.22 (m, 9H). – **^{13}C NMR** (125 MHz, CDCl$_3$): δ = 34.43, 35.01, 99.19, 116.38, 118.62, 119.15, 123.99, 124.65, 124.89, 125.37, 126.33, 126.94, 127.22, 128.22, 128.43, 130.76, 131.22, 131.39, 131.51, 134.01, 136.42, 138.90, 146.79, 148.09. – **MS** (EI, 80 eV, 250 °C): *m/z* (rel. Int.) = 483 (100) [M]$^+$. **C$_{27}$H$_{18}$IN (483.34):** calcd. C 67.09, H 3.75, N 2.90; found C 66.93, H 3.43, N 2.74.

2-(But-3-enyl)-4-(pyren-1-yl)-benzonitrile (69)



Procedure as described for **21**:

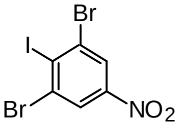
65: 1.05 g, 2.59 mmol; DDQ: 58 mg, 0.26 mmol, 0.10 eq.; acetonitrile: 100 ml; water: 10 ml; 10 h at room temperature; chromatography through a short column of silica gel (hexane:ethyl acetate = 5:1); yield: 0.88 g (95 %) of aldehyde **68** as a clear yellowish oil.

Without further purification and characterization a Wittig reaction was performed (as desribed for **15**, procedure a):

Triphenylmethylphosphoniumiodide: 1.98 g, 4.90 mmol, 2.00 eq.; tetrahydrofuran: 100 ml, *n*-butyllithium (1.6 M solution in hexane): 2.90 ml, 4.64 mmol, 1.89 eq.; **68**: 0.88 g, 2.45 mmol in 10 ml tetrahydrofuran; column chromatography on silica gel (hexane:ethyl acetate = 10:1) gave 0.62 g (70 %) of olefin **69** as colorless crystals.

– **M.p.** 102 °C. – **R_f** = 0.37 (hexane:ethyl acetate = 10:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.54 (m, 2H), 3.07 (t, ^3J = 7.6 Hz, 2H), 5.09 (m, 2H), 5.90 (m, 1H), 7.53 (d, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H), 7.57 (s, 1H), 7.78 (d, ^3J = 7.8 Hz, 1H), 7.91 (d, ^3J = 7.9 Hz, 1H), 8.00-8.23 (m, 8H). – **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 34.30, 34.67, 111.13, 116.13, 118.17, 124.37, 124.67, 124.73, 124.91, 125.19, 125.55, 126.24, 127.10, 127.23, 127.97, 128.09, 128.25, 128.73, 130.80, 131.23, 131.40, 131.82, 132.76, 135.60, 136.74, 145.68, 145.90. – **MS** (EI, 80 eV, 170 °C): *m/z* (rel. Int.) = 357 (100) $[M]^+$. **HRMS**: *m/z* calcd. for **$C_{27}H_{19}N$** 357.15175; found 357.15466.

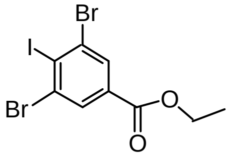
3,5-Dibromo-4-iodo-nitrobenzene (72)



To a mechanically stirred suspension of the 2,6-dibromo-4-nitro-aniline **70** (10.27 g, 34.71 mmol), 50 g ice and sulfuric acid (96 %, 60 ml) was added a solution of sodium nitrate (4.11 g, 59.57 mmol, 1.72 eq.) in 30 ml of water. The yellow suspension was stirred for additional 30 min, followed by the addition of potassium iodide (9.95 g, 59.94 mmol, 1.73 eq., in 30 ml water). After two hours the precipitate was sucked off and washed with water thoroughly. The residue was recrystallized from acetone to yield **72** (12.20 g, 86 %) as orange-brown long needles.

– **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 8.34 (s, 2H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 118.46, 118.89, 125.23, 132.09. – **MS** (EI, 80 eV, 90 °C): *m/z* (rel. Int.) = 409 (49) $[C_6H_2{}^{81}Br_2O]^+$, 407 (100) $[C_6H_2{}^{79}Br^{81}BrO]^+$, 405 (51) $[C_6H_2{}^{79}Br_2O]^+$. – **IR** (KBr): $\tilde{n}$ = 1516 (*NO* [ν_{as}], s), 1335 (*NO* [ν_s], s) cm^{-1}. – **$C_6H_2Br_2INO_2$ (406.80)**: calcd. C 17.72, H 0.50, N 3.44; found C 17.92, H 0.50, N 3.35.

3,5-Dibromo-4-iodo-benzoic acid ethyl ester (73)



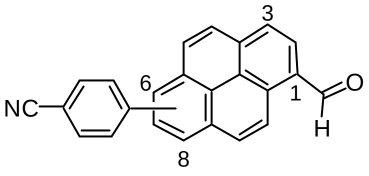
Procedure as described for **72**:

4-Amino-3,5-dibromo-benzoic acid ethyl ester **71** (12.24 g, 37.89 mmol); 50 g ice; sulfuric acid (96 %, 60 ml); sodium nitrate (4.30 g, 62.32 mmol, 1.65 eq.) in 25 ml of water; potassium iodide (10.50 g, 63.25 mmol, 1.67 eq.) in 25 ml water. The residue was recrystallized from ethanol to yield 11.97 g of **73** (73 %) as colorless crystals.

– **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 1.40 (t, 3H), 4.38 (q, 2H), 8.14 (s, 2H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 14.22, 61.96, 115.45, 131.50, 132.70, 144.10, 163.93. – **MS** (EI, 80 eV, 100 °C): *m/z* (rel. Int.) = 436 (50) $[C_9H_7{}^{81}Br_2IO_2]^+$, 434 (100) $[C_9H_7{}^{79}Br^{81}BrIO_2]^+$, 432 (53) $[C_9H_7{}^{79}Br_2IO_2]^+$. – **IR** (KBr): $\tilde{n}$ = 1707 (*C=O*, vs), 1264 (*C-O*, vs) cm^{-1}. – **$C_9H_7Br_2IO_2$ (433.86)**: calcd. C 24.91, H 1.63; found C 24.95, H 1.49.

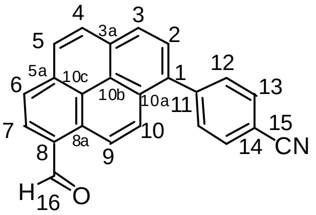
7.4.8 Compounds of Chapter 4.5.2

X-(4-Benzonitrile)-pyrene-1-carbaldehyde, three isomers (X = 3, 6 or 8) (76)



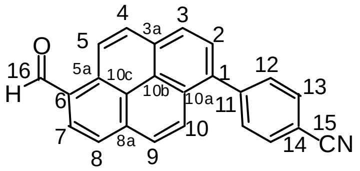
To a solution of 11.50 g (37.91 mmol) of 4-pyren-1-yl-benzonitrile **45b** and 4.30 ml (47.54 mmol, 1.25 eq.) dichloromethyl methylether in 250 ml dichloromethane at 0 °C 11.5 ml (104.9 mmol, 2.77 eq.) titanium-tetrachloride was added within 30 min. The dark mixture was stirred at room temperature over night. 100 ml of water were added, the phases separated, and the aqueous one was extracted with dichloromethane (5x). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (dichloromethane). Yield: 62 % (7.79 g) of **76** a mixture of regioisomers (3-, 6-, and 8-formyl isomer). By recrystallization of suitable fractions it was possible to obtain pure (**^{1}H NMR**) samples of the 6- and the 8-isomer. The structure of8-(4-benzonitrile)-pyrene-1-carbaldehyde was solved by x-ray analysis. See chapter 7.5.1 for details.

8-(4-Benzonitrile)-pyrene-1-carbaldehyde (76)



Orange crystals. – **M.p.** 239 °C. – **R_f** = 0.28 (hexane:ethyl acetate = 3:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.73 (d, ^3J = 8.5 Hz, 2H, *H-12*), 7.86 (d, ^3J = 8.5 Hz, 2H, *H-13*), 8.00 (d, ^3J = 7.5 Hz, 1H, *H-2*), 8.13 (d, ^3J = 9.0 Hz, 1H, *H-5*), 8.24 (d, ^3J = 9.0 Hz, 1H, *H-4*), 8.26 (d, ^3J = 9.0 Hz, 1H, *H-10*), 8.29 (d, ^3J = 7.5 Hz, 1H, *H-6*), 8.34 (d, ^3J = 7.5 Hz, 1H, *H-3*), 8.45 (d, ^3J = 7.5 Hz, 1H, *H-7*), 9.38 (d, ^3J = 9.0 Hz, 1H, *H-9*), 10.73 (s, 1H, *H-16*). – **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 111.47 (*C-14*), 118.84 (*C-15*), 123.87 (*C-9*), 124.37 (*C-10b*), 125.19 (*C-6*), 126.79 (*C-3*), 127.45 (*C-10a*), 127.59 (*C-8*), 127.77 (*C-10*), 127.84 (*C-2, C-5*), 130.59 (*C-4*), 131.05 (*C-3a*), 131.36 (*C-12, C-8a*), 131.80 (*C-7*), 132.29 (*C-13*), 135.71 (*C-5a*), 137.18 (*C-1*), 145.30 (*C-11*), 193.00 (*C-16*). – **MS** (EI, 80 eV, 120 °C): *m/z* (%) = 331 (100) $[M]^+$, 330 (24) $[M\text{-}H]^+$, 304 (26) $[M\text{-}HCN]^+$, 303 (59) $[M\text{-}CO]^+$, 166 (5) $[M]^{2+}$. – **IR** (KBr): $\tilde{n}$ = 2227 (*CN*, s), 1677 (*CO*, vs) cm^{-1}. – **$C_{24}H_{13}NO$ (331.37)**: calcd. C 86.99, H 3.95, N 4.23; found C 86.53, H 3.82, N 4.09.

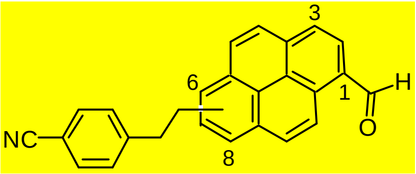
6-(4- Benzonitrile)-pyrene-1-carbaldehyde (76)



Yellow crystals. – **M.p.** 253 °C. – ***R_f*** = 0.26 (hexane:ethyl acetate = 3:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.78 (d, ^3J = 8.2 Hz, 2H, *H-12*), 7.82 (d, ^3J = 8.2 Hz, 2H, *H-13*), 7.96 (d, ^3J = 7.5 Hz, 1H, *H-2*), 8.02 (d, ^3J = 9.5 Hz, 1H, *H-9*), 8.13 (d, ^3J = 9.0 Hz, 1H, *H-10*), 8.21 (d, ^3J = 7.5 Hz, 1H, *H-8*), 8.28 (d, ^3J = 9.0 Hz, 1H, *H-4*), 8.30 (d, ^3J = 7.5 Hz, 1H, *H-3*), 8.41 (d, ^3J = 8.1 Hz, 1H, *H-7*), 9.42 (d, ^3J = 9.5 Hz, 1H, *H-5*), 10.72 (s, 1H, *H-16*). – **^{13}C NMR** (125

MHz, $CDCl_3$): δ = 111.45 (*C-14*), 118.81 (*C-15*), 123.63 (*C-5*), 124.34 (*C-10b*), 124.82 (*C-8, C-10c*), 126.57 (*C-3*), 127.63 (*C-10*), 127.73 (*C-6*), 127.86 (*C-2*), 127.97 (*C-9*), 128.12 (*C-10a*), 130.46 (*C-3a*), 130.74 (*C-4*), 131.35 (*C-12, C-5a*), 131.87 (*C-7*), 132.27 (*C-13*), 135.04 (*C-8a*), 137.43 (*C-1*), 145.47 (*C-11*), 193.09 (*C-16*). – **IR** (KBr): $\tilde{n}$ = 2221 (*CN*, m), 1682 (*CO*, vs) cm^{-1}. – **$C_{24}H_{13}NO$ (331.37)**.

X-[2-(4-Benzonitrile)-ethyl]-pyrene-1-carbaldehyde, three isomers (X = 3, 6 and 8) (77)



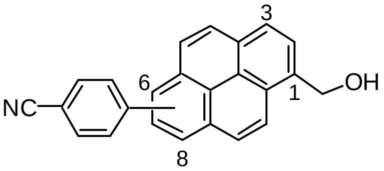
Procedure as described for **76**:

4-(2-Pyren-1-yl-ethyl)-benzonitrile **57**: 27.90 g (84.18 mmol); dichloromethyl methylether: 8.90 ml (98.40 mmol, 1.17 eq.); dichloromethane: 500 ml; titanium-tetrachloride: 21.5 ml (196.08 mmol, 2.33 eq.); yield: 21.72 g (72 %) of a mixture of regioisomers (3-, 6-, and 8-formyl isomers).

The values are given for a mixture of the three isomers.

– **R_f** = 0.47 (hexane:ethyl acetate = 2:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.22 (m, 2H), 3.65 (m, 2H), 7.22, 7.28 (2·d, 2H), 7.55 (m, 2H), 7.75 (m, 1H), 8.04-8.47 (m, 2H), 9.32, 9.38, 9.47 (3·d, ^3J = 9.0 Hz, 1H), 10.74, 10.77 (2·s, 1H). – **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 34.76, 34.96, 34.99, 37.61, 38.14, 38.23, 110.05, 110.07, 110.16, 118.96, 119.01, 48 signals between 122.43 and 137.00, 146.70, 146.76, 146.79, 192.72, 193.12, 193.22. – **MS** (EI, 80 eV, 300 °C): *m/z* (%) = 359 (53) [*M*]$^+$, 243 (100) [$M\text{-}CH_2PhCN$]$^+$, 215 (42) [$M\text{-}CH_2PhCN\text{-}CO$]$^+$. – **IR** (KBr): $\tilde{n}$ = 2224 (*CN*, m), 1669 (*CO*, vs) cm^{-1}. – **$C_{26}H_{17}NO$ (359.42)**: calcd. C 86.88, H 4.77, N 3.90; found C 86.48, H 4.71, N 3.88.

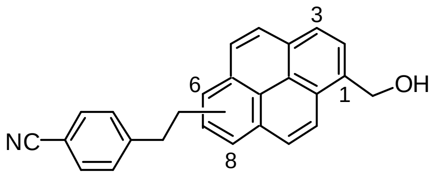
[X-(4-Benzonitrile)-pyren-1-yl]-methanol, three isomers (X = 3, 6 or 8) (78)



11.95 g (36.06 mmol) of X-(4-benzonitrile)-pyrene-1-carbaldehyde **76** was solved in 500 ml tetrahydrofuran, and 1000 ml *iso*-propanol were added. After addition of 7.25 g (191.65 mmol, 5.32 eq.) sodium borohydride, the reaction mixture was stirred for 2 h at ambient temperature. The unreacted sodium borohydride was hydrolyzed by dropwise addition diluted hydrochloric acid to the ice-cooled mixture until no more hydrogen evolution occurred. The organic solvents were distilled off, and the residue was extracted with dichloromethane (3x). The combined organic layers were dried, filtered and the solvent evaporated. Column chromatography (dichloromethane to dichloromethane:methanol = 20:1) gave 11.8 g (98 %) of a mixture of the three regioisomers of [X-(4-benzonitrile)-pyren-1-yl]-methanol **78**. The data are given for a small sample of a pure isomer that was obtained by fractionated crystallization.

– **R_f** = 0.30 (hexane:ethyl acetate = 1:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 5.07 (s, 2H), 7.58 (d, ^3J = 8.2 Hz, 2H), 7.71 (d, ^3J = 8.2 Hz, 2H), 7.78 (d, ^3J = 7.9 Hz, 1H), 7.90 (m, 2H), 7.94 (d, ^3J = 7.9 Hz, 1H), 8.04 (m, 2H), 8.12 (d, ^3J = 7.9 Hz, 1H), 8.29 (d, ^3J = 9.0 Hz, 1H). – **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 73.19, 110.95, 118.95, 123.93, 124.15, 124.73, 124.93, 127.19, 127.33, 127.57, 128.18, 128.23, 129.54, 130.84, 130.86, 131.24, 131.89, 132.10, 135.44, 146.02. – **MS** (EI, 80 eV, 60 °C): *m/z* (%) = 333 (100) [*M*]$^+$, 317 (49), [*M-O*]$^+$. – **$C_{24}H_{15}NO$ (333.38)**: calcd. C 86.46, H 4.54, N 4.20; found C 86.33, H 4.75, N 3.98.

{X-[2-(4-Benzonitrile)-ethyl]-pyren-1-yl}-methanol, three isomers (X = 3, 6 or 8) (79)



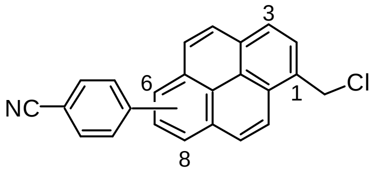
Procedure as described for **78**:

X-[2-(4-Benzonitrile)-ethyl]-pyrene-1-carbaldehyde **77**: 27.42 g (76.29 mmol); sodium borohydride: 14.27 g (377.21 mmol, 4.94 eq.); *iso*-propanol: 750 ml; yield: 24.76 g (85 %) of a mixture of the three regioisomers of **79**.

The data are given for a sample of a mixture of the 3- and 6- or 8-isomer.

– **R_f** = 0.22 (hexane:ethyl acetate = 1:1). – **^{1}H NMR** (250 MHz, $CDCl_3$): δ =2.03 (s, 1H), 3.13 (m, 2H), 3.56 (m, 2H), 5.30, 5.36 (2·s, 2H), 7.18 (m, 2H), 7.48 (m, 2H), 7.66, 7.77 (m,s, 1H), 7.98-8.37 (m, 7H). – **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 34.65, 37.78, 63.26, 63.51, 109.76, 118.95, 122.58, 122.71, 123.06, 124.73, 124.95, 125.12, 125.28, 125.93, 126.77, 126.96, 127.16, 127.39, 128.39, 129.09, 129.17, 130.79, 130.90, 131.30, 132.06, 133.47, 133.68, 134.27, 134.73, 147.05, 153.33. – **MS** (EI, 80 eV, 150 °C): *m/z* (%) = 361 (61) [*M*]$^+$, 245 (100) [*M-CH$_2$PhCN*]$^+$. – **IR** (KBr): $\tilde{n}$ = 2225 (*CN*, s) cm^{-1}. – **$C_{26}H_{19}NO$ (361.44)**: calcd. C 86.40, H 5.30, N 3.88; found C 85.93, H 5.19, N 3.75.

1-Chloromethyl-X-(4-benzonitrile)-pyrene, one isomer (X = ?) (80)

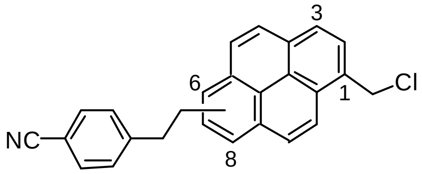


To a suspension of **78** (9.87 g, 29.61 mmol) in 350 ml dichloromethane was added dropwise a solution of thionyl chloride in 50 ml dichloromethane at room temperature (40 min). The clear solution was stirred until gas evolution stopped (3 h). To the ice cooled solution aqueous sodium hydroxide (1 M, 150 ml) was added carefully, and the phases were separated. The aqueous one was extracted with dichloromethane (2x), the combined organic layers were dried over $MgSO_4$, filtered and and the solvent evaporated. The resulting brownish residue was recrystallized from dichloromethane / methanol to give 8.60 g (83 %) of **80** as an amorphous solid.

The reaction proceeded quantitatively as the TLC showed no alkohol. The reduced yield may be due to loss of product in the recrystallization step. It was found that the benzyl chloride was not stable on silica gel (2D TLC). The data given are for the 6- or 8-isomer.

– **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 5.38 (s, 2H), 7.76 (d, 2H), 7.89 (d, 2H), 7.98 (d, 1H), 8.07-8.10 (m, 3H), 8.19 (d, 1H), 8.26-8.33 (m, 2H), 8.48 (d, 1H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 44.51, 111.30, 118.85, 123.40, 123.62, 124.96, 125.05, 125.29, 125.41, 126.53, 127.44, 127.88, 127.91, 127.97, 128.03, 128.84, 129.43, 130.71, 131.30, 132.20, 136.04, 145.80. – **MS** (EI, 80 eV, 250 °C): *m/z* (%) = 353 (14) $[C_{24}H_{14}{}^{37}ClN]^+$, 351 (40) $[C_{24}H_{14}{}^{35}ClN]^+$, 316 (100) $[M\text{-}Cl]^+$. – **HRMS**: *m/z* calcd. for $\mathbf{C_{24}H_{14}ClN}$ 351.08148; found 351.08365.

1-Chloromethyl-X-[2-(4-benzonitrile)-ethyl]-pyrene, one isomer (X = 6 or 8) (81)



Procedure as described for **80**:

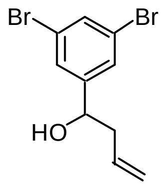
79: 20.0 g (55.3 mmol); thionyl chloride: 40 ml (548 mmol, 9.9 eq.); dichloromethane: 600 ml; yield: 15.8 g (75 %) of **81** as a yellow amorphous solid.

The reaction proceeded quantitatively as the TLC showed no alcohol. The reduced yield may be due to loss of product in the recrystallization step. It was found that the benzyl chloride was not stable on silica gel (2D TLC). The data given are for the 6- or 8-isomer.

– **M.p.** 153 °C. – **^{1}H NMR** (270 MHz, $CDCl_3$): δ = 3.12 (t, ^3J = 7.5 Hz, 2H), 3.55 (t, ^3J = 7.5

Hz, 2H), 5.28 (s, 2H), 7.15 (d, ${}^3J$ = 8.0 Hz, 2H), 7.49 (d, ${}^3J$ = 8.0 Hz, 2H), 7.65 (d, ${}^3J$ = 7.6 Hz, 1H), 7.95-8.16 (m, 6H), 8.29 (d, ${}^3J$ = 9.3 Hz, 1H). – **^{13}C NMR** (68 MHz, $CDCl_3$): δ = 34.91, 37.96, 44.88, 109.93, 119.07, 122.17, 123.35, 124.65, 124.99, 125.42, 127.42, 127.61, 127.76, 128.10, 128.46, 128.54, 128.76, 129.29, 129.36, 129.61, 130.35, 131.57, 132.16, 135.31, 146.97. – **MS** (EI, 80 eV, 220 °C): *m/z* (%) = 381 (10) $[C_{26}H_{18}{}^{37}ClN]^+$, 379 (26) $[C_{26}H_{18}{}^{35}ClN]^+$, 344 (9) $[M\text{-}Cl]^+$, 265 (34) $[C_{26}H_{18}{}^{37}ClN\text{-}CH_2PhCN]^+$, 263 (100) $[C_{26}H_{18}{}^{35}ClN\text{-}CH_2PhCN]^+$, 228 (95) $[M\text{-}Cl\text{-}CH_2PhCN]^+$. – **IR** (KBr): $\tilde{\nu}$ = 2223 (*CN*, s) cm^{-1}. – **HRMS**: *m/z* calcd. for $\mathbf{C_{26}H_{18}ClN}$ 379.11278; found 379.11444.

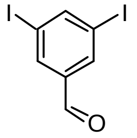
1-(3,5-Dibromo-phenyl)-but-3-en-1-ol (84)



18.00 ml (106.83 mmol, 1.53 eq.) allyl-trimethoxysilane was added dropwise to a suspension of 18.50 g (70.10 mmol) 3,5-dibromo-benzaldehyde **9**, 23.01 g (208.97 mmol, 2.98 eq.) catechol and triethyl amine (50 ml, 358.73 mmol, 5.12 eq.). The mixture was stirred at 70 °C for 24 h. The acidified (25 % hydrochloric acid) suspension was extracted with dichloromethane (5x), the combined organic phases were washed with brine, then dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexane:ethyl acetate = 10:1), and the product was distilled in vacuo to give 17.96 g (84 %) of **84** as a colorless liquid.

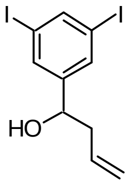
– **B.p.** 95 °C/3·10^{-2} mbar. – **R_f** = 0.30 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.29 (s, 1H, O*H*), 2.40 (m, 1H, CH_2), 2.46 (m, 1H, CH_2), 4.65 (m, 1H, C*H*OH), 5.26 (m, 2H, CH=CH_2), 5.73 (m, 1H, C*H*=CH$_2$), 7.41 (s, 2H), 7.55 (s, 1H). – **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 43.65 (*C*H$_2$), 71.77 (*C*HOH), 119.38 (CH=*C*H$_2$), 122.85 ($C_{aromatic}$-*Br*), 127.60 ($C_{aromatic}$-H), 132.90, 133.27 ($C_{aromatic}$-H, *C*H=CH$_2$), 147.63 ($C_{aromatic}$-CH$_2$). – **MS** (EI, 80 eV, 40 °C): *m/z* (%) = 306 (6) $[C_{10}H_{10}{}^{79}Br^{81}BrO]^+$, 265 (100), $[M\text{-}C_3H_5]^+$. – **IR** (KBr): $\tilde{\nu}$ = 3375 (st, br), 3075, 3004, 2978, 2906 (m), 1641 (m), 1585, 1557, 1425 (st) cm^{-1}. – **$C_{10}H_{10}Br_2O$ (305.99)**: calcd. C 39.25, H 3.29; found C 39.09, H 3.07.

3,5-Diiodo-benzaldehyde (82)



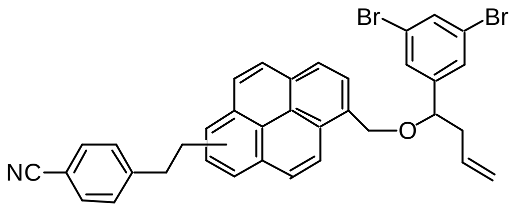
Procedure as described for 1-allyl-3,5-diiodo-benzene **4**:
1,3,5-Triiodo-benzene **3**: 17.39 g (38.15 mmol); *n*-butyl lithium: 28.00 ml of a 1.6 M solution in hexane (44.80 mmol, 1.17 eq.); toluene: 650 ml; *N,N*-dimethyl formamide, p.a.: 10.0 ml (119.0 mmol, 3.12 eq.). Chromatographic separation through silical gel (hexane:ethyl acetate = 10:1) gave 9.02 g (66 %) of **82** as colorless crystals.
When diethylether or tetrahydrofuran at –78 °C was used instead of toluene, the product was accompanied by butylated side-products.
– **M.p.** 133-134 °C. – **R$_f$** = 0.46 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (270 MHz, $CDCl_3$): δ = 8.14 (d, ^4J = 1.8 Hz, 2H), 8.28 (t, ^4J = 1.8 Hz, 1H), 9.83 (s, 1H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 95.27, 137.63, 138.89, 150.47, 189.04. – **MS** (EI, 80 eV, 40 °C): *m/z* (rel. Int.) = 358 (100) $[C_7H_4I_2O]^+$, 127 (14) $[I]^+$. – **IR** (KBr): $\tilde{n}$ = 1686, 1696 (*CO*, vs) cm^{-1}. – **$C_7H_4I_2O$ (357.92)**: calcd. C 23.49, H 1.13; found C 23.47, H 0.91.

1-(3,5-Diiodo-phenyl)-but-3-en-1-ol (85)



Procedure as described for **84**.
– **M.p.** 65-66 °C. – **R$_f$** = 0.33 (hexane:ethyl acetate = 6:1). – **$[a]^{25}_{D}$** = -0.052 (1.605 g/mol, $CDCl_3$). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.18 (s, 1H, O*H*), 2.38 (m, 1H, CH_2CH=CH_2), 2.47 (m, 1H, CH_2CH=CH_2), 4.60 (m, 1H, C*H*OH), 5.16 (m, 2H, CH=CH_2), 5.74 (m, 1H, C*H*=CH_2), 7.63 (s, 2H), 7.92 (s, 1H). – **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 43.75 (CH_2CH=CH_2), 71.47 (*C*HOH), 94.83 (*C*-I), 119.48 (CH=*C*H_2), 133.37, 134.13 ($C_{aromatic}$-H, *C*H=CH_2), 144.01 ($C_{aromatic}$-H). 147.81 ($C_{aromatic}$-CH_2). – **MS** (EI, 80 eV, 60 °C): *m/z* (%) = 400 (16) $[M]^+$, 359 (100), $[M\text{-}C_3H_5]^+$. – **$C_{10}H_{10}I_2O$ (399.99)**: calcd. C 30.03, H 2.52; found C 29.93, H 2.49.

1-[2-(4-Benzonitrile)-ethyl]-X-[1-(3,5-dibromo-phenyl)-but-3-enyloxymethyl]-pyrene (X = 6,8) (86)

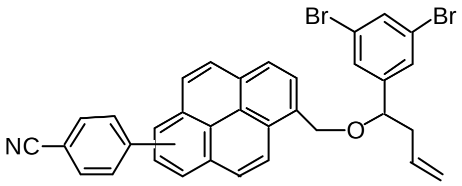


Procedure as described for **87**:

Sodium hydride: 0.252 g of a 60 % suspension in mineral oil (6.30 mmol, 1.01 eq.); tetrahydrofuran: 10 ml; 1-(3,5-dibromo-phenyl)-but-3-en-1-ol **84**: 2.39 g (7.81 mmol, 1.25 eq.); **81**: 2.37 g (6.24 mmol); [15]K-5: 0.13 ml (0.66 mmol, 0.1 eq.); additional 50 ml tetrahydrofuran; recrystallization from diethylether; yield 3.30 g (82 %) of **86** as a bright yellow solid.

– **M.p.** 138 °C. – $\mathbf{R_f}$ = 0.48 (hexane:ethyl acetate = 3:1). – $\mathbf{^1H}$**-NMR** (500 MHz, $CDCl_3$): δ = 2.32 (m, 1H), 2.50 (m, 1H), 3.11 (t, ^3J = 8 Hz, 2H), 3.54 (t, ^3J = 8 Hz, 2H), 4.31 (m, 1H), 4.88-4.95 (m, 3H), 5.07 (d, ^3J = 12 Hz, 1H), 5.63 (m, 1H), 7.13 (d, ^3J = 8.4 Hz, 2H), 7.39 (s, 2H), 7.44 (d, ^3J = 8.4 Hz, 2H), 7.52 (s, 1H), 7.61 (d, ^3J = 8.0 Hz, 1H), 7.84 (d, ^3J = 7.6 Hz, 2H), 7.98-8.01 (m, 3H), 8.05 (d, ^3J = 7.6 Hz, 1H), 8.10-8.13 (m, 2H). – $\mathbf{^{13}C}$**-NMR** (125 MHz, $CDCl_3$): δ = 34.98, 37.99, 42.44, 69.57, 80.14, 109.92, 117.80, 119.04, 122.88, 123.08, 123.63, 124.43, 124.66, 125.09, 125.11, 125.17, 126.86, 127.24, 127.43, 127.55, 127.86, 128.60, 128.75, 129.08, 129.32, 129.52, 129.63, 129.76, 130.82, 131.04, 132.16, 133.30, 133.73, 134.85, 146.18, 147.08. – **MS** (EI, 80 eV, 230 °C): *m/z* (%) = 651 (6) $[C_{36}H_{27}{}^{81}Br_2NO]^+$, 649 (12) $[C_{36}H_{27}{}^{79}Br^{81}BrNO]^+$, 647 (6) $[C_{36}H_{27}{}^{79}Br_2NO]^+$, 533 (25) $[M\text{-}CH_2PhCN]^+$, 228 (100) $[pyrene(CH_2)_2]^+$. – $\mathbf{C_{36}H_{27}Br_2NO}$ **(649.41)**: calcd. C 66.58, H 4.19, N 2.16; found C 66.39, H 4.02, N 1.96.

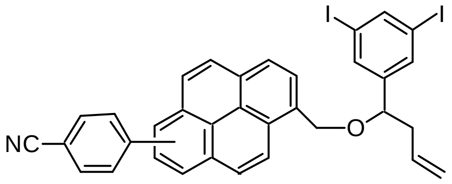
1-(4-Benzonitrile)-X-[1-(3,5-dibromo-phenyl)-but-3-enyloxymethyl]-pyrene, one isomer (X = 6, 8) (87)



To a suspension of sodium hydride (0.332 g of a 60 % suspension in mineral oil, 8.65 mmol, 2.03 eq.) in 5 ml tetrahydrofuran was added carefully a solution of 1-(3,5-dibromo-phenyl)-but-3-en-1-ol **84** (2.57 g, 8.40 mmol, 1.97 eq.) in 5 ml tetrahydrofuran . After one hour 1-chloromethyl-X-(4-benzonitrile)-pyrene **80** (1.50 g, 4.26 mmol), [15]-crown-5 (0.094 g, 0.43 mmol, 0.1 eq.) and 50 ml tetrahydrofuran were added, and the solution was stirred overnight. A small amount of silica gel was added and the solvent was removed. The residue was purified by column chromatography on silica gel (dichloromethane) to yield 2.21 g (83 %) of **87** as greenish glassy material that was not recrystallized successfully.

– **R_f** = 0.58 (dichloromethane). – **^{1}H-NMR** (250 MHz, $CDCl_3$): δ = 2.37 (m, 1H), 2.54 (m, 1H), 4.34 (t, ^3J = 7.0 Hz, 1H), 4.93-5.02 (m, 3H), 5.11 (d, ^3J = 12 Hz, 1H), 5.69 (m, 1H), 7.42 (s, 2H), 7.55 (s, 1H), 7.70 (d, ^3J = 7.5 Hz, 2H), 7.81 (d, ^3J = 7.5 Hz, 2H), 7.93 (m, 2H), 8.05 (m, 6H). – **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 42.32, 69.42, 80.24, 111.13, 117.82, 118.89, 123.01, 124.26, 124.58, 124.94, 125.03, 125.15, 127.22, 127.39, 127.88, 128.03, 128.74, 129.06, 129.89, 131.13, 131.28, 131.36, 131.64, 132.14, 133.27, 133.62, 135.57, 145.92, 146.07, 154.64. – **MS** (EI, 80 eV, 200 °C): *m/z* (%) = 621 (18) [$C_{34}H_{21}{}^{81}Br_2NO$]$^+$, 619 (34) [$C_{34}H_{21}{}^{79}Br^{81}BrNO$]$^+$, 617 (18) [$C_{34}H_{21}{}^{79}Br_2NO$]$^+$, 315 (100) [*$H_2C$-pyrene-phenyl-CN*]$^+$. The spectrum matches the calculated isotope pattern of [*M-2H*]$^+$. A possible explanation is the thermic formation of a cyclic isomer (5,7-dibromo-1-[(4-benzonitrile)-pyren-1-yl]-1,2-dihydro-naphthalene). – **MS** (pos. FAB; Xe, MNBA, CH_2Cl_2): *m/z* (%) = 623 (13) [$C_{34}H_{23}{}^{81}Br_2NO$]$^+$, 621 (23) [$C_{34}H_{23}{}^{79}Br^{81}BrNO$]$^+$, 619 (10) [$C_{34}H_{23}{}^{79}Br_2NO$]$^+$, 315 (100) [*$H_2C$-pyrene-phenyl-CN*]$^+$. – **HRMS**: *m/z* calcd. for **$C_{34}H_{21}Br_2NO$** 616.998987; found 616.99450.

1-(4-Benzonitrile)-X-[1-(3,5-diiodo-phenyl)-but-3-enyloxymethyl]-pyrene, one isomer (X = 6 or 8) (88)



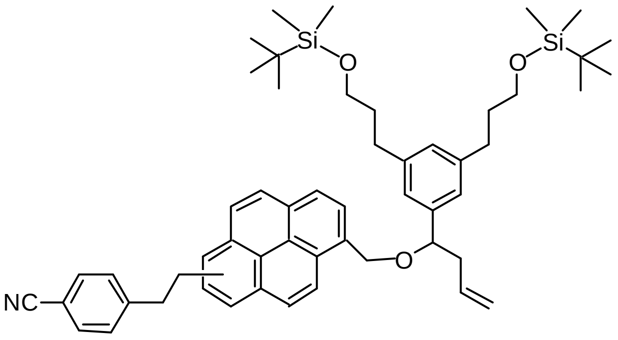
Procedure as described for **87**:

Sodium hydride: 0.093 g of a 60 % suspension in mineral oil (2.32 mmol, 2.00 eq.); tetrahydrofuran: 10 ml; 1-(3,5-diiodo-phenyl)-but-3-en-1-ol **84**: 0.90 g (2.25 mmol, 1.94 eq.); benzyl chloride **81**: 0.41 g (1.16 mmol); [15]K-5: 0.03 ml (0.15 mmol, 0.13 eq.); additional 50 ml tetrahydrofuran; recrystallization from diethylether; yield 0.70 g (85 %) of **86** as a bright yellow amorphous solid.

– **R**$_f$ = 0.60 (dichloromethane). – **^{1}H-NMR** (250 MHz, CDCl$_3$): δ = 2.34 (m, 1H), 2.48 (m, 1H), 4.25 (m, 1H), 4.90-5.07 (m, 4H), 5.64 (m, 1H), 7.57 (s, 2H), 7.66-8.21 (m, 13). – **^{13}C-NMR** (63 MHz, CDCl$_3$): δ = 42.36, 69.66, 80.09, 94.80, 111.05, 117.78, 118.92, 123.31, 124.17, 124.69, 125.06, 125.63, 126.37, 127.25, 127.44, 127.66, 128.08, 128.47, 130.61, 131.36, 132.18, 133.73, 135.27, 135.63, 144.31, 146.23. – **MS** (EI, 80 eV, 230 °C): *m/z* (%) = 715 (9) [*M*]$^+$, 588 (3) [*M-2H-I*]$^+$, 315 (100) [*H$_2$C-pyrene-phenyl-CN*]$^+$. — **HRMS**: *m/z* calcd. for **C$_{34}$H$_{22}$I$_2$NO** 713.979094; found 713.97479.

7.4.9 Compounds of Chapter 4.6

1-(1-{3,5-Bis-[3-(*tert*-butyl-dimethyl-silanyloxy)-propyl]-phenyl}-but-3-enyloxymethyl)-X-[2-(4-benzonitrile)-ethyl]-pyrene (X = 6, 8) (89)

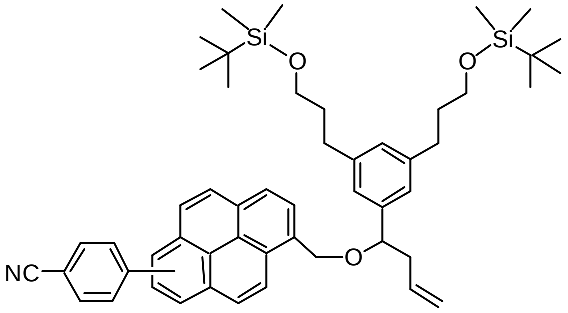


Procedure as described for **90**:

Allyloxy-dimethyl-*tert*-butyl-silane **30**: 5.0 ml (23.53 mmol, 2.62 eq.); 9-BBN: 47.0 ml of a 0.5 M solution in tetrahydrofuran (23.50 mmol, 2.61 eq.); aqueous sodium hydroxide (1 M): 20 ml; **86**: 5.84 g (2.09 mmol); Pd(PPh$_3$)$_4$: 0.54 g (4.7·10^{-4} mol, 2.6 mol-% per coupling); additional tetrahydrofuran: 20 ml; 4.35 g (58 %) of **89** as a highly viscous oil.

– **R$_f$** = 0.50 (dichloromethane). – **^{1}H NMR** (500 MHz, CDCl$_3$): δ = -0.02 (s, 12H), 0.83 (s, 18H), 1.77 (m, 4H), 2.37 (m, 1H), 2.57 (m, 1H), 2.62 (t, ^3J = 7.7 Hz, 4H), 3.08 (t, ^3J = 7.5 Hz, 2H), 3.49 (t, ^3J = 7.5 Hz, 2H), 3.58 (t, ^3J = 7.9 Hz, 4H), 4.35 (m, 1H), 4.86-5.07 (m, 3H), 5.09 (d, ^3J = 11.8 Hz, 1H), 5.71 (m, 1H), 6.94 (s, 1H), 7.00 (s, 2H), 7.11 (d, ^3J = 8.1 Hz, 2H), 7.42 (d, ^3J = 8.1 Hz, 2H), 7.55 (d, ^3J = 7.8 Hz, 1H), 7.84 (d, ^3J = 7.6 Hz, 1H), 7.90 (m, 2H), 7.94 (d, ^3J = 7.8 Hz, 1 H), 8.02 (d, ^3J = 7.6 Hz, 1H), 8.15 (d, ^3J = 9.5 Hz, 1H), 8.27 (d, ^3J = 9.5 Hz, 1H). – **^{13}C NMR** (126 MHz, CDCl$_3$): δ = -5.29, 18.31, 25.93, 32.04, 34.45, 34.88, 37.86, 42.75, 62.40, 68.87, 81.46, 109.81, 116.67, 122.78, 123.96, 124.47, 124.60, 124.86, 125.08, 125.16, 126.86, 127.20, 127.35, 128.15, 128.22, 128.24, 128.25, 128.26, 129.03, 129.26, 130.12, 131.36, 131.55, 132.12, 134.58, 135.16, 141.71, 142.36, 147.08. – **MS** (EI, 80 eV, 280 °C): *m/z* (%) = 835 (19) [*M*]$^+$, 820 (2) [*M-CH$_3$*]$^+$, 778 (8) [*M-^{t}Bu*]$^+$, 344 (100) [*H$_2$C-pyrene-ethyl-benzonitrile*]$^+$. – **$C_{54}H_{69}NO_3Si_2$ (836.30)**: calcd. C 77.55, H 8.32, N 1.67; found C 77.21, H 8.24, N 1.44.

1-(1-{3,5-Bis-[3-(*tert*-butyl-dimethyl-silanyloxy)-propyl]-phenyl}-but-3-enyloxymethyl)-X-(4-benzonitrile)-pyrene (X = 6 or 8) (90)

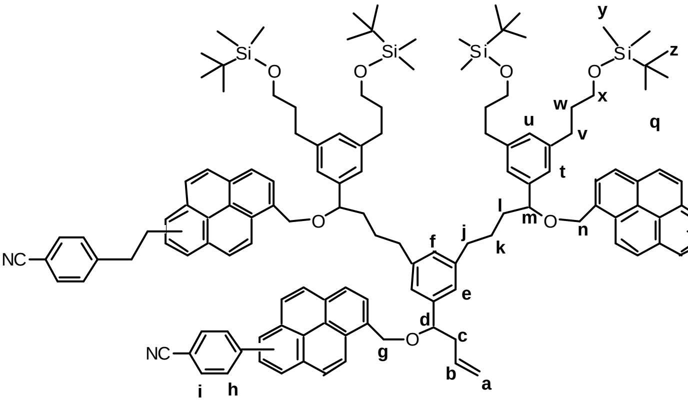


Allyloxy-dimethyl-*tert*-butyl-silane **30** (1.33 ml, 6.26 mmol, 2.99 eq.) was added to a solution of 9-BBN (12.55 ml of a 0.5 M solution in tetrahydrofuran, 6.28 mmol, 3.00 eq.) at 0 °C, and the solution was stirred for 18 h at ambient temperature. After addition of aqueous sodium hydroxide (1 M, 20 ml), **86** (1.30 g, 2.09 mmol), the catalyst precursor Pd(PPh$_3$)$_4$ (0.15 g, $1.3 \cdot 10^{-4}$ mol, 3.1 mol-% per coupling), and additional tetrahydrofuran (20 ml) the suspension was stirred for 17 h at 60 °C. Extractive work-up with diethylether and column chromatography on silica gel (dichloromethane) gave 0.88 g (52 %) of **90** as a highly viscous oil.

– **R$_f$** = 0.47 (dichloromethane). – **^{1}H NMR** (500 MHz, CDCl$_3$): δ = 0.07 (s, 12H), 0.92 (s, 18H), 1.87 (m, 4H), 2.51 (m, 1H), 2.63-2.69 (m, 5H), 3.65 (t, ^3J = 8 Hz, 4H), 4.48 (m, 1H), 4.95-5.05 (m, 3H), 5.14 (d, ^3J = 12 Hz, 1H), 5.77 (m, 1H), 7.00 (s, 1H), 7.07 (s, 2H), 7.73 (d, ^3J = 7.5 Hz, 2H), 7.85 (d, ^3J = 7.5 Hz, 2H), 7.92 (d, ^3J = 7.8 Hz, 1H), 7.99 (d, ^3J = 7.8 Hz, 1H), 8.05-8.11 (m, 3H), 8.17 (d, ^3J = 9.5 Hz, 1H), 8.22 (d, ^3J = 7.8 Hz, 1H), 8.29 (d, ^3J = 9.5

Hz, 1H).– ^{13}**C NMR** (126 MHz, $CDCl_3$): δ = -5.28, 18.31, 25.95, 32.06, 34.45, 42.69, 62.41, 68.80, 81.76, 111.09, 116.71, 118.91, 124.25, 124.49, 124.62, 124.86, 124.99, 125.02, 125.17, 127.15, 127.46, 127.93, 128.11, 128.25, 128.42, 129.06, 131.29, 131.40, 131.42, 132.14, 132.20, 134.94, 135.09, 135.39, 141.68, 142.41, 146.07. – **MS** (EI, 80 eV, 230 °C): *m/z* (%) = 807 (8) $[M]^+$, 792 (<1) $[M\text{-}CH_3]^+$, 750 (3) $[M\text{-}{}^tBu]^+$, 316 (100) $[H_2C\text{-pyrene-benzonitrile}]^+$. – **$C_{52}H_{65}NO_3Si_2$ (808.25)**: calcd. C 77.27, H 8.11, N 1.73; found C 76.95, H 8.04, N 1.67.

G2 Dendron 91



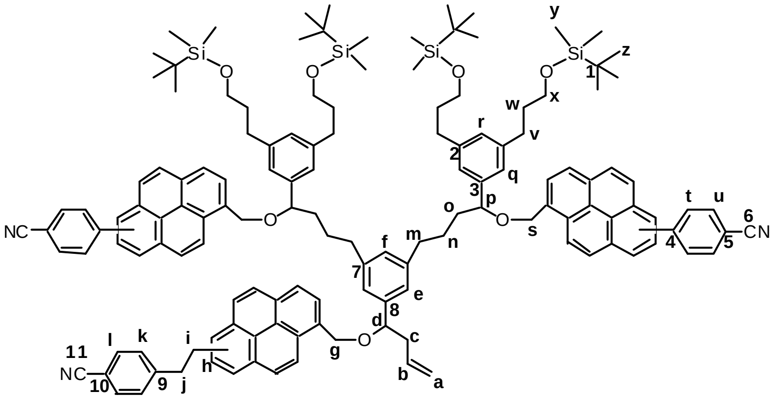
Procedure as described for **90**:

89: 3.20 g (3.85 mmol); 9-BBN: 9.00 ml of a 0.5 M solution in tetrahydrofuran (4.50 mmol, 1.17 eq.); aqueous sodium hydroxide (1 M): 15 ml; **87**: 0.95 g (1.53 mmol, 0.40 eq.); $Pd(PPh_3)_4$: 70 mg ($6.1\cdot10^{-5}$ mol, 2.0 mol-% per coupling); additional tetrahydrofuran: 15 ml; isolated yield after prepurification by column chromatography on silica gel (dichloromethane), preparative GPC-separation, precipitation from methanol, centrifugation and lyophilization from benzene: 350 mg (11 %) of **91** as a yellow amorphous solid. The conversion lies somewhat higher as other fractions also contained the product.

– **R_f** = 0.30 (hexane:ethyl acetate = 3:1). – ^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 0.02 (s, 24H, *H-y*), 0.89 (s, 36, *H-z*), 1.53 (m, 4H, *H-k*), 1.70 (m, 2H, *H-l*), 1.84 (m, 10H, *H-l', H-w*), 2.30 (m, 1H, *H-c'*), 2.45 (m, 5H, *H-c, H-j*), 2.66 (m, 8H, *H-v*), 3.04 (m, 4H, *H-p*), 3.46 (m, 4H, *H-o*), 3.62 (m, 8H, *H-x*), 4.22 (m, 1H, *H-d*), 4.36 (m, 2H, *H-m*), 4.74-5.08 (m, 8H, *H-a, H-g, H-n,*), 5.67 (m, 1H, *H-b*), 6.71 (s, 1H, *H-f*), 6.87 (s, 2H, *H-u*), 6.97 (s, 2H, *H-e*), 7.04 (s, 4H, *H-t*), 7.13 (d, 2H, *H-r*), 7.39 (d, 2H, *H-s*), 7.47-7.75 (m, 10H, *H-i, H-h, Py-H*), 7.85-8.25 (m, 22H, *Py-H*) – ^{13}**C NMR** (126 MHz, $CDCl_3$): δ = -5.25, 18.34, 25.98, 27.87, 29.70, 32.15, 34.44, 34.53, 34.94, 35.65, 37.90, 38.16, 38.72, 42.66, 62.52, 68.78, 68.98, 81.75, 109.99, 111.07, 116.80, 118.97, 122.58, 122.82, 123.34, 123.78, 124.41, 124.65, 124.90, 126.04, 126.24, 126.75, 126.92, 127.16, 127.38, 127.55, 128.13, 129.23, 129.34, 129.74, 130.86, 131.25, 131.74, 132.15, 132.28, 134.60, 135.04, 141.46, 142.50, 144.91, 147.12. – **MS** (MALDI-

TOF, dithranol): *m/z* (%) = 1985 $[M\text{-}OSiMe_2{}^tBu+Na]^+$, 2157 (50), 2158 (100), 2159 (94), 2160 (76), 2161 (54), 2162 (41) $[M+H+Na]^+$, 2173 $[M+H+K]^+$. – **$C_{142}H_{163}N_3O_7Si_4$ (2136.17)**: calcd. C 79.84, H 7.69, N 1.97; found C 79.47, H 7.22, N 1.61.

G2 Dendron 92

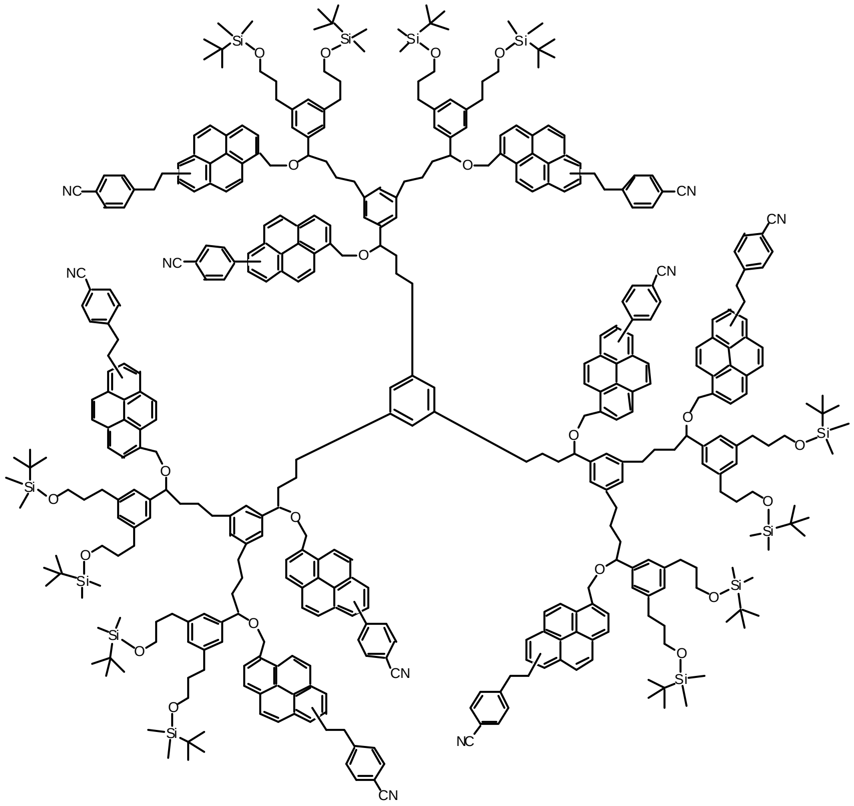


Procedure as described for **90**:

90: 790 mg (0.98 mmol); 9-BBN: 2.50 ml of a 0.5 M solution in tetrahydrofuran (1.25 mmol, 1.28 eq.); aqueous sodium hydroxide (1 M): 5 ml; **86**: 165 mg (0.25 mmol, 0.26 eq.); $Pd(PPh_3)_4$: 5 mg ($4.3\cdot10^{-6}$ mol, 3.5 mol-% per coupling); additional tetrahydrofuran: 10 ml; isolated yield after prepurification by column chromatography on silica gel (dichloromethane), preparative GPC-separation, precipitation from methanol, centrifugation and lyophilization from benzene: 270 mg (50 %) of **92** as a yellow amorphous solid. The conversion lies somewhat higher as other fractions also contained the product.

– **R_f** = 0.21 (hexane:ethyl acetate = 3:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.04 (s, 24H, *H-y*), 0.90 (s, 36, *H-z*), 1.60 (m, 4H, *H-n*), 1.72 (m, 2H, *H-o*), 1.83 (m, 8H, *H-w*), 1.94 (m, 2H, *H-o'*), 2.29 (m, 1H, *H-c'*), 2.46 (m, 4H, *H-m*), 2.51 (m, 1H, *H-c*), 2.66 (t, ^3J = 7.9 Hz, 8H, *H-v*), 3.17 (t, ^3J = 7.5 Hz, 2H, *H-j*), 3.62 (m, 10H, *H-i*, *H-x*), 4.24 (t, ^3J = 6.7 Hz, 1H, *H-d*), 4.39 (m, 2H, *H-p*), 4.72 (d, ^3J = 11.8 Hz, 1H, *H-g'*), 4.85-4.97 (m, 5H, *H-a*, *H-g*, *H-s*), 5.09 (d, ^3J = 11.8 Hz, 2H, *H-s'*), 5.65 (m, 1H, *H-b*), 6.72 (s, 1H, *H-f*), 6.89 (s, 2H, *H-r*), 6.98 (s, 2H, *H-e*), 7.05 (s, 4H, *H-p*), 7.23 (d, ^3J = 7.9 Hz, 2H, *H-k*), 7.54 (d, ^3J = 7.9 Hz, 2H, *H-l*), 7.62 (d, ^3J = 7.5 Hz, 4H, *H-t*), 7.75 (m, 5H, *H-h*, *H-u*), 7.83 (d, ^3J = 7.9 Hz, 2H), 7.91-7.99 (m, 13H), 8.08-8.23 (m, 8H) – **^{13}C NMR** (126 MHz, $CDCl_3$): δ = -5.33 (*C-y*), 18.31 (*C-1*), 25.94 (*C-z*), 27.89 (*C-n*), 32.11 (*C-w*), 34.46 (*C-v*), 34.97 (*C-j*), 35.61 (*C-o*), 37.99 (*C-i*), 38.09 (*C-m*), 42.59 (*C-c*), 62.44 (*C-x*), 68.63 (*C-p*), 68.82 (*C-d*), 81.33 (*C-g*), 81.95 (*C-s*), 109.95 (*C-10*), 110.96 (*C-5*), 116.66 (*C-a*), 118.88 (*C-6*), 119.03 (*C-11*), 122.53, 123.14, 124.22, 124.33, 124.41, 124.84, 124.91, 124.97, 125.06, 125.18, 127.07, 127.11, 127.19, 127.25, 127.45, 127.53, 127.74, 127.81, 128.05, 128.15, 128.18, 128.52, 128.94, 129.30, 129.56, 129.73, 130.69, 131.21, 131.27, 131.34, 131.37, 131.65, 132.10, 132.18, 132.29, 133.01, 134.50, 134.54, 135.01, 135.27, 141.56, 141.63 (*C-3*, *C-8*), 142.44, 142.48 (*C-2*, *C-7*), 145.94 (*C-4*), 147.16 (*C-9*). – **MS** (MALDI-TOF, dithranol): *m/z* (rel. %) = 1957 $[M\text{-}OSiMe_2{}^tBu\text{-}C_3H_5+Na]^+$, 2129 (51), 2130 (100), 2131 (96), 2132 (66), 2133 (39), 2134 (22) $[M+H+Na]^+$; 2145 $[M+H+K]^+$. – **$C_{140}H_{159}N_3O_7Si_4$ (2108.12)**: calcd. C 79.76, H 7.60, N 1.99; found C 79.50, H 7.17, N 1.91.

G2 Dendrimer 93

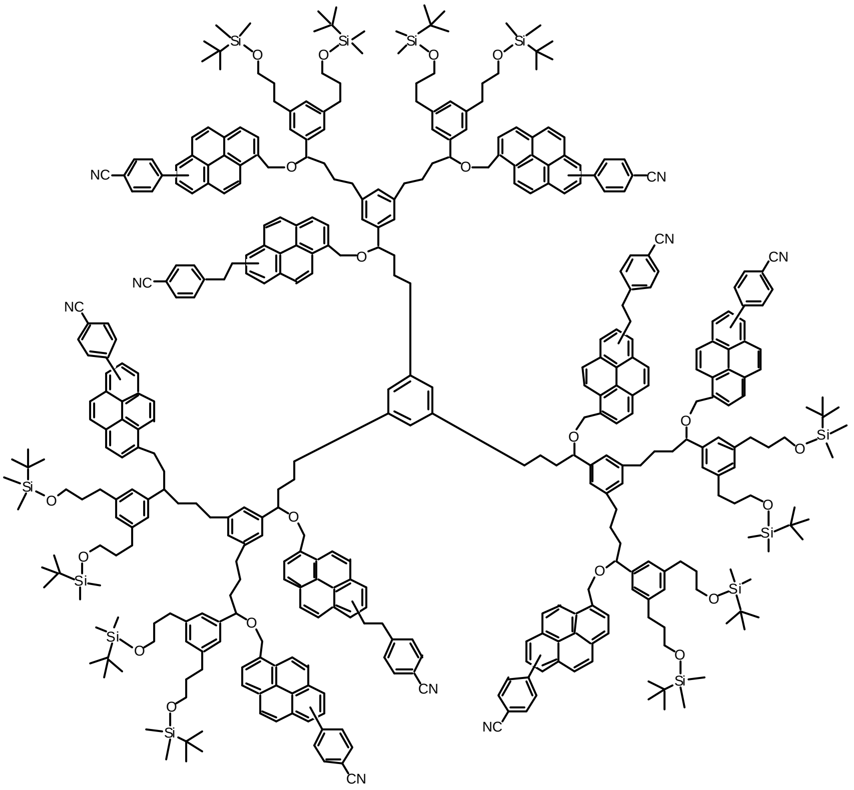


Procedure as described for **90**:

91: 180 mg (0.084 mmol); 9-BBN: 0.55 ml of a 0.5 M solution in tetrahydrofuran (0.28 mmol, 3.33 eq.); aqueous sodium hydroxide (1 M): 1.0 ml; **3**: 9.7 mg (0.021 mmol, 0.25 eq.); $Pd(PPh_3)_4$: 2 mg ($1.7 \cdot 10^{-6}$ mol, 2.7 mol-% per coupling); additional tetrahydrofuran: 5 ml; prepurification by column chromatography on silica gel (dichloromethane), preparative GPC-separation, precipitation from methanol, centrifugation and lyophilization from benzene: gave 3 mg of **93** as a yellow amorphous solid. Other fractions obtained by preparative GPC-separation were the one- and twofold coupled analog (6 and 18 mg). All fractions were not characterized by further than GPC analysis.

– **$C_{432}H_{495}N_9O_{21}Si_{12}$ (6486.63)**.

G2 Dendrimer 94

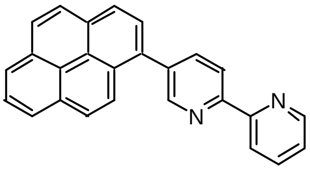


Procedure as described for **90**:

92: 183 mg (0.087 mmol); 9-BBN: 0.26 ml of a 0.5 M solution in tetrahydrofuran (0.13 mmol, 1.50 eq.); aqueous sodium hydroxide (1 M): 1.5 ml; **3**: 11 mg (0.024 mmol, 0.28 eq.); $Pd(PPh_3)_4$: 2 mg ($1.7 \cdot 10^{-6}$ mol, 2.4 mol-% per coupling); additional tetrahydrofuran: 3 ml; isolated yield after prepurification by column chromatography on silica gel (dichloromethane), preparative GPC-separation, precipitation from methanol, centrifugation and lyophilization from benzene: 7 mg of **94** as a yellow amorphous solid. Other fractions obtained by preparative GPC-separation were the one- and twofold coupled analog (8 and 32 mg). All fractions were not sufficiently characterized since the differences in the NMR spectra were too little, and in the MALDI-TOF mass spec only fragments were identified. – **$C_{426}H_{483}N_9O_{21}Si_{12}$ (6402.47)**: calcd. C 79.92, H 7.60, N 1.97; found C 78.96, H 7.39, N 1.84.

7.4.10 Compounds of Chapter 4.7

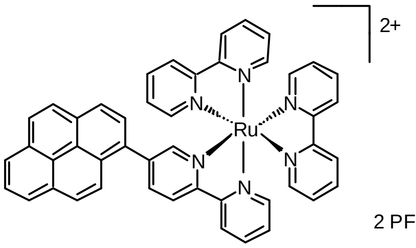
5-Pyren-1-yl-2,2'-bipyridine (99)



Procedure as described for **45e**.

– **M.p.** 172-173 °C. – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.34 (t, ^{3}J = 5.0 Hz, 1H), 7.86 (dt, ^{3}J = 7.5 Hz, ^{4}J = 1.5 Hz, 1H), 7.97-8.25 (m, 10H), 8.52 (d, ^{3}J = 8.0 Hz, 1H), 8.61 (d, ^{3}J=8.0 Hz, 1H), 8.75 (d, ^{3}J = 5.0 Hz, 1H), 8.97 (d, ^{4}J = 1.5 Hz, 1H). – **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 120.68, 121.12, 123.77, 124.32, 124.65, 124.74, 124.88, 125.08, 125.39, 126.12, 127.24, 127.45, 127.83, 128.06, 128.62, 130.76, 131.10, 131.30, 133.29, 136.84, 137.03, 138.74, 149.20, 150.37, 154.72, 155.79. – **MS** (EI, 80 eV, 130 °C): *m/z* (%) = 356 (100) $[M]^{+}$. – **HRMS**: *m/z* calcd. for $\mathbf{C_{26}H_{16}N_2}$ 356.13135; found 356.13467.

rac-[Ruthenium(II)-bis(2,2'-bipyridine)(5-pyren-1-yl-2,2'-bipyridine)]-$(PF_6)_2$ (100)



A suspension of **99** (60 mg, 0.17 mmol) and *cis/trans*-bis(2,2′-bipyridine)dichloro ruthenium(II)·x H_2O (86 mg) in aqueous ethanol (30 ml, 1:1 v/v) was refluxed for 19 h. The solvent was evaporated, and the residue chromatographed on silica gel with a 7:2:1-mixture of methanol/2M NH_4Cl/nitromethane. Water was added to the eluate and the resulting mixture extracted with chloroform. After evaporation of the chloroform the remaining red solid was dissolved in methanol (3 ml) and a saturated solution of NH_4PF_6 in methanol (2 ml) was added. After standing overnight the mixture was centrifuged, the solvent was decanted and the residue dried in vacuo to give racemic **100** (0.15 g, 0.14 mmol, 83 %).

The structure of **100** was solved by x-ray structure analysis, details are given in section 7.5.2. – **M.p.** >210 °C (decomp.). – **^{1}H NMR** (500 MHz, d_3-acetonitrile): δ = 7.14 (dt, ^{3}J = 6.7 Hz, ^{4}J = 1.5 Hz, 1H), 7.40 (m, 5H), 7.68 (d, ^{3}J = 5.7 Hz, 1H), 7.73 (dt, ^{3}J = 7.5 Hz, ^{4}J = 1.5 Hz, 1H), 7.81 (t, ^{3}J = 6.0 Hz, 2H), 7.85 (s, ^{4}J = 2.2 Hz, 1H), 7.89 (m, 2H), 8.00 (d, ^{3}J = 5.7 Hz, 1H), 8.04-8.14 (m, 7H), 8.18 (dt, ^{3}J = 7.7 Hz, ^{4}J = 1.5 Hz, 1H), 8.22 (d, ^{3}J = 8.2 Hz, 1H), 8.24

(d, ^3J = 7.7 Hz, 1H), 8.29 (d, ^3J = 8.2 Hz, 2H), 8.45 (d, ^3J = 8.2 Hz, 1H), 8.51 (d, ^3J = 8.2 Hz, 2H), 8.61 (d, ^3J = 8.2 Hz, 1H), 8.64 (d, ^3J = 8.2 Hz, 1H), 8.67 (d, ^3J = 8.2 Hz, 1H). – **^{13}C NMR** (125 MHz, d_3-acetonitrile): δ = 123.63, 124.84, 124.95, 125.07, 125.09, 125.20, 125.87, 126.48, 126.90, 127.51, 127.67, 127.97, 128.24, 128.38, 128.42, 128.53, 128.67, 128.80, 129.25, 129.40, 131.23, 131.33, 131.98, 132.53, 138.34, 138.65, 138.71, 138.85, 139.87, 140.88, 152.55, 152.58, 152.62, 152.76, 152.83, 156.36, 157.63, 157.69, 157.74, 157.77. – **MS** (pos. FAB; Xe, MNBA, CH_2Cl_2): *m/z* (%) = 915 (4) [*M-PF$_6$*]$^+$, 770 (1) [*M-2PF$_6$*]$^+$, 614 (2) [*M-2PF$_6$-bipy*]$^+$, 455 (1) [*M-2PF$_6$-2bipy*]$^+$, 413 (4) [*Ru(bipy)$_2$*]$^+$, 357 (2) [*Pyrene+bipy*]$^+$. – **$C_{46}H_{32}F_{12}N_6P_2Ru$ (1059.79)**: calcd. C 52.13, H 3.04, N 7.93; found C 51.67, H 3.25, N 7.70.

7.4.11 Compounds of Chapter 4.8

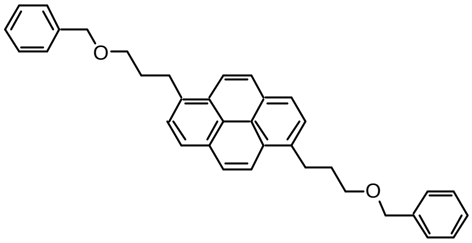
Bis-(3-benzyloxy-propyl)-pyrene (103) and 1,3,6-tris-(3-benzyloxy-propyl)-pyrene (106)

Procedure as described for **6**:

Allylbenzylether **5**: 2.86 g, 19.30 mmol; 9-BBN: 2.42 g, 19.83 mmol; toluene: 100 ml; aqueous sodium hydroxide: 25 ml (3 M); a mixture of dibromopyrenes (34 % 1,8-, 21 % 1,6-, 2 % 1,3-dibromopyrene) and tribromopyrene (43 %, all according to analytical HPLC): 2.22 g, max. 6.2 mmol; $Pd(PPh_3)_4$: 0.42 g, 0.36 mmol.

DC has shown four distinct spots, two of them were isolated by column chromatography on silica gel (hexane, then hexane:ethyl acetate = 20:1):

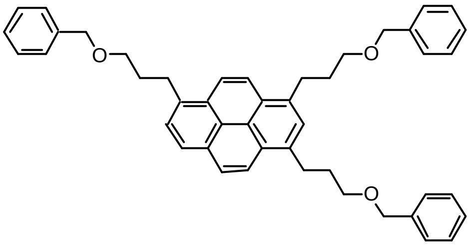
1,6-Bis-(3-benzyloxy-propyl)-pyrene (103)



Recrystallized from dichloromethane/methanol, yield: 0.92 of **103** as a yellowish amorphous solid.

– **M.p.** 98-101 °C. – **R$_f$** = 0.31 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.18 (m, 4H), 3.46 (m, 4H), 3.58 (m, 4H), 4.56 (s, 4H), 7.32-7.42 (m, 10H), 7.84 (d, ^3J = 7.6 Hz, 2H), 8.05 (d, ^3J = 9.3 Hz, 2H), 8.08 (d, ^3J = 7.6 Hz, 2H), 8.26 (d, ^3J = 9.3 Hz, 2H). – **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 29.96, 31.65, 69.45, 72.97, 23 signals between 122.59 and 131.13, 136.07, 138.53 (values taken from the 1,6-/1,8-isomers mixture). – **MS** (EI, 80 eV, 240 °C): *m/z* (rel. Int.) = 498 (100) [*M*]$^+$, 407 (7) [*M-CH$_2$Bn*]$^+$, 316 (6) [*M-2CH$_2$Bn*]$^+$, 91 (26) [*Bn*]$^+$. – **HRMS**: *m/z* calcd. for **$C_{36}H_{34}O_2$** 498.2558811; found 498.25387.

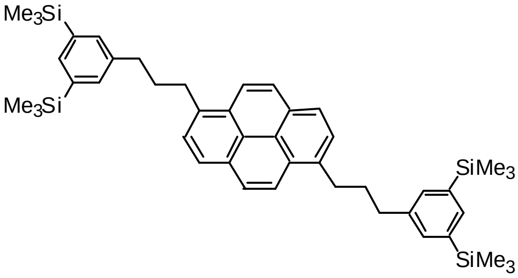
1,3,6-Tris-(3-benzyloxy-propyl)-pyrene (106)



Yield: 1.40 g as a slightly yellowish oil.

– **R$_f$** = 0.24 (hexane:ethyl acetate = 6:1). – **^{1}H NMR** (500 MHz, CDCl$_3$): δ = 2.20 (m, 6H), 3.45 (m, 6H), 3.61 (m, 6H), 4.59 (s, 6H), 7.33-7.46 (m, 15H), 7.76 (s, 1H), 7.86 (d, ^3J = 7.6 Hz, 1H), 8.01 (d, ^3J = 9.0 Hz, 1H), 8.08 (d, ^3J = 7.6 Hz, 1H), 8.28 (m, 3H). – **^{13}C NMR** (63 MHz, CDCl$_3$): δ = 29.99, 31.77, 69.66, 72.97, 122.40, 122.61, 123.25, 124.38, 125.78, 125.95, 126.52, 127.19, 127.48, 127.62, 127.83, 128.08, 128.34, 128.75, 128.90, 129.87, 135.42, 135.64, 135.78, 138.66. – **MS** (EI, 80 eV, 250 °C): *m/z* (rel. Int.) = 646 (80) [*M*]$^+$, 91 (100) [*C$_7$H$_7$*]$^+$. – **HRMS**: *m/z* calcd. for **$C_{46}H_{46}O_3$** 646.344696; found 646.34930.

1,6-Bis-[3-(bis-3,5-trimethylsilanyl-phenyl)-propyl]-pyrene (109)

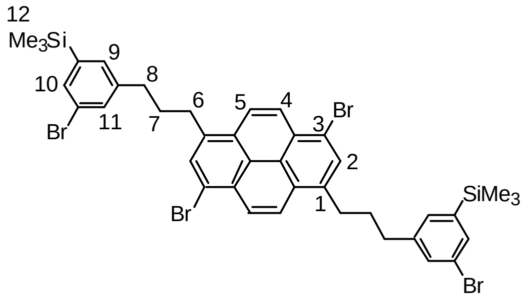


Procedure as described for **6**:

1-Allyl-3,5-bis(trimethylsilanyl)-benzene **108**: 3.30 g, 12.60 mmol; 9-BBN (0.5 M solution in tetrahydrofuran): 28. 0 ml, 14.0 mmol; aqueous sodium hydroxide (3 M, 8 ml); dibromopyrene **107**: 0.88 g, 2.44 mmol (88.5 % 1,6-isomer, according to analytical HPLC); Pd(PPh$_3$)$_4$: 0.16 g, 0.14 mmol; yield: 1.58 g (74 %) of **109** as a clear yellowish oil.

– **R$_f$** = 0.53 (hexane:ethyl acetate = 20:1). – **^{1}H NMR** (270 MHz, CDCl$_3$): δ = 0.31 (s, 36H), 2.24 (m, 4H), 2.84 (t, 4H), 3.40 (t, 4H), 7.41 (s, 4H), 7.56 (s, 2H), 7.88 (d, ^3J = 7.5 Hz, 2H), 7.98-8.24 (m, 6H). – **^{13}C NMR** (63 MHz, CDCl$_3$): δ = -1.02, 33.24, 33.33, 36.12, 122.55, 124.49, 125.50, 127.25, 127.32, 128.96, 129.60, 134.05, 135.73, 136.52, 139.46, 140.27. – **MS** (EI, 80 eV, 170 °C): *m/z* (rel. Int.) = 727 (71) [*M*]$^+$, 726 (100) [*M-H*]$^+$. – **HRMS**: *m/z* calcd. for **$C_{46}H_{62}Si_4$** 726.392866; found 726.39587.

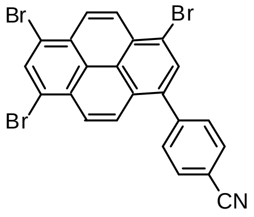
1,6-Dibromo-3,6-bis-[3-(3-bromo-5-trimethylsilanyl-phenyl)-propyl]-pyrene (112)



To a solution of pyrene **109** (1.50 g, 2.06 mmol) in *N*,*N*-dimethyl formamide (20 ml) was added a solution of *N*-bromo succinimide (5.25 g, 29.50 mmol) in 25 ml *N*,*N*-dimethyl formamide within 5 min. The solution was stirred for 2 h at room temperature when brine (20 ml) and dichloromethane (100 ml) were added. Usual extractive work-up with dichloromethane and column chromatography on silica gel (hexane, then hexane:ethyl acetate = 20:1) gave the tetrabromo compound **112** (1.40 g, 76 %) as a yellow solid, which was the only identifyable product.

– **R$_f$** = 0.62 (hexane:ethyl acetate = 20:1). – **^{1}H NMR** (270 MHz, CDCl$_3$): δ = 0.26 (s, 18H, *H-12*), 2.15 (m, 4H, *H-7*), 2.75 (t, 4H, *H-8*), 3.29 (t, 4H, *H-6*), 7.26 (s, 2H, *H-9*), 7.36 (s, 2H, *H-11*), 7.46 (s, 2H, *H-10*), 8.08 (s, 2H, *H-2*), 8.09 (d, ^3J = 9.5 Hz, 2H, *H-5*), 8.37 (d, ^3J = 9.5 Hz, 2H, *H-4*). – **MS** (EI, 80 eV, 270 °C): *m/z* (rel. Int.) = 898 (100) $[M]^+$, isotopic pattern matches the calculated one. – **$C_{40}H_{42}Br_4Si_2$ (898.56)**

4-(3,6,8-Tribromo-pyren-1-yl)-benzonitrile (113)



To a solution of 4-pyren-1-yl-benzonitrile **45b** (0.76 g, 2.51 mmol) in 20 ml dichloromethane was added a solution of bromine (0.50 ml, 9.71 mmol, 3.87 eq.) in 20 ml dichloromethane. Product precipitated and the suspension thickened, therefore additional 150 ml dichloromethane were added, and the suspension was refluxed for 18 h. After cooling the solid was filtered off, washed with methanol and dried in vacuo to yield 1.22 g (90 %) of **113** as a bright yellow amorphous solid.

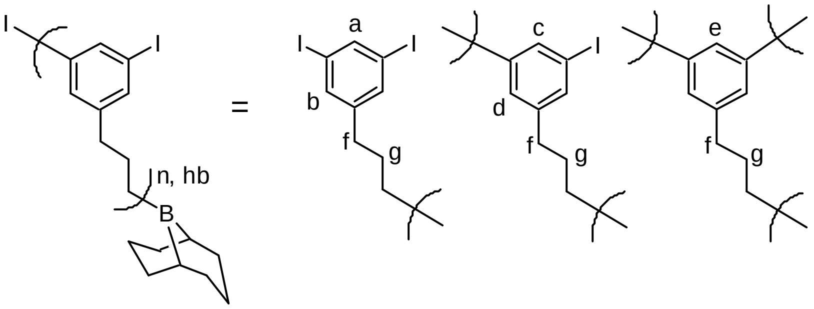
The compound is not sufficiently soluble in common organic solvents, therefore no NMR data were obtained.

– **M.p.** >295 °C. –**MS** (EI, 80 eV, 290 °C): *m/z* (%) = 541 (99) $[C_{23}H_{10}{}^{79}Br_2{}^{81}Br_1N]^+$, 539 (100) $[C_{23}H_{10}{}^{79}Br_3N]^+$. – **IR** (KBr): $\tilde{n}$ = 2229 (*CN*, m) cm^{-1}. – **$C_{23}H_{10}BrN$ (540.04)**: calcd.

C 51.15, H 1.87, N 2.59; found C 50.80, H 2.00, N 2.36.

7.4.12 Compound of Chapter 4.9

Poly-{9-[3-(3,5-diiodo-phenyl)-propyl]-9-bora-bicyclo[3.3.1]nonane} (115)



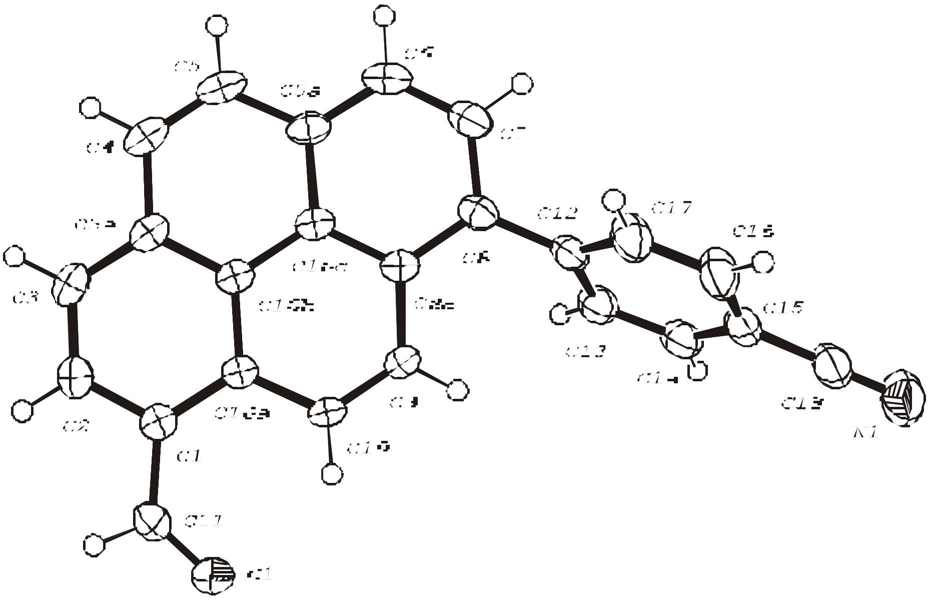
Typical procedure:

A mixture of 9-BBN (3.2 ml of a 0.5 M solution in tetrahydrofuran, 1.60 mmol, 1.02 eq.) and 1-allyl-3,5-diiodo-benzene **4** (0.58 g, 1.57 mmol) was stirred for one day at room temperature. After addition of aqueous sodium hydroxide (3 M, 1.50 ml, 4.50 mmol, 2.87 eq.) and additional tetrahydrofuran (10 ml) the suspension was degassed. The catalyst precursor $Pd(PPh_3)_4$ (38.3 mg, $3.31 \cdot 10^{-5}$ mol, 1.05 mol-% per coupling) was added and the suspension was stirred under gentle reflux for 20 h. The reaction mixture was poured into 200 ml methanol, and the polymer was allowed to precipitate for one day. The turbid suspension was centrifugated, and the resulting solid was lyophilized from benzene to yield 0.38 g (94 %) of polymer **115** as a creamy white solid.

– **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.85 (s, 2H, *H-g*), 2.52 (s, br, 4H, *H-f*), 6.76 (s, br, *H-e*), 6.88 (s, br, *H-d*), 7.30 (s, br, *H-c*), 7.42 (s, br, *H-b*), 7.82 (s, br, *H-a*). – **MS** (MALDI-TOF, DHB): *m/z* = 2333 $[(M)_{n=9}]^+$, 2207 $[(M)_{n=9}\text{-}I]^+$, 2089 $[(M)_{n=8}]^+$, 1963 $[(M)_{n=8}\text{-}I]^+$, 1845 $[(M)_{n=7}]^+$, 1719 $[(M)_{n=7}\text{-}I]^+$, 1601 $[(M)_{n=6}]^+$, 1475 $[(M)_{n=6}\text{-}I]^+$, 1357 $[(M)_{n=5}]^+$, 1231 $[(M)_{n=5}\text{-}I]^+$, 1113 $[(M)_{n=4}]^+$, 987 $[(M)_{n=4}\text{-}I]^+$, 869 $[(M)_{n=3}]^+$, 743 $[(M)_{n=3}\text{-}I]^+$. – **$[C_{10}H_{11}I]_n$ (258.20)**: calcd. C 44.29, H 3.72; found C 46.46, H 3.89.

7.5 Crystal Structure Data

7.5.1 8-(4-Benzonitrile)-pyrene-1-carbaldehyde (**76**)



Caution: The numeration in chapter 4.5.2 is different.

Crystal data and structure refinement:

Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P2(1)/c (No. 14)
Unit cell dimensions	a = 14.874(2) Å, b = 6.788(1) Å, c = 16.801(2) Å α = 90°, β = 108.737(2)°, γ= 90°
Z	4
Density	1.271 g/mol
Volume	1606.3(3) $Å^3$
Crystal size	(0.06 · 0.15 · 0.73) mm
Theta range for data collection	(1.45 to 26.37)°
Reflections collected / unique	14277 / 3285 [R(int) = 0.0480]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3285 / 0 / 236
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.1025
R indices (all data)	R1 = 0.0763, wR2 = 0.1204

Bond lengths [Å]:

C(1)-C(2)	1.393(2)	C(8A)-C(10C)	1.420(2)
C(1)-C(10A)	1.415(2)	C(8A)-C(9)	1.432(2)
C(1)-C(11)	1.469(2)	C(9)-C(10)	1.351(2)
C(2)-C(3)	1.374(2)	C(10)-C(10A)	1.430(2)
C(3)-C(3A)	1.392(2)	C(10A)-C(10B)	1.424(2)
C(3A)-C(10B)	1.425(2)	C(10B)-C(10C)	1.426(2)
C(3A)-C(4)	1.434(2)	C(11)-O(1)	1.208(2)
C(4)-C(5)	1.331(2)	C(12)-C(17)	1.389(2)
C(5)-C(5A)	1.435(2)	C(12)-C(13)	1.394(2)
C(5A)-C(6)	1.388(2)	C(13)-C(14)	1.378(2)
C(5A)-C(10C)	1.424(2)	C(14)-C(15)	1.388(2)
C(6)-C(7)	1.376(2)	C(15)-C(16)	1.387(2)
C(7)-C(8)	1.393(2)	C(15)-C(18)	1.439(3)
C(8)-C(8A)	1.413(2)	C(16)-C(17)	1.375(2)
C(8)-C(12)	1.488(2)	C(18)-N(1)	1.145(2)

Angles [°]:

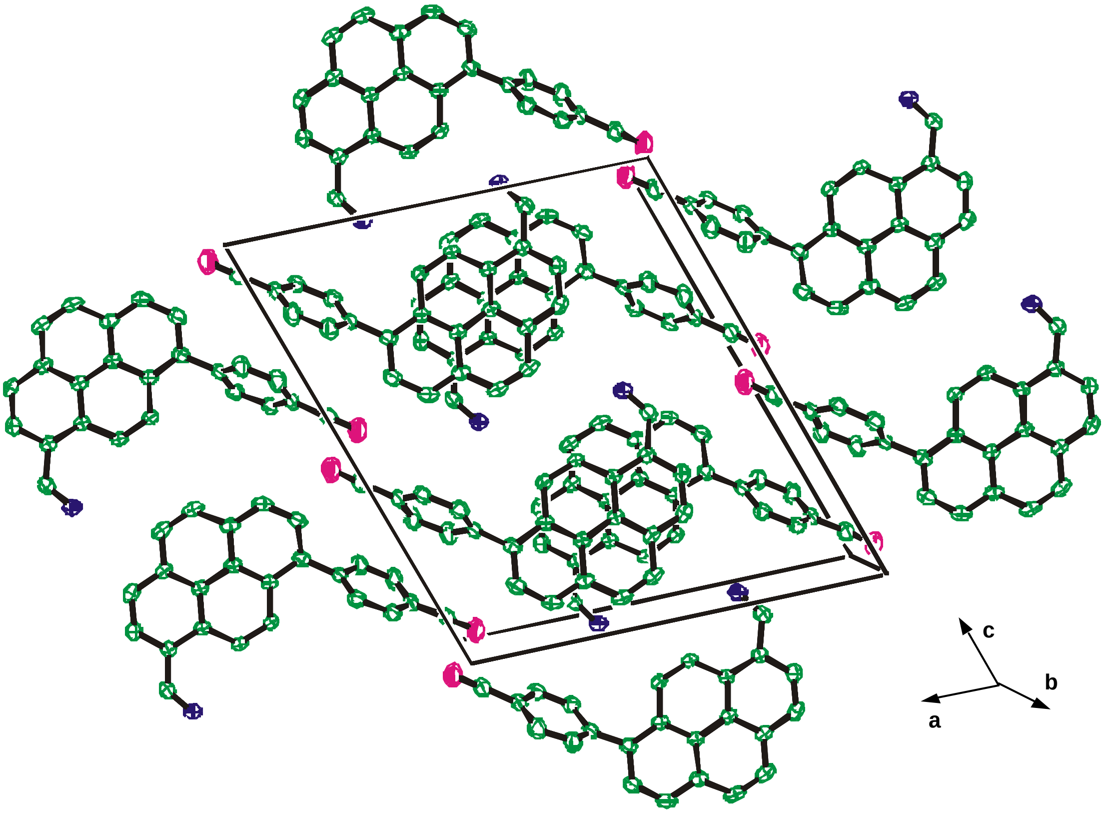
C(2)-C(1)-C(10A)	120.0(2)	C(9)-C(10)-C(10A)	121.6(2)
C(2)-C(1)-C(11)	115.1 (2)	C(1)-C(10A)-C(10B)	118.4(2)
C(10A)-C(1)-C(11)	124.9 (2)	C(1)-C(10A)-C(10)	123.9(2)
C(3)-C(2)-C(1)	121.6(2)	C(10B)-C(10A)-C(10)	117.8(2)
C(2)-C(3)-C(3A)	120.7(2)	C(10A)-C(10B)-C(3A)	120.2(2)
C(3)-C(3A)-C(10B)	119.2(2)	C(10A)-C(10B)-C(10C)	120.4(2)
C(3)-C(3A)-C(4)	121.8(2)	C(3A)-C(10B)-C(10C)	119.4(2)
C(10B)-C(3A)-C(4)	119.0(2)	C(8A)-C(10C)-C(5A)	119.9(2)
C(5)-C(4)-C(3A)	121.4(2)	C(8A)-C(10C)-C(10B)	120.3(2)
C(4)-C(5)-C(5A)	121.7(2)	C(5A)-C(10C)-C(10B)	119.8(2)
C(6)-C(5A)-C(10C)	118.9(2)	O(1)-C(11)-C(1)	128.6(2)
C(6)-C(5A)-C(5)	122.5(2)	C(17)-C(12)-C(13)	118.(2)
C(10C)-C(5A)-C(5)	118.7(2)	C(17)-C(12)-C(8)	120.1(2)
C(7)-C(6)-C(5A)	121.1(2)	C(13)-C(12)-C(8)	121.9(2)
C(6)-C(7)-C(8)	121.5(2)	C(14)-C(13)-C(12)	121.0(2)
C(7)-C(8)-C(8A)	1193 (2)	C(13)-C(14)-C(15)	120.0(2)
C(7)-C(8)-C(12)	119.0(2)	C(16)-C(15)-C(14)	119.7(2)
C(8A)-C(8)-C(12)	121.6(2)	C(16)-C(15)-C(18)	120.6(2)
C(8)-C(8A)-C(10C)	119.2(2)	C(14)-C(15)-C(18)	119.7(2)
C(8)-C(8A)-C(9)	123.1(2)	C(17)-C(16)-C(15)	119.7(2)
C(10C)-C(8A)-C(9)	117.6(2)	C(16)-C(17)-C(12)	121.6(2)
C(10)-C(9)-C(8A)	122.2(2)	N(1)-C(18)-C(15)	179.4(2)

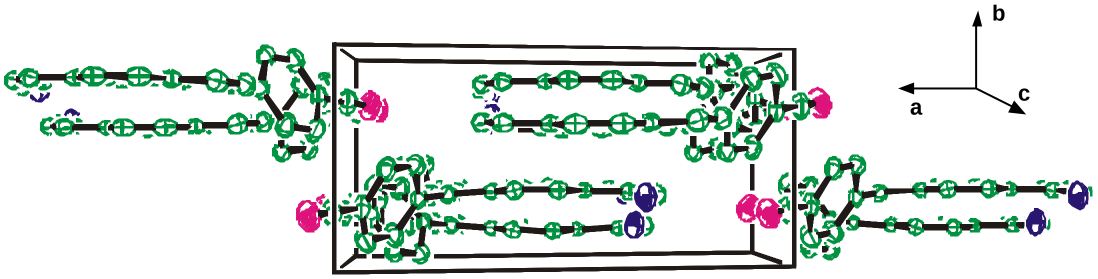
Torsion angles [°]:

C(10A)-C(1)-C(2)-C(3)	-0.1(2)	C(4)-C(3A)-C(10B)-C(10A)	-179.4(2)
C(11)-C(1)-C(2)-C(3)	178.6(2)	C(3)-C(3A)-C(10B)-C(10C)	-178.4(2)
C(1)-C(2)-C(3)-C(3A)	-0.8(2)	C(4)-C(3A)-C(10B)-C(10C)	1.1(2)
C(2)-C(3)-C(3A)-C(10B)	0.3(2)	C(8)-C(8A)-C(10C)-C(5A)	2.8(2)
C(2)-C(3)-C(3A)-C(4)	-179.2(2)	C(9)-C(8A)-C(10C)-C(5A)	-178.8(2)
C(3)-C(3A)-C(4)-C(5)	178.5(2)	C(8)-C(8A)-C(10C)-C(10B)	-176.2(2)
C(10B)-C(3A)-C(4)-C(5)	-1.0(2)	C(9)-C(8A)-C(10C)-C(10B)	2.2(2)
C(3A)-C(4)-C(5)-C(5A)	-0.6(2)	C(6)-C(5A)-C(10C)-C(8A)	-1.4(2)
C(4)-C(5)-C(5A)-C(6)	-177.5(2)	C(5)-C(5A)-C(10C)-C(8A)	179.0(2)
C(4)-C(5)-C(5A)-C(10C)	2.1(2)	C(6)-C(5A)-C(10C)-C(10B)	177.6(2)
C(10C)-C(5A)-C(6)-C(7)	-1.3(2)	C(5)-C(5A)-C(10C)-C(10B)	-1.9(2)
C(5)-C(5A)-C(6)-C(7)	178.2(2)	C(10A)-C(10B)-C(10C)-C(8A)	0.0(2)
C(5A)-C(6)-C(7)-C(8)	2.7(3)	C(3A)-C(10B)-C(10C)-C(8A)	179.4(2)
C(6)-C(7)-C(8)-C(8A)	-1.3(2)	C(10A)-C(10B)-C(10C)-C(5A)	-179.1(2)
C(6)-C(7)-C(8)-C(12)	-179.0(2)	C(3A)-C(10B)-C(10C)-C(5A)	0.4(2)
C(7)-C(8)-C(8A)-C(10C)	-1.5(2)	C(2)-C(1)-C(11)-O(1)	-176.7(2)

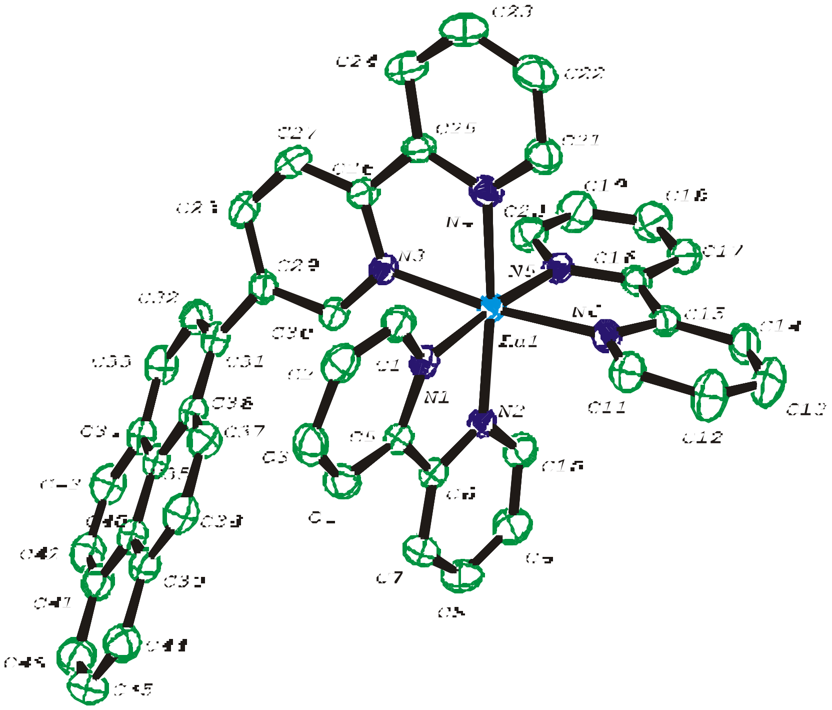
C(12)-C(8)-C(8A)-C(10C)	176.1(2)	C(10A)-C(1)-C(11)-O(1)	1.9(3)
C(7)-C(8)-C(8A)-C(9)	-179.8(2)	C(7)-C(8)-C(12)-C(17)	60.7(2)
C(12)-C(8)-C(8A)-C(9)	-2.2(2)	C(8A)-C(8)-C(12)-C(17)	-117.0(2)
C(8)-C(8A)-C(9)-C(10)	176.3(2)	C(7)-C(8)-C(12)-C(13)	-118.3(2)
C(10C)-C(8A)-C(9)-C(10)	-2.1(2)	C(8A)-C(8)-C(12)-C(13)	64.1(2)
C(8A)-C(9)-C(10)-C(10A)	-0.3(2)	C(17)-C(12)-C(13)-C(14)	-0.2(2)
C(2)-C(1)-C(10A)-C(10B)	1.4(2)	C(8)-C(12)-C(13)-C(14)	178.8(2)
C(11)-C(1)-C(10A)-C(10B)	-177.1(2)	C(12)-C(13)-C(14)-C(15)	0.9(2)
C(2)-C(1)-C(10A)-C(10)	-178.7(2)	C(13)-C(14)-C(15)-C(16)	-1.3(3)
C(11)-C(1)-C(10A)-C(10)	2.7(2)	C(13)-C(14)-C(15)-C(18)	178.2(2)
C(9)-C(10)-C(10A)-C(1)	-177.4(2)	C(14)-C(15)-C(16)-C(17)	0.9(3)
C(9)-C(10)-C(10A)-C(10B)	2.5(2)	C(18)-C(15)-C(16)-C(17)	-178.6(2)
C(1)-C(10A)-C(10B)-C(3A)	-1.9(2)	C(15)-C(16)-C(17)-C(12)	-0.2(3)
C(10)-C(10A)-C(10B)-C(3A)	178.2(2)	C(13)-C(12)-C(17)-C(16)	-0.2(3)
C(1)-C(10A)-C(10B)-C(10C)	177.6(2)	C(8)-C(12)-C(17)-C(16)	-179.2(2)
C(10)-C(10A)-C(10B)-C(10C)	-2.3(2)	C(16)-C(15)-C(18)-N(1)	148.0(3)
C(3)-C(3A)-C(10B)-C(10A)	1.1(2)	C(14)-C(15)-C(18)-N(1)	-32.0(3)

Crystal Lattice and Unit Cell:





7.5.2 *rac*-[Ruthenium(II)-bis(2,2′-bipyridine)(5-pyren-1-yl-2,2′-bipyridine)]·$(PF_6)_2$·$(CH_2Cl_2)_3$ (**100**)[266]



Caution: The numeration in chapter 4.7 is different.

Crystal data and structure refinement:

Temperature	-120 °C
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, C2/c (No. 15)
Unit cell dimensions	a = 20.926(3), b = 12.369(2), c = 41.031(6) α = 90°, β = 93.113(2)°, γ= 90°
Z	8
Density	1.639 g/mol
Volume	10604(3)$Å^3$
Crystal size	(0.65 · 0.53 · 0.20) mm
Theta range for data collection	(3.83 to 27.51)°
Reflections collected / unique	48759 / 11920 [R(int) = 0.0481]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11920 / 0 / 730
Final R indices [I>2sigma(I)]	R1 = 0.0589, wR2 = 0.1480
R indices (all data)	R1 = 0.0674, wR2 = 0.1530

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[266] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163286. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: ++44-1223-336 033, e-mail: deposit@ccdc.cam.ac.uk).

Bond lengths [Å]:

Ru(1)-N(6)	2.054(3)	C(7)-C(8)	1.384(6)
Ru(1)-N(4)	2.058(3)	C(9)-C(8)	1.381(7)
Ru(1)-N(5)	2.059(3)	C(9)-C(10)	1.387(6)
Ru(1)-N(1)	2.060(3)	C(24)-C(23)	1.378(7)
Ru(1)-N(2)	2.064(3)	C(24)-C(25)	1.400(5)
Ru(1)-N(3)	2.063(3)	C(22)-C(21)	1.379(6)
N(1)-C(1)	1.344(5)	C(22)-C(23)	1.378(7)
N(1)-C(5)	1.357(4)	C(45)-C(46)	1.380(7)
N(2)-C(10)	1.343(5)	C(38)-C(37)	1.353(6)
N(2)-C(6)	1.365(5)	C(20)-C(19)	1.387(6)
N(3)-C(30)	1.339(5)	C(12)-C(13)	1.369(7)
N(3)-C(26)	1.362(4)	C(12)-C(11)	1.368(6)
N(4)-C(21)	1.344(5)	C(19)-C(18)	1.382(7)
N(4)-C(25)	1.364(5)	P(1)-F(3)#1	1.596(2)
N(5)-C(20)	1.339(5)	P(1)-F(3)	1.596(2)
N(5)-C(16)	1.365(5)	P(1)-F(2)	1.599(3)
N(6)-C(11)	1.338(5)	P(1)-F(2)#1	1.599(3)
N(6)-C(15)	1.369(5)	P(1)-F(1)#1	1.600(2)
C(6)-C(7)	1.392(5)	P(1)-F(1)	1.600(2)
C(6)-C(5)	1.474(5)	P(2)-F(6)#2	1.494(5)
C(31)-C(32)	1.399(6)	P(2)-F(6)	1.494(5)
C(31)-C(36)	1.419(5)	P(2)-F(5)#2	1.511(5)
C(31)-C(29)	1.480(5)	P(2)-F(5)	1.511(6)
C(2)-C(3)	1.385(6)	P(2)-F(4)#2	1.519(4)
C(2)-C(1)	1.381(5)	P(2)-F(4)	1.519(4)
C(36)-C(35)	1.425(5)	P(3)-F(9)	1.508(4)
C(36)-C(37)	1.441(5)	P(3)-F(8)	1.527(5)
C(17)-C(18)	1.379(7)	P(3)-F(10)	1.581(4)
C(17)-C(16)	1.390(5)	P(3)-F(11)	1.591(5)
C(4)-C(3)	1.377(6)	P(3)-F(7)	1.598(4)
C(4)-C(5)	1.389(5)	P(3)-F(12)	1.603(5)
C(29)-C(30)	1.392(5)	Cl(1)-C(1L)	1.760(8)
C(29)-C(28)	1.397(5)	Cl(2)-C(1L)	1.759(7)
C(41)-C(46)	1.400(6)	Cl(4)-C(2L)	1.711(9)
C(41)-C(40)	1.420(6)	Cl(5)-C(3L)	1.736(2)
C(41)-C(42)	1.430(6)	C(2L)-Cl(31)	1.580(2)
C(39)-C(44)	1.397(6)	C(2L)-Cl(3)	1.760(1)
C(39)-C(40)	1.420(6)	C(3L)-Cl(61)	1.379(2)
C(39)-C(38)	1.440(6)	C(3L)-Cl(6)	2.010(2)
C(16)-C(15)	1.470(6)	Cl(3)-Cl(31)	1.701(2)
C(43)-C(42)	1.348(7)	Cl(6)-Cl(61)	0.903(1)
C(43)-C(34)	1.436(6)	C(15)-C(14)	1.383(5)
C(44)-C(45)	1.383(7)	C(35)-C(40)	1.428(5)
C(34)-C(33)	1.391(6)	C(27)-C(28)	1.372(6)
C(34)-C(35)	1.425(5)	C(14)-C(13)	1.384(7)
C(26)-C(27)	1.398(5)	C(33)-C(32)	1.380(6)
C(26)-C(25)	1.459(5)		

Angles [°]:

N(6)-Ru(1)-N(4)	97.0(2)	C(27)-C(28)-C(29)	119.8(4)
N(6)-Ru(1)-N(5)	79.2(2)	C(8)-C(9)-C(10)	118.6(4)
N(4)-Ru(1)-N(5)	90.1(2)	C(23)-C(24)-C(25)	119.5(4)
N(6)-Ru(1)-N(1)	98.3(2)	C(39)-C(40)-C(41)	119.5(4)
N(4)-Ru(1)-N(1)	95.5(2)	C(39)-C(40)-C(35)	120.3(3)
N(5)-Ru(1)-N(1)	174.2(2)	C(41)-C(40)-C(35)	120.2(4)
N(6)-Ru(1)-N(2)	87.7(2)	C(43)-C(42)-C(41)	121.3(4)
N(4)-Ru(1)-N(2)	173.1(2)	C(21)-C(22)-C(23)	118.8(4)
N(5)-Ru(1)-N(2)	95.9(2)	C(44)-C(45)-C(46)	121.0(4)

N(1)-Ru(1)-N(2)	78.7(2)	N(4)-C(25)-C(24)	120.6(4)
N(6)-Ru(1)-N(3)	174.3(2)	N(4)-C(25)-C(26)	115.0(3)
N(4)-Ru(1)-N(3)	78.6(2)	C(24)-C(25)-C(26)	124.3(4)
N(5)-Ru(1)-N(3)	97.2(2)	C(37)-C(38)-C(39)	121.7(4)
N(1)-Ru(1)-N(3)	85.7(2)	N(4)-C(21)-C(22)	122.9(4)
N(2)-Ru(1)-N(3)	97.1(2)	C(33)-C(32)-C(31)	120.8(4)
C(1)-N(1)-C(5)	118.7(3)	N(5)-C(20)-C(19)	122.3(4)
C(1)-N(1)-Ru(1)	125.6(2)	C(13)-C(12)-C(11)	119.4(4)
C(5)-N(1)-Ru(1)	115.4(2)	C(45)-C(46)-C(41)	120.6(4)
C(10)-N(2)-C(6)	118.1(3)	N(2)-C(10)-C(9)	123.1(4)
C(10)-N(2)-Ru(1)	126.6(3)	N(6)-C(11)-C(12)	122.8(4)
C(6)-N(2)-Ru(1)	115.3(2)	C(7)-C(8)-C(9)	119.4(4)
C(30)-N(3)-C(26)	119.2(3)	C(18)-C(19)-C(20)	119.0(4)
C(30)-N(3)-Ru(1)	125.1(2)	C(12)-C(13)-C(14)	119.3(4)
C(26)-N(3)-Ru(1)	115.6(2)	C(24)-C(23)-C(22)	119.5(4)
C(21)-N(4)-C(25)	118.7(3)	C(19)-C(18)-C(17)	119.2(4)
C(21)-N(4)-Ru(1)	125.6(3)	C(38)-C(37)-C(36)	121.5(4)
C(25)-N(4)-Ru(1)	115.7(2)	F(3)#1-P(1)-F(3)	180.0(1)
C(20)-N(5)-C(16)	119.0(3)	F(3)#1-P(1)-F(2)	89.83(2)
C(20)-N(5)-Ru(1)	125.7(3)	F(3)-P(1)-F(2)	90.17(2)
C(16)-N(5)-Ru(1)	115.4(2)	F(3)#1-P(1)-F(2)#1	90.2(2)
C(11)-N(6)-C(15)	118.3(3)	F(3)-P(1)-F(2)#1	89.8(2)
C(11)-N(6)-Ru(1)	126.2(3)	F(2)-P(1)-F(2)#1	180.0(2)
C(15)-N(6)-Ru(1)	115.4(2)	F(3)#1-P(1)-F(1)#1	90.7(2)
N(2)-C(6)-C(7)	121.4(4)	F(3)-P(1)-F(1)#1	89.3(2)
N(2)-C(6)-C(5)	114.7(3)	F(2)-P(1)-F(1)#1	90.3(2)
C(7)-C(6)-C(5)	123.8(4)	F(2)#1-P(1)-F(1)#1	89.7(2)
C(32)-C(31)-C(36)	119.4(4)	F(3)#1-P(1)-F(1)	89.3(2)
C(32)-C(31)-C(29)	118.7(4)	F(3)-P(1)-F(1)	90.7(2)
C(36)-C(31)-C(29)	121.7(3)	F(2)-P(1)-F(1)	89.7(2)
C(3)-C(2)-C(1)	119.0(4)	F(2)#1-P(1)-F(1)	90.3(2)
C(31)-C(36)-C(35)	119.1(3)	F(1)#1-P(1)-F(1)	180.0(2)
C(31)-C(36)-C(37)	122.9(4)	F(6)#2-P(2)-F(6)	94.7(8)
C(35)-C(36)-C(37)	117.9(3)	F(6)#2-P(2)-F(5)#2	83.7(5)
C(18)-C(17)-C(16)	119.7(4)	F(6)-P(2)-F(5)#2	178.3(7)
C(3)-C(4)-C(5)	119.6(4)	F(6)#2-P(2)-F(5)	178.3(7)
C(30)-C(29)-C(28)	117.3(4)	F(6)-P(2)-F(5)	83.7(5)
C(30)-C(29)-C(31)	119.2(3)	F(5)#2-P(2)-F(5)	98.0(9)
C(28)-C(29)-C(31)	123.4(3)	F(6)#2-P(2)-F(4)#2	89.0(4)
C(4)-C(3)-C(2)	119.0(4)	F(6)-P(2)-F(4)#2	94.8(4)
N(3)-C(30)-C(29)	123.3(3)	F(5)#2-P(2)-F(4)#2	85.6(4)
C(46)-C(41)-C(40)	119.1(4)	F(5)-P(2)-F(4)#2	90.8(4)
C(46)-C(41)-C(42)	122.1(4)	F(6)#2-P(2)-F(4)	94.8(4)
C(40)-C(41)-C(42)	118.8(4)	F(6)-P(2)-F(4)	89.0(4)
C(44)-C(39)-C(40)	119.4(4)	F(5)#2-P(2)-F(4)	90.8(4)
C(44)-C(39)-C(38)	122.5(4)	F(5)-P(2)-F(4)	85.6(4)
C(40)-C(39)-C(38)	118.1(4)	F(4)#2-P(2)-F(4)	174.5(8)
N(5)-C(16)-C(17)	120.9(4)	F(9)-P(3)-F(8)	97.7(5)
N(5)-C(16)-C(15)	115.0(3)	F(9)-P(3)-F(10)	91.6(3)
C(17)-C(16)-C(15)	124.1(4)	F(8)-P(3)-F(10)	90.0(3)
C(42)-C(43)-C(34)	121.6(4)	F(9)-P(3)-F(11)	90.9(4)
C(45)-C(44)-C(39)	120.4(4)	F(8)-P(3)-F(11)	171.3(4)
N(1)-C(1)-C(2)	122.4(4)	F(10)-P(3)-F(11)	90.7(3)
C(33)-C(34)-C(35)	118.5(4)	F(9)-P(3)-F(7)	91.2(3)
C(33)-C(34)-C(43)	122.9(4)	F(8)-P(3)-F(7)	90.4(3)
C(35)-C(34)-C(43)	118.6(4)	F(10)-P(3)-F(7)	177.1(2)
N(3)-C(26)-C(27)	120.1(4)	F(11)-P(3)-F(7)	88.5(2)
N(3)-C(26)-C(25)	115.0(3)	F(9)-P(3)-F(12)	175.1(4)
C(27)-C(26)-C(25)	124.9(3)	F(8)-P(3)-F(12)	86.9(4)
N(6)-C(15)-C(14)	121.0(4)	F(10)-P(3)-F(12)	90.0(3)
N(6)-C(15)-C(16)	114.7(3)	F(11)-P(3)-F(12)	84.5(3)
C(14)-C(15)-C(16)	124.2(4)	F(7)-P(3)-F(12)	87.2(2)
C(36)-C(35)-C(34)	120.2(4)	Cl(2)-C(1L)-Cl(1)	108.8(4)
C(36)-C(35)-C(40)	120.4(3)	Cl(31)-C(2L)-Cl(4)	122.1(8)

C(34)-C(35)-C(40)	119.4(4)	Cl(31)-C(2L)-Cl(3)	60.9(5)
C(28)-C(27)-C(26)	120.1(4)	Cl(4)-C(2L)-Cl(3)	110.7(6)
N(1)-C(5)-C(4)	121.2(3)	Cl(61)-C(3L)-Cl(5)	113.7(5)
N(1)-C(5)-C(6)	114.9(3)	Cl(61)-C(3L)-Cl(6)	22.4(5)
C(4)-C(5)-C(6)	123.9(3)	Cl(5)-C(3L)-Cl(6)	110.2(4)
C(13)-C(14)-C(15)	119.2(4)	C(2L)-Cl(3)-Cl(31)	54.3(5)
C(32)-C(33)-C(34)	121.9(4)	C(2L)-Cl(31)-Cl(3)	64.8(6)
C(8)-C(7)-C(6)	119.3(4)	Cl(61)-Cl(6)-C(3L)	35.6(6)

Torsion angles [°]:

N(6)-Ru(1)-N(1)-C(1) 90.8(3)	C(11)-N(6)-C(15)-C(14) 3.1(5)
N(4)-Ru(1)-N(1)-C(1) -7.1(3)	Ru(1)-N(6)-C(15)-C(14) -173.7(3)
N(5)-Ru(1)-N(1)-C(1) 154.6(2)	C(11)-N(6)-C(15)-C(16) -176.8(3)
N(2)-Ru(1)-N(1)-C(1) 176.7(3)	Ru(1)-N(6)-C(15)-C(16) 6.5(4)
N(3)-Ru(1)-N(1)-C(1) -85.2(3)	N(5)-C(16)-C(15)-N(6) -4.2(4)
N(6)-Ru(1)-N(1)-C(5) -95.1(3)	C(17)-C(16)-C(15)-N(6) 174.6(3)
N(4)-Ru(1)-N(1)-C(5) 167.0(2)	N(5)-C(16)-C(15)-C(14) 175.9(3)
N(5)-Ru(1)-N(1)-C(5) -31.4(2)	C(17)-C(16)-C(15)-C(14) -5.3(6)
N(2)-Ru(1)-N(1)-C(5) -9.2(2)	C(31)-C(36)-C(35)-C(34) -0.6(5)
N(3)-Ru(1)-N(1)-C(5) 88.9(3)	C(37)-C(36)-C(35)-C(34) 176.5(3)
N(6)-Ru(1)-N(2)-C(10) -71.5(3)	C(31)-C(36)-C(35)-C(40) 179.9(3)
N(4)-Ru(1)-N(2)-C(10) 156.3(9)	C(37)-C(36)-C(35)-C(40) -2.9(5)
N(5)-Ru(1)-N(2)-C(10) 7.3(3)	C(33)-C(34)-C(35)-C(36) -2.4(5)
N(1)-Ru(1)-N(2)-C(10) -170.5(3)	C(43)-C(34)-C(35)-C(36) 178.5(3)
N(3)-Ru(1)-N(2)-C(10) 105.3(3)	C(33)-C(34)-C(35)-C(40) 177.1(3)
N(6)-Ru(1)-N(2)-C(6) 106.3(3)	C(43)-C(34)-C(35)-C(40) -2.1(5)
N(4)-Ru(1)-N(2)-C(6) -25.9(12)	N(3)-C(26)-C(27)-C(28) 3.4(6)
N(5)-Ru(1)-N(2)-C(6) -174.9(3)	C(25)-C(26)-C(27)-C(28) -174.7(4)
N(1)-Ru(1)-N(2)-C(6) 7.3(2)	C(1)-N(1)-C(5)-C(4) 2.1(5)
N(3)-Ru(1)-N(2)-C(6) -76.9(3)	Ru(1)-N(1)-C(5)-C(4) -172.4(3)
N(6)-Ru(1)-N(3)-C(30) 145.9(2)	C(1)-N(1)-C(5)-C(6) -175.9(3)
N(4)-Ru(1)-N(3)-C(30) -174.8(3)	Ru(1)-N(1)-C(5)-C(6) 9.6(4)
N(5)-Ru(1)-N(3)-C(30) 96.6(3)	C(3)-C(4)-C(5)-N(1) -0.1(6)
N(1)-Ru(1)-N(3)-C(30) -78.3(3)	C(3)-C(4)-C(5)-C(6) 177.8(4)
N(2)-Ru(1)-N(3)-C(30) -0.3(3)	N(2)-C(6)-C(5)-N(1) -3.3(5)
N(6)-Ru(1)-N(3)-C(26) -37.5(2)	C(7)-C(6)-C(5)-N(1) 173.5(4)
N(4)-Ru(1)-N(3)-C(26) 1.9(3)	N(2)-C(6)-C(5)-C(4) 178.7(3)
N(5)-Ru(1)-N(3)-C(26) -86.8(3)	C(7)-C(6)-C(5)-C(4) -4.4(6)
N(1)-Ru(1)-N(3)-C(26) 98.3(3)	N(6)-C(15)-C(14)-C(13) -2.1(6)
N(2)-Ru(1)-N(3)-C(26) 176.4(3)	C(16)-C(15)-C(14)-C(13) 177.8(4)
N(6)-Ru(1)-N(4)-C(21) -7.9(3)	C(35)-C(34)-C(33)-C(32) 2.7(6)
N(5)-Ru(1)-N(4)-C(21) -87.0(3)	C(43)-C(34)-C(33)-C(32) -178.2(4)
N(1)-Ru(1)-N(4)-C(21) 91.1(3)	N(2)-C(6)-C(7)-C(8) 3.2(6)
N(2)-Ru(1)-N(4)-C(21) 123.8(1)	C(5)-C(6)-C(7)-C(8) -173.5(4)
N(3)-Ru(1)-N(4)-C(21) 175.7(3)	C(26)-C(27)-C(28)-C(29) 0.3(7)
N(6)-Ru(1)-N(4)-C(25) 175.1(3)	C(30)-C(29)-C(28)-C(27) -3.7(6)
N(5)-Ru(1)-N(4)-C(25) 96.0(3)	C(31)-C(29)-C(28)-C(27) 179.2(4)
N(1)-Ru(1)-N(4)-C(25) -85.8(3)	C(44)-C(39)-C(40)-C(41) 0.9(6)
N(2)-Ru(1)-N(4)-C(25) -53.2(2)	C(38)-C(39)-C(40)-C(41) -178.5(3)
N(3)-Ru(1)-N(4)-C(25) -1.3(3)	C(44)-C(39)-C(40)-C(35) -178.7(4)
N(6)-Ru(1)-N(5)-C(20) -177.7(3)	C(38)-C(39)-C(40)-C(35) 1.8(5)
N(4)-Ru(1)-N(5)-C(20) -80.7(3)	C(46)-C(41)-C(40)-C(39) -0.8(6)
N(1)-Ru(1)-N(5)-C(20) 117.6(2)	C(42)-C(41)-C(40)-C(39) -180.0(4)
N(2)-Ru(1)-N(5)-C(20) 95.8(3)	C(46)-C(41)-C(40)-C(35) 178.8(4)
N(3)-Ru(1)-N(5)-C(20) -2.1(3)	C(42)-C(41)-C(40)-C(35) -0.3(6)
N(6)-Ru(1)-N(5)-C(16) 2.6(2)	C(36)-C(35)-C(40)-C(39) 0.7(5)
N(4)-Ru(1)-N(5)-C(16) 99.7(3)	C(34)-C(35)-C(40)-C(39) -178.7(3)
N(1)-Ru(1)-N(5)-C(16) -62.0(2)	C(36)-C(35)-C(40)-C(41) -178.9(3)
N(2)-Ru(1)-N(5)-C(16) -83.8(3)	C(34)-C(35)-C(40)-C(41) 1.6(5)
N(3)-Ru(1)-N(5)-C(16) 178.2(2)	C(34)-C(43)-C(42)-C(41) 0.1(7)
N(4)-Ru(1)-N(6)-C(11) 89.8(3)	C(46)-C(41)-C(42)-C(43) -179.7(4)
N(5)-Ru(1)-N(6)-C(11) 178.5(3)	C(40)-C(41)-C(42)-C(43) -0.5(6)

N(1)-Ru(1)-N(6)-C(11) -6.8(3)
N(2)-Ru(1)-N(6)-C(11) -85.1(3)
N(3)-Ru(1)-N(6)-C(11) 128.6(2)
N(4)-Ru(1)-N(6)-C(15) -93.7(2)
N(5)-Ru(1)-N(6)-C(15) -5.0(2)
N(1)-Ru(1)-N(6)-C(15) 169.7(2)
N(2)-Ru(1)-N(6)-C(15) 91.4(2)
N(3)-Ru(1)-N(6)-C(15) -55.0(2)
C(10)-N(2)-C(6)-C(7) -3.4(5)
Ru(1)-N(2)-C(6)-C(7) 178.5(3)
C(10)-N(2)-C(6)-C(5) 173.5(3)
Ru(1)-N(2)-C(6)-C(5) -4.5(4)
C(32)-C(31)-C(36)-C(35) 3.4(5)
C(29)-C(31)-C(36)-C(35) -173.0(3)
C(32)-C(31)-C(36)-C(37) -173.6(4)
C(29)-C(31)-C(36)-C(37) 10.0(6)
C(32)-C(31)-C(29)-C(30) -122.9(4)
C(36)-C(31)-C(29)-C(30) 53.5(5)
C(32)-C(31)-C(29)-C(28) 54.2(5)
C(36)-C(31)-C(29)-C(28) -129.5(4)
C(5)-C(4)-C(3)-C(2) -2.3(6)
C(1)-C(2)-C(3)-C(4) 2.6(6)
C(26)-N(3)-C(30)-C(29) 0.0(5)
Ru(1)-N(3)-C(30)-C(29) 176.5(3)
C(28)-C(29)-C(30)-N(3) 3.6(6)
C(31)-C(29)-C(30)-N(3) -179.1(3)
C(20)-N(5)-C(16)-C(17) 1.5(5)
Ru(1)-N(5)-C(16)-C(17) -178.9(3)
C(20)-N(5)-C(16)-C(15) -179.7(3)
Ru(1)-N(5)-C(16)-C(15) 0.0(4)
C(18)-C(17)-C(16)-N(5) -1.2(6)
C(18)-C(17)-C(16)-C(15) 180.0(4)
C(40)-C(39)-C(44)-C(45) -0.4(6)
C(38)-C(39)-C(44)-C(45) 179.0(4)
C(5)-N(1)-C(1)-C(2) -1.8(5)
Ru(1)-N(1)-C(1)-C(2) 172.1(3)
C(3)-C(2)-C(1)-N(1) -0.5(6)
C(42)-C(43)-C(34)-C(33) -177.9(4)
C(42)-C(43)-C(34)-C(35) 1.2(6)
C(30)-N(3)-C(26)-C(27) -3.6(5)
Ru(1)-N(3)-C(26)-C(27) 179.6(3)
C(30)-N(3)-C(26)-C(25) 174.7(3)
Ru(1)-N(3)-C(26)-C(25) -2.1(4)

C(39)-C(44)-C(45)-C(46) -0.3(7)
C(21)-N(4)-C(25)-C(24) -0.1(6)
Ru(1)-N(4)-C(25)-C(24) 177.1(3)
C(21)-N(4)-C(25)-C(26) -176.6(3)
Ru(1)-N(4)-C(25)-C(26) 0.5(4)
C(23)-C(24)-C(25)-N(4) -0.4(7)
C(23)-C(24)-C(25)-C(26) 175.8(4)
N(3)-C(26)-C(25)-N(4) 1.1(5)
C(27)-C(26)-C(25)-N(4) 179.2(4)
N(3)-C(26)-C(25)-C(24) -175.4(4)
C(27)-C(26)-C(25)-C(24) 2.8(7)
C(44)-C(39)-C(38)-C(37) 178.3(4)
C(40)-C(39)-C(38)-C(37) -2.2(6)
C(25)-N(4)-C(21)-C(22) -0.1(6)
Ru(1)-N(4)-C(21)-C(22) -177.0(3)
C(23)-C(22)-C(21)-N(4) 0.8(7)
C(34)-C(33)-C(32)-C(31) 0.1(6)
C(36)-C(31)-C(32)-C(33) -3.2(6)
C(29)-C(31)-C(32)-C(33) 173.3(4)
C(16)-N(5)-C(20)-C(19) -0.1(6)
Ru(1)-N(5)-C(20)-C(19) -179.7(3)
C(44)-C(45)-C(46)-C(41) 0.4(7)
C(40)-C(41)-C(46)-C(45) 0.2(7)
C(42)-C(41)-C(46)-C(45) 179.3(4)
C(6)-N(2)-C(10)-C(9) 1.1(6)
Ru(1)-N(2)-C(10)-C(9) 178.9(3)
C(8)-C(9)-C(10)-N(2) 1.5(7)
C(15)-N(6)-C(11)-C(12) -1.9(6)
Ru(1)-N(6)-C(11)-C(12) 174.5(3)
C(13)-C(12)-C(11)-N(6) -0.4(7)
C(6)-C(7)-C(8)-C(9) -0.4(7)
C(10)-C(9)-C(8)-C(7) -1.8(7)
N(5)-C(20)-C(19)-C(18) -1.5(7)
C(11)-C(12)-C(13)-C(14) 1.5(7)
C(15)-C(14)-C(13)-C(12) -0.2(7)
C(25)-C(24)-C(23)-C(22) 1.1(8)
C(21)-C(22)-C(23)-C(24) -1.3(8)
C(20)-C(19)-C(18)-C(17) 1.7(7)
C(16)-C(17)-C(18)-C(19) -0.4(7)
C(39)-C(38)-C(37)-C(36) 0.0(6)
C(31)-C(36)-C(37)-C(38) 179.6(4)
C(35)-C(36)-C(37)-C(38) 2.6(6)

Crystal Lattice (in part):