Supporting Information

for

Synthesis of 6,13-difluoropentacene

Matthias W. Tripp and Ulrich Koert

*Beilstein J. Org. Chem.* **2020**, *16*, 2136–2140. doi:10.3762/bjoc.16.181

Experimental details, spectroscopic and analytical data of all new compounds
Table of contents

1. Methods and materials .................................................................................................................. S3
2. Synthesis of 6,13-difluoropentacene ............................................................................................ S5
3. NMR spectra of all compounds .................................................................................................... S12
4. References ...................................................................................................................................... S19
1. Methods and materials

General information

All anhydrous reactions were carried out using flame-dried glassware under argon atmosphere. All solvents were distilled by rotary evaporation. THF for anhydrous reactions was dried with KOH and subsequently distilled from sodium/benzophenone and from Solvona® respectively. All other solvents employed under anhydrous and/or anaerobic conditions were bought in anhydrous form. C₆D₆ for NMR measurements was degassed three times by freeze-pump-thaw cycles prior to use. All commercially available reagents and reactants were used without further purification unless otherwise noted. Reactions were monitored by thin layer chromatography (TLC) using Merck Silica Gel 60 F₂₅₄ and visualized by fluorescence quenching under UV-light. In addition, TLC-plates were stained using a cerium sulfate/phosphomolybdic acid stain or a potassium permanganate stain. Chromatographic purification of products was performed on Macherey-Nagel Silica Gel 60 (230–400 mesh) using a forced flow of eluents. All crude products were adsorbed onto silica by dissolving in an appropriate solvent and removing the solvent under reduced pressure. Concentration under reduced pressure was performed by rotary evaporation at 40 °C and appropriate pressure and by exposing to high vacuum at room temperature if necessary.

NMR-Spectroscopy

NMR spectra were recorded on a Bruker AVIII HD250, AVII 300, AVIII HD300, AVIII 500 or AVIII HD500 spectrometer at room temperature unless otherwise mentioned. Chemical shifts are reported in ppm with the solvent resonance as internal standard. All reported ¹⁹F-NMR spectra are proton decoupled ¹⁹F{¹H}-measurements and referenced to external CFCl₃. Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet and combination thereof. Due to the low solubility of compounds 5 & 16 no ¹³C NMR spectra were obtained. All correlations of atoms from NMR spectra of new compounds could be achieved via additional 2D-NMR data (HSQC- and HMBC-spectra) which is not shown within this Supporting Information.
High resolution mass spectrometry

HR-ESI and APCI mass spectra were acquired with a Finnigan LTQ-FT Ultra mass spectrometer (Thermo Fischer Scientific). EI mass spectra were acquired with an AccuTOF GCv (Jeol) mass spectrometer.

Infrared spectroscopy

FTIR spectra were recorded on a BRUKER IFS 200 spectrometer. Intensities are reported as follows: s = strong, m = medium, w = weak.

Melting points

Melting points were determined on a MP70 (Mettler Toledo) using one end closed capillary tubes.

UV–vis spectroscopy

UV–vis-spectra have been acquired with a Thermo Scientific Multiskan Go using quartz rectangular cuvettes (Teflon cover, 10 mm light path, 3.5 mL) by Aldrich.
2. Synthesis of 6,13-difluoropentacene

1,4-Difluoroanthracene-9,10-dione (11)[1]

Following an adapted procedure of Krapcho et al., a suspension of phthalic anhydride (4.30 g, 29.0 mmol, 1.00 equiv) and AlCl₃ (15.4 g, 116 mmol, 4.00 equiv) in 1,4-difluorobenzene 10 (30 mL, 290 mmol, 10.0 equiv) was stirred at 100 °C for 45 h. Excess 1,4-difluorobenzene (26 mL, 253 mmol, 8.72 eq.) was reisolated via distillation and the residue was taken up in CHCl₃ (250 mL) and 1 M a. HCl (170 mL). The layers were separated and the aqueous layer extracted with CHCl₃ (3 × 80 mL). The combined organic layers were dried over MgSO₄ and the solvent was removed under reduced pressure. The residue was dissolved in CHCl₃ (20 mL) and n-hexane (45 mL) was added. The mixture was incubated at −20 °C for 16 h and the precipitate was filtered and dried under reduced pressure.

The crude 2-(2,5-difluorobenzoyl)benzoic acid was suspended in polyphosphoric acid (41.2 g) and the suspension was stirred at 140 °C for 2 h. The mixture was cooled to room temperature and poured into ice-water (200 mL) and CH₂Cl₂ (200 mL) and neutralized to pH = 7 using K₂CO₃. The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 150 mL). The combined organic layers were dried over MgSO₄ and filtered over Alox (basic). The crude product was adsorbed onto silica and purified via column chromatography (n-hexane/CHCl₃ 3:7) to obtain anthraquinone 11 (3.72 g, 15.2 mmol, 53% over two steps) as yellow solid.

**TLC:** \[ R_f = 0.44 \text{ (n-pentane/EtOAc 5:1).} \]

**¹H-NMR:** 250 MHz, CDCl₃; \( \delta = 8.26 \text{ (dd, } J = 5.8, 3.3 \text{ Hz, } 2H, H6 & H7), 7.81 \text{ (dd, } J = 5.8, 3.3 \text{ Hz, } 2H, H5 & H8), 7.51-7.46 \text{ (m, } 2H, H2 & H3) \text{ ppm.} \)

**¹³C-NMR:** 75 MHz, CDCl₃; \( \delta = 180.7 \text{ (s, } 2C, C9 & C10), 157.8 \text{ (dd, } J = 268.5, 4.0 \text{ Hz, } 2C, C1 & C4), 134.5 \text{ (s, } 2C, C5 & C8), 133.4 \text{ (s, } 2C, C11 \text{ &} \)
C12), 127.1 (s, 2C, C6 & C7), 124.7 (dd, J = 19.5, 15.1 Hz, 2C, C2 & C3), 121.8 (d, J = 2.2 Hz, 2C, C13 & C14) ppm.

**19F-NMR:** 235 MHz, CDCl₃; δ = −114.3 (s, 2F, F1 & F4) ppm.

**HR-MS:** EI(+); m/z calc. for C₁₄H₆F₂O₂ [M]⁺: 244.03359, found: 244.03415.

**FT-IR:** film; ν̃ = 3087 (w), 2926 (w), 1777 (w), 1715 (w), 1679 (s), 1591 (m), 1497 (w), 1469 (w), 1416 (m), 1337 (m), 1311 (w), 1287 (w), 1253 (s), 1170 (w), 1082 (w), 1064 (w), 1024 (w), 935 (w), 892 (w), 870 (w), 843 (w), 819 (w), 798 (w), 746 (w), 722 (m), 690 (w), 653 (w), 565 (w), 421 (w) cm⁻¹.

**m.p.:** 232 °C (CDCl₃).

### 1,4-Difluoroanthracene (9)

A suspension of anthraquinone 11 (200 mg, 819 µmol, 1.00 equiv), zinc powder (214 mg, 3.28 mmol, 4.00 equiv) and CuSO₄·5H₂O (10 mg, 41.0 µmol, 0.05 equiv) in 1,4-dioxane (4.0 mL) and aq NH₃ (25%, 4.0 mL) was stirred at 85 °C for 25 h in a pressure tube under vigorous stirring. The suspension was filtered over celite and washed with 2 M aq HCl (60 mL). The aqueous layer was reextracted with EtOAc (2 × 60 mL) and the combined organic layers were washed with brine (30 mL) and dried over MgSO₄. The crude product was adsorbed onto silica and purified via column chromatography (n-pentane) to obtain anthracene 9 (166 mg, 775 µmol, 95%) as colorless solid.

**TLC:** Rᵣ = 0.81 (n-pentane/EtOAc 50:1).
**1H-NMR:** 500 MHz, CDCl$_3$; $\delta = 8.65$ (s, 2H, $H9$ & $H10$), 8.06 (dd, $J = 6.4, 3.3$ Hz, 2H, $H5$ & $H8$), 7.55 (dd, $J = 6.6, 3.2$ Hz, 2H, $H6$ & $H7$), 7.00 (dd, $J = 7.4, 6.7$ Hz, 2H, $H2$ & $H3$) ppm.

**13C-NMR:** 126 MHz, CDCl$_3$; $\delta = 154.9$ (dd, $J = 252.4, 6.0$ Hz, 2C, $C1$ & $C4$), 132.1 (s, 2C, $C11$ & $C12$), 128.7 (s, 2C, $C5$ & $C8$), 126.8 (s, 2C, $C6$ & $C7$), 123.3 (dd, $J = 14.5, 11.0$ Hz, 2C, $C13$ & $C14$), 120.1 (t, $J = 2.7$ Hz, 2C, $C9$ & $C10$), 106.5 (dd, $J = 19.0, 12.4$ Hz, 2C, $C2$ & $C3$) ppm.

**19F-NMR:** 283 MHz, CDCl$_3$; $\delta = -127.0$ (s, 2F, $F1$ & $F4$) ppm.

**HR-MS:** EI($+$); $m/z$ calc. for C$_{14}$H$_8$F$_2$ [M]: 214.05941, found: 214.05990.

**FT-IR:** film; $\tilde{\nu} = 3058$ (w), 2960 (w), 2928 (w), 2855 (w), 2254 (w), 1650 (w), 1581 (w), 1462 (w), 1382 (w), 1320 (w), 1261 (w), 1237 (w), 1202 (w), 1139 (w), 1096 (w), 1019 (w), 957 (w), 904 (s), 818 (w), 725 (s), 650 (w), 612 (w), 468 (w), 434 (w) cm$^{-1}$.

**m.p.:** 107 °C (CDCl$_3$).

2-(1,4-Difluoroanthracene-2-carbonyl)benzoic acid (12)

\[
\begin{align*}
\text{9 [214.21]} & \quad \text{1) LDA} \\
& \quad \text{2) phthalic anhydride} \\
& \quad \text{THF} \\
& \quad -100 \text{ °C to rt, 2 h} \\
& \quad 82\% \\
\rightarrow & \quad \text{12 [362.33]}
\end{align*}
\]

$n$-BuLi (2.5 M in $n$-hexane, 196 µL, 490 µmol, 1.05 equiv) was added dropwise to a solution of $N,N$-diisopropylamine (72.2 µL, 514 µmol, 1.10 equiv) in THF (1.2 mL) at 0 °C. The mixture was stirred at 0 °C for 15 min and then cooled to −78 °C. A solution of anthracene 9 (100 mg, 467 µmol, 1.00 eq.) in THF (1.0 mL) was added dropwise and the resulting orange solution was stirred at −78 °C for 15 min. The mixture was added to a suspension of phthalic anhydride (83 mg, 560 µmol, 1.20 equiv) in THF (1.8 mL) at −100 °C and stirred at this temperature for 1 h. The cooling bath was removed and the solution was stirred additional 1 h at room temperature before 2 M aq HCl (25 mL) was added. The mixture was extracted with EtOAc ($2 \times 30$ mL) and the combined organic layers were dried over MgSO$_4$. The crude product was adsorbed
onto silica and purified via column chromatography (n-pentane/EtOAc/AcOH 5:1:0.1) to obtain carboxylic acid 12 (138 mg, 381 µmol, 82%) as yellow solid.

**TLC:** \( R_f = 0.26 \) (n-pentane/EtOAc/AcOH 4:1:0.1).

**\(^1\)H-NMR:** 500 MHz, acetone-\(d_6\); \( \delta = 11.64 \) (s, 1H, COOH), 8.76 (s, 1H, \( H_{ar} \)), 8.75 (s, 1H, \( H_{ar} \)), 8.25 (d, \( J = 8.4 \) Hz, 1H, \( H_{ar} \)), 8.19 (d, \( J = 8.4 \) Hz, 1H, \( H_{ar} \)), 8.15 (d, \( J = 7.5 \) Hz, 1H, \( H_{ar} \)), 7.81 (td, \( J = 7.5, 1.0 \) Hz, 1H, \( H_{ar} \)), 7.74-7.65 (m, 3H, 3 \( \times \) \( H_{ar} \)), 7.59-7.56 (m, 2H, 2 \( \times \) \( H_{ar} \)) ppm.

**\(^{13}\)C-NMR:** 126 MHz, acetone-\(d_6\); \( \delta = 192.7 \) (s, 1C, CO), 167.4 (s, 1C, COOH), 156.5 (d, \( J = 265.0 \) Hz, 1C, CF), 155.4 (dd, \( J = 250.0, 3.0 \) Hz, 1C, CF), 145.6 (s, 1C, \( C_{ar} \)), 134.4 (s, 1C, \( C_{ar} \)), 133.7 (s, 1C, \( C_{ar} \)), 133.3 (d, \( J = 2.0 \) Hz, 1C, \( C_{ar} \)), 131.0 (s, 1C, \( C_{ar} \)), 130.5 (s, 1C, \( C_{ar} \)), 129.7 (s, 1C, \( C_{ar} \)), 129.5 (s, 1C, \( C_{ar} \)), 129.4 (s, 1C, \( C_{ar} \)), 129.1 (s, 1C, \( C_{ar} \)), 128.4 (s, 1C, \( C_{ar} \)), 127.6 (s, 1C, \( C_{ar} \)), 125.3-125.1 (m, 1C, \( C_{ar} \)), 123.7-123.5 (m, 2C, 2 \( \times \) \( C_{ar} \)), 120.8 (s, 1C, \( C_{ar} \)), 119.0-118.9 (m, 1C, \( C_{ar} \)), 106.2 (d, \( J = 24.0 \) Hz, 1C, \( C_{ar} \)) ppm.

**\(^{19}\)F-NMR:** 235 MHz, acetone-\(d_6\); \( \delta = -119.4 \) (d, \( J = 22.2 \) Hz, 1F), \( -127.7 \) (d, \( J = 22.0 \) Hz, 1F) ppm.

**HR-MS:** ESI(−); \( m/z \) calc. for C\(_{22}\)H\(_{11}\)F\(_2\)O\(_3\) [M-H]−: 361.0682, found: 361.0683.

**FT-IR:** film; \( \tilde{\nu} = 3058 \) (w), 2658 (w), 2542 (w), 1774 (w), 1691 (w), 1665 (w), 1639 (s), 1596 (w), 1577 (w), 1541 (w), 1488 (w), 1438 (w), 1410 (w), 1389 (w), 1369 (s), 1329 (m), 1285 (w), 1265 (w), 1233 (s), 1164 (w), 1142 (m), 1109 (w), 1076 (w), 1056 (w), 974 (w), 885 (m), 829 (w), 771 (w), 736 (s), 712 (w), 667 (m), 644 (w), 559 (w), 471 (m) cm\(^{-1}\).

**m.p.:** 203 °C decomposition (toluene).
6,13-Difluoropentacene-5,14-dione (16)

A suspension of carboxylic acid 12 (30 mg, 82.8 µmol, 1.00 equiv) in polyphosphoric acid (1.30 g) was stirred at 140 °C for 3 h. The mixture was cooled to room temperature and taken up in CH₂Cl₂ (30 mL) and H₂O (30 mL). The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (2 × 30 mL). The combined organic layers were dried over MgSO₄ and the solvent was removed under reduced pressure to obtain the crude pentacenequinone 16 as red solid, which was used in the next step without further purification.

**TLC:** \( R_f = 0.49 \) (CH₂Cl₂).

**¹H-NMR:** 300 MHz, CD₂Cl₂; \( \delta = 8.98 \) (s, 2H, H7 & H12), 8.33 (dd, \( J = 5.8, 3.3 \) Hz, 2H, 2×Har.), 8.20 (dd, \( J = 6.4, 3.3 \) Hz, 2H, 2×Har.), 7.84 (dd, \( J = 5.8, 3.3 \) Hz, 2H, 2×Har.), 7.73 (dd, \( J = 6.5, 3.2 \) Hz, 2H, 2×Har.) ppm.

**¹⁹F-NMR:** 235 MHz, CD₂Cl₂; \( \delta = -117.9 \) (s, 2F, F6 & F13) ppm.

**HR-MS:** EI(+); \( m/z \) calc. for C₂₂H₁₀F₂O₂ [M]⁺: 344.06489, found: 344.06531.

**FT-IR:** film; \( \tilde{\nu} = 2957 \) (w), 2920 (s), 2851 (w), 1775 (w), 1744 (w), 1678 (m), 1587 (w), 1530 (w), 1446 (m), 1384 (w), 1364 (w), 1344 (w), 1284 (w), 1256 (s), 1152 (w), 1092 (w), 1011 (s), 978 (w), 886 (w), 800 (s), 748 (w), 725 (m), 532 (w), 467 (w) cm⁻¹.

**m.p.:** 238 °C decomposition (CH₂Cl₂).
6,13-Difluoro-5,14-dihydropentacene-5,14-diol (13)

A suspension of pentacenequinone 16 (crude, ≈82.8 µmol, 1.00 equiv) and NaBH₄ (16 mg, 414 µmol, 5.00 equiv) in THF (3.1 mL) and EtOH (2.0 mL) was stirred at room temperature under exclusion of light. After 2.5 h, additional NaBH₄ (16 mg, 414 µmol, 5.00 equiv) was added and the mixture was stirred for another 1.5 h. The reaction was cooled to 0 °C and quenched with silica (1.00 g) until gas evolution stopped. The crude product was adsorbed onto the silica and purified via column chromatography (n-pentane/Et₂O 3:2 → 0:1) to obtain diol 13 (7 mg, 20.1 µmol, 24% over two steps) as yellow solid.

**TLC:** \[ R_f = 0.31 \text{ (CH}_2\text{Cl}_2/\text{EtOAc 20:1).} \]

**¹H-NMR:** 300 MHz, CD₂Cl₂; \[ δ = 8.72 \text{ (s, 2H, } H7 \text{ & } H12), 8.11 \text{ (dd, } J = 6.5, 3.4 \text{ Hz, } 2H, 2 \times H_{ar}), 7.78 \text{ (dd, } J = 5.7, 3.4 \text{ Hz, } 2H, 2 \times H_{ar}), 7.59 \text{ (dd, } J = 6.6, 3.2 \text{ Hz, } 2H, 2 \times H_{ar}), 7.48 \text{ (dd, } J = 5.7, 3.3 \text{ Hz, } 2H, 2 \times H_{ar}), 6.37 \text{ (d, } J = 2.3 \text{ Hz, } 2H, H5 \text{ & } H14), 2.88 \text{ (s, } 2H, 2 \times OH) \text{ ppm.} \]

**¹⁹F-NMR:** 235 MHz, CD₂Cl₂; \[ δ = -131.1 \text{ (s, 2F, } F6 \text{ & } F13) \text{ ppm.} \]

**HR-MS:** APCI(−); \[ m/z \text{ calc. for C}_{22}H_{11}F_{2}O \text{ [M-H₂O-H]}^{-}: 329.0783, \text{ found: 329.0794.} \]

**FT-IR:** film; \[ ν = 3315 \text{ (s), 3108 (w), 2976 (w), 2927 (w), 2721 (w), 1681 (w), 1653 (w), 1612 (w), 1563 (w), 1477 (m), 1388 (m), 1368 (s), 1341 (w), 1317 (w), 1236 (w), 1175 (w), 1139 (w), 1027 (m), 991 (s), 972 (w), 935 (w), 900 (m), 809 (w), 781 (w), 759 (s), 741 (w), 726 (w), 664 (w), 635 (w), 552 (w), 530 (w), 480 (w), 460 (w) cm}^{-1}. \]

**m.p.:** 82 °C decomposition (Et₂O).
6,13-Difluoropentacene (F2PEN, 5)

2 mL aq HCl (0.20 mL) was added dropwise to a suspension of diol 13 (6 mg, 17.2 µmol, 1.00 equiv) and SnCl₂ (33 mg, 172 µmol, 10.0 equiv) in degassed 1,4-dioxane (1.6 mL). The mixture was stirred vigorously for 30 min at room temperature under exclusion of light. The precipitate was centrifuged (13,000 rpm, 3 min) and washed with H₂O (1.0 mL) and acetone (1.0 mL) to obtain F2PEN 5 (4 mg, 12.7 µmol, 74%) as dark purple solid.

**¹H-NMR:** 300 MHz, C₆D₆; δ = 8.82 (s, 4H, H₅ & H₇ & H₁₂ & H₁₄), 7.63 (dd, J = 6.6, 3.2 Hz, 4H, H₁ & H₄ & H₈ & H₁₁), 7.04 (dd, J = 6.7, 3.2 Hz, 4H, H₂ & H₃ & H₉ & H₁₀) ppm.

**¹⁹F-NMR:** 235 MHz, C₆D₆; δ = −132.1 (s, 2F, F₆ & F₁₃) ppm.

**HR-MS:** EI (+); m/z calc. for C₂₂H₁₂F₂ [M]+: 314.09071, found: 314.09089.

**FT-IR:** neat; ν = 3042 (w), 2960 (w), 2919 (w), 1740 (w), 1670 (w), 1612 (w), 1572 (w), 1485 (w), 1447 (m), 1358 (s), 1341 (w), 1293 (w), 1270 (w), 1205 (w), 1180 (w), 1133 (w), 1050 (w), 1003 (m), 952 (w), 925 (w), 865 (s), 762 (w), 734 (s), 671 (m), 629 (w), 565 (w), 536 (w), 513 (w), 482 (w), 455 (s) cm⁻¹.

**m.p.:** 288 °C decomposition (1,4-dioxane).
3. NMR spectra of all compounds

$^1$H-NMR, 250 MHz, CDCl$_3$

$^{13}$C-NMR, 75 MHz, CDCl$_3$
$^{19}$F-NMR, 235 MHz, CDCl$_3$

$^1$H-NMR, 500 MHz, CDCl$_3$
$^1$H-NMR, 126 MHz,
CDCl$_3$

$^1$C-NMR, 126 MHz,
CDCl$_3$

$^19$F-NMR, 283 MHz,
CDCl$_3$
$^{1}\text{H-NMR, 500 MHz, acetone-}d_6$

$^{13}\text{C-NMR, 126 MHz, acetone-}d_6$
$^{19}$F-NMR, 283 MHz, acetone-$d_6$

$^1$H-NMR, 300 MHz, CD$_2$Cl$_2$
16

$^{19}$F-NMR, 235 MHz,
CD$_2$Cl$_2$

13

$^1$H-NMR, 300 MHz,
CD$_2$Cl$_2$
19F-NMR, 235 MHz, CD2Cl2

1H-NMR, 300 MHz, C6D6

13C-satellites of C6D6
4. References

1. Krapcho, A. P.; Getahun, Z. *Synth. Commun.* **1985**, *15*, 907-910.