Palladium Catalysed C–H Arylation of Pyrenes: Access to a New Class of Exfoliating Agents for Water-Based Graphene Dispersions

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1. General Information

Tetrahydrofuran (THF) and toluene were dried using a PureSolv solvent purification system. All other solvents and reagents used were purchased from commercial suppliers and used without further purification. 1H-NMR spectra were obtained at room temperature on a Bruker 400 MHz or 500 MHz spectrometer. 13C-NMR spectra were obtained at 100 or 125 MHz, respectively. 19F-NMR spectra were obtained at 376 or 471 MHz, respectively. All NMR spectra were processed using MestReNova NMR software. Chemical shifts are reported in parts per million (ppm) and coupling constants (J) are reported in Hz. Splitting patterns are reported as follows: singlet (s), doublet (d), triplet (t), quadruplet (q), quintuplet (quint), doublet of doublets (dd), doublet of doublets of doublets (ddd), multiplet (m), etc. NMR signals were assigned using the appropriate 2D NMR experiments (i.e. HSQC and HMBC) when necessary. TLC analysis was carried out on aluminium sheets coated with silica gel and visualised using potassium permanganate solution and/or UV light. Infra-red spectra were recorded as evaporated films or neat using FT/IR spectrometers. Melting points were measured on solids as obtained after chromatography. Mass spectra were obtained using positive or negative electrospray (ESI), atmospheric pressure chemical ionization (APCI) or atmospheric solids analysis probe (ASAP).
For details on Liquid Fase Exfoliation and the subsequent analyses (AFM, Raman, Zeta-Potential and UV-Vis), see the corresponding sections.

2. Optimisation Tables

Table S1. Non-decarboxylative C–H ortho-arylation.\textsuperscript{a}

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{entry} & \text{Pd cat. (mol\%)} & \text{acid (equiv)} & 3a - \text{NMR yield (isolated yield)} & 1 (\text{NMR RSM}) \\
\hline
1 & Pd(OAc)\textsubscript{2} & AcOH (1.5) & 82 & 17 \\
2 & PEPPSI-IPr & AcOH (1.5) & 84 & 16 \\
3 & Pd(OAc)\textsubscript{2} & AcOH (1 M) & 9 & 26 \\
4 & PEPPSI-IPr & AcOH (1 M) & - & 31 \\
5 & Pd(OAc)\textsubscript{2} & TFA (1.5) & 28 & 29 \\
\hline
6\textsuperscript{b} & Pd(OAc)\textsubscript{2} & AcOH (1.5) & 89 & - \\
7\textsuperscript{b,c} & Pd(OAc)\textsubscript{2} & AcOH (1.5) & (80) & N/A \\
\hline
\end{array}
\]
\textsuperscript{a}Reactions run at 0.203 mmol scale; NMR yields determined with MeNO\textsubscript{2} as internal standard. \textsuperscript{b}Extra NMe\textsubscript{4}Cl (0.80 mmol) and KOAc (0.80 mmol) added after 24 h and stirred for another 21 h at 120 °C. \textsuperscript{c}Reaction run at 1.00 mmol scale.

Table S2. Iododecarboxylation.\textsuperscript{a}

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{entry} & \text{Solvent} & T (\degree\text{C}) & I\textsubscript{2} (\text{equiv}) & K\textsubscript{3}PO\textsubscript{4} (\text{equiv}) & 4a - \text{NMR yield (isolated yield)} \\
\hline
1 & MeCN (0.2 M) & 100 & 4 & 1 & <34 \\
2 & 1,4-dioxane (1.0 M) & 150 & 4 & 1 & - \\
3 & o-DCB (1.0 M) & 150 & 4 & 1 & ~50 \\
4 & o-DCB (1.0 M) & 150 & 3 & 1 & ~50 \\
5 & o-DCB (1.0 M) & 150 & 2 & 1 & ~50 \\
6 & o-DCB (1.0 M) & 120 & 3 & 1 & 49 \\
7 & o-DCB (1.0 M) & 100 & 3 & 1 & 43 \\
8 & o-DCB (1.0 M) & 120 & 2 & 1 & 47 \\
\hline
\end{array}
\]
Decarboxylative C–H ortho-arylation.

Table S3. Decarboxylative C–H ortho-arylation.\(^a\)

| entry | 2a (equiv) | Pd cat. (mol%) | AgX (equiv) | acid (equiv) | T (˚C) | time   | 5a - NMR yield (isolated yield) |
|-------|------------|----------------|-------------|--------------|--------|--------|---------------------------------|
| 1     | 3          | Pd(OAc)\(_2\) (2) | Ag\(_2\)CO\(_3\) (1) | TFA (3.5) | 130    | 3 days | -                               |
| 2     | 10         | Pd(OAc)\(_2\) (2) | Ag\(_2\)CO\(_3\) (1) | TFA (3.5) | 130    | 3 days | -                               |
| 3     | 3          | Pd(OAc)\(_2\) (2) | Ag\(_2\)CO\(_3\) (1) | AcOH (3.5) | 130    | 19 h   | 30                              |
| 4     | 3          | Pd(OAc)\(_2\) (2) | Ag\(_2\)CO\(_3\) (1) | AcOH (7.0) | 130    | 19 h   | 50                              |
| 5     | 3          | Pd(OAc)\(_2\) (2) | AgOAc (2)    | AcOH (3.5) | 130    | 19 h   | 58                              |
| 6\(^b\) | 3          | Pd(OAc)\(_2\) (2) | Ag\(_2\)CO\(_3\) (1) | AcOH (3.5) | 130    | 19 h   | <5                               |
| 7     | 3          | Pd(OAc)\(_2\) (2) | AgOAc (2)    | AcOH (7.0) | 130    | 19 h   | 50                              |
| 8     | 3          | Pd(OAc)\(_2\) (2) | AgOAc (2)    | AcOH (14.0)| 130    | 19 h   | 44                              |
| 9     | 3          | Pd(OAc)\(_2\) (2) | Ag\(_2\)CO\(_3\) (1) | AcOH (3.5) | 130    | 3 days | 61                              |
| 10    | 10         | Pd(OAc)\(_2\) (2) | Ag\(_2\)CO\(_3\) (1) | AcOH (3.5) | 130    | 3 days | 54                              |
| 11    | 3          | Pd(OAc)\(_2\) (2) | AgOAc (2)    | AcOH (3.5) | 130    | 3 days | 57                              |
| 12    | 3          | PEPSSI-IPr (2)    | AgOAc (2)    | AcOH (3.5) | 130    | 17 h   | 36                              |
| 13    | 3          | PEPSSI-IPr (2)    | Ag\(_2\)CO\(_3\) (1) | AcOH (3.5) | 150    | 19 h   | 57                              |
| 14    | 3          | PEPSSI-IPr (2)    | Ag\(_2\)CO\(_3\) (0.5) | AcOH (3.5) | 150    | 19 h   | 32                              |
| 15    | 3          | PEPSSI-IPr (2)    | AgOAc (2)    | AcOH (3.5) | 150    | 19 h   | 63                              |

\(^a\)Reactions run at 0.1 mmol scale. NMR yields determined with MeNO\(_2\) as internal standard.
| Entry | Phenylacetylene (equiv) | Pd cat. (mol%) | NEt₃ | solvent   | 6a - NMR yield (isolated yield) | 4a (NMR RSM) |
|-------|------------------------|---------------|------|-----------|-------------------------------|--------------|
| 1     | 1.1                    | PdCl₂(PPh₃)₂ (20 mol%) | 0.044 M | -         | 36                            | -            |
| 2     | 1.0                    | Pd[PPh₃]₄ (5 mol%)        | 1.5 equiv THF (0.1 M) | 15      | 64                            |
| 3     | 3.0                    | Pd[PPh₃]₄ (5 mol%)        | 1.5 equiv THF (0.1 M) | -       | 81                            |
| 4     | 3.0                    | PdCl₂(PPh₃)₂ (20 mol%) | 0.044 M | -         | 75 (58)                       | -            |
| 5     | 3.0                    | Pd[PPh₃]₄ (20 mol%)        | 0.044 M | -         | 72                            | -            |
| 6     | 3.0                    | PdCl₂(PPh₃)₂ (20 mol%) | 1.5 equiv THF (0.1 M) | 15      | 56                            |

*Reactions run at 0.0347 mmol (15 mg) scale; NMR yield determined with MeNO₂ as internal standard.

| Entry | Phenylacetylene (equiv) | Pd cat. (mol%) | NEt₃ | solvent   | 6a - NMR yield (isolated yield) | 4a (NMR RSM) |
|-------|------------------------|---------------|------|-----------|-------------------------------|--------------|
| 1     | 1.1                    | PdCl₂(PPh₃)₂ (20 mol%) | 0.044 M | -         | 36                            | -            |
| 2     | 1.0                    | Pd[PPh₃]₄ (5 mol%)        | 1.5 equiv THF (0.1 M) | 15      | 64                            |
| 3     | 3.0                    | Pd[PPh₃]₄ (5 mol%)        | 1.5 equiv THF (0.1 M) | -       | 81                            |
| 4     | 3.0                    | PdCl₂(PPh₃)₂ (20 mol%) | 0.044 M | -         | 75 (58)                       | -            |
| 5     | 3.0                    | Pd[PPh₃]₄ (20 mol%)        | 0.044 M | -         | 72                            | -            |
| 6     | 3.0                    | PdCl₂(PPh₃)₂ (20 mol%) | 1.5 equiv THF (0.1 M) | 15      | 56                            |

*Reactions run at 0.0347 mmol (15 mg) scale; NMR yield determined with MeNO₂ as internal standard.

3. Synthesis and characterisation
General Procedure A: Palladium catalysed non-decarboxylative ortho-arylation of pyrene-1-carboxylic acid

2-(3,5-Dimethylphenyl)pyrene-1-carboxylic acid (3a)

A microwave vial fitted with a Teflon-coated stirring bar was loaded with pyrene-1-carboxylic acid (246 mg, 1.00 mmol), 5-iodo-ortho-xylene (433 µL, 3.00 mmol), Pd(OAc)$_2$ (13.5 mg, 0.06 mmol), KOAc (196 mg, 2.00 mmol), NMe$_2$Cl (138 mg, 1.26 mmol) and acetic acid (87 µL, 1.50 mmol). The vial was sealed under air and the mixture was stirred at 120 °C. After cooling to room temperature, the mixture was partitioned between 2 M aqueous HCl (15 mL) and EtOAc (20 mL) and the organic fraction was filtered through a short plug of Celite. After removing volatiles under vacuum (70 °C) and EtOAc (232-235 °C). $^1$H-NMR (400 MHz, DMSO-$d_6$) δ 2.38 (s, CH$_3$, 6 H), 7.11 (s, ArH, 1 H), 7.28 (s, ArH, 2 H), 8.09-8.21 (m, ArH, 2 H), 8.23-8.42 (m, ArH, 6 H), 13.57 (bs, CO$_2$H, 1 H) ppm; $^{13}$C-NMR (125 MHz, DMSO-$d_6$) δ 21.1 (CH$_3$), 122.5 (ArC), 123.4 (ArC), 124.1 (ArCH), 125.8 (ArCH), 126.0 (ArCH), 126.1 (ArCH), 126.7 (ArCH), 126.8 (ArC), 126.9 (ArCH), 127.2 (ArCH), 128.5 (ArCH), 128.9 (ArCH), 129.0 (ArCH), 129.4 (ArC), 130.1 (ArC), 130.7 (ArC), 131.0 (ArC), 136.6 (ArC), 137.4 (ArC), 140.6 (ArC), 170.6 (ArCO$_2$H) ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 3035, 2916, 1690, 1597, 1407, 1275; HRMS calcld for C$_{25}$H$_{19}$O$_2$ [M+H]$^+$: 351.1380, found 351.1368.

2-(4-Methylphenyl)pyrene-1-carboxylic acid (3b)

Prepared according to general procedure A using pyrene-1-carboxylic acid (246 mg, 1.00 mmol) and 4-iodotoluene (654 mg, 3.00 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 50:50) to yield the title product as a pale orange solid (252 mg, 80%). mp (EtOAc) 254-257 °C. $^1$H-NMR (500 MHz, DMSO-$d_6$) δ 2.41 (s, CH$_3$, 3 H), 7.35 (d, J = 8.0 Hz, ArH, 2 H), 7.56 (d, J = 8.0 Hz, ArH, 2 H), 8.14 (t, J = 7.8 Hz, ArH, 1 H), 8.18 (d, J = 9.0 Hz, ArH, 1 H), 8.26 (d, J = 8.5 Hz, ArH, 1 H), 8.29 (d, J = 8.5 Hz, ArH, 1 H), 8.31-8.35 (m, ArH, 2 H), 8.36-8.40 (m, ArH, 2 H), 13.53 (bs, CO$_2$H, 1 H) ppm; $^{13}$C-NMR (125 MHz, DMSO-$d_6$) δ 20.8 (CH$_3$), 122.4 (ArC), 123.4 (ArC), 124.1 (ArCH), 125.8 (ArCH), 126.0 (ArCH), 126.1 (ArCH), 126.7 (ArCH), 126.9 (ArCH), 127.2 (ArCH), 128.5 (ArCH), 128.9 (ArCH), 129.1 (ArCH), 129.6 (ArC), 130.1 (ArC), 130.7 (ArC), 131.0 (ArC), 136.3 (ArC), 136.9 (ArC), 137.8 (ArC), 170.6 (CO$_2$H) ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 3037, 1682, 1596, 1512, 1404, 1267; HRMS calcld for C$_{25}$H$_{17}$O$_2$ [M–H]$^-$: 335.1078, found 335.1070.
2-(3-Tolyl)pyrene-1-carboxylic acid (3c)

Prepared according to general procedure A using pyrene-1-carboxylic acid (100 mg, 0.406 mmol) and 3-iodotoluene (157 µL, 1.22 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 60:40) to yield the title product as an orange solid (102 mg, 75%), mp (CH$_2$Cl$_2$) 188-191 °C. $^1$H-NMR (400 MHz, DMSO-d$_6$) δ 2.43 (s, CH$_3$, 3 H), 7.29 (d, J = 7.2 Hz, ArH, 1 H), 7.39-7.53 (m, ArH, 1 H), 8.14 (t, J = 7.6 Hz, ArH, 1 H), 8.19 (d, J = 9.2 Hz, ArH, 1 H), 8.27 (d, J = 9.2 Hz, ArH, 1 H), 8.30 (d, J = 9.2 Hz, ArH, 1 H), 8.32-8.41 (m, ArH, 4 H), 13.57 (s, CO$_2$H, 1 H) ppm; $^{13}$C-NMR (125 MHz, DMSO-d$_6$) δ 21.2 (C(CH$_3$)$_3$), 122.5 (ArC), 123.4 (ArC), 124.1 (ArCH), 125.8 (ArCH), 126.1 (ArCH), 126.7 (ArCH), 126.9 (ArC), 127.2 (ArCH), 128.3 (ArCH), 128.4 (ArCH), 128.6 (ArCH), 129.0 (ArCH), 129.7 (ArCH), 130.1 (ArC), 130.7 (ArC), 136.5 (ArC), 137.6 (ArC), 140.7 (ArC), 170.5 (ArCO$_2$H) ppm, one ArC was not observed; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 2916, 1682, 1597, 1411, 1279; HRMS calcd for C$_{24}$H$_{15}$O$_2$ [M–H]$: 335.1078, found 335.1080.

2-(4-tert-Butylphenyl)pyrene-1-carboxylic acid (3d)

Prepared according to general procedure A using pyrene-1-carboxylic acid (100 mg, 0.406 mmol) and 1-(tert-butyl)-1-iodobenzene (216 µL, 1.22 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 50:50) to yield the title product as a pale orange solid (99 mg, 64%), mp (CH$_2$Cl$_2$) 210-213 °C. $^1$H-NMR (500 MHz, DMSO-d$_6$) δ 1.37 (s, C(C(CH$_3$)$_3$), 9 H), 7.57 (d, J = 8.3 Hz, ArH, 2 H), 7.62 (d, J = 8.3 Hz, ArH, 2 H), 8.14 (t, J = 7.8 Hz, ArH, 1 H), 8.18 (d, J = 9.5 Hz, ArH, 1 H), 8.25 (d, J = 9.0 Hz, ArH, 1 H), 8.29 (d, J = 9.0 Hz, ArH, 1 H), 8.31-8.36 (m, ArH, 2 H), 8.36-8.40 (m, ArH, 2 H), 13.56 (bs, CO$_2$H, 1 H) ppm; $^{13}$C-NMR (125 MHz, DMSO-d$_6$) δ 31.2 (C(CH$_3$)$_3$), 34.4 (C(CH$_3$)$_3$), 122.4 (ArC), 123.4 (ArC), 124.1 (ArCH), 125.4 (ArCH), 125.8 (ArCH), 126.1 (ArCH), 126.7 (ArCH), 126.8 (ArC), 127.2 (ArCH), 128.5 (ArCH), 128.7 (ArCH), 129.0 (ArCH), 129.5 (ArC), 130.1 (ArC), 130.7 (ArC), 131.0 (ArC), 136.2 (ArC), 137.8 (ArC), 150.0 (ArC), 170.6 (ArCO$_2$H) ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 2916, 1682, 1597, 1411, 1279; HRMS calcd for C$_{27}$H$_{21}$O$_2$ [M–H]$: 377.1547, found 377.1546.

2-(4-Methoxyphenyl)pyrene-1-carboxylic acid (3e)
Prepared according to general procedure A, but using a tick glass wall pressure tube as reaction vessel with pyrene-1-carboxylic acid (739 mg, 3.00 mmol) and 4-iodoanisole (2.11 g, 9.00 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 30:70) to yield the title product as an orange solid (790 mg, 75%), mp (CH$_2$Cl$_2$) 180–183 °C. $^1$H-NMR (500 MHz, DMSO-d$_6$) δ 3.85 (s, OCH$_3$, 3 H), 7.11 (d, $J$ = 8.0 Hz, ArH, 2 H), 7.61 (d, $J$ = 8.0 Hz, ArH, 2 H), 8.13 (t, $J$ = 7.5 Hz, ArH, 1 H), 8.18 (d, $J$ = 9.5 Hz, ArH, 1 H), 8.25 (d, $J$ = 9.3 Hz, ArH, 1 H), 8.28 (d, $J$ = 9.3 Hz, ArH, 1 H), 8.30–8.35 (m, ArH, 2 H), 8.35–8.39 (m, ArH, 2 H), 13.53 (bs, CO$_2$H, 1 H) ppm; $^{13}$C-NMR (125 MHz, DMSO-d$_6$) δ 55.2 (OCH$_3$), 114.0 (ArC), 122.3 (ArC), 123.4 (ArC), 124.1 (ArC), 125.8 (ArC), 126.0 (ArC), 126.7 (ArC), 126.9 (ArC), 127.2 (ArC), 128.5 (ArC), 128.9 (ArC), 129.5 (ArC), 130.0 (ArC), 130.2 (ArC), 130.7 (ArC), 131.0 (ArC), 132.9 (ArC), 136.0 (ArC), 159.0 (ArC), 170.7 (ArCO$_2$H) ppm; IR $\nu_{\text{max}}$(neat/cm$^{-1}$): 2960, 1681, 1512, 1248, 1174, 1028, 827; HRMS calcd for C$_{24}$H$_{15}$O$_3$ [M–H]$^-$: 351.1027, found 351.1028.

2-Phenylpyrene-1-carboxylic acid (3f)

Prepared according to general procedure A using pyrene-1-carboxylic acid (100 mg, 0.406 mmol) and iodobenzene (137 µL, 1.22 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 50:50) to yield the title product as a brown solid (109 mg, 83%), mp (CH$_2$Cl$_2$) 222-225 °C. $^1$H-NMR (500 MHz, DMSO-d$_6$) δ 7.49 (t, $J$ = 7.4 Hz, ArH, 1 H), 7.55 (t, $J$ = 7.4 Hz, ArH, 2 H), 7.68 (d, $J$ = 7.4 Hz, ArH, 2 H), 8.15 (t, $J$ = 7.6 Hz, ArH, 1 H), 8.21 (d, $J$ = 9.2 Hz, ArH, 1 H), 8.27 (d, $J$ = 9.0 Hz, ArH, 1 H), 8.30 (d, $J$ = 9.0 Hz, ArH, 1 H), 8.32-8.43 (m, ArH, 4 H), 13.57 (bs, CO$_2$H, 1 H) ppm; $^{13}$C-NMR (125 MHz, DMSO-d$_6$) δ 122.5 (ArC), 123.4 (ArC), 124.1 (ArC), 125.9 (ArC), 126.1 (ArC), 126.1 (ArC), 126.8 (ArC), 126.9 (ArC), 127.2 (ArC), 127.6 (ArC), 128.5 (ArC), 128.6 (ArC), 129.0 (ArC), 129.0 (ArC), 129.5 (ArC), 130.1 (ArC), 130.7 (ArC), 131.0 (ArC), 136.4 (ArC), 140.7 (ArC), 170.5 (ArCO$_2$H) ppm; IR $\nu_{\text{max}}$(neat/cm$^{-1}$): 1679, 1596, 1406, 1271, 882, 840, 827; HRMS calcd for C$_{23}$H$_{13}$O$_2$ [M–H]$^-$: 321.0921, found 321.0913.

2-(4-Bromophenyl)pyrene-1-carboxylic acid (3g)
Prepared according to general procedure A using pyrene-1-carboxylic acid (100 mg, 0.406 mmol) and 4-bromiodobenzene (345 mg, 1.22 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 50:50) to yield the title product as a pale brown solid (106 mg, 65%). 1H-NMR (500 MHz, DMSO-d6) δ 7.61 (d, J = 8.4 Hz, ArH, 2 H), 7.75 (d, J = 8.4 Hz, ArH, 2 H), 8.15 (t, J = 7.6 Hz, ArH, 1 H), 8.21 (d, J = 9.2 Hz, ArH, 1 H), 8.26 (d, J = 9.0 Hz, ArH, 1 H), 8.30 (d, J = 9.0 Hz, ArH, 1 H), 8.33-8.37 (m, ArH, 2 H), 8.37-8.42 (m, ArH, 2 H), 13.65 (bs, CO2H, 1 H) ppm; 13C-NMR (125 MHz, DMSO-d6) δ 121.8 (ArC), 123.1 (ArC), 123.8 (ArC), 124.5 (ArCH), 126.3 (ArCH), 126.4 (ArCH), 126.7 (ArCH), 127.3 (ArCH), 127.4 (ArC), 127.7 (ArCH), 129.2 (ArCH), 129.6 (ArCH), 130.6 (ArC), 131.2 (ArC), 131.6 (ArCH), 131.9 (ArCH), 135.6 (ArC), 140.4 (ArC), 170.8 (ArCO2H) ppm, 2 quaternary C were not observed; IR νmax (neat/cm⁻¹): 3038, 1687, 1597, 1486, 1411, 1274, 1009, 880; HRMS calcd for C23H12O2Br [M–H]: 399.0015, found 399.0029.

2-(3-Bromophenyl)pyrene-1-carboxylic acid (3i)

Prepared according to general procedure A using pyrene-1-carboxylic acid (100 mg, 0.406 mmol) and 3-bromiodobenzene (156 μL, 1.22 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 70:30) to yield the title product as a pale brown solid (112 mg, 69%). 1H-NMR (400 MHz, DMSO-d6) δ 7.52 (t, J = 8.0 Hz, ArH, 1 H), 7.64-7.73 (m, ArH, 2 H), 7.85 (t, J = 1.8 Hz, ArH, 1 H), 8.16 (t, J = 7.6 Hz, ArH, 1 H), 8.21 (d, J = 9.2 Hz, ArH, 1 H), 8.28 (d, J = 8.8 Hz, ArH, 1 H), 8.32 (d, J = 8.8 Hz, ArH, 1 H), 8.36 (d, J = 9.6 Hz, ArH, 1 H), 8.38-8.43 (m, ArH, 3 H), 13.73 (s, CO2H, 1 H) ppm; 13C-NMR (125 MHz, DMSO-d6) δ 121.7 (ArC), 122.8 (ArC), 123.3 (ArC), 124.1 (ArCH), 126.0 (ArCH), 126.0 (ArCH), 126.3 (ArCH), 126.9 (ArCH), 127.2 (ArCH), 128.2 (ArCH), 128.8 (ArCH), 129.2 (ArCH), 129.2 (ArC), 130.1 (ArC), 130.5 (ArCH), 130.7 (ArCH), 130.8 (ArC), 131.1 (ArC), 131.5 (ArCH), 134.8 (ArC), 143.1 (ArC), 170.3 (ArCO2H) ppm; IR νmax (neat/cm⁻¹): 2919, 1662, 1593, 1385, 1350, 1295; HRMS calcd for C23H12O2Br [M–H]: 399.0015, found 399.0029.

2-(3-Chlorophenyl)pyrene-1-carboxylic acid (3i)

Prepared according to general procedure A using pyrene-1-carboxylic acid (100 mg, 0.406 mmol) and 3-chloriodobenzene (151 μL, 1.22 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 50:50) to yield the title product as a pale brown solid (116 mg, 80%). 1H-NMR (500 MHz, DMSO-d6) δ 7.56 (dt, J = 7.5, 1.8 Hz, ArH, 1 H), 7.59 (t, J = 7.5 Hz, ArH, 1 H), 7.63 (dt, J = 7.5, 1.8 Hz, ArH, 1 H), 7.71 (t, J = 1.8 Hz, ArH, 1 H), 8.16 (t, J = 7.8 Hz, ArH, 1 H), 8.21 (d, J = 9.3 Hz, ArH, 1 H), 8.28 (d, J = 9.0 Hz, ArH, 1 H), 8.32...
(d, J = 9.0 Hz, ArH, 1 H), 8.36 (d, J = 9.3 Hz, ArH, 1 H), 8.38-8.43 (ArH, 3 H), 13.71 (s, CO₂H, 1 H) ppm; ¹³C-NMR (125 MHz, DMSO-d₆) δ 122.8 (ArC), 123.3 (ArC), 124.1 (ArCH), 126.0 (ArCH), 126.0 (ArCH), 126.3 (ArCH), 126.9 (ArCH), 127.0 (ArC), 127.2 (ArCH), 127.6 (ArCH), 127.8 (ArCH), 128.7 (ArCH), 128.8 (ArCH), 129.2 (ArCH), 130.1 (ArC), 130.4 (ArCH), 130.8 (ArC), 131.1 (ArC), 133.1 (ArC), 134.8 (ArC), 142.8 (ArC), 170.3 (ArCO₂H) ppm, one ArC was not observed; IR νₘₐₓ (neat/cm⁻¹): 2929, 1652, 1595, 1387, 1307; HRMS caled for C₂₃H₁₆O₃Cl [M–H]: 355.0531, found 355.0536.

2-(3,5-Dichlorophenyl)pyrene-1-carboxylic acid (3j)

\[ \text{HO-} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \text{Ar} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \text{Pyrene-COOH} \]

Prepared according to general procedure A using pyrene-1-carboxylic acid (100 mg, 0.406 mmol) and 3,5-dichloriodobenzene (333 mg, 1.22 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 60:40) to yield the title product as a brown solid (121 mg, 76%), mp (CH₂Cl₂) 215-218 °C. ¹H-NMR (400 MHz, DMSO-d₆) δ 7.70 (d, J = 2.0 Hz, ArH, 2 H), 7.77 (t, J = 2.0 Hz, ArH, 1 H), 8.17 (t, J = 7.6 Hz, ArH, 1 H), 8.23 (d, J = 9.2 Hz, ArH, 1 H), 8.28 (d, J = 9.2 Hz, ArH, 1 H), 8.34 (d, J = 9.2 Hz, ArH, 1 H), 8.37 (d, J = 9.6 Hz, ArH, 1 H), 8.39-8.45 (m, ArH, 3 H), 13.87 (s, CO₂H, 1 H) ppm; ¹³C-NMR (125 MHz, DMSO-d₆) δ 123.0 (ArC), 123.2 (ArC), 124.0 (ArCH), 126.0 (ArCH), 126.1 (ArCH), 126.4 (ArCH), 127.0 (ArCH), 127.1 (ArC), 127.2 (ArCH), 127.3 (ArCH), 127.7 (ArCH), 129.0 (ArCH), 129.3 (ArCH), 129.4 (ArC), 129.5 (ArC), 131.2 (ArC), 133.5 (ArC), 144.2 (ArC), 170.2 (ArCO₂H) ppm, one ArC was not observed; IR νₘₐₓ (neat/cm⁻¹): 3038, 1712, 1589, 1559, 1201, 1148; HRMS caled for C₂₃H₁₆O₃Cl [M–H]: 389.0131, found 389.0147.

2-(3,5-Bis(trifluoromethyl)phenyl)pyrene-1-carboxylic acid (3k)

\[ \text{HO-} \begin{array}{c} \text{CF₃} \\ \text{CF₃} \end{array} \text{Ar} \begin{array}{c} \text{CF₃} \\ \text{CF₃} \end{array} \text{Pyrene-COOH} \]

Prepared according to general procedure A using pyrene-1-carboxylic acid (100 mg, 0.406 mmol) and 1-iodo-3,5-bis(trifluoromethyl)benzene (216 µL, 1.22 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 50:50) to yield the title product as a pale orange solid (161 mg, 87%), mp (CH₂Cl₂) >260 °C. ¹H-NMR (500 MHz, DMSO-d₆) δ 8.19 (t, J = 7.8 Hz, ArH, 1 H), 8.24-8.46 (m, ArH, 9 H), 8.52 (s, ArH, 1 H), 13.92 (bs, CO₂H, 1 H) ppm; ¹³C-NMR (125 MHz, DMSO-d₆) δ 121.5 (m, ArCH), 123.2 (ArC), 123.2 (ArC), 123.4 (q, J = 271.1 Hz, ArCCF₃), 124.1 (ArCH), 126.1 (ArCH), 126.2 (ArCH), 126.4 (ArCH), 127.1 (ArCH), 127.2 (ArCH), 129.1 (ArCH), 129.3 (ArC), 129.4 (ArCH), 129.7 (q, J = 3.3 Hz, ArCH), 130.2 (ArC), 130.5 (q, J = 32.7 Hz, ArCCF₃), 130.8 (ArC), 131.2 (ArC), 133.3 (ArC), 143.3 (ArC), 170.2
(ArCO₂H) ppm; ¹⁹F-NMR (471 MHz, DMSO-d₆) δ –61.1 ppm; IR νₘₐₓ (neat/cm⁻¹): 2930, 1678, 1379, 1285, 1171, 1117; HRMS calcd for C₂₅H₁₆O₃F₅ [M–H]: 457.0669, found 457.0672.

2-(3-Nitrophenyl)pyrene-1-carboxylic acid (3l)

Prepared according to general procedure A using pyrene-1-carboxylic acid (100 mg, 0.406 mmol) and 3-nitriodobenzene (304 mg, 1.22 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 20:80) to yield the title product as an orange solid (123 mg, 82%), mp (CH₂Cl₂) 222-225 °C. ¹H-NMR (500 MHz, DMSO-d₆) δ 7.88 (t, J = 8.0 Hz, ArH, 1 H), 8.14 (ddd, J = 8.0, 2.0, 1.0 Hz, ArH, 1 H), 8.18 (t, J = 8.0 Hz, ArH, 1 H), 8.26 (d, J = 9.0 Hz, ArH, 1 H), 8.31 (d, J = 9.0 Hz, ArH, 1 H), 8.33-8.40 (m, ArH, 3 H), 8.40-8.44 (m, ArH, 2 H), 8.47 (s, ArH, 1 H), 8.49 (t, J = 2.0 Hz, ArH, 1 H), 13.82 (s, CO₂H, 1 H) ppm; ¹³C-NMR (125 MHz, DMSO-d₆) δ 122.6 (ArCH), 123.0 (ArC), 123.2 (ArC), 123.4 (ArCH), 124.1 (ArCH), 126.0 (ArCH), 126.1 (ArCH), 126.4 (ArCH), 127.1 (ArCH), 127.3 (ArC), 127.2 (ArCH), 129.0 (ArCH), 129.4 (ArCH), 130.2 (ArC), 130.2 (ArCH), 130.8 (ArC), 131.3 (ArC), 134.1 (ArC), 135.7 (ArCH), 142.3 (ArC), 147.8 (ArC), 170.2 (ArCO₂H) ppm, one ArC was not observed; IR νₘₐₓ (neat/cm⁻¹): 1674, 1520, 1349; HRMS calcd for C₂₅H₁₆O₃N [M–H]: 366.0772, found 366.0774.

2-(3-(Trifluoromethyl)phenyl)pyrene-1-carboxylic acid (3m)

Prepared according to general procedure A using pyrene-1-carboxylic acid (100 mg, 0.406 mmol) and 3-trifluoromethyliodobenzene (176 µL, 1.22 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 60:40) to yield the title product as a pale brown solid (133 mg, 84%), mp (CH₂Cl₂) 230-233 °C. ¹H-NMR (400 MHz, DMSO-d₆) δ 7.81 (t, J = 8.0 Hz, ArH, 1 H), 7.87 (d, J = 8.0 Hz, ArH, 1 H), 7.95-8.01 (m, ArH, 2 H), 8.17 (t, J = 7.6 Hz, ArH, 1 H), 8.23 (d, J = 9.2 Hz, ArH, 1 H), 8.30 (d, J = 8.8 Hz, ArH, 1 H), 8.33 (d, J = 8.8 Hz, ArH, 1 H), 8.37 (d, J = 9.2 Hz, ArH, 1 H), 8.39-8.46 (m, ArH, 3 H), 13.77 (s, CO₂H, 1 H) ppm; ¹³C-NMR (125 MHz, DMSO-d₆) δ 122.8 (ArC), 123.3 (ArC), 124.1 (ArCH), 124.2 (q, J = 271.3 Hz, ArCCF₃), 124.4 (q, J = Hz, ArCH), 125.4 (q, J = Hz, ArCH), 126.0 (ArCH), 126.1 (ArCH), 126.3 (ArCH), 127.0 (ArCH), 127.0 (ArC), 127.2 (ArCH), 128.9 (ArCH), 129.3 (q, J = 31.3 Hz, ArCCF₃), 129.3 (ArCH), 129.7 (ArCH), 130.1 (ArC), 130.8 (ArC), 131.2 (ArC), 133.2 (ArCH), 134.8 (ArC), 141.7 (ArC), 170.3 (ArCO₂H) ppm, one ArC was not observed; ¹⁹F-NMR (471 MHz, DMSO-d₆) –60.9 ppm; IR νₘₐₓ (neat/cm⁻¹): 3037, 1683, 1337, 1274, 1121; HRMS calcd for C₂₅H₁₆O₃F₃ [M–H]: 389.0795, found 389.0796.
2-(3-Cyanophenyl)pyrene-1-carboxylic acid (3n)

Prepared according to general procedure A using pyrene-1-carboxylic acid (100 mg, 0.406 mmol) and 3-iodobenzonitrile (279 mg, 1.22 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 30:70) to yield the title product as a pale orange solid (104 mg, 74%). mp (CH$_2$Cl$_2$) 215-217 °C. $^1$H-NMR (500 MHz, acetone-d$_6$) $\delta$ 7.77 (t, $J = 8.0$ Hz, ArH, 1 H), 7.89 (d, $J = 8.0$ Hz, ArH, 1 H), 8.03 (d, $J = 8.0$ Hz, ArH, 1 H), 8.08 (s, ArH, 1 H), 8.16 (t, $J = 7.5$ Hz, ArH, 1 H), 8.26 (d, $J = 9.0$ Hz, ArH, 1 H), 8.29-8.42 (m, ArH, 6 H), 12.06 (bs, CO$_2$H, 1 H) ppm; $^{13}$C-NMR (125 MHz, acetone-d$_6$) $\delta$ 113.3 (ArC), 119.3 (ArCN), 124.5 (ArC), 124.8 (ArC), 125.2 (ArCH), 126.9 (ArCH), 127.0 (ArCH), 127.2 (ArCH), 127.8 (ArCH), 128.1 (ArCH), 128.9 (ArC), 129.7 (ArC), 130.0 (ArCH), 130.2 (ArCH), 130.5 (ArCH), 131.6 (ArC), 132.1 (ArCH), 132.2 (ArC), 132.8 (ArC), 133.4 (ArCH), 134.7 (ArCH), 136.1 (ArC), 143.6 (ArC), 170.5 (ArCO$_2$H) ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 3043, 2229, 1722, 1695, 1597, 1404, 1245; HRMS calcd for C$_{25}$H$_{15}$O$_2$N [M–H]: 346.0874, found 346.0874.

2-(3-(Methoxycarbonyl)phenyl)pyrene-1-carboxylic acid (3o)

Prepared according to general procedure A using pyrene-1-carboxylic acid (100 mg, 0.406 mmol) and methyl 3-iodobenzoate (320 mg, 1.22 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 30:70) to yield the title product as an orange solid (105 mg, 68%). mp (CH$_2$Cl$_2$) 201-204 °C. $^1$H-NMR (400 MHz, DMSO-d$_6$) $\delta$ 3.91 (s, CO$_2$CH$_3$, 3 H), 7.72 (t, $J = 7.6$ Hz, ArH, 1 H), 7.95 (ddd, $J = 7.6$, 1.6, 1.2 Hz, ArH, 1 H), 8.08 (dt, $J = 7.6$, 1.2 Hz, ArH, 1 H), 8.16 (t, $J = 7.6$ Hz, ArH, 1 H), 8.21-8.26 (m, ArH, 2 H), 8.30 (d, $J = 9.0$ Hz, ArH, 1 H), 8.33 (d, $J = 9.0$ Hz, ArH, 1 H), 8.37 (d, $J = 8.8$ Hz, ArH, 1 H), 8.38-8.43 (m, ArH, 3 H), 13.69 (s, CO$_2$H, 1 H) ppm; $^{13}$C-NMR (125 MHz, DMSO-d$_6$) $\delta$ 52.4 (ArCO$_2$CH$_3$), 122.8 (ArC), 123.3 (ArC), 124.1 (ArCH), 124.1 (ArC), 126.0 (ArCH), 126.0 (ArCH), 126.3 (ArCH), 126.9 (ArCH), 127.0 (ArC), 127.2 (ArCH), 128.3 (ArCH), 128.8 (ArCH), 129.2 (ArCH), 129.5 (ArCH), 129.9 (ArC), 130.1 (ArC), 130.7 (ArC), 131.2 (ArC), 133.8 (ArCH), 135.4 (ArC), 141.2 (ArC), 166.1 (ArCO$_2$CH$_3$), 170.3 (ArCO$_2$H) ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 3166, 1716, 1683, 1594, 1436, 1207; HRMS calcd for C$_{25}$H$_{15}$O$_4$ [M–H]: 379.0976, found 379.0974.
2-(4-(Methoxycarbonyl)phenyl)pyrene-1-carboxylic acid (3p)

Prepared according to general procedure A, but using a tick glass wall pressure tube as reaction vessel with pyrene-1-carboxylic acid (739 mg, 3.00 mmol) and methyl 4-iodobenzoate (2.36 g, 9.00 mmol). The crude product was purified by silica flash column chromatography (hexane/ EtOAc, 100:0 to 40:60) to yield the title product as an orange solid (1.06 g, 90%), mp (CH₂Cl₂) 225-227 ºC. ¹H-NMR (500 MHz, DMSO-d₆) δ 3.92 (s, OCH₃, 3 H), 7.82 (d, J = 7.5 Hz, ArH, 2 H), 8.13 (d, J = 7.5 Hz, ArH, 2 H), 8.17 (t, J = 7.5 Hz, ArH, 1 H), 8.24 (d, J = 9.3 Hz, ArH, 1 H), 8.29 (d, J = 9.0 Hz, ArH, 1 H), 8.33 (d, J = 9.0 Hz, ArH, 1 H), 8.37 (d, J = 9.3 Hz, ArH, 1 H), 8.39-8.43 (m, ArH, 3 H), 13.68 (bs, CO₂H, 1 H) ppm; ¹³C-NMR (125 MHz, DMSO-d₆) δ 52.3 (OCH₃), 122.9 (ArC), 123.3 (ArC), 124.1 (ArCH), 125.9 (ArCH), 126.0 (ArCH), 126.3 (ArCH), 127.0 (ArCH), 127.1 (ArC), 127.2 (ArCH), 128.7 (ArC), 128.9 (ArCH), 129.2 (ArCH), 129.3 (ArC), 129.4 (ArCH), 130.1 (ArC), 130.8 (ArC), 131.1 (ArC), 135.4 (ArC), 145.6 (ArC), 166.1 (CO₂CH₃), 170.3 (CO₂H) ppm; IR νmax (neat/cm⁻¹): 3042, 2924, 1723, 1669, 1427, 1298, 1280; HRMS calcd for C₂₅H₂₅O₄ [M–H]: 379.0976, found 379.0977.

General Procedure B: Iododecarboxylation of pyrenecarboxylic acids

2-(3,5-Dimethylphenyl)-1-iodopyrene (4a)

To a flame dried microwave vial fitted with a Teflon-coated stirring bar and loaded with 3a (500 mg, 1.43 mmol), iodine (1.09 g, 4.29 mmol) and dry K₂PO₄ (303 mg, 1.43 mmol) was added dry 1,2-dichlorobenzene (7.2 mL). The vial was sealed under air and the mixture was stirred at 120 ºC for 21 h. After cooling to room temperature, the reaction was quenched with 10% aqueous Na₂S₂O₃ / saturated aqueous Na₂CO₃ (1:1, 20 mL) and extracted with CH₂Cl₂ (3 × 15 mL). The organic layer was washed with brine, dried (MgSO₄) and concentrated under reduced pressure. The crude product was purified by silica flash column chromatography (hexane) to yield the title product as an off-white solid (422 mg, 68%), mp (CH₂Cl₂) 160-163 ºC. ¹H-NMR (400 MHz, CDCl₃) δ 2.45 (s, CH₃, 6 H), 7.13 (s, ArH, 3 H), 8.00-8.09 (m, ArH, 2 H), 8.10-8.17 (m, ArH, 2 H), 8.18-8.30 (m, ArH, 3 H), 8.58 (d, J = 9.2 Hz, ArH, 1 H) ppm; ¹³C-NMR (100 MHz, CDCl₃) δ 21.4 (CH₃), 101.7 (ArC), 123.7 (ArC), 124.2 (ArC), 125.5 (ArCH), 125.8 (ArCH), 125.9 (ArCH), 126.4 (ArCH), 127.0 (ArCH), 127.8 (ArCH), 128.3 (ArCH), 129.2 (ArCH), 129.6 (ArCH), 130.8 (ArC), 130.8 (ArC), 131.1 (ArC), 132.5 (ArCH), 133.2 (ArC), 137.3 (ArC), 145.8 (ArC), 146.1 (ArC) ppm; IR νmax (neat/cm⁻¹): 3033, 2915, 1602, 1587, 1422, 1008, 881; HRMS calcd for C₂₅H₂₂I [M⁺]: 432.0369, found 432.0359.
1-Iodo-2-(4-methylphenyl)pyrene (4b)

Prepared according to general procedure B using 3b (404 mg, 1.20 mmol). The crude product was purified by silica flash column chromatography (hexane/CH$_2$Cl$_2$, 100:0 to 98:2) to yield the title product as a pale yellow solid (404 mg, 81%), mp (CH$_2$Cl$_2$) 90-93 °C. $^1$H-NMR (400 MHz, CDCl$_3$) δ 2.51 (s, C$_7$H$_3$, 3 H), 7.35 (d, $J = 8.2$ Hz, ArH, 2 H), 7.42 (d, $J = 8.2$ Hz, ArH, 2 H), 7.99-8.09 (m, ArH, 2 H), 8.10-8.16 (m, ArH, 2 H), 8.17-8.30 (m, ArH, 3 H), 8.57 (d, $J = 9.2$ Hz, ArH, 1 H) ppm; $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 21.4 (C$_7$H$_3$), 101.9 (ArC$I$), 123.8 (ArC), 124.3 (ArC), 125.6 (ArC), 125.8 (ArC), 126.1 (ArC), 126.4 (ArC), 127.0 (ArC), 128.4 (ArC), 129.7 (ArC), 129.8 (ArC), 130.8 (ArC), 130.9 (ArC), 131.1 (ArC), 132.5 (ArC), 133.3 (ArC), 137.4 (ArC), 143.4 (ArC), 145.5 (ArC) ppm; IR ν$_{max}$ (neat/cm$^{-1}$): 2921, 2852, 1739, 1588, 1509, 1447, 1177, 1002; HRMS calcd for C$_{23}$H$_{16}$I$^+ [M+H]^+$: 419.0291, found 419.0284.

1-Iodo-2-(3-methylphenyl)pyrene (4c)

Prepared according to general procedure B using 3c (34 mg, 0.100 mmol). The crude product was purified by silica flash column chromatography (hexane) to yield the title product as a pale yellow solid (31 mg, 74%), mp (CH$_2$Cl$_2$) 103-105 °C. $^1$H-NMR (400 MHz, CDCl$_3$) δ 2.50 (s, C$_7$H$_3$, 3 H), 7.29-7.36 (m, ArH, 3 H), 7.40-7.46 (m, ArH, 1 H), 8.01 (d, $J = 8.8$ Hz, ArH, 1 H), 8.05 (t, $J = 7.6$ Hz, ArH, 1 H), 8.09-8.15 (m, ArH, 2 H), 8.18 (d, $J = 9.4$ Hz, ArH, 1 H), 8.20-8.29 (m, ArH, 2 H), 8.56 (d, $J = 9.4$ Hz, ArH, 1 H) ppm; $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 21.6 (CH$_3$), 101.7 (ArC$I$), 123.7 (ArC), 124.2 (ArC), 125.5 (ArC), 125.8 (ArC), 125.9 (ArC), 126.4 (ArC), 126.9 (ArC), 127.1 (ArC), 127.7 (ArC), 128.3 (ArC), 128.7 (ArC), 129.7 (ArC), 130.6 (ArC), 130.8 (ArC), 130.8 (ArC), 131.0 (ArC), 132.5 (ArC), 133.2 (ArC), 137.5 (ArC), 145.6 (ArC), 146.1 (ArC) ppm; IR ν$_{max}$ (neat/cm$^{-1}$): 3042, 2920, 1587, 1422; HRMS calcd for C$_{13}$H$_{16}$I$^+ [M+H]^+$: 419.0291, found 419.0285.

2-(4-tert-Butylphenyl)-1-iodopyrene (4d)

Prepared according to general procedure B using 3d (38 mg, 0.100 mmol). The crude product was purified by silica flash column chromatography (hexane) to yield the title product as a white solid (28 mg, 61%), mp (CH$_2$Cl$_2$) 130-133 °C. $^1$H-NMR (400 MHz, CDCl$_3$) δ 1.45 (s, C(CH$_3$)$_3$, 9 H), 7.46 (d, $J$
= 8.2 Hz, ArH, 2 H), 7.55 (d, J = 8.2 Hz, ArH, 2 H), 7.99-8.09 (m, ArH, 2 H), 8.11-8.16 (m, ArH, 2 H), 8.18-8.31 (m, ArH, 3 H), 8.58 (d, J = 9.2 Hz, ArH, 1 H) ppm; $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 31.5 (C(CH$_3$)$_3$), 34.7 (C(CH$_3$)$_3$), 101.9 (ArCl), 123.8 (ArC), 124.3 (ArC), 124.8 (ArCH), 125.6 (ArCH), 125.8 (ArCH), 126.2 (ArCH), 126.4 (ArCH), 127.0 (ArCH), 128.3 (ArCH), 129.6 (ArCH), 129.7 (ArCH), 130.8 (ArC), 130.9 (ArC), 131.1 (ArC), 132.6 (ArCH), 133.3 (ArC), 143.2 (ArC), 145.6 (ArC), 150.5 (ArC) ppm; IR $\nu_{max}$ (neat/cm$^{-1}$): 3041, 2949, 1578, 1509, 1420, 1397, 1360, 1180, 1115, 877; HRMS calcd for C$_{26}$H$_{21}$I [M$^+$]: 460.0682, found 460.0681.

1-Iodo-2-(4-methoxyphenyl)pyrene (4e)

![Image of 1-Iodo-2-(4-methoxyphenyl)pyrene (4e)]

Prepared according to general procedure B using 3e (400 mg, 1.13 mmol). The crude product was purified by silica flash column chromatography (hexane/CH$_2$Cl$_2$, 100:0 to 90:10) to yield the title product as a white solid (370 mg, 75%). $^{1}$H-NMR (400 MHz, CDCl$_3$) δ 3.94 (s, OCH$_3$, 3 H), 7.06 (d, J = 8.4 Hz, ArH, 2 H), 7.45 (d, J = 8.4 Hz, ArH, 2 H), 7.99-8.10 (m, ArH, 2 H), 8.11-8.17 (m, ArH, 2 H), 8.18-8.29 (m, ArH, 3 H), 8.57 (d, J = 9.2 Hz, ArH, 1 H) ppm; $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 55.4 (OCH$_3$), 102.4 (ArCl), 113.3 (ArCH), 115.0 (ArC), 123.8 (ArC), 124.3 (ArC), 125.6 (ArCH), 125.9 (ArCH), 126.2 (ArCH), 126.4 (ArCH), 127.0 (ArCH), 128.4 (ArCH), 129.7 (ArCH), 130.9 (ArC), 130.9 (ArC), 131.1 (ArC), 131.1 (ArC), 132.6 (ArCH), 133.4 (ArC), 138.9 (ArC), 145.2 (ArC), 159.1 (ArC) ppm; IR $\nu_{max}$ (neat/cm$^{-1}$): 3033, 2836, 1609, 1511, 1286, 1242, 1174, 1024; HRMS calcd for C$_{23}$H$_{19}$OI [M$^+$]: 434.0162, found 434.0162.

1-Iodo-2-phenylpyrene (3f)

![Image of 1-Iodo-2-phenylpyrene (3f)]

Prepared according to general procedure B using 3f (81 mg, 0.250 mmol). The crude product was purified by silica flash column chromatography (hexane/CH$_2$Cl$_2$, 100:0 to 98:2) to yield the title product as a yellow solid (27 mg, 27%). $^{1}$H-NMR (400 MHz, CDCl$_3$) δ 7.48-7.57 (m, ArH, 5 H), 8.01 (d, J = 9.2 Hz, ArH, 1 H), 8.05 (t, J = 7.6 Hz, ArH, 1 H), 8.10-8.14 (m, ArH, 2 H), 8.18 (d, J = 9.2 Hz, ArH, 1 H), 8.20-8.28 (m, ArH, 2 H), 8.56 (d, J = 9.2 Hz, ArH, 1 H) ppm; $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 101.6 (ArCl), 123.7 (ArC), 124.3 (ArC), 125.6 (ArCH), 125.9 (ArCH), 126.4 (ArCH), 126.9 (ArCH), 127.6 (ArCH), 127.9 (ArCH), 128.4 (ArCH), 129.7 (ArCH), 129.9 (ArCH), 130.8 (ArC), 130.8 (ArC), 131.1 (ArC), 132.4 (ArCH), 133.3 (ArC), 145.5 (ArC), 146.2 (ArC) ppm; IR $\nu_{max}$ (neat/cm$^{-1}$): 3047, 1587, 1495, 1421, 1180, 1005, 839, 820; HRMS calcd for C$_{22}$H$_{18}$I [M+H$^+$]: 405.0135, found 405.0136.
2-(4-Bromophenyl)-1-iodopyrene (4g)

Prepared according to general procedure B using 3g (100 mg, 0.250 mmol). The crude product was purified by silica flash column chromatography (hexane) to yield the title product as a pale yellow solid (37 mg, 31%), mp (CH₂Cl₂) 172-175 °C. ¹H-NMR (400 MHz, CDCl₃) δ 7.39 (d, J = 8.4 Hz, ArH, 2 H), 7.67 (d, J = 8.4 Hz, ArH, 2 H), 7.98 (d, J = 8.8 Hz, ArH, 1 H), 8.02-8.08 (m, ArH, 2 H), 8.11 (d, J = 8.8 Hz, ArH, 1 H), 8.14-8.27 (m, ArH, 3 H), 8.52 (d, J = 9.2 Hz, ArH, 1 H) ppm; ¹³C-NMR (100 MHz, CDCl₃) δ 101.1 (ArC), 122.0 (ArC), 123.6 (ArC), 124.4 (ArC), 125.6 (ArC), 125.7 (ArC), 126.0 (ArC), 126.5 (ArC), 126.8 (ArC), 128.5 (ArC), 129.9 (ArC), 131.0 (ArC), 131.1 (ArC), 131.6 (ArC), 133.3 (ArC), 144.2 (ArC), 145.0 (ArC) ppm; IR ν max (neat/cm⁻¹): 3044, 2922, 1586, 1488, 1422, 1179, 1068, 1011, 840, 829, 819; HRMS calcd for C₂₂H₁₃BrI [M+H]⁺: 482.9240, found 482.9242.

1-Iodo-2-(3-bromophenyl)pyrene (4h)

Prepared according to general procedure B using 3h (40 mg, 0.100 mmol). The crude product was purified by silica flash column chromatography (hexane) to yield the title product as a pale yellow solid (34 mg, 70%), mp (CH₂Cl₂) 147-150 °C. ¹H-NMR (400 MHz, CDCl₃) δ 7.40 (t, J = 7.6 Hz, ArH, 1 H), 7.46 (dt, J = 7.6, 1.2 Hz, ArH, 1 H), 7.64 (ddd, J = 7.6, 1.6, 1.2 Hz, ArH, 1 H), 7.68 (t, J = 7.6, 1.6 Hz, ArH, 1 H), 7.99 (d, J = 9.0 Hz, ArH, 1 H), 8.02-8.09 (m, ArH, 2 H), 8.12 (d, J = 9.0 Hz, ArH, 1 H), 8.17 (d, J = 9.6 Hz, ArH, 1 H), 8.20-8.28 (m, ArH, 2 H), 8.51 (d. J = 9.2 Hz, ArH, 1 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 100.9 (ArC), 121.8 (ArC), 123.5 (ArC), 124.4 (ArC), 125.6 (ArC), 125.7 (ArC), 126.0 (ArC), 126.5 (ArC), 126.8 (ArC), 128.5 (ArC), 128.7 (ArC), 129.4 (ArC), 129.9 (ArC), 130.7 (ArC), 130.8 (ArC), 131.0 (ArC), 131.2 (ArC), 132.2 (ArC), 132.9 (ArC), 133.3 (ArC), 143.8 (ArC), 148.0 (ArC) ppm; IR ν max (neat/cm⁻¹): 3046, 2924, 2853, 1587, 1558, 1473, 1422; HRMS calcd for C₂₂H₁₂BrI [M⁺]: 481.9162, found 481.9155.

1-Iodo-2-(3-chlorophenyl)pyrene (4i)

Prepared according to general procedure B using 3i (36 mg, 0.100 mmol). The crude product was purified by silica flash column chromatography (hexane) to yield the title product as a pale yellow...
solid (30 mg, 68%), mp (CH₂Cl₂) 135-138 °C. ¹H-NMR (400 MHz, CDCl₃) δ 7.40 (dt, J = 6.6, 2.0 Hz, ArH, 1 H), 7.43-7.50 (m, ArH, 2 H), 7.50-7.53 (m, ArH, 1 H), 7.99 (d, J = 9.0 Hz, ArH, 1 H), 8.03-8.09 (m, ArH, 2 H), 8.12 (d, J = 9.0 Hz, ArH, 1 H), 8.18 (d, J = 9.2 Hz, ArH, 1 H), 8.21-8.28 (m, ArH, 2 H), 8.52 (d, J = 9.2 Hz, ArH, 1 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 100.9 (ArCl), 123.6 (ArC), 124.4 (ArC), 125.6 (ArCH), 125.7 (ArCH), 126.0 (ArCH), 126.6 (ArCH), 126.8 (ArCH), 127.8 (ArCH), 128.3 (ArCH), 128.5 (ArCH), 129.1 (ArCH), 129.9 (ArCH), 130.0 (ArCH), 130.8 (ArC), 130.8 (ArC), 131.0 (ArC), 132.3 (ArCH), 133.3 (ArC), 133.7 (ArC), 143.9 (ArC), 147.7 (ArC) ppm; IR νmax (neat/cm⁻¹): 3046, 2925, 1587, 1563, 1474, 1422; HRMS calcd for C₂₂H₁₂ClI [M]⁺: 437.9667, found 437.9660.

1-Iodo-2-(3,5-dichlorophenyl)pyrene (4j)

Prepared according to general procedure B using 3j (39 mg, 0.100 mmol). The crude product was purified by silica flash column chromatography (hexane) to yield the title product as an off-white solid (19 mg, 42%), mp (CH₂Cl₂) 175-178 °C. ¹H-NMR (500 MHz, CDCl₃) δ 7.41 (d, J = 1.5 Hz, ArH, 2 H), 7.50 (bs, ArH, 1 H), 8.00 (d, J = 8.8 Hz, ArH, 1 H), 8.04 (s, ArH, 1 H), 8.07 (t, J = 7.5 Hz, ArH, 1 H), 8.15 (d, J = 8.8 Hz, ArH, 1 H), 8.20 (d, J = 9.5 Hz, ArH, 1 H), 8.23-8.29 (m, ArH, 2 H), 8.52 (d, J = 9.5 Hz, ArH, 1 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 100.3 (ArCl), 123.5 (ArC), 124.6 (ArC), 125.4 (ArCH), 125.9 (ArCH), 126.1 (ArCH), 126.7 (ArCH), 126.8 (ArCH), 127.8 (ArCH), 128.6 (ArCH), 128.8 (ArCH), 130.1 (ArCH), 130.9 (ArC), 130.9 (ArC), 131.1 (ArC), 132.2 (ArCH), 133.4 (ArC), 134.4 (ArCCl), 142.6 (ArC), 148.6 (ArC) ppm; IR νmax (neat/cm⁻¹): 2923, 1584, 1558, 1411, 1097; HRMS calcd for C₂₂H₁₁ClI [M]⁺: 471.9277, found 471.9277.

2-(3,5-Bis(trifluoromethyl)phenyl)-1-iodopyrene (4k)

Prepared according to general procedure B using 3k (46 mg, 0.100 mmol). The crude product was purified by silica flash column chromatography (hexane/CH₂Cl₂; 100:0 to 70:30) to yield the title product as an off-white solid (21 mg, 39%), mp (CH₂Cl₂) 220-222 °C. ¹H-NMR (400 MHz, CDCl₃) δ 8.02 (s, ArH, 3 H), 8.06 (d, J = 8.8 Hz, ArH, 1 H), 8.09-8.14 (m, ArH, 2 H), 8.20 (d, J = 8.8 Hz, ArH, 1 H), 8.24-8.35 (m, ArH, 3 H), 8.55 (d, J = 9.2 Hz, ArH, 1 H) ppm; ¹³C-NMR (100 MHz, CDCl₃) δ 100.1 (ArCl), 121.5 (hept, J = 3.8 Hz, ArCH), 123.4 (hept, J = 271.2 Hz, ArCCF₃), 123.5 (ArC), 124.8 (ArC), 125.5 (ArCH), 126.0 (ArCH), 126.3 (ArCH), 126.7 (ArCH), 126.9 (ArCH), 129.0 (ArCH), 130.4 (ArCH), 130.4 (m, ArCH), 130.9 (ArC), 131.1 (ArC), 131.2 (ArC), 131.3 (q, J = 33.2 Hz, ArCCF₃), 132.1 (ArCH), 133.6 (ArC), 142.1 (ArC), 147.7 (ArC), ppm; ¹⁹F-NMR (376 MHz,
CDCl₃ δ −62.7 ppm; IR ν max (neat/cm⁻¹): 2921, 1375, 1278, 1172, 1117; HRMS calcd for C₂₃H₁₂F₃I [M⁺]: 539.9804, found 539.9781.

1-Iodo-2-(3-nitrophenyl)pyrene (4l)

Prepared according to general procedure B using 3l (37 mg, 0.100 mmol). The crude product was purified by silica flash column chromatography (hexane/CH₂Cl₂, 100:0 to 85:15) to yield the title product as a yellow solid (12 mg, 26%). mp (CH₂Cl₂) 195-198 °C. ¹H-NMR (400 MHz, CDCl₃) δ 7.71 (t, J = 7.8 Hz, ArH, 1 H), 7.87 (d, J = 7.8 Hz, ArH, 1 H), 8.04 (d, J = 9.2 Hz, ArH, 1 H), 8.06-8.13 (m, ArH, 2 H), 8.18 (d, J = 9.2 Hz, ArH, 1 H), 8.23 (d, J = 9.4 Hz, ArH, 1 H), 8.25-8.33 (m, ArH, 2 H), 8.34-8.40 (m, ArH, 1 H), 8.40-8.44 (m, ArH, 1 H), 8.53 (d, J = 9.4 Hz, ArH, 1 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 100.4 (ArCl), 122.7 (ArCH), 123.6 (ArC), 124.7 (ArC), 125.0 (ArCH), 125.6 (ArCH), 126.0 (ArCH), 126.3 (ArCH), 126.8 (ArCH), 126.8 (ArCH), 128.9 (ArCH), 128.9 (ArCH), 130.2 (ArC), 130.9 (ArC), 131.1 (ArC), 131.2 (ArC), 132.2 (ArCH), 133.6 (ArC), 136.3 (ArCH), 142.8 (ArC), 147.5 (ArC), 147.9 (ArC) ppm; IR ν max (neat/cm⁻¹): 2922, 2854, 1525, 1350; HRMS calcd for C₂₃H₁₂O₂NI [M⁺]: 448.9907, found 448.9898.

1-Iodo-2-(4-methoxyphenyl)pyrene (4m)

Prepared according to general procedure B using 3m (39 mg, 0.100 mmol). The crude product was purified by silica flash column chromatography (hexane) to yield the title product as an off-white solid (33 mg, 71%). mp (CH₂Cl₂) 120-123 °C. ¹H-NMR (400 MHz, CDCl₃) δ 7.66 (t, J = 7.6 Hz, ArH, 1 H), 7.72 (d, J = 7.6 Hz, ArH, 1 H), 7.77 (d, J = 7.6 Hz, ArH, 1 H), 7.81 (s, ArH, 1 H), 8.02 (d, J = 9.0 Hz, ArH, 1 H), 8.05-8.12 (m, ArH, 2 H), 8.15 (d, J = 9.0 Hz, ArH, 1 H), 8.20 (d, J = 9.2 Hz, ArH, 1 H), 8.22-8.31 (m, ArH, 2 H), 8.54 (d, J = 9.2 Hz, ArH, 1 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 100.9 (ArCl), 123.6 (ArC), 124.2 (q, J = 270.7 Hz, ArCCl₃), 124.4 (q, J = 3.8 Hz, ArCH), 124.5 (ArC), 125.7 (ArCH), 125.8 (ArCH), 126.1 (ArCH), 126.6 (ArCH), 126.8 (ArCH), 126.9 (q, J = 3.8 Hz, ArCH), 128.4 (ArCH), 128.7 (ArCH), 129.9 (ArCH), 130.3 (q, J = 32.2 Hz, ArCCF₃), 130.9 (ArC), 130.9 (ArC), 131.1 (ArC), 132.3 (ArCH), 133.4 (q, J = 1.2 Hz, ArCH), 133.4 (ArC), 143.8 (ArCH), 146.7 (ArC) ppm; ¹⁹F-NMR (471 MHz, DMSO-d₆) δ −62.4 ppm; IR ν max (neat/cm⁻¹): 3046, 1587, 1420, 1343, 1329, 1165, 1123; HRMS calcd for C₂₃H₁₂F₃I [M⁺]: 471.9930, found 471.9926.
1-Iodo-2-(3-cyanophenyl)pyrene (4n)

Prepared according to general procedure B using 3n (35 mg, 0.100 mmol). The crude product was purified by silica flash column chromatography (hexane/CH2Cl2, 100:0 to 70:30) to yield the title product as a pale yellow solid (17 mg, 40%). {H-NMR (500 MHz, CDCl3) δ 7.64 (t, J = 7.8 Hz, ArH, 1 H), 7.74-7.83 (m, ArH, 3 H), 8.03 (d, J = 8.8 Hz, ArH, 1 H), 8.05-8.11 (m, ArH, 2 H), 8.17 (d, J = 8.8 Hz, ArH, 1 H), 8.23 (d, J = 9.2 Hz, ArH, 1 H), 8.25-8.32 (m, ArH, 2 H), 8.54 (d, J = 9.2 Hz, ArH, 1 H) ppm; 13C-NMR (100 MHz, CDCl3) δ 100.5 (ArCl), 112.2 (ArC), 118.8 (ArCN), 123.5 (ArC), 124.6 (ArC), 125.5 (ArCH), 125.9 (ArCH), 126.2 (ArCH), 126.7 (ArCH), 126.8 (ArCH), 128.8 (ArCH), 130.2 (ArCH), 130.8 (ArC), 131.0 (ArC), 131.1 (ArC), 131.3 (ArCH), 132.1 (ArCH), 133.5 (ArCH + ArC), 134.5 (ArCH), 142.9 (ArC), 147.1 (ArC) ppm; IR νmax (neat/cm−1): 3046, 2923, 2228, 1579, 1481, 1414, 1263, 1007; HRMS calcd for C23H12Ni [M]+: 429.0009, found 429.0018.

1-Iodo-2-(3-(methoxycarbonyl)phenyl)pyrene (4o)

Prepared according to general procedure B using 3o (38 mg, 0.100 mmol). The crude product was purified by silica flash column chromatography (hexane/CH2Cl2, 100:0 to 50:50) to yield the title product as an off-white solid (32 mg, 69%). {H-NMR (400 MHz, CDCl3) δ 3.97 (s, CO2CH3, 3 H), 7.61 (t, J = 7.6 Hz, ArH, 1 H), 7.73 (d, J = 7.6 Hz, ArH, 1 H), 8.01 (d, J = 8.8 Hz, ArH, 1 H), 8.06 (t, J = 7.6 Hz, ArH, 1 H), 8.10 (1, ArH, 1 H), 8.13 (d, J = 8.8 Hz, ArH, 1 H), 8.16-8.30 (m, ArH, 5 H), 8.53 (d, J = 9.2 Hz, ArH, 1 H) ppm; 13C-NMR (125 MHz, CDCl3) δ 52.2 (CO2CH3), 101.1 (ArCl), 123.6 (ArC), 124.4 (ArC), 125.7 (ArCH), 125.8 (ArCH), 126.0 (ArCH), 126.5 (ArCH), 126.9 (ArCH), 128.0 (ArCH), 128.5 (ArCH), 128.8 (ArCH), 129.9 (ArCH), 130.8 (ArC), 130.9 (ArC), 131.0 (ArCH), 131.1 (ArC), 132.3 (ArCH), 133.4 (ArC), 134.5 (ArCH), 144.3 (ArC), 146.3 (ArC), 167.0 (CO2CH3) ppm; IR νmax (neat/cm−1): 3035, 2949, 1720, 1583, 1436, 1281, 1258; HRMS calcd for C32H16O2I [M+H]+: 463.0189, found 463.0181.

1-Iodo-2-(4-(methoxycarbonyl)phenyl)pyrene (4p)
Prepared according to general procedure B using 3p (100 mg, 0.263 mmol). The crude product was purified by silica flash column chromatography (hexane/CH₂Cl₂, 100:0 to 40:60) to yield the title product as a pale yellow solid (45 mg, 37%). ¹H-NMR (500 MHz, CDCl₃) δ 4.01 (s, CO₂CH₃, 3 H), 7.60 (d, J = 8.0 Hz, ArH, 2 H), 8.04 (d, J = 8.8 Hz, ArH, 1 H), 8.06-8.11 (m, ArH, 2 H), 8.16 (d, J = 8.8 Hz, ArH, 1 H), 8.19-8.24 (m, ArH, 3 H), 8.25 (d, J = 7.5 Hz, ArH, 1 H), 8.29 (d, J = 7.5 Hz, ArH, 1 H), 8.55 (d, J = 9.5 Hz, ArH, 1 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 52.2 (CO₂CH₃), 100.5 (ArCl), 123.7 (ArC), 124.5 (ArC), 125.5 (ArCH), 125.8 (ArCH), 126.1 (ArCH), 126.9 (ArCH), 128.6 (ArCH), 129.3 (ArCH), 129.4 (ArC), 130.0 (ArCH), 130.1 (ArCH), 130.9 (ArC), 131.1 (ArC), 132.3 (ArCH), 133.4 (ArC), 144.5 (ArC), 150.6 (ArC), 167.0 (CO₂CH₃) ppm; IR νₘₐₓ (neat/cm⁻¹): 3046, 2946, 1720, 1608, 1434, 1275, 1116, 1099; HRMS calcd for C₂₃H₁₆O₂I [M+H]⁺: 463.0189, found 463.0186.

General Procedure C: Palladium catalysed decarboxylative ortho-arylation of pyrene-1-carboxylic acid

2-(3,5-Dimethylphenyl)pyrene (5a)

A microwave vial fitted with a Teflon-coated stirring bar was loaded with pyrene-1-carboxylic acid (50 mg, 0.203 mmol), PEPPSI-IPr (2.8 mg, 4.06 μmol), Ag₂CO₃ (56 mg, 0.203 mmol), 5-iodo-orthoxylene (88 μL, 0.609 mmol) and acetic acid (0.2 mL). The vial was sealed under air and the mixture was stirred at 150 °C for 19 h. After cooling to room temperature the reaction mixture was diluted with CH₂Cl₂ and filtered through a short plug of Celite. The crude product was purified by silica flash column chromatography (hexane/CH₂Cl₂, 100:0 to 98:2) to yield the title product as a yellow solid (38 mg, 61%), mp (CH₂Cl₂) 140-143 °C. ¹H-NMR (400 MHz, CDCl₃) δ 2.49 (s, CH₃, 6 H), 7.10 (s, ArH, 1 H), 7.53 (s, ArH, 2 H), 8.01 (t, J = 7.6 Hz, ArH, 1 H), 8.11 (d, J = 9.0 Hz, ArH, 2 H), 8.14 (d, J = 9.0 Hz, ArH, 2 H), 8.20 (d, J = 7.6 Hz, ArH, 2 H), 8.40 (s, ArH, 2 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 21.5 (CH₃), 123.8 (ArCH), 123.8 (ArC), 124.6 (ArC), 125.0 (ArCH), 125.8 (ArCH), 126.0 (ArCH), 127.5 (ArCH), 127.7 (ArCH), 129.0 (ArCH), 131.1 (ArC), 131.5 (ArC), 138.5 (ArC), 139.1 (ArC), 141.5 (ArC) ppm; IR νₘₐₓ (neat/cm⁻¹):3037, 2914, 1598, 1440, 877, 848, 841, 819 ; HRMS calcd for C₂₃H₁₆O₂I [M+H]⁺: 307.1481, found 307.1473.

2-(4-Methylphenyl)pyrene (5b)

Prepared according to general procedure C using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and 4-iodotoluene (133 mg, 0.609 mmol). The crude product was purified by silica flash column chromatography (hexane/CH₂Cl₂, 100:0 to 98:2) to yield the title product as a yellow solid (64 mg, 41%). ¹H-NMR (400 MHz, CDCl₃) δ 2.49 (s, CH₃, 6 H), 7.06 (d, J = 8.0 Hz, ArH, 2 H), 8.04 (d, J = 8.8 Hz, ArH, 1 H), 8.06-8.11 (m, ArH, 2 H), 8.16 (d, J = 8.8 Hz, ArH, 1 H), 8.19-8.24 (m, ArH, 3 H), 8.25 (d, J = 7.5 Hz, ArH, 1 H), 8.29 (d, J = 7.5 Hz, ArH, 1 H), 8.55 (d, J = 9.5 Hz, ArH, 1 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 52.2 (CO₂CH₃), 100.5 (ArCl), 123.7 (ArC), 124.5 (ArC), 125.5 (ArCH), 125.8 (ArCH), 126.1 (ArCH), 126.9 (ArCH), 128.6 (ArCH), 129.3 (ArCH), 129.4 (ArC), 130.0 (ArCH), 130.1 (ArCH), 130.9 (ArC), 131.1 (ArC), 132.3 (ArCH), 133.4 (ArC), 144.5 (ArC), 150.6 (ArC), 167.0 (CO₂CH₃) ppm; IR νₘₐₓ (neat/cm⁻¹):3046, 2946, 1720, 1608, 1434, 1275, 1116, 1099; HRMS calcd for C₂₃H₁₈I [M+H]⁺: 430.0893, found 430.0886.

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chromatography (hexane/CH\textsubscript{2}Cl\textsubscript{2}, 100:0 to 98:2) to yield the title product as a bright yellow solid (30 mg, 51%), mp (CH\textsubscript{2}Cl\textsubscript{2}) 110-114 °C. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 2.48 (s, CH\textsubscript{3}, 3 H), 7.38 (d, \(J = 7.4\) Hz, ArH, 2 H), 7.81 (d, \(J = 7.4\) Hz, ArH, 2 H), 8.01 (t, \(J = 7.8\) Hz, ArH, 1 H), 8.11 (d, \(J = 8.8\) Hz, ArH, 2 H), 8.14 (d, \(J = 8.8\) Hz, ArH, 2 H), 8.20 (d, \(J = 7.8\) Hz, ArH, 2 H), 8.40 ppm; \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 21.2 (CH\textsubscript{3}), 123.5 (ArCH), 123.7 (ArC), 124.6 (ArC), 125.1 (ArCH), 125.8 (ArCH), 127.5 (ArCH), 127.7 (ArCH), 127.9 (ArCH), 129.7 (ArCH), 131.1 (ArC), 131.5 (ArC), 132.7 (ArC), 138.6 (ArC), 138.8 (ArC) ppm; IR \(\nu_{\text{max}}\) (neat/cm\textsuperscript{-1}): 3039, 2920, 2853, 1601, 1513, 1441, 1178, 882, 825; HRMS calcd for C\textsubscript{23}H\textsubscript{17} [M+H]\textsuperscript{+}: 293.1325, found 293.1315.

2-(3-Methylphenyl)pyrene (5c)

![2-(3-Methylphenyl)pyrene (5c)](image)

Prepared according to general procedure C using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and 3-iodotoluene (78 \(\mu\)L, 0.609 mmol). The crude product was purified by silica flash column chromatography (hexane/CH\textsubscript{2}Cl\textsubscript{2}, 100:0 to 98:2) to yield the title product as a bright yellow solid (30 mg, 51%), mp (CH\textsubscript{2}Cl\textsubscript{2}) 118-121 °C. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 2.53 (s, CH\textsubscript{3}, 3 H), 7.26-7.30 (m, ArH, 1 H), 7.47 (t, \(J = 7.6\) Hz, ArH, 1 H), 7.68-7.75 (m, ArH, 2 H), 8.02 ppm; \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 21.6 (CH\textsubscript{3}), 123.5 (ArCH), 123.7 (ArC), 123.8 (ArC), 124.6 (ArC), 125.2 (ArC), 125.3 (ArC), 127.6 (ArC), 127.7 (ArC), 128.2 (ArC), 128.9 (ArCH), 131.1 (ArC), 131.5 (ArC), 138.6 (ArC), 139.0 (ArC), 141.5 (ArC) ppm; IR \(\nu_{\text{max}}\) (neat/cm\textsuperscript{-1}): 3039, 2923, 2852, 1601, 1491, 1442, 1178; HRMS calcd for C\textsubscript{23}H\textsubscript{17} [M+H]\textsuperscript{+}: 293.1325, found 293.1316.

2-(4-tert-Butylphenyl)pyrene (5d)

![2-(4-tert-Butylphenyl)pyrene (5d)](image)

Prepared according to general procedure C using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and 4-tert-butyliodobenzene (110 \(\mu\)L, 0.609 mmol). The crude product was purified by silica flash column chromatography (hexane/CH\textsubscript{2}Cl\textsubscript{2}, 100:0 to 90:10) to yield the title product as a bright yellow solid (35 mg, 52%), mp (CH\textsubscript{2}Cl\textsubscript{2}) 188-190 °C. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 1.43 (s, C(CH\textsubscript{3})\textsubscript{3}, 9 H), 7.60 (d, \(J = 8.4\) Hz, ArH, 2 H), 7.85 (d, \(J = 8.4\) Hz, ArH, 2 H), 8.01 (t, \(J = 7.4\) Hz, ArH, 1 H), 8.11 (d, \(J = 8.8\) Hz, ArH, 2 H), 8.14 ppm; \textsuperscript{13}C-NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 21.2 (CH\textsubscript{3}), 31.4 (C(CH\textsubscript{3})\textsubscript{3}), 34.6 (C(CH\textsubscript{3})\textsubscript{3}), 123.6 (ArCH), 123.8 (ArC), 124.6 (ArC), 125.1 (ArCH), 125.8 (ArCH), 126.0 (ArCH), 127.5 (ArCH), 127.7 (ArCH), 131.1 (ArC), 138.6 (ArC), 138.7 (ArC), 150.5 (ArC) ppm; IR \(\nu_{\text{max}}\) (neat/cm\textsuperscript{-1}): 3039, 2962, 2904, 1600, 1511, 1464, 1370, 1360, 879, 831; HRMS calcd for C\textsubscript{29}H\textsubscript{23} [M+H]\textsuperscript{+}: 335.1794, found 335.1790.
2-(4-methoxyphenyl)pyrene (5e)

Prepared according to general procedure C using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and 4-iodoanisole (143 mg, 0.609 mmol). The crude product was purified by silica flash column chromatography (hexane/CH$_2$Cl$_2$, 100:0 to 88:12) to yield the title product as a yellow solid (30 mg, 48%), mp (CH$_2$Cl$_2$) 145–148 ºC. $^1$H-NMR (400 MHz, CDCl$_3$) δ 3.92 (s, OCH$_3$, 3 H), 7.11 (d, $J = 8.6$ Hz, ArH, 2 H), 7.84 (d, $J = 8.6$ Hz, ArH, 2 H), 8.01 (t, $J = 7.8$ Hz, ArH, 1 H), 8.07–8.15 (m, ArH, 4 H), 8.19 (d, $J = 7.8$ Hz, ArH, 2 H), 8.37 (s, ArH, 2 H) ppm; $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 55.4 (OCH$_3$), 114.4 (ArC), 115.9 (OCH$_3$), 123.2 (ArCH), 123.5 (ArC), 124.6 (ArC), 125.0 (ArCH), 125.7 (ArCH), 127.5 (ArCH), 127.7 (ArCH), 129.0 (ArCH), 131.0 (ArC), 131.5 (ArC), 133.9 (ArC), 138.5 (ArC), 159.3 (ArC) ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 3036, 3931, 1605, 1514, 1283, 1251, 1115; HRMS calcd for C$_{23}$H$_{17}$O $[\text{M+H}]^+$: 309.1274, found 309.1267.

2-Phenylpyrene (5f)

Prepared according to general procedure C using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and iodobenzene (68 µL, 0.609 mmol). The crude product was purified by silica flash column chromatography (hexane/CH$_2$Cl$_2$, 100:0 to 98:2) to yield the title product as a yellow solid (25 mg, 44%), mp (CH$_2$Cl$_2$) 158-162 ºC. $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.46 (t, $J = 7.3$ Hz, ArH, 1 H), 7.58 (t, $J = 7.3$ Hz, ArH, 2 H), 7.91 (d, $J = 7.3$ Hz, ArH, 2 H), 8.03 (t, $J = 7.8$ Hz, ArH, 1 H), 8.12 (d, $J = 9.2$ Hz, ArH, 2 H), 8.15 (d, $J = 9.2$ Hz, ArH, 2 H), 8.21 (d, $J = 7.8$ Hz, ArH, 2 H), 8.42 (s, ArH, 2 H) ppm; $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 123.7 (ArCH), 123.9 (ArC), 124.6 (ArC), 125.1 (ArCH), 125.9 (ArCH), 127.4 (ArCH), 127.5 (ArCH), 127.8 (ArCH), 128.1 (ArCH), 131.1 (ArC), 131.5 (ArC), 138.9 (ArC), 141.5 (ArC) ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 3041, 2926, 1597, 1495, 1441, 1419, 881, 842, 823; HRMS calcd for C$_{22}$H$_{15}$ [M+H]$^+$: 279.1168, found 279.1159.

2-(4-Bromophenyl)pyrene (5g)

Prepared according to general procedure C using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and 4-bromoiodobenzene (172 mg, 0.609 mmol). The crude product was purified by silica flash column...
chromatography (hexane/CH$_2$Cl$_2$, 100:0 to 98:2) to yield the title product as a bright yellow solid (46 mg, 63%). $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.69 (d, $J = 8.4$ Hz, ArH, 2 H), 7.77 (d, $J = 8.4$ Hz, ArH, 2 H), 8.03 (t, $J = 7.6$ Hz, ArH, 4 H), 8.13 (s, ArH, 4 H), 8.21 (d, $J = 7.6$ Hz, ArH, 2 H), 8.36 (s, ArH, 2 H) ppm; $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 121.8 (ArC), 123.3 (ArC, H), 124.0 (ArC), 124.5 (ArC), 125.3 (ArCH), 126.0 (ArCH), 127.4 (ArCH), 128.0 (ArCH), 129.6 (ArCH), 131.1 (ArC), 131.6 (ArC), 132.1 (ArCH), 137.6 (ArC) ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 3040, 2922, 1602, 1491, 1440, 1179, 1074, 1008, 883, 841, 828; HRMS calcd for C$_{22}$H$_{14}$Br [M+H]$^+$: 357.0273, found 357.0266.

2-(3-Bromophenyl)pyrene (5h)

Prepared according to general procedure C using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and 3-bromoiodobenzene (78 µL, 0.609 mmol). The crude product was purified by silica flash column chromatography (hexane/CH$_2$Cl$_2$, 100:0 to 98:2) to yield the title product as a bright yellow solid (32 mg, 44%). $^1$H-NMR (500 MHz, CDCl$_3$) δ 7.43 (t, $J = 7.8$ Hz, ArH, 1 H), 7.58 (d, $J = 7.8$ Hz, ArH, 1 H), 7.82 (d, $J = 7.8$ Hz, ArH, 1 H), 8.01-8.07 (m, ArH, 2 H), 8.09-8.16 (m, ArH, 2 H), 8.21 (d, $J = 7.8$ Hz, ArH, 2 H), 8.36 (s, ArH, 2 H) ppm; $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 123.1 (ArC), 123.5 (ArC, H), 124.1 (ArC), 124.4 (ArC), 125.3 (ArCH), 126.1 (ArCH), 126.6 (ArCH), 127.4 (ArCH), 128.0 (ArCH), 130.3 (ArCH), 130.5 (ArCH), 131.0 (ArCH), 131.1 (ArC), 131.6 (ArC), 134.3 (ArC) ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 3040, 2921, 1593, 1560, 1480, 1439, 871, 841; HRMS calcd for C$_{22}$H$_{14}$Br [M+H]$^+$: 357.0273, found 357.0267.

2-(3-Chlorophenyl)pyrene (5i)

Prepared according to general procedure C using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and 3-chloroiodobenzene (75 µL, 0.609 mmol). The crude product was purified by silica flash column chromatography (hexane/CH$_2$Cl$_2$, 100:0 to 98:2) to yield the title product as a bright yellow solid (35 mg, 55%). $^1$H-NMR (500 MHz, CDCl$_3$) δ 7.42 (ddd, $J = 7.6$, 2.0, 1.0 Hz, ArH, 1 H), 7.49 (t, $J = 7.6$ Hz, ArH, 1 H), 7.77 (d, $J = 7.6$ Hz, ArH, 1 H), 7.89 (s, ArH, 1 H), 8.03 (t, $J = 7.3$ Hz, ArH, 1 H), 8.07-8.17 (m, ArH, 4 H), 8.21 (d, $J = 7.3$ Hz, ArH, 2 H), 8.37 (s, ArH, 2 H) ppm; $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 123.5 (ArCH), 124.1 (ArC), 124.4 (ArC), 125.3 (ArCH), 126.1 (ArCH), 126.6 (ArCH), 127.4 (ArCH), 128.0 (ArCH), 130.1 (ArCH), 130.5 (ArCH), 131.0 (ArCH), 131.1 (ArC), 131.6 (ArC), 134.8 (ArC) ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 3040, 2923, 1594, 1565, 1440, 871, 841; HRMS calcd for C$_{22}$H$_{13}$Cl [M]$^+$: 312.0700, found 312.0700.
2-(3,5-Dichlorophenyl)pyrene (5j)

Prepared according to general procedure C using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and 3,5-dichloroiodobenzene (166 mg, 0.609 mmol). The crude product was purified by silica flash column chromatography (hexane) to yield the title product as a yellow solid (40 mg, 57%), mp (CH$_2$Cl$_2$) 200-203 ºC. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (bs, ArH, 1 H), 7.77 (d, $J$ = 1.2 Hz, ArH, 2 H), 8.05 (t, $J$ = 7.6 Hz, ArH, 1 H), 8.10-8.18 (m, ArH, 4 H), 8.23 (d, $J$ = 7.6 Hz, ArH, 2 H), 8.34 (s, ArH, 2 H) ppm; $^{13}$C-NMR (125 MHz, CDCl$_3$) $\delta$ 123.3 (ArC$_H$), 124.4 (ArC$_H$), 124.4 (ArC$_H$), 125.4 (ArCH), 126.3 (ArCH), 126.5 (ArCH), 127.3 (ArCH), 127.3 (ArCH), 128.2 (ArCH), 131.2 (ArC), 131.7 (ArC), 135.4 (ArC), 136.0 (ArC), 144.6 (ArC) ppm; IR $\nu_{max}$ (neat/cm$^{-1}$): 3033, 1588, 1559, 1426, 1411, 849; HRMS calcd for C$_{22}$H$_{13}$Cl$_2$[M+H]$^+$: 347.0389, found 347.0387.

Alternatively, the product was prepared by decarboxylation of 3i in the following manner: A microwave vial fitted with a Teflon-coated stirring bar was loaded with 3i (20 mg, 43.6 µmol), Ag$_2$CO$_3$ (12 mg, 43.6 µmol) and dry DMSO (620 µL). The vial was sealed under air and the resulting mixture was stirred at 140 ºC for 15 h. After cooling to room temperature the mixture was loaded into a silica column and eluted with hexane. The title compound was obtained as an off-white solid (12 mg, 66%). Analysis of the product showed the same spectroscopic data as the detailed above.

2-(3,5-Bis(trifluoromethyl)phenyl)pyrene (5k)

Prepared according to general procedure C using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and 3,5-bis(trifluoromethyl)iodobenzene (108 µL, 0.609 mmol). The crude product was purified by silica flash column chromatography (hexane) to yield the title product as an off-white solid (10 mg, 12%), mp (CH$_2$Cl$_2$) 210-213 ºC. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (bs, ArH, 1 H), 8.07 (t, $J$ = 8.0 Hz, ArH, 1 H), 8.14-8.19 (m, ArH, 4 H), 8.39 (s, ArH, 2 H) ppm; $^{13}$C-NMR (125 MHz, CDCl$_3$) $\delta$ 121.0 (hept, $J$ = 3.9 Hz, ArCH), 123.3 (ArCH), 123.5 (q, $J$ = 271.0 Hz, ArCCF$_3$), 124.3 (ArC), 124.5 (ArC), 125.6 (ArCH), 126.4 (ArCH), 127.2 (ArCH), 128.1 (q, $J$ = 2.6 Hz, ArCH), 128.5 (ArCH), 131.2 (ArC), 131.8 (ArC), 132.3 (q, $J$ = 33.0 Hz, ArCCF$_3$), 135.6 (ArC), 143.7 (ArC) ppm; $^{19}$F-NMR (471 MHz, CDCl$_3$) –62.7 ppm; IR $\nu_{max}$ (neat/cm$^{-1}$): 2922, 1375, 1276, 1161, 1123; HRMS calcd for C$_{24}$H$_{13}$F$_6$[M+H]$^+$: 415.0916, found 415.0910.

Alternatively, the product was prepared by decarboxylation of 3i in the following manner: A microwave vial fitted with a Teflon-coated stirring bar was loaded with 3i (20 mg, 43.6 µmol), Ag$_2$CO$_3$ (12 mg, 43.6 µmol) and dry DMSO (620 µL). The vial was sealed under air and the resulting mixture was stirred at 140 ºC for 15 h. After cooling to room temperature the mixture was loaded into a silica column and eluted with hexane. The title compound was obtained as an off-white solid (12 mg, 66%). Analysis of the product showed the same spectroscopic data as the detailed above.
2-(3-nitrophenyl)pyrene (5l)

Prepared according to general procedure C using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and 3-iodonitrobenzene (152 mg, 0.609 mmol). The crude product was purified by silica flash column chromatography (hexane/CH$_2$Cl$_2$, 100:0 to 70:30) to yield the title product as a bright yellow solid (26 mg, 40%), mp (CH$_2$Cl$_2$) 222-224 ºC. $^1$H-NMR (500 MHz, CDCl$_3$) δ 7.74 (t, $J = 8.0$ Hz, ArH, 1 H), 8.06 (t, $J = 7.5$ Hz, ArH, 1 H), 8.16 (s, ArH, 4 H), 8.20-8.27 (m, ArH, 3 H), 8.30 (d, $J = 8.0$ Hz, ArH, 1 H), 8.42 (s, ArH, 1 H) ppm; $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 122.1 (ArC$_H$), 122.8 (ArC$_H$), 123.4 (ArC$_H$), 124.3 (ArC), 124.4 (ArC), 125.5 (ArCH), 126.3 (ArCH), 127.3 (ArCH), 128.3 (ArCH), 129.9 (ArCH), 131.2 (ArC), 131.8 (ArC), 133.9 (ArCH), 136.1 (ArC), 143.3 (ArC), 148.9 (ArC) ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 3043, 1525, 1346, 1311, 870; HRMS calcd for C$_{22}$H$_{14}$O$_2$N [M+H]$^+$: 324.1019, found 324.1016.

2-(3-trifluoromethylphenyl)pyrene (5m)

Prepared according to general procedure C using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and 3-trifluoromethyliodobenzene (88 µL, 0.609 mmol). The crude product was purified by silica flash column chromatography (hexane) to yield the title product as a yellow solid (29 mg, 41%), mp (CH$_2$Cl$_2$) 128-131 ºC. $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.64-7.76 (m, ArH, 2 H), 8.00-8.07 (m, ArH, 2 H), 8.08-8.18 (m, ArH, 5 H), 8.21 (d, $J = 7.8$ Hz, ArH, 2 H), 8.37 (s, ArH, 2 H) ppm; $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 123.5 (ArCH), 124.1 (q, $J = 3.8$ Hz, ArCH), 124.2 (ArC), 124.3 (q, $J = 270.8$ Hz, ArCCF$_3$), 124.4 (ArC), 124.8 (q, $J = 3.8$ Hz, ArCH), 125.3 (ArCH), 126.2 (ArCH), 127.4 (ArCH), 128.1 (ArCH), 129.4 (ArCH), 131.1 (ArC), 131.3 (q, $J = 1.2$ Hz, ArCH), 131.4 (q, $J = 32.0$ Hz, ArCCF$_3$), 131.7 (ArC), 137.2 (ArC), 142.3 (ArC) ppm; $^{19}$F-NMR (471 MHz, CDCl$_3$) –62.4 ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 3041, 1598, 1435, 1336, 1292, 1165, 1122; HRMS calcd for C$_{23}$H$_{14}$F$_3$ [M+H]$^+$: 347.1042, found 347.1037.

2-(3-Cyanophenyl)pyrene (5n)

A microwave vial fitted with a Teflon-coated stirring bar was loaded with 3i (20 mg, 57.6 µmol), Ag$_2$CO$_3$ (16 mg, 57.6 µmol) and dry DMSO (820 µL). The vial was sealed under air and the resulting
mixture was stirred at 140 °C for 15 h. After cooling to room temperature the mixture was loaded into a silica column and eluted with hexane/CH₂Cl₂ (80:20). The title compound was obtained as a pale yellow solid (9 mg, 52%), mp (CH₂Cl₂) 190-192 °C. ¹H-NMR (500 MHz, CDCl₃) δ 7.66 (t, J = 7.7 Hz, ArH, 1 H), 7.73 (d, J = 7.7 Hz, ArH, 1 H), 8.05 (t, J = 7.5 Hz, ArH, 1 H), 8.08-8.20 (m, ArH, 6 H), 8.23 (d, J = 7.5 Hz, ArH, 2 H), 8.35 (s, ArH, 2 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 113.2 (ArC), 118.9 (ArCN), 123.3 (ArCH), 124.3 (ArC), 124.5 (ArCH), 126.3 (ArCH), 127.3 (ArCH), 128.3 (ArCH), 129.8 (ArCH), 130.8 (ArCH), 131.2 (ArC), 131.5 (ArCH), 131.7 (ArC), 132.3 (ArCH), 136.3 (ArC), 142.8 (ArC) ppm; IR νmax (neat/cm⁻¹): 3042, 2921, 2228, 1599, 1483, 1445, 1414, 1178; HRMS calcd for C₂₃H₁₄N [M+H]⁺: 304.1121, found 304.1117.

Methyl 3-(pyren-2-yl)benzoate (5o)

![Methyl 3-(pyren-2-yl)benzoate](image)

Prepared according to general procedure C using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and methyl 3-iodobenzoate (160 mg, 0.609 mmol). The crude product was purified by silica flash column chromatography (hexane/CH₂Cl₂, 100:0 to 60:40) to yield the title product as a yellow solid (38 mg, 56%), mp (CH₂Cl₂) 145-148 °C. ¹H-NMR (400 MHz, CDCl₃) δ 4.02 (s, CO₂CH₃, 3 H), 7.62 (t, J = 7.6 Hz, ArH, 1 H), 8.02 (t, J = 7.6 Hz, ArH, 1 H), 8.05-8.15 (m, ArH, 6 H), 8.19 (d, J = 7.6 Hz, ArH, 2 H), 8.40 (s, ArH, 2 H), 8.58 (bs, ArH, 1 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 52.2 (CO₂OCH₃), 123.5 (ArCH), 124.0 (ArC), 124.4 (ArC), 125.2 (ArCH), 126.0 (ArCH), 127.4 (ArCH), 127.9 (ArCH), 128.4 (ArCH), 129.0 (ArCH), 130.8 (ArC), 131.1 (ArC), 131.5 (ArC), 132.3 (ArCH), 137.5 (ArC), 141.7 (ArC), 167.1 (CO₂OCH₃) ppm; IR νmax (neat/cm⁻¹): 3036, 2951, 1719, 1435, 1281, 1260; HRMS calcd for C₂₂H₁₆O₂ [M+H]⁺: 336.1145, found 336.1142.

Methyl 4-(pyren-2-yl)benzoate (5p)

![Methyl 4-(pyren-2-yl)benzoate](image)

Prepared according to general procedure C using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and methyl 4-iodobenzoate (160 mg, 0.609 mmol). The crude product was purified by silica flash column chromatography (hexane/CH₂Cl₂, 100:0 to 60:40) to yield the title product as a bright yellow solid (42 mg, 62%), mp (CH₂Cl₂) 168-170 °C. ¹H-NMR (500 MHz, CDCl₃) δ 4.00 (s, CO₂CH₃, 3 H), 7.98 (d, J = 8.5 Hz, ArH, 2 H), 8.04 (t, J = 7.8 Hz, ArH, 1 H), 8.13 (d, J = 9.0 Hz, ArH, 2 H), 8.15 (d, J = 9.0 Hz, ArH, 2 H), 8.19-8.27 (m, ArH, 4 H), 8.43 (s, ArH, 2 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 52.2 (CO₂CH₃), 123.6 (ArCH), 124.3 (ArC), 124.4 (ArC), 125.3 (ArCH), 126.2 (ArCH), 127.4 (ArCH), 127.9 (ArCH), 128.0 (ArCH), 129.0 (ArC), 130.3 (ArCH), 131.2 (ArC), 131.6 (ArC), 137.5 (ArC), 146.0 (ArC), 167.1 (CO₂CH₃) ppm; IR νmax (neat/cm⁻¹): 3041, 2950, 1722, 1608, 1434, 1285, 1275, 1112; HRMS calcd for C₂₃H₁₅O₂ [M+H]⁺: 337.1223, found 337.1219.
General Procedure D: Ruthenium catalysed non-decarbonylative ortho-arylation of pyrene-1-carboxylic acid

2-(Thiophen-2-yl)pyrene-1-carboxylic acid (3q)

A microwave vial fitted with a Teflon-coated stirring bar was loaded with pyrene-1-carboxylic acid (50 mg, 0.203 mmol), 2-bromothiophene (24 μL, 0.254 mmol), [Ru(p-cymene)Cl₂]₂ (5.0 mg, 0.008 mmol), PCy₃ (4.5 mg, 0.016 mmol), K₂CO₃ (28 mg, 0.203 mmol) and NMP (800 μL, 0.25 M) inside the glovebox. The vial was sealed and taken out of the glovebox. The reaction mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the reaction mixture was quenched with 2 M aqueous HCl (100 μL). Internal standard dibromomethane (0.2 mmol) was added to the crude. Aliquot of approximately 50 μL was taken out by syringe. Each aliquot was diluted with DMSO-d₆ (600 μL) and passed through a short plug of Celite into a NMR tube. The crude was monitored by quantitative ¹H NMR. The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 30:70) to yield the title product as an off white solid (30 mg, 45%), mp (CH₂Cl₂) 220-222 °C. ¹H-NMR (500 MHz, DMSO-d₆) δ 7.24 (d, J = 5.0, 3.5 Hz, ArH, 1 H), 7.50 (d, J = 3.5 Hz, ArH, 1 H), 7.74 (d, J = 5.0 Hz, ArH, 1 H), 8.09 (d, J = 10.5 Hz, ArH, 1 H), 8.12 (t, J = 7.8 Hz, ArH, 1 H), 8.23-8.31 (m, ArH, 3 H), 8.32-8.38 (m, ArH, 2 H), 8.44 (s, ArH, 1 H), 14.03 (bs, CO₂H, 1 H) ppm; ¹³C-NMR (125 MHz, DMSO-d₆) δ 123.2 (ArC), 123.8 (ArC), 124.7 (ArCH), 126.1 (ArCH), 126.3 (ArCH), 126.6 (ArCH), 127.3 (ArCH), 127.7 (ArC), 127.9 (ArCH), 128.6 (ArCH), 128.9 (ArCH), 129.0 (ArCH), 129.5 (ArCH), 130.6 (ArC), 131.2 (ArC), 131.3 (ArC), 142.0 (ArC), 171.1 (CO₂H) ppm; IR ν max (neat/cm⁻¹): 3402, 2255, 1652, 1247, 1049, 1023, 997; HRMS calcd for C₂₀H₁₅O₂S [M+H]⁺: 329.0636, found 329.0641.

2-(5-Methylthiophen-2-yl)pyrene-1-carboxylic acid (3r)

Prepared according to general procedure D using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and 2-iodo-5-methylthiophene (31 μL, 0.254 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 60:40) to yield the title product as an orange solid (24 mg, 35%), mp (CH₂Cl₂) 236-238 °C. ¹H-NMR (500 MHz, DMSO-d₆) δ 2.55 (s, CH₃, 3 H), 6.94 (d, J = 3.5 Hz, ArH, 1 H), 7.27 (d, J = 3.5 Hz, ArH, 1 H), 8.07-8.15 (m, ArH, 2 H), 8.21-8.29 (m, ArH, 2 H), 8.33 (d, J = 9.5 Hz, ArH, 1 H), 8.34-8.38 (m, ArH, 2 H), 8.39 (s, ArH, 1 H), 13.79 (bs, CO₂H, 1 H) ppm; ¹³C-NMR (125 MHz, DMSO-d₆) δ 15.4 (CH₃), 123.0 (ArC), 123.8 (ArC), 124.4 (ArCH), 125.8 (ArCH), 126.4 (ArCH), 126.7 (ArCH), 127.0 (ArCH), 127.3 (ArCH), 127.9 (ArCH), 127.5 (ArCH), 128.6 (ArCH), 129.0 (ArC), 129.2 (ArCH), 129.5 (ArC), 129.7 (ArCH), 130.5 (ArC), 131.1 (ArC), 131.5 (ArC), 139.4 (ArC), 141.5 (ArC), 171.0 (CO₂H) ppm; IR ν max (neat/cm⁻¹): 3407,
1732, 1652, 1374, 1243, 1045, 1024, 1003; HRMS calcd for C_{22}H_{15}O_{2}S [M+H]^+: 343.0793, found 343.0798.

2-(1-Methylindol-5-yl)pyrene-1-carboxylic acid (3s)

Prepared according to general procedure D using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and 5-bromo-1-methylindole (53 mg, 0.254 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 40:60) to yield the title product as an orange solid (32 mg, 42%), mp (CH_2Cl_2) >220 °C. ^1H-NMR (500 MHz, DMSO-d_6) δ 3.87 (s, CH_3, 3 H), 6.54 (d, J = 3.0 Hz, ArH, 1 H), 7.43 (d, J = 8.5 Hz, ArH, 1 H), 7.49 (d, J = 8.5 Hz, ArH, 1 H), 7.59 (d, J = 8.5 Hz, ArH, 1 H), 7.86 (s, ArH, 1 H), 8.12 (t, J = 7.8 Hz, ArH, 1 H), 8.20 (d, J = 9.5 Hz, ArH, 1 H), 8.24-8.29 (m, ArH, 2 H), 8.30-8.40 (m, ArH, 4 H), 13.45 (bs, CO_2H, 1 H) ppm; ^13C-NMR (125 MHz, DMSO-d_6) δ 33.1 (CH), 101.2 (ArCH), 110.2 (ArCH), 121.3 (ArCH), 122.6 (ArC), 123.0 (ArCH), 123.9 (ArC), 124.6 (ArCH), 126.1 (ArCH), 126.4 (ArCH), 127.0 (ArCH), 127.0 (ArCH), 127.3 (ArC), 127.7 (ArCH), 128.7 (ArC), 128.8 (ArCH), 129.2 (ArC), 130.4 (ArC), 130.5 (ArC), 130.9 (ArCH), 131.1 (ArC), 131.4 (ArC), 132.1 (ArC), 136.4 (ArC), 138.2 (ArC), 171.3 (CO_2H) ppm; IR ν_max (neat/cm^{-1}): 3402, 2255, 2129, 1652, 1149, 1023, 996;

2-(2,6-Dichloropyridin-4-yl)pyrene-1-carboxylic acid (3t)

Prepared according to general procedure D using pyrene-1-carboxylic acid (50 mg, 0.203 mmol) and 2,6-dichloro-4-iodopyridine (70 mg, 0.254 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 40:60) to yield the title product as an orange solid (46 mg, 58%), mp (CH_2Cl_2) >250 °C. ^1H-NMR (500 MHz, DMSO-d_6) δ 7.83 (s, ArH, 2 H), 8.16 (t, J = 7.8 Hz, ArH, 1 H), 8.20-8.42 (m, ArH, 6 H), 8.43 (s, ArH, 1 H), 14.00 (bs, CO_2H, 1 H) ppm; ^13C-NMR (125 MHz, DMSO-d_6) δ 123.5 (ArC), 123.9 (ArCH), 124.0 (ArC), 124.5 (ArCH), 126.2 (ArCH), 126.7 (ArCH), 127.0 (ArCH), 127.5 (ArCH), 127.7 (ArCH), 127.8 (ArC), 129.0 (ArC), 129.7 (ArCH), 130.0 (ArCH), 130.6 (ArC), 131.3 (ArC), 131.7 (ArC), 131.8 (ArC), 149.7 (ArC), 155.6 (ArC), 170.3 (CO_2H) ppm; IR ν_max (neat/cm^{-1}): 3394, 1651, 1023, 999; ESI-MS found for C_{22}H_{13}O_{2}S [M−H]: 390.0 (100%), 392.1, 394.0.
**General Procedure E: Sonogashira coupling of 2-aryl-1-iodopyrenes**

**2-(3,5-Dimethylphenyl)-1-(phenylethynyl)pyrene (6a)**

A flame dried Schlenk tube fitted with a Teflon coated stirring bar and loaded with 4a (20 mg, 46.3 μmol), PdCl₂(PPh₃)₂ (6.5 mg, 9.26 μmol) and CuI (1.8 mg, 9.26 μmol) was evacuated and refilled with N₂. Then, degassed Et₃N (1.1 mL) and phenylacetylene (15 μL, 0.139 mmol) were added and the tube was sealed under N₂ before stirring it at room temperature. After 19 h the reaction mixture was diluted with CH₂Cl₂ and filtered through Celite. The organic layer was washed with saturated aqueous NH₄Cl (2 × 3 mL) and H₂O (2 × 3 mL), dried (MgSO₄) and concentrated under reduced pressure. The crude product was purified by silica flash column chromatography (hexane/EtOAc 1:1) to yield the title product as a pale yellow solid (11 mg, 58%), mp (CH₂Cl₂) 129-132 °C. ¹H-NMR (500 MHz, CDCl₃) δ 2.49 (s, Ar(CH₃)₂), 7.15 (s, ArH, 1 H), 7.32-7.41 (m, ArH, 3 H), 7.49-7.56 (m, ArH, 4 H), 8.04 (t, J = 7.5 Hz, ArH, 1 H), 8.07 (d, J = 9.0 Hz, ArH, 1 H), 8.12 (d, J = 9.0 Hz, ArH, 1 H), 8.18-8.27 (m, ArH, 4 H), 8.82 (d, J = 9.0 Hz, ArH, 1 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 21.5 (Ar(CH₃)₂), 88.5 (C=C), 98.6 (C=C), 116.3 (ArC), 123.5 (ArC), 123.8 (ArC), 124.2 (ArC), 125.6 (ArCH), 125.8 (ArCH), 126.1 (ArCH), 126.2 (ArCH), 127.3 (ArCH), 128.1 (ArCH), 128.2 (ArCH), 128.3 (ArCH), 128.4 (ArCH), 128.6 (ArCH), 129.1 (ArC), 130.9 (ArC), 131.0 (ArC), 131.2 (ArC), 131.4 (ArCH), 132.3 (ArC), 137.3 (ArC), 141.2 (ArC), 142.3 (ArC) ppm; IR νmax (neat/cm⁻¹): 3037, 2919, 2857, 1597, 1490, 1442, 1179; HRMS calcd for C₃₂H₂₅N [M+H]+: 407.1794, found 407.1775.

**2-(3,5-Dimethylphenyl)-1-(4-trifluoromethylphenylethynyl)pyrene (6b)**

Prepared according to general procedure E using 4a (20 mg, 46.3 μmol) and 4-(trifluoromethyl)phenylacetylene (23 μL, 0.139 mmol). The crude product was purified by silica flash column chromatography (hexane) to yield the title product as a bright yellow solid (11 mg, 50%), mp (CH₂Cl₂) 145-148 °C. ¹H-NMR (400 MHz, CDCl₃) δ 2.48 (s, Ar(CH₃)₂), 6 H), 7.16 (s, ArH, 1 H), 7.50 (s, ArH, 2 H), 7.56 (d, J = 8.2 Hz, ArH, 2 H), 7.63 (d, J = 8.2 Hz, ArH, 2 H), 8.02-8.11 (m, ArH, 2 H), 8.14 (d, J = 8.8 Hz, ArH, 1 H), 8.19-8.31 (m, ArH, 4 H), 8.77 (d, J = 8.8 Hz, ArH, 1 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 21.5 (CH₃), 91.1 (C=C), 97.0 (C=C), 115.5 (ArC), 122.9 (ArC), 124.0 (q,
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J = 270.4 \text{ Hz, ArC}, 124.2 \text{ (ArC), 125.3 (q, } J = 3.8 \text{ Hz, ArCH), 125.8 \text{ (ArCH), 125.8 (ArCH), 125.8 (ArCH), 125.9 (ArCH), 126.3 (ArCH), 127.3 (ArCH), 127.6 (q, } J = 1.4 \text{ Hz, ArC), 128.1 (ArCH), 128.8 \text{ (ArCH), 128.9 (ArCH), 129.2 (ArCH), 129.7 (q, } J = 32.4 \text{ Hz, ArC), 130.9 (ArC), 131.2 (ArC), 131.4 \text{ (ArC), 131.5 (ArCH), 132.5 (ArC), 137.4 (ArC), 141.1 \text{ (ArC), 142.7 \text{ (ArC ppm; } ^{19}\text{F-NMR (376 MHz, CDCl}_3) \delta -62.7 \text{ ppm; IR } v_{\text{max}} \text{ (neat/cm }^{-1}) \text{): 1312, 1322, 1166, 1125, 1066, 840; HRMS calcld for } C_{30}H_{32}F_3 [M+H]^+ : 475.1668, \text{ found 475.1649.}}
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2-(3,5-Dimethylphenyl)-1-(trimethylsilylethynyl)pyrene (6c)

Prepared according to general procedure E using 4a (20 mg, 46.3 \text{ mmol}) and trimethylsilylacetylene (19 \text{ \mu L, 0.139 mmol}). The crude product was purified by silica flash column chromatography (hexane) to yield the title product as a yellow solid (11 mg, 59\%). \text{ H-NMR (500 MHz, CDCl}_3) \delta 0.28 \text{ (s, Si(CH}_3)_3, 9 H), 2.46 \text{ (s, Ar(CH}_3)_2, 6 H), 7.10 \text{ (s, ArH, 1 H), 7.47 \text{ (s, ArH, 2 H), 8.01-8.07 (m, ArH, 2 H), 8.11 (d, } J = 8.5 \text{ Hz, ArH, 1 H), 8.17 \text{ (s, ArH, 1 H), 8.19-8.23 (m, ArH, 2 H), 8.24 (d, } J = 7.5 \text{ Hz, ArH, 1 H), 8.72 (d, } J = 9.0 \text{ Hz, ArH, 1 H ppm; } ^{13}\text{C-NMR (125 MHz, CDCl}_3) \delta 0.0 \text{ (Si(CH}_3)_3, 21.4 \text{ (Ar(CH}_3)_2, 103.3 \text{ (C=C), 104.0 \text{ (C=C), 116.2 \text{ (ArC), 123.3 \text{ (ArC), 124.1 \text{ (ArC), 125.6 \text{ (ArCH), 125.7 \text{ (ArCH), 125.8 \text{ (ArCH), 126.1 \text{ (ArCH), 126.2 \text{ (ArCH), 127.3 \text{ (ArCH), 128.0 \text{ (ArCH), 128.5 \text{ (ArCH), 128.6 \text{ (ArCH), 129.0 \text{ (ArCH), 130.9 \text{ (ArC), 131.0 \text{ (ArC), 131.1 \text{ (ArC), 132.8 \text{ (ArC), 137.2 \text{ (ArCH), 141.0 \text{ (ArC), 142.6 \text{ (ArC ppm; IR } v_{\text{max}} \text{ (neat/cm }^{-1}) : 3039, 2957, 2917, 1597, 1436, 1247, 1180, 879; HRMS calcld for } C_{55}H_{56}Si [M+H]^+ : 403.1877, \text{ found 403.1875.}}
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2-(4-Methylphenyl)-1-(phenylethynyl)pyrene (6d)

Prepared according to general procedure E using 4b (30 mg, 71.7 \text{ \mu mol}) and phenylacetylene (24 \text{ \mu L, 0.215 mmol}). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 96.4) to yield the title product as a yellow solid (21 mg, 75\%). \text{ H-NMR (400 MHz, CDCl}_3) \delta 2.52 \text{ (s, CH}_3, 3 H), 7.32-7.44 \text{ (m, ArH, 5 H), 7.53 (dd, } J = 7.8, 1.8 \text{ Hz, ArH, 2 H), 7.81 (d, } J = 8.0 \text{ Hz, ArH, 2 H), 7.99-8.10 (m, ArH, 2 H), 8.12 (d, } J = 8.8 \text{ Hz, ArH, 1 H), 8.18-8.29 (m, ArH, 4 H), 8.82 (d, } J = 9.2 \text{ Hz, ArH, 1 H ppm; } ^{13}\text{C-NMR (125 MHz, CDCl}_3) \delta 21.4 \text{ (CH}_3, 88.5 \text{ (C=C), 98.4 \text{ (C=C), 116.4 \text{ (ArC), 123.5 \text{ (ArC), 123.8 \text{ (ArC), 124.2 \text{ (ArC), 125.6 \text{ (ArCH),}}}
}
125.7 (ArCH), 125.9 (ArCH), 126.1 (ArCH), 126.2 (ArCH), 127.3 (ArCH), 128.2 (ArCH), 128.4 (ArCH), 128.6 (ArCH), 128.7 (ArCH), 130.1 (ArC), 131.0 (ArC), 131.2 (ArC), 131.4 (ArCH), 132.4 (ArC), 137.2 (ArC), 138.5 (ArC), 142.0 (ArC) ppm; IR ν_{max} (neat/cm⁻¹): 3040, 1512, 841, 827; HRMS calcd for C_{31}H_{21}[M+H]^+: 393.1638, found 393.1634.

2-(4-Methylphenyl)-1-(trimethylsilylethynyl)pyrene (6e)

Prepared according to general procedure E using 4b (30 mg, 71.7 μmol) and trimethylsilylacetylene (30 μL, 0.215 mmol). The crude product was purified by silica flash column chromatography (hexane) to yield the title product as a pale yellow solid (14 mg, 50%), mp (CH₂Cl₂) 134–138 °C. \(^1\)H-NMR (400 MHz, CDCl₃) δ 0.26 (s, Si(CH₃)₃, 9 H), 2.48 (s, ArCH₃, 3 H), 7.32 (d, J = 7.8 Hz, ArH, 2 H), 7.74 (d, J = 7.8 Hz, ArH, 2 H), 8.00-8.05 (m, ArH, 2 H), 8.10 (d, J = 9.0 Hz, ArH, 1 H), 8.14-8.25 (m, ArH, 4 H), 8.71 (d, J = 9.5 Hz, ArH, 1 H) ppm; \(^1\)C-NMR (125 MHz, CDCl₃) δ –0.1 (Si(CH₃)₃), 21.3 (ArCH₃), 103.4 (C≡C), 104.2 (C≡C), 116.2 (ArC), 123.3 (ArC), 124.1 (ArC), 125.6 (ArCH), 125.7 (ArCH), 126.1 (ArCH), 126.2 (ArCH), 127.3 (ArCH), 128.5 (ArCH), 128.6 (ArCH), 130.1 (ArCH), 130.9 (ArC), 131.0 (ArC), 131.1 (ArC), 132.8 (ArC), 137.1 (ArC), 138.2 (ArC), 142.3 (ArC) ppm; IR ν_{max} (neat/cm⁻¹): 3040, 2956, 2919, 2144, 1596, 1581, 1512, 1434, 1248, 1184; HRMS calcd for C_{28}H_{25}Si [M+H]^+: 389.1720, found 389.1715.

1-(4-Fluorophenylethynyl)-2-(4-methylphenyl)pyrene (6f)

Prepared according to general procedure E using 4b (209 mg, 0.50 mmol) and 1-ethynyl-4-fluorobenzene (172 μL, 1.50 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 90:10) to yield the title product as a pale yellow solid (139 mg, 69%), mp (CH₂Cl₂) 160–163 °C. \(^1\)H-NMR (500 MHz, CDCl₃) δ 2.52 (s, ArCH₃, 3 H), 7.08 (t, J = 8.0 Hz, ArH, 2 H), 7.38 (d, J = 7.8 Hz, ArH, 2 H), 7.49 (dd, J = 8.0, 6.0 Hz, ArH, 2 H), 7.79 (d, J = 7.8 Hz, ArH, 2 H), 8.01-8.09 (m, ArH, 2 H), 8.12 (d, J = 9.0 Hz, ArH, 1 H), 8.18-8.28 (m, ArH, 4 H), 8.77 (d, J = 9.0 Hz, ArH, 1 H) ppm; \(^1\)C-NMR (125 MHz, CDCl₃) δ 21.3 (ArCH₃), 88.2 (C≡C), 97.3 (C≡C), 115.7 (d, J = 21.9 Hz, ArCH), 116.2 (ArC), 119.9 (d, J = 3.5 Hz, ArC), 123.5 (ArC), 124.2 (ArC), 125.7 (ArCH), 125.7 (ArCH), 125.8 (ArCH), 126.0 (ArCH), 126.2 (ArCH), 127.3 (ArCH), 127.3 (ArCH), 128.8 (ArC), 128.8 (ArC), 131.9 (ArC), 138.2 (ArC), 142.3 (ArC) ppm; IR ν_{max} (neat/cm⁻¹): 3040, 2956, 2919, 2144, 1596, 1581, 1512, 1434, 1248, 1184; HRMS calcd for C_{28}H_{25}F [M+H]^+: 393.1720, found 393.1715.
128.5 (ArCH), 128.6 (ArCH), 128.7 (ArCH), 130.1 (ArCH), 131.0 (ArC), 131.2 (ArC),
132.4 (ArC), 133.2 (d, J = 8.3 Hz, ArCH), 137.3 (ArC), 138.5 (ArC), 142.0 (ArC), 162.5 (d, J = 248.0 Hz, ArCF) ppm; 19F-NMR (471 MHz, CDCl3) δ −110.9 ppm; IR νmax (neat/cm−1): 3040, 1717, 1597,
1508, 1226, 1177, 1152, 821; HRMS calcd for C31H20F [M+H]+: 411.1544, found 411.1542.

2-(4-Methoxyphenyl)-1-(phenylethynyl)pyrene (6g)

Prepared according to general procedure E using 4e (217 mg, 0.50 mmol) and phenylacetylene (165 µL, 1.50 mmol). The crude product was purified by silica flash column chromatography (hexane) to yield the title product as a yellow solid (148 mg, 72%), mp (CH2Cl2) 158−161 ºC. 1H-NMR (500 MHz, CDCl3) δ 3.95 (s, OC6H3, 3 H), 7.12 (d, J = 8.3 Hz, ArH, 2 H), 7.32−7.44 (m, ArH, 3 H), 7.55 (d, J = 7.0 Hz, ArH, 2 H), 7.86 (d, J = 8.3 Hz, ArH, 2 H), 7.99−8.07 (m, ArH, 2 H), 8.10 (d, J = 9.0 Hz, ArH, 1 H), 8.17−8.28 (m, ArH, 4 H), 8.80 (d, J = 9.0 Hz, ArH, 1 H) ppm; 13C-NMR (125 MHz, CDCl3) δ 55.4 (OCC6H3), 88.5 (C=C), 98.4 (C=C), 113.4 (ArCH), 116.3 (ArC), 123.4 (ArC), 123.8 (ArC), 124.2 (ArC), 125.6 (ArCH), 125.7 (ArCH), 126.0 (ArCH), 126.1 (ArCH), 127.3 (ArCH), 128.2 (ArCH), 128.4 (ArCH), 128.6 (ArCH), 130.9 (ArC), 131.0 (ArC), 131.2 (ArC), 131.4 (ArCH × 2), 132.4 (ArC), 133.9 (ArC), 141.6 (ArC), 159.2 (ArC) ppm; IR νmax (neat/cm−1): 1597, 1509, 1440, 1243, 1178, 1028, 894; HRMS calcd for C31H21O [M+H]+: 409.1587, found 409.1583.

General Procedure F: Suzuki coupling of 2-aryl-1-iodopyrenes

2-(3,5-Dimethylphenyl)-1-(4-ethoxycarbonylphenyl)pyrene (7a)

A flame dried Schlenk tube fitted with a Teflon coated stirring bar and loaded with 4a (15 mg, 34.7 µmol), 4-(methoxycarbonyl)phenylboronic acid (7.5 mg, 41.6 µmol), Pd(PPh3)4 (4.8 mg, 4.16 µmol) and Na2CO3 (26 mg, 0.250 mmol) was evacuated and refilled with N2. Then, degassed THF (5.0 mL) and degassed H2O (1.2 mL) were added and the tube was sealed under N2 before stirring it at 100 ºC for 19 h. After cooling to room temperature, the reaction was quenched with saturated aqueous NH4Cl and extracted with CH2Cl2 (3 × 3 mL). The organic layer was washed with brine, dried (MgSO4) and concentrated under reduced pressure. The crude product was purified by silica flash column chromatography (hexane/CH2Cl2, 100:0 to 0:100) to yield the title product as a pale yellow solid (10
mg, 65%), mp (CH₂Cl₂) 190-193 °C. ¹H-NMR (400 MHz, CDCl₃) δ 2.23 (s, Ar(CH₃)₂, 6 H), 3.97 (s, CO₂CH₃, 3 H), 6.86 (s, ArH, 1 H), 6.88 (s, ArH, 2 H), 7.41 (d, J = 8.0 Hz, ArH, 2 H), 7.84 (d, J = 9.2 Hz, ArH, 1 H), 7.98-8.09 (m, ArH, 4 H), 8.11 (d, J = 9.2 Hz, ArH, 1 H), 8.14 (d, J = 9.2 Hz, ArH, 1 H), 8.18 (d, J = 7.2 Hz, ArH, 1 H), 8.23 (d, J = 7.6 Hz, ArH, 1 H), 8.25 (s, ArH, 1 H) ppm; ¹³C-NMR (100 MHz, CDCl₃) δ 21.2 Ar(C(CO₂)), 130.8 (ArH), 131.4 (ArC), 131.7 (ArC), 132.8 (ArC), 134.9 (ArC), 137.1 (ArC), 139.4 (ArC), 141.6 (ArC), 144.9 (ArC), 156.4 (ArC), 212.3 (Ar(CO₂)) ppm; IR νmax (neat/cm⁻¹): 3038, 2921, 1721, 1607, 1434, 1274, 1111, 1100; HRMS calcd for C₃₅H₂₇O₂ [M+H]+: 441.1849, found 441.1830.

2-(3,5-Dimethylphenyl)-1-(4-methoxyphenyl)pyrene (7b)

A flame dried Schlenk tube fitted with a Teflon coated stirring bar and loaded with 4a (15 mg, 34.7 µmol), 4-(methoxy)phenylboronic acid (7.5 mg, 41.6 µmol), Pd(PPh₃)₄ (4.0 mg, 3.47 µmol) and K₂CO₃ (48 mg, 0.347 mmol) was evacuated and refilled with N₂. Then, degassed THF (1.7 mL), degassed EtOH (0.4 mL) and degassed H₂O (0.5 mL) were added and the tube was sealed under N₂ before stirring it at 100 °C for 14 h. After cooling to room temperature, the reaction was quenched with saturated aqueous NH₄Cl and extracted with CH₂Cl₂ (3 × 3 mL). The organic layer was washed with brine, dried (MgSO₄) and concentrated under reduced pressure. The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 99.5:0.5) to yield the title product as a pale yellow solid (10 mg, 70%), mp (CH₂Cl₂) 156-159 °C. ¹H-NMR (400 MHz, CDCl₃) δ 2.25 (s, Ar(CH₃)₂, 6 H), 3.87 (s, OCH₃, 3 H), 6.84-6.96 (m, ArH, 5 H), 7.23 (d, J = 8.4 Hz, ArH, 2 H), 7.94-8.04 (m, ArH, 3 H), 8.11 (s, ArH, 2 H), 8.16 (d, J = 7.6 Hz, ArH, 1 H), 8.20 (d, J = 7.6 Hz, ArH, 1 H), 8.24 (s, ArH, 1 H) ppm; ¹³C-NMR (100 MHz, CDCl₃) δ 21.3 (Ar(CH₃)₂), 55.3 (OCH₃), 113.2 (ArCH), 124.0 (ArC), 124.7 (ArC), 124.8 (ArCH), 125.0 (ArCH), 125.9 (ArCH), 126.2 (ArCH), 126.6 (ArCH), 127.3 (ArCH), 127.4 (ArCH), 127.5 (ArCH), 127.8 (ArCH), 128.4 (ArCH), 129.9 (ArC), 130.3 (ArC), 130.8 (ArC), 131.4 (ArC), 131.7 (ArC), 132.8 (ArCH), 135.9 (ArC), 136.9 (ArC), 139.8 (ArC), 142.2 (ArC), 158.4 (ArC) ppm; IR νmax (neat/cm⁻¹): 3035, 2914, 1607, 1515, 1437, 1291, 1243, 1175, 1036; HRMS calcd for C₃₇H₂₅O [M+H]+: 413.1900, found 413.1899.
Prepared according to general procedure F using 4b (102 mg, 0.243 mmol), 4-(methoxy)phenylboronic acid (44 mg, 0.292 mmol), Pd(PPh3)4 (28 mg, 24.3 μmol) and K2CO3 (336 mg, 2.43 mmol). The crude product was purified by silica flash column chromatography (hexane/EtOAc, 100:0 to 98:2) to yield the title product as a yellow solid (78 mg, 81%), mp (CH2Cl2) 197–200 °C. 1H-NMR (500 MHz, CDCl3) δ 2.35 (s, ArCH3, 3 H), 3.88 (s, ArOCH3, 3 H), 6.92 (d, J = 8.8 Hz, ArH, 2 H), 7.08 (d, J = 7.8 Hz, ArH, 2 H), 7.18 (d, J = 7.8 Hz, ArH, 2 H), 7.22 (d, J = 8.8 Hz, ArH, 2 H), 7.96 (d, J = 9.5 Hz, ArH, 1 H), 7.98-8.04 (m, ArH, 2 H), 8.08-8.12 (m, ArH, 2 H), 8.16 (d, J = 7.0 Hz, ArH, 1 H), 8.20 (d, J = 7.5 Hz, ArH, 1 H), 8.24 (s, ArH, 1 H), ppm; 13C-NMR (125 MHz, CDCl3) δ 21.1 (ArCH3), 55.2 (ArOCH3), 113.3 (ArCH), 123.9 (ArC), 124.7 (ArC), 124.8 (ArCH), 125.0 (ArCH), 125.9 (ArCH), 126.1 (ArCH), 126.7 (ArCH), 127.4 (ArCH), 127.4 (ArCH), 127.6 (ArCH), 128.4 (ArCH), 129.9 (ArC), 130.3 (ArCH), 130.3 (ArC), 130.8 (ArC), 131.4 (ArC), 131.7 (ArC), 132.8 (ArCH), 135.7 (ArC), 135.9 (ArC), 139.4 (ArC), 139.5 (ArC), 158.4 (ArC) ppm; IR νmax (neat/cm–1): 3039, 2957, 2916, 2852, 1733, 1607, 1512, 1463, 1435, 1326, 1175; HRMS calcd for C30H23O [M+H]+: 399.1743, found 399.1742.

2-(6-(4-Methoxyphenyl)-7-(p-tolyl)pyren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8)

In an argon-filled glovebox, to a microwave vial charged with 7e (50 mg, 0.125 mmol), bispinacalotetaboron (32 mg, 0.125), 4,4’-di-tert-butyl-2,2’-bipyridine (0.6 mg, 2.26 μmol) and [Ir(µ-MeOH)cod]2 (0.75 mg, 1.13 μmol) was added cyclohexane (0.38 mL). The vial was sealed, taken out of the glovebox and the mixture was stirred at 80 °C for 22 h. After cooling to room temperature, the mixture was filtered through Celite with CH2Cl2 and volatiles were removed under reduced pressure. The crude product was purified by silica column chromatography (hexane/MeOH)cod2 (0.75 mg, 1.13 μmol) was added cyclohexane (0.38 mL). The vial was sealed, taken out of the glovebox and the mixture was stirred at 80 °C for 22 h. After cooling to room temperature, the mixture was filtered through Celite with CH2Cl2 and volatiles were removed under reduced pressure. The crude product was purified by silica flash column chromatography (hexane/MeOH)cod2 (0.75 mg, 1.13 μmol) was added cyclohexane (0.38 mL). The vial was sealed, taken out of the glovebox and the mixture was stirred at 80 °C for 22 h. After cooling to room temperature, the mixture was filtered through Celite with CH2Cl2 and volatiles were removed under reduced pressure. The crude product was purified by silica flash column chromatography (hexane/MeOH)cod2 (0.75 mg, 1.13 μmol) was added cyclohexane (0.38 mL). The vial was sealed, taken out of the glovebox and the mixture was stirred at 80 °C for 22 h. After cooling to room temperature, the mixture was filtered through Celite with CH2Cl2 and volatiles were removed under reduced pressure. The crude product was purified by silica flash column chromatography (hexane/MeOH)cod2 (0.75 mg, 1.13 μmol) was added cyclohexane (0.38 mL). The vial was sealed, taken out of the glovebox and the mixture was stirred at 80 °C for 22 h. After cooling to room temperature, the mixture was filtered through Celite with CH2Cl2 and volatiles were removed under reduced pressure.
1-(Hydroxymethyl)-2-(p-tolyl)pyrene (9a)

To a flame dried Schlenk tube charged with a solution of 3b (50 mg, 0.149 mmol) in dry THF (1.5 mL) under N₂ was added dropwise BH₂·SMe₂ (113 μL, 1.19 mmol). The tube was sealed and the resulting mixture was stirred at 50 ºC for 18 h. After cooling to room temperature the reaction was carefully quenched by dropwise addition of H₂O (1.5 mL) and extracted with EtOAc (3 × 3 mL). The organic layer was washed with brine, dried (MgSO₄) and concentrated under reduced pressure. The crude product was loaded onto a short silica plug, washed with hexane/EtOAc (98:2) and collected with hexane/EtOAc (50:50). The title product was obtained as a pale orange solid (35 mg, 73%), mp (CH₂Cl₂) 170-173 ºC. ¹H-NMR (500 MHz, CDCl₃) δ 1.78 (bs, OH, 1 H), 2.50 (s, CH₃, 3 H), 5.27-5.33 (m, CH₂OH, 2 H), 7.35 (d, J = 7.3 Hz, ArH, 2 H), 7.51 (d, J = 7.3 Hz, ArH, 2 H), 8.01-8.07 (m, ArH, 2 H), 8.08-8.15 (m, ArH, 2 H), 8.18-8.28 (m, ArH, 3 H), 8.57 (d, J = 9.5 Hz, ArH, 1 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 21.2 (CH₂), 59.8 (CH₂OH), 123.9 (ArCH), 124.3 (ArC), 124.6 (ArC), 125.4 (ArCH), 125.4 (ArCH), 126.0 (ArCH), 126.7 (ArCH), 127.3 (ArCH), 128.1 (ArCH), 128.5 (ArCH), 128.9 (ArCH), 130.3 (ArCH), 130.6 (ArC), 130.9 (ArC), 131.0 (ArC), 131.1 (ArC), 137.1 (ArC), 138.7 (ArC), 140.7 (ArC) ppm; IR νmax (neat/cm⁻¹): 3347, 3031, 2919, 1599, 1511, 1437, 1180, 996, 839, 825; HRMS calcd for C₂₃H₁₉OK [M+K]+: 361.0989, found 361.0977.

Methyl 4-(1-(hydroxymethyl)pyren-2-yl)benzoate (9b)

To a vial charged with 3p (57 mg, 0.15 mmol) at 0 ºC under N₂ was added thionyl chloride (220 μL, 3.0 mmol) and the resulting mixture was then stirred at 70 ºC for 16 h. After cooling to room temperature the reaction mixture was diluted with toluene before removing volatiles under vaccum. The crude acid chloride was then dissolved in dry THF (1.1 mL) before adding NaBH₄ (28 mg, 0.75 mmol) in one portion. The vial was sealed and the resulting mixture was stirred at 50 ºC for 44 h. After cooling to 0ºC the reaction was carefully quenched with H₂O. The aqueous layer was extracted with EtOAc (3 × 10 mL) and the combined organic fractions were dried (MgSO₄) and concentrated under vaccum. The crude product was purified by silica column chromatography (pentane/EtOAc, 100:0 to 75:25) to yield the title product as a pale yellow solid (39 mg, 71%), mp (CH₂Cl₂) 164-168 ºC. ¹H-NMR (500 MHz, CDCl₃) δ 1.83 (t, J = 4.5 Hz, CH₂OH, 1 H), 4.01 (s, CO₂CH₃, 3 H), 5.27 (d, J = 4.5 Hz, CH₂OH, 2 H), 7.72 (d, J = 8.0 Hz, ArH, 2 H), 8.02-8.10 (m, ArH, 2 H), 8.11-8.17 (m, ArH, 2 H), 8.19-8.29 (m, ArH, 5 H), 8.57 (d, J = 9.0 Hz, ArH, 1 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 52.3 (CO₂), 59.7 (CH₂OH), 123.7 (ArCH), 124.5 (ArC), 124.6 (ArC), 125.6 (ArCH), 125.7 (ArCH), 126.2 (ArCH), 126.2 (ArCH), 127.2 (ArCH), 128.4 (ArCH), 128.8 (ArCH), 129.1 (ArC), 129.5 (ArCH), 130.1 (ArCH), 130.4 (ArC), 130.5 (ArC), 130.6 (ArC), 131.0 (ArC).
(ArC), 131.2 (ArC), 139.6 (ArC), 146.5 (ArC), 167.0 (CO$_2$CH$_3$) ppm; IR $v_{\text{max}}$ (neat/cm$^{-1}$): 3333, 2928, 1725, 1610, 1434, 1274, 1180, 1115; HRMS calcd for C$_{23}$H$_1$_O$_3$ [M–H]: 365.1183, found 365.1184.

(2-(4-(Hydroxymethyl)phenyl)pyren-1-yl)methanol (9c)

![Structure of (2-(4-(Hydroxymethyl)phenyl)pyren-1-yl)methanol](image)

To a flame dried Schlenk tube charged with a solution of 3p (50 mg, 0.131 mmol) in dry THF (1.3 mL) under N$_2$ was added dropwise BH$_2$·SMe$_2$ (100 µL, 1.05 mmol). The tube was sealed under N$_2$ and the resulting mixture was stirred at 55 °C for 18 h. After cooling to room temperature the reaction was quenched by addition of H$_2$O (1.5 mL) and extracted with EtOAc (3 × 3 mL). The organic layer was washed with brine, dried (MgSO$_4$), and concentrated under reduced pressure. The crude product was purified by silica flash column chromatography (hexane/EtOAc, 50:50 to hexane/MeOH, 95:5) to yield the title product as a yellow solid (29 mg, 65%), mp (EtOAc) 210–212 ºC. $^1$H-NMR (500 MHz, MeOD-d$_4$) $\delta$ 4.74 (s, CH$_2$OH), 5.16 (m, ArCH$_2$OH), 5.31 (d, $J$ = 7.5 Hz, ArH), 7.53 (d, $J$ = 7.5 Hz, ArH), 8.04 (t, $J$ = 7.8 Hz, ArH), 8.06-8.15 (m, ArH), 8.20-8.29 (m, ArH), 8.62 (d, $J$ = 9.0 Hz, ArH) ppm; $^{13}$C-NMR (125 MHz, MeOD-d$_4$) $\delta$ 59.7 (CH$_2$OH), 125.5 (ArC), 125.6 (ArC), 125.7 (ArC), 126.4 (ArC), 127.2 (ArCH), 127.5 (ArCH), 127.8 (ArCH), 128.4 (ArCH), 129.0 (ArCH), 129.1 (ArCH), 131.2 (ArCH), 132.0 (ArC), 132.1 (ArC), 132.3 (ArC), 132.6 (ArC), 141.8 (ArC), 142.1 (ArC), 142.2 (ArC) ppm; IR $v_{\text{max}}$ (neat/cm$^{-1}$): 3324, 2924, 2854, 1411, 1178, 994; HRMS calcd for C$_{24}$H$_{18}$O$_3$Na [M+Na]: 361.1199, found 361.1199.

1-(Hydroxymethyl)-2-(3,5-bis(trifluoromethyl)phenyl)pyrene (9d)

![Structure of 1-(Hydroxymethyl)-2-(3,5-bis(trifluoromethyl)phenyl)pyrene](image)

To a flame dried Schlenk tube charged with a solution of 3k (46 mg, 0.100 mmol) in dry THF (1.0 mL) under N$_2$ was added dropwise BH$_2$·SMe$_2$ (76 µL, 0.800 mmol). The tube was sealed under N$_2$ and the resulting mixture was stirred at 55 °C for 18 h. After cooling to room temperature the reaction was carefully quenched by dropwise addition of H$_2$O (1.5 mL) and extracted with EtOAc (3 × 3 mL). The organic layer was washed with brine, dried (MgSO$_4$) and concentrated under reduced pressure. The crude product was purified by silica column chromatography (hexane/EtOAc, 100:0 to 60:40). The title product was obtained as an off-white solid (31 mg, 70%), mp (CH$_3$Cl) >260 ºC. $^1$H-NMR (500 MHz, acetone-d$_6$) $\delta$ 5.16-5.21 (m, ArCH$_2$OH), 8.12 (t, $J$ = 7.5 Hz, ArH), 8.19 (bs, ArH), 8.21 (d, $J$ = 9.0 Hz, ArH), 8.24 (d, $J$ = 9.0 Hz, ArH), 8.31-8.39 (m, ArH), 8.43 (bs, ArH), 8.71 (d, $J$ = 9.5 Hz, ArH) ppm; $^{13}$C-NMR (125 MHz, acetone-d$_6$) $\delta$ 59.2 and 59.3 (ArCH$_2$OH), 121.9 (hept, $J$ = 4.0 Hz, ArCH), 124.6 (q, $J$ = 270.4 Hz, ArCF$_3$), 125.1 (ArC), 125.5 (ArCH), 125.5 (ArC), 126.5 (ArCH), 126.6 (ArCH), 127.2 (ArCH), 127.5 (ArCH), 128.2 (ArCH), 1434, 1274, 1180, 1115; HRMS calcd for C$_{24}$H$_{18}$O$_3$Na [M+Na]: 361.1199, found 361.1199.
129.1 (ArCH), 129.2 (ArCH), 131.5-131.6 (m, ArCH), 131.7 (ArC), 131.8 (q, J = 32.9 Hz, ArC), 131.9 (ArC), 132.3 (ArC), 132.9 and 132.9 (ArC), 138.5 (ArC), 145.3 (ArC) ppm; $^{19}$F-NMR (471 MHz, acetone-d$_6$) –63.1 ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 3356, 2924, 2851, 1382, 1280, 1175, 1120; HRMS calcd for C$_{25}$H$_{14}$OF$_6$ [M$^+$]: 444.0943, found 444.0935.

$N,N,N$-Trimethyl-1-(2-(p-tolyl)pyren-1-yl) methanammonium bromide (10a)

To a solution of 9a (15 mg, 46.5 $\mu$mol), in dry THF (470 $\mu$L) at 0 °C under N$_2$ was added PBr$_3$ (2.2 $\mu$L, 23.3 $\mu$mol ). The resulting mixture was allowed to slowly warm to room temperature. After 18 h the reaction was quenched with H$_2$O (0.5 mL) and extracted with EtOAc (3 × 3 mL). The organic layer was washed with brine, dried (MgSO$_4$) and concentrated under reduced pressure. The crude product was filtered through a short plug of silica (hexane/EtOAc, 90:10) to yield the benzylic bromide as a yellow solid, which was used without further purification. The bromide was then dissolved in THF (0.3 mL) and a 4.2 M solution of trimethylamine in EtOH (0.3 mL, 1.26 m) was added. The vial was sealed and the mixture stirred at 55 °C for 3 h. After cooling to room temperature, volatiles were removed under vaccum and the crude product was triturated in THF/Et$_2$O. The resulting solid was filtered under vaccum and washed with Et$_2$O. The solid was dried and the title product was obtained as a pale yellow solid (10 mg, 48% over 2 steps), mp (Et$_2$O) 151-154 °C.

$1$-(2-(4-(Methoxycarbonyl)phenyl)pyren-1-yl)-$N,N,N$-trimethylmethanammonium bromide (10b)

To a solution of 9b (35 mg, 95.5 $\mu$mol), in dry CH$_2$Cl$_2$ (1.0 mL) at 0 °C under N$_2$ was added PBr$_3$ (4.5 $\mu$L, 47.8 $\mu$mol ). The resulting mixture was allowed to slowly warm to room temperature. After 5
h the reaction was quenched with H2O (0.5 mL) and extracted with EtOAc (3 × 3 mL). The organic layer was washed with brine, dried (MgSO4) and concentrated under reduced pressure. The crude product was filtered through a short plug of silica (hexane/EtOAc, 50:50) to yield the benzylic bromide as a yellow solid, which was used without further purification. The bromide was then dissolved in THF (0.6 mL) and a 4.2 M solution of trimethylamine in EtOH (0.6 mL, 2.52 mmol) was added. The vial was sealed and the mixture stirred at 55 °C for 17 h. After cooling to room temperature, the solid residue was re-dissolved in as little MeOH as possible and Et2O was added to precipitate the product. The precipitate was filtered and washed with Et2O. The solid was dried and the title product was obtained as a pale brown solid (37 mg, 79% over 2 steps, mp (Et2O), decomposes above 160 °C. 1H-NMR (400 MHz, MeOD-d4) δ 2.88 (s, CH3N(CH3)3, 9 H), 3.99 (s, CO2CH3, 3 H), 5.38 (d, J = 14.4 Hz, CH2N(CH3)3, 1 H), 5.76 (d, J = 14.4 Hz, CH2N(CH3)3, 1 H), 7.57-8.02 (m, ArH, 2 H), 8.12-8.49 (m, ArH, 9 H), 8.75 (d, J = 9.6 Hz, ArH, 1 H) ppm; 13C-NMR (125 MHz, MeOD-d4) δ 52.9 (CO2CH3), 54.0 (CH2N(CH3)3), 62.9 (CH2N(CH3)3), 118.7 (ArC), 124.6 (ArCH), 125.2 (ArC), 125.6 (ArC), 127.7 (ArCH), 128.1 (ArCH), 128.2 (ArCH), 128.3 (ArCH), 129.1 (ArCH), 131.0 (ArC), 131.2 (ArCH), 131.3 (ArCH), 131.6 (ArC), 131.8-132.4 (ArCH × 2), 132.6 (ArC), 134.5 (ArC), 134.5 (ArC), 144.1 (ArC), 147.6 (ArC), 168.0 (CO2CH3) ppm; IR νmax (neat/cm−1): 3424, 3016, 2950, 1717, 1608, 1598, 1485, 1434, 1326, 1286, 1182, 1104; HRMS calcd for C29H32O2N [M]+: 408.1958, found 408.1946.

\[ N,N,N\text{-trimethyl-1-}(2\text{-}4\text{-}((\text{trimethylammonio})\text{methyl})\text{phenyl})\text{pyren-1-yl})\text{methanammonium bromide (10c)} \]

To a solution of 9c (23 mg, 68.0 μmol), in dry CH2Cl2 (680 μL) at 0 °C under N2 was added PBr3 (6.8 μL, 68.0 μmol). The resulting mixture was allowed to slowly warm to room temperature. After 5 h the reaction was quenched with H2O (0.5 mL) and extracted with EtOAc (3 × 3 mL). The organic layer was washed with brine, dried (MgSO4) and concentrated under reduced pressure. The crude product was filtered through a short plug of silica (hexane/CH2Cl2, 50:50) to yield the dibromide as a pale yellow solid, which was used without further purification. The dibromide was then dissolved in THF (1.0 mL) and a 4.2 M solution of trimethylamine in EtOH (1.0 mL, 4.20 mmol) was added. The vial was sealed and the mixture stirred at 55 °C for 6 h. After cooling to room temperature, volatiles were removed under vacuum and the crude product was triturated in THF. The resulting solid was filtered under vacuum and washed with THF. The solid was dried and the title product was obtained as a yellow solid (16 mg, 40% over 2 steps, mp (MeOH), decomposes above 190 °C. 1H-NMR (400 MHz, MeOD-d4) δ 2.92 (s, ArCH2N(CH3)3, 9 H), 3.26 (s, ArCH2N(CH3)3, 9 H), 7.91 (m, ArCH2N(CH3)3, 1 H), 8.18 (t, J = 7.6 Hz, ArH, 1 H), 8.23 (d, J = 8.8 Hz, ArH, 1 H), 8.31-8.37 (m, ArH, 2 H), 8.48 (d, J = 9.0 Hz, ArH, 1 H), 8.77 (d, J = 9.0 Hz, ArH, 1 H) ppm; 13C-NMR (125 MHz, MeOD-d4) δ 53.4 (J = 3.9 Hz, ArCH2N(CH3)3), 54.1 (ArCH2N(CH3)3), 63.0 (ArCH2N(CH3)3), 70.0 (ArCH2N), 118.8 (ArC), 124.7 (ArCH), 125.2 (ArC), 125.6 (ArC), 127.7 (ArCH), 128.1 (ArCH), 128.2 (ArCH), 128.2 (ArCH), 129.0 (ArC), 129.2 (ArCH), 131.2 (ArCH), 131.3...
(ArCH), 131.6 (ArC), 132.6 (ArC), 132.7 (ArCH), 134.5 (ArC), 134.5 (ArCH), 135.2 (ArCH), 144.0 (ArC), 145.4 (ArC) ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 3393, 3007, 2922, 1596, 1476, 1414, 1377, 970, 892, 864, 845; HRMS calc'd for C$_{30}$H$_{34}$N$_2$ [M$^+$]: 211.1356, found 211.1348.

1-(2-(3,5-Bis(trifluoromethyl)phenyl)pyren-1-yl)-N,N,N-trimethylmethanammonium bromide (10d)

To a solution of 9d (30 mg, 67.5 $\mu$mol), in dry CH$_2$Cl$_2$ (680 $\mu$L) at 0 °C under N$_2$ was added PBr$_3$ (3.0 $\mu$L, 33.8 $\mu$mol). The resulting mixture was allowed to slowly warm to room temperature. After 13 h the reaction was quenched with H$_2$O (0.5 mL) and extracted with EtOAc (3 × 3 mL). The organic layer was washed with brine, dried (MgSO$_4$) and concentrated under reduced pressure. The crude product was purified by silica column chromatography (hexane/EtOAc, 100:0 to 80:20) to yield the benzyl bromide as a pale yellow solid. The benzyl bromide was then dissolved in THF (0.5 mL) and a 4.2 M solution of trimethylamine in EtOH (245 $\mu$L, 1.03 mmol) was added. The vial was sealed and the mixture stirred at 55 °C for 5 h. After cooling to room temperature, volatiles were removed under vaccum and the crude product was triturated in Et$_2$O. The resulting solid was allowed to settle, the supernatant was removed and the solid dried under vacuum. The title product was obtained as a white solid (19 mg, 50% over 2 steps), mp (Et$_2$O) 145–148 ºC.

**1-(Bromomethyl)pyrene (S1)**

To a suspension of 1-pyrenemethanol (5.00 g, 21.5 mmol) in dry toluene (250 mL) at 0 °C, PBr$_3$ (1.0 mL, 10.8 mmol) was added dropwise. The resulting mixture was stirred at 0 °C for 1.5 h and then at room temperature for 1 h. The reaction was quenched by careful addition of saturated aqueous Na$_2$CO$_3$ (25 mL). Layers were separated and the organic fraction was washed with H$_2$O (2 × 12 mL).
and brine (2 × 12 mL). The organic layer was concentrated to obtain the title product as an off-white solid (6.21 g, 98%), mp (toluene): decomposes above 125 °C. $^1$H-NMR (400 MHz, CDCl$_3$) δ 5.28 (s, CH$_2$, 2 H), 8.02-8.16 (m, ArH, 5 H), 8.21-8.30 (m, ArH, 3 H), 8.41 (d, $J$ = 9.2 Hz, ArH, 1 H) ppm; $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 32.2 (CH$_2$), 122.8 (ArC), 124.6 (ArC), 124.9 (ArC), 125.1 (ArC), 125.6 (ArCH), 125.6 (ArCH), 126.3 (ArCH), 127.3 (ArCH), 127.7 (ArCH), 128.0 (ArCH), 128.2 (ArCH), 129.1 (ArC), 130.6 (ArC), 130.8 (ArC), 131.2 (ArC), 132.0 (ArC) ppm; IR $\nu_{\text{max}}$ (neat/cm$^{-1}$): 3037, 1917, 1587, 1418, 1311, 1201, 1184, 1084, 840; HRMS calcd for C$_{17}$H$_{12}$Br [M]$^+$: 295.0117, found 295.0112.

$N_N_N$-Trimethyl-N-(1-pyrenylmethyl)ammonium bromide (11)

A solution of trimethylamine in ethanol (4.2 M, 14.7 mL, 62.0 mmol) was added to a flask charged with S1 (1.00 g, 3.39 mmol). The flask was sealed under air and the mixture stirred at 60 °C for 18 h. After cooling to room temperature volatiles were removed under vacuum. The resulting solid was triturated in Et$_2$O, filtered and washed with more Et$_2$O. The title product was obtained as an off-white solid (1.25 mg, 98%), mp (MeOH): decomposes above 170 °C. $^1$H-NMR (500 MHz, MeOD-d$_4$) δ 3.24 (s, N(CH$_3$)$_3$, 9 H), 5.36 (s, CH$_2$, 2 H), 8.13 (t, $J$ = 7.8 Hz, ArH, 1 H), 8.19 (d, $J$ = 9.0 Hz, ArH, 1 H), 8.22-8.29 (m, ArH, 2 H), 8.31-8.40 (m, ArH, 4 H), 8.60 (d, $J$ = 9.5 Hz, ArH, 1 H) ppm; $^{13}$C-NMR (125 MHz, MeOD-d$_4$) δ 53.6 (t, $J$ = 4.0 Hz, N(CH$_3$)$_3$), 67.0 (t, $J$ = 2.4 Hz, ArCH$_2$N), 121.9 (ArC), 123.6 (ArCH), 125.5 (ArC), 125.9 (ArCH), 126.2 (ArC), 127.3 (ArCH), 127.7 (ArCH), 127.9 (ArCH), 128.3 (ArCH), 130.5 (ArCH), 132.0 (ArCH), 131.7 (ArC), 132.6 (ArC), 133.1 (ArCH), 133.2 (ArC), 134.8 (ArC) ppm
4. NMR spectra

2-(3,5-Dimethylphenyl)pyrene-1-carboxylic acid (3a)

$^1$H-NMR (400 MHz, DMSO-d$_6$)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$)
2-(4-Methylphenyl)pyrene-1-carboxylic acid (3b)

$^1$H-NMR (500 MHz, DMSO-d$_6$)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$)
2-(3-Tolyl)pyrene-1-carboxylic acid (3c)

$^1$H-NMR (400 MHz, DMSO-d$_6$)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$)
2-(4-tert-Butylphenyl)pyrene-1-carboxylic acid (3d)

$^1$H-NMR (500 MHz, DMSO-d$_6$)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$)
2-(4-Methoxyphenyl)pyrene-1-carboxylic acid (3e)

$^1$H-NMR (500 MHz, DMSO-d$_6$)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$)
2-Phenylpyrene-1-carboxylic acid (3f)

$^1$H-NMR (500 MHz, DMSO-d$_6$)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$)
2-(4-Bromophenyl)pyrene-1-carboxylic acid (3g)

$^1$H-NMR (500 MHz, DMSO-d$_6$)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$)
2-(3-Bromophenyl)pyrene-1-carboxylic acid (3h)

$^1$H-NMR (400 MHz, DMSO-d$_6$)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$)
2-(3-Chlorophenyl)pyrene-1-carboxylic acid (3i)

$^1$H-NMR (400 MHz, DMSO-$d_6$)

$^{13}$C-NMR (125 MHz, DMSO-$d_6$)
2-(3,5-Dichlorophenyl)pyrene-1-carboxylic acid (3j)

$^1$H-NMR (400 MHz, DMSO-d$_6$)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$)
2-(3,5-Bis(trifluoromethyl)phenyl)pyrene-1-carboxylic acid (3k)

$^1$H-NMR (500 MHz, DMSO-$d_6$)

$^{13}$C-NMR (125 MHz, DMSO-$d_6$)
$^{19}$F-NMR (471 MHz, DMSO-d$_6$)
2-(3-Nitrophenyl)pyrene-1-carboxylic acid (3l)

$^1$H-NMR (400 MHz, DMSO-d$_6$)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$)
2-(3-(Trifluoromethyl)phenyl)pyrene-1-carboxylic acid (3m)

$^1$H-NMR (400 MHz, DMSO-d$_6$)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$)
$^{19}$F-NMR (471 MHz, DMSO-$d_6$)
2-(3-Cyanophenyl)pyrene-1-carboxylic acid (3n)

$^1$H-NMR (500 MHz, acetone-d$_6$)

$^{13}$C-NMR (125 MHz, acetone-d$_6$)
2-(3-(Methoxycarbonyl)phenyl)pyrene-1-carboxylic acid (3o)

$^1$H-NMR (400 MHz, DMSO-$d_6$)

$^{13}$C-NMR (125 MHz, DMSO-$d_6$)
2-(4-(Methoxycarbonyl)phenyl)pyrene-1-carboxylic acid (3p)

$^{1}$H-NMR (500 MHz, DMSO-$d_6$)

$^{13}$C-NMR (125 MHz, DMSO-$d_6$)
2-(Thiophen-2-yl)pyrene-1-carboxylic acid (3q)

$^1$H-NMR (500 MHz, DMSO-d$_6$)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$)
2-(5-Methylthiophen-2-yl)pyrene-1-carboxylic acid (3r)

$^1$H-NMR (500 MHz, DMSO-$d_6$)

$^{13}$C-NMR (125 MHz, DMSO-$d_6$)
2-(1-Methylindol-5-yl)pyrene-1-carboxylic acid (3s)

$^1$H-NMR (500 MHz, DMSO-d$_6$)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$)
2-(2,6-Dichloropyridin-4-yl)pyrene-1-carboxylic acid (3t)

$^1$H-NMR (500 MHz, DMSO-d$_6$)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$)
2-(3,5-Dimethylphenyl)-1-iodopyrene (4a)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
1-Iodo-2-(4-methylphenyl)pyrene (4b)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
1-Iodo-2-(3-methylphenyl)pyrene (4c)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
2-(4-\textit{tert}-Butylphenyl)-1-iodopyrene (4d)

$^1$H-NMR (400 MHz, CDCl$_3$)

\[ \text{\includegraphics[width=\textwidth]{hnmr_4d}} \]

$^{13}$C-NMR (125 MHz, CDCl$_3$)

\[ \text{\includegraphics[width=\textwidth]{cnmr_4d}} \]
1-Iodo-2-(4-methoxyphenyl)pyrene (4e)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
1-Iodo-2-phenylpyrene (4f)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
2-(4-Bromophenyl)-1-iodopyrene (4g)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
1-Iodo-2-(3-bromophenyl)pyrene (4h)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
1-Iodo-2-(3-chlorophenyl)pyrene (4i)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
1-Iodo-2-(3,5-dichlorophenyl)pyrene (4j)

$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
2-(3,5-Bis(trifluoromethyl)phenyl)-1-iodopyrene (4k)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)

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$^{19}$F-NMR (376 MHz, DMSO-$d_6$)
1-Iodo-2-(3-nitrophenyl)pyrene (4l)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
1-Iodo-2-(4-methoxyphenyl)pyrene (4m)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
$^{19}\text{F-NMR (471 MHz, DMSO-d}_6\text{)}$
1-Iodo-2-(3-cyanophenyl)pyrene (4n)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
1-Iodo-2-(3-(methoxycarbonyl)phenyl)pyrene (4o)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
1-Iodo-2-(4-(methoxycarbonyl)phenyl)pyrene (4p)

$^1$H-NMR (500 MHz, CDCl₃)

$^{13}$C-NMR (125 MHz, CDCl₃)
(3,5-Dimethylphenyl)pyrene (5a)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
2-(4-Methylphenyl)pyrene (5b)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
2-(3-Methylphenyl)pyrene (5c)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
2-(4-tert-Butylphenyl)pyrene (5d)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)

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2-(4-methoxyphenyl)pyrene (5e)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
2-Phenylpyrene (5f)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
2-(4-Bromophenyl)pyrene (5g)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
2-(3-Bromophenyl)pyrene (5h)

$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
2-(3-Chlorophenyl)pyrene (5i)

$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
2-(3,5-Dichlorophenyl)pyrene (5j)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
2-(3,5-Bis(trifluoromethyl)phenyl)pyrene (5k)

$^{1}$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
$^{19}$F-NMR (471 MHz, CDCl$_3$)
2-(3-nitrophenyl)pyrene (5l)

$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
2-(3-trifluoromethylphenyl)pyrene (5m)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
$^{19}$F-NMR (471 MHz, CDCl$_3$)
2-(3-Cyanophenyl)pyrene (5n)

$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)

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Methyl 3-(pyren-2-yl)benzoate (5o)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
Methyl 4-(pyren-2-yl)benzoate (5p)

$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
2-(3,5-Dimethylphenyl)-1-(phenylethynyl)pyrene (6a)

$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
2-(3,5-Dimethylphenyl)-1-(4-trifluoromethylphenylethynyl)pyrene (6b)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
$^{19}$F-NMR (376 MHz, CDCl$_3$)
2-(3,5-Dimethylphenyl)-1-(trimethylsilylethynyl)pyrene (6c)

$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
2-(4-Methylphenyl)-1-(phenylethynyl)pyrene (6d)

$^1\text{H-NMR} \ (400 \text{ MHz, CDCl}_3)$

$^{13}\text{C-NMR} \ (125 \text{ MHz, CDCl}_3)$
2-(4-Methylphenyl)-1-(trimethylsilylethynyl)pyrene (6e)

$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
1-(4-Fluorophenylethynyl)-2-(4-methylphenyl)pyrene (6f)

$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
$^{19}$F-NMR (471 MHz, CDCl$_3$)
2-(4-Methoxyphenyl)-1-(phenylethynyl)pyrene (6g)

$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
2-(3,5-Dimethylphenyl)-1-(4-ethoxycarbonylphenyl)pyrene (7a)

\(^1\)H-NMR (400 MHz, CDCl\(_3\))

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\))
2-(3,5-Dimethylphenyl)-1-(4-methoxyphenyl)pyrene (7b)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
1-(4-Methoxyphenyl)-2-(4-methylphenyl)pyrene (7c)

$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
2-(6-(4-Methoxyphenyl)-7-(p-tolyl)pyren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
1-(Hydroxymethyl)-2-(p-tolyl)pyrene (9a)

$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)

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Methyl 4-(1-(hydroxymethyl)pyren-2-yl)benzoate (9b)

$^1$H-NMR (500 MHz, CDCl₃)

$^{13}$C-NMR (125 MHz, CDCl₃)
(2-(4-(Hydroxymethyl)phenyl)pyren-1-yl)methanol (9c)

$^1$H-NMR (500 MHz, MeOD-$d_4$)

$^{13}$C-NMR (125 MHz, MeOD-$d_4$)
1-(Hydroxymethyl)-2-(3,5-bis(trifluoromethyl)phenyl)pyrene (9d)

$^1$H-NMR (500 MHz, acetone-$d_6$)

$^{13}$C-NMR (125 MHz, acetone-$d_6$)
$^{19}$F-NMR (471 MHz, acetone-d$_6$)
$N,N,N$-Trimethyl-1-(2-(p-tolyl)pyren-1-yl)methanammonium bromide (10a)

$^1$H-NMR (500 MHz, MeOD-$d_4$)

$^{13}$C-NMR (125 MHz, MeOD-$d_4$)
1-(2-(4-(Methoxycarbonyl)phenyl)pyren-1-yl)-N,N,N-trimethylmethanammonium bromide (10b)

$^1$H-NMR (400 MHz, MeOD-d$_4$)

$^{13}$C-NMR (125 MHz, MeOD-d$_4$)
$N,N,N$-trimethyl-$1$-(2-($4$-((trimethylammonio)methyl)phenyl)pyren-$1$-yl)methanammonium bromide (10c)

$^1$H-NMR (400 MHz, MeOD-$d_4$)

$^{13}$C-NMR (125 MHz, MeOD-$d_4$)
1-(2-(3,5-Bis(trifluoromethyl)phenyl)pyren-1-yl)-N,N,N-trimethylmethanammonium bromide (10d)

$^1$H-NMR (400 MHz, MeOD-$d_4$)

$^{13}$C-NMR (100 MHz, MeOD-$d_4$)
$^{19}$F-NMR (376 MHz, MeOD-$d_4$)
1-(Bromomethyl)pyrene (S1)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
$N,N,N$-Trimethyl-$N$-(1-pyrenylmethyl)ammonium bromide (11)

$^1$H-NMR (500 MHz, MeOD-d$_4$)

$^{13}$C-NMR (125 MHz, MeOD-d$_4$)
5. Liquid Phase Exfoliation

The LPE process was performed in the following way: 30 mg of graphite (Graphexel ltd.) was added to 10 mL of de-ionized water, previously mixed with 4 mg of the prepared pyrene derivatives. The mixture was sonicated at 600 W for 7 days using a Hilsonic bath sonicator fit with a chiller to keep temperature constant at 20 ºC. Un-exfoliated graphite was removed by 2-steps centrifugation at 3500 rpm (903 g) for 20 minutes. After each centrifugation step, the supernatant containing dispersed exfoliated graphite in water was collected and analysed. Dispersions were diluted (×10) for visual inspection.
6. AFM Analysis

A Bruker Atomic Force Microscope (MultiMode 8) in Peak Force Tapping mode, equipped with ScanAsyst-Air tips is used to determine the lateral size distribution of the flakes. The sample was prepared by drop casting the solution on a clean silicon substrate and subsequent annealing at 250 °C for 2 hours. Lateral dimension and thickness distributions of graphene nanosheets were carried out using Gwyddion scanning probe microscopy data processing software (Figure S1).

Figure S1. AFM images of graphene nanosheets drop-casted on silicon substrate.
7. Raman Analysis

Micro Raman measurements were carried out with a Renishaw Invia Raman spectrometer with excitation energy of 514.5 nm at 1.0 mW power. A 100X objective with a NA of 0.85 and 2400 grooves/mm grating was used for the characterization. Graphene dispersions were drop cast onto silicon substrates and measurements were performed on isolated and individual flakes. Typically about 30 flakes were measured for each sample (Table S5). The Raman peaks are fitted with Lorentzian lineshape.

Table S5. Raman analysis summary.

| Compound | SLG<sup>a</sup> | FLG<sup>b</sup> | Thick layers | Total (%) |
|----------|----------------|----------------|--------------|-----------|
| 10a      | 20.0%          | 80.0%          | 0%           | 100.0     |
| 10b      | 6.7%           | 93.3%          | 0%           | 100.0     |
| 10c      | 6.7%           | 93.3%          | 0%           | 100.0     |
| 10d      | 5.9%           | 94.1%          | 0%           | 100.0     |
| 11       | 26.7%          | 73.3%          | 0%           | 100.0     |

<sup>a</sup>Single-layer graphene. <sup>b</sup>Few-layer graphene.

The Raman analysis is performed using a qualitative protocol for analyzing LPE graphene, which was introduced in our previous works. In details, the 2D peak was fitted with a Lorentzian lineshape and the coefficient of determination, $R^2$, was used to discriminate between a single layer ($n = 1$, symmetric peak), a few layers ($2 \leq n \leq 10$, asymmetric 2D peak) and graphitic ($n > 10$ with AB stacking, characteristic peak shape with shoulder) material. Figure S2 shows typical Raman spectra corresponding to LPE single-layer graphene (SLG), few-layer graphene (FLG) and thick flakes measured on the graphene dispersions obtained with pyrene derivatives. This analysis provides qualitative information on the thickness distribution.

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8. Zeta-Potential Measurements

Electrophoretic mobility (μ) was measured using a ZetaSizer Nano ZS (Malvern Instruments, UK) in the folded capillary cells at 25°C and the natural pH. The equipment software automatically converted the μ to zeta-potential (ζ) values by Henry’s equation: \[ \mu = 2\varepsilon\zeta F(\kappa a)/3\eta \] where ε is dielectric constant, η is the solution viscosity and F(κa) is the Henry’s function which is approximated to the value of 1.5 using Smoluchowski approximation for polar media, valid for dispersed particles of any shape including plate-like particles. All values for samples are mean values, calculated from triplicate measurements.

9. UV-Vis Spectroscopy

The final concentration of graphene dispersed in the solution was determined using UV-Vis spectroscopy. The UV-Vis spectrum of graphene appears flat and featureless in the visible-IR region, so the absorption is measured at 660 nm. The Beer-Lambert law is used to derive the concentration by assuming an absorption coefficient of 2460 L·g⁻¹·m⁻¹ at 660 nm. A Perkin-Elmer l-900 UV-Vis-NIR spectrophotometer was used to acquire the spectra.

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