Regioselective ortho-Functionalization of Bromofluorenecarbaldehydes using TMPMgCl·LiCl

Supporting Information

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1 General Information

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. All chemicals were purchased from commercial suppliers and either used as received or purified according to Purification of Common Laboratory Chemicals.\textsuperscript{1} Dry tetrahydrofuran (THF), dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}) and acetonitrile (MeCN) were obtained from an inert PS-MD-6 solvent purification system. All other solvents were dried using standard methods.\textsuperscript{1} Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by \textsuperscript{1}H-NMR spectroscopy.

Thin layer chromatography was performed on fluorescence indicator marked precoated silica gel 60 plates (Macherey-Nagel, ALUGRAM Xtra SIL G/UV\textsubscript{254}) and visualized by UV light (254 nm/366 nm). Flash column chromatography was performed on silica gel (0.040 – 0.063 mm) with the solvents given in the procedures. Retention factors were determined at chamber saturation at 25 °C. Developments were carried out between 3.0 – 3.5 cm.

NMR spectra were recorded on a Bruker Avance 360WB spectrometer at 20 °C. Chemical shifts for \textsuperscript{1}H-NMR spectra are reported as \(\delta\) (parts per million) relative to the residual proton signal of CDCl\textsubscript{3} at 7.26 ppm (s), C\textsubscript{6}D\textsubscript{6} at 7.16 ppm (s) or DMSO-d\textsubscript{6} at 2.50 ppm (quin). Chemical shifts for \textsuperscript{13}C-NMR spectra are reported as \(\delta\) (parts per million) relative to the signal of CDCl\textsubscript{3} at 77.0 ppm (t), C\textsubscript{6}D\textsubscript{6} at 128.1 ppm (t) or DMSO-d\textsubscript{6} at 39.5 ppm (sept). The following abbreviations are used to describe splitting patterns: br. = broad, s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, ddt = doublet of doublet of triplets, t = triplet, td = triplet of doublets, tt = triplet of triplets, q = quartet, sept = septet, m = multiplet. Coupling constants \(J\) are given in Hertz.

ESI and APCI mass spectra were recorded on an Advion Expression CMS\textsuperscript{1} via ASAP probe or direct inlet. High resolution (HR) EI mass spectra were recorded on a double focusing mass spectrometer ThermoQuest MAT 95 XL from Finnigan MAT. HR-ESI mass spectra were recorded on a Bruker impact II. All Signals are reported with the quotient from mass to charge m/z.

IR spectra were recorded on a Nicolet Thermo iS10 scientific spectrometer with a diamond ATR unit. The absorption bands are reported in cm\textsupscript{-1} with indicated relative intensities: s (strong, 0 – 33 % T); m (medium, 34 – 66 % T), w (weak, 67 – 100 % T), and br (broad).
Melting points of solids, compounds that solidified after chromatography, were measured on a Büchi M-5600 Melting Point apparatus and are uncorrected. The measurements were performed with a heating rate of 5 °C/min and the melting points are reported in °C.

Low temperature reactions (−78 °C or −40 °C) were cooled using a Julabo FT902 cryostat. If not otherwise noted, solvents were removed on a Büchi Rotavapor R-300 with 40 °C water bath temperature.
## 2 Optimization of the Reaction Conditions

![Reaction Scheme](image)

<table>
<thead>
<tr>
<th>entry( ^a )</th>
<th>directing group</th>
<th>metal base( ^b )</th>
<th>equivalents( ^c )</th>
<th>temperature</th>
<th>time</th>
<th>yield [%]</th>
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<td>1</td>
<td>2 OXO</td>
<td>LDA</td>
<td>1.0 – 3.0</td>
<td>-78 °C</td>
<td>1 h</td>
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<tr>
<td>3</td>
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<td>4</td>
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<td>1 h</td>
<td>---</td>
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<td>3.0</td>
<td>25 °C</td>
<td>6 h</td>
<td>85</td>
</tr>
</tbody>
</table>

\( ^a \)Reactions were conducted with 0.2 mmol of 2 or 3 respectively and freshly prepared metalation agent in anhydrous THF (0.5 mL, 0.4 M) under nitrogen atmosphere. \( ^b \)LDA = Lithium diisopropylamide was prepared by dissolving \( N,N \)-Diisopropylamine (1.0 eq) in anhydrous THF (0.3 M) and cooling to 0 °C. \( n \)BuLi (1.0 eq, 2.5 M in hexane) was added in one portion and the mixture was stirred for ten minutes at 0 °C. \( ^c \)Reactions with LDA were conducted with 1.0, 2.0 and 3.0 equivalents respectively at the given temperature.
3 Preparation of Starting Materials

3.1 Preparation of Metalation Agents and Salt Solutions

3.1.1 Preparation of the reagent iPrMgCl·LiCl

A slightly modified literature procedure was used. LiCl (4.24 g, 100 mmol, 1.00 eq) was placed in a heat gun-dried and nitrogen-flushed Schlenk flask and heated *in vacuo* at 140 °C by heat gun for five hours. Magnesium turnings (2.67 g, 110 mmol, 1.10 eq) were placed in another heat gun-dried and nitrogen-flushed Schlenk flask and the dried LiCl and anhydrous THF (50 mL) were added. 2-Chloropropane (9.14 mL, 100 mmol, 1.00 eq) in anhydrous THF (50 mL) was slowly added at 25 °C through a dropping funnel. After approximately 1/5 of addition the mixture was slightly warmed with a heat gun until the reaction started (within ten minutes). When the reaction started the remaining solution was added dropwise and stirring was continued for 18 hours. After complete addition the temperature of the mixture rose until it started to boil. To remove excess of magnesium the grey solution was cannulated to another heat gun-dried and nitrogen-flushed Schlenk flask. The Grignard reagent was titrated prior to use against I₂ (0.50 – 0.60 mmol) in anhydrous THF (2 mL) at 0 °C which resulted in a conversion of 92 – 96 %. Color change from dark violet to pale brown indicated the end of the titration.

3.1.2 Preparation of the reagent TMPMgCl·LiCl

A slightly modified literature procedure was used. A heat gun-dried and nitrogen-flushed Schlenk flask was charged with freshly titrated iPrMgCl-LiCl (75.0 mL, 90.0 mmol, 1.00 eq, 1.20 M). TMP (16.0 mL, 94.5 mmol, 1.05 eq) was added through a rubber septum to the vigorously stirred Grignard solution via syringe pump (0.5 mL/min) at 25 °C. The reaction mixture was stirred at 25 °C for 48 hours, while the solution turned dark green. The base was titrated prior to use against benzoic acid (122 mg, 1.00 mmol) using (4-Phenylazo)diphenylamine (3 mg) as indicator in anhydrous THF (2.00 mL) at 0 °C which resulted in a conversion of 96 – 99 %. Color change from orange to dark violet indicated the end of the titration.
3.1.3 Preparation of CuCN·2LiCl solution

A reported literature procedure was used. A heat gun-dried and nitrogen-flushed Schlenk flask was charged with CuCN (40.0 mmol, 3.58 g) and LiCl (80.0 mmol, 3.39 g) and heated in vacuo at 140 °C for 5 h. After cooling to 25 °C, anhydrous THF (40 mL) was added and stirring was continued until the salts were dissolved, providing a 1.00 M solution.

3.1.4 Preparation of ZnCl₂ solution

A reported literature procedure was used. A heat gun-dried and nitrogen-flushed Schlenk flask was charged with ZnCl₂ (10.0 mmol, 1.36 g) and heated in vacuo at 140 °C for 5 h. After cooling to 25 °C, anhydrous THF (10 mL) was added and stirring was continued until the salt was dissolved, providing a 1.00 M solution.

3.2 Preparation of 2,7-difunctionalized Fluorenes (1a, 2 and 3)

3.2.1 2,7-Dibromo-9H-fluorene (S1)

A modified literature procedure was used. Fluorene (8.31 g, 50.0 mmol, 1.00 eq) was dissolved in chloroform (83 mL, 0.6 M) and iron powder (279 mg, 5.00 mmol, 0.10 eq) was added. The solution was cooled in a water/ice bath to 0 °C. Bromine (5.38 mL, 105 mmol, 2.10 eq) in chloroform (42 mL) was added through a dropping funnel over one hour in the dark to the vigorously stirred mixture. After complete addition the mixture was stirred for an additional three hours at 0 °C. Saturated Na₂S₂O₅ solution (100 mL) was slowly added at the same temperature and stirring was continued for 30 minutes. Chloroform (100 mL) was added, the phases were separated and the aqueous layer was extracted with chloroform (2 × 100 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. S1 (16.1 g, 49.7 mmol, 99 %) was isolated as a colorless solid. If desired the product can be recrystallized from chloroform.

R_f = 0.61 (SiO₂, CH). Mp.: 164 – 166 °C. ¹H-NMR (360 MHz, CDCl₃): δ = 7.64 (d, J_HH = 1.6 Hz, 2H), 7.57 (d, J_HH = 8.1 Hz, 2H), 7.49 (dd, J_HH = 8.2 Hz, J_HH = 1.8 Hz, 2H), 3.83 (s, 2H) ppm. ¹³C{¹H}-NMR (91 MHz, CDCl₃): δ = 144.9 (2x), 139.8 (2x), 130.2 (2x), 128.4 (2x), 121.3 (2x), 121.1 (2x), 36.7 ppm. IR
(ATR, neat): $\tilde{\nu} = 3049$ (w), 2919 (w), 1881 (w), 1766 (w), 1568 (w), 1453 (m), 1391 (m), 1159 (m), 1054 (m), 1005 (w), 931 (w), 807 (s), 685 (m), 662 (m) cm$^{-1}$. MS (EI, 70 eV): $m/z = 321.8 \ [C_{13}H_{8}^{79}Br_2]^+$. The analytical data are in accordance with the literature.\(^9\)

### 3.2.2 2,7-Dibromo-9,9-dimethyl-9H-fluorene (S2)

![Chemical structure of S2](image)

A modified literature procedure was used.\(^{10}\) **S1** (16.2 g, 50.0 mmol, 1.00 eq) was suspended in DMSO (83 mL, 0.6 M) and potassium iodide (830 mg, 5.00 mmol, 0.10 eq) was added. To the water bath-cooled and vigorously stirred mixture were added potassium hydroxide pellets (11.2 g, 200 mmol, 4.00 eq). The reaction was stirred for one hour, while the solution turned intensive red. Methyl iodide (7.78 mL, 125 mmol, 2.50 eq) was added via syringe pump (0.15 mL/min) through a rubber septum and stirring was continued at 25 °C for 18 hours. Excess of methyl iodide was quenched by addition of triethylamine (13.9 mL, 100 mmol, 2.00 eq). The mixture was stirred for 30 minutes, poured into water (500 mL) and extracted with CH$_2$Cl$_2$ (4 × 100 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO$_2$, CH) afforded **S2** (16.2 g, 46.0 mmol, 92%) as a colorless solid. If desired the product can be recrystallized from cyclohexane.

$R_f = 0.68$ (SiO$_2$, CH). **Mp.:** 177 – 179 °C. $^1$H-NMR (360 MHz, CDCl$_3$): $\delta = 7.55$ (d, $^4J_{HH} = 1.8$ Hz, 2H), 7.54 (d, $^3J_{HH} = 8.1$ Hz, 2H), 7.46 (dd, $^3J_{HH} = 8.1$ Hz, $^4J_{HH} = 1.8$ Hz, 2H), 1.47 (s, 6H) ppm. $^{13}$C($^1$H)-NMR (91 MHz, CDCl$_3$): $\delta = 155.4$ (2x), 137.3 (2x), 130.5 (2x), 126.3 (2x), 121.6 (4x), 47.4, 27.0 (2x) ppm. IR (ATR, neat): $\tilde{\nu} = 2962$ (m), 2920 (w), 2856 (w), 1861 (w), 1727 (w), 1597 (w), 1577 (w), 1447 (m), 1397 (m), 1259 (m), 1083 (m), 1058 (m), 1001 (m), 865 (m), 824 (m), 791 (s), 729 (m), 667 (m) cm$^{-1}$. MS (EI, 70 eV): $m/z = 349.9 \ [C_{15}H_{12}^{79}Br_2]^+$. The analytical data are in accordance with the literature.\(^{11}\)

### 3.2.3 7-Bromo-9,9-dimethyl-9H-fluorene-2-carbaldehyde (1a)

![Chemical structure of 1a](image)
A modified literature procedure was used. A heat gun-dried and nitrogen-flushed Schlenk flask was charged with S2 (14.1 g, 40.0 mmol, 1.00 eq) and anhydrous THF (200 mL, 0.2 M) was added. The solution was cooled to –78 °C and nBuLi (16.8 mL, 42.0 mmol, 1.05 eq, 2.5 M in hexane) in anhydrous THF was added via syringe pump (0.2 mL/min) through a rubber septum to the vigorously stirred mixture. The intensive red solution was stirred for one hour at –78 °C and anhydrous DMF (6.19 mL, 80.0 mmol, 2.00 eq) in anhydrous THF (8 mL) was added via syringe pump (0.4 mL/min) through the rubber septum. Stirring was continued for 10 hours while the mixture was allowed to warm slowly to 25 °C. HCl (100 mL, 1.0 M) was poured in small portions to the reaction and the mixture was stirred rapidly for 30 minutes. The phases were separated and the aqueous layer was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were dried over anhydrous Na2SO4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO2, CH:EE 20:1 v:v) afforded 1a (10.9 g, 36.0 mmol, 90 %) as a colorless solid.

Rf = 0.26 (SiO2, CH:EE 20:1 v:v). Mp.: 147 – 149 °C. 1H-NMR (360 MHz, CDCl3): δ = 10.06 (s, 1H), 7.96 (d, 3JHH = 1.5 Hz, 1H), 7.87 (dd, 3JHH = 7.8 Hz, 4JHH = 1.3 Hz, 1H), 7.82 (d, 3JHH = 7.8 Hz, 1H), 7.65 (d, 3JHH = 8.1 Hz, 1H), 7.61 (d, 4JHH = 1.6 Hz, 1H), 7.51 (dd, 3JHH = 8.1 Hz, 4JHH = 1.7 Hz, 1H), 1.52 (s, 6H) ppm. 13C{1H}-NMR (91 MHz, CDCl3): δ = 192.2, 157.0, 154.1, 144.6, 136.8, 135.9, 130.8, 130.7, 126.6, 123.2, 122.7, 120.5, 47.4, 26.9 (2x) ppm. IR (ATR, neat): ν = 2963 (w), 2924 (w), 2814 (w), 2783 (w), 2708 (w), 1695 (s), 1683 (s), 1605 (m), 1405 (m), 1247 (m), 1175 (s), 1060 (m), 883 (s), 810 (s), 795 (s), 755 (s), 733 (s), 658 (m) cm−1. MS (APCI): m/z = 301.1 [C16H1379BrO+H]+. The analytical data are in accordance with the literature.

3.2.4 2-(7-Bromo-9,9-dimethyl-9H-fluoren-2-yl)-1,3-dioxolane (2)

A modified literature procedure was used.13 1a (904 mg, 3.00 mmol, 1.00 eq) was dissolved in PhMe (10 mL, 0.3 M) and ethylene glycol (336 µL, 6.00 mmol, 2.00 eq) and pTsOH (114 mg, 600 µmol, 0.20 eq) were added. 4 Å MS (3.00 g) was added and the mixture was heated to 120 °C and slowly stirred for ten hours. The organic phase was washed with saturated NaHCO3 solution (2 × 20 mL), dried over anhydrous Na2SO4, filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO2, CH:EE 20:1 v:v) afforded 2 (692 mg, 2.00 mmol, 67 %) as a colorless solid. If desired the product can be recrystallized from cyclohexane.
R_f = 0.19 (SiO_2, CH:EE 20:1 v:v). Mp.: 115 – 117 °C. ^1H-NMR (360 MHz, CDCl_3): δ = 7.69 (d, ^3J_HH = 7.7 Hz, 1H), 7.62 – 7.53 (m, 3H), 7.51 – 7.43 (m, 2H), 5.87 (s, 1H), 4.25 – 4.03 (m, 4H), 1.49 (s, 6H) ppm. ^13C[^1H]-NMR (91 MHz, CDCl_3): δ = 156.1, 153.5, 139.3, 137.8, 137.3, 130.2, 126.3, 125.9, 121.7, 121.4, 120.8, 120.1, 104.0, 65.5 (2x), 47.3, 27.1 (2x) ppm. IR (ATR, neat): ν̃ = 2958 (w), 2889 (w), 1454 (w), 1401 (m), 1260 (w), 1250 (w), 121.7, 121.4, 120.8, 120.1, 104.0, 65.5 (2x) cm^-1. HR-MS (EI, 70 eV): calculated for C_{18}H_{17}79BrO_2⁺ [M]^+: m/z = 344.04064, found: 344.04034 (Dev.: –0.30 mu; –0.88 ppm).

3.2.5 2-(7-Bromo-9,9-dimethyl-9H-fluoren-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (3)

A modified literature procedure was used. ^14 1a (3.01 g, 10.0 mmol, 1.00 eq) and 2-amino-2-methylpropan-1-ol (1.78 g, 20.0 mmol, 2.00 eq) were dissolved in CH_2Cl_2 (40 mL, 0.25 M) and 4 Å MS (5.00 g) was added. The mixture was slowly stirred for 18 hours at 25 °C whereupon NBS (3.56 g, 20.0 mmol, 2.00 eq) was added in one portion and stirring was continued for another three hours at the same temperature. All solids were filtered off and the organic phase was washed with saturated NaHCO_3 solution (2 × 50 mL). The combined aqueous phases were extracted with CH_2Cl_2 (2 × 50 mL). All organic phases were combined and washed with saturated Na_2S_2O_3 solution (50 mL) and the aqueous phase was extracted with CH_2Cl_2 (20 mL). The combined organic phases were dried over anhydrous MgSO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2, CH:EE 15:1 v:v) afforded 3 (3.41 g, 9.21 mmol, 92 %) as a colorless foam.

R_f = 0.17 (SiO_2, CH:EE 15:1 v:v). Mp.: 62 – 64 °C. ^1H-NMR (360 MHz, CDCl_3): δ = 8.02 (d, ^4J_HH = 1.4 Hz, 1H), 7.92 (dd, ^3J_HH = 7.9 Hz, ^4J_HH = 1.5 Hz, 1H), 7.69 (d, ^3J_HH = 7.9 Hz, 1H), 7.58 (d, ^3J_HH = 8.0 Hz, 1H), 7.56 (d, ^4J_HH = 1.8 Hz, 1H), 7.46 (dd, ^3J_HH = 8.0 Hz, ^4J_HH = 1.9 Hz, 1H), 4.12 (s, 2H), 1.48 (s, 6H), 1.41 (s, 6H) ppm. ^13C[^1H]-NMR (91 MHz, CDCl_3): δ = 162.3, 156.4, 153.3, 141.2, 137.4, 130.4, 127.8, 127.2, 126.4, 122.7, 122.1, 122.0, 119.9, 79.2, 67.7, 47.4, 28.6 (2x), 26.9 (2x) ppm. IR (ATR, neat): ν̃ = 2962 (w), 2924 (w), 2359 (w), 1641 (s), 1452 (m), 1403 (m), 1355 (m), 1308 (s), 1262 (s), 1202 (s), 1086 (m), 1060 (s), 968 (m), 815 (s), 774 (m), 738 (s), 716 (s) cm^-1. HR-MS (EI, 70 eV): calculated for C_{20}H_{20}79BrNO⁺ [M]^+: m/z = 369.07228, found: 369.07227 (Dev.: –0.01 mu; –0.02 ppm).
3.3 Preparation of Electrophiles

3.3.1 Tosyl azide (5a)

![Structural formula](image)

A slightly modified literature procedure was used. Sodium azide (3.58 g, 55.0 mmol, 1.10 eq) was dissolved in acetone (25 mL) and water (15 mL) to give a colorless solution. Separately, pTsCl (9.53 g, 50.0 mmol, 1.00 eq) was dissolved in acetone (25 mL) and added to the water bath cooled sodium azide solution in one portion. The mixture was stirred for two hours at 25 °C, while two phases were formed. Acetone was removed on a rotatory evaporator (bath temperature 30 °C). The aqueous phase was diluted with CH₂Cl₂ (30 mL) and the phases were separated. The organic phase was washed with water (2 × 10 mL), dried over anhydrous Na₂SO₄, filtered and the solvent was removed on a rotatory evaporator (water bath temperature 30 °C) to afford 5a (9.57 g, 48.5 mmol, 97 %) as a colorless liquid, which solidified upon standing at 20 °C.

Rₛ = 0.39 (SiO₂, CH:EE 10:1 v:v). ¹H-NMR (360 MHz, CDCl₃): δ = 7.88 – 7.82 (AA'XX', 2H), 7.44 – 7.38 (AA'XX', 2H), 2.48 (s, 3H) ppm. ¹³C{¹H}-NMR (91 MHz, CDCl₃): δ = 146.3, 135.6, 130.4 (2x), 127.7 (2x), 21.9 ppm. IR (ATR, neat): ν = 2357 (w), 2121 (s), 1595 (w), 1495 (w), 1450 (w), 1366 (s), 1307 (w), 1297 (w), 1162 (s), 1120 (m), 1084 (s), 1018 (w), 813 (m), 743 (s), 702 (m), 657 (s) cm⁻¹. MS (EI, 70 eV): m/z = 196.9 [M]⁺. The analytical data are in accordance with the literature.

3.3.2 (3-Bromoprop-1-yn-1-yl)triisopropylsilane (5b)

![Structural formula](image)

A slightly modified literature procedure was used. A heat gun-dried and nitrogen-flushed Schlenk flask was charged with NaHMDS (3.67 g, 20.0 mmol, 1.00 eq) dissolved in anhydrous THF (40.0 mL, 0.5 M) and cooled to −78 °C. Propargyl bromide (2.3 mL, 20.0 mmol, 1.00 eq, 80 % in PhMe) was added via syringe pump (0.4 mL/min) and stirring was continued for further ten minutes at −78 °C, while the mixture turned purple. Chlorotriisopropylsilane (4.28 mL, 20.0 mmol, 1.00 eq) was added via syringe pump (0.4 mL/min) and the mixture was stirred for another hour at −78 °C. It was allowed to warm slowly to 25 °C and stirred for a total of three hours. Saturated NH₄Cl solution (10 mL) and water (10 mL) were
added, the phases separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (4 × 40 mL). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO$_2$, CH) provided 5b (2.96 g, 10.8 mmol, 54 %) as a slightly yellow oil.

R$_f$ = 0.71 (SiO$_2$, CH). $^1$H-NMR (360 MHz, CDCl$_3$): δ = 3.95 (s, 2H), 1.07 (s, 21H) ppm. $^{13}$C($^1$H)-NMR (91 MHz, CDCl$_3$): δ = 102.0, 89.3, 18.7 (6x), 15.2, 11.3 (3x) ppm. IR (ATR, neat): $\tilde{\nu}$ = 2942 (m), 2891 (w), 2865 (m), 1463 (m), 1383 (w), 1242 (w), 1202 (s), 1171 (w), 1072 (w), 1035 (s), 995 (m), 919 (m), 882 (s), 676 (s), 661 (s) cm$^{-1}$. MS (EI, 70 eV): m/z = 274.0 [M]$^+$. The analytical data are in accordance with the literature.$^{18}$

### 3.3.3 Triisopropyl((trimethylsilyl)ethynyl)silane (S3)

A slightly modified literature procedure was used.$^{19}$ A heat gun-dried and nitrogen-flushed Schlenk flask was charged with ethynyltrimethylsilane (6.23 mL, 45 mmol, 1.00 eq), dissolved in anhydrous THF (40.0 mL, 0.5 M) and cooled to –78 °C. nBuLi (18.0 mL, 45.0 mmol, 1.00 eq, 2.5 M in hexane) was added via syringe pump (2.0 mL/min) to the cooled solution whereupon the cooling bath was removed and a water/ice bath was placed under the flask. Stirring at 0 °C for five minutes was followed by recooling to –78 °C and addition of triisopropylsilyl chloride (9.63 mL, 45.0 mmol, 1.00 eq) via syringe pump (0.4 mL/min). After complete addition the mixture was allowed to warm to 25 °C and stirred for 24 hours in all. Saturated NH$_4$Cl solution (100 mL) was added and the phases were separated. The aqueous layer was extracted with Et$_2$O (3 × 80 mL) and the combined organic layers were washed with water (80 mL) and saturated NaCl solution (80 mL). The organic layer was dried over anhydrous MgSO$_4$, filtered and the solvent was removed under reduced pressure to afford the crude product as a slightly yellow liquid. Distillation of the crude product (55 – 57 °C/0.3 mbar) afforded S3 (11.0 g, 43.3 mmol, 96 %) as a colorless liquid.

$^1$H-NMR (360 MHz, CDCl$_3$): δ = 1.08 – 1.04 (m, 21H), 0.17 (s, 9H) ppm. $^{13}$C($^1$H)-NMR (91 MHz, CDCl$_3$): δ = 116.3, 110.3, 18.7 (6x), 11.2 (3x), 0.2 (3x) ppm. IR (ATR, neat): $\tilde{\nu}$ = 2959 (w), 2943 (w), 2895 (w), 2866 (w), 1463 (w), 1383 (w), 1367 (w), 1249 (m), 1072 (w), 1017 (w), 996 (w), 919 (w), 883
(m), 855 (s), 839 (s), 760 (s), 699 (w), 674 (s), 658 (m) cm\(^{-1}\). **MS (EI, 70 eV):** \(m/z = 254.3 [M]^+\). The analytical data are in accordance with the literature.\(^{19}\)

### 3.3.4 1-Hydroxy-1\(\lambda^3\)-benzo[\(d\)][1,2]iodaoxol-3(1\(H\))-one (S4, 2-Iodosylbenzoic acid)

![Chemical Structure]

A slightly modified literature procedure was used.\(^{20}\) NaIO\(_4\) (11.2 g, 51.5 mmol, 1.03 equiv.) and 2-iodobenzoic acid (12.4 g, 50.0 mmol, 1.00 eq) were suspended in AcOH/H\(_2\)O (75 mL, 1:2 v:v). The mixture was heated under reflux for four hours, diluted with H\(_2\)O (200 mL) and then cooled to 25 °C in the dark. After one hour the resulting product was collected by filtration, washed with ice-water (3 \(\times\) 50 mL) and cold acetone (3 \(\times\) 50 mL) and then dried open to air in the dark overnight to give S4 (12.8 g, 48.5 mmol, 97 %) as a colorless solid.

**Mp.:** 248 – 250 °C. **\(^1\)H-NMR (360 MHz, DMSO-\(d_6\)):** \(\delta = 8.06\) (br. s, 1H), 8.01 (dd, \(^3\)J\(_{HH}\) = 7.5 Hz, \(^4\)J\(_{HH}\) = 1.5 Hz, 1H), 7.95 (ddd, \(^3\)J\(_{HH}\) = 8.5 Hz, \(^3\)J\(_{HH}\) = 7.2 Hz, \(^4\)J\(_{HH}\) = 1.6 Hz, 1H), 7.84 (dd, \(^3\)J\(_{HH}\) = 8.2 Hz, \(^4\)J\(_{HH}\) = 1.0 Hz, 1H), 7.69 (td, \(^3\)J\(_{HH}\) = 7.3 Hz, \(^4\)J\(_{HH}\) = 1.1 Hz, 1H) ppm. **\(^{13}\)C{\(^1\)H}-NMR (91 MHz, DMSO-\(d_6\)):** \(\delta = 167.8, 134.5, 131.5, 131.1, 130.4, 126.3, 120.5\) ppm. **IR (ATR, neat):** \(\nu = 3082\) (w), 3059 (w), 2808 (br), 2384 (br), 1600 (m), 1584 (m), 1557 (m), 1452 (w), 1439 (m), 1338 (s), 1301 (m), 1159 (w), 1148 (m), 1111 (w), 1017 (w), 991 (w), 964 (w), 884 (w), 832 (m), 797 (w), 739 (s), 693 (s), 675 (m) cm\(^{-1}\). **MS (APCI):** \(m/z = 264.9 [M+H]^+\). The analytical data are in accordance with the literature.\(^{20}\)

### 3.3.5 1-((Triisopropylsilyl)ethynyl)-1\(\lambda^3\)-benzo[\(d\)][1,2]iodaoxol-3(1\(H\))-one (5c, TIPS-EBX)

![Chemical Structure]

A slightly modified literature procedure was used.\(^{21}\) S4 (7.92 g, 30.0 mmol, 1.00 eq) was suspended in anhydrous MeCN (240 mL, 0.125 M) and TMSOTf (5.97 mL, 33.0 mmol, 1.10 eq) was added dropwise over 15 min. The mixture was stirred for 30 min at 25 °C and afterwards S3 (8.40 mL, 33.0 mmol, 1.10 eq) was added dropwise via a dropping funnel over 15 min. The mixture was stirred for another 30 min and then pyridine (2.66 mL, 33.0 mmol, 1.10 eq) was added and after 10 min, the mixture was concentrated under reduced pressure. The residue was dissolved in CH\(_2\)Cl\(_2\) (75 mL) and extracted with 1 N HCl (75 mL). The
aqueous phase was extracted with \( \text{CH}_2\text{Cl}_2 \) (75 mL) and the combined organic phases were washed with saturated NaHCO\(_3\) solution (50 mL), dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. The resulting product was recrystallized from MeCN to give \( 5c \) (11.3 g, 26.4 mmol, 88 %) as a colorless crystalline solid. 

**Mp.:** 173 – 175 °C decomp. 

\( ^1\text{H}-\text{NMR (360 MHz, CDCl}_3\): } \delta = 8.45 – 8.38 \text{ (m, 1H), 8.32 – 8.26 \text{ (m, 1H), 7.79 – 7.72 \text{ (m, 2H), 1.23 – 1.09 \text{ (m, 21H) ppm.}} \)

\( ^{13}\text{C}^{[1}\text{H]}-\text{NMR (91 MHz, CDCl}_3\): } \delta = 166.5, 134.8, 132.6, 131.7, 131.5, 126.2, 115.7, 114.4, 64.8, 18.6 (6x), 11.3 (3x) ppm. 

**IR (ATR, neat):** \( \nu = 2943 \text{ (m), 2863 \text{ (m), 2359 \text{ (w), 1614 \text{ (s), 1602 \text{ (s), 1558 \text{ (m), 1461 \text{ (m), 1437 \text{ (m), 1381 \text{ (w), 1366 \text{ (w), 1326 \text{ (m), 1293 \text{ (m), 1250 \text{ (w), 1155 \text{ (w), 1111 \text{ (w), 1075 \text{ (w), 1016 \text{ (w), 993 \text{ (w), 919 \text{ (w), 883 \text{ (m), 829 \text{ (m), 745 \text{ (s), 702 \text{ (s), 681 \text{ (s cm}^{-1}. \text{ MS (APCI): } m/z = 429.0 \text{ [M+H]^+} \) .

The analytical data are in accordance with the literature.\(^{21}\)

### 3.3.6 Mesityl(phenyl)iodonium trifluoromethanesulfonate (5d)

A slightly modified literature procedure was used.\(^{22}\) Iodobenzene (557 µL, 5.00 mmol, 1.00 eq) and \( m\text{-CPBA} \) (65 % active oxidant, 1.46 g, 5.50 mmol, 1.10 eq) were dissolved in \( \text{CH}_2\text{Cl}_2 \) (20 mL, 0.25 M) and mesitylene (765 µL, 5.50 mmol, 1.10 eq) was added dropwise. The mixture was cooled to 0 °C and trifluoromethanesulfonic acid (527 µL, 6.00 mmol, 1.20 eq) was added dropwise, whereupon the mixture turned into a dark red. During slowly warming to 25 °C within 12 hours the dark color disappeared. Volatile components were removed under reduced pressure and the residue was suspended in Et\(_2\)O (20 mL). The suspension was stored at –25 °C for two hours and the formed crystals were filtered off, washed with ice cooled Et\(_2\)O (3 × 10 mL) and dried under reduced pressure to afford \( 5d \) (1.75 g, 3.71 mmol, 74 %) as a colorless solid. 

**Mp.:** 146 – 148 °C. 

\( ^1\text{H}-\text{NMR (360 MHz, DMSO-d}_6\): } \delta = 7.98 \text{ (dd, } \frac{3J_{HH}}{} = 8.4 \text{ Hz, } \frac{4J_{HH}}{} = 1.0 \text{ Hz, 2H), 7.64 \text{ (tt, } \frac{3J_{HH}}{} = 6.9 \text{ Hz, } \frac{4J_{HH}}{} = 1.1 \text{ Hz, 1H), 7.50 \text{ (t, } \frac{3J_{HH}}{} = 7.7 \text{ Hz, 2H), 7.22 \text{ (s, 2H), 2.60 \text{ (s, 6H), 2.29 \text{ (s, 3H) ppm.}} \)

\( ^{13}\text{C}^{[1}\text{H]}-\text{NMR (91 MHz, DMSO-d}_6\): } \delta = 143.1, 141.6 (2x), 134.5 (2x), 131.9 (2x), 131.8, 129.8 (2x), 122.6, 114.5, 26.3 (2x), 20.5 ppm. 

**IR (ATR, neat):** \( \nu = 3059 \text{ (w), 3000 \text{ (w), 2919 \text{ (w), 2359 \text{ (w), 1583 \text{ (w), 1567 \text{ (w), 1474 \text{ (w), 1444 \text{ (m), 1381 \text{ (w), 1245 \text{ (s), 1222 \text{ (s), 1157 \text{ (s), 1069 \text{ (w), 1024 \text{ (s), 992 \text{ (m), 984 \text{ (m), 944 \text{ (m), 918 \text{ (w), 856 \text{ (m), 757 \text{ (w), 740 \text{ (s), 683 \text{ (m), 654 \text{ (w cm}^{-1. \text{ MS (ESI): } m/z = 323.0 \text{ [M–OTf]^+} \) .

The analytical data are in accordance with the literature.\(^{21}\)
3.3.7 4,4-Dimethyl-2-(p-tolyl)-4,5-dihydrooxazole (S5)

A modified literature procedure was used.\textsuperscript{14} p-Tolualdehyde (8.41 g, 70.0 mmol, 1.00 eq) and 2-amino-2-methylpropan-1-ol (12.5 g, 140 mmol, 2.00 eq) were dissolved in CH\textsubscript{2}Cl\textsubscript{2} (175 mL, 0.4 M) and 4 Å MS (25.0 g) was added. After 18 hours of slowly stirring at 25 °C NBS (24.9 g, 140.0 mmol, 2.00 eq) was added in one portion and stirring was continued for another four hours at 25 °C. All solids were filtered off and the organic phase was washed with saturated NaHCO\textsubscript{3} solution (3 × 100 mL). The combined aqueous phases were extracted with CH\textsubscript{2}Cl\textsubscript{2} (2 × 100 mL). All organic phases were washed with saturated NaS\textsubscript{2}O\textsubscript{3} solution (100 mL) and the aqueous phase was extracted with CH\textsubscript{2}Cl\textsubscript{2} (50 mL). The combined organic phases were dried over anhydrous MgSO\textsubscript{4} and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO\textsubscript{2}, CH:EE 10:1 to 5:1 v:v) afforded S5 (13.0 g, 68.7 mmol, 98 %) as a pale brown solid with a characteristic nougat odor.

R\textsubscript{f} = 0.16 (SiO\textsubscript{2}, CH:EE 10:1 v:v). Mp.: 42 – 44 °C. \textsuperscript{1}H-NMR (360 MHz, CDCl\textsubscript{3}): \( \delta = 7.81 \) (d, \( ^{3}J_{HH} = 7.7 \) Hz, 1H), 7.19 (d, \( ^{3}J_{HH} = 7.8 \) Hz, 1H), 4.07 (s, 2H), 2.37 (s, 3H), 1.36 (s, 6H) ppm. \textsuperscript{13}C{\textsuperscript{1}H}-NMR (91 MHz, CDCl\textsubscript{3}): \( \delta = 162.2, 141.6, 129.1 \) (2x), 128.3 (2x), 125.3, 79.1, 67.6, 28.5 (2x), 21.6 ppm. IR (ATR, neat): \( \bar{\nu} = 2970 \) (w), 2924 (w), 2894 (w), 1642 (m), 1510 (m), 1463 (w), 1409 (w), 1364 (w), 1353 (m), 1316 (m), 1302 (m), 1250 (w), 1193 (w), 1173 (m), 1065 (s), 1019 (m), 992 (w), 965 (m), 917 (m), 871 (w), 829 (s), 727 (s), 682 (s) cm\textsuperscript{-1}. MS (APCI): m/z = 190.1 [M+H]\textsuperscript{+}. The analytical data are in accordance with the literature.\textsuperscript{24}

3.3.8 2-(4-(Bromomethyl)phenyl)-4,4-dimethyl-4,5-dihydrooxazole (5g)

A modified literature procedure was used.\textsuperscript{25} S5 (568 mg, 3.00 mmol, 1.00 eq) was dissolved in CCl\textsubscript{4} (10 mL, 0.3 M) and NBS (534 mg, 3.00 mmol, 1.00 eq) was added in one portion. AIBN (24.3 mg, 150 \( \mu \)mol, 0.05 eq) was added and the mixture was heated to 100 °C for five hours. After cooling to 25 °C the mixture was directly filtered over anhydrous Na\textsubscript{2}SO\textsubscript{4} and the solids were washed with CCl\textsubscript{4} (20 mL). The solvent was evaporated under reduced pressure and purification was conducted by flash column chromatography (SiO\textsubscript{2},
CH:EE 10:1 v:v) to provide 5g (631 mg, 2.35 mmol, 78 %) as a colorless solid.

R_f = 0.11 (SiO_2, CH:EE 10:1 v:v). Mp.: 77 – 79 °C. \(^1\)H-NMR (360 MHz, CDCl_3): \(\delta = 7.94 – 7.87\) (AA’XX’, 2H), 7.45 – 7.39 (AA’XX’, 2H), 4.49 (s, 2H), 4.11 (s, 2H), 1.38 (s, 6H) ppm. \(^1\)C\(^{1}\)H-NMR (91 MHz, CDCl_3): \(\delta = 161.6, 140.9, 129.1\) (2x), 128.8 (2x), 128.2, 79.3, 67.8, 32.8, 28.6 (2x) ppm. IR (ATR, neat): \(\tilde{\nu} = 2965\) (w), 2926 (w), 2898 (w), 1644 (m), 1511 (w), 1458 (w), 1415 (m), 1357 (m), 1320 (m), 1299 (m), 1228 (w), 1194 (w), 1177 (m), 1068 (s), 1018 (m), 987 (w), 960 (m), 918 (w), 870 (w), 849 (m), 835 (m), 819 (m), 747 (w), 688 (s) cm\(^{-1}\). HR-MS (EI, 70 eV): calculated for C_{12}H_{14}\(^79\)BrNO\(^+\) [M]\(^+\): m/z = 267.02533, found: 267.02514 (Dev.: –0.19 mu; –0.70 ppm). The analytical data are in accordance with the literature.\(^{26}\)
4 General Procedures

4.1 General Procedure for the Deprotonation of Bromofluorene 3 (GP1)

A heat gun-dried and nitrogen-flushed Schlenk tube, equipped with a magnetic stirring bar and a rubber septum, was charged with 3 (1.00 eq) and evacuated for one hour. The flask was flushed with nitrogen and anhydrous THF (0.4 M) was added. Dropwise addition of TMPMgCl·LiCl (3.00 eq) via syringe through the rubber septum at 25 °C was followed by stirring for four hours under the same conditions. Separately, a heat gun-dried and nitrogen-flushed Schlenk tube was charged with the electrophile (3.00 eq) in anhydrous THF. The Schlenk tube, containing the dark red metalation solution, was cooled to −15 °C and the electrophile solution was added via syringe pump (0.3 mL/min) through the rubber septum. After complete addition the brown mixture was stirred for the indicated time while it was allowed to warm to 25 °C. Full consumption of the starting material was followed by aqueous workup. The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure on a rotary evaporator. Purification of the crude product was conducted by flash column chromatography.

4.2 General Procedure for the Conversion of Cuprates (GP2)

According to GP1, the freshly prepared organomagnesium species was cooled to −40 °C, and CuCN·2LiCl (3.00 eq, 1.00 M in THF) was added via syringe pump (0.3 mL/min) through the rubber septum and stirring was continued for 30 minutes under the same conditions. Separately, a heat gun-dried and nitrogen-flushed Schlenk tube was charged with the electrophile (3.00 eq) in anhydrous THF. The electrophile solution was added at −40 °C via syringe pump (0.3 mL/min) through the rubber septum to the brown solution. Stirring for one hour at −40 °C was followed by stirring for four hours while the mixture was allowed to warm to 25 °C. Full consumption of the starting material was followed by aqueous workup. The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure on a rotary evaporator. Purification of the crude product was conducted by flash column chromatography.

4.3 General Procedure for Cross-Coupling reactions (GP3)

According to GP1, to the freshly prepared organomagnesium species was added ZnCl₂ (3.00 eq, 1.00 M in THF) via syringe pump (0.3 mL/min) through the rubber septum at 25 °C and stirring was continued for 30 minutes at the same conditions. Separately, a heat gun-dried and nitrogen-flushed Schlenk tube was charged with the electrophile (3.00 eq) and Pd(PPh₃)₄ (0.05 eq) in anhydrous THF. The catalyst/electrophile solution was added at 25 °C via syringe pump (0.3 mL/min) through the rubber septum to the brown
solution. Stirring for 24 hours at 25 °C was followed by aqueous workup. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure on a rotary evaporator. Purification of the crude product was conducted by flash column chromatography.

4.4 General Procedure for Lactonization reactions (GP4)

Benzyl alcohol (1.00 eq) was suspended in 4 N HCl (0.2 M) and heated to 100 °C for six hours. After cooling to 25 °C and aqueous workup, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure on a rotary evaporator. Purification of the crude product was conducted by flash column chromatography.
4.5 Preparation of 2,3,7-Trisubstituted Fluorenes (6a–t)

4.5.1 2-(7-Bromo-3-iodo-9,9-dimethyl-9H-fluoren-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (6a)

Prepared according to GP1 from 3 (74.1 mg, 200 µmol, 1.00 eq) in anhydrous THF (0.5 mL, 0.4 M) and TMPMgCl-LiCl (500 µL, 600 µmol, 3.00 eq) in anhydrous THF (0.5 mL) was added and the reaction mixture was stirred for two hours. The reaction was quenched with water (5 mL) and saturated Na$_2$S$_2$O$_3$ solution (5 mL). CH$_2$Cl$_2$ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (4 × 10 mL). Purification by flash column chromatography (SiO$_2$, CH:EE 8:1 v:v) afforded 6a (85.1 mg, 172 µmol, 86 %) as a colorless foam. 

R$_f$ = 0.27 (SiO$_2$, CH:EE 8:1 v:v). Mp.: 68 – 70 °C decomp. $^1$H-NMR (360 MHz, CDCl$_3$): $\delta$ = 8.18 (s, 1H, H–4), 7.61 (s, 1H, H–1), 7.54 (d, $^4$J$_{HH}$ = 1.8 Hz, 1H, H–8), 7.52 (d, $^3$J$_{HH}$ = 8.1 Hz, 1H, H–5), 7.46 (dd, $^3$J$_{HH}$ = 8.1 Hz, 1H, H–6), 4.16 (s, 2H, H–12), 1.44 (s, 6H, H–14), 1.44 (s, 6H, H–10) ppm. $^{13}$C{$^1$H}-NMR (91 MHz, CDCl$_3$): $\delta$ = 163.5 (C–11), 156.4 (C–9a), 153.2 (C–8a), 142.2 (C–4a), 136.2 (C–4b), 132.9 (C–2), 132.1 (C–4), 130.8 (C–6), 126.7 (C–8), 125.3 (C–1), 122.9 (C–7), 122.4 (C–5), 93.4 (C–3), 79.8 (C–12), 68.6 (C–13), 47.6 (C–9), 28.7 (2x, C–14), 27.0 (2x, C–10) ppm. IR (ATR, neat): $\tilde{\nu}$ = 2961 (m), 2924 (w), 2889 (w), 1652 (m), 1602 (m), 1448 (s), 1395 (m), 1377 (w), 1362 (m), 1346 (m), 1298 (m), 1264 (s), 1202 (s), 1079 (s), 1061 (s), 1013 (w), 967 (s), 938 (m), 879 (m), 818 (s), 804 (s), 741 (m), 670 (w) cm$^{-1}$. HR-MS (EI, 70 eV): calculated for C$_{20}$H$_{19}$BrINO+ [M]$^+$: m/z = 494.96893, found: 494.96850 (Dev.: –0.43 mu; –0.86 ppm).

4.5.2 2-(3,7-Dibromo-9,9-dimethyl-9H-fluoren-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (6b)

Prepared according to GP1 from 3 (148 mg, 400 µmol, 1.00 eq) in anhydrous THF (1.0 mL, 0.4 M) and TMPMgCl-LiCl (1.26 mL, 1.20 mmol, 3.00 eq, 0.95 M). 1,2-Dibromotetrachloroethane (391 mg, 1.20 mmol, 3.00 eq) in anhydrous THF (1 mL) was added and the reaction mixture was stirred for two hours. The reaction was quenched with water (5 mL) and CH$_2$Cl$_2$ (10 mL) was added, the phases were separated...
and the aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL). Purification by flash column chromatography (SiO₂, CH:EE 8:1 v:v) afforded 6b (131 mg, 292 µmol, 73 %) as a yellowish foam.

Rᵢ = 0.24 (SiO₂, CH:EE 8:1 v:v). Mp.: 62 – 64 °C decomp. ¹H-NMR (360 MHz, CDCl₃): δ = 7.90 (s, 1H), 7.66 (s, 1H), 7.55 (d, ³JHH = 1.8 Hz, 1H), 7.52 (d, ³JHH = 8.2 Hz, 1H), 7.47 (dd, ³JHH = 8.1 Hz, ⁴JHH = 1.8 Hz, 1H), 4.16 (s, 2H), 1.45 (s, 6H), 1.44 (s, 6H) ppm. ¹³C{¹H}-NMR (91 MHz, CDCl₃): δ = 162.2, 156.3, 152.0, 141.9, 136.2, 130.6, 128.8, 126.5, 125.2, 122.7, 122.2, 120.8, 79.5, 68.2, 47.3, 28.4 (2x), 26.8 (2x) ppm. IR (ATR, neat): ν = 2962 (m), 2925 (w), 2880 (w), 1645 (m), 1607 (m), 1450 (m), 1398 (m), 1362 (m), 1348 (m), 1299 (m), 1265 (m), 1202 (m), 1084 (s), 1061 (m), 1019 (m), 968 (m), 940 (m), 876 (m), 811 (s), 768 (w), 740 (m), 670 (w) cm⁻¹. HR-MS (EI, 70 eV): calculated for C₂₀H₁₉₅Br₂NO⁺ [M⁺]: m/z = 446.98279, found: 446.98227 (Dev.: –0.52 µu; –1.16 ppm).

4.5.3 2-(3-Azido-7-bromo-9,9-dimethyl-9H-fluoren-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (6c)

Prepared according to GP1 from 3 (148 mg, 400 µmol, 1.00 eq) in anhydrous THF (1.0 mL, 0.4 M) and TMPMgCl·LiCl (1.21 mL, 1.20 mmol, 3.00 eq, 0.99 M). 5a (183 µL, 1.20 mmol, 3.00 eq) in anhydrous THF (1 mL) was added and the reaction mixture was stirred for three hours. The reaction was quenched with saturated NH₄Cl solution (5 mL) and water (5 mL). CH₂Cl₂ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL). Purification by flash column chromatography (SiO₂, CH:EE 8:1 v:v) afforded 6c (125 mg, 304 µmol, 76 %) as a colorless solid.

Rᵢ = 0.21 (SiO₂, CH:EE 8:1 v:v). Mp.: 162 – 164 °C. ¹H-NMR (360 MHz, CDCl₃): δ = 7.80 (s, 1H), 7.59 (d, ³JHH = 8.1 Hz, 1H), 7.56 (d, ³JHH = 1.7 Hz, 1H), 7.49 (dd, ³JHH = 8.1 Hz, ⁴JHH = 1.8 Hz, 1H), 7.47 (s, 1H), 4.13 (s, 2H), 1.47 (s, 6H), 1.43 (s, 6H) ppm. ¹³C{¹H}-NMR (91 MHz, CDCl₃): δ = 160.5, 156.8, 149.4, 142.1, 138.7, 136.5, 130.6, 126.5, 125.6, 122.8, 122.2, 119.4, 111.0, 79.0, 68.2, 47.3, 28.5 (2x), 27.0 (2x) ppm. IR (ATR, neat): ν = 2964 (m), 2926 (w), 2886 (w), 2100 (s), 1633 (m), 1466 (m), 1450 (m), 1425 (m), 1406 (m), 1361 (m), 1285 (s), 1266 (m), 1203 (m), 1122 (m), 1091 (m), 1064 (s), 1048 (m), 972 (m), 944 (m), 901 (w), 847 (m), 822 (m), 811 (s), 748 (m), 675 (w), 661 (w) cm⁻¹. HR-MS (APCI): calculated for C₂₀H₂₀BrN₄O⁺ [M+H⁺]: m/z = 411.08150, found: 411.08185 (Dev.: 0.35 µu; 0.85 ppm).
4.5.4 7-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-y1)-9,9-dimethyl-9H-fluorene-3-carbonitrile (6d)

Prepared according to GP1 from 3 (74.1 mg, 200 µmol, 1.00 eq) in anhydrous THF (0.5 mL, 0.4 M) and TMPMgCl-LiCl (667 µL, 600 µmol, 3.00 eq, 0.90 M). Tosyl cyanide (109 mg, 600 µmol, 3.00 eq) in anhydrous THF (5 mL) was added and the reaction mixture was stirred for two hours. The reaction was quenched with saturated NH₄Cl solution (5 mL) and water (5 mL). CH₂Cl₂ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL). Purification by flash column chromatography (SiO₂, CH:EE 8:1 v:v) afforded 6d (48.0 mg, 121 µmol, 61 %) as a yellowish solid.

Rᶠ = 0.18 (SiO₂, CH:EE 8:1 v:v). Mp.: 141 – 143 °C. ¹H-NMR (360 MHz, CDCl₃): δ = 8.08 (s, 1H), 8.02 (s, 1H), 7.62 (d, ³JHH = 8.1 Hz, 1H), 7.60 (d, ⁴JHH = 1.7 Hz, 1H), 7.53 (dd, ³JHH = 8.1 Hz, ⁴JHH = 1.8 Hz, 1H), 4.23 (s, 2H), 1.51 (s, 6H), 1.45 (s, 6H) ppm. ¹³C{¹H}-NMR (91 MHz, CDCl₃): δ = 160.3, 157.5, 156.1, 141.4, 135.5, 131.0, 129.7, 126.7, 126.0, 124.8, 123.6, 122.5, 118.3, 111.1, 79.9, 68.4, 48.1, 28.4 (2x), 26.6 (2x) ppm. IR (ATR, neat): ʋ = 2965 (w), 2925 (w), 2867 (w), 2224 (w), 1634 (m), 1616 (w), 1599 (w), 1562 (w), 1464 (m), 1450 (m), 1399 (m), 1360 (m), 1296 (m), 1267 (m), 1203 (m), 1089 (m), 1066 (s), 968 (m), 943 (m), 917 (m), 879 (m), 870 (m), 814 (s), 768 (m), 750 (m), 655 (m) cm⁻¹. HR-MS (APCI): calculated for C₂₁H₂₀⁷⁹BrN₂O⁺ [M+H]⁺: m/z = 395.07535, found: 395.07591 (Dev.: 0.56 mu; 1.41 ppm).

4.5.5 Ethyl 7-bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-y1)-9,9-dimethyl-9H-fluorene-3-carboxylate (6e)

Prepared according to GP1 from 3 (148 mg, 400 µmol, 1.00 eq) in anhydrous THF (1.0 mL, 0.4 M) and TMPMgCl-LiCl (1.21 mL, 1.20 mmol, 3.00 eq, 0.99 M). Ethyl cyanoformate (111 µL, 1.20 mmol, 3.00 eq) in anhydrous THF (1 mL) was added and the reaction mixture was stirred for two hours. The reaction was quenched with saturated NH₄Cl solution (5 mL) and water (5 mL). CH₂Cl₂ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL). Purification by flash column chromatography (SiO₂, CH:EE 8:1 v:v) afforded 6e (158 mg, 357 µmol, 89 %) as a colorless foam.
R_f = 0.15 (SiO_2, CH:EE 8:1 v:v). Mp.: 55 – 57 °C. ^1H-NMR (360 MHz, CDCl_3): δ = 8.00 (d, ^3J_{HH} = 0.6 Hz, 1H), 7.79 (d, ^5J_{HH} = 0.6 Hz, 1H), 7.61 (dd, ^3J_{HH} = 8.1 Hz, ^5J_{HH} = 0.5 Hz, 1H), 7.57 (dd, ^4J_{HH} = 1.8 Hz, ^5J_{HH} = 0.5 Hz, 1H), 7.49 (dd, ^3J_{HH} = 8.1 Hz, ^4J_{HH} = 1.8 Hz, 1H), 4.38 (q, ^3J_{HH} = 7.2 Hz, 2H), 4.11 (s, 2H), 1.48 (s, 6H), 1.42 (s, 6H), 1.39 (t, ^3J_{HH} = 7.2 Hz, 3H) ppm. ^13C{^1H}-NMR (91 MHz, CDCl_3): δ = 168.2, 162.7, 156.2, 155.7, 140.6, 136.6, 132.3, 130.6, 127.5, 126.4, 124.4, 122.3, 120.8, 79.9, 68.1, 61.7, 47.7, 28.4 (2x), 26.8 (2x), 14.4 ppm.

IR (ATR, neat): ν̃ = 2964 (m), 2927 (w), 2899 (w), 1724 (s), 1651 (m), 1462 (m), 1411 (w), 1365 (m), 1353 (m), 1018 (m), 971 (m), 946 (m), 904 (m), 872 (w), 822 (s), 771 (m), 746 (m), 662 (w) cm⁻¹. HR-MS (APCI): Calculated for C_{23}H_{25}BrNO_3^+[M+H]^+: m/z = 442.10123, found: 442.10205 (Dev.: 0.82 μu; 1.86 ppm).

4.5.6 tert-Butyl 7-bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-9,9-dimethyl-9H-fluorene-3-carboxylate (6f)

Prepared according to GP1 from 3 (148 mg, 400 μmol, 1.00 eq) in anhydrous THF (1.0 mL, 0.4 M) and TMPMgCl·LiCl (1.33 mL, 1.20 mmol, 3.00 eq, 0.90 M). Di-tert-butyl dicarbonate (262 mg, 1.20 mmol, 3.00 eq) in anhydrous THF (1 mL) was added and the reaction mixture was stirred for three hours. The reaction was quenched with saturated NH_4Cl solution (5 mL) and water (5 mL). CH_2Cl_2 (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH_2Cl_2 (4 × 10 mL). Purification by flash column chromatography (SiO_2, CH:EE 8:1 v:v) afforded 6f (153 mg, 325 μmol, 81%) as a colorless foam.

R_f = 0.21 (SiO_2, CH:EE 8:1 v:v). Mp.: 171 – 173 °C. ^1H-NMR (360 MHz, CDCl_3): δ = 7.86 (d, ^5J_{HH} = 0.5 Hz, 1H), 7.81 (d, ^5J_{HH} = 0.5 Hz, 1H), 7.62 (d, ^3J_{HH} = 8.1 Hz, 1H), 7.56 (d, ^4J_{HH} = 1.7 Hz, 1H), 7.49 (dd, ^3J_{HH} = 8.1 Hz, ^4J_{HH} = 1.8 Hz, 1H), 4.12 (s, 2H), 1.61 (s, 9H), 1.48 (s, 6H), 1.43 (s, 6H) ppm. ^13C{^1H}-NMR (91 MHz, CDCl_3): δ = 167.6, 162.7, 156.3, 155.0, 140.5, 136.8, 134.4, 130.6, 126.6, 126.4, 124.4, 122.5, 122.3, 120.3, 82.0, 79.7, 68.1, 47.6, 28.4 (2x), 28.2 (3x), 26.8 (2x) ppm. IR (ATR, neat): ν̃ = 2965 (w), 2927 (w), 1718 (s), 1651 (m), 1568 (w), 1457 (m), 1405 (w), 1392 (w), 1361 (s), 1302 (m), 1253 (s), 1202 (m), 1164 (s), 1106 (s), 1042 (m), 990 (m), 971 (m), 946 (m), 903 (m), 846 (m), 822 (s), 805 (m), 785 (m), 772 (m), 736 (m), 668 (m) cm⁻¹. HR-MS (APCI): Calculated for C_{25}H_{29}BrNO_3^+[M+H]^+: m/z = 470.13253, found: 470.13252 (Dev.: −0.01 μu; −0.03 ppm).
4.5.7 7-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-y1)-9,9-dimethyl-9H-fluoren-3-ol (6g)

**Procedure A:** Prepared according to GP1 from 3 (2.22 g, 6.00 mmol, 1.00 eq) in anhydrous THF (15 mL, 0.4 M) and TMPMgCl·LiCl (15.0 mL, 18.0 mmol, 3.00 eq, 1.20 M). The septum was removed, placed aslopes on the opening of the flask and stirring at 25 °C was continued for 48 hours while the solution turned bright red. The reaction was quenched with saturated NH₄Cl solution (40 mL) and water (40 mL). CH₂Cl₂ (60 mL) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (4 × 60 mL). Purification by flash column chromatography (SiO₂, CH:EE 20:1 v:v) afforded 6g (1.76 g, 4.56 mmol, 76 %) as a colorless solid. If desired the product can be recrystallized from acetonitrile.

**Procedure B:** Prepared according to GP1 from 3 (148 mg, 400 µmol, 1.00 eq) in anhydrous THF (1.0 mL, 0.4 M) and TMPMgCl·LiCl (1.00 mL, 1.20 mmol, 3.00 eq, 1.20 M). For generating moisture free air a column was packed with silica gel with humidity indicator. Air was purged through the column and sparged via cannula through anhydrous THF. The resulting atmosphere was guided into the reaction tube. Pressure equalization was achieved with a needle in the septum of the reaction vessel. Running this system for 16 hours was followed by quenching with saturated NH₄Cl solution (5 mL) and water (5 mL). CH₂Cl₂ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (4 × 15 mL). Purification by flash column chromatography (SiO₂, CH:EE 20:1 v:v) afforded 6g (114 mg, 295 µmol, 74 %) as a slightly yellow solid.

$$R_f = 0.48 \text{ (SiO}_2, \text{ CH:EE 20:1 v:v).}$$ **Mp.:** 150 – 152 °C. **¹H-NMR (360 MHz, CDCl₃):** \(\delta = 12.37 \text{ (br. s, 1H)}, 7.66 \text{ (s, 1H)}, 7.57 \text{ (d, } 3_J_{HH} = 8.0 \text{ Hz, 1H)}, 7.55 \text{ (d, } 4_J_{HH} = 1.8 \text{ Hz, 1H)}, 7.47 \text{ (dd, } 3_J_{HH} = 8.1 \text{ Hz, } 4_J_{HH} = 1.8 \text{ Hz, 1H)}, 7.31 \text{ (s, 1H)}, 4.13 \text{ (s, 2H)}, 1.46 \text{ (s, 6H)}, 1.42 \text{ (s, 6H) ppm.}$$ **¹³C{¹H}-NMR (91 MHz, CDCl₃):** \(\delta = 163.8, 160.0, 157.1, 143.4, 143.3, 137.5, 130.4, 126.4, 122.4, 122.4, 121.7, 109.9, 107.9, 78.5, 67.3, 46.7, 28.7 \text{ (2x)}, 27.4 \text{ (2x) ppm.}$$ **IR (ATR, neat):** \(\nu = 2959 \text{ (w), 2922 \text{ (w), 2893 \text{ (w), 2862 \text{ (w), 1734 \text{ (w), 1635 \text{ (s), 1584 \text{ (m), 1454 \text{ (m), 1389 \text{ (m), 1375 \text{ (m), 1310 \text{ (m), 1269 \text{ (s), 1218 \text{ (m), 1200 \text{ (s), 1129 \text{ (w), 1096 \text{ (m), 1063 \text{ (m), 1052 \text{ (s), 975 \text{ (m), 949 \text{ (m), 916 \text{ (w), 896 \text{ (m), 866 \text{ (m), 827 \text{ (m), 819 \text{ (s), 804 \text{ (s), 757 \text{ (m), 726 \text{ (m), 656 \text{ (s) cm}^{-1.}}$$ **HR-MS (APCI):** calculated for C₂₀H₂₁⁷⁹BrNO₂⁺ [M+H]⁺: m/z = 386.07502, found: 386.07565 (Dev.: 0.63 mu; 1.63 ppm).
4.5.8 2-(3-Allyl-7-bromo-9,9dimethyl-9H-fluoren-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (6h)

Prepared according to GP1 from 3 (74.1 mg, 200 µmol, 1.00 eq) in anhydrous THF (0.5 mL, 0.4 M) and TMPMgCl·LiCl (500 µL, 600 µmol, 3.00 eq, 1.20 M). An allylation reaction was performed according to GP2 using CuCN·2LiCl (600 µL, 600 µmol, 3.00 eq, 1.00 M) and allyl bromide (51.9 µL, 600 µmol, 3.00 eq) in anhydrous THF (1 mL). The reaction was quenched with saturated NH₄Cl solution (5 mL) and water (5 mL). CH₂Cl₂ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL). Purification by flash column chromatography (SiO₂, CH:EE 20:1 v:v) afforded 6h (68.0 mg, 166 µmol, 83 %) as a colorless solid.

Rᵣ = 0.21 (SiO₂, CH:EE 20:1 v:v). Mp.: 107 – 109 °C. ¹H-NMR (360 MHz, CDCl₃): δ = 7.78 (s, 1H), 7.59 (d, 3J_HH = 8.1 Hz, 1H), 7.56 (s, 1H), 7.55 (d, 4J_HH = 2.0 Hz, 1H), 7.46 (dd, 3J_HH = 8.1 Hz, 4J_HH = 1.8 Hz, 1H), 6.03 (ddt, 3J_HH = 16.8 Hz, 3J_HH = 10.1 Hz, 4J_HH = 6.6 Hz, 1H), 5.16 – 5.02 (m, 2H), 4.10 (s, 2H), 3.84 (dt, 3J_HH = 6.6 Hz, 4J_HH = 1.5 Hz, 2H), 1.47 (s, 6H), 1.41 (s, 6H) ppm. ¹³C{¹H}-NMR (91 MHz, CDCl₃): δ = 163.0, 156.7, 150.9, 140.6, 139.8, 137.8, 137.5, 130.3, 126.8, 126.4, 124.4, 122.0, 121.9 (2x), 115.8, 78.9, 68.0, 47.2, 38.7, 28.6 (2x), 27.1 (2x) ppm. IR (ATR, neat): ʋ = 2963 (w), 2923 (w), 2865 (w), 1633 (s), 1567 (w), 1477 (w), 1462 (w), 1407 (m), 1359 (m), 1303 (m), 1259 (m), 1196 (m), 1138 (w), 1087 (m), 1062 (m), 1041 (s), 994 (m), 973 (m), 950 (w), 904 (s), 884 (m), 869 (w), 824 (s), 775 (w), 737 (w), 657 (w) cm⁻¹. HR-MS (APCI): calculated for C₂₃H₂₂BrNO⁺ [M+H]⁺: m/z = 410.11140, found: 410.11210 (Dev.: 0.70 mu; 1.70 ppm).

4.5.9 2-(7-Bromo-9,9-dimethyl-3-(3-triisopropylsilyl)prop-2-yn-1-yl)-9H-fluoren-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (6i)

S22
Prepared according to GP1 from 3 (74.1 mg, 200 µmol, 1.00 eq) in anhydrous THF (0.5 mL, 0.4 M) and TMPMgCl-LiCl (667 µL, 600 µmol, 3.00 eq, 0.90 M). A propargylation reaction was performed according to GP2 using CuCN-2LiCl (600 µL, 600 µmol, 3.00 eq, 1.00 M) and 5b (165 mg, 600 µmol, 3.00 eq) in anhydrous THF (1 mL). The reaction was quenched with saturated NH₄Cl solution (5 mL) and water (5 mL). CH₂Cl₂ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL). Purification by flash column chromatography (SiO₂, CH:EE 20:1 v:v) afforded 6i (83.8 mg, 148 µmol, 74 %) as a yellow solid.

\[ R_f = 0.37 \text{ (SiO}_2, \text{CH:EE 20:1 v:v)}. \text{Mp.: 60 – 62 °C.} \text{H-NMR (360 MHz, CDCl}_3)\] \( \delta = 8.25 \text{ (s, 1H), 7.84 (s, 1H), 7.58 – 7.54 (m, 2H), 7.49 (dd,} J_{HH} = 8.1 \text{ Hz,} J_{HH} = 1.9 \text{ Hz, 1H), 4.23 (s, 2H), 4.07 (s, 2H), 1.48 (s, 6H), 1.40 (s, 6H), 1.15 (s, 21H) ppm.} \text{C\{H\}-NMR (91 MHz, CDCl}_3)\] \( \delta = 162.0, 156.7, 151.2, 140.7, 137.7, 136.6, 130.5, 126.4, 125.7, 124.1, 122.0, 121.9, 120.9, 106.3, 84.2, 78.4, 68.4, 47.3, 28.7 (2x), 27.0 (2x), 25.9, 18.9 (6x), 11.5 (3x) ppm. \text{IR (ATR, neat):} \tilde{\nu} = 2959 \text{ (m), 2941 (m), 2889 (w), 2863 (m), 2170 (w), 1635 (m), 1599 (w), 1567 (w), 1462 (m), 1410 (m), 1382 (w), 1361 (m), 1312 (m), 1259 (m), 1199 (m), 1087 (m), 1061 (m), 1043 (s), 1027 (m), 994 (m), 974 (m), 946 (w), 920 (m), 881 (s), 820 (s), 771 (w), 744 (m), 672 (s) cm}^{-1}. \text{HR-MS (APCI):} \text{calculated for C}_{32}H_{43}BrNOSi}^+ [M+H]^+: m/z = 564.22918, \text{found: 564.22963 (Dev.: 0.45 mu; 0.80 ppm).} \]

4.5.10 2-(7-Bromo-9,9-di methyl-3-((triisopropyl silyl)ethynyl)-9H-fluoren-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (6j)

Prepared according to GP1 from 3 (74.1 mg, 200 µmol, 1.00 eq) in anhydrous THF (0.5 mL, 0.4 M) and TMPMgCl-LiCl (857 µL, 600 µmol, 3.00 eq, 0.70 M). An alkynylation reaction was performed according to GP2 using CuCN-2LiCl (600 µL, 600 µmol, 3.00 eq, 1.00 M) and 5c (257 mg, 600 µmol, 3.00 eq) in anhydrous THF (3 mL). Instantaneously blue discoloring at 5c addition was observed. The reaction was quenched with saturated NH₄Cl solution (5 mL) and water (5 mL). CH₂Cl₂ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL). Purification by flash column chromatography (SiO₂, CH:EE 8:1 v:v) afforded 6j (89.0 mg, 162 µmol, 81 %) as a yellow solid.

\[ R_f = 0.16 \text{ (SiO}_2, \text{CH:EE 8:1 v:v)}. \text{Mp.: 218 – 220 °C.} \text{H-NMR (360 MHz, CDCl}_3)\] \( \delta = 8.17 \text{ (s, 1H), 8.14 (s, 1H), 7.62 (d,} J_{HH} = 1.9 \text{ Hz, 1H), 7.61 (d,} J_{HH} = 7.6 \text{ Hz, 1H), 7.54 (dd,} J_{HH} = 8.1 \text{ Hz,} J_{HH} = 1.7 \text{ Hz, 1H),} \text{S23} \)
4.31 (s, 2H), 1.79 (s, 6H), 1.70 (sept, \( ^3J_{HH} = 7.4 \text{ Hz} \), 3H), 1.52 (s, 6H), 1.25 (s, 9H), 1.23 (s, 9H) ppm. 

\(^{13}\text{C}\{^1\text{H}\}\text{-NMR (91 MHz, CDCl}_3\): \( \delta = 164.0, 156.6, 154.5, 142.7, 135.7, 130.9, 126.7, 126.3, 124.9, 123.8, 123.5, 122.6, 121.0, 110.7, 108.4, 80.6, 70.3, 47.7, 29.0 (2x), 26.8 (2x), 19.2 (6x), 12.7 (3x) ppm. IR (ATR, neat): \( \tilde{\nu} = 2956 \text{ (m)}, 2937 \text{ (m)}, 2859 \text{ (m)}, 2359 \text{ (w)}, 1960 \text{ (w)}, 1610 \text{ (s)}, 1561 \text{ (w)}, 1455 \text{ (m)}, 1409 \text{ (m)}, 1394 \text{ (w)}, 1374 \text{ (s)}, 1312 \text{ (m)}, 1287 \text{ (m)}, 1253 \text{ (m)}, 1208 \text{ (m)}, 1173 \text{ (w)}, 1101 \text{ (m)}, 1069 \text{ (s)}, 985 \text{ (m)}, 970 \text{ (m)}, 912 \text{ (m)}, 903 \text{ (m)}, 876 \text{ (s)}, 842 \text{ (w)}, 817 \text{ (s)}, 767 \text{ (m)}, 748 \text{ (s)}, 673 \text{ (s)} \text{ cm}^{-1}. \) HR-MS (APCI): calculated for \( \text{C}_{31}\text{H}_{41}\text{BrNOSi}^+ [M+H]^+ : m/z = 550.21353, \) found: 550.21342 (Dev.: \(-0.09 \mu\text{u}; -0.21 \text{ ppm}). 

4.5.11 2-(7-Bromo-9,9-dimethyl-3-phenyl-9H-fluoren-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (6k)

Prepared according to GP1 from 3 (74.1 mg, 200 \( \mu\text{mol}, 1.00 \text{ eq}) in anhydrous THF (0.5 mL, 0.4 M) and TMPMgCl-LiCl (500 \( \mu\text{L}, 600 \mu\text{mol}, 3.00 \text{ eq}, 1.20 \text{ M}). A phenylation reaction was performed according to GP2 using CuCN-2LiCl (600 \( \mu\text{L}, 600 \mu\text{mol}, 3.00 \text{ eq}, 1.00 \text{ M}) and 5d (283 mg, 600 \mu\text{mol}, 3.00 eq) in anhydrous THF (5 mL). The reaction was quenched with saturated NH\(_4\)Cl solution (5 mL) and water (5 mL). CH\(_2\)Cl\(_2\) (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH\(_2\)Cl\(_2\) (4 \( \times \) 10 mL). Purification by flash column chromatography (SiO\(_2\), CH:EE 8:1 v:v) afforded 6k (38.2 mg, 85.6 \( \mu\text{mol}, 43 \% \)) as a yellowish oil.

\( \text{R}_f = 0.19 \) (SiO\(_2\), CH:EE 8:1 v:v). \(^1\text{H}\)-NMR (360 MHz, CDCl\(_3\)): \( \delta = 7.78 \text{ (s, 1H)}, 7.68 \text{ (s, 1H)}, 7.59 \text{ (d, } ^3J_{HH} = 8.0 \text{ Hz, 1H}), 7.59 \text{ (d, } ^4J_{HH} = 1.8 \text{ Hz, 1H}), 7.52 \text{ – } 7.30 \text{ (m, 6H)}, 3.79 \text{ (s, 2H)}, 1.53 \text{ (s, 6H)}, 1.33 \text{ (s, 6H)} \text{ ppm.} \) 

\(^{13}\text{C}\{^1\text{H}\}\text{-NMR (91 MHz, CDCl}_3\): \( \delta = 164.3, 156.5, 151.9, 141.6, 141.4, 140.5, 137.4, 130.4, 128.5 \text{ (2x), 128.2 (2x), 127.3, 127.3, 126.4, 124.6, 122.1, 122.0, 121.9, 79.6, 67.6, 47.4, 28.2 (2x), 27.1 (2x) ppm. IR (ATR, neat): \( \tilde{\nu} = 2961 \text{ (m)}, 2924 \text{ (w)}, 2866 \text{ (w)}, 1645 \text{ (m)}, 1600 \text{ (w)}, 1455 \text{ (m)}, 1400 \text{ (m)}, 1358 \text{ (m)}, 1341 \text{ (w), 1300 (w), 1286 (w), 1266 (m), 1200 (m), 1092 (w), 1066 (m), 1033 (m), 1010 (w), 990 (m), 969 (m), 941 (w), 905 (m), 887 (m), 819 (s), 768 (s), 753 (m), 728 (s), 699 (s), 674 (m) cm}^{-1}. \) HR-MS (APCI): calculated for \( \text{C}_{26}\text{H}_{25}\text{BrNO}^+ [M+H]^+ : m/z = 446.11140, \) found: 446.11137 (Dev.: \(-0.03 \mu\text{u}; -0.08 \text{ ppm}).
4.5.12 (7-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-9,9-dimethyl-9H-fluoren-3-yl)(phenyl) methanone (6l)

Prepared according to GP1 from 3 (148 mg, 400 µmol, 1.00 eq) in anhydrous THF (1.0 mL, 0.4 M) and TMPMgCl·LiCl (1.00 mL, 1.20 mmol, 3.00 eq, 1.20 M). An acylation reaction was performed according to GP2 using CuCN·2LiCl (1.20 mL, 1.20 mmol, 3.00 eq, 1.00 M) and 5e (139 µL, 1.20 mmol, 3.00 eq) in anhydrous THF (1 mL). The reaction was quenched with saturated NH₄Cl solution (5 mL) and water (5 mL). CH₂Cl₂ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL). Purification by flash column chromatography (SiO₂, CH:EE 10:1 v:v) afforded 6l (148 mg, 312 µmol, 78 %) as a colorless oil.

R_f = 0.10 (SiO₂, CH:EE 10:1 v:v). ¹H-NMR (360 MHz, CDCl₃): δ = 7.93 (s, 1H), 7.81 (s, 1H), 7.76 (d, ³J_HH = 7.6 Hz, 2H), 7.58 (d, ³J_HH = 7.5 Hz, 2H), 7.56 – 7.36 (m, 4H), 3.55 (s, 2H), 1.53 (s, 6H), 1.04 (s, 6H) ppm. ¹³C[¹H]-NMR (91 MHz, CDCl₃): δ = 197.0, 161.6, 156.3, 155.0, 141.3, 139.5, 137.9, 136.6, 132.7, 130.6, 129.3 (2x), 128.5 (2x), 126.4, 126.3, 123.5, 122.7, 122.3, 120.4, 79.3, 67.9, 47.7, 27.9 (2x), 26.8 (2x) ppm. IR (ATR, neat): GetProperty=2963 (w), 2925 (w), 2893 (w), 2867 (w), 1667 (m), 1649 (m), 1598 (w), 1448 (m), 1406 (w), 1383 (w), 1355 (m), 1301 (m), 1260 (m), 1202 (m), 1177 (w), 1134 (w), 1088 (w), 1063 (m), 1047 (m), 1026 (w), 973 (m), 955 (m), 935 (m), 906 (m), 881 (m), 818 (m), 774 (w), 759 (w), 727 (s), 715 (s), 696 (s), 673 (m) cm⁻¹. HR-MS (APCI): calculated for C_{27}H_{25}BrNO_{2}⁺ [M+H]⁺: m/z = 474.10632, found: 474.10666 (Dev.: 0.34 µu; 0.71 ppm).

4.5.13 (7-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-9,9-dimethyl-9H-fluoren-3-yl)(4-nitrophenyl)methanone (6m)

S25
Prepared according to GP1 from 3 (74.1 mg, 200 µmol, 1.00 eq) in anhydrous THF (0.5 mL, 0.4 M) and TMPMgCl-LiCl (500 µL, 600 µmol, 3.00 eq, 1.20 M). An acylation reaction was performed according to GP2 using CuCN-2LiCl (600 µL, 600 µmol, 3.00 eq, 1.00 M) and 5f (111 mg, 600 µmol, 3.00 eq) in anhydrous THF (3 mL). The reaction was quenched with saturated NH₄Cl solution (5 mL) and water (5 mL). CH₂Cl₂ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL). Purification by flash column chromatography (SiO₂, CH:EE 8:1 v:v) afforded 6m (75.0 mg, 144 µmol, 72 %) as a yellow oil.

Rf = 0.16 (SiO₂, CH:EE 8:1 v:v). ¹H-NMR (360 MHz, CDCl₃): δ = 8.31 – 8.21 (AA'XX', 2H), 7.97 (d, 3JHH = 0.5 Hz, 1H), 7.79 (d, 3JHH = 0.6 Hz, 1H), 7.61 (d, 4JHH = 1.8 Hz, 1H), 7.60 (d, 3JHH = 8.3 Hz, 1H), 7.50 (dd, 3JHH = 8.1 Hz, 4JHH = 1.8 Hz, 1H), 3.67 (s, 2H), 1.55 (s, 6H), 1.01 (s, 6H) ppm.

¹³C{¹H}-NMR (91 MHz, CDCl₃): δ = 195.2, 160.7, 156.4, 155.7, 149.9, 143.0, 141.7, 138.6, 136.4, 130.0 (2x), 126.6, 125.8, 123.7 (2x), 123.6, 123.1, 122.4, 120.4, 79.4, 68.3, 47.8, 27.9 (2x), 26.8 (2x) ppm.

IR (ATR, neat): 𝜈̃ = 2964 (w), 2926 (w), 2897 (w), 2867 (w), 2251 (w), 2213 (w), 1677 (m), 1646 (m), 1603 (m), 1564 (w), 1525 (m), 1461 (w), 1410 (w), 1384 (w), 1362 (w), 1342 (s), 1319 (w), 1250 (m), 1202 (w), 1134 (w), 1106 (w), 1088 (m), 1063 (m), 1049 (m), 1013 (w), 974 (m), 955 (m), 935 (m), 906 (s), 867 (m), 853 (m), 811 (s), 781 (w), 758 (m), 723 (s), 681 (m) cm⁻¹. HR-MS (APCI): calculated for C₂₇H₃₇BrN₂O₄⁺ [M+H]⁺: m/z = 519.09140, found: 519.09183 (Dev.: 0.43 mu; 0.83 ppm).

4.5.14 2-(4-((7-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-9,9-dimethyl-9H-fluoren-3-yl) methyl)phenyl)-4,4-dimethyl-4,5-dihydrooxazole (6n)

Prepared according to GP1 from 3 (74.1 mg, 200 µmol, 1.00 eq) in anhydrous THF (0.5 mL, 0.4 M) and TMPMgCl-LiCl (500 µL, 600 µmol, 3.00 eq, 1.20 M). A benzylation reaction was performed according to GP2 using CuCN-2LiCl (600 µL, 600 µmol, 3.00 eq, 1.00 M) and 5g (161 mg, 600 µmol, 3.00 eq) in anhydrous THF (1 mL). The reaction was quenched with saturated NH₄Cl solution (5 mL) and water (5 mL). CH₂Cl₂ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL). Purification by flash column chromatography (SiO₂, CH:EE 8:1 v:v) afforded 6n (92.2 mg, 144 µmol, 72 %) as a yellow oil.
165 µmol, 83 %) as a colorless solid.

\[ R_f = 0.17 \] (SiO₂, CH:EE 4:1 v:v). **Mp.:** 137 – 139 °C. **¹H-NMR (360 MHz, CDCl₃):** \( \delta = 7.88 – 7.80 \) (AA'XX', 2H), 7.78 (s, 1H), 7.54 (d, \( J_{HH} = 1.7 \) Hz, 1H), 7.50 (d, \( J_{HH} = 8.1 \) Hz, 1H), 7.45 (s, 1H), 7.43 (dd, \( J_{HH} = 8.1 \) Hz, \( J_{HH} = 1.8 \) Hz, 1H), 7.26 – 7.18 (AA'XX', 2H), 4.51 (s, 2H), 4.08 (s, 2H), 3.99 (s, 2H), 1.48 (s, 6H), 1.37 (s, 6H), 1.30 (s, 6H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃):** \( \delta = 162.7, 162.2, 156.6, 151.2, 144.9, 140.6, 139.8, 137.4, 130.3, 129.1 \) (2x), 128.3 (2x), 127.1, 126.4, 125.8, 124.6, 122.7, 122.1, 122.0, 79.1, 78.7, 68.0, 67.6, 47.3, 40.0, 28.6 (2x), 28.5 (2x), 27.0 (2x) ppm. **IR (ATR, neat):** \( \nu = 2961 \text{ (m)}, 2923 \text{ (w)}, 2895 \text{ (w)}, 2864 \text{ (w)}, 1636 \text{ (s)}, 1610 \text{ (m)}, 1563 \text{ (w)}, 1511 \text{ (w)}, 1461 \text{ (m)}, 1416 \text{ (m)}, 1407 \text{ (w)}, 1354 \text{ (m)}, 1301 \text{ (s)}, 1187 \text{ (s)}, 1087 \text{ (m)}, 1059 \text{ (s)}, 1040 \text{ (s)}, 1020 \text{ (s)}, 994 \text{ (m)}, 977 \text{ (m)}, 948 \text{ (m)}, 922 \text{ (m)}, 904 \text{ (s)}, 881 \text{ (m)}, 835 \text{ (m)}, 823 \text{ (s)}, 805 \text{ (m)}, 777 \text{ (m)}, 730 \text{ (s)}, 715 \text{ (s)}, 687 \text{ (s)}, 669 \text{ (m)} \text{ cm}^{-1}. **HR-MS (APCI):** calculated for C₃₂H₃₄BrN₂O₂ \[ \text{[M+H]}^+ \]: m/z = 557.17982, found: 557.18050 (Dev.: 0.68 mu; 1.23 ppm).

**4.5.15 2-(7-Bromo-9,9-dimethyl-3-(4-nitrophenyl)-9H-fluoren-2-yl)-4,4-dimethyl-4,5-dihydro oxazole (60)**

![Diagram](image)

Prepared according to GP1 from 3 (74.1 mg, 200 µmol, 1.00 eq) in anhydrous THF (0.5 mL, 0.4 M) and TMPMgCl·LiCl (500 µL, 600 µmol, 3.00 eq, 1.20 M). A cross-coupling reaction was performed according to GP3 using ZnCl₂ (600 µL, 600 µmol, 3.00 eq, 1.00 M), 5h (149 mg, 600 µmol, 3.00 eq) and Pd(PPh₃)₄ (11.6 mg, 10.0 µmol, 0.05 eq) in anhydrous THF (1 mL). The reaction was quenched with saturated NH₄Cl solution (5 mL) and water (5 mL). CH₂Cl₂ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL). Purification by flash column chromatography (SiO₂, CH:EE 6:1 v:v) afforded 6o (82.9 mg, 169 µmol, 84 %) as a colorless solid.

\[ R_f = 0.13 \] (SiO₂, CH:EE 6:1 v:v). **Mp.:** 192 – 194 °C. **¹H-NMR (360 MHz, CDCl₃):** \( \delta = 8.32 – 8.23 \) (AA'XX', 2H), 7.87 (s, 1H), 7.64 (s, 1H), 7.63 – 7.55 (m, 4H), 7.49 (dd, \( J_{HH} = 8.2 \) Hz, \( J_{HH} = 1.7 \) Hz, 1H), 3.81 (s, 2H), 1.53 (s, 6H), 1.31 (s, 6H) ppm. **¹H-NMR (360 MHz, C₆D₆):** \( \delta = 8.15 \) (s, 1H), 8.04 – 7.96 (AA'XX', 2H), 7.45 (d, \( J_{HH} = 1.8 \) Hz, 1H), 7.32 (dd, \( J_{HH} = 8.1 \) Hz, \( J_{HH} = 1.7 \) Hz, 1H), 7.32 (s, 1H), 7.17 – 7.10 (m, 3H), 3.46 (s, 2H), 1.13 (s, 6H), 1.08 (s, 6H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃):** \( \delta = 163.2, 156.5, 153.3, 148.7, 147.1, 140.9, 139.2, 136.8, 130.6, 129.5 \) (2x), 126.9, 126.5, 124.9, 123.3 (2x), 122.6, 122.1, 121.7, 79.5, 67.9, 47.5, 28.2 (2x), 26.9 (2x) ppm. **¹³C{¹H}-NMR (91 MHz, C₆D₆):** \( \delta = 162.3, 156.8, \)
153.4, 148.9, 147.5, 140.8, 140.1, 137.1, 130.9, 129.8 (2x), 127.5, 126.7, 125.3, 123.2 (2x), 123.0, 122.4, 122.2, 79.1, 68.1, 47.4, 28.1 (2x), 26.5 (2x) ppm. IR (ATR, neat): $\tilde{\nu} = 2962$ (w), 2926 (w), 2868 (w), 1633 (m), 1597 (m), 1509 (s), 1456 (m), 1361 (m), 1340 (s), 1295 (m), 1268 (m), 1200 (m), 1133 (w), 1106 (m), 1068 (m), 1051 (m), 1017 (m), 970 (m), 945 (m), 914 (m), 882 (m), 861 (m), 853 (s), 818 (s), 775 (m), 764 (m), 750 (m), 730 (m), 703 (s), 672 (m), 661 (m) cm$^{-1}$. HR-MS (APCI): calculated for C$_{26}$H$_{24}$BrN$_2$O$_3$ $^{+}$ [M+H]$^{+}$: m/z = 491.09648, found: 491.09614 (Dev.: $-$0.34 mu; $-$0.70 ppm).

4.5.16 Ethyl 4-(7-bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-9,9-dimethyl-9H-fluoren-3-yl) benzoate (6p)

Prepared according to GP1 from 3 (74.1 mg, 200 µmol, 1.00 eq) in anhydrous THF (0.5 mL, 0.4 M) and TMPMgCl·LiCl (500 µL, 600 µmol, 3.00 eq, 1.20 M). A cross-coupling reaction was performed according to GP3 using ZnCl$_2$ (600 µL, 600 µmol, 3.00 eq, 1.00 M), 5i (101 µL, 600 µmol, 3.00 eq) and Pd(PPh$_3$)$_4$ (11.6 mg, 10.0 µmol, 0.05 eq) in anhydrous THF (1 mL). The reaction was quenched with saturated NH$_4$Cl solution (5 mL) and water (5 mL). CH$_2$Cl$_2$ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (4 × 10 mL). Purification by flash column chromatography (SiO$_2$, CH:EE 6:1 v:v) afforded 6p (95.0 mg, 183 µmol, 92 %) as a colorless solid.  

$R_f$ = 0.11 (SiO$_2$, CH:EE 6:1 v:v). Mp.: 158 – 160 °C. $^1$H-NMR (360 MHz, CDCl$_3$): $\delta = 8.14 – 8.05$ (AA'XX', 2H), 7.82 (s, 1H), 7.66 (s, 1H), 7.61 – 7.57 (m, 2H), 7.56 – 7.47 (AA'XX', 2H), 7.47 (dd, $^3$$J_{HH} =$ 8.2 Hz, $^4$$J_{HH} =$ 1.7 Hz, 1H), 4.41 (q, $^3$$J_{HH} =$ 7.1 Hz, 2H), 3.78 (s, 2H), 1.53 (s, 6H), 1.42 (t, $^3$$J_{HH} =$ 7.1 Hz, 3H), 1.33 (s, 6H) ppm. $^1$H-NMR (360 MHz, C$_6$D$_6$): $\delta = 8.34 – 8.26$ (AA'XX', 2H), 8.16 (s, 1H), 7.50 – 7.43 (AA'XX', 2H), 7.46 (s, 1H), 7.44 (d, $^4$$J_{HH} =$ 1.7 Hz, 1H), 7.30 (dd, $^3$$J_{HH} =$ 8.1 Hz, $^4$$J_{HH} =$ 1.7 Hz, 1H), 7.10 (d, $^3$$J_{HH} =$ 8.1 Hz, 1H), 4.18 (q, $^3$$J_{HH} =$ 7.1 Hz, 2H), 3.48 (s, 2H), 1.14 (s, 6H), 1.12 (s, 6H), 1.05 (t, $^3$$J_{HH} =$ 7.1 Hz, 3H) ppm. $^{13}$C($^1$H)-NMR (91 MHz, CDCl$_3$): $\delta =$ 166.7, 163.9, 156.5, 152.6, 146.4, 140.7, 140.4, 137.1, 130.5, 129.4 (2x), 129.3, 128.5 (2x), 127.1, 126.4, 124.8, 122.3, 122.0, 121.8, 79.6, 67.7, 61.1, 47.4, 28.2 (2x), 27.0 (2x), 14.5 ppm. $^{13}$C($^1$H)-NMR (91 MHz, C$_6$D$_6$): $\delta =$ 166.3, 163.1, 156.8, 152.8, 147.2, 141.3, 140.7, 137.4, 130.8, 130.0, 129.6 (2x), 129.2 (2x), 127.9, 126.6, 125.2, 122.7, 122.4 (2x), 79.2, 68.0, 60.9, 47.3, 28.2 (2x), 26.5 (2x), 14.4 ppm. IR (ATR, neat): $\tilde{\nu} = 2960$ (w), 2925 (w), 2866 (w), 1709 (s), 1652 (m), 1609 (m), 1575 (w), 1466 (w), 1406 (w), 1361 (m), 1306 (w), 1271 (s), 1204 (m), 1176 (m), 1100 (s), 1066 (m), 1051 (s), 1023 (m), 1008 (m), 963 (m), 943 (m), 917 (m), 901 (w), 859 (m), 829 (s), 821 (s), 818 (s), 775 (m), 764 (m), 750 (m), 730 (m), 703 (s), 672 (m), 661 (m) cm$^{-1}$. HR-MS (APCI): calculated for C$_{26}$H$_{24}$BrN$_2$O$_3$ $^{+}$ [M+H]$^{+}$: m/z = 491.09648, found: 491.09614 (Dev.: $-$0.34 mu; $-$0.70 ppm).
775 (s), 754 (s), 731 (w), 710 (s), 674 (m), 664 (m) cm

4.5.17 2-(7-Bromo-3-(4-methoxyphenyl)-9,9-dimethyl-9H-fluoren-2-yl)-4,4-dimethyl-4,5-dihydro oxazole (6q)

Prepared according to GP1 from 3 (74.1 mg, 200 µmol, 1.00 eq) in anhydrous THF (0.5 mL, 0.4 M) and TMPMgCl·LiCl (500 µL, 600 µmol, 3.00 eq, 1.20 M). A cross-coupling reaction was performed according to GP3 using ZnCl₂ (600 µL, 600 µmol, 3.00 eq, 1.00 M), 5j (140 mg, 600 µmol, 3.00 eq) and Pd(PPh₃)₄ (11.6 mg, 10.0 µmol, 0.05 eq) in anhydrous THF (1 mL). The reaction was quenched with saturated NH₄Cl solution (5 mL) and water (5 mL). CH₂Cl₂ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL). Purification by flash column chromatography (SiO₂, CH:EE 6:1 v:v) afforded 6q (81.1 mg, 170 µmol, 85 %) as a colorless solid.

Rᵣ = 0.12 (SiO₂, CH:EE 6:1 v:v). Mp.: 131 – 133 °C. ¹H-NMR (360 MHz, CDCl₃): δ = 7.76 (s, 1H), 7.65 (s, 1H), 7.60 – 7.56 (m, 2H), 7.47 (dd, 3JHH = 8.2 Hz, 4JHH = 1.7 Hz, 1H), 7.43 – 7.34 (AA'XX', 2H), 7.00 – 6.91 (AA'XX', 2H), 3.86 (s, 3H), 3.82 (s, 2H), 1.52 (s, 6H), 1.35 (s, 6H) ppm. ¹H-NMR (360 MHz, C₆D₆): δ = 8.13 (s, 1H), 7.61 (s, 1H), 7.45 (d, 4JHH = 1.7 Hz, 1H), 7.48 – 7.40 (AA'XX', 2H), 7.29 (dd, 3JHH = 8.1 Hz, 4JHH = 1.8 Hz, 1H), 7.11 (d, 3JHH = 8.1 Hz, 1H), 6.93 – 6.85 (AA'XX', 2H), 3.57 (s, 2H), 3.37 (s, 3H), 1.19 (s, 6H), 1.16 (s, 6H) ppm. ¹³C{¹H}-NMR (91 MHz, CDCl₃): δ = 164.5, 159.1, 156.6, 151.6, 141.0, 140.5, 137.4, 134.1, 130.4, 129.6 (2x), 127.2, 126.4, 124.7, 122.1, 122.0, 121.8, 113.6 (2x), 79.7, 67.5, 55.4, 47.4, 28.2 (2x), 27.1 (2x) ppm. ¹³C{¹H}-NMR (91 MHz, C₆D₆): δ = 163.9, 159.6, 156.9, 151.9, 142.0, 140.6, 137.7, 134.9, 130.7, 130.2 (2x), 128.2, 126.6, 125.2, 122.6, 122.4, 122.3, 113.8 (2x), 79.3, 67.8, 54.9, 47.3, 28.3 (2x), 26.7 (2x) ppm. IR (ATR, neat): ν = 2965 (w), 2928 (w), 2198 (w), 1643 (m), 1607 (m), 1516 (m), 1454 (m), 1425 (w), 1356 (w), 1296 (m), 1267 (w), 1247 (s), 1200 (m), 1177 (s), 1112 (w), 1093 (w), 1070 (m), 1035 (m), 1017 (w), 987 (m), 969 (m), 934 (m), 905 (m), 889 (m), 878 (m), 842 (s), 820 (s), 807 (s), 772 (w), 759 (m), 735 (s), 724 (s), 680 (m), 654 (m) cm⁻¹. HR-MS (APCI): calculated for C₂₇H₂₇BrNO₂⁺ [M+H]⁺: m/z = 476.12197, found: 476.12232 (Dev.: 0.35 µ; 0.73 ppm).
4.5.18 (7-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-9,9-dimethyl-9H-fluoren-3-yl)(3-nitrophenyl)methanol (S6)

Prepared according to GP1 from 3 (148 mg, 400 µmol, 1.00 eq) in anhydrous THF (1.0 mL, 0.4 M) and TMPMgCl·LiCl (1.00 mL, 1.20 mmol, 3.00 eq, 1.20 M). 5k (181 mg, 1.20 mmol, 3.00 eq) in anhydrous THF (1 mL) was added and the reaction mixture was stirred for four hours. The reaction was quenched with saturated NH₄Cl solution (5 mL) and water (5 mL). CH₂Cl₂ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL). Purification by flash column chromatography (SiO₂, DCM then CH:EE 10:1 v:v) afforded S6 (127 mg, 244 µmol, 61 %) as a yellow oil, which was directly used for the next step.

4.5.19 7-Bromo-9,9-dimethyl-3-(3-nitrophenyl)-3,9-dihydro-1H-fluroeno[2,3-c]furan-1-one (6r)

Prepared according to GP4 from S6 (104 mg, 200 µmol, 1.00 eq) in 4 N HCl (1.0 mL, 0.2 M). After cooling to 25 °C, saturated NaHCO₃ solution (10 mL) and CH₂Cl₂ (10 mL) were added. The phases were separated and the aqueous phase was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic phases were washed with saturated NaHCO₃ solution (10 mL), dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO₂, CH:EE 8:1 v:v) afforded 6r (68.2 mg, 151 µmol, 76 %) as a yellow solid.

Rᵣ = 0.23 (SiO₂, CH:EE 8:1 v:v). Mp.: 171 – 173 °C. ¹H-NMR (360 MHz, CDCl₃): δ = 8.30 – 8.21 (m, 2H), 8.00 (d, ²JHH = 0.8 Hz, 1H), 7.71 (dt, ³JHH = 7.7 Hz, ⁴JHH = 1.4 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.61 (d, ⁴JHH = 1.8 Hz, 1H), 7.58 (d, ³JHH = 8.1 Hz, 1H), 7.57 (s, 1H), 7.48 (dd, ³JHH = 8.1 Hz, ⁴JHH = 1.8 Hz, 1H),
6.53 (s, 1H), 1.53 (s, 3H), 1.53 (s, 3H) ppm. \[^{13}\text{C}\{^1\text{H}\} \text{-NMR}\ (91\ \text{MHz, CDCl}_3): \ \delta = 170.1, 156.8, 155.7, 148.7, 148.7, 145.7, 139.1, 135.9, 133.0, 130.9, 126.7, 124.4, 124.3, 123.9, 122.7, 122.1, 120.3, 113.8, 81.1, 47.2, 27.1, 26.9 ppm.\]

IR (ATR, neat): \( \tilde{\nu} = 2923\ (w), 2859\ (w), 1758\ (s), 1615\ (m), 1529\ (s), 1474\ (m), 1455\ (m), 1434\ (w), 1407\ (w), 1346\ (w), 1294\ (m), 1270\ (m), 1256\ (m), 1204\ (w), 1181\ (s), 1150\ (m), 1083\ (m), 1062\ (m), 1039\ (s), 1017\ (s), 895\ (m), 883\ (m), 831\ (s), 816\ (m), 802\ (m), 780\ (m), 766\ (m), 729\ (s), 722\ (s), 704\ (m), 689\ (s), 673\ (s)\ cm^{-1}.\)

HR-MS (APCI): calculated for C\(_{23}\)H\(_{17}\)\(\text{BrNO}_4^+\) [M+H]\(^+\): m/z = 450.0335, found: 450.0355 (Dev.: 0.00 mu; 0.02 ppm).

### 4.5.20

**7-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-9,9-dimethyl-9H-fluoren-3-yl)(4-bromo phenyl)methanol (S7)**

![Image](image1)

Prepared according to GP1 from 3 (148 mg, 400 \(\mu\)mol, 1.00 eq) in anhydrous THF (1.0 mL, 0.4 M) and TMPMgCl·LiCl (1.00 mL, 1.20 mmol, 3.00 eq, 1.20 M). 5l (222 mg, 1.20 mmol, 3.00 eq) in anhydrous THF (1 mL) was added and the reaction mixture was stirred for four hours. The reaction was quenched with saturated NH\(_4\)Cl solution (5 mL) and water (5 mL). CH\(_2\)Cl\(_2\) (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH\(_2\)Cl\(_2\) (4 \(\times\) 10 mL). Purification by flash column chromatography (SiO\(_2\), DCM then CH:EE 10:1 v:v) afforded S7 (161 mg, 290 \(\mu\)mol, 72 \%) as a yellow oil, which was directly used for the next step.

### 4.5.21

**7-Bromo-3-(4-bromophenyl)-9,9-dimethyl-3,9-dihydro-1H-fluoro[2,3-c]furan-1-one (6s)**

![Image](image2)

Prepared according to GP4 from S7 (111 mg, 200 \(\mu\)mol, 1.00 eq) in 4 N HCl (1.0 mL, 0.2 M). After cooling to 25 °C, saturated NaHCO\(_3\) solution (10 mL) and CH\(_2\)Cl\(_2\) (10 mL) were added. The phases were separated
and the aqueous phase was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic phases were washed with saturated NaHCO$_3$ solution (10 mL), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO$_2$, CH:EE 10:1 v:v) afforded 6s (81.0 mg, 167 µmol, 84 %) as a colorless solid.

$R_f = 0.25$ (SiO$_2$, CH:EE 10:1 v:v). M.p.: 243 – 245 °C. $^1$H-NMR (360 MHz, CDCl$_3$): $\delta = 7.96$ (s, 1H), 7.61 (d, $^4J_{HH} = 1.7$ Hz, 1H), 7.57 (d, $^3J_{HH} = 8.1$ Hz, 1H), 7.58 – 7.50 (AA'XX', 2H), 7.53 (s, 1H), 7.48 (dd, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 1.8$ Hz, 1H), 7.25 – 7.20 (AA'XX', 2H), 6.39 (s, 1H), 1.53 (s, 3H), 1.52 (s, 3H) ppm.

$^{13}$C($^1$H)-NMR (91 MHz, CDCl$_3$): $\delta = 170.5, 156.9, 155.4, 149.4, 145.4, 136.1, 135.8, 132.4 (2x), 130.8, 128.8 (2x), 126.7, 124.6, 123.7, 123.6, 122.7, 120.0, 114.0, 81.9, 47.2, 27.1, 27.0 ppm. IR (ATR, neat): $\tilde{\nu} = 2971$ (w), 2926 (w), 2863 (w), 1771 (s), 1732 (m), 1617 (m), 1599 (m), 1482 (m), 1455 (m), 1434 (w), 1402 (m), 1315 (m), 1269 (m), 1253 (m), 1200 (m), 1179 (m), 1144 (m), 1084 (m), 1061 (m), 1039 (s), 1019 (m), 1005 (s), 976 (m), 949 (m), 893 (w), 847 (w), 818 (s), 804 (s), 774 (s), 760 (m), 725 (m), 671 (m) cm$^{-1}$. HR-MS (APCI): calculated for C$_{23}$H$_{17}$Br$_2$O$_2$ [M+H]$^+$: m/z = 482.95898, found: 482.95924 (Dev.: 0.26 mu; 0.55 ppm).

4.5.22 (7-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-9,9-dimethyl-9H-fluoren-3-yl)(4-methoxy phenyl)methanol (S8)

Prepared according to GP1 from 3 (148 mg, 400 µmol, 1.00 eq) in anhydrous THF (1.0 mL, 0.4 M) and TMPMgCl·LiCl (1.00 mL, 1.20 mmol, 3.00 eq, 1.20 M). Freshly distilled 5m (146 µL, 1.20 mmol, 3.00 eq) in anhydrous THF (1 mL) was added and the reaction mixture was stirred for four hours. The reaction was quenched with saturated NH$_4$Cl solution (5 mL) and water (5 mL). CH$_2$Cl$_2$ (10 mL) was added, the phases were separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (4 × 10 mL). Purification by flash column chromatography (SiO$_2$, DCM then CH:EE 10:1 v:v) afforded S8 (135 mg, 267 µmol, 67 %) as a yellow oil, which was directly used for the next step.
4.5.23 7-Bromo-3-(4-methoxyphenyl)-9,9-dimethyl-3,9-dihydro-1H-fluoreno[2,3-c]furan-1-one (6t)

Prepared according to GP4 from S8 (101 mg, 200 µmol, 1.00 eq) in 4 N HCl (1.0 mL, 0.2 M). After cooling to 25 °C, saturated NaHCO₃ solution (10 mL) and CH₂Cl₂ (10 mL) were added. The phases were separated and the aqueous phase was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic phases were washed with saturated NaHCO₃ solution (10 mL), dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO₂, CH:EE 10:1 v:v) afforded 6t (76.0 mg, 175 µmol, 87 %) as a colorless solid.

Rᶠ = 0.17 (SiO₂, CH:EE 10:1 v:v). Mp.: 196 – 198 °C. ¹H-NMR (360 MHz, CDCl₃): δ = 7.97 (s, 1H), 7.61 (d, ⁴JHH = 1.7 Hz, 1H), 7.55 (d, ³JHH = 8.6 Hz, 1H), 7.54 (s, 1H), 7.47 (dd, ³JHH = 8.2 Hz, ⁴JHH = 1.8 Hz, 1H), 7.29 – 7.20 (AA'XX', 2H), 6.97 – 6.87 (AA'XX', 2H), 6.40 (s, 1H), 3.81 (s, 3H), 1.54 (s, 3H), 1.53 (s, 3H) ppm. ¹³C{¹H}-NMR (91 MHz, CDCl₃): δ = 170.8, 160.5, 156.8, 155.1, 150.0, 145.1, 136.2, 130.7, 129.0 (2x), 128.6, 126.7, 125.1, 123.5, 122.6, 119.8, 114.5 (2x), 114.2, 82.8, 55.5, 47.1, 27.2, 27.0 ppm. IR (ATR, neat): ν = 2954 (w), 2925 (w), 2859 (w), 2840 (w), 1733 (s), 1609 (m), 1513 (m), 1484 (w), 1466 (w), 1436 (w), 1408 (w), 1343 (m), 1325 (m), 1303 (m), 1287 (m), 1252 (s), 1183 (s), 1153 (m), 1133 (m), 1088 (m), 1059 (m), 1049 (m), 1029 (s), 958 (m), 937 (m), 899 (m), 883 (m), 828 (s), 820 (s), 787 (m), 776 (m), 761 (m), 724 (m), 689 (m) cm⁻¹. HR-MS (APCI): calculated for C₂₃H₂₀⁷⁹BrO₃⁺ [M+H]^+: m/z = 435.05903, found: 435.05938 (Dev.: 0.35 µu; 0.80 ppm).
4.6 Preparation of Azido-Bromofluorenecarbaldehyde 11

4.6.1 7-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-9,9-dimethyl-9H-fluorene-3-carbaldehyde (7)

Prepared according to GP1 from 3 (3.70 g, 10.0 mmol, 1.00 eq) in anhydrous THF (25.0 mL, 0.4 M) and TMPMgCl·LiCl (25.0 mL, 30.0 mmol, 3.00 eq, 1.20 M). DMF (3.10 mL, 40.0 mmol, 4.00 eq) in anhydrous THF (10 mL) was added and the reaction mixture was stirred for two hours. The reaction was quenched with water (50 mL). Ethyl acetate (80 mL) was added, the phases were separated and the aqueous layer was extracted with ethyl acetate (4 × 80 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure on a rotary evaporator (30 °C water bath temperature). The product was used without further purification for the next reaction step. If desired, the aldehyde 7 can be isolated as a colorless solid by washing the crude product with small amounts of ice cooled cyclohexane.

R$_f$ = 0.33 (SiO$_2$, CH:EE 6:1 v:v). Mp.: 178 – 180 °C decom. $^1$H-NMR (360 MHz, CDCl$_3$): $\delta$ = 10.75 (s, 1H), 8.26 (s, 1H), 7.93 (s, 1H), 7.67 (d, $^3$$J_{HH}$ = 8.1 Hz, 1H), 7.58 (s, 1H), 7.51 (d, $^3$$J_{HH}$ = 8.0 Hz, 1H), 4.19 (s, 2H), 1.51 (s, 6H), 1.44 (s, 6H) ppm. $^{13}$C($^1$H)-NMR (91 MHz, CDCl$_3$): $\delta$ = 192.5, 160.7, 158.1, 156.1, 141.2, 136.5, 136.1, 130.8, 129.5, 126.5, 124.4, 122.9, 122.6, 119.7, 79.5, 68.9, 47.8, 28.6 (2x), 26.8 (2x) ppm. IR (ATR, neat): $\tilde{\nu}$ = 2966 (w), 2926 (w), 2359 (w), 2324 (w), 1682 (s), 1643 (m), 1613 (m), 1463 (m), 1409 (m), 1358 (m), 1302 (m), 1268 (m), 1200 (m), 1146 (m), 1086 (m), 1062 (s), 1038 (s), 973 (s), 899 (s), 810 (s), 743 (s) cm$^{-1}$. HR-MS (EI, 70 eV): calculated for C$_{21}$H$_{20}^{79}$BrNO$_2$+ [M]$^+$: m/z = 397.06719, found: 397.06645 (Dev.: −0.74 mu; −1.87 ppm).

4.6.2 (7-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-9,9-dimethyl-9H-fluoren-3-yl)methanol (8)
A modified literature procedure was used.\(^\text{27}\) The crude product 7 (10.0 mmol, 1.00 eq) was dissolved in THF:MeOH (25.0 mL, 1:1 v:v, 0.4 M) and cooled to 0 °C. NaBH\(_4\) (757 mg, 20.0 mmol, 2.00 eq) was added at once and stirring was continued for 90 minutes while the temperature was maintained. Water (25 mL) was added dropwise at 0 °C to stop the reaction, CH\(_2\)Cl\(_2\) (50 mL) was added and the phases were separated. The aqueous layer was extracted with CH\(_2\)Cl\(_2\) (4 × 50 mL) and the combined organic layers were dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO\(_2\), CH:EE 10:1 to 6:1 v:v) afforded 8 (3.16 g, 7.89 mmol, 79 % over two steps) as a colorless solid. If necessary the product can be washed with cyclohexane to remove yellow impurities.

R\(_f\) = 0.06 (SiO\(_2\), CH:EE 10:1 v:v). R\(_f\) = 0.22 (SiO\(_2\), CH:EE 6:1 v:v). Mp.: 179 – 181 °C. \(^1\)H-NMR (360 MHz, CDCl\(_3\)): \(\delta = 7.91\) (s, 1H), 7.68 (s, 1H), 7.61 (d, \(^3J_{IH} = 8.0\) Hz, 1H), 7.57 (d, \(^4J_{IH} = 1.8\) Hz, 1H), 7.49 (dd, \(^3J_{IH} = 8.0\) Hz, \(^4J_{IH} = 1.8\) Hz, 1H), 6.77 (br. s, 1H), 4.74 (s, 2H), 4.17 (s, 2H), 1.48 (s, 6H), 1.43 (s, 6H) ppm. \(^1\)C\{\(^1\)H\}-NMR (91 MHz, CDCl\(_3\)): \(\delta = 162.4, 156.7, 152.5, 141.9, 141.4, 137.2, 130.6, 126.4, 126.0, 124.4, 122.4, 122.2 (2x), 78.9, 68.2, 64.9, 47.3, 28.6 (2x), 26.9 (2x) ppm. IR (ATR, neat): \(\tilde{\nu} = 3184\) (br), 3050 (w), 2962 (w), 2947 (w), 2926 (w), 2864 (w), 2360 (w), 1635 (s), 1567 (w), 1459 (m), 1366 (m), 1307 (m), 1298 (m), 1089 (m), 1064 (s), 1050 (s), 1019 (s), 974 (m), 950 (s), 899 (m), 885 (m), 830 (s), 819 (s), 740 (s), 724 (s), 654 (s) cm\(^{-1}\). HR-MS (EI, 70 eV): calculated for C\(_{21}\)H\(_{22}\)\(^{79}\)BrNO\(_2\)\([\text{M}]^+\): m/z = 399.08284, found: 399.08234 (Dev.: ± 0.50 mu; ± 1.25 ppm).

4.6.3 7-Bromo-9,9-dimethyl-3,9-dihydro-1H-fluorenoc[2,3-c]furan-1-one (9)

A modified literature procedure was used.\(^\text{28}\) 8 (160 mg, 400 µmol, 1.00 eq) was suspended in 4 N HCl (2.00 mL, 0.4 M) and heated to 120 °C. After stirring for six hours at this temperature the mixture was allowed to cool to 25 °C and saturated NaHCO\(_3\) solution (10 mL) and CH\(_2\)Cl\(_2\) (10 mL) were added. The phases were separated and the aqueous phase was extracted with CH\(_2\)Cl\(_2\) (3 × 10 mL). The combined organic phases were washed with saturated NaHCO\(_3\) solution (10 mL), dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO\(_2\), CH:EE 6:1 v:v) afforded 9 (120 mg, 365 µmol, 91 %) as a colorless solid.
R_f = 0.22 (SiO_2, CH:EE 6:1 v:v). Mp.: 215 – 217 °C. ^1H-NMR (360 MHz, CDCl_3): δ = 7.94 (d, J_HH = 0.9 Hz, 1H), 7.75 (d, J_HH = 0.8 Hz, 1H), 7.65 (d, J_HH = 8.1 Hz, 1H), 7.62 (d, J_HH = 1.8 Hz, 1H), 7.52 (dd, J_HH = 8.1 Hz, J_HH = 1.8 Hz, 1H), 5.37 (s, 2H), 1.51 (s, 6H) ppm. ^13C{^1H}-NMR (91 MHz, CDCl_3): δ = 171.4, 156.9, 154.9, 146.7, 144.9, 136.3, 130.8, 126.8, 125.0, 123.5, 122.5, 121.3, 113.4, 69.8, 47.1, 27.1 (2x) ppm. IR (ATR, neat): v = 2910 (w), 2869 (w), 2360 (w), 1755 (s), 1622 (m), 1452 (m), 1345 (s), 1252 (m), 1184 (s), 1081 (m), 1055 (m), 1034 (s), 1006 (s), 953 (w), 884 (m), 870 (m), 822 (s), 777 (s), 762 (s) cm⁻¹. HR-MS (EI, 70 eV): calculated for C_{17}H_{13}BrO_2·[M]^+: m/z = 328.00934, found: 328.00958 (Dev.: 0.24 mu; 0.72 ppm).

4.6.4 2-(3-(Azidomethyl)-7-bromo-9,9-dimethyl-9H-fluoren-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (10)

A modified literature procedure was used.²⁹ 8 (1.00 g, 2.50 mmol, 1.00 eq) was dissolved in PhMe (12.5 mL, 0.2 M) and DBU (485 µL, 3.25 mmol, 1.30 eq) was added via syringe pump (0.5 mL/min) at 25 °C. The mixture was stirred for ten minutes, whereupon DPPA (645 µL, 3.00 mmol, 1.20 eq) was added via syringe pump (0.3 mL/min). After complete addition the suspension was stirred for 15 hours at 25 °C. Due to incomplete consumption of the immediately formed phosphate, NaN_3 (163 mg, 2.50 mmol, 1.00 eq) was added and the mixture was heated to 60 °C for four hours. Saturated NH_4Cl solution (10 mL) and CH_2Cl_2 (30 mL) were added, the phases separated and the aqueous phase was extracted with CH_2Cl_2 (4 × 40 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2, CH:EE 15:1 v:v) provided 10 (921 mg, 2.17 mmol, 87 %) as a colorless oil. The oil solidified upon standing at 25 °C to form a colorless solid.

R_f = 0.34 (SiO_2, CH:EE 15:1 v:v). Mp.: 122 – 124 °C. ^1H-NMR (360 MHz, CDCl_3): δ = 7.94 (s, 1H), 7.75 (s, 1H), 7.62 (d, J_HH = 8.1 Hz, 1H), 7.57 (d, J_HH = 1.8 Hz, 1H), 7.49 (dd, J_HH = 8.1 Hz, J_HH = 1.8 Hz, 1H), 4.95 (s, 2H), 4.12 (s, 2H), 1.49 (s, 6H), 1.42 (s, 6H) ppm. ^13C{^1H}-NMR (91 MHz, CDCl_3): δ = 161.5, 156.6, 152.8, 141.0, 137.1, 135.8, 130.5, 126.4, 126.0, 124.6, 122.4, 122.2, 121.3, 78.7, 68.5, 53.6, 47.4, 28.5 (2x), 26.9 (2x) ppm. IR (ATR, neat): v = 2964 (w), 2924 (w), 2359 (w), 2359 (w), 2103 (s), 1637 (m), 1458 (m), 1409 (m), 1360 (m), 1327 (m), 1301 (s), 1261 (s), 1200 (m), 1087 (m), 1061 (m), 1038 (s), 974 (m), 951

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HR-MS (APCI): calculated for C_{21}H_{22}BrN_{4}O^{+} [M+H]^+: m/z = 425.09715, found: 425.09753 (Dev.: 0.38 mu; 0.90 ppm).

4.6.5 3-(Azidomethyl)-7-bromo-9,9-dimethyl-9H-fluorene-2-caraldehyde (11)

A modified literature procedure was used.\(^{30}\) 10 (319 mg, 750 µmol, 1.00 eq) was dissolved in CH_{2}Cl_{2} (2.50 mL, 0.3 M) and MeOTf (164 µL, 1.50 mmol, 2.00 eq) was added via syringe in one portion at 25 °C. After stirring for two and a half hours at the same temperature the solution was cooled to 0 °C. A solution of NaBH\(_{4}\) (56.8 mg, 1.50 mmol, 2.00 eq) in THF:MeOH (2.5 mL, 4:1 v:v, 0.3 M) was added via syringe within five minutes and stirring was continued at 0 °C for another two and a half hours. Saturated NH\(_{4}\)Cl solution (5 mL), water (5 mL) and CH\(_{2}\)Cl\(_{2}\) (10 mL) were added and the phases separated. The aqueous layer was extracted with CH\(_{2}\)Cl\(_{2}\) (4 x 20 mL) and the combined organic phases were dried over Na\(_{2}\)SO\(_{4}\). After filtration and solvent evaporation under reduced pressure, the residue was redissolved in THF:H\(_{2}\)O (2.5 mL, 4:1 v:v, 0.3 M). Oxalic acid dihydrate (189 mg, 1.50 mmol, 2.00 eq) was added at 25 °C and the mixture was stirred for 20 hours at the same temperature. Saturated NaHCO\(_{3}\) solution (10 mL), water (10 mL) and CH\(_{2}\)Cl\(_{2}\) (20 mL) were added and the phases separated. The aqueous layer was extracted with CH\(_{2}\)Cl\(_{2}\) (4 x 20 mL), the combined organic phases were dried over anhydrous Na\(_{2}\)SO\(_{4}\), filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO\(_{2}\), CH:EE 20:1 v:v) afforded 11 (230 mg, 646 µmol, 86 %) as a colorless oil. Upon standing at 25 °C the oil solidified very slowly to form a colorless solid.

R\(_{f}\) = 0.27 (SiO\(_{2}\), CH:EE 20:1 v:v). Mp.: 103 – 105 °C. \(^{1}\)H-NMR (360 MHz, CDCl\(_{3}\)): \(\delta = 10.20\) (s, 1H, CHO), 7.90 (s, 1H, H–1), 7.84 (s, 1H, H–4), 7.69 (d, \(^{3}\)J\(_{HH} = 8.1\) Hz, 1H, H–5), 7.62 (d, \(^{4}\)J\(_{HH} = 1.7\) Hz, 1H, H–8), 7.53 (dd, \(^{3}\)J\(_{HH} = 8.1\) Hz, \(^{4}\)J\(_{HH} = 1.8\) Hz, 1H, H–6), 4.95 (s, 2H, CH\(_{2}\)), 1.53 (s, 6H, 2xCH\(_{3}\)) ppm. \(^{13}\)C\({}^{1}\)H-NMR (91 MHz, CDCl\(_{3}\)): \(\delta = 192.3\) (C–11), 157.1 (C–8a), 153.3 (C–9a), 144.0 (C–4a), 137.5 (C–3), 136.5 (C–4b), 132.7 (C–2), 130.9 (C–6), 128.4 (C–1), 126.7 (C–8), 123.5 (C–7), 122.9 (C–5), 121.2 (C–4), 52.5 (C–12), 47.4 (C–9), 26.8 (2x, C–10) ppm. IR (ATR, neat): \(\tilde{\nu} = 2965\) (w), 2929 (w), 2860 (w), 2735 (w), 2359 (w), 2103 (s), 1682 (s), 1616 (m), 1599 (m) 1558 (s), 1452 (m), 1425 (m), 1361 (m), 1294 (m), 1254 (m), 1178 (s), 1151 (s), 1060 (m), 965 (m), 887 (m), 877 (m), 828 (s), 796 (s), 774 (m), 746 (s), 737 (s), 674
(m) cm$^{-1}$. **HR-MS (EI, 70 eV):** calculated for C$_{17}$H$_{14}^{79}$BrN$_3$O$^+$ [M]$^+$: m/z = 355.03148, found: 355.03133 (Dev.: –0.15 μu; –0.41 ppm).

### 4.6.6 7-Bromo-9,9-dimethyl-3-((4-octyl-1H-1,2,3-triazol-1-yl)methyl)-9H-fluorene-2-carbaldehyde (12)

![Chemical Structure]

A modified literature procedure was used.$^{31}$ In a screw-cap vial 11 (35.6 mg, 100 μmol, 1.00 eq) and 1-Decyne (19.0 μL, 105 μmol, 1.05 eq) were dissolved in CHCl$_3$ (1.00 mL, 0.1 M). CuSO$_4$·5 H$_2$O (10 μmol, 0.10 eq) and sodium ascorbate (50 μmol, 0.50 eq) were suspended separately in water (125 μL) and added to the reaction vial. The heterogeneous mixture was stirred vigorously at 25 °C for 24 h and directly purified by flash column chromatography (SiO$_2$, CH:EE 3:1 v:v) to provide 12 (45.2 mg, 91.4 μmol, 91 %) as a yellowish oil.

$^{1}$H-NMR (360 MHz, CDCl$_3$): δ = 10.18 (s, 1H), 7.86 (s, 1H), 7.59 (d, $^4$J$_{HH}$ = 1.7 Hz, 1H), 7.54 (d, $^3$J$_{HH}$ = 8.1 Hz, 1H), 7.48 (dd, $^3$J$_{HH}$ = 8.1 Hz, $^4$J$_{HH}$ = 1.7 Hz, 1H), 7.46 – 7.44 (m, 2H), 6.04 (s, 2H), 2.71 (t, $^3$J$_{HH}$ = 7.6 Hz, 2H), 1.66 (p, $^3$J$_{HH}$ = 7.4 Hz, 2H), 1.51 (s, 6H), 1.39 – 1.18 (m, 10H), 0.85 (t, $^3$J$_{HH}$ = 6.8 Hz, 3H) ppm. $^{13}$C{$_{^1}$H}-NMR (91 MHz, CDCl$_3$): δ = 192.7, 156.6, 153.2, 148.5, 143.9, 136.4, 135.8, 131.9, 130.5, 129.3, 126.2, 123.3, 122.6, 121.5, 121.4, 121.4, 50.6, 47.0, 31.6, 29.2, 29.1, 29.0, 29.0, 26.4 (2x), 25.5, 22.4, 13.9 ppm. IR (ATR, neat): $\tilde{\nu}$ = 2923 (m), 2853 (m), 1684 (s), 1614 (m), 1561 (m), 1457 (m), 1405 (m), 1362 (w), 1251 (m), 1217 (w), 1179 (s), 1047 (m), 966 (m), 907 (w), 876 (w), 821 (m), 800 (m), 771 (m), 732 (s), 672 (w) cm$^{-1}$. **HR-MS (EI, 70 eV):** calculated for C$_{27}$H$_{32}^{79}$BrN$_3$O$^+$ [M]$^+$: m/z = 493.17233, found: 493.17229 (Dev.: –0.04 μu; –0.07 ppm).
5 References

6 NMR Spectra
Br

5b, CDCl₃
6g, CDCl₃