Clickable Azide-Functionalized Bromo-Aryl-Aldehydes – Synthesis and Photophysical Characterization

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In this article we describe the functionalization of bromo aryl aldehyde-based fluorophores with azide functionalities, their Cu-catalyzed attachment to alkynes and the effect of these functionalizations on their emission properties.

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Abstract

Herein we present the facile synthesis of three azide-functionalized fluorophores and their covalent attachment as triazoles in Huisgen-type cycloaddition with model alkynes. Besides two *ortho*- and *para*-bromo-substituted benzaldehydes, the azide functionalization of a fluorene-based structure will be presented. The copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) of the so synthesized azide-functionalized bromocarbaldehydes with terminal alkynes exhibiting different degree of steric demand was performed in high efficiency. Finally, we investigated the photophysical properties of the azide-functionalized arenes and their covalently linked

triazole derivatives to gain deeper insight towards the effect of these covalent linkers on their emission behavior.

Keywords

fluorenes, bromo-arylaldehydes, click-chemistry, phosphorescence, fluorescence

Introduction

Small organic luminophores exhibiting room-temperature phosphorescence (RTP) have attracted great attention due to promising applications in optoelectronic devices [1–8], biological imaging [9–12] and chemical sensing [13–15]. Referring to the Jablonski diagram (see Scheme 1a) [16, 17], upon excitation from the singlet ground state (S_0) to higher singlet states (S_n), followed by internal conversion (IC), either non-radiative or radiative decay to S_0 can occur. While the latter decay (fluorescence) takes place without change in electron spin, phosphorescence is defined as the radiative transition from the lowest excited triplet state (T_1) to the singlet ground state (S_0) [18–21]. Triplet state excitons are generated by the spin-forbidden intersystem crossing (ISC) process from the first excited singlet state (S_1). Pursuant to the El-Sayed rule (see Scheme 1b) [22, 23], ISC is spin allowed from $^1(n, \pi^*)$ to $^3(\pi, \pi^*)$ and from $^1(\pi, \pi^*)$ to $^3(n, \pi^*)$ excited states, while ISC is spin-forbidden from $^1(n, \pi^*)$ to $^3(n, \pi^*)$ and from $^1(\pi, \pi^*)$ to $^3(\pi, \pi^*)$ excited states, owing to poor orbital overlap, resulting in decreased spin-orbit coupling.

Scheme 1: a) Schematic depiction of the Jablonski diagram; b) Schematic representation of El-Sayed's rule.

Quenching processes of triplet states, induced by molecular motions, oxygen or humidity, restrict the versatile application of such organic materials [24]. Thus, low temperatures [25–27] or inert conditions [28] are necessary to facilitate afterglow emission.

Most phosphorescence studies are focused on metal complexes, due to a strong heavy atom-induced spin-orbit coupling [29–33]. Considering the high price and potential of toxicity of many metal-complexes, pure organic phosphors are highly desirable [16, 17, 34–37]. Two approaches are applied to achieve organic phosphors. (1) Introduction of non-metal heavy atoms such as halogens (Br or I) or functionalities containing lone pairs, in particular carbonyls, nitrogen, sulfur and phosphorus derivatives which

facilitate the ISC process from S_1 to T_n and thus increase the spin-orbital coupling [38–47]. Also, decreasing the singlet-triplet splitting energy (ΔE_{ST}) caused by intramolecular charge-transfer (ICT) interactions is an approved method [48, 49]. (2) Significant reduction of nonradiative transitions can be achieved by the host-guest method [50–52] or by crystallization [53–57]. In difference to liquid phase, the highly ordered packing and the restriction of molecular motions in the crystalline state favor persistent luminescence.

The promotion of ISC processes through intermolecular halogen bonding to generate efficient RTP was initially investigated by Kim *et al.* [58]. They developed the minimalistic 2,5-dihexyloxy-4-bromobenzaldehyde **1** [59–63] which shows weak fluorescence in solution, but exhibits green phosphorescence with a quantum yield of $\Phi_P = 2.9\%$ in the crystalline state. This behavior is caused by intermolecular halogen bonds from the carbonyl-oxygen to an adjacent bromine-atom (Figure 1a).

Literature examples:

Figure 1: Top: Literature examples of organic compounds showing RTP in the crystalline state (a) and in solution (b). Bottom: Azide-linked derivatives presented in this work.

Despite multifarious examples of RTP in the crystalline state, purely organic compounds showing RTP in solution are rare [64–69]. Takeuchi *et al.* [28] reported a

bromofluorencarbaldehyde **2** which shows blue fluorescence in chloroform at 298 K under air and green phosphorescence under argon with a phosphorescence quantum yield of $\Phi_P = 5.9\%$ (Figure 1b). This observation is reasoned by a strong (π , π^*) character of the T₂-state.

Although phosphorescent organic compounds are well investigated towards their photophysical properties in the crystalline state, in solution or physically embedded in polymer matrices, there is a significant lack of possibilities [61] for their targeted covalent attachment to higher structures. This is due to missing synthetic strategies to incorporate suitable linkable functionalities into those luminophores.

Our group is highly interested in the *de novo* synthesis of small organic luminophores and in this regard we recently developed efficient methods for the synthesis of ESIPT-based luminophores [70, 71]. Herein, we present the efficient functionalization of derivatives of the potent luminophores **1** and **2** with “clickable” azide functionalities to target structures **3-5** and further investigated the influence of this functionalization, both in the unlinked azide state and the linked triazole state, on the emission properties of these compounds (Figure 1).

Results and Discussion

Syntheses

para*- and *ortho*-Bromobenzaldehyde **3** and **4*

We initiated our synthetic investigations towards azide-functionalized *para*-bromobenzaldehyde **3** in a two-step sequence. Condensation with 2-amino-2-methylpropan-1-ol and oxidation with NBS yielded the oxazoline **6** in good yield. Directed *ortho*-metalation utilizing TMPMgCl·LiCl under mild conditions and subsequent smooth formylation with DMF afforded benzaldehyde **7**. Due to rapid

decomposition of **7** under ambient and acidic conditions, rapid aqueous work-up was conducted, followed by reduction with NaBH₄, yielding the corresponding primary alcohol **8** in 81% over two steps. The transformation to azide **9** was accomplished by deprotonation using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and reaction with diphenylphosphoryl azide (DPPA) in excellent yield. Finally, the oxazoline group, which acted as directing and protecting group, was removed in a three-step sequence of *N*-methylation, reduction of the *in situ* formed iminium ion and acidic hydrolysis. This afforded the azide-functionalized *para*-bromobenzaldehyde **3** in 78% yield and an overall yield of 56% (starting from 4-bromobenzaldehyde).

Scheme 2: Reaction conditions: **para-Bromobenzaldehyde 3:** a) 1) 2-amino-2-methylpropan-1-ol, 4 Å MS, CH₂Cl₂, 25 °C, 18 h; 2) NBS, CH₂Cl₂, 25 °C, 5 h, 91%; b) 1) TMPMgCl·LiCl, THF, 25 °C, 4 h; 2) DMF, THF, 0 °C to 25 °C, 1.5 h; c) NaBH₄, THF:MeOH 1:1, 0 °C, 1 h, 81% (2 steps); d) DPPA, DBU, PhMe, 25 °C, 18 h, 98%; e) 1) MeOTf, CH₂Cl₂, 25 °C, 2.5 h; 2) NaBH₄, THF:MeOH 4:1 v:v, 0 °C, 2.5 h; 3) oxalic acid, THF:H₂O 4:1 v:v, 25 °C, 20 h, 78%. Overall yield from 4-bromobenzaldehyde to **3**: 56% (5 steps). **ortho-Bromobenzaldehyde 4:** f) 1) 2-amino-2-methylpropan-1-ol, 4 Å MS, CH₂Cl₂, 25 °C, 18 h; 2) NBS, CH₂Cl₂, 25 °C, 4 h, 98%; g) 1) TMPMgCl·LiCl, THF, 25 °C, 4 h; 2) (CBrCl₂)₂, THF, 0 °C to 25 °C, 10 h, 76%; h) NBS, AIBN, CCl₄, 100 °C, 7 h, 66%; i) NaN₃, DMF, 25 °C, 4 h, 99%; j) 1) MeOTf, CH₂Cl₂, 25 °C, 2.5 h; 2) NaBH₄, THF:MeOH 4:1 v:v, 0 °C, 2.5 h; 3) oxalic acid, THF:H₂O 4:1 v:v, 25 °C, 20 h, 85%. Overall yield from 4-methylbenzaldehyde to **4**: 41% (5 steps).

Azide-functionalized *ortho*-bromobenzaldehyde **4** was prepared by a similar route as aldehyde **3**. Initially, oxazoline formation from 4-methylbenzaldehyde yielded 2-aryloxazoline **10** in almost quantitative yield. Introduction of the *ortho*-bromine substituent was again accomplished by metalation using $\text{TMPMgCl}\cdot\text{LiCl}$ and subsequent reaction with 1,2-dibromotetrachloroethane to afford **11** in 76% yield. A second bromination at benzylic position provided the dibrominated derivative **12** in 66% yield. Substitution reaction of benzyl bromide with sodium azide delivered primary azide **13** in quantitative yield. Again, final back-conversion of the oxazoline group to the corresponding aldehyde afforded azide-functionalized *ortho*-bromobenzaldehyde **4** in 85% yield and an overall yield of 41% (starting from 4-methylbenzaldehyde).

Bromofluorenecarbaldehyde **5**

The synthetic route to azide-functionalized 7-bromofluorene-2-carbaldehyde **5** started from unfunctionalized fluorene. Double bromination to **14**, followed by double methylation of the methylene bridge to **15** and a lithiation/formylation sequence afforded 7-bromofluorene-2-carbaldehyde **16** in excellent yield over three steps. Conversion to the 2-aryloxazoline **17** was accomplished in 92% yield using the same method as described for the synthesis of **6** and **10**. *ortho*-Metalation with $\text{TMPMgCl}\cdot\text{LiCl}$ [70] and conversion of the magnesiated species with DMF to carbaldehyde **18** was followed by reduction with NaBH_4 to give the primary alcohol **19**. In contrast to benzaldehyde **7**, carbaldehyde **18** showed no decomposition at ambient temperature. While acidic hydrolysis of **19** provided exocyclic γ -lactone **20**, substitution reaction with DPPA/NaN_3 yielded the primary azide in 87% yield. In accordance to previous deprotection reactions, fluorene **21** was converted by means of a three-step sequence to the desired azide-functionalized 7-bromofluorene-2-carbaldehyde **5** in 86% yield and an overall yield of 45% (starting from fluorene). The molecular structure of **5** could be verified by X-ray diffraction (XRD, see Scheme 3).

Scheme 3: Reaction conditions: a) Br₂, Fe-powder, CHCl₃, 0 °C, 4 h, 99%; b) KOH, KI, MeI, DMSO, 25 °C, 18 h, 92%; c) 1) *n*BuLi, THF, –78 °C, 1 h; 2) DMF, THF, –78 °C to 25 °C, 10 h, 90%; d) 1) 2-amino-2-methylpropan-1-ol, 4 Å MS, CH₂Cl₂, 25 °C, 18 h; 2) NBS, CH₂Cl₂, 25 °C, 3 h, 92%; e) 1) TMPMgCl·LiCl, THF, 25 °C, 4 h; 2) DMF, THF, –15 °C to 25 °C, 2 h; f) NaBH₄, THF:MeOH 1:1 v:v, 0 °C, 1.5 h, 79% (2 steps); g) HCl (4 N), 120 °C, 6 h, 91%; h) 1) DPPA, DBU, PhMe, 25 °C, 15 h; 2) NaN₃, PhMe, 60 °C, 4 h, 87%; i) 1) MeOTf, CH₂Cl₂, 25 °C, 2.5 h; 2) NaBH₄, THF:MeOH 4:1 v:v, 0 °C, 2.5 h; 3) oxalic acid, THF:H₂O 4:1 v:v, 25 °C, 20 h, 86%. Overall yield to **5**: 45% (8 steps). The molecular structure of **5** shows 50% probability ellipsoids.

Derivatization of fluorenyl methanol **19**

To gain deeper insights about the emission behavior of fluorenes bearing different functional groups in the side chains, fluorenyl methanol **19** was subjected to derivatization reactions. Deprotonation and subsequent methylation afforded methoxy derivative **22**, which was then converted into the methoxy-functionalized 7-bromofluorene-2-carbaldehyde **23** in 75% yield. Implementation of potent leaving groups in the side chain as complement linkable functionalities *via* S_N-reaction was

initiated by mesylation. Unfortunately, the mesylated fluorene showed such a high reactivity that rapid decomposition occurred. However, bromination was conducted by various substitution methods delivering benzyl bromide **24**, which upon isolation cyclized to iminium bromide **25** in high yields. To suppress this unexpected cyclization, careful fine-adjustment of the work-up conditions were made. Here, upon complete formation of **24**, rapid filtration of the reaction mixture through a plug of neutral alumina, solvent evaporation and quick conversion in the next step was successfully applied. Deprotection to the carbaldehyde was performed using the well applied three-step methylation/reduction/hydrolysis sequence. Methylation of the oxazoline nitrogen afforded iminium salt **26**, which was reduced to oxazolidine **27**. Again, similar to **25**, cyclization took place and ammonium triflate **28** was isolated in 56% yield (starting from **24**). In contrast to the cyclization of oxazoline **24**, oxazolidine **27** cyclized already during the reaction, caused by the increased basicity of the ring nitrogen.

General approach:

Derivatization:

Scheme 4: Reaction conditions: a) 1) NaH, THF, 0 °C, 30 min; 2) MeI, THF, 0 °C to 25 °C, 2 h, 99%; b) 1) MeOTf, CH₂Cl₂, 25 °C, 3 h; 2) NaBH₄, THF:MeOH 4:1 v:v, 0 °C, 3 h; 3) oxalic acid, THF:H₂O 4:1 v:v, 25 °C, 24 h, 75%. Overall yield from fluorene to **23**: 44% (8 steps). c) CBr₄, PPh₃, CH₂Cl₂, 0 °C to 25 °C, 2 h, 95%; or NBS, PPh₃, CH₂Cl₂, 0 °C to 25 °C, 2 h, 91%; or PBr₃, CH₂Cl₂, 0 °C to 25 °C, 2 h, 92%; d) MeOTf, CH₂Cl₂, 25 °C, 3 h; e) NaBH₄, THF:MeOH 4:1 v:v, 0 °C, 3 h. Overall yield from **24** to **28**: 56% (2 steps).

CuAAC reactions of bromocarbaldehydes

We further investigated the reactivity of azide-functionalized bromocarbaldehydes **3**, **4** and **5** in copper(I)-catalyzed azide-alkyne cycloaddition reactions (CuAAC). For this, we treated the azide-functionalized luminophores with alkynes exhibiting different degree of steric demand, including 1-decyne **29**, phenyl acetylene **30**, 1-ethynyladamantane **31** and 1,3-di-*tert*-butyl-5-ethynylbenzene **32** (see Scheme 5). All triazoles **33-44**, based on the bromocarbaldehydes **3**, **4** and **5** were successfully isolated in excellent yields of > 90%. As a further model functionalization, the sterically demanding adamantly substituted triazole **42** was subjected to a methylation reaction with Meerwein's salt (trimethyloxonium tetrafluoroborate) to deliver the *N*-methylated triazole **45** in 83% yield.

a) CuAAC reactions

b) Methylation reaction

Scheme 5: a) CuAAC reactions of azide-functionalized bromocarbaldehydes **3**, **4** and **5** with terminal alkynes to triazoles **33**–**44**. General reaction conditions for CuAAC reactions: Azide (1.00 eq), terminal alkyne (1.05 eq), $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ (0.1 eq), Na ascorbate (0.50 eq), CHCl_3 , (0.1 M) and water (12.5 mM) at 25 °C for 48 h. b) Methylation reaction of adamantly substituted triazole **42** with Meerwein's salt (trimethyloxonium tetrafluoroborate).

Photophysical properties

We finally examined the photophysical properties of both the azides and the triazoles. UV-Vis absorption measurements of *para*-Bromobenzaldehyde **3** and *ortho*-

Bromobenzaldehyde **4** as well as the corresponding triazoles **33-40** were conducted in chloroform. Intense absorption bands below 270 nm are observed, which can be attributed to typical π - π^* transitions deriving from the single-benzene core. In addition, unstructured absorption bands above 290 nm are observed, while *ortho*-derivatives exhibit more broadened bands than the *para*-derivatives (see Figure 2a and S1-S11). Emission spectra for *para*-bromocarbaldehyde **3** and adamantyl-triazole **34** in the solid-state show maxima at 440 nm (for compound **3**) and 416 nm (for compound **34**) (see Figure 2b). Additionally, fluorescence half lifetimes (τ) of **3** and **34** were determined by time correlated single photon counting (TCSPC), indicating low half-lifetimes of 2.21 ns (for compound **3**) and 3.23 ns (for compound **34**) for lower populated species (see Figure S6). Quantum yields (Φ) of both derivatives are below 1% in the solid-state. In chloroform no luminescence was detected for the *para*-derivatives. All *ortho*-derivatives exhibit no luminescence neither in solution nor in the solid-state [72].

Figure 2: a) Normalized UV-Vis absorption spectra of **3** (blue line), **34** (green line), **4** (yellow line) and **38** (red line) in CHCl₃. b) Normalized emission spectra of **3** (navy line), **34** (olive line) in CHCl₃ after bubbling with argon for 30 minutes.

These observations for *para*- and *ortho*-bromobenzaldehydes indicate that phosphorescence is quenched in these systems yielding only weak fluorescence. This may be owing to the azide-moiety either as functional group or as part of the triazole heterocycle. Similar observations were already made on luminescent materials [73, 74].

Fluorene derivatives were subjected to photophysical measurements as well. UV-Vis absorption spectra of bromofluorenecarbaldehydes **5** and **16** show intense absorption bands at 331 and 330 nm. Furthermore, adamantyl-triazole **42** and the corresponding tetrafluoroborate salt **45** exhibit similar absorption properties, while the methylated species **45** shows a comparable slightly red-shifted absorption band (see Figure 3a and S12-S14). Emission measurements of carbaldehydes **5** and **16** reveal that solid-state emission bands are more blue-shifted than emission bands in solution (see Figure 3b). Similar observations were made for adamantyl-triazole **42** and tetrafluoroborate salt **45** with maxima at 510 nm and 540 nm (see Figure 3c). However, TCSPC demonstrate that solely fluorescence is observed in all physical states for all investigated compounds with a maximum half-lifetime τ of 11.6 ns for methylated triazole **45** in chloroform (see Figure 3d). Quantum yields Φ were determined to be < 1% for all structures. Further fluorene derivatives – methoxymethyl carbaldehyde **23**, iminium bromide **25** and ammonium triflate **28** – exhibit intense absorption maxima around 320 nm (see Figure S13). For **25** and **28**, emission maxima in the solid-state were red-shifted compared to emission bands in chloroform solution (see Figure S31 and S33). **23** Exhibits a deep violet emission maximum at 360 nm in chloroform solution and no emission in the solid-state (see Figure S30). Half-lifetimes τ were defined up to 8.66 ns for iminium bromide **25**, with quantum yields Φ below 1% (see Figure S32). The absence of any long living triplet species in all fluorene derivatives in

solution as well as in the solid-state again indicates undesirable quenching events induced by the azide functionalities, similar to *para*- and *ortho*-bromobenzaldehydes.

Figure 3: a) Normalized UV-Vis absorption spectra of **5** (blue line), **16** (green line), **42** (yellow line) and **45** (red line) in CHCl₃. b) Normalized emission spectra of **5** (in solution, blue line and solid-state, green line) and **16** (in solution, yellow line and solid-state, red line). c) Normalized emission spectra of **42** (in solution, blue line and solid-state, green line) and **45** (in solution, yellow line and solid-state, red line). d) Time resolved emission decay curves of **5** (in solution, blue dots and solid-state, green dots), **42** (in solution, yellow dots) and **45** (in solution, red dots) at 25 °C. In all diluted measurements ($c = 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) CHCl₃ was used as solvent and solutions were sparged with argon for 30 minutes.

Conclusion

In summary, azide-functionalized *ortho*- and *para*-bromo benzaldehydes and fluorene derivatives were successfully synthesized. The azide bearing arenes were efficiently linked with even sterically highly demanding alkynes in a copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC). Initial photophysical investigations of azide-functionalized bromocarbaldehydes and fluorenes revealed that the azide-moiety and the triazole heterocycle efficiently quench phosphorescent transitions. Efforts of installing other functional groups suitable for covalent connections or modification of the alkyl bridge between the arene and the azide are underway in our laboratories.

Supporting Information

Supporting Information File 1:

Detailed experimental procedures, characterization data, photophysical properties, and copies of NMR spectra.

Supporting Information File 2:

Crystallographic data for compound **5**.

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Clickable Azide-functionalized Bromo-Aryl-Aldehydes – Synthesis and Photophysical Characterization

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*.^[1] Anhydrous tetrahydrofuran (THF) and dichloromethane (CH₂Cl₂) were obtained from an *inert* PS-MD-6 solvent purification system. All other solvents were dried using standard methods.^[1] Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by ¹H-NMR spectroscopy.

Thin layer chromatography was performed on fluorescence indicator marked precoated silica gel 60 plates (*Macherey-Nagel*, ALUGRAM Xtra SIL G/UV₂₅₄) and visualized by UV light (254 nm/366 nm) or staining solution. KMnO₄ staining solution was prepared using the following recipe: KMnO₄ (1.5 g), K₂CO₃ (10 g) and aqueous NaOH (1.25 mL, 10 %) in water (200 mL). Flash column chromatography was performed on silica gel (0.040 – 0.063 mm) with the solvents given in the procedures. Abbreviations for solvents used: CH = cyclohexane, EE = ethyl acetate. Retention factors were determined at chamber saturation at 25 °C. Developments were carried out between 3.0 – 3.5 cm. If not otherwise stated, crude products were adsorbed on silica gel (up to twice the amount of crude product mass) prior to purification by flash column chromatography.

NMR spectra were recorded on a *Bruker* Avance 360WB spectrometer, a *Bruker* Avance Neo 600 MHz spectrometer with BBO probe head and a *Bruker* Avance Neo 600 MHz spectrometer with TXI probe head at 23 °C. Chemical shifts for ¹H-NMR spectra are reported as δ (parts per million) relative to the residual proton signal of CDCl₃ at 7.26 ppm (s), MeOD-*d*₄ at 3.31 ppm (p). Chemical shifts for ¹³C-NMR spectra are reported as δ (parts per million) relative to the signal of CDCl₃ at 77.0 ppm (t), MeOD-*d*₄ at 49.0 ppm (sept). Chemical shifts for ¹⁹F-NMR spectra are reported as δ (parts per million) relative to the signal of Si(CH₃)₄ at 0.0 ppm. 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, t = triplet, p = pentet, m = multiplet. Coupling constants *J* are given in Hertz.

ESI and APCI mass spectra were recorded on an *Advion* Expression CMS^L via ASAP probe or direct inlet. EI mass spectra were obtained from an Agilent 7890B GC System with an Agilent 5977A MSD mass spectrometer. As column a HP-5M5 (5%-phenyl)-methylpolysiloxane was used. High resolution (HR) EI mass spectra were recorded on a double focusing mass spectrometer ThermoQuest MAT 95 XL from *Finnigan* MAT. HR-ESI and HR-APCI 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^{-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) 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.

Absorption measurements were performed either using an *Agilent* Cary 5000 UV-Vis-NIR spectrophotometer or a *Shimadzu* UV-2700 UV-Vis spectrophotometer. Emission measurements were performed using an *Edinburgh Instruments* FLS 1000 photoluminescence spectrometer. Absolute quantum yields were measured using an *Edinburgh* integrating sphere. TCSPC measurements were performed using a fast response MCP-PMT detector on the FLS 1000 and a 376 nm *Edinburgh* EPL Laser as excitation source with 10 – 20 MHz repetition rate and 80 ps pulse width. All measurements were performed at 23 °C room temperature in Quartz Cuvettes with 10 mm path length by *Hellma Analytics*.

1

Single crystals were grown as described in the procedure below. Intensity data of suitable crystals were collected on a *Bruker* Venture D8 diffractometer at 100 K with Mo-K α (0.71073 Å) radiation. All structures were solved by direct methods and refined based on F^2 by use of the SHELX program package as implemented in Olex2.[2, 3] All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a rigid model. Crystal and refinement data are collected in Tables S4-22. Figures were created using Olex2. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

2 Experimental Procedures

2.1 Preparation of Metalation Agents

2.1.1 Preparation of the Reagent *i*PrMgCl·LiCl

A slightly modified literature procedure was used.[4] 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[5] 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.

2.1.2 Preparation of the Reagent TMPMgCl·LiCl

A slightly modified literature procedure was used.[6] A heat gun-dried and nitrogen-flushed *Schlenk* flask was charged with freshly titrated *i*PrMgCl·LiCl (75.0 mL, 90.0 mmol, 1.00 eq, 1.20 M). Freshly distilled 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[7] 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.

2.2 Preparation of 2-(Azidomethyl)-4-bromobenzaldehyde (3)

Reaction conditions: a) 1) 2-amino-2-methylpropan-1-ol, 4 Å MS, CH₂Cl₂, 25 °C, 18 h; 2) NBS, CH₂Cl₂, 25 °C, 5 h, 91 %; b) 1) TMPMgCl·LiCl, THF, 25 °C, 4 h; 2) DMF, THF, 0 °C to 25 °C, 1.5 h; c) NaBH₄, THF:MeOH 1:1, 0 °C, 1 h, 81 % (2 steps); d) DPPA, DBU, PhMe, 25 °C, 18 h, 98 %; e) 1) MeOTf, CH₂Cl₂, 25 °C, 2.5 h; 2) NaBH₄, THF:MeOH 4:1 v:v, 0 °C, 2.5 h; 3) oxalic acid, THF:H₂O 4:1 v:v, 25 °C, 20 h, 78 %. Overall yield: 56 % (5 steps).

2.2.1 2-(4-Bromophenyl)-4,4-dimethyl-4,5-dihydrooxazole (6)

A modified literature procedure was used.[8] 4-Bromobenzaldehyde (5.55 g, 30.0 mmol, 1.00 eq) and 2-amino-2-methylpropan-1-ol (5.35 g, 60.0 mmol, 2.00 eq) were dissolved in CH₂Cl₂ (100 mL, 0.3 M) and 4 Å MS (20.0 g) was added. After 18 hours of slowly stirring at 25 °C NBS (10.7 g, 60.0 mmol, 2.00 eq) was added in one portion and stirring was continued for another five hours at 25 °C. All solids were filtered off and the organic phase was washed with saturated NaHCO₃ solution (100 mL). The combined aqueous phases were extracted with CH₂Cl₂ (3 × 50 mL). All organic phases were washed with saturated NaS₂O₃ solution (100 mL) and the aqueous phase was extracted with CH₂Cl₂ (50 mL). The combined organic phases were dried over anhydrous MgSO₄, filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, CH:EE 10:1 v:v) afforded **6** (6.97 g, 27.4 mmol, 91 %) as a colorless oil which solidified upon standing to form a pale brown solid.

R_f = 0.26 (SiO₂, CH:EE 10:1 v:v). **Mp.**: 38 – 40 °C. **¹H-NMR (360 MHz, CDCl₃):** δ = 7.83 – 7.74 (AA'XX', 2H), 7.57 – 7.47 (AA'XX', 2H), 4.09 (s, 2H), 1.36 (s, 6H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃):** δ = 161.4, 131.6 (2x), 129.9 (2x), 127.1, 125.9, 79.3, 67.9, 28.5 (2x) ppm. **IR (ATR, neat):** $\tilde{\nu}$ = 2969 (m), 2624(w), 2897 (w), 1642 (s), 1591 (m), 1479 (m), 1459 (m), 1397 (m), 1357 (m), 1315 (m), 1296 (m), 1177 (m), 1070 (s), 1063 (s), 1009 (s), 964 (m), 923 (m), 835 (s), 824 (m), 726 (s), 712

(m), 676 (s) cm^{-1} . MS (APCI): $m/z = 254.0$ [$\text{C}_{11}\text{H}_{12}^{79}\text{BrNO}+\text{H}$] $^{+}$. **HR-MS (APCI):** calculated for $\text{C}_{11}\text{H}_{13}^{79}\text{BrNO}^{+}$ [$\text{M}+\text{H}$] $^{+}$: $m/z = 254.01750$, found: 254.01748 (Dev.: -0.02 mu; -0.10 ppm). The analytical data are in accordance with the literature.[9]

2.2.2 5-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)benzaldehyde (7)

A modified literature procedure was used.[9] A heat gun-dried and nitrogen-flushed *Schlenk* flask, equipped with a magnetic stirring bar and a rubber septum was charged with **6** (3.30 g, 13.0 mmol, 1.00 eq) and evacuated for half an hour. The flask was flushed with nitrogen and anhydrous THF (32.5 mL, 0.4 M) was added. Addition of $\text{TMPMgCl}\cdot\text{LiCl}$ (26.0 mL, 26.0 mmol, 2.00 eq, 1.00 M in THF) *via* syringe within three minutes at 25 °C was followed by stirring for three hours at the same conditions. DMF (4.03 mL, 52.0 mmol, 4.00 eq) was diluted in anhydrous THF (10 mL) and added *via* syringe pump (0.5 mL/min) to the dark red solution at 0 °C. After complete addition the mixture was stirred for one and a half hours while it was allowed to warm to 25 °C. Full consumption of the starting material was followed by diluting with water (50 mL) and ethyl acetate (50 mL). The phases were separated and the aqueous layer was extracted with ethyl acetate (4×50 mL). The combined organic phases were dried over anhydrous NaSO_4 , filtered and concentrated under reduced pressure on a rotary evaporator at 30 °C. Due to its sensibility, the crude product was directly used for the next step. If desired the product can be isolated by rapid flash column chromatography (SiO_2 , CH:EE 10:1 v:v) to afford **7** as a yellowish oil.

$R_f = 0.23$ (SiO_2 , CH:EE 10:1 v:v). **$^1\text{H-NMR}$ (360 MHz, CDCl_3):** $\delta = 10.71$ (s, 1H), 8.05 (d, $^4J_{\text{HH}} = 2.1$ Hz, 1H), 7.78 (d, $^3J_{\text{HH}} = 8.3$ Hz, 1H), 7.71 (dd, $^3J_{\text{HH}} = 8.3$ Hz, $^4J_{\text{HH}} = 2.1$ Hz, 1H), 4.14 (s, 2H), 1.39 (s, 6H) ppm. **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (91 MHz, CDCl_3):** $\delta = 191.3, 159.6, 137.4, 135.9, 131.6, 131.0, 128.6, 125.9, 79.5, 69.0, 28.5$ (2x) ppm. **IR (ATR, neat):** $\tilde{\nu} = 2967$ (w), 2928 (w), 2894 (w), 1687 (s), 1644 (m), 1582 (m), 1563 (w), 1478 (w), 1381 (w), 1364 (w), 1351 (m), 1305 (m), 1284 (w), 1251 (w), 1212 (w), 1182 (m), 1129 (w), 1082 (w), 1046 (s), 987 (w), 963 (m), 922 (w), 881 (w), 865 (w), 836 (m), 819 (w), 712 (m), 677 (m) cm^{-1} . **MS (APCI):** $m/z = 282.0$ [$\text{C}_{12}\text{H}_{12}^{79}\text{BrNO}_2+\text{H}$] $^{+}$. **HR-MS (ESI):** calculated for $\text{C}_{12}\text{H}_{13}^{79}\text{BrNO}_2^{+}$ [$\text{M}+\text{H}$] $^{+}$: $m/z = 282.01242$, found: 282.01244 (Dev.: 0.02 mu; 0.07 ppm).

2.2.3 (5-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)methanol (**8**)

A modified literature procedure was used.[10] The crude benzaldehyde **7** (13.0 mmol, 1.00 eq) was dissolved in THF:MeOH (26 mL, 1:1 v:v, 0.5 M) and cooled to 0 °C. NaBH₄ (984 mg, 26.0 mmol, 2.00 eq) was added and stirring was continued for two more hours while the mixture was allowed to warm slowly to 25 °C. Saturated NH₄Cl solution (20 mL), ethyl acetate (20 mL) and water (30 mL) were added successively and the phases were separated. The aqueous layer was extracted with ethyl acetate (4 × 50 mL), the combined organic phases were dried over anhydrous NaSO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO₂, CH:EE 10:1 v:v) afforded **8** (2.98 g, 10.5 mmol, 81 % over two steps) as a colorless oil.

R_f = 0.17 (SiO₂, CH:EE 10:1 v:v). **¹H-NMR (360 MHz, CDCl₃)**: δ = 7.71 (d, ³J_{HH} = 8.2 Hz, 1H), 7.51 (d, ⁴J_{HH} = 2.1 Hz, 1H), 7.47 (dd, ³J_{HH} = 8.3 Hz, ⁴J_{HH} = 2.1 Hz, 1H), 6.65 (t, ³J_{HH} = 7.6 Hz, 1H), 4.59 (d, ³J_{HH} = 7.6 Hz, 2H), 4.12 (s, 2H), 1.39 (s, 6H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 161.6, 144.0, 133.4, 131.6, 130.8, 126.0, 125.7, 78.9, 68.2, 64.1, 28.5 (2x) ppm. **IR (ATR, neat)**: $\tilde{\nu}$ = 3270 (w), 2966 (w), 2928 (w), 2895 (w), 1636 (s), 1586 (w), 1561 (w), 1462 (w), 1386 (w), 1352 (m), 1308 (m), 1284 (w), 1186 (m), 1090 (m), 1054 (s), 1032 (s), 963 (m), 875 (w), 844 (m), 826 (m), 706 (m), 679 (m) cm⁻¹. **MS (APCI)**: m/z = 284.0 [C₁₂H₁₄⁷⁹BrNO₂+H]⁺. **HR-MS (EI, 70 eV)**: calculated for C₁₂H₁₄⁷⁹BrNO₂⁺ [M]⁺: m/z = 283.02024, found: 283.02011 (Dev.: -0.13 mu; -0.47 ppm).

2.2.4 2-(2-(Azidomethyl)-4-bromophenyl)-4,4-dimethyl-4,5-dihydrooxazole (**9**)

A modified literature procedure was used.[11] **8** (1.42 g, 5.00 mmol, 1.00 eq) was dissolved in PhMe (16.7 mL, 0.3 M) and DBU (970 μL, 6.50 mmol, 1.30 eq) was added *via* syringe pump (1.0 mL/min) at 25 °C. The mixture was stirred for ten minutes and DPPA (1.29 mL, 6.00 mmol, 1.20 eq) was added *via* syringe pump (0.3 mL/min). After complete addition the suspension was stirred for 18 hours at 25 °C. Saturated NH₄Cl solution (50 mL) and ethyl acetate (100 mL) were added and the phases separated. The aqueous phase was extracted with ethyl acetate (3 × 50 mL) and the combined organic phases were dried over anhydrous NaSO₄. After filtration the solvent was removed under reduced pressure and purification was conducted by flash column chromatography (SiO₂, CH:EE 15:1 v:v) to provide **9** (1.52 g, 4.92 mmol, 98 %) as a colorless liquid.

R_f = 0.30 (SiO₂, CH:EE 15:1 v:v). **Mp.:** around 0 °C. **¹H-NMR (360 MHz, CDCl₃):** δ = 7.75 (d, ³ J_{HH} = 8.4 Hz, 1H), 7.62 (d, ⁴ J_{HH} = 2.1 Hz, 1H), 7.49 (dd, ³ J_{HH} = 8.4 Hz, ⁴ J_{HH} = 2.0 Hz, 1H), 4.87 (s, 2H), 4.06 (s, 2H), 1.37 (s, 6H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃):** δ = 160.4, 138.4, 132.3, 131.7, 131.1, 125.6, 125.6, 78.6, 68.6, 52.8, 28.5 (2x) ppm. **IR (ATR, neat):** $\tilde{\nu}$ = 2966 (w), 2929 (w), 2892 (w), 2099 (s), 1642 (m), 1588 (w), 1564 (w), 1481 (w), 1350 (w), 1338 (w), 1304 (m), 1277 (m), 1212 (w), 1184 (m), 1090 (w), 1042 (s), 967 (w), 923 (w), 872 (w), 830 (m), 741 (w), 679 (w) cm⁻¹. **MS (APCI):** m/z = 309.0 [C₁₂H₁₃⁷⁹BrN₄O+H]⁺. **HR-MS (ESI):** calculated for C₁₂H₁₃⁷⁹BrN₄O⁺ [M+H]⁺: m/z = 309.03455, found: 309.03499 (Dev.: 0.44 mu; 1.43 ppm).

2.2.5 2-(Azidomethyl)-4-bromobenzaldehyde (3)

A modified literature procedure was used.[12] **9** (1.86 g, 6.00 mmol, 1.00 eq) was dissolved in CH₂Cl₂ (20.0 mL, 0.3 M) and MeOTf (1.31 mL, 12.0 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 NaBH₄ (454 mg, 12.0 mmol, 2.00 eq) in THF:MeOH (20.0 mL, 4:1 v:v, 0.3 M) was added *via* syringe within 20 minutes and stirring was continued at 0 °C for another two and a half hours. Saturated NH₄Cl solution (20 mL), water (20 mL) and CH₂Cl₂ (40 mL) were added and the phases separated. The aqueous layer was extracted with CH₂Cl₂ (3 × 50 mL) and the combined organic phases were dried over anhydrous Na₂SO₄. After filtration and solvent evaporation under reduced pressure, the residue was redissolved in THF:H₂O (20.0 mL, 4:1 v:v, 0.3 M). Oxalic acid dihydrate (1.51 g, 12.0 mmol, 2.00 eq) was added at 25 °C and the mixture was stirred for 18 hours at the same temperature. Saturated NaHCO₃ solution (20 mL), water (20 mL) and CH₂Cl₂ (40 mL) were added and the phases separated. The aqueous layer was extracted with CH₂Cl₂ (4 × 40 mL) and the combined organic phases were dried over anhydrous Na₂SO₄. Filtration and solvent evaporation under reduced pressure and purification by flash column chromatography (SiO₂, CH:EE 20:1 v:v) afforded **3** (1.12 g, 4.67 mmol, 78 %) as an off-white solid.

R_f = 0.24 (SiO₂, CH:EE 20:1 v:v). **Mp.:** 47 – 49 °C. **¹H-NMR (360 MHz, CDCl₃):** δ = 10.07 (d, ⁵ J_{HH} = 0.1 Hz 1H, CHO), 7.76 – 7.73 (m, 1H, H-3), 7.73 – 7.66 (m, 2H, H-5, H-6), 4.88 (s, 2H, CH₂) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃):** δ = 192.0 (C-7), 139.3 (C-2), 135.9 (C-6), 132.4 (C-3), 132.1 (C-1), 131.8 (C-5), 129.8 (C-4), 51.7 (C-8) ppm. **IR (ATR, neat):** $\tilde{\nu}$ = 3098 (w), 2928 (w), 2849 (w), 2751 (w), 2114 (m), 1687 (m), 1593 (m), 1556 (m), 1426 (m), 1378 (w), 1338 (m), 1292 (m), 1223 (w), 1197 (m), 1086 (m), 979 (w), 933 (m), 885 (m), 872 (m), 828 (w), 802 (s), 701 (w), 688 (m) cm⁻¹. **MS (ESI):** m/z = 262.1 [C₈H₆⁷⁹BrN₃O+Na]⁺. **HR-MS (ESI):** calculated for C₈H₆⁷⁹BrN₃O⁺ [M+Na]⁺: m/z

=261.95864, found: 261.95890 (Dev.: 0.26 mu; 0.97 ppm). The analytical data are in accordance with the literature.[13]

2.3 Preparation of 4-(Azidomethyl)-2-bromobenzaldehyde (4)

Reaction conditions: a) 1) 2-amino-2-methylpropan-1-ol, 4 Å MS, CH₂Cl₂, 25 °C, 18 h; 2) NBS, CH₂Cl₂, 25 °C, 4 h, 98 %; b) NBS, AIBN, CCl₄, 100 °C, 5 h, 78 %; c) NaN₃, DMF, 25 °C, 4 h, 90 %; d) 1) TMPMgCl·LiCl, THF, 25 °C, 4 h; 2) (CBrCl₂)₂, THF, 0 °C to 25 °C, 10 h, 76 %; e) NBS, AIBN, CCl₄, 100 °C, 7 h, 66 %; f) NaN₃, DMF, 25 °C, 4 h, 99 %; g) 1) MeOTf, CH₂Cl₂, 25 °C, 2.5 h; 2) NaBH₄, THF:MeOH 4:1 v:v, 0 °C, 2.5 h; 3) oxalic acid, THF:H₂O 4:1 v:v, 25 °C, 20 h, 85 %. Overall yield: 41 % (5 steps).

2.3.1 4,4-Dimethyl-2-(*p*-tolyl)-4,5-dihydrooxazole (10)

A modified literature procedure was used.[8] *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 CH₂Cl₂ (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 NaHCO₃ solution (3 × 100 mL). The combined aqueous phases were extracted with CH₂Cl₂ (2 × 100 mL). All organic phases were washed with saturated NaS₂O₃ solution (100 mL) and the aqueous phase was extracted with CH₂Cl₂ (50 mL).

The combined organic phases were dried over anhydrous MgSO_4 , filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2 , CH:EE 10:1 to 5:1 v:v) afforded **10** (13.0 g, 68.7 mmol, 98 %) as a pale brown solid with a characteristic nougat odor.

R_f = 0.16 (SiO_2 , CH:EE 10:1 v:v). **Mp.**: 42 – 44 °C. **^1H -NMR (360 MHz, CDCl_3)**: δ = 7.81 (d, $^3J_{\text{HH}}$ = 7.7 Hz, 2H), 7.19 (d, $^3J_{\text{HH}}$ = 7.8 Hz, 2H), 4.07 (s, 2H), 2.37 (s, 3H), 1.36 (s, 6H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ -NMR (91 MHz, CDCl_3)**: δ = 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)**: $\tilde{\nu}$ = 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^{-1} . **MS (APCI)**: m/z = 190.1 $[\text{M}+\text{H}]^+$. The analytical data are in accordance with the literature.[14]

2.3.2 2-(4-(Bromomethyl)phenyl)-4,4-dimethyl-4,5-dihydrooxazole (**S1**)

A modified literature procedure was used.[15] **10** (568 mg, 3.00 mmol, 1.00 eq) was dissolved in CCl_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 μmol , 0.05 eq) was added and the mixture was heated to 100 °C (oil bath temperature) for five hours. After cooling to 25 °C the mixture was directly filtered over anhydrous Na_2SO_4 and the solids were washed with CCl_4 (20 mL). The solvent was evaporated under reduced pressure and purification was conducted by flash column chromatography (SiO_2 , CH:EE 10:1 v:v) to provide **S1** (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. **^1H -NMR (360 MHz, CDCl_3)**: δ = 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. **$^{13}\text{C}\{^1\text{H}\}$ -NMR (91 MHz, CDCl_3)**: δ = 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} . **MS (APCI)**: m/z = 267.9 $[\text{C}_{12}\text{H}_{14}^{79}\text{BrNO}+\text{H}]^+$. **HR-MS (EI, 70 eV)**: calculated for $\text{C}_{12}\text{H}_{14}^{79}\text{BrNO}^+$ $[\text{M}]^+$: m/z = 267.02533, found: 267.02514 (Dev.: –0.19 mu; –0.70 ppm). The analytical data are in accordance with the literature.[16]

2.3.3 2-(4-(Azidomethyl)phenyl)-4,4-dimethyl-4,5-dihydrooxazole (S2)

A modified literature procedure was used.[13] **S1** (992 mg, 3.70 mmol, 1.00 eq) was dissolved in DMF (12.3 mL, 0.3 M) and NaN₃ (481 mg, 7.40 mmol, 2.00 eq) was added in one portion. After stirring for four hours at 25 °C water (20 mL) and CH₂Cl₂ (50 mL) were added and the phases separated. The aqueous phase was extracted with CH₂Cl₂ (6 × 50 mL) and the combined organic phases were dried over anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, CH:EE 10:1 to 5:1 v:v) provided **S2** (771 mg, 3.35 mmol, 90 %) as a colorless liquid.

R_f = 0.09 (SiO₂, CH:EE 10:1 v:v). **R_f** = 0.23 (SiO₂, CH:EE 5:1 v:v). **¹H-NMR (360 MHz, CDCl₃):** δ = 7.98 – 7.92 (AA'XX', 2H), 7.39 – 7.32 (AA'XX', 2H), 4.38 (s, 2H), 4.11 (s, 2H), 1.38 (s, 6H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃):** δ = 161.3, 138.2, 128.5 (2x), 127.8, 127.7 (2x), 78.9, 67.4, 54.1, 28.2 (2x) ppm. **IR (ATR, neat):** $\tilde{\nu}$ = 2967 (w), 2928 (w), 2893 (w), 2094 (s), 1647 (s), 1513 (w), 1462 (w), 1417 (m), 1352 (m), 1316 (m), 1297 (m), 1247 (m), 1179 (m), 1064 (s), 1019 (m), 991 (w), 965 (m), 920 (w), 844 (m), 802 (m), 730 (m), 693 (m) cm⁻¹. **MS (APCI):** m/z = 231.0 [C₁₂H₁₄N₄O+H]⁺. **HR-MS (EI, 70 eV):** calculated for C₁₂H₁₄N₄O⁺ [M]⁺: m/z = 230.11621, found: 230.11607 (Dev.: -0.14 mu; -0.62 ppm).

2.3.4 2-(2-Bromo-4-methylphenyl)-4,4-dimethyl-4,5-dihydrooxazole (11)

A modified literature procedure was used.[9] A heat gun-dried and nitrogen-flushed *Schlenk* flask, equipped with a magnetic stirring bar and a rubber septum was charged with **11** (1.51 g, 8.00 mmol, 1.00 eq) and evacuated for half an hour. The flask was flushed with nitrogen and anhydrous THF (20.0 mL, 0.4 M) was added. Addition of TMPMgCl·LiCl (24.0 mL, 24.0 mmol, 3.00 eq, 1.00 M in THF) *via* syringe within two minutes at 25 °C was followed by stirring for four hours at the same conditions. 1,2-Dibromotetrachloroethane (7.82 g, 24.0 mmol, 3.00 eq) was diluted in anhydrous THF (12 mL) and added *via* syringe pump (0.5 mL/min) to the dark red solution at 0 °C. After complete addition the mixture was allowed to warm to 25 °C and stirred for a total of ten hours. Saturated NH₄Cl solution (20 mL), water (50 mL) and CH₂Cl₂ (50 mL) were added and the phases separated. The aqueous phase was extracted with CH₂Cl₂ (3 × 50 mL) and the combined organic phases were dried over

anhydrous Na₂SO₄. Filtration, solvent evaporation under reduced pressure and purification by flash column chromatography (SiO₂, CH:EE 10:1 v:v) afforded **11** (1.62 g, 6.04 mmol, 76 %) as a slightly yellow liquid.

R_f = 0.15 (SiO₂, CH:EE 10:1 v:v). **¹H-NMR (360 MHz, CDCl₃)**: δ = 7.54 (d, ³J_{HH} = 7.8 Hz, 1H), 7.44 (d, ⁴J_{HH} = 0.6 Hz, 1H), 7.12 (dd, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 0.8 Hz, 1H), 4.11 (s, 2H), 2.34 (s, 3H), 1.40 (s, 6H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 161.5, 141.9, 133.9, 130.8, 127.6, 127.0, 121.3, 79.0, 67.7, 28.0, 20.8 ppm. **IR (ATR, neat)**: $\tilde{\nu}$ = 2965 (w), 2926 (w), 2889 (w), 1651 (m), 1604 (w), 1493 (w), 1460 (w), 1390 (w), 1363 (w), 1349 (m), 1308 (m), 1264 (w), 1248 (w), 1188 (w), 1084 (s), 1027 (s), 963 (m), 920 (w), 877 (w), 827 (m), 812 (m), 736 (m), 682 (w), 671 (m) cm⁻¹. **MS (APCI)**: m/z = 267.9 [C₁₂H₁₄⁷⁹BrNO+H]⁺. **HR-MS (EI, 70 eV)**: calculated for C₁₂H₁₄⁷⁹BrNO⁺ [M]⁺: m/z = 267.02533, found: 267.02509 (Dev.: -0.24 mu; -0.89 ppm). The analytical data are in accordance with the literature.[17]

2.3.5 2-(2-Bromo-4-(bromomethyl)phenyl)-4,4-dimethyl-4,5-dihydrooxazole (12)

2.3.6 2-(4-(Azidomethyl)-2-bromophenyl)-4,4-dimethyl-4,5-dihydrooxazole (13)

A modified literature procedure was used.[13] **12** (521 mg, 1.50 mmol, 1.00 eq) was dissolved in DMF (5.00 mL, 0.3 M) and NaN₃ (195 mg, 3.00 mmol, 2.00 eq) was added in one portion. After stirring for four hours at 25 °C water (20 mL) and CH₂Cl₂ (50 mL) were added and the phases separated. The aqueous phase was extracted with CH₂Cl₂ (6 × 50 mL) and the combined organic phases were dried over anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, CH:EE 10:1 to 5:1 v:v) provided **13** (457 mg, 1.48 mmol, 99 %) as a colorless liquid.

R_f = 0.10 (SiO₂, CH:EE 10:1 v:v). **R_f** = 0.24 (SiO₂, CH:EE 5:1 v:v). **¹H-NMR (360 MHz, CDCl₃):** δ = 7.67 (d, ³J_{HH} = 7.9 Hz, 1H), 7.59 (d, ⁴J_{HH} = 1.7 Hz, 1H), 7.28 (dd, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 1.7 Hz, 1H), 4.36 (s, 2H), 4.14 (s, 2H), 1.41 (s, 6H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃):** δ = 161.4, 139.4, 133.1, 131.8, 130.2, 126.6, 122.3, 79.6, 68.3, 53.7, 28.4 ppm. **IR (ATR, neat):** $\tilde{\nu}$ = 2966 (w), 2928 (w), 2891 (w), 2095 (s), 1652 (m), 1604 (w), 1492 (w), 1461 (w), 1397 (m), 1350 (m), 1338 (m), 1308 (m), 1280 (m), 1247 (m), 1189 (m), 1086 (s), 1028 (s), 961 (m), 920 (m), 888 (m), 826 (m), 813 (m), 738 (w), 686 (m) cm⁻¹. **MS (APCI):** m/z = 309.0 [C₁₂H₁₃⁷⁹BrN₄O+H]⁺. **HR-MS (EI, 70 eV):** calculated for C₁₂H₁₃⁷⁹BrN₄O⁺ [M]⁺: m/z = 308.02672, found: 308.02707 (Dev.: 0.35 mu; 1.12 ppm).

2.3.7 4-(Azidomethyl)-2-bromobenzaldehyde (4)

A modified literature procedure was used.[12] **13** (928 mg, 3.00 mmol, 1.00 eq) was dissolved in CH₂Cl₂ (10.0 mL, 0.3 M) and MeOTf (656 μL, 6.00 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 NaBH₄ (227 mg, 6.00 mmol, 2.00 eq) in THF:MeOH (10.0 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 NH₄Cl solution (10 mL), water (20 mL) and CH₂Cl₂ (20 mL) were added and the phases separated. The aqueous layer was extracted with CH₂Cl₂ (4 × 20 mL) and the combined organic phases were dried over anhydrous Na₂SO₄. After filtration and solvent evaporation under reduced pressure, the residue was redissolved in THF:H₂O (10.0 mL, 4:1 v:v, 0.3 M). Oxalic acid dihydrate (756 mg, 6.00 mmol, 2.00 eq) was added at 25 °C and the mixture was stirred for 16 hours at the same

temperature. Saturated NaHCO₃ solution (10 mL), water (20 mL) and CH₂Cl₂ (40 mL) were added and the phases separated. The aqueous layer was extracted with CH₂Cl₂ (4 × 20 mL) and the combined organic phases were dried over anhydrous Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. Purification by flash column chromatography (SiO₂, CH:EE 5:1 v:v) afforded **4** (614 mg, 2.56 mmol, 85 %) as a colorless oil which solidified very slowly upon standing at 25 °C.

R_f = 0.54 (SiO₂, CH:EE 5:1 v:v). **Mp.**: 26 – 28 °C. **¹H-NMR (360 MHz, CDCl₃)**: δ = 10.34 (d, ⁴J_{HH} = 0.8 Hz, 1H, CHO), 7.92 (d, ³J_{HH} = 8.0 Hz, 1H, H-6), 7.63 (dd, ⁴J_{HH} = 1.6 Hz, ⁵J_{HH} = 0.8 Hz, 1H, H-3), 7.38 (ddd, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 1.6 Hz, ⁵J_{HH} = 0.8 Hz, 1H, H-5), 4.43 (s, 2H, CH₂) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 191.0 (C-7), 143.2 (C-4), 132.9 (C-1), 132.7 (C-3), 130.0 (C-6), 127.2 (C-2), 126.9 (C-5), 53.3 (C-8) ppm. **IR (ATR, neat)**: $\tilde{\nu}$ = 3084 (w), 2920 (w), 2859 (w), 2758 (w), 2227 (w), 2116 (s), 1684 (s), 1599 (s), 1558 (m), 1483 (w), 1427 (m), 1403 (m), 1387 (m), 1339 (s), 1275 (s), 1207 (s), 1140 (m), 1038 (m), 966 (m), 957 (m), 881 (m), 872 (m), 821 (s), 797 (s), 733 (w), 681 (m) cm⁻¹. **MS (EI, 70 eV)**: m/z = 238.8 [C₈H₆⁷⁹BrN₃O]⁺. **HR-MS (EI, 70 eV)**: calculated for C₈H₆⁷⁹BrN₃O⁺ [M]⁺: m/z = 238.96888, found: 238.96872 (Dev.: -0.16 mu; -0.65 ppm).

2.4 Preparation of Highly Functionalized Fluorenes (5), (23), (25) & (28)

Reaction conditions: a) Br₂, Fe-powder, CHCl₃, 0 °C, 4 h, 99 %; b) KOH, KI, MeI, DMSO, 25 °C, 18 h, 92 %; c) 1) *n*BuLi, THF, −78 °C, 1 h; 2) DMF, THF, −78 °C to 25 °C, 10 h, 90 %; d) 1) 2-amino-2-methylpropan-1-ol, 4 Å MS, CH₂Cl₂, 25 °C, 18 h; 2) NBS, CH₂Cl₂, 25 °C, 3 h, 92 %; e) 1) TMPMgCl·LiCl, THF, 25 °C, 4 h; 2) DMF, THF, −15 °C to 25 °C, 2 h; f) NaBH₄, THF:MeOH 1:1 v:v, 0 °C, 1.5 h, 79 % (2 steps); g) HCl (4 N), 120 °C, 6 h, 91 %; h) 1) DPPA, DBU, PhMe, 25 °C, 15 h; 2) NaN₃, PhMe, 60 °C, 4 h, 87 %; i) 1) MeOTf, CH₂Cl₂, 25 °C, 2.5 h; 2) NaBH₄, THF:MeOH 4:1 v:v, 0 °C, 2.5 h; 3) oxalic acid, THF:H₂O 4:1 v:v, 25 °C, 20 h, 86 % – overall yield to **5**: 45 % (8 steps); j) 1) NaH, THF, 0 °C, 30 min; 2) MeI, THF, 0 °C to 25 °C, 2 h, 99 %; k) 1) MeOTf, CH₂Cl₂, 25 °C, 3 h; 2) NaBH₄, THF:MeOH 4:1 v:v, 0 °C, 3 h; 3) oxalic acid, THF:H₂O 4:1 v:v, 25 °C, 24 h, 75 % – overall yield to **23**: 44 % (8 steps); l) CBr₄, PPh₃, CH₂Cl₂, 0 °C to 25 °C, 2 h, 95 %; m) NBS, PPh₃, CH₂Cl₂, 0 °C

to 25 °C, 2 h, 91 %; n) PBr₃, CH₂Cl₂, 0 °C to 25 °C, 2 h, 92 %; o) MeOTf, CH₂Cl₂, 25 °C, 3 h; p) NaBH₄, THF:MeOH 4:1 v:v, 0 °C, 3 h, 56 % from **19**.

2.4.1 2,7-Dibromo-9H-fluorene (**14**)

A modified literature procedure was used.[18] Fluorene (8.31 g, 50.0 mmol, 1.00 eq) was dissolved in CHCl₃ (83 mL, 0.6 M) and Fe-powder (279 mg, 5.00 mmol, 0.10 eq) was added. The solution was cooled to 0 °C in a water/ice bath. Br₂ (5.38 mL, 105 mmol, 2.10 eq) in CHCl₃ (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. CHCl₃ (100 mL) was added, the phases were separated and the aqueous layer was extracted with CHCl₃ (2 × 100 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure on a rotary evaporator. **14** (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, ⁴ J_{HH} = 1.6 Hz, 2H), 7.57 (d, ³ J_{HH} = 8.1 Hz, 2H), 7.49 (dd, ³ J_{HH} = 8.2 Hz, ⁴ 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), 1760 (w), 1568 (w), 1453 (w), 1391 (m), 1159 (w), 1054 (m), 1005 (w), 952 (w), 931 (w), 807 (s), 685 (m), 662 (m) cm⁻¹. **MS (EI, 70 eV)**: m/z = 321.8 [C₁₃H₈⁷⁹Br₂]⁺. The analytical data are in accordance with the literature.[19]

2.4.2 2,7-Dibromo-9,9-dimethyl-9H-fluorene (**15**)

A modified literature procedure was used.[20] **14** (16.2 g, 50.0 mmol, 1.00 eq) was suspended in DMSO (83 mL, 0.6 M) and KI (830 mg, 5.00 mmol, 0.10 eq) was added. To the water bath-cooled and vigorously stirred mixture were added KOH pellets (11.2 g, 200 mmol, 4.00 eq). The reaction was stirred for one hour, while the solution turned intensive red. MeI (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 MeI was quenched by addition of NEt₃ (13.9 mL, 100 mmol, 2.00 eq). The mixture was stirred

for 30 minutes, poured into water (500 mL) and extracted with CH₂Cl₂ (4 × 100 mL). The combined organic layers were dried over anhydrous NaSO₄, filtered and concentrated under reduced pressure on a rotary evaporator. Purification by flash column chromatography (SiO₂, CH) afforded **15** (16.2 g, 46.0 mmol, 92 %) as a colorless solid. If desired the product can be recrystallized from cyclohexane.

R_f = 0.68 (SiO₂, CH). **Mp.**: 177 – 179 °C. **¹H-NMR (360 MHz, CDCl₃)**: δ = 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. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 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 [C₁₅H₁₂⁷⁹Br₂]⁺. The analytical data are in accordance with the literature.[21]

2.4.3 7-Bromo-9,9-dimethyl-9H-fluorene-2-carbaldehyde (**16**)

A modified literature procedure was used.[20] A heat gun-dried and nitrogen-flushed *Schlenk* flask was charged with **15** (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 *n*BuLi (16.8 mL, 42.0 mmol, 1.05 eq, 2.5 M in hexane) 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 (5.85 g, 6.19 mL, 80.0 mmol, 2.00 eq) in anhydrous THF (8 mL) was added *via* syringe pump (0.4 mL/min) through a 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 into the reaction in small portions 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 on a rotary evaporator. Purification by flash column chromatography (SiO₂, CH:EE 20:1 v:v) afforded **16** (10.9 g, 36.0 mmol, 90 %) as a colorless solid.

R_f = 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, ⁴J_{HH} = 1.5 Hz, 1H), 7.87 (dd, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.3 Hz, 1H), 7.82 (d, ³J_{HH} = 7.8 Hz, 1H), 7.65 (d, ³J_{HH} = 8.1 Hz, 1H), 7.61 (d, ⁴J_{HH} = 1.6 Hz, 1H), 7.51 (dd, ³J_{HH} = 8.1 Hz, ⁴J_{HH} = 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)**: $\tilde{\nu}$ = 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 (m),

810 (s), 795 (s), 755 (s), 733 (s), 658 (m) cm^{-1} . **MS (APCI):** $m/z = 301.1$ $[\text{C}_{16}\text{H}_{13}^{79}\text{BrO}+\text{H}]^+$. The analytical data are in accordance with the literature.[22]

2.4.4 2-(7-Bromo-9,9-dimethyl-9H-fluoren-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (17)

A modified literature procedure was used.[8] **16** (3.01 g, 10.0 mmol, 1.00 eq) and 2-amino-2-methylpropan-1-ol (1.78 g, 1.91 mL, 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 $\text{Na}_2\text{S}_2\text{O}_3$ 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 on a rotary evaporator. Purification by flash column chromatography (SiO_2 , CH:EE 15:1 v:v) afforded **17** (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. **$^1\text{H-NMR}$ (360 MHz, CDCl_3):** $\delta = 8.02$ (d, $^4J_{\text{HH}} = 1.4$ Hz, 1H), 7.92 (dd, $^3J_{\text{HH}} = 7.9$ Hz, $^4J_{\text{HH}} = 1.5$ Hz, 1H), 7.69 (d, $^3J_{\text{HH}} = 7.9$ Hz, 1H), 7.58 (d, $^3J_{\text{HH}} = 8.0$ Hz, 1H), 7.56 (d, $^4J_{\text{HH}} = 1.8$ Hz, 1H), 7.46 (dd, $^3J_{\text{HH}} = 8.0$ Hz, $^4J_{\text{HH}} = 1.9$ Hz, 1H), 4.12 (s, 2H), 1.48 (s, 6H), 1.41 (s, 6H) ppm. **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (91 MHz, CDCl_3):** $\delta = 162.3, 156.4, 153.3, 141.2, 137.4, 130.4, 127.8, 127.2, 126.4, 122.7, 122.1, 122.0, 119.9, 79.2, 67.7, 47.4, 28.6$ (2x), 26.9 (2x) ppm. **IR (ATR, neat):** $\tilde{\nu} = 2962$ (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} . **MS (APCI):** $m/z = 370.2$ $[\text{C}_{20}\text{H}_{20}^{79}\text{BrNO}+\text{H}]^+$. **HR-MS (EI, 70 eV):** calculated for $\text{C}_{20}\text{H}_{20}^{79}\text{BrNO}^+$ $[\text{M}]^+$: $m/z = 369.07228$, found: 369.07227 (Dev.: -0.01 mu; -0.02 ppm). The analytical data are in accordance with the literature.[23]

2.4.5 7-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-9,9-dimethyl-9H-fluorene-3-carbaldehyde (18)

A literature procedure was used.[23] A heat gun-dried and nitrogen-flushed *Schlenk* flask, equipped with a magnetic stirring bar and a rubber septum, was charged with **17** (3.70 g, 10.0 mmol, 1.00 eq) and evacuated for half an hour. The flask was flushed with nitrogen and anhydrous THF (25.0 mL, 0.4 M) was added. Addition of $\text{TMPMgCl} \cdot \text{LiCl}$ (25.0 mL, 30.0 mmol, 3.00 eq, 1.20 M) *via* syringe through the rubber septum within five minutes at 25 °C was followed by stirring for four hours under the same conditions. DMF (3.10 mL, 40.0 mmol, 4.00 eq) was diluted in anhydrous THF (10 mL) and added *via* syringe pump (0.3 mL/min) through the rubber septum to the dark red solution at –15 °C. After complete addition the brown mixture was stirred for another two hours while it was allowed to warm to 25 °C. Full consumption of the starting material was followed by diluting with water (50 mL) and ethyl acetate (80 mL). 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_2SO_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 **18** 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 decomp. **^1H -NMR (360 MHz, CDCl_3):** δ = 10.75 (s, 1H), 8.26 (s, 1H), 7.93 (s, 1H), 7.67 (d, $^3J_{\text{HH}} = 8.1$ Hz, 1H), 7.58 (s, 1H), 7.51 (d, $^3J_{\text{HH}} = 8.0$ Hz, 1H), 4.19 (s, 2H), 1.51 (s, 6H), 1.44 (s, 6H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ -NMR (91 MHz, CDCl_3):** δ = 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} . **MS (APCI):** m/z = 398.1 [$\text{C}_{21}\text{H}_{20}^{79}\text{BrNO}_2 + \text{H}$] $^+$. **HR-MS (EI, 70 eV):** calculated for $\text{C}_{21}\text{H}_{20}^{79}\text{BrNO}_2^+$ [M] $^+$: m/z = 397.06719, found: 397.06645 (Dev.: –0.74 mu; –1.87 ppm). The analytical data are in accordance with the literature.[23]

2.4.6 (7-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-9,9-dimethyl-9H-fluoren-3-yl)methanol (**19**)

A modified literature procedure was used.[10] The crude aldehyde **18** (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_2Cl_2 (50 mL) was added and the phases were separated. The aqueous layer was extracted with CH_2Cl_2 (4 × 50 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced

pressure. Purification by flash column chromatography (SiO₂, CH:EE 10:1 to 6:1 v:v) afforded **19** (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. CDCl₃, used for NMR analysis, must be free of acids, due to decomposition of **19** in acidic media. Therefore, CDCl₃ was flushed over neutral alumina.

R_f = 0.06 (SiO₂, CH:EE 10:1 v:v). **R_f** = 0.22 (SiO₂, CH:EE 6:1 v:v). **Mp.**: 179 – 181 °C. **¹H-NMR (360 MHz, CDCl₃)**: δ = 7.91 (s, 1H), 7.68 (s, 1H), 7.61 (d, ³J_{HH} = 8.0 Hz, 1H), 7.57 (d, ⁴J_{HH} = 1.8 Hz, 1H), 7.49 (dd, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 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. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 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), 1204 (s), 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. **MS (APCI)**: m/z = 400.2 [C₂₁H₂₂⁷⁹BrNO₂+H]⁺. **HR-MS (EI, 70 eV)**: calculated for C₂₁H₂₂⁷⁹BrNO₂⁺ [M]⁺: m/z = 399.08284, found: 399.08234 (Dev.: -0.50 mu; -1.25 ppm). The analytical data are in accordance with the literature.[23]

2.4.7 7-Bromo-9,9-dimethyl-3,9-dihydro-1H-fluoreno[2,3-c]furan-1-one (20)

A modified literature procedure was used.[24] **19** (160 mg, 400 μmol, 1.00 eq) was suspended in 4 N HCl (2.00 mL, 0.4 M) and heated to 120 °C (oil bath temperature). After stirring for six hours at this temperature the mixture was allowed to cool to 25 °C and 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 6:1 v:v) afforded **20** (120 mg, 365 μmol, 91 %) as a colorless solid.

R_f = 0.22 (SiO₂, CH:EE 6:1 v:v). **Mp.**: 215 – 217 °C. **¹H-NMR (360 MHz, CDCl₃)**: δ = 7.94 (d, ⁵J_{HH} = 0.9 Hz, 1H), 7.75 (d, ⁵J_{HH} = 0.8 Hz, 1H), 7.65 (d, ³J_{HH} = 8.1 Hz, 1H), 7.62 (d, ⁴J_{HH} = 1.8 Hz, 1H), 7.52 (dd, ³J_{HH} = 8.1 Hz, ⁴J_{HH} = 1.8 Hz, 1H), 5.37 (s, 2H), 1.51 (s, 6H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 171.4, 156.9, 154.9, 146.7, 144.9, 136.3, 130.8, 126.8, 125.0, 123.5, 122.5, 120.1, 113.4, 69.8, 47.1, 27.1 (2x) ppm. **IR (ATR, neat)**: $\tilde{\nu}$ = 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} . **MS (APCI):** $m/z = 329.1$ $[\text{C}_{17}\text{H}_{13}^{79}\text{BrO}_2 + \text{H}]^+$. **HR-MS (EI, 70 eV):** calculated for $\text{C}_{17}\text{H}_{13}^{79}\text{BrO}_2^+ [\text{M}]^+$: $m/z = 328.00934$, found: 328.00958 (Dev.: 0.24 mu; 0.72 ppm). The analytical data are in accordance with the literature.[23]

2.4.8 2-(3-(Azidomethyl)-7-bromo-9,9-dimethyl-9H-fluoren-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (21)

A modified literature procedure was used.[11] **19** (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 intermediately formed phosphate, NaN_3 (163 mg, 2.50 mmol, 1.00 eq) was added and the mixture was heated to 60 °C (oil bath temperature) 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 $\times$ 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 **21** (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. **$^1\text{H-NMR}$ (360 MHz, CDCl_3):** $\delta = 7.94$ (s, 1H), 7.75 (s, 1H), 7.62 (d, $^3J_{\text{HH}} = 8.1$ Hz, 1H), 7.57 (d, $^4J_{\text{HH}} = 1.8$ Hz, 1H), 7.49 (dd, $^3J_{\text{HH}} = 8.1$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, 1H), 4.95 (s, 2H), 4.12 (s, 2H), 1.49 (s, 6H), 1.42 (s, 6H) ppm. **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (91 MHz, CDCl_3):** $\delta = 161.5, 156.6, 152.8, 141.0, 137.1, 135.8, 130.5, 126.4, 126.0, 124.6, 122.4, 122.2, 121.3, 78.7, 68.5, 53.6, 47.4, 28.5$ (2x), 26.9 (2x) ppm. **IR (ATR, neat):** $\tilde{\nu} = 2964$ (w), 2924 (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 (m), 908 (m), 872 (m), 812 (s), 767 (m), 742 (s) cm^{-1} . **MS (APCI):** $m/z = 425.2$ $[\text{C}_{21}\text{H}_{21}^{79}\text{BrN}_4\text{O} + \text{H}]^+$. **HR-MS (APCI):** calculated for $\text{C}_{21}\text{H}_{22}^{79}\text{BrN}_4\text{O}^+ [\text{M} + \text{H}]^+$: $m/z = 425.09715$, found: 425.09753 (Dev.: 0.38 mu; 0.90 ppm). The analytical data are in accordance with the literature.[23]

2.4.9 3-(Azidomethyl)-7-bromo-9,9-dimethyl-9H-fluorene-2-carbaldehyde (**5**)

A modified literature procedure was used.[12] **21** (319 mg, 750 μ mol, 1.00 eq) was dissolved in CH₂Cl₂ (2.50 mL, 0.3 M) and MeOTf (164 μ L, 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 NaBH₄ (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 NH₄Cl solution (5 mL), water (5 mL) and CH₂Cl₂ (10 mL) were added and the phases were separated. The aqueous layer was extracted with CH₂Cl₂ (4 $\times$ 20 mL) and the combined organic phases were dried over anhydrous Na₂SO₄. After filtration and solvent evaporation under reduced pressure, the residue was redissolved in THF:H₂O (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 NaHCO₃ solution (10 mL), water (10 mL) and CH₂Cl₂ (20 mL) were added and the phases separated. The aqueous layer was extracted with CH₂Cl₂ (4 $\times$ 20 mL), the combined organic phases were 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 **5** (230 mg, 646 μ mol, 86 %) as a colorless oil. Upon standing at 25 °C the oil solidified very slowly to form a colorless solid. Single crystals suitable for X-ray analysis were grown by slow diffusion of cyclohexane into a CH₂Cl₂ solution.

R_f = 0.27 (SiO₂, CH:EE 20:1 v:v). **Mp.**: 103 – 105 °C. **¹H-NMR (360 MHz, CDCl₃)**: δ = 10.20 (s, 1H, CHO), 7.90 (s, 1H, H-1), 7.84 (s, 1H, H-4), 7.69 (d, ³J_{HH} = 8.1 Hz, 1H, H-5), 7.62 (d, ⁴J_{HH} = 1.7 Hz, 1H, H-8), 7.53 (dd, ³J_{HH} = 8.1 Hz, ⁴J_{HH} = 1.8 Hz, 1H, H-6), 4.95 (s, 2H, CH₂), 1.53 (s, 6H, 2xCH₃) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 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. **MS (EI, 70 eV)**: m/z = 354.9 [C₁₇H₁₄⁷⁹Br]⁺. **HR-MS (EI, 70 eV)**: calculated for C₁₇H₁₄⁷⁹BrN₃O⁺ [M]⁺: m/z = 355.03148, found: 355.03133 (Dev.: -0.15 mu; -0.41 ppm). The analytical data are in accordance with the literature.[23]

2.4.10 2-(7-Bromo-3-(methoxymethyl)-9,9-dimethyl-9H-fluoren-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (22)

A slightly modified literature procedure was used.[25] A heat gun-dried and nitrogen-flushed *Schlenk* tube, equipped with a magnetic stirring bar and a rubber septum, was charged with **19** (200 mg, 500 μmol , 1.00 eq). The tube was flushed with nitrogen, anhydrous THF (5.00 mL, 0.1 M) was added and the colorless solution was cooled to 0 $^{\circ}\text{C}$. NaH (40.0 mg, 1.00 mmol, 2.00 eq, 60 % in mineral oil) was added at once and the mixture was stirred at 0 $^{\circ}\text{C}$ for 30 minutes. MeI (68.5 μL , 156 mg, 1.10 mmol, 2.20 eq) was dropwise added *via* syringe at 0 $^{\circ}\text{C}$ and the mixture was stirred for two hours while it was allowed to warm to 25 $^{\circ}\text{C}$. Saturated NH_4Cl solution (10 mL) and CH_2Cl_2 (10 mL) were added and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (4 $\times$ 10 mL) and 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 5:1 v:v) provided **22** (206 mg, 497 μmol , 99 %) as a colorless oil, which solidified rapidly upon standing at 25 $^{\circ}\text{C}$.

R_f = 0.34 (SiO_2 , CH:EE 5:1 v:v). **Mp.**: 151 – 153 $^{\circ}\text{C}$. **$^1\text{H-NMR}$ (601 MHz, CDCl_3):** δ = 7.90 (s, 1H), 7.84 (s, 1H), 7.63 (d, $^3J_{\text{HH}}$ = 8.1 Hz, 1H), 7.56 (d, $^4J_{\text{HH}}$ = 1.7 Hz, 1H), 7.47 (dd, $^3J_{\text{HH}}$ = 8.1 Hz, $^4J_{\text{HH}}$ = 1.8 Hz, 1H), 4.88 (s, 2H), 4.10 (s, 2H), 3.50 (s, 3H), 1.48 (s, 6H), 1.41 (s, 6H) ppm. **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (151 MHz, CDCl_3):** δ = 162.1, 156.6, 151.8, 140.7, 138.8, 137.6, 130.4, 126.4, 125.5, 124.1, 122.2, 122.0, 119.4, 78.7, 73.0, 68.3, 58.8, 47.3, 28.6 (2x), 27.0 (2x) ppm. **IR (ATR, neat):** $\tilde{\nu}$ = 2960 (w), 2921 (w), 2896 (w), 2804 (w), 1640 (m), 1601 (w), 1566 (w), 1483 (w), 1458 (w), 1430 (w), 1411 (w), 1384 (w), 1355 (m), 1302 (w), 1285 (w), 1262 (m), 1191 (m), 1161 (m), 1110 (s), 1084 (m), 1060 (m), 1035 (s), 971 (m), 945 (m), 921 (m), 869 (m), 901 (m), 882 (m), 820 (m), 809 (s), 765 (m), 742 (m), 672 (w) cm^{-1} . **MS (ESI):** m/z = 413.9 [$\text{C}_{22}\text{H}_{24}^{79}\text{BrNO}_2 + \text{H}$] $^{+}$. **HR-MS (ESI):** calculated for $\text{C}_{22}\text{H}_{25}^{79}\text{BrNO}_2^{+}$ [$\text{M} + \text{H}$] $^{+}$: m/z = 414.10632, found: 414.10617 (Dev.: -0.15 mu; -0.35 ppm); calculated for $\text{C}_{22}\text{H}_{24}^{79}\text{BrNNaO}_2^{+}$ [$\text{M} + \text{Na}$] $^{+}$: m/z = 436.08826, found: 436.08811 (Dev.: -0.15 mu; -0.34 ppm).

2.4.11 7-Bromo-3-(methoxymethyl)-9,9-dimethyl-9H-fluorene-2-carbaldehyde (23)

A modified literature procedure was used.[12] **22** (82.9 mg, 200 μmol , 1.00 eq) was dissolved in CH_2Cl_2 (1.00 mL, 0.2 M) and MeOTf (43.8 μL , 400 μmol , 2.00 eq) was added *via* syringe in one portion at

25 °C. After stirring for three hours at the same temperature the solution was cooled to 0 °C. A solution of NaBH₄ (15.1 mg, 400 μmol, 2.00 eq) in THF:MeOH (1.0 mL, 4:1 v:v, 0.4 M) was added *via* syringe within five minutes and stirring was continued at 0 °C for another three hours. Saturated NH₄Cl solution (5 mL), water (5 mL) and CH₂Cl₂ (10 mL) were added and the phases were separated. The aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL) and the combined organic phases were dried over anhydrous Na₂SO₄. After filtration and solvent evaporation under reduced pressure, the residue was redissolved in THF:H₂O (1.0 mL, 4:1 v:v, 0.2 M). Oxalic acid dihydrate (50.4 mg, 400 μmol, 2.00 eq) was added at 25 °C and the mixture was stirred for 24 hours under the same conditions. Saturated NaHCO₃ solution (5 mL), water (5 mL) and CH₂Cl₂ (10 mL) were added and the phases were separated. The aqueous layer was extracted with CH₂Cl₂ (4 × 10 mL), the combined organic phases were dried over anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, CH:EE 10:1 v:v) afforded **23** (51.6 mg, 150 μmol, 75 %) as a colorless solid.

R_f = 0.18 (SiO₂, CH:EE 10:1 v:v). **Mp.**: 62 – 64 °C. **¹H-NMR (600 MHz, CDCl₃)**: δ = 10.26 (s, 1H), 7.92 (s, 1H), 7.91 (s, 1H), 7.68 (d, ³J_{HH} = 8.1 Hz, 1H), 7.61 (d, ⁴J_{HH} = 1.6 Hz, 1H), 7.51 (dd, ³J_{HH} = 8.1 Hz, ⁴J_{HH} = 1.7 Hz, 1H), 4.93 (s, 2H), 3.54 (s, 3H), 1.51 (s, 6H) ppm. **¹³C{¹H}-NMR (151 MHz, CDCl₃)**: δ = 192.2, 157.2, 152.6, 143.8, 141.0, 136.9, 132.8, 130.7, 126.6, 126.2, 123.2, 122.8, 120.0, 72.2, 58.9, 47.4, 26.9 (2x) ppm. **IR (ATR, neat)**: $\tilde{\nu}$ = 2956 (w), 2923 (w), 2864 (w), 2820 (w), 2721 (w), 1682 (s), 1614 (m), 1598 (m), 1559 (s), 1471 (m), 1444 (m), 1405 (m), 1384 (m), 1361 (w), 1334 (m), 1302 (w), 1282 (w), 1245 (m), 1222 (w), 1178 (s), 1156 (m), 1134 (m), 1104 (s), 1079 (m), 1057 (m), 980 (s), 907 (m), 886 (m), 838 (m), 825 (s), 798 (s), 772 (m), 729 (s), 673 (m) cm⁻¹. **MS (ESI)**: m/z = 413.9 [C₂₂H₂₄⁷⁹BrNO₂+H]⁺. **HR-MS (ESI)**: calculated for C₁₈H₁₇⁷⁹BrNaO₂⁺ [M+Na]⁺: m/z = 367.03041, found: 367.03027 (Dev.: -0.14 mu; -0.39 ppm); calculated for C₃₆H₃₄⁷⁹Br₂NaO₄⁺ [2M+Na]⁺: m/z = 711.07160, found: 711.07146 (Dev.: -0.14 mu; -0.20 ppm).

2.4.12 9-Bromo-3,3,11,11-tetramethyl-2,3,5,11-tetrahydroindeno[1,2-f]oxazolo[2,3-a]isoindol-4-ium bromide (**25**)

Reaction conditions: a) CBr₄, PPh₃, CH₂Cl₂, 0 °C to 25 °C, 2 h, 95 %; b) NBS, PPh₃, CH₂Cl₂, 0 °C to 25 °C, 2 h, 91 %; c) PBr₃, CH₂Cl₂, 0 °C to 25 °C, 2 h, 92 %; d) spontaneous during/upon workup.

For a): A slightly modified literature procedure was used.[26] A heat gun-dried and nitrogen-flushed *Schlenk* tube, equipped with a magnetic stirring bar and a rubber septum, was charged with **19** (80.1 mg,

200 μmol , 1.00 eq). The tube was flushed with nitrogen, anhydrous CH_2Cl_2 (2.00 mL, 0.1 M) was added and the colorless solution was cooled to 0 °C. PPh_3 (78.7 mg, 300 μmol , 1.50 eq) and CBr_4 (99.5 mg, 300 μmol , 1.50 eq) were added subsequently and the mixture was stirred for two hours while it was allowed to warm to 25 °C – the initial dark yellow color disappeared in the course of the reaction. After full conversion the reaction mixture was directly flushed through a plug of neutral alumina using CH_2Cl_2 . The solvent was removed under reduced pressure to afford the cyclized iminium bromide **25** (88.3 mg, 191 μmol , 95 %) as a colorless foam.

For b): A slightly modified literature procedure was used.[27] A heat gun-dried and nitrogen-flushed *Schlenk* tube, equipped with a magnetic stirring bar and a rubber septum, was charged with **19** (80.1 mg, 200 μmol , 1.00 eq). The tube was flushed with nitrogen, anhydrous CH_2Cl_2 (2.00 mL, 0.1 M) was added and the colorless solution was cooled to 0 °C. PPh_3 (78.7 mg, 300 μmol , 1.50 eq) and NBS (53.4 mg, 300 μmol , 1.50 eq) were added subsequently and the mixture was stirred for two hours while it was allowed to warm to 25 °C – the mixture stayed slightly yellow in the course of the reaction. After full conversion the reaction mixture was directly flushed through a plug of neutral alumina using CH_2Cl_2 . The solvent was removed under reduced pressure to afford the cyclized iminium bromide **25** (84.5 mg, 182 μmol , 91 %) as a colorless foam.

For c): A slightly modified literature procedure was used.[28] A heat gun-dried and nitrogen-flushed *Schlenk* tube, equipped with a magnetic stirring bar and a rubber septum, was charged with **19** (80.1 mg, 200 μmol , 1.00 eq). The tube was flushed with nitrogen, anhydrous CH_2Cl_2 (2.00 mL, 0.1 M) was added and the colorless solution was cooled to 0 °C. PBr_3 (28.5 mL, 81.2 mg, 300 μmol , 1.50 eq) was added dropwise and the mixture was stirred for two hours while it was allowed to warm to 25 °C – the mixture stayed colorless in the course of the reaction. After full conversion the reaction mixture was directly flushed through a plug of neutral alumina using CH_2Cl_2 . The solvent was removed under reduced pressure to afford the cyclized iminium bromide **25** (85.2 mg, 184 μmol , 92 %) as a colorless foam.

24: R_f = 0.44 (SiO_2 , CH:EE 6:1 v:v). **HR-MS (ESI):** calculated for $\text{C}_{21}\text{H}_{22}^{79}\text{Br}_2\text{NO}^+$ $[\text{M}+\text{H}]^+$: m/z = 462.00626, found: 462.00581 (Dev.: -0.46 mu; -0.99 ppm); calculated for $\text{C}_{21}\text{H}_{21}^{79}\text{Br}_2\text{NNaO}^+$ $[\text{M}+\text{Na}]^+$: m/z = 483.98821, found: 483.98779 (Dev.: -0.42 mu; -0.87 ppm); calculated for $\text{C}_{21}\text{H}_{21}^{79}\text{Br}_2\text{KNO}^+$ $[\text{M}+\text{K}]^+$: m/z = 499.96215, found: 499.96202 (Dev.: -0.13 mu; -0.26 ppm); calculated for $\text{C}_{42}\text{H}_{43}^{79}\text{Br}_4\text{N}_2\text{O}_2^+$ $[2\text{M}+\text{H}]^+$: m/z = 923.00525, found: 923.00458 (Dev.: -0.67 mu; -0.73 ppm); calculated for $\text{C}_{42}\text{H}_{42}^{79}\text{Br}_4\text{N}_2\text{NaO}_2^+$ $[2\text{M}+\text{Na}]^+$: m/z = 944.98720, found: 944.98614 (Dev.: -1.06 mu; -1.12 ppm); calculated for $\text{C}_{42}\text{H}_{42}^{79}\text{Br}_4\text{KN}_2\text{O}_2^+$ $[2\text{M}+\text{K}]^+$: m/z = 960.96114, found: 960.96237 (Dev.: 1.24 mu; 1.29 ppm).

25: R_f = 0.18 (SiO_2 , CH:EE 6:1 v:v). **Mp.:** 108 – 110 °C. **$^1\text{H-NMR}$ (601 MHz, CDCl_3):** δ = 7.85 (s, 1H, H-1), 7.69 (s, 1H, H-4), 7.61 (d, $^3J_{\text{HH}}$ = 8.1 Hz, 1H, H-5), 7.59 (d, $^4J_{\text{HH}}$ = 1.7 Hz, 1H, H-8), 7.49

(dd, $^3J_{\text{HH}} = 8.1$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, 1H, H-6), 4.60 (s, 2H, H-15), 4.16 (s, 2H, H-12), 1.69 (s, 6H, H-14), 1.50 (s, 6H, H-10) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (151 MHz, CDCl_3): $\delta = 169.2$ (C=N⁺), 156.6 (C-8a), 153.8 (C-9a), 142.0 (C-4a), 140.6 (C-3), 137.2 (C-4b), 133.2 (C-2), 130.5 (C-6), 126.6 (C-8), 122.4 (C-7), 122.0 (C-5), 117.8 (C-1), 114.0 (C-4), 56.7 (C-13), 50.0 (C-15), 47.1 (C-9), 41.7 (C-12), 27.2 (C-10), 25.4 (C-14) ppm. IR (ATR, neat): $\tilde{\nu} = 2960$ (w), 2922 (w), 2860 (w), 1669 (s), 1622 (m), 1486 (w), 1436 (m), 1388 (s), 1362 (m), 1314 (w), 1247 (s), 1200 (s), 1182 (m), 1142 (m), 1088 (m), 1065 (m), 976 (w), 951 (w), 875 (m), 822 (s), 780 (s), 765 (m), 737 (m), 703 (m), 660 (m) cm^{-1} . MS (ESI): $m/z = 382.0$ [$\text{C}_{21}\text{H}_{21}^{79}\text{BrNO}^+$]. HR-MS (ESI): calculated for $\text{C}_{21}\text{H}_{21}^{79}\text{BrNO}^+$ [$\text{M}-\text{Br}^-$]⁺: $m/z = 382.08010$, found: 382.07985 (Dev.: -0.25 mu; -0.65 ppm).

2.4.13 9-Bromo-3,3,4,11,11-pentamethyl-2,3,4,5,11,12b-hexahydroindeno[1,2-f]oxazolo[2,3-a]isoindol-4-ium trifluoromethanesulfonate (**28**)

Reaction conditions: a) CBr_4 , PPh_3 , CH_2Cl_2 , 0 °C to 25 °C, 2 h, rapid filtration over neutral alumina b) MeOTf, CH_2Cl_2 , 25 °C, 3 h; c) NaBH_4 , THF:MeOH 4:1 v:v, 0 °C, 3 h; d) during reaction, 56 % from **19**.

Slightly modified literature procedures were used.[12, 26] A heat gun-dried and nitrogen-flushed Schlenk tube, equipped with a magnetic stirring bar and a rubber septum, was charged with **19** (160 mg, 400 μmol , 1.00 eq). The tube was flushed with nitrogen, anhydrous CH_2Cl_2 (2.00 mL, 0.1 M) was added and the colorless solution was cooled to 0 °C. PPh_3 (157 mg, 600 μmol , 1.50 eq) and CBr_4 (199 mg, 600 μmol , 1.50 eq) were added subsequently and the mixture was stirred for two hours while it was allowed to warm to 25 °C – the initial dark yellow color disappeared in the course of the reaction. After full conversion the reaction mixture was rapidly flushed through a plug of neutral alumina using CH_2Cl_2 . The solvent was removed under reduced pressure on a rotary evaporator (30 °C water bath temperature) to obtain primarily the benzyl bromide **24** as a colorless foam.

The crude was dissolved in CH_2Cl_2 (2.00 mL, 0.2 M) and MeOTf (87.5 μL , 800 μmol , 2.00 eq) was added *via* syringe in one portion at 25 °C. After stirring for three hours at the same temperature the solution was cooled to 0 °C. A solution of NaBH_4 (30.3 mg, 800 μmol , 2.00 eq) in THF:MeOH (1.0 mL, 4:1 v:v, 0.4 M) was added *via* syringe within five minutes and stirring was continued at 0 °C for another

three hours. Saturated NH_4Cl solution (5 mL), water (5 mL) and CH_2Cl_2 (10 mL) were added and the phases were separated. The aqueous layer was extracted with CH_2Cl_2 (4×10 mL) and the combined organic phases were dried over anhydrous Na_2SO_4 , filtered and the solvent was removed under reduced pressure. Due to unexpected cyclization a further acidic hydrolysis using oxalic acid becomes impossible. Purification by flash column chromatography (SiO_2 , CH_2Cl_2 :MeOH 15:1 v:v) afforded the ammonium triflate **28** (87.7 mg, 223 μmol , 56 % from **19**) as a colorless foam.

R_f = 0.14 (SiO_2 , CH_2Cl_2 :MeOH 15:1 v:v). **Mp.**: 205 – 222 °C (very long decomp.). **^1H -NMR (601 MHz, MeOD- d_4)**: δ = 7.86 (s, 1H, H-4), 7.77 (d, $^3J_{\text{HH}}$ = 8.1 Hz, 1H, H-5), 7.73 (s, 1H, H-1), 7.72 (d, $^4J_{\text{HH}}$ = 1.7 Hz, 1H, H-8), 7.54 (dd, $^3J_{\text{HH}}$ = 8.1 Hz, $^4J_{\text{HH}}$ = 1.6 Hz, 1H, H-6), 6.56 (s, 1H, H-11), 5.43 (d, $^2J_{\text{HH}}$ = 14.9 Hz, 1H, H-15), 4.73 (d, $^2J_{\text{HH}}$ = 14.9 Hz, 1H, H-15), 4.35 (d, $^2J_{\text{HH}}$ = 9.8 Hz, 1H, H-12), 4.31 (d, $^2J_{\text{HH}}$ = 9.8 Hz, 1H, H-12), 3.26 (s, 3H, H-16), 1.77 (s, 3H, H-14), 1.69 (s, 3H, H-14), 1.51 (s, 3H, H-10), 1.51 (s, 3H, H-10) ppm. **$^{13}\text{C}\{^1\text{H}\}$ -NMR (151 MHz, MeOD- d_4)**: δ = 157.7 (C-8a), 156.7 (C-9a), 143.5 (C-4a), 137.9 (C-4b), 135.7 (C-3), 133.2 (C-2), 131.7 (C-6), 127.6 (C-8), 123.6 (C-7), 123.4 (C-5), 121.8 (q, CF_3 , $^1J_{\text{CF}}$ = 318.4 Hz), 120.8 (C-1), 116.5 (C-4), 107.5 (C-11), 79.1 (C-12), 75.6 (C-13), 65.8 (C-15), 48.4 (C-9), 44.2 (C-16), 27.1 (C-10), 27.0 (C-10), 23.2 (C-14), 18.8 (C-14) ppm. **$^{19}\text{F}\{^1\text{H}\}$ -NMR (565 MHz, MeOD- d_4)**: δ = -80.09 (s) ppm. **IR (ATR, neat)**: $\tilde{\nu}$ = 2965 (w), 2927 (w), 1623 (w), 1601 (w), 1475 (w), 1457 (w), 1436 (w), 1405 (w), 1388 (w), 1360 (w), 1251 (s), 1224 (s), 1190 (m), 1154 (s), 1086 (m), 1050 (m), 1028 (s), 968 (m), 918 (m), 878 (m), 820 (m), 755 (m), 676 (w) cm^{-1} . **MS (ESI)**: m/z = 397.8 [$\text{C}_{22}\text{H}_{25}^{79}\text{BrNO}$] $^+$. **HR-MS (ESI)**: calculated for $\text{C}_{22}\text{H}_{25}^{79}\text{BrNO}$ [M-OTf^-] $^+$: m/z = 398.11140, found: 398.11122 (Dev.: -0.18 mu; -0.45 ppm).

2.4.14 Attempted Preparation of (7-bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-9,9-dimethyl-9H-fluoren-3-yl)methyl methanesulfonate (**S3**)

A slightly modified literature procedure was used.[29] A heat gun-dried and nitrogen-flushed *Schlenk* tube, equipped with a magnetic stirring bar and a rubber septum, was charged with **19** (400 mg, 1.00 mmol, 1.00 eq). The tube was flushed with nitrogen, anhydrous CH_2Cl_2 (5.00 mL, 0.2 M) was added and the colorless solution was cooled to 0 °C. NEt_3 (152 mg, 209 μL , 1.50 mmol, 1.50 eq) and MsCl (160 mg, 108 μL , 1.40 mmol, 1.40 eq) were added successively and the mixture was stirred at 0 °C for one hour. Despite complete conversion of **19**, only traces of **S3** were observed.

2.5 Preparation of Sterically Hindered Alkynes

2.5.1 Preparation of (3*r*,5*r*,7*r*)-1-ethynyladamantane (**31**)

A modified literature procedure was used.[30] Initially a fresh LDA solution was prepared. Therefore, a heat gun-dried and nitrogen-flushed *Schlenk* flask, equipped with a magnetic stirring bar and a rubber septum, was charged with anhydrous THF (16.7 mL) and *N,N*-diisopropylamine (1.69 mL, 12.0 mmol, 1.20 eq) was added. The solution was cooled to $-78\text{ }^{\circ}\text{C}$ and *n*BuLi (4.40 mL, 11.0 mmol, 1.10 eq, 2.50 M in hexane) was added in one portion, whereupon the solution turned slightly yellow. After stirring for 30 minutes at the same temperature 1-((3*r*,5*r*,7*r*)-adamantan-1-yl)ethan-1-one (1.78 g, 10.0 mmol, 1.00 eq), dissolved in anhydrous THF (12.5 mL), was added dropwise *via* syringe pump (0.5 mL/min) to the LDA solution. After complete addition the solution was stirred at $-78\text{ }^{\circ}\text{C}$ for an additional one hour and then diethyl chlorophosphate (1.59 mL, 11.0 mmol, 1.10 eq) was added *via* syringe pump (0.5 mL/min), whereupon the mixture was stirred for one more hour under the same conditions. The cooling bath was removed and the mixture was stirred for three more hours while it was allowed to warm to $25\text{ }^{\circ}\text{C}$. In a separately heat gun-dried and nitrogen-flushed *Schlenk* flask, equipped with a magnetic stirring bar and a rubber septum, was prepared a second LDA solution. Therefore, *N,N*-diisopropylamine (2.96 mL, 21.0 mmol, 2.10 eq) was added to anhydrous THF (25.0 mL) and the solution was cooled to $-78\text{ }^{\circ}\text{C}$. *n*BuLi (8.00 mL, 20.0 mmol, 2.00 eq, 2.50 M in hexane) was added in one portion and the slightly yellow solution was stirred for 30 minutes at the same temperature. The phosphate containing solution was added *via* syringe pump (1.0 mL/min) to the second LDA solution at $-78\text{ }^{\circ}\text{C}$ and stirred under these conditions for two hours. Then the mixture was allowed to warm slowly to $25\text{ }^{\circ}\text{C}$ and stirred for 12 hours in all. Saturated NH₄Cl solution (40 mL) and water (20 mL) were added and the phases separated. The aqueous layer was extracted with ethyl acetate (3 × 40 mL) and the combined organic layers were dried over anhydrous Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. Purification by flash column chromatography (SiO₂, CH) afforded **31** (735 mg, 4.59 mmol, 46 %) as a colorless solid.

R_f = 0.74 (SiO₂, CH, staining with KMnO₄). **Mp.**: $79 - 81\text{ }^{\circ}\text{C}$. **¹H-NMR (360 MHz, CDCl₃)**: δ = 2.10 (s, 1H), 1.95 (br. s, 3H), 1.88 (d, $^3J_{\text{HH}}$ = 2.8 Hz, 6H), 1.68 (t, $^3J_{\text{HH}}$ = 3.1 Hz, 6H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 93.2, 66.7, 42.9 (3x), 36.4 (3x), 29.5, 28.0 (3x) ppm. **IR (ATR, neat)**: $\tilde{\nu}$ = 3304 (m), 2900 (s), 2849 (s), 2657 (w), 2104 (w), 1450 (s), 1356 (w), 1343 (w), 1314 (w), 1227 (m), 1182

(w), 1132 (w), 1098 (m), 1023 (w), 975 (w), 932 (w), 811 (m), 772 (w), 699 (w) cm^{-1} . **MS (EI, 70 eV):** $m/z = 160.1$ $[\text{M}]^+$. The analytical data are in accordance with the literature.[30]

2.5.2 Preparation of 1,3-di-*tert*-butyl-5-ethynylbenzene (32)

Reaction conditions: a) 1) NBS, AIBN, PhH, 90 °C, 16 h; 2) $(\text{CH}_2)_6\text{N}_4$, EtOH:H₂O 1:1 v:v, 90 °C 4 h; (3) conc. HCl, 90 °C, 0.5 h, 80 %; b) PPh_3 , Zn, CBr_4 , CH_2Cl_2 , 0 °C to 25 °C, 3 h, 96 %; c) $n\text{BuLi}$, THF, -78 °C to 25 °C, 5 h, 89 %.

2.5.2.1 3,5-Di-*tert*-butylbenzaldehyde (S4)

A modified literature procedure was used.[31] 1,3-Di-*tert*-butyl-5-methylbenzene (3.07 g, 15.0 mmol, 1.00 eq) was dissolved in benzene (15.0 mL, 1.0 M) and NBS (1.50 g, 22.5 mmol, 1.50 eq) and AIBN (123 mg, 750 μmol , 0.05 eq) were added. The mixture was heated to 100 °C (oil bath temperature) and stirred for 16 hours at this temperature. After cooling to 25 °C, the mixture was filtered through Celite® and washed with ethyl acetate (~50 mL). The solution was concentrated under reduced pressure to afford a brown oil, which was used without further purification. The crude product was dissolved in EtOH:H₂O (15 mL 1:1 v:v) and hexamethylenetetramine (6.31 g, 45.0 mmol, 3.00 eq) was added in one portion. Heating for four hours at 100 °C (oil bath temperature) was followed by the addition of concentrated HCl and heating was continued for another 30 minutes. Ethanol was removed under reduced pressure by rotary evaporation and water (35 mL) and ethyl acetate (50 mL) were added. The phases were separated and the aqueous phase was extracted with ethyl acetate (3 $\times$ 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2 , CH:EE 50:1 v:v) afforded **S4** (2.61 g, 12.0 mmol, 80 %) as a colorless oil, which slowly solidified upon standing at 25 °C.

$R_f = 0.09$ (SiO_2 , CH). $R_f = 0.26$ (SiO_2 , CH:EE 50:1 v:v). **Mp.:** 83 – 85 °C. **^1H -NMR (360 MHz, CDCl_3):** $\delta = 10.01$ (s, 1H), 7.76 – 7.69 (m, 3H), 1.37 (s, 18H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ -NMR (91 MHz, CDCl_3):** $\delta = 193.4$, 152.0 (2x), 136.3, 129.0, 124.3 (2x), 35.1 (2x), 31.5 (6x) ppm. **IR (ATR, neat):** $\tilde{\nu} = 2960$ (m), 2905 (w), 2868 (w), 2817 (w), 2734 (w), 1686 (s), 1591 (m), 1474 (m), 1463 (m), 1388 (m), 1363 (m), 1325

(w), 1305 (w), 1278 (w), 1250 (m), 1189 (s), 1127 (w), 1011 (w), 948 (w), 900 (w), 882 (m), 818 (m), 768 (w), 706 (s), 699 (s) cm^{-1} . **MS (EI, 70 eV):** $m/z = 218.1$ $[\text{M}]^+$. The analytical data are in accordance with the literature.[32]

2.5.2.2 1,3-Di-*tert*-butyl-5-(2,2-dibromovinyl)benzene (S5)

A modified literature procedure was used.[33] A heat gun-dried and nitrogen-flushed *Schlenk* flask, equipped with a magnetic stirring bar and a rubber septum, was charged with PPh_3 (4.72 g, 18.0 mmol, 2.00 eq) and anhydrous CH_2Cl_2 (45 mL) was added. Zinc dust (particle $< 10\text{ }\mu\text{m}$) was added in one portion and the suspension was cooled to $0\text{ }^\circ\text{C}$. CBr_4 (5.97 g, 18.0 mmol, 2.00 eq) was added in one portion whereupon the suspension turned dirty green. The mixture was allowed to warm slowly to ambient temperature and stirred for 24 hours, while the color turned deep red. **S4** (1.97 g, 9.00 mmol, 1.00 eq) was dissolved in anhydrous CH_2Cl_2 (15 mL) and added *via* syringe pump (1.0 mL/min) to the ice cooled ($0\text{ }^\circ\text{C}$) mixture. Stirring was continued for three more hours while the mixture was allowed to warm to $25\text{ }^\circ\text{C}$. Filtration through a short plug of Celite[®] and washing with CH_2Cl_2 (150 mL) was followed by removing of the solvent under reduced pressure. Purification by flash column chromatography (SiO_2 , CH) afforded **S5** (3.23 g, 8.63 mmol, 96 %) as a colorless oil which slowly solidified upon standing at $25\text{ }^\circ\text{C}$.

$R_f = 0.78$ (SiO_2 , CH). **Mp.:** $41 - 44\text{ }^\circ\text{C}$. **^1H -NMR (360 MHz, CDCl_3):** $\delta = 7.52$ (br. s, 1H), $7.43 - 7.37$ (m, 3H), 1.34 (s, 18H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ -NMR (91 MHz, CDCl_3):** $\delta = 150.9$ (2x), 137.9 , 134.5 , 122.9 (2x), 122.8 , 88.7 , 35.0 (2x), 31.5 (6x) ppm. **IR (ATR, neat):** $\tilde{\nu} = 3308$ (w), 2961 (s), 2903 (s), 2853 (m), 2733 (w), 2105 (w), 1687 (s), 1593 (m), 1475 (m), 1451 (m), 1389 (m), 1363 (s), 1305 (w), 1278 (w), 1249 (m), 1189 (s), 1127 (w), 1098 (w), 1011 (w), 949 (w), 900 (m), 882 (s), 827 (m), 817 (m), 799 (m), 767 (w), 705 (s) cm^{-1} . **MS (EI, 70 eV):** $m/z = 371.9$ $[\text{C}_{16}\text{H}_{22}^{79}\text{Br}_2]^+$. **HR-MS (EI, 70 eV):** calculated for $\text{C}_{16}\text{H}_{22}^{79}\text{Br}_2^+$ $[\text{M}]^+$: $m/z = 372.00883$, found: 372.00842 (Dev.: 0.41 mu ; 1.10 ppm). The analytical data are in accordance with the literature.[33]

2.5.3 1,3-Di-*tert*-butyl-5-ethynylbenzene (**32**)

A modified literature procedure was used.[33] A heat gun-dried and nitrogen-flushed *Schlenk* flask, equipped with a magnetic stirring bar and a rubber septum, was charged with **S5** (1.87 g, 5.00 mmol, 1.00 eq) and dissolved in anhydrous THF (12.5 mL, 0.4 M). The solution was cooled to $-78\text{ }^{\circ}\text{C}$ and *n*BuLi (6.00 mL, 15.0 mmol, 3.00 eq, 2.50 M in hexane) was added *via* syringe pump (1.0 mL/min). Stirring was continued for one hour at $-78\text{ }^{\circ}\text{C}$, then the cooling bath was removed while it was allowed to warm slowly to $25\text{ }^{\circ}\text{C}$ and stirred for four hours in all. Cooling to $0\text{ }^{\circ}\text{C}$ was followed by the dropwise addition of saturated NH_4Cl solution (10 mL). Water (10 mL) and CH_2Cl_2 (10 mL) were added and the phases separated. The aqueous phase was extracted with CH_2Cl_2 ($3 \times 20\text{ mL}$), the combined organic phases dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2 , CH) provided **32** (949 mg, 4.43 mmol, 89 %) as a colorless solid.

$R_f = 0.66$ (SiO_2 , CH). **Mp.**: $83 - 85\text{ }^{\circ}\text{C}$. **$^1\text{H-NMR}$ (360 MHz, CDCl_3)**: $\delta = 7.45 - 7.38$ (m, 1H), $7.38 - 7.32$ (m, 2H), 3.03 (s, 1H), 1.31 (s, 18H) ppm. **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (91 MHz, CDCl_3)**: $\delta = 151.0$ (2x), 126.5 (2x), 123.4 , 121.1 , 85.0 , 75.9 , 34.9 (2x), 31.4 (6x) ppm. **IR (ATR, neat)**: $\tilde{\nu} = 3272$ (m), 2951 (s), 2903 (m), 2868 (m), 1776 (w), 1591 (m), 1477 (m), 1460 (m), 1422 (m), 1392 (w), 1364 (s), 1316 (w), 1248 (m), 1192 (m), 1137 (w), 1025 (w), 935 (w), 914 (w), 900 (m), 883 (s), 710 (s), 673 (s) cm^{-1} . **MS (EI, 70 eV)**: $m/z = 214.1$ $[\text{M}]^+$. **HR-MS (EI, 70 eV)**: calculated for $\text{C}_{16}\text{H}_{22}^+$ $[\text{M}]^+$: $m/z = 214.17215$, found: 214.17143 (Dev.: 0.72 mu; 3.36 ppm). The analytical data are in accordance with the literature.[33]

2.6 Copper-Catalyzed Azide-Alkyne Cycloadditions (CuAAC)

2.6.1 General Procedure for the CuAACs (GP1)

A modified literature procedure was used.[34] In a screw-cap vial azide (100 μmol , 1.00 eq) and terminal alkyne (105 μmol , 1.05 eq) were dissolved in CHCl_3 (1.00 mL, 0.1 M). $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ (2.4 mg, 10 μmol , 0.10 eq) and sodium ascorbate (9.9 mg, 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 the indicated time and directly purified by flash column chromatography.

2.6.2 4-Bromo-2-((4-octyl-1H-1,2,3-triazol-1-yl)methyl)benzaldehyde (**33**)

33

According to GP1 the reaction of **3** (24.0 mg, 100 μmol , 1.00 eq) and 1-decyne (19.0 μL , 105 μmol , 1.05 eq) provided after 24 hours reaction time and subsequent flash column chromatography (SiO_2 , $\text{CH}:\text{EE}$ 3:1 v:v) **32** (35.5 mg, 93.8 μmol , 94 %) as a colorless solid.

R_f = 0.33 (SiO_2 , $\text{CH}:\text{EE}$ 3:1 v:v). **Mp.**: 82 – 84 °C. **^1H -NMR (360 MHz, CDCl_3)**: δ = 10.08 (d, $^4J_{\text{HH}}$ = 0.6 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.39 (s, 1H), 7.22 – 7.16 (m, 1H), 5.94 (s, 2H), 2.71 (t, $^3J_{\text{HH}}$ = 7.6 Hz, 2H), 1.66 (p, $^3J_{\text{HH}}$ = 7.9 Hz, 2H), 1.39 – 1.20 (m, 10H), 0.86 (t, $^3J_{\text{HH}}$ = 7.2 Hz, 3H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ -NMR (91 MHz, CDCl_3)**: δ = 192.6, 149.1, 138.6, 136.7, 132.9, 132.3, 131.8, 130.1, 121.7, 50.2, 32.0, 29.5, 29.4, 29.4, 29.3, 25.8, 22.8, 14.2 ppm. **IR (ATR, neat)**: $\tilde{\nu}$ = 3056 (w), 2950 (w), 2921 (m), 2850 (m), 2782 (w), 1686 (s), 1583 (s), 1562 (m), 1466 (w), 1435 (m), 1334 (m), 1288 (w), 1210 (m), 1196 (m), 1174 (m), 1141 (m), 1097 (m), 1079 (m), 1055 (m), 1033 (w), 866 (s), 834 (m), 803 (s), 721 (m), 670 (w) cm^{-1} . **MS (APCI)**: m/z = 378.1 [$\text{C}_{18}\text{H}_{24}^{79}\text{BrN}_3\text{O}+\text{H}$] $^+$. **HR-MS (EI, 70 eV)**: calculated for $\text{C}_{18}\text{H}_{24}^{79}\text{BrN}_3\text{O}^+$ [M] $^+$: m/z = 377.10973, found: 377.10924 (Dev.: –0.49 mu; –1.29 ppm); calculated for $\text{C}_{18}\text{H}_{24}^{81}\text{BrN}_3\text{O}^+$ [M] $^+$: m/z = 379.10768, found: 379.10780 (Dev.: 0.12 mu; 0.32 ppm).

2.6.3 2-((4-((1*s*,3*s*)-Adamantan-1-yl)-1*H*-1,2,3-triazol-1-yl)methyl)-4-bromobenzaldehyde (**34**)

34

According to GP1 the reaction of **3** (24.0 mg, 100 μ mol, 1.00 eq) and **31** (16.8 mg, 105 μ mol, 1.05 eq) provided after three days reaction time and subsequent flash column chromatography (SiO₂, CH:EE 4:1 v:v) **34** (38.9 mg, 97.2 μ mol, 97 %) as a colorless solid.

R_f = 0.23 (SiO₂, CH:EE 4:1 v:v). **Mp.**: 131 – 133 °C. **¹H-NMR (360 MHz, CDCl₃)**: δ = 10.08 (s, 1H), 7.69 (d, ⁴*J*_{HH} = 1.6 Hz, 2H), 7.34 (s, 1H), 7.24 – 7.19 (m, 1H), 5.93 (s, 2H), 2.08 – 2.02 (m, 3H), 1.96 (d, ³*J*_{HH} = 2.9 Hz, 6H), 1.82 – 1.71 (m, 6H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 192.6, 158.5, 138.6, 136.6, 133.1, 132.3, 131.8, 130.0, 119.5, 50.1, 42.6 (3x), 36.8 (3x), 32.8, 28.5 (3x) ppm. **IR (ATR, neat)**: $\tilde{\nu}$ = 2906 (m), 2848 (m), 1694 (s), 1587 (m), 1558 (m), 1479 (w), 1456 (m), 1413 (w), 1385 (w), 1340 (m), 1309 (m), 1290 (m), 1212 (m), 1186 (m), 1170 (m), 1146 (m), 1077 (m), 1047 (m), 1001 (m), 976 (w), 888 (s), 852 (w), 804 (s), 754 (m), 723 (m), 701 (m), 683 (m), 661 (m) cm⁻¹. **MS (APCI)**: *m/z* = 400.1 [C₂₀H₂₂⁷⁹BrN₃O+H]⁺. **HR-MS (ESI)**: calculated for C₂₀H₂₃⁷⁹BrN₃O⁺ [M+H]⁺: *m/z* = 400.10190, found: 400.10175 (Dev.: -0.15 mu; -0.37 ppm).

2.6.4 4-Bromo-2-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)benzaldehyde (**35**)

35

According to GP1 the reaction of **3** (24.0 mg, 100 μ mol, 1.00 eq) and phenylacetylene (11.5 μ L, 105 μ mol, 1.05 eq) provided after 24 hours reaction time and subsequent flash column chromatography (SiO₂, CH:EE 3:1 v:v) **35** (33.8 mg, 98.7 μ mol, 99 %) as a colorless solid.

R_f = 0.27 (SiO₂, CH:EE 3:1 v:v). **Mp.**: 157 – 159 °C. **¹H-NMR (360 MHz, CDCl₃)**: δ = 10.08 (d, ⁴*J*_{HH} = 0.6 Hz, 1H), 7.92 (s, 1H), 7.87 – 7.79 (m, 2H), 7.72 – 7.70 (m, 2H), 7.44 – 7.38 (m, 2H), 7.37 – 7.35 (m, 1H), 7.35 – 7.30 (m, 1H), 6.02 (s, 2H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 192.7, 148.1,

138.0, 136.9, 133.3, 132.5, 131.8, 130.5, 130.1, 129.0 (2x), 128.4, 125.8 (2x), 120.7, 50.4 ppm. **IR (ATR, neat):** $\tilde{\nu}$ = 3082 (w), 2876 (w), 2777 (w), 1686 (s), 1582 (m), 1563 (m), 1466 (m), 1433 (m), 1400 (w), 1349 (w), 1288 (w), 1214 (m), 1202 (m), 1172 (m), 1099 (w), 1084 (m), 1047 (m), 1029 (w), 978 (m), 915 (w), 865 (m), 833 (m), 804 (m), 781 (m), 765 (s), 714 (m), 692 (s), 671 (m), 657 (m) cm^{-1} . **MS (APCI):** m/z = 342.0 $[\text{C}_{16}\text{H}_{12}^{79}\text{BrN}_3\text{O}+\text{H}]^+$. **HR-MS (EI, 70 eV):** calculated for $\text{C}_{16}\text{H}_{12}^{79}\text{BrN}_3\text{O}^+$ $[\text{M}]^+$: m/z = 341.01583, found: 341.01570 (Dev.: -0.13 mu; -0.37 ppm).

2.6.5 4-Bromo-2-((4-(3,5-di-*tert*-butylphenyl)-1*H*-1,2,3-triazol-1-yl)methyl)benzaldehyde (**36**)

36

According to GP1 the reaction of **3** (24.0 mg, 100 μmol , 1.00 eq) and **32** (22.5 mg, 105 μmol , 1.05 eq) provided after three days reaction time and subsequent flash column chromatography (SiO_2 , CH:EE 4:1 v:v) **36** (43.6 mg, 96.0 μmol , 96 %) as a colorless solid.

R_f = 0.31 (SiO_2 , CH:EE 4:1 v:v). **Mp.:** 132 – 134 $^\circ\text{C}$. **$^1\text{H-NMR}$ (360 MHz, CDCl_3):** δ = 10.10 (s, 1H), 7.91 (s, 1H), 7.71 (d, $^5J_{\text{HH}}$ = 1.0 Hz, 2H), 7.69 (d, $^4J_{\text{HH}}$ = 1.8 Hz, 2H), 7.43 (t, $^4J_{\text{HH}}$ = 1.8 Hz, 1H), 7.31 (s, 1H), 6.06 (s, 2H), 1.37 (s, 18H) ppm. **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (91 MHz, CDCl_3):** δ = 192.7, 151.5 (2x), 149.1, 138.3, 136.8, 133.0, 132.4, 131.8, 130.2, 129.6, 122.7, 120.6 (2x), 120.3, 50.4, 35.1 (2x), 31.6 (6x) ppm. **IR (ATR, neat):** $\tilde{\nu}$ = 2962 (m), 2903 (m), 2847 (w), 1698 (s), 1590 (m), 1562 (s), 1447 (m), 1419 (m), 1393 (m), 1361 (m), 1343 (m), 1287 (m), 1249 (m), 1225 (m), 1201 (m), 1183 (m), 1097 (m), 1080 (m), 1064 (m), 1051 (s), 1001 (w), 968 (m), 902 (s), 879 (s), 848 (m), 826 (s), 816 (s), 785 (s), 768 (s), 727 (s), 718 (s), 709 (s), 685 (m), 673 (m), 660 (m) cm^{-1} . **MS (APCI):** m/z = 454.0 $[\text{C}_{24}\text{H}_{28}^{79}\text{BrN}_3\text{O}+\text{H}]^+$. **HR-MS (ESI):** calculated for $\text{C}_{24}\text{H}_{29}^{79}\text{BrN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: m/z = 454.14885, found: 454.14826 (Dev.: -0.59 mu; -1.30 ppm).

2.6.6 2-Bromo-4-((4-octyl-1*H*-1,2,3-triazol-1-yl)methyl)benzaldehyde (**37**)

37

According to GP1 the reaction of **4** (24.0 mg, 100 μ mol, 1.00 eq) and 1-decyne (19.0 μ L, 105 μ mol, 1.05 eq) provided after 24 hours reaction time and subsequent flash column chromatography (SiO₂, CH:EE 3:1 v:v) **37** (34.7 mg, 91.7 μ mol, 92 %) as a colorless solid.

R_f = 0.14 (SiO₂, CH:EE 3:1 v:v). **Mp.**: 75 – 77 °C. **¹H-NMR (360 MHz, CDCl₃)**: δ = 10.30 (d, ⁴J_{HH} = 0.8 Hz, 1H), 7.87 (d, ³J_{HH} = 8.0 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.30 – 7.21 (m, 2H), 5.53 (s, 2H), 2.70 (t, ³J_{HH} = 7.7 Hz, 2H), 1.64 (p, ³J_{HH} = 7.9 Hz, 2H), 1.36 – 1.19 (m, 10H), 0.84 (t, ³J_{HH} = 6.8 Hz, 3H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 191.1, 149.6, 142.9, 133.5, 132.8, 130.5, 127.6, 127.1, 120.9, 52.8, 31.9, 29.4, 29.4, 29.3, 29.3, 25.8, 22.7, 14.2 ppm. **IR (ATR, neat)**: $\tilde{\nu}$ = 3061 (w), 2951 (w), 2918 (m), 2848 (m), 1687 (s), 1600 (m), 1558 (m), 1466 (m), 1432 (m), 1408 (m), 1389 (m), 1349 (m), 1291 (w), 1260 (m), 1202 (s), 1137 (m), 1079 (w), 1052 (m), 1036 (m), 977 (w), 889 (w), 866 (m), 826 (m), 805 (s), 781 (s), 765 (m), 721 (m), 692 (m), 674 (m) cm⁻¹. **MS (APCI)**: m/z = 378.1 [C₁₈H₂₄⁷⁹BrN₃O+H]⁺. **HR-MS (EI, 70 eV)**: calculated for C₁₈H₂₄⁷⁹BrN₃O⁺ [M]⁺: m/z = 377.10973, found: 377.10955 (Dev.: -0.18 mu; -0.47 ppm).

2.6.7 4-((4-((1*s*,3*s*)-Adamantan-1-yl)-1*H*-1,2,3-triazol-1-yl)methyl)-2-bromobenzaldehyde (**38**)

38

According to GP1 the reaction of **4** (24.0 mg, 100 μ mol, 1.00 eq) and **31** (16.8 mg, 105 μ mol, 1.05 eq) provided after 24 hours reaction time and subsequent flash column chromatography (SiO₂, CH:EE 3:1 v:v) **38** (38.7 mg, 96.7 μ mol, 97 %) as a colorless solid.

R_f = 0.24 (SiO₂, CH:EE 3:1 v:v). **Mp.**: 99 – 101 °C. **¹H-NMR (360 MHz, CDCl₃)**: δ = 10.31 (s, 1H), 7.88 (d, ³J_{HH} = 8.0 Hz, 1H), 7.51 (d, ⁴J_{HH} = 1.7 Hz, 1H), 7.26 (dd, ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 1.6 Hz, 1H), 7.21 (s, 1H), 5.52 (s, 2H), 2.08 – 2.00 (m, 3H), 1.95 (d, ³J_{HH} = 2.9 Hz, 6H), 1.81 – 1.70 (m, 6H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 191.2, 159.1, 142.9, 133.5, 133.0, 130.6, 127.6, 127.3, 118.7, 52.8, 42.6 (3x), 36.7 (3x), 32.8, 28.5 (3x) ppm. **IR (ATR, neat)**: $\tilde{\nu}$ = 2900 (s), 2847 (m), 1689 (s), 1599 (m), 1562 (w), 1539 (w), 1450 (w), 1406 (w), 1387 (m), 1343 (w), 1303 (w), 1286 (w), 1266 (m), 1205 (s), 1140 (w), 1101 (w), 1073 (w), 1042 (s), 1002 (m), 975 (w), 925 (w), 898 (w), 845 (m), 811 (w), 788 (s), 771 (m), 755 (s), 724 (s), 676 (m) cm⁻¹. **MS (APCI)**: m/z = 400.0 [C₂₀H₂₂⁷⁹BrN₃O+H]⁺. **HR-MS**

(ESI): calculated for $C_{20}H_{23}^{79}BrN_3O^+$ $[M+H]^+$: $m/z = 400.10190$, found: 400.10166 (Dev.: -0.24 mu; -0.59 ppm).

2.6.8 2-Bromo-4-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)benzaldehyde (39)

39

According to GP1 the reaction of **4** (24.0 mg, 100 μ mol, 1.00 eq) and phenylacetylene (11.5 μ L, 105 μ mol, 1.05 eq) provided after 24 hours reaction time and subsequent flash column chromatography (SiO_2 , CH:EE 3:1 v:v) **39** (33.1 mg, 96.7 μ mol, 97 %) as a colorless solid.

$R_f = 0.13$ (SiO_2 , CH:EE 3:1 v:v). **Mp.**: 141 – 143 $^{\circ}C$. **1H -NMR (360 MHz, $CDCl_3$)**: $\delta = 10.32$ (d, $^4J_{HH} = 0.8$ Hz, 1H), 7.90 (d, $^3J_{HH} = 8.0$ Hz, 1H), 7.86 – 7.77 (m, 2H), 7.77 (s, 1H), 7.55 (d, $^4J_{HH} = 1.6$ Hz, 1H), 7.44 – 7.39 (m, 2H), 7.37 – 7.30 (m, 2H), 5.61 (s, 2H) ppm. **$^{13}C\{^1H\}$ -NMR (91 MHz, $CDCl_3$)**: $\delta = 191.1, 148.8, 142.5, 133.7, 133.0, 130.6, 130.2, 129.0$ (2x), 128.6, 127.7, 127.2, 125.8 (2x), 119.8, 53.0 ppm. **IR (ATR, neat)**: $\tilde{\nu} = 3084$ (w), 2858 (w), 1687 (m), 1584 (m), 1563 (w), 1465 (m), 1426 (w), 1403 (m), 1383 (w), 1344 (w), 1224 (m), 1201 (m), 1179 (m), 1148 (w), 1084 (m), 1047 (m), 1039 (m), 978 (m), 914 (w), 865 (w), 845 (w), 825 (m), 805 (m), 782 (m), 763 (s), 710 (m), 692 (s), 677 (m), 654 (m) cm^{-1} . **MS (APCI)**: $m/z = 342.0$ $[C_{16}H_{12}^{79}BrN_3O+H]^+$. **HR-MS (EI, 70 eV)**: calculated for $C_{16}H_{12}^{79}BrN_3O^+$ $[M]^+$: $m/z = 341.01583$, found: 341.01565 (Dev.: -0.18 mu; -0.51 ppm).

2.6.9 2-Bromo-4-((4-(3,5-di-*tert*-butylphenyl)-1*H*-1,2,3-triazol-1-yl)methyl)benzaldehyde (40)

40

According to GP1 the reaction of **4** (24.0 mg, 100 μ mol, 1.00 eq) and **32** (22.5 mg, 105 μ mol, 1.05 eq) provided after 24 hours reaction time and subsequent flash column chromatography (SiO_2 , CH:EE 3:1 v:v) **40** (42.9 mg, 94.4 μ mol, 94 %) as a colorless solid.

R_f = 0.34 (SiO₂, CH:EE 3:1 v:v). **Mp.**: 190 – 192 °C. **¹H-NMR (360 MHz, CDCl₃)**: δ = 10.36 (s, 1H), 7.94 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.82 (s, 1H), 7.70 (d, $^4J_{HH}$ = 1.8 Hz, 2H), 7.58 (d, $^4J_{HH}$ = 1.7 Hz, 1H), 7.46 (t, $^4J_{HH}$ = 1.9 Hz, 1H), 7.35 (ddd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, $^5J_{HH}$ = 0.8 Hz, 1H), 5.66 (s, 2H), 1.39 (s, 18H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 191.2, 151.6 (2x), 149.7, 142.7, 133.6, 132.9, 130.6, 129.4, 127.7, 127.1, 122.9, 120.3 (2x), 119.8, 53.0, 35.1 (2x), 31.5 (6x) ppm. **IR (ATR, neat)**: $\tilde{\nu}$ = 3104 (w), 3067 (w), 2961 (m), 2865 (w), 1699 (s), 1599 (m), 1546 (w), 1474 (w), 1463 (w), 1444 (w), 1420 (w), 1405 (w), 1386 (m), 1363 (m), 1279 (w), 1264 (m), 1248 (m), 1224 (m), 1199 (m), 1139 (w), 1099 (w), 1054 (m), 1042 (m), 1008 (w), 882 (m), 839 (m), 781 (s), 745 (m), 714 (s), 677 (m) cm⁻¹. **MS (APCI)**: m/z = 454.1 [C₂₄H₂₈⁷⁹BrN₃O+H]⁺. **HR-MS (ESI)**: calculated for C₂₄H₂₉⁷⁹BrN₃O⁺ [M+H]⁺: m/z = 454.14885, found: 454.14914 (Dev.: 0.28 mu; 0.63 ppm).

2.6.10 7-Bromo-9,9-dimethyl-3-((4-octyl-1H-1,2,3-triazol-1-yl)methyl)-9H-fluorene-2-carbaldehyde (41)

41

According to GP1 the reaction of **5** (35.6 mg, 100 μ mol, 1.00 eq) and 1-decyne (19.0 μ L, 105 μ mol, 1.05 eq) provided after 24 hours reaction time and subsequent flash column chromatography (SiO₂, CH:EE 3:1 v:v) **41** (45.2 mg, 91.4 μ mol, 91 %) as a yellowish oil.

R_f = 0.22 (SiO₂, CH:EE 3:1 v:v). **¹H-NMR (360 MHz, CDCl₃)**: δ = 10.18 (s, 1H), 7.86 (s, 1H), 7.59 (d, $^4J_{HH}$ = 1.7 Hz, 1H), 7.54 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.48 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.7 Hz, 1H), 7.46 – 7.44 (m, 2H), 6.04 (s, 2H), 2.71 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 1.66 (p, $^3J_{HH}$ = 7.4 Hz, 2H), 1.51 (s, 6H), 1.39 – 1.18 (m, 10H), 0.85 (t, $^3J_{HH}$ = 6.8 Hz, 3H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: 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, 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), 1600 (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. **MS (APCI)**: m/z = 494.1 [C₂₇H₃₂⁷⁹BrN₃O+H]⁺. **HR-MS (EI, 70 eV)**: calculated for C₂₇H₃₂⁷⁹BrN₃O⁺ [M]⁺: m/z = 493.17233, found: 493.17229 (Dev.: -0.04 mu; -0.07 ppm).

2.6.11 3-((4-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-1*H*-1,2,3-triazol-1-yl)methyl)-7-bromo-9,9-dimethyl-9*H*-fluorene-2-carbaldehyde (42)

42

According to GPI **5** (107 mg, 300 μmol , 1.00 eq) and **31** (50.5 mg, 315 μmol , 1.05 eq) were dissolved in CHCl_3 (3.00 mL, 0.1 M). $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ (7.2 mg, 30 μmol , 0.10 eq) and sodium ascorbate (29.7 mg, 150 μmol , 0.50 eq) were suspended separately in water (375 μL) and added to the reaction vial. The heterogeneous mixture was stirred vigorously at 25 $^\circ\text{C}$ for three days and directly purified by flash column chromatography (SiO_2 , CH:EE 3:1 v:v) **42** (153 mg, 296 μmol , 99 %) as a colorless oil, which solidified upon standing at 25 $^\circ\text{C}$.

R_f = 0.33 (SiO_2 , CH:EE 3:1 v:v). **Mp.**: 123 – 125 $^\circ\text{C}$. **$^1\text{H-NMR}$ (360 MHz, CDCl_3):** δ = 10.18 (s, 1H), 7.86 (s, 1H), 7.59 (s, 1H), 7.53 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 1H), 7.49 (d, $^3J_{\text{HH}}$ = 7.9 Hz, 1H), 7.45 (s, 1H), 7.39 (s, 1H), 6.03 (s, 2H), 2.04 (s, 3H), 1.97 (s, 6H), 1.75 (s, 6H), 1.50 (s, 6H) ppm. **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (91 MHz, CDCl_3):** δ = 193.1, 158.4, 157.0, 153.5, 144.2, 136.8, 136.2, 132.3, 130.9, 129.5, 126.6, 123.6, 122.9, 122.1, 119.4, 50.8, 47.4, 42.6 (3x), 36.8 (3x), 32.8, 28.5 (3x), 26.7 (2x) ppm. **IR (ATR, neat):** $\tilde{\nu}$ = 2903 (m), 2847 (m), 1677 (s), 1615 (m), 1563 (m), 1448 (m), 1427 (m), 1408 (w), 1361 (w), 1344 (w), 1312 (w), 1253 (m), 1213 (w), 1182 (m), 1167 (m), 1128 (w), 1101 (w), 1081 (w), 1063 (m), 1049 (m), 1001 (w), 967 (m), 905 (m), 880 (w), 827 (s), 806 (m), 789 (m), 767 (m), 726 (s), 672 (m) cm^{-1} . **MS (APCI):** m/z = 516.1 [$\text{C}_{29}\text{H}_{30}^{79}\text{BrN}_3\text{O} + \text{H}$] $^+$. **HR-MS (APCI):** calculated for $\text{C}_{29}\text{H}_{31}^{79}\text{BrN}_3\text{O}^+$ [$\text{M} + \text{H}$] $^+$: m/z = 516.16450, found: 516.16445 (Dev.: -0.05 mu ; -0.10 ppm).

2.6.12 7-Bromo-9,9-dimethyl-3-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)-9*H*-fluorene-2-carbaldehyde (43)

43

According to GP1 the reaction of **5** (35.6 mg, 100 μ mol, 1.00 eq) and phenylacetylene (11.5 μ L, 105 μ mol, 1.05 eq) provided after 48 hours reaction time and subsequent flash column chromatography (SiO₂, CH:EE 3:1 v:v) **43** (42.9 mg, 93.6 μ mol, 94 %) as a colorless foam.

R_f = 0.24 (SiO₂, CH:EE 3:1 v:v). **Mp.**: 76 – 86 °C (very long melting). **¹H-NMR (360 MHz, CDCl₃)**: δ = 10.19 (s, 1H), 7.98 (s, 1H), 7.87 (s, 1H), 7.88 – 7.79 (m, 2H), 7.61 – 7.59 (m, 2H), 7.57 (d, ³J_{HH} = 8.2 Hz, 1H), 7.48 (dd, ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 1.7 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.34 – 7.28 (m, 1H), 6.13 (s, 2H), 1.51 (s, 6H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 192.9, 156.6, 153.4, 147.7, 144.0, 135.8, 135.7, 132.0, 130.6, 130.3, 129.6, 128.6 (2x), 127.9, 126.2, 125.5 (2x), 123.4, 122.7, 122.0, 120.4, 50.8, 47.1, 26.4 (2x) ppm. **IR (ATR, neat)**: $\tilde{\nu}$ = 2961 (w), 2924 (w), 2858 (w), 1683 (s), 1614 (m), 1600 (w), 1561 (m), 1463 (w), 1406 (w), 1251 (m), 1179 (m), 1076 (m), 1045 (m), 965 (m), 907 (w), 822 (m), 810 (m), 763 (s), 732 (s), 694 (s), 672 (m) cm⁻¹. **MS (APCI)**: m/z = 458.0 [C₂₅H₂₀⁷⁹BrN₃O+H]⁺. **HR-MS (EI, 70 eV)**: calculated for C₂₅H₂₀⁷⁹BrN₃O⁺ [M]⁺: m/z = 457.07843, found: 457.07831 (Dev.: -0.12 mu; -0.25 ppm).

2.6.13 7-Bromo-3-((4-(3,5-di-*tert*-butylphenyl)-1*H*-1,2,3-triazol-1-yl)methyl)-9,9-dimethyl-9*H*-fluorene-2-carbaldehyde (**44**)

According to GP1 the reaction of **5** (35.6 mg, 100 μ mol, 1.00 eq) and **32** (22.5 mg, 105 μ mol, 1.05 eq) provided after six days reaction time and subsequent flash column chromatography (SiO₂, CH:EE 3:1 v:v) **44** (55.9 mg, 98.0 μ mol, 98 %) as a colorless solid.

R_f = 0.47 (SiO₂, CH:EE 3:1 v:v). **Mp.**: 210 – 212 °C. **¹H-NMR (360 MHz, CDCl₃)**: δ = 10.21 (s, 1H), 7.97 (s, 1H), 7.88 (s, 1H), 7.70 (d, J = 1.8 Hz, 2H), 7.60 (d, J = 1.7 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.54 (s, 1H), 7.48 (dd, J = 8.2, 1.8 Hz, 1H), 7.42 (t, J = 1.8 Hz, 1H), 6.16 (s, 2H), 1.52 (s, 6H), 1.36 (s, 18H) ppm. **¹³C{¹H}-NMR (91 MHz, CDCl₃)**: δ = 193.3, 157.0, 153.6, 151.4 (2x), 149.0, 144.3, 136.6, 136.1, 132.2, 130.9, 129.8 (2x), 126.6, 123.7, 123.1, 122.6, 121.8, 120.6, 120.2 (2x), 51.1, 47.4, 35.1 (2x), 31.6 (6x), 26.7 (2x) ppm. **IR (ATR, neat)**: $\tilde{\nu}$ = 2960 (m), 2903 (w), 2866 (w), 1686 (s), 1613 (m), 1600 (m), 1563 (m), 1462 (m), 1420 (m), 1393 (m), 1362 (s), 1281 (m), 1250 (s), 1224 (m), 1179 (s), 1091 (m), 1047 (m), 967 (m), 900 (m), 876 (s), 847 (m), 821 (s), 810 (s), 730 (s), 708 (s), 673 (m), 661

(m) cm^{-1} . **MS (APCI):** $m/z = 570.1$ $[\text{C}_{33}\text{H}_{36}^{79}\text{BrN}_3\text{O}+\text{H}]^+$. **HR-MS (APCI):** calculated for $\text{C}_{33}\text{H}_{37}^{79}\text{BrN}_3\text{O}^+ [\text{M}+\text{H}]^+$: $m/z = 570.21145$, found: 570.21154 (Dev.: 0.09 mu; 0.15 ppm).

2.7 Methylation Reaction of Adamantyl substituted triazole 42

2.7.1 4-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-1-((7-bromo-2-formyl-9,9-dimethyl-9*H*-fluoren-3-yl)methyl)-3-methyl-1*H*-1,2,3-triazol-3-ium tetrafluoroborate (45)

A modified literature procedure was used.[35] A heat gun-dried and nitrogen-flushed *Schlenk* flask, equipped with a magnetic stirring bar and a rubber septum, was charged with **42** (25.8 mg, 50.0 μmol , 1.00 eq) and dissolved in anhydrous CH_2Cl_2 (3.33 mL, 15 mM). Trimethyloxonium tetrafluoroborate (7.40 mg, 50.0 μmol , 1.00 eq) was added in one portion at 25 $^\circ\text{C}$ whereupon the mixture turned slightly yellow. After stirring for two days under these conditions, methanol (1.0 mL) was added and the mixture was stirred for 30 minutes under air. All volatile components were removed under reduced pressure and the oily yellow residue was purified by flash column chromatography (CH_2Cl_2 :MeOH 15:1 v:v) to provide **45** (25.7 mg, 41.6 μmol , 83 %) as a colorless solid. If desired the product can be precipitated by dissolving in CH_2Cl_2 and addition of diethyl ether until a white precipitate is formed.

R_f = 0.33 (SiO_2 , DCM:MeOH 15:1 v:v). **Mp.:** 249 – 251 $^\circ\text{C}$ decomp. **^1H -NMR (360 MHz, CDCl_3):** δ = 10.10 (s, 1H), 8.22 (s, 1H), 8.20 (s, 1H), 7.92 (s, 1H), 7.86 (d, $^3J_{\text{HH}}$ = 8.1 Hz, 1H), 7.59 (d, $^4J_{\text{HH}}$ = 1.7 Hz, 1H), 7.52 (dd, $^3J_{\text{HH}}$ = 8.2 Hz, $^4J_{\text{HH}}$ = 1.8 Hz, 1H), 6.17 (s, 2H), 4.31 (s, 3H), 2.11 (s, 3H), 2.07 – 2.02 (m, 6H), 1.78 – 1.72 (m, 6H), 1.53 (s, 6H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ -NMR (91 MHz, CDCl_3):** δ = 193.1, 158.7, 156.8, 155.4, 151.0, 145.0, 136.0, 133.0, 131.2, 130.7, 130.0, 128.2, 126.4, 126.3, 124.0, 54.7, 47.6, 41.0, 39.5 (3x), 35.8 (3x), 33.8, 27.7 (3x), 26.6 (2x) ppm. **IR (ATR, neat):** $\tilde{\nu}$ = 2909 (m), 2850 (w), 2734 (w), 1703 (s), 1615 (w), 1600 (w), 1562 (m), 1456 (w), 1406 (w), 1380 (w), 1356 (w), 1325 (w), 1311 (w), 1284 (w), 1251 (w), 1251 (w), 1231 (w), 1180 (m), 1166 (w), 1137 (w), 1106 (m), 1057 (s), 1026 (s), 963 (m), 884 (m), 867 (w), 827 (s), 811 (m), 785 (m), 773 (m), 736 (m), 700 (w), 674 (w), 655 (w) cm^{-1} . **MS (ESI):** $m/z = 530.2$ $[\text{C}_{30}\text{H}_{33}^{79}\text{BrN}_3\text{O}]^+$. **HR-MS (ESI):** calculated for $\text{C}_{30}\text{H}_{33}^{79}\text{BrN}_3\text{O}^+ [\text{M}]^+$: $m/z = 530.18015$, found: 530.17960 (Dev.: -0.55 mu; -1.04 ppm).

3 Optical Properties

3.1 2-(Azidomethyl)-4-bromobenzaldehyde (**3**) & Derivatives

Figure S1: Normalized absorption spectra of **6** (black line), **7** (blue line), **8** (green line), **9** (yellow line) and **3** (red line) in chloroform solution ($c = 10^{-5} \text{ mol L}^{-1}$).

Figure S2: Normalized absorption spectra of **33** (blue line), **34** (green line), **35** (yellow line) and **36** (red line) in chloroform solution ($c = 10^{-5} \text{ mol L}^{-1}$).

Figure S3: Absorption spectra of **3** at various concentration in chloroform solution.

Figure S4: Linear regression for extinction coefficient determination (with respect to Figure S3): $\epsilon_{267} = 13.900 \text{ L mol}^{-1} \text{ cm}^{-1}$.

Figure S5: Normalized absorption spectra of **3** (blue line) and **34** (green line) in chloroform solution ($c = 10^{-5}$ mol L^{-1}) after bubbling with argon for 30 minutes and normalized emission spectra of **3** (yellow line), **34** (red line) in the solid-state.

Figure S6: Fluorescence decay profile of **3** and **34** in the solid-state with excitation at 376 nm.

3: $\tau_1 = 0.796 \pm 0.006$ (84.4%) ns; $\tau_2 = 3.228 \pm 0.115$ (15.6%) ns; $\chi^2 = 1.081$.

34: $\tau_1 = 0.516 \pm 0.006$ (50.2%) ns; $\tau_2 = 2.212 \pm 0.022$ (49.8%) ns; $\chi^2 = 1.069$.

3.2 4-(Azidomethyl)-2-bromobenzaldehyde (**4**) & Derivatives

Figure S7: Normalized absorption spectra of **10** (black line), **S1** (navy line), **S2** (blue line), **11** (green line), **12** (yellow line), **13** (orange line) and **4** (red line) in chloroform solution ($c = 10^{-5} \text{ mol L}^{-1}$).

Figure S8: Normalized absorption spectra of **37** (blue line), **38** (green line), **39** (yellow line), **40** (red line) in chloroform solution ($c = 10^{-5} \text{ mol L}^{-1}$).

Figure S9: Absorption spectra of **4** at various concentration in chloroform solution.

Figure S10: Linear regression for extinction coefficient determination (with respect to Figure S9): $\epsilon_{259} = 9.180 \text{ L mol}^{-1} \text{ cm}^{-1}$.

Figure S11: Linear regression for extinction coefficient determination (with respect to Figure S9): $\epsilon_{300} = 1.440 \text{ L mol}^{-1} \text{ cm}^{-1}$.

3.3 3-(Azidomethyl)-7-bromo-9,9-dimethyl-9H-fluorene-2-carbaldehyde (5) & Derivatives

Figure S12: Normalized absorption spectra of **14** (black line), **15** (navy line), **16** (blue line), **17** (green line), **18** (light green line), **19** (yellow line), **20** (orange line), **21** (red line) and **6** (wine line) in chloroform solution ($c = 10^{-5} \text{ mol L}^{-1}$).

Figure S13: Normalized absorption spectra of **22** (blue line), **23** (green line), **25** (yellow line), **28** (red line) in chloroform solution ($c = 10^{-5} \text{ mol L}^{-1}$).

Figure S14: Normalized absorption spectra of **41** (black line), **42** (blue line), **43** (green line), **44** (yellow line), **45** (red line) in chloroform solution ($c = 10^{-5} \text{ mol L}^{-1}$).

Figure S15: Normalized absorption (black line) and emission (red line) spectra of **16** in chloroform solution ($c = 10^{-5} \text{ mol L}^{-1}$) after bubbling with argon for 30 minutes. Emission was monitored by excitation at the absorption maximum wavelength of 330 nm. Emission maximum at 528 nm.

Figure S16: Fluorescence decay profile of **16** in chloroform solution ($c = 10^{-5} \text{ mol L}^{-1}$) after bubbling with argon for 30 minutes with excitation at 376 nm: $\tau_1 = 1.186 \pm 0.010$ (54.7%) ns; $\tau_2 = 11.50 \pm 0.26$ (45.3%) ns; $\chi^2 = 1.247$. Emission was detected at 530 nm.

Figure S17: Normalized excitation (blue line) and emission (red line) spectra of **16** in the solid-state. Emission was monitored by excitation at the absorption wavelength of 396 nm and excitation was monitored at fluorescence maximum wavelength of 424 nm.

Figure S18: Fluorescence decay profile of **16** in the solid-state with excitation at 376 nm: $\tau_1 = 0.286 \pm 0.002$ (54.4%) ns; $\tau_2 = 0.872 \pm 0.006$ (45.6%) ns; $\chi^2 = 1.283$.

Figure S19: Normalized emission spectra of **19** in chloroform solution (blue line, $c = 10^{-5} \text{ mol L}^{-1}$) after bubbling with argon for 30 minutes and the solid-state (red line). Quantum yield in the solid-state was determined to 6.0 %.

Figure S20: Fluorescence decay profile of **19** in the solid-state with excitation at 376 nm: $\tau_1 = 0.554 \pm 0.001$ (85.3%) ns; $\tau_2 = 2.043 \pm 0.020$ (14.7%) ns; $\chi^2 = 1.430$.

Figure S21: Normalized emission spectrum of **20** in the solid-state. Quantum yield in the solid-state was determined to 12.6 %.

Figure S22: Fluorescence decay profile of **20** in the solid-state with excitation at 376 nm: $\tau = 0.587 \pm 0.001$ ns; $\chi^2 = 1.430$. Emission was detected at 407 nm.

Figure S23: Normalized emission spectra of **21** in chloroform solution (blue line, $c = 10^{-5}$ mol L $^{-1}$) after bubbling with argon for 30 minutes and the solid-state (red line).

Figure S24: Fluorescence decay profile of **21** in chloroform solution (blue dots, detection at 400 nm) after bubbling with argon for 30 minutes and the solid-state (red dots, detection at 392 nm) with excitation at 376 nm. CHCl $_3$: $\tau_1 = 0.442 \pm 0.011$ (12.9%) ns; $\tau_2 = 1.697 \pm 0.020$ (54.6%) ns; $\tau_3 = 7.630 \pm 0.080$ (32.5%) ns; $\chi^2 = 1.199$. Solid-state: $\tau_1 = 0.378 \pm 0.002$ (73.5%) ns; $\tau_2 = 1.648 \pm 0.013$ (26.5%) ns; $\chi^2 = 1.274$.

Figure S25: Fluorescence decay profile of **21** in chloroform solution (blue dots, detection at 550 nm) after bubbling with argon for 30 minutes and the solid-state (red dots, detection at 527 nm) with excitation at 376 nm. CHCl_3 : $\tau_1 = 2.137 \pm 0.030$ (40.5%) ns; $\tau_2 = 5.747 \pm 0.058$ (59.5%) ns; $\chi^2 = 1.404$. Solid-state: $\tau_1 = 1.503 \pm 0.008$ (45.2%) ns; $\tau_2 = 6.153 \pm 0.027$ (54.8%) ns; $\chi^2 = 1.445$.

Figure S26: Normalized emission spectra of **5** in chloroform solution (blue line, $c = 10^{-5} \text{ mol L}^{-1}$) under air, in chloroform solution (green line, $c = 10^{-5} \text{ mol L}^{-1}$) after bubbling with argon for 30 minutes and the solid-state (red line).

Figure S27: Fluorescence decay profile of **5** in chloroform solution under air (blue dots, detection at 450 nm), in chloroform solution after bubbling with argon for 30 minutes (green dots, detection at 450 nm) and the solid-state (red dots, detection at 446 nm) with excitation at 376 nm.

CHCl₃ (air): $\tau_1 = 1.459 \pm 0.004$ (72.2%) ns; $\tau_2 = 5.692 \pm 0.030$ (27.8%) ns; $\chi^2 = 1.353$.

CHCl₃ (argon): $\tau_1 = 1.709 \pm 0.004$ (77.1%) ns; $\tau_2 = 6.288 \pm 0.045$ (22.9%) ns; $\chi^2 = 1.265$.

Solid-state: $\tau_1 = 0.637 \pm 0.003$ (66.2%) ns; $\tau_2 = 2.601 \pm 0.015$ (33.8%) ns; $\chi^2 = 1.183$.

Figure S28: Absorption spectra of **5** at various concentration in chloroform solution.

Figure S29: Linear regression for extinction coefficient determination (with respect to Figure S28): $\epsilon_{331} = 24.220 \text{ L mol}^{-1} \text{ cm}^{-1}$.

Figure S30: Normalized emission spectra of **22** in chloroform solution (blue line, $c = 10^{-5} \text{ mol L}^{-1}$, excitation at 280 nm) and (green line, excitation at 300 nm) and of **23** in chloroform solution (yellow line, $c = 10^{-5} \text{ mol L}^{-1}$, excitation at 300 nm) and (red line, excitation at 317 nm) after bubbling with argon for 30 minutes.

Figure S31: Normalized emission spectra of **25** in chloroform solution (blue line, $c = 10^{-5} \text{ mol L}^{-1}$) after bubbling with argon for 30 minutes and the solid-state (red line).

Figure S32: Fluorescence decay profile of **25** in chloroform solution (blue dots, detection at 430 nm) after bubbling with argon for 30 minutes and the solid-state (red dots, detection at 560 nm) with excitation at 376 nm.

CHCl_3 : $\tau_1 = 1.505 \pm 0.027$ (5.5%) ns; $\tau_2 = 8.661 \pm 0.009$ (94.5%) ns; $\chi^2 = 1.135$.

Solid-state: $\tau_1 = 0.876 \pm 0.005$ (44.9%) ns; $\tau_2 = 2.826 \pm 0.010$ (55.1%) ns; $\chi^2 = 1.404$.

Figure S33: Normalized emission spectra of **28** in chloroform solution (blue line, $c = 10^{-5}$ mol L $^{-1}$) after bubbling with argon for 30 minutes and the solid-state (red line).

Figure S34: Fluorescence decay profile of **28** in the solid-state with excitation at 376 nm: $\tau_1 = 2.564 \pm 0.009$ ns (93.0%); $\tau_2 = 5.513 \pm 0.158$ (7.1%) ns; $\chi^2 = 1.099$. Emission was detected at 480 nm.

Figure S35: Normalized emission spectra of **42** in chloroform solution (blue line, $c = 10^{-5} \text{ mol L}^{-1}$) after bubbling with argon for 30 minutes and the solid-state (red line).

Figure S36: Fluorescence decay profile of **42** in chloroform solution ($c = 10^{-5} \text{ mol L}^{-1}$) after bubbling with argon for 30 minutes with excitation at 376 nm: $\tau_1 = 1.004 \pm 0.010$ (57.7%) ns; $\tau_2 = 6.171 \pm 0.104$ (42.3%) ns; $\chi^2 = 1.285$. Emission was detected at 540 nm.

Figure S37: Fluorescence decay profile of **42** in the solid-state with excitation at 376 nm: $\tau_1 = 0.871 \pm 0.002$ ns (90.7%); $\tau_2 = 4.805 \pm 0.049$ (9.3%) ns; $\chi^2 = 1.457$. Emission was detected at 442 nm.

Figure S38: Absorption spectra of **42** at various concentration in chloroform solution.

Figure S39: Linear regression for extinction coefficient determination (with respect to Figure S38): $\epsilon_{331} = 20.450$ L mol⁻¹ cm⁻¹.

Figure S40: Normalized emission spectra of **45** in chloroform solution (blue line, $c = 10^{-5}$ mol L⁻¹) under air, in chloroform solution (green line, $c = 10^{-5}$ mol L⁻¹) after bubbling with argon for 30 minutes and the solid-state (red line).

Figure S41: Fluorescence decay profile of **45** in chloroform solution (blue dots, detection at 540 nm) after bubbling with argon for 30 minutes and the solid-state (red dots, detection at 580 nm) with excitation at 376 nm.

CHCl₃: $\tau_1 = 1.824 \pm 0.018$ (51.3%) ns; $\tau_2 = 11.56 \pm 0.31$ (48.7%) ns; $\chi^2 = 1.225$.

Solid-state: $\tau_1 = 1.076 \pm 0.006$ (43.9%) ns; $\tau_2 = 4.050 \pm 0.018$ (56.1%) ns; $\chi^2 = 1.435$.

Figure S42: Absorption spectra of **45** at various concentration in chloroform solution.

Figure S43: Linear regression for extinction coefficient determination (with respect to Figure S42): $\epsilon_{334} = 54.460$ L mol⁻¹ cm⁻¹.

4 Crystal Structure of 3-(Azidomethyl)-7-bromo-9,9-dimethyl-9*H*-fluorene-2-carbaldehyde (**5**)

4.1 Crystal Data for (**5**)

Figure S1: Asymmetric unit of **5** with atom labels.

Table S2: Crystal data and structure refinement for **5**.

Empirical formula	C ₁₇ H ₁₄ BrN ₃ O
Formula weight, g mol ⁻¹	356.22
Crystal system	Triclinic
Crystal size, mm ³	0.3 × 0.2 × 0.2
Space group (number)	P-1 (2)
a/Å	8.2141(3)
b/Å	12.7921(4)
c/Å	16.1129(6)
α/°	107.8710(10)
β/°	102.8730(10)
γ/°	99.2410(10)
Volume/Å ³	1522.30(9)

Z	4
$\rho_{\text{calc}}, \text{g/cm}^3$	1.554
μ/mm^{-1}	2.705
$F(000)$	720
2θ range for data collection/ $^\circ$	5.18 to 61.22
	$-11 \leq h \leq 11$
Index ranges	$-18 \leq k \leq 18$
	$-23 \leq l \leq 23$
No. of reflections collected	53013
No. of independent reflections	9309 [$R_{\text{int}} = 0.0274$, $R_{\text{sigma}} = 0.0219$]
Data/restraints/parameters	9309/0/401
Goodness-of-fit on F^2	1.081
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0246$, $wR_2 = 0.0540$
Final R indexes [all data]	$R_1 = 0.0310$, $wR_2 = 0.0561$
Largest diff. peak/hole/ $e \text{ \AA}^{-3}$	0.60/−0.46
Completeness to $\theta = 25.242^\circ$	99.9 %
CCDC number	1989134

Table S3: Fractional Atomic Coordinates [$\text{\AA}^2$] and Equivalent Isotropic Displacement Parameters [$\text{\AA}^2$] for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U_{eq}
Br1	0.62959(2)	0.87935(2)	0.88875(2)	0.01738(4)
O1	0.33038(13)	0.46964(9)	0.13714(7)	0.0220(2)
N1	0.79293(15)	0.48548(11)	0.32343(8)	0.0190(2)
N2	0.87272(16)	0.42834(11)	0.27937(8)	0.0204(2)
N3	0.95945(19)	0.37986(15)	0.24644(10)	0.0381(4)
C1	0.28731(16)	0.63068(11)	0.35404(9)	0.0144(2)
H1	0.181517	0.646152	0.329310	0.017
C2	0.36981(16)	0.56857(11)	0.29586(9)	0.0132(2)
C3	0.52889(16)	0.54570(10)	0.33167(8)	0.0113(2)
C4	0.59980(16)	0.58406(10)	0.42580(8)	0.0117(2)
H4	0.705325	0.568757	0.451174	0.014
C4A	0.51590(16)	0.64483(10)	0.48263(8)	0.0115(2)
C4B	0.56563(16)	0.69502(10)	0.58212(8)	0.0115(2)
C5	0.70807(16)	0.69389(11)	0.64733(9)	0.0134(2)
H5	0.791526	0.655539	0.629495	0.016
C6	0.72612(17)	0.74983(11)	0.73898(9)	0.0136(2)

H6	0.822249	0.750274	0.784673	0.016
C7	0.60132(16)	0.80525(11)	0.76293(9)	0.0127(2)
C8	0.45795(16)	0.80749(11)	0.69884(9)	0.0138(2)
H8	0.374611	0.845824	0.716874	0.017
C8A	0.44162(16)	0.75146(11)	0.60754(9)	0.0123(2)
C9	0.29979(16)	0.74108(11)	0.52397(9)	0.0137(2)
C9A	0.36006(16)	0.66938(11)	0.44743(9)	0.0124(2)
C10	0.12230(17)	0.68180(13)	0.52496(10)	0.0200(3)
H10A	0.036244	0.669237	0.467621	0.030
H10B	0.090161	0.729581	0.576028	0.030
H10C	0.127354	0.608788	0.531852	0.030
C11	0.29608(19)	0.85823(12)	0.51709(10)	0.0197(3)
H11A	0.410171	0.895712	0.517395	0.030
H11B	0.264871	0.904650	0.569130	0.030
H11C	0.210823	0.848851	0.460379	0.030
C12	0.28224(17)	0.52849(12)	0.19717(9)	0.0178(3)
H12	0.179054	0.550673	0.178968	0.021
C13	0.61929(16)	0.48143(11)	0.26895(8)	0.0129(2)
H13A	0.551907	0.401722	0.237200	0.016
H13B	0.629690	0.515846	0.222492	0.016
Br1*	-0.22890(2)	1.00015(2)	0.14743(2)	0.01550(4)
O1*	0.89725(13)	0.61783(9)	0.17610(7)	0.0191(2)
N1*	0.88357(14)	0.89128(9)	0.40051(8)	0.0143(2)
N2*	0.81665(15)	0.88222(10)	0.46022(8)	0.0158(2)
N3*	0.76277(19)	0.88614(12)	0.51975(9)	0.0285(3)
C1*	0.51351(16)	0.69391(11)	0.08530(9)	0.0121(2)
H1*	0.499974	0.649222	0.023855	0.015
C2*	0.65942(16)	0.70333(11)	0.15443(9)	0.0117(2)
C3*	0.68417(16)	0.77256(10)	0.24610(8)	0.0111(2)
C4*	0.55942(16)	0.82955(11)	0.26659(8)	0.0112(2)
H4*	0.573964	0.876650	0.327514	0.013
C4A*	0.41258(15)	0.81752(10)	0.19750(8)	0.0100(2)
C4B*	0.26634(16)	0.86909(10)	0.20113(8)	0.0106(2)
C5*	0.23047(16)	0.94449(11)	0.27376(8)	0.0121(2)
H5*	0.306336	0.969258	0.333719	0.015
C6*	0.08156(17)	0.98299(11)	0.25707(9)	0.0129(2)
H6*	0.054806	1.034677	0.305587	0.016

C7*	-0.02773(16)	0.94503(11)	0.16862(9)	0.0120(2)
C8*	0.00514(16)	0.86908(11)	0.09497(9)	0.0121(2)
H8*	-0.071691	0.843831	0.035221	0.014
C8A*	0.15437(15)	0.83179(10)	0.11232(8)	0.0102(2)
C9*	0.22183(16)	0.75194(10)	0.04453(8)	0.0105(2)
C9A*	0.38937(15)	0.74993(10)	0.10694(8)	0.0102(2)
C10*	0.09774(16)	0.63361(11)	-0.00032(9)	0.0142(2)
H10D	-0.013154	0.638890	-0.034819	0.021
H10E	0.080477	0.603261	0.046861	0.021
H10F	0.146688	0.583159	-0.041645	0.021
C11*	0.25559(18)	0.79907(12)	-0.02848(9)	0.0156(2)
H11D	0.146586	0.804420	-0.064864	0.023
H11E	0.306879	0.748393	-0.068189	0.023
H11F	0.334881	0.874536	0.000948	0.023
C12*	0.78038(17)	0.63657(11)	0.12570(9)	0.0148(2)
H12*	0.766049	0.605275	0.062135	0.018
C13*	0.84582(16)	0.78619(11)	0.31997(8)	0.0128(2)
H13C	0.832009	0.719942	0.339569	0.015
H13D	0.944912	0.787400	0.294493	0.015

Table S4: Bond Lengths for **5**.

Atom–Atom	Length [Å]	Atom–Atom	Length [Å]
Br1–C7	1.8980(13)	Br1*–C7*	1.9013(12)
O1–C12	1.2157(17)	O1*–C12*	1.2185(16)
N1–N2	1.2291(16)	N1*–N2*	1.2349(16)
N1–C13	1.4826(16)	N1*–C13*	1.4844(16)
N2–N3	1.1321(18)	N2*–N3*	1.1337(18)
C1–H1	0.9500	C1*–H1*	0.9500
C1–C2	1.4028(18)	C1*–C2*	1.4029(17)
C1–C9A	1.3833(18)	C1*–C9A*	1.3837(17)
C2–C3	1.4200(17)	C2*–C3*	1.4188(17)
C2–C12	1.4766(18)	C2*–C12*	1.4716(17)
C3–C4	1.3922(17)	C3*–C4*	1.3905(17)
C3–C13	1.5064(18)	C3*–C13*	1.5180(17)
C4–H4	0.9500	C4*–H4*	0.9500
C4–C4A	1.3907(17)	C4*–C4A*	1.3981(17)
C4A–C4B	1.4632(17)	C4A*–C4B*	1.4641(17)

C4A–C9A	1.4050(17)	C4A*–C9A*	1.4007(17)
C4B–C5	1.3928(17)	C4B*–C5*	1.3925(17)
C4B–C8A	1.4027(17)	C4B*–C8A*	1.4053(17)
C5–H5	0.9500	C5*–H5*	0.9500
C5–C6	1.3910(18)	C5*–C6*	1.3926(17)
C6–H6	0.9500	C6*–H6*	0.9500
C6–C7	1.3943(18)	C6*–C7*	1.3922(18)
C7–C8	1.3933(18)	C7*–C8*	1.3944(18)
C8–H8	0.9500	C8*–H8*	0.9500
C8–C8A	1.3892(18)	C8*–C8A*	1.3875(17)
C8A–C9	1.5263(17)	C8A*–C9*	1.5199(17)
C9–C9A	1.5267(18)	C9*–C9A*	1.5219(17)
C9–C10	1.5374(19)	C9*–C10*	1.5353(17)
C9–C11	1.5409(19)	C9*–C11*	1.5335(17)
C10–H10A	0.9800	C10*–H10D	0.9800
C10–H10B	0.9800	C10*–H10E	0.9800
C10–H10C	0.9800	C10*–H10F	0.9800
C11–H11A	0.9800	C11*–H11D	0.9800
C11–H11B	0.9800	C11*–H11E	0.9800
C11–H11C	0.9800	C11*–H11F	0.9800
C12–H12	0.9500	C12*–H12*	0.9500
C13–H13A	0.9900	C13*–H13C	0.9900
C13–H13B	0.9900	C13*–H13D	0.9900

Table S5: Bond Angles for **5**.

Atom–Atom–Atom	Angle [°]	Atom–Atom–Atom	Angle [°]
N2–N1–C13	114.01(11)	N2*–N1*–C13*	115.47(11)
N3–N2–N1	173.21(14)	N3*–N2*–N1*	172.57(14)
C2–C1–H1	120.0	C2*–C1*–H1*	120.1
C9A–C1–H1	120.0	C9A*–C1*–H1*	120.1
C9A–C1–C2	119.98(12)	C9A*–C1*–C2*	119.76(11)
C1–C2–C3	120.73(11)	C1*–C2*–C3*	120.79(11)
C1–C2–C12	116.65(11)	C1*–C2*–C12*	115.95(11)
C3–C2–C12	122.62(12)	C3*–C2*–C12*	123.25(11)
C2–C3–C13	120.59(11)	C2*–C3*–C13*	120.55(11)
C4–C3–C2	118.72(11)	C4*–C3*–C2*	118.76(11)
C4–C3–C13	120.69(11)	C4*–C3*–C13*	120.68(11)

C3–C4–H4	120.1	C3*–C4*–H4*	120.0
C4A–C4–C3	119.89(11)	C3*–C4*–C4A*	119.97(11)
C4A–C4–H4	120.1	C4A*–C4*–H4*	120.0
C4–C4A–C4B	129.90(11)	C4*–C4A*–C4B*	130.38(11)
C4–C4A–C9A	121.56(11)	C4*–C4A*–C9A*	121.10(11)
C9A–C4A–C4B	108.52(11)	C9A*–C4A*–C4B*	108.49(10)
C5–C4B–C4A	130.36(12)	C5*–C4B*–C4A*	131.05(11)
C5–C4B–C8A	121.10(12)	C5*–C4B*–C8A*	120.85(11)
C8A–C4B–C4A	108.53(11)	C8A*–C4B*–C4A*	108.09(10)
C4B–C5–H5	120.5	C4B*–C5*–H5*	120.5
C6–C5–C4B	118.92(12)	C4B*–C5*–C6*	118.91(11)
C6–C5–H5	120.5	C6*–C5*–H5*	120.5
C5–C6–H6	120.4	C5*–C6*–H6*	120.3
C5–C6–C7	119.15(12)	C7*–C6*–C5*	119.37(11)
C7–C6–H6	120.4	C7*–C6*–H6*	120.3
C6–C7–Br1	117.83(9)	C6*–C7*–Br1*	118.55(9)
C8–C7–Br1	119.29(10)	C6*–C7*–C8*	122.69(11)
C8–C7–C6	122.88(12)	C8*–C7*–Br1*	118.77(9)
C7–C8–H8	121.3	C7*–C8*–H8*	121.3
C8A–C8–C7	117.40(12)	C8A*–C8*–C7*	117.44(11)
C8A–C8–H8	121.3	C8A*–C8*–H8*	121.3
C4B–C8A–C9	111.03(11)	C4B*–C8A*–C9*	111.33(10)
C8–C8A–C4B	120.56(12)	C8*–C8A*–C4B*	120.74(11)
C8–C8A–C9	128.41(12)	C8*–C8A*–C9*	127.93(11)
C8A–C9–C9A	100.99(10)	C8A*–C9*–C9A*	100.86(9)
C8A–C9–C10	111.47(11)	C8A*–C9*–C10*	111.25(10)
C8A–C9–C11	110.98(11)	C8A*–C9*–C11*	111.67(10)
C9A–C9–C10	112.16(11)	C9A*–C9*–C10*	111.31(10)
C9A–C9–C11	110.84(11)	C9A*–C9*–C11*	111.24(10)
C10–C9–C11	110.14(11)	C11*–C9*–C10*	110.23(10)
C1–C9A–C4A	119.11(12)	C1*–C9A*–C4A*	119.58(11)
C1–C9A–C9	129.96(11)	C1*–C9A*–C9*	129.19(11)
C4A–C9A–C9	110.91(11)	C4A*–C9A*–C9*	111.22(10)
C9–C10–H10A	109.5	C9*–C10*–H10D	109.5
C9–C10–H10B	109.5	C9*–C10*–H10E	109.5
C9–C10–H10C	109.5	C9*–C10*–H10F	109.5
H10A–C10–H10B	109.5	H10D–C10*–H10E	109.5

H10A–C10–H10C	109.5	H10D–C10*–H10F	109.5
H10B–C10–H10C	109.5	H10E–C10*–H10F	109.5
C9–C11–H11A	109.5	C9*–C11*–H11D	109.5
C9–C11–H11B	109.5	C9*–C11*–H11E	109.5
C9–C11–H11C	109.5	C9*–C11*–H11F	109.5
H11A–C11–H11B	109.5	H11D–C11*–H11E	109.5
H11A–C11–H11C	109.5	H11D–C11*–H11F	109.5
H11B–C11–H11C	109.5	H11E–C11*–H11F	109.5
O1–C12–C2	125.83(12)	O1*–C12*–C2*	125.87(12)
O1–C12–H12	117.1	O1*–C12*–H12*	117.1
C2–C12–H12	117.1	C2*–C12*–H12*	117.1
N1–C13–C3	108.94(10)	N1*–C13*–C3*	112.68(10)
N1–C13–H13A	109.9	N1*–C13*–H13C	109.1
N1–C13–H13B	109.9	N1*–C13*–H13D	109.1
C3–C13–H13A	109.9	C3*–C13*–H13C	109.1
C3–C13–H13B	109.9	C3*–C13*–H13D	109.1
H13A–C13–H13B	108.3	H13C–C13*–H13D	107.8

Table S5: Torsion Angles for **5**.

Atom–Atom–Atom–Atom	Torsion Angle [°]	Atom–Atom–Atom–Atom	Torsion Angle [°]
Br1–C7–C8–C8A	-179.52(9)	Br1*–C7*–C8*–C8A*	178.96(9)
N2–N1–C13–C3	174.96(12)	N2*–N1*–C13*–C3*	89.13(14)
C1–C2–C3–C4	1.34(19)	C1*–C2*–C3*–C4*	1.11(18)
C1–C2–C3–C13	-178.51(12)	C1*–C2*–C3*–C13*	-177.50(11)
C1–C2–C12–O1	-176.60(14)	C1*–C2*–C12*–O1*	-166.75(13)
C2–C1–C9A–C4A	-0.49(19)	C2*–C1*–C9A*–C4A*	1.37(18)
C2–C1–C9A–C9	177.71(13)	C2*–C1*–C9A*–C9*	-179.65(12)
C2–C3–C4–C4A	-0.87(18)	C2*–C3*–C4*–C4A*	0.36(18)
C2–C3–C13–N1	171.26(11)	C2*–C3*–C13*–N1*	157.56(11)
C3–C2–C12–O1	2.9(2)	C3*–C2*–C12*–O1*	12.4(2)
C3–C4–C4A–C4B	-178.81(12)	C3*–C4*–C4A*–C4B*	-178.88(12)
C3–C4–C4A–C9A	-0.27(19)	C3*–C4*–C4A*–C9A*	-0.96(18)
C4–C3–C13–N1	-8.58(16)	C4*–C3*–C13*–N1*	-21.03(16)
C4–C4A–C4B–C5	-1.5(2)	C4*–C4A*–C4B*–C5*	-0.1(2)
C4–C4A–C4B–C8A	177.87(13)	C4*–C4A*–C4B*–C8A*	178.41(13)
C4–C4A–C9A–C1	0.96(19)	C4*–C4A*–C9A*–C1*	0.09(18)
C4–C4A–C9A–C9	-177.56(11)	C4*–C4A*–C9A*–C9*	-179.06(11)

C4A–C4B–C5–C6	179.44(13)	C4A*–C4B*–C5*–C6*	178.13(12)
C4A–C4B–C8A–C8	-179.69(11)	C4A*–C4B*–C8A*–C8*	-178.84(11)
C4A–C4B–C8A–C9	0.06(14)	C4A*–C4B*–C8A*–C9*	0.27(14)
C4B–C4A–C9A–C1	179.78(12)	C4B*–C4A*–C9A*–C1*	178.42(11)
C4B–C4A–C9A–C9	1.26(14)	C4B*–C4A*–C9A*–C9*	-0.73(14)
C4B–C5–C6–C7	0.05(19)	C4B*–C5*–C6*–C7*	0.23(19)
C4B–C8A–C9–C9A	0.64(14)	C4B*–C8A*–C9*–C9A*	-0.65(13)
C4B–C8A–C9–C10	119.93(12)	C4B*–C8A*–C9*–C10*	117.48(11)
C4B–C8A–C9–C11	-116.91(12)	C4B*–C8A*–C9*–C11*	-118.90(12)
C5–C4B–C8A–C8	-0.21(19)	C5*–C4B*–C8A*–C8*	-0.14(19)
C5–C4B–C8A–C9	179.54(11)	C5*–C4B*–C8A*–C9*	178.97(11)
C5–C6–C7–Br1	179.42(10)	C5*–C6*–C7*–Br1*	-179.32(9)
C5–C6–C7–C8	-0.1(2)	C5*–C6*–C7*–C8*	0.13(19)
C6–C7–C8–C8A	-0.03(19)	C6*–C7*–C8*–C8A*	-0.49(19)
C7–C8–C8A–C4B	0.17(19)	C7*–C8*–C8A*–C4B*	0.49(18)
C7–C8–C8A–C9	-179.53(12)	C7*–C8*–C8A*–C9*	-178.46(12)
C8–C8A–C9–C9A	-179.64(13)	C8*–C8A*–C9*–C9A*	178.38(12)
C8–C8A–C9–C10	-60.35(18)	C8*–C8A*–C9*–C10*	-63.49(16)
C8–C8A–C9–C11	62.81(17)	C8*–C8A*–C9*–C11*	60.14(16)
C8A–C4B–C5–C6	0.09(19)	C8A*–C4B*–C5*–C6*	-0.23(19)
C8A–C9–C9A–C1	-179.47(13)	C8A*–C9*–C9A*–C1*	-178.21(12)
C8A–C9–C9A–C4A	-1.15(14)	C8A*–C9*–C9A*–C4A*	0.84(13)
C9A–C1–C2–C3	-0.65(19)	C9A*–C1*–C2*–C3*	-1.99(19)
C9A–C1–C2–C12	178.89(12)	C9A*–C1*–C2*–C12*	177.21(11)
C9A–C4A–C4B–C5	179.76(13)	C9A*–C4A*–C4B*–C5*	-178.23(13)
C9A–C4A–C4B–C8A	-0.82(14)	C9A*–C4A*–C4B*–C8A*	0.29(14)
C10–C9–C9A–C1	61.74(18)	C10*–C9*–C9A*–C1*	63.70(16)
C10–C9–C9A–C4A	-119.94(12)	C10*–C9*–C9A*–C4A*	-117.25(11)
C11–C9–C9A–C1	-61.81(18)	C11*–C9*–C9A*–C1*	-59.66(17)
C11–C9–C9A–C4A	116.50(12)	C11*–C9*–C9A*–C4A*	119.39(11)
C12–C2–C3–C4	-178.18(12)	C12*–C2*–C3*–C4*	-178.02(12)
C12–C2–C3–C13	1.97(19)	C12*–C2*–C3*–C13*	3.37(19)
C13–C3–C4–C4A	178.97(11)	C13*–C3*–C4*–C4A*	178.97(11)

4.2 Crystal Packing Views of (5)

Figure S2: Unit cell packing view of a **5** crystal along the *a*-axis.

Figure S3: Unit cell packing view of a **5** crystal along the *b*-axis.

Figure S4: Unit cell packing view of a **5** crystal along the *c*-axis.

5 References

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6 NMR-Spectra

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