“Golden” Cascade Cyclization to Benzo[c]-Phenantridines

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1. General Information

All employed chemicals were purchased from commercial suppliers (ABCR, TCI, Carbolution, Acros, Alfa Aesar, Chempur, Merck and Sigma Aldrich). Anhydrous solvents were dispensed from the solvent purification system MB SPS 800. THF and NEt₃ for Sonogashira cross couplings were degassed using freeze pump techniques. Deuterated solvents were bought from Euriso Top or Sigma Aldrich. Melting points were measured in open glass capillaries on a Stuart SMP10 melting point apparatus and have not been corrected. Rf-values were determined by aluminium sheets coated with silica gel produced by Merck (TLC Silica gel 60 F254). Visualization of substances proceeded either by employing a colouring reagent (vanillin, ninhydrin) or exposing the TLC plate to ultraviolet light (254 and 366 nm). Infrared spectra were recorded on a FT IR spectrometer (Bruker LUMOS) with a Germanium ATR-crystal. The solvent or matrix is denoted in brackets. For the most significant bands the wave number (cm⁻¹) is given. NMR spectra were, if not mentioned otherwise, recorded at room temperature at the chemistry department of Heidelberg University under the direction of Dr. J. Graf on the following spectrometers: Bruker Avance III 300 (300 MHz), Bruker Avance DRX 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz) and Bruker Avance III 600 (600 MHz). Chemical shifts are given in ppm and coupling constants in Hz. ¹H and ¹³C spectra were calibrated in relation to deuterated solvents according to Fulmer et al.[1]. The following abbreviations were used to describe the observed multiplicities: for ¹H NMR spectra: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dd = doublet of a doublet, dt = doublet of triplet; for ¹³C NMR spectra: s = quaternary carbon, d = CH carbon, t = CH₂ carbon and q = CH₃ carbon. ¹³C NMR spectra are proton and fluorine decoupled and interpreted with help of DEPT- and/or 2D spectra. All spectra were integrated and processed using the TopSpin 3.5 software. Mass spectra and high-resolution mass spectra (HR/MS) were recorded at the chemical department of Heidelberg University under the direction of Dr. J. Gross. EI spectra were measured on a JEOL JMS 700 spectrometer, ESI spectra on a Bruker ApexQe hybrid 9.4 T FT-ICR (also for MALDI spectra) or a Finnigan LCQ spectrometer. GC/MS spectra were measured on an Agilent 7890A gas chromatograph, coupled with an Agilent 5975C mass selective detector. An OPTIMA 5 cross-linked methyl silicone capillary column (30 Mesh, 0.25 mm, 0.25 μm) was employed. Nitrogen served as carrier gas. UV-Vis spectra were recorded on a Jasco UV-VIS V-670. Fluorescence spectra were recorded on a Jasco FT6500. X-Ray structures were measured on a Stoe Stadivari or Bruker Smart APEX II instrument. All data were processed using the Mercury 3.8 software. For flash column chromatography silica gel of Sigma-Aldrich (silica gel, pore size 60 Å, 230-400 mesh particle size, particle size 40-63 μm) was used as stationary phase. As eluents different mixtures of petroleum ether (PE) and ethyl acetate (EA) or DCM were used.

If not mentioned differently, all reactions were carried out at normal laboratory conditions.
2. General Procedures

GP1: Sonogashira Cross Coupling

A Schlenk flask was evacuated and backfilled with nitrogen for three times. 1.00 eq of the aryl halide was dissolved in a degassed 1:1 solution of THF and NEt₃ and the Palladium catalyst was added. After stirring for 10 min at room temperature, the corresponding alkyne and copper(I)-iodide were added. The mixture was stirred at the given temperature for the given time until full conversion. The progress of the reaction was controlled by GC/MS and/or TLC. After the reaction was finished, solvents were removed under reduced pressure and the residue was adsorbed onto Celite®. The crude product was purified using flash column chromatography.

GP2: Reductive Amination

According to a slightly modified procedure of Takemoto et al.[2] 1.00 eq of the aldehyde was dissolved in MeCN (and - if needed - DCM for better solubility). 2.00 eq tert-butyl carbamate were added and the reaction mixture was cooled down to 0 °C. Subsequently, 2.00 eq triethylsilane and 1.30 eq trifluoracetic acid were added dropwise. The solution was then stirred for 30 min, warmed up to room temperature and stirred overnight. After full conversion was observed by TLC, the reaction mixture was diluted with Et₂O and quenched with an aqueous NaHCO₃ solution. The aqueous phase was extracted with Et₂O and the combined organic layer was washed with brine and dried over Sodium sulphate. After filtration, the crude product was adsorbed onto Celite® and purified by flash column chromatography.

GP3: Gold Catalysis

1.00 eq of the corresponding alkyne was dissolved in dichloroethane and 2.5 mol% JohnPhosAu(MeCN)SbF₆ were added. The mixture was stirred at 50 °C until the TLC showed full conversion. The solvent was evaporated under reduced pressure. The resulting crude product was adsorbed onto Celite® and purified by flash column chromatography.

GP4: Cleavage of the Boc-Group

1.00 eq of the corresponding Boc-protected secondary amine was heated up to 200 °C under nitrogen atmosphere for the given time. The conversion was detected via ¹H NMR of the mixture. After full conversion was observed, the residue was dissolved in chloroform and flushed with air for given time. After removing of the solvent, the corresponding benzo[c]phenanthridine was obtained as a solid in quantitative yield.
3. Gold Catalysis Screening
For the screening of the gold catalyzed step all test reactions were carried out in an NMR-
tube. For the reaction 0.5 mL of a 50 mM stock solution of *tert*-butyl (2-((2-(phenylethynyl)-
phenyl)ethynyl)benzyl)carbamate (5a) and hexamethylbenzene as internal standard in CDCl₃
were used (corresponding to 25.0 µmol of each per reaction). All catalysts were added as
salts. Conversion and yields of the intermediate and the expected product were calculated by
integration of characteristic signals - namely the benzylic protons - against the internal
standard with fixed integrals. To observe the reaction progress, control NMRs were measured
after 2 h and 5 h.
4. Experimental Section

2-((Trimethylsilyl)ethynyl)benzaldehyde

This compound was synthesized in a three step synthesis from \( p \)-phenylene-

![TMB](image)
diamine according to a previously reported procedure.[3]

\[ R_f: 0.60 \text{ (silica gel, PE:EA = 10:1)}; \ H NMR (CD_2Cl_2, 500.1 MHz): \delta[ppm] = 0.29 \text{ (s, 9H), 7.44-7.47 (m, 1H), 7.54-7.59 (m, 2H), 7.88 (d, J_H-H = 7.7 Hz, 1H), 10.54 (s, 1H)}. \]

Analytics confirm to previously reported data.[3]

2-(Phenylethynyl)benzaldehyde

This compound was synthesized in a three step synthesis from \( p \)-phenylenediamine according to a previously reported procedure.[3]

![Ph](image)

\[ R_f: 0.67 \text{ (silica gel, PE:EA = 5:1)}; \ H NMR (CDCl_3, 500.1 MHz): \delta[ppm] = 7.38-7.40 \text{ (m, 3H), 7.46 (t, J_H-H = 7.8 Hz, 1H), 7.56-7.61 (m, 3H), 7.65 (d, J_H-H = 7.7 Hz, 1H), 7.96 (d, J_H-H = 7.8 Hz, 1H), 10.66 (s, 1H)}. \]

Analytics confirm to previously reported data.[3]

1-Ethynyl-2-(phenylethynyl)benzene

This compound was synthesized in a three step synthesis from \( p \)-phenylenediamine according to a previously reported procedure.[3]

![Ph](image)

\[ R_f: 0.48 \text{ (silica gel, PE:EA = 10:1)}; \ H NMR (CDCl_3, 500.1 MHz): \delta[ppm] = 3.38 \text{ (s, 1H), 7.28-7.38 (m, 5H), 7.54-7.59 (m, 4H)}. \]

Analytics confirm to previously reported data.[3]

Naphthalene-2,3-diyl bis(trifluoromethanesulfonate)

In a baked-out schlenk flask 10.0 eq triethylamine (19.0 g, 26.0 mL, 187 mmol)

![TMSOTf](image)

were added at -78 °C to a solution of 1.00 eq naphthalene-2,3-diol (3.00 g,

![TMSOTf](image) 18.7 mmol) in 150 mL DCM. The mixture was allowed to warm up to room
temperature and stirred 2 h at this temperature. After re-cooling down to -78 °C 4.50 eq of trifluoromethanesulfonic anhydride (23.8 g, 14.2 mL, 84.3 mmol) were added dropwise. The mixture was again allowed to warm up to room temperature and stirred overnight. After quenching with water, the organic layer was washed with diluted hydrochloric acid and again with water. The aqueous layer was extracted with DCM and the combined organic layers were dried over MgSO₄. The solvent was evaporated under reduced pressure and the residue was dissolved in DCM and adsorbed onto Celite®. The crude product was purified by flash column chromatography (silica gel, PE to PE:EA = 10:1). A colorless solid was obtained (7.10 g, 16.7 mmol, 89%).

Rf: 0.46 (silica gel, PE:EA = 1:2); ³¹H NMR (CDCl₃, 500.1 MHz): δ[ppm] = 7.67-7.69 (dd, ³JH-H = 6.3 Hz, ⁴JH-H = 3.2 Hz, 2H), 7.92-7.94 (m, 4H); ¹⁹F NMR (CDCl₃, 470.6 MHz): δ[ppm] = -72.9 (s, 6F).

Analytics confirm to previously reported data.[⁴]

3-(Phenylethynyl)naphthalen-2-yl trifluoromethanesulfonate

According to GP1, 1.10 eq ethynylbenzene (167 mg, 2.73 mmol) and later 2 mol% copper(I) iodide (9.60 mg, 50.4 µmol) were added to a mixture of 1.00 eq naphthalene-2,3-diyl bis(trifluoromethanesulfonate) (1.07 g, 2.52 mmol) and 2 mol% PdCl₂(PPh₃)₂ (35.4 mg, 50.4 µmol) in 40 mL solvent. The solution was stirred over night at room temperature and treated according to GP1 (silica gel, PE:EA = 30:1). A beige solid was obtained (884 mg, 2.35 mmol, 93%).

Mp: 107 °C; Rf: 0.56 (silica gel, PE:EA = 10:1); IR (ATR): ν[cm⁻¹] = 2219, 1602, 1502, 1420, 1249, 1206, 1136, 1054, 958, 921, 891, 875, 816, 749, 725, 687, 608; ¹H NMR (CDCl₃, 500.2 MHz): δ[ppm] = 7.39-7.40 (m, 3H), 7.57-7.61 (m, 2H), 7.63-7.65 (m, 2H), 7.77 (s, 1H), 7.85-7.88 (m, 2H), 8.16 (s, 1H); ¹³C NMR (¹⁹F) (CDCl₃, 125.8 MHz): δ[ppm] = 83.2 (s, 1C), 96.0 (s, 1C), 116.3 (s, 1C), 118.9 (s, 1C), 119.8 (d, 1C), 122.5 (s, 1C), 127.9 (d, 1C), 127.9 (d, 1C), 128.1 (d, 1C), 128.3 (d, 1C), 128.6 (d, 2C), 129.2 (d, 1C), 131.9 (d, 2C), 132.1 (s, 1C), 132.7 (s, 1C), 134.2 (d, 1C), 146.7 (s, 1C); ¹⁹F NMR (CDCl₃, 470.7 MHz): δ[ppm] = -73.4 (3F); HRMS (EI+): C₁₉H₁₁F₃O₃S⁺, calculated: 376.03755 [M⁺], observed: 376.03679 [M⁺].

tert-Butyl (2-((trimethylsilyl)ethynyl)benzyl)carbamate

According to GP2 1.00 eq 2-((trimethylsilyl)ethynyl)benzaldehyde (9.42 g, 46.6 mmol) was dissolved in 200 mL MeCN and 5 mL DCM. 2.00 eq tert-butyl carbamate (10.9 g, 93.1 mmol) were added and the reaction mixture was cooled down to 0 °C. 2.00 eq triethylsilane (10.8 g, 14.9 mL, 93.1 mmol) and 1.30 eq trifluoroacetic acid (6.90 g, 4.66 mL, 60.5 mmol) were added dropwise. After stirring the solution for 30 min the reaction was warmed up to room temperature, stirred overnight
and treated according to GP2 (silica gel, PE:EA = 20:1). A yellow oil was obtained (13.8 g, 45.4 mmol, 98%).

$^1$H NMR (CDCl$_3$, 300.5 MHz): $\delta$[ppm] = 0.27 (s, 9H), 1.45 (s, 9H), 4.45 (d, $^3J_{H-H} = 5.9$ Hz, 2H), 5.10 (s, 1H), 7.18-7.23 (m, 1H), 7.26-7.35 (m, 2H), 7.45 (d, $^3J_{H-H} = 7.2$ Hz, 1H).

Analytics confirm to previously reported data.$^5$

**tert-Butyl (2-ethynylbenzyl)carbamate**

1.00 eq of 2-((trimethylsilyl)ethynyl)benzaldehyde (13.7 g, 45.1 mmol) was dissolved in 300 mL methanol. 2.00 eq K$_2$CO$_3$ (12.5 g, 90.4 mmol) were added and the reaction mixture was stirred at room temperature for 3 h. The solution was concentrated under reduced pressure, quenched with water and extracted with DCM. The combined organic layer was dried over sodium sulphate and filtered over a pad of Celite$^8$. The solvent was removed under reduced pressure to obtain a reddish solid (9.81 g, 42.4 mmol, 94%).

$^1$H NMR (CDCl$_3$, 300.5 MHz): $\delta$[ppm] = 1.45 (s, 9H), 3.32 (s, 1H), 4.47 (d, $^3J_{H-H} = 5.8$ Hz, 2H), 5.02 (s, 1H), 7.20-7.25 (m, 1H), 7.30-7.38 (m, 2H), 7.48-7.50 (d, $^3J_{H-H} = 7.5$ Hz, 1H).

Analytics confirm to previously reported data.$^5$

**1,4-Dibromo-2,5-bis(bromomethyl)benzene**

According to a procedure from Chen et al.$^6$, in baked-out Schlenk flask 1.00 eq 1,4-dibromo-2,5-dimethylbenzene (5.00 g, 18.9 mmol) and 2.20 eq N-bromosuccinimide (7.42 g, 41.7 mmol) were dissolved in 110 mL dry benzene. The reaction mixture was stirred at 60 °C for 2 h. 5 mol% azobisisobutyronitrile (156 mg, 947 µmol) were added and the mixture was stirred for 15 h at 80 °C. The solution was quenched with water and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over sodium sulphate and the solvents were evaporated under reduced pressure. The residue was purified by recrystallization in ethanol. The precipitate was filtered and washed with ice-cold ethanol to give a colourless solid (4.88 g, 11.6 mmol, 61%).

R$_f$: 0.39 (silica gel, PE:EA = 5:1); $^1$H-NMR (CDCl$_3$, 300.5 MHz): $\delta$[ppm] = 4.51 (s, 4H), 7.66 (s, 2H).

Analytics confirm to previously reported data.$^6$
Di-tert-butyl ((2,5-dibromo-1,4-phenylene)bis(methylene))dicarbamate

According to a modified procedure from Yaghi et al.,\textsuperscript{[7]} 1.00 eq 1,4-dibromo-2,5-bis(bromomethyl)benzene (4.85 g, 11.5 mmol) and 4.00 eq sodium azid (2.99 g, 46.0 mmol) were dissolved in a baked-out Schlenk flask in 100 mL dry dimethylformamide. The reaction mixture was stirred at 65 °C for 15 h and then quenched with 100 mL ethanol. The organic layer was extracted with deionized water and diethylether, dried over sodium sulfate and the solvent was removed under reduced pressure until a volume of 10 mL. The concentrated solution was dissolved with 100 mL dry tetrahydrofuran and the solution was concentrated again up to a volume of 10 mL. This procedure was repeated three times. After the concentrate was dissolved in 100 mL dry tetrahydrofuran and flooded with nitrogen, 2.20 eq triphenylphosphane (6.64 g, 25.3 mmol) were added and the dark red reaction mixture was stirred at 60 °C for 2 h. 8 mL water was then added and the now clear red reaction mixture was stirred at 65 °C for 15 h. After the mixture was cooled down to room temperature, 2.50 eq di-tert-butyl dicarbonate (6.27 g, 6.60 mL, 28.8 mmol) were added and the reaction mixture was stirred at room temperature for 8 h. 2.20 eq ethanolamine (1.13 g, 18.5 mmol, 1.12 mL) were added and the mixture was stirred at room temperature for 2 h and 1 h at 50 °C. The solvent was removed under reduced pressure and the residue was dissolved in 110 mL ethylacetate. The organic layer was washed with ionized water and brine, dried over sodium sulfate and the solvent was removed under reduced pressure. The crude solid was purified by column chromatography (silica gel, DCM:EA = 1:1 to DCM). The product was obtained as a light orange solid (3.73 g, 7.55 mmol, 66%).

\(R_f\): 0.27 (silica gel, PE:EA = 5:1);\textsuperscript{1H-NMR} (CDCl\textsubscript{3}, 300.5 MHz): \(\delta[ppm] = 1.46 \text{ (s, 18H), 4.32 \ (d, }^{3}J_{H-H} = 5.50 \text{ Hz, 4H), 4.99 \ (m, 2H), 7.52 \ (s, 2H).\)

Analytics confirm to previously reported data.\textsuperscript{[7]}

((2,5-Dibromo-1,4-phenylene)bis(ethyne-2,1-diyl))dibenzene

According to GP1, 2.10 eq phenylactelyene (691 mg, 743 µL, 6.77 mmol) and later 2 mol% copper(I) iodide (11.7 mg, 61.5 µmol) were added to a mixture of 1.00 eq 1,4-dibromo-2,5-diiodobenzene (1.50 g, 3.08 mmol) and 2 mol% PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (43.2 mg, 61.5 µmol) in 30 mL solvent. The solution was stirred for 2 h at room temperature and treated according to GP1 (silica gel, PE). A light yellow solid was obtained (1.24 g, 2.84 mmol, 92%).

\(R_f\): 0.65 (silica gel, PE); \textsuperscript{1H NMR} (CDCl\textsubscript{3}, 300.5 MHz): \(\delta[ppm] = 7.37-7.39 \text{ (m, 6H), 7.56-7.60 \ (m, } 4H), 7.79 \ (s, 2H).\)

Analytics confirm to previously reported data.\textsuperscript{[8]}

\[\text{PhPh} \ 	ext{PhPh} \ \text{BrBr} \ 	ext{BrBr} \ \text{BrBr} \ 	ext{BrBr} \ \text{HHNN} \ 	ext{NNHH} \ \text{BocBoc} \ 	ext{BocBoc} \]
**tert-Butyl (2-((2-bromophenyl)ethynyl)benzyl)carbamate**

According to GP1, 1.00 eq tert-butyl (2-ethynylbenzyl)carbamate (5.00 g, 21.6 mmol) and later 2 mol% copper(I) iodide (82.9 mg, 436 µmol) were added to a mixture of 1.00 eq 1-bromo-2-iodo-benzene (6.12 g, 21.6 mmol) and 1 mol% PdCl$_2$(PPh$_3$)$_2$ (151 mg, 216 µmol) in 300 mL solvent. The solution was stirred overnight at room temperature and treated according to GP1 (silica gel, PE:EA = 10:1). A yellowish solid was obtained (7.41 g, 19.2 mmol, 89%).

Mp: 76 °C; Rf: 0.30 (silica gel, PE:EA = 10:1); IR (ATR): v [cm$^{-1}$] = 3432, 3350, 3063, 2976, 2930, 2216, 1715, 1506, 1466, 1433, 1391, 1365, 1249, 1167, 1045, 1025, 933, 857, 757, 697, 653;

$^1$H NMR ((CD$_3$)$_2$CO, 500.2 MHz): $\delta$ (ppm) = 1.43 (s, 9H), 4.60 (d, $^3$J$_{H-H}$ = 6.2 Hz, 2H), 6.49 (s, 1H), 7.31-7.37 (m, 3H), 7.40-7.47 (m, 3H), 7.59 (d, $^3$J$_{H-H}$ = 7.5 Hz, 1H), 7.71-7.74 (m, 2H);

$^{13}$C NMR ((CD$_3$)$_2$CO, 125.8 MHz): $\delta$ (ppm) = 28.6 (q, 3C), 43.5 (t, 1C), 78.9 (s, 1C), 92.4 (s, 1C), 93.3 (s, 1C), 121.9 (s, 1C), 125.6 (s, 1C), 126.0 (s, 1C), 127.8 (d, 1C), 128.0 (d, 1C), 128.5 (d, 1C), 130.0 (d, 1C), 131.0 (d, 1C), 133.0 (d, 1C), 133.4 (d, 1C), 134.5 (d, 1C), 142.8 (s, 1C), 156.8 (s, 1C);

HRMS (EI+): C$_{20}$H$_{20}$NO$_2$Br$_7$+, calculated: 385.06719 [M$^+$], observed: 385.06570 [M$^+$].

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**tert-Butyl (2-((2-bromo-4-fluorophenyl)ethynyl)benzyl)carbamate**

According to GP1, 1.00 eq tert-butyl (2-ethynylbenzyl)carbamate (615 mg, 2.66 mmol) and later 2 mol% copper(I) iodide (10.1 mg, 53.2 µmol) were added to a mixture of 1.00 eq 2-bromo-4-fluoro-1-iodobenzene (800 mg, 2.66 mmol) and 2 mol% PdCl$_2$(PPh$_3$)$_2$ (37.3 mg, 53.2 µmol) in 40 mL solvent. The solution was stirred for 64 h at room temperature and treated according to GP1 (silica gel, PE:EA = 10:1). A beige solid was obtained (916 mg, 2.27 mmol, 85%).

Mp: 80 °C; Rf: 0.28 (silica gel, PE:EA = 10:1); IR (ATR): v [cm$^{-1}$] = 3355, 3067, 2975, 2894, 1685, 1593, 1538, 1494, 1477, 1390, 1364, 1273, 1253, 1173, 1051, 1032, 959, 938, 892, 861, 832, 796, 759, 705, 642; $^1$H NMR ((CD$_3$)$_2$CO, 500.2 MHz): $\delta$ (ppm) = 1.42 (s, 9H), 4.59 (d, $^3$J$_{H-H}$ = 6.2 Hz, 2H), 6.49 (s, 1H), 7.26-7.34 (m, 2H), 7.40-7.46 (m, 2H), 7.57-7.61 (m, 2H), 7.79 (dd, $^3$J$_{H-H}$ = 6.0 Hz, $^3$J$_{H-H}$ = 8.6 Hz, 1H);

$^{13}$C NMR ((CD$_3$)$_2$CO, 125.8 MHz): $\delta$ (ppm) = 28.6 (q, 3C), 43.5 (t, 1C), 79.0 (s, 1C), 92.2 (s, 1C), 92.3 (s, 1C), 116.0 (d, 1C), 120.8 (d, 1C), 121.8 (s, 1C), 122.7 (s, 1C), 126.3 (s, 1C), 127.8 (d, 1C), 128.0 (d, 1C), 130.0 (d, 1C), 133.0 (d, 1C), 135.9 (d, 1C), 142.8 (s, 1C), 156.8 (s, 1C), 162.9 (s, 1C);

$^{19}$F NMR ((CD$_3$)$_2$CO, 470.7 MHz): $\delta$ (ppm) = -105.0 (1F); HRMS (EI+): C$_{20}$H$_{19}$FNO$_2$Br$_7$+, calculated: 403.05777 [M$^+$], observed: 403.05700 [M$^+$].
**tert-Butyl (2-((2-bromo-4-methylphenyl)ethynyl)benzyl)carbamate**

According to GP1, 1.00 eq tert-butyl (2-ethynylbenzyl)carbamate (623 mg, 2.69 mmol) and later 2 mol% copper(I) iodide (10.3 mg, 53.9 µmol) were added to a mixture of 1.00 eq 2-bromo-1-iodo-4-methylbenzene (800 mg, 2.69 mmol) and 2 mol% PdCl$_2$(PPh$_3$)$_2$ (37.8 mg, 53.9 µmol) in 40 mL solvent. The solution was stirred overnight at room temperature and treated according to GP1 (silica gel, PE:EA = 10:1). A beige solid was obtained (949 mg, 2.37 mmol, 88%).

**Mp**: 121 °C; **Rf**: 0.37 (silica gel, PE:EA = 10:1); **IR** (ATR): ν [cm$^{-1}$] = 3359, 2976, 2931, 2216, 1688, 1534, 1497, 1478, 1449, 1390, 1363, 1269, 1250, 1166, 1090, 1049, 1039, 957, 936, 869, 823, 779, 756, 649; **$^1$H NMR** ((CD$_3$)$_2$CO, 400.3 MHz): δ [ppm] = 1.43 (s, 9H), 2.38 (s, 3H), 4.59 (d, $^3$J$_{H-H}$ = 6.0 Hz, 2H), 6.41 (s, 1H), 7.25-7.33 (m, 2H), 7.38-7.45 (m, 2H), 7.56-7.60 (m, 3H); **$^{13}$C NMR** ((CD$_3$)$_2$CO, 100.7 MHz): δ [ppm] = 21.1 (q, 1C), 28.7 (q, 3C), 43.7 (t, 1C), 79.0 (s, 1C), 91.7 (s, 1C), 93.5 (s, 1C), 122.3 (s, 1C), 123.0 (s, 1C), 125.3 (s, 1C), 127.8 (d, 1C), 128.0 (d, 1C), 129.3 (d, 1C), 129.8 (d, 1C), 132.9 (d, 1C), 133.8 (d, 1C), 134.2 (d, 1C), 141.8 (s, 1C), 142.7 (s, 1C), 156.8 (s, 1C); **HRMS** (EI+): C$_{21}$H$_{22}$BrNO$_2$+, calculated: 399.08284 [M+], observed: 399.08182 [M+].

**5-Fluoro-2-((2-(phenylethynyl)phenyl)ethynyl)benzaldehyde**

According to GP1, 1.10 eq 1-ethynyl-2-(phenylethynyl)benzene (1.10 g, 5.42 mmol) and later 2 mol% copper(I) iodide (18.8 mg, 98.5 µmol) were added to a mixture of 1.00 eq 2-bromo-5-fluorobenzaldehyde (1.00 g, 4.93 mmol) and 2 mol% PdCl$_2$(PPh$_3$)$_2$ (69.2 mg, 98.5 µmol) in 40 mL solvent. The solution was stirred overnight at room temperature and treated according to GP1 (silica gel, PE:EA = 20:1). A yellow solid was obtained (1.53 g, 4.72 mmol, 96%).

**Mp**: 81 °C; **Rf**: 0.44 (silica gel, PE:EA = 10:1); **IR** (ATR): ν [cm$^{-1}$] = 3371, 3063, 2852, 2749, 2216, 1695, 1602, 1495, 1441, 1420, 1390, 1314, 1291, 1266, 1208, 1145, 965, 887, 827, 758, 691, 621; **$^1$H NMR** (CD$_2$Cl$_2$, 500.2 MHz): δ [ppm] = 7.31-7.35 (m, 1H), 7.38-7.41 (m, 5H), 7.55-7.56 (m, 2H), 7.63 (m, 3H), 7.70-7.72 (m, 1H), 10.72 (d, $^4$J$_{H-H}$ = 2.4 Hz, 1H); **$^{13}$C NMR** ($^{19}$F) (CD$_2$Cl$_2$, 125.8 MHz): δ [ppm] = 88.1 (s, 1C), 88.2 (s, 1C), 94.2 (s, 1C), 94.9 (s, 1C), 113.8 (d, 1C), 121.7 (d, 1C), 123.1 (s, 1C), 123.2 (s, 1C), 124.8 (s, 1C), 126.2 (s, 1C), 128.7 (d, 1C), 128.9 (d, 2C), 129.2 (d, 1C), 129.4 (d, 1C), 132.0 (d, 2C), 132.5 (d, 1C), 132.7 (d, 1C), 135.8 (d, 1C), 138.3 (s, 1C), 163.0 (s, 1C), 190.8 (d, 1C); **$^{19}$F NMR** (CD$_2$Cl$_2$, 470.7 MHz): δ [ppm] = -109.5 (1F); **HRMS** (EI+): C$_{23}$H$_{13}$FO+, calculated: 324.09449 [M+], observed: 324.09306 [M+].
4,5-Dimethoxy-2-((2-(phenylethynyl)phenyl)ethynyl)benzaldehyde

According to GP1, 1.10 eq 1-ethynyl-2-(phenylethynyl)benzene (907 mg, 4.48 mmol) and later 2 mol% copper(I) iodide (15.5 mg, 81.6 µmol) were added to a mixture of 1.00 eq 2-bromo-4,5-dimethoxybenzaldehyde (1.00 g, 4.08 mmol) and 2 mol% PdCl₂(PPh₃)₂ (57.0 mg, 81.6 µmol) in 40 mL solvent. The solution was stirred overnight at 50 °C and treated according to GP1 (silica gel, PE:EA = 10:1 to 5:1 to 3:1). An orange solid was obtained (694 mg, 1.89 mmol, 46%).

Mp: 135 °C; Rф: 0.36 (silica gel, PE:EA = 3:1); IR (ATR): ν[cm⁻¹] = 3002, 2971, 2933, 2831, 2211, 1675, 1587, 1504, 1461, 1444, 1398, 1359, 1304, 1263, 1237, 1219, 1162, 1104, 1080, 1039, 1006, 927, 895, 867, 761, 748, 699, 631; ¹H NMR (CDCl₃, 400.3 MHz): δ[ppm] = 3.82 (s, 3H), 3.95 (s, 3H), 7.05 (s, 1H), 7.33-7.36 (m, 5H), 7.42 (s, 1H), 7.56-7.60 (m, 4H), 10.62 (s, 1H); ¹³C NMR (CDCl₃, 100.7 MHz): δ[ppm] = 56.3 (q, 1C), 56.3 (q, 1C), 88.2 (s, 1C), 89.1 (s, 1C), 94.0 (s, 1C), 94.0 (s, 1C), 108.3 (d, 1C), 114.6 (d, 1C), 121.7 (s, 1C), 123.1 (s, 1C), 125.2 (s, 1C), 126.1 (s, 1C), 128.3 (d, 1C), 128.6 (d, 2C), 128.7 (d, 1C), 128.8 (d, 1C), 130.4 (s, 1C), 131.9 (d, 2C), 131.9 (d, 1C), 132.3 (d, 1C), 150.1 (s, 1C), 153.8 (s, 1C), 190.6 (d, 1C); HRMS (EI+): C₂₅H₁₈O₃⁺, calculated: 366.12505 [M⁺], observed: 366.12448 [M⁺].

tert-Butyl (2-((2-(phenylethynyl)phenyl)ethynyl)benzyl)carbamate, 5a

According to GP1, 1.85 eq ethynylbenzene (167 mg, 1.64 mmol) and later 2 mol% copper(I) iodide (3.40 mg, 17.8 µmol) were added to a mixture of 1.00 eq tert-butyl (2-((2-bromophenyl)ethynyl)benzyl)carbamate (342 mg, 885 µmol) and 2 mol% PdCl₂(PPh₃)₂ (12.5 mg, 17.8 µmol) in 20 mL solvent. The solution was stirred overnight at 50 °C and for further 5 h at 80 °C. 2 mol% Pd(PPh₃)₄ (20.5 mg, 17.7 µmol) were added and the reaction mixture was stirred at 80 °C for 64 h and then treated according to GP1 (silica gel, PE:EA = 20:1). An orange solid was obtained (290 mg, 712 µmol, 80%).

Mp: 70 °C; Rф: 0.53 (silica gel, PE:EA = 10:1); IR (ATR): ν[cm⁻¹] = 3397, 2973, 2876, 1698, 1597, 1512, 1449, 1389, 1362, 1303, 1243, 1164, 1135, 1047, 1024, 947, 916, 884, 864, 803, 754, 689; ¹H NMR (CDCl₃, 400.3 MHz): δ[ppm] = 1.43 (s, 9H), 4.64 (d, 3J₃H-H = 6.2 Hz, 2H), 6.39 (m, 1H), 7.27-7.31 (m, 1H), 7.37-7.47 (m, 7H), 7.58-7.66 (m, 4H), 7.69-7.71 (m, 1H); ¹³C NMR (CDCl₃, 100.7 MHz): δ[ppm] = 28.7 (q, 3C), 43.6 (t, 1C), 78.9 (s, 1C), 88.9 (s, 1C), 92.0 (s, 1C), 93.7 (s, 1C), 94.2 (s, 1C), 122.2 (s, 1C), 123.8 (s, 1C), 126.1 (s, 1C), 126.3 (s, 1C), 127.7 (d, 1C), 127.8 (d, 1C), 129.4 (d, 1C), 129.4 (d, 1C), 129.5 (d, 2C), 129.6 (d, 1C), 129.8 (d, 1C), 132.5 (d, 2C), 133.0 (d, 1C), 133.1 (d, 1C), 142.7 (s, 1C), 156.7 (s, 1C); HRMS (ESI+): C₂₀H₁₆ONa⁺, calculated: 430.1777 [M+Na⁺], observed: 430.1778 [M+Na⁺].
**tert-Butyl (5-fluoro-2-((2-(phenylethynyl)phenyl)ethynyl)benzyl)carbamate, 5b**

According to GP2, 1.00 eq of the corresponding aldehyde (1.51 g, 4.65 mmol) was dissolved in 50 mL MeCN and 5 mL DCM. 2.00 eq tert-butyl carbamate (1.09 g, 9.29 mmol) were added and the reaction mixture was cooled down to 0 °C. 2.00 eq triethylsilane (1.09 g, 1.50 mL, 9.39 mmol) and 1.40 eq trifluoroacetic acid (740 mg, 500 µL, 6.49 mmol) were added dropwise. After stirring the solution for 30 min the formed precipitate was filtrated and washed with cold MeCN. A beige solid was obtained (690 mg, 1.62 mmol, 35%).

**Mp**: 114 °C; **Rf**: 0.29 (silica gel, PE:EA = 10:1); **IR** (ATR): ν [cm⁻¹] = 3369, 3067, 2971, 1682, 1605, 1581, 1527, 1494, 1431, 1388, 1363, 1301, 1273, 1250, 1212, 1166, 1080, 1045, 962, 930, 875, 814, 784, 753, 691; **1H NMR** (CDCl₃, 500.2 MHz): δ [ppm] = 1.41 (s, 9H), 4.52 (d, 3JH-H = 5.8 Hz, 2H), 5.03 (m, 1H), 6.94 (d, 3JH-H = 8.3 Hz, 1H), 7.10 (d, 3JH-H = 9.1 Hz, 1H), 7.34-7.36 (m, 5H), 7.51-7.59 (m, 5H); **13C NMR** (CDCl₃, 125.8 MHz): δ [ppm] = 28.5 (q, 3C), 43.2 (t, 1C), 79.7 (s, 1C), 88.3 (s, 1C), 90.3 (s, 1C), 92.8 (s, 1C), 93.5 (s, 1C), 114.5 (d, 1C), 115.1 (d, 1C), 117.9 (s, 1C), 123.1 (s, 1C), 125.4 (s, 1C), 125.6 (s, 1C), 128.3 (d, 1C), 128.4 (d, 1C), 128.6 (d, 2C), 128.8 (d, 1C), 131.8 (d, 2C), 132.1 (d, 1C), 132.3 (d, 1C), 134.2 (d, 1C), 144.1 (s, 1C), 155.9 (s, 1C), 162.9 (s, 1C); **19F NMR** (CDCl₃, 470.7 MHz): δ [ppm] = -109.7 (1F); **HRMS** (ESI (+)): C₂₈H₂₄FNO₂Na⁺, calculated: 448.1683 [M++Na], observed: 448.1685 [M++Na].

**tert-Butyl (4,5-dimethoxy-2-((2-(phenylethynyl)phenyl)ethynyl)benzyl)carbamate, 5c**

According to GP2, 1.00 eq of the corresponding aldehyde (675 mg, 1.84 mmol) was dissolved in 150 mL MeCN and 12 mL DCM. 2.00 eq tert-butyl carbamate (432 mg, 3.69 mmol) were added and the reaction mixture was cooled down to 0 °C. 2.00 eq triethylsilane (430 mg, 590 µL, 3.69 mmol) and 1.27 eq trifluoroacetic acid (266 mg, 180 µL, 2.34 mmol) were added dropwise. After stirring the solution for 30 min the reaction was warmed up to room temperature and stirred overnight. Additional 0.50 eq tert-butyl carbamate (108 mg, 921 µmol), 0.51 eq triethylsilane (109 mg, 150 µL, 940 µmol) and 0.35 eq trifluoroacetic acid (74.0 mg, 50.0 µL, 649 µmol) were added. After stirring overnight at 50 °C, the mixture was treated according to GP2 (silica gel, PE:EA = 5:1 to 3:1 to 1:1). An orange solid was obtained (307 mg, 656 µmol, 36%).

**Mp**: 123 °C; **Rf**: 0.22 (silica gel, PE:EA = 3:1); **IR** (ATR): ν [cm⁻¹] = 3368, 2992, 2971, 2932, 2831, 2208, 1686, 1607, 1514, 1494, 1464, 1428, 1391, 1365, 1348, 1283, 1243, 1210, 1173, 1101, 1079, 1039, 996, 934, 865, 756, 737, 691, 637; **1H NMR** (CDCl₃, 400.3 MHz): δ [ppm] = 1.41 (s, 9H), 3.77 (s, 3H), 3.89 (s, 3H), 4.48 (d, 3JH-H = 5.9 Hz, 2H), 5.04 (m, 1H), 6.93 (s, 1H), 7.01 (s, 1H), 7.29-7.35 (m, 5H), 7.55-7.58 (m, 4H); **13C NMR** (CDCl₃, 100.7 MHz): δ [ppm] = 28.5 (q, 3C), 43.2 (t, 1C), 56.0 (q, 1C), 56.1 (q, 1C), 79.4 (s, 1C), 88.5 (s, 1C), 91.6 (s, 1C), 91.8 (s, 1C), 93.5 (s, 1C), 111.7 (d, 1C), 114.1 (s, 1C), 114.7 (d, 1C), 123.3 (s, 1C), 125.5 (s, 1C), 126.0 (s, 1C), 128.1 (d, 1C), 128.3 (d, 1C), 128.5 (d, 2C), 128.7 (d, 1C), 131.8 (d, 3C), 132.2 (d, 1C), 134.9 (s, 1C), 148.0 (s,
1C), 149.9 (s, 1C), 156.1 (s, 1C); HRMS (EI+): C$_{30}$H$_{29}$NO$_4^+$, calculated: 467.20911 [M$^+$], observed: 467.20974 [M$^+$].

**tert-Butyl (2-((4-fluoro-2-(phenylethynyl)phenyl)ethynyl)benzyl)carbamate, 5d**

According to GP1, 2.00 eq of ethynylbenzene (253 mg, 272 µL 2.47 mmol) and later 3 mol% copper(I) iodide (7.40 mg, 38.8 µmol) were added to a mixture of 1.00 eq *tert*-butyl (2-((2-bromo-4-fluorophenyl)ethynyl)benzyl)-carbamate (500 mg, 1.24 mmol) and 4 mol% Pd(PPh$_3$)$_4$ (57.2 mg, 49.5 µmol) in 40 mL solvent. The solution was stirred overnight at 80 °C and treated according to GP1 (silica gel, PE:EA = 10:1). A brown solid was obtained (521 mg, 1.22 mmol, 99%).

**Mp**: 95-98 °C; **Rf**: 0.44 (silica gel, PE:EA = 5:1); **IR** (ATR): $\nu$ [cm$^{-1}$] = 2973, 2873, 1687, 1598, 1500, 1390, 1244, 1197, 1163, 1046, 956, 862, 827, 755, 689; **$^1$H NMR** ((CD$_3$)$_2$CO, 500.2 MHz): $\delta$ [ppm] = 1.42 (s, 9H), 4.59 (d, $^3$$J_{H-H}$ = 6.1 Hz, 2H), 6.46 (m, 1H) 7.25-7.31 (m, 2H), 7.38-7.46 (m, 6H), 7.58 (d, $^3$$J_{H-H}$ = 7.5 Hz, 1H), 7.62-7.64 (m, 2H), 7.76 (dd, $^3$$J_{H-H}$ = 5.9 Hz, $^2$$J_{H-H}$ = 8.7 Hz, 1H); **$^{13}$C NMR** ($^{19}$F) ((CD$_3$)$_2$CO, 125.8 MHz): $\delta$ [ppm] = 28.6 (q, 3C), 43.5 (t, 1C), 78.9 (s, 1C), 87.7 (s, 1C), 91.7 (s, 1C), 92.7 (s, 1C), 95.3 (s, 1C), 117.1 (d, 1C), 119.5 (d, 1C), 122.0 (s, 1C), 122.8 (s, 1C), 123.2 (s, 1C), 127.7 (d, 1C), 127.7 (d, 1C), 128.1 (s, 1C), 129.6 (d, 2C), 129.8 (d, 1C), 130.0 (d, 1C), 132.6 (d, 2C), 132.9 (d, 1C), 135.3 (d, 1C), 142.7 (s, 1C), 156.7 (s, 1C), 162.8 (s, 1C); **$^{19}$F NMR** ((CD$_3$)$_2$CO, 470.7 MHz): $\delta$ [ppm] = -112.2 (1F); HRMS (EI+): C$_{28}$H$_{24}$FNO$_2^+$, calculated: 425.17856 [M$^+$], observed: 425.17791 [M$^+$].

**tert-Butyl (2-((4-methyl-2-(phenylethynyl)phenyl)ethynyl)benzyl)carbamate, 5e**

According to GP1, 2.00 eq of ethynylbenzene (255 mg, 274 µL, 2.50 mmol) and later 3 mol% copper(I) iodide (7.60 mg, 40.0 µmol) were added to a mixture of 1.00 eq *tert*-butyl (2-((2-bromo-4-methylphenyl)ethynyl)benzyl)-carbamate (500 mg, 1.24 mmol) and 4 mol% Pd(PPh$_3$)$_4$ (57.7 mg, 50.0 µmol) in 40 mL solvent. The solution was stirred for 40 h at 80 °C and additional 0.50 eq of ethynylbenzene (63.8 mg, 68.6 µL, 625 µmol) and 2 mol% Pd(PPh$_3$)$_4$ (28.9 mg, 25.0 µmol) were added. After stirring overnight at 80 °C, the mixture was treated according to GP1 (silica gel, PE:EA = 20:1). A brown solid was obtained (428 mg, 1.02 mmol, 81%).

**Mp**: 101-104 °C; **Rf**: 0.48 (silica gel, PE:EA = 5:1); **IR** (ATR): $\nu$ [cm$^{-1}$] = 3376, 2983, 2924, 1682, 1525, 1497, 1443, 1392, 1364, 1305, 1274, 1170, 1138, 1021, 919, 874, 823, 751, 691, 617; **$^1$H NMR** ((CD$_3$)$_2$CO, 300.2 MHz): $\delta$ [ppm] = 1.42 (s, 9H), 2.39 (s, 3H), 4.59 (d, $^3$$J_{H-H}$ = 6.2 Hz, 2H), 6.38 (m, 1H), 7.26-7.31 (m, 2H), 7.35-7.43 (m, 5H), 7.47 (s, 1H), 7.55-7.62 (m, 4H); **$^{13}$C NMR** ((CD$_3$)$_2$CO, 75.5 MHz): $\delta$ [ppm] = 21.2 (q, 1C), 28.7 (q, 3C), 43.6 (t, 1C), 78.9 (s, 1C), 89.1 (s, 1C), 91.3 (s, 1C), 93.8 (s, 1C), 93.9 (s, 1C), 122.4 (s, 1C), 123.4 (s, 1C), 123.9 (s, 1C), 126.0 (s, 1C), 127.7 (d, 2C), 129.5 (d, 2C), 129.6 (d, 2C), 130.3 (d, 1C), 132.5 (d, 2C), 132.9 (d, 1C), 135.3 (d, 1C), 142.7 (s, 1C), 156.7 (s, 1C), 162.8 (s, 1C), 167.1 (s, 1C).
tert-Butyl (2-((3-(phenylethynyl)naphthalen-2-yl)ethynyl)benzyl)carbamate, 5f

According to GP1, 1.20 eq tert-butyl (2-ethynylbenzyl)carbamate (553 mg, 2.39 mmol) and later 2 mol% copper(I) iodide (7.60 mg, 39.9 µmol) were added to a mixture of 1.00 eq 3-(phenylethynyl)naphthalen-2-yl trifluoromethanesulfonate (750 mg, 1.99 mmol) and 2 mol% PdCl$_2$(PPh$_3$)$_2$ (31.7 mg, 45.2 µmol) in 40 mL solvent. The solution was stirred overnight at room temperature and additional 0.40 eq tert-butyl (2-ethynylbenzyl)carbamate (184 mg, 797 µmol) were added. After stirring for 64 h at 50 °C, the mixture was treated according to GP1 (silica gel, PE:EA = 10:1). A beige solid was obtained (627 mg, 1.37 mmol, 69%).

**Mp:** 119 °C; **Rf:** 0.43 (silica gel, PE:EA = 5:1); **IR** (ATR): $\nu$[cm$^{-1}$] = 3362, 2970, 1678, 1510, 1494, 1364, 1247, 1168, 1126, 1047, 1025, 953, 895, 756, 748, 693; **$^1$H NMR** ((CD$_3$)$_2$CO, 400.3 MHz): $\delta$[ppm] = 1.43 (s, 9H), 4.65 (d, $^3$$J_{H-H} = 5.9$ Hz, 2H), 6.41 (m, 1H), 7.31 (dt, $^3$$J_{H-H} = 7.4$ Hz, $^4$$J_{H-H} = 1.2$ Hz, 1H), 7.39-7.46 (m, 5H), 7.58-7.66 (m, 5H), 7.96-7.98 (m, 2H), 8.23 (s, 1H), 8.30 (s, 1H); **$^{13}$C NMR** ((CD$_3$)$_2$CO, 100.7 MHz): $\delta$[ppm] = 28.7 (q, 3C), 43.6 (t, 1C), 78.9 (s, 1C), 89.1 (s, 1C), 91.4 (s, 1C), 93.7 (s, 1C), 94.0 (s, 1C), 122.3 (s, 1C), 122.7 (s, 1C), 122.9 (s, 1C), 123.9 (s, 1C), 127.8 (d, 1C), 127.8 (d, 1C), 128.6 (d, 2C), 128.6 (d, 2C), 129.6 (d, 2C), 129.6 (d, 1C), 129.8 (d, 1C), 132.5 (d, 2C), 133.1 (d, 1C), 133.2 (d, 1C), 133.5 (s, 1C), 133.5 (s, 1C), 142.8 (s, 1C), 156.8 (s, 1C); **HRMS** (EI+): C$_{32}$H$_{27}$NO$_2$+, calculated: 457.20363 [M+], observed: 457.20254 [M+].

ter t-Butyl (2-((2-(oct-1-yn-1-yl)phenyl)ethynyl)benzyl)carbamate, 5g

According to GP1, 1.80 eq oct-1-yne (254 mg, 340 µL, 2.30 mmol) and later 2 mol% copper(I) iodide (4.93 mg, 25.9 µmol) were added to a mixture of 1.00 eq tert-butyl (2-((2-bromophenyl)ethynyl)-benzyl)carbamate (500 mg, 1.29 mmol) and 2 mol% Pd(PPh$_3$)$_4$ (29.9 mg, 25.9 µmol) in 20 mL solvent. The solution was stirred overnight at 60 °C and additional 4 mol% Pd(PPh$_3$)$_4$ (59.8 mg, 51.6 µmol) were added. After stirring for 88 h at 80 °C, the mixture was treated according to GP1 (silica gel, PE:EA = 20:1). A green solid was obtained (407 mg, 979 µmol, 76%).

**Mp:** 47 °C; **Rf:** 0.62 (silica gel, PE:EA = 5:1); **IR** (ATR): $\nu$[cm$^{-1}$] = 3432, 3357, 3061, 2957, 2931, 2858, 2227, 1956, 1925, 1717, 1504, 1453, 1391, 1366, 1250, 1171, 1048, 950, 933, 858, 758; **$^1$H NMR** ((CD$_3$)$_2$CO, 500.2 MHz): $\delta$[ppm] = 0.85-0.88 (m, 3H), 1.28-1.31 (m, 4H), 1.44 (s, 9H), 1.47-1.52 (m, 2H), 1.61-1.66 (m, 2H), 2.54 (t, $^3$$J_{H-H} = 7.1$ Hz, 2H), 4.64 (d, $^3$$J_{H-H} = 6.2$ Hz, 2H), 6.52 (m, 1H), 7.28-7.32 (m, 1H), 7.34-7.37 (m, 2H), 7.38-7.45 (m, 2H), 7.46-7.49 (m, 1H), 7.55 (d, $^3$$J_{H-H} = 7.8$ Hz, 1H), 7.60-7.62 (m, 1H); **$^{13}$C NMR** ((CD$_3$)$_2$CO, 125.8 MHz): $\delta$[ppm] = 14.3 (q, 1C),
**tert-Butyl (2-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)benzyl)carbamate, 5h**

According to GP1, 2.00 eq ethynyltrimethylsilane (255 mg, 360 µL, 2.60 mmol) and later 4 mol% copper(I) iodide (9.90 mg, 51.8 µmol) were added to a mixture of 1.00 eq tert-butyl (2-((2-bromophenyl)ethynyl)benzyl)carbamate (500 mg, 1.29 mmol) and 4 mol% Pd(PPh₃)₄ (59.8 mg, 51.8 µmol) in 30 mL solvent. The solution was stirred overnight at 60 °C and additional 0.50 eq ethynyltrimethylsilane (63.6 mg, 90.0 µL, 647 µmol) were added and the reaction mixture was stirred at 80 °C overnight. Again, 0.50 eq ethynyltrimethylsilane (63.6 mg, 90.0 µL, 647 µmol) and 2 mol% Pd(PPh₃)₄ (30.0 mg, 25.9 µmol) were added. After stirring for 88 h at 70 °C, the mixture was treated according to GP1 (silica gel, PE:EA = 20:1). A beige solid was obtained (279 mg, 692 µmol, 53%).

**Mp**: 107 °C; **Rf**: 0.57 (silica gel, PE:EA = 5:1); **IR** (ATR): ν [cm⁻¹] = 3365, 3053, 3001, 2975, 2152, 1682, 1530, 1491, 1365, 1292, 1247, 1211, 1165, 1049, 953, 871, 841, 755, 646; **¹H NMR** ((CD₃)₂CO, 500.2 MHz): δ [ppm] = 0.27 (s, 9H), 1.43 (s, 9H), 4.61 (d, J₁H-H = 6.2 Hz, 2H), 6.52 (m, 1H), 7.32 (t, J₃H-H = 7.2 Hz, 1H), 7.38-7.46 (m, 4H), 7.55-7.59 (m, 2H), 7.67 (d, J₃H-H = 7.8 Hz, 1H); **¹³C NMR** ((CD₃)₂CO, 125.8 MHz): δ [ppm] = 0.0 (q, 3C), 28.6 (q, 3C), 43.5 (t, 1C), 78.9 (s, 1C), 91.8 (s, 1C), 93.6 (s, 1C), 99.2 (s, 1C), 104.4 (s, 1C), 122.1 (s, 1C), 126.0 (s, 1C), 126.4 (s, 1C), 127.7 (d, 1C), 127.8 (d, 1C), 129.3 (d, 1C), 129.6 (d, 1C), 129.8 (d, 1C), 133.3 (d, 1C), 133.3 (d, 1C), 133.5 (d, 1C), 142.7 (s, 1C), 156.8 (s, 1C); **HRMS** (EI+): C₂₈H₃₃NO₂⁺, calculated: 415.25058 [M⁺], observed: 415.248884 [M⁺].

**tert-Butyl (2-((2-ethynylphenyl)ethynyl)benzyl)carbamate, 5i**

1.00 eq of tert-butyl (2-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)benzyl)carbamate (204 mg, 505 µmol) was dissolved in 20 mL methanol and 3 mL DCM. 2.00 eq K₂CO₃ (140 mg, 1.01 mmol) were added and the reaction mixture was stirred at room temperature for 3 h until TLC showed full conversion. 20 mL DCM and 20 mL deionized water were added. The aqueous phase was extracted with DCM and the combined organic layer was dried over sodium sulphate. The solution was filtrated and the solvent was removed under reduced pressure. The crude product was adsorbed onto Celite® and purified by flash column chromatography (silica gel, PE:EA = 30:1 to 20:1). A yellowish oil was obtained (55.6 mg, 168 µmol, 53%).
**Rf**: 0.50 (silica gel, PE:EA = 5:1); **IR** (ATR): ν [cm⁻¹] = 3102, 3068, 2934, 2841, 1718, 1670, 1612, 1507, 1446, 1383, 1355, 1303, 1228, 1190, 1160, 1104, 1065, 1042, 953, 853, 700, 632; **1H NMR** ((CD₃)₂CO, 500.2 MHz): δ [ppm] = 1.43 (s, 9H), 3.98 (s, 1H), 4.61 (d, J₆-H = 6.1 Hz, 2H), 6.41 (m, 1H), 7.31 (dt, J₈-H = 7.4 Hz, J₆-H = 1.2 Hz, 1H), 7.38-7.48 (m, 4H), 7.56-7.61 (m, 2H), 7.65-7.68 (m, 1H); **13C NMR** ((CD₃)₂CO, 100.7 MHz): δ [ppm] = 28.6 (q, 3C), 43.6 (t, 1C), 78.9 (s, 1C), 82.9 (s, 1C), 83.6 (d, 1C), 91.8 (s, 1C), 93.3 (s, 1C), 122.1 (s, 1C), 125.3 (s, 1C), 126.8 (s, 1C), 127.7 (d, 1C), 127.8 (d, 1C), 129.3 (d, 1C), 129.7 (d, 1C), 132.8 (d, 1C), 133.0 (d, 1C), 133.3 (d, 1C), 142.6 (s, 1C), 156.8 (s, 1C); **HRMS** (EI⁺): C₂₂H₂₁NO₂⁺, calculated: 331.15668 [M⁺], observed: 331.15584 [M⁺].

**Di-tert-butyl** (((2,5-bis(phenylethynyl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(2,1-phenylene))bis(methylene)dicarbamate, **5j**

According to GP1, 2.00 eq 3,3-dimethylbut-1-yne (213 mg, 320 µL, 2.59 mmol) and later 4 mol% copper(I) iodide (9.90 mg, 51.8 µmol) were added to a mixture of 1.00 eq tert-butyl (2-((2-bromophenyl)ethynyl)benzyl)carbamate (500 mg, 1.29 mmol) and 4 mol% Pd(PPh₃)₄ (59.8 mg, 51.8 µmol) in 30 mL solvent. The solution was stirred for 40 h at 60 °C and additional 1.00 eq 3,3-dimethylbut-1-yne (106 mg, 160 µL, 1.29 mmol) and 2 mol% Pd(PPh₃)₄ (30.0 mg, 25.9 µmol) were added. After stirring for 88 h at 70 °C, the mixture was treated according to GP1 (silica gel, PE:EA = 20:1). A colorless solid was obtained (226 mg, 584 µmol, 45%).

**Mp**: 95 °C; **Rf**: 0.56 (silica gel, PE:EA = 5:1); **IR** (ATR): ν [cm⁻¹] = 3433, 3346, 3062, 2970, 2929, 2868, 2237, 1703, 1492, 1453, 1391, 1365, 1249, 1169, 1048, 933, 857, 757; **1H NMR** ((CD₃)₂CO, 500.2 MHz): δ [ppm] = 1.35 (s, 9H), 1.43 (s, 9H), 4.61 (d, J₆-H = 6.2 Hz, 2H), 6.53 (m, 1H), 7.31 (t, J₈-H = 7.3 Hz, 1H), 7.34-7.47 (m, 5H), 7.57 (d, J₆-H = 7.7 Hz, 1H), 7.63-7.64 (m, 1H); **13C NMR** ((CD₃)₂CO, 125.8 MHz): δ [ppm] = 28.6 (q, 3C), 28.8 (s, 1C), 31.3 (q, 3C), 43.6 (t, 1C), 78.9 (s, 1C), 78.9 (s, 1C), 91.1 (s, 1C), 94.1 (s, 1C), 103.5 (s, 1C), 122.3 (s, 1C), 125.9 (s, 1C), 126.9 (s, 1C), 127.6 (d, 1C), 127.7 (d, 1C), 128.5 (d, 1C), 129.2 (d, 1C), 129.6 (d, 1C), 132.9 (d, 1C), 133.1 (d, 1C), 133.1 (d, 1C), 142.6 (s, 1C), 156.8 (s, 1C); **HRMS** (EI⁺): C₂₂H₂₁NO₂⁺, calculated: 387.21928 [M⁺], observed: 387.21937 [M⁺].

**Di-tert-butyl** (((2,5-bis(phenylethynyl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(2,1-phenylene))bis(methylene)dicarbamate, **5k**

According to GP1, 2.40 eq tert-butyl (2-ethynylbenzyl)carbamate (763 mg, 3.30 mmol) and later 4 mol% copper(I) iodide (10.4 mg, 55.0 µmol) were added to a mixture of 1.00 eq ((2,5-dibromo-1,4-phenylene)bis(ethyne-2,1-diyl))dibenzene (600 mg, 1.38 mmol) and 4 mol% PdCl₂(PPh₃)₂ (38.6 mg, 55.0 µmol) in 36 mL solvent. After stirring for 15 h at 65 °C, the solvent was removed under reduced pressure and the residue was adsorbed onto Celite®. The crude product was filtered through
a pad of silica gel (around 10 cm high) to remove major impurities using a mixture of PE and EA and afterwards DCM. Solvents were evaporated and the crude product was precipitated from a hot mixture of EA. The precipitate was filtered and dried under vacuum. A colourless solid was obtained (881 mg, 1.20 mmol, 87%).

**Mp**: 184-186 °C; **Rf**: 0.4 (silica gel, PE:EA = 1:2); **IR** (ATR): ν [cm⁻¹] = 3367, 2981, 2205, 1685, 1525, 1502, 1365, 1272, 1168, 930, 752, 690; **¹H NMR** (CD₂Cl₂, 400.3 MHz): δ [ppm] = 1.41 (s, 18H), 4.54 (d, 3Jₕ=H= 6.2 Hz, 4H), 5.08 (m, 2H), 7.27-7.31 (m, 2H), 7.35-7.43 (m, 10H), 7.57-7.62 (m, 6H), 7.84 (s, 2H); **¹³C NMR** (CD₂Cl₂, 100.7 MHz): δ [ppm] = 28.5 (q, 6C), 43.7 (t, 2C), 79.6 (s, 2C), 87.6 (s, 2C), 92.4 (s, 2C), 93.6 (s, 2C), 95.9 s, 2C), 121.9 (s, 2C), 123.0 (s, 2C), 125.5 (s, 2C), 125.6 (s, 2C), 127.6 (d, 2C), 128.2 (d, 2C), 129.0 (d, 4C), 129.4 (d, 2C), 129.7 (d, 2C), 132.2 (d, 4C), 132.9 (d, 2C), 136.0 (d, 2C), 141.9 (s, 2C), 156.1 (s, 2C); **HRMS** (ESI+): C₅₀H₄₄N₂NaO₄⁺, calculated: 759.3193 [M+Na +], observed: 739.3202 [M+Na +]; **UV/VIS** (DCM, 8.00 µg/mL): λ [nm] (log ε) = 300 (4.88), 317 (5.12), 352 (4.71), 368 (4.67), 379 (4.44); **Fluorescence** (DCM): λ<sub>Anr</sub> = 370 nm, λ<sub>Max</sub> = 393 nm; **Quantum yield**: Φ = 65%.

**Di-tert-butyl ((2,5-bis((2-phenylethynyl)phenyl)ethynyl)-1,4-phenylene)bis(methylene))dicarbamate, 5l**

According to GP1, 2.40 eq 1-ethynyl-2-(phenylethynyl)benzene (785 mg, 3.88 mmol) and later 5 mol% copper(I) iodide (15.4 mg, 80.9 µmol) were added to a mixture of 1.00 eq di-tert-butyl ((2,5-dibromo-1,4-phenylene)bis(methylene))dicarbamate (800 mg, 1.62 mmol) and 10 mol% Pd(PPh₃)₄ (187 mg, 161 µmol) in 42 mL solvent. After stirring for 15 h at 65 °C, the solvent was removed under reduced pressure and the residue was adsorbed onto Celite®. The crude product was filtered through a pad of silica gel (around 10 cm high) to remove major impurities using a mixture of PE and EA and afterwards DCM. Solvents were evaporated and the crude product was precipitated from a hot mixture of EA. The precipitate was filtered and dried under vacuum. A beige solid was obtained (430 mg, 584 µmol, 36%).

**Mp**: 200 °C; **Rf**: 0.22 (silica gel, PE:EA = 5:1); **IR** (ATR): ν [cm⁻¹] = 3372, 3057, 2982, 2965, 1693, 1527, 1388, 1270, 1166, 942, 752; **¹H NMR** (CDCl₃, 400.3 MHz): δ [ppm] = 1.38 (s, 18H), 4.47 (d, 3Jₕ=H= 5.1 Hz, 4H), 5.03 (m, 2H), 7.33-7.36 (m, 12H), 7.54-7.60 (m, 8H); **¹³C NMR** (CDCl₃, 100.6 MHz): δ [ppm] = 28.5 (q, 6C), 43.1 (t, 2C), 79.5 (s, 2C), 88.3 (s, 2C), 91.2 (s, 2C), 93.7 (s, 2C), 94.8 (s, 2C), 122.6 (s, 2C), 123.1 (s, 2C), 125.4 (s, 2C), 125.8 (s, 2C), 128.3 (d, 2C), 128.6 (d, 2C), 128.6 (d, 4C), 128.8 (d, 2C), 131.9 (d, 4C), 132.1 (d, 2C), 132.3 (d, 2C), 132.4 (d, 2C), 140.1 (s, 2C), 155.8 (s, 2C); **HRMS** (ESI+): C₅₀H₄₈N₃O₄⁺, calculated: 754.3639 [M+Na⁺], observed: 754.3668 [M+Na⁺]; **UV/VIS** (DCM, 9.20 µg/mL): λ [nm] (log ε) = 242 (4.58), 285 (4.67), 348 (4.53), 367 (4.45); **Fluorescence** (DCM): λ<sub>Anr</sub> = 350 nm, λ<sub>Max</sub> = 384 nm; **Quantum yield**: Φ = 74%. 

![Diagram](attachment:di-tert-butyl ((2,5-bis((2-phenylethynyl)phenyl)ethynyl)-1,4-phenylene)bis(methylene))dicarbamate, 5l.png)
Gold catalysis

tert-Butyl 11-phenylbenzo[4]phenanthridine-5(6H)-carboxylate, 6a

According to GP3, 1.00 eq of tert-butyl (2-((2-(phenylethynyl)phenyl)ethynyl)-benzyl) carbamate (1.30 g, 3.19 mmol) was dissolved in 70 mL DCE. 2.5 mol% JohnPhosAu(MeCN)SbF₆ (61.6 mg, 79.8 µmol) were added and the reaction mixture was stirred at 50 °C for 1.5 h. The solvent was removed under reduced pressure and treated as described in GP3 (silica gel, PE:EA = 20:1 to 10:1). A yellow solid was obtained (1.23 g, 3.03 mmol, 95%).

Mp: 74 °C; Rf: 0.73 (silica gel, PE:EA = 5:1); IR (ATR): ν [cm⁻¹] = 3057, 2976, 2930, 1702, 1560, 1493, 1480, 1446, 1389, 1366, 1343, 1308, 1245, 1228, 1151, 1131, 1094, 1030, 993, 957, 897, 856, 828, 760, 738, 701, 634; ¹H NMR ((CD₃)₂CO, 400.3 MHz): δ [ppm] = 1.25 (s, 9H), 4.29 (d, 2J_H-H = 14.6 Hz, 1H), 5.38 (d, 2J_H-H = 14.6 Hz, 1H), 6.88-6.94 (m, 2H), 7.20 (dt, 3J_H-H = 7.1 Hz, 4J_H-H = 1.6 Hz, 1H), 7.38-7.43 (m, 6H), 7.53-7.60 (m, 2H), 7.79 (s, 1H), 7.93-7.96 (m, 1H); ¹³C NMR ((CD₃)₂CO, 150.9 MHz): δ [ppm] = 28.1 (q, 3C), 49.3 (t, 1C), 81.3 (s, 1C), 126.4 (d, 2C), 126.6 (d, 1C), 127.1 (d, 1C), 127.5 (d, 1C), 127.9 (d, 1C), 128.8 (d, 1C), 129.3 (s, 1C), 129.4 (d, 1C), 129.6 (d, 1C), 129.8 (d, 1C), 130.3 (s, 1C), 132.5 (s, 1C), 134.0 (s, 1C), 137.9 (s, 1C), 138.3 (s, 1C), 143.3 (s, 1C), 154.3 (s, 1C); HRMS (El+): C₂₈H₂₅NO₂⁺, calculated: 407.18798 [M⁺], observed: 407.18848 [M⁺].

Four carbons (1s, 3d) were not detectable (very broad signals between 129-130 ppm).

tert-Butyl 8-fluoro-11-phenylbenzo[4]phenanthridine-5(6H)-carboxylate, 6b

According to GP3, 1.00 eq of tert-butyl (5-fluoro-2-((2-(phenylethynyl)phenyl)ethynyl)-benzyl)-carbamate (250 mg, 588 µmol) was dissolved in 25 mL DCE. 2.5 mol% JohnPhosAu(MeCN)SbF₆ (11.3 mg, 14.7 µmol) were added and the reaction mixture was stirred at 50 °C for 2 h. The solvent was removed under reduced pressure and treated as described in GP3 (silica gel, PE:EA = 20:1). An orange solid was obtained (225 mg, 529 µmol, 90%).

Mp: 103 °C; Rf: 0.48 (silica gel, PE:EA = 10:1); IR (ATR): ν [cm⁻¹] = 3057, 2978, 1703, 1562, 1488, 1386, 1367, 1342, 1305, 1272, 1238, 1150, 1124, 1030, 997, 960, 890, 858, 829, 792, 769, 701, 650; ¹H NMR ((CD₃)₂CO, 500.2 MHz): δ [ppm] = 1.25 (s, 9H), 4.31 (d, 2J_H-H = 14.8 Hz, 1H), 5.40 (d, 2J_H-H = 14.8 Hz, 1H), 6.71 (dt, 3J_H-H = 8.8 Hz, 4J_H-H = 2.8 Hz, 1H), 6.88 (dd, 3J_H-H = 5.7 Hz, 3J_H-H = 8.8 Hz, 1H), 7.27 (dd, 3J_H-H = 8.8 Hz, 4J_H-H = 2.6 Hz, 1H), 7.39-7.40 (m, 3H), 7.54-7.61 (m, 2H), 7.80 (s, 1H), 7.95 (d, 3J_H-H = 8.2 Hz, 1H), 8.03 (d, 3J_H-H = 8.4 Hz, 1H); ¹³C NMR (¹⁹F) ((CD₃)₂CO, 125.8 MHz): δ [ppm] = -116.3 (1F); HRMS (El+): C₂₈H₂₄FNO₂⁺, calculated: 425.17856 [M⁺], observed: 425.17749 [M⁺].
Two hydrogens were not detectable. (very broad aromatic signal).

Four carbon signals (4d) were not detectable (very broad signals between 129-130 ppm).

**tert-Butyl 8,9-dimethoxy-11-phenylbenzo[c]phenanthridine-5(6H)-carboxylate, 6c**

According to GP3, 1.00 eq of tert-butyl (4,5-dimethoxy-2-((2-(phenylethynyl)phenyl) ethynyl)-benzyl)carbamate (275 mg, 588 µmol) was dissolved in 25 mL DCE with 2.5 mol% JohnPhosAu(MeCN)SbF$_6$ (11.4 mg, 14.7 µmol). The reaction mixture was stirred for 4.5 h at 50 °C and further 2.5 mol% JohnPhosAu(MeCN)SbF$_6$ (11.4 mg, 14.7 µmol) were added. After stirring at 50 °C for one hour, the mixture was treated as described in GP3 (silica gel, PE:EA = 10:1). A yellow solid was obtained (122 mg, 260 µmol, 44%).

Mp: 197 °C; Rf: 0.31 (silica gel, PE:EA = 5:1); IR (ATR): ν[cm$^{-1}$] = 2977, 2936, 2835, 1691, 1607, 1516, 1489, 1449, 1366, 1327, 1279, 1250, 1223, 1161, 1140, 1100, 1053, 1038, 1025, 1004, 950, 884, 856, 838, 792, 758, 701, 671, 615; $^1$H NMR ((CD$_3$)$_2$CO, 500.2 MHz): δ[ppm] = 1.23 (s, 9H), 3.14 (s, 3H), 3.85 (s, 3H), 4.21 (d, $^2$J$_{H-H}$ = 14.6 Hz, 1H), 5.32 (d, $^2$J$_{H-H}$ = 12.2 Hz, 1H), 6.45 (s, 1H), 7.03 (s, 1H), 7.38-7.57 (m, 6H), 7.76 (s, 1H), 7.92 (d, $^3$J$_{H-H}$ = 8.1 Hz, 1H), 8.01 (d, $^3$J$_{H-H}$ = 8.3 Hz, 1H); $^{13}$C NMR ((CD$_3$)$_2$CO, 125.8 MHz): δ[ppm] = 28.1 (q, 3C), 48.3 (t, 1C), 55.0 (q, 1C), 56.0 (q, 1C), 81.2 (s, 1C), 109.7 (d, 1C), 113.8 (d, 1C), 124.7 (s, 1C), 126.3 (d, 1C), 126.5 (d, 1C), 127.0 (d, 1C), 127.9 (d, 1C), 128.8 (d, 1C), 129.3 (d, 1C), 129.5 (s, 1C), 130.8 (s, 1C), 133.5 (s, 1C), 138.1 (s, 1C), 143.8 (s, 1C), 148.1 (s, 1C), 149.4 (s, 1C), 154.4 (s, 1C); HRMS (EI+): C$_{30}$H$_{29}$NO$_4$+, calculated: 467.20911 [M$^+$], observed: 467.20845 [M$^+$].

One hydrogen was not detectable (very broad aromatic signal).

Six carbons (2s, 4d) were not detectable (very broad signals between 129-130 ppm).

**tert-Butyl 2-fluoro-11-phenylbenzo[c]phenanthridine-5(6H)-carboxylate, 6d**

According to GP3, 1.00 eq of tert-butyl (2-((4-fluoro-2-(phenylethynyl)phenyl)ethynyl)-benzyl)carbamate (250 mg, 588 µmol) was dissolved in 25 mL DCE. 2.5 mol% JohnPhosAu(MeCN)SbF$_6$ (11.3 mg, 14.7 µmol) were added. The reaction mixture was stirred at 50 °C for 2 h. The solvent was removed under reduced pressure and treated as described in GP3 (silica gel, PE:EA = 20:1). A yellow solid was obtained (167 mg, 392 µmol, 67%).

Mp: 101 °C; Rf: 0.65 (silica gel, PE:EA = 5:1); IR (ATR): ν[cm$^{-1}$] = 2977, 2930, 1701, 1631, 1561, 1481, 1450, 1392, 1367, 1338, 1291, 1242, 1224, 1151, 1127, 1029, 994, 954, 894, 856, 833, 776, 754, 735, 701, 628; $^1$H NMR ((CD$_3$)$_2$CO, 500.2 MHz): δ[ppm] = 1.25 (s, 9H), 4.30 (d, $^2$J$_{H-H}$ = 14.6 Hz, 1H), 5.37 (d, $^2$J$_{H-H}$ = 14.5 Hz, 1H), 6.87 (d, $^3$J$_{H-H}$ = 7.8 Hz, 1H), 6.92 (t, $^3$J$_{H-H}$ = 7.8 Hz, 1H), 7.21 (t, $^3$J$_{H-H}$ = 7.5 Hz, 1H), 7.39-7.44 (m, 7H), 7.67 (dd, $^3$J$_{H-H}$ = 9.9 Hz, $^4$J$_{H-H}$ = 2.6 Hz, 1H), 7.79 (s, 1H), 8.10 (dd, $^3$J$_{H-H}$ = 9.3 Hz, $^3$J$_{H-H}$ = 5.8 Hz, 1H); $^{13}$C NMR ($^{19}$F) ((CD$_3$)$_2$CO, 125.8 MHz):
δ[ppm] = 28.1 (q, 3C), 49.3 (t, 1C), 81.6 (s, 1C), 111.6 (d, 1C), 116.7 (d, 1C), 126.4 (d, 1C), 126.5 (s, 1C), 127.1 (d, 1C), 127.9 (d, 1C), 128.1 (d, 1C), 129.0 (d, 1C), 129.4 (s, 1C), 129.6 (d, 1C), 129.7 (d, 1C), 130.2 (s, 1C), 132.3 (s, 1C), 134.9 (s, 1C), 137.7 (s, 1C), 139.7 (s, 1C), 143.0 (s, 1C), 162.0 (s, 1C); 19F NMR ((CD3)2CO, 470.7 MHz): δ[ppm] = -115.7 (1F); HRMS (EI+): C28H24FNO2+, calculated: 425.17856 [M+], observed: 425.17711 [M+].

Five carbons (1s, 4d) were not detectable (very broad signals between 129-130 ppm).

**tert-Butyl 2-methyl-11-phenylbenzo[c]phenanthridine-5(6H)-carboxylate, 6e**

According to GP3, 1.00 eq of tert-butyl (2-((4-methyl-2-(phenylethynyl)-phenyl)-ethyl)benzyl)carbamate (248 mg, 588 µmol) was dissolved in 25 mL DCE. 2.5 mol% JohnPhosAu(MeCN)SbF6 (11.4 mg, 14.8 µmol) were added. The reaction mixture was stirred at 50 °C for 1 h. The solvent was removed under reduced pressure and treated as described in GP3 (silica gel, PE:EA = 20:1). A yellow solid was obtained (237 mg, 564 µmol, 96%).

Mp: 105 °C; Rf: 0.66 (silica gel, PE:EA = 5:1); IR (ATR): ν[cm⁻¹] = 2974, 2927, 2869, 1700, 1629, 1595, 1481, 1450, 1389, 1366, 1340, 1298, 1265, 1245, 1220, 1154, 1133, 1029, 993, 895, 858, 832, 774, 752, 736, 701, 652, 627; ¹H NMR ((CD3)2CO, 500.2 MHz): δ[ppm] = 1.25 (s, 9H), 2.52 (s, 3H), 4.27 (d, JH-H = 14.6 Hz, 1H), 5.36 (d, JH-H = 13.4 Hz, 1H), 6.85-6.92 (m, 2H), 7.19 (dt, JH-H = 7.4 Hz, 1H), 7.37-7.44 (m, 6H), 7.68 (s, 1H), 7.71 (s, 1H), 7.93 (d, JH-H = 8.7 Hz, 1H); ¹³C NMR ((CD3)2CO, 125.8 MHz): δ[ppm] = 21.6 (q, 1C), 28.1 (q, 3C), 49.3 (t, 1C), 81.3 (s, 1C), 126.1 (s, 1C), 126.3 (d, 2C), 127.0 (d, 1C), 127.5 (s, 1C), 127.7 (d, 2C), 127.9 (d, 1C), 128.8 (d, 1C), 129.1 (d, 1C), 129.3 (d, 1C), 129.7 (d, 1C), 130.3 (s, 1C), 132.7 (s, 1C), 134.3 (s, 1C), 137.2 (s, 1C), 137.7 (s, 1C), 138.3 (s, 1C), 143.4 (s, 1C), 154.3 (s, 1C); HRMS (EI+): C29H27NO2+, calculated: 421.20363 [M+], observed: 421.20293 [M+].

One hydrogen was not detectable. (very broad aromatic signal).

Three carbons (3d) were not detectable.

**tert-Butyl 5-phenylnaphtho[2,3-c]phenanthridine-13(14H)-carboxylate, 6f**

According to GP3, 1.00 eq of tert-butyl (2-((3-(phenylethynyl)naphthalen-2-yl)ethyl)benzyl)carbamate (269 mg, 588 µmol) was dissolved in 25 mL DCE. 2.5 mol% JohnPhosAu(MeCN)SbF6 (11.4 mg, 14.7 µmol) were added and the reaction mixture was stirred at 50 °C for 2 h. The solvent was removed under reduced pressure and treated as described in GP3 (silica gel, PE:EA = 15:1). A yellow solid was obtained (242 mg, 529 µmol, 90%).

Mp: 144 °C; Rf: 0.60 (silica gel, PE:EA = 5:1); IR (ATR): ν[cm⁻¹] = 3055, 2975, 1702, 1436, 1366, 1336, 1242, 1153, 956, 895, 859, 741, 701; ¹H NMR ((CD3)2CO, 300.2 MHz): δ[ppm] = 1.20 (s, 9H), 4.38 (d, JH-H = 14.7 Hz, 1H), 5.47 (d, JH-H = 14.7 Hz, 1H), 6.87-6.97 (m, 2H), 7.22 (dt,
$^{3}J_{H-H} = 7.1$ Hz, $^{4}J_{H-H} = 1.6$ Hz, 1H), 7.33-7.47 (m, 6H), 7.50-7.57 (m, 2H), 7.97 (s, 1H), 8.07-8.10 (m, 1H), 8.14-8.17 (m, 1H), 8.57 (s, 1H), 8.66 (s, 1H); $^{13}$C NMR ((CD$_3$)$_2$CO, 75.5 MHz): $\delta$[ppm] = 28.1 (q, 3C), 49.6 (t, 1C), 81.4 (s, 1C), 125.4 (d, 1C), 126.4 (d, 1C), 126.8 (d, 1C), 126.9 (d, 1C), 127.1 (d, 1C), 127.2 (d, 1C), 127.6 (s, 1C), 128.0 (d, 2C), 128.9 (d, 1C), 129.4 (d, 2C), 129.7 (d, 1C), 129.8 (d, 1C), 129.9 (d, 1C), 129.8 (d, 1C), 130.3 (d, 1C), 132.1 (s, 1C), 132.6 (s, 1C), 132.6 (s, 1C), 133.2 (s, 1C), 133.2 (s, 1C), 133.2 (s, 1C), 137.7 (s, 1C), 138.0 (s, 1C), 143.3 (s, 1C), 154.4 (s, 1C); HRMS (EI+): C$_{32}$H$_{27}$NO$_2^+$, calculated: 457.20363 [M+], observed: 457.20531 [M+].

Three carbons (2s, 1d) were not detectable.

tert-Butyl 11-hexylbenzo[c]phenanthridine-5(6H)-carboxylate, 6g

According to GP3, 1.00 eq of tert-butyl (2-((2-(oct-1-yn-1-yl)phenyl)ethynyl)-benzyl)-carbamate (244 mg, 587 µmol) was dissolved in 25 mL 1,2-dichloro-ethane. 2.5 mol% JohnPhosAu(MeCN)SbF$_6$ (11.4 mg, 14.8 µmol) were added. The reaction mixture was stirred at 50 °C for 1 h. The solvent was removed under reduced pressure and treated as described in GP3 (silica gel, PE:EA = 20:1). A yellow solid was obtained (239 mg, 576 µmol, 98%).

Mp: 118 °C; Rf: 0.71 (silica gel, PE:EA = 1:5); IR (ATR): $\nu$[cm$^{-1}$] = 2960, 2926, 2852, 1692, 1560, 1435, 1390, 1365, 1337, 1293, 1245, 1150, 1132, 1093, 929, 858, 765, 621; $^1$H NMR ((CD$_3$)$_2$CO, 400.3 MHz): $\delta$[ppm] = 0.84-0.87 (m, 3H), 1.23 (s, 9H), 1.28-1.30 (m, 4H), 1.37-1.39 (m, 2H), 1.66-1.79 (m, 2H), 3.08-3.12 (m, 1H), 3.23-3.27 (m, 1H), 4.04 (d, $^{2}J_{H-H} = 14.8$ Hz, 1H), 5.29 (d, $^{2}J_{H-H} = 14.7$ Hz, 1H), 7.37 (dt, $^{3}J_{H-H} = 7.4$ Hz, $^{4}J_{H-H} = 1.0$ Hz, 1H), 7.44 (dt, $^{3}J_{H-H} = 7.5$ Hz, $^{4}J_{H-H}$ = 1.1 Hz, 1H), 7.46-7.50 (m, 3H), 7.81 (s, 1H), 7.84-7.86 (m, 1H), 7.93-7.98 (m, 2H); $^{13}$C NMR ((CD$_3$)$_2$CO, 100.7 MHz): $\delta$[ppm] = 14.3 (q, 1C), 23.2 (t, 1C), 28.2 (q, 3C), 30.0 (t, 1C), 32.0 (t, 1C), 32.3 (t, 1C), 35.4 (t, 1C), 49.5 (t, 1C), 81.1 (s, 1C), 125.9 (d, 1C), 126.1 (d, 1C), 126.7 (d, 1C), 127.1 128.0 (d, 1C), 128.1 (d, 1C), 128.1 (d, 1C), 128.4 (d, 2C), 128.7 (s, 1C), 133.3 (s, 1C), 134.2 (s, 1C), 137.5 (s, 1C), 138.0 (s, 1C), 138.8 (s, 1C), 154.4 (s, 1C); HRMS (EI+): C$_{32}$H$_{27}$NO$_2^+$, calculated: 457.20585 [M+], observed: 457.20531 [M+].

One carbon (1s) was not detectable.

tert-butyl 3-(2-(3,3-dimethylbut-1-yn-1-yl)phenyl)isoquinoline-2(1H)-carboxylate, 7j

According to GP3, 1.00 eq of tert-butyl (2-((2-(3,3-dimethylbut-1-yn-1-yl)-phenyl)-ethynyl)benzyl)carbamate (182 mg, 470 µmol) was dissolved in 20 mL DCE. 2.5 mol% JohnPhosAu(MeCN)SbF$_6$ (9.10 mg, 11.7 µmol) were added. The reaction mixture was stirred at 50 °C for 2 h. The solvent was removed under reduced pressure and treated as described in GP3 (silica gel, PE:EA = 20:1). A colorless solid was obtained (159 mg, 411 µmol, 87%).

Mp: 124 °C; Rf: 0.67 (silica gel, PE:EA = 5:1); IR (ATR): $\nu$[cm$^{-1}$] = 2971, 2927, 2864, 2239, 1697, 1612, 1474, 1446, 1365, 1312, 1234, 1157, 1129, 987, 941, 866, 828, 791, 761, 744, 726, 630,
$^1$H NMR ((CD$_3$)$_2$CO, 500.2 MHz): $\delta$[ppm] = 1.04 (s, 9H), 1.33 (s, 9H), 4.91 (s, 2H), 6.35 (s, 1H), 7.23-7.32 (m, 5H), 7.35 (dt, $^3\lambda_{H-H}$ = 7.5 Hz, $^4\lambda_{H-H}$ = 1.5 Hz, 1H), 7.42 (dd, $^3\lambda_{H-H}$ = 7.5 Hz, $^4\lambda_{H-H}$ = 1.5 Hz, 1H), 7.49 (dd, $^3\lambda_{H-H}$ = 7.6 Hz, $^4\lambda_{H-H}$ = 1.4 Hz, 1H); $^{13}$C NMR ((CD$_3$)$_2$CO, 125.8 MHz): $\delta$[ppm] = 27.8 (q, 3C), 28.7 (s, 1C), 31.5 (q, 3C), 47.6 (t, 1C), 78.6 (s, 1C), 80.6 (s, 1C), 102.7 (s, 1C), 116.7 (d, 1C), 122.9 (s, 1C), 125.8 (d, 1C), 125.9 (d, 1C), 128.1 (d, 1C), 128.2 (d, 1C), 128.4 (d, 1C), 128.6 (d, 1C), 128.7 (d, 1C), 132.8 (s, 1C), 133.6 (s, 1C), 133.6 (d, 1C), 141.0 (s, 1C), 142.1 (s, 1C), 152.5 (s, 1C); HRMS (EI+): C$_{26}$H$_{29}$NO$_2^+$, calculated: 387.21928 [M+], observed: 387.22032 [M+].

Di-tert-butyl 8,17-diphenyl-6,15-dihydrobenzo[c]benzo[7,8]quinolino[4,3-j]phenanthridine-5,14-dicarboxylate, 6k

According to GP3, 1.00 eq (400 mg, 543 µmol) was dissolved in 50 mL DCE. 5 mol% JohnPhosAu(MeCN)SbF$_6$ (21.0 mg, 27.1 µmol) were added and the reaction mixture was stirred at 50 °C for 5 h. The solvent was removed under reduced pressure and the residue was adsorbed onto Celite®. The crude product was filtered through a pad of silica gel (around 10 cm high) to remove major impurities using a mixture of PE and EA and afterwards DCM. Solvents were evaporated and the crude product was directly used for the next step.

Di-tert-butyl 5,14-diphenyl-9,18-dihydrobenzo[1,2-c,4,5-c']diphenanthridine-8,17-dicarboxylate, 6l

According to GP3, 1.00 eq (800 mg, 1.09 mmol) was dissolved in 150 mL DCE. 5 mol% JohnPhosAu(MeCN)SbF$_6$ (41.9 mg, 54.3 µmol) were added and the reaction mixture was stirred at 50 °C for 2 h. The solvent was removed under reduced pressure and the residue was adsorbed onto Celite®. The crude product was filtered through a pad of silica gel (around 10 cm high) to remove major impurities using a mixture of PE and EA and afterwards DCM. Solvents were evaporated and the crude product was precipitated from a hot mixture of EA and PE. The precipitate was filtered and dried under vacuum. The title compound was obtained as a greenish solid in two isomers (523 mg, 710 µmol, 65%, major:minor isomer = 2:1).

$^1$H-NMR (CDCl$_3$, 600.2 MHz): $\delta$[ppm] = 1.21 (bs, 18H), 4.36 (d, $^2\lambda_{H-H}$= 14.5 Hz, 2H), 5.43 (m, 2H), 6.86-6.96 (m, 4H), 7.17-7.21 (m, 2H), 7.23-7.75 (m, 12H), 7.88 (s, 2H)$^b$, 7.90 (s, 2H)$^b$, 8.56 (s, 2H)$^b$, 8.59 (s, 2H)$^b$

$^a$ major isomer, $^b$ minor isomer
Boc cleavage and Oxidation

11-Phenylbenzo[c]phenanthridine, 13a

According to GP4, 1.00 eq of tert-butyl 11-phenylbenzo[c]phenanthridine-5(6H)-carboxylate (500 mg, 1.23 mmol) was heated up to 200 °C under nitrogen atmosphere for overall 6 h. The reaction was treated according to GP4 (3 h air treatment) and the title compound was obtained as a brownish solid in quantitative yield (375 mg, 1.23 mmol).

Mp: 169 °C; Rf: 0.22 (silica gel, PE:EA = 5:1); IR (ATR): ν[cm⁻¹] = 3066, 3026, 1954, 1935, 1615, 1586, 1520, 1494, 1471, 1437, 1372, 1284, 1251, 1217, 1077, 1030, 977, 960, 933, 919, 899, 860, 815, 762, 706, 655, 608; ¹H NMR (CDCl₃, 400.3 MHz): δ[ppm] = 7.34-7.39 (m, 1H), 7.48-7.53 (m, 5H), 7.56-7.60 (m, 1H), 7.64 (d, 3JH-H = 8.7 Hz, 1H), 7.96-7.97 (m, 1H), 7.76-7.80 (m, 1H), 7.88 (s, 1H), 7.94 (d, 3JH-H = 7.9 Hz, 1H), 8.10 (dd, 3JH-H = 7.9 Hz, 1H), 9.46 (d, 3JH-H = 8.2 Hz, 1H), 9.50 (s, 1H); ¹³C NMR (CDCl₃, 100.7 MHz): δ[ppm] = 120.5 (s, 1C), 125.2 (d, 1C), 126.8 (d, 1C), 127.1 (d, 1C), 127.2 (d, 1C), 127.5 (d, 1C), 127.6 (d, 1C), 128.0 (d, 1C), 128.7 (d, 1C), 129.1 (d, 2C), 129.3 (d, 2C), 129.5 (d, 1C), 130.9 (d, 1C), 131.6 (s, 1C), 132.4 (s, 1C), 133.3 (s, 1C), 137.6 (s, 1C), 142.8 (s, 1C), 144.5 (s, 1C), 152.6 (d, 1C); HRMS (EI+): C₂₃H₁₅N⁺, calculated: 305.11990 [M⁺], observed: 305.11910 [M⁺].

8-Fluoro-11-phenylbenzo[c]phenanthridine, 13b

According to GP4, 1.00 eq of tert-butyl 8-fluoro-11-phenylbenzo[c]phenanthridine-5(6H)-carboxylate (100 mg, 235 µmol) was heated up to 200 °C under nitrogen atmosphere for overall 6 h. The reaction was treated according to GP4 (3 h air treatment) and the title compound was obtained as a brownish solid in quantitative yield (76.0 mg, 235 µmol).

Mp: 166 °C; Rf: 0.31 (silica gel, PE:EA = 5:1); IR (ATR): ν[cm⁻¹] = 3057, 3010, 1940, 1904, 1868, 1619, 1587, 1571, 1523, 1493, 1463, 1443, 1412, 1357, 1279, 1223, 1149, 1136, 1073, 1024, 968, 953, 936, 899, 865, 834, 801, 765, 746, 714, 695, 665, 651; ¹H NMR (CDCl₃, 500.2 MHz): δ[ppm] = 7.10-7.14 (m, 1H), 7.46-7.54 (m, 5H), 7.64 (dd, 3JH-H = 9.5 Hz, 3JH-H = 5.1 Hz, 1H), 7.70-7.73 (m, 2H), 7.77-7.81 (m, 1H), 7.89 (s, 1H), 7.95 (d, 3JH-H = 7.9 Hz, 1H), 9.42-9.45 (m, 2H); ¹³C NMR (¹⁹F) (CDCl₃, 125.8 MHz): δ[ppm] = 112.2 (d, 1C), 119.1 (d, 1C), 120.4 (s, 1C), 125.0 (d, 1C), 127.4 (d, 1C), 127.6 (d, 1C), 127.8 (d, 1C), 128.1 (d, 1C), 129.2 (d, 2C), 129.3 (d, 2C), 129.9 (d, 1C), 130.1 (s, 1C), 131.4 (d, 1C), 132.3 (s, 1C), 137.1 (s, 1C), 144.1 (s, 1C), 151.4 (d, 1C), 160.6 (s, 1C); ¹⁹F NMR (CDCl₃, 470.7 MHz): δ[ppm] = -113.2 (1F); HRMS (EI+): C₂₃H₁₄F⁺N⁺, calculated: 323.11048 [M⁺], observed: 323.11068 [M⁺].

Three carbons (3s) were not detectable.
8,9-Dimethoxy-11-phenylbenzo[c]phenanthridine, 13c

According to GP4, 1.00 eq of tert-butyl 8,9-dimethoxy-11-phenylbenzo[c]phenanthridine-5(6H)-carboxylate (50.0 mg, 107 µmol) was heated up to 200 °C under nitrogen atmosphere for overall 4 h. The reaction was treated according to GP4 (1 h air treatment) and the title compound was obtained as a yellow solid in quantitative yield (39.1 mg, 107 µmol).

\( \text{Mp}: 185 ^\circ \text{C}; \ \text{Rf}: 0.65 \) (silica gel, PE:EA = 1:1); \( \text{IR} \) (ATR): \( \nu[\text{cm}^{-1}] = 3162, 3060, 2994, 2958, 2932, 1617, 1588, 1518, 1480, 1462, 1422, 1392, 1296, 1275, 1261, 1225, 1200, 1188, 1155, 1074, 1050, 1027, 993, 944, 927, 909, 891, 854, 834, 800, 771, 757, 732, 711, 700, 684, 646, 626, 616; \( ^1\text{H NMR} \) (CDCl\(_3\), 300.5 MHz): \( \delta[\text{ppm}] = 3.31 \) (s, 3H), 4.01 (s, 3H), 7.11 (s, 1H), 7.29 (s, 1H), 7.41-7.54 (m, 5H), 7.64-7.70 (m, 1H), 7.73-7.78 (m, 2H), 7.90 (d, \( ^3J_{HH} = 7.8 \) Hz, 1H), 9.27 (s, 1H), 9.41 (d, \( ^3J_{HH} = 8.3 \) Hz, 1H); \( ^{13}\text{C NMR} \) (CDCl\(_3\), 75.6 MHz): \( \delta[\text{ppm}] = 55.0 \) (q, 1C), 56.0 (q, 1C), 106.9 (d, 1C), 107.6 (d, 1C), 119.8 (s, 1C), 123.8 (s, 1C), 124.9 (d, 1C), 126.9 (d, 1C), 127.4 (d, 1C), 127.6 (d, 1C), 128.9 (s, 1C), 129.1 (d, 2C), 129.6 (d, 2C), 130.1 (d, 1C), 131.9 (s, 1C), 131.9 (s, 1C), 137.1 (s, 1C), 142.2 (s, 1C), 144.9 (s, 1C), 149.2 (s, 1C), 150.4 (d, 1C), 151.0 (s, 1C); \( \text{HRMS} \) (EI+): C\(_{25}\)H\(_{19}\)NO\(_2\)\(^+\), calculated: 365.14103 \[M^+\], observed: 365.14029 \[M^+\].

2-Fluoro-11-phenylbenzo[c]phenanthridine, 13d

According to GP4, 1.00 eq of tert-butyl 2-fluoro-11-phenylbenzo[c]phenanthridine-5(6H)-carboxylate (100 mg, 235 µmol) was heated up to 200 °C under nitrogen atmosphere for overall 6 h. The reaction was treated according to GP4 (2 h air treatment) and the title compound was obtained as a brownish solid in quantitative yield (76.0 mg, 235 µmol).

\( \text{Mp}: 166 ^\circ \text{C}; \ \text{Rf}: 0.26 \) (silica gel, PE:EA = 5:1); \( \text{IR} \) (ATR): \( \nu[\text{cm}^{-1}] = 3060, 1920, 1858, 1624, 1575, 1522, 1493, 1468, 1447, 1427, 1376, 1352, 1301, 1279, 1246, 1213, 1147, 1121, 1074, 1028, 968, 927, 895, 848, 834, 803, 780, 756, 701, 656; \( ^1\text{H NMR} \) (CDCl\(_3\), 500.2 MHz): \( \delta[\text{ppm}] = 7.36-7.39 \) (m, 1H), 7.46-7.56 (m, 7H), 7.57-7.61 (m, 2H), 7.80 (s, 1H), 8.10 (d, \( ^3J_{HH} = 8.0 \) Hz, 1H), 9.46-9.48 (m, 2H); \( ^{13}\text{C NMR} \) (\( ^{19}\text{F} \)) (CDCl\(_3\), 125.8 MHz): \( \delta[\text{ppm}] = 111.1 \) (d, 1C), 116.7 (d, 1C), 119.9 (s, 1C), 126.9 (d, 1C), 127.1 (d, 1C), 127.8 (d, 1C), 128.1 (d, 1C), 128.3 (s, 1C), 128.9 (d, 1C), 129.1 (d, 2C), 129.2 (d, 2C), 129.8 (d, 1C), 130.1 (d, 1C), 133.2 (s, 1C), 133.5 (s, 1C), 139.0 (s, 1C), 142.5 (s, 1C), 144.0 (s, 1C), 152.8 (d, 1C), 162.5 (s, 1C); \( ^{19}\text{F NMR} \) (CDCl\(_3\), 470.7 MHz): \( \delta[\text{ppm}] = -113.0 \) (1F); \( \text{HRMS} \) (EI+): C\(_{23}\)H\(_{14}\)FN\(^+\), calculated: 323.11048 \[M^+\], observed: 323.11057 \[M^+\].

One carbon (1s) was not detectable.
2-Methyl-11-phenylbenzo[c]phenanthridine, 13e

According to GP4, 1.00 eq of tert-butyl 2-methyl-11-phenylbenzo[c]-phenanthridine-5(6H)-carboxylate (150 mg, 356 µmol) was heated up to 200 °C under nitrogen atmosphere for overall 3 h. The reaction was treated according to GP4 (3 h air treatment) and the title compound was obtained as a yellow solid in quantitative yield (114 mg, 356 µmol).

Mp: 195 °C; Rf: 0.25 (silica gel, PE:EA = 5:1); IR (ATR): ν [cm⁻¹] = 3058, 3030, 2913, 2854, 1614, 1591, 1523, 1492, 1467, 1443, 1369, 1280, 1250, 1217, 1160, 1135, 1073, 1026, 959, 948, 921, 902, 884, 869, 833, 803, 773, 760, 749, 696, 655, 616; ¹H NMR (CDCl₃, 500.2 MHz): δ[ppm] = 2.61 (s, 3H), 7.34-7.38 (m, 1H), 7.47-7.53 (m, 5H), 7.56 (t, ³J_H⁻H = 7.9 Hz, 1H), 7.61 (d, ³J_H⁻H = 8.7 Hz, 2H), 7.71 (s, 1H), 7.80 (s, 1H), 8.09 (d, ³J_H⁻H = 7.9 Hz, 1H), 9.33 (d, ³J_H⁻H = 8.6 Hz, 1H), 9.48 (s, 1H); ¹³C NMR (CDCl₃, 125.8 MHz): δ[ppm] = 21.9 (q, 1C), 119.9 (s, 1C), 125.0 (d, 1C), 126.6 (d, 1C), 126.8 (d, 1C), 127.1 (d, 1C), 127.5 (d, 1C), 127.8 (s, 1C), 128.8 (d, 1C), 129.1 (d, 2C), 129.3 (d, 2C), 129.3 (d, 1C), 129.5 (s, 1C), 129.5 (d, 1C), 130.7 (d, 1C), 132.6 (s, 1C), 133.4 (s, 1C), 137.6 (s, 1C), 138.0 (s, 1C), 144.5 (s, 1C), 152.4 (d, 1C); HRMS (EI+): C₂₄H₁₇N⁺, calculated: 319.13555 [M⁺], observed: 319.13446 [M⁺].

One carbon (1s) was not detectable.

5-Phenylnaphtho[2,3-c]phenanthridine, 13f

According to GP4, 1.00 eq of tert-butyl 5-phenylnaphtho[2,3-c]phenanthridine-13(14H)-carboxylate (150 mg, 328 µmol) was heated up to 200 °C under nitrogen atmosphere for overall 7 h. The reaction was treated according to GP4 (8 h air treatment). Due to significant impurities the residue was dissolved in chloroform and filtrated over silica gel. A yellow solid was obtained (44.9 mg, 126 µmol, 39%).

Mp: 206-208 °C; Rf: 0.19 (silica gel, PE:EA = 5:1); IR (ATR): ν [cm⁻¹] = 3051, 3029, 2958, 2924, 2852, 1947, 1810, 1739, 1615, 1600, 1583, 1536, 1492, 1478, 1444, 1392, 1274, 1231, 1193, 1133, 1025, 951, 935, 907, 871, 809, 793, 739, 700, 686, 653, 615; ¹H NMR (CDCl₃, 300.5 MHz): δ[ppm] = 7.34-7.39 (m, 1H), 7.51-7.64 (m, 9H), 7.96 (s, 1H), 8.07-8.13 (m, 2H), 8.27-8.30 (m, 1H), 8.45 (s, 1H), 9.54 (s, 1H), 9.98 (s, 1H); ¹³C NMR (CDCl₃, 150.9 MHz): δ[ppm] = 120.4 (s, 1C), 124.6 (d, 1C), 125.9 (d, 1C), 126.0 (d, 1C), 126.3 (d, 1C), 126.7 (d, 1C), 127.2 (d, 1C), 127.6 (d, 1C), 127.9 (d, 1C), 128.3 (s, 1C), 128.7 (d, 1C), 129.1 (d, 2C), 129.2 (d, 2C), 129.3 (d, 1C), 129.5 (d, 1C), 130.7 (s, 1C), 131.3 (d, 1C), 132.5 (s, 1C), 133.0 (s, 1C), 133.3 (s, 1C), 137.4 (s, 1C), 143.7 (s, 1C), 144.4 (s, 1C), 152.4 (d, 1C); HRMS (EI+): C₂₇H₁₇N⁺, calculated: 355.13555 [M⁺], observed: 355.13504 [M⁺].
11-Hexylbenzo[c]phenanthridine, 13g

According to GP4, 1.00 eq of tert-butyl 11-hexylbenzo[c]phenanthridine-5(6H)-carboxylate (150 mg, 361 µmol) was heated up to 200 °C under nitrogen atmosphere for overall 6 h. The reaction was treated according to GP4 (5.5 h air treatment) and the title compound was obtained as a brown solid in quantitative yield (113.2 mg, 361 µmol).

** Mp: 65 °C; Rf: 0.28 (silica gel, PE:EA = 5:1); IR (ATR): ν [cm⁻¹] = 3055, 2951, 2929, 2853, 1615, 1592, 1573, 1524, 1463, 1373, 1268, 1218, 1034, 956, 935, 906, 875, 856, 848, 760, 743, 726, 658, 618; H NMR (CDCl₃, 500.2 MHz): δ [ppm] = 0.92 (t, 3JH-H = 7.1 Hz, 3H), 1.33-1.41 (m, 4H), 1.53-1.58 (m, 2H), 1.89-1.94 (m, 2H), 3.53 (t, 3JH-H = 7.8 Hz, 2H), 7.66-7.76 (m, 3H), 7.86-7.91 (m, 3H), 8.18 (dd, 3JH-H = 7.9 Hz, 4JH-H = 1.0 Hz, 1H), 8.84 (d, 3JH-H = 8.7 Hz, 1H), 9.40 (d, 3JH-H = 8.1 Hz, 1H), 9.47 (s, 1H); C NMR (CDCl₃, 125.8 MHz): δ [ppm] = 14.2 (q, 1C), 22.8 (t, 1C), 29.6 (t, 1C), 30.7 (t, 1C), 31.9 (t, 1C), 38.7 (t, 1C), 121.6 (s, 1C), 125.3 (d, 1C), 126.5 (d, 1C), 126.7 (d, 1C), 126.8 (d, 1C), 127.8 (d, 1C), 127.9 (s, 1C), 129.4 (d, 1C), 130.0 (d, 1C), 130.5 (d, 1C), 131.1 (s, 1C), 132.7 (s, 1C), 133.7 (s, 1C), 137.2 (s, 1C), 143.0 (s, 1C), 151.9 (d, 1C); HRMS (EI+): C23H23N+ calculated: 313.18250 [M+], observed: 313.18132 [M+].

5,14-Diphenylbenzo[1,2-c4,5-c’]diphenanthridine, 13k

According to GP4, 1.00 eq 6k (250 mg, 339 µmol) was heated up to 200 °C under nitrogen atmosphere for overall 6 h. The reaction was treated according to GP4 (8 h air treatment). The crude product was filtered through a pad of silica gel (around 10 cm high) to remove major impurities using a mixture of PE and EA and afterwards DCM. Solvents were evaporated and the crude product was precipitated from a hot mixture of EA and PE. The precipitate was filtered and dried under vacuum. A yellow solid was obtained (139 mg, 261 µmol, 77%).

** Mp: >300°C; Rf: 0.36 (silica gel, PE:EA = 5:1); IR (ATR): ν [cm⁻¹] = 3059, 3023, 1837, 1615, 1581, 1539, 1493, 1223, 911, 767, 753; H NMR (d₂-TCE, 400.3 MHz): δ [ppm] = 7.44 (t, 3JH-H = 7.5 Hz, 2H), 7.58-7.69 (m, 14H), 8.18 (d, 3JH-H = 7.7 Hz, 2H), 8.29 (s, 2H), 9.61 (s, 2H), 10.05 (s, 2H); C NMR (d₂-TCE, 100.7 MHz): δ [ppm] = 120.7 (s, 2C), 123.9 (d, 2C), 126.8 (d, 2C), 127.0 (d, 2C), 127.5 (d, 2C), 128.0 (s, 2C), 128.5 (d, 2C), 129.0 (d, 4C), 129.0 (d, 4C), 129.4 (d, 2C), 130.9 (s, 2C), 131.0 (s, 2C), 131.7 (d, 2C), 132.9 (s, 2C), 137.5 (s, 2C), 142.7 (s, 2C), 143.8 (s, 2C), 152.4 (d, 2C); HRMS (EI+): C₆₀H₃₅N₂⁺ calculated: 313.18250 [M⁺], observed: 313.18132 [M⁺]; UV/VIS (DCM; 7.00 µg/mL): λ [nm] (logε) = 279 (4.46), 315 (4.92), 333 (4.69), 363 (4.05), 384 (4.12), 405 (4.13); Fluorescence (DCM): λMax = 405 nm, λMax = 449 nm, 424 nm; Quantum yield: Φ = 26%
According to GP4, 237 mg of the residue containing 6l were heated up to 200 °C under nitrogen atmosphere for overall 5 h. The reaction was treated according to GP4 (6 h air treatment). The crude product was filtered through a pad of silica gel (around 10 cm high) to remove major impurities using a mixture of PE and EA and afterwards DCM. Solvents were evaporated and the crude product was precipitated from a hot mixture of EA and PE. The precipitate was filtered and dried under vacuum. A yellow solid was obtained (96.0 mg, 180 µmol, 33% over two steps).

**Mp.:** >300 °C; **Rf:** 0.59 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm⁻¹] = 3043, 1592, 1549, 1495, 1442, 1339, 930, 889, 772, 753; **¹H NMR** (d₂-TCE, 500.2 MHz, 373 K): δ[ppm] = 7.64-7.72 (m, 10H), 7.76-7.83 (m, 4H), 8.02-8.03 (m, 4H), 8.27 (s, 2H), 9.08 (s, 2H), 9.48 (d, 3JH-H= 8.2 Hz, 2H); **¹³C NMR** (d₂-TCE, 125.8 MHz, 373 K): δ[ppm] = 119.3 (s, 2C), 125.3 (d, 2C), 126.8 (d, 2C), 127.2 (d, 2C), 127.4 (s, 2C), 127.8 (d, 4C), 128.1 (d, 2C), 129.1 (d, 4C), 129.3 (d, 4C), 129.6 (s, 2C), 130.4 (d, 2C), 131.6 (s, 2C), 132.5 (s, 2C), 137.6 (s, 2C), 143.9 (s, 2C), 154.7 (s, 2C); **HRMS** (EI⁺): C₄₀H₂₄N₂⁺, calculated: 532.1934 [M⁺], observed: 532.1944 [M⁺]; **UV/VIS** (DCM; 5.00 µg/mL): λ[nm] (logε) = 263 (4.70), 291 (4.81), 316 (4.74), 329 (4.81), 335 (4.75), 365 (4.00), 401 (3.91), 425 (3.98); **Fluorescence** (DCM): λAnr = 425 nm, λMax = 464 nm, 439 nm; **Quantum yield:** Φ = 27%

One carbon (1s) was not detectable.
5. NMR Spectra

$^1$H NMR spectrum of 3-(Phenylethynyl)naphthalen-2-yl trifluoromethanesulfonate in CDCl$_3$ at 500.2 MHz.

$^{13}$C NMR ($^{19}$F) spectrum of 3-(Phenylethynyl)naphthalen-2-yl trifluoromethanesulfonate in CDCl$_3$ at 125.8 MHz.
$^{19}$F NMR spectrum of 3-(Phenylethynyl)naphthalen-2-yl trifluoromethanesulfonate in CDCl$_3$ at 470.7 MHz.
$^1$H NMR spectrum of tert-Butyl (2-((2-bromophenyl)ethynyl)benzyl)carbamate in (CD$_3$)$_2$CO at 500.2 MHz.

$^{13}$C NMR spectrum of tert-Butyl (2-((2-bromophenyl)ethynyl)benzyl)carbamate in (CD$_3$)$_2$CO at 125.8 MHz.
$^1$H NMR spectrum of 5-Fluoro-2-((2-(phenylethynyl)phenyl)ethynyl)benzaldehyde in CD$_2$Cl$_2$ at 500.2 MHz.

$^{13}$C NMR ($^{19}$F) spectrum of 5-Fluoro-2-((2-(phenylethynyl)phenyl)ethynyl)benzaldehyde in CD$_2$Cl$_2$ at 125.8 MHz.
$^{19}$F NMR spectrum of 5-Fluoro-2-((2-(phenylethynyl)phenyl)ethynyl)benzaldehyde in CD$_2$Cl$_2$ at 470.7 MHz.
$^1$H NMR spectrum of 4,5-Dimethoxy-2-((2-(phenylethynyl)phenyl)ethynyl)benzaldehyde in CDCl$_3$ at 400.3 MHz.

$^{13}$C NMR spectrum of 4,5-Dimethoxy-2-((2-(phenylethynyl)phenyl)ethynyl)benzaldehyde in CDCl$_3$ at 100.7 MHz.
$^1$H NMR spectrum of tert-Butyl (2-((2-bromo-4-fluorophenyl)ethynyl)benzyl)carbamate in (CD$_3$)$_2$CO at 500.2 MHz.

$^{13}$C NMR ($^{19}$F) spectrum of tert-Butyl (2-((2-bromo-4-fluorophenyl)ethynyl)benzyl)carbamate in (CD$_3$)$_2$CO at 125.8 MHz.
$^{19}$F NMR spectrum of tert-Butyl (2-((2-bromo-4-fluorophenyl)ethynyl)benzyl)carbamate in (CD$_3$)$_2$CO at 470.7 MHz.
$^1$H NMR spectrum of tert-Butyl (2-((2-bromo-4-methylphenyl)ethynyl)benzyl)carbamate in (CD$_3$)$_2$CO at 400.3 MHz.

$^{13}$C NMR spectrum of tert-Butyl (2-((2-bromo-4-methylphenyl)ethynyl)benzyl)carbamate in (CD$_3$)$_2$CO at 100.7 MHz.
$^1$H NMR spectrum of 5a in (CD$_3$)$_2$CO at 400.3 MHz.

$^{13}$C NMR spectrum of 5a in (CD$_3$)$_2$CO at 100.7 MHz.
$^1$H NMR spectrum of 5b in CDCl$_3$ at 500.2 MHz.

$^{13}$C NMR ($^{19}$F) spectrum of 5b in CDCl$_3$ at 125.8 MHz.
$^{19}$F NMR spectrum of 5b in CDCl$_3$ at 470.7 MHz.
$^1$H NMR spectrum of $5c$ in CDCl$_3$ at 400.3 MHz.

$^{13}$C NMR spectrum of $5c$ in CDCl$_3$ at 100.7 MHz.
$^1$H NMR spectrum of 5d in (CD$_3$)$_2$CO at 500.2 MHz.

$^{13}$C NMR ($^{19}$F) spectrum of 5d in (CD$_3$)$_2$CO at 125.8 MHz.
$^{19}$F NMR spectrum of 5d in (CD$_3$)$_2$CO at 470.7 MHz.
$^1$H NMR spectrum of 5e in (CD$_3$)$_2$CO at 300.2 MHz.

$^{13}$C NMR spectrum of 5e in (CD$_3$)$_2$CO at 75.5 MHz.
$^1$H NMR spectrum of 5f in (CD$_3$)$_2$CO at 400.3 MHz.

$^{13}$C NMR spectrum of 5f in (CD$_3$)$_2$CO at 100.7 MHz.
$^1$H NMR spectrum of 5g in (CD$_3$)$_2$CO at 500.2 MHz.

$^{13}$C NMR spectrum of 5g in (CD$_3$)$_2$CO at 125.8 MHz.
$^1$H NMR spectrum of 5h in (CD$_3$)$_2$CO at 500.2 MHz.

$^{13}$C NMR spectrum of 5h in (CD$_3$)$_2$CO at 125.8 MHz.
$^1$H NMR spectrum of 5i in (CD$_3$)$_2$CO at 500.2 MHz.

$^{13}$C NMR spectrum of 5i in (CD$_3$)$_2$CO at 125.8 MHz.
$^1$H NMR spectrum of 5j in (CD$_3$)$_2$CO at 500.2 MHz.

$^{13}$C NMR spectrum of 5j in (CD$_3$)$_2$CO at 125.8 MHz.
$^1$H NMR spectrum of $5k$ in CD$_2$Cl$_2$ at 400.3 MHz.

$^{13}$C NMR spectrum of $5k$ in CD$_2$Cl$_2$ at 100.7 MHz.
$^1$H NMR spectrum of $5I$ in CDCl$_3$ at 400.3 MHz.

$^{13}$C NMR spectrum of $5I$ in CDCl$_3$ at 100.7 MHz.
\(^1\)H NMR spectrum of 6a in (CD\(_3\))\(_2\)CO at 400.3 MHz.

\(^{13}\)C NMR spectrum of 6a in (CD\(_3\))\(_2\)CO at 150.9 MHz.
$^1$H NMR spectrum of $6b$ in (CD$_3$)$_2$CO at 500.2 MHz.

$^{13}$C NMR spectrum of $6b$ in (CD$_3$)$_2$CO at 125.8 MHz.
$^{19}$F NMR spectrum of 6b in $(CD_3)_2CO$ at 470.7 MHz.
$^1$H NMR spectrum of 6c in CDCl$_3$ at 500.2 MHz.

$^{13}$C NMR spectrum of 6c in CDCl$_3$ at 125.8 MHz.
$^1$H NMR spectrum of 6d in (CD$_3$)$_2$CO at 500.2 MHz.

$^{13}$C NMR spectrum of 6d in (CD$_3$)$_2$CO at 125.8 MHz.
$^{19}$F NMR spectrum of 6d in (CD$_3$)$_2$CO at 470.7 MHz.
\( ^1\)H NMR spectrum of 6e in (CD\(_3\))\(_2\)CO at 500.2 MHz.

\( ^{13}\)C NMR spectrum of 6e in (CD\(_3\))\(_2\)CO at 125.8 MHz.
\(^1\)H NMR spectrum of 6f in (CD\(_3\)\(_2\)CO at 300.2 MHz.

\(^1\)C NMR spectrum of 6f in (CD\(_3\)\(_2\)CO at 75.5 MHz.
$^1$H NMR spectrum of 6g in (CD$_3$)$_2$CO at 400.3 MHz.

$^{13}$C NMR spectrum of 6g in (CD$_3$)$_2$CO at 100.7 MHz.
$^1$H NMR spectrum of 7j in (CD$_3$)$_2$CO at 500.2 MHz.

$^{13}$C NMR spectrum of 7j in (CD$_3$)$_2$CO at 125.8 MHz.
$^1$H NMR spectrum of 6k in CDCl$_3$ at 600.2 MHz.
$^1$H NMR spectrum of 13a in CDCl$_3$ at 400.3 MHz.

$^{13}$C NMR spectrum of 13a in CDCl$_3$ at 100.7 MHz.
$^1$H NMR spectrum of $^{13b}$ in CDCl$_3$ at 500.2 MHz.

$^{13}$C NMR spectrum of $^{13b}$ in CDCl$_3$ at 125.8 MHz.
$^{19}$F NMR spectrum of 13b in CDCl$_3$ at 470.7 MHz.
$^1$H NMR spectrum of 13c in CDCl$_3$ at 300.5 MHz.

$^{13}$C NMR spectrum of 13c in CDCl$_3$ at 75.6 MHz.
$^1$H NMR spectrum of 13d in CDCl$_3$ at 500.2 MHz.

$^{13}$C NMR spectrum of 13d in CDCl$_3$ at 125.8 MHz.
$^{19}$F NMR spectrum of **13d** in CDCl$_3$ at 470.7 MHz.
$^1$H NMR spectrum of **13e** in CDCl$_3$ at 500.2 MHz.

$^{13}$C NMR spectrum of **13e** in CDCl$_3$ at 125.8 MHz.
$^1$H NMR spectrum of 13f in CDCl$_3$ at 300.5 MHz.

$^{13}$C NMR spectrum of 13f in (CD$_3$)$_2$CO at 150.9 MHz.
$^1$H NMR spectrum of $^{13}$g in CDCl$_3$ at 500.2 MHz.

$^{13}$C NMR spectrum of $^{13}$g in CDCl$_3$ at 125.8 MHz.
$^1$H NMR spectrum of 13k in d$_2$-TCE at 400.3 MHz.

$^{13}$C NMR spectrum of 13k in d$_2$-TCE at 100.7 MHz.
$^1$H NMR spectrum of 13l in d$_2$-TCE at 500.2 MHz (373 K).

$^{13}$C NMR spectrum of 13l in d$_2$-TCE at 125.8 MHz (373 K).
6. Absorption and Emission Spectra

Figure SI1: Absorption spectra of 13k and 13l in DCM.

Figure SI2: Emission spectra of 13k and 13l in DCM.
7. Calculations and NMR experiments for the rotation barrier

Relaxed scans in steps of 2 degrees were performed on the PBE0-D3/aug-pcseg-1 level of theory using the TeraChem software package.[9,10]

Figure SI3: Relaxed scan (in steps of 2 degrees) of the highlighted dihedral angle involving the boc group.
Figure SI4: Relaxed scan (in steps of 2 degrees) of the highlighted dihedral angle involving the phenyl group.

Figure SI5: $^1$H NMR spectrum of the aromatic region (7.80-8.00 ppm) of $6k$ in CDCl$_3$ at different temperatures with a coalescence temperature of 318 K.
8. AFM/SEM Images

Figure SI6: Atomic force microscopy (AFM) images (left: amplitude, right: topography) of 13k deposited by thermal sublimation in vacuum onto a silicon substrate coated with thermally grown silicon dioxide, atomic-layer-deposited aluminum oxide and an alkylphosphonic acid self-assembled monolayer.

Figure SI7: Scanning electron microscopy (SEM) image of 13k deposited by thermal sublimation in vacuum onto a silicon substrate coated with thermally grown silicon dioxide, atomic-layer-deposited aluminum oxide and a fluoroalkylphosphonic acid self-assembled monolayer.
FigureSI8: AFM images (left: amplitude, right: topography) of 13I deposited by thermal sublimation in vacuum onto a silicon substrate coated with thermally grown silicon dioxide, atomic-layer-deposited aluminum oxide and an alkylphosphonic acid self-assembled monolayer.

FigureSI9: SEM image of 13I deposited by thermal sublimation in vacuum onto a silicon substrate coated with thermally grown silicon dioxide, atomic-layer-deposited aluminum oxide and a fluoroalkylphosphonic acid self-assembled monolayer.
9. X-Ray Crystallography

Table SI1: Crystal data and structure refinement for 6c (CCDC 2087651).

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                            | C_{30}H_{29}NO_4                          |
| Formula weight                                | 467.54                                    |
| Temperature                                   | 200(2) K                                  |
| Wavelength                                    | 0.71073 Å                                 |
| Crystal system                                | orthorhombic                              |
| Space group                                   | P2_12_1                                    |
| Z                                             | 4                                          |
| Unit cell dimensions                          | a = 6.0063(6) Å, b = 19.183(2) Å, c = 21.328(2) Å |
| Volume                                        | 2457.3(5) Å                               |
| Density (calculated)                         | 1.26 g/cm³                                 |
| Absorption coefficient                        | 0.08 mm⁻¹                                  |
| Crystal shape                                 | column                                     |
| Crystal size                                  | 0.127 x 0.040 x 0.026 mm³                  |
| Crystal colour                                | colourless                                 |
| Theta range for data collection               | 1.4 to 23.0 deg.                          |
| Index ranges                                  | -6 ≤ h ≤ 6, -21 ≤ k ≤ 21, -23 ≤ l ≤ 23    |
| Reflections collected                         | 12751                                      |
| Independent reflections                      | 3444 (R(int) = 0.1257)                    |
| Observed reflections                          | 2108 (I > 2σ(I))                          |
| Absorption correction                         | Semi-empirical from equivalents           |
| Max. and min. transmission                    | 0.96 and 0.83                             |
| Refinement method                             | Full-matrix least-squares on F²           |
| Data/restraints/parameters                    | 3444 / 0 / 321                            |
| Goodness-of-fit on F²                         | 0.98                                       |
| Final R indices (I>2σ(I))                     | R₁ = 0.060, wR₂ = 0.113                   |
| Absolute structure parameter                  | -3.2(10)                                  |
| Largest diff. peak and hole                   | 0.18 and -0.29 eÅ⁻³                       |
Table SI2: Crystal data and structure refinement for 6k (CCDC 2087652).

| Parameter                          | Value                                      |
|------------------------------------|--------------------------------------------|
| Empirical formula                  | C₅₀H₄₄N₂O₄                                 |
| Formula weight                     | 736.87                                     |
| Temperature                        | 200(2) K                                   |
| Wavelength                         | 1.54178 Å                                  |
| Crystal system                     | monoclinic                                 |
| Space group                        | C2/c                                       |
| Z                                  | 4                                          |
| Unit cell dimensions               | a = 30.647(3) Å                            |
|                                    | b = 6.1402(4) Å                            |
|                                    | c = 21.8472(16) Å                         |
|                                    | α = 90 deg.                                |
|                                    | β = 100.504(6) deg.                       |
|                                    | γ = 90 deg.                                |
| Volume                             | 4042.2(5) Å                               |
| Density (calculated)               | 1.21 g/cm³                                 |
| Absorption coefficient             | 0.60 mm⁻¹                                  |
| Crystal shape                      | plate                                      |
| Crystal size                       | 0.147 x 0.046 x 0.012 mm³                  |
| Crystal colour                     | yellow                                     |
| Theta range for data collection    | 2.9 to 57.9 deg.                           |
| Index ranges                       | -33 ≤ h ≤ 33, -4 ≤ k ≤ 6, -23 ≤ l ≤ 18    |
| Reflections collected              | 9863                                       |
| Independent reflections            | 2779 (R(int) = 0.0979)                     |
| Observed reflections               | 1409 (I > 2σ(I))                          |
| Absorption correction              | Semi-empirical from equivalents            |
| Max. and min. transmission         | 1.24 and 0.74                             |
| Refinement method                  | Full-matrix least-squares on F²           |
| Data/restraints/parameters         | 2779 / 0 / 256                             |
| Goodness-of-fit on F²              | 1.00                                       |
| Final R indices (I > 2σ(I))        | R1 = 0.061, wR2 = 0.106                    |
| Largest diff. peak and hole        | 0.20 and -0.20 eÅ⁻³                        |
Table SI3: Crystal data and structure refinement for 13a (CCDC 2087653).

| Crystal data and structure refinement for 13a (CCDC 2087653). |
|---------------------------------------------------------------|
| **Empirical formula** | C_{23}H_{15}N |
| **Formula weight** | 305.36 |
| **Temperature** | 200(2) K |
| **Wavelength** | 0.71073 Å |
| **Crystal system** | monoclinic |
| **Space group** | P2_1/c |
| **Z** | 4 |
| **Unit cell dimensions** | 
| a | 11.3680(4) Å | α = 90 deg. |
| b | 11.9253(4) Å | β = 114.026(2) deg. |
| c | 12.3919(4) Å | γ = 90 deg. |
| **Volume** | 1534.39(9) Å³ |
| **Density (calculated)** | 1.32 g/cm³ |
| **Absorption coefficient** | 0.08 mm⁻¹ |
| **Crystal shape** | column |
| **Crystal size** | 0.164 x 0.084 x 0.033 mm³ |
| **Crystal colour** | colourless |
| **Theta range for data collection** | 2.0 to 25.1 deg. |
| **Index ranges** | -13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14 |
| **Reflections collected** | 13987 |
| **Independent reflections** | 2722 (R(int) = 0.0563) |
| **Observed reflections** | 1845 (I > 2σ(I)) |
| **Absorption correction** | Semi-empirical from equivalents |
| **Max. and min. transmission** | 0.96 and 0.90 |
| **Refinement method** | Full-matrix least-squares on F² |
| **Data/restraints/parameters** | 2722 / 0 / 217 |
| **Goodness-of-fit on F²** | 1.04 |
| **Final R indices (I>2σ(I))** | R1 = 0.047, wR2 = 0.108 |
| **Largest diff. peak and hole** | 0.16 and -0.19 eÅ⁻³ |
Table SI4: Crystal data and structure refinement for 13f (CCDC 2087654).

| Property                                      | Value                        |
|-----------------------------------------------|------------------------------|
| Empirical formula                            | C_{27}H_{17}N                |
| Formula weight                                | 355.42                       |
| Temperature                                   | 200(2) K                     |
| Wavelength                                    | 0.71073 Å                    |
| Crystal system                                | orthorhombic                 |
| Space group                                   | P2_12_12_1                   |
| Z                                             | 4                            |
| Unit cell dimensions                          | a = 7.8601(4) Å, α = 90 deg. |
|                                              | b = 10.6012(6) Å, β = 90 deg.|
|                                              | c = 21.5960(11) Å, γ = 90 deg.|
| Volume                                        | 1799.52(16) Å^3              |
| Density (calculated)                          | 1.31 g/cm^3                  |
| Absorption coefficient                        | 0.08 mm^{-1}                 |
| Crystal shape                                 | plank                        |
| Crystal size                                  | 0.311 x 0.172 x 0.076 mm^3   |
| Crystal colour                                | brown                        |
| Theta range for data collection               | 1.9 to 31.5 deg.             |
| Index ranges                                  | -10 ≤ h ≤ 11, -15 ≤ k ≤ 15, -29 ≤ l ≤ 31 |
| Reflections collected                         | 15602                        |
| Independent reflections                       | 5844 (R(int) = 0.0342)       |
| Observed reflections                          | 4030 (I > 2σ(I))             |
| Absorption correction                         | Semi-empirical from equivalents|
| Max. and min. transmission                    | 0.96 and 0.91                |
| Refinement method                             | Full-matrix least-squares on F^2|
| Data/restraints/parameters                     | 5844 / 0 / 253               |
| Goodness-of-fit on F^2                        | 1.03                         |
| Final R indices (I>2sigma(I))                 | R1 = 0.058, wR2 = 0.110      |
| Absolute structure parameter                  | -1.8(10)                     |
| Largest diff. peak and hole                   | 0.20 and -0.23 eÅ^3          |
Table SI5: Crystal data and structure refinement for 13k (CCDC 2087655).

- **Empirical formula**: $C_{40}H_{24}N_{2}$
- **Formula weight**: 532.61
- **Temperature**: 200(2) K
- **Wavelength**: 0.71073 Å
- **Crystal system**: monoclinic
- **Space group**: P2$_1$/n
- **Z**: 2
- **Unit cell dimensions**:
  - $a = 5.9570(4)$ Å, $\alpha = 90$ deg.
  - $b = 20.9412(15)$ Å, $\beta = 104.072(2)$ deg.
  - $c = 10.9419(8)$ Å, $\gamma = 90$ deg.
- **Volume**: 1324.01(16) Å$^3$
- **Density (calculated)**: 1.34 g/cm$^3$
- **Absorption coefficient**: 0.08 mm$^{-1}$
- **Crystal shape**: brick
- **Crystal size**: 0.197 x 0.107 x 0.052 mm$^3$
- **Crystal colour**: orange
- **Theta range for data collection**: 1.9 to 28.3 deg.
- **Index ranges**: $-7 \leq h \leq 7$, $-26 \leq k \leq 26$, $-13 \leq l \leq 14$
- **Reflections collected**: 14293
- **Independent reflections**: 3019 (R(int) = 0.0479)
- **Observed reflections**: 1931 ($I > 2\sigma(I)$)
- **Absorption correction**: Semi-empirical from equivalents
- **Max. and min. transmission**: 0.96 and 0.90
- **Refinement method**: Full-matrix least-squares on $F^2$
- **Data/restraints/parameters**: 3019 / 0 / 190
- **Goodness-of-fit on $F^2$**: 1.05
- **Final R indices ($I>2\sigma(I)$)**: $R1 = 0.054$, $wR2 = 0.122$
- **Largest diff. peak and hole**: 0.25 and -0.17 eÅ$^{-3}$
Table SI6: Crystal data and structure refinement for 13l (CCDC 2087656).

| Parameter                      | Value                                         |
|--------------------------------|-----------------------------------------------|
| Empirical formula             | C₄₀H₂₄N₂                                       |
| Formula weight                | 532.61                                        |
| Temperature                   | 200(2) K                                      |
| Wavelength                    | 0.71073 Å                                     |
| Crystal system                | monoclinic                                    |
| Space group                   | P2₁/c                                         |
| Z                              | 2                                             |
| Unit cell dimensions          | a = 11.6891(6) Å, α = 90 deg.                |
|                               | b = 7.2017(3) Å, β = 104.454(2) deg.         |
|                               | c = 16.3768(8) Å, γ = 90 deg.                |
| Volume                        | 1334.99(11) Å                                 |
| Density (calculated)          | 1.33 g/cm³                                     |
| Absorption coefficient        | 0.08 mm⁻¹                                      |
| Crystal shape                 | brick                                          |
| Crystal size                  | 0.090 x 0.055 x 0.028 mm³                     |
| Crystal colour                | brown                                          |
| Theta range for data collection| 1.8 to 23.1 deg.                              |
| Index ranges                  | -12≤h≤12, -7≤k≤7, -18≤l≤18                    |
| Reflections collected         | 9953                                          |
| Independent reflections       | 1864 (R(int) = 0.1302)                        |
| Observed reflections          | 1291 (I > 2σ(I))                              |
| Absorption correction         | Semi-empirical from equivalents               |
| Max. and min. transmission    | 0.96 and 0.93                                 |
| Refinement method             | Full-matrix least-squares on F²               |
| Data/restraints/parameters    | 1864 / 0 / 190                                |
| Goodness-of-fit on F²         | 1.00                                          |
| Final R indices (I>2σ(I))     | R1 = 0.045, wR2 = 0.104                      |
| Largest diff. peak and hole   | 0.16 and -0.21 eÅ⁻³                            |
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