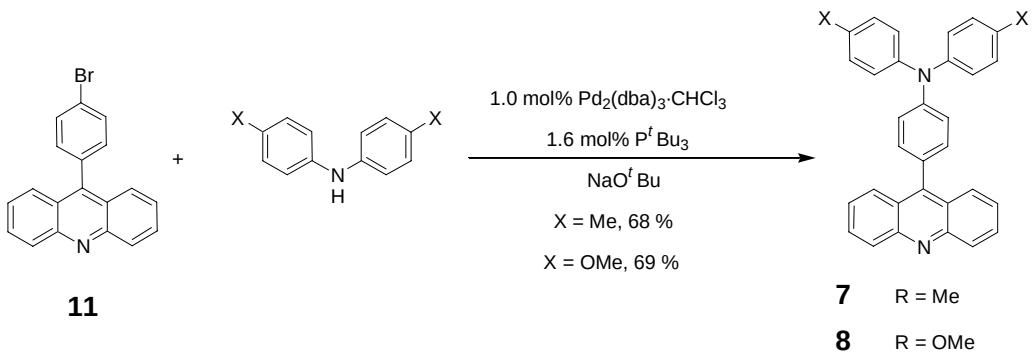
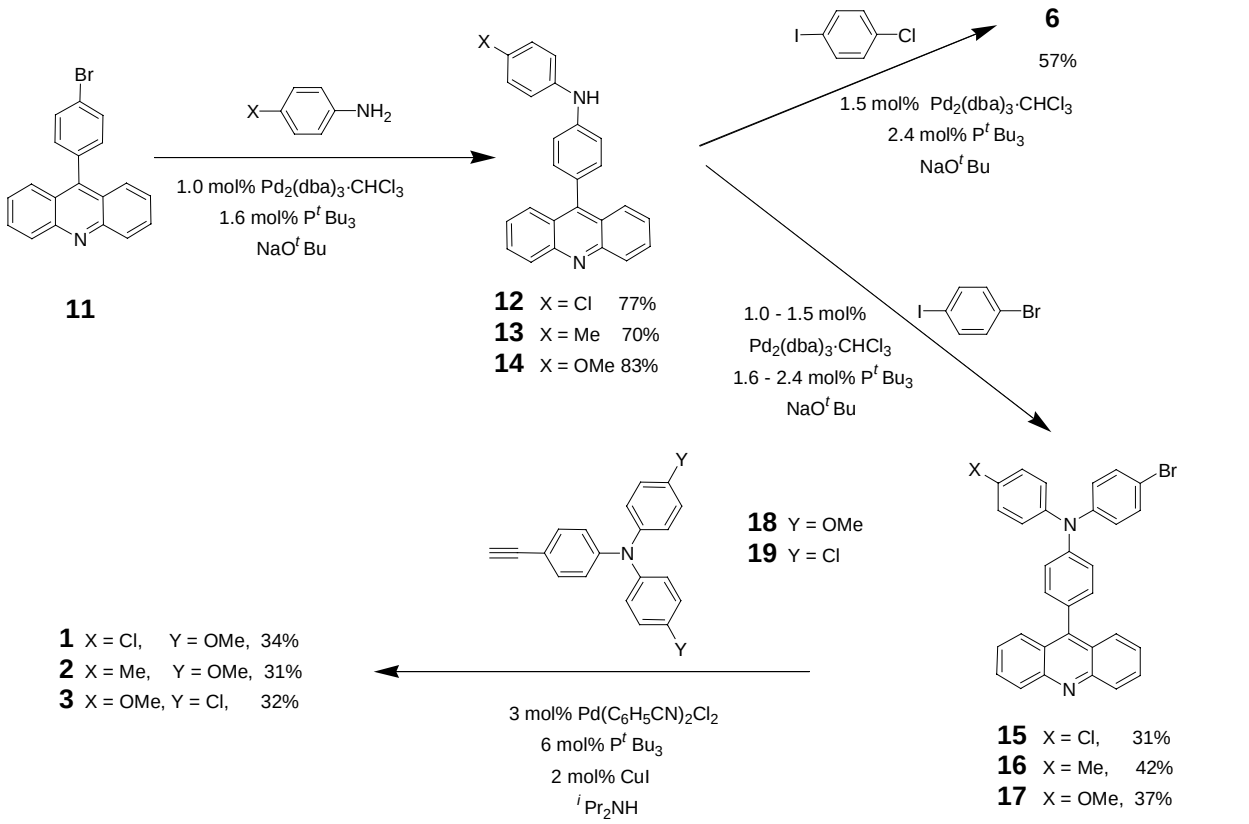
Suppprting Information

Synthesis

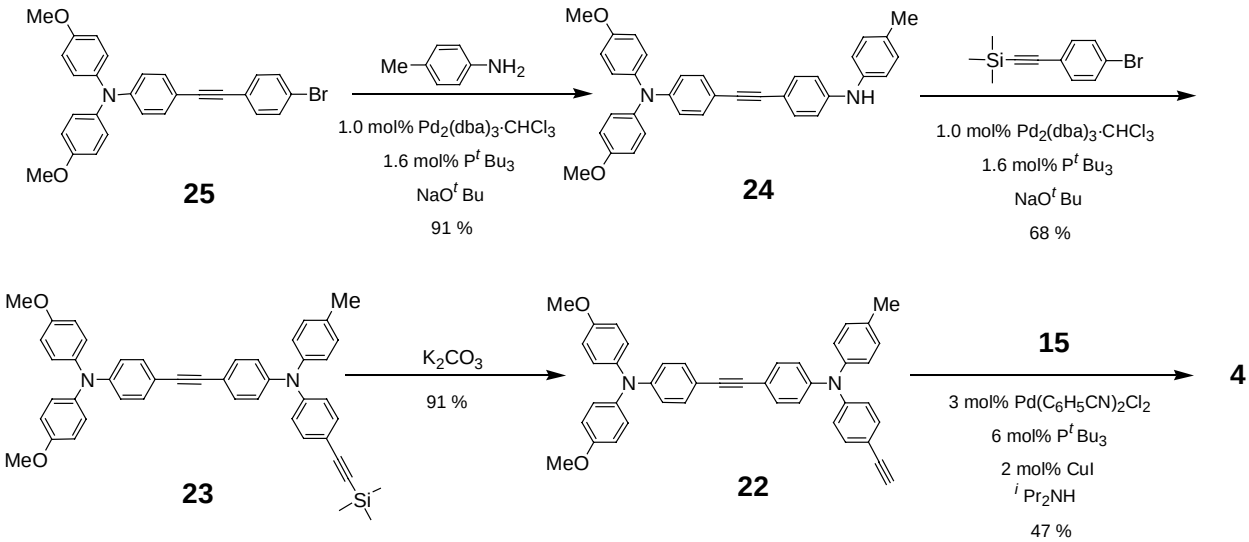
The synthetic approaches to the cascades **1-5** and to the model compounds **6-8** are described in Schemes S1-S4. C-N couplings were achieved by palladium(0) catalyzed reactions. In these reactions we take advantage of the different reactivity of chlorine, bromine and iodine substituted arenes (e.g. synthesis and follow-up reactions of **15**). The alkyne-arene couplings were accomplished by the usual Hagihara-Sonogashira protocols. For both types of coupling reactions we used P^tBu_3 as the ligand to palladium. The yields given in the Schemes are those of purified material; moderate yields are due to the sensitivity of the triarylamines towards oxidation during purification as well as to homocoupling of the terminal alkynes under Hagihara-Sonogashira conditions.



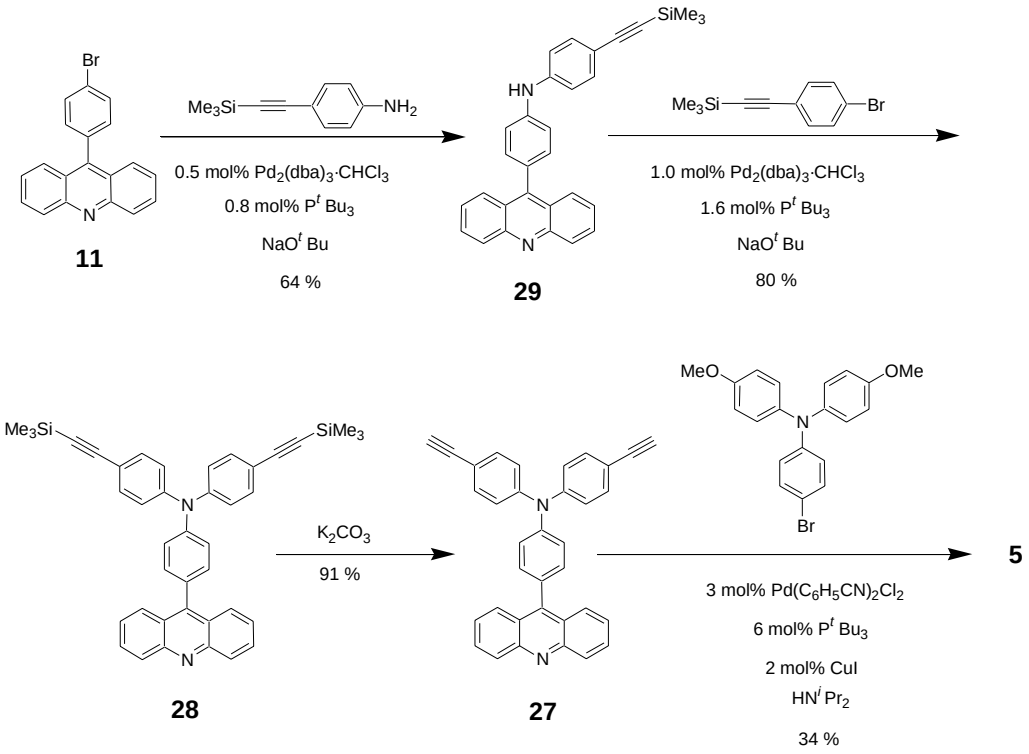
Scheme S1



Scheme S2



Scheme S3



Scheme S4

General procedure for the palladium catalyzed amination of aryl halides (general method A): A solution of the aryl halide (1.1 equivalents), aryl amine (1.0 equivalents), sodium *tert*-butoxide (1.25 equivalents), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.5 – 2.0 mol% Pd) and dppf (bis(diphenylphosphino)ferrocene) (0.75 equivalents per Pd atom) were heated in dry toluene under nitrogen atmosphere at 75 – 90 °C for 1 to 3 d. After having removed the solvent in vacuo we dissolved the residue in dichloromethane and washed it with water. The organic layer was dried over $MgSO_4$ and the solvent was removed. Column chromatography (neutral aluminum oxide, activity V) or flash chromatography (silica gel) was used to purify the crude product.

General procedure for the palladium catalyzed amination of aryl halides (general method B): A mixture of the aryl halide (1.1 equivalents), aryl amine (1.0 equivalents), sodium *tert*-butoxide (1.25 equivalents), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.5 – 2.0 mol% Pd) and P^tBu_3 (solution in hexane, 0.8 equivalents per Pd atom) in dry toluene was stirred under nitrogen atmosphere at 40 °C for 1 to 3 d. The solvent amount was reduced in vacuo, the residue was dissolved in dichloromethane and washed with water. The organic layer was dried over $MgSO_4$ and the solvent was removed. The crude product was purified either by column chromatography (neutral aluminum oxide, activity V) or by flash chromatography (silica gel).

Sonogashira coupling of aryl halides with acetylenes (general method C): To a solution of the aryl halide (1.0 equivalents), the acetylene (1.1 – 1.25 equivalents), $Pd(C_6H_5CN)_2Cl_2$ (3 mol%) and cuprous iodide (2 mol%) in dioxane P^tBu_3 (solution in hexane, 6 mol%) and diisopropylamine (1.1 equivalents) were added and the mixture was stirred under nitrogen atmosphere at room temperature for 1 to 3 d. The solvent was removed in vacuo, the residue was dissolved in dichloromethane and washed with water. The organic layer was dried over $MgSO_4$ and the solvent was removed. The crude product can be purified either by column chromatography (neutral aluminum oxide, activity V) or flash chromatographie (silica gel).

***N*-(4-Bromophenyl)-*N*,*N*-di(4-methoxyphenyl)amine (26)**: Following **general method A** the compound was prepared from di(4-methoxyphenyl)amine (3.00 g, 13.1 mmol), 4-bromoiodobenzene (4.64 g, 16.4 mmol), sodium *tert*-butoxide (1,89 g, 19.7 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (68 mg, 66 μmol) and dppf (56 mg, 0.10 mmol) in toluene (20 ml). Flash chromatography (silica gel, dichloromethane/petrol ether 1:2) gave 4.40 g (11.5 mmol, 88 %) of a brown solid. Mp 96 – 98 °C (lit.[1] 91 – 92 °C). ^{1}H NMR (250 MHz, [D_6]-acetone): δ 7.29 (AA', 2H, bromophenyl), 7.06 (AA', 4H, methoxyphenyl), 6.91 (BB', 4H, methoxyphenyl), 6.74 (BB', 2H, bromophenyl), 3.79 (s, 6H, methoxy).

***N*-(4-Chlorophenyl)-*N*-(4-(trimethylsilylethynyl)phenyl)amine (21)**: Synthesis followed **general method B** using 4-(trimethylsilylethynyl)bromobenzene[2] (1.30 g, 5.13 mmol), 4-chloroaniline (786 mg, 6.16 mmol), sodium *tert*-butoxide (567 mg, 5.90 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (27 mg, 26 μmol) and P^tBu_3 (0.13 ml of a 10% solution in hexane, 42 μmol) in toluene (10 ml). Flash chromatography (silica gel, dichloromethane/petrol ether 1:3) yielded 1.18 g (3.93 mmol, 77 %) of a brown solid. Mp 101 – 103 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.34 (AA', 2H, phenyl), 7.25 (AA', 2H, phenyl), 7.05 (BB', 2H, phenyl), 6.95 (BB', 2H, phenyl), 5.91 (s, 1H, NH), 0.23 (s, 9H, trimethylsilyl). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 143.8, 141.1, 133.5, 129.7, 126.8, 120.5, 116.7, 115.3, 105.7, 92.8, 0.1. $C_{17}H_{18}ClNSi$ calcd C 68.09, H 6.05, N 4.67 found C 67.92, H 6.05, N 4.26.

***N*,*N*-Di(4-chlorophenyl)-*N*-(4-(trimethylsilylethynyl)phenyl)amine (20)**: Applying **general method B** the compound was prepared from *N*-(4-chlorophenyl)-*N*-(4-(trimethyl-silylethynyl)phenyl)amine **21** (1.27 g, 4.24 mmol), 4-chloroiodobenzene (1.21 g, 5.09 mmol), sodium tert-butoxide (489 mg, 5.09 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (22 mg, 21 μmol) and P^tBu_3 (0.10 ml of a 10% solution in hexane, 34 μmol) in toluene (10 ml). After flash chromatography (silica gel, dichloromethane/petrol ether 1:4) 1.17 g of a yellow solid was obtained, which was contaminated with about 5 % of an unknown byproduct that could not be removed. The crude

product was used without further purification. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 7.31 (AA', 2H, phenyl), 7.24, (AA', 4H, chlorophenyl), 7.01 (BB', 4H, chlorophenyl), 6.93 (BB', 2H, phenyl), 0.23 (s, 9H, trimethylsilyl).

***N*,*N*-Di(4-chlorophenyl)-*N*-(4-ethynylphenyl)amine (19)**: *N*,*N*-Di(4-chlorophenyl)-*N*-(4-(trimethylsilylethynyl)phenyl)amine **20** (700 mg of the crude product from the previous step, 2.07 mmol) and potassium carbonate (506 mg, 3.66 mmol) were dissolved in dry methanol (10 ml) and the mixture was stirred under nitrogen atmosphere at room temperature for 12 h. The solvent was removed in vacuo, the residue was dissolved in dichloromethane and washed with water. The organic layer was dried over $MgSO_4$ and the solvent was removed. Flash chromatography (silica gel, dichloromethane/petrol ether 1:4) yielded 570 mg of a yellow solid which was contaminated with about 5 % of an unknown compound that could not be separated. The crude product was used without further purification. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.35 (AA', 2H, phenyl), 7.25 (AA', 4H, chlorophenyl), 7.02 (BB', 4H, chlorphenyl), 6.95 (BB', 2H, phenyl), 3.09 (s, 1H, ethynyl).

***N*,*N*-Di(4-methoxyphenyl)-*N*-(4-(4-(*N*'-(4-methylphenyl)amino)phenyl)ethynylphenyl)amine (24)**: Preparation followed **general method B** from *N*-(4-(4-bromophenyl)ethynylphenyl)-*N*,*N*-di(4-methoxyphenyl)amine[3] **25** (690 mg, 1.42 mmol), *p*-toluidine (182 mg, 1.70 mmol), sodium *tert*-butoxide (171 mg, 1.78 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (15 mg, 14 μmol) and P^tBu_3 (0.07 ml of a 10 % solution in hexane, 23 μmol) in toluene (5 ml). After column chromatography (neutral aluminum oxide, activity V, petrol ether) 660 mg (1.30 mmol, 91 %) of a yellow solid were obtained. Mp 123 – 125 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.34 (AA', 2H, phenyl), 7.27 (AA', 2H, phenyl), 7.12 (AA', 2H, phenyl), 7.07 (AA', 4H, phenyl), 7.04 (BB', 2H, phenyl), 6.94 (BB', 2H, phenyl), 6.86 (BB', 4H, phenyl), 6.81 (BB', 2H, phenyl), 5.84 (s, 1H, NH), 3.79 (s, 6H, methoxy), 2.11 (s, 3H, methyl). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 156.9, 148.9, 144.5, 140.6, 139.6, 132.9, 132.4, 132.3, 130.3, 127.5, 120.1, 119.4, 115.9, 115.1, 114.72, 114.71, 88.7, 88.6, 55.8, 20.8. HRMS (EI): calcd for $C_{35}H_{30}N_2O_2$ 510.2307 found 510.2300.

***N*,*N*-Di(4-methoxyphenyl)-*N*-(4-(4-(*N*'-(4-methylphenyl)-*N*'-(4-(trimethylsilylethynyl)phenyl)-amino)phenyl)ethynylphenyl)amine (23)**: The reaction mixture contained *N,N*-di(4-methoxyphenyl)-*N*-(4-(4-(*N*'-(4-methylphenyl)amino)phenyl)-ethynylphenyl)amine **24** (590 mg, 1.29 mmol), 4-(trimethylsilylethynyl)bromobenzene[2] (360 mg, 1.42 mmol), sodium *tert*-butoxide (155 mg, 1.61 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (13 mg, 13 μmol) and P^tBu_3 (0.06 ml of a 10% solution in hexane, 21 μmol) in toluene (5 ml) following **general method B**. Flash chromatography (silica gel, dichloromethane/petrol ether 1:2)

yielded 600 mg (879 μmol, 68 %) of a yellow solid. Mp 106 – 110 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.34 (AA', 2H, phenyl), 7.30 (AA', 2H, phenyl), 7.27 (BB', 2H, phenyl), 7.14 (AA', 2H, phenyl), 7.07 (AA', 4H, phenyl), 7.01 (AA', 2H, phenyl), 6.98 (BB', 2H, phenyl), 6.95 (BB', 2H, phenyl), 6.86 (BB', 4H, phenyl), 6.81 (BB', 2H, phenyl), 3.79 (s, 6H, methoxy), 2.33 (s, 3H, methyl), 0.23 (s, 9H, trimethylsilyl). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 156.9, 149.2, 148.1, 147.3, 144.4, 140.5, 134.9, 133.2, 132.6, 132.5, 130.6, 127.6, 126.4, 123.5, 122.8, 119.3, 117.9, 116.7, 115.2, 114.3, 105.6, 93.5, 89.8, 88.3, 55.8, 21.0, 0.1. HRMS (EI): calcd for $C_{46}H_{42}N_2O_2Si$ 682.3016 found 682.3015.

***N*,*N*-Di(4-methoxyphenyl)-*N*-(4-(4-(*N*'-(4-methylphenyl)-*N*'-(4-ethynylphenyl)amino)-phenyl)ethynylphenyl)amine (22)**: *N*,*N*-Di(4-methoxyphenyl)-*N*-(4-(4-(*N*'-(4-methylphenyl)-*N*'-(4-(trimethylsilylethynyl)phenyl)amino)phenyl)ethynylphenyl)amine **23** (500 mg, 732 μmol) and potassium carbonate (132 mg, 952 μmol) were dissolved in a mixture of methanol (10 ml) and dichloromethane (10 ml). The mixture was stirred under nitrogen atmosphere at room temperature for 12 h. The solvent was removed in vacuo and the residue was dissolved in dichloromethane and washed with water. The organic layer was dried over $MgSO_4$ and the solvent was removed. Flash chromatography (silica gel, dichloromethane/petrol ether 1:2) gave 410 mg (671 μmol, 91 %) of a yellow solid. Mp 184 – 186 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.35 (AA', 2H, phenyl), 7.33 (AA', 2H, phenyl), 7.27 (AA', 2H, phenyl), 7.14 (AA', 2H, phenyl), 7.07 (AA', 4H, phenyl), 7.03 – 6.95 (6H, phenyl), 6.86 (BB', 4H, phenyl), 6.81 (BB', 2H, phenyl), 3.79 (s, 6H, methoxy), 3.07 (s, 1H, ethynyl), 2.34 (s, 3H, methyl). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 157.0, 149.2, 148.4, 147.2, 144.3, 140.5, 134.9, 133.4, 132.6, 132.5, 130.6, 127.6, 126.4, 123.6, 122.7, 119.3, 118.0, 115.5, 115.2, 114.3, 89.8, 88.3, 84.0, 76.6, 55.8, 21.0. $C_{43}H_{34}N_2O_2$ calcd C 84.56, H 5.61, N 4.59 found C 84.22, H 5.84, N 4.47.

9-(4-Bromophenyl)acridine (11): A mixture of diphenylamine (15.0 g, 88.5 mmol), 4-bromobenzoic acid (26.7 g, 133 mmol) and zinc bromide (49.8 g, 221 mmol) was heated in an oil bath at 180 – 200 °C for 6 d. The solid green residue was dissolved in boiling ethanol (600 ml) and the solution was added to water (1000 ml). After addition of concentrated ammonia the brown precipitate was filtered and washed with methanol (10 ml). To remove a great part of unreacted 4-bromobenzoic acid the crude product was dissolved in dichloromethane and the insoluble 4-bromobenzoic acid was filtered off. Flash chromatography (silica gel, dichloromethane/ethyl acetate 20:1) yielded a brown residue which was further purified in boiling methanol (150 ml) and filtration of the yellow product (12.5 g, 37.4 mmol, 42 %). Mp 238 – 244 °C (lit. 234 °C[4]). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.31 (m, 2H, acridine), 7.79 (ddd, $^{3}J_{HH}$ = 8.6 Hz, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 1.6 Hz, 2H, acridine),7.76 (AA', 2H, phenyl), 7.68 (m, 2H,

acridine), 7.45 (ddd, $^3J_{HH}$ =8.7 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, acridine), 7.33 (BB', 2H, phenyl).

9-(4-(*N*-(4-Chlorophenyl)amino)phenyl)acridine (12): According to **general method B** a mixture of 9-(4-bromophenyl)acridine **11** (1.70 g, 5.09 mmol), 4-chloroaniline (811 mg, 6.36 mmol), sodium *tert*-butoxide (611 mg, 6.36 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (66 mg, 64 μmol) and P^tBu_3 (0.31 ml of a 10% solution in hexane, 0.10 mmol) was stirred in dry toluene at 40 °C for 2 d. Flash chromatography (silica gel, CH_2Cl_2/ethyl acetate 20:1) of the crude product yielded a yellow solid (1.50 g, 3.94 mmol, 77 %). Mp 189 – 191 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.23 (ddd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.2 Hz, $^5J_{HH}$ = 0.7 Hz, 2H, acridine), 7.85 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.7 Hz, 2H, acridine), 7.77 (ddd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, acridine), 7.46 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, acridine), 7.36 (AA', 2H, phenyl), 7.32 – 7.26 (AA'BB', 4H, phenyl), 7.20 (BB', 2H, phenyl), 6.16 (s, 1H, NH). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 149.4, 147.5, 143.6, 141.8, 132.2, 130.1, 130.0, 129.7, 128.5, 127.3, 126.3, 125.80, 125.77, 119.9, 117.4. HRMS (EI): calcd for $C_{25}H_{17}ClN_2$ 380.1080 found 380.1080.

9-(4-(*N*-(4-Methylphenyl)amino)phenyl)acridine (13): 9-(4-Bromophenyl)acridine **11** (1.00 g, 2.99 mmol), *p*-toluidine (401 mg, 3.74 mmol), sodium *tert*-butoxide (359 mg, 3.74 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (31 mg, 30 μmol) and P^tBu_3 (0.14 ml of a 10% solution in hexane, 48 μmol) were stirred in dry toluene (10 ml) at 40 °C for 2 d (**general method B**). The crude product was purified by column chromatography (neutral aluminum oxide, activity V, CH_2Cl_2/petrol ether 1:2). Yield: 750 mg (2.08 mmol, 70 %) of a yellow solid. Mp 212 – 214 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.22 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.2 Hz, $^5J_{HH}$ = 0.7 Hz, 2H, acridine), 7.87 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.7 Hz, 2H, acridine), 7.77 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, acridine), 7.45 (ddd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, acridine), 7.32 (AA', 2H, phenyl), 7.23 (BB', 2H, phenyl), 7.17 (AA'BB', 4H, phenyl), 6.01 (bs, 1H, NH), 2.34 (s, 3H, methyl). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 149.4, 147.8, 144.9, 140.1, 132.2, 132.1, 130.3, 130.1, 130.0, 127.4, 127.2, 125.8, 125.7, 120.0, 116.1, 20.8. HRMS (EI): calcd for $C_{26}H_{20}N_2$ 360.1626 found 360.1627.

9-(4-(*N*-(4-Methoxyphenyl)amino)phenyl)acridine (14): Applying **general method B** a mixture of 9-(4-bromophenyl)acridine **11** (1.50 g, 4.49 mmol), 4-aminoanisole (691 mg, 5.61 mmol), sodium *tert*-butoxide (530 mg, 5.51 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (47 mg, 45 μmol) and P^tBu_3 (0.22 ml of a 10% solution in hexane, 72 μmol) in toluene (20 ml) was stirred at 40 °C for 2 d. Purification of the crude product by column chromatography (neutral aluminum oxide, activity V, using a gradient of dichlormethane/petrolether 1:2 → 1:1) yielded 1.40 g (3.72

mmol, 83 %) of a yellow solid. Mp 205 – 206 °C. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ 8.20 (ddd, $^{3}J_{HH}$ = 8.7 Hz, $^{4}J_{HH}$ = 1.0 Hz, $^{5}J_{HH}$ = 0.7 Hz, 2H, acridine), 7.88 (ddd, $^{3}J_{HH}$ = 8.8 Hz, $^{4}J_{HH}$ = 1.1 Hz, $^{5}J_{HH}$ = 0.6 Hz, 2H, acridine), 7.81 (ddd, $^{3}J_{HH}$ = 8.8 Hz, $^{3}J_{HH}$ = 6.6 Hz, $^{4}J_{HH}$ = 1.5 Hz, 2H, acridine), 7.51 (ddd, $^{3}J_{HH}$ = 8.7 Hz, $^{3}J_{HH}$ = 6.6 Hz, $^{4}J_{HH}$ = 1.1 Hz, 2H, acridine), 7.48 (bs, 1H, NH), 7.31 (AA', 2H, phenyl), 7.28 (AA', 2H, phenyl), 7.24 (BB', 2H, phenyl), 6.96 (BB', 2H, phenyl), 3.80 (s, 3H, methoxy). ^{13}C NMR (101 MHz, [D$_6$]-acetone): δ 156.4, 150.0, 148.3, 147.3, 136.5, 132.4, 130.7, 130.6, 127.8, 126.3, 126.2, 126.0, 123.2, 115.5, 115.3, 55.8. HRMS (EI): calcd for $C_{26}H_{20}N_2O$ 376.1576 found 376.1574.

9-(4-(*N*-(4-Bromophenyl)-*N*-(4-chlorophenyl)amino)phenyl)acridine (15): **General method B** was applied starting from 9-(4-(N-(4-chlorophenyl)amino)phenyl)acridine **12** (1.00 g, 2.63 mmol), 4-bromoiodobenzene (931 mg, 3.29 mmol), sodium *tert*-butoxide (316 mg, 3.29 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (41 mg, 39 μmol) and P^{t}Bu$_3$ (0.19 ml of a 10% solution in hexane, 63 μmol) in toluene (15 ml). Flash chromatography (silica gel, dichloromethane/ethyl acetate 20:1) yielded 440 mg (821 μmol, 31 %) of a yellow solid. Mp 260 – 264 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.23 (ddd, $^{3}J_{HH}$ = 8.8 Hz, $^{4}J_{HH}$ = 1.2 Hz, $^{5}J_{HH}$ = 0.8 Hz, 2H, acridine), 7.85 (ddd, $^{3}J_{HH}$ = 8.8 Hz, $^{4}J_{HH}$ = 1.4 Hz, $^{5}J_{HH}$ = 0.7 Hz, 2H, acridine), 7.78 (ddd, $^{3}J_{HH}$ = 8.7 Hz, $^{3}J_{HH}$ = 6.5 Hz, $^{4}J_{HH}$ = 1.4 Hz, 2H, acridine), 7.48 (ddd, $^{3}J_{HH}$ = 8.7 Hz, $^{3}J_{HH}$ = 6.5 Hz, $^{4}J_{HH}$ = 1.2 Hz, 2H, acridine), 7.46 (AA', 2H, phenyl), 7.36 (AA', 2H, phenyl), 7.32 (AA', 2H, phenyl), 7.28 (BB', 2H, phenyl), 7.19 (BB', 2H, phenyl), 7.13 (BB', 2H, phenyl). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 149.3, 147.6, 147.0, 146.9, 146.3, 132.9, 132.1, 130.8, 130.2, 130.1, 130.0, 128.9, 127.2, 126.4, 126.3, 125.9, 125.6, 123.7, 116.3. $C_{31}H_{20}BrClN_2$ calcd C 69.48, H 3.76, N 5.23 found C 69.31, H 3.88, N 5.33.

9-(4-(*N*-(4-Bromophenyl)-*N*-(4-methylphenyl)amino)phenyl)acridine (16): A solution of 9-(4-(*N*-(4-methylphenyl)amino)phenyl)acridine **13** (700 mg, 1.94 mmol), 4-bromoiodobenzene (823 mg, 2.91 mmol), sodium tert-butoxide (234 mg, 2.43 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (30 mg, 29 μmol) and dppf (24 mg, 43 μmol) in toluene (5 ml) was heated to 75 °C for 2 d according to **general method A**. The crude product was purified by column chromatography (neutral aluminum oxide, activity V, dichloromethane/petrolether 1:2). Yield: 420 mg (815 μmol, 42 %) of a yellow solid. Mp 247 – 250 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.22 (ddd, $^{3}J_{HH}$ = 8.7 Hz, $^{4}J_{HH}$ = 1.1 Hz, $^{5}J_{HH}$ = 0.7 Hz, 2H, acridine), 7.87 (ddd, $^{3}J_{HH}$ = 8.7 Hz, $^{4}J_{HH}$ = 1.3 Hz, $^{5}J_{HH}$ = 0.6 Hz, 2H, acridine), 7.78 (ddd, $^{3}J_{HH}$ = 8.7 Hz, $^{3}J_{HH}$ = 6.6 Hz, $^{4}J_{HH}$ = 1.4 Hz, 2H, acridine), 7.48 (ddd, $^{3}J_{HH}$ = 8.8 Hz, $^{3}J_{HH}$ = 6.6 Hz, $^{4}J_{HH}$ = 1.2 Hz, 2H, acridine), 7.41 (AA', 2H, phenyl), 7.32 (AA', 2H, phenyl), 7.25 (BB', 2H, phenyl), 7.20 (AA', 2H, phenyl), 7.15 (BB', 2H, phenyl), 7.10 (BB', 2H, phenyl), 2.36 (s, 3H, methyl). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 149.4, 148.1, 147.4,

147.3, 144.8, 134.6, 132.6, 131.9, 130.7, 130.13, 130.10, 129.8, 127.3, 126.1, 125.8, 125.68, 125.65, 122.9, 115.3, 21.0. HRMS (EI): calcd for $C_{32}H_{23}BrN_2$ 514.1045 found 514.1038.

9-(4-(*N*-(4-Bromophenyl)-*N*-(4-methoxyphenyl)amino)phenyl)acridine (17): According to **general method B** 9-(4-(*N*-(4-methoxyphenyl)amino)phenyl)acridine **14** (1.00 g, 2.66 mmol), 4-bromoiodobenzene (902 mg, 3.19 mmol), sodium tert-butoxide (307 mg, 3.19 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (28 mg, 27 μmol) and P^tBu_3 (0.13 ml of a 10% solution in hexane, 43 μmol) in toluene (15 ml) were stirred at 40 °C for 2 d. Flash chromatography (silica gel, dichloromethane/ethyl acetate 10:1) yielded 520 mg (978 μmol, 37 %) of an orange solid. Mp 193 – 195 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.22 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.1 Hz, $^5J_{HH}$ = 0.8 Hz, 2H, acridine), 7.87 (ddd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.8 Hz, 2H, acridine), 7.77 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, acridine), 7.47 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, acridine), 7.40 (AA', 2H, phenyl), 7.31 (AA', 2H, phenyl), 7.23 (BB', 2H, phenyl), 7.22 (AA', 2H, phenyl), 7.09 (BB', 2H, phenyl), 6.95 (BB', 2H, phenyl), 3.83 (s, 3H, methoxy). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 157.7, 149.4, 148.3, 147.5, 147.3, 140.2, 132.5, 131.9, 130.13, 130.11, 129.4, 128.4, 127.3, 125.8, 125.7, 125.1, 122.2, 115.5, 114.9, 55.9. $C_{32}H_{23}BrN_2O$ calcd C 72.32, H 4.36, N 5.27 found C 71.99, H 4.32, N 5.36.

9-(4-(*N*-(4-Trimethylsilylethynyl)phenyl)amino)phenyl)acridine (29): Following **general method B** 4-trimethylsilylethynylaniline[5] (1.50 g, 7.92 mmol), 9-(4-bromophenyl)acridine (3.17 g, 9.50 mmol), sodium *tert*-butoxide (913 mg, 9.50 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (41 mg, 40 μmol) and P^tBu_3 (0.19 ml of a 10% solution in hexane, 64 μmol) in toluene (15 ml) were stirred for 2 d at 40 °C. The crude product was purified by column chromatography (neutral aluminum oxide, activity V, dichloromethane/petrol ether 1:2) to yield 2.25 g (5.08 mmol, 64 %) of a yellow solid. Mp 227 – 229 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.23 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.3 Hz, $^5J_{HH}$ = 0.8 Hz, 2H, acridine), 7.84 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.7 Hz, 2H, acridine), 7.77 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, acridine), 7.46 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, acridine), 7.42 (AA', 2H, phenyl), 7.39 (AA', 2H, phenyl), 7.35 (BB', 2H, phenyl), 7.15 (BB', 2H, phenyl), 6.27 (s, 1H, NH), 0.25 (s, 9H, trimethylsilyl). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 149.4, 147.3, 143.7, 142.7, 133.6, 132.1, 130.15, 130.06, 129.2, 127.3, 125.8, 125.7, 118.4, 117.1, 115.5, 105.7, 92.9, 0.1. $C_{30}H_{26}N_2Si$ calcd C 81.41, H 5.92, N 6.33 found C 81.29, H 6.13, N 6.11.

9-(4-(*N*,*N*-Di(4-trimethylsilylethynyl)phenyl)amino)phenyl)acridine (28): Preparation followed **general method B** from 4-(trimethylsilylethynyl)bromobenzene[2] (500 mg, 1.97 mmol), 9-(4-(*N*-(4-Trimethylsilylethynyl)phenyl)amino)phenyl)acridine **29** (832 mg, 1.88 mmol), sodium *tert*-butoxide (226 mg, 2.35 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (19 mg, 19 μmol) and

P^tBu_3 (0.09 ml of a 10% solution in hexane, 30 μmol) in toluene (5 ml). Column chromatography (neutral aluminum oxide, activity V, dichloromethane/petrol ether 1:2) yielded 930 mg (1.51 mmol, 80 %) of a yellow solid. Mp > 285 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.23 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.3 Hz, $^5J_{HH}$ = 0.8 Hz, 2H, acridine), 7.85 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.8 Hz, 2H, acridine), 7.78 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, acridine), 7.49 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, acridine), 7.42 (AA', 4H, phenyl), 7.38 (AA', 2H, phenyl), 7.32 (BB', 2H, phenyl), 7.16 (BB', 4H, phenyl), 0.25 (s, 18H, trimethylsilyl). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 149.3, 147.6, 147.2, 146.9, 133.5, 132.2, 131.4, 130.2, 130.1, 127.2, 126.0, 125.6, 124.8, 124.2, 118.1, 105.3, 94.1, 0.0. $C_{41}H_{38}N_2Si_2$ calcd C 80.08, H 6.23, N 4.56 found C 79.99, H 6.39, N 4.19.

9-(4-(*N*,*N*-Di(4-ethynylphenyl)amino)phenyl)acridine (27): To a solution of 9-(4-(*N*,*N*-Di(4-trimethylsilylethynyl)phenyl)amino)phenyl)acridine **28** (700 mg, 1.14 mmol) in methanol (20 ml) and dichloromethane (5 ml) potassium carbonate (236 mg, 1.71 mmol) was added and the mixture was stirred under nitrogen atmosphere for 12 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in dichloromethane and washed with water. The organic layer was dried over $MgSO_4$ and the solvent was removed. Column chromatography (neutral aluminum oxide, activity V, dichloromethane/petrol ether 1:2) yielded 490 mg (1.04 mmol, 91 %) of a yellow solid. Mp 110 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.23 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.2 Hz, $^5J_{HH}$ = 0.8 Hz, 2H, acridine), 7.85 (ddd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.7 Hz, 2H, acridine), 7.79 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, acridine), 7.49 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, acridine), 7.46 (AA', 4H, phenyl), 7.39 (AA', 2H, phenyl), 7.33 (BB', 2H, phenyl), 7.18 (BB', 4H, phenyl), 3.13 (s, 2H, ethynyl). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 149.3, 147.9, 147.1, 146.9, 133.7, 132.2, 131.6, 130.2, 130.1, 127.2, 126.0, 125.5, 125.0, 124.2, 116.9, 83.8, 77.1. $C_{35}H_{22}N_2$ calcd C 89.33, H 4.71, N 5.95 found C 89.12, H 4.75, N 5.87.

9-(4-(*N*,*N*-Di(4-chlorophenyl)amino)phenyl)acridine (6): **General method B** was used to synthesize **(6)** starting from 9-(4-(*N*-(4-chlorophenyl)amino)phenyl)acridine **12** (300 mg, 788 μmol), 4-chloroiodobenzene (235 mg, 985 μmol), sodium *tert*-butoxide (95 mg, 0.99 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (12 mg, 12 μmol) and P^tBu_3 (0.06 ml of a 10% solution in hexane, 19 μmol) in toluene (5 ml). Flash chromatography (silica gel, dichloromethane/ethyl acetate 20:1) gave the crude product which was precipitated from dichloromethane/methanol to yield 220 mg (448 μmol, 57 %) of a yellow powder. Mp 256 – 257 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.23 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.1 Hz, $^5J_{HH}$ = 0.7 Hz, 2H, acridine), 7.85 (ddd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.7 Hz, 2H, acridine), 7.78 (ddd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, acridine), 7.48 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, acridine), 7.35 (AA',

2H, phenyl), 7.32 (AA', 4H, phenyl), 7.28 (BB', 2H, phenyl), 7.18 (BB', 4H, phenyl). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 149.3, 147.7, 147.0, 146.3, 132.1, 130.7, 130.16, 130.14, 129.9, 128.8, 127.2, 126.2, 125.9, 125.6, 123.6. HRMS (EI): calcd for $C_{31}H_{20}Cl_2N_2$ 490.1004 found 490.0999.

9-(4-(*N*,*N*-Di(4-methylphenyl)amino)phenyl)acridine (7): Compound **(7)** was prepared from 9-(4-bromophenyl)acridine **11** (400 mg, 1.20 mmol), di-*p*-tolylamine (249 mg, 1.26 mmol), sodium *tert*-butoxide (144 mg, 1.50 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (12 mg, 12 μmol) and P^tBu_3 (0.06 ml of a 10% solution in hexane, 19 μmol) in toluene (3 ml) (**general method B**). Flash chromatography (silica gel, dichloromethane) and subsequent column chromatography (neutral aluminum oxide, activity V, dichloromethane/petrol ether 1:5) resulted in 370 mg (821 μmol, 68 %) of a bright yellow solid. Mp 230 – 232 °C. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 8.22 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.2 Hz, $^5J_{HH}$ = 0.8 Hz, 2H, acridine), 7.90 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.8 Hz, 2H, acridine), 7.77 (ddd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, acridine), 7.47 (ddd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, acridine), 7.27 (AA', 2H, phenyl), 7.19 (BB', 2H, phenyl), 7.18 – 7.12 (AA'BB', 8H, phenyl), 2.35 (s, 6H, methyl). ^{13}C NMR (63 MHz, CD_2Cl_2): δ 149.3, 148.6, 147.6, 145.4, 133.7, 131.7, 130.4 (2x), 130.1, 130.0, 128.3, 127.4, 125.7, 125.6, 121.4, 20.9. $C_{33}H_{26}N_2$ calcd C 87.97, H 5.82, N 6.22 found C 87.71, H 6.04, N 5.92.

9-(4-(*N*,*N*-Di(4-methoxyphenyl)amino)phenyl)acridine (8): Compound **(8)** was synthesized via **general method B** using 9-(4-bromophenyl)acridine **11** (500 mg, 1.50 mmol), di(4-methoxyphenyl)amine (362 mg, 1.58 mmol), sodium *tert*-butoxide (181 mg, 1.88 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (16 mg, 16 μmol) and P^tBu_3 (0.07 ml of a 10% solution in hexane, 24 μmol) in toluene (5 ml). Flash chromatography (silica gel, dichloromethane/ethyl acetate 20:1) and precipitation of the crude product from dichloromethane/methanol yielded 495 mg (1.03 mmol, 69 %) of a yellow solid. Mp 230 – 231 °C. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 8.20 (m, 2H, acridine), 7.90 (ddd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.7 Hz, 2H, acridine), 7.76 (ddd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, acridine), 7.46 (ddd, $^3J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, acridine), 7.24 (AA', 2H, phenyl), 7.22 (AA', 4H, phenyl), 7.09 (BB', 2H, phenyl), 6.91 (BB', 4H, phenyl), 3.81 (s, 6H, methoxy). ^{13}C NMR (63 MHz, CD_2Cl_2): δ 156.8, 149.4, 149.3, 147.8, 140.8, 131.7, 130.1, 130.0, 127.6, 127.4, 127.1, 125.7, 125.6, 119.3, 115.2, 55.8. HRMS (EI): calcd for $C_{33}H_{26}N_2O_2$ 482.1994 found 482.1993.

9-(4-(*N*-(4-chlorophenyl)-*N*-(4-(4-(*N*',*N*'-di(4-methoxyphenyl)amino)phenyl)ethynyl-phenyl)amino)phenyl)acridin (1): Following **general method C** compound **(1)** was prepared from 9-(4-(*N*-(4-bromophenyl)-*N*-(4-chlorophenyl)amino)phenyl)acridine **15** (400

mg, 746 μmol), *N*,*N*-di(4-methoxyphenyl)-*N*-(4-ethynylphenyl)amine[6] **18** (283 mg, 858 μmol), $Pd(C_6H_5CN)_2Cl_2$ (8.6 mg, 22 μmol), cuprous iodide (2.8 mg, 15 μmol), P^tBu_3 (0.14 ml of a 10% solution in hexane, 45 μmol) and diisopropylamine (0.13 ml, 0.90 mmol) in dioxane (5 ml). Column chromatography (neutral aluminum oxide, activity V, dichloromethane/petrol ether 1:2) and precipitation of the crude product from dichloromethane/methanol gave 200 mg (255 μmol, 34 %) of a yellow powder. Mp 150 °C dec. ^{1}H NMR (600 MHz, [D$_6$]-acetone): δ 8.22 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.1 Hz, $^5J_{HH}$ = 0.8 Hz, 2H, acridine), 7.85 (ddd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 1.3 Hz, $^5J_{HH}$ = 0.8 Hz, 2H, acridine), 7.84 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, acridine), 7.54 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, acridine), 7.49 (AA', 2H, phenyl), 7.47 (AA', 2H, phenyl), 7.43 (AA', 2H, phenyl), 7.39 (BB', 2H, phenyl), 7.32 (AA', 2H, phenyl), 7.30 (BB', 2H, phenyl), 7.22 (BB', 2H, phenyl), 7.10 (AA', 4H, phenyl), 6.79 (BB', 4H, phenyl), 3.80 (s, 6H, methoxy). ^{13}C NMR (151 MHz, [D$_6$]-acetone): δ 157.8, 150.0, 149.9, 148.1, 147.9, 147.3, 147.0, 140.8, 133.4, 133.1, 132.7, 131.5, 130.8, 130.7, 130.6, 129.3, 128.3, 127.6, 127.4, 126.7, 125.9, 124.7, 124.6, 119.3, 119.2, 115.8, 114.6, 90.6, 88.6, 55.8. HRMS (EI): calcd for $C_{53}H_{38}ClN_3O_2$ 783.2653 found 783.2667.

9-(4-(*N*-(4-(4-(*N*',*N*'-Di(4-methoxyphenyl)amino)phenyl)ethynylphenyl)-*N*-(4-methyl-phenyl)amino)phenyl)acridine (2): Compound **(2)** was synthesized via **general method C** from 9-(4-(*N*-(4-bromophenyl)-*N*-(4-methylphenyl)amino)phenyl)acridine **16** (300 mg, 582 μmol), *N*,*N*-di(4-methoxyphenyl)-*N*-(4-ethynylphenyl)amine[6] **18** (220 mg, 669 μmol), $Pd(C_6H_5CN)_2Cl_2$ (6.7 mg, 18 μmol), cuprous iodide (2.2 mg, 12 μmol), P^tBu_3 (0.11 ml of a 10% solution in hexane, 35 μmol) and diisopropylamine (0.10 ml, 0.70 mmol) in dioxane (5 ml). The crude product was purified by column chromatography (neutral aluminum oxide, activity V, dichloromethane/petrol ether 1:2) and subsequent precipitation from dichloro-methane/methanol. Yield: 140 mg (183 μmol, 31 %) of a yellow solid. Mp 137 °C dec. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 8.22 (m, 2H, acridine), 7.88 (m, 2H, acridine), 7.78 (m, 2H, acridine), 7.48 (m, 2H, acridine), 7.41 (AA', 2H, phenyl), 7.34 (AA', 2H, phenyl), 7.30 (AA', 2H, phenyl), 7.29 (BB', 2H, phenyl), 7.21 (AA', 2H, phenyl), 7.18 (BB', 2H, phenyl), 7.15 (BB', 2H, phenyl), 7.07 (AA', 4H, phenyl), 6.86 (BB', 4H, phenyl), 6.81 (BB', 2H, phenyl), 3.79 (s, 6H, methoxy), 2.37 (s, 3H, methyl). ^{13}C NMR (151 MHz, CD_2Cl_2): δ 156.9, 149.3, 149.2, 148.0, 147.8, 147.3, 144.7, 140.5, 134.8, 132.6, 132.5, 131.9, 130.7, 130.2, 130.1, 130.0, 127.6, 127.3, 126.4, 125.8, 125.6, 123.4, 123.1, 119.3, 117.5, 115.2, 114.3, 89.6, 88.4, 55.8, 21.0. HRMS (EI): calcd for $C_{54}H_{41}N_3O_2$ 763.3199 found 763.3210.

9-(4-(*N*-(4-(4-(*N*',*N*'-Di(4-chlorophenyl)amino)phenyl)ethynylphenyl)-*N*-(4-methoxy-phenyl)amino)phenyl)acridin (3): Following **general method C** compound **(3)** was prepared from *N*,*N*-di(4-chlorophenyl)-*N*-(4-ethynylphenyl)amine **19** (229 mg, 677 μmol), 9-

(4-(*N*-(4-bromophenyl)-*N*-(4-methoxyphenyl)amino)phenyl)acridine **17** (300 mg, 564 μmol), $Pd(C_6H_5CN)_2Cl_2$ (6.5 mg, 17 μmol), cuprous iodide (2.1 mg, 11 μmol), P^tBu_3 (0.10 ml of a 10% solution in hexane, 34 μmol) and diisopropylamine (0.09 ml, 0.62 mmol) in dioxane (3 ml). Flash chromatography (silica gel, dichloromethane/ethyl acetate 20:1) yielded 143 mg (181 μmol, 32 %) of a yellow powder. Mp 147 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8,22 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.1 Hz, $^5J_{HH}$ = 0.8 Hz, 2H, acridine), 7.88 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.8 Hz, 2H, acridine), 7.78 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, acridine), 7.48 (ddd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, acridine), 7.42 (AA', 2H, phenyl), 7.39 (AA', 2H, phenyl), 7.34 (AA', 2H, phenyl), 7.29 (BB', 2H, phenyl), 7.254 (AA', 4H, phenyl), 7.249 (AA', 2H, phenyl), 7.14 (BB', 2H, phenyl), 7.03 (BB', 4H, phenyl), 6.99 (BB', 2H, phenyl), 6.97 (BB', 2H, phenyl), 3.84 (s, 3H, methoxy). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 157.6, 149.4, 148.2, 148.0, 147.29, 147.27, 146.0, 140.0, 132.9, 132.8, 131.9, 130.14, 130.12, 129.9, 128.9, 128.6, 127.3, 126.2, 125.8 (2x), 125.7, 123.3, 123.0, 122.2, 118.0, 116.5, 115.5, 89.6, 88.8, 55.9. HRMS (EI): calcd for $C_{52}H_{35}Cl_2N_3O$ 787.2157 found 787.2156.

9-(4-(*N*-(4-Chlorophenyl)-*N*-(4-(4-(*N*'-(4-(4-(*N*'',*N*''-di(4-methoxyphenyl)amino)phenyl)-ethynylphenyl)-*N*'-(4-methylphenyl)amino)phenyl)ethynylphenyl)amino)phenyl)-acridine (4): Compound **(4)** was prepared from 9-(4-(*N*-(4-(bromophenyl)-*N*-(4-chloro-phenyl)amino)phenyl)acridine **15** (150 mg, 280 μmol), *N*,*N*-di(4-methoxyphenyl)-*N*-(4-(4-(*N*'-(4-methylphenyl)-*N*'-(4-ethynylphenyl)amino)phenyl)ethynylphenyl)amine **22** (188 mg, 308 μmol), $Pd(C_6H_5CN)_2Cl_2$ (3.2 mg, 8.4 μmol), cuprous iodide (1.1 mg, 5.6 μmol), P^tBu_3 (0.05 ml of a 10% solution in hexane, 17 μmol) and diisopropylamine (0.05 ml, 0.34 mmol) in dioxane (3 ml) using **general method C**. Column chromatography (neutral aluminum oxide, activity V, using a gradient of dichloromethane/petrol ether 1:2 → 2:3 as eluent) yielded 140 mg (131 μmol, 47 %) of a yellow solid. Mp 163 °C dec. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 8.23 (m, 2H, acridine), 7.86 (m, 2H, acridine), 7.79 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, acridine), 7.49 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, acridine), 7.46 (AA', 2H, phenyl), 7.39 – 7.31 (10H, phenyl), 7.27 (AA', 2H, phenyl), 7.22 (BB', 2H, phenyl), 7.18 (BB', 2H, phenyl), 7.15 (AA', 2H, phenyl), 7.07 (AA', 4H, phenyl), 7.03 (BB', 2H, phenyl), 7.02 – 6.99 (AA'BB', 4H, phenyl), 6.86 (BB', 4H, phenyl), 6.81 (BB', 2H, phenyl), 3.79 (s, 6H, methoxy), 2.34 (s, 3H, methyl). ^{13}C NMR (151 MHz, CD_2Cl_2): δ 156.9, 149.3, 149.2, 147.8, 147.5, 147.4, 147.3, 147.0, 146.2, 144.4, 140.5, 134.8, 133.0, 132.7, 132.6, 132.5, 132.2, 131.0, 130.6, 130.2, 130.1, 130.0, 129.1, 127.6, 127.2, 126.7, 126.4, 125.9, 125.6, 124.2, 123.8, 123.4, 123.0, 119.3, 118.1, 117.8, 117.0, 115.2, 114.3, 89.8, 89.6, 89.0, 88.3, 55.8, 21.0. HRMS (EI): calcd for $C_{74}H_{53}ClN_4O_2$ 1064.3857 found 1064.3879.

9-(4-(*N*,*N*-Bis(4-(4-(*N*',*N*'-di(4-methoxyphenyl)amino)phenyl)ethynylphenyl)amino)-phenyl)acridine (5): Preparation followed **general method C** using 9-(4-(*N*,*N*-di(4-ethynylphenyl)amino)phenyl)acridine **27** (300 mg, 638 μmol), *N*-(4-bromophenyl)-*N*,*N*-di(4-methoxyphenyl)amine **26** (588 mg, 1.53 mmol), $Pd(C_6H_5CN)_2Cl_2$ (7.3 mg, 19 μmol), cuprous iodide (2.4 mg, 13 μmol), P^tBu_3 (0.11 ml of a 10% solution in hexane, 38 μmol) and diisopropylamine (0.22 ml, 1.6 mmol) in dioxane (15 ml). Column chromatography (neutral aluminum oxide, activity V, dichloromethane/petrol ether 1:3) yielded 232 mg (215 μmol, 34 %) of a yellow solid. Mp 145 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.23 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.1 Hz, $^5J_{HH}$ = 0.8 Hz, 2H, acridine), 7.87 (ddd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.2 Hz, $^5J_{HH}$ = 0.6 Hz, 2H, acridine), 7.79 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, acridine), 7.49 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, acridine), 7.46 (AA', 4H, phenyl), 7.38 – 7.35 (AA'BB', 4H, phenyl), ,7.30 (AA', 4H, phenyl), 7.21 (BB', 4H, phenyl), 7.08 (AA', 8H, phenyl), 6.86 (BB', 8H, phenyl), 6.81 (BB', 4H, phenyl), 3.79 (s, 12H, methoxy). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 157.0, 149.4, 149.3, 147.4, 147.06, 147.04, 140.5, 132.8, 132.6, 132.2, 131.1, 130.2, 130.1, 127.6, 127.2, 125.9, 125.6, 124.6, 124.4, 119.2, 118.8, 115.2, 114.1, 90.1, 88.2, 55.8. HRMS (EI): calcd for $C_{75}H_{56}N_4O_4$ 1076.4302 found 1076.4319.

X-Ray Structure Analysis

Slow evaporation of a solution of **8** in CH_2Cl_2/MeOH yielded crystals suitable for X-ray crystallographic investigation. The most important structural results are the planar trigonal coordinate amine nitrogen (angle sum 360°), the strongly twisted anisyl groups (71.8° and 75.6° relative to the amine plane), the slightly twisted phenylene group (10.9° relative to the amine plane) and the almost perpendicular phenyl-acridine dihedral angle (83.7°). The amine plane has a 85.6° dihedral angle vs. the acridine.

The data set was collected at low temperature using an oil-coated shock-cooled crystal on a Bruker APEX-CCD diffractometer with Mo-K_α (λ = 71.073 pm) radiation equipped with a low temperature device at 173(2) K. The structures were solved by direct methods (SHELXS-NT 97)[7] and refined by full-matrix least squares methods against F^2 (SHELXL-NT 97).[8] All non-hydrogen atoms were refined anisotropically. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-261335. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (Internat.)+44-1223/336-033, e-mail: deposit@ccdc.cam.ac.uk].

Monoclinic, space group: $P2_1/c$; cell dimensions: a = 8.3516(19) Å, b = 30.307(7) Å, c = 9.825(2) Å, $\alpha = \gamma = 90°$, β = 92.697(4)°; V = 2484.1(10) Å^3; Z = 4, calculated density: ρ = 1.290 g/cm^3; crystal size: 0.2 mm × 0.2 mm × 0.2 mm; scan angles: 1.34° < θ < 25.58°;

number of collected reflexes: 43467, independent reflexes: 4627; Goodness-of-fit für F^2: 1.048; R1 = 0.0366, w*R*2 = 0.0961 für $I > 2\sigma(I)$; *R*1 = 0.0399, w*R*2 = 0.0984 for all reflexes; minimal and maximal residual electron density: -0.217/0.167 eÅ^{-3}; numeric absorption correction.

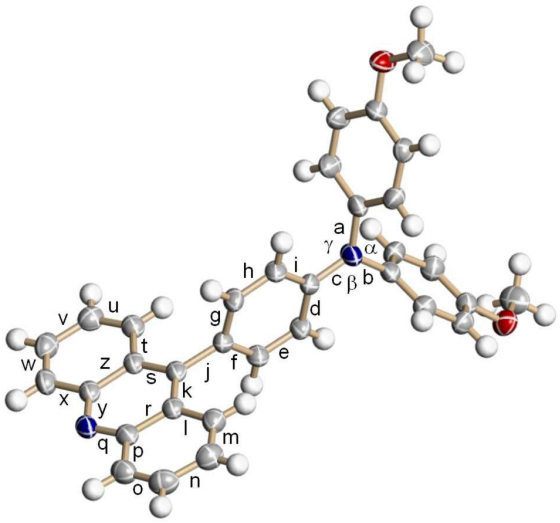


Table S1. Selected bond angles and distances of **8**.

	17
α	116.28(9)°
β	121.19(9)°
γ	122.53(9)°
a	1.4355(15) Å
b	1.4365(15) Å
c	1.3903(14) Å
d	1.4004(16) Å
e	1.3844(16) Å
f	1.3870(16) Å
g	1.3929(16) Å
h	1.3838(16) Å
i	1.3995(16) Å
j	1.4968(15) Å
k	1.4050(16) Å
l	1.4265(17) Å
m	1.3592(17) Å
n	1.4170(19) Å
o	1.3575(19) Å
p	1.4287(17) Å
q	1.3432(16) Å
r	1.4373(15) Å
s	1.4026(16) Å
t	1.4262(17) Å
u	1.3567(19) Å
v	1.420(2) Å
w	1.358(2) Å
x	1.4240(17) Å
y	1.3461(16) Å
z	1.4320(16) Å

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