Supporting Information for
Synthesis of 9-substituted acridines from bis(bromophenyl)amine

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General Experimental:

Reagents and anhydrous solvents were purchased from Sigma-Aldrich or Alfa Aesar. All other chemicals were used without purification unless otherwise noted. NMR spectra were acquired on a JEOL 400 MHz NMR spectrometer with chloroform-d$_1$ ($\delta_H = 7.26$ ppm $\delta_C = 77.23$ ppm ) or acetone-d$_6$($\delta_H = 2.05$ ppm $\delta_C = 206.26$ ppm). All coupling constants were generated by the MestReNova program and were uncorrected. Chromatography was performed with Biotage KP-SIL™ or KP-NH™ cartridges or Silicycle silica gel (porosity = 60 Å, particle size 40-63 μm). Microwave reactions were run on the Discover Microwave System by CEM Corporation. HRMS was acquired with an Agilent 7200 GC/QTOF or Bruker Bio TOF II with Electrospray Ionization.
Synthesis of bis(bromophenyl)amine (3):

To a flame dried 35 mL microwave vial with a teflon cap, 16 mL of anhydrous toluene was added followed by 3.18 g (33.1 mmol) of sodium tert-butoxide then 2.6 mL (23 mmol) of 2-bromoaniline (1) and 3.0 mL (23 mmol) of 2-bromoiodobenzene (2) dropwise and stirred. The ligand DPEPhos, 103 mg (0.190 mmol), and 29.8 mg (0.133 mmol) Pd(OAc)$_2$ were added then heated 30 minutes at 150 °C in a microwave reactor. The product was extracted with 3 x 35 mL of dichloromethane and the combined organic layer was washed with water (3 x 150mL). The organic layer was dried over magnesium sulfate and concentrated in vacuo. The resulting product was recrystallized from ethanol to yield white or gray needle-like crystals in 68 % yield.

**MP** 59.8-60.7 °C

**$^1$H-NMR** (400 MHz, CDCl$_3$) δ: 7.58 (dd, J = 8.0 Hz, 1.6 Hz, 2H), 7.30 (dd, J = 8.0 Hz, 1.6 Hz, 2H), 7.22 (td, J = 8.4 Hz, 1.2 Hz, 2H), 6.84 (td, J = 7.6 Hz, 2.0 Hz, 2H), 6.44 (s, 1H)

**$^{13}$C-NMR** (100 MHz, CDCl$_3$) δ: 140.13, 133.39, 128.23, 122.67, 118.08, 114.38

**HRMS** (EI) calc. for C$_{12}$H$_9$Br$_2$N 324.9102, found 324.9094

**UV-Vis** (CH$_2$Cl$_2$) λ max (ε, cm$^{-1}$M$^{-1}$) 287 (39000)

Synthesis of bis(tolan)amine (4a):

To a flame dried 35mL microwave vial with a teflon cap, 25 mL of diisopropylamine was added via syringe and degassed with nitrogen for ten minutes. To this vessel 510 mg (1.6 mmol) of bis(2-bromophenyl)amine (3), 140 mg (0.74 mmol) CuI, and 111 mg Pd(PPh$_3$)$_2$Cl$_2$ (0.16 mmol) were added sequentially while stirring under nitrogen. Subsequently 0.84 mL of phenyl acetylene was added dropwise via syringe over 30 min followed by heating for 2.5 hours at 120 °C in a microwave reactor. Upon completion, the reaction was poured over ice and extracted into dichloromethane (3 × 50mL). The combined organic layer was washed with water (3 × 100mL) then concentrated in vacuo. The reaction was then purified using a KP-NH™ flash column using hexanes and ethyl acetate to produce a yellow solid in 63 % yield.

**MP** 136.6-137.1 °C

**$^1$H-NMR** (400 MHz, CDCl$_3$) δ: 7.53 (dd, J = 1.4 Hz, 7.7 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.38 (m, 5H), 7.28 (t, J = 7.3 Hz, 2H), 7.22-7.17 (m, 2H), 7.13 (t, J = 7.2 Hz, 4H), 6.90 (t, J = 7.6 Hz, 2H)

**$^{13}$C-NMR** (100 MHz, CDCl$_3$) δ: 143.2, 132.9, 131.7, 129.4, 128.4, 128.3, 122.9, 120.1, 115.3, 112.2, 96.2, 85.6

**HRMS** (ESI) calc. for C$_{28}$H$_{19}$NNa $[M + Na]^+$ 392.141519, found 392.1433

**UV-Vis** (CH$_2$Cl$_2$) λ max (ε, cm$^{-1}$M$^{-1}$) 279 (160000), 312 (37000), 340 (44000)
General Procedure for the synthesis of 9-substituted acridine (5a-f) derivatives:

**Microwave Heating:**
To a flame dried 35 mL microwave vial with a teflon coated cap, 25 mL of ethylene diamine was added via syringe and degassed with nitrogen for 20 minutes. To this vessel was added 504 mg (1.5 mmol) of bis(2-bromophenyl)amine (3), 66 mg (0.30 mmol) of copper iodide, and 219 mg (0.30 mmol) of bis(triphenylphosphine)palladium dichloride sequentially while stirring under nitrogen. Next 3.0 mmol of aryl acetylene was added dropwise via syringe. The reaction flask was heated for 1.5 hours at 180 °C in a microwave reactor. Upon completion, the reaction was then poured over ice, extracted into dichloromethane (3 x 35 mL) and the combined organic layers were washed with water three times before purifying on an amine treated KP-NH™ silica flash column using hexanes and ethyl acetate as eluent. Fractions include primarily bis(tolan)amines (4a-f), 9-substituted acridines (5a-f), and carbazole (6) depending on conditions.

**Conventional Heating:**
To a flame dried 150 mL pressure vessel, 25 mL of ethylene diamine was added via syringe and degassed with nitrogen for 20 minutes. To this vessel was added 504 mg (1.5 mmol) of bis(2-bromophenyl)amine (3), 66 mg (0.30 mmol) of copper iodide, and 219 mg (0.30 mmol) of bis(triphenylphosphine)palladium dichloride sequentially while stirring under nitrogen. Next 3.0 mmol of aryl acetylene was added dropwise via syringe. The reaction flask was heated for 1.5 hours in an oil bath set to 180 °C. Upon completion, the reaction was then poured over ice, extracted into dichloromethane (3 x 35 mL) and the combined organic layers were washed with water three times before purifying on an amine treated KP-NH™ silica flash column using hexanes and ethyl acetate as eluent. Fractions include primarily bis(tolan)amines (4a-f), 9-substituted acridines (5a-f), and carbazole (6) depending on conditions.

**Preparation of 9-benzylacridine (5a):**
The general procedure for the synthesis of 9-substituted acridine derivatives above was followed with 0.33 mL (3.0 mmol) phenyl acetylene. The reaction produced a mustard yellow solid in 203 mg (53%) yield by microwave heating. Conventional heating produces 217 mg (55%) yield.

**MP** 160.6-163.6 °C **\(^1^H-NMR\) (400 MHz, CDCl\(_3\)) δ: 8.25 (t, J = 8.0 Hz, 4H), 7.77 (t, J = 4.0 Hz, 2H), 7.53 (td, J = 8.0 Hz,1.2 Hz 2H), 7.24-7.16 (m, 3H), 7.11 (d, J = 6.8 Hz, 2H), 5.03 (s, 2H) **\(^1^3^C-NMR\) (100 MHz, CDCl\(_3\)) δ: 149.0, 143.6, 139.5, 130.5, 130.0, 128.9, 128.3, 126.2, 126.2 125.8, 124.9, 33.3 **HRMS** (ESI) calc. for C\(_{20}\)H\(_{16}\)N 270.1283, found 270.1204 **UV-Vis** (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (\(\varepsilon\), cm\(^{-1}\)M\(^{-1}\)) 255 (120000), 280 (sh,5100), 343 (5700), 361 (8600), 387 (38000)
Preparation of 9-(4-methylbenzyl)acridine (5b):

The general procedure for the synthesis of 9-substituted acridine derivatives above was followed with 0.39 mL (3.0 mmol) 4-ethynyltoluene. The reaction produced a pale white solid in 236 mg (55%) yield. Conventional heating produces 184 mg (40%) yield.

**MP** 160.6-163.6 °C  
**1H-NMR** (400 MHz, CDCl3) δ: 8.25 (dd J = 8.9 Hz, 9.1 Hz, 4H) 7.77 (dd, J = 1.2 Hz, 8.8 Hz, 8.8 Hz, 2H), 7.52 (dd, J = 1.2 Hz, 8.8 Hz, 8.9 Hz, 2H), 7.01 (aa′bb′ J = 8.4 Hz, 8.4 Hz, 4.8 Hz, 4H), 4.99 (s, 2H), 2.26 (s, 3H)  
**13C-NMR** (100 MHz, CDCl3) δ: 149.04, 143.90, 136.42, 136.16, 130.49, 129.95, 129.52, 128.12, 126.16, 125.80, 124.94, 32.89, 21.11  
**HRMS** (ESI) calc. for C21H18N [M+1]^+ 284.1439, found 284.1431

**UV-Vis** (CH2Cl2) λ max (ε, cm⁻¹M⁻¹) 255 (130000), 247 (sh,55000), 342 (6100), 362 (9100), 387 (3000)

Preparation of 9-(4-methoxybenzyl)acridine (5c):

The general procedure for the synthesis of 9-substituted acridine derivatives above was followed with 0.39 mL (3.0 mmol) 4-ethynylanisole. The reaction produced a light cream colored solid in 155 mg (35%) yield. Conventional heating produces 162 mg (36%) yield.

**MP** 135.9-138.7 °C  
**1H-NMR** (400 MHz, CDCl3) δ: 8.25 (dd J = 7.8 Hz, 8.0 Hz, 4H), 7.77 (dd, J = .8 Hz, 8.5 Hz, 8.6 Hz, 2H), 7.53 (dd, J = 1.1 Hz, 8.6 Hz, 8.5 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 6.75 (d, J = 8.8 Hz, 2H), 4.96 (s, 2H), 3.72 (s, 3H)  
**13C-NMR** (100 MHz, CDCl3) δ: 158.2, 149.0, 144.0, 131.5, 130.5, 130.0, 129.2, 126.1, 125.7, 124.9, 114.2, 55.4, 32.4  
**HRMS** (ESI) calc. for C21H18NO 300.1388, found 300.1381

**UV-Vis** (CH2Cl2) λ max (ε, cm⁻¹M⁻¹) 255 (430000), 247 (sh,180000), 344 (19000), 361 (28000), 387 (14000)

Preparation of 9-(4-fluorobenzyl)acridine (5d):

The general procedure for the synthesis of 9-substituted acridine derivatives above was followed with 0.35 mL (3.0 mmol) 1-ethynyl-4-fluorobenzene. The reaction produced a toffee-colored solid in 119 mg (27%) yield. Conventional heating produces 78 mg (18%) yield.

**MP** 163.6-165.9 °C  
**1H-NMR** (400 MHz, DMSO) δ: 8.45 (d, J = 9.0 Hz, 2H), 8.18 (d, J = 8.5 Hz, 2H), 7.85 (dd, J = 7.7 Hz, 8.8 Hz, 2H), 7.64 (dd, J = 7.5 Hz, 8.8 Hz, 2H), 7.17 (dd, J = 8.8 Hz, 8.5 Hz, 2H), 7.04 (t, J = 8.8 Hz, 2H), 5.10 (s, 2H)  
**13C-NMR** (100 MHz, CDCl3) δ: 149.1, 143.2, 130.7, 130.0, 129.7, 129.6, 126.3, 125.7, 126.4, 125.7, 124.7, 115.8, 115.6, 32.5  
**HRMS** (EI) calc. for C20H14FN 287.1111, found 287.1108

**UV-Vis** (CH2Cl2) λ max (ε, cm⁻¹M⁻¹) 255 (470000), 343 (23000), 360 (35000), 385 (16000)
Preparation of 9-heptylacridine (5e):

The general procedure for the synthesis of 9-substituted acridine derivatives above was followed with 0.45 mL (3.0 mmol) 1-octyne. The reaction produced a light red oil in 78 mg (19%) yield.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 8.23 (dd, J = 8.8 Hz, 8.8 Hz, 2H), 7.76 (dd, J = 7.7 Hz, 8.6 Hz, 2H), 7.56 (dd, J = 8.4 Hz, 8.6 Hz, 2H), 3.61 (t, J = 8.0 Hz, 2H), 1.82 (p, J = 7.8 Hz, 2H), 1.57 (p, J = 7.2 Hz, 2H), 1.40 (p, J = 6.9 Hz, 2H), 1.33-1.29 (m, 4H), .89 (t, J = 6.7 Hz, 3H)

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 148.9, 142.1, 136.6, 129.9, 128.5, 126.0, 125.7, 125.0, 124.5, 35.8, 32.0, 31.11, 31.04, 27.7 HRMS (EI) calc. for C$_{20}$H$_{23}$N 277.1831, found 277.1817 UV-Vis (CH$_2$Cl$_2$) $\lambda_{max}$ (ε, cm$^{-1}$M$^{-1}$) 255 (320000), 247 (sh,130000), 359 (190000), 388 (8500)

Preparation of 9-(4-phenylbutyl)acridine (5f):

The general procedure for the synthesis of 9-substituted acridine derivatives above was followed with 0.46 mL (3.0 mmol) 5-phenyl-1-pentyne. The reaction produced a pale green oil in 50 mg (10%) yield.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 8.22 (d, J = 8.7 Hz, 2H), 8.21 (d, J = 8.6 Hz, 2H), 7.76 (ddd, J = 8.4 Hz, .7 Hz, 8.6 Hz, 2H), 7.55 (ddd, J = 8.6 Hz, 10.3 Hz, 1.0 Hz, 2H), 7.28 (t, 2H), 7.21-7.16 (mp, 3H), 3.64 (t, J = 7.9 Hz, 2H), 2.70 (t, J = 6.9 Hz, 2H), 1.93-1.84 (brm, 4H) $^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 148.8, 142.1, 136.6, 129.9, 128.5, 126.0, 125.7, 125.0, 124.5, 35.8, 32.0, 31.11, 31.04, 27.7 HRMS (EI) calc. for C$_{23}$H$_{21}$N 311.1674, found 311.1685 UV-Vis (CH$_2$Cl$_2$) $\lambda_{max}$ (ε, cm$^{-1}$M$^{-1}$) 255 (890000), 247 (sh,400000), 360 (59000), 386 (2600)
Spectra for all molecules:

Bis(bromophenyl)amine (3):

\[ \text{1H-NMR (400 MHz, CDCl}_3) \]

\[ \text{13C-NMR (100 MHz, CDCl}_3) \]
Bis(tolan)amine (4a):

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

\[ 1^\text{3C}-\text{NMR} \ (100 \text{ MHz, CDCl}_3) \]
Generic Display Report (all)
9-(Benzyl)acridine (5a):

\[ \text{1H-NMR (400 MHz, CDCl}_3) \]

\[ \text{13C-NMR (100 MHz, CDCl}_3) \]
9-(4-Methylbenzyl)acridine (5b):
Generic Display Report (all)

Wavelength (nm)

Absorbance
9-(4-Methoxybenzyl)acridine (5c):

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

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

5c
9-(4-Fluorobenzyl)acridine (5d):

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

$^1$H-NMR (400 MHz, DMSO)
9-Heptylacridine (5e):

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

$^{13}$C-NMR (100 MHz, CDCl$_3$)
9-(4-Phenylbutyl)acridine (5f):

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

$\text{C-NMR (100 MHz, CDCl}_3\text{)}$
