

General procedure for amination reactions using a 1:1 ratio of Pd(dba)₂ and P(*t*-Bu)₃. In a drybox, the aryl halide, amine, and sodium *tert*-butoxide were weighed into a reaction vessel. For convenience, Pd(dba)₂, or Pd(OAc)₂ and tri-*tert*-butyl phosphine were weighed in a separate vial; toluene was added to this vial, and the resulting mixture was added to the reaction flask containing the other reagents, followed by the remaining toluene. The resulting mixture was removed from the box and stirred at the given temperature. The reaction times and catalyst loading were not minimized.

Compound 1. The general amination procedure was followed using aminodiphenylmethane (1.83 g, 10.00 mmol), 4-bromochlorobenzene (4.60 g, 24.03 mmol), sodium *tert*-butoxide (2.88 g, 30.00 mmol), Pd(dba)₂ (115 mg, 0.208 mmol), tri-*tert*-butyl phosphine (32 mg, 0.16 mmol) and 30 mL of toluene to give a purple mixture. The reaction vessel was removed from the drybox and stirred at room temperature. After 16 h, the brown slurry was poured into a saturated aqueous solution of ammonium chloride and extracted two times with toluene. The combined organic layers were dried over magnesium sulfate and evaporated under vacuum. The crude material was adsorbed onto silica gel and purified by flash chromatography using 25% toluene/hexanes to give 3.75 g (93%) of **1** as a colorless oil. ¹H NMR (500 MHz, C₆D₆) δ 6.05 (s, 1 H), 6.52 (d, *J* = 9.0 Hz, 4 H), 6.90 (d, *J* = 9.0 Hz, 4 H), 6.93-7.03 (m, 10 H). ¹³C NMR (125 MHz, C₆D₆) δ 69.17, 124.96, 127.47, 127.61, 128.47, 129.18, 129.55, 140.70, 145.98. Anal Calcd for C₂₅H₁₉NCl₂: C, 74.26; H, 4.74; N, 3.46. Found: C, 74.05; H, 4.74; N, 3.37. HRMS Calcd for C₂₅H₁₉NCl₂: 403.0895. Found: 403.0900.

Compound 2. The general amination procedure was followed using **1** (564 mg, 1.39 mmol, 1.00 equiv), di-*p*-tolylamine (605 mg, 3.07 mmol), sodium *tert*-butoxide (400 mg, 4.17 mmol), Pd(dba)₂ (32 mg, 0.055 mmol), tri-*tert*-butyl phosphine (9.0 mg, 0.044 mmol) and 17 mL of toluene to give a purple mixture. The reaction vessel was removed from the box and stirred at 100-105 °C. After 13.5 h, the brown mixture was poured into a saturated aqueous solution of ammonium chloride and extracted two times with toluene.

The combined organic layers were washed with brine, dried over magnesium sulfate and evaporated under vacuum to give a brown oil. Crystallization from EtOAc/EtOH gave 769 mg (77%) of **2** as an off-white solid. ^1H NMR (500 MHz, C_6D_6) δ 2.09 (s, 12 H), 6.20 (s, 1H), 6.82 (d, J = 9.0 Hz, 4 H), 6.88 (d, J = 8.5 Hz, 8 H), 6.93 (d, J = 9.0 Hz, 4 H), 6.99-7.05 (m, 14 H), 7.17 (d, J = 6.5 Hz, 4 H). ^{13}C NMR (125 MHz, C_6D_6) δ 20.72, 69.67, 124.10, 124.52, 125.30, 127.03, 128.29, 129.93, 130.07, 131.58, 142.05, 142.82, 142.95, 146.39. Anal. Calcd for $\text{C}_{53}\text{H}_{47}\text{N}_3$: C, 87.69; H, 6.53; N, 5.79. Found: C, 87.46; H, 6.57; N, 5.63. MS (MALDI) 725.42.

Compound 3. Cyclohexene (27 mL) was added to a mixture of **2** (2.00 g, 2.75 mmol) and 400 mg of 10% palladium on carbon in a round bottom flask to give a black slurry. The flask was sealed with a rubber septum, which was wired to the flask. The reaction vessel was heated at 75-80° C in an oil bath. After 25 h, the slurry was filtered through Celite and adsorbed onto silica gel. Purification by flash chromatography using 40% toluene/hexanes gave 1.29 g (84%) of **3** as a white solid identical to that previously prepared.³³ ^1H NMR (500 MHz, C_6D_6) δ 2.10 (s, 12 H), 4.87 (s, 1 H), 6.74 (d, J = 8.5 Hz, 4 H), 6.92 (d, J = 8.5 Hz, 8 H), 7.06 (d, J = 9.0 Hz, 4 H), 7.13 (d, J = 8.5 Hz, 8 H). ^{13}C NMR (125 MHz, C_6D_6) δ 21.12, 119.50, 124.30, 126.62, 130.53, 131.90, 139.77, 142.44, 146.98.

Compound 5. The general amination procedure was followed using **1** (220 mg, 0.54 mmol, 1.00 equiv), **3** (612 mg, 1.09 mmol), sodium *tert*-butoxide (157 mg, 1.63 mmol), $\text{Pd}(\text{dba})_2$ (12 mg, 0.022 mmol), tri-*tert*-butyl phosphine (3.5 mg, 0.017 mmol) and 10 mL of toluene to give a purple mixture. The reaction vessel was removed from the box and stirred at 100 °C. After 7.5 h, the brown mixture was poured into a saturated aqueous solution of sodium chloride and extracted three times with toluene. The combined organic layers were dried over magnesium sulfate and evaporated under vacuum. Purification by crystallization from THF/EtOH gave 579 mg (73%) of **5** as a light green solid that was judged to be >95% pure by NMR spectroscopy and was used

without further purification. ^1H NMR (500 MHz, C_6D_6) δ 2.08 (s, 24 H), 6.19 (s, 1 H), 6.79 (d, $J = 9.0$ Hz, 4 H), 6.84-7.04 (m, 46 H), 7.11 (d, $J = 8.0$ Hz, 16 H). ^{13}C NMR (125 MHz, C_6D_6) δ 21.13, 70.03, 124.77, 124.93, 125.13, 125.51, 125.77, 127.49, 128.70, 130.30, 130.59, 132.28, 142.32, 142.81, 143.37, 143.66, 143.68, 146.70. Anal. Calcd for $\text{C}_{105}\text{H}_{91}\text{N}_7$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.50; H, 6.33; N, 6.76. MS (MALDI) 1451.44.

Compound 6. Cyclohexene (8 mL) was added to a mixture of **5** (467 mg, 0.322 mmol) and 94 mg of 10% palladium on carbon in 7 mL of THF in a small vial. The sealed vial was heated at 75-80° C in an oil bath. After 24 h, the slurry was filtered through Celite, and the filtrate was evaporated under vacuum. The crude product was crystallized from THF/EtOH to give 279 mg (75%) of **9** as a green solid identical to that previously prepared.³³ ^1H NMR (500 MHz, C_6D_6) δ 2.08 (s, 24 H), 4.83 (s, 1 H), 6.71 (d, $J = 9.0$ Hz, 4 H), 6.89 (d, $J = 8.5$ Hz, 16 H), 7.07-7.14 (m, 36 H). ^{13}C NMR (125 MHz, C_6D_6) δ 21.32, 119.54, 124.76, 124.90, 125.63, 126.74, 130.59, 132.28, 132.45, 142.02, 143.58, 143.90, 146.73.

TAA-G3. In a drybox, **6** (142 mg, 0.110 mmol, 3.00 equiv) was combined with tris(4-bromophenyl)amine (17.8 mg, 0.0370 mmol, 1 equiv), sodium *tert*-butoxide (17.5 mg, 0.185 mmol, 5.00 equiv), $\text{Pd}(\text{dba})_2$ (1.0 mg, 0.00185 mmol, 0.05 equiv) and tri-*tert* butyl phosphine (0.30 mg, 0.0015 mmol, 0.040 equiv) in 5.0 mL of toluene. The reaction was stirred at room temperature for 3 d. After this time, the reaction mixture was adsorbed onto a silica gel plug (5 g), and the product was rapidly eluted using toluene/hexanes (4/1) to give 134.0 mg (89 %) of **4** as light yellowish-green solid. ^1H NMR (500 MHz, C_6D_6) δ 2.12 (s, 72 H), 6.88 (d, $J = 8.2$ Hz, 48 H), 7.03-7.14 (m, 152 H). ^{13}C NMR (100 MHz, C_6D_6) δ 21.16, 124.88, 125.37, 125.39, 125.58, 130.62, 132.39, 143.35, 143.60, 143.70, 144.03, 146.62. MALDI-MS m/z 4091.3, requires $4\cdot 2\text{H}^+$ 4091.3. Anal Calcd. for $\text{C}_{294}\text{H}_{252}\text{N}_{22}$: C, 86.27; H, 6.21; N, 7.53. Found: C, 84.36, Ash 2.02; H, 6.27; N, 7.30.

Steady State Fluorescence Spectra of TAA-G1, TAA-G2, TAA-G3 in THF λ_{ex} = 390nm.

