Supplementary Information for: Bridged Triarylamines - A New Class of Heterohelicenes

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General Information. All chemicals were purchased from major chemical suppliers and were used without further purification. Flash chromatography was performed using ICN flash silica gel, 230-400 mesh. All ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX300 MHz spectrometer. Chemical shifts (δ) and coupling constants (J) are reported in parts per million and Hertz, respectively. The abbreviations for splitting patterns are s, singlet; br s, broad singlet; d, doublet, t, triplet; q, quartet; and combinations therein (i.e. dd, doublet of doublets). Elemental analyses were performed in the Microanalysis Laboratory, University of Massachusetts at Amherst, by Dr. Greg Dabkowski. Mass spectral data were obtained at the University of Massachusetts Mass Spectrometry Facility which is supported, in part, by the National Science Foundation grant CHE-9974648. X-ray data were collected using a Nonius kappa-CCD diffractometer with $\text{MoK}\alpha$ ($\lambda=0.71072$ Å) as the incident radiation. Diffraction data were collected at ambient temperature unless otherwise stated. The raw data were integrated, refined, scaled, and corrected for Lorentz polarization and absorption effects, if necessary, using the programs DENZO and SCALEPAK, supplied by Nonius. Structure solutions and refinements were done (on F_o^2) using a suite

of programs such as SIR97, SIR92, LSQ, SHELXS and SHELXL that are contained within the Nonius MAXUS module. All structures were checked for any missing symmetry using MISSYM of PLATON. Absorption spectra were collected using a Hewlett-Packard 8452A Diode Array Spectrophotometer. Emission spectra were collected using a Shimadzu RF-5301 PC Spectrofluorophotometer. A scaling factor was applied to both absorption and emission spectra for this publication in order to place the maximum wavelength intensities on a similar scale, for ease of viewing. Cyclic voltammetry was carried out using a BAS CV-50W voltammetric analyzer with a glassy carbon working electrode, a platinum auxiliary electrode, and a silver wire pseudo reference electrode. A scan rate of 250 mV/s was employed. Ferrocene/ferrocenium was added as an internal reference. The values were then adjusted to values versus standard calomel electrode given ferrocene/ferrocenium $E_{1/2}=0.307$ V vs. SCE. All electrochemical experiments were carried out using analyte concentrations of 10^{-3} M in dichloromethane and electrolyte (tetrabutylammonium hexafluorophosphate) concentrations of 0.1 M. Air was removed from the solvent and replaced with argon through several freeze/pump/thaw cycles.

Synthesis of mixed symmetric (5) and unsymmetric (6) bridged triarylamines. 2, 2'-[(4-Methylphenyl)imino]bisbenzoicacid-dimethylester **4** (0.939 g, 2.5 mmol) was hydrolyzed with NaOH (0.6 g,

15 mmol) in 25 mL of refluxing ethanol/water (1:1) for 2 h. The resulting acid was precipitated with concentrated HCl and dried under vacuum. The solid was then dispersed in dichloromethane (15 mL) with a few drops of DMF and then oxalylchloride (0.44 mL, 5.1 mmol) was added dropwise. The reaction was refluxed for 1 h and FeCl₃ (1.62 g, 10 mmol) added. After refluxing for an additional 12 h, the reaction was filtered through celite and concentrated. Flash chromatography in using 20:1 chloroform/acetone as the eluent gave 0.417 g (53% yield) of the bridged triarylamine as a mixture of symmetric **5** and unsymmetric **6** isomers. Recrystallization from chloroform/hexane gave the symmetric isomer **5** in a more pure form. The proton NMR spectra of both the mixture and symmetric product are shown below. Also, the elemental analysis of the mixture gives: Anal. Calcd. For C₂₁H₁₃NO₂: C=81.01, H=4.21, N=4.50; Found: C=80.85, H=4.05, N=4.45. For the symmetric isomer **5**, *Crystal data*: C₂₁H₁₃NO₂, *M* = 311.34, Monoclinic, *P* 2₁/*n*, *a* = 3.9442(2) Å, *b* = 10.3945(4) Å, *c* = 34.639(2) Å, α = 90.00°, β = 91.58 (10)°, γ = 90.00°, *V* = 1419.60(10) Å³, *Z* = 4, μ = 0.094 mm⁻¹, *T* = 298 K, data/parameters = 2400 /97, converging to *R*₁ = 0.1151, *wR*₂ = 0.2906 (on 1349, *I* > 2σ(*I*) observed data); *R*₁ = 0.1871, *wR*₂ = 0.3509 (all data), residual electron density: 0.599 e/Å³.

Dinaphthylamine. A 100 mL Schlenk flask equipped with a magnetic stir bar was charged with 1-aminonaphthalene (8.591 g, 60.0 mmol), Pd₂(dba)₃ (1.094 g, 1.2 mmol), 1,1' bis (diphenylphosphino) ferrocene (0.998 g, 1.8 mmol), and sodium-*t*-butoxide (7.208 g, 75.0 mmol). Air was removed and replaced by argon. Dry toluene (40 mL) was added through a septum followed by the addition of 1-bromonaphthalene (8.34 mL, 60.0 mmol). The septum was replaced with a glass stopper and the reaction stirred for 48 h at 110 °C. The resulting mixture was cooled to room temperature and the solids filtered out with CH₂Cl₂ as a wash solvent. Solvents were removed by rotary evaporation. The residue was purified by flash chromatography with 2:1 hexane/dichloromethane as the eluent to give the product as a yellow solid. Re-crystallization

from dichloromethane layered with hexane gave the product as yellow crystals (13.243 g, 82%). ^1H NMR: (CDCl_3) δ 8.08 (d, $J=8.0$ Hz, 2H), 7.89 (d, $J=7.5$ Hz, 2H), 7.50 (m, 6H), 7.34 (t, $J=7.9$ Hz, 2H), 7.02 (d, $J=7.4$ Hz, 2H), 6.34 (br s, 1H). ^{13}C NMR (300 MHz, CDCl_3) δ 140.24, 134.60, 128.58, 126.87, 126.16, 126.07, 125.62, 122.34, 121.76, 115.38. HRMS Calcd For $\text{C}_{20}\text{H}_{15}\text{N}$: 269.1204 Found: 269.1202. *Crystal data*: $\text{C}_{20}\text{H}_{15}\text{N}$, $M = 269.347$, Monoclinic, $P 2_1/c$, $a = 10.4907(7)$ Å, $b = 10.9269(7)$ Å, $c = 14.5995(12)$ Å, $\alpha = 90.00^\circ$, $\beta = 120(18)^\circ$, $\gamma = 90.00^\circ$, $V = 1431.8(2)$ Å³, $Z = 4$, $\mu = 0.072$ mm⁻¹, $T = 298$ K, data/parameters = 2494/192, converging to $R_1 = 0.0640$, $wR_2 = 0.1743$ (on 1660, $I > 2\sigma(I)$ observed data); $R_1 = 0.0985$, $wR_2 = 0.2057$ (all data), residual electron density: 0.436 e/Å³.

2D Spectra for **1**:

2D Spectra for **2**:

2D Spectra for **3**: