Supporting Information for

An Effective Synthesis of N,N-diphenyl carbazolium salts

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I. General Experimental Details

All materials, unless otherwise stated, were purchased from commercial sources and utilized without further purification. Schlenk glassware was flame-dried under vacuum prior to use. Deoxygenation was performed by bubbling Ar for 10 min. followed by 3 freeze-thaw-pump cycles (for liquids) or by evacuation of the reaction vessel from the atmosphere and backfilling with Ar (for solids). Xylenes were passed through alumina column and deoxygenated. PhI was deoxygenated. Flash column chromatography was conducted with silica gel 60 (230-400 mesh) from Merck. TLC was conducted on silica gel 60 F$_{254}$ plates from Merck. Freeze-drying was performed on a Labconco FreeZone 2.5 Plus model lyophilizer for 20 h.

All $^1$H and $^{13}$C (proton decoupled) NMR spectra were recorded using AVANCE 300 MHz, AVANCE II 400 MHz, AVANCE 500 MHz or AVANCE III 600 MHz Bruker spectrometer at the Technion NMR facilities. Chemical shifts (δ) are reported in ppm, relative to residual solvent signals as internal reference.\(^1\) Coupling constants (J) are reported in hertz (Hz). Peak multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), dt (double triplet), br (broad) and m (multiplet). High-resolution mass spectrometry was performed in a Waters LCT Premier Mass Spectrometer (ESI) and a Bruker maxis impact with APCI solid probe.
II. Synthetic Procedures

2,2′-diaminobiphenyl (A):

In a 3 L beaker flask, glacial acetic acid (190 mL) was added to a stirred solution of 2,2′-dinitrobiphenyl (13.00 g, 53.23 mmol) in absolute ethanol (1.9 L), followed by portionwise addition of zinc powder (75.00 g, 1147 mmol) during 2 min. After the exothermic reaction subsided (10 min) the beaker was left stirring for additional 5 min, after which it was allowed to reach RT. The yellow-green reaction mixture was filtered, and the unreacted zinc powder washed with small amounts of ethanol (caution – the fine activated zinc powder reacts exothermically when exposed to the atmosphere), and the filtrate concentrated to a thick syrup, which was dissolved in 16% HCl (80 mL). The aqueous phase was extracted with CHCl₃ (5 x 20 mL), until no color was observed in the organic phase, and then added slowly to 25% NH₄OH (1 L), for liberation of the amine and complexation of Zn (II). The free amine was extracted with CHCl₃ (4 x 100 mL), and the organic phase washed with water (40 mL), and dried over Na₂SO₄. After the solvent was removed in vacuo, A was obtained as a light brown oil which solidified to an off-white solid, which could be used without further purification (9.23 g, 94%). ^H and ^13C NMR spectra according to literature.² (Rₜ = 0.28, CHCl₃).

2-amino,2′-(N,N-diphenylamino)biphenyl (B) and 2-(N-phenylamino),2′-(N,N-diphenylamino)biphenyl (F):

A (9.00 g, 48.9 mmol) was deoxygenated in a 250 mL flame dried Schlenk flask. Xylenes (135 mL) were added via a syringe, and to the resulted solution KO'Bu (12.09 g 107.7 mmol) was added under argon. The mixture was stirred for 10 min during which a brown-yellow color developed. Iodobenzene (20.93 g, 11.5 mL, 102.6 mmol) was
injected to the Schlenk flask under argon, followed by CuI (1.86 g, 9.77 mmol), and o-phenanthroline (1.76 g, 9.77 mmol). The mixture was stirred at 125°C for 3.5 h, after which it was allowed to reach RT. The mixture was filtered, and the filtration cake washed with small amounts of CHCl₃ (ca. 70 mL). The solids were dissolved in 25% NH₄OH (200 mL), the dark green-blue aqueous phase was swiftly extracted with CHCl₃ (2 x 30 mL), and the organic phase added to the filtrate. (Caution: the aqueous phase is acidified before disposal to avoid formation of explosive Ni₃ via Cu(I)/Cu(II) catalyzed aerobic iodide oxidation). The filtrate was concentrated to a dark paste, which was dissolved in CHCl₃ (200 mL), and extracted with small amounts of 25% NH₄OH, until the aqueous phase was free from the copper complexes color. The organic phase was then extracted with 0.1 M HCl (3 x 250 mL) for separation of the unreacted A and phenanthroline, which could be recycled. The organic phase was washed with aq. sat. NaHCO₃, then with water, dried over Na₂SO₄, filtered, and the solvent removed in vacuo to give a dark paste which consisted of a mixture of B and F (ca. 7:3 mol ratio) along with small amounts of other aromatic compounds, xylenes and CHCl₃, which was used for the next step without further purification. Samples of pure B (Rᶠ = 0.57, CHCl₃) and F (Rᶠ = 0.80, CHCl₃) were obtained by column chromatography of this mixture (90% conversion, 60% and 25% yield of B and F, respectively, from A).

NMR of B: ¹H NMR (400 MHz, CDCl₃) δ 7.66, (d, J = 8.0 Hz, 1H), 7.59, (d, J = 8.0 Hz, 1H), 7.53 (dt, J = 8.0, 1.3 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.25 (t, J = 8.0 Hz, 4H, Ph-m), 7.12 (t, J = 8.0 Hz, 2H, Ph-p), 7.07-7.02 (m, 6H), 6.75 (t, J = 8.0 Hz, 1H), 6.58 (d, J = 8.0 Hz, 1H), 3.38 (s, br., 2H, NH₂). ¹³C NMR (75 MHz, CDCl₃) δ 147.34 (C(Ph)-N, 2C), 146.04 (C-N, 1C), 143.35(C-N, 1C), 136.82 (C-C, 1C), 132.46(C-H(biphenyl), 1C),
130.10(C-H(biphenyl), 1C), 128.86(C-H(biphenyl), 1C), 128.62(C-H(biphenyl), 1C), 128.50(C-H(Ph), 4C), 127.89(C-H(biphenyl), 1C), 125.25(C-H(biphenyl), 1C), 125.10 (C-C, 1C), 122.02 (C-H(Ph), 4C), 121.36(C-H(Ph), 2C), 118.03(C-H(biphenyl), 1C), 115.26(C-H(biphenyl), 1C). APCI-HRMS: m/z calcd for C_{24}H_{21}N_{2} [M+H]^+: 337.1699; found 337.1719 (-5.8 ppm).

NMR of F: \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.44 (d, \(J = 7.3\) Hz, 1H), 7.36 (dt, \(J = 7.3, 1.6\) Hz, 1H), 7.32 (dd, \(J = 7.3, 1.4\) Hz, 1H), 7.23(t, \(J = 7.3\) Hz, 1H), 7.16 (t, \(J = 7.3, 2H\)), 7.09-7.05 (m, 5H), 7.02-6.98 (m, 2H), 6.87-6.83 (m, 7H), 6.78 (d, \(J = 7.3, 2H, o\-PhNH\)), 6.71, (t, \(J = 7.3, 1H\)), 5.31 (s, br., 1H, NHPh). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 147.50 (C(Ph)-N, 2C), 146.53 (C-N, 1C), 143.21 (C-N, 1C), 140.29 (C-N, 1C), 137.56, 137.01, 132.82, 131.03, 130.34, 129.55, 129.15 (C-H(Ph), 2C), 129.05, 128.93 (C-H(NPh\(_2\)), 4C), 127.86, 125.59, 122.44 (C-H(NPh\(_2\)), 4C), 121.98 (C-H(Ph), 2C), 120.60, 118.11 (C-H(Ph), 2C), 116.7. APCI-HRMS: m/z calcd for C_{30}H_{25}N_{2} [M+H]^+: 413.2012; found 413.1985 (-6.5 ppm).

2-amino,2′-(N-phenylamino)biphenyl (D):\(^3\)

In a similar manner to the synthesis of B and F, A (100 mg, 0.543 mmol) was reacted for 3.5 h at 125°C in a 20 mL Schlenk tube with iodobenzene (110 mg, 0.539 mmol), KO\(_2\)Bu (61 mg, 0.54 mmol), Cul (21 mg, 0.11 mmol), and o-phenanthroline (29 mg, 0.16 mmol) in xylenes (2 mL). After the xylenes and solids were removed, the organic phase was extracted with 10% wt aqueous H\(_3\)PO\(_4\) (3 x 10 mL), which extracted the unreacted A and phenanthroline, followed by extraction with 25% wt HCl (3 x 10 mL). The aqueous phase was washed with CHCl\(_3\) (10 mL), and solid Na\(_2\)CO\(_3\) was added slowly to liberate the amine until basic pH was reached (water was added to dissolve the
precipitating salts). The mixture was extracted with CHCl₃ (3 x 10 mL), the organic phase washed with water (10 mL), dried over Na₂SO₄, filtered, and the solvent removed in vacuo to give a residue, chiefly consisted of a mixture of D and small amounts of other aromatic compounds. Pure D (20 mg, 14% yield) were obtained by column chromatography of this mixture. Rᵣ = 0.48, CHCl₃.

¹H NMR (601 MHz, C₂D₂Cl₄) δ 7.42, (d, J = 12 Hz, 1H), 7.29-7.30, (m, 1H), 7.28-7.25, (m, 3H), 7.24-7.21, (m, 1H), 7.18 (dd, J = 12, 6 Hz, 1H), 7.07 (d, J = 12 Hz, 2H, Ph), 7.01 (m, 1H), 6.94 (m, 1H), 6.88 (m, 1H), 6.82 (m, 1H), 5.98 (s, br., 1H, NPh) 3.74 (s, br., 2H, NH₂). ¹³C NMR (151 MHz, C₂D₂Cl₄) δ 143.80 (C-N), 142.68 (C-N), 141.00 (C-N), 131.51, 131.14, 129.24 (2C, Ph), 128.91, 128.46, 127.68, 124.37, 121.19, 120.75, 119.00, 118.66 (2C, Ph), 115.99, 115.65. APCI-HRMS: m/z calcd for C₁₈H₁₇N₂ [M+H]⁺: 261.1386; found 261.1384 (-0.8 ppm).

**N,N-diphenylcarbazolium acetate⁴ and hexafluorophosphate (C).**

In a 100 mL Erlenmeyer beaker, the mixture of amines B and F (4.36 g) was dissolved in glacial acetic acid (53 mL). The solution was cooled to 0-5°C using an ice bath, and the solidified acetic acid solution was crushed by a steel spatula. A solution of NaNO₂ (4.15 g, 60.2 mmol) in water (5.5 mL) was added, and the resulted dark slurry was stirred mechanically (using a spatula) for 20 min. Urea prills (3.32 g, 55.3 mmol) were then added, and the mixture was stirred mechanically (using a spatula) for 1 h at 40°C, during which black tar separated. The reaction mixture was concentrated under reduced pressure, and the residue was dissolved in CHCl₃ (50 mL), filtered, and the filtration cake was washed with small amounts of CHCl₃. The solvent was removed in vacuo, and the dark residue partitioned between ether (40 mL) and water (10 mL).
organic phase was extracted with water (5 mL), and the volume of the united aqueous phase was reduced to ca. 6 mL in vacuo, and extracted with small amounts of ether until no color is seen in the organic phase. Removal of water and acetic acid from the yellow aqueous phase by reduced pressure azeotropic distillation with toluene and freeze-drying affords C (acetate) as a highly hygroscopic yellow solid, which still contained acetic acid and water. Pure C was obtained by addition of 75% (w/v) aqueous solution of NH₄PF₆ (5 mL) to the concentrated solution of the acetate. The resulted light yellow precipitate was collected, washed with small amounts of water, and dried under reduced pressure (857 mg, 21.5% yield from B).

NMR of C (acetate): ¹H NMR (500 MHz, D₂O) δ 8.05 (d, J = 10.0 Hz, 2H, biphenyl), 7.64, (t, J = 10.0 Hz, 2H), 7.60 (d, J = 10.0 Hz, 2H, biphenyl), 7.47 (m, 4H), 7.37 (t, J = 10.0 Hz, 4H, o-Ph), 7.29, (d, J = 10.0 Hz, 4H, o-Ph), 1.95 (CH₃COOD/CH₃COO⁻).

¹³C NMR (126 MHz, D₂O) δ 180.79 (br., CH₃COOD), 163.32, 150.28 (2C), 147.02 (2C), 132.79, 131.95, 131.50, 131.18, 130.69, 123.71, 122.74, 121.95, 49.50 (CH₃OD), 23.51 (br., CH₃COOD/CH₃COO⁻).

NMR of C (PF₆⁻): ¹H NMR (400 MHz, CD₃CN) δ 8.21 (d, J = 8.0 Hz, 2H, biphenyl), 7.81 (t, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.67-7.62 (m, 4H), 7.56 (t, J = 8.0 Hz, 4H, m-Ph), 7.47 (d, J = 8.0 Hz, 4H, o-Ph), 13C NMR (75 MHz, CD₃CN) δ 151.31 (2C), 147.74 (2C), 133.40 (C-H(biphenyl), 2C), 132.53 (C-H(biphenyl), 2C), 132.19 (C-H(biphenyl), 2C), 131.88 (C-H(Ph), 4C), 131.52 (C-C(biphenyl), 2C), 124.53 (C-H(biphenyl), 2C), 123.55 (C-H(Ph), 4C). ¹⁹F NMR (377 MHz, CD₃CN) δ -72.82 (d, J₁=707 Hz⁵, P-F). ESI-HRMS: m/z calcd for C₂₄H₁₈N [M-PF₆]⁺: 320.1439; found 320.1420 (-5.9 ppm).
III. NMR Spectra

Figure S1. $^1$H NMR of B in CDCl$_3$.

Figure S2. $^{13}$C NMR of B in CDCl$_3$.
Figure S3. $^1$H NMR of F in CDCl$_3$.

Figure S4. $^{13}$C NMR of F in CDCl$_3$. 
Figure S5. $^1$H NMR of D in C$_2$D$_2$Cl$_4$.

Figure S6. $^{13}$C NMR of D in CDCl$_3$. 
Figure S7. $^1$H NMR of C (acetate) in D$_2$O.

Figure S8. $^{13}$C NMR of C (acetate) in D$_2$O (MeOH was added for reference).
Figure S9. $^1$H NMR of C (PF$_6^-$) in CD$_3$CN.

Figure S10. $^{13}$C NMR of C (PF$_6^-$) in CD$_3$CN.
Figure S11. $^{19}$F NMR of C (PF$_6^-$) in CD$_3$CN.
IV. References


