Supplementary Information

A Density-Controlled Scaffolding Strategy for Covalent Functionalization of Carbon-Fiber Microelectrodes

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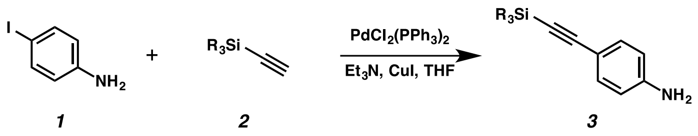
General Information. Unless otherwise specified, all commercially available reagents were purchased from Sigma-Aldrich and used without further purification. Anhydrous Et_2O, PhMe, *n*-hexane, MeCN, DMF, DMSO, CH_2Cl_2 were purchased from Fisher, THF was purchased from EMD, and PhH was purchased from Sigma-Aldrich. These were passed through a commercial solvent purification system (2 columns of alumina) and used without further drying. Triethylamine, diisopropylamine, pyridine, and Hünig's base were distilled over CaH_2 immediately prior to use. Unless otherwise noted, all reactions were performed in flame-dried glassware under 1 atm of pre-purified anhydrous N_2 or argon gas. ^1H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Mercury-400 MHz or a Varian VNMRS-500MHz spectrometer with a multinuclear broadband probe at ambient temperature unless otherwise stated. Chemical shifts are reported in parts per million relative to residual solvent peaks (as established by Stoltz, et. al. in *Organometallics* **2010**, *29*, 2176). All ^{13}C spectra are recorded with complete proton decoupling. High-resolution mass spectral analyses were performed by the Lumigen Instrument Center, Wayne State University. All purifications were performed on SiliaFlash® P60 40-63µm (230-400 mesh) 60Å Irregular Silica Gels (cat. # R12030B) or on a Biotage Isolera IV flash purification system using SNAP cartridges (cat. # FSKO-1107-XXXX). Thin layer chromatography was performed using glass-backed SiliaPlate™ TLC Plates (cat. # TLG-R10011B-323) cut to the desired size then visualized with short-wave UV lamps and $KMnO_4$, CAM, PMA, or Anisaldehyde stains prepared according to standard recipes. All yields refer to chromatographically and spectroscopically pure products. IR data was obtained on a Varian/Digilab Excalibur 3100 High Resolution FT-IR, and optical rotation data was collected on a Perkin-Elmer 341 automated Polarimeter at the concentration noted.

Azidomethylferrocene was synthesized according to literature procedures.[1]

Experimental Procedures and Spectroscopic Data.



4-((trimethylsilyl)ethynyl)aniline (3a):

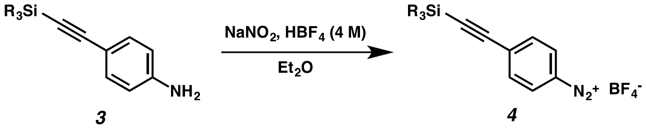
4-Iodoaniline (426 mg, 1.94 mmol), copper(I) iodide (37 mg, 0.0.195 mmol), triphenylphosphine (51 mg, 0.195 mmol), and Pd(PPh$_3$)$_2$Cl$_2$ (68 mg, 0.097 mmol) were dissolved in dry THF (4.3 mL) and triethylamine (2.4 mL) was added at room temperature with exclusion of light, then the solution was degassed by 3 freeze pump and thaw cycles. After 10 min stirring, trimethylsilylacetylene (220 mg, 316 μL, 2.24 mmol) was added dropwise to this solution. After 16 h, the reaction mixture was filtered through celite and precipitates were washed with ethyl acetate (20 mL). Then the filtrate was washed with distilled water and the layer were separated, the aqueous layer was extracted with EtOAc (3 x 20 mL), then the combined organic extracts were washed with brine, dried over anhydrous MgSO$_4$ and the solvent was removed under reduced pressure and the crude was purified by column chromatography with 0-20% EtOAc/Hexane gradient isolated as a slight yellow solid (367 mg, >99% yield). NMR data matched literature.[2, 3]

4-((tert-butyldimethylsilyl)ethynyl)aniline (3b):

4-Iodoaniline (500 mg, 2.283 mmol), copper(I) iodide (43 mg, 0.228 mmol), triphenylphosphine (60 mg, 0.228 mmol), and Pd(PPh$_3$)$_2$Cl$_2$ (80 mg, 0.114 mmol) were dissolved in dry THF (5.1 mL) and triethylamine (2.8 mL) was added at room temperature with exclusion of light, then the solution was degassed by 3 freeze pump and thaw cycles. After 10 min stirring, *t*-butyldimethylsilylacetylene (368 mg, 453 μL, 2.63 mmol) was added dropwise to this solution. After 16 h, the reaction mixture was filtered through celite and precipitates were washed with ethyl acetate (20 mL). Then the filtrate was washed with distilled water and the layer were separated, the aqueous layer was extracted with EtOAc (3 x 20 mL), then the combined organic extracts were washed with brine, dried over anhydrous MgSO$_4$ and the solvent was removed under reduced pressure and the crude was purified by column chromatography with 0-20% EtOAc/Hexane gradient isolated as a slight white solid (513 mg, 97% yield); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 – 7.26 (m, *J* = 8.6 Hz, 2H), 6.58 (d, *J* = 8.6 Hz, 2H), 0.98 (s, 9H), 0.16 (s, 5H); ^{13}C NMR (101 MHz, CDCL$_3$) δ 146.7, 133.4, 114.5, 112.7, 106.6, 89.6, 77.3, 77.0, 76.7, 26.2, 16.8, -4.5; IR

4-((triisopropylsilyl)ethynyl)aniline (3c):

4-Iodoaniline (500 mg, 2.283 mmol), copper(I) iodide (43 mg, 0.228 mmol), triphenylphosphine (60 mg, 0.228 mmol), and Pd(PPh$_3$)$_2$Cl$_2$ (80 mg, 0.114 mmol) were dissolved in dry THF (5.1 mL) and triethylamine (2.8 mL) was added at room temperature with exclusion of light, then the solution was degassed by 3 freeze pump and thaw cycles. After 10 min stirring, triisoprpylsilylacetylene (478 mg, 589 μL, 2.63 mmol) was added dropwise to this solution. After 16 h, the reaction mixture was filtered through celite and precipitates were washed with ethyl acetate (20 mL). Then the filtrate was washed with distilled water and the layer were separated, the aqueous layer was extracted with EtOAc (3 x 20 mL), then the combined organic extracts were washed with brine, dried over anhydrous MgSO$_4$ and the solvent was removed under reduced pressure and the crude was purified by column chromatography with 0-20% EtOAc/Hexane gradient isolated as a slight yellow oil (560 mg, 90% yield). NMR data matched literature.[2, 3]



4-((trimethylsilyl)ethynyl)benzenediazonium tetrafluoroborate (4a):

The aniline (**3a**) (310 mg, 1.64 mmol) was dissolved in ether (1 mL) then water (0.9 mL) and 48w% aqueous HBF_4 (1 mL) were added the mixture was cooled to 0 °C then $NaNO_2$ was added slowly. The reaction was allowed to warm up to ambient temperature in melting ice bath and stirred over night with the flask opened to allow the ether to evaporate. The reaction was filtered through a Büchner funnel, the precipitate was washed with ice cold 5wt% aqueous $NaBF_4$ (5 mL), then ice cold water (5 mL), then ice cold methanol (5 mL), then ice cold ether (5 mL), affording beige solid (390 mg, 83% yield). NMR spectra matched literature.[2, 3]

4-((tert-butyldimethylsilyl)ethynyl)benzenediazonium tetrafluoroborate (4b):

The aniline (**3b**) (195 mg, 0.843 mmol) was dissolved in ether (1 mL) then water (1.1 mL) and 48w% aqueous HBF_4 (1 mL) were added the mixture was cooled to 0 °C then $NaNO_2$ (290 mg, 4.213 mmol) was added slowly then allowed to warm up to ambient temperature in melting ice bath and stirred over night then with the flask opened to let the ether to evaporate. The reaction was filtered through a Büchner funnel, the precipitate was washed with ice cold 5wt% aqueous $NaBF_4$ (5 mL), then ice cold water (5 mL), then ice cold methanol (5 mL), then ice cold ether (5 mL), affording beige solid (222 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCL_3$) δ 8.55 (d, J = 8.9 Hz, 2H), 7.73 (d, J = 8.9 Hz, 2H), 0.98 (s, 9H), 0.21 (s, 6H);^{13}C NMR (101 MHz, $CDCL_3$) δ 136.55, 134.11, 132.75, 112.47, 108.06, 102.47, 77.32, 77.00, 76.68, 26.02, 16.70, -5.04; HRMS [M^+] m/z ES calc'd for $[C_{10}H_{14}O_2]^+$: 189.0886; observed: 189.1388; IR 2937, 2874, 1736, 1450 cm^{-1}.

4-((triisopropylsilyl)ethynyl)benzenediazonium tetrafluoroborate (4c)

The aniline (**3c**) (200 mg, 0.731 mmol) was dissolved in ether (1 mL) then water (0.9 mL) and 48w% aqueous HBF_4 (1 mL) were added the mixture was cooled to 0 °C then $NaNO_2$ (252 mg, 3.656 mmol) was added slowly then allowed to warm up to ambient temperature in melting ice bath and stirred over night with the flask opened to allow the ether to evaporate. The reaction was filtered through a Büchner funnel, the precipitate was washed with ice cold 5wt% aqueous $NaBF_4$ (5 mL), then ice cold water (5 mL), then ice cold methanol (5 mL) then ice cold ether (5 mL), affording beige solid (198 mg, 72% yield). NMR spectra matched literature.[2, 3]

References.

1. C. G. Hardy, L. Ren, T. C. Tamboue and C. Tang, *Journal of Polymer Science Part A: Polymer Chemistry*, 2011, 49, 1409-1420.
2. Y. R. Leroux, H. Fei, J. M. Noel, C. Roux and P. Hapiot, *Journal of the American Chemical Society*, 2010, 132, 14039-14041.
3. Y. R. Leroux and P. Hapiot, *Chemistry of Materials*, 2013, 25, 489-495.