Supporting Information

for the Article entitled

Ferrocene-Based Nanoelectronics: Regioselective Syntheses and Electrochemical Characterization of α-Monothiol and α,ω – Dithiol, Phenylethynyl-conjugated, 2,5-Diethynylpyridyl- and pyridinium-linked Diferrocene Frameworks Having an End-to-End Distance of ~ 4 nm

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Full experimental details, including synthesis and analytical characterization of all new compounds including solution electrochemical characterization (23 pages).

Experimental Details.

General. All reactions were performed under a nitrogen atmosphere using standard Schlenk line techniques. All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Tetrahydrofuran (THF) was distilled from Na-benzophenone under nitrogen. Methylene chloride, diisopropylamine (DIPA), and *N*,*N*-diisopropylethylamine (Hunig's Base) were distilled from calcium hydride under nitrogen. Other solvents were HPLC grade or higher. Compounds **47**, iodoferrocene, 1,1'-diiodoferrocene, ethynylferrocene, 2,5-diiodopyridine, 2,5-diethynylpyridine, 3-iodopyridine, *S*-acetyl-4-iodothiophenol, 1-bromo-4-iodo-2,5-dimethoxybenzene, (2,5-dimethoxyphenyl)ethyne, 1,4-diethynylbenzene, and1-ethynyl-4-[2-(triisopropylsilyl)ethynyl]benzene were prepared according to literature procedures. Thin-layer chromatography (TLC) analysis was performed using EM Science silica gel 60 (F254) plates (0.25 mm), and the eluted plates were observed under a UV detector. Chromatographic purifications were performed by flash chromatography on EM Science silica gel (230-400 mesh). ^{1}H and ^{13}C NMR spectra were taken in acetone-d_6, methylene chloride-d_2, or chloroform-*d* at 400 and 100 MHz, respectively. High-resolution mass spectra were obtained in either EI or FAB mode. Chemical analyses were performed by Midwest Microlab.

Preparation of 20. Compound **20** was prepared using 5.64 g (16.4 mmol) of 1-bromo-4-iodo-2,5-dimethoxybenzene, 3.30 g (18.1 mmol) of triisopropylsilylacetylene, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), and 150 ml of DIPA. The reaction mixture was stirred at room temperature for 24 h, at which time, 3.22 g (32.8 mmol) of trimethylsilylacetylene were added by syringe. After an additional 24 h, the solvent was removed in vacuo, and the crude product was purified via column chromatography on silica gel using a 3:1 hexane/ CH_2Cl_2 solvent system to

provide 5.57 g (82%) of bis-silyl-protected diyne. Data: ^{1}H NMR ($CDCl_3$) δ 0.27 (s, 9H), 1.14 (s, 21H), 3.81 (s, 3H), 3.84 (s, 3H), 6.88 (s, 1H), 6.91 (s, 1H). The entire portion of this product (5.57 g, 13.4 mmol) was dissolved in 100 ml of a 1:1 THF/MeOH solvent mixture to which 40 ml of aqueous 1 M NaOH were added. The reaction mixture was stirred for 3 h, quenched with 150 ml of water, and extracted with 3 x 150 ml CH_2Cl_2. The organic layers were combined, dried with Na_2SO_4, and the solvent was removed in vacuo. The residue was purified via column chromatography on silica gel using a 3:1 hexane/ CH_2Cl_2 solvent system to provide 4.06 g (89%) of **20**. Data for **20**: ^{1}H NMR ($(CD_3)_2CO$) δ 1.15 (s, 21H), 3.83 (s, 3H), 3.85 (s, 3H), 3.88 (s, 1H), 7.04 (s, 1H), 7.05 (s, 1H); ^{13}C NMR ($(CD_3)_2CO$) δ 12.0, 19.0, 56.6, 56.8, 80.5, 84.5, 96.9, 103.9, 113.5, 114.9, 116.4, 117.3, 155.4, 155.5; UV (CH_2Cl_2) (ε) λ (nm) 268 (14428), 282 (12364), 340 (12812); HRMS (EI) calcd for $C_{21}H_{30}OSi$ 342.2015 (M^+), found 342.2017.

General Procedure for Palladium-Catalyzed Coupling Reactions. A solution of an aryl halide, terminal acetylene, $Pd(PPh_3)_2Cl_2$, and a copper salt (CuI, $Cu(OAc)_2$, or $Cu(OAc)_2 \bullet H_2O$) in either diisopropylamine or a THF/Hunig's Base solvent mixture was deoxygenated using three freeze-pump-thaw cycles and after the last cycle the flask was backfilled with nitrogen (unless otherwise indicated). The reaction mixture was then stirred at approximately 50 °C for 24-48 hours. The progress of the reaction was monitored by TLC analysis. When the reaction was complete, the solvents were removed in vacuo and the residue was then taken up in CH_2Cl_2 and filtered through a short silica gel column assembled in a fritted funnel. Further purification of the crude product was done via column chromatography.

Preparation of 9. Compound **9** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 6.00 g (13.7 mmol) of 1,1'-diiodoferrocene, 2.09 g (11.5 mmol) of triisopropylsilylacetylene, $Pd(PPh_3)_2Cl_2$ (8 mol%), $Cu(OAc)_2 \bullet H_2O$ (8 mol%),

130 ml of DIPA, and heated to 70 ˚C. The crude product was purified by column chromatography on silica gel using a 100% hexanes solvent system to yield a mixture of starting material and the desired intermediate 1-iodo-1'-((triisopropylsilyl)ethynyl)ferrocene. Data for 1-iodo-1'-((triisopropylsilyl)ethynyl)ferrocene: ^{1}H NMR ($CDCl_3$) δ 1.13 (br s, 21H), 4.20 (t, 4H, *J* = 2.0 Hz), 4.39 (t, 2H, *J* = 2.0 Hz), 4.40 (t, 2H, *J* = 2.0 Hz). The above mixture was dissolved in 10 ml of CH_2Cl_2 and 12 ml of a solution of TBAF (1 M in THF) was added dropwise. The reaction mixture was stirred for 20 minutes, after which time the solvents were removed in vacuo. The resulting crude material was purified via column chromatography (100% hexanes) to provide 2.36 g of recovered 1,1'-diiodoferrocene (R_f = 0.67) and 1.64 g (60% overall yield based on recovered 1,1'-diiodoferrocene) of **9** (R_f = 0.36). Data for **9**: ^{1}H NMR ($(CD_3)_2CO$) δ 3.28 (s, 1H), 4.27 (t, 4H, *J* = 2.0 Hz), 4.42 (t, 2H, *J* = 2.0 Hz), 4.44 (t, 2H, *J* = 2.0 Hz); ^{13}C NMR ($(CD_3)_2CO$) δ 40.4, 67.1, 71.6, 72.6, 75.1, 76.4, 77.1, 81.7; UV (CH_2Cl_2) (ε) λ (nm) 446 (259); HRMS (EI) calcd for $C_{12}H_9FeI$ 335.9098 (M^+), found 335.9094.

Preparation of 12. Compound **12** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 482 mg (1.43 mmol) of **9**, 398 mg (1.43 mmol) of *S*-acetyl-4-iodothiophenol, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), and 11 ml of THF/Hunig's base (1:1). The crude product was purified by column chromatography on silica gel using a 1:1 CH_2Cl_2/hexane solvent system. The desired fractions were pooled to yield 556 mg (80%) of the title compound. Data for **12**: ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3H), 4.23 (t, 2H, *J* = 2.0 Hz), 4.28 (t, 2H, *J* = 2.0 Hz), 4.45 (t, 2H, *J* = 2.0 Hz), 4.48 (t, 2H, *J* = 2.0 Hz), 7.37 (d, 2H, *J* = 8.4 Hz), 7.54 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (CD_2Cl_2) δ 30.9, 42.0, 67.9, 71.7, 73.0, 75.0, 77.3, 86.8, 89.9, 125.9, 128.5, 132.6, 135.2, 194.2; UV (CH_2Cl_2) (ε) λ (nm) 270 (14741), 314 (14962), 452 (571); HRMS (FAB) calcd for $C_{20}H_{15}OISFe$ 485.9238 (M^+), found 485.9229.

Preparation of 16. Compound **16** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 292 mg (0.87 mmol) of **9**, 144 mg (0.43 mmol) of 2,5-diiodopyridine, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), and 6 ml of THF/Hunig's base (1:1). The crude product was purified by column chromatography on silica gel using a 5:1 CH_2Cl_2/hexane solvent system. The desired fractions were pooled to yield 282 mg (87%) of the title compound. Data for **16**: ^{1}H NMR ($(CD_3)_2CO$) δ 4.345 (t, 2H, *J* = 2.0 Hz), 4.350 (t, 2H, *J* = 2.0 Hz), 4.405 (t, 2H, *J* = 2.0 Hz), 4.411 (t, 2H, *J* = 2.0 Hz), 4.523 (t, 2H, *J* = 2.0 Hz), 4.527 (t, 2H, *J* = 2.0 Hz), 4.541 (t, 2H, *J* = 2.0 Hz), 4.572 (t, 2H, *J* = 2.0 Hz), 7.57 (d, 1H, *J* = 8.3 Hz), 7.89 (dd, 1H, *J* = 2.0, 8.3 Hz), 8.69 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR (CD_2Cl_2) δ 41.3, 41.7, 66.3, 67.0, 71.3, 71.5, 72.7, 73.0, 74.6, 74.8, 76.9, 84.1, 87.0, 89.9, 92.7, 119.8, 126.5, 138.4, 142.1, 152.6; UV (CH_2Cl_2) (ε) λ (nm) 288 (25817), 334 (38026), 452 (3878); HRMS (FAB) calcd for $C_{29}H_{20}NFe_2I_2$ 747.8384 (M+1), found 747.8353.

Preparation of 22. Compound **22** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 1.06 g (2.41 mmol) of 1,1'-diiodoferrocene **10**, 1.81 g (5.30 mmol) of **20**, $Pd(PPh_3)_2Cl_2$ (8 mol%), $Cu(OAc)_2$ (8 mol%), 14 ml of DIPA, and heated to 90 ºC. The crude product was purified by column chromatography on silica gel using a 1:1 hexanes/CH_2Cl_2 solvent system. The desired fractions were pooled to yield 868 mg (42%) of the bis-silyl-protected intermediate **21**. Data for **21**: ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 42H), 3.78 (s, 6H), 3.86 (s, 6H), 4.36 (t, 4H, *J* = 1.6 Hz), 4.60 (t, 4H, *J* = 1.6 Hz), 6.92 (s, 4H). To a solution of 303 mg (0.349 mmol) of **21** in 10 ml of CH_2Cl_2 was added 2.2 equiv of TBAF (1 M in THF). The reaction mixture was stirred at room temperature for 15 min, after which time the solvents were removed in vacuo. The crude residue was purified via column chromatography on silica gel using a 6:1 CH_2Cl_2/hexanes solvent system to provide 161 mg (84%) of the desired product.

Data for **22**: ^{1}H NMR ($CDCl_3$) δ 3.40 (s, 2H), 3.82 (s, 6H), 3.83 (s, 6H), 4.37 (t, 4H, *J* = 1.6 Hz), 4.60 (t, 4H, *J* = 1.6 Hz), 6.92 (s, 2H), 6.94 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 56.5, 56.6, 66.7, 71.6, 73.5, 80.2, 82.48, 82.54, 111.5, 115.0, 115.6, 116.4, 153.9, 154.7; UV (CH_2Cl_2) (ε) λ (nm) 276 (43014), 308 (22959), 352 (38433), 452 (1909); Anal. calcd for $C_{34}H_{26}O_4Fe$: C, 73.65; H, 4.74. Found: C, 73.32; H, 4.79.

Preparation of 1. Compound **1** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 342 mg (0.616 mmol) of **22**, 378 mg (1.36 mmol) of *S*-acetyl-4-iodothiophenol, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), 5 ml of THF, and 0.5 ml of Hunig's base. The crude product was purified by column chromatography on silica gel using a solvent gradient (6:1 CH_2Cl_2/hexanes to 100% CH_2Cl_2). The desired fractions were pooled to yield 255 mg (50%) of the title compound. Data for **1**: ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 6H), 3.84 (s, 6H), 3.87 (s, 6H), 4.43 (bs, 4H), 4.67 (bs, 4H), 6.93 (bs, 2H), 6.97 (bs, 2H), 7.38 (d, 4H, *J* = 8.4 Hz), 7.57 (d, 4H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 30.5, 56.6, 66.9, 71.6, 73.5, 82.8, 87.7, 93.7, 94.2, 112.5, 114.6, 115.7, 115.8, 124.7, 128.2, 132.4, 134.3, 154.0, 154.2, 193.7; UV (CH_2Cl_2) (ε) λ (nm) 312 (57358), 368 (62572), 452 (3758); HRMS (FAB) calcd for $C_{50}H_{38}O_6S_2Fe$ 854.1459 (M^+), found 854.1460. Anal. calcd for $C_{50}H_{38}O_6S_2Fe$: C, 70.30; H, 4.49. Found: C, 69.96; H, 4.53.

Preparation of 23. Compound **23** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 194 mg (0.26 mmol) of **16**, 631 mg (1.84 mmol) of **20**, $Pd(PPh_3)_2Cl_2$ (8 mol%), $Cu(OAc)_2$ (8 mol%), 5 ml of THF, 0.6 ml of Hunig's base, and heated to 90 ºC. The crude product was purified by column chromatography on silica gel using a 100% CH_2Cl_2 solvent system. The desired fractions were pooled to yield 214 mg of a mixture of the mono- and bis-silyl-protected intermediates. Data for bis-silyl-protected intermediate: ^{1}H

NMR ($(CD_3)_2CO$) δ 1.15 (s, 42H), 3.82 (s, 3H), 3.83 (s, 3H), 3.85 (s, 3H), 3.86 (s, 3H), 4.44 (m, 4H), 4.46 (t, 2H, *J* = 2.0 Hz), 4.48 (t, 2H, *J* = 2.0 Hz), 4.59 (m, 4H), 4.62 (t, 2H, *J* = 2.0 Hz), 4.65 (t, 2H, *J* = 2.0 Hz), 6.99 (s, 1H), 7.00 (s, 1H), 7.01 (s, 2H), 7.34 (d, 1H, *J* = 8.3 Hz), 7.64 (dd, 1H, *J* = 2.0, 8.3 Hz), 8.59 (d, 1H, *J* = 2.0 Hz). To a solution of the above-mentioned mixture of mono- and bis-silyl-protected intermediates in 10 ml of CH_2Cl_2 was added 2.2 equiv of a solution of TBAF (1 M in THF). The reaction mixture was stirred at room temperature for 15 min, after which time the solvents were removed in vacuo. The crude residue was purified via column chromatography on silica gel using a 100% CH_2Cl_2 solvent system to provide 30 mg (16% overall yield) of the desired product. Data for **23**: ^{1}H NMR ($(CD_3)_2CO$) δ 3.81 (s, 3H), 3.82 (s, 3H), 3.856 (s, 3H), 3.862 (s, 3H), 3.89 (s, 2H), 4.45 (m, 6H), 4.47 (t, 2H, *J* = 2.0 Hz), 4.61 (m, 4H), 4.63 (t, 2H, *J* = 2.0 Hz), 4.66 (t, 2H, *J* = 2.0 Hz), 6.95 (s, 1H), 6.96 (s, 1H), 7.005 (s, 1H), 7.009 (s, 1H), 7.24 (d, 1H, *J* = 8.3 Hz), 7.53 (dd, 1H, *J* = 2.0, 8.3 Hz), 8.51 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR ($(CD_3)_2CO$) δ 56.6, 56.79, 56.84, 66.8, 67.3, 68.28, 68.33, 71.9, 72.0, 72.1, 72.4, 73.9, 74.0, 74.2, 80.8, 83.8, 84.4, 87.5, 89.9, 93.0, 93.4, 112.72, 112.75, 115.46, 115.51, 116.2, 116.3, 117.2, 120.1, 126.8, 138.4, 142.6, 152.6, 154.68, 154.75, 155.6; UV (CH_2Cl_2) (ε) λ (nm) 276 (38241), 304 (30430), 352 (40114), 450 (3738); HRMS (FAB) calcd for $C_{53}H_{38}NO_4Fe_2$ 864.1500 (M+1), found 864.1508.

Preparation of 3. Compound **3** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 46 mg (54 μmol) of **23**, 50 mg (179 μmol) of *S*-acetyl-4-iodothiophenol, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), 2.5 ml of THF, and 0.4 ml of Hunig's base. The crude product was purified by column chromatography on silica gel using a 1:1 hexane/EtOAc solvent system. The desired fractions were pooled to yield 27 mg (43%) of the title compound. Data for **3**: ^{1}H NMR (CD_2Cl_2) δ 2.42 (s, 6H), 3.84 (s, 6H), 3.85 (s, 6H), 4.37

(m, 6H), 4.39 (t, 2H, *J* = 2.0 Hz), 4.56 (t, 2H, *J* = 2.0 Hz), 4.57 (t, 2H, *J* = 2.0 Hz), 4.59 (t, 2H, *J* = 2.0 Hz), 4.60 (t, 2H, *J* = 2.0 Hz), 6.90 (s, 1H), 6.91 (s, 1H), 6.96 (s, 2H), 7.15 (d, 1H, *J* = 8.0 Hz), 7.39 (d, 4H, *J* = 8.4 Hz), 7.43 (dd, 1H, *J* = 2.0, 8.0 Hz), 7.55 (d, 4H, *J* = 8.4 Hz), 8.48 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR (CD_2Cl_2) δ 30.5, 56.8, 66.2, 66.9, 67.7, 71.5, 71.6, 71.9, 73.4, 73.5, 73.8, 83.5, 84.1, 87.0, 88.1, 89.7, 92.4, 93.2, 94.05, 94.09, 112.59, 112.65, 114.81, 114.86, 115.8, 115.9, 116.00, 116.05, 152.3, 154.15, 154.19, 154.5, 193.6; UV (CH_2Cl_2) (ε) λ (nm) 312 (36379), 370 (36109), 458 (3831); HRMS (FAB) calcd for $C_{69}H_{49}NO_6S_2Fe_2$ 1296.0754 (M^+), found 1296.0731.

Preparation of 4. Compound **4** was prepared using 27 mg (23 μmol) of **3**, 20 mg (0.14 mmol) of iodomethane in 2 ml of CH_2Cl_2 and 1 ml of CH_3CN. The reaction mixture was heated to 55 ˚C and stirred for 18 h. When the reaction was complete by TLC analysis (100% CH_2Cl_2) the solvent was removed in vacuo. The residue was dissolved in a minimum amount of CH_2Cl_2 and placed on top of a short silica gel column assembled in a fritted funnel by pipete. The residue was washed with 200 ml of CH_2Cl_2 to remove any non-polar impurities and then filtered through the pad of silica gel using 150 ml of acetone. The solvent was removed in vacuo and the residue was dissolved in a minimum amount of CH_3CN and 0.5 g of ammonium hexafluorophosphate was added. Distilled water was added to the solution to precipitate the desired product and the solid was then isolated via suction filtration, washed with ample amounts of distilled water, and dried in a vacuum oven overnight to yield 19 mg (63%) of the title compound. Data for **4**: ^{1}H NMR (CD_2Cl_2) δ 2.43 (s, 6H), 3.72 (s, 3H), 3.75 (s, 3H), 3.80 (s, 3H), 3.82 (s, 3H), 3.96 (s, 3H), 4.315 (t, 2H, *J* = 2.0 Hz), 4.324 (t, 2H, *J* = 2.0 Hz), 4.35 (t, 2H, *J* = 2.0 Hz), 4.47 (t, 2H, *J* = 2.0 Hz), 4.50 (t, 2H, *J* = 2.0 Hz), 4.53 (t, 2H, *J* = 2.0 Hz), 4.55 (t, 2H, *J* = 2.0 Hz), 4.58 (t, 2H, *J* = 2.0 Hz), 6.64 (s, 1H), 6.70 (s, 1H), 6.73 (s, 1H), 6.77 (s, 1H), 7.24 (d,

2H, *J* = 8.3 Hz), 7.25 (d, 1H, *J* = 8.3 Hz), 7.26 (d, 2H, *J* = 8.3 Hz), 7.35 (d, 2H, *J* = 8.3 Hz), 7.37 (d, 2H, *J* = 8.3 Hz), 7.63 (d, 1H, *J* = 8.3 Hz), 7.76 (s, 1H); ^{13}C NMR (CD_2Cl_2) δ 30.5, 47.7, 56.89, 56.94, 57.0, 62.8, 65.7, 69.0, 70.1, 71.1, 71.5, 71.9, 73.0, 73.3, 73.5, 73.6, 74.2, 80.1, 81.1, 84.1, 84.5, 87.3, 91.9, 92.7, 95.06, 95.14, 99.8, 112.2, 113.0, 113.3, 113.8, 115.24, 115.3, 115.81, 115.84, 116.3, 123.0, 124.3, 124.4, 128.8, 128.91, 128.92, 132.3, 132.4, 134.57, 134.60, 134.7, 135.5, 142.5, 145.5, 153.4, 153.5, 154.2, 154.4, 193.5; UV (CH_2Cl_2) (ε) λ (nm) 312 (33909), 364 (35431), 600 (2759); HRMS (FAB) calcd for $C_{70}H_{52}NO_6S_2Fe_2$ 1178.1935 (M^+), found 1178.1987.

Preparation of 25. Compound **25** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 643 mg (1.91 mmol) of **9**, 394 mg (1.92 mmol) of 3-iodopyridine, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), and 8 ml of THF/Hunig's base (1:1). The crude product was purified by column chromatography on silica gel using a 2:1 hexane/EtOAc solvent system. The desired fractions were pooled to yield 628 mg (80%) of the title compound. Data for **25**: ^{1}H NMR ($(CD_3)_2CO$) δ 4.33 (t, 2H, *J* = 2.0 Hz), 4.38 (t, 2H, *J* = 2.0 Hz), 4.51 (t, 2H, *J* = 2.0 Hz), 4.52 (t, 2H, *J* = 2.0 Hz), 7.39 (dd, 1H, *J* = 4.4, 8.0), 7.89 (ddd, 1H, *J* = 1.6, 4.4, 8.0 Hz), 8.55 (dd, 1H, *J* = 1.6, 4.4 Hz), 8.73 (d, 1H, *J* = 1.6 Hz); ^{13}C NMR ($(CD_3)_2CO$) δ 41.7, 67.6, 71.7, 72.8, 74.9, 77.3, 84.2, 91.3, 121.6, 124.1, 138.8, 149.2, 152.6; UV (CH_2Cl_2) (ε) λ (nm) 254 (9641), 306 (8124), 346 (1176), 452 (341); HRMS (FAB) calcd for $C_{17}H_{13}NFeI$ 413.9442 (M+1), found 413.9435.

Preparation of 27. Compound **27** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 588 mg (1.42 mmol) of **25**, 380 mg (2.34 mmol) of (2,5-dimethoxyphenyl)ethyne, $Pd(PPh_3)_2Cl_2$ (8 mol%), $Cu(OAc)_2$ (8 mol%), 4 ml of THF, and 2 ml Hunig's base. The crude product was purified by column chromatography on silica gel using

a 1:1 hexane/EtOAc solvent system. The desired fractions were pooled to yield 343 mg (54%) of the title compound. Data for **27**: ^{1}H NMR ($(CD_3)_2CO$) δ 3.72 (s, 3H), 3.82 (s, 3H), 4.41 (t, 2H, *J* = 2.0 Hz), 4.44 (t, 2H, *J* = 2.0 Hz), 4.56 (t, 2H, *J* = 2.0 Hz), 4.61 (t, 2H, *J* = 2.0 Hz), 6.85-6.92 (m, 3H), 7.27 (dd, 1H, *J* = 4.4, 8.0), 7.72 (ddd, 1H, *J* = 1.6, 4.4, 8.0 Hz), 8.48 (dd, 1H, *J* = 1.6, 4.4 Hz), 8.62 (d, 1H, *J* = 1.6 Hz); ^{13}C NMR ($(CD_3)_2CO$) δ 55.9, 56.6, 67.1, 68.5, 71.7, 72.0, 73.8, 74.0, 83.89, 83.94, 91.3, 91.4, 113.3, 114.4, 115.8, 118.6, 121.6, 123.9, 138.6, 148.9, 152.5, 154.2, 155.4; UV (CH_2Cl_2) (ε) λ (nm) 254 (25132), 310 (18632), 456 (998); HRMS (EI) calcd for $C_{27}H_{21}NO_2Fe$ 447.0922 (M^+), found 447.0925.

Preparation of 29. Compound **29** was prepared using 130 mg (0.29 mmol) of **27**, 247 mg (1.74 mmol) of iodomethane in 2 ml of CH_2Cl_2 and 1 ml of CH_3CN. The reaction mixture was heated to 55 ˚C and stirred for 18 h. When the reaction was complete by TLC analysis (100% CH_2Cl_2) the solvent was removed in vacuo. The residue was dissolved in a minimum amount of CH_2Cl_2 and placed on top of a short silica gel column assembled in a fritted funnel by pipete. The residue was washed with 200 ml of CH_2Cl_2 to remove any non-polar impurities and then filtered through the pad of silica gel using 150 ml of acetone. The solvent was removed in vacuo and the residue was dissolved in a minimum amount of CH_3CN and 0.5 g of ammonium hexafluorophosphate was added. Distilled water was added to the solution to precipitate the desired product and the solid was then isolated via suction filtration, washed with ample amounts of distilled water, and dried in a vacuum oven overnight to yield 118 mg (67%) of the title compound as an orange solid. Data for **29**: ^{1}H NMR ($(CD_3)_2CO$) δ 3.75 (s, 3H), 3.78 (s, 3H), 4.44 (t, 2H, *J* = 1.6 Hz), 4.49 (s, 3H), 4.54 (t, 2H, *J* = 1.6 Hz), 4.57 (t, 2H, *J* = 1.6 Hz), 4.66 (t, 2H, *J* = 1.6 Hz), 6.74-6.86 (m, 3H), 8.01 (dd, 1H, *J* = 6.8, 8.0 Hz), 8.42 (d, 1H, *J* = 8.0 Hz), 8.88 (d, 1H, *J* = 6.0 Hz), 8.97 (s, 1H); ^{13}C NMR ($(CD_3)_2CO$) δ 49.2, 56.0, 56.7, 65.5, 69.7, 71.6, 72.5,

73.5, 74.1, 80.8, 84.6, 90.5, 97.4, 113.3, 114.4, 115.3, 118.7, 126.3, 128.7, 143.9, 146.4, 147.5, 154.1, 155.1; UV (CH_2Cl_2) (ε) λ (nm) 282 (20775), 322 (19935), 496 (1886); HRMS (FAB) calcd for $C_{28}H_{24}NO_2Fe$ 462.1156 (M^+), found 462.1143.

Preparation of 24. Compound **24** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 106 mg (0.32 mmol) of **9**, 56 mg (0.35 mmol) of 2-bromopyridine, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), and 3 ml of THF/Hunig's base (1:1). The crude product was purified by column chromatography on silica gel using a 2:1 hexane/EtOAc solvent system. The desired fractions were pooled to yield 108 mg (83%) of the title compound. Data for **24**: ^{1}H NMR ($(CD_3)_2CO$) δ 4.34 (t, 2H, *J* = 2.0 Hz), 4.38 (t, 2H, *J* = 2.0 Hz), 4.51 (t, 2H, *J* = 2.0 Hz), 4.55 (t, 2H, *J* = 2.0 Hz), 7.34 (ddd, 1H, *J* = 1.2, 4.8, 7.6 Hz), 7.56 (ddd, 1H, *J* = 1.2, 1.2, 8.0 Hz), 7.78 (ddd, 1H, *J* = 1.6, 7.6, 7.6 Hz), 8.58 (ddd, 1H, *J* = 0.8, 1.6, 4.8 Hz); ^{13}C NMR ($(CD_3)_2CO$) δ 41.3, 67.0, 71.8, 73.1, 75.0, 77.2, 87.5, 87.7, 123.4, 127.7, 136.9, 144.5, 150.8; UV (CH_2Cl_2) (ε) λ (nm) 276 (11121), 310 (12572), 452 (540); HRMS (FAB) calcd for $C_{17}H_{13}NFeI$ 413.9442 (M+1), found 413.9461.

Preparation of 26. Compound **26** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 669 mg (1.62 mmol) of **24**, 528 mg (3.25 mmol) of (2,5-dimethoxyphenyl)ethyne, $Pd(PPh_3)_2Cl_2$ (8 mol%), $Cu(OAc)_2$ (8 mol%), 4 ml of THF, and 2 ml Hunig's base. The crude product was purified by column chromatography on silica gel using a 1:1 hexane/EtOAc solvent system. The desired fractions were pooled to yield 343 mg (54%) of the title compound. Data for **26**: ^{1}H NMR ($(CD_3)_2CO$) δ 3.73 (s, 3H), 3.82 (s, 3H), 4.40 (t, 2H, *J* = 2.0 Hz), 4.45 (t, 2H, *J* = 2.0 Hz), 4.57 (t, 2H, *J* = 2.0 Hz), 4.63 (t, 2H, *J* = 2.0 Hz), 6.86-6.93 (m, 3H), 7.28 (ddd, 1H, *J* = 1.2, 4.8, 7.6 Hz), 7.42 (d, 1H, *J* = 8.0 Hz), 7.67 (ddd, 1H, *J* = 1.6, 7.6, 7.6 Hz), 8.53 (d, 1H, *J* = 4.8); ^{13}C NMR ($(CD_3)_2CO$) δ 55.9, 56.6, 66.6, 68.4, 71.8, 72.2,

73.8, 74.1, 83.8, 87.3, 87.9, 91.4, 113.3, 114.4, 115.8, 118.6, 123.2, 127.6, 136.8, 144.6, 150.7, 154.2, 155.4; UV (CH_2Cl_2) (ε) λ (nm) 314 (34563), 448 (1979); HRMS (EI) calcd for $C_{27}H_{21}NO_2Fe$ 447.0922 (M^+), found 447.0919.

Preparation of 28. Compound **28** was prepared using 111 mg (0.25 mmol) of **26**, 213 mg (1.50 mmol) of iodomethane in 3 ml of CH_2Cl_2 and 2 ml of CH_3CN. The reaction mixture was heated to 55 ˚C and stirred for 18 h. When the reaction was complete by TLC analysis (100% CH_2Cl_2) the solvent was removed in vacuo. The residue was dissolved in a minimum amount of CH_2Cl_2 and placed on top of a short silica gel column assembled in a fritted funnel by pipette. The residue was washed with 200 ml of CH_2Cl_2 to remove any non-polar impurities and then filtered through the pad of silica gel using 150 ml of acetone. The solvent was removed in vacuo and the residue was dissolved in a minimum amount of CH_3CN and 0.5 g of ammonium hexafluorophosphate was added. Distilled water was added to the solution to precipitate the desired product and the solid was then isolated via suction filtration, washed with ample amounts of distilled water, and dried in a vacuum oven overnight to yield 78 mg (52%) of the title compound as an purple solid. Data for **28**: ^{1}H NMR ($(CD_3)_2CO$) δ 3.72 (s, 3H), 3.80 (s, 3H), 4.40 (s, 3H), 4.50 (t, 2H, *J* = 1.6 Hz), 4.65 (t, 2H, *J* = 1.6 Hz), 4.72 (t, 2H, *J* = 1.6 Hz), 4.89 (t, 2H, *J* = 1.6 Hz), 6.68-6.86 (m, 3H), 7.91 (t, 1H, *J* = 6.4 Hz), 8.03 (d, 1H, *J* = 8.0 Hz), 8.40 (t, 1H, *J* = 8.0 Hz), 8.77 (d, 1H, *J* = 6.0 Hz); ^{13}C NMR ($(CD_3)_2CO$) δ 47.9, 55.9, 56.6, 63.3, 70.6, 71.9, 73.7, 73.8, 79.7, 84.9, 90.1, 109.6, 113.1, 113.7, 115.6, 118.4, 125.8, 131.1, 139.5, 144.8, 146.8, 154.0, 154.8; UV (CH_2Cl_2) (ε) λ (nm) 258 (15618), 290 (13770), 328 (16775), 554 (2205); HRMS (FAB) calcd for $C_{28}H_{24}NO_2Fe$ 462.1156 (M^+), found 462.1141.

Preparation of 18. Compound **18** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 76 mg (226 μmol) of **9**, 83 mg (226 μmol) of **30**,

$Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), and 4 ml of THF/Hunig's base (1:1). The crude product was purified by column chromatography on silica gel using a 5:1 CH_2Cl_2/hexane solvent system. The desired fractions were pooled to yield 116 mg (82%) of the title compound. Data for **18**: ^{1}H NMR ($(CD_3)_2CO$) δ 4.28 (s, 5H), 4.35 (t, 2H, *J* = 2.0 Hz), 4.36 (t, 2H, *J* = 2.0 Hz), 4.41 (t, 2H, *J* = 2.0 Hz), 4.53 (t, 2H, *J* = 2.0 Hz), 4.57 (br t, 4H), 7.56 (d, 1H, *J* = 8.3 Hz), 7.84 (dd, 1H, *J* = 2.0, 8.3 Hz), 8.64 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ 41.1, 64.4, 66.1, 69.5, 70.3, 71.4, 71.8, 73.0, 74.6, 76.6, 82.8, 86.7, 90.1, 94.1, 119.8, 126.3, 138.2, 141.8, 152.4; UV (CH_2Cl_2) (ε) λ (nm) 332 (35281), 450 (4299); HRMS (FAB) calcd for $C_{29}H_{21}NFe_2I$ 621.9418 (M+1), found 621.9432; Anal. calcd for $C_{29}H_{20}NFe_2I$: C, 56.08; H, 3.25; N, 2.26. Found: C, 55.74; H, 3.14; N, 2.16.

Preparation of 19. Compound **19** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 304 mg (0.49 mmol) of **18**, 385 mg (3.92 mmol) of trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), 28 ml of THF/Hunig's base (1:1). The crude product was purified by column chromatography on silica gel using a 3:1 CH_2Cl_2/hexane solvent system. The desired fractions were pooled to yield 232 mg (80%) of the silyl-protected intermediate **19**.

Preparation of 32. Compound **32** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 415 mg (0.67 mmol) of **18**, 404 mg (1.18 mmol) of **20**, $Pd(PPh_3)_2Cl_2$ (8 mol%), $Cu(OAc)_2$ (8 mol%), 5 ml of THF, and 1 ml of Hunig's base. The crude product was purified by column chromatography on silica gel using a 6:1 CH_2Cl_2/hexane solvent system. The desired fractions were pooled to yield 169 mg (30%) of the silyl-protected intermediate **31**. Data for **31**: ^{1}H NMR ($(CD_3)_2CO$) δ 1.15 (s, 21H), 3.83 (s, 3H), 3.86 (s, 3H), 4.28 (s, 5H), 4.35 (t, 4H, *J* = 2.0 Hz), 4.45 (t, 2H, *J* = 2.0 Hz), 4.48 (t, 2H, *J* = 2.0 Hz), 4.57 (t,

4H, *J* = 2.0 Hz), 4.60 (t, 2H, *J* = 2.0 Hz), 4.66 (t, 2H, *J* = 2.0 Hz), 7.01 (s, 1H), 7.02 (s, 1H), 7.42 (d, 1H, *J* = 8.3 Hz), 7.75 (dd, 1H, *J* = 2.0, 8.3 Hz), 8.62 (d, 1H, *J* = 2.0 Hz). To a solution of 77 mg (92 μmol) of **31** in 10 ml of CH_2Cl_2 was added 1.1 equiv of a solution of TBAF (1 M in THF). The reaction mixture was stirred at room temperature for 15 min, after which time the solvents were removed in vacuo. The crude residue was purified via column chromatography on silica gel using a 100% CH_2Cl_2 solvent system to provide 55 mg (88%) of the desired product. Data for **32**: ^{1}H NMR ($(CD_3)_2CO$) δ 3.82 (s, 3H), 3.86 (s, 3H), 3.89 (s, 1H), 4.29 (s, 5H), 4.35 (t, 2H, *J* = 2.0 Hz), 4.44 (t, 2H, *J* = 2.0 Hz), 4.48 (t, 2H, *J* = 2.0 Hz), 4.57 (t, 2H, *J* = 2.0 Hz), 4.60 (t, 2H, *J* = 2.0 Hz), 4.66 (t, 2H, *J* = 2.0 Hz), 6.95 (s, 1H), 7.01 (s, 1H), 7.36 (d, 1H, *J* = 8.3 Hz), 7.69 (dd, 1H, *J* = 2.0, 8.3 Hz), 8.56 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR (CD_2Cl_2) δ 56.6, 56.7, 64.6, 66.1, 67.6, 69.7, 70.5, 71.6, 72.0, 73.4, 73.8, 80.4, 82.5, 82.9, 83.2, 86.9, 89.7, 93.1, 94.0, 111.6, 115.0, 115.7, 116.6, 119.8, 126.2, 138.0, 141.9, 152.3, 154.0, 154.9; UV (CH_2Cl_2) (ε) λ (nm) 276 (44377), 308 (40282), 338 (49490), 454 (5219); HRMS (FAB) calcd for $C_{41}H_{30}NO_2Fe_2$ 680.0975 (M+1), found 680.0950.

Preparation of 5. Compound **5** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 45 mg (66 μmol) of **32**, 40 mg (144 μmol) of *S*-acetyl-4-iodothiophenol, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), 2.5 ml of THF, and 0.3 ml of Hunig's base. The crude product was purified by column chromatography on silica gel using a 3:1 hexane/EtOAc solvent system. The desired fractions were pooled to yield 36 mg (65%) of the title compound. Data for **5**: ^{1}H NMR ($(CD_3)_2CO$) δ 2.45 (s, 3H), 3.86 (s, 3H), 3.88 (s, 3H), 4.26 (s, 5H), 4.32 (t, 2H, *J* = 2.0 Hz), 4.45 (t, 2H, *J* = 2.0 Hz), 4.48 (t, 2H, *J* = 2.0 Hz), 4.52 (t, 2H, *J* = 2.0 Hz), 4.61 (t, 2H, *J* = 2.0 Hz), 4.67 (t, 2H, *J* = 2.0 Hz), 6.97 (s, 1H), 7.08 (s, 1H), 7.35 (d, 1H, *J* = 8.3 Hz), 7.46 (d, 2H, *J* = 8.4 Hz), 7.59 (d, 2H, *J* = 8.4 Hz), 7.68 (dd, 1H, *J* = 2.0, 8.3

Hz), 8.56 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR (CD_2Cl_2) δ 30.5, 56.7, 64.6, 66.2, 67.7, 69.7, 70.4, 71.6, 71.94, 71.97, 73.4, 73.8, 82.9, 83.5, 86.9, 88.0, 89.6, 93.2, 93.9, 94.0, 112.5, 114.8, 115.85, 115.93, 119.8, 124.8, 126.3, 128.8, 132.4, 134.7, 138.0, 141.9, 152.3, 154.2, 154.4, 193.6; UV (CH_2Cl_2) (ε) λ (nm) 314 (36780), 342 (31185), 372 (31993), 452 (3650); HRMS (FAB) calcd for $C_{49}H_{36}NO_3SFe_2$ 830.1115 (M+1), found 830.1110; Anal. calcd for $C_{49}H_{35}NO_3SFe_2$: C, 70.93; H, 4.26; N, 1.69. Found: C, 71.20; H, 4.59; N, 1.72.

Preparation of 7. Compound **7** was prepared using 24 mg (29 μmol) of **5**, 24 mg (0.17 mmol) of iodomethane in 2 ml of CH_2Cl_2 and 1 ml of CH_3CN. The reaction mixture was heated to 55 ˚C and stirred for 18 h. When the reaction was complete by TLC analysis (100% CH_2Cl_2) the solvent was removed in vacuo. The residue was dissolved in a minimum amount of CH_2Cl_2 and placed on top of a short silica gel column assembled in a fritted funnel by pipete. The residue was washed with 200 ml of CH_2Cl_2 to remove any non-polar impurities and then filtered through the pad of silica gel using 150 ml of acetone. The solvent was removed in vacuo and the residue was dissolved in a minimum amount of CH_3CN and 0.5 g of ammonium hexafluorophosphate was added. Distilled water was added to the solution to precipitate the desired product and the brown solid was then isolated via suction filtration, washed with ample amounts of distilled water, and dried in a vacuum oven overnight to yield 21 mg (74%) of the title compound. Data for **7**: ^{1}H NMR ($(CD_3)_2CO$) δ 2.46 (s, 3H), 3.86 (s, 3H), 3.88 (s, 3H), 4.24 (s, 5H), 4.34 (t, 2H, *J* = 1.6 Hz), 4.44 (s, 3H), 4.47 (t, 2H, *J* = 1.6 Hz), 4.53 (t, 2H, *J* = 1.6 Hz), 4.70 (t, 2H, *J* = 1.6 Hz), 4.76 (t, 2H, *J* = 1.6 Hz), 4.93 (t, 2H, *J* = 1.6 Hz), 6.88 (s, 1H), 6.99 (s, 1H), 7.41 (d, 2H, *J* = 8.0 Hz), 7.49 (d, 2H, *J* = 8.0 Hz), 7.98 (d, 1H, *J* = 8.4 Hz), 8.36 (dd, 1H, *J* = 2.0, 8.4 Hz), 8.97 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR (CD_2Cl_2) δ 30.5, 48.0, 56.98, 57.04, 62.0, 62.5, 70.1, 70.8, 70.9, 71.8, 72.8, 73.67, 73.73, 74.5, 79.2, 79.8, 84.5, 87.4, 92.1, 95.0, 102.7,

113.0, 113.4, 114.0, 115.5, 116.4, 123.1, 124.4, 129.0, 129.9, 132.4, 134.6, 136.1, 143.7, 146.4, 153.7, 154.5, 193.5; UV (CH_2Cl_2) (ε) λ (nm) 312 (31342), 366 (31845), 586 (4699); HRMS (FAB) calcd for $C_{50}H_{38}NO_3SFe_2$ 844.1271 (M^+), found 844.1300.

Preparation of 35 and 36. Compounds **35** and **36** were prepared using the general procedure for the palladium-catalyzed coupling reaction using 399 mg (1.90 mmol) of ethynylferrocene, 824 mg (2.49 mmol) of 2,5-diiodopyridine, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), and 15 ml of THF/Hunig's base (1:1). The crude mixture of products was purified by column chromatography on silica gel using a 3:1 CH_2Cl_2/hexane solvent system. The desired fractions were pooled to yield 350 mg (45%) of **35** (R_f = 0.34) and 132 mg (17%) of **36** (R_f = 0.43). Data for **35**: ^{1}H NMR ($(CD_3)_2CO$) δ 4.27 (s, 5H), 4.37 (t, 2H, *J* = 2.0 Hz), 4.59 (t, 2H, *J* = 2.0 Hz), 7.37 (d, 1H, *J* = 8.3 Hz), 8.16 (dd, 1H, *J* = 2.0, 8.3 Hz), 8.80 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ 63.5, 69.6, 70.3, 72.1, 84.9, 91.5, 128.2, 142.8, 144.5, 156.1; UV (CH_2Cl_2) (ε) λ (nm) 260 (21963), 304 (24422), 358 (4794), 452 (1455); HRMS (FAB) calcd for $C_{17}H_{12}NFeI$ 412.9364 (M^+), found 412.9346; Anal. calcd for $C_{17}H_{12}NFeI$: C, 49.43; H, 2.93; N, 3.39. Found: C, 49.37; H, 3.05; N, 3.31. Data for **36**: ^{1}H NMR ($(CD_3)_2CO$) δ 4.27 (s, 5H), 4.35 (t, 2H, *J* = 2.0 Hz), 4.56 (t, 2H, *J* = 2.0 Hz), 7.56 (dd, 1H, *J* = 2.0, 8.3 Hz), 7.86 (d, 1H, *J* = 8.3 Hz), 8.44 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ 64.0, 69.5, 70.3, 71.8, 81.6, 94.2, 115.6, 121.0, 134.4, 139.5, 152.7; UV (CH_2Cl_2) (ε) λ (nm) 262 (24017), 300 (24186), 356 (4291), 452 (1191); HRMS (FAB) calcd for $C_{17}H_{12}NFeI$ 412.9364 (M^+), found 412.9369.

Preparation of 34. Compound **34** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 594 mg (1.77 mmol) of **9**, 655 mg (1.59 mmol) of **35**, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), and 15 ml of THF/Hunig's base (1:1). The crude product was purified by column chromatography on silica gel using a 5:1 CH_2Cl_2/hexane solvent

system. The desired fractions were pooled to yield 659 mg (67%) of the title compound. Data for **34**: ^{1}H NMR ($(CD_3)_2CO$) δ 4.26 (s, 5H), 4.32 (t, 2H, *J* = 2.0 Hz), 4.35 (t, 2H, *J* = 2.0 Hz), 4.37 (t, 2H, *J* = 2.0 Hz), 4.49 (t, 2H, *J* = 2.0 Hz), 4.51 (t, 2H, *J* = 2.0 Hz), 4.57 (t, 2H, *J* = 2.0 Hz), 7.49 (d, 1H, *J* = 8.3 Hz), 7.84 (dd, 1H, *J* = 2.0, 8.3 Hz), 8.65 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ 41.6, 63.8, 66.8, 69.6, 70.3, 71.1, 72.1, 72.5, 74.3, 76.6, 84.1, 85.7, 91.8, 92.6, 119.4, 126.1, 138.4, 142.1, 152.4; UV (CH_2Cl_2) (ε) λ (nm) 332 (32750), 452 (3949); HRMS (FAB) calcd for $C_{29}H_{21}NFe_2I$ 621.9418 (M+1), found 621.9419; Anal. calcd for $C_{29}H_{20}NFe_2I$: C, 56.08; H, 3.25; N, 2.26. Found: C, 55.83; H, 3.32; N, 2.24.

Preparation of 6. Compound **6** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 533 mg (0.86 mmol) of **34**, 450 mg (1.31 mmol) of **20**, $Pd(PPh_3)_2Cl_2$ (8 mol%), $Cu(OAc)_2$ (8 mol%), 5 ml of THF, and 1 ml of Hunig's base. The crude product was purified by column chromatography on silica gel using a 6:1 CH_2Cl_2/hexane solvent system. The desired fractions were pooled to yield 295 mg (41%) of the silyl-protected intermediate. Data for the silyl-protected intermediate: ^{1}H NMR ($(CD_3)_2CO$) δ 1.15 (s, 21H), 3.82 (s, 3H), 3.86 (s, 3H), 4.28 (s, 5H), 4.38 (t, 4H, *J* = 2.0 Hz), 4.45 (t, 2H, *J* = 2.0 Hz), 4.46 (t, 2H, *J* = 2.0 Hz), 4.59 (t, 4H, *J* = 2.0 Hz), 4.60 (t, 2H, *J* = 2.0 Hz), 4.63 (t, 2H, *J* = 2.0 Hz), 6.99 (s, 1H), 7.02 (s, 1H), 7.42 (d, 1H, *J* = 8.3 Hz), 7.71 (dd, 1H, *J* = 2.0, 8.3 Hz), 8.61 (d, 1H, *J* = 2.0 Hz). To a solution of 295 mg (0.35 mmol) of the silyl-protected intermediate in 10 ml of CH_2Cl_2 was added 1.1 equiv of a solution of TBAF (1 M in THF). The reaction mixture was stirred at room temperature for 15 min, after which time the solvents were removed in vacuo. The crude residue was purified via column chromatography on silica gel using a 100% CH_2Cl_2 solvent system to provide 142 mg (60%) of the desired deprotected product. Data for the deprotected product: ^{1}H NMR ($(CD_3)_2CO$) δ 3.81 (s, 3H), 3.86 (s, 3H), 3.88 (s, 1H), 4.30 (s, 5H), 4.37 (t, 2H,

J = 2.0 Hz), 4.44 (t, 2H, *J* = 2.0 Hz), 4.46 (t, 2H, *J* = 2.0 Hz), 4.59 (t, 2H, *J* = 2.0 Hz), 4.60 (t, 2H, *J* = 2.0 Hz), 4.63 (t, 2H, *J* = 2.0 Hz), 6.94 (s, 1H), 7.00 (s, 1H), 7.36 (d, 1H, *J* = 8.3 Hz), 7.65 (dd, 1H, *J* = 2.0, 8.3 Hz), 8.56 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR (CD_2Cl_2) δ 56.6, 56.7, 64.1, 66.8, 67.5, 69.9, 70.5, 71.5, 71.7, 72.2, 73.4 73.5, 80.4, 82.6, 83.2, 84.0, 85.9, 91.1, 92.3, 93.1, 111.7, 115.0, 115.6, 116.6, 119.5, 126.1, 138.0, 142.1, 152.4, 154.0, 155.0; UV (CH_2Cl_2) (ε) λ (nm) 276 (25607), 306 (23966), 336 (29527), 454 (3048); HRMS (FAB) calcd for $C_{41}H_{30}NO_2Fe_2$ 680.0975 (M+1), found 680.0947. To a solution of 65 mg (96 μmol) of the deprotected product in 4 ml of THF and 0.5 ml of Hunig's base, 60 mg (215 μmol) of *S*-acetyl-4-iodothiophenol, $Pd(PPh_3)_2Cl_2$ (4 mol%), and CuI (4 mol%) were added. The crude product was purified by column chromatography on silica gel using a 3:1 hexane/EtOAc solvent system. The desired fractions were pooled to yield 47 mg (60%) of the title compound. Data for **6**: ^{1}H NMR ($(CD_3)_2CO$) δ 2.45 (s, 3H), 3.85 (s, 3H), 3.87 (s, 3H), 4.26 (s, 5H), 4.34 (t, 2H, *J* = 2.0 Hz), 4.45 (t, 2H, *J* = 2.0 Hz), 4.47 (t, 2H, *J* = 2.0 Hz), 4.54 (t, 2H, *J* = 2.0 Hz), 4.60 (t, 2H, *J* = 2.0 Hz), 4.64 (t, 2H, *J* = 2.0 Hz), 6.96 (s, 1H), 7.07 (s, 1H), 7.36 (d, 1H, *J* = 8.3 Hz), 7.46 (d, 2H, *J* = 8.4 Hz), 7.59 (d, 2H, *J* = 8.4 Hz), 7.64 (dd, 1H, *J* = 2.0, 8.3 Hz), 8.56 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR (CD_2Cl_2) δ 30.5, 56.7, 56.8, 64.0, 66.8, 67.7, 69.9, 70.5, 71.5, 71.7, 72.3, 73.4, 73.5, 83.5, 84.0, 85.9, 88.0, 91.2, 92.4, 93.2, 94.1, 112.6, 114.8, 115.8, 116.0, 119.5, 124.8, 126.1, 128.8, 132.4, 134.7, 138.0, 142.1, 152.4, 154.1, 154.5, 193.6; UV (CH_2Cl_2) (ε) λ (nm) 314 (37105), 340 (31283), 370 (31941), 452 (3697); HRMS (FAB) calcd for $C_{49}H_{36}NO_3SFe_2$ 830.1115, found 830.1093; Anal. calcd for $C_{49}H_{35}NO_3SFe_2$: C, 70.93; H, 4.26; N, 1.69. Found: C, 70.51; H, 4.35; N, 1.72.

Preparation of 8. Compound **8** was prepared using 38 mg (46 μmol) of **6**, 39 mg (0.28 mmol) of iodomethane in 2 ml of CH_2Cl_2 and 1 ml of CH_3CN. The reaction mixture was heated to 55 ˚C and stirred for 18 h. When the reaction was complete by TLC analysis (100% CH_2Cl_2)

the solvent was removed in vacuo. The residue was dissolved in a minimum amount of CH_2Cl_2 and placed on top of a short silica gel column assembled in a fritted funnel by pipette. The residue was washed with 200 ml of CH_2Cl_2 to remove any non-polar impurities and then filtered through the pad of silica gel using 150 ml of acetone. The solvent was removed in vacuo and the residue was dissolved in a minimum amount of CH_3CN and 0.5 g of ammonium hexafluorophosphate was added. Distilled water was added to the solution to precipitate the desired product and the dark purple solid was then isolated via suction filtration, washed with ample amounts of distilled water, and dried in a vacuum oven overnight to yield 36 mg (78%) of the title compound. Data for **8**: ^{1}H NMR (CD_2Cl_2) δ 2.43 (s, 3H), 3.79 (s, 3H), 3.85 (s, 3H), 4.19 (s, 3H), 4.27 (s, 5H), 4.40 (t, 2H, *J* = 1.6 Hz), 4.46 (t, 2H, *J* = 1.6 Hz), 4.49 (t, 2H, *J* = 1.6 Hz), 4.56 (t, 2H, *J* = 1.6 Hz), 4.62 (t, 2H, *J* = 1.6 Hz), 4.69 (t, 2H, *J* = 1.6 Hz), 6.81 (s, 1H), 6.83 (s, 1H), 7.30 (d, 2H, *J* = 8.4 Hz), 7.43 (d, 2H, *J* = 8.4 Hz), 7.64 (d, 1H, *J* = 8.4 Hz), 7.97 (dd, 1H, *J* = 2.0, 8.4 Hz), 8.20 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR (CD_2Cl_2) δ 30.5, 47.9, 57.0, 57.1, 59.4, 65.4, 69.0, 71.3, 71.4, 72.2, 72.6, 73.3, 73.5, 73.8, 78.6, 81.1, 84.1, 87.4, 92.9, 94.9, 99.8, 112.5, 115.2, 115.6, 115.97, 116.01, 123.4, 124.4, 129.0, 130.1, 132.4, 134.7, 135.6, 143.9, 146.8, 153.8, 154.4, 193.5; UV (CH_2Cl_2) (ε) λ (nm) 316 (35401), 370 (46727), 590 (8350); HRMS (FAB) calcd for $C_{50}H_{38}NO_3SFe_2$ 844.1271 (M^+), found 844.1281.

Preparation of 38. Compound **38** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 1.00 g (3.21 mmol) of iodoferrocene, 992 mg (2.90 mmol) of **20**, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), 25 ml of THF/Hunig's base (1:1). The crude product was purified by column chromatography on silica gel using a 2:1 hexanes/CH_2Cl_2 solvent system. The desired fractions were pooled to yield 415 mg (27%) of the silyl-protected intermediate **37**. Data for **37**: ^{1}H NMR (CD_2Cl_2) δ 1.15 (s, 21H), 3.84 (s, 3H), 3.86 (s, 3H), 4.26

(s, 5H), 4.28 (t, 2H, J = 2.0 Hz), 4.51 (t, 2H, J = 2.0 Hz), 6.94 (s, 1H), 6.96 (s, 1H); ^{13}C NMR (CD_2Cl_2) δ 11.9, 19.0, 56.9, 57.1, 65.6, 69.6, 70.6, 72.0, 82.3, 94.6, 97.2, 103.6, 113.6, 114.8, 116.37, 116.39, 154.3, 155.3. To a solution of 323 mg (0.61 mmol) of **37** in 8 ml of CH_2Cl_2 was added 1.1 equiv of a solution of TBAF (1 M in THF). The reaction mixture was stirred at room temperature for 15 min, after which time the solvents were removed in vacuo. The crude residue was purified via column chromatography on silica gel using a 2:1 hexanes/CH_2Cl_2 solvent system to provide 232 mg (84%) of the desired product. Data for **38**: ^{1}H NMR (CD_2Cl_2) δ 3.39 (s, 1H), 3.83 (s, 3H), 3.84 (s, 3H), 4.24 (s, 5H), 4.26 (t, 2H, J = 2.0 Hz), 4.50 (t, 2H, J = 2.0 Hz), 6.955 (s, 1H), 6.961 (s, 1H).; ^{13}C NMR (CD_2Cl_2) δ 56.85, 56.91, 65.4, 69.7, 70.6, 72.0, 80.5, 82.1, 82.7, 94.9, 111.6, 115.4, 115.9, 116.8, 154.2, 155.2; UV (CH_2Cl_2) (ε) λ (nm) 276 (21442), 306 (14058), 350 (17170), 450 (1494); HRMS (EI) calcd for $C_{22}H_{18}O_2Fe$ 370.0656 (M^+), found 370.0643.

Preparation of 39. Compound **39** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 205 mg (0.55 mmol) of **38**, 1.55 g (4.69 mmol) of 1,4-diiodobenzene, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), 30 ml of THF, and 26 ml of Hunig's base. The crude product was purified by column chromatography on silica gel using a solvent gradient system (2:1 hexanes/CH_2Cl_2 to 1:1 hexanes/CH_2Cl_2). The desired fractions were pooled to yield 192 mg (61%) of the title compound. Data for **39**: ^{1}H NMR (CD_2Cl_2) δ 3.861 (s, 3H), 3.864 (s, 3H), 4.25 (s, 5H), 4.27 (t, 2H, J = 2.0 Hz), 4.50 (t, 2H, J = 2.0 Hz), 6.98 (s, 1H), 7.00 (s, 1H), 7.27 (d, 2H, J = 8.4 Hz), 7.70 (d, 2H, J = 8.4 Hz); ^{13}C NMR (CD_2Cl_2) δ 56.92, 56.94, 65.5, 69.7, 70.6, 72.0, 82.3, 87.9, 94.0, 94.7, 94.9, 112.6, 115.1, 116.0, 116.1, 123.4, 133.5, 138.2, 154.4, 154.6; UV (CH_2Cl_2) (ε) λ (nm) 312 (42543), 364 (43504), 448 (3269); HRMS (FAB) calcd for $C_{28}H_{21}O_2FeI$ 571.9936 (M^+), found 571.9950.

Preparation of 41. Compound **41** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 190 mg (0.33 mmol) of **39**, 181 mg (0.53 mmol) of **20**, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), 5 ml of THF/Hunig's base (1:1). The crude product was purified by column chromatography on silica gel using a 1:1 hexanes/CH_2Cl_2 solvent system. The desired fractions were pooled to yield 195 mg (75%) of silyl-protected intermediate **40**. Data for **40**: ^{1}H NMR (CD_2Cl_2) δ 1.14 (s, 21H), 3.83 (s, 3H), 3.86 (s, 3H), 3.87 (s, 3H), 3.88 (s, 3H), 4.25 (s, 5H), 4.27 (t, 2H, *J* = 2.0 Hz), 4.51 (t, 2H, *J* = 2.0 Hz), 6.95 (s, 1H), 6.99 (s, 1H), 7.00 (s, 1H), 7.02 (s, 1H), 7.53 (bs, 4H). To a solution of 195 mg (0.246 mmol) of **40** in 10 ml of CH_2Cl_2 was added 1.1 equiv of a solution of TBAF (1 M in THF). The reaction mixture was stirred at room temperature for 15 min, after which time the solvents were removed in vacuo. The crude residue was purified via column chromatography on silica gel using a solvent gradient system (1:1 hexanes/CH_2Cl_2 to 1:2 hexanes/CH_2Cl_2) to provide 140 mg (90%) of the desired product. Data for **41**: ^{1}H NMR (CD_2Cl_2) δ 3.41 (s, 1H), 3.84 (s, 3H), 3.85 (s, 3H), 3.87 (s, 3H), 3.88 (s, 2H), 4.25 (s, 5H), 4.27 (t, 2H, *J* = 2.0 Hz), 4.51 (t, 2H, *J* = 2.0 Hz), 6.99 (s, 1H), 7.00 (s, 1H), 7.018 (s, 1H), 7.022 (s, 1H), 7.24 (bs, 4H); ^{13}C NMR (CD_2Cl_2) δ 56.86, 56.91, 57.0, 65.5, 69.7, 70.6, 72.0, 80.3, 82.3, 83.2, 88.0, 88.6, 94.7, 95.0, 95.1, 112.68, 112.73, 114.2, 115.1, 115.97, 116.02, 116.1, 116.8, 123.5, 123.9, 132.05, 132.10, 154.37, 154.41, 154.6, 155.1; UV (CH_2Cl_2) (ε) λ (nm) 264 (18021), 320 (30020), 380 (45772); HRMS (FAB) calcd for $C_{40}H_{30}O_4Fe$ 630.1493 (M^+), found 630.1503.

Preparation of 42. Compound **42** was prepared using the general procedure for the palladium-catalyzed coupling reaction using 137 mg (0.22 mmol) of **41**, 100 mg (0.36 mmol) of *S*-acetyl-4-iodothiophenol, $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%), 2 ml of THF, and 1.5 ml of Hunig's base. The crude product was purified by column chromatography on silica gel using a

100% CH_2Cl_2 solvent system. The desired fractions were pooled to yield 92 mg (55%) of the title compound. Data for **42**: ^{1}H NMR (CD_2Cl_2) δ 2.41 (s, 3H), 3.88 (s, 3H), 3.885 (s, 3H), 3.886 (s, 3H), 3.89 (s, 3H), 4.25 (s, 5H), 4.27 (t, 2H, *J* = 2.0 Hz), 4.51 (t, 2H, *J* = 2.0 Hz), 6.99 (s, 1H), 7.02 (s, 1H), 7.05 (s, 2H), 7.41 (d, 2H, *J* = 8.4 Hz), 7.54 (bs, 4H), 7.57 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (CD_2Cl_2) δ 30.7, 56.9, 57.0, 65.5, 69.7, 70.6, 72.0, 82.3, 88.0, 88.3, 88.6, 94.6, 94.7, 95.0, 95.2, 112.7, 113.7, 113.9, 115.1, 115.99, 116.11, 116.16, 123.6, 123.9, 124.9, 129.2, 132.1, 132.1, 132.6, 134.9, 154.4, 154.6, 154.6, 193.8; UV (CH_2Cl_2) (ε) λ (nm) 280 (15956), 324 (25737), 390 (45020); HRMS (FAB) calcd for $C_{48}H_{36}O_5SFe$ 780.1633 (M^+), found 780.1639; Anal. calcd for $C_{48}H_{36}O_5SFe$: C, 73.84; H, 4.66. Found: C, 73.55; H, 4.71.

General Procedure for the Preparation of Arenethiols from the Thioacetates. As a general procedure, to a stirred solution of the thioacetate (86 μmol) in CH_2Cl_2 (1.5 ml) under nitrogen at 0 ºC was added dropwise a solution of sodium thiomethoxide (1.5 equiv) in 0.5 ml of methanol. The mixture was stirred at 0 ºC for 15 minutes. The solution was then added into 5 ml of 0.1 M HCl and extracted with CH_2Cl_2 (3 x 10 ml). The combined organic layers were washed with brine (2 x 10 ml), dried over $MgSO_4$, filtered, and concentrated to yield an orange residue. The crude material was filtered through a short pad of silica gel using 100 ml of CH_2Cl_2 and the solvent was removed in vacuo to give the arenethiol in 50% to 80% yield.

Solution Electrochemical Characterization. Methylene chloride (HPLC grade) was distilled from calcium hydride under nitrogen. The tetrabutylammonium tetrakis(pentafluorophenyl)borate salt was prepared by the metathesis of an aqueous solution of $Li[B(C_6F_5)_4] \cdot 2.5Et_2O$ and a solution of [*n*-Bu_4N]Br in methanol. The white precipitate was isolated via suction filtration and washed with water, recrystallized from CH_2Cl_2/Et_2O twice, and then dried in a vacuum oven at room temperature for several days. A standard three-electrode

cell was utilized under ambient temperatures under an atmosphere of argon. A glassy carbon disk was used as the working electrode and the counter electrode was a Pt wire. The reference electrode was a silver wire but all potentials were recorded relative to the decamethylferrocene/decamethylferrocenium couple through the addition of this internal standard at the end of each electrochemical analysis. Electrochemical measurements were conducted using a Princeton Applied Research model 273A potentiostat. A program written using the LabVIEW™ 6i software package controlled the measurement procedure. All CV traces were taken at a scan rate of 0.1 V s^{-1}. Differential pulse voltammetry experiments utilized a pulse amplitude of 50 mV and step potential of 2 mV.