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Synthesis and Fluorescence Properties of "Manisyl" (4-Methoxy-2,6-dimethylphenyl) Substituted Terpyridine and Bipyridine and Phenanthroline

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Experimental

Materials and Methods

^{1}H- and ^{13}C NMR spectra were recorded on Varian (Mercury 300/400 MHz) spectrometers with tetramethylsilane (TMS) as an internal standard. High-resolution mass spectral analyses were performed by the University California Riverside mass spectrometry facility in DEI mode. UV-Vis spectra were recorded on a Perkin Elmer UV/VIS/NIR Spectrometer Lambda 19. Fluorescence spectra were recorded on a Perkin Elmer LS50B Luminescence Spectrometer. All experiments were carried out under argon in freshly distilled anhydrous solvents unless otherwise noted. Commercial chemicals were used as supplied. Column chromatography was performed using neutral 4-5% deactivated aluminum oxide (Brockmann II) and silica gel (230-425 mesh) from Fisher Scientific Co. Melting points are uncorrected and were recorded on a Mel-Temp Laboratory Device.

2-bromo-5-iodopyridine (1c)

To a solution of 2,5-dibromopyridine (10.0 g, 42.2 mmol) in diethyl ether (400 mL) was added *n*-BuLi (27.7 mL of 1.6 M, 44.3 mmol) via syringe at –78 °C over ten minutes. The orange-red lithiated intermediate was slowly quenched by addition of a room temperature solution of iodine (11.3 g, 44.3 mmol) in diethyl ether (200 mL) via cannula. The orange-red color dissipated upon addition of I_2 and the solution was warmed to room temperature. The mixture was stirred for an additional two hours, quenched with aqueous sodium bisulfite and basified with saturated aqueous sodium bicarbonate. The organic layer was removed and the aqueous layer was extracted two times with diethyl ether (100 mL). The combined organic layers were washed two times with brine (300 mL), dried over magnesium sulfate, filtered and evaporated to yield a light brown crystalline solid (10.9g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.57 (d, *J* = 2.0 Hz, 1H), 7.80 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H).

4-bromo-3,5-dimethylanisole (4-bromomanisole) (3)

To a solution of 3,5-dimethylanisole (100 g, 0.73 moles) in acetic acid (500 mL) at 0 °C was added a solution of bromine (117.3 g, 0.73 mol) in acetic acid (250 mL) drop wise, over 4 hours. After addition, the reaction mixture was stirred for an additional 45 minutes. This solution was warmed to room temperature, neutralized with saturated aqueous sodium carbonate and extracted with dichloromethane (500 mL). The organic layer was washed with water (200 mL), brine (200 mL), dried over magnesium sulfate, filtered and evaporated. The crude product was purified by three consecutive short path fractional distillations under reduced pressure to yield a clear colorless liquid (110 g, 70%). Spectral data matches that of the literature. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.63 (s, 2H), 3.74 (s, 3H), 2.36 (s, 6H).

2-bromo-6-manisylpyridine (4)

To a solution of 4-bromo-3,5-dimethylanisole (**3**) (5.00 g, 23.3 mmol) in THF (200 mL) at –78 °C was added *n*-BuLi (14.5 mL of 1.6 M, 23.3 mmol). To this mixture was added a 0 °C solution of zinc chloride (3.16 g, 23.3 mmol) in THF (50 mL) via cannula and allowed to warm to room temperature. Subsequently a solution of 2,6-dibromopyridine (**1b**) (4.96 g, 21.1 mmol) and palladium tetrakistriphenylphosphine (1.32 g, 1.1 mmol) was added to the organozinc intermediate via cannula. The reaction was heated at reflux for 15 hours then cooled to room temperature and added to dichloromethane (150 mL). The organic mixture was extracted vigorously with saturated aqueous EDTA and basified with saturated aqueous sodium bicarbonate. The organic layer was removed, washed with water (150 mL), dried over magnesium sulfate, filtered, and evaporated to yield yellow viscous oil. The crude golden solid was purified by column chromatography on silica gel with 7:3 dichloromethane/hexane as the eluent to yield a white crystalline solid (3.7 g, 61%). Mp 75-77 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.58 (t, *J* = 7.5 Hz, 1H), 7.42 (dd, *J* = 1.0, 7.5 Hz, 1H), 7.16 (dd, *J* = 1.0, 7.5 Hz, 1H), 6.62 (s, 2H), 3.78 (s, 3H), 2.03 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.71, 158.99, 141.51, 138.34, 137.25, 131.82, 125.81, 123.93, 112.85, 55.19, 20.67. HRMS $[M - H]^+$: found 290.0183; calcd ($C_{14}H_{13}NOBr$) 290.0181.

2-bromo-5-manisylpyridine (5)

To a solution of 4-bromo-3,5-dimethylanisole (**3**) (6.00 g, 27.9 mmol) in THF (200 mL) at –78 °C was added *n*-BuLi (17.4 mL of 1.6 M, 27.9 mmol) over ten minutes. To this mixture was added a 0 °C solution of zinc chloride (3.79 g, 27.9 mmol) in THF (50 mL) via cannula and allowed to warm to room temperature. Subsequently a solution of 2-bromo-5-iodopyridine (**1c**) (7.38 g, 26.5 mmol) and palladium tetrakistriphenylphosphine (1.62 g, 1.4 mmol) in THF (50 mL) was added to the organozinc intermediate via cannula. The reaction was heated at reflux for approximately 15 hours, cooled to room temperature, and added to dichloromethane (200 mL). The organic mixture was extracted vigorously with saturated aqueous EDTA (150 mL) and basified with saturated aqueous sodium bicarbonate. The organic layer was separated, washed with water (100 mL), dried over magnesium sulfate, filtered, and evaporated to yield dark yellow viscous oil. The crude oil was purified by column chromatography on silica gel with 3:2 dichloromethane/hexane as the eluent to yield a light yellow crystalline solid (6.54 g, 85%). Mp 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.18 (d, J = 2.0 Hz, 1H), 7.55 (d, J = 8.8 Hz, 1H), 7.36 (dd, J = 2.0, 8.8 Hz, 1H), 6.68 (s, 2H), 3.82 (s, 3H), 2.02 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.92, 150.81, 140.21, 139.83, 137.50, 135.60, 128.78, 127.69, 112.96, 55.22, 21.30.

4-manisylpyridine

To a solution of 4-bromomanisole (**3**) (8.27 g, 38.5 mmol) in THF (75 mL) at –78 °C was added *n*-BuLi (24.0 mL of 1.6 M, 38.5 mmol). To this mixture was added a 0 °C solution of zinc chloride (5.32 g, 38.5 mmol) in THF (25 mL) via cannula and allowed to warm to room temperature. Subsequently a solution of 4-bromopyridine hydrochloride (**1e**) (3.00 g, 15.4 mmol) and palladium tetrakistriphenylphosphine (0.89 g, 0.80 mmol) was added to the organozinc intermediate via cannula. The reaction was heated at reflux for 15 hours then cooled to room temperature and added to dichloromethane (300 mL). The organic mixture was extracted vigorously with saturated aqueous EDTA and basified with saturated aqueous sodium bicarbonate. The organic layer was removed, washed with water (300 mL), dried over magnesium sulfate, filtered, and evaporated to yield an oily solid. The crude solid was purified by column chromatography on aluminum oxide with 7:3 dichloromethane/hexanes as the eluent to yield a colorless crystalline solid (3.20 g, 98%). Mp = 98-101 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.65 (d, *J* = 6.0 Hz, 2H), 7.09 (d, *J* = 6.0 Hz, 2H), 6.67 (s, 2H), 3.82 (s, 3H), 2.01 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.67, 149.78, 149.16, 136.55, 131.54, 125.00, 112.80, 55.17, 21.01. HRMS *m/z*: found 213.1153; calcd ($C_{14}H_{15}NO$) 213.1154.

2-amino-4-manisylpyridine

To a solution of freshly prepared sodium amide (.686 g, 17.6 mmol) in N,N-dimethylaniline (6 mL) was added 4-manisylpyridine (1.5 g, 7.04 mmol) and heated to 160 °C for 12 hours. Upon cooling, the reaction mixture was poured into water (25 mL) and extracted twice with dichloromethane (75 mL). Combined organic layers were dried over magnesium sulfate, filtered, solvent removed. The oily crude was purified by column chromatography on aluminum oxide with 6:4 dichloromethane/hexanes followed by 100% dichloromethane, then 100% chloroform as the eluent to yield a tan crystalline solid (0.95 g, 60%). Mp = 147-148 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.10 (d, *J* = 5.5 Hz, 1H), 6.65 (s, 2H), 6.46 (dd, *J* = 1.5, 5.5 Hz, 1H), 6.30 (d, *J* = 1.5 Hz, 1H), 4.53 (bs, 2H), 3.81 (s, 3H), 2.04 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.48, 158.40, 150.99, 148.01, 136.52, 132.18, 115.74, 112.58, 109.40, 55.13, 20.85. HRMS *m/z*: found 228.1253; calcd ($C_{14}H_{16}N_2O$) 228.1263.

2-iodo-4-manisylpyridine (6)

To a solution of 2-amino-4manisylpyridine (0.400 g, 1.75 mmol) and iodine (0.445g, 1.75 mmol) in benzene (25 mL), was slowly added isoamyl nitrite (0.260 mL, 1.93 mmol) via syringe. Contents were heated to reflux for 12 hours. Upon cooling, the reaction is quenched with aqueous sodium bisulfite and extracted twice with dichloromethane. Combined organic layers were dried, filtered, and reduced to dryness. Crude product was purified by column chromatography on silica gel with 8:2 dichloromethane/hexanes as the eluent to yield a white crystalline solid (0.275 g, 46%). Mp = 101-103 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.40 (d, *J* = 6.0 Hz, 1H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.07 (dd, *J* = 2.0, 6.0 Hz, 1H), 6.66 (s, 2H), 3.82 (s, 3H), 2.02 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.97, 151.24, 150.45, 136.47, 135.86, 129.88, 124.58, 118.43, 112.93, 55.21, 21.05. HRMS *m/z*: found 339.0119; calcd ($C_{14}H_{14}NOI$) 339.0120.

3-manisylpyridine (7)

To a solution of 4-bromomanisole (**3**) (1.00 g, 4.65 mmol) in THF (25 mL) at –78 °C was added *n*-BuLi (2.9 mL of 1.6 M, 4.65 mmol). To this mixture was added a 0 °C solution of zinc chloride (0.635 g, 4.65 mmol) in THF (10 mL) via cannula and allowed to warm to room temperature. Subsequently a solution of 3-bromopyridine (**1a**) (0.725 g, 4.65 mmol) and palladium tetrakistriphenylphosphine (0.270 g, 0.23 mmol) was added to the organozinc intermediate via cannula. The reaction was heated at reflux for 15 hours then cooled to room temperature and added to dichloromethane (100 mL). The organic mixture was extracted vigorously with saturated aqueous EDTA and basified with saturated aqueous sodium bicarbonate. The organic layer was removed, washed with water (100 mL), dried over magnesium sulfate, filtered, and evaporated to yield viscous oil. The crude oil was purified by column chromatography on aluminum oxide with 100% dichloromethane as the eluent to yield a colorless crystalline solid (0.744 g, 75%). Mp 53-55 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.57 (dd, *J* = 2.0, 5.0 Hz, 1H), 8.40 (dd, *J* = 0.5, 2.0 Hz, 1H), 7.47 (dt, *J* = 2.0, 8.0 Hz, 1H), 7.33 (ddd, *J* = 0.5, 5.0, 8.0 Hz, 1H), 6.67, (s, 2H), 3.81 (s, 3H), 2.00 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.63, 150.44, 147.80, 137.58, 137.10, 136.28, 130.29, 123.16, 112.76, 55.18, 21.30. Uv-Vis (CH_3CN) λ_{max}, nm (ε): 247 (sh $7.0x10^3$), 285 (sh $3.3x10^3$). HRMS *m/z*: found 213.1150; calcd ($C_{14}H_{15}NO$) 213.1154.

3,8-dimanisyl-1,10-phenanthroline (8)

To a solution of 4-bromo-3,5-dimethylanisole (**3**) (0.192 g, 0.893 mmol) in THF (15 mL) at –78 °C was added *n*-BuLi (0.57 mL of 1.6 M, 0.913 mmol). To this mixture was added a 0 °C solution of zinc chloride (0.124 g, 0.913 mmol) in THF (5 mL) via cannula and allowed to warm to room temperature. Subsequently this solution was added, via cannula, to a solution of 3,8-dibromo-1,10-phenanthroline (**2c**) (0.150 g, 0.446 mmol) and palladium tetrakistriphenylphosphine (0.026 g, 0.022 mmol) in THF (5 mL). The reaction was heated at reflux for 15 hours then cooled to room temperature and added to dichloromethane (50 mL). The organic mixture was extracted vigorously with saturated aqueous EDTA and basified with saturated aqueous sodium bicarbonate. The organic layer was removed, washed with water (50 mL), dried over magnesium sulfate, filtered, and evaporated to yield a golden solid. The crude golden solid was purified by column chromatography on aluminum oxide with dichloromethane as the eluent to yield a white crystalline solid (0.140 g, 70%). Mp 248-249 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.00 (d, *J* = 2.2 Hz, 2H), 8.06 (d, *J* = 2.2 Hz, 2H), 7.83 (s, 2H), 6.74 (s, 4H), 3.84 (s, 6H), 2.06 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.88, 151.78, 144.61, 137.83, 136.16, 135.78, 130.04, 128.18, 126.61, 112.95, 55.27, 21.46. Uv-Vis (CH_3CN) λ_{max}, nm (ε): 237 ($8.0x10^4$), 270 ($5.3x10^4$). HRMS *m/z*: found 448.2156; calcd ($C_{30}H_{28}N_2O_2$) 448.2151.

2,9-dimanisyl-1,10-phenanthroline (9)

To a solution of 4-bromo-3,5-dimethylanisole (**3**) (0.299 g, 1.39 mmol) in THF (15 mL) at –78 °C was added *n*-BuLi (0.87 mL of 1.6 M, 1.39 mmol). To this mixture was added a 0 °C solution of zinc chloride (0.189 g, 1.39 mmol) in THF (5 mL) via cannula and allowed to warm to room temperature. Subsequently this solution was added, via cannula, to a solution of 2,9-diiodo-1,10-phenanthroline (**2a**) (0.200 g, 0.463 mmol) and palladium tetrakistriphenylphosphine (0.027 g, 0.023 mmol) in THF (5 mL). The reaction was heated at reflux for 15 hours then cooled to room temperature and added to dichloromethane (50 mL). The organic mixture was extracted vigorously with saturated aqueous EDTA and basified with saturated aqueous sodium bicarbonate. The organic layer was removed, washed with water (50 mL), dried over magnesium sulfate, filtered, and evaporated to yield a golden solid. The crude solid was purified by column chromatography on aluminum oxide with 60:40 – 80:20 dichloromethane/hexane as the eluent to yield a white solid (0.143g, 69%). Mp 234-235 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.26 (d, *J* = 8.0 Hz, 2H), 7.83 (s, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 6.64 (s, 4H), 3.79 (s, 6H), 2.15 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.64, 158.78, 145.94, 137.83, 135.60, 133.69, 126.94, 126.03, 125.19, 113.00, 55.18, 21.11. Uv-Vis (CH_3CN) λ_{max}, nm (ε): 234 ($6.9x10^4$), 266 ($2.9x10^4$). HRMS $[M – H]^+$: found 447.2065; calcd ($C_{30}H_{27}N_2O_2$) 447.2073.

4,7-dimanisyl-1,10-phenanthroline (10)

To a solution of 4-bromo-3,5-dimethylanisole (**3**) (0.223 g, 1.04 mmol) in THF (15 mL) at –78 °C was added *n*-BuLi (0.65 mL of 1.6 M, 1.04 mmol). To this mixture was added a 0 °C solution of zinc chloride (0.141 g, 1.04 mmol) in THF (5 mL) via cannula and allowed to warm to room temperature. Subsequently this solution was added, via cannula, to a solution of 4,7-dibromo-1,10-phenanthroline (**2d**) (0.116 g, 0.345 mmol) and palladium tetrakistriphenylphosphine (0.040 g, 0.035 mmol) in THF (5 mL). The reaction was heated at reflux for 15 hours then cooled to room temperature and added to dichloromethane (75 mL). The organic mixture was extracted vigorously with saturated aqueous EDTA and basified with saturated aqueous sodium bicarbonate. The organic layer was removed, washed with water (75 mL), dried over magnesium sulfate, filtered, and evaporated to yield a crude oily solid. The crude solid was purified by column chromatography on aluminum oxide with 100% dichloromethane as the eluent to yield pink crystalline solid (0.021 g, 14%). Mp = decomposes 255 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.26 (d, *J* = 4.5 Hz, 2H), 7.45 (d, *J* = 4.5 Hz, 2H), 7.27 (s, 2H), 6.73 (s, 4H), 3.85 (s, 6H), 1.89 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.03, 150.04, 147.80, 146.72, 137.34, 129.22, 127.72, 124.20, 123.78, 112.82, 55.25, 20.83. Uv-Vis (CH_3CN) λ_{max}, nm (ε): 200 ($1.3x10^5$), 235 ($6.9x10^4$), 267 ($5.5x10^4$). HRMS *m/z*: found 448.2160; calcd ($C_{30}H_{28}N_2O_2$) 448.2151.

2,8-dimanisyl-1,10-phenanthroline (11)

To a solution of 4-bromo-3,5-dimethylanisole (**3**) (0.586 g, 2.73 mmol) in THF (20 mL) at –78 °C was added *n*-BuLi (1.70 mL of 1.6 M, 2.73 mmol). To this mixture was added a 0 °C solution of zinc chloride (0.370 g, 2.73 mmol) in THF (5 mL) via cannula and allowed to warm to room temperature. Subsequently this solution was added, via cannula, to a solution of 3-bromo-9-iodo-1,10-phenanthroline (**2b**) (0.350 g, 0.909 mmol) and palladium tetrakistriphenylphosphine (0.053 g, 0.045 mmol) in THF (5 mL). The reaction was heated at reflux for 15 hours then cooled to room temperature and added to dichloromethane (75 mL). The organic mixture was extracted vigorously with saturated aqueous EDTA and basified with saturated aqueous sodium bicarbonate. The organic layer was removed, washed with water (75 mL), dried over magnesium sulfate, filtered, and evaporated to yield a crude solid. The crude solid was purified by column chromatography on aluminum oxide with 1:1 – 100:0 dichloromethane/hexane as the eluent to yield a pale yellow solid (0.274 g, 67%). Mp 244-245 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.99 (d, *J* = 2.0 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 2.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 6.73 (s, 2H), 6.99 (s, 2H), 3.83 (s, 3H), 3.82 (s, 3H), 2.10 (s, 6H), 2.06 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.41, 158.79, 158.76, 151.70, 146.03, 144.70, 137.85, 137.51, 136.16, 135.88, 135.54, 134.06, 130.11, 128.44, 126.78, 126.49, 126.12, 124.89, 112.91, 112.69, 55.24, 21.51, 21.02. Uv-Vis (CH_3CN) λ_{max}, nm (ε): 236 (1.1×10^5), 269 (5.5×10^4). HRMS *m/z*: found 448.2155; calcd ($C_{30}H_{28}N_2O_2$) 448.2151.

6’6’’-dimanisyl-2,2’:6’,2’’-terpyridine (12)

To a solution of 2-bromo-6-manisylpyridine (**4**) (1.00 g, 3.42 mmol) in THF (30 mL) at –78 °C was added *n*-BuLi (2.25 mL of 1.6 M, 3.59 mmol). To this mixture was added a 0 °C solution of zinc chloride (0.488 g, 3.59 mmol) in THF (10 mL) via cannula and allowed to warmed to room temperature. Subsequently a solution of 2,6-dibromopyridine (**1b**) (0.404 g, 3.59 mmol) and palladium tetrakistriphenylphosphine (0.198 g, 0.171 mmol) in THF (10 mL) was added to the organozinc intermediate via cannula. The mixture was heated at reflux for 20 hours, cooled to room temperature, and placed in freezer. The white precipitate was filtered, washed with cold THF and dried. The precipitate was dissolved in dichloromethane and extracted vigorously for several hours with saturated aqueous EDTA, and basified with saturated aqueous sodium bicarbonate. The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated to afford a white crystalline solid (0.415 g, 48%). Mp 215-216 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.57 (dd, *J* = 1.2, 8.0 Hz, 2H), 8.43 (d, *J* = 8.0 Hz, 2H), 7.90 (t, *J* = 8.0 Hz, 2H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.24 (dd, *J* = 1.2, 8.0 Hz, 2H), 6.69 (s, 4H), 3.82 (s, 6H), 2.12 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.75, 158.67, 155.91, 155.31, 137.54, 137.43, 136.76, 133.49, 124.99, 121.27, 118.72, 112.95, 55.25, 20.95. Uv-Vis (CH_3CN) λ_{max}, nm (ε): 282 (3.6×10^4). HRMS $[M - H]^+$: found 500.2336; calcd ($C_{33}H_{30}N_3O_2$) 500.2338.

5',5''-dimanisyl-2,2':6',2''-terpyridine (13)

To a solution of 2-bromo-5-manisylpyridine (**5**) (3.85 g, 13.2 mmol) in THF (200 mL) at –78 °C was added *n*-BuLi (8.6 mL of 1.6 M, 13.8 mmol). To this mixture was added a 0 °C solution of zinc chloride (1.88 g, 13.8 mmol) in THF (50 mL) via cannula and allowed to warm to room temperature. Subsequently a solution of 2,6-dibromopyridine (**1b**) (1.56 g, 6.6 mmol) and palladium tetrakistriphenylphosphine (0.76 g, 0.66 mmol) in THF (50 mL) was added to the organozinc intermediate via cannula. The mixture was heated at reflux for 20 hours, cooled to room temperature, and placed in freezer. The white precipitate was filtered, washed with cold THF and dried. The white precipitate was dissolved in dichloromethane and extracted vigorously with saturated aqueous EDTA, and basified with sodium bicarbonate. The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated to afford a white crystalline solid (2.05 g, 62%). Mp 224-225 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.72 (d, *J* = 8.0 Hz, 2H), 8.52 (d, *J* = 2.0 Hz, 2H), 8.51 (d, *J* = 8.0 Hz, 2H), 8.01 (t, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 2.0, 8.0

Hz, 2H), 6.73 (s, 4H), 3.85 (s, 6H), 2.09 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.72, 155.12, 154.35, 149.79, 138.16, 137.86, 137.72, 136.52, 130.23, 120.72, 120.70, 112.87, 55.23, 21.38. Uv-Vis (CH_3CN) λ_{max}, nm (ε): 234 ($4.6x10^4$), 286 ($4.0x10^4$). HRMS *m/z*: found 501.2418; calcd ($C_{33}H_{31}N_3O_2$) 501.2416.

4,4’’-dimanisyl-2,2’:6’,2’’-terpyridine (14)

To a solution of 2-iodo-4manisylpyridine (**6**) (0.500 g, 1.47 mmol) in THF (15 mL) at –78 °C was added *n*-BuLi (0.97 mL of 1.6 M, 1.55 mmol). To this mixture was added a 0 °C solution of zinc chloride (0.221 g, 1.62 mmol) in THF (7 mL) via cannula. Subsequently a solution of 2,6-dibromopyridine (**1b**) (0.174 g, 0.738 mmol) and palladium tetrakistriphenylphosphine (0.085 g, 0.074 mmol) was added to the organozinc intermediate via cannula. The reaction was heated at reflux for 15 hours then cooled to room temperature and added to dichloromethane (75 mL). The organic mixture was extracted vigorously with saturated aqueous EDTA and basified with saturated aqueous sodium bicarbonate. The organic layer was removed, washed with water (100 mL), dried over magnesium sulfate, filtered, and evaporated to yield an oily solid. The crude solid was purified by column chromatography on aluminum oxide with 3:2 dichloromethane/hexanes as the eluent to yield a bright yellow solid that was dissolved in a minimal amount of THF with zinc chloride (2 equiv.) and was heated to reflux for twenty minutes. Upon cooling the flask was placed in freezer to induce precipitation. The white precipitate was filtered washed with cold THF and dried. The precipitate was dissolved in dichloromethane and extracted vigorously with saturated aqueous EDTA, and basified with saturated aqueous sodium bicarbonate. The organic layer was separated and evaporated to dryness to afford a white solid (0.040 g, 11%). Mp = 259-261 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.73 (d, *J* = 5.0 Hz, 2H), 8.56 (d, *J* = 8.1 Hz, 2H), 8.34 (d, *J* = 1.5 Hz, 2H), 8.00 (t, 8.1 Hz, 1H), 7.12 (dd, *J* = 1.5, 5.0 Hz, 2H), 6.69 (s, 4H), 3.83 (s, 6H), 2.05 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.70, 156.22, 155.49, 150.12, 149.08, 137.70, 136.83, 131.99, 125.21, 122.00, 121.36, 112.86, 55.19, 21.20. Uv-Vis (CH_3CN) λ_{max}, nm (ε): 200 ($1.1x10^5$), 250 ($2.5x10^4$), 279 ($1.9x10^4$), 303 (sh $1.4x10^4$), 318 (sh $5.7x10^3$). HRMS $[M – H]^+$: found 500.2357; calcd ($C_{33}H_{30}N_3O_2$) 500.2338.

6,6’-dimanisyl-2,2’-bipyridine (15)

To a solution of 2-bromo-6-manisylpyridine (**4**) (0.150 g, 0.514 mmol) in THF (15 mL) at –78 °C was added *n*-BuLi (0.34 mL of 1.6 M, 0.539 mmol). To this mixture was added a 0 °C solution of zinc chloride (0.073 g, 0.539 mmol) in THF (5 mL) via cannula and allowed to warm to room temperature. Subsequently a solution of 2-bromo-6-manisylpyridine (**4**) (0.150 g, 0.514 mmol) and palladium tetrakistriphenylphosphine (0.029 g, 0.03 mmol) was added to the organozinc intermediate via cannula. The reaction was heated at reflux for 15 hours then cooled to room temperature and added to dichloromethane (75 mL). The organic mixture was extracted vigorously with saturated aqueous EDTA and basified with saturated aqueous sodium bicarbonate. The organic layer was removed, washed with water (75 mL), dried over magnesium sulfate, filtered, and evaporated to yield crude solid. The crude solid was purified by column chromatography on aluminum oxide with 7:3 hexane/dichloromethane as the eluent to yield white solid (0.125 g, 59%). Mp 231-235 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.34 (dd, *J* = 1.0, 7.8 Hz, 2H), 7.88 (t, *J* = 7.8 Hz, 2H), 7.19 (dd, *J* = 1.0, 7.8 Hz, 2H), 6.69 (s, 4H), 3.82 (s, 6H), 2.12 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.63, 158.62, 156.00, 137.43, 136.74, 133.55, 124.89, 119.08, 112.90, 55.24, 20.96. Uv-Vis (CH_3CN) λ_{max}, nm (ε): 245 (sh 2.3×10^4), 282 (2.2×10^4). HRMS $[M - H]^+$: found 423.2068; calcd ($C_{28}H_{27}N_2O_2$) 423.2073.

5,6’-dimanisyl-2,2’-bipyridine (16)

To a solution of 2-bromo-5-manisylpyridine (**5**) (0.100 g, 0.340 mmol) in THF (15 mL) at –78 °C was added *n*-BuLi (0.23 mL of 1.6 M, 0.36 mmol). To this mixture was added a 0 °C solution of zinc chloride (0.047 g, 0.36 mmol) in THF (5 mL) via cannula and allowed to warm to room temperature. Subsequently a solution of 2-bromo-6-manisylpyridine (**4**) (0.100 g, 0.340 mmol) and palladium tetrakistriphenylphosphine (0.020 g, 0.02 mmol) was added to the organozinc intermediate via cannula. The reaction was heated at reflux for 15 hours cooled to room temperature, and placed in freezer. The white precipitate was filtered, washed with cold THF and dried. The precipitate was dissolved in dichloromethane and extracted vigorously with saturated aqueous EDTA, and basified with saturates aqueous sodium bicarbonate. The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated to afford a white solid (0.45 g, 31%). Mp 164-166 °C. ^1H NMR (300 MHz, $CDCl_3$, δ): 8.48 (d, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 2.0 Hz, 1H), 8.37 (dd, *J* = 1.0, 7.5 Hz, 1H), 7.88 (t, *J* = 7.5 Hz, 1H), 7.56 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.23 (dd, *J* = 1.0, 7.5 Hz, 1H), 6.69 (s, 4H), 3.82 (s, 3H), 3.81 (s, 3H), 2.12 (s, 6H), 2.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.86, 158.67, 155.66, 154.60, 149.68, 138.16, 137.72, 137.39, 136.90, 136.35, 133.49, 130.29, 124.96, 121.09, 118.53, 112.91, 112.84, 55.24, 21.38, 20.93. Uv-Vis (CH_3CN) λ_{max}, nm (ε): 238 (2.5×10^4), 290 (2.6×10^4). HRMS $[M - H]^+$: found 423.2074; calcd ($C_{28}H_{27}N_2O_2$) 423.2073.

5,5’-dimanisyl-2,2’-bipyridine (17)

To a solution of 2-bromo-5-manisylpyridine (**5**) (0.300 g, 1.03 mmol) in THF (15 mL) at –78 °C was added *n*-BuLi (0.67 mL of 1.6 M, 1.08 mmol). To this mixture was added a 0 °C solution of zinc chloride (0.147 g, 1.08 mmol) in THF (5 mL) via cannula and allowed to warm to room temperature. Subsequently a solution of 2-bromo-5-manisylpyridine (**5**) (0.300 g, 1.03 mmol) and palladium tetrakistriphenylphosphine (0.059 g, 0.05 mmol) was added to the organozinc intermediate via cannula. The reaction was heated at reflux for 15 hours then cooled to room temperature and added to dichloromethane (75 mL). The organic mixture was extracted vigorously with saturated aqueous EDTA and basified with saturated aqueous sodium bicarbonate. The organic layer was removed, washed with water (75 mL), dried over magnesium sulfate, filtered, and evaporated to yield crude solid. The crude solid was purified by column chromatography on aluminum oxide with 7:3 – 4:6 hexane/dichloromethane as the eluent to yield a pale yellow solid (0.259 g, 59%). Mp 257-258 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.49 (d, *J* = 2.5 Hz, 2H), 8.48 (d, *J* = 7.8 Hz, 2H), 7.64 (dd, *J* = 2.5, 7.8 Hz, 2H), 6.70 (s, 4H), 3.82 (s, 6H), 2.06 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.70, 154.21, 149.93, 138.26, 137.70, 136.41, 130.20, 120.52, 112.86, 55.23, 21.36. Uv-Vis (CH_3CN) λ_{max}, nm (ε): 243 (2.2×10^4), 296 (3.0×10^4). HRMS *m/z*: found 424.2144; calcd ($C_{28}H_{28}N_2O_2$) 424.2151.

5-manisyl-2,2’-bipyridine (18)

To a solution of 2-bromo-5-manisylpyridine (**5**) (0.300 g, 1.03 mmol) in THF (15 mL) at –78 °C was added *n*-BuLi (0.67 mL of 1.6 M, 1.08 mmol). To this mixture was added a 0 °C solution of zinc chloride (0.147 g, 1.08 mmol) in THF (5 mL) via cannula and allowed to warm to room temperature. Subsequently a solution of 2-bromopyridine (**1d**) (0.160 g, 1.03 mmol) and palladium tetrakistriphenylphosphine (0.059 g, 0.05 mmol) was added to the organozinc intermediate via cannula. The reaction was heated at reflux for 15 hours cooled to room temperature, and placed in freezer. The white precipitate was filtered, washed with cold THF and dried. The precipitate was dissolved in dichloromethane and extracted vigorously with saturated aqueous EDTA, and basified with saturated aqueous sodium bicarbonate. The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated to afford a white solid (0.175 g, 59%). Mp 94-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.69 (d, J = 4.0 Hz, 1H), 8.45 (d, J = 17.0 Hz, 1H), 8.44 (d, J = 17.0 Hz, 1H), 8.43 (d, J = 19.0 Hz, 1H), 7.83 (m, 1H), 7.62 (dd, J = 2.5, 8.0 Hz, 1H), 7.31 (m, 1H), 6.69 (s, 2H), 3.82 (s, 3H), 2.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.69, 155.87, 154.26, 149.83, 149.06, 138.22, 137.70, 136.80, 136.45, 130.16, 123.54, 120.82, 120.62, 112.84, 55.22, 21.36. Uv-Vis (CH_3CN) λ_{max}, nm (ε): 238 ($1.9x10^4$), 286 ($2.3X10^4$). HRMS *m/z*: found 290.1410; calcd ($C_{19}H_{18}N_2O$) 290.1419.

4,4’-manisyl-2,2’-bipyridine (19)

To a solution of 2-iodo-4-manisylpyridine (**6**) (0.050 g, 0.15 mmol) in THF (10 mL) at –78 °C was added *n*-BuLi (0.10 mL of 1.6 M, 0.15 mmol). To this mixture was added a 0 °C solution of zinc chloride (0.021 g, 0.15 mmol) in THF (5 mL) via cannula and allowed to warm to room temperature. Subsequently a solution of 2-iodo-4-manisylpyridine (**6**) (0.045 g, 0.13 mmol) and palladium tetrakistriphenylphosphine (0.009 g, 7.5 μmol) was added to the organozinc intermediate via cannula. The reaction was heated at reflux for 15 hours cooled to room temperature, and placed in freezer. The white precipitate was filtered, washed with cold THF and dried. The precipitate was dissolved in dichloromethane and extracted vigorously with saturated aqueous EDTA, and basified with saturated aqueous sodium bicarbonate. The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated to afford a white solid (0.012 g, 21%). Mp = 272-274 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.70 (d, *J* = 5.0 Hz, 1H), 8.30 (d, *J* = 1.5 Hz, 1H), 7.13 (dd, *J* = 1.5, 5.0 Hz, 1H), 6.69 (s, 2H), 3.83 (s, 6H), 2.07 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.64, 156.15, 150.30, 149.27, 136.63, 131.86, 125.09, 122.41, 112.76, 55.20, 21.17. Uv-Vis (CH_3CN) λ_{max}, nm (ε): 203 (1.39.2x10^4), 248 (1.9x10^4), 282 (1.8x10^4). HRMS $[M – H]^+$: found 423.2060; calcd ($C_{28}H_{27}N_2O_2$) 423.2073.

2-(5-manisyl-2-pyridyl)-8-bromo-1,10-penanthroline (20)

To a solution of 2-bromo-5-manisylpyridine (**5**) (0.398 g, 1.36 mmol) in THF (20 mL) at –78 °C was added *n*-BuLi (0.89 mL of 1.6 M, 1.43 mmol). To this mixture was added a 0 °C solution of zinc chloride (0.195 g, 1.43 mmol) in THF (5 mL) via cannula and allowed to warm to room temperature while stirring. Subsequently a solution of 3-bromo-9-iodo-1,10-phenanthroline (**2b**) (0.500 g, 1.30 mmol) and palladium tetrakistriphenylphosphine (0.075 g, 0.065 mmol) in THF (5 mL) was added to the organozinc intermediate via cannula. The mixture was heated at reflux for 20 hours, cooled to room temperature, and placed in freezer. The precipitate was filtered, washed with cold THF and dried. The precipitate was dissolved in dichloromethane and extracted vigorously with saturated aqueous EDTA, and basified with saturated aqueous sodium bicarbonate. The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated to afford a white crystalline solid (468 mg, 77%). Mp 112-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.20 (d, *J* = 2.5 Hz, 1H), 8.95 (d, *J* = 8.0 Hz, 1H), 8.81 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 2.0 Hz, 1H), 8.39 (d, *J* = 2.5 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.72 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 6.70 (s, 2H), 3.82 (s, 3H), 2.06

(s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 158.72, 156.50, 154.21, 151.01, 149.75, 145.32, 144.36, 138.48, 137.69, 137.41, 137.07, 136.94, 130.18, 129.91, 128.50, 127.84, 125.44, 122.41, 121.02, 119.63, 112.86, 55.23, 21.37. HRMS *m/z*: found 471.0750; calcd ($C_{26}H_{20}N_3OBr$) 471.0769.

2-(5-manisyl-2-pyridyl)-8-manisyl-1,10-penanthroline (21)

To a solution of 4-bromomanisole (**3**) (0.206 g, 0.957 mmol) in THF (20 mL) at –78 °C was added *n*-BuLi (0.60 mL of 1.6 M, 0.957 mmol). To this mixture was added a 0 °C solution of zinc chloride (0.130 g, 0.957 mmol) in THF (5 mL) via cannula and allowed to warm to room temperature. Subsequently a solution of 2-(5-manisyl-2-pyridyl)-8-bromo-1,10-penanthroline (**20**) (0.300 g, 0.638 mmol) and palladium tetrakistriphenylphosphine (0.055 g, 0.048 mmol) in THF (5 mL) was added to the organozinc intermediate via cannula. The mixture was heated at reflux for 20 hours, cooled to room temperature, and placed in freezer. The white precipitate was filtered, washed with cold THF and dried. The precipitate was dissolved in dichloromethane and extracted vigorously with saturated aqueous EDTA, and basified with saturated aqueous sodium bicarbonate. The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated to afford a white crystalline solid (270 mg, 81%). Mp 130-134 °C. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 9.05 (d, *J* = 2.0 Hz, 1H), 9.04 (d, *J* = 8.0 Hz, 1H), 8.83 (d, *J* = 8.5 Hz, 1H), 8.53 (d, *J* = 2.0 Hz, 1H), 8.41 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 2.0 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.72 (dd, *J* = 2.0, 8.0 Hz, 1H), 6.74 (s, 2H), 6.70 (s, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 2.07 (s, 6H), 2.05 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 158.85, 158.67, 156.12, 145.37, 151.80, 149.63, 145.51, 144.67, 138.38, 137.83, 137.67, 136.89, 136.41, 135.84, 130.23, 130.01, 128.66, 128.49, 126.62, 122.41, 120.56, 112.88, 112.82, 55.23, 55.20, 21.43, 21.34. Uv-Vis (CH_3CN) λ_{max}, nm (ε): 240 ($6.3x10^4$), 296 ($4.3x10^4$), 354 ($8.7x10^3$). HRMS *m/z*: found 525.2407; calcd ($C_{35}H_{31}N_3O_2$) 525.2416.

Fluorescence quantum yields (Φ_f)

Fluorescence quantum yields were determined with optically thin solutions (OD = 0.05) at room temperature using the method of comparison described by Demas, and Crosby. Argon purged, and isoabsorptive solutions of standard (9,10-diphenylanthracene) and samples **7-19, 21** were excited at wavelengths of maximum absorption for each sample. Quantum yields (Φ_f) were calculated using equation (1) where f_{unk} is the fluorescence quantum yield of the unknown, f_{std} is the fluorescence quantum yield of the standard (0.91 in ethanol), A_{unk} and A_{std} are the absorbance values of the unknown and the standard at the excitation wavelength (λ_{ex}) respectively, I_{unk} and I_{std} are the integrated values for fluorescence emissions of the unknown and standard respectively, and h_{unk} and h_{std} are the refractive indexes of the corresponding solvents, acetonitrile and ethanol respectively.

$$f_{unk} = f_{std}\left(\frac{I_{unk}}{A_{unk}}\right)\left(\frac{A_{std}}{I_{std}}\right)\left(\frac{h_{unk}}{h_{std}}\right)^2 \qquad \text{equation (1)}$$

Fluorescence emissions spectra were converted from nm to cm^{-1} prior to integration. Repetitive measurements suggest a 5% precision for the values determined via this method.