Supporting Information

Regioselective [2+2+2] Cycloaddition of a Nickel-Benzyne Complex with 1,3-Diynes

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Experimental Section

General. Unless otherwise specified, all starting materials were obtained from commercially available sources and used without further purification. All air- or moisture-sensitive reactions were performed under an atmosphere of dry argon utilizing standard Schlenk line techniques. Toluene was distilled from sodium metal while acetonitrile, methylene chloride, and triethylamine were distilled from calcium hydride. Methanol was distilled from magnesium powder. Nickel-benzyne **1b** was prepared by reduction of the 2-bromoaryl-nickel(II) bromide salt using sodium amalgam according to literature procedures¹ and recrystallized prior to use. Analytical thin layer chromatography was performed using EM Science F₂₅₄ precoated silica gel 60 plates. Eluting solvents are reported as percentages according to volume. Visualization was accomplished with UV-light, ceric ammonium molybdate (CAM) or potassium permanganate. Flash column chromatography was carried out with silica gel 60 (230-400 mesh). Melting points were obtained on a 115V 50/60 Hz Fisher-Johns melting point apparatus from Fisher-Scientific.

All ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on Varian Unity 400 or 500 MHz spectrometers using CDCl₃. Chemical shifts are expressed in ppm (δ) using residual solvent as internal standard. In the case of ¹⁹F NMR spectra, a solution of 1% CF₃C₆D₅ in chloroform was used as the standard. Coupling constants (*J*) are reported in Hertz (Hz), and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), or m (multiplet). High resolution and low resolution Electron Ionization (EI) mass spectra were obtained with Micromass 70 VSE spectrometer. Low resolution Field Ionization (FI) mass spectra were performed on the Micromass 70 VSE spectrometer. High and low resolution Electron Spray

¹ (a) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, 4, 1992-2000.
(b) Bennett, M. A.; Wenger, E. *Organometallics* **1995**, 14, 1267-1277.

Ionization (ESI) mass spectra were performed on a Micromass Quattro I spectrometer. Infrared Spectroscopy was obtained using a Perkin Elmer spectrophotometer referenced to a polystyrene standard. Samples were prepared as thin films on a NaCl salt plate by evaporation of chloroform or dichloromethane solutions. Peaks are reported in wavenumbers (cm^{-1}) as strong (s), medium (m), weak (w), and broad (br).

The UV absorption spectra were recorded using 1 cm quartz cells on a Hewlett Packard UV spectrophotometer. The data is presented graphically with molar absorptivity, ϵ , in $\text{M}^{-1}\text{cm}^{-1}$ plotted versus the wavelength in nm. Fluorescence emission spectra were recorded on a Photon Technology International (PTI) QM-1 fluorimeter, and were corrected for the wavelength dependence of detector sensitivity and excitation light source output. All UV and fluorescence spectra were recorded using a 1 cm quartz cuvette in the right angle geometry at room temperature.

Reaction of nickel benzyne **1a with diyne **2a**.** To a solution of **1a**^{1a} (22 mg, 39 μmol , 1 equiv) in 1.0 mL of degassed cyclohexane was added 3,5-octadiyne **2a** (6.2 μL , 47 μmol , 1.2 equiv). The reaction mixture was stirred at 23 $^{\circ}\text{C}$ for 20 min, then at 75 $^{\circ}\text{C}$ for 2 h. The solvent was removed in vacuo, and the residue purified by silica gel flash column chromatography (cyclohexane) to give 6.7 mg of a 3:7 mixture of naphthalene **3a** and benzene **5**: TLC R_f = 0.23 (cyclohexane).

Data for **3a**: ^1H NMR (500 MHz, CDCl_3) δ 8.03-8.01 (m, 2H, H_{aryl}), 7.49-7.47 (m, 2H, H_{aryl}), 3.29 (q, J = 7.5 Hz, 4H, ArCH_2), 2.58 (q, J = 7.5 Hz, 4H, $\text{ArC}\equiv\text{CCH}_2$), 1.33 (t, J = 7.5 Hz, 6H, CH_3), 1.28 (t, J = 7.6 Hz, 6H, CH_3); LRMS (FI): 288.3.

Data for **5**: ^1H NMR (500 MHz, CDCl_3) δ 2.96 (q, J = 7.6 Hz, 2H, ArCH_2), 2.82 (q, J = 7.5 Hz, 2H, ArCH_2), 2.80 (q, J = 7.5 Hz, 2H, ArCH_2), 2.52 (q, J = 7.3 Hz, 2H, $\text{ArC}\equiv\text{CCH}_2$), 2.51 (q, J = 7.4 Hz, 2H, $\text{ArC}\equiv\text{CCH}_2$), 2.48 (q, J = 7.4 Hz, 2H, $\text{ArC}\equiv\text{CCH}_2$), 1.281 (t, J = 7.5 Hz, 3H, CH_3), 1.276 (t, J = 7.5 Hz, 3H, CH_3), 1.26 (t, J = 7.6 Hz, 3H, CH_3), 1.18 (t, J = 7.4 Hz, 3H, CH_3), 1.153 (t, J = 7.5 Hz, 3H, CH_3), 1.150 (t, J = 7.4 Hz, 3H, CH_3); LRMS (FI): 318.3.

2c R = CO₂Et

2e R = *n*-Bu

2f R = CH₂OMe

2j R =

General Procedure for Synthesis of 1,3-Diynes 2c, 2e, 2f, and 2j. A solution of the respective terminal alkyne in CH₃CN was exposed to air in the presence of Cu(OAc)₂·H₂O at various temperatures. The reactions were considered complete when TLC indicated either consumption of the alkyne starting material, or no further change in the reaction. The solvent was removed by rotary evaporation under reduced pressure and all purification of the resulting 1,3-diynes was carried out using silica gel flash column chromatography.

2c

Hexa-2,4-diynedioic acid diethyl ester (2c). To a solution of Cu(OAc)₂·H₂O (1.43 g, 7.16 mmol, 1 equiv) in CH₃CN (68 mL) was added ethyl propiolate (690 μL, 6.8 mmol, 1 equiv). The mixture was stirred at 23 °C for 5 h. The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (20% EtOAc/hexane) to give 510 mg (77%) of **2c** as a colorless oil which was highly unstable to light and decomposed rapidly upon isolation. The product was purified immediately before use by flash column chromatography and concentrated in vacuo while wrapped in foil to prevent decomposition from light exposure: TLC R_f = 0.53 (20% EtOAc/hexane); ¹H NMR (500 MHz, CDCl₃) δ 4.28 (q, *J* = 7 Hz, 4H, OCH₂), 1.33 (t, *J* = 7 Hz, 6H, OCH₂CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 152, 72.5, 67.8, 63.1, 13.8; IR (thin film): ν 2986 (w), 2922 (w), 2360 (w), 2157 (m), 1715 (s), 1467 (w), 1366 (w), 1309 (m), 1219 (s), 1129 (w), 1018 (m), 856 (w), 742 (w); HRMS (EI⁺): calcd for C₁₀H₁₀O₄: 194.0579, found: 194.0583.

11d

5,7-Dodecadiyne (2e). To a solution of Cu(OAc)₂·H₂O (3.73 g, 18.7 mmol, 7.2 equiv) in CH₃CN (12 mL) was added 1-hexyne (300 μL, 2.6 mmol, 1 equiv) and the flask was equipped with a reflux condenser. The solution was heated at reflux for 7 h, then cooled to rt and concentrated in vacuo. The crude oil was purified by silica gel flash column chromatography (hexane), to yield 210 mg (100%) of **2e** as a colorless oil: TLC R_f = 0.85 (5% EtOAc/hexane);

^1H NMR (400 MHz, CDCl_3) δ 2.25 (t, $J = 7$ Hz, 4H, $\text{C}\equiv\text{CCH}_2$), 1.47 – 1.52 (m, 4H, $\text{CH}_2\text{CH}_2\text{Me}$), 1.38 – 1.44 (m, 4H, CH_2Me), 0.90 (t, $J = 7.3$ Hz, 6H, CH_3); ^{13}C NMR (126 MHz, CDCl_3) δ 77.5, 65.1, 30.3, 21.9, 18.8, 13.5; IR (thin film): ν 2958 (s), 2873 (s), 2833 (m), 2171 (w), 2141 (w) 1465 (m), 740 (m); HRMS (EI^+): calcd for $\text{C}_{12}\text{H}_{18}$: 162.1409, found: 162.1407.

1,6-Dimethoxy-2,4-hexadiyne (2f). To a solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (3.77 g, 18.8 mmol, 7.8 equiv) in CH_3CN (12 mL), was added methyl propargyl ether (300 μL , 3.6 mmol, 1 equiv). The flask was equipped with a reflux condenser and the solution was heated at reflux for 12 h. The solvent was removed by rotary evaporation and the residue was purified by silica gel flash column chromatography (30% EtOAc/hexane) to afford 241 mg (98%) of **2f** as a colorless oil: TLC $R_f = 0.53$ (30% EtOAc/hexane); ^1H NMR (500 MHz, CDCl_3) δ 4.17 (s, 4H, CH_2), 3.39 (s, 6H, CH_3); ^{13}C NMR (126 MHz, CDCl_3) δ 75.2, 70.5, 60.1, 57.8; IR (thin film): ν 2935 (s), 2826 (s), 2256 (w), 2151 (w), 1716 (m), 1352 (s), 1187 (s), 1098 (s), 800 (w); HRMS (EI^+): calcd for $\text{C}_8\text{H}_{10}\text{O}_2$: 138.0681, found: 138.0684.

2,7-Di-tert-butoxy-3,5-octadiyne (2j). To a solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (200 mg, 1.0 mmol, 1 equiv) in CH_3CN (10 mL) was added *tert*-butyl 1-methyl-2-propynyl ether (160 μL , 1.0 mmol, 1 equiv). The reaction was stirred at 23 $^\circ\text{C}$ in air for 7 h. The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (10% EtOAc/hexane) to give 110 mg (88%) of **2j**² as a colorless oil: TLC $R_f = 0.39$ (10% EtOAc/hexane); ^1H NMR (400 MHz, CDCl_3) δ 4.30 (q, $J = 6.6$ Hz, 2H, CHMe), 1.37 (d, $J = 6.7$ Hz, 6H, CHCH_3), 1.24 (s, 9H, $\text{OC}(\text{CH}_3)_3$); ^{13}C NMR (126 MHz, CDCl_3) δ 81.8, 74.9, 67.7, 58.0, 28.0, 23.9; IR (thin film): ν 2978 (s), 2934 (m), 2360 (w), 1462 (w), 1367 (s), 1194 (s), 1088 (s), 970 (m), 844 (w); LRMS (FI^+): 250.2.

² Although **2j** is formed as a diastereomeric mixture from the racemic terminal alkyne, there was no spectroscopic difference detected between the two compounds.

1,8-Bis(*tert*-butyl-dimethyl-silynyloxy)-octa-3,5-diyne (2d). A solution of 3-butynol (76 μ L, 1.0 mmol, 1 equiv) in CH_2Cl_2 (10 mL) and cooled to 0 $^\circ\text{C}$. Triethylamine (170 μ L, 1.2 mmol, 1.2 equiv) was added followed by *tert*-butyldimethylsilyl chloride (156 mg, 1.00 mmol, 1 equiv) and a catalytic amount of 4-(dimethylamino)-pyridine (DMAP, $\sim$ 5 mg). The reaction was allowed to stir while gradually warming from 0 to 23 $^\circ\text{C}$ over 8 h. Acetonitrile (10 mL) was added to the reaction mixture followed by $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (200 mg, 1 mmol, 1 equiv). The reaction was stirred in air for 12 h, then the solvent was removed by rotary evaporation. Purification by silica gel flash column chromatography (20% EtOAc/Hexane) yielded 67 mg (36%) of **2d** as a colorless oil: TLC R_f = 0.75 (20% EtOAc/hexane); ^1H NMR (400 MHz, CDCl_3) δ 3.72 (t, J = 7 Hz, 4H, TBSOCH_2), 2.45 (t, J = 7 Hz, 4H, $\text{TBSOCH}_2\text{CH}_2$), 0.89 (s, 18H, $\text{OSi}(\text{Me})_2\text{C}(\text{CH}_3)_3$), 0.07 (s, 12H, $\text{OSi}(\text{CH}_3)_2$); ^{13}C NMR (126 MHz, CDCl_3) δ 74.5, 66.2, 61.5, 25.8, 23.6, 18.3, 5.37; IR (thin film): ν 2955 (m), 2929 (m), 2857 (m), 1770 (m), 1471 (w), 1383 (w), 1248 (s), 1105 (s), 1056 (s), 913 (m), 837 (s), 777 (m), 741 (w); HRMS (ESI^+): calcd for $\text{C}_{20}\text{H}_{39}\text{O}_2\text{Si}_2$ ($\text{M}+1$): 367.2489, found: 367.2484 ($\text{M}+1$).

Deca-4,6-diyne-1,10-dioic acid dimethyl ester (2g). 4-Pentynoic acid (50 mg, 510 μ mol, 1 equiv) was dissolved in CH_3OH (0.5 mL) and CH_3CN (4.5 mL). The solution was cooled to 0 $^\circ\text{C}$ and trimethylsilyldiazomethane (510 μ L, 1.02 mmol, 2 equiv) was added dropwise over 5 min. The reaction was stirred for 2 h as it gradually warmed to 23 $^\circ\text{C}$. To this mixture was added $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (102 mg, 510 μ mol, 1 equiv), and the reaction mixture was exposed to air. After 12 h the solvent was removed by rotary evaporation and the residue was purified by silica gel flash column chromatography (20% EtOAc/Hexane) to yield 43 mg (76%) of **2g** as a yellow oil: TLC R_f = 0.37 (30% EtOAc/hexane); ^1H NMR (400 MHz, CDCl_3) δ 3.70 (s, 6H, OCH_3), 2.54 – 2.57 (m, 8H, $\text{C}\equiv\text{CCH}_2\text{CH}_2$); ^{13}C NMR (100 MHz, CDCl_3) δ 172, 75.7, 65.7, 51.9, 32.7, 15.1; IR (thin film): ν 2954 (m), 2255 (w), 1738 (s), 1436 (m), 1362 (m), 1199 (s), 1167 (s), 1024 (s), 833 (w); HRMS (EI^+): calcd for $\text{C}_{12}\text{H}_{14}\text{O}_4$: 222.0892, found: 222.0892.

1,6-Acetoxy-2,4-hexadiyne (2h). A mixture of 2,4-hexadiyne-1,6-diol (225 mg, 2.04 mmol, 1 equiv), pyridine (8.2 mL, 100 mmol, 50 equiv), and acetic anhydride (9.6 mL, 100 mmol, 50 equiv) was heated to 100 °C for 5 h. The reaction was cooled to 23 °C and toluene (200 mL) was added to facilitate the removal of residual pyridine by rotary evaporation. Purification by silica gel flash column chromatography (15% EtOAc/hexane) gave 340 mg (86%) of **2h** as a white solid: TL: R_f = 0.37 (30% EtOAc/hexane); m.p. 29-31 °C; ^1H NMR (500 MHz, CDCl_3) δ 4.73 (s, 4H, CH_2), 2.10 (s, 6H, COCH_3); ^{13}C NMR (126 MHz, CDCl_3) δ 170.0, 73.6, 70.2, 52.1, 20.5; IR (thin film): ν 2943 (m), 2263 (w), 2200 (w), 2152 (w), 2040 (w), 1750 (s), 1430 (s), 1356 (s), 1220 (s), 1031 (s); HRMS (EI^+): calcd for $\text{C}_{10}\text{H}_{10}\text{O}_4$: 194.0579, found: 194.0579.

General Procedure for [2+2+2] Cycloadditions of Benzyne **1b** with Diynes (**2b-i**).

Procedure A. A solution of the 1,3-diyne **2** in toluene (0.1 M, 2.2 equiv) was treated with PEt_3 (5 equiv), deoxygenated by Ar sparge, and heated to 60 °C. Recrystallized Ni-benzyne **1b** (1 equiv) was added, and the reaction mixture was stirred at 60 °C until the reaction was complete. The solvent was removed in vacuo and the resulting residue was purified by silica gel flash column chromatography.

Procedure B. A solution of the 1,3-diyne **2** in toluene was deoxygenated by Ar sparge and brought to the necessary temperature for the reaction to proceed. Recrystallized Ni-benzyne **1b** (1 equiv) was added and the reaction was stirred until complete. The solvent was removed in vacuo and the resulting residues were purified by silica gel flash column chromatography.

Naphthalene (3b). Following Procedure A, 1,4-diphenyl-1,3-butadiyne (11 mg, 54 μmol , 2.1 equiv), triethylphosphine (19 μL , 130 μmol , 5 equiv), and recrystallized Ni-benzyne **1b** (15 mg, 26 μmol , 1 equiv) were reacted in toluene (642 μL) at 60 $^{\circ}\text{C}$ for 1 h. The residue was purified by silica gel flash column chromatography (hexane) to give 11 mg of **3b** (85%) as a white solid: TLC R_f = 0.35 (5% EtOAc/hexane); m.p. 188-191 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.50-7.61 (m, 10H, H_{phenyl}), 7.38 (t, J = 10 Hz, 2H, H_{aryl}), 7.16-7.32 (m, 10H, H_{phenyl}); ^{13}C NMR (126 MHz, CDCl_3) δ 150 (dd, J = 253, 17.5 Hz), 143, 142, 138, 131, 130, 128.4, 128.3, 128.2, 128.0, 123, 122, 113 (dd, J = 13, 7.0 Hz), 97.3, 88.3; ^{19}F NMR (470 MHz, CDCl_3) δ -135 (t, J = 10 Hz, 2F); IR (thin film): ν 3057 (w), 2919 (w), 2355 (w), 2216 (w), 1597 (w), 1514 (m), 1493 (m), 913 (s); HRMS (EI^+): calcd for $\text{C}_{38}\text{H}_{22}\text{F}_2$: 516.1690, found: 516.1691; ϵ_{max} (306 nm) = $6.81 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

Naphthalene (3c). Following Procedure B, diyne **2c**³ (164 mg, 845 μmol , 10 equiv) was dissolved in toluene (1.7 mL), deoxygenated by Ar sparge, and cooled to -78 $^{\circ}\text{C}$. Recrystallized Ni-benzyne **1b** (51 mg, 86 μmol , 1 equiv) was added to the flask and the reaction mixture was stirred at -78 $^{\circ}\text{C}$ for 30 minutes and then allowed to warm slowly to room temperature. After 12 h the crude residue was purified by silica gel flash column chromatography (30% EtOAc/hexane) to give 35 mg (82%) of **3c** as a white solid: TLC R_f = 0.70 (40% EtOAc/hexane); m.p. 117-120 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.82 (t, J = 10 Hz, 2H, H_{aryl}), 4.58 (q, J = 7 Hz, 4H, CO_2CH_2), 4.32 (q, J = 7 Hz, 4H, $\text{C}\equiv\text{CCO}_2\text{CH}_2$), 1.49 (t, J = 7 Hz, 6H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.37 (t, J = 7 Hz, 6H, $\text{C}\equiv\text{CCO}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (126 MHz, CDCl_3) δ 165, 153, 152 (dd, J = 260, 7 Hz), 138, 127 (t, J = 5 Hz), 119, 113 (dd, J = 14, 6.3 Hz) 88.9, 79.4, 63.1, 62.4, 14.0, 13.9; ^{19}F NMR (376 MHz, CDCl_3) δ -128 (t, J = 10 Hz, 2F); IR (thin film): ν 2987 (w), 2922 (w),

³ For handling of diyne **2c**, see the procedure for its preparation.

2225 (m), 1711 (s), 1519 (w), 1378 (m), 1274 (s), 1247 (s), 1220 (s), 1149 (m), 1018 (m), 871 (w), 748 (w); HRMS (EI⁺): calcd for C₂₆H₂₂O₈F₂: 500.1288, found: 500.1288; ϵ_{max} (279 nm) = 6.04 x 10⁴ M⁻¹cm⁻¹.

3d

Naphthalene (3d). Following Procedure A, diyne **2d** (10 mg, 27 μ mol, 1.8 equiv), triethylphosphine (11 μ L, 74 μ mol, 5 equiv), and recrystallized Ni-benzynes **1b** (9.0 mg, 15 μ mol, 1 equiv) were reacted in toluene (300 μ L) at 60 °C for 13 h. The solvent was removed in vacuo and the crude oil was purified by silica gel flash column chromatography (1% EtOAc/hexane) to afford 8.5 mg (74%) of **3d** as a yellow oil: TLC R_f = 0.31 (5% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.85 (t, *J* = 10 Hz, 2H, H_{aryl}), 3.88 (t, *J* = 7 Hz, 4H, ArCH₂CH₂O), 3.84 (t, *J* = 7.4 Hz, 4H, C $\equiv$ CCH₂CH₂O), 3.42 (t, *J* = 7 Hz, 4H, ArCH₂CH₂O), 2.76 (t, *J* = 7.4 Hz, 4H, C $\equiv$ CCH₂CH₂O), 0.92 (s, 18H, OSi(CH₃)₃), 0.84 (s, 18H, OSi(CH₃)₃), 0.10 (s, 12H, OSi(CH₃)₂), 0.068 (s, 12H, OSi(CH₃)₂); ¹³C NMR (101 Hz, CDCl₃) δ 150 (dd, *J* = 252, 17.5 Hz), 136, 129 (t, *J* = 4 Hz), 123, 112 (dd, *J* = 12.4, 6.6 Hz), 94.7, 80.0, 62.8, 62.1, 36.0, 24.3, 18.3, 18.2, -5.27, -5.47; ¹⁹F NMR (376 MHz, CDCl₃) δ -137 (t, *J* = 9 Hz, 2F); IR (thin film): ν 2929 (s), 2857 (s), 2226 (w), 1733 (w), 1634 (w), 1523 (m), 1472 (m), 1383 (m), 1361 (m), 125 (s), 1101 (s), 836 (s), 776 (s); HRMS (EI⁺): calcd for C₄₆H₇₈O₄F₂Si₄: 844.4945, found: 844.4943; ϵ_{max} (268 nm) = 8.32 x 10⁴ M⁻¹cm⁻¹.

3e

Naphthalene (3e). Following Procedure A, 5,7-dodecadiyne (**2e**) (2 M in toluene, 280 μ L, 56 μ mol, 2.2 equiv), triethylphosphine (18 μ L, 120 μ mol, 5 equiv), and recrystallized Ni-benzynes **1b** (14 mg, 24 μ mol, 1 equiv) were reacted in toluene (220 μ L) at 60 °C for 2 h. The crude oil was purified by silica gel flash column chromatography (hexane) to afford 6.8 mg

(68%) of **3e** as a yellow oil: TLC R_f = 0.54 (5% EtOAc/hexane); ^1H NMR (500 MHz, CDCl_3) δ 7.68 (t, J = 10.2 Hz, 2H, H_{aryl}), 3.13 – 3.18 (m, 4H, ArCH_2), 2.55 (t, J = 7 Hz, 4H, $\text{C}\equiv\text{CCH}_2$), 1.42-1.7 (br m, 16H, CH_2), 0.97 (t, J = 12 Hz, 6H, CH_3); ^{13}C NMR (126 MHz, CDCl_3) δ 149 (dd, J = 251, 17.3 Hz), 139 (t, J = 1.5 Hz), 128 (t, J = 4 Hz), 123, 111 (dd, J = 12, 6.0 Hz), 98.0, 79.1, 32.4, 31.4, 31.0, 23.1, 22.0, 19.4, 14.0, 13.8; ^{19}F NMR (470 MHz, CDCl_3) δ -137 (t, J = 11 Hz, 2F); IR (thin film): ν 2957 (s), 2931 (s), 2872 (m), 2362 (w), 2227 (w), 1521 (s), 1263 (m), 866 (m); HRMS (EI^+): calcd for $\text{C}_{30}\text{H}_{34}\text{F}_2$: 436.2941, found: 436.2942; ϵ_{max} (269 nm) = $7.22 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$.

Naphthalene (3f). Following Procedure A, a flask was charged with toluene (1.3 mL), recrystallized Ni-benzynes **1b** (40 mg, 68 μmol , 1 equiv), and triethylphosphine (50 μL , 340 μmol , 5 equiv). The solution was deoxygenated by Ar sparge and heated to 60 $^\circ\text{C}$. Diyne **2f** (20 mg, 150 μmol , 2.2 equiv) was dissolved in toluene (3 mL) and added via a syringe pump at 40 $\mu\text{L}/\text{min}$. The addition was complete after 75 min, following which the reaction was stirred at 60 $^\circ\text{C}$ for 13 h. The crude oil was purified by silica gel flash column chromatography (15% EtOAc/hexane) to give 10 mg (40%) of **3f** as a white solid: TLC R_f = 0.31 (20% EtOAc/hexane); m.p. 84-88 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.98 (t, J = 10 Hz, 2H, H_{aryl}), 5.10 (s, 4H, ArCH_2), 4.47 (s, 4H, $\text{C}\equiv\text{CCH}_2$), 3.54 (s, 6H, OCH_3), 3.42 (s, 6H, OCH_3); ^{13}C NMR δ 150 (dd, J = 254, 16.8 Hz), 136, 129 (t, J = 4.7 Hz), 123, 112 (dd, J = 13, 7.0 Hz), 93.9, 83.4, 70.3, 60.5, 58, 57.8; ^{19}F NMR (376 MHz, CDCl_3) δ -134.03 (t, J = 10 Hz, 2F); IR (thin film): ν 2927 (m), 2814 (m), 2210 (w), 1712 (w), 1522 (m), 1448 (m), 1271 (m), 1188 (m), 1094 (s), 949 (m); HRMS (EI^+): calcd for $\text{C}_{22}\text{H}_{22}\text{O}_4\text{F}_2$: 388.1486, found: 388.1491; ϵ_{max} (264 nm) = $1.04 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$.

3g

Naphthalene (3g). Following Procedure A, diyne **2g** (24 mg, 110 μmol , 2.2 equiv), triethylphosphine (50 μL , 340 μmol , 5 equiv), and recrystallized Ni-benzene **1b** (28.5 mg, 48.1 μmol , 1 equiv) were reacted in toluene (980 μL) at 60 $^{\circ}\text{C}$ for 13.5 h. The solvent was removed in vacuo and the crude oil was purified by silica gel flash column chromatography (20% EtOAc/hexane) to give 7.6 mg (28%) of **3g** as a yellow oil: TLC R_f = 0.35 (40% EtOAc/hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.74 (t, J = 10 Hz, 2H, H_{aryl}), 3.73 (s, 6H, OCH_3), 3.72 (s, 6H, OCH_3), 3.46 (t, J = 8.3 Hz, 4H, ArCH_2), 2.88 (t, J = 7.5 Hz, 4H, $\text{C}\equiv\text{CCH}_2$), 2.71 (t, J = 7.4 Hz, 4H, $\text{C}\equiv\text{CCH}_2\text{CH}_2$), 2.60 (t, J = 8.3 Hz, 4H, ArCH_2CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 173, 172, 150 (dd, J = 254, 17.2 Hz), 138, 128 (t, J = 4.2 Hz), 123, 111 (dd, J = 13.3, 6.5 Hz), 97.0, 78.5, 51.8, 51.7, 33.7, 33.3, 26.7, 15.6; ^{19}F NMR (376 MHz, CDCl_3) δ -135 (t, J = 10 Hz, 2F); IR (thin film): ν 2929 (s), 2853 (m), 2230 (w), 1738 (s), 1605 (w), 1524 (m), 1438 (m), 1396 (w), 1366 (w), 1264 (m), 1197 (m), 1169 (m), 854 (w); HRMS (EI^+): calcd for $\text{C}_{30}\text{H}_{30}\text{O}_8\text{F}_2$: 556.1909, found: 556.1911; ϵ_{max} (267 nm) = $1.03 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$.

3h

Naphthalene (3h). Following Procedure B, diyne **2h** (37 mg, 190 μmol , 2.2 equiv) and recrystallized Ni-benzene **1b** (51 mg, 86 μmol , 1 equiv) were reacted in toluene (8.4 mL) at 60 $^{\circ}\text{C}$ for 15 h. The crude oil was purified by silica gel flash column chromatography (25% EtOAc/hexane) to afford 11 mg (27%) of **3h** as a white solid: TLC R_f = 0.19 (30% EtOAc/hexane); m.p. 176-178 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.80 (t, J = 10 Hz, 2H, H_{aryl}), 5.69 (s, 4H, ArCH_2), 5.03 (s, 4H, $\text{C}\equiv\text{CCH}_2$), 2.17 (s, 6H, $\text{CH}_2\text{O}_2\text{CCH}_3$), 2.11 (s, 6H, $\text{CH}_2\text{O}_2\text{CCH}_3$); ^{13}C NMR (126 MHz, CDCl_3) δ 171, 170, 151 (dd, J = 256, 17.2 Hz), 136, 129 (t, J = 4.8 Hz), 124, 112 (dd, J = 14, 6.0 Hz), 93.1, 82.2, 61.9, 52.5, 20.8, 20.7; ^{19}F NMR

(376 MHz, CDCl₃) δ -132.68 (t, J = 10 Hz, 2F); IR (thin film): ν 2918 (m), 2852 (m), 2257 (w), 1739 (s), 1526 (m), 1445 (w), 1372 (m), 1235 (s), 1028 (m), 961 (w), 748 (w); HRMS (EI⁺): calcd for C₂₆H₂₂O₈F₂: 500.1283, found: 500.1288; ϵ_{max} (265 nm) = 1.40 x 10⁵ M⁻¹cm⁻¹.

Naphthalene (3i). Following Procedure A, diyne **2i** (47 mg, 240 μ mol, 2.2 equiv), triethylphosphine (81 μ L, 550 μ mol, 5 equiv), and recrystallized Ni-benzyne **1b** (62 mg, 100 μ mol, 1 equiv) were reacted in toluene (2.2 mL) at 60 °C for 9 h. The crude oil was purified by silica gel flash column chromatography (hexane) to give 11 mg (21%) of naphthalene **3i** as a waxy white solid: TLC R_f = 0.75 (5% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 8.00 (t, J = 11 Hz, 2H, H_{aryl}) 0.60, (s, 18H, SiCH₃), 0.29 (s, 18H, SiCH₃); ¹³C NMR (126 MHz, CDCl₃) δ 149 (dd, J = 252, 17.2 Hz), 143, 134 (t, J = 4.5 Hz), 130, 114 (dd, J = 12.5, 6.5 Hz), 105, 104, 2.86, -0.15; ¹⁹F NMR (470 MHz, CDCl₃) δ -136.8 (t, J = 11 Hz, 2F); IR (thin film): ν 2924 (s), 2854 (s), 2359 (m), 2315 (w), 2146 (w), 1513 (w), 1460 (m), 1376 (m), 1251 (m), 1092 (w), 1027 (w), 847 (w); HRMS (EI⁺): calcd for C₂₆H₃₈F₂Si₄: 500.2023, found: 500.2019; ϵ_{max} (278 nm) = 1.11 x 10⁵ M⁻¹cm⁻¹.

Naphthalene (10). Following Procedure A, diyne **2j** (20 mg, 180 μ mol, 2.2 equiv), triethylphosphine (27 μ L, 180 μ mol, 5 equiv), and recrystallized Ni-benzyne **1b** (22 mg, 36 μ mol, 1 equiv) were reacted in toluene (800 μ L) at 60 °C for 13 h. The solvent was removed in vacuo and the crude oil was purified by silica gel flash column chromatography (10% EtOAc/hexane) to give 12.5 mg (40%) of **10** as a mixture of diastereomers: TLC R_f = 0.41 (10% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 8.88 – 8.78 (m, 2H), 8.3 – 8.2 (m, 0.2H),

8.1 - 7.9 (m, 0.3H), 6.0 – 5.85 (m, 0.4H), 5.81 – 5.72 (m, 2H), 5.6 – 5.45 (m, 0.6H), 4.70 – 4.58 (m, 2.5H), 1.6 – 1.55 (m, 11H), 1.52 – 1.49 (m, 7H), 1.36 and 1.35 (overlapping singlets, 5.3H), 1.333, 1.329, and 1.322 (overlapping singlets, 18.7H), 1.14 – 1.06 (m, 24H); ^{19}F NMR (376 MHz, CDCl_3) δ –136.2 to –136.4 (m, 2F), –137.4 to –137.8 (m, 0.6F); IR (thin film): ν 3101 (w), 2975 (s), 2931 (s), 2862 (m), 1732 (w), 1517 (s), 1443 (m), 1390 (m), 1367 (m), 1332 (m), 1259 (s), 1234 (m), 1195 (s), 1087 (s), 965 (m), 818 (m); HRMS (EI^+): calcd for $\text{C}_{38}\text{H}_{54}\text{O}_4\text{F}_2$: 612.3990, found: 612.3982; ϵ_{max} (266 nm) = $1.50 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$.

1,4-Diphenyl-2,3-bis(2-phenylethynyl) naphthalene (11). 2-Bromoaryl-nickel(II) bromide salt (**4**) was synthesized according to literature procedures.¹ A solution of **4** (200mg, 280 μM , 1 equiv) in THF (7 mL) was treated with sodium amalgam (1% wt/wt, 660 μL , 3.9 mmol, 14 equiv) and allowed to stir for 3 h. The solvent was removed in vacuo and the residue was dissolved in hot cyclohexane and filtered through celite while maintaining an inert atmosphere. The cyclohexane was removed in vacuo to afford the crude benzyne **1a**.

1,4-Diphenyl-1,3-butadiene (**2b**) (124 mg, 614 μmol , 2.2 equiv) was dissolved in toluene (2.3 mL) and triethylphosphine (200 μL , 1.39 mmol, 5 equiv) was added. The solution was deoxygenated by Ar sparge, heated to 60 $^{\circ}\text{C}$, and added to the crude Ni-benzyne **1a**. Toluene (3.1 mL) was used to rinse the residual diyne and triethylphosphine, then deoxygenated, and added to the reaction mixture. The reaction was heated at 60 $^{\circ}\text{C}$ for 3 h and then cooled to room temperature. The solvent was removed in vacuo and the residue was purified by silica gel flash column chromatography (hexane) to afford 65 mg (48%) of **11** as a white solid which resulted in a crystals suitable for x-ray analysis: TLC R_f = 0.48 (5% EtOAc/hexane); m.p. 225-227 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.67 (dd, J = 6.6, 3.3 Hz, 2H, H_{aryl}) 7.52-7.61 (m, 10H, H_{phenyl}), 7.41 (dd, J = 6.6, 3.3 Hz, 2H, H_{aryl}) 7.21-7.28 (m, 10H, H_{phenyl}); ^{13}C NMR (126 MHz, CDCl_3) δ 143, 139, 132, 131, 130, 128.1, 128.1, 128.0, 127.7, 127, 126.7, 123.5, 121.6, 96.8, 88.9; IR (thin film): ν 3059 (m), 2919 (m), 2850 (w), 2216 (w), 1954 (w), 1596 (m), 1492 (s), 755 (s); HRMS (EI): calcd for $\text{C}_{38}\text{H}_{24}$: 480.1878, found: 480.1878; ϵ_{max} (306 nm) = $2.99 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$.

General Procedures for UV and Fluorescence Measurements.

UV sample preparation and measurement. Solutions were prepared in spectrophotometric grade chloroform using serial dilutions from an initial stock solution. The stock solutions were prepared by transferring between 2 and 60 mg of each compound to a volumetric flask.⁴ Spectra were recorded for each compound at 2 – 4 different concentrations. Molar absorptivity was calculated using the equation:

$$\epsilon = \text{Absorbance} / [\text{concentration(M)} * \text{pathlength(cm)}]$$

Fluorescence sample preparation and measurement. Fluorescence solutions were prepared from serial dilutions of the UV stock solutions by dilution until they possessed a UV absorbance of approximately 0.1. Three compounds, **3b**, **3h**, and **11** were further diluted to absorbances of 0.04, 0.03, and 0.01 respectively in order to obtain the fluorescence emission spectra within the limits of the detector. Each sample was excited at its λ_{max} and the resulting emission spectra were corrected for the wavelength dependence of detector sensitivity and excitation light source output, and normalized to an absorbance of 0.1.

Figure 1. UV and Fluorescence spectra for naphthalenes, **3d-h** and **10** in chloroform.

⁴ Masses were measured using a Mettler Toledo MT5 analytical balance.

Figure 2. UV and Fluorescence spectra for naphthalenes, **3c** and **3i** in chloroform.

Figure 3. UV and Fluorescence spectra for naphthalenes, **3b** and **11** in chloroform.