

Supporting Information

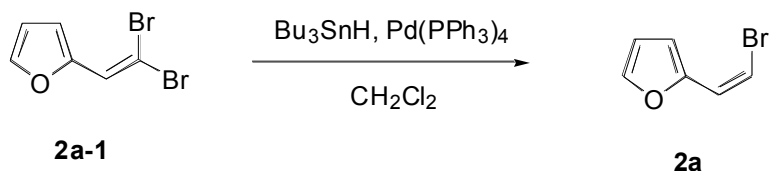
Practical Synthesis of (Z)-Polyaromatic and Heteroaromatic Vinylacetylenes

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Cheryl Harrison and Thomas Corprew

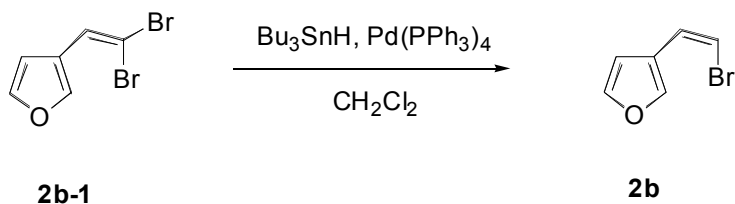
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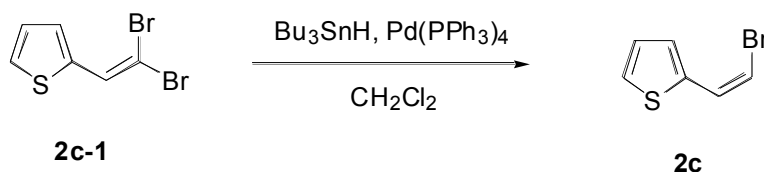


(Z)-2-(2-bromovinyl) furan 2a: Prepared according to a procedure reported by Herz¹ and coworkers. A mixture of a prepared dibromide **2a-1** (4.00 g, 0.016 mol) in the presence Pd(PPh₃)₄ (0.4 g, 0.0003 mol) was stirred in CH₂Cl₂ (60 mL) at room temperature under nitrogen atmosphere. *n*-Bu₃SnH (5.8 g, 0.02 mol) was slowly added *via* syringe and the mixture was stirred for additional 3hr. The reaction mixture was then poured into 100 mL KF 5% solution and stirring resumed at room temperature for 18hr. The suspension of the tin-by products that resulted was filtered by suction filtration. The filtrate was extracted with CH₂Cl₂ (2 x 40 mL), washed with brine, dried (Na₂SO₄) and concentrated to dryness *in vacuo*. The residue was immediately purified by chromatography over silica gel-15% KF mixture² (petroleum ether-EtOAc, 10:1) to yield pure (Z) compound **2a** (1.1 g, 41%) as a yellow oil. Spectroscopic data obtained for **2a** were in agreement with that reported in the literature.³ ¹H-NMR (300 MHz, CDCl₃) δ 6.3 (1H, d, *J* = 8.1Hz), 6.5 (1H, m), 7.0 (1H, d, *J* = 8.1Hz), 7.1 (1H, d, *J* = 2.7Hz), 7.4 (1H, s); ¹³C NMR (75 MHz, CDCl₃) δ 104.5, 111.7, 111.9, 122.4, 142.3, 150.8.

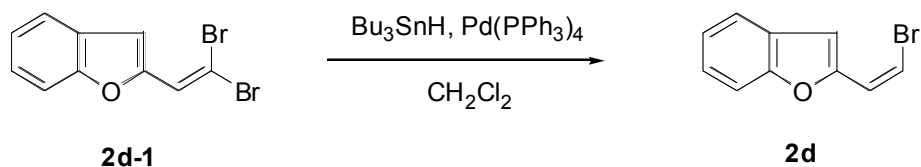


(Z)-3-(2-bromovinyl) furan 2b: Compound **2b** was synthesized analogously to compound **2a** from dibromide **2b-1** (9.88 g, 39.2 mmol), Pd[PPh₃]₄ (0.91 g, 0.78 mmol), and *n*-Bu₃SnH (11.48 mL, 43 mmol) in 60mL of CH₂Cl₂. Yield; (2.03 g, 30%) as a

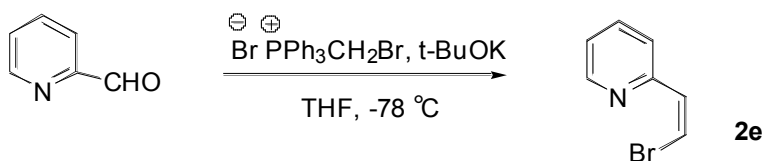
yellow oil. ^1H -NMR (300 MHz, CDCl_3) δ 6.31 (1H, d, $J = 7.8\text{ Hz}$), 6.87 (1H, s), 6.93 (1H, d, $J = 7.8\text{ Hz}$), 7.43 (1H, dd, $J = 2.7, 1.5\text{ Hz}$), 7.93 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 106.1, 110.7, 123.8, 128.7, 143.2, 144.1.



(Z)-2-(2-bromovinyl) thiophene 2c: To a stirred solution of dibromothiophene **2c-1** (9.04 g, 33.7 mmol) and $\text{Pd[PPh}_3)_4$ (0.78 g, 0.67 mmol) in dried CH_2Cl_2 (100 mL) was added *n*- Bu_3SnH (9.90 mL, 37.1 mmol) via a syringe, and the mixture was stirred overnight. The mixture was hydrolyzed by the addition of aqueous potassium fluoride (9.80 g, 169 mmol in 40 mL H_2O). After 90 min, the precipitated tin salts were filtered under vacuum and the residual solution was extracted with CH_2Cl_2 (2 x 40 mL). The organic layer was washed with brine and water, dried over sodium sulfate and concentrated. Purification of the residue by flash column chromatography on basic alumina and finely ground KF (90:10%, w/w)² using hexanes as eluent furnished the product as a yellow oil. Yield; (3.83 g, 60%). Spectroscopic data obtained for **2c** were consistent with that reported in the literature.¹ ^1H NMR (300 MHz, CDCl_3) δ 6.32 (1H, d, $J = 8.0\text{ Hz}$), 7.07 (1H, dd, $J = 5.2, 3.7\text{ Hz}$), 7.29-7.34 (2H, m) 7.39 (1H, d, $J = 5.2\text{ Hz}$); ^{13}C NMR (125 MHz, CDCl_3) δ 104.1, 126.3, 126.8, 130.1, 138.1.

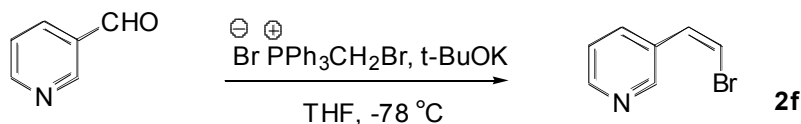


(Z)-2-(2-bromovinyl) benzofuran 2d: Compound **2d** was synthesized analogously to compound **2a** from dibromide **2d-1** (5.00 g, 16 mmol), $\text{Pd(PPh}_3)_4$ (0.4 g, 0.3 mmol), and $n\text{-Bu}_3\text{SnH}$ (5.8 g, 20 mmol) in 60 mL of CH_2Cl_2 . Yield; (2.6 g, 71%) as a yellow oil. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 6.56 (1H, d, $J = 9.3$ Hz), 7.19 (1H, d, $J = 9.3$ Hz), 7.20 (2H, m), 7.41 (2H, m), 7.52 (1H, d, $J = 6.9$ Hz); ^{13}C (75 MHz, CDCl_3) δ 107.9, 108.6, 111.4, 121.7, 122.8, 123.3, 125.5, 128.7, 133.8, 134.1.

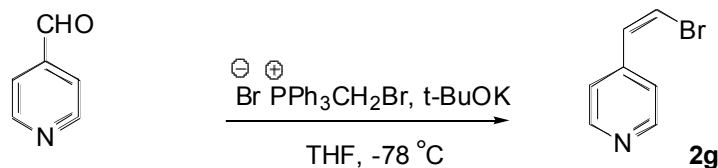


(Z)-2-(2-bromovinyl) pyridine 2e: Prepared according to the procedure described by Matsumoto and Kuroda.⁴ To a cooled (-78 °C) suspension of bromomethyltriphenylphosphonium bromide (25.27 g, 50.0 mmol) in dried THF (150 mL) under a nitrogen atmosphere, was added potassium *tert*-butoxide (6.57 g, 50.0 mmol). The resulting yellow mixture was stirred at the indicated temperature for 1 hr. A solution of 2-pyridine carboxaldehyde (5 mL, 42.0 mmol) in dried THF (10 mL) was then introduced via a syringe. The temperature was maintained at -78 °C, and the mixture was stirred an additional 5 hrs. The mixture was diluted with 80 mL of petroleum ether, and filtered under vacuum. Evaporation of the solvent and purification by flash column chromatography (silica gel, 30% ethyl acetate in petroleum ether) gave vinyl bromide (7.29 g, 95%) as a yellow oil. The product contains *Z* and *E* isomers in 9:1 *Z/E* ratio.

^1H NMR (*cis* **2e**⁵) (500 MHz, CDCl_3) _ 6.66 (1H, d, $J = 8.5$ Hz), 7.23 (1H, ddd, $J = 8.0$, 5.0, 1.5 Hz), 7.26 (1H, d, $J = 8.5$ Hz), 7.69 (1H, td, $J = 8.0$, 1.5 Hz), 8.01 (1H, td, $J = 8.0$, 1.5 Hz), 8.64 (1H, td, $J = 5.0$, 1.5 Hz); ^{13}C NMR (75 MHz, CDCl_3) _ 109.4, 122.9, 123.9, 133.4, 136.1, 149.7, 154.0.

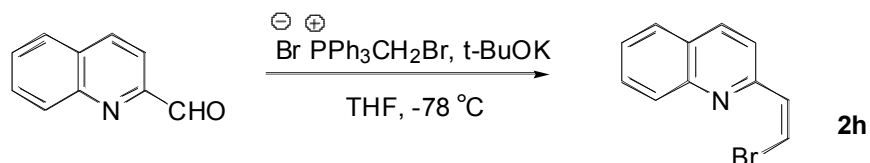


(Z)-3-(3-bromovinyl) pyridine 2f: Synthesized analogously to **2e**, from bromomethyltriphenylphosphonium bromide (6.04 g, 13.85 mmol), potassium *tert*-butoxide (1.55 g, 13.85 mmol) and 3-pyridinecarboxaldehyde (1.0 mL, 10.65 mmol) in 60 mL of anhydrous THF. Purification by flash column chromatography on silica gel (20% ethyl acetate in hexanes) yielded 1.80 g (91%) of the product as a colorless oil. The product was found to be contaminated with the E isomer (95:5, *Z:E*). ^1H NMR (*Z* isomer⁵) (300 MHz, CDCl_3) _ 6.55 (1H, d, $J = 8.1$ Hz), 7.03 (1H, d, $J = 8.1$ Hz), 7.28 (1H, dd, $J = 7.8$, 4.5 Hz), 8.11 (1H, dt, $J = 7.8$, 1.5 Hz), 8.51 (1H, d, $J = 4.5$ Hz), 8.73 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) _ 109.4, 123.3, 129.4, 131.2, 135.7, 149.3, 150.5.

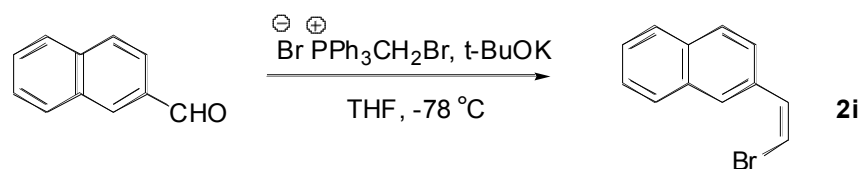


(Z)-4-(3-bromovinyl) pyridine 2 g: Compound **2 g** was synthesized analogously to **2e**, from bromomethyltriphenylphosphonium bromide (12.96 g, 29.7 mmol), potassium *tert*-butoxide (3.34 g, 29.7 mmol) and 4-pyridinecarboxaldehyde (2.0 mL, 21.2 mmol) in 70 mL of dried THF. The crude was purified by flash column chromatography on silica gel

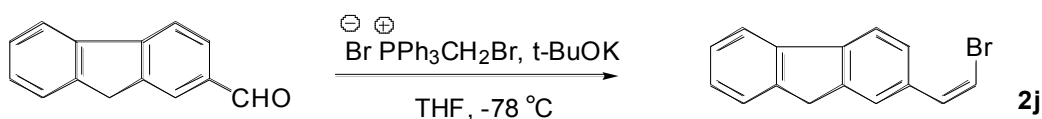
using 3:2 hexanes/ ethyl acetate as eluent. Due to its very limited stability, this compound was used immediately. Spectral data obtained for **2g** was in agreement with that reported in the literature.⁵ ¹H NMR (300 MHz, CDCl₃) _ 6.68 (1H, d, *J* = 8.3 Hz), 7.05 (1H, d, *J* = 8.3 Hz), 7.56 (2H, dd, *J* = 4.5, 1.7 Hz), 8.64 (2H, dd, *J* = 4.5, 1.7 Hz).



Synthesis of (Z)-2-(bromovinyl) quinoline 2h: Compound **2h** was synthesized analogously to **2e**, from bromomethyltriphenylphosphonium bromide (20.81 g, 47.72 mmol), potassium *tert*-butoxide (5.36 g, 47.72 mmol) and 2-quinoline carboxaldehyde (6.00 g, 38.18 mmol) in 200 mL of anhydrous THF. Purification by flash column chromatography on silica gel (10:1 petroleum ether/ ethyl acetate) gave 6.59 g (80%) product as a yellow oil. The product contains *Z* and *E* isomers in 13:1 *Z/E* ratio. ¹H NMR (*Z* isomer⁵) (300 MHz, CDCl₃) _ 6.79 (1H, d, *J* = 8.1 Hz), 7.45 (1H, d, *J* = 8.1 Hz), 7.55 (1H, td, *J* = 6.9, 1.2 Hz), 7.72 (1H, td, *J* = 6.9, 1.2 Hz), 7.81 (1H, dd, *J* = 8.1, 1.2 Hz), 8.07, (1H, d, *J* = 8.6 Hz), 8.11, (1H, d, *J* = 8.6 Hz), 8.17, (1H, d, *J* = 8.6 Hz); ¹³C NMR (75 MHz, CDCl₃) _ 110.70, 121.50, 127.14, 127.54, 127.78, 129.61, 130.01, 134.05, 136.14, 148.23, 154.59.

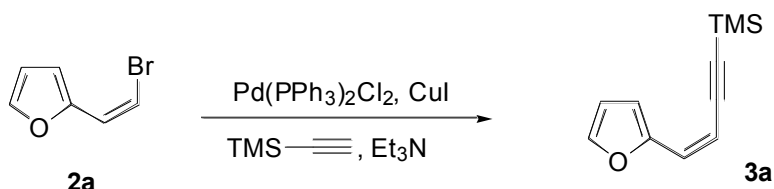


(Z)-2-(2-bromovinyl) naphthalene 2i: Compound **2i** was synthesized analogously to **2e** from bromomethyltriphenylphosphonium bromide (19.55 g, 44.82 mmol), potassium *tert*-butoxide (5.03 g, 44.82 mmol) and 2-naphthalene carboxaldehyde (5.00 g, 32.01 mmol) in 150 mL of dried THF. The crude was purified by flash column chromatography on basic alumina using petroleum ether as eluent to give 6.88 g (92%) of the product as colorless crystals. (mp = 77-79 °C); Spectral data were consistent with that reported in the literature.⁵ ¹H NMR (300 MHz, CDCl₃): δ 6.52 (1H, d, J = 8.1 Hz), 7.24 (1H, d, J = 8.1 Hz), 7.46-7.54 (2H, m), 7.80-7.90 (4H, m), 8.17 (1H, s); ¹³C NMR (75 MHz, CDCl₃) δ 106.7, 126.3, 126.4, 126.5, 127.6, 127.7, 128.3, 128.6, 132.4, 133.0, 133.1, 136.9.

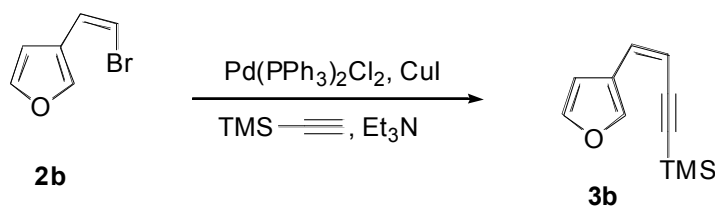


(Z)-3-(2-bromo-vinyl)-9H-fluorene 2j: Synthesized analogously to **2e**, from bromomethyltriphenylphosphonium bromide (8.72 g, 20 mmol), potassium *tert*-butoxide (1.93 g, 16.9 mmol) and fluorene-2-carboxaldehyde (3.0 g, 15.0 mmol) in 100 mL of anhydrous THF. Purification by flash column chromatography on silica gel (20:1 hexanes /ethyl acetate) yielded 1.90 g (46%) of the product as pure white crystals. ¹H-NMR (300MHz, CDCl₃) δ 3.8(s, 2H), 6.39 (1H, d, J = 8.1Hz), 7.0 (1H, d, J = 8.1Hz), 7.1(2H, m), 7.4 (1H, d, J = 6.6Hz), 7.6(1H, d, J = 6.6Hz), 7.7(2H,m), 7.8 (1H,s); ¹³C-NMR (75MHz, CDC₃,) δ 37.2, 105.9, 119.9, 120.4, 125.3, 127.1, 127.3, 128.4, 132.9,

133.6, 141.5, 142.2, 143.4, 143.9; HRMS calculated for $C_{15}H_{11}Br$ 270.0044, found 270.0027.

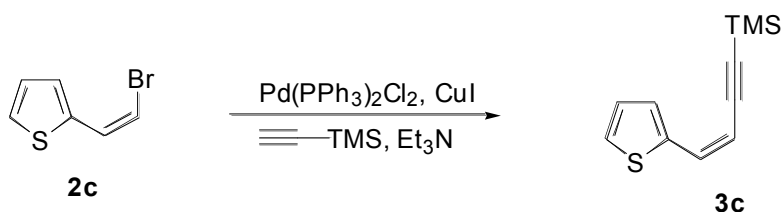


(Z)- 2-(4-Trimethylsilylbut-1-en-3-ynyl) furan 3a: While stirring, copper iodide (0.60 g, 0.3 mmol) and $\text{Pd}[(\text{PPh}_3)_2\text{Cl}_2]$ (0.41 g, 0.6 mmol) were added to a solution of vinylbromide **2a** (5.0 g, 29 mmol) in 90 mL of Et_3N . After 5 min, trimethylsilylacetylene (4.35 g, 43 mmol) was introduced to the reaction mixture which was stirred for 3 hrs at room temperature. The mixture was filtered through a pad of celite and concentrated. The residue was dissolved in 40 mL of diethyl ether and washed with water. The organic layer was dried over magnesium sulfate and concentrated. The crude product was chromatographed on silica gel using 10:1 hexanes / ethyl acetate as eluent to give the product as a brown oil. Yield; 5.50 g (100%). $^1\text{H-NMR}$ (300MHz, CDCl_3) δ 0.23 (9H, s), 5.51 (1H, d, $J = 11.7\text{Hz}$), 6.53 (1H, d, $J = 11.7\text{Hz}$), 7.0 (1H, s), 7.4 (1H, d, $J = 1.5\text{Hz}$), 7.8 (1H, s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 0.0, 103.6, 104.4, 111.1, 111.7, 126.0, 128.3, 141.9, 152.6; HRMS calculated for $C_{11}H_{14}\text{OSi}$ 190.0814, found 190.0818.

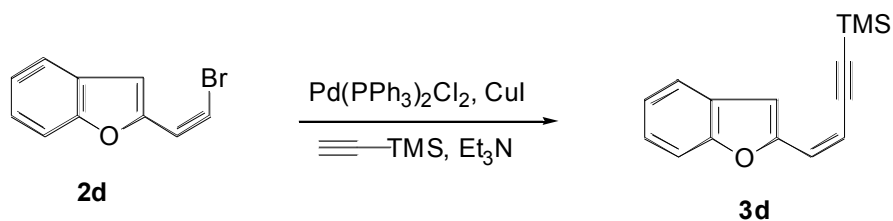


(Z)- 3-(4-Trimethylsilylbut-1-en-3-ynyl) furan 3b: Synthesized analogously to compound **3a** from CuI (0.39 g, 2.04 mmol), $\text{Pd}[(\text{PPh}_3)_2\text{Cl}_2]$ (0.29 g, 0.41 mmol),

trimethylsilyl acetylene (3.50 mL, 24.5 mmol) and vinylbromide **2b** (3.54 g, 20.4 mmol) in 75 mL of Et₃N. Yield; 2.12 g (55%) as a yellow oil. ¹H-NMR (300MHz, CDCl₃) _ 0.24 (9H, s), 5.56 (1H, d, *J* = 12Hz), 6.53 (1H, d, *J* = 12Hz), 7.01 (1H, d, *J* = 1.5Hz), 7.38 (1H, s), 7.83 (1H, s); ¹³C NMR (75 MHz, CDCl₃) _ 0.0, 102.3, 104.1, 106.3, 109.8, 123.4, 130.3, 142.7, 143.2.

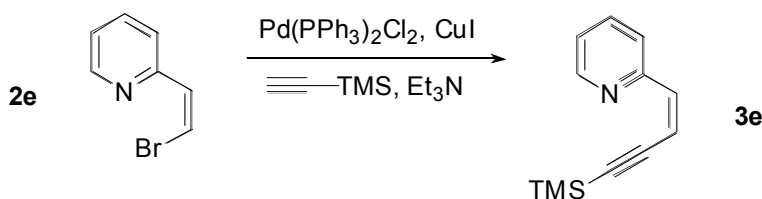


(Z)- 2-(4-Trimethylsilylbut-1-en-3-ynyl) thiophene 3c: Synthesized analogously to compound **3a** from CuI (0.29 g, 1.54 mmol), Pd[(PPh₃)₂Cl₂] (0.43 g, 0.61 mmol), trimethylsilyl acetylene (5.60 mL, 39.9 mmol) and vinylbromide **2c** (5.80 g, 30.7 mmol) in 70 mL of Et₃N overnight. Yield; 5.12 g (81%) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) _ 0.33 (9H, s), 5.59 (1H, d, *J* = 11.5 Hz), 6.91 (1H, d, *J* = 11.5 Hz), 7.04 (1H, dd, *J* = 8.5, 3.5 Hz), 7.31 (1H, d, *J* = 3.5 Hz), 7.36 (1H, d, *J* = 8.5 Hz); ¹³C NMR (75 MHz, CDCl₃) _ 0.0, 103.9, 104.8, 105.4, 126.6, 127.3, 130.1, 133.6, 140.9.



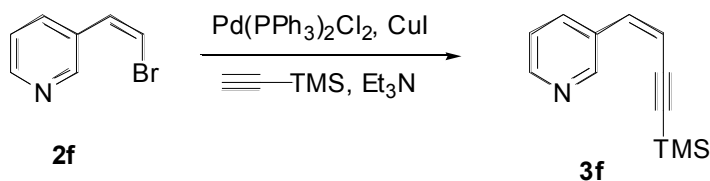
(Z)-2-(4-Trimethylsilylbut-1-en-3-ynyl)-benzofuran 3d: Synthesized analogously to compound **3a** from CuI (0.2 g, 0.0009 mol), Pd[(PPh₃)₂Cl₂] (0.14 g, 0.0002 mol), trimethylsilyl acetylene (1.5 g, 0.015 mol) and vinylbromide **2d** (2.2 g, 0.01 mol) in 70

mL of Et₃N for 3hrs. Yield; 1.83 g (99.5%) as a dark brown oil. ¹H NMR (300 MHz, CDCl₃) δ 0.19 (9H, s), 5.58 (1H, d, J = 12Hz), 6.54 (1H, d, J = 12Hz), 7.0 (4H, m), 7.3 (1H, d, J = 7.5Hz); ¹³C NMR (75 MHz, CDCl₃) δ 0.0, 103.6, 105.4, 107.6, 108.5, 111.3, 121.6, 123.2, 125.4, 128.3, 128.8, 154.1; HRMS calculated for C₁₅H₁₆OSi 240.0970, found, 240.0969.

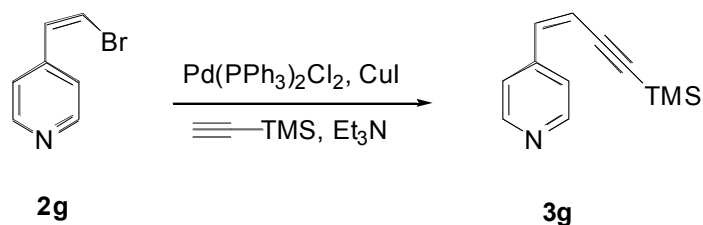


(Z)-2-(4-Trimethylsilanyl-but-1-en-3-ynyl)-pyridine 3e: To a solution of monobromide **2e** (2.60 g, 14.1 mmol) in Et₃N (50 mL) was added Pd[(PPh₃)₂Cl₂] (0.19 g, 0.03 mmol). After stirring for 10 min, CuI (0.13 g, 0.07 mmol) and trimethylsilylacetylene (2.40 mL, 16.9 mmol) were added to the mixture. The resulting mixture was stirred further for 6 hrs at room temperature. After evaporation of the solvent under reduced pressure, the residue was dissolved in diethyl ether (40 mL) and filtered through Celite. The ether solution was washed with water, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography on silica gel using petroleum ether/ ethyl acetate (15:1 \rightarrow 10:1) as eluent to afford the titled compound. Yield: 2.83 g (100%) as yellow oil.⁶ ¹H NMR (300 MHz, CDCl₃) δ 0.25 (9H, s), δ 5.96 (1H, d, J = 12.3 Hz), 6.88 (1H, d, J = 12.3 Hz), 7.24 (1H, ddd, J = 6.6, 4.8, 1.2 Hz), 7.69 (1H, td, J = 6.4, 2.0 Hz), 8.46 (1H, d, J = 8.1 Hz), 8.60 (1H, d, J = 4.8 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 0.0, 103.3, 104.2, 111, 123.2, 136, 140.9, 149.6, 155.3; MS (EI) m/z (rel. intensity) 201 (M⁺, 0), 200 (base), 186 (60), 170 (17), 156 (20), 141

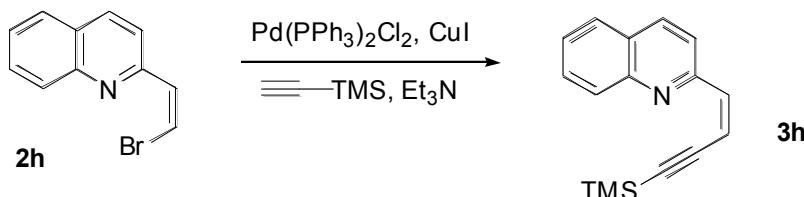
(10), 132 (35), 130 (6), 106 (6), 83 (5), 78 (5), 67 (5), 53 (5); HRMS calculated for $C_{12}H_{15}NSi$ 201.0974, found 201.0935; IR: (neat cm^{-1}) 3057, 2966, 2341, 2141, 2067, 1584, 1392, 1250, 1153, 1050, 1020, 986, 836.



(Z)-3-(4-Trimethylsilylbut-1-en-3-ynyl)pyridine 3f: Compound **3f** was synthesized analogously to **3e** from vinyl bromide **2f** (4.70 g, 25.6 mmol), trimethylsilylacetylene (4.34 mL, 30.7 mmol), CuI (0.97 g, 5.1 mmol), and Pd[(PPh₃)₂Cl₂] (0.36 g, 0.51 mmol) in 100 mL of triethylamine. The crude was purified by flash column chromatography on silica gel using 10:1 hexanes/ ethyl acetate and later increasing the polarity to 4:1 hexanes/ ethyl acetate to yield the titled compound (4.31 g, 84%) as yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 0.25 (9H, s), 5.84 (1H, d, J = 12 Hz), 6.63 (1H, d, J = 12 Hz), 7.28 (1H, dd, J = 8.1, 4.2 Hz), 8.42 (1H, dt, J = 8.1, 2.1 Hz), 8.50 (1H, d, J = 4.2), 8.86 (1H, s); ¹³C NMR (75 MHz, CDCl₃) δ 0.0, 103.2, 104, 110.2, 123.3, 132.4, 135.2, 136.3, 149.6, 150.7; MS (EI) m/z (rel. intensity) 201 (M^+ , 75), 186 (base), 170 (15), 156 (34), 142 (5), 130 (5), 115 (4), 103 (3), 85 (6), 67 (3), 55 (3), 43 (3); HRMS calculated for $C_{12}H_{15}NSi$ 210.0974, found 201.0968.

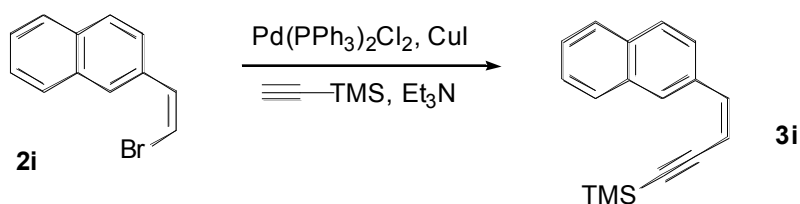


(Z)-4-(4-Trimethylsilylbut-1-en-3-ynyl)pyridine 3g: Compound **3g** was obtained using a procedure analogous to that of compound **3e** from vinyl bromide **2g**, trimethylsilylacetylene (3.60 mL, 25.4 mmol), CuI (0.20 g, 1.1 mmol), and Pd[(PPh₃)₂Cl₂] (0.30 g, 0.04 mmol) in 50 mL of Et₃N. The crude was purified by flash column chromatography on silica gel using 1:1 hexanes/ethyl acetate as the eluent. The product (1.92 g, 45%, 2 steps) was obtained as yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 0.24 (9 H, s), δ 5.92 (1H, d, *J* = 12 Hz), 6.59 (1H, d, *J* = 12 Hz), 7.71 (2H, d, *J* = 6.3 Hz), 8.59 (2H, d, *J* = 4.8 Hz), ¹³C NMR (75 MHz, CDCl₃) δ 0.05, 102.8, 105.8, 112.9; HRMS calculated for C₁₂H₁₅NSi 201.0974, found 201.0969.

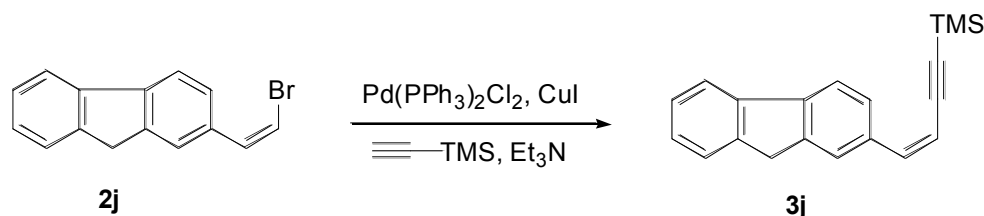


(Z)-2-(4-Trimethylsilylbut-1-en-3-ynyl)quinoline 3h: Compound **3h** was synthesized analogously to **3e** from vinyl bromide **2h** (5.92 g, 25.30 mmol), trimethylsilylacetylene (4.30 mL, 30.36 mmol), CuI (0.24 g, 1.27 mmol), and Pd[(PPh₃)₂Cl₂] (0.44 g, 0.06 mmol) in 100 mL of triethylamine. The residue was purified by flash column chromatography on silica gel using 15:1 hexanes/ ethyl acetate as eluent. The protected quinoline-enyne was obtained as a yellow solid (4.83 g, 76%). (mp = 49-51 °C); ¹H NMR (300 MHz, CDCl₃) δ 0.25, (9H, s), 6.10 (1H, d, *J* = 12.3 Hz), 7.06 (1H, d,

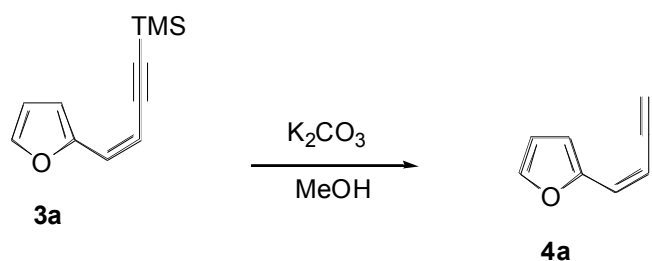
$J = 12.3$ Hz), 7.52 (1H, td, $J = 6.9, 1.2$ Hz), 7.70 (1H, td, $J = 6.9, 1.2$ Hz), 7.78 (1H, d, $J = 8.1$), 8.05 (1H, d, $J = 8.7$), 8.13 (1H, d, $J = 8.7$), 8.58 (1H, d, $J = 8.7$); ^{13}C NMR (75 MHz, CDCl_3) δ 0.00, 103.16, 104.51, 112.59, 120.93, 127.04, 127.66, 127.75, 129.73, 129.87, 135.96, 141.21, 148.22, 155.59; MS (EI) m/z (rel. intensity) 251 (M^+ , 48), 236 (35), 220 (14), 206 (20), 191 (24), 178 (base), 156 (11), 128 (10), 110 (9), 101 (4), 75 (5), 73 (89), 53 (5), 43 (4); HRMS calculated for $\text{C}_{16}\text{H}_{17}\text{NSi}$ 251.1130, found 251.1140; IR, (in CHCl_3 , cm^{-1}) 2871, 2360, 1597, 1251, 1007, 911, 840, 741.



(Z)-2-(4-Trimethylsilylbut-1-en-3-ynyl) naphthalene 3i: Compound **3i** was synthesized analogously to **3e** from vinyl bromide **2i** (6.88 g, 29.5 mmol), trimethylsilylacetylene (5.00 mL, 35.4 mmol), CuI (0.97 g, 1.5 mmol), and Pd[(PPh₃)₂Cl₂] (0.52 g, 0.74 mmol) in 80 mL of triethylamine. The residue was purified by flash column chromatography on silica gel using 9:1 petroleum ether/ ethyl acetate as eluent to give 5.58 g (75%) of the product as white solid. Spectroscopic data obtained for **3i** were consistent with that reported in the literature⁷. ^1H NMR (300 MHz, CDCl_3) δ 0.25 (9H, s), 5.51 (1H, d, $J = 12.0$ Hz), 6.52 (1H, d, $J = 12.0$ Hz), 7.21 (2H, m), 7.55 (3H, m), 7.78 (1H, d, $J = 8.4$ Hz), 8.07 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 0.03, 102.60, 104.05, 107.74, 107.77, 126.37, 126.58, 126.64, 127.77, 128.53, 128.61, 133.35, 133.53, 134.11, 139.98; MS (EI) m/z (rel. intensity) 250 (M^+ , 87), 235 (base), 219 (25), 205 (12), 189 (20), 178 (5), 165 (9), 152 (9), 117 (12); HRMS calculated for $\text{C}_{17}\text{H}_{18}\text{Si}$ 250.1178, found 250.1183.

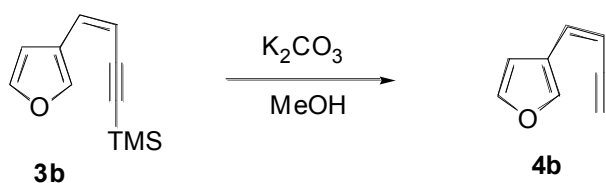


(Z)-4-(9H-fluoren-3-yl)-but-3-en-1-ynyl]-trimethylsilane 3j: Compound **3j** was synthesized analogously to **3e** from vinyl bromide **2j** (1.7 g, 6.3 mmol), trimethylsilylacetylene (0.743 g, 7.56 mmol), CuI (0.12 g, 0.63 mmol), and Pd[(PPh₃)₂Cl₂] (0.088 g, 0.126 mmol) in 75 mL of triethylamine. The residue was purified by flash column chromatography on silica gel using 15:1 hexanes/ ethyl acetate as eluent. The TMS-protected fluorine-enyne **3j** was obtained as a yellow solid (1.65 g, 97.6 % mp = 51-53 °C); ¹H-NMR (300 MHz, CDCl₃) _ 0.28 (s, 9H), 3.81 (2H, s), 5.73 (1H, d, *J* = 12Hz), 6.74 (1H, d, *J* = 12Hz), 7.31 (2H, m), 7.55 (1H, d, *J* = 7.8Hz), 7.76 (3H, m), 8.22 (1H, s); ¹³C-NMR (300 MHz, CDCl₃) _ 0.0, 36.9, 102.4, 104.5, 106.4, 119.6, 120.2, 125.0, 125.2, 126.9, 127.1, 128.5, 135.2, 140.4, 141.4, 142.4, 143.2, 143.9; MS (EI) *m/z* (relative intensity) 190 (M⁺, 100%), 175 (base), 192 (4), 191 (19), 160 (6), 147 (20), 145 (19), 115 (38), 105 (4), 87 (7), 75 (6); HRMS calculated for C₂₁H₂₀Si 300.1334, found 288.1338.

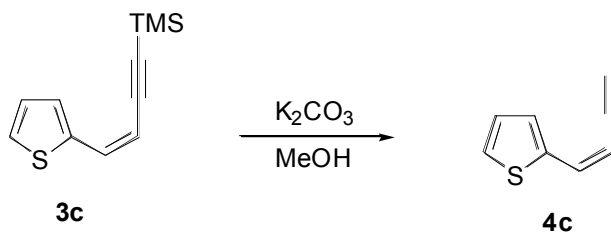


(Z)-2-(But-1-en-3-ynyl) furan 4a: To a solution of silylated enyne **3a** (3.0 g, 0.016 mol) in methanol (50 mL) was added potassium carbonate (3.30 g, 0.03 mol). The mixture

was stirred at room temperature for 2 hours. The mixture was then concentrated and the residue dissolved in diethyl ether and washed with water, dried over sodium sulfate and evaporated under reduced pressure. The crude was purified by flash column chromatography on silica gel using 20:1 hexanes/ ethyl acetate to yield the titled compound as yellow oil (1.80 g, 95 %). Spectroscopic data obtained for **4a** were identical to the literature data.⁸ ¹H NMR (300 MHz, CDCl₃) _ 3.4 (1H, s), 5.5 (1H, d, *J* = 12Hz), 6.3 (1H, m), 6.6 (1H, d, *J* = 12Hz), 7.0 (1H, d, *J* = 3.3Hz), 7.3 (1H, s).

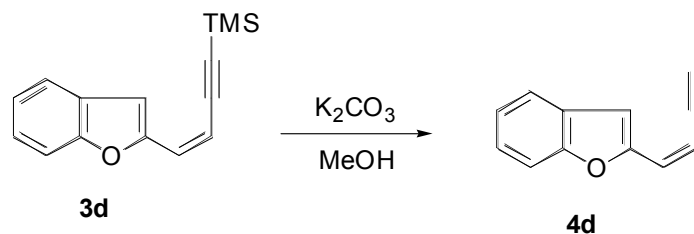


(Z)-3-(But-1-en-3-ynyl) furan 4b: Synthesized analogously to compound **4a** from **3b** (0.68 g, 0.0035 mol), and K₂CO₃ (0.98 g, 0.007 mol) for 1 hr. Due to the very unstable nature of this compound, a pure sample could not be obtained for spectroscopic experiments to be performed.

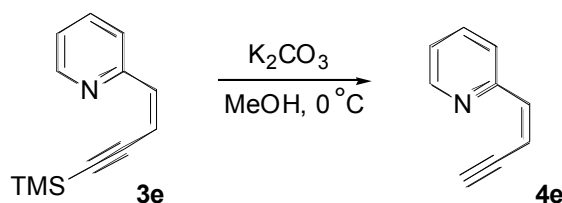


(Z)-2-(But-1-en-3-ynyl) thiophene 4c: Synthesized analogously to compound **4a** from **3c** (3.04 g, 14.7mmol), and K₂CO₃ (2.44 g, 17.7 mmol) for 2 hr. The crude was purified by flash column chromatography on silica gel using 20:1 hexanes/ ethyl acetate to yield the titled compound as yellow oil (1.31 g, 67 %). Spectral data for **4c** were identical to

the literature data.⁸ ^1H NMR (500 MHz, CDCl_3) δ 3.53 (1H, d, $J = 2.5$ Hz), 5.53 (1H, dd, $J = 11.5, 2.5$ Hz), 6.93 (1H, d, $J = 11.5$ Hz), 7.03 (1H, dd, $J = 5.0, 3.0$ Hz), 7.34 (2H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 82.4, 87.1, 103.8, 126.8, 127.3, 129.9, 134.1, 140.

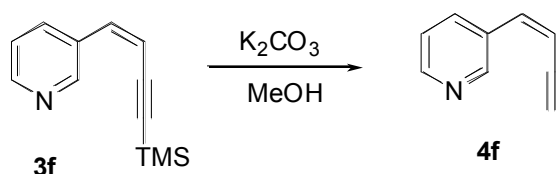


(Z)-2-But-1-en-3-ynylbenzofuran 4d: Synthesized analogously to compound **4a** from **3d** (0.97 g, 0.004 mol), and K_2CO_3 (0.84 g, 0.006 mol) for 12 hr. The crude was purified by flash column chromatography on silica gel using 20:1 hexanes/ ethyl acetate to yield the titled compound as a dark brown oil (0.37 g, 55 %). ^1H -NMR(300MHz, CDCl_3) δ 3.64 (1H, s), 5.79 (1H, d, $J = 11.7\text{Hz}$), 6.84 (1H, d, $J = 11.7\text{Hz}$), 7.34 (2H, m), 7.50 (2H, d, $J = 6\text{Hz}$), 7.64 (1H, d, $J = 7.2\text{Hz}$); ^{13}C -NMR (75MHz, CDCl_3) δ 82.0, 87.1, 107.5, 111.5, 121.7, 123.3, 125.6, 128.8, 129.3, 153.7, 154.4; MS (EI) m/z (relative intensity) 168 (M^+ , 100%), 139 (base), 138 (6), 113 (14), 94 (7), 86 (6), 66 (5), 50 (60, 18 (7); HRMS calculated for $\text{C}_{12}\text{H}_8\text{O}$ 168.0575, found 168.0582.

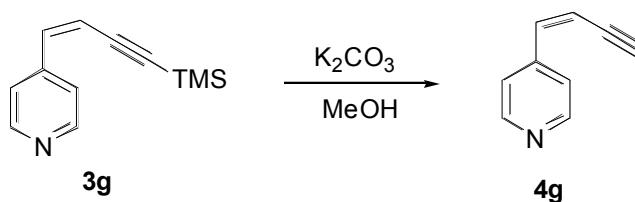


(Z)-2-(But-1-en-3-ynyl) pyridine 4e: A solution of silylated enyne **3e** (0.10 g, 0.49 mmol) in 50 mL of methanol was cooled to 0 °C and then potassium carbonate (0.14 g, 0.99 mmol) was added to the mixture. The mixture was stirred for 1 hr at the indicated

temperature, diluted with a saturated solution of sodium bicarbonate and extracted with hexanes. The organic layer was dried over sodium sulfate and concentrated on a rotary evaporator. The crude was used immediately. Due to the very unstable nature of this compound, a pure sample could not be obtained for spectroscopic experiments to be performed. However, this compound has been reported in the literature.⁶

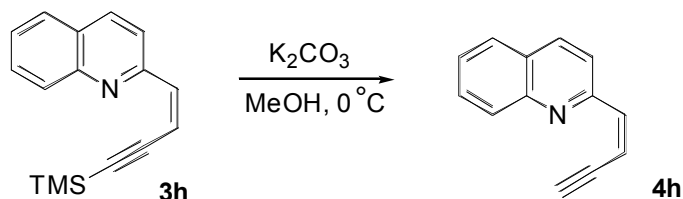


(Z) -3-(But-1-en-3-ynyl) pyridine 4f: Compound **4f** was synthesized analogously to **4a** from silyl capped enyne **3f** (0.40 g, 1.99 mmol), and K_2CO_3 (0.33 g, 2.39 mmol) in 40 mL of MeOH. The crude was purified by flash column chromatography on silica gel using 3:1 hexanes/ ethyl acetate to yield the product as a yellow oil (0.24 g, 95%). Spectral data obtained for **4f** were identical to the literature data.⁸ ^1H NMR (300 MHz, CDCl_3) δ 3.37 (1H, dd, $J = 2.7, 1.2$ Hz), 5.76 (1H, dd, $J = 12, 2.7$ Hz), 6.64 (1H, d, $J = 12$ Hz), 7.23 (1H, dd, $J = 8.1, 4.8$, Hz), 8.31 (1H, dt, $J = 8.1, 2.1$ Hz), 8.45 (1H, dd, $J = 4.8, 2.1$ Hz), 8.80 (1H, d, $J = 1.8$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 81.5, 85.7, 109.2, 123.4, 132, 137, 149.6, 150.5.

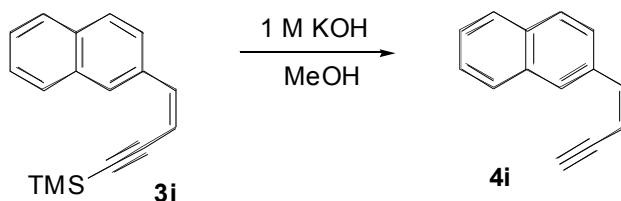


(Z) -4-(But-1-en-3-ynyl) pyridine 4g: Compound **4g** was synthesized analogously to **4a** from silyl capped enyne **3g** (0.10 g, 0.49 mmol), and K_2CO_3 (0.14 g, 0.99 mmol) in 40

mL of MeOH for 1 hr. Due to the very unstable nature of this compound, a pure sample could not be obtained for spectroscopic experiments to be performed.

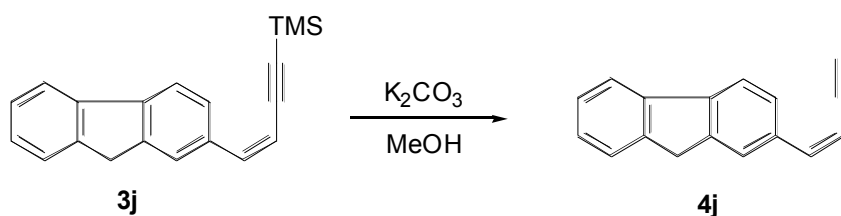


(Z)-2-(But-1-en-3-ynyl) quinoline 4h: Compound **4h** was synthesized analogously to **4e** from silyl capped enyne **3h** (0.2 g, 0.08 mmol), and K_2CO_3 (0.2 g, 0.16 mmol) in 40 mL of MeOH. The crude was purified by flash column chromatography on neutral alumina using 5:1 hexanes/ ethyl acetate as the eluent to yield the product as a brown solid (0.13 g, 94%). 1H NMR (300 MHz, $CDCl_3$) δ 3.47 (1H, dd, $J = 0.9, 2.7$ Hz), 6.08 (1H, dd, $J = 12.3, 2.7$ Hz), 7.12 (1H, d, $J = 12.3$ Hz), 7.54 (1H, td, $J = 6.9, 1.2$ Hz), 7.68 (1H, td, $J = 6.9, 1.2$ Hz), 7.80 (1H, d, $J = 8.4$ Hz), 8.06 (1H, d, $J = 8.4$ Hz), 8.16 (1H, d, $J = 8.4$ Hz), 8.51 (1H, d, $J = 8.4$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 81.50, 86.06, 111.48, 120.72, 127.12, 127.68, 127.76, 129.69, 129.93, 136.30, 142.01, 148.17, 155.23.



(Z)-2-(But-1-en-3-ynyl) naphthalene 4i: To (5.40 g, 21.58 mmol) of silylated naphthalyl enyne **3i** in 120 mL of methanol was added 40 mL of 1M potassium hydroxide solution. The mixture was stirred under nitrogen for 2 hrs. The mixture was diluted with 25 mL of saturated ammonium chloride, extracted with diethyl ether (4 x 30

mL) and dried over sodium sulfate. The crude was chromatographed on silica gel using petroleum ether as eluent. Yield; 3.70 g (100%) as a white solid. Spectral data for **4i** were consistent with the literature data.⁷ (mp = 84-87 °C); ¹H NMR (300 MHz, CDCl₃) _ 3.42 (1H, d, *J* = 2.7 Hz), 5.79 (1H, dd, *J* = 12.3, 2.7 Hz), 6.89 (1H, d, *J* = 12.3 Hz), 7.45 (2H, m), 7.85 (3H, m), 8.15 (1H, dd, *J* = 9.0, 1.8 Hz), 8.21 (1H, s); ¹³C NMR (75 MHz, CDCl₃) _ 82.36, 84.54, 106.84, 126.13, 126.47, 126.79, 127.86, 128.06, 128.66, 128.96, 133.39, 133.63, 133.95, 140.95.



(Z) 2-But-1-en-3-ynyl-9H-fluorene 4j: Compound **4j** was synthesized analogously to compound **4a** from silyl capped enyne **3j** (0.80 g, 2.0 mmol), K₂CO₃ (0.76 g, 5.0 mmol) in 30 mL of MeOH. The crude was purified by flash column chromatography on silica gel using hexanes to yield the product as a white solid (0.57 g, 97 %). ¹H NMR (300MHz, CDCl₃) _ 3.43 (1H, s), 3.92 (2H, s), 5.71 (1H, d, *J* = 12 Hz), 6.82 (1H, d, *J* = 12.3 Hz), 7.28 (2H, m), 7.44 (1H, d, *J* = 7.5 Hz), 7.79 (3H, m), 8.12 (1H, s); ¹³C-NMR (75MHz, CDCl₃) _ 37.1, 82.6, 84.4, 84.6, 105.6, 119.9, 120.4, 125.3, 127.1, 127.3, 128.2, 135.0, 141.1, 141.5, 142.6, 143.4, 144.1.

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