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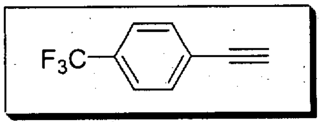
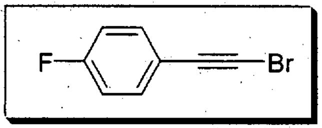
Experimental Section

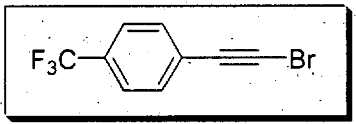
General. All reactions were run under a dry Ar atmosphere. Reactions were monitored by GC analysis of reaction aliquots. GC yields were determined by using a hydrocarbon as the internal standard. GC analysis was performed on HP6890 Gas Chromatography using HP-5 capillary column (30 m x 0.32 mm, 0.5 μM film) on a column packed with SE-30 on Chemosorb W. Column chromatography was carried out on 230–400 mesh silica gel. IR spectra were recorded Perkin-Elmer FT-IR 2000. ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini-200, Varian Inova-300 spectrometers. THF is distilled from sodium/benzophenone. $ZnBr_2$ was flame-dried under vacuum. $Pd(PPh_3)_4$,[a] (*E*)-chroloiodoethylene[b], (*E*)-bromoiodoethylene[c], 4-ethynyl-1-nitrobenzene[d], 4-ethynyl-1-methoxybenzene[d], 4-ethynyl-1-fluorobenzene[d], 4-(2′-bromoethynyl)-toluene[e] were prepared as reported in the literature. The starting materials were purchased from commercial sources and used as received.



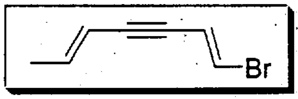
4-Ethynyl-1-trifluoromethylbenzene[f]: To a solution of lithium acetylide, ethylenediamine complex (2.1 g of 90 wt%, 20 mmol) in THF (5 mL), was added anhydrous $ZnBr_2$ (5.0 g, 22 mmol) in THF (11 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. 4-Trifluoromethyl-1-iodobenzene (4.6 g, 17 mmol) and $Pd(PPh_3)_4$ (323 mg, 2 mol%) were added to the reaction mixture at 0 °C, which was then stirred at 25 °C overnight. The reaction mixture was quenched with aqueous NH_4Cl, extracted with ether, dried over $MgSO_4$, and concentrated. Blub-to-blub distillation afforded 1.67 g (58%) of the title product as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 3.17 (s, 1 H), 7.55 (s, 4 H) ppm ; ^{13}C NMR ($CDCl_3$) δ 79.57, 82.19, 123.83 (q, J = 267.0 Hz), 125.26 (q, J = 3.8 Hz, 2C), 125.96, 130.62 (q, J = 32.7 Hz), 132.40 (2C) ppm.



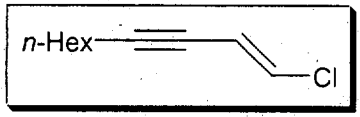
4-(2′-Bromoethynyl)-1-fluorobenzene[g]**: Representative Procedure for the Synthesis of Alkynylbromide**: To a solution of 4-ethynyl-1-fluorobenzene (110 mg, 0.92 mmol) in THF (4 mL) was added *n*-BuLi (0.40 mL of 2.5 M hexane solution, 1.0 mmol) at –78 °C. The reaction mixture was stirred at this temperature for 30 min, treated with *N*-bromosuccinimide (178 mg, 1.0 mmol), gradually warmed to 25 °C, and then stirred overnight. The reaction mixture was quenched with aqueous NH_4Cl, extracted with ether, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, pentane) afforded 145 mg (79 %) of the title product as a white solid: ^1H NMR ($CDCl_3$) δ 6.9–7.1 (m, 2 H), 7.3–7.5 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ 49.54 (d, $J = 2.0$ Hz), 79.00, 115.62 (d, $J = 22.2$ Hz, 2C), 118.75 (d, $J = 3.5$ Hz), 133.89 (d, $J = 8.1$ Hz, 2C), 162.66 (d, $J = 250.3$ Hz) ppm.



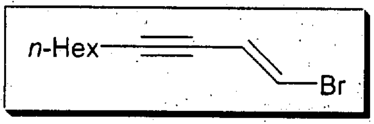
4-(2′-Bromoethynyl)-1-trifluoromethylbenzene: The title compound was prepared from 4-ethynyl-1-trifluoromethylbenzene (141 mg, 0.83 mmol) and *N*-bromosuccinimide (178 mg, 1.0 mmol). Purification by column chromatography (silica gel, pentane) afforded 131 mg (65 %) of the product as a white solid: ^1H NMR ($CDCl_3$) δ 7.4–7.7 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$) δ 52.97, 78.82, 123.81 (q, $J = 272.0$ Hz), 125.28 (q, $J = 3.7$ Hz, 2C), 126.48, 130.45 (q, $J = 32.7$ Hz), 132.28 ppm.



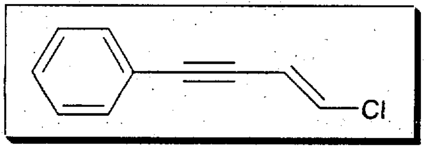
1-Bromo-1, 5-heptadien-3-yne: To a 0.5 M solution of ethynylmagnesium bromide in THF (50 mL, 25 mmol) was added at 0 °C $ZnBr_2$ (5.6 g, 25 mmol) in THF (25 mL). The reaction mixture was stirred for 30 min., then (*E*)-1-bromopropene (1.81 g, 15 mmol) and $Pd(PPh_3)_4$ (345 mg, 2 mol%) were added. After stirring at 25 °C overnight, the reaction mixture was first treated with water (0.14 g, 8 mmol) and then distilled to another flask cooled at –78 °C. The distillate was warmed to 25 °C, and then cooled to –78 °C. *n*-BuLi (6 mL of 2.5 M hexane solution, 15 mmol) was added at –78 °C. The reaction mixture was stirred at –78 °C for 30 min., treated with a solution of anhydrous $ZnBr_2$ (3.4 g, 15 mmol) in THF (15 mL), and warmed to 0 °C. (*E*)-Bromoiodoethylene (3.50 g, 15 mmol) and $Pd(PPh_3)_4$ (345 mg, 2 mol%) were added to the reaction mixture at 0 °C which was then stirred at 25 °C for 1 h. The reaction mixture was quenched with aqueous NH_4Cl, extracted with ether, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, pentane) afforded 1.85 g (72%) of the title product as a colorless liquid: ^1H NMR ($CDCl_3$) δ 1.83 (dd, J = 6.8, 1.6 Hz, 3H), 5.5-5.7 (m, 1 H), 6.23 (dq, J = 15.7, 6.8 Hz, 1 H), 6.33 (dd, J = 14.0, 2.2 Hz, 1H), 6.67 (d, J = 14.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.82, 84.21, 90.56, 110.31, 117.50, 117.70, 140.84; HRMS calcd for C_7H_7Br 169.9731, found 169.9735.



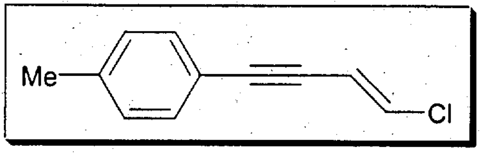
(*E*)-1-Chloro-1-decen-3-yne[h]: **Representative Procedure for the Synthesis of Haloenyne Derivatives:** To a solution of 1-octyne (1.1 g, 10 mmol) in THF (15 mL) was added *n*-BuLi (4.0 mL of 2.5 M hexane solution, 10 mmol) at –78 °C. The reaction mixture was stirred at –78 °C for 30 min., treated with a solution of anhydrous $ZnBr_2$ (3.0 g, 13 mmol) in THF (10 mL), and warmed to 0 °C. (*E*)-Chloroiodoethylene (1.9 g, 10 mmol) and $Pd(PPh_3)_4$ (231 mg, 2 mol%) were added to the reaction mixture at 0 °C, which was then stirred at 25 °C for 1 h. The reaction mixture was quenched with aqueous NH_4Cl, extracted with ether, dried over anhydrous $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, pentane) afforded 1.46 g (86%) of the title product as a colorless liquid: ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 6.8 Hz, 3 H), 1.2–1.6 (m, 8 H), 2.27 (td, J = 7.0, 2.3 Hz, 2 H), 5.89 (dt, J = 13.6, 2.3 Hz, 1 H), 6.40 (d, J = 13.6 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$) δ 13.99, 19.38, 22.52, 28.46, 28.54, 31.30, 75.65, 93.43, 114.30, 128.63 ppm.



(*E*)-1-Bromo-1-decen-3-yne[i]: The title compound was prepared from 1-octyne (0.9 mL, 6.0 mmol) and (*E*)-bromoiodoethylene (1.4 g, 6.0 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 94% yield. Purification by column chromatography (silica gel, pentane) afforded 0.96 g (74 %) of the title product as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 6.8 Hz, 3 H), 1.2–1.6 (m, 8 H), 2.24 (td, J = 6.9, 2.3 Hz, 2 H), 6.15 (dt, J = 14.0, 2.3 Hz, 1 H), 6.54 (d, J = 14.0 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$) δ 14.00, 19.40, 22.50, 28.35, 28.52, 31.28, 77.19, 93.23, 116.85, 118.04 ppm; *E* / *Z* ratio is 95 : 5 based on ^{13}C NMR; IR (neat) 2930, 2858, 2332, 2217 cm^{-1}; MS (CI, 70 eV) m/z (relative intensity) 273 (43), 271 (38), 216 (M$^+$, 31), 214 (M$^+$ 31), 192 (35), 191 (100), 149 (32), 147 (30), 135 (98).

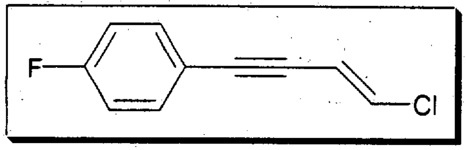


(*E*)-1-Chloro-4-phenyl-1-buten-3-yne[i]**:** The title compound was prepared from phenylacetylene (1.1 mL, 10.0 mmol) and (*E*)-chloroiodoethylene (1.88 g, 10.0 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 89% yield. Purification by column chromatography (silica gel, pentane) afforded 1.31 g (81%) of the title product as a white solid: ^{1}H NMR ($CDCl_3$) δ 6.12 (d, J = 13.5 Hz, 1 H), 6.58 (d, J = 13.5 Hz, 1 H), 7.25–7.35 (m, 3 H), 7.35–7.45 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ 84.37, 91.93, 113.81, 122.58, 128.31 (2C), 128.55, 130.08, 131.46 (2C) ppm.

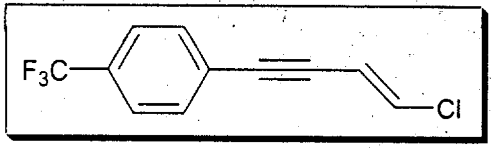


(*E*)-1-Chloro-4-(4′-toluenyl)-1-buten-3-yne: The title compound was prepared from 4-ethynyltoluene (0.63 mL, 5.0 mmol) and (*E*)-chloroiodoethylene (1.13 g, 6.0

mmol). Purification by column chromatography (silica gel, pentane) afforded 0.80 g (4.5 mmol, 90%) of the title product as a white solid: ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3 H), 6.13 (d, *J* = 13.6 Hz, 1 H), 6.58 (d, *J* = 13.6 Hz, 1 H), 7.11 (d, *J* = 8.1 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ 21.48, 83.76, 92.14, 113.97, 119.51, 129.13 (2C), 129.67, 131.38 (2C), 138.81 ppm; IR (nujol) 3076, 3028, 2205 cm^{-1}; HRMS calcd for $C_{11}H_9Cl$ 176.0393, found 176.0393.

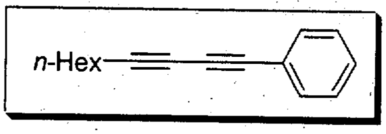


(*E*)-1-Chloro-4-(4′-fluorophenyl)-1-buten-3-yne: The title compound was prepared from 4-ethynyl-1-fluorobenzene (0.84 g, 7.0 mmol) and (*E*)-chloroiodoethylene (1.32 g, 7.0 mmol). Purification by column chromatography (silica gel, pentane) afforded 1.1 g (86%) of the title product as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 6.10 (dd, *J* = 1.7, 13.6 Hz, 1 H), 6.57 (dd, *J* = 2.1, 13.6 Hz, 1 H), 6.9–7.0 (m, 2 H), 7.3–7.4 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ 84.10 (d, *J* = 1.5 Hz), 90.83, 113.60, 115.57 (d, *J* = 22.2 Hz, 2C), 118.67 (d, *J* = 3.5 Hz), 130.18, 133.32 (d, *J* = 8.6 Hz, 2C), 162.57 (d, *J* = 250.3 Hz) ppm; IR (neat) 2973, 2209 cm^{-1}; MS (CI, 70 eV) m/z (relative intensity) 182 (M$^+$+2, 35), 180 (M$^+$, 100), 145 (86), 125 (48), 75 (15).

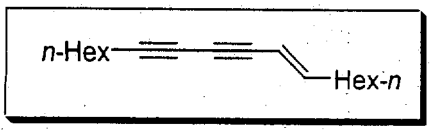


(*E*)-1-Chloro-4-(4′-trifluoromethylphenyl)-1-buten-3-yne: The title compound was prepared from 4-ethynyl-1-trifluoromethylbenzene (0.68 g, 4.0 mmol) and (*E*)-chloroiodoethylene (0.75 g, 4.0 mmol). Purification by column chromatography (silica gel, pentane) afforded 0.77 g (84%) of the title product as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 6.12 (d, *J* = 13.6 Hz, 1 H), 6.65 (d, *J* = 13.6 Hz, 1 H), 7.4–7.6 (m, 5 H) ppm; ^{13}C NMR ($CDCl_3$) δ 86.64, 90.34, 113.36, 123.87 (q, *J* = 271.9 Hz), 125.25 (q, *J* = 3.7 Hz, 2C), 126.44, 130.30 (q, *J* = 33.2 Hz), 131.51, 131.69 (2C) ppm; IR (neat) 3076, 2208

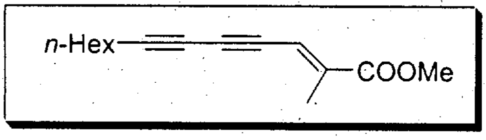
cm^{-1}; MS (CI, 70 eV) m/z (relative intensity) 289 (31), 287 (100), 275 (12), 273 (39), 232 (18), 231 (17), 230 (M^+, 56).



1-Phenyl-deca-1, 3-diyne[k]: **Representative Procedure for the Pd-Catalyzed Synthesis of Conjugated Diynes from Chloroenyne Derivatives (Method A):** To a solution of (*E*)-1-chloro-1-decen-3-yne (171 mg, 1.0 mmol) in THF (3 mL) was added *n*-BuLi (0.8 mL of 2.5 M hexane solution, 2.0 mmol) at –78 °C. The reaction mixture was stirred first at –78 °C for 30 min and then at –30 °C for 30 min, treated with a solution of anhydrous $ZnBr_2$ (270 mg, 1.2 mmol) in THF (1 mL), and warmed to 0 °C. Iodobenzene (204 mg, 1.0 mmol) and $Pd(PPh_3)_4$ (23 mg, 2 mol%) were added to the reaction mixture at 0 °C, which was then stirred at 25 °C for 3 h. Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 93% yield. The reaction mixture was quenched with aqueous NH_4Cl, extracted with ether, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, pentane) afforded 152 mg (72%) of the title product as a colorless liquid: ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 6.8 Hz, 3 H), 1.2–1.6 (m, 8 H), 2.34 (t, J = 6.9 Hz, 2 H), 7.2–7.6 (m, 5 H) ppm; ^{13}C NMR ($CDCl_3$) δ 14.00, 19.55, 22.48, 28.21, 28.53, 31.26, 65.04, 74.42, 74.64, 84.82, 122.11, 128.27 (2C), 128.72, 132.43 (2C) ppm; IR (neat) 2245 cm^{-1}. **Representative Procedure for the Pd-Catalyzed Synthesis of Conjugated Diynes from Bromoenyne Derivatives (Method B):** To a solution of (*E*)-1-bromo-1-decen-3-yne (215 mg, 1.0 mmol) in THF (3 mL) was added LDA (1.1 mL of 2.0 M heptane/ethylbenzene solution, 2.2 mmol) at -78 °C. The reaction mixture was stirred at –78 °C for 30 min, treated with a solution of anhydrous $ZnBr_2$ (270 mg, 1.2 mmol) in THF (1 mL), and warmed to 0 °C. Iodobenzene (204 mg, 1.0 mmol) and $Pd(PPh_3)_4$ (23 mg, 2 mol%) were added to the reaction mixture at 0 °C, which was then stirred at 25 °C for 1 h. The reaction mixture was quenched with aqueous NH_4Cl, extracted with ether, dried over anhydrous $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, pentane) afforded 189 mg (90%) of the title compound.

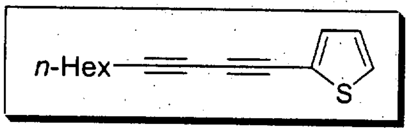


(*E*)-7-Octadecen-9, 11-diyne: Method A: The title compound was prepared from (*E*)-1-chloro-1-decen-3-yne (128 mg, 0.75 mmol) and (*E*)-1-iodo-1-octene (179 mg, 0.75 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 84% yield. Purification by column chromatography (silica gel, pentane) afforded 130 mg (71%) of the product as a colorless liquid: ^{1}H NMR (CDCl$_3$) δ 0.8–1.0 (m, 6 H), 1.2–1.6 (m, 16 H), 2.06 (q, *J* = 6.8 Hz, 2 H), 2.26 (t, *J* = 6.9 Hz, 2 H), 5.43 (d, *J* = 16.5 Hz, 1H), 6.22 (m, 1 H) ppm; ^{13}C NMR (CDCl$_3$) δ 13.96, 19.47, 22.48, 22.53, 28.27, 28.51, 28.71, 31.26, 31.58, 33.17, 65.22, 72.87, 73.88, 83.43, 108.63, 147.99 ppm; IR (neat) 2929, 2858, 2361, 2339, 2232 cm^{-1}; MS (CI, 70 eV) m/z (relative intensity) 244 (M$^+$, 14), 215 (5), 131 (23), 117 (24), 91 (36), 43 (100); HRMS calcd for $C_{18}H_{28}$ 244.2191, found 244.2189.

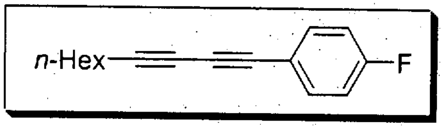


(*E*)-2-Methyl-2-tridecen-4, 6-diynoic Acid Methyl Ester: Method A: The title compound was prepared from (*E*)-1-chloro-1-decen-3-yne (128 mg, 0.75 mmol) and (*E*)-3-bromo-2-methylacrylic acid methyl ester (134 mg, 0.75 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 84% yield. Purification by column chromatography (silica gel, 95/5 pentane/ether) afforded 126 mg (72%) of the title product as a yellow liquid: ^{1}H NMR (CDCl$_3$) δ 0.85 (t, *J* = 6.7 Hz, 3 H), 1.2–1.6 (m, 8 H), 2.04 (s, 3 H), 2.32 (t, *J* = 7.0 Hz, 2 H), 3.71 (s, 3 H), 6.57 (s, 1 H) ppm; ^{13}C NMR (CDCl$_3$) δ 13.90, 15.51, 19.65, 22.40, 28.01, 28.47, 31.17, 52.02, 64.84, 70.96, 65.22, 86.06, 89.05, 118.68, 141.63, 167.04 ppm; IR (neat) 2932, 2860, 2361, 2339, 2229, 1719 cm^{-1}; MS (CI, 70 eV) m/z (relative intensity) 232 (M$^+$, 12), 217 (5), 203 (6), 115 (26), 91 (39), 77 (50), 43 (100); HRMS calcd for $C_{15}H_{20}O_2$ 232.1463, found 232.1465. **Method B**: The title compound was prepared from (*E*)-1-bromo-1-

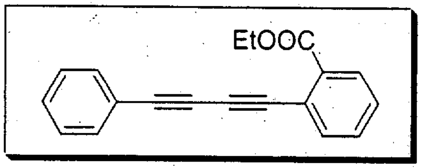
decen-3-yne (215 mg, 1 mmol) and (*E*)-3-bromo-2-methylacrylic acid methyl ester (178 mg, 1 mmol). Purification by column chromatography (silica gel, 95/5 pentane/ether) afforded 154 mg (88%) of the title compound.



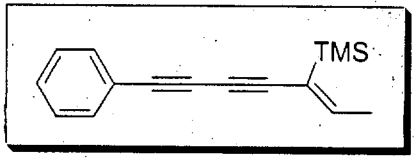
1-(2′-Thiophenyl)-deca-1, 3-diyne: **Method A:** The title compound was prepared from (*E*)-1-chloro-1-decen-3-yne (128 mg, 0.75 mmol) and 2-iodothiophene (158 mg, 0.75 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 93% yield. Purification by column chromatography (pentane) afforded 130 mg (80%) of the title product as a yellow liquid: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 6.8 Hz, 3 H), 1.2–1.6 (m, 8 H), 2.34 (t, *J* = 6.9 Hz, 2 H), 6.9 – 7.0 (m, 1 H), 7.2–7.3 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ 14.00, 19.65, 22.48, 28.15, 28.51, 31.24, 64.95, 67.62, 78.52, 87.05, 122.43, 126.93, 127.90, 133.73 ppm; IR (neat) 2930, 2859, 2361, 2339, 2232 cm^{-1}; MS (CI, 70 eV) m/z (relative intensity) 216 (M^{+}, 100), 201 (14), 187 (72), 173 (56), 145 (91), 45 (40); HRMS calcd for $C_{14}H_{16}S$ 216.0973, found 216.0968.



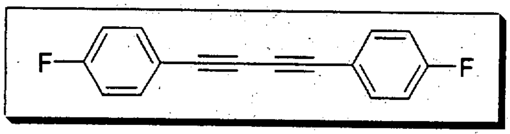
1-(4′-Fluorophenyl)-deca-1, 3-diyne: **Method A:** The title compound was prepared from (*E*)-1-chloro-1-decen-3-yne (85 mg, 0.50 mmol) and 4-fluoro-1-iodobenzene (111 mg, 0.50 mmol). Purification by column chromatography (silica gel, pentane) afforded 88 mg (72%) of the title product as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 6.8 Hz, 3 H), 1.2–1.6 (m, 8 H), 2.35 (t, *J* = 6.9 Hz, 2 H), 6.9–7.1 (m, 2 H), 7.4– 7.5 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ 13.98, 19.52, 22.48, 28.19, 28.53, 31.26, 64.90 (d, *J* = 1.0 Hz), 73.54, 74.17 (d, *J* = 2.0 Hz), 84.83, 115.67 (d, *J* = 22.2 Hz, 2C), 118.21 (d, *J* = 3.0 Hz), 134.40 (d, *J* = 8.6 Hz, 2C), 162.73 (d, *J* = 250.8 Hz) ppm; IR (neat) 2246, 2155 cm^{-1}; MS (CI, 70 eV) m/z (relative intensity) 285 (100), 229 (M^++1, 35), 228 (M^+, 29); HRMS calcd for $C_{16}H_{17}F$ 228.1314, found 228.1312.



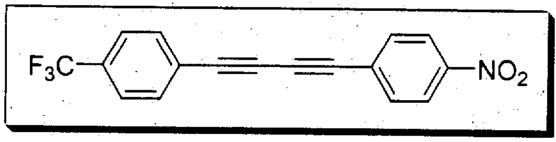
Ethyl 2-(4-Phenylbuta-1, 3-diynyl)-benzoate: Method A: The title compound was prepared from (*E*)-1-chloro-4-phenyl-1-buten-3-yne (122 mg, 0.75 mmol) and ethyl 2-iodobenzoate (207 mg, 0.75 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 78% yield. Purification by column chromatography (silica gel, 95/5 pentane/ether) afforded 150 mg (73%) of the title product as a yellow liquid: ^{1}H NMR ($CDCl_3$) δ 1.43 (t, *J* = 7.1 Hz, 3 H), 4.42 (q, *J* = 7.1 Hz, 2 H), 7.0–8.0 (m, 9 H) ppm; ^{13}C NMR ($CDCl_3$) δ 14.06, 61.24, 74.02, 78.68, 79.82, 83.04, 121.60, 122.23, 128.29 (2C), 128.55, 129.13, 130.45, 131.60, 132.34 (2C), 132.79, 134.89, 165.52 ppm; IR (neat) 2983, 2936, 2215 cm^{-1}; MS (CI, 70 eV) m/z (relative intensity) 277 (M^++2, 31), 275 (M^+, 100), 247 (4); HRMS calcd for $C_{19}H_{14}O_2$ 274.0994, found 2274.0990.



(*E*)-(1-Ethylidene-5-phenylpenta-2, 4-diynyl)-trimethylsilane: Method A: The title compound was prepared from (*E*)-1-chloro-4-phenyl-1-buten-3-yne (122 mg, 0.75 mmol) and (*E*)-(1-iodo-propenyl)-trimethylsilane (178 mg, 0.75 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 85% yield. Purification by column chromatography (silica gel, pentane) afforded 127 mg (71%) of the title product as a yellow liquid: ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 9 H), 2.02 (d, *J* = 6.6 Hz, 3 H), 6.38 (q, *J* = 6.6 Hz, 1 H), 7.25–7.35 (m, 3 H), 7.45–7.55 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ -1.92 (3C), 19.05, 74.49, 81.39, 81.55, 82.46, 122.40, 124.48, 128.33 (2C), 128.75, 132.25 (2C), 150.33 ppm; IR (neat) 2958, 2904, 2204, 2128 cm^{-1}; MS (CI, 70 eV) m/z (relative intensity) 297 (6), 296 (26), 295 (100), 255 (13), 239 (M^{+}+1, 6), 73 (5); HRMS calcd for $C_{16}H_{18}Si$ 238.1178, found 238.1175.

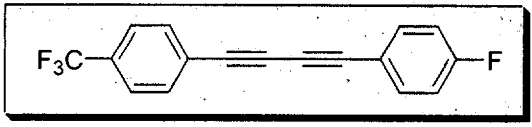


1, 4-Bis(4′-fluorophenyl)-buta-1, 3-diyne^{l}: Method A: The title compound was prepared from (*E*)-1-chloro-4-(4′-fluorophenyl)-1-buten-3-yne (135 mg, 0.75 mmol) and 4-fluoro-1-iodobenzene (200 mg, 0.90 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 86% yield. Purification by column chromatography (silica gel, pentane) afforded 131 mg (73%) of the title product as a white solid: ^{1}H NMR ($CDCl_3$) δ 7.0–7.2 (m, 4 H), 7.4–7.6 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$) δ 73.53 (2C), 80.41 (2C), 115.89 (d, J = 22.2 Hz, 4C), 117.78 (2C), 134.53 (d, J = 8.6 Hz, 4C), 163.05 (d, J = 251.8 Hz, 2C) ppm; IR (nujol) 2144 cm^{-1}; MS (CI, 70 eV) m/z (relative intensity) 391 (5), 333 (6), 331 (22), 296 (17), 295 (100), 257 (8), 239 (M^{+}+1, 6). **Representative Procedure for the Synthesis of Conjugated Diynes by Cadiot-Chodkiewicz Reaction (Method C):** To a solution of 4-ethynyl-1-fluorobenzene (90 mg, 0.75 mmol) in EtOH (4 mL) was added hydroxylamine hydrochloride (42 mg, 0.60 mmol), cuprous chloride (7.0 mg, 0.071 mmol), and *n*-propylamine (79 mg, 1.4 mmol). 4-(2′-Bromoethynyl)-1-fluorobenzene (149 mg, 0.75 mmol) in EtOH (1 mL) was added to the reaction mixture, which was then stirred at 25 °C overnight. Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 57% yield. The reaction mixture was quenched with water, extracted with ether, dried over $MgSO_4$, and concentrated. Purification on column chromatography (silica gel, pentane) afforded 86 mg (48%) of the title product.

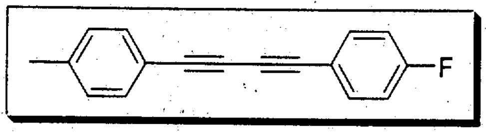


1-(4′-Nitrophenyl)-4-(4″-trifluoromethylphenyl)-buta-1, 3-diyne: Method A: The title compound was prepared from (*E*)-1-chloro-4-(4′-trifluoromethylphenyl)-1-

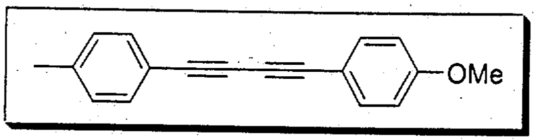
buten-3-yne (173 mg, 0.75 mmol) and 1-iodo-4-nitrobenzene (187 mg, 0.75 mmol). Purification by column chromatography (silica gel, 3/1 pentane/CH_2Cl_2) afforded 205 mg (87%) of the title product as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 7.6–7.7 (m, 6 H), 8.2–8.3 (m, 2 H) ppm; ^{13}C NMR (CD_3COCD_3) δ 75.71, 77.86, 81.19, 82.75, 124.70 (2C), 125.84 , 126.57 (q, J = 3.8 Hz, 2C), 127.07 (q, J = 204.1 Hz), 131.70 (q, J = 32.4 Hz), 134.10 (2C), 134.54 (2C), 139.82, 148.99 ppm; IR (nujol) 3107, 2361, 2341, 2211 cm^{-1}; MS (CI, 70 eV) m/z (relative intensity) 317 (M^++2, 13) 316 (M^++1, 100); HRMS calcd for $C_{17}H_8F_3NO_2$ 315.0507, found 315.0502.



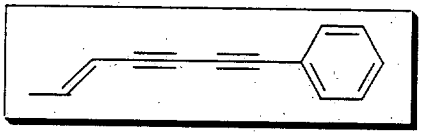
1-(4′-Fluorophenyl)-4-(4″-trifluoromethylphenyl)-buta-1, 3-diyne: Method A: The title compound was prepared from (*E*)-1-chloro-4-(4′-trifluoromethylphenyl)-1-buten-3-yne (173 mg, 0.75 mmol) and 4-fluoro-1-iodobenzene (200 mg, 0.90 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 78% yield. Purification by column chromatography (silica gel, pentane) afforded 157 mg (73%) of the title product as a white solid: ^{1}H NMR ($CDCl_3$) δ 7.0–7.2 (m, 2 H), 7.4–7.7 (m, 6 H) ppm; ^{13}C NMR ($CDCl_3$) δ 73.24, 76.05, 79.78, 81.72, 115.97 (d, J = 22.2 Hz, 2C), 117.49 (d, J = 3.5 Hz), 123.75 (q, J = 275.0 Hz), 125.37 (q, J = 3.7 Hz, 2C), 125.58, 131.18 (q, J = 32.7 Hz), 132.69 (2C), 134.65 (d, J = 8.6 Hz, 2C), 163.22 (d, J = 251.8 Hz) ppm; IR (nujol) 2361, 2340, 2217 cm^{-1}; MS (CI, 70 eV) m/z (relative intensity) 346 (11), 345 (100), 331 (6), 289 (3), 288 (M^+, 11); HRMS calcd for $C_{17}H_8F_4$ 288.0562, found 288.0558. **Method C**: The title compound was prepared from 4-ethynyl-1-fluorobenzene (90 mg, 0.75 mmol) and 4-(2′-bromoethynyl)-1-trifluoromethylbenzene (187 mg, 0.75 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound 40% yield, along with 1,4-bis(4′-trifluoromethylphenyl)-buta-1, 3-diyne as a by-product in 24 % yield. Purification by column chromatography (silica gel, pentane) afforded 82 mg (38%) of the title product.



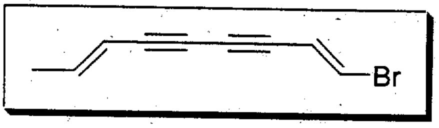
1-(4′-Fluorophenyl)-4-(4″-toluenyl)-buta-1, 3-diyne: **Method A**: **(I)** The title compound was prepared from (*E*)-1-chloro-4-(4′-toluenyl)-1-buten-3-yne (115 mg, 0.65 mmol) and 4-fluoro-1-iodobenzene (160 mg, 0.72 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 93% yield. Purification by column chromatography (silica gel, pentane) afforded 133 mg (88%) of the title product as a white solid: ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3 H), 6.9–7.1 (m, 2 H), 7.0–7.2 (m, 2 H), 7.35–7.45 (m, 2 H), 7.45–7.55 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ 21.57, 73.15, 73.87, 80.09, 81.85, 115.81 (d, J = 22.2 Hz, 2C), 118.01 (d, J = 3.0 Hz), 118.52, 129.21 (2C), 132.39 (2C), 134.44 (d, J = 8.6 Hz, 2C), 139.65, 162.92 (d, J = 251.3 Hz) ppm; IR (nujol) 3000, 2359, 2214, 2141 cm^{-1}; HRMS calcd for $C_{17}H_{11}F$ 234.0845, found 234.0836. **(II)** The title compound was prepared from (*E*)-1-chloro-4-(4′- fluorophenyl)-1-buten-3-yne (68 mg, 0.38 mmol) and 4-iodotoluene (98 mg, 0.45 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 81% yield. **Method C**: **(I)** The title compound was prepared from 4-ethynyl-1-fluorobenzene (90 mg, 0.75 mmol) and 4-(2′-bromoethynyl)-toluene (146 mg, 0.75 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 55% yield, along with 1, 4-bis(4′-toluenyl)-buta-1, 3-diyne and 1,4-bis(4′-fluorophenyl)-buta-1, 3-diyne as by-products, in 26 and 8% yields, respectively. Purification by column chromatography (silica gel, pentane) afforded 60 mg (34%) of the title product. **(II)** The title compound was prepared from 4-ethynyltoluene (44 mg, 0.38 mmol) and 4-(2′-bromoethynyl)-1-fluorobenzene (74 mg, 0.38 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 48% yield, along with 1, 4-bis(4′-fluorophenyl)-buta-1, 3-diyne as a by-product in 16% yield.



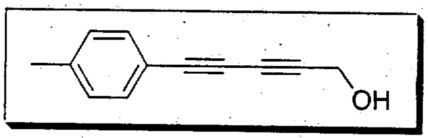
1-(4′- Methoxyphenyl)-4-(4″- toluenyl)-buta-1, 3-diyne: Method A: The title compound was prepared from (*E*)-1-chloro-4-(4′-toluenyl)-1-buten-3-yne (90 mg, 0.51 mmol) and 4-iodoanisole (129 mg, 0.55 mmol). Analysis of an aliquot of the reaction mixture by GC indicated the formation of the title compound in 76% yield. Purification by column chromatography (silica gel, pentane) afforded 93 mg (74%) of the title product as a white solid: ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3 H), 3.81 (s, 3 H), 6.8–6.9 (m, 2 H), 7.1–7.2 (m, 2 H), 7.35–7.5 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$) δ 21.58, 55.30, 72.85, 73.53, 81.30, 81.45, 113.82, 114.12 (2C), 118.86, 129.18 (2C), 132.33 (2C), 134.05 (2C), 139.37, 160.28 ppm; IR (nujol) 2361, 2215, 2138 cm^{-1}; MS (CI, 70 eV) m/z (relative intensity) 304 (23), 303 (100), 247 (M^{+}+1, 28); HRMS calcd for $C_{18}H_{14}O$ 246.1045, found 246.1039. **Method C**: The title compound was prepared from 4-ethynyl-1-methoxybenzene (99 mg, 0.75 mmol) and 4-(2′-bromoethynyl)-toluene (146 mg, 0.75 mmol). Purification by column chromatography (silica gel, 95/5 pentane/ether) afforded 62 mg (34%) of the title product, along with 1, 4-bis(4′-toluenyl)-buta-1, 3-diyne 17 mg (20%) as a by-product. NMR data of 1, 4-bis(4′-toluenyl)-buta-1, 3-diyne: ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 6 H), 7.1–7.2 (m, 4 H), 7.35–7.5 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$) δ 21.60 (2C), 73.44 (2C), 81.52 (2C), 118.78 (2C), 129.20 (4C), 132.38 (4C), 139.48 (2C) ppm.



(2*E*)-7-Phenyl-2-hepten-4, 6-diyne[k]: Method B: The title compound was prepared from (1*E*, 5*E*)-1-bromo-1, 5-heptadien-3-yne (171 mg, 1.0 mmol) and iodobenzene (204 mg, 1.0 mmol). Purification by column chromatography (silica gel, pentane) afforded 129 mg (78%) of the title compound as a liquid: ^{1}H NMR ($CDCl_3$) δ 1.90 (dd, J = 6.9, 1.8 Hz, 3 H), 5.67 (dq, J = 15.8, 1.8 Hz, 1 H), 6.42 (dt, J = 15.8, 6.9 Hz, 1 H), 7.3–7.6 (m, 5 H) ppm; ^{13}C NMR (CDCl$_3$) δ 18.89, 72.19, 74.09, 80.38, 80.77, 109.76, 121.88, 128.31, 128.93, 132.32, 143.80 ppm.



(1*E*, 7*E*)-1-Bromo-1, 7-nonadien-3, 5-diyne: Method B: The title compound was prepared from (1*E*, 5*E*)-1-bromo-1, 5-heptadien-3-yne (171 mg, 1.0 mmol) and (*E*)-bromoiodoethylene (233 mg, 1.0 mmol). Purification by column chromatography (silica gel, pentane) afforded 138 mg (71%) of the title compound as a colorless liquid: ^{1}H NMR (CDCl$_3$) δ 1.82 (dd, J = 6.9, 1.8 Hz, 3 H), 5.56 (ddq, J = 15.8, 1.8, and 1 Hz, 1 H), 6.27 (dd, J = 14.2, 1 Hz, 1 H), 6.37 (dq, J = 15.8, 6.9 Hz, 1 H), 6.86 (d, J = 14.2 Hz, 1 H) ppm; ^{13}C NMR (CDCl$_3$) δ 18.94, 71.92, 76.35, 76.72, 82.03, 109.64, 116.71, 121.75, 144.39 ppm; IR (neat) 2928, 2361, 2202, 1550, 1438, 1197, 946, 913 cm^{-1}; HRMS calcd for C_9H_7Br 193.9731, found 193.9735.



5-*p*-Tolylpenta-2, 4-diyn-1-ol^m: To a solution of (*E*)-1-chloro-4-(4′-toluenyl)-1-buten-3-yne (132 mg, 0.75 mmol) in THF (3 mL) was added *n*-BuLi (0.66 mL of 2.5 M hexane solution, 1.65 mmol) at –78 °C. The reaction mixture was first stirred at –78 °C for 30 min and then at –30 °C for 30 min, treated with paraformaldehyde (68 mg, 2.3 mmol). The reaction mixture was gradually warmed to 25 °C, stirred overnight. The reaction mixture was quenched with water, extracted with ether, dried over Na$_2$SO$_4$, and concentrated. Purification by column chromatography (silica gel, 3/1 pentane/ether) afforded 115 mg (90% yield) of the title compound as a white solid: ^{1}H NMR (CDCl$_3$) δ 2.32 (s, 3 H), 2.8–3.0 (brs, 1 H), 4.42 (s, 2 H), 7.05–7.15 (m, 2 H), 7.3–7.4 (m, 2 H) ppm; ^{13}C NMR (CDCl$_3$) δ 21.45, 51.36, 70.34, 72.57, 78.72, 80.13, 118.10, 129.07 (2C), 132.41 (2C), 139.62 ppm.

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