Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for:

(*Z*)-Selective cross-dimerization of arylacetylenes with silylacetylenes catalyzed by vinylideneruthenium complexes

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Experimental Section

General Procedure and Materials. All manipulations were performed under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was purified by passing successively through the columns of an activated copper catalyst (BASF, R3-11) and P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a Varian Mercury 300 (^{1}H NMR, 300.11 MHz; ^{13}C NMR, 75.46 MHz) spectrometer. Chemical shifts are reported in δ (ppm), referenced to the ^{1}H (of residual protons) and ^{13}C signals of deuterated solvents. Mass spectra were measured with a Shimadzu QP-5000 GC-mass spectrometer (EI, 70 eV). GLC analysis was performed on a Shimadzu GC-14B instrument equipped with a FID detector and a capillary column CBP-1 (25 m × 0.25 mm).

Dichloromethane was dried over CaH_2 and distilled prior to use. $RuCl_2(=C=CHY)L_2$ (L = PPr^i_3, Y = Ph (**1**-Pr^i); L = PCy_3, Y = Ph (**1**-Cy); L = PPh_3, Y = *t*-Bu (**1**-Ph)) were prepared according to literatures.[1] 2-Ethynyltoluene (**2c**), 4-ethynylanisole (**2d**), 2-ethynylthiophene (**2e**), and 2-ethynylfluorene (**2f**) were synthesized by Sonogashira coupling reactions of the corresponding iodoarenes with (trimethylsilyl)acetylene followed by desilylation with K_2CO_3 in MeOH.[2] All other chemicals were obtained from commercial suppliers and used without further purification.

Homo-Dimerization of Arylacetylenes. A typical procedure (run 2 in Table 1) was reported in ref. 3. Identification data of the following compounds were consistent with those reported: (*Z*)-1,4-diphenyl-1-buten-3-yne ((*Z*)-**5a**),[4] (*Z*)-1,4-di(4-tolyl)-1-buten-3-yne ((*Z*)-**5b**),[5] (*Z*)-1,4-di(2-tolyl)-1-buten-3-yne ((*Z*)-**5c**),[5] (*Z*)-1,4-bis(2-fluorenyl)-1-buten-3-yne ((*Z*)-**5f**),[4] 2,4-bis(trimethylsilyl)-1-buten-3-yne (*gem*-**6m**).[6]

Identification Data for (*Z*)-1,4-Bis(4-methoxyphenyl)-1-buten-3-yne ((*Z*)-5d). Orange oil. ^{1}H NMR ($CDCl_3$): δ 7.92–7.87 (m, 2H, Ar), 7.45–7.41 (m, 2H, Ar), 6.93–6.86 (m, 4H, Ar), 6.60 (d, *J* = 11.9 Hz, 1H, ArC*H*=), 5.79 (d, *J* = 11.9 Hz, 1H, =CHC≡C), 3.84, 3.83 (each s, 6H, OMe). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.6, 159.5 (each s, Ar), 137.3 (s, Ar*C*H=), 132.8, 130.1, 114.0, 113.6 (each s, Ar), 105.1 (s, =*C*HC≡C), 95.4, 87.4 (each s, C≡C), 55.3, 55.2 (each s, OMe). MS, *m*/*z* (rel intensity, %): 264 (M^+, 100), 249 (34), 234 (9), 221 (22), 206 (18), 190 (12), 178 (30), 152 (14), 132 (13), 94 (16), 76 (18), 63 (13). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.55; H, 6.23.

(*Z*)-1,4-Bis(2-thienyl)-1-buten-3-yne ((*Z*)-5e). Red oil. ^{1}H NMR ($CDCl_3$): δ 7.38–7.33 (m, 3H, Ar), 7.29–7.27 (m, 1H, Ar), 7.06, 7.04 (each dd, *J* = 4.2, 0.9 Hz, 2H, Ar), 6.96 (dt, *J* = 11.4 Hz, 1H, ArC*H*=), 5.77 (d, *J* = 11.4 Hz, 1H, =CHC≡C). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 140.8 (s, Ar*C*H=), 132.2, 131.8, 129.7, 127.8, 127.2, 126.4, 123.5 (each s, Ar), 104.1 (s, =CHC≡C), 92.4, 92.2 (each s, C≡C). MS, *m*/*z* (rel intensity, %): 216 (M^+, 100), 184 (21), 171 (63), 108 (14), 86 (17), 69 (20). Anal. Calcd for $C_{12}H_8S_2$: C, 66.63; H, 3.73. Found: C, 67.03; H, 3.78.

Cross-Dimerization between Arylacetylenes and Silylacetylenes. A typical procedure is as follows (run 3 in Table 2). To a solution of 4-ethynyltoluene (**2a**) (116 mg, 1.00 mmol), *N*-methylpyrrolidine (17 mg, 0.20 mmol), and anisole (31 mg, internal standard for GLC analysis) in CH_2Cl_2 (1.0 mL) were successively added (trimethylsilyl)acetylene (**3m**) (0.98 g, 10 mmol) and **1**-Pr^i (30 mg, 0.050 mmol) at room temperature. The reaction mixture was stirred for 16 h. GLC analysis revealed the formation of **4am**, **5a** and **6m** in 93, 5 (based on **2a**) and 24% (based on **3m**) yields, respectively. Volatile materials were removed by pumping. The dark red oily

residue was purified by flash column chromatography over silica gel eluted with hexane. Homo-dimer **6m** was eluted first. Then the eluate containing cross-dimer **4am** was obtained. Evaporation of the eluate afforded **4am** having a (*Z*):(*E*):*gem* ratio of 93:0:7 (167 mg, 78%) as a colorless oil. Further chromatographic purification gave geometrically pure (*Z*)-**4am** (107 mg, 50%). All the reactions in Tables 2 and 3 were similarly carried out. Cross-dimerization products **4** were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, mass spectrometry and elemental analysis, except for **4an** (run 6 in Table 3), which could not be separated from **5a** and **6n** by column chromatography.

Identification Data for (*Z*)-1-(4-Tolyl)-4-trimethylsilyl-1-buten-3-yne ((*Z*)-4am). ^{1}H NMR ($CDCl_3$): δ 7.82, 7.17 (each d, *J* = 8.2 Hz, 4H, Ar), 6.63 (d, *J* = 12.1 Hz, 1H, ArC*H*=), 5.65 (d, *J* = 12.1 Hz, 1H, =CHC≡C), 2.37 (s, 3H, Me), 0.26 (s, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 139.8 (s, Ar*C*H=), 138.7, 133.7, 128.8 (each s, Ar), 106.1 (s, =*C*HC≡C), 104.0, 101.9 (each s, C≡C), 21.4 (s, Me), –0.2 (s, $SiMe_3$). MS, *m*/*z* (relative intensity, %): 214 (M^+, 51), 199 (100), 183 (37), 167 (14), 155 (14), 141 (9), 115 (10), 99 (25), 73 (9), 59 (10). Anal. Calcd for $C_{14}H_{18}Si$: C, 78.44; H, 8.46. Found: C, 78.09; H, 8.38.

(*Z*)-1-Phenyl-4-trimethylsilyl-1-buten-3-yne ((*Z*)-4bm). ^{1}H NMR ($CDCl_3$): δ 7.92–7.89 (m, 2H, Ph), 7.36–7.30 (m, 3H, Ph), 6.66 (d, *J* = 12.0 Hz, 1H, PhC*H*=), 5.71 (d, *J* = 12.0 Hz, 1H, =CHC≡C), 0.22 (s, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 139.8 (s, Ph*C*H=), 136.8, 128.8, 128.6, 128.1 (each s, Ph), 107.2 (s, =*C*HC≡C), 103.7, 102.2 (each s, C≡C), –0.3 (s, $SiMe_3$). MS, *m*/*z* (relative intensity, %): 200 (M^+, 39), 185 (100), 169 (17), 155 (14), 141 (10), 129 (10), 115 (10), 92 (10), 77 (7), 53 (27). Anal. Calcd for $C_{13}H_{16}Si$: C, 77.93; H, 8.05. Found: C, 77.81; H, 8.09.

(*Z*)-1-(2-Tolyl)-4-trimethylsilyl-1-buten-3-yne ((*Z*)-4cm). ^{1}H NMR ($CDCl_3$): δ 8.30–8.26 (m, 1H, Ar), 7.23–7.16 (m, 3H, Ar), 6.88 (d, *J* = 12.1 Hz, 1H, ArC*H*=), 5.76 (d, *J* = 12.1 Hz, 1H, =CHC≡C), 2.34 (s, 3H, Me), 0.21 (s, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.8 (s, Ar*C*H=), 136.5, 134.8, 130.0, 128.5, 128.1, 125.3 (each s, Ar), 107.9 (s, =*C*HC≡C), 103.5, 101.0

(each s, C≡C), 19.8 (s, Me), –0.3 (s, $SiMe_3$). MS, *m*/*z* (relative intensity, %): 214 (M^+, 69), 199 (96), 183 (98), 171 (29), 155 (46), 141 (46), 115 (24), 99 (36), 86 (15), 73 (100), 59 (27). Anal. Calcd for $C_{14}H_{18}Si$: C, 78.44; H, 8.46. Found: C, 78.33; H, 8.37.

(*Z*)-1-(4-Methoxyphenyl)-4-trimethylsilyl-1-buten-3-yne ((*Z*)-4dm). ^1H NMR ($CDCl_3$): δ 7.89–7.87 (m, 2H, Ar), 6.90–6.86 (m, 2H, Ar), 6.59 (d, *J* = 12.1 Hz, 1H, ArCH=), 5.59 (d, *J* = 12.1 Hz, 1H, =CHC≡C), 3.84 (s, 3H, OMe), 0.26 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.8 (s, Ar), 139.4 (s, Ph*C*H=), 130.3, 129.4, 113.4 (each s, Ph), 104.7 (s, =*C*HC≡C), 104.2, 101.4 (each s, C≡C), 55.3 (s, OMe), –0.2 (s, $SiMe_3$). MS, *m*/*z* (relative intensity, %): 230 (M^+ 81), 215 (100), 200 (5), 185 (30), 169 (12), 155 (14), 141 (25), 128 (9), 115 (16), 107 (36), 86 (9), 73 (28), 59 (18). Anal. Calcd for Calcd for $C_{14}H_{18}OSi$: C, 72.99; H, 7.88. Found: C, 72.70; H, 7.87.

(*Z*)-1-(2-Thienyl)-4-trimethylsilyl-1-buten-3-yne ((*Z*)-4em). ^1H NMR ($CDCl_3$): δ 7.34 (d, *J* = 5.0 Hz, 1H, Ar), 7.30 (d, *J* = 3.7 Hz, 1H, Ar), 7.03 (dd, *J* = 5.0, 3.7 Hz, 1H, Ar), 6.90 (d, *J* = 11.0 Hz, 1H, ArC*H*=), 5.56 (d, *J* = 11.0 Hz, 1H, =CHC≡C), 0.29 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.7 (s, Ar*C*H=), 133.3, 129.8, 127.0, 126.3 (each s, Ar), 105.2 (s, =*C*HC≡C), 104.5, 103.6 (each s, C≡C), 0.3 (s, $SiMe_3$). MS, *m*/*z* (relative intensity, %): 206 (M^+, 53), 191 (100), 165 (14), 147 (13), 115 (27), 95 (18), 75 (14). Anal. Calcd for $C_{11}H_{14}SSi$: C, 64.02; H, 6.84. Found: C, 63.78; H, 6.97.

(*Z*)-1-(2-Fluorenyl)-4-trimethylsilyl-1-buten-3-yne ((*Z*)-4fm). ^1H NMR ($CDCl_3$): δ 8.33 (br s, 1H, Ar), 7.84–7.75 (m, 3H, Ar), 7.59–7.55 (m, 1H, Ar), 7.43–7.31 (m, 2H, Ar), 6.75 (d, *J* = 11.9 Hz, 1H, ArCH=), 5.73 (d, *J* = 11.9 Hz, 1H, =CHC≡C), 3.92 (s, 2H, CH_2), 0.33 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.8, 143.1, 142.2, 141.3 (each s, Ar), 140.2 (s, Ar*C*H=), 135.1, 128.3, 127.0, 126.8, 125.0, 124.9, 120.1, 119.5 (each s, Ar), 106.3 (s, =*C*HC≡C), 104.3, 102.3 (each s, C≡C), 36.8 (s, CH_2), –0.2 (s, $SiMe_3$). MS, *m*/*z* (relative intensity, %): 288 (M^+ 100), 273 (54), 257 (23), 245 (25), 229 (15), 215 (40), 136 (85), 121 (14), 108 (9), 73 (26), 59 (12). Anal. Calcd for $C_{20}H_{20}Si$: C, 83.28; H, 6.99. Found: C, 83.44; H, 7.09.

(*Z*)-1-(4-Tolyl)-4-dimethylphenylsilyl-1-buten-3-yne ((*Z*)-4an). ^{1}H NMR ($CDCl_3$): δ 7.81 (d, *J* = 8.2 Hz, 2H, C_6H_4), 7.72–7.67 (m, 2H, SiPh), 7.44–7.38 (m, 3H, SiPh), 7.12 (d, *J* = 8.2 Hz, 2H, C_6H_4), 6.66 (d, *J* = 12.1 Hz, 1H, ArCH=), 5.70 (d, *J* = 12.1 Hz, 1H, =CHC≡C), 2.36 (s, 3H, MeC_6H_4), 0.51 (s, 6H, $SiMe_2$). MS, *m*/*z* (relative intensity, %): *m*/*z* 276 (M^+, 38), 261 (100), 245 (7), 215 (14), 183 (25), 159 (36), 130 (26), 105 (20), 91 (9), 77 (7).

(*Z*)-1-(4-Tolyl)-4-triisopropylsilyl-1-buten-3-yne ((*Z*)-4ao). ^{1}H NMR ($CDCl_3$): δ 7.88 (d, *J* = 8.1 Hz, 2H, C_6H_4), 7.14 (d, *J* = 8.1 Hz, 2H, C_6H_4), 6.60 (d, *J* = 12.1 Hz, 1H, ArCH=), 5.70 (d, *J* = 12.1 Hz, 1H, =C*H*C≡C), 2.36 (s, 3H, Me), 1.14 (apparent s, 21H, C*H*(CH_3)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 139.1 (s, Ar*C*H=), 138.6, 133.8, 128.8 (each s, Ar), 106.5 (s, =*C*HC≡C), 105.5, 98.8 (each s, C≡C), 21.4 (s, Me), 18.7 (s, CH(*C*H_3)$_2$), 11.4 (s, *C*H(CH_3)$_2$). MS, *m*/*z* (relative intensity, %): 298 (M^+, 19), 255 (67), 199 (53), 185 (73), 171 (37), 159 (21), 141 (13), 115 (9), 99 (84), 92 (42), 73 (24), 59 (100). Anal. Calcd for $C_{20}H_{30}Si$: C, 80.46; H, 10.13. Found: C, 80.19; H, 10.25.

Desilylation of (*Z*)-4am–fm. A typical procedure is as follows. To a solution of (*Z*)-**4am** (61 mg, 0.28 mmol) in MeOH (2.8 mL) was added K_2CO_3 (46 mg, 0.33 mmol). The mixture was stirred for 1 h and then quenched with water (*ca*. 2 mL). The mixture was extracted with ether (2 mL×3), and the combined organic layers were dried over anhydrous $MgSO_4$. After the drying agent was filtered off, the solution was concentrated to dryness to give a brown oil. The crude product was purified by silica gel column chromatography using hexane as an eluent to afford a yellow oil of (*Z*)-1-(4-tolyl)-1-buten-3-yne (38 mg, 96%). Desilylations of (*Z*)-**4bm**–**fm** were similarly carried out. Identification data of the following compounds were consistent with those reported: (*Z*)-1-phenyl-1-buten-3-yne,[7] (*Z*)-1-(4-methoxyphenyl)-1-buten-3-yne,[7] (*Z*)-1-(2-thienyl)-1-buten-3-yne.[8]

(*Z*)-1-(4-Tolyl)-1-buten-3-yne. ^{1}H NMR ($CDCl_3$): δ 7.77, 7.17 (each d, *J* = 7.9 Hz, 4H, Ar), 6.68 (d, *J* = 12.1 Hz, 1H, ArC*H*=), 5.62 (dd, *J* = 12.1, 2.7 Hz, 1H, =CHC≡C), 3.34 (d, *J* = 2.7 Hz, 1H, C≡CH), 2.36 (s, 3H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 140.5 (s, Ar*C*H=), 138.8, 133.4,

129.0, 128.7 (each s, Ar), 105.2 (s, =*C*HC≡C), 83.2, 82.2 (each s, C≡C), 21.4 (s, Me). MS, *m*/*z* (relative intensity, %): 141 (M^+–1, 100), 115 (44), 70 (15), 58 (14), 51 (12). Anal. Calcd for $C_{11}H_{10}$: C, 92.91; H, 7.09. Found: C, 92.83; H, 7.09.

(*Z*)-1-(2-Tolyl)-1-buten-3-yne. Pale yellow oil (93% yield). ^{1}H NMR ($CDCl_3$): δ 8.13–8.10 (m, 1H, Ar), 7.23–7.19 (m, 3H, Ar), 6.94 (d, *J* = 12.1 Hz, 1H, ArC*H*=), 5.74 (dd, *J* = 12.1, 2.7 Hz, 1H, =CHC≡C), 3.17 (d, *J* = 2.7 Hz, 1H, C≡CH), 2.33 (s, 3H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$): 139.0 (s, Ar*C*H=), 136.4, 130.1, 128.6, 128.0, 125.6 (each s, Ar), 107.3 (s, =*C*HC≡C), 82.8 (s, C≡C), 19.8 (s, Me). MS, *m*/*z* (relative intensity, %): 141 (M^+–1, 100), 115 (45), 70 (20), 58 (14), 51 (12). Anal. Calcd for $C_{11}H_{10}$: C, 92.91; H, 7.09. Found: C, 92.62; H, 7.17.

(*Z*)-1-(2-Fluorenyl)-1-buten-3-yne. Pale yellow solid (96% yield). ^{1}H NMR ($CDCl_3$):δ 8.13 (br s, 1H, Ar), 7.92–7.76 (m, 3H, Ar), 7.58–7.54 (m, 1H, Ar), 7.43–7.31 (m, 2H, Ar), 6.80 (dd, *J* = 12.1, 0.6 Hz, 1H, ArC*H*=), 5.70 (dd, *J* = 12.1, 2.7 Hz, 1H, =CHC≡C), 3.93 (s, 2H, CH_2), 3.44 (dd, *J* = 2.7, 0.6 Hz, C≡CH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 143.8, 143.2, 142.3, 141.2 (each s, Ar), 140.9 (s, Ar*C*H=), 134.7, 127.9, 127.0, 126.8, 125.1, 125.1, 120.1, 119.7 (each s, Ar), 105.4 (s, =*C*HC≡C), 84.3, 82.4 (each s, C≡C), 36.9 (s, CH_2). MS, *m*/*z* (relative intensity, %): 215 (M^+–1, 100), 189 (7), 163 (6), 107 (37), 94 (43). Anal. Calcd for $C_{17}H_{12}$: C, 94.41; H, 5.59. Found: C, 94.22; H, 5.60.

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References

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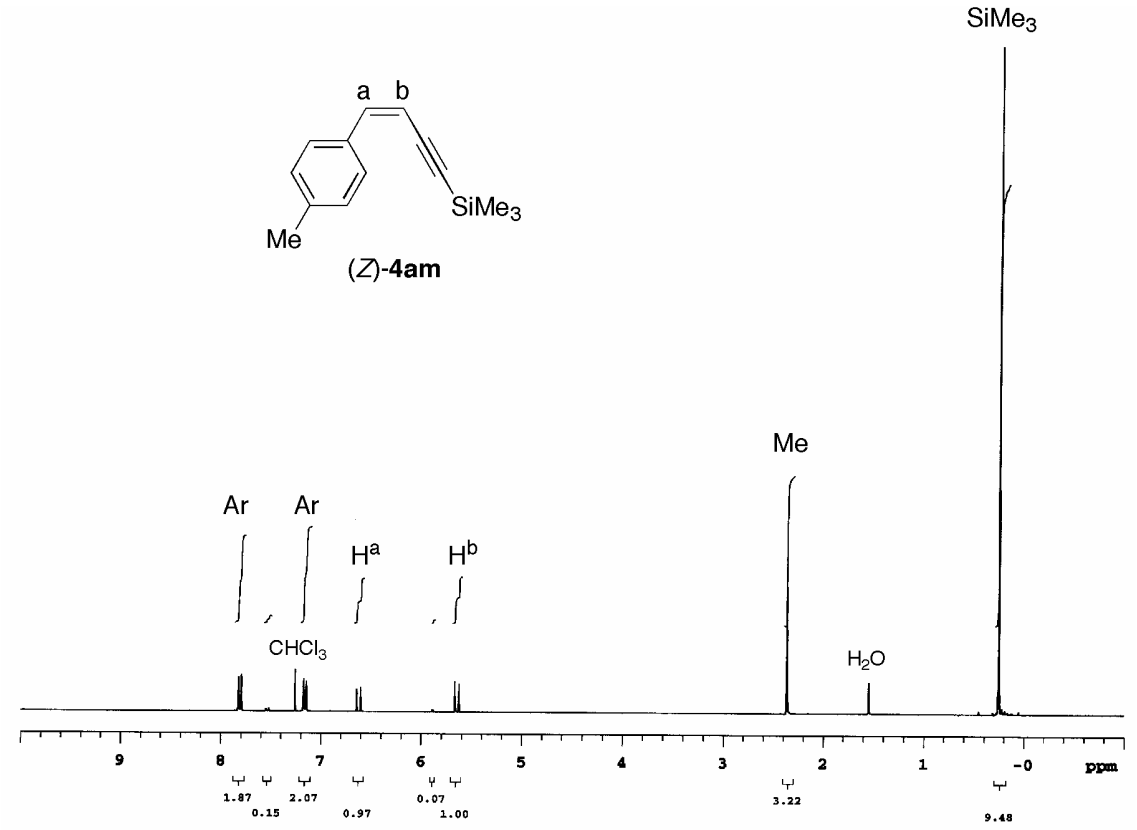

Figure S1. ^{1}H NMR spectrum of **4am** ((*Z*):(*E*):*gem* = 93:0:7) in $CDCl_3$ (300 MHz).

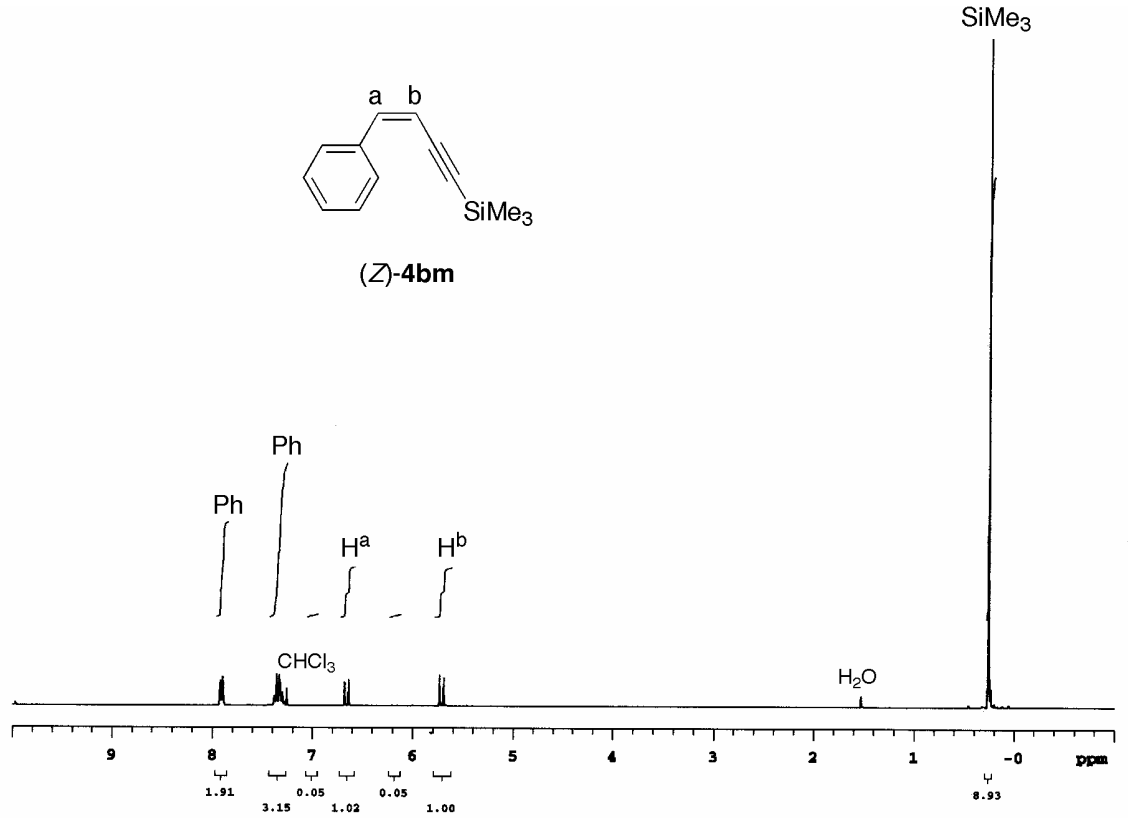

Figure S2. ^{1}H NMR spectrum of **4bm** ((*Z*):(*E*):*gem* = 95:5:0) in $CDCl_3$ (300 MHz).

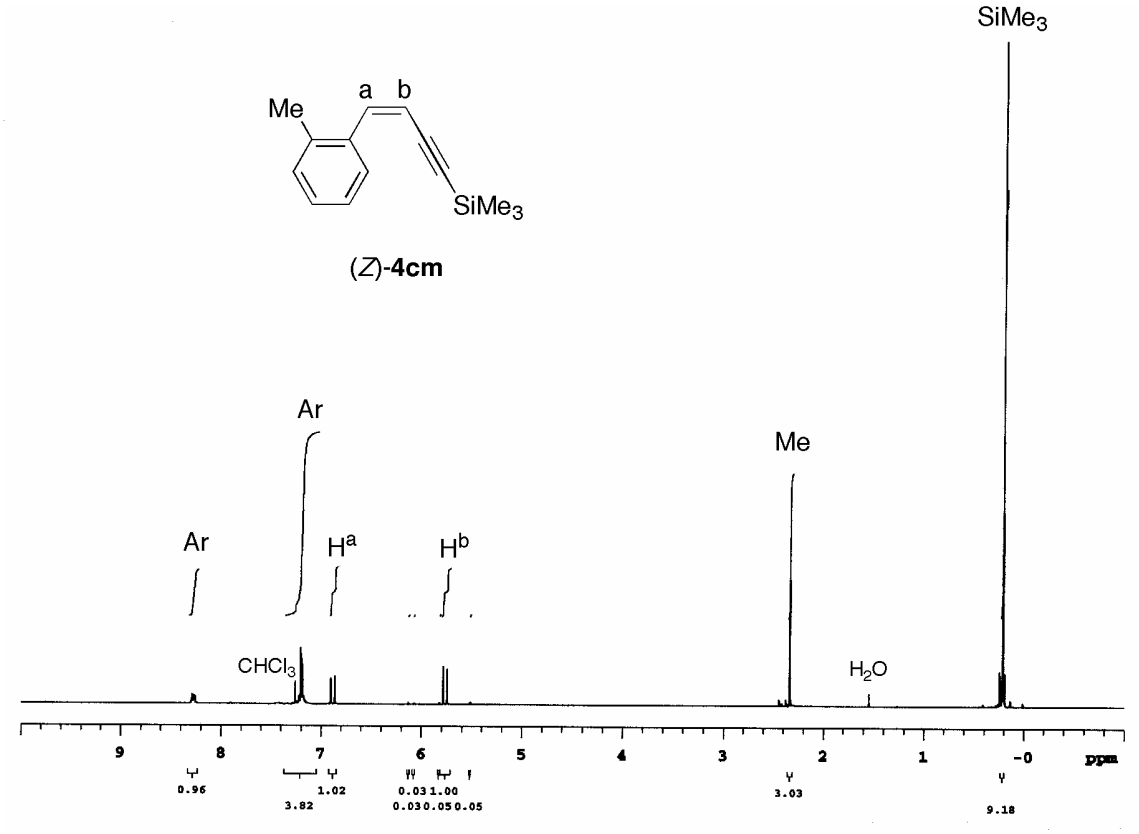

Figure S3. ^{1}H NMR spectrum of **4cm** ((*Z*):(*E*):*gem* = 90:5:5) in $CDCl_3$ (300 MHz).

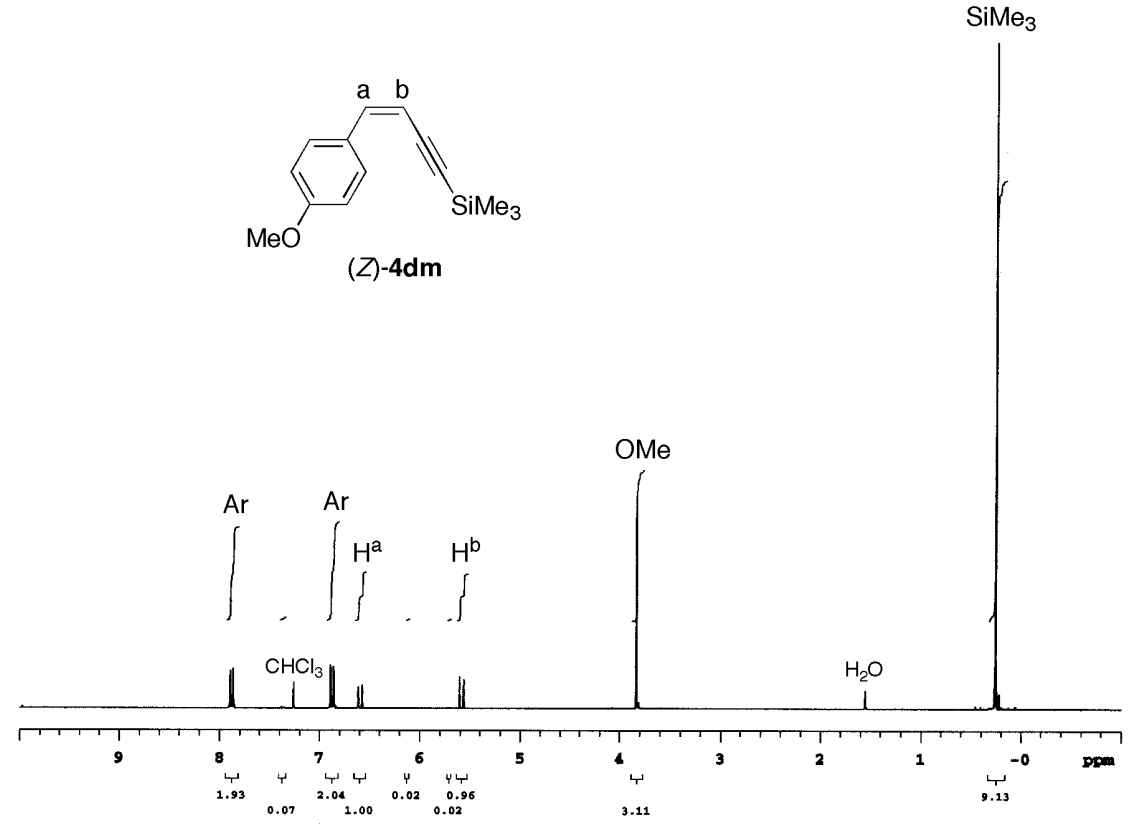

Figure S4. ^{1}H NMR spectrum of **4dm** ((*Z*):(*E*):*gem* = 98:0:2) in $CDCl_3$ (300 MHz).

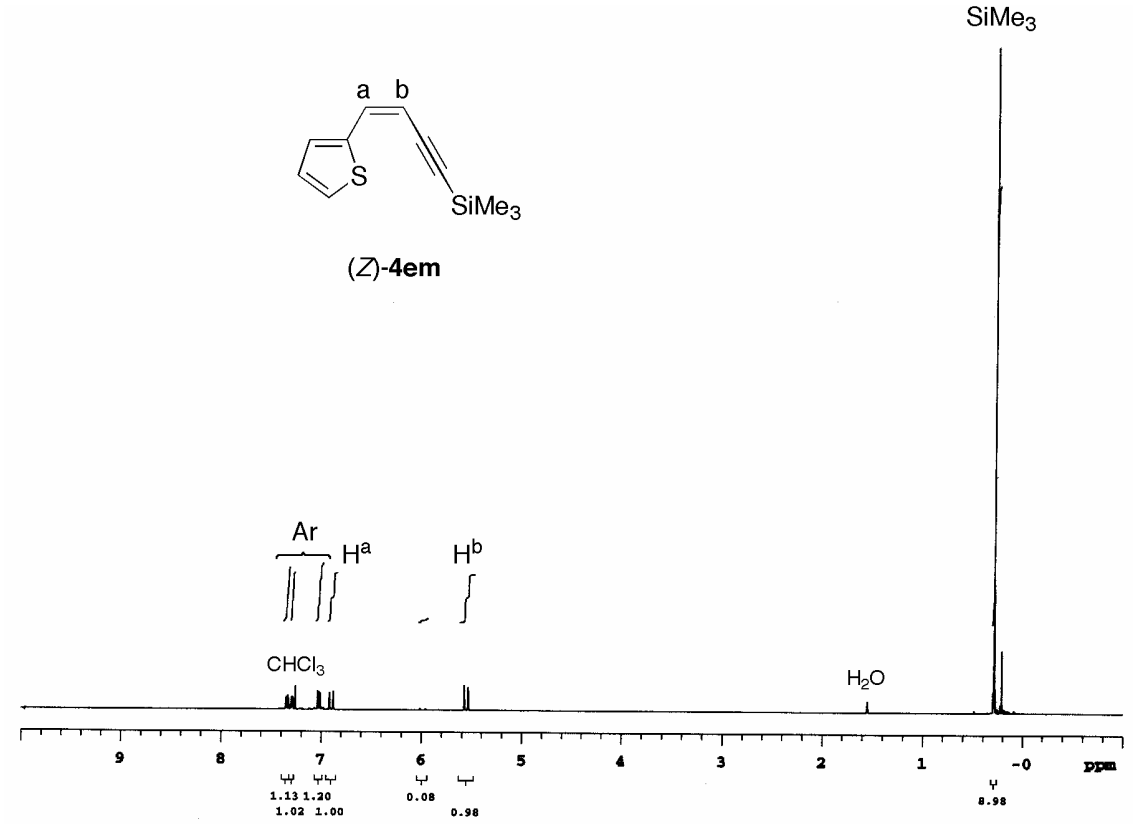

Figure S5. ^{1}H NMR spectrum of **4em** ((*Z*):(*E*):*gem* = 93:7:0) in $CDCl_3$ (300 MHz).

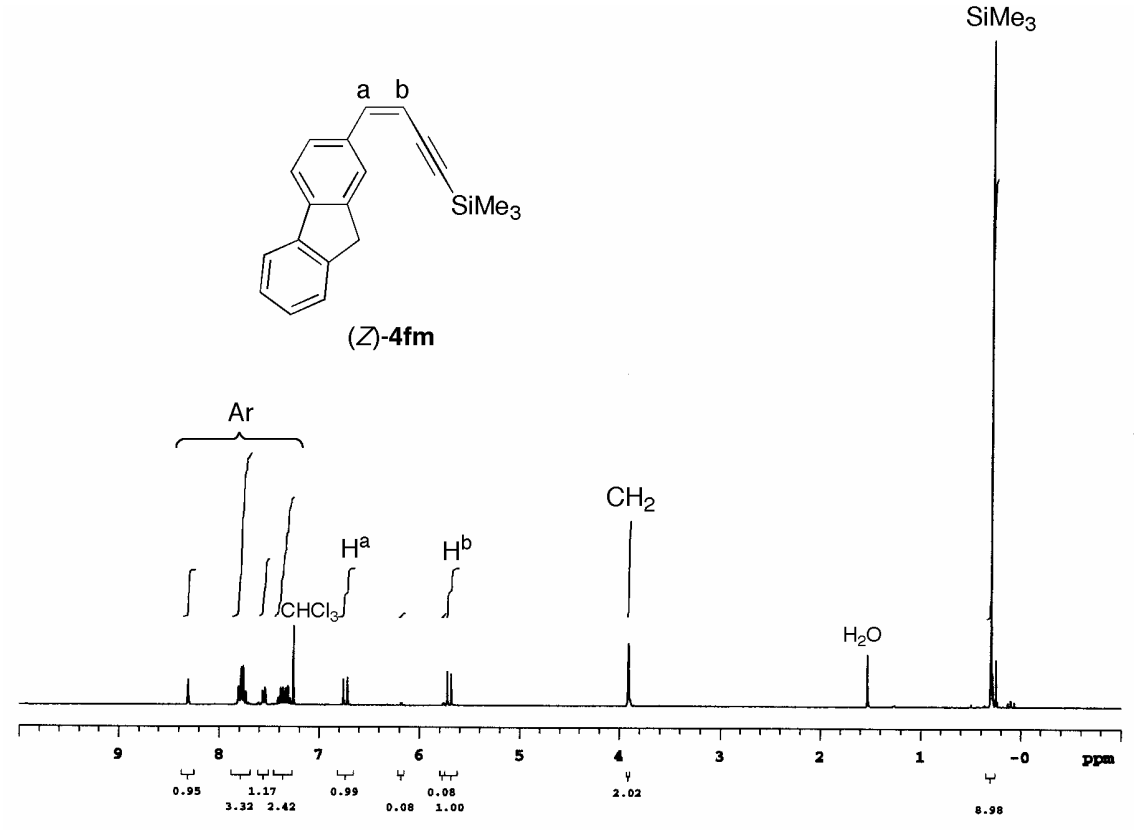

Figure S6. ^{1}H NMR spectrum of **4fm** ((*Z*):(*E*):*gem* = 93:0:7) in $CDCl_3$ (300 MHz).

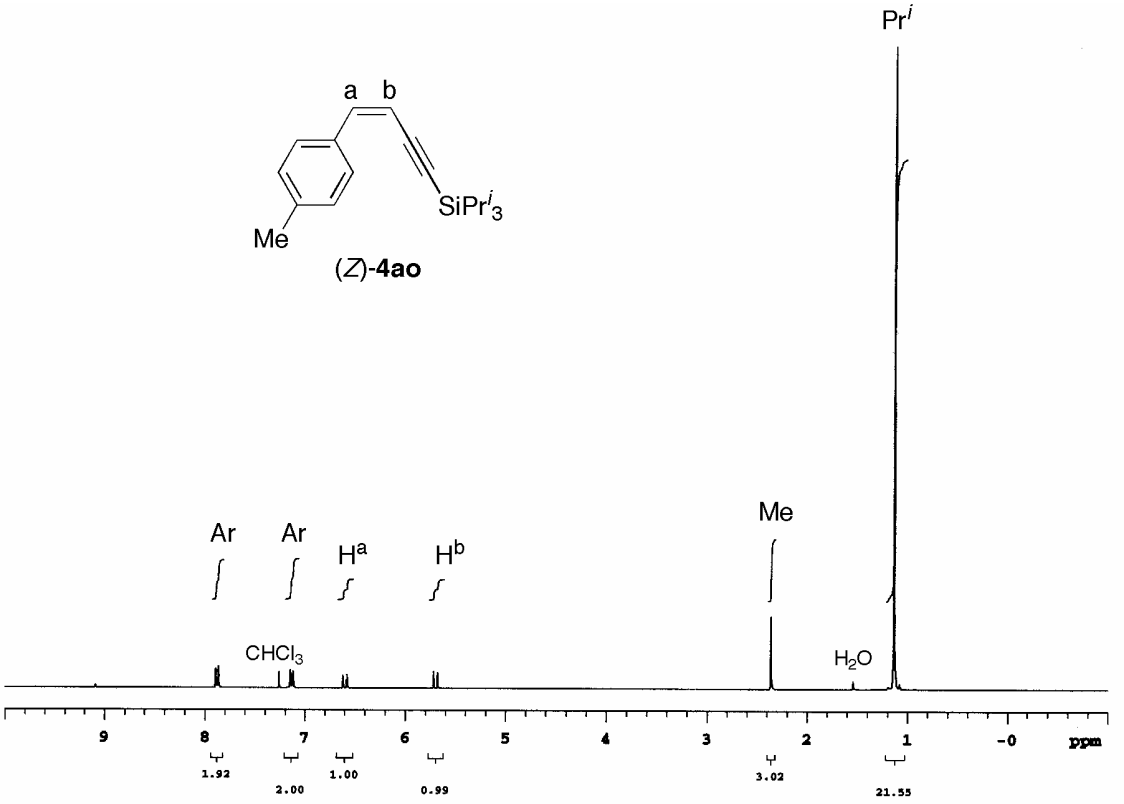

Figure S7. ^{1}H NMR spectrum of **4ao** ((*Z*):(*E*):*gem* = 100:0:0) in $CDCl_3$ (300 MHz).