Supporting Information

Copper-Catalyzed Allylations of Zirconocene Intermediates Generated from *o*-Alkenyl or *o*-Alkynylbenzyl Ether Derivatives and Zirconocene-butene Complex

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Experimental Details

General. Infrared (IR) spectra were recorded on a FT-IR spectrophotometer, ν_{max} in cm^{-1} . ^1H NMR spectra were recorded on a 300 MHz or 400 MHz spectrometer. Chemical shifts are reported in ppm with the solvent resonance as internal standard (CHCl_3 : δ 7.26 ppm). ^{13}C NMR spectra were recorded on a 75.5 MHz 100 MHz spectrometer. Chemical shifts are reported in ppm with the solvent resonance as internal standard (CDCl_3 : δ 77.0 ppm). ^{19}F NMR spectra were recorded on a 282 MHz spectrometer. Chemical shifts are reported in ppm with α,α,α -trifluorotoluene resonance as an internal standard ($\text{C}_6\text{H}_5\text{CF}_3$: δ 0 ppm).

Thin-layer chromatography (TLC) was performed using pre-coated plates (0.25 mm) with a UV lamp, PMA or basic KMnO_4 for detection. Column chromatography was performed on silica gel (100-210 μm particle size), or on a flash silica gel (40-50 μm particle size). Medium-pressure liquid chromatography (MPLC) was performed on a 40 x 300 mm I.D. prepacked column with a UV detector.

Moisture sensitive reactions were performed under an argon atmosphere in flame-dried glassware equipped with a magnetic stirring bar. Tetrahydrofuran (THF), diethyl ether, dichloromethane, *N,N*-dimethylformamide (DMF), toluene and benzene were purchased as dehydrated solvents, and used without further purification. *n*-Butyllithium was titrated with diphenylacetic acid before use. Other commercially available reagents were used as obtained.

A. Typical procedure for the allylations of *o*-vinylbenzylzirconocene intermediates.

To a solution of Cp_2ZrCl_2 (153 mg, 0.53 mmol) in THF (5 mL) was added *n*-BuLi (1.6 M solution in *n*-hexane, 0.66 mL, 1.05 mmol) at -78°C and stirred for 1 h. To this solution was added a solution of **1a** (112 mg, 0.50 mmol) in THF (2 mL) and gradually warmed to room temperature, and stirred for 3 h. To this reaction mixture was added a solution of allyl bromide (65 μL , 0.75 mmol) in THF (1 mL) and CuCl (5 mg, 0.05 mmol), and then the mixture was

refluxed for 5 h. After cooling to room temperature, 1 M HCl aq was added, and the mixture was extracted with ether. The combined organic layer was washed with brine, dried over anhydrous MgSO_4 , and the filtrate was concentrated to dryness under reduced pressure. The residue was purified by flash chromatography (*n*-hexane), and further purification was carried out by MPLC (*n*-hexane) to give **4a** (70 mg, 88 %).

4a

1-(3-Butenyl)-2-vinylbenzene (4a): Colorless oil. IR (liquid film): 2937, 1641, 1484, 991, 911, 772, 753. ^1H NMR (CDCl_3 , 300 MHz): δ 7.53-7.49 (1H, m), 7.26-7.15 (3H, m), 7.02 (1H, dd, $J=17.3$, 10.8 Hz), 5.90 (1H, dddd, $J=17.0$, 10.3, 6.7, 6.4 Hz), 5.68 (1H, dd, $J=17.3$, 1.5 Hz), 5.33 (1H, dd, $J=10.8$, 1.5 Hz), 5.12-4.99 (2H, m), 2.83-2.77 (2H, m), 2.39-2.31 (2H, m). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 139.0, 137.8, 136.2, 134.3, 129.3, 127.5, 126.1, 125.6, 115.3, 114.7, 35.2, 32.9. EI-MS (m/z): 158 (M^+). Anal. Calcd. for $\text{C}_{12}\text{H}_{14}$: C, 91.08; H, 8.92. Found: C, 91.06; H, 8.79.

4b

2-(3-Butenyl)-4-methoxy-1-vinylbenzene (4b): Colorless oil. IR (liquid film): 2934, 1607, 1498, 1251, 910, 814. ^1H NMR (CDCl_3 , 300 MHz): δ 7.46 (1H, d, $J=8.5$ Hz), 6.92 (1H, dd, $J=17.3$, 10.8 Hz), 6.78-6.70 (2H, m), 5.89 (1H, dddd, $J=16.8$, 10.4, 6.7, 6.4 Hz), 5.57 (1H, dd, $J=17.3$, 0.9 Hz), 5.21 (1H, dd, $J=10.8$, 0.9 Hz), 5.08 (1H, dd, $J=16.8$, 1.2 Hz), 5.01 (1H, d, $J=10.4$ Hz), 3.82 (3H, s), 2.79-2.74 (2H, m), 2.38-2.30 (2H, m). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 157.6, 139.2, 136.5, 132.4, 127.7, 125.4, 113.5, 113.3, 112.0, 110.3, 54.0, 33.8, 31.8. EI-

MS (m/z): 188 (M^+). Anal. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.57; O, 8.50. Found: C, 83.07; H, 8.52.

2-(3-Butenyl)-4-fluoro-1-vinylbenzene (4c): Colorless oil. IR (liquid film): 1608, 1493, 1247, 1153, 913. 1H NMR ($CDCl_3$, 300 MHz): δ 7.45 (1H, dd, $J=8.2, 5.9$ Hz), 6.96-6.84 (3H, m), 5.86 (1H, dddd, $J=17.0, 10.3, 6.7, 6.4$ Hz), 5.59 (1H, dd, $J=17.3, 1.2$ Hz), 5.29 (1H, dd, $J=10.8, 1.2$ Hz), 5.10-4.99 (2H, m), 2.79-2.73 (2H, m), 2.37-2.29 (2H, m). ^{19}F NMR ($CDCl_3$, 282.3 MHz): δ -51.98 (ddd, $J=9.9, 7.9, 6.0$ Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 162.0 (d, $J=245.3$ Hz), 141.2 (d, $J=16.9$ Hz), 137.3 (s), 133.4 (s), 132.4 (d, $J=3.5$ Hz), 127.3 (d, $J=8.1$ Hz), 115.7 (d, $J=20.7$ Hz), 115.2 (s), 115.1 (s), 113.1 (d, $J=21.3$ Hz), 34.7 (s), 32.8 (s). EI-MS (m/z): 176 (M^+). Anal. Calcd. for $C_{12}H_{13}F$: C, 81.78; H, 7.44; F, 10.78. Found: C, 81.76; H, 7.55.

1-(3-Chloro-3-butenyl)-2-vinylbenzene (4d): Colorless oil. IR (liquid film): 1635, 1484, 1190, 1162, 990, 914, 883, 773, 754. 1H NMR ($CDCl_3$, 300 MHz): δ 7.52-7.46 (1H, m), 7.23-7.14 (3H, m), 7.00 (1H, dd, $J=17.3, 10.8$ Hz), 5.67 (1H, dd, $J=17.3, 1.5$ Hz), 5.34 (1H, dd, $J=10.8, 1.5$ Hz), 5.16 (1H, d, $J=1.2$ Hz), 5.10 (1H, dd, $J=1.2, 0.9$ Hz), 2.99-2.93 (2H, m), 2.61-2.55 (2H, m). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 141.7, 137.6, 136.3, 134.0, 129.4, 127.6, 126.5, 125.7, 115.8, 112.4, 40.6, 31.5. EI-MS (m/z): 192 (M^+). Anal. Calcd. for $C_{12}H_{13}Cl$: C, 74.80; H, 6.80; Cl, 18.40. Found: C, 74.92; H, 6.84.

1-(3-Bromo-3-butenyl)-2-vinylbenzene (4e): Colorless oil. IR (liquid film): 1629, 1484, 1183, 1121, 990, 914, 883, 773, 754. ^1H NMR (CDCl_3 , 300 MHz): δ 7.53-7.49 (1H, m), 7.26-7.17 (3H, m), 7.01 (1H, dd, $J=17.3$, 10.8 Hz), 5.68 (1H, dd, $J=17.3$, 1.5 Hz), 5.55 (1H, d, $J=1.5$ Hz), 5.41 (1H, d, $J=1.5$ Hz), 5.35 (1H, dd, $J=10.8$, 1.5 Hz), 3.00-2.94 (2H, m), 2.70-2.65 (2H, m). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 137.5, 136.3, 134.0, 133.3, 129.4, 127.6, 126.5, 125.7, 116.8, 115.8, 42.8, 32.2. EI-MS (m/z): 236 (M^+). Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{Br}$: C, 60.78; H, 5.53; Br, 33.70. Found: C, 61.18; H, 5.63.

Methyl 2-(2-vinylphenethyl)acrylate (4f): Colorless oil. IR (liquid film): 2951, 1722, 1630, 1440, 1198, 1138, 774. ^1H NMR (CDCl_3 , 300 MHz): δ 7.52-7.49 (1H, m), 7.22-7.12 (3H, m), 7.04 (1H, dd, $J=17.3$, 11.1 Hz), 6.16 (1H, d, $J=1.2$ Hz), 5.67 (1H, dd, $J=17.3$, 1.5 Hz), 5.53 (1H, dd, $J=1.5$, 1.2 Hz), 5.32 (1H, dd, $J=11.1$, 1.5 Hz), 3.78 (3H, s), 2.89-2.83 (2H, m), 2.59-2.54 (2H, m). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 167.2, 139.7, 138.5, 136.3, 134.2, 129.4, 127.6, 126.3, 125.5, 125.3, 115.4, 51.9, 33.8, 32.7. EI-MS (m/z): 216 (M^+). Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_2$: C, 77.75; H, 7.46; O, 14.80. Found: C, 77.51; H, 7.38.

1-(2,3-Butadienyl)-2-vinylbenzene (4g): Colorless oil. IR (neat): 1955, 1626, 846. ^1H NMR (CDCl_3 , 300 MHz): δ 7.50-7.22 (4H, m), 7.01 (1H, dd, $J=17.4$, 11.0 Hz), 5.68 (1H, dd, $J=17.4$,
S5

1.5 Hz), 5.33 (1H, dd, $J=11.0, 1.5$ Hz), 5.32-5.10 (1H, m), 4.73-4.67 (2H, m), 3.46-3.41 (2H, m). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 208.8, 137.3, 136.7, 134.6, 129.4, 127.8, 126.7, 125.7, 115.5, 89.4, 75.4, 32.6. EI-MS (m/z): 156 (M^+). Anal. Calcd. for $\text{C}_{12}\text{H}_{12}$: C, 92.26; H, 7.74. Found: C, 92.30; H, 7.73.

B. Typical procedure for the allylations of α -trimethylsilylethynylbenzylzirconocene intermediates.

To a solution of Cp_2ZrCl_2 (175 mg, 0.60 mmol) in THF (5 mL) was added $n\text{-BuLi}$ (1.6 M solution in $n\text{-hexane}$, 0.75 mL, 1.20 mmol) at -78°C and stirred for 1 h. To this solution was added a solution of **5a** (109 mg, 0.50 mmol) in THF (2 mL) and gradually warmed to room temperature, and stirred for 5 h. To this reaction mixture was added a solution of allyl bromide (65 μL , 0.75 mmol) in THF (1 mL) and CuCl (5 mg, 0.05 mmol), and then the mixture was refluxed for 5 h. After cooling to room temperature, 1 M HCl aq was added, and the mixture was extracted with ether. The combined organic layer was washed with brine, dried over anhydrous MgSO_4 , and the filtrate was concentrated to dryness under reduced pressure. The residue was purified by flash chromatography ($n\text{-hexane}$), and further purification was carried out by MPLC ($n\text{-hexane}$) to give **7a** (91 mg, 80 %).

{2-[2-(3-Butenyl)phenyl]ethynyl}trimethylsilane (7a): Colorless oil. IR (liquid film): 2157, 1250, 869, 843, 758. ^1H NMR (CDCl_3 , 300 MHz): δ 7.46-7.10 (4H, m), 5.89 (1H, dddd, $J=17.0, 10.8, 6.7, 6.5$ Hz), 5.10-4.97 (2H, m), 2.91-2.85 (2H, m), 2.45-2.36 (2H, m), 0.28 (9H, s). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 144.2, 138.0, 132.2, 128.6, 128.3, 125.6, 122.3, 114.6, 103.7, 97.9,

34.7, 34.4, 0.3. EI-MS (m/z): 228 (M^+). Anal. Calcd. for $C_{15}H_{20}Si$: C, 78.88; H, 8.83; Si, 12.30. Found: C, 78.77; H, 8.86.

{2-[2-(3-Butenyl)-4-methoxyphenyl]ethynyl}trimethylsilane (7b): Colorless oil. IR (liquid film): 2959, 2151, 1492, 1250, 1220, 1040, 861, 843. 1H NMR ($CDCl_3$, 300 MHz): δ 7.38 (1H, d, $J=8.2$ Hz), 6.72-6.66 (2H, m), 5.89 (1H, dddd, $J=17.0, 10.3, 6.7, 6.4$ Hz), 5.10-4.96 (2H, m), 3.80 (3H, s), 2.87-2.82 (2H, m), 2.44-2.36 (2H, m), 0.26 (9H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 159.4, 146.1, 137.9, 133.6, 114.7, 114.4, 111.1, 103.9, 96.2, 55.3, 34.7, 34.6, 0.4. EI-MS (m/z): 258 (M^+). Anal. Calcd. for $C_{16}H_{22}OSi$: C, 74.36; H, 8.58; O, 6.19; Si, 10.87. Found: C, 73.99; H, 8.63.

{2-[2-(3-Butenyl)-4-fluorophenyl]ethynyl}trimethylsilane (7c): Colorless oil. IR (liquid film): 2961, 2157, 1489, 1252, 1210, 861, 844. 1H NMR ($CDCl_3$, 300 MHz): δ 7.44-7.37 (1H, m), 6.91-6.80 (2H, m), 5.87 (1H, dddd, $J=17.0, 10.3, 6.7, 6.4$ Hz), 5.10-4.98 (2H, m), 2.89-2.84 (2H, m), 2.44-2.36 (2H, m), 0.27 (9H, s). ^{19}F NMR ($CDCl_3$, 282.3 MHz): δ -47.74 (ddd, $J=9.9, 7.9, 6.0$ Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 162.2 (d, $J=248.2$ Hz), 147.0 (d, $J=7.5$ Hz), 137.4 (s), 133.9 (d, $J=8.6$ Hz), 118.5 (d, $J=3.4$ Hz), 115.6 (d, $J=21.9$ Hz), 115.0 (s), 112.8 (d, $J=21.9$ Hz), 102.7 (s), 97.6 (s), 34.4 (s), 34.3 (s), 0.2 (s). EI-MS (m/z): 246 (M^+). Anal. Calcd. for $C_{15}H_{19}FSi$: C, 73.12; H, 7.77; F, 7.71; Si, 11.40. Found: C, 73.13; H, 7.89.

{2-[2-(3-Bromo-3-butenyl)phenyl]ethynyl}trimethylsilane (7d): Colorless oil. IR (liquid film): 2959, 2157, 1630, 1482, 1250, 869, 843, 758. ^1H NMR (CDCl_3 , 300 MHz): δ 7.50 (1H, dd, $J=7.6, 0.9$ Hz), 7.31-7.17 (3H, m), 5.59 (1H, dd, $J=1.5, 1.2$ Hz), 5.45 (1H, dd, $J=1.5$ Hz), 3.13-3.07 (2H, m), 2.84-2.79 (2H, m), 0.33 (9H, s). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 142.6, 133.5, 132.3, 128.9, 128.4, 126.0, 122.4, 116.7, 103.3, 98.3, 42.2, 33.7, 0.3. EI-MS (m/z): 227 (M-Br) $^+$. Anal. Calcd. for $\text{C}_{15}\text{H}_{19}\text{BrSi}$: C, 58.63; H, 6.23; Br, 26.00; Si, 9.14. Found: C, 58.48; H, 6.24.

{2-[2-(2,3-Butadienyl)phenyl]ethynyl}trimethylsilane (7e): Colorless oil. IR (liquid film): 2960, 2157, 1956, 1482, 1250, 870, 842, 758. ^1H NMR (CDCl_3 , 300 MHz): δ 7.47-7.43 (1H, m), 7.28-7.13 (3H, m), 5.33 (1H, tt, $J=7.3, 6.7$ Hz), 4.72 (2H, dt, $J=6.4, 2.9$ Hz), 3.55 (2H, dt, $J=7.3, 2.9$ Hz), 0.28 (9H, s). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 208.6, 142.4, 132.2, 128.5, 128.4, 125.9, 122.3, 103.4, 98.4, 88.7, 75.1, 33.9, 0.3. EI-MS (m/z): 226 (M^+). Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{Si}$: C, 79.58; H, 8.01; Si, 12.41. Found: C, 79.50; H, 8.13.

C. Typical procedure for synthesis of (3-butynyl)-derivatives.

To a solution of diisopropylamine (140 μL , 1.00 mmol) in THF (5 mL) was added *n*-BuLi (1.6 M solution in *n*-hexane, 0.63 mL, 1.00 mmol) at 0 $^\circ\text{C}$ and stirred for 0.5 h. To this solution was added a solution of **4e** (119 mg, 0.50 mmol) in THF (2 mL) and the mixture was gradually warmed to room temperature. After being stirred for 3 h at room temperature, the reaction

mixture was quenched by 1 M HCl aq at 0 °C and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous MgSO₄, and the filtrate was concentrated to dryness. The residue was purified by flash chromatography (*n*-hexane), and further purification was carried out by MPLC (*n*-hexane) to give **10** (66 mg, 83 %).

1-(3-Butynyl)-2-vinylbenzene (10): Colorless oil. IR (liquid film): 1484, 991, 915, 773, 640. ¹H NMR (CDCl₃, 300 MHz): δ 7.56-7.52 (1H, m), 7.29-7.23 (3H, m), 7.02 (1H, dd, *J*=17.3, 11.1 Hz), 5.71 (1H, dd, *J*=17.3, 1.5 Hz), 5.38 (1H, dd, *J*=11.1, 1.5 Hz), 2.99 (2H, t, *J*=7.8 Hz), 2.49 (2H, dt, *J*=7.8, 2.6 Hz), 2.05 (1H, t, *J*=2.6 Hz). ¹³C NMR (CDCl₃, 75.5 MHz): δ 137.4, 136.3, 134.0, 129.3, 127.6, 126.7, 125.8, 115.9, 83.7, 69.0, 32.5, 20.2. EI-MS (*m/z*): 156 (M⁺). Anal. Calcd. for C₁₂H₁₂: C, 92.26; H, 7.74. Found: C, 92.26; H, 7.84.

{2-[2-(3-Butynyl)phenyl]ethynyl}trimethylsilane (11): Colorless oil. IR (neat): 2958, 2155, 1482, 1449, 1250. ¹H NMR (CDCl₃, 300 MHz): δ 7.48-7.16 (4H, m), 3.04 (2H, t, *J*=7.6 Hz), 2.57 (2H, dt, *J*=7.6, 2.6 Hz), 2.00 (1H, t, *J*=2.6 Hz). ¹³C NMR (CDCl₃, 75.5 MHz): δ 142.5, 132.2, 128.9, 128.4, 126.1, 122.3, 103.2, 98.5, 83.8, 68.7, 34.1, 19.4, 0.2. EI-MS (*m/z*): 226 (M⁺).

D. Dane's diene and its fluorine analogue synthesis.

D-1. Typical procedure for desilylation, To a solution of **7b** (129 mg, 0.50 mmol) in THF (5 mL) was added tetrabutylammonium fluoride (about 1.0 M solution in THF, 0.75 mL, 0.75 mmol) and stirred for 3 h at room temperature. The mixture was poured into water and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous MgSO_4 , and the filtrate was concentrated to dryness. The residue was purified by column chromatography (*n*-hexane / ether = 50 / 1), and further purification was carried out by MPLC (*n*-hexane / ethyl acetate = 20 / 1) to give **12a** (89 mg, 96 %).

2-(3-Butenyl)-1-ethynyl-4-methoxybenzene (12a): Colorless oil. IR (liquid film): 2102, 1607, 1495, 1241, 1161, 1039, 914, 811. ^1H NMR (CDCl_3 , 300 MHz): δ 7.42 (1H, d, $J=8.2$ Hz), 6.75-6.68 (2H, m), 5.88 (1H, dddd, $J=17.0, 10.3, 6.7, 6.4$ Hz), 5.07 (1H, dd, $J=17.0, 1.7$ Hz), 5.02-4.98 (1H, m), 3.81 (3H, s), 3.19 (1H, s), 2.88 (2H, t, $J=7.8$ Hz), 2.46-2.37 (2H, m). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 159.6, 146.0, 137.8, 134.0, 114.8, 114.4, 113.6, 111.2, 82.3, 79.3, 55.3, 34.6, 34.3. EI-MS (m/z): 186 (M^+). Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}$: C, 83.83; H, 7.58; O, 8.59. Found: C, 83.72; H, 7.39.

2-(3-Butenyl)-1-ethynyl-4-fluorobenzene (12b): Colorless oil. IR (liquid film): 1642, 1609, 1582, 1489, 1275, 1237, 1152, 916, 871, 820. ^1H NMR (CDCl_3 , 300 MHz): δ 7.45 (1H, dd, $J=8.5, 5.9$ Hz), 6.93-6.82 (2H, m), 5.87 (1H, dddd, $J=17.0, 10.3, 6.7, 6.4$ Hz), 5.09-4.98 (2H,

m), 3.23 (1H, s), 2.89 (2H, t, $J=7.8$ Hz), 2.45-2.37 (2H, m). ^{19}F NMR (CDCl_3 , 282.3 MHz): δ -47.46 (ddd, $J=9.9$, 7.9, 6.0 Hz). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 162.3 (d, $J=248.8$ Hz), 147.0 (d, $J=8.1$ Hz), 137.3 (s), 134.4 (d, $J=8.6$ Hz), 117.4 (d, $J=3.2$ Hz), 115.6, (d, $J=21.3$ Hz), 115.1 (s), 113.0 (d, $J=21.9$ Hz), 81.3 (s), 80.4 (s), 34.3 (s), 34.0 (s). EI-MS (m/z): 174 (M^+). Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{F}$: C, 82.73; H, 6.36; F, 10.91. Found: C, 82.78; H, 6.54.

D-2. Typical procedure for the intramolecular enyne metathesis. To a 2nd generation Grubbs catalyst (10.6 mg, 12.5 μmol) was added a solution of **12a** (46.6 mg, 250.0 μmol) in CH_2Cl_2 (2.5 mL) and stirred for 16 h at room temperature. After solvent was removed under reduced pressure, the residue was purified by column chromatography (*n*-hexane / ether = 50 / 1), and further purification was carried out by MPLC (*n*-hexane / ethyl acetate = 20 / 1) to give Dane's diene (**13a**) (35.1 mg, 75 %).

7-Methoxy-4-vinyl-1,2-dihydronaphthalene (Dane's diene) (13a): The structure was confirmed by comparison of spectrum data with the authentic sample.¹

¹ Woski, S. A.; Koreeda, M. *J. Org. Chem.* **1992**, 57, 5736.

7-Fluoro-4-vinyl-1,2-dihydronaphthalene (13b): Colorless oil. IR (liquid film): 2935, 1608, 1583, 1493, 1428, 1270, 1242, 831. ^1H NMR (CDCl_3 , 300 MHz): δ 7.32-7.26 (1H, m), 6.91-6.85 (2H, m), 6.59 (1H, ddd, $J=17.3$, 11.0, 1.2 Hz), 6.15 (1H, t, $J=4.8$ Hz), 5.52 (1H, dd, $J=17.3$, 1.8 Hz), 5.21 (1H, dd, $J=10.8$, 1.8 Hz), 2.75 (2H, t, $J=7.9$ Hz), 2.34-2.27 (2H, m). ^{19}F NMR (CDCl_3 , 282.3 MHz): δ -52.39 (ddd, $J=9.9$, 7.9, 6.0 Hz). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 161.3 (d, $J=245.3$ Hz), 138.9 (d, $J=7.5$ Hz), 135.7 (s), 135.2 (s), 130.0 (s), 125.3 (d, $J=2.3$ Hz), 125.2 (d, $J=8.1$ Hz), 115.2 (s), 114.5 (d, $J=21.9$ Hz), 112.5 (d, $J=21.3$ Hz), 28.6 (s), 23.1 (s). EI-MS (m/z): 174 (M^+). Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{F}$: C, 82.73; H, 6.36; F, 10.91. Found: C, 82.33; H, 6.55.

E. Preparation of 1-[(benzyloxy)methyl]-2-vinylbenzene 1a.

E-1. Experimental procedure for preparation of 1a. To a suspension of NaH (55 % assay, 262 mg, 6.0 mmol) in THF (5 mL) was added a solution of (2-vinylphenyl)methanol (**14**)² (671 mg, 5.0 mmol) in THF (5 mL) at 0 °C, and stirred for 0.5 hr at same temperature. To the mixture was added benzyl bromide (0.71 mL, 6.0 mmol), and stirred for overnight at room temperature. After cooling to 0 °C, saturated NH_4Cl aq was added carefully, and extracted with ether. The organic layer was washed with brine, dried over anhydrous MgSO_4 , and the filtrate was concentrated to dryness under reduced pressure. The residue was purified by column chromatography (*n*-hexane to *n*-hexane / ethyl acetate = 20 / 1) to give **1a** (1.08 g, 96 %).

² Compound **14** was prepared from phthalide according to the literature; Boland, W.; Ney, P.; Jaenicke, L. *Synthesis* **1980**, 1015.

1-[(Benzyloxy)methyl]-2-vinylbenzene (1a): Colorless oil. IR (neat): 1644. ^1H NMR (CDCl_3 , 300 MHz): δ 7.59-7.27 (9H, m), 7.01 (1H, dd, $J=17.5$, 11.0 Hz), 5.35 (1H, dd, $J=11.0$, 1.3 Hz), 5.22 (1H, dd, $J=17.5$, 1.3 Hz), 4.64 (2H, s), 4.60 (2H, s). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 137.9, 136.9, 134.7, 133.8, 129.0, 128.1, 127.9, 127.6, 127.4, 125.5, 115.7, 72.1, 70.2. EI-MS (m/z): 224 (M^+). Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}$: C, 85.68; H, 7.19; O, 7.13. Found: C, 85.49; H, 7.24.

F. Preparation of 4-substituted styrene derivatives, 1b and 1c.

F-1-1. Experimental procedure for preparation of 16a. To a solution of 2-bromo-5-methoxybenzoic acid (**15**) (4.62 g, 20.0 mmol) in THF (50 mL), BH_3 -THF complex (1.07 M in THF, 28.0 mL, 30.0 mmol) was added dropwise at 0 °C, and then stirred for 3.5 h at room temperature. The reaction mixture was cooled to 0 °C, 1M HCl aq was added carefully, and extracted with ether. The organic layer was washed with water, saturated NaHCO_3 aq, and brine. The organic layer was dried over anhydrous MgSO_4 , and the filtrate was concentrated to dryness under reduced pressure. The residue was purified by column chromatography (n -hexane / ethyl acetate = 4 / 1) to give **16a** (4.28 g, 99 %).

(2-Bromo-5-methoxyphenyl)methanol (16a): White powder. mp: 46.5-48.5 °C. IR (KBr): 1472, 1297, 1239, 1065, 1056, 1017, 808, 792. ¹H NMR (CDCl₃, 300 MHz): δ 7.40 (1H, d, *J*=8.8 Hz), 7.05 (1H, d, *J*=3.0 Hz), 6.70 (1H, dd, *J*=8.8, 3.0 Hz), 4.69 (2H, d, *J*=6.1 Hz), 3.80 (3H, s), 2.27 (1H, t, *J*=6.1 Hz). ¹³C NMR (CDCl₃, 75.5 MHz): δ 158.9, 140.5, 132.9, 114.6, 114.0, 112.3, 65.0, 55.6. EI-MS (*m/z*): 216 (M⁺). Anal. Calcd. for C₈H₉BrO₂: C, 44.27; H, 4.18; Br, 36.81; O, 14.74. Found: C, 43.99; H, 4.22.

F-1-2. Experimental procedure for preparation of 16b. To a solution of 2-bromo-5-fluorobenzaldehyde (**17**) (5.00 g, 24.6 mmol) in THF (50 mL), DIBAL (0.95 M in *n*-hexane, 28.5 mL, 27.1 mmol) was added dropwise at 0 °C, and then stirred for 2.5 h at same temperature. To the reaction mixture, 2M HCl aq was added carefully, and extracted with ether. The organic layer was washed with brine, dried over anhydrous MgSO₄, and the filtrate was concentrated to dryness under reduced pressure. The residue was purified by column chromatography (*n*-hexane / ethyl acetate = 4 / 1) to give **16b** (5.00 g, 99 %).

(2-Bromo-5-fluorophenyl)methanol (16b): White powder. mp: 92-94 °C (lit. 88-90 °C). The structure was confirmed by comparison of spectrum data with the literature.³

³ Stará, I. G.; Starý, I.; Kollárovič, A.; Teplý, F.; Šaman, D.; Fiedler, P. *Collect. Czech. Chem. Commun.*, **1999**, 64, 649.

F-2. Typical procedure for benzyl etherification.

To a suspension of NaH (55 % assay, 890 mg, 20.4 mmol) in THF (20 mL) was added a solution of **16a** (3.69 g, 17.0 mmol) in THF (20 mL) at 0 °C, and stirred for 0.5 h. To the mixture was added benzyl bromide (2.43 mL, 20.4 mmol), and stirred for overnight at room temperature. After cooling to 0 °C, saturated NH₄Cl aq was added carefully, and extracted with ether. The organic layer was washed with brine, dried over anhydrous MgSO₄, and the filtrate was concentrated to dryness under reduced pressure. The residue was purified by column chromatography (*n*-hexane to *n*-hexane / ethyl acetate = 10 / 1) to give **18a** (5.22 g, quant).

2-[(Benzyloxy)methyl]-1-bromo-4-methoxybenzene (18a): Colorless oil. IR (liquid film): 1595, 1575, 1475, 1298, 1274, 1164, 1098, 1056, 1018, 737, 698. ¹H NMR (CDCl₃, 300 MHz): δ 7.46-7.16 (7H, m), 6.74 (1H, dd, *J*=8.5, 2.9 Hz), 4.69 (2H, s), 4.64 (2H, s), 3.82 (3H, s). ¹³C NMR (CDCl₃, 75.5 MHz): δ 158.7, 138.4, 137.7, 132.8, 128.2, 127.5, 114.4, 114.2, 112.6, 72.7, 71.5, 55.5. EI-MS (*m/z*): 306 (M⁺). Anal. Calcd. for C₁₅H₁₅BrO₂: C, 58.65; H, 4.92; Br, 26.01; O, 10.42. Found: C, 58.82; H, 4.89.

2-[(Benzyloxy)methyl]-1-bromo-4-fluorobenzene (18b): Benzyl ether **18b** (5.74 g, 97 %) was prepared from **16b** (4.10 g, 20.0 mmol). Colorless oil. IR (liquid film): 1607, 1582, 1469, 1413, 1357, 1268, 1152, 1115, 1092, 1030, 959, 874, 810, 737, 697. ¹H NMR (CDCl₃, 300

MHz): δ 7.53-7.34 (7H, m), 6.91 (1H, dd, $J=8.2, 2.9$ Hz), 4.71 (2H, s), 4.64 (2H, s). ^{19}F NMR (CDCl_3 , 282.3 MHz): δ -51.43 (m). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 161.8 (d, $J=245.3$ Hz), 139.9 (d, $J=7.5$ Hz), 137.5 (s), 133.2 (d, $J=8.1$ Hz), 128.2 (s), 127.6 (s), 127.5 (s), 115.71 (d, $J=8.6$ Hz), 115.68 (d, $J=4.6$ Hz), 115.4 (d, $J=7.5$ Hz), 72.9 (s), 71.0 (s). EI-MS (m/z): 294 (M^+). Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{BrFO}$: C, 56.97; H, 4.10; Br, 27.07; F, 6.44; O, 5.42. Found: C, 57.20; H, 4.17.

F-3. Typical procedure for formylation.

To a solution of **18a** (4.91 g, 16.0 mmol) in THF (50 mL) was added $n\text{-BuLi}$ (1.59 M solution in $n\text{-hexane}$, 11.1 mL, 17.6 mmol) at -78°C , and stirred for 0.5 h. To the reaction mixture, DMF (1.9 mL, 24.0 mmol) was added dropwise, and then gradually warmed to room temperature, and stirred for 3.5 h. The reaction mixture was quenched by 1M HCl aq, and extracted with ether. The organic layer was washed with brine, dried over anhydrous MgSO_4 , and the filtrate was concentrated to dryness under reduced pressure. The residue was purified by column chromatography ($n\text{-hexane}$ / ethyl acetate = 50 / 1 to 10 / 1) to give **19a** (3.72 g, 91 %).

2-[(Benzyloxy)methyl]-4-methoxybenzaldehyde (19a): Colorless oil. IR (liquid film): 1687, 1603, 1568, 1287, 816, 734, 699. ^1H NMR (CDCl_3 , 300 MHz): δ 10.02 (1H, s), 7.79 (1H, d, $J=8.5$ Hz), 7.43-7.27 (6H, m), 6.92 (1H, dd, $J=8.5, 2.3$ Hz), 5.01 (2H, s), 4.69 (2H, s), 3.89 (3H, s). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 190.7, 163.7, 143.5, 137.8, 135.5, 128.2, 127.43, 127.39,

126.4, 113.1, 112.1, 72.8, 69.5, 55.5. HRMS Calcd. for $C_{16}H_{16}O_3$: 257.1178 (M+H)⁺. Found: 257.1178. Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29; O, 18.73. Found: C, 75.18; H, 6.29.

19b

2-[(Benzyloxy)methyl]-4-fluorobenzaldehyde (19b): Benzaldehyde **19b** (3.27 g, 89 %) was prepared from **18b** (4.43 g, 15.0 mmol). Colorless oil. IR (liquid film): 1699, 1609, 1584, 1355, 1220, 1114, 1074, 969, 880, 822, 738, 699. ¹H NMR (CDCl₃, 300 MHz): δ 10.09 (1H, s), 7.86 (1H, dd, *J*=8.5, 5.6 Hz), 7.51-7.30 (6H, m), 7.13 (1H, dt, *J*=8.2, 2.4 Hz), 5.00 (2H, s), 4.70 (2H, s). ¹⁹F NMR (CDCl₃, 282.3 MHz): δ -39.66 (q, *J*=7.9 Hz). ¹³C NMR (CDCl₃, 75.5 MHz): δ 190.4 (s), 165.5 (d, *J*=255.1 Hz), 144.5 (d, *J*=9.2 Hz), 137.4 (s), 135.4 (d, *J*=9.8 Hz), 129.1 (s), 128.0 (s), 127.3 (d, *J*=9.8 Hz), 127.2 (s), 114.6 (d, *J*=23.6 Hz), 113.9 (d, *J*=21.9 Hz), 72.7 (s), 68.8 (s). HRMS Calcd. for $C_{15}H_{13}FO_2$: 245.0978 (M+H)⁺. Found: 245.0981. Anal. Calcd. for $C_{15}H_{13}FO_2$: C, 73.76; H, 5.36; F, 7.78; O, 13.10. Found: C, 73.66; H, 5.57.

F-4. Typical procedure for Wittig reaction.

To a suspension of methyl triphenylphosphonium bromide (2.68 g, 7.5 mmol) in THF (20 mL) was added *n*-BuLi (1.59 M solution in *n*-hexane, 4.72 mL, 7.5 mmol) at 0 °C, and stirred for 1 h. To the resultant red solution was added a solution of **19a** (1.28 g, 5.0 mmol) in THF (10 mL), and stirred for 4.5 h at room temperature. The reaction mixture was quenched by water, and extracted with ether. The organic layer was washed with brine, dried over anhydrous MgSO₄, and the filtrate was concentrated to dryness under reduced pressure. The residue was purified by column chromatography (*n*-hexane / ethyl acetate = 50 / 1) to give **1b** (1.24 g, 98 %).

2-[(Benzyloxy)methyl]-4-methoxy-1-vinylbenzene (1b): Colorless oil. IR (liquid film): 1608, 1496, 1298, 1255, 1027, 908, 738, 698. ¹H NMR (CDCl₃, 300 MHz): δ 7.50 (1H, d, *J*=8.5 Hz), 7.41-7.30 (5H, m), 6.98-6.83 (3H, m), 5.58 (1H, dd, *J*=17.3, 1.2 Hz), 5.22 (1H, dd, *J*=11.1, 1.2 Hz), 4.61-5.9 (4H, m), 3.84 (3H, s). ¹³C NMR (CDCl₃, 75.5 MHz): δ 158.8, 137.8, 136.2, 133.1, 129.2, 128.1, 127.5, 127.3, 126.7, 113.9, 113.6, 113.3, 72.1, 70.0, 55.2. EI-MS (*m/z*): 254 (*M*⁺). Anal. Calcd. for C₁₇H₁₈O₂: C, 80.28; H, 7.13; O, 12.58. Found: C, 80.26; H, 7.20.

2-[(Benzyloxy)methyl]-4-fluoro-1-vinylbenzene (1c): Styrene **1c** (2.25 g, 93 %) was prepared from **19b** (2.44 g, 10.0 mmol). Colorless oil. IR (liquid film): 2861, 1608, 1492, 1253, 1072, 875, 737, 698. ¹H NMR (CDCl₃, 300 MHz): δ 7.49 (1H, dd, *J*=8.5, 5.6 Hz), 7.33 (5H, m),

7.15 (1H, dd, $J=9.7, 2.6$ Hz), 6.98 (1H, dd, $J=8.5, 2.6$ Hz), 6.89 (1H, dd, $J=17.3, 10.8$ Hz), 5.61 (1H, d, $J=17.3$ Hz), 5.30 (1H, d, $J=10.8$ Hz), 4.60 (2H, s), 4.59 (2H, s). ^{19}F NMR (CDCl_3 , 282.3 MHz): δ -51.40 (ddd, $J=9.9, 7.9, 6.0$). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 161.9 (d, $J=246.5$ Hz), 137.6 (s), 137.3 (d, $J=8.6$ Hz), 132.6 (s), 132.3 (d, $J=2.9$ Hz), 128.1 (s), 127.4 (s), 127.1 (d, $J=8.1$ Hz), 115.493 (s), 115.490 (s), 114.9 (d, $J=24.9$ Hz), 114.4 (d, $J=21.3$ Hz), 72.3 (s), 69.3 (s). EI-MS (m/z): 242 (M^+). Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{FO}$: C, 79.32; H, 6.24; F, 7.84; O, 6.60. Found: C, 79.43; H, 6.36.

G. Preparation of phenylacetylene derivatives 5a.

G-1. Experimental procedure for preparation of 5a. To a solution of (2-bromophenylethynyl)trimethylsilane (**20**) (1.27 g, 5.0 mmol) was added $n\text{-BuLi}$ (1.49 M solution in $n\text{-hexane}$, 3.4 mL, 5.0 mmol) at -78°C , and stirred for 0.5 h. To the mixture was added chloromethyl methyl ether (0.46 mL, 6.0 mmol) in a dropwise manner. The mixture was warmed gradually to room temperature and stirred for 5 h. To the reaction mixture was added 1M HCl aq, and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous MgSO_4 , and the filtrate was concentrated to dryness under reduced pressure. The residue was purified by column chromatography ($n\text{-hexane}$ / ether = 200 / 1) to give **5a** (0.96 g, 88 %).

{2-[2-(Methoxymethyl)phenyl]ethynyl}trimethylsilane (5a): Colorless oil. IR (liquid film): 2960, 2157, 1250, 868, 843, 760. ^1H NMR (CDCl_3 , 300 MHz): δ 7.48-7.21 (4H, m), 4.63 (2H, s), 3.46 (3H, s), 0.28 (9H, s). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 140.1, 132.0, 128.4, 127.1, 126.9, 121.5, 102.5, 98.7, 72.5, 58.5, 0.2. HRMS Calcd. for $\text{C}_{13}\text{H}_{18}\text{OSi}$: 219.1205 ($\text{M}+\text{H}$) $^+$. Found: 219.1208. Anal. Calcd. for $\text{C}_{13}\text{H}_{18}\text{OSi}$: C, 71.50; H, 8.31; O, 7.33; Si, 12.86. Found: C, 71.26; H, 8.37.

H. Preparation of 4-substituted phenylacetylene derivatives 5b and 5c.

H-1. Methyl etherification. Methyl ether **21a** or **21b** were prepared from **13a** or **13b** according to the procedure described in section F-2 using methyl iodide instead of benzyl bromide.

1-Bromo-4-methoxy-2-(methoxymethyl)benzene (21a)⁴: Methyl ether **21a** (2.24 g, 97 %) was obtained from **16a** (2.17 g, 10.0 mmol). Colorless oil. IR (neat): 1595, 1575, 1472, 1298, 1274, 1240, 1195, 1165, 1107. ^1H NMR (CDCl_3 , 300 MHz): δ 7.40 (1H, d, $J=8.8$ Hz), 7.04 (1H, d, $J=3.2$ Hz), 6.71 (1H, dd, $J=8.8, 3.2$ Hz), 4.49 (2H, s), 3.81 (3H, s), 3.48 (3H, s). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 158.8, 138.3, 132.8, 114.7, 113.9, 112.5, 73.8, 58.7, 55.5. EI-MS (m/z): 230 (M^+).

⁴ Kanapure, S. P.; Das, K. G.; Bhawal, B. M. *Synth. Commun.* **1984**, *14*, 1205.

21b

1-Bromo-4-fluoro-2-(methoxymethyl)benzene (21b): Methyl ether **21b** (2.19 g, quant) was obtained from **16b** (2.05 g, 10.0 mmol). Colorless oil. IR (liquid film): 2931, 2825, 1582, 1466, 1414, 1381, 1268, 1195, 1154, 1120, 1098, 1033, 875, 810, 619, 585. ^1H NMR (CDCl_3 , 300 MHz): δ 7.47 (1H, dd, $J=8.5$, 5.1 Hz), 7.22 (1H, dd, $J=9.7$, 3.2 Hz), 6.87 (1H, dt, $J=8.5$, 3.2 Hz), 4.48 (2H, s), 3.49 (3H, s). ^{19}F NMR (CDCl_3 , 282.3 MHz): δ -51.50 (dt, $J=13.9$, 9.9 Hz). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 161.8 (d, $J=245.9$ Hz), 139.8 (d, $J=6.9$ Hz), 133.1 (d, $J=8.1$ Hz), 115.51 (d, $J=2.9$ Hz), 115.49 (d, $J=5.2$ Hz), 115.2 (d, $J=6.9$ Hz), 73.2 (s), 58.6 (s). EI-MS (m/z): 218 (M^+). Anal. Calcd. for $\text{C}_8\text{H}_8\text{BrFO}$: C, 43.86; H, 3.68; Br, 36.48; F, 8.67; O, 7.30. Found: C, 43.94; H, 3.87.

H-2. Formylation. Benzaldehyde derivatives **22a** or **22b** were prepared from **21a** or **21b** according the procedure described in section F-3.

22a

4-Methoxy-2-(methoxymethyl)benzaldehyde (22a)⁵: Benzaldehyde **22a** (1.10 g, 87%) was obtained from **21a** (1.62 g, 7.0 mmol). Colorless oil. IR (liquid film): 1688, 1603, 1568, 1288, 1248, 1093, 1037, 818. ^1H NMR (CDCl_3 , 300 MHz): δ 10.01 (1H, s), 7.78 (1H, d, $J=8.5$ Hz),

⁵ Bhawal *et al.* prepared **22a** from **21a** by preparation of Grignard reagent of **21a**. See reference 7.

7.19 (1H, d, $J=2.5$ Hz), 6.92 (1H, dd, $J=8.5, 2.5$ Hz), 4.88 (2H, s), 3.90 (3H, s), 3.50 (3H, s).
 ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 190.2, 163.3, 143.1, 135.1, 125.9, 112.4, 111.7, 71.3, 58.2, 55.1. HRMS Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_3$: 181.0865 ($\text{M}+\text{H}$) $^+$. Found: 181.0865. Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_3$: C, 66.65; H, 6.71; O, 26.64. Found: C, 66.34; H, 0.04.

22b

4-Fluoro-2-(methoxymethyl)benzaldehyde (22b): Benzaldehyde **22b** (1.30 g, 86%) was obtained from **21b** (1.97 g, 9.0 mmol). Colorless oil. IR (neat): 1697, 1608, 1583, 1271, 1197. ^1H NMR (CDCl_3 , 300 MHz): δ 10.09 (1H, s), 7.85 (1H, dd, $J=8.5, 5.6$ Hz), 7.41 (1H, dd, $J=10.0, 2.5$ Hz), 7.12 (1H, dd, $J=8.5, 2.5$ Hz), 4.88 (2H, s), 3.51 (3H, s), 3.50 (3H, s). ^{19}F NMR (CDCl_3 , 282.3 MHz): δ -39.74 (ddd, $J=9.9, 7.9, 6.0$ Hz). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 190.4 (s), 165.5 (d, $J=255.7$ Hz), 144.5 (d, $J=8.6$ Hz), 135.4 (d, $J=9.8$ Hz), 122.1 (s), 114.3 (d, $J=23.6$ Hz), 113.8 (d, $J=22.5$ Hz), 71.0 (s), 58.4 (s). EI-MS (m/z): 168 (M^+). Anal. Calcd. for $\text{C}_9\text{H}_9\text{FO}_2$: C, 64.28; H, 5.39; F, 11.30; O, 19.03. Found: C, 64.62; H, 5.53.

H-3. Typical procedure for dibromo-olefination.⁶

To a solution of triphenylphosphine (4.72 g, 18.0 mmol) in CH₂Cl₂ (50 mL) was added carbon tetrabromide (2.98 g, 9.0 mmol) at 0 °C, and stirred for 15 min. To the resultant red solution was added a solution of **22a** (1.08 g, 6.0 mmol) in CH₂Cl₂ (10 mL), and stirred for 1 h at room temperature. The reaction mixture was quenched by water, and extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄, and the filtrate was concentrated to dryness under reduced pressure. The residue was purified by column chromatography (*n*-hexane / ethyl acetate = 20 / 1) to give **23a** (1.98 g, 98 %).

1-(2,2-Dibromovinyl)-4-methoxy-2-(methoxymethyl)benzene (23a): White semisolid. IR (liquid film): 2930, 1607, 1571, 1494, 1465, 1283, 1249, 1194, 1164, 1092, 1042, 871. ¹H NMR (CDCl₃, 300 MHz): δ 7.51 (1H, s), 7.43 (1H, d, *J*=8.5 Hz), 6.95 (1H, d, *J*=2.9 Hz), 6.84 (1H, dd, *J*=8.5, 2.9 Hz), 4.39 (2H, s), 3.83 (3H, s), 3.41 (3H, s). ¹³C NMR (CDCl₃, 75.5 MHz): δ 159.1, 137.2, 134.9, 129.6, 126.7, 113.4, 112.5, 90.7, 72.2, 58.2, 55.1. HRMS Calcd. for C₁₁H₁₂Br₂O₂: 334.9282 (M+H)⁺. Found: 334.9393. Anal. Calcd. for C₁₁H₁₂Br₂O₂: C, 39.32; H, 3.60; Br, 47.56; O, 9.52. Found: C, 39.50; H, 3.94.

⁶ Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 13, 3769.

1-(2,2-Dibromo-vinyl)-4-fluoro-2-(methoxymethyl)benzene (23b): Dibromo-olefin **23b** (1.95 g, 86%) was obtained from **22b** (1.18 g, 7.0 mmol). Due to the instability⁷ of **23b**, the compound was used immediately for the next reaction after purification by a silica gel column chromatography. White semisolid. ¹H NMR (CDCl₃, 300 MHz): δ 7.48 (1H, s), 7.42 (1H, dd, $J=8.4, 5.7$ Hz), 7.15 (1H, dd, $J=9.4, 2.6$ Hz), 7.00 (1H, dd, $J=8.4, 2.6$ Hz), 4.39 (2H, s), 3.43 (3H, s). ¹⁹F NMR (CDCl₃, 282.3 MHz): δ -49.26 (dt, $J=13.9, 7.9$). ¹³C NMR (CDCl₃, 75.5 MHz): δ 162.2 (d, $J=248.2$ Hz), 138.5 (d, $J=7.5$ Hz), 134.5 (s), 130.35 (d, $J=3.1$ Hz), 130.32 (d, $J=8.1$ Hz), 114.9 (d, $J=22.5$ Hz), 114.3 (d, $J=21.3$ Hz), 92.5 (s), 71.8 (d, $J=1.1$ Hz), 58.6 (s).

H-4. Typical procedure for synthesis of phenylacetylene derivatives.

To a solution of **23a** (1.62 g, 5.0 mmol) in THF (20 mL) was added *n*-BuLi (1.39 M solution in *n*-hexane, 7.91 mL, 11.0 mmol) at -78 °C, and stirred for 0.5 h at the same temperature. To the mixture, chlorotrimethylsilane (1.27 mL, 10.0 mmol) was added dropwise, and then warmed gradually to room temperature. After stirring for 3 h, 1M HCl aq was added and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous MgSO₄, and the filtrate was concentrated to dryness under reduced pressure. The residue was purified by column chromatography (*n*-hexane / ether = 50 / 1) to give **5b** (1.07 g, 86 %).

⁷ Due to the rapid decomposition of **23b**, analyses by IR, elemental analysis and mass spectrum have not been carried out.

5b

{2-[4-Methoxy-2-(methoxymethyl)phenyl]ethynyl}trimethylsilane (5b): Colorless oil. IR (liquid film): 2959, 2151, 1607, 1494, 1300, 1250, 1096, 1040, 862, 843, 760. ^1H NMR (CDCl_3 , 300 MHz): δ 7.38 (1H, d, $J=8.5$ Hz), 7.00 (1H, d, $J=2.6$ Hz), 6.75 (1H, dd, $J=8.5$, 2.6 Hz), 4.61 (2H, s), 3.83 (3H, s), 3.46 (3H, s), 0.27 (9H, s). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 159.7, 142.2, 133.4, 113.4, 112.9, 112.1, 102.6, 97.1, 72.4, 58.6, 55.3, 0.3. HRMS Calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2\text{Si}$: 249.1311 ($\text{M}+\text{H}$) $^+$. Found: 249.1317. Anal. Calcd. for $\text{C}_{13}\text{H}_{18}\text{OSi}$: C, 67.70; H, 8.12; O, 12.88; Si, 11.31. Found: C, 67.50; H, 8.04.

5c

{2-[4-Fluoro-2-(methoxymethyl)phenyl]ethynyl}trimethylsilane (5c): Phenylacetylene **5c** (686 mg, 58 %) was obtained from **23b** (1.62 g, 5.0 mmol). Colorless oil. IR (neat): 2156, 1606, 1488, 1252, 1185, 1152, 1119. ^1H NMR (CDCl_3 , 300 MHz): δ 7.42 (1H, dd, $J=8.4$, 5.6 Hz), 7.18 (1H, dd, $J=9.7$, 2.8 Hz), 6.90 (1H, dt, $J=8.4$, 2.8 Hz), 4.60 (2H, s), 3.47 (3H, s), 0.27 (9H, s). ^{19}F NMR (CDCl_3 , 282.3 MHz): δ -49.90 (m). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 162.5 (d, $J=249.3$ Hz), 143.4 (d, $J=8.1$ Hz), 133.7 (d, $J=8.6$ Hz), 117.0 (d, $J=3.5$ Hz), 114.0 (d, $J=22.5$ Hz), 113.9 (d, $J=23.0$ Hz), 101.4 (s), 98.7 (s), 72.0 (d, $J=1.2$ Hz), 58.7 (s), 0.19 (s). EI-MS (m/z): 236 (M^+). Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{FOSi}$: C, 66.06; H, 7.25; F, 8.04; O, 6.77; Si, 11.88. Found: C, 66.11; H, 7.33.

I. Preparation of phenylallene derivative 6.

I-1. Experimental procedure for preparation of 6. To a solution of 1-bromo-2-(methoxymethyl)benzene (**24**)⁸ (1.08 g, 5.4 mmol) was added *n*-BuLi (1.49 M solution in *n*-hexane, 4.3 mL, 5.9 mmol) at -78 °C, and stirred for 0.5 h at same temperature. To the mixture, CuI (1.53 g, 8.1 mmol) was added in one portion, and then stirred for 2 h at room temperature. After cooling to 0 °C, propargyl bromide (0.81 mL, 10.7 mmol) was added dropwise, and stirred for 5 h at room temperature. To the reaction mixture, saturated NH₄Cl aq was added, filtration with Celite, and the filtrate was extracted with ether. The organic layer was washed with brine, dried over anhydrous MgSO₄, and the filtrate was concentrated to dryness under reduced pressure. The residue was purified by column chromatography (*n*-hexane / ether = 200 / 1), and further purification was carried out by MPLC (*n*-hexane / ethyl acetate = 50 / 1) to give very unstable **6** (611 mg, 35 %).

1-(Methoxymethyl)-2-(1,2-propadienyl)benzene (6): Colorless oil. ¹H NMR (CDCl₃, 300 MHz): δ 7.50-7.19 (4H, m), 6.48 (1H, t, *J*=6.7 Hz), 5.14 (2H, d, *J*=6.7 Hz), 4.53 (2H, s), 3.41 (3H, s). ¹³C NMR (CDCl₃, 75.5 MHz): δ 209.9, 134.1, 132.4, 129.2, 127.9, 127.3, 126.4, 90.4, 78.0, 72.8, 58.0. EI-MS (*m/z*): 160 (M⁺). Anal. Calcd. for C₁₁H₁₂O: C, 82.46; H, 7.55; O, 9.99. Found: C, 82.04; H, 7.64.

⁸ (a) Reich, H. J.; Goldenberg, W. S.; Sanders, A. W.; Jantzi, K. L.; Tzschucke, C. C. *J. Am. Chem. Soc.* **2003**, 125, 3509. (b) Christenson, B.; Hallnemo, G.; Ullenius, C. *Tetrahedron* **1991**, 47, 4739.