Supporting Information

Zirconocene-Mediated and/or Catalyzed Unprecedented Coupling Reactions of Alkoxymethyl-Substituted Styrene Derivatives

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Experimental Details

A. General.

Infrared (IR) spectra were recorded on a FT-IR spectrophotometer, ν_{max} in cm^{-1}.

^{1}H 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 or 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 ($C_6H_5CF_3$: 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.

Preparations of *o*-(benzyloxymethyl)styrene derivatives *o*-**4a**~**c** were described previous literature.[1]

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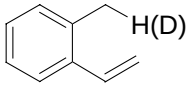
[1] Ikeuchi, Y.; Taguchi, T.; Hanzawa, Y. *J. Org. Chem.* **2005**, *70*, 756.

B-1. Typical procedure for generation of benzyl-zirconocene intermediates

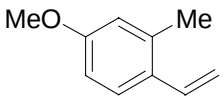
To a solution of Cp_2ZrCl_2 (153 mg, 0.53 mmol) in THF (5 mL) was added *n*-BuLi (1.6 M solution in *n*-hexane, 0.66 mL, 1.05 mmol) at -78 ^oC and stirred for 1h at the same temperature. To this solution was added a solution of *o*-**4a** (112 mg, 0.50 mmol) in THF (2 mL) and gradually warmed to room temperature, and stirred for 3 h. To this reaction mixture, 1 M HCl (aq) was added, and extracted with ether. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and the filtrate was concentrated to dryness. The residue was purified by flash chromatography (*n*-hexane) to give **8a** (52 mg, 88 %).



8a

1-Methy-2-vinylbenzene (8a): The structure was confirmed by comparison of spectrum data from a commercially available sample.

1-Methy-*d*$_1$-2-vinylbenzene (8a-D**)**: This product was prepared by using 10% DCl/D_2O instead of 1M HCl (aq). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.50-7.47 (1H, m), 7.21-7.16 (3H, m), 6.96 (1H, dd, *J*=17.4, 11.0 Hz), 5.69 (1H, dd, *J*=17.4, 1.4 Hz), 5.23 (1H, dd, *J*=11.0, 1.4 Hz), 2.46 (2H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.4, 134.8, 130.2, 127.6, 126.1, 125.3, 115.2, 111.5, 19.4 (t). EI-MS (*m/z*): 119 (M^+).

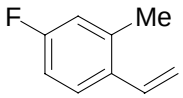


8b

4-Methoxy-2-methyl-1-vinylbenzene (*o*-8b)[2]: Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.43 (1H, d, *J*=8.5 Hz), 6.88 (1H, dd, J=17.3, 11.1 Hz), 6.76-6.70 (2H, m), 5.55 (1H, dd, *J*=17.3, 1.5 Hz), 5.29 (1H, dd, *J*=11.1, 1.5 Hz), 3.82 (3H, s), 2.36 (3H, s). ^{13}C NMR ($CDCl_3$,

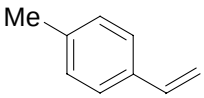
[2] Quelet, R. *Bull. Soc. Chim. Fr.* **1940**, *1*, 905.

75.5 MHz): δ 158.8, 136.7, 134.0, 129.4, 126.3, 115.3, 112.9, 111.5, 55.3, 20.1. HRMS Calcd. for $C_{10}H_{12}O$: 148.0888 (M^+). Found: 148.0882.



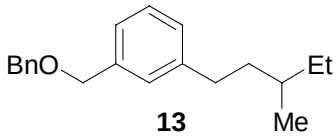
8c

4-Fluoro-2-methyl-1-vinylbenzene (8c)[3]: Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.45-7.40 (1H, m), 6.91-6.82 (3H, m), 6.76-6.70 (2H, m), 5.57 (1H, dd, *J*=17.6, 1.0 Hz), 5.27 (1H, dd, *J*=11.0, 1.0 Hz), 2.35 (3H, s). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -52.36 (m). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 162.3 (d, *J*=245.3 Hz), 137.8 (d, *J*=8.1 Hz), 134.0 (s), 133.1 (s), 127.2 (d, *J*=8.1 Hz), 116.9 (d, *J*=20.7 Hz), 115.1 (d, *J*=1.7 Hz), 113.1 (d, *J*=20.7 Hz), 20.3 (s). HRMS Calcd. for C_9H_9F: 136.0688 (M^+). Found: 136.0693.



11

1-Methy-4-vinylbenzene (11): This compound was prepared from *p*-**4** according to the typical procedure, and the structure was confirmed by comparison of spectrum data with commercially available sample.



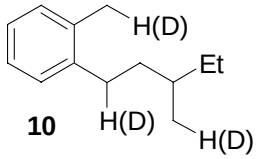
13

1-[(Benzyloxy)methyl]-3-(3-methylpentyl)benzene (13): This compound was prepared from *m*-**4** according to the typical procedure. Colorless oil. IR (liquid film): 3030, 2960, 2928, 2857, 1455, 1359, 1096, 1074, 791, 736, 698. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40-7.10 (9H,

[3] Sianesi, D. *Gazz. Chim. Ital.* **1959**, *89*, 1749.

m), 4.57 (3H, s), 4.55 (3H, s), 2.74-2.52 (2H, m), 1.71-1.13 (5H, m), 0.94 (3H, d, *J*=6.4 Hz), 0.89 (3H, t, *J*=7.2 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.1, 138.1, 137.9, 128.2, 128.1, 127.6, 127.5, 127.4, 124.9, 72.2, 72.1, 38.6, 34.3, 33.6, 29.5, 19.3, 11.5. HRMS Calcd. for $C_{13}H_{19}$: 175.1487 $(M\text{-}BnOH+H)^+$. Found: 175.1487. Anal. Calcd. for $C_{20}H_{26}O$: C, 85.06; H, 9.28; O, 5.67. Found: C, 84.92; H, 9.21.

B-2. Typical procedure for butene-coupling reactions of benzyl-zirconocene intermediates : To a solution of Cp_2ZrCl_2 (307 mg, 0.53 mmol) in THF (5 mL) was added *n*-BuLi (1.6 M solution in *n*-hexane, 1.31 mL, 2.10 mmol) at -78 ^{o}C and stirred for 1h at same temperature. To this solution was added a solution of *o*-**4a** (112 mg, 0.50 mmol) in THF (2 mL) and gradually warmed to room temperature, and stirred for 3 h. To this reaction mixture, 1 M HCl (aq) was added, and extracted with ether. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and the filtrate was concentrated to dryness. The residue was purified by flash chromatography (*n*-hexane) to give **10** (70 mg, 79 %).

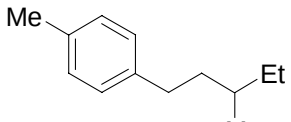


10

1-Methyl-2-(3-methylpentyl)benzene (10): Colorless oil. IR (neat): 2961, 2928, 2873, 1906, 1605, 1493, 739. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.25-7.13 (4H, m), 2.78-2.56 (2H, m), 2.37 (3H, s), 1.66-1.25 (5H, m), 1.02 (3H, d, *J*=6.1 Hz), 0.96 (3H, t, *J*=7.2 Hz).^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 141.4, 135.7, 130.1, 128.7, 125.9, 125.7, 37.3, 34.7, 30.9, 29.4, 19.23, 19.19, 11.4. EI-MS (*m/z*): 176 (M^+). Anal. Calcd. for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.66; H, 11.27.

1-Methyl-*d*$_1$-2-(3-methyl-*d*$_1$-pentyl-1-*d*$_1$)benzene (10-D): This product was prepared by using 10% DCl/D_2O instead of 1M HCl (aq). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.25-7.13 (4H, m), 2.68-2.49 (1H, m), 2.34 (2H, s), 1.66-1.14 (5H, m), 1.08-0.88 (5H, m). ^{13}C NMR

($CDCl_3$, 75.5 MHz): δ 141.4, 135.7, 130.1, 128.7, 125.9, 125.7, 37.3, 34.6, 30.76 (t), 29.4, 19.0 (t), 18.9 (t), 11.9. EI-MS (*m/z*): 179 (M^+).

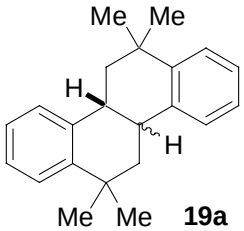


12

1-Methyl-4-(3-methylpentyl)benzene (12): Colorless oil. IR (liquid film): 2961, 2925, 2874, 2858, 1515, 1461, 1378, 807. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.21-7.01 (4H, m), 2.70-2.49 (2H, m), 2.34 (3H, s), 1.71-1.14 (5H, m), 0.95 (3H, d, *J*=6.0 Hz), 0.90 (3H, t, *J*=7.2 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 140.1, 134.9, 128.9, 128.2, 38.7, 34.1, 33.1, 29.4, 21.0, 19.1, 11.3. EI-MS (*m/z*): 176 (M^+). Anal. Calcd. for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.35; H, 11.32.

C. Typical procedure for homo-coupling reactions under catalytic conditions

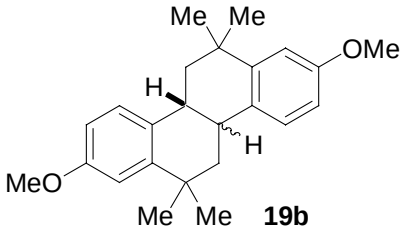
To a solution of **17b** (88 mg, 0.50 mmol) and Cp_2ZrCl_2 (14.6 mg, 0.05 mmol) in THF (5.2 mL) was added *n*-BuMgCl (0.84 M solution in THF, 1.79 mL, 1.50 mmol) at room temperature and refluxed for 5h. To this reaction mixture was added by 1N HCl (aq) at 0 ^oC, and extracted with ether. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and the filtrate was concentrated to dryness. The residue was purified by flash chromatography (*n*-hexane) to give **19a** (59 mg, 81 %) as a mixture of *trans/cis* = 3.0. Recrystallization from EtOH gave a *trans*-**19a** as a single isomer.



19a

***trans*-6,6,12,12-Tetramethyl-4b,5,6,10b,11,12-hexahydrochrysene (*trans*-19a)**: Colorless crystalline solid. mp (EtOH): 169.5-172.0 ^{o}C. IR (KBr): 2955, 2905, 2854, 1485, 1344, 755, 743. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.18 (8H, m), 2.88 (2H, dd, J=11.0, 1.0 Hz), 2.44 (2H, dd, *J*=12.5, 1.0 Hz), 1.71 (2H, dd, *J*=12.5, 11.1 Hz), 1.44 (12H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.8, 138.9, 127.0, 126.1, 125.6, 125.4, 44.0, 38.6, 35.3, 33.1, 32.6. EI-MS (*m/z*): 290 (M^+). Anal. Calcd. for $C_{22}H_{26}$: C, 90.73; H, 9.27. Found: C, 91.03; H, 9.23.

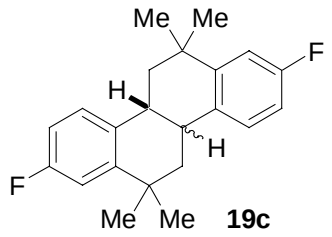
***cis*-isomer (*cis*-19a)**: Colorless crystalline solid. mp (ether): 161.4-163.4 ^{o}C. IR (KBr): 2955, 2853, 1485, 1443, 1361, 754, 743. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43-7.15 (8H, m), 3.25 (2H, dd, *J*=13.1, 4.2 Hz), 1.99 (2H, br.t, *J*=13.1 Hz), 1.69 (2H, dd, *J*=14.2, 4.2 Hz), 1.40 (6H, s), 1.35 (6H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.0, 140.0, 129.5, 126.4, 125.7, 125.3, 43.4, 35.3, 34.8, 31.3, 30.3.



19b

***trans*-2,8-Dimethoxy-6,6,12,12-tetramethyl-4b,5,6,10b,11,12-hexahydrochrysene (*trans*-19b)**: Colorless crystalline solid. mp (ether): 213.3-215.3 ^{o}C. IR (KBr): 2955, 1611, 1573, 1489, 1287, 1231, 1076, 1044, 874, 801. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33 (2H, d, *J*=8.8 Hz), 6.94 (2H, d, *J*=2.6 Hz), 6.76 (2H, dd, *J*=8.8, 2.6 Hz), 3.83 (6H, s), 2.76 (2H, br.d, *J*=9.7 Hz), 2.38 (2H, br.d, *J*=13.8 Hz), 1.66 (2H, br.t, *J*=12.3 Hz), 1.45 (12H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 157.5, 147.1, 131.1, 126.1, 112.6, 110.8, 55.3, 44.3, 38.3, 35.6, 33.2, 32.8. HRMS Calcd. for $C_{24}H_{31}O_2$: 351.2324 $(M+H)^+$. Found: 352.2340. Anal. Calcd. for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63; O, 9.13. Found: C, 82.01; H, 8.66.

***cis*-isomer (*cis*-19b)**: Colorless crystalline solid. mp (ether): 113.7-114.7 ^{o}C. IR (KBr): 2957, 1612, 1573, 1493, 1463, 1287, 1247, 1229, 1195, 1171, 1077, 1045, 873, 800. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.09 (2H, d, *J*=8.5 Hz), 6.89 (2H, d, *J*=2.6 Hz), 6.76 (2H, dd, *J*=8.5, 2.6 Hz), 3.82 (6H, s), 3.18 (2H, br.d, *J*=12.9 Hz), 1.93 (2H, br.t, *J*=12.9 Hz), 1.63 (2H, br.d, *J*=14.7 Hz), 1.39 (6H, s), 1.34 (6H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 157.5, 146.1, 132.2, 130.2, 111.5, 111.4, 55.3, 45.2, 35.1, 34.7, 32.7, 31.4.

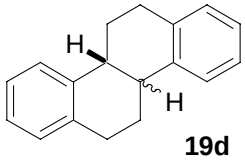


19c

***trans*-2,8-Difluoro-6,6,12,12-tetramethyl-4b,5,6,10b,11,12-hexahydrochrysene (*trans*-19c)**: Colorless crystalline solid. mp (ether): 201.0-202.0 ^{o}C. IR (KBr): 2966, 2942, 2862, 1608, 1584, 1486, 1272, 1211, 1179, 939, 925, 884, 813, 770, 517, 483. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35 (2H, dd, *J*=8.4, 6.0 Hz), 7.07 (2H, dd, *J*=10.7, 2.7 Hz), 6.88 (2H, dt, *J*=8.4, 2.7 Hz), 2.77 (2H, br.d, *J*=13.2 Hz), 2.38 (2H, br.d, *J*=13.2 Hz), 1.68 (2H, br.t, *J*=12.5 Hz), 1.41 (12H, s). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -54.16 (dt, *J*=9.9, 7.9 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 161.2 (d, *J*=242.4 Hz), 147.9 (d, *J*=5.8 Hz), 133.9 (d, *J*=2.9 Hz), 126.7 (d, *J*=7.5 Hz), 113.2 (d, *J*=20.7 Hz), 112.5 (d, *J*=20.7 Hz), 44.1 (s), 38.3 (s), 35.7 (s), 33.1 (s), 32.6 (s). EI-MS (*m/z*): 326 (M^{+}). Anal. Calcd. for $C_{22}H_{24}F_2$: C, 80.95; H, 7.41; F, 11.64. Found: C, 81.05; H, 7.51.

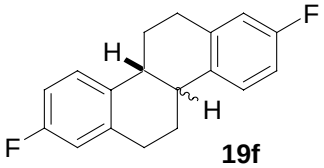
***cis*-isomer (*cis*-19c)**: Crystalline solid. mp (ether): 170.5-172.5 ^{o}C. IR (KBr): 2959, 2917, 1610, 1586, 1498, 1483, 1273, 1209, 1174, 935, 875, 811, 774. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.11 (2H, dd, *J*=8.5, 6.2 Hz), 7.03 (2H, dd, *J*=10.8, 2.6 Hz), 6.87 (2H, dt, *J*=8.5, 2.6 Hz), 3.20 (2H, br.d, *J*=13.1 Hz), 1.92 (2H, br.t, *J*=13.1 Hz), 1.63 (2H, br.d, *J*=14.4 Hz), 1.41 (6H, s), 1.34 (6H, s). ^{19}F NMR ($CDCl_3$, 283 MHz): δ -53.82 (dt, *J*=9.9, 4.0 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz):

δ 161.1 (d, *J*=241.8 Hz), 146.9 (d, *J*=6.3 Hz), 135.0 (d, *J*=2.3 Hz), 130.7 (d, *J*=8.1 Hz), 113.0 (d, *J*=21.3 Hz), 112.5 (d, *J*=20.7 Hz), 44.7 (s), 35.2 (s), 34.8 (s), 32.6 (s), 31.3 (s).



19d

4b,5,6,10b,11,12-Hexahydrochrysene (19d)[4]: The structure was confirmed by comparison of spectrum data with the authentic sample prepared according to the literature[4].



19f

2,8-Difluoro-4b,5,6,10b,11,12-hexahydrochrysene (19f): Although a small amount of pure *cis*-isomer was isolated and analyzed for X-ray, it was difficult to separate to each isomer by recrystallization or MPLC. Thus, the data described below were obtained as a mixture of *trans* / *cis* isomers (1.5 / 1). Colorless crystalline solid. Mp (ether): 128.3-129.3 ^{o}C. IR (KBr): 2959, 2927, 1613, 1590, 1495, 1259, 1223, 1146, 1099, 967, 926, 879, 822, 779, 720. ^{1}H NMR ($CDCl_3$, 300 MHz): [*trans*-isomer] δ 7.18 (1H, dd, *J*=8.6, 5.7 Hz), 6.92-6.77 (2H, m), 3.08-1.26 (5H, m); [*cis*-isomer] δ 7.32 (1H, dd, *J*=8.5, 5.6 Hz), 6.92-6.77 (2H, m), 3.08-1.26 (5H, m). ^{19}F NMR ($CDCl_3$, 283 MHz): δ -54.63 (ddd, J_{H-F}=9.9, 7.9, 6.0 Hz, *trans*-isomer), -54.89 (ddd, J_{H-F}=9.4, 7.9, 5.9 Hz, *cis*-isomer). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ [*trans*-isomer] 160.6 (d, J_{C-F}=243.6 Hz), 137.8 (d, J_{C-F}=6.9 Hz), 135.9 (d, J_{C-F}=2.9 Hz), 130.6 (d, J_{C-F}=5.2 Hz), 114.6 (d, J_{C-F}=20.2 Hz), 112.9 (d, J_{C-F}=21.9 Hz), 37.9, 30.2, 29.2; [*cis*-isomer] 160.8 (d, J_{C-F}=243.0 Hz), 138.7 (d, J_{C-F}=6.9 Hz), 135.4 (d, J_{C-F}=2.9 Hz), 126.8 (d, J_{C-F}=8.0 Hz), 114.7 (d, J_{C-F}=20.7 Hz),

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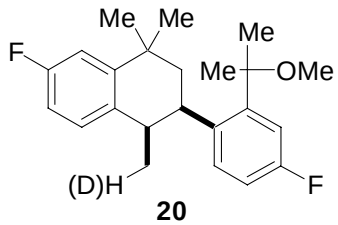
[4] Levy, L. A.; Sashikumar, V. P. *J. Org. Chem.* **1985**, *50*, 1760.

113.0 (d, $J_{C\text{-}F}$=21.3 Hz), 40.6, 30.0, 27.5. EI-MS (*m/z*): 270 (M^+). Anal. Calcd. for $C_{18}H_{16}F_2$: C, 79.98; H, 5.97; F, 14.06. Found: C, 79.99; H, 6.22.



20

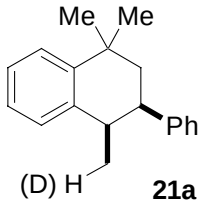
***cis*-7-Fluoro-3-[4-fluoro-2-(1-methoxy-1-methylethyl)phenyl]-1,1,4-trimethyl-1,2,3,4-tetrahydronapthalene (20)**: Colorless crystalline solid. mp (ether): 162.0-164.0 ^oC. IR (KBr): 2971, 1608, 1583, 1484, 1274, 1243, 1184, 1067, 940, 828, 560. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.29 (1H, dd, *J*=8.5, 6.5 Hz), 7.07-6.92 (4H, m), 6.80 (1H, dt, *J*=8.5, 2.6 Hz), 4.38 (1H, ddd, *J*=13.3, 4.7, 2.1 Hz), 3.07-3.01 (1H, m), 3.06 (3H, s), 2.33 (1H, br.t, *J*=13.3 Hz), 1.61 (6H, s), 1.49 (1H, br.d, *J*=13.3 Hz), 1.40 (3H, s), 1.36 (3H, s), 1.12 (3H, d, *J*=7.3 Hz). ^{19}F NMR ($CDCl_3$, 283 MHz): δ -54.08 (1F, ddd, *J*=7.9, 5.9, 4.0 Hz), -54.33 (1F, ddd, *J*=7.9, 5.9, 4.0 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 161.1 (d, *J*=241.9 Hz), 160.4 (d, *J*=243.0 Hz), 146.3 (d, *J*=6.3 Hz), 144.9 (d, *J*=5.8 Hz), 139.4 (d, *J*=3.5 Hz), 138.0 (d, *J*=2.9 Hz), 131.5 (d, *J*=7.5 Hz), 130.4 (d, *J*=8.1 Hz), 114.2 (d, *J*=21.8 Hz), 112.9 (d, *J*=20.7 Hz), 112.6 (d, *J*=21.4 Hz), 78.2 (d, *J*=1.7 Hz), 51.0 (s), 40.5 (s), 38.8 (s), 36.3 (s), 34.5 (s), 32.6 (s), 32.1 (s), 29.3 (s), 28.2 (s), 19.4 (s). HRMS Calcd. for $C_{22}H_{25}F_2$: 327.1924 (M - MeOH + H)$^+$. Found: 327.1909. Anal. Calcd. for $C_{23}H_{28}F_2O$: C, 77.06; H, 7.87; F, 10.60; O, 4.46. Found: C, 77.02; H, 7.70.

***cis*-7-Fluoro-3-[4-fluoro-2-(1-methoxy-1-methylethyl)phenyl]-1,1,(4-d_1)-trimethyl-1,2,3,4-tetrahydronapthalene (20-D)**: ^1H NMR ($CDCl_3$, 300 MHz): δ 7.29 (1H, dd, *J*=8.5, 6.5 Hz), 7.07-6.92 (4H, m), 6.80 (1H, dt, *J*=8.5, 2.6 Hz), 4.38 (1H, ddd, *J*=13.3, 4.7, 2.1 Hz), 3.07-3.01 (1H, m), 3.06 (3H, s), 2.33 (1H, br.t, *J*=13.3 Hz), 1.61 (6H, s), 1.49 (1H, br.d, *J*=13.3 Hz), 1.40 (3H, s), 1.36 (3H, s), 1.12 (2H, dd, *J*=7.0, 4.7 Hz). ^{19}F NMR ($CDCl_3$, 283 MHz): δ -54.08 (1F,

ddd, *J*=7.9, 5.9, 4.0 Hz), -54.33 (1F, ddd, *J*=7.9, 5.9, 4.0 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 161.1 (d, *J*=241.9 Hz), 160.4 (d, *J*=243.0 Hz), 146.3 (d, *J*=6.3 Hz), 144.9 (d, *J*=5.8 Hz), 139.4 (d, *J*=3.5 Hz), 138.0 (d, *J*=2.9 Hz), 131.5 (d, *J*=7.5 Hz), 130.4 (d, *J*=8.1 Hz), 114.2 (d, *J*=21.8 Hz), 112.9 (d, *J*=20.7 Hz), 112.6 (d, *J*=21.4 Hz), 78.2 (d, *J*=1.7 Hz), 51.0 (s), 40.5 (s), 38.8 (s), 36.3 (s), 34.5 (s), 32.6 (s), 32.1 (s), 29.3 (s), 28.2 (s), 19.4 (t). HRMS Calcd. for $C_{22}H_{24}DF_2$: 328.1987 $(M - MeOH + H)^+$. Found: 328.1985.

D. Typical procedure for hetero-coupling reactions

To a solution of Cp_2ZrCl_2 (175 mg, 0.60 mmol) in THF (5 mL) was added *n*-BuLi (1.6 M solution in *n*-hexane, 0.75 mL, 1.20 mmol) at -78 ^{o}C and stirred for 1h at same temperature. To this solution was added a solution of **17b** (88 mg, 0.50 mmol) and **5a** (156 mg, 1.50 mmol) in THF (2 mL) and gradually warmed to room temperature, and stirred for 3h. To this reaction mixture, 1 M HCl (aq) was added, and extracted with ether. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, 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 **21a** (106 mg, 85 %).

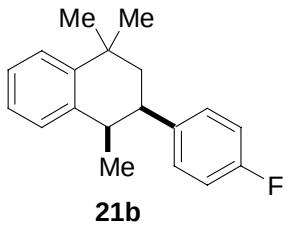


21a

1,1,4-Trimethyl-3-phenyl-1,2,3,4-tetrahydronaphthalene (21a): Colorless crystalline solid. mp (ether): 75.4-76.4 ^{o}C. IR (KBr): 2962, 2931, 1487, 1452, 1040, 763, 751, 699. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37-7.31 (3H, m), 7.26-6.97 (6H, m), 3.38 (1H, ddd, *J*=13.6, 4.8, 1.9 Hz), 3.09 (1H, dq, *J*=7.2, 4.8 Hz), 2.25 (1H, dd, 13.6, 13.0 Hz), 1.73 (1H, dd, *J*=13.0, 1.9 Hz), 1.44 (3H, s), 1.31 (3H, s), 0.87 (3H, d, *J*=7.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.8, 144.4,

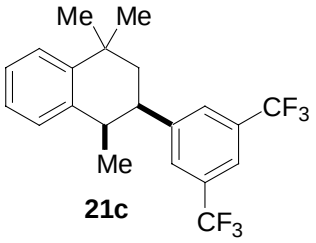
142.1, 129.2, 128.2, 127.8, 126.9, 126.2, 126.0, 125.6, 40.4, 39.4, 37.2, 35.2, 32.7, 32.3, 18.1. EI-MS (*m/z*): 250 (M^+). Anal. Calcd. for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.25; H, 8.46.

1,1,4-Trimethyl-4-*d*$_1$-3-phenyl-1,2,3,4-tetrahydronaphthalene (21a-D): Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.54-7.23 (9H, m), 3.56 (1H, ddd, *J*=13.5, 5.0, 2.0 Hz), 3.26 (1H, dt, *J*=7.0, 5.0 Hz), 2.42 (1H, dd, *J*=13.5, 12.9 Hz), 1.90 (1H, dd, *J*=12.9, 2.0 Hz), 1.61 (3H, s), 1.49 (3H, s), 1.03 (2H, d, *J*=7.0 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 144.5, 144.1, 141.8, 129.0, 128.0, 127.6, 126.7, 126.0, 125.8, 125.4, 40.5, 39.5, 37.4, 35.3, 32.8, 32.4, 18.0 (t). EI-MS (*m/z*): 251 (M^+).



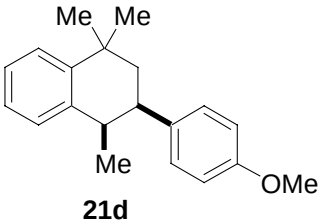
21b

3-(4-Fluorophenyl)-1,1,4-trimethyl-1,2,3,4-tetrahydronaphthalene (21b): White powder. mp (ether): 91.6-93.6 ^{o}C. IR (KBr): 2968, 2934, 2883, 2869, 1508, 1488, 1220, 1159, 1093, 1040, 838, 764, 557, 505. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.39-7.36 (1H, m), 7.24-7.01 (7H, m), 3.37 (1H, ddd, *J*=13.5, 5.2, 1.9 Hz), 3.07 (1H, dq, *J*=7.2, 5.2 Hz), 2.23 (1H, dd, *J*=13.5, 13.2 Hz), 1.73 (1H, dd, *J*=13.2, 1.9 Hz), 1.46 (3H, s), 1.33 (3H, s), 0.88 (3H, d, *J*=7.2 Hz). ^{19}F NMR (283 MHz, $CDCl_3$): δ -54.42 (ddd, *J*=9.9, 6.0, 4.0 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 161.0 (d, *J*=242.4 Hz), 144.0 (s), 141.6 (s), 140.2 (d, *J*=3.5 Hz), 129.0 (s), 128.9 (d, *J*=7.5 Hz), 126.7 (s), 126.1 (s), 125.4 (s), 114.8 (d, *J*=20.7 Hz), 40.5 (s), 38.9 (s), 37.6 (s), 35.4 (s), 32.9 (s), 32.4 (s), 18.2 (s). EI-MS (*m/z*): 268 (M^+). Anal. Calcd. for $C_{19}H_{21}F$: C, 85.03; H, 7.89; F, 7.08. Found: C, 84.88; H, 7.83.



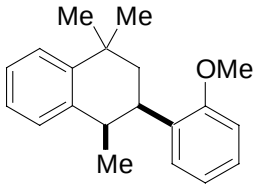
21c

3-[3,5-Bis(trifluoromethyl)phenyl)-1,1,4-trimethyl-1,2,3,4-tetrahydronaphthalene (21c): White powder. mp (ether): 74.7-75.7 ^{o}C. IR (KBr): 2964, 1368, 1278, 1167, 1134, 896, 757, 707, 684. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.77 (1H, br.s), 7.70 (2H, br.s), 7.40-7.37 (1H, m), 7.26-7.08 (3H, m), 3.52 (1H, ddd, *J*=13.6, 4.5, 2.1 Hz), 3.15 (1H, dq, *J*=6.9, 4.5 Hz), 2.31 (1H, dd, *J*=13.6, 13.0 Hz), 3.53 (dd, *J*=13.0, 2.1 Hz), 1.50 (3H, s), 1.35 (3H, s), 0.89 (3H, d, *J*=6.9 Hz). ^{19}F NMR (283 MHz, CDCl3): δ 0.04 (s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 147.1, 143.6, 140.6, 131.5, 131.0, 128.9, 127.8, 126.8, 126.4, 125.7, 125.1, 121.5, 120.0, 40.1, 39.8, 37.1, 35.4, 32.8, 32.3, 18.1. EI-MS (*m/z*): 386 (M^+).



21d

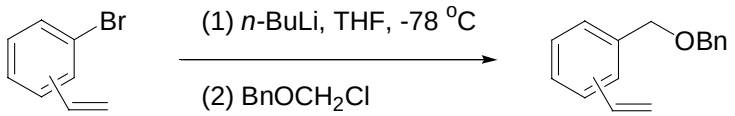
3-(4-Methoxyphenyl)-1,1,4-trimethyl-1,2,3,4-tetrahydronaphthalene (21d): Colorless oil. IR (liquid film): 2963, 2926, 1513, 1250, 1180, 1040, 834, 755. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40-7.37 (1H, m), 7.24-7.09 (5H, m), 6.94-6.89 (2H, m), 3.84 (3H, s), 3.36 (1H, ddd, *J*=13.5, 4.7, 2.1 Hz), 3.08 (1H, dq, *J*=7.0, 4.7 Hz), 2.25 (1H, dd, *J*=13.5, 13.2 Hz), 1.73 (1H, dd, *J*=13.2, 2.1 Hz), 1.46 (3H, s), 1.34 (3H, s), 0.90 (3H, d, *J*=7.0 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 157.5, 144.1, 141.9, 136.7, 129.0, 128.4, 126.7, 125.9, 125.3, 113.4, 113.4, 55.3, 40.7, 38.7, 37.7, 35.4, 32.9, 32.4, 18.2. EI-MS (*m/z*): 280 (M^+). Anal. Calcd. for $C_{20}H_{24}O$: C, 85.67; H, 8.63; O, 5.71. Found: C, 85.56; H, 8.79.



21e

3-(2-Methoxyphenyl)-1,1,4-trimethyl-1,2,3,4-tetrahydronaphthalene (21e): White solid. mp (ether): 74.5-75.5 ^{o}C. IR (KBr): 2958, 2926, 1494, 1463, 1246, 1102, 1032, 758. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40-7.36 (1H, m), 7.25-7.11 (5H, m), 6.97 (1H, dd, *J*=7.3, 0.9 Hz), 6.89 (1H, dt, *J*=8.2, 0.9 Hz), 3.82 (3H, s), 3.76 (1H, ddd, *J*=13.5, 4.7, 2.0 Hz), 3.29 (1H, dq, *J*=7.2, 4.7 Hz), 2.30 (1H, dd, *J*=13.5, 13.2 Hz), 1.62 (1H, dd, *J*=13.2, 2.0 Hz), 1.46 (3H, s), 1.35 (3H, s), 0.88 (3H, d, *J*=7.3 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 157.0, 144.2, 142.5, 132.8, 129.3, 127.7, 126.7, 126.6, 125.7, 125.2, 119.9, 109.8, 55.3, 37.8, 35.4, 33.0, 32.7, 32.4, 18.8. EI-MS (*m/z*): 280 (M^+). Anal. Calcd. for $C_{20}H_{24}O$: C, 85.67; H, 8.63; O, 5.71. Found: C, 85.63; H, 8.70.

E. Preparation of *m*- and *p*-4a

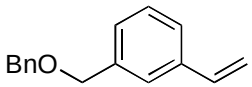


m- or *p*-**27** *m*- or *p*-**4**

Typical procedure

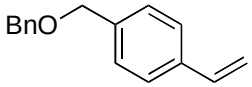
To a solution of 3-bromostyrene (*m*-**27**) (549 mg, 3.0 mmol) in THF (15mL) was added *n*-BuLi (1.46 M solution in *n*-hexane, 2.1 mL, 3.0 mmol) at -78 ^{o}C, and stirred for 0.5 h. To the mixture was added benzyl chloromethyl ether (0.44 mL, 3.2 mmol) in a dropwise manner. The mixture was warmed gradually to room temperature and stirred for 5 h. To the reaction mixture was added saturated NH_4Cl (aq) at 0 ^{o}C, 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 / ethyl acetate = 100 / 1) to give *m*-**4a** (575 mg, 85 %).



m-**4**

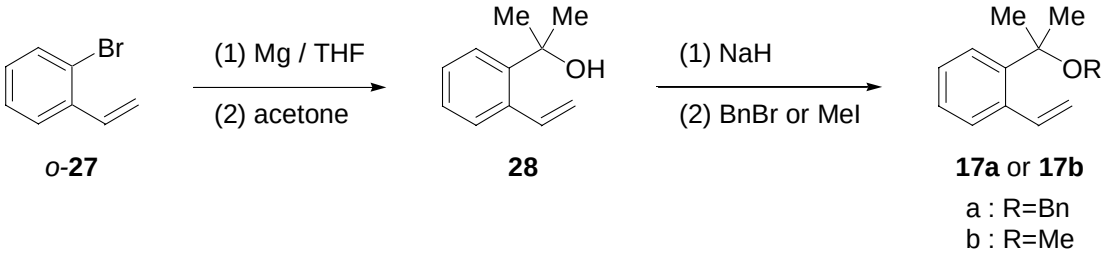
1-[(Benzyloxy)methyl]-3-vinylbenzene (*m*-4): Colorless oil. IR (liquid film): 3030, 2855, 1630, 1512, 1497, 1455, 1406, 1361, 1210, 1094, 1074, 991, 909, 827, 737, 698. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42-7.25 (9H, m), 6.73 (1H, dd, *J*=17.6, 10.8 Hz), 5.77 (1H, dd, *J*=17.6, 0.9 Hz), 5.27 (1H, dd, *J*=10.8, 0.9 Hz), 4.58 (2H, s), 4.57 (2H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 138.3, 138.0, 137.5, 136.5, 128.4, 128.2, 127.6, 127.4, 127.0, 125.4, 125.3, 113.9, 72.2, 72.0. EI-MS (*m/z*): 224 (M^+). Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19; O, 7.13. Found: C, 85.56; H, 7.19.



p-**4**

1-[(Benzyloxy)methyl]-4-vinylbenzene (*p*-4): This product (1.04 g, 93%) was prepared from 4-bromostyrene (*p*-**27**) (915 mg, 5 mmol) according to the typical procedure. Colorless oil. IR (liquid film): 3030, 2857, 1455, 1358, 1091. 1074, 991, 909, 798, 737, 714, 698. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.45-7.32 (9H, m), 6.75 (1H, dd, *J*=17.6, 10.9 Hz), 5.78 (1H, dd, *J*=17.6, 0.9 Hz), 5.27 (1H, dd, *J*=10.9, 0.9 Hz), 4.58 (4H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 138.2, 137.8, 136.9, 136.5, 128.3, 127.9, 127.7, 127.6, 113.7, 72.0, 71.7. EI-MS (*m/z*): 224 (M^+). Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19; O, 7.13. Found: C, 85.60; H, 7.24.

F. Preparation of *o*-(alkoxy-isopropyl)styrene derivatives (17a,b)



o-**27** **28** **17a** or **17b**

a : R=Bn
b : R=Me

F-1. Typical procedure for Grignard reaction

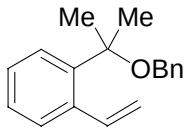
To a suspension of magnesium turnings (549 mg, 22.5 mmol) in THF (20 mL) was added a solution of 2-bromostyrene (*o*-**27**) (1.88 mL, 15 mmol) in THF (10 mL) at 0 ^{o}C over 1h, and stirred for 1h at room temperature. To the mixture was added slowly a solution of acetone (2.20 mL. 30.0 mmol) in THF (5 mL) at 0 ^{o}C, and stirred for 5h. After cooling to 0 ^{o}C, to the reaction mixture was added saturated NH_4Cl (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*-hexane / ethyl acetate = 20 / 1) to give **28** (1.40 g, 58 %).

2-(2-Vinylphenyl)-2-propanol (28): Semisolid. IR (KBr): 3378, 2977, 1478, 1365, 1165, 1144, 913, 759. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.64 (1H, dd, *J*=17.3, 10.8 Hz), 7.49-7.43 (2H, m), 7.25-7.23 (2H, m), 5.52 (1H, dd, *J*=17.3, 1.8 Hz), 5.28 (1H, dd, *J*=10.8, 1.8 Hz), 1.67 (6H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 144.5, 137.9, 137.0, 128.3, 127.2, 127.1, 124.8, 115.0, 73.6, 31.5. EI-MS (*m/z*): 162 (M^+). Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70; O, 9.86. Found: C, 81.32; H, 8.42.

F-2. Typical procedure for etherification

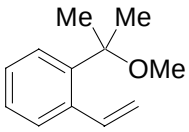
To a suspension of NaH (55%, 52 mg, 1.2 mmol) in THF (5 mL) was added a solution of **28** (162 mg, 1.0 mmol) in THF (5 mL) at 0 ^{o}C, and stirred for 1h. To the reaction mixture was added benzyl bromide (0.14 mL, 1.2 mmol) and stirred for overnight at room temperature. After cooling to 0 ^{o}C, saturated NH_4Cl aq was added, 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 = 100 / 1) to give **17a** (89 mg, 35 %).



17a

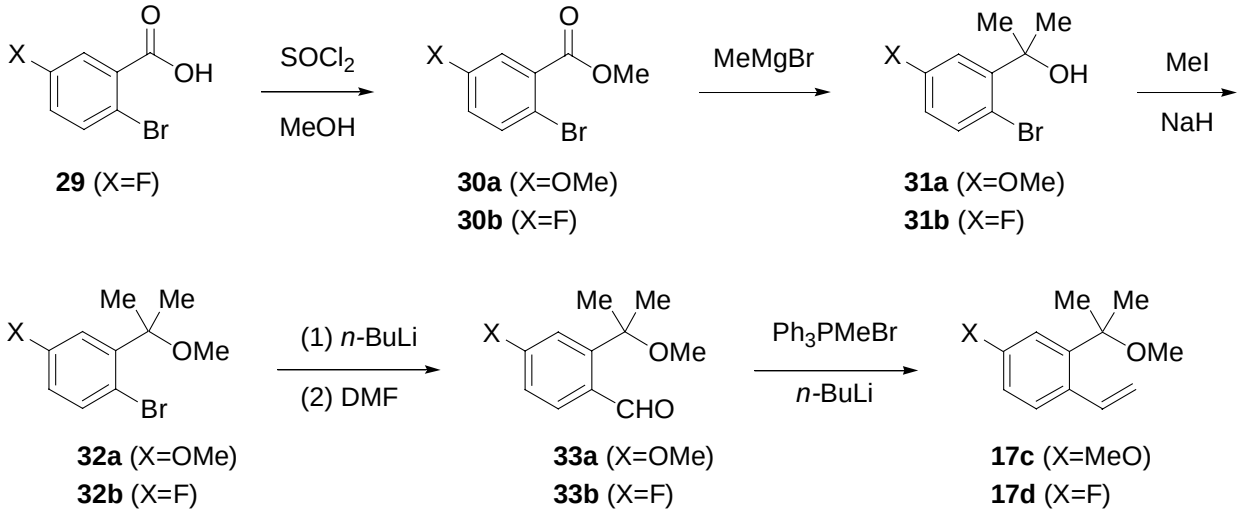
1-[1-(Benzyloxy)-1-methylethyl]-2-vinylbenzene (17a): Colorless oil. IR (liquid film): 2981, 1381, 1157, 1060, 913, 773, 759, 734, 699. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.75 (1H, dd, *J*=17.4, 10.8 Hz), 7.59-7.55 (1H, m), 7.38-7.20 (8H, m), 5.56 (1H, dd, *J*=17.4, 1.8 Hz), 5.22 (1H, dd, *J*=10.8, 1.8 Hz), 4.16 (2H, s), 1.73 (6H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 141.2, 139.0, 137.7, 137.5, 128.0, 127.7, 127.6, 127.4, 127.2, 127.0, 126.6, 114.7, 78.5, 65.3, 28.8. EI-MS (*m/z*): 252 (M^+). Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99; O, 6.34. Found: C, 85.66; H, 7.97.



17b

1-[1-(Methoxy)-1-methylethyl]-2-vinylbenzene (17b): This product (1.34 g, 95%) was prepared from alcohol **28** (1.30 g, 8.0 mmol) by using of methyl iodide instead of benzyl bromide. Colorless oil. IR (liquid film): 2981, 2934, 1170, 1074, 912, 758. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62 (1H, dd, *J*=17.4, 10.8 Hz), 7.51-7.47 (1H, m), 7.28-7.18 (3H, m), 5.50 (1H, dd, *J*=17.4, 1.8 Hz), 5.21 (1H, dd, *J*=10.8, 1.8 Hz), 3.00 (3H, s), 1.60 (6H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 141.1, 137.7, 137.5, 127.7, 127.3, 127.1, 126.7, 114.3, 78.3, 50.5, 28.3. EI-MS (*m/z*): 176 (M^+). Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15; O, 9.08. Found: C, 81.89; H, 9.00.

G. Preparation of substituted *o*-(alkoxy-isopropyl)styrene derivatives (17c,d)



29 (X=F)

30a (X=OMe)
30b (X=F)

31a (X=OMe)
31b (X=F)

32a (X=OMe)
32b (X=F)

33a (X=OMe)
33b (X=F)

17c (X=MeO)
17d (X=F)

G-1. Experimental procedure for esterification

To a solution of 2-bromo-5-fluorobenzoic acid (**29**) (2.00 g, 9.13 mmol) in methanol (40 mL) was added thionyl chloride (1.0 mL, 13.7 mmol) at 0 ^{o}C over 1h, and stirred for overnight at room temperature, and then refluxed for 8h. After cooling to room temperature, the solvent was concentrated to dryness under reduced pressure. The residue was diluted with ether, and washed with sat. $NaHCO_3$ (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 = 20 / 1) to give **30b** (2.17 g, quant).

Methyl 2-bromo-5-fluorobenzoate (30b): Colorless oil. IR (liquid film): 1739, 1469, 1437, 1302, 1249, 1204, 1034. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63 (1H, dd, *J*=8.7, 5.1 Hz), 7.53 (1H, dd, J=8.7, 3.3 Hz), 7.11-7.04 (1H, m), 3.95 (3H, s). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -50.92 (ddd, *J*=9.9, 7.9, 4.0 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 165.0 (s), 161.0 (d, *J*=247.6 Hz), 135.5 (d, *J*=7.5 Hz), 133.2 (d, *J*=8.6 Hz), 120.0 (d, *J*=22.5 Hz), 118.3 (d, *J*=24.2 Hz), 115.9 (d, *J*=4.0 Hz), 52.8 (s). EI-MS (*m/z*): 232 (M^+). Anal. Calcd. for $C_8H_6BrFO_2$: C, 41.23; H, 2.60; Br, 34.29; F, 8.15; O, 13.73. Found: C, 41.40; H, 2.90.

G-2. Typical procedure for Grignard reaction

To a solution of MeMgBr (0.93 M in THF, 53.8 mL, 50 mmol) in THF was added a solution of methyl 2-bromo-5-methoxybenzoate (**30a**)[5] (4.90 g, 20 mmol) in THF (20 mL) at 0 ^{o}C, and stirred for 10h at room temperature. To the mixture was added saturated NH_4Cl (aq) at 0 ^{o}C, 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 / ethyl acetate = 20 / 1 to 4 / 1) to give **31a** (4.54 g, 93 %).

2-(2-Bromo-5-methoxyphenyl)-2-propanol (31a): Colorless crystalline solid. mp (ether): 96.8-97.8 ^{o}C. IR (KBr): 3343, 1569, 1459, 1291, 1242, 1165, 1047, 1014, 886, 805, 605. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46 (1H, d, *J*=8.8 Hz), 7.26 (1H, d, *J*=3.2 Hz), 6.65 (1H, dd, *J*=8.8, 3.2 Hz), 3.81 (3H, s), 2.71 (1H, s), 1.75 (6H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 158.6, 147.0, 135.4, 113.6, 113.1, 110.4, 73.4, 55.5, 29.5. EI-MS (*m/z*): 244 (M^+). Anal. Calcd. for $C_{10}H_{13}BrO_2$: C, 49.00; H, 5.35; Br, 32.60; O, 13.05. Found: C, 48.81; H, 5.46.

2-(2-Bromo-5-fluorophenyl)-2-propanol (31b): This product (1.97 g, 8.5 mmol, 99% yield) was prepared from ester **30b** (2.00 g, 8.6 mmol). Semisolid. IR (KBr): 3434, 1576, 1456, 1262, 1024, 811, 610. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55-7.43 (2H, m), 6.86-6.80 (1H, m), 1.75 (6H, s). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -51.08 (ddd, *J*=7.9, 5.9, 4.0 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 161.7 (d, *J*=245.0 Hz), 148.5 (d, *J*=6.3 Hz), 135.9 (d, *J*=8.1 Hz), 115.1 (d, *J*=22.5 Hz), 114.6 (d, *J*=24.8 Hz), 113.9 (d, *J*=3.5 Hz), 73.3 (s), 29.3 (s). EI-MS (*m/z*): 232 (M^+). Anal. Calcd. for $C_9H_{10}BrFO$: C, 46.38; H, 4.32; Br, 34.28; F, 8.15; O, 6.86. Found: C, 46.17; H, 4.37.

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[5] Commercially available.

G-3. Typical procedure for etherification

To a solution of **31a** (3.68 g, 15.0 mmol) in THF (50 mL) was added NaH (55%, 982 mg, 22.5 mmol) at 0 ^{o}C, and stirred for 1h. To the reaction mixture was added methyl iodide (1.4 mL, 22.5 mmol), and stirred for 6h at room temperature. After cooling to 0 ^{o}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 = 10 / 1) to give **32a** (3.84 g, 99 %).

1-Bromo-4-methoxy-2-(1-methoxy-1-methylethyl)benzene (32a): Colorless oil. IR (liquid film): 2979, 2936, 1465, 1290, 1175, 1074, 1049, 1019, 806, 604. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.50 (1H, d, *J*=8.8 Hz), 7.01 (1H, d, *J*=3.2 Hz), 6.66 (1H, dd, *J*=8.8, 3.2 Hz), 3.81 (3H, s), 3.12 (3H, s), 1.67 (6H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 158.2, 143.9, 135.8, 115.4, 112.7, 111.2, 77.7, 55.3, 50.5, 26.6. EI-MS (*m/z*): 258 (M^+). Anal. Calcd. for $C_{11}H_{15}BrO_2$: C, 50.98; H, 5.83; Br, 30.83; O, 12.35. Found: C, 51.12; H, 5.82.

1-Bromo-4-fluoro-2-(1-methoxy-1-methylethyl)benzene (32b): This product (1.81 g, 7.3 mmol, 92% yield) was prepared from ester **31b** (1.86 g, 8.0 mmol). Colorless oil. IR (liquid film): 1462, 1265, 1175, 1073, 1026, 812, 610. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56 (1H, dd, *J*=8.8, 5.6 Hz), 7.19 (1H, dd, *J*=10.8, 3.2 Hz), 6.83 (1H, ddd, *J*=8.8, 7.2, 3.2 Hz), 3.13 (3H, s), 1.67, (6H, s). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -51.75 (ddd, *J*=7.9, 6.0, 4.0 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 161.5 (d, *J*=245.3 Hz), 145.5 (d, *J*=5.4 Hz), 136.4 (d, *J*=8.1 Hz), 116.0 (d, *J*=24.2 Hz), 115.2 (d, *J*=22.5 Hz), 114.9 (d, *J*=2.9 Hz), 77.7 (s), 50.6 (s), 26.4 (s). EI-MS

(*m/z*): 246 (M^+). Anal. Calcd. for $C_{10}H_{12}BrFO$: C, 48.61; H, 4.89; Br, 32.34; F, 7.69; O, 6.47. Found: C, 48.95; H, 4.98.

G-4. Typical procedure for formylation

To a solution of **32a** (3.11 g, 12.0 mmol) in THF (30 mL) was added *n*-BuLi (1.37 M in *n*-hexane, 10.5 mL, 14.4 mmol) at -78 ^oC, and stirred for 0.5h. To the reaction mixture was added DMF (1.4 mL, 18.0 mmol), and stirred for overnight at room temperature. To the reaction mixture was added saturated NH_4Cl (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*-hexane / ethyl acetate = 10 / 1) to give **33a** (2.20 g, 88 %).

4-Methoxy-2-(1-methoxy-1-methylethyl)benzaldehyde (33a): Colorless oil. IR (liquid film): 1678, 1598, 1305, 1255, 1072, 1039, 820, 562. ^1H NMR ($CDCl_3$, 300 MHz): δ 10.81 (1H, s), 8.00 (1H, d, *J*=8.5 Hz), 6.88-6.82 (2H, m), 3.88 (3H, s), 3.07 (3H, s), 1.67 (6H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 192.2, 162.8, 149.1, 131.0, 128.6, 113.8, 110.9, 78.2, 55.4, 50.5, 29.2. EI-MS (*m/z*): 208 (M^+). Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74; O, 23.05. Found: C, 69.16; H, 7.62.

4-Fluoro-2-(1-methoxy-1-methylethyl)benzaldehyde (33b): This product (1.14 g, 5.8 mmol, 90% yield) was prepared from bromide **32b** (1.61 g, 6.5 mmol). Colorless oil. IR (liquid film): 1686, 1605, 1580, 1254, 1196, 1064, 821. ^1H NMR ($CDCl_3$, 300 MHz): δ 10.83 (1H, s), 7.96 (1H, dd, *J*=8.5, 6.2 Hz), 7.08-7.00 (2H, m), 3.08 (3H, s), 1.68 (6H, s). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -41.82 (ddd, J=7.9, 6.0, 4.0). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 191.2 (s), 164.5 (d, *J*=252.8 Hz), 149.9 (d, *J*=6.9 Hz), 131.8 (d, *J*=2.3 Hz), 131.0 (d, *J*=9.2 Hz), 113.89 (d, *J*=23.6 Hz), 113.87 (d, *J*=24.8 Hz), 77.8 (s), 50.1 (s), 28.7 (s). EI-MS (*m/z*): 181 $(M\text{-}Me)^+$. Anal. Calcd. for $C_{11}H_{13}FO_2$: C, 67.33; H, 6.68; F, 9.68; O, 16.31. Found: C, 67.28, H, 6.48.

G-5. Typical procedure for Wittig reaction

To a suspension of methyltriphenylphosphonium bromide (4.07 g, 11.4 mmol) in THF (40 mL) was added *n*-BuLi (1.57 M in *n*-hexane, 7.3 mL, 11.4 mmol) at 0 ^{o}C, and stirred for 1h. To the mixture was added a solution of **33a** (1.98 g, 9.5 mmol) in THF (20 mL), and stirred for overnight at room temperature. To the reaction mixture was added water, 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 / ethyl acetate = 50 / 1) to give **17c** (1.57 g, 80 %).

4-Methoxy-2-(1-methoxy-1-methylethyl)-1-vinylbenzene (17c): Colorless oil. IR (liquid film): 2980, 2936, 1606, 1483, 1294, 1260, 1074, 1050, 808. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55 (1H, dd, J=17.3, 10.8 Hz), 7.46 (1H, d, *J*=8.5 Hz), 6.84-6.77 (2H, m), 5.42 (1H, dd, J=17.3, 1.8 Hz), 5.13 (1H, dd, J=10.8, 1.8 Hz), 3.82 (3H, s), 3.02 (3H, s), 1.60 (6H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 158.5, 142.7, 136.8, 130.3, 128.7, 113.8, 112.5, 110.9, 78.1, 55.0, 50.4, 28.0. EI-MS (*m/z*): 206 (M^+). Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80; O, 15.51. Found: C, 75.79; H, 8.70.

4-Fluoro-2-(1-methoxy-1-methylethyl)-1-vinylbenzene (17d): This product (0.87 g, 4.5 mmol, 86% yield) was prepared from bromide **33b** (1.02 g, 5.2 mmol). Colorless oil. IR (liquid film): 2983, 2935, 1605, 1482, 1255, 1198, 1172, 1074, 943, 912, 871, 828, 811, 730. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.54 (1H, dd, J=17.3, 10.8 Hz), 7.46 (1H, dd, *J*=8.5, 6.2 Hz), 7.00-6.92 (2H, m), 5.45 (1H, dd, J=17.3, 1.5 Hz), 5.20 (1H, dd, J=10.8, 1.5 Hz), 3.02 (3H, s), 1.59 (6H, s). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -51.86 (ddd, J=7.9, 5.9, 4.0 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 161.7 (d, J=244.7 Hz), 143.7 (d, J=6.3 Hz), 136.4 (s), 133.7 (d, J=3.5 Hz), 129.2 (d, J=7.5 Hz), 114.0 (s), 113.9 (d, J=23.0 Hz), 113.7 (d, J=20.7 Hz), 77.8 (s), 50.3 (s), 27.8 (s).

EI-MS (*m/z*): 194 (M^+). Anal. Calcd. for $C_{12}H_{15}FO$: C, 74.20; H, 7.78; F, 9.78; O, 8.24. Found: C, 74.20; H, 7.81.