Supporting Information**for Fluorotetraphenylbismuth: A New Reagent for Efficient Regioselective
 α -Phenylation of Carbonyl Compounds**

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Synthesis of Fluorotetraphenylbismuth (Ph_4BiF) (1). To a solution of Ph_3BiF_2 (2.39 g, 5.00 mmol)¹ and phenylboronic acid (671 mg, 5.50 mmol) in CH_2Cl_2 (50 mL) was added $\text{BF}_3 \cdot \text{OEt}_2$ (950 μL , 7.50 mmol) at 0 °C and the reaction solution was stirred for 30 min at this temperature. Then, the solution was allowed to warm to room temperature and stirring was continued for additional 3 h. After complete removal of CH_2Cl_2 under reduced pressure, cesium fluoride (3.80 g, 25.0 mmol) and acetonitrile (10 mL) were added. While stirring overnight at room temperature, Ph_4BiF was precipitated as a white solid, which was filtered through a glass filter with the aid of a small amount of acetonitrile. The crude Ph_4BiF was dissolved in CH_2Cl_2 and insoluble inorganic salts were filtered off. Recrystallization using hexane as co-solvent afforded essentially pure Ph_4BiF as a colorless prism (1, 2.14 g, 3.99 mmol, 80 %). ^1H NMR (400 MHz, CDCl_3) δ 7.90-7.85 (8H, m), 7.52-7.44 (12H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 148.91, 135.65, 130.50, 130.15; ^{19}F NMR (376 MHz, CDCl_3 , at -78 °C) δ -84.6; IR (KBr) 3039, 2984, 1564, 1468, 1435, 1326, 1301, 1169, 1045, 1011, 993, 848, 727, 689 cm^{-1} . Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{FBi}$: C, 53.74; H, 3.76; F, 3.54. Found: C, 54.02; H, 3.68; F, 3.25. mp 135 °C (partially decomposed).

Synthesis of Fluoro(2-phenylethenyl)tris(*p*-tolyl)bismuth (2). To a mixture of (2-phenylethenyl)tris(*p*-tolyl)bismuthonium tetrafluoroborate (3.36 g, 5.00 mmol)² and cesium fluoride (3.80 g, 25.0 mmol) was added acetonitrile (16.6 mL) and the reaction mixture was stirred for 3 h at room temperature. After evaporation of the solvent, the residue was filtered with CH_2Cl_2 to remove the inorganic salts. The filtrate was concentrated again and dried thoroughly under vacuum to give analytically pure fluoro(2-phenylethenyl)tris(*p*-tolyl)bismuth as light yellow powder (2, 2.98 g, 4.93 mmol, 99%). ^1H NMR (400 MHz, CDCl_3) δ 8.06 (1H, d, J = 16.6 Hz, $\text{CH}=\text{CH}$), 7.76 (6H, d, J = 7.9 Hz, Ar-H), 7.43-7.40 (2H, m, Ar-H), 7.37-7.27 (10H, m, Ar-H and $\text{CH}=\text{CH}$), 2.39 (9H, s, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 147.81, 144.94, 140.15, 137.53, 136.42, 135.41, 131.06, 129.10, 128.51, 126.99, 21.39; ^{19}F NMR (376 MHz, CDCl_3) δ -84.8; IR (KBr) 3049, 2920, 2806, 2199, 1591, 1566, 1487, 1447, 1389, 1310, 1207, 1186, 1115, 1053, 1003, 922, 795 cm^{-1} . Anal. Calcd for $\text{C}_{29}\text{H}_{28}\text{FBi}$: C, 57.62; H, 4.67; F, 3.14. Found: C, 56.71; H, 4.66; F, 2.97.

General Procedure for Selective Phenylation of Enol Silyl Ethers and Ketene Silyl Acetals.

Regioselective Monophenylation of 1-Tetralone (entry 1 in Table 1). To a suspension of Ph_4BiF (1, 177.0 mg, 0.33 mmol) in THF (1 mL) was added 1-trimethylsiloxy-3,4-dihydronaphthalene (65.5 mg, 0.3 mmol) at $-40\text{ }^\circ\text{C}$ under argon atmosphere and the cooling bath was removed immediately. After being stirred at room temperature for 10 min, saturated NH_4Cl was added to the reaction mixture and extractive workup was performed with AcOEt. The organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (AcOEt/hexane = 1:15 as eluent) to give 2-phenyl-1-tetralone almost quantitatively (65.7 mg, 0.295 mmol, 99%). ^1H NMR (400 MHz, CDCl_3) δ 8.10 (1H, d, $J = 7.9$ Hz, Ar-H), 7.50 (1H, t, $J = 7.5$ Hz, Ar-H), 7.36-7.18 (7H, m, Ar-H), 3.80 (1H, dd, $J = 7.9, 7.9$ Hz, $\text{C}(=\text{O})\text{CHPh}$), 3.17-3.01 (2H, m, ArCH_2), 2.47-2.41 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}$); ^{13}C NMR (100 MHz, CDCl_3) δ 197.93, 143.90, 139.59, 133.30, 132.73, 128.65, 128.40, 128.30, 127.68, 126.80, 126.65, 54.42, 31.25, 28.84; IR (neat) 3061, 3028, 2951, 2896, 1890, 1674, 1599, 1452, 1425, 1312, 1221, 1150, 1009, 959, 897, 826, 758, 733, 714, 696 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{16}\text{H}_{14}\text{ONa}$: 245.0937 ($[\text{M}+\text{Na}]^+$). Found: 245.0928 ($[\text{M}+\text{Na}]^+$).

The following phenylation products are all known: 2-Phenyl-1-indanone³; 2-Phenylcyclopentanone⁴; 6-Methyl-2-phenylcyclohexanone⁴; 2-Methyl-2-phenylcyclohexanone⁴; 1,4-Diphenyl-2-butanone⁵; 2-Phenylacetophenone⁶; 2-Phenylpropiophenone⁶; 2-Methyl-2-phenylpropiophenone⁶; Phenyl 2-Phenylpropanoate⁷; Ethyl 2-Methyl-2-phenylpropanoate⁸

General Procedure for 2-Phenylethenylation of Enol Silyl Ethers and Ketene Silyl Acetals.

To a solution of fluoro(2-phenylethenyl)tris(*p*-tolyl)bismuth (2, 217.6 mg, 0.36 mmol) in THF (1 mL) was added enol silyl ether or ketene silyl acetal (0.30 mmol) at $-40\text{ }^\circ\text{C}$ under argon atmosphere. After being stirred at this temperature for 30 min, saturated NH_4Cl was added to the reaction mixture and extractive workup was performed with AcOEt. The organic extracts were dried over Na_2SO_4 and concentrated. Purification of the residue by flash column chromatography on silica gel (AcOEt/hexane as eluent) afforded the corresponding 2-phenylethenylated product in high yield.

2-(2-Phenylethenyl)-1-tetralone: ^1H NMR (400 MHz, CDCl_3) δ 8.07 (1H, d, $J = 7.9$ Hz, Ar-H), 7.51-7.19 (8H, m, Ar-H), 6.57-6.49 (2H, m, $\text{CH}=\text{CHPh}$), 3.45-3.39 (1H, m, $\text{C}(=\text{O})\text{CHC}=\text{C}$), 3.14-3.02 (2H, m, ArCH_2), 2.43-2.31 (1H, m, $\text{CH}_2\text{CH}_2\text{CH}$), 2.25-2.15 (1H, m, $\text{CH}_2\text{CH}_2\text{CH}$); ^{13}C NMR (100 MHz, CDCl_3) δ 197.85, 143.76, 136.94, 133.31, 132.19, 131.87, 128.61, 128.38, 127.57, 127.31, 126.98, 126.63, 126.21, 50.88, 29.49, 28.25; IR (neat) 2937, 1682, 1599, 1454, 1296, 1221, 964, 739, 692 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{16}\text{ONa}$: 271.1093 ($[\text{M}+\text{Na}]^+$). Found: 271.1132 ($[\text{M}+\text{Na}]^+$).

2-(2-Phenylethenyl)-6-methylcyclohexanone: ^1H NMR (400 MHz, CDCl_3) *cis* isomer: δ 7.38 (2H, d, $J = 7.5$ Hz, Ph), 7.29 (2H, t, $J = 7.5$ Hz, Ph), 7.20 (1H, t, $J = 7.5$ Hz, Ph), 6.49 (1H, dd, $J =$

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7.5, 16.2 Hz, $\text{CH}=\text{CHPh}$), 6.36 (1H, d, $J = 16.2$ Hz, $\text{CH}=\text{CHPh}$), 3.23-3.15 (1H, m, $\text{C}(=\text{O})\text{CHC}=\text{C}$), 2.53-2.42 (1H, m, $\text{C}(=\text{O})\text{CHCH}_3$), 2.25-2.19 (1H, m, $\text{CH}_2\text{CHC}=\text{C}$), 2.18-2.11 (1H, m, CH_2CHCH_3), 1.95-1.78 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.69 (1H, dq, $J = 4.4$, 12.7 Hz, $\text{CH}_2\text{CHC}=\text{C}$), 1.42 (1H, dq, $J = 4.4$, 12.7 Hz, CH_2CHCH_3), 1.05 (3H, d, $J = 6.3$ Hz, CH_3); *trans* isomer: δ 7.36 (2H, d, $J = 7.5$ Hz, Ph), 7.30 (2H, t, $J = 7.5$ Hz, Ph), 7.22 (1H, t, $J = 7.5$ Hz, Ph), 6.45 (1H, d, $J = 16.2$ Hz, $\text{CH}=\text{CHPh}$), 6.35 (1H, dd, $J = 6.7$, 16.2 Hz, $\text{CH}=\text{CHPh}$), 3.38-3.33 (1H, m, $\text{C}(=\text{O})\text{CHC}=\text{C}$), 2.70-2.60 (1H, m, $\text{C}(=\text{O})\text{CHCH}_3$), 2.09-1.87 (4H, m, CH_2), 1.82-1.76 (1H, m, $\text{CH}_2\text{CHC}=\text{C}$), 1.55-1.47 (1H, m, CH_2CHCH_3), 1.08 (3H, d, $J = 6.7$ Hz, CH_3); ^{13}C NMR (100 MHz, CDCl_3) *cis* isomer: δ 212.19, 137.18, 130.82, 128.33, 127.86, 127.11, 126.16, 54.25, 45.70, 37.06, 35.96, 25.40, 14.68; *trans* isomer: δ 213.17, 136.66, 131.83, 128.30, 127.29, 127.18, 125.97, 52.97, 42.95, 35.58, 33.25, 20.88, 15.19; IR (neat) 2930, 2856, 1707, 1448, 1126, 964, 752, 694 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{15}\text{H}_{19}\text{O}$: 215.1430 ($[\text{M}+\text{H}]^+$). Found: 215.1430 ($[\text{M}+\text{H}]^+$).

2-Methyl-1,4-diphenyl-3-buten-1-one: ^1H NMR (400 MHz, CDCl_3) δ 8.03-8.00 (2H, m, Ph), 7.58-7.53 (1H, m, Ph), 7.49-7.44 (2H, m, Ph), 7.35-7.18 (5H, m, Ph), 6.53 (1H, d, $J = 15.8$ Hz, $\text{CH}=\text{CHPh}$), 6.36 (1H, dd, $J = 7.9$, 15.8 Hz, $\text{CH}=\text{CHPh}$), 4.32 (1H, dq, $J = 6.7$, 7.9 Hz, $\text{C}(=\text{O})\text{CHCH}_3$), 1.43 (3H, d, $J = 6.7$ Hz, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 200.84, 136.76, 136.22, 132.92, 131.52, 129.61, 128.52, 128.46, 128.40, 127.41, 126.13, 44.89, 17.80; IR (neat) 2980, 1682, 1597, 1495, 1448, 1202, 972, 706, 692 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{17}\text{H}_{17}\text{O}$: 237.1274 ($[\text{M}+\text{H}]^+$). Found: 237.1297 ($[\text{M}+\text{H}]^+$).

2,2-Dimethyl-1,4-diphenyl-3-buten-1-one: ^1H NMR (400 MHz, CDCl_3) δ 7.88 (2H, d, $J = 7.5$ Hz, Ph), 7.50-7.20 (8H, m, Ph), 6.53 (2H, s, $\text{C}(=\text{O})\text{CH}=\text{CHPh}$), 1.49 (6H, s, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 204.24, 136.86, 135.07, 131.59, 129.12, 128.97, 128.53, 127.96, 127.49, 126.16, 124.51, 49.60, 26.60; IR (neat) 2972, 1676, 1597, 1447, 1244, 1163, 968, 748, 692 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{18}\text{ONa}$: 273.1250 ($[\text{M}+\text{Na}]^+$). Found: 273.1200 ($[\text{M}+\text{Na}]^+$).

Phenyl 2-Methyl-4-phenyl-3-buten-1-one: ^1H NMR (400 MHz, CDCl_3) δ 7.46-7.30 (6H, m, Ph), 7.28-7.18 (2H, m, Ph), 7.09 (2H, d, $J = 8.7$ Hz, Ph), 6.61 (1H, d, $J = 15.8$ Hz, $\text{CH}=\text{CHPh}$), 6.39 (1H, dd, $J = 7.9$, 15.8 Hz, $\text{CH}=\text{CHPh}$), 3.56 (1H, dq, $J = 7.1$, 7.9 Hz, $\text{C}(=\text{O})\text{CHCH}_3$), 1.51 (3H, d, $J = 7.1$ Hz, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 172.77, 150.64, 136.62, 131.72, 129.27, 128.47, 127.91, 127.58, 126.27, 125.71, 121.35, 43.35, 17.54; IR (neat) 2980, 1757, 1593, 1493, 1455, 1196, 1163, 1142, 1070, 968, 746, 691 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Na}$: 275.1043 ($[\text{M}+\text{Na}]^+$). Found: 275.1041 ($[\text{M}+\text{Na}]^+$).

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