Revised

Supporting Information
for (2,7-Disubstituted-1,8-biphenylenedioxy)bis(dimethylaluminum) as
Bidentate Organoaluminum Lewis Acids: Elucidation and Synthetic
Utility of the Double Electrophilic Activation Phenomenon

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General. Infrared (IR) spectra were recorded on a Shimadzu FT-IR 8100A spectrometer. ^1H and ^{13}C NMR spectra were measured on a Varian Gemini-200 (200 MHz), Gemini-300 (300 MHz) and JEOL JNM-FX400 (400 MHz) spectrometers. All experiments were carried out under an atmosphere of dry argon. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel (E. Merck 9385). Microanalyses were accomplished at the Center for Instrumental Analysis, Hokkaido University and the Center of Elemental Analysis, School of Pharmaceutical Sciences, Kyoto University. The high-resolution mass spectra (HRMS) were conducted at the School of Agriculture, Hokkaido University and the School of Engineering, Kyoto University. In experiments requiring dry solvents, ether and tetrahydrofuran (THF) were purchased from Kanto Chemical Co., Ltd. as "Dehydrated". Hexane was dried over sodium metal. Methylene chloride was stored over 4Å molecular sieves. Pyridine was stored over KOH pellets. DMF and *N,N,N',N'*-tetramethylethylenediamine were distilled and stored over 4Å molecular sieves. Trimethylaluminum was kindly supplied by Tosoh-Finechem. Co. Ltd., Japan. Benzaldehyde and cyclohexanecarboxaldehyde were distilled under reduced pressure. Other simple chemicals were purchased and used as such.

Representative Synthetic Scheme for the Preparation of 2,7-Disubstituted-1,8-biphenylenediols. *N*-Pivaloyl-*m*-anisidine (3).¹ To a solution of *m*-anisidine (11.2 mL, 100 mmol), pyridine (16.2 mL, 200 mmol) and 4-(dimethylamino)pyridine (122 mg, 1 mmol) in dry CH_2Cl_2 (200 mL) was added pivaloyl chloride (13.5 mL, 110 mmol) dropwise at 0 °C. The resulting

mixture was stirred for 1 h at that temperature, and poured into ice-cooled 1 N HCl. The organic layer was separated and the aqueous phase was extracted with ether. The combined organic extracts were washed with 1 N HCl and brine, and dried over Na₂SO₄. Evaporation of solvents and purification of the residue by column chromatography on silica gel (EtOAc/CH₂Cl₂/hexane = 1:9:10 as eluant) gave *N*-pivaloyl-*m*-anisidine (**3**, 20.7 g, 100 mmol, quantitative yield) as a white solid: ¹H NMR (300 MHz, CDCl₃) δ 7.39 (1H, dd, *J* = 1.8, 2.4 Hz, Ar-H), 7.30 (1H, br s, N-H), 7.21 (1H, dd, *J* = 7.8, 8.1 Hz, Ar-H), 6.93 (1H, ddd, *J* = 0.6, 1.8, 7.8 Hz, Ar-H), 6.66 (1H, ddd, *J* = 0.6, 2.4, 8.1 Hz, Ar-H), 3.81 (3H, s, OCH₃), 1.32 (9H, s, *t*-Bu); IR (KBr) 3315, 2970, 1643, 1609, 1531, 1450, 1425, 1367, 1298, 1281, 1121, 1182, 1153, 1036, 959, 853, 789, 689 cm⁻¹. MS: *m/z* 207 (M⁺, 100%), 192, 164, 149, 137, 123, 94, 93, 69, 57. HRMS Calcd for C₁₂H₁₇NO₂: 207.1259 (M⁺). Found: 207.1252 (M⁺). Anal. Calcd: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.56; H, 8.16; N, 6.74.

2-Bromo-*N*-pivaloyl-*m*-anisidine (4**).**² To a solution of *N*-pivaloyl-*m*-anisidine (**3**, 24.9 g, 120 mmol) in dry THF (250 mL) was added a 1.6 M hexane solution of BuLi (157.5 mL, 252 mmol) dropwise over 15 min at 0 °C. After 12 h of stirring at 0 °C, the solution was cooled to -78 °C and 1,2-dibromoethane (12.4 mL, 144 mmol) was added dropwise. Then, the resulting mixture was allowed to warm to room temperature. When the generation of ethylene gas was ceased, the reaction should be completed. The solution was poured into ice-cooled 1 N HCl and the organic layer was separated. The aqueous layer was extracted with ether and the combined organic extracts were washed with brine, and dried over Na₂SO₄. The solvents were evaporated and the residual oil was treated with hexane until white solid was precipitated, which is unreacted starting material. The solid was filtered off and washed with hexane, and the filtrate was concentrated. Purification of the residue by column chromatography on silica gel (CH₂Cl₂/hexane = 1:1 as eluant) gave 2-bromo-*N*-pivaloyl-*m*-anisidine (**4**, 31.1 g, 108.5 mmol, 90% yield) as a yellow oil: ¹H NMR (300 MHz, CDCl₃) δ 8.15 (1 H, br s, N-H), 8.07 (1H, dd, *J* = 1.3, 8.3 Hz, Ar-H), 7.27 (1H, dd, *J* = 8.3, 8.3 Hz, Ar-H), 6.64 (1H, dd, *J* = 1.3, 8.3 Hz, Ar-H), 3.89 (3H, s, OCH₃), 1.36 (9H, s, *t*-Bu); IR (liquid film) 3416, 2963, 2872, 1693, 1597, 1526, 1472, 1412, 1366, 1294, 1263, 1180, 1161, 1078, 1032, 947, 775 cm⁻¹. MS: *m/z* 285 (M⁺), 242, 228, 206 (100%), 201, 158, 69, 57. HRMS Calcd for C₁₂H₁₆BrNO₂: 285.0364 (M⁺). Found: 285.0363 (M⁺). Anal. Calcd: C, 50.37; H, 5.64; N, 4.89. Found: C, 50.50; H, 5.44; N, 4.72.

2-Bromo-*m*-anisidine (5).³ 2-Bromo-*N*-pivaloyl-*m*-anisidine (**4**, 28.6 g, 100 mmol) obtained above was dissolved into 1,4-dioxane (100 mL) and *conc.* HCl (100 mL), and heated to reflux for 3 h. The dark-brown mixture was cooled to 0 °C, and neutralized by the addition of cold aqueous NaOH. The mixture was then extracted with ether and the organic extracts were washed with saturated Na₂SO₃, and dried over Na₂SO₄. The solvents were removed by evaporation and the residual brown oil, crude 2-bromo-*m*-anisidine (**5**), was used for the next step without purification. The analytical sample was purified by column chromatography on silica gel (CH₂Cl₂/hexane = 1:4 as eluant) to give a white solid: ¹H NMR (300 MHz, CDCl₃) δ 7.05 (1H, dd, *J* = 8.1, 8.1 Hz, Ar-H), 6.42 (1H, dd, *J* = 1.2, 8.1 Hz, Ar-H), 6.32 (1H, dd, *J* = 1.2, 8.1 Hz, Ar-H), 4.16 (2H, br s, NH₂), 3.87 (3H, s, OCH₃); IR (liquid film) 3416, 3300, 3194, 2945, 2841, 1624, 1593, 1474, 1437, 1325, 1261, 1142, 1097, 1063, 1024, 762, 704 cm⁻¹. MS: *m/z* 201 (M⁺, 100%), 171, 158. HRMS Calcd for C₇H₈NO: 200.9789 (M⁺). Found: 200.9789 (M⁺). Anal. Calcd: C, 41.61; H, 3.99; N, 6.93. Found: C, 41.56; H, 3.86; N, 6.79.

2-Bromo-3-iodoanisole (6). To a solution of crude 2-bromo-*m*-anisidine (**5**, *ca.* 20.2 g, 100 mmol) in *conc.* HCl (100 mL) was added NaNO₂ (8.3 g, 120 mmol) dissolved in water (10 mL) dropwise at 0 °C followed by the addition of a solution of KI (49.8 g, 300 mmol) in water at that temperature. After the addition was completed, the whole mixture was heated to 80 °C and stirred there for 2 h. The resulting mixture was cooled to 0 °C and neutralized by aqueous NaOH, then extracted with ether. The combined organic extracts were dried over Na₂SO₄. The solvents were evaporated and the residue was purified by column chromatography on silica gel (CH₂Cl₂/hexane = 1:9 as eluant) to afford 2-bromo-3-iodoanisole (**6**, 24.7 g, 79.0 mmol, 79% yield) as a light-orange solid: ¹H NMR (300 MHz, CDCl₃) δ 7.49 (1H, dd, *J* = 1.2, 7.8 Hz, Ar-H), 7.01 (1H, dd, *J* = 7.8, 8.1 Hz, Ar-H), 6.86 (1H, dd, *J* = 1.2, 8.1 Hz, Ar-H), 3.88 (3H, s, OCH₃); IR (KBr) 2936, 2833, 1568, 1466, 1420, 1285, 1186, 1142, 1096, 1038, 1015, 816, 772 cm⁻¹. MS: *m/z* 312 (M⁺, 100%), 297, 269, 218, 190, 142, 127, 79. HRMS Calcd for C₇H₆BrIO: 311.8647 (M⁺). Found: 311.8647 (M⁺). Anal. Calcd: C, 26.87; H, 1.93. Found: C, 26.82; H, 1.93.

2,2'-Dibromo-3,3'-dimethoxybiphenyl (7). The flask containing Zn/Cu couple (5.1 g, 78 mmol) and 1,2-dibromoethane (0.4 mL) in dry THF (100 mL) was heated to reflux for 30 min. After cooling to room temperature, trimethylsilyl chloride (0.4 mL) was added and the mixture was stirred for 15 min at room temperature, and then 2-bromo-3-iodoanisole (**6**, 12.2 g, 39 mmol) in dry DMF

(10 mL) was introduced. The mixture was heated to reflux until the starting material was almost disappeared on TLC (about 2 h, 2-bromoanisole was observed instead of the starting material). The requisite zinc reagent thus prepared was transferred by cannula to another flask containing 2-bromo-3-iodoanisole (**6**, 9.8 g, 31.2 mmol), Pd(PPh₃)₄ (2.25 g, 1.95 mmol) in dry THF (100 mL). The whole mixture was carefully degassed and heated to 40 °C for 12 h. After the reaction was completed, the mixture was poured into ice-cooled 1 N HCl. Extractive workup was performed with ether. The organic extracts were washed with brine, dried over Na₂SO₄ and concentrated. Purification of the residue by column chromatography on silica gel (CH₂Cl₂/hexane = 1:3 as eluant) furnished 2,2'-dibromo-3,3'-dimethoxybiphenyl (**7**, 10.4 g, 27.98 mmol, 90% yield) as a white solid: ¹H NMR (300 MHz, CDCl₃) δ 7.34 (2H, dd, *J* = 7.5, 8.4 Hz, Ar-H), 6.94 (2H, dd, *J* = 1.5, 8.4 Hz, Ar-H), 6.85 (2H, dd, *J* = 1.5, 7.5 Hz, Ar-H), 3.96 (6H, s, OCH₃); IR (KBr) 2959, 2936, 2835, 1570, 1462, 1421, 1319, 1288, 1271, 1184, 1144, 1097, 1072, 1018, 779, 719, 665 cm⁻¹. MS: *m/z* 370 (M⁺), 327, 291 (100%), 276, 261, 233, 212, 197, 169, 63. HRMS Calcd for C₁₄H₁₂O₂Br₂: 369.9204 (M⁺). Found: 369.9204 (M⁺). Anal. Calcd: C, 45.20; H, 3.25. Found: C, 45.31; H, 3.30.

1,8-Dimethoxybiphenylene (8). 2,2'-Dibromo-3,3'-dimethoxybiphenyl (**7**, 2.03 g, 5.45 mmol) in dry THF (150 mL) was treated with a 1.6 M hexane solution of BuLi (7.5 mL, 12 mmol) at -78 °C for 30 min. To this solution was added a 0.5 M THF solution of ZnCl₂ (12 mL, 6.0 mmol) dropwise at that temperature. After 30 min, anhydrous CuCl₂ (2.2 g, 16.4 mmol, dried by heat under reduced pressure before use) was added in one portion and the resulting mixture was allowed to warm to room temperature, and vigorously stirred overnight. The reaction was quenched with 1 N HCl and extracted with ether. The combined extracts were washed with brine and dried over Na₂SO₄. The solvents were removed by evaporation and the residue was purified by silica gel column chromatography (CH₂Cl₂/hexane = 1:3 as eluant) to afford 1,8-dimethoxybiphenylene (**8**, 688 mg, 3.24 mmol, 54% yield) as a light-yellow solid: ¹H NMR (300 MHz, CDCl₃) δ 6.71 (2H, dd, *J* = 6.6, 9.0 Hz, Ar-H), 6.41 (2H, dd, *J* = 0.6, 9.0 Hz, Ar-H), 6.28 (2H, dd, *J* = 0.6, 6.6 Hz, Ar-H), 3.85 (6H, s, OCH₃); IR (KBr) 2964, 2941, 2835, 1665, 1585, 1470, 1433, 1394, 1290, 1267, 1219, 1178, 1142, 1045, 922, 766, 694 cm⁻¹. MS: *m/z* 212 (M⁺, 100%), 197, 169, 126, 106, 69. HRMS Calcd for C₁₄H₁₂O₂: 212.0837 (M⁺). Found: 212.0839 (M⁺).

2,7-Dibromo-1,8-dimethoxybiphenylene (9). To a solution of *N,N,N',N'*-tetramethylethylenediamine (4.43 mL, 29.4 mmol) in dry ether (50 mL) was added a 1.6 M hexane solution of BuLi (18.5 mL, 29.4 mmol) dropwise at 0 °C. After 30 min of stirring, 1,8-dimethoxybiphenylene (**8**, 1.79 g, 8.41 mmol) was introduced. The mixture was allowed to warm to room temperature and stirred overnight. The resulting mixture was then cooled to -78 °C and diluted with dry THF (50 mL) followed by the addition of 1,2-dibromo-1,1,2,2-tetrafluoroethane (3.51 mL, 29.4 mmol). The reaction mixture was gradually warmed to room temperature. Completion of the bromination was confirmed by TLC analysis. The mixture was poured into 1 N HCl, extracted with ether and dried over Na₂SO₄. After removal of solvents, the residue was purified by column chromatography on silica gel (CH₂Cl₂/hexane = 1:7 as eluant) to give 2,7-dibromo-1,8-dimethoxybiphenylene (**9**, 2.79 g, 7.56 mmol, 90% yield) as a yellow solid: ¹H NMR (300 MHz, CDCl₃) δ 7.05 (2H, d, *J* = 7.2 Hz, Ar-H), 6.28 (2H, d, *J* = 7.2 Hz, Ar-H), 3.96 (6H, s, OCH₃); IR (KBr) 2943, 1655, 1578, 1460, 1391, 1273, 1250, 1036, 1011, 997, 926, 808, 677 cm⁻¹. MS: *m/z* 368 (M⁺, 100%), 325, 310, 295, 282, 246, 216, 203, 137, 124, 69. HRMS Calcd for C₁₄H₁₀O₂Br₂: 367.9048 (M⁺). Found: 367.9050 (M⁺). Anal. Calcd: C, 45.44; H, 2.72. Found: C, 45.72; H, 2.64.

1,8-Biphenylenediol (1f, R = H).⁴⁻⁶ To a solution of **8** (212 mg, 1 mmol) in dry CH₂Cl₂ (5 mL) was added BBr₃ (209 μL, 2.2 mmol) dropwise at 0 °C. After the reaction was completed, cold water was added carefully at that temperature. Extractive workup was performed with ether and the organic extracts were dried over Na₂SO₄. Evaporation of solvents and purification of the residue by silica gel column chromatography (CH₂Cl₂/ether = 7:1 as eluant) afforded 1,8-biphenylenediol (**1f**, 166 mg, 0.9 mmol, 90% yield) as a yellow solid: ¹H NMR (400 MHz, THF-d₈) δ 7.84 (2H, br s, OH), 6.49 (2H, dd, *J* = 6.4, 8.8 Hz, Ar-H), 6.17 (2H, d, *J* = 8.8 Hz, Ar-H), 6.12 (2H, d, *J* = 6.4 Hz, Ar-H); IR (KBr) 3331, 1686, 1622, 1458, 1433, 1356, 1256, 1202, 1159, 1140, 951, 835, 764, 694 cm⁻¹. MS: *m/z* 184 (M⁺, 100%), 155, 138, 92, 69. HRMS Calcd for C₁₂H₈O₂: 184.0524 (M⁺). Found: 184.0521 (M⁺).

General Method for Nickel-Catalyzed Coupling of 9 with Grignard Reagents. To a mixture of **9** (370 mg, 1 mmol) and NiCl₂(dppe) (26 mg, 0.05 mmol, 5 mol%) in dry ether (5 mL) was added the requisite Grignard reagent (*ca.* 3 equiv) at 0 °C. The whole mixture was degassed and heated to reflux until the starting material was consumed. The reaction mixture was diluted with ether

and excess reagents were quenched by the slow addition of methanol at 0 °C. This was then poured into 1 N HCl, extracted with ether and dried over Na₂SO₄. Removal of solvents and purification of the residue by column chromatography on silica gel (CH₂Cl₂/hexane as eluant) afforded the coupling product **10** in almost quantitative yield. Subsequent demethylation with BBr₃ (2.2 equiv) in CH₂Cl₂ at 0 °C gave the corresponding 2,7-disubstituted-1,8-biphenylenediol **1** in good to moderate yields.

2,7-Dimethyl-1,8-dimethoxybiphenylene (10a).^{4b} ¹H NMR (400 MHz, CDCl₃) δ 6.55 (2H, d, *J* = 7.2 Hz, Ar-H), 6.25 (2H, d, *J* = 7.2 Hz, Ar-H), 3.88 (6H, s, OCH₃), 2.09 (6H, s, ArCH₃); IR (KBr) 3065, 2941, 2855, 1666, 1589, 1464, 1400, 1285, 1246, 1184, 1115, 1036, 1009, 808 cm⁻¹.

2,7-Dimethyl-1,8-biphenylenediol (1a).^{4b} ¹H NMR (300 MHz, CDCl₃) δ 6.51 (2H, d, *J* = 6.9 Hz, Ar-H), 6.21 (2H, d, *J* = 6.9 Hz, Ar-H), 4.96 (2H, br s, OH), 2.10 (6H, s, CH₃); IR (KBr) 3369, 2920, 1678, 1624, 1460, 1408, 1340, 1263, 1236, 1211, 1117, 1011, 937, 916, 847, 797 cm⁻¹.

2,7-Diphenyl-1,8-dimethoxybiphenylene (10b). ¹H NMR (300 MHz, CDCl₃) δ 7.49-7.31 (10H, m, Ph), 6.77 (2H, d, *J* = 6.9 Hz, Ar-H), 6.49 (2H, d, *J* = 6.9 Hz, Ar-H), 3.69 (6H, s, OCH₃); IR (KBr) 3061, 2984, 2934, 1665, 1597, 1582, 1472, 1412, 1396, 1364, 1258, 1236, 1036, 1009, 829, 770, 700 cm⁻¹. MS: *m/z* 364 (M⁺, 100%), 348, 334, 321, 305, 276, 274, 182. HRMS Calcd for C₂₆H₂₀O₂: 364.1463 (M⁺). Found: 364.1461 (M⁺). Anal. Calcd: C, 85.69; H, 5.53. Found: C, 85.96; H, 5.80.

2,7-Diphenyl-1,8-biphenylenediol (1b). ¹H NMR (300 MHz, CDCl₃) δ 7.47-7.36 (10H, m, Ph), 6.70 (2H, d, *J* = 6.9 Hz, Ar-H), 6.43 (2H, d, *J* = 6.9 Hz, Ar-H), 5.07 (2H, br s, OH); IR (KBr) 3499, 3369, 3061, 3026, 1670, 1618, 1597, 1474, 1458, 1420, 1652, 1275, 1219, 1142, 818, 762, 700 cm⁻¹. MS: *m/z* 336 (M⁺, 100%), 318, 307, 289, 276, 168. HRMS Calcd for C₂₄H₁₆O₂: 336.1150 (M⁺). Found: 336.1152 (M⁺). Anal. Calcd: C, 85.69; H, 4.79. Found: C, 85.77; H, 4.99.

2,7-Dioctyl-1,8-dimethoxybiphenylene (10c). ¹H NMR (400 MHz, CDCl₃) δ 6.53 (2H, d, *J* = 6.8 Hz, Ar-H), 6.27 (2H, d, *J* = 6.8 Hz, Ar-H), 3.87 (6H, s, OCH₃), 2.41 (4H, t, *J* = 5.7 Hz, ArCH₂(CH₂)₆CH₃), 1.54-1.20 (24H, m, ArCH₂(CH₂)₆CH₃), 0.88 (6H, t, *J* = 6.8 Hz, ArCH₂(CH₂)₆CH₃); IR (liquid film) 2926, 2855, 1665, 1585, 1483, 1466, 1416, 1252, 1238, 1043, 1011, 812, 723 cm⁻¹. MS: *m/z* 436 (M⁺, 100%), 337, 323, 239. HRMS Calcd for C₃₀H₄₄O₂:

436.3341 (M^+). Found: 436.3342 (M^+). Anal. Calcd: C, 82.52; H, 10.16. Found: C, 82.63; H, 10.42.

2,7-Dioctyl-1,8-biphenylenediol (1c). ^1H NMR (300 MHz, CDCl_3) δ 6.47 (2H, d, J = 6.9 Hz, Ar-H), 6.22 (2H, d, J = 6.9 Hz, Ar-H), 4.89 (2H, br s, OH), 2.41 (4H, t, J = 7.5 Hz, $\text{ArCH}_2(\text{CH}_2)_6\text{CH}_3$), 1.60-1.20 (24H, m, $\text{ArCH}_2(\text{CH}_2)_6\text{CH}_3$), 0.88 (6H, t, J = 6.8 Hz, $\text{ArCH}_2(\text{CH}_2)_6\text{CH}_3$); IR (KBr) 3396, 2922, 2849, 1676, 1626, 1468, 1429, 1410, 1329, 1298, 1238, 1180, 1123, 949, 810, 789 cm^{-1} . MS: m/z 408 (M^+ , 100%), 309, 210, 182. HRMS Calcd for $\text{C}_{28}\text{H}_{40}\text{O}_2$: 408.3028 (M^+). Found: 408.3031 (M^+). Anal. Calcd: C, 82.30; H, 9.87. Found: C, 82.27; H, 9.92.

2,7-Diisopropyl-1,8-dimethoxybiphenylene (10d). ^1H NMR (300 MHz, CDCl_3) δ 6.61 (2H, d, J = 6.9 Hz, Ar-H), 6.33 (2H, d, J = 6.9 Hz, Ar-H), 3.90 (6H, s, OCH_3), 3.10 (2H, sept, J = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$), 1.15 (12H, d, J = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$); IR (KBr) 2963, 2870, 1665, 1583, 1483, 1447, 1412, 1321, 1238, 1167, 1111, 1034, 1005, 816, 754 cm^{-1} . MS: m/z 296 (M^+ , 100%), 281, 266, 251, 219, 202, 178, 165, 152, 133, 115, 89. HRMS Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_2$: 296.1776 (M^+). Found: 296.1777 (M^+).

2,7-Diisopropyl-1,8-biphenylenediol (1d). ^1H NMR (300 MHz, CDCl_3) δ 6.55 (2H, d, J = 7.2 Hz, Ar-H), 6.27 (2H, d, J = 7.2 Hz, Ar-H), 4.87 (2H, br s, OH), 2.94 (2H, sept, J = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$), 1.21 (12H, d, J = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$); IR (KBr) 3512, 3418, 2963, 2870, 1672, 1620, 1601, 1458, 1431, 1410, 1387, 1317, 1219, 1198, 1146, 1069, 947, 843, 814, 731, 656 cm^{-1} . MS: m/z 268 (M^+ , 100%), 253, 239, 238, 237, 223, 220, 191, 178, 165, 152, 139, 134, 119, 69. HRMS Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2$: 268.1463 (M^+). Found: 268.1468 (M^+).

2,7-Dicyclohexyl-1,8-dimethoxybiphenylene (10e). ^1H NMR (300 MHz, CDCl_3) δ 6.58 (2H, d, J = 6.9 Hz, Ar-H), 6.32 (2H, d, J = 6.9 Hz, Ar-H), 3.88 (6H, s, OCH_3), 2.70 (2H, m, ArCH), 1.83-1.10 (20H, m, $2(\text{CH}_2)_5$); IR (KBr) 2924, 2851, 1655, 1578, 1474, 1448, 1416, 1352, 1304, 1244, 1223, 1173, 1140, 1111, 1011, 822 cm^{-1} . MS: m/z 376 (M^+ , 100%), 333, 320, 307, 294, 251, 145, 69. HRMS Calcd for $\text{C}_{26}\text{H}_{32}\text{O}_2$: 376.2402 (M^+). Found: 376.2408 (M^+).

2,7-Dicyclohexyl-1,8-biphenylenediol (1e). ^1H NMR (400 MHz, CDCl_3) δ 6.52 (2H, d, J = 6.8 Hz, Ar-H), 6.25 (2H, d, J = 6.8 Hz, Ar-H), 5.41 (2H, br s, OH), 2.57 (2H, m, ArCH), 1.85-1.20 (20H, m, $2(\text{CH}_2)_5$); IR (KBr) 3427, 2926, 2851, 1674, 1616, 1448, 1302, 1223, 1132,

808 cm⁻¹. MS: *m/z* 348 (M⁺, 100%), 305, 292, 279, 223, 197, 152. HRMS Calcd for C₂₄H₂₈O₂: 348.2089 (M⁺). Found: 348.2090 (M⁺).

Preparation of 3,5-Di-*tert*-butylphenyl Magnesium Bromide. Mg turnings (87 mg, 3.6 mmol) were vigorously stirred and dry THF (1.5 mL) was added to the flask. Then 1,2-dibromoethane (310 μL, 3.6 mmol) was added dropwise with reflux to generate anhydrous MgBr₂. In the meantime, 3,5-di-*tert*-butylbromobenzene (808 mg, 3 mmol)⁷ was lithiated by the treatment with a 1.6 M hexane solution of BuLi (1.88 mL, 3 mmol) in THF (3 mL) at -78 °C for 30 min and transferred to the solution of anhydrous MgBr₂ prepared above at -78 °C. The resulting mixture was allowed to warm to 0 °C and stirred there for 1 h to give a THF solution of the title compound.

2,7-Bis(3,5-di-*tert*-butylphenyl)-1,8-dimethoxybiphenylene (10g). ¹H NMR (400 MHz, CDCl₃) δ 7.37 (2H, dd, *J* = 1.6, 1.6 Hz, Ar-H), 7.32 (4H, d, *J* = 1.6 Hz, Ar-H), 6.79 (2H, d, *J* = 6.8 Hz, Ar-H), 6.48 (2H, d, *J* = 6.8 Hz, Ar-H), 3.69 (6H, s, OCH₃), 1.36 (36H, s, *t*-Bu); IR (KBr) 3067, 2964, 2866, 1662, 1593, 1477, 1408, 1393, 1362, 1248, 1040, 1009, 901, 878, 858, 818, 716 cm⁻¹. MS: *m/z* 588 (M⁺, 100%), 573, 532, 531, 516, 501, 486, 294, 279, 57. HRMS Calcd for C₄₂H₅₂O₂: 588.3967 (M⁺). Found: 588.3971 (M⁺).

2,7-Bis(3,5-di-*tert*-butylphenyl)-1,8-biphenylenediol (1g). ¹H NMR (300 MHz, CDCl₃) δ 7.45 (2H, dd, *J* = 1.5, 1.5 Hz, Ar-H), 7.28 (4H, d, *J* = 1.5 Hz, Ar-H), 6.72 (2H, d, *J* = 6.6 Hz, Ar-H), 6.43 (2H, d, *J* = 6.6 Hz, Ar-H), 5.15 (2H, s, OH), 1.36 (36H, s, *t*-Bu); IR (KBr) 3537, 3071, 2961, 2868, 1686, 1593, 1477, 1416, 1364, 1304, 1248, 1200, 1140, 878, 814, 714 cm⁻¹. MS: *m/z* 560 (M⁺, 100%), 545, 504, 503, 488, 473, 431, 280, 265, 57. HRMS Calcd for C₄₀H₄₈O₂: 560.3654 (M⁺). Found: 560.3649 (M⁺).

[2,7-Bis(3,5-di-*tert*-butylphenyl)-1,8-biphenylenedioxy]bis(dimethylaluminum) (2g) Dimer. To a stirred solution of **1g** (468 mg, 0.834 mmol) in dry hexane (5 mL) was added a 1 M hexane solution of Me₃Al (1.67 mL, 1.67 mmol) at room temperature. After 2 h of stirring, light-yellow powder was precipitated. The mixture was then stood for about 1 h and the supernatant was removed. The resulting solid, desired bis-Al dimer, was washed with dry hexane several times and dried under reduced pressure. The solid thus obtained was found to be air-stable and easy to handle under open-air condition. The yield of the bis-Al dimer was approximately 30%: ¹H NMR (400 MHz, CDCl₃) δ 7.42 (4H, dd, *J* = 2.0, 2.0 Hz, Ar-H), 6.99 (8H, d, *J* = 2.0 Hz, Ar-H), 6.52 (4H, d, *J* = 6.8 Hz, Ar-H), 6.42 (4H, d, *J* = 6.8 Hz, Ar-H), 1.30 (72H, s, *t*-Bu), -1.09 (24H, s, CH₃); ¹³C

NMR (75 MHz, CD₂Cl₂) δ 150.2, 148.6, 141.7, 138.8, 138.1, 136.2, 132.5, 123.1, 122.8, 115.1, 34.4, 30.7, -7.1. The powder of bis-Al dimer was dissolved into minimum quantity of CH₂Cl₂ with heat. Excess of dry hexane was added *very carefully* onto the layer of the CH₂Cl₂ solution of bis-Al dimer. The biphasic mixture was stood as such at room temperature. Slow diffusion of the solvents over a day gave a single crystal of colorless prism, which was mounted on a glass capillary. Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated MoK α radiation ($\lambda = 0.71069$ Å) to a maximum 2θ value of 55°. All of the crystallographic calculations were performed using teXsan software package of the Molecular Structure Corp. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using SIR-92. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. The crystallographic data were summarized in the following table.

empirical formula	C ₄₄ H ₅₈ Al ₂ O ₂
formula weight	672.90
crystal system	monoclinic
space group	C2/c (No. 15)
<i>a</i> , Å	22.5771(7)
<i>b</i> , Å	18.7762(5)
<i>c</i> , Å	21.5639(6)
<i>V</i> , Å ³	8288.8(4)
<i>Z</i>	10
<i>D</i> _{calc} , g/cm ³	1.348
<i>T</i> , °C	-100
μ (MoK α), cm ⁻¹	1.28
no. of reflns measd	38947
no. of reflns obsd	9487
no. of variable	434
<i>R</i>	0.066
<i>R</i> _w	0.161
goodness of fit	1.19

General Procedure for the Reduction of Acetophenone with Bis(organoaluminum)

Reagents 2. A suspension of 2,7-dimethyl-1,8-biphenylenediol (**1a**, 117 mg, 0.55 mmol) in dry CH₂Cl₂ (5 mL) was degassed carefully with stirring, and a 1 M hexane solution of Me₃Al (1.1 mL,

1.1 mmol) was added at room temperature. Evolution of methane gas was observed and the mixture turned into wine-red as suspended biphenylenediol was completely dissolved. After 30 min, the solution was cooled to $-78\text{ }^{\circ}\text{C}$. Acetophenone (58 μL , 0.5 mmol) was added followed by the addition of Bu_3SnH (148 μL , 0.55 mmol) at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for 5 h at that temperature and quenched with 1 N HCl. Usual workup and purification by silica gel column chromatography (CH_2Cl_2 as eluant) gave 2-phenethyl alcohol (55 mg, 0.45 mmol, 91% yield) as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.26 (5H, m, Ph), 4.91 (1H, dq, $J = 3.6, 6.3$ Hz, O-CH), 1.79 (1H, d, $J = 3.6$ Hz, OH), 1.51 (3H, d, $J = 6.3$ Hz, CH_3). 2,7-Dimethyl-1,8-biphenylenediol was easily recovered quantitatively by the elution with $\text{CH}_2\text{Cl}_2/\text{ether} = 19:1$ to 9:1.

Reduction of 5-Nonanone. A solution of bis(organoaluminium) reagent **2a** (0.55 mmol) in CH_2Cl_2 (5 mL) was prepared in a similar manner as described above, and 5-nonanone (86 μL , 0.5 mmol) was added dropwise followed by the addition of Bu_3SnH (148 μL , 0.55 mmol) at $-78\text{ }^{\circ}\text{C}$. The reaction was completed within 20 min. The mixture was poured into ice-cooled 1 N HCl and extracted with ether. The ethereal extracts were washed with brine and dried over Na_2SO_4 . Evaporation of solvents and purification of the residue by column chromatography on silica gel (CH_2Cl_2 as eluant) gave 5-nonanol (62 mg, 0.43 mmol, 86% yield) as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 3.59 (1H, m, O-CH), 1.50-1.25 (13H, m, $\text{CH}_3(\text{CH}_2)_3\text{CHOH}$), 0.91 (6H, t, $J = 7.2$ Hz, CH_3).

Mukaiyama Aldol Reaction. Benzaldehyde (51 μL , 0.5 mmol) was added to a solution of *in situ* prepared **2a** (0.55 mmol) in CH_2Cl_2 (5 mL) at $-78\text{ }^{\circ}\text{C}$ followed by the addition of 1-(trimethylsiloxy)-1-cyclohexene (107 μL , 0.55 mmol). The reaction was monitored by TLC analysis and completion was confirmed after 3.5 h. The whole mixture was poured into 1 N HCl and extracted with ether. The ethereal extracts were washed with saturated NaHCO_3 and brine, and dried over Na_2SO_4 . The solvents were removed by evaporation and the residue was purified by column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane} = 1:2$ to CH_2Cl_2 as eluant) to give the corresponding aldol product, 2-(1'-trimethylsiloxybenzyl)-1-cyclohexanone [**12** ($\text{R} = \text{SiMe}_3$)]⁸ (121 mg, 0.44 mmol, 87% yield, *erythro/threo* = 1:3): ^1H NMR (300 MHz, CDCl_3) *erythro* isomer: 7.39-7.15 (5H, m, Ph), 5.54 (1H, d, $J = 5.2$ Hz, O-CH), 2.60-1.15 (9H, m, CH and CH_2), 0.21 (9H, s, $\text{Si}(\text{CH}_3)_3$); *threo* isomer: 7.40-7.20 (5H, m, Ph), 5.28 (1H, d, $J = 8.1$ Hz, O-CH), 2.80-1.15 (9H, m, CH and CH_2), 0.20 (9H, s, $\text{Si}(\text{CH}_3)_3$).

Mukaiyama Michael Addition. Ketene silyl acetal **13**⁹ (96 mg, 0.55 mmol) was added to a solution of the complex of benzalacetone (73 mg, 0.5 mmol) with **2a** (0.55 mmol) in CH₂Cl₂ (5 mL) at -78 °C. The mixture was stirred for 15 min at that temperature and then poured into 1 N HCl. Extractive workup was carried out with ether and the combined extracts were dried over Na₂SO₄. Evaporation of solvents and purification of the residue by column chromatography on silica gel afforded 1,4-adduct **15** and **16** in the form of enol silyl ether (117 mg, 0.36 mmol, 73% combined yield) with silyl ether of 1,2-adduct **17** (12.3 mg, 0.038 mmol, 8% yield): ¹H NMR (300 MHz, CDCl₃) 1,4-adduct **15** (Z-isomer): δ 7.27-7.13 (5H, m, Ph), 4.92 (1H, dd, *J* = 0.9, 10.5 Hz, PhC-CH=C), 3.98 (1H, d, *J* = 10.5 Hz, PhCH), 3.58 (3H, s, CO₂CH₃), 1.80 (3H, d, *J* = 0.9 Hz, -C=C-CH₃), 1.14 (6H, s, C(CH₃)₂CO₂CH₃), 0.05 (9H, s, Si(CH₃)₃); 1,4-adduct **16** (E-isomer): δ 7.27-7.13 (5H, m, Ph), 5.14 (1H, dd, *J* = 0.9, 10.5 Hz, PhC-CH=C), 3.69 (1H, d, *J* = 10.5 Hz, PhCH), 3.61 (3H, s, CO₂CH₃), 1.69 (3H, d, *J* = 0.9 Hz, C=CCH₃), 1.10 (6H, s, C(CH₃)₂CO₂CH₃), 0.19 (9H, s, Si(CH₃)₃); IR (liquid film, Z/E = 41:59 mixture) 2953, 1736, 1666, 1470, 1452, 1433, 1387, 1366, 1254, 1190, 1128, 1032, 1011, 986, 905, 847, 752, 704 cm⁻¹. MS (Z/E = 41:59 mixture): *m/z* 320 (M⁺), 305, 289, 219 (100%), 145, 129, 73. Anal. Calcd for C₁₈H₂₈O₃Si: C, 67.46; H, 8.81. Found: C, 67.27; H, 8.61. The structure of Z-isomer was confirmed by NOE measurement.

1,2-adduct **17**: δ 7.37-7.26 (5H, m, Ph), 6.46 (1H, d, *J* = 16.2 Hz, PhCH=C-), 6.37 (1H, d, *J* = 16.2 Hz, PhC=CH-), 3.64 (3H, s, CO₂CH₃), 1.48 (3H, s, PhC=C-CCH₃), 1.19 (6H, s, C(CH₃)₂CO₂CH₃), 0.10 (9H, s, Si(CH₃)₃).

General Procedure for Selective Activation of Carbonyls in the Presence of Acetals: To a solution of **2a** (0.55 mmol) in CH₂Cl₂ (5 mL) were added benzaldehyde (51 μL, 0.5 mmol) and its dimethyl acetal (75 μL, 0.5 mmol) at -78 °C. After 5 min of stirring, 1-(trimethylsiloxy)-1-cyclohexene (97 μL, 0.5 mmol) was introduced. The reaction mixture was stirred at -78 °C for 3 h and poured into 1 N HCl. Extractive workup was preformed with ether. The combined extracts were washed with saturated NaHCO₃ and brine, and then dried over Na₂SO₄.

Evaporation of solvents and purification of the residual oil by column chromatography on silica gel (2 times, CH_2Cl_2 and EtOAc/hexane = 1:20 to 1:5 as eluants) gave aldol adducts **12** and **18**¹⁰ as a pale yellow oil (84% combined yield; ratio of **12**/**18** = 97:3). **12** (R = H)¹¹: ^1H NMR (300 MHz, CDCl_3) *erythro* isomer: δ 7.35-7.25 (5H, m, Ph), 5.40 (1H, d, J = 2.7 Hz, O-CH), 3.02 (1H, d, J = 2.7 Hz, OH), 2.70-1.10 (9H, m, CH and CH_2). *threo* isomer: δ 7.35-7.26 (5H, m, Ph), 4.79 (1H, dd, J = 2.7, 9.0 Hz, O-CH), 3.96 (1H, d, J = 2.7 Hz, OH), 2.70-1.10 (9H, m, CH and CH_2). **18**: *erythro* isomer: ^1H NMR (200 MHz, CDCl_3) δ 7.45-7.20 (5H, m, Ph), 4.79 (1H, d, J = 4.3 Hz, O-CH), 3.26 (3H, s, O- CH_3), 2.52-2.36 (2H, m, CH), 2.33-2.14 (1H, m, CH), 2.08-1.40 (6H, m, CH); IR (liquid film) 2939, 2864, 2826, 1713, 1493, 1452, 1362, 1310, 1221, 1184, 1128, 1099, 1078, 1030, 949, 916, 733, 702. *threo* isomer: ^1H NMR (200 MHz, CDCl_3) δ 7.45-7.25 (5H, m, Ph), 4.55 (1H, d, J = 8.6 Hz, O-CH), 3.20 (3H, s, O- CH_3), 2.72 (1H, ddd, J = 5.0, 8.6, 10.6 Hz, CH), 2.55-2.30 (2H, m, CH), 2.06-1.88 (1H, m, CH), 1.84-1.67 (2H, m, CH), 1.67-1.44 (2H, m, CH), 1.32-1.10 (1H, m, CH); IR (liquid film) 2934, 2862, 2822, 1717, 1495, 1452, 1367, 1348, 1308, 1246, 1215, 1182, 1094, 1028, 968, 908, 804, 777, 748, 704 cm^{-1} .

3-Hydroxy-2,2-dimethylcyclohexanepropionic Acid Methyl Ester (19a).¹² ^1H NMR (200 MHz, CDCl_3) δ 3.69 (3H, s, CO_2CH_3), 3.34 (1H, dd, J = 2.9, 8.8 Hz, O-CH), 2.84 (1H, d, J = 8.8 Hz, OH), 1.80-1.10 (11H, m, C_6H_{11}), 1.27 (3H, s, CH_3), 1.18 (3H, s, CH_3); IR (liquid film) 3516, 2924, 2855, 1736, 1450, 1389, 1259, 1192, 1138, 1113, 1030, 993, 864 cm^{-1} .

3-Methoxy-2,2-dimethylcyclohexanepropionic Acid Methyl Ester (20a). ^1H NMR (400 MHz, CDCl_3) δ 3.66 (3H, s, OCH_3), 3.45 (3H, s, CO_2CH_3), 3.17 (1H, d, J = 6.0 Hz, O-CH), 1.90-1.02 (11H, m, C_6H_{11}), 1.24 (3H, s, $\text{C}(\text{CH}_3)_2\text{CO}_2\text{CH}_3$), 1.11 (3H, s, $\text{C}(\text{CH}_3)_2\text{CO}_2\text{CH}_3$); IR (liquid film) 2928, 2853, 1738, 1472, 1448, 1387, 1362, 1265, 1190, 1140, 1109, 982, 962, 891, 866 cm^{-1} . MS: m/z 213 ($[\text{M}-\text{CH}_3]^+$), 197 ($[\text{M}-\text{OCH}_3]^+$), 145, 128, 127, 95, 75 (100%). Anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{O}_3$: C, 68.38; H, 10.59. Found: C, 68.29; H, 10.83.

3-Hydroxy-2,2-dimethyldecanoic Acid Methyl Ester (19b).¹³ ^1H NMR (200 MHz, CDCl_3) δ 3.70 (3H, s, CO_2CH_3), 3.60 (1H, m, O-CH), 2.34 (1H, d, J = 6.8 Hz, OH), 1.50-1.10 (12H, m, CH_2), 1.19 (3H, s, $\text{C}(\text{CH}_3)_2\text{CO}_2\text{CH}_3$), 1.17 (3H, s, $\text{C}(\text{CH}_3)_2\text{CO}_2\text{CH}_3$), 0.88 (3H, t, J = 6.9 Hz, CH_3); IR (liquid film) 3502, 2941, 2858, 1732, 1468, 1435, 1389, 1271, 1194, 1142, 1076, 989, 862 cm^{-1} .

3-Methoxy-2,2-dimethyldecanoic Acid Methyl Ester (20b). ^1H NMR (200 MHz, CDCl_3) δ 3.68 (3H, s, CO_2CH_3), 3.43 (3H, s, O- CH_3), 3.35 (1H, dd, $J = 3.0, 12.0$ Hz, O-CH), 1.65-1.20 (12H, m, CH_2), 1.19 (3H, s, $\text{C}(\text{CH}_3)_2\text{CO}_2\text{CH}_3$), 1.10 (3H, s, $\text{C}(\text{CH}_3)_2\text{CO}_2\text{CH}_3$), 0.89 (3H, t, $J = 6.7$ Hz, CH_3); IR (liquid film) 2957, 2855, 1732, 1468, 1387, 1366, 1271, 1190, 1140, 1099, 989, 947, 866, 770 cm^{-1} . MS: m/z 213 ($[\text{M}-\text{OCH}_3]^+$), 145, 143 (100%), 111. Anal. Calcd for $\text{C}_{14}\text{H}_{28}\text{O}_3$: C, 68.81; H, 11.55. Found: C, 69.01; H, 11.81.

3-Hydroxy-2,2-dimethylbenzenepropionic Acid Methyl Ester (19c).¹² ^1H NMR (200 MHz, CDCl_3) δ 7.40-7.24 (5H, m, Ph), 4.90 (1H, d, $J = 4.0$ Hz, O-CH), 3.73 (3H, s, CO_2CH_3), 3.09 (1H, d, $J = 4.0$ Hz, OH), 1.17 (3H, s, CH_3), 1.11 (3H, s, CH_3); IR (KBr) 3454, 3065, 2978, 2893, 1697, 1472, 1452, 1367, 1346, 1294, 1277, 1202, 1161, 1051, 1013, 887, 772, 745, 706 cm^{-1} .

3-Methoxy-2,2-dimethylbenzenepropionic Acid Methyl Ester (20c).¹⁴ ^1H NMR (200 MHz, CDCl_3) δ 7.40-7.20 (5H, m, Ph), 4.48 (1H, s, O-CH), 3.72 (3H, s, CO_2CH_3), 3.20 (3H, s, O- CH_3), 1.11 (3H, s, CH_3), 1.01 (3H, s, CH_3); IR (liquid film) 2984, 2949, 2883, 2824, 1740, 1472, 1454, 1387, 1364, 1256, 1192, 1165, 1132, 1099, 770, 748, 706 cm^{-1} .

3-Hydroxy-2,2,3-trimethyldodecanoic Acid Methyl Ester (19d). ^1H NMR (200 MHz, CDCl_3) δ 3.72 (3H, s, CO_2CH_3), 3.50 (1H, s, OH), 1.60-1.20 (16H, m, CH_2), 1.24 (3H, s, CH_3), 1.20 (3H, s, CH_3), 1.10 (3H, s, CH_3), 0.88 (3H, t, $J = 6.7$ Hz, CH_2CH_3); IR (liquid film) 3512, 2920, 2855, 1728, 1709, 1468, 1393, 1377, 1279, 1192, 1146, 1099 cm^{-1} . MS: m/z 257 ($[\text{M}-\text{CH}_3]^+$), 241 ($[\text{M}-\text{OCH}_3]^+$), 225, 171, 155, 145 (100%), 113, 102. Anal. Calcd for $\text{C}_{16}\text{H}_{32}\text{O}_3$: C, 70.54; H, 11.84. Found: C, 70.74; H, 12.06.

3-Methoxy-2,2,3-trimethyldodecanoic Acid Methyl Ester (20d). ^1H NMR (200 MHz, CDCl_3) δ 3.66 (3H, s, CO_2CH_3), 3.24 (3H, s, O- CH_3), 1.70-1.20 (16H, m, CH_2), 1.22 (3H, s, CH_3), 1.21 (3H, s, CH_3), 1.20 (3H, s, CH_3), 0.88 (3H, t, $J = 6.7$ Hz, CH_2CH_3); IR (liquid film) 2926, 2855, 1728, 1468, 1377, 1269, 1186, 1126, 1103 cm^{-1} . MS: m/z 271 ($[\text{M}-\text{CH}_3]^+$), 255 ($[\text{M}-\text{OCH}_3]^+$), 239, 185 (100%), 159, 145, 127, 99. Anal. Calcd for $\text{C}_{17}\text{H}_{34}\text{O}_3$: C, 71.28; H, 11.96. Found: C, 71.58; H, 12.26.

3-Hydroxy-2,2,3-trimethylbenzenepropionic Acid Methyl Ester (19e).¹⁵ ^1H NMR (200 MHz, CDCl_3) δ 7.50-7.20 (5H, m, Ph), 4.38 (1H, s, OH), 3.69 (3H, s, CO_2CH_3), 1.61 (3H,

s, PhCCH₃), 1.17 (3H, s, CH₃), 1.15 (3H, s, CH₃); IR (liquid film) 3491, 2984, 2951, 1722, 1703, 1474, 1447, 1375, 1279, 1204, 1150, 1113, 1069, 768, 706 cm⁻¹.

3-Methoxy-2,2,3-trimethylbenzenepropionic Acid Methyl Ester (20e). ¹H NMR (200 MHz, CDCl₃) δ 7.40-7.20 (5H, m, Ph), 3.56 (3H, s, CO₂CH₃), 3.11 (3H, s, O-CH₃), 1.68 (3H, s, PhCCH₃), 1.14 (3H, s, CH₃), 1.11 (3H, s, CH₃); IR (liquid film) 2986, 2949, 2829, 1724, 1688, 1447, 1375, 1271, 1151, 1119, 1072, 1047, 708 cm⁻¹. MS: *m/z* 221 ([M-CH₃]⁺), 205 ([M-OCH₃]⁺), 177, 135 (100%), 105, 91. Anal. Calcd for C₁₄H₂₀O₃: C, 71.16; H, 8.53. Found: C, 71.42; H, 8.67.

α-(2-Propenyl)cyclohexanemethanol (19f).¹⁶ ¹H NMR (300 MHz, CDCl₃) δ 5.85 (1H, m, CH=CH₂), 5.19-5.12 (2H, m, CH=CH₂), 3.40 (1H, m, O-CH), 2.23 (2H, m, CH₂-C=C), 1.90-1.61 (5H, m, CH), 1.58 (1H, br s, OH), 1.42-0.95 (6H, m, CH).

(1-Methoxy-3-butenyl)cyclohexane (20f).¹⁷ ¹H NMR (200 MHz, CDCl₃) δ 5.85 (1H, dddd, *J* = 7.0, 7.0, 10.0, 17.2 Hz, CH=CH₂), 5.07 (1H, dd, *J* = 1.8, 17.2 Hz, CH=CH₂ (*Z*)), 5.04 (1H, dd, *J* = 1.8, 10.0 Hz, CH=CH₂ (*E*)), 3.35 (3H, s, O-CH₃), 2.94 (1H, ddd, *J* = 5.5, 5.5, 5.5 Hz, O-CH), 2.25 (2H, m, CH₂-C=C), 1.85-1.60 (4H, m, CH), 1.48 (1H, m, CH), 1.35-0.85 (6H, m, CH); IR (liquid film) 2928, 2853, 1641, 1450, 1354, 1150, 1101, 1000, 910 cm⁻¹.

α-(2-Propenyl)benzylalcohol (19g).¹⁸ ¹H NMR (300 MHz, CDCl₃) δ 7.25-7.39 (5H, m, Ph), 5.82 (1H, m, CH=CH₂), 5.21-5.13 (2H, m, CH=CH₂), 4.74 (1H, m, O-CH), 2.59-2.43 (2H, m, CH₂-C=C), 2.08 (1H, br s, OH).

(1-Methoxy-3-butenyl)benzene (20g).¹⁹ ¹H NMR (200 MHz, CDCl₃) δ 7.40-7.25 (5H, m, Ph), 5.77 (1H, dddd, *J* = 7.0, 7.0, 10.2, 18.2 Hz, CH=CH₂), 5.05 (1H, dd, *J* = 1.6, 18.2 Hz, CH=CH₂ (*Z*)), 5.03 (1H, dd, *J* = 1.6, 10.2 Hz, CH=CH₂ (*E*)), 4.17 (1H, dd, *J* = 6.0, 7.4 Hz, O-CH), 3.22 (3H, s, O-CH₃), 2.57 (1H, ddd, *J* = 7.0, 7.4, 14.4 Hz, CH₂-C=C), 2.40 (1H, ddd, *J* = 6.0, 7.0, 14.4 Hz, CH₂-C=C); IR (liquid film) 3076, 3028, 2982, 2934, 2822, 1641, 1493, 1454, 1358, 1101, 916, 758, 702 cm⁻¹.

Preparation of Allyl Vinyl Ether 21.²⁰ The mixture of cinnamyl alcohol (1.34 g, 10 mmol), mercury acetate (2.14 g, 7 mmol), and ethyl vinyl ether (15 mL) was stirred at room temperature for 3 h. This mixture was poured into 5% aqueous KOH, extracted with hexane and dried over Na₂SO₄. The solvents were evaporated and the residual oil was purified by column chromatography on silica gel (hexane as eluant) to give cinnamyl vinyl ether (**21**, 1.17 g, 7.3 mmol, 73% yield) as a colorless

oil: ^1H NMR (300 MHz, CDCl_3) δ 7.42-7.25 (5H, m, Ph), 6.66 (1H, d, J = 16.2 Hz, PhCH=C), 6.52 (1H, dd, J = 6.9, 14.4 Hz, O-CH=C), 6.32 (1H, dt, J = 6.0, 16.2 Hz, PhC=CH), 4.41 (2H, d, J = 6.0 Hz, O-CH₂), 4.28 (1H, dd, J = 2.1, 14.4 Hz, O-C=CH₂ (Z)), 4.07 (1 H, dd, J = 2.1, 6.9 Hz, O-C=CH₂ (E)); IR (liquid film) 3061, 3028, 2909, 2862, 1636, 1614, 1495, 1450, 1373, 1319, 1194, 1153, 1055, 964, 822, 745, 692 cm^{-1} .

Claisen Rearrangement of Allyl Vinyl Ether 21. A solution of **2a** (0.55 mmol) in CH_2Cl_2 (5 mL) was prepared as already described, and cooled to 0 °C. Cinnamyl vinyl ether **21** (80 mg, 0.5 mmol) was added dropwise and the mixture was stirred for 1 h. The reaction was quenched with 1 N HCl, extracted with ether and dried over Na_2SO_4 . Evaporation of solvents and purification of the residue by silica gel column chromatography (CH_2Cl_2 as eluant) gave a colorless oil, 3-phenyl-1-hexen-5-ol (**22**,²⁰ 84 mg, 0.48 mmol, 96% yield) as a mixture of two diastereomers (44:56): ^1H NMR (300 MHz, CDCl_3) δ 7.34-7.17 (5H, m, Ph), 6.08-5.88, 5.13-5.01 (3H, m, PhC-CH=CH₂), 3.73 (0.44H, m, PhCH (minor isomer)), 3.63 (0.56H, m, PhCH (major isomer)), 3.50 (1H, m, O-CH), 1.95-1.75 (2H, m, PhCCH₂C), 1.43 (0.56H, d, J = 4.2 Hz, OH (major isomer)), 1.31 (0.44H, d, J = 4.8 Hz, OH (minor isomer)), 1.22 (1.32H, d, J = 7.2 Hz, CH₃ (minor isomer)), 1.07 (1.68H, d, J = 6.3 Hz, CH₃ (major isomer)); IR (liquid film) 3354, 3082, 3028, 2966, 2930, 1638, 1601, 1493, 1454, 1414, 1375, 1126, 1063, 1020, 995, 947, 916, 845, 756, 702, 681 cm^{-1} .

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