Supporting Information

Pd(0)-Catalyzed Amphiphilic Allylation of Aldehydes with Vinyl Epoxide

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Experimental Section

Reactions employed oven-dried glassware unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator (Merck, Silica gel 60F₂₅₄). Flash chromatography columns were packed with 230-400 mesh silica gel as a slurry in hexane. Gradient flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Proton and carbon NMR data were obtained with a JEOL-GX400 with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured with a JEOL JMS-DX303.

Solvents and Reagents

Tetrahydrofuran was dried and distilled from benzophenone and sodium immediately prior to use under nitrogen atmosphere. Pd(PPh₃)₄ and Pd(acac)₂ (Nakalai), Et₃B (1.0 M hexane solution, KANTO and 1.0 M THF solution, Aldrich),

tri(n-butyl)phosphine (Tokyo Kasei Kogyo Co., Ltd), triphenylphosphine, triethylphosphite, DPPE, and DPPF (Aldrich), were purchased and used without further purification. The following aldehydes and epoxides were purchased and distilled prior to use by Kugelrohr apparatus.

General Procedure for α -Alkylation of Aldehydes with Vinyl Epoxide (Scheme 2): To a solution of Pd(PPh₃)₄ (57.8 mg, 0.05 mmol), in dry DMSO (2.5 ml), were successively added diphenylacetaldehyde (196.2 mg, 1.0 mmol) and vinyl epoxide (84.1 mg, 1.2 mmol) via syringe at ambient temperature under N₂. The mixture (brown solution all through the reaction) was stirred at ambient temperature for 1 h. The mixture was diluted with EtOAc and washed with brine. The extract was dried (MgSO₄) and concentrated in vacuo and the residual oil was subjected to column chromatography over silica gel (hexane/EtOAc = 2/1 v./v.) to give **1a** (242 mg, 91%, *R_f* = 0.27; hexane/EtOAc = 2/1 v./v.).

6-Hydroxy-2,2-diphenylhex-4-enal (1a): IR (neat) 3383 (w), 3059 (w), 1722 (w), 1599 (w), 1097 (m), 758 (m), 700 (s) cm⁻¹; ¹H NMR (C₆D₆, 400 MHz, *E* isomer) δ 3.00 (d, *J* = 6.8 Hz, 2 H), 3.64 (br s, 2 H), 5.29-5.35 (dm, *J* = 15.4 Hz, 1 H), 5.45 (dt, *J* = 15.4, 6.8 Hz, 1 H), 6.93-7.07 (m, 10 H), 9.67 (s, 1 H); ¹H NMR (C₆D₆, 400 MHz, *Z* isomer) δ 3.00 (d, *J* = 6.8 Hz, 2 H), 3.77 (br s, 2 H), 5.29-5.37 (m, 1 H), 5.48-5.54 (dm, *J* = 6.8 Hz, 1 H), 6.93-7.07 (m, 10 H), 9.61 (s, 1 H); ¹³C NMR (C₆D₆, 100 MHz, *E* isomer) δ 37.6, 63.0, 63.8, 126.5, 127.2, 128.6, 129.3, 133.7, 140.2, 197.4; ¹³C NMR (C₆D₆, 100 MHz, *Z* isomer) δ 32.4, 58.3, 63.9, 126.4, 127.3, 128.7, 129.2, 132.4, 140.0, 197.3. High-resolution MS, calcd for C₁₈H₁₈O₂: 266.1307, found *m/z* (relative intensity): 266.1337 (M⁺, 67), 237 (73), 195 (100).

5-(Hydroxymethyl)-2,2-diphenylhex-4-enal (1b): IR (neat) 3344 (w), 3059 (w), 3026 (w), 1722 (s), 1599 (w), 1015 (m), 756 (m), 700 (s) cm⁻¹; ¹H NMR (CDCl₃,

400 MHz, *E* isomer) δ 1.40 (s, 3 H), 3.04 (d, J = 7.0 Hz, 2 H), 3.81 (s, 2 H), 5.31 (t, J = 7.0 Hz, 1 H), 7.17-7.20 (m, 4 H), 7.26-7.30 (m, 2 H), 7.32-7.36 (m, 4 H), 9.82 (s, 1 H); ^1H NMR (CDCl_3 , 400 MHz, *Z* isomer) δ 1.64 (s, 3 H), 3.06 (d, J = 7.8 Hz, 2 H), 3.76 (s, 1 H), 3.77 (s, 1 H), 5.16 (t, J = 7.8 Hz, 1 H), 7.17-7.19 (m, 4 H), 7.30-7.33 (m, 2 H), 7.36-7.40 (m, 4 H), 9.81 (s, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz, *E* isomer) δ 13.6, 32.5, 64.0, 120.5, 127.4, 128.6, 129.2, 138.0, 139.7, 198.6; ^{13}C NMR (CDCl_3 , 100 MHz, *Z* isomer) δ 21.5, 32.3, 61.3, 68.7, 122.3, 127.4, 128.5, 129.0, 137.7, 139.6, 198.1. High-resolution MS, calcd for $\text{C}_{19}\text{H}_{20}\text{O}_2$: 280.1463, found m/z (relative intensity): 280.1461 (M^+ , 85), 249 (44), 195 (100).

6-Hydroxy-2-methyl-2-phenylhex-4-enal (1c): IR (neat) 3383 (m), 3088 (w), 1722 (s), 1599 (w), 1373 (m), 1082 (m), 762 (m), 700 (s) cm^{-1} ; ^1H NMR (C_6D_6 , 400 MHz, *E* isomer) δ 1.63 (s, 3 H), 2.44 (dd, J = 7.0, 14.2 Hz, 1 H), 2.48 (dd, J = 7.0, 14.2 Hz, 1 H), 3.66 (br s, 2 H), 5.28 (dt, J = 15.4, 7.0 Hz, 1 H), 5.35-5.41 (dm, J = 15.4 Hz, 1 H), 6.94-7.10 (m, 5 H), 9.26 (s, 1 H); ^1H NMR (C_6D_6 , 400 MHz, *Z* isomer) δ 1.10 (s, 3 H), 2.44 (dd, J = 7.0, 14.2 Hz, 1 H), 2.48 (dd, J = 7.0, 14.2 Hz, 1 H), 3.79 (br s, 2 H), 5.10-5.17 (dm, J = 11.5 Hz, 1 H), 5.50 (dt, J = 11.5, 7.0 Hz, 1 H), 6.94-7.10 (m, 5 H), 9.22 (s, 1 H). Anal. calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: C, 76.44; H, 7.90. Found: C, 76.53; H, 7.76.

6-Hydroxy-2-(4-isobutylphenyl)-2-methylhex-4-enal (1d): IR (neat) 3379 (m), 3030 (w), 1720 (s), 1604 (w), 1380 (w), 1272 (w), 848 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, *E* isomer) δ 0.89 (d, J = 7.0 Hz, 6 H), 1.41 (s, 3 H), 1.85 (m, 1 H), 2.45 (d, J = 7.0 Hz, 2 H), 2.62 (dd, J = 7.3, 13.9 Hz, 1 H), 2.65 (dd, J = 7.3, 13.9 Hz, 1 H), 4.01 (d, J = 5.7 Hz, 2 H), 5.45 (dt, J = 15.3, 7.3 Hz, 1 H), 5.65 (dt, J = 15.3, 5.7 Hz, 1 H), 7.11-7.16 (m, 4 H), 9.48 (s, 1 H); ^1H NMR (CDCl_3 , 400 MHz, *Z* isomer) δ 0.89 (d, J = 7.0 Hz, 6 H), 1.45 (s, 3 H), 1.85 (m, 1 H), 2.53 (d, J = 7.0 Hz, 2 H), 2.62 (dd, J = 7.3, 13.9 Hz, 1 H), 2.65 (dd, J = 7.3, 13.9 Hz, 1 H), 4.01 (d, J = 5.7

Hz, 2 H), 5.33 (dt, $J = 7.3, 11.2$ Hz, 1 H), 5.63 (dt, $J = 5.7, 11.2$ Hz, 1 H), 7.11-7.16 (m, 4 H), 9.49 (s, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz, *E* isomer) δ 18.9, 22.3, 30.1, 38.8, 44.8, 53.4, 63.2, 126.6, 127.0, 129.4, 132.8, 136.4, 140.7, 201.7; ^{13}C NMR (CDCl_3 , 100 MHz, *Z* isomer) δ 18.6, 22.3, 34.0, 38.9, 44.9, 53.6, 58.2, 126.7, 126.8, 129.4, 132.8, 136.1, 140.8, 201.7. High-resolution MS, calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2$: 260.1776, found m/z (relative intensity): 260.1743 (M^+ , 100), 243 (17), 242 (59). Anal. calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2$: C, 78.42; H, 9.29. Found: C, 78.44; H, 9.40.

2-Ethyl-6-hydroxy-2-phenylhex-4-enal (1e): IR (neat) 3402 (m), 3030 (w), 1720 (vs), 1604 (w), 1249 (w), 1087 (w), 1002 (m), 756 (m), 702 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, *E* isomer) δ 0.79 (t, $J = 7.4$ Hz, 3 H), 1.59 (br s, 1 H), 1.97 (q, $J = 7.4$ Hz, 2 H), 2.65 (ddm, $J = 12.0, 7.0$ Hz, 1 H), 2.68 (ddm, $J = 12.0, 7.0$ Hz, 1 H), 4.01 (d, $J = 7.2$ Hz, 2 H), 5.41 (dtm, $J = 15.4, 7.2$ Hz, 1 H), 5.64 (dt, $J = 15.4, 7.0$ Hz, 1 H), 7.17-7.39 (m, 5 H), 9.49 (s, 1 H); ^1H NMR (CDCl_3 , 400 MHz, *Z* isomer) δ 0.84 (t, $J = 7.5$ Hz, 3 H), 1.59 (br s, 1 H), 2.03 (q, $J = 7.5$ Hz, 2 H), 2.68 (ddm, $J = 14.5, 8.5$ Hz, 1 H), 2.73 (ddm, $J = 14.5, 8.5$ Hz, 1 H), 3.98 (d, $J = 7.7$ Hz, 2 H), 5.30 (dtm, $J = 11.1, 7.7$ Hz, 1 H), 5.65 (dt, $J = 11.1, 8.5$ Hz, 1 H), 7.17-7.39 (m, 5 H), 9.53 (s, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz, *E* isomer) δ 8.1, 24.8, 34.7, 57.6, 63.3, 126.6, 127.2, 127.5, 128.7, 132.8, 138.3, 202.3; ^{13}C NMR (CDCl_3 , 100 MHz, *Z* isomer) δ 8.4, 24.9, 30.3, 57.8, 58.3, 126.4, 127.4, 127.6, 128.7, 131.5, 138.5, 202.4. High-resolution MS, calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$: 218.1307, found m/z (relative intensity): 218.1301 (M^+ , 100), 201 (19), 189 (20).

2-(4-Chlorophenyl)-6-hydroxy-2-isopropylhex-4-enal (1f): IR (neat) 3410 (s), 2970 (m), 2878 (m), 1720 (s), 1096 (m), 1011 (m), 825 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, *E* isomer) δ 0.83 (d, $J = 6.9$ Hz, 3 H), 0.92 (d, $J = 6.9$ Hz, 3 H), 1.61 (br s, 1 H), 2.40 (sept, $J = 6.9$ Hz, 1 H), 2.62 (dd, $J = 7.1, 13.9$ Hz, 1 H), 2.74 (dd, $J = 7.1,$

13.9 Hz, 1 H), 4.00 (d, $J = 5.7$ Hz, 2 H), 5.43 (dt, $J = 15.4, 7.1$ Hz, 1 H), 5.63 (dt, $J = 15.4, 5.7$ Hz, 1 H), 7.09-7.12 (m, 2 H), 7.34-7.39 (m, 2 H), 9.74 (s, 1 H); ^1H NMR (CDCl_3 , 400 MHz, *Z* isomer) δ 0.88 (d, $J = 6.9$ Hz, 3 H), 0.95 (d, $J = 6.9$ Hz, 3 H), 1.61 (br s, 1 H), 2.39 (sept, $J = 6.9$ Hz, 1 H), 2.69 (dd, $J = 7.1, 13.9$ Hz, 1 H), 2.74 (dm, $J = 13.9$ Hz, 1 H), 4.05 (dm, $J = 5.6$ Hz, 2 H), 5.28 (dt, $J = 7.1, 11.1$ Hz, 1 H), 5.64 (dt, $J = 11.1, 5.6$ Hz, 1 H), 7.09-7.12 (m, 2 H), 7.34-7.39 (m, 2 H), 9.80 (s, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz, *E* isomer) δ 17.6, 18.3, 31.6, 35.4, 60.2, 63.2, 126.5, 128.4, 129.9, 133.0, 133.2, 136.0, 203.4 ; ^{13}C NMR (CDCl_3 , 100 MHz, *Z* isomer) δ 17.8, 18.2, 30.8, 32.3, 58.4, 60.3, 126.2, 128.6, 129.7, 131.37, 133.1, 136.4, 203.7. High-resolution MS, calcd for $\text{C}_{15}\text{H}_{19}\text{ClO}_2$: 266.1074, found m/z (relative intensity): 266.1042 (M^+ , 100), 249 (17), 235 (15).

2-Benzyl-6-hydroxy-2-phenylhex-4-enal (1g): IR (neat) 3425 (s), 3032 (m), 2862 (m), 2715 (s), 2361 (w), 1720 (m), 1597 (w), 1011 (m), 702 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, *E* isomer) δ 2.03 (br s, 1 H), 2.66 (d, $J = 6.9$ Hz, 2 H), 3.18 (d, $J = 13.9$ Hz, 1 H), 3.24 (d, $J = 13.9$ Hz, 1 H), 4.04 (dd, $J = 1.1, 6.6$ Hz, 2 H), 5.58 (dtm, $J = 15.4, 6.9$ Hz, 1 H), 5.69 (dtm, $J = 15.4, 6.6$ Hz, 1 H), 6.77 (d, $J = 2.7$ Hz, 1 H), 6.78 (dm, $J = 2.7$ Hz, 1 H), 7.07-7.38 (m, 8 H), 9.64 (s, 1 H); ^1H NMR (CDCl_3 , 400 MHz, *Z* isomer) δ 2.03 (br s, 1 H), 2.60 (d, $J = 6.9$ Hz, 2 H), 3.23 (d, $J = 13.9$ Hz, 1 H), 3.32 (d, $J = 13.9$ Hz, 1 H), 4.04 (dm, $J = 6.6$ Hz, 2 H), 5.44 (dtm, $J = 11.0, 6.9$ Hz, 1 H), 5.66 (dtm, $J = 11.0, 6.6$ Hz, 1 H), 6.82 (d, $J = 3.0$ Hz, 1 H), 6.84 (t, $J = 3.0$ Hz, 1 H), 7.07-7.38 (m, 8 H), 9.66 (s, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz, *E* isomer) δ 34.8, 39.7, 58.5, 63.2, 126.2, 126.4, 127.5, 127.8, 127.9, 128.7, 130.3, 133.7, 136.2, 137.9, 202.0; ^{13}C NMR (CDCl_3 , 100 MHz, *Z* isomer) δ 29.9, 39.6, 58.5, 58.6, 126.0, 126.9, 127.6, 127.9, 128.0, 128.8, 131.8, 133.7, 136.1, 137.8, 201.9; High-resolution MS, calcd for $\text{C}_{19}\text{H}_{20}\text{O}_2$: 280.1463, found m/z (relative intensity): 280.1454 (M^+ , 100), 263 (27). Anal. calcd for $\text{C}_{19}\text{H}_{20}\text{O}_2$: C, 81.40; H, 7.19. Found: C, 81.50; H, 7.11.

2-(2-Furanyl)methyl-6-hydroxy-2-phenylhex-4-enal (1h): IR (neat) 3407 (s), 2917 (m), 1722 (s), 1504 (m), 1009 (m), 700 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, *E* isomer) δ 1.52 (br s, 1 H), 2.64 (dd, $J = 7.4, 14.0$ Hz, 1 H), 2.75 (dd, $J = 7.4, 14.0$ Hz, 1 H), 3.24 (d, $J = 15.2$ Hz, 1 H), 3.34 (d, $J = 15.2$ Hz, 1 H), 4.03 (d, $J = 5.7$ Hz, 2 H), 5.49 (dt, $J = 15.6, 7.4$ Hz, 1 H), 5.68 (dt, $J = 15.6, 5.7$ Hz, 1 H), 5.82 (d, $J = 3.1$ Hz, 1 H), 6.20 (dm, $J = 3.1$ Hz, 1 H), 7.16-7.45 (m, 6 H), 9.62 (s, 1 H); ^1H NMR (CDCl_3 , 400 MHz, *Z* isomer) δ 1.52 (br s, 1 H), 2.60 (dd, $J = 7.4, 14.0$ Hz, 1 H), 2.76 (dd, $J = 7.4, 14.0$ Hz, 1 H), 3.25 (d, $J = 15.4$ Hz, 1 H), 3.38 (d, $J = 15.4$ Hz, 1 H), 3.97 (dm, $J = 3.2$ Hz, 2 H), 5.36 (dt, $J = 11.0, 7.4$ Hz, 1 H), 5.80 (dt, $J = 11.0, 3.2$ Hz, 1 H), 5.87 (dm, $J = 2.9$ Hz, 1 H), 6.22 (dm, $J = 2.9$ Hz, 1 H), 7.16-7.45 (m, 6 H), 9.64 (s, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz, *E* isomer) δ 31.5, 35.3, 57.6, 63.3, 108.2, 110.1, 126.2, 127.5, 128.7, 132.0, 133.7, 137.4, 141.4, 150.9, 200.9; ^{13}C NMR (CDCl_3 , 100 MHz, *Z* isomer) δ 30.6, 31.2, 57.7, 58.4, 108.2, 110.2, 126.0, 127.6, 128.5, 128.8, 130.5, 133.7, 137.3, 150.7, 200.9. High-resolution MS, calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3$: 270.1256, found m/z (relative intensity): 270.1257 (M^+ , 76), 252 (100). Anal. calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3$: C, 75.53; H, 6.71. Found: C, 75.49, H, 6.66.

1-(4-Hydroxybut-2-enyl)cyclohexanecarbaldehyde (1i): IR (neat) 3400 (m), 2932 (s), 2856 (m), 1724 (m), 1045 (m), 976 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, *E* isomer) δ 1.21-1.91 (m, 10 H), 2.18 (d, $J = 7.3$ Hz, 2 H), 4.08 (d, $J = 5.6$ Hz, 2 H), 5.54 (dt, $J = 15.4, 7.3$ Hz, 1 H), 5.66 (dt, $J = 15.4, 5.6$ Hz, 1 H), 9.44 (s, 1 H); ^1H NMR (CDCl_3 , 400 MHz, *Z* isomer) δ 1.21-1.91 (m, 10 H), 2.22 (d, $J = 8.1$ Hz, 2 H), 4.17 (d, $J = 6.8$ Hz, 2 H), 5.43 (dt, $J = 11.0, 8.1$ Hz, 1 H), 5.72 (dt, $J = 11.0, 6.8$ Hz, 1 H), 9.45 (s, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz, *E* isomer) δ 22.4, 25.6, 30.9, 39.1, 49.8, 65.5, 126.5, 131.5, 206.8; ^{13}C NMR (CDCl_3 , 100 MHz, *Z* isomer) δ 22.4, 25.7, 30.9, 33.8, 50.0, 58.3, 126.5, 133.0, 206.8. High-resolution MS, calcd for $\text{C}_{11}\text{H}_{18}\text{O}_2$: 182.1307, found m/z (relative intensity): 182.1283 (M^+ , 86), 165 (100),

153 (78).

2,2-Diethyl-6-hydroxyhex-4-enal (1j): IR (neat) 3400 (m), 2968 (s), 1724 (s), 1043 (m), 1009 (m), 974 (m), 783 (w) cm^{-1} ; ^1H NMR (C_6D_6 , 400 MHz, *E* isomer) δ 0.60 (t, $J = 7.6$ Hz, 6 H), 1.26 (q, $J = 7.6$ Hz, 4 H), 2.03 (d, $J = 7.0$ Hz, 2 H), 3.75-3.76 (m, 2 H), 5.37 (dt, $J = 15.4, 7.0$ Hz, 1 H), 5.43 (dm, $J = 15.4$ Hz, 1 H), 9.19 (s, 1 H); ^1H NMR (C_6D_6 , 400 MHz, *Z* isomer) δ 0.57 (t, $J = 7.6$ Hz, 6 H), 1.23 (q, $J = 7.6$ Hz, 4 H), 2.03 (d, $J = 7.6$ Hz, 2 H), 3.93 (d, $J = 6.6$ Hz, 2 H), 5.17 (dt, $J = 11.1, 7.6$ Hz, 1 H), 5.55 (dt, $J = 11.1, 6.6$ Hz, 1 H), 9.15 (s, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz, *E* isomer) δ 7.9, 24.3, 33.4, 52.6, 63.1, 126.3, 132.6, 207.0; ^{13}C NMR (CDCl_3 , 100 MHz, *Z* isomer) δ 7.9, 24.5, 28.4, 52.6, 58.2, 126.0, 131.3, 206.9. High-resolution MS, calcd for $\text{C}_{10}\text{H}_{18}\text{O}_2$: 170.1307, found m/z (relative intensity): 170.1294 (M^+ , 10), 152 (100), 141 (40).

1-(4-Hydroxy-3-methylbut-2-enyl)cyclohexanecarbaldehyde (1k): IR (neat) 3381 (s), 2932 (s), 1724 (s), 1005 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, *E* isomer) δ 1.20-1.40 (m, 6 H), 1.48-1.64 (dm, $J = 5.9$ Hz, 3 H), 1.80 (s, 3 H), 1.87-2.00 (m, 2 H), 2.20 (d, $J = 8.0$ Hz, 2 H), 4.09 (br d, $J = 5.9$ Hz, 2 H), 5.19 (t, $J = 8.0$ Hz, 1 H), 9.44 (s, 1 H); ^1H NMR (CDCl_3 , 400 MHz, *Z* isomer) δ 1.20-1.40 (m, 6 H), 1.48-1.64 (dm, $J = 5.9$ Hz, 3 H), 1.65 (s, 3 H), 1.87-2.00 (m, 2 H), 2.19 (d, $J = 8.0$ Hz, 2 H), 3.99 (br d, $J = 5.9$ Hz, 2 H), 5.33 (t, $J = 8.0$ Hz, 1 H), 9.51 (s, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz, *E* isomer) δ 21.5, 22.5, 25.6, 30.9, 34.0, 50.1, 61.3, 121.7, 137.3, 207.0; ^{13}C NMR (CDCl_3 , 100 MHz, *Z* isomer) δ 22.6, 22.8, 25.7, 32.0, 34.4, 50.3, 68.6, 119.3, 137.7, 206.6. High-resolution MS, calcd for $\text{C}_{12}\text{H}_{20}\text{O}_2$: 196.1463, Found m/z (relative intensity): 196.1467 (M^+ , 8), 178 (21), 165 (100), 163 (25).

General Procedure for the Intramolecular Nucleophilic Alkylation of Aldehydes (run 1, Table 1): To a solution of $\text{Pd}(\text{acac})_2$ (30.5 mg, 0.1 mmol), PBU_3

(40.4 mg, 0.2 mmol), and **1a** (266.3 mg, 1.0 mmol) in dry THF (5 ml) were added triethylborane (3.0 mmol, 1.0 M hexane solution) via syringe under N₂. The blown solution was stirred at room temperature for 8 h. The mixture was diluted with EtOAc and washed with brine. The extract was dried (MgSO₄) and concentrated in vacuo and residual oil was subjected to column chromatography over neutral silica gel (hexane/EtOAc = 16/1 v./v.) to give **2a** (205.0 mg, 82%, *R_f* = 0.66; hexane/EtOAc = 2/1 v./v.).

2,2-Diphenyl-4-vinylcyclobutanol (2a): IR (neat) 3435 (w), 1638 (w), 1599 (w), 1115 (m), 916 (m), 748 (m), 700 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz, *trans* isomer) δ 1.60 (d, *J* = 11.7 Hz, 1 H), 1.86 (dd, *J* = 10.6, 11.7 Hz, 1 H), 2.69 (ddt, *J* = 7.1, 10.6, 8.8 Hz, 1 H), 3.06 (dd, *J* = 8.8, 11.7 Hz, 1 H), 4.46 (dd, *J* = 8.8, 11.7 Hz, 1 H), 5.02 (d, *J* = 10.3 Hz, 1 H), 5.07 (d, *J* = 17.2 Hz, 1 H), 5.94 (ddd, *J* = 7.1, 10.3, 17.2 Hz, 1 H), 7.11-7.41 (m, 10 H); ¹H NMR (CDCl₃, 400 MHz, *cis* isomer) δ 1.72 (br s, 1 H), 2.62 (ddm, *J* = 7.8, 11.7 Hz, 1 H), 3.01 (dd, *J* = 6.6, 11.7 Hz, 1 H), 3.23 (tt, *J* = 6.6, 7.8 Hz, 1 H), 5.02 (dm, *J* = 6.6 Hz, 1 H), 5.10 (dm, *J* = 17.2 Hz, 1 H), 5.13 (dm, *J* = 10.3 Hz, 1 H), 5.82 (ddd, *J* = 7.8, 10.3, 17.2 Hz, 1 H), 7.11-7.41 (m, 10 H); ¹³C NMR (CDCl₃, 100 MHz, *trans* isomer) δ 30.7, 47.3, 56.0, 77.4, 114.9, 125.9, 126.3, 126.8, 128.4, 128.7, 138.9, 139.5, 149.7; ¹³C NMR (CDCl₃, 100 MHz, *cis* isomer) δ 33.5, 41.3, 56.1, 75.9, 118.1, 125.9, 126.2, 128.0, 128.5, 136.1, 142.7, 148.9. High-resolution MS, calcd for C₁₈H₁₈O: 250.1358, found *m/z* (relative intensity): 250.0350 (M⁺, 100).

2,2-Diphenyl-4-(prop-1-en-2-yl)cyclobutanol (2b): IR (neat) 3526 (w), 3036 (w), 1647 (w), 1599 (w), 1119 (m), 889 (w), 752 (m), 700 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz, *trans* isomer) δ 1.64 (d, *J* = 11.2 Hz, 1 H), 1.76 (s, 3 H), 1.91 (dm, *J* =

11.5 Hz, 1 H), 2.64 (tm, $J = 8.8$ Hz, 1 H), 3.02 (dd, $J = 8.8, 11.5$ Hz, 1 H), 4.50 (dd, $J = 8.8, 11.2$ Hz, 1 H), 4.75 (s, 1 H), 4.77 (br s, 1 H), 7.13-7.40 (m, 10 H); ^{13}C NMR (CDCl_3 , 100 MHz, *trans* isomer) δ 19.8, 28.5, 49.0, 54.1, 75.9, 108.3, 124.9, 125.2, 125.7, 127.3, 127.7, 129.0, 131.4, 138.6, 144.7, 148.7. High-resolution MS, calcd for $\text{M}^+ - \text{H}_2\text{O}$: 246.1409, found m/z (relative intensity): 246.1417 ($\text{M}^+ - \text{H}_2\text{O}$, 100).

2-Methyl-2-phenyl-4-vinylcyclobutanol (2c): IR (neat) 3421 (m), 3026 (w), 1637 (w), 1602 (w), 1494 (m), 912 (m), 748 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, *trans* isomer) δ 1.42 (s, 3 H), 1.75 (t, $J = 10.4$ Hz, 1 H), 2.06 (br s, 1 H), 2.10 (t, $J = 10.4$ Hz, 1 H), 2.86 (ddt, $J = 7.0, 7.7, 10.4$ Hz, 1 H), 4.09 (d, $J = 7.7$ Hz, 1 H), 4.99 (dm, $J = 10.3$ Hz, 1 H), 5.07 (dm, $J = 17.1$ Hz, 1 H), 5.91 (ddd, $J = 7.0, 10.3, 17.1$ Hz, 1H), 7.15-7.33 (m, 5 H); ^1H NMR (CDCl_3 , 400 MHz, *cis* isomer) δ 1.37 (s, 3 H), 2.02 (dm, $J = 11.7$ Hz, 1 H), 2.40 (dm, $J = 11.7$ Hz, 1 H), 3.21 (ddm, $J = 7.1, 8.0$ Hz, 1 H), 4.54 (dm, $J = 8.0$ Hz, 1 H), 5.20 (br d, $J = 17.5$ Hz, 1 H), 5.32 (br d, $J = 10.5$ Hz, 1 H), 6.11 (ddd, $J = 7.1, 10.5, 17.5$ Hz, 1 H), 7.21-7.43 (m, 5 H); ^{13}C NMR (CDCl_3 , 100 MHz, *trans* isomer) δ 22.8, 31.8, 45.5, 46.3, 78.5, 114.4, 124.9, 125.7, 128.4, 139.5, 150.8; ^{13}C NMR (CDCl_3 , 100 MHz, *cis* isomer) δ 24.9, 32.8, 40.6, 48.7, 74.9, 117.9, 124.9, 125.5, 128.2, 137.1, 150.9. High-resolution MS, calcd for $\text{C}_{13}\text{H}_{16}\text{O}$: 188.1201, found m/z (relative intensity): 188.1186 (M^+ , 100), 170 (77).

2-Ethyl-2-phenyl-4-vinylcyclobutanol (2e): IR (neat) 3379 (m), 3078 (w), 3024 (w), 1635 (w), 1103 (m), 1072 (m), 910 (m), 763 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, major isomer) δ 0.73 (t, $J = 7.4$ Hz, 3 H), 1.69 (t, $J = 10.4$ Hz, 1 H), 1.85 (q, $J = 7.4$ Hz, 2 H), 2.16 (br s, 1 H), 2.18 (t, $J = 10.4$ Hz, 1 H), 2.87 (ddt, $J = 7.0, 8.0, 10.4$ Hz, 1H), 4.09 (d, $J = 8.0$ Hz, 1 H), 4.99 (dm, $J = 10.3$ Hz, 1 H), 5.07 (dm, $J =$

17.1 Hz, 1 H), 5.89 (ddd, $J = 7.0, 10.3, 17.1$ Hz, 1 H), 7.15-7.31 (m, 5 H); ^{13}C NMR (CDCl_3 , 100 MHz, major isomer) δ 8.4, 27.2, 28.4, 45.7, 50.8, 79.7, 114.3, 125.5, 125.8, 127.8, 139.6, 148.7. High-resolution MS, calcd for $\text{C}_{14}\text{H}_{18}\text{O}$: 202.1358, found m/z (relative intensity): 202.1338 (M^+ , 100), 185 (17), 184 (67), 173 (18).

2-(4-Chlorophenyl)-2-isopropyl-4-vinylcyclobutanol (2f): IR (neat) 3410 (s), 3078 (m), 1720 (w), 1643 (w), 1489 (w), 1088 (m), 826 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, **major isomer**) δ 0.78 (d, $J = 6.6$ Hz, 6 H), 1.48 (t, $J = 10.4$ Hz, 1 H), 2.16 (sept, $J = 6.6$ Hz, 1 H), 2.26 (t, $J = 10.4$ Hz, 1 H), 2.79 (ddt, $J = 7.0, 8.3, 10.4$ Hz, 1 H), 4.06 (d, $J = 8.3$ Hz, 1 H), 4.89 (d, $J = 10.3$ Hz, 1 H), 4.96 (d, $J = 17.2$ Hz, 1 H), 5.76 (ddd, $J = 7.0, 10.3, 17.2$ Hz, 1 H), 6.98 (d, $J = 8.5$ Hz, 2 H), 7.16 (d, $J = 8.5$ Hz, 2 H); ^1H NMR (C_6D_6 , 400 MHz, **other isomer-1**) δ 0.56 (d, $J = 6.8$ Hz, 3 H), 0.73 (d, $J = 6.8$ Hz, 3 H), 1.62 (sept, $J = 6.8$ Hz, 1 H), 2.01 (dd, $J = 11.8, 8.1$ Hz, 1 H), 2.30 (dd, $J = 11.8, 8.5$ Hz, 1 H), 2.67 (ddt, $J = 8.5, 8.1, 7.0$ Hz, 1 H), 4.28 (d, $J = 8.5$ Hz, 1 H), 4.97 (d, $J = 17.3$ Hz, 1 H), 4.98 (d, $J = 10.1$ Hz, 1 H), 5.82 (ddd, $J = 17.3, 10.1, 7.0$ Hz, 1 H), 6.90 (d, $J = 8.5$ Hz, 2 H), 7.30 (d, $J = 8.5$ Hz, 2 H); ^1H NMR (C_6D_6 , 400 MHz, **other isomer-2**) δ 0.57 (d, $J = 6.8$ Hz, 3 H), 0.66 (d, $J = 6.8$ Hz, 3 H), 2.07 (dd, $J = 11.8, 8.1$ Hz, 1 H), 2.30 (dd, $J = 11.8, 8.5$ Hz, 1 H), 2.23 (sept, $J = 6.8$ Hz, 1 H), 2.67 (ddt, $J = 8.5, 8.1, 7.0$ Hz, 1 H), 3.76 (t, $J = 7.1$ Hz, 1 H), 5.00 (d, $J = 17.0$ Hz, 1 H), 5.09 (d, $J = 10.4$ Hz, 1 H), 5.81 (ddd, $J = 17.0, 10.4, 7.0$ Hz, 1 H), 6.90 (d, $J = 8.5$ Hz, 2 H), 7.30 (d, $J = 8.5$ Hz, 2 H); ^1H NMR (CDCl_3 , 400 MHz, **other isomer-3**) δ 0.65 (d, $J = 6.8$ Hz, 3 H), 0.72 (d, $J = 6.8$ Hz, 3 H), 1.50 (d, $J = 7.1$ Hz, 1 H), 1.91 (sept, $J = 6.8$ Hz, 1 H), 2.19 (dd, $J = 11.7, 8.3$ Hz, 1 H), 2.30 (dd, $J = 11.7, 7.6$ Hz, 1 H), 3.15 (ddt, $J = 8.3, 7.6, 7.1$ Hz, 1 H), 4.32 (t, $J = 7.1$ Hz, 1 H), 5.00 (d, $J = 17.4$ Hz, 1 H), 5.08 (d, $J = 10.3$ Hz, 1 H), 5.60 (ddd, $J = 17.4, 10.3, 7.3$ Hz, 1 H), 7.05 (d, $J = 8.5$ Hz, 2 H), 7.21 (d, $J = 8.5$ Hz, 2 H); ^{13}C NMR (CDCl_3 , 100 MHz, **major isomer**) δ 18.3, 19.7, 29.9, 30.2, 45.8, 53.6, 80.5, 114.4, 127.3, 128.7, 131.2, 139.5, 145.5; ^{13}C NMR (C_6D_6 , 100 MHz, **other isomer-1**) δ

16.4, 19.2, 31.6, 34.4, 45.8, 54.2, 76.9, 117.2, 130.0, 137.0, 142.3; ^{13}C NMR (C_6D_6 , 100 MHz, **other isomer-2**) δ 17.7, 18.0, 28.1, 39.1, 39.5, 55.7, 77.9, 114.2, 131.4, 137.3, 139.6; ^{13}C NMR (CDCl_3 , 100 MHz, **other isomer-3**) δ 16.4, 31.0, 35.5, 38.3, 53.6, 73.8, 116.9, 126.3, 129.7, 135.2, 137.2. High-resolution MS, Calcd for $\text{C}_{15}\text{H}_{19}\text{ClO}$: 250.1124, found m/z (relative intensity): 250.1082 (M^+ , 100), 235 (16).

2-[(Furan-2-yl)methyl]-2-phenyl-4-vinylcyclobutanol (2h): IR (neat) 3402 (s), 2932 (m), 1597 (w), 1096 (m), 1011 (w), 918 (w), 918 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, *trans* isomer) δ 1.75 (t, $J = 10.4$ Hz, 1 H), 2.42 (dm, $J = 10.4$ Hz, 1 H), 2.59 (ddm, $J = 6.9, 8.3$ Hz, 1 H), 2.73 (d, $J = 8.3$ Hz, 1 H), 3.03 (d, $J = 15.0$ Hz, 1 H), 3.20 (d, $J = 15.0$ Hz, 1 H), 4.17 (t, $J = 8.3$ Hz, 1 H), 4.96 (dm, $J = 10.3$ Hz, 1 H), 5.02 (dm, $J = 17.2$ Hz, 1 H), 5.79 (dm, $J = 3.2$ Hz, 1 H), 5.85 (ddd, $J = 6.9, 10.3, 17.2$ Hz, 1 H), 6.22 (dd, $J = 1.8, 3.2$ Hz, 1H), 7.07-7.25 (m, 5 H), 7.28 (dm, $J = 1.8$ Hz, 1 H); ^1H NMR (CDCl_3 , 400 MHz, *cis* isomer) δ 1.75 (t, $J = 10.4$ Hz, 1 H), 2.42 (dm, $J = 10.4$ Hz, 1 H), 2.59 (ddm, $J = 6.9, 8.3$ Hz, 1 H), 3.07 (d, $J = 11.9$ Hz, 1 H), 3.09 (d, $J = 11.9$ Hz, 1 H), 4.64 (br t, $J = 8.3$ Hz, 1 H), 5.23 (dm, $J = 17.2$ Hz, 1 H), 5.32 (dm, $J = 17.2$ Hz, 1 H), 5.55 (br d, $J = 3.2$ Hz, 1 H), 6.10 (ddd, $J = 6.9, 10.3, 17.2$ Hz, 1 H), 6.12 (dd, $J = 1.8, 3.2$ Hz, 1H), 7.07-7.28 (m, 6 H), 7.28 (dm, $J = 1.8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, *trans* isomer); δ 14.6, 19.9, 30.7, 36.0, 64.5, 93.2, 95.7, 99.7, 110.7, 111.1, 113.3, 124.6, 126.3, 134.2, 137.9; ^{13}C NMR (CDCl_3 , 100 MHz, *cis* isomer) δ 16.2, 21.2, 25.1, 36.9, 61.4, 92.7, 95.3, 99.7, 110.7, 111.1, 111.4, 122.0, 126.1, 134.2, 137.9. High-resolution MS, calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2$: 254.1307, found m/z (relative intensity): 254.1298 (M^+ , 100), 236 (77). Anal. calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2$: C, 80.28; H, 7.13. Found: C, 80.08, H, 7.30.

2-Vinyl-spiro[3.5]nonan-1-ol (2i): IR (neat) 3341 (w), 3078 (w), 2926 (s), 2853 (m), 1638 (w), 1090 (m), 1061 (m), 908 (m) cm^{-1} ; ^1H NMR (C_6D_6 , 400 MHz, *trans* isomer) δ 0.98 (dm, $J = 10.5$ Hz, 1 H), 1.16-1.61 (m, 10 H), 1.65 (dd, $J = 9.6, 10.5$ Hz, 1 H), 2.54 (ddm, $J = 7.9, 9.6$ Hz, 1 H), 3.41 (d, $J = 7.9$ Hz, 1 H), 4.99 (d, $J = 10.2$ Hz, 1 H), 5.05 (d, $J = 17.1$ Hz, 1 H), 5.85-5.93 (ddm, $J = 10.2, 17.1$ Hz, 1 H); ^1H NMR (C_6D_6 , 400 MHz, *cis* isomer) δ 0.80-0.94 (m, 2 H), 1.18-1.26 (m, 8 H), 1.53 (dd, $J = 7.3, 11.7$ Hz, 1 H), 1.61 (dd, $J = 7.3, 11.7$ Hz, 1 H), 1.82-1.89 (m, 1 H), 2.88 (quint, $J = 7.3$ Hz, 1 H), 3.76 (d, $J = 7.3$ Hz, 1 H), 5.02 (dm, $J = 17.4$ Hz, 1 H), 5.09 (dm, $J = 10.5$ Hz, 1 H), 5.91 (ddd, $J = 7.3, 10.5, 17.4$ Hz, 1 H); ^{13}C NMR (C_6D_6 , 75 MHz, *trans* isomer) δ 22.8, 23.5, 26.7, 29.9, 30.8, 39.1, 43.1, 45.0, 79.8, 113.5, 140.8; ^{13}C NMR (C_6D_6 , 75 MHz, *cis* isomer) δ 22.9, 23.3, 26.5, 32.0, 33.5, 37.6, 39.4, 42.9, 75.6, 116.5, 138.1. High-resolution MS, calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: 166.1358, found m/z (relative intensity): 166.1339 (M^+ , 44), 149 (100).

2,2-Diethyl-4-vinylcyclobutanol (2j): IR (neat) 3452 (w), 2963 (s), 2936 (s), 1636 (w), 1097 (m), 908 (m), 700 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, *trans* isomer) δ 0.81 (t, $J = 7.4$ Hz, 3 H), 0.87 (t, $J = 7.4$ Hz, 3 H), 1.05 (t, $J = 9.6$ Hz, 1 H), 1.28-1.67 (m, 4 H), 1.76 (t, $J = 9.6$ Hz, 1 H), 2.63 (ddt, $J = 6.4, 6.9, 9.6$ Hz, 1 H), 3.69 (br t, $J = 6.4$ Hz, 1 H), 4.96 (dm, $J = 10.3$ Hz, 1 H), 5.01 (dm, $J = 17.2$ Hz, 1 H), 5.90 (ddd, $J = 6.9, 10.3, 17.2$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz, *trans* isomer) δ 7.8, 8.2, 21.9, 29.6, 30.6, 44.7, 45.2, 78.8, 113.6, 140.3; ^1H NMR (CDCl_3 , 400 MHz, *cis* isomer) δ 0.78 (t, $J = 7.4$ Hz, 3 H), 0.81 (t, $J = 7.4$ Hz, 3 H), 1.37-1.71 (m, 7 H), 3.12 (ddm, $J = 6.8, 7.8$ Hz, 1 H), 4.00 (d, $J = 7.8$ Hz, 1 H), 5.11 (dm, $J = 17.3$ Hz, 1 H), 5.22 (dm, $J = 10.4$ Hz, 1 H), 5.96 (ddd, $J = 6.8, 10.4, 17.3$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz, *cis* isomer) δ 7.8, 8.3, 21.8, 29.7, 30.6, 44.7, 45.4, 70.8, 113.5, 140.2. High-resolution MS, calcd for $\text{C}_{10}\text{H}_{18}\text{O}$: 154.1358, found m/z (relative intensity): 154.1304 (M^+ , 94), 125(100).

2k

cis-4-(Prop-1-en-2-yl) spiro[3.5]nonan-1-ol (2k): IR (neat) 3439 (s), 2926 (s), 1647 (m), 1067 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.28-1.58 (m, 10 H), 1.63 (d, $J = 7.8$ Hz, 1 H), 1.70 (ddd, $J = 2.9, 7.8, 11.0$ Hz, 1 H), 1.73 (br s, 3 H), 1.82 (dd, $J = 7.8, 11.0$ Hz, 1 H), 3.06 (q, $J = 7.8$ Hz, 1 H), 3.96 (dt, $J = 2.9, 7.8$ Hz, 1 H), 4.82 (br s, 1 H), 5.10 (br s, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 21.7, 21.8, 21.9, 22.0, 25.2, 31.1, 35.3, 40.0, 40.5, 73.6, 111.2, 142.9. High-resolution MS, calcd for $\text{C}_{12}\text{H}_{20}\text{O}$: 180.1514, Found m/z (relative intensity): 180.1502 (M^+ , 30), 162 (100).

3

2-Cyclohexyl-4-vinyl-1,3-dioxolane (3): IR (neat) 2984 (w), 2928 (s), 2855 (s), 1136 (s), 988 (s), 964 (m), 889 (m), 677 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, major isomer) δ 1.05-1.29 (m, 5 H), 1.56 (dm, $J = 4.8$ Hz, 1 H), 1.70-1.82 (m, 5 H), 3.51 (dm, $J = 8.1$ Hz, 1 H), 4.14 (dm, $J = 8.1$ Hz, 1 H), 4.42 (m, 1 H), 4.77 (dm, $J = 4.8$ Hz, 1 H), 5.21 (d, $J = 10.3$ Hz, 1 H), 5.33 (d, $J = 17.2$ Hz, 1 H), 5.82 (ddm, $J = 10.3, 17.2$ Hz, 1 H); ^1H NMR (CDCl_3 , 400 MHz, minor isomer) δ 1.05-1.29 (m, 5 H), 1.68 (dm, $J = 4.9$ Hz, 1 H), 1.70-1.82 (m, 5 H), 3.56 (dm, $J = 7.7$ Hz, 1 H), 3.97 (dm, $J = 7.7$ Hz, 1 H), 4.42 (m, 1 H), 4.69 (d, $J = 4.9$ Hz, 1 H), 5.21 (d, $J = 10.3$ Hz, 1 H), 5.34 (d, $J = 17.2$ Hz, 1 H), 5.83 (ddm, $J = 10.3, 17.2$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz, major isomer) δ 25.8, 26.5, 27.3, 42.0, 70.2, 77.0, 107.8, 117.7, 135.8; ^{13}C NMR (CDCl_3 , 100 MHz, minor isomer) δ 25.8, 26.5, 27.2, 41.8, 69.7, 77.6, 108.2, 117.9, 135.9. High-resolution MS, calcd for $\text{M}^+ - \text{C}_6\text{H}_{11}$: 99.0466, found m/z (relative intensity): 99.0466 ($\text{M}^+ - \text{C}_6\text{H}_{11}$, 100).

4

Tetrahydro-3,3-diphenyl-5-vinylfuran-2-ol (4): IR (KBr) 3410 (s), 2901 (m),

1040 (s), 767 (m), 752 (s), 700 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, major isomer) δ 2.37 (d, $J = 3.2$ Hz, 1 H), 2.46 (dm, $J = 11.7$ Hz, 1 H), 2.82 (dd, $J = 10.5$, 11.7 Hz, 1 H), 4.39 (dm, $J = 10.5$ Hz, 1 H), 5.15 (d, $J = 10.0$ Hz, 1H), 5.25 (d, $J = 17.2$ Hz, 1 H), 5.99 (ddm, $J = 10.0$, 17.2 Hz, 1 H), 6.06 (d, $J = 3.2$ Hz, 1 H), 7.16-7.41 (m, 10 H); ^{13}C NMR (CDCl_3 , 100 MHz, major isomer) δ 40.7, 61.0, 79.8, 101.1, 116.2, 126.1, 126.3, 126.9, 128.0, 128.1, 128.2, 139.0, 143.0, 144.6; ^1H NMR (CDCl_3 , 400 MHz, minor isomer) δ 2.40 (dd, $J = 7.5$, 12.9 Hz, 1 H), 3.27 (dm, $J = 12.9$ Hz, 1 H), 4.90 (tm, $J = 7.5$ Hz, 1 H), 4.99 (d, $J = 10.2$ Hz, 1 H), 5.25 (d, $J = 17.2$ Hz, 1 H), 5.59 (ddd, $J = 7.5$, 10.2, 17.2 Hz, 1 H), 6.06 (d, $J = 3.2$ Hz, 1 H), 7.16-7.41 (m, 10 H); ^{13}C NMR (CDCl_3 , 100 MHz, minor isomer) δ 42.1, 61.0, 78.0, 101.6, 115.4, 126.1, 126.5, 127.3, 128.0, 128.2, 128.3, 138.6, 143.0, 144.6. Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$: C, 81.17; H, 6.81; Found: C, 80.78; H, 6.99.

1-(3-Methylbut-2-enyl)cyclohexanecarbaldehyde (5): IR (neat) 2932 (s), 1726 (s), 1450 (s), 1121 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.18-1.39 (m, 6 H), 1.50-1.61 (m, 2 H), 1.59 (s, 3 H), 1.69 (s, 3 H), 1.79-2.00 (m, 2 H), 2.10 (d, $J = 7.5$ Hz, 2 H), 5.02 (t, $J = 7.5$ Hz, 1 H), 9.44 (s, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 17.0, 21.9, 24.9, 25.1, 30.0, 34.4, 49.7, 117.0, 133.8, 206.6. High-resolution MS, calcd for $\text{C}_{12}\text{H}_{20}\text{O}$: 180.1514, Found m/z (relative intensity): 180.1510 (M^+ , 100).

^1H NMR spectra