Supporting Information

Triethylborane-mediated Hydrogallation and Hydroindation: Novel Access to Organogalliums and Organoindiums

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Instrumentation and Materials

^1H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken on a Varian GEMINI 300 spectrometer in CDCl_3 as a solvent, and chemical shifts were given in δ value with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. The elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. Gallium trichloride and triethylborane were purchased from Aldrich Chemicals and were diluted to prepare a 1.0 M hexane solution to handle easily. Red-Al[®] (70wt% in toluene) was obtained from Nacalai Tesque Inc., and was diluted with toluene to prepare a 2.0 M solution. These solutions were stored under argon. Anhydrous indium trichloride was purchased from

Aldrich Chemicals and was dried in a reaction flask carefully under reduced pressure (0.5 torr) by heating with a hair drier for 2 min before use. Diisobutylaluminium hydride (DIBAL-H) and triethylborane were purchased from Aldrich and were diluted with hexane to prepare 1.0 M solutions. 1,3-Dimethyl-2-imidazolidinone (DMI) was purchased from Wako Pure Chemicals and was distilled from CaH_2 before use. Tris(dibenzylideneacetone)dipalladium ($\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$) was prepared according to the literature.¹ Trifurylphosphine was prepared by treatment of phosphorous trichloride with furyllithium.

Experimental Section

The reaction was performed in a reaction flask equipped with a toy balloon that was filled with argon unless otherwise noted. Oxygen, which is necessary to produce an ethyl radical from triethylborane, penetrates the balloon easily. Any further addition of oxygen is not necessary.

Typical Procedure for Triethylborane-induced Hydrogallation of Alkynes.

A hexane solution of gallium trichloride (1.0 M, 1.5 mL, 1.5 mmol) was mixed with a toluene solution of Red-Al® (2.0 M, 0.375 mL, 0.75 mmol) at 0 °C in THF (5 mL) under an argon atmosphere, and the mixture was stirred for 30 min. To the solution, 1-dodecyne (166 mg, 1.0 mmol) and a hexane solution of triethylborane (1.0 M, 0.20 mL, 0.20 mmol) were sequentially added, and then the whole mixture was stirred for 4 h. Quenching with 1.0 M HCl and extraction with hexane (10 mL $\times$ 3) followed by silica gel column purification provided 141 mg of 1-dodecene (84% yield).

Cross-Coupling Reaction of Aryl Halides with Alkenylgallium Prepared via Hydrogallation

Dichlorogallane (3.0 mmol) was prepared in THF (7.5 mL) as aforementioned. To the solution,

¹ Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, 65, 253.

1-dodecyne (249 mg, 1.5 mmol) and triethylborane (1.0 M hexane solution, 0.30 mL, 0.30 mmol) were sequentially added at 0 °C and the resulting mixture was stirred for 5 h. After removal of THF by reducing a pressure (0.5 Torr), a residue was dissolved with dimethylsulfoxide (5 mL). To the solution, 3-iodoanisole (234 mg, 1.0 mmol) and a palladium complex, prepared from $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (10 mg, 0.010 mmol) and tri-*o*-tolylphosphine (12.2 mg, 0.040 mmol) in DMSO (1 mL) in another reaction flask, was successively added and the whole mixture was heated at 80 °C for 4 h. Acidic workup followed by silica gel column purification afforded **9a** (*E/Z* = 66/34, 85.1 mg, 0.31 mmol) and **10a** (49.4 mg, 0.18 mmol).

Procedure for Triethylborane-induced Hydrogallation of Alkenes.

A gallium hydride reagent (2.0 mmol) was prepared in THF (5 mL) at 0 °C as aforementioned. At the same temperature, 1-dodecene (168 mg, 1.0 mmol) and triethylborane (1.0 M solution of hexane, 1.0 mL, 1.0 mmol) were added successively and resulting mixture was stirred for 4 h. Methyl lithium (1.2 M, solution of ether, 7.5 mL, 9.0 mmol) was added at 0 °C and the mixture was stirred for 1 h. The resulting mixture was warmed up to room temperature. After an addition of 12 M hydrochloric acid (10 mL), the whole mixture was stirred for additionally 1 h. Extractive workup with hexane (10 mL $\times$ 3) followed by silica gel column chromatography afforded dodecane (145 mg, 0.85 mmol).

Procedure for Hydrogallation of Allenes.

Under an argon atmosphere, a hexane solution of gallium trichloride (1.0 M, 2.25 mL, 2.25 mmol) was treated with a hexane solution of DIBAL-H (1.0 M 2.25 mL, 2.25 mmol) in THF (10 mL) at 0 °C, and the mixture was stirred for 30 min. Then, 1,2-tridecadiene (271 mg, 1.5 mmol) and a hexane solution of triethylborane (1.0 M, 2.0 mL, 2.0 mmol) were successively added. The mixture was stirred for 8 h. Benzaldehyde (106 mg, 1.0 mmol) was added to the reaction mixture.

The whole mixture was stirred for 1 h, and was quenched with 1.0 M HCl (10 mL). Extraction (hexane/ethyl acetate = 5/1, 10 mL × 3) followed by silica gel column chromatography afforded **13** (173 mg, 0.60 mmol, 51/49 isomeric mixture) with dimerization product **11** (22 mg, 0.060 mmol).

Typical Procedure for Hydroindation of Alkynes.

Anhydrous indium trichloride (299 mg, 1.35 mmol) was placed in a reaction flask and heated with a hair drier in vacuo for 2 min. The indium salt was dissolved with 4 mL of THF at 25 °C under an argon atmosphere. The solution turned to a white suspension upon cooling to –78 °C. Diisobutylaluminum hydride (1.0 M hexane solution, 1.3 mL, 1.3 mmol) was then added dropwise to the suspension at –78 °C. The mixture was stirred for 30 min to prepare dichloroindium hydride. To the resulting mixture, 1-dodecyne (166 mg, 1.0 mmol) and triethylborane (1.0 M hexane solution, 0.20 mL, 0.20 mmol) were added in sequence and the resulting mixture was stirred for 2.5 h at –78 °C. Iodine (1.5 g, 6.0 mmol) was added to the reaction mixture. After being stirred for 30 min at –78 °C, the reaction mixture was poured into saturated sodium hydrogen carbonate solution. Sodium thiosulfate solution was added. The product was extracted with hexane (10 mL × 3). Concentration followed by silica gel column purification afforded (*Z*)-1-iodo-1-dodecene (271 mg, 0.92 mmol) as a colorless oil in 92% yield.

Radical Cyclization of Enyne 16 with Indium Hydride Reagent.

Under an argon atmosphere, dichloroindium hydride (1.0 mmol) was prepared in THF (4 mL) at 0 °C as aforementioned. The solution was warmed up to room temperature, and then **16** (182 mg, 1.0 mmol in 1 mL of THF) and a hexane solution of triethylborane (0.10 mL, 0.10 mmol) were successively added. After being stirred for 2 h, the reaction was quenched with 1.0 M hydrochloric acid (10 mL). Extraction (hexane/ethyl acetate = 5/1, 10 mL × 3) followed by silica gel column purification afforded the cyclized product **17** (55mg, 0.30 mmol) along with the starting material **16**

(91 mg, 0.50 mmol).

Cross-Coupling Reaction of Aryl Halides with Alkenylindiums Prepared by Hydroindation.

Anhydrous indium trichloride (343 mg, 1.55 mmol) was dried and dissolved with THF (4 mL) under argon. After dropwise addition of a hexane solution of diisobutylaluminium hydride (1.0 M, 1.5 mL, 1.5 mmol) at $-78\text{ }^{\circ}\text{C}$, the mixture was stirred for 30 min. To the mixture, 1-octyne (143 mg, 1.3 mmol) and triethylborane (1.0 M hexane solution, 0.20 mL, 0.20 mmol) were added sequentially, and the mixture was stirred for 2.5 h. After warming to $25\text{ }^{\circ}\text{C}$, 1,3-dimethyl-2-imidazolidinone (3 mL) and iodobenzene (204 mg, 1.0 mmol) were successively added. A palladium-trifurylphosphine complex, prepared from $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (2.5 mg, 0.0025 mmol) and trifurylphosphine (3.5 mg, 0.015 mmol) in THF (1 mL) in another reaction flask, was introduced by a syringe. The resulting mixture was heated at reflux for 30 min. Extractive workup with water (20 mL) and hexane (10 mL $\times$ 3) followed by silica gel column purification provided 177 mg of *b*-hexylstyrene (**20a**, *E/Z* = 5/95, 0.94 mmol) in 94% yield.

Characterization Data

Spectral data for **15d**², **20a**³ were found in the literatures.

Benzyl 5-Iodo-4-pentenyl Ether (15a, *E/Z* = 1/99): IR (neat) 2937, 2856, 1609, 1454, 1364, 1275, 1105, 735, 696 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.76 (quint, *J* = 6.9 Hz, 2H), 2.21–2.29 (m, 2H), 3.51 (t, *J* = 6.6 Hz, 2H), 4.52 (s, 2H), 5.99 (d, *J* = 14.4 Hz, 0.01H), 6.15–6.24 (m, 1.98H), 6.51 (dt, *J* = 14.4, 7.2 Hz, 0.01H), 7.26–7.34 (m, 1H), 7.35 (d, *J* = 4.2 Hz, 4H); ^{13}C NMR

² Ma, S.; Lu, X.; Li, Z. *J. Org. Chem.* **1992**, 57, 709–713.

³ Kataoka, Y.; Takai, K.; Oshima, K.; Utimoto, K. *J. Org. Chem.* **1992**, 57, 1615–1618.

(CDCl₃) For major isomer: δ 28.02, 31.52, 69.50, 72.95, 82.70, 127.62, 127.73, 128.45, 138.63, 140.89. Found: C, 47.98; H, 5.00%. Calcd for C₁₂H₁₅IO: C, 47.70; H, 5.00%.

Ethyl (Z)-9-Iodo-8-nonenoate (15b): IR (neat) 2932, 2856, 1738, 1609, 1464, 1373, 1182, 1034 cm⁻¹; ¹H NMR (CDCl₃) δ 1.25 (t, J = 7.2 Hz, 3H), 1.29–1.50 (m, 6H), 1.62 (quint, J = 7.2 Hz, 2H), 2.13 (q, J = 6.6 Hz, 2H), 2.29 (t, J = 7.5 Hz, 2H), 4.12 (q, J = 7.2 Hz, 2H), 6.03–6.08 (m, 2H); ¹³C NMR (CDCl₃) δ 14.07, 24.65, 27.53, 28.48, 28.72, 34.09, 34.38, 59.94, 82.21, 141.12, 173.59. Found: C, 42.79; H, 5.96%. Calcd for C₁₁H₁₉IO₂: C, 42.60; H, 6.17%.

(Z)-6-Iodo-5-hexen-1-ol (15c): IR (neat) 3460, 2947, 2852, 1744, 1605, 1466, 1366, 1244, 1047 cm⁻¹; ¹H NMR (CDCl₃) δ 1.51 (quint, J = 7.5 Hz, 2H), 1.68 (quint, J = 7.5 Hz, 2H), 2.06 (d, J = 1.2 Hz, 1H), 2.17 (dt, J = 6.9, 6.9 Hz, 2H), 4.08 (dt, J = 1.2, 6.6 Hz, 2H), 6.13–6.25 (m, 2H); ¹³C NMR (CDCl₃) δ 24.16, 27.81, 34.02, 64.04, 82.83, 140.62. HRMS Found 225.9857. Calcd for C₆H₁₁IO 225.9855.

(Z)-13-Iodo-12-tridecen-5-one (15e): IR (neat) 2924, 2853, 1715, 1610, 1466, 1377, 1279, 1128, 1047 cm⁻¹; ¹H NMR (CDCl₃) δ 0.91 (t, J = 7.5 Hz, 3H), 1.24–1.48 (m, 8H), 1.50–1.62 (m, 4H), 2.13 (q, J = 6.6 Hz, 2H), 2.40 (t, J = 7.5 Hz, 4H), 6.12–6.20 (m, 2H); ¹³C NMR (CDCl₃) δ 13.71, 22.24, 23.60, 25.86, 27.62, 28.72, 28.92, 34.47, 42.44, 42.60, 82.24, 141.35, 211.65. Found: C, 48.50; H, 6.93%. Calcd for C₁₃H₂₃IO: C, 48.46; H, 7.19%. HRMS Found 322.0810. Calcd for C₁₃H₂₃IO (M⁺) 322.0794.

9-Iodo-8-nonenoic Acid (15f, *E/Z* = 3/97): IR (neat) 3051, 2932, 2856, 1709, 1412, 1271, 941 cm⁻¹; ¹H NMR (CDCl₃) δ 1.28–1.56 (m, 6H), 1.64 (t, J = 7.5 Hz, 2H), 2.05 (q, J = 7.2 Hz, 0.06H), 2.14 (q, J = 6.9 Hz, 1.94H), 2.36 (t, J = 7.5 Hz, 2H), 5.98 (dt, J = 14.4, 1.6 Hz, 0.03H),

6.12–6.21 (m, 1.94H), 6.50 (dt, $J = 14.4, 7.2$ Hz, 0.03H), 11.78 (bs, 1H); ^{13}C NMR (CDCl_3)
For major isomer: δ 24.35, 27.52, 28.46, 28.65, 33.91, 34.39, 82.35, 141.19, 180.58. Found: C, 38.49; H, 5.34%. Calcd for $\text{C}_9\text{H}_{15}\text{IO}_2$: C, 38.32; H, 5.36%.

(Z)-1-Iodo-1,11-dodecadiene (15g): IR (neat) 3074, 2926, 2855, 1641, 1611, 1462, 1281, 991, 910 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.24–1.48 (m, 12H), 2.04 (q, $J = 7.2$ Hz, 2H), 2.09–2.17 (m, 2H), 4.93 (dq, $J = 8.7, 1.2$ Hz, 1H), 5.00 (dq, $J = 17.1, 1.5$ Hz, 1H), 5.82 (ddt, $J = 10.2, 17.1, 6.6$ Hz, 1H), 6.12–6.21 (m, 2H); ^{13}C NMR (CDCl_3) δ 27.88, 28.82, 28.99 (2C), 29.28 (2C), 33.70, 34.60, 82.10, 114.18, 139.29, 141.55. Found: C, 49.30; H, 7.02%. Calcd for $\text{C}_{12}\text{H}_{21}\text{I}$: C, 49.33; H, 7.24%.

4,4-Bis(methoxymethyl)-6-hepten-1-yne (16): IR (neat) 3292, 2934, 2876, 2100, 1641, 1452, 1200, 1109, 914 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.97 (t, $J = 1.8$ Hz, 1H), 2.17 (dt, $J = 7.5, 1.2$ Hz, 2H), 2.21 (d, $J = 1.8$ Hz, 2H), 3.25 (d, $J = 2.1$ Hz, 4H), 3.33 (s, 6H), 5.05–5.15 (m, 2H), 5.80 (ddt, $J = 10.2, 17.1, 7.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 21.98, 36.15, 41.65, 59.27, 70.10, 74.22, 81.22, 118.11, 133.74. Found: C, 72.35; H, 10.03%. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 72.49; H, 9.95%.

4-Methyl-1,1-bis(methoxymethyl)-3-methylenecyclopentane (17): IR (neat) 2924, 2874, 1659, 1456, 1200, 1109, 970, 881 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.07 (d, $J = 6.9$ Hz, 3H), 1.07 (dd, $J = 10.8, 12.9$ Hz, 1H), 1.89 (dd, $J = 8.1, 12.9$ Hz, 1H), 2.23–2.25 (m, 2H), 2.46–2.59 (m, 1H), 3.23 (d, $J = 1.2$ Hz, 2H), 3.24 (s, 2H), 3.34 (d, $J = 2.1$ Hz, 6H), 4.72–4.76 (m, 1H), 4.82 (s, 1H); ^{13}C NMR (CDCl_3) δ 18.43, 36.52, 39.49, 40.38, 45.28, 59.14, 59.17, 75.71, 77.33, 104.41, 156.61. Found: C, 71.97; H, 11.10%. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 71.70; H, 10.94%.

2-(1-Octenyl)nitrobenzene (20b, *E/Z* = 5/95): IR (neat) 2924, 2852, 1608, 1572, 1527, 1647, 1346, 962, 857, 784, 757 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.85(t, J = 6.9 Hz, 3H), 1.15–1.53 (m, 8H), 2.08 (dq, J = 1.8, 7.2 Hz, 1.90H), 2.26 (q, J = 7.2 Hz, 0.10H), 5.82 (dt, J = 11.7, 7.5 Hz, 0.95H), 6.24 (dt, J = 15.6, 7.5 Hz, 0.05H), 6.69 (d, J = 11.7 Hz, 0.95H), 6.83 (d, J = 15.9 Hz, 0.05H), 7.30–7.43 (m, 2H), 7.47–7.60 (m, 1H), 7.86 (dd, J = 0.9, 8.1 Hz, 0.05H), 7.98 (dd, J = 0.9, 7.8 Hz, 0.95H); ^{13}C NMR (CDCl_3) For major isomer: δ 1308, 22.37, 28.28, 28.64, 29.30, 31.45, 124.38, 124.98, 127.61, 131.90, 132.50, 133.00, 134.90, 148.57, for minor isomer: δ 13.89, 22.44, 28.69, 28.81, 31.54, 33.03, 124.32, 124.90, 127.31, 128.41, 132.74, 133.44, 136.98, 147.79. Found: C, 72.31; H, 8.36%. Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2$: C, 72.07; H, 8.21%.

4-(1-Octenyl)nitrobenzene (20c, *E/Z* = 5/95): IR (neat) 2957, 2928, 2856, 2448, 1649, 1597, 1493, 1466, 1342, 1273, 1180, 1109, 1013, 968, 962, 856, 827, 793, 766, 745, 706, 691 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.87 (t, J = 6.9 Hz, 3H), 1.20–1.40 (m, 6H), 1.40–1.55 (m, 2H), 2.22–2.36 (m, 2H), 5.87 (dt, J = 11.7, 7.5 Hz, 0.95H), 6.44 (s, 0.05H), 6.45 (dd, J = 2.4, 6.3 Hz, 1H), 7.40 (d, J = 8.7 Hz, 1.90H), 7.44 (d, J = 9.0 Hz, 0.10H), 8.14 (d, J = 9.0 Hz, 0.10H), 8.18 (d, J = 9.3 Hz, 1.90H); ^{13}C NMR (CDCl_3) For major isomer: δ 14.06, 22.66, 28.92, 29.05, 29.75, 31.74, 123.72, 127.29, 129.60, 137.48, 144.87, 146.56, for minor isomer: δ 14.10, 22.73, 29.01, 29.08, 31.80, 33.33, 124.19, 126.59, 128.39, 136.97, 144.82, 146.80. Found: C, 72.02; H, 8.34%. Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2$: C, 72.07; H, 8.21%.

Butyl 2-[(*Z*)-1-Octenyl]benzoate (20d): IR (neat) 2959, 2853, 1726, 1605, 1472, 1256, 1134, 1082 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.85 (t, J = 7.2 Hz, 3H), 0.97 (t, J = 7.5 Hz, 3H), 1.12–1.33 (m, 6H), 1.38 (quint, J = 7.5 Hz, 2H), 1.48 (quint, J = 7.5 Hz, 2H), 1.73 (quint, J = 7.2 Hz, 2H), 2.11 (dq, J = 1.8, 7.2 Hz, 2H), 4.28 (t, J = 6.6 Hz, 2H), 5.71 (dt, J = 11.7, 7.2 Hz, 1H), 6.85 (d, J = 11.4 Hz, 1H), 7.29 (t, J = 7.5 Hz, 2H), 7.45 (dt, J = 1.2, 7.5 Hz, 1H), 7.93 (dd, J = 1.2, 7.3 Hz,

1H); ¹³C NMR (CDCl₃) δ 13.55, 13.87, 19.18, 22.44, 28.14, 28.76, 26.61, 30.64, 31.55, 64.65, 126.54, 128.80, 129.86, 130.34, 130.78, 131.34, 132.18, 139.14, 167.56. Found: C, 79.03; H, 9.74%. Calcd for C₁₉H₂₈O₂: C, 79.12; H, 9.78%.

3-(1-Octenyl)anisole (20e, *E/Z* = 5/95): IR (neat) 2926, 2835, 1599, 1578, 1489, 1464, 1433, 1256, 1150, 1051, 787, 689 cm⁻¹; ¹H NMR (CDCl₃) δ 0.87 (t, *J* = 6.9 Hz, 3H), 1.20–1.38 (m, 6H), 1.44 (quint, *J* = 7.2 Hz, 2H), 2.19 (q, *J* = 7.2 Hz, 0.10H), 2.33 (q, *J* = 7.2 Hz, 1.90H), 3.79 (s, 3H), 5.65 (dt, *J* = 11.4, 7.2 Hz, 0.95H), 6.21 (dt, *J* = 15.9, 7.2 Hz, 0.05H), 6.34 (d, *J* = 15.9 Hz, 0.05H), 6.37 (d, *J* = 11.7 Hz, 0.95H), 6.70–6.95 (m, 3H), 7.19 (t, *J* = 7.8 Hz, 0.05H), 7.23 (t, *J* = 7.8 Hz, 0.95H); ¹³C NMR (CDCl₃) For major isomer: δ 14.09, 22.70, 28.82, 29.13, 30.04, 31.84, 55.23, 112.20, 114.59, 121.59, 128.90, 129.28, 133.76, 139.53, 159.75, for minor isomer: δ 14.12, 22.46, 29.01, 29.42, 30.41, 33.11, 55.19, 111.57, 112.61, 118.86, 129.65, 129.92, 131.81, 139.77, 160.16. Found: C, 82.38; H, 10.16%. Calcd for C₁₅H₂₂O: C, 82.52; H, 10.16%.

2-[(*Z*)-1-Octenyl]pyridine (20f): IR (neat) 2926, 2855, 1585, 1468, 806, 743 cm⁻¹; ¹H NMR (CDCl₃) δ 0.87 (t, *J* = 6.9 Hz, 3H), 1.23–1.40 (m, 6H), 1.47 (quint, *J* = 7.5 Hz, 2H), 2.57 (dq, *J* = 1.8, 7.5 Hz, 2H), 5.88 (dt, *J* = 12.3, 7.2 Hz, 1H), 6.46 (dt, *J* = 12.0, 1.8 Hz, 1H), 7.08 (ddd, *J* = 1.2, 4.8, 7.5 Hz, 1H), 7.23 (dq, *J* = 8.1, 0.9 Hz, 1H), 7.61 (dt, *J* = 1.2, 7.5 Hz, 1H), 8.59 (dq, *J* = 4.8, 0.9 Hz, 1H); ¹³C NMR (CDCl₃) δ 13.86, 22.42, 28.67, 28.85, 29.56, 31.56, 120.99, 123.72, 128.50, 135.83, 137.45, 149.27, 156.97. Found: C, 82.58; H, 9.99%. Calcd for C₁₃H₁₉N: C, 82.48; H, 10.12%.

(*Z*)-1-(4-Methylphenyl)-1-octene (20g): IR (neat) 3004, 2922, 2852, 1513, 1459, 823, 722 cm⁻¹; ¹H NMR (CDCl₃) δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.20–1.38 (m, 6H), 1.44 (quint, *J* = 7.2 Hz,

2H), 2.31 (ddt, $J = 2.1, 6.9, 7.2$ Hz, 2H), 2.33 (s, 3H), 5.61 (dt, $J = 11.7, 6.9$ Hz, 1H), 6.36 (d, $J = 11.7$ Hz, 1H), 7.17 (q, $J = 8.4$ Hz, 4H); ^{13}C NMR (CDCl_3) δ 14.08, 21.17, 22.69, 28.78, 29.13, 30.09, 31.84, 128.84, 128.94, 129.05, 132.79, 135.31, 136.28. Found: C, 88.98; H, 10.83%. Calcd for $\text{C}_{15}\text{H}_{22}$: C, 89.04; H, 10.96%.

3-[(Z)-1-Octenyl]phenol (20h): IR (neat) 3333, 2925, 2855, 1580, 1450, 1342, 1246, 791, 689 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.87 (t, $J = 6.9$ Hz, 3H), 1.19–1.37 (m, 6H), 1.43 (quint, $J = 7.5$ Hz, 2H), 2.31 (dq, $J = 1.5, 7.5$ Hz, 2H), 5.04 (bs, 1H), 5.65 (dt, $J = 11.7, 7.5$ Hz, 1H), 6.33 (d, $J = 11.7$ Hz, 1H), 6.70 (dd, $J = 1.8, 8.1$ Hz, 1H), 6.76 (s, 1H), 6.86 (d, $J = 7.5$ Hz, 1H), 7.19 (t, $J = 7.8$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 13.91, 22.49, 28.61, 28.90, 29.81, 31.62, 113.48, 115.61, 121.61, 128.33, 129.36, 133.85, 139.65, 155.31. Found: C, 82.05; H, 9.91%. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}$: C, 82.30; H, 9.87%.

Ethyl (Z)-9-Phenyl-8-nonenoate (20i): IR (neat) 2935, 2864, 1726, 1600, 1499, 1186, 1035, 768, 704 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.25 (t, $J = 7.2$ Hz, 3H), 1.26–1.40 (m, 4H), 1.39–1.53 (m, 2H), 1.61 (quint, $J = 7.2$ Hz, 2H), 2.27 (t, $J = 7.5$ Hz, 2H), 2.32 (dq, $J = 1.8, 7.2$ Hz, 2H), 4.12 (q, $J = 7.2$ Hz, 2H), 5.65 (dt, $J = 11.7, 7.2$ Hz, 1H), 6.41 (d, $J = 11.4$ Hz, 1H), 7.20–7.36 (m, 5H); ^{13}C NMR (CDCl_3) δ 14.12, 24.80, 28.41, 28.82, 28.88, 29.65, 34.25, 60.10, 126.50, 128.17, 128.81, 128.92, 133.08, 137.88, 173.97. HRMS Found 260.1774. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2$ (M^+) 260.1766.

Ethyl (Z)-9-(4-Nitrophenyl)-8-nonenoate (20j): IR (neat) 2932, 2856, 1732, 1597, 1518, 1342, 1182, 856 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.25 (t, $J = 7.2$ Hz, 3H), 1.24–1.37 (m, 4H), 1.48 (quint, $J = 7.5$ Hz, 2H), 1.62 (quint, $J = 7.5$ Hz, 2H), 2.28 (t, $J = 7.5$ Hz, 2H), 2.32 (dq, $J = 1.8, 7.2$ Hz, 2H), 4.12 (q, $J = 4.2$ Hz, 2H), 5.86 (dt, $J = 11.7, 7.5$ Hz, 1H), 6.45 (d, $J = 11.7$ Hz, 1H), 7.31 (d,

$J = 8.4$ Hz, 2H), 8.18 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 14.14, 24.71, 28.60, 28.78 (2C), 29.34, 34.13, 60.07, 123.38, 127.01, 129.23, 136.87, 144.36, 146.03, 173.63. Found: C, 66.75; H, 7.71%. Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_4$: C, 66.86; H, 7.59%.

***t*-Butyldimethylsilyl (Z)-3-Phenyl-2-propenyl Ether (20k)**: IR (neat) 2935, 2864, 1600, 1598, 1472, 1256, 1105, 837, 773, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.04 (s, 6H), 0.88 (s, 9H), 1.69 (quint, $J = 6.9$ Hz, 2H), 3.41 (dq, $J = 1.5, 7.5$ Hz, 2H), 3.65 (t, $J = 6.6$ Hz, 2H), 5.68 (dt, $J = 11.7, 7.5$ Hz, 1H), 6.43 (d, $J = 11.7$ Hz, 1H), 7.19–7.36 (m, 5H); ^{13}C NMR (CDCl_3) δ –5.47, 18.21, 24.96, 25.84, 32.97, 62.59, 126.54, 128.19, 128.84, 129.21, 132.59, 137.78. Found: C, 73.59; H, 10.34%. Calcd for $\text{C}_{17}\text{H}_{28}\text{OSi}$: C, 73.85; H, 10.21%.

***t*-Butyldimethylsilyl 5-(4-Nitrophenyl)-4-pentenyl Ether (20l, *E/Z* = 5/95)**: IR (neat) 2947, 2853, 1599, 1524, 1348, 1256, 1105, 843, 773 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.02 (s, 5.70H), 0.06 (s, 0.30H), 0.86 (s, 8.55H), 0.91 (s, 0.45H), 1.69 (quint, $J = 6.9$ Hz, 1.90H), 1.72 (quint, $J = 6.9$ Hz, 0.10H), 2.31–2.37 (m, 0.10H), 2.42 (q, $J = 7.5$ Hz, 1.90H), 3.64 (t, $J = 6.0$ Hz, 1.90H), 3.67 (t, $J = 6.3$ Hz, 0.10H), 5.89 (dt, $J = 11.7, 7.5$ Hz, 0.95H), 6.44–6.50 (m, 1.05H), 7.43 (d, $J = 8.7$ Hz, 1.90H), 7.45 (d, $J = 8.1$ Hz, 0.10H), 8.16 (d, $J = 8.1$ Hz, 0.10H), 8.18 (d, $J = 8.1$ Hz, 1.90H); ^{13}C NMR (CDCl_3) For major isomer: δ –5.51, 18.15, 25.15, 25.76, 32.56, 62.19, 123.55, 126.40, 129.44, 136.65, 144.50, 146.60, for minor isomer: δ –5.46, 18.20, 25.83, 29.54, 31.94, 62.29, 124.04, 127.47, 128.45, 136.19, 144.47, 146.55. Found: C, 63.40; H, 8.30%. Calcd for $\text{C}_{17}\text{H}_{27}\text{NO}_3\text{Si}$: C, 63.51; H, 8.47%.

(Z)-6-(4-Nitrophenyl)-5-hexen-1-ol (20m): IR (neat) 3356, 2936, 2862, 1595, 1514, 1342, 1109, 1067, 856 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.49–1.66 (m, 5H), 2.37 (dq, $J = 1.8, 7.2$ Hz, 2H), 3.65 (t, $J = 6.0$ Hz, 2H), 5.87 (dt, $J = 12.0, 7.2$ Hz, 1H), 6.48 (d, $J = 11.7$ Hz, 1H), 7.41 (d, $J = 8.4$ Hz,

2H), 8.19 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 25.81, 28.43, 32.13, 62.47, 123.46, 127.31, 129.30, 136.56, 144.33, 146.11. Found: C, 65.19; H, 6.94%. Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_3$: C, 65.14; H, 6.83%.

(Z)-6-(3-Methoxyphenyl)-5-hexen-1-ol (20n): IR (neat) 3344, 2936, 1596, 1576, 1489, 1454, 1433, 1256, 1148, 1049, 789, 691cm^{-1} ; ^1H NMR (CDCl_3) δ 1.46–1.65 (m, 4H), 1.97 (bs, 1H), 2.37 (dq, $J = 1.8, 7.2$ Hz, 2H), 3.62 (t, $J = 6.3$ Hz, 2H), 3.81 (s, 3H), 5.66 (dt, $J = 7.2, 11.7$ Hz, 1H), 6.41 (d, $J = 11.4$ Hz, 1H), 6.75–6.83 (m, 2H), 6.87 (d, $J = 7.5$ Hz, 1H), 7.25 (t, $J = 7.8$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 25.88, 28.17, 32.11, 55.06, 62.57, 111.97, 114.40, 121.32, 129.05, 129.11, 132.93, 139.10, 159.47. HRMS Found 206.1298. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$ (M^+) 206.1307.

(Z)-6-(3-Hydroxyphenyl)-5-hexen-1-ol (20o): IR (neat) 3301, 2937, 2860, 1580, 1450, 1252, 793, 681 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.46–1.65 (m, 4H), 2.30 (q, $J = 7.2$ Hz, 2H), 2.43 (bs, 1H), 3.65 (t, $J = 6.0$ Hz, 2H), 5.63 (dt, $J = 11.4, 7.2$ Hz, 1H), 6.35 (d, $J = 11.4$ Hz, 1H), 6.72 (dd, $J = 1.8, 7.8$ Hz, 1H), 6.77 (d, $J = 7.5$ Hz, 1H), 6.82 (s, 1H), 6.99 (bs, 1H), 7.17 (t, $J = 7.8$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 25.66, 27.99, 31.89, 62.48, 113.74, 115.46, 121.22, 129.08, 129.43, 132.77, 139.21, 155.82.

(Z)-1-(3-Methoxyphenyl)-5-phenylmethoxy-1-petene (20p): IR (neat) 2936, 2856, 1597, 1576, 1489, 1454, 1433, 1256, 1105, 1049, 876, 791, 737, 696 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.76 (quint, $J = 7.2$ Hz, 2H), 2.44 (dq, $J = 1.5, 7.2$ Hz, 2H), 3.50 (t, $J = 7.2$ Hz, 2H), 3.79 (s, 3H), 4.47 (s, 2H), 5.66 (dt, $J = 11.7, 7.5$ Hz, 1H), 6.41 (d, $J = 11.7$ Hz, 1H), 6.78 (d, $J = 8.7$ Hz, 1H), 6.82 (s, 1H), 6.89 (d, $J = 7.5$ Hz, 1H), 7.20–7.38 (m, 6H); ^{13}C NMR (CDCl_3) δ 25.26, 29.90, 55.11, 69.73, 72.90, 112.16, 114.38, 121.39, 127.55, 127.68, 128.40, 129.17, 129.31, 132.61, 138.68, 139.09, 159.57. Found: C, 80.55; H, 7.81%. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2$: C, 80.82; H, 7.85%.

1-(3-Methoxyphenyl)-3-phenylmethoxy-1-propene (20q, *E/Z* = 11/89): IR (neat) 3329, 3028, 2937, 2835, 1599, 1578, 1491, 1454, 1258, 1150, 1047, 791, 739, 696 cm⁻¹; ¹H NMR (CDCl₃) δ 3.77 (s, 2.67H), 3.84 (s, 0.33H), 4.18 (dd, *J* = 1.5, 6.3 Hz, 0.22H), 4.30 (dd, *J* = 1.5, 6.3 Hz, 1.78H), 4.52 (s, 1.78H), 4.56 (s, 0.22H), 5.90 (dt, *J* = 12.0, 6.3 Hz, 0.89H), 6.31 (dt, *J* = 15.9, 6.3 Hz, 0.11H), 6.59 (d, *J* = 12.0 Hz, 0.89H), 6.60 (d, *J* = 17.1 Hz, 0.11H), 6.75–6.83 (m, 2.67H), 6.85–7.00 (m, 0.33H), 7.19–7.40 (m, 6H); ¹³C NMR (CDCl₃) For major isomer: δ 55.28, 67.14, 72.63, 113.00, 114.58, 121.54, 127.85, 128.04, 128.60, 129.42, 129.49, 131.99, 138.31, 138.48, 159.80, for minor isomer: δ 55.38, 70.82, 72.35, 111.99, 113.20, 113.62, 119.41, 119.93, 126.72, 128.64, 129.75, 129.94, 132.57, 160.14. HRMS Found 254.1309. Calcd for C₁₇H₁₈O₂ (M⁺) 254.1307.