

Supporting Information for

Silver-Catalyzed Regioselective Carbomagnesiation of Alkynes with Alkyl Halides and Grignard Reagents

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Table S1. Screening of catalysts and ligands.

$$\text{Ph}-\text{C}\equiv\text{C}-\text{H} + \text{Cy-I} + i\text{Bu-MgCl} \xrightarrow[\text{Et}_2\text{O}, -10\text{ }^\circ\text{C}, 1\text{ h}]{\text{Catalyst (8 mol\% on Ag), Ligand (8 mol\% on P), H}^+} \text{Ph}-\text{C}(\text{H})=\text{C}(\text{H})-\text{Cy} \text{ (3e)} + \text{Ph}-\text{C}(\text{H})=\text{C}(\text{H})-i\text{Bu} \text{ (4d)}$$

entry	catalyst	ligand	Yield of 3e (%) ^a	<i>E/Z</i> ^a	Yield of 4d (%) ^a	<i>E/Z</i> ^a
1	AgOTs	PPh ₃	67	35/65	2	36/64
2	AgOTs	P(<i>p</i> -ClC ₆ H ₄) ₃	70	29/71	3	29/71
3	AgOTs	P(<i>p</i> -CF ₃ C ₆ H ₄) ₃	65	26/74	3	28/72
4	AgOTs	P(<i>p</i> -MeC ₆ H ₄) ₃	79	32/68	3	35/65
5	AgOTs	P(<i>o</i> -MeC ₆ H ₄) ₃	58	18/82	2	22/78
6	AgOTs	PPh ₂ Me	48	36/64	2	37/63
7	AgOTs	P <i>n</i> Bu ₃	70	34/66	3	35/65
8	AgOTs	PCy ₃	7	33/67	n.d.	-
9	AgOTs	dppb	9	30/70	n.d.	-
10	Ag ₂ SO ₄	P(<i>p</i> -MeC ₆ H ₄) ₃	46	29/71	2	34/66
11	Ag ₂ PO ₄	P(<i>p</i> -MeC ₆ H ₄) ₃	64	30/70	2	33/67
12	Ag ₂ CO ₃	P(<i>p</i> -MeC ₆ H ₄) ₃	60	30/70	2	33/67
13	AgOCOCH ₃	P(<i>p</i> -MeC ₆ H ₄) ₃	61	32/68	3	35/65
14	AgOCOCF ₃	P(<i>p</i> -MeC ₆ H ₄) ₃	72	33/67	3	37/63
15	Ag ₂ O	P(<i>p</i> -MeC ₆ H ₄) ₃	11	32/68	1	38/62
16	AgOTf	P(<i>p</i> -MeC ₆ H ₄) ₃	66	30/70	3	34/66

^a GC yield.

Effects of catalysts and ligands were screened using phenylacetylene, cyclohexyl iodide, and *i*BuMgCl and the results were summarized in Table S1. Triarylphosphines bearing electron-withdrawing or donating substituents at *p*-position showed little effect on yields and selectivities (entries 1–4). Sterically-hindered P(*o*-MeC₆H₄)₃ afforded product **3e** with highest stereoselectivity in *E/Z* = 18/82, though yield slightly decreased (entry 5). P(*n*Bu)₃ gave similar yield but sterically hindered phosphine PCy₃ and diphosphine ligands were not effective (entries 6–9). Next, various silver salts were tested with P(*p*-MeC₆H₄)₃ as a ligand. Although Ag₂SO₄ and Ag₂O were not effective, other silver salts afforded **3e** in similar yields as AgOTs. In all cases, formation of direct carbomagnesiation product **4d** was suppressed. Thus we chose the AgOTs and PPh₃ system as the standard conditions.

General

¹H NMR and ¹³C NMR spectra were recorded with a JEOL JNM-Alice 400 (400 MHz and 100 MHz, respectively) spectrometer. Chemical shifts were reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were recorded with a JASCO Corporation FT/IR-4200 instrument. Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. GC Mass spectra (EI) were obtained using a JMS-mate operating in the electron impact mode (70 eV) equipped with a RTX-5 30MX.25MMX.25U column. HPLC separations were performed on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908) equipped with JAIGEL-1H and -2H columns (GPC) using CHCl₃ as an eluent. Column chromatography was conducted using Biotage Isolera version 1. 3. 1 equipped with KP-Sil column (silica gel 20 μm). Elemental analyses were performed on a Perkin Elmer 240C apparatus. GC analysis was performed on a Shimadzu GC-2014 instrument equipped with a GL Sciences InertCap 5 capillary column. GC yields were determined using decane as an internal standard. Phenylacetylene, 2-ethynyltoluene, 3-ethynyltoluene, 4-ethynyltoluene, 4-ethynylanisole, 4-ethynyltrifluorotoluene, *t*Bu-MgCl, *s*Bu-MgCl, *n*Bu-MgCl, *i*Bu-MgCl, allyl bromide, 1-bromopentane, 1-iodoadamantane, iodine, acetaldehyde, (dimethylphenyl)silylacetylene (Aldrich Chemical Company), P(*t*Bu)₃ (Hokko-chemical-Industry), dehydrated diethyl ether (Kanto Chemical Company), decane (Kishida Chemical Company), 2-bromo-2-methylbutane, 2-iodo-2-methylpropane, 2-iodobutane, 1-iodobutane, iodocyclohexane, Pd(dba)₂, iodobenzene (Tokyo Chemical Industry Company), AgOTs, PPh₃, D₂O, and dehydrated toluene (Wako Pure Chemical Industries) were purchased and used as received. 2-Iodo-2-methylbutane,^{S1} 6-iodo-1-phenyl-1-hexyne (**13a**),^{S2} 6-bromo-1-phenyl-1-hexyne (**13b**),^{S3} and 2-iodoethanal butyl 3-phenyl-2-propynyl acetal (**13c**)^{S4} were prepared according to the literature.

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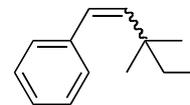
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Typical Procedures and Characterization Data for the Isolated Compounds

3,3-Dimethyl-1-phenyl-1-pentene (**3b**):^{S5}



A mixture of phenyl acetylene (102.1 mg, 1.0 mmol), 2-iodo-2-methylbutane (357.9 mg, 1.8 mmol), PPh₃ (21.1 mg, 0.08 mmol), and AgOTs (22.3 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et₂O, 0.6 mL, 1.2 mmol) at -10 °C. After stirring for 1 h at same temperature, aqueous 1N HCl was added to the solution at room temperature. The product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane) afforded 148.4 mg (85%) of **3b** as a mixture of stereoisomers (*E/Z* = 18/82); IR (NaCl) 3079, 3058, 3023, 2964, 2876, 1599, 1492, 1462, 1378, 1362, 1217, 1071, 1028, 1006, 969, 825, 755, 719, 698, 652 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.16 (m, 5H), 6.48 (d, *J* = 12.7 Hz, 0.82H), 6.27 (d, *J* = 16.1 Hz, 0.18H), 6.17 (d, *J* = 16.1 Hz, 0.18H), 5.49 (d, *J* = 12.7 Hz, 0.82H), 1.41 (q, *J* = 7.3 Hz, 0.36H), 1.31 (q, *J* = 7.3 Hz, 1.64H), 1.07 (s, 1.08H), 0.89 (s, 4.92H), 0.83 (t, *J* = 7.3 Hz, 0.54H), 0.83 (t, *J* = 7.3 Hz, 2.46H); ¹³C NMR (100 MHz, CDCl₃) (*Z* isomer): δ 141.4, 139.5, 128.8, 128.0, 127.5, 126.1, 37.5, 36.7, 28.5, 9.2; (*E* isomer): δ 140.6, 138.1, 128.5, 126.7, 126.0, 125.8, 36.4, 35.5, 26.7, 9.0; MS (EI) *m/z* (relative intensity, %) (*Z* isomer): 174 (M⁺, 10), 159 (5), 146(13), 145 (100), 130 (8), 129 (6), 128 (7), 117 (17), 115 (6), 105 (5), 91 (13); (*E* isomer): 174 (M⁺, 17), 159 (6), 146(13), 145 (100), 130 (7), 129 (6), 128 (6), 117 (16), 115 (6), 105 (5), 91 (13); HRMS (EI) calcd for C₁₃H₁₈ 174.1409 (*Z* isomer): found 174.1413; (*E* isomer): found 174.1401.

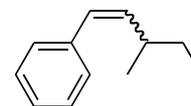
3,3-Dimethyl-1-phenyl-1-butene (**5a**):^{S6}



A mixture of phenyl acetylene (103.0 mg, 1.0 mmol), 2-iodo-2-methylpropane (332.1 mg, 1.8 mmol), PPh₃ (20.8 mg, 0.08 mmol), and AgOTs (22.2 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et₂O, 0.6 mL, 1.2 mmol) at -10 °C. After stirring for 1 h at same temperature, aqueous 1N HCl was added to the solution at room temperature. The product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane) afforded 130.6 mg (81%) of **5a** as a mixture of stereoisomers (*E/Z* = 22/78); IR (NaCl) 3079, 3058, 3026, 2959, 2903, 2867, 1599, 1492, 1475, 1461, 1444, 1362, 1201, 1072, 1028, 967, 918, 746, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.17 (m, 5H), 6.41 (d, *J* = 12.7 Hz, 0.78H), 6.29-6.27 (m, 0.44H), 5.60 (d, *J* = 12.7 Hz, 0.78H), 1.12 (s, 1.98H), 0.98 (s, 7.02H); ¹³C NMR (100 MHz, CDCl₃) (*Z* isomer): δ 142.8, 139.6, 129.1, 127.7, 127.3, 126.3, 34.3, 31.4; (*E* isomer): δ 142.0, 138.2, 128.6, 126.9, 126.2, 124.7, 33.5, 29.8; MS (EI) *m/z* (relative intensity, %) (*Z* isomer): 160 (M⁺,

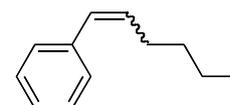
33), 146 (13), 145 (100), 130 (12), 129 (7), 128 (9), 117 (20), 115 (7), 105 (7), 91 (19), 77 (5); (*E* isomer): 160 (M^+ , 36), 146 (12), 145 (100), 130 (9), 129 (6), 128 (8), 117 (16), 115 (6), 105 (6), 91 (15), 77(4); HRMS (EI) calcd for $C_{12}H_{16}$ 160.1252 (*Z* isomer): found 160.1255; (*E* isomer): found 160.1248.

3-Methyl-1-phenyl-1-pentene (**5b**):^{S6}



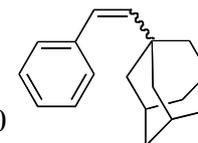
A mixture of phenyl acetylene (103.0 mg, 1.0 mmol), 2-iodobutane (333.6 mg, 1.8 mmol), PPh_3 (21.0 mg, 0.08 mmol), and AgOTs (22.4 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et_2O , 0.6 mL, 1.2 mmol) via syringe pump for 1 h at $-10\text{ }^\circ\text{C}$. The reaction mixture was stirred at that temperature for 2 h after completion of the addition of the Grignard reagent. Then aqueous 1N HCl was added to the solution at room temperature. The product was extracted with ether, dried over $MgSO_4$, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by HPLC with $CHCl_3$ as an eluent afforded 107.3 mg (67%) of **5b** as a mixture of stereoisomers (*E/Z* = 30/70); IR (NaCl) 3080, 3058, 3025, 3000, 2961, 2925, 2872, 1600, 1493, 1455, 1377, 1073, 1029, 964, 916, 798, 778, 746, 696 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.16 (m, 5H), 6.40-6.32 (m, 1H), 6.09 (dd, $J = 15.6, 7.8$ Hz, 0.3H), 5.43 (dd, $J = 11.0, 11.0$ Hz, 0.70H), 2.71-2.60 (m, 0.7H), 2.24-2.17 (m, 0.3H), 1.45-1.29 (m, 2H), 1.07 (d, $J = 6.8$ Hz, 0.9H), 1.03 (d, $J = 6.9$ Hz, 2.1H), 0.93-0.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 139.4, 136.8, 128.6, 128.1, 127.5, 126.4, 33.8, 30.3, 20.7, 11.8; (*E* isomer): δ 138.0, 136.8, 128.5, 128.1, 126.7, 126.0, 38.9, 29.8, 20.2, 11.9; MS (EI) m/z (relative intensity, %) (*Z* isomer): 160 (M^+ , 21), 145 (6), 132 (10), 131 (100), 129 (7), 128 (5), 117 (5), 116 (8), 115 (9), 104 (8), 91 (23), 77 (3); (*E* isomer): 160 (M^+ , 24), 145 (6), 132 (10), 131 (100), 129 (7), 128 (5), 117 (5), 116 (8), 115 (8), 104 (8), 91 (21), 77 (3); HRMS (EI) calcd for $C_{12}H_{16}$ 160.1252 (*Z* isomer): found 160.1256; (*E* isomer): found 160.1258.

1-Phenyl-1-hexene (**5c**):^{S6}



A mixture of phenyl acetylene (103.2 mg, 1.0 mmol), 1-iodobutane (332.9 mg, 1.8 mmol), PPh_3 (21.0 mg, 0.08 mmol), and AgOTs (22.5 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et_2O , 0.6 mL, 1.2 mmol) via syringe pump for 1 h at $-10\text{ }^\circ\text{C}$. The reaction mixture was stirred at that temperature for 2 h after completion of the addition of the Grignard reagent. Then aqueous 1N HCl was added to the solution at room temperature and the product was analyzed by GC with decane as an internal standard.

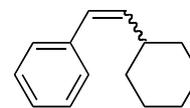
1-(1-Adamantyl)-2-Phenylethene (**5d**):^{S7}



A mixture of phenyl acetylene (100.0 mg, 0.98 mmol), 1-iodoadamantane (470.0 mg, 1.8 mmol), PPh_3 (21.0 mg, 0.08 mmol), and AgOTs (22.4 mg, 0.08 mmol) was added *i*-butyl

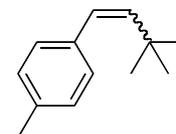
magnesium chloride (2.0 M in Et₂O, 0.6 mL, 1.2 mmol) at -10 °C. After stirring for 4 h at same temperature, aqueous 1N HCl was added to the solution at room temperature. The product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by HPLC with CHCl₃ as an eluent afforded 99.3 mg (43%) of **5d** as a mixture of stereoisomers (*E/Z* = 32/68); IR (NaCl) 3077, 3056, 3024, 2990, 2902, 2846, 1599, 1490, 1450, 1344, 1316, 1101, 1069, 1028, 965, 916, 816, 773, 746, 711, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.15 (m, 5H), 6.39 (d, *J* = 12.7 Hz, 0.68H), 6.24 (d, *J* = 16.1 Hz, 0.32H), 6.10 (d, *J* = 16.1 Hz, 0.32H), 5.36 (d, *J* = 12.7 Hz, 0.68H), 2.02-1.26 (m, 4.8H) 1.85-1.55 (m, 10.2H); ¹³C NMR (100 MHz, CDCl₃) (*Z* isomer): δ 143.0, 139.7, 129.0, 127.4, 127.0, 126.1, 43.1, 36.7, 36.6, 28.5; (*E* isomer): δ 142.1, 138.2, 128.5, 126.7, 126.0, 124.5, 42.2, 36.7, 35.2, 28.5; MS (EI) *m/z* (relative intensity, %) (*Z* isomer): 239 (18), 238 (M⁺, 100), 237 (6), 195 (5), 182 (11), 181 (55), 168 (2), 167 (5), 166 (6), 165 (5), 155 (4), 154 (3), 153 (3), 144 (10), 143 (7), 142 (19), 141(7), 129 (12), 128 (8), 117 (5), 115 (6), 105 (5), 104 (5), 103 (6), 93 (6), 91 (14), 79 (5), 77 (5); (*E* isomer): 239 (21), 238 (M⁺, 100), 237 (6), 195 (6), 182 (14), 181 (59), 168 (3), 167 (7), 166 (5), 165 (6), 155 (5), 154 (2), 153 (4), 144 (7), 143 (6), 142 (18), 141(7), 129 (13), 128 (9), 117 (5), 115 (5), 105 (4), 104 (6), 103 (6), 93 (6), 91 (13), 79 (4), 77 (4); HRMS (EI) calcd for C₁₈H₂₂ 238.1722 (*Z* isomer): found 238.1722; (*E* isomer): found 228.1725.

2-Cyclohexyl-1-phenylethene (**5e**):^{S6}



A mixture of phenyl acetylene (102.9 mg, 1.0 mmol), 2-iodocyclohexane (379.7 mg, 1.8 mmol), PPh₃ (21.3 mg, 0.08 mmol), and AgOTs (22.1 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et₂O, 0.6 mL, 1.2 mmol) via syringe pump for 1 h at -10 °C. The reaction mixture was stirred at that temperature for 2 h after completion of the addition of the Grignard reagent. Then aqueous 1N HCl was added to the solution at room temperature and the product was analyzed by GC with decane as an internal standard.

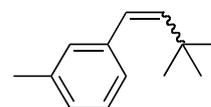
3,3-Dimethyl-1-(4-methylphenyl)-1-butene (**5f**):^{S6}



A mixture of 4-ethynyltoluene (114.1 mg, 0.99 mmol), 2-iodo-2-methylpropane (327.7 mg, 1.8 mmol), PPh₃ (21.2 mg, 0.08 mmol), and AgOTs (22.2 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et₂O, 0.6 mL, 1.2 mmol) at -10 °C. After stirring for 1 h at same temperature, aqueous 1N HCl was added to the solution at room temperature. The product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane) afforded 130.1 mg (76%) of **3f** as a mixture of stereoisomers (*E/Z* = 35/65); IR (NaCl) 3022,

2993, 2958, 2902, 2866, 1512, 1475, 1461, 1362, 1200, 1109, 1022, 969, 902, 849, 799, 775, 740 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.11-7.05 (m, 4H), 6.37 (d, $J = 12.7$ Hz, 0.65H), 6.25-6.22 (m, 0.70H), 5.55 (d, $J = 12.7$ Hz, 0.65H), 2.33 (s, 1.95H), 2.32 (s, 1.05H), 1.11 (s, 3.15H), 0.99 (s, 5.85H); ^{13}C NMR (100 MHz, CDCl_3) (*Z* isomer): δ 142.5, 136.3, 135.7, 128.8, 128.2, 127.1, 34.1, 31.2, 21.1; (*E* isomer): δ 140.8, 136.4, 135.2, 129.1, 125.9, 124.3, 33.3, 29.6, 21.1; MS (EI) m/z (relative intensity, %) (*Z* isomer): 174 (M^+ , 33), 160 (13), 159 (100), 144 (14), 131 (10), 129 (8), 128 (8), 117 (7), 115 (6), 105 (13), 91 (5), 77 (3); (*E* isomer): 174 (M^+ , 37), 160 (13), 159 (100), 144 (11), 131 (8), 129 (6), 128 (7), 117 (5), 115 (5), 105 (10), 91 (3), 77 (2); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{18}$ 174.1409 (*Z* isomer): found 174.1411; (*E* isomer): found 174.1405.

3,3-Dimethyl-1-(3-methylphenyl)-1-butene (**5g**):^{S6}



A mixture of 3-ethynyltoluene (117.1 mg, 1.0 mmol), 2-iodo-2-methylpropane (331.1 mg, 1.8 mmol), PPh_3 (21.2 mg, 0.08 mmol), and AgOTs (22.3 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et_2O , 0.6 mL, 1.2 mmol) at -10 $^\circ\text{C}$. After stirring for 1 h at same temperature, aqueous 1N HCl was added to the solution at room temperature. The product was extracted with ether, dried over MgSO_4 , filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane) afforded 139.5 mg (79%) of **5g** as a mixture of stereoisomers (*E/Z* = 26/74); IR (NaCl) 2958, 2903, 2866, 1603, 1583, 1475, 1461, 1361, 1218, 1201, 1090, 970, 902, 878, 812, 766, 738, 703 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.14 (m, 1H), 7.02-6.97 (m, 3H), 6.38 (d, $J = 12.7$ Hz, 0.74H), 6.26-6.25 (m, 0.52H), 5.57 (d, $J = 12.7$ Hz, 0.74H), 2.33 (m, 3H), 1.11 (s, 2.34H), 0.98 (s, 6.66H); ^{13}C NMR (100 MHz, CDCl_3) (*Z* isomer): δ 142.4, 139.3, 137.0, 129.6, 127.4, 127.2, 126.8, 126.0, 34.2, 31.2, 21.4; (*E* isomer): δ 141.6, 138.0, 137.9, 128.4, 127.5, 126.7, 124.5, 123.2, 33.3, 29.6, 21.4; MS (EI) m/z (relative intensity, %) (*Z* isomer): 174 (M^+ , 36), 160 (13), 159 (100), 144 (14), 131 (13), 129 (9), 128 (9), 119 (4), 117 (8), 115 (8), 105 (14), 91 (5), 77 (3); (*E* isomer): 174 (M^+ , 38), 160 (12), 159 (100), 144 (12), 131 (12), 129 (8), 128 (9), 119 (3), 117 (7), 115 (6), 105 (12), 91 (5), 77 (3); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{18}$ 174.1409 (*Z* isomer): found 174.1403 (*E* isomer): found 174.1406; Anal. Calcd for $\text{C}_{13}\text{H}_{18}$: C, 89.59; H, 10.41. found: C, 89.44; H, 10.38.

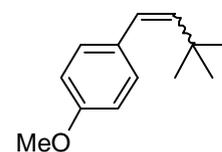
3,3-Dimethyl-1-(2-methylphenyl)-1-butene (**5h**):^{S6}



A mixture of 2-ethynyltoluene (115.2 mg, 1.0 mmol), 2-iodo-2-methylpropane (332.4 mg, 1.8 mmol), PPh_3 (21.0 mg, 0.08 mmol), and AgOTs (22.4 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et_2O , 0.6 mL, 1.2 mmol) at -10 $^\circ\text{C}$. After stirring for 1 h at same temperature, aqueous 1N HCl was added to the solution at room temperature. The product was

extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane) afforded 146.5 mg (85%) of **5h** as a mixture of stereoisomers (*E/Z* = 3/97); IR (NaCl) 3061, 3019, 2988, 2958, 2904, 2866, 1488, 1475, 1461, 1361, 1234, 1205, 1045, 944, 901, 805, 751, 739, 721 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) (*Z* isomer): δ 7.14-7.09 (m, 4H), 6.26 (d, *J* = 12.7 Hz, 1H), 5.61 (d, *J* = 12.7 Hz, 1H), 2.24 (s, 3H), 0.93 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) (*Z* isomer): δ 142.1, 138.9, 135.7, 129.5, 129.2, 126.6, 126.2, 124.8, 34.3, 30.8, 20.3; MS (EI) *m/z* (relative intensity, %) (*Z* isomer): 174 (M⁺, 39), 160 (14), 159 (100), 145 (4), 144 (13), 131 (14), 129 (9), 128 (9), 117 (11), 115 (9), 105 (13), 104 (7), 91 (5), 77 (3); HRMS (EI) calcd for C₁₃H₁₈ 174.1409 found 174.1413; Anal. Calcd for C₁₃H₁₈: C, 89.59; H, 10.41. found: C, 89.31; H, 10.45.

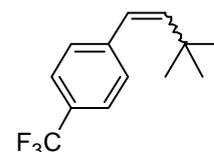
3,3-Dimethyl-1-(4-methoxyphenyl)-1-butene (**5i**):^{S6}



A mixture of 4-ethynylanisole (130.0 mg, 0.98 mmol), 2-iodo-2-methylpropane (331.4 mg, 1.8 mmol), PPh₃ (21.5 mg, 0.08 mmol), and AgOTs (22.1 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et₂O, 0.6 mL, 1.2 mmol) at -10 °C. After stirring for 1 h at same temperature, aqueous 1N HCl was added to the solution at room temperature. The product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane/ethyl acetate = 19/1) afforded 138.1mg (73%) of **5i** as a mixture of stereoisomers (*E/Z* = 50/50); IR (NaCl) 2995, 2957, 2903, 2866, 2835, 1607, 1510, 1464, 1442, 1362, 1302, 1285, 1247, 1201, 1173, 1107, 1038, 969, 851, 815, 783 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.8 Hz 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.85-6.81 (m, 2H), 6.35 (d, *J* = 12.7 Hz, 0.5H), 6.25 (d, *J* = 16.1 Hz, 0.5H), 6.12 (d, *J* = 16.1 Hz, 0.5H), 5.56 (d, *J* = 12.7 Hz, 0.5H), 3.80 (s, 1.5H), 3.80 (s, 1.5H), 1.11 (s, 4.5H), 0.99 (s, 4.5H); ¹³C NMR (100 MHz, CDCl₃) (*Z* isomer): δ 158.0, 142.5, 131.6, 130.0, 126.7, 112.9, 55.2, 34.0, 31.2; (*E* isomer): δ 158.6, 139.8, 130.8, 127.0, 123.8, 113.9, 55.3, 33.2, 29.7; MS (EI) *m/z* (relative intensity, %) (*Z* isomer): 190 (M⁺, 32), 176 (13), 175 (100), 160 (11), 146 (3), 145 (4), 128 (3), 121 (8), 115 (4), 91 (4), 77 (2); (*E* isomer): 190 (M⁺, 35), 176 (12), 175 (100), 160 (10), 146 (3), 145 (3), 128 (3), 121 (8), 115 (3), 91 (3), 77 (2); HRMS (EI) calcd for C₁₃H₁₈O 190.1358 (*Z* isomer): found 190.1359 (*E* isomer): found 190.1364; Anal. Calcd for C₁₃H₁₈O: C, 82.06; H, 9.53. found: C, 81.77; H, 9.38.

3,3-Dimethyl-1-(4-trifluoromethylphenyl)-1-butene (**5j**):^{S6}

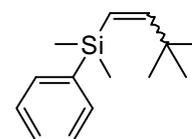
A mixture of 4-ethynyltrifluoromethylbenzene (170.5 mg, 1.0 mmol), 2-iodo-2-methylpropane (334.3 mg, 1.8 mmol), PPh₃ (21.9 mg, 0.08 mmol), and



AgOTs (21.9 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et₂O, 0.6 mL, 1.2 mmol) at -10 °C. After stirring for 1 h at same temperature, aqueous 1N HCl was added to the solution at room temperature. The product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by HPLC with CHCl₃ as an eluent afforded 142.5 mg (63%) of **5j** as a mixture of stereoisomers (*E/Z* = 11/89); IR (NaCl) 2962, 2905, 2869, 1616, 1476, 1465, 1406, 1363, 1325, 1165, 1127, 1106, 1066, 1018, 903, 862, 815, 732 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.54-7.28 (m, 4H), 6.38 (d, *J* = 12.7 Hz, 0.89H), 6.34 (d, *J* = 4.4 Hz, 0.11H), 6.34 (d, *J* = 4.4 Hz, 0.11H), 5.68 (d, *J* = 12.7 Hz, 0.89H), 1.13 (s, 0.99H), 0.97 (s, 8.01H); ¹³C NMR (100 MHz, CDCl₃) (*Z* isomer): δ 143.9, 143.3, 129.2, 128.5 (q, *J* = 32.1 Hz), 125.6, 124.5 (q, *J* = 4.1 Hz), 124.6 (q, *J* = 270.8 Hz), 34.3, 31.2; MS (EI) *m/z* (relative intensity, %) (*Z* isomer): 228 (M⁺, 28), 214 (13), 213 (100), 209 (5), 185 (21), 173 (7), 165 (7), 159 (16), 144 (4), 129 (5), 128 (5); (*E* isomer): 228 (M⁺, 31), 214 (12), 213 (100), 209 (5), 185 (18), 173 (6), 165 (5), 159 (16), 144 (3), 129 (4), 128 (4); HRMS (EI) calcd for C₁₃H₁₅F₃ 228.1126 (*Z* isomer): found 228.1122 (*E* isomer): found 228.1129; Anal. Calcd for C₁₃H₁₅F₃: C, 68.41; H, 6.62. found: C, 68.49; H, 6.62.

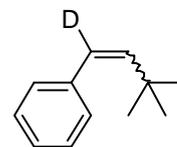
3,3-Dimethyl-1-(dimethylphenylsilyl)-1-butene (**5l**):^{S6}

A mixture of (dimethylphenylsilyl)acetylene (156.3 mg, 1.0 mmol), 2-iodo-2-methylpropane (327.7 mg, 1.8 mmol), PPh₃ (21.3 mg, 0.08 mmol), and AgOTs (22.1 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et₂O, 0.6 mL, 1.2 mmol) via syringe pump for 1 h at -10 °C. The reaction mixture was stirred at that temperature for 8 h after completion of the addition of the Grignard reagent. Then aqueous 1N HCl was added to the solution at room temperature. The product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane) and HPLC with CHCl₃ as an eluent afforded 110.1 mg (52%) of **5l** as a mixture of stereoisomers (*E/Z* = 9/91); IR (NaCl) 3069, 2958, 2901, 2866, 1950, 1878, 1815, 1611, 1475, 1462, 1427, 1362, 1248, 1113, 994, 824 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.52-7.33 (m, 5H), 6.48 (d, *J* = 15.1 Hz, 0.09H), 6.13 (d, *J* = 19.0 Hz, 0.91H), 5.65 (d, *J* = 19.0 Hz, 0.91H), 5.50 (d, *J* = 15.1 Hz, 0.09H), 1.01 (s, 8.19H), 0.96 (s, 0.81H), 0.41 (s, 0.54H), 0.32 (s, 5.46H); ¹³C NMR (100 MHz, CDCl₃) (*Z* isomer): δ 159.5, 139.6, 133.8, 128.7, 127.7, 120.3, 35.2, 29.1, -2.3; (*E* isomer): δ 161.7, 140.9, 133.7, 128.6, 127.6, 122.6, 35.6, 30.1, 0.8; MS (EI) *m/z* (relative intensity, %) (*Z* isomer): 218 (M⁺, 20), 203 (72), 161 (96), 135 (100), 121 (48), 73 (26); HRMS (EI) calcd for C₁₄H₂₂Si 218.1491 (*Z* isomer): found 218.1484.



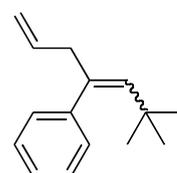
1-Deuterio-3,3-dimethyl-1-phenyl-1-butene (**8a**):^{S6}

A mixture of phenyl acetylene (102.0 mg, 1.0 mmol), 2-iodo-2-methylpropane (338.1 mg, 1.8 mmol), PPh₃ (21.2 mg, 0.08 mmol), and AgOTs (22.5 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et₂O, 0.6 mL, 1.2 mmol) at -10 °C. After stirring for 1 h, D₂O was added to the solution at -10 °C. After stirring for 30 min at room temperature, aqueous 1N HCl was added to the solution. The product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane) afforded 125.4 mg (78%) of **8a** as a mixture of stereoisomers (*E/Z* = 22/78); IR (NaCl) 3079, 3059, 3022, 2959, 2902, 2867, 1599, 1492, 1475, 1462, 1442, 1362, 1201, 1028, 919, 902, 772, 744, 721, 696 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.17 (m, 5H), 6.25 (t, *J* = 2.0 Hz, 0.22H), 5.60 (t, *J* = 2.0 Hz, 0.78H), 1.12 (s, 1.98H), 0.98 (s, 7.02H); ¹³C NMR (100 MHz, CDCl₃) (*Z* isomer): δ 142.5, 139.3, 128.9, 127.5, 126.8 (t, *J* = 23.9 Hz), 126.2, 34.1, 31.2; (*E* isomer): δ 141.7, 137.9, 128.4, 126.7, 126.0, 124.2 (t, *J* = 23.1 Hz), 33.3, 29.6; MS (EI) *m/z* (relative intensity, %) (*Z* isomer): 161 (M⁺, 29), 147 (12), 146 (100), 131 (9), 130 (8), 129 (7), 118 (12), 117 (6), 116 (5), 106 (5), 92 (11), 91 (5); (*E* isomer): 161 (M⁺, 31), 147 (14), 146 (100), 131 (9), 130 (8), 129 (7), 118 (10), 117 (5), 116 (5), 106 (4), 92 (10), 91 (4); HRMS (EI) calcd for C₁₂H₁₅D 161.1314 (*Z* isomer): found 161.1310 (*E* isomer): found 161.1322; Anal. Calcd for C₁₂H₁₅D: C, 89.38; H and D, 10.62. found: C, 89.17; H and D, 10.83.



6,6-Dimethyl-4-phenyl-1,4-heptadiene (**8b**):^{S8}

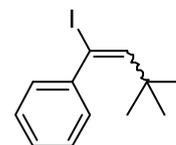
A mixture of phenyl acetylene (102.4 mg, 1.0 mmol), 2-iodo-2-methylpropane (334.9 mg, 1.8 mmol), PPh₃ (21.1 mg, 0.08 mmol), and AgOTs (22.4 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et₂O, 0.6 mL, 1.2 mmol) at -10 °C. After stirring for 1 h, dry Et₂O (0.6 mL) and Allyl iodide (341.0 mg, 2.0 mmol) were added to the solution at -10 °C. After stirring for 1 h at room temperature, aqueous 1N HCl was added to the solution. The product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane) and HPLC with CHCl₃ as an eluent afforded 132.1 mg (66%) of **8b** as a mixture of stereoisomers (*E/Z* = 24/76); IR (NaCl) 3078, 3058, 3020, 2957, 2902, 2867, 1638, 1599, 1493, 1474, 1463, 1442, 1362, 1222, 1200, 1071, 995, 912, 764, 747, 703 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.08 (m, 5H), 5.82-5.72 (m, 1H), 5.75 (s, 0.24H), 5.43-5.42 (m, 0.76H), 5.05-4.91 (m, 2H), 3.42-3.40 (m, 0.48H), 2.94-2.91 (m, 1.52H), 1.21 (s, 2.16H), 0.85 (s, 6.84H); ¹³C NMR (100 MHz, CDCl₃) (*Z* isomer): δ 142.3, 137.8, 137.0, 136.6, 129.0, 127.5, 126.2, 115.8, 46.7, 33.3, 31.4; (*E* isomer): δ 144.6, 140.8, 136.5, 136.4, 128.0, 126.7, 126.4, 115.8, 34.5, 33.1, 31.3; MS (EI) *m/z*



(relative intensity, %) (*Z* isomer): 201 (9), 200 (M^+ , 51), 186 (13), 185 (90), 172 (5), 171 (6), 160 (10), 159 (74), 158 (18), 157 (62), 156 (7), 155 (7), 153 (6), 152 (4), 145 (8), 144 (55), 143 (77), 142 (20), 141 (19), 131 (20), 130 (37), 129 (100), 128 (50), 127 (14), 119 (8), 118 (8), 117 (65), 116 (7), 115 (34), 107 (7), 106 (3), 105 (28), 103 (10), 102 (7), 92 (6), 91 (75), 79 (5), 78 (4), 77 (16), 57 (17), 55 (6), 41 (13); (*E* isomer): 201 (11), 200 (M^+ , 61), 186 (14), 185 (91), 172 (5), 171 (8), 160 (10), 159 (69), 158 (18), 157 (61), 156 (8), 155 (12), 153 (7), 152 (4), 145 (6), 144 (60), 143 (78), 142 (16), 141 (16), 131 (20), 130 (37), 129 (100), 128 (57), 127 (14), 119 (8), 118 (7), 117 (63), 116 (9), 115 (31), 107 (6), 106 (3), 105 (31), 103 (11), 102 (6), 92 (9), 91 (77), 79 (5), 78 (5), 77 (15), 69 (7), 65 (5), 57 (17), 55 (7), 41 (11); HRMS (EI) calcd for $C_{15}H_{20}$ 200.1565 (*Z* isomer): found 200.1571 (*E* isomer): found 200.1565.

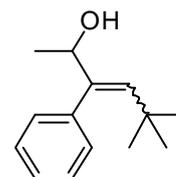
3,3-Dimethyl-1-iodo-1-phenyl-1-butene (**8c**):^{S9}

A mixture of phenyl acetylene (104.2 mg, 1.0 mmol), 2-iodo-2-methylpropane (339.5 mg, 1.8 mmol), PPh_3 (21.1 mg, 0.08 mmol), and AgOTs (21.9 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et_2O , 0.6 mL, 1.2 mmol) at -10 °C. After stirring for 1 h, dry Et_2O (0.6 mL) and I_2 (509.1 mg, 2.0 mmol) were added to the solution at -10 °C. After stirring for 1 h at room temperature, aqueous 1N HCl was added to the solution. The product was extracted with ether, dried over $MgSO_4$, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane) afforded 208.9 mg (72%) of **8c** as a mixture of stereoisomers (*E/Z* = 79/21); IR (NaCl) 3077, 3056, 3016, 2959, 2900, 2867, 1593, 1487, 1474, 1460, 1442, 1362, 1256, 1217, 1200, 1070, 1028, 917, 861, 830, 767, 746, 698, 683 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.21 (m, 5H), 6.47 (s, 0.79H), 6.24 (s, 0.21H), 1.29 (s, 1.89H), 0.89 (s, 7.11H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer): δ 148.1, 145.9, 128.4, 127.9, 127.8, 97.4, 33.9, 29.6; (*E* isomer): δ 152.4, 144.2, 128.0, 127.9, 127.8, 93.7, 38.1, 30.6; MS (EI) *m/z* (relative intensity, %) (*Z* isomer): 286 (M^+ , 6), 160 (16), 159 (100), 144 (10), 143 (7), 131 (6), 130 (4), 129 (21), 128 (16), 127 (5), 118 (3), 117 (32), 115 (9), 105 (5), 103 (7), 102 (7), 91 (5), 57 (32); (*E* isomer): 286 (M^+ , 3), 160 (13), 159 (100), 144 (7), 143 (5), 131 (5), 130 (3), 129 (17), 128 (14), 127 (5), 118 (3), 117 (27), 115 (7), 105 (4), 103 (7), 102 (8), 91 (4), 57 (35); HRMS (EI) calcd for $C_{12}H_{15}I$ 286.0218 (*Z* isomer): found 286.0226 (*E* isomer): found 286.0231; Anal. Calcd for $C_{12}H_{15}I$: C, 50.37; H, 5.28. found: C, 50.57; H, 5.12.



5,5-Dimethyl-3-phenyl-3-hexene-2-ol (**8d**):

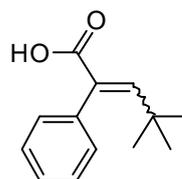
A mixture of phenyl acetylene (103.1 mg, 1.0 mmol), 2-iodo-2-methylpropane (331.2 mg, 1.8 mmol), PPh_3 (21.3 mg, 0.08 mmol), and AgOTs (22.3 mg, 0.08 mmol) was



added *i*-butyl magnesium chloride (2.0 M in Et₂O, 0.6 mL, 1.2 mmol) at -10 °C. After stirring for 1 h, dry Et₂O (0.6 mL) and acetaldehyde (4.0 mmol) were added to the solution at -10 °C. After stirring for 3 h at room temperature, aqueous 1N HCl was added to the solution. The product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane/ethyl acetate/ethanol = 8/1/1) afforded 144.8 mg (70%) of **8d** as a mixture of stereoisomers (*E/Z* = 70/30); IR (NaCl) 3368, 3057, 3019, 2959, 2902, 2868, 1599, 1575, 1493, 1475, 1463, 1442, 1363, 1220, 1116, 1056, 1030, 876, 760, 703 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.11 (m, 5H), 5.66 (s, 0.70H), 5.51 (s, 0.30H), 5.28 (q, *J* = 6.4 Hz, 0.30H), 4.32 (q, *J* = 6.4 Hz, 0.70H), 1.54 (s, 1H), 1.24 (s, 2.70H), 1.22 (d, *J* = 6.4 Hz, 0.90H), 1.17 (d, *J* = 6.4 Hz, 2.10H), 0.85 (s, 6.30H); ¹³C NMR (100 MHz, CDCl₃) (*Z* isomer): δ 142.9, 142.1, 141.4, 129.2, 127.7, 126.7, 65.2, 32.7, 31.9, 22.0; (*E* isomer): δ 141.7, 138.3, 137.3, 130.1, 127.5, 126.7, 74.1, 33.1, 31.2, 22.2; MS (EI) *m/z* (relative intensity, %) (*Z* isomer): 204 (M⁺, 9), 189 (6), 187 (3), 186 (11), 172 (6), 171 (38), 161 (11), 160 (2), 159 (8), 158 (2), 157 (14), 156 (10), 148 (13), 147 (100), 146 (98), 145 (31), 144 (7), 143 (19), 142 (6), 141 (6), 134 (6), 133 (7), 132 (2), 131 (15), 130 (7), 129 (24), 128 (20), 127 (8), 119 (5), 118 (5), 117 (63), 116 (5), 115 (16), 105 (32), 104 (5), 103 (10), 102 (6), 91 (30), 78 (5), 77 (15), 59 (31), 57 (16), 43 (24), 41 (10); (*E* isomer): 204 (M⁺, 5), 189 (7), 187 (3), 186 (12), 172 (5), 171 (39), 161 (12), 160 (4), 159 (9), 158 (3), 157 (14), 156 (10), 148 (14), 147 (100), 146 (81), 145 (31), 144 (6), 143 (17), 142 (4), 141 (6), 134 (7), 133 (7), 131 (13), 130 (6), 129 (25), 128 (20), 127 (6), 119 (4), 118 (5), 117 (52), 116 (4), 115 (14), 105 (26), 104 (5), 103 (10), 102 (7), 91 (24), 78 (3), 77 (10), 59 (22), 57 (18), 43 (22), 41 (9); HRMS (EI) calcd for C₁₄H₂₀O 204.1514 (*Z* isomer): found 204.1508 (*E* isomer): found 204.1514.

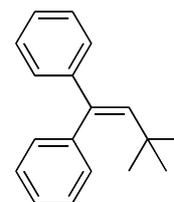
4,4-Dimethyl-2-phenyl-2-pentenoic acid (**8e**):^{S6}

A mixture of phenyl acetylene (104.1 mg, 1.0 mmol), 2-iodo-2-methylpropane (333.9 mg, 1.8 mmol), PPh₃ (21.1 mg, 0.08 mmol), and AgOTf (22.5 mg, 0.08 mmol) was added *i*-butyl magnesium (2.0 M in Et₂O, 0.6 mL, 1.2 mmol) at -10 °C. After stirring for 1 h, dry Et₂O (0.6 mL) and CO₂ were added to the solution at -10 °C. Aqueous 1N HCl was added to the solution and the product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane/ethyl acetate = 1/1 with 1% acetic acid) afforded 161.0 mg (77%) of **8e** as a mixture of stereoisomers (*E/Z* = 82/18); Mp: 104-127 °C; IR (KBr) 3057, 2964, 2869, 2622, 1673, 1631, 1598, 1463, 1444, 1421, 1366, 1300, 1267, 1207, 950, 922, 784, 702, 607 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 11.2 (s, 1.0H), δ 7.37-7.13 (m, 5.82H), 5.92 (s, 0.18H),



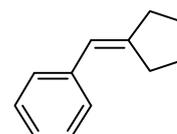
1.21 (s, 1.62H), 0.92 (s, 7.38H); ^{13}C NMR (100 MHz, CDCl_3) (*Z* isomer): δ 176.3, 143.7, 137.7, 131.4, 128.5, 127.7, 126.3, 33.9, 29.7; (*E* isomer): 173.9, 155.9, 135.6, 130.7, 130.0, 127.6, 127.5, 34.4, 30.2; MS (EI) m/z (relative intensity, %) (*Z* isomer): 206 (4), 205 (15), 204 (M^+ , 92), 203 (3), 190 (6), 189 (31), 187 (5), 186 (13), 185 (3), 172 (6), 171 (13), 169 (3), 163 (3), 161 (15), 160 (3), 159 (21), 158 (5), 157 (4), 148 (4), 147 (5), 146 (36), 145 (20), 144 (18), 143 (100), 142 (9), 141 (12), 139 (4), 133 (5), 131 (14), 130 (9), 129 (24), 128 (47), 127 (17), 118 (17), 117 (57), 116 (6), 115 (30), 105 (5), 104 (4), 103 (16), 102 (11), 91 (20), 89 (5), 79 (5), 78 (7), 77 (14), 75 (5), 59 (17); (*E* isomer): 206 (2), 205 (15), 204 (M^+ , 100), 203 (3), 190 (5), 189 (34), 187 (3), 186 (13), 185 (2), 172 (2), 171 (17), 161 (12), 160 (3), 159 (20), 158 (5), 157 (6), 148 (4), 147 (6), 146 (32), 145 (18), 144 (17), 143 (97), 142 (6), 141 (9), 139 (2), 133 (4), 131 (9), 130 (6), 129 (22), 128 (49), 127 (13), 118 (19), 117 (55), 116 (9), 115 (23), 105 (6), 103 (11), 102 (8), 91 (15), 89 (2), 79 (2), 78 (6), 77 (13), 75 (3), 59 (23); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$ 204.1150 (*Z* isomer): found 204.1148 (*E* isomer): found 204.1150; Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$: C, 76.44; H, 7.90. found: C, 76.15; H, 7.74.

3,3-Dimethyl-1,1-diphenyl-1-butene (**8f**):^{S10}



A mixture of phenyl acetylene (100.3 mg, 0.98 mmol), 2-iodo-2-methylpropane (332.1 mg, 1.8 mmol), PPh_3 (21.3 mg, 0.08 mmol), and AgOTs (22.3 mg, 0.08 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et_2O , 0.6 mL, 1.2 mmol) at $-10\text{ }^\circ\text{C}$. After stirring for 1 h, the mixture was warmed to room temperature. A solution of $\text{Pd}(\text{dba})_2$ (28.6 mg, 0.05 mmol), $\text{P}(t\text{-Bu})_3$ (21.0 mg, 0.10 mmol), and iodobenzene (409.3 mg, 2.0 mmol) in dry toluene (2.4 mL) was added to the mixture. After stirring for 2 h at room temperature, aqueous 1N HCl was added to the solution. The product was extracted with ether, dried over MgSO_4 , filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane) afforded 168.9 mg (73%) of **8f**. IR (NaCl) 3079, 3057, 3022, 2957, 2901, 2866, 1597, 1494, 1475, 1460, 1073, 1030, 782, 763, 752, 726, 702, 640 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.7.15 (m, 10H), 6.09 (s, 1H), 0.96 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.9, 140.6, 140.0, 138.8, 130.2, 127.8, 127.6, 126.7, 126.6, 126.4, 33.8, 31.2; MS (EI) m/z (relative intensity, %) 237 (12), 236 (M^+ , 64), 222 (19), 221 (100), 193 (10), 192 (6), 191 (8), 179 (8), 178 (14), 167 (6), 166 (4), 165 (16), 144 (7), 143 (51), 129 (6), 128 (12), 105 (14), 91 (27); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{20}$ 236.1565 found 236.1559; Anal. Calcd for $\text{C}_{18}\text{H}_{20}$: C, 91.27; H, 8.53. found: C, 91.27; H, 8.46.

Benzylidenecyclopentane (**15a**):^{S10}

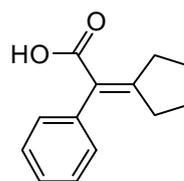


A mixture of 6-iodo-1-phenyl-1-hexyne (281.0 mg, 0.99 mmol), PPh_3 (21.5 mg, 0.082

mmol), and AgOTs (22.0 mg, 0.078 mmol) was added *i*-butyl magnesium chloride (2.0 M in Et₂O, 0.6 mL, 1.2 mmol) via syringe pump for 1 h at -10 °C. The reaction mixture was stirred at that temperature for 3 h after completion of the addition of the Grignard reagent. Then saturated aqueous NH₄Cl was added to the solution at room temperature. The product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane) afforded 124.0 mg (79%) of **15a**. IR (NaCl) 3083, 3056, 3023, 2954, 2867, 2832, 1654, 1600, 1490, 1447, 1430, 910, 862, 747, 694 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.13 (m, 5H), 6.37-6.35 (m, 1H), 2.57-2.47 (m, 4H), 1.81-1.74 (m, 2H), 1.70-1.63 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 147.2, 138.9, 128.2, 127.9, 125.6, 120.8, 35.9, 31.2, 27.2, 25.7; MS (EI) *m/z* (relative intensity, %) (*Z* isomer): 159 (14), 158 (M⁺, 100), 157 (7), 143 (16), 142 (5), 141 (5), 130 (27), 129 (48), 128 (23), 117 (49), 116 (9), 115 (33), 92 (5), 91 (24), 80 (10), 79 (7), 77 (7), 67 (47), 66 (9), 65 (5); HRMS (EI) calcd for C₁₂H₁₄ 158.1096 found 158.1100.

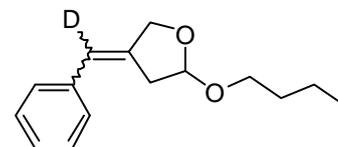
1-Cyclopentylidene-1-phenylacetic acid (**15b**):^{S11}

A mixture of 6-iodo-1-phenyl-1-hexyne (284.0 mg, 1.0 mmol), PPh₃ (20.9 mg, 0.080 mmol), and AgOTs (22.4 mg, 0.080 mmol) was added *i*-butyl magnesium (2.0 M in Et₂O, 0.6 mL, 1.2 mmol) via syringe pump for 1 h at -10 °C. The reaction mixture was stirred at that temperature for 3 h after completion of the addition of the Grignard reagent. Dry Et₂O (0.6 mL) and CO₂ were added to the solution at -10 °C. Then saturated aqueous NH₄Cl was added to the solution at room temperature. The product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane/ethyl acetate = 8/2 to 4/6) afforded 151.2 mg (75%) of **15b**. Mp: 132 °C; IR (KBr) 3058, 2958, 2869, 2816, 2631, 1678, 1615, 1597, 1495, 1444, 1414, 1286, 1275, 1252, 949, 920, 891, 726, 699, 651 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 12.23 (s, 1H), 7.37-7.16 (m, 5H), 2.91-2.88 (m, 2H), 2.22-2.18 (m, 2H), 1.80-1.73 (m, 2H), 1.62-1.55 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 172.4, 168.1, 138.7, 129.3, 128.2, 127.0, 124.9, 36.0, 34.6, 26.8, 25.7; MS (EI) *m/z* (relative intensity, %) 203 (14), 202 (M⁺, 100), 185 (6), 184 (39), 173 (8), 157 (22), 156 (26), 155 (20), 142 (7), 141 (14), 130 (5), 129 (37), 128 (31), 127 (9), 118 (6), 117 (6), 116 (7), 115 (35), 91 (18), 78 (5), 77 (9), 67 (8); HRMS (EI) calcd for C₁₃H₁₄O₂ 202.0994 found 202.0996.



2-Butoxy-4-(phenyl[²H]methylene)tetrahydrofuran (15c):

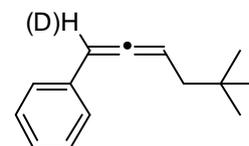
A mixture of 2-iodoethanal butyl 3-phenyl-2-propynyl acetal (355.0 mg, 0.99 mmol), AgOTs (22.4 mg, 0.080 mmol), and dichloroethane (0.3 mL) was added *i*-butyl magnesium chloride (2.0 M in THF, 0.6 mL, 1.2 mmol)



at 25 °C. After stirring for 3 h, D₂O was added to the solution at 25 °C. Then saturated aqueous NH₄Cl was added to the solution and the product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane/ethyl acetate = 10/0 to 8/2) afforded 185.9 mg (80%) of **15c** as a mixture of stereoisomers (*E/Z* = 42/58); IR (NaCl) 3055, 3023, 2957, 2930, 2869, 1601, 1496, 1463, 1445, 1422, 1350, 1179, 1097, 1036, 927, 767, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.12 (m, 5H), 5.34 (d, *J* = 7.1 Hz, 0.57H), 5.22 (d, *J* = 5.0 Hz, 0.43H), 4.69 (m, 0.86H), 4.64-4.52 (m, 1.14H), 3.75-3.68 (m, 1.0H), 3.47-3.40 (m, 1.0H), 2.96-2.91 (m, 1.0H), 2.86-2.82 (m, 0.57H), 2.74-2.70 (m, 0.43H), 1.58-1.51 (m, 2.0H), 1.40-1.31 (m, 2.0H), 0.91 (t, *J* = 7.3 Hz, 3.0H); ¹³C NMR (100 MHz, CDCl₃) (*Z* isomer): δ 138.5, 137.3, 128.3, 127.9, 126.4, 119.7 (t, *J* = 23.1 Hz), 104.3, 70.7, 67.1, 37.8, 31.6, 19.3, 13.8; (*E* isomer): δ 138.9, 137.3, 128.4, 127.8, 126.5, 121.1 (t, *J* = 23.1 Hz), 102.1, 67.8, 67.0, 41.0, 31.6, 19.3, 13.8; MS (EI) *m/z* (relative intensity, %) 160 (M⁺, 13), 132 (28), 131 (100), 130 (55), 129 (14), 128 (5), 117 (5), 116 (24), 115 (9), 92 (7), 91(5), 85 (5), 57 (5), 56 (10); HRMS (EI) calcd for C₁₅H₁₉DO₂ 233.1526 found 233.1523.

5,5-Dimethyl-1-phenyl-1,2-hexadiene (20):

A mixture of 1-phenylbuta-3-ene-1-yn (127.0 mg, 0.99 mmol), 2-iodo-2-methylpropane (334.1 mg, 1.8 mmol), PPh₃ (21.0 mg, 0.080 mmol), AgOTs (22.6 mg, 0.080 mmol), and TMEDA (207.8 mg, 1.8 mmol) was added



i-butyl magnesium chloride (2.0 M in THF, 0.6 mL, 1.2 mmol) at 0 °C. After stirring for 17 h, H₂O or D₂O was added to the solution at same temperature. Then aqueous 1N HCl was added to the solution and the product was extracted with ether, dried over MgSO₄, filtered on celite, and evaporated to give crude product. The volatile compounds were removed in vacuo and purification by silica gel column chromatography (*n*-hexane) afforded 128.0 mg (69%) and 136 mg (73%) of **20** and **20-d₁**, respectively. Spectral data for **20**: IR (NaCl) 3063, 3032, 2955, 1949, 1598, 1494, 1460, 1364, 1257, 1241, 1198, 1157, 1071, 1028, 909, 886, 868 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.16-7.30 (m, 5H), 6.09 (dt, *J* = 6.4, 2.6 Hz, 1H), 5.53 (dt, *J* = 8.3, 6.4 Hz, 1H), 2.03 (dd, *J* = 8.3, 2.6 Hz, 2H), 0.97 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) 206.2, 135.1, 128.5, 126.6, 126.5, 93.3, 91.8, 43.5, 31.1, 29.1; MS (EI) *m/z* (relative intensity, %) 186 (M⁺, 15), 171 (10), 143 (10), 130 (100), 129 (65), 115 (28), 91 (10), 57 (50); HRMS

(EI) calcd for C₁₄H₁₈ 186.1409 found 186.1405; Anal. Calcd for C₁₄H₁₈: C, 90.26; H, 9.74. found: C, 89.99; H, 9.71.

¹H NMR for **20-d₁**: ¹H NMR (400 MHz, CDCl₃) δ 7.16-7.30 (m, 5H), 5.53 (t, *J* = 8.3 Hz, 1H), 2.03 (d, *J* = 8.3 Hz, 2H), 0.97 (s, 9H).

Copies of ^1H and ^{13}C NMR Spectra of Isolated Products

