Supporting Information

Ni-Catalyzed Regioselective Three-Component Coupling of Alkyl Halides, Arylalkynes, or Enynes with Ar-M (M = MgX, ZnX)

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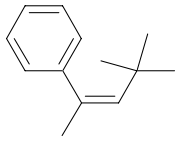
General

^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL JNM-Alice 400 spectrometer (400 MHz and 100 MHz, respectively). Chemical shifts are given in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were obtained with a Perkin-Elmer FT-IR (Model 1600). Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. GC Mass analyses (EI) were run using a JEOL JMS-mate operating in the electron impact mode (70 eV) equipped with a RTX-5 30MX.25MMX.25U column. Elemental analyses were performed on a Perkin Elmer 240C apparatus.

(Z)- 4,4-dimethyl-2-phenyl-2-pentene (**1a**):



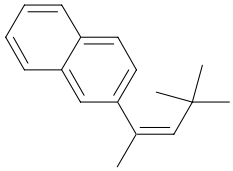
1a

To a mixture of phenylacetylene (49 mg, 0.48 mmol), 2-iodo-2-methylpropane (184 mg, 1.0 mmol), catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) and dppb (21 mg, 0.05 mmol) in Et_2O (2.5 mL) was added methylmagnesium bromide (3.0 M in Et_2O, 0.35 mL, 1.0 mmol) at 0 °C under nitrogen. After stirring for 1 h at 25 °C, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 60 mg (73%) of **1a**.

IR(NaCl): 3058, 3021, 2958, 2866, 1600, 1494, 1475, 1446, 1432, 1395, 1360, 1074, 1029, 779, 764, 779, 728, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.30-7.19 (m, 3H), 7.14-7.11 (m, 2H), 5.44 (q, *J* = 1.4 Hz, 1H), 1.94 (d, *J* = 1.4 Hz, 3H), 0.85 (s, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 5.44 caused 4.9% enhancement of allyl protons (vinyl-CH_3) δ 1.94; ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 143.8, 137.0, 134.6, 128.3, 127.7, 126.1, 33.3, 31.4, 29.5; MS (EI) *m/z* (relative intensity, %): 174 (M, 50), 160

(13), 159 (100), 144 (10), 131 (19), 129 (13), 128 (14), 117 (72), 115 (13), 105 (13), 92 (15); HRMS (EI) calcd for $C_{13}H_{18}$: 174.1409, found 174.1419. Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. found: C, 89.59; H, 10.38.

(Z)-4,4-dimethyl-2-naphthyl-2-pentene (**1b**):



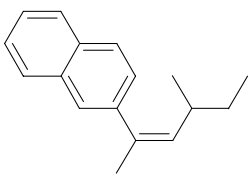
1b

To a mixture of 2-naphthylacetylene (74 mg, 0.48 mmol), 2-iodo-2-methylpropane (184 mg, 1.0 mmol), catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) and dppb (21 mg, 0.05 mmol) in Et_2O (2.5 mL) was added methylmagnesium bromide (3.0 M in Et_2O, 0.35 mL, 1.0 mmol) at 0 °C under nitrogen. After stirring for 1 h at 25 °C, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 86 mg (79%) of **1b**.

To a mixture of 2-naphthylacetylene (74 mg, 0.48 mmol), 2-bromo-2-methyl-propane (140 mg, 1.0 mmol), catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) and dppb (21 mg, 0.05 mmol) in Et_2O (2.5 mL) was added methylmagnesium iodide (1.0 M in Et_2O, 1.0 mL, 1.0 mmol) at 0 °C under nitrogen. After stirring for 4 h at 25 °C, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 65 mg (60%) of **1b**.

IR(NaCl): 3054, 2958, 2904, 2865, 1598, 1504, 1474, 1462, 1446, 1434, 1360, 1199, 1016, 894, 855, 819, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.83-7.76 (m, 3H), 7.58 (t, *J* = 0.7 Hz, 1H), 7.48-7.41 (m, 2H), 7.29 (dd, *J* = 1.7, 8.3 Hz, 1H), 5.53 (q, *J* = 1.5 Hz, 1H), 2.01 (d, *J* = 1.5 Hz, 3H), 0.87 (s, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 5.53 caused 7.7% enhancement of allyl protons (vinyl-CH_3) δ 2.01; ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 141.3, 137.5, 134.4, 133.1, 132.0, 127.7, 127.6, 127.3, 127.2, 126.4, 125.9, 125.4, 33.4, 31.5, 29.4; MS (EI) *m/z* (relative intensity, %): 224 (M, 47), 210 (17), 209 (100), 194 (16), 179 (28), 178 (13), 167 (19), 165 (15), 152 (12), 105 (13), 92 (15); HRMS (EI) calcd for $C_{17}H_{20}$: 224.1565, found 224.1557. Anal. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99. found: C, 90.76; H, 8.88.

(Z)-4-methyl-2-naphthyl-2-hexene (**1c**):

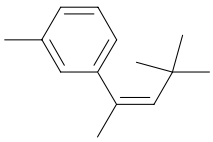


1c

To a mixture of 2-naphthylacetylene (73 mg, 0.48 mmol), 2-iodobutane (186 mg, 1.0 mmol), catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) and dppb (21 mg, 0.05 mmol) in Et_2O (2.5 mL) was added methylmagnesium bromide (3.0 M in Et_2O, 0.35 mL, 1.0 mmol) at 0 °C under nitrogen. After stirring for 5 h at 25 °C, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 57 mg (54%) of **1c** as a mixture of stereoisomers (*E*/*Z* = 3/97).

IR(NaCl): 3056, 2960, 2924, 2865, 2870, 2852, 1508, 1455, 1375, 854, 818, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.83-7.79 (m, 3H), 7.60 (s, 1H), 7.48-7.42 (m, 2H), 7.31 (dd, *J* = 1.1, 8.4 Hz, 1H), 5.28 (d, *J* = 10.1 Hz, 1H), 2.19-2.02 (m, 1H), 2.10 (s, 3H), 1.28-1.21 (m, 2H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.78 (t, *J* = 7.4 Hz, 3H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 5.28 caused 7.9% enhancement of allyl protons (vinyl-CH_3) δ 2.10; ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 140.4, 135.0, 134.5, 133.3, 132.1, 127.8, 127.6, 127.5, 126.8, 126.2, 125.9, 125.4, 34.7, 30.3, 25.9, 21.1, 11.9; MS (EI) *m/z* (relative intensity, %): 224 (M, 43), 209 (15), 196 (16), 195 (100), 180 (20), 179 (16), 178 (13), 168 (7), 167 (12), 166 (9), 165 (29), 153 (13), 152 (10), 141 (7), 128 (6) ; HRMS (EI) calcd for $C_{17}H_{20}$: 224.1565, found 224.1566. Anal. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99. found: C, 90.76; H, 8.98.

(Z)-4,4-dimethyl-2-(3-methylphenyl)-2-pentene (**1e**):



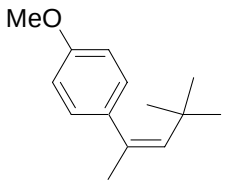
1e

To a mixture of 3-ethynyltoluene (58 mg, 0.48 mmol), 2-iodo-2-methylpropane (184 mg, 1.0 mmol), catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) and dppb (21 mg, 0.05 mmol) in Et_2O (2.5 mL) was added methylmagnesium bromide (3.0 M in Et_2O, 0.35 mL, 1.0 mmol) at 0 °C under nitrogen. After stirring for 1 h at 25 °C, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 70 mg (77%) of **1e**.

Isolated yield 77% (70 mg, colorless liquid)

IR(NaCl): 3033, 2958, 2865, 1602, 1475, 1462, 1446, 1433, 1360, 1204, 1020, 788, 770, 710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.17 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.94-6.91 (m, 2H), 5.41 (q, *J* = 1.5 Hz, 1H), 2.34 (s, 3H), 1.93 (d, *J* = 1.5 Hz, 3H), 0.85 (s, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 5.41 caused 8.5% enhancement of allyl protons (vinyl-CH_3) δ 1.93; ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 143.7, 137.1, 136.7, 134.7, 129.0, 127.5, 126.8, 125.4, 33.3, 31.4, 29.5, 21.4; MS (EI) *m/z* (relative intensity, %): 188 (M, 53), 174 (14), 173 (100), 158 (11), 145 (12), 143 (9), 131 (42), 119 (8), 115 (8); HRMS (EI) calcd for $C_{14}H_{20}$: 188.1565, found 188.1559. Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. found: C, 89.19; H, 10.61.

(Z)-2-(4-methoxylphenyl)-4,4-dimethyl-2-pentene (**1f**):

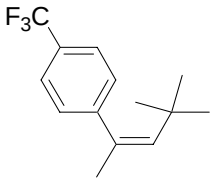


1f

To a mixture of 4-ethynylanisole (61 mg, 0.46 mmol), 2-iodo-2-methylpropane (184 mg, 1.0 mmol), catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) and dppb (21 mg, 0.05 mmol) in Et_2O (2.5 mL) was added methylmagnesium bromide (3.0 M in Et_2O, 0.35 mL, 1.0 mmol) at 0 °C under nitrogen. After stirring for 1 h at 25 °C, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (pentane/ether = 98/2) gave 74 mg (78%) of **1f**.

IR(NaCl): 2957, 2905, 2864, 1608, 1509, 1463, 1286, 1244, 1174, 1037, 831, 675 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.04 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.43 (q, *J* = 1.2 Hz, 1H), 3.80 (s, 3H), 1.92 (d, *J* = 1.2 Hz, 3H), 0.85 (s, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 5.43 caused 11.0% enhancement of allyl protons (vinyl-CH_3) δ 1.92; ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 160.0, 137.2, 136.0, 134.2, 129.3, 113.1, 55.2, 33.3, 31.4, 30.0; MS (EI) *m/z* (relative intensity, %): 204 (M, 37), 190 (16), 189 (100), 174 (14), 159 (7), 147 (9); HRMS (EI) calcd for $C_{14}H_{20}O$: 204.1514, found 204.1521. Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. found: C, 82.03; H, 9.81.

(Z)-2-(4-trifluoromethylphenyl)-4,4-dimethyl-2-pentene (**1g**):



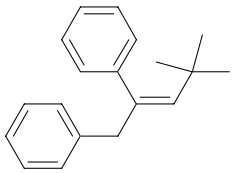
1g

To a mixture of 4-ethynyltrifluoromethylbenzene (75 mg, 0.44 mmol), 2-iodo-2-methylpropane (184 mg, 1.0 mmol), catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) and dppb (21 mg, 0.05 mmol) in Et_2O (2.5 mL) was added methylmagnesium bromide (3.0 M in Et_2O, 0.35 mL, 1.0 mmol) at 0 °C under nitrogen. After stirring for 1 h at 25 °C, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 63 mg (68%) of **1g**.

IR(NaCl): 2961, 2905, 2868, 1614, 1324, 1165, 1128, 1106, 1078, 1063, 1019, 843, 620 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 5.49 (q, *J* = 1.5 Hz, 1H), 1.94 (d, *J*

= 1.5 Hz, 3H), 0.85 (s, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 5.49 caused 14.2% enhancement of allyl protons (vinyl-CH_3) δ 1.94; ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 147.8 (q, *J* = 1.7 Hz,) 138.0, 133.1, 128.7, 128.4 (q, *J* = 32.3 Hz), 124.8 (q, *J* = 4.1 Hz,), 124.3 (q, *J* = 272.3 Hz,), 33.4, 31.4, 29.1; MS (EI) *m/z* (relative intensity, %): 242 (M, 53), 228 (14), 227 (100), 223 (9), 199 (21), 185 (73), 173 (53), 165 (14), 159 (17), 128 (9), 115 (10), 43 (68), 41 (11); HRMS (EI) calcd for $C_{14}H_{17}F_3$: 242.1282, found 242.1286. Anal. Calcd for $C_{14}H_{17}F_3$: C, 69.40; H, 7.07. found: C, 69.29; H, 7.08.

(Z)-4,4-dimethyl-1,2-diphenyl-2-pentene (**1h**):

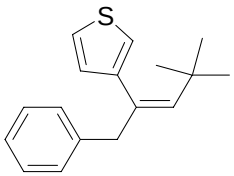


1h

To a mixture of phenylacetylene (50 mg, 0.49 mmol), 2-iodo-2-methylpropane (184 mg, 1.0 mmol), catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) and dppb (21 mg, 0.05 mmol) in Et_2O (2.5 mL) was added benzylmagnesium chloride (1.0 M in Et_2O, 1.0 mL, 1.0 mmol) at 0 °C under nitrogen. After stirring for 1 h at 25 °C, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 78 mg (64%) of **1h**.

IR(NaCl): 3079, 3060, 3027, 2956, 2901, 2866, 1600, 1494, 1474, 1454, 1441, 1360, 1030, 762, 746, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.23-7.13 (m, 6H), 7.06-7.04 (m, 2H), 6.90-6.87 (m, 2H), 5.53 (t, *J* = 1.2 Hz, 1H), 3.48 (s, 2H), 0.86 (s, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 5.53 caused 7.6% enhancement of allyl protons (vinyl-CH_2) δ 3.48; ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 139.8, 138.8, 138.0, 129.2, 129.1, 128.0, 127.3, 126.1, 125.9, 49.0, 33.4, 31.4; MS (EI) *m/z* (relative intensity, %): 250 (M, 56), 207 (20), 178 (14), 160 (11), 159 (100), 158 (12), 157 (44), 129 (24), 128 (14), 119 (16), 117 (31), 115 (16), 105 (21), 91 (74), 57 (13); HRMS (EI) calcd for $C_{19}H_{22}$: 250.1721, found 250.1728. Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. found: C, 91.00; H, 8.86.

(Z)-4,4-dimethyl-1-phenyl-2-(3-thienyl)-2-pentene (**1i**):

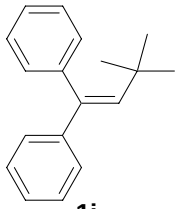


1i

To a mixture of 3-ethynylthiophene (74 mg, 0.49 mmol), 2-iodo-2-methylpropane (184 mg, 1.0 mmol), catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) and dppb (21 mg, 0.05 mmol) in Et_2O (2.5 mL) was added benzylmagnesium chloride (1.0 M in Et_2O, 1.0 mL, 1.0 mmol) at 0 °C under nitrogen. After stirring for 1 h at 25 °C, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 100 mg (80%) of **1i**.

IR(NaCl): 3027, 2955, 2900, 2865, 1494, 1474, 1453, 1359, 857, 794, 768, 746, 701, 682 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.25-7.05 (m, 6H), 6.65-6.62 (m, 2H), 6.64 (dt, *J* = 1.4, 4.9 Hz 1H), 5.61 (s, 1H), 3.44 (s, 2H), 0.86 (s, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 5.61 caused 5.7% enhancement of allyl protons (vinyl-CH_2) δ 3.44; ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 141.1, 140.7, 140.0, 133.1, 129.1, 129.0, 128.0, 125.9, 123.8, 121.7, 48.5, 33.3, 31.1; MS (EI) *m/z* (relative intensity, %): 256 (M, 99), 242 (12), 241 (57), 213 (12), 185 (11), 166 (14), 165 (100), 157 (31), 129 (20), 119 (13), 115 (14), 111 (13), 97 (27), 91 (38), 57 (17); HRMS (EI) calcd for $C_{17}H_{20}S$: 256.1286, found 256.1296. Anal. Calcd for $C_{17}H_{20}S$: C, 79.63; H, 7.86. found: C, 79.49; H, 7.98.

3,3-dimethyl-1,1-diphenyl-1-butene (**1j**):

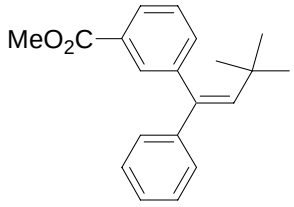


1j

A mixture of $ZnCl_2$ (0.5 M in THF, 1.2 mL, 0.6 mmol) and phenylmagnesium bromide (2.0 M in THF, 0.6 mL, 1.2 mmol) in CH_3CN (1.8 mL) was stirred at 0 °C for 10 min under nitrogen. To the resulting solution was added phenylacetylene (49 mg, 0.48 mmol), 2-iodo-2-methylpropane (110 mg, 0.6 mmol), dppb (21 mg, 0.05 mmol), and then catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) at 0 °C. After stirring for 1 h at 25 °C, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by HPLC with $CHCl_3$ as an eluent gave 93 mg (82%) of **1j**.

IR(NaCl): 3057, 3022, 2958, 2902, 2866, 1494, 1475, 1461, 1444, 1360, 782, 763, 752, 726, 702, 640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.36-7.15 (m, 10H), 6.08 (s, 1H), 0.96 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 144.1, 140.8, 141.0, 139.0, 130.3, 128.0, 127.7, 126.8. 126.7, 126.5, 34.0, 31.3; MS (EI) *m/z* (relative intensity, %): 236 (M, 61), 222 (18), 221 (100), 193 (11), 191 (11), 178 (17), 165 (18), 143 (60), 128 (17), 105 (19), 91 (36); HRMS (EI) calcd for $C_{18}H_{20}$: 236.1565, found 236.1550. Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. found: C, 91.23; H, 8.38.

(Z)-1-(3-methoxycarbonyphenyl)-3,3-dimethyl-1-phenyl-1-butene (**1k**):

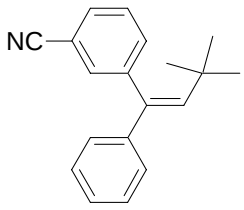


1k

A mixture of $ZnCl_2$ (0.5 M in THF, 1.2 mL, 0.6 mmol) and phenylmagnesium bromide (2.0 M in THF, 0.6 mL, 1.2 mmol) in CH_3CN (1.8 mL) was stirred at 0 °C for 10 min under nitrogen. To the resulting solution was added 3-methoxycarbonylphenylacetylene (75 mg, 0.47 mmol), 2-iodo-2-methylpropane (110 mg, 0.6 mmol), dppb (21 mg, 0.05 mmol), and then catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) at 0 °C. After stirring for 1 h at 25 °C, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (hexane/CH_2Cl_2 = 1/1) gave 93 mg (68%) of **1k** as a mixture of stereoisomers (*E*/*Z* = 2/98).

mp: 55-57 °C; IR(NaCl): 2955, 1725, 1439, 1290, 1258, 1156, 1105, 763, 749, 706 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.99 (dt, *J* = 1.7, 7.3 Hz, 1H), 7.89 (t, *J* = 1.7 Hz, 1H), 7.45-7.15 (m, 7H), 6.12 (s, 1H), 3.91 (s, 3H), 0.95 (s, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 6.12 caused 9.5% enhancement of phenyl protons (vinyl-C*CH*) δ 7.15; ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 167.1, 143.6, 141.1, 140.9, 138.0, 134.9, 131.3, 129.8, 128.1, 128.1, 128.0, 127.0, 126.8, 52.1, 34.1, 31.4; MS (EI) *m/z* (relative intensity, %): 294 (M, 75), 280 (20), 279 (100), 247 (27), 235 (44), 205 (19), 165 (18), 143 (29), 124 (16), 105 (18), 91 (19); HRMS (EI) calcd for $C_{20}H_{22}O_2$: 294.1620, found 294.1636. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. found: C, 81.53; H, 7.67.

(Z)-1-(3-cyanophenyl)-3,3-dimethyl-1-phenyl-1-butene (**1l**):

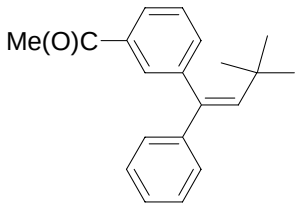


1l

A mixture of $ZnCl_2$ (0.5 M in THF, 1.2 mL, 0.6 mmol) and phenylmagnesium bromide (2.0 M in THF, 0.6 mL, 1.2 mmol) in CH_3CN (1.8 mL) was stirred at 0 °C for 10 min under nitrogen. To the resulting solution was added 3-cyanophenylacetylene (61 mg, 0.48 mmol), 2-iodo-2-methylpropane (110 mg, 0.6 mmol), dppb (21 mg, 0.05 mmol), and then catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) at 0 °C. After stirring for 1 h at 25 °C, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (hexane/CH_2Cl_2 = 1/1) gave 70 mg (56%) of **1l** as a mixture of stereoisomers (*E*/*Z* = 4/96).

mp: 88-90 °C; IR(NaCl): 2960, 2902, 2867, 2229, 1575, 1476, 1462, 1445, 1363, 791, 752, 710, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.62-7.10 (m, 9H), 6.14 (s, 1H), 3.91 (s, 3H), 0.95 (s, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 6.14 caused 6.2% enhancement of phenyl protons (vinyl-C*CH*) δ 7.11; ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 142.9, 142.2, 141.7, 136.8, 134.8, 133.7, 130.7, 128.7, 128.2, 127.1, 126.8, 118.8, 112.1, 34.1, 31.4; MS (EI) *m/z* (relative intensity, %): 261 (M, 47), 247 (20), 246 (100), 190 (12), 168 (23), 130 (18), 116 (12), 91 (12); HRMS (EI) calcd for $C_{14}H_{19}N$: 261.1517, found 261.1514. Anal. Calcd for $C_{14}H_{19}N$: C, 87.31; H, 7.33.; N, 5.36. found: C, 87.03; H, 7.24.; N, 5.29.

(Z)-1-(3-acetylphenyl)-3,3-dimethyl-1-phenyl-1-butene (**1m**):

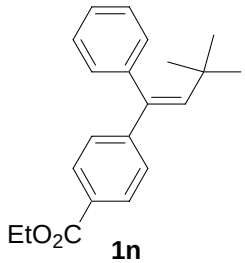


1m

A mixture of $ZnCl_2$ (0.5 M in THF, 1.2 mL, 0.6 mmol) and phenylmagnesium bromide (2.0 M in THF, 0.6 mL, 1.2 mmol) in CH_3CN (1.8 mL) was stirred at 0 °C for 10 min under nitrogen. To the resulting solution was added 3-acetylphenylacetylene (69 mg, 0.48 mmol), 2-iodo-2-methylpropane (110 mg, 0.6 mmol), dppb (21 mg, 0.05 mmol), and then catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) at 0 °C. After stirring for 1 h at 25 °C, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (hexane/ether = 8/2) gave 53 mg (40%) of **1m** as a mixture of stereoisomers (*E*/*Z* = 3/97).

IR(NaCl): 2959, 2902, 2866, 1688, 1475, 1426, 1357, 1283, 1253, 792, 772, 752, 708, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.91 (dt, *J* = 1.7, 7.3 Hz, 1H), 7.80 (t, *J* = 1.7 Hz, 1H), 7.47-7.14 (m, 7H), 6.13 (s, 1H), 3.91 (s, 3H), 0.95 (s, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 6.13 caused 7.0% enhancement of phenyl protons (vinyl-C*CH*) δ 7.13; ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 198.1, 143.5, 141.3, 140.9, 138.0, 136.7, 135.1, 130.1, 128.1, 126.9, 126.9, 126.8, 34.0, 31.4, 26.7; MS (EI) *m/z* (relative intensity, %): 278 (M, 100), 264 (23), 263 (99), 235 (45), 221 (23), 205 (16), 178 (14), 165 (18), 143 (18), 124 (17), 91 (18), 43 (100); HRMS (EI) calcd for $C_{20}H_{22}O$: 278.1671, found 278.1662. Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. found: C, 86.05; H, 7.90.

(E)-1-(4-ethoxycarbonyphenyl)-3,3-dimethyl-1-phenyl-1-butene (**1n**):

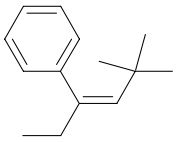


1n

A mixture of 4-(ethoxycarbonyl)phenylzinc iodide (0.5 M in THF, 1.5 mL, 0.75 mmol) and trimethylsilylmethylmagnesium chloride (0.58 M in THF, 1.25 mL, 0.75 mmol) in CH_3CN (2.7 mL) was stirred at 0 °C for 10 min under nitrogen. To the resulting solution was added phenylacetylene (77 mg, 0.49 mmol), 2-iodo-2-methylpropane (110 mg, 0.6 mmol), dppb (21 mg, 0.05 mmol), and then catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) at 0 °C. After stirring for 1 h at 25 °C, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by HPLC with $CHCl_3$ as an eluent gave 72 mg (47%) of **1n**.

IR(NaCl): 2959, 2903, 1716, 1606, 1366, 1276, 1250, 1182, 1105, 1021, 853, 758, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 8.02 (d, *J* = 7.7 Hz, 2H), 7.30-7.13 (m, 7H), 6.11 (s, 1H), 3.93 (s, 3H), 0.95 (s, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 6.11 caused 9.4% enhancement of phenyl protons (vinyl-C*CH*) δ 7.14; ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 167.1, 146.1, 143.3, 140.7, 138.1, 130.4, 129.1, 128.7, 128.1, 126.8, 126.8, 52.1, 34.0, 31.3; MS (EI) *m/z* (relative intensity, %): 294 (M, 62), 280 (18), 279 (89), 247 (25), 236 (20), 235 (100), 205 (24), 165 (18), 157 (22), 143 (33), 124 (19), 105 (26), 91 (26); HRMS (EI) calcd for $C_{20}H_{22}O_2$: 294.1620, found 294.1634. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. found: C, 81.32; H, 7.38.

(Z)- 2,2-dimethyl-4-phenyl-3-hexene (**2a**):



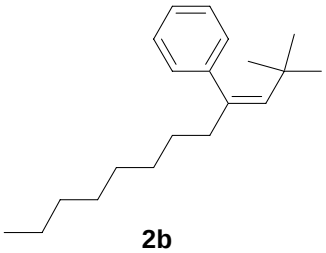
2a

To a mixture of phenylacetylene (50 mg, 0.48 mmol), 2-iodo-2-methylpropane (184 mg, 1.0 mmol), catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) and dppb (21 mg, 0.05 mmol) in Et_2O (2.5 mL) was added ethylmagnesium chloride (2.0 M in Et_2O, 0.5 mL, 1.0 mmol) at 0 °C under nitrogen. After stirring for 3 h, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by HPLC with $CHCl_3$ as an eluent gave 67 mg (72%) of **2a**.

IR(NaCl): 2957, 2903, 2871, 1494, 1475, 1461, 1446, 1360, 771, 756, 726, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.30-7.19 (m, 3H), 7.10-7.07 (m, 2H), 5.39 (t, *J* = 1.4 Hz 1H), 2.22-2.16 (m, 2H), 0.92 (t, *J* = 7.5 Hz 3H), 0.84 (s, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 5.39 caused 6.2% enhancement of allyl protons (vinyl-CH_2) δ 2.22-2.16; ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 142.6,

140.4, 135.7, 129.0, 127.4, 126.0, 35.3, 33.1, 31.5; MS (EI) *m/z* (relative intensity, %): 188 (M, 78), 173 (51), 160 (13), 159 (93), 145 (18), 143 (10), 131 (100), 129 (16), 128 (18), 117 (60), 115 (18), 105 (13), 91 (30), 57 (18); HRMS (EI) calcd for $C_{14}H_{20}$: 188.1565, found 188.1566. Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. found: C, 89.25; H, 10.60.

(Z)- 2,2-dimethyl-4-phenyl-3-dodecene (**2b**):

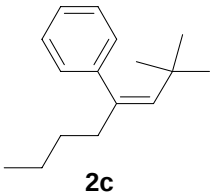


2b

To a mixture of phenylacetylene (50 mg, 0.49 mmol), 2-iodo-2-methylpropane (184 mg, 1.0 mmol), catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) and dppb (21 mg, 0.05 mmol) in Et_2O (2.5 mL) was added octylmagnesium bromide (2.0 M in Et_2O, 0.5 mL, 1.0 mmol) at 0 °C under nitrogen. After stirring for 3 h, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 112 mg (84%) of **2b**.

IR(NaCl): 2956, 2927, 2855, 1463, 1441, 1359, 769, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.29-7.19 (m, 3H), 7.09-7.07 (m, 2H), 5.39 (s, 1H), 2.17 (t, *J* = 6.8 Hz, 2H), 1.33-1.18 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.84 (s, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 5.39 caused 7.3% enhancement of allyl protons (vinyl-CH_2) δ 2.17;^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 142.6, 138.8, 136.9, 129.0, 127.4, 126.0, 42.5, 33.2, 31.9, 31.5, 29.5, 29.3, 29.1, 27.9, 22.7, 14.1; MS (EI) *m/z* (relative intensity, %): 272 (M, 26), 257 (21), 174 (17), 160 (14), 159 (100), 145 (39), 143 (10), 131 (27), 118 (43), 117 (32), 91 (24), 69 (10), 57 (12); HRMS (EI) calcd for $C_{20}H_{32}$: 272.2504, found 272.2513. Anal. Calcd for $C_{20}H_{32}$: C, 88.16; H, 11.84. found: C, 88.14; H, 11.68.

(Z)- 2,2-dimethyl-4-phenyl-3-octene (**2c**):



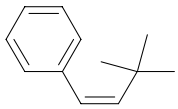
2c

To a mixture of phenylacetylene (50 mg, 0.48 mmol), 2-iodo-2-methylpropane (184 mg, 1.0 mmol), catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) and dppb (21 mg, 0.05 mmol) in Et_2O (2.5 mL) was added

buthyllmagnesium chloride (2.0 M in Et_2O, 0.5 mL, 1.0 mmol) at 0 °C under nitrogen. After stirring for 3 h, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 85 mg (81%) of **2c**.

IR(NaCl): 2957, 2861, 1493, 1475, 1466, 1441, 1359, 765, 725, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.29-7.19 (m, 3H), 7.10-7.07 (m, 2H), 5.40 (s, 1H), 2.17 (d, *J* = 6.8 Hz, 2H), 1.32-1.20 (m, 4H), 0.86 (t, *J* = 6.8 Hz, 3H) 0.87-0.82 (m, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 5.40 caused 5.6% enhancement of allyl protons (vinyl-CH_2) δ 2.17;^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 142.6, 138.7, 136.8, 129.0, 127.4, 126.0, 42.2, 33.2, 31.5, 30.2, 22.2, 14.0; MS (EI) *m/z* (relative intensity, %): 216 (M, 42), 201 (27), 174 (11), 160 (13), 159 (100), 145 (51), 131 (37), 128 (11), 118 (19), 117 (46), 115 (12), 91 (28), 69 (10); HRMS (EI) calcd for $C_{16}H_{24}$: 216.1878, found 216.1887. Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. found: C, 88.89; H, 10.89.

(Z)- 3,3-dimethyl-1-phenyl-1-butene (**3**):

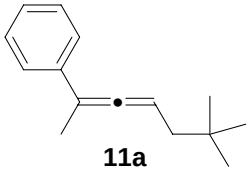


3

To a mixture of phenylacetylene (49 mg, 0.48 mmol), 2-iodo-2-methylpropane (184 mg, 1.0 mmol), catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol) and dppb (21 mg, 0.05 mmol) in Et_2O (2.5 mL) was added *tert*-butylmagnesium chloride (2.0 M in Et_2O, 0.5 mL, 1.0 mmol) at 0 °C under nitrogen. After stirring for 3 h, aqueous 1 N HCl was added to the solution, and the product was extracted with ether, dried over $MgSO_4$ and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 62 mg (81%) of **3**.

IR(NaCl): 3021, 2993, 2959, 2904, 2867, 1492, 1476, 1462, 1360, 1201, 754, 729, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(*Z* isomer): δ 7.29-7.25 (m, 2H), 7.21-7.17 (m, 3H), 6.41 (d, *J* = 12.7 Hz, 1H), 5.60 (d, *J* = 12.7 Hz, 1H), 0.98 (s, 9H); NOE difference measurement: irradiation of vinyl proton (vinyl-*H*) at δ 5.60 caused 8.2% enhancement of allyl protons (vinyl-CH_3) δ 6.41; ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 142.6, 139.4, 128.9, 127.5, 127.1, 126.2, 34.2, 31.2; MS (EI) *m/z* (relative intensity, %): 160 (M, 29), 146 (11), 145 (100), 130 (12), 128 (9), 115 (8), 105 (8), 117 (19), 91 (20); HRMS (EI) calcd for $C_{12}H_{16}$: 160.1252, found 160.1243. Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. found: C, 89.84; H, 10.02.

6,6-dimethyl-2-phenyl-hepta-2,3-diene (**11a**):

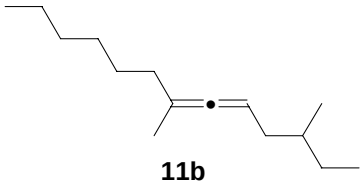


11a

A mixture of $ZnCl_2$ (0.5 M in THF, 2.0 mL, 1.0 mmol) and methylmagnesium bromide (1.0 M in THF, 2.0 mL, 2.0 mmol) was stirred for 10 min under nitrogen. To the resulting solution was added 4-phenyl-but-1-en-3-yne (64 mg, 0.50 mmol), 2-iodo-2-methylpropane (110 mg, 0.6 mmol), dppb (21 mg, 0.05 mmol), and then catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol). After stirring for 12 h at 25 °C, a saturated aqueous NH_4Cl was added to the solution, and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 77 mg (77%) of **11a**.

IR(NaCl): 2955, 2866, 1949, 1740, 1493, 1475, 1445, 1314, 1027, 759, 692, 604 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.33-7.29 (m, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 5.44-5.38 (m, 1H), 2.09 (d, *J* = 2.9 Hz, 3H), 2.00 (d, *J* = 7.9 Hz, 2H), 0.97 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.3, 137.7, 128.2, 126.2, 125.6, 98.9, 89.8, 43.7, 31.1, 29.2, 17.2; MS (EI) *m/z* (relative intensity, %): 200 (M, 8), 145 (10), 144 (75), 143 (47), 141 (9), 130 (10), 129 (100), 128 (42), 127 (10), 115 (8), 91 (7), 57 (27); HRMS (EI) calcd for $C_{15}H_{20}$: 200.1565, found 200.1574.

3,7-dimethyl-trideca-5,6-diene (**11b**):



11b

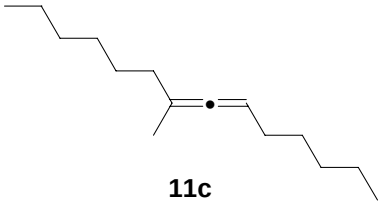
A mixture of $ZnCl_2$ (0.5 M in THF, 2.0 mL, 1.0 mmol) and methylmagnesium bromide (1.0 M in THF, 2.0 mL, 2.0 mmol) was stirred for 10 min under nitrogen. To the resulting solution was added dec-1-en-3-yne (63 mg, 0.46 mmol), 2-iodobutane (110 mg, 0.6 mmol), dppb (21 mg, 0.05 mmol), and then catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol). After stirring for 15 h at 25 °C, a saturated aqueous NH_4Cl was added to the solution, and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 75 mg (78%) of **11b**.

A mixture of $ZnCl_2$ (0.5 M in THF, 2.0 mL, 1.0 mmol) and methylmagnesium bromide (1.0 M in THF, 2.0 mL, 2.0 mmol) was stirred for 10 min under nitrogen. To the resulting solution was added dec-1-en-3-yne (63 mg, 0.46 mmol), 2-bromobutane (82 mg, 0.6 mmol), dppb (21 mg, 0.05 mmol), and then catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol). After stirring for 12 h at reflux, a saturated aqueous NH_4Cl was added to the solution, and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by HPLC with $CHCl_3$ as an eluent gave 57 mg (60%) of **11b**.

IR(NaCl): 2959, 2927, 2873, 2856, 1965, 1461, 1377, 607 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.96-4.90 (m, 1H), 2.00-1.75 (m, 4H), 1.66 (d, *J* = 2.9 Hz, 3H), 1.43-1.13 (m, 11H), 0.90-0.85 (m, 9H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 201.8, 98.5, 88.4, 36.7, 34.8, 34.1, 31.8, 29.0 (2C), 27.6, 22.7, 19.2, 19.1, 14.1, 11.4; MS (EI) *m/z* (relative intensity, %): 208 (M, 2), 152 (40), 138 (38), 137 (11), 123 (33), 109 (82), 96 (20), 95 (100), 83 (11), 82 (77), 81 (83), 79 (16), 69 (22), 68 (58), 67 (29), 57 (20), 55 (23), 53 (10), 43 (14), 41 (34); HRMS (EI) calcd for $C_{15}H_{28}$: 208.2191, found 208.2183.

3,7-dimethyl-tetradeca-6,7-diene (**11c**):

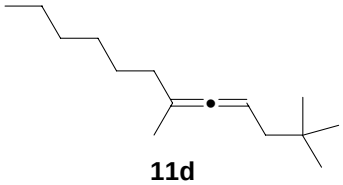


11c

A mixture of $ZnCl_2$ (0.5 M in THF, 2.0 mL, 1.0 mmol) and methylmagnesium bromide (1.0 M in THF, 2.0 mL, 2.0 mmol) was stirred for 10 min under nitrogen. To the resulting solution was added dec-1-en-3-yne (68 mg, 0.50 mmol), 1-iodobutane (110 mg, 0.6 mmol), dppb (21 mg, 0.05 mmol), and then catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol). After stirring for 20 h at 50 °C, a saturated aqueous NH_4Cl was added to the solution, and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by HPLC with $CHCl_3$ as an eluent gave 52 mg (50%) of **11c**.

IR(NaCl): 2957, 2926, 2872, 2856, 1965, 1466, 1378, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.00-4.96 (m, 1H), 1.97-1.89 (m, 4H), 1.66 (d, *J* = 2.9 Hz, 3H), 1.40-1.28 (m, 13H), 0.90-0.87 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 99.2, 90.1, 34.1, 31.8, 31.3, 29.3, 29.0, 27.5, 22.7, 22.5, 19.3, 14.1, 14.1; MS (EI) *m/z* (relative intensity, %): 208 (M, 1), 152 (31), 138 (46), 123 (21), 109 (21), 96 (17), 95 (100), 82 (75), 81 (75), 79 (14), 69 (19), 68 (65), 67 (30), 55 (22), 41 (18); HRMS (EI) calcd for $C_{15}H_{28}$: 208.2191, found 208.2199.

2,2,6-trimethyl-dodeca-4,5-diene (**11d**):

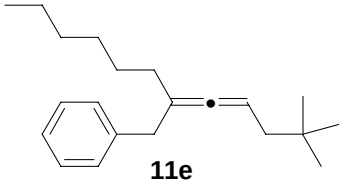


11d

A mixture of $ZnCl_2$ (0.5 M in THF, 2.0 mL, 1.0 mmol) and methylmagnesium bromide (1.0 M in THF, 2.0 mL, 2.0 mmol) was stirred for 10 min under nitrogen. To the resulting solution was added dec-1-en-3-yne (64 mg, 0.47 mmol), 2-bromo-2-methylpropane (82 mg, 0.6 mmol), dppb (21 mg, 0.05 mmol), and then catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol). After stirring for 20 h at 50 °C, a saturated aqueous NH_4Cl was added to the solution, and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 68 mg (70%) of **11d**.

IR(NaCl): 2956, 2930, 2859, 1965, 1466, 1390, 1364, 1242, 1198, 814 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.98-4.92 (m, 1H), 1.94-1.86 (m, 2H), 1.84 (d, *J* = 7.8 Hz, 2H), 1.66 (d, *J* = 2.9 Hz, 3H), 1.42-1.28 (m, 8H), 0.90 (s, 9H), (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)(*Z* isomer): δ 202.6, 97.7, 86.7, 44.4, 34.1, 31.8, 31.0, 29.1, 29.0, 27.6, 22.7, 19.2, 14.1; MS (EI) *m/z* (relative intensity, %): 208 (M, 1), 138 (43), 123 (11), 109 (12), 95 (31), 82 (79), 81 (27), 67 (12), 57 (100), 55 (10), 41 (19); HRMS (EI) calcd for $C_{15}H_{28}$: 208.2191, found 208.2186.

2,2-dimethyl-6-(phenylmethyl)-dodeca-4,5-diene (**11e**):

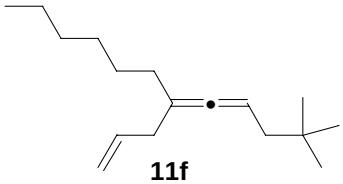


11e

A mixture of $ZnCl_2$ (0.5 M in THF, 2.0 mL, 1.0 mmol) and benzylmagnesium chloride (1.0 M in Et_2O, 2.0 mL, 2.0 mmol) was stirred for 10 min under nitrogen. To the resulting solution was added dec-1-en-3-yne (66 mg, 0.48 mmol), 2-iodo-2-methylpropane (110 mg, 0.6 mmol), dppb (21 mg, 0.05 mmol), and then catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol). After stirring for 12 h at 25 °C, a saturated aqueous NH_4Cl was added to the solution, and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by column chromatography on silica gel (pentane) gave 74 mg (54%) of **11e**.

IR(NaCl): 3028, 2955, 2928, 2859, 1961, 1494, 1465, 1454, 1364, 1242, 733, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.29-7.24 (m, 2H), 7.21-7.16 (m, 3H), 5.07-5.01 (m, 1H), 3.27 (d, *J* = 2.0 Hz, 2H), 1.91-1.82 (m, 4H), 1.41-1.20 (m, 8H), 0.91 (s, 9H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.3, 140.2, 128.9, 128.1, 126.0, 102.1, 88.2, 44.4, 40.2, 31.8, 31.7, 31.0, 29.1, 29.0, 27.6, 22.6, 14.1; MS (EI) *m/z* (relative intensity, %): 284 (M, 8), 227 (21), 214 (28), 199 (12), 158 (35), 157 (26), 144 (14), 143 (100), 129 (29), 128 (12), 91 (55), 57 (84), 41 (16); HRMS (EI) calcd for $C_{21}H_{32}$: 284.2504, found 284.2498.

4-hexyl-8,8-dimethyl-nona-1,4,5-triene (**11f**):



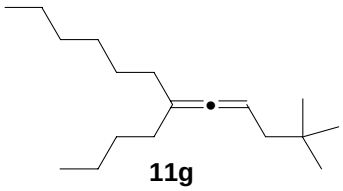
11f

A mixture of $ZnCl_2$ (0.5 M in THF, 2.0 mL, 1.0 mmol) and allylmagnesium chloride (2.0 M in THF, 1.0 mL, 2.0 mmol) was stirred for 10 min under nitrogen. To the resulting solution was added dec-1-en-3-yne (66 mg, 0.49 mmol), 2-iodo-2-methylpropane (110 mg, 0.6 mmol), dppb (21 mg, 0.05 mmol), and then catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol). After stirring for 20 h at 25 °C, a saturated aqueous NH_4Cl was added to the

solution, and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by HPLC with $CHCl_3$ as an eluent gave 63 mg (56%) of **11f**.

IR(NaCl): 2956, 2929, 2859, 1960, 1466, 1390, 1378, 1364, 1242, 1198, 727 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.87-5.76 (m, 1H), 5.08-4.98 (m, 3H), 2.69 (d, *J* = 6.3 Hz, 2H), 1.94-1.90 (m, 2H), 1.87 (d, *J* = 7.8 Hz, 2H), 1.42-1.28 (m, 8H), 1.41-1.20 (m, 8H), 0.91 (s, 9H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.5, 136.6, 115.3, 101.1, 88.5, 44.5, 37.8, 32.2, 31.8, 31.0, 29.1, 29.0, 27.6, 22.6, 14.1; MS (EI) *m/z* (relative intensity, %): 234 (M, 2), 177 (17), 121 (12), 108 (36), 107 (26), 93 (51), 91 (13), 79 (24), 77 (10), 57 (100), 55 (10), 41 (19); HRMS (EI) calcd for $C_{17}H_{30}$: 234.2347, found 234.2359.

6-butyl-2,2-dimethyl-dodeca-4,5-diene (**11g**):



11g

A mixture of $ZnCl_2$ (0.5 M in THF, 2.0 mL, 1.0 mmol) and butylmagnesium bromide (2.0 M in THF, 1.0 mL, 2.0 mmol) in cyclohexane (3.0 mL) was stirred for 10 min under nitrogen. To the resulting solution was added dec-1-en-3-yne (64 mg, 0.47 mmol), 2-iodo-2-methylpropane (110 mg, 0.6 mmol), dppb (21 mg, 0.05 mmol), and then catalytic amounts of $Ni(acac)_2$ (10 mg, 0.04 mmol). After stirring for 12 h at 25 °C, a saturated aqueous NH_4Cl was added to the solution, and the product was extracted with ether, dried over Na_2SO_4 and evaporated to give crude product. Purification by HPLC with $CHCl_3$ as an eluent gave 77 mg (66%) of **11g**.

IR(NaCl): 2955, 2929, 2859, 1962, 1638, 1467, 1432, 1364, 1242, 991, 912 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.02-4.95 (m, 1H), 1.91-1.83 (m, 6H), 1.38-1.26 (m, 12H), 0.92-0.85 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.0, 102.7, 88.2, 44.6, 32.7, 32.4, 31.8, 31.0, 29.2, 29.1, 27.8, 22.7, 22.4, 14.1, 14.0; MS (EI) *m/z* (relative intensity, %): 250 (M, 3), 180 (14), 138 (28), 137 (14), 124 (34), 123 (15), 109 (31), 95 (32), 82 (67), 81 (25), 79 (10), 69 (10), 67 (21), 57 (100), 55 (13), 41 (13); HRMS (EI) calcd for $C_{18}H_{34}$: 250.2661, found 250.2666.