

Supporting Information

Matched Coupling of Propargylic Carbonates with Cyclopropanols

Penglin Wu,^a Minqiang Jia,^{a,*} Weilong Lin,^b Shengming Ma^{a,b,*}

^a Research Center for Molecular Recognition and Synthesis, Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, P. R. China

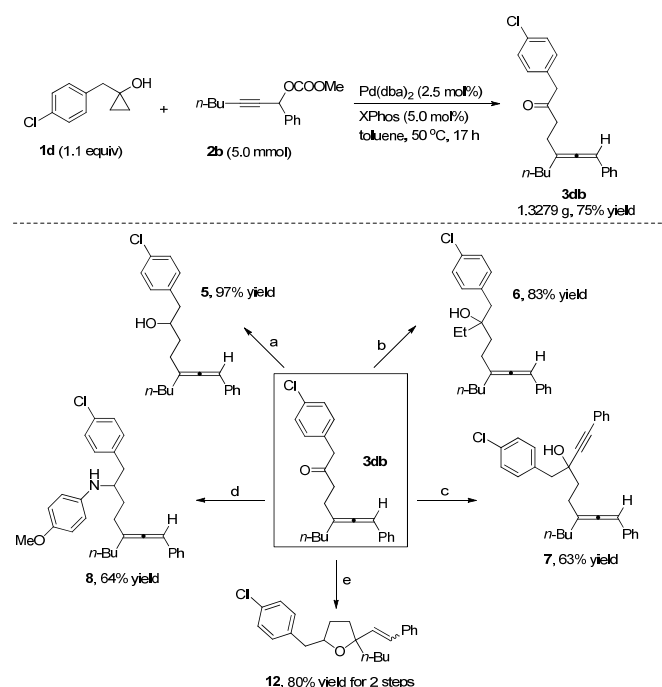
^b State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, P. R. China

Fax: (+86)21-64167510 E-mail: masm@sioc.ac.cn

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General Information. NMR spectra were taken with an Agilent-400 spectrometer (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR). Chemical shifts were recorded in ppm in relative to the TMS in CDCl_3 and coupling constants were reported in Hz. All reactions were carried out in flame-dried Schlenk tubes. $\text{Pd}(\text{dba})_2$ was purchased from J&K Chemicals; Xphos was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. Toluene was dried over sodium wire with benzophenone as the indicator and distilled freshly before use. All the temperatures are referred to the oil baths, acetone/dry ice bath, or ice/water bath used. NMR yields and recovery of starting material were determined by ^1H NMR analysis of the related reaction mixtures using dibromomethane as the internal standard. Cyclopropanols **1a-1c**,^{1a} **1d**,^{1b} **1e-1f**,^{1a} **1g-1i**,^{1c} **1j**,^{1d} **1k**,^{1e} **1l**,^{1a} were synthesized according to the reported procedures. Propargylic carbonates **2a-2e**,^{2b} (*R*)-**2e**,^{2b} **2h-2l**,^{2b} (*R*)-**2g**,^{2b,2d} (*R*)-**2m**,^{2b,2d} and propargylic acetate **10a**³ were synthesized from propargylic alcohols⁴ according to the reported procedures.

Scheme S1. Gram-scale synthesis and transformations of **3db**



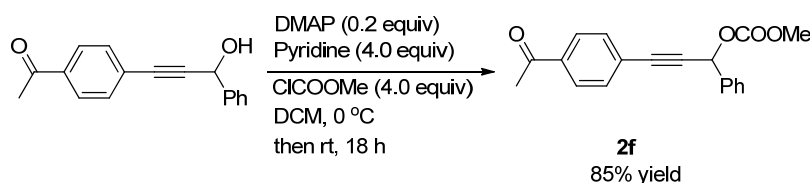
Reaction conditions: ^a NaBH_4 (1.5 equiv), MeOH, 0 °C, then rt, 2 h; ^b EtMgCl (2 equiv), THF, 0 °C, 2 h; ^c 1) phenylacetylene (2 equiv), *n*-BuLi (1.6 equiv), THF, -78 °C, then rt 30 min; 2) **3db** in THF, -78 °C, then rt, 3 h; ^d PMPNH₂ (2 equiv), NaBH₃CN (3 equiv), AcOH (1.75 equiv), MeOH, rt, 28 h. ^e 1) NaBH_4 (1.5 equiv), MeOH, 0 °C, then rt, 1 h, workup; 2) $\text{PPh}_3\text{AuNTf}_2$ (3 mol%), DCM, rt, 15 h.

Experimental details and analytical data

I. Synthesis of propargylic carbonates **2f**, **2g**, (*R*)-**2g**, and (*R*)-**2m**^{2b,2d}

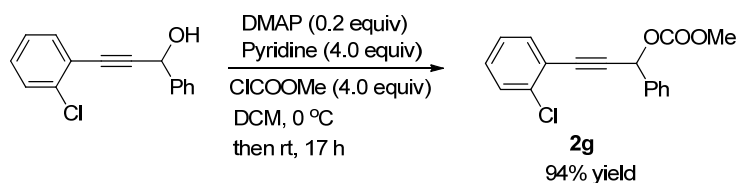
(1) Synthesis of 3-(4-acetylphenyl)-1-phenylprop-2-ynyl methyl carbonate

(**2f**)^{2b,2d} (wpl-1-75)



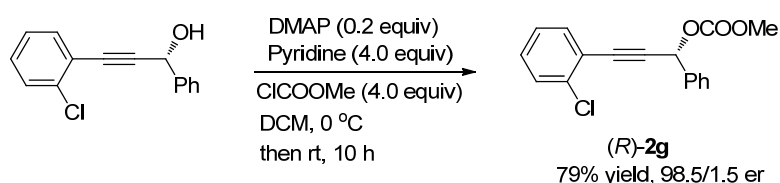
To a three-necked flask were added 3-(4-acetylphenyl)-1-phenylprop-2-yn-1-ol^{2d} (1.52 g, 6.0 mmol), CH₂Cl₂ (20 mL), and DMAP (0.1470 g, 1.2 mmol). After being cooled to 0 °C with stirring, pyridine (2.0 mL, d = 0.983 g/mL, 1.966 g, 24.9 mmol) and methyl chloroformate (1.85 mL, d = 1.223 g/mL, 2.2626 g, 24.0 mmol) were added sequentially. The resulting mixture was naturally warmed up to room temperature, stirred overnight (18 h), and diluted with CH₂Cl₂ (40 mL). This CH₂Cl₂ solution was washed sequentially with water (40 mL), 1 mol/L HCl (aq) (30 mL × 3), a solution of NaCl (aq), dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 40/1 (0.4 L) to 20/1] to afford **2f** (1.5919 g, 85%) as an oil: ¹H NMR (400 MHz, CDCl₃) δ = 7.91 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.61 (dd, *J* = 7.8, 1.8 Hz, 2 H, ArH), 7.56 (d, *J* = 8.4 Hz, 2 H, ArH), 7.47-7.36 (m, 3 H, ArH), 6.54 (s, 1 H, CH), 3.84 (s, 3 H, CH₃), 2.60 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 197.3, 154.8, 136.7, 136.1, 132.0, 129.4, 128.8, 128.2, 127.8, 126.7, 88.0, 87.0, 70.0, 55.2, 26.6; IR (neat, cm⁻¹): ν = 2229, 1749, 1684, 1602, 1557, 1496, 1440, 1403, 1243, 1046; MS (70 eV, EI) *m/z* (%): 308 (M⁺, 47.24), 189 (100); HRMS calcd for C₁₉H₁₆O₄ [M⁺]: 308.1049, found: 308.1055.

(2) Synthesis of 3-(2-chlorophenyl)-1-phenylprop-2-ynyl methyl carbonate (**2g**)^{2b} (jmq4-43)



To a three-necked flask were added 3-(2-chlorophenyl)-1-phenylprop-2-yn-1-ol⁵ (2.30 g, 9.5 mmol) and CH₂Cl₂ (20 mL). After being cooled with an ice/water bath with stirring, DMAP (0.2340 g, 1.9 mmol) and pyridine (3.05 mL, d = 0.983 g/mL, 2.998 g, 37.9 mmol) were added sequentially. Then methyl chloroformate (2.9 mL, d = 1.223 g/mL, 3.5467 g, 37.9 mmol) was added slowly. After the addition, the resulting mixture was warmed up naturally to room temperature and stirred overnight (17 h). The resulting mixture was then diluted with CH₂Cl₂ (20 mL), and the CH₂Cl₂ solution was washed with water (20 mL), 1 mol/L HCl (aq) (20 mL × 3), dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 30/1 (1.6 L)] to afford **2g** (2.6703 g, 94%) as an oil: ¹H NMR (400 MHz, CDCl₃) δ = 7.66 (dd, *J* = 8.0, 1.6 Hz, 2 H, ArH), 7.51 (dd, *J* = 7.4 Hz, 1.8 Hz, 1 H, ArH), 7.47-7.35 (m, 4 H, ArH), 7.32-7.27 (m, 1 H, ArH), 7.25-7.16 (m, 1 H, ArH), 6.58 (s, 1 H, CH), 3.83 (s, 3 H, Me); ¹³C NMR (100 MHz, CDCl₃) δ = 154.9, 136.4, 136.1, 133.6, 129.9, 129.29, 129.27, 128.7, 128.0, 126.4, 121.9, 89.8, 84.7, 70.1, 55.1; IR (neat, cm⁻¹): 1746, 1474, 1439, 1249, 1193; MS (70 eV, EI) *m/z* (%): 302 [M⁺(³⁷Cl), 8.40], 300 [M⁺(³⁵Cl), 23.33], 189 (100); HRMS Calcd for C₁₇H₁₃³⁵ClO₃ (M⁺): 300.0553, Found: 300.0549.

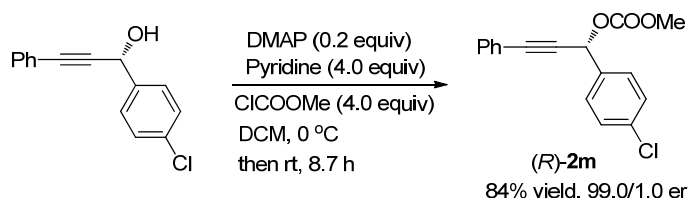
(3) Synthesis of (*R*)-3-(2-chlorophenyl)-1-phenylprop-2-ynyl methyl carbonate ((*R*)-2g) (jmq4-31)



To a three-necked flask were added (*R*)-3-(2-chlorophenyl)-1-phenylprop-2-ynol^{6a} (2.20 g, 9.06 mmol) and CH₂Cl₂ (18 mL). After being cooled with an ice/water bath, DMAP (0.2215 g, 1.8 mmol) and pyridine (2.9 mL, d = 0.983 g/mL, 2.8507 g, 36.0 mmol) were added sequentially with stirring. Then methyl chloroformate (2.8 mL, d =

1.223 g/mL, 3.4244 g, 36.2 mmol) was added slowly. The resulting mixture was naturally warmed up to room temperature and stirred for 10 h. The resulting mixture was then diluted with CH₂Cl₂ (20 mL) and this CH₂Cl₂ solution was washed with water (20 mL), 1 mol/L HCl (aq) (20 mL × 3), dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 100/1 (0.4 L) to 40/1 (1.2 L)] to afford (*R*)-**2g** (2.1368 g, 79%) as an oil: 98.5/1.5 er (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 214 nm, t_R (major) = 6.1 min, t_R (minor) = 7.4 min); $[\alpha]_D^{20}$ = +55.6 (c = 1.08, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 7.66 (dd, J = 7.8, 1.8 Hz, 2 H, ArH), 7.51 (dd, J = 7.4, 1.8 Hz, 1 H, ArH), 7.47-7.35 (m, 4 H, ArH), 7.32-7.17 (m, 2 H, ArH), 6.58 (s, 1 H, CH), 3.83 (s, 3 H, Me); ¹³C NMR (100 MHz, CDCl₃) δ = 154.9, 136.4, 136.1, 133.6, 129.9, 129.31, 129.28, 128.7, 128.0, 126.4, 121.9, 89.8, 84.7, 70.2, 55.1; IR (neat, cm⁻¹): 1746, 1474, 1439, 1249, 1064, 1034; MS (70 eV, EI) m/z (%): 302 [M^+ (³⁷Cl), 9.89], 300 [M^+ (³⁵Cl), 27.67], 189 (100); HRMS Calcd for C₁₇H₁₃³⁵ClO₃ (M^+): 300.0553, Found: 300.0556.

(4) Synthesis of (*R*)-1-(4-chlorophenyl)-3-phenylprop-2-ynyl methyl carbonate ((*R*)-2m**) (lj1-2)**

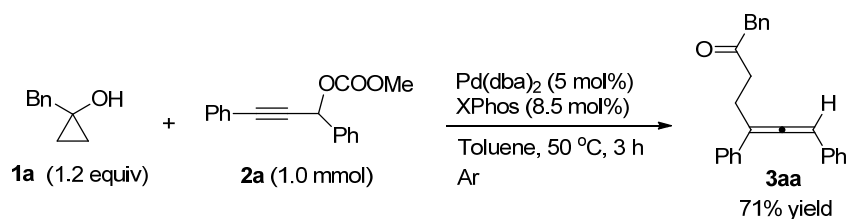


To a three-necked flask were added (*R*)-1-(4-chlorophenyl)-3-phenylprop-2-ynol^{6b-c} (1.8512 g, 7.62 mmol), and CH₂Cl₂ (20 mL). The resulting mixture was stirred and cooled with an ice/water bath. DMAP (0.1870 g, 1.53 mmol) and pyridine (2.5 mL, d = 0.983 g/mL, 2.4575 g, 31.1 mmol) were added sequentially. Then methyl chloroformate (2.4 mL, d = 1.223 g/mL, 2.9352 g, 31.1 mmol) was added slowly. The resulting mixture was warmed up naturally to room temperature and stirred for 8.7 h. The resulting mixture was then diluted with CH₂Cl₂ (20 mL) and the CH₂Cl₂ solution was washed with water (30 mL), 1 mol/L HCl (aq) (30 mL × 3), dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified by column

chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 80/1 (0.8 L) to 40/1 (0.8 L)] to afford (*R*)-**2m** (1.9348 g, 84%) as an oil: 99.0/1.0 er (HPLC conditions: Chiralcel OJ-H column, hexane/*i*-PrOH = 90/10, 0.7 mL/min, λ = 214 nm, t_R (minor) = 16.0 min, t_R (major) = 17.5 min); $[\alpha]_D^{20}$ = +30.6 (c = 0.85, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 7.55 (d, J = 8.4 Hz, 2 H, ArH), 7.46 (dd, J = 7.4, 1.8 Hz, 2 H, ArH), 7.38-7.34 (m, 2 H, ArH), 7.33-7.27 (m, 3 H, ArH), 6.50 (s, 1 H, CH), 3.80 (s, 3 H, Me); ¹³C NMR (100 MHz, CDCl₃) δ = 154.7, 135.1, 135.0, 131.8, 129.1, 129.0, 128.8, 128.2, 121.6, 88.2, 84.3, 69.3, 55.1; IR (neat, cm⁻¹): 2230, 1746, 1597, 1489, 1440, 1411, 1326, 1292, 1254, 1243, 1193, 1178, 1089, 1071, 1032, 1015; MS (70 eV, EI) m/z (%): 302 [M^+ (³⁷Cl), 9.68], 300 [M^+ (³⁵Cl), 28.30], 225 (100); HRMS Calcd for C₁₇H₁₃³⁵ClO₃ (M^+): 300.0553, Found: 300.0556.

II. Palladium-catalyzed synthesis of 3,4-allenyl ketones **3**

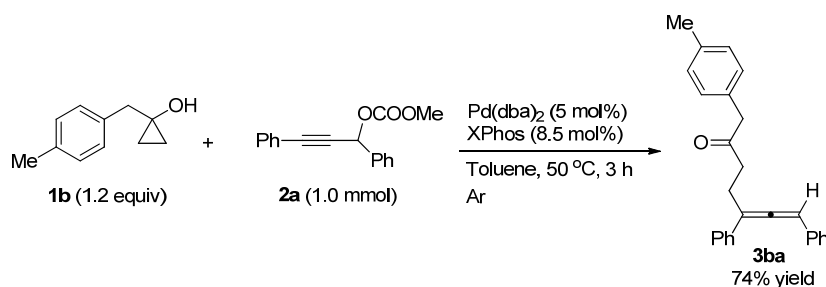
(1) 1,5,7-Triphenylhepta-5,6-dien-2-one (**3aa**) (jmq3-152)



Typical Procedure I: To a flame-dried Schlenk tube were added Pd(dba)₂ (28.8 mg, 0.05 mmol) and XPhos (41.2 mg, 0.085 mmol) under Ar atmosphere. Compound **1a** (liquid, 177.6 mg, 1.2 mmol)/toluene (2.5 mL) and **2a** (266.5 mg, 1.0 mmol)/toluene (2.5 mL) were then added sequentially under Ar atmosphere at room temperature. The Schlenk tube was then stirred at 50 °C until completion of the reaction as monitored by TLC (3 h). The crude reaction mixture was filtrated through a short column of silica gel (height: 2 cm, Φ : 3.5 cm) eluted with ethyl acetate (80 mL). After evaporation, the residue was purified by chromatography on silica gel to afford **3aa** (240.3 mg, 71%) [eluent: petroleum ether/ethyl acetate = 40/1 (1.6 L)] as a white solid: m.p. = 60.4-61.3 °C (petroleum ether/dichloromethane); ¹H NMR (400 MHz, CDCl₃) δ = 7.41 (d, J = 7.2 Hz, 2 H, ArH), 7.36-7.15 (m, 11 H, ArH), 7.03 (d, J = 6.8 Hz, 2 H, ArH), 6.55-6.43 (m, 1 H, =CH), 3.61 (d, J = 15.6 Hz, 1 H, one proton of PhCH₂), 3.56

(d, $J = 15.6$ Hz, 1 H, one proton of PhCH_2), 2.95-2.65 (m, 4 H, $2 \times \text{CH}_2$); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 207.0, 205.7, 135.5, 134.0, 133.9, 129.4, 128.7, 128.49, 128.46, 127.3, 127.2, 126.81, 126.76, 125.9, 109.3, 99.3, 50.1, 39.8, 23.5$; IR (neat, cm^{-1}): 3029, 2897, 1936, 1715, 1595, 1493, 1446, 1416, 1363, 1308, 1074, 1027; MS (70 eV, EI) m/z (%): 338 (M^+ , 17.58), 204 (100); Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{O}$: C 88.72, H 6.55; Found: C 88.80, H 6.55.

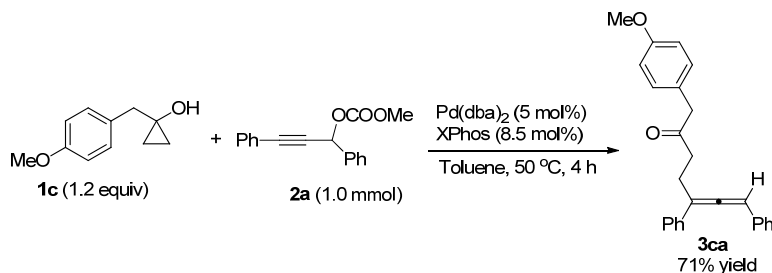
(2) 5,7-Diphenyl-1-(*p*-tolyl)hepta-5,6-dien-2-one (3ba) (jmq3-156)



Typical Procedure II: To a flame-dried Schlenk tube were added $\text{Pd}(\text{dba})_2$ (28.9 mg, 0.05 mmol) and XPhos (41.2 mg, 0.085 mmol) under Ar atmosphere. Compound **1b** (solid, 199.9 mg, 1.2 mmol), **2a** (266.5 mg, 1.0 mmol), and toluene (5.0 mL) were then added sequentially under Ar atmosphere at room temperature. The Schlenk tube was then stirred at 50 °C until completion of the reaction as monitored by TLC (3 h). The crude reaction mixture was filtrated through a short column of silica gel (height: 2 cm, Φ : 3.5 cm) eluted with ethyl acetate (60 mL). After evaporation, the residue was purified by chromatography on silica gel to afford **3ba** (261.3 mg, 74%) [eluent: petroleum ether/ethyl acetate = 40/1 (1.6 L)] as a white solid: m.p. = 72.0-74.2 °C (petroleum ether/dichloromethane); ^1H NMR (400 MHz, CDCl_3) $\delta = 7.41$ (d, $J = 7.2$ Hz, 2 H, ArH), 7.36-7.25 (m, 6 H, ArH), 7.25-7.18 (m, 2 H, ArH), 7.04 (d, $J = 7.6$ Hz, 2 H, ArH), 6.93 (d, $J = 8.4$ Hz, 2 H, ArH), 6.52-6.46 (m, 1 H, =CH), 3.58 (d, $J = 15.2$ Hz, 1 H, one proton of CH_2Ar), 3.53 (d, $J = 15.6$ Hz, 1 H, one proton of CH_2Ar), 2.90-2.65 (m, 4 H, $2 \times \text{CH}_2$), 2.29 (s, 3 H, Me); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 207.3, 205.7, 136.4, 135.6, 134.0, 131.0, 129.2, 128.7, 128.5, 127.23, 127.20, 126.8, 125.9, 109.3, 99.3, 49.8, 39.7, 23.6, 21.0$; IR (neat, cm^{-1}): 3030, 2897, 1933, 1713, 1595, 1516, 1492, 1460, 1446, 1411, 1366, 1314, 1106, 1083, 1026; MS (70 eV, EI) m/z (%): 352 (M^+ , 26.21), 204 (100); Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{O}$: C 88.60, H 6.86;

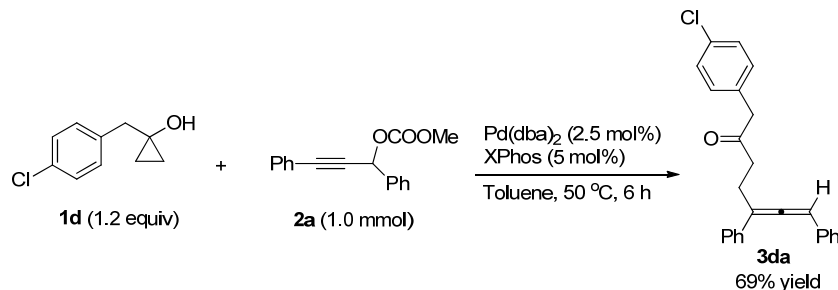
Found: C 88.33, H 6.87.

(3) 1-(4-Methoxyphenyl)-5,7-diphenylhepta-5,6-dien-2-one (3ca) (jmq3-151)



Following **Typical Procedure I**, the reaction of $\text{Pd}(\text{dba})_2$ (28.8 mg, 0.05 mmol), XPhos (41.2 mg, 0.085 mmol), **1c** (213.9 mg, 1.2 mmol)/toluene (2.5 mL), and **2a** (266.5 mg, 1.0 mmol)/toluene (2.5 mL) for 4 h afforded **3ca** (260.4 mg, 71%) [eluent: petroleum ether/ethyl acetate = 30/1 (2.0 L)] as a white solid: m.p. = 86.5-87.4 °C (petroleum ether/dichloromethane); ^1H NMR (400 MHz, CDCl_3) δ = 7.42 (d, J = 7.6 Hz, 2 H, ArH), 7.36-7.28 (m, 6 H, ArH), 7.26-7.17 (m, 2 H, ArH), 6.96 (d, J = 8.8 Hz, 2 H, ArH), 6.77 (d, J = 8.8 Hz, 2 H, ArH), 6.54-6.48 (m, 1 H, =CH), 3.77 (s, 3 H, OMe), 3.58 (d, J = 15.6 Hz, 1 H, one proton of CH_2Ar), 3.52 (d, J = 15.6 Hz, 1 H, one proton of CH_2Ar), 2.94-2.66 (m, 4 H, $2 \times \text{CH}_2$); ^{13}C NMR (100 MHz, CDCl_3) δ = 207.6, 205.7, 158.5, 135.6, 134.0, 130.4, 128.8, 128.5, 127.3, 127.2, 126.8, 126.1, 126.0, 114.0, 109.4, 99.4, 55.2, 49.3, 39.6, 23.6; IR (neat, cm^{-1}): 3050, 3030, 2957, 2899, 1933, 1710, 1612, 1595, 1511, 1493, 1242, 1079, 1029; MS (70 eV, EI) m/z (%): 368 (M^+ , 19.25), 121 (100); Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{O}_2$: C 84.75, H 6.57; Found: C 84.87, H 6.58.

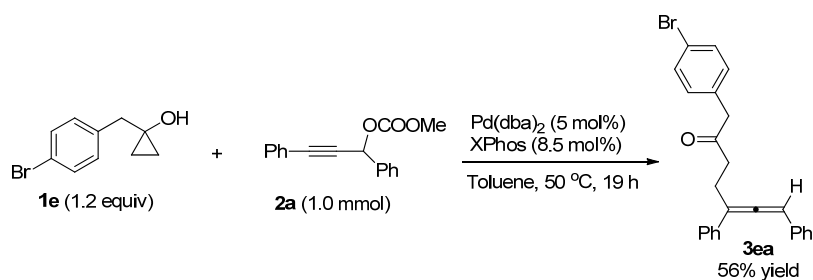
(4) 1-(4-Chlorophenyl)-5,7-diphenylhepta-5,6-dien-2-one (3da) (wpl-1-77)



Following **Typical Procedure II**, the reaction of $\text{Pd}(\text{dba})_2$ (14.4 mg, 0.025 mmol), XPhos (23.9 mg, 0.085 mmol), **1d** (219.0 mg, 1.2 mmol), and **2a** (265.9 mg, 1.0 mmol)/toluene (5.0 mL) for 6 h afforded **3da** (257.2 mg, 69%) (eluent: petroleum

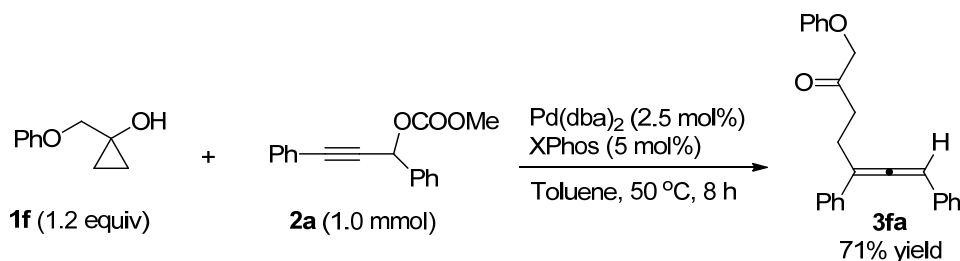
ether/ethyl acetate for the first run, then all the products was collected and treated with the second run of chromatography, eluent: petroleum ether/dichloromethane = 2/1) as a white solid: m.p. = 122.0-122.5 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, CDCl_3): δ = 7.42 (d, J = 7.2 Hz, 2 H, ArH), 7.36-7.10 (m, 10 H, ArH), 6.92 (d, J = 8.4 Hz, 2 H, ArH), 6.51 (t, J = 3.0 Hz, 1 H, =CH), 3.61 (d, 1 H, J = 15.6 Hz, one proton of CH_2Ar), 3.54 (d, J = 15.2 Hz, 1 H, one proton of CH_2Ar), 3.08-2.58 (m, 4 H, $2 \times \text{CH}_2$); ^{13}C NMR (100 MHz, CDCl_3): δ = 206.3, 205.7, 135.6, 133.9, 132.8, 132.4, 130.8, 128.8, 128.6, 128.5, 127.4, 127.3, 126.8, 126.0, 109.4, 99.5, 49.3, 39.9, 23.5; IR (neat, cm^{-1}): ν = 1931, 1716, 1595, 1491, 1102, 1028, 1014; MS (70 eV, EI) m/z (%): 374 [$\text{M}^+(\text{}^{37}\text{Cl})$, 5.31], 372 [$\text{M}^+(\text{}^{35}\text{Cl})$, 13.74], 204 (100); Anal. Calcd for $\text{C}_{25}\text{H}_{21}\text{OCl}$: C 80.53, H 5.68; found: C 80.54, H 5.83.

(5) 1-(4-Bromophenyl)-5,7-diphenylhepta-5,6-dien-2-one (3ea) (jmq3-160)



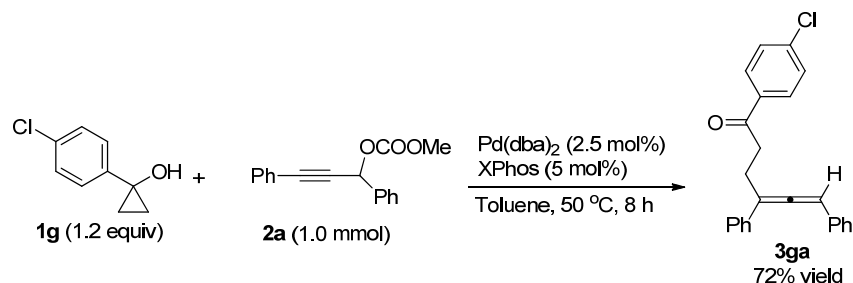
Following Typical Procedure II, the reaction of $\text{Pd}(\text{dba})_2$ (28.8 mg, 0.05 mmol), XPhos (41.1 mg, 0.085 mmol), **1e** (272.9 mg, 1.2 mmol), and **2a** (266.4 mg, 1.0 mmol) /toluene (5.0 mL) for 19 h afforded **3ea** (233.2 mg, 56%) [eluent: petroleum ether/dichloromethane/ethyl acetate = 50/1/1 (1.6 L)] as a white solid: m.p. = 123.3-125.0 °C (petroleum ether/dichloromethane); ^1H NMR (400 MHz, CDCl_3) δ = 7.42 (d, J = 7.2 Hz, 2 H, ArH), 7.36-7.17 (m, 10 H, ArH), 6.85 (d, J = 8.8 Hz, 2 H, ArH), 6.50 (t, J = 3.4 Hz, 1 H, =CH), 3.58 (d, J = 16.0 Hz, 1 H, one proton of CH_2Ar), 3.51 (d, J = 16.4 Hz, 1 H, one proton of CH_2Ar), 2.95-2.65 (m, 4 H, $2 \times \text{CH}_2$); ^{13}C NMR (100 MHz, CDCl_3) δ = 206.2, 205.7, 135.5, 133.9, 132.9, 131.5, 131.1, 128.8, 128.5, 127.4, 127.3, 126.8, 125.9, 120.9, 109.3, 99.5, 49.3, 39.9, 23.4; IR (neat, cm^{-1}): 2898, 1931, 1715, 1593, 1487, 1446, 1328, 1069, 1028, 1010; MS (70 eV, EI) m/z (%): 418 [$\text{M}^+(\text{}^{81}\text{Br})$, 7.68], 416 [$\text{M}^+(\text{}^{79}\text{Br})$, 7.89], 204 (100). Anal. Calcd for $\text{C}_{25}\text{H}_{21}\text{BrO}$: C 71.95, H 5.07; Found: C 72.03, H 5.03.

(6) 1-Phenoxy-5,7-diphenylhepta-5,6-dien-2-one (3fa) (jmq4-56)



Following Typical Procedure II, the reaction of Pd(dba)_2 (14.3 mg, 0.025 mmol), XPhos (23.8 mg, 0.05 mmol), **1f** (197.4 mg, 1.2 mmol), and **2a** (266.3 mg, 1.0 mmol) /toluene (5.0 mL) for 8 h afforded **3fa** (251.3 mg, 71% yield) [petroleum ether/ethyl acetate = 60/1 (0.4 L) to 40/1 (2.0 L) for the first run provided pure product **3fa** and some impure product. The impure product was treated with the second run of chromatography (eluent: petroleum ether/ethyl acetate = 60/1 to 40/1) to get another batch of pure product] as an oil: ^1H NMR (400 MHz, CDCl_3) δ = 7.44 (d, J = 7.6 Hz, 2 H, ArH), 7.44-7.16 (m, 10 H, ArH), 6.94 (t, J = 7.4 Hz, 1 H, ArH), 6.76 (d, J = 7.6 Hz, 2 H, ArH), 6.63-6.48 (m, 1 H, =CH), 4.45 (d, J = 16.4 Hz, 1 H, one proton of OCH_2), 4.39 (d, J = 16.8 Hz, 1 H, one proton of OCH_2), 3.12-2.74 (m, 4 H, $2 \times \text{CH}_2$); ^{13}C NMR (100 MHz, CDCl_3) δ = 206.6, 205.7, 157.6, 135.5, 133.8, 129.5, 128.7, 128.5, 127.32, 127.29, 126.7, 126.0, 121.5, 114.5, 109.2, 99.5, 72.8, 36.8, 23.1; IR (neat, cm^{-1}): 1934, 1738, 1682, 1597, 1490, 1433, 1288, 1240, 1086, 1072, 1029; MS (70 eV, EI) m/z (%): 354 (M^+ , 7.31), 204 (100); HRMS Calcd for $\text{C}_{25}\text{H}_{22}\text{O}_2$ (M^+): 354.1620, Found: 354.1617.

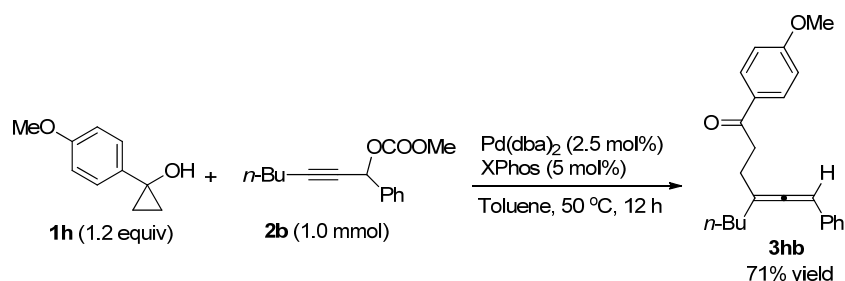
(7) 1-(4-Chlorophenyl)-4,6-diphenylhexa-4,5-dien-1-one (3ga) (jmq4-108)



Following Typical Procedure II, the reaction of Pd(dba)_2 (14.4 mg, 0.025 mmol), XPhos (23.9 mg, 0.05 mmol), **1g** (202.5 mg, 1.2 mmol), and **2a** (266.3 mg, 1.0 mmol) /toluene (5.0 mL) for 8 h afforded **3ga** (256.7 mg, 72%) [eluent: petroleum ether/ethyl

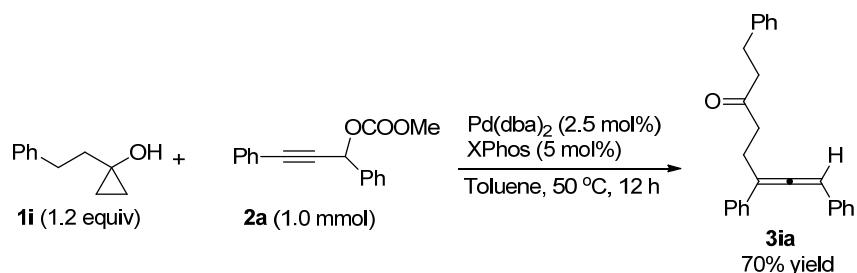
acetate = 80/1 (1.6 L)] as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ = 7.76 (dd, J = 7.0, 1.8 Hz, 2 H, ArH), 7.48 (dd, J = 8.8, 1.2 Hz, 2 H, ArH), 7.38-7.14 (m, 10 H, ArH), 6.49 (t, J = 7.4 Hz, 1 H, =CH), 3.27-3.18 (m, 2 H, CH_2), 3.15-2.93 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ = 205.8, 197.9, 139.2, 135.6, 135.3, 133.9, 129.3, 128.6, 128.5, 127.3, 127.2, 126.7, 126.0, 109.3, 99.5, 36.3, 24.2; IR (neat, cm^{-1}): 1933, 1682, 1588, 1572, 1492, 1446, 1398, 1359, 1200, 1175, 1091, 1074, 1012; MS (70 eV, EI) m/z (%): 360 [$\text{M}^+(\text{Cl})$, 5.22], 358 [$\text{M}^+(\text{Cl})$, 13.79], 105 (100); HRMS Calcd for $\text{C}_{24}\text{H}_{19}\text{O}^{35}\text{Cl}$ (M^+): 358.1124, Found: 358.1126.

(8) 4-Butyl-1-(4-methoxyphenyl)-6-phenylhexa-4,5-dien-1-one (3hb) (jmq4-102)



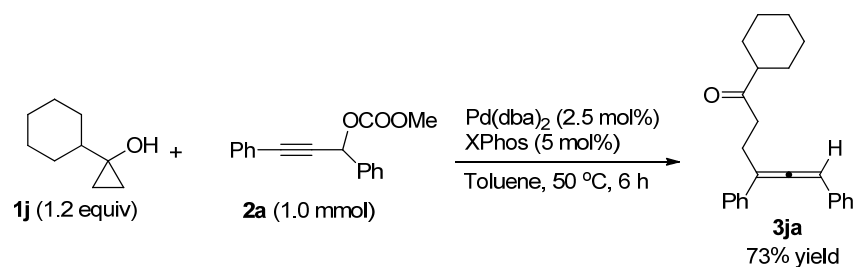
Following Typical Procedure II, the reaction of $\text{Pd}(\text{dba})_2$ (14.3 mg, 0.025 mmol), XPhos (23.8 mg, 0.05 mmol), **1h** (197.4 mg, 1.2 mmol), **2b** (246.3 mg, 1.0 mmol)/toluene (5.0 mL) for 12 h afforded **3hb** (237.3 mg, 71% yield) [eluent: petroleum ether/ethyl acetate = 80/1 (1.6 L)] as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ = 7.85 (dt, J = 9.2, 2.4 Hz, 2 H, ArH), 7.35-7.10 (m, 5 H, ArH), 6.84 (dt, J = 9.2, 2.4 Hz, 2 H, ArH), 6.12 (quint, J = 3.2 Hz, 1 H, =CH), 3.83 (s, 3 H, OMe), 3.20-2.98 (m, 2 H, $\text{CH}_2\text{C}=\text{C}$), 2.64-2.38 (m, 2 H, CH_2), 2.16 (t, J = 7.2 Hz, 2 H, CH_2), 1.55-1.42 (m, 2 H, CH_2), 1.40-1.32 (m, 2 H, CH_2), 0.89 (t, J = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ = 201.6, 198.1, 163.2, 135.6, 130.13, 130.07, 128.4, 126.41, 126.35, 113.4, 108.5, 96.8, 55.3, 35.9, 32.9, 29.8, 26.8, 22.4, 13.9; IR (neat, cm^{-1}): 2956, 2927, 1946, 1675, 1599, 1575, 1510, 1496, 1460, 1417, 1360, 1256, 1212, 1168, 1028; MS (70 eV, EI) m/z (%): 334 (M^+ , 29.11), 135 (100); HRMS Calcd for $\text{C}_{23}\text{H}_{26}\text{O}_2$ (M^+): 334.1933, Found: 334.1929.

(9) 1,6,8-Triphenylocta-6,7-dien-3-one (3ia) (wpl-1-135)



Following Typical Procedure II, the reaction of Pd(dba)_2 (14.5 mg, 0.025 mmol), XPhos (24.0 mg, 0.05 mmol), **1i** (194.5 mg, 1.2 mmol), and **2a** (266.2 mg, 1.0 mmol) /toluene (5.0 mL) for 12 h afforded **3ia** (247.7 mg, 70%) [eluent: petroleum ether/ethyl acetate = 60/1 (0.8 L) to 40/1 (1.2 L)] as a white solid: m.p. = 86-87 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, CDCl_3): δ = 7.44 (d, J = 8.4 Hz, 2 H, ArH), 7.38-7.25 (m, 6 H, ArH), 7.25-7.17 (m, 4 H, ArH), 7.15 (t, J = 7.2 Hz, 1 H, ArH), 7.03 (d, J = 6.8 Hz, 2 H, ArH), 6.51 (t, J = 3.4 Hz, 1 H, =CH), 2.98-2.50 (m, 8 H, 4 \times CH_2); ^{13}C NMR (100 MHz, CDCl_3): δ = 208.7, 205.7, 141.1, 135.6, 134.0, 128.8, 128.5, 128.4, 128.3, 127.33, 127.27, 126.8, 125.99, 125.96, 109.4, 99.4, 44.8, 40.4, 29.5, 23.6; IR (neat, cm^{-1}): ν = 1929, 1707, 1596, 1492, 1447, 1402, 1376, 1094, 1073, 1030, 1001; MS (70 eV, EI) m/z (%): 352 (M^+ , 19.56), 204 (100); Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{O}$: C 88.60, H 6.86; found: C 88.66, H 6.89.

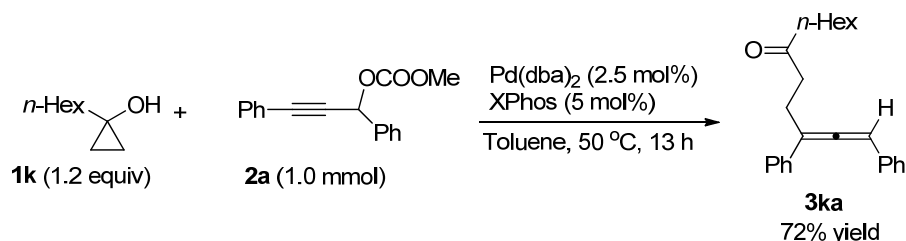
(10) 1-Cyclohexyl-4,6-diphenylhexa-4,5-dien-1-one (3ja) (jmq4-111)



Following Typical Procedure I, the reaction of Pd(dba)_2 (14.4 mg, 0.025 mmol), XPhos (23.9 mg, 0.05 mmol), **1j** (168.5 mg, 1.2 mmol)/toluene (2.5 mL), and **2a** (266.3 mg, 1.0 mmol)/toluene (2.5 mL) for 6 h afforded **3ja** (242.2 mg, 73%) [eluent: petroleum ether/ethyl acetate = 100/1 (0.4 L) to 80/1 (1.2 L)] as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ = 7.45 (d, J = 7.2 Hz, 2 H, ArH), 7.36-7.26 (m, 6 H, ArH), 7.25-7.12 (m, 2 H, ArH), 6.54 (t, J = 3.2 Hz, 1 H, =CH), 2.95-2.66 (m, 4 H, 2 \times CH_2), 2.30-2.14 (m, 1 H, one proton of *c*-Hex), 1.86-1.52 (m, 5 H, 5 protons of *c*-Hex),

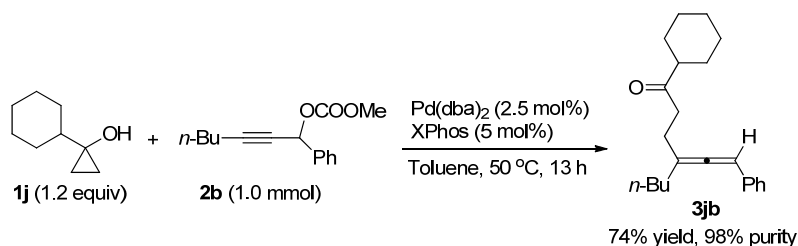
1.34-1.02 (m, 5 H, 5 protons of *c*-Hex); ^{13}C NMR (100 MHz, CDCl_3) δ = 212.7, 205.7, 135.7, 134.1, 128.7, 128.4, 127.2, 126.7, 126.0, 109.5, 99.1, 50.8, 38.4, 28.5, 28.2, 25.7, 25.6, 26.5, 23.6; IR (neat, cm^{-1}): 2927, 2852, 1934, 1704, 1596, 1493, 1446, 1093, 1073, 1028; MS (70 eV, EI) m/z (%): 330 (M^+ , 12.12), 161 (100); HRMS Calcd for $\text{C}_{24}\text{H}_{26}\text{O}$ (M^+): 330.1984, Found: 330.1988.

(11) 1,3-Diphenyldodeca-1,2-dien-6-one (3ka) (wpl-1-148)



Following Typical Procedure II, the reaction of Pd(dba)_2 (14.4 mg, 0.025 mmol), XPhos (23.8 mg, 0.05 mmol), **1k** (170.3 mg, 1.2 mmol), and **2a** (266.4 mg, 1.0 mmol) /toluene (5.0 mL) for 13 h afforded **3ka** (239.2 mg, 72%) [eluent: petroleum ether/ethyl acetate = 100/1 (0.4 L) to 60/1 (0.4 L) to 40/1 (0.4 L)] as a white solid: m.p. = 49-50 $^\circ\text{C}$ (petroleum ether/ethyl acetate), ^1H NMR (400 MHz, CDCl_3): δ = 7.46 (d, J = 7.6 Hz, 2 H, ArH), 7.35-7.26 (m, 6 H, ArH), 7.25-7.14 (m, 2 H, ArH), 6.55 (t, J = 3.2 Hz, 1 H, =CH), 2.96-2.76 (m, 2 H, CH_2), 2.73-2.61 (m, 2 H, CH_2), 2.40-2.25 (m, 2 H, CH_2), 1.52-1.36 (m, 2 H, CH_2), 1.32-1.10 (m, 6 H, $3 \times \text{CH}_2$), 0.85 (t, J = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ = 210.0, 205.7, 135.7, 134.1, 128.7, 128.5, 127.2, 126.7, 126.0, 109.4, 99.3, 43.1, 40.3, 31.5, 28.8, 23.7, 23.6, 22.4, 14.0; IR (neat, cm^{-1}): ν = 2955, 2930, 2864, 2847, 1933, 1704, 1595, 1492, 1461, 1445, 1409, 1373, 1092; MS (70 eV, EI) m/z (%): 332 (M^+ , 14.91), 204 (100); Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{O}$: C 86.70, H 8.49; found: C 86.40, H 8.48.

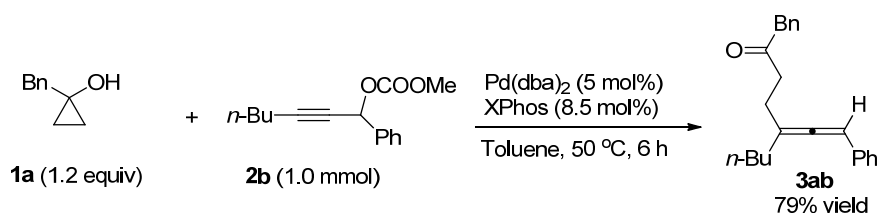
(12) 4-Butyl-1-cyclohexyl-6-phenylhexa-4,5-dien-1-one (3jb) (jmq4-107)



Following Typical Procedure I, the reaction of Pd(dba)_2 (14.4 mg, 0.025 mmol),

XPhos (23.9 mg, 0.05 mmol), **1j** (168.7 mg, 1.2 mmol)/toluene (2.5 mL), and **2b** (246.3 mg, 1.0 mmol)/toluene (2.5 mL) for 13 h afforded **3jb** (234.0 mg, 74%, 98% purity) [petroleum ether/ethyl acetate = 80/1 (0.4 L) to 60/1 (0.8 L) for the first run. All the product was collected and treated with the second run of chromatography (eluent: petroleum ether/ethyl acetate = 100/1 (1.6 L)] as an oil: ¹H NMR (400 MHz, CDCl₃) δ = 7.32-7.10 (m, 5 H, ArH), 6.14 (t, *J* = 3.2 Hz, 1 H, =CH), 2.59 (t, *J* = 6.2 Hz, 2 H, CH₂), 2.44-2.16 (m, 3 H, CH + CH₂), 2.11 (t, *J* = 7.0 Hz, 2 H, CH₂), 1.85-1.52 (m, 5 H, CH + 2 × CH₂), 1.52-1.02 (m, 9 H, CH + 4 × CH₂), 0.88 (t, *J* = 7.4 Hz, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 213.1, 201.5, 135.7, 128.5, 126.5, 126.4, 108.6, 96.8, 50.8, 38.2, 33.0, 29.7, 28.5, 28.2, 26.0, 25.8, 25.6, 25.5, 22.4, 13.9; IR (neat, cm⁻¹): 2926, 2854, 1947, 1707, 1495, 1448, 1403, 1374, 1265, 1143, 1071, 1028; MS (70 eV, EI) *m/z* (%): 310 (M⁺, 17.94), 142 (100); HRMS Calcd for C₂₂H₃₀O (M⁺): 310.2297, Found: 310.2299.

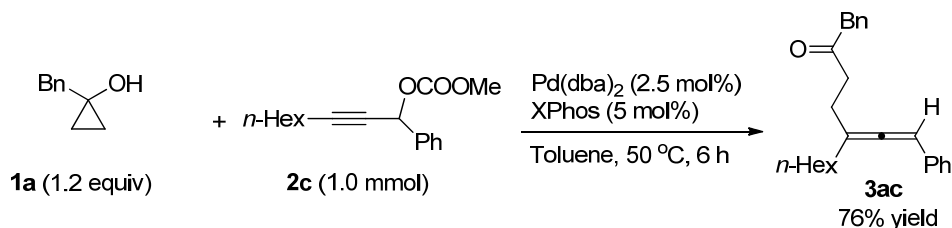
(13) 5-Butyl-1,7-diphenylhepta-5,6-dien-2-one (3ab) (jmq3-164)



Following typical Procedure I, the reaction of Pd(dba)₂ (28.8 mg, 0.05 mmol), XPhos (41.2 mg, 0.085 mmol), **1a** (177.9 mg, 1.2 mmol)/toluene (2.5 mL), and **2b** (246.4 mg, 1.0 mmol)/toluene (2.5 mL) for 6 h afforded **3ab** (251.4 mg, 79%) [eluent: petroleum ether/ethyl acetate = 80/1 (2.0 L)] as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ = 7.28 (t, *J* = 7.2 Hz, 2 H, ArH), 7.26-7.15 (m, 6 H, ArH), 7.07-6.96 (m, 2 H, ArH), 6.11 (quint, *J* = 3.2 Hz, 1 H, =CH), 3.57 (d, *J* = 15.6 Hz, 1 H, one proton of PhCH₂), 3.51 (d, *J* = 16.0 Hz, 1 H, one proton of PhCH₂), 2.63-2.50 (m, 2 H, CH₂), 2.45-2.32 (m, 1 H, one proton of CH₂), 2.31-2.20 (m, 1 H, one proton of CH₂), 2.13-2.00 (m, 2 H, CH₂), 1.53-1.36 (m, 2 H, CH₂), 1.36-1.20 (m, 2 H, CH₂), 0.86 (t, *J* = 7.2 Hz, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 207.2, 201.4, 135.5, 134.1, 129.3, 128.5, 128.4, 126.7, 126.6, 126.4, 108.4, 96.9, 50.0, 39.6, 32.8, 29.6, 25.9, 22.3,

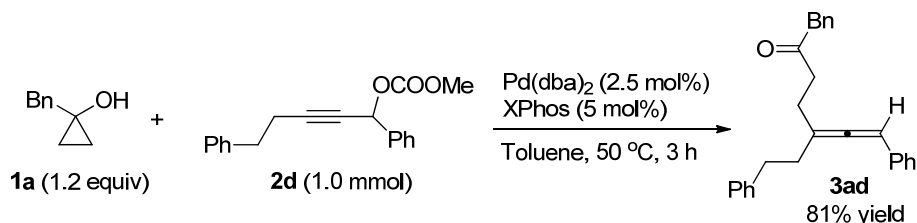
13.8; IR (neat, cm^{-1}): 2956, 2927, 1947, 1714, 1598, 1496, 1455, 1405, 1360, 1334, 1072, 1029; MS (70 eV, EI) m/z (%): 318 (M^+ , 8.57), 142 (100); HRMS Calcd for $\text{C}_{23}\text{H}_{26}\text{O}$ (M^+): 318.1984, Found: 318.1980.

(14) 5-Hexyl-1,7-diphenylhepta-5,6-dien-2-one (3ac) (jmq4-5)



Following Typical Procedure I, the reaction of $\text{Pd}(\text{dba})_2$ (14.4 mg, 0.025 mmol), XPhos (23.9 mg, 0.05 mmol), **1a** (178.0 mg, 1.2 mmol)/toluene (2.5 mL), and **2c** (274.4 mg, 1.0 mmol)/toluene (2.5 mL) for 6 h afforded **3ac** (263.3 mg, 76%) [eluent: petroleum ether/ethyl acetate = 80/1 (1.6 L)] as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ = 7.29 (t, J = 7.4 Hz, 2 H, ArH), 7.26-7.12 (m, 6 H, ArH), 7.02 (d, J = 8.0 Hz, 2 H, ArH), 6.11 (quint, J = 3.2 Hz, 1 H, =CH), 3.59 (d, J = 15.6 Hz, 1 H, one proton of PhCH_2), 3.52 (d, J = 15.6 Hz, 1 H, one proton of PhCH_2), 2.68-2.52 (m, 2 H, CH_2), 2.48-2.18 (m, 2 H, CH_2), 2.07 (td, J = 7.2, 2.4 Hz, 2 H, CH_2), 1.55-1.38 (m, 2 H, CH_2), 1.38-1.15 (m, 6 H, $3 \times \text{CH}_2$), 0.84 (t, J = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ = 207.3, 201.5, 135.5, 134.1, 129.4, 128.52, 128.46, 126.8, 126.6, 126.4, 108.4, 96.9, 50.1, 39.7, 33.2, 31.6, 29.0, 27.5, 26.0, 22.6, 14.0; IR (neat, cm^{-1}): 2925, 2856, 1947, 1714, 1598, 1496, 1455, 1405, 1359, 1072; MS (70 eV, EI) m/z (%): 346 (M^+ , 5.60), 142 (100); HRMS Calcd for $\text{C}_{25}\text{H}_{30}\text{O}$ (M^+): 346.2297, Found: 346.2299.

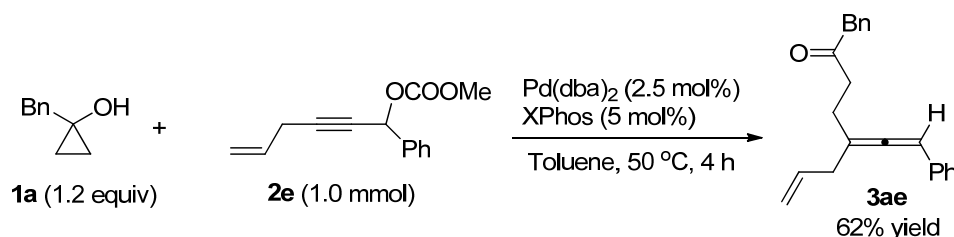
(15) 5-Phenethyl-1,7-diphenylhepta-5,6-dien-2-one (3ad) (jmq3-186)



Following typical Procedure I, the reaction of $\text{Pd}(\text{dba})_2$ (14.4 mg, 0.025 mmol), XPhos (23.9 mg, 0.05 mmol), **1a** (179.0 mg, 1.2 mmol)/toluene (2.5 mL), and **2d**

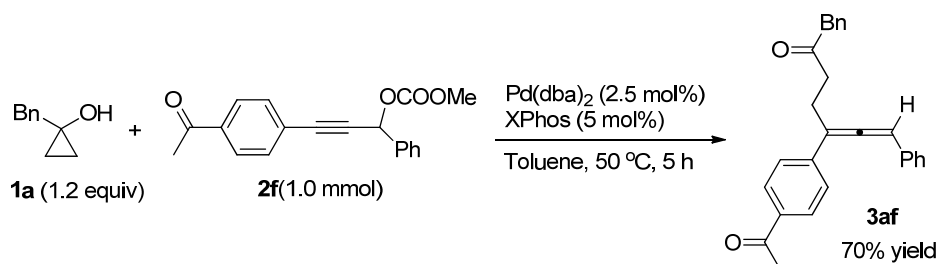
(294.3 mg, 1.0 mmol)/toluene (2.5 mL) for 3 h afforded **3ad** (295.1 mg, 81%) [eluent: petroleum ether/ethyl acetate = 80/1 (2.0 L)] as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ = 7.32-7.08 (m, 13 H, ArH), 7.02 (dd, J = 7.8, 1.8 Hz, 2 H, ArH), 6.12 (quint, J = 3.2 Hz, 1 H, =CH), 3.57 (d, J = 15.6 Hz, 1 H, one proton of PhCH_2), 3.51 (d, J = 15.6 Hz, 1 H, one proton of PhCH_2), 2.85-2.71 (m, 2 H, CH_2), 2.67-2.52 (m, 2 H, CH_2), 2.49-2.24 (m, 4 H, $2 \times \text{CH}_2$); ^{13}C NMR (100 MHz, CDCl_3) δ = 207.2, 201.5, 141.7, 135.2, 134.1, 129.4, 128.51, 128.46, 128.3, 128.2, 126.8, 126.7, 126.5, 125.8, 107.8, 97.5, 50.1, 39.6, 34.8, 33.8, 26.0; IR (neat, cm^{-1}): 1948, 1712, 1599, 1495, 1453, 1072, 1029; MS (ESI) m/z = 389 ($\text{M}+\text{Na}^+$), 384 ($\text{M}+\text{NH}_4^+$), 367 ($\text{M}+\text{H}^+$); HRMS Calcd for $\text{C}_{27}\text{H}_{26}\text{O}$ (M^+): 366.1984, Found: 366.1980.

(16) 5-Allyl-1,7-diphenylhepta-5,6-dien-2-one (3ae) (jmq4-23)



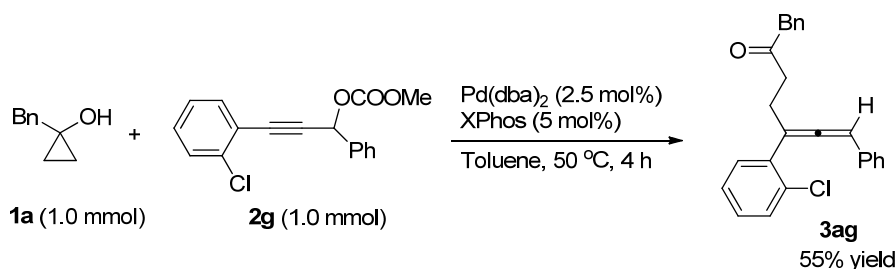
Following typical Procedure I, the reaction of $\text{Pd}(\text{dba})_2$ (14.4 mg, 0.025 mmol), XPhos (23.9 mg, 0.05 mmol), **1a** (177.9 mg, 1.2 mmol)/toluene (2.5 mL), and **2e** (230.3 mg, 1.0 mmol)/toluene (2.5 mL) for 4 h afforded **3ae** (188.6 mg, 62%) [eluent: petroleum ether/ethyl acetate = 60/1 (2.0 L)] as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ = 7.44-7.12 (m, 8 H, ArH), 7.09-6.93 (m, 2 H, ArH), 6.13 (quint, J = 3.0 Hz, 1 H, =CH), 5.93-5.74 (m, 1 H, =CH), 5.10 (dd, J = 16.8, 1.6 Hz, 1 H, one proton of = CH_2), 5.02 (dt, J = 10.4, 0.8 Hz, 1 H, one proton of = CH_2), 3.59 (d, J = 15.6 Hz, 1 H, one proton of PhCH_2), 3.53 (d, J = 15.2 Hz, 1 H, one proton of PhCH_2), 2.84 (d, J = 6.4 Hz, 2 H, CH_2), 2.74-2.51 (m, 2 H, CH_2), 2.48-2.34 (m, 1 H, one proton of CH_2), 2.34-2.16 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ = 207.2, 201.8, 135.3, 135.1, 134.1, 129.4, 128.6, 128.5, 126.8, 126.5, 116.4, 106.8, 97.1, 50.1, 39.6, 37.9, 25.6; IR (neat, cm^{-1}): 1949, 1711, 1598, 1495, 1454, 1407, 1241, 1071, 1029; MS (70 eV, EI) m/z (%): 302 (M^+ , 7.72), 91 (100); HRMS Calcd for $\text{C}_{22}\text{H}_{22}\text{O}$ (M^+): 302.1671, Found: 302.1669.

(17) 5-(4-Acetylphenyl)-1,7-diphenylhepta-5,6-dien-2-one (3af) (jmq4-24)



Following typical Procedure I, the reaction of Pd(dba)₂ (14.5 mg, 0.025 mmol), XPhos (23.9 mg, 0.05 mmol), **1a** (177.9 mg, 1.2 mmol)/toluene (2.5 mL), and **2f** (308.4 mg, 1.0 mmol)/toluene (2.5 mL) for 5 h afforded **3af** (268.3 mg, 70%) [eluent: petroleum ether/ethyl acetate = 50/1 (0.4 L) to 25/1 (1.2 L) to 8/1 (0.8 L)] as a white solid: m.p. = 75.4-76.8 °C (petroleum ether/dichloromethane); ¹H NMR (400 MHz, CDCl₃) δ = 7.88 (d, *J* = 8.0 Hz, 2 H, ArH), 7.49 (d, *J* = 8.4 Hz, 2 H, ArH), 7.40-7.15 (m, 8 H, ArH), 7.03 (dd, *J* = 7.2, 2.0 Hz, 2 H, ArH), 6.56 (t, *J* = 3.2 Hz, 1 H, =CH), 3.64 (d, *J* = 15.6 Hz, 1 H, one proton of PhCH₂), 3.58 (d, *J* = 15.6 Hz, 1 H, one proton of PhCH₂), 2.98-2.70 (m, 4 H, 2 × CH₂), 2.56 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 206.81, 206.75, 197.5, 140.7, 135.7, 133.9, 133.2, 129.3, 128.8, 128.6, 128.5, 127.6, 126.9, 126.0, 108.9, 99.9, 50.2, 39.6, 26.5, 23.3; IR (neat, cm⁻¹): 1931, 1708, 1678, 1598, 1496, 1456, 1408, 1264, 1183, 1089, 1072, 1032; MS (70 eV, EI) *m/z* (%): 380 (M⁺, 25.32), 91 (100); HRMS Calcd for C₂₇H₂₄O₂ (M⁺): 380.1776, Found: 380.1784.

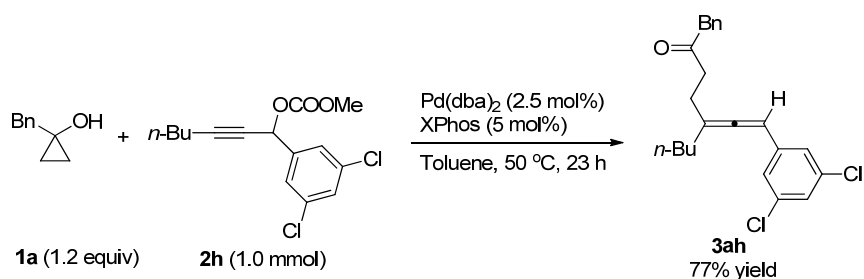
(18) 5-(2-Chlorophenyl)-1,7-diphenylhepta-5,6-dien-2-one (3ag) (jmq4-45)



Following Typical Procedure I, the reaction of Pd(dba)₂ (14.6 mg, 0.025 mmol), XPhos (23.9 mg, 0.05 mmol), **1a** (177.7 mg, 1.2 mmol)/toluene (2.5 mL), and **2g** (300.8 mg, 1.0 mmol)/toluene (2.5 mL) for 4 h afforded **3ag** (205.7 mg, 55%) [eluent: petroleum ether/ethyl acetate = 50/1 (2.0 L)] as a colorless oil: ¹H NMR (400 MHz,

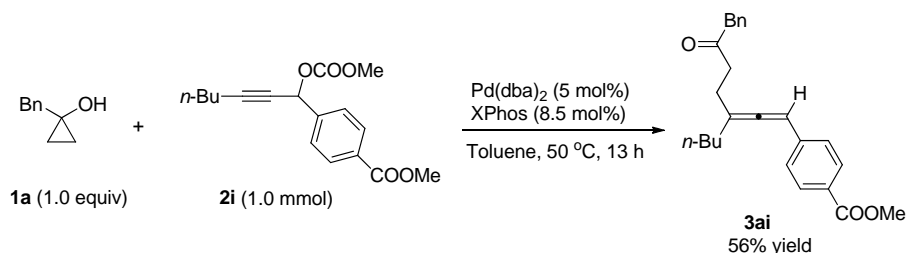
CDCl₃) δ = 7.45-7.12 (m, 12 H, ArH), 7.05 (d, J = 6.4 Hz, 2 H, ArH), 6.29 (t, J = 3.0 Hz, 1 H, =CH), 3.63 (d, J = 15.6 Hz, 1 H, one proton of PhCH₂), 3.58 (d, J = 15.6 Hz, 1 H, one proton of PhCH₂), 2.86-2.62 (m, 4 H, 2 \times CH₂); ¹³C NMR (100 MHz, CDCl₃) δ = 206.9, 203.8, 136.4, 134.1, 132.8, 130.1, 129.9, 129.4, 128.63, 128.55, 127.2, 127.1, 126.9, 126.8, 107.5, 97.3, 50.1, 39.8, 26.9; IR (neat, cm⁻¹): 1948, 1712, 1598, 1495, 1473, 1456, 1434, 1062, 1032; MS (70 eV, EI) m/z (%): 374 [M⁺(³⁷Cl), 13.65], 372 [M⁺(³⁵Cl), 40.75], 203 (100); HRMS Calcd for C₂₅H₂₁³⁵ClO (M⁺): 372.1281, Found: 372.1276.

(19) 5-Butyl-7-(3,5-dichlorophenyl)-1-phenylhepta-5,6-dien-2-one (3ah) (jmq4-1)



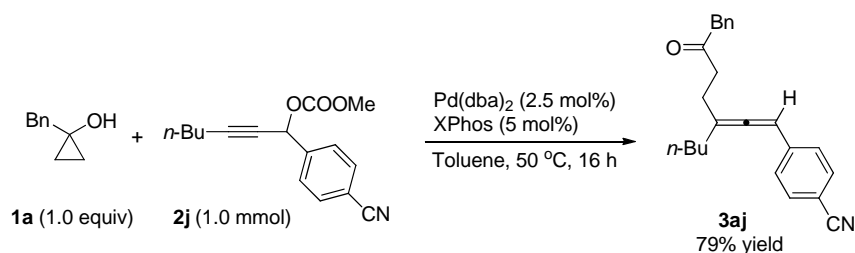
Following Typical Procedure I, the reaction of Pd(dba)₂ (14.3 mg, 0.025 mmol), XPhos (23.8 mg, 0.05 mmol), **1a** (178.5 mg, 1.2 mmol)/toluene (2.5 mL), and **2h** (315.2 mg, 1.0 mmol)/toluene (2.5 mL) for 23 h afforded **3ah** (298.6 mg, 77%) [petroleum ether/ethyl acetate = 70/1 (2.0 L) for the first run. Then all the product was treated with the second run of chromatography (eluent: petroleum ether/ethyl acetate = 80/1 (2.0 L))] as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ = 7.30-7.18 (m, 3 H, ArH), 7.15 (t, J = 2.0 Hz, 1 H, ArH), 7.12-7.05 (m, 2 H, ArH), 7.05-6.99 (m, 2 H, ArH), 5.94 (quint, J = 3.2 Hz, 1 H, =CH), 3.61 (d, J = 15.2 Hz, 1 H, one proton of PhCH₂), 3.56 (d, J = 15.2 Hz, 1 H, one proton of PhCH₂), 2.59 (t, J = 6.8 Hz, 2 H, CH₂), 2.44-2.20 (m, 2 H, CH₂), 2.16-1.98 (m, 2 H, CH₂), 1.50-1.20 (m, 4 H, 2 \times CH₂), 0.87 (t, J = 7.2 Hz, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 206.9, 202.2, 139.0, 135.0, 134.0, 129.3, 128.5, 126.9, 126.3, 124.6, 109.8, 95.2, 50.1, 39.5, 32.6, 29.5, 25.7, 22.3, 13.8; IR (neat, cm⁻¹): 2956, 2927, 1949, 1714, 1584, 1563, 1496, 1454, 1431, 1375, 1360, 1113, 1087, 1031; MS (ESI) m/z = 411 [M(^{37,35}Cl₂)+Na]⁺; 409 [M(^{35,35}Cl₂)+Na]⁺; HRMS Calcd for C₂₃H₂₄^{35,35}Cl₂O (M⁺): 386.1204, Found: 386.1207.

(20) 5-Butyl-7-(4-(methoxycarbonyl)phenyl)-1-phenylhepta-5,6-dien-2-one (3ai) (wpl-1-92)



Following Typical Procedure I, the reaction of Pd(dba)₂ (28.7 mg, 0.05 mmol), XPhos (40.6 mg, 0.085 mmol), **1a** (148.2 mg, 1.0 mmol)/toluene (2.5 mL), and **2i** (303.7 mg, 1.0 mmol)/toluene (2.5 mL) for 13 h afforded **3ai** (209.3 mg, 56 %) [petroleum ether/ethyl acetate = 80/1 (1.2 L) to 40/1 (1.0 L) was used for for the first run. Then all the product was treated with the second run of chromatography (eluent: petroleum ether/ethyl acetate = 80/1 (1.2 L) to 40/1 (1.2 L))] as a colorless oil: ¹H NMR (400 MHz, CDCl₃): δ = 7.96 (d, *J* = 8.8 Hz, 2 H, ArH), 7.30-7.18 (m, 5 H, ArH), 7.10-6.97 (m, 2 H, ArH), 6.12 (quint, *J* = 3.2 Hz, 1 H, =CH), 3.92 (s, 3 H, CH₃), 3.59 (d, *J* = 15.2 Hz, 1 H, one proton of Bn), 3.54 (d, *J* = 15.2 Hz, 1 H, one proton of Bn), 2.72-2.51 (m, 2 H, CH₂), 2.48-2.20 (m, 2 H, CH₂), 2.18-2.03 (m, 2 H, CH₂), 1.52-1.40 (m, 2 H, CH₂), 1.39-1.27 (m, 2 H, CH₂), 0.86 (t, *J* = 7.2 Hz, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 207.1, 202.9, 166.9, 140.6, 134.0, 129.9, 129.3, 128.5, 128.1, 126.9, 126.2, 109.0, 96.5, 52.0, 50.2, 39.6, 32.7, 29.6, 25.9, 22.4, 13.8; IR (neat, cm⁻¹): ν = 2953, 2927, 1945, 1713, 1605, 1496, 1273, 1190, 1173, 1107, 1016; MS (70 eV, EI) *m/z* (%): 376 (M⁺, 14.02), 200 (100); HRMS calcd for C₂₅H₂₈O₃ (M⁺): 376.2038, found: 376.2041.

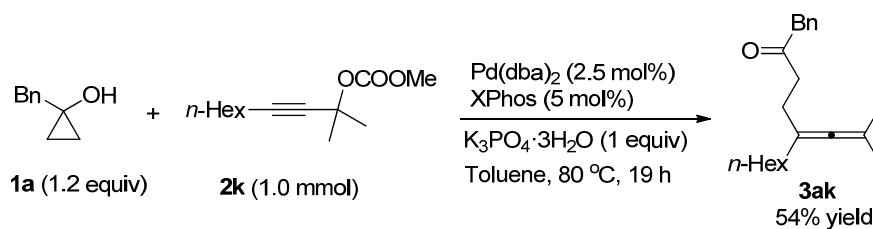
(21) 5-Butyl-7-(4-cyanophenyl)-1-phenylhepta-5,6-dien-2-one (3aj) (jmq4-22)



Following Typical Procedure I, the reaction of Pd(dba)₂ (14.5 mg, 0.025 mmol), XPhos (23.9 mg, 0.05 mmol), **1a** (148.1 mg, 1.0 mmol)/toluene (2.5 mL), and **2j**

(271.3 mg, 1.0 mmol)/toluene (2.5 mL) in for 16 h afforded **3aj** (271.2 mg, 79%) [eluent: petroleum ether/ethyl acetate = 60/1 (0.4 L) to 40/1 (1.2 L) to 30/1 (0.8 L)] as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ = 7.53 (d, J = 8.0 Hz, 2 H, ArH), 7.27-7.15 (m, 5 H, ArH), 7.08-6.95 (m, 2 H, ArH), 6.09 (t, J = 3.2 Hz, 1 H, =CH), 3.58 (d, J = 15.2 Hz, 1 H, one proton of Bn), 3.52 (d, J = 15.2 Hz, 1 H, one proton of Bn), 2.72-2.50 (m, 2 H, CH_2), 2.50-2.35 (m, 1 H, one proton of CH_2), 2.35-2.18 (m, 1 H, one proton of CH_2), 2.18-1.98 (m, 2 H, CH_2), 1.52-1.20 (m, 4 H, $2 \times \text{CH}_2$), 0.86 (t, J = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ = 206.8, 203.2, 140.7, 133.8, 132.2, 129.2, 128.4, 126.8, 126.7, 119.1, 109.5, 96.1, 50.0, 39.3, 32.5, 29.5, 25.6, 22.3, 13.8; IR (neat, cm^{-1}): 2956, 2927, 2858, 2224, 1945, 1713, 1603, 1498, 1454, 1393, 1359, 1334, 1204, 1172, 1071; MS (70 eV, EI) m/z (%): 343 (M^+ , 17.68), 91 (100); HRMS Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}$ (M^+): 343.1936, Found: 343.1939.

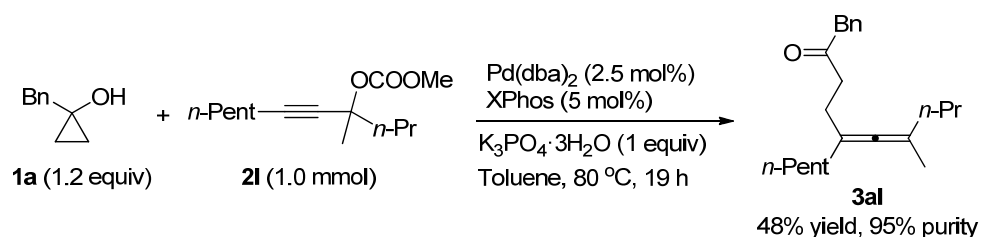
(22) 5-Hexyl-7-methyl-1-phenylocta-5,6-dien-2-one (3ak) (wpl1-147)



Typical Procedure III: To a flame-dried Schlenk tube were added $\text{Pd}(\text{dba})_2$ (14.2 mg, 0.025 mmol), XPhos (24.2 mg, 0.05 mmol), and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ (266.3 mg, 1.0 mmol) under Ar atmosphere. Compound **1a** (177.7 mg, 1.2 mmol) and **2k** (226.3 mg, 1.0 mmol)/toluene (5.0 mL) were then added sequentially under Ar atmosphere at room temperature. The resulting mixture was then stirred at 80 °C until completion of the reaction as monitored by NMR (19 h). The crude reaction mixture was filtrated through a short column of silica gel (height: 2 cm, Φ : 3.5 cm) eluted with ethyl acetate (60 mL). After evaporation, the residue was purified by chromatography on silica gel to afford **3ak** (161.2 mg, 54%) [eluent: petroleum ether/ethyl acetate = 100/1 (0.8 L)] as a colorless oil: ^1H NMR (400 MHz, CDCl_3): δ = 7.43-7.15 (m, 5 H, ArH), 3.67 (s, 2 H, CH_2 of Bn), 2.52 (t, J = 7.0 Hz, 2 H, CH_2), 2.15 (t, J = 7.0 Hz, 2 H, CH_2), 1.88 (t, J = 7.0 Hz, 2 H, CH_2), 1.61 (s, 6 H, $2 \times \text{CH}_3$), 1.43-1.20 (m, 8 H, $4 \times$

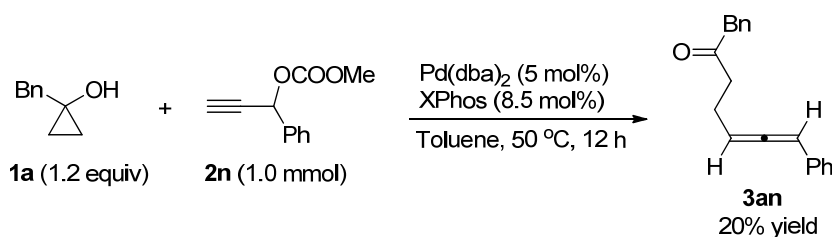
CH₂), 0.87 (t, *J* = 6.6 Hz, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 207.8, 198.0, 134.4, 129.4, 128.6, 126.8, 101.4, 97.1, 50.1, 40.2, 33.2, 31.8, 28.9, 27.6, 26.6, 22.7, 20.9, 14.1; IR (neat, cm⁻¹): ν = 2924, 2855, 1714, 1602, 1496, 1454, 1360, 1264, 1187, 1074, 1031; MS (70 eV, EI) *m/z* (%): 298 (M⁺, 6.60), 91 (100); HRMS calcd for C₂₁H₃₀O (M⁺): 298.2297, found: 298.2293.

(23) 7-Methyl-5-pentyl-1-phenyldeca-5,6-dien-2-one (3al) (wpl1-149)



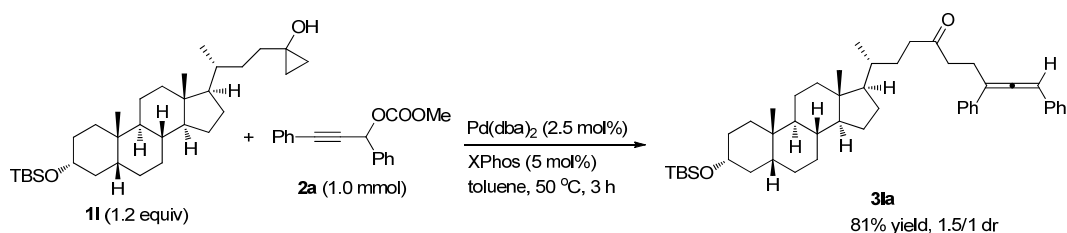
Following Typical Procedure III, the reaction of Pd(dba)₂ (14.4 mg, 0.025 mmol), XPhos (23.5 mg, 0.05 mmol), K₃PO₄·3H₂O (266.4 mg, 1.0 mmol), **1a** (177.9 mg, 1.2 mmol), and **2l** (240.0 mg, 1.0 mmol)/toluene (5.0 mL) at 80 °C for 19 h afforded **3al** (156.0 mg, 95% purity, 48%) [petroleum ether/ethyl acetate = 100/1 (1.2 L) was used for the first run. Then all the product was treated with the second run of chromatography(eluent: petroleum ether/ethyl acetate = 100/1)] as a colorless oil: ¹H NMR (400 MHz, CDCl₃): δ = 7.38-7.15 (m, 5 H, ArH), 3.67 (s, 2 H, CH₂ of Bn), 2.55-2.46 (m, 2 H, CH₂), 2.20-2.11 (m, 2 H, CH₂), 1.92-1.80 (m, 4 H, 2 × CH₂), 1.59 (s, 3 H, CH₃), 1.42-1.19 (m, 8 H, 4 × CH₂), 0.93-0.82 (m, 6 H, 2 × CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 207.9, 197.6, 134.4, 129.4, 128.6, 126.8, 102.6, 101.4, 50.1, 40.3, 36.7, 33.3, 31.5, 27.4, 26.6, 22.5, 21.0, 19.4, 14.1, 14.0; IR (neat, cm⁻¹): ν = 2956, 2927, 2871, 1714, 1496, 1455, 1408, 1359, 1260, 1089, 1074, 1031; MS (70 eV, EI) *m/z* (%): 312 (M⁺, 5.98), 91 (100); HRMS calcd for C₂₂H₃₂O[M⁺]: 312.2453, found: 312.2455.

(24) 1, 7-Diphenylhepta-5,6-dien-2-one (3an) (wpl2-141)



To a flame-dried Schlenk tube were added Pd(dba)₂ (28.6 mg, 0.05 mmol) and XPhos (40.4 mg, 0.085 mmol) under Ar atmosphere. Compound **1a** (liquid, 177.7 mg, 1.2 mmol)/toluene (1.0 mL), **2n** (190.3 mg, 1.0 mmol)/toluene (1.0 mL), and toluene (3.0 mL) were then added sequentially under Ar atmosphere at room temperature. The resulting mixture was then stirred at 50 °C until completion of the reaction as monitored by TLC (12 h). The crude reaction mixture was filtrated through a short column of silica gel (height: 3 cm, Φ : 3.5 cm) eluted with ethyl acetate (60 mL). After evaporation, the residue was purified by chromatography on silica gel to afford **3an** (52.1 mg, 20%) [eluent: petroleum ether/ethyl acetate = 100/1 (2.0 L)] as a colorless oil: ¹H NMR (400 MHz, CDCl₃): δ = 7.50-7.15 (m, 8 H, ArH), 7.10 (d, J = 7.6 Hz, 2 H, ArH), 6.17-6.07 (m, 1 H, =CH), 5.60 (q, J = 6.0 Hz, 1 H, =CH), 3.65 (d, J = 15.2 Hz, 1 H, one proton of CH₂Ph), 3.61 (d, J = 15.6 Hz, 1 H, one proton of CH₂Ph), 2.74-2.56 (m, 2 H, CH₂), 2.51-2.30 (m, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 207.2, 204.8, 134.5, 134.1, 129.4, 128.59, 128.58, 126.91, 126.88, 126.6, 96.1, 94.1, 50.1, 40.4, 22.2; IR (neat, cm⁻¹): ν = 3061, 3029, 2915, 1948, 1710, 1597, 1495, 1454, 1406, 1359, 1311, 1267, 1203, 1072, 1029; MS (70 eV, EI) m/z (%): 262 (M⁺, 30.50), 128 (100); HRMS calcd for C₁₉H₁₈O [M⁺]: 262.1358, found: 262.1360.

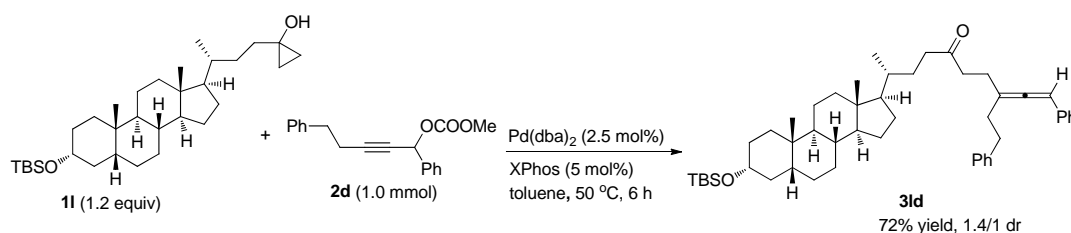
(25) Steroidal skeleton containing allene **3la** (jmq3-193)



Following Typical Procedure II, the reaction of Pd(dba)₂ (14.4 mg, 0.025 mmol), XPhos (23.7 mg, 0.05 mmol), **11** (584.5 mg, 1.2 mmol), and **2a** (266.3 mg, 1.0 mmol)/toluene (5.0 mL) for 3 h afforded **3la** (563.8 mg, 81%, dr = 1.5/1) [eluent: petroleum ether/ethyl acetate = 200/1 (0.4 L) to 100/1 (1.6 L)] as a white foam. The dr ratio of **3la** was determined to be 1.5/1 by HPLC (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 214 nm, t_R (major) = 4.0 min, t_R (minor) = 5.5 min); ¹H NMR (400 MHz, CDCl₃) δ = 7.46 (d, J = 8.0 Hz, 2 H, ArH), 7.40-7.28

(m, 6 H, ArH), 7.26-7.16 (m, 2 H, ArH), 6.56 (t, $J = 3.4$ Hz, 1 H, =CH), 3.65-3.50 (m, 1 H, CH), 3.00-2.64 (m, 4 H, $2 \times \text{CH}_2$), 2.48-2.14 (m, 2 H, CH_2), 1.98-1.66 (m, 5 H, CH + $2 \times \text{CH}_2$), 1.65-0.94 (m, 21 H), 0.90 (s, 12 H, CH_3 + *t*-Bu), 0.79 (d, $J = 6.4$ Hz, 3 H, CH_3), 0.59 (s, 3 H, CH_3), 0.07 (s, 6 H, SiMe_2); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 210.4, 205.7, 135.7, 134.0, 128.7, 128.5, 127.3, 127.2, 126.8, 126.0, 109.5, 99.29, 99.28, 72.8, 56.3, 55.9, 55.8, 42.6, 42.2, 40.3, 40.1, 40.06, 39.9, 36.9, 35.8, 35.5, 35.1, 34.5, 30.98, 29.52, 29.50, 28.11, 28.10, 27.3, 26.4, 25.9, 24.1, 23.6, 23.4, 20.7, 18.3, 12.0, -4.6$; IR (neat, cm^{-1}): 2926, 2856, 1935, 1715, 1597, 1494, 1461, 1447, 1409, 1372, 1250, 1093, 1076; MS (ESI): m/z 693 ($\text{M}+\text{H}$) $^+$, 710 ($\text{M}+\text{NH}_4$) $^+$; HRMS Calcd for $\text{C}_{47}\text{H}_{72}\text{NO}_2\text{Si}$ ($\text{M}+\text{NH}_4$) $^+$: 710.5327, Found: 710.5324; Anal. Calcd for $\text{C}_{47}\text{H}_{68}\text{O}_2\text{Si}$: C 81.44, H 9.89; found: C 80.43, H 9.87.

(26) Steroidal skeleton containing allene **3ld (jmq4-6)**

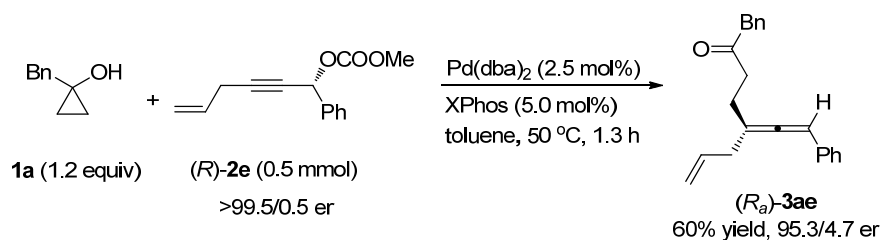


Following Typical Procedure II, the reaction of $\text{Pd}(\text{dba})_2$ (14.3 mg, 0.025 mmol), XPhos (23.9 mg, 0.05 mmol), **11** (584.8 mg, 1.2 mmol), and **2d** (294.3 mg, 1.0 mmol) /toluene (5.0 mL) for 6 h afforded **3ld** (518.1 mg, 72%, dr = 1.4/1) [eluent: petroleum ether/ethyl acetate = 200/1 (0.4 L) to 100/1 (1.6 L)] as a colorless oil: The dr ratio of **3ld** was determined to be 1.4/1 by HPLC (HPLC conditions: (*S,S*)-whelk-O 1 column, hexane/*i*-PrOH = 95/5, 0.2 mL/min, $\lambda = 214$ nm, $t_{\text{R}}(\text{minor}) = 29.1$ min, $t_{\text{R}}(\text{major}) = 30.5$ min); ^1H NMR (400 MHz, CDCl_3) $\delta = 7.40\text{--}7.07$ (m, 10 H, ArH), 6.16 (t, $J = 3.0$ Hz, 1 H, =CH), 3.70-3.50 (m, 1 H, CH of CHOTBS), 2.80 (t, $J = 1.8$ Hz, 2 H, COCH_2), 2.66-2.54 (m, 2 H, CH_2CO), 2.54-2.10 (m, 6 H), 1.97-0.95 (m, 26 H), 0.94-0.85 (m, 12 H, CH_3 + *t*-Bu), 0.77 (d, $J = 6.0$ Hz, 3 H, CH_3), 0.58 (d, $J = 2.0$ Hz, 3 H, CH_3), 0.06 (s, 6 H, SiMe_2); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 210.6, 201.5, 141.7, 135.2, 128.5, 128.3, 128.2, 126.7, 126.4, 125.7, 107.9, 97.47, 97.46, 72.7, 56.3, 55.84, 55.78, 42.6, 42.2, 40.11, 40.06, 40.04, 40.03, 39.8, 36.8, 35.8, 35.5, 35.09, 35.08, 34.9,$

34.5, 33.8, 31.0, 29.47, 29.44, 28.07, 28.06, 27.2, 26.3, 26.1, 25.9, 24.1, 23.3, 20.7, 18.3, 11.9, -4.6; IR (neat, cm^{-1}): 2927, 2857, 1948, 1716, 1600, 1496, 1451, 1406, 1372, 1251, 1094, 1077; MS (ESI): m/z 743 ($\text{M}+\text{Na}$)⁺, 738 ($\text{M}+\text{NH}_4$)⁺, 721 ($\text{M}+\text{H}$)⁺; HRMS Calcd for $\text{C}_{49}\text{H}_{76}\text{NO}_2\text{Si}$ ($\text{M}+\text{NH}_4$)⁺: 738.5640, Found: 738.5635. Anal. Calcd for $\text{C}_{49}\text{H}_{72}\text{O}_2\text{Si}$: C 81.61, H 10.06; found: C 81.84, H 10.10.

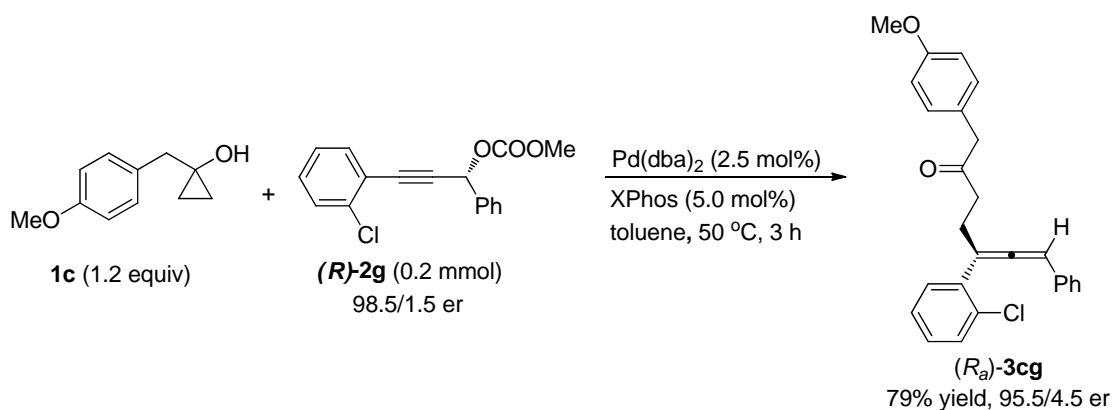
Chirality transfer:

(1) (*R_a*)-5-Allyl-1,7-diphenylhepta-5,6-dien-2-one ((*R_a*)-3ae) (jmq4-120)



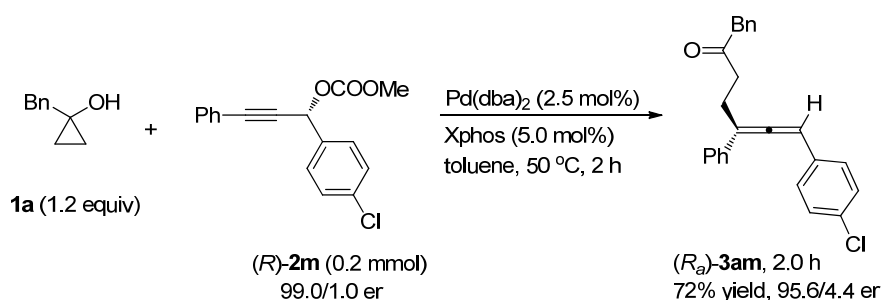
Following Typical Procedure I, the reaction of Pd(dba)₂ (7.2 mg, 0.0125 mmol), XPhos (12.0 mg, 0.025 mmol), **1a** (89.2 mg, 0.6 mmol)/toluene (1.0 mL), and (*R*)-**2e** (115.2 mg, 0.5 mmol, > 99.5/0.5 er)/toluene (1.5 mL) for 1.3 h afforded (*R_a*)-**3ae** (90.3 mg, 60%) [eluent: petroleum ether/ethyl acetate = 60/1 (0.4 L) to 50/1 (0.8 L)] as a colorless oil: 95.3/4.7 er (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 100/1, 1.0 mL/min, λ = 214 nm, t_R (major) = 9.7 min, t_R (minor) = 10.3 min); $[\alpha]_D^{25}$ = +44.6 (c = 1.0, CHCl_3); ¹H NMR (400 MHz, CDCl_3) δ = 7.36-7.14 (m, 8 H, ArH), 7.09-6.93 (m, 2 H, ArH), 6.13 (quint, J = 3.2 Hz, 1 H, =CH), 5.90-5.76 (m, 1 H, =CH), 5.10 (dd, J = 16.8, 1.6 Hz, 1 H, one proton of =CH₂), 5.02 (dd, J = 10.2, 1.4 Hz, 1 H, one proton of =CH₂), 3.59 (d, J = 15.6 Hz, 1 H, one proton of PhCH₂), 3.53 (d, J = 15.2 Hz, 1 H, one proton of PhCH₂), 2.84 (d, J = 6.4 Hz, 2 H, CH₂), 2.72-2.51 (m, 2 H, CH₂), 2.48-2.20 (m, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl_3) δ = 207.2, 201.9, 135.3, 135.2, 134.1, 129.4, 128.6, 128.5, 126.8, 126.5, 116.4, 106.8, 97.1, 50.1, 39.6, 37.9, 25.6; IR (neat, cm^{-1}): 2976, 1948, 1712, 1598, 1495, 1407, 1360, 1071, 1029; MS (70 eV, EI) m/z (%): 302 (M^+ , 6.78), 91 (100); HRMS Calcd for $\text{C}_{22}\text{H}_{22}\text{O}$ (M^+): 302.1671, Found: 302.1674.

(2) (*R_a*)-5-(2-Chlorophenyl)-1-(4-methoxyphenyl)-7-phenylhepta-5,6-dien-2-one ((*R_a*)-3cg) (jmq4-124)



Following Typical Procedure I, the reaction of Pd(dba)_2 (2.9 mg, 0.005 mmol), XPhos (4.8 mg, 0.01 mmol), **1c** (42.9 mg, 0.24 mmol)/toluene (0.5 mL), and $(R)\text{-2g}$ (60.2 mg, 0.2 mmol, 98.5/1.5 er)/toluene (0.5 mL) for 3 h afforded $(R_a)\text{-3cg}$ (63.4 mg, 79%) [eluent: petroleum ether/ethyl acetate = 40/1 (0.4 L) to 30/1 (0.8 L) to 20/1 (0.4 L)] as a colorless oil: 95.5/4.5 er (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 90/10, 1.0 mL/min, $\lambda = 214$ nm, $t_{\text{R}}(\text{major}) = 11.8$ min, $t_{\text{R}}(\text{minor}) = 16.0$ min); $[\alpha]_{\text{D}}^{20} = -158.0$ ($c = 0.408$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) $\delta = 7.44\text{--}7.26$ (m, 6 H, ArH), 7.25–7.11 (m, 3 H, ArH), 6.96 (d, $J = 8.8$ Hz, 2 H, ArH), 6.78 (d, $J = 8.8$ Hz, 2 H, ArH), 6.29 (t, $J = 3.4$ Hz, 1 H, =CH), 3.76 (s, 3 H, OMe), 3.57 (d, $J = 15.6$ Hz, 1 H, one proton of ArCH_2), 3.52 (d, $J = 15.6$ Hz, 1 H, one proton of ArCH_2), 2.86–2.54 (m, 4 H, $2 \times \text{CH}_2$); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 207.4, 203.9, 158.5, 136.4, 134.1, 132.8, 130.4, 130.1, 129.9, 128.6, 128.5, 127.2, 127.1, 126.8, 126.1, 114.0, 107.5, 97.3, 55.2, 49.2, 39.6, 26.9$; IR (neat, cm^{-1}): 1947, 1711, 1611, 1584, 1511, 1461, 1435, 1406, 1300, 1245, 1177, 1113, 1063, 1032; MS (70 eV, EI) m/z (%): 404 [$\text{M}^+(\text{C}^{37}\text{Cl})$, 3.43], 402 [$\text{M}^+(\text{C}^{35}\text{Cl})$, 9.45], 121 (100); HRMS Calcd for $\text{C}_{26}\text{H}_{23}^{35}\text{ClO}_2$ (M^+): 402.1387, Found: 402.1392.

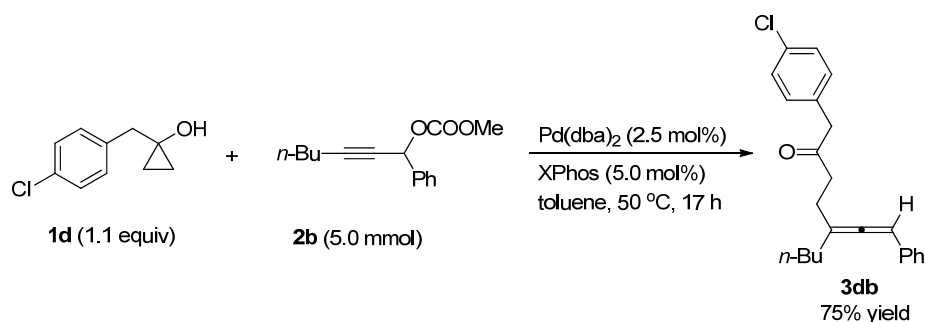
(3) $(R_a)\text{-7-(4-Chlorophenyl)-1,5-diphenylhepta-5,6-dien-2-one}$ ($(R_a)\text{-3am}$)
(jmq5-29)



Following Typical Procedure I, the reaction of Pd(dba)₂ (2.9 mg, 0.005 mmol), XPhos (4.9 mg, 0.01 mmol), **1a** (35.8 mg, 0.24 mmol)/toluene (0.5 mL), and (*R*)-**2m** (60.2 mg, 0.2 mmol, 99.0/1.0 er)/toluene (0.5 mL) for 2 h afforded (*R_a*)-**3am** (53.5 mg, 72%) [eluent: petroleum ether/ethyl acetate = 60/1 (0.4 L) to 40/1 (1.2 L)] as a solid: m.p. 88.8-89.3 °C (petroleum ether/dichloromethane); 95.6/4.4 er (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 214 nm, *t_R*(major) = 8.6 min, *t_R*(minor) = 13.2 min); [α]_D²⁰ = -248.3 (c = 0.44, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 7.39 (d, *J* = 7.6 Hz, 2 H, ArH), 7.36-7.15 (m, 10 H, ArH), 7.12-6.94 (m, 2 H, ArH), 6.50-6.40 (m, 1 H, =CH), 3.62 (d, *J* = 15.2 Hz, 1 H, one proton of Bn), 3.56 (d, *J* = 15.2 Hz, 1 H, one proton of Bn), 3.01-2.65 (m, 4 H, 2 × CH₂); ¹³C NMR (100 MHz, CDCl₃) δ = 206.8, 205.8, 135.3, 133.9, 132.8, 132.5, 129.3, 128.9, 128.5, 128.0, 127.4, 126.9, 126.0, 109.8, 98.4, 50.2, 39.7, 23.5; IR (neat, cm⁻¹): 3026, 2892, 1930, 1716, 1596, 1487, 1453, 1428, 1407, 1380, 1313, 1229, 1083, 1073, 1030, 1013; MS (70 eV, EI) *m/z* (%): 374 [M⁺(³⁷Cl), 7.93], 372 [M⁺(³⁵Cl), 23.25], 91 (100); Anal. Calcd for C₂₅H₂₁ClO: C 80.53, H 5.68; found: C 80.48, H 5.70.

III. Gram-scale synthesis and transformations of product **3db**.

Gram scale reaction: 5-Butyl-1-(4-chlorophenyl)-7-phenylhepta-5,6-dien-2-one (3db) (jmq4-49)

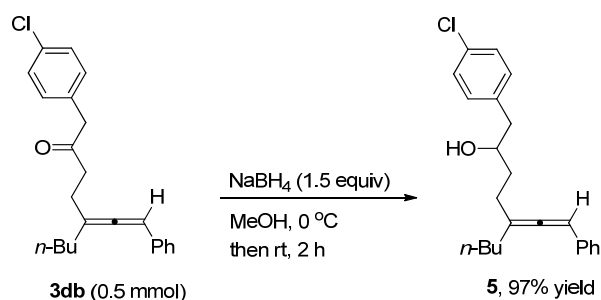


Following Typical Procedure II, the reaction of Pd(dba)₂ (71.9 mg, 0.125 mmol), XPhos (119.4 mg, 0.25 mmol), **1d** (1.0050 g, 5.5 mmol), and **2b** (1.2320 g, 5.0 mmol) in toluene (5.0 mL), and toluene (20.0 mL) for 17 h afforded 75% yield of **3db** (1.3279 g) [eluent: petroleum ether/ethyl acetate = 100/1 (0.8 L) to 60/1 (1.6 L)] as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ = 7.35-7.27 (m, 2 H, ArH), 7.25-7.12 (m, 5 H, ArH), 6.89 (d, *J* = 8.4 Hz, 2 H, ArH), 6.11 (quint, *J* = 3.2 Hz, 1 H, =CH), 3.56 (d,

$J = 16.0$ Hz, 1 H, one proton of PhCH₂), 3.49 (d, $J = 15.6$ Hz, 1 H, one proton of PhCH₂), 2.73-2.51 (m, 2 H, CH₂), 2.48-2.36 (m, 1 H, one proton of CH₂), 2.35-2.20 (m, 1 H, one proton of CH₂), 2.08 (t, $J = 6.8$ Hz, 2 H, CH₂), 1.54-1.40 (m, 2 H, CH₂), 1.40-1.24 (m, 2 H, CH₂), 0.87 (t, $J = 7.2$ Hz, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) $\delta = 206.6, 201.4, 135.4, 132.7, 132.5, 130.8, 128.6, 128.5, 126.7, 126.4, 108.5, 97.1, 49.2, 39.8, 32.9, 29.7, 25.9, 22.4, 13.9$; IR (neat, cm⁻¹): 2955, 2927, 2871, 2859, 1945, 1715, 1597, 1492, 1461, 1406, 1360, 1089, 1073, 1016; MS (70 eV, EI) m/z (%): 354 [$M^+(^{37}\text{Cl})$, 1.35], 352 [$M^+(^{35}\text{Cl})$, 4.74], 142 (100); HRMS Calcd for C₂₃H₂₅³⁵ClO (M^+): 352.1594, Found: 352.1597.

Transformations of product 3db:

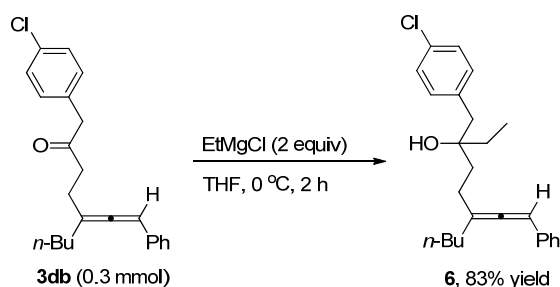
(1) Reduction with NaBH₄ for the synthesis of 5-butyl-1-(4-chlorophenyl)-7-phenylhepta-5,6-dien-2-ol (5) (jmq4-54, wpl-2-16)



To a flame-dried Schlenk tube were added **3db** (176.5 mg, 0.5 mmol) and MeOH (5.0 mL). The solution was cooled to 0 °C and NaBH₄ (29.0 mg, 0.75 mmol, 1.5 equiv) was added slowly. The resulting mixture was allowed to warm up to room temperature and stirred at rt for 2 h. The resulting mixture was then cooled to 0 °C and quenched with water (10 mL) and the aqueous layer was extracted by EtOAc (15 mL \times 3). The combined organic phase was washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. After evaporation, the residue was purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 20/1 (1.2 L)] to afford **5** (172.1 mg, 97%) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) $\delta = 7.40\text{--}7.14$ (m, 7 H, ArH), 7.09 (d, $J = 8.0$ Hz, 1 H, ArH), 6.89 (d, $J = 8.8$ Hz, 1 H, ArH), 6.27-6.02 (m, 1 H, =CH), 3.96-3.84 (m, 1 H, CH), 2.85-2.46 (m, 2 H, CH₂), 2.38-1.98 (m, 4 H, 2 \times CH₂), 1.82-1.58 (m, 2 H, CH₂), 1.57-1.40 (m, 3 H, CH₂ + OH),

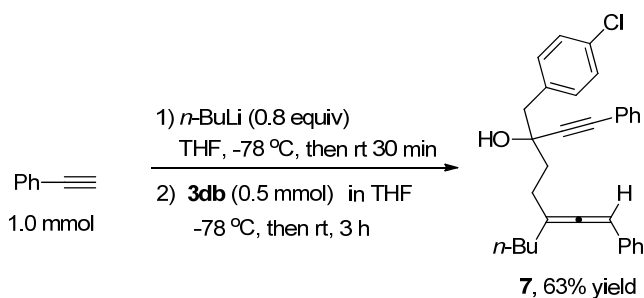
1.39-1.26 (m, 2 H, CH₂), 0.88 (t, *J* = 7.4 Hz, 3 H, CH₃); IR (neat, cm⁻¹): 2925, 2857, 1946, 1894, 1597, 1491, 1461, 1406, 1089, 1071, 1015; MS (70 eV, EI) *m/z* (%): 356 [M⁺(³⁷Cl), 0.65], 354 [M⁺(³⁵Cl), 2.34], 129 (100); HRMS Calcd for C₂₃H₂₇³⁵ClO (M⁺): 354.1750, Found: 354.1754; Anal. Calcd for C₂₃H₂₇ClO: C 77.83, H 7.67; found: C 77.75, H 7.77.

(2) Reaction with EtMgCl for the synthesis of 6-butyl-3-(4-chlorobenzyl)-8-phenylocta-6,7-dien-3-ol (6) (jmq4-67, wpl-2-18)



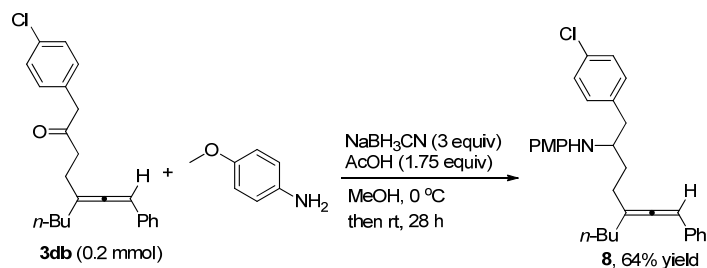
To a flame-dried Schlenk tube was added a solution of **3db** (105.9 mg, 0.3 mmol) in THF (1.5 mL). The solution was cooled to 0 °C and EtMgCl (2.0 M in THF, 0.6 mmol, 0.2 mL + 0.1 mL) was added slowly. After being stirred at 0 °C for 2 h, the resulting mixture was quenched with water at 0 °C (10 mL) and the aqueous layer was extracted by EtOAc (10 mL × 3). The combined organic phase was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. After evaporation, the residue was purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 40/1 (1.2 L)] to afford **6** (95.2 mg, 83% yield) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ = 7.43-6.98 (m, 9 H, ArH), 6.26-6.03 (m, 1 H, =CH), [the major isomer: 2.70 (s), the minor isomer 2.69 (s), 2 H, CH₂ of ArCH₂], 2.25-2.00 (m, 4 H, 2 × CH₂), 1.70-1.52 (m, 2 H, CH₂), 1.50-1.40 (m, 4 H, 2 × CH₂), 1.40-1.28 (m, 2 H, CH₂), 1.18 (s, 1 H, OH), 1.00-0.80 (m, 6 H, 2 × CH₃); IR (neat, cm⁻¹): 2956, 2927, 2872, 2857, 1946, 1597, 1491, 1459, 1406, 1378, 1111, 1092, 1029, 1016; MS (MALDI) *m/z*: 400 (M+NH₄)⁺; HRMS Calcd for C₂₅H₃₁³⁵ClO (M⁺): 382.2063, Found: 382.2069; Anal. Calcd for C₂₅H₃₁ClO: C 78.41, H 8.16; found: C 78.31, H 8.14.

(3) Synthesis of 6-butyl-3-(4-chlorophenylmethyl)-1,8-phenyl-nona-1-yn-6,7-dien-3-ol (7) (jmq4-61, wpl-2-17)



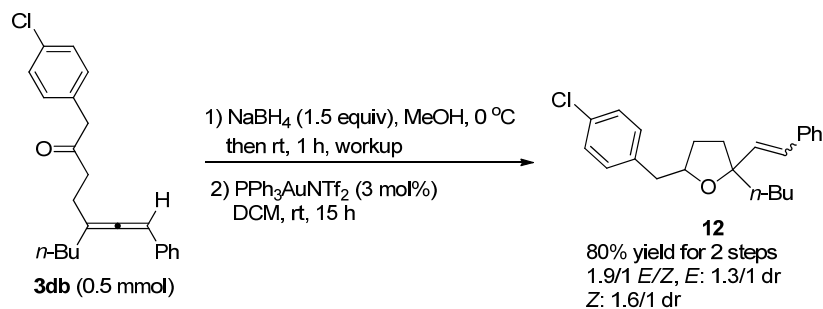
To a flame-dried Schlenk tube were added phenylacetylene (102.8 mg, 1.0 mmol) and THF (0.5 mL) under Ar. The resulting mixture was cooled to -78 °C, then *n*-BuLi (2.5 M in hexane, 0.32 mL, 0.8 mmol) was added dropwise. After the addition, the resulting mixture was stirred at room temperature for 30 min. The resulting mixture was cooled to -78 °C, and a solution of **3db** (176.5 mg, 0.5 mmol) in THF (1.5 mL) was added dropwise. The resulting mixture was stirred at room temperature for 3 h, and then cooled to 0 °C, quenched with H₂O (10 mL), extracted with ethyl ether (15 mL × 3), and dried over anhydrous Na₂SO₄. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 60/1 (2.4 L)] to afford **7** (142.2 mg, 63%) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ = 7.44-7.10 (m, 14 H, ArH), 6.26-6.04 (m, 1 H, =CH), 2.99 (d, *J* = 13.6 Hz, 1 H, one proton of CH₂Ar), 2.92 (d, *J* = 13.2 Hz, 1 H, one proton of CH₂Ar), 2.54-2.32 (m, 2 H, CH₂), 2.24-2.10 (m, 2 H, CH₂), 2.08 (s, 1 H, OH), 2.07-1.86 (m, 2 H, CH₂), 1.55-1.44 (m, 2 H, CH₂), 1.40-1.28 (m, 2 H, CH₂), 0.88 (t, *J* = 7.4 Hz, 3 H, CH₃); IR (neat, cm⁻¹): 3559, 3415, 2954, 2924, 2857, 2323, 2228, 1947, 1597, 1490, 1459, 1406, 1378, 1110, 1029, 1016; MS (70 eV, EI) *m/z* (%): 456 [*M*⁺(³⁷Cl), 2.23], 454 [*M*⁺(³⁵Cl), 5.99], 329 (100); HRMS Calcd for C₃₁H₃₁³⁵ClO (*M*⁺): 454.2063, Found: 454.2065; Anal. Calcd for C₃₁H₃₁ClO: C 81.83, H 6.87; found: C 81.40, H 7.07.

(4) Reductive amination with amine and NaBH₃CN for the synthesis of *N*-(5-butyl-1-(4-chlorophenyl)-7-phenylhepta-5,6-dien-2-yl)-4-methoxyaniline (8**) (jmq4-72, wpl-2-20)**



To a flame-dried Schlenk tube were added $4\text{-MeOC}_6\text{H}_4\text{NH}_2$ (49.5 mg, 0.4 mmol) and a solution of **3db** (70.7 mg, 0.2 mmol) in MeOH (2.0 mL). AcOH (20 μL , $d = 1.049\text{ g/mL}$, 21.0 mg, 0.35 mmol) was then added, and the resulting solution was cooled with an ice/water bath. NaBH_3CN (37.9 mg, 0.6 mmol, 3 equiv) was added slowly. After addition, the resulting mixture was stirred at room temperature for 28 h before the reaction was cooled with an ice/water bath and quenched with water (10 mL). The aqueous layer was extracted by EtOAc (10 mL \times 3). The combined organic phase was washed with brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. After evaporation, the residue was purified by preparative thin layer chromatography on silica gel (20 \times 20 cm) to afford 64% yield of **8** (59.3 mg, 64% yield) (petroleum ether/ethyl acetate = 40/1 was used for the first run. This TLC plate was re-eluted with petroleum ether/ethyl acetate = 25/1) as an oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.40-7.08 (m, 7 H, ArH), 7.00 (d, J = 8.0 Hz, 1 H, ArH), 6.90 (d, J = 8.0 Hz, 1 H, ArH), 6.75 (t, J = 8.4 Hz, 2 H, ArH), 6.56-6.44 (m, 2 H, ArH), 6.07 (q, J = 2.8 Hz, 1 H, =CH), [the major isomer: 3.74 (s), the minor isomer 3.73 (s), 3 H, MeO], 3.63-3.47 (m, 1 H, NH), 2.86-2.57 (m, 2 H, CH_2 of ArCH_2), 2.36-2.06 (m, 2 H, CH and one proton of CH_2), 2.06-1.92 (m, 2 H, CH_2), 1.80-1.62 (m, 1 H, one proton of CH_2), 1.56-1.17 (m, 6 H, 3 \times CH_2), 0.85 (t, J = 7.2 Hz, 3 H, CH_3); IR (neat, cm^{-1}): 2952, 2927, 1946, 1597, 1509, 1491, 1462, 1407, 1234, 1178, 1107, 1038, 1015; MS (ESI) m/z = 462 [$\text{M}(^{37}\text{Cl})+\text{H}$] $^+$, 460 [$\text{M}(^{35}\text{Cl})+\text{H}$] $^+$; HRMS Calcd for $\text{C}_{30}\text{H}_{34}^{35}\text{ClNO}$ (M^+): 459.2329, Found: 459.2331; Anal. Calcd for $\text{C}_{30}\text{H}_{34}\text{ClNO}$: C 78.32, H 7.45, N 3.04; found: C 78.43, H 7.37, N 2.96.

(5) One-pot reduction-cyclization for the synthesis of 2-butyl-5-(4-chlorobenzyl)-2-styryltetrahydrofuran (12) (jmq4-65)

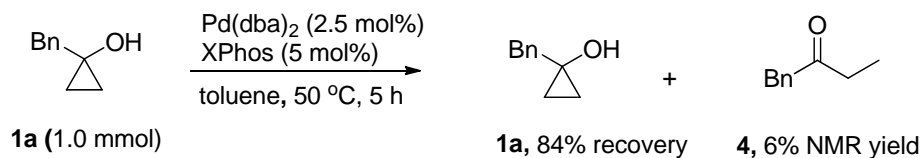


To a flame-dried Schlenk tube were added **3db** (105.9 mg, 0.3 mmol) and MeOH (3.0 mL) under Ar atmosphere. The solution was cooled to 0 °C and NaBH₄ (17.2 mg, 0.45 mmol, 1.5 equiv) was added slowly. The resulting mixture was warmed up to room temperature, stirred at rt for 1 h, cooled to 0 °C, quenched with water (10 mL), and extracted by EtOAc (15 mL × 3). The combined organic phase was washed with brine (20 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. After evaporation, the residue was used directly for next step.

To a flame-dried Schlenk tube were added PPh₃AuNTf₂ (6.8 mg, 0.009 mmol) and a solution of the above-prepared crude product in dichloromethane solution (3.0 mL). The resulting mixture was stirred at room temperature for 15 h. After concentration under reduced pressure, the crude product was purified by flash column chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 50/1 (1.2 L)] to provide **12** (85.5 mg, 80% yield for 2 steps, 1.9/1 *E/Z*, *E*: 1.3/1 dr, *Z*: 1.6/1 dr) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.50-6.89 (m, 9 H, ArH), 6.62-6.33 (m, 1 H, =CH), [*E*, the minor isomer: 6.23 (d, *J* = 16.0 Hz), the major isomer: 6.15 (d, *J* = 16.0 Hz); *Z*, the minor isomer: 5.71 (d, *J* = 12.8 Hz), the major isomer: 5.59 (d, *J* = 13.2 Hz), 1 H, =CH], 4.17-3.60 (m, 1 H, CH), 3.18-2.30 (m, 2 H, CH₂), 2.02-1.10 (m, 10 H, 5 × CH₂), 1.01-0.80 (m, 3 H, CH₃); IR (neat): ν = 2955, 2930, 2860, 1598, 1491, 1447, 1407, 1377, 1299, 1194, 1090, 1042, 1015 cm⁻¹; MS (70 eV, EI) *m/z* (%): 356 [M⁺(³⁷Cl), 0.79], 354 [M⁺(³⁵Cl), 2.35], 297 (100); Anal. Calcd for C₂₃H₂₇ClO: C 77.83, H 7.67; found: C 77.58, H 7.60; HRMS Calcd for C₂₃H₂₇³⁵ClO (M⁺): 354.1750, Found: 354.1746.

IV. Mechanistic studies

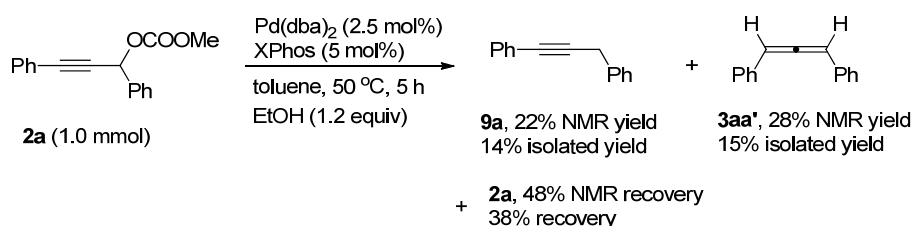
(1) Reaction of cyclopropanol **1a** under standard conditions (jmq4-38)



To a flame-dried Schlenk tube were added Pd(dba)₂ (14.4 mg, 0.025 mmol) and XPhos (23.8 mg, 0.05 mmol) under Ar atmosphere. A solution of **1a** (148.2 mg, 1.0 mmol) in toluene (5.0 mL) was added under Ar atmosphere at room temperature and the resulting mixture was stirred at 50 °C for 5 h and filtrated through a short column of silica gel eluted with ethyl acetate (80 mL). After evaporation, the residue was analyzed with the NMR spectrum in CDCl₃ with CH₂Br₂ (43.8 mg) as the internal standard-the recovery of **1a**^{1a} and NMR yield of compound **4**⁸ were determined to be 84% and 6%, respectively.

(2) Reaction of propargylic carbonate **2a** with alcohol under standard conditions

1) Reaction of propargylic carbonate **2a** with EtOH under standard conditions (jmq4-39)



To a flame-dried Schlenk tube were added Pd(dba)₂ (14.3 mg, 0.025 mmol) and XPhos (23.8 mg, 0.05 mmol) under Ar atmosphere. Compound **2a** (266.3 mg, 1.0 mmol)/toluene (5.0 mL) and EtOH (70.1 μL, d = 0.789 g/mL, 55.3 mg, 1.2 mmol) were then added sequentially under Ar atmosphere at room temperature. The Schlenk tube was then stirred at 50 °C for 5 h. Then the crude reaction mixture was filtrated through a short column of silica gel eluted with ethyl acetate (80 mL). After evaporation, the residue was characterized by crude NMR in CDCl₃ with CH₂Br₂ (44.3 mg) as the internal standard. The recovery of **2a**^{2b} and NMR yield of compounds **9a**^{9a} and **3aa'**^{9b} were determined to be 48%, 22%, and 28%, respectively. Then the crude mixture was concentrated and purified by silica gel column chromatography [eluent: petroleum ether/ethyl acetate = 200/1 (0.8 L) to petroleum

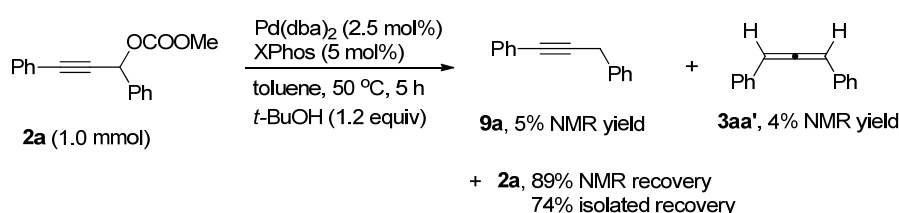
ether/ethyl acetate = 30/1 (0.8 L)] to provide **2a** (102.3 mg, 38% recovery), **9a** (27.4 mg, 14% yield) and **3aa'** (29.0 mg, 15% yield).

9a:^{9a} oil; ¹H NMR (400 MHz, CDCl₃) δ = 7.55-7.24 (m, 10 H, ArH), 3.83 (s, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ = 136.7, 131.6, 128.5, 128.2, 127.9, 127.8, 126.6, 123.6, 87.5, 82.6, 25.7; IR (neat, cm⁻¹): 3061, 3030, 2198, 1692, 1641, 1598, 1582, 1490, 1451, 1416, 1316, 1286, 1207, 1174, 1070, 1028, 1013; MS (70 eV, EI) *m/z* (%): 192 (M⁺, 44.9), 121 (100).

3aa':^{9b} oil; ¹H NMR (400 MHz, CDCl₃) δ = 7.48-7.20 (m, 10 H, ArH), 6.59 (s, 2 H, 2 × =CH).

2a:^{2b} oil; ¹H NMR (400 MHz, CDCl₃) δ = 7.70-7.56 (m, 2 H, PhH), 7.54-7.45 (m, 2 H, ArH), 7.44-7.37 (m, 3 H, ArH), 7.35-7.27 (m, 3 H, ArH), 6.53 (s, 1 H, CH), 3.82 (s, 3 H, MeO).

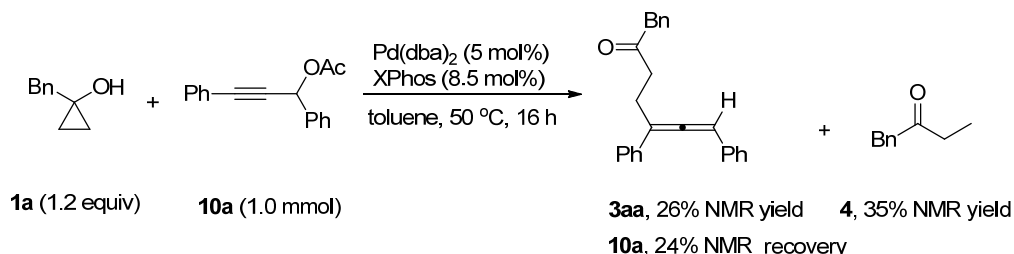
2) Reaction of propargylic carbonate **2a** with *t*-BuOH under standard conditions (jmq5-66)



To a flame-dried Schlenk tube were added Pd(dba)₂ (14.3 mg, 0.025 mmol) and XPhos (23.8 mg, 0.05 mmol) under Ar atmosphere. Compound **2a** (266.3 mg, 1.0 mmol)/toluene (5.0 mL) and *t*-BuOH (110.0 μL, d = 0.81 g/mL, 89.1 mg, 1.2 mmol) were then added sequentially under Ar atmosphere at room temperature. The Schlenk tube was then stirred at 50 °C for 5 h. Then the crude reaction mixture was filtrated through a short column of silica gel eluted with ethyl ether (50 mL). After evaporation, the residue was analyzed with the ¹H NMR spectrum in CDCl₃ with CH₂Br₂ (17.5 μL) as the internal standard. The recovery of **2a**^{2b} and NMR yields of compounds **9a**^{9a} and **3aa'**^{9b} were determined to be 89%, 5%, and 4%, respectively. Then the crude mixture was concentrated and purified by silica gel column chromatography [eluent: petroleum ether/ethyl acetate = 200/1 (1.2 L) to petroleum ether/ethyl acetate = 30/1

(0.8 L)] to provide **2a** (197.9 mg, 74% yield) and trace amounts of impure **9a** and **3aa'**.

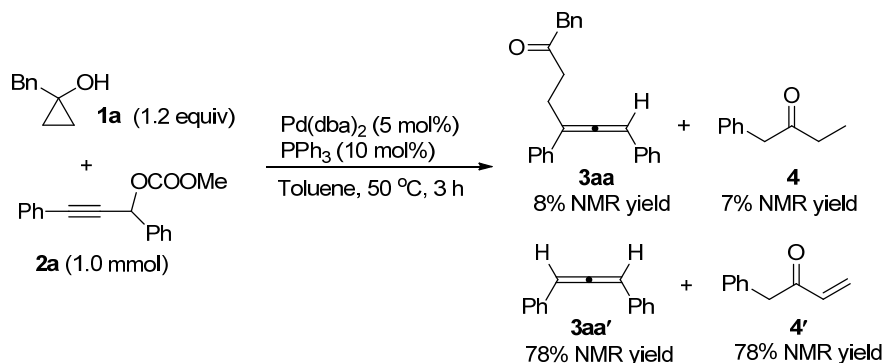
(3) Reaction of propargylic acetate **10a** with cyclopropanol **1a** under standard conditions (jmq4-164)



To a flame-dried Schlenk tube were added Pd(dba)₂ (23.9 mg, 0.05 mmol) and XPhos (40.6 mg, 0.085 mmol) under Ar atmosphere. Compound **1a** (178.5 mg, 1.0 mmol)/toluene (2.5 mL) and **10a** (250.3 mg, 1.0 mmol)/toluene (2.5 mL) were then added sequentially under Ar atmosphere at room temperature. The resulting mixture was then stirred at 50 °C for 16 h and filtrated through a short column of silica gel eluted with ethyl acetate (60 mL). After evaporation, the residue was analyzed with the ¹H NMR spectrum in CDCl₃ with CH₂Br₂ (44.0 mg) as the internal standard. The recovery of **10a**,³ NMR yield of **4**,⁸ and allene product **3aa** were determined to be 24%, 35%, and 26%.

V. Characterization of the byproducts

1) Characterization of the byproducts **3aa'** and **4'** (jmq4-199)



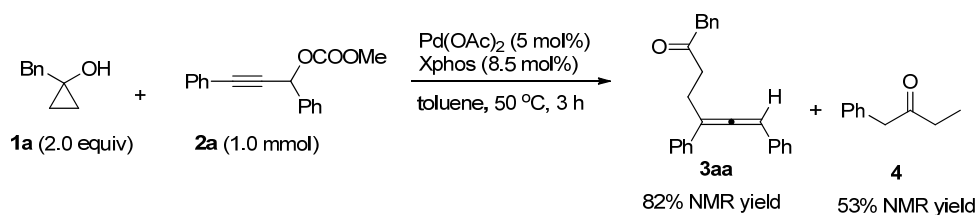
To a flame-dried Schlenk tube were added Pd(dba)₂ (28.7 mg, 0.05 mmol) and PPh₃ (26.2 mg, 0.10 mmol) under Ar atmosphere. Compound **1a** (178.1 mg, 1.2 mmol)/toluene (2.5 mL) and **2a** (266.3 mg, 1.0 mmol)/toluene (2.5 mL) were then added sequentially under Ar atmosphere at room temperature. The Schlenk tube was

then stirred at 50 °C until completion of the reaction as monitored by TLC (3 h). The crude reaction mixture was filtrated through a short column of silica gel (height: 2 cm, Φ : 3.5 cm) eluted with ethyl acetate (60 mL). After evaporation, the residue was analyzed with the ^1H NMR spectrum in CDCl_3 with CH_2Br_2 (44.4 mg) as the internal standard. All the residue was then purified by chromatography on silica gel to afford **3aa'**^{9b} (138.2 mg, 72%) and **4'**^{9c} (80.2 mg, 55%) [eluent: petroleum ether (0.4 L) to petroleum ether/ ethyl ether = 30/1, (1.2 L)].

3aa'^{9b} oil; ^1H NMR (400 MHz, CDCl_3) δ = 7.44-7.27 (m, 8 H, ArH), 7.26-7.18 (m, 2 H, ArH), 6.59 (s, 2 H, $2 \times =\text{CH}$); ^{13}C NMR (100 MHz, CDCl_3) δ = 207.8, 133.6, 128.7, 127.3, 127.0, 98.4; IR (neat, cm^{-1}): 1936, 1701, 1597, 1492, 1450, 1310, 1072, 1028; MS (70 eV, EI) m/z (%): 192 (M^+ , 100).

4'^{9c} oil; ^1H NMR (400 MHz, CDCl_3) δ = 7.36-7.15 (m, 5 H, ArH), 6.39 (dd, J = 17.4, 10.6 Hz, 1 H, $=\text{CH}$), 6.29 (dd, J = 17.4, 1.4 Hz, 1 H, one proton of $=\text{CH}_2$), 5.80 (dd, J = 10.0, 1.2 Hz, 1 H, one proton of $=\text{CH}_2$), 3.86 (s, 2 H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ = 197.6, 135.5, 134.0, 129.4, 128.9, 128.6, 126.9, 47.0; IR (neat, cm^{-1}): 2924, 1706, 1495, 1454, 1399, 1184, 1075, 1031; MS (ESI) m/z 169 ($\text{M}+\text{Na}$)⁺, 147 ($\text{M}+\text{H}$)⁺.

2) Characterization of the byproduct 4 (jmq5-50)



To a flame-dried Schlenk tube were added $\text{Pd}(\text{OAc})_2$ (11.3 mg, 0.05 mmol) and XPhos (40.5 mg, 0.085 mmol) under Ar atmosphere. Compound **1a** (296.6 mg, 2.0 mmol)/toluene (2.5 mL) and **2a** (266.5 mg, 1.0 mmol)/toluene (2.5 mL) were then added sequentially under Ar atmosphere at room temperature. The Schlenk tube was then stirred at 50 °C until completion of the reaction as monitored by TLC (3 h). The crude reaction mixture was filtrated through a short column of silica gel (height: 2 cm, Φ : 3.5 cm) eluted with ethyl ether (50 mL). After evaporation, the residue was

purified by chromatography on silica gel to afford **3aa** and **4** [eluent: petroleum ether/ethyl acetate = 80/1 (2.0 L)].

3aa: white solid; ^1H NMR (400 MHz, CDCl_3) δ = 7.41 (d, J = 7.2 Hz, 2 H, ArH), 7.36-7.16 (m, 11 H, ArH), 7.04 (d, J = 6.4 Hz, 2 H, ArH), 6.50 (s, 1 H, =CH), 3.62 (d, J = 15.6 Hz, 1 H, one proton of PhCH_2), 3.57 (d, J = 15.6 Hz, 1 H, one proton of PhCH_2), 2.97-2.65 (m, 4 H, $2 \times \text{CH}_2$); ^{13}C NMR (100 MHz, CDCl_3) δ = 207.0, 205.7, 135.6, 134.0, 129.4, 128.8, 128.53, 128.49, 127.3, 127.2, 126.85, 126.80, 126.0, 109.3, 99.3, 50.2, 39.8, 23.6.

4:^{9d} colorless oil; ^1H NMR (400 MHz, CDCl_3) δ = 7.50-7.15 (m, 5 H, ArH), 3.68 (s, 2 H, CH_2Ar), 2.47 (q, J = 7.2 Hz, 2 H, CH_2), 1.03 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ = 209.0, 134.5, 129.4, 128.7, 126.9, 49.8, 35.2, 7.7; IR (neat, cm^{-1}): 2957, 2926, 2854, 1738, 1716, 1666, 1604, 1494, 1451, 1369, 1335, 1262, 1231, 1078, 1017; MS (70 eV, EI) m/z (%): 148 (M^+ , 16.13), 57 (100).

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