Tri(*o*-tolyl)phosphine for Highly Efficient Suzuki Coupling of Propargylic Carbonates with Boronic Acids

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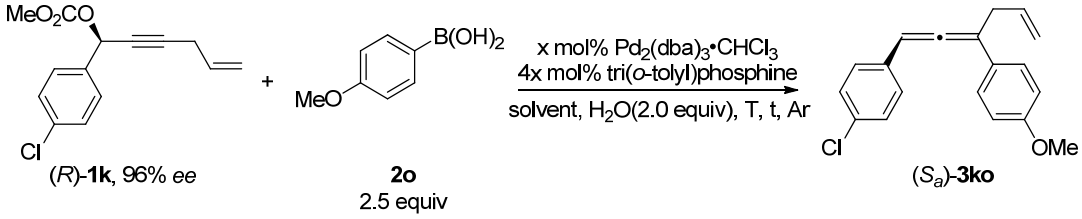
General Information. NMR spectra were taken with an Agilent-400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR) in $CDCl_3$. All ^{1}H NMR experiments were measured with tetramethylsilane (0 ppm) or the signal of residual $CHCl_3$ (7.26 ppm) in $CDCl_3$ as the internal reference; ^{13}C NMR experiments were measured in relative to the signal of $CDCl_3$ (77.16 ppm); ^{19}F NMR experiments were measured in relative to the signal of $CFCl_3$ (0 ppm) in $CDCl_3$. All reactions were carried out in oven-dried Schlenk bottles. $Pd_2(dba)_3{\cdot}CHCl_3$ was purchased from J&K Chemicals; tris(*o*-tolyl)phosphine was purchased from Tokyo Chemical Industry Co., Ltd. Organoboronic acids were all commercially available: phenylboronic acid was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and recrystallized from ethyl acetate before use; other arylboronic acids (98% purity) were purchased from Shanghai Boka Chemical Technology Co., Ltd (Shanghai, China) and used as received. Petroleum ether (b.p. 60-90 ^{o}C) was purchased from Shanghai Titan Scientific Co., Ltd. Dioxane was dried over sodium wire with benzophenone as the indicator and distilled freshly before use. The starting racemic propargylic carbonates and the enantioenriched propargylic carbonates (*R*)-**1p** were synthesized from commercially or easily available propargylic alcohols[1] according to the reported procedures.[2] Optically active propargylic carbonate (*R*)-**1k** was synthesized from the optically active terminal propargylic alcohol[3] via coupling with allyl bromide according to the literature method.[4]

Table S1. Optimization of reaction conditions for chirality transfer

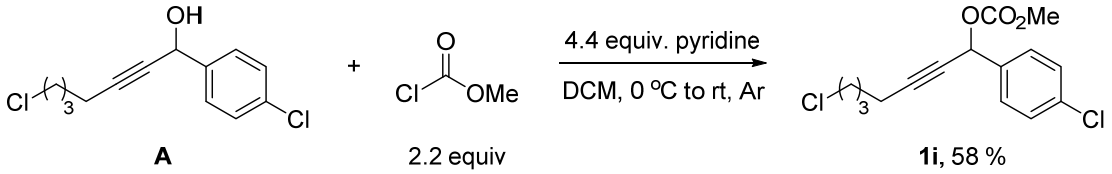


Entry	x	solvent	T/°C	t	yield/%[a]	recovery of (*R*)-**1k**/%[a]	*ee* of S_a-**3ko**/%
1[c]	3	dioxane	rt	5 min	99	9	91
2[d]	3	Et_2O	0	4.1 h	16	79	96
3[d]	3	dioxane:Et_2O= 5:2	0	18 h	82[b]	/	93
4[c]	5	dioxane:Et_2O= 5:2	0	13.1 h	>99	/	91

[a] The yield and recovery were determined by ^{1}H NMR analysis. [b] isolated yield. [c] The recation was conducted on 1.0 mmol scale. [d] The recation was conducted on 0.5 mmol scale.

Experimental details and analytical data

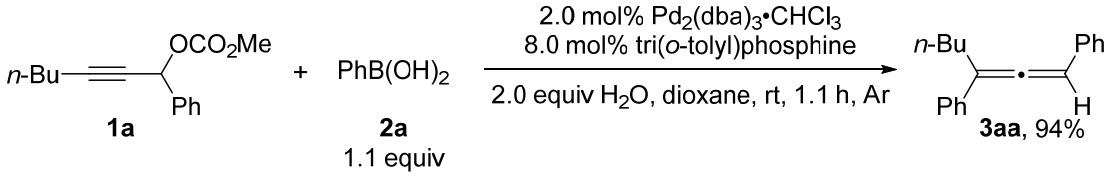
Preparation of 7-chloro-1-(4-chlorophenyl)hept-2-ynyl methyl carbonate (1i, xjz-1-009)



To an oven-dried round-flask were added 7-chloro-1-(4-chlorophenyl)hept-2-yn-1-ol (2.1606 g, 8.4 mmol), pyridine (2.97 mL, d = 0.983 g/cm^3, 2.9195 g, 37.0 mmol), and anhydrous DCM (10 mL) under argon. After cooling to 0 °C via an ice-water bath, methyl chloroformate (1.44 mL, d = 1.213 g/cm^3, 1.7467 g, 18.5 mmol) was added dropwise to the mixture over 2 min. The resulting mixture was naturally warmed up to room temperature and stirred overnight. The reaction was quenched with 1 M HCl (aq.) and extracted with DCM three times. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel to afford **1i** (1.5398 g, 58%) [eluent: petroleum ether/ethyl acetate = 100:1 (200 mL), then petroleum ether/ethyl acetate = 60:1 (300 mL), then petroleum ether/ethyl acetate = 50:1 (400 mL), then petroleum ether/ethyl acetate = 40:1 (800 mL)]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.52-7.43 (m, 2 H, Ar-H), 7.41-7.30 (m, 2 H, Ar-H), 6.24 (t, *J* = 2.0 Hz, 1 H, CH), 3.80 (s, 3 H, OCH_3), 3.55 (t, *J* = 6.6 Hz, 2 H, CH_2), 2.32 (td, J_1 = 7.0 Hz, J_2 = 2.1 Hz, 2 H, CH_2), 1.93-1.80 (m, 2 H, CH_2), 1.75-1.65 (m, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 154.9, 135.5, 135.2, 129.2, 129.0, 88.9, 76.6, 69.4, 55.2, 44.5, 31.6, 25.5, 18.3; **IR** (neat): ν = 2955, 2233, 1746, 1491, 1440, 1247, 1089 cm^{-1}; **MS** (70 eV, EI) m/z (%): 316 (M^+(^{35}Cl, ^{37}Cl), 2.37), 314 (M^+(^{35}Cl, ^{35}Cl), 3.81), 203 (100); **HRMS** Calcd. for $C_{15}H_{16}{}^{35,35}Cl_2O_3$ [M^+]: 314.0477; found 314.0481.

Pd-Catalyzed synthesis of allenes 3

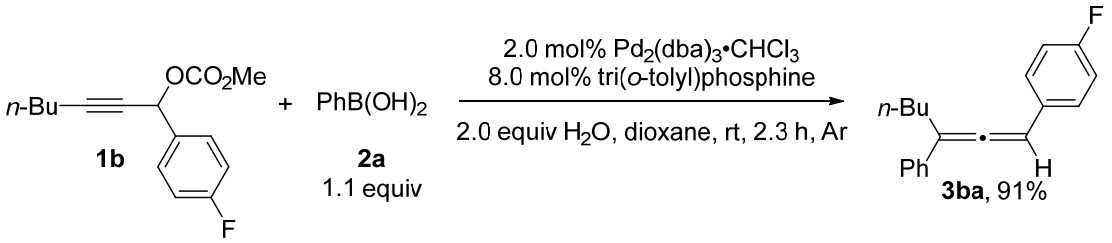
(1) Preparation of 1,3-diphenyl-1,2-heptadiene (3aa, xjz-1-102)



Typical Procedure I: To an oven-dried Schlenk tube were added $Pd_2(dba)_3{\cdot}CHCl_3$ (20.5 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.6 mg, 0.08 mmol), and **2a** (134.5 mg, 1.1 mmol). After replacing air with argon for three times at rt by vacuum, **1a** (246.3 mg, 1.0 mmol), freshly distilled dioxane (2.0 mL), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) were added sequentially. The resulting mixture was stirred for 1.1 h at rt and then filtered through a short pad of silica gel with Et_2O (25.0 mL) as the eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel to afford **3aa**[5] (233.5 mg, 94%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.52-7.39 (m, 2 H, Ar-H), 7.38-7.24 (m, 6 H, Ar-H), 7.23-7.14 (m, 2 H, Ar-H), 6.51 (t, *J* = 3.2 Hz, 1 H, =CH), 2.64-2.48 (m, 2 H, CH_2), 1.69-1.50 (m, 2 H, CH_2), 1.49-1.37 (m, 2 H, CH_2), 0.91 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 206.6, 136.4, 134.8, 128.8, 128.6, 127.12, 127.08, 126.9, 126.2, 110.1, 98.0, 30.3, 30.0, 22.8, 14.1; **IR** (neat): ν = 3027, 2955, 2927, 2858, 1932, 1596, 1492, 1459, 1446, 1073, 1028 cm^{-1}; **MS** (70 eV, EI) m/z (%): 249 (M^++1, 2.15), 248 (M^+, 8.82), 206 (100).

The following compounds were prepared according to this Typical Procedure.

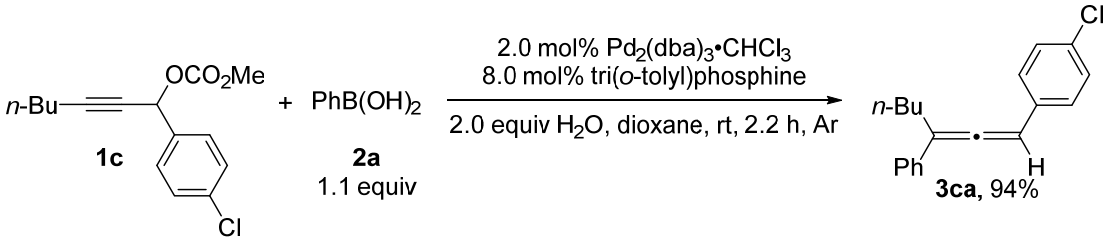
(2) Preparation of 1-(4-fluorophenyl)-3-phenyl-1,2-heptadiene (3ba, xjz-1-062)



The reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ (20.6 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.8 mg, 0.08 mmol), **2a** (133.6 mg, 1.1 mmol), **1b** (264.2 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL)

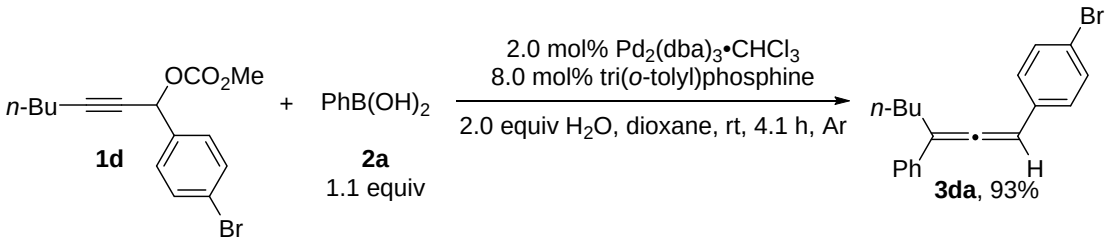
afforded **3ba** (242.3 mg, 91%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.6 Hz, 2 H, Ar-H), 7.36-7.25 (m, 4 H, Ar-H), 7.25-7.18 (m, 1 H, Ar-H), 6.99 (d, *J* = 8.2 Hz, 2 H, Ar-H), 6.49 (t, *J* = 3.0 Hz, 1 H, =CH), 2.63-2.48 (m, 2 H, CH_2), 1.68-1.49 (m, 2 H, CH_2), 1.48-1.37 (m, 2 H, CH_2), 0.91 (t, *J* = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 206.3 (d, *J* = 2.3 Hz), 163.3 (d, *J* = 245.2 Hz), 136.3, 130.79 (d, *J* = 3.0 Hz), 128.7, 128.3 (d, *J* = 8.3 Hz), 127.2, 126.2, 115.9 (d, *J* = 21.2 Hz), 110.3, 97.0, 30.2, 30.0, 22.8, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -115.9; **IR** (neat): ν = 3061, 2956, 2927, 2859, 1933, 1600, 1506, 1464, 1453, 1224, 1154, 1093 cm^{-1}; **MS** (70 eV, EI) m/z (%): 267 (M^++1, 1.94), 266 (M^+, 8.05), 105 (100); **HRMS** calcd for $C_{19}H_{19}F$ [M^+]: 266.1471; found 266.1469.

(3) Preparation of 1-(4-chlorophenyl)-3-phenyl-1,2-heptadiene (3ca, xjz-1-063)



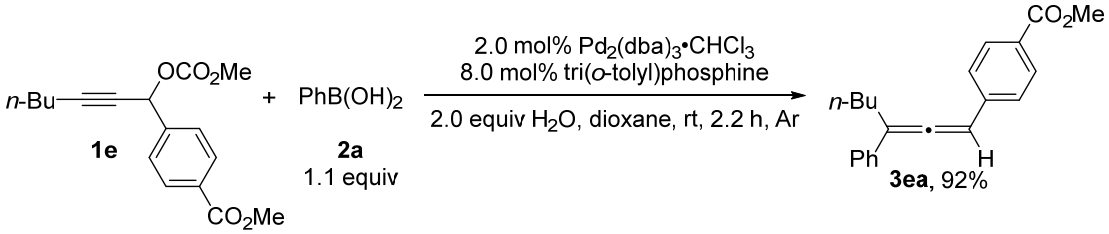
The reaction of $Pd_2(dba)_3$·$CHCl_3$ (20.9 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.8 mg, 0.08 mmol), **2a** (134.1 mg, 1.1 mmol), **1c** (280.5 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3ca**[6] (266.3 mg, 94%) [eluent: petroleum ether]: solid; **m.p.** 53.5-54.3 ^oC [petroleum ether]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.6 Hz, 2 H, Ar-H), 7.36-7.28 (m, 2 H, Ar-H), 7.27-7.17 (m, 5 H, Ar-H), 6.47 (s, 1 H, =CH), 2.63-2.48 (m, 2 H, CH_2), 1.66-1.50 (m, 2 H, CH_2), 1.48-1.37 (m, 2 H, CH_2), 0.91 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 206.8, 136.0, 133.4, 132.6, 129.0, 128.7, 128.0, 127.3, 126.2, 110.6, 97.1, 30.2, 30.0, 22.8, 14.1; **IR** (neat): ν = 3058, 2952, 2931, 2894, 2856, 1933, 1594, 1489, 1465, 1448, 1379, 1089, 1071, 1012 cm^{-1}; **MS** (70 eV, EI) m/z (%): 284 (M^+(^{37}Cl), 1.83), 282 (M^+(^{35}Cl), 4.89), 205 (100).

(4) Preparation of 1-(4-bromophenyl)-3-phenyl-1,2-heptadiene (3da, xjz-1-064)



The reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ (20.7 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.3 mg, 0.08 mmol), **2a** (134.4 mg, 1.1 mmol), **1d** (325.7 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3da**[7] (304.3 mg, 93%) [eluent: petroleum ether]: solid; **m.p.** 60.2-60.4 ^oC [petroleum ether (b.p. 60-90 ^oC)]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.47-7.37 (m, 4 H, Ar-H), 7.33-7.29 (m, 2 H, Ar-H), 7.26-7.14 (m, 3 H, Ar-H), 6.46 (t, *J* = 3.0 Hz, 1 H, =CH), 2.63-2.48 (m, 2 H, CH_2), 1.65-1.48 (m, 2 H, CH_2), 1.47-1.35 (m, 2 H, CH_2), 0.91 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 206.8, 136.0, 133.9, 131.9, 128.7, 128.4, 127.3, 126.2, 120.7, 110.6, 97.2, 30.2, 29.9, 22.8, 14.1; **IR** (neat): ν = 3057, 2952, 2931, 2856, 1934, 1594, 1485, 1466, 1378, 1196, 1069, 1009 cm^{-1}; **MS** (70 eV, EI) m/z (%): 328 (M^+(^{81}Br), 3.26), 326 (M^+(^{79}Br), 3.19), 205 (100).

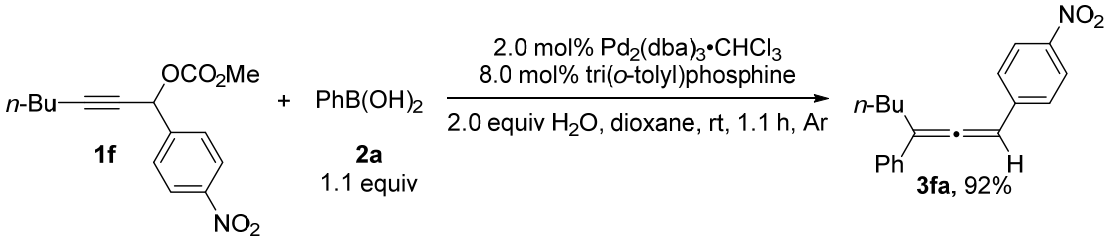
(5) Preparation of 1-(methoxycarbonylphenyl)-3-phenyl-1,2-heptadiene (3ea, xjz-1-066)



The reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ (20.3 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.2 mg, 0.08 mmol), **2a** (134.4 mg, 1.1 mmol), **1e** (304.8 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3ea**[8] (282.3 mg, 92%) [First run: eluent: petroleum ether/ethyl acetate = 40:1 (40 mL), then petroleum ether/ethyl acetate = 20:1 (180 mL) got the impure product. Second run: petroleum ether (300 mL), then petroleum ether/ethyl acetate = 80:1 (80 mL), then petroleum ether/ethyl acetate = 40:1 (240 mL) got the pure product.]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.43 (d, *J* = 7.6 Hz, 2 H, Ar-H), 7.38 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.35-7.28 (m, 2 H, Ar-H), 7.26-7.19 (m, 1

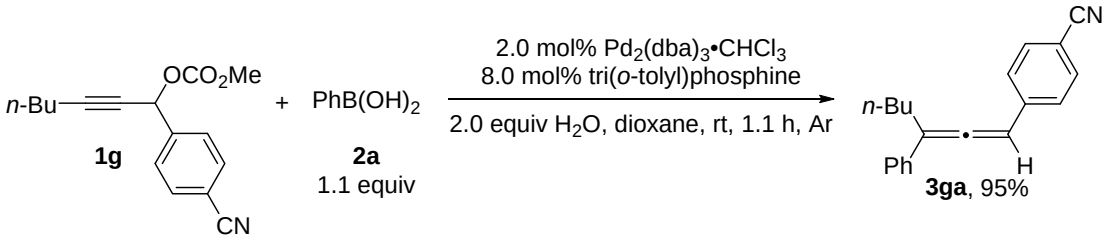
H, Ar-H), 6.55 (t, *J* = 3.0 Hz, 1 H, =CH), 3.89 (s, 3 H, OCH_3), 2.64-2.50 (m, 2 H, CH_2), 1.65-1.50 (m, 2 H, CH_2), 1.49-1.38 (m, 2 H, CH_2), 0.91 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 208.0, 167.0, 139.9, 135.7, 130.2, 128.7, 128.6, 127.4, 126.7, 126.3, 110.6, 97.5, 52.1, 30.2, 29.9, 22.7, 14.1; **IR** (neat): ν = 3031, 2953, 2928, 2859, 1931, 1717, 1605, 1493, 1451, 1434, 1272, 1173, 1016 cm^{-1}; **MS** (70 eV, EI) m/z (%): 307 (M^++1, 1.92), 306 (M^+, 8.57), 205 (100).

(6) Preparation of 1-(4-nitrophenyl)-3-phenyl-1,2-heptadiene (3fa, xjz-1-067)



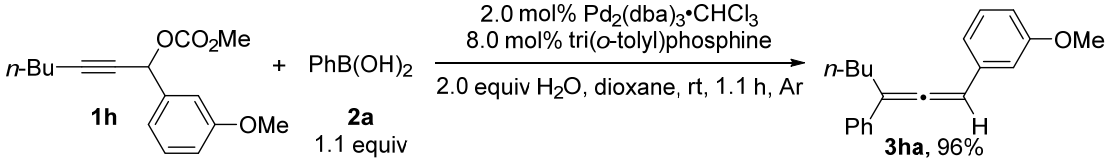
The reaction of $Pd_2(dba)_3$·$CHCl_3$ (20.7 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.0 mg, 0.08 mmol), **2a** (133.7 mg, 1.1 mmol), **1f** (291.5 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3fa** (270.8 mg, 92%) [First run: eluent: petroleum ether (100 mL), then petroleum ether/ethyl acetate = 40:1 (320 mL) got the impure product. Second run: petroleum ether (300 mL), then petroleum ether/ethyl acetate = 40:1 (300 mL) got the pure product.]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 6.8 Hz, 2 H, Ar-H), 7.50-7.39 (m, 4 H, Ar-H), 7.38-7.30 (m, 2 H, Ar-H), 7.30-7.20 (m, 1 H, Ar-H), 6.59 (t, *J* = 2.8 Hz, 1 H, =CH), 2.63-2.57 (m, 2 H, CH_2), 1.63-1.53 (m, 2 H, CH_2), 1.48-1.41 (m, 2 H, CH_2), 0.92 (t, *J* = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 208.9, 146.6, 142.2, 135.1, 128.8, 127.7, 127.2, 126.3, 124.3, 111.3, 96.9, 30.1, 29.9, 22.7, 14.1; **IR** (neat): ν = 2956, 2928, 2858, 1930, 1592, 1513, 1492, 1451, 1337, 1107 cm^{-1}; **MS** (70 eV, EI) m/z (%): 294 (M^++1, 1.86), 293 (M^+, 10.05), 204 (100); **HRMS** calcd. for $C_{19}H_{19}NO_2$ [M^+]: 293.1416; found 293.1414.

(7) Preparation of 1-(4-cyanophenyl)-3-phenyl-1,2-heptadiene (3ga, xjz-1-072)



The reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ (20.4 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.8 mg, 0.08 mmol), **2a** (134.3 mg, 1.1 mmol), **1g** (271.7 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3ga**[8] (259.4 mg, 95%) [eluent: petroleum ether (300 mL), then petroleum ether/ethyl acetate = 40:1 (~240 mL)]: oil; **m.p.** 82.7-82.9 ^oC [petroleum ether]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.47-7.37 (m, 4 H, Ar-H), 7.37-7.29 (m, 2 H, Ar-H), 7.28-7.21 (m, 1 H, Ar-H), 6.53 (t, *J* = 2.8 Hz, 1 H, =CH), 2.68-2.51 (m, 2 H, CH_2), 1.66-1.50 (m, 2 H, CH_2), 1.49-1.38 (m, 2 H, CH_2), 0.92 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 208.2, 140.1, 135.3, 132.6, 128.8, 127.6, 127.2, 126.3, 119.2, 111.2, 110.2, 97.2, 30.1, 29.9, 22.7, 14.0; **IR** (neat): ν = 2955, 2922, 2854, 2228, 1933, 1604, 1493, 1464, 1452, 1379, 1205, 1175, 1075, 1031 cm^{-1}; **MS** (70 eV, EI) m/z (%): 274 (M^++1, 1.52), 273 (M^+, 7.32), 231 (100).

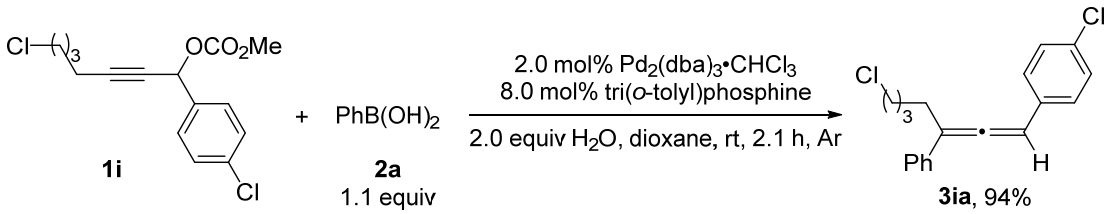
(8) Preparation of 1-(3-methoxyphenyl)-3-phenyl-1,2-heptadiene (3ha, xjz-1-077)



The reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ (20.5 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.5 mg, 0.08 mmol), **2a** (134.1 mg, 1.1 mmol), **1h** (275.9 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3ha** (268.0 mg, 96%) [eluent: petroleum ether (400 mL), then petroleum ether/ethyl acetate = 80:1 (~160 mL) to 60:1 (240 mL)]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.29 (t, *J* = 7.6 Hz, 2 H, Ar-H), 7.31-7.15 (m, 2 H, Ar-H), 6.98-6.86 (m, 2 H, Ar-H), 6.74 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H, Ar-H), 6.49 (t, *J* = 2.8 Hz, 1 H, =CH), 3.74 (s, 3 H, OCH_3), 2.63-2.48 (m, 2 H, CH_2),

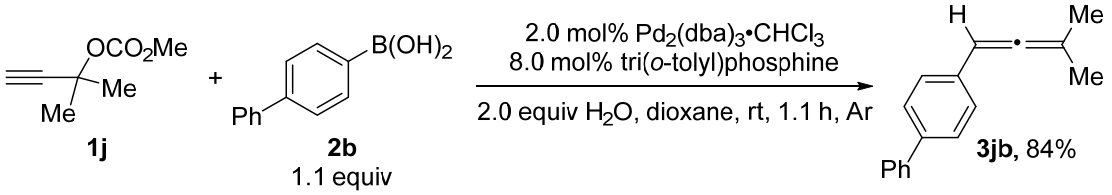
1.67-1.51 (m, 2 H, CH_2), 1.50-1.36 (m, 2 H, CH_2), 0.91 (t, J = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 206.7, 160.1, 136.31, 136.27, 129.8, 128.6, 127.1, 126.2, 119.5, 112.7, 112.1, 110.1, 97.9, 55.2, 30.2, 30.0, 22.8, 14.1; **IR** (neat): ν = 2955, 2928, 2858, 1933, 1596, 1581, 1490, 1464, 1450, 1437, 1284, 1260, 1144, 1043 cm^{-1}; **MS** (70 eV, EI) m/z (%): 279 (M^++1, 2.46), 278 (M^+, 10.73), 105 (100); **HRMS** calcd. for $C_{20}H_{22}O$ [M^+]: 278.1671; found 278.1670.

(9) Preparation of 1-(4-chlorophenyl)-3-phenyl-7-chloro-1,2-heptadiene (3ia, xjz-1-076)



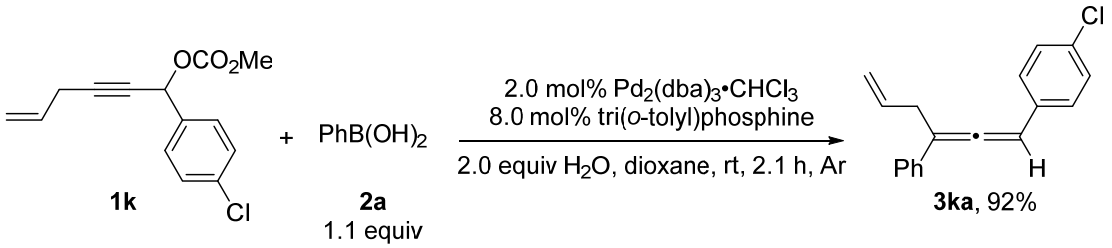
The reaction of $Pd_2(dba)_3$·$CHCl_3$ (21.1 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.1 mg, 0.08 mmol), **2a** (134.4 mg, 1.1 mmol), **1i** (315.7 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3ia** (303.2 mg, 94%, 99% purity) [eluent: petroleum ether (500 mL), then petroleum ether/ethyl acetate = 40:1 (~360 mL)]: solid; **m.p.** 61.3-61.5 ^oC [petroleum ether]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.2 Hz, 2 H, Ar-H), 7.32 (t, J = 7.4 Hz, 2 H, Ar-H), 7.39-7.28 (m, 5 H, Ar-H), 6.51 (t, J = 3.0 Hz, 1 H, =CH), 3.52 (t, J = 6.6 Hz, 2 H, CH_2), 2.69-2.50 (m, 2 H, CH_2), 1.97-1.84 (m, 2 H, CH_2), 1.82-1.65 (m, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 206.6, 135.7, 133.1, 132.8, 129.0, 128.7, 128.0, 127.5, 126.2, 110.0, 97.5, 44.8, 32.4, 29.4, 25.2; **IR** (neat): ν = 2942, 2861, 1929, 1899, 1593, 1489, 1459, 1450, 1431, 1380, 1330, 1090, 1064, 1012 cm^{-1}; **MS** (70 eV, EI) m/z (%): 320 (M^+(^{37}Cl, ^{37}Cl), 1.09), 318 (M^+(^{35}Cl, ^{37}Cl), 5.00), 316 (M^+(^{35}Cl, ^{35}Cl), 7.55), 205 (100); Anal. Calcd. for $C_{19}H_{18}Cl_2$: C 71.93, H 5.72; found C 71.38, H 5.69.

(10) Preparation of 1-(4-phenylphenyl)-3-methyl-1,2-butadiene (3jb, xjz-1-099)



The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.6 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.0 mg, 0.08 mmol), **2b** (217.6 mg, 1.1 mmol), **1j** (142.6 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3jb** (185.1 mg, 84%) [eluent: petroleum ether]: solid; **m.p.** 63.6-63.9 ^oC [petroleum ether]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.65-7.48 (m, 4 H, Ar-H), 7.47-7.38 (m, 2 H, Ar-H), 7.37-7.27 (m, 3 H, Ar-H), 6.07-5.99 (m, 1 H, =CH), 1.83 (d, *J* = 3.2 Hz, 6 H, 2 x CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 203.5, 141.1, 139.4, 135.2, 128.9, 127.4, 127.23, 127.17, 127.0, 99.4, 92.4, 20.4; **IR** (neat): ν = 3063, 3032, 2981, 2935, 2905, 2849, 1954, 1596, 1486, 1447, 1390, 1378, 1358, 1213, 1003 cm^{-1}; **MS** (70 eV, EI) m/z (%): 221 (M^++1, 17.68), 220 (M^+, 95.09), 205 (100); Anal. Calcd. for $C_{17}H_{16}$: C 92.68, H 7.32; found C 92.55, H 7.36.

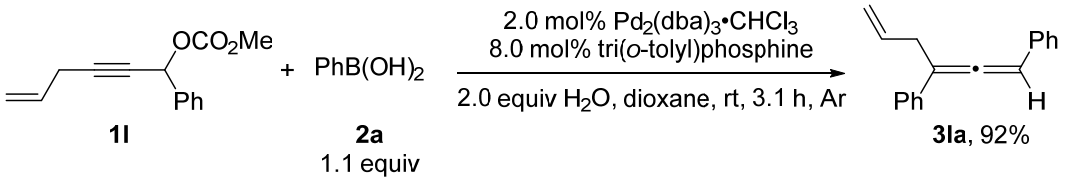
(11) Preparation of 1-(4-chlorophenyl)-3-phenyl-1,2,5-hexatriene (3ka, xjz-1-148



The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (21.2 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.4 mg, 0.08 mmol), **2a** (134.4 mg, 1.1 mmol), **1k** (265.1 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3ka**[9] (246.5 mg, 92%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.52-7.39 (m, 2 H, Ar-H), 7.36-7.28 (m, 2 H, Ar-H), 7.28-7.19 (m, 5 H, Ar-H), 6.50 (t, *J* = 2.8 Hz, 1 H, =CH), 6.03-5.90 (m, 1 H, =CH), 5.20 (ddd, J_1 = 17.2 Hz, J_2 = 3.2 Hz, J_3 = 1.6 Hz, 1 H, one proton of $=CH_2$), 5.09 (dd, J_1 = 10.2 Hz, J_2 = 1.4 Hz, 1 H, one proton of $=CH_2$), 3.42-3.27 (m, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 207.1, 135.41, 135.39, 133.0, 132.8, 129.0, 128.7, 128.1, 127.5, 126.3,

116.9, 108.9, 97.4, 34.9; **IR** (neat): ν = 3080, 3059, 3030, 2978, 2905, 1933, 1639, 1596, 1488, 1450, 1380, 1089, 1012 cm^{-1}; **MS** (70 eV, EI) m/z (%): 268 (M^+(^{37}Cl), 12.55), 266 (M^+(^{35}Cl), 45.90), 105 (100).

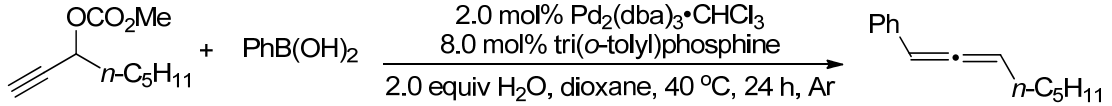
(12) Preparation of 1,3-diphenyl-1,2,5-hexatriene (3la, xjz-1-153)



1l **2a** (1.1 equiv) **3la**, 92%

The reaction of $Pd_2(dba)_3$·$CHCl_3$ (20.4 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.8 mg, 0.08 mmol), **2a** (134.3 mg, 1.1 mmol), **1l** (229.9 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3la**[9] (213.3 mg, 92%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 7.6 Hz, 2 H, Ar-H), 7.39-7.25 (m, 6 H, Ar-H), 7.25-7.16 (m, 2 H, Ar-H), 6.54 (t, *J* = 2.6 Hz, 1 H, =CH), 6.04-5.93 (m, 1 H, =CH), 5.20 (dd, J_1 = 17.2 Hz, J_2 = 1.6 Hz, 1 H, one proton of $=CH_2$), 5.08 (dd, J_1 = 10.4 Hz, J_2 = 1.6 Hz, 1 H, one proton of $=CH_2$), 3.42-3.27 (m, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 207.0, 135.7, 135.6, 134.5, 128.9, 128.6, 127.3, 127.0, 126.3, 116.7, 108.4, 98.2, 35.0; **IR** (neat): ν = 1933, 1639, 1596, 1492, 1459, 1446, 1073, 1028 cm^{-1}; **MS** (70 eV, EI) m/z (%): 233 (M^++1, 11.75), 232 (M^+, 57.40), 191 (100).

(13) Preparation of 1-phenyl-1,2-octadiene (3na, xjz-1-164)

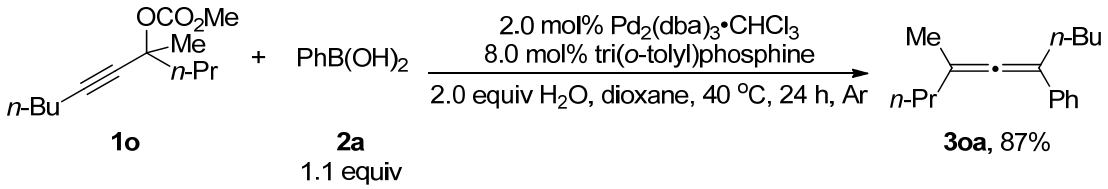


1n **2a** (1.1 equiv) **3na**, 36%, 8% recovery of **1n**

The reaction of $Pd_2(dba)_3$·$CHCl_3$ (10.8 mg, 0.01 mmol), tri(*o*-tolyl)phosphine (12.2 mg, 0.04 mmol), **2a** (66.8 mg, 0.55 mmol), **1n** (92.0 mg, 0.5 mmol), and H_2O (18.0 μL, d = 1.0 g/cm^3, 18.0 mg, 1.0 mmol) in freshly distilled dioxane (1.0 mL) afforded **3na**[10] (33.9 mg, 36%) [eluent: petroleum ether (60-90 °C)] (8% recovery of **1n** as determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as internal

standard): oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 4.8 Hz, 4 H, Ar-H), 7.20-7.15 (m, 1 H, Ar-H), 6.12 (dt, J_1 = 6.4 Hz, J_2 = 3.1 Hz, 1 H, =CH), 5.56 (q, *J* = 6.7 Hz, 1 H, =CH), 2.12 (qd, J_1 = 7.2 Hz, J_2 = 2.8 Hz, 2 H, CH_2), 1.53-1.42 (m, 2 H, CH_2), 1.40-1.25 (m, 4 H, 2×CH_2), 0.89 (t, *J* = 7.0 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 205.3, 135.3, 128.7, 126.72, 126.70, 95.2, 94.7, 31.5, 29.0, 28.9, 22.6, 14.2; **IR** (neat): ν = 2926, 2860, 1948, 1712, 1595, 1456 cm^{-1}; **MS** (70 eV, EI) m/z (%): 186 (M^+, 1.36), 130 (100).

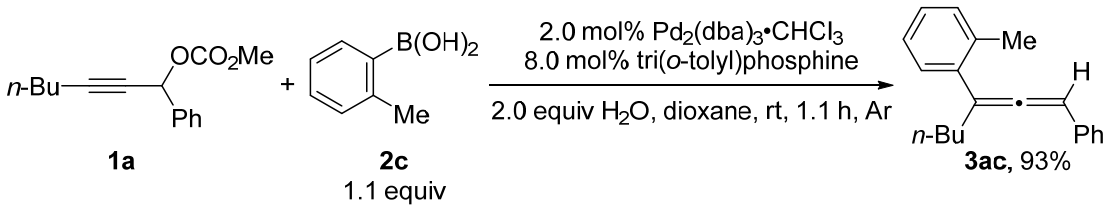
(14) Preparation of 4-methyl-6-phenyl-4,5-decadiene (3oa, xjz-1-166)



1o **2a** 1.1 equiv **3oa**, 87%

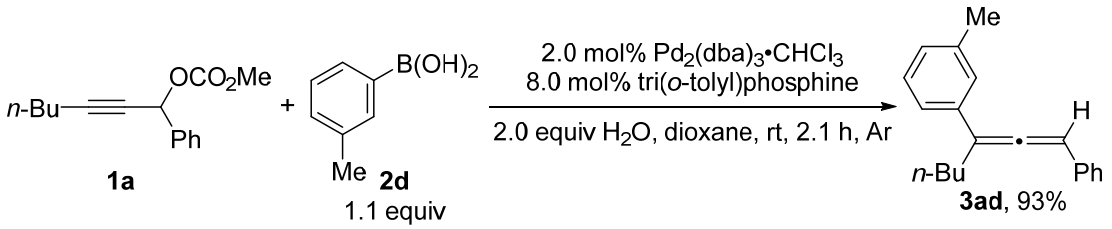
The reaction of $Pd_2(dba)_3$·$CHCl_3$ (21.0 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.7 mg, 0.08 mmol), **2a** (134.2 mg, 1.1 mmol), **1o** (226.6 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3oa** (198.9 mg, 87%) [eluent: petroleum ether (60-90 °C)/DCM/Et_2O = 200:1:1 (100+0.5+0.5) mL)]; oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.28 (t, *J* = 7.6 Hz, 2 H, Ar-H), 7.14 (t, *J* = 7.6 Hz, 1 H, Ar-H), 2.39 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.05 (t, *J* = 7.8 Hz, 2 H, CH_2), 1.78 (s, 3 H, CH_3), 1.56-1.35 (m, 6 H, 3×CH_2), 0.93 (t, *J* = 7.2 Hz, 6 H, 2×CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 201.5, 138.7, 128.3, 126.1, 126.0, 104.6, 102.7, 36.7, 30.5, 30.1, 22.7, 21.1, 19.0, 14.21, 14.19; **IR** (neat): ν = 3056, 2956, 2865, 1947, 1596, 1492, 1454, 1372 cm^{-1}; **MS** (70 eV, EI) m/z (%): 229 (M^++1, 1.65), 228 (M^+, 8.52), 143 (100); **HRMS** calcd. for $C_{17}H_{24}$ [M^+]: 228.1878; found: 228.1879.

(15) **Preparation of 1-phenyl-3-(2-methylphenyl)-1,2-heptadiene (3ac, xjz-1-081)**



The reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ (21.2 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.3 mg, 0.08 mmol), **2c** (149.9 mg, 1.1 mmol), **1a** (246.4 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in dioxane (2.0 mL) afforded **3ac**[8] (243.6 mg, 93%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.37-7.24 (m, 5 H, Ar-H), 7.22-7.10 (m, 4 H, Ar-H), 6.24 (t, *J* = 3.0 Hz, 1 H, =CH), 2.52-2.39 (m, 2 H, CH_2), 2.36 (s, 3 H, CH_3), 1.60-1.46 (m, 2 H, CH_2), 1.45-1.34 (m, 2 H, CH_2), 0.89 (t, *J* = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 204.1, 137.6, 136.0, 135.2, 130.6, 128.7, 128.1, 127.1, 126.9, 126.8, 125.9, 109.1, 95.3, 34.0, 30.2, 22.7, 20.8, 14.1; **IR** (neat): ν = 3062, 3028, 2955, 2926, 2857, 1941, 1598, 1487, 1456, 1377 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 263 (M^++1, 2.42), 262 (M^+, 8.38), 205 (100).

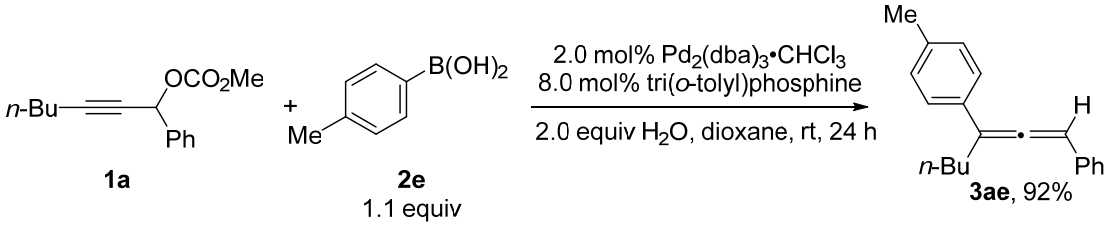
(16) Preparation of 1-phenyl-3-(3-methylphenyl)-1,2-heptadiene (3ad, xjz-1-082)



The reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ (20.5 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.0 mg, 0.08 mmol), **2d** (150.0 mg, 1.1 mmol), **1a** (245.7 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3ad** (243.7 mg, 93%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.40-7.23 (m, 6 H, Ar-H), 7.22-7.15 (m, 2 H, Ar-H), 7.02 (d, *J* = 7.6 Hz, 1 H, Ar-H), 6.50 (t, *J* = 3.0 Hz, 1 H, =CH), 2.62-2.47 (m, 2 H, CH_2), 2.32 (s, 3 H, CH_3), 1.67-1.50 (m, 2 H, CH_2), 1.49-1.37 (m, 2 H, CH_2), 0.91 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 206.6, 138.2, 136.3, 134.9, 128.8, 128.5, 128.0, 127.04, 126.96, 126.89, 123.3, 110.1, 97.8, 30.3, 30.1, 22.8, 21.7, 14.1; **IR** (neat): ν = 3028, 2955, 2926, 2859, 1932, 1599, 1493, 1456, 1378, 1027 cm^{-1}; **MS** (70 eV, EI) m/z (%): 263 (M^++1, 1.99), 262 (M^+, 8.24), 119 (100); **HRMS** calcd. for

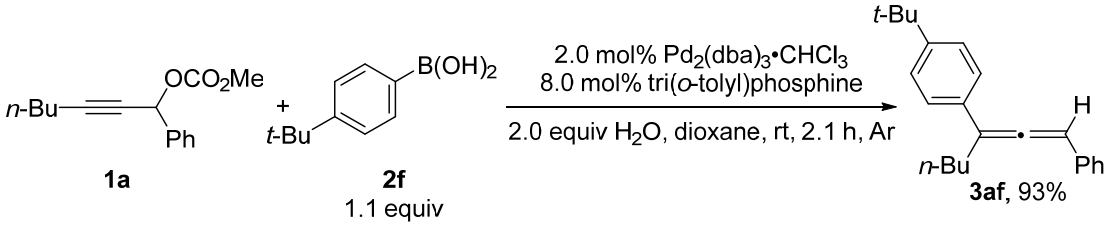
$C_{20}H_{22}$ [M^+]: 262.1722; found 262.1718.

(17) Preparation of 1-phenyl-3-(4-methylphenyl)-1,2-heptadiene (3ae, xjz-1-106)



The reaction of $Pd_2(dba)_3$·$CHCl_3$ (21.1 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.4 mg, 0.08 mmol), **2e** (149.5 mg, 1.1 mmol), **1a** (246.7 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3ae** (241.6 mg, 92%) [eluent: petroleum ether]: solid; **m.p.** 44.3-47.7 ^oC [petroleum ether]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.40-7.23 (m, 6 H, Ar-H), 7.21-7.14 (m, 1 H, Ar-H), 7.13-7.07 (m, 2 H, Ar-H), 6.49 (t, *J* = 2.8 Hz, 1 H, =CH), 2.62-2.46 (m, 2 H, CH_2), 2.31 (s, 3 H, CH_3), 1.68-1.50 (m, 2 H, CH_2), 1.49-1.36 (m, 2 H, CH_2), 0.90 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 206.4, 136.9, 135.0, 133.4, 129.3, 128.8, 127.0, 126.9, 126.2, 109.9, 97.8, 30.3, 30.1, 22.8, 21.2, 14.1; **IR** (neat): ν = 3064, 3029, 2949, 2921, 2855, 1935, 1597, 1509, 1495, 1458, 1329, 1183, 1109, 1072, 1025 cm^{-1}; **MS** (70 eV, EI) m/z (%): 263 (M^++1, 3.59), 262 (M^+, 16.48), 220 (100); Anal. Calcd. for $C_{20}H_{22}$: C 91.55, H 8.45; found C 91.66, H 8.56.

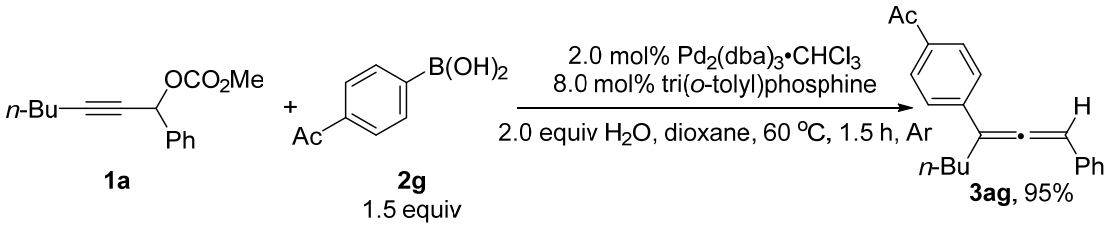
(18) Preparation of 1-phenyl-3-(4-*tert*-butylphenyl)-1,2-heptadiene (3af, xjz-1-089)



The reaction of $Pd_2(dba)_3$·$CHCl_3$ (20.6 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.4 mg, 0.08 mmol), **2f** (196.1 mg, 1.1 mmol), **1a** (246.5 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3af** (283.7 mg, 93%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz,

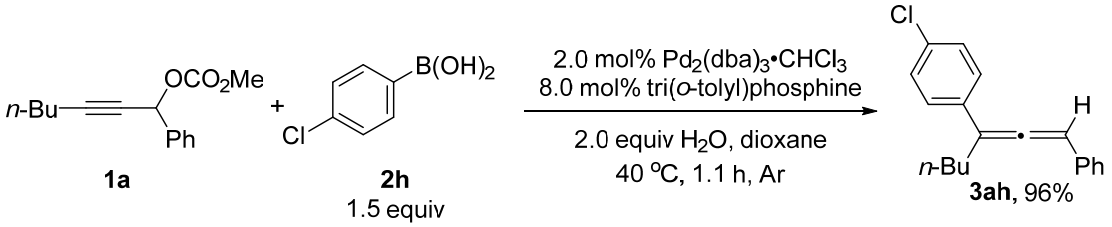
$CDCl_3$): δ = 7.42-7.37 (m, 2 H, Ar-H), 7.36-7.30 (m, 4 H, Ar-H), 7.30-7.24 (m, 2 H, Ar-H), 7.22-7.14 (m, 1 H, Ar-H), 6.50 (t, *J* = 3.2 Hz, 1 H, =CH), 2.62-2.48 (m, 2 H, CH_2), 1.69-1.52 (m, 2 H, CH_2) 1.48-1.34 (m, 2 H, CH_2), 1.30 (s, 9 H, 3 x CH_3), 0.91 (t, *J* = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 206.6, 150.1, 135.0, 133.4, 128.8, 127.0, 126.9, 125.9, 125.6, 109.8, 97.9, 34.6, 31.4, 30.3, 30.0, 22.8, 14.1; **IR** (neat): ν = 3030, 2957, 2867, 1933, 1598, 1509, 1495, 1459, 1363, 1269, 1201, 1118, 1017 cm^{-1}; **MS** (ESI) *m/z*: 305 ($M+H^+$); **HRMS** calcd. for $C_{23}H_{28}$ [M^+]: 304.2191; found 304.2200.

(19) Preparation of 1-phenyl-3-(4-acetylphenyl)-1,2-heptadiene (3ag, xjz-1-112)



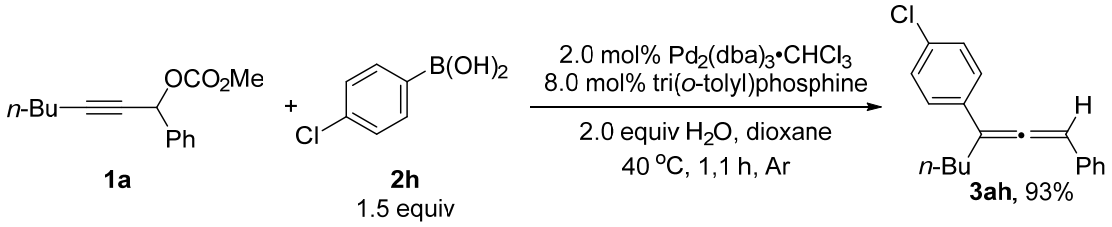
The reaction of $Pd_2(dba)_3$·$CHCl_3$ (20.5 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.6 mg, 0.08 mmol), **2f** (245.8 mg, 1.5 mmol), **1a** (246.5 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) at 60 °C afforded **3ag** (276.4 mg, 95%) [eluent: petroleum ether/ethyl acetate = 80:1]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.93-7.85 (m, 2 H, Ar-H), 7.52 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.37-7.27 (m, 4 H, Ar-H), 7.26-7.18 (m, 1 H, Ar-H), 6.58 (t, *J* = 3.0 Hz, 1 H, =CH), 2.65-2.49 (m, 5 H, CH_2 and CH_3CO), 1.69-1.51 (m, 2 H, CH_2), 1.49-1.39 (m, 2 H, CH_2), 0.92 (t, *J* = 7.6 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 207.7, 197.6, 141.5, 135.7, 134.1, 128.9, 128.7, 127.4, 127.0, 126.2, 109.7, 98.5, 30.2, 29.8, 26.7, 22.7, 14.1; **IR** (neat): ν = 2927, 2858, 1929, 1679, 1599, 1494, 1458, 1412, 1356, 1265, 1184, 1014 cm^{-1}; **MS** (70 eV, EI) m/z (%): 291 (M^++1, 5.74), 290 (M^+, 21.38), 147 (100); **HRMS** calcd. for $C_{21}H_{22}O$ [M^+]: 290.1671; found 290.1673.

(20) Preparation of 1-phenyl-3-(4-chlorophenyl)-1,2-heptadiene (3ah, xjz-1-114)



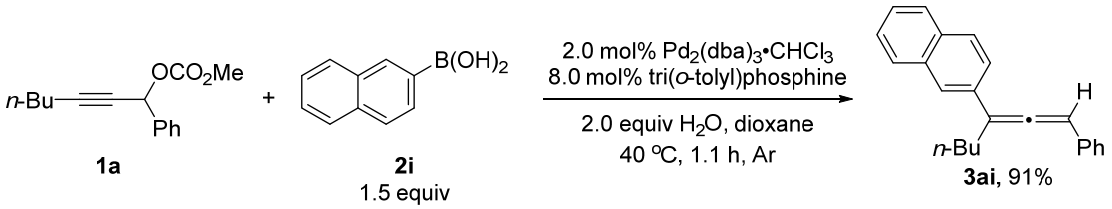
The reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ (21.2 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.8 mg, 0.08 mmol), **2g** (234.7 mg, 1.5 mmol), **1a** (246.3 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) at 40 °C afforded **3ah** (270.8 mg, 96%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.40-7.22 (m, 8 H, Ar-H), 7.22-7.17 (m, 1 H, Ar-H), 6.52 (t, *J* = 3.2 Hz, 1 H, =CH), 2.60-2.43 (m, 2 H, CH_2), 1.66-1.48 (m, 2 H, CH_2), 1.47-1.36 (m, 2 H, CH_2), 0.91 (t, *J* = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 206.6, 134.9, 134.5, 132.8, 128.9, 128.7, 127.5, 127.3, 126.9, 109.3, 98.3, 30.2, 30.0, 22.7, 14.1; **IR** (neat): ν = 2956, 2927, 2858, 1933, 1597, 1489, 1458, 1409, 1093, 1011 cm^{-1}; **MS** (70 eV, EI) m/z (%): 284 (M^+(^{37}Cl), 3.56), 282 (M^+(^{35}Cl), 10.37), 240 (100); **HRMS** calcd. for $C_{19}H_{19}{}^{35}Cl$ [M^+]: 282.1175; found 282.1172.

Gram-scale reaction for preparation of 3ah (xjz-1-117)



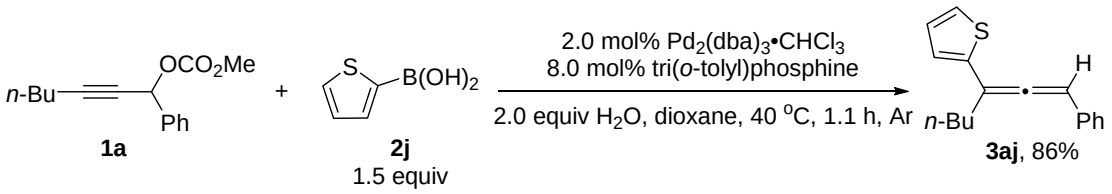
The reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ (124.3 mg, 0.12 mmol), tri(*o*-tolyl)phosphine (146.4 mg, 0.48 mmol), **2g** (1407.5 mg, 9.0 mmol), **1a** (1477.0 mg, 6.0 mmol), and H_2O (216.0 μL, d = 1.0 g/cm^3, 216.0 mg, 12.0 mmol) in freshly distilled dioxane (12.0 mL) afforded **3ah** (1571.7 mg, 93%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.40-7.21 (m, 8 H, Ar-H), 7.20-7.14 (m, 1 H, Ar-H), 6.51 (t, *J* = 3.0 Hz, 1 H, =CH), 2.57-2.42 (m, 2 H, CH_2), 1.64-1.48 (m, 2 H, CH_2), 1.47-1.34 (m, 2 H, CH_2), 0.90 (t, *J* = 7.2 Hz, 3 H, CH_3).

(21) Preparation of 1-phenyl-3-(2-naphthyl)-1,2-heptadiene (3ai, xjz-1-115)



The reaction of $Pd_2(dba)_3$·$CHCl_3$ (21.1 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.7 mg, 0.08 mmol), **2i** (257.7 mg, 1.5 mmol), **1a** (246.2 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3ai** (272.5 mg, 91%) [eluent: petroleum ether]: solid; **m.p.** 47.0-49.6 °C [petroleum ether]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.86-7.77 (m, 2 H, Ar-H), 7.74 (d, *J* = 7.2 Hz, 1 H, Ar-H), 7.70 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.60 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1 H, Ar-H), 7.46-7.33 (m, 4 H, Ar-H), 7.29 (t, *J* = 7.6 Hz, 2 H, Ar-H), 7.22-7.15 (m, 1 H, Ar-H), 6.58 (t, *J* = 2.8 Hz, 1 H, =CH), 2.76-2.59 (m, 2 H, CH_2), 1.73-1.56 (m, 2 H, CH_2), 1.53-1.38 (m, 2 H, CH_2), 0.93 (t, *J* = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 207.4, 134.8, 133.8, 133.7, 132.7, 128.9, 128.2, 128.0, 127.7, 127.2, 127.0, 126.2, 125.9, 125.5, 123.9, 110.3, 98.3, 30.3, 30.0, 22.8, 14.2; **IR** (neat): ν = 3055, 2954, 2926, 2857, 1928, 1628, 1596, 1494, 1457, 1436, 1272, 1128, 1026 cm^{-1}; **MS** (70 eV, EI) m/z (%): 299 (M^++1, 9.23), 298 (M^+, 35.55), 256 (100); Anal. Calcd. for $C_{23}H_{22}$: C 92.57, H 7.43; found C 92.32, H 7.55.

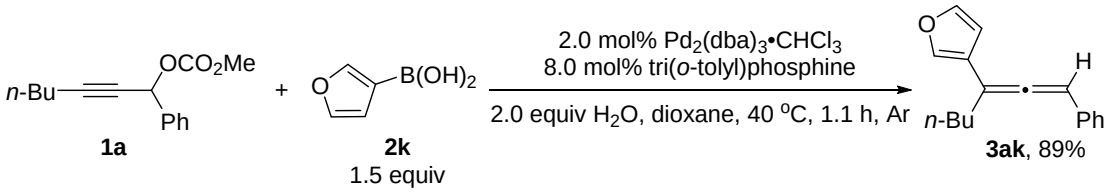
(22) Preparation of 1-phenyl-3-(2-thienyl)-1,2-heptadiene (3aj, xjz-1-116)



The reaction of $Pd_2(dba)_3$·$CHCl_3$ (20.8 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.8 mg, 0.08 mmol), **2j** (191.8 mg, 1.5 mmol), **1a** (246.0 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3aj** (217.8 mg, 86%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.28-7.24 (m, 4 H, Ar-H), 7.23-7.17 (m, 1 H, Ar-H), 7.16-7.12 (m, 1 H, Ar-H), 7.02-6.98 (m, 1 H, Ar-H), 6.98-6.93 (m, 1 H, Ar-H), 6.51 (t, *J* = 3.0 Hz, 1 H, =CH), 2.61-2.46 (m, 2 H, CH_2), 1.70-1.51 (m, 2 H, CH_2), 1.48-1.36 (m, 2 H, CH_2),

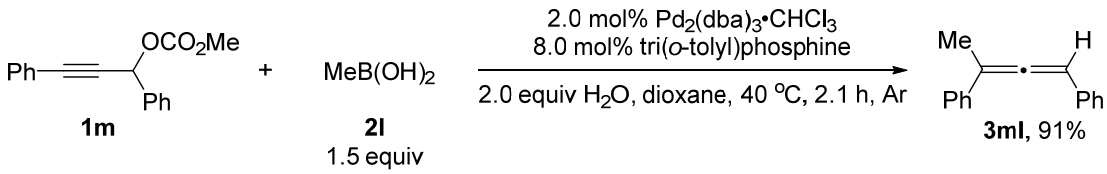
0.91 (t, J = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 205.8, 141.4, 134.4, 128.8, 127.6, 127.3, 127.2, 124.6, 123.3, 105.9, 98.4, 31.4, 30.2, 22.7, 14.1; **IR** (neat): ν = 3061, 3023, 2954, 2928, 2858, 1944, 1596, 1492, 1449, 1378, 1233, 1073, 1029 cm^{-1}; **MS** (70 eV, EI) m/z (%): 255 (M^++1, 5.46), 254 (M^+, 29.36), 111 (100); **HRMS** calcd. for $C_{17}H_{18}S$ [M^+]: 254.1129; found 254.1130.

(23) Preparation of 1-phenyl-3-(3-furyl)-1,2-heptadiene (3ak, xjz-1-118)



The reaction of $Pd_2(dba)_3$·$CHCl_3$ (20.5 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.8 mg, 0.08 mmol), **2k** (174.4 mg, 1.5 mmol), **1a** (246.5 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3ak** (212.4 mg, 89%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.43 (s, 1 H, Ar-H), 7.38-7.25 (m, 5 H, Ar-H), 7.25-7.16 (m, 1 H, Ar-H), 6.45 (t, J = 2.8 Hz, 1 H, =CH), 6.42-6.35 (m, 1 H, Ar-H), 2.48-2.31 (m, 2 H, CH_2), 1.66-1.53 (m, 2 H, CH_2), 1.48-1.34 (m, 2 H, CH_2), 0.90 (t, J = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 205.4, 143.3, 138.6, 134.9, 128.8, 127.1, 127.0, 123.0, 109.4, 102.9, 97.5, 30.6, 30.1, 22.7, 14.1; **IR** (neat): ν = 3062, 3028, 2956, 2927, 2859, 1936, 1598, 1494, 1457, 1377, 1154, 1071, 1032 cm^{-1}; **MS** (70 eV, EI) m/z (%): 239 (M^++1, 4.98), 238 (M^+, 22.38), 196 (100); **HRMS** calcd. for $C_{17}H_{18}O$ [M^+]: 238.1358; found 238.1355.

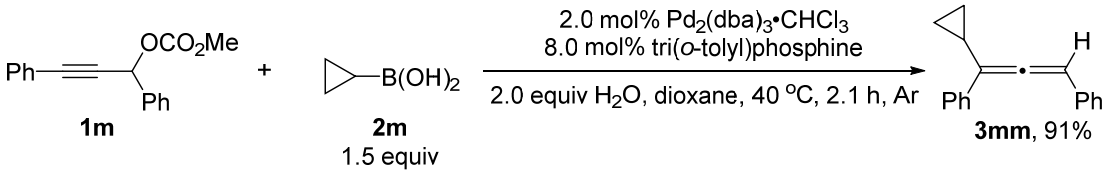
(24) Preparation of 1,3-diphenyl-1,2-butadiene (3ml, xjz-1-131)



The reaction of $Pd_2(dba)_3$·$CHCl_3$ (20.3 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.1 mg, 0.08 mmol), **2l** (93.0 mg, 97% purity, 1.5 mmol), **1m** (266.7 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0

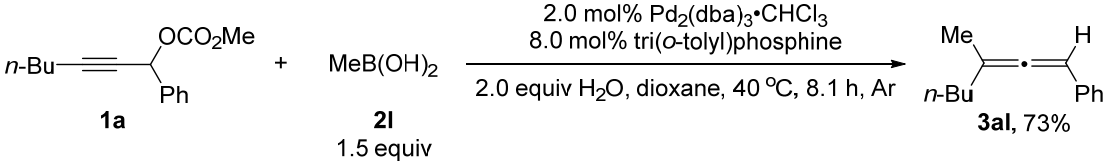
mL) afforded **3ml**[11] (188.0 mg, 91%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 6.8 Hz, 2 H, Ar-H), 7.37-7.26 (m, 6 H, Ar-H), 7.25-7.15 (m, 2 H, Ar-H), 6.47 (q, *J* = 2.8 Hz, 1 H, =CH), 2.22 (d, *J* = 2.8 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 207.0, 136.5, 134.7, 128.8, 128.6, 127.17, 127.15, 127.0, 126.0, 104.7, 96.7, 16.9; **IR** (neat): ν = 3057, 3023, 2975, 2930, 1935, 1597, 1492, 1443, 1371, 1179, 1156, 1067, 1026 cm^{-1}; **MS** (70 eV, EI) m/z (%): 207 (M^++1, 15.88), 206 (M^+, 80.72), 191 (100).

(25) Preparation of 1-cyclopropyl-1,3-diphenylpropadiene (3mm, xjz-1-134)



The reaction of $Pd_2(dba)_3$·$CHCl_3$ (20.5 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.8 mg, 0.08 mmol), **2m** (132.0 mg, 1.5 mmol, 98% purity), **1m** (265.9 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3mm**[12] (212.5 mg, 91%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 7.2 Hz, 2 H, Furyl-H), 7.37-7.27 (m, 6 H, Ar-H), 7.26-7.15 (m, 2 H, Ar-H), 6.54 (d, *J* = 2.4 Hz, 1 H, =CH), 1.74-1.63 (m, 1 H, CH), 0.95-0.84 (m, 2 H, CH_2), 0.67-0.53 (m, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 205.9, 136.6, 134.4, 128.9, 128.6, 127.32, 127.26, 126.9, 126.5, 113.4, 99.1, 11.2, 7.5, 7.0; **IR** (neat): ν = 3081, 3061, 3026, 3001, 1931, 1596, 1578, 1491, 1446, 1073, 1049, 1021 cm^{-1}; **MS** (70 eV, EI) m/z (%): 233 (M^++1, 3.86), 232 (M^+, 19.43), 105 (100).

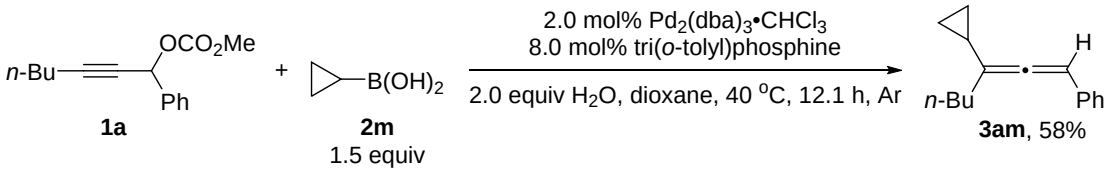
(26) Preparation of 1-phenyl-3-methyl-1,2-heptadiene (3al, xjz-1-141)



The reaction of $Pd_2(dba)_3$·$CHCl_3$ (21.1 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.4 mg, 0.08 mmol), **2l** (93.0 mg, 97% purity, 1.5 mmol), **1a** (246.7 mg, 1.0 mmol),

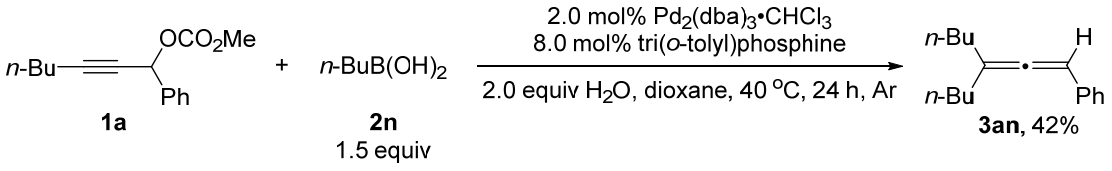
and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3al**[11] (136.5 mg, 73%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.34-7.23 (m, 4 H, Ar-H), 7.20-7.12 (m, 1 H, Ar-H), 6.08-6.02 (m, 1 H, =CH), 2.15-2.02 (m, 2 H, CH_2), 1.80 (d, *J* = 2.8 Hz, 3 H, CH_3), 1.53-1.42 (m, 2 H, CH_2), 1.41-1.29 (m, 2 H, CH_2), 0.89 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 202.8, 136.3, 128.6, 126.6, 126.5, 103.9, 93.9, 33.9, 29.9, 22.6, 19.0, 14.1; **IR** (neat): ν = 3082, 3002, 2956, 2927, 2858, 1943, 1597, 1495, 1459, 1378, 1072, 1018 cm^{-1}; **MS** (70 eV, EI) m/z (%): 186 (M^+, 2.93), 129 (100).

(27) Preparation of 1-phenyl-3-cyclopropyl-1,2-heptadiene (3am, xjz-1-142)



The reaction of $Pd_2(dba)_3$·$CHCl_3$ (21.2 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (24.9 mg, 0.08 mmol), **2m** (131.3 mg, 98% purity, 1.5 mmol), **1a** (245.9 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3am**[13] (123.8 mg, 58%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.33-7.19 (m, 4 H, Ar-H), 7.18-7.11 (m, 1 H, Ar-H), 6.20-6.12 (m, 1 H, =CH), 2.26-2.09 (m, 2 H, CH_2), 1.58-1.44 (m, 2 H, CH_2), 1.44-1.29 (m, 2 H, CH_2), 1.28-1.16 (m, 1 H, CH), 0.89 (t, *J* = 7.2 Hz, 3 H, CH_3), 0.75-0.60 (m, 2 H, CH_2), 0.52-0.39 (m, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 201.5, 136.0, 128.6, 126.6, 126.5, 112.3, 96.7, 32.8, 30.2, 22.7, 14.1, 12.8, 7.3, 6.5; **IR** (neat): ν = 3029, 2956, 2927, 2858, 1950, 1598, 1581, 1496, 1463, 1444, 1369, 1200, 1071 cm^{-1}; **MS** (70 eV, EI) m/z (%): 213 (M^++1, 1.25), 212 (M^+, 6.67), 141 (100).

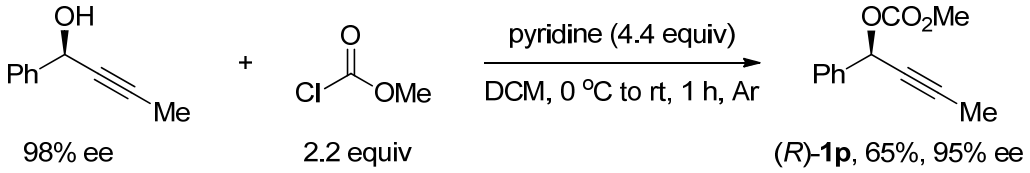
(28) Preparation of 1-phenyl-3-butyl-1,2-heptadiene (3an, xjz-1-136)



The reaction of $Pd_2(dba)_3$·$CHCl_3$ (20.4 mg, 0.02 mmol), tri(*o*-tolyl)phosphine

(24.2 mg, 0.08 mmol), **2n** (156.4 mg, 98% purity, 1.5 mmol), **1a** (246.5 mg, 1.0 mmol), and H_2O (36.0 μL, d = 1.0 g/cm^3, 36.0 mg, 2.0 mmol) in freshly distilled dioxane (2.0 mL) afforded **3an** (95.1 mg, 42%) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.33-7.21 (m, 4 H, Ar-H), 7.20-7.09 (m, 1 H, Ar-H), 6.16-6.03 (m, 1 H, =CH), 2.18-1.99 (m, 4 H, 2 x CH_2), 1.55-1.41 (m, 4 H, 2 x CH_2), 1.40-1.27 (m, 4 H, 2 x CH_2), 0.88 (t, *J* = 7.4 Hz, 6 H, 2 x CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 202.4, 136.4, 128.6, 126.5, 126.4, 108.9, 95.4, 32.7, 30.0, 22.7, 14.1; **IR** (neat): ν = 3031, 2956, 2926, 2858, 1947, 1598, 1495, 1460, 1378, 1071, 1027 cm^{-1}; **MS** (70 eV, EI) m/z (%): 228 (M^+, 3.52), 129 (100); **HRMS** calcd. for $C_{17}H_{24}$ [M^+]: 228.1878; found 228.1876.

Preparation of (*R*)-1-phenylbuta-2-ynyl methyl carbonate ((*R*)-1p, xjz-1-182)

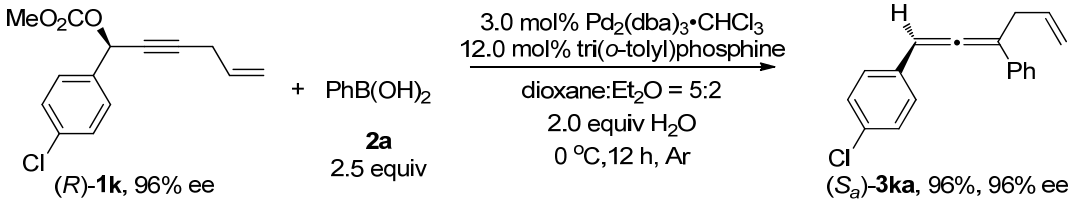


To a round-flask were added (*R*)-1-phenylbuta-2-yn-1-ol (0.8405 g, 5.7 mmol, 98% *ee*), DCM (11.4 mL), and pyridine (2.0 mL, d = 0.983 g/cm^3, 1.966 g, 24.9 mmol) under argon. After cooling to 0 °C with an ice-water bath, methyl chloroformate (1.0 mL, d = 1.223 g/cm^3, 1.223 g, 12.9 mmol) was added dropwise to the mixture over 5 min. After the addition, the resulting mixture was stirred at this temperature for 10 min, the resulting mixture was naturally warmed up to room temperature and stirred at rt for 1 h. The reaction was quenched with 3 M HCl (aq.) (7 mL) then extracted with DCM (10 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel to afford (*R*)-**1p** (0.7599 g, 65%, 95% *ee*) [eluent: petroleum ether (60-90 ^{o}C)/ethyl acetate = 40:1 (205 mL), then petroleum ether (60-90 ^{o}C)/ethyl acetate = 20:1 (210 mL)]: oil; HPLC conditions: OJ-H column, hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R (major) = 12.5 min, t_R (minor) = 16.6 min; $[\alpha]_D^{26}$ = + 14.6 (*c* = 1.025, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ =

7.57-7.50 (m, 2 H, Ar-H), 7.42-7.32 (m, 3 H, Ar-H), 6.26 (q, J = 2.4 Hz, 1 H, CH), 3.80 (s, 3 H, OCH_3), 1.91 (d, J = 2.0 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 155.1, 137.0, 129.1, 128.7, 127.7, 85.1, 75.4, 70.2, 55.1, 3.9; **IR** (neat): ν = 2239, 1746, 1443, 1247, 1146 cm^{-1}; **MS** (70 eV, EI) m/z (%): 204 (M^+, 2.70), 128 (100); **HRMS** calcd. for $C_{12}H_{12}O_3$ [M^+]: 204.0786; found: 204.0792.

Highly enantioselective synthesis of allenes by chirality transfer

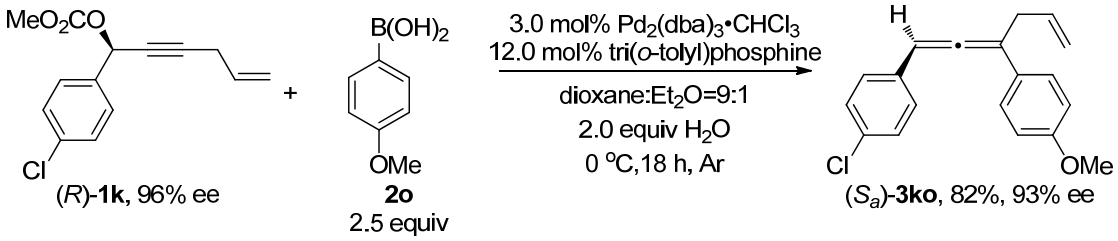
(1) Preparation of (S_a)-1-(4-chlorophenyl)-3-phenyl-1,2,5-hexatriene ((S_a)-3ka, xjz-1-147)



Typical Procedure II. To an oven-dried Schlenk tube were added $Pd_2(dba)_3$·$CHCl_3$ (15.7 mg, 0.015 mmol), tri(*o*-tolyl)phosphine (18.3 mg, 0.06 mmol), and **2a** (152.6 mg, 1.25 mmol). After replacing air with argon for three times under vacuum, the tube was cooled to 0 °C. Then (*R*)-**1k** (132.8 mg, 0.5 mmol, 96% ee), mixed solvents (1.4 mL, from the mixture of dioxane (5.0 mL) and Et_2O (2.0 mL)) pre-cooled at 0 °C under Ar, and H_2O (18.0 μL, d = 1.0 g/cm^3, 18.0 mg, 1.0 mmol) were added. The resulting mixture was stirred for 12 h at 0 °C as monitored by TLC, and then passed through a short pad of silica gel with Et_2O (10 mL) as eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel to afford (S_a)-**3ka** (127.4 mg, 96%, 96% ee) [eluent: petroleum ether]: oil; HPLC conditions: OJ-H column, hexane/*i*-PrOH = 100/1, 1.0 mL/min, λ = 214 nm, t_R (minor) = 7.8 min, t_R (major) = 9.1 min; $[\alpha]_D^{20}$ = + 402.5 (*c* = 0.97, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 7.6 Hz, 2 H, Ar-H), 7.36-7.28 (m, 2 H, Ar-H), 7.27-7.19 (m, 5 H, Ar-H), 6.50 (t, J = 2.8 Hz, 1 H, =CH), 6.03-5.90 (m, 1 H, =CH), 5.20 (dd, J_1 = 17.0 Hz, J_2 = 1.4 Hz, 1 H, one proton of $=CH_2$), 5.08 (dd, J_1 = 10.4 Hz, J_2 = 1.6 Hz, 1 H, one proton of $=CH_2$), 3.44-3.26 (m, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 207.1, 135.39, 135.37, 133.0, 132.8, 129.0, 128.7, 128.1,

127.4, 126.3, 116.8, 108.9, 97.3, 34.9; **IR** (neat): ν = 1933, 1639, 1596, 1488, 1450, 1089, 1032, 1012 cm^{-1}; **MS** (70 eV, EI) m/z (%): 268 (M^+(^{37}Cl), 3.67), 266 (M^+(^{35}Cl), 9.07), 105 (100); **HRMS** calcd. for $C_{18}H_{15}{}^{35}Cl$ [M^+]: 266.0862; found 266.0865.

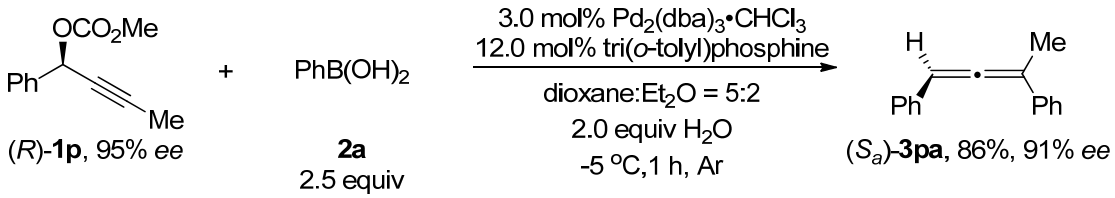
(2) **Preparation of (S_a)-1-(4-chlorophenyl)-3-(4-methoxylphenyl)-1,2,5-hexatriene ((S_a)-3ko, xjz-1-156)**



Following Typical Procedure II, to an oven-dried Schlenk tube were added $Pd_2(dba)_3$·$CHCl_3$ (15.9 mg, 0.015 mmol), tri(*o*-tolyl)phosphine (18.2 mg, 0.06 mmol), and **2a** (194.2 mg, 1.25 mmol). After replacing air with argon for three times under vacuum, the tube was cooled to 0 °C. Then (*R*)-**1k** (132.6 mg, 0.5 mmol, 96% ee), mixed solvents (1.4 mL, from the mixture of dioxane (5.0 mL) and Et_2O (2.0 mL)) pre-cooled at 0 °C under Ar, and H_2O (18.0 μL, d = 1.0 g/cm^3, 18.0 mg, 1.0 mmol) were added. The resulting mixture was stirred for 18 h at 0 °C as monitored by TLC, and then passed through a short pad of silica gel with Et_2O (10 mL) as eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel to afford (S_a)-**3ka**[14] (122.2 mg, 82%, 93% ee) [eluent: petroleum ether]: solid; **m.p.**: 74.0-75.2 °C (ee > 99%); HPLC conditions: OJ-H column, hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R (minor) = 10.6 min, t_R (major) = 19.9 min; $[\alpha]_D^{31}$ = + 456.9 (*c* = 0.99, $CHCl_3$) [Reported $[\alpha]_D^{31}$ = + 457.0 (*c* = 0.98, $CHCl_3$), ee = 94%]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.25 (s, 4 H, Ar-H), 6.86 (d, *J* = 8.4 Hz, 2 H, Ar-H), 6.48 (s, 1 H, =CH), 6.05-5.87 (m, 1 H, =CH), 5.19 (d, *J* = 16.8 Hz, 1 H, one proton of $=CH_2$), 5.08 (d, *J* = 8.4 Hz, 1 H, one proton of $=CH_2$), 3.79 (s, 3 H, OCH_3), 3.40-3.23 (m, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 206.7, 159.1, 135.5, 133.3, 132.7, 129.0, 128.1, 127.5, 127.4, 116.7, 114.1, 108.4, 97.2, 55.4, 35.1; **IR** (neat): ν = 3074, 2910, 2879, 2839, 1935, 1642, 1605, 1573, 1510, 1488, 1291, 1249, 1176, 1084, 1031 cm^{-1}; **MS** (70 eV,

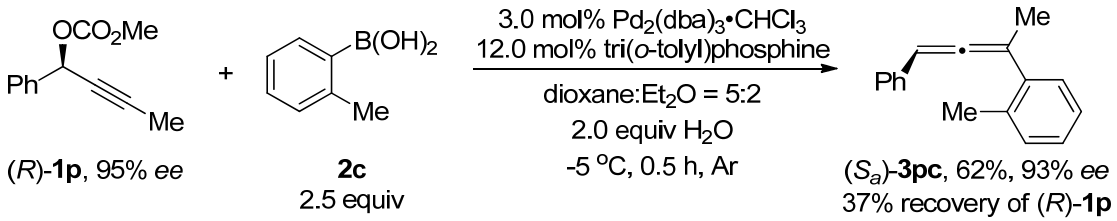
EI) m/z (%): 298 (M^+(^{35}Cl), 23.38), 296 (M^+(^{35}Cl), 74.33), 255 (100).

(3) Preparation of (S_a)-1,3-diphenyl-1,2-butadiene ((S_a)-3pa, xjz-1-192)



Typical Procedure III: To an oven-dried Schlenk tube were added $Pd_2(dba)_3$•$CHCl_3$ (6.2 mg, 0.006 mmol), tri(*o*-tolyl)phosphine (7.5 mg, 0.024 mmol), and **2a** (61.2 mg, 0.5 mmol). After replacing air with argon for three times under vacuum, freshly distilled dioxane (0.4 mL) and freshly distilled Et_2O (0.16 mL) were added sequentially. After the tube was cooled to -5 ^oC, (*R*)-**1p** (41.1 mg, 0.2 mmol, 95% ee) and H_2O (7.2 μL, d = 1.0 g/cm^3, 7.2 mg, 0.4 mmol) were added sequentially. The resulting mixture was stirred for 1 h at -5 ^oC as monitored by TLC. The resulting mixture was filtered through a short pad of silica gel eluted with Et_2O (15 mL, pre-cooled at -5 ^oC). After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel to afford (***S*$_a$**)-**3pa** (35.7 mg, 86%, 91% ee) [eluent: petroleum ether (60-90 ^oC)]: oil; HPLC conditions: OZ-H column, hexane/*i*-PrOH = 100/0, 1.0 mL/min, λ = 214 nm, t_R (minor) = 6.1 min, t_R (major) = 7.5 min; $[\alpha]_D^{30}$ = + 417.4 (*c* = 1.01, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.37-7.25 (m, 6 H, Ar-H), 7.25-7.17 (m, 2 H, Ar-H), 6.47 (q, *J* = 2.7 Hz, 1 H, =CH), 2.22 (d, *J* = 3.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 207.0, 136.5, 134.7, 128.8, 128.6, 127.17, 127.15, 127.0, 126.0, 104.7, 96.7, 16.9; **IR** (neat): ν = 1935, 1593, 1489, 1445 cm^{-1}; **MS** (70 eV, EI) m/z (%): 207 (M^++1, 21.36), 206 (M^+, 100); **HRMS** calcd. for $C_{16}H_{14}$ [M^+]: 266.1096; found: 266.1100.

(4) Preparation of (S_a)-1-phenyl-3-(2-methylphenyl)-1,2-butadiene ((S_a)-3pc, xjz-1-196)



Following **Typical Procedure III,** the reaction of $Pd_2(dba)_3$·$CHCl_3$ (6.2 mg, 0.006 mmol), tri(*o*-tolyl)phosphine (7.4 mg, 0.024 mmol), **2c** (68.2 mg, 0.5 mmol), (*R*)-**1p** (40.8 mg, 0.2 mmol, 95% ee), and H_2O (7.2 μL, d = 1.0 g/cm^3, 7.2 mg, 0.4 mmol) in freshly distilled dioxane (0.4 mL) and freshly distilled Et_2O (0.16 mL) afforded (***S**$_a$*)-**3pc** (27.3 mg, 62%, 93% ee) [eluent: petroleum ether (60-90 °C)] (37% recovery of (*R*)-**1p** as determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as internal standard): oil; HPLC conditions: OJ-H column, hexane/*i*-PrOH = 100/0, 1.0 mL/min, λ = 214 nm, t_R (major) = 17.7 min, t_R (minor) = 22.8 min; $[\alpha]_D^{30}$ = + 506.4 (*c* = 1.015, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.36-7.27 (m, 5 H, Ar-H), 7.23-7.12 (m, 4 H, Ar-H), 6.20 (q, *J* = 2.8 Hz, 1 H, =CH), 2.38 (s, 3 H, CH_3), 2.18 (d, *J* = 3.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 205.2, 137.6, 136.1, 135.2, 130.8, 128.7, 127.7, 127.2, 127.1, 126.9, 126.1, 103.8, 94.1, 21.0, 20.6; **IR** (neat): ν = 3020, 2971, 1938, 1594, 1489, 1451, 1372 cm^{-1}; **MS** (70 eV, EI) m/z (%): 221 (M^++1, 10.61), 220 (M^+, 51.27), 205 (100); **HRMS** calcd. for $C_{17}H_{16}$ [M^+]: 220.1252; found: 220.1251.

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