Highly regioselective iridium-catalyzed and samarium-promoted coupling of allylic carbonates with ketones: New approach toward homoallylic alcohols

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Experimental section

General: $^1$H, $^{13}$C, and $^{19}$F NMR spectra were recorded as solutions in CDCl$_3$ with a Bruker NMR (400 MHz) spectrometer. The chemical shifts are reported in $\delta$ units downfield from the Me$_4$Si internal reference. High-resolution mass spectra were obtained with a Finnigan VG Platform or a Finnigan MAT 95S.

Reaction procedure for preparation of 3: [Ir(COD)Cl]$_2$ (2.6 mg, 0.004 mmol) was dissolved in THF (5 mL) with SmI$_2$ (0.1 M) in a Schlenk tube under argon. Allylic carbonate 1 (0.2 mmol) and ketone 2a (0.3 mmol) or 2b (0.4 mmol) were dissolved in THF (2.5 mL), then the solution was slowly added to the Schlenk tube via a syringe pump during 1 h. The mixture was stirred for an additional period of 5 h. The crude reaction mixture was filtered through celite and the solvent was removed by rotary evaporation. The crude residue was purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10) to give the desired products.

Procedure for preparation of 3ea,3ja: compound 3a or 3j (0.10 mmol) was dissolved in EtOH (2 mL) with 10% Pd/C (3 mg) in a Schlenk tube under H$_2$. The solution was stirred at 60 °C in 12 h. The solvent was removed by rotary evaporation. Then the crude residue was purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10) to give the desired product 3ea, 3ja.

Procedure for preparation of 3eb,3jb: 3ea or 3ja (0.10 mmol) was dissolved in dry DCM (2 mL) in a Schlenk tube under argon. Diethylaminosulfur trifluoride (DAST) (0.15 mmol) was added by a syringe at room temperature. The solution was stirred for 5 min, and then NaHCO$_3$ solution (2 mL, 1.5 M) was added. After stirred for an additional 5 min, the mixture was extracted with DCM. The organic layer was dried with MgSO$_4$ and the solvent was removed under reduced pressure. Then the crude residue was purified by flash column chromatography (petroleum ether) to give the desired product 3eb, 3jb.

1-Cinnamylcyclohexanol (3a). Colorless oil. Yield: 35.9 mg (83%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.41 (d, $J$ = 7.3 Hz, 2H), 7.33 (t, $J$ = 7.5 Hz, 2H), 7.24 (t, $J$ = 7.2 Hz, 1H), 6.49 (d, $J$ = 15.9 Hz, 1H), 6.34 (dt, $J$ = 15.8, 7.5 Hz, 2H), 2.40 (d, $J$ = 7.5 Hz, 2H), 1.71-1.46 (m, 10H).

(E)-1-(3-(3-Methoxyphenyl)allyl)cyclohexanol (3b). Colorless oil. Yield: 37.4 mg (76%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.23 (dd, $J$ = 16.1, 8.2 Hz, 1H), 6.96 (d, $J$ = 7.6 Hz, 1H), 6.91 (s, 1H), 6.77 (d, $J$ = 8.2 Hz, 1H), 6.42 (d, $J$ = 15.9 Hz, 1H), 6.31 (dt, $J$ = 15.4, 7.7 Hz, 1H), 3.81 (s, 3H), 2.36 (d, $J$ = 7.4 Hz, 2H), 1.65-1.45 (m, 10H). $^{13}$C NMR (100 Hz, CDCl$_3$) $\delta$ = 159.8, 138.9, 133.5, 129.5, 125.8, 118.8, 112.9, 111.5, 71.6, 55.2, 45.9, 37.6, 25.8, 22.2. HRMS (ESI) calcd for C$_{16}$H$_{22}$O$_2$Na, [M+Na]$^+$: 269.1517, Found: 269.1474. IR(KBr): $\nu_{\text{max}}$ (cm$^{-1}$) = 3780, 3610, 3453, 3125, 2450, 1555, 1450, 1230, 1157, 1142, 1121, 1055, 998, 755, 600, 490.

(E)-1-(3-(p-Tolyl)allyl)cyclohexanol (3c). Colorless oil. Yield: 33.0 mg (72%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.30 (d, $J$ = 8.0 Hz, 2H), 7.14 (d, $J$ = 7.9 Hz, 2H), 6.45 (d, $J$ = 15.8 Hz, 1H), 6.29 (dt, $J$ = 15.6, 7.8 Hz, 1H), 2.38 (d, $J$ = 7.7 Hz, 2H), 2.36 (s, 3H), 1.70-1.47 (m, 10H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 135.9, 132.7, 132.3, 128.7, 127.3, 126.3, 71.6, 45.9, 37.6, 29.7, 25.7, 22.3. HRMS (ESI) calcd for C$_{16}$H$_{22}$ONa, [M+Na]$^+$: 253.1568, Found: 253.1558. IR(KBr): $\nu_{\text{max}}$ (cm$^{-1}$) = 3770, 3650, 3443, 3225, 2450, 1505, 1220, 1150, 1117, 1040, 740, 600.

(E)-1-(3-(2-Chlorophenyl)allyl)cyclohexanol (3d). Colorless oil. Yield: 25.0 mg (50%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.53 (dd, $J$ = 7.6, 1.3 Hz, 1H), 7.37-7.31 (m, 1H), 7.17 (m, 2H), 6.82 (d, $J$ = 15.8 Hz, 1H), 6.30
yield: 28.6 mg (99%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.62 (d, $J$ = 7.2 Hz, 2H), 7.55 (d, $J$ = 8.1 Hz, 2H), 7.46 (t, $J$ = 7.6 Hz, 2H), 7.35 (t, $J$ = 7.3 Hz, 1H), 7.29 (d, $J$ = 8.3 Hz, 2H), 2.69 (t, $J$ = 7.7 Hz, 2H), 1.82-1.71 (m, 2H), 1.65-1.42 (m, 10H), 1.39-1.21 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 141.7, 141.2, 138.7, 138.8, 128.7, 127.1, 127.0, 71.4, 42.1, 37.5, 36.0, 25.9, 24.8, 22.3. HRMS (ESI) calcd for C$_{21}$H$_{26}$ONa. [M+Na]$^+$: 317.1881, Found: 317.1890. IR(KBr): $\nu$ = 3052, 2954, 1659, 1491, 1446, 1236, 1197, 1157, 1129, 1074, 1035, 958, 887, 827, 795, 765, 721, 665, 607, 512.

(4-3-(1-Fluorocyclohexyl)propyl)-1,1'-biphenyl (3eb). Colorless oil. Yield: 22.1 mg (75%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.62 (d, $J$ = 7.3 Hz, 2H), 7.55 (d, $J$ = 8.0 Hz, 2H), 7.46 (t, $J$ = 7.6 Hz, 2H), 7.36 (t, $J$ = 7.3 Hz, 1H), 7.30 (d, $J$ = 8.3 Hz, 2H), 2.70 (t, $J$ = 7.5 Hz, 2H), 1.91-1.75 (m, 4H), 1.73-1.60 (m, 5H), 1.58-1.44 (m, 3H), 1.41-1.23 (m, 2H). $^1$F NMR (377 MHz, CDCl$_3$) $\delta$ = -155.6. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 166.5, 139.9, 132.3, 132.2, 129.7, 126.1, 124.6, 122.9, 121.7, 64.8, 30.7, 29.7, 21.3, 19.2, 19.1, 13.7. HRMS (ESI) calcd for C$_{21}$H$_{26}$ONa. [M+Na]$^+$: 319.1838, Found: 319.1830. IR(KBr): $\nu$ = 3052, 2954, 1659, 1491, 1446, 1236, 1197, 1157, 1129, 1074, 1035, 958, 887, 827, 795, 765, 721, 665, 607, 512.

(E)-2-Methyl-5-phenylpent-4-en-2-ol (3f). Colorless oil. Yield: 31.3 mg (89%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.38 (d, $J$ = 7.3 Hz, 2H), 7.31 (t, $J$ = 7.5 Hz, 2H), 7.23 (dd, $J$ = 6.7, 6.7 Hz, 1H), 6.47 (d, $J$ = 15.8 Hz, 1H), 6.30 (dt, $J$ = 15.5, 7.8 Hz, 1H), 2.39 (d, $J$ = 7.5 Hz, 2H), 1.28 (s, 6H).

(E)-2-Methyl-5-(p-tolyl)pent-4-en-2-ol (3g). Colorless oil. Yield: 29.6 mg (78%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.28 (d, $J$ = 8.0 Hz, 2H), 7.12 (d, $J$ = 7.9 Hz, 2H), 6.43 (d, $J$ = 15.8 Hz, 1H), 6.24 (dt, $J$ = 15.5, 7.8 Hz, 1H), 2.37 (d, $J$ = 7.5 Hz, 2H), 2.33 (s, 3H), 1.27 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 137.1, 134.6, 133.6, 129.3, 126.1, 124.7, 70.9, 47.4, 29.3, 21.2. HRMS (ESI) calcd for C$_{13}$H$_{18}$ONa. [M+Na]$^+$: 213.1255, Found: 213.1250. IR(KBr): $\nu$ = 3790, 3600, 3458, 3112, 2583, 1595, 1480, 1208, 1186, 1132, 1086, 795, 665, 508.

(E)-5-(4-Methoxyphenyl)-2-methylpent-4-en-2-ol (3h). Colorless oil. Yield: 30.9 mg (75%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.31 (d, $J$ = 8.6 Hz, 2H), 6.85 (d, $J$ = 8.6 Hz, 2H), 6.41 (d, $J$ = 15.8 Hz, 1H), 6.14 (dt, $J$ = 15.5, 7.6 Hz, 1H), 3.81 (s, 3H), 2.36 (d, $J$ = 7.6 Hz, 2H), 1.27 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 159.0, 133.2, 130.2, 127.3, 123.4, 114.0, 70.9, 55.3, 47.3, 29.2. HRMS (ESI) calcd for C$_{13}$H$_{18}$O$_2$Na. [M+Na]$^+$: 229.1204, Found: 229.1211. IR(KBr): $\nu$ = 3785, 3605, 3450, 3120, 2443, 1555, 1440, 1233, 1168, 1145, 1132, 1065, 777, 615, 500.

(E)-2-Methyl-5-(naphthalen-1-yl)pent-4-en-2-ol (3i). Colorless oil. Yield: 24.4 mg (54%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.31 (d, $J$ = 8.6 Hz, 2H), 7.28 (d, $J$ = 8.6 Hz, 2H), 6.41 (d, $J$ = 15.5, 7.6 Hz, 1H), 3.81 (s, 3H), 2.36 (d, $J$ = 7.6 Hz, 2H), 1.27 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 137.1, 134.6, 133.6, 129.3, 126.1, 124.7, 70.9, 47.4, 29.3, 21.2. HRMS (ESI) calcd for C$_{13}$H$_{18}$ONa. [M+Na]$^+$: 213.1255, Found: 213.1250. IR(KBr): $\nu$ = 3790, 3600, 3458, 3112, 2583, 1595, 1480, 1208, 1186, 1132, 1086, 795, 665, 508.
MHz, CDCl₃) δ = 8.12 (d, J = 7.8 Hz, 1H), 7.87-7.83 (m, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 7.1 Hz, 1H), 7.54-7.41 (m, 3H), 7.21 (d, J = 15.5 Hz, 1H), 6.31 (dt, J = 15.4, 7.6 Hz, 1H), 2.51 (d, J = 7.6 Hz, 2H), 1.33 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ = 135.2, 133.6, 131.1, 131.0, 129.2, 128.5, 127.7, 126.0, 125.8, 125.7, 123.8, 123.8, 71.0, 47.8, 29.3. HRMS (ESI) calcd for C₁₆H₁₈ONa. [M+Na]⁺: 249.1255, Found: 249.1257. IR(KBr): ν max (cm⁻¹) = 3800, 3750, 3554, 3085, 2395, 1600, 1480, 1250, 1158, 1100, 1085, 968, 727, 650, 490.

(E)-5-[(1',1'-Biphenyl)-4-yl]-2-methylpent-4-en-2-ol (3j). White solid. Melting point 94−95°C. Yield: 21.7 mg (43%). ¹H NMR (400 MHz, CDCl₃) δ = 7.63 (d, J = 7.4 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.47 (dd, J = 10.2, 8.2 Hz, 4H), 7.37 (t, J = 7.3 Hz, 1H), 6.54 (d, J = 15.8 Hz, 1H), 6.39 (dt, J = 15.5, 7.8 Hz, 1H), 2.44 (d, J = 7.5 Hz, 2H), 1.32 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ = 140.8, 140.1, 136.4, 133.2, 128.8, 127.3, 126.9, 126.6, 126.0, 71.0, 47.4, 29.3. HRMS (ESI) calcd for C₁₈H₂₀ONa. [M+Na]⁺: 275.1412, Found: 275.1420. IR(KBr): ν max (cm⁻¹) = 3810, 3790, 3533, 3145, 2650, 1575, 1478, 1211, 1137, 1100, 1055, 915, 705, 618, 500.

5-[(1',1'-Biphenyl)-4-yl]-2-methylpentan-2-ol (3ja). White solid. Melting point 80−81°C. Yield: 21.7 mg (99%). ¹H NMR (400 MHz, CDCl₃) δ = 7.58 (d, J = 7.7 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.26 (d, J = 8.5 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H), 1.77-1.69 (m, 2H), 1.54 (dd, J = 11.2, 5.5 Hz, 2H), 1.22 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ = 141.6, 141.1, 138.7, 128.8, 128.7, 127.1, 127.0, 43.5, 36.0, 29.3, 26.3. HRMS (ESI) calcd for C₁₈H₂₂ONa. [M+Na]⁺: 277.1568, Found: 277.1573. IR(KBr): ν max (cm⁻¹) = 3910, 3720, 3358, 3205, 2650, 1745, 1500, 1600, 1157, 1121, 1050, 775, 615.

4-(4-Fluoro-4-methylpentyl)-1,1'-biphenyl (3jb). White solid. Melting point 49−50°C. Yield: 18.2 mg (71%). ¹H NMR (400 MHz, CDCl₃) δ = 7.61 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.29 (d, J = 7.6 Hz, 2H), 2.70 (t, J = 7.4 Hz, 2H), 1.84-1.65 (m, 4H), 1.40 (s, 3H), 1.35 (s, 3H), 1.35 (s, 3H). ¹⁹F NMR (377 MHz, CDCl₃) δ = -137.5. ¹³C NMR (100 MHz, CDCl₃) δ = 141.4, 141.1, 138.8, 128.8, 128.7, 127.1, 127.0, 41.1, 40.9, 35.7, 26.8, 26.6, 25.8, 25.8. HRMS (ESI) calcd for C₁₈H₂₁FNa. [M+Na]⁺: 279.1525, Found: 279.1519. IR(KBr): ν max (cm⁻¹) = 3905, 3715, 3370, 3115, 2785, 1768, 1620, 1605, 1142, 1115, 1035, 760, 610.

Procedure for the preparation of 3a from Grignard reagent such as (E)-cinnamylmagnesium chloride: (E)-Cinnamylmagnesium chloride (0.20 mmol, 2 mL) made according to a known procedure³ was added by a syringe into a Schlenk tube under argon. Then a solution of cyclohexanone (0.30 mmol, 1.5 eq) and THF (1 mL) was slowly added into the reaction mixture by a syringe. The mixture was stirred for 12 h. The crude reaction mixture was filtered through celite and the solvent was removed by rotary evaporation. The crude residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:10) to give the desired product 3a in 46% yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.41 (d, J = 7.3 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.24 (t, J = 7.2 Hz, 1H), 6.49 (d, J = 15.9 Hz, 1H), 6.34 (dt, J = 15.8, 7.5 Hz, 2H), 2.40 (d, J = 7.5 Hz, 2H), 1.71-1.46 (m, 10H).
$^1$H NMR spectra

![NMR spectra of compounds 3a and 3b](image-url)
$^{13}$C NMR spectra

![$^{13}$C NMR spectra for compounds 3b and 3c](image-url)
$^{19}$F NMR spectra

![Chemical Structures](image-url)
References