Supporting Information for

Enantioselective tandem reaction over a site-isolated bifunctional catalyst

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CONTENTS

Experimental part and Data of chiral products............................................................. 2
Figure S1. The FT-IR spectrum of catalyst 3................................................................. 11
Figure S2. The solid-state $^{13}$C CP MAS NMR spectra of the fresh catalyst 5
and the recycled catalyst 5 .................................................................................................. 12
Figure S3. The solid-state $^{31}$P CP MAS NMR spectrum of catalyst 5......................... 13
Figure S4. The solid-state $^{29}$Si CP MAS NMR spectrum of catalyst 5. ..................... 13
Figure S5. The small-angle powder XRD pattern of catalyst 5................................. 14
Figure S6. The nitrogen adsorption-desorption isotherm of catalyst 5......................... 15
Figure S7. The TEM images of the fresh catalyst 5 and the recycled catalyst 5........... 16
Table S1. Optimizing reaction conditions for the tandem Sonogashira coupling–ATH
of 4-iodoacetophenone and phenylacetylene............................................................... 17
Figure S8. Characterizations of chiral products.......................................................... 18
Figure S9. HPLC analyses for chiral products............................................................ 57
Table S2. Reusability of catalyst 5............................................................................. 83
Figure S10. Reusability of catalyst 5 ......................................................................... 83
Experimental

1). General. All experiments, which are sensitive to moisture or air, were carried out under an Ar atmosphere using the standard Schlenk techniques. Diphenyl(2-(triethoxysilyl)ethyl)phosphine, tetraethoxysilane (TEOS), 1,4-bis(triethoxysilyl)ethane, cetyltrimethylammonium bromide (CTAB), fluorocarbon surfactant (FC-4: \( \text{C}_3\text{F}_2\text{O(CF(CF_3)CF_2O)_2CF(CF_3)CONH(CH}_2\text{}_3\text{N}^+(\text{C}_2\text{H}_5)_2\text{CH}_3\text{I}^-) \)), 4-(2-(trimethoxysilyl)ethyl)benzene-1-sulfonyl chloride, 4-(methylphenylsulfonyl)-1,2-diphenylethylenediamine \([(S,S)-\text{TsDPEN}]\), surfactant P123 \((\text{CH}_2\text{-CH}_2\text{O})_{20}(\text{CH}_2\text{(CH}_3\text{)CH}_2\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20})\), \([\text{mesityleneRuCl}_2]_2\) were purchased from Sigma-Aldrich Company Ltd and used as received. Compound of \((S,S)-4-(\text{trimethoxysilyl})\text{ethyl})\text{phenylsulfonyl-1,2-diphenylethylenediamine} [J. Mater. Chem., 2010, 20, 1970.] and bis[(diphenylphosphino)ethyltriethoxysilane]palladium dichloride [J. Catal. 1998, 178, 284] were synthesized according to the reported literature.

2). Characterization. Ru, Pd loading amounts in the catalyst was analyzed using an inductively coupled plasma optical emission spectrometer (ICP, Varian VISTA-MPX). Fourier transform infrared (FTIR) spectra were collected on a Nicolet Magna 550 spectrometer using KBr method. X-ray powder diffraction (XRD) was carried out on a Rigaku D/Max-RB diffractometer with CuKα radiation. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6380LV microscope operating at 20 kV. Transmission electron microscopy (TEM) images were performed on a JEOL JEM2010 electron microscope at an acceleration voltage of 220 kV. Nitrogen adsorption isotherms were measured at 77 K with a Quantachrome Nova 4000 analyzer. The samples were measured after being outgassed at 423 K overnight. Pore size distributions were calculated by using the BJH model. The specific surface areas (SBET) of samples were determined from the linear parts of BET plots \((p/p_0 = 0.05-1.00)\). Solid state NMR experiments were explored on a Bruker AVANCE spectrometer at a magnetic field strength of 9.4 T with \(^1\text{H}\) frequency of 400.1 MHz, \(^{13}\text{C}\) frequency of 100.5 MHz and \(^{29}\text{Si}\) frequency of 79.4 MHz, and \(^{31}\text{P}\) frequency of 169.3 MHz with 4 mm rotor at two spinning frequency of 5.5 kHz and 8.0 kHz, TPPM decoupling is applied in the during acquisition period. \(^1\text{H}\) cross polarization in all solid state NMR experiments was employed using a contact time of 2 ms and the pulse lengths of 4 μs.
3). Preparation of Catalyst 5. In a typical synthesis, (The first step for the synthesis of mesoporous yolk functionalized with chiral siloxane) 0.10 g (0.27 mmol) of cetyltrimethylammonium bromide (CTAB) was completely dissolved in 45.0 mL of aqueous sodium hydroxide (0.35 mL, 2.0 N). The mixture was stirred at room temperature for 0.5 h. Subsequently, 0.18 g (0.50 mmol) of 1,2-bis(triethoxysilyl)ethane (1), 0.125 g (0.25 mmol) of (S,S)-4-(trimethoxysilyl)ethylphenylsulfonyl-1,2-diphenylethlenediamine (2) and 0.43 g of (2.07 mmol) of tetraethoxysilane (TEOS) was added at room temperature under vigorous stirring. Finally, 0.40 mL of ethyl acetate was added and the mixture was stirred at 80 °C for 2 h. (The second step for the coating above yolk with a SiO2-coated layer) After cooling the above mixture down to 38 °C, an aqueous solution (80 mL of water, 50 mL of ethanol, 0.30 g (0.82 mmol) of CTAB and 1.0 mL (25 wt%) of NH3·H2O) was added and the mixture was stirred 38 °C for 0.5 h. Subsequently, 0.5 mL, 0.47 g (2.26 mmol) of TEOS was added and the mixture was stirred at 38 °C for another 2 h. (The third step for the coating above SiO2-coated yolk with an ethylene-bridged organopalladium-functionalized silica layer) An aqueous solution (3 mL of water containing 0.04 g (0.044 mmol) of FC-4 ([C3F7O(CF(CF3)CF2O)2CF(CF3)CONH(CH2)3N+(C2H5)2CH3]I), 0.08 g (0.22 mmol) of CTAB and 0.20 mL (25 wt%) of NH3·H2O) was added and the mixture was stirred at 38 °C for 0.5 h. Then, 0.89 g of 1,2-bis(triethoxysilyl)ethane (2.50 mmol) in 2 mL of ethanol and 0.116 g (0.125 mmol) of bis[(diphenylphosphino)ethyltriethoxysilane)]palladium dichloride (3) (2 min later) were added subsequently under vigorous stirring for 1.5 h. Finally, the temperature was raised to 80 °C and the mixture was stirred at 80 °C for another 3 h. After cooling the above mixture down to room temperature, the solid was collected by filtration. (The fourth step for the selective etching) To remove the surfactant and form yolk-shell structured mesoporous nanoparticles, the collected solids (1.22 g) were dispersed in 120 mL of solution (80 mg (1.0 mmol) of ammonium nitrate in 120 mL (95%) of ethanol), and the mixture was stirred at 60 °C for 10 h. After cooling the above mixture down to room temperature, the solid was filtered and washed with excess water and ethanol, and dried at ambient temperature under vacuum overnight to afford Shell@SiO2@Yolk as a light−yellow powder (0.86 g). (The fifth step for the complexation) 50.0 mg of [MesityleneRuCl2]2 (4) (0.086 mmol) was added to a suspension of Shell@SiO2@Yolk (0.50 g) in 20.0 mL of dry CH2Cl2 at room temperature, and the resulting mixture was stirred at 25 °C for 12 h. The mixture was
filtered through filter paper and then rinsed with excess CH₂Cl₂. After Soxhlet extraction for 24 h in CH₂Cl₂ to remove homogeneous and unreacted starting materials, the solid was dried at ambient temperature under vacuum overnight to afford PdPPh₂@MesityleneRuArDPEN@MNPs (5) (0.52 g) as a red powder. ICP analysis showed that the Pd and Ru loadings were 5.38 mg (0.0508 mmol of Pd) and 10.12 mg (0.099 mmol of Ru) per gram of catalyst, respectively. IR (KBr) cm⁻¹: 3424.9 (s), 3061.8 (w), 2977.6 (w), 2921.9 (w), 1636.4 (m), 1496.6 (w), 1449.9 (w), 1412.4 (w), 1384.6 (w), 1077.1 (s), 787.7 (m), 695.2 (m), 573.4 (w), 545.6 (w), 462.1 (m).¹³C CP/MAS NMR (161.9 MHz): 147.7, 138.9, 128.1 (C of Ph and Ar groups), 105.5, 102.5 (C of mesitylene groups), 76.5, 71.6 (CH of –NCHPh), 59.8 (CH₂ of –OCH₂CH₃), 53.4 (–NCH₂⁻ or –NCH₃ of CTAB), 29.8 (CH₂ of –CH₂P), 22.9 (CH₂ of –CH₂Ar), 20.5 (CH₃ of mesitylene), 18.0 (CH₃ of –OCH₂CH₃, and –CH₃ or –CH₂⁻ of CTAB), 4.8 (–CH₂Si–) ppm; ³¹P MAS NMR (169.3 MHz): 39.2 (cis), 29.8 (trans) ppm. ²⁹Si MAS NMR (79.4 MHz): T² (δ = –58.7 ppm), T³ (δ = –66.4 ppm), Q² (δ = –96.3 ppm), Q³ (δ = –102.2 ppm), Q⁴ (δ = –111.8 ppm).

4). General procedure for one-pot tandem reaction. A typical procedure was as follows. Catalyst 5 (19.68 mg, 1.00 μmol of Pd and 1.95 μmol of Ru, based on ICP analysis), K₂CO₃ (13.80 mg, 0.10 mmol), HCO₂Na (68.0 mg, 1.0 mmol), iodoacetophenones (0.10 mmol), aryne (0.11 mmol), and 4.0 mL of the mixed solvents (H₂O/MeOH, v/v = 1/3) were added sequentially to a 10.0 mL round-bottom flask. The mixture was then stirred at 60 °C for 10-16 h. During this period, the reaction was monitored constantly by TLC. After completion of the reaction, the catalyst was separated by centrifugation (10,000 rpm) for the recycling experiment. The aqueous solution was extracted with ethyl ether (3 × 3.0 mL). The combined ethyl ether extracts were washed with brine twice and then dehydrated with Na₂SO₄. After evaporation of ethyl ether, the residue was purified by silica gel flash column chromatography to afford the desired products.
5). Data of chiral products

6a. (S)-1-(4-(phenylethynyl)phenyl)ethanol. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.57–7.53 (m, 4H), 7.40–7.35 (m, 5H), 4.95–4.90 (q, $J = 8.0$ Hz, 1H), 2.09 (s, 1H), 1.53–1.51 (d, $J = 8.0$ Hz, 3H); $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$): δ 146.30, 141.99, 131.88, 128.63, 128.52, 125.71, 123.6 , 122.49, 89.61, 70.21, 25.34; GC/MS (m/z): 222; HPLC (OD-H, elute: Hexanes/i-PrOH = 97/3, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t$_1$ = 16.3 min (major), t$_2$ = 20.7 min.

6b. (S)-1-(4-((4-fluorophenyl)ethynyl)phenyl)ethanol. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.54–7.04 (m, 8H), 4.96–4.91 (q, $J = 8.0$ Hz, 1H), 1.90 (s, 1H), 1.53–1.51 (d, $J = 8.0$ Hz, 3H); $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$): δ 162.72 (d, $J = 250$ Hz), 146.29, 133.67 (d, $J = 8.3$ Hz), 131.93, 125.67, 122.34, 119.58 (d, $J = 3.6$ Hz), 115.87 (d, $J = 22$ Hz), 89.15, 88.45, 70.30, 25.38; GC/MS (m/z): 240; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t$_1$ = 16.5 min (major), t$_2$ = 18.9 min.

6c. (S)-1-(4-((3-fluorophenyl)ethynyl)phenyl)ethanol. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.52–7.20 (m, 8H), 4.95–4.90 (q, $J = 8.0$ Hz, 1H), 1.78 (s, 1H), 1.51–1.49 (d, $J = 8.0$ Hz, 3H); $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$): δ 162.85 (d, $J = 250$ Hz), 146.59, 133.67, 132.08, 130.17 (d, $J = 7.7$ Hz), 115.76 (d, $J = 21$ Hz), 124.19 (d, $J = 3.5$ Hz), 122.12, (d, $J = 15$ Hz) , 94.55, 82.83, 70.29, 25.37; GC/MS (m/z): 240; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t$_1$ = 19.9 min (major), t$_2$ = 23.1 min.

6d. (S)-1-(4-((2-fluorophenyl)ethynyl)phenyl)ethanol. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.57–7.12 (m, 8H), 4.96–4.91 (q, $J = 8.0$ Hz, 1H), 1.93 (s, 1H), 1.53–1.51 (d, $J = 8.0$ Hz, 3H); $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$): δ 162.87 (d, $J = 250$ Hz), 146.34, 133.68, 130.24 (d, $J = 7.8$ Hz), 128.95, 128.80, 125.97, 124.20 (d, $J = 13$ Hz), 123.23, 115.76 (d, $J = 21$ Hz) , 112.09 (d, $J = 15$ Hz), 94.88, 83.00, 70.25, 25.41; GC/MS (m/z): 240; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t$_1$ = 21.9 min (major), t$_2$ = 26.2 min.
6e. (S)-1-((4-chlorophenyl)ethynyl)phenyl)ethanol. \(^1\)H NMR (400 MHz, CDCl\(_3\)):
\[ \delta 7.53-7.33 \text{ (m, 8H), 4.95-4.90} \text{ (q, } J = 4.0 \text{ Hz, 1H), 1.98} \text{ (s, 1H), 1.52-1.51} \text{ (d, } J = 4.0 \text{ Hz, 3H)}; \]
\[^{13}\text{C}\{1\text{H}\} \text{ NMR (101 MHz, CDCl}_3\): } \delta 146.43, 134.37, 133.03, 131.98, 128.93, 125.68, 122.19, 121.20, 90.41, 88.41, 70.31, 25.40; GC/MS (m/z): 300; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), \( t_1 = 19.2 \text{ min (major), } t_2 = 21.6 \text{ min.} \)

6f. (S)-1-((4-bromophenyl)ethynyl)phenyl)ethanol. \(^1\)H NMR (400 MHz, CDCl\(_3\)):
\[ \delta 7.54-7.04 \text{ (m, 8H), 4.96-4.91} \text{ (q, } J = 8.0 \text{ Hz, 1H), 1.90} \text{ (s, 1H), 1.53-1.51} \text{ (d, } J = 8.0 \text{ Hz, 3H)}; \]
\[^{13}\text{C}\{1\text{H}\} \text{ NMR (101 MHz, CDCl}_3\): } \delta 145.20, 131.99, 130.73, 130.60, 124.43, 121.44, 12.22, 120.94, 89.34, 87.21, 69.07, 24.15; GC/MS (m/z): 300; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), \( t_1 = 20.4 \text{ min (major), } t_2 = 23.4 \text{ min.} \)

6g. (S)-1-((p-tolylethynyl)phenyl)ethanol. \(^1\)H NMR (400 MHz, CDCl\(_3\)):
\[ \delta 7.51-7.49 \text{ (m, 2H), 7.48-7.43} \text{ (m, 2H), 7.41-7.36} \text{ (m, 2H), 7.33-7.14} \text{ (m, 2H), 4.93-4.88} \text{ (q, } J = 8.0 \text{ Hz, 1H), 2.37} \text{ (s, 3H), 1.87} \text{ (s, H), 1.50-1.49} \text{ (d, } J = 8.0 \text{ Hz, 3H)}; \]
\[^{13}\text{C}\{1\text{H}\} \text{ NMR (101 MHz, CDCl}_3\): } \delta 146.13, 138.25, 132.43, 131.98, 129.40, 128.92, 128.49, 125.63, 123.30, 122.66, 89.75, 89.16, 70.32, 25.36, 21.47; GC/MS (m/z): 236; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), \( t_1 = 19.9 \text{ min (major), } t_2 = 22.5 \text{ min.} \)

6h. (S)-1-((m-tolylethynyl)phenyl)ethanol. \(^1\)H NMR (400 MHz, CDCl\(_3\)):
\[ \delta 7.54-7.52 \text{ (m, 2H), 7.39-7.35} \text{ (m, 2H), 7.28-7.16} \text{ (m, 2H), 4.96-4.91} \text{ (q, } J = 8.0 \text{ Hz, 1H), 2.38} \text{ (s, 3H), 1.53-1.51} \text{ (d, } J = 8.0 \text{ Hz, 3H)}; \]
\[^{13}\text{C}\{1\text{H}\} \text{ NMR (101 MHz, CDCl}_3\): } \delta 146.13, 138.25, 132.43, 131.98, 129.40, 128.92, 128.49, 125.63, 123.30, 122.66, 89.75, 89.16, 70.32, 25.36, 21.47; GC/MS (m/z): 236; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), \( t_1 = 19.6 \text{ min (major), } t_2 = 24.1 \text{ min.} \)
6i. (S)-1-(4-((4-methoxyphenyl)ethynyl)phenyl)ethanol. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.53-6.89 (m, 8H), 4.94–4.89 (q, J = 8.0 Hz, 1H), 3.84 (s, 3H), 2.00 (s, 1H), 1.52–1.50 (d, J = 8.0 Hz, 3H); \(^1\)C\{\(^1\)H\} NMR (101 MHz, CDCl\(_3\)): δ 159.85, 145.85, 133.88, 131.81, 125.60, 122.90, 115.62, 114.24, 89.53, 88.16, 70.34, 55.52, 25.34; GC/MS (m/z): 252; HPLC (OD-H, elute: Hexanes/i-PrOH = 95/5, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t\(_1\) = 16.1 min (major), t\(_2\) = 20.7 min.

6j. (S)-1-(4-((3-methoxyphenyl)ethynyl)phenyl)ethanol. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.55-6.90 (m, 8H), 4.91–4.86 (q, J = 8.0 Hz, 1H), 3.83 (s, 3H), 2.43 (s, 1H), 1.59–1.48 (d, J = 8.0 Hz, 3H); \(^1\)C\{\(^1\)H\} NMR (101 MHz, CDCl\(_3\)): δ 159.58, 146.41, 132.01, 129.66, 126.20, 125.65, 116.60, 115.17, 89.46, 89.32, 70.30, 55.52, 25.37; GC/MS (m/z): 252; HPLC (OD-H, elute: Hexanes/i-PrOH = 95/5, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t\(_1\) = 14.5 min (major), t\(_2\) = 17.3 min.

6k. (S)-4-((4-(1-hydroxyethyl)phenyl)ethynyl)benzonitrile. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.69-7.18 (m, 8H), 4.92–4.87 (q, J = 8.0 Hz, 1H), 1.73 (s, 1H), 1.52–1.50 (d, J = 8.0 Hz, 3H); \(^1\)C\{\(^1\)H\} NMR (101 MHz, CDCl\(_3\)): δ 146.97, 132.06, 131.97, 128.27, 125.57, 121.22, 118.55, 111.43, 90.70, 87.66, 70.02, 25.24; GC/MS (m/z): 247; HPLC (AD-H, elute: Hexanes/i-PrOH = 95/5, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t\(_1\) = 33.8 min (major), t\(_2\) = 4.2 min.

6l. (S)-1-(4-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)ethanol. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.66–7.38 (m, 8H), 4.96–4.91 (q, J = 8.0 Hz, 1H), 2.07 (s, 1H), 1.53–1.51 (d, J = 8.0 Hz, 3H); \(^1\)C\{\(^1\)H\} NMR (101 MHz, CDCl\(_3\)): δ 146.62, 131.19, 131.80, 130.05 (q, J = 32.7 Hz), 127.12, 125.51, 125.28 (q, J = 3.7 Hz), 122.61, 121.57, 91.65, 87.92, 70.05, 25.18; GC/MS (m/z): 300; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t\(_1\) = 20.8 min (major), t\(_2\) = 23.1 min.
6m. (S)-1-(3-(phenylethynyl)phenyl)ethanol. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.59–7.35 (m, 9H), 4.95–4.90 (q, $J=8.0$ Hz, 1H), 2.05 (s, 1H), 1.54–1.52 (d, $J=8.0$ Hz, 3H); $^{13}$C{1H} NMR (101 MHz, CDCl$_3$): $\delta$ 146.28, 131.86, 130.85, 128.86, 128.78, 125.62, 123.64, 123.44, 89.63, 89.55, 70.29, 25.41; GC/MS (m/z): 222; HPLC (OD-H, elute: Hexanes/i-PrOH = 97/3, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t$_1$ = 16.5 min (major), t$_2$ = 22.7 min.

6n. (S)-1-(3-((4-fluorophenyl)ethynyl)phenyl)ethanol. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.46–7.04 (m, 8H), 4.95–4.90 (q, $J=8.0$ Hz, 1H), 2.01 (s, 1H), 1.52–1.50 (d, $J=8.0$ Hz, 3H); $^{13}$C{1H} NMR (101 MHz, CDCl$_3$): $\delta$ 162.86 (d, $J=250$ Hz), 146.59, 133.67, 132.08, 130.17 (d, $J=7.7$ Hz), 125.64, 124.19 (d, $J=3.5$ Hz), 122.16 (d, $J=15$ Hz), 115.75 (d, $J=21$Hz), 112.16 (d, $J=15$ Hz), 94.51, 82.83, 70.29, 25.37; GC/MS (m/z): 240; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t$_1$ = 16.5 min (major), t$_2$ = 18.9 min.

6o. (S)-1-(3-((3-fluorophenyl)ethynyl)phenyl)ethanol. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.58–7.06 (m, 8H), 4.94–4.89 (q, $J=8.0$ Hz, 1H), 2.19 (s, 1H), 1.53–1.51 (d, $J=8.0$ Hz, 3H); $^{13}$C{1H} NMR (101 MHz, CDCl$_3$): $\delta$ 162.63 (d, $J=250$ Hz), 146.37, 130.81, 130.17 (d, $J=8.6$ Hz), 128.93, 128.84, 127.73 (d, $J=3.1$ Hz), 125.98, 125.29 (d, $J=9.8$ Hz), 123.12, 118.59 (d, $J=2.3$ Hz), 94.44, 88.32, 70.23, 25.45; GC/MS (m/z): 240; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t$_1$ = 20.4 min (major), t$_2$ = 25.1 min.

6p. (S)-1-(3-((2-fluorophenyl)ethynyl)phenyl)ethanol. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39–7.10 (m, 8H), 4.94–4.89 (q, $J=6.40$ Hz, 1H), 2.15 (s, 1H), 1.55–1.51 (d, $J=6.40$ Hz, 3H); $^{13}$C{1H} NMR (101 MHz, CDCl$_3$): $\delta$ 164.12, 161.62, 146.34, 133.69, 130.94, 130.28, 130.20, 128.94, 128.80, 124.18, 115.43, 94.58, 82.90, 70.24, 25.41; GC/MS (m/z): 240; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t$_1$ = 24.7 min (major), t$_2$ = 26.7 min.
6q. (S)-1-(3-((4-chlorophenyl)ethynyl)phenyl)ethanol. \[^{1}H\]NMR (400 MHz, CDCl\(_3\)):
\[\delta 7.89-7.33 (m, 8H), 4.92–4.87 (q, J = 8.0 Hz, 1H), 2.28 (s, 1H), 1.52–1.50 (d, J = 8.0 Hz, 3H); \[^{13}C\]{1H}NMR (101 MHz, CDCl\(_3\)):
\[\delta 146.17, 134.32, 132.84, 130.59, 128.74, 128.66, 128.61, 125.68, 123.03, 121.73, 90.36, 88.31, 69.97, 55.52, 25.21; \] GC/MS (m/z): 256; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t\(_1\) = 23.8 min (major), t\(_2\) = 26.6 min.

6r. (S)-1-(3-((4-bromophenyl)ethynyl)phenyl)ethanol. \[^{1}H\]NMR (400 MHz, CDCl\(_3\)):
\[\delta 7.57-7.35 (m, 8H), 4.93–4.88 (q, J = 4.0 Hz, 1H), 2.12 (s, 1H), 1.52–1.51 (d, J = 4.0 Hz, 3H); \[^{13}C\]{1H}NMR (101 MHz, CDCl\(_3\)):
\[\delta 146.15, 133.04, 131.65, 130.60, 128.63, 128.62, 125.68, 123.04, 122.55, 122.19, 90.49, 88.55, 70.01, 25.23; \] GC/MS (m/z): 300; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t\(_1\) = 24.0 min (major), t\(_2\) = 27.3 min.

6s. (S)-1-(3-(p-tolylethynyl)phenyl)ethanol. \[^{1}H\]NMR (400 MHz, CDCl\(_3\)):
\[\delta 7.51–7.14 (m, 8H), 4.93–4.88 (q, J = 4.0 Hz, 1H), 2.37 (s, 3H), 1.87 (s, 1H), 1.50–1.49 (d, J = 4.0 Hz, 3H); \[^{13}C\]{1H}NMR (101 MHz, CDCl\(_3\)):
\[\delta 146.32, 138.69, 131.77, 130.77, 129.40, 128.83, 128.77, 125.50, 123.80, 123.80, 89.86, 89.00, 70.25, 25.39, 21.75; \] GC/MS (m/z): 236; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t\(_1\) = 22.7 min (major), t\(_2\) = 24.0 min.

6t. (S)-1-(3-(m-tolylethynyl)phenyl)ethanol. \[^{1}H\]NMR (400 MHz, CDCl\(_3\)):
\[\delta 7.54–7.16 (m, 8H), 4.96–4.91 (q, J = 8.0 Hz, 1H), 2.38 (s, 3H), 1.88 (s, 1H), 1.53–1.51 (d, J = 8.0 Hz, 3H); \[^{13}C\]{1H}NMR (101 MHz, CDCl\(_3\)):
\[\delta 146.28, 138.26, 132.44, 130.83, 129.46, 128.94, 128.49, 125.55, 123.73, 123.24, 89.84, 89.23, 70.28, 25.39, 21.46; \] GC/MS (m/z): 236; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t\(_1\) = 20.9 min (major), t\(_2\) = 27.3 min.
6u. (S)-1-(3-((3-methoxyphenyl)ethynyl)phenyl)ethanol. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.53-6.88 (m, 8H), 4.94–4.89 (q, $J = 8.0$ Hz, 1H), 3.84 (s, 3H), 2.00 (s, 1H), 1.53–1.51 (d, $J = 8.0$ Hz, 3H); $^{13}$C{1H} NMR (101 MHz, CDCl$_3$): $\delta$ 159.88, 146.26, 133.31, 130.68, 128.75, 128.71, 125.31, 123.95, 115.96, 114.27, 89.66, 88.28, 7029, 55.52, 25.39; GC/MS (m/z): 252; HPLC (OD-H, elute: Hexanes/i-PrOH = 95/5, detector: 254 nm, flow rate: 1 mL/min, 25 °C), $t_1$ = 16.6 min (major), $t_2$ = 19.8 min.

6v. (S)-1-(3-((3-methoxyphenyl)ethynyl)phenyl)ethanol. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55-6.90 (m, 8H), 4.91–4.86 (q, $J = 12.0$ Hz, 1H), 3.83 (s, 3H), 2.43 (s, 1H), 1.51–1.48 (d, $J = 12.0$ Hz, 3H); $^{13}$C{1H} NMR (101 MHz, CDCl$_3$): $\delta$ 159.58, 146.32, 130.85, 129.68, 128.91, 128.80, 116.60, 125.71, 123.31, 116.61, 115.23, 89.57, 89.43, 70.23, 55.52, 25.40; GC/MS (m/z): 252; HPLC (OD-H, elute: Hexanes/i-PrOH = 95/5, detector: 254 nm, flow rate: 1 mL/min, 25 °C), $t_1$ = 13.2 min (major), $t_2$ = 16.6 min.

6w. (S)-1-(3-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)ethanol. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.66-7.37 (m, 8H), 4.95–4.90 (q, $J = 8.0$ Hz, 1H), 2.13 (s, 1H), 1.53–1.51 (d, $J = 8.0$ Hz, 3H); $^{13}$C{1H} NMR (101 MHz, CDCl$_3$): $\delta$ 146.24, 131.82, 130.73, 130.02 (q, $J = 32.5$ Hz), 128.78, 128.66, 127.07, 126.01, 125.30 (q, $J = 3.3$ Hz), 122.67, 91.74, 87.98, 69.95, 55.52, 25.21; GC/MS (m/z): 290; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), $t_1$ = 18.9 min (major), $t_2$ = 23.9 min.

6x. (S)-1-(4-(hex-1-yn-1-yl)phenyl)ethanol $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.40–7.28 (dd, $J = 8.0$ Hz, 4H), 4.92–4.87 (q, $J = 8.0$ Hz, 1H), 2.14–2.11 (t, $J = 8.0$ Hz, 1H), 1.84 (s, 1H), 1.64–1.45 (m, 7H), 0.98–0.95 (t, $J = 8.0$ Hz, 3H); $^{13}$C{1H} NMR (101 MHz, CDCl$_3$): $\delta$ 145.28, 131.89, 125.16, 123.44, 90.59, 80.55, 70.33, 31.07, 25.32, 22.25, 19.33, 13.87; GC/MS (m/z): 266; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), $t_1$ = 12.4 min (major), $t_2$ = 17.5 min.
6y. (S,S)-1,1'-(ethyne-1,2-diylbis(4,1-phenylene))diethanol. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.54–7.37 (m, 8H), 4.96–4.91 (q, $J$ = 4.0 Hz, 2H), 1.53 (s, 2H), 1.53–1.50 (t, $J$ = 4.0 Hz, 6H); $^{13}$C{1H} NMR (101 MHz, CDCl$_3$): $\delta$ 146.17, 132.0, 125.62, 122.57, 89.38, 70.35, 25.39; GC/MS (m/z): 266; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), $t_1$ = 33.8 min (major), $t_2$ = 53.6 min.

6z. (S)-1-(3-((4-((S)-1-hydroxyethyl)phenyl)ethynyl)phenyl)ethanol. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55–7.34 (m, 8H), 4.91–4.86 (q, $J$ = 4.0 Hz, 2H), 2.25 (s, 2H), 1.53–1.48 (d, $J$ = 4.0 Hz, 6H); $^{13}$C{1H} NMR (101 MHz, CDCl$_3$): $\delta$ 146.09, 146.02, 131.77, 130.61, 128.65, 128.56, 125.45, 125.42, 123.37, 122.22, 89.30, 89.27, 70.07, 70.01, 25.17, 25.12; GC/MS (m/z): 266; HPLC (OD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), $t_1$ = 33.6 min (major), $t_2$ = 37.6 min.

**Figure S1.** The FT-IR spectrum catalyst 5.
**Figure S2.** The solid-state $^{13}$C CP MAS NMR spectra of the fresh catalyst 5 and the recycled catalyst 5.
**Figure S3.** The solid-state $^{31}$P CP MAS NMR spectrum of catalyst 5.

![Catalyst 5 spectrum](image)

**Figure S4.** The solid-state $^{29}$Si CP MAS NMR spectrum of catalyst 5.

![Catalyst 5 spectrum](image)
Figure S5. The small-angle powder XRD pattern catalyst 5.
Figure S6. The nitrogen adsorption-desorption isotherms of catalyst 5.
Figure S7. The TEM images of the fresh catalyst 5 and the recycled catalyst 5.

TEM images of the fresh catalyst 5

TEM of the recycled catalyst 5
Table S1. Optimizing reaction conditions for the tandem Sonogashira coupling–ATH of 4-iodoacetophenone and phenylacetylene.\textsuperscript{a}

![Chemical structure](image)

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\textsuperscript{a} Reaction conditions: catalyst 5 (19.68 mg, 1.00 μmol of Pd and 1.95 μmol of Ru, based on ICP analysis), \( \text{K}_2\text{CO}_3 \) (13.80 mg, 0.10 mmol), \( \text{HCO}_2\text{Na} \) (68.0 mg, 1.0 mmol), iodoacetophenones (0.10 mmol), phenylacetylene (0.11 mmol), and 4.0 mL of solvents. \( \textsuperscript{b} \) TOF (TOF = number of moles of substrate converted per mole of catalyst per hour).
Figure S8. Characterizations of chiral products.

6a (Entry 1 in Table 1): (S)-1-(4-(phenylethynyl)phenyl)ethanol
6b (Entry 2 in Table 1): (S)-1-(4-((4-fluorophenyl)ethynyl)phenyl)ethanol
6c \textit{(Entry 3 in Table 1)}: (S)-1-(4-((3-fluorophenyl)ethynyl)phenyl)ethanol
6d (Entry 4 in Table 1): (S)-1-(4-((2-fluorophenyl)ethynyl)phenyl)ethanol
6e (Entry 5 in Table 1): (S)-1-(4-((4-chlorophenyl)ethynyl)phenyl)ethanol
6f (Entry 6 in Table 1): (S)-1-(4-((4-bromophenyl)ethynyl)phenyl)ethanol
6g (Entry 7 in Table 1): (S)-1-(4-(p-tolylethynyl)phenyl)ethanol
6h (Entry 8 in Table 1): (S)-1-(4-(m-tolylethynyl)phenyl)ethanol (5h)
6i (Entry 9 in Table 1): (S)-1-((4-methoxyphenyl)ethynyl)phenyl)ethanol
6j (Entry 10 in Table 1): (S)-1-(4-((3-methoxyphenyl)ethynyl)phenyl)ethanol
(S)-1-(4-(4-methoxyphenyl)ethynyl)phenyl)ethanol

Chemical Formula: C_{17}H_{16}O_{2}

Molecular Weight: 252.12
6k (Entry 11 in Table 1): (S)-4-((4-(1-hydroxyethyl)phenyl)ethynyl)benzonitrile
61 (Entry 12 in Table 1): (S)-1-(4-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)ethanol
6m (Entry 13 in Table 1): (S)-1-(3-(phenylethynyl)phenyl)ethanol
6n (Entry 14 in Table 1): (S)-1-(3-((4-fluorophenyl)ethynyl)phenyl)ethanol
60 (Entry 15 in Table 1): (S)-1-(3-((3-fluorophenyl)ethyl)phenyl)ethanol
6p (Entry 16 in Table 1): (S)-1-((3-(2-fluorophenyl)ethynyl)phenyl)ethanol
(S)-1-(3-((2-fluorophenyl)ethynyl)phenyl)ethanol

Chemical Formula: $C_{16}H_{13}FO$
Molecular Weight: 240.10
6q (Entry 17 in Table 1): (S)-1-(3-((4-chlorophenyl)ethynyl)phenyl)ethanol
6r (Entry 18 in Table 1): (S)-1-((4-bromophenyl)ethynyl)phenyl)ethanol
6s (Entry 19 in Table 1): (S)-1-(4-(p-tolylethynyl)phenyl)ethanol
6t (Entry 20 in Table 1): (S)-1-(4-(m-tolyethyl)phenyl)ethanol
6u (Entry 21 in Table 1): (S)-1-(4-((4-methoxyphenyl)ethynyl)phenyl)ethanol
**6v (Entry 22 in Table 1):** (S)-1-(4-((3-methoxyphenyl)ethynyl)phenyl)ethanol
6w *(Entry 23 in Table 1)*: (S)-1-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)ethanol
6x (Entry 24 in Table 1): (S)-1-(4-(hex-1-yn-1-yl)phenyl)ethanol
Scheme 3: (1S,1'S)-1,1'-(ethyne-1,2-diylbis(4,1-phenylene))diethanol
$6z$ (Scheme 3): (S)-1-[(4-((S)-1-hydroxyethyl)phenyl)ethynyl]phenyl)ethanol
Figure 9. HPLC analyses for chiral products

6a (*Entry 1 in Table 1*): (S)-1-(4-(phenylethynyl)phenyl)ethanol
6b (Entry 2 in Table 1): (S)-1-(4-((4-fluorophenyl)ethynyl)phenyl)ethanol
6c (Entry 3 in Table 1): (S)-1-(4-((3-fluorophenyl)ethynyl)phenyl)ethanol
6d (*Entry 4 in Table 1*): (S)-1-(4-((2-fluorophenyl)ethynyl)phenyl)ethanol 5(d)

![Organic structure diagram](image)

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6f (Entry 6 in Table 1): (S)-1-(4-((4-bromophenyl)ethynyl)phenyl)ethanol
6g (Entry 7 in Table 1): (S)-1-(4-(p-tolylethynyl)phenyl)ethanol
6h (Entry 8 in Table 1): (S)-1-(4-(m-tolylethynyl)phenyl)ethanol
6i \textit{(Entry 9 in Table 1)}: (S)-1-((4-methoxyphenyl)ethyl(phenyl)ethanol 5(i)
6j (Entry 10 in Table 1): (S)-1-(4-((3-methoxyphenyl)ethynyl)phenyl)ethanol

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61 (Entry 12 in Table 1):

(S)-1-(4-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)ethanol
6m (Entry 13 in Table 1): (S)-1-(3-(phenylethynyl)phenyl)ethanol
6n (Entry 14 in Table 1): (S)-1-(3-((4-fluorophenyl)ethynyl)phenyl)ethanol
60 (Entry 15 in Table 1): (S)-1-((3-fluorophenyl)ethynyl)phenyl)ethanol 5(o)
6p *(Entry 16 in Table 1)*: (S)-1-(3-((2-fluorophenyl)ethynyl)phenyl)ethanol
6q (Entry 17 in Table 1): (S)-1-(3-((4-chlorophenyl)ethynyl)phenyl)ethanol
6r (*Entry 18 in Table 1*): (S)-1-((4-bromophenyl)ethynyl)phenyl)ethanol
6s (Entry 19 in Table 1): (S)-1-(3-(p-tolylethynyl)phenyl)ethanol
**6t (Entry 20 in Table 1): (S)-1-(3-(m-tolylethynyl)phenyl)ethanol**

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</table>
6u (Entry 21 in Table 1): (S)-1-(3-((4-methoxyphenyl)ethynyl)phenyl)ethanol
6v (Entry 22 in Table 1): (S)-1-((3-methoxyphenyl)ethynyl)phenyl)ethanol
6w (Entry 23 in Table 1):

*(S)*-1-((3-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)ethanol
6x (Entry 24 in Table 1):

(S)-1-(4-(hex-1-yn-1-yl)phenyl)ethanol
6v (Scheme 2): (1S,1'S)-1,1'-(ethyne-1,2-diylbis(4,1-phenylene))diethanol
6z (Scheme 2): (S)-1-(3-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)ethanol
Table S1. Reusability of catalyst 5 for the enantioselective tandem Sonogashira coupling-ATH reaction of 4-iodoacetophenone and phenylacetylene.[a]

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<td>ee [%]</td>
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</tbody>
</table>

[a] Reaction conditions: catalyst 5 (196.80 mg), K₂CO₃ (138.0 mg, 1.0 mmol), HCO₂Na (680.0 mg, 10.0 mmol), iodoacetophenones (1.0 mmol), aryne (1.10 mmol), and 40.0 mL of the mixed solvents (H₂O/MeOH v/v = 1/3), reaction temperature (60 °C), reaction time (16 h).

Figure 10. Reusability of catalyst 5 for the Sonogashira coupling-ATH reaction of 4-iodoacetophenone and phenylacetylene.

Recycle 2

Recycle 3
Recycle 4

Recycle 5

Recycle 6