Supplementary Material (ESI) for Chemical Communications

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excess was determined by chiral HPLC (DAICEL CHIRALCEL OD-H, eluent: hexane/isopropanol = 9/1, flow: 0.5 mL/min, detection at 254 nm, 97% ee).

**Spectral Data**

**(S)-4-Methyl-1-phenyl-pent-2-yne-1,4-diol (4a):** Known compound (CAS No. 321855-44-1)

Colorless solid; IR (KBr) 3375, 2981, 1638, 1454, 1379, 1164, 1090, 1059 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.54 (s, 6H), 2.94 (brs, 1H), 3.24 (brs, 1H), 5.46 (d, \(J = 5.5\) Hz, 1H), 7.31-7.39 (m, 3H), 7.51 (brd, \(J = 7.1\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 31.2, 31.3, 64.4, 65.2, 81.8, 91.3, 126.6, 128.3, 128.6, 140.5; ESI-MS \(m/z\) 213 [M+Na\(^+\)]; \([\alpha\]\(_D\)\(^{25}\) \(-17.9\) (c 0.79, CHCl\(_3\)); HPLC (DAICEL CHIRALCEL OD-H, 2-propanol/hexane 10/90, flow 0.5 mL/min, detection at 254 nm) \(t_R\) 12.6 min (major) and 14.7 min (minor).

**(S)-1-(4-Chloro-phenyl)-4-methyl-pent-2-yne-1,4-diol (4b):**

Colorless solid; IR (KBr) 3389, 2982, 1490, 1164 cm\(^{-1}\); 1H NMR (CDCl\(_3\)) \(\delta\) 1.49 (s, 6H), 5.37 (s, 1H), 7.28 (d, \(J = 8.2\) Hz, 2H), 7.39 (d, \(J = 8.2\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 31.1, 31.1, 63.3, 65.1, 81.5, 91.4, 128.0, 128.6, 134.0, 139.0; ESI-MS \(m/z\) 247 [M+Na\(^+\)]; HRMS calcd. for C\(_{12}\)H\(_{12}\)ClO \([M-OH]^{+}\): 207.0571, found 207.0569; \([\alpha\]\(_D\)\(^{27}\) \(-15.5\) (c 0.87, CHCl\(_3\)); HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 10/90, flow 0.5 mL/min, detection at 254 nm) \(t_R\) 21.3 min (major) and 23.5 min (minor).

**(S)-1-(4-Methoxy-phenyl)-4-methyl-pent-2-yne-1,4-diol (4c):**

Colorless solid; IR (KBr) 3374, 2980, 1611, 1512, 1247, 1173 cm\(^{-1}\); 1H NMR (CDCl\(_3\)) \(\delta\) 1.51 (s, 6H), 3.23 (brs, 1H), 3.45 (brs, 1H), 3.78 (s, 3H), 5.38 (s, 1H), 6.86 (d, \(J = 8.6\) Hz, 2H), 7.41 (d, \(J = 8.6\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 31.2, 31.2, 55.2, 63.8, 65.1, 82.0, 91.1, 113.8, 128.1, 132.9, 159.5; ESI-MS \(m/z\) 243 [M+Na\(^+\)]; HRMS calcd. for C\(_{13}\)H\(_{15}\)O\(_2\) \([M-OH]^{+}\): 203.1067, found 203.1067; \([\alpha\]\(_D\)\(^{26}\) \(-22.3\) (c 0.91, CHCl\(_3\)); HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 10/90, flow 0.5 mL/min, detection at 254 nm) \(t_R\) 33.0 min (major) and 36.6 min (minor).

**(S)-1-Furan-2-yl-4-methyl-pent-2-yne-1,4-diol (4d):** Known compound (CAS No. 99186-44-4 (for racemic compound))

Colorless oil; IR (neat) 3346, 2982, 1379, 1234, 1166 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.50 (s, 6H), 3.85 (brs, 1H), 4.29 (brs, 1H), 5.44 (s, 1H), 6.30 (dd, \(J = 1.2, 3.4\) Hz, 1H), 6.40 (d, \(J = 3.4\) Hz, 1H), 7.36 (d, \(J = 1.2\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 30.9, 31.0, 57.6, 65.0, 79.4, 90.3, 107.7, 110.3, 142.8, 152.9; ESI-MS \(m/z\) 203 [M+Na\(^+\)]; \([\alpha\]\(_D\)\(^{25}\) \(-10.6\) (c 1.53, CHCl\(_3\)); HPLC (DAICEL CHIRALCEL OD-H, 2-propanol/hexane 10/90, flow 0.5 mL/min, detection at 254 nm) \(t_R\) 28.4 min (minor) and 50.9 min (major).

**(S)-4-Methyl-1-thiophen-3-yl-pent-2-yne-1,4-diol (4e):**
Colorless oil; IR (neat) 3344, 2981, 1377, 1233, 1164 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.51 (s, 6H), 3.85 (brs, 1H), 4.24 (brs, 1H), 5.46 (s, 1H), 7.16 (d, \(J = 5.2\) Hz, 1H), 7.27 (dd, \(J = 3.5, 5.2\) Hz, 1H), 7.34 (brs, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 31.0, 31.1, 60.0, 81.7, 90.3, 122.6, 126.2, 126.4, 141.9; ESI-MS \(m/z\) 219 [M+Na]; HRMS calcd. for C\(_{10}\)H\(_{13}\)O\(_2\)SCS [M+Cs] \(^+\): 328.9612, found 328.9609; \([\alpha]_D^{25}\) –13.0 (c 1.21, CHCl\(_3\)); HPLC (DAICEL CHIRALCEL OD-H, 2-propanol/hexane 10/90, flow 0.5 mL/min, detection at 254 nm) \(t_R\) 14.7 min (major) and 17.0 min (minor).

(S)-2,7-Dimethyl-oct-3-yne-2,5-diol (4f): Known compound (CAS No. 2398-42-7) for racemic compound

Colorless oil; IR (neat) 3390, 2957, 1366, 1235, 1166 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.89-0.92 (m, 6H), 1.49 (s, 6H), 1.51-1.53 (m, 1H), 1.58-1.63 (m, 1H), 1.76-1.84 (m, 1H), 3.27 (brs, 1H), 3.41 (brs, 1H), 4.40 (t, \(J = 7.4\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 22.4, 22.5, 24.7, 31.3, 31.3, 46.7, 60.6, 65.0, 83.4, 89.4; ESI-MS \(m/z\) 193 [M+Na]; \([\alpha]_D^{29}\) –11.8 (c 1.02, CHCl\(_3\)); HPLC (after conversion to corresponding 3,5-dinitrobenzoate) (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 10/90, flow 1.0 mL/min, detection at 254 nm) \(t_R\) 22.3 min (major) and 24.3 min (minor).

(S)-2,6-Dimethyl-hept-3-yne-2,5-diol (4g): Known compound (CAS No. 321903-25-7)

Colorless oil; IR (neat) 3374, 2979, 1380, 1235, 1166 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.94-0.97 (m, 6H), 1.48 (s, 3H), 1.46 (s, 3H), 1.75-1.86 (m, 1H), 4.04 (d, \(J = 5.8\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 19.1, 20.2, 31.3, 31.4, 34.4, 65.0, 67.5, 81.7, 90.3; ESI-MS \(m/z\) 157 [M+Na]; \([\alpha]_D^{31}\) +1.83 (c 0.77, CHCl\(_3\)); HPLC (after conversion to corresponding 3,5-dinitrobenzoate) (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 10/90, flow 1.0 mL/min, detection at 254 nm) \(t_R\) 24.2 min (major) and 33.8 min (minor).

(S)-1-Cyclohexyl-4-methyl-pent-2-yne-1,4-diol (4h): Known compound (CAS No. 321855-40-7)

Colorless oil; IR (neat) 3357, 2926, 1450, 1233, 1163, 1084 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.96-1.24 (m, 5H), 1.45-1.51 (m, 7H), 1.63-1.83 (m, 5H), 3.27 (brs, 1H), 3.49 (brs, 1H), 4.11 (d, \(J = 6.1\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 25.8, 26.3, 28.1, 28.6, 31.3, 43.9, 64.9, 66.8, 82.0, 90.3; ESI-MS \(m/z\) 219 [M+Na]; \([\alpha]_D^{29}\)
+6.68 (c 1.14, CHCl₃); HPLC (after conversion to corresponding 3,5-dinitrobenzoate) (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 10/90, flow 1.0 mL/min, detection at 254 nm) \( t_R \) 23.5 min (minor) and 47.1 min (major).

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\text{(S)-2,6,6-Trimethyl-hept-3-yne-2,5-diol (4i):} \text{ Known compound (CAS No. 321855-41-8)}
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Colorless oil; IR (neat) 3374, 2978, 1364, 1233, 1165 cm\(^{-1}\); \(^1\)H NMR (CDCl₃) \( \delta \) 0.95 (s, 9H), 1.49 (s, 3H), 1.50 (s, 3H), 2.81 (brs, 1H), 3.11 (brs, 1H), 3.99 (s, 1H); \(^{13}\)C NMR (CDCl₃) \( \delta \) 25.3, 31.3, 31.4, 35.7, 65.0, 71.0, 81.8, 90.4; ESI-MS \( m/z \) 193 [M+Na]\(^+\); \([\alpha]_D^{21} -2.71 (c 1.15, CHCl₃); HPLC (after conversion to corresponding benzoate) (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 10/90, flow 0.3 mL/min, detection at 254 nm) \( t_R \) 18.9 min (minor) and 20.1 min (major).

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\text{(S)-2-Methyl-7-phenyl-hept-6-en-3-yne-2,5-diol (4j):} \text{ Known compound (CAS No. 321855-45-2)}
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Colorless solid; IR (KBr) 3332, 2980, 1449, 1378, 1232, 1164 cm\(^{-1}\); \(^1\)H NMR (CDCl₃) \( \delta \) 1.54 (s, 6H), 3.70 (brs, 1H), 3.97 (brs, 1H), 5.07 (d, \( J = 5.7 \) Hz, 1H), 6.27 (dd, \( J = 5.7, 15.5 \) Hz, 1H), 6.71 (d, \( J = 15.5 \) Hz, 1H), 7.22-7.30 (m, 3H), 7.36 (d, \( J = 8.1 \) Hz, 2H); \(^{13}\)C NMR (CDCl₃) \( \delta \) 31.2, 31.2, 62.5, 65.1, 81.1, 91.0, 126.7, 128.0, 128.0, 128.3, 128.4, 128.5, 131.7, 136.0; ESI-MS \( m/z \) 239 [M+Na]\(^+\); \([\alpha]_D^{27} +4.58 (c 2.88, CHCl₃); HPLC (DAICEL CHIRALCEL OD-H, 2-propanol/hexane 10/90, flow 0.5 mL/min, detection at 254 nm) \( t_R \) 19.4 min (major) and 21.4 min (minor).

**Deprotection:**

To a 20 mL round-bottomed flask, 4a (500 mg, 2.63 mmol) and DMF (5.0 mL) was charged. To the resulting solution was added imidazole (537.2 mg, 7.89 mmol) and TIPSCl (0.843 mL, 3.94 mmol) was added at 0 °C successively. Then the mixture was warmed up to room temperature and stirred over night. The reaction was quenched with water and extracted with diethyl ether for 3 times. Collected organic layer was washed with water then brine, and dried over Na₂SO₄. After filtration of Na₂SO₄, the organic solvent was evaporated and the residue was purified by flash column chromatography (silica gel, eluent: hexane/Et₂O = 100/0 – 85/15) to give 5a as a colorless oil.

To a test tube, MS 5A (6.5 mg) and K₂CO₃ (2.81 mg, 25.9 µmol) was charged and dried with heat gun under reduced pressure. After cooling down to room temperature, argon was charged in the test tube and xylenes (0.7 mL) was added. The resulting slurry was stirred for 1 minute, then 18-crown-6 (2.74 mg, 10.4...
µmol) was added. Again stirring for 1 minute, 5a (22.5 mg, 64.8 µmol) in xylenes (0.2 mL) was added by syringe, followed by washing with xylenes 3 times (0.2 mL x 3). The reaction mixture was stirred for 44 h at 145 °C (oil bath temperature). The reaction was monitored by TLC analysis. After cooling to room temperature, the reaction was quenched with water, extracted with diethyl ether for 3 times. Combined organic layers were washed with brine, and dried over Na2SO4. After filtration of Na2SO4, the organic solvent was evaporated and the residue was purified by flash column chromatography (silica gel, eluent: hexane 100%) to give 6a (14.26 mg, 49.4 µmol, 76% yield) as a colorless oil.

Spectral Data  
(R)-Triisopropyl-(1-phenyl-prop-2-ynloxy)-silane (6a): Known compound (CAS No. 321855-62-3)  
Colorless oil; IR (neat) 2944, 2867, 1093, 1065 cm⁻¹; ¹H NMR (CDCl₃) δ 1.08 (d, J = 7.3 Hz, 9H), 1.13 (d, J = 7.0 Hz, 9H), 1.17-1.25 (m 3H), 2.54 (d, J = 2.2 Hz, 1H), 5.57 (d, J = 2.2 Hz, 1H), 7.29 (dd, J = 7.4, 7.4 Hz, 1H), 7.36 (d, J = 7.4, 7.7 Hz, 2H), 7.52 (d, J = 7.7 Hz, 2H); ¹³C NMR (CDCl₃) δ 12.2, 18.0, 64.7, 73.4, 85.2, 125.8, 127.7, 128.3, 141.9; ESI-MS m/z 311 [M+Na⁺]; [α]D²⁵ –5.7 (c 1.21, CHCl₃).

Mass Spectrometry Analyses:  
A flame-dried test tube was charged with (S)-BINOL (28.6 mg, 0.1 mmol) and InBr₃ (35.4 mg, 0.1 mmol) under Argon atmosphere. To the tube was added dry CH₂Cl₂ (0.5 mL), and the mixture was stirred for 1 h. Then, benzaldehyde (3a) (40.7 µL, 0.4 mmol) was added at room temperature. After the resulting solution was stirred for 15 minutes, a portion of the resulting solution (75 µL) was then diluted with CH₂Cl₂ (1.0 mL) and iPrOH (0.1 mL). The resulting clear solution was analyzed by Waters micromass ZQ (ESI-MS). ESI-MS analysis was performed in cation mode under the following conditions: capillary: 3.8 kV; cone: 95 V; source temp: 80 °C; desolvation temp.: 100 °C; syringe pump: 10 µL/min. The obtained spectrum is shown in Figure S1.

**Figure S1.** ESI-MS of indium(III)/binol = 1:1 mixture in CH₂Cl₂/iPrOH. m/z: 275 [InBr₂]⁺, 561 [binol/InBr₂]⁺, 847 [binol x 2/InBr₂]⁺.
In addition to a major of InBr$_3^+$ ($m/z$ 275), peaks corresponding to [binol/InBr$_2$]$^+$ ($m/z$ 561) and [binol x 2/InBr$_2$]$^+$ ($m/z$ 847) were observed. Although the chart supported the complexation of indium(III) with BINOL, further mechanistic studies are required to elucidate the structure of the InBr$_3$/BINOL complex.