Supporting Information
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**Experimental Section**

**General**

All manipulations were carried out under an argon atmosphere in dried and degassed solvents. All solvents were dried and degassed by standard methods and all aldehydes, dimethylzinc and diethylzinc were commercially available. Melting points were determined using a standard melting point apparatus and are uncorrected. The reactions were monitored by thin layer chromatography (TLC). NMR spectra were measured in CDCl₃ on a 400 NMR spectrometer (400 MHz) with TMS as an internal reference. Optical rotations were measured with a SEPA-200 high sensitive polarimeter. Enantiomeric excess (ee) determination was carried out using a chiral OD-H column. Solvent, 80:20 hexane/isopropanol; Flow rate 1 mL.min⁻¹; 254 nm UV Detection. High resolution mass spectra (HRMS) were measured with EI.

**Characterization of the corresponding chiral products:**

**Methyl 4-(4-bromophenyl)-4-hydroxybut-2-ynoate:** 57% yield. 83% ee determined by HPLC analysis (Chiralcel AD-H column, IPA : hexane = 10 : 90). Retention time: $t_{\text{minor}} = 9.08$ min, $t_{\text{major}} = 10.58$ min. $^1$H NMR (400 MHz, CDCl₃) $\delta$: 2.76 (br, 1H), 3.80 (s, 3H), 5.54 (s, 1H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 8.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl₃) $\delta$: 53.5, 63.9, 78.1, 86.6, 123.4, 128.8, 132.4, 137.9, 154.2.

**Methyl 4-(4-chlorophenyl)-4-hydroxybut-2-ynoate:** 74% yield. 82% ee determined by HPLC analysis (Chiralcel AD-H column, IPA : hexane = 10 : 90). Retention time: $t_{\text{minor}} = 8.55$ min, $t_{\text{major}} = 9.74$ min. $^1$H NMR (400 MHz, CDCl₃) $\delta$: 2.69 (d, $J = 5.6$ Hz, 1H), 3.80 (s, 3H), 5.56 (d, $J = 5.6$ Hz, 1H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl₃) $\delta$: 53.5, 63.8, 78.0, 86.7, 128.5, 129.4, 135.2, 137.4, 154.2.
Methyl 4-hydroxy-4-p-tolylbut-2-ynoate: 61% yield. 82% ee determined by HPLC analysis (Chiralcel AD-H column, IPA : hexane = 10 : 90). Retention time: $t_{\text{minor}} = 9.24 \text{ min}$, $t_{\text{major}} = 10.55 \text{ min}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 2.36 (s, 3H), 2.54 (d, $J = 5.2 \text{ Hz}$, 1H), 3.79 (s, 3H), 5.53 (d, $J = 3.6 \text{ Hz}$, 1H), 7.20 (d, $J = 8.0 \text{ Hz}$, 2H), 7.40 (d, $J = 8.0 \text{ Hz}$, 2H); $^{13}$CNMR (100 MHz, CDCl$_3$) $\delta$: 21.6, 53.3, 64.4, 77.7, 87.5, 127.1, 129.9, 136.1, 139.2, 154.4.

Methyl 4-(2-chlorophenyl)-4-hydroxybut-2-ynoate: 75% yield. 81% ee determined by HPLC analysis (Chiralcel OD-H column, IPA : hexane = 10 : 90). Retention time: $t_{\text{minor}} = 8.01 \text{ min}$, $t_{\text{major}} = 8.77 \text{ min}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 2.91 (d, $J = 5.6 \text{ Hz}$, 1H), 3.79 (s, 3H), 5.93 (d, $J = 5.6 \text{ Hz}$, 1H), 7.27–7.36 (m, 2H), 7.39–7.41 (m, 1H), 7.69–7.71 (m, 1H); $^{13}$CNMR (100 MHz, CDCl$_3$) $\delta$: 53.4, 61.7, 77.4, 86.3, 127.8, 128.7, 130.2, 130.5, 132.9, 136.4, 154.3.

Methyl 4-(4-fluorophenyl)-4-hydroxybut-2-ynoate: 66% yield. 79% ee determined by HPLC analysis (Chiralcel AD-H column, IPA : hexane = 10 : 90). Retention time: $t_{\text{minor}} = 8.29 \text{ min}$, $t_{\text{major}} = 9.09 \text{ min}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 2.71 (d, $J = 5.2 \text{ Hz}$, 1H), 3.80 (s, 3H), 5.56 (d, $J = 3.6 \text{ Hz}$, 1H), 7.08 (t, $J = 8.8 \text{ Hz}$, 2H), 7.48-7.51 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 53.4, 63.9, 78.1, 86.8, 116.1–116.3 (d, $J = 21.7 \text{ Hz}$), 129.0–129.1 (d, $J = 8.4 \text{ Hz}$), 134.8–134.9 (d, $J = 2.3 \text{ Hz}$), 154.2, 164.7.

Methyl 4-(3-chlorophenyl)-4-hydroxybut-2-ynoate: 57% yield. 80% ee determined by HPLC analysis (Chiralcel OD-H column, IPA : hexane = 8 : 92). Retention time: $t_{\text{minor}} = 12.19 \text{ min}$, $t_{\text{major}} = 10.87 \text{ min}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 2.80 (d, $J = 6.0 \text{ Hz}$, 1H), 3.80 (s, 3H), 5.56 (d, $J = 4.4 \text{ Hz}$, 1H), 7.33–7.34 (m, 2H), 7.39–7.41 (m, 1H), 7.52 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 53.5, 63.9, 78.1, 86.5, 125.2, 127.2, 129.5, 130.5, 135.1, 140.8, 154.2.

Methyl 4-hydroxy-4-(naphthalen-4-yl)but-2-ynoate: 73% yield. 83% ee determined by HPLC analysis (Chiralcel AD-H column, IPA : hexane = 10 : 90). Retention time: $t_{\text{minor}} = 13.54 \text{ min}$, $t_{\text{major}} = 16.34 \text{ min}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 2.62 (d, $J = 6.0 \text{ Hz}$, 1H), 3.79 (s, 3H), 6.23 (d, $J = 6.0 \text{ Hz}$, 1H), 7.46–7.61 (m, 3H), 7.80 (d, $J = 7.2 \text{ Hz}$, 1H), 7.88 (t, $J = 8.0 \text{ Hz}$, 2H), 8.23 (d, $J = 8.4 \text{ Hz}$, 1H); $^{13}$C
NMR (100 MHz, CDCl₃) δ: 53.3, 62.9, 78.4, 87.1, 123.9, 125.4, 125.6, 126.5, 127.2, 129.2, 130.3, 130.7, 134.1, 134.4, 154.3.

**Methyl 4-hydroxy-4-(naphthalen-2-yl)but-2-ynoate:** 43% yield. 73% ee determined by HPLC analysis (Chiralcel AD-H column, IPA : hexane = 10 : 90). Retention time: $t_{\text{minor}} = 15.37$ min, $t_{\text{major}} = 19.34$ min. $^1$H NMR (400 MHz, CDCl₃) δ: 2.64 (d, $J = 5.2$ Hz, 1H), 3.80 (s, 3H), 5.74 (d, $J = 3.6$ Hz, 1H), 7.50–7.53 (m, 2H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.84–7.89 (m, 3H), 7.97 (s, 1H); $^{13}$C NMR (100 MHz, CDCl₃) δ: 53.4, 64.8, 78.2, 87.1, 124.7, 126.2, 126.9, 127.1, 128.2, 128.7, 129.3, 133.5, 133.8, 136.2, 154.3.

**Methyl 4-hydroxy-4-(4-methoxyphenyl)but-2-ynoate:** 47% yield. 63% ee determined by HPLC analysis (Chiralcel AD-H column, IPA : hexane = 10 : 90). Retention time: $t_{\text{minor}} = 14.47$ min, $t_{\text{major}} = 16.91$ min. $^1$H NMR (400 MHz, CDCl₃) δ: 2.41 (br, 1H), 3.80 (s, 3H), 3.82 (s, 3H), 5.52 (s, 1H), 6.92 (d, $J = 8.8$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl₃) δ: 53.4, 55.8, 64.2, 70.8, 87.4, 114.6, 128.6, 131.3, 154.3, 160.4.

**Ethyl 4-hydroxy-4-phenylbut-2-ynoate:** 81% yield. 81% ee determined by HPLC analysis (Chiralcel OD-H column, IPA : hexane = 20 : 80). Retention time: $t_{\text{minor}} = 8.77$ min, $t_{\text{major}} = 9.54$ min. $^1$H NMR (400 MHz, CDCl₃) δ: 1.32 (d, $J = 7.2$ Hz, 3H), 2.55 (d, $J = 6.0$ Hz, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 5.58 (d, $J = 5.2$ Hz, 1H), 7.35–7.43 (m, 3H), 7.53 (d, $J = 7.2$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl₃) δ: 14.3, 62.8, 64.4, 78.1, 87.0, 127.1, 129.2, 139.0, 154.0.

**Ethyl 4-hydroxy-4-(naphthalen-4-yl)but-2-ynoate:** 76% yield. 77% ee determined by HPLC analysis (Chiralcel AD-H column, IPA : hexane = 10 : 90). Retention time: $t_{\text{minor}} = 12.82$ min, $t_{\text{major}} = 16.52$ min. $^1$H NMR (400 MHz, CDCl₃) δ: 1.31 (t, $J = 7.2$ Hz, 3H), 2.66 (d, $J = 6.0$ Hz, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 6.23 (d, $J = 5.6$ Hz, 1H), 7.46–7.61 (m, 3H), 7.80 (d, $J = 7.2$ Hz, 1H), 7.88 (t, $J = 8.0$ Hz, 2H), 8.23 (d, $J = 8.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl₃) δ: 14.3, 62.7, 62.8, 78.8, 86.7, 124.0, 125.4, 125.6, 126.4, 127.1, 129.2, 130.2, 130.7, 134.1, 134.3, 154.0.

**Ethyl 4-hydroxy-4-(naphthalen-3-yl)but-2-ynoate:** 70% yield. 74% ee determined by HPLC analysis (Chiralcel AD-H column, IPA : hexane = 10 : 90). Retention time:
$t_{\text{minor}} = 15.17 \text{ min, } t_{\text{major}} = 16.79 \text{ min.} \ ^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta: \ 1.33 \ (t, \ J = 7.2 \text{ Hz, 3H}), \ 2.58 \ (d, \ J = 5.6 \text{ Hz, 1H}), \ 4.27 \ (q, \ J = 7.2 \text{ Hz, 2H}), \ 5.75 \ (d, \ J = 8.0 \text{ Hz, 1H}), \ 7.51–7.53 \ (m, 2H), \ 7.61–7.64 \ (m, 1H), \ 7.84–7.90 \ (m, 3H), \ 7.98 \ (s, 1H); \ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta: \ 14.3, \ 62.8, \ 64.6, \ 78.3, \ 87.0, \ 124.7, \ 126.1, \ 126.8, \ 126.9, \ 128.1, \ 128.6, \ 129.1, \ 133.4, \ 133.7, \ 136.3, \ 154.0.$
Copies of $^1H$, $^{13}C$ NMR Spectra for Products:
CDCl₃

H₂O

ppm (δ)
CDCl₃

OH

H₂O

CDCl₃

ppm (δ)

159.014  133.985  127.915  79.972  77.940  77.500  77.480  62.775  14.346

CDCl₃

ppm (δ)