Supporting Information


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Table 1. Screening reaction conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>AgX</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>ee (%)</th>
<th>yield(%)</th>
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<td>(S)-MeO-biphenp</td>
<td>AgOTf</td>
<td>DCM</td>
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<td>40</td>
<td>-11</td>
<td>48</td>
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<td>(R)-C&lt;sub&gt;1&lt;/sub&gt;-tunephos</td>
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<td>21</td>
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<sup>a</sup> Reaction conditions: AuCl(SMe<sub>2</sub>) (5 mol%), ligand (3 mol%) and AgX (5 mol%), 1a/2a = 0.40 mmol/0.22 mmol, 4Å molecular sieves (60 mg), solvent (3 mL), Ar. <sup>b</sup> 4Å MS was not used. <sup>c</sup> (1S, 4S)-3a was isolated in 51% with 77% ee. <sup>d</sup> AuCl(SMe<sub>2</sub>) (1 mol%), (S)-L<sub>6</sub> (0.6 mol%) and AgSbF<sub>6</sub> (1 mol%) of catalyst were used, 1a/2a = 4.0 mmol/2.2 mmol.
We also paid our attention on the asymmetric [4+3] annulation of 2-nonsubstituted cyclopropyl ketone 1q. After reacting with nitrone 2a under the optimized reaction conditions, heterobicyclic cycloadduct 3q is isolated in 75% yield with 82% ee, indicating the present reaction conditions are applicable to the 2-non-substituted cyclopropyl ketones [Eq (1)].

\[
\begin{align*}
\text{MeC} & \text{C} \text{C} \text{C} \text{C} \text{Ph} \\
\text{O} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{N} - \text{O} \quad \text{Ph} \\
\end{align*}
\]

\[
\begin{align*}
\text{AuCl(SMe)}_{2} (5 \text{ mol}) & \\
\text{(S)-MeO-dibm-biphep} (3 \text{ mol}) & \\
\text{AgSbF}_{6} (5 \text{ mol}) & \\
\text{DCE, 4Å MS, rt} & \\
\text{75% yield} & \\
\end{align*}
\]

\[
\begin{align*}
\text{MeC} & \text{C} \text{C} \text{C} \text{C} \text{Me} \\
\text{O} & \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \text{Ph} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \\
\text{Me} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Br} & \\
\text{Me} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \\
\end{align*}
\]

Figure 1. X-ray structure of \((1R, 2S)-1k\)
**General:** All Lewis acid and ligand are commercially available. All reactions were carried out under nitrogen or argon atmosphere. All solvents were fresh distilled from calcium hydride. \(^1\)H and \(^{13}\)C NMR spectra were obtained using a Bruker DPX-400 spectrometer in CDCl\(_3\). Splitting patterns were designed as s (singlet), d (doublet), t (triplet), m (multiplet) and q (quartet). Compounds 1a-q and 4 were prepared according to the procedure of literature\(^1\). The data of compound 1a-1b, 1e-1g, 1m and 1p were consistent with those in the literature\(^2\). Compounds 2a-2f were synthesized according to the procedure of literature\(^3\). Compound 6 was synthesized according to the procedure of literature\(^4\). The data of compound 3p and 5 were consistent with those in the literature.\(^5\)

**General procedure for kinetic resolution of ketone 1.**

**Conditions A** (Small Scale) (Scale of 1/2 = 0.4/0.22 mmol): Me\(_2\)SAuCl (3.2 mg, 0.011mmol), (S)-MeO-dtbm-biphep (7.6 mg, 0.0066 mmol) and DCE (3 mL) was added to the dry Schlenk tube under Ar or N\(_2\). After stirring for two hours, AgSbF\(_6\) (3.7 mg, 0.011 mmol) was added to the mixture. The mixture was then stirred for another 15 mins at rt. To the resulting mixture was added activated molecular sieves 4Å (50 mg). The mixture was stirred for 30 minutes and then nitrone 2 (0.22 mmol,) and ketone 1 (0.4 mmol) were added. The resulting mixture was stirred at rt until the reaction was complete (monitored by TLC).The reaction was quenched by saturated NaCl. After standard work-up, the residue was purified by flash column chromatography on silica gel (hexanes/DCM/EA = 50:10:1).

**Conditions B** (large Scale) (Scale of 1/2 = 4.0/2.2 mmol): The procedure is same as the small scale with the use of Me\(_2\)SAuCl (32.0 mg, 0.11mmol), (S)-MeO-dtbm-biphep (76.0 mg, 0.066 mmol), DCE (15 mL), AgSbF\(_6\) (37 mg, 0.11 mmol), activated molecular sieves 4Å (300 mg). nitrone 2a (2.2 mmol) and ketone 1a (4.0 mmol).

1. 1-((1R, 2S)-2-phenyl-1-(phenylethynyl)cyclopropyl)ethanone (1a).

![Structure of 1a]

\(^1\)H NMR (400 MHz, CDCl\(_3\))  δ 7.38 - 7.18 (m, 8 H), 7.16 - 7.08 (m, 2 H), 3.04 (t, J = 8.8 Hz, 1 H), 2.59 (s, 3 H), 2.20 (dd, J = 8.8, 4.0 Hz, 1 H), 1.86 (dd, J = 7.6, 4.0 Hz, 1 H).

**Conditions A:** the reaction under conditions A afforded the recovered 1a in 43% yield with 92% ee.

The ee was determined by chiral HPLC (Daicel OD-H column, hexanes : isopropanol = 98 : 2, 0.8 
ml/min, \(\lambda = 230\) nm: \(t_\text{R} = 7.45\) min, \(t_\text{R} = 8.67\) min.)

2. 1-((1R, 2S)-1-(naphthalen-1-ylethynyl)-2-phenylcyclopropyl)ethanone (1b).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 - 7.69 (m, 2 H), 7.53 - 7.28 (m, 10 H), 3.16 (t, $J = 8.0$ Hz, 1 H), 2.69 (s, 3 H), 2.26 (dd, $J = 9.2$, 3.2 Hz, 1 H), 1.99 (dd, $J = 8.0$, 4.4 Hz, 1 H).

**Conditions B:** The reaction under conditions B afforded the recovered 1b in 34% yield with 95% ee. The ee was determined by chiral HPLC (Daicel OD-H column, hexanes : isopropanol = 95 : 5, 0.8 ml/min, $\lambda = 220$ nm: $t_R = 9.42$ min, $t_R = 15.13$ min.).

3. **1-((1R, 2S)-2-phenyl-1-(p-tolylethynyl)cyclopropyl)ethanone (1c).**

Light yellow solid, m.p.27-30 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 - 7.35 (m, 2 H), 7.35-7.26 (m, 3H), 7.12 - 7.10 (m, 4 H), 3.06 (t, $J = 8.0$ Hz, 1 H), 2.62 (s, 3 H), 2.34 (s, 3 H), 2.23 (t, $J = 5.2$, 4.0 Hz, 1 H), 1.87 (t, $J = 4.0$, 3.6 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 205.05, 138.05, 135.90, 131.18, 128.89, 128.63, 127.88, 127.14, 119.84, 86.47, 84.44, 39.06, 33.30, 29.57, 26.42, 21.38 ppm; MS (EI) m/z (%): 274 [M]$^+$ (42.24), 215 (100); HRMS calcd for C$_{20}$H$_{18}$O: 274.1358, found: 274.1357.

**Conditions A:** The reaction under conditions A afforded the recovered 1c in 41% yield with 90% ee. The ee was determined by chiral HPLC (Daicel OD-H column, hexanes : isopropanol = 98 : 2, 0.8 ml/min, $\lambda = 220$ nm: $t_R = 7.05$ min, $t_R = 8.45$ min.)

4. **1-((1R, 2S)-1-((4-bromophenyl)ethynyl)-2-phenylcyclopropyl)ethanone (1d).**

Light yellow solid, m.p.45-48 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 -7.31 (m, 4 H), 7.22 -7.29 (m, 3 H), 6.95 (d, $J = 8.4$ Hz, 2 H), 3.06 (t, $J = 8.4$ Hz, 1 H), 2.57 (s, 3 H), 2.20 (dd, $J = 8.8$, 4.0 Hz, 1 H), 1.86 (dd, $J = 8.0$, 4.4 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 204.45, 135.72, 132.72, 131.41, 128.65, 127.96, 127.29, 122.14, 121.85, 88.64, 83.27, 39.21, 33.23, 29.58, 26.35 ppm; MS (EI) m/z (%): 338 [M]$^+$ (1.52), 43 (100); HRMS calcd for C$_{19}$H$_{15}$OBr: 338.0306, found: 338.0302.
**Conditions B** The reaction under conditions B afforded the recovered 1d in 42% yield with 93% ee. The ee was determined by chiral HPLC (Daicel OD-H column, hexanes : isopropanol = 95 : 5, 0.8 ml/min, $\lambda$ = 220 nm: $t_R = 6.64$ min, $t_R = 7.75$ min.).

5. 1-((1R, 2S)-1-(cyclohex-1-en-1-ylethynyl)-2-phenylcyclopropyl)ethanone (1e).

![Structure of 1e]

$^1$H NMR (400 MHz, CDCl$_3$) 7.35 - 7.18 (m, 5 H), 5.81 (s, 1 H), 2.94 (t, $J$ = 8.4 Hz, 1 H), 2.51 (s, 3 H), 2.12 (dd, $J$ = 9.2, 4.0 Hz, 1 H), 2.05 - 1.94 (m, 2 H), 1.91 - 1.82 (m, 2 H), 1.72 (dd, $J$ = 7.6, 4.0 Hz, 1 H), 1.57 - 1.46 (m, 4 H).

**Conditions A**: The reaction under conditions A afforded the recovered 1e in 41% yield with 35% ee. The ee was determined by chiral HPLC (Daicel OD-H column, hexanes : isopropanol = 95 : 5, 0.8 ml/min, $\lambda$ = 230 nm: $t_R = 5.43$ min, $t_R = 6.06$ min.).

6. 1-((1R,2S)-1-(hex-1-yn-1-yl)-2-phenylcyclopropyl)ethanone (1f)

![Structure of 1f]

$^1$H NMR (400 MHz, CDCl$_3$) 7.36 - 7.11 (m, 5 H), 2.87 (t, $J$ = 8.4 Hz, 1 H), 2.50 (s, 3 H), 2.08 - 2.04 (m, 2 H), 2.04 - 2.01 (m, 1 H), 1.64 - 1.66 (m, 1 H), 1.30 - 1.22 (m, 2 H), 1.21 - 1.11 (m, 2 H), 0.80 (t, $J$ = 7.6 Hz, 3 H).

**Conditions A**: The reaction under conditions A afforded the recovered 1f in 30% yield with 32% ee. The ee was determined by chiral HPLC (Daicel OD-H column, hexanes : isopropanol = 95 : 5, 0.8 ml/min, $\lambda$ = 230 nm: $t_R = 5.05$ min, $t_R = 5.35$ min.).

7. 1-((1R,2S)-2-(4-methoxyphenyl)-1-(phenylethynyl)cyclopropyl)ethanone (1g)

![Structure of 1g]
1H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.33 - 7.11 (m, 7 H), 6.94 - 6.83 (m, 2 H), 3.81 (s, 3 H), 2.99 (t, J = 8.4 Hz, 1 H), 2.58 (s, 3 H), 2.19 (t, J = 4.4 Hz, 1 H), 1.79 (dd, J = 8.4, 4.4 Hz, 1 H).

**Conditions B:** The reaction under conditions B afforded the recovered 1g in 35% yield with 93% ee. The ee was determined by chiral HPLC (Daicel OD-H column, hexanes : isopropanol = 98 : 2, 0.8 ml/min, λ = 220 nm: t\textsubscript{R} = 9.99 min, t\textsubscript{R} = 10.30 min).

8. 1-((1R,2S)-1-(phenylethynyl)-2-(p-tolyl)cyclopropyl)ethanone (1h).

![Chemical Structure](image)

Light yellow solid, m.p.46-48 °C. 1H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.26 -7.20 (m, 3 H), 7.20 -7.1 (m, 6 H), 2.30 (t, J = 8.4 Hz, 1 H), 2.58 (s, 3 H), 2.36 (s, 3 H), 2.19 (dd, J = 6.9, 4.4 Hz, 1 H), 1.82 (dd, J = 8.4, 4.4 Hz, 1 H); 13C NMR (100 MHz, CDCl\textsubscript{3}) δ 205.03, 136.87, 132.73, 131.29, 128.62, 128.46, 128.14, 127.92, 123.02, 87.46, 84.32, 39.20, 33.32, 29.61, 26.57, 21.13 ppm; MS (EI) m/z (%): 274 [M]\textsuperscript{+} (22.28), 215 (100); HRMS calcd for C\textsubscript{20} H\textsubscript{18}O: 274.1358, found: 274.1357.

**Conditions B:** The reaction under conditions B afforded the recovered 1h in 42% yield with 96% ee. The ee was determined by chiral HPLC (Daicel OJ-H column, hexanes : isopropanol = 98 : 2, 0.8 ml/min, λ = 230 nm: t\textsubscript{R} = 11.17 min, t\textsubscript{R} = 12.04 min).

9. 1-((1R,2S)-2-(4-chlorophenyl)-1-(phenylethynyl)cyclopropyl)ethanone (1i).

![Chemical Structure](image)

Light yellow solid, m.p.44-47 °C. 1H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.29 - 7.35 (m, 2 H), 7.19 - 7.29 (m, 5 H), 7.11 - 7.19 (m, 2 H), 2.30 (t, J = 8.4 Hz, 1 H), 2.59 (s, 3 H), 2.19 (dd, J = 9.2, 4.0 Hz, 1 H), 1.79 (dd, J = 7.6, 4.0 Hz, 1 H); 13C NMR (100 MHz, CDCl\textsubscript{3}) δ 204.71, 134.47, 133.02, 131.31, 129.93, 128.27, 128.18, 128.07, 122.67, 86.82, 84.68, 38.12, 33.15, 29.63, 26.60 ppm; MS (EI) m/z (%): 294 [M]\textsuperscript{+} (12.73), 43 (100); HRMS calcd for C\textsubscript{19} H\textsubscript{15}OCl: 294.0811, found: 294.0810.
**Condition B:** The reaction under conditions B afforded the recovered 1i in 44% yield with 97% ee. The ee was determined by chiral HPLC (Daicel OJ-H column, hexanes : isopropanol = 98 : 2, 0.8 ml/min, \( \lambda = 230 \) nm: \( t_R = 18.58 \) min, \( t_R = 23.24 \) min.).

10. **1-((1R,2R)-2-(2-bromophenyl)-1-(phenylethynyl)cyclopropyl)ethanone (1j).**

![Structure of 1j](image)

Oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 7.63 \) (d, \( J = 7.6 \) Hz, 1 H), 7.36 - 7.27 (m, 1 H), 7.25 - 7.12 (m, 5 H), 7.02 - 6.93 (m, 2 H), 3.03 (t, \( J = 8.4 \) Hz, 1 H), 2.65 (s, 3 H), 2.26 (dd, \( J = 8.4, 4.0 \) Hz, 1 H), 1.88 (dd, \( J = 6.8, 4.0 \) Hz, 1 H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta 205.00, 136.27, 132.36, 131.33, 129.57, 128.82, 128.08, 127.90, 127.45, 127.01, 122.83, 86.85, 83.16, 40.32, 32.17, 29.43, 25.59 ppm; MS (EI) m/z (%): 338 [M]\(^+\) (4.88), 43 (100); HRMS calcd for C\(_{19}\)H\(_{15}\)OBr: 338.0306, found: 338.0303.

**Conditions A:** The reaction under conditions A afforded the recovered 1j in 41% yield with 98% ee. The ee was determined by chiral HPLC (Daicel AD-H column, hexanes : isopropanol = 98 : 2, 0.8 ml/min, \( \lambda = 220 \) nm: \( t_R = 7.19 \) min, \( t_R = 7.69 \) min.).

11. **1-((1R,2S)-2-(4-bromophenyl)-1-(phenylethynyl)cyclopropyl)ethanone (1k).**

Light yellow solid, m.p.69-72 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 7.52 - 7.42 \) (m, 2 H), 7.31 - 7.22 (m, 3 H), 7.20 - 7.10 (m, 4 H), 2.98 (t, \( J = 8.4 \) Hz, 1 H), 2.59 (s, 3 H), 2.18 (dd, \( J = 8.8, 4.0 \) Hz, 1 H), 1.79 (dd, \( J = 6.4, 4.0 \) Hz, 1 H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta 204.63, 135.02, 131.01, 130.28, 128.27, 128.18, 122.65, 121.13, 86.79, 84.73, 38.12, 33.11, 29.60,26.53 ppm; MS (EI) m/z (%): 338 [M]\(^+\) (3.43), 43 (100); HRMS calcd for C\(_{19}\)H\(_{15}\)OBr: 338.0306, found: 338.0302.

**Conditions A:** The reaction under conditions A afforded the recovered 1k in 42% yield with 98% ee. The ee was determined by chiral HPLC (Daicel OD-H column, hexanes : isopropanol = 95 : 5, 0.8 ml/min, \( \lambda = 230 \) nm: \( t_R = 7.40 \) min, \( t_R = 7.90 \) min.).
12. 1-((1R,2R)-2-butyl-1-(phenylethynyl)cyclopropyl)ethanone (1l)

![Diagram of molecule](image)

Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51-7.39 (m, 2 H), 7.38-7.28 (m, 3 H), 2.54 (s, 3 H), 1.83 (dd, $J$ = 8.8, 3.2 Hz, 1 H), 1.80-1.69 (m, 1 H), 1.69-1.57 (m, 2 H), 1.54-1.34 (m, 4 H), 1.10 (dd, $J$ = 7.2, 3.2 Hz, 1 H), 0.92 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.00, 131.50, 128.30, 127.98, 123.34, 88.27, 82.70, 35.08, 31.02, 30.01, 29.89, 29.45, 29.06, 22.41, 14.04 ppm; MS (EI) m/z (%): 240 [M]$^+$ (31.11), 43(100); HRMS calcd for C$_{17}$H$_{20}$O: 240.1514, found: 240.1514.

**Condition A:** The reaction under conditions A afforded the recovered 1l in 43% yield with 27% ee. The ee was determined by chiral HPLC (Daicel OJ-3 column, hexanes : isopropanol = 98 : 2, 0.8 ml/min, $\lambda$= 254 nm: $t_R$ = 5.78 min, $t_R$ = 6.29 min. ).

13. Phenyl((1R,2S)-2-phenyl-1-(phenylethynyl)cyclopropyl)methanone (1m).

![Diagram of molecule](image)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 - 8.02 (m, 2 H), 7.58 - 7.30 (m, 8 H), 7.24 - 7.30 (m, 3 H), 7.05 - 6.91 (m, 2 H), 3.04 (t, $J$ = 7.6 Hz, 1 H), 3.02 (dd, $J$ = 9.2, 4.8 Hz, 1 H), 1.96 (dd, $J$ = 10.8, 4.8 Hz, 1 H).

**Condition B:** The reaction under conditions B afforded the recovered 1m in 37% yield with 99% ee. The ee was determined by chiral HPLC (Daicel OD-H column, hexanes : isopropanol = 95 : 5, 0.8 ml/min, $\lambda$= 220 nm: $t_R$ = 6.35 min, $t_R$ = 7.27 min. ).

14. ((1R,2S)-2-(4-chlorophenyl)-1-(phenylethynyl)cyclopropyl)(phenyl)methanone (1n).

![Diagram of molecule](image)
Light yellow solid, m.p.60-62 °C. $^1$H NMR (400 MHz, CDCl₃) δ 8.10 - 8.01 (m, 2 H), 7.60 - 7.50 (m, 1 H), 7.48 - 7.40 (m, 2 H), 7.40 - 7.33 (m, 2 H), 7.43 - 7.27 (m, 2 H), 7.24 - 7.12 (m, 3 H), 7.06 - 6.94 (m, 2 H), 3.00 (t, $J = 8.4$ Hz, 1 H), 2.50 (dd, $J = 8.4$, 4.8 Hz, 1 H), 1.90 (t, $J = 6.0$ Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl₃) δ 196.42, 136.62, 134.48, 133.16, 132.69, 131.12, 129.95, 129.20, 128.23, 128.15, 127.98, 122.80, 87.74, 85.30, 36.84, 31.95, 23.81 ppm; MS (EI) m/z (%): 356 [M]+ (5.92), 105 (100); HRMS calcd for C$_{24}$H$_{17}$OCl: 356.0968, found: 356.0970.

**Condition B:** The reaction under conditions B afforded the recovered 1n in 49% yield with 92% ee.
The ee was determined by chiral HPLC (Daicel AD-H column, hexanes : isopropanol = 98 : 2, 0.8 ml/min, $\lambda = 220$ nm: $t_R = 8.71$ min, $t_R = 9.45$ min ).

15. (4-chlorophenyl)((1$^R$,2$^S$)-2-phenyl-1-(phenylethynyl)cyclopropyl)methanone (1o).

![Chemical structure of 1o](image)

Light yellow solid, m.p.44-47 °C. $^1$H NMR (400 MHz, CDCl₃) δ 8.08 - 7.98 (m, 2 H), 7.44 - 7.31 (m, 7 H), 7.22 - 7.12 (m, 3 H), 7.04 -6.94 (m, 2 H), 3.02 (t, $J = 8.4$ Hz, 1 H), 2.51 (dd, $J = 9.2$, 4.8 Hz, 1 H), 1.96 (t, $J = 6.0$ Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl₃) δ 195.47, 138.92, 135.54, 135.03, 131.10, 130.67, 128.63, 128.26, 128.10, 127.96, 127.42, 122.79, 87.77, 85.13, 38.22, 31.99, 23.65 ppm; MS (EI) m/z (%): 356 [M]+ (2.47), 43 (100); HRMS calcd for C$_{24}$H$_{17}$OCl: 356.0968, found: 356.0967.

**Condition A:** The reaction under conditions A afforded the recovered 1o in 37% yield with 97% ee.
The ee was determined by chiral HPLC (Daicel AD-H column, hexanes : isopropanol = 98 : 2, 0.8 ml/min, $\lambda = 220$ nm: $t_R = 8.07$ min, $t_R = 8.80$ min ).

16. 1-((1$^R$,2$^S$)-2-(4-methoxyphenyl)-1-((4-methoxyphenyl)ethynyl)cyclopropyl)ethanone (1p)

![Chemical structure of 1p](image)

$^1$H NMR (400 MHz, CDCl₃) δ 7.20 (d, $J = 8.4$ Hz, 2 H), 7.10 (d, $J = 8.8$ Hz, 2 H), 6.88 (d, $J = 8.4$ Hz, 2 H), 6.76 (d, $J = 8.8$ Hz, 2 H), 3.81 (s, 3 H), 3.78 (s, 3 H), 2.96 (t, $J = 8.4$ Hz, 1 H), 2.57 (s, 3 H), 2.22-2.12 (m, 1 H), 1.79-1.72 (m, 1 H).
**Condition A**: The reaction under conditions A afforded the recovered 1p in 39% yield with 68% ee. The ee was determined by chiral HPLC (Daicel OD-H column, hexanes:isopropanol = 99:1, 0.8 ml/min, λ= 230 nm: tR = 26.81 min, tR = 30.16 min ).

**Condition B**: The reaction under conditions B afforded the recovered 1p in 24% yield with 87% ee. The ee was determined by chiral HPLC (Daicel OD-H column, hexanes:isopropanol = 98:2, 0.8 ml/min, λ= 230 nm: tR = 13.90 min, tR = 14.69 min ).

17. **1-(1-(phenylethynyl)cyclopropyl)ethanone (1q)**

![1q](image)

^H NMR (400 MHz, CDCl3) δ 7.39 - 7.46 (m, 2 H), 7.35 - 7.28 (m, 3 H), 2.56 (s, 3 H), 1.62 (dd, J = 2.4, 1.6 Hz, 2 H), 1.39 (t, J = 1.6 Hz, 2 H).

18. **(1S,4S)-4,8-bis(4-methoxyphenyl)-6-methyl-1,2-diphenyl-1,2,4,5-tetrahydrofuro[3,4-d][1,2]oxazepine (3p)**

![3p](image)

^H NMR (400 MHz, CDCl3) δ 7.30 (d, J = 8.4 Hz, 2 H), 7.26-7.22 (m, 5 H), 7.20-7.12 (m, 4 H), 6.92-6.80 (m, 7 H), 6.07 (s, 1 H), 5.03 (d, J = 10.4 Hz, 1 H), 3.81 (s, 3 H), 3.80 (s, 3 H), 3.19 (dd, J = 15.2, 11.2 Hz, 2 H), 2.97 (d, J = 15.2 Hz, 1 H), 2.33 (s, 3 H).

**Condition A**: The reaction under conditions A afforded the recovered 3p in 54% yield with 97% ee. The ee was determined by chiral HPLC (Daicel OD-H column, hexanes:isopropanol = 95:5, 0.8 ml/min, λ= 230 nm: tR = 8.16 min, tR = 8.78 min ).

**Table 2, entry 2**: The reaction afforded the recovered 3p in 87% yield with 91% ee. The ee was determined by chiral HPLC (Daicel OD-H column, hexanes:isopropanol = 95:5, 0.8 ml/min, λ= 230 nm: tR = 8.46 min, tR = 9.13 min ).

**Condition B**: The reaction under conditions B afforded the recovered 3p in 46% yield with 96% ee. The ee was determined by chiral HPLC (Daicel OD-H column, hexanes:isopropanol = 95:5, 0.8 ml/min, λ= 230 nm: tR = 8.76 min, tR = 9.67 min ).
19. 6-methyl-1,2,8-triphenyl-1,2,4,5-tetrahydrofuro[3,4-d][1,2]oxazepine(3q).

Me₂SAuCl (6.4 mg, 0.02 mmol), (S)-L₆ (15.2 mg, 0.012 mmol) and DCE (2 mL) was added to the dry Schlenk tube in glove box. After stirring for two hours, AgSbF₆ (7.4 mg, 0.002 mmol) was added to the mixture. The mixture was stirred for another 15 mins at rt. To the resulting solution was added activated molecular sieves 4Å MS (60 mg). The mixture was stirred for 30 minutes and then nitron 2 (0.3 mmol, 59.1 mg) and ketone 1q (0.2 mmol, 36.9 mg) were added. The resulting mixture was then stirred under N₂ at rt until the reaction was complete after 87 hours (monitored by TLC). The reaction was quenched by saturated NaCl. After standard work-up, the residue was purified by flash column chromatography on silica gel (hexanes/DCM/EA = 50:10:1) to afford the pure product 3q (56.9 mg) in 75% yield with 82% ee.

Solid, m.p.127-130 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.4 - 7.05 (m, 12 H), 6.96 - 6.82 (m, 3 H), 6.09 (s, 1 H), 4.25 (d, J = 11.6 Hz, 1 H), 4.01 (t, J = 12.0 Hz, 1 H), 3.04 (t, J = 12.0 Hz, 1 H), 2.68 (d, J = 15.2 Hz, 1 H), 2.32 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 149.67, 147.10, 147.02, 138.00, 130.89, 128.77, 128.73, 128.52, 127.97, 127.46, 127.09, 125.81, 122.10, 121.25, 119.55, 116.12, 73.68, 67.06, 27.47, 11.72; MS (EI) m/z (%): 381 [M⁺] (18.28), 77 (100); HRMS calcd for C₂₆H₂₃NO₂: 381.1729, found: 381.1724.

The ee was determined by chiral HPLC (Daicel AS-H column, hexanes : isopropanol = 98 : 2, 0.8 ml/min, λ = 220 nm: tᵣ = 5.99 min, tᵣ = 6.51 min ).

20. 3-(2-methoxy-2-phenylethyl)-2-methyl-5-phenylfuran (4).

The reaction afforded the product 4 in 99% yield with 86% ee according to the procedure of reference.

¹H NMR (400 MHz, CDCl₃) δ 7.63 - 7.52 (m, 2 H), 7.37 - 7.15 (m, 8 H), 6.38 (s, 1 H), 4.24 (t, J = 6.4 Hz, 1 H), 3.24 (s, 3 H), 2.87 (dd, J = 14.4, 6.4 Hz, 1 H), 2.66 (dd, J = 14.4, 6.8 Hz, 1 H), 1.98 (s, 3 H).
The ee was determined by chiral HPLC (Daicel OD-H column, hexanes : isopropanol = 98 : 2, 0.8 ml/min, $\lambda$= 220 nm: $t_R$ = 6.40 min, $t_R$ = 7.08 min.)

21. 1-(2,3,6-triphenyl-4-(phenylethynyl)-1,2-oxazinan-4-yl)ethanone (5).

![Structure of 5](image)

The reaction of 1a with nitrone 2a under the catalysis of Sc(OTf)$_3$ afford the pure product 5 in 90% yield with d.r. = 11:1. The major isomer is with 72% ee.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66 -7.29 (m, 12 H), 7.21 - 7.05 (m, 7 H), 6.88 - 6.76 (m, 1 H), 5.57 (d, $J$ = 11.6 Hz, 1 H), 5.26 (s, 1 H), 3.02 (t, $J$ = 13.2 Hz, 1 H), 2.35 (s, 3 H), 2.21 (d, $J$ = 14.0 Hz, 1 H).

The ee was determined by chiral HPLC (Daicel AS-H column, hexanes : isopropanol = 80 : 20, 0.8 ml/min, $\lambda$= 220 nm: $t_R$ = 7.02 min, $t_R$ = 9.44 min.)

22. 1-Methyl-3,6-diphenyl-4-(p-tolyl)-6,7-dihydro-4H-furo[3,4-c]pyran (6).

![Structure of 6](image)

The reaction of 1a with aldehyde under the catalysis of gold(I) afforded compound 6 in 90% yield with 79% ee according to the procedure of [4+3] cycloaddition reaction.

White solid, m.p. 64-67°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 - 6.57(m, 14 H), 6.03 (s, 1 H), 4.74 (d, $J$ = 11.2 Hz, 1 H), 2.83 (d, $J$ = 14.8 Hz, 1 H), 2.73 (dd, $J$ = 14.8, 11.2 Hz, 1 H), 2.32 (s, 3 H), 2.24 (s, 3 H);

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.19, 144.89, 142.21, 137.79, 137.16, 130.70, 128.88 (2 C), 128.25, 127.77, 127.45, 126.13, 126.01, 125.23, 119.23, 117.66, 77.76, 76.88, 29.82, 21.15, 11.67; MS (EI) m/z (%): 380 [M]$^+$ (14.05), 259 (100); HRMS calcd for C$_{27}$H$_{24}$O$_2$: 380.1776, found: 380.1778.

The ee was determined by chiral HPLC (Daicel OD-H column, hexanes : isopropanol = 95 : 5, 0.8 ml/min, $\lambda$= 220 nm: $t_R$ = 5.96 min, $t_R$ = 6.87 min.)

23. 1-((1R,2S)-2-phenyl-1-(phenylethynyl)cyclopropyl)ethanone O-methyl oxime (7).
The reaction of 1a with O-methylhydroxylamine hydrochloride under the sodium acetate afforded 7 in yield 95% with 96% ee.

Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 - 7.01 (m, 10 H), 3.87 (s, 3 H), 2.67 (t, $J = 7.6$ Hz, 1 H), 2.16 (dd, $J = 5.2$, 2.8 Hz, 1 H), 2.13 (s, 3 H), 1.67 (dd, $J = 4.4$, 0.8 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.91, 137.19, 131.41, 128.56, 128.02, 127.83, 127.65, 126.64, 123.29, 88.64, 82.22, 61.57, 34.28, 26.53, 20.86, 13.86 ppm; MS (EI) m/z (%): 289 [M]$^+$ (42.90), 215 (100); HRMS calcd for C$_{20}$H$_{19}$NO: 289.1467, found: 289.1468.

The ee was determined by chiral HPLC (Daicel OD-3 column, hexanes : isopropanol = 98 : 2, 0.8 ml/min, $\lambda = 254$ nm: $t_R = 6.0$ min, $t_R = 8.06$ min).

References

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zyq-5-50 H

Electronic Supplementary Material (ESI) for Chemical Communications
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Electronic Supplementary Material (ESI) for Chemical Communications
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zyq-3-137 H

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Electronic Supplementary Material (ESI) for Chemical Communications
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\(\text{O} \rightarrow \text{Ph} \)

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Area Percent Report

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**Area Report**

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**Dilution:** 1.0000

**Two Multipliers & Dilution Factors with IN70s**

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**Two Multipliers & Dilution Factors with IN70s**

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