Supporting Information for

Photoinduced Wolff rearrangement/Pd-catalyzed [3+2] cycloaddition sequence: an unexpected route to tetrahydrofurans

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1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. $^1$H NMR spectra were recorded on 400 MHz spectrophotometers. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. $^{13}$C NMR spectra were recorded on Varian Mercury 100 MHz with complete proton decoupling spectrophotometers (CDCl$_3$: 77.0 ppm; CD$_3$OD: 3.31 ppm, 4.87 ppm). $^{31}$P NMR spectra were recorded on Varian Mercury 162 MHz spectrophotometers. HRMS was recorded on Bruker ultrafleXtreme MALDITOF/TOF mass spectrometer.

All the solvents were treated according to standard methods and all chemicals were used without purification. The vinylcyclopropanes$^1$ and diazo compounds$^2$ were prepared by following the literature report.

2. Preparation and Characterization Data of Hybrid P,S Ligands

Achiral and chiral hybrid P,S ligands were synthesized according to our previous methods.$^3$

2.1 General procedure for the synthesis of ligand L5

\[
\begin{align*}
\text{Br-S-} & + \text{PhCHO} & \xrightarrow{\text{TFE, NaBH}_4, \text{rt}} & \text{Br-S-} \\
\text{NH}_2 & & \text{NH}_2 \\
\text{PhH} & & \text{NH}_2 \\
& & \text{NH}_2
\end{align*}
\]

To a solution of benzaldehyde (0.95 mL, 9.5 mmol) in trifluoroethane (48 mL), was added achiral amine (2.19 g, 9.5 mmol). After 2 hours, NaBH$_4$ (2.01 g, 19 mmol) was added to the reaction mixture in portions at 0 °C. The mixture was stirred at room temperature overnight. Water (20 mL) was added to quench the reaction and the mixture was extracted with CH$_2$Cl$_2$ (3*10 mL). The organic layers were dried over Na$_2$SO$_4$ and filtered, and the solvents were evaporated in vacuo. The residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate (7: 1) to afford the corresponding product as white solid in 55% yield.

\[
\begin{align*}
\text{Br-S-} & + \text{PhOH} & \xrightarrow{\text{PCl}_3, \text{Et}_3\text{N, Toluene, 0°C-rt}} & \text{Br-S-} \\
\text{NH}_2 & & \text{NH}_2 \\
\text{BnN-} & & \text{BnN-} \\
\text{OPh} & & \text{OPh}
\end{align*}
\]

To a solution of achiral amine (1.76 g, 5.5 mmol) and Et$_3$N (0.84 g, 6 mmol) in toluene, was
added the solution of PCl₃ (0.75 g, 5.5 mmol) in toluene dropwise, stirring for 6 hours at 70 °C. After the reaction mixture was cooled to room temperature, Et₃N (1.27 g, 12.6 mmol) was added dropwise and PhOH (1.04 g, 11 mmol) was added at -20 °C, stirring for 20 mins at the temperature. The reaction mixture was stirred for 12 hours at room temperature. The solvents were evaporated in vacuo. The residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate (20: 1) to afford the corresponding product white solid in 53% yield.

2.2 Characterization data of the ligand L5

**Diphenyl benzyl(2-((4-bromophenyl)thio)ethyl)phosphoramidite (L5)**

![Chemical structure](Image)

Yield of 56% as a white solid. **¹H NMR** (400 MHz, Methanol-d₄) δ = 7.34 (m, J = 10.8, 4.7 Hz, 6H), 7.26 (t, J = 7.3 Hz, 5H), 7.14 – 7.08 (m, 4H), 7.06 (d, J = 7.6 Hz, 4H), 4.41 (d, J = 9.0 Hz, 2H), 3.24 (q, J = 9.0, 8.5 Hz, 2H), 2.96 – 2.89 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ = 153.5, 153.4, 138.0, 137.9, 134.9, 131.9, 130.5, 129.7, 128.5, 128.4, 127.4, 123.3, 123.3, 120.2, 120.1, 119.7, 49.4, 49.2, 43.8, 43.6, 32.3, 32.3. **³¹P NMR** (162 MHz, CDCl₃) δ = 139.7. **M.P.:** 43 – 46 °C; **HRMS (ESI)** for C_{17}H_{16}N₂O [M + H]^+: calcd 538.0605, found 538.0599.

References


3. General Procedure and Characterization Data of Products

3.1 General procedure for the synthesis of 4

[Chemical reaction diagram]

**General procedures:** Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with α-diazoketones 1 (0.4 mmol, 2.0 equiv) and anhydrous DCE (2 mL). The resulting solution was stirred for 4 h at room temperature ([Procedure A]) or for 8 h at -10 °C ([Procedure B]) under the irradiation of 6 W blue LEDs. To another flame-dried 10 mL Schlenk tube, Pd(dbta)3•CHCl3 (0.005 mmol, 2.5 mol%), L5 (0.01 mmol, 5 mol%) and anhydrous DCE (2 mL) were added and the resulting solution was stirred for 10 min at room temperature. After that, the reaction solution in the first Schlenk together with VCPs 3 (0.2 mmol, 1.0 equiv.) were moved to the second one. The resulting solution was stirred until complete conversion of VCPs 3 (monitored by TLC). DCE was removed under the reduced pressure and the residue was purified by flash column chromatography on silica gel (petrol ether/ethyl acetate = 50/1 to 25/1) to afford the tetrahydrofuran product 4.

3.2 Characterization data of products

**(Z)-2-(1-Phenylethylidene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4aa)**

Procedure A, white solid, 96% yield. $^1$H NMR (400 MHz, CDCl₃) δ = 7.51 – 7.46 (m, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.27 (d, J = 12.7 Hz, 1H), 5.87 (m, 1H), 5.46 – 5.33 (m, 2H), 4.89 – 4.81 (m, 1H), 3.09 (dd, J = 13.0, 5.5 Hz, 1H), 2.69 (dd, J = 13.1, 8.6 Hz, 1H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, CDCl₃) δ = 141.2, 138.0, 132.9, 128.1, 127.8, 127.5, 120.1, 113.4, 113.3, 113.2, 80.5, 44.2, 35.1, 18.3. M.P.: 59 – 61 °C. IR (KBr, ν / cm⁻¹) 3131, 2361, 1676, 1398, 1137, 694. HRMS (ESI) for C₁₆H₁₄N₂O [M + OH]⁺: calcd 267.1139, found 267.1132.

**(Z)-2-(1-(p-Tolyl)ethylidene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4ab)**

Procedure A, white solid, 99% yield. $^1$H NMR (400 MHz, CDCl₃) δ = 7.39 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 5.87 (m, 1H), 5.47 – 5.31 (m, 2H), 4.83 (q, J = 6.6 Hz, 1H), 3.08 (dd, J = 13.0, 5.5 Hz, 1H), 2.69 (dd, J = 13.0, 8.6 Hz, 1H), 2.35 (s, 3H), 2.28 (s, 3H). $^{13}$C NMR (100 MHz, CDCl₃) δ = 140.7, 137.3, 135.0, 132.9,
128.8, 127.7, 120.0, 113.4, 113.3, 113.2, 80.4, 44.2, 35.0, 21.2, 18.3. M.P.: 80 – 85 °C. IR (KBr, ν / cm⁻¹) 3132, 2362, 1641, 1400, 1155, 615. HRMS (ESI) for C₁₃H₁₆N₂O [M + Na]⁺: calcd 287.1160, found 287.1156.

(Z)-2-(1-(4-Fluorophenyl)ethylidene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4ac)

Procedure A, white solid, 98% yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.48 (d, J = 8.5, 5.4 Hz, 2H), 7.05 (t, J = 8.6 Hz, 2H), 5.87 (m, 1H), 5.48 – 5.33 (m, 2H), 4.86 (q, J = 6.1 Hz, 1H), 3.10 (dd, J = 13.1, 5.5 Hz, 1H), 2.70 (dd, J = 13.1, 8.7 Hz, 1H), 2.28 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 141.6, 136.8, 132.7, 131.2, 129.5, 121.4, 120.4, 113.1, 113.0, 112.1, 80.8, 44.1, 35.2, 18.1. ¹⁹F NMR (377 MHz, CDCl₃) δ -114.0. M.P.: 47 – 49 °C. IR (KBr, ν / cm⁻¹) 3132, 2361, 1646, 1510, 1399, 1156, 760. HRMS (ESI) for C₁₇H₁₃FN₂O [M + Na]⁺: calcd 291.0910, found 291.0906.

(Z)-2-(1-(4-Chlorophenyl)ethylidene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4ad)

Procedure A, white solid, 93% yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.44 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 5.87 (m, 1H), 5.48 – 5.29 (m, 2H), 4.86 (q, J = 6.5 Hz, 1H), 3.10 (dd, J = 13.1, 5.5 Hz, 1H), 2.69 (dd, J = 13.1, 8.7 Hz, 1H), 2.28 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 141.7, 136.3, 133.2, 132.7, 129.3, 128.3, 120.4, 113.2, 113.1, 112.1, 80.8, 44.1, 35.2, 18.2. M.P.: 85 – 87 °C. IR (KBr, ν / cm⁻¹) 3132, 2361, 1649, 1492, 1400, 1155, 614. HRMS (ESI) for C₁₈H₁₅ClN₂O [M + Na]⁺: calcd 307.0614, found 307.0617.

(Z)-2-(1-(4-Bromophenyl)ethylidene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4ae)

Procedure A, white solid, 96% yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.48 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 5.86 (m, 1H), 5.62 – 5.33 (m, 2H), 4.86 (d, J = 7.6 Hz, 1H), 3.10 (dd, J = 13.1, 5.5 Hz, 1H), 2.70 (dd, J = 13.1, 8.7 Hz, 1H), 2.28 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.2, 141.3, 139.3, 132.8, 129.1, 120.3, 120.1, 113.8, 113.3, 113.2, 112.9, 80.5, 55.2, 44.1, 35.1, 18.4. M.P.: 95 – 99 °C. IR (KBr, ν / cm⁻¹) 3132, 2361, 1639, 1490, 1400, 1155, 614. HRMS (ESI) for C₁₈H₁₃BrN₂O [M + Na]⁺: calcd 351.0109, found 351.0108.

(Z)-2-(1-(3-Fluorophenyl)ethylidene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4af)

Procedure A, white solid, 95% yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.32 (d, J = 6.3 Hz, 1H), 7.26 (d, J = 14.0 Hz, 2H), 6.97 (t, J = 8.2 Hz, 1H), 5.88 (m, 1H), 5.49 – 5.35 (m, 2H), 4.89 (q, J = 6.6 Hz, 1H), 3.10 (dd, J = 13.1, 5.5 Hz, 1H), 2.70 (dd, J = 13.1, 8.6 Hz, 1H), 2.31 – 2.27 (m, 3H). ¹³C NMR
(100 MHz, CDCl\textsubscript{3}) δ = 163.7, 161.3, 142.1, 140.0, 139.9, 132.7, 129.6, 129.5, 123.5, 123.5, 120.4, 115.2, 115.0, 114.5, 114.3, 113.2, 113.0, 112.0, 112.0, 80.9, 44.1, 35.3, 18.1. \textsuperscript{19}F NMR (377 MHz, CDCl\textsubscript{3}) δ -113.2. M.P.: 98 – 101 °C. IR (KBr, ν / cm\textsuperscript{-1}) 3128, 2361, 1651, 1489, 1400, 1144, 690. HRMS (ESI) for C\textsubscript{16}H\textsubscript{13}FN\textsubscript{2}O [M + Na\textsuperscript{+}]: calcd 291.0910, found 291.0913.

(Z)-2-(1-(3-Chlorophenyl)ethylidene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4ag)

Procedure A, white solid, 96% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ = 7.49 (s, 1H), 7.37 (d, J = 7.7 Hz, 1H), 7.32 – 7.23 (m, 2H), 5.87 (m, 1H), 5.48 – 5.34 (m, 2H), 4.88 (q, J = 6.6 Hz, 1H), 3.10 (dd, J = 13.1, 5.5 Hz, 1H), 2.70 (dd, J = 13.1, 8.6 Hz, 1H), 2.28 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ = 142.1, 139.7, 134.0, 132.6, 129.3, 128.1, 127.5, 126.0, 120.3, 113.1, 113.0, 111.9, 80.8, 77.3, 77.0, 76.7, 44.1, 35.2, 18.1. M.P.: 78 – 81 °C. IR (KBr, ν / cm\textsuperscript{-1}) 3163, 2361, 1639, 1474, 1401, 1157, 615. HRMS (ESI) for C\textsubscript{16}H\textsubscript{13}ClN\textsubscript{2}O [M + Na\textsuperscript{+}]: calcd 307.0614, found 307.0612.

(Z)-2-(1-(3-Methoxyphenyl)ethylidene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4ah)

Procedure A, yellow oil, 98% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ = 7.29 (d, J = 7.9 Hz, 1H), 7.07 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.6 Hz, 1H), 5.87 (m, 1H), 5.48 – 5.34 (m, 2H), 4.85 (q, J = 6.6 Hz, 1H), 3.81 (s, 3H), 3.09 (dd, J = 13.1, 5.5 Hz, 1H), 2.70 (dd, J = 13.0, 8.6 Hz, 1H), 2.29 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ = 163.0, 160.5, 141.2, 133.8, 133.8, 132.7, 129.7, 129.6, 120.3, 115.1, 114.9, 113.3, 113.1, 112.2, 80.6, 44.1, 18.3. IR (KBr, ν / cm\textsuperscript{-1}) 3132, 2361, 1639, 1474, 1401, 1157, 615. HRMS (ESI) for C\textsubscript{17}H\textsubscript{16}N\textsubscript{2}O\textsubscript{2} [M + Na\textsuperscript{+}]: calcd 303.1109, found 303.1098.

(Z)-2-(1-(2-Chlorophenyl)ethylidene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4ai)

Procedure A, yellow oil, 87% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ = 7.41 (d, J = 7.3 Hz, 1H), 7.27 (s, 1H), 7.22 (t, J = 6.5 Hz, 2H), 5.80 (m, 1H), 5.42 – 5.28 (m, 2H), 4.81 (q, J = 6.7 Hz, 1H), 3.09 (dd, J = 13.1, 5.7 Hz, 1H), 2.70 (dd, J = 13.1, 8.1 Hz, 1H), 2.21 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ = 142.1, 137.5, 132.9, 132.8, 129.7, 129.7, 128.8, 126.8, 120.0, 113.1, 113.0, 112.1, 80.3, 44.3, 34.0, 18.4. IR (KBr, ν / cm\textsuperscript{-1}) 3132, 2361, 1638, 1472, 1400, 1163, 614. HRMS (ESI) for C\textsubscript{16}H\textsubscript{15}ClN\textsubscript{2}O [M + Na\textsuperscript{+}]: calcd 307.0614, found 307.0609.
(Z)-2-(1-(Naphthalen-2-yl)ethylidene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4aj)

Procedure A, white solid, 95% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.92$ (s, 1H), 7.82 (dd, $J = 9.1$, 4.2 Hz, 3H), 7.64 (d, $J = 8.6$ Hz, 1H), 7.47 (d, $J = 9.5$ Hz, 2H), 5.88 (m, 1H), 5.48 – 5.32 (m, 2H), 4.88 (q, $J = 6.6$ Hz, 1H), 3.12 (dd, $J = 13.1$, 5.5 Hz, 1H), 2.72 (dd, $J = 13.0$, 8.6 Hz, 1H), 2.44 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 141.5, 135.5, 133.0, 132.8, 132.5, 128.2, 127.5, 127.5, 126.9, 126.2, 126.1, 126.0, 120.1, 113.4, 113.3, 113.2, 80.6, 44.2, 35.1, 18.5. M.P.: 73 – 76 °C. IR (KBr, $\nu$ / cm$^{-1}$) 3133, 2366, 1641, 1399, 1153, 615. HRMS (ESI) for C$_{20}$H$_{16}$N$_2$O $[M + Na]^{+}$: calcd 323.1160, found 323.1168.

(Z)-2-(1-Phenylpropyldene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4ak)

Procedure B, yellow oil, 95% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.37$ (d, $J =$ 4.3 Hz, 4H), 7.28 (q, $J =$ 4.4 Hz, 1H), 5.84 (m, 1H), 5.44 – 5.28 (m, 2H), 4.78 (q, $J =$ 6.5 Hz, 1H), 3.06 (dd, $J =$ 13.0, 5.5 Hz, 1H), 2.75 – 2.63 (m, 3H), 1.03 (t, $J =$ 7.3 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 141.0, 136.6, 132.9, 128.4, 128.2, 127.4, 120.1, 119.9, 113.9, 113.7, 80.1, 44.3, 34.5, 25.5, 11.7. IR (KBr, $\nu$ / cm$^{-1}$) 3130, 2361, 1651, 1400, 1152, 698. HRMS (ESI) for C$_{17}$H$_{16}$N$_2$O $[M + Na]^{+}$: calcd 287.1160, found 287.1152.

(Z)-2-(1-Phenylpentylidene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4al)

Procedure B, colorless oil, 61% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.35$ – 7.34 (m, 4H), 7.28 (d, $J =$ 5.3 Hz, 1H), 5.84 (m, 1H), 5.48 – 5.26 (m, 2H), 4.78 (q, $J =$ 6.8 Hz, 1H), 3.07 (dd, $J =$ 13.0, 5.5 Hz, 1H), 2.75 – 2.47 (m, 3H), 1.37 (d, $J =$ 6.9 Hz, 4H), 0.98 – 0.73 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 141.0, 136.6, 132.9, 128.3, 128.2, 127.4, 119.9, 119.2, 113.9, 113.7, 80.0, 44.4, 34.5, 32.1, 29.5, 22.6, 13.8. IR (KBr, $\nu$ / cm$^{-1}$) 3234, 2361, 1618, 1399, 1154, 617. HRMS (ESI) for C$_{19}$H$_{20}$N$_2$O $[M + Na]^{+}$: calcd 315.1474, found 315.1469.

(Z)-2-(3-Methyl-1-phenylbutyldiene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4am)

Procedure B, colorless oil, 61% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.35$ (d, $J =$ 6.3 Hz, 4H), 7.26 (d, $J =$ 11.6 Hz, 1H), 5.82 (m, 1H), 5.43 – 5.25 (m, 2H), 4.77 (q, $J =$ 6.5 Hz, 1H), 3.05 (dd, $J =$ 13.0, 5.5 Hz, 1H), 2.67 (dd, $J =$ 13.0, 8.4 Hz, 1H), 2.55 (d, $J =$ 7.3 Hz, 2H), 1.58 (s, 1H), 0.92 (d, $J =$ 6.6 Hz, 6H). $^{13}$C
NMR (100 MHz, CDCl$_3$) $\delta$ = 136.5, 133.0, 129.0, 128.4, 128.1, 127.3, 119.9, 118.7, 114.1, 113.8, 79.9, 77.3, 77.0, 76.7, 44.5, 40.4, 34.4, 26.9, 22.1, 21.8. IR (KBr, $\nu$ / cm$^{-1}$) 3131, 2362, 1653, 1400, 1153, 702. HRMS (ESI) for C$_9$H$_{30}$N$_2$O: calcd 315.1474, found 315.1475.

(Z)-2-(1,2-Diphenylethyldiene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4an)

Procedure B, white solid, 65% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.31 (d, $J$ = 7.0 Hz, 2H), 7.23 (d, $J$ = 7.8 Hz, 2H), 7.18 (d, $J$ = 5.9 Hz, 5H), 7.12 (dd, $J$ = 6.1, 2.2 Hz, 1H), 5.88 (m, 1H), 5.50 – 5.32 (m, 2H), 4.88 (q, $J$ = 6.4 Hz, 1H), 4.13 – 4.01 (m, 2H), 3.13 (dd, $J$ = 13.0, 5.5 Hz, 1H), 2.75 (dd, $J$ = 13.0, 8.5 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 142.6, 136.9, 136.3, 132.8, 128.8, 128.6, 128.0, 127.4, 126.4, 120.2, 117.1, 113.7, 113.5, 80.3, 44.5, 37.7, 34.8. M.P.: 119 – 124 °C. IR (KBr, $\nu$ / cm$^{-1}$) 3130, 2360, 1639, 1400, 1153, 700. HRMS (ESI) for C$_9$H$_{18}$N$_2$O [M + Na]$^+$: calcd 349.1317, found 349.1311

2-(diphenylmethylene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4ao)

Procedure A, white solid, 98% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.46 (t, $J$ = 7.8 Hz, 3H), 7.40 (d, $J$ = 9.0 Hz, 4H), 7.31 (dd, $J$ = 13.0, 5.6 Hz, 3H), 7.23 (d, $J$ = 7.3 Hz, 1H), 5.99 (m, 1H), 5.59 – 5.42 (m, 2H), 5.09 – 5.02 (m, 1H), 3.06 (dd, $J$ = 12.8, 5.1 Hz, 1H), 2.67 (dd, $J$ = 12.8, 9.7 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 142.5, 137.5, 136.6, 132.8, 131.1, 129.2, 129.0, 128.7, 128.0, 127.5, 120.6, 119.7, 113.8, 111.9, 80.9, 45.1, 36.8. M.P.: 135 – 138 °C. IR (KBr, $\nu$ / cm$^{-1}$) 3128, 2361, 1645, 1401, 1153, 699; HRMS (ESI) for C$_{22}$H$_{16}$N$_2$O [M + Na]$^+$: calcd 335.1161, found 335.1158.

(E)-2-(2-(Benzyloxy)-1-phenylethyldiene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4ap)

Procedure B, yellow oil, 91% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.40 – 7.29 (m, 9H), 7.25 (s, 1H), 5.79 (m, 1H), 5.39 – 5.23 (m, 2H), 4.74 (q, $J$ = 6.5 Hz, 1H), 4.44 (s, 2H), 3.49 (t, $J$ = 6.4 Hz, 2H), 3.01 (dd, $J$ = 13.1, 5.5 Hz, 1H), 2.85 – 2.67 (m, 2H), 2.63 (dd, $J$ = 13.0, 8.6 Hz, 1H), 1.72 (dd, $J$ = 15.8, 6.2 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 141.3, 138.5, 136.3, 132.8, 128.4, 128.3, 128.2, 127.5, 127.5, 127.4, 120.0, 118.5, 113.8, 113.6, 80.1, 72.7, 69.6, 44.3, 34.5, 29.0, 27.5. IR (KBr, $\nu$ / cm$^{-1}$) 3131, 2361, 1668, 1400, 1152, 699. HRMS (ESI) for C$_{25}$H$_{24}$N$_2$O$_2$ [M + Na]$^+$: calcd 407.1735, found 407.1731.

(Z)-2-(1-Phenylhex-yn-1-ylidene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4aq)

Procedure B, yellow oil, 73% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.37 (d, $J$ = 4.5 Hz, 4H), 7.29 (d, $J$ = 5.7 Hz, 1H), 5.84 (m, 1H), 5.43 – 5.29 (m, 2H), 4.80 (q, $J$ = 6.5 Hz, 1H), 3.07 (dd, $J$ = 13.1, 5.5 Hz, 1H), 2.61 (s, 2H), 1.74 (s, 3H).

S8
(Z)-2-(1-Phenylpent-4-en-1-ylidene)-5-vinylidihydrofuran-3,3(2H)-dicarbonitrile (4ar)

Procedure B, yellow oil, 65% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.36$ (d, $J = 3.8$ Hz, 4H), 7.32 – 7.28 (m, 1H), 5.84 (m, 2H), 5.44 – 5.27 (m, 2H), 5.04 – 4.95 (m, 2H), 4.83 – 4.75 (m, 1H), 3.07 (dd, $J = 13.0$, 5.5 Hz, 1H), 2.78 – 2.64 (m, 3H), 2.18 – 2.09 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 141.5$, 138.1, 128.1, 127.9, 127.9, 127.3, 124.6, 113.5, 113.3, 112.8, 80.9, 44.6, 35.2, 31.8, 30.6, 22.1, 18.3, 13.8. IR (KBr, $\nu / \text{cm}^{-1}$) 3130, 2930, 2361, 1656, 1400, 1252, 1164, 697. HRMS (ESI) for C$_{20}$H$_{18}$N$_2$O $[\text{M} + \text{Na}]^+$: calcd 325.1317, found 325.1315.
Scheme S1. Other VCPs failed to provide tetrahydrofuran products

4. X-Ray Crystal Structure of Product 4ae
5. Preliminary Trials on the Asymmetric Variant

\[
\begin{align*}
1a & \xrightarrow{0.2 \text{ M in toluene, } \text{rt}, 4 \text{ h}} 2a \quad \xrightarrow{\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3 \ (2.5 \text{ mol\%})} \xrightarrow{1.0 \text{ eq. of } 3a \text{, rt, 20 mins}} \text{chiral } 4aa: \\
2a & \quad \xrightarrow{\text{L6-17 (2.5 mol\%)}} 3a
\end{align*}
\]

**Trost ligand (L7):** 0% yield

**MonoPhos (L8):** 0% yield

**PHOX ligand (L9):** 0% yield

**L6 (R = Br):** 91% yield, 75:25 er

**L11 (R = OMe):** 74% yield, 71:29 er

**L12 (R = F):** 95% yield, 72:28 er

**L13 (R = H):** 79% yield, 72:28 er

**L14:** 34% yield, 66:34 er

**L15:** 93% yield, 73:27 er

**L16:** 94% yield, 73:27 er

**L17:** 41% yield, 63:27 er

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*a*Conditions: 1a (0.4 mmol) in 2 mL of dry toluene was irradiated at rt under 6 W blue LEDs for 4 h; then, the resulting solution 2a together with 3a (0.2 mmol) were added to the pre-prepared solution of Pd_2(dba)_3·CHCl_3 (2.5 mol%) and chiral ligand (5 mol%) in 2 mL of dry toluene and stirred at rt for 20 minutes; isolated yield; er values were determined by chiral HPLC.

**Procedure C with L6:** Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with 1a (0.4 mmol, 2.0 equiv) and anhydrous toluene (2 mL). The resulting solution was stirred for 4 h at 25°C under 6 W blue LEDs. Then, another one flame-dried 10 mL Schlenk tube was charged with Pd_2(dba)_3·CHCl_3 (0.005 mmol, 2.5 mol%), L6 (0.01 mmol, 5 mol%), and anhydrous toluene (2 mL) were added, the resulting solution was stirred for 10 min at 25°C, then 2 (0.2 mmol, 1.0 equiv.) and 3 (0.2 mmol, 1.0 equiv.) were added together. The resulting solution was stirred until complete conversion of VCP 3a (monitored by TLC). Solvent was removed under the reduced pressure and the residue was purified by flash column chromatography on silica gel (petrol ether/ethyl acetate = 50/1 to 25/1) to afford the tetrahydrofuran product 4aa.
(Z)-2-(1-phenylethylidene)-5-vinylidihydropuran-3,3(2H)-dicarbonitrile (chiral 4aa)

White solid, 91% yield, 75:25 er, [α]D25 = 16.25 (c = 1.0, CHCl3). The er value was determined by HPLC (Chiralpak AS, column, hexane/i-PrOH, 98:2 v/v, flow rate 0.8 mL/min, λ = 254 nm, 25 °C; tR (minor) = 19.442 min; tR (major) = 20.453 min).

6. Copies of HPLC Spectra

$^1$H NMR Spectrum of L5

$^{13}$C NMR Spectrum of L5
$^{31}$P NMR Spectrum of L5

$^1$H NMR Spectrum of 4aa
$^{13}$C NMR Spectrum of 4aa

$^1$H NMR Spectrum of 4ab
$^{13}$C NMR Spectrum of 4ab

$^{1}$H NMR Spectrum of 4ac
$^{13}$C NMR Spectrum of 4ac

F NMR Spectrum of 4ac
$^1$H NMR Spectrum of 4ad

$^{13}$C NMR Spectrum of 4ad
$^{1}$H NMR Spectrum of 4ae

$^{13}$C NMR Spectrum of 4ae
$^1$H NMR Spectrum of 4af

$^{13}$C NMR Spectrum of 4af
$^{19}$F NMR Spectrum of 4af

$^1$H NMR Spectrum of 4ag
$^{13}$C NMR Spectrum of $4ag$

$^1$H NMR Spectrum of $4ah$
$^{13}$C NMR Spectrum of 4ah

$^1$H NMR Spectrum of 4ai
$^{13}$C NMR Spectrum of 4ai

$^1$H NMR Spectrum of 4aj
$^{13}$C NMR Spectrum of 4aj

$^1$H NMR Spectrum of 4ak

S25
$^{13}$C NMR Spectrum of 4ak

$^1$H NMR Spectrum of 4ai
$^{13}$C NMR Spectrum of 4al

$^1$H NMR Spectrum of 4am
$^{13}$C NMR Spectrum of 4am

$^{1}$H NMR Spectrum of 4an
$^{13}$C NMR Spectrum of 4an

$^1$H NMR Spectrum of 4ao
$^{13}$C NMR Spectrum of 4ao

$^1$H NMR Spectrum of 4ap
$^{13}$C NMR Spectrum of 4ap

$^1$H NMR Spectrum of 4aq
$^{13}$C NMR Spectrum of 4ar

$^1$H NMR Spectrum of 4ba
$^{13}$C NMR Spectrum of $4ba$

$^1$H NMR Spectrum of $4ca$
$^{13}$C NMR Spectrum of 4ca

**J.501: 0.1.FID**

(NMR spectrum and compound structure)