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1. General Information

Unless stated otherwise, all reactions were conducted in pressure tubes under N₂. All solvents were received from commercial sources without further purification. Commercially available reagents were used as received. Non-commercially available substrates were synthesized following reported protocols. Thin-layer chromatography (TLC) was visualized using a combination of UV and potassium permanganate staining techniques. Silica gel (particle size 40 – 63 µm) was used for flash column chromatography. NMR spectra were recorded on Bruker AV 400 spectrometer at 400 MHz (¹H NMR), 100 MHz (¹³C NMR). Proton and carbon chemical shifts are reported relative to the solvent used as an internal reference. High-resolution mass spectra were recorded on an IonSpec FT-ICR mass spectrometer with ESI resource.

2. Reaction Optimization

\[ \text{Ph} \equiv \text{Ph} \xrightarrow{[\text{Ir(COD)Cl}]_2 (2.5 \text{ mol} \%)} \text{Ph} \equiv \text{Ph} + \text{Ph} \equiv \text{Ph} \]

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[^a] Yields were determined by GC analysis.

Table 1 Effect of DPPE amount on the stereoselectivity. 1,2-Diphenylethyne (0.2 mmol), ethanol (4 mmol), [Ir(COD)Cl]₂ (10 µmol), THF (1.5 mL), at 120 °C under N₂ for 22 h. [a] Yields were determined by GC analysis.
Table 2 Effects of COD amount and other ligand on the stereoselectivity. 1,2-Diphenylethyne (0.2 mmol), ethanol (4 mmol), [Ir(COD)Cl]₂ (10 µmol), DPPE (0.04 mmol), THF (1.5 mL), at 120 °C under N₂ for 40 h. [a] Yields were determined by GC analysis. [b] COE = cyclooctene.

3. Typical Procedure for Synthesis of (E)-1,2-diphenylethene

To a 15 mL pressure tube were added diarylacetylene 1 (0.20 mmol), [Ir(cod)Cl]₂ (5 µmol, 3.6 mg), DPPE (0.04 mmol, 15.9 mg) under N₂, and then EtOH (4 mmol, 232 µL) and THF (1.5 mL) were added. The resulting solution was stirred at 120 °C for 22 h. After the reaction was completed, the solution was cooled to room temperature, and diluted with ethyl acetate (10 mL). The combined organic phases were washed with brine, and the aqueous phase was extracted with ethyl acetate. The organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by column chromatography (n-Hexane or n-Hex/EtOAc = 100:1 to 40:1) to afford the desired product.
2a: (E)-1,2-diphenylethene.\textsuperscript{[1]} White solid (33 mg, 92% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.49 (m, 4H), 7.34 (m, 4H), 7.26 – 7.22 (m, 2H), 7.09 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 137.4, 128.8, 127.7, 126.6.

2b: (E)-1-chloro-4-styrylbenzene.\textsuperscript{[1]} White solid (36 mg, 84% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.51 – 7.49 (m, 2H), 7.45 – 7.43 (m, 2H), 7.38 – 7.25 (m, 5H), 7.11 – 7.02 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 137.1, 136.0, 133.3, 129.5, 129.0, 128.9, 128.0, 127.8, 127.5, 126.7.

2c: (E)-1-chloro-3-styrylbenzene.\textsuperscript{[1]} White solid (36 mg, 84% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.51 – 7.49 (m, 3H), 7.38 – 7.34 (m, 3H), 7.29 – 7.21 (m, 3H), 7.11 (d, \(J = 16.3\) Hz, 1H), 7.02 (d, \(J = 16.3\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 139.4, 137.0, 134.8, 130.3, 130.0, 128.9, 128.2, 127.6, 127.4, 126.8, 126.4, 124.9.

2d: (E)-1-bromo-4-styrylbenzene.\textsuperscript{[2]} White solid (44 mg, 85% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.48 – 7.43 (m, 4H), 7.35 – 7.31 (m, 4H), 7.23 (t, \(J = 7.2\) Hz, 1H), 7.02 (d, \(J = 16.0\) Hz, 1H), 6.95 (d, \(J = 16.0\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 137.1, 136.4, 131.9, 129.6, 128.9, 128.1, 128.1, 127.6, 126.7, 121.5.

2e: (E)-1-bromo-3-styrylbenzene.\textsuperscript{[3]} White solid (47 mg, 91% yield). \(^1\)H NMR (400
2f: (E)-1-methoxy-2-styrylbenzene,\(^\text{[2]}\) White solid (56 mg, 83% yield).\(^\text{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.61 – 7.59 (m, 1H), 7.55 – 7.53 (m, 2H), 7.49 (d, \(J = 16.4\) Hz, 1H), 7.35 (t, \(J = 7.6\) Hz, 2H), 7.27-7.22 (m, 2H), 7.12 (d, \(J = 16.4\) Hz, 1H), 6.97 (t, \(J = 7.6\) Hz, 1H), 6.91 (m, d, \(J = 8.0\) Hz, 1H), 3.90 (s, 3H); \(^\text{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.1, 138.1, 129.3, 128.8, 128.7, 127.5, 126.7, 126.6, 126.6, 123.7, 120.9, 111.1, 55.7.

2g: (E)-2-(3-bromophenyl)-1-(4-bromophenyl)ethene,\(^\text{[2]}\) White solid (56 mg, 83% yield).\(^\text{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.65 (t, 1H), 7.49 (d, \(J = 8.0\) Hz, 2H), 7.41 – 7.35 (m, 4H), 7.22 (t, \(J = 7.6\) Hz, 1H), 7.03 (d, \(J = 16.8\) Hz, 1H), 6.99 (d, \(J = 16.8\) Hz, 1H); \(^\text{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 139.3, 135.9, 132.0, 130.8, 130.4, 129.4, 129.0, 128.2, 128.0, 125.4, 123.1, 122.0.

2h: (E)-1, 2-bis(4-bromophenyl)ethene,\(^\text{[4]}\) White solid (58 mg, 86% yield).\(^\text{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.36 (d, \(J = 8.4\) Hz, 4H), 7.08 (d, \(J = 8.4\) Hz, 4H), 6.54 (s, 2H); \(^\text{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 135.8, 131.7, 130.6, 129.9, 121.4.
2i: (E)-1-(4-bromostyryl)-3-chlorobenzene, White solid (48 mg, 82% yield). 
$^{1}$HNMR (400 MHz, CDCl$_3$): $\delta$ 7.50 – 7.48 (m, 3H), 7.38 – 7.35 (m, 3H), 7.29 (t, $J$ = 8.0 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.02 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 139.0, 135.9, 134.9, 132.0, 130.1, 129.0, 128.2, 128.1, 127.9, 126.5, 124.9, 122.0; HRMS(ESI) m/z Calcd for C$_{14}$H$_{10}$BrCl 291.9654, Found 291.9644.

![Structure of (E)-1-(4-bromostyryl)-3-chlorobenzene](image)

2j: (E)-1-(4-bromostyryl)-4-chlorobenzene.$^{[5]}$ White solid (47 mg, 80% yield). $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.37 – 7.34 (m, 2H), 7.22 – 7.08 (m, 6H), 6.59 – 6.51 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 135.9, 135.4, 133.2, 131.7, 130.6, 130.3, 129.8, 129.8, 128.7, 121.4.

![Structure of (E)-1-(4-bromostyryl)-4-chlorobenzene](image)

2k: (E)-1-(4-bromostyryl)-3-methylbenzene, White solid (49 mg, 90% yield). $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48 – 7.46 (m, 2H), 7.38 – 7.35 (m, 2H), 7.31 – 7.29 (m, 2H), 7.24 – 7.21 (m, 1H), 7.09 (d, $J$ = 7.2 Hz, 1H), 7.06 (d, $J$ = 16.4 Hz, 1H), 7.00 (d, $J$ = 16.4 Hz, 1H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.4, 137.0, 136.5, 131.9, 129.7, 128.9, 128.8, 128.1, 127.4, 127.3, 123.9, 121.3, 21.6; HRMS(ESI) m/z Calcd for C$_{13}$H$_{13}$Br [M+H]$^+$ 273.0279, Found 273.0281.

![Structure of (E)-1-(4-bromostyryl)-3-methylbenzene](image)

2l: (E)-1-(4-bromostyryl)-4-methylbenzene.$^{[5]}$ White solid (41 mg, 75% yield). $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7. 48 – 7. 45 (m, 2H), 7.41 – 7.35 (m, 4H), 7.18 – 7.16 (m, 2H), 7.07 (d, $J$ = 16.4 Hz, 1H), 6.98 (d, $J$ = 16.4 Hz, 1H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.0, 136.6, 134.3, 131.9, 129.6, 129.5, 128.0, 126.6, 126.5, 121.2, 21.4.
2m: (E)-1-(4-bromostyryl)-4-fluorobenzene,[6] White solid (50 mg, 90% yield). $^1$H NMR (400 MHz, CDCl₃): $\delta$ 7.49 – 7.45 (m, 4H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.07 – 7.03 (m, 3H), 6.94 (d, $J = 16.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl₃) $\delta$ 162.6 (d, $J_{C-F} = 240$ Hz), 136.3, 133.3, 132.0, 128.3 (d, $J_{C-F} = 10$ Hz), 128.0, 127.3 (d, $J_{C-F} = 2.0$ Hz), 121.5, 116.0, 115.9 (d, $J_{C-F} = 20.0$ Hz).

2n: (E)-1-(4-bromostyryl)naphthalene,[7] White solid (53 mg, 86% yield). $^1$H NMR (400 MHz, CDCl₃): $\delta$ 8. 20 (d, $J = 8.0$ Hz, 1H), 7.89 – 7.81 (m, 3H), 7.74 (d, $J = 7.2$ Hz, 1H), 7.57 – 7.46 (m, 7H), 7.08 (d, $J = 16.0$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl₃) $\delta$ 136.7, 134.8, 133.9, 132.0, 131.5, 130.6, 128.8, 128.5, 128.3, 126.7, 126.4, 126.1, 125.8, 123.8, 121.7.

2o: (E)-1-(3-bromostyryl)-3-methylbenzene,[8] White solid (50 mg, 91% yield). $^1$H NMR (400 MHz, CDCl₃): $\delta$ 7.64 (t, $J = 4.0$ Hz, 1H), 7.40 – 7.34 (m, 2H), 7.31 – 7.28 (m, 2H), 7.24 – 7.18 (m, 2H), 7.09 (d, $J = 8.0$ Hz, 1H ), 7.06 (d, $J = 16.0$ Hz, 1H), 6.98 (d, $J = 16.0$ Hz, 1H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, CDCl₃) $\delta$ 139.7, 138.4, 136.8, 130.4, 130.4, 130.3, 129.3, 129.0, 128.8, 127.5, 127.0, 125.3, 124.0, 123.0, 21.6.

2p: (E)-2-(3-bromostyryl)naphthalene,[9] White solid (54 mg, 87% yield). $^1$H NMR (400 MHz, CDCl₃): $\delta$ 7.85 – 7.71 (m, 6H), 7.51 – 7.39 (m, 4H), 7.29 – 7.23 (m, 2H),
7.15 (d, J = 16.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 139.7, 134.4, 133.8, 133.3, 130.6, 130.4, 129.4, 128.6, 128.2, 127.9, 127.5, 127.2, 126.6, 125.4, 123.5, 123.1.

**2q: (E)-2-(3-chlorophenyl)-1-(4-chlorophenyl)ethene,** $^{[8]}$ White solid (39 mg, 78% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.48 (s, 1H), 7.43 – 7.41 (m, 2H), 7.36 – 7.30 (m, 3H), 7.28 – 7.22 (m, 2H), 7.05 (d, J = 16.4 Hz, 1H), 6.98 (d, J = 16.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 139.0, 135.5, 134.9, 133.8, 130.1, 129.1, 128.9, 128.0, 127.9, 127.9, 126.5, 124.9.

**2r: (E)-1-(4-chlorostyryl)-3-bromobenzene,** $^{[8]}$ White solid (49 mg, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.65 (s, 1H), 7.44 – 7.32 (m, 6H), 7.24 – 7.20 (m, 1H), 7.05 (d, J = 16.0 Hz, 1H), 6.98 (d, J = 16.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 139.3, 135.4, 133.8, 130.8, 130.4, 129.4, 129.1, 129.0, 127.9, 127.8, 125.4, 123.1.

**2s: (E)-1-(4-chlorostyryl)-3-methylbenzene,** $^{[10]}$ White solid (42 mg, 92% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.43 – 7.40 (m, 2H), 7.32 – 7.29 (m, 4H), 7.24 – 7.22 (m, 1H), 7.09 (d, J = 7.6 Hz, 1H), 7.04 (s, 2H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.4, 137.0, 136.1, 133.5, 129.5, 129.0, 128.8, 128.8, 127.8, 127.4, 127.3, 123.9, 21.6.

**2t: (E)-2-(4-chlorostyrylnaphthalene,** $^{[11]}$ White solid (47mg, 89% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.85 – 7.71 (m, 5H), 7.51 – 7.44 (m, 4H), 7.37 – 7.33 (m, 2H),
7.25 (d, J = 16.0 Hz, 1H), 7.18 (d, J = 16.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$
136.0, 134.6, 133.8, 133.4, 133.3, 129.6, 129.0, 128.2, 127.9, 127.8, 127.0, 126.6, 126.2, 123.5.

![Image of compound 2u](image_url)

**2u: (E)-1-(3-chlorostyryl)-4-methylbenzene**$^{[5]}$ White solid (38 mg, 84% yield). $^1$H
NMR (400 MHz, CDCl$_3$): $\delta$ 7.49 (s, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 8.0 Hz, 1H), 7.22 – 7.17 (m, 3H), 7.09 (d, J = 16.0 Hz, 1H), 6.98 (d, J = 16.0 Hz, 1H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.6, 139.2, 134.7, 134.2, 130.2, 130.0, 129.6, 127.4, 126.7, 126.3, 126.3, 124.8, 21.4.

![Image of compound 2v](image_url)

**2v: (E)-1-(4-chlorostyryl)-4-methylbenzene**$^{[5]}$ White solid (35 mg, 77% yield). $^1$H
NMR (400 MHz, CDCl$_3$): $\delta$ 7.44 – 7.40 (m, 4H), 7.33 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 16.0 Hz, 1H), 7.00 (d, J = 16.0 Hz, 1H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.0, 136.2, 134.3, 133.0, 129.6, 129.4, 128.9, 127.7, 126.6, 126.5, 21.4.

![Image of compound 2w](image_url)

**2w: (E)-1-(3-bromostyryl)-4-methylbenzene**$^{[12]}$ White solid (49 mg, 90% yield). $^1$H
NMR (400 MHz, CDCl$_3$): $\delta$ 7.66 (s, 1H), 7.40 – 7.36 (m, 4H), 7.23 – 7.17 (m, 3H), 7.08 (d, J = 16.0 Hz, 1H), 6.97 (d, J = 16.0 Hz, 1H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.9, 138.2, 134.1, 130.3, 130.3, 130.2, 129.6, 129.2, 126.7, 126.2, 125.2, 123.0, 21.4.
2x: *(E)-1-(3,5-dimethoxystyryl)-4-fluorobenzene,* [13] White solid (44 mg, 86% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48 – 7.45 (m, 2H), 7.06 – 6.92 (m, 3H), 6.94 (d, $J = 16.4$ Hz, 1H), 6.66 (d, $J = 2.0$ Hz, 2H), 6.40 (t, $J = 2.4$ Hz, 1H), 3.83 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 162.6 (d, $J_{C-F} = 246.0$ Hz), 161.2, 139.3, 133.5, 128.6 (d, $J_{C-F} = 2.0$ Hz), 128.2 (d, $J_{C-F} = 5.0$ Hz), 128.1, 115.8 (d, $J_{C-F} = 21.0$ Hz), 104.7, 100.5, 55.5.

2y: *(E)-1-(3,5-dimethoxystyryl)benzene,* [3] White solid (38 mg, 80% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.51 – 7.49 (m, 2H), 7.37 – 7.33 (m, 2H), 7.28 – 7.24 (m, 1H), 7.09 (d, $J = 16.4$ Hz, 1H), 7.03 (d, $J = 16.4$ Hz, 1H), 6.7 (d, $J = 2.4$ Hz, 2H), 6.40 (t, $J = 2.0$ Hz, 1H), 3.82 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.1, 139.5, 137.3, 129.3, 128.8, 128.8, 127.9, 126.7, 104.7, 100.1, 55.5.

2z: *(E)-1,2-bis(4-methoxyphenyl)ethene,* [11] White solid (35 mg, 73% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.44 – 7.41 (m, 4H), 6.93 (s, 2H), 6.90 – 6.87 (m, 4H), 3.82 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.2, 130.6, 127.6, 126.3, 114.3, 55.5.

2a: *(E)-1-(4-propylstyryl)-4-methoxybenzene,* White solid (35 mg, 70% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.46 – 7.41 (m, 4H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.04 (d, $J = 16.0$ Hz, 1H), 6.96 (d, $J = 16.0$ Hz, 1H), 6.92 – 6.89 (m, 2H), 3.83 (s, 3H), 2.59 (t, $J =
8.0 Hz, 2H), 1.70 – 1.61 (m, 2H), 0.96 (t, J = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.3, 142.1, 135.2, 130.5, 128.9, 127.7, 127.4, 126.7, 126.3, 114.2, 55.5, 37.9, 24.7, 14.0; HRMS (ESI) m/z Calcd for C$_{18}$H$_{20}$O [M+H]$^+$ 253.1592, Found 253.1581.

![Chemical Structure](image)

2β: (E)-1-styryl-3,5-bis(trifluoromethyl)benzene.$^{[14]}$ White solid (46 mg, 73% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.92 (s, 2H), 7.74 (s, 1H), 7.55 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 7.35 – 7.32 (m, 1H), 7.20 (d, J = 16.4 Hz, 1H), 7.20 (d, J = 16.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.6, 136.2, 132.7, 132.2 (d, $J_{C,F}$ = 33.0 Hz), 129.1, 128.9, 127.1, 126.3 (d, $J_{C,F}$ = 3.4 Hz), 125.7, 123.5 (d, $J_{C,F}$ = 271.1 Hz), 121.0-120.9 (m).

![Chemical Structure](image)

2γ: (E)-1-styryl-4-(trifluoromethyl)benzene.$^{[11]}$ White solid (41 mg, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 (s, 4H), 7.54 (m, 2H), 7.38 (t, J = 8.0 Hz, 2H), 7.35 – 7.32 (m, 1H), 7.25 (d, J = 16.4 Hz, 1H), 7.14 (d, J = 16.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 141.0, 136.8, 131.4, 129.6, 129.3, 129.0, 128.4, 127.3, 126.9, 126.7, 125.8 (q, $J_{C,F}$ = 3.8 Hz).

![Chemical Structure](image)

2ε: (E)-prop-1-en-1-ylbenzene.$^{[15]}$ Colorless liquid (20 mg, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33 – 7.26 (m, 4H), 7.20 – 7.16 (m, 1H), 6.40 (dd, J = 16.0, 1.2 Hz, 1H), 6.28 – 6.19 (m, 1H), 1.88 (dd, J = 6.4, 1.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.1, 131.2, 128.6, 126.9, 126.0, 125.8, 18.6.

![Chemical Structure](image)

2ψ: (E)-dec-5-ene.$^{[16]}$ Colorless liquid (20 mg, 70% yield). $^1$H NMR (400 MHz,
CDCl₃): δ 5.40 – 5.36 (m, 2H), 1.98 – 1.97 (m, 4H), 1.34 – 1.27 (m, 8H), 0.89 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 130.5, 32.5, 32.0, 22.4, 14.1.

2η: (E)-tetradec-7-ene,[¹⁷] Colorless liquid (28 mg, 72% yield). ¹H NMR (400 MHz, CDCl₃): δ 5.40 – 5.34 (m, 2H), 2.03 – 1.95 (m, 4H), 1.30 – 1.27 (m, 16H), 0.88 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 130.5, 32.8, 32.0, 29.8, 29.0, 22.8, 14.3.

O

2A: Methyl cinnamate,[¹⁸] White solid (25 mg, 76% yield). ¹H NMR (400 MHz, CDCl₃): δ 7770 (d, J = 16.0 Hz, 1H), 7.54-7.52 (m, 2H), 7.40-7.38 (m, 3H), 6.45 (d, J = 16.0 Hz, 1H), 3.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 167.7, 145.1, 134.5, 130.5, 129.0, 128.2, 117.9, 51.9.

2B: 2-vinylnapthalene,[¹⁵] White solid (24 mg, 79% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.82 – 7.76 (m, 4H), 7.64 (dd, J = 8.0, 1.6Hz, 1H), 7.49 – 7.42 (m, 2H), 6.89 (dd, J = 17.6, 11.2 Hz, 1H), 5.88 (d, J = 17.6 Hz, 1H), 5.35 (d, J =14.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 137.1, 135.2, 133.7, 133.3, 128.3, 128.2, 127.8, 126.5, 126.4, 126.1, 123.3, 114.3.

2C: 1-methyl-4-vinylbenzene,[¹⁵] Colorless liquid (22 mg, 93% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.36 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.74 (dd, J = 17.6, 11.2 Hz, 1H), 5.75 (d, J = 17.6 Hz, 1H), 5.23 (d, J = 10.8 Hz, 1H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 137.7, 136.8, 134.9, 129.3, 126.2, 112.8, 21.3.

2D: 1-chloro-4-vinylbenzene,[¹⁵] Colorless liquid (25 mg, 91% yield). ¹H NMR (400
MHz, CDCl₃): δ 7.34-7.25 (m, 4H), 6.66 (dd, J = 17.6, 11.2 Hz, 1H), 5.72 (d, J = 17.6 Hz, 1H), 5.26 (d, J = 11.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 136.2, 135.8, 133.6, 128.8, 127.6, 114.6.

4, Deprotection of (E)-1,2-bis(4-methoxyphenyl)ethene

To a solution of (E)-1,2-bis(4-methoxyphenyl)ethene (0.2 mmol) in anhydrous DCM (6 mL) maintained under nitrogen at −20 °C with stirring was added BBr₃ dropwise (0.34 g, 1.34 mmol, 30% in DCM). The mixture, maintained under nitrogen with stirring, was allowed to warm up to room temperature for 4 – 5 h, and then it was poured into water (10 mL) and extracted with DCM (3×10 mL). The collected organic phases were washed with brine (10 mL) and then dried over Na₂SO₄. After filtration, the solvent was evaporated and the residue purified by column chromatography on silica gel using 6:4 hexane–acetone.

Pinosylvin,[¹⁹] White solid (33 mg, 77.8% yield). ¹H NMR (400 MHz, (CD₃)₂CO): δ 8.04 (s, 2H), 7.40 (d, J = 8.8 Hz, 4H), 6.96 (s, 2H), 6.83 (d, J = 8.8 Hz, 4H); ¹³C NMR (100 MHz, (CD₃)₂CO): δ 157.7, 130.5, 128.3, 126.5, 116.4.

5, Deprotection of 3-Mesityl-2'-methoxy-[1,1'-binaphthalene]-2-ol

To a solution of (E)-1,3-dimethoxy-5-styrylbenzene (0.2 mmol) in anhydrous DCM (6
mL) maintained under nitrogen at –20 °C with stirring was added BBr₃ dropwise (0.34 g, 1.34 mmol, 30% in DCM). The mixture, maintained under nitrogen with stirring, was allowed to warm up to room temperature for 4 – 5 h, and then it was poured into water (10 mL) and extracted with DCM (3×10 mL). The collected organic phases were washed with brine (10 mL) and then dried over Na₂SO₄. After filtration, the solvent was evaporated and the residue purified by column chromatography on silica gel using 6:4 hexane–acetone.

4,4′-dihydroxystilbene (DHS),[13] White solid (35 mg, 83% yield). ¹H NMR (400 MHz, (CD₃)₂CO): δ 7.57 (d, J = 7.2 Hz, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H), 7.10 (s, 2H), 6.60 (d, J = 2.0 Hz, 2H), 6.32 (t, J = 2.4 Hz, 1H); ¹³C NMR (100 MHz, (CD₃)₂CO): δ 159.6, 140.4, 138.4, 129.8, 129.5, 129.2, 128.3, 127.3, 105.9, 103.1.

6. Typical Procedure for Synthesis of (Z)-1,2-diarylethene

To a 15 mL pressure tube were added diphenylacetylene 1 (0.20 mmol), [Ir(cod)Cl]₂ (5 μmol, 3.6 mg), DPPE (0.04 mmol, 15.9 mg) under N₂, and then EtOH (4 mmol, 232 μL), COD (0.4 mmol, 49 μL) and THF (1.5 mL) were added. The resulting solution was stirred at 120 °C for 44 h. After the reaction was completed, the solution was cooled to room temperature, and diluted with ethyl acetate (10 mL). The combined organic phases were washed with brine, and the aqueous phase was extracted with ethyl acetate. The organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by column chromatography (n-Hexane or n-Hex/EtOAc = 100:1 to 40:1) to afford the desired...
product.

3a: (Z)-1,2-diphenylethene,[1] Colorless liquid (30 mg, 84% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.27 – 7.21 (m, 10H), 6.63 – 6.60 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.4, 130.4, 130.4, 129.0, 129.0, 128.4, 128.3, 127.2, 127.2.

3b: (Z)-1-chloro-2-styrylbenzene,[20] Colorless liquid (37 mg, 81% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.42 – 7.40 (m, 1H), 7.21 – 7.15 (m, 7H), 7.06 – 7.02 (m, 1H), 6.73 (d, $J$ = 12.4 Hz 1H), 6.68 (d, $J$ = 12.4 Hz 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 136.6, 136.2, 133.8, 131.8, 130.9, 129.7, 129.1, 128.6, 128.3, 127.5, 127.4, 126.5.

3c: (Z)-1-fluoro-2-styrylbenzene,[20] Colorless liquid (44 mg, 80% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.23 – 7.17 (m, 7H), 7.07 – 7.02 (m, 1H), 7.95 – 7.91 (m, 1H), 6.73 (d, $J$ = 12.4 Hz 1H), 6.63 (d, $J$ = 12.4 Hz 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.5 (d, $J_{C,F}$ = 246.2 Hz), 136.9, 132.4, 130.6 (d, $J_{C,F}$ = 3.5 Hz); 129.1 (d, $J_{C,F}$ = 8.2 Hz), 128.9, 128.4, 127.5, 125.2 (d, $J_{C,F}$ = 14.4 Hz), 123.7 (d, $J_{C,F}$ = 3.5 Hz), 122.8 (d, $J_{C,F}$ = 3.3 Hz), 115.7 (d, $J_{C,F}$ = 21.8 Hz).

3d: (Z)-1-methoxy-2-styrylbenzene,[21] Colorless liquid (36 mg, 79% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.24 – 7.12 (m, 7H), 6.89 (d, $J$ = 8.0 Hz, 1H), 6.77 – 6.73 (m, 1H), 6.69 (d, $J$ = 12.4 Hz, 1H), 6.62 (d, $J$ = 12.4 Hz, 1H), 3.82 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 157.2, 137.3, 130.2, 130.1, 128.9, 128.6, 128.0, 126.9, 126.2, 125.8, 120.2, 110.7, 55.5.
3e: **(Z)-1-(4-chlorostyryl)-4-methylbenzene**, Colorless liquid (37 mg, 81% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.18 (s, 4H), 7.13 – 7.03 (m, 4H), 6.59 (d, $J = 12.4$ Hz, 1H), 6.48 (d, $J = 12.4$ Hz, 1H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.3, 136.0, 134.0, 132.7, 131.0, 130.3, 129.2, 128.9, 128.5, 128.4, 21.4; HRMS(ESI) m/z Calcd for C$_{13}$H$_{13}$Cl [M+H]$^+$ 229.0784, Found 229.0789.

3f: **(Z)-1-(4-bromostyryl)-4-methylbenzene**.$^{[22]}$ Colorless liquid (44 mg, 80% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.36 – 7.33 (m, 2H), 7.13 – 7.03 (m, 6H), 6.60 (d, $J = 12.0$ Hz, 1H), 6.46 (d, $J = 12.0$ Hz, 1H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.3, 136.5, 134.0, 131.5, 131.1, 130.7, 129.2, 128.8, 128.4, 120.9, 21.4.

3g: **(Z)-1-(3-chlorostyryl)-4-methylbenzene**.$^{[8]}$ Colorless liquid (36 mg, 79% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.26 (s, 1H), 7.17 – 7.11 (m, 5H), 7.06 – 7.04 (m, 2H), 6.61 (d, $J = 12.4$ Hz, 1H), 6.47 (d, $J = 12.4$ Hz, 1H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.5, 137.4, 134.2, 133.8, 131.7, 129.6, 129.2, 129.0, 128.9, 128.1, 127.2, 127.1, 21.4.

3h: **(Z)-1-(4-propylstyryl)-4-methoxybenzene**, Colorless liquid (39 mg, 78% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.23 – 7.19 (m, 4H), 7.05 (d, $J = 8.0$ Hz, 2H), 6.79 – 6.75 (m, 2H), 6.49 (s, 2H), 3.80 (s, 3H), 2.56 (t, $J = 8.0$ Hz, 2H), 1.68 – 1.59 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.7, 141.6, 135.0, 130.2,
130.1, 129.2, 128.9, 128.8, 128.4, 113.7, 55.3, 37.9, 24.6, 14.0; HRMS(ESI) m/z Calcd for C₁₈H₂₀O [M+H⁺] 253.1514, Found 253.1582.

3i: (Z)-1,2-bis(4-methoxyphenyl)ethene,[23] Colorless liquid (34 mg, 71% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.22 – 7.20 (m, 4H), 6.79 – 6.77 (m, 4H), 6.46 (s, 2H), 3.80 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 158.7, 130.2, 130.1, 128.5, 113.7, 55.3.

3j: (Z)-1,2-bis(4-methoxyphenyl)ethene,[24] Colorless liquid (39 mg, 75% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.25 – 7.22 (m, 2H), 6.93 (t, J = 8.4 Hz, 2H), 6.57 – 6.50 (m, 2H), 6.39 – 6.38 (m, 2H), 6.33 – 6.32 (m, 1H), 3.66 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 163.2, 160.8, 139.0, 133.3 (d, J_C-F = 3.4 Hz), 130.8 (d, J_C-F = 7.9 Hz), 130.7, 130.4 (d, J_C-F = 1.2 Hz), 129.6, 115.2 (d, J_C-F = 21.3 Hz), 106.8, 100.0, 55.3.

3k: (Z)-1-styryl-3,5-bis(trifluoromethyl)benzene,[25] Colorless liquid (47 mg, 75% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.67 – 7.64 (m, 3H), 7.28 – 7.26 (m, 3H), 7.19 – 7.17 (m, 2H), 6.84 (d, J = 12.4 Hz, 1H), 6.59 (d, J = 12.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 139.3, 135.8, 134.1, 131.6 (q, J_C-F = 33.4 Hz), 129.2 (m), 128.8 (d, J_C-F = 8.8 Hz), 128.3, 127.2, 124.7, 122.0, 120.8-120.7 (m).

3l: (Z)-2-(3-chlorophenyl)-1-(4-chlorophenyl)ethene, Colorless liquid (35 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.22 – 7.13 (m, 7H), 7.10 – 7.07 (m, 1H), 6.58 (d, J = 12.0 Hz, 1H), 6.54 (d, J = 12.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 138.9,
HRMS(ESI) m/z Calcd for C_{14}H_{10}Cl_{2} 248.0160, Found 248.0165.

3m: (Z)-1-(4-chlorostyryl)naphthalene, Colorless liquid (41 mg, 78% yield).

{\textsuperscript{1}}HNMR (400 MHz, CDCl{\textsubscript{3}}): \(\delta\) 8.06 – 8.04 (m, 1H), 7.90 – 7.88 (m, 1H), 7.79(d, \(J = 8.0\) Hz, 1H), 7.54 – 7.47 (m, 2H), 7.38 – 7.32 (m, 2H), 7.10 – 6.99 (m, 5H), 6.79 (d, \(J = 12.0\) Hz, 1H); \{\textsuperscript{13}\}C NMR (100 MHz, CDCl{\textsubscript{3}}): \(\delta\) 135.3, 135.0, 133.8, 132.8, 131.6, 130.9, 130.4, 129.4, 128.6, 128.4, 127.9, 126.5, 126.3, 126.2, 125.7, 124.9; HRMS(ESI) m/z Calcd for C_{18}H_{13}Cl [M+H]+ 265.0784, Found 265.0788.

7. Gram-scale Synthesis

\[
\begin{align*}
\text{Ph} \equiv \equiv \text{Ph} + \text{EtOH} & \xrightarrow{[\text{Ir(cod)Cl}]_2 (2.5 \, \text{mol} \%), \text{DPPE (0.2 eq)}}^\text{THF (33 mL), N}_2, 130 \, ^\circ\text{C, 72 h}} \text{Ph} \equiv \equiv \text{Ph} \\
\end{align*}
\]

Gram-scale

79% yield

According to the typical procedure: To a 250 mL pressure tube were added diphenylacetylene 1 (5.62 mmol, 1.0 g), [Ir(cod)Cl]{\textsubscript{2}} (141 \, \mu\text{mol}, 94 mg), DPPE (1.12 mmol, 447 mg) under N\textsubscript{2}, and then EtOH (56.2 mmol, 3.26 mL), and THF (33 mL) were added. The resulting solution was stirred at 130 °C for 72 h. After column purification (n-Hexane), coupling product was obtained (0.8 g, 79% yield).

8. Deuterium Labeling Experiments

To a 15 mL pressure tube were added diphenylacetylene 1 (0.20 mmol), [Ir(cod)Cl]{\textsubscript{2}} (5 \, \mu\text{mol}, 3.6mg), DPPE (0.04 mmol, 15.9mg) under N\textsubscript{2}, and then C\textsubscript{2}D\textsubscript{5}OH or C\textsubscript{2}H\textsubscript{5}OD (4 mmol, 232 \, \mu\text{L}), COD (0.4 mmol, 49 \, \mu\text{L}), THF or tetrahydrofuran-d8 (1.5 mL) were added. The resulting solution was stirred at 120 °C for 44 h. After the reaction was completed, the solution was cooled to room temperature, and diluted with ethyl acetate (10 mL). The combined organic phases were washed with brine, and the aqueous phase was extracted with ethyl acetate. The organic phase was dried...
over anhydrous Na$_2$SO$_4$, filtered and concentrated in \textit{vacuo}. The crude product was purified by column chromatography ($n$-Hexane) to afford the desired cis-stilbene 3a or di-deuterated product 3a'.

\[ 3a 
\]

\[ 3a' 
\]

9. Zebrafish Experiments

At 6 hpf, embryos were screened under anatomical microscope to remove the morphologically abnormal individuals. Around 10 healthy embryos were loaded into
each well of 96-well plate in E3 solution. At the setting time, E3 solutions were replaced with different pino-sylvin or DHS treatment solutions. The control and treated groups were analyzed at different intervals. At 55 hpf, the Tg(fli1a:nEGFP) zebrafish embryos were collected for imaging. At 55 hpf, for confocal imaging embryos were anesthetized with E3/0.16 mg/mL tricaine/1% 1-phenyl-2-thiourea (Sigma) and embedded in 0.8% low melt agarose. Confocal imaging was performed with a Leica TCS-SP8 LSM. Analysis was performed using Imaris software.

10. Possible Mechanism

![Possible mechanism diagram]

Figure 1 Possible mechanism

References


11. NMR Spectra

![NMR Spectrum Diagram](image-url)
1r-P complex

$^3$P NMR (162 MHz, CDCl$_3$)

2a
2k

[Chemical structure image]

2l

[Chemical structure image]
2w

2x
3a

3b
3g

3h