Supporting Information
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Supporting Information

Stereoselective Rh-Catalyzed Isomerization of Stereoisomeric Mixtures of Arylalkenes

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1. General Information

Unless otherwise noted, all reactions were conducted in oven–dried vials with a magnetic stir bar under nitrogen atmosphere. Solvents were purified under nitrogen using a solvent purification system. [RhCl(cod)]$_2$ was prepared according to literature procedure and all characterization data are in accordance with the literature.$^1$ Phosphine ligands, bases and bis(pinacolate)diboron (B$_2$pin$_2$) were all purchased from Energy Chemicals Inc. and used as received. Analytical thin layer chromatography (TLC) was performed using silica gel plates. Visualisation was by ultraviolet fluorescence, and/or phosphomolybdic acid, and/or KMnO$_4$. Flash column chromatography was performed using EM Science (200–300 mesh) silica gel.

$^1$H–Nuclear Magnetic Resonance ($^1$H–NMR) and $^{13}$C–Nuclear Magnetic Resonance ($^{13}$C–NMR) spectra were recorded on Bruker 400 MHz at 20 °C with CDCl$_3$ as solvent and tetramethylsilane as an internal standard. The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet, br = broad), coupling constant $J$ (Hz) and integration. High resolution mass spectra were recorded on a Bruker Maxis System. IR spectra were collected on a Spectrum BX FTIR from Perkin–Elmer and reported in unit of cm$^{-1}$. 
2. Optimization of Conditions

Table S1. B$_2$Pin$_2$-loading evaluation$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>B$_2$Pin$_2$ (eq)</th>
<th>yield (%)$^b$ ($E$-1a/2a)</th>
<th>ratio($E$/Z)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^c$</td>
<td>1.1</td>
<td>0/75</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.7</td>
<td>6/61</td>
<td>&gt;15:1</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>68/15</td>
<td>15:1</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>92/&lt;5</td>
<td>15:1</td>
</tr>
</tbody>
</table>

$^a$All reactions were carried out with 1a (0.30 mmol), B$_2$pin$_2$ (0.015 mmol), [Rh(cod)Cl]$_2$ (3 mol%), and Xantphos (9 mol%) in 1 mL DME at 60 °C. $^b$Yields were determined by $^1$H NMR analysis with CH$_2$Br$_2$ as an internal standard. DME = 1,2-dimethoxyethane. $^c$80 °C, 19h. The ratio of E/Z was determined by $^1$H NMR.

Table S2. Reaction temperature evaluation$^d$

<table>
<thead>
<tr>
<th>entry</th>
<th>T (°C)</th>
<th>yield (%)$^d$ ($E$-1a)</th>
<th>ratio($E$/Z)$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>64</td>
<td>1.7:1</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>78</td>
<td>6.5:1</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>92</td>
<td>15:1</td>
</tr>
</tbody>
</table>
All reactions were carried out with 1a (0.30 mmol), B$_2$pin$_2$ (0.015 mmol), [Rh(cod)Cl]$_2$ (3 mol%) and Xantphos (9 mol%) in 1 mL DME. Yields were determined by $^1$H NMR analysis with CH$_2$Br$_2$ as an internal standard. DME = 1,2-dimethoxyethane. The ratio of $E$/Z was determined by $^1$H NMR.

Table S3. Time-loading evaluation$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>time (h)</th>
<th>yield (%)$^b$ (E-1a)</th>
<th>ratio($E$/Z)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>78</td>
<td>7:1</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>84</td>
<td>10:1</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>90</td>
<td>13:1</td>
</tr>
</tbody>
</table>

$^a$All reactions were carried out with 1a (0.30 mmol), B$_2$pin$_2$ (0.015 mmol), [Rh(cod)Cl]$_2$ (3 mol%) and Xantphos (9 mol%) in 1 mL DME at 60 °C. Yields were determined by $^1$H NMR analysis with CH$_2$Br$_2$ as an internal standard. DME = 1,2-dimethoxyethane. The ratio of $E$/Z was determined by $^1$H NMR.

Table S4. Solvent evaluation$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>yield (%)$^b$ (E-1a)</th>
<th>ratio($E$/Z)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCE</td>
<td>87</td>
<td>15:1</td>
</tr>
<tr>
<td>2</td>
<td>EtOAc</td>
<td>91</td>
<td>&gt;15:1</td>
</tr>
<tr>
<td>3</td>
<td>DMA</td>
<td>90</td>
<td>15:1</td>
</tr>
<tr>
<td>4</td>
<td>1,4–dioxane</td>
<td>90</td>
<td>15:1</td>
</tr>
</tbody>
</table>
All reactions were carried out with \( \text{1a} \) (0.30 mmol), \( \text{B} \text{2pin}_2 \) (0.015 mmol), \([\text{Rh(cod)}\text{Cl}]_2 \) (3 mol\%) and Xantphos (9 mol\%). \(^b\)Yields were determined by \(^1\)H NMR analysis with \( \text{CH}_2\text{Br}_2 \) as an internal standard. IPE = isopropyl ether, DME = 1,2-dimethoxyethane, DMA = \( N,N \)-dimethylacetamide. \(^c\)The ratio of \( E/Z \) was determined by \(^1\)H NMR. \(^d\)\( \text{B} \text{2pin}_2 \) was replaced by MeOH. \(^e\)\( \text{B} \text{2pin}_2 \) was replaced by \( \text{iPrOH} \).

### Table S5. Ligand evaluation\(^d\)

<table>
<thead>
<tr>
<th>entry</th>
<th>ligand</th>
<th>yield (%)(( E-\text{1a} ))</th>
<th>ratio((E/Z))(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PCys</td>
<td>70</td>
<td>2.5:1</td>
</tr>
<tr>
<td>2</td>
<td>PEtPPh(_2)</td>
<td>64</td>
<td>2.4:1</td>
</tr>
<tr>
<td>3</td>
<td>PPh(_3)</td>
<td>69</td>
<td>2.4:1</td>
</tr>
<tr>
<td>5</td>
<td>P(OPh)(_3)</td>
<td>65</td>
<td>2.3:1</td>
</tr>
<tr>
<td>6</td>
<td>DPEPhos</td>
<td>90</td>
<td>15:1</td>
</tr>
<tr>
<td>7</td>
<td>Xantphos</td>
<td>92</td>
<td>15:1</td>
</tr>
<tr>
<td>8</td>
<td>DPPB</td>
<td>70</td>
<td>2.5:1</td>
</tr>
<tr>
<td>9</td>
<td>DPPP</td>
<td>66</td>
<td>2.1:1</td>
</tr>
<tr>
<td>10</td>
<td>DPPE</td>
<td>74</td>
<td>4.6:1</td>
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</tbody>
</table>

\(^a\)All reactions were carried out with \( \text{1a} \) (0.30 mmol), \( \text{B} \text{2pin}_2 \) (0.015 mmol), \([\text{Rh(cod)}\text{Cl}]_2 \) (3 mol%) and ligand (18 mol% for monodentate phosphines and 9 mol% for bidentate phosphines) in 1 mL DME at 60 °C. \(^b\)Yields were determined by \(^1\)H NMR analysis with \( \text{CH}_2\text{Br}_2 \) as an internal standard. DME = 1,2-dimethoxyethane. \(^c\)The ratio of \( E/Z \) was determined by \(^1\)H NMR.
3. Synthesis and Characterization of Substrates

**General procedure A**

To a suspension of butyltriphenylphosphonium (10 mmol, 1.0 eq) in THF (30 mL) were added ‘BuLi (1.2 eq) at −78 °C, and the resulting mixture was stirred at ambient temperature for 3h. Then, the corresponding aldehyde (10 mmol) was added and stirred for 5 h. The mixture was quenched with saturated aqueous NH4Cl and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na2SO4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the corresponding alkenes.

1a, 1c, 1d, 1e, 1f, 1g, 1h, 1i, 1j, 1k, 1l, 1m, 1n, 1o, 1p, 1q, 1r, 1s, 1t, 1u, 1v, 1w, 1x, and 1y were prepared according to general procedure A. 1b were prepared using NaH instead of ‘BuLi. The data are in accordance with the literatures.
Synthesis of S1: To a solution of 1,6-hexanediol (11.8 g, 80 mmol) and imidazole (6.30 g, 92 mmol) in dry CH$_2$Cl$_2$ (20 mL) was added TBSCI (13.27 g, 8.09 mmol) at ambient temperature. The reaction mixture was stirred for 2 h. The reaction was quenched with H$_2$O, extracted with CH$_2$Cl$_2$, dried with Na$_2$SO$_4$, filtered and concentrated. The residue was purified by silica gel flash chromatography (PE/EtOAc = 10:1) to afford the desired product (16.33 g, 88%).

Synthesis of S2: To a solution of S1 (16.24 g, 70 mmol) in dry CH$_2$Cl$_2$ (20 mL) was added PCC (13.27 g, 84 mmol) at ambient temperature. The reaction mixture was stirred for 3 h. The reaction was quenched with H$_2$O, extracted with CH$_2$Cl$_2$, dried with Na$_2$SO$_4$, filtered and concentrated. The residue was purified by silica gel flash chromatography (PE/EtOAc= 20:1) to afford the desired product (6.33 g, 41%).

Synthesis of S3: To a suspension of benzyltriphenylphosphonium bromide (10 mmol, 1.0 eq) in THF (30 mL) were added BuLi (1.2 eq) at −78 °C, and the resulting mixture was stirred for 3 h. Then, S2 (10 mmol) was added and stirred for 5 h. The mixture was quenched with saturated aqueous NH$_4$Cl and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the corresponding compound.
Synthesis of S4: The S3 (3.03 g, 10 mmol) was dissolved in THF (15 mL) and cooled to 0 °C. TBAF (15 ml, 1.0 mol/L) was then added dropwise to the reaction mixture. After stirred for 2 h, the resulting suspension was diluted with EtOAc and quenched by saturated aqueous NH₄Cl. The mixture was extracted by EtOAc (10 mL x 3), dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (PE/EtOAc = 10:1–3:1) to afford the product as a colorless liquid (1.48 g, 78%).

1t, 1r¹³, and 1s were prepared by general procedure B.

1. Synthesis of N,N-dimethyl-4-(pent-1-en-1-yl)aniline (1c)

Follow the general procedure A, the title compound was isolated as a colorless oil by flash chromatography with ethyl acetate/petroleum ether (1:30) as an eluent (1.58 g, 84%).

$E/Z = 1/1.64$.

(Z): $^1$H NMR (400 MHz, CDCl₃) δ 7.25–7.16 (m, 2H), 6.74–6.64 (m, 2H), 6.34–6.25 (m, 1H), 5.53–5.43 (m, 1H), 2.92 (s, 6H), 2.36–2.29 (m, 2H), 1.53–1.41 (m, 2H), 0.94 (t, $J = 7.2$ Hz, 3H).

(Z): $^{13}$C NMR (100 MHz, CDCl₃) δ 149.3, 130.0, 129.9, 128.7, 126.6, 112.3, 40.7, 31.1, 23.5, 14.1.

(E): $^1$H NMR (400 MHz, CDCl₃) δ 7.25–7.16 (m, 2H), 6.74–6.64 (m, 2H), 6.34–6.25 (m, 1H), 6.08–5.95 (m, 1H), 2.90 (s, 6H), 2.19–2.10 (m, 2H), 1.53–1.41 (m, 2H), 0.94 (t, $J = 7.2$ Hz, 3H).
(E): $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.8, 129.7, 127.0, 126.94, 126.87, 112.8, 40.8, 35.3, 23.0, 13.9.


IR (neat, cm$^{-1}$): 2956, 2926, 1612, 1522, 1352, 1165, 962, 825.

2. Synthesis of methyl(4-(pent-1-en-1-yl)phenyl)sulfane (1e)

Follow the general procedure A, the title compound was isolated as a colorless oil by flash chromatography with ethyl acetate/petroleum ether (1:50) as an eluent (1.59 g, 83%).

$E/Z = 1/1.16$.

(Z): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22–7.19 (m, 4H), 6.39–6.29 (m, 1H), 5.70–5.58 (m, 1H), 2.47 (s, 3H), 2.34–2.25 (m, 2H), 1.53–1.42 (m, 2H), 0.97–0.89 (m, 3H).

(Z): $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.5, 134.9, 133.0, 129.3, 128.3, 126.5, 30.9, 23.3, 16.0, 14.0.

(E): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26 (d, $J =$ 7.9 Hz, 2H), 7.18 (d, $J =$ 8.1 Hz, 2H), 6.39–6.29 (m, 1H), 6.23–6.13 (m, 1H), 2.46 (s, 3H), 2.21–2.13 (m, 2H), 1.53–1.42 (m, 2H), 0.97–0.89 (m, 3H).

(E): $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.6, 135.2, 130.7, 129.3, 127.0, 126.5, 35.2, 22.7, 16.2, 13.9.


IR (neat, cm$^{-1}$): 2958, 2924, 2870, 1493, 1464, 1458, 1437, 1093, 966, 839, 793.
3. Synthesis of 4-(pent-1-en-1-yl)-1,1'-biphenyl (1f)

Follow the general procedure A, the title compound was isolated as a yellow solid by flash chromatography with ethyl acetate/petroleum ether (1:30) as an eluent (1.75 g, 79%).

\[ E/Z = 1/1.51 \]

(Z): \( ^1 \text{H NMR (400 MHz, CDCl}_3 \) δ 7.62–7.50 (m, 4H), 7.45–7.29 (m, 5H), 6.47–6.37 (m, 1H), 5.74–5.64 (m, 1H), 2.41–2.31 (m, 2H), 1.55–1.44 (m, 2H), 0.96 (t, \( J = 7.6 \) Hz, 3H).

(E): \( ^1 \text{H NMR (400 MHz, CDCl}_3 \) δ 7.62–7.50 (m, 4H), 7.45–7.29 (m, 5H), 6.47–6.37 (m, 1H), 6.31–6.21 (m, 1H), 2.24–2.16 (m, 2H), 1.55–1.44 (m, 2H), 0.96 (t, \( J = 7.6 \) Hz, 3H).

(E): \( ^13 \text{C NMR (100 MHz, CDCl}_3 \) δ 141.0, 139.6, 137.1, 131.3, 129.6, 128.9, 127.31, 127.25, 127.0, 126.5, 35.3, 22.7, 14.0.

(Z): \( ^13 \text{C NMR (100 MHz, CDCl}_3 \) δ 141.0, 139.3, 137.0, 133.5, 129.4, 128.9, 128.5, 127.3, 127.1, 126.9, 31.0, 23.3, 14.0.

HRMS (APCI): Calcd for C\(_{17}\)H\(_{19}\) + [M+H]\(^+\): 223.1481; Found: 223.1481.

IR (neat, cm\(^{-1}\)): 2976, 2958, 2929, 1487, 1379, 1371, 1348, 1311, 1147, 1128, 764.

4. Synthesis of tert-butyldimethyl(4-(pent-1-en-1-yl)phenoxy)silane (1g)

\[
\begin{align*}
&\text{PhCHO} \\
&\text{1) TBSCI (1.1 eq), imidazole (1.15 eq)} \\
&\text{DCM, rt, overnight} \\
&\text{2) \(^{\beta}\text{BuLi (1.2 eq), THF, -78^\circ C - rt}} \\
&\text{\(^{\beta}\text{BuPh}_2\text{Br (1 eq)}} \\
&\text{TBSO} \\
&\text{1g}
\end{align*}
\]

Synthesis of S5: To a solution of 4-hydroxybenzaldehyde (1.18 g, 5 mmol) and
imidazole (0.630 g, 5.75 mmol) in dry CH$_2$Cl$_2$ (20 mL) was added TBSCl (1.32 g, 5.06 mmol) at ambient temperature. The reaction mixture was stirred for overnight. The reaction was quenched with H$_2$O, extracted with CH$_2$Cl$_2$, dried with Na$_2$SO$_4$, filtered and concentrated. The residue was purified by silica gel flash chromatography (PE/EtOAc= 20:1) to afford the desired product (1.21 g, 88%).

Synthesis of 1g: Follow the general procedure A, 1g was isolated as a colorless oil by flash chromatography with ethyl acetate/petroleum ether (1:30) as an eluent (0.98g, 81%).

$E/Z = 1/0.69.$

(Z): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.15 (d, $J = 7.5$ Hz, 2H), 6.76 (d, $J = 7.7$ Hz, 2H), 6.36–6.27 (m, 1H), 5.62–5.51 (m, 1H), 2.33–2.25 (m, 2H), 1.53–1.41 (m, 2H), 0.98 (s, 9H), 0.94 (t, $J = 7.5$ Hz, 3H), 0.20 (s, 6H).

(E): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.20 (d, $J = 8.2$ Hz, 2H), 6.79 (d, $J = 8.2$ Hz, 2H), 6.36–6.27 (m, 1H), 6.13–5.99 (m, 1H), 2.19–2.10 (m, 2H), 1.53–1.41 (m, 2H), 0.98 (s, 9H), 0.94 (t, $J = 7.5$ Hz, 3H), 0.18 (s, 6H).

(Z): $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.4, 131.6, 131.2, 130.0, 128.5, 119.8, 30.9, 25.9, 23.4, 18.4, 14.0, -4.3.

(E): $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.8, 131.5, 129.5, 129.0, 127.0, 120.3, 35.3, 25.9, 22.8, 18.4, 13.9, -4.3.


IR (neat, cm$^{-1}$): 2958, 2929, 1604, 1512, 1263, 1255, 916, 839, 781.

5. Synthesis of 2-(pent-1-en-1-yl)thiophene (1o)
Follow the general procedure A, the title compound was isolated as a colorless oil by flash chromatography with ethyl acetate/petroleum ether (1:20) as an eluent (1.23 g, 86%).

\[ E/Z = 1/1.74. \]

(Z): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.22 (d, J = 4.8 \text{ Hz}, 1\text{H}), 7.00–6.82 (m, 2\text{H}), 6.68–6.42 (m, 1\text{H}), 6.10–6.01 (m, 1\text{H}), 2.18–2.11 (m, 2\text{H}), 1.56–1.42 (m, 2\text{H}), 1.01–0.91 (m, 3\text{H}).\)

(Z): \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 141.0, 131.2, 127.1, 126.8, 125.0, 122.0, 31.5, 22.9, 14.1.\)

(E): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.06 (d, J = 5.1 \text{ Hz}, 1\text{H}), 7.00–6.82 (m, 2\text{H}), 6.68–6.42 (m, 1\text{H}), 5.63–5.51 (m, 1\text{H}), 2.43–2.35 (m, 2\text{H}), 1.56–1.42 (m, 2\text{H}), 1.01–0.91 (m, 3\text{H}).\)

(E): \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 143.3, 131.1, 127.3, 124.2, 123.3, 123.1, 35.1, 22.6, 13.9.\)

HRMS (APCI): Calcd for C\(_9\)H\(_{13}\)S\(^+\) [M+H]\(^+\): 153.0732; Found: 153.0732.

IR (neat, cm\(^{-1}\)): 2958, 2927, 2872, 1461, 1436, 1376, 955, 852, 827, 692.

6. **Synthesis of 4-(pent-1-en-1-yl)pyridine (1p)**

\[ \text{Follow the general procedure A, the title compound was isolated as a colorless oil by flash chromatography with ethyl acetate/petroleum ether (1:10) as an eluent (1.22 g, 88%).} \]

\[ E/Z = 1/1.30. \]
(Z): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.55 (d, $J = 6.1$ Hz, 2H), 7.15 (d, $J = 6.0$ Hz, 2H), 6.37–6.28 (m, 1H), 5.89–5.81 (m, 1H), 2.34–2.27 (m, 2H), 1.56–1.43 (m, 2H), 0.99–0.91 (m, 3H).

(Z): $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.7, 145.2, 137.2, 126.7, 123.5, 30.8, 22.9, 13.8.

(E): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.49 (d, $J = 6.1$ Hz, 2H), 7.19 (d, $J = 6.1$ Hz, 2H), 6.51–6.42 (m, 1H), 6.37–6.28 (m, 1H), 2.25–2.18 (m, 2H), 1.56–1.43 (m, 2H), 0.99–0.91 (m, 3H).

(E): $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.0, 145.3, 136.2, 127.9, 120.6, 35.1, 22.2, 13.8.


IR (neat, cm$^{-1}$): 2958, 2927, 2871, 2854, 1596, 1463, 1417, 966.

7. Synthesis of (4,8-dimethylnona-1,7-dien-1-yl)benzene (1q)

Follow the general procedure A, the title compound was isolated as a colorless oil by flash chromatography with petroleum ether as an eluent (1.98 g, 87%).

$E/Z = 1/0.45$.

(Z): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43–7.09 (m, 5H), 6.45 (d, $J = 11.9$ Hz, 1H), 5.72–5.63 (m, 1H), 5.14–5.05 (m, 1H), 2.38–2.29 (m, 1H), 2.10–1.90 (m, 4H), 1.68 (s, 3H), 1.61 (s, 3H), 1.46–1.31 (m, 1H), 1.23–1.13 (m, 1H), 0.93 (d, $J = 6.9$ Hz, 3H).

(Z): $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.0, 132.0, 129.8, 129.6, 128.9, 128.2, 126.5, 124.9, 36.9, 35.8, 33.5, 25.9, 25.7, 19.7, 17.8.
**Synthesis of (7-methoxyhept-1-en-1-yl)benzene (1s)**

**S4** was prepared by the general procedure B. To a solution of **S4** (0.95 g, 5 mmol) in dry THF (15 mL) was added NaH (0.21 g, 5.25 mmol) under 0 °C. The resulting suspension was stirred at ambient temperature for 30 min, followed by adding MeI (0.34 mL, 1.1 eq) dropwise. After completion of the starting material, the reaction was quenched with water and extracted by EtOAc (15 mL x 3). The organic layer was dried over anhydrous Na₂SO₄, filtered, concentrated and then purified by silica gel flash column chromatography (PE/EtOAc = 20:1) to provide the title compound as a colorless oil (0.90 g, 88%).

**IR (neat, cm⁻¹):** 2962, 2912, 2870, 2854, 1558, 1448, 1374, 964, 741, 692.

8. **Synthesis of (7-methoxyhept-1-en-1-yl)benzene (1s)**

**S4** was prepared by the general procedure B. To a solution of **S4** (0.95 g, 5 mmol) in dry THF (15 mL) was added NaH (0.21 g, 5.25 mmol) under 0 °C. The resulting suspension was stirred at ambient temperature for 30 min, followed by adding MeI (0.34 mL, 1.1 eq) dropwise. After completion of the starting material, the reaction was quenched with water and extracted by EtOAc (15 mL x 3). The organic layer was dried over anhydrous Na₂SO₄, filtered, concentrated and then purified by silica gel flash column chromatography (PE/EtOAc = 20:1) to provide the title compound as a colorless oil (0.90 g, 88%).

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**IR (neat, cm⁻¹):** 2962, 2912, 2870, 2854, 1558, 1448, 1374, 964, 741, 692.
(E): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37–7.15 (m, 5H), 6.43–6.33 (m, 1H), 6.26–6.16 (m, 1H), 3.36 (t, $J$ = 7.1 Hz, 2H), 3.32 (s, 3H), 2.15–2.12 (m, 2H), 1.64–1.54 (m, 2H), 1.53–1.44 (m, 2H), 1.44–1.34 (m, 2H).

(Z): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37–7.15 (m, 5H), 6.43–6.33 (m, 1H), 6.26–6.16 (m, 1H), 4.61–4.49 (m, 1H), 3.90–3.82 (m, 1H), 3.80–3.69 (m, 1H), 3.59–3.46 (m, 1H), 3.43–3.34 (m, 1H), 2.37–2.30 (m, 2H), 1.88–1.77 (m, 1H), 1.72–1.37 (m, 11H).

HRMS (APCI): Calcd for C$_{14}$H$_{21}$O$^+$ [M+H]$^+$: 205.1587; Found: 205.1587.

IR (neat, cm$^{-1}$): 2929, 2856, 2827, 1120, 964, 744, 692.

9. Synthesis of 2-((7-phenylhept-6-en-1-yl)oxy)tetrahydro-2H-pyran (1t)

S4 was prepared by the general procedure B. To a solution of S4 (380 mg, 2.0 mmol) and pyridinium $p$-toluenesulfonate (PPTS) (50.3 mg, 0.2 mmol) in CH$_2$Cl$_2$ (4 mL) was added 3,4-dihydro-2H-pyran (252 mg, 3.0 mmol) at room temperature. The reaction mixture was stirred for 12 h and concentrated under reduced pressure. The crude material was purified by silica gel chromatography (PE/EtOAc = 25/1) to afford the title compound a colorless oil (504 mg, 92%).

$E/Z = 1/0.26$.

(Z): $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.9, 131.1, 128.92, 128.85, 128.2, 126.5, 99.0, 67.7, 62.5, 30.0, 29.3, 28.7, 26.1, 26.0, 19.83, 19.81.
\( (E) : ^1H \text{NMR (400 MHz, CDCl}_3 \) \( \delta \) 7.37–7.15 (m, 5H), 6.43–6.34 (m, 1H), 6.26–6.17 (m, 1H), 4.61–4.49 (m, 1H), 3.90–3.82 (m, 1H), 3.80–3.69 (m, 1H), 3.59–3.46 (m, 1H), 3.43–3.34 (m, 1H), 2.25–2.30 (m, 2H), 1.88–1.77 (m, 1H), 1.72–1.37 (m, 11H).

\( (E) : ^13C \text{NMR (100 MHz, CDCl}_3 \) \( \delta \) 138.0, 133.1, 130.0, 128.6, 126.9, 126.0, 99.0, 67.7, 62.5, 33.1, 30.9, 29.7, 29.3, 26.0, 25.6, 19.8.


IR (neat, cm\(^{-1}\)) : 2958, 2929, 2856, 1639, 1255, 1103, 1049, 958.

10. Synthesis of 1-(4-styrylphenyl)propan-1-one (1ab)

Synthesis of S6: To a solution of BnPh\(_3\)Br (5.16 g, 12 mmol) in THF (30 mL) was added NaH (640 mg, 16 mmol) at 0 °C. The reaction mixture was stirred for 2 h. Then, 4-bromobenzaldehyde (1.46 g, 8 mmol) was added and stirred for 2 h. The mixture was quenched with saturated aqueous NH\(_4\)Cl and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The crude material was purified by silica gel chromatography (PE) to afford the title compound (1.69 g, 82%).

Synthesis of S7: To a solution of S6 (1.29 g, 5 mmol) in THF (30 mL) were added \(^{11}\)BuLi (1.2 eq) at \(-78 \) °C, and the resulting mixture was stirred 1 h. Then, propionaldehyde (319 mg, 5.5 mmol) was added and stirred at room temperature for
12 h. The mixture was quenched with saturated aqueous NH₄Cl and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification of the residue by column chromatograph (PE/EtOAc = 20/1) gave S7 (830 mg, 70%).

Synthesis of 1ab: To a solution of S7 (476 mg, 2 mmol) in dry CH₂Cl₂ (20 mL) was added PCC (647 mg, 3 mmol) at ambient temperature. The reaction mixture was stirred for 3 h. The reaction was quenched with H₂O, extracted with CH₂Cl₂, dried with Na₂SO₄, filtered and concentrated. The residue was purified by silica gel flash chromatography (PE/EtOAc= 30:1) to afford the desired product (396 mg, 84%). E/Z = 1/1.2. The data are in accordance with the literatures.¹⁵

11. Synthesis of 4-styrylphenyl pivalate (1ac)

Synthesis of S8: To a solution of 4-hydroxybenzaldehyde (1.89 g, 8 mmol) and imidazole (1.04 g, 9.2 mmol) in dry CH₂Cl₂ (20 mL) was added TBSCI (2.32 g, 8.8 mmol) at ambient temperature. The reaction mixture was stirred for overnight. The reaction was quenched with H₂O, extracted with CH₂Cl₂, dried with Na₂SO₄, filtered and concentrated. The residue was purified by silica gel flash chromatography (PE/EtOAc= 20:1) to afford the desired product (1.66 g, 88%).

Synthesis of S9: To a solution of BnPh₃Br (3.22 g, 12 mmol) in THF (30 mL) was added NaH (400 mg, 10 mmol) at 0 °C. The reaction mixture was stirred for 2 h. Then, S8 (1.18 g, 5 mmol) was added and stirred for 2 h. The mixture was quenched
with saturated aqueous NH₄Cl and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude material was purified by silica gel chromatography (PE) to afford the title compound (1.22 g, 79%).

Synthesis of S10: The S9 (1.24 g, 4 mmol) was dissolved in THF (15 mL) and cooled to 0 °C. TBAF (5 ml, 1.0 mol/L) was then added dropwise to the reaction mixture. After stirred for 2 h, the resulting suspension was diluted with EtOAc and quenched by saturated aqueous NH₄Cl. The mixture was extracted by EtOAc (10 mL x 3), dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (PE/EtOAc = 10:1) to afford the product as a colorless liquid (624 mg, 78%).

Synthesis of 1ac: To a solution of S10 (392 mg, 2 mmol), pivaloyl chloride (360 mg, 3 mmol) in dry CH₂Cl₂ (20 mL) was added Et₃N (1.5 eq) at 0 °C. The reaction mixture was stirred for 3 h. The reaction was quenched with H₂O, extracted with CH₂Cl₂, dried with Na₂SO₄, filtered and concentrated. The residue was purified by silica gel flash chromatography (PE/EtOAc= 30:1) to afford the desired product (454 mg, 81%). \( E/Z = 1/1 \). The data are in accordance with the literatures.¹⁶

12. Synthesis of (Z)-pent-1-en-1-ylbenzene (Z-1a)

A dried 50ml flask was added indobenzene (1.63 g, 8 mmol), Pd(PPh₃)₂Cl₂ (84 mg, 0.12mmol), CuI (46 mg, 0.24 mmol), triethylamine (2.02 g, 20 mmol) and THF (20 L). The flask was purged with nitrogen and 1-pentin (8.8 mmol) were added via
syringe. After the addition, the reaction mixture was stirred overnight at room temperature. The resulting mixture was filtered to remove the ammonium salt, and the filtrate was concentrated in vacuo. Purification of the residue by column chromatograph (petroleum ether) gave S6 (910 mg, 79%).

To a solution of S11 (576 mg, 4 mmol) and quinoline (0.14 ml, 1.20 mmol) in hexane (10 mL) was added 5% Lindlar catalyst (122.2 mg). The reaction flask was fitted with a balloon of hydrogen and stirred at room temperature, monitoring by TLC analysis upon completion (6 h), the reaction was filtered and concentrated in vacuo. Purification by flash column chromatography (eluent: CH2Cl2) afforded Z-1a (508.8 mg, 87%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl3) δ 7.38-7.15 (m, 5H), 6.41 (1H, d, $J = 11.5$ Hz), 5.70-5.62 (m, 1H), 2.35-2.27 (m, 2H), 1.53-1.44 (m, 2H), 0.93 (t, 3H, $J = 7.4$ Hz).

$^{13}$C NMR (100 MHz, CDCl3) δ 138.0, 133.1, 129.0, 128.9, 128.2, 126.5, 30.8, 23.3, 13.9.

These spectroscopic data match those previously reported.17

13. Synthesis of (E)-(3-methoxyprop-1-en-1-yl)benzene (E-1ad)

To a solution of S12 (0.67 g, 5 mmol) in dry THF (15 mL) was added NaH (0.21 g, 5.25 mmol) under 0 °C. The resulting suspension was stirred at ambient temperature for 30 min, followed by adding MeI (0.34 mL, 1.1 eq) dropwise. After completion of the starting material, the reaction was quenched with water and extracted by EtOAc (15 mL x 3). The organic layer was dried over anhydrous Na2SO4, filtered, concentrated and then purified by silica gel flash column chromatography (PE/EtOAc = 20:1) to provide the title compound as a colorless oil (0.64 g, 86%).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41-7.36 (m, 2H), 7.31 (t, $J = 7.5$ Hz, 1H), 7.26-7.20 (m, 2H), 6.61 (d, $J = 16.0$ Hz, 1H), 6.32-6.23 (m, 1H), 4.08 (d, $J = 6.6$ Hz, 2H), 3.38 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.8, 132.5, 128.7, 127.8, 126.6, 126.1, 73.2, 58.1.

These spectroscopic data match those previously reported.$^{18}$

4. References


5. Copies of $^1$H and $^{13}$C Spectra