Cobalt Catalyzed Stereodivergent Semi-hydrogenation of Alkynes using H$_2$O as the Hydrogen Source

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Table of Contents

1. General information ........................................................................................................S2
2. Optimization table for Z-selective transfer hydrogenation of 1a ........ S2
3. Optimization table for E-selective transfer hydrogenation of 1a ........ S3
4. General procedure ........................................................................................................S5
5. Control and deuterium labeling experiments ......................................................... S6
6. Characterization data of Z-alkene products ............................................................. S10
7. Characterization data of E-alkene products ............................................................. S14
8. Reference ....................................................................................................................... S19
9. NMR spectra ................................................................................................................. S20
1. General information

Unless stated otherwise, all reactions were carried out under argon atmosphere. \(^1\)H NMR spectra were recorded using a Bruker 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. \(^13\)C NMR spectra were obtained at 101 MHz and referenced to the internal solvent signals. Commercially available reagents and solvents were used without further purification unless indicated otherwise.

2. Optimization table for Z-selective transfer hydrogenation of 1a

Table S1

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Co]</th>
<th>Solvent</th>
<th>Metal</th>
<th>Temp((^\circ)C)</th>
<th>Time(h)</th>
<th>Yield(^b)</th>
<th>Z/E(^c)</th>
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<tbody>
<tr>
<td>1</td>
<td>CoI(_2)</td>
<td>CH(_3)CN</td>
<td>Zn</td>
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<td>48</td>
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<td>-</td>
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<td>76%</td>
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<td>60</td>
<td>72</td>
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<td>72</td>
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<td>-</td>
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<tr>
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<td>CoI(_2)</td>
<td>Toluene</td>
<td>Zn</td>
<td>60</td>
<td>72</td>
<td>trace</td>
<td>-</td>
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<tr>
<td>6</td>
<td>CoI(_2)</td>
<td>DMF</td>
<td>Zn</td>
<td>60</td>
<td>72</td>
<td>trace</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>CoI(_2)</td>
<td>DMSO</td>
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<td>72</td>
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<td>-</td>
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<td>Metal</td>
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<td>Temp (°C)</td>
<td>Time (h)</td>
<td>Yield</td>
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**3. Optimization table for E-selective transfer hydrogenation of 1a**

**Table S2**

**Reaction Conditions:** 1a (0.2 mmol), [Co] (0.01 mmol), Zn powder (0.6 mmol), H₂O (2 mmol) in solvent (2 mL). The total yield of Z and E-alkenes was determined by ¹H NMR spectroscopy using 1,3-benzodioxole as internal standard. The Z/E ratio was determined by ¹H NMR spectroscopy using 1,3-benzodioxole as internal standard. ²Added 0.02 mmol CoI₂. ³Added 0.4 mmol Zn powder. ⁴Added 0.8 mmol Zn powder. ⁵Added 1 mmol H₂O. ⁶Added 3 mmol H₂O.
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<th>Entry</th>
<th>Catalyst</th>
<th>Ligand</th>
<th>Solvent</th>
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<th>Time (min)</th>
<th>Yield (%)</th>
<th>Ratio</th>
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<td>CH₃CN</td>
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<tr>
<td>29</td>
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<td>dppe</td>
<td>Zn</td>
<td>CH₃CN</td>
<td>60</td>
<td>12</td>
<td>98%</td>
</tr>
</tbody>
</table>

*Reaction conditions: 1a (0.2 mmol), [Co] (0.01 mmol), ligand (0.012 mmol), Zn powder (0.6 mmol), H₂O (2 mmol) in solvent (2 mL). bThe total yield of Z and E-alkenes was determined by ¹H NMR spectroscopy using 1,3-benzodioxole as internal standard. *The Z/E ratio was determined by ¹H NMR spectroscopy using 1,3-benzodioxole as internal standard. dAdded 0.024 mmol PPh₃. eAdded 0.4 mmol Zn powder. fAdded 0.8 mmol Zn powder. gAdded 1 mmol H₂O. hAdded 3 mmol H₂O.
4. General procedure

a) General procedure for the transfer semi-hydrogenation of internal alkynes 
affording cis-alkene: Under argon atmosphere, CoI₂ (3.1 mg, 0.01 mmol, 5 mol%), Zinc powder (39.2 mg, 0.6 mmol, 3.0 equiv), alkyne (0.2 mmol), H₂O (36 μL, 2 mmol, 10.0 equiv) and methanol (2 mL) were added sequentially to a 25 mL Schlenk tube equipped with a magnetic stir bar. The reaction was stirred for 72-84 hour at 60 °C. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give cis-alkene product. The yield and Z/E ratios were determined by ¹H NMR spectroscopy using 1,3-benzodioxole as internal standard.

b) General procedure for the transfer semi-hydrogenation of internal alkynes 
affording trans-alkene: Under argon atmosphere, CoI₂ (3.1 mg, 0.01 mmol, 5 mol%), dppe (4.8 mg, 0.012 mmol, 6 mol%) and acetonitrile (1 mL) were added sequentially to a 25 mL Schlenk tube equipped with a magnetic stir bar. The reaction was stirred for 0.5 hour at room temperature, and then Zinc powder (39.2 mg, 0.6 mmol, 3.0 equiv), alkyne (0.2 mmol), H₂O (36 μL, 2 mmol, 10.0 equiv), and acetonitrile (1 mL) were added sequentially to the reaction. Finally the reaction was stirred for 10-12 hour at 60 °C. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give trans-alkene product, the yield and Z/E ratios are determined by ¹H NMR spectroscopy using 1,3-benzodioxole as internal standard.

c) General procedure for the preparation of internal alkynes¹

\[
\begin{align*}
\text{R}^1 \text{H} \text{R}^2 \text{X} + \text{Ph} & \xrightarrow{\text{PdCl}_2, \text{PPh}_3, \text{CuI}} \text{Et}_3 \text{N/THF,rt or 80°C} \\
\text{R}^1 & \text{Ph} \text{R}^2 \text{X} \\
\text{X} = & \text{Br, I}
\end{align*}
\]

The corresponding aryl bromide or aryl iodide (3 mmol, 1 equiv), PdCl₂ (10.6 mg, 0.06 mmol, 2 mol%), PPh₃ (47.2 mg 0.18 mmol, 6 mol%), CuI (11.4 mg, 0.06 mmol, 2 mol%) and phenylacetylene (3.3 mmol, 1.1 equiv) were added to a 50 mL Schlenk flask with a stir bar under nitrogen atmosphere. Then tetrahydrofuran (5 mL) and triethylamine (5 mL) were added
sequentially. The reaction mixture was then stirred at room temperature or 80 °C overnight. Afterwards, 10 mL of water was added and the reaction mixture was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine and dried over Na₂SO₄. After filtration, the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of petroleum ether or ethyl acetate/petroleum ether to give internal alkyne substrates. The yields were not optimized for the synthesis of alkynes.

**d) Synthesis of E-resveratrol**

For the synthesis of E-resveratrol, 1,3-dimethoxy-5-((4-methoxyphenyl)ethynyl)benzene 4 was reduced to the E-alkene intermediate 5 using our standard catalytic system for the E-selective transfer hydrogenation of alkynes. Then 5 (0.3 mmol) was demethylated using BBr₃ (1.2 mmol) in DCM according to the procedure provided in the literature² and the final product E-resveratrol (6) was obtained in 82% yield (56.1 mg, white solid).

**5. Control and deuterium labeling experiments**

According to the general procedure for the transfer semi-hydrogenation of internal alkynes, using D₂O instead of H₂O, using CD₃OD or CD₃OH or CH₃OD instead of CH₃OH, deuteration experiments were carried out. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with petroleum ether to give alkene product or alkene deuterated product.
Table S3: Control and deuterium labeling experiments

1a (0.2 mmol)

Co₂ (5 mol%) Zn (3 equiv)
MeOH, 60 °C, 84h
No H₂O
Trace (GC-MS)

1a (0.2 mmol)

Co₂ (5 mol%) Zn (3 equiv)
MeOH, 60 °C, 84h
H₂ (1 atm)
Trace (GC-MS)

1a (0.2 mmol)

Co₂ (5 mol%) Zn (3 equiv)
MeOH, 60 °C, 96h
D₂O (10 equiv)
82% isolated yield

1a (0.2 mmol)

Co₂ (5 mol%) Zn (3 equiv)
H₂O (10 equiv)
CD₃OD, 60 °C, 96h
88% isolated yield
d

1a (0.2 mmol)

Co₂ (5 mol%) Zn (3 equiv)
H₂O (10 equiv)
CH₃OD, 60 °C, 120h
80% isolated yield
e

1a (0.2 mmol)

Co₂ (5 mol%) Zn (3 equiv)
D₂O (10 equiv)
CD₃OD, 60 °C, 120h
85% isolated yield (75% D incorporated)
f

1a (0.2 mmol)

Co₂ (5 mol%) Zn (3 equiv)
H₂O (10 equiv)
CD₃OH, 60 °C, 84h
84% isolated yield
g

1a (0.1 mmol)

Co₂ (5 mol%) Zn (3 equiv)
D₂O (10 equiv)
CD₃OH, 60 °C, 84h
80% isolated yield
h

1a (0.2 mmol)

Co₂ (5 mol%) dppa (6 mol%) Zn (3 equiv)
MeCN, 60 °C, 12h
D₂O (10 equiv)
(20%) D (45%)
(20%) D (20%)
i

Isolated yield: 86%

2a (Z)

Co₂ (5 mol%) dppa (6 mol%) Zn (3 equiv)
MeCN, 60 °C, 12h
H₂O (10 equiv)
No Z to E isomerization

2a (Z)

3a (E)

Co₂ (5 mol%) Zn (3 equiv)
MeOH, 60 °C, 84h
No E to Z isomerization

3a (E)
6. Characterization data of Z-alkene products

(Z)-1,2-diphenylethene

Yield: 98% (by NMR), colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.30 – 7.12 (m, 10H), 6.59 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 137.28, 130.30, 128.94, 128.28, 127.16.

(Z)-1-methyl-4-styrylbenzene

Yield: 95% (by NMR), colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 – 7.18 (m, 5H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.02 (d, $J = 7.9$ Hz, 2H), 6.55 (s, 2H), 2.31 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.51, 136.90, 130.22, 129.57, 129.03 – 128.71, 128.22, 127.00, 21.28.

(Z)-1-methyl-3-styrylbenzene

Yield: 97% (by NMR), colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27 – 7.17 (m, 5H), 7.14 – 6.96 (m, 4H), 6.56 (s, 2H), 2.25 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.82, 137.28, 130.39, 130.10, 129.64, 128.92, 128.16, 127.89, 127.09, 125.90, 21.40.

(Z)-1-methyl-2-styrylbenzene

Yield: 70% (by NMR), colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 – 7.09 (m, 8H), 7.05 (t, $J = 7.8$ Hz, 1H), 6.69 – 6.58 (m, 2H), 2.28 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.03, 136.09, 130.47, 130.04, 129.51, 128.87, 128.06, 127.10, 125.68, 19.88.
(Z)-1-ethyl-4-styrylbenzene

Yield: 95% (by NMR), colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 – 7.15 (m, 7H), 7.04 (d, $J = 8.3$ Hz, 2H), 6.55 (s, 2H), 2.60 (q, $J = 7.6$ Hz, 2H), 1.21 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.29, 137.56, 134.52, 130.26, 129.58, 128.89, 128.25, 127.73, 127.02, 28.64, 15.48.

(Z)-1-methoxy-4-styrylbenzene

Yield: 96% (by NMR), colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 – 7.14 (m, 7H), 6.74 (d, $J = 8.8$ Hz, 2H), 6.51 (s, 2H), 3.76 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.71, 137.56, 134.52, 130.26, 129.81, 128.83, 128.29, 126.96, 113.63, 55.22.

(Z)-1-((tert-butyl)-4-styrylbenzene

Yield: 81% (by NMR), colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 – 7.13 (m, 9H), 6.55 (s, 2H), 1.29 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.19, 137.63, 134.21, 130.12, 129.60, 128.61, 128.25, 127.00, 125.12, 34.58, 31.32.

(Z)-1-chloro-4-styrylbenzene

Yield: 92% (by NMR), colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26 – 7.14 (m, 9H), 6.57 (dd, $J = 39.6$, 12.2 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 136.87, 135.65, 132.75, 130.96, 130.24, 128.88, 128.40, 127.34.
(Z)-1-fluoro-4-styrylbenzene

Yield: 95% (by NMR), colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 – 7.16 (m, 7H), 6.90 (t, $J$ = 8.8 Hz, 2H), 6.56 (q, $J$ = 12.2 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.06, 160.60, 130.55, 130.27, 129.09, 128.84, 128.33, 127.22, 115.28, 115.07.

(Z)-1-bromo-4-styrylbenzene

Yield: 98% (by NMR), colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 (d, $J$ = 8.4 Hz, 2H), 7.26 – 7.18 (m, 5H), 7.10 (d, $J$ = 8.3 Hz, 2H), 6.56 (dd, $J$ = 52.0, 12.2 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 136.85, 136.13, 131.40, 131.06, 130.58, 128.90, 128.40, 127.39, 120.97.

(Z)-1-styryl-4-(trifluoromethyl)benzene

Yield: 50% (by NMR), white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J$ = 8.2 Hz, 2H), 7.33 (d, $J$ = 8.3 Hz, 2H), 7.26 – 7.19 (m, 5H), 6.65 (dd, $J$ = 50.9, 12.3 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.90, 136.54, 132.33, 129.15, 128.79, 128.44, 127.59, 125.17 122.84.

(Z)-2-styrylthiophene

Yield: 54% (by NMR), faint yellow liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.29 (m, 5H), 7.09 (d, $J$ = 5.2 Hz, 1H), 6.97 (d, $J$ = 3.5 Hz, 1H), 6.89 (dd, $J$ = 5.0, 3.6 Hz, 1H), 6.64 (dd, $J$ = 49.4, 12.0 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.76, 137.34, 128.84, 128.52, 128.15, 127.51, 126.42, 125.52, 123.35.
methyl (Z)-4-styrylbenzoate\(^1\)

![Chemical structure of methyl (Z)-4-styrylbenzoate](image)

Yield: 94\% (by NMR), colorless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\))  δ 7.89 (d, \(J = 8.4\) Hz, 2H), 7.30 (d, \(J = 8.1\) Hz, 2H), 7.21 (d, \(J = 1.9\) Hz, 5H), 6.65 (dd, \(J = 41.3, 12.3\) Hz, 2H), 3.88 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\))  δ 166.94, 142.13, 136.68, 132.26, 129.57, 129.24, 128.90, 128.59, 128.39, 127.56, 52.10.

(Z)-4-styrylbenzonitrile\(^1\)

![Chemical structure of (Z)-4-styrylbenzonitrile](image)

Yield: 21\% (by NMR), yellow solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\))  δ 7.50 (d, \(J = 8.2\) Hz, 2H), 7.32 (d, \(J = 8.2\) Hz, 2H), 7.26 – 7.17 (m, 5H), 6.67 (dd, \(J = 77.6, 12.2\) Hz, 2H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\))  δ 141.04, 135.18, 132.28, 130.99, 128.50, 127.73, 127.40, 126.79 (s), 117.94, 109.41.

(Z)-4-styrylphenol\(^5\)

![Chemical structure of (Z)-4-styrylphenol](image)

Yield: 64\% (by NMR), white solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\))  δ 7.29 – 7.21 (m, 5H), 7.14 (d, \(J = 8.6\) Hz, 2H), 6.69 (d, \(J = 8.7\) Hz, 2H), 6.52 (s, 2H), 4.91 (s, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\))  δ 153.51, 136.49, 129.32, 128.63, 127.80, 127.20, 125.89, 114.04.

(Z)-4-styrylaniline\(^1\)

![Chemical structure of (Z)-4-styrylaniline](image)

Yield: 78\% (by NMR), faint yellow liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\))  δ 7.32 – 7.16 (m, 5H), 7.07 (d, \(J = 8.4\) Hz, 2H), 6.56 – 6.50 (m, 2H), 6.45 (q, \(J = 12.2\) Hz, 2H), 3.61 (s, 2H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\))  δ 145.46, 137.93, 130.11, 128.78, 128.15, 127.58, 126.68, 114.67.
methyl (Z)-3-phenylacrylate

\[
\begin{align*}
&\text{COOMe} \\
&2q
\end{align*}
\]

Yield: 55% (by NMR), colorless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.60 (dd, J = 7.5, 1.7 \text{ Hz}, 2H), 7.38 – 7.33 \text{ (m, 3H)}, 6.97 \text{ (d, } J = 12.6 \text{ Hz, 1H), 5.97 \text{ (d, } J = 12.6 \text{ Hz, 1H), 3.72 \text{ (s, 3H).}}\)

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 165.58, 142.42, 133.69, 128.67, 128.06, 127.01, 118.22, 50.38.\)

\((Z)\)-dodec-6-ene

\[
\begin{align*}
&\text{} \\
&2r
\end{align*}
\]

Yield: 93% (by NMR), colorless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 5.35 \text{ (t, } J = 4.6 \text{ Hz, 2H), 2.02 \text{ (dd, } J = 12.4, 6.7 \text{ Hz, 4H), 1.36 – 1.25 \text{ (m, 12H), 0.89 \text{ (t, } J = 6.8 \text{ Hz, 6H).}}\)

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 129.92, 31.55, 29.48, 27.19, 22.60, 14.10.\)

7. Characterization data of E-alkene products

\((E)\)-1,2-diphenylethene

\[
\begin{align*}
&\text{} \\
&3a
\end{align*}
\]

Yield: 99% (by NMR), white solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.50 \text{ (d, } J = 7.7 \text{ Hz, 4H), 7.34 \text{ (t, } J = 7.6 \text{ Hz, 4H), 7.25 \text{ (dd, } J = 8.4, 6.2 \text{ Hz, 2H), 7.10 \text{ (d, } J = 2.4 \text{ Hz, 2H).}}\)

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 137.39, 128.78, 127.72, 126.61.\)

\((E)\)-1-methyl-4-styrylbenzene

\[
\begin{align*}
&\text{} \\
&3b
\end{align*}
\]

Yield: 99% (by NMR), white solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.51 – 7.45 \text{ (m, 2H), 7.40 \text{ (d, } J = 8.0 \text{ Hz, 2H), 7.33 \text{ (t, } J = 7.6 \text{ Hz, 2H), 7.26 – 7.20 \text{ (m, 1H), 7.15 \text{ (d, } J = 7.8 \text{ Hz, 2H), 7.06 \text{ (d, } J = 2.3 \text{ Hz, 2H), 2.34 \text{ (s, 3H).}}\)

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 137.59, 134.60, 129.49, 128.71, 127.75, 127.49, 126.50, 21.36.\)
(E)-1-methyl-3-styrylbenzene

\[
\begin{array}{c}
\text{3c}
\end{array}
\]

Yield: 93% (by NMR), white solid.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.50 (dd, \(J = 8.2, 1.2\) Hz, 2H), 7.34 (dt, \(J = 10.7, 8.3\) Hz, 4H), 7.25 (dd, \(J = 11.3, 4.5\) Hz, 2H), 7.08 (d, \(J = 0.9\) Hz, 3H), 2.37 (s, 3H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 138.28, 137.38, 128.68, 127.61, 127.27, 126.54, 123.77, 21.52.

(E)-1-methyl-2-styrylbenzene

\[
\begin{array}{c}
\text{3d}
\end{array}
\]

Yield: 94% (by NMR), colorless liquid.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.59 (d, \(J = 7.0\) Hz, 1H), 7.54 – 7.49 (m, 2H), 7.39 – 7.18 (m, 7H), 6.99 (d, \(J = 16.2\) Hz, 1H), 2.43 (s, 3H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 137.70, 136.43, 135.86, 130.45, 130.03, 128.73, 127.62, 126.58, 126.25, 125.39, 19.99.

(E)-1-ethyl-4-styrylbenzene

\[
\begin{array}{c}
\text{3e}
\end{array}
\]

Yield: 93% (by NMR), white solid.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.50 (dd, \(J = 8.2, 1.1\) Hz, 2H), 7.44 (d, \(J = 8.2\) Hz, 2H), 7.34 (t, \(J = 7.6\) Hz, 2H), 7.26 – 7.17 (m, 3H), 7.08 (d, \(J = 3.3\) Hz, 2H), 2.65 (q, \(J = 7.6\) Hz, 2H), 1.24 (t, \(J = 7.6\) Hz, 3H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.99, 137.57, 134.84, 128.69, 128.26, 127.80, 127.46, 126.51, 28.71, 15.62.

(E)-1-methoxy-4-styrylbenzene

\[
\begin{array}{c}
\text{3f}
\end{array}
\]

Yield: 98% (by NMR), white solid.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.46 (dd, \(J = 14.5, 8.0\) Hz, 4H), 7.33 (t, \(J = 7.6\) Hz, 2H), 7.25 – 7.19 (m, 1H), 7.01 (dd, \(J = 38.4, 16.3\) Hz, 2H), 6.89 (d, \(J = 8.8\) Hz, 2H), 3.80 (s, 3H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 159.34, 137.68, 130.17, 128.71, 128.25, 127.78, 127.27, 126.64, 126.31, 114.17, 55.36.
(E)-1-(tert-butyl)-4-styrylbenzene

\[
\begin{align*}
\text{Yield: 90\% (by NMR), white solid.} \\
^1\text{H NMR (400 MHz, CDCl}_3) \delta 7.56 & - 7.47 (m, 4H), 7.44 - 7.35 (m, 4H), 7.28 (d, J = 7.3 Hz, 1H), 7.12 (d, J = 2.7 Hz, 2H), 1.37 (s, 9H). \\
^13\text{C NMR (101 MHz, CDCl}_3) \delta 150.83, 137.58, 134.60, 128.62, 127.97, 127.47, 126.39, 125.67, 34.68, 31.35.
\end{align*}
\]

(E)-1-chloro-4-styrylbenzene

\[
\begin{align*}
\text{Yield: 95\% (by NMR), white solid.} \\
^1\text{H NMR (400 MHz, CDCl}_3) \delta 7.49 & (d, J = 7.2 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.38 - 7.24 (m, 5H), 7.04 (d, J = 2.9 Hz, 2H). \\
^13\text{C NMR (101 MHz, CDCl}_3) \delta 137.01, 135.87, 133.20, 129.33, 128.84, 127.93, 127.71, 127.39, 126.60.
\end{align*}
\]

(E)-1-fluoro-4-styrylbenzene

\[
\begin{align*}
\text{Yield: 97\% (by NMR), white solid.} \\
^1\text{H NMR (400 MHz, CDCl}_3) \delta 7.48 & (td, J = 8.5, 3.4 Hz, 4H), 7.35 (dd, J = 8.2, 6.9 Hz, 2H), 7.28 - 7.23 (m, 1H), 7.10 - 6.97 (m, 4H). \\
^13\text{C NMR (101 MHz, CDCl}_3) \delta 163.59, 161.14, 137.19, 133.53, 128.76, 128.50, 128.02, 127.72, 127.50, 126.48, 115.77, 115.56.
\end{align*}
\]

(E)-1-bromo-4-styrylbenzene

\[
\begin{align*}
\text{Yield: 70\% (by NMR), white solid.} \\
^1\text{H NMR (400 MHz, CDCl}_3) \delta 7.56 & - 7.45 (m, 4H), 7.38 (dd, J = 8.1, 6.2 Hz, 4H), 7.32 - 7.26 (m, 1H), 7.07 (q, J = 16.3 Hz, 2H). \\
^13\text{C NMR (101 MHz, CDCl}_3) \delta 136.91, 136.23, 131.75, 129.38, 128.73, 127.92, 127.36, 126.54, 121.29.
\end{align*}
\]
(E)-1-styryl-4-(trifluoromethyl)benzene

![Chemical Structure]

Yield: 95% (by NMR), white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (s, 4H), 7.57 – 7.53 (m, 2H), 7.40 (t, $J$ = 7.4 Hz, 2H), 7.32 (t, $J$ = 7.3 Hz, 1H), 7.17 (q, $J$ = 16.4 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.81, 136.64, 131.2, 128.84, 128.33, 127.13, 126.81, 126.60, 125.66.

(E)-2-styrylthiophene

![Chemical Structure]

Yield: 76% (by NMR), faint yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (d, $J$ = 7.4 Hz, 2H), 7.35 (t, $J$ = 7.6 Hz, 2H), 7.26 – 7.18 (m, 3H), 7.07 (d, $J$ = 3.4 Hz, 1H), 7.01 (dd, $J$ = 5.0, 3.6 Hz, 1H), 6.93 (d, $J$ = 16.1 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.87, 136.94, 128.69, 128.30, 127.59, 126.19, 124.33, 121.76.

Methyl (E)-4-styrylbenzoate

![Chemical Structure]

Yield: 84% (by NMR), white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 (d, $J$ = 8.4 Hz, 2H), 7.55 (dd, $J$ = 11.3, 7.8 Hz, 4H), 7.38 (dd, $J$ = 8.1, 6.8 Hz, 2H), 7.31 (dt, $J$ = 9.4, 4.3 Hz, 1H), 7.17 (dd, $J$ = 38.3, 16.4 Hz, 2H), 3.93 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.92, 141.83, 136.75, 131.24, 130.06, 128.82, 128.28, 127.57, 126.82, 126.35, 52.13.

(E)-4-styrylbenzonitrile

![Chemical Structure]

Yield: 79% (by NMR), white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (dd, $J$ = 21.9, 8.4 Hz, 4H), 7.54 (d, $J$ = 7.1 Hz, 2H), 7.39 (dd, $J$ = 8.1, 6.6 Hz, 2H), 7.33 (dt, $J$ = 9.5, 4.3 Hz, 1H), 7.15 (dd, $J$ = 51.5, 16.3 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.85, 136.30, 132.47, 128.90, 128.69, 127.05 – 126.64, 119.10, 110.57.
(E)-4-styrylphenol

\[ \text{H} \text{NMR (400 MHz, CDCl}_3\text{) } \delta 7.49 (d, J = 7.3 \text{ Hz, 2H}), 7.41 (d, J = 8.5 \text{ Hz, 2H}), 7.35 (t, J = 7.6 \text{ Hz, 2H}), 7.23 (d, J = 7.3 \text{ Hz, 1H}), 7.01 (q, J = 16.3 \text{ Hz, 2H}), 6.83 (d, J = 8.6 \text{ Hz, 2H}), 4.96 (s, 1H). \]

\[ \text{C NMR (101 MHz, CDCl}_3\text{) } \delta 155.24, 137.58, 130.34, 128.65, 128.02, 127.25, 126.67, 126.25, 115.61. \]

Yield: 92% (by NMR), faint yellow solid.

(E)-4-styrylaniline

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.47 (d, J = 7.4 \text{ Hz, 2H}), 7.33 (dd, J = 8.1, 6.6 \text{ Hz, 4H}), 7.21 (t, J = 7.4 \text{ Hz, 1H}), 6.97 (dd, J = 43.8, 16.3 \text{ Hz, 2H}), 6.67 (d, J = 8.5 \text{ Hz, 2H}), 3.73 (s, 2H). \]

\[ \text{C NMR (101 MHz, CDCl}_3\text{) } \delta 146.18, 137.96, 128.67, 127.78, 126.93, 126.13, 125.12, 115.23. \]

Yield: 73% (by NMR), faint yellow solid.

methyl cinnamate

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.70 (d, J = 16.0 \text{ Hz, 1H}), 7.56 – 7.47 (m, 2H), 7.42 – 7.31 (m, 3H), 6.44 (d, J = 16.0 \text{ Hz, 1H}), 3.80 (s, 3H). \]

\[ \text{C NMR (101 MHz, CDCl}_3\text{) } \delta 167.50, 144.95, 134.43, 130.38, 128.96, 128.15, 117.85, 51.77. \]

Yield: 24% (by NMR), white solid.

(E)-1,3-dimethoxy-5-(4-methoxystyryl)benzene

Isolated yield: 84%, yellow liquid.

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.44 (d, J = 8.7 \text{ Hz, 2H}), 7.04 (d, J = 16.3 \text{ Hz, 1H}), 6.94 – 6.84 (m, 3H), 6.65 (d, J = 2.2 \text{ Hz, 2H}), 6.37 (t, J = 2.2 \text{ Hz, 1H}), 3.82 (s, 9H). \]

\[ \text{C NMR (101 MHz, CDCl}_3\text{) } \delta 160.98, 159.41, 139.72, 129.92, 128.75, 127.84, 126.57, 114.16, 104.33, 99.62, 55.38. \]
(E)-5-(4-hydroxystyryl)benzene-1,3-diol

Isolated yield: 82%, white solid.

$^1$H NMR (400 MHz, MeOD) $\delta$ 7.31 (d, $J = 8.6$ Hz, 2H), 6.92 (d, $J = 16.3$ Hz, 1H), 6.75 (t, $J = 12.4$ Hz, 3H), 6.43 (d, $J = 2.1$ Hz, 2H), 6.14 (t, $J = 2.1$ Hz, 1H).

$^{13}$C NMR (101 MHz, MeOD) $\delta$ 159.63, 158.33, 141.37, 130.45, 129.46, 128.88, 127.01, 116.54, 105.85, 102.68.

8. Reference


9. NMR Spectra

- Spectra for compound 2a shown with chemical shifts.
\begin{align*}
\text{S35}
\end{align*}