# Cobalt Catalyzed Stereodivergent Semi-hydrogenation of Alkynes using H<sub>2</sub>O as the Hydrogen Source

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## 1. General information

Unless stated otherwise, all reactions were carried out under argon atmosphere. <sup>1</sup>H NMR spectra were recorded using a Bruker 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. <sup>13</sup>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<sup>a</sup>

$ \begin{array}{c c} \hline & \underline{[Co], Zn, H_2O} \\ \hline & \underline{Solvent, Temp} \\ 1a \\ \begin{array}{c} \hline & 2a (Z) \\ \hline & 3a (E) \\ \end{array} $									
Entry	[Co]	Solvent	Metal	Temp(°C)	Time(h)	Yield <sup>b</sup>	<b>Z/E</b> <sup>c</sup>		
1	CoI <sub>2</sub>	CH <sub>3</sub> CN	Zn	60	48	trace	-		
2	CoI <sub>2</sub>	CH <sub>3</sub> OH	Zn	60	48	76%	90:10		
					84	98%	90:10		
3	CoI <sub>2</sub>	1,4-dioxane	Zn	60	72	trace	-		
4	$CoI_2$	DCE	Zn	60	72	trace	-		
5	$CoI_2$	Toluene	Zn	60	72	trace	-		
6	CoI <sub>2</sub>	DMF	Zn	60	72	trace	-		
7	CoI <sub>2</sub>	DMSO	Zn	60	72	trace	-		
8	CoI <sub>2</sub>	THF	Zn	60	72	18%	-		
9 <sup>d</sup>	CoI <sub>2</sub>	CH <sub>3</sub> OH	Zn	60	78	98%	91: 9		
10	CoI <sub>2</sub>	EtOH	Zn	60	84	75%	90:10		
11	CoI <sub>2</sub>	<sup>i</sup> PrOH	Zn	60	84	37%	85:15		
12	CoI <sub>2</sub>	TFE	Zn	60	84	19%	-		
13	CoBr <sub>2</sub>	CH <sub>3</sub> OH	Zn	60	84	98%	87:13		
14	CoCl <sub>2</sub>	CH <sub>3</sub> OH	Zn	60	84	13%	-		

Table S1

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15	Co(OAc) <sub>2</sub>	CH <sub>3</sub> OH	Zn	60	84	63%	93: 7
16	Co(acac) <sub>2</sub>	CH <sub>3</sub> OH	Zn	60	84	trace	-
17	$CoI_2$	CH <sub>3</sub> OH	Zn	40	84	39%	84:16
18	$\mathrm{CoI}_2$	CH <sub>3</sub> OH	Zn	80	84	97%	90:10
19	$\mathrm{CoI}_2$	CH <sub>3</sub> OH	Mn	60	84	14%	-
20	$\mathrm{CoI}_2$	CH <sub>3</sub> OH	Fe	60	84	trace	-
21	$CoI_2$	CH <sub>3</sub> OH	Mg	60	84	trace	-
22 <sup>e</sup>	$CoI_2$	CH <sub>3</sub> OH	Zn	60	84	14%	-
$2^{\mathrm{f}}$	$\mathrm{CoI}_2$	CH <sub>3</sub> OH	Zn	60	72	98%	87:13
24 <sup>g</sup>	$\mathrm{CoI}_2$	CH <sub>3</sub> OH	Zn	60	84	19%	-
25 <sup>h</sup>	CoI <sub>2</sub>	CH <sub>3</sub> OH	Zn	60	84	10%	-

<sup>a</sup>Reaction Conditions: 1a (0.2 mmol), [Co] (0.01 mmol), Zn powder (0.6 mmol), H<sub>2</sub>O (2 mmol) in solvent (2 mL). <sup>b</sup>The total yield of Z and E-alkenes was determined by <sup>1</sup>H NMR spectroscopy using 1,3-benzodioxole as internal standard. "The Z/E ratio was determined by <sup>1</sup>H NMR spectroscopy using 1,3-benzodioxole as internal standard. <sup>d</sup>Added 0.02 mmol CoI<sub>2</sub>. <sup>e</sup>Added 0.4 mmol Zn powder. <sup>f</sup>Added 0.8 mmol Zn powder. <sup>g</sup>Added 1 mmol H<sub>2</sub>O. <sup>h</sup>Added 3 mmol H<sub>2</sub>O.

## 3. Optimization table for *E*-selective transfer hydrogenation of 1a<sup>a</sup>

Table S2

$ \begin{array}{c} \hline \\ 1a \\ \hline 2a (Z) \\ \hline 3a (E) \end{array} $									
Entry	[Co]	Ligand	Metal	Solvent	Temp(°C)	Time(h)	<b>Yield</b> <sup>b</sup>	<b>Z/E</b> <sup>c</sup>	
1	CoI <sub>2</sub> (dppp)	-	Zn	CH <sub>3</sub> CN	60	6	97%	12:88	
				CH <sub>3</sub> OH	60	72	trace	-	
$2^d$	$CoI_2$	PPh <sub>3</sub>	Zn	CH <sub>3</sub> CN	60	48	14%	-	
3	$CoI_2$	dppm	Zn	CH <sub>3</sub> CN	60	72	67%	23:77	
4	CoI <sub>2</sub>	dppe	Zn	CH <sub>3</sub> CN	60	10	99%	3:97	
5	CoI <sub>2</sub>	dppf	Zn	CH <sub>3</sub> CN	60	24	99%	55:45	

6	$CoI_2$	1,10-phen	Zn	CH <sub>3</sub> CN	60	72	49%	51:49
7	CoI <sub>2</sub>	( <u>+</u> )-BINAP	Zn	CH <sub>3</sub> CN	60	48	10%	-
8	CoI <sub>2</sub>	xantphos	Zn	CH <sub>3</sub> CN	60	24	99%	20:80
9	CoI <sub>2</sub>	dppb	Zn	CH <sub>3</sub> CN	60	72	95%	41:59
10	CoI <sub>2</sub>	dppen	Zn	CH <sub>3</sub> CN	60	36	99%	5 :95
11	CoI <sub>2</sub>	dppe	Zn	CH <sub>3</sub> OH	60	48	trace	-
12	CoI <sub>2</sub>	dppe	Zn	THF	60	48	77%	26:74
13	CoI <sub>2</sub>	dppe	Zn	1,4-dioxane	60	48	89%	20:80
14	$CoI_2$	dppe	Zn	Toluene	60	48	15%	-
15	$CoI_2$	dppe	Zn	DMSO	60	48	14%	-
16	$CoI_2$	dppe	Zn	DMF	60	48	63%	17:83
17	CoBr <sub>2</sub>	dppe	Zn	CH <sub>3</sub> CN	60	16	96%	3 :97
18	$CoCl_2$	dppe	Zn	CH <sub>3</sub> CN	60	18	95%	4 :96
19	Co(OAc) <sub>2</sub>	dppe	Zn	CH <sub>3</sub> CN	60	48	36%	49:51
20	Co(acac)₂	dppe	Zn	CH <sub>3</sub> CN	60	48	trace	-
21	$CoI_2$	dppe	Zn	CH <sub>3</sub> CN	40	48	58%	7 :93
22	$CoI_2$	dppe	Zn	CH <sub>3</sub> CN	80	8	99%	4 :96
23	CoI <sub>2</sub>	dppe	Mn	CH <sub>3</sub> CN	60	48	trace	-
24	$CoI_2$	dppe	Fe	CH <sub>3</sub> CN	60	48	trace	-
25	CoI <sub>2</sub>	dppe	Mg	CH <sub>3</sub> CN	60	48	trace	-
26 <sup>e</sup>	CoI <sub>2</sub>	dppe	Zn	CH <sub>3</sub> CN	60	24	80%	14:86
27 <sup>f</sup>	CoI <sub>2</sub>	dppe	Zn	CH <sub>3</sub> CN	60	10	99%	7 :93
28 <sup>g</sup>	CoI <sub>2</sub>	dppe	Zn	CH <sub>3</sub> CN	60	12	98%	4 :96
29 <sup>h</sup>	$CoI_2$	dppe	Zn	CH <sub>3</sub> CN	60	12	98%	7 :93

<sup>*a*</sup>*Reaction conditions:* **1a** (0.2 mmol), [Co] (0.01 mmol), ligand (0.012 mmol), Zn powder (0.6 mmol), H<sub>2</sub>O (2 mmol) in solvent (2 mL). <sup>*b*</sup>The total yield of *Z* and *E*-alkenes was determined by <sup>1</sup>H NMR spectroscopy using 1,3-benzodioxole as internal standard. <sup>*c*</sup>The *Z/E* ratio was determined by <sup>1</sup>H NMR spectroscopy using 1,3-benzodioxole as internal standard. <sup>*d*</sup>Added 0.024 mmol PPh<sub>3</sub>. <sup>*e*</sup>Added 0.4 mmol Zn powder. <sup>*f*</sup>Added 0.8 mmol Zn powder. <sup>*g*</sup>Added 1 mmol H<sub>2</sub>O. <sup>*h*</sup>Added 3 mmol H<sub>2</sub>O.

## 4. General procedure

- a) General procedure for the transfer semi-hydrogenation of internal alkynes affording *cis*-alkene: Under argon atmosphere, CoI<sub>2</sub> (3.1 mg, 0.01 mmol, 5 mol%), Zinc powder (39.2 mg, 0.6 mmol, 3.0 equiv), alkyne (0.2 mmol), H<sub>2</sub>O (36  $\mu$ L, 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 <sup>1</sup>H 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, CoI<sub>2</sub> (3.1mg, 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), H<sub>2</sub>O (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 <sup>1</sup>H NMR spectroscopy using 1,3-benzodioxole as internal standard.

#### c) General procedure for the preparation of internal alkynes<sup>1</sup>



The corresponding aryl bromide or aryl iodide (3 mmol, 1 equiv),  $PdCl_2$  (10.6 mg, 0.06 mmol, 2 mol%),  $PPh_3$  (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 ( $3 \times 10$  mL). The combined organic fractions were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. 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 BBr<sub>3</sub> (1.2 mmol) in DCM according to the procedure provided in the literature<sup>2</sup> 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  $D_2O$  instead of  $H_2O$ , using  $CD_3OD$  or  $CD_3OH$  or  $CH_3OD$  instead of  $CH_3OH$ , 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















## 6. Characterization data of Z-alkene products

## (Z)-1,2-diphenylethene<sup>1</sup>

2a

Yield: 98% (by NMR), colorless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.30 – 7.12 (m, 10H), 6.59 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 137.28, 130.30, 128.94, 128.28, 127.16.

## (Z)-1-methyl-4-styrylbenzene<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.51, 136.90, 130.22, 129.57, 129.03 – 128.71, 128.22, 127.00, 21.28.

## (Z)-1-methyl-3-styrylbenzene<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27 – 7.17 (m, 5H), 7.14 – 6.96 (m, 4H), 6.56 (s, 2H), 2.25 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 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<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 – 7.09 (m, 8H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.69 – 6.58 (m, 2H), 2.28 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 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<sup>3</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 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<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28 – 7.14 (m, 7H), 6.74 (d, J = 8.8 Hz, 2H), 6.51 (s, 2H), 3.76 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.71, 137.66, 130.21, 129.81, 128.83, 128.29, 126.96, 113.63, 55.22.

## (Z)-1-(tert-butyl)-4-styrylbenzene<sup>4</sup>



Yield: 81% (by NMR), colorless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 – 7.13 (m, 9H), 6.55 (s, 2H), 1.29 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.19, 137.63, 134.21, 130.12, 129.60, 128.85, 128.61, 128.25, 127.00, 125.12, 34.58, 31.32.

## (Z)-1-chloro-4-styrylbenzene<sup>1</sup>



Yield: 92% (by NMR), colorless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.26 – 7.14 (m, 9H), 6.57 (dd, *J* = 39.6, 12.2 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  136.87, 135.65, 132.75, 130.96, 130.24, 128.88, 128.40, 127.34.

### (Z)-1-fluoro-4-styrylbenzene<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 – 7.16 (m, 7H), 6.90 (t, *J* = 8.8 Hz, 2H), 6.56 (q, *J* = 12.2 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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<sup>5</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.85, 136.13, 131.40, 131.06, 130.58, 128.90, 128.40, 127.39, 120.97.

### (Z)-1-styryl-4-(trifluoromethyl)benzene<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.76, 137.34, 128.84, 128.52, 128.15, 127.51, 126.42, 125.52, 123.35.

### methyl (Z)-4-styrylbenzoate<sup>1</sup>



COOMe

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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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<sup>5</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.51, 136.49, 129.32, 128.63, 127.80, 127.20, 125.89, 114.04.

#### (Z)-4-styrylaniline<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.46, 137.93, 130.11, 128.78, 128.15, 127.58, 126.68, 114.67.

## methyl (Z)-3-phenylacrylate<sup>6</sup>

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

<sup>1</sup>H NMR (400 MHz, CDCl3) δ 7.60 (dd, J = 7.5, 1.7 Hz, 2H), 7.38 – 7.33 (m, 3H), 6.97 (d, J = 12.6 Hz, 1H), 5.97 (d, J = 12.6 Hz, 1H), 3.72 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl3) δ 165.58, 142.42, 133.69, 128.67, 128.06, 127.01, 118.22, 50.38.

## (Z)-dodec-6-ene<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.35 (t, *J* = 4.6 Hz, 2H), 2.02 (dd, *J* = 12.4, 6.7 Hz, 4H), 1.36 – 1.25 (m, 12H), 0.89 (t, *J* = 6.8 Hz, 6H).

 $^{13}\text{C}$  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<sup>1</sup>

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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 (d, J = 7.7 Hz, 4H), 7.34 (t, J = 7.6 Hz, 4H), 7.25 (dd, J = 8.4, 6.2 Hz, 2H), 7.10 (d, J = 2.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.39, 128.78, 127.72, 126.61.

## (E)-1-methyl-4-styrylbenzene<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51 – 7.45 (m, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.15 (d, J = 7.8 Hz, 2H), 7.06 (d, J = 2.3 Hz, 2H), 2.34 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.59, 134.60, 129.49, 128.71, 127.75, 127.49, 126.50, 21.36. (E)-1-methyl-3-styrylbenzene<sup>1</sup>



Yield: 93% (by NMR), white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.28, 137.38, 128.68, 127.61, 127.27, 126.54, 123.77, 21.52.

#### (*E*)-1-methyl-2-styrylbenzene<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 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<sup>7</sup>



Yield: 93% (by NMR), white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 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<sup>1</sup>



Yield: 98% (by NMR), white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 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<sup>8</sup>



Yield: 90% (by NMR), white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.83, 137.58, 134.60, 128.62, 127.97, 127.47, 126.39, 125.67, 34.68, 31.35.

#### (*E*)-1-chloro-4-styrylbenzene<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.01, 135.87, 133.20, 129.33, 128.84, 127.93, 127.71, 127.39, 126.60.

#### (*E*)-1-fluoro-4-styrylbenzene<sup>1</sup>



Yield: 97% (by NMR), white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.59, 161.14, 137.19, 133.53, 128.76, 128.50, 128.02, 127.72, 127.50, 126.48, 115.77, 115.56.

### (*E*)-1-bromo-4-styrylbenzene<sup>5</sup>



Yield: 70% (by NMR), white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.91, 136.23, 131.75, 129.38, 128.73, 127.92, 127.36, 126.54, 121.29.

(*E*)-1-styryl-4-(trifluoromethyl)benzene<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.81, 136.64, 131.2, 128.84, 128.33, 127.13, 126.81, 126.60, 125.66.

#### (*E*)-2-styrylthiophene<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.87, 136.94, 128.69, 128.30, 127.59, 126.19, 124.33, 121.76.

## methyl (E)-4-styrylbenzoate<sup>1</sup>



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

1H NMR (400 MHz, CDCl3)  $\delta$  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). 13C NMR (101 MHz, CDCl3)  $\delta$  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<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  141.85, 136.30, 132.47, 128.90, 128.69, 127.05 – 126.64, 119.10, 110.57. (*E*)-4-styrylphenol<sup>5</sup>

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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 (d, *J* = 7.3 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.01 (q, *J* = 16.3 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.96 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  155.24, 137.58, 130.34, 128.65, 128.02, 127.25, 126.67, 126.25, 115.61.

(E)-4-styrylaniline<sup>1</sup>



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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 (d, *J* = 7.4 Hz, 2H), 7.33 (dd, *J* = 8.1, 6.6 Hz, 4H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.97 (dd, *J* = 43.8, 16.3 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 2H), 3.73 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  146.18, 137.96, 128.67, 127.78, 126.93, 126.13, 125.12, 115.23.

### methyl cinnamate<sup>9</sup>

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

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d, *J* = 16.0 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.42 – 7.31 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H).

 $^{13}\text{C}$  NMR (101 MHz, CDCl\_3)  $\delta$  167.50, 144.95, 134.43, 130.38, 128.96, 128.15, 117.85, 51.77.

### (*E*)-1,3-dimethoxy-5-(4-methoxystyryl)benzene<sup>2</sup>



Isolated yield: 84%, yellow liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 16.3 Hz, 1H), 6.94 – 6.84 (m, 3H), 6.65 (d, J = 2.2 Hz, 2H), 6.37 (t, J = 2.2 Hz, 1H), 3.82 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 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<sup>2</sup>



Isolated yield: 82%, white solid.

<sup>1</sup>H NMR (400 MHz, MeOD) δ 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). <sup>13</sup>C NMR (101 MHz, MeOD) δ 159.63, 158.33, 141.37, 130.45, 129.46, 128.88, 127.01, 116.54,

105.85, 102.68.

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## 9. NMR Spectra















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