Supporting Information

Stereoselective Synthesis of Vinyl Iodides through Copper(I)-Catalyzed Finkelstein-Type Halide Exchange Reaction

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1. Synthesis of the Bromides

To a suspension of α,β-unsaturated aromatic carboxylic acid (20.0 mmol) and KBr (4.76 g, 40.0 mmol) a solution of Na$_2$MoO$_4$·2H$_2$O (242.0 mg, 1.0 mmol) in water (5.0 mL) and H$_2$O$_2$ (15.0 mL) was added dropwise at room temperature (25 °C). A rapid reaction took place and the temperature immediately rose to a high temperature within 30 min. The reaction mixture was stirred for a period time until it was cooled down. And then the product as well as the unreacted acid were extracted with CH$_2$Cl$_2$ (20 mL) for 3 times. The corresponding (E)-β-bromostyrene 1 was separated from the starting material by column chromatography in good yield.$^{[1]}$

\[ \text{Scheme S1. Preparation of (E)-β-bromostyrenes} \]

In a round-bottomed flask equipped with a magnetic stirring bar was charged with erythro-α,β-dibromo-β-phenylpropionionic acid (3.08 g, 10.0 mol), sodium azide (1.30 g, 20.0 mmol), and dry N,N-dimethylformamide (DMF, 50 mL). The reaction mixture was stirred at room temperature for 8 h and poured into a mixture of ether (30 mL) and water (30 mL). The organic layer was separated, washed with water (10 mL) for 3 times, and then was dried over magnesium sulfate. The corresponding (Z)-β-bromostyrene (1j) was separated from the starting material by column chromatography in good yield.$^{[2]}$

\[ \text{Scheme S2. Preparation of (Z)-β-bromostyrene} \]

**Preparation of Bromomethyltriphenylphosphonium Bromide:**

Triphenylphosphine (15.00 g, 57.25 mmol) and dibromomethane (19.92 g, 114.48 mmol) were dissolved in dried toluene (125 mL), and then the reaction mixture was refluxed for 7 days. After the reaction mixture was cooled to 0 °C, the crystal obtained was filtered and washed with toluene to yield the phosphonium salt (16.50 g, 66%) as a white solid.$^{[3]}$

To a cooled (-78 °C) suspension of bromomethyltriphenylphosphonium bromide (6.04 g, 13.85 mmol) in dried THF (60 mL) under nitrogen atmosphere, was added potassium tert-butoxide (1.55 g, 13.85 mmol). The resulting yellow mixture was stirred at the indicated temperature for 1 h. A solution of furfural (1.04 mL, 12.59 mmol) in dried THF (5
S3 mL) was then introduced via a syringe. The temperature was maintained at –78 °C, and the mixture was stirred for additional 5 h. The mixture was diluted with petroleum ether (80 mL), and filtered under reduced pressure. The residue obtained was purified by column chromatography (silica gel, 30% ethyl acetate in petroleum ether) to afford 2-(2-Bromovinyl)furan (1k, 1.02 g) as yellow oil with 1:1 ratio of Z-isomer to E-isomer.^[4]

\[
\text{Scheme S3. Preparation of 2-(2-bromovinyl)furan}
\]

To a cooled (-78 °C) suspension of bromomethyltriphenylphosphonium bromide (6.04 g, 13.85 mmol) in dried THF (60 mL) under nitrogen atmosphere, was added potassium tert-butoxide (1.55 g, 13.85 mmol). The resulting yellow mixture was stirred at the indicated temperature for 1 h. A solution of 3-phenylpropionaldehyde (1.67 mL, 12.59 mmol) in dried THF (5 mL) was then introduced via a syringe. The temperature was maintained at –78 °C, and the mixture was stirred for additional 5 h. The mixture was diluted with petroleum ether (80 mL), and filtered under reduced pressure. The residue obtained was purified by column chromatography (silica gel, petroleum ether) to afford (4-Bromobut-3-en-1-yl)benzene (1l, 1.28 g) as colorless oil with 3:1 ratio of Z-isomer to E-isomer.^[5]

\[
\text{Scheme S4. Preparation of (4-bromobut-3-en-1-yl)benzene}
\]

To a cooled (-78 °C) suspension of bromomethyltriphenylphosphonium bromide (6.04 g, 13.85 mmol) in dried THF (60 mL) under nitrogen atmosphere, was added potassium tert-butoxide (1.55 g, 13.85 mmol). The resulting yellow mixture was stirred at the indicated temperature for 1 h. A solution of 2-phenylpropionaldehyde (1.67 mL, 12.59 mmol) in dried THF (5 mL) was then introduced via a syringe. The temperature was maintained at –78 °C, and the mixture was stirred for additional 5 h. The mixture was diluted with petroleum ether (80 mL), and filtered under reduced pressure. The residue obtained was purified by column chromatography (silica gel, petroleum ether) to afford (3-bromo-1-methyl-2-propen-1-yl)benzene (1m, 1.22 g) as colorless oil with 1:1 ratio of Z-isomer to E-isomer.^[5]
2. Characterization Data

**(E)-β-Bromostyrene (1a)**\(^{[6]}\)

Yield: 75%, 2.75 g, colorless oil. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.30–7.21 (m, 5H), 7.05 (d, \(J = 14.0\) Hz, 1H), 6.70 (d, \(J = 14.0\) Hz, 1H).

**(E)-β-Bromo-4-methylstyrene (1b)**\(^{[6]}\)

Yield: 81%, 3.19 g, white solid. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.18(d, 2H), 7.12 (d, \(J = 8.0\) Hz, 2H), 7.05 (d, \(J = 14.0\) Hz, 1H), 6.69 (d, \(J = 14.0\) Hz, 1H), 2.32 (s, 3H).

**(E)-β-Bromo-4-methoxystyrene (1c)**\(^{[7]}\)

Yield: 83%, 3.54 g, white solid. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.12 (dd, \(J = 6.8, 2.0\) Hz, 2H), 6.95 (d, \(J = 14.0\) Hz, 1H), 6.77 (dd, \(J = 6.8, 2.0\) Hz, 2H), 6.51 (d, \(J = 14.0\) Hz, 1H), 3.70 (s, 3H).

**(E)-β-Bromo-3,4-dimethoxystyrene (1d)**\(^{[8]}\)

Yield: 70%, 3.40 g, white solid. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.03 (d, \(J = 14.0\) Hz, 1H), 6.86–6.80 (m, 3H), 6.62 (d, \(J = 14.0\) Hz, 1H), 3.91–3.88 (m, 6H).

**(E)-β-Bromo-3,4-methylene dioxy styrene (1e)**\(^{[8]}\)
Yield: 81%, 3.68 g, white solid. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 6.97 (d, $J = 14.0$ Hz, 1H), 6.78 (d, $J = 1.2$ Hz, 1H) 6.74–6.70 (m, 2H), 6.56 (d, $J = 14.0$ Hz, 1H), 5.93 (s, 2H).

**(E)-β-Bromo-4-fluorostyrene (1f)**

Yield: 72%, 2.89 g, yellowish solid. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.26–7.23 (m, 2H), 7.06–6.98 (m, 3H), 6.67 (d, $J = 14.4$ Hz, 1H).

**(E)-β-Bromo-4-chlorostyrene (1g)**

Yield: 74%, 3.22 g, white solid. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.28 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $J = 8.8$ Hz, 2H), 7.04 (d, $J = 14.4$ Hz, 1H), 6.75 (d, $J = 14.0$ Hz, 1H).

**(E)-β-Bromo-3-chlorostyrene (1h)**

Yield: 47%, 2.04 g, yellowish oil. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.29–7.25 (m, 3H), 7.18–7.15 (m, 1H), 7.05 (d, $J = 14.0$ Hz, 1H), 6.81 (d, $J = 14.0$ Hz, 1H).

**(E)-β-Bromo-2-chlorostyrene (1i)**

Yield: 65%, 2.83 g, yellowish oil. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.43 (d, $J = 14.0$ Hz, 1H), 7.34–7.30 (m, 2H), 7.20–7.17 (m, 2H), 6.74 (d, $J = 14.0$ Hz, 1H).

**(Z)-β-Bromostyrene (1j)**

Yield: 72%, 1.32 g, yellow oil. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.66 (d, $J = 6.8$ Hz, 2H), 7.36–7.27 (m, 3H), 7.02 (d, $J = 8.0$ Hz, 1H), 6.39 (d, $J = 8.0$ Hz, 1H).

**2-(2-Bromovinyl)furan (1k)**

Yield: 47%, 1.02 g, yellow oil. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.42 (d, $J = 1.6$ Hz, 1H),
7.34 (d, J = 1.2 Hz, 1H), 7.08 (d, J = 3.6 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 14.0 Hz, 1H), 6.70 (d, J = 14.0 Hz, 1H), 6.46 (dd, J = 3.6, 2.0 Hz, 1H), 6.35 (dd, J = 3.2, 1.6 Hz, 1H), 6.28 (d, J = 8.4 Hz, 1H), 6.23 (d, J = 3.2 Hz, 1H).

(4-Bromobut-3-en-1-yl)benzene (1l)\(^9\)

Yield: 48%, 1.28 g, colorless oil. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.34−7.13 (m, 10H), 6.22−6.14 (m, 2H), 6.11−6.00 (m, 2H), 2.74−2.67 (m, 4H), 2.54−2.49 (m, 3H), 2.33 (q, J = 7.6 Hz, 1H).

(3-bromo-1-methyl-2-propen-1-yl)benzene (1m)\(^10\)

Yield: 46%, 1.22 g, colorless oil. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.31−7.36 (m, 10H), 6.37−6.32 (m, 1H), 6.20−6.13 (m, 2H), 6.05−6.01 (d, J=13.6 Hz, 1H), 4.05−3.98 (m, 1H), 3.50−3.43 (m, 1H), 1.36(t, J = 7.2 Hz, 6H).

3. References

4. Copies of $^1$H NMR Spectra of Starting Materials

$^1$H NMR, 400 MHz, CDCl$_3$
$^{1}$H NMR, 400 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

![NMR Spectrum](image1)

![NMR Spectrum](image2)
\(^1\)H NMR, 400 MHz, CDCl\(_3\)

![NMR spectrum 1](image1)

\(^1\)H NMR, 400 MHz, CDCl\(_3\)

![NMR spectrum 2](image2)

\(^1\)H NMR, 400 MHz, CDCl\(_3\)

![NMR spectrum 3](image3)
$^1$H NMR, 400 MHz, CDCl$_3$
5. Copies of $^1$H and $^{13}$C NMR Spectra of Products

$^1$H NMR, 400 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
$^{13}$C NMR, 100 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
\begin{align*}
\text{\textsuperscript{13}C NMR, 100 MHz, CDCl\textsubscript{3}}\\
\text{49.42} & - \quad 144.53 & - \quad 131.02 \\
\text{77.40} & - \quad 78.77 & - \quad 55.84 \\
\end{align*}

\begin{align*}
\text{\textsuperscript{1}H NMR, 400 MHz, CDCl\textsubscript{3}}\\
7.32 & - \quad 6.791 & - \quad 6.639 & - \quad 6.596 \\
5.98 & - \quad 5.98 & - \quad 5.98 \\
4.21 & - \quad 4.871 & - \quad 4.914 & - \quad 4.914 \\
3.00 & - \quad 3.00 & - \quad 3.00 & - \quad 3.00 \\
1.00 & - \quad 1.00 & - \quad 1.00 & - \quad 1.00 \\
0.00 & - \quad 0.00 & - \quad 0.00 & - \quad 0.00 \\
\end{align*}
$^{13}$C NMR, 100 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$

S18
$^{13}$C NMR, 100 MHz, CDCl$_3$

![Carbon NMR spectrum]

$^1$H NMR, 400 MHz, CDCl$_3$

![Hydrogen NMR spectrum]
$^1$H NMR, 500 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$