Electronic Supplementary Information (ESI) for

**Rhodium acetate/base-catalyzed N-silylation of indole derivatives with hydrosilanes**

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**Experimental Details**

**General:** GC analyses were performed on Shimadzu GC-2014 with a FID detector equipped with a TC-1 or a TC-5 capillary column. Mass spectra were recorded on Shimadzu GCMS-QP2010 equipped with a TC-5HT or an InertCap 5MS/Sil capillary column. Liquid-state NMR spectra were recorded on a JEOL JNM-EX-270 (1H, 270.0 MHz; 13C, 67.80 MHz) or a JEOL ECA-500 (1H, 500.0 MHz; 13C, 124.50 MHz) spectrometer. CSI-MS spectra were measured with JEOL T 100-CS. Rh2(OAc)4 was obtained from Aldrich (reagent grade) and used as received. Other metal salts and complexes were obtained from Wako Pure Chemical Industries, Kanto Chemical, TCI, or Aldrich (reagent grade) and used as received. TBA2WO4 was prepared according to the literature procedure and handled in a glove box under Ar (O2 < 1.0 ppm, H2O < 1.0 ppm). Other bases were obtained from Kanto Chemical or TCI and used as received. Indoles, pyrrole, carbazole, and silanes were obtained from TCI and used as received. Acetonitrile was purified by The Ultimate Solvent System (Glass Contour Company). Other solvents (dehydrated grade) were obtained from Wako Pure Chemical Industries, Kanto Chemical, or Aldrich and used in a glove box.

**Typical procedure for N-silylation of indoles:** The catalytic N-silylation of indoles with silanes was carried out in a Schlenk tube. In a glove box, TBA2WO4 (10 μmol) was dissolved in acetonitrile (2 mL). To a mixture of Rh2(OAc)4 (5 μmol) and 1a (0.5 mmol) were added the...
acetonitrile solution of TBA$_2$WO$_4$ and 2a (2.5 mmol) under a continuous Ar flow. The reaction mixture was stirred at 50 °C for 2 h, and the progress was monitored by GC (>99% yield). The reaction mixture of 3aa was evaporated by a vacuum line, followed by the addition of hexane (2 mL) under a continuous Ar flow. The resulting yellow solution was subjected to flash column chromatography on silica gel using hexane to afford 3aa as colorless oils in 79% yield.

**Compound data**

**Compound 3aa (Table 1, entry 1)**

![Structure of 3aa]

CAS Registry Number: 1343516-53-9; $^1$H NMR (500.0 MHz, CDCl$_3$, TMS): 0.770 (s, 6H), 6.61 (d, $J$ = 2.8 Hz, 1H), 7.03–7.11 (m, 2H), 7.14 (d, $J$ = 2.8 Hz, 1H), 7.25 (d, $J$ = 7.9 Hz, 1H), 7.35 (t, $J$ = 7.4 Hz, 2H), 7.40 (t, $J$ = 7.4 Hz, 1H), 7.51 (d, $J$ = 6.2 Hz, 2H), 7.63 (d, $J$ = 7.9 Hz, 1H); $^{13}$C($^1$H) NMR (124.5 MHz, CDCl$_3$, TMS): −1.06, 105.3, 113.7, 120.3, 121.1, 121.8, 128.6, 130.6, 130.8, 132.0, 134.1, 135.6, 140.7; MS (EI) m/z (%): 252 (24), 251 (100) [M$^+$], 250 (33), 236 (31), 136 (14), 135 (99), 117 (10), 107 (11), 105 (11).

**Compound 3ab (Table 1, entry 2)**

![Structure of 3ab]

CAS Registry Number: 1343516-48-2; MS (EI) m/z (%): 314 (27), 313 (99) [M$^+$], 312 (22), 298 (10), 198 (17), 197 (100), 195 (12), 118 (12), 105 (14).

**Compound 3ac (Table 1, entry 3)**

![Structure of 3ac]

CAS Registry Number: 1256710-30-1; MS (EI) m/z (%): 376 (31), 375 (91) [M$^+$], 374 (15), 260 (24), 259 (100), 181 (22), 149 (18), 105 (12).
**Compound 3ad (Table 1, entry 4)**

![Chemical Structure](image)

CAS Registry Number: 1343516-56-2; \(^1\)H NMR (500.0 MHz, CDCl\(_3\), TMS): 0.964 (t, \(J = 7.4\) Hz, 9H), 1.05 (q, \(J = 7.9\) Hz, 6H), 6.60 (d, \(J = 3.4\) Hz, 1H), 7.10–7.17 (m, 3H), 7.49 (d, \(J = 7.9\) Hz, 1H), 7.64 (d, \(J = 7.4\) Hz, 1H); \(^{13}\)C\{\(^1\)H\} NMR (124.5 MHz, CDCl\(_3\), TMS): 4.59, 7.03, 104.9, 113.2, 120.2, 121.1, 121.7, 130.7, 131.8, 140.7; MS (EI) m/z (%): 232 (21), 231 (100) [M\(^+\)], 203 (25), 202 (76), 175 (17), 174 (91), 146 (57), 144 (12), 117 (13), 87 (27), 73 (10), 59 (17).

**Compound 3ae (Table 1, entry 5)**

![Chemical Structure](image)

CAS Registry Number: 40899-73-8; MS (EI) m/z (%): 231 (36) [M\(^+\)], 176 (10), 175 (47), 174 (100).

**Compound 3ba (Table 2, entry 2)**

![Chemical Structure](image)

CAS Registry Number: 1343516-54-0; \(^1\)H NMR (500.0 MHz, CDCl\(_3\), TMS): 0.835 (s, 6H), 2.33 (s, 3H), 6.34 (s, 1H), 6.96 (t, \(J = 7.9\) Hz, 1H), 7.04 (t, \(J = 7.4\) Hz, 1H), 7.25 (s, 1H), 7.33–7.42 (m, 3H), 7.47–7.50 (m, 3H); \(^{13}\)C\{\(^1\)H\} NMR (124.5 MHz, CDCl\(_3\), TMS): 1.71, 17.3, 106.3, 113.8, 119.7, 120.2, 120.8, 128.6, 130.3, 131.8, 133.8, 137.6, 142.0, 142.4; MS (EI) m/z (%): 266 (17), 265 (71) [M\(^+\)], 264 (10), 187 (20), 136 (14), 135 (100), 107 (10).

**Compound 3ca (Table 2, entry 3)**

![Chemical Structure](image)

\(^1\)H NMR (500.0 MHz, CDCl\(_3\), TMS): 0.373 (s, 6H), 6.59 (s, 1H), 7.02 (t, \(J = 7.6\) Hz, 1H), 7.11 (t, \(J = 7.6\) Hz, 1H), 7.26–7.40 (m, 9H), 7.48 (d, \(J = 6.8\) Hz, 2H), 7.61 (d, \(J = 8.0\) Hz, 1H); \(^{13}\)C\{\(^1\)H\} NMR (124.5 MHz, CDCl\(_3\), TMS): 1.25, 107.8, 115.0, 120.5, 120.7, 121.6, 128.2, 128.3, 128.5, 130.1, 130.2, 131.7, 133.7, 136.4, 137.9, 142.7, 146.5.
Compound 3da (Table 2, entry 4)

\[ \text{MeSiMe}_2\text{Ph} \]

\(^1\)H NMR (500.0 MHz, CDCl\(_3\), TMS): 0.753 (s, 6H), 2.31 (s, 3H), 6.90 (s, 1H), 7.05 (t, \(J = 7.4\) Hz, 1H), 7.10 (t, \(J = 7.4\) Hz, 1H), 7.20 (d, \(J = 6.8\) Hz, 2H), 7.35 (t, \(J = 6.8\) Hz, 2H), 7.40 (t, \(J = 6.8\) Hz, 1H), 7.52 (d, \(J = 7.4\) Hz, 2H), 7.55 (d, \(J = 7.4\) Hz, 1H); \(^{13}\)C\(^{\text{\(\text{H}\)}}\) NMR (124.5 MHz, CDCl\(_3\), TMS): −0.82, 10.0, 113.6, 114.2, 119.2, 119.8, 121.7, 128.0, 128.5, 130.5, 132.4, 134.2, 136.0, 141.1; MS (EI) \(m/z\) (%): 266 (25), 265 (100) \([M^+]\), 264 (31), 250 (19), 136 (13), 135 (94), 107 (10).

Compound 3ea (Table 2, entry 5)

\[ \text{MeSiMe}_2\text{Ph} \]

\(^1\)H NMR (500.0 MHz, CDCl\(_3\), TMS): 0.761 (s, 6H), 2.40 (s, 3H), 6.53 (d, \(J = 3.4\) Hz, 1H), 6.88 (dd, \(J = 1.4, 8.2\) Hz, 1H), 7.10−7.14 (m, 2H), 7.33−7.37 (m, 2H), 7.39−7.42 (m, 2H), 7.49 (dd, \(J = 1.7, 7.9\) Hz, 2H); \(^{13}\)C\(^{\text{\(\text{H}\)}}\) NMR (124.5 MHz, CDCl\(_3\), TMS): −1.07, 21.7, 104.9, 113.3, 120.8, 123.3, 128.5, 129.6, 130.6, 130.9, 132.3, 134.1, 135.8, 138.9; MS (EI) \(m/z\) (%): 266 (25), 265 (100) \([M^+]\), 264 (31), 250 (36), 136 (11), 135 (79), 107 (10).

Compound 3fa (Table 2, entry 6)

\[ \text{Cl} \quad \text{MeSiMe}_2\text{Ph} \]

\(^1\)H NMR (500.0 MHz, CDCl\(_3\), TMS): 0.779 (s, 6H), 6.55 (d, \(J = 2.8\) Hz, 1H), 6.99 (dd, \(J = 2.0, 8.8\) Hz, 1H), 7.11 (d, \(J = 9.1\) Hz, 1H), 7.17 (d, \(J = 3.4\) Hz, 1H), 7.38 (t, \(J = 7.0\) Hz, 2H), 7.44 (t, \(J = 7.4\) Hz, 1H), 7.50 (d, \(J = 6.8\) Hz, 2H), 7.58 (d, \(J = 2.3\) Hz, 1H); \(^{13}\)C\(^{\text{\(\text{H}\)}}\) NMR (124.5 MHz, CDCl\(_3\), TMS): −1.11, 105.0, 114.5, 120.5, 122.1, 126.1, 128.7, 130.8, 132.3, 133.1, 134.1, 135.2, 139.0.

Compound 3ga (Table 2, entry 7)

\[ \text{Br} \quad \text{MeSiMe}_2\text{Ph} \]

\(^1\)H NMR (500.0 MHz, CDCl\(_3\), TMS): 0.773 (s, 6H), 6.55 (d, \(J = 3.4\) Hz, 1H), 7.07 (d, \(J = 9.1\) Hz, 1H), 7.12 (d, \(J = 8.5\) Hz, 1H), 7.15 (d, \(J = 3.4\) Hz, 1H), 7.37 (t, \(J = 7.2\) Hz, 2H), 7.43 (t, \(J = 7.4\) Hz, 1H), 7.49 (d, \(J = 7.9\) Hz, 1H), 7.74 (s, 1H); \(^{13}\)C\(^{\text{\(\text{H}\)}}\) NMR (124.5 MHz, CDCl\(_3\),
TMS): −1.12, 104.9, 113.8, 115.0, 123.6, 124.6, 128.7, 130.8, 132.1, 133.8, 134.1, 135.1, 139.3; MS (EI) m/z (%): 331 (39) [M⁺], 330 (11), 329 (39) [M⁺], 136 (14), 135 (100).

**Compound 3ha (Table 2, entry 8)**

\[
\text{MeO} \quad \begin{array}{c}
\text{N} \\
\text{SiMe}_2\text{Ph}
\end{array}
\]

\^{1}H NMR (500.0 MHz, CDCl₃, TMS): 0.756 (s, 6H), 3.80 (s, 3H), 6.54 (d, \(J = 2.8\) Hz, 1H), 6.71 (dd, \(J = 2.5, 8.8\) Hz, 1H), 7.09−7.12 (m, 3H), 7.35 (t, \(J = 7.1\) Hz, 2H), 7.41 (tt, \(J = 2.5, 7.4\) Hz, 1H), 7.50 (dd, \(J = 1.1, 7.9\) Hz, 2H); \^{13}C\{\^{1}H\} NMR (124.5 MHz, CDCl₃, TMS): −1.07, 56.0, 102.9, 105.2, 111.8, 114.2, 128.5, 130.6, 131.6, 132.5, 134.1, 135.6, 135.7, 154.6; MS (EI) m/z (%): 282 (24), 281 (100) [M⁺], 266 (36), 136 (13), 135 (98), 107 (11).

**Compound 3ia (Table 2, entry 9)**

\[
\text{Me} \quad \begin{array}{c}
\text{N} \\
\text{SiMe}_2\text{Ph}
\end{array}
\]

\^{1}H NMR (500.0 MHz, CDCl₃, TMS): 0.796 (s, 6H), 2.27 (s, 3H), 6.65 (d, \(J = 2.9\) Hz, 1H), 6.86 (d, \(J = 7.4\) Hz, 1H), 7.03 (t, \(J = 7.4\) Hz, 1H), 7.30−7.33 (m, 3H), 7.36−7.41 (m, 3H), 7.50 (d, \(J = 7.9\) Hz, 1H); \^{13}C\{\^{1}H\} NMR (124.5 MHz, CDCl₃, TMS): 2.38, 21.9, 105.7, 118.8, 120.9, 123.1, 124.9, 128.6, 130.2, 132.5, 133.2, 133.4, 138.6, 140.5.

**Compound 5aa (Table 2, entry 10)**

\[
\text{SiMe}_2\text{Ph}
\]

\^{1}H NMR (500.0 MHz, CDCl₃, TMS): 0.681 (s, 6H), 6.34 (s, 2H), 6.79 (s, 2H), 7.35−7.43 (m, 3H), 7.47 (d, \(J = 6.8\) Hz, 2H); \^{13}C\{\^{1}H\} NMR (124.5 MHz, CDCl₃, TMS): −1.37, 111.4, 124.0, 128.4, 130.6, 134.0, 135.9; MS (EI) m/z (%): 202 (19), 201 (99) [M⁺], 200 (73), 187 (10), 186 (55), 184 (17), 136 (14), 135 (100), 107 (12), 105 (18), 93 (23).

**Compound 7aa (Table 2, entry 11)**

\[
\text{SiMe}_2\text{Ph}
\]

\^{1}H NMR (500.0 MHz, CDCl₃, TMS): 0.924 (s, 6H), 7.20−7.28 (m, 4H), 7.37 (t, \(J = 7.4\) Hz, 4H), 7.43 (t, \(J = 6.8\) Hz, 1H), 7.57 (d, \(J = 7.3\) Hz, 2H), 8.07 (d, \(J = 8.0\) Hz, 2H); \^{13}C\{\^{1}H\} NMR (124.5 MHz, CDCl₃, TMS): 0.87, 113.9, 120.0, 120.3, 125.7, 126.7, 128.7, 130.5, 134.1,
136.9, 144.7; MS (EI) \( m/z \) (%): 302 (21), 301 (82) \([M^+],\) 300 (12), 286 (18), 136 (14), 135 (100), 107 (10).

References


Table S1. N-Silylation of indole (1a) with dimethylphenylsilane (2a) using various metal catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh₂(OAc)₄</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2ᵇ</td>
<td>Rh₂(OAc)₄</td>
<td>83</td>
<td>83</td>
</tr>
<tr>
<td>3</td>
<td>Cu(OAc)₂·H₂O</td>
<td>&lt;1</td>
<td>nd</td>
</tr>
<tr>
<td>4</td>
<td>AgOAc</td>
<td>&lt;1</td>
<td>nd</td>
</tr>
<tr>
<td>5</td>
<td>AuBr₃</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>Pd(OAc)₂</td>
<td>&lt;1</td>
<td>nd</td>
</tr>
<tr>
<td>7</td>
<td>Co(OAc)₂·4H₂O</td>
<td>&lt;1</td>
<td>nd</td>
</tr>
<tr>
<td>8</td>
<td>Ni(OAc)₂·4H₂O</td>
<td>&lt;1</td>
<td>nd</td>
</tr>
<tr>
<td>9</td>
<td>Zn(OAc)₂·2H₂O</td>
<td>1</td>
<td>nd</td>
</tr>
<tr>
<td>10</td>
<td>Ru(acac)₃</td>
<td>&lt;1</td>
<td>nd</td>
</tr>
<tr>
<td>11</td>
<td><a href="OAc">Ru₃(μ₃-O)(OAc)₆(H₂O)₃</a></td>
<td>&lt;1</td>
<td>nd</td>
</tr>
<tr>
<td>12</td>
<td>[RuCl₂(p-cymene)]₂</td>
<td>1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>13</td>
<td>Pt(acac)₂</td>
<td>&lt;1</td>
<td>nd</td>
</tr>
<tr>
<td>14</td>
<td>Pt(OAc)₂·2AcOH</td>
<td>20</td>
<td>16</td>
</tr>
<tr>
<td>15</td>
<td>[IrCl₂Cp⁺]₂</td>
<td>&lt;1</td>
<td>nd</td>
</tr>
<tr>
<td>16</td>
<td>None</td>
<td>&lt;1</td>
<td>nd</td>
</tr>
</tbody>
</table>

ᵇ Reaction conditions: Metal catalyst (metal: 2 mol% with respect to 1a), TBA₂WO₄ (2 mol% with respect to 1a), 1a (0.5 mmol), 2a (2.5 mmol), CH₃CN (2 mL), Ar (1 atm), 50 °C, 2 h. Conversions and yields were based on 1a and determined by GC analysis. nd = not detected. ᵇ 2a (1.0 mmol).
Table S2. N-Silylation of indole (1a) with dimethylphenylsilane (2a) using various Rh-based catalysts

[Diagram of the N-silylation reaction]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh₂(OAc)₄</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>Rh₂(pfb)₄</td>
<td>25</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>RhCl₃·nH₂O</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>[RhCl₂(Cp*)₂]</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>[Rh(cod)Cl]₂</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>Rh(PPh₃)₃Cl</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>[Rh(CO)₂Cl]₂</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>Rh(OH)/TiO₂</td>
<td>&lt;1</td>
<td>nd</td>
</tr>
</tbody>
</table>

*a Reaction conditions: Rh-Based catalyst (Rh: 2 mol% with respect to 1a), TBA₂WO₄ (2 mol% with respect to 1a), 1a (0.5 mmol), 2a (2.5 mmol), CH₃CN (2 mL), Ar (1 atm), 50 °C, 2 h. Conversions and yields were based on 1a and determined by GC analysis. nd = not detected.*
Table S3. N-Silylation of indole (1a) with dimethylphenylsilane (2a) using various bases\textsuperscript{a}

\[
\begin{align*}
\text{Entry} & \quad \text{Base} & \quad \text{Conv. (\%)} & \quad \text{Yield (\%)} \\
1 & \text{TBA}_2\text{WO}_4 & >99 & >99 \\
2 & \text{KO}^\text{t}\text{-Bu} & 71 & 69 \\
3 & \text{K}_2\text{CO}_3 & 66 & 66 \\
4 & \text{TBAOH} & 63 & 63 \\
5 & \text{K}_3\text{PO}_4 & 34 & 33 \\
6 & \text{Cs}_2\text{CO}_3 & 17 & 13 \\
7 & \text{TBA}_4[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2] & 16 & 15 \\
8 & \text{TBA}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] & \text{nd} & \text{nd} \\
9 & \text{Et}_3\text{N} & <1 & \text{nd} \\
10 & \text{DBU} & 5 & 2 \\
11 & \text{None} & <1 & \text{nd} \\
\end{align*}
\]

\textsuperscript{a}Reaction conditions: Rh\textsubscript{2}(OAc)\textsubscript{4} (1 mol\% with respect to 1a), base (2 mol\% with respect to 1a), 1a (0.5 mmol), 2a (2.5 mmol), CH\textsubscript{3}CN (2 mL), Ar (1 atm), 50 °C, 2 h. Conversions and yields were based on 1a and determined by GC analysis. nd = not detected.
Table S4. Effect of solvents on the N-silylation of indole (1a) with dimethylphenylsilane (2a)*

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetonitrile</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>Benzonitrile</td>
<td>82</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>DMSO</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>4</td>
<td>DMF</td>
<td>26</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>DCE</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>6</td>
<td>Acetone</td>
<td>5</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

* Reaction conditions: Rh₂(OAc)₄ (1 mol% with respect to 1a), TBA₂WO₄ (2 mol% with respect to 1a), 1a (0.5 mmol), 2a (2.5 mmol), solvent (2 mL), Ar (1 atm), 50 °C, 2 h. Conversions and yields were based on 1a and determined by GC analysis. The hydrosilylation of acetone proceeded.
**Fig. S1** Positive ion CSI-MS spectra of a) TBA₂WO₄, b) Rh₂(OAc)₄, TBA₂WO₄, and 2a (Rh₂(OAc)₄:TBA₂WO₄=1:1:40), and c) Rh₂(OAc)₄ and TBA₂WO₄ (Rh₂(OAc)₄:TBA₂WO₄ = 1:1) in acetonitrile. The signal sets A, B, C, D, E, and F are possibly assignable to [TBA₃WO₄]⁺, [TBA₄(WO₄)₂]⁺, [TBA₂OAc]⁺, [TBA₂(PhMe₂Si)WO₄(PhMe₂SiOAc)]⁺, [TBA₂WO₄(Rh₂(OAc)₄)]⁺, and [TBA₂WO₄(Rh₂(OAc)₄)₂]⁺, respectively. The asterisk is probably due to Rh₂(OAc)₄ and/or the solvent. The lines in the inset are the calculated pattern for [TBA₂(PhMe₂Si)WO₄(PhMe₂SiOAc)]⁺.
Fig. S2 $^1$H NMR spectrum of Rh$_2$(OAc)$_4$ and 2a in acetonitrile-$d_3$. The signals A, B, and C are possibly assignable to H$_2$, the SiH proton of 2a, the OH proton of dimethylphenylsilanol, respectively. Conditions: Rh$_2$(OAc)$_4$ (25 mM), 2a (10 mM).
Fig. S3 $^1$H NMR spectra of a) 1a and b) 1a and TBA$_2$WO$_4$ in acetonitrile-$d_3$. Conditions: 1a (50 mM), TBA$_2$WO$_4$ (50 mM), −20 °C.
Scheme S1 Proposed catalytic cycle (Base = O-donor bases such as TBA₂WO₄, KOt-Bu, K₂CO₃, TBAOH, K₃PO₄, and Cs₂CO₃).