Supporting Information

Scalable Pinacol Coupling Reaction Utilizing Inorganic Electride
[Ca$_2$N]$^+$:e$^-$ as an Electron Donor

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General Methods

Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F254. $^1$H NMR spectra were recorded on a Varian at 500 MHz in CDCl$_3$ ($\delta$ 7.26 ppm) or DMSO-$d_6$ ($\delta$ 2.50 ppm), $^{13}$C NMR spectral measurements were performed at 125 MHz using CDCl$_3$ ($\delta$ 77.16 ppm) or DMSO-$d_6$($\delta$ 39.52 ppm). The terms m, s, d, t, q, quint., and sept. represent multiplet, singlet, doublet, triplet, quadruplet, quintuplet, and septet, respectively, and the term br means a broad signal. Commercial grade reagents and solvents were used without further purification.

The measurement of X-ray diffraction patterns for Ca(OMe)$_2$ was made over a 20 range from 5° to 40° along with a step size of 0.02° and scanning speed was set at 1° at 1°min$^{-1}$ with filtered Cu K$_\alpha$ radiation $\lambda$=0.15418 nm (Rigaku Smart Lab, Japan).

Ion chromatography was performed on Metrohm 833 IC plus with conductivity detector (solvent: 1.7mM HNO$_3$ + 0.7mM PDCA in DI water, temperature: room temperature, fluent speed : 0.9mL/min). Analytic sample was prepared by the following procedure: Each sample was taken from the individual reaction mixture using micro-glass filters. To make more accurate analysis, it diluted with deionized water (200 times less than in the original sample).

Synthesis of dicalcium nitride [Ca$_2$N]$^+$$^-$$e^{-}$ electride

A stoichiometric polycrystalline dicalcium nitride ([Ca$_2$N]$^+$$^-$$e^{-}$) was synthesized by the solid-state reaction of calcium nitride(Ca$_3$N$_2$) powders and calcium metals. Mixture of Ca$_3$N$_2$ powders and calcium chips at a molar ratio of 1:1 were pressed into a pellet form under pressure (20–30 MPa). The pellet was fully covered with molybdenum foil and annealed at 800 °C for 48 hrs under vacuum (~10$^{-3}$ Pa). Then, the sample was quenched into water. To improve homogeneity of dicalcium nitride [Ca$_2$N]$^+$$^-$$e^{-}$, the synthesized sample was ground into a powder in an agate mortar in nitrogen-filled glovebox and re-annealed under the same conditions.

Procedure for pinacol coupling reaction of aromatic aldehyde

Dicalcium nitride [Ca$_2$N]$^+$$^-$$e^{-}$ (94 mg, 1 mmol) was added to a suspension of aldehyde (0.5 mmol) in dry THF and MeOH in 1:1 mixture at room temperature. The reaction was stirred until TLC analysis indicated complete consumption of the starting material, and then the reaction mixture was quenched with water and 5% HCl and, extracted with EtOAc or Et$_2$O (5 mL×3). The combined organic layers were dried over MgSO$_4$ and concentrated under vacuum. The crude residue was purified by flash chromatography on silica gel (EtOAc/Hexanes) to give the corresponding 1,2-vic-diol.
Characterization Data for Products

1,2-Bis(4-chlorophenyl)ethane-1,2-diol (Table 2, Entry 1)

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{Cl} & \quad \text{Cl} \\
\text{2a}
\end{align*}
\]

The physical and spectral data were identical to those previously reported for this compound.\(^1\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(dl\) [\emph{meso}] \(\delta\): 6.95-7.31 (m, 8H), 4.60[4.82] (s, 2H); \(^1\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 137.93, 137.78, 133.88, 128.40, 128.36, 128.33, 78.55, 77.16 ppm.

1,2-Bis(4-fluorophenyl)ethane-1,2-diol (Table 2, Entry 2)

\[
\begin{align*}
\text{F} & \quad \text{F} \\
\text{2b}
\end{align*}
\]

The physical and spectral data were identical to those previously reported for this compound.\(^3\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(dl\) [\emph{meso}] \(\delta\): 6.85-7.20 (m, 8H), 4.61[4.82] (s, 2H); \(^1\)C NMR (125 MHz, CDCl\(_3\)) \(dl\) [\emph{meso}] \(\delta\): 162.55[162.63] (d, \(J = 175\) Hz), 135.48[135.31] (d, \(J = 2.5\) Hz), 128.76[128.82] (d, \(J = 6.25\) Hz), 115.21[115.20] (d, \(J = 15\) Hz), 78.86[77.39] ppm.

1,2-Bis(3-(trifluoromethyl)phenyl)ethane-1,2-diol (Table 2, Entry 3)

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{F} \\
\text{2c}
\end{align*}
\]

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(dl\) [\emph{meso}] \(\delta\): 7.25-7.62 (m, 8H), 5.70[5.63] (s, 2H), 4.85[4.71] (s, 2H) \(^1\)C NMR (125 MHz, DMSO-\(d_6\)) \(dl\) [\emph{meso}] \(\delta\): 143.32[144.22], 131.11[131.47], 128.13[128.36], 128.05 [128.24] (q, \(J = 22.5\) Hz), 124.38[124.43] (q, \(J = 193\) Hz), 123.53[123.76] (q, \(J = 2.5\) Hz), 123.35(q, \(J = 2.5\)Hz), 75.83[76.10] ppm.
1,2-Bis(3-bromophenyl)ethane-1,2-diol (Table 2, Entry 4)

![2d](image)

The physical and spectral data were identical to those previously reported for this compound.\(^3\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(dl\) [meso] \(\delta\): 6.89-7.47 (m, 8H), 4.60[4.77] (s, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(dl\) [meso] \(\delta\): 141.97[141.88], 131.36[131.37], 129.99[130.23], 129.84[129.83], 125.81[125.87], 122.56[122.53], 78.37[77.28] ppm.

1,2-Bis(3-chlorophenyl)ethane-1,2-diol (Table 2, Entry 5)

![2e](image)

The physical and spectral data were identical to those previously reported for this compound.\(^4\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(dl\) [meso] \(\delta\): 7.08-7.70 (m, 8H), 4.62[4.79] (s, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(dl\) [meso] \(\delta\): 141.59[141.49], 134.27[134.24], 129.45[129.42], 128.32, 126.96[127.19], 125.22[125.27], 77.20[78.32] ppm.

1,2-Bis(2-chlorophenyl)ethane-1,2-diol (Table 2, Entry 6)

![2f](image)

The physical and spectral data were identical to those previously reported for this compound.\(^3\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(dl\) [meso] \(\delta\): 7.08-7.70 (m, 8H), 5.58[5.34] (s, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(dl\) [meso] \(\delta\): 137.36[136.51], 132.74[133.50], 129.58[129.00], 129.29[129.25], 128.94[128.88], 73.12[72.21] ppm.
1,2-Diphenylethane-1,2-diol (Table 2, Entry 7)

![Chemical Structure](image)

The physical and spectral data were identical to those previously reported for this compound.\(^1\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(dl\) [meso] \(\delta\): 7.11-7.40 (m, 10H), 4.69[4.82] (s, 2H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)) \(dl\) [meso] \(\delta\): 139.96[139.88], 128.27[128.38], 128.07[128.25], 127.07[127.22], 79.24[78.23] ppm.

1,2-Di(naphthalene-2-yl)ethane-1,2-diol (Table 2, Entry 8)

![Chemical Structure](image)

The physical and spectral data were identical to those previously reported for this compound.\(^1\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(dl\) [meso] \(\delta\): 7.26-7.86 (m, 14H), 5.54[5.41] (s, 2H), 4.90[4.83] (s, 2H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 138.31, 131.90, 131.70, 126.83, 126.51, 126.19, 124.98, 124.83, 124.61, 124.55, 77.49 ppm.

1,2-Di-\(m\)-tolylethane-1,2-diol (Table 2, Entry 9)

![Chemical Structure](image)

The physical and spectral data were identical to those previously reported for this compound.\(^3\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(dl\) [meso] \(\delta\): 6.86-7.29 (m, 8H), 4.67[4.72] (s, 2H), 2.28[2.34] (s, 3H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)) \(dl\) [meso] \(\delta\): 140.09[140.07], 137.90[138.17], 128.74[129.11], 128.13[128.37], 127.58[127.92], 124.11[124.40], 78.92[78.38] ppm.
1,2-Bis(3-methoxyphenyl)ethane-1,2-diol (Table 2, Entry 10)

The physical and spectral data were identical to those previously reported for this compound.¹

¹¹H NMR (500 MHz, CDCl₃) dl [meso] δ: 6.64-7.31 (m, 8H), 4.65[4.77] (s, 2H), 3.70[3.73] (s, 6H); ¹³C NMR (125 MHz, CDCl₃) dl [meso] δ: 159.52[159.66], 141.64[141.53], 129.28[129.38], 119.37[119.57], 113.80[114.10], 112.33[112.41], 78.98[78.10], 55.31[55.33] ppm.

2,2,5,5-Tetramethylhexane-3,4-diol (Table 2, Entry 11)

The physical and spectral data were identical to those previously reported for this compound.⁵

¹¹H NMR (500 MHz, CDCl₃) dl [meso] δ: 3.33[3.25] (s, 2H), 0.91[1.01] (s, 18H); ¹³C NMR (125 MHz, CDCl₃) dl [meso] δ: 75.12[80.57], 35.39[35.84], 25.99[26.73] ppm.

2,3-Diphenylbutane-2,3-diol (Table 2, Entry 12)

The physical and spectral data were identical to those previously reported for this compound.²

¹¹H NMR (500 MHz, CDCl₃) dl [meso] δ: 7.14-7.30 (m, 10H), 2.57[2.27] (s, 2H), 1.50[1.58] (s, 6H); ¹³C NMR (125 MHz, CDCl₃) dl [meso] δ: 143.54[143.90], 127.50[127.43], 127.29[127.19], 127.05[127.04], 78.98[78.72], 25.09[25.25] ppm.
References

1,2-Bis(4-chlorophenyl)ethane-1,2-diol (Table 2, Entry1)
1,2-Bis(4-fluorophenyl)ethane-1,2-diol (Table 2, Entry 2)

[Chemical structure image]

[1H NMR spectrum]

[13C NMR spectrum]
1,2-Bis(3-(trifluoromethyl)phenyl)ethane-1,2-diol (Table 2, Entry 3)
1,2-Bis(3-bromophenyl)ethane-1,2diol (Table 2, Entry 4)
1,2-Bis(3-chlorophenyl)ethane-1,2-diol (Table 2, Entry 5)
1,2-Bis(2-chlorophenyl)ethane-1,2-diol (Table 2, Entry 6)
1,2-Diphenylethane-1,2diol (Table 2, Entry 7)
1,2-Di(naphthalene-2-yl)ethane-1,2-diol (Table 2, Entry 8)

![Chemical Structure](image)

### Spectral Data

**H NMR (CDCl3):**

- δ (ppm): 2.85, 11.86, 0.16, 0.89, 0.16, 1.00, 0.82, 1.67, 4.09
- δ (ppm): 2.50, 2.50, 2.50, 3.33, 4.83, 4.90, 5.41, 5.54, 7.31, 7.31, 7.33, 7.33, 7.40, 7.41, 7.42, 7.42, 7.67, 7.68, 7.70, 7.73, 7.74, 7.74, 7.75, 7.79, 7.80, 7.80, 7.81

**C NMR (CDCl3):**

- δ (ppm): 130.40, 130.62, 130.77, 131.97, 132.30, 132.62, 137.48, 137.69, 144.09

**Notes:**

- Yeji-naphthyl
- Yeji-naphthyl

**Additional Details:**

- 2h
1,2-Di-<i>m</i>-tolyethane-1,2-diol (Table 2, Entry 9)
1,2-Bis(3-methoxyphenyl)ethane-1,2-diol (Table 2, Entry 10)
2,2,5,5-Tetramethylhexane-3,4-diol (Table 2, Entry 11)
2,3-Diphenylbutane-2,3-diol (Table 2, Entry 12)
Calibrations and Results of Ion Chromatography

1) NH\textsubscript{4}\textsuperscript{+} cation calibration curve

Function: \( A = 4.15059 \times 10^{-3} + 0.0211598 \times Q \)
Relative standard deviation: 2.732093%
Correlation coefficient: 0.999834

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc.(mg/L)</th>
<th>Volume((\mu)L)</th>
<th>Dilution</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard 1</td>
<td>0.500</td>
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<td>1.0</td>
<td>0.109</td>
</tr>
<tr>
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<tr>
<td>Standard 4</td>
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<td>10</td>
<td>1.0</td>
<td>2.109</td>
</tr>
</tbody>
</table>

2) Ca\textsuperscript{2+} cation calibration curve

Function: \( A = 0.00617120 + 0.0154480 \times Q \)
Relative standard deviation: 1.194612%
Correlation coefficient: 0.999950
<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc.(mg/L)</th>
<th>Volume(μL)</th>
<th>Dilution</th>
<th>Area</th>
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</thead>
<tbody>
<tr>
<td>Standard 1</td>
<td>0.500</td>
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<td>1.0</td>
<td>0.138</td>
</tr>
<tr>
<td>Standard 2</td>
<td>1.000</td>
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<td>1.0</td>
<td>0.211</td>
</tr>
<tr>
<td>Standard 3</td>
<td>5.000</td>
<td>10</td>
<td>1.0</td>
<td>0.844</td>
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<tr>
<td>Standard 4</td>
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<td>10</td>
<td>1.0</td>
<td>1.602</td>
</tr>
</tbody>
</table>

3) THF Sample Result

![Graph showing cation concentrations over time]

Sample

<table>
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<tr>
<th>Component</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electride</td>
<td>[Ca₂N]⁺·e⁻ (94 mg, 1 mmol)</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>4-chlorobenzaldehyde (70.3 mg, 0.5 mmol)</td>
</tr>
<tr>
<td>Solvent</td>
<td>THF 4 mL</td>
</tr>
<tr>
<td>Washed Solvent</td>
<td>THF 8 mL</td>
</tr>
<tr>
<td>Dilution</td>
<td>200 times</td>
</tr>
<tr>
<td>Pressure / Flow</td>
<td>7.88 MPa / 0.700 mL/min</td>
</tr>
</tbody>
</table>

Result

<table>
<thead>
<tr>
<th>Peak #</th>
<th>Retention Time (min)</th>
<th>Area (μS/cm)×min</th>
<th>Height (μS/cm)</th>
<th>Concentration (ppm)</th>
<th>Component name</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.1127</td>
<td>0.351</td>
<td>invalid</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>3.523</td>
<td>0.2556</td>
<td>2.205</td>
<td>0.025</td>
<td>Na</td>
</tr>
<tr>
<td>3</td>
<td>4.748</td>
<td>0.0181</td>
<td>0.117</td>
<td>0.096</td>
<td>K</td>
</tr>
<tr>
<td>4</td>
<td>9.813</td>
<td>0.1364</td>
<td>0.385</td>
<td>0.483</td>
<td>Ca</td>
</tr>
</tbody>
</table>
### 4) MeOH Sample Result

![Baseline and peaks](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Ca$_2$N]$^+\cdot$e$^-$ (94 mg, 1 mmol)</th>
<th>4-chlorobenzaldehyde (70.3 mg, 0.5 mmol)</th>
<th>MeOH 4 mL</th>
<th>MeOH 4 mL</th>
<th>200 times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electride</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aldehyde</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Washed Solvent</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dilution</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Pressure / Flow</td>
<td></td>
<td></td>
<td>7.88 MPa</td>
<td>0.700 mL/min</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Result</th>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak #</td>
<td>Retention Time (min)</td>
<td>Area ($\mu$S/cm)$\times$min</td>
<td>Height ($\mu$S/cm)</td>
<td>Concentration (ppm)</td>
<td>Component name</td>
</tr>
<tr>
<td>-------------------------</td>
<td>---------------------------------------</td>
<td>----------------------------------------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>1</td>
<td>3.530</td>
<td>0.2902</td>
<td>2.543</td>
<td>0.208</td>
<td>Na</td>
</tr>
<tr>
<td>2</td>
<td>3.852</td>
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<td>2.841</td>
<td>1.674</td>
<td>NH$_4$</td>
</tr>
<tr>
<td>3</td>
<td>4.752</td>
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<td>0.122</td>
<td>K</td>
</tr>
<tr>
<td>4</td>
<td>9.768</td>
<td>0.3036</td>
<td>0.858</td>
<td>1.566</td>
<td>Ca</td>
</tr>
</tbody>
</table>
5) MeOH/THF Sample Result

![Graph showing cation concentration over time.]

### Sample

<table>
<thead>
<tr>
<th>Component</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electride</td>
<td>([\text{Ca}_2\text{N}]^+\cdot\text{e}^-) (94 mg, 1 mmol)</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>4-chlorobenzaldehyde (70.3 mg, 0.5 mmol)</td>
</tr>
<tr>
<td>Solvent</td>
<td>MeOH 2 mL / THF 2 mL</td>
</tr>
<tr>
<td>Washed Solvent</td>
<td>MeOH 8 mL</td>
</tr>
<tr>
<td>Dilution</td>
<td>200 times</td>
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<tr>
<td>Pressure / Flow</td>
<td>7.88 MPa / 0.700 mL/min</td>
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</tbody>
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### Result

<table>
<thead>
<tr>
<th>Peak #</th>
<th>Retention Time (min)</th>
<th>Area ((\mu\text{S/cm})\times\text{min})</th>
<th>Height ((\mu\text{S/cm}))</th>
<th>Concentration (ppm)</th>
<th>Component name</th>
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</tr>
<tr>
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<td>0.2661</td>
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<td>NH(_4)</td>
</tr>
<tr>
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<td>4.753</td>
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<td>0.140</td>
<td>0.137</td>
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<tr>
<td>4</td>
<td>9.783</td>
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<td>0.648</td>
<td>1.093</td>
<td>Ca</td>
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</table>