Supporting Information for

Nickel-Catalyzed Highly Regioselective Hydrocyanation of Alkenes with Zn(CN)₂

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General Methods. Unless noted, all reactions were carried out using standard Schlenk
technique under an argon atmosphere or a dry box technique under a nitrogen atmosphere. Tetrahydrofuran and toluene were distilled from sodium and benzophenone. 1,4-dioxane was distilled from sodium. Acetonitrile was dried using Innovative Technology Solvent Purifier. N, N-Dimethylformamide (Superdry), Xantphos, DPEphos, dppf, dppp, neocuproine and 2,2′:6′,2″-terpyridine were purchased from J&K Chemical Company. PPh₃, P(OPh)₃ and dppb were purchased from TCI. Ni(COD)₂, NiI₂, Ni(acac)₂ and Ni(ClO₄)₂·6H₂O were purchased from Strem Chemicals Inc. NiCl₂(DME) and NiBr₂(DME) were purchased from Sigma-Aldrich. NiCl₂·6H₂O, NiCl₂, dppe, Zn(CN)₂, and DMAP were purchased from Alfa Aesar. Zinc powder (99.8%, -100 mesh) and Mn powder (APS<10 micron, 99.6% metals basis) were purchased from Alfa Aesar. Al powder (200 mesh) was purchased from Acros Organics. Before using, zinc powder was stirred with 1 M HCl aqueous solution, filtered and washed thoroughly with water, acetone and diethyl ether and dried under vacuum. Unless noted, all commercial reagents were used without further purification. ¹H and ¹³C NMR spectra were recorded at room temperature in CDCl₃ (containing 0.03% TMS) on Varian or Agilent XL-400 MHz spectrometer. ¹H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) or solvent residual peak (chloroform, δ = 7.26 ppm) as internal reference; ¹³C NMR spectra was recorded with CDCl₃ (δ = 77.00 ppm) as internal reference. High-resolution mass spectra were obtained by using Waters Micromass GCT Premier mass spectrometer, Agilent Technologies 6224 TOF LC/MS or Thermo Fisher Scientific LTQ FT Ultra mass spectrometers. The IR spectra were measured on a ThermoFisher Nicolet FT-IR spectrometer.

Note: It was noted that partial dehydration of NiCl₂·6H₂O stored in a nitrogen-filled glove box for a long time might occur. In order to obtain the accurate experimental data, NiCl₂·6H₂O used in this study was stored under air (outside of glove box), which was brought into the glove box and used immediately for every experiment.

Caution! Zinc cyanide is toxic and should be handled with extra care. The crude reaction mixture or the aqueous layer should not be exposed to acidic conditions as formation of hydrogen cyanide is possible.
Alkenes were synthesized according to the published methods. For the characterization of the new alkene substrates, see the following:

To a solution of 7-hydroxy-3-(4-methoxyphenyl)-4H-chromen-4-one (2.68 g, 10 mmol) and Et₃N (2.02 g, 20 mmol) in DCM (50 mL) was added Tf₂O (3.10 g, 11 mmol) at 0 °C under Argon, then the mixture was warmed up to room temperature and stirred for another 2 h. The reaction was quenched with saturated NH₄Cl and extracted with DCM. The combined organic layers were dried over Na₂SO₄, filtered and concentrated in vacuum. The residue was purified by column chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 2:1) to give 3-(4-methoxyphenyl)-4-oxo-4H-chromen-7-yl trifluoromethanesulfonate (s-1u) in 69% yield (2.76 g) as a white solid. M.p.: 125.0-126.3 °C. ¹H NMR (400 M, CDCl₃): δ 3.84 (s, 3H), 6.97 (d, J = 8.8 Hz, 2H), 7.33 (dd, J = 8.8, 2.4 Hz, 1H), 7.45 (d, J = 2.0 Hz, 1H), 7.49 (d, J = 8.8 Hz, 2H), 8.01 (s, 1H), 8.40 (d, J = 8.8 Hz, 1H). ¹³C NMR (100 M, CDCl₃): δ 55.26, 111.39, 114.04, 118.47, 118.63 (q, ¹J_C-F = 321.3 Hz), 123.08, 124.14, 125.62, 129.12, 130.00, 152.02, 152.80, 156.27, 159.86, 175.11. IR (neat): 3097, 3076, 3058, 2954, 2907, 2836, 1644, 1612, 1568, 1516, 1424, 1400, 1292, 1250, 1212, 1182, 1168, 1132, 1095, 1029, 952, 883, 864, 824, 801, 788, 782, 689, 659 cm⁻¹. HRMS (ESI) calcd for C₁₇H₁₂F₃O₆S[M+H]⁺: 401.0301, found 401.0298.

To a solution of s-1u (1.20 g, 3 mmol), Pd(PPh₃)₂Cl₂ (210.6 mg, 0.3 mmol) and LiCl (127.2 mg, 3 mol) in DMF (18 mL) was added tributyl(vinyl)stannane (1.05 g, 3.3 mmol) dropwise under Argon. The mixture was heated at 90 °C for 4 h. After completion the reaction
mixture was cooled down to room temperature and diluted with Et₂O and washed with 1 M HCl(aq.), then washed with saturated NaHCO₃(aq.) and brine. The combined aqueous layers were extracted once with Et₂O. The combined organic layers were dried over Na₂SO₄, filtered and concentrated in vacuum. The residue was purified by column chromatography on silica gel (eluent: petroleum ether / dichloromethane / ethyl acetate = 6:1:1) to give 3-(4-methoxyphenyl)-7-vinyl-4H-chromen-4-one (1u) in 76% yield (637.7 mg) as a white solid. M.p.: 154.0-155.1 °C. ¹H NMR (400 M, CDCl₃): δ 3.83 (s, 3H), 5.48 (d, J = 11.2 Hz, 1H), 5.94 (d, J = 17.6, Hz, 1H), 6.79 (dd, J = 17.6, 11.2 Hz, 1H), 6.96–6.98 (m, 2H), 7.41 (s, 1H), 7.46–7.52 (m, 3H), 7.96 (s, 1H), 8.24 (d, J = 8.4 Hz, 1H). ¹³C NMR (100 M, CDCl₃): δ 55.26, 113.91, 115.37, 117.81, 122.83, 123.62, 124.03, 124.97, 126.49, 130.02, 135.32, 142.89, 152.49, 156.44, 159.55, 176.06. IR (neat): 3092, 3076, 3040, 3011, 2972, 2930, 2838, 1624, 1609, 1557, 1439, 1407, 1358, 1291, 1253, 1233, 1176, 1106, 1024, 985, 927, 901, 886, 878, 830, 821, 802, 791, 767, 717 cm⁻¹. HRMS (ESI) calcd for C₁₈H₁₅O₃ [M+H]⁺: 279.1016, found 279.1007.

**Optimization studies for Ni-catalyzed hydrocyanation of aryl alkenes.**

**General procedure for optimization studies.**

The reaction was conducted in an oven-dried screw-cap vial (4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, NiCl₂·6H₂O (3.6 mg, 0.015 mmol) [or other Ni(II) salts], Xantphos (10.4 mg, 0.018 mmol) [or other ligands], Zinc powder (3.9 mg, 0.06 mmol) [or other reductants], Zn(CN)₂ (28.2 mg, 0.24 mmol), dioxane or other solvents (1.5 mL) and 1-methyl-4-vinylbenzene (35.5 mg, 0.3 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then H₂O (30 µL or x equiv) was added to the vial. After the reaction mixture was stirred at 80 °C, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was dissolved in CDCl₃. The NMR yields were obtained by ¹H NMR analysis of the crude mixture using mesitylene (36.1 mg, 0.3 mmol) as an internal standard. In some cases, the reaction mixture was quenched by 10% NH₃·H₂O aqueous solution and extracted with ethyl acetate. The combined organic layers were washed with water and saturated NaCl solution, dried over anhydrous Na₂SO₄ (for
entries 1-4).

Table S1. Optimization studies for Ni-catalyzed hydrocyanation of aryl alkenes.\(^a\)

<table>
<thead>
<tr>
<th>entry</th>
<th>deviation from conditions shown in eq 1</th>
<th>yield (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2a</td>
</tr>
<tr>
<td>1</td>
<td>none</td>
<td>89</td>
</tr>
<tr>
<td>2</td>
<td>dioxane/H(_2)O = 25/1</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1.0 equiv H(_2)O was used</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>2.0 equiv H(_2)O was used</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>NiCl(_2) instead of NiCl(_2)·6H(_2)O</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>NiCl(_2)(DME) instead of NiCl(_2)·6H(_2)O</td>
<td>87</td>
</tr>
<tr>
<td>7</td>
<td>NiBr(_2)(DME) instead of NiCl(_2)·6H(_2)O</td>
<td>78</td>
</tr>
<tr>
<td>8</td>
<td>Ni(_2) instead of NiCl(_2)·6H(_2)O</td>
<td>79</td>
</tr>
<tr>
<td>9</td>
<td>Ni(CIO(_4))(_2)·6H(_2)O instead of NiCl(_2)·6H(_2)O</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>Ni(acac)(_2) instead of NiCl(_2)·6H(_2)O</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>10 mol% PPh(_3) or P(Ph)(_3) instead of 6 mol% dppf</td>
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</tr>
<tr>
<td>12</td>
<td>dppe instead of dppf</td>
<td>8</td>
</tr>
<tr>
<td>13</td>
<td>dppp instead of dppf</td>
<td>37</td>
</tr>
<tr>
<td>14</td>
<td>dppb instead of dppf</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>Xantphos instead of dppf</td>
<td>96</td>
</tr>
<tr>
<td>16</td>
<td>DPEPhos instead of dppf</td>
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<tr>
<td>17</td>
<td>neocuproine instead of dppf</td>
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<tr>
<td>18</td>
<td>terpyridine instead of dppf</td>
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</tr>
<tr>
<td>19</td>
<td>Xantphos instead of dppf, toluene instead of dioxane</td>
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</tr>
<tr>
<td>20</td>
<td>Xantphos instead of dppf, MeCN instead of dioxane</td>
<td>49</td>
</tr>
<tr>
<td>21</td>
<td>Xantphos instead of dppf, THF instead of dioxane</td>
<td>95</td>
</tr>
<tr>
<td>22</td>
<td>Xantphos instead of dppf, DMF instead of dioxane</td>
<td>26</td>
</tr>
<tr>
<td>23(^c)</td>
<td>Xantphos instead of dppf, 0.6 equiv Zn(CN)(_2) was used</td>
<td>97</td>
</tr>
<tr>
<td>24(^c,d)</td>
<td>Xantphos instead of dppf, Mn instead of Zn</td>
<td>73</td>
</tr>
<tr>
<td>25(^c,d)</td>
<td>Xantphos instead of dppf, Al instead of Zn</td>
<td>2</td>
</tr>
<tr>
<td>26(^c,d)</td>
<td>Without either of NiCl(_2)·6H(_2)O, Xantphos or Zn</td>
<td>0</td>
</tr>
<tr>
<td>27(^c,d)</td>
<td>Without H(_2)O</td>
<td>25</td>
</tr>
</tbody>
</table>

\(^{a}\) 1a (0.3 mmol), Zn(CN)\(_2\) (0.24 mmol), NiCl\(_2\)·6H\(_2\)O (0.015 mmol), dppf (0.018 mmol) and zinc powder (0.06 mmol) in dioxane/H\(_2\)O (1.5 mL/0.03 mL) at 80 °C for 12 h.  
\(^{b}\) Determined by \(^1\)H NMR of the crude reaction mixture using mesitylene as an internal standard.  
\(^{c}\) The reaction time was 4 h.  
\(^{d}\) 0.6 equiv Zn(CN)\(_2\) was used.
Ni-Catalyzed hydrocyanation of aryl/heteroaryl alkenes.

Typical procedure for the synthesis of 2a.

\[
\begin{align*}
\text{Ar} & \quad + \quad \text{Zn(CN)}_2 \\
& \quad \text{0.6 equiv} \\
\longrightarrow & \quad \text{CN} \\
\text{Me} & \quad \text{Ar} \\
\end{align*}
\]

for 2a, Ar = 4-MeC₆H₄

The reaction was conducted in an oven-dried screw-cap vial (8 mL) equipped with a magnetic stir bar. The vial containing NiCl₂·6H₂O was equipped with a septum cap, which was pierced by a needle and introduced into the antechamber of nitrogen-filled glovebox. Before transferring into the inside of the glovebox, it was evacuated and back-filled with nitrogen for three times (ca. 5 min). In a nitrogen-filled glove box, NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), dioxane (2.5 mL) and 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then H₂O (50 μL) was added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1 to 50:1) to give the desired product 2a in 93% yield (67.5 mg) as a colorless oil.

2-\text{p}-\text{Tolylpropanenitrile (2a).} \quad ^1\text{H NMR (400 M, CDCl}_3\text{): } \delta \text{ 1.62 (d, } J = 7.2 \text{ Hz, 3H), 2.35 (s, 3H), 3.86 (q, } J = 7.2 \text{ Hz, 1H), 7.18 (d, } J = 8.0 \text{ Hz, 2H), 7.25 (d, } J = 8.4 \text{ Hz, 2H).} \quad ^{13}\text{C NMR (100 M, CDCl}_3\text{): } \delta \text{ 20.98, 21.44, 30.80, 121.73, 126.52, 129.71, 134.05, 137.78. The spectroscopic data are in agreement with that previously reported.} \quad ¹
2-Phenylpropanenitrile (2b). NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), styrene (52.1 mg, 0.5 mmol) and H$_2$O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) afforded the product 2b in 88% yield (57.4 mg) as a colorless oil. $^1$H NMR (400 M, CDCl$_3$): δ 1.62 (d, $J = 7.2$ Hz, 3H), 3.89 (q, $J = 7.2$ Hz, 1H), 7.29-7.40 (m, 5H). $^{13}$C NMR (100 M, CDCl$_3$): δ 21.34, 31.10, 121.51, 126.58, 129.02, 136.96. The spectroscopic data are in agreement with that previously reported.$^1$

2-o-Tolylpropanenitrile (2c). $^1$H NMR (400 M, CDCl$_3$): δ 1.60 (d, $J = 7.2$ Hz, 3H), 2.35 (s, 3H), 4.03 (q, $J = 7.2$ Hz, 1H), 7.17-7.27 (m, 3H), 7.43-7.45 (m, 1H). $^{13}$C NMR (100 M, CDCl$_3$): δ 18.90, 19.93, 28.05, 121.72, 126.59, 126.88, 128.02, 130.90, 134.69, 135.17. The spectroscopic data are in agreement with that previously reported.$^2$

3-o-Tolylpropanenitrile (3c). $^1$H NMR (400 M, CDCl$_3$): δ 2.33 (s, 3H), 2.58 (t, $J = 7.6$ Hz, 2H), 2.98 (t, $J = 7.6$ Hz, 2H), 7.15-7.20 (m, 4H). $^{13}$C NMR (100 M, CDCl$_3$): δ 17.97, 19.14, 28.84, 119.19, 126.45, 127.33, 128.67, 130.61, 135.74, 136.18. The spectroscopic data are in agreement with that previously reported.$^3$
2-(4-Isobutylphenyl)propanenitrile (2d). NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 1-isobutyl-4-vinylbenzene (80.1 mg, 0.5 mmol) and H$_2$O (50 μL) were stirred at 80 °C for 6 h. Purification by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) afforded the product 2d in 75% yield (70.0 mg) as a colorless oil. 

$^1$H NMR (400 M, CDCl$_3$): δ 0.90 (d, J = 6.8 Hz, 6H), 1.62 (d, J = 7.6 Hz, 3H), 1.80-1.90 (m, 1H), 2.47 (d, J = 7.2 Hz, 2H), 3.86 (q, J = 7.2 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H). $^{13}$C NMR (100 M, CDCl$_3$): δ 21.34, 22.22, 30.09, 30.78, 44.85, 121.73, 126.34, 129.72, 134.22, 141.53. The spectroscopic data are in agreement with that previously reported.\(^4\)

2-(4-Methoxyphenyl)propanenitrile (2e). NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 1-methoxy-4-vinylbenzene (67.1 mg, 0.5 mmol) and H$_2$O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product 2e in 92% yield (73.9 mg) as a colorless oil. $^1$H NMR (400 M, CDCl$_3$): δ 1.60 (d, J = 7.6 Hz, 3H), 3.80 (s, 3H), 3.84 (q, J = 7.6 Hz, 1H), 6.89-6.92 (m, 2H), 7.25-7.27 (m, 2H). $^{13}$C NMR (100 M, CDCl$_3$): δ 21.39, 30.31, 55.22, 114.36, 121.79, 127.72, 128.98, 159.18. The spectroscopic data are in agreement with that previously reported.\(^5\)
2-(3,5-Dimethoxyphenyl)propanitrile (2f). NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 1,3-dimethoxy-5-vinylbenzene (82.1 mg, 0.5 mmol) and H₂O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product 2f in 95% yield (91.3 mg) as a colorless oil. ¹H NMR (400 M, CDCl₃): δ 1.62 (d, J = 7.2 Hz, 3H), 3.79-3.84 (m, 7H), 6.40 (t, J = 2.0 Hz, 1H), 6.49 (d, J = 2.0 Hz, 2H). ¹³C NMR (100 M, CDCl₃): δ 21.12, 31.19, 55.24, 99.52, 104.75, 121.35, 139.12, 161.14. IR (neat): 2985, 2941, 2839, 2242, 1596, 1457, 1429, 1349, 1328, 1296, 1204, 1152, 1051, 836, 735, 694 cm⁻¹. HRMS (ESI) calcd for C₁₁H₁₄NO₂ [M+H]⁺: 192.1019, found 192.1017.

2-(4-Hydroxyphenyl)propanitrile (2g). NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 4-vinylphenol (60.1 mg, 0.5 mmol) and H₂O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1 to 3:1) afforded the product 2g in 87% yield (63.7 mg) as a colorless oil. ¹H NMR (400 M, CDCl₃): δ 1.59 (d, J = 7.6 Hz, 3H), 3.84 (q, J = 7.2 Hz, 1H), 6.59 (s, 1H), 6.82-6.86 (m, 2H), 7.17 (d, J = 8.8 Hz, 2H). ¹³C NMR (100 M, CDCl₃): δ 21.21, 30.30, 115.97, 121.95, 127.88, 128.44, 155.67. IR (neat): 3344, 3022, 2988, 2936, 2254, 1613, 1591, 1515, 1441, 1372, 1356, 1343, 1274, 1264, 1216, 1185, 1174, 1107, 1083, 1054, 987, 837, 818, 732 cm⁻¹. HRMS (EI) calcd for C₉H₉NO [M]⁺: 147.0684, found 147.0679.
2-(4-Aminophenyl)propanenitrile (2h). NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 4-vinylaniline (59.6 mg, 0.5 mmol) and H$_2$O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 1:1) afforded the product 2h in 89% yield (64.7 mg) as a light yellow oil. $^1$H NMR (400 M, CDCl$_3$): $\delta$ 1.56 (d, $J = 7.2$ Hz, 3H), 3.72 (s, 2H), 3.76 (q, $J = 7.2$ Hz, 1H), 6.64 (d, $J = 8.4$ Hz, 2H), 7.09 (d, $J = 8.8$ Hz, 2H). $^{13}$C NMR (100 M, CDCl$_3$): $\delta$ 21.25, 30.19, 115.20, 122.10, 126.39, 127.46, 146.18. IR (neat): 3460, 3369, 3225, 2983, 2924, 2853, 2238, 1623, 1516, 1452, 1378, 1285, 1183, 1130, 1084, 988, 826 cm$^{-1}$. HRMS (ESI) calcd for C$_9$H$_{11}$N$_2$ [M+H]$^+$: 147.0917, found 147.0914.

2-(4-Fluorophenyl)propanenitrile (2i). NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 1-fluoro-4-vinylbenzene (61.1 mg, 0.5 mmol) and H$_2$O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1 to 20:1) afforded the product 2i in 81% yield (60.4 mg) as a colorless oil. $^1$H NMR (400 M, CDCl$_3$): $\delta$ 1.63 (d, $J = 7.2$ Hz, 3H), 3.90 (q, $J = 7.2$ Hz, 1H), 7.05-7.09 (m, 2H), 7.31-7.35 (m, 2H). $^{13}$C NMR (100 M, CDCl$_3$): $\delta$ 21.37, 30.44, 115.97 (d, $^2$J$_{C-F}$ = 8.4 Hz), 121.34, 128.35 (d, $^3$J$_{C-F}$ = 8.4 Hz), 132.77 (d, $^4$J$_{C-F}$ = 3.8 Hz), 162.22 (d, $^1$J$_{C-F}$ = 247.3 Hz). The spectroscopic data are in agreement with that previously reported.5
2-(4-(Trifluoromethyl)phenyl)propanenitrile (2j). NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 1-(trifluoromethyl)-4-vinylbenzene (86.1 mg, 0.5 mmol) and H₂O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product 2j in 84% yield (84.0 mg) as a colorless oil. ¹H NMR (400 M, CDCl₃): δ 1.67 (d, J = 7.2 Hz, 3H), 3.99 (q, J = 7.2 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H). ¹³C NMR (100 M, CDCl₃): δ 21.13, 31.01, 120.72, 123.75 (q, ¹J_C-F = 272.4 Hz), 126.08 (q, ³J_C-F = 3.8 Hz), 127.15, 130.35 (q, ²J_C-F = 32.9 Hz), 140.94 (q, ⁵J_C-F = 1.5 Hz). The spectroscopic data are in agreement with that previously reported.⁶

4-(1-Cyanoethyl)benzonitrile (2k). NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 4-vinylbenzonitrile (64.6 mg, 0.5 mmol) and H₂O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the product 2k in 85% yield (66.2 mg) as a colorless oil. ¹H NMR (400 M, CDCl₃): δ 1.68 (d, J = 7.6 Hz, 3H), 4.02 (q, J = 7.2 Hz, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H). ¹³C NMR (100 M, CDCl₃): δ 20.93, 31.11, 112.01, 118.01, 120.26, 127.52, 132.81, 142.00. The spectroscopic data are in agreement with that previously reported.⁷
2-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanenitrile (2l).

NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (115.1 mg, 0.5 mmol) and H₂O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1 to 10:1) afforded the product 2l in 77% yield (98.8 mg) as a white solid. M.p.: 100.1-101.4 °C. ¹H NMR (400 M, CDCl₃): δ 1.34 (s, 12H), 1.62 (d, J = 7.2 Hz, 3H), 3.90 (q, J = 7.2 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H). ¹³C NMR (100 M, CDCl₃): δ 21.29, 24.72, 31.23, 83.82, 121.24, 125.91, 135.47, 139.88. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (neat): 2983, 2920, 2239, 1614, 1521, 1454, 1412, 1398, 1358, 1333, 1282, 1267, 1167, 1138, 1094, 1021, 963, 856, 833, 675, 656 cm⁻¹. HRMS (ESI) calcd for C₁₅H₂₄O₂N₂₁₀B [M+NH₄]⁺: 274.1962, found 274.1961.

2-(Biphenyl-4-yl)propanenitrile (2m). NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), dioxane (2.5 mL) and H₂O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1 to 20:1) afforded the product 2m in 95% yield (98.3 mg) as a white solid. ¹H NMR (400 M, CDCl₃): δ 1.63 (d, J = 7.2 Hz, 3H), 3.90 (q, J = 7.2 Hz, 1H), 7.32-7.44 (m, 5H), 7.57 (t, J = 8.4 Hz, 4H). ¹³C NMR (100 M, CDCl₃): δ 21.26, 30.76, 121.47, 126.93, 127.03, 127.48, 127.67, 128.74, 135.89, 140.07, 140.88. The spectroscopic data are in agreement with that previously reported.⁵
2-(Naphthalen-2-yl)propanenitrile (2n). NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), 2-vinyl-6-naphthalene (77.1 mg, 0.5 mmol), dioxane (2.5 mL) and H₂O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1 to 20:1) afforded the product 2n in 91% yield (82.4 mg) as a white solid. \(^1\)H NMR (400 M, CDCl₃): δ 1.66 (d, \(J = 7.2\) Hz, 3H), 3.99 (q, \(J = 7.2\) Hz, 1H), 7.37 (dd, \(J = 8.6, 2.0\) Hz, 1H), 7.45-7.50 (m, 2H), 7.79-7.83 (m, 4H). \(^{13}\)C NMR (100 M, CDCl₃): δ 21.22, 31.20, 121.50, 124.26, 125.41, 126.33, 126.57, 127.57, 127.70, 128.98, 132.60, 133.14, 134.19. The spectroscopic data are in agreement with that previously reported.\(^1\)

2-(6-Methoxynaphthalen-2-yl)propanenitrile (2o). NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), 2-methoxy-6-vinyl-6-naphthalene (82.1 mg, 0.5 mmol), dioxane (2.5 mL) and H₂O (50 μL) were stirred at 80 °C for 8 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product 2o in 98% yield (103.7 mg) as a white solid. \(^1\)H NMR (400 M, CDCl₃): δ 1.65 (d, \(J = 7.2\) Hz, 3H), 3.87 (s, 3H), 3.95 (q, \(J = 7.2\) Hz, 1H), 7.09 (d, \(J = 2.0\) Hz, 1H), 7.15 (dd, \(J = 9.0, 2.0\) Hz, 1H), 7.34 (dd, \(J = 8.4, 1.2\) Hz, 1H), 7.67-7.72 (m, 3H). \(^{13}\)C NMR (100 M, CDCl₃): δ 21.19, 30.98, 55.12, 105.49, 119.37, 121.65, 124.75, 125.18, 127.72, 128.57, 129.12, 131.85, 133.83, 157.90. The spectroscopic data are in agreement with that previously reported.\(^8\)
3-Phenylbutanenitrile (2p). NiCl₂·6H₂O (5.9 mg, 0.025 mmol), dppf (16.6 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), ZnI₂ (79.8 mg, 0.25 mmol), MeCN (2.5 mL), prop-1-en-2-ylbenzene (59.1 mg, 0.5 mmol) and H₂O (18 μL) were stirred at 80 °C for 8 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product 2p in 75% yield (54.4 mg) as a colorless oil. ¹H NMR (400 M, CDCl₃): δ 1.45 (d, J = 6.8 Hz, 3H), 2.51-2.64 (m, 2H), 3.11-3.20 (m, 1H), 7.23-7.28 (m, 3H), 7.33-7.36 (m, 2H). ¹³C NMR (100 M, CDCl₃): δ 20.60, 26.27, 36.44, 118.55, 126.48, 127.25, 128.79, 143.07. The spectroscopic data are in agreement with that previously reported.⁹

2-(Pyridin-3-yl)propanenitrile (2q). NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 3-vinylpyridine (52.6 mg, 0.5 mmol) and H₂O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 1:1) afforded the product 2q in 83% yield (54.6 mg) as a colorless oil. ¹H NMR (400 M, CDCl₃): δ 1.68 (d, J = 7.2 Hz, 3H), 3.98 (q, J = 7.2 Hz, 1H), 7.34-7.37 (m, 1H), 7.75 (d, J = 8.0 Hz, 1H), 8.60-8.62 (m, 2H). ¹³C NMR (100 M, CDCl₃): δ 20.99, 28.78, 120.42, 123.74, 132.72, 134.12, 148.02, 149.34. IR (neat): 3037, 2988, 2941, 2243, 1577, 1481, 1455, 1426, 1301, 1181, 1129, 1089, 1043, 1027, 990, 810, 711 cm⁻¹. HRMS (ESI) calcd for C₈H₉N₂ [M+H]⁺: 133.0760, found 133.0758.

3-(Pyridin-2-yl)propanenitrile (2r). NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg,
0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 2-vinylpyridine (52.6 mg, 0.5 mmol) and H₂O (50 μL) were stirred at 80 °C for 3.5 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 1:1) afforded the product 2r in 91% yield (60.4 mg) as a colorless oil. ¹H NMR (400 M, CDCl₃): δ 2.84 (t, J = 7.2 Hz, 2H), 3.11 (t, J = 7.2 Hz, 2H), 7.17-7.23 (m, 2H), 7.65 (td, J = 7.6, 0.8 Hz, 1H), 8.55 (d, J = 4.8 Hz, 1H). ¹³C NMR (100 M, CDCl₃): δ 16.37, 33.09, 119.27, 121.98, 122.90, 136.55, 149.36, 156.97. The spectroscopic data are in agreement with that previously reported.¹⁰

[Diagram of 2r]

2-(1H-Indol-3-yl)propanenitrile (2s). NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), 3-vinyl-1H-indole (71.6 mg, 0.5 mmol), dioxane (2.5 mL) and H₂O (50 μL) were stirred at 80 °C for 8 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the product 2s in 87% yield (73.8 mg) as a colorless oil. ¹H NMR (400 M, CDCl₃): δ 1.67 (d, J = 7.2 Hz, 3H), 4.08 (q, J = 7.2 Hz, 1H), 7.04 (d, J = 1.6 Hz, 1H), 7.12-7.22 (m, 2H), 7.31 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 8.28 (s, 1H). ¹³C NMR (100 M, CDCl₃): δ 19.39, 22.66, 111.36, 111.62, 118.17, 119.86, 121.66, 121.98, 122.50, 124.94, 136.33. IR (neat): 3409, 3063, 2983, 2943, 2240, 1618, 1457, 1421, 1355, 1339, 1248, 1225, 1100, 1032, 1012, 909, 819, 765, 739 cm⁻¹. HRMS (El) calcd for C₁₁H₁₀N₂ [M]⁺: 170.0844, found 170.0842.

[Diagram of 2s]

2-(Benzol[b]thiophen-2-yl)propanenitrile (2t). NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos
(17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), 2-vinylbenzo[b]thiophene (80.1 mg, 0.5 mmol), dioxane (2.5 mL) and H$_2$O (50 μL) were stirred at 80 °C for 8 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product 2t in 84% yield (79.0 mg) as a white solid. M.p.: 81.0-82.0 °C. $^1$H NMR (400 M, CDCl$_3$): δ 1.73 (d, $J$ = 7.2 Hz, 3H), 4.16 (q, $J$ = 7.2 Hz, 1H), 7.27-7.36 (m, 3H), 7.69-7.71 (m, 1H), 7.76 (d, $J$ = 7.6 Hz, 1H). $^{13}$C NMR (100 M, CDCl$_3$): δ 20.87, 27.20, 120.09, 122.11, 122.17, 123.58, 124.63, 124.69, 138.96, 139.24, 139.66. IR (neat): 3056, 2993, 2983, 2938, 2925, 2241, 1459, 1435, 1376, 1205, 1156, 1143, 1129, 1057, 967, 943, 876, 841, 823, 728, 679, 666 cm$^{-1}$. HRMS (EI) calcd for C$_{11}$H$_9$NS [M]$^+$: 187.0456, found 187.0459.

![Image](2-3-(4-Methoxyphenyl)-4-oxo-4H-chromen-7-yl)propanonitrile (2u). NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), 3-(4-methoxyphenyl)-7-vinyl-4H-chromen-4-one (139.2 mg, 0.5 mmol), dioxane (2.5 mL) and H$_2$O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) afforded the product 2u in 86% yield (131.0 mg) as a white solid. M.p.: 147.8-149.1 °C. $^1$H NMR (400 M, CDCl$_3$): δ 1.70 (d, $J$ = 7.2 Hz, 3H), 3.82 (s, 3H), 4.05 (q, $J$ = 7.2 Hz, 1H), 6.96 (d, $J$ = 8.8 Hz, 2H), 7.37 (d, $J$ = 8.4 Hz, 1H), 7.49 (d, $J$ = 8.8 Hz, 3H), 7.99 (s, 1H), 8.29 (d, $J$ = 8.4 Hz, 1H). $^{13}$C NMR (100 M, CDCl$_3$): δ 20.99, 31.04, 55.16, 113.83, 116.18, 120.41, 123.54, 123.84, 125.04, 127.38, 129.89, 142.81, 152.51, 156.09, 159.54, 175.66. IR (neat): 3081, 2961, 2937, 2909, 2833, 2246, 1637, 1624, 1606, 1574, 1562, 1511, 1437, 1371, 1357 1289, 1246, 1229, 1195, 1178, 1116, 1107, 1028, 902, 887, 837, 818, 805, 789, 701 cm$^{-1}$. HRMS (ESI) calcd for C$_{19}$H$_{16}$NO$_3$ [M+H]$^+$: 306.1125, found 306.1117.
2-((8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)propanenitrile (2v). NiCl\(_2\)·6H\(_2\)O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)\(_2\) (35.2 mg, 0.3 mmol), (8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (140.2 mg, 0.5 mmol), dioxane (2.5 mL) and H\(_2\)O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) afforded the product 2v (dr = 1:1 determined by HPLC) in 95% yield (146.0 mg) as a colorless oil. \(^1\)H NMR (400 M, CDCl\(_3\)): \(\delta\) 0.91 (s, 3H), 1.40-1.67 (m, 9H), 1.95-2.19 (m, 4H), 2.26-2.31 (m, 1H), 2.39-2.44 (m, 1H), 2.50 (dd, \(J\) = 18.6, 8.6 Hz, 1H), 2.91-2.95 (m, 2H), 3.84 (q, \(J\) = 7.2 Hz, 1H), 7.10-7.13 (m, 2H), 7.30 (d, \(J\) = 7.6 Hz, 1H). \(^{13}\)C NMR (100 M, CDCl\(_3\)): \(\delta\) 13.62, 21.20, 21.23, 21.35, 25.46, 26.13, 29.12, 29.15, 30.50, 30.52, 31.33, 35.62, 37.78, 44.02, 47.71, 50.21, 121.57, 123.85, 125.94, 127.03, 134.29, 134.31, 137.26, 139.47, 220.51. IR (neat): 3369, 2927, 2859, 2239, 1732, 1498, 1454, 1404, 1373, 1243, 1086, 1050, 1008, 819 cm\(^{-1}\). HRMS (EI) calcd for C\(_{21}\)H\(_{25}\)NO [M]+: 307.1936, found 307.1943.

(E)-2-Methyl-4-phenylbut-3-enenitrile (2w). NiCl\(_2\)·6H\(_2\)O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)\(_2\) (35.2 mg, 0.3 mmol), dioxane (2.5 mL), (E)-buta-1,3-dien-1-ylbenzene (65.1 mg, 0.5 mmol) and H\(_2\)O (50 μL) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) afforded the product 2w in 80% yield (63.0 mg) as a colorless oil. \(^1\)H NMR (400 M, CDCl\(_3\)): \(\delta\) 1.49 (d, \(J\) = 6.8 Hz, 3H), 3.45-3.52 (m, 1H), 6.06 (dd, \(J\) = 15.8, 6.4 Hz,
1H), 6.71 (d, J = 16.0 Hz, 1H), 7.24-7.38 (m, 5H). $^{13}$C NMR (100 M, CDCl$_3$): δ 18.95, 28.27, 120.81, 124.23, 126.45, 128.17, 128.63, 132.41, 135.60. The spectroscopic data are in agreement with that previously reported.$^5$

Isolation of 4a’ at the early stage of the hydrocyanation of 4a.

**Diagram:**

$$
\text{NiCl}_2\cdot 6\text{H}_2\text{O} (5.9 \text{ mg}, 0.025 \text{ mmol}), \text{Xantphos} (17.4 \text{ mg}, 0.03 \text{ mmol}), \text{Zinc powder} (6.5 \text{ mg}, 0.1 \text{ mmol}), \text{Zn(CN)}_2 (35.2 \text{ mg}, 0.3 \text{ mmol}), \text{dioxane} (2.5 \text{ mL}), 2\text{-allylnaphthalene} (84.1 \text{ mg}, 0.5 \text{ mmol}) \text{ and } \text{H}_2\text{O} (50 \mu\text{L}) \text{ were stirred at } 80\,\text{oC} \text{ for } 4 \text{ h. The mixture was filtered through a pad of silica gel and washed with ether. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: pentane) to give the product 4a’ (E/Z = 33.3:1) in 94% yield (78.9 mg) as a colorless oil. For E-4a’: $^1$H NMR (400 M, CDCl$_3$): δ 1.90 (dd, J = 6.8, 1.6 Hz, 3H), 6.28-6.37 (m, 1H), 6.52 (d, J = 16.0 Hz, 1H), 7.35-7.42 (m, 2H), 7.51-7.54 (m, 1H), 7.61 (s, 1H), 7.70-7.75 (m, 3H). $^{13}$C NMR (100 M, CDCl$_3$): δ 18.60, 123.45, 125.16, 125.37, 126.05, 126.11, 127.58, 127.79, 128.01, 131.12, 132.58, 133.67, 135.33. The spectroscopic data are in agreement with that previously reported.$^{11}$ For partial $^1$H NMR of Z-4a’: $^1$H NMR (400 M, CDCl$_3$): δ 1.95 (dd, J = 6.8, 1.6 Hz, 3H), 5.81-5.89 (m, 1H). The spectroscopic data are in agreement with that previously reported.$^{12}$

2-(Naphthalen-2-yl)butanenitrile (5). This product was synthesized following the procedure described for Ni-catalyzed hydrocyanation of aryl alkenes. NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3
mmol), dioxane (2.5 mL), 2-allylnaphthalene (84.1 mg, 0.5 mmol) and H₂O (50 μL) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product 5 in 88% yield (85.9 mg) as a colorless oil. ¹H NMR (400 M, CDCl₃): δ 1.07 (t, J = 7.2 Hz, 3H), 1.95-2.03 (m, 2H), 3.86 (t, J = 7.2 Hz, 1H), 7.36 (dd, J = 8.6, 1.6 Hz, 1H), 7.46-7.51 (m, 2H), 7.79-7.84 (m, 4H). ¹³C NMR (100 M, CDCl₃): δ 11.36, 28.93, 38.88, 120.67, 124.71, 126.24, 126.33, 126.57, 127.59, 127.73, 128.87, 132.66, 132.88, 133.14. IR (neat): 3055, 2970, 2932, 2875, 2236, 1600, 1508, 1458, 1370, 1268, 893, 857, 816, 786, 748 cm⁻¹. HRMS (EI) calcd for C₁₄H₁₃N [M]+: 195.1048, found 195.1042.

**Optimization studies for Ni-catalyzed hydrocyanation of aliphatic alkenes.**

**General procedure for optimization studies.**

The reaction was conducted in an oven-dried screw-cap vial (4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, Ni(ClO₄)₂·6H₂O (5.5 mg, 0.015 mmol) [or other Ni(II) salts], dppp (7.4 mg, 0.018 mmol) [or other ligands], Zinc powder (19.6 mg, 0.3 mmol), Zn(CN)₂ (21.1 mg, 0.18 mmol), DMAP (36.7 mg, 0.3 mmol) [or other additives], acetonitrile (1.5 mL), 2-allylnaphthalene (50.5 mg, 0.3 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then H₂O (10.8 μL, 0.6 mmol) was added to the vial. After the reaction mixture was stirred at 80 °C for 24 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was dissolved in CDCl₃. The NMR yields were obtained by ¹H NMR analysis of the crude mixture using mesitylene (36.1 mg, 0.3 mmol) as an internal standard.
Table S2. Optimization studies for Ni-catalyzed hydrocyanation of aliphatic alkenes.

![chemical structure](image)

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<sup>a</sup> Determined by <sup>1</sup>H NMR of the crude reaction mixture using mesitylene as an internal standard. <sup>b</sup> Overall yields of the E- and Z-isomers of 4a<sup>a</sup> and the ratio of E/Z isomers are shown in parentheses if Z-isomers exist. <sup>c</sup> 24 h. <sup>d</sup> 10 mol% Ni(CIO₄)₂·6H₂O and 12 mol% dppp were used. <sup>e</sup> Without H₂O.

Synthesis of 6a-6m and 7a-7m.

Typical procedure for the synthesis of 6a and 7a.
The reaction was conducted in an oven-dried screw-cap vial (8 mL) equipped with a magnetic stir bar. The vial containing Ni(ClO$_4$)$_2$·6H$_2$O was equipped with a septum cap, which was pierced by a needle and introduced into the antechamber of nitrogen-filled glovebox. Before transferring into the inside of the glovebox, it was evacuated and back-filled with nitrogen for three times (ca. 5 min). In a nitrogen-filled glove box, Ni(ClO$_4$)$_2$·6H$_2$O (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), 2-allylnaphthalene (84.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then H$_2$O (18 μL, 1 mmol) was added to the vial. After the reaction mixture was stirred at 80 °C for 24 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to give the desired product 6a in 78% yield (76.2 mg) as a white solid and 7a in 9% yield (8.8 mg) as a white solid.

**4-(Naphthalen-2-yl)butanenitrile (6a).** $^1$H NMR (400 M, CDCl$_3$): $\delta$ 1.94-2.01 (m, 2H), 2.23 (t, $J$ = 7.2 Hz, 2H), 2.86 (t, $J$ = 7.2 Hz, 2H), 7.25 (dd, $J$ = 8.2, 1.6 Hz, 1H), 7.39-7.46 (m, 2H), 7.58 (s, 1H), 7.75-7.79 (m, 3H). $^{13}$C NMR (100 M, CDCl$_3$): $\delta$ 16.22, 26.60, 34.31, 119.47, 125.45, 126.09, 126.69, 127.35, 127.53, 128.25, 132.07, 133.38, 137.03. The spectroscopic data are in agreement with that previously reported.$^{13}$

**2-Methyl-3-(naphthalen-2-yl)propanenitrile (7a).** $^1$H NMR (400 M, CDCl$_3$): $\delta$ 1.36 (d, $J$ =
6.8 Hz, 3H), 2.92-3.01 (m, 2H), 3.09-3.14 (m, 1H), 7.34 (dd, $J = 8.6, 1.6$ Hz, 1H), 7.46-7.49 (m, 2H), 7.69 (s, 1H), 7.80-7.83 (m, 3H). $^{13}$C NMR (100 M, CDCl$_3$): δ 17.62, 27.42, 40.11, 122.54, 125.88, 126.27, 126.93, 127.65, 127.84, 128.46, 132.52, 133.40, 134.27. The spectroscopic data are in agreement with that previously reported.$^{14}$

![Image of 6b and 7b](image)

Ni(ClO$_4$)$_2$·6H$_2$O (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), 1-allyl-4-methoxybenzene (74.1 mg, 0.5 mmol) and H$_2$O (18 µL, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to give the desired product 6b and 7b in 81% overall yield (70.6 mg) as a colorless oil (6b:7b = 8.3:1).

4-(4-Methoxyphenyl)butanenitrile (6b). $^1$H NMR (400 M, CDCl$_3$): δ 1.89-1.96 (m, 2H), 2.28 (t, $J = 7.2$ Hz, 2H), 2.70 (t, $J = 7.2$ Hz, 2H), 3.78 (s, 3H), 6.84 (d, $J = 8.4$ Hz, 2H), 7.09 (d, $J = 8.4$ Hz, 2H). $^{13}$C NMR (100 M, CDCl$_3$): δ 16.10, 26.95, 33.29, 55.09, 113.89, 119.47, 129.25, 131.58, 158.08. The spectroscopic data are in agreement with that previously reported.$^{15}$

3-(4-Methoxyphenyl)-2-methylpropanenitrile (7b). Partial $^1$H NMR (400 M, CDCl$_3$): δ 1.30 (d, $J = 6.4$ Hz, 3H), 2.77-2.87 (m, 3H), 3.78 (s, 3H), 7.14 (d, $J = 8.8$ Hz, 2H), partial $^{13}$C NMR (400 M, CDCl$_3$): δ 17.34, 27.61, 38.96, 113.90, 129.95. The spectroscopic data are in agreement with that previously reported.$^{14}$

Ni(ClO$_4$)$_2$·6H$_2$O (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), but-3-en-1-ylbenzene (66.1 mg, 0.5 mmol) and H$_2$O (18 µL, 1 mmol) were stirred at 80 °C for
Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1 to 20:1) to give the desired product 6c in 81% yield (64.3 mg) as a colorless oil and 7c in 12% yield (9.2 mg) as a colorless oil.

5-Phenylpentanenitrile (6c). \(^1\)H NMR (400 M, CDCl\(_3\)): \(\delta\) 1.62-1.69 (m, 2H), 1.73-1.81 (m, 2H), 2.31 (t, \(J = 7.2\) Hz, 2H), 2.64 (t, \(J = 7.2\) Hz, 2H), 7.15-7.21 (m, 3H), 7.26-7.30 (m, 2H). \(^{13}\)C NMR (100 M, CDCl\(_3\)): \(\delta\) 16.92, 24.71, 30.14, 34.85, 119.54, 125.95, 128.24, 128.35, 141.12. The spectroscopic data are in agreement with that previously reported.\(^{16}\)

2-Methyl-4-phenylbutanenitrile (7c). \(^1\)H NMR (400 M, CDCl\(_3\)): \(\delta\) 1.33 (d, \(J = 7.2\) Hz, 3H), 1.79-1.88 (m, 1H), 1.91-2.01 (m, 1H), 2.53-2.62 (m, 1H), 2.71-2.79 (m, 1H), 2.84-2.91 (m, 1H), 7.19-7.26 (m, 3H), 7.29-7.33 (m, 2H). \(^{13}\)C NMR (100 M, CDCl\(_3\)): \(\delta\) 17.97, 24.81, 33.15, 35.71, 122.74, 126.38, 128.38, 128.61, 140.11. The spectroscopic data are in agreement with that previously reported.\(^{2}\)

Undecanenitrile (6d). \(^1\)H NMR (400 M, CDCl\(_3\)): \(\delta\) 0.88 (t, \(J = 6.8\) Hz, 3H), 1.20-1.32 (m, 12H), 1.41-1.46 (m, 2H), 1.62-1.69 (m, 2H), 2.33 (t, \(J = 7.2\) Hz, 2H). \(^{13}\)C NMR (100 M, CDCl\(_3\)): \(\delta\) 13.96, 16.98, 22.54, 25.26, 28.54, 28.64, 29.13, 29.19, 29.34, 31.73, 119.73. The spectroscopic data are in agreement with that previously reported.\(^{17}\)

2-Methyldecanenitrile (7d). Partial \(^1\)H NMR (400 M, CDCl\(_3\)): \(\delta\) 0.88 (t, \(J = 6.8\) Hz, 3H), 2.55-2.64 (m, 1H), partial \(^{13}\)C NMR (400 M, CDCl\(_3\)): \(\delta\) 17.90, 25.38, 26.91, 28.95, 29.05, 29.20, 31.69, 33.95. The \(^1\)H NMR spectroscopic data are in agreement with that previously reported.\(^{18}\)
3-Cyclohexylpropanenitrile (6e). Ni(ClO₄)₂·6H₂O (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), vinylcyclohexane (55.1 mg, 0.5 mmol) and H₂O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to give the desired product 6e in 80% yield (55.0 mg) as a colorless oil. ¹H NMR (400 M, CDCl₃): δ 0.87-0.95 (m, 2H), 1.09-1.30 (m, 3H), 1.35-1.44 (m, 1H), 1.55 (q, J = 7.2 Hz, 2H), 1.65-1.74 (m, 5H), 2.35 (t, J = 7.2 Hz, 2H). ¹³C NMR (100 M, CDCl₃): δ 14.49, 25.81, 26.17, 32.36, 32.42, 36.43, 119.96. The spectroscopic data are in agreement with that previously reported.

Ni(ClO₄)₂·6H₂O (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), acetonitrile (2.5 mL), 2-allylisooindoline-1,3-dione (93.6 mg, 0.5 mmol) and H₂O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Purification by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to give the desired product 6f in 78% yield (83.5 mg) as a colorless oil and 7f in 17% yield (18.2 mg) as a white solid.

4-(1,3-Dioxoisooindolin-2-yl)butanenitrile (6f). ¹H NMR (400 M, CDCl₃): δ 2.05-2.12 (m, 2H), 2.45 (t, J = 7.2 Hz, 2H), 3.82 (t, J = 6.4 Hz, 2H), 7.73-7.77 (m, 2H), 7.84-7.88 (m, 2H). ¹³C NMR (100 M, CDCl₃): δ 14.95, 24.60, 36.50, 118.70, 123.30, 131.70, 134.11, 168.10. The spectroscopic data are in agreement with that previously reported.

3-(1,3-Dioxoisooindolin-2-yl)-2-methylpropanenitrile (7f). ¹H NMR (400 M, CDCl₃): δ 1.40 (d, J = 6.8 Hz, 3H), 3.19-3.28 (m, 1H), 3.77 (dd, J = 13.8, 6.8 Hz, 1H), 4.02 (dd, J = 13.6, 8.4 Hz, 1H), 7.76-7.79 (m, 2H), 7.87-7.91 (m, 2H). ¹³C NMR (100 M, CDCl₃): δ 15.54, 25.23,
40.09, 120.37, 123.68, 131.59, 134.40, 167.69. The spectroscopic data are in agreement with that previously reported.\textsuperscript{21}

\begin{center}
\includegraphics[width=0.2\textwidth]{6g}
\end{center}

\textbf{4-(Phenylamino)butanenitrile (6g).} Ni(ClO\textsubscript{4})\textsubscript{2} \cdot 6H\textsubscript{2}O (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)\textsubscript{2} (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), N-allylaniline (66.6 mg, 0.5 mmol) and H\textsubscript{2}O (18 \mu L, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) to give the product \textit{6g} in 81\% yield (64.9 mg) as a light yellow oil. \textsuperscript{1}H NMR (400 M, CDCl\textsubscript{3}): \(\delta\) 1.88-1.95 (m, 2H), 2.42 (t, \(J = 6.8\) Hz, 2H), 3.26 (t, \(J = 6.8\) Hz, 2H), 3.73 (s, 1H), 6.60 (d, \(J = 8.0\) Hz, 2H), 6.72 (t, \(J = 7.6\) Hz, 1H), 7.18 (t, \(J = 8.0\) Hz, 2H). \textsuperscript{13}C NMR (100 M, CDCl\textsubscript{3}): \(\delta\) 14.61, 25.00, 42.07, 112.65, 117.65, 119.39, 129.24, 147.43. The spectroscopic data are in agreement with that previously reported.\textsuperscript{22}

\begin{center}
\includegraphics[width=0.2\textwidth]{6h}
\end{center}

\textbf{4-((tert-Butyldimethylsilyl)oxy)-6-phenylhexanenitrile (6h).} Ni(ClO\textsubscript{4})\textsubscript{2} \cdot 6H\textsubscript{2}O (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)\textsubscript{2} (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), \textit{tert}-butyldimethyl((5-phenylpent-1-en-3-yl)oxy)silane (138.3 mg, 0.5 mmol) and H\textsubscript{2}O (18 \mu L, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to give the desired product \textit{6h} in 80\% yield (120.7 mg) as a colorless oil. \textsuperscript{1}H NMR (400 M, CDCl\textsubscript{3}): \(\delta\) 0.12 (d, \(J = 2.0\) Hz, 6H), 0.95 (s, 9H), 1.77-1.94 (m, 4H), 2.43 (t, \(J = 7.2\) Hz, 2H), 2.66 (t, \(J = 8.4\) Hz, 2H), 3.85-3.90 (m, 1H), 7.19-7.24 (m, 3H), 7.30-7.34 (m, 2H). \textsuperscript{13}C NMR (100 M, CDCl\textsubscript{3}): \(\delta\) -4.74, -4.44, 12.97, 17.92, 25.73, 31.19, 32.10, 38.52, 69.70, 119.85, 125.86, 128.15, 128.39, 141.64. IR (neat): 3084, 3060, 3026, 2952, 2929, 2857, 2246, 1603, 1495, 1469, 1453, 1362, 1254, 1092, 993, 834, 774, 746, 698, 663 cm\textsuperscript{-1}. HRMS (EI) calcd for C\textsubscript{18}H\textsubscript{29}NOSi [M]\textsuperscript{+}: 303.2018, found 303.2010.
Ni(ClO$_4$)$_2$·6H$_2$O (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), (but-3-en-1-yloxy)(tert-butyl)diphenylsilane (155.3 mg, 0.5 mmol) and H$_2$O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Purification by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to give the desired product 6i in 74% yield (124.3 mg) as a colorless oil and 7i in 7% yield (11.5 mg) as a colorless oil.

5-((tert-Butyldiphenylsilyl)oxy)pentanenitrile (6i). $^1$H NMR (400 M, CDCl$_3$): δ 1.06 (s, 9H), 1.64-1.71 (m, 2H), 1.73-1.81 (m, 2H), 2.30 (t, $J$ = 7.2 Hz, 2H), 3.69 (t, $J$ = 6.0 Hz, 2H), 7.35-7.43 (m, 6H), 7.64-7.66 (m, 4H). $^{13}$C NMR (100 M, CDCl$_3$): δ 16.74, 19.05, 22.09, 26.73, 31.08, 62.52, 119.62, 127.60, 129.60, 133.45, 135.38. IR (neat): 3071, 3045, 2931, 2857, 2244, 1590, 1472, 1427, 1385, 1186, 1109, 1007, 974, 822, 740, 700, 686 cm$^{-1}$. HRMS (ESI) calcd for C$_{21}$H$_{31}$N$_2$O$^+$: 355.2200, found 355.2199.

4-((tert-Butyldiphenylsilyl)oxy)-2-methylbutanenitrile (7i). $^1$H NMR (400 M, CDCl$_3$): δ 1.06 (s, 9H), 1.32 (d, $J$ = 7.2 Hz, 3H), 1.68-1.79 (m, 1H), 1.81-1.89 (m, 1H), 2.92-3.01 (m, 1H), 3.73-3.85 (m, 2H), 7.37-7.46 (m, 6H), 7.64-7.67 (m, 4H). $^{13}$C NMR (100 M, CDCl$_3$): δ 17.76, 19.18, 21.94, 26.79, 36.70, 60.53, 122.91, 127.75, 127.76, 129.78, 129.80, 133.15, 133.35, 135.45, 135.51. IR (neat): 3071, 2931, 2857, 2239, 1587, 1472, 1428, 1388, 1110, 998, 981, 902, 822, 738, 700, 687 cm$^{-1}$. HRMS (ESI) calcd for C$_{21}$H$_{31}$N$_2$O$^+$: 355.2200, found 355.2196.

Ni(ClO$_4$)$_2$·6H$_2$O (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), pent-4-en-1-ol (43.1 mg, 0.5 mmol) and H$_2$O (18 μL, 1 mmol) were stirred at 80 °C for 24 h.
Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate =3:2) to give the desired product 6j and 7j in 89% overall yield (50.4 mg) as a colorless oil (6j:7j = 9.1:1).

6-Hydroxyhexanenitrile (6j). \(^1\)H NMR (400 M, CDCl\(_3\)): \(\delta \) 1.49-1.64 (m, 4H), 1.67-1.74 (m, 2H), 2.27 (s, 1H), 2.38 (t, \(J = 7.2 \) Hz, 2H), 3.64 (t, \(J = 6.4 \) Hz, 2H). \(^{13}\)C NMR (100 M, CDCl\(_3\)): \(\delta \) 16.98, 24.85, 25.01, 31.53, 61.98, 119.68. The spectroscopic data are in agreement with that previously reported.\(^{23}\)

5-Hydroxy-2-methylpentanenitrile (7j). Partial \(^1\)H NMR (400 M, CDCl\(_3\)): \(\delta \) 1.34 (d, \(J = 7.2 \) Hz, 3H), 2.64-2.73 (m, 1H), partial \(^{13}\)C NMR (100 M, CDCl\(_3\)): \(\delta \) 17.87, 25.24, 29.77, 30.38, 61.54.

\[\text{EtO} \text{CN}\]

6k

Ethyl 5-cyanopentanoate (6k). \(\text{Ni(ClO}_4)_2\cdot6\text{H}_2\text{O} \) (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), \(\text{Zn(CN)}_2\) (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), ethyl pent-4-enoate (64.1 mg, 0.5 mmol) and \(\text{H}_2\text{O} \) (18 \(\mu\)L, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1 to 3:1) to give the desired product 6k in 74% yield (57.5 mg) as a colorless oil. \(^1\)H NMR (400 M, CDCl\(_3\)): \(\delta \) 1.26 (t, \(J = 7.2 \) Hz, 3H), 1.68-1.82 (m, 4H), 2.34-2.41 (m, 4H), 4.14 (q, \(J = 7.2 \) Hz, 2H). \(^{13}\)C NMR (100 M, CDCl\(_3\)): \(\delta \) 14.00, 16.74, 23.69, 24.61, 33.09, 60.28, 119.21, 172.58. The spectroscopic data are in agreement with that previously reported.\(^{17}\)

\[\text{O} \text{CN}\]

6l

4-(2-Oxocyclohexyl)butanenitrile (6l). \(\text{Ni(ClO}_4)_2\cdot6\text{H}_2\text{O} \) (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), \(\text{Zn(CN)}_2\) (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), 2-allylcyclohexan-1-one (69.1 mg, 0.5 mmol) and \(\text{H}_2\text{O} \) (18 \(\mu\)L, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel
(eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) to give the desired product 6l in 68% yield (56.4 mg) as a colorless oil. $^1$H NMR (400 M, CDCl$_3$): δ 1.32-1.46 (m, 2H), 1.58-1.78 (m, 4H), 1.82-1.92 (m, 2H), 2.05-2.14 (m, 2H), 2.28-2.42 (m, 5H). $^{13}$C NMR (100 M, CDCl$_3$): δ 17.17, 23.08, 24.81, 27.77, 28.60, 33.97, 41.90, 49.75, 119.50, 212.26. The spectroscopic data are in agreement with that previously reported.$^{24}$

12-Oxododecanenitrile (6m). Ni(ClO$_4$)$_2$·6H$_2$O (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), undec-10-enal (84.1 mg, 0.5 mmol) and H$_2$O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) to give the desired product 6m in 58% yield (57.1 mg) as a colorless oil. $^1$H NMR (400 M, CDCl$_3$): δ 1.26-1.30 (m, 10H), 1.39-1.46 (m, 2H), 1.59-1.69 (m, 4H), 2.34 (t, $J$ = 7.2 Hz, 2H), 2.41-2.45 (m, 2H), 9.76 (s, 1H). $^{13}$C NMR (100 M, CDCl$_3$): δ 16.96, 21.88, 25.20, 28.47, 28.56, 28.95, 29.05, 29.09, 29.11, 43.73, 119.74, 202.80. The spectroscopic data are in agreement with that previously reported.$^{25}$

Synthesis of 6n-6s.

Typical procedure for the synthesis of 6n.

The reaction was conducted in an oven-dried screw-cap vial (8 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), dppf (16.6 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), acetonitrile (2.5 mL), diethyl allylphosphonate (89.1 mg, 0.5 mmol) were added sequentially
to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then H₂O (18 μL, 1 mmol) was added to the vial. After the reaction mixture was stirred at 80 °C for 12 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: ethyl acetate) to give the desired product 6n in 85% yield (86.9 mg) as a colorless oil.

\[(EtO)_2P\overset{\text{CN}}{\longrightarrow}\]

6n

**Diethyl (3-cyanopropyl)phosphonate (6n).** ¹H NMR (400 M, CDCl₃): δ 1.34 (t, J = 7.2 Hz, 6H), 1.85-2.03 (m, 4H), 2.52 (t, J = 6.8 Hz, 2H), 4.07-4.17 (m, 4H). ¹³C NMR (100 M, CDCl₃): δ 16.17 (d, ³J C-P = 5.7 Hz), 17.46 (d, ²J C-P = 15.4 Hz), 18.90 (d, ³J C-P = 4.5 Hz), 24.20 (d, ¹J C-P = 142.6 Hz), 61.59 (d, ²J C-P = 6.1 Hz), 118.63. ³¹P NMR (162 M, CDCl₃): δ 29.28. IR (neat): 3458, 2979, 2927, 2909, 2244, 1233, 1163, 1024, 957, 784, 733 cm⁻¹. HRMS (ESI) calcd for C₆H₁₈N₂O₃P [M+NH₄]⁺: 223.1206, found 223.1201.

\[(EtO)_2P\overset{\text{CN}}{\longrightarrow}\]

6o

**3-(2-Oxopyrrolidin-1-yl)propanenitrile (6o).** NiCl₂·6H₂O (5.9 mg, 0.025 mmol), dppf (16.6 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), acetonitrile (2.5 mL), 1-vinylpyrrolidin-2-one (55.6 mg, 0.5 mmol) and H₂O (18 μL, 1 mmol) were stirred at 80 °C for 12 h. Column chromatography on silica gel (eluent: ethyl acetate) to give the desired product 6o in 80% yield (55.4 mg) as a colorless oil. ¹H NMR (400 M, CDCl₃): δ 2.06-2.14 (m, 2H), 2.41 (t, J = 8.0 Hz, 2H), 2.64 (t, J = 6.4 Hz, 2H), 3.55-3.59 (m, 4H). ¹³C NMR (100 M, CDCl₃): δ 16.39, 17.98, 30.43, 38.82, 47.87, 117.96, 175.44. The spectroscopic data are in agreement with that previously reported.²⁶
3-(9H-Carbazol-9-yl)propanitrile (6p). \(\text{NiCl}_2\cdot6\text{H}_2\text{O}\) (5.9 mg, 0.025 mmol), dpff (16.6 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), \(\text{Zn(CN)}_2\) (35.2 mg, 0.3 mmol), 9-vinyl-9H-carbazole (96.6 mg, 0.5 mmol), acetonitrile (2.5 mL) and \(\text{H}_2\text{O}\) (18 \(\mu\text{L}, 1\ \text{mmol}) were stirred at 80 °C for 12 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) afforded the product 6p in 97% yield (106.8 mg) as a white solid. M.p.: 149.0-150.2 °C.

\(^1\text{H NMR}\) (400 M, CDCl\(_3\)): \(\delta\) 2.62 (t, \(J = 7.2\ \text{Hz}, 2\text{H}\)), 4.41 (t, \(J = 7.2\ \text{Hz}, 2\text{H}\)), 7.20-7.28 (m, 4H), 7.41 (t, \(J = 7.6\ \text{Hz}, 2\text{H}\)), 8.03 (d, \(J = 7.6\ \text{Hz}, 2\text{H}\)). \(^{13}\text{C NMR}\) (100 M, CDCl\(_3\)): \(\delta\) 17.02, 38.54, 108.09, 117.35, 119.75, 120.50, 123.09, 125.99, 139.34. IR (neat): 3045, 2956, 2930, 2244, 1593, 1485, 1459, 1419, 1383, 1353, 1333, 1327, 1261, 1225, 1198, 1152, 1123, 1066, 744, 724 cm\(^{-1}\). HRMS (EI) calcd for C\(_{15}\)H\(_{12}\)N\(_2\)[M]\(^+\): 220.1000, found 220.1005.

2-Cyanoethyl pivalate (6q). \(\text{NiCl}_2\cdot6\text{H}_2\text{O}\) (5.9 mg, 0.025 mmol), dpff (16.6 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), \(\text{Zn(CN)}_2\) (35.2 mg, 0.3 mmol), acetonitrile (2.5 mL), vinyl pivalate (64.1 mg, 0.5 mmol) and \(\text{H}_2\text{O}\) (18 \(\mu\text{L}, 1\ \text{mmol}) were stirred at 80 °C for 12 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the product 6q in 53% yield (41.1 mg) as a colorless oil. \(^1\text{H NMR}\) (400 M, CDCl\(_3\)): \(\delta\) 1.24 (s, 9H), 2.72 (t, \(J = 6.4\ \text{Hz}, 2\text{H}\)), 4.27 (t, \(J = 6.4\ \text{Hz}, 2\text{H}\)). \(^{13}\text{C NMR}\) (100 M, CDCl\(_3\)): \(\delta\) 17.89, 26.95, 38.69, 58.43, 116.68, 177.91. The spectroscopic data are in agreement with that previously reported.\(^{27}\)
NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), dppf (16.6 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), acetonitrile (2.5 mL), dimethyl(phenyl)(vinyl)silane (81.2 mg, 0.5 mmol) and H$_2$O (18 μL, 1 mmol) were stirred at 80 °C for 12 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product 6r and 7r in 86% overall yield (81.3 mg) as a colorless oil (6r:7r = 16.7:1).

3-(Dimethyl(phenyl)silyl)propanenitrile (6r). $^1$H NMR (400 M, CDCl$_3$): δ 0.34 (s, 6H), 1.11-1.15 (m, 2H), 2.22-2.26 (m, 2H), 7.35-7.38 (m, 3H), 7.47-7.49 (m, 2H). $^{13}$C NMR (100 M, CDCl$_3$): δ -3.67, 11.77, 11.95, 121.02, 127.95, 129.41, 133.34, 136.46. The spectroscopic data are in agreement with that previously reported.$^{28}$

2-(Dimethyl(phenyl)silyl)propanenitrile (7r). Partial $^1$H NMR (400 M, CDCl$_3$): δ 0.48 (d, $J$ = 0.8 Hz, 6H), 1.22 (d, $J$ = 7.2 Hz, 3H), 1.98 (q, $J$ = 7.2 Hz, 1H), 7.54-7.57 (m, 2H). Partial $^{13}$C NMR (100 M, CDCl$_3$): δ -5.69, -5.09, 11.43, 11.86, 128.02, 130.04, 133.76. The $^1$H NMR spectroscopic data are in agreement with that previously reported.$^{29}$

3-(Phenylsulfonyl)propanenitrile (6s). NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), dppf (16.6 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), (vinylsulfonyl)benzene (84.1 mg, 0.5 mmol), acetonitrile (2.5 mL) and H$_2$O (18 μL, 1 mmol) were stirred at 80 °C for 12 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2:1) afforded the product 6s in 86% yield (84.0 mg) as a white solid. $^1$H NMR (400 M, CDCl$_3$): δ 2.81 (t, $J$ = 7.6 Hz, 2H), 3.41 (t, $J$ = 7.6 Hz, 2H), 7.62 (t, $J$ = 7.6 Hz, 2H), 7.72 (t, $J$ = 7.6 Hz, 1H), 7.93 (d, $J$ = 7.6 Hz, 2H). $^{13}$C NMR (100 M, CDCl$_3$): δ 11.79, 50.75, 116.09, 128.04, 129.57, 134.51, 137.27. The spectroscopic data are in agreement with that previously reported.$^{30}$

Synthesis of 8.
5-Phenethyldihydrofuran-2(3H)-one (8). Ni(ClO$_4$)$_2$·6H$_2$O (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), 5-phenylpent-1-en-3-ol (81.1 mg, 0.5 mmol) and H$_2$O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to give the product 8 in 67% yield (63.5 mg) as a colorless oil. $^1$H NMR (400 M, CDCl$_3$): δ 1.80-1.94 (m, 2H), 1.99-2.08 (m, 1H), 2.24-2.33 (m, 1H), 2.49-2.53 (m, 2H), 2.68-2.85 (m, 2H), 4.41-4.48 (m, 1H), 7.18-7.21 (m, 3H), 7.27-7.30 (m, 2H). $^{13}$C NMR (100 M, CDCl$_3$): δ 27.77, 28.63, 31.44, 37.13, 79.76, 125.99, 128.26, 128.35, 140.58, 177.03. The spectroscopic data are in agreement with that previously reported.$^{31}$

**Gram scale study:**

To an oven-dried sealable Schlenk tube were added NiCl$_2$·6H$_2$O (0.5 mmol, 118.8 mg), Xantphos (0.6 mmol, 347.2 mg), Zn (2 mmol, 130.8 mg) and Zn(CN)$_2$ (6 mmol, 704.5 mg). The tube was evacuated and back-filled with argon for three times, then dioxane (50 mL), 1a (10 mmol, 1.18 g) and water (1 mL) were added sequentially under argon. The tube was sealed and the mixture was stirred at 80 °C for 6 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and dissolved in 20 mL ethyl acetate, then 3 mL 30% H$_2$O$_2$ was added to the solution and the mixture was stirred at room temperature for 10 min. The reaction was quenched by saturated Na$_2$S$_2$O$_3$ and extracted with ethyl acetate, the organic layers was combined, washed by saturated NaCl and dried over anhydrous Na$_2$SO$_4$. The mixture was filtered and the solvent
was evaporated under the reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to give the desired product 2a in 86% yield (1.25 g) as a colorless oil.

Control experiments.

(1) Reaction of 1a in the absence of water.

In a nitrogen-filled glove box, NiCl$_2$(DME) (5.5 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL) and 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was dissolved in CDCl$_3$. The NMR yields were obtained by $^1$H NMR analysis of the crude mixture using mesitylene (60.1 mg, 0.5 mmol) as an internal standard. The desired product 2a was not detected.

(2) Deuterium labeling experiments.

a) NiCl$_2$·6H$_2$O-catalyzed deuterium labeling experiment of 1a with D$_2$O.

In a nitrogen-filled glove box, NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL) and 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then D$_2$O (50 μL) was added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture
was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to give the desired product 2a-d in 91% yield (66.8 mg) as a colorless oil. 

\[ \delta 1.57-1.60 \text{ (m, 2.19H), 2.33 (s, 3H), 3.81-3.87 (m, 0.67H), 7.17 (d, } J = 8.0 \text{ Hz, 2H), 7.22 (d, } J = 8.0 \text{ Hz, 2H).} \]

\[ \delta 20.87, 21.06 \text{ (t, } J = 19.4 \text{ Hz), 21.22, 21.31, 30.51, 30.59, 30.66, 121.65, 126.42, 129.61, 133.97, 137.64.} \]

b) NiCl\(_2\)(DME)-catalyzed deuterium labeling experiment of 1a with D\(_2\)O.

In a nitrogen-filled glove box, NiCl\(_2\)(DME) (5.5 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)\(_2\) (35.2 mg, 0.3 mmol), dioxane (2.5 mL) and 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then D\(_2\)O (50 μL) was added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1 to 50:1) to give the desired product 2a-d in 89% yield (65.0 mg) as a colorless oil. 

\[ \delta 1.57-1.61 \text{ (m, 2.11H), 2.34 (s, 3H), 3.82-3.87 (m, 0.65H), 7.17 (d, } J = 8.0 \text{ Hz, 2H), 7.23 (d, } J = 8.0 \text{ Hz, 2H).} \]

\[ \delta 20.89, 21.06 \text{ (t, } J = 20.1 \text{ Hz), 21.24, 21.34, 30.45, 30.54, 30.61, 30.69, 121.67, 126.43, 129.63, 133.99, 137.67.} \]

IR (neat): 3053, 3027, 2984, 2923, 2873, 2240, 1514, 1453, 1379, 1284, 1116, 1083, 1051, 1021, 814, 720 cm\(^{-1}\).

c) NiCl\(_2\)·6H\(_2\)O-catalyzed deuterium labeling experiment of 2a with D\(_2\)O.
In a nitrogen-filled glove box, NiCl$_2$·6H$_2$O (5.5 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL) and 2a (72.6 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then D$_2$O (50 μL) was added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1 to 50:1) to give product 2a in 90% yield (65.3 mg) as a colorless oil.

(3) Ni(cod)$_2$-catalyzed hydrocyanation of 1a.

In a nitrogen-filled glove box, Ni(cod)$_2$ (6.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol) and dioxane (2.5 mL) were stirred for at room temperature 10 min. Then Zn(CN)$_2$ (35.2 mg, 0.3 mmol) and 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) were added sequentially to the mixture. The vial cap was then securely fitted and taken outside the glove box, then H$_2$O (50 μL) was added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1 to 50:1) to give the desired product 2a in 90% yield (65.3 mg) as a colorless oil.

(4) NiCl(dppf)$_2$-catalyzed hydrocyanation of 1a.
In a nitrogen-filled glove box, NiCl(dppf) (9.7 mg, 0.015 mmol), Zn(CN)$_2$ (21.1 mg, 0.18 mmol), dioxane (1.5 mL), 1-methyl-4-vinylbenzene (35.5 mg, 0.3 mmol) were added sequentially to the vial. The vial cap was then securely fitted and taken outside the glove box, then H$_2$O (30 μL) was added to the vial. After the reaction mixture was stirred at 80 °C for 8 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to give the desired product 2a in 85% yield (37.0 mg) as a colorless oil.

It is unlikely that the reaction goes through Ni(I) species involving transmetalation of Ni-Cl with Zn(CN)$_2$ to form a Ni(I)-CN species followed by addition of Ni(I)-CN to the alkene and protonation (Scheme S1), since it is hard to explain the observed regioselectivity and deuterium labeling results. For regioselectivity, the formation of intermediate 18 would lead to the branched isomer. However, it is not stable compared to $\eta^3$-benzyl nickel species. Deuterium labeling experiment indicated that deuterium was found in both benzylic position and methyl group. To explain the formation of the product bearing a D atom at the benzylic position, intermediate 21 should be formed (Scheme S2). However, 21 was not observed during the reaction. In addition, the intermediate 22 was also unfavored due to the steric effect.
Scheme S1. Unfavored reaction pathway for Ni(I)-catalyzed hydrocyanation reaction

Scheme S2

(5) Reaction of 1a in the presence of TMSCN/MeOH.

In a nitrogen-filled glove box, NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), dioxane (2.5 mL), 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) and TMSCN (99.2 mg, 1 mmol) were added sequentially to a screw-cap
vial. The vial cap was then securely fitted and taken outside the glove box, then H₂O (50 μL) and MeOH (32 mg, 1 mmol) were added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was dissolved in CDCl₃. The NMR yields were obtained by ¹H NMR analysis of the crude mixture using mesitylene (60.1 mg, 0.5 mmol) as an internal standard. The desired product 2a was not formed and 83% of starting material 1a was observed. Column chromatography on silica gel (eluent: pentane) afforded the 1a in 63% yield (37.0 mg) as a colorless liquid.

(6) Mercury poisoning experiment.

In a nitrogen-filled glove box, NiCl₂·6H₂O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)₂ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) and Hg (501.5 mg, 2.5 mmol, 100 equiv respect to Ni) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then H₂O (50 μL) was added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was dissolved in CDCl₃. The NMR yields were obtained by ¹H NMR analysis of the crude mixture using mesitylene (60.1 mg, 0.5 mmol) as an internal standard. 95% NMR yield of the desired product 2a was observed.

(7) Ni-catalyzed hydrocyanation of 1a using MeOH or PhCOOH as the hydrogen source.
In a nitrogen-filled glove box, NiCl$_2$(DME) (5.5 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL) and 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then MeOH (32 mg, 1.0 mmol) was added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was dissolved in CDCl$_3$. The NMR yields were obtained by $^1$H NMR analysis of the crude mixture using mesitylene (60.1 mg, 0.5 mmol) as an internal standard. 11% NMR yield of the desired product 2a was observed.

In a nitrogen-filled glove box, NiCl$_2$(DME) (5.5 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), PhCOOH (122.1 mg, 1.0 mmol), dioxane (2.5 mL) and 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was dissolved in CDCl$_3$. The NMR yields were obtained by $^1$H NMR analysis of the crude mixture using mesitylene (60.1 mg, 0.5 mmol) as an internal standard. 6% NMR yield of the desired product 2a was observed.
References


MeO

2e

Me

CN
CN
MeO
Me

2o
2p
2t
$\mathbf{2v \ d.r = 1:1}$
2w

CN

Me
4a' (E/Z = 33.3:1)
$4a'$ ($E/Z = 33.3:1$)
6a

[Chemical structure image]
MeO\(^{6\text{b}}\) + MeO\(^{7\text{b}}\) (\(6\text{b}:7\text{b} = 8.3:1\))
(6b:7b = 8.3:1)
Ph\textsubscript{6c}CN
$6d$ $+ \quad 7d$

$\text{(6d:7d} = 12.5:1)$
(6d:7d = 12.5:1)
6e
$6\text{e}$
TBDPSO\(\text{CN}\)

6i
TBDPSO-\text{CN}

6i
\[ \text{HO} \text{CN} + \text{HO} \text{CN} \]

\((6j:7j = 9:1:1)\)
$\text{HOCH}_2\text{CN} + \text{HOCH}_2\text{CN}$

$(6j:7j = 9:1:1)$
Me₂PhSiCN + Me₂PhSiCN

(6r:7r = 16.7:1)
\[
\text{Me}_2\text{PhSi} - \text{CN} \quad + \quad \text{Me}_2\text{PhSi} - \text{CN}
\]

(\(6r:7r = 16.7:1\))
$2a-d$, $91\%$

$33\%$ D

$27\%$ D
2a-d, 91%

33% D

27% D
2a-d, 89%

NC
H(D) ↫ 35% D

Me

CH₃(D) ↫ 30% D