Ni-catalyzed hydrocyanation of alkenes with formamide as the cyano source

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Caution 1: All reactions were run in thick-wall pressure-proof glass tube (Chemglass brand microwave tube, CG-4920-01) to avoid the possible crack of the reactor.

Caution 2: All work-up and purifications were done in the fume-hood. The reaction wastes were treated by 10% FeSO$_4$ aqueous solution and collected separately to avoid possible safety risk of cyanide.

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I. General information

Unless otherwise noted, all commercially available compounds were used as purchased without further purification. Dry solvents (toluene, ethyl acetate, dichloromethane, acetonitrile, chlorobenzene, fluorobenzene, trifluoromethyl benzene) were used as commercially available. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) or Sorbent Silica Gel 60 F254 plates. The developed chromatography was analyzed by UV lamp (254 nm). High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ESI). Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Chemical shifts for $^1$H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: $\delta$ 7.26 ppm). Chemical shifts for $^{13}$C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (CDCl$_3$: $\delta$ 77.16 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.
II. General experimental procedure

**Method A:** for the hydrocyanation of **alkenes (3a-3m, 3t-3v):**

An oven-dried reaction vessel was charged with styrene (1a, 0.2 mmol, 20.8 mg), Ni(acac)₂ (10 mol%, 5.2 mg), Zn powder (20 mol%, 2.6 mg), Xantphos (15 mol%, 17.4 mg) and formamide (1.0 mL) under argon atmosphere. The vessel was sealed, heated and stirred at 150 °C (oil bath temperature) for 24 h. After the resulting mixture was cooled to room temperature, added with 10 mL brine and extracted with ethyl acetate (3×10 mL). The organic layer was combined, washed with brine (2×10 mL), dried with anhydrous sodium sulfate and filtered. The filtrate was condensed in vacuo to remove solvent and further purified by column chromatography on silica gel with a mixture of EtOAc / petroleum ether as eluent to give the product (3a, 21.2 mg) in 81% yield.

**Method B:** for the hydrocyanation of **1,2-diarylethene (3n-3s):**

An oven-dried reaction vessel was charged with 1,2-diphenylethene (1n, 0.2 mmol, 36.0 mg), Ni(acac)₂ (10 mol%, 5.2 mg), Zn powder (20 mol%, 2.6 mg), Xantphos (15 mol%, 17.4 mg), and formamide (1.0 mL) under argon atmosphere. The vessel was sealed, heated and stirred at 155 °C (oil bath temperature) for 36 h. After the resulting mixture was cooled to room temperature, added with 10 mL brine and extracted with ethyl acetate (3×10 mL). The organic layer was combined, washed with brine (2×10 mL), dried with anhydrous sodium sulfate and filtered. The filtrate was condensed in vacuo to remove solvent and further purified by column chromatography on silica gel with a mixture of EtOAc / petroleum (1:15) ether as eluent to give the product (3n, 32.3 mg) in 78% yield.

### III. Conditions optimization

<table>
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<th>Change from the “standard conditions”</th>
<th>3a (%)</th>
<th>1a (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>5 mol% Ni(acac)₂</td>
<td>30</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>10 mol% Ni(acac)₂</td>
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<td>8</td>
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<td>4</td>
<td>10 mol% Ni(OAc)₂</td>
<td>48</td>
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<td>5</td>
<td>10 mol% NiBr₂</td>
<td>36</td>
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<td>6</td>
<td>10 mol% NiF₂</td>
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<tr>
<td>7</td>
<td>10 mol% Ni(OAc)₂</td>
<td>66</td>
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<tr>
<td>9</td>
<td>10 mol% Xantphos</td>
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<tr>
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<td>15 mol% Xantphos</td>
<td>81</td>
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<tr>
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<td>15 mol% PPh₃</td>
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<tr>
<td>13</td>
<td>15 mol% PyPPh₂</td>
<td>8</td>
<td>55</td>
</tr>
</tbody>
</table>
14  15 mol% Dpephos       10  51
15  10 mol% Dpephos + 10% DPPP  12  56
16  10 mol% Dpephos + 10% BINAP  18  51
17  **20 mol% Zn**       **81**  **8**
18  40 mol% Zn          41  12
19  20 mol% Mn         40  45
20  20 mol% Mg         34  48
21  20 mol% HCO$_2$H      54  22
22  20 mol% HCO$_2$NH$_4$   48  25
23  140 °C            44  36
24  **150 °C**        **81**  **8**
25  160 °C            28  12

*aConditions: Styrene (1a, 0.2 mmol, 20.8 mg), Ni(acac)$_2$ (10 mol%, 5.2 mg), Zn powder (20 mol%, 2.6 mg), Xantphos (15 mol%, 17.4 mg), formamide (1.0 mL) were reacted at 150 °C (oil bath temperature) for 24 h under argon atmosphere. *bYields and recovered 1a were tested by GC with an internal standard.

### IV. Mechanistic experiments

**(1) Detection of cyanide anion by indicator paper**

Picrate paper was prepared by wetting filter paper with a solution of sodium bicarbonate (5.0 g) and picric acid (0.5 g) in 100 mL of water. After drying the paper, it was cut as strips and inserted into a 10 mL reaction vessel (A). Another oven-dried reaction vessel (B) was charged with Ni(acac)$_2$ (0.01 mmol, 10 mol%), Zn powder (20 mol%, 2.6 mg, with or without), Xantphos (0.015 mmol, 15 mol%), formamide (1.0 mL) under argon. The reaction vessel was sealed, heated and stirred at 150 °C (oil bath temperature) for 12 h. Then, the reaction vessel B was cooled to r.t., connected to the reaction vessel (A) in head-to-head model and sealed the joint by rubber stopper immediately. Then, this reaction B was heated at 80 °C for 1 h. The test paper was changed from yellow to red, indicating the presence of cyanide anion.

\[
\text{(a) } 2\text{H}^+ + \text{CN}^- + \text{NH}_4^+ \rightarrow \text{HCN} + \text{HCO}_2\text{NH}_4^+ 
\]

**detected by picrate paper**

**detected by $^{13}$C NMR**

**(2) Detection of ammonium formate ($\text{HCO}_2\text{NH}_4^+$) by $^{13}$C NMR.**

Ni(acac)$_2$ (10 mol%, 5.2 mg), Zn powder (20 mol%, 2.6 mg), Xantphos (15 mol%, 17.4 mg), and formamide (1.0 mL) were reacted at 150 °C for 12 h under argon atmosphere in the sealed reaction vessel. After cooled to room temperature, 0.1 mL of the reaction mixture was transferred into the NMR tube and 0.4 mL of DMSO-$d_6$ was added as an internal standard for $^{13}$C NMR measurements. The ammonium formate was detected by the $^{13}$C NMR at 167.36 ppm (C=O), which was identical with the literature reports. Authentic sample of ammonium formate (5 mg) was further added into the same NMR tube and recorded the $^{13}$C NMR spectrum again, to find that the chemical shift of added ammonium formate was same as the signal of the previously observed one.
(3) Ni-catalyzed migrative isomerization

An oven-dried reaction vessel was charged with 1-methoxy-4-(prop-1-en-1-yl)benzene (1l, 0.21 mmol, 31.1 mg), Ni(acac)$_2$ (10 mol%, 5.2 mg), Zn powder (20 mol%, 2.6 mg), Xantphos (15 mol%, 17.4 mg), and formamide (1.0 mL) under argon atmosphere. The vessel was sealed, heated and stirred at 150 °C (oil bath temperature) for 8 h. After the resulting mixture was cooled to room temperature, added with 10 mL brine and extracted with ethyl acetate (3x10 mL). The organic layer was combined, washed with brine (2x10 mL), dried with anhydrous sodium sulfate and filtered. Then, we carefully isolated the reaction mixture, two main-products (1l' and 3l) were obtained and characterized. Their yields were determined by the $^1$H NMR of reaction mixture using CH$_3$NO$_2$ (0.25 mmol, 15.3 mg) as the internal standard.

V. Spectra data of products 3a-3v, 4v and 5a

(3a) 2-phenylpropanenitrile

The title compound was prepared according to the general procedure described above by the reaction between styrene (1a) with formamide, and purified by standard extraction and concentration procedures to provide yellow oil (20.4 mg, 78%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 - 7.31 (m, 5H), 3.91 (q, $J = 7.2$ Hz, 1H), 1.65 (d, $J = 7.2$ Hz,
$^3$H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.18, 129.28, 128.18, 126.83, 121.72, 31.39, 21.61. IR (cm$^{-1}$): 2984, 2935, 2241, 1495, 1453, 1403, 1232, 699.

(3b) 2-(4-butylphenyl)propanenitrile$^2$

![Image of 2-(4-butylphenyl)propanenitrile](image)

The title compound was prepared according to the general procedure described above by the reaction between 1-(tert-butyl)-4-vinylbenzene (1b) with formamide, and purified by standard extraction and concentration procedures to provide yellow oil (30.2 mg, 73%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (d, $J$ = 8.4 Hz, 2H), 7.29 (d, $J$ = 8.4 Hz, 2H), 3.89 (q, $J$ = 7.6 Hz, 1H), 1.64 (d, $J$ = 7.6 Hz, 3H), 1.08 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 135.66, 134.20, 129.47, 128.24, 121.24, 42.69, 30.86, 23.56, 21.50. IR (cm$^{-1}$): 2931, 2871, 2859, 2241, 1654, 1513, 1086, 833.

(3c) 2-(p-tolyl)propanenitrile$^1$

![Image of 2-(p-tolyl)propanenitrile](image)

The title compound was prepared according to the general procedure described above by the reaction between 1-methyl-4-vinylbenzene (1c) with formamide, and purified by standard extraction and concentration procedures to provide yellow oil (21.7 mg, 75%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24 (d, $J$ = 8.4 Hz, 2H), 7.19 (d, $J$ = 8.0 Hz, 2H), 3.87 (q, $J$ = 7.2 Hz, 1H), 2.35 (s, 3H), 1.63 (d, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.00, 134.22, 129.91, 126.71, 121.91, 31.01, 21.64, 21.18. IR (cm$^{-1}$): 2360, 2240, 1685, 1514, 1403.

(3d) 2-(4-methoxyphenyl)propanenitrile$^1$

![Image of 2-(4-methoxyphenyl)propanenitrile](image)

The title compound was prepared according to the general procedure described above by the reaction between 1-methoxy-4-vinylbenzene (1d) with formamide, and purified by standard extraction and concentration procedures to provide yellow oil (23.2 mg, 72%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 - 7.25 (m, 2H), 6.93 - 6.89 (m, 2H), 3.87 (q, $J$ = 7.6 Hz, 1H), 3.81 (s, 3H), 1.62 (d, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.41, 129.20, 127.97, 122.00, 114.60, 55.48, 30.60, 21.66. IR (cm$^{-1}$): 2984, 2938, 2240, 1612, 1514, 1250, 1181, 832.

(3e) 2-(2-methoxyphenyl)propanenitrile$^6$

![Image of 2-(2-methoxyphenyl)propanenitrile](image)
The title compound was prepared according to the general procedure described above by the reaction between 1-methoxy-2-vinylbenzene (1e) with formamide, and purified by standard extraction and concentration procedures to provide oil (22.5 mg, 70%).

1H NMR (400 MHz, CDCl₃) δ 7.42 (dd, J = 7.6, 1.6 Hz, 1H), 7.31 (td, J = 7.6, 1.6 Hz, 1H), 6.98 (tt, J = 21.6, 10.8 Hz, 1H), 6.90 (d, J = 8.2 Hz, 1H), 4.25 (q, J = 7.2 Hz, 1H), 3.87 (s, 3H), 1.58 (d, J = 7.2 Hz, 3H). 13C NMR (100 MHz, CDCl₃) δ 156.13, 129.44, 127.72, 125.47, 122.15, 121.10, 110.85, 55.58, 25.74, 19.64. IR (cm⁻¹): 2940, 2840, 2242, 1601, 1250, 1028, 755.

(3f) 2-(4-fluorophenyl)propanenitrile

The title compound was prepared according to the general procedure described above by the reaction between 1-fluoro-4-vinylbenzene (1f) with formamide, and purified by standard extraction and concentration procedures to provide oil (17.3 mg, 58%).

1H NMR (400 MHz, CDCl₃) δ 7.38 - 7.29 (m, 4H), 3.89 (q, J = 7.2 Hz, 1H), 1.63 (d, J = 7.2 Hz, 3H). 13C NMR (100 MHz, CDCl₃) δ 162.51 (d, J = 245.7 Hz), 129.74 (d, J = 8.2 Hz), 125.77, 117.80, 116.22 (d, J = 21.8 Hz), 33.13, 23.03. IR (cm⁻¹): 2919, 2853, 1648, 1462, 1305, 1231, 962.

(3g) 2-(4-chlorophenyl)propanenitrile

The title compound was prepared according to the general procedure described above by the reaction between 1-chloro-4-vinylbenzene (1g) with formamide, and purified by standard extraction and concentration procedures to provide oil (16.5 mg, 50%).

1H NMR (400 MHz, CDCl₃) δ 7.38 - 7.28 (m, 4H), 3.89 (q, J = 7.2 Hz, 1H), 1.63 (d, J = 7.2 Hz, 3H). 13C NMR (100 MHz, CDCl₃) δ 135.65, 134.21, 129.48, 128.24, 121.25, 30.87, 21.51. IR (cm⁻¹): 2987, 2243, 1493, 1095, 827.

(3h) 2-(naphthalen-2-yl)propanenitrile

The title compound was prepared according to the general procedure described above by the reaction between 2-vinylnaphthalene (1h) with formamide, and purified by standard extraction and concentration procedures to provide white solid (26.2 mg, 72%).

1H NMR (400 MHz, CDCl₃) δ 7.89 - 7.84 (m, 4H), 7.54 - 7.50 (m, 2H), 7.43 (dd, J = 7.6 Hz, 0.8 Hz, 1H), 4.07 (q, J = 7.2 Hz, 1H), 1.73 (d, J = 7.6 Hz, 3H). 13C NMR (100 MHz, CDCl₃) δ 134.44, 133.44, 132.90, 129.28, 127.99, 127.86, 126.87, 126.63, 125.72, 124.55, 121.74, 31.57, 21.59. IR (cm⁻¹): 3055, 2988, 2932, 2241, 1601, 1509, 1453, 1372, 1148, 821, 750.
(3i) octanenitrile
\[ \text{C}_8\text{H}_{17} \rightarrow \text{CN} \]

The title compound was prepared according to the general procedure described above by the reaction between heptane (1i) with formamide, and purified by standard extraction and concentration procedures to provide oil (16.8 mg, 67%).

\[ ^1\text{H} \text{ NMR (400 MHz, CDCl}_3 \] \delta 2.34 (t, \( J = 7.2 \text{ Hz}, 2\text{H} \)), 1.69 - 1.62 (m, 2H), 1.46 - 1.41 (m, 2H), 1.36 - 1.30 (m, 6H), 0.91 - 0.87 (m, 3H). \[ ^{13}\text{C} \text{ NMR (100 MHz, CDCl}_3 \] \delta 119.83, 31.44, 28.56, 28.38, 25.33, 22.47, 17.04, 13.95. IR (cm\(^{-1}\)): 2958, 2927, 2246, 1260, 1011.

(3j) nonanenitrile
\[ \text{C}_9\text{H}_{19} \rightarrow \text{CN} \]

The title compound was prepared according to the general procedure described above by the reaction between oct-1-ene (1j) with formamide, and purified by standard extraction and concentration procedures to provide oil (17.7 mg, 64%).

\[ ^1\text{H} \text{ NMR (400 MHz, CDCl}_3 \] \delta 2.34 (t, \( J = 7.2 \text{ Hz}, 2\text{H} \)), 1.65 (q, \( J = 7.2 \text{ Hz}, 2\text{H} \)), 1.46 - 1.41 (m, 2H), 1.31 - 1.28 (m, 8H), 0.90 - 0.87 (m, 3H). \[ ^{13}\text{C} \text{ NMR (100 MHz, CDCl}_3 \] \delta 120.00, 31.81, 29.08, 28.84, 28.78, 25.48, 22.71, 17.25, 14.17. IR (cm\(^{-1}\)): 2987, 2243, 1493, 1095, 827.

(3k) 2-phenylbutanenitrile
\[ \text{C}_9\text{H}_{11} \rightarrow \text{CN} \]

The title compound was prepared according to the general procedure described above by the reaction between allylbenzene (1k) with formamide, and purified by standard extraction and concentration procedures to provide oil (18.0 mg, 64%).

\[ ^1\text{H} \text{ NMR (400 MHz, CDCl}_3 \] \delta 7.41 - 7.30 (m, 5H), 3.74 (t, \( J = 7.2 \text{ Hz}, 1\text{H} \)), 1.99 - 1.91 (m, 2H), 1.08 (t, \( J = 7.2 \text{ Hz}, 3\text{H} \)). \[ ^{13}\text{C} \text{ NMR (100 MHz, CDCl}_3 \] \delta 135.86, 129.16, 127.82, 121.14, 114.44, 55.42, 38.20, 29.33, 11.64. IR (cm\(^{-1}\)): 3040, 2963, 2241, 1600, 1458, 1327, 752, 700.

(3l) 2-(4-methoxyphenyl)butanenitrile
\[ \text{MeO} \text{C}_9\text{H}_{11} \rightarrow \text{CN} \]

The title compound was prepared according to the general procedure described above by the reaction between 1-methoxy-4-(prop-1-en-1-yl)benzene (1l) with formamide, and purified by standard extraction and concentration procedures to provide oil (26.6 mg, 76%).

\[ ^1\text{H} \text{ NMR (400 MHz, CDCl}_3 \] \delta 7.23 (d, \( J = 8.4 \text{ Hz}, 2\text{H} \)), 6.90 (d, \( J = 8.4 \text{ Hz}, 2\text{H} \)), 3.81 (s, 3H), 3.68 (t, \( J = 7.2 \text{ Hz}, 1\text{H} \)), 1.95 - 1.89 (m, 2H), 1.06(t, \( J = 7.2 \text{ Hz}, 3\text{H} \)). \[ ^{13}\text{C} \text{ NMR (100 MHz, CDCl}_3 \] \delta 159.36, 128.40, 127.82, 121.14, 114.44, 55.42, 38.20, 29.33, 11.53. IR (cm\(^{-1}\)): 2955, 2925, 2870, 2239, 1611, 1459, 828.
(3m) 2-phenylpentanenitrile

The title compound was prepared according to the general procedure described above by the reaction between but-3-en-1-ylbenzene (1m) with formamide, and purified by standard extraction and concentration procedures to provide oil (24.1 mg, 76%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 - 7.30 (m, 5H), 3.79 (q, $J$ = 7.6 Hz, 1H), 1.96 - 1.79 (m, 2H), 1.56 - 1.46 (m, 2H), 0.96 (t, $J$ = 7.6 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.18, 129.18, 128.12, 127.38, 121.06, 77.48, 77.16, 76.84, 38.04, 37.32, 20.45, 13.56. IR (cm$^{-1}$): 3065, 3033, 2962, 2874, 2239, 1602, 1495, 1455, 1383, 1031, 757, 699.

(3n) 2,3-diphenylpropanenitrile

The title compound was prepared according to the general procedure described above by the reaction between 1,2-diphenylethene (1n) with formamide, and purified by standard extraction and concentration procedures to provide white solid (32.3 mg, 78%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 - 7.25 (m, 8H), 7.15-7.26 (m, 2H), 4.00 (dd, $J$ = 8.4, 6.4 Hz, 1H), 3.22 - 3.11 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.39, 135.34, 129.32, 129.12, 128.72, 128.30, 127.59, 127.48, 120.46, 42.29, 39.89. IR (cm$^{-1}$): 3087, 3063, 3031, 2241, 1497, 1455, 755, 698. Melting point: 55-56 °C.

(3o) 2,3-di-p-tolylpropanenitrile

The title compound was prepared according to the general procedure described above by the reaction between 1,2-di-p-tolylethene (1o) with formamide, and purified by standard extraction and concentration procedures to provide white solid (34.3 mg, 73%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.16 (s, 4H), 7.10 (d, $J$ = 8.0 Hz, 2H), 7.04 (d, $J$ = 8.0 Hz, 2H), 3.93 (dd, $J$ = 8.4, 6.5 Hz, 1H), 3.16 - 3.03 (m, 2H), 2.35 (s, 3H), 2.32 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.07, 137.07, 133.51, 132.47, 129.77, 129.42, 129.19, 127.46, 120.77, 42.00, 39.74, 21.23. IR (cm$^{-1}$): 3024, 2923, 2862, 2240, 1701, 1514, 1112, 813. Melting point: 65-66 °C.

(3p) 2,3-bis(4-methoxyphenyl)propanenitrile

The title compound was prepared according to the general procedure described above by the
reaction between 1,2-bis(4-methoxyphenyl)ethene (1p) with formamide, and purified by standard extraction and concentration procedures to provide white solid (38.4 mg, 72%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.16 - 7.14 (m, 2H), 7.05 - 7.02 (m, 2H), 6.88 - 6.86 (m, 2H), 6.83 - 6.81 (m, 2H), 3.91 (dd, \(J = 8.0, 6.8\) Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.14 - 3.02 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 159.47, 158.93, 130.45, 128.78, 128.53, 127.35, 120.87, 114.43, 114.07, 55.45, 55.36, 41.59, 39.35. IR (cm\(^{-1}\)): 2938, 2839, 2241, 1611, 1510, 1457, 1178, 1027, 827. Melting point: 117-118 °C.

**3q** 2,3-bis(4-fluorophenyl)propanenitrile\(^{10}\)

\[
\begin{array}{c}
\text{CN} \\
\text{F} \\
\text{F}
\end{array}
\]

The title compound was prepared according to the general procedure described above by the reaction between 1,2-bis(4-fluorophenyl)ethene (1q) with formamide, and purified by standard extraction and concentration procedures to provide white solid (34.1 mg, 70%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.20 - 7.15 (m, 2H), 7.07 - 7.01 (m, 4H), 7.00 - 6.95 (m, 2H), 3.97 (t, \(J = 7.2\) Hz, 1H), 3.18 - 3.06 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 163.68 (d, \(J = 29.5\) Hz), 161.22 (d, \(J = 27.9\) Hz), 131.67 (d, \(J = 3.3\) Hz), 130.98 (d, \(J = 8.1\) Hz), 130.73 (d, \(J = 3.3\) Hz), 129.36 (d, \(J = 8.2\) Hz), 120.13, 116.16 (d, \(J = 21.7\) Hz), 115.68 (d, \(J = 21.3\) Hz), 41.39, 39.11. IR (cm\(^{-1}\)): 2924, 2854, 2242, 1891, 1602, 1223, 1016, 831. Melting point: 95-96 °C.

**3r** 2,3-di(naphthalen-1-yl)propanenitrile\(^{11}\)

\[
\begin{array}{c}
\text{CN} \\
\text{CN}
\end{array}
\]

The title compound was prepared according to the general procedure described above by the reaction between 1,2-di(naphthalen-1-yl)ethene (1r) with formamide, and purified by standard extraction and concentration procedures to provide white solid (40.5 mg, 66%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.98 - 7.86 (m, 5H), 7.81 - 7.78 (m, 1H), 7.66 (d, \(J = 6.4\) Hz, 1H), 7.57 - 7.48 (m, 5H), 7.42 - 7.38 (m, 2H), 4.91 (t, \(J = 7.4\) Hz, 1H), 3.80 (d, \(J = 7.6\) Hz, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 134.18, 134.10, 132.66, 131.67, 131.63, 130.31, 129.49, 129.34, 129.32, 128.44, 128.00, 127.09, 126.58, 126.29, 126.16, 125.93, 125.65, 125.61, 122.82, 122.21, 120.92, 38.04, 35.66. IR (cm\(^{-1}\)): 3060, 2240, 1598, 1511, 1396, 797, 776. Melting point: 134-135°C.

**3s** 2,3-bis(3,5-dimethylphenyl)propanenitrile

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\text{CN} \\
\end{array}
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The title compound was prepared according to the general procedure described above by the reaction between 1,2-bis(3,5-dimethylphenyl)ethene (1s) with formamide, and purified by
standard extraction and concentration procedures to provide white solid (34.6 mg, 66%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.96 (s, 1H), 6.92 (s, 3H), 6.82 (s, 2H), 3.88 (dd, $J$ = 8.8, 6.4 Hz, 1H), 3.03 (dd, $J$ = 9.2, 5.6 Hz, 2H), 2.32 (s, 6H), 2.30 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.79, 138.22, 136.71, 135.64, 129.82, 129.06, 127.03, 125.26, 120.77, 42.44, 40.07, 21.34. IR (cm$^{-1}$): 3016, 2919, 2862, 2240, 1607, 1465, 849, 699 cm$^{-1}$. HRMS: calcd. for C$_{19}$H$_{21}$NNa$^+ [M+Na]^+$: 286.1566, Found: 286.1571. Melting point: 144-145 °C.

(3k) 2-phenylbutanenitrile$^4$

![2-phenylbutanenitrile](image)

The title compound was prepared according to the general procedure described above by the reaction between prop-1-en-1-ylbenzene ($^{1}$k') with formamide, and purified by standard extraction and concentration procedures to provide oil (17.98 mg, 62%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 - 7.30 (m, 5H), 3.74 (t, $J$ = 7.2 Hz, 1H), 1.99 - 1.91 (m, 2H), 1.08 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 135.86, 129.16, 128.15, 127.43, 120.90, 39.07, 29.37, 11.64. IR (cm$^{-1}$): 3040, 2963, 2241, 1600, 1458, 1327, 752, 700.

(3l) 2-(4-methoxyphenyl)butanenitrile$^5$

![2-(4-methoxyphenyl)butanenitrile](image)

The title compound was prepared according to the general procedure described above by the reaction between 1-methoxy-4-(prop-1-en-1-yl)benzene ($^{1}$l') with formamide, and purified by standard extraction and concentration procedures to provide oil (26.6 mg, 76%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.23 (d, $J$ = 8.4 Hz, 2H), 6.90 (d, $J$ = 8.4 Hz, 2H), 3.81 (s, 3H), 3.68 (t, $J$ = 7.2 Hz, 1H), 1.95 - 1.89 (m, 2H), 1.06 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.36, 128.40, 127.82, 121.14, 114.44, 55.42, 38.20, 29.33, 11.53. IR (cm$^{-1}$): 2955, 2925, 2870, 2239, 1611, 1459, 828.

(3t) cyclohexanecarbonitrile$^{12}$

![cyclohexanecarbonitrile](image)

The title compound was prepared according to the general procedure described above by the reaction between cyclohexene ($^{1}$t) with formamide, and purified by standard extraction and concentration procedures to provide oil (14.8 mg, 68%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.75 - 2.67 (m, 1H), 1.95 (d, $J$ = 13.2 Hz, 2H), 1.85 - 1.81 (m, 2H), 1.67 - 1.57 (m, 2H), 1.45 - 1.18 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 104.44, 47.08, 42.01, 31.37, 27.19, 26.13, 26.04. IR (cm$^{-1}$): 2928, 2853, 2245, 1450, 1423.

(3u) 2-butylheptanenitrile
The title compound was prepared according to the general procedure described above by the reaction between methyl dec-5-yne (1u) with formamide, and purified by standard extraction and concentration procedures to provide colorless oil (21.0 mg, 63%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 2.55 - 2.47 (m, 1H), 1.67 - 1.47 (m, 6H), 1.42 - 1.26 (m, 8H), 0.94 - 0.88 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 122.64, 32.36, 32.09, 31.78, 31.41, 29.41, 26.97, 22.53, 22.36, 14.08, 13.95. IR (cm$^{-1}$): 2237, 1647, 1466, 669. HRMS: calcd. for C$_{11}$H$_{21}$NNa$^+$ [M+Na$^+$]: 190.1566, Found: 190.1569.

(3v) pent-4-enenitrile

The title compound was prepared according to the general procedure described above by the reaction between 1,3-butadiene (1v) with formamide.

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.89 - 5.78 (m, 1H), 5.21 - 5.15 (m, 2H), 2.47 - 2.38 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 134.23, 119.27, 117.78, 29.38, 17.04. IR (cm$^{-1}$): 2922, 2852, 2240, 1462, 1019.

(4v) adiponitrile

The title compound was prepared according to the general procedure described above by the reaction between methyl pent-4-enenitrile (3v) with formamide, and purified by standard extraction and concentration procedures to provide colorless oil (6.1 mg, 28%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 2.48 - 2.43 (m, 4H), 1.86 - 1.79 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 118.89, 24.07, 16.42. IR (cm$^{-1}$): 2947, 2245, 1425, 913, 743.

(5a) 2-phenylpropanamide

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.36 - 7.25 (m, 5H), 6.08 (s, 1H), 5.45 (s, 1H), 3.59 (q, $J = 6.8$ Hz, 1H), 1.51 (d, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.09, 141.35, 129.03, 127.68, 127.43, 46.68, 18.41. IR (cm$^{-1}$): 3361, 3185, 2801, 1451, 1287, 1264, 1114, 656.

VI. Reference


**VII. Copies of \( ^1 \text{H} \) and \( ^{13} \text{C} \) NMR spectra of products 3a-3v, 4v, and 5a**
3a
3l

36
\( 3p \)
\[
\text{3u}
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