Supporting Information

Palladium-Catalyzed Cyanide Metathesis: Utilization of Benzyl Cyanide as an Operator-Benign Reagent for Aryl Halide Cyanations

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1. General experimental details:

Melting points were recorded on a BÜCHI 535. NMR spectra were obtained on a Bruker AVANCE DMX500 spectrometer operating at 500 MHz or 400 MHz for $^1$H-NMR, 125 MHz or 100 MHz for $^{13}$C-NMR in CDCl$_3$. Chemicals were either purchased or purified by standard techniques without special instructions. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, m = multiplet. Coupling constants $J$, were reported in hertz unit(Hz). Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl$_3$ as an internal standard. $^{13}$C NMR spectra were obtained by using the same NMR spectrometers and chemical shifts were reported in ppm referenced to the center line of a triplet at 77.36 ppm of CDCl$_3$.

Typical experimental procedures for the reaction of aryl halide and benzyl cyanide:

A 25mL round-bottom flask was charged with aryl halide (1 mmol), benzyl cyanide (176 mg, 1.5 mmol), K$_2$CO$_3$ (690 mg, 5 mmol), n-Bu$_4$NBr (322 mg, 1 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), and DMF (5 mL). The reaction mixture was stirred at 90 °C (oil bath) for 8 h. After cooling to room temperature, the resultant mixture was added to 30mL water, extracted with DCM (3×5 mL), and dried over anhydrous Na$_2$SO$_4$. The dichloromethane was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel to give the products.

Procedure for 1c to 2c in 5 mmol scale: 1c (1.17 g, 5 mmol), benzyl cyanide (878 mg, 7.5 mmol), K$_2$CO$_3$ (3.45 g, 25 mmol), n-Bu$_4$NBr (1.61 g, 5 mmol), Pd(OAc)$_2$ (56 mg, 0.25 mmol), and DMF (30 mL). The reaction gave 2c (345 mg) in 52% yield along with 4,4'-dimethoxy-1,1'-biphenyl (226 mg) in 42% yield.

Procedure for the reaction of 1p with benzyl cyanide in 5 mmol scale: 1p (1.23 g, 5 mmol), benzyl cyanide (878 mg, 7.5 mmol), K$_2$CO$_3$ (3.45 g, 25 mmol), n-Bu$_4$NBr (1.61 g, 5 mmol), Pd(OAc)$_2$ (56 mg, 0.25 mmol), and DMF (30 mL). The reaction gave a mixture (440 mg) of 2na and 2nb in 46% yield.
## 2. Optimization of reaction conditions for the preparation of 2j

### Table S1 Screening of reaction condition of 9-bromoanthracene and benzyl cyanide catalyzed by palladium

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pd Cat.</th>
<th>Base (equiv.)</th>
<th>n-BuNX (equiv.)</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Yield(%)</th>
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<td>86</td>
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<td>n.d.</td>
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<td>trace</td>
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<td>n-BuBr (1)</td>
<td>DMF</td>
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<td>6</td>
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</table>

*Reaction conditions: unless otherwise specified, the reaction was carried out under air, 8 h. † Isolated yield. ‡ under N₂.
3. Spectral data for the products:

2-aminobenzonitrile (2a)

\[
\text{NH}_2
\]

brown solid, m.p. 49-50 °C (Lit.\textsuperscript{1}, 48-50 °C)

\(^1\)H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 7.38 (d, \(J = 7.8\) Hz, 1H), 7.34-7.31 (m, 1H), 6.75-6.72 (m, 2H), 4.43 (s, 2H).

\(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta\) 149.9, 134.3, 132.6, 118.2, 117.9, 115.4, 96.2.

4-aminobenzonitrile (2b)

\[
\text{H}_2\text{N} \hspace{1cm} \text{CN}
\]

yellow solid, m.p. 85-87 °C (Lit.\textsuperscript{1}, 84-86 °C)

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.42 (d, \(J = 8.5\) Hz, 2H), 6.65 (d, \(J = 8.5\) Hz, 2H), 4.18 (s, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 150.6, 134.1, 120.5, 114.7, 100.4.

4-methoxybenzonitrile (2c)

\[
\text{H}_3\text{CO} \hspace{1cm} \text{CN}
\]

white solid, m.p. 60-61 °C (Lit.\textsuperscript{2}, 60-62 °C)

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.59 (d, \(J = 8.6\) Hz, 2H), 6.96 (d, \(J = 8.6\) Hz, 2H), 3.86 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 163.1, 134.2, 119.5, 115.0, 104.2, 55.8.

4-methylbenzonitrile (2d)

\[
\text{H}_3\text{C} \hspace{1cm} \text{CN}
\]

white solid, m.p. 29-30 °C (Lit.\textsuperscript{3}, 29-30 °C)

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.53 (d, \(J = 7.6\) Hz, 2H), 7.27 (d, \(J = 7.6\) Hz, 2H), 2.42 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 143.9, 132.2, 130.0, 119.4, 109.4, 22.0.

4-hydroxybenzonitrile (2e)

\[
\text{HO} \hspace{1cm} \text{CN}
\]

white solid, m.p. 112-113 °C (Lit.\textsuperscript{4}, 111-113 °C)

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.57 (d, \(J = 8.4\) Hz, 2H), 6.95 (d, \(J = 8.4\) Hz, 2H), 6.58 (s, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 160.4, 134.6, 119.5, 116.8, 103.5.
4-benzoylbenzonitrile (2f)

white solid, m.p. 113-114 °C (Lit. 5, 113-114 °C)

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$ 7.88 (d, $J = 8.0$ Hz, 2H), 7.81-7.78 (m, 4H), 7.65 (dd, $J_1 = J_2 = 7.2$ Hz, 1H), 7.52 (dd, $J_1 = J_2 = 7.6$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) : $\delta$ 195.3, 141.5, 136.5, 133.6, 132.4, 130.5, 130.3, 128.9, 118.3, 115.9.

4-acetylbenzonitrile (2g)

white solid, m.p. 57-58 °C (Lit. 6, 56-58 °C)

$^1$H NMR (500 MHz, CDCl$_3$) : $\delta$ 8.05 (d, $J = 8.3$ Hz, 2H), 7.79 (d, $J = 8.3$ Hz, 2H), 2.66 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) : $\delta$ 196.8, 140.2, 132.8, 129.0, 118.2, 116.7, 27.1.

3-cyanopyridine (2h)

white solid, m.p. 51-52 °C (Lit. 7, 50-51 °C)

$^1$H NMR (500 MHz, CDCl$_3$) : $\delta$ 8.92 (s, 1H), 8.85-8.84 (m, 1H), 8.00 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.5$ Hz, 1H), 7.49-7.46 (m, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$) : $\delta$ 153.2, 152.7, 139.5, 123.8, 116.7, 110.3.

1-naphthonitrile (2i)

white solid, m.p. 36-37 °C (Lit. 2, 35-36 °C)

$^1$H NMR (500 MHz, CDCl$_3$) : $\delta$ 8.21 (d, $J = 8.3$ Hz, 1H), 8.05 (d, $J = 8.3$ Hz, 1H), 7.89 (dd, $J_1 = 9.0$ Hz, $J_2 = 7.5$ Hz, 2H), 7.67 (dd, $J_1 = 7.0$ Hz, $J_2 = 7.5$ Hz, 1H), 7.60 (dd, $J_1 = 8.0$ Hz, $J_2 = 7.0$ Hz, 1H), 7.50 (dd, $J_1 = 7.5$ Hz, $J_2 = 8.0$ Hz, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$) : $\delta$ 133.5, 133.1, 132.6, 128.9, 128.8, 127.8, 125.3, 125.1, 118.1, 110.4.
anthracene-9-carbonitrile (2j)

![Chemical structure of anthracene-9-carbonitrile]

yellow solid, m.p. 175-176 °C (Lit.\textsuperscript{8}, 173-177 °C)

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$ 8.60 (s, 1H), 8.37 (d, $J = 8.4$ Hz, 2H), 8.03 (d, $J = 8.4$ Hz, 2H), 7.68 (dd, $J_1 = J_2 = 7.6$ Hz, 2H), 7.55 (dd, $J_1 = J_2 = 7.6$ Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) : $\delta$ 133.5, 133.0, 130.8, 129.2, 129.2, 126.6, 125.5, 117.5, 105.5.

9,9-dibutyl-9H-fluorene-2-carbonitrile (2k)

![Chemical structure of 9,9-dibutyl-9H-fluorene-2-carbonitrile]

white solid, m.p. 103-104 °C

$^1$H NMR (500 MHz, CDCl$_3$) : $\delta$ 7.77-7.73 (m, 2H), 7.64-7.61 (m, 2H), 7.39-7.37 (m, 3H), 2.01-1.95 (m, 4H), 1.11-1.03 (m, 4H), 0.67 (t, $J = 7.4$ Hz, 6H), 0.58-0.48 (m, 4H).

$^{13}$C NMR (125 MHz, CDCl$_3$) : $\delta$ 151.7, 151.6, 146.0, 139.4, 131.5, 129.2, 127.5, 126.7, 123.4, 121.1, 120.5, 120.2, 110.1, 55.7, 40.2, 26.1, 23.2, 14.0.

IR (KBr) : 2951, 2929, 2860, 2220, 1466, 1452, 831, 737, 590 cm$^{-1}$.


9-heptyl-9H-carbazole-3,6-dicarbonitrile (2l)

![Chemical structure of 9-heptyl-9H-carbazole-3,6-dicarbonitrile]

yellow solid, m.p. 172-173 °C

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$ 8.41 (s, 2H), 7.79 (d, $J = 8.6$ Hz, 2H), 7.53 (d, $J = 8.6$ Hz, 2H), 4.36 (t, $J = 7.2$ Hz, 2H), 1.94-1.83 (m, 2H), 1.35-1.25 (m, 8H), 0.86 (t, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) : $\delta$ 143.0, 130.6, 126.0, 122.4, 120.1, 110.5, 103.7, 44.1, 31.9, 29.2, 29.1, 27.4, 22.8, 14.3.

IR (KBr) : 2926, 2856, 2220, 1596, 1483, 821, 593 cm$^{-1}$.

HRMS : cacl. for C$_{21}$H$_{23}$N$_3$ $[M^+]$, 315.1735; found, 315.1737.
9-heptyl-6-iodo-9H-carbazole-3-carbonitrile (2m)

![Chemical Structure Image]

brown solid, m.p. 117-118 °C

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$ 8.39 (s, 1H), 8.31 (s, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 1H), 4.28 (t, $J = 7.2$ Hz, 2H), 1.89-1.79 (m, 2H), 1.32-1.24 (m, 8H), 0.85 (t, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) : $\delta$ 142.2, 140.4, 135.6, 129.9, 129.8, 125.7, 124.6, 121.9, 120.6, 111.6, 109.9, 102.4, 83.1, 43.8, 31.9, 29.3, 29.1, 27.4, 22.8, 14.3.

IR (KBr) : 3474, 3414, 2928, 2853, 2221, 1479, 802 cm$^{-1}$.

HRMS : cacld. for C$_{20}$H$_{21}$IN$_2$ [M+], 416.0749; found, 416.0747.

4. The detection of CN$^-$ by the picric acid strip

Preparation of the picric acid strip:

Picric acid strip was prepared by wetting filter paper with a solution of 5.0 g of sodium bicarbonate and 0.5 g picric acid in 100 mL water. After drying the paper, it was cut into strips for use.

Strip test of the cyanide anion:

Tartaric acid (0.2 g) and the target solution (1.5 mL) were added into a flask. A sealed plastic vial, with a number of holes and a strip inside, was placed above the reaction mixture. The flask was heated in the water bath under 80 °C for 20 minutes. The strip turned red indicating the existence of CN$^-$.10

Table S2 Detection of CN$^-$ by the picric acid strip$^a$

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<th>9-Br anthracene 0.5 mmol</th>
<th>Pd(OAc)$_2$ 0.025 mmol</th>
<th>n-Bu$_4$NBr 0.5 mmol</th>
<th>K$_2$CO$_3$ 2.5 mmol</th>
<th>Cyanation reagent 0.75 mmol</th>
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$^a$ Reaction conditions: The mixture was heated under 90 °C in 3 mL DMF for 2 h. $^b$ 0.25 mmol K$_3$[Fe(CN)$_6$] or NaCN was tested.
5. References

6. $^1$H NMR and $^{13}$C NMR of the products

Figure S1 $^1$H-NMR spectrum of 2a

Figure S2 $^{13}$C-NMR spectrum of 2a
Figure S3 ¹H-NMR spectrum of 2b

Figure S4 ¹³C-NMR spectrum of 2b
Figure S5 $^1$H-NMR spectrum of 2c

Figure S6 $^{13}$C-NMR spectrum of 2c
Figure S7: $^1$H-NMR spectrum of 2d

![1H-NMR Spectrum of 2d](image)

Figure S8: $^{13}$C-NMR spectrum of 2d

![13C-NMR Spectrum of 2d](image)
Figure S9 $^1$H-NMR spectrum of 2e

Figure S10 $^{13}$C-NMR spectrum of 2e
Figure S11 $^1$H-NMR spectrum of 2f

Figure S12 $^{13}$C-NMR spectrum of 2f
Figure S13 $^1$H-NMR spectrum of 2g

Figure S14 $^{13}$C-NMR spectrum of 2g
Figure S15 $^1$H-NMR spectrum of 2h

Figure S16 $^{13}$C-NMR spectrum of 2h
**Figure S17** $^1$H-NMR spectrum of 2i

**Figure S18** $^{13}$C-NMR spectrum of 2i
Figure S19 $^1$H-NMR spectrum of 2j

Figure S20 $^{13}$C-NMR spectrum of 2j
Figure S21 $^1$H-NMR spectrum of 2k

Figure S22 $^{13}$C-NMR spectrum of 2k
Figure S23 ¹H-NMR spectrum of 2l

Figure S24 ¹³C-NMR spectrum of 2l
Figure S25 $^1$H-NMR spectrum of 2m

Figure S26 $^{13}$C-NMR spectrum of 2m
7. Other data

Figure S27 \(^1\)H-NMR spectrum of 4,4'-dimethyl-1,1'-biphenyl

![\(^1\)H-NMR spectrum of 4,4'-dimethyl-1,1'-biphenyl](image)

Figure S28 \(^{13}\)C-NMR spectrum of 4,4'-dimethyl-1,1'-biphenyl

![\(^{13}\)C-NMR spectrum of 4,4'-dimethyl-1,1'-biphenyl](image)
Figure S29 $^1$H-NMR spectrum of 4,4'-dimethoxy-1,1'-biphenyl

Figure S30 $^{13}$C-NMR spectrum of 4,4'-dimethoxy-1,1'-biphenyl
Figure S31 $^1$H-NMR spectrum of the mixture of 2na and 2nb
Figure S32 GC-MS result of the mixture of 2na and 2nb