Electronic Supplementary Information

Synthesis of Arylacetonitrile Derivatives: Ni-catalyzed Reaction of Benzyl Chlorides and Trimethylsilyl Cyanide under Base-free Conditions

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**General**

GLC analysis was performed with a flame ionization detector using a 0.22 × 25 m capillary column (BP-5). $^1$H and $^{13}$C NMR were measured at 400 and 100 MHz, respectively, in CDCl$_3$ with Me$_4$Si as the internal standard. The products were characterized by $^1$H NMR, $^{13}$C NMR, HMOC, HMBC.

All reagents were commercially available and used without any purification.

**Experimental Section**

A typical reaction procedure for the preparation of 3a (entry 13, Table 1):

A mixture of phenylacetonitrile (1a) (127 mg, 1 mmol), trimethylsilyl cyanide (2) (397 mg, 4 mmol), Ni(cod)$_2$ (28 mg, 0.2 mmol), PPh$_3$ (52 mg, 0.2 mmol), and toluene (1 mL) was stirred for 16 h at 60 °C under Ar. The yields of the products were estimated from the peak areas based on the internal standard technique using GC and 3a was obtained in 97% yield. The products (3a) was isolated by silica gel column chromatography ($n$-hexane:EtOAc=100:0 to 10:1 as eluent) in 83% yield (97 mg) as yellow liquid.

A typical reaction procedure for the preparation of 3a (Scheme 1):

A mixture of Ni($\eta^3$-CH$_2$Ph)(PCy$_2$Ph)Cl (6) (182 mg, 0.4 mmol) with TMSCN (2) (159 mg, 1.6 mmol) and toluene (3 mL) was stirred for 40 h at 100 °C under Ar. The yields of the products were estimated from the peak areas based on the internal standard technique using GC and 3a was obtained in 29% yield.
Compounds \(3a\)-\(3d\), \(3e\), \(3g\), \(3h\), \(3i\), \(3j\), and \(3k\) are known compounds and reported previously.

\(3a\) : colorless liquid; \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.71 (s, 2H), 7.32-7.36 (m, 5H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 23.4 (CH\(_2\)), 117.8 (C), 127.8 (2CH), 128.0 (CH), 129.0 (2CH), 129.8 (C)

\(3b\) : colorless liquid; \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.34 (s, 3H), 3.67 (s, 2H), 7.15 (d, \(J = 8.4\) Hz, 2H), 7.19 (d, \(J = 8.4\) Hz, 2H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 20.9 (CH\(_3\)), 23.1 (CH\(_2\)), 118.0 (C), 126.8 (C), 127.7 (2CH), 129.7 (2CH), 137.7 (C)

\(3c\) : colorless liquid; \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.67 (s, 2H), 3.80 (s, 3H), 6.89 (d, \(J = 8.4\) Hz, 2H), 7.23 (d, \(J = 8.4\) Hz, 2H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 22.7 (CH\(_2\)), 55.3 (CH\(_3\)), 114.4 (2CH), 118.2 (C), 121.7 (C), 129.0 (2CH), 159.3 (C)

\(3d\) : colorless liquid; \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.72 (s, 2H), 7.06 (t, \(J = 8.8\) Hz, 2H), 7.29 (dd, \(J = 5.2, 5.6\) Hz, 2H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 22.7 (CH\(_2\)), 115.9 (\(J = 22\) Hz, 2CH), 117.7 (C), 125.6 (\(J = 2.9\) Hz, C), 129.5 (\(J = 8.5\) Hz, 2CH), 162.2 (\(J = 246\) Hz, C)

\(3e\) : white solid; m.p. 60.9-61.2 °C (ref\(^3\) 61-62 °C), \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.67 (s, 2H), 3.80 (s, 3H), 7.34 (d, \(J = 7.6\) Hz, 2H), 7.97 (d, \(J = 7.6\) Hz, 2H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 23.6 (CH\(_2\)), 52.2 (CH\(_3\)), 117.1 (C), 127.9 (2CH), 130.3 (2CH), 134.8 (C), 166.3 (C)

\(3f\) : colorless liquid; \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.47 (s, 9H), 3.61(s, 2H), 7.22 (d, \(J = 6.4\) Hz, 2H), 7.52 (d, \(J = 6.8\) Hz, 2H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 23.5 (CH\(_2\)), 50.7 (3CH), 117.5 (C), 127.4 (2CH), 129.4 (C), 132.3 (C), 135.4 (2CH); IR (neat, cm\(^{-1}\)) 3020, 2250, 1604, 1458, 1124, 797; GC-MS (EI) \(m/z\) (relative intensity) 237 (9) [M]+, 121 (100), 91 (8), 77 (8), 41 (7); HRMS (EI) \(m/z\) caled for C\(_{11}\)H\(_{15}\)NO\(_3\)Si, [M]+ 237.0821, found 237.0824

\(3g\) : colorless liquid; \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.27 (s, 3H), 3.60 (s, 2H), 7.01-7.24 (m, 4H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 21.3 (CH\(_3\)), 23.5 (CH\(_2\)), 124.9 (C), 128.6 (CH), 127.7 (CH), 129.0 (CH), 129.7 (CH), 139.0 (C)
3h: colorless liquid; $^1$H-NMR (400 MHz, CDCl$_3$) δ 2.26 (s, 3H), 3.59 (s, 2H), 7.00-7.23 (m, 4H); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 19.2 (CH$_3$), 21.8 (CH$_2$), 117.5 (C), 126.7 (CH), 128.3 (CH), 128.5 (CH), 130.6 (CH), 136.0 (C)

3i: colorless liquid; $^1$H-NMR (400 MHz, CDCl$_3$) δ 2.26 (s, 3H), 2.35 (s, 6H), 3.59 (s, 2H), 6.89 (s, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 17.3 (CH$_3$), 19.9 (2CH$_3$), 20.8 (CH$_2$), 117.4 (C), 124.4 (C), 129.3 (2CH), 136.4 (C), 137.8 (C)

3j: beiji solid; m.p. 78-80 °C, $^1$H-NMR (400 MHz, CDCl$_3$) δ 3.68 (s, 2H), 7.17-7.68 (s, 7H); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 23.5 (CH$_2$), 117.8 (C), 125.3 (CH), 126.3 (CH), 126.6 (CH), 126.7 (CH), 127.1 (C), 127.5 (CH), 127.6 (CH), 128.8 (CH), 132.5 (C), 133.1 (C)

3k: colorless liquid; $^1$H-NMR (400 MHz, CDCl$_3$) δ 1.57 (d, $J$ = 7.6 Hz, 3H), 3.83 (q, $J$ = 7.2 Hz, 1H), 7.27-7.32 (m, 5H); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 21.4 (CH$_3$), 31.2 (CH), 121.6 (C), 126.7 (CH), 128.0 (CH), 129.1 (2CH), 137.0 (C)

References
$^1$H NMR

\[
\begin{align*}
\text{CN} \\
\text{3a}
\end{align*}
\]

$^{13}$C NMR
$^1$H NMR

$^{13}$C NMR
$^1$H NMR

\[ \text{CN} \quad 3c \]

$^{13}$C NMR
$^1$H NMR

$^13$C NMR
$^1$H NMR

$^{13}$C NMR
$^{1}H$ NMR

$^{13}C$ NMR
$^1$H NMR

$^1$C NMR
$^1$H NMR

$^1$H NMR

$^{13}$C NMR

$^{13}$C NMR
$^1$H NMR

$^{13}$C NMR
$^1$H NMR

\[ \begin{align*}
    \text{CN} & \quad 3k \\
\end{align*} \]

$^{13}$C NMR