

### Supplementary data

#### Solvent-free mechanochemical and one-pot reductive benzylizations of malononitrile and 4-methylaniline using Hantzsch 1,4-dihydropyridine as the reductant

**Ze Zhang, Jie Gao, Jing-Jing Xia and Guan-Wu Wang\***

*Hefei National Laboratory for Physical Sciences at Microscale, Hefei, Anhui 230026, P. R. China and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China.*

*Fax & Tel (+86) 551 360 7864; E-mail: gwang@ustc.edu.cn*

#### Melting points for compounds **3** and **5** with related references.

Compound	m. p. (lit.) / °C
<b>3a</b>	90-91 (89, <sup>1</sup> 86-89 <sup>2</sup> )
<b>3b</b>	91-92 (90-91 <sup>1</sup> )
<b>3c</b>	149-150 (150 <sup>2</sup> )
<b>3d</b>	118-119 (118 <sup>2</sup> )
<b>3e</b>	132-133 (132 <sup>3</sup> )
<b>3f</b>	85-86
<b>3g</b>	81-82 (oil <sup>1</sup> )
<b>3h</b>	94-95
<b>3i</b>	90-91 (91-92 <sup>4</sup> )
<b>5a</b>	88-90 (89 <sup>5</sup> )
<b>5b</b>	89-91 (90-92 <sup>6</sup> )
<b>5c</b>	69-70 (68-70 <sup>5,7,8</sup> )
<b>5d</b>	92-93 (90-92 <sup>8</sup> )
<b>5e</b>	47-48 (47-48 <sup>7</sup> )
<b>5f</b>	71-72 (72 <sup>9</sup> )
<b>5g</b>	60-61
<b>5h</b>	62-63
<b>5i</b>	oil (19-20 <sup>8,10</sup> )

## References

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Spectral data (IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR) for compounds **3f-3h**, **5g** and **5h**.

**2-(2-nitro-benzyl)-malononitrile (3f):** IR (KBr) 2930 (s), 2262 (m), 1521 (vs), 1350 (vs)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (dd,  $J = 8.1, 1.1$  Hz, ArH, 1 H), 7.74 (td,  $J = 7.5, 1.2$  Hz, ArH, 1 H), 7.62 (td,  $J = 7.9, 1.4$  Hz, ArH, 1 H), 7.57 (dd,  $J = 7.5, 1.2$  Hz, ArH, 1 H), 4.46 (t,  $J = 7.8$  Hz, CH, 1 H), 3.59 (d,  $J = 7.8$  Hz,  $\text{CH}_2$ , 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.79, 134.59, 133.99, 130.54, 128.33, 126.07, 111.99 (2 CN), 35.23, 23.70.

**2-(3,4-dichloro-benzyl)-malononitrile (3g):** IR (KBr) 2915 (vs), 2258 (m), 1474 (vs), 1402 (s), 1033 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J = 8.2$  Hz, ArH, 1 H), 7.44 (d,  $J = 2.1$  Hz, ArH, 1 H), 7.20 (dd,  $J = 8.2, 2.1$  Hz, ArH, 1 H), 3.94 (t,  $J = 6.8$  Hz, CH, 1 H), 3.26 (d,  $J = 6.8$  Hz,  $\text{CH}_2$ , 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.39, 132.93, 132.84, 131.30, 131.16, 128.60, 111.85 (2 CN), 35.48, 24.61.

**2-(2,4-dichloro-benzyl)-malononitrile (3h):** IR (KBr) 2914 (vs), 2258 (m), 1474 (vs), 1402 (s), 1033 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (d,  $J = 8.6$  Hz, ArH, 1 H), 7.39 (d,  $J = 2.3$  Hz, ArH, 1 H), 7.34 (dd,  $J = 8.6, 2.3$  Hz, ArH, 1 H), 4.11 (t,  $J = 7.8$  Hz, CH, 1 H), 3.42 (d,  $J = 7.8$  Hz,  $\text{CH}_2$ , 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.58, 132.35, 132.29, 131.69, 131.26, 130.61, 111.74 (2 CN), 34.57, 22.48.

**(2,4-dichloro-benzyl)-*p*-tolyl-amine (5g):** IR (KBr) 3418 (vs), 1619 (m), 1522 (s), 807 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J = 1.9$  Hz, ArH, 1 H), 7.34 (d,  $J = 8.2$  Hz, ArH, 1 H), 7.14 (dd,  $J = 8.2, 1.9$  Hz, ArH, 1 H), 6.96 (d,  $J = 8.3$  Hz, ArH, 2 H), 6.47 (d,  $J = 8.3$  Hz, ArH, 2 H), 4.22 (s,  $\text{CH}_2$ , 2 H), 3.83 (br, NH, 1 H), 2.22 (s,  $\text{CH}_3$ , 3 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.32, 140.35, 132.64, 130.91, 130.56, 129.90 (2 C), 129.15, 127.27, 126.57, 113.10 (2 C), 47.51, 20.48.

**(3,4-dichloro-benzyl)-*p*-tolyl-amine (5h):** IR (KBr) 3414 (vs), 1618 (m), 1521 (s), 808 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 2.5$  Hz, ArH, 1 H), 7.27 (d,  $J = 8.4$  Hz, ArH, 1 H), 7.14 (dd,  $J = 8.4, 2.5$  Hz, ArH, 1 H), 6.97 (d,  $J = 8.3$  Hz, ArH, 2 H), 6.49 (d,  $J = 8.3$  Hz, ArH, 2 H), 4.34 (s,  $\text{CH}_2$ , 2 H), 4.02 (br, NH, 1 H), 2.23 (s,  $\text{CH}_3$ , 3 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.23, 139.03, 133.10, 131.27, 130.60, 129.95 (2 C), 128.80, 128.35, 127.36, 113.12 (2 C), 46.18, 20.50.