



SUPPLEMENTARY MATERIAL TO

**A clean and efficient, L-proline-catalyzed synthesis of polysubstituted benzenes in the ionic liquid [bmim][PF<sub>6</sub>]**

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J. Serb. Chem. Soc. 77 (10) (2012) 1345–1352

ANALYTICAL AND SPECTRAL DATA FOR SELECTED PRODUCTS

*5'-Amino-4-nitro-[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (3a)*. Yellow needles; yield: 76 %; m.p. 242–244 °C (244–246 °C<sup>1</sup>); <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 6.34 (2H, *s*, amino group), 7.35–7.44 (3H, *m*, phenyl ring), 7.53–7.58 (2H, *m*, phenyl ring), 7.65–7.71 (2H, *m*, phenyl ring), 7.90 (1H, *s*, phenyl ring), 8.20 (2H, *d*, *J* = 7.3 Hz, phenyl ring).

*5'-Amino-4,4''-dinitro-[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (3b)*. Yellow rods; yield: 54 %; m.p. 350–351 °C (352–353 °C<sup>1</sup>); <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 6.54 (2H, *s*, amino group), 6.98 (1H, *s*, phenyl ring), 7.65–7.67 (4H, *m*, phenyl ring), 7.69–7.70 (4H, *m*, phenyl ring).

*5'-Amino-2-methoxy-[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (3c)*. White solid; yield: 65 %; m.p. 165–167 °C (168–169 °C<sup>2</sup>); <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 3.72 (3H, *s*, methoxy group), 5.92 (2H, *s*, amino group), 6.79–6.81 (2H, *m*, phenyl ring), 7.09–7.12 (2H, *m*, phenyl ring), 7.37–7.43 (4H, *m*, phenyl ring), 7.75–7.77 (2H, *m*, phenyl ring).

*3-Amino-5-(furan-2-yl)biphenyl-2,4-dicarbonitrile (3d)*. Yellow solid; yield: 82 %; m.p. > 350 °C; Anal. Calcd. for C<sub>18</sub>H<sub>11</sub>N<sub>3</sub>O: C, 75.78; H, 3.89; N, 14.73 %. Found: C, 75.82; H, 3.94; N, 14.66 %; IR (KBr, cm<sup>-1</sup>): 3474 (ArN–H), 3359 (ArN–H), 2926 (ArC–H), 2215 (ArC≡N), 1653 (ArN–H), 1540 (ArC=C), 1291 (ArC–N), 1049 (ArC–O), 826; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 6.30 (2H, *s*, amino group), 6.67–6.69 (2H, *m*, furan ring), 7.41–7.42 (2H, *d*, *J* = 3.6 Hz, phenyl ring), 7.54 (1H, *s*, furan ring), 7.83 (2H, *d*, *J* = 1.6 Hz, phenyl ring), 8.16 (2H, *d*, *J* = 1.5 Hz, phenyl ring); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 88.70, 91.60, 112.52, 112.72, 113.37, 116.04, 116.07, 128.05, 128.49, 128.87, 136.26, 138.38, 141.44, 144.94, 148.41, 154.68; MS (*m/z*): 285 (M<sup>+</sup>).

*3-Amino-5-(furan-2-yl)-4'-nitro-biphenyl-2,4-dicarbonitrile (3e)*. Yellow solid; yield: 74 %; m.p. 277–278 °C; Anal. Calcd. for C<sub>18</sub>H<sub>10</sub>N<sub>4</sub>O<sub>3</sub>: C, 65.45; H, 3.05; N, 16.96 %. Found: C, 65.76; H, 3.27; N, 16.72 %; IR (KBr, cm<sup>-1</sup>): 3468

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(ArN–H), 3358 (ArN–H), 2927 (ArC–H), 2221 (ArC≡N), 1544 (ArC=C), 1284 (ArC–N); <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 6.60 (2H, *s*, amino group), 6.66–6.68 (1H, *m*, phenyl ring), 7.19 (1H, *s*, phenyl ring), 7.44 (1H, *d*, *J* = 3.5 Hz, phenyl ring), 7.77 (1H, *d*, *J* = 1.7 Hz, phenyl ring), 7.82–7.84 (2H, *m*, phenyl ring), 8.36–8.38 (2H, *m*, phenyl ring); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 89.96, 93.01, 99.49, 112.50, 112.90, 114.01, 115.32, 115.78, 123.52, 129.52, 136.48, 143.68, 144.80, 147.21, 147.77, 148.41, 154.17; MS (*m/z*): 331 (M<sup>+</sup>).

*3-Amino-4'-nitro-5-(2-thienyl)biphenyl-2,4-dicarbonitrile (3f)*. Yellow solid; yield: 68 %; m.p. 272–273 °C; Anal. Calcd. for C<sub>18</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>S: C, 62.42; H, 2.91; N, 16.18, S, 9.26 %. Found: C, 62.68; H, 2.96; N, 16.34, S, 9.22 %; IR (KBr, cm<sup>-1</sup>): 3472 (ArN–H), 3382 (ArN–H), 2936 (ArC–H), 2224 (ArC≡N), 1535 (ArC=C), 1326 (ArC–N), 760; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 6.74 (2H, *s*, amino group), 6.91 (1H, *s*, phenyl ring), 7.22 (1H, *t*, *J* = 4.6 Hz, phenyl ring), 7.70–7.73 (2H, *m*, phenyl ring), 7.84 (2H, *d*, *J* = 8.6 Hz, phenyl ring), 8.36 (2H, *d*, *J* = 8.6 Hz, phenyl ring); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 96.73, 96.77, 115.00, 115.29, 117.52, 123.54, 128.06, 128.82, 129.68, 133.24, 138.04, 141.75, 143.45, 147.34, 152.28, 154.31; MS (*m/z*): 347 (M<sup>+</sup>).

*2-Amino-4,6-bis(furan-2-yl)-1,3-benzenedicarbonitrile (3g)*. Yellow solid; yield: 84 %; m.p. 318 °C; Anal. Calcd. for C<sub>16</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>: C, 69.81; H, 3.30; N, 15.27 %. Found: C, 69.85; H, 3.33; N, 15.25 %. IR (KBr, cm<sup>-1</sup>): 3475 (ArN–H), 3376 (ArN–H), 2926 (ArC–H), 2212 (ArC≡N), 1654 (ArN–H), 1540 (ArC=C), 1301 (ArC–N), 1032 (ArC–O), 862, 754; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 6.58 (2H, *s*, amino group), 6.90–6.95 (2H, *m*, furan ring), 7.21–7.25 (2H, *m*, furan ring), 7.53 (1H, *s*, phenyl ring), 7.87 (2H, *d*, *J* = 1.7 Hz, furan ring); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 93.34, 115.24, 117.83, 121.53, 126.16, 128.71, 134.98, 146.39, 154.60; MS (*m/z*): 275 (M<sup>+</sup>).

*2-Amino-4-(furan-2-yl)-6-(1H-pyrrol-2-yl)-1,3-benzenedicarbonitrile (3h)*. Green solid; yield: 72 %; m.p. 329 °C; Anal. Calcd. for C<sub>16</sub>H<sub>10</sub>N<sub>4</sub>O: C, 70.06; H, 3.67; N, 20.43 %. Found: C, 70.18; H, 3.72; N, 20.41 %; IR (KBr, cm<sup>-1</sup>): 3458 (ArN–H), 3260 (ArN–H), 3131, 3088 (ArC–H), 2293 (ArC≡N), 1649 (ArN–H), 1555 (ArC=C), 1342 (ArC–N), 1053 (ArC–O), 790; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 6.58 (2H, *s*, amino group), 6.67–6.69 (1H, *m*, pyrrole ring), 7.21–7.23 (1H, *t*, *J* = 4.4 Hz, pyrrole ring), 7.25 (1H, *s*, phenyl ring), 7.42–7.43 (1H, *d*, *J* = 3.5 Hz, pyrrole ring), 7.69–7.70 (2H, *m*, furan ring), 7.83 (*d*, 1H, *J* = 1.6 Hz, furan ring), 8.10 (1H, *s*, pyrrole ring); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 92.98, 108.98, 109.49, 111.41, 114.92, 117.83, 121.53, 126.16, 128.71, 133.35, 134.98, 137.20, 146.39, 155.07, 163.00; MS (*m/z*): 274 (M<sup>+</sup>).

*2-Amino-4-(furan-2-yl)-6-(pyridin-3-yl)-1,3-benzenedicarbonitrile (3i)*. Yellow solid; yield: 79 %; m.p. 315 °C; Anal. Calcd. for C<sub>17</sub>H<sub>10</sub>N<sub>4</sub>O: C, 71.32; H, 3.52; N, 19.57 %. Found: C, 71.44; H, 3.67; N, 19.56 %; IR (KBr, cm<sup>-1</sup>): 3472 (ArN–H), 3365 (ArN–H), 2925 (ArC–H), 2212 (ArC≡N), 1637 (ArN–H), 1540

(ArC=C), 1296 (ArC-N), 1039 (ArC-O), 824;  $^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 6.21 (2H, *s*, amino group), 6.78–6.82 (2H, *m*, furan ring), 7.11 (1H, *s*, pyridine ring), 7.42 (1H, *d*,  $J = 3.6$  Hz, furan ring), 7.53 (1H, *s*, phenyl ring), 7.87 (1H, *d*,  $J = 1.7$  Hz, pyridine ring), 8.21 (1H, *d*,  $J = 1.8$  Hz, pyridine ring), 8.52 (1H, *s*, pyridine ring);  $^{13}\text{C-NMR}$  (100 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 92.58, 93.34, 109.49, 112.10, 117.83, 121.53, 126.16, 128.71, 133.35, 134.98, 145.82, 146.39, 150.48, 154.00, 155.07; MS ( $m/z$ ): 286 ( $\text{M}^+$ ).

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