## **Supporting Information:**

# A metal free reduction of aryl-*N*-nitrosamines to corresponding hydrazines using sustainable reductant thiourea dioxide

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#### 1. General information

All the reactions were performed in round bottom flask at appropriate temperature mentioned in the manuscript. Solvents and chemicals were purchased from commercial sources and used without further purifications. Thin layer chromatography was performed using pre-coated plates obtained from E. Merck (TLC silica gel 60 F<sub>254</sub>). The NMR spectra were recorded on Bruker Avance 500 MHz NMR spectrometer and/or Bruker Avance 400 MHz in CDCl<sub>3</sub> Solvent. Mass spectra (HRMS) were measured on water's Quattro Micro V 4.1. The purification of the products were performed on silica gel (60-120 mesh) using a mixture of ethyl acetate and hexane. All the products were characterized by proton and carbon NMR as well as mass spectrometry. In proton NMR, TMS is calibrated to 0 ppm and in <sup>13</sup>C NMR CDCl<sub>3</sub> peak is calibrated to 77.0 ppm.

#### 2. Experimental procedure for the reduction of *N*-nitrosamines

*N*-nitrosamine (1.0 mmol) was allowed to stir in methanol (2 mL) approximately for 5 min at 50  $^{\circ}$ C to which aqueous solution of sodium hydroxide (1 M, 6 equiv.) followed by thiourea dioxide (TDO) (3 equiv.) was added. The reaction was allowed to stir for 3-4 h and the progress of the reaction was monitored by TLC. After completion, the reaction mixture was diluted with chloroform and washed with water. The organic layer was dried over anhydrous sodium sulphate, concentrated and subjected for column chromatography (SiO<sub>2</sub>: ethyl acetate/hexane) to obtain corresponding pure substituted *N*-aryl hydrazines.

#### 3. Experimental procedure for the one-pot synthesis of N,N-disubstituted hydrazines

At the beginning, secondary amine (1 mmol) was converted to corresponding *N*nitrosamine using 1.2 equiv. *tert*-butyl nitrite in 25 mL flask at room temperature to which methanol (2 mL) was added. Then the reaction mixture was kept at pre-heated oil-bath at 50 °C to which aqueous solution of sodium hydroxide (1 M, 6 equiv.) followed by thiourea dioxide (TDO) (3 equiv.) was added. The resulting mixture was allowed to stir for 4 h at same temperature. After completion, the reaction mixture was diluted with chloroform and washed with water. The organic layer was dried over anhydrous sodium sulphate, concentrated and subjected for column chromatography (SiO<sub>2</sub>: ethyl acetate/hexane) to obtain corresponding pure aryl hydrazine.

#### 4. Experimental procedure for the reduction of *N*-nitroso dialkylamine:

*N*-nitroso dibenzylamine (1.0 mmol) was allowed to stir in methanol (2 mL) approximately for 5 min at 50  $^{\circ}$ C to which aqueous solution of sodium hydroxide (1 M, 10 equiv.) followed by thiourea dioxide (TDO, 5. equiv.) was added. The reaction was allowed to stir for 6 h and the progress of the reaction was monitored by TLC. After completion, the reaction mixture was diluted with chloroform and washed with water. The organic layer was dried over anhydrous sodium sulphate, concentrated and subjected for column chromatography (SiO<sub>2</sub>: ethyl acetate/hexane) to obtain corresponding pure substituted *N*,*N*-dibenzyl hydrazine (**2w**).

#### 5. Analytical Data of the Products

5.1 *N*-benzyl *N*-phenyl hydrazine (**2a**) was obtained as white solid (160 mg, 81%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 – 7.17 (m, 7H), 7.02 (d, *J* = 7.7 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 4.52 (s, 2H, Benzylic-CH<sub>2</sub>), 3.47 (brs, 2H, NH<sub>2</sub>).<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  151.7, 137.5, 129.0, 128.6, 127.8, 127.3, 118.5, 113.6, 60.3. HRMS: Calc. for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 199.1235, Obser.: 199.1226 .



5.2 *N*-(4-methylbenzyl)-*N*-phenylhydrazine (**2b**) was obtained as yellow solid (180 mg, 78%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.27 – 7.22 (m, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 4.53 (s, 2H, Benzylic-CH<sub>2</sub>), 3.50 (brs, NH<sub>2</sub>), 2.33 (s, 3H, aryl-CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  151.8, 137.0, 134.3, 129.3, 129.0, 127.9, 118.5, 113.7, 60.1, 21.0. HRMS: Calc. for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 213.1392, Obser.: 213.1385



5.3 *N*-(4-methoxybenzyl)-*N*-phenylhydrazine (**2c**) was obtained as white solid (173 mg, 76%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.26 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.3 Hz,

2H), 6.87 (d, J = 8.4 Hz, 2H), 6.82 (t, J = 7.2 Hz, 1H), 4.52 (s, 2H, Benzylic-CH<sub>2</sub>), 3.80 (s, 3H, Aryl-OCH<sub>3</sub>), 3.49 (s, 2H, NH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  158.9, 151.7, 129.2 (2C), 129.0, 118.6, 114.0, 113.9, 59.8, 55.2. HRMS: Calc. for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 229.1341, Obser.: 229.1332



5.4 *N*-(4-chlorobenzyl)-*N*-phenylhydrazine (**2d**) was obtained as white solid (186 mg, 80%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.23 – 7.14 (m, 6H), 6.96 (d, *J* = 7.7 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 4.47 (s, 2H, Benzylic-CH<sub>2</sub>), 3.50 (brs, 2H, NH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  151.5, 136.2, 133.0, 129.1 (2C), 128.7, 118.8, 113.5, 59.7. HRMS: Calc. for C<sub>13</sub>H<sub>13</sub>ClN<sub>2</sub> [M+H]<sup>+</sup>: 233.0846, Obser.: 233.0835.



5.5 *N*-benzyl-*N*-(4-methylphenyl) hydrazine (**2e**) was obtained as white solid (165 mg, 78%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 – 7.27 (m, 5H), 7.07 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 4.52 (s, 2H, Benzylic-CH<sub>2</sub>), 3.49 (brs, 2H, NH<sub>2</sub>), 2.27 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  149.7, 137.6, 129.5, 128.6, 128.1, 128.0, 127.3, 114.1, 61.0, 20.3. HRMS: Calc. for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 213.1392, Obser. : 213.1382.



5.6 *N*-benzyl-*N*-(4-chlorophenyl) hydrazine (**2f**) was obtained as white solid (165 mg, 71%) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (t, *J* = 7.3 Hz, 2H), 7.32 – 7.24 (m, 3H), 7.19 (d, *J* = 8.9 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 4.56 (s, 2H, Benzylic-CH<sub>2</sub>), 3.53 (brs, 2H, NH<sub>2</sub>).<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  150.3, 136.8, 128.8, 128.7, 127.8, 127.5, 123.2, 114.8, 60.2. HRMS: Calc. for C<sub>13</sub>H<sub>13</sub>ClN<sub>2</sub> [M+H]<sup>+</sup>: 233.0846, Obser. : 233.0833.



5.7 *N*-(4-bromobenzyl)-*N*-phenylhydrazine (**2g**) was obtained as white solid (207 mg, 75%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 – 7.27 (m, 5H), 7.26 (d, *J* = 7.4 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 4.57 (s, 2H, Benzylic-CH<sub>2</sub>), 3.53 (s, 2H, NH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  150.6, 136.8, 131.7, 128.7, 127.7, 127.5, 115.2, 110.3, 60.0. HRMS: Calc. for C<sub>13</sub>H<sub>13</sub>BrN<sub>2</sub> [M+H]<sup>+</sup>: 277.0340, Obser. : 277.0333.



5.8 *N*-benzyl-(4-fluorophenyl) hydrazine (**2h**) was obtained as yellow solid (156 mg, 72%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 (t, *J* = 8.4 Hz, 2H), 7.24 – 7.21 (m, 3H), 7.04 – 6.96 (m, 2H), 6.88 (t, *J* = 8.7 Hz, 2H), 4.43 (s, 2H, Benzylic-CH<sub>2</sub>), 3.41 (brs, 2H, NH<sub>2</sub>).<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  156.6 (d, *J*<sub>C-F</sub> =237.5 Hz), 148.3, 148.3, 137.0, 128.7, 128.1, 127.5, 115.6 (d, *J*<sub>C-F</sub> =7.4 Hz), 115.3 (d, *J*<sub>C-F</sub> =22.2 Hz), 61.7. HRMS: Calc. for C<sub>13</sub>H<sub>13</sub>FN<sub>2</sub> [M+H]<sup>+</sup>: 217.1141, Obser.: 217.1145



5.9 *N*-benzyl-(2-methoxyphenyl) hydrazine (**2i**) was obtained as yellow liquid (157 mg, 69%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 – 7.29 (m, 4H), 7.29 (dd, *J* = 5.9, 2.9 Hz, 1H), 7.15 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.95 – 6.90 (m, 2H), 4.31 (s, 2H, Benzylic-CH<sub>2</sub>), 3.93 (s, 3H, OCH<sub>3</sub>), 3.52 (brs, 2H, NH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  151.6, 141.9, 137.5, 129.1, 128.3, 127.3, 123.6, 120.8, 119.7, 111.3, 63.4, 55.5. HRMS: Calc. for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 229.1341, Obser. : 229.1334.



5.10 *N*-(4-methoxybenzyl)-(4-chlorophenyl) hydrazine (**2j**) was obtained as pale brown solid (194 mg, 74%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 – 7.17 (m, 4H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 4.46 (s, 2H, Benzylic-CH<sub>2</sub>), 3.79 (s, 3H, Aryl-OCH<sub>3</sub>), 3.45 (s, 2H, NH<sub>2</sub>).<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  159.1, 150.3, 129.2, 128.7, 128.6, 123.2, 115.1, 114.1, 59.6, 55.2. HRMS: Calc. for C<sub>14</sub>H<sub>15</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup>: 263.0951, Obser.: 263.0947.



5.11 *N*-(4-chlorobenzyl)-(4-methylphenyl) hydrazine (**2k**) was obtained as pale yellow solid (185 mg, 75%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.21 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 4.41 (s, 2H, Benzylic-CH<sub>2</sub>), 3.44 (s, 2H, NH<sub>2</sub>), 2.20 (s, 3H, Aryl-CH<sub>3</sub>).<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  149.5, 136.3, 133.0, 129.6, 129.3, 128.7, 128.3, 114.0, 60.3, 20.3. HRMS: Calc. for C<sub>14</sub>H<sub>15</sub>ClN<sub>2</sub> [M+H]<sup>+</sup>: 247.1002, Obser.: 247.0990



5.12 *N*-(4-bromophenyl)-*N*-(4-methoxybenzyl) hydrazine (**2I**) was obtained as white solid (236 mg, 77%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 7.7 Hz, 2H), 4.47 (s, 2H, Bezylic-CH<sub>2</sub>), 3.78 (s, 3H, Aryl-OCH<sub>3</sub>), 3.45 (s, 2H, NH<sub>2</sub>).<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  159.1, 150.7, 131.6, 129.2, 128.5, 115.5, 114.1, 110.4, 59.5, 55.2. HRMS: Calc. for C<sub>14</sub>H<sub>15</sub>BrN<sub>2</sub>O [M+H]<sup>+</sup>: 307.0446, Obser. : 307.0431.



5.13 *N*-(4-methylbenzyl)-(4-bromophenyl) hydrazine (**2m**) was obtained as yellow solid (229 mg, 79%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.16 (d, *J* = 9.0 Hz, 2H), 7.13 (s, 4H), 7.01 (d, *J* = 9.0 Hz, 2H), 4.49 (s, 2H, Bezylic-CH<sub>2</sub>), 3.47 (s, 2H, NH<sub>2</sub>), 2.32 (s, 3H, Aryl-CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  150.3, 137.2, 133.6, 129.4, 128.7, 127.8, 123.1, 114.9, 60.0, 21.0. HRMS: Calc. for C<sub>14</sub>H<sub>15</sub>BrN<sub>2</sub> [M+H]<sup>+</sup>: 291.0497, Obser.: 291.0491.



5.14 *N*-(4-chlorobenzyl)-*N*-4-methyl hydrazine (**2n**) was obtained as white solid (179 mg, 73%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 7.30 (d, *J* = 9.0 Hz, 2H), 7.14 (m, 4H), 6.97 (d, *J* = 9.0 Hz, 2H), 4.51 (s, 2H, Benzylic-CH<sub>2</sub>), 3.49 (s, 2H, NH<sub>2</sub>), 2.32 (s, 3H, Aryl-CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  150.3, 137.2, 133.6, 129.3, 128.7, 127.8, 123.1, 114.9, 60.2, 21.0. HRMS: Calc. for C<sub>14</sub>H<sub>15</sub>ClN<sub>2</sub> [M+H]<sup>+</sup>: 247.1002, Obser.: 247.0997



5.15 *N*-(4-bromophenyl)-*N*-(4-chlorobenzyl) hydrazine (**2o**) was obtained as white solid (234 mg, 76%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 – 7.25 (m, 4H), 7.18 (d, *J* = 6.3 Hz, 2H), 6.92 (d, *J* = 6.6 Hz, 2H), 4.52 (s, 2H, Benzylic-CH<sub>2</sub>), 3.53 (s, 2H, NH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  150.4, 135.4, 133.3, 131.7, 129.0, 128.9, 115.2, 110.7, 59.5. HRMS: Calc. for C<sub>13</sub>H<sub>12</sub>BrClN<sub>2</sub> [M+H]<sup>+</sup>: 310.9951, Obser. : 310.9927



5.16 *N*-(4-methylbenzyl)-*N*-(4-methoxyphenyl) hydrazine (**2p**) was obtained as red liquid (169 mg,70%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.21 (m, 2H), 7.16 – 7.11 (m, 3H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 2H), 4.27 (s, 2H, Benzylic-CH<sub>2</sub>), 3.93 (s, 3H, Aryl-OCH<sub>3</sub>), 3.38 (brs, 2H, NH<sub>2</sub>), 2.34 (s, 3H, Aryl-CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  151.5, 141.9, 136.9, 134.3, 129.1, 129.0, 123.5, 120.8, 119.7, 111.3, 63.1, 55.5, 21.1. HRMS: Calc. for C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 243.1497, Obser. : 243.1419



5.17 *N*-methyl–*N*-phenyl hydrazine (**2q**) was obtained as yellow liquid (112 mg, 89%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 – 7.11 (m, 2H), 6.93 (d, *J* = 7.7 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 3.62 (brs, 2H, NH<sub>2</sub>), 3.03 (s, 3H, *N*-CH<sub>3</sub>).<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  152.6, 128.9, 118.5, 113.4, 44.5. HRMS: Calc. for C<sub>7</sub>H<sub>10</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 123.0922, Obser. : 123.0929



5.18 *N*-ethyl-*N*-phenyl hydrazine (**2r**) was obtained as yellow liquid (118 mg, 87%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.18 (m, 2H), 6.91 (d, *J* = 7.2 Hz, 2H), 6.71 (m, 1H), 3.39 (q, *J* = 7.1 Hz, 4H (together CH<sub>2</sub> and broad peak of amine)), 1.10 (t, *J* = 7.1 Hz, 3H, CH<sub>3</sub>).<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  148.4, 129.1, 117.1, 112.7, 38.4, 14.8. HRMS: Calc. for C<sub>8</sub>H<sub>12</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 137.1079, Obser. : 137.1068



5.19 *N*-isopropyl-*N*-phenyl hydrazine (**2s**) was obtained as yellow liquid (109 mg, 73%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.20 – 7.15 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.70 (t, *J* = 7.4 Hz, 1H), 4.00 (q, *J* = 6.4 Hz, 1H, *iso*-propyl-CH), 3.17 (s, 2H, CH<sub>2</sub>), 1.08 (d, *J* = 6.6 Hz, 6H, 2CH<sub>3</sub>). <sup>13</sup>C

NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  151.5, 129.0, 118.0, 113.7, 50.6, 17.6. HRMS: Calc. for C<sub>9</sub>H<sub>14</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 151.1235, Obser.: 151.1227



5.20 *N*-diphenyl hydrazine (**2t**) was obtained as white solid (144 mg, 81%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>).  $\delta$  7.28 (t, *J* = 7.8 Hz, 4H), 7.25 – 7.17 (m, 4H), 6.97 (t, *J* = 7.3 Hz, 2H), 3.77 (brs, 2H, NH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  149.1, 129.0, 121.9, 119.4. HRMS: Calc. for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub> [M+H]<sup>+</sup>:185.1079, Obser.: 185.1067



5.21 *N*-allyl *N*-phenyl hydrazine (**2u**) was obtained as dark yellow liquid (102 mg, 69%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.17 (t, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 5.80 (m, 1H), 5.27 – 5.17 (m, 2H), 3.95 (d, *J* = 5.8 Hz, 2H, CH<sub>2</sub>), 3.50 (brs, 2H, NH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  151.3, 132.6, 128.9, 118.6, 118.5, 113.7, 58.8. HRMS: Calc. for C<sub>9</sub>H<sub>12</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 149.1079, Obser. : 148.1068



5.22 *N*-propargyl-*N*-phenyl hydrazine (**2v**) was obtained as brown liquid (103 mg, 71%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.88 (t, *J* = 7.3 Hz, 1H), 4.18 (d, *J* = 2.3 Hz, 2H, propargyl-CH<sub>2</sub>), 3.77 (brs, 2H, NH<sub>2</sub>), 2.18 (t, *J* = 2.3 Hz, 1H, propargyl-CH) <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  150.5, 128.9, 120.0, 115.1, 78.0, 73.2, 46.0. HRMS: Calc. for C<sub>9</sub>H<sub>10</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 147.0922, Obser.: 147.0915.



5.23 *N*,*N*-dibenzyl hydrazine (**2w**) was obtained as white solid (74 mg, 33%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.47–7.25 (m, 10H), 3.73 (s, 4H, Benzylic-CH<sub>2</sub>), 2.81 (brs, 2H,NH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  137.8, 129.0, 128.3, 127.2, 64.8. HRMS: Calc. for C<sub>14</sub>H<sub>11</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 213.1392, Obser.: 213.1384.





### 6. <sup>1</sup>H and <sup>13</sup>C NMR of *N*,*N*-disubstituted hydrazines

Figure 6.1 <sup>1</sup>H and <sup>13</sup>C NMR of product 2a



Figure 6.2 <sup>1</sup>H and <sup>13</sup>C NMR of product 2b



Figure 6.3 <sup>1</sup>H and <sup>13</sup>C NMR of product 2c



Figure 6.4 <sup>1</sup>H and <sup>13</sup>C NMR of product 2d



Figure 6.5 <sup>1</sup>H and <sup>13</sup>C NMR of product 2e



Figure 6.6 <sup>1</sup>H and <sup>13</sup>C NMR of product 2f



Figure 6.7  $^{1}$ H and  $^{13}$ C NMR of product 2g



Figure 6.8 <sup>1</sup>H and <sup>13</sup>C NMR of product 2h



Figure 6.9 <sup>1</sup>H and <sup>13</sup>C NMR of product 2i



Figure 6.10 <sup>1</sup>H and <sup>13</sup>C NMR of product 2j



Figure 6.11 <sup>1</sup>H and <sup>13</sup>C NMR of product 2k



Figure 6.12 <sup>1</sup>H and <sup>13</sup>C NMR of product 2I



Figure 6.13 <sup>1</sup>H and <sup>13</sup>C NMR of product 2m



Figure 6.14 <sup>1</sup>H and <sup>13</sup>C NMR of product 2n



Figure 6.15 <sup>1</sup>H and <sup>13</sup>C NMR of product 20



Figure 6.16 <sup>1</sup>H and <sup>13</sup>C NMR of product 2p



Figure 6.17 <sup>1</sup>H and <sup>13</sup>C NMR of product 2q



Figure 6.18 <sup>1</sup>H and <sup>13</sup>C NMR of product 2r



Figure 6.19 <sup>1</sup>H and <sup>13</sup>C NMR of product 2s



Figure 6.20 <sup>1</sup>H and <sup>13</sup>C NMR of product 2t



Figure 6.21 <sup>1</sup>H and <sup>13</sup>C NMR of product 2u



Figure 6.22 <sup>1</sup>H and <sup>13</sup>C NMR of product 2v



Figure 6.23 <sup>1</sup>H and <sup>13</sup>C NMR of product 2w