

Iridium/Graphene Nanostructured Catalyst for the N-Alkylation of Amines to Synthesize Nitrogen-containing Derivatives and Heterocyclic Compounds

**Supporting Information**

Iridium/Graphene Nanostructured Catalyst for the N-  
Alkylation of Amines to Synthesize Nitrogen-containing  
Derivatives and Heterocyclic Compounds

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### Characterization of the Catalyzed Products

*N*-benzylaniline (**1a**). It was obtained as yellow oil, yield 92 % (169 mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.37-7.32 (m, Ar, 4H), 7.27-7.24 (m, Ar, 1H), 7.18-7.15 (m, Ar, 2H), 6.72-6.69 (t, Ar, 1H), 6.64-6.62 (d, Ar, 2H,  $J_{\text{HH}} = 7.8\text{Hz}$ ), 4.32 (s,  $\text{CH}_2$ , 2H), 4.01 (br. s, NH, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 148.1, 139.3, 129.2, 128.6, 127.4, 127.2, 117.5, 112.7, 48.2. HRMS (ESI/APCI):  $m/z = 184.1114$  g/mol, calc'd. for  $\text{C}_{13}\text{H}_{14}\text{N}$ : 184.1121 g/mol. FTIR IR (ATR):  $\nu = 3410(\text{w})$ , 3022 (w), 1604 (m), 1507 (m), 1320 (w), 1261 (m), 731(s)  $\text{cm}^{-1}$

*N*-(4-methoxybenzyl)aniline (**1b**). It was obtained as yellow oil, yield 93 % (199mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.28-7.26 (d,  $J_{\text{HH}} = 8.4\text{Hz}$ , 2H, Ar), 7.17-7.14 (m, 2H, Ar), 6.87-6.85 (m, 2H, Ar), 6.71-6.68 (t, 1H, Ar), 6.62-6.61 (m, 2H, Ar), 4.23 (br. s, NH, 1H), 3.90 (d,  $J_{\text{HH}} = 13.2\text{Hz}$ , 1H), 3.78 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 158.8, 148.1, 131.3, 129.2, 128.7, 117.4, 113.9, 112.7, 55.2, 47.7. HRMS (ESI/APCI):  $m/z = 214.1222$  g/mol, calc'd. for  $\text{C}_{14}\text{H}_{16}\text{NO}$   $[\text{M}]^+$  : 214.1226 g/mol. FTIR IR (ATR):  $\nu = 3410$  (w), 3029 (w), 2835 (w), 1604(s), 1507 (s), 1238(s), 1171(m), 1029 (m), 820 (m), 746 (s)  $\text{cm}^{-1}$ .

*N*-(*p*-chlorobenzyl)aniline (**1c**). It was obtained as colorless oil, yield 85 % (185mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.28 (s, 3H, Ar), 7.16-7.13 (m, 2H, Ar), 6.72-6.69 (m, 1H, Ar), 6.59-6.58 (m, 2H, Ar), 4.29(d, 2H,  $J_{\text{HH}} = 5.4\text{Hz}$ ), 4.04 (br. s, NH,

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<sup>1</sup>H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150MHz) δ (ppm) = 147.7, 137.9, 132.8, 129.2, 128.7, 128.6, 117.7, 112.8, 47.5. HRMS (ESI/APCI): *m/z* = 218.0731 g/mol, calc'd. for C<sub>13</sub>H<sub>13</sub>NCl [M]<sup>+</sup>: 218.0731 g/mol. FTIR IR (ATR): ν = 3417 (w), 3044 (w), 2843 (w), 1604(s), 1499 (s), 1320(m), 1253(m), 1089 (m), 813(m), 746 (s) cm<sup>-1</sup>.

*benzyl(4-methoxyphenyl)amine (1d)*. It was obtained as yellow oil, yield 90 % (193mg);

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600MHz) δ (ppm) = 7.36-7.31 (m, Ar, 4H), 7.26-7.24 (t, Ar, 1H), 6.76-6.75 (m, Ar, 2H), 6.58-6.59 (m, Ar, 2H), 4.26 (s, CH<sub>2</sub>, 2H), 3.72 (s, CH<sub>3</sub>, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150MHz) δ (ppm) = 152.1, 142.4, 139.6, 128.57, 127.52, 127.15, 114.8, 114.0, 55.7, 49.2. HRMS (ESI/APCI): *m/z* = 214.1222 g/mol, calc'd. for C<sub>14</sub>H<sub>16</sub>NO [M]<sup>+</sup>: 214.1226 g/mol. FTIR IR (ATR): ν = 3402 (w), 3029 (w), 2835 (w), 1514(s), 1231 (s), 1178 (w), 1029 (m), 820 (m), 738 (m) cm<sup>-1</sup>.

*N-(4-chlorophenyl)benzylamine (1e)*. It was obtained as yellow oil, yield 80 % (174mg);

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600MHz) δ (ppm) = 7.33-7.19 (m, Ar, 4H), 7.10-7.06 (m, Ar, 2H), 6.54-6.51 (m, Ar, 2H), 4.61 (s, 1H), 4.29-4.28 (d, CH<sub>2</sub>, 2H, J<sub>HH</sub> = 6.0Hz), 4.04(br. s, NH, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150MHz) δ (ppm) = 146.6, 138.9, 128.9, 128.6, 127.39, 127.35, 127.0, 126.5, 122.0, 113.8, 54.4, 48.3. HRMS (ESI/APCI): *m/z* = 218.07311 g/mol, calc'd. for C<sub>13</sub>H<sub>13</sub>NCl [M]<sup>+</sup>: 218.07310 g/mol. FTIR IR (ATR): ν = 3410 (w), 3029 (w), 2850 (w), 1596(s), 1499 (s), 1313 (m), 1178 (w), 1089 (w), 813 (m), 731 (m) cm<sup>-1</sup>.

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*N-Benzyl-3,5-dimethoxyaniline (If)*. It was obtained as yellow oil, yield 90 % (219mg);

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.34-7.30 (m, Ar, 4H), 7.26-7.24 (t, Ar, 1H), 5.877-5.870 (m, Ar, 1H), 5.817-5.814(d, Ar, 2H, JHH = 1.8Hz), 4.28 (s, CH<sub>2</sub>, 2H), 4.03 (br. s, NH, 1H), 3.71 (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 161.6, 150.0, 139.2, 128.6, 127.5, 127.2, 91.6, 89.8, 55.1, 48.3. HRMS (ESI/APCI):  $m/z$  = 244.1333 g/mol, calc'd. for  $\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}$   $[\text{M}]^+$ : 244.1332 g/mol. FTIR IR (ATR):  $\nu$  = 3402 (w), 3007 (w), 2843 (w), 1596(s), 1455 (m), 1201(s), 1149(s), 1067 (m), 805(m), 731 (m)  $\text{cm}^{-1}$ .

*N-benzyl-(2-fluorophenyl)amine (Ig)*. It was obtained as yellow oil, yield 87 %

(176mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.37-7.32 (m, Ar, 4H), 7.28-7.24 (m, Ar, 1H), 6.98-6.92 (m, Ar, 2H), 6.67-6.64 (m, Ar, 1H), 6.63-6.59 (m, Ar, 1H), 4.36-4.35 (d, 2H, JHH = 5.4Hz), 4.30 (br. s, NH, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 152.2, 150.6, 138.9, 136.5, 128.6, 127.3, 124.5, 116.7, 114.4, 114.2, 112.2, 47.8. HRMS (ESI/APCI):  $m/z$  = 202.1020 g/mol, calc'd. for  $\text{C}_{13}\text{H}_{13}\text{NF}$   $[\text{M}]^+$ : 202.1027 g/mol. FTIR IR (ATR):  $\nu$  = 3432(w), 3029(w), 2925(w), 1619(m), 1514(s), 1335(m), 1246(m), 1186(m), 746(s)  $\text{cm}^{-1}$ .

*N-ethyl-N-phenylamine (Ih)*. It was obtained as colorless oil, yield 80 % (98mg);  $^1\text{H}$

NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.24-7.14 (m, Ar, 2H), 6.68-6.66 (t, Ar, 1H), 6.59-6.58 (d, Ar, 2H, JHH = 7.8Hz), 3.52 (br. s, NH, 1H), 3.10-3.08 (q, 2H), 0.92-0.81 (t,

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3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 148.0, 129.8, 116.5, 112.1, 45.0, 15.6.

HRMS (ESI/APCI):  $m/z$  = 122.0965 g/mol, calc'd. for  $\text{C}_8\text{H}_{12}\text{N} [\text{M}]^+$ : 122.0964 g/mol.

FTIR IR (ATR):  $\nu$  = 3410 (w), 3051 (w), 2925 (m), 2857 (m), 1604 (s), 1507 (s), 1462 (s), 1320 (m), 1261 (m), 1149 (m), 1029 (s), 746 (s)  $\text{cm}^{-1}$ .

*N-propylaniline (Ii)*. It was obtained as colorless oil, yield 68 % (93mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.16-7.14 (m, Ar, 2H), 6.68-6.65 (t, Ar, 1H), 6.60-6.58 (t, Ar, 2H), 3.61 (br. s, NH, 1H), 3.07-3.05 (t, 2H), 1.64-1.60 (m,  $\text{CH}_2$ , 2H), 0.99-0.97 (t, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 148.4, 129.2, 117.0, 112.6, 45.7, 22.7, 11.6.

HRMS (ESI/APCI):  $m/z$  = 136.1120 g/mol, calc'd. for  $\text{C}_9\text{H}_{14}\text{N} [\text{M}]^+$ : 136.1121 g/mol.

FTIR IR (ATR):  $\nu$  = 3410(w), 3022 (w), 2962 (w), 2932 (w), 1604 (m), 1507 (m), 1320 (m), 1253 (m), 1149 (w), 865(w), 746 (m)  $\text{cm}^{-1}$

*N-(n-butyl)aniline (Ij)*. It was obtained as colorless oil, yield 75 % (113mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.16-7.13 (m, Ar, 2H), 6.67-6.65 (m, Ar, 1H), 6.59-6.57 (m, Ar, 2H), 3.56 (br. s, NH, 1H), 3.10-3.07 (t, 2H), 1.61-1.54 (m, 2H), 1.44-1.38 (m, 2H), 0.95-0.92 (t, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 148.5, 129.1, 117.0, 112.6, 43.6, 31.6, 20.2, 13.9. HRMS (ESI/APCI):  $m/z$  = 150.1274 g/mol, calc'd. for  $\text{C}_{10}\text{H}_{16}\text{N} [\text{M}]^+$ : 150.1277 g/mol. FTIR IR (ATR):  $\nu$  = 3417 (w), 3051 (w), 2932 (m), 2865 (m), 1604 (s), 1507 (s), 1320 (m), 1261 (m), 738 (s)  $\text{cm}^{-1}$ .

*N-hexylaniline (Ik)*. It was obtained as colorless oil, yield 72 % (128mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.16-7.13 (m, Ar, 2H), 6.67-6.65 (m, Ar, 1H), 6.59-6.57 (m, Ar, 2H), 3.56 (br. s, NH, 1H), 3.10-3.07 (t, 2H), 1.61-1.54 (m, 2H), 1.44-1.38 (m, 2H), 0.95-0.92 (t, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 148.5, 129.1, 117.0, 112.6, 43.6, 31.6, 28.7, 27.3, 23.2, 13.9. HRMS (ESI/APCI):  $m/z$  = 178.2920 g/mol, calc'd. for  $\text{C}_{12}\text{H}_{20}\text{N}^+ [\text{M}]^+$ : 178.2919g/mol. FTIR IR (ATR):  $\nu$  = 3402 (w), 3059

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(w), 2925 (m), 2857 (w), 1604 (s), 1507 (s), 1320 (m), 1253 (m), 1178 (w), 865 (w), 746 (s)  $\text{cm}^{-1}$

*4-Methoxy-N-(1-phenylethyl)aniline (II)*. It was obtained as yellow oil, yield 79 % (179mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.50-7.48 (m, Ar, 2H), 7.18-7.16 (m, Ar, 2H), 6.89-6.65 (m, Ar, 3H), 6.60-6.58 (m, Ar, 2H), 4.20-4.17 (q, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 154.1, 148.5, 147.4, 142.5, 130.65, 129.1, 117.0, 112.6, 50.3, 30.8. HRMS (ESI/APCI):  $m/z$  = 228.3075 g/mol, calc'd. for  $\text{C}_{15}\text{H}_{18}\text{NO}^+$   $[\text{M}]^+$ : 228.3073 g/mol. FTIR IR (ATR):  $\nu$  = 3387 (m), 3216 (w), 2917 (m), 2843 (w), 1634 (m), 1507 (s), 1462 (s), 1298 (w), 1231 (s), 1126 (w), 1029 (s), 820 (s)  $\text{cm}^{-1}$ .

*N-Isopropylaniline (Im)*. It was obtained as colorless oil, yield 90 % (123mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.15-7.13 (m, Ar, 2H), 6.69-6.67 (m, Ar, 1H), 6.60-6.58 (m, Ar, 2H), 3.39-3.36 (m, 1H), 1.09-1.08 (d, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 148.4, 129.2, 117.0, 112.6, 51.8, 21.8. HRMS (ESI/APCI):  $m/z$  = 136.1120 g/mol, calc'd. for  $\text{C}_9\text{H}_{14}\text{N}$   $[\text{M}]^+$ : 136.1121 g/mol. FTIR IR (ATR):  $\nu$  = 3395(w), 3059(w), 1634(m), 1581(s), 1462(m), 1268(m), 738(s)  $\text{cm}^{-1}$ .

*N-Isopropyl-p-anisidine (In)*. It was obtained as colorless oil, yield 92 % (153mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.50-7.48 (m, Ar, 2H), 6.96-6.93 (m, Ar, 2H), 4.49-4.43 (m, 1H), 1.09-1.08 (d, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 154.1, 147.4, 142.5, 130.65, 55.8, 52.8, 49.5, 22.0. HRMS (ESI/APCI):  $m/z$  = 166.1223 g/mol, calc'd. for  $\text{C}_{10}\text{H}_{16}\text{ON}$   $[\text{M}]^+$ : 166.1226 g/mol. FTIR IR (ATR):  $\nu$  = 3365(w), 2962(w), 1619(w), 1507(s), 1231(s), 1171(m), 1037(m), 820(m)  $\text{cm}^{-1}$ .

*N-benzylpyridin-2-amine (Io)*. It was obtained as yellow solid (mp: 93-95°C), yield 95 % (176mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 8.8-8.1 (m, Ar, 1H), 7.39-7.36 (m, Ar, 1H), 7.35-7.30 (m, Ar, 4H), 7.27-7.24 (m, Ar, 1H), 6.58-6.56 (m, 1H), 6.35-6.35 (t, 1H), 4.85 (br. s, NH, 1H), 4.49 (d, 2H,  $J_{\text{HH}} = 6.0\text{Hz}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$

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(ppm) = 158.6, 148.2, 139.1, 137.4, 128.6, 127.3, 127.2, 113.1, 106.7, 46.3. HRMS (ESI/APCI):  $m/z = 185.1067$  g/mol, calc'd. for  $C_{12}H_{13}N_2 [M]^+$ : 185.1073 g/mol. FTIR IR (ATR):  $\nu = 3216(m), 3022(w), 29777(w), 1574(s), 1522(m), 1440(s), 1335(m), 1149(m), 1081(m) \text{ cm}^{-1}$ .

*o*-(benzylamino)phenol (**1p**). It was obtained as yellow oil, yield 75 % (150mg);  $^1H$  NMR ( $CDCl_3$ , 600MHz)  $\delta$  (ppm) = 11.0 (br. s, OH, 1H), 7.37-7.32 (m, Ar, 4H), 7.28-7.24 (m, Ar, 1H), 7.18-7.02 (m, Ar, 2H), 6.85-6.73 (m, Ar, 1H), 6.65-6.60 (m, Ar, 1H), 4.56-4.45 (d, 2H,  $J_{HH} = 5.4\text{Hz}$ ), 4.50 (br. s, NH, 1H).  $^{13}C$  NMR ( $CDCl_3$ , 150MHz)  $\delta$  (ppm) = 155.1, 155.3, 130.1, 138.5, 130.2, 129.5, 126.3, 118.6, 115.2, 114.5, 110.0, 47.8. HRMS (ESI/APCI):  $m/z = 200.2542$  g/mol, calc'd. for  $C_{13}H_{14}NO^+ [M]^+$ : 200.2545 g/mol. FTIR IR (ATR):  $\nu = 3100-3500(br), 3037(w), 2925(w), 2843(w), 1581(m), 1492(m), 1447(m), 1358(m), 1238(m), 1029(w), 731(s) \text{ cm}^{-1}$

2-(benzylamino)pyrimidine (**1q**). It was obtained as yellow oil, yield 56 % (104mg);  $^1H$  NMR ( $CDCl_3$ , 600MHz)  $\delta$  (ppm) = 8.25-8.24 (d, Ar, 2H,  $J_{HH} = 4.8\text{Hz}$ ), 7.35-7.30 (m, Ar, 3H), 7.26-7.24 (m, Ar, 2H), 6.53-6.51 (t, Ar, 1H), 5.54 (br.s, NH, 1H), 4.63 (d, 2H,  $J_{HH} = 4.0\text{Hz}$ ).  $^{13}C$  NMR ( $CDCl_3$ , 150MHz)  $\delta$  (ppm) = 162.2, 158.0, 139.0, 128.5, 127.4, 127.2, 110.8, 45.4. HRMS (ESI/APCI):  $m/z = 186.1019$  g/mol, calc'd. for  $C_{11}H_{12}N_3 [M]^+$ : 186.1026 g/mol. FTIR IR (ATR):  $\nu = 3231(m), 3029(w), 2857(m), 1574(s), 1529(s), 1447(s), 1261(s), 1067(m), 746(s) \text{ cm}^{-1}$ .

(1*H*-benzoimidazol-2-yl)benzylamine (**1r**). It was obtained as yellow oil, yield 85 % (191mg);  $^1H$  NMR ( $CDCl_3$ , 600MHz)  $\delta$  (ppm) = 7.36-7.30 (m, Ar, 4H), 7.29-7.24 (m, Ar, 4H), 7.04-7.02 (m, Ar, 2H), 4.58 (s, Ar,NH, 2H).  $^{13}C$  NMR ( $CDCl_3$ , 150MHz)  $\delta$  (ppm) = 154.5, 138.0, 128.9, 127.8, 127.3, 120.8, 112.4, 47.3. HRMS (ESI/APCI):  $m/z = 224.1176$  g/mol, calc'd. for  $C_{14}H_{14}N_3 [M]^+$ : 224.1182 g/mol. FTIR IR (ATR):  $\nu = 3395(w), 3059(w), 1634(m), 1581(s), 1462(m), 738(s) \text{ cm}^{-1}$ .

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*N-methyl-N-phenyl-benzenemethanamine (2a)*. It was obtained as colorless oil, yield 82 % (163mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.35-7.30 (m, Ar, 4H), 7.25-7.22 (m, Ar, 1H), 7.15-7.13 (m, Ar, 2H), 6.70-6.67 (t, Ar, 1H), 6.68-6.64 (d, Ar, 2H,  $J_{\text{HH}} = 7.8\text{Hz}$ ), 4.35 (s,  $\text{CH}_2$ , 2H), 3.10 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 148.7, 139.8, 129.6, 128.8, 127.8, 127.5, 117.2, 112.5, 48.0, 45.7. HRMS (ESI/APCI):  $m/z = 198.2821$  g/mol, calc'd. for  $\text{C}_{14}\text{H}_{16}\text{N}^+ [\text{M}]^+$ : 198.2819 g/mol. FTIR IR (ATR):  $\nu = 3029$  (w), 2925 (w), 2857 (w), 1596 (s), 1499 (s), 1455 (m), 1350 (m), 1111(m) , 1029(m), 940(m), 746(s) , 723(s)  $\text{cm}^{-1}$

*N-benzyl-N-(4-chloro-benzyl)-aniline (2b)*. It was obtained as colorless oil, yield 80 % (247mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.31-7.29 (m, Ar, 4H), 7.24-7.22 (m, Ar, 6H), 7.16-7.13 (m, Ar, 2H), 6.72-6.67 (m, Ar, 2H), 4.63-4.60 (d, Ar, 2H,  $J_{\text{HH}} = 23.4\text{Hz}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 149.1, 138.5, 132.8, 129.1, 128.6, 127.8, 127.0, 126.8, 126.6, 116.6, 117.7, 112.3, 54.5, 49.8. HRMS (ESI/APCI):  $m/z = 308.8225$  g/mol, calc'd. for  $\text{C}_{20}\text{H}_{19}\text{NCl}^+ [\text{M}]^+$ : 308.8226 g/mol. FTIR IR (ATR):  $\nu = 3051$  (w), 2902 (w), 2857 (w), 1596 (m), 1492 (m), 1358 (m), 1231 (m), 955 (m) , 805(m), 731 (s),  $\text{cm}^{-1}$

*N,N-dibenzylaniline (2c)*. It was obtained as yellow solid (mp: 68-70°C), yield 86 % (236mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.31-7.29 (m, Ar, 4H), 7.24-7.22 (m, Ar, 6H), 7.16-7.13 (m, Ar, 2H), 6.72-6.67 (m, Ar, 2H), 4.63-4.60 (d, Ar, 2H,  $J_{\text{HH}} = 23.4\text{Hz}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 149.1, 138.5, 129.1, 128.6, 126.8, 126.6, 116.6, 112.3, 54.1. HRMS (ESI/APCI):  $m/z = 274.1588$  g/mol, calc'd. for  $\text{C}_{20}\text{H}_{20}\text{N} [\text{M}]^+$ : 274.1590 g/mol. FTIR IR (ATR):  $\nu = 3037$  (w), 2917 (m), 1596 (s), 1499 (s), 1455 (m), 1358 (m) 1231 (m), 1029 (w), 955 (m), 731 (s)  $\text{cm}^{-1}$

*N-phenylpyrrolidine (3a)*. It was obtained as colorless oil, yield 80 % (119mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.17-7.26 (m, 3H), 6.93-6.96 (m, 2H), 6.75-6.96(m,

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1H), 3.38–3.44 (m, 4H), 2.01–2.07 (m, 3H). HRMS (ESI/APCI):  $m/z = 148.2231$  g/mol, calc'd. for  $C_{13}H_{14}N$ : 148.2234 g/mol. FTIR IR (ATR):  $\nu = 3059$  (w), 3029 (w), 2962 (m), 2925(s), 2835(m), 1604(m), 1596(s), 1507(s), 1462 (m), 1365 (s), 1358 (w), 1238(w), 1186 (m), 1156 (m), 992 (m), 746 (s), 686 (s)  $cm^{-1}$

*N*-(4-chlorophenyl) pyrrolidine (**3b**). It was obtained as colorless oil, yield 85 % (155mg);  $^1H$  NMR ( $CDCl_3$ , 600MHz)  $\delta$  (ppm) = 7.37–7.42 (m, 3H), 7.07–7.09 (m, 1H), 2.83–2.85 (m, 4H), 2.19–2.22 (m, 4H). HRMS (ESI/APCI):  $m/z = 182.6683$  g/mol, calc'd. for  $C_{11}H_{13}NCl^+ [M]^+$  : 182.6686 g/mol. FTIR (ATR):  $\nu = 2962$ (w), 2925(s), 2857(m), 1738(s), 1604(m), 1470(m), 1462(m), 1373(s), 275(w), 1231(s), 1156(w), 1074(w), 1014(w), 798(m)  $cm^{-1}$ .

*N*-(4-methoxyphenyl) pyrrolidine (**3c**). It was obtained as colorless oil, yield 89 % (159mg);  $^1H$  NMR ( $CDCl_3$ , 600MHz)  $\delta$  (ppm) = 6.62–6.74 (m, 4H), 3.79 (s, 3H), 3.38–3.43(t, J=6 Hz 4H), 2.01–2.06 (t, J=6 Hz 4H), 2.01–1.98 (m, 4H).  $^{13}C$  NMR ( $CDCl_3$ , 150MHz)  $\delta$  (ppm) = 149.2, 141.1, 116.1, 114.1, 78.1, 56.1, 51.1, 25.9. HRMS (ESI/APCI):  $m/z = 178.2485$  g/mol, calc'd. for  $C_{11}H_{16}NO^+ [M]^+$ : 178.2488 g/mol. FTIR (ATR):  $\nu = 3044$ (w), 2947(m), 2925(s), 2857(m), 1619 (w), 1514(m), 1484(w), 1462(m), 1365(m), 1275(w), 1238(m), 1178(w), 1156(w), 1044(m), 970(w), 805(s), 731(w)  $cm^{-1}$ .

*N*-phenylpiperidine (**3d**). It was obtained as colorless oil, yield 75 % (122mg);  $^1H$  NMR ( $CDCl_3$ , 600MHz)  $\delta$  (ppm) = 7.26 (t, 2H, J=7 Hz), 6.99 (d, 2H, J=7 Hz), 6.86 (t, 1H, J=7 Hz), 3.17 (t, 4H, J=6.7 Hz), 1.75 (m, 4H), 1.61 (t, 2H, J=4.8 Hz).  $^{13}C$  NMR ( $CDCl_3$ , 150MHz)  $\delta$  (ppm) = 151.6, 129.0, 119.7, 116.7, 60.0, 25.7, 24.2. HRMS (ESI/APCI):  $m/z = 162.2495$  g/mol, calc'd. for  $C_{11}H_{16}N^+ [M]^+$ : 162.2498 g/mol. FTIR IR (ATR):  $\nu = 2932$  (m), 2853 (m), 2805 (m), 1597 (s), 1494 (s), 1450 (m), 1384 (m), 1235 (s), 1220 (s), 1131 (m), 917 (m), 753 (s)  $cm^{-1}$ .

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*N*-(4-methoxyphenyl) piperidine (**3e**). It was obtained as colorless oil, yield 78 % (150mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 6.93–6.90 (m, 2H), 6.84–6.81 (m, 2 H), 3.76 (s, 3 H), 3.03–3.01(m, 4 H), 1.74–1.70 (m, 4 H), 1.56–1.52 (m, 2 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 154.0, 145.2, 119.0, 114.3, 55.6, 52.7, 25.8, 23.9. HRMS (ESI/APCI):  $m/z$  = 192.2753g/mol, calc'd. for  $\text{C}_{12}\text{H}_{18}\text{NO}^+$   $[\text{M}]^+$ : 192.2752 g/mol. FTIR (ATR):  $\nu$  = 2932(m), 2850(w), 2800(w), 1507(s), 1447 (m), 1238(s), 1178(m), 1119(m), 1037(s), 917(m),858(w),820(s),798(w),701(w)  $\text{cm}^{-1}$ .

1-(piperidine-1-yl) pyridine (**3f**). It was obtained as y colorless oil, yield 70 % (114mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 8.17 (s, 1H), 7.46 (t,  $J$  = 8Hz, 1H), 6.67 (d,  $J$  = 7Hz, 1H), 6.54 (dd,  $J$  = 4.9, 0.9 Hz, 1H), 3.54(s, 4H), 1.67 (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 159.1, 147.2, 137.7, 112.3, 107.4, 46.5, 25.4, 24.6. HRMS (ESI/APCI):  $m/z$  =163.2381 g/mol, calc'd. for  $\text{C}_{10}\text{H}_{15}\text{N}_2^+$   $[\text{M}]^+$ : 163.2380 g/mol. FTIR (ATR):  $\nu$  = 3007(w), 2925(m),2850(m), 1596(s), 1484(s), 1432(s), 1380(w), 1313(m), 1246(s),1156(w), 1126(m), 1022(w), 850(w), 768 (s),732(w)  $\text{cm}^{-1}$ .

1-methyl-4-(pyridin-2-yl) piperazine (**3g**). It was obtained as colorless oil, yield 70 % (125mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 48 (dd, 1H), 7.46 (ddd, 1H), 7.18 – 7.26 (m, 2H), 3.97-3.99 (m, 4H), 2.34-2.36 (m, 4H), 1.99-2.01(m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 138.9 , 133.2, 132.1, 130.4, 129.6, 59.9, 58.6, 52.9. HRMS (ESI/APCI):  $m/z$  = 178.2522g/mol, calc'd. for  $\text{C}_{10}\text{H}_{16}\text{N}_3^+$   $[\text{M}]^+$ : 178.2525 g/mol. IR(ATR) :  $\nu$  = 3328(s), 2932(m), 2865(m), 1626(m), 1604 (s), 1529 (w), 1514(s), 1447(m), 1156(w), 1052(m), 1029(w), 887(w),858(w),768(s),701(w)  $\text{cm}^{-1}$ .

Benzylpiperazine (**3h**). It was obtained as colorless oil, yield 90 % (160mg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  (ppm) = 7.29-7.22 (m, Ar, 5H), 3.56-3.40 (m, 4H), 2.89-2.86 (m, 4H), 2.41 (br. s, NH , 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz)  $\delta$  (ppm) = 137.8, 129.2, 128.1, 127.0, 64.0, 54.1, 45.8. HRMS (ESI/APCI):  $m/z$  = 177.2642 g/mol, calc'd. for

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$C_{11}H_{17}N_2^+$   $[M]^+$ : 177.2644g/mol. FTIR (ATR):  $\nu$  = 3320(s), 3029(w),2940(m),2820(m), 1641(s),1544 (m), 1492(w), 1455(s),1417(m), 1268(s), 1134(m), 999(s),910(w), 738(s)  $cm^{-1}$ .

*1-methyl-4-phenyl piperazine (3i)*. It was obtained as colorless oil, yield 75 % (133mg);  $^1H$  NMR ( $CDCl_3$ , 600MHz)  $\delta$  (ppm) = 7.26-7.31 (m, Ar, 2H), 7.05-7.09 (m, Ar, 1H), 6.92-6.99 (m, Ar, 2H), 3.63 (t, J = 4.6 Hz, 4H), 2.85-2.87 (m, 7H).  $^{13}C$  NMR ( $CDCl_3$ , 150MHz)  $\delta$  (ppm) = 149.3, 129.4, 121.8, 117.2, 55.4, 46.9, 43.6. HRMS (ESI/APCI):  $m/z$  = 177.2646 g/mol, calc'd. for  $C_{11}H_{17}N_2^+$   $[M]^+$ : 177.2644 g/mol.. FTIR (ATR):  $\nu$  = 3059(w), 2940(m), 2850(w), 2798(s), 1596(s), 1499 (s), 1455(m), 1373(w), 1335(w), 1417(m), 1268(s), 1134(m), 999(s), 910(w), 738(s)  $cm^{-1}$ .

*Hydroxyine*. It was obtained as yellow solid (mp: 190-192°C), yield 55 % (total yield of the tandem reaction, 207mg);  $^1H$  NMR ( $CDCl_3$ , 600MHz)  $\delta$  (ppm) = 7.16-7.37 (m, Ar, 10H), 4.19 (s, 1H), 3.44-3.56 (m, 6H), 2.38-2.57 (m, 8H), 1.16 (t, 2H, JHH = 6Hz).  $^{13}C$  NMR ( $CDCl_3$ , 150MHz)  $\delta$  (ppm) = 142.0, 141.1, 132.4, 129.1, 128.3, 127.8, 126.9, 75.5, 67.9, 66.3, 66.1, 57.9, 57.5, 53.9, 51.4, 15.0. HRMS (ESI/APCI):  $m/z$  = 375.9088 g/mol, calc'd. for  $C_{21}H_{28}ClN_2O_2^+$   $[M]^+$ : 375.9086 g/mol. FTIR (ATR):  $\nu$  = 3300 (S), 3081 (w),3074 (w), 3014 (w),2954 (w), 2910 (w),2865 (w) ,2835 (w), 1604 (s), 1574 (s), 1529 (s), 1447 (s), 1246 (m), 1037(m), 820(s), 768(s)  $cm^{-1}$

*Cyclizine*. It was obtained as yellow solid (mp: 105-107°C), yield 60 % (160mg);  $^1H$  NMR ( $CDCl_3$ , 600MHz)  $\delta$  (ppm) = 7.44-7.17 (m, 10H, Ph), 4.26 (s, 1H, N-CH), 3.31 (s, 8H, N-CH), 2.30 (s, 3H, N-CH<sub>3</sub>).  $^{13}C$  NMR ( $CDCl_3$ , 150MHz)  $\delta$  (ppm) = 142.6, 128.3, 127.9, 126.7, 77.4, 56.3, 46.2 HRMS (ESI/APCI):  $m/z$  = 267.3861 g/mol, calc'd. for  $C_{18}H_{23}N_2$   $[M]^+$ : 267.3863 g/mol. FTIR (ATR):  $\nu$  = 3059(w), 3029(w), 2925(m),

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2857(w), 1619(s), 1492(m), 1447(m), 1275(m) ,1149(w), 1074(w), 1029(w), 984(w),

925(w), 858(w), 746(s), 701(s)  $\text{cm}^{-1}$ .