# A one-pot parallel reductive amination of aldehydes with heteroaromatic amines 

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## Analytical data for the selected compounds

## $N$-(4-fluorobenzyl)-5-methylisoxazol-3-amine (Entry 1, in Table 1)



Yield: $143 \mathrm{mg}, 69 \%$; yellowish solid, $\mathrm{mp} 78-80^{\circ} \mathrm{C}$. IR $(\mathrm{KBr}): v\left(\mathrm{~cm}^{-1}\right) 3270,3110,3086,3049$, 2928, 2862, 1632, 1573, 1506, 1217, 1155; ${ }^{\mathbf{1}} \mathbf{H}$ NMR ( 500 MHz , DMSO-d $\mathrm{d}_{6}$ ): $\delta(\mathrm{ppm}) 2.20(\mathrm{~s}$, $\left.3 \mathrm{H}, \mathrm{CH}_{3}\right), 4.20\left(\mathrm{~d}, \mathrm{~J}=6.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 5.65(\mathrm{~d}, \mathrm{~J}=0.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Het}), 6.53(\mathrm{t}, \mathrm{J}=5.2 \mathrm{~Hz}, 1 \mathrm{H}$, NH ), 7.13 (t, J = $8.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{Ar}), 7.35$ (m, 2H, Ar); ${ }^{\mathbf{1 3}} \mathbf{C}$ NMR ( 125 MHz, DMSO-d ${ }_{6}$ ): $\delta(\mathrm{ppm})$ 12.1, 45.9, 93.7, 114.9 (d, J = 21 Hz ), 129.4 (d, J = 8 Hz ), 136.2 (d, J = 3 Hz ), 161.0 (d, J = 245 Hz ), 164.4, 167.6; MS (APCI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{11} \mathrm{H}_{12} \mathrm{FN}_{2} \mathrm{O}$ : 207.1; found: 207.0; Anal. Calcd.: C, 64.07; H, 5.38; N, 13.58; found C, 63.80; H, 5.10; N, 13.70.

## $N$-(2-chlorobenzyl)-5-methylisoxazol-3-amine (Entry 2, in Table 1)



Yield: $51 \mathrm{mg}, 23 \%$; yellow solid, $\mathrm{mp} 105-107^{\circ} \mathrm{C}$; IR (KBr): $v\left(\mathrm{~cm}^{-1}\right) 3255,3187,3072,2929$, 2871, 1627, 1560, 1520, 1356, 1050; ${ }^{1} \mathbf{H}$ NMR ( 500 MHz , DMSO-d ${ }^{2}$ ): $\delta(\mathrm{ppm}) 2.21$ (s, 3H, $\mathrm{CH}_{3}$ ), 4.30 (d, J = $6.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}$ ), 5.69 ( $\mathrm{s}, 1 \mathrm{H}, \mathrm{Het}$ ), 6.59 (t, J = $6.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}$ ), 7.29 (m, 2H, Ar), 7.42 (m, 2H, Ar); ${ }^{13}$ C NMR ( 125 MHz, DMSO-d ${ }^{2}$ ): $\delta(\mathrm{ppm}) 12.1,44.3,93.6,127.1,128.6$, $129.0,129.2,132.3,136.9,164.2,167.8 ; \mathbf{M S}$ (APCI) $m / z[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{11} \mathrm{H}_{12} \mathrm{ClN}_{2} \mathrm{O}$ : 223.1; found: 222.8; Anal. Calcd.: C, 59.33; H, 4.98; N, 12.58; found C, 59.10; H, 5.15; N, 12.45 .
$N$-(2,3-dimethoxybenzyl)benzo[d]oxazol-2-amine (Entry 3, in Table 1)


Yield: $241 \mathrm{mg}, 84 \%$; yellow solid, $\mathrm{mp} 79-81^{\circ} \mathrm{C}$; $\mathbf{I R}(\mathrm{KBr}): v\left(\mathrm{~cm}^{-1}\right) 3170,3053,3000,2961$, 2905, 2832, 1680, 1586, 1480, 1457, 1266, 1243, 1063; ${ }^{1}$ H NMR ( 500 MHz, DMSO-d ${ }_{6}$ ): $\delta$ (ppm) 3.78(s, 3H, CH3), $3.80\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 4.53\left(\mathrm{~d}, \mathrm{~J}=5.9 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 6.92-6.99(\mathrm{~m}, 3 \mathrm{H}$, Ar), 7.02 (t, J = 7.9 Hz, 1H, Ar), 7.1 (t, J = $7.3 \mathrm{~Hz}, 1 \mathrm{H}, ~ A r), 7.23(\mathrm{~d}, \mathrm{~J}=7.7 \mathrm{~Hz}, 1 \mathrm{H}, ~ A r), 7.33$ (d, $\mathrm{J}=7.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 8.34(\mathrm{t}, \mathrm{J}=5.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}) ;{ }^{13} \mathbf{C}$ NMR ( 125 MHz, DMSO-d ${ }^{2}$ ): $\delta(\mathrm{ppm})$ 40.7, 55.8, 60.2, 108.6, 112.0, 115.6, 120.0, 120.2, 123.7, 123.9, 132.3, 143.3, 146.4, 148.2, 152.4, 162.5; MS (APCI) m/z [M+H] ${ }^{+}$calculated for $\mathrm{C}_{16} \mathrm{H}_{17} \mathrm{~N}_{2} \mathrm{O}_{3}$ : 285.1; found: 285.0; Anal. Calcd.: C, 67.59 ; H, 5.67 ; N, 9.85 ; found C, $67.20 ; \mathrm{H}, 5.90$; N, 9.55 .
$N$-(3,4,5-trimethoxybenzyl)benzo[d]oxazol-2-amine (Entry 4, in Table 1)


Yield: $100 \mathrm{mg}, 32 \%$; whitish solid, mp $112-114^{\circ} \mathrm{C}$; IR (KBr): $v\left(\mathrm{~cm}^{-1}\right) 3335,3250,3178,3063$, 2954, 2937, 1677, 1648, 1586, 1457, 1415, 1247, 1128; ${ }^{1}$ H NMR ( 500 MHz, DMSO-d ${ }_{6}$ ): $\delta$ (ppm) 3.63 (s, $3 \mathrm{H}, \mathrm{CH}_{3}$ ), 3.75 ( $\mathrm{s}, 6 \mathrm{H}, 2 \mathrm{CH}_{3}$ ), $4.46\left(\mathrm{~d}, \mathrm{~J}=6.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 6.72$ (s, 2H, Ar), 6.98 (t, J = $7.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 7.10(\mathrm{t}, \mathrm{J}=7.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 7.24(\mathrm{~d}, \mathrm{~J}=7.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 7.34$ (d, J = $7.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 7.41$ (t, J = $5.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}$ ); ${ }^{13} \mathrm{C}$ NMR ( 125 MHz , DMSO-d $\mathrm{d}_{6}: \delta(\mathrm{ppm}) 46.1$, 55.9, 60.1, 104.7, 108.7, 115.6, 120.3, 123.7, 134.7, 136.6, 143.2, 148.2, 152.9, 162.5; MS (APCI) $m / z[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{17} \mathrm{H}_{19} \mathrm{~N}_{2} \mathrm{O}_{4}$ : 315.2; found: 315.0; Anal. Calcd.: C, 64.96; H , 5.77; N, 8.91; found C, 65.05; H, 5.90; N, 8.80.
$N$-benzyl-3-methyl-1,2,4-oxadiazol-5-amine (Entry 5, in Table 1)


Yield: 113 mg , $60 \%$; yellowish solid, $\mathrm{mp} 108-110^{\circ} \mathrm{C}$; IR (KBr): v $\left(\mathrm{cm}^{-1}\right) 3293,3178,3069$, 2930, 2882, 1661, 1414, 1355, 1302, 1010; ${ }^{1} \mathbf{H}$ NMR ( 500 MHz, DMSO-d ${ }_{6}$ ): $\delta(\mathrm{ppm}) 2.08$ (s, $3 \mathrm{H}, \mathrm{CH}_{3}$ ), $4.44\left(\mathrm{~d}, \mathrm{~J}=6.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 7.22-7.28(\mathrm{~m}, 1 \mathrm{H}, \mathrm{Ar}), 7.29-7.38(\mathrm{~m}, 4 \mathrm{H}, \mathrm{Ar}), 8.75$ (t, J = $5.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}$ ); ${ }^{13} \mathbf{C}$ NMR ( 125 MHz, DMSO-d $)_{6}$ : $\delta(\mathrm{ppm}) 11.5,46.4,127.2,127.3$, 128.5, 138.7, 167.0, 171.4; MS (APCI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{10} \mathrm{H}_{12} \mathrm{~N}_{3} \mathrm{O}: 190.1$; found: 190.0; Anal. Calcd.: C, 63.48; H, 5.86; N, 22.21; found C, 63.20; H, 6.05; N, 22.10.

## $N$-(4-fluorobenzyl)-3-methyl-1,2,4-oxadiazol-5-amine (Entry 6, in Table 1)



Yield: $89 \mathrm{mg}, 43 \%$; yellowish solid, $\mathrm{mp} 82-84^{\circ} \mathrm{C}$; IR (KBr): $v\left(\mathrm{~cm}^{-1}\right) 3299,3201,3161,3072$, 2964, 2868, 1661, 1507, 1415, 1326, 1210, 1007; ${ }^{1} \mathbf{H}$ NMR ( 500 MHz, DMSO-d ${ }_{6}$ ): $\delta(\mathrm{ppm}) 2.08$ $\left(\mathrm{s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 4.40\left(\mathrm{~d}, \mathrm{~J}=6.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 7.16(\mathrm{t}, \mathrm{J}=8.8 \mathrm{H}, 2 \mathrm{H}, \mathrm{Ar}), 7.35(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ar}), 8.70$ $(\mathrm{m}, 1 \mathrm{H}, \mathrm{NH}) ;{ }^{13} \mathbf{C}$ NMR ( 125 MHz, DMSO-d $\mathrm{d}_{6}$ ): $\delta(\mathrm{ppm}) 11.5,45.7,115.2(\mathrm{~d}, \mathrm{~J}=21 \mathrm{~Hz}), 129.3$ (d, J = 8 Hz ), $134.8(\mathrm{~d}, \mathrm{~J}=3 \mathrm{~Hz}), 161.0(\mathrm{~d}, \mathrm{~J}=244 \mathrm{~Hz}), 166.9,171.3$; MS (APCI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{H}]^{+}$ calculated for $\mathrm{C}_{10} \mathrm{H}_{11} \mathrm{FN}_{3} \mathrm{O}$ : 208.1; found: 207.8; Anal. Calcd.: C, 57.97; H, 4.86; N, 20.28; found C, $57.80 ; \mathrm{H}, 5.00 ; \mathrm{N}, 20.44$.

## $N$-(2,3-dimethoxybenzyl)-[1,2,4]triazolo[4,3-a]pyridin-3-amine (Entry 11, in Table 1)



Yield: $57 \mathrm{mg}, 20 \%$; white solid, mp $182-184^{\circ} \mathrm{C}$; IR (KBr): $v\left(\mathrm{~cm}^{-1}\right) 3431,3181,3053,3003$, 2954, 2924, 2832, 1635, 1598, 1592, 1486, 1230, 1088, 1003; ${ }^{1} \mathbf{H}$ NMR ( 500 MHz, DMSO-d $_{6}$ ): $\delta(\mathrm{ppm}) 3.79\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.81\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 4.60\left(\mathrm{~d}, \mathrm{~J}=5.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 6.73(\mathrm{t}, \mathrm{J}=6.5$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{NH}$ ), 7.02 (m, 5H, Ar), 7.43 (d, J = $9.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}$ ), 8.16 (d, J = $7.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}) ;{ }^{13} \mathrm{C}$ NMR ( 125 MHz, DMSO-d ${ }_{6}$ ): $\delta(\mathrm{ppm}) 41.3,55.8,60.2,111.4,111.9,115.5,120.5,122.4,123.8$, $125.5,132.9,146.2,146.6,148.7,152.4 ;$ MS (APCI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{15} \mathrm{H}_{17} \mathrm{~N}_{4} \mathrm{O}_{2}$ : 285.1; found: 285.1; Anal. Calcd.: C, 63.37; H, 5.67; N, 19.71; found C, 63.44; H, 5.83; N, 19.83.

## $N$-benzyl-5-methylthiazol-2-amine (Entry 13, in Table 1)



Yield: $161 \mathrm{mg}, 79 \%$; yellow solid, $\mathrm{mp} 98-100^{\circ} \mathrm{C}$; IR (KBr): v $\left(\mathrm{cm}^{-1}\right) 3165,3063,2967,2915$, 2855, 1569, 1536, 1510, 1467, 1283, 1145; ${ }^{1} \mathbf{H}$ NMR ( 500 MHz , DMSO-d $\mathrm{d}_{6}$ ): $\delta(\mathrm{ppm}) 2.18$ ( s , $\left.3 \mathrm{H}, \mathrm{CH}_{3}\right), 4.38\left(\mathrm{~d}, \mathrm{~J}=4.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 6.65(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}), 7.23(\mathrm{~m}, 1 \mathrm{H}, \mathrm{Ar}), 7.31(\mathrm{~m}, 4 \mathrm{H}, \mathrm{Ar})$, 7.81 (m, 1H, NH); ${ }^{13}$ C NMR (125 MHz, DMSO-d ${ }_{6}$ ): $\delta(\mathrm{ppm}) 11.7,47.5,119.5,126.9,127.4$, 128.3, 135.5, 139.6, 167.6; MS (APCI) $m / z[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{11} \mathrm{H}_{13} \mathrm{~N}_{2} \mathrm{~S}: 205.1$; found: 205.0; Anal. Calcd.: C, 64.67; H, 5.92; N, 13.71; found C, 64.55; H, 6.06; N, 13.85.
$N$-((2,3-dihydrobenzo[b][1,4]dioxin-6-yl)methyl)-6-(methylsulfonyl)benzo[d]thiazol-2amine (Entry 15, in Table 1)


Yield: $177 \mathrm{mg}, 47 \%$; white solid, mp $282-284^{\circ} \mathrm{C}$; IR (KBr): v $\left(\mathrm{cm}^{-1}\right) 3217,3194,3082,3030$, 2941, 2895, 1612, 1572, 1510, 1303, 1280, 1141; ${ }^{1} \mathbf{H}$ NMR ( 500 MHz, DMSO-d ${ }_{6}$ ): $\delta(\mathrm{ppm}) 3.17$ ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{CH}_{3}$ ), $4.20\left(\mathrm{~s}, 4 \mathrm{H}, 2 \mathrm{CH}_{2} \mathrm{O}\right), 4.50\left(\mathrm{~d}, \mathrm{~J}=4.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 6.82(\mathrm{~s}, 2 \mathrm{H}, \mathrm{Ar}), 6.87(\mathrm{~s}, 1 \mathrm{H}$, Ar), 7.53 (d, J = $8.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}$ ), 7.72 (d, J = $8.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}$ ), $8.28(\mathrm{~s}, 1 \mathrm{H}, \mathrm{Ar}), 8.90(\mathrm{~m}, 1 \mathrm{H}$, NH ); ${ }^{13}$ C NMR ( 125 MHz, DMSO- $_{6}$ ): $\delta(\mathrm{ppm}) 44.3,46.9,64.1,64.2,116.3,117.1,117.8$, $120.5,120.9,125.0,131.1,131.4,132.6,142.7,143.3,156.5,169.6$; MS (APCI) $m / z[\mathrm{M}+\mathrm{H}]^{+}$ calculated for $\mathrm{C}_{17} \mathrm{H}_{17} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{~S}_{2}$ : 377.1; found: 377.0; Anal. Calcd.: C, 54.24; H, 4.28; N, 7.44; found C, 54.10; H, 4.40; N, 7.60.

## $N$-(2-chlorobenzyl)-1,3,4-thiadiazol-2-amine (Entry 17, in Table 1)



Yield: $153 \mathrm{mg}, 68 \%$; yellow solid, $\mathrm{Mp} 87-89^{\circ} \mathrm{C}$; IR (KBr): $v\left(\mathrm{~cm}^{-1}\right) 3188,3065,2987,2790$, 1556, 1497, 1437, 1040; ${ }^{1}$ H NMR ( 500 MHz , DMSO-d ${ }_{6}$ ): $\delta(\mathrm{ppm}) 4.61$ (m, 2H, CH2 $), 7.30$ (m, $2 \mathrm{H}, \mathrm{Ar}), 7.44$ (m, 2H, Ar), 8.32 (br. s, 1H, NH), 8.66 (s, 1H, Het); ${ }^{13}$ C NMR ( 125 MHz , DMSO$\mathrm{d}_{6}$ ): $\delta(\mathrm{ppm}) 46.1,127.3,129.0,129.3,129.4,132.6,135.8,142.9,168.2$; MS (APCI) $\mathrm{m} / \mathrm{z}$ $[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{9} \mathrm{H}_{9} \mathrm{ClN}_{3} \mathrm{~S}$ : 226.0; found: 225.8; Anal. Calcd.: C, 47.90 ; H, 3.57; N, 18.62; found C, 47.83; H, 3.65; N, 18.70.
$N$-((2,3-dihydrobenzo[b][1,4]dioxin-6-yl)methyl)-1,3,4-thiadiazol-2-amine (Entry 18, in Table 1)


Yield: $114 \mathrm{mg}, 46 \%$; white solid, $\mathrm{mp} 117-119^{\circ} \mathrm{C}$; IR (KBr): $v\left(\mathrm{~cm}^{-1}\right)$ 3204, 3086, 2997, 2947, 2924, 2882, 1590, 1566, 1506, 1441, 1319, 1283, 1260, 1072, 1050; ${ }^{1} \mathbf{H}$ NMR ( 500 MHz , DMSO-d $\mathrm{d}_{6}$ ) $\delta(\mathrm{ppm}) 4.20\left(\mathrm{~s}, 4 \mathrm{H}, 2 \mathrm{CH}_{2} \mathrm{O}\right), 4.35\left(\mathrm{~d}, \mathrm{~J}=5.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 6.80(\mathrm{~s}, 2 \mathrm{H}, \mathrm{Ar}), 6.84$ ( $\mathrm{s}, 1 \mathrm{H}, \mathrm{Ar}$ ), 8.19 (t, J = $4.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}$ ), 8.61 ( $\mathrm{s}, 1 \mathrm{H}, \mathrm{Het}$ ); ${ }^{13} \mathrm{C}$ NMR ( 125 MHz, DMSO- $\mathrm{d}_{6}$ ): $\delta$ (ppm) 47.9, 64.1, 64.2, 116.4, 116.9, 120.6, 131.7, 142.5, 142.6, 143.2, 168.5; MS (APCI) $m / z$
$[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{11} \mathrm{H}_{12} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{~S}: 250.1$; found: 249.8; Anal. Calcd.: C, 53.00 ; H, 4.45; N, 16.86; found C, 52.85 ; H, 4.65; N, 16.74.

## $N$-(2,3-dimethoxybenzyl)-3-methylpyridin-2-amine (Entry 19, in Table 1)



Yield: $83 \mathrm{mg}, 32 \%$; white solid, mp 84-86 ${ }^{\circ} \mathrm{C}$; IR (KBr): $v\left(\mathrm{~cm}^{-1}\right)$ 3417, 3008, 2963, 2936, 2899, 2836, 1598, 1507, 1480, 1275, 1060; ${ }^{1} \mathbf{H}$ NMR ( 500 MHz, DMSO-d 6 ): $\delta$ (ppm) 2.11 (s, 3H, $\left.\mathrm{CH}_{3}\right), 3.79\left(\mathrm{~s}, 6 \mathrm{H}, 2 \mathrm{OCH}_{3}\right), 4.60\left(\mathrm{~d}, \mathrm{~J}=5.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 6.24(\mathrm{t}, \mathrm{J}=5.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}), 6.43(\mathrm{~m}$, $1 \mathrm{H}, \mathrm{Py}), 6.81(\mathrm{~d}, \mathrm{~J}=7.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 6.88(\mathrm{~d}, \mathrm{~J}=7.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 6.94(\mathrm{t}, \mathrm{J}=7.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar})$, 7.22 (d, J = 6.4 Hz, Py), 7.80 (d, J = $3.8 \mathrm{~Hz}, 1 \mathrm{H}$, Py); ${ }^{13}$ C NMR ( 125 MHz, DMSO-d ): $\delta(\mathrm{ppm}$ ) 17.0, 38.9, 55.7, 59.9, 111.1, 111.8, 116.6, 119.7, 123.6, 134.6, 136.4, 144.9, 146.3, 152.2, 156.8; MS (APCI) $m / z[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{15} \mathrm{H}_{19} \mathrm{~N}_{2} \mathrm{O}_{2}$ : 259.1; found: 259.0; Anal. Calcd.: C, 69.74; H, 7.02; N, 10.84; found C, 69.53; H, 7.13; N, 10.67.

4-((dimethylamino)methyl)- N -(3,4,5-trimethoxybenzyl)pyridin-2-amine (Entry 21, in Table 1)


Yield: 315 mg , $95 \%$; yellowish solid, mp $102-104^{\circ} \mathrm{C}$; IR (KBr): v $\left(\mathrm{cm}^{-1}\right) 3411,3217,3076$, 2997, 2963, 2944, 2855, 2813, 2776, 1599, 1576, 1503, 1454, 1250, 1158; ${ }^{\mathbf{1}} \mathbf{H}$ NMR ( 500 MHz , DMSO-d $\mathrm{d}_{6}$ : $\delta(\mathrm{ppm}) 2.11\left(\mathrm{~s}, 6 \mathrm{H}, 2 \mathrm{NCH}_{3}\right), 3.63\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 3073\left(\mathrm{~s}, 6 \mathrm{H}, 2 \mathrm{CH}_{3}\right), 4.42(\mathrm{~d}, \mathrm{~J}=5.5$ $\mathrm{Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}$ ), 6.43 (d, J = $5.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Py}$ ), 6.50 ( $\mathrm{s}, 1 \mathrm{H}, \mathrm{Py}$ ), 6.67 (s, 2H, Ar), $6.90(\mathrm{t}, \mathrm{J}=4.8 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{NH}), 7.90\left(\mathrm{~d}, \mathrm{~J}=5.2 \mathrm{~Hz}, 1 \mathrm{H}\right.$, Py); ${ }^{13} \mathbf{C}$ NMR ( 125 MHz, DMSO-d $_{6}$ ): $\delta(\mathrm{ppm}) 44.7,45.1$, $55.8,60.0,62.7,104.6,107.7,112.4,136.2,136.4,147.4,148.4,152.8,159.1 ;$ MS (APCI) $\mathrm{m} / \mathrm{z}$ $[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{18} \mathrm{H}_{26} \mathrm{~N}_{3} \mathrm{O}_{3}$ : 332.2; found: 332.0; Anal. Calcd.: C, 65.23; H, 7.60; N, 12.68 ; found $\mathrm{C}, 65.11 ; \mathrm{H}, 7.75$; N, 12.60 .

## $N$-benzyl-4-(4-methyl-4H-1,2,4-triazol-3-yl)pyridin-2-amine (Entry 23, in Table 1)



Yield: $111 \mathrm{mg}, 42 \%$; yellowish solid, $\mathrm{mp} 146-148^{\circ} \mathrm{C}$; IR (KBr): v $\left(\mathrm{cm}^{-1}\right) 3273,3181,3131$, 3105, 3065, 3036, 2977, 2918, 1615, 1549, 1497, 1194; ${ }^{1} \mathbf{H}$ NMR ( 500 MHz , DMSO-d ${ }_{6}$ ): $\delta$ (ppm) 3.72 (s, 3H, NCH3 ), 4.53 (d, J = $5.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}$ ), $6.84(\mathrm{~d}, \mathrm{~J}=5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Py}), 6.88$ ( s , $1 \mathrm{H}, \mathrm{Py}$ ), 7.22 (t, J = $7.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}$ ), 7.31 (m, 2H, Ar), 7.35 (m, 3H, NH + Ar), 8.11 (d, J = 5.2 $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{Py}), 8.58$ (s, 1H, Het); ${ }^{13}$ C NMR ( 125 MHz , DMSO-d $\mathrm{d}_{6}$ ): $\delta(\mathrm{ppm}) 32.2,44.3,106.9$, $110.3,126.7,127.3,128.3,135.0,140.4,146.7,148.5,151.9,159.1 ; \mathbf{M S}$ (APCI) $m / z[\mathrm{M}+\mathrm{H}]^{+}$ calculated for $\mathrm{C}_{15} \mathrm{H}_{16} \mathrm{~N}_{5}$ : 266.1; found: 266.1; Anal. Calcd.: C, 67.90 ; H, 5.70; N, 26.40; found C, 67.75; H, 5.85; N, 26.30.


Yield: $75 \mathrm{mg}, 25 \%$; yellowish solid, $\mathrm{mp} 186-188^{\circ} \mathrm{C}$; IR (KBr): $v\left(\mathrm{~cm}^{-1}\right) 3293,3250,3095,3046$, 2941, 2915, 1618, 1553, 1500, 1286, 1197, 1040; ${ }^{1}$ H NMR ( 500 MHz, DMSO-d ${ }_{6}$ ): $\delta$ (ppm) 3.75 (s, 3H, NCH ${ }_{3}$ ), $4.60\left(\mathrm{~d}, \mathrm{~J}=5.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 6.87(\mathrm{~d}, \mathrm{~J}=5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Py}), 6.96(\mathrm{~s}, 1 \mathrm{H}$, Py), 7.28 (m, 2H, Ar), 7.39 (m, 2H, Ar), 7.44 (d, J = $7.7 \mathrm{~Hz}, 1 \mathrm{H}, \operatorname{Py}$ ), 8.09 (d, J = $5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}$ ), 8.59 (s, $1 \mathrm{H}, \mathrm{Het}) ;{ }^{13} \mathrm{C}$ NMR ( 125 MHz, DMSO-d $\mathrm{d}_{6}$ ): $\delta$ (ppm) 32.3, 42.1, 107.2, 110.6, 127.2, 128.5, 128.8, 129.2, 132.3, 135.1, 137.4, 146.8, 148.4, 151.8, 158.8; MS (APCI) $m / z[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{15} \mathrm{H}_{15} \mathrm{ClN}_{5}$ : 300.1; found: 300.0; Anal. Calcd.: C, 60.10 ; H, 4.71; N, 23.36; found C, 60.05 ; H, 4.85; N, 23.23.

## (3-chloro-6-(4-fluorobenzylamino)pyridin-2-yl)methanol (Entry 27, in Table 1)



Yield: $198 \mathrm{mg}, 74 \%$; yellow solid, $\mathrm{mp} 58-60^{\circ} \mathrm{C}$; $\mathbf{I R}(\mathrm{KBr}): v\left(\mathrm{~cm}^{-1}\right) 3332,3046,2918,2866$, 1595, 1507, 1408, 1220, 1076; ${ }^{1}$ H NMR ( 500 MHz , DMSO-d $)_{6}$ : $\delta(\mathrm{ppm}) 4.43\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 4.48$ (d, J = 5.6, 2H, CH 2 ), 4.77 (br. s, 1H, OH), 6.44 (d, J = $8.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}$ ), 7.12 (t, J = $8.8 \mathrm{~Hz}, 2 \mathrm{H}$, Ar), $7.30(\mathrm{t}, \mathrm{J}=5.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}), 7.38(\mathrm{~m}, 3 \mathrm{H}, \mathrm{Ar}) ;{ }^{13} \mathbf{C}$ NMR ( 125 MHz, DMSO-d $\mathrm{d}_{6}$ ): $\delta(\mathrm{ppm})$ 43.7, 61.7, 108.3, 115.0 ( $\mathrm{d}, \mathrm{J}=20 \mathrm{~Hz}$ ), 115.2, 129.3 (d, J = 9 Hz ), $136.5(\mathrm{~d}, \mathrm{~J}=2.5 \mathrm{~Hz}), 137.9$, 138.1, 153.4, 156.6, 161.2 (d, J = 243 Hz ); MS (APCI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{13} \mathrm{H}_{13} \mathrm{ClFN}_{2} \mathrm{O}: 267.1$; found: 267.2; Anal. Calcd.: C, 58.55 ; H, 4.54; N, 10.50; found C, 58.45; H, 4.66; N, 10.34.

## $N$-(3,4,5-trimethoxybenzyl)pyridin-3-amine (Entry 30, in Table 1)



Yield: $230 \mathrm{mg}, 84 \%$; brownish solid, $\mathrm{mp} 91-93^{\circ} \mathrm{C}$; $\mathbf{I R}(\mathrm{KBr}): v\left(\mathrm{~cm}^{-1}\right) 3257,3112,3056,3000$, 2931, 2832, 2826, 1595, 1540, 1507, 1467, 1418, 1422, 1337, 1233, 1130, 1010; ${ }^{1} \mathbf{H}$ NMR (500 MHz, DMSO-d 6 ): $\delta(\mathrm{ppm}) 3.65\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 3.74\left(\mathrm{~s}, 6 \mathrm{H}, 2 \mathrm{CH}_{3}\right), 4.23\left(\mathrm{~d}, \mathrm{~J}=5.5 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)$, 6.46 (t, J = $5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}$ ), 6.72 (s, 2H, Ar), 6.93 (m, 1H, Py), 7.04 (m, 1H, Py), 7.78 (s, 1H, Py), 8.06 (s, 1H, Py); ${ }^{13}$ C NMR ( 125 MHz , DMSO-d 6 ): $\delta$ (ppm) 46.6, 55.8, 60.0, 104.6, 117.9, 123.6, 135.4, 135.7, 136.4, 137.2, 144.8, 153.0; MS (APCI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{15} \mathrm{H}_{19} \mathrm{~N}_{2} \mathrm{O}_{3}$ : 275.1; found: 275.0; Anal. Calcd.: C, 65.68 ; H, 6.61; N, 10.21; found C, 65.55 ; H, 6.75; N, 10.14.
$N$-((2,3-dihydrobenzo[b][1,4]dioxin-6-yl)methyl)-2-methylpyridin-3-amine (Entry 31, in Table 1)


Yield: $92 \mathrm{mg}, 36 \%$; yellowish solid, $\mathrm{mp} 103-105^{\circ} \mathrm{C}$; IR (KBr): $v\left(\mathrm{~cm}^{-1}\right) 3434,3030,2993,2938$, 2871, 1579, 1506, 1467, 1302, 1277, 1060; ${ }^{1} \mathbf{H}$ NMR ( $500 \mathrm{MHz}, ~ D M S O-\mathrm{d}_{6}$ ): $\delta(\mathrm{ppm}) 2.35$ (s, $3 \mathrm{H}, \mathrm{CH}_{3}$ ), 4.18 ( $\mathrm{s}, 4 \mathrm{H}, 2 \mathrm{CH}_{2}$ ), 4.22 (d, J = $5.9 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}$ ), 5.85 (d, J = $\left.5.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}\right), 6.64$ (d, J = $8.1 \mathrm{~Hz}, 1 \mathrm{H}$, Py), 6.80 (m, 3H, Ar), $6.88\left(\mathrm{~m}, 1 \mathrm{H}\right.$, Py), $7.63\left(\mathrm{~d}, \mathrm{~J}=4.6 \mathrm{~Hz}, 1 \mathrm{H}\right.$, Py); ${ }^{13} \mathrm{C}$ NMR ( 125 MHz, DMSO-d6): $\delta(\mathrm{ppm}) 21.0,45.3,64.0,64.1,115.3,115.6,116.9,119.8,121.7$, $132.8,135.6,142.0,142.2,143.3,143.7$; MS (APCI) $m / z[M+H]^{+}$calculated for $\mathrm{C}_{15} \mathrm{H}_{17} \mathrm{~N}_{2} \mathrm{O}_{2}$ : 257.1; found: 257.0; Anal. Calcd.: C, 70.29; H, 6.29; N, 10.93; found C, 70.12; H, 6.45; N, 10.86.

## Methyl 5-(benzylamino)nicotinate (Entry 33, in Table 1)



Yield: $177 \mathrm{mg}, 73 \%$; whitish solid, mp $128-130^{\circ} \mathrm{C}$; IR (KBr): $v\left(\mathrm{~cm}^{-1}\right) 3253,3049,3007,2951$, 2860, 1717, 1597, 1418, 1315, 1224, 1099; ${ }^{1} \mathbf{H}$ NMR ( 500 MHz , DMSO-d $\mathrm{d}_{6}$ : $\delta(\mathrm{ppm}) 3.80$ (s, $\left.3 \mathrm{H}, \mathrm{CH}_{3}\right), 4.35\left(\mathrm{~d}, \mathrm{~J}=5.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 6.89(\mathrm{t}, \mathrm{J}=5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}), 7.23(\mathrm{t}, \mathrm{J}=7.1 \mathrm{~Hz}, 1 \mathrm{H}$, Ar), $7.26-7.40(\mathrm{~m}, 5 \mathrm{H}, 4 \mathrm{Ar}+1 \mathrm{Py}), 8.22$ (s, 1 H, Py), $8.30\left(\mathrm{~s}, 1 \mathrm{H}\right.$, Py); ${ }^{13}$ C NMR ( 125 MHz , DMSO-d $\mathrm{d}_{6}$ : $\delta(\mathrm{ppm}) 46.0,52.2,117.6,125.6,127.0,127.3,128.5,137.3,139.1,139.3,144.6$, 165.9; MS (APCI) $m / z[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{14} \mathrm{H}_{15} \mathrm{~N}_{2} \mathrm{O}_{2}$ : 242.1 ; found: 243.0; Anal. Calcd.: C, 69.41 ; H, 5.82; N, 11.56; found C, 69.33; H, 5.96; N, 11.50.

## N -(2,3-dimethoxybenzyl)-6-(methylsulfonyl)pyridin-3-amine (Entry 35, in Table 1)



Yield: $161 \mathrm{mg}, 50 \%$; white solid, $\mathrm{mp} 142-144^{\circ} \mathrm{C}$; IR (KBr): $v\left(\mathrm{~cm}^{-1}\right) 3243,3078,3003,2934$, 2835, 1579, 1477, 1302, 1161, 1125; ${ }^{1} \mathbf{H}$ NMR ( 500 MHz, DMSO-d ${ }_{6}$ ): $\delta$ (ppm) 3.09 (s, 3H, $\mathrm{SO}_{2} \mathrm{CH}_{3}$ ), 3.78 (s, $3 \mathrm{H}, \mathrm{OCH}_{3}$ ), $3.80\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right.$ ), $4.36\left(\mathrm{~d}, \mathrm{~J}=5.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 6.86(\mathrm{~d}, \mathrm{~J}=6.9$ Hz, 1H, Py), 7.01 (m, 3H, Ar), 7.35 (t, J = 5.4, 1H, NH), 7.69 (d, J = 8.6 Hz, Py), 8.09 (d, J = 2.2 $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{Py}$ ); ${ }^{13}$ C NMR ( 125 MHz, DMSO-d 6 ): $\delta$ (ppm) 40.7, 40.9, 55.8, 60.4, 112.2, 116.5, $120.2,122.6,124.1,131.5,135.2,143.6,146.7,147.6,152.5$; MS (APCI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{15} \mathrm{H}_{19} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{~S}$ : 323.1; found: 323.1; Anal. Calcd.: C, 55.89 ; H, 5.63 ; N, 8.69; found C, 55.80 ; H, 5.70; N, 8.59.

## $N$-(4-fluorobenzyl)-1,3-dimethyl-1H-pyrazolo[3,4-b]pyridin-5-amine (Entry 40, in Table 1)



Yield: $59 \mathrm{mg}, 22 \%$; white solid, $\mathrm{mp} 96-98^{\circ} \mathrm{C}$; $\mathbf{I R}(\mathrm{KBr}): v\left(\mathrm{~cm}^{-1}\right) 3290,3046,2928,2839,1602$, 1507, 1477, 1224, 1151; ${ }^{1} \mathbf{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{DMSO}-\mathrm{d}_{6}$ ): $\delta(\mathrm{ppm}) 2.64$ (s, $3 \mathrm{H}, \mathrm{CH}_{3}$ ), 3.86 ( 3 H , $\left.\mathrm{NCH}_{3}\right), 4.29\left(\mathrm{~d}, \mathrm{~J}=5.9 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 6.25(\mathrm{t}, \mathrm{J}=5.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}), 7.04(\mathrm{~d}, \mathrm{~J}=2.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Het})$, $7.15(\mathrm{t}, \mathrm{J}=8.9 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{Ar}), 7.44(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ar}), 8.16(\mathrm{~d}, \mathrm{~J}=2.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Het}) ;{ }^{13} \mathbf{C}$ NMR ( 125 MHz, DMSO-d $\mathrm{d}_{6}$ : $\delta(\mathrm{ppm}) 12.1,33.2,46.5,106.3,114.4,115.1(\mathrm{~d}, \mathrm{~J}=21 \mathrm{~Hz}), 129.4(\mathrm{~d}, \mathrm{~J}=7.5$ $\mathrm{Hz}), 135.9(\mathrm{~d}, \mathrm{~J}=3.8 \mathrm{~Hz}), 137.2,139.7,140.3,144.3,145.8,161.3(\mathrm{~d}, \mathrm{~J}=239 \mathrm{~Hz}) ; \mathbf{M S}$ (APCI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{15} \mathrm{H}_{16} \mathrm{FN} 4$ : 271.1; found: 271.0; Anal. Calcd.: C, 66.65; H, 5.59; N, 20.73; found C, 66.60; H, 5.73; N, 20.55.

## LC-MS spectra of the crude mixtures.



Figure S1. Entry 1, in Table 1: peak was assigned to the product (rt 1.15 min ).


Figure S2. Entry 2, in Table 1: peaks were assigned to the starting amine (rt 0.3 min ), the aldehyde ( rt 0.99 min ), the tertiary amine $(\mathrm{rt} 1.02 \mathrm{~min})$, the intermediate imine ( rt 1.16 min ), and the product ( rt 1.23 min ).


Figure S3. Entry 3, in Table 1: peaks were assigned to the starting amine (rt 0.64 min ) and the product (rt 1.29 min ).


Figure S4. Entry 4, in Table 1: peaks were assigned to the starting amine (rt 0.65 min ), the aldehyde (rt 1.08 min ) and the product ( rt 1.23 min ).


Figure S5. Entry 5, in Table 1: peak was assigned to the product (rt 1.02 min ).


Figure S6. Entry 6, in Table 1: peak was assigned to the product (rt 1.06 min ).


Figure S7. Entry 7, in Table 1: peaks were assigned to the starting amine (rt 0.66 min ) and the product (rt 1.00 min ).


Figure S8. Entry 8, in Table 1: peak was assigned to the product (rt 0.65 min$)$.


Figure S9. Entry 9, in Table 1: peaks were assigned to the starting amine (rt 0.91 min ) and the product (rt 1.17 min ).


Figure S10. Entry 10, in Table 1: peaks were assigned to the starting amine ( rt 0.89 min ) and the product (rt 1.12 min ).


Figure S11. Entry 11, in Table 1: peak was assigned to the product (rt 0.87 min ).


Figure S12. Entry 12, in Table 1: peaks were assigned to the product (rt 0.86 min ), the aldehyde (rt 0.99 min ), and the intermediate imine ( rt 1.14 min ).


Figure S13. Entry 13, in Table 1: peak was assigned to the product (rt 0.86 min$)$.


Figure S14. Entry 14, in Table 1: peaks were assigned to the product (rt 0.91 min ) and the aldehyde (rt 1.08 min ).


Figure S15. Entry 15, in Table 1: peaks were assigned to the starting amine (rt 0.73 min ), the aldehyde ( 1.05 min ), and the product ( rt 1.2 min ).


Figure S 16. Entry 16, in Table 1: peaks were assigned to the starting amine (rt 0.73 min ), the aldehyde ( 1.08 min ), and the product ( rt 1.17 min ).


Figure S17. Entry 17, in Table 1: peak was assigned to the product (rt 1.05 min ).


Figure S18. Entry 18, in Table 1: peaks were assigned to the product (rt 0.96 min ) and the aldehyde (rt 1.01 min ).


Figure S19. Entry 19, in Table 1: peaks were assigned to the product (rt 0.87 min ), the aldehyde (rt 0.98 min ), and the intermediate imine ( rt 1.07 min ).


Figure S20. Entry 20, in Table 1: peaks were assigned to the product (rt 0.83 min ) and the aldehyde (rt 1.03 min ).


Figure S21. Entry 21, in Table 1: peak was assigned to the product (rt 0.66 min$)$.


Figure S22. Entry 22, in Table 1: peak was assigned to the product (rt 0.67 min ).


Figure S23. Entry 23, in Table 1: peak was assigned to the product (rt 0.73 min$)$.


Figure S24. Entry 24, in Table 1: peaks were assigned to the product (rt 0.86 min ), the aldehyde $(0.99 \mathrm{~min})$, and the tertiary amine ( 1.1 min ).


Figure S25. Entry 25, in Table 1: peak was assigned to the product (rt 1.25 min ).


Figure S26. Entry 26, in Table 1: peaks were assigned to the starting amine ( rt 0.29 min ) and the product (rt 0.78 min ).


Figure S27. Entry 27, in Table 1: peak was assigned to the product (rt 1.12 min$)$.


Figure S28. Entry 28, in Table 1: peaks were assigned to the aldehyde (rt 1.03 min ) and the product (rt 1.1 min ).


Figure S29. Entry 29, in Table 1: peak was assigned to the product (rt 0.78 min ).


Figure S30. Entry 30, in Table 1: peaks were assigned to the product (rt 0.83 min ) and the aldehyde (rt 1.08 min ).


Figure S31. Entry 31, in Table 1: peaks were assigned to the product (rt 0.86 min ), the aldehyde (rt 0.97 min ), and the tertiary amine ( rt 1.16 min ).


Figure S32. Entry 32, in Table 1: peaks were assigned to the product (rt 0.83 min ), the aldehyde (rt 1.04 min ), and the tertiary amine ( rt 1.1 min ).


Figure S33. Entry 33, in Table 1: peak was assigned to the product (rt 1.02 min ).


Figure S34. Entry 34, in Table 1: peaks were assigned to the starting amine (rt 0.26 min ), the product (rt 1.04 min ), and the aldehyde (rt 1.07 min ).


Figure S35. Entry 35, in Table 1: peaks were assigned to the starting amine (rt 0.45 min ) and the product (rt 1.03 min ).


Figure S36. Entry 36, in Table 1: peaks were assigned to the starting amine (rt 0.34 min ), the aldehyde ( rt 1.08 min ), and the product $(\mathrm{rt} 1.11 \mathrm{~min})$.


Figure S37. Entry 37, in Table 1: peaks were assigned to the side product (rt 1.00 min ) and the product (rt 1.13 min ).

Possible structure of the side product



Figure S38. Entry 38, in Table 1: peaks were assigned to the product (rt 0.90 min ) and the starting amine (rt 0.99 min ).


Figure S39. Entry 39, in Table 1: peaks were assigned to the starting amine (rt 0.61 min ), the acylated starting amine ( rt 0.77 min ), the aldehyde ( rt 0.84 min ), and the product ( rt 1.16 min ).


Figure S40. Entry 40, in Table 1: peaks were assigned to the starting amine (rt 0.58 min ), the aldehyde ( rt 0.88 min ), and the product ( rt 1.19 g min ).

NMR spectra for the selected compounds


Entry 1 , in Table 1


Entry 2, in Table 1







Entry 4, in Table 1


Entry 5, in Table 1


Entry 6 , in Table 1


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Entry 11, in Table 1


Entry 13, in Table 1


Entry 15, in Table 1


Entry 17, in Table 1


Entry 18, in Table 1


Entry 19, in Table 1


Entry 22, in Table 1


Entry 23, in Table 1

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Entry 24, in Table 1


Entry 27, in Table 1


Entry 30, in Table 1


Entry 31, in Table 1


Entry 33, in Table 1

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Entry 36, in Table 1


Entry 40, in Table 1

