Supporting Information

Efficient halogenation of 2-aminopyrazine

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**General**

Microwave assisted reactions were carried out in a CEM Discover LabMate instrument and the temperature vessel was measured by an IR sensor. The reactions were monitored by thin-layer chromatography (TLC) analysis using silica gel (60 F254, Merck) plates. Compounds were visualized by UV irradiation. Column chromatography was performed with silica gel 60 (230-400 mesh, 0.040-0.063 mm) and automatic column chromatography was performed with a CombiFlash Rf system with UV-vis (PN 68-5230-008) detector and RediSep Rf 4 and 12 g silica gel column. Melting points (mp) were obtained on a MFB-595010M Gallenkamp apparatus with digital thermometer in open capillary tubes and are reported without correction. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Gemini-400 (100 MHz). Chemical shifts are reported in parts per million (ppm) relative to the central peak of the solvent: CDCl$_3$ ($\delta$, 7.26 (H) and 77.16 (C)), CD$_3$OD ($\delta$, 3.31 (H) and 49.45 (C)), DMSO-$d_6$($\delta$, 2.49 (H) and 39.51 (C)) as internal standards. The following abbreviations are used for the proton spectra multiplicities: s, singlet, d, doublet, t, triplet, q, quadruplet, m, multiplet. Coupling constants ($J$) were reported in Hertz (Hz). All reagents were of high quality or were purified before use. Organic solvents were of analytical grade or were purified by standard procedures.

**Analytical data**

a) **2-Amino-5-iodopyrazine**

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$(ppm), 7.83 (s, 1H, H-3); 8.21 (s, 1H, H-6)

Mp: 110-113 °C

b) **2-Amino-3,5-diiodopyrazine**

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$(ppm), 7.99 (s, 2H, H-6)

c) **2-Amino-5-chloropyrazine**

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$(ppm), 7.77 (s, 1H, H-3); 8.00 (s, 1H, H-6)

Mp: 127-128 °C (bibliography 129-130 °C)

d) **2-Amino-3,5-dichloropyrazine**

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$(ppm), 5.12 (bs, 2H, NH$_2$); 7.97 (s, 1H, H-6)

Mp: 115-118 °C

e) **2-Amino-5-bromopyrazine**

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$(ppm), 7.76 (s, 1H, H-3); 8.10 (s, 1H, H-6)
b) 2-Amino-3,5-dibromopyrazine

$^1$H-NMR (400 MHz, CDCl$_3$) δ (ppm), 5.18 (bs, 2H, NH$_2$); 8.04 (s, 1H, H-6)

$^{13}$C-NMR (100.6 MHz, CDCl$_3$) δ (ppm), 123.6 (C-3); 124.0 (C5-); 143.1 (CH, C-6); 151.9 (C-2)

Mp: 118-120 °C (bibliography 117-118 °C)$^3$

References

2-Amino-3,5-dibromopyrazine - $^1$H-NMR (400 MHz, CDCl$_3$)

2-Amino-5-bromopyrazine - $^1$H-NMR (400 MHz, CDCl$_3$)
2-Amino-3,5-dichloropyrazine - $^1$H-NMR (400 MHz, CDCl$_3$)

2-Amino-5-chloropyrazine - $^1$H-NMR (400 MHz, CDCl$_3$)
2-Amino-3,5-diiodopyrazine - $^1$H-NMR (400 MHz, CDCl$_3$)

2-Amino-5-iodopyrazine - $^1$H-NMR (400 MHz, CDCl$_3$)