

Synthesis of Tetra(imidazol-4(5)-yl)pyrazine and Tetrapyrazilpyrazine

Carolina B. P. Ligiéro; Luis G. T. A. Duarte; Paulo C. M. L. Miranda

Instituto de Química, Universidade Estadual de Campinas, SP

*e-mail corresponding author: miranda@iqm.unicamp.br

Keywords: Supramolecular chemistry, benzoin condensation, polyheteroaromatic ligands

INTRODUCTION

N-heterocyclic bridging ligands are able of forming complexes with metals allowing the construction of functional supramolecular systems.

We present the synthesis of two new building blocks designed for the construction of tridimensional arrays: 2,3,5,6-tetra(pyrazin-2-yl)pyrazine (**1**) and 2,3,4,6-tetra(imidazol-4(5)-yl)pyrazine (**2**).

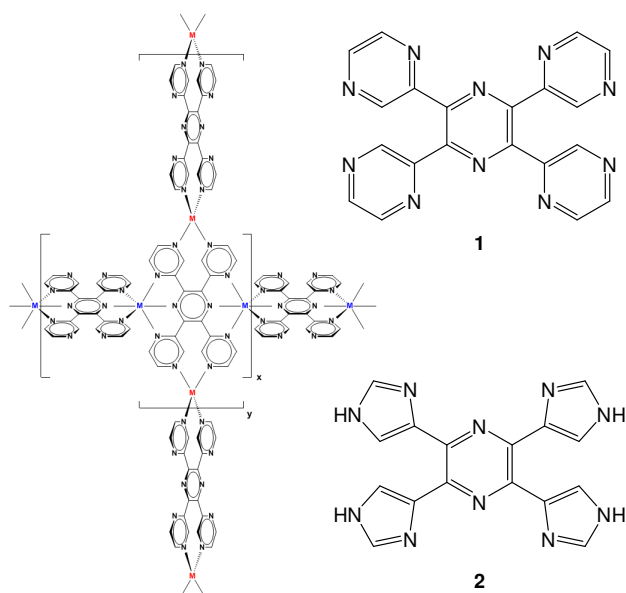
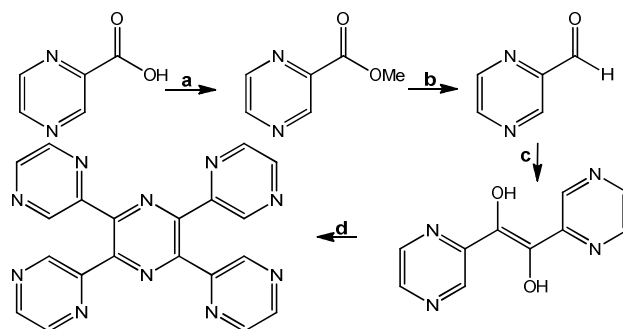


Figure 1. Tetrapyrazilpyrazine (**1**) and tetra(imidazol-4(5)-yl)pyrazine (**2**).

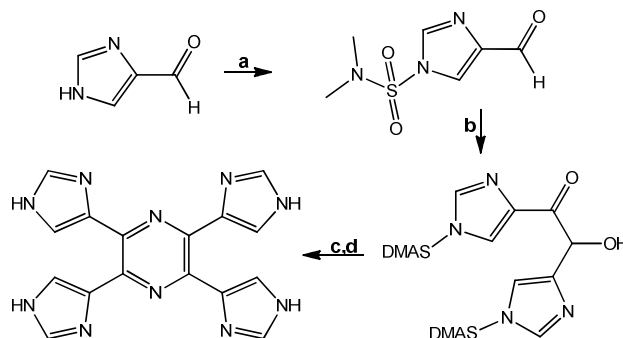
RESULTS AND DISCUSSION

Tetrapyrazilpyrazine was prepared in a four step route from pyrazinecarboxylic acid with 15% of global yield (**Scheme 1**) from benzoin coupling strategy.¹ Tetra(imidazol-4(5)yl)pyrazine was also synthesized by benzoin condensation strategy, but in this case we used 4(5)-imidazolecarbaldehyde as starting material (**Scheme 2**). Protection with sulfamoyl group was critical to activate the aldehyde carbonyl in the benzoin condensation. Many other protecting groups failed in performing this reaction. With BOC, acetyl and tosyl as protecting groups ANRORC degradation products prevail over benzoin coupling.



a) MeOH, H₂SO₄ (cat), 72h, rt., 93% **b)** LiAlH₄, THF, 1.5h, -82°C, 63% **c)** KCN (cat), water, rt., 1h, 73% **d)** NH₄OAc, DMF, 80°C, 36%.

Scheme 1. Synthesis of tetrapyrazilpyrazine.



a) NaH, DMF, rt, 1.5h and then DMASCl, rt, 24h, 68% **b)** 3-(benzyl)-5-(2-hydroxyethyl)-4-methylthiazolium chloride, EtOH, 50°C, 30 min, 93% **c)** NH₄OAc, pyridine, 100°C, 2h, 20% **d)** HCl 6M, 100°C, 64%.

Scheme 2. Synthesis of tetra(imidazol-4(5)yl)pyrazine.

CONCLUSION

Two new ligands for supramolecular assembling were successfully synthesized from simple heteroaromatic compounds in few steps.

ACKNOWLEDGEMENTS

CNPQ, CAPES, FAPESP, INCT-INOMAT.

REFERENCES

- Torres, S. F.; Hutchison, G. R.; Stolzberg, L. J.; Abruña, H. D. *J. Am. Chem. Soc.* **2006**, *128*, 1513.
- Ligiéro, C. B. P.; Visentin, L. C.; Giacomini, R.; Filgueiras, C. A. L.; Miranda, P. C. M. L. *Tetrahedron Lett.* **2009**, *50*, 4030.