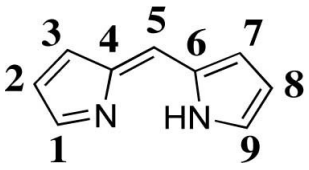
Synthesis and Applications of Dipyrrins

Dipyrrins, as shown in Figure 1 with their accepted numbering scheme, are an interesting class of molecules with intense molar absorptivities in the visible region.

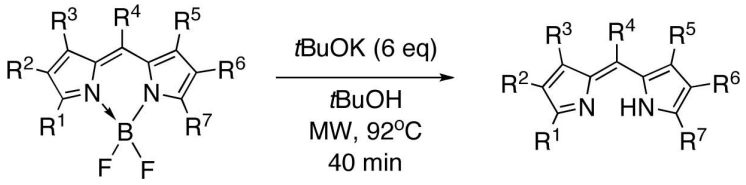
Figure 1. **Basic structure and numbering of the dipyrrin unit**



The chemical manipulation of dipyrrinato complexes is more common in the literature than the chemical manipulation of the dipyrrin itself as the nitrogen atoms of the dipyrrin are effectively protected by the species to which they are coordinated. Manipulations of zinc, cobalt and palladium dipyrrinato complexes are known[1] and, while a wide variety of synthetic modifications can be carried out on these dipyrrinato complexes, strongly acidic and reductive conditions must be avoided to prevent decomplexation.[1] We have recently explored the synthesis of a series of dipyrrinato alkali metal complexes[2,3] and are currently looking at using these complexes as synthetic building blocks to previously unexplored dipyrrinato metal complexes.

The most well explored dipyrrinato complexes are BF_2 complexes, also called *F*-BODIPYs. These compounds are chemically robust, highly stable and emit sharp fluorescence peaks with high quantum yields.[4,5] *F*-BODIPYs are routinely synthesized in high yields by trapping the parent dipyrrin as its BF_2 complex. Our recent work has focused on the development of a general method for the removal of the BF_2 group from an *F*-BODIPY to generate the corresponding dipyrrin. Our procedure involves heating a sealed mixture of an *F*-BODIPY and 6 equivalents of potassium *tert*-butoxide in *tert*-butanol to 92 °C under 600 W microwave irradiation for 40 min (Figure 2), followed by an aqueous basic work-up to give the deprotected dipyrrin product.[6]

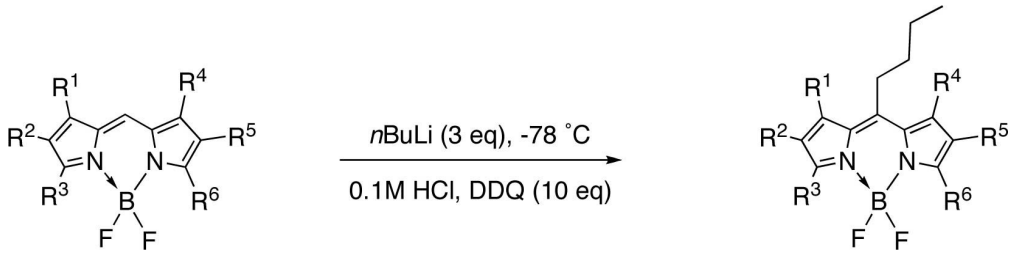
Figure 2. **Microwave-promoted deprotection of *F*-BODIPYs**



The development of this methodology allows the use of the BF_2 group as a dipyrrin protecting group. Further investigations into the mechanism and reagents used in this deprotection reaction are currently ongoing.

Investigations into the *meso*-modification of *F*-BODIPYS have also been undertaken as a possible synthetic route to novel dipyrrins. *F*-BODIPYs have been successfully monoalkylated at the *meso*-position using *n*-butyllithium (Figure 3).[6] This represents a new, higher yielding method for the generation of *meso*-alkylated *F*-BODIPYs in moderate yields.

Figure 3. ***meso*-Modification of *F*-BODIPYs**



Extension of this methodology to arylation using aryllithium reagents was unsuccessful; however, extension of the methodology to other alkyllithium reagents to generate *meso*-substituted *F*-BODIPYs, with additional sites for functionalization is currently under investigation.

In summary, our research interests in this area include the synthesis of new dipyrrins and new main group and transition metal coordinated dipyrirnato complexes and the investigation of their properties (e.g. fluorescence, chirooptical properties). Once synthetic methodologies have been developed and the properties of the synthesized dipyrrins and dipyrrinato complexes have been investigated and explored, we then want to investigate the development of these compounds for use in possible applications (e.g. chemical sensors, functional materials).

References

(1) Wood, T. E.; Thompson, A. *Chem. Rev.* **2007**, *107*, 1831–1861.
(2) Al-Sheikh Ali, A.; Cipot-Wechsler, J.; Crawford, S. M.; Selim, O.; Stoddard, R. L.; Cameron, T. S.; Thompson, A. *Can. J. Chem.* **2010**, *88*, 725–735.
(3) Cipot-Wechsler, J.; Al-Sheikh Ali, A.; Chapman, E. E.; Cameron, T. S.; Thompson, A. *Inorg. Chem.* **2007**, *46*, 10947–10949.
(4) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891–4932.
(5) Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 1184–1201.
(6) Crawford, S. M.; Thompson, A. *Org. Lett.* **2010**, *12*, 1424–1427.