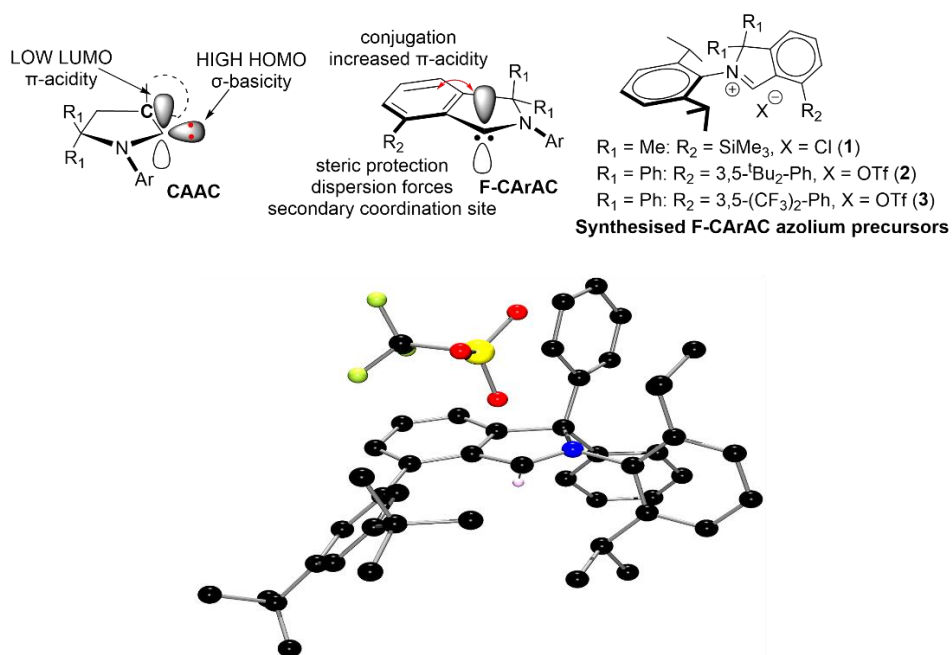


## Synthesis of Fused-Cyclic Aryl Amino Carbene Ligand Precursors

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Since the introduction of singlet state, thermally stable and crystalline Cyclic-Alkyl-Amino Carbenes (CAACs) by Bertrand *et.al.* (**Figure 1**)<sup>[1]</sup>, suffice to say that this type of 2e<sup>-</sup> donor ligands have made their indelible mark in diverse areas of chemistry<sup>[2]</sup>. This is due to their enhanced  $\sigma$ -donation and  $\pi$ -acidity, which can stabilize low-coordinate, as well as electron-rich species, respectively. Fused Cyclic-Aryl-Amino Carbenes (F-CArACs)<sup>[3]</sup> take these advantageous attributes even further, especially regarding their  $\pi$ -acceptor properties thanks to conjugation built in their design (**Figure 1**). To this end, we present new synthetic routes leading to the preparation of expanded F-CArAC ligands' azolium precursors, incorporating ancillary arene or SiR<sub>3</sub> moieties in their architecture (**Figure 1**). We envisage that including these groups (R<sub>2</sub> in **Figure 1**) into the F-CArAC ligand scaffold will offer steric protection, engender further stabilisation *via* dispersion forces and additionally, in the case when R<sub>2</sub> is an arene, provide a second site for metal centres to form an M-arene  $\pi$ -complex.



**Figure 1:** Top: From left to right: CAAC, F-CArAC, synthesised F-CArAc azolium precursors; Bottom: Molecular structure of F-CArAc azolium precursor (2).

### References:

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