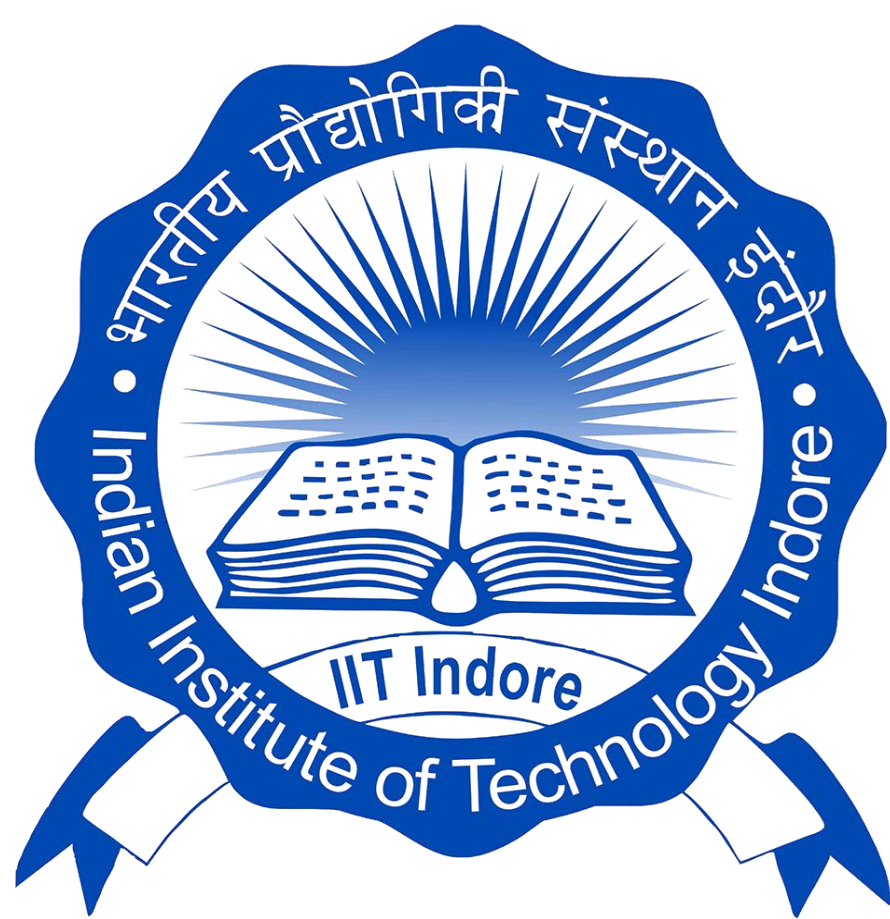


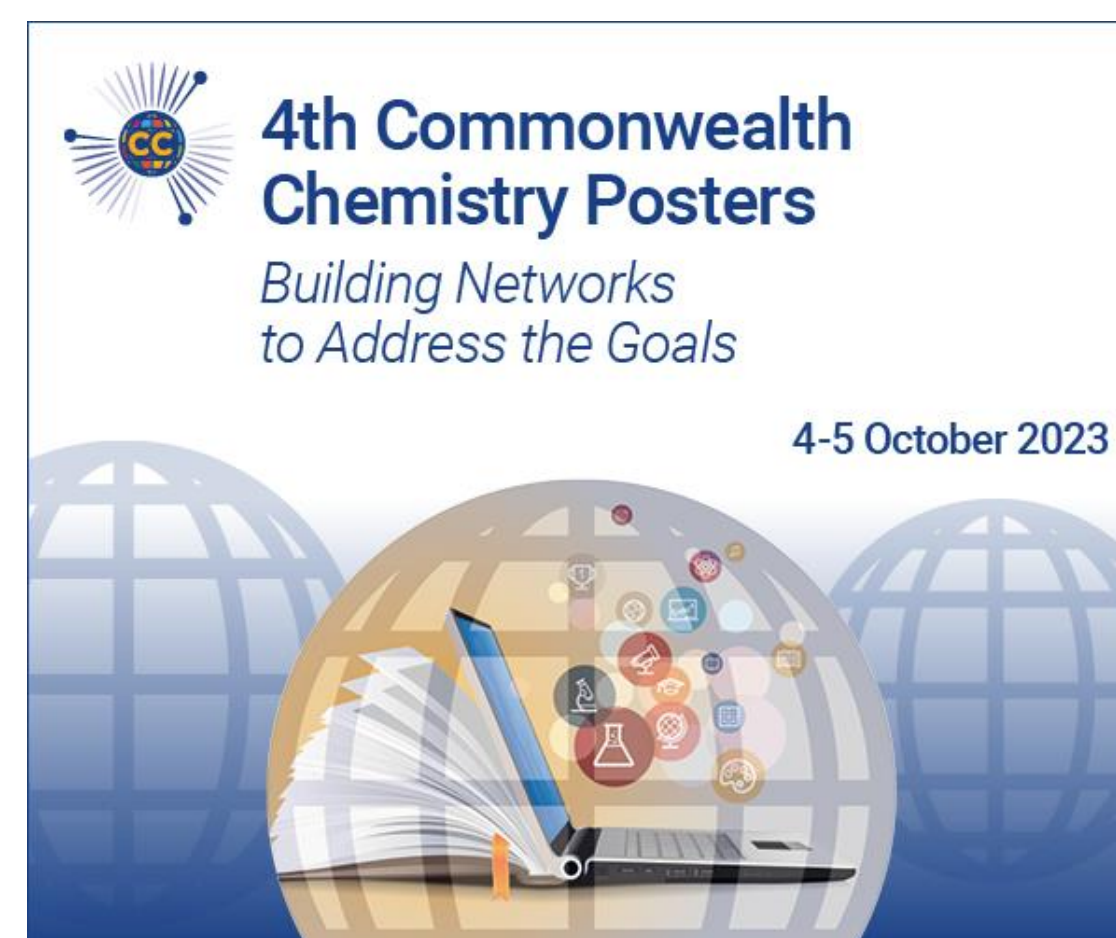


Base-free synthesis of benchtop stable Ru(III)-NHC complexes from Ruthenium(III) chloride trihydrate and their use as precursors for Ru(II)-NHC complexes

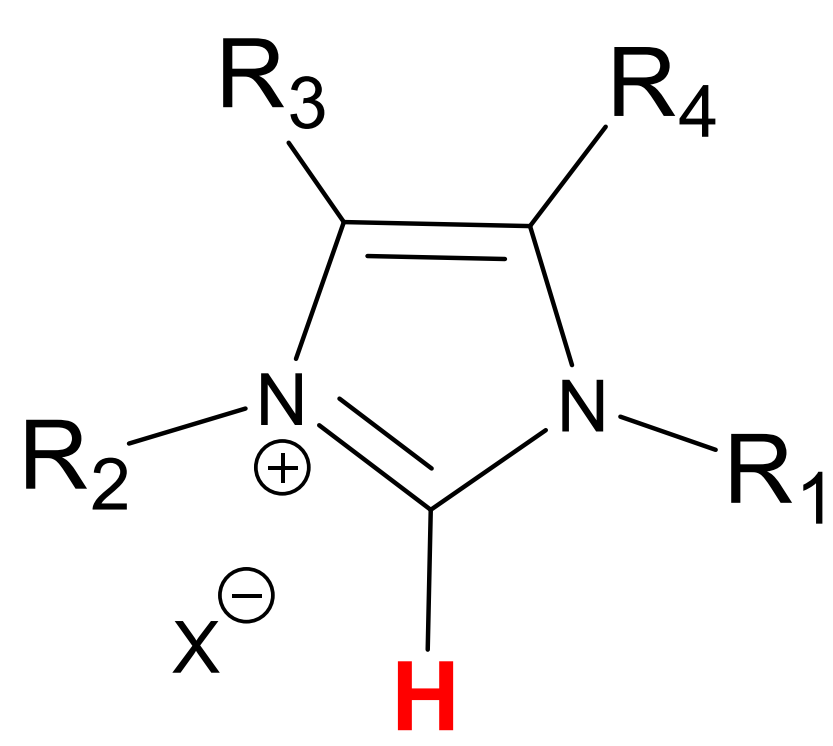
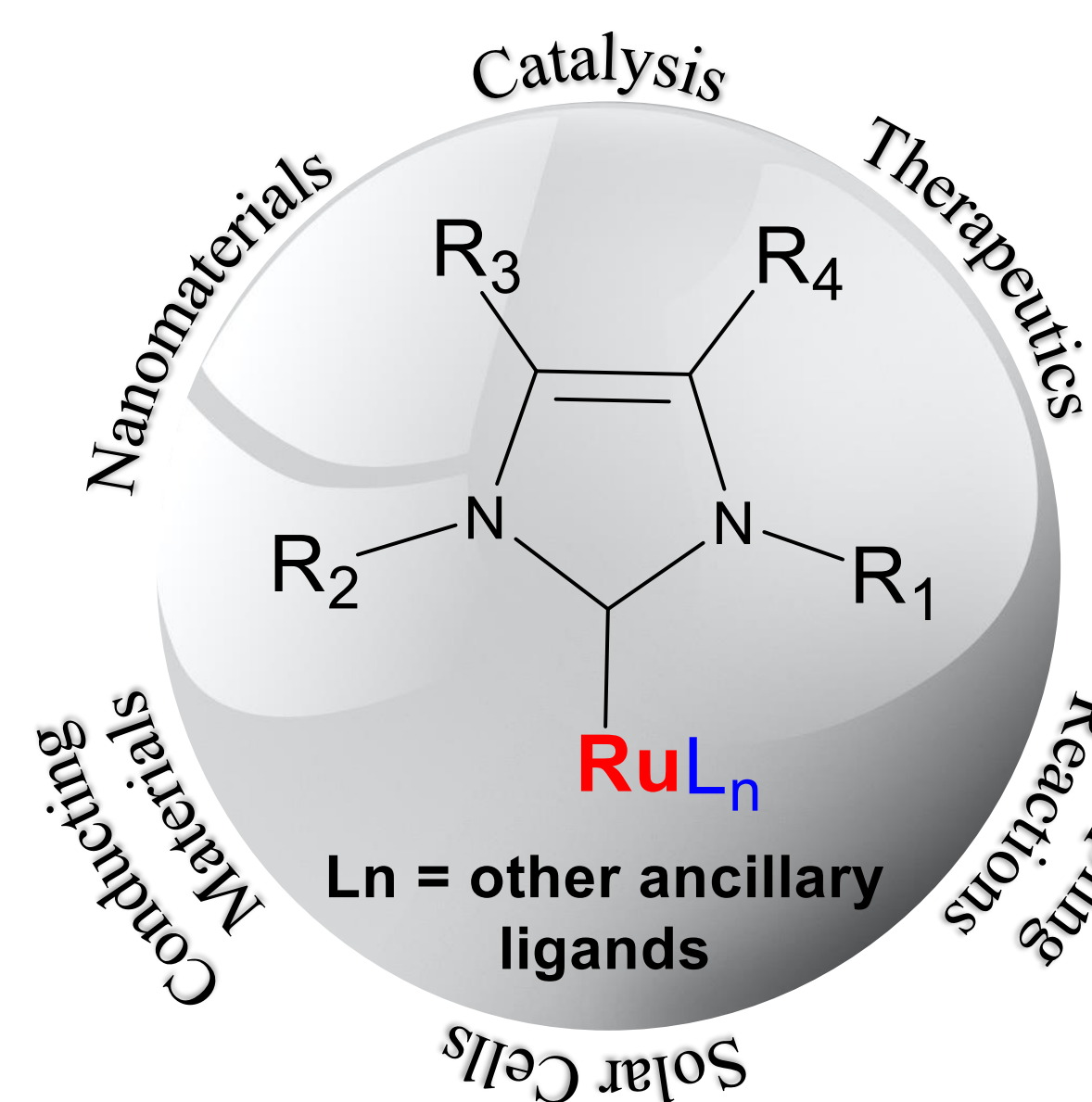
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Ru-NHC complexes in^[1]:



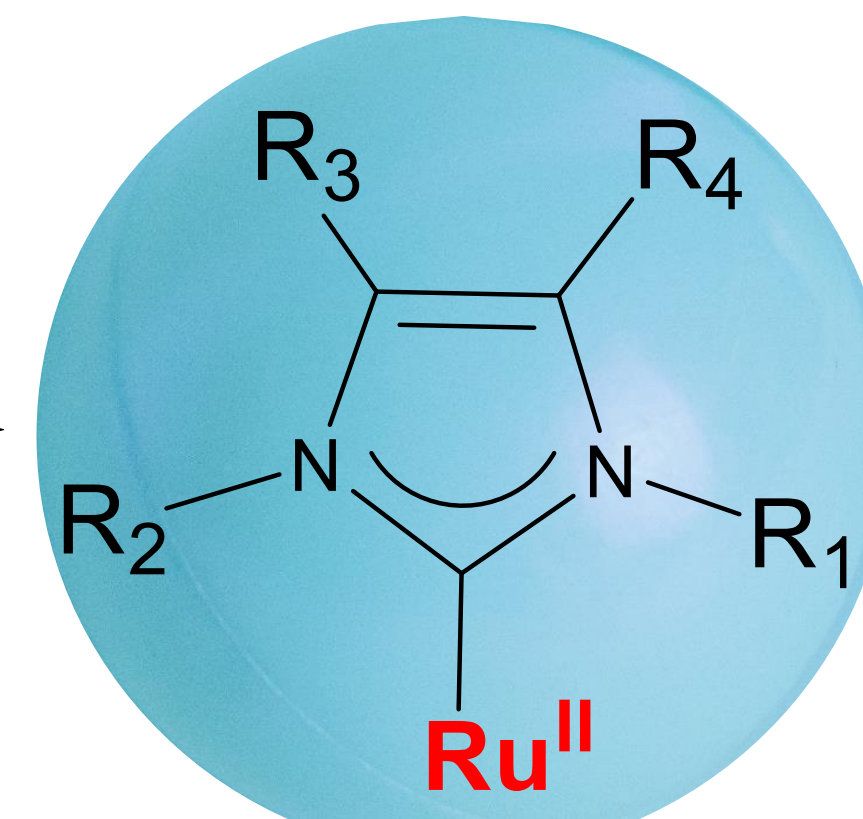
[Ru] can be any suitable metal precursor like [RuCl₂(PPh₃)₃], [Ru(Cl)(p-cymene)]₂, [Ru(Cl)₂(DMSO)₄] etc.

How they can be formed:

1. Deprotonation of azolium salt
2. Metalation using [Ru] (involves base)

1. Formation of Ag(I)/Cu(I)-NHC
2. Transmetalation using [Ru] (involves undesired side products)

Metal assisted C-H activation of C4/C2-H imidazolium proton
involves: no base, less or no side products
can be done in green solvents



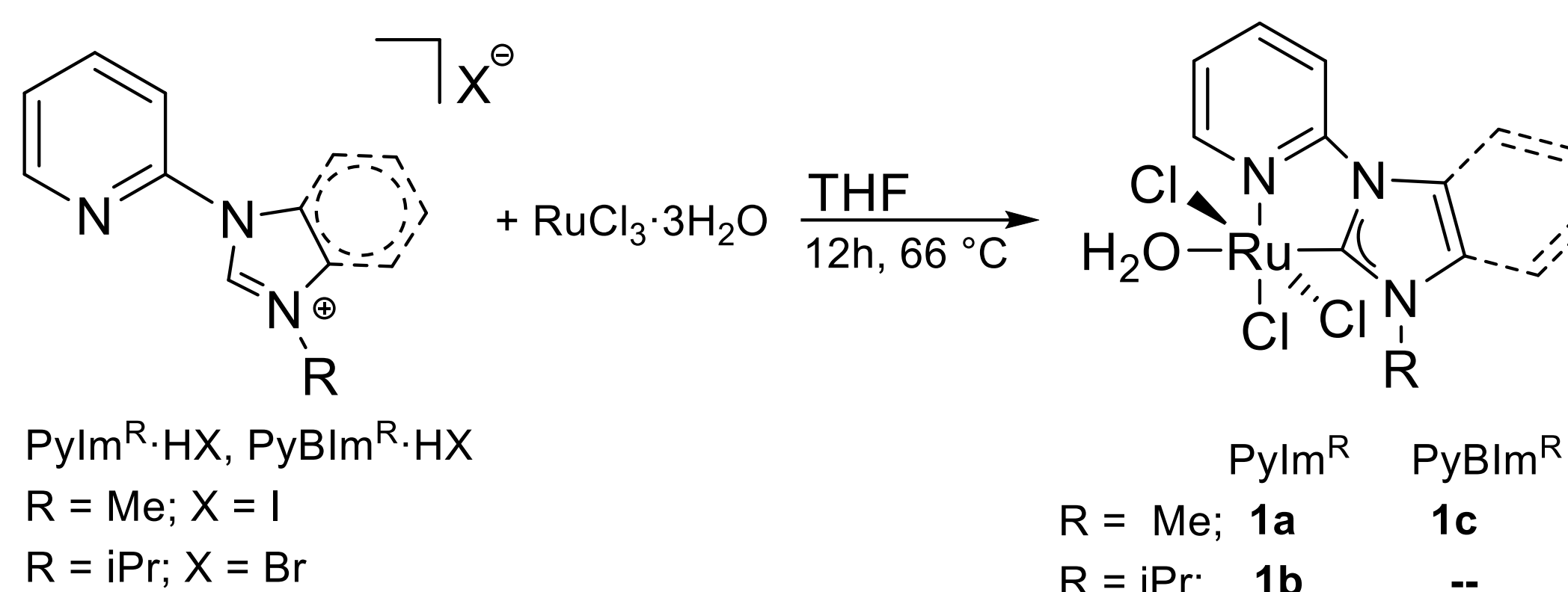
So far...

- No Ru precursor with an NHC ligand is reported till date..
- No reports on synthesis of Ru(III)-NHC complex directly from RuCl₃·3H₂O..
- Role of ion pairs during the synthesis of Ru-NHC complexes has been studied till date...
- A few Ru(III)-NHC complexes^[2] are known, which are formed by oxidizing Ru(II)-NHC complexes..

Objectives

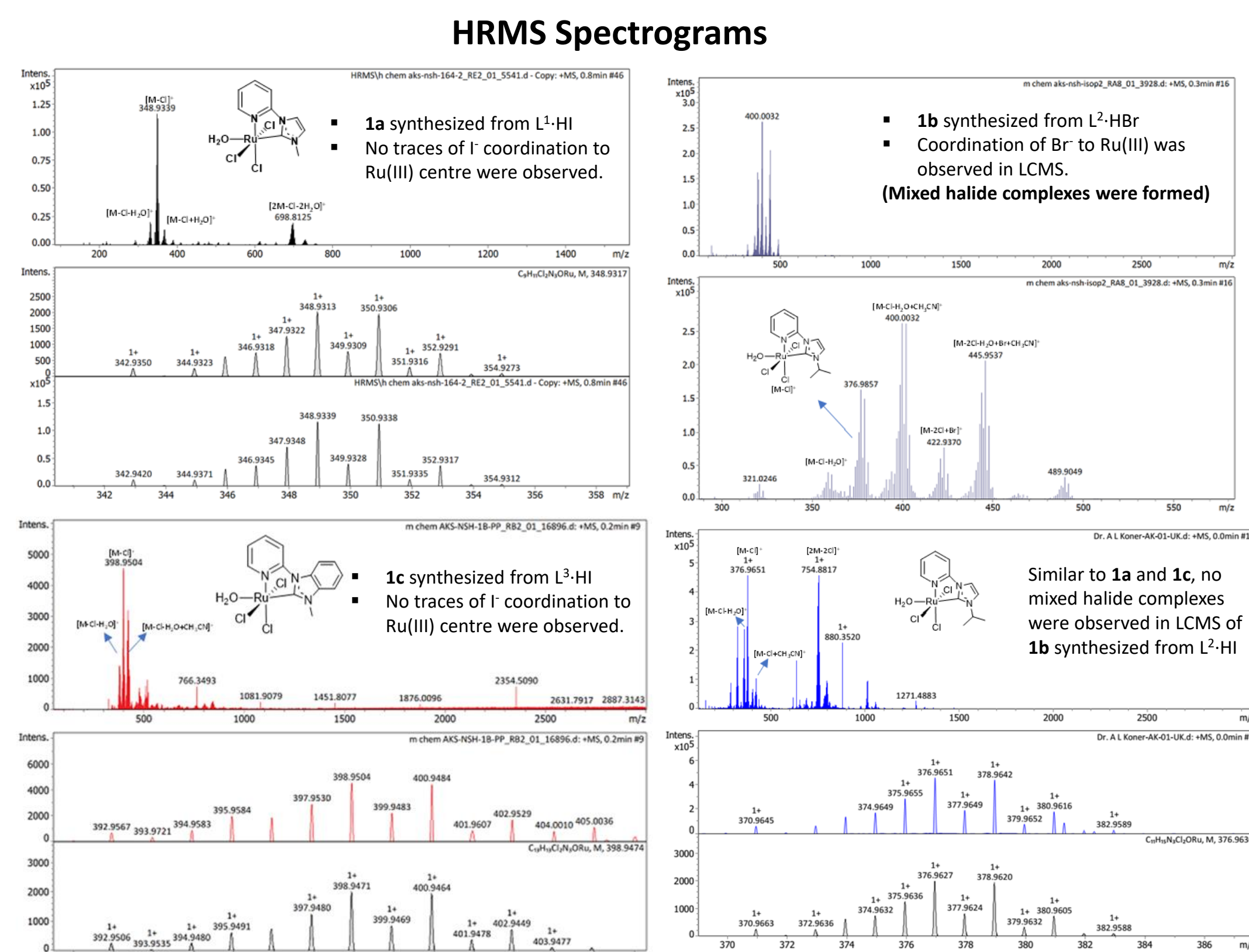
- To synthesize a series of Ru(III)-NHC complexes (**1a-c**) based on pyridine functionalized (benz)imidazolydene bidentate ligand framework via electrophilic C-H activation in presence of Lewis acidic Ru(III) centre.
- To utilize the Ru(III)-NHC complexes (**1a-c**) as the metal precursors for the corresponding Ru(II)-PyNHC-(PPh₃) complexes (**2a-c**) and Ru(II)-PyNHC-(CNC^{Me}) complexes (**3a-c**).

Synthesis of Ru(III)-NHC Complexes 1a-c:

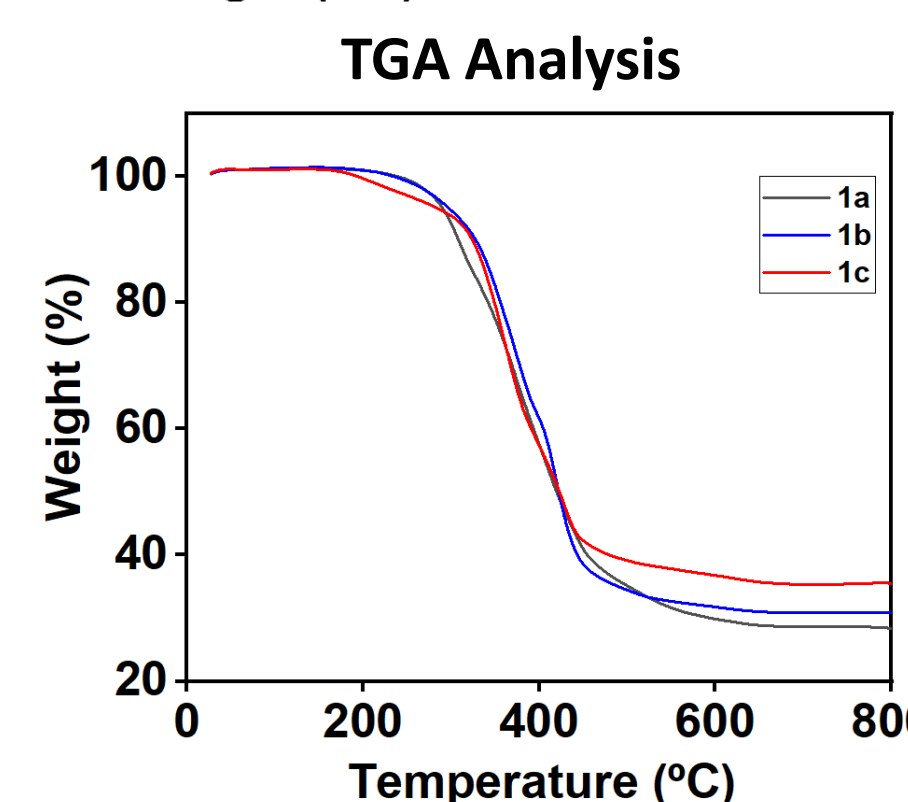
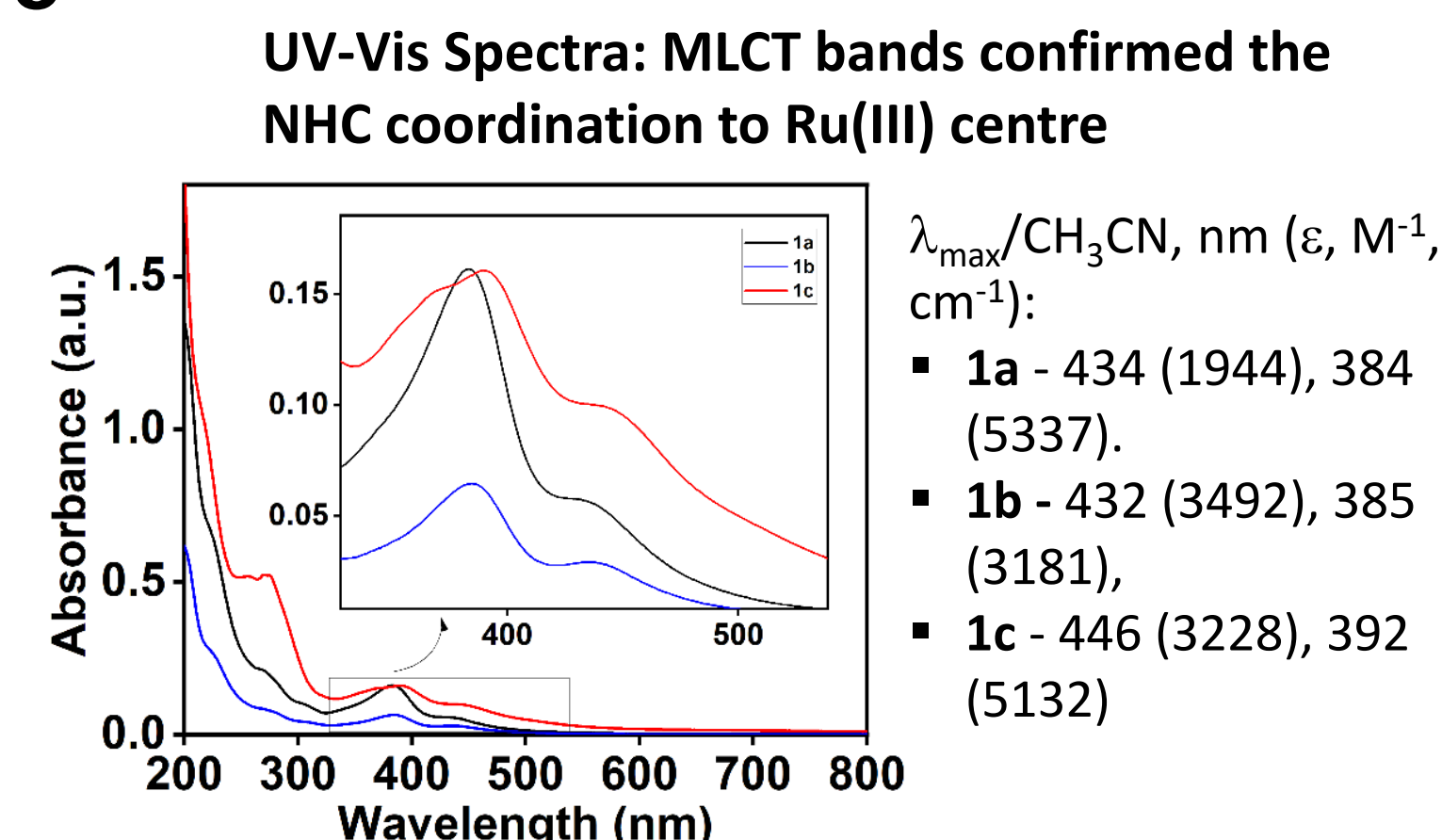
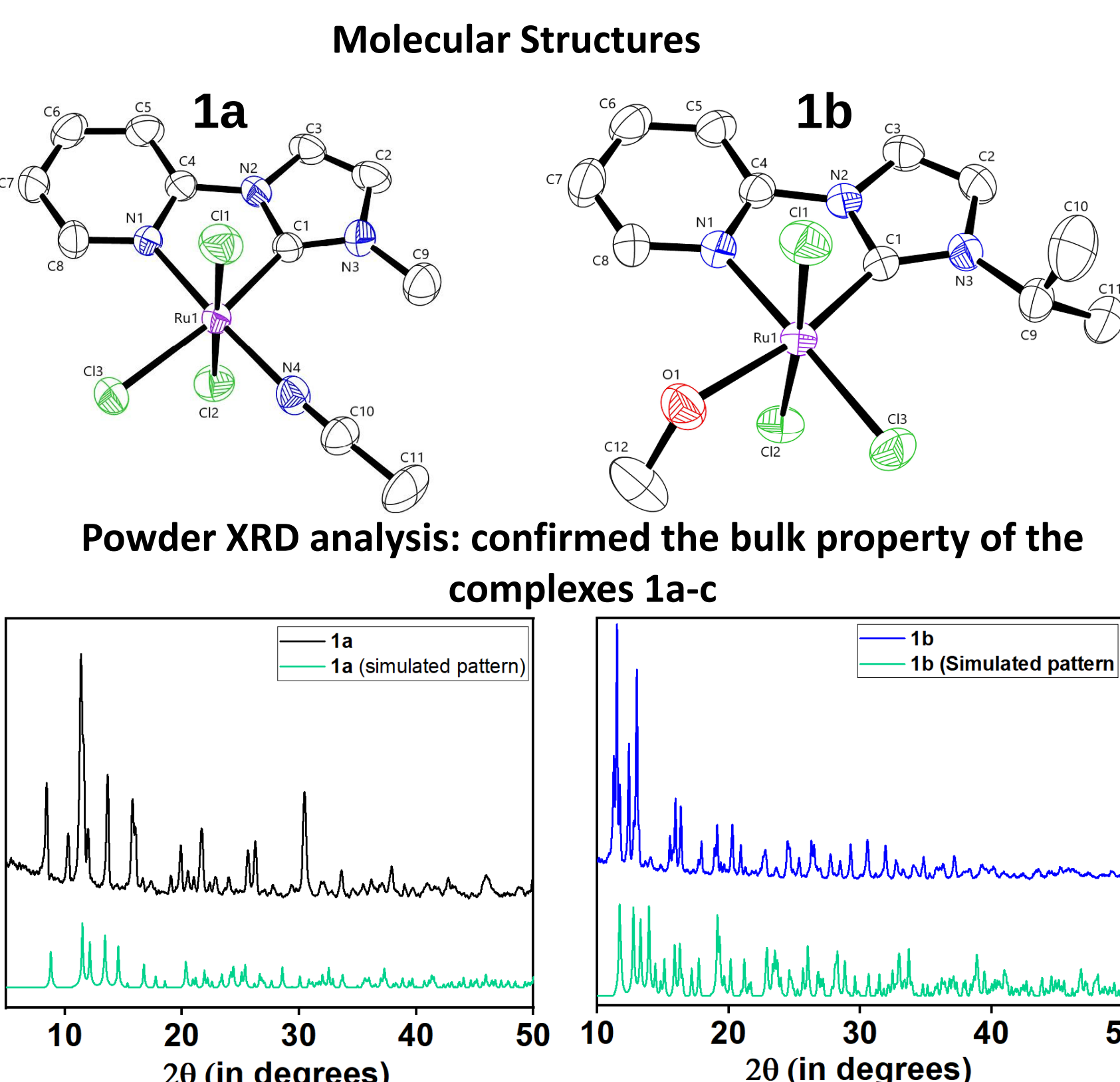


- Base-free synthesis
 - Scalable
 - No reaction was observed with Ligand precursors, L-HX, X = Cl, BF₄, PF₆.
- Complexes **1a-c** are:
- Air- and moisture stable
 - Bench-top stable
 - Can serve as the metal precursor for Ru(II)-NHC complexes

Spectroscopic characterization of Ru(III)-NHC complexes 1a-c

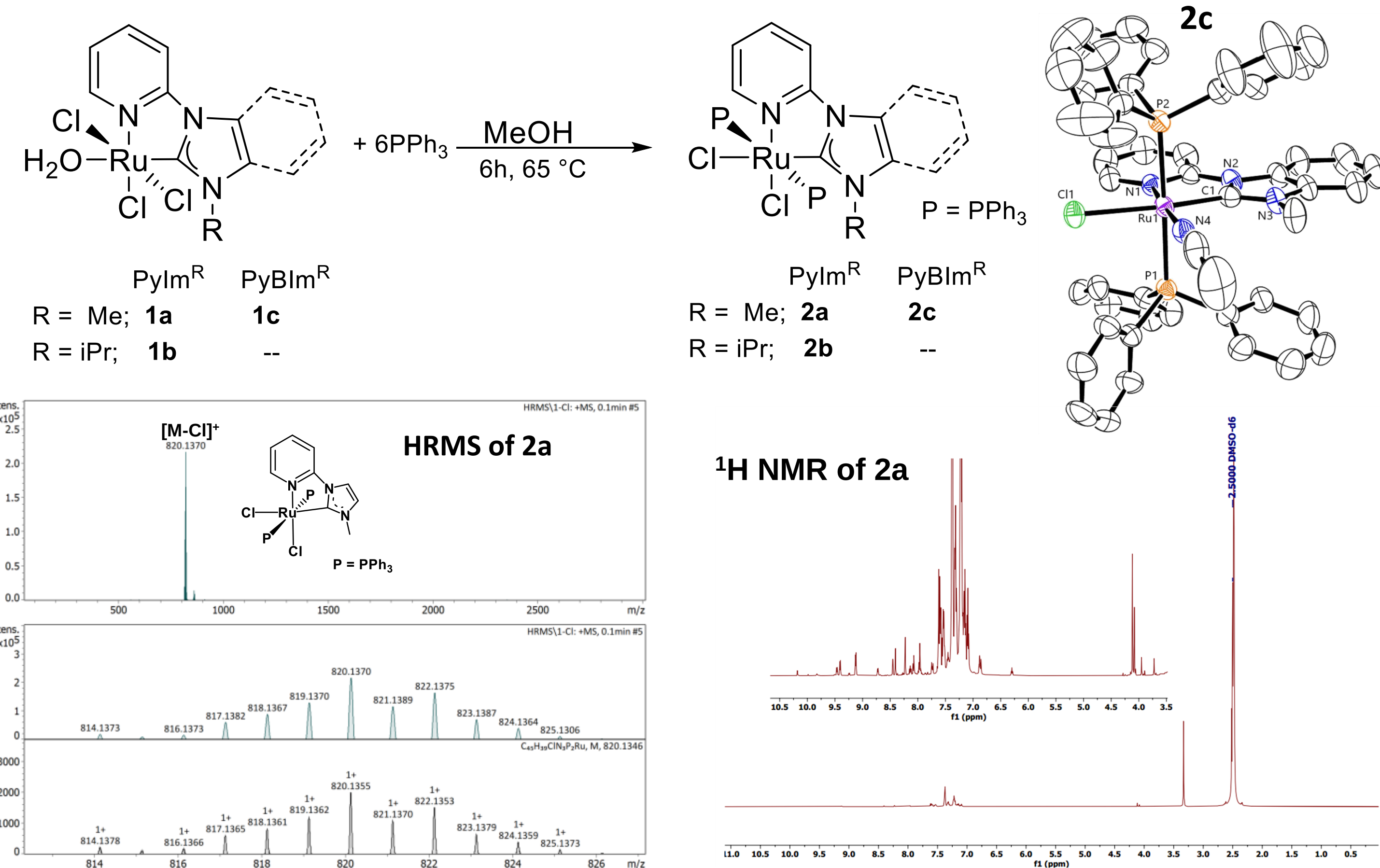


Switching over to L²-H from L¹-H

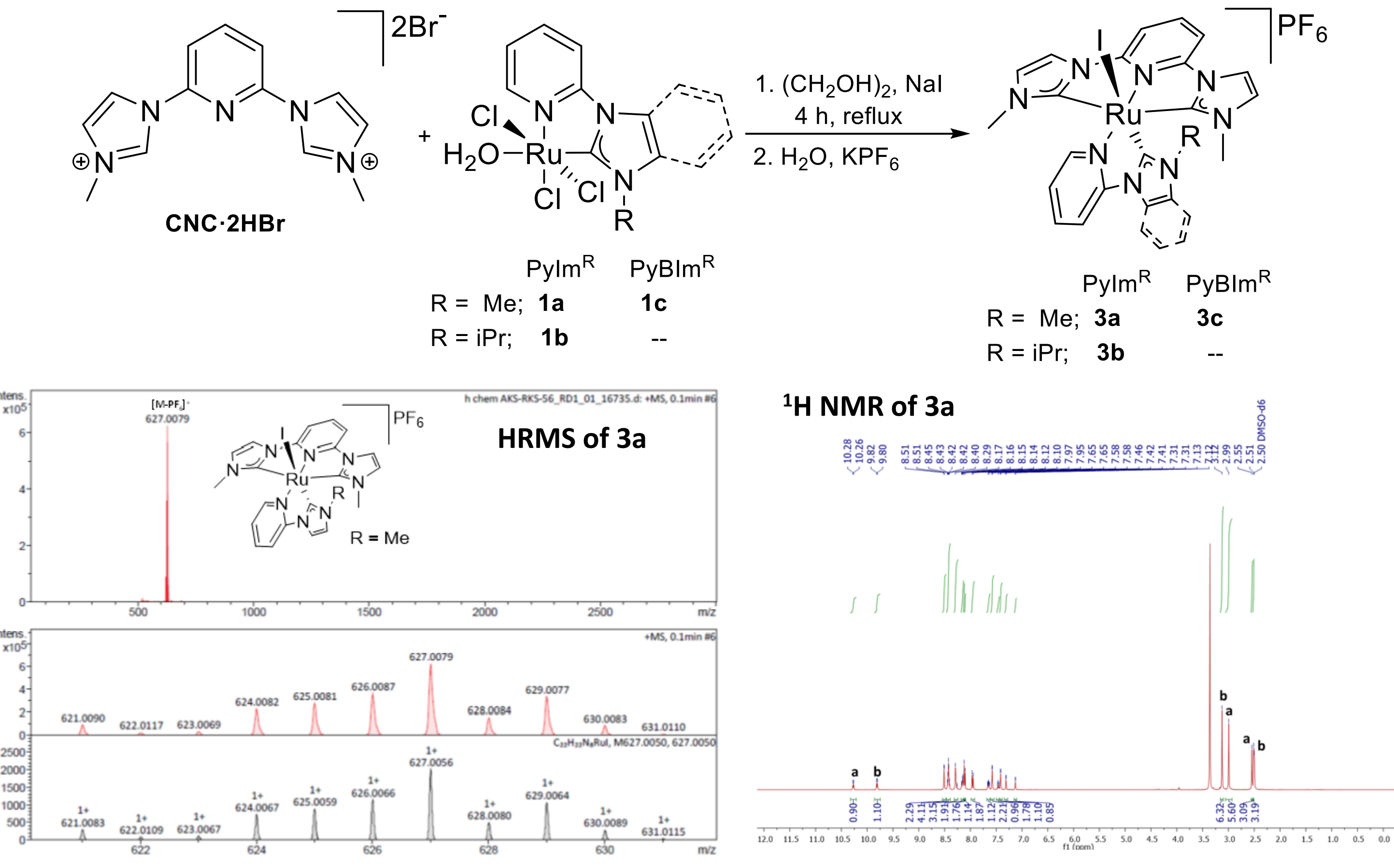


Use of Ru(III)-NHC complexes 1a-c as the precursor for Ru(II)-NHC complexes

Synthesis of Ru(II)-PyNHC-(PPh₃) Complexes 2a-c from Ru(III)-PyNHC complexes 1a-c



Synthesis of Ru(II)-PyNHC-(CNC^{Me}) Complexes 3a-c from Ru(III)-PyNHC complexes 1a-c



Conclusions

- A series of new, benchtop stable Ru(III)-NHC complexes **1a-c** has been synthesized from the bidentate Py(B/Im)^R-HI (R = Me, and iPr) ligand precursors and RuCl₃·3H₂O, following a base-free route.
- The role of ion pairs in ligand precursors, on the synthesis of Ru(III)-NHC complexes **1a-c** has been observed.
- These Ru(III) complexes serve as metal precursors for the preparation of new Ru(II)-NHC-(PPh₃) complexes (**2a-c**) and Ru(II)-NHC-CNC^{Me} (**3a-c**).
- All complexes have been characterized by usual characterization techniques.

References

- [1] a) P. Nareddy, F. Jordan and M. Szostak, *ACS Catal.*, 2017, 7, 5721–5745, b) S. Thota, D. A. Rodrigues, D. C. Crans and E. J. Barreiro, *J. Med. Chem.*, 2018, 61, 5805–5821, c) S. Aghazada, I. Zimmermann, V. Scutelnic and M. K. Nazeeruddin, *Organometallics*, 2017, 36, 2397–2403.
- [2] a) S. Hitzel, C. Färber, C. Bruhn and U. Siemeling, *Organometallics*, 2014, 33, 425–428, b) P. L. Arnold and A. C. Scarisbrick, *Organometallics*, 2004, 23, 2519–2521.
- [3] N. Shahid, R. K. Singh, N. Srivastava and A. K. Singh, *Dalton Trans.*, 2023, Accepted Manuscript (doi.org/10.1039/D3DT00243H).

Future Scope

These Ru(III)-NHC complexes **1a-c** allow easy access to new Ru(II)-NHC complexes with different ancillary ligands, for novel applications.

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