A tin-complexation strategy for use in acylation methods in the preparation of 1,9-diacyldipyrromethanes.

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ABSTRACT Phenothiazinyl-dipyrromethane with Vilsmeier reagent, or with acid chloride typically affords a mixture of 1-, 1,8-, and 1,9-diformyl(or acyl)-dipyrromethanes. Acyl- and formyldipirromethanes typically afford amorphous powder upon attempted crystallization and streak expensively on column chromatography. To facilitate isolation of 1,9-diacyl respectively 1,9-diformyl species, the crude mixture is treated with dialkyl-tin-dichloride (R_2SnCl_2). The tin-complexation process is selective for 1,9-diformyl(acyl) species, yielding a hydrophobic 1,9-diformyl(acyl)dipyrromethane-dialkyltin complex.

Acknowledgments:

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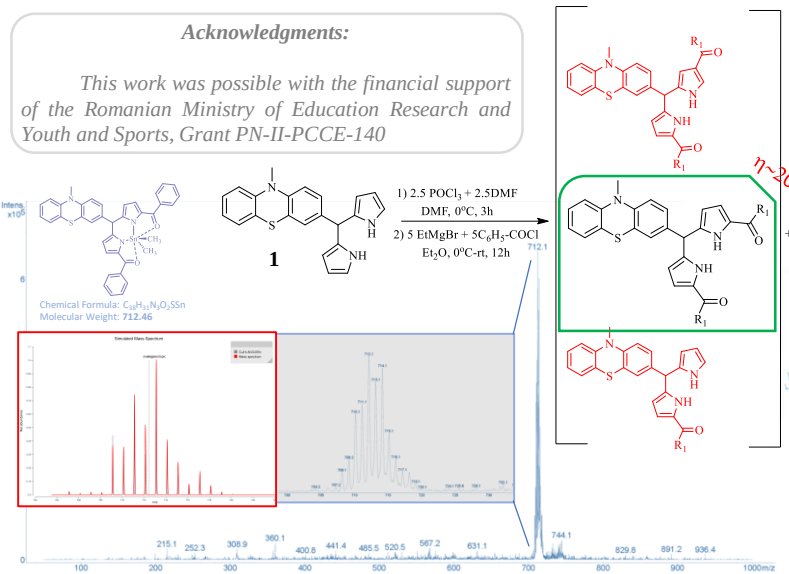
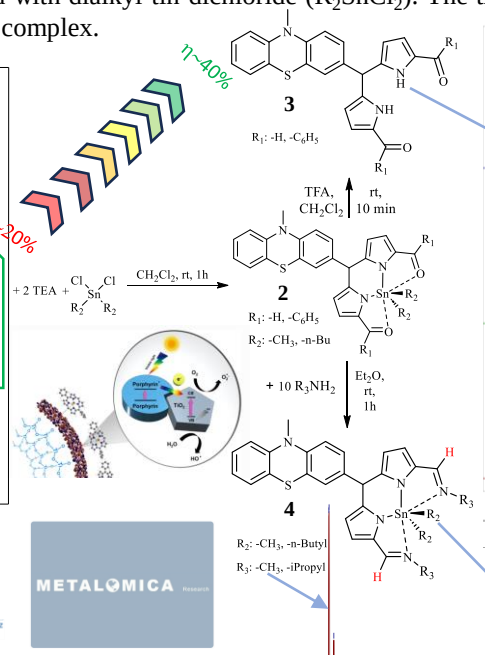
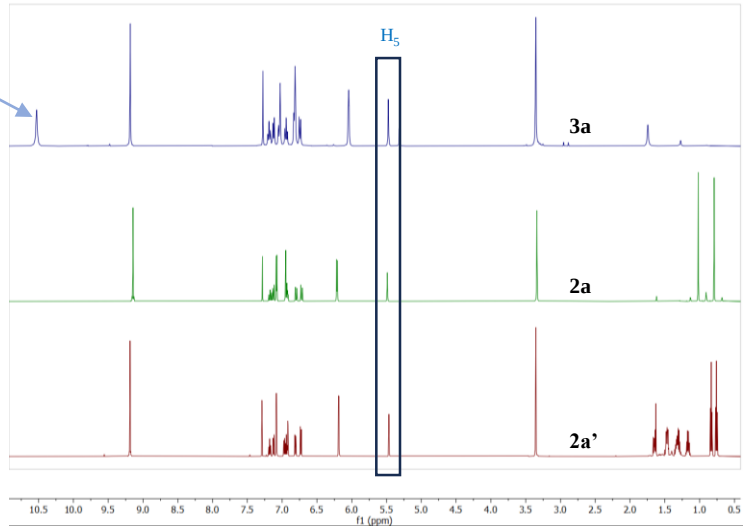
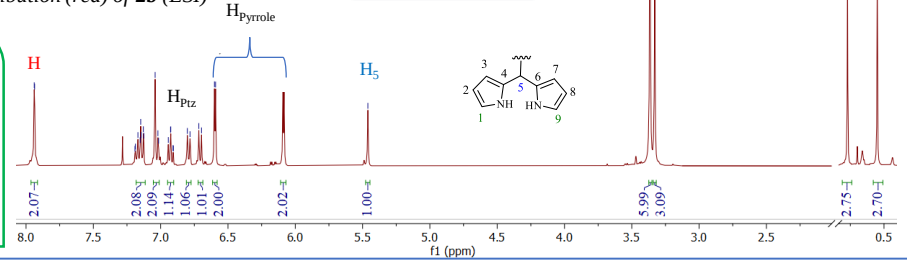


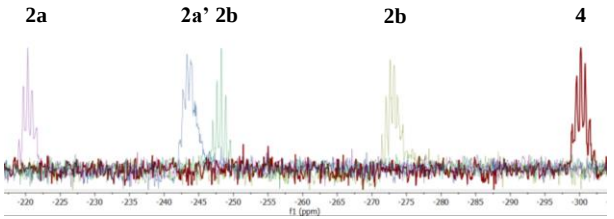
*MS spectrum (blue) and simulated isotope distribution (red) of **2b** (ESI)*





^{1}H-NMR spectra of 1,9-diformyl-phenothiazinyl-dipyrromethane and their dialkyltin complexes (400MHz, $CDCl_3$)





^{119}Sn-NMR spectra of phenothiazinyl-dipyrromethane dialkyltin complexes (149MHz, $CDCl_3$)

Conclusion: *The corresponding tin complexes was readily isolated by column chromatography, the fast moving yellow fraction were collected and concentrated to dryness. This procedure proved viable for small-scale preparation, but partial decomplexation upon chromatographic separation limited larger scale implementation*

References

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Equipments:

Bruker ASCEND 400 and 600 MHz NMR spectrometer;
Bruker FT-IR Vector 22 spectrophotometer;
Shimadzu QP-2010 PLUS mass spectrometer;
HRMS Thermo Scientific LTQ Orbitrap XL