Metal-containing ionic liquids used as catalysts in the recycling of PET waste

Ţincu Robert-Andrei, Florina Teodorescu*, Emeric Bartha

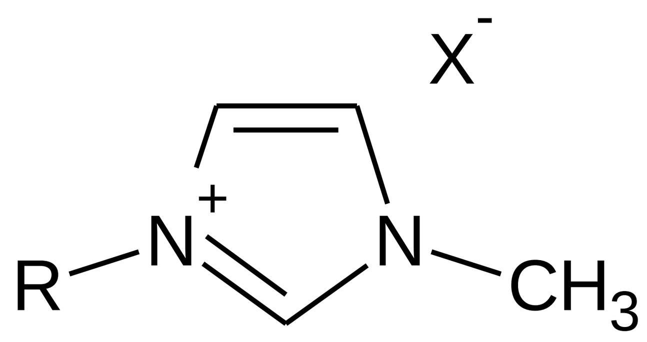
*‘‘C.D. Nenitzescu’’ Center for Organic Chemistry, 202 B Spl. Independenței, S6, 060023 Bucharest, Romania, *florina.teodorescu@gmail.com*

INTRODUCTION

PET, or poly(ethylene terephthalate), is a non-biodegradable post-consumer waste [1]. Aromatic polyester-polyols (APPs) are produced via glycolysis of PET wastes with different diols using a range of catalysts [2]. The most common catalysts employed today are inorganic metal salts or, more recently, organic compounds (such as super-bases or ionic liquids). Because of its unique properties, such as thermal stability, electrochemical stability, low flammability, and structural flexibility of the cation and anion, ionic liquids have stimulated the interest of researchers as potential green solvents and/or catalysts. Ionic liquids have been used as solvents and/or catalysts in polymer breakdown. In a low-pressure, low-temperature environment, PET degrades efficiently with ionic liquids without producing hazardous compounds. By adding water via filtering, the ionic liquid can be separated from the chemicals generated, allowing the ionic liquid to be reused [3].

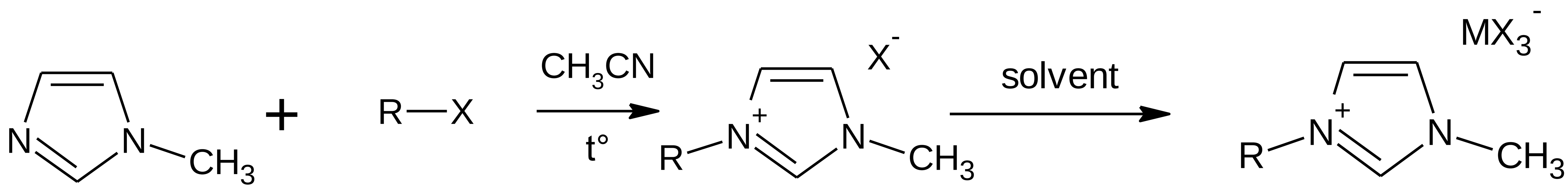
OBJECTIVE

The aim of our work was to obtain, characterize and test a variety in the glycolysis of PET. Following the synthesis, the compounds were analyzed by NMR and FTIR and then tested for PET glycolysis using ethylene glycol (EG) as diol. After each reaction it was calculated the conversion (based on the quantity of PET unreacted) and the selectivity (based on the quantity of isolated monomer, by precipitation from cold water). In addition, some optimum reaction parameters were determined.

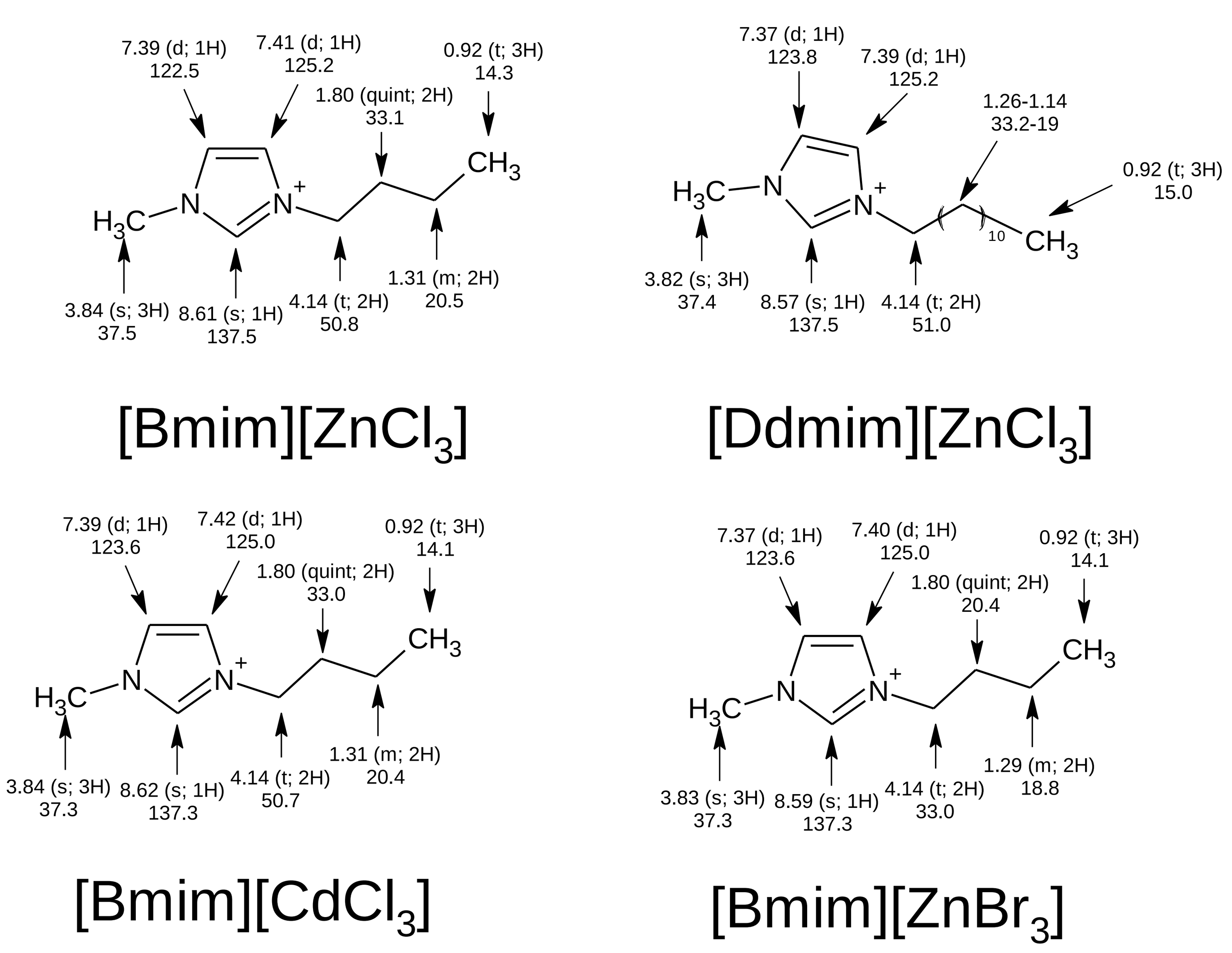


Catalyst	R	X
[Bmim][$ZnCl_3$]	C_4H_9	$ZnCl_3$
[Ddmim][$ZnCl_3$]	$C_{12}H_{25}$	$ZnCl_3$
[Bmim][$CdCl_3$]	C_4H_9	$CdCl_3$
[Bmim][$ZnBr_3$]	C_4H_9	$ZnBr_3$

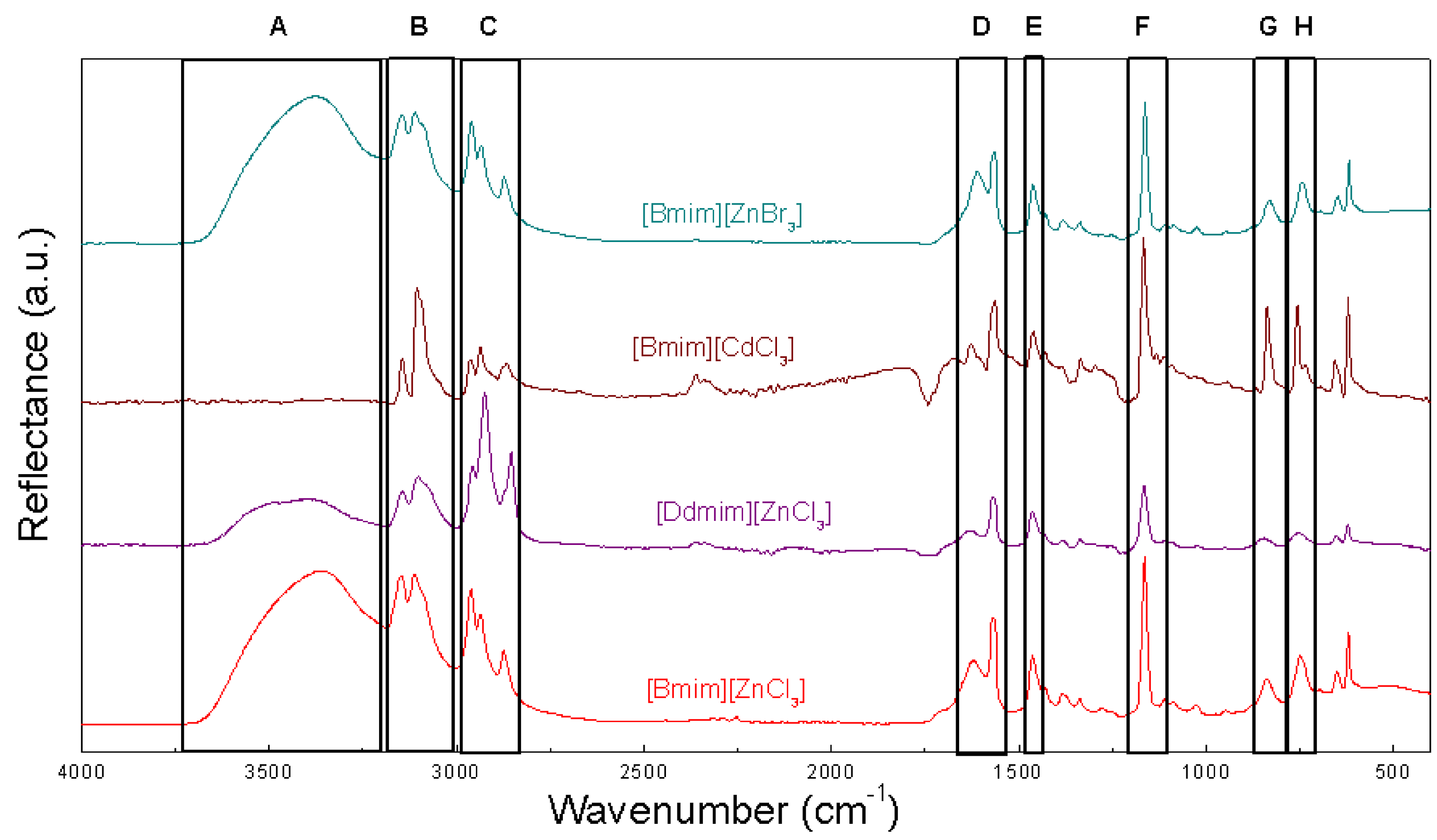
SYNTHESIS AND CHARACTERIZATION OF CATALYSTS



(^{1}H-,^{13}C-) NMR spectra

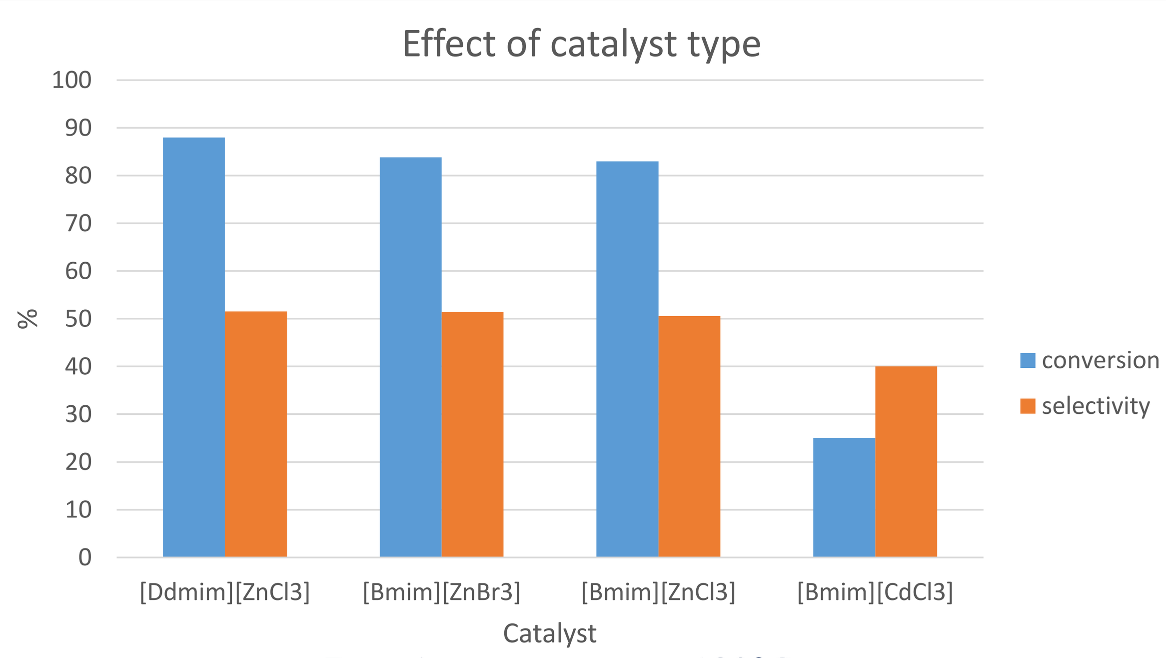


FT-IR spectra

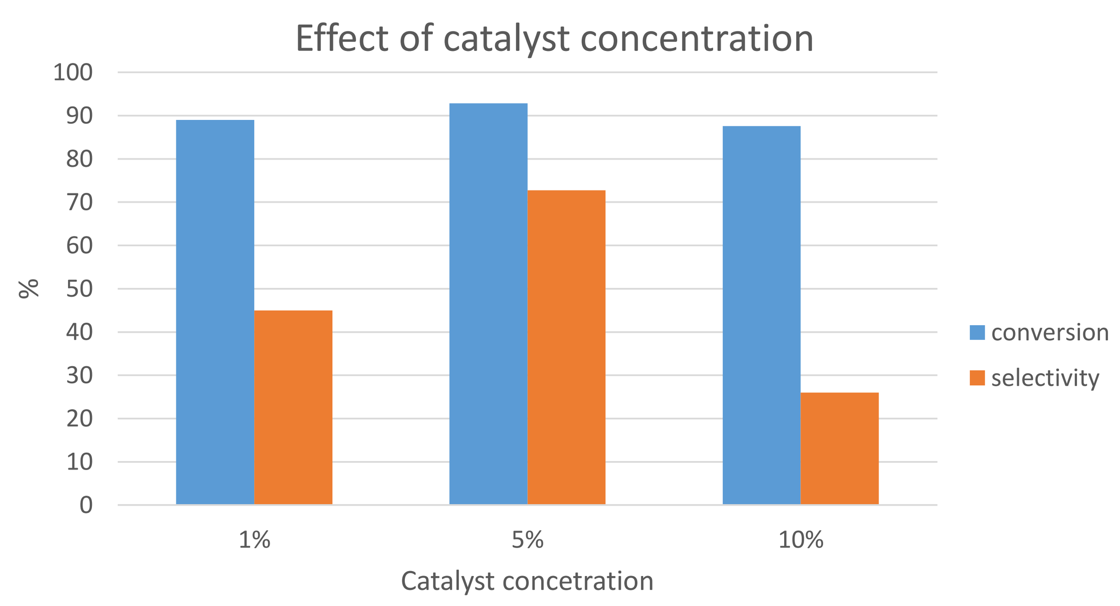


Legend: A – water; B – aromatic C=C; C – C-H stretch; D – C=C & C=N stretch; E – C-C deformation; F – MX_3^- ; G – C-N vibration; H – C-C vibration

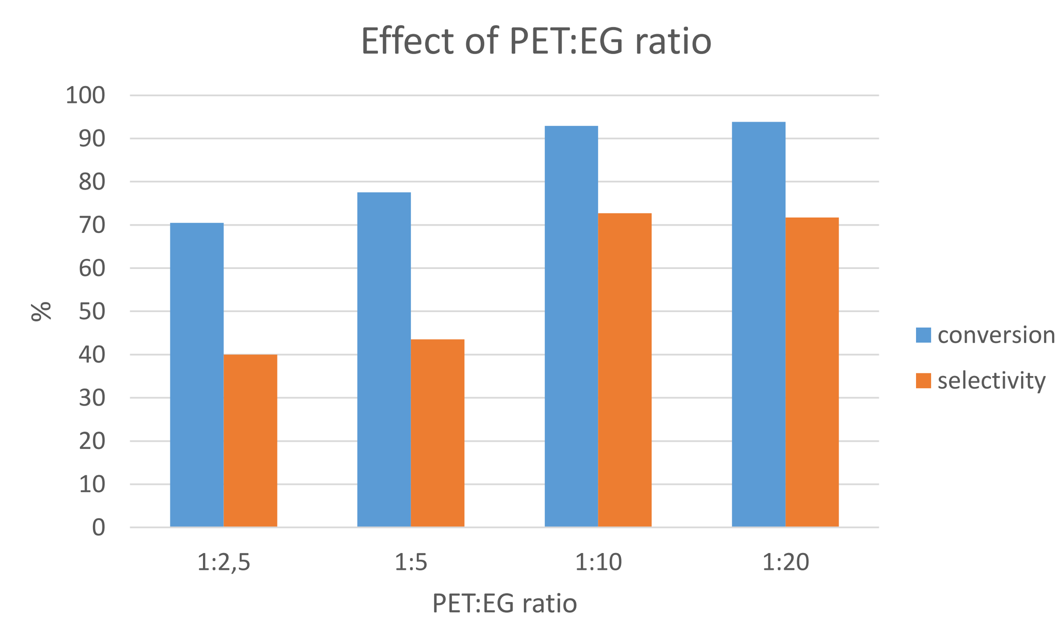
PET GLYCOLYSIS REACTION PARAMETER OPTIMIZATION



- Reaction temperature: 180°C
- Reaction time: 4 h
- PET:EG = 1:10
- Catalyst concentration: 1% molar
- **Optimum catalyst: [Ddmim]$ZnCl_3$**



- Reaction temperature: 180°C
- Reaction time: 4 h
- PET:EG = 1:10
- Catalyst: [Ddmim]$ZnCl_3$
- **Optimum concentration: 5% molar**



- Reaction temperature: 180°C
- Reaction time: 4 h
- Catalyst concentration: 5%
- Catalyst: [Ddmim]$ZnCl_3$
- **Optimum ratio: 1:10**

CONCLUSIONS

• Metal-containing ionic liquids were synthesized is a two step reaction, starting from N-methylimidazole and characterized by nuclear magnetic resonance spectroscopy (NMR) and infrared spectroscopy (FTIR);

• Optimum reaction parameters were determined;

• The new catalyst ([Ddmim]$ZnCl_3$) leads to the best conversion (~90%) and the best selectivity in BHET (~70%) The catalyst loading was 5% molar with respect to PET and the molar ratio was PET:EG=1:10.

REFERENCES

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[3] Shuangjun, C., Weihe, S., Haidong, C. et al., J Therm Anal Calorim 143 (2021), 3489–3497.

ACKNOWLEDGEMENTS

This work was supported by the Executive Agency for Higher Education, Research, Development and Innovation (UEFISCDI): PN-III-P2-2.1-PTE-2019-0355.