

The idea of creating a pollution-free environment has urged the chemical industries to perform reactions under

Synthesis of 1a and 2a

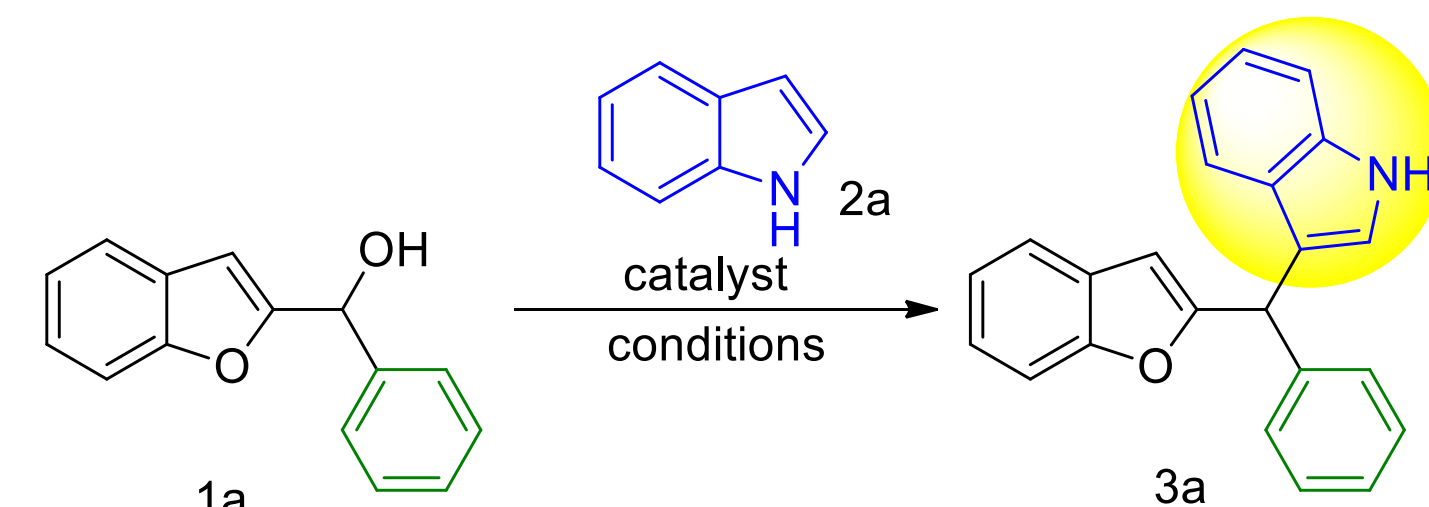
greener conditions

Considering the diverse potential of TRAMs having anticancer, and antibacterial properties as well as their potent cytotoxic activities, and applications in dyes and colorants

it is highly desirable to develop a sustainable strategy to access unsymmetrically substituted triarylmethanes (TRAMs).

The dehydrative substitution reaction in an aqueous medium is a highly challenging operation

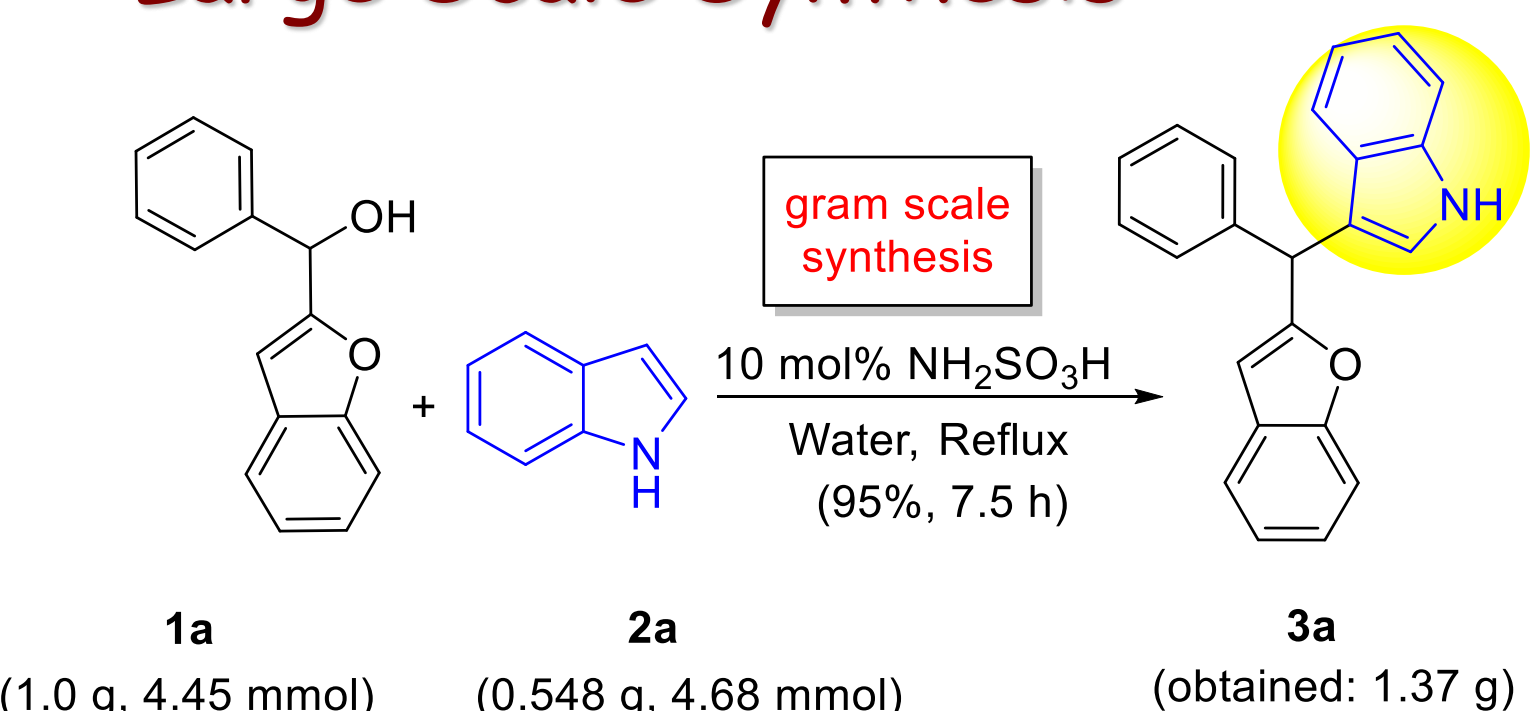
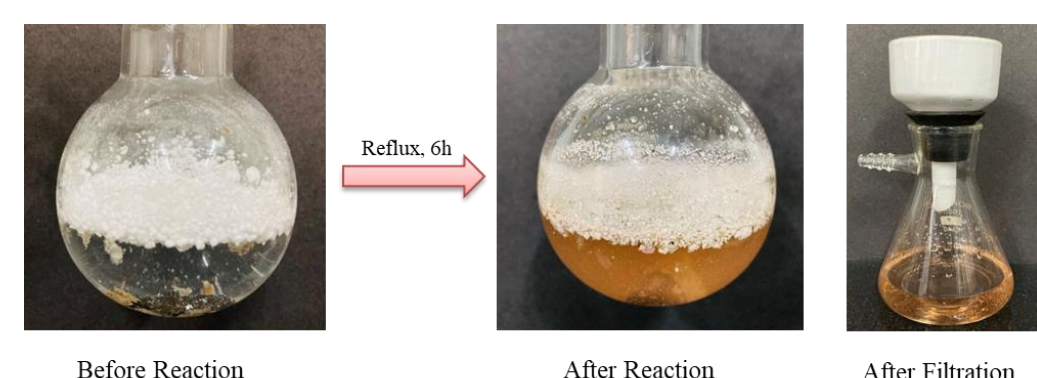
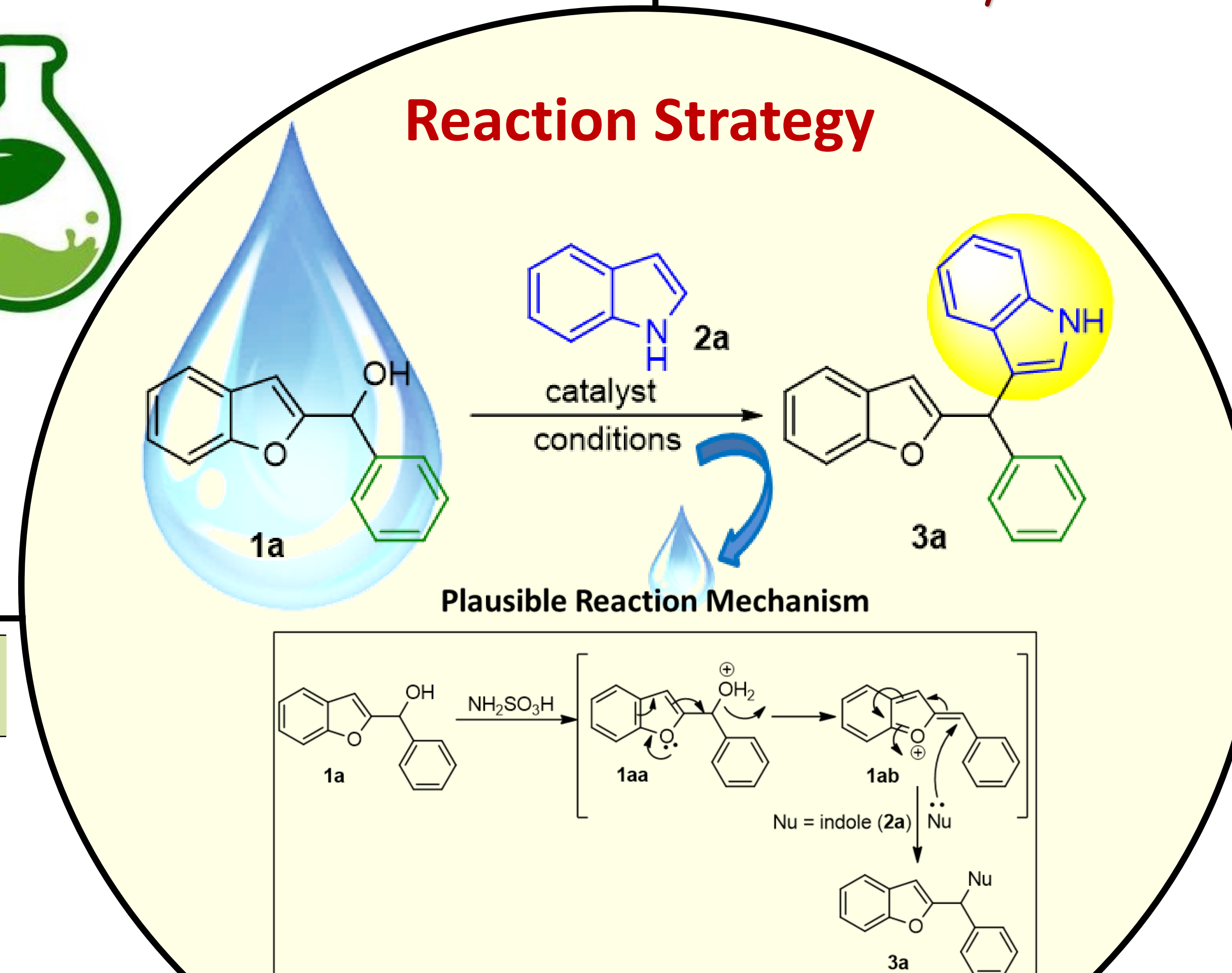
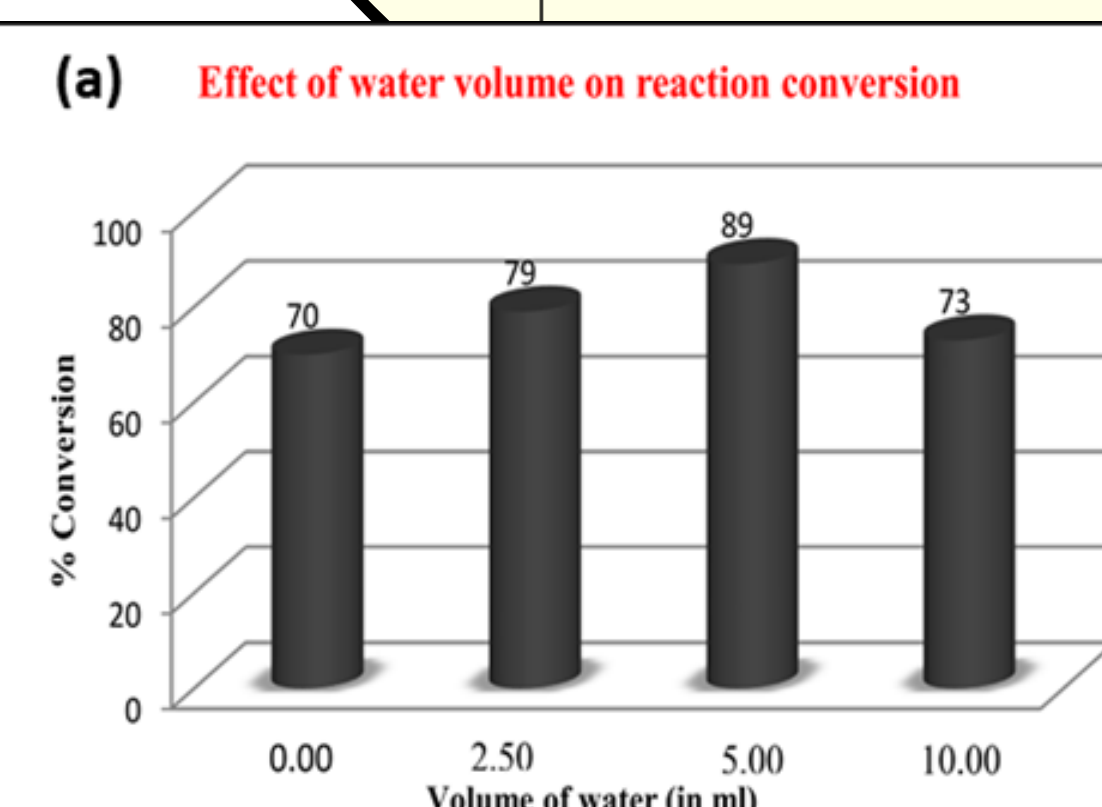
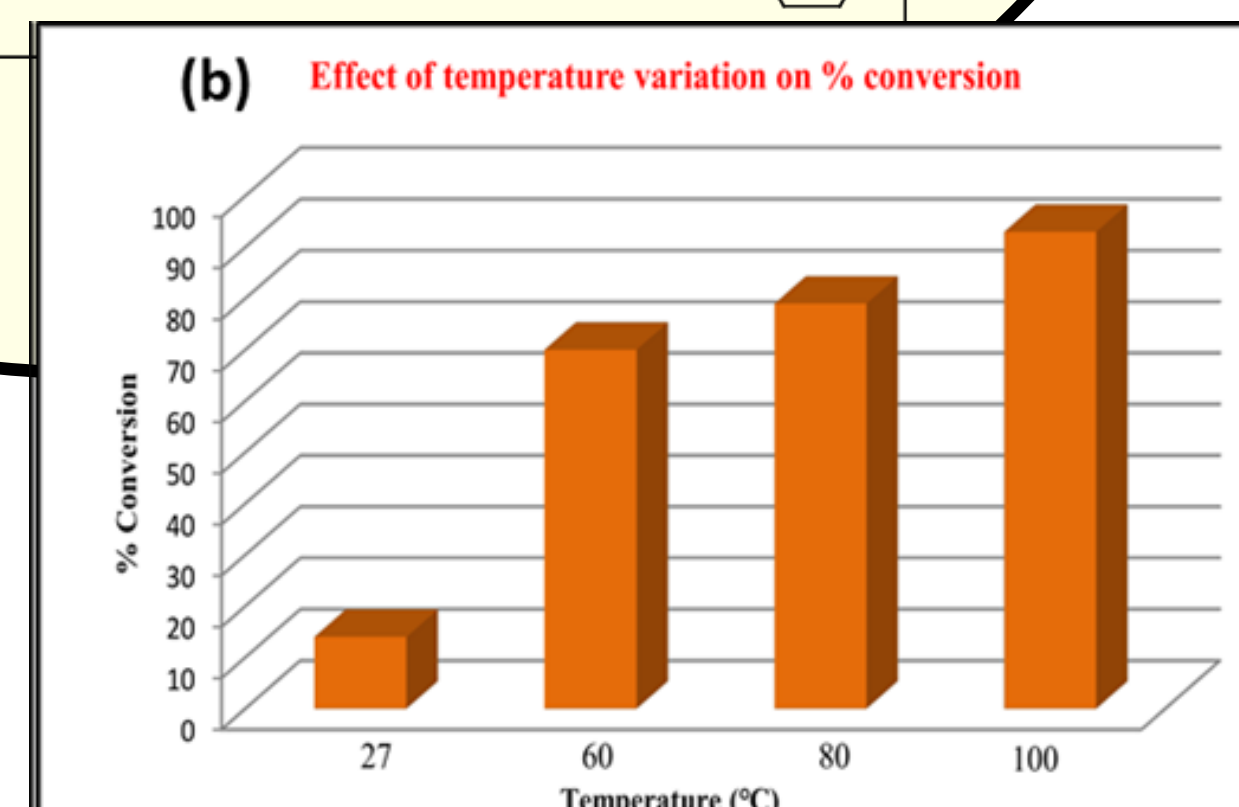
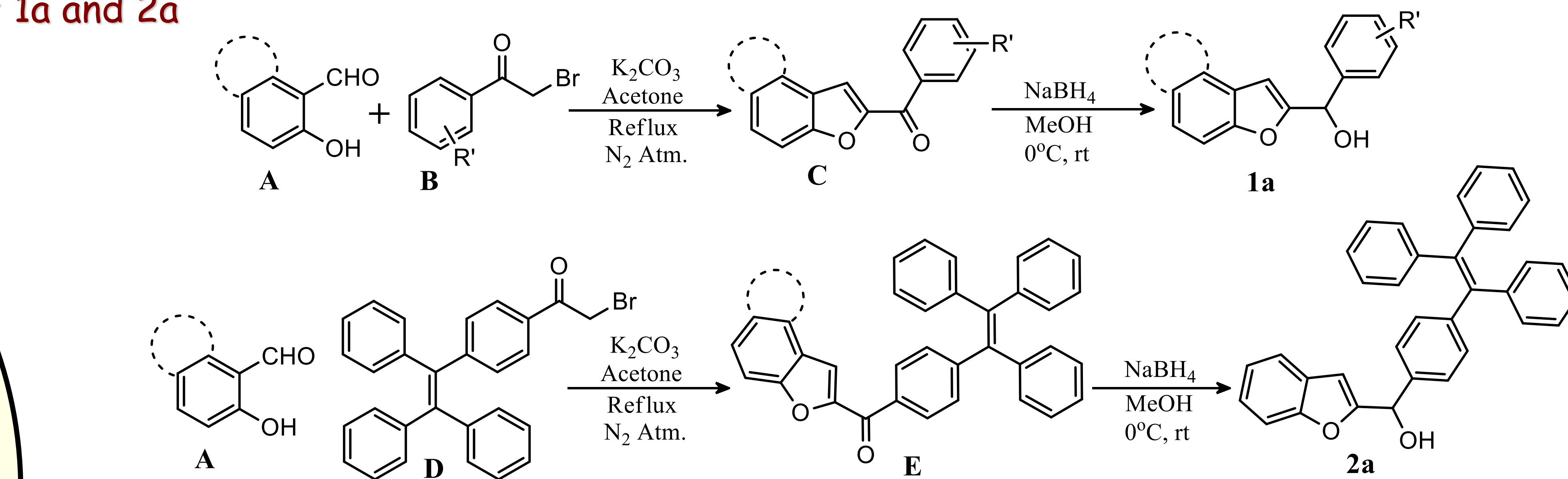
The need for a robust and cheap catalytic system for the dehydrative substitution reaction to address the challenges associated with the scalability of the process, catalyst, and solvent recyclability is highly desirable



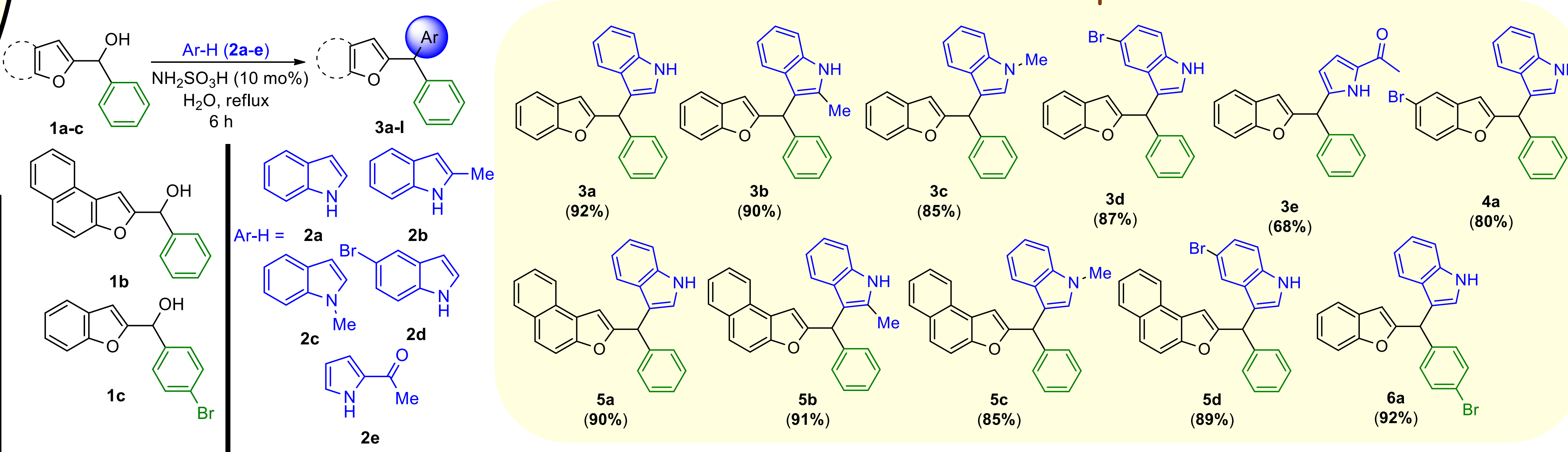
Results and Discussion

Entry	Conditions and catalysts employed	Time (Min.)	% Yield ^b
1	<i>p</i> -TSA; grinding	15	30
2	<i>p</i> -TSA/Na ₂ SO ₄ -grinding	25	25
3	FeCl ₃ -grinding	20	<20 ^c
4	InCl ₃ -grinding	20	50 ^c
5	AlCl ₃ -grinding	25	50 ^c
6	PMA-grinding	20	25 ^c
7	HClO ₄	20	20
8	NH ₂ SO ₃ H-grinding	15	75 ^c
9	NH ₂ SO ₃ H-H ₂ O-reflux (20 mol%)	360	95
10	NH ₂ SO ₃ H-H ₂ O-reflux (10 mol%)	360	92
11	NH ₂ SO ₃ H-H ₂ O-reflux (5 mol%)	360	80
12	No catalyst-H ₂ O-reflux	360	- ^d

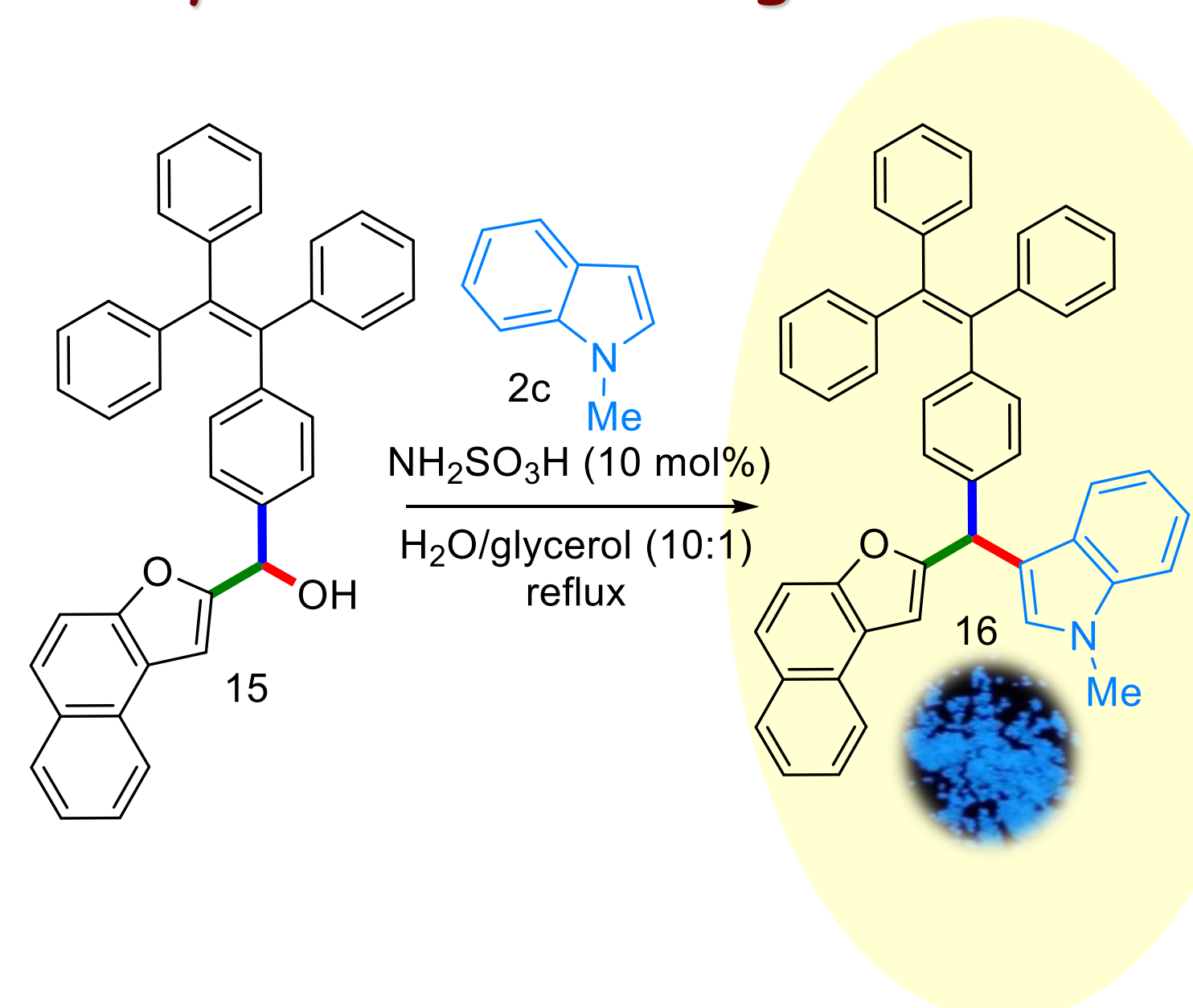
Large Scale Synthesis



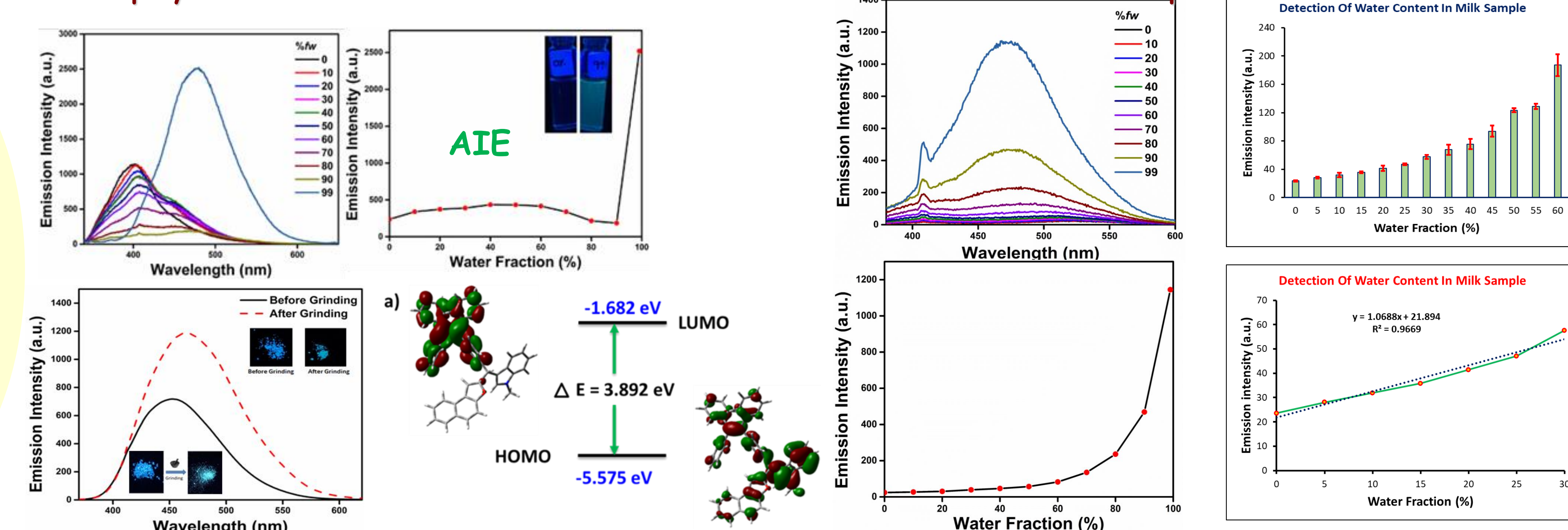
Substrate Scope



Synthesis of AIEgen



Photophysical Studies and Detection of Added Water in Milk Sample



Green Chemistry Metrics

Raw materials consumed	Batch wise production (considering a set of 6 operations)	Current production involving reusing the effluent containing dissolved sulfamic acid
Starting material 1a	1.8 g	1.8 g
Starting material 2a	0.987 g	0.987 g
Catalyst	0.077 g (10 mol%)	0.012 g (10 mol%)
Water	90 ml	15 ml
		Isolated product = 2.441 g % yield = 94.06

Conclusion: 1. Development of sulfamic acid-mediated dehydrative substitution reaction in water to access unsymmetrically substituted TRAMs in good to excellent yield

2. Demonstrated that the same effluent can be re-employed for at least six consecutive batches without compromising the product yield and purity

3. Consumed 6 times lesser solvent and catalyst as compared to the conventional batch-wise operation

4. Methodology was further extended towards developing a green synthetic route to access TRAM

based solid-state emitting material with AIE behaviour

5. Designed luminogen was further engaged to monitor the water added as diluent to the milk sample

References

1. Saha *et. al.* *ChemPlusChem* **2022**, 87, e202200150

Acknowledgements: DST-PURSE, India, UGC-FRP India, TEQIP-III