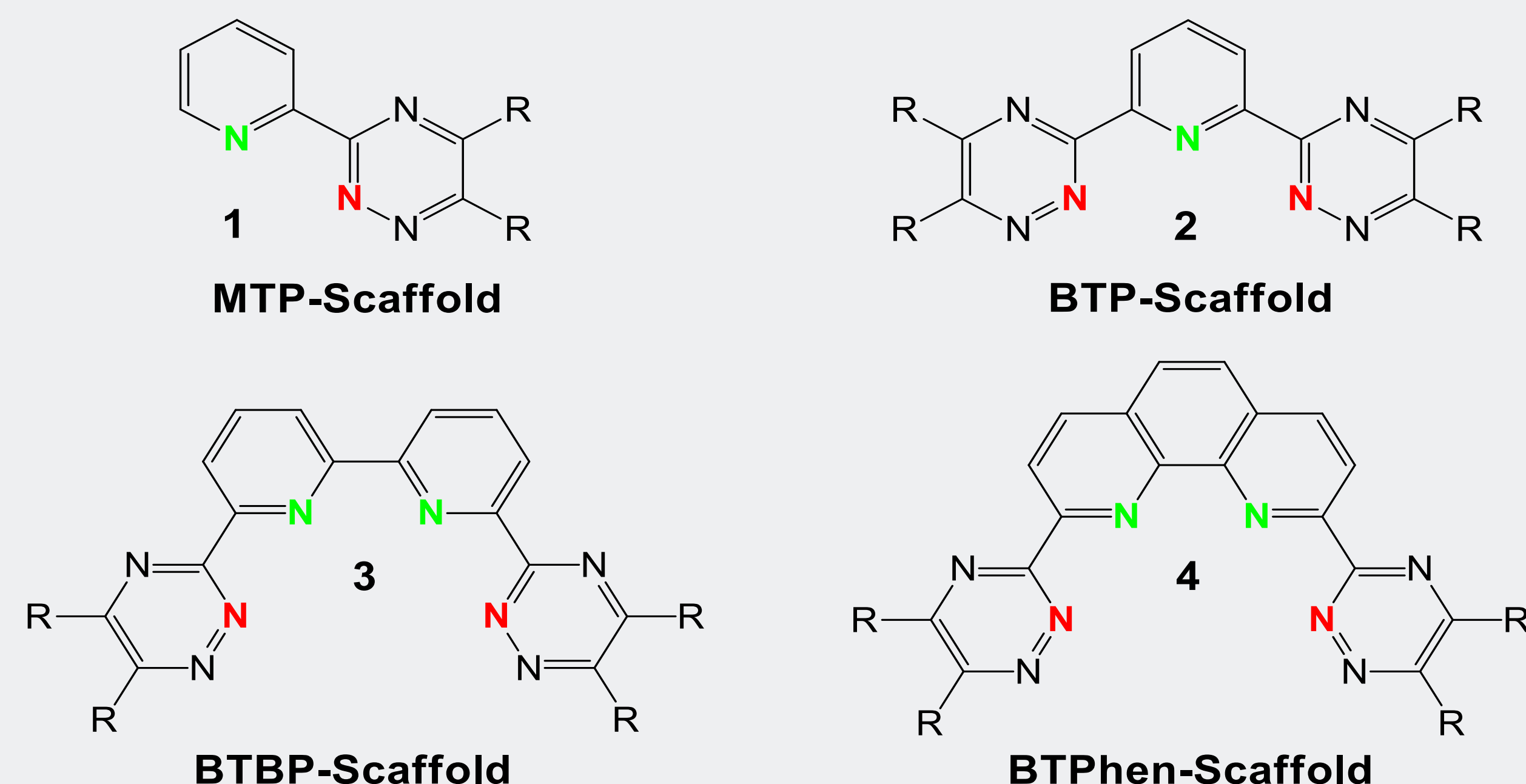


Introduction

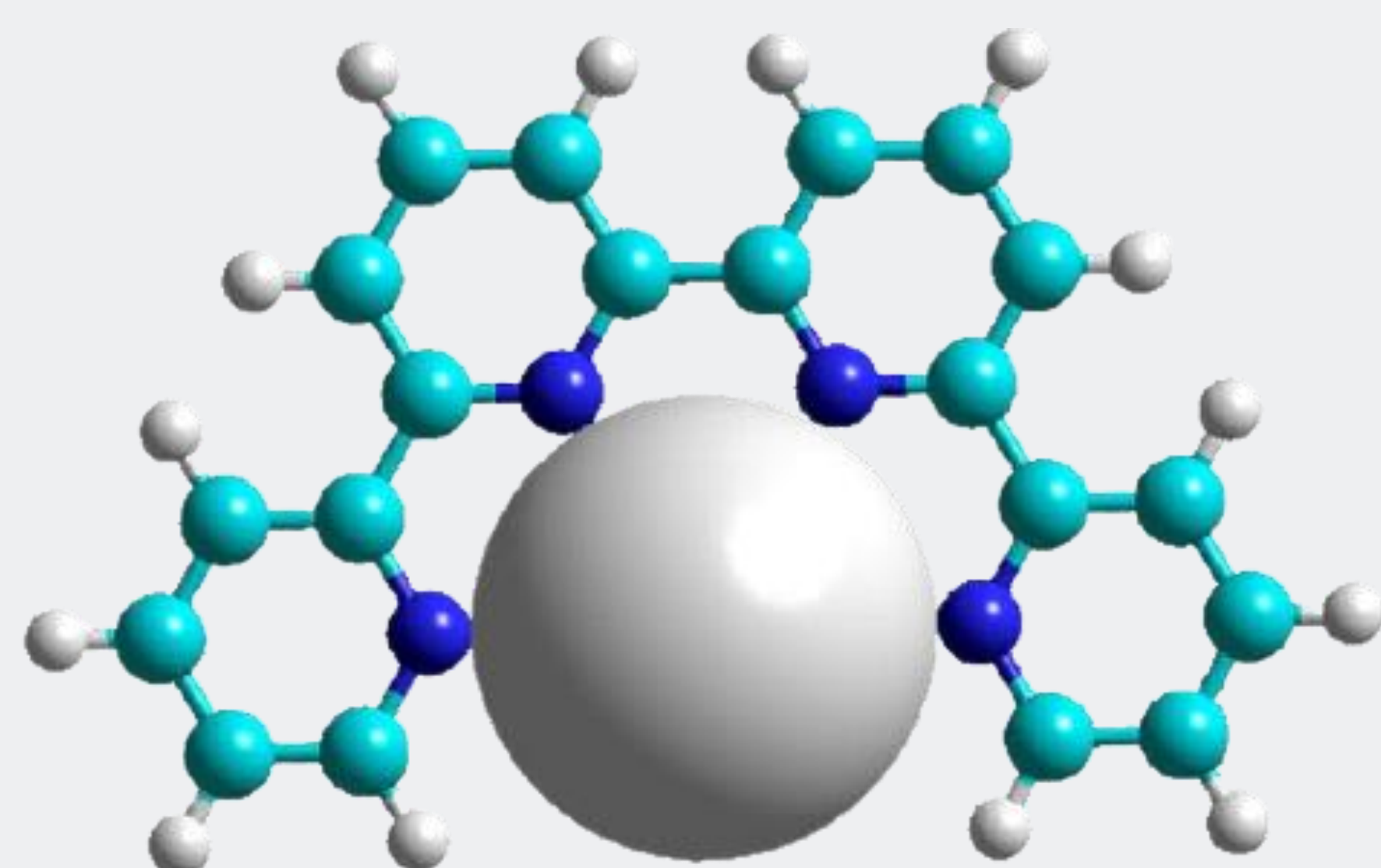
Ongoing efforts in this laboratory continue to design and synthesize novel N-heterocyclic complexant scaffolds for their employment in chemoselective minor actinide separations of spent nuclear fuel.¹ Recovery and remediation of hazardous radioactive isotopes utilized in nuclear fuel in an energy efficient, cost-effective, and environmentally friendly way has been an area of intense research focus in recent years as the need for alternative energy sources has surged. Desired separation processes require extraction of An(III) over Ln(III) in nonpolar solvent systems without degradation over a viable time-scale.² Traditional separation techniques present challenges since these elements have similar atomic radii and other physical properties.

Figure 1. Common soft-N-donor 1,2,4-triazine scaffolds

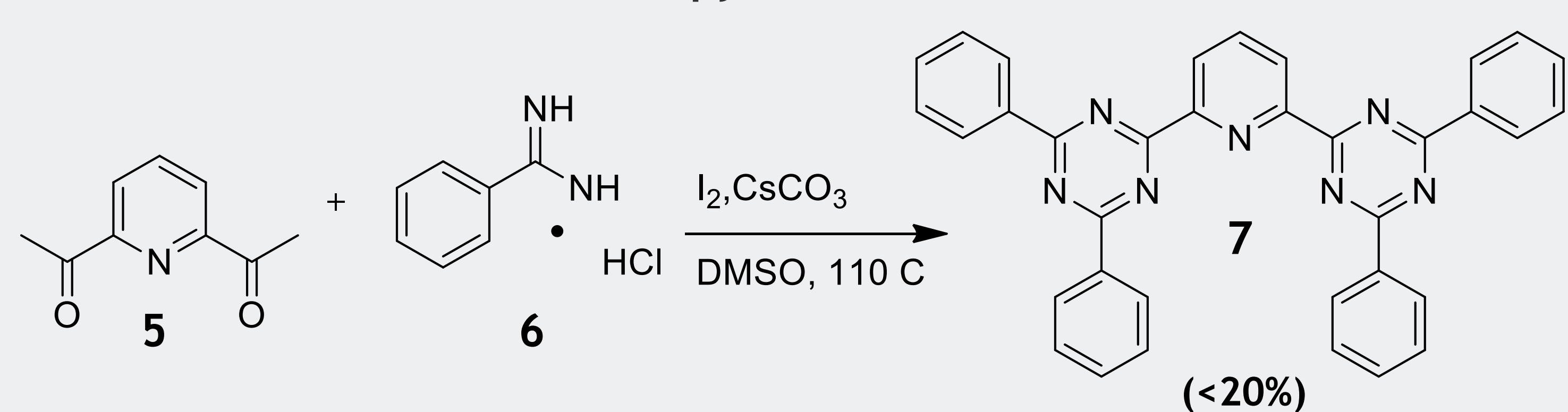


The above scaffolds provide Lewis-basic Nitrogenous zones that chelate to the desired metal to enable extraction. These are all afforded via condensation or metal-mediated coupling. Figure 2 shows a physical representation of a complexant chelated to a metal ion.

Figure 2. BTBP-like Complexant Chelated to Radioactive Metal Ion.³



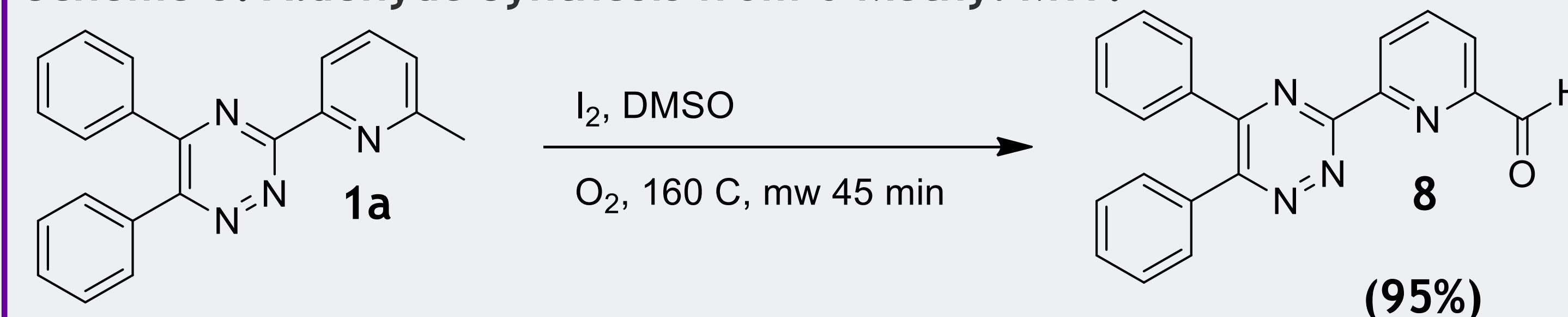
Scheme 1. Oxidative Cyclizations of pyridinyl diketones with Benzamidine salts to Afford Terpy-like scaffolds.⁴



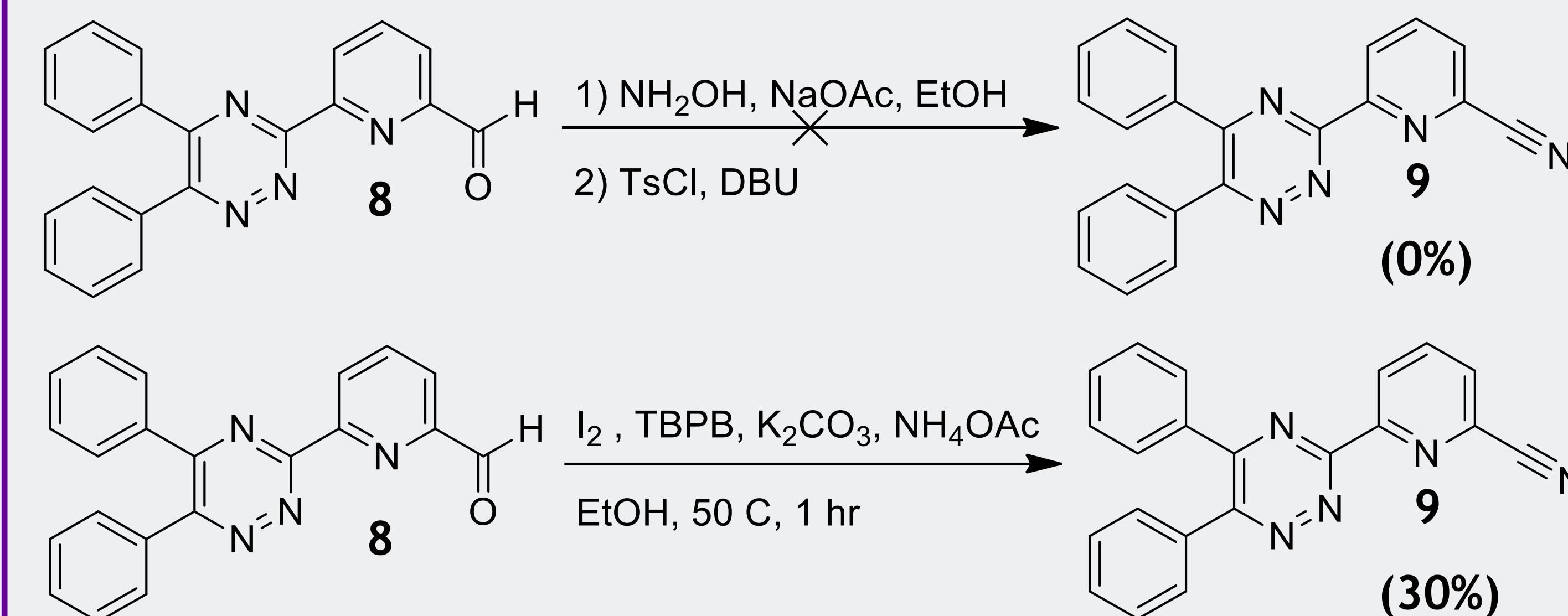
Current Results

The goal of this project is to gain access to diversified scaffolds in order to test their viability in separation assays. Due to the solubility issues of previous synthons, exploring new motifs for their topographic geographies is of high interest. Schemes 3,4, and 6 outline a new methodology to obtain a highly sought after asymmetric BTP from MTP.

Scheme 3. Aldehyde Synthesis from 6-Methyl-MTP.

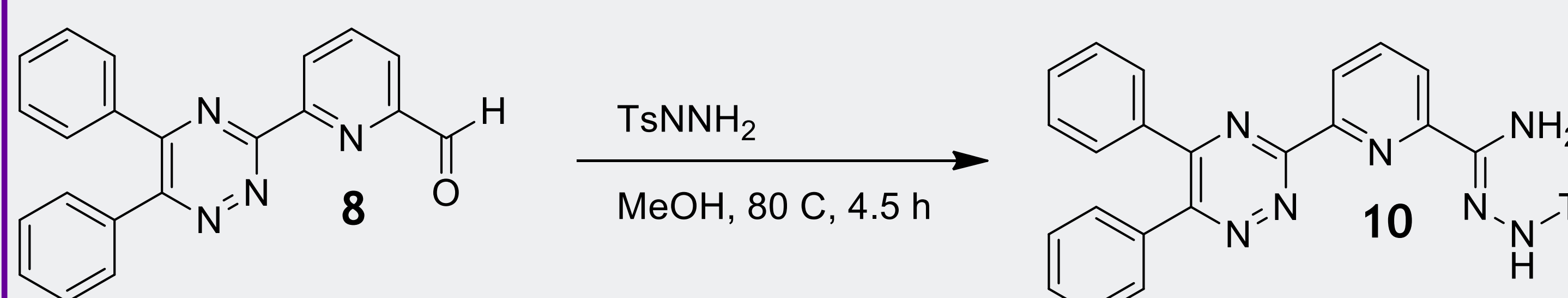


Scheme 4. Cyano Derivatization via two pathways.⁵



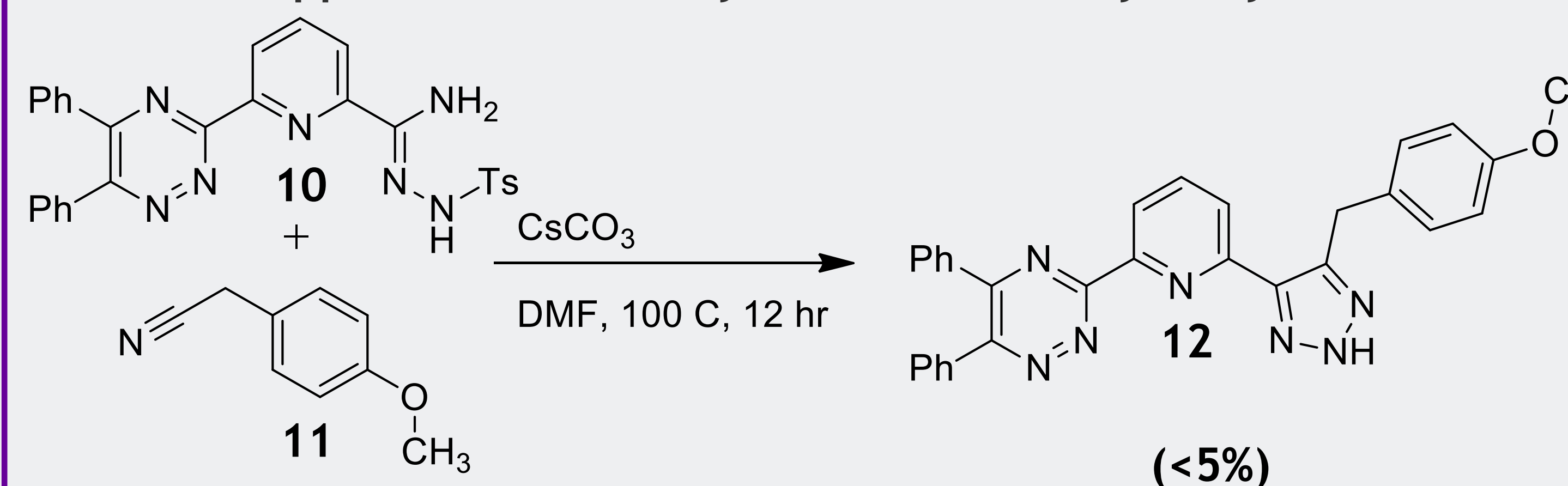
In lieu of using the above reaction pathways, forming a tosyl hydrazone that can then cyclize via basic conditions with a commercially available carbonitrile to form the 1,2,3-triazole motif.

Table 1. Tosyl Hydrazone Solvent Optimization



Entry	Solvent	Conversion(%)	Yield(%)
1	EtOH	100	0
2	IPA	100	0
3	MeOH	100	80

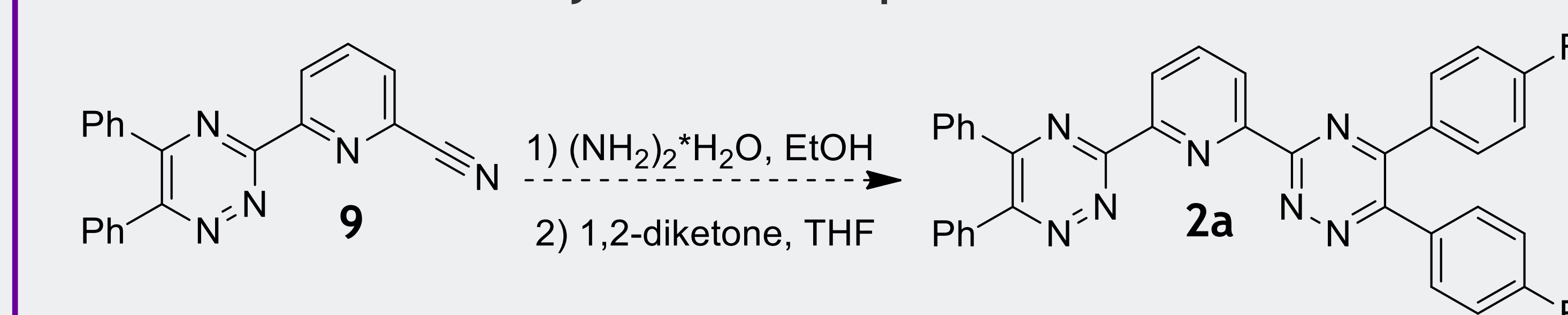
Scheme 5. Approach to Diversely Functionalized Pyridinyl Triazoles.⁶



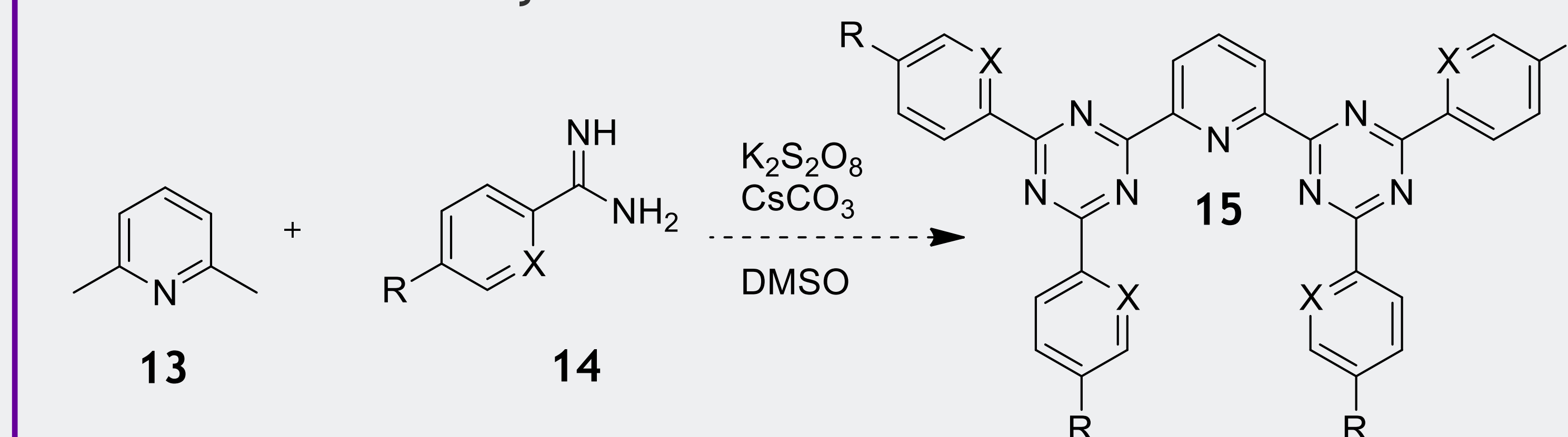
Future Directions

Future work will leverage the results obtained for further investigation into symmetric and unsymmetric novel complexants using these method and others described. Schemes 6,7, and 8 are future experiments to be performed to obtain novel complexants. This work is a continuation of an overall effort to design and synthesize complexant scaffolds via a wide range of modular strategies.⁷

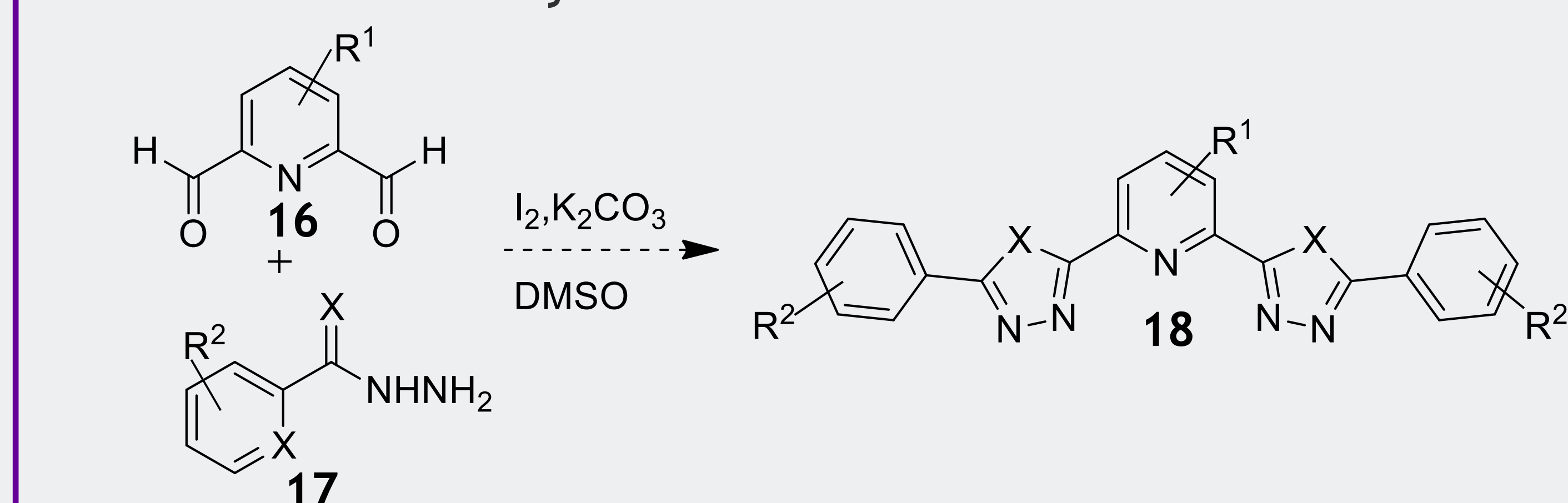
Scheme 6. Diversified Asymmetric Complexant Scaffolds



Scheme 7. Oxidative Cyclizations with Benzamidine Derivatives.⁸



Scheme 8. Oxidative Cyclizations with Benzamidine Derivatives.⁹



Acknowledgements

Financial support for this work was provided by an award from the U.S. Department of Energy, Basic Energy Sciences, Separations Award: DOE-SC0018033. NSF MRI 1531870 is also gratefully acknowledged for the acquisition of the University's 500 MHz NMR spectrometer (2015)

References

- 1) Panak, P. J.; Geist, A. *Chem. Rev.* 2013, 113,1199-1236.
- 2) Tevepaugh, K. N.; Carrick J. D.; Tai, S.; Coonce, J. G.; Delmau, L. G.; Ensor D. D. *Solvent Extr. Ion Exch.* 2016, 34, 13-25.
- 3) Ballance, Daniel G, et. *Inorganica Chimica Acta*, Volume 488,2019,Pages 19-27,
- 4) Bhanage, J. *Org. Chem.* 2017
- 5) RSC Adv., 2017, 7, 1484
- 6) Manna, *Org. Lett.*
- 7) Zhan, *Eur. J. Org. Chem.* 2020
- 8) Zhu, et.al. *Tetrahedron* 2020, 130887