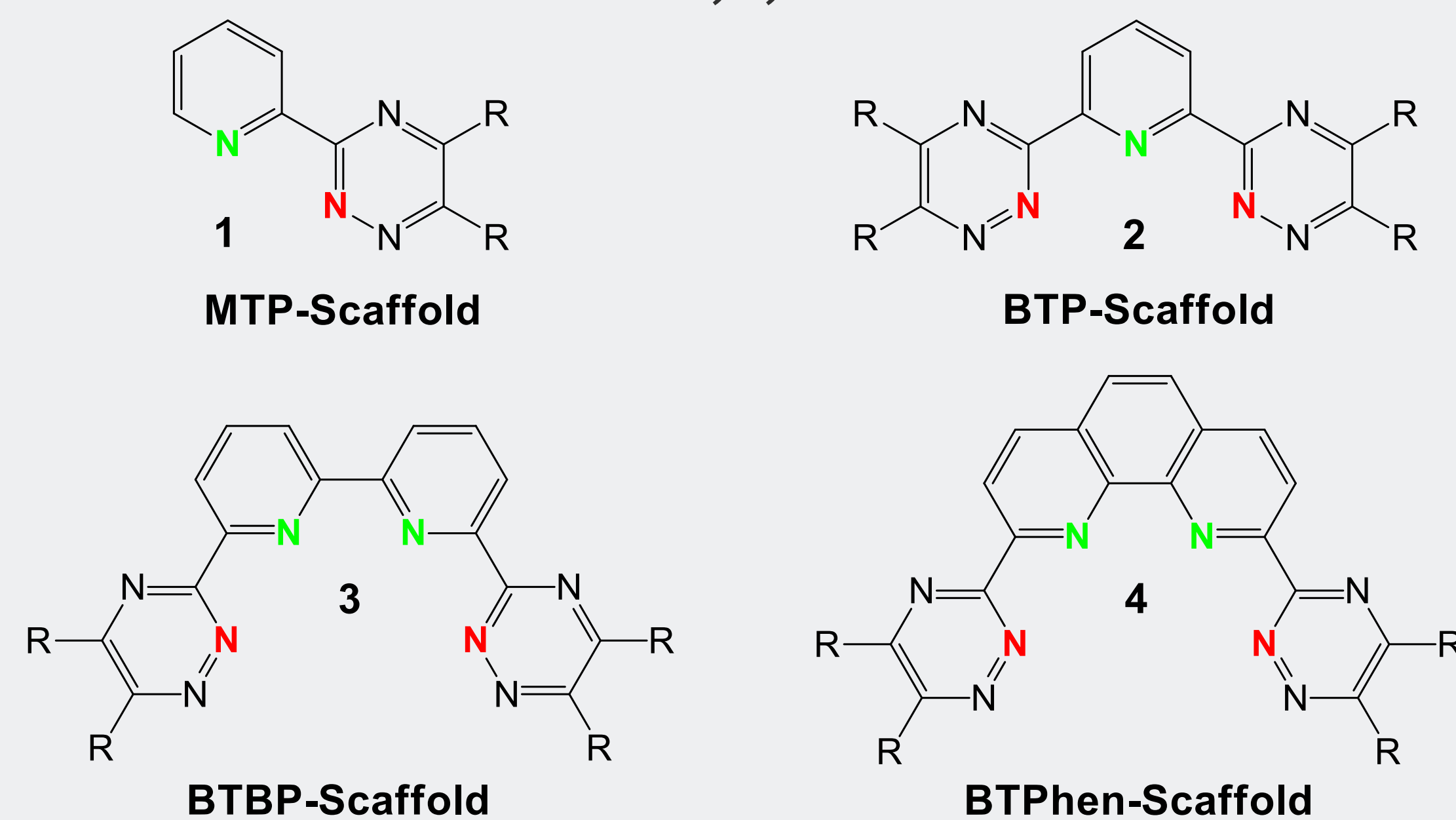


Introduction

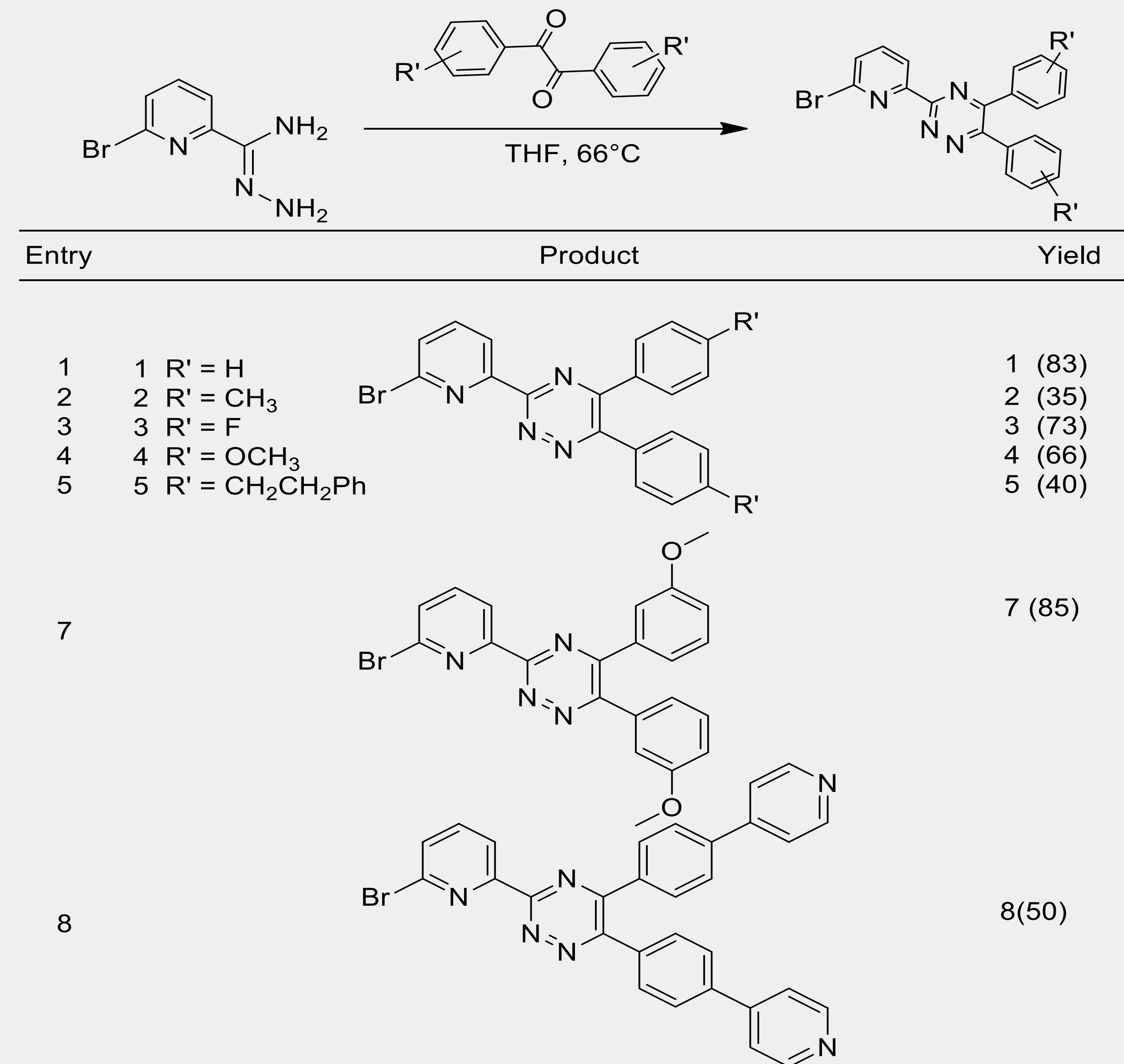
Ongoing efforts in this laboratory continue to design and synthesize novel N-heterocyclic complexant scaffolds for their employment in chemoselective minor actinide separations of spent nuclear fuel.¹ Recovery and remediation of hazardous radioactive isotopes utilized in nuclear fuel in an energy efficient, cost-effective, and environmentally friendly way has been an area of intense research focus for the past few years as the need for alternative energy sources has increased. 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 condensation reaction to afford the bromo-MTP scaffold is the second step after the hydrazone synthesis. This scaffold provides the starting material for the homocoupling that affords the BTBP scaffold.

Table 1. Functionalized Bromo-MTP Scaffolds



Current Results

The goal of this project was to develop and optimize a reaction pathway that afforded the BTBP scaffold. The work began with screening catalysts and ligands. Metals and additives were screened as well in this process to afford final optimized conditions seen in entry 15 in Table 2.

Table 2. Optimization of BTBP synthesis

entry	catalyst	ligand	metal	additive	solvent	temp (°C)	time (h)	conv (%) ^a
1	NiBr ₂ ·3H ₂ O	Phenanthroline	Mn(0)	-----	DMF	40-140	48	0*
2	Pd ₂ (dba) ₃	XPhos	Zn(0)	TFA	DMAc	66-110	48	0*
3	Pd ₂ (dba) ₃	CyPF-tBu	Zn(0)	TFA	Tol	110	24	0
4	Pd(OAc) ₂	RuPhos	Zn(0)	TFA, CuI	DMF	115	48	0
5	Pd(OAc) ₂	XantPhos	Zn(0)	TFA, CuI	DMF	115	48	0
6	Pd ₂ (dba) ₃	CyPF-tBu	Zn(0)	TFA, CuI	DMF	115	48	10
7	Pd(dppf) ₂ Cl ₂	-----	Zn(0)	TEA, CuI	MTBE	55	36	0
8	Pd ₂ (dba) ₃	CyPF-tBu	Zn(0)	CuI	DMF	115	36	30
9	Pd ₂ (dba) ₃	<i>t</i> -BuBrettPhos	Zn(0)	CuI, TMEDA	DMF	115	18	90
10	Pd ₂ (dba) ₃	dppf	Zn(0)	CuI, TMEDA	DMF	115	18	95
11	Pd ₂ (dba) ₃	CyPF-tBu	Zn(0)	CuI, TMEDA	DMSO	115	18	0
12	Pd ₂ (dba) ₃	CyPF-tBu	Zn(0)	CuI	DMF	150	18	90
13	Pd ₂ (dba) ₃	CyPF-tBu	Zn(0)	Cu(0), TMEDA	DMF	115	18	99
14	Pd ₂ (dba) ₃	CyPF-tBu	Zn(0)	CuI, TMEDA	DMF	115	18	99
15	Pd ₂ (dba) ₃	CyPF-tBu	Zn(0)	CuI, TMEDA, DMF	Tol	115	18	99

Table 3. Scope Investigation Towards 2,2'-Bipyridines

Entry	Product	Yield ^b
1		1 (45)
2		2 (93)
3		3 (62)
4		4 (0)
5		5 (pending)
6		6 (10)
7		7 (pending)
8		8 (pending)

Future Directions

Future work will leverage the results obtained for further investigation into symmetric and unsymmetric novel complexants using this optimized method (Table 4). Purification optimization will also continue so pure products can be afforded in higher yields. This work is a continuation of an overall effort to design and synthesize complexant scaffolds via a wide range of modular strategies.⁶

Table 4. Diversified Symmetric Complexant Scaffolds

Entry	Product	Yield
1		1 (98)
2		2 (25)
3		3 (52)
4		4 (10)
5		5 (<5)
6		6 (20)
7		7 (85)
8		8 (<5)

Acknowledgements

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