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Sustainable chemical synthesis of high added-value aromatic compounds through the photochemical valorization of lignin

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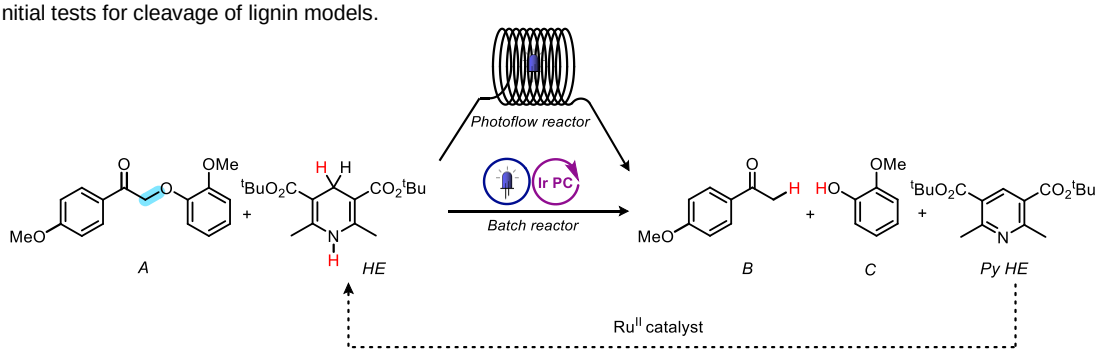
ABSTRACT

Lignin is nature's most abundant source of aromatic compounds and constitutes an attractive renewable resource to produce aromatic commodity chemicals.[1] Bearing this in mind, we propose the conversion of lignin into aromatic platform chemicals through the development of a continuous flow photocatalytic methodology for the reductive cleavage of lignin models using Hantzsch esters (HE) as a source of hydrogen.[2] In this strategy, HE is oxidized leading to the formation of the respective pyridine coproduct, which could be recycled back to the HE through catalytic hydrogenation using Ruthenium(II) catalysts.[3] In batch reactions, lignin model A was cleaved with HE in the presence of Iridium photocatalysts, providing products B and C in 84% yield at room temperature in 5 hours. Under continuous flow conditions, products B and C were obtained in 75% and 70% yield, respectively, in just 15 minutes. Following the optimization of reaction conditions, we plan to evaluate more complex lignin models and lignin itself.

Table 1. Initial tests for cleavage of lignin models.



Entry	Catalyst (loading)	Time	Condition	Conversion (%)	Yield B/C (%)
1	$[Ir(ppy)_2(dtbbpy)]PF_6$ (0.3%)	5 h	Batch	100	84/84
2	$[Ru(bpy)_3]Cl_2$ (0.5%)	4 h	Batch	40	29/24
3	$[Ru(bpy)_3]Cl_2$ (0.5%)	20 h	Batch	40	40/36
4	Eosin Y (1%)	20 h	Batch	82	*traces*
5	Rhodamine G (1%)	20 h	Batch	75	5/2
6	Fluorescein (1%)	20 h	Batch	0	*no reaction*
7	$[Ir(ppy)_2(dtbbpy)]PF_6$ (0.5%)	15 min	Flow	95	**75/70**
8	$[Ir(ppy)_2(dtbbpy)]PF_6$ (0.5%)	10 min	Flow	86	57/51

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