



Polarity-Reversed Trifluoroacetyl Radical Three-Component Assembly of Alkene-Heteroarene Frameworks via Consecutive Photoinduced Electron Transfer

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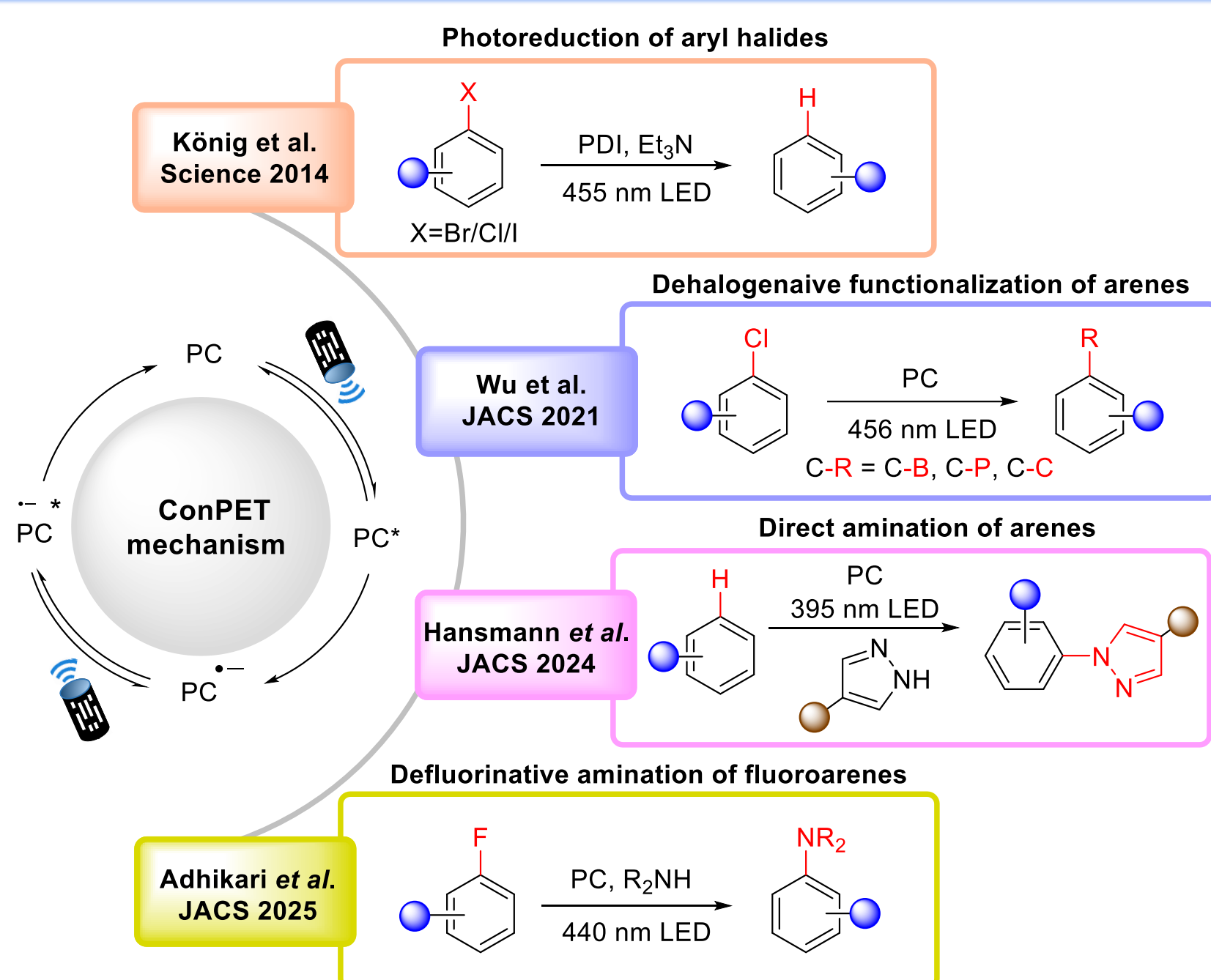
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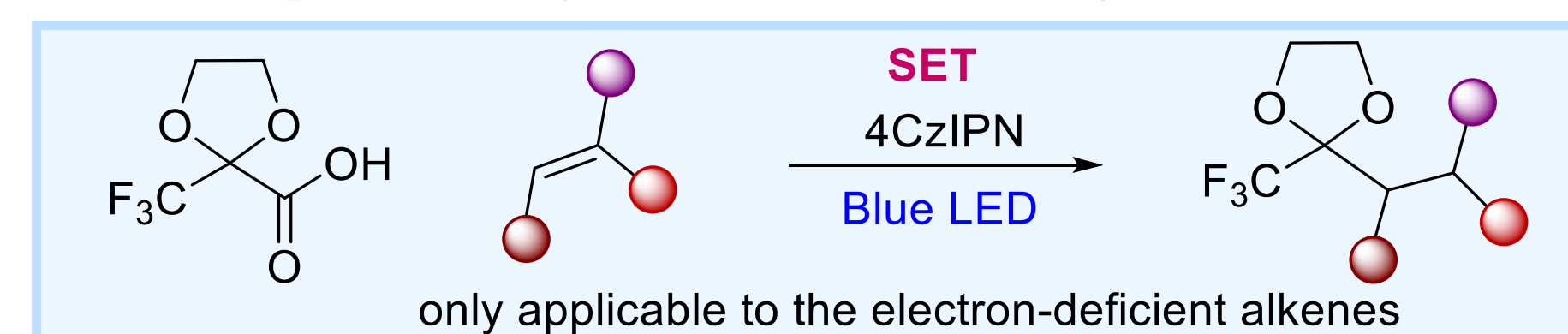
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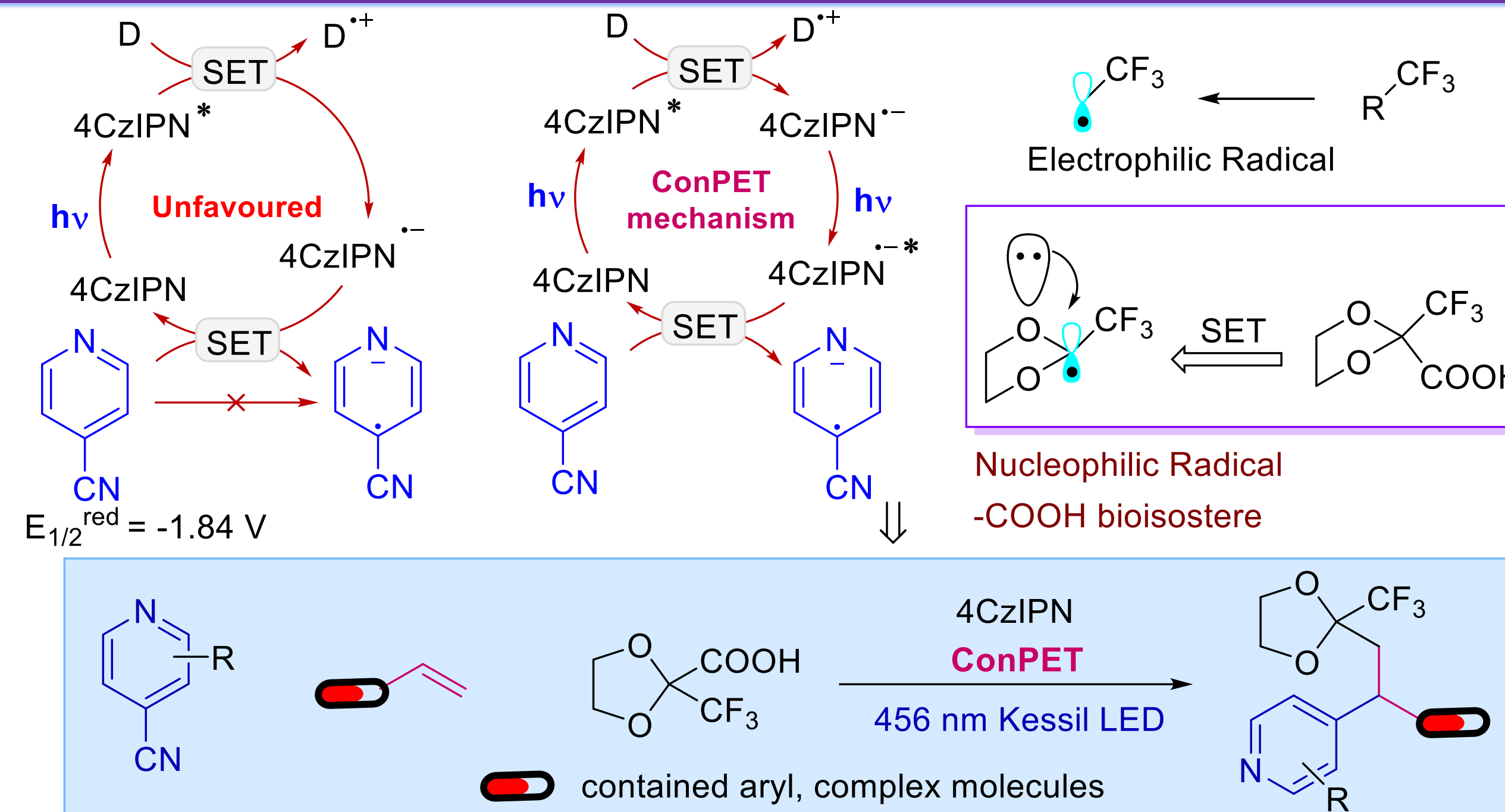
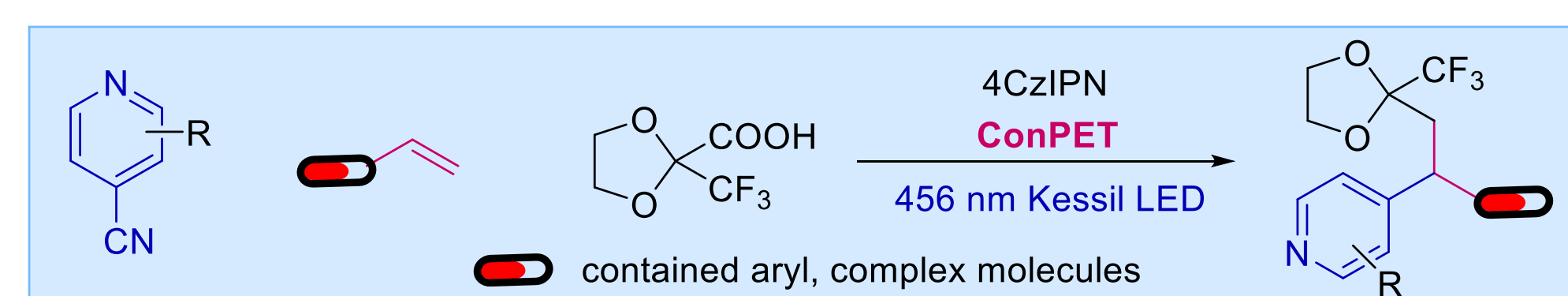
Abstract: The incorporation of fluorinated motifs, particularly CF₃CO groups, into electron-deficient molecular frameworks remains a persistent challenge due to the intrinsic electrophilic character. Herein, we report a three-component, mild and efficient protocol that achieves both trifluoroacetylation and heteroarylation of broad class of alkenes. Our strategy employs a masked trifluoroacetyl precursor to invert the native electrophilicity of the CF₃CO unit. Mechanistically, the reaction operates via a consecutive photoinduced electron transfer (ConPET) pathway involving two-photon excitation process. This protocol is compatible with late-stage functionalization of structurally complex unsaturated coupling partner and proposed mechanism is corroborated by a detailed mechanistic study.



(a) Two component hydrotrifluoroacetylation of alkenes

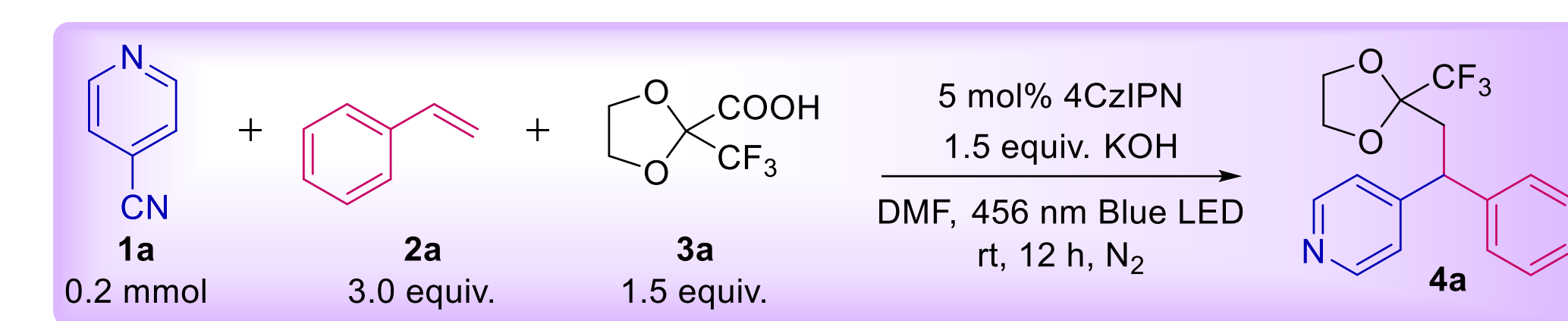


(b) This work: Three component, modular access to pyridyl-trifluoroacetyl-ation of alkenes via masked acyl group

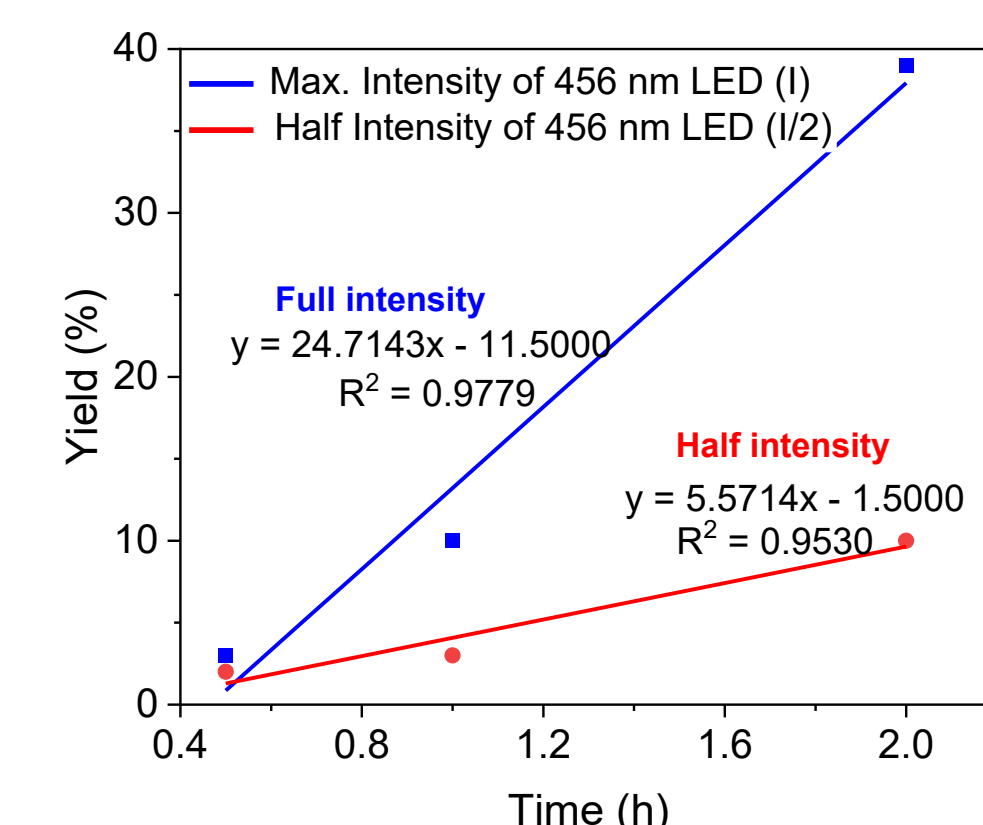
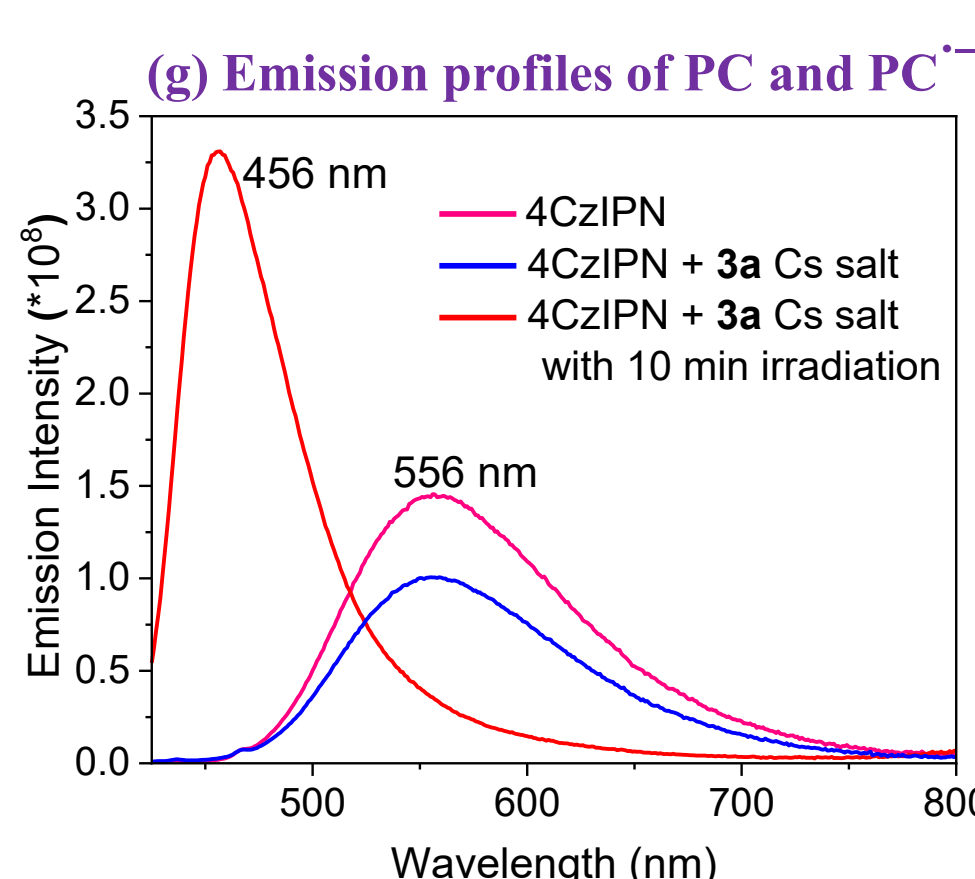
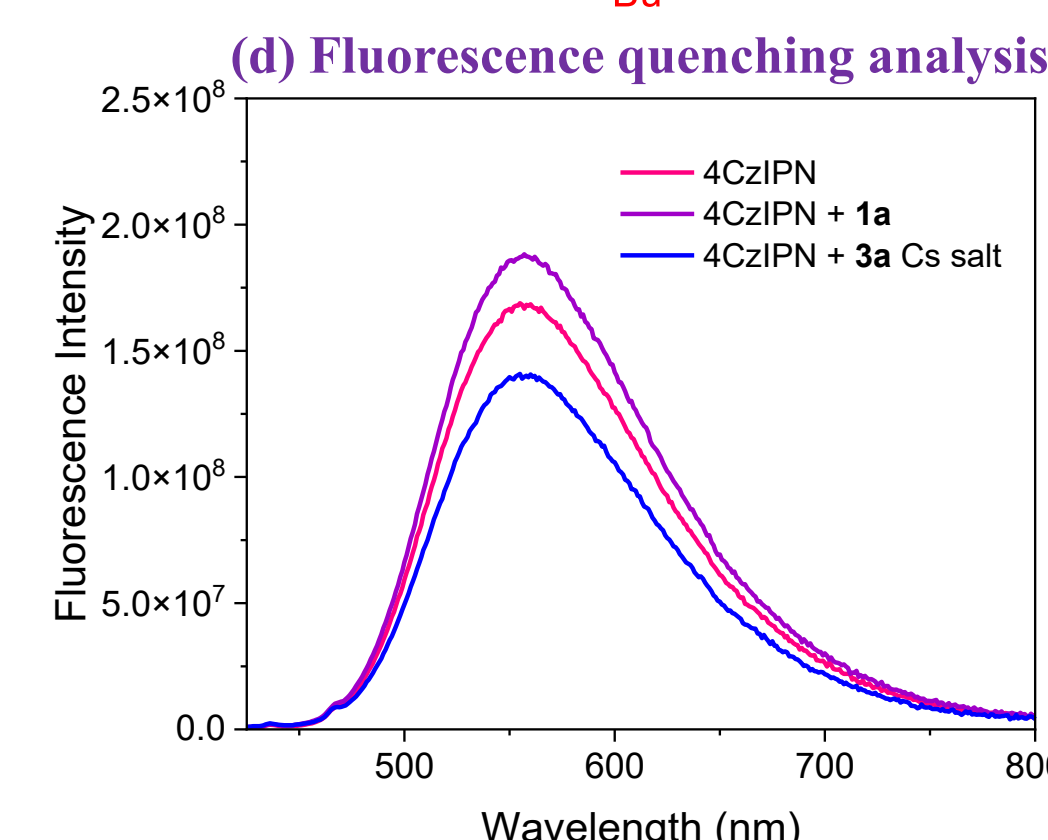
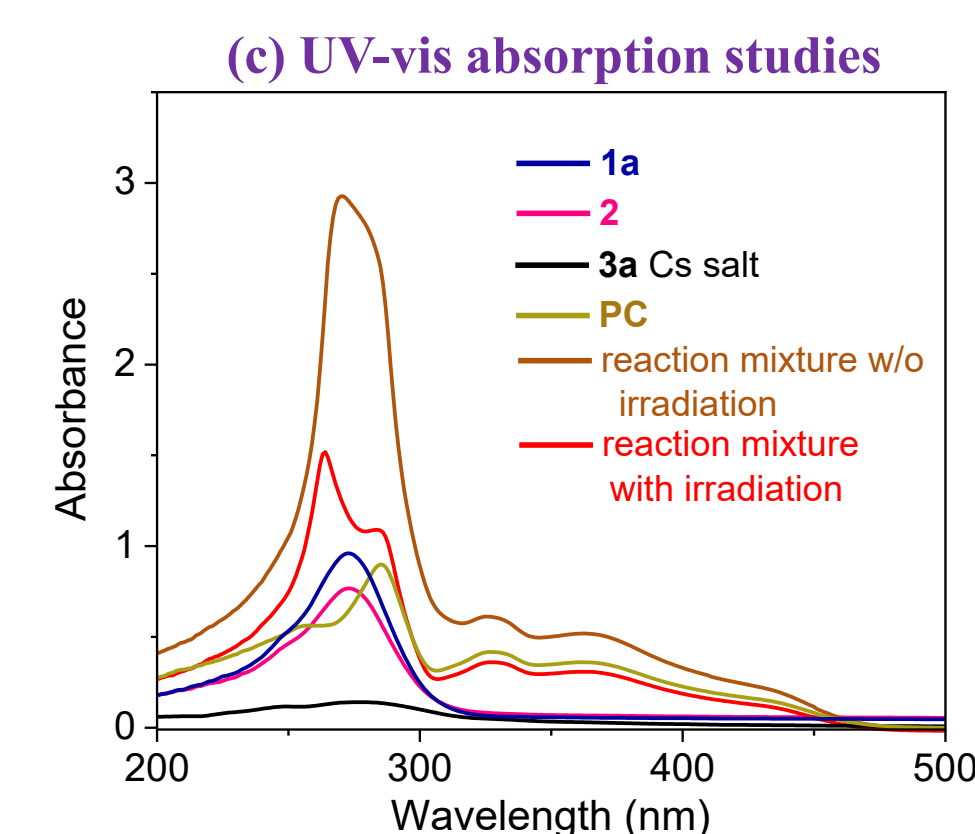
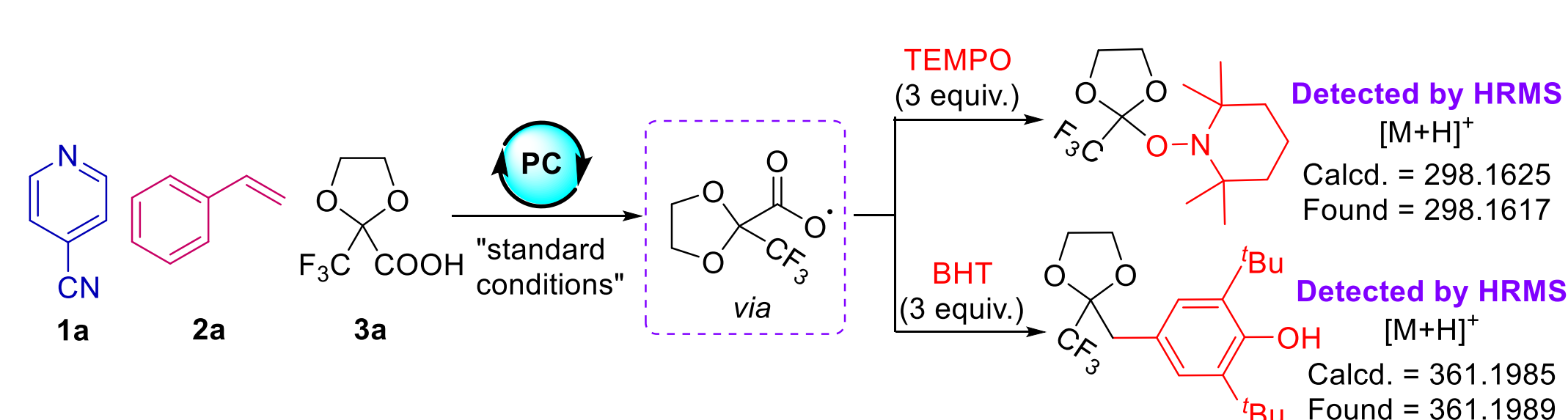


(c) Optimization table

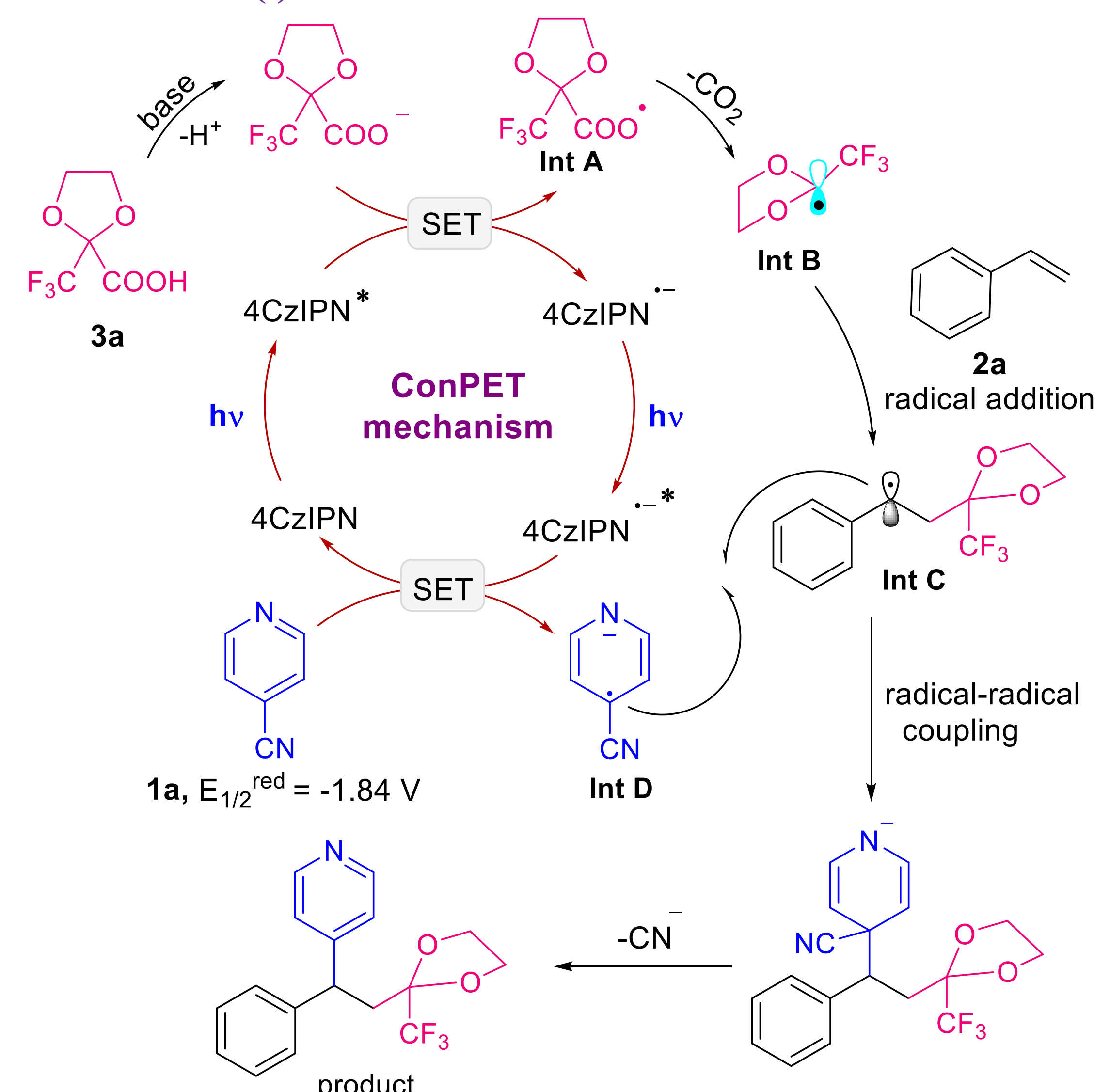
Entry	variation from the standard conditions	Yield 4a(%)
1.	None	70
2.	DBU, DABCO and Cs ₂ CO ₃ instead of KOH	0, 0, 40
3.	DMSO, MeCN, EtOAc instead of DMF	65, 35, 0
4.	Eosin Y instead of 4CzIPN	0
5.	Ru-complexes instead of 4CzIPN	0
6.	390 nm LED, White LED	55, 59
7.	CF ₃ COOH, CF ₃ COCOOH	0, 0



Entry	deviation from the standard conditions	Yield 4a(%)
1.	No light	0
2.	No photocatalyst	0
3.	No base	0
4.	Oxygen environment	15
5.	60 °C (dark)	0
6.	TEMPO, BHT	0, 0



(i) Plausible reaction mechanism



(1) Selected Examples

