

Table S1 Optimization of the reaction conditions^a

Entry	E ⁺	Solvent	Base	Time/h	Yield (%) ^b
1	I ₂	THF	—	24	Trace
2	I ₂	CHCl ₃	—	24	33
3	I ₂	ClCH ₂ CH ₂ Cl	—	24	63
4	I ₂	CH ₂ Cl ₂	—	24	75
5	I ₂	Toluene	—	24	44
6	I ₂	Xylene	—	24	48
7	I ₂	ClCH ₂ CH ₂ Cl	NaHCO ₃	12	85
8	I₂	CH₂Cl₂	NaHCO₃	12	95
9	I ₂	CH ₂ Cl ₂	K ₂ CO ₃	12	84
10	I ₂	CH ₂ Cl ₂	K ₃ PO ₄	12	76
11	I ₂	CH ₂ Cl ₂	KOBu ^t	12	0
12	I ₂	CH ₂ Cl ₂	CH ₃ ONa	12	0
13	NIS	CH ₂ Cl ₂	NaHCO ₃	12	0
14	ICl	CH ₂ Cl ₂	NaHCO ₃	12	78
15	I ₂	CH ₂ Cl ₂ (dry)	NaHCO ₃	12	64
16	I ₂	CH ₂ Cl ₂ (5%aq)	NaHCO ₃	12	66

^a Reaction conditions: unless indicated otherwise, all reactions were run by employing 0.25 mmol of enynebenzaldehyde, 2 equiv. of electrophile and 2 equiv. of base in 3 mL of solvent stirred at room temperature. ^b Isolated yields.