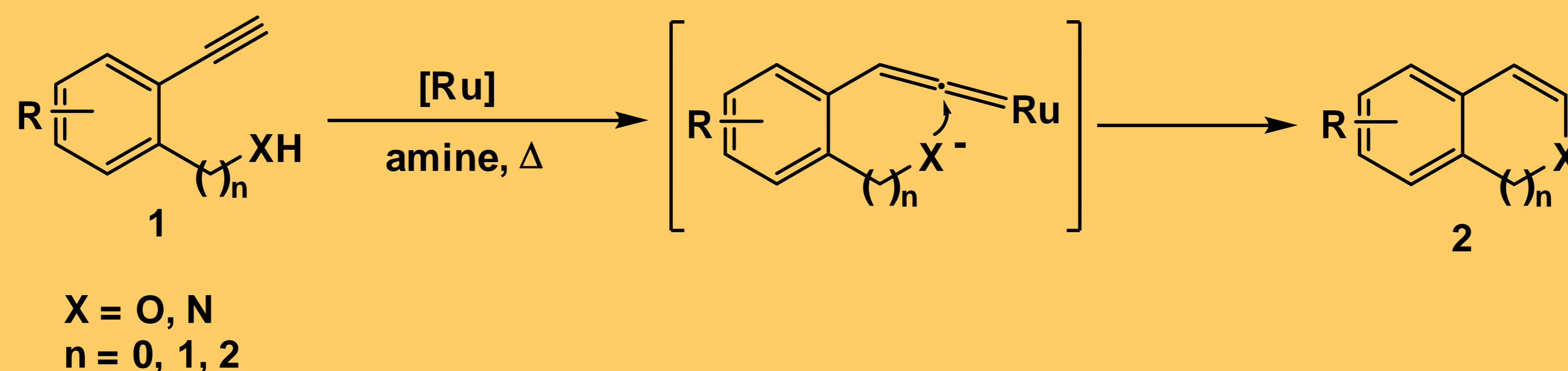


Heterocyclic compounds are widely spread in Nature. The development of new metal-catalyzed cyclizations can offer powerful means to synthesize these compounds.¹ An attractive approach to this end, under the basis of atom economy,² makes use of catalytic metal vinylidenes.³ Herein we present new 5-, 6- and 7-endo cyclizations of aromatic α,ω -alkynols and alkynylamines to the corresponding heterocyclic compounds.



Oxygen

5-membered rings \Rightarrow Benzofurans

Entry	Substrate	Product	Yield (%) [a]
1			84
2			30 [b]
3			82

[a] 10% CpRu(PPh₃)₂Cl, pyridine, 90°C, 2-6 h [b] 10% CpRu(PPh₃)₂Cl, n-BuNH₂, 90°C, 5-8h

Nitrogen

5-membered rings \Rightarrow Indoles

Entry	Substrate	Product	Yield (%) [a]
1			54
2			80
3			98

[a] 10% CpRu(PPh₃)₂Cl, pyridine, 90°C, 1-2h

6-membered rings \Rightarrow Isochromenes

Entry	Substrate	Product	Yield (%) [a]
1			86
2			60
3			65 [b]

[a] 10% CpRu(PPh₃)₂Cl, n-BuNH₂, 90°C, 2-6 h [b] 10% CpRu(PPh₃)₂Cl, pyridine, 90°C, 5-8h

6-membered rings \Rightarrow Isoquinolines

Entry	Substrate	Product	Yield (%) [a]
1			82
2			80

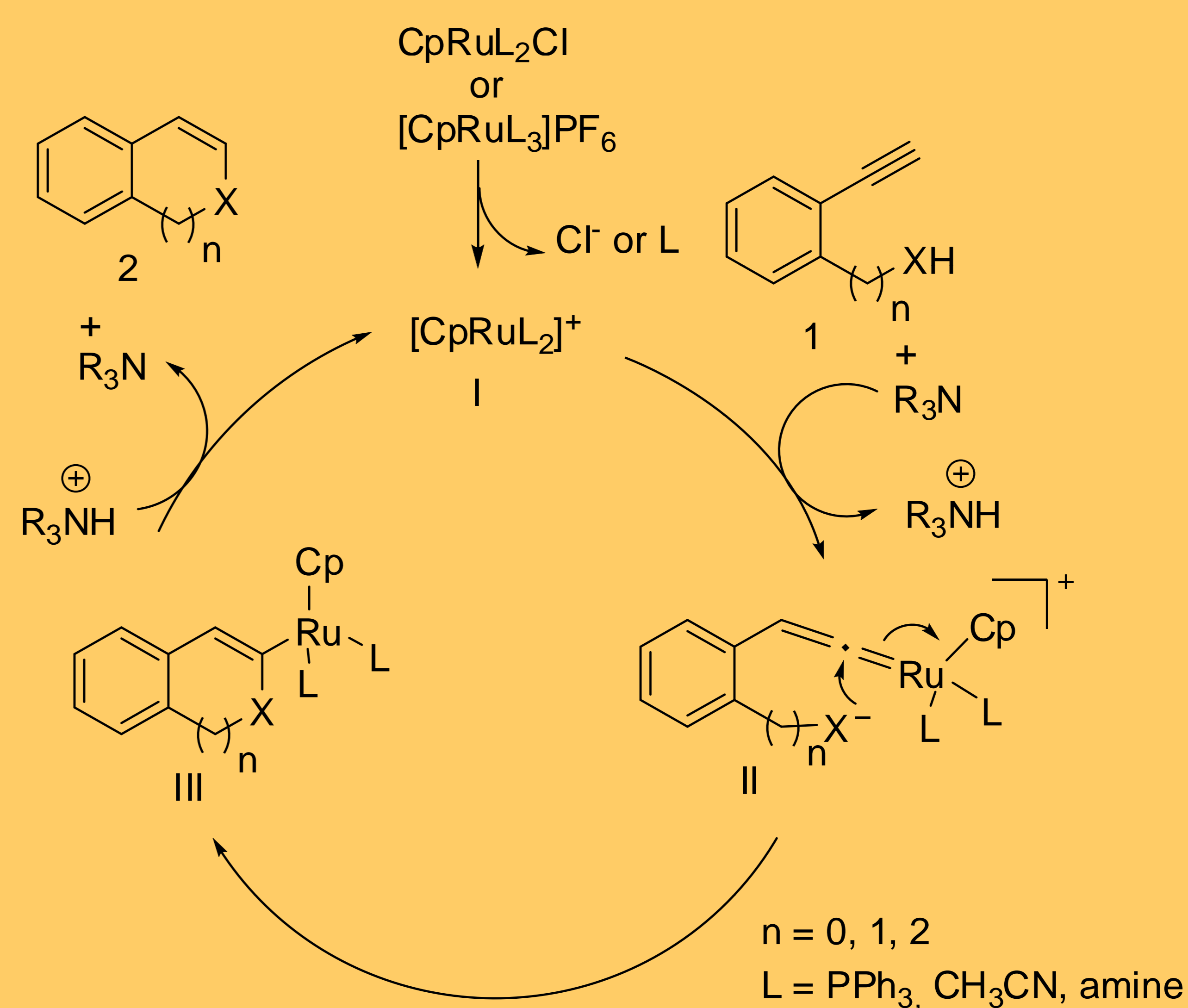
[a] 10% CpRu(PPh₃)₂Cl, pyridine, 90°C, 1-2h

7-membered rings \Rightarrow 3-Benzoxepines

Entry	Substrate	Product	Yield (%) [a]
1			40
2			38
3			32

[a] 10% [CpRu(CH₃CN)]PF₆, pyridine, 90°C, 1-4h

Catalytic cycle



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