Rhodium(I)-Catalyzed Ene–Allene–Allene [2+2+2] Cycloadditions: Stereoselective Synthesis of Complex *trans*-Fused Carbocycles

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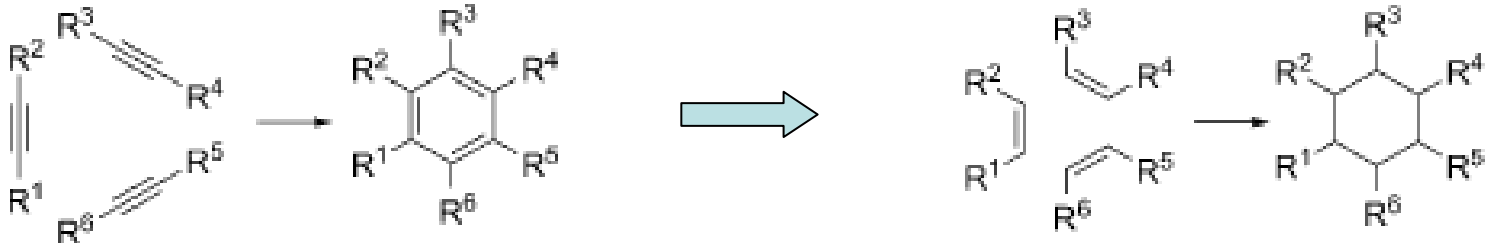
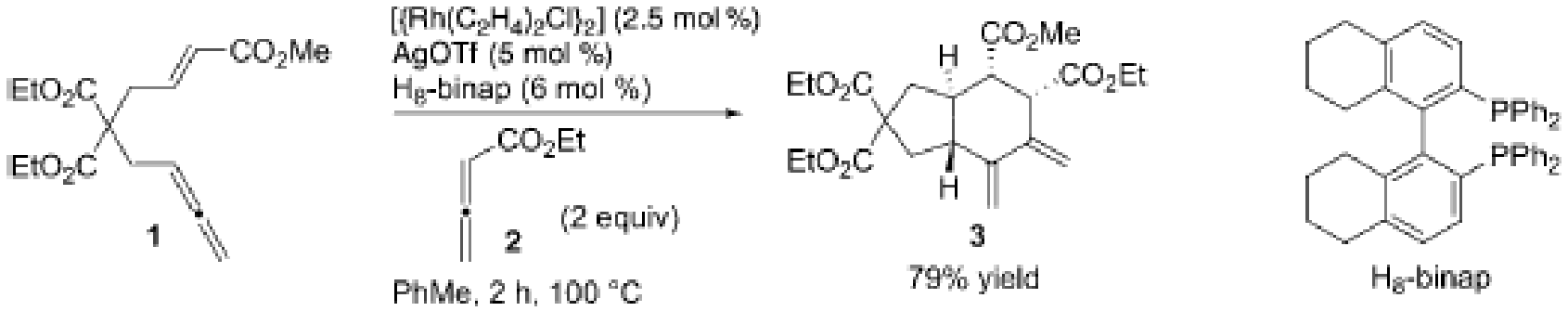
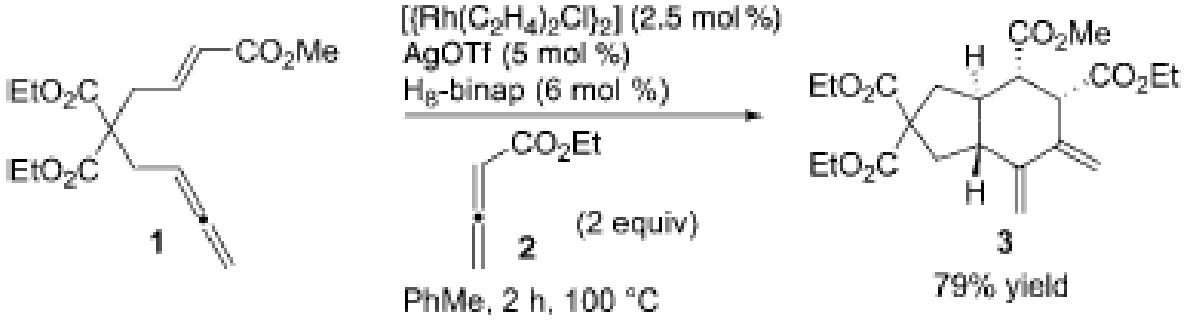
Cycloaddition de type [2+2+2]



Synthèse de cycles à 6 chaînons complexes à partir de molécules simples à une seule étape

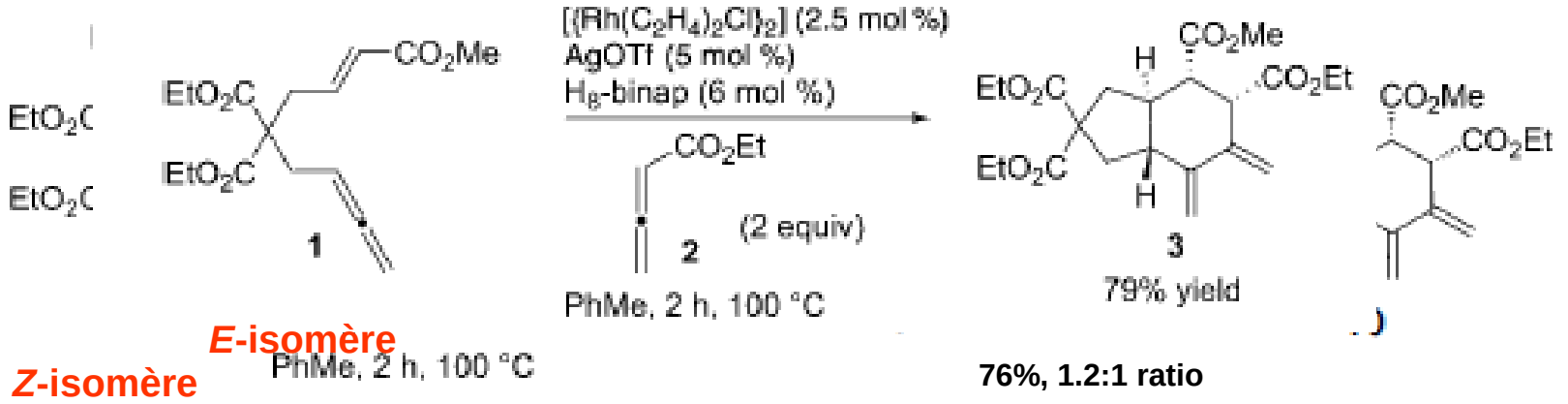


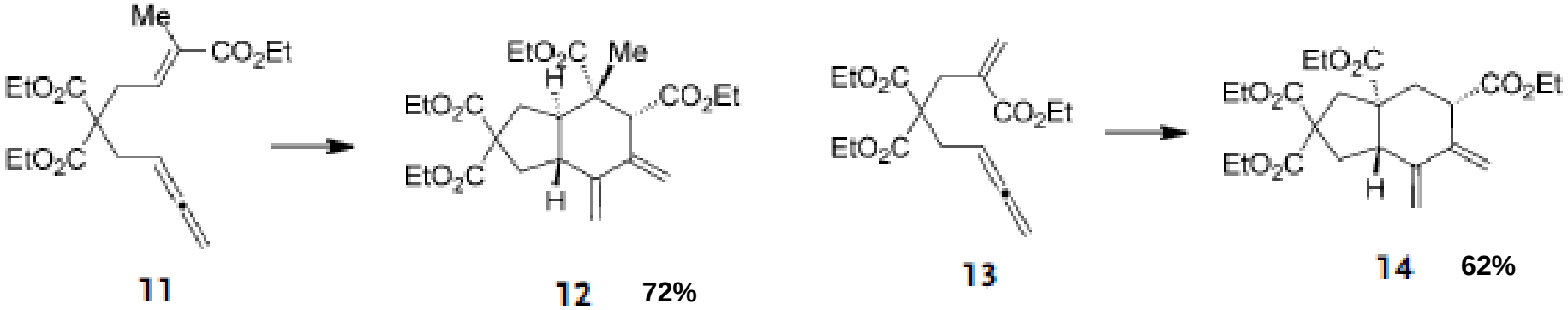
Optimisation des conditions de réaction



Entry	Variation from standard conditions	Yield [%][b]
1	none	79
2	$[\{Rh(coe)_2Cl\}_2]$ instead of $[\{Rh(C_2H_4)_2Cl\}_2]$, 2 h	76
3	$[\{Rh(nbd)Cl\}_2]$ instead of $[\{Rh(C_2H_4)_2Cl\}_2]$, 7.5 h	61
4	$[Rh(PPh_3)_3Cl]$/AgOTf instead of $[\{Rh(C_2H_4)_2Cl\}_2]$/ H_8-binap/AgOTf	<2
5	$[RhCl(PPh_3)_3]$ instead of $[\{Rh(C_2H_4)_2Cl\}_2]$/H_8-binap/AgOTf	<2
6	BINAP instead of H_8-binap, 3.5 h	68
7	No AgOTf	59
8	$AgBF_4$ instead of AgOTf, 1 h	60
9	80 °C instead of 100 °C	55
10	dioxane, 80 °C instead of $PhCH_3$, 100 °C	32
11	$[\{Rh(coe)_2Cl\}_2]$/DCE instead of $[\{Rh(C_2H_4)_2Cl\}_2]$/$PhCH_3$	47
12	1.1 equiv allene instead of 2.0 equiv allene, 3 h	54
13	5.0 equiv allene instead of 2.0 equiv allene	58

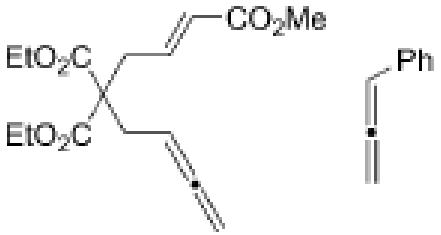
Influence de la configuration de C=C dans ene-allène sur la stéréosélectivité



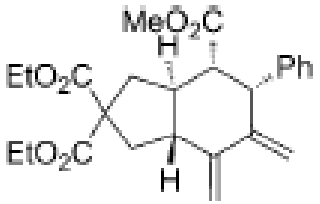


Champs d'application de cette cycloaddition du type ene-allène-allène

Variation d'allène

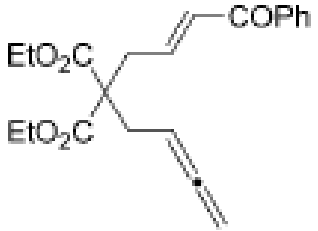


1

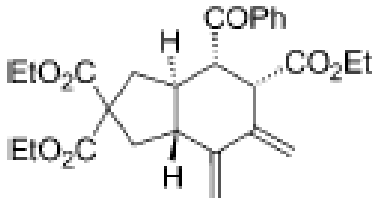


4 59%

Variation de component alcène

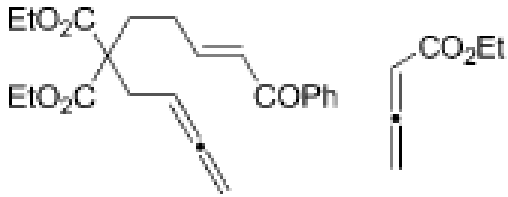


5

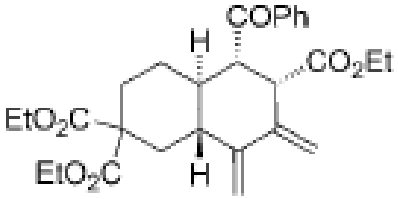


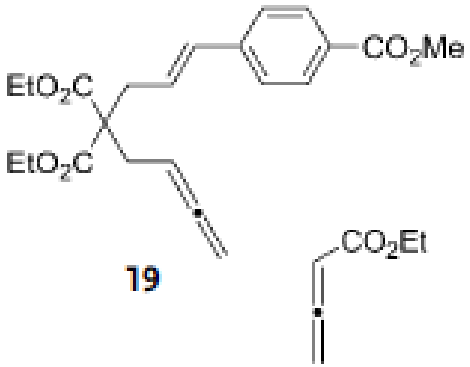
6 61%

Variation de pont ene-allène

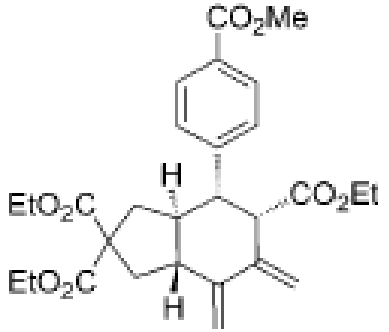


15 16 48%

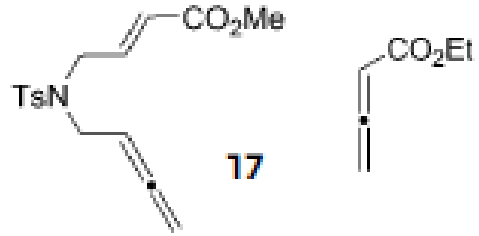




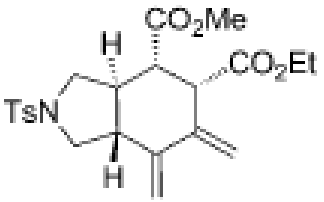
19



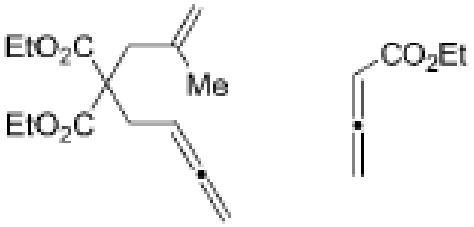
20 63%



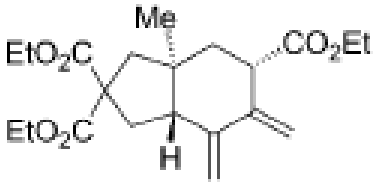
17



18 45%

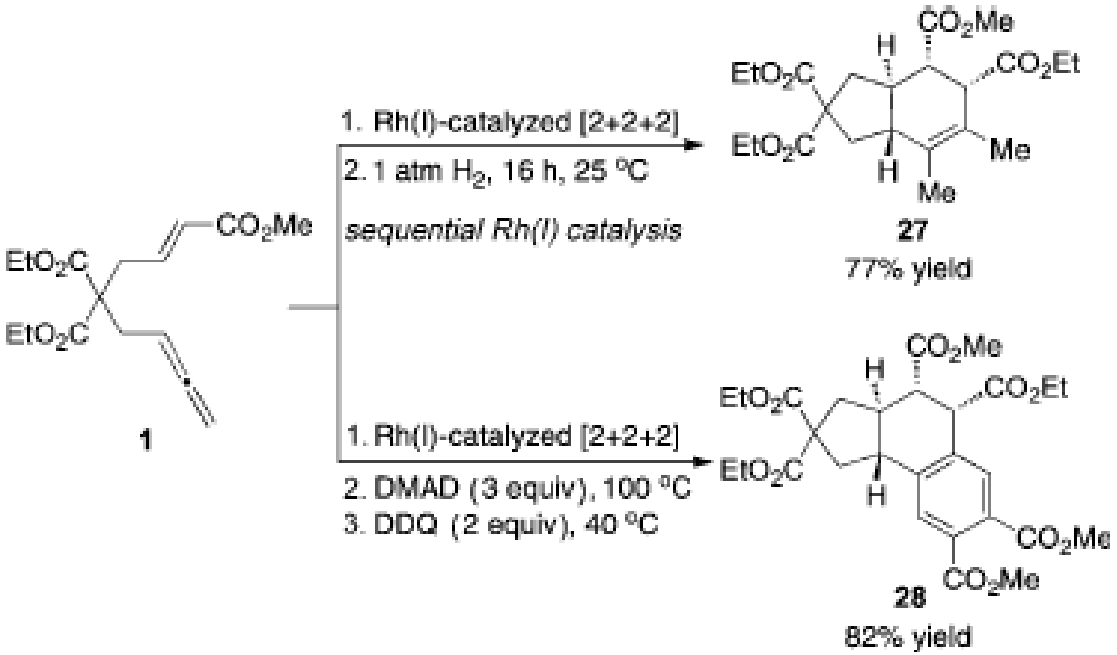


23

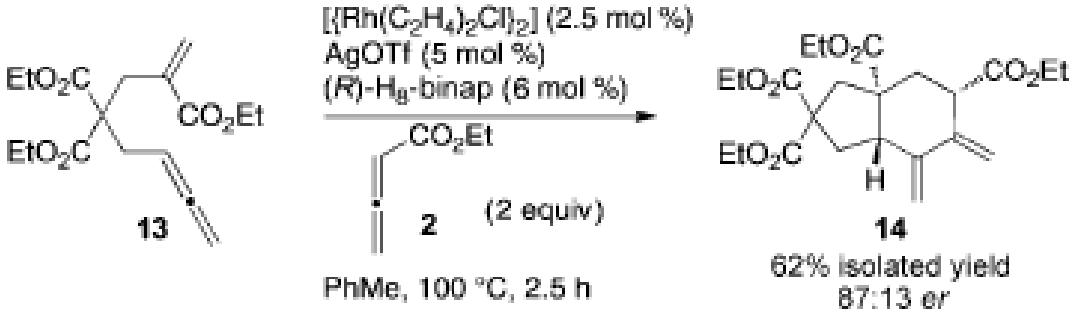


24 27%

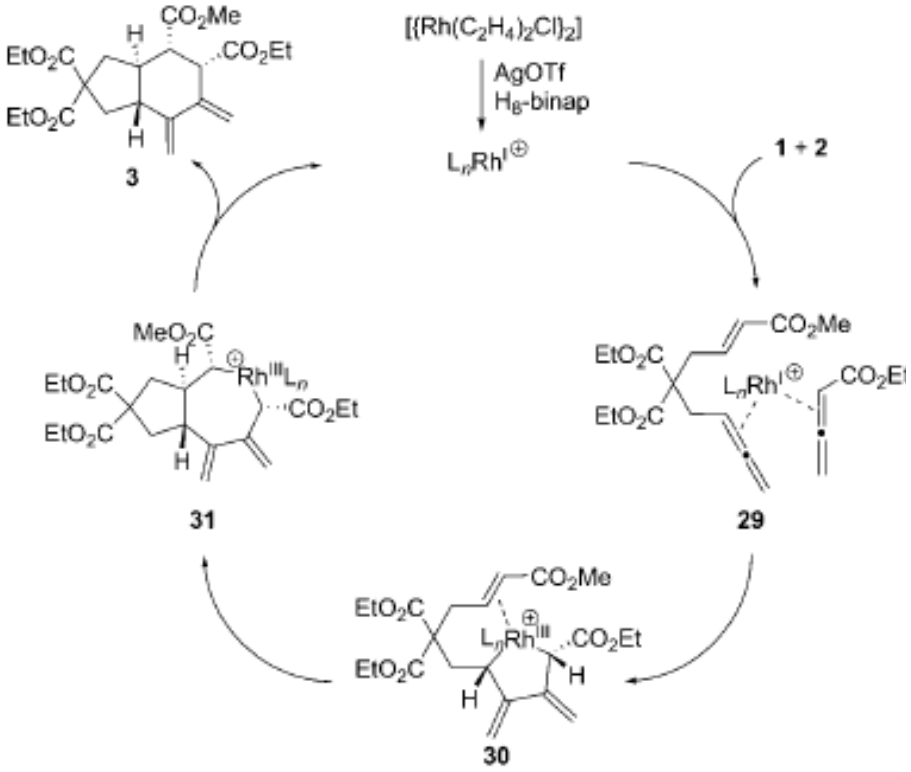
Transformations consécutives des produits *trans*-hydrindane *in situ*

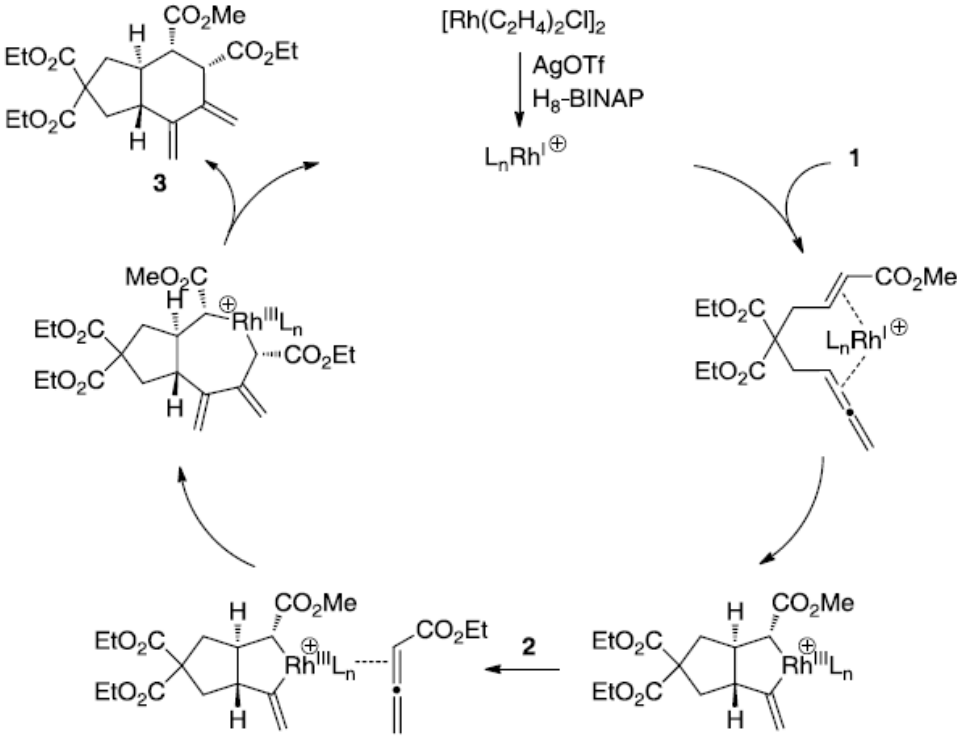


Version énantiosélective de la cycloaddition ene-allène-allène



Deux mécanismes possibles pour cette transformation





Couplage de deux fragment allénique suivi par insertion d'alcène

Couplage intramoléculaire entre les fragments alcène et allène suivi par insertion de deuxième molécule d'allène