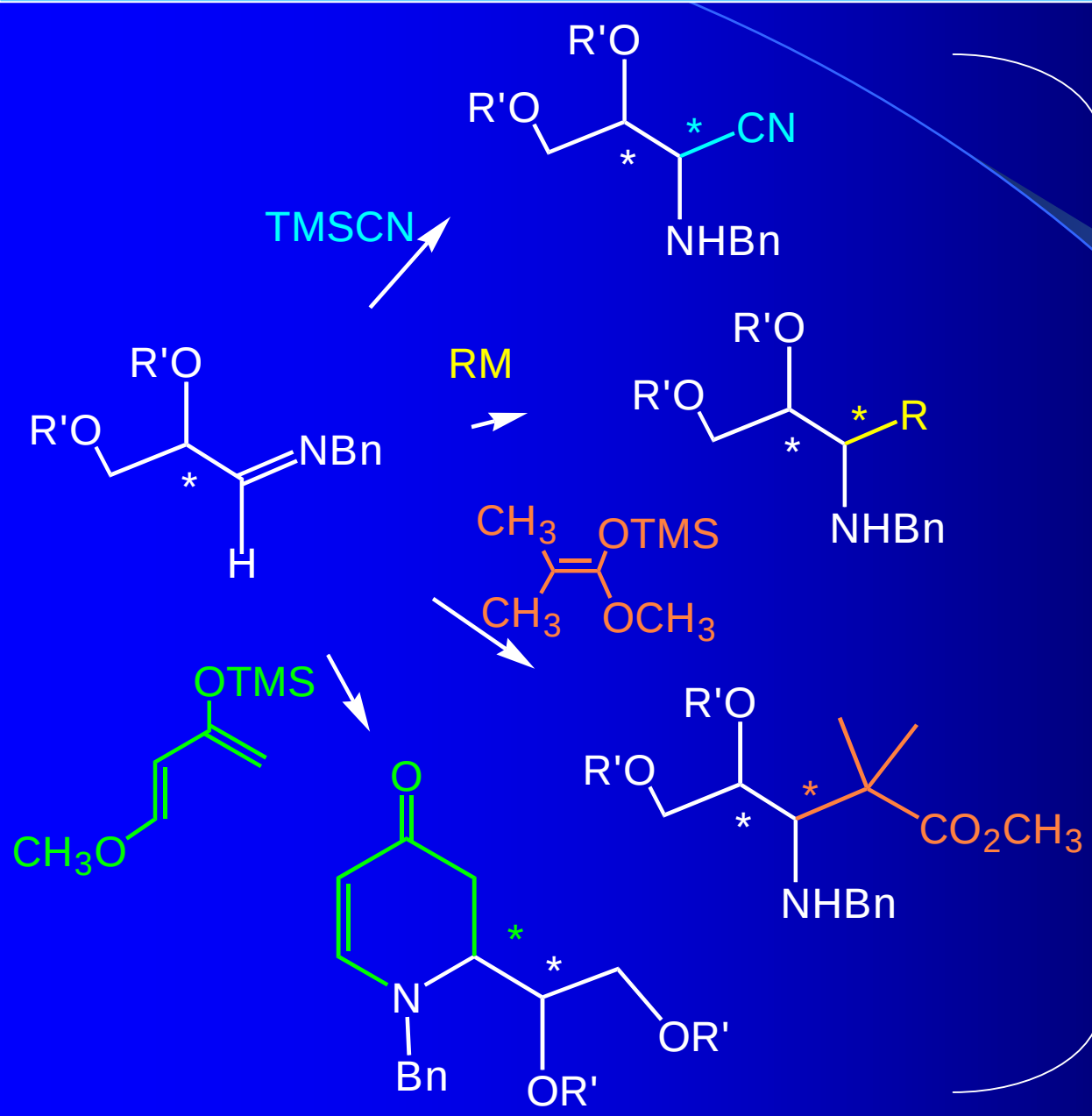
Derivados Carbonílicos de D-gliceraldehído

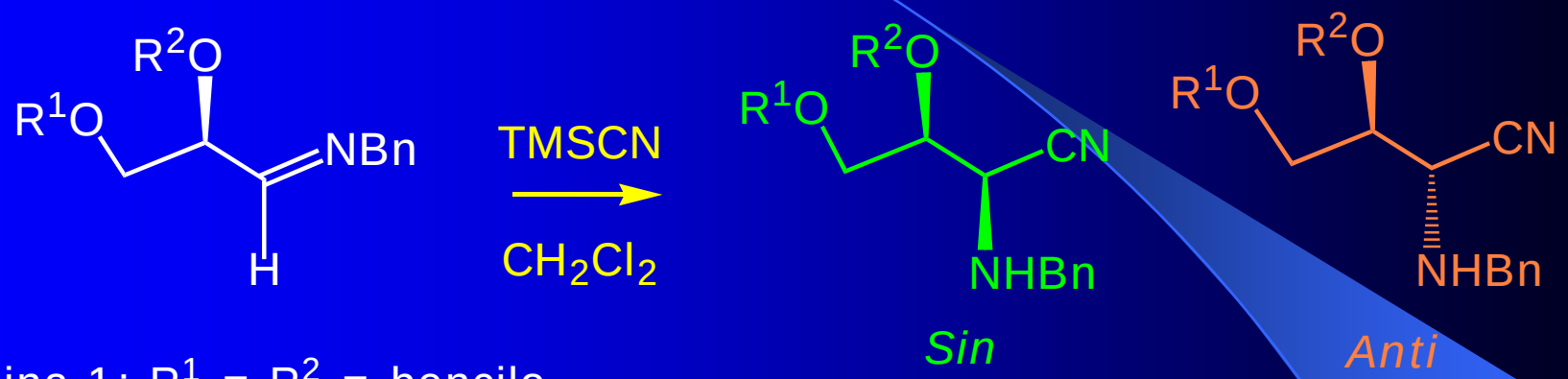
Reactividad de iminas



PRODUCTOS BIOACTIVOS ENANTIOPUROS

LIGANDOS QUIRALES

Reacción con TMSCN

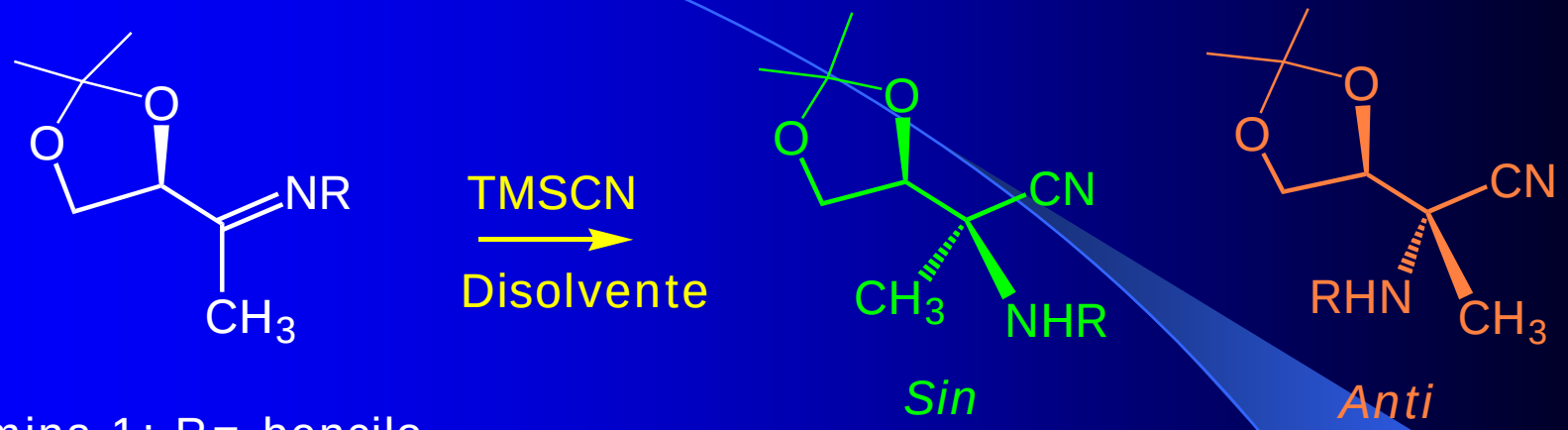


Imina 1: R^1 = R^2 = bencilo

Imina 2: R^1-R^1 = isopropilideno

Imina 3: R^1 =TBS, R^2= bencilo

Imina	Rdto.(%)	r.d.(*sin*/*anti*)
1	74	90/10
2	77	88/12
3	75	85/15

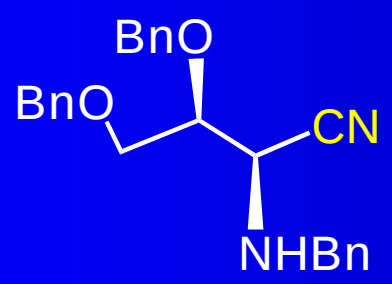


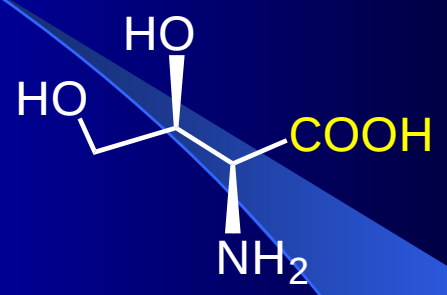
Imina 1: R= bencilo
Imina 2: R= *(S)*-α-metilbencilo

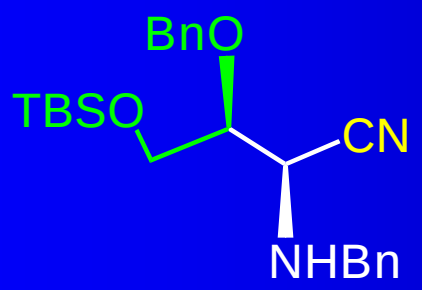
Imina	Disolvente	Rdto.(%)	r.d.(*sin*/*anti*)
2	CH_2Cl_2	84	87/13
2	Isopropanol	73	41/59
4	CH_2Cl_2	79	98/2

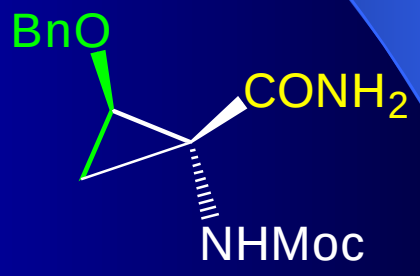
Transformaciones I

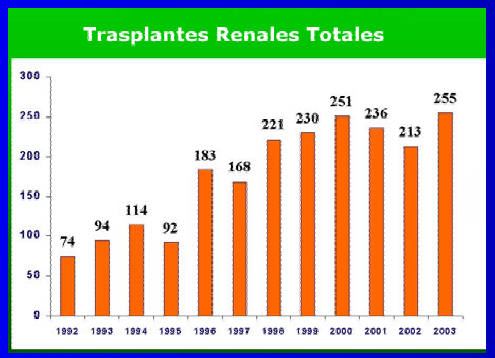
- **β-Hidroxi-α-aminoácidos**



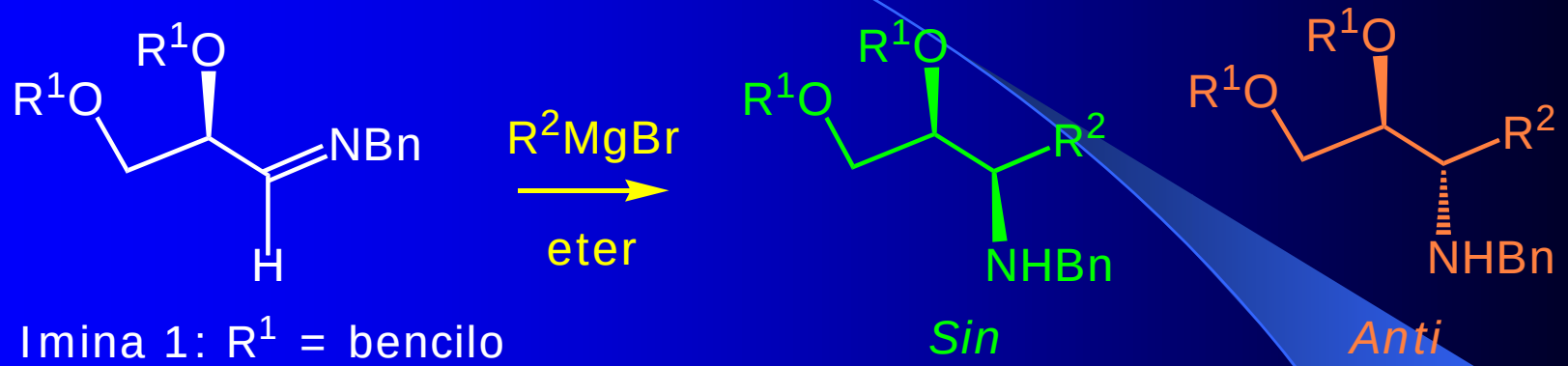








Reacción con organometálicos

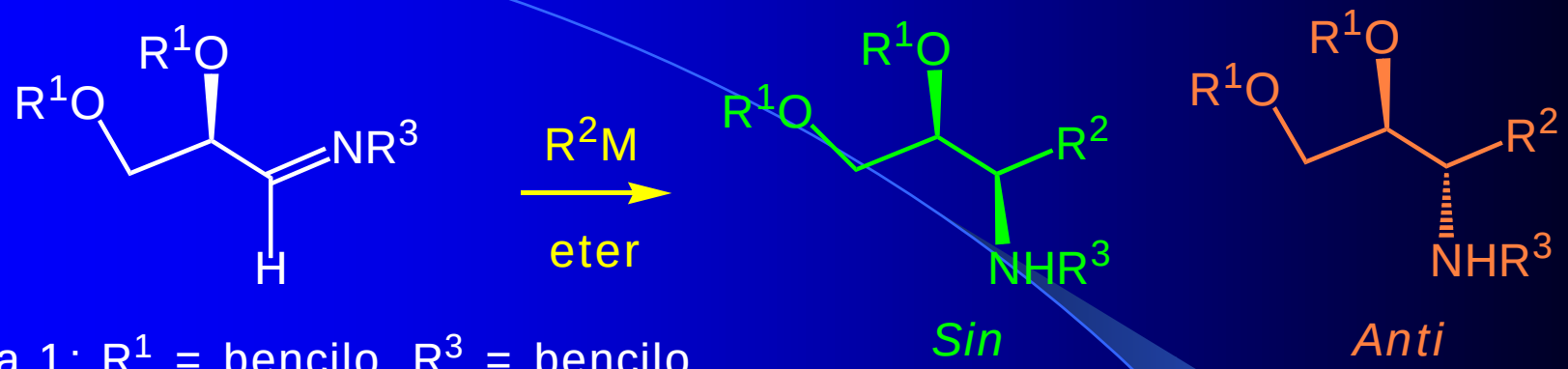


Sin *Anti*

Imina 1: R^1 = bencilo

Imina 2: R^1 = isopropilideno

Imina	R^2MgBr	Rdto.(%)	r.d.(*sin*/*anti*)
1	CH_3MgBr	64	98/2
2	CH_3MgBr	34	55/35
1	$C_6H_5CH_2MgBr$	68	98/2
2	$C_6H_5CH_2MgBr$	75	98/2
1	C_6H_5MgBr	78	98/2
2	C_6H_5MgBr	69	2/98

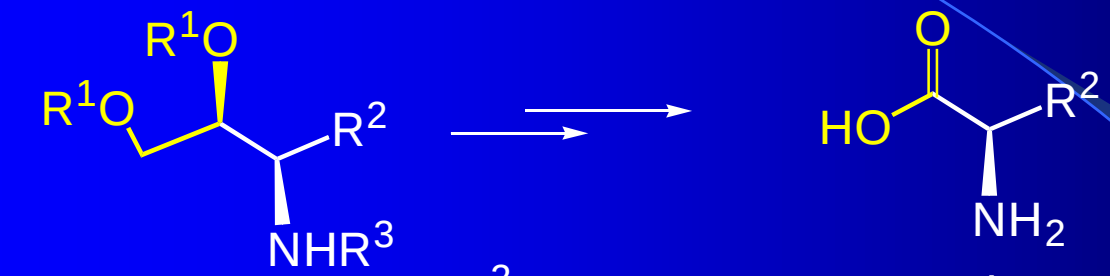


Imina 1: R^1 = bencilo, R^3 = bencilo
Imina 2: R^1 = isopropilideno, R^3 = bencilo
Imina 5: R^1 = bencilo, R^3 = *(S)*-α-metilbencilo
Imina 6: R^1 = bencilo, R^3 = *(R)*-α-metilbencilo

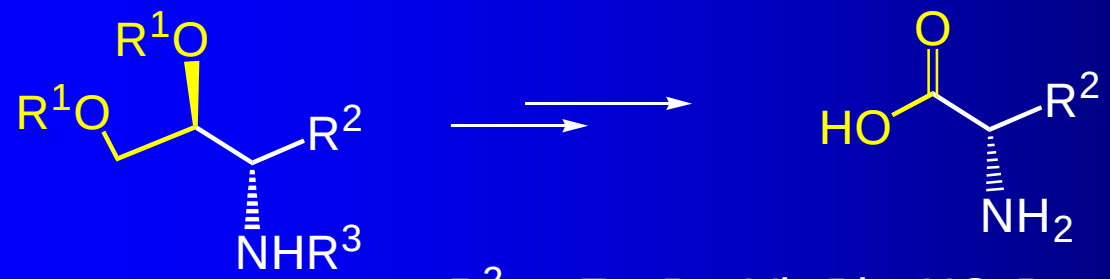
Imina	R^2M	Aditivo	Rdto.(%)	r.d.(*sin*/*anti*)
1	$CH_2{=}CHMgBr$	-----	80	98/2
2	$CH_2{=}CHMgBr$	-----	97	2/98
5	$CH_2{=}CHCH_2MgBr$	-----	65	98/2
6	$CH_2{=}CHCH_2BBN$	-----	70	2/98
2	$TBSOCH_2C{\equiv}CLi$	-----	55	88/12
2	$TBSOCH_2C{\equiv}CLi$	$BF_3{\cdot}OEt_2$	60	10/90

Transformaciones II

- **α-aminoácidos**

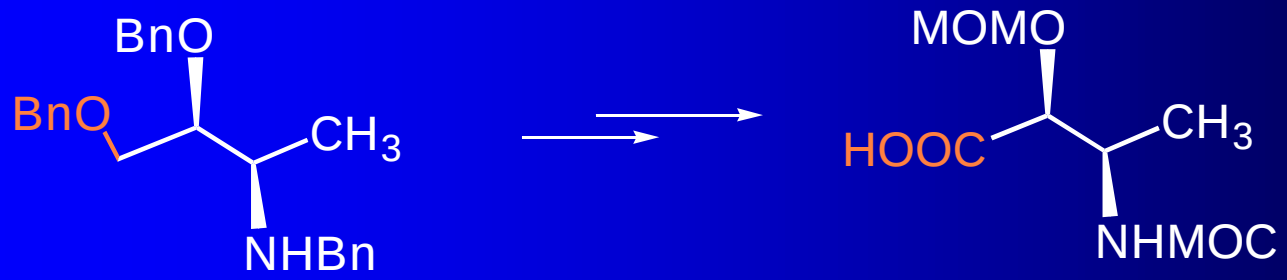


R^2 = Me, Et, Pr, Bn, Ph

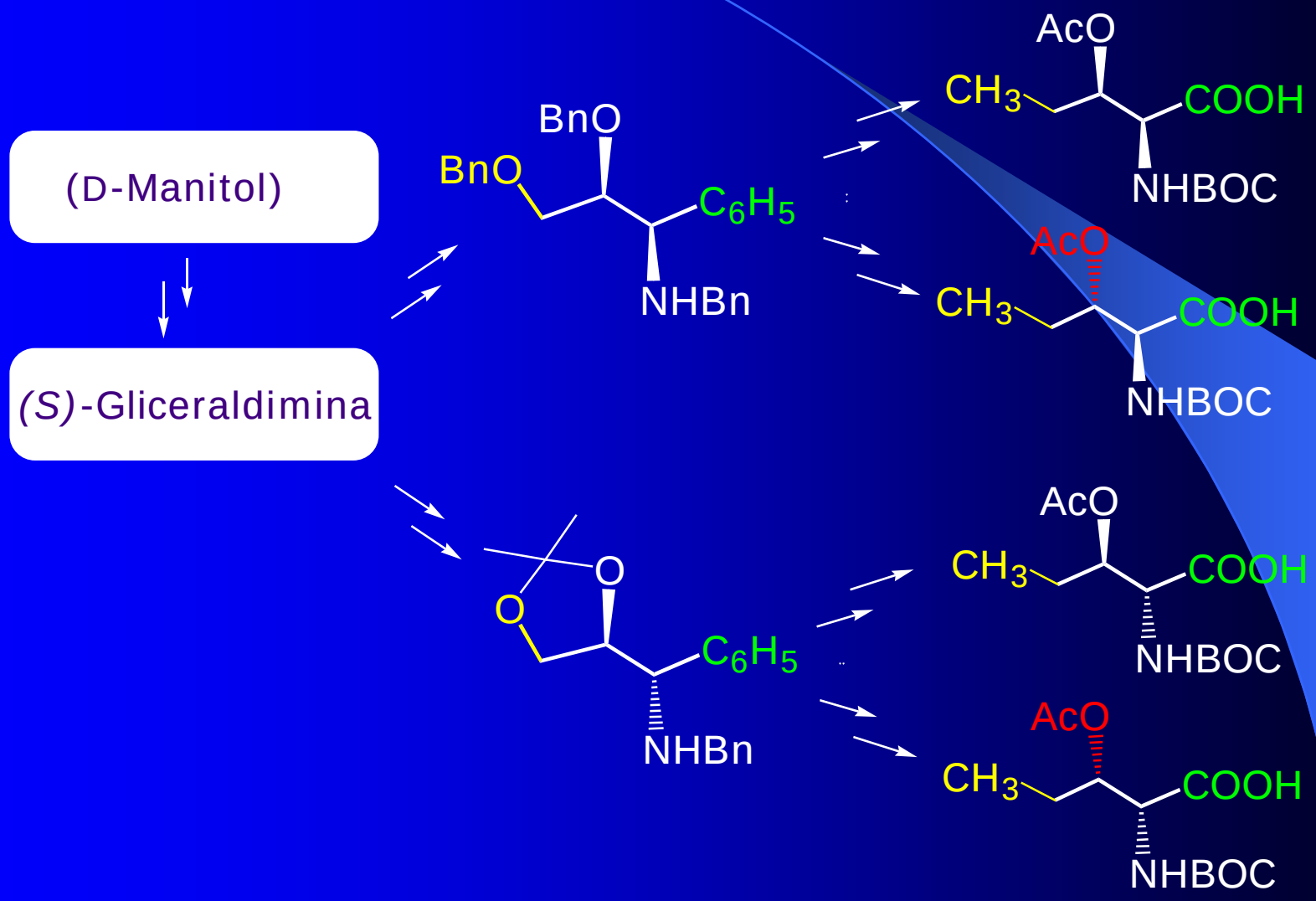


R^2 = Et, Pr, Vi, Ph, HO-Pr

- **α-Hidroxi-β-aminoácidos**



β-Hidroxi-α-aminoácidos

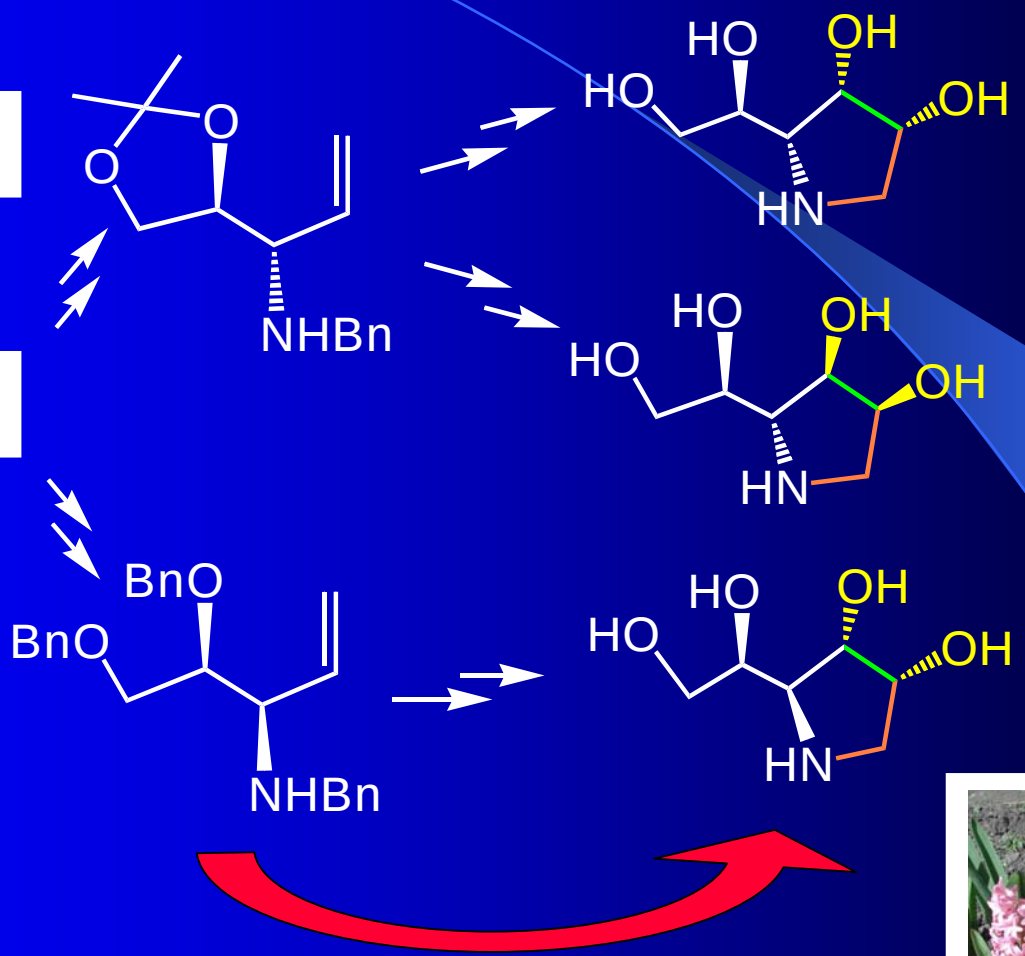


Aminoazucares: 1,4-dideoxi-1,4-iminohexitoles

(D-Manitol)

↓

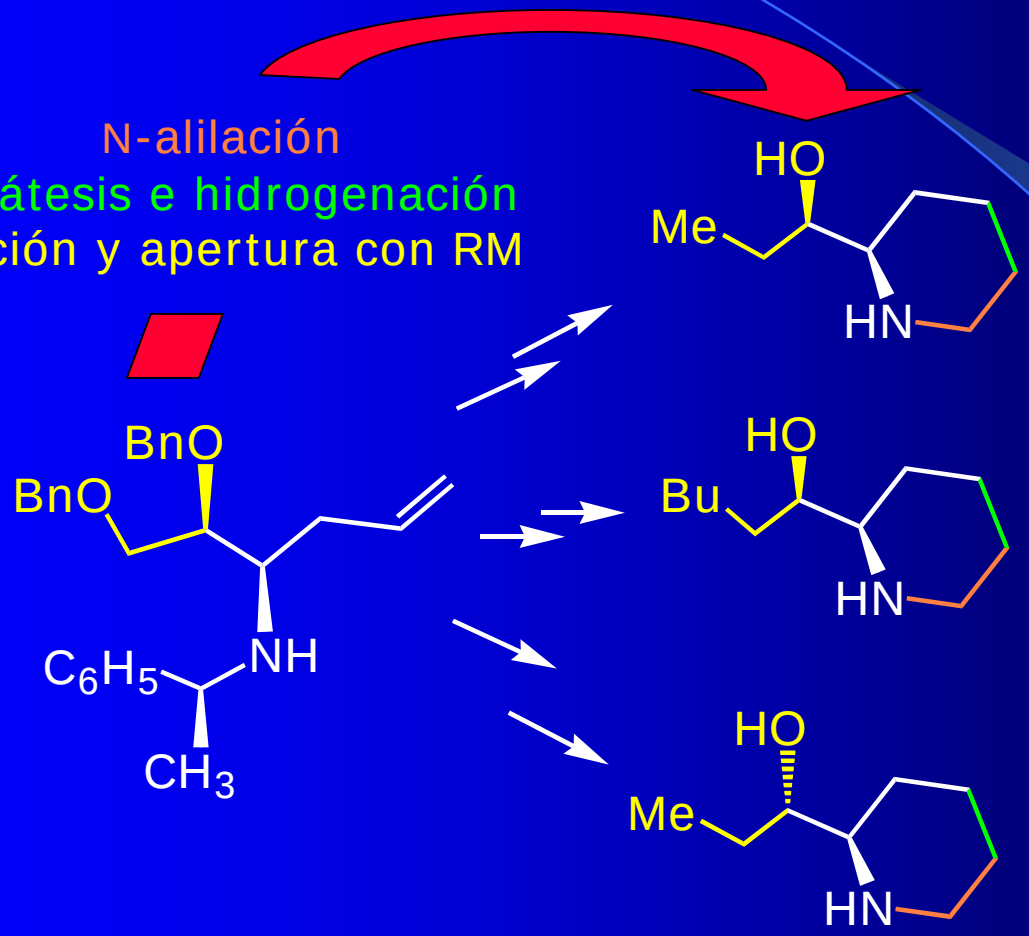
(S)-Gliceraldimina



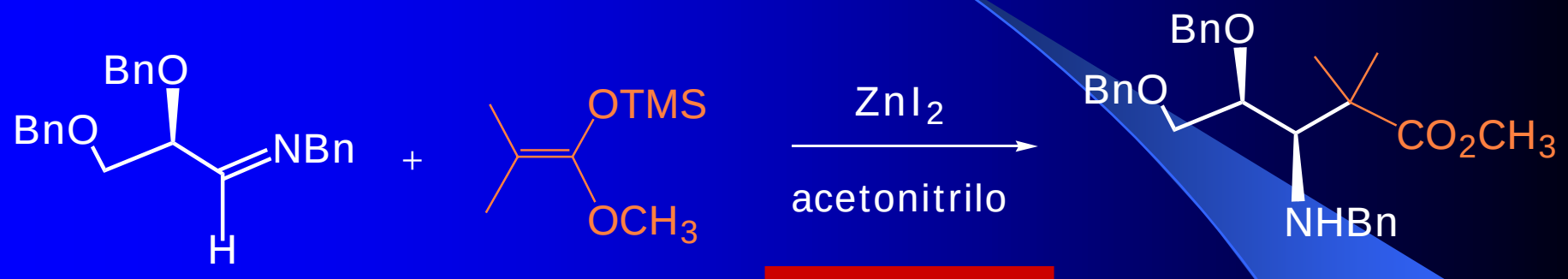
N-alilación o acilación
Metátesis
Dihidroxilación

Alcaloides: conhidrina

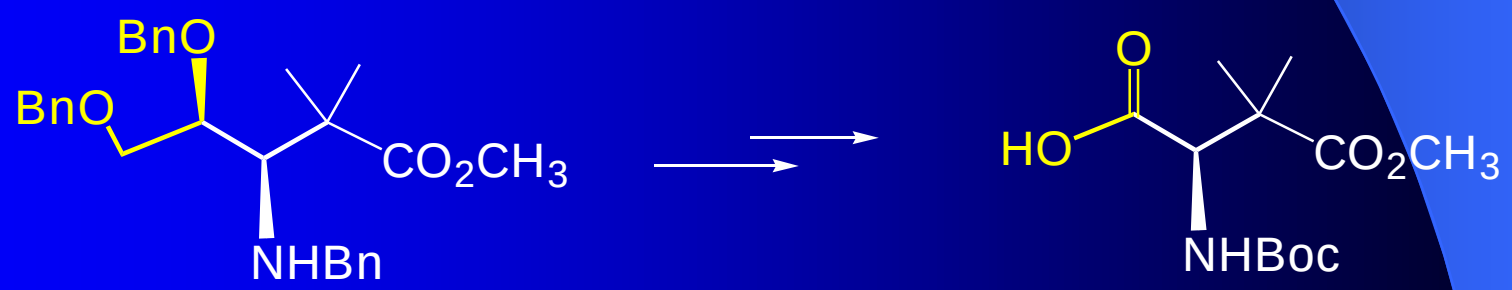
N-alilación
Metátesis e hidrogenación
Epoxidación y apertura con RM



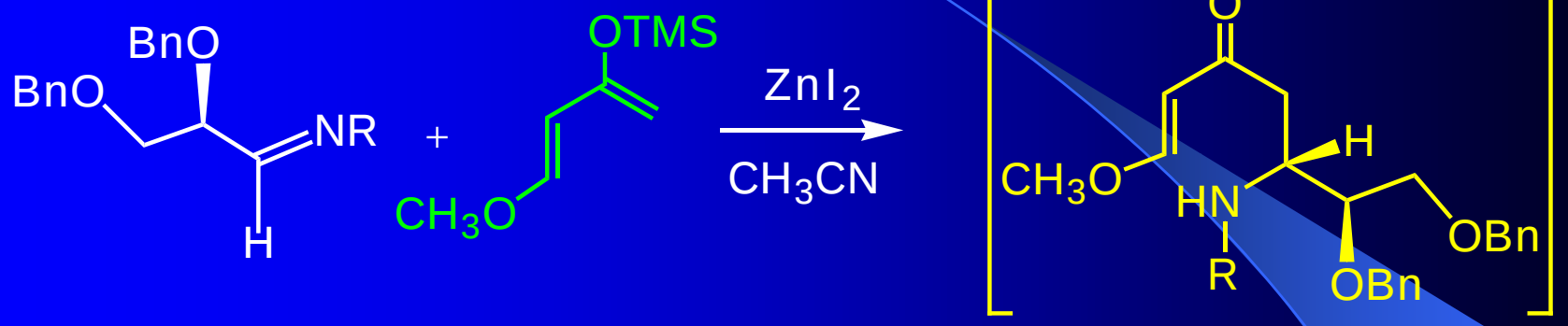
Reacción de Mannich



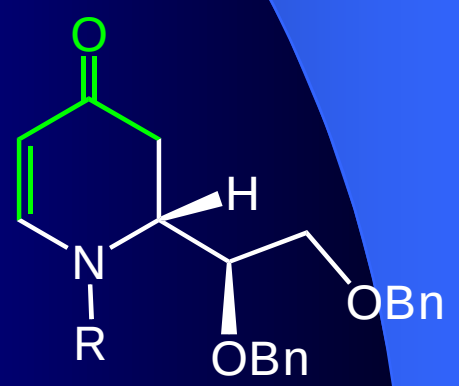
Rdto = 78%



Reacción de HeteroDiels-Alder



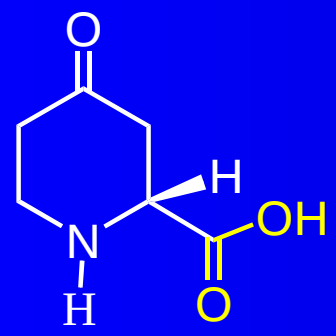
Mecanismo : tándem Mannich-Michael

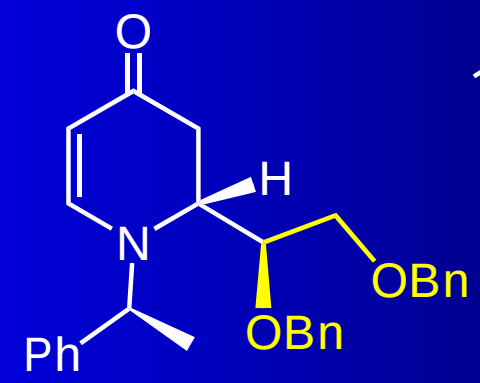


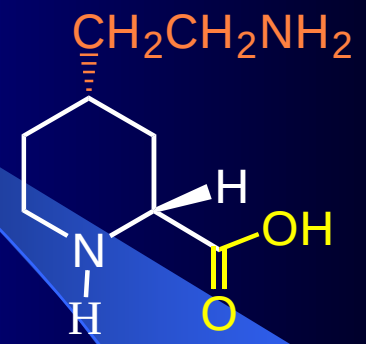
R	Rdto.(%)	r.d.
Bencilo	88	95/5
(S)-α-metilbencilo	75	> 98/2

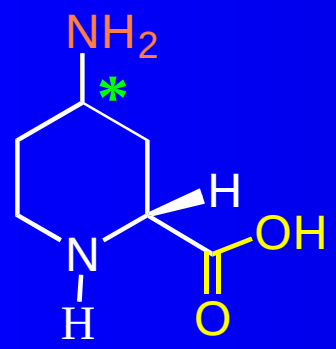
Transformaciones III

- **Derivados del ácido pipecólico**

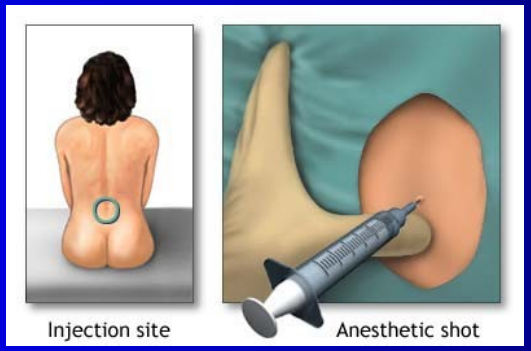


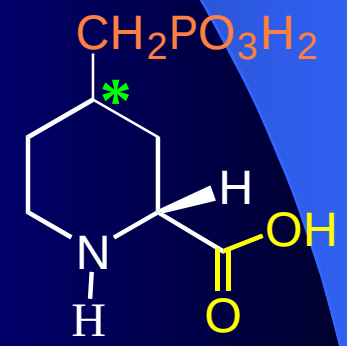






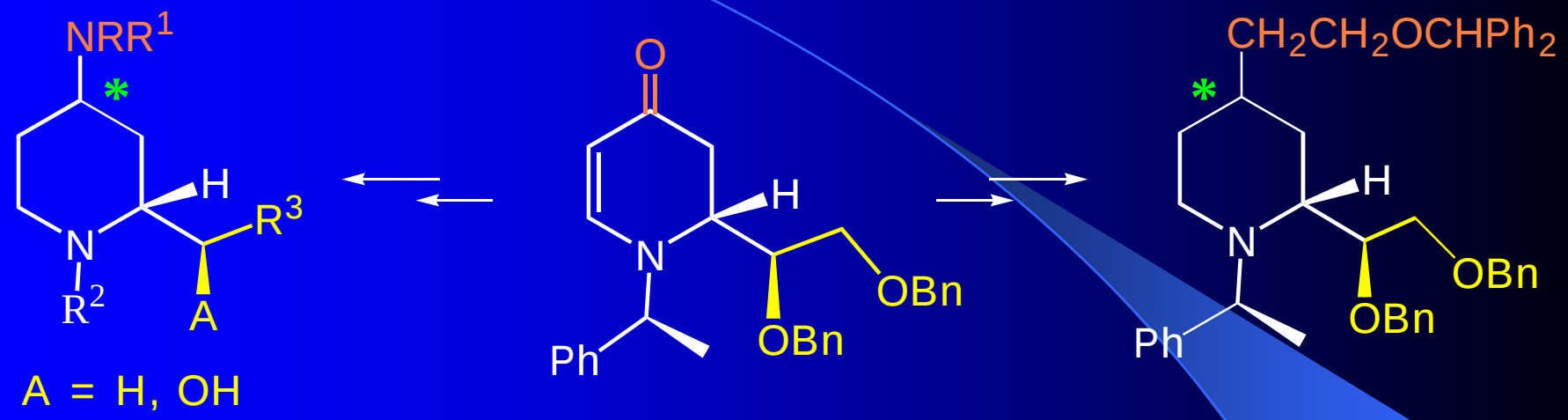
Síntesis estereodivergente
(*isómeros cis* y *trans*)





Síntesis estereodivergente
(*isómeros cis* (Selfotel) y *trans*)

Piperidinas sustituidas en posiciones 2 y 4



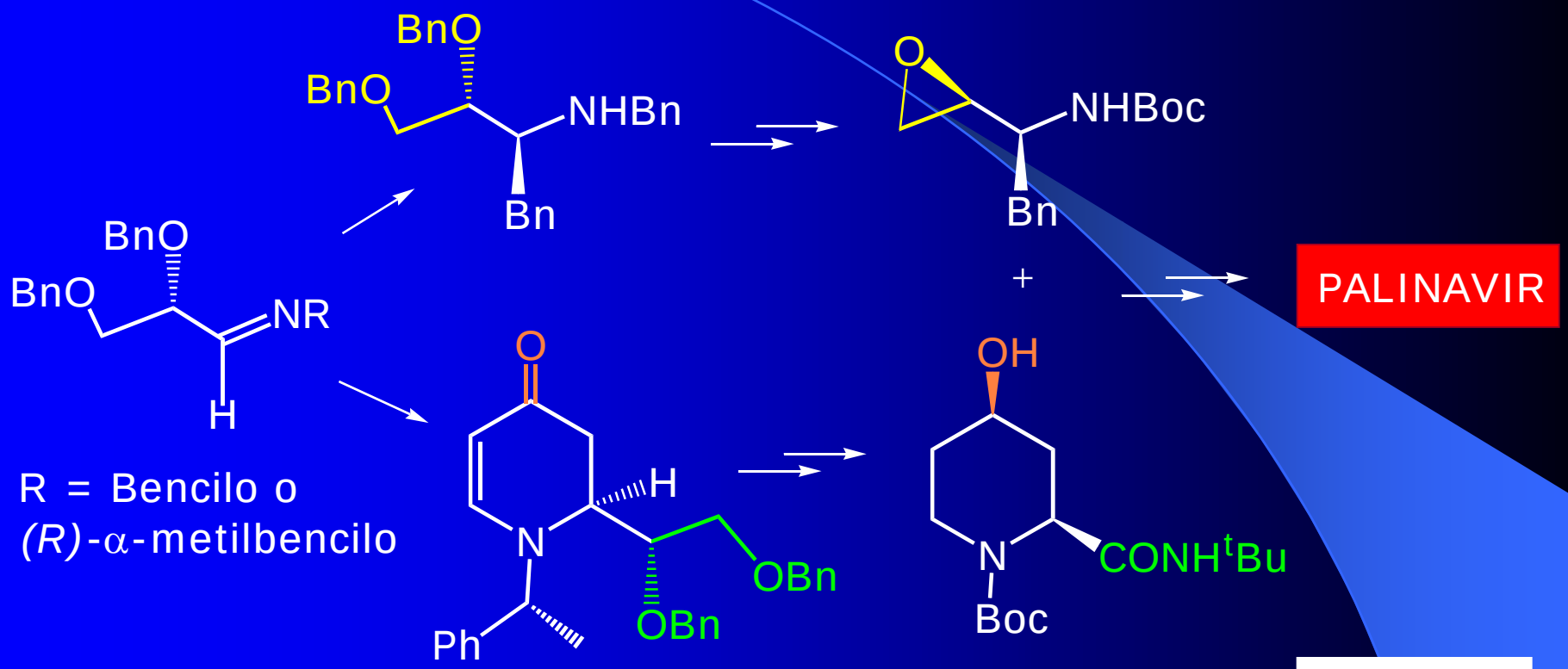
A = H, OH

Síntesis estereodivergente
(*isómeros cis y trans*)

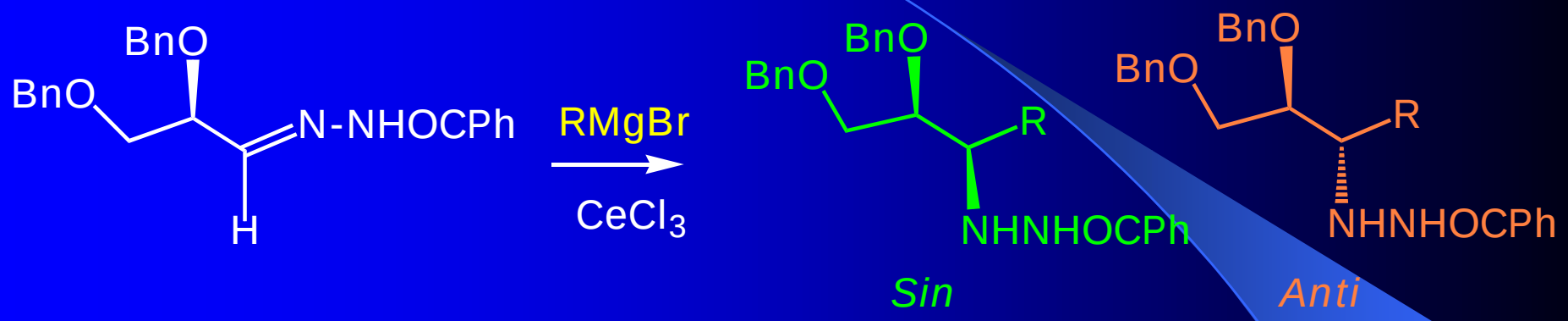
Síntesis estereodivergente
(*isómeros cis y trans*)

(Actividad sobre el sistema nervioso central)

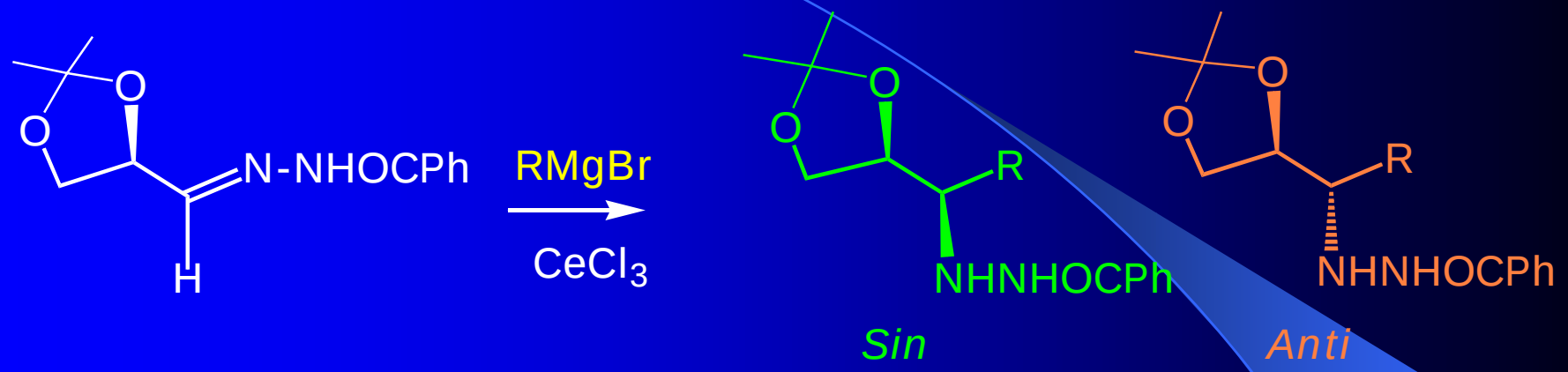
Inhibidores de la proteasa del VIH



Reactividad de hidrazonas



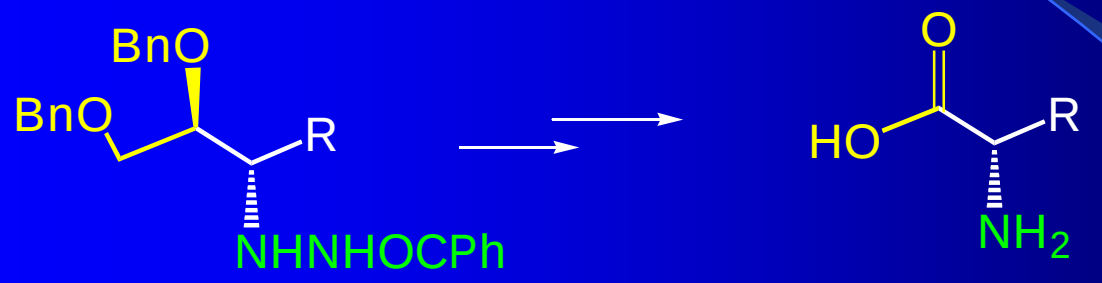
R	Rdto.(%)	r.d.(*sin*/*anti*)
CH_3	100	13/87
C_6H_5	86	14/86
$CH_2{=}CH$	71	14/86
$C_6H_5CH_2$	75	25/75
$(CH_3)_2CH$	67	25/75



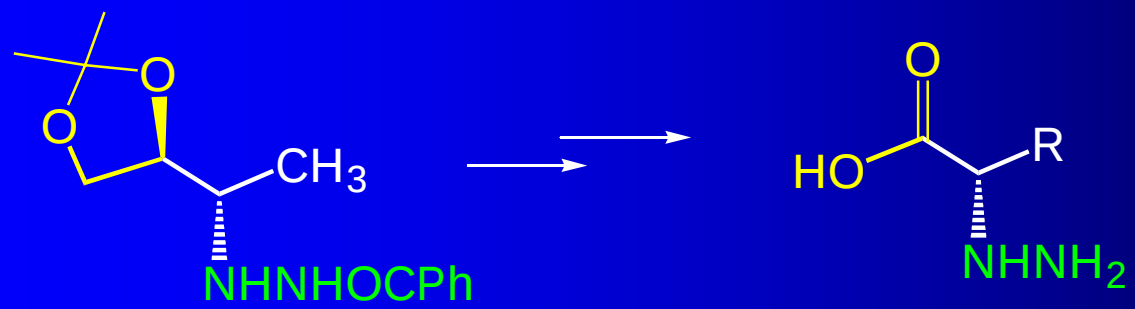
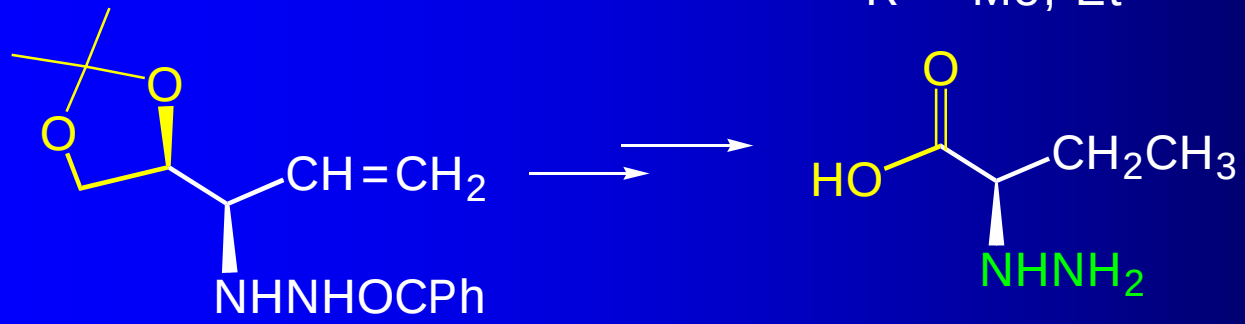
R	Rdto.(%)	r.d.(*sin*/*anti*)
CH_3	82	10/90
$CH_2{=}CH$	71	80/20
$(CH_3)_2CH$	79	84/16

Transformaciones IV

- **α-Aminoácidos y α-hidracinoácidos**



R = Me, Et, Ph, Bn, i-Pr



R = Me, Et