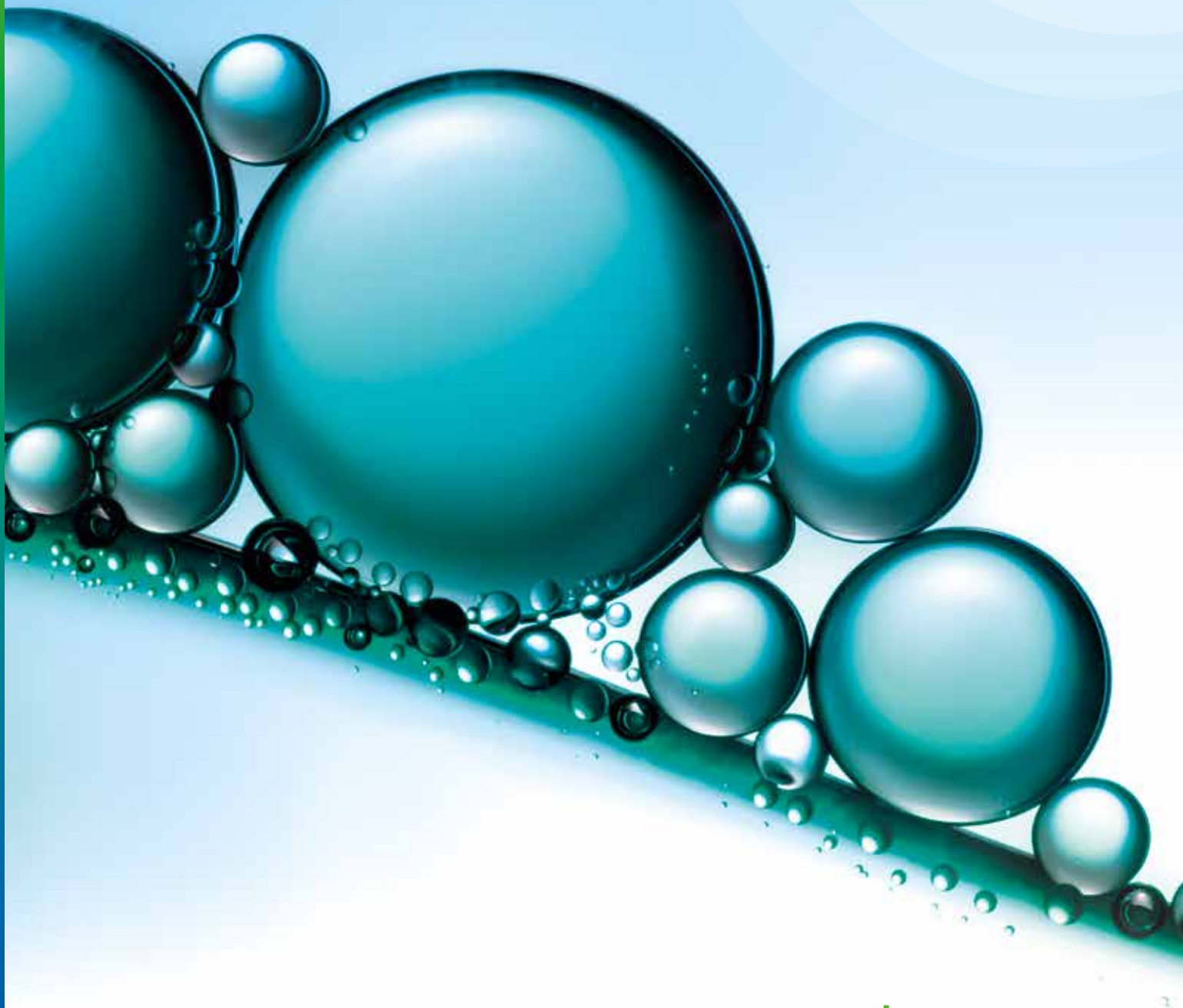
umicore
Precious Metals Chemistry



Umicore M Catalysts

Alkene Metathesis Catalysts

Find the right product for you at Umicore PMC

Different catalyst families allow for a fast screening of your most efficient metathesis synthetic step

UMICORE METATHESIS CATALYSTS – KEY FACTS AT A GLANCE

- ✓ Product availability:
  - » IP included in kg price
  - » Customer friendly license models
- ✓ Technical advantages:
  - » Broad tolerance of functional groups
  - » Excellent stability to air and moisture
  - » Thermal stability improved by N-heterocyclic carbene ligands
  - » High efficiency in straightforward RCM and CM using boomerang-type catalysts

ALKENE METATHESIS HAS GAINED EXTENSIVE USE IN INDUSTRIAL AND ACADEMIC SYNTHETIC CHEMISTRY AS A POWERFUL METHODOLOGY FOR ELEGANT, EFFICIENT AND ATOM-ECONOMICAL FORMATION OF CARBON-CARBON DOUBLE BONDS.[1]

SINCE ITS DISCOVERY IN POLYMER CHEMISTRY IN THE EARLY 1960s AND THE NOBEL PRIZE IN CHEMISTRY IN 2005 AWARDED TO CHAUVIN, GRUBBS AND SCHROCK[2], THE CATALYTIC REACTION HAS BEEN USED IN A BROAD RANGE OF APPLICATIONS SPANNING FROM PHARMACEUTICALS TO AGROCHEMICALS TO POLYMERS TO PETRO- CHEMICALS TO RENEWABLES.

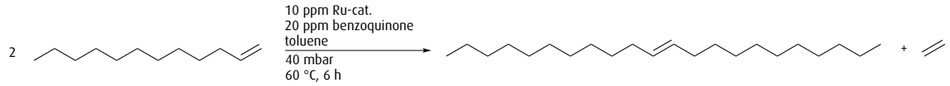
In the last ten years, we have expanded our metathesis portfolio to include new, well-defined catalyst families bearing unique stabilities, activities, initiation rates and a wide-ranging functional group tolerance. The ability to handle these catalyst families under air without any special techniques (Schlenk or glove box) gives this synthetic method further advantages when preparing your chemicals or materials, such as:

- » A clean and sustainable synthetic method
- » A shorter synthetic route
- » Safer, cost-effective, and environmentally-friendly industrial processes
- » Less to no formation of by-products

Regardless of whether you need to perform a self or cross metathesis (SM/CM), enyne metathesis, ring closing metathesis (RCM) or ring opening metathesis polymerization (ROMP), we provide you the right choice.

SELF METATHESIS (SM)[3]

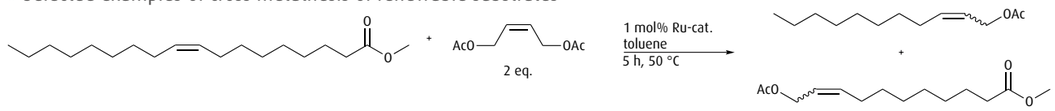
» Excellent selectivities in the self-metathesis of 1-dodecene even at low catalyst loadings



Catalyst	Yield SM products [%]	Selectivity SM products [%]	TON
M1	6	99	2688
Grubbs I	6	99	2912
Hoveyda I	15	99	7720
M2	78	82	41289
Grubbs II	62	98	31500
M51	27	96	13855
Hoveyda II	34	98	17429
Grela II	50	98	25702

CROSS METATHESIS (CM)[4]

» Selected examples of cross metathesis of renewable substrates

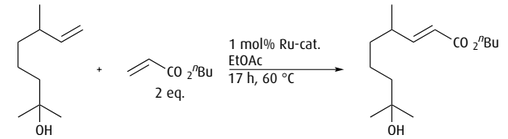


Catalyst	Conversion [%][a]	Selectivity SM products [%][b]
M2	72	86/83
M20	26	83/81
M22	13	85/83
M23	75	87/82
M31	72	86/83

[a] determined by GC, [b] calculated for the both E/Z isomers

CROSS METATHESIS (CM)[4]

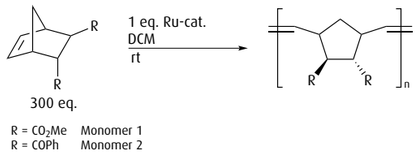
» Cross metathesis of terpenic compounds



Catalyst	Yield [%]
M2	68
Grubbs II	25
M71 SIMes	63
M71 SIPr	71
M73 SIMes	67
M73 SIPr	73

RING OPENING METATHESIS POLYMERIZATION (ROMP)[5]

» Cross metathesis of terpenic compounds

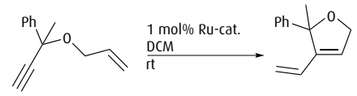


Catalyst	Mn [g/mol][a]		PDI[a]	
	Monomer 1	Monomer 2	Monomer 1	Monomer 2
M2	290 (6)	375 (72)	2.3 (6)	2.1 (6)
M31	60 (0.1)	55 (4)	1.05 (0.1)	1.06 (4)

[a] time [h]

RING CLOSING METATHESIS (RCM)[6]

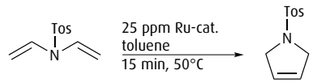
» Enyne metathesis of a model substrate



Catalyst	Time [h]	Conversion [%][a]
M2	24	63
M20	0.75	>99
M23	0.25	>99
M31	24	12

[a] determined by ^{1}H-NMR

» Ring closing metathesis of a typical model substrate

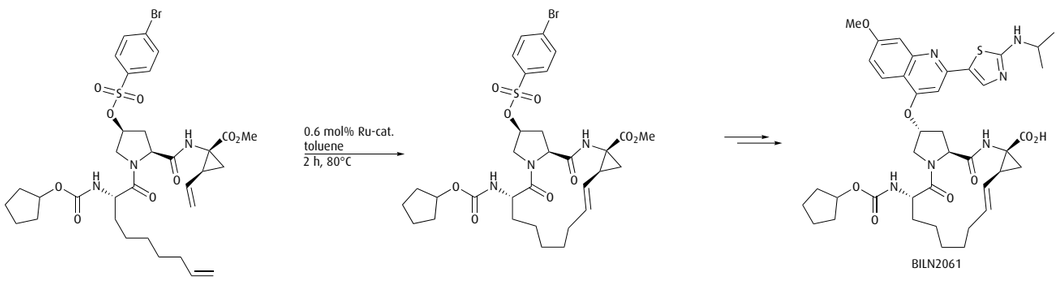


Catalyst	Conversion [%][a]
Grubbs II	61
M31	60
M61 SIMes	84
M61 SIPr	98
Hoveyda II	70

[a] determined by GC

RING CLOSING METATHESIS (RCM)[6]

» Total synthesis of BILN2061 (Ciluprevir), a hepatitis C virus (HCV) NS3 protease inhibitor involving a ring closing metathesis step to form a macro cycle.



Catalyst	Yield [%]
M51	95
Hoveyda II	89
Grubbs II	93

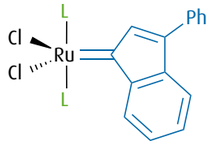
[a] determined by HPLC

References:

[1] a) R. H. Grubbs in Handbook of Olefin Metathesis, Wiley VCH, Weinheim, 2003
b) R. H. Grubbs et al., Chem. Rev. 2010, 110, 1746; c) K. Grela et al., Sci. of Synth., 2010, 47a, 327
[2] http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2005/popular-chemistryprize2005.pdf
[3] a) Adv. Synth. Catal. 2013, 355, 1997
b) Grubbs I [172222-30-9], Grubbs II [246047-72-3], Hoveyda I [203714-71-0], Hoveyda II [301224-40-8], Grela II [502964-52-5]
[4] a) Green Chem. 2014, 16, 1579
b) Synthesis 2011, 13, 2125
[5] Chem. Eur. J. 2011, 17, 5045
[6] a) Chem. Comm. 2011, 47, 5022
b) Chem. Eur. J. 2012, 18, 12845
c) Organomet. 2011, 30, 4144

Umicore M Catalyst Portfolio

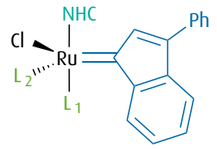
Umicore M1 series – Grubbs 1st Generation Type
Ru Indenylidene Metathesis Catalysts



L	Trade Name	CAS No.	Product No.
PCy_3	Umicore M1[a]	250220-36-1	3000034559
$P(^tBu)_2$(phobane)	Umicore M11[b]	894423-99-5	3000034563

[a] WO 2010 037550, WO 2014 001291 and US 9 604 205 apply.
[b] WO 2007 010453 applies.

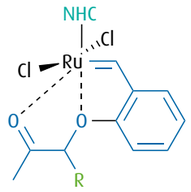
Umicore M2 series (incl. 3/8 series) – Grubbs 2nd Generation Type
Ru Indenylidene Metathesis Catalysts



NHC	L_1	L_2	Trade Name	CAS No.	Product No.
SIPr	PPh_3	Cl	Umicore M23	1307233-23-3	3000036123
SIMes	PCy_3	Cl	Umicore M2	536724-67-1	3000034561
	PPh_3	Cl	Umicore M20	340810-50-6	3000036116
	Cl	$P(O^iPr)_3$	Umicore M22	1255536-61-8	3000036115
	py	Cl	Umicore M31	1031262-76-6	3000034565
		Cl	Umicore M81 SIMes	1228169-92-3	3000036143

WO 2000 15339, US 10 873 026 and foreign equivalents apply. For use in pharmaceutical applications.

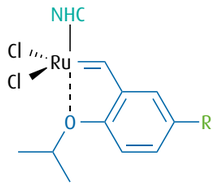
Umicore M5 series – Grubbs 2nd Generation Type
Ru Oxygen Chelated Benzylidene Metathesis Catalysts



NHC	R	Trade Name	CAS No.	Product No.
SIMes	Me	Umicore M51	1031262-71-1	3000034567
	H	Umicore M52	1014701-61-1	3000034571

WO 2008 034552 applies.

Umicore M7 series – Hoveyda-Grubbs 2nd Generation Type
Ru Benzylidene Metathesis Catalysts

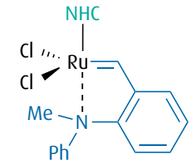


NHC	R	Trade Name	CAS No.	Product No.
SIMes	$NH(CO)CF_3$	Umicore M71 SIMes	1025728-56-6	3000034576
	$NH(CO)C_6F_5$	Umicore M72 SIMes	1030618-02-0	3000036136
	$NH(CO)O^tBu$	Umicore M73 SIMes	1025728-57-7	3000034574
	NH(CO)(CO)Et	Umicore M74 SIMes	1030618-11-1	3000036140
SIPr	$NH(CO)CF_3$	Umicore M71 SIPr	1212008-99-5	3000036112
	$NH(CO)C_6F_5$	Umicore M72 SIPr	1354710-90-9	3000036137
	$NH(CO)O^tBu$	Umicore M73 SIPr	1212009-05-6	3000034573
	NH(CO)(CO)Et	Umicore M74 SIPr	1212009-08-9	3000036139

WO 2008 065187 applies.

Umicore M Catalyst Portfolio

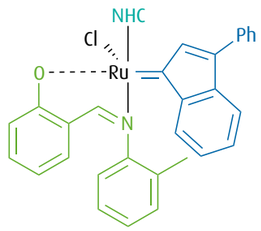
Umicore M6 series – Grubbs 2nd Generation Type
Ru Nitrogen Chelated Benzylidene Metathesis Catalysts



NHC	Trade Name	CAS No.	Product No.
SIMes	Umicore M61 SIMes	1416427-09-2	3000034579
SIPr	Umicore M61 SIPr	1416427-12-7	3000034577

EP 2 825 522 applies.

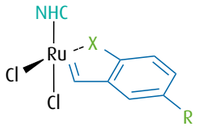
Umicore M4 series – Grubbs 2nd Generation Type
Ru Schiff Base Indenylidene Metathesis Catalyst



NHC	Trade Name	CAS No.	Product No.
SIMes	Umicore M42	934538-12-2	3000034564

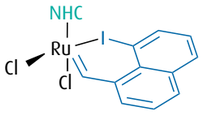
EP 1 468 004 B1, US 2002 0349956 and foreign equivalents apply.
Not to be used in the metathesis of DCPD derivates.

Umicore M9 series – Grubbs 2nd Generation Type
Ru Halogen Chelated Benzylidene Metathesis Catalysts



NHC	X	R	Trade Name	CAS No.	Product No.
SIMes	I	H	Umicore M91	1415725-62-0	3000036076
	Br	NMe_2	Umicore M93	1415725-68-6	3000036078

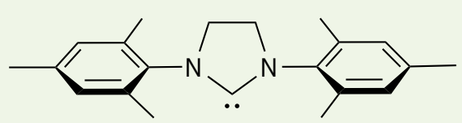
WO 2012 168183 applies.



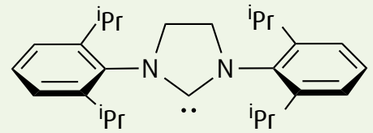
SIMes	Umicore M92	1415725-73-3	3000036077

WO 2012 168183 applies.

Legend:



SIMes



SIPr

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Haven't found the right metathesis catalyst, yet? Please ask our team for advice on how to innovate your process. We have the answer to your problems.

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