

# Apeiron's olefin metathesis catalysts

## Apeiron's catalyst offerings

Apeiron Synthesis has developed a growing portfolio of over twenty exceptional metathesis catalysts designed to accommodate a wide range of applications, with catalyst availability from gram to multi-kilogram quantities, suitable for applications in R&D as well as in large scale production. Our technology platform offers customers:

- Broad and growing portfolio of catalysts with applications to all metathesis reaction types.
- Catalysts optimized for continuous flow - with high turnover and extended reusability.
- High efficiency catalysts for metathesis in water, at room temperature and on solid support.
- Extensive metathesis centered know-how, unique tools and process chemistry expertise that combine to meet challenging chemistry objectives.

A variety systems of catalyst-activator and catalyst-retardant applicable in metathesis polymerization reactions.

Apeiron Synthesis is dedicated to providing products and services that transform our customers' chemistry to save time and money with cost effective, efficient, sustainable processes.

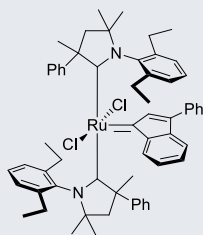
### How does it work:

Our technology platform is highly modular, enabling us to manufacture catalysts incorporating process-specific structural modifications in the labile (ionic and benzylidene) and non-labile (NHC and CAAC) ligands. Apeiron takes advantage of proprietary technology that is the result of our in-house research program as well as intellectual property licensed from leading European industrial and academic partners.

**We specialize in modifications of the NHC and CAAC ligand to append customized utility tags - affording novel catalyst traits for process-specific requirements, such as altered solubility profiles, simpler post-reaction work-up or easier removal of ruthenium residues from products.**

### Validation by Industry

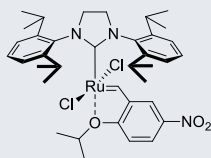
Apeiron's catalysts have been extensively tested and some have also become industry standards. When compared to other options, our catalysts have demonstrated clear superiority with respect to reaction time, temperature, dilution factor, reactivity and selectivity.



## UltraCat

AS2086 CAS: 2055540-61-7

- Versatile catalyst, excellent for CM of terminal, type 1 olefins. Excellent for ethenolysis, very good for mRCM and RCM leading to small/medium rings.
- Compatible with toluene, ethyl acetate, dimethylcarbonate, CPME, neat substrate in the temp. range of 40 to 85°C.
- High stability allows handling in air.



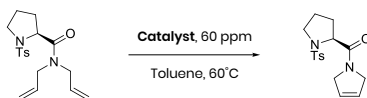
## nitro-Grela SIPr

AS2033 CAS: 928795-51-1

- General purpose catalyst, very good for CM of terminal and disubstituted trans olefins of type 1. Very good for RCM with sterically non-demanding substrates leading to small/medium rings and for CM with electron deficient partners such as acrylates. Less sensitive to small impurities than nitro-Grela catalyst.
- Compatible with toluene, ethyl acetate, dimethylcarbonate, CPME, DCM, DCE, neat substrate in the temp. range of RT to 110°C.
- High stability allows handling in air.

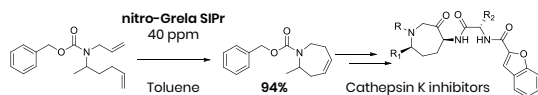
# Ring-closing metathesis (RCM)

RCM of small/medium rings

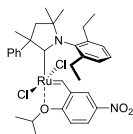


Catalyst	Loading [ppm]	GC yield [%]	TON
UltraCat	60	92	15 300
Grubbs II	60	50	8 300

R. Gowin, A. Kozakiewicz, P. A. Gurka, P. Dąbrowski, K. Skowroński 'Bis(Cyclic Alkyl Amino Carbene) Ruthenium Complexes: A Versatile, Highly Efficient Tool for Olefin Metathesis' *Angew. Chem. Int. Ed.* 56, 910, (2017).

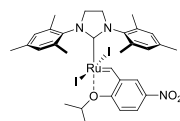


Other catalysts suitable for this transformation:



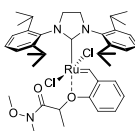
UltraNitroCat

AS2091 CAS: 2106819-64-9



nitro-Grela I<sub>2</sub>

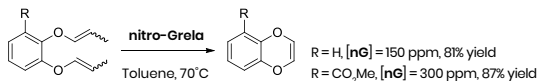
AS2052 CAS: 1874264-99-9



GreenCat

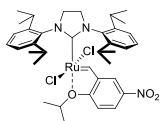
AS2034 CAS: 1448663-06-6

## RCM of sterically demanding substrates



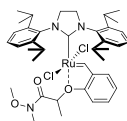
E. Cheng, B. Qu, Y. Zhang, Z. P. Cannone, J. C. Leung, S. Toyuhnikov, K. D. Nguyen, N. Haddad, S. Biswas, X. Hou, K. Kozackiewicz, M. Chwalba, A. Tracz, S. Czarnocki, J. J. Song, M. C. Kozłowski, C. H. Sonnarayake, A. Venetillo, catalytic system for enantioselective synthesis of 2-substituted 1,4-benzodioxanes" *Chem. Sci.*, 10, 4339–4345, (2019).

Other catalysts suitable for this transformation:



**nitro-Grela SIPr**

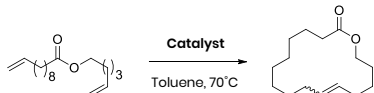
**AS2033** CAS: 928795-51-1



**GreenCat**

**AS2034** CAS: 1448663-06-6

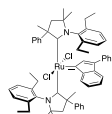
## Macrocyclic Ring-Closing Metathesis (mRCM)



Catalyst	Loading [ppm]	C [mM]	GC Yield [%]	TON
CatMETium RF2	30	5	<1	<300
Grubbs II	30	5	12	4 000
<b>UltraNitroCat</b>	<b>30</b>	<b>5</b>	<b>90</b>	<b>30 000</b>
<b>UltraNitroCat</b>	<b>10</b>	<b>20</b>	<b>62</b>	<b>62 000</b>

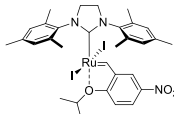
R. Gavin, A. Tracz, M. Chwalba, A. Kozackiewicz, B. Trzaskowski, K. Skowerski "Cyclic Alkyl Amino Ruthenium Complexes—Efficient Catalysts for Macrocyclization and Acrylonitrile Cross Metathesis" *ACS Catal.*, 7, 8, 6443–5449, (2017).

Other catalysts suitable for this transformation:



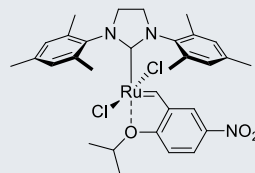
**UltraCat**

**AS2086** CAS: 2055540-61-7



**nitro-Grela I<sub>2</sub>**

**AS2052** CAS: 1874264-99-9

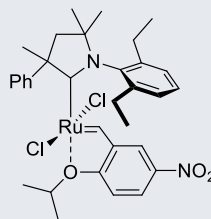


## nitro-Grela

**AS2032**

CAS: 502964-52-5

- Universal catalyst which provides good results in a wide spectrum of transformations. High selectivity in cross metathesis (CM) reactions between type 1 olefins (rapid homodimerization, homodimers consumable) and an electron deficient partner. Very good for metathesis with sterically demanding substrates.
- Compatible with toluene, ethyl acetate, dimethylcarbonate, CPME, DCM, DCE, neat substrate in the temp. range of RT to 100°C.
- High stability allows handling in air.

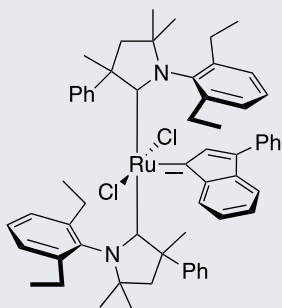


## UltraNitroCat

**AS2091**

CAS: 2106819-64-9

- Shows unmatched efficiency in cross metathesis with acrylonitrile and in macrocyclization. Very good for RCM leading to formation of small and medium rings.
- Compatible with toluene, ethyl acetate, dimethylcarbonate, CPME, DCM, DCE, neat substrate in the temp. range of RT to 85°C.
- High stability allows handling in air.



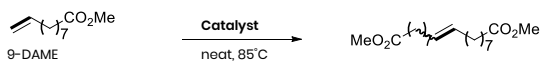
## UltraCat

AS2086 CAS: 2055540-61-7

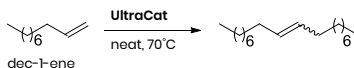
- Versatile catalyst, excellent for CM of terminal, type 1 olefins; excellent for ethenolysis, very good for mRCM and RCM leading to small/medium rings.
- Compatible with toluene, ethyl acetate, dimethylcarbonate, CPME; neat substrate in the temperature range of 40 to 85°C.
- High stability allows handling in air.

# Cross Metathesis (CM)

CM of terminal, type-1 olefins



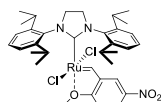
Catalyst	Loading [ppm]	GC yield [%]	TON
Hov-II	1 (4x0.25)	12	60 000
Gru-II	1 (4x0.25)	<1	-
UltraCat	1 (4x0.25)	88	440 000
	0.5 (2x0.25)	66	660 000
	0.25	41	820 000



Catalyst	Loading [ppm]	GC yield [%]	TON
UltraCat	0.2	84	2 100 000
	0.15	75	2 500 000
	0.1	59	2 950 000
	0.05	34	3 400 000

R. Gawin, A. Kozakiewicz, P. A. Gurka, P. Dąbrowski, K. Skowerski "Bis(Cyclic Alkyl) Amino Carbene" Ruthenium Complexes: A Versatile, Highly Efficient Tool for Olefin Metathesis" *Angew. Chem. Int. Ed.*, 56, 910, (2017).

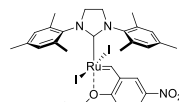
Other catalysts suitable for this transformation:



nitro-Grela SIPr

AS2033

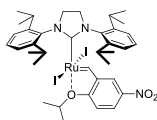
CAS: 928795-51-1



nitro-Grela I<sub>2</sub>

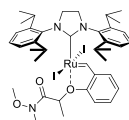
AS2052

CAS: 1874264-99-9



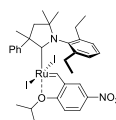
nitro-Grela SIPr I<sub>2</sub>

AS2053



GreenCat I<sub>2</sub>

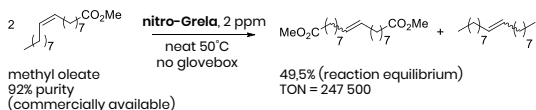
AS2094



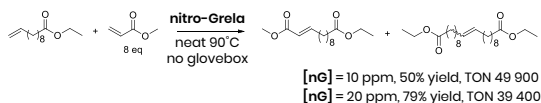
UltraNitroCat I<sub>2</sub>

AS2092

## CM of internal olefins & sterically demanding substrates

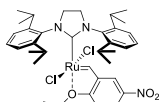


## CM with electron deficient alkenes



K. Kaczanowska, B. Trzaskowski, A. Peszczyńska, A. Tracz, R. Gawin, T. K. Olszewski, K. Skowroński "Cross metathesis with acrylates: N-heterocyclic carbene (NHC) versus cyclic alkyl amino carbene (CAAC)-based ruthenium catalysts, an unanticipated influence of the carbene type on efficiency and selectivity of the reaction" *ChemCatChem*, 12, 24, 6366–6374, (2020).

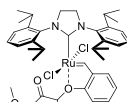
### Other catalysts suitable for this transformation:



**nitro-Grela SiPr**

**AS2033**

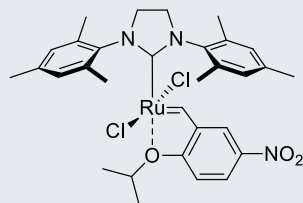
CAS: 928795-51-1



**GreenCat**

**AS2034**

CAS: 1448663-06-6



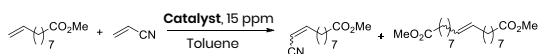
## nitro-Grela

**AS2032**

CAS: 502964-52-5

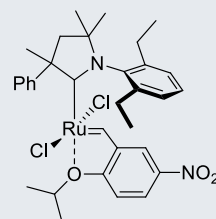
- Universal catalyst which provides good results in a wide spectrum of transformations. High selectivity in cross metathesis (CM) reactions between type 1 olefins (rapid homodimerization, homodimers consumable) and an electron deficient partner. Very good for metathesis with sterically demanding substrates.
- Compatible with toluene, ethyl acetate, dimethylcarbonate, CPME, DCM, DCE, neat substrate in the temp. range of RT to 100°C.
- High stability allows handling in air.

## CM with acrylonitrile



Catalyst	Loading [ppm]	GC yield [%]	TON
UltraNitroCat	75	75	38 000
nitro-Grela	34	81	18 400

R. Gawin, A. Tracz, M. Chwałka, A. Kozakiewicz, B. Trzaskowski, K. Skowroński "Cyclic Alkyl Amino Ruthenium Complexes—Efficient Catalysts for Macrocyclization and Acrylonitrile Cross Metathesis" *ACS Catal.*, 7, 8, 6443–5449, (2017).

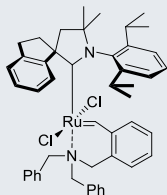


## UltraNitroCat

**AS2091**

CAS: 2106819-64-9

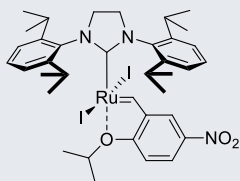
- Shows unmatched efficiency in cross metathesis with acrylonitrile and in macrocyclization. Very good for RCM leading to formation of small and medium rings.
- Compatible with toluene, ethyl acetate, dimethylcarbonate, CPME, DCM, DCE, neat substrate in the temp. range of RT to 85°C.
- High stability allows handling in air.



## SlashCat

AS2153

- Shows unmatched efficiency in ethenolysis.
- Compatible with toluene, ethyl acetate, dimethylcarbonate, neat substrate in the temp. range of 30 to 85°C.
- High stability allows handling in air.



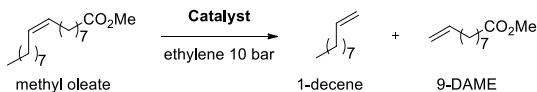
## nitro-Grela SIPr I<sub>2</sub>

AS2053

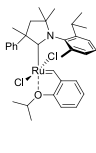
CAS: 1874265-00-5

- Excellent for CM of terminal, type 1 olefins. Provides improved selectivity in metathesis of substrate bearing unprotected -OH and -COOH groups. Very good for RCM with sterically non-demanding substrates leading to small/medium rings. Less sensitive to small impurities than nitro-Grela and nitro-Grela-SIPr catalysts. Suppressed C=C double bond migration.
- Compatible with toluene, ethyl acetate, dimethylcarbonate, CPME, DCM, DCE, neat substrate in the temperature range of 40 to 110°C.
- High stability allows handling in air.

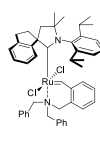
## Ethenolysis



Catalyst	Loading [ppm]	Conversion [%]	Selectivity [%]	TON
Reference	1	41	92	378 000
catalyst*	0.5	25	94	472 000
	0.25	16	97	604 000
SlashCat	1	60	96	574 000
	0.5	43	98	848 000
	0.25	32	99	1 260 000

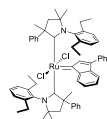


\*reference catalyst

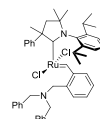


SlashCat AS2153

Other catalysts suitable for this transformation:



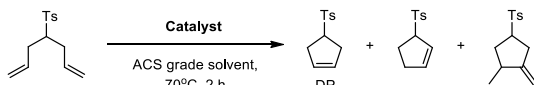
UltraCat AS2086



AS2131

## Metathesis

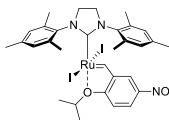
under challenging conditions  
(low grade solvents, impurities, acidic functional groups)



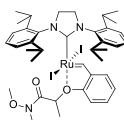
Catalyst	Solvent	Selectivity [%]	GC Yield [%]
nitro-Grela	Toluene	89	54
	iPrOH	72	21
nitro-Grela SIPr I <sub>2</sub>	Toluene	99	99
	iPrOH	97	94

A. Tracz, M. Matczak, K. Urbaniak, K. Skowierski 'Nitro-Grela'-type complexes containing iodides – robust and selective catalysts for olefin metathesis under challenging conditions' *Baistain J. Org. Chem.*, 11, 1823-1832, (2015).

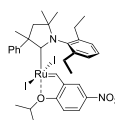
Other recommended catalysts:



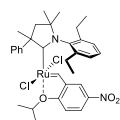
nitro-Grela I<sub>2</sub> AS2052



GreenCat I<sub>2</sub> AS2094



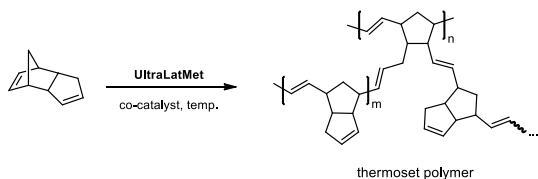
UltraNitroCat I<sub>2</sub> AS2092



UltraNitroCat AS2091

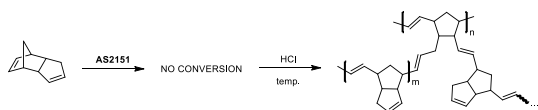
# Ring Opening Meta-thesis Polymerization

Latent catalysts activated by **metal complexes**

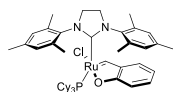


R. Gawin, A. Kazakiewicz, P. A. Gurka, P. Dąbrowski, K. Skowerski, Bis(Cyclic Alkyl Amino Carbons) Ruthenium Complexes: A Versatile, Highly Efficient Tool for Olefin Metathesis *Angew. Chem., Int. Ed.* 56, 910, (2017).

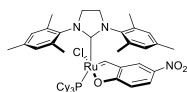
Latent catalysts activated by **acid**



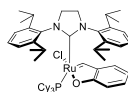
Other catalysts activated by acid:



**LatMet**  
AS2035

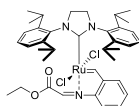
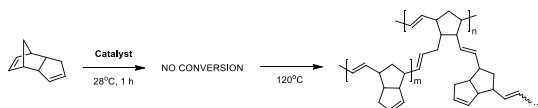


**Nitro-LatMet**  
AS2036



**LatMet SIPR**  
AS2037

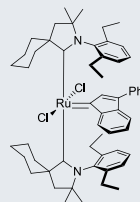
Latent catalysts activated by **temperature**



Other catalysts  
activated by  
temperature:

**HeatMet SIPR**  
AS2056

S. J. Czarnocki, I. Czelusniak, T. K. Olszowski, M. Malinska, K. Wozniak, K. Grela, "Rational and Then Serendipitous Formation of Aza Analogues of Hoveyda-Type Catalysts Containing a Chelating Ester Group Leading to a Polymerization Catalyst Family" *ACS Catal.* 7, 415 – 421, (2017).

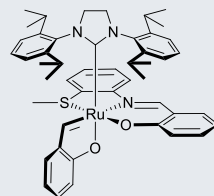


## UltraLatMet

AS2098

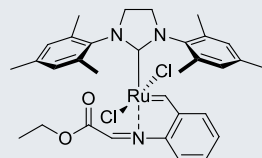
2501978-79-4

- Latent catalyst for ROMP activated by co-catalyst - HCl free activation.
- Two component formulations with shelf life up to 12 months.
- Adjustable gelation time ranging from minutes to days.



AS2151

- excellent latency and shelf life can be stored at room temp. for 3-6 months
- High activity after activation - short working time.



## HeatMet

AS2055

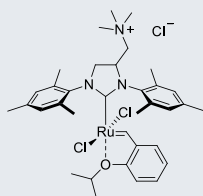
2248443-33-4

- No activation additives required.
- Good working time.
- Good for slow curing of large parts.

## Contact:

**Apeiron Synthesis S. A.** | info@apeiron-synthesis.com  
Wrocław Technology Park, Duńska 9, 54-427 Wrocław, Poland

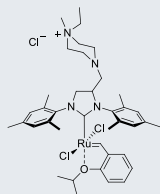
**Cengiz Azap** | PhD Chief Commercial Officer  
cengiz.azap@apeiron-synthesis.com | mobile: +49 176 8142 0090



## StickyCat Cl

**AS2040** 1452227-72-3

- Simple removal of residual ruthenium by extraction with water or work-up with silica gel.
- Residual ruthenium < 5 ppm.
- High activity in the temperature range of 40 – 110°C.
- Designed to be deposited on solid support to increase reusability or for continuous flow applications
- Good solubility in neat water (up to 60 mg/ml).
- High stability in non-degassed water.



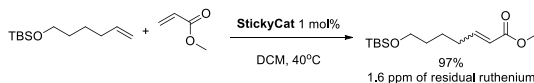
## AquaMet

**AS2038** 1414707-08-6

- Water soluble catalyst; also in some chlorinated organic solvents (DCM, chloroform).

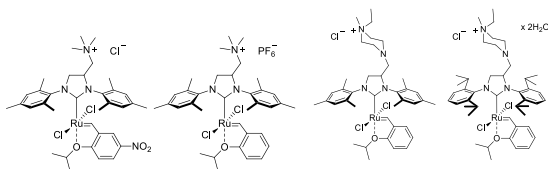
# Ammonium Tagged Catalysts

Catalysts enabling removal of residual ruthenium



K. Stowerski, C. Wierzbicka, G. Szczepaniak, Ł. Gultajski, M. Błonieć, K. Grela "Easily removable olefin metathesis catalysts" *Green Chem.*, 14, 3264-3268, (2012).

other catalysts in this group:



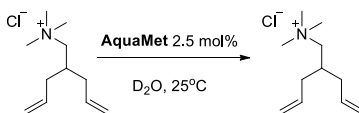
**nitro-StickyCat Cl**  
**AS2041**

**StickyCat PF<sub>6</sub>**  
**AS2054**

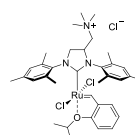
**AquaMet**  
**AS2038**

**FixCat**  
**AS2061**

## Metathesis in aqueous media



Other catalysts in this group:



**StickyCat Cl**  
**AS2040**

K. Stowerski, C. Wierzbicka, G. Szczepaniak, Ł. Gultajski, M. Błonieć, K. Grela "Easily removable olefin metathesis catalysts" *Green Chem.*, 14, 3264-3268, (2012).