Universidad Zaragoza

Year : 2020/21

60459 - Asymmetric catalysis

Syllabus Information

Academic Year: 2020/21
Subject: 60459 - Asymmetric catalysis
Faculty / School: 100 - Facultad de Ciencias
Degree: 543 - Master's in Molecular Chemistry and Homogeneous Catalysis
ECTS: 2.0
Year: 1
Semester: Second semester
Subject Type: Optional
Module: ---

1.General information

1.1.Aims of the course

The objective of the subject is to study the general principles of asymmetric catalysis, and the main catalytic systems based on chiral transition metal compounds, emphasizing the study of the reaction mechanisms.

1.2.Context and importance of this course in the degree

Asymmetric Catalysis is a fundamental area inside the Catalysis that is closely related to other areas of Chemistry, such as Organometallic Chemistry and, Inorganic and Organic Chemistry. *Asymmetric Catalysis* is an optional subject of 2 ECTS scheduled in the second semester. The subject is included the optional module *Horizons in Molecular Chemistry*. The learning outcomes in this field are complemented by those of the three subjects included in the obligatory module of the master: *Catalysis*, *Synthetic Strategies in Advanced Organic Synthesis* and *Molecular Design in Inorganic and Organometallic Chemistry*. Moreover, *Asymmetric Catalysis* is closely related to the other subjects of the optional module: *Supramolecular Chemistry*, *Chemistry of Advanced Materials*, *Chemistry at the Frontiers of th the Biology or Sustainable* Chemistry and Catalysis.

1.3.Recommendations to take this course

It is recommended to have basic concepts of Inorganic Chemistry, Organic, Organometallic and Catalysis.

2.Learning goals

2.1.Competences

To identify concepts related to the catalytic activity of chiral compounds and their application in the synthesis of optically active compounds.

To apply the acquired knowledge to interpret potential catalyst applications depending on their nature.

To interpret and evaluate the most important parameters that characterize the enantioselective catalytic reactions.

To design and evaluate organic reactions catalyzed by chiral transition metal compounds.

2.2.Learning goals

To know the general principles of stereochemistry and stereodifferentiation in catalysis.

To know the most important enantioselective catalytic processes.

To analyse the most relevant parameters that characterize the efficiency of a catalyst in asymmetric reactions.

To evaluate the potential in asymmetric catalysis of homogeneous catalysts according to their nature.

To understand and interpret new knowledge in asymmetric catalysis.

2.3.Importance of learning goals

Learning outcomes of the subject are of great importance due to the significance of the field of study. Because of important industries such as agrochemicals, the flavors and fragrances, polymers and especially the pharmaceutical, produce and demand enantiopure compounds, the asymmetric synthesis is a discipline that plays a central role in current chemistry.

Among the different methods available for the preparation of enantiopure compounds, asymmetric catalysis is a competitive methodology, and among different types of catalysts, the best expectations are focused on the use of transition metals complexes.

3.Assessment (1st and 2nd call)

3.1.Assessment tasks (description of tasks, marking system and assessment criteria)

Continuous assessment of this subject is based on the following activities:

1.- Class participation, exercises and questions proposed by the teacher (40%).

2.- Oral presentation and group discussion of the contents of selected scientific papers (60%).

The students that have not passed the subject or wish to improve their score have the option to carry out a global test, either in the first or the second call, that will represent 100% of the final student's grade.

The number of official examination calls per registration and their use will be subjected to the statements of the *Regulation of Permanence in Master Studies* and the *Regulation of the Learning Assessment*

(https://ciencias.unizar.es/normativas-asuntos-academicos). The latest document will also regulate the general design and scoring criteria of the assessment activities, as well as the exam schedules and timetable for the post-examination review.

4.Methodology, learning tasks, syllabus and resources

4.1.Methodological overview

The learning process designed for the course is essentially based on participative and interactive theoretical sessions that will be complemented with seminars and personalized tutoring classes. In order to encourage the scientific communication skills we propose the oral presentation of relevant scientific results and their discussion.

4.2.Learning tasks

The course includes the following learning tasks:

- Participative and interactive theoretical sessions (1.5 ECTS).
- Seminars (0.5 ECTS).
- Personalized tutoring classes

Teaching and assessment activities will be carried out in the classroom with all students in person unless, due to the health situation, the provisions issued by the competent authorities and by the University of Zaragoza arrange to carry them out by telematics means. If the number of enrolled students exceeds the established capacity of the classroom, the teaching will follow the guidelines of the Faculty of Sciences and/or the University of Zaragoza. Tutorial activity will be carried out mainly in remote using on-line tools.

4.3.Syllabus

The course will address the following topics:

Introduction to asymmetric catalysis

Topic 1. Introduction to asymmetric catalysis (2 h)
Enantioselective synthesis and catalysis. Synthetic routes of optically active compounds. Asymmetric catalysis by transition metal complexes. Stereochemical terminology.

Asymmetric catalytic reactions

Topic 2. Asymmetric metal-catalyzed hydrogenation in homogeneous phase (4.5 h)
Rhodium-Catalyzed Hydrogenation. Development of chiral phosphorous ligands. First examples of asymmetric hydrogenations. Industrial synthesis of L-DOPA. Catalytic precursors. Detection of intermediates. Unsaturated route. Dihydride route. Theoretical calculations. Mechanism of the asymmetric hydrogenation of olefins by rhodium-diphosphane complexes: integrated mechanism. Hydrogenation of olefins catalyzed by monodentate phosphane-Rh complexes. Non-linear effects. Hydrogenation of "largely" functionalized olefins.

Topic 3. Asymmetric metal-catalyzed transfer hydrogenation in homogeneous phase (3.5 h)
Transfer hydrogenation reactions. Meerwein-Schmidt-Ponforf-Verley reduction: mechanism. Asymmetric versions. Transfer hydrogenation catalyzed by transition metal complexes. Hydride mechanism. Noyori's mechanism. Amino-carboxylate complexes as asymmetric transfer hydrogenation catalysts: a case study.

Topic 4. Asymmetric metal-catalyzed Diels-Alder reactions (2.5 h)
Diels-Alder reactions. Activity, selectivity, enantioselectivity. Dienes, dienophiles and catalysts. Mechanistic considerations. Catalytic systems. One point binding half-sandwich catalyst: origin of enantioselectivity.

Topic 5. Asymmetric metal-catalyzed Friedel-Crafts reactions (2.5 h)
Friedel-Crafts reactions. Friedel-Crafts alkylation reactions. Hydroxyalkylation reactions. Aza-Friedel-Crafts reactions. Reactions of *trans-b*-nitrostyrenes with indoles: origin of enantioselectivity.

Topic 6. Asymmetric metal-catalyzed allylic alkylations (2.5 h)
Allylic alkylation reactions. Mechanistic studies. Catalysts. Selectivity. Enantiodiscrimination: Enantiofacial complexation and ionization, ionization of enantiotopic leaving group, enantioface exchange in the allyl complex, attack at enantioselective termini of the allyl, enantiofaces of prochiral nucleophiles. Dynamic kinetic asymmetric transformations. Recent developments in asymmetric allylic alkylations.

Topic 7. Asymmetric transition metal-catalyzed oxidations (2.5 h)
Oxidation reactions, olefin oxidation, industrial importance. Asymmetric epoxidation. Epoxidation of allylic alcohols. Epoxidation of alkenes other than allylic alcohols. Catalytic asymmetric dihydroxilation. Catalytic asymmetric oxygenations with the oxidants H_2O_2 and O_2.

4.4.Course planning and calendar

Further information concerning the timetable, classroom, assessment dates and other details regarding this course, will be provided on the first day of class or please refer to the Faculty of Science website https://ciencias.unizar.es.

The submission of assignments will be done according to the schedule to be announced in advance.

Students will be provided with diverse teaching material either at reprography or through the University's virtual platform https://moodle2.unizar.es/add.

The programmed activities will take place during the second semester in weekly two-hour sessions. The information about schedules, calendars and exams is available at the websites of the Sciences Faculty, https://ciencias.unizar.es/calendario-y-horarios, and the Master, http://masterqmch.unizar.es.

4.5.Bibliography and recommended resources