| Teaching Guide | | | | |
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| Identifying Data | | | | 2016/17 |
| Subject (*) | Síntese estereoselectiva | | Code | 610509012 |
| Study programme | Mestrado en Investigación Química e Química Industrial (plan 2016) | | | |
| Descriptors | | | | |
| Cycle | Period | Year | Type | Credits |
| Official Master's Degree | Yearly | First | Optativa | 3 |
| Language | Spanish | | | |
| Teaching method | Face-to-face | | | |
| Prerequisites | | | | |
| Department | Química Fundamental | | | |
| Coordinador | Perez Sestelo, Jose | E-mail | jose.perez.sestelo@udc.es | |
| Lecturers | Perez Sestelo, Jose | E-mail | jose.perez.sestelo@udc.es | |
| Web | miiquimica.webnode.es | | | |
| General description | the subject is part of module 2: Synthetic Chemistry. It is primarily related to the subjects of this module, but has some relationship to some subjects of Chemical Biology (Chemistry of Biomolecules, Medicinal Chemistry and Chemistry of Natural Products) and Nanochemistry and New Materials (Molecular Materials, etc.) tracks.<br>The subject covers the study of the generation of (new) stereocenters starting from substrates that contain stereocenters or proestereogenic units (C=C or C=X bonds). Therefore, incorporates fundamental concepts for the training in synthesis, such as the analysis of the Stereochemistry in chemical reactions, the conformational analysis of organic compounds and the reactivity models, including the diastereoselectivity induced by the substrate, the chiral auxiliary or a chiral-non racemic additive (catalyst, ligand). | | | |

| Study programme competences | |
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| Code | Study programme competences |
| A1 | Define concepts, principles, theories and specialized facts of different areas of chemistry. |
| A2 | Suggest alternatives for solving complex chemical problems related to the different areas of chemistry. |
| A4 | Innovate in the methods of synthesis and chemical analysis related to the different areas of chemistry |
| A7 | Operate with advanced instrumentation for chemical analysis and structural determination. |
| A8 | Analyze and use the data obtained independently in complex laboratory experiments and relating them with the chemical, physical or biological appropriate techniques, including the use of primary literature sources |
| B1 | Possess knowledge and understanding to provide a basis or opportunity for originality in developing and / or applying ideas, often within a research context |
| B2 | Students should apply their knowledge and ability to solve problems in new or unfamiliar environments within broader (or multidisciplinary) contexts related to their field of study. |
| B3 | Students should be able to integrate knowledge and handle complexity, and formulate judgments based on information that was incomplete or limited, include reflecting on social and ethical responsibilities linked to the application of their knowledge and judgments. |
| B4 | Students should be able to communicate their conclusions, and the knowledge and the reasons that support them to specialists and non-specialists in a clear and unambiguous manner |
| B5 | Students must possess learning skills to allow them to continue studying in a way that will have to be largely self-directed or autonomous. |
| B7 | Identify information from scientific literature by using appropriate channels and integrate such information to raise and contextualize a research topic |
| B10 | Use of scientific terminology in English to explain the experimental results in the context of the chemical profession |
| B11 | Apply correctly the new technologies to gather and organize the information to solve problems in the professional activity. |

| Learning outcomes | | | |
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| Learning outcomes | Study programme competences | | |
| ? Use of the terms and definitions of chemical reactivity, and the proper description of stereoselective reactions | AC1 | BC10 | |

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| ? Ability to use and communicate, both in written and oral forms, the basic concepts of dynamic stereochemistry in Organic Chemistry | | BC2<br>BC4<br>BC10 | |
| ? Be familiar with the tridimensional representation of molecules, building the capacity to estimate their possible conformations. | | BC1<br>BC2<br>BC3<br>BC7<br>BC10 | |
| ? Capacity to visualise molecular structures using models generated by quantum mechanical computations. | AC2<br>AC4<br>AC7 | BC1<br>BC2<br>BC3<br>BC7<br>BC11 | |
| ? Understand the relationship between the tridimensional structure of the organic compounds and their reactivity | | BC1<br>BC2<br>BC10 | |
| ? Understand the structural properties and the reactivity of the prostereogenic centers in those processes that generate new stereogenic elements. | AC1 | BC1 | |
| ? Rationally explain the outcome of a chemical reaction in terms of the Stereochemistry | | BC1<br>BC4<br>BC7 | |
| ? To know the main classes of reactions that generate stereocenters, and understand their mechanisms. | AC1 | BC1<br>BC3<br>BC4<br>BC10 | |
| ? Understand the stereoelectronic effects and their role in chemical reactivity | AC1 | BC1<br>BC4<br>BC5 | |
| ? Understand the value of the analysis of transition structures in chemical reactions, and be able to visualise those generated by quantum mechanical computations | AC2<br>AC4<br>AC7 | BC1<br>BC2<br>BC3<br>BC7<br>BC11 | |
| ? Understand how the chirality of enantiopure compounds can be transmited to other chiral non-racemic products through chemical transformations | AC1<br>AC8 | BC1<br>BC2<br>BC5<br>BC10 | |
| ? Quantity the relative ration of diastereoisomers and enantiomers using phisical and chemical methods. | AC1 | | |
| ? Predict the outcome of a chemical reaction that generates novel stereocenters | AC1 | BC1 | |
| ? Propose synthetic sequences for the preparation of chiral non-racemic molecules. | AC1 | BC4<br>BC5<br>BC11 | |
| ? Acquire and utilize the existing literature on synthetic processes in which stereocenters are generated. | | BC7<br>BC10 | |

| Contents | |
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| Topic | Sub-topic |
| Chapter 1. Stereochemistry in chemical reactions | Chirality. Stereogenic units. Topicity. Diastereoselectivity and enantioselectivity. The ?chiral pool?: chiral auxiliaries and chiral ligands. Kinetic resolution |

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| Chapter 2. Conformational analysis and chemical reactivity | Conformational control of the diastereoselectivity. Conformational analysis. Allylic tension. Stereoelectronic effects. The Curtin-Hammett principle. |
| Chapter 3. Additions to C=C trigonal centers | Additions to C=C bonds. Diastereoselective epoxidations of acyclic and cyclic olefins. Enantioselective epoxidations (Sharpless, Jacobsen, Shi). Synthetic applications of epoxyalcohols. Diastereoselective dihydroxylations of acyclic and cyclic olefins. Sharpless enantioselective dihydroxylation (SAD). Sharpless enantioselective aminohydroxylation (SAA). Diastereoselective olefin hydrogenation. Enantioselective hydrogenación |
| Chapter 4. Additions to C=O trigonal centers. | Addition to C=X bonds. Sterecontrol in nucleophilic additions to carbonyl groups in acyclic and cyclic compounds. 1,2 and 1,3-Asymmetric induction models. Enantioselective additions to  ketones. Nucleophilic additions to imines and sulfinamides. |
| Chapter 5. Conjugate additions to C=C-C=X systems | Conjugate additions to C=C-C=O systems. Diastereoselective conjugate additions. Catalytic asymmetric conjugate additions. Reduction of conjugated systems. Asymmetric epoxidation of enones. |
| Chapter 6. Additions to C=C-X systems | Additions to C=C-OM bonds. Regio- y stereoselective synthesis of enolates. Diastereoselective reactions of chiral enolates: alkylation, halogenation, amination and hydroxilation. Diastereoselective reactions of chiral azaenolates |
| Chapter 7. Reactions between trigonal centers | Reactions between trigonal centers: generation of two or more stereocenters. Aldol reaction: control of the diastereoselectivity. The Zimmerman-Traxler model. Organocatalyzed aldol reactions. Aldol Mukaiyama reaction of latent enolates. Double diastereoselection: chiral centers on the components of the aldol reaction. Addition of allyl organometals to carbonyl groups. Allylic boranes. Allylic stannanes and silanes: catalysis by chiral Lewis acids and bases. Addition of allyl organometals to imines. Diastereoselectivity in Diels-Alder cycloadditions |

| Planning | | | | |
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| Methodologies / tests | Competencies | Ordinary class hours | Student?s personal work hours | Total hours |
| Guest lecture / keynote speech | A1 A4 B1 B3 B4 B5 B7 B10 B11 | 12 | 24 | 36 |
| Seminar | A2 A4 A8 B2 B3 B4 B5 B7 B10 B11 | 5 | 20 | 25 |
| ICT practicals | A7 A8 B1 B3 B5 | 2 | 4 | 6 |
| Objective test | A1 A2 A4 A8 B1 B5 | 3 | 3 | 6 |
| Personalized attention | | 2 | 0 | 2 |
| **(*)The information in the planning table is for guidance only and does not take into account the heterogeneity of the students.** | | | | |

| Methodologies | |
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| Methodologies | Description |
| Guest lecture / keynote speech | It will be held 12 sessions of lectures in one group where the theoretical contents of the course will be presented with illustrative examples. It will consist mainly of PowerPoint presentations. Copies of these presentations will be made available to the students in advance of the course via the virtual campus. This will allow the students to study ahead the contents of the course and will facilitate the monitoring of explanations. Attendance to these lectures is mandatory |
| Seminar | 4 sessions in small group seminars where students will present the work proposed by the professor followed by a discussion section. Students will have access to the proposed exercises and papers in advance via the virtual campus of the course. Attendance to these classes is mandatory |
| ICT practicals | 3 sessions in small group seminars where students will have the opportunity to visualize the transition structures generated by computational methods that correspond to the main reaction of the course. Attendance to these classes is mandatory. |

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| Objective test | A written exam will be performed with the purpose to measure the knowledge adquired during the course |

| Personalized attention | |
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| **Methodologies** | **Description** |
| Guest lecture / keynote speech<br>Seminar<br>ICT practicals<br>Objective test | Tutoring scheduled by the professor and coordinated by the Centre. It will be 2 hours per student and will involve the supervision of proposed work, clarifying doubts, etc. Attendance to these classes is mandatory. |

| Assessment | | | |
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| **Methodologies** | **Competencies** | **Description** | **Qualification** |
| Seminar | A2 A4 A8 B2 B3 B4 B5 B7 B10 B11 | Continuous assessment (N1) will be 40% of the qualification and will consist of two components: interactive class in small groups (seminars) and interactive class in very small groups (tutorials). Seminars and tutorials include the following: resolution of exercises and practical cases (15%), realization of homework and reports (10%), oral presentations [(papers, reviews and practical cases), 10%] and oral questions during the course (5%). | 40 |
| Objective test | A1 A2 A4 A8 B1 B5 | The final exam (N2) will cover all the contents of the course. | 60 |

| Assessment comments |
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| The student's score will result of applying the following formula:<br>Final score = 0.4 x N1 + 0.6 x N2<br>N1 and N2 are the marks corresponding to the continuous assessment (0-10 scale) and the final exam (0-10 scale), respectively.<br>The repeaters will have the same system of class attendance than those who study the course for first time. |

| Sources of information | |
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| **Basic** | - Koskinen, A. M. P (2012). Asymmetric Synthesis of Natural Products. Wiley, New York<br>- Mulzer, J.; , Jacobsen, E. N.; Pfaltz, A.; Yamamoto, Y. (1999). Basic Principles of Asymmetric Synthesis, In Comprehensive Asymmetric Catalysis. Springer, Heidelberg<br>- Corey, E. J.; Kürti, L.  (2010). Enantioselective Chemical Synthesis. Methods, Logic and Practice. Direct Book Publishing: LLC |
| **Complementary** | - Atkinson, R. S. (1995). Stereoselective Synthesis. Chichester, UK:John Wiley & Sons<br>- Procter, G. (1996). Asymmetric Synthesis. Oxford University Press, Oxford<br>- Ager, D. J.; East, M. B. (1996). Asymmetric Synthetic Methodology. CRC Press, Boca Raton, FL<br>- Corey, E. J.; Kürti, L.  (2010). Enantioselective Chemical Synthesis.Methods, Logic and Practice. Direct Book Publishing: LLC |

| Recommendations |
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| **Subjects that it is recommended to have taken before** |
| Profundización en Química Orgánica/610509004<br>Análise Estrutural Avanzado/610509005 |
| **Subjects that are recommended to be taken simultaneously** |
| Compostos organometálicos en síntese e catálise /610509011 |
| **Subjects that continue the syllabus** |
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| **Other comments** |

The students should review the theoretical concepts introduced in each chapter using the reference manual and the material provided by the professor. Those students, which have significant difficulties when working the proposed activities, should contact with the professor during the tutorials, in order to analyze the problem and to receive the necessary support.
The professor will analyze with those students who do not successfully pass the evaluation, and so wish, their difficulties in learning the course content. Additional material (questions, exercises, tests, etc..) to strengthen the learning of the course might be also provided.