



## Teaching Guide

| Teaching Guide           |  |        |                           |           |
|--------------------------|--|--------|---------------------------|-----------|
| Identifying Data         |  |        |                           | 2022/23   |
| Subject (*)              | Synthetic Applications of Organometallic compounds   |        | Code                      | 610509112 |
| Study programme          | Mestrado Universitario en Investigación Química e Química Industrial (Plan 2020)   |        |                           |           |
| Descriptors              |  |        |                           |           |
| Cycle                    | Period   | Year   | Type                      | Credits   |
| Official Master's Degree | 2nd four-month period  | First  | Optional                  | 3         |
| Language                 | Spanish  |        |                           |           |
| Teaching method          | Face-to-face   |        |                           |           |
| Prerequisites            |  |        |                           |           |
| Department               | Química  |        |                           |           |
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| Lecturers                | Perez Sestelo, Jose  | E-mail | jose.perez.sestelo@udc.es |           |
|                          | Sarandeses Da Costa, Luis Alberto  |        | luis.sarandeses@udc.es    |           |
| Web                      | www.usc.es/gl/centros/quimica/curso/master.html  |        |                           |           |
| General description      | <p>This matter is basic in the specialty Synthetic Chemistry because it studies the reactivity of organometallic compounds and their applications in synthesis and catalysis. The concepts addressed in this matter are useful in others of other modules such as Chemical Structure and Reactivity, Nanochemistry and New Materials and Biological Chemistry.</p> <p>This matter is related to others such as Organometallic Compounds and Advanced Coordination Chemistry, which cover general aspects of the structure and reactivity of the organometallic compounds and the coordination metal complexes.</p> <p>The use of organometallic compounds and catalysis by transition metals are fundamental tools of today's synthetic chemistry, both in their academic and industrial aspects. The current organic synthesis involves the development of more selective and sustainable processes, objectives for which organometallic compounds and catalysis are frequently required.</p> |        |                           |           |

## Study programme competences

| 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.   |
| A3   | Innovate in the methods of synthesis and chemical analysis related to the different areas of chemistry  |
| A6   | Design processes involving the treatment or disposal of hazardous chemicals   |
| 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.                                 |
| 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

| Learning outcomes   | Study programme competences |     |  |
|---|-----------------------------|-----|--|
| To understand the basis of catalytic cycles from the point of view of reaction coordinates and potential energy surfaces. | AC1                         | BC5 |  |
|   | AC6                         |     |  |
|   | AC8                         |     |  |

|   |     |      |  |
|---|-----|------|--|
| To understand the applications in synthesis of the diversity of processes of formation of bonds mediated by organometallic compounds. | AC2 | BC1  |  |
|   | AC3 | BC2  |  |
|   | AC6 | BC4  |  |
|   |     | BC7  |  |
|   |     | BC10 |  |
|   |     | BC11 |  |
| Propose synthetic sequences with key disconnections based on synthetic processes of organometallic compounds.                         | AC2 | BC1  |  |
|   | AC3 | BC2  |  |
|   | AC6 | BC4  |  |
|   |     | BC7  |  |
|   |     | BC11 |  |

| Contents  |   |
|---|---|
| Topic   | Sub-topic   |
| Topic 1. Energy principles and fundamentals of organometallic catalytic cycles.       | ? General concepts<br>? Thermodynamics and kinetics of the catalytic cycle of reactions catalysed by transition metals.<br>? Application: Pd catalyzed cross coupling; Synergy between computational and experimental results.  |
| Topic 2. Cross-coupling reactions and Heck reaction.                                  | ? Cross-coupling reactions. Generalities. Leaving groups. Metals. Selectivity.<br>? Carbon-carbon bond formation reactions: organometallic compounds of Li, Zn, Al, Zr, Sn, Cu; Compounds of B and Si; Other metals; Enolates.<br>? Carbon-heteroatom bond formation reactions.<br>? Heck reaction. Components of the reaction. Inter- and intramolecular reactions.<br>Asymmetric Heck Reactions. Heck reactions with organometallic species.  |
| Topic 3. Insertion reactions.   | ? Carbonylative reactions. Generalities. Mechanism.<br>? Carbonylative coupling reactions.<br>? Hydroformylation reactions.<br>? Carbonylation reactions with carbonyl complexes.<br>? Carboxylation.<br>? Decarbonylative reactions and decarbonylative couplings.<br>? Other insertion reactions with zirconium and titanium.   |
| Topic 4. Reactions of $\eta^3$ -allyl complexes.                                      | ? Palladium $\eta^3$ -allyl complexes (1. Synthesis and properties; 2. Regioselectivity and stereoselectivity).<br>? Allylic substitution reactions catalyzed by palladium complexes (1. Allylic alkylation; 2. Amination, etherification and allyl reduction; 3. Cyclization reactions through alkene insertion processes; 4. Cycloaddition reactions via trimethylenemethane intermediates) .<br>? Allylic substitution reactions catalyzed by complexes of other transition metals (Iridium, Nickel, Iron, Molybdenum).<br>? Alkylation reactions with alkynes and alenes catalyzed by Rh complexes. |
| Topic 5. Reactions of electrophilic complexes of alkenes, alkynes, dienes and arenes. | ? Alkyl insertion reactions and Heck, Suzuki, etc., tandem reactions.<br>? Insertion reactions mediated by other metals (Zr and Ti).<br>? Electrophilic additions on alkenes and alkynes.<br>? Reaction of Nicholas and Pauson-Khand.<br>? Reactions of alkenes with palladium in high oxidation state.<br>? Synthetic applications of $\eta^4$ -dienyl complexes and $\eta^6$ -arenes.   |



|   |   |
|---|---|
| Topic 6. Reactivity of metal carbenes.      | ? Characteristics of carbenes.<br>? Carbenes of transition metals. Structure and types.<br>? Transformations involving carbenes of transition metals.<br>? Olefin metathesis.   |
| Topic 7. Activation reactions of C-H bonds. | ? Introduction to the activation of C-H bonds: relevancy, difficulties and mechanisms of activation.<br>? Reactions of insertion of carbenes and nitrenes<br>? Ir-catalyzed borilation reactions<br>? Functionalization of alkanes and arenes catalyzed by Pd(II): oxygenation, arylation, halogenation, oxidative Heck reaction. |

| Planning  |  |                      |                               |             |
|---|--|----------------------|-------------------------------|-------------|
| Methodologies / tests   | Competencies                             | Ordinary class hours | Student?s personal work hours | Total hours |
| Seminar   | A1 A2 A3 A6 A8 B1<br>B2 B4 B5 B7 B10 B11 | 7                    | 18                            | 25          |
| Mixed objective/subjective test   | A1 A2 A3 B2 B5                           | 3                    | 0                             | 3           |
| Guest lecture / keynote speech  | A1 A8 B1 B2 B7 B10<br>B11                | 12                   | 33                            | 45          |
| 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                   |   |
|---------------------------------|---|
| Methodologies                   | Description   |
| Seminar                         | Seminars held with teachers of the Master, or with professionals invited from industry, the administration or other universities.<br>Interactive sessions related to the different subjects with debates and exchange of opinions with students.<br>Resolution of practical exercises (problems, test questions, interpretation and processing of information, evaluation of scientific publications, etc.).<br>Additionally, during the seminars the possibility of carrying out other methodologies is contemplated:<br>- Works, individually or in groups, on scientific topics related to the different subjects of the Master.<br>- Oral presentation of papers, reports, etc., including discussion with teachers and students.<br>- Use of specialized computer programs and internet. Online teaching support (Virtual Campus). |
| Mixed objective/subjective test | A final written exam is scheduled, which will allow to objectively evaluate the degree of assimilation and the ability to apply the contents of the subject by the student. The objective test will include a unique type of questions, which will be related to the structure, reactivity and synthesis of organic compounds, and will allow to determine if the answers are correct.  |
| Guest lecture / keynote speech  | Theoretical classes. Lectures (use of blackboard, computer, cannon), complemented with the tools of virtual teaching.   |

| Personalized attention                    |  |
|---|--|
| Methodologies                             | Description  |
| Seminar<br>Guest lecture / keynote speech | Two individual or small group tutorials are programmed to check the comprehension of the subject and to complement the student's formation through solving doubts and other questions. |

| Assessment    |              |             |               |
|---------------|--------------|-------------|---------------|
| Methodologies | Competencies | Description | Qualification |

|                                       |  |  |    |
|---------------------------------------|--|--|----|
| Seminar                               | A1 A2 A3 A6 A8 B1<br>B2 B4 B5 B7 B10 B11 | Continuous evaluation will have a weight of 40% in the grade of the subject and will consist of the following components: problem solving and practical cases (15%), oral presentation [(practical cases, problems), 10%] and oral questions during Course (10%) and attendance and participation (10%). | 40 |
| Mixed<br>objective/subjective<br>test | A1 A2 A3 B2 B5                           | The final exam will cover all the contents of the subject.   | 60 |

#### Assessment comments

The evaluation of this subject will be done through continuous evaluation and the completion of a final exam.

Repeating students will have the same attendance regime for classes as those who study the subject for the first time.

Continuous evaluation (N1) will have a 40% weight in the subject's qualification and will consist of the following components: problem solving and practical cases (15%), oral presentation [(practical cases, problems), 10%] and questions Oral during the course (10%) and attendance and participation (10%).

The final exam (N2) will cover all the contents of the subject.

The qualification of the student will be obtained as a result of applying the following formula: Final note = maximum (0.4 x N1 + 0.6 x N2)

N1 being the numeric note corresponding to the continuous evaluation (scale 0-10) and N2 the numerical note of the final exam (scale 0-10).

#### Sources of information

|                      |   |
|----------------------|---|
| <b>Basic</b>         | <ul style="list-style-type: none"> <li>- Bates, R. (2012). Organic Synthesis Using Transition Metals, 2nd Ed.. Wiley</li> <li>- Hegedus, L. S. (1999). Transition Metals in the Synthesis of Complex Organic Molecules, 2nd Ed.. University Science Books</li> </ul>  |
| <b>Complementary</b> | <ul style="list-style-type: none"> <li>- Luther, G. W. (2016). Reactivity of Transition Metal Complexes: Thermodynamics, Kinetics and Catalysis, in Inorganic Chemistry for Geochemistry and Environmental Sciences: Fundamentals and Applications. Wiley</li> <li>- Cybulski, A.; Moulijn, J. A.; Stankiewicz, A. (2010). Novel Concepts in Catalysis and Chemical Reactors: Improving the Efficiency for the Future. Wiley-VCH</li> <li>- Ananikov, V. P. (2015). Understanding Organometallic Reaction Mechanisms and Catalysis: Computational and Experimental Tools. Wiley-VCH</li> <li>- Negishi, E., Ed. (2002). Handbook of Organopalladium Chemistry for Organic Synthesis. Wiley</li> <li>- De Meijere, A., Bräse, S., Oestreich, M. (2014). Metal-Catalyzed Cross-Coupling Reactions and More. Wiley-VCH</li> <li>- Beller, M., Bolm, C. (2004). Transition Metals for Organic Synthesis, 2nd Ed.. Wiley-VCH</li> <li>- Kazmaier, U. (2012). Transition Metal Catalyzed Enantioselective Allylic Substitution in Organic Synthesis. Springer-Verlag</li> <li>- Crabtree, R. H. (2005). The Organometallic Chemistry of the Transition Metals, 4th Ed.. Wiley</li> <li>- Yu, J.-Q. (2016). Science of Synthesis: Catalytic Transformations via C-H Activation Vol. 1 &amp; 2. Thieme</li> </ul> |

#### Recommendations

##### Subjects that it is recommended to have taken before

Industrial Processes and Sustainability/610509104

Organometallic Chemistry/610509111

Advanced Structural Determination/610509103

Structure and Reactivity of Organic Compounds /610509114

##### Subjects that are recommended to be taken simultaneously

Stereoselective Synthesis/610509113

##### Subjects that continue the syllabus

#### Other comments



(\*)The teaching guide is the document in which the URV publishes the information about all its courses. It is a public document and cannot be modified. Only in exceptional cases can it be revised by the competent agent or duly revised so that it is in line with current legislation.