

Data Subject				
Code	34205			
Name	Organic Chemistry III			
Cycle	Grade			
ECTS Credits	6.0			
Academic year	2020 - 2021			
Study (s)		Contor	Acad Deried	
Study (s) Degree		Center	Acad. Period	
			year	
1110 - Degree in Cł	nemistry	Faculty of Chemistry	3 Second term	
Subject-matter				
Degree		Subject-matter	Character	
1110 - Degree in Ch	nemistry	9 - Organic Chemistry	Obligatory	
Coordination				
Name	2	Department		

# SUMMARY

The subject Organic Chemistry III that is taught in the third year of the Degree in Chemistry is a continuation and deepening of the knowledge acquired in the subjects Organic Chemistry I and II that are taught in the second year of the Degree.

Organic Chemistry is the branch of Chemistry that studies the structure, reactivity and synthesis of carbon compounds. Its study covers the behavior of many millions of chemicals with diverse properties, which constitutes one of the great challenges for teaching this discipline: to show Organic Chemistry as a logical and consistent body of interrelated ideas and not as a mere collection of facts without any connection between them.



The relevance of Organic Chemistry gives an idea of the fact that this discipline goes beyond purely academic limits and is an important part of life itself. Lipids, carbohydrates, proteins and nucleic acids, all essential compounds for life, are organic compounds. So are many substances that facilitate our daily life, such as textile fibers, medicines, antioxidants, etc.

The knowledge of the structure of organic compounds leads to the understanding of their reactivity and, consequently, the understanding of the biological processes in which many organic compounds are involved. Furthermore, the knowledge of the reactivity of organic compounds allowed us to design new synthetic methods and to prepare organic compounds with useful properties but without undesirable side effects. Such syntheses should be carried out in a sustainable manner, that is, with a minimum generation of waste.

The study of the Organic Chemistry III subject is based on the knowledge acquired in the previous subjects of Organic Chemistry I and II and, of course, in the General Chemistry I and II subjects. Based on this knowledge, a systematic study will be carried out on some functional groups that complete those already seen, as well as on different bifunctional organic compounds, including the most representative groups of natural products. This study will be completed, on the one hand, with an introduction to the synthesis design and, on the other, with an introduction to the processes catalysed by transition metals and pericyclic reactions.

The objectives to achieve in this subject can be summarised as follows:

• To identify the different functional groups present in the polyfunctional organic molecules, their relative positions and to understand the interactions between them.

• To study the reactivity and methods to obtain organic compounds containing phosphorus, sulfur and silicon.

• To design simple syntheses of organic compounds from the indicated starting products and involving synthetic sequences of up to 5 stages.

• To study the reactivity and methods to obtain monocyclic and simple bicyclic aromatic compounds with hexagonal heterocyclic ring.

• To study the reactivity and methods to obtain monocyclic and simple bicyclic aromatic compounds with pentagonal heterocyclic ring.

• To know the general aspects and the basic mechanism steps of the processes catalysed by transition metals.



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• To know the general aspects and the basic mechanism guidelines of pericyclic reactions.

• To identify the main groups of natural products in primary and secondary metabolism, and to know their importance.

# PREVIOUS KNOWLEDGE

Relationship to other subjects of the same degree

1108 - Degree in Chemistry V1-2009 :

1110 - Degree in Chemistry V2-2018 :

1929 - Double Degree in Physics and Chemistry :

#### 1934 - Programa de doble Grado Química-Ingeniería Química\_2023 :

#### R4-OBLIGATION TO HAVE SUCCESSFULLY COMPLETED THE COURSE

- 34183 General Chemistry I
- 34184 General Chemistry II
- 34183 General Chemistry I
- 34184 General Chemistry II
- 34183 General Chemistry I
- 34184 General Chemistry II
- 34183 General Chemistry I
- 34184 General Chemistry II

#### **Other requirements**

The study of Organic Chemistry III is based on the knowledge acquired in Organic Chemistry I and II. The structure and reactivity of the functional groups studied in Organic Chemistry I and II is important to understand the more complex systems that will be studied here. To strengthen the knowledge of the nomenclature and the representation of organic compounds, including their configurations and conformations is also essential.

## OUTCOMES

#### 1110 - Degree in Chemistry

- Develop capacity for analysis, synthesis and critical thinking.
- Show inductive and deductive reasoning ability.



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- Demonstrate leadership and management skills, entrepreneurship, initiative, creativity, organization, planning, control, leadership, decision making and negotiation.
- Solve problems effectively.
- Demonstrate ability to communicate information, ideas, problems and solutions to both specialist and non-specialist audiences and using information technology, as appropriate.
- Demonstrate a commitment to ethics, equality values and social responsibility as a citizen and as a professional.
- Learn autonomously.
- Demonstrate the ability to adapt to new situations.
- Acquire a permanent sensitivity to quality, the environment, sustainable development and the prevention of occupational hazards.
- Demonstrate knowledge of the main aspects of chemical terminology, nomenclature, conventions and units.
- Interpret the variation of the characteristic properties of chemical elements according to the periodic table.
- Demonstrate knowledge of the main types of chemical reaction and their main characteristics.
- Demonstrate knowledge of the principles of thermodynamics and kinetics and their applications in chemistry.
- Ability to recognise chemical elements and their compounds: preparation, structure, reactivity, properties and applications.
- Demonstrate knowledge and understanding of essential facts, concepts, principles and theories related to the areas of chemistry.
- Solve qualitative and quantitative problems following previously developed models.
- Recognise and analyse new problems and plan strategies to solve them.
- Evaluate, interpret and synthesise chemical data and information.
- Recognise and evaluate chemical processes in daily life.
- Develop sustainable and environmentally friendly methods.
- Relate chemistry with other disciplines.
- Students must be able to apply their knowledge to their work or vocation in a professional manner and have acquired the competences required for the preparation and defence of arguments and for problem solving in their field of study.
- Students must have the ability to gather and interpret relevant data (usually in their field of study) to make judgements that take relevant social, scientific or ethical issues into consideration.
- Students must be able to communicate information, ideas, problems and solutions to both expert and lay audiences.



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- Students must have developed the learning skills needed to undertake further study with a high degree of autonomy.
- Express oneself correctly, both orally and in writing, in any of the official languages of the Valencian Community.
- Have basic skills in the use of information and communication technology and properly manage the information obtained.

# LEARNING OUTCOMES

The previous section includes the competences contained in the document VERIFICA. This subject addresses part of the learning results of the matter Organic Chemistry that allow to acquire specific knowledge of chemistry, cognitive skills and general skills recommended by the EUROPEAN CHEMISTRY THEMATIC NETWORK (ECTN) for the Chemistry Eurobachelor® Label. The following table lists the learning outcomes acquired in the subject Organic Chemistry III related to the competences of the degree in Chemistry.

The learning process should allow the degree graduates to demonstrate:		
	Competences of the subject ORGANIC CHEMISTRY III that contemplate the learning outcomes EUROBACHELOR®	
The kinetics of chemical change, including catalysis; the mechanistic interpretation of chemical reactions	Demonstrate knowledge of the principles of thermodynamics and kinetics and their applications in chemistry (CE6).	
	Demonstrate knowledge of the main types of chemical reaction and their main characteristics.(CE4)	
The properties of aliphatic, aromatic, heterocyclic and organometallic compounds.	Ability to recognise chemical elements and their compounds: preparation, structure, reactivity, properties and applications (CE7).	
	Demonstrate knowledge of the principles, procedures and techniques for the determination, separation, identification and	



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	characterisation of chemical compounds (CE8). Show knowledge of the structure and reactivity of the main classes of biomolecules and the chemistry of the main biological processes (CE12).
The nature and behaviour of functional groups in organic molecules	Demonstrate knowledge of the main types of chemical reaction and their main characteristics.(CE4) Ability to recognise chemical elements and their compounds: preparation, structure, reactivity, properties and applications (CE7). Demonstrate knowledge of the principles, procedures and techniques for the determination, separation, identification and characterisation of chemical compounds (CE8).
Major synthetic pathways in organic chemistry, involving functional group interconversions and carbon- carbon and carbon- heteroatom bond formation	Demonstrate knowledge of the main types of chemical reaction and their main characteristics.(CE4) Ability to recognise chemical elements and their compounds: preparation, structure, reactivity, properties and applications (CE7). Demonstrate knowledge of the principles, procedures and techniques for the determination, separation, identification and characterisation of chemical compounds (CE8). Show knowledge of the structure and reactivity of the main classes of biomolecules and the chemistry of the main biological processes (CE12).
The structure and reactivity of important classes of biomolecules and the chemistry of important biological processes	Show knowledge of the structure and reactivity of the main classes of biomolecules and the chemistry of the main biological processes (CE12). Relate chemistry with other disciplines CE26).



COMPETENCES AND COGNITIVE SKILLS				
The learning process should allow the degree graduates to demonstrate:				
2	Competences of the subject ORGANIC CHEMISTRY III that contemplate the learnin outcomes EUROBACHELOR®			
Ability to demonstrate knowledge and understanding of the facts, concepts, principles and fundamental theories related to the topics mentioned above.				
Ability to apply this knowledge and understanding to the solution of common qualitative and quantitative problems.	Solve qualitative and quantitative problems following previously developed models (CE14). Recognise and analyse new problems and plan strategies to solve them (CE15). Understand the qualitative and quantitative aspect of chemical problems (CE24).			
Competences to present and argue scientific issues orally and in writing to a specialized audience.	Relate chemistry with other disciplines (CE26). Prepare reports, surveys and industrial and environmental projects in the field of chemistry (CE27). Demonstrate ability to communicate information, ideas, problems and solutions to both specialist and non-specialist audiences and using information technology, as appropriate. (CG6). Students must be able to communicate information ideas, problems and solutions to both expert and lay audiences (CB4).			



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GENERAL COMPETENC	ES		
The learning process should allow the degree graduates to demonstrate:			
	Competences of the subject ORGANIC CHEMISTRY III that contemplate the learning outcomes EUROBACHELOR®		
Ability to apply practical knowledge to solve problems related to qualitative and quantitative information.	Solve problems effectively (CG4). Solve qualitative and quantitative problems following previously developed models (CE14). Relate theory and experimentation (CE22). Recognise and evaluate chemical processes in daily life (CE23). Understand the qualitative and quantitative aspects of chemical problems (CE24).		
management, in relation to primary and secondary sources, including	Demonstrate ability to communicate information, ideas, problems and solutions to both specialist and non-specialist audiences and using information technology, as appropriate (CG6). Have basic skills in the use of information and communication technology and properly manage the information obtained (CT2).		
Skills related to information technology such as word processing, spreadsheet, recording and storage of data, internet use related to the subjects.	Demonstrate ability to communicate information, ideas, problems and solutions to both specialist and non-specialist audiences and using information technology, as appropriate (CG6). Have basic skills in the use of information and communication technology and properly manage the information obtained (CT2).		
Interpersonal skills to Interact with other people and get involved in team	Demonstrate ability to work in teams both in interdisciplinary teams and in an international context (CG5).		



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work.	Demonstrate a commitment to ethics, equality values and social responsibility as a citizen and as a professional (CG7).	
	Demonstrate the ability to adapt to new situations (CG9).	

# **DESCRIPTION OF CONTENTS**

#### 1. Unsaturated carbonyl compounds.

Unsaturated carbonyl compounds. Additional stability of , -unsaturated carbonyl compounds regarding unconjugated ones. Reactions of , -unsaturated carbonyl compounds: 1,2-addition (direct addition) and 1,4-addition (conjugate addition or addition of Michael). Factors that control the conjugate addition. Reaction conditions: kinetic vs. thermodynamic control. Nature of , -unsaturated carbonyl compound. Nature of the nucleophile: hard or soft nucleophiles. Addition of heteroatomic nucleophiles. Conjugated additions of carbon nucleophiles. Addition of organometallic compounds: organolithium, organomagnesians and organocuprates. Vinology principle. Conjugate substitution reactions. Nucleophilic epoxidation. Addition of enolate anions. Robinsons anellation reaction. Conjugated reactions of other electronically deficient alkenes.

#### 2. Sulfur, silicon and phosphorus compounds.

Properties, preparation and reactivity of the main organic functions with phosphorus: phosphines and salts of phosphonium, phosphates and phosphonates. Phosphorus Ilures. Wittig olefination reaction and related reactions. Properties, preparation and reactivity of the main organic functions with sulfur: thioalcohols and thioethers, sulfoxides and sulphones, and sulfonic acids. Anions stabilized by sulfur: sulfur ylides. Sulfoxide elimination reactions. Julia olefination reaction. Properties, preparation and reactivity of the main organic functions with silicon. Nucleophilic substitution on silicon. Protective groups based on silicon. Stabilisation of carbaniones by silicon. Olephination reaction of Peterson. Stabilisation of carbocations by silicon. Reactivity of aryl silanes, vinyl silanes and allyl silanes. Synthetic applications.

#### 3. Retrosynthetic analysis.

Retrosynthetic disconnection. Synthon concept: idealised reagents. Fundamental strategies of disconnection. Disconnections CHeteroatom. Synthesis of several stages: the problem of chemoselectivity. Protection of functional groups. Interconversion of functional groups. Disconnections involving two functional groups: 1,2 disconnections, 1,3 disconnections. CC disconnections: CC 1,1 disconnections, CC 1,2 disconnections. Giving and accepting synthons. CC disconnections of two functional groups: 1,3-difunctionalised compounds, 1,5-difunctionalised compounds. Natural reactivity and umpolung.





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#### 4. Aromatic heterocyclic compounds: structure and reactivity.

Types of heterocyclic compounds. Nomenclature of heterocyclic compounds. Relevant saturated and aromatic heterocycles. Aromatic heterocycles of six links: pyridine. Reactivity of pyridine: reactions of pyridine nitrogen, reactions by carbonate positions. Derivatives of pyridine: pyridones, N-pyridine oxides. Aromatic heterocycles of six links with more than one heteroatom: diazines. Aromatic heterocycles of five links: pyrrole, furan and thiophene. Reactivity of pentagonal heterocycles. Heterocycles of five members with more than one nitrogen atom: azoles. Benzofused heterocycles. Benzopyridines: quinoline and isoquinoline. Five-member heterocycles fused to benzene: indole.

Main approaches for the synthesis of aromatic heterocycles: modification of existing rings, construction of the heterocyclic ring by ionic reactions, construction of the heterocyclic ring by cycloadditions. Retrosynthetic analysis in the synthesis of heterocycles: disconnection of carbon-heteroatom bonds. Pyrroles, thiophenes and furans from 1,4-dicarbonyl compounds. Hantzsch synthesis of pyridines. Other synthesis of pyridines: Synthesis of Guareschi. Synthesis of pyrazoles and pyridazines from dicarbonyl compounds and hydrazine. Synthesis of pyrimidines from 1,3-dicarbonyl compounds and amidines. Azole synthesis. Synthesis of quinolines and isoquinolines. The synthesis of Fischer indoles.

#### 5. Organometallic transition metals reagents.

Organometalic compounds of transition metals: general aspects, hapticity. The rule of the 18 electrons. Bonding in transition metal complexes. Basic mechanistic guidelines for organometallic complexes. Exchange of ligands. Oxidising addition and reductive elimination. Migratory insertion. Transmetallation. Transition metals in organic synthesis: catalytic processes. Reactions of palladium organometallics. Reactions through complexes: coupling reactions of halides with alkenes (Heck reactions) and alkynes (Sonogashira reaction); Reactions of coupling of halides with organometallic (reactions of Negishi, Suzuki and Stille); Reactions of coupling with amines (Buchwald-Hartwig reactions). Reactions through complexes: nucleophilic addition to alkene-palladium complexes (Wacker reaction). Reactions through allyl complexes: nucleophilic addition to 3-allyl palladium complexes (allylic substitution reactions). Reactions through acyl-palladium complexes: carbonylation reactions.

#### 6. Pericyclic reactions

lonic vs. pericyclic reactions. Molecular orbitals of conjugated systems. Control of pericyclic reactions by Frontier Molecular Orbitals. Electrocyclic reactions. Stereochemistry of electrocyclic thermal reactions. Electrocyclic photochemical reactions. Cycloaddition reactions: cycloadditions [2+2] and [4+2]. Stereochemistry of cycloaddition reactions. Signatropic rearrangements. Some examples of signatropic rearrangements. Summary of the rules for pericyclic reactions.

#### 7. Natural Products

Introduction: primary and secondary metabolites. Primary metabolites: Carbohydrates. Classification. Monosaccharides and representation of the stereochemistry. Cyclic structures of monosaccharides. Structure of glucose. Anomeric carbon and glycosidic bond. Disaccharides and polysaccharides. Amino acids. Peptides and proteins. Peptide synthesis. Structure of proteins. Enzymes and co-enzymes. Nucleic acids: Composition and structure. Secondary metabolites: Waxes, fats and oils. Soaps.



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### Prostaglandins. Terpenes. Steroids.

# WORKLOAD

ACTIVITY		Hours	% To be attended
Theory classes		51,00	100
Tutorials	0520	9,00	100
Study and independent work		90,00	0
	TOTAL	150,00	

# **TEACHING METHODOLOGY**

The subject is designed so that the student is the protagonist of his/her own learning. The subject structure is:

• Theory classes and questions.- Theory lessons will introduce the students to the most fundamental aspects of the subject. The question sessions will be dedicated to the application of the

specific knowledge that students have acquired in theory classes. Students must have previously worked on the questions to be solved. The answers will be discussed in class by both the teacher and the students. The classes should be complemented by personal study time.

• Tutoring.- In them the overall learning process of the students will be evaluated. In the tutorial sessions the professor could entrust written reports to the students. Furthermore, the tutorials will serve to solve any doubts that may have arisen during the classes and guide students on the most convenient work methods.

• Seminars-Talks: The Seminars-Talks will deal with complementary aspects of their formation in Organic Chemistry and will be dedicated to the presentation by a specialist of a relevant topic in current Chemistry. For this task, students will attend the event and answer a questionnaire prepared by the teacher.

# **EVALUATION**

For learning assessment, the teacher can use two modalities. The student must opt for one of them and communicate his choice to the secretary of the department according to the written form available. The student must communicate the prefered modality during the first month of the semester. On behalf of the teacher's programming, the student will be evaluated with the B modality if there is no communication within this first month period.



The minimum global qualification to pass the subject in any modality will be 5 points out of 10.

### FIRST CALL

#### **Modality** A

Continuous evaluation through the course. In this case, the following sections will be considered:

**1. Direct evaluation by the teacher (5%):** this evaluation will take into account different aspects, among which include:

Assistance and reasoned and clear participation in the discussions and questions in the class

Progress in the use of the language specific to organic chemistry

Troubleshooting and raising doubts

Critical spirit

**2. Tutorials and Seminars-Talks (globally 15%):** In this section the following aspects will be considered:

Assistance

Content and written presentation of the exercises proposed by the teacher (if applicable).

Rational and clear participation in the discussions.

**3. Exams (80%):** will be held on the date indicated by the Faculty and will be common to all groups of the subject. It will consist of theoretical and practical questions related to the subject explained during the teaching period. The global passing of the subject will necessarily entail having obtained a minimum score of 5 out of 10 points on the exam.

#### **Modality B**

Evaluation with only a written exam on the contents of the subject dealt with in theory classes and tutorials, so that the teacher can thus assess whether the student has acquired the skills and knowledge related to the subject. This exam will be 100% of the overall score.

The exam will be held on the date indicated by the Faculty and will be common to all groups of the subject. In this modality, the teacher may take into account the participation of students in theory classes and tutorials for the final grade.

#### SECOND CALL



In the second call evaluation for students who have chosen modality A, the grade obtained by the student in the first call for sections 1 and 2 will be maintained but, section 3 will be re-evaluated.

# REFERENCES

#### Basic

- CLAYDEN, J.; GREEVES, N.; WARREN, S. Organic Chemistry, 2 Ed., Oxford University Press: Oxford, 2012. Disponible en formato papel y electrónico en la biblioteca.
- McMURRY, J. Organic Chemistry, 9 Ed., Cengage Learning, 2016. Disponible en formato electrónico en la biblioteca.
- CLAYDEN, J.; WARREN, S. Solutions manual to accompany Organic Chemistry, 2 Ed., Oxford University Press: Oxford, 2013. Disponible en formato papel en la biblioteca.
- BRUICE, P. Y. Química Orgánica, 5 Ed., Pearson Prentice Hall, 2008. Disponible en formato papel y electrónico en la biblioteca.
- WADE, L. G. Química Orgánica, 9 Ed., Pearson Prentice Hall, 2017. Disponible en formato electrónico en la biblioteca.
- WADE, L. G. Química Orgánica, 7 Ed., Pearson Prentice Hall, 2012. Disponible en formato papel y electrónico en la biblioteca.
- VOLLHARDT, K. P. C. Química Orgánica Estructura y Función, 5 Ed., Ediciones Omega, 2007. Disponible en formato papel en la biblioteca.
- ChemBioOffice Ultra, Perkin Elmer (CambridgeSoft) Amplia selección de aplicaciones y funcionalidades que permite a químicos y biólogos dibujar, formular, modelar y editar estructuras moleculares químicas y biológicas así como simular espectros de RMN de protón y carbono.

#### **Additional**

- CAREY, F. A.; SUNDBERG, R. J. Advanced Organic Chemistry, 4 Ed., Plenum Press, 2000.
- CARROLL, F. A. Perspectives on Structure and Mechanism in Organic Chemistry, Brooks/Cole Publishing Company, 1998.
- WARREN, S.; WYATT, P. Organic Synthesis. The Disconnection Approach, 2 Ed., John Wiley and Sons, 2009.
- SMITH, M. B. Organic Synthesis, 2 Ed. Mc Graw Hill Higher Education, 2002.
- CARDA, M.; MARCO, J. A.; MURGA, J.; FALOMIR, E. Análisis retrosintético y síntesis orgánica. Resolución de ejemplos prácticos, Publicacions de la Universitat Jaume I: Castellón, 2010.
- JOULE, J. A.; MILLS, K. Mills, Heterocyclic Chemistry, 4 Ed., Blackwell Publishing, 2003.
- MARCO, J. A. Química de los Productos Naturales, Editorial Síntesis: Madrid, 2006.



# **ADDENDUM COVID-19**

This addendum will only be activated if the health situation requires so and with the prior agreement of the Governing Council

### Contents

1.- The contents initially indicated in the teaching guide are maintained.

#### Workload and temporary teaching planning

Regarding the workload:

1.- The different activities described in the Teaching Guide are maintained with the intended dedication.

### Regarding the temporary teaching planning:

1.- The material to follow the theory/tutoring/classroom-seminar classes allows to continue the temporary teaching planning both in days and schedule, whether the teaching is face-to-face in the classroom or not.

### **Teaching Methodology**

#### Theory subjects:

<u>Situation of minimal attendance</u>: In theory classes and tutorials the occupation will be, at most, 30% of their usual occupation. Teaching will be online. Students who have a laboratory session before or after theory classes, and the time to travel is longer than the time established in the schedules, will be able to follow the class in person in the classroom assigned in the schedules. When there are students in this situation, classes will be taught by synchronous videoconference in the group classroom.

<u>Maximum face-to-face situation</u>: In theory classes and tutorials, the occupation will respect the sanitary restrictions that limit the capacity of the classrooms. Depending on the capacity of the classroom and the number of students enrolled, it may be necessary that part of the students have to follow the classes synchronously. If this situation arises, the students will attend the group classroom in weekly rotating shifts (preferably in alphabetical order), so as to ensure that the percentage of attendance of all the students enrolled in the subject is the same.

<u>Confinement situation</u>: If for health reasons it is not possible to continue with hybrid teaching, totally or partially affecting the classes of the subject, these will be replaced by synchronous non-face-to-face sessions following the established schedules and using the virtual classroom tools.



The methodology used for non-face-to-face classes shall be:

- 1. Synchronously using virtual classroom tools
- 3. Resolution of exercises and questionnaires

In the case of students confined to home due to COVID, they will be ensured on-line teaching through available virtual classroom tools.

## Evaluation

2. The evaluation system described in the Teaching Guide of the subject in which the various evaluable activities have been specified as well as their contribution to the final grade of the subject is maintained.

The continuous evaluation modality will be strengthened (Modality A). In the case of students who, for exceptional reasons, cannot follow this evaluation modality, they will be able to opt for the evaluation with a single exam (Modality B). In this case, the student must notify this election before the first month of the course by sending an email to the secretariat of the Department (secorgan@uv.es) and the teacher of the subject.

If there is a closure of the facilities for health reasons affecting the development of any face-to-face evaluable activity of the subject, it will be replaced by a test of a similar nature that will be carried out in virtual mode using the computer tools licensed by the University of Valencia. The contribution of each evaluable activity to the final grade of the subject will remain unchanged, as set out in this guide.

### References

1. 1. The literature recommended in the Teaching Guide is maintained since it is accessible, and it is complemented by notes, slides and problems uploaded to the Virtual Classroom as material of the course.