



UNIVERSITÀ DEGLI STUDI DI PALERMO

DEPARTMENT	Fisica e Chimica - Emilio Segrè		
ACADEMIC YEAR	2021/2022		
MASTER'S DEGREE (MSC)	CHEMISTRY		
SUBJECT	ORGANIC SPECIAL SYNTHESSES AND LABORATORY		
TYPE OF EDUCATIONAL ACTIVITY	B		
AMBIT	50485-Discipline chimiche organiche		
CODE	16503		
SCIENTIFIC SECTOR(S)	CHIM/06		
HEAD PROFESSOR(S)	GIACALONE FRANCESCO	Professore Ordinario	Univ. di PALERMO
OTHER PROFESSOR(S)			
CREDITS	6		
INDIVIDUAL STUDY (Hrs)	81		
COURSE ACTIVITY (Hrs)	69		
PROPAEDEUTICAL SUBJECTS			
MUTUALIZATION			
YEAR	1		
TERM (SEMESTER)	1° semester		
ATTENDANCE	Mandatory		
EVALUATION	Out of 30		
TEACHER OFFICE HOURS	GIACALONE FRANCESCO Wednesday 11:00 - 12:30 Studio Prof. Giacalone (studio PT084) - Dip. STEBICEF, sez. Chimica		

PREREQUISITES	organic chemistry
LEARNING OUTCOMES	<p>Knowledge and understanding Ken of asymmetric synthesis concepts. Introduction on homogeneous and heterogeneous catalysis and to the chemistry of carbon nanoforms Assessment - oral exam - laboratory reports</p> <p>Applying knowledge and understanding Ability to independently organize a multistep synthesis and the subsequent characterization of the products obtained Assessment - oral exam - laboratory reports</p> <p>Making judgements To be able to foresee selectivity in an asymmetric process choosing the proper conditions in order to obtain a given isomer. To be able to assess the chemical structure of the obtained products with the help of spectroscopy. To be able to plan the functionalization of carbon nanoforms Assessment - oral exam -continuous monitoring and interaction during lectures and laboratory experiences</p> <p>Communication Ability in the use of the proper scientific language in the description of asymmetric synthesis, organocatalysis and chemistry of carbon nanoforms. Assessment - oral exam -continuous monitoring and interaction during lectures and laboratory experiences - laboratory reports</p> <p>Lifelong learning skills Ability in the comprehension of scientific textbooks on asymmetric synthesis and chemistry of carbon nanoforms. Ability to stay updated and to extend the knowledge of the subjects through specific scientific research papers. Assessment - oral exam -continuous monitoring and interaction during lectures and laboratory experiences</p>
ASSESSMENT METHODS	<p>The following criteria will be taken into account for the final assessment of the exam:</p> <ul style="list-style-type: none"> - Active and continued supervision in laboratory through the observation of every single student during the experiments. - Evaluation of knowledge and written communication skills through the analysis of reports on laboratory experiences. - Oral exam aimed to the determination of student's theoretical knowledge and student's oral communication skills. The interview starts from the corrections on the reports and it follows with questions on the course topics. <p>The final assessment is given over 30 points and it is composed by the assessment of laboratory work and reports and by the interview assessment. The oral exam will be evaluated taking into account:</p> <ul style="list-style-type: none"> a) Basic knowledge of the course topics and limited capacity to apply them during the discussion (18-21); b) Good knowledge of the course topics and good capacity to apply them during the discussion (22-25); c) Very good knowledge of the course arguments and capacity to apply them during the discussion even if in a not completely independent manner (26-28); d) Excellent knowledge of all the course topics and excellent capacity to apply them during the discussion with the proper language (29-30L).
EDUCATIONAL OBJECTIVES	<p>The aim of the theoretical course is to furnish the principles for carrying out asymmetric reactions in organic synthesis. The student will be confident with the concept of homogeneous and heterogeneous organocatalysis. One of the main topics will regard reactivity and characterization of carbon nanoforms such as fullerenes, nanotubes, nanohorns, graphene etc.</p> <p>During the laboratory course the student will acquire the ability to carry out a multistep synthesis even with the use of inert atmosphere. The student will be able to separate racemic mixtures, to carry out asymmetric synthesis by means of homogeneous and heterogeneous catalysis (and organocatalysis) and to functionalism fullerene. Finally, the student will knows scientific search engines and how to use it properly.</p>

TEACHING METHODS	lectures, laboratory experiences
SUGGESTED BIBLIOGRAPHY	G. Procter, Sintesi Asimmetrica, EdiSES, 2000 P.I. Dalko, Enantioselective Organocatalysis, Wiley 2007 A. Hirsch, M. Brettreich, Fullerenes – Chemistry and Reactivity, Wiley 2005 Articoli di letteratura e Appunti di lezione

SYLLABUS

Hrs	Frontal teaching
3	Carbon nanoforms: Fullerene. Properties, preparation and purification. Reactivity: nucleophilic additions, hydroalkylations, cyclopropanation, amines addition. Cycloadditions: Diels-Alder, 1,3-dipolar, benzyne addition
1	Carbon nanotubes: single-, double- and multi-walled. Properties and preparation. Reactivity: Oxidation, amidation, esterification, fluorination. Cycloadditions: nitrenes and azides, Bingel reaction, Prato's reaction, Tour reaction, reaction with disulfides and radical reactions.
1	Non covalent functionalization of carbon nanotubes. Spectroscopic and analytic techniques for the characterization: TGA, Raman, XPS, TEM, SEM, AFM
1	Carbon nanohorns: properties and preparation. Reactivity Graphene and graphene oxide: properties, preparation and reactivity Nanodiamonds: properties, preparation and reactivity
2	Asymmetric synthesis: fundamentals. Synthesis of enantiopure compounds: racemate resolution (diastereomeric salts, kinetic resolution, dynamic kinetic resolution), chiral pool approach, stereoselective syntheses
1	Analytic and spectroscopic techniques for the determination of optical purity. Polarimetry, NMR and chiral column chromatography (HPLC and GC)
2	Asymmetric synthesis. Additions to carbonyl compounds: use of chiral substrate, reactant or auxiliary. Chiral catalyst and chiral amplification. Allylmetal addition to aldehydes and ketones. Allylboranes additions to aldehydes and ketones. Asymmetric catalytic cyanohydrations
2	Substitution in chiral enolates. Chiral auxiliary, base and reactant
2	Asymmetric aldol reactions. Aldol stereochemistry and transition states involved in the aldol reaction. Chiral substrate, chiral reactant, chiral auxiliary
2	Addition to C-C double bonds. Asymmetric Diels-Alder reactions: with chiral auxiliary, with chiral reactant. Chiral catalyst based on Al, B or Ti. Asymmetric conjugated additions. Enantioselective hydroboration. Homologation
3	Asymmetric reductions. Catalytic hydrogenations. Rhodium and Ruthenium catalysts. Sulfoxides as chiral auxiliaries. Chiral reactants, Corey-Bakshi-Shibata reduction. Asymmetric oxidations. Sharpless' Oxidation. Kinetic resolution of allyl alcohols. Jacobsen' asymmetric epoxidation. Asymmetric dihydroxylation
4	Organocatalysis. Principles, catalysts, mechanisms and reactions. Activation modes: aminocatalysis, Bronsted acids and bases, Lewis acids and bases, hydrogen bonds, transfer phase catalysis. Heterogeneous organocatalysis. How, when and why. Supports and catalysts, advantages and disadvantages of heterogeneous catalysis. Examples of organocatalysed reactions.
Hrs	Workshops
1	Laboratory safety procedures and rules. Delivering of glassware for the experiences
8	Synthesis of N-methylfulleropyrrolidine through Prato's Reaction. Chromatographic purification
8	Kinetic resolution of a 1,2-trans-cyclohexyldiamine racemic mixture and assessment of optical purity by means of HPLC with chiral column
8	Sharpless' Asymmetric Epoxidation of geraniol. Purification by column chromatography
8	Asymmetric aldol reaction promoted by an organocatalyst. Purification of the aldol and determination of optical purity by means of HPLC with chiral column
4	Bibliometrics. Impact factor and H-index. Making bibliographic research with Scopus, ISI WoS and SCI-finder. How to apply the proper filters.
4	Spectroscopic characterization, by means of NMR, of the products synthesized during the course
4	How to use ChemDraw for the representation of molecules and reaction schemes