Chem 353 Syllabus

Optical properties: optical rotation, optical purity, enantiomeric excess. Diastereomers.

Electrophilic addition reactions of alkenes and alkynes. Markovnikov's rule: empirical basis, application. Stereochemistry (syn/anti/not specific additions), product stereochemistry.

Alkenes:
Review preparations via elimination of alkyl halides and alcohols.
Reactions: heterogeneous catalaytic hydrogenation, hydrohalogenation (HX, inc. radical HBr), hydration (H3O+, BH3, oxymercuration), halogenation, halohydration (HOX, X2/H2O), epoxidation with peracids, ozonolysis (oxidative and reductive work ups), dihydroxylation (KMnO4 and cat. OsO4)

Alkynes: internal and terminal subtypes.
Review preparations via elimination and alkylation reactions.
Reactions: reductions (cat. H2, Lindlar's cat., dissolving metal (Na/NH3 and Na/THF then MeOH), halogenation, hydrohalogenation (HX and excess HX), hydration (H3O+, tautomerisation), hydroboration.

Organic synthesis: analysis and design. Basic retrosynthetic principles. Protecting groups.

Dienes and allylic systems: terminology, structure, bonding, subtypes, preparation.
Addition reactions with HX, X2, Diels-Alder. Kinetic and thermodynamic control.

Epoxides: Reactions with nucleophiles. Regioselectivity for unsymmetrical epoxides based on reaction conditions and pathway.

Aromatic systems:
Benzene: structure, bonding, physical and chemical properties, reactivity implications.
Aromaticity, resonance energy, criteria for aromaticity (inc. heteroaromatic and ions), Huckel rule.

Electrophilic aromatic substitution reactions of benzene systems: Nitration, alkylation, acylation, sulfonation, halogenation. Scope and limitations.
Substitutent effects: activating or deactivating, directing effects. Implications on properties (e.g. reactivity, acidity/basicity)
Reactions of aromatic substituents: review radical, nucleophilic substitutions, eliminations.
Oxidation of alkyl groups. Reduction of nitro groups. Diazotisation. Reaction of diazonium salts.
Synthesis of disubstituted and polysubstituted benzenes considering directing effects etc.

Introduction to organometallic compounds: Grignard and related reagents (organolithium, cuprates), hydride reagents (LiAlH4 and NaBH4). Structure, reactivity.

Preparations of alcohols from carbonyl groups by reaction with organometallics and hydride reagents.

Relative reactivity of carbonyl containing functional groups.

Reactions of alcohols with carboxylic acid derivatives to give esters.
Oxidation of alcohols (using chromium reagents)
Diols: properties, preparation and reactions of.

Nucleophilic addition reactions of aldehydes and ketones:
Hydration, addition of alcohols to give acetals and ketals (potential protecting groups), cyanohydrins, organometallic reagents including hydrides, the Wittig reaction, reactions with primary amine derivatives.

Carboxylic acids and derivatives: structure, bonding, physical and chemical properties, preparations.
Reactions: Nucleophilic acyl substitution of carboxylic acid derivatives for interconversion reactions (emphasis on preparations of acid derivatives and hydrolysis of acid derivatives) and reactions with organometallic and hydride reagents.

Enols and enolates of aldehydes, ketones and esters: acidity, preparation.
Reactions as nucleophiles in alkylation and condensation reactions (aldol, Claisen, Dieckmann). Active methylene compounds. Decarboxylation of beta-keto systems.

As time allows: Conjugate additions to conjugated ketones and aldehydes.

Laboratory experiments (10 experiments)

1. Molecular models (stereochemistry)
2. Distillation
3. Polymers and plastics
4. Synthesis of Biodiesel
5. Selectivity using sodium borohydride
6. Grignard reaction
7. Aldol reaction
8. Identification of unknowns (3 laboratory sessions)