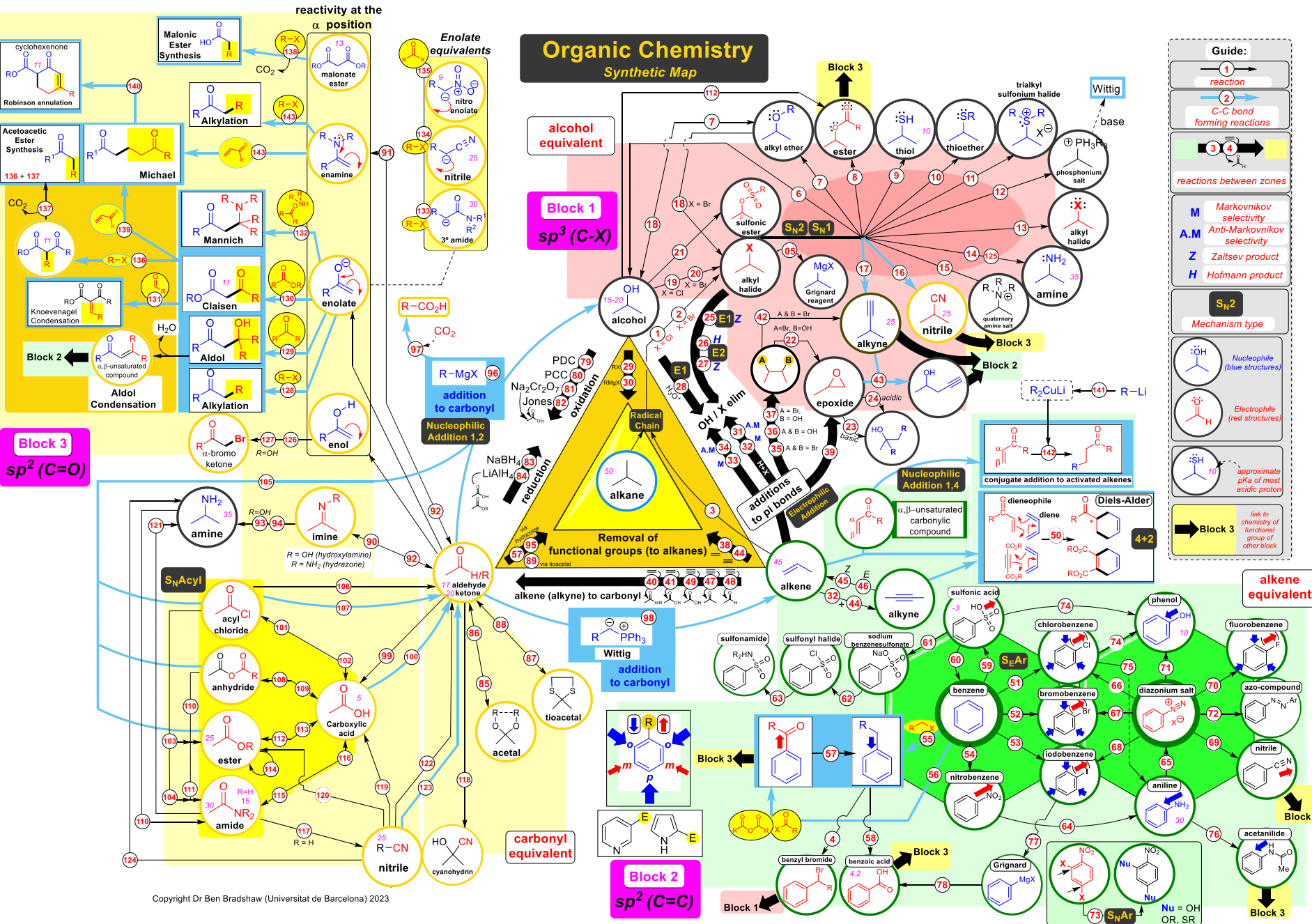


Organic Chemistry Synthetic Map



Guide:

- 1 → reaction
- 2 ↔ C-C bond forming reactions
- 3 → 4 → reactions between zones

M Markovnikov selectivity
A.M Anti-Markovnikov selectivity
Z Zaitsev product
H Hofmann product

S_N2
Mechanism type

- Nucleophile (blue structures)
- Electrophile (red structures)
- approximate pK_a of most acidic proton

→ **Block 3** link to chemistry of functional group of other block

Block 3
 sp² (C=O)

Block 1
 sp³ (C-X)

Block 2
 sp² (C=C)

Block 1	
01	Radical Chlorination of alkanes: $\text{Cl}_2, \text{hu or } \Delta$
02	Radical Bromination of alkanes: $\text{Br}_2, \text{hu or } \Delta$
03	Radical Bromination of allylic alkanes: $\text{NBS}, \text{hu or } \Delta$
04	Benzylic bromination: $\text{NBS}, \text{hu or } \Delta$
05	Grignard formation: Mg
06	Formation of alcohols ($\text{S}_{\text{N}}2$) – NaOH
07	Williamson Ether Synthesis ($\text{S}_{\text{N}}2$): (i) RONa, RX
08	Formation of esters ($\text{S}_{\text{N}}2$): NaCO_2R ($\text{S}_{\text{N}}1$): RCO_2H
09	Formation of thiols ($\text{S}_{\text{N}}2$): NaSH
10	Formation of thioethers ($\text{S}_{\text{N}}2$): NaSR
11	Formation of trialkylsulfonium salts ($\text{S}_{\text{N}}2$): RSR
12	Formation of phosphonium salts ($\text{S}_{\text{N}}2$): PR_3
13	Interconversion of halogens ($\text{S}_{\text{N}}2$): (Finkelstein): NaI
14	Formation of amines ($\text{S}_{\text{N}}2$): Excess NH_3
15	Alkylation of tertiary amines ($\text{S}_{\text{N}}2$): R_3N
16	Formation of nitriles ($\text{S}_{\text{N}}2$): NaCN
17	Alkylation of acetylide ions ($\text{S}_{\text{N}}2$): $\text{Acetylene} + \text{NaNH}_2$
18	Cleavage of ethers under acidic conditions: HBr
19	Chlorination of alcohols ($\text{S}_{\text{N}}2$) $\text{SOCl}_2, \text{pyridine}$
20	Bromination of alcohols ($\text{S}_{\text{N}}2$) PBr_3 ($\text{S}_{\text{N}}1$) HBr
21	Alcohol to leaving group: $\text{TsCl}/\text{MsCl}, \text{base}$
22	Formation of epoxides via halohydrins: $\text{NaOH}, \text{H}_2\text{O}$
23	Opening epoxides with Nu under basic conditions ($\text{Nu} = \text{RNH}_2, \text{RONa}, \text{NaCN}, \text{NaSH}, \text{RMgBr}, \text{LiAlH}_4$)
24	Opening epoxides with Nu under acidic conditions: $\text{H}_2\text{SO}_4, (\text{Nu} = \text{H}_2\text{O}, \text{ROH})$
25	Elimination [E1] of 2° or 3° alkyl halides: H_2O
26	Elimination [E2] with impeded base: $t\text{-BuOK}$
27	Elimination [E2] of 1→3° alkyl halides: $\text{NaOMe}, \text{MeOH}$
28	Elimination [E1] of ROH (→Z): $\text{H}_2\text{SO}_4 \& \text{H}_2\text{O}$.
29	Conversion of alkyl halide to alkane ($\text{S}_{\text{N}}2$): LiAlH_4
30	Conversion of Grignard to alkane: H_2O

Block 2	
31	Addition of HX to alkenes. HCl or HBr
32	Radical addition of HBr: HBr, ROOR
33	Hydration of alkenes: $\text{H}_2\text{O} \& \text{dil. } \text{H}_2\text{SO}_4$
34	Hydroboration: (i) BH_3 , (ii) $\text{H}_2\text{O}_2, \text{NaOH}$
35	Addition of halogen: Br_2
36	Dihydroxylation of alkenes: OsO_4
37	Formation of halohydrins: $\text{Br}_2, \text{H}_2\text{O}$
38	Hydrogenation of alkenes: $\text{Pd/C}, \text{H}_2$
39	Epoxidation: mcpba
40	Reductive ozonolysis: O_3 , then Zn, AcOH
41	Oxidative ozonolysis: O_3 , then $\text{H}_2\text{O}_2, \text{HCOOH}$
42	Convert 1,2 dihaloalkanes to alkynes: $2x \text{NaNH}_2$
43	Ring opening of epoxides with acetylide ions: Alkyne + NaNH_2 then add to epoxide
44	Hydrogenation of alkynes: Pt/H_2
45	Lindlar Reduction to Z alkenes Lindlar catalyst, H_2
46	Reduction of alkynes to E alkenes: Na/NH_3
47	Hydration of alkynes: $\text{HgSO}_4, \text{H}_2\text{O}, \text{H}^+$

48	Hydroboration of alkynes: (i) R_2BH , (ii) $\text{H}_2\text{O}_2, \text{NaOH}$
49	Ozonolysis of alkynes: (i) O_3 (ii) $\text{Zn}, \text{H}_2\text{O}$
50	Diels-Alder Reaction: Δ
51	Aromatic Chlorination: $\text{Cl}_2/\text{AlCl}_3$
52	Aromatic Bromination: $\text{Br}_2/\text{FeBr}_3$
53	Aromatic Iodination: I_2/CuCl_2
54	Aromatic Nitration: $\text{HNO}_3/\text{H}_2\text{SO}_4$
55	Friedel-Crafts Alkylation: RX/AlX_3
56	Friedel-Crafts Acylation: Acyl chloride or anhydride/AlX_3
57	Clemmensen Reduction: $\text{Zn}(\text{Hg}), \text{HCl}$
58	Benzylic Oxidation: $\text{KMNO}_4, \text{NaOH}$ or $\text{Na}_2\text{Cr}_2\text{O}_7$
59	Aromatic Sulfonation: Fuming H_2SO_4
60	Aromatic Desulfonation: dilute H_2SO_4
61	Deprotonation of benzenesulfonic acids: NaOH
62	Synthesis of Benzenesulfonyls: PCl_5
63	Synthesis of sulfonamides: Amine
64	Nitro reduction: $\text{Zn}(\text{Hg})/\text{HCl}$, or Fe/HCl or $\text{Pd/C}, \text{H}_2$
65	Formation of diazo compounds: NaNO_2/HCl
66	Sandemeyer Reaction: CuCl
67	Sandemeyer Reaction: CuBr
68	Sandemeyer Reaction: KI
69	Sandemeyer Reaction: CuCN
70	Shiemann Reaction: $\text{HBF}_4 (\text{X} = \text{F})$
71	Hydrolysis of diazonium salts: $\text{H}^+/\text{H}_2\text{O}, \Delta$
72	Diazo coupling: phenols or anilines
73	Nucleophilic Aromatic Substitution: $\text{Nu} = \text{H}_2\text{O}, \text{RNH}_2, \text{ROH}, \text{RSH}$
74	Fusion with NaOH: $\text{NaOH } 350^\circ\text{C}$
75	Formation of anilines: $\text{PhCl}, \text{NaNH}_2, \text{NH}_3$
76	Formation of acetanilides: acid chloride or anhydride, piridine
77	Carboxylation: CO_2 then H_3O^+
78	Metalation (Grignard formation): Mg

Block 3	
79	PDC Oxidation: $\text{pyH-Cr}_2\text{O}_7$ (PDC)
80	PCC Oxidation: $\text{pyH-CrO}_3\text{Cl}$
81	Potassium Dichromate Oxidation: $\text{K}_2\text{Cr}_2\text{O}_7$
82	Jones Oxidation. $\text{CrO}_3, \text{H}_2\text{SO}_4, \text{acetone}$
83	NaBH_4 reduction: NaBH_4
84	LiAlH_4 reduction of carbonyls: LiAlH_4
85	Formation of acetals. ROH or $\text{HOCH}_2\text{CH}_2\text{OH}/\text{cat } \text{H}^+$
86	Deprotection of acetals: $\text{H}_2\text{O}/\text{H}^+$
87	Formation of thioacetals: $\text{HSCH}_2\text{CH}_2\text{SH}/\text{ZnCl}_2$
88	Hydrolysis of thioacetals : $\text{H}_2\text{O}, \text{HgCl}_2, \text{CaCO}_3$
89	Desulfurization of thioacetals to alkanes: Raney Ni/H_2
90	Imine formation: R^1NH_2 (amine 1°)
91	Enamine formation: $\text{R}^1\text{R}^2\text{NH}$ (amine 2°)
92	Hydrolysis of imines and enamines: H_3O^+
93	Reductive amination to primary amine: $\text{NH}_2\text{OH}, \text{H}_2, \text{Ni}$
94	Reductive amination: NaCNBH_3
95	Wolff-Kishner reduction: $\text{NH}_2\text{NH}_2/\Delta$
96	Addition of Grignards to aldehydes & ketones: RMgBr
97	Addition of Grignards to CO_2 : (Grignard + CO_2)
98	Wittig Reaction: $\text{XPh}_3\text{PR}, \text{base}$ (BuLi or NaH)

99	Oxidation of aldehydes to carboxylic acids: Ag_2O
100	Addition of organolithiums to carboxylic acids: RLi (2 eq.)
101	Preparation of acid chlorides: SOCl_2
102	Hydrolysis of acid chlorides: H_2O
103	Esterification of acid chlorides: $\text{ROH}, \text{pyridine}$
104	Preparation of amides from acid chlorides: R_2NH
105	Double addition of organometallics to acid chlorides, anhydrides or esters to give alcohols: RMgBr (2 equiv.)
106	$\text{LiAl}(\text{OR})_3\text{H}$ acid chloride to aldehydes: $\text{LiAl}(\text{OR})_3\text{H}$
107	Acid chloride to ketone: R_2CuLi
108	Preparation of anhydrides: acid chloride + RCOOH
109	Hydrolysis of anhydrides: H_2O
110	Esterification of Anhydrides: $\text{ROH}, \text{pyridine}$
111	Preparation of amides from anhydrides: $\text{R}_2\text{NH}, \text{base}$
112	Fischer Esterification: $\text{ROH}, \text{cat } \text{H}_3\text{O}^+$
113	Hydrolysis of esters (Saponification): $\text{NaOH}, \text{H}_2\text{O}$
114	Transesterification: R^1OH
115	Preparation of amides from carboxylic acids: NH_3, Δ
116	Hydrolysis of amides catalyzed by acid: $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$
117	Formation of nitriles from amides: SOCl_2
118	Formation de cyanohydrins: NaCN, HCl
119	Hydrolysis of nitriles: H_3O^+
120	Alcoholysis of nitriles: formation of esters: $\text{ROH}, \text{H}_3\text{O}^+$
121	LiAlH_4 reduction of amides to amines: LiAlH_4
122	Reduction of nitriles to aldehydes: DIBALH:
123	Conversion of nitriles to ketones: RMgX then H_2O
124	Reduction of nitriles to amines: LiAlH_4
125	Gabriel amine synthesis (→amines 1 ^a): (i) Pthalimide, KOH, RX (ii) NH_2NH_2 or H_3O^+
126	Halogenation of enols: Br_2/AcOH
127	Hell-Volhard-Zelinsky Halogenation Reaction: $\text{Br}_2, \text{PBr}_3$ (ii) H_2O
128	Alkylation at the α position : (i) LDA (ii) RX
129	Aldol Condensation: Base (KOH) + aldehyde o ketone
130	Claisen Condensation: NaOH or NaOR Intramolecular Version. Dieckmann Cyclisation
131	Knoevenagel Condensation: piperidine, aldehyde
132	Mannich Reaction: $(\text{CH}_3)_2\text{NH}, \text{CH}_2=\text{O}$
133	Alkylation of amides 3 ^a at the α position: NaNH_2, RX
134	Alkylation of nitriles: (i) NaOEt (ii) RBr
135	Nitroaldol reaction: NaOH + aldehyde or ketone
136	Alkylation of β -ketoesters: (i) NaOEt (ii) RBr
137	Decarboxylation de β -ketoesters: $\text{H}_3\text{O}^+/\Delta$
138	Malonic ester synthesis: (i) NaOEt (ii) RBr (iii) $\text{H}_3\text{O}^+/\Delta$
139	Michael Reaction - Conjugate addition 1,4: $\text{Nu} = \text{NaCN}, \text{H}_2\text{O}, \text{RNH}_2, \text{R}_2\text{CuLi}$
140	Robinson Annulation: Base (NaOH)
141	Formation of cuprates: Grignard or Organolithium + CuI
142	Addition of cuprates to electron deficient alkenes: R_2CuLi
143	Stork enamine alkylation: pyrrolidine, then $\text{RX}, \text{acyl chloride}$ or Michael acceptor or (ii) H_3O^+