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DEFINITIONS OF SPORE KEYPHRASES (RXN_TYPE'S)

GENERAL RULES AND DEFINITIONS:

GENERAL RULE 1: In reactions with more than one reactant, corresponding keyphrases often apply to the two coupling partners (e.g. "N-alkylation" for Reactant 1, "amination" for Reactant 2). As a general rule, appropriate keyphrases are assigned to all reactants of a given reaction, regardless of the size of the particular compound.

GENERAL RULE 2: Keyphrases are assigned to the actual reactant-to-product conversion; the transformations of the likely intermediates of the reaction mechanism (as opposed to intermediates of a multi-step reaction) are usually not taken into account.

GENERAL RULE 3: Keyphrases are only assigned to transformations of the reactants of a reaction, and not to transformations of catalysts or reagents. However, the transformation that a reagent effects is of course considered. Thus, in a reaction

$R\text{-}CO\text{-}Cl$ (+ reagent NH_3) -> $R\text{-}CO\text{-}NH_2$

the keyphrase "amidation", induced by the reagent ammonia, is assigned while the keyphrases "N-acylation" is not, since the compound undergoing N-acylation is only a reagent.

Note to the Keyphrases in Chapter C: Apart from chapter C8 (Ring Systems), all but four of the keyphrases apply to reactions leading to either cyclic or acyclic products (thus, both open-chain ester formations and lactonizations will have the keyphrase "esterification"). These four exceptions are the "...-alkylation", terms (C-/N-/O-/S-alkylation), which are only used for the formation of open-chain C-C, C-N, C-O or C-S bonds (otherwise, all cycloadditions and many heterocyclic syntheses would formally have to be regarded as "C/N/O/S-alkylation").

DEFINITIONS: "Aryl" includes aromatic heterocycles; "alkyl" includes benzyl, alkenyl, alkynyl, and non-aromatic carbocycles or heterocycles (linked via a carbon atom).

A) SUPPORTS AND PROTECTING GROUPS:

Coupling

polymer coupling	Assignment according to SPORE guidelines.
ligand coupling	Assignment according to SPORE guidelines.
tag coupling	Attachment of tags/encoding information.

Cleavage

polymer cleavage	Assignment according to SPORE guidelines.
ligand cleavage	Assignment according to SPORE guidelines.
tag cleavage	Removal of tags/encoding information.

Protection

O-protection	Protection of alcohols, carboxylic acids
N-protection	Protection of amines, N-heterocycles, amides etc.
S-protection	Protection of thiols and thiocarboxylic acids
carbonyl protection	Protection of carbonyl groups (e.g. as acetals)
protection, others	Protection of any other functional group

Deprotection

O-deprotection	Deprotection of alcohols, carboxylic acids
N-deprotection	Deprotection of amines, N-heterocycles, amides etc,
S-deprotection	Deprotection of thiols and thiocarboxylic acids
carbonyl deprotection	Carbonyl regeneration (e.g. by acetal cleavage)
deprotection, others	Deprotection of any other functional group

analytical cleavage Cleavage of a bond other than the ligand linkage for analytical purposes (using supports containing more than one cleavage site, e.g. "analytical construct resins").

cyclorelease Release of a ligand from a support by a cyclization reaction. This keyphrase is only assigned to transformations where the ligand release is an integral part of the cyclization mechanism (e. g. in an intramolecular attack of an amine on an ester linkage to give a lactam product) and not to reactions where the ring closure occurs after the release of the ligand (e.g. in a lactone formation after the release of a hydroxy ester).
For application of the additional term "traceless cleavage": cf. the comments given for that keyphrase.
Additional keyphrases: "ring closure", "ligand cleavage", possibly "polymer cleavage" and appropriate terms of chapter C8 – Ring Systems.

intra-resin reaction For reactions in which one of the products results from site-site interactions on the polymeric support, and for reactions where the TOPICS datafield describes crosslinking processes (or the absence of such processes) during the synthetic sequence (this excludes intermolecular reactions of soluble non-crosslinked polymers).

linker activation Assigned to the activation of safety-catch-type linkages (not necessarily ‘linkers’ as support components) for subsequent ligand release; e.g., by N-alkylation of acylsulfonamide linkages, S-oxidation of sulfide linkages, or removal of deactivating protecting groups.

linker derivatization For reactions (or individual steps of a multistep reaction) describing the (re)functionalization of a linker (e. g. the transformation of a hydroxy group to a halide or carbonate prior to attachment of an amine ligand), or for reactions of synthetic precursors of the linker (in practical terms: reactions with a "stable" POLYMER_LINKAGE and no data for the LIGAND_LINKAGE datafields).

mixed beads method For reactions in a mix-and-split strategy, in which mixtures of beads (not MicroTubes or tea-bags or similar multibead or other carriers) bearing different ligands are subjected in one pot to the same reaction conditions.

multipolymer system For reactions involving more than one polymer, e.g. in resin-to-resin transfer reactions, or in reactions of a polymer-supported reactant with a polymer-bound reagent or catalyst.

polymer derivatization For reactions (or individual steps of a multistep reaction) which have entries in POLYMER_NAME (and, possibly, LOADING or POLYMER_DATA) but no entries in the other support-related fields. In practical terms, this applies to reactions describing the functionalization or derivatization of polymers and to those which do not fit into the polymer-linker-ligand concept of the database.

polymer preparation For reactions in which the synthesis of a polmer framework (by polymerization reactions) or basic polymer type (e.g. by grafting processes) is described in the TOPICS datafield.

polymer-supported reagent For reactions where the TOPICS datafield describes the use of a synthesized, polymer-supported compound as a reagent/catalyst/metal ligand in solution-phase reactions (excluding "reagents" which provide C-containing fragments – these compounds are classified as "reactants" in the SPORE and CIRX databases).

reaction without polymers Reactions where neither reactants nor products are attached to a polymeric support (usually linker-ligand reactions); this keyword is not assigned to reactions where only the first or last step(s) of a multi-step reaction are carried out in solution.

scavenger resin Reactions describing the preparation of a scavenger resin and/or a novel application of a non-standard scavenger resin (with details in the TOPICS datafield).

soluble-polymer reaction Reactions using soluble polymers (usually polyethylene glycol and its derivatives.

"traceless cleavage..." terms A strict definition of "traceless cleavage" confines this term to reactions where the product released from a support contains no remnants of the ligand linkage. In accordance with the usage of this term in the literature, however, there are some types of "traceless cleavage" which are not entirely "traceless" (see below).

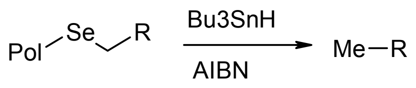
To permit more specific searches in the database, the diverse transformations reckoned as traceless cleavage reactions are further classified in SPORE by the type of bond or structure formed in the cleavage process; this information is cited in parentheses after the keyphrase "traceless cleavage":

traceless cleavage (H-alkyl)
traceless cleavage (H-aryl)
traceless cleavage (C-C)
traceless cleavage (olefin)
traceless cleavage (alkyne)
traceless cleavage (new func. group)
traceless cleavage (tert. amine)
traceless cleavage (N-heterocycle)
traceless cleavage (aromatization)
traceless cleavage (heterocyclization)

In some of these subgroups, the strict definition of a "traceless" cleavage is extended to include further reactions, e. g. in metathesis reactions of the "(olefin)" group (one carbon atom of the released olefin is derived from the ligand linkage, an alkene), and in the formation of heterocycles or tert. amines where a non-carbon atom of the ligand linkage provides the heteroatom of a heterocyclic scaffold, or the nitrogen of the tert. amine.
In contrast to the widespread use of the term "traceless" for any cyclization/cleavage reaction (indicating that a desired functionalized heterocycle is formed "tracelessly"), these reactions are not necessarily regarded as "traceless" in SPORE (they are all accessible, however, via the keyphrase "cyclorelease"). The most common cyclorelease reaction is a transformation where the heterocyclic product (of the lactam- or lactone-type) contains a carbonyl group of the ligand linkage, and reactions of this type are not regarded as "traceless" in SPORE.

Notes: In some cases, more than one traceless cleavage term will have to be assigned to a particular reaction (e. g. in a heterocyclization proceeding with concurrent aromatization). Furthermore, the assignment of some "traceless cleavage" terms is less stringent than the "cyclorelease" term in 2-step reactions, where they may be assigned (in one-pot transformations) even if some relevant structural features are only introduced in the second step of the reaction.

traceless cleavage (H-alkyl)
For cleavage reactions where a (non-aromatic) C-H bond replaces the ligand linkage.



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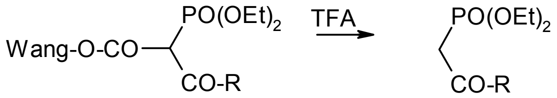

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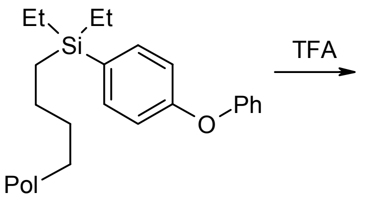
traceless cleavage (H-aryl)
For cleavage reactions where the ligand linkage to an arene is replaced with a C-H bond.



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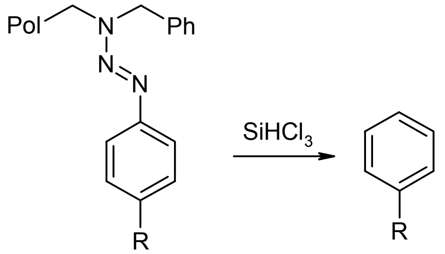

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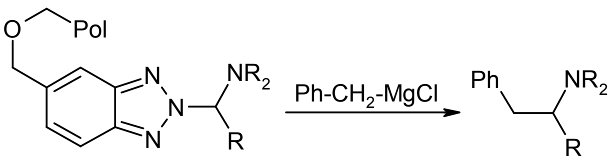
traceless cleavage (C-C)
For various cleavage reactions where a C-C bond replaces the ligand linkage.



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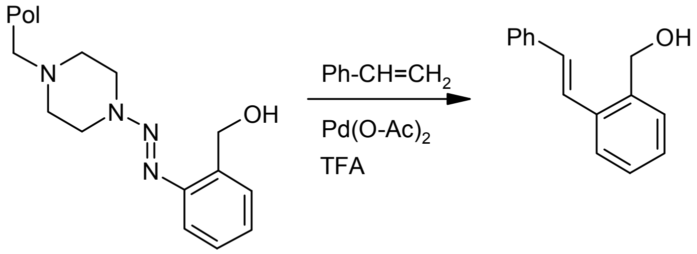

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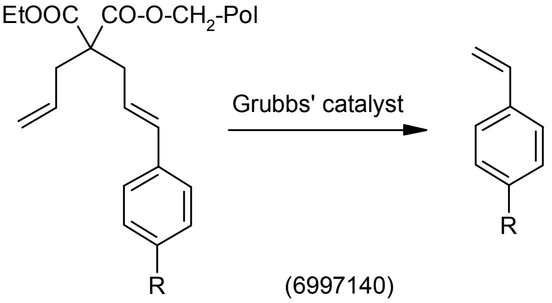
traceless cleavage (olefin)
For reactions where the cleavage of the ligand linkage results in the release of an olefin.



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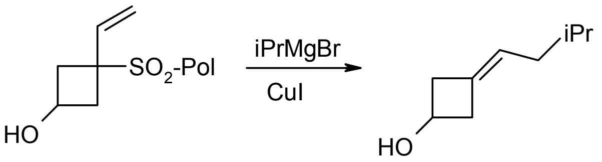

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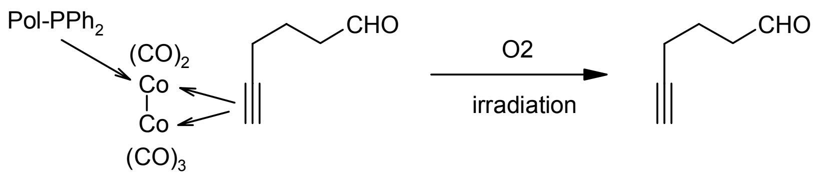
traceless cleavage (alkyne)

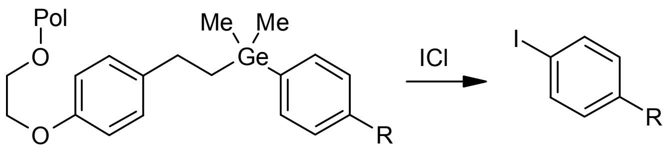
For cleavage reactions proceeding with release of an alkyne.



(6999179)

traceless cleavage (new func. group)

For cleavage reactions where a new type of functional group replaces the ligand linkage.



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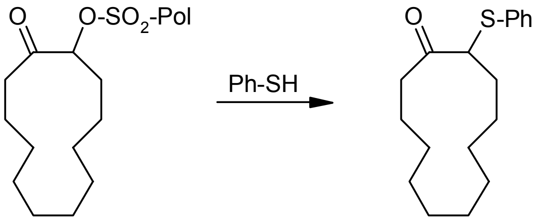

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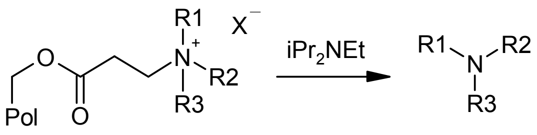
traceless cleavage (tert. amine)

For the release of tert. amines (including heterocycles) by Hofmann elimination or other procedures.



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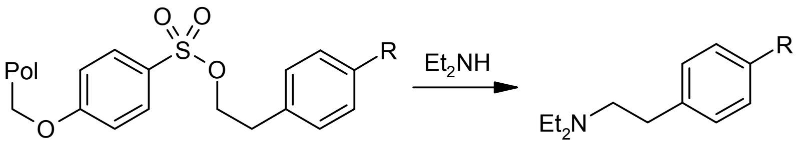
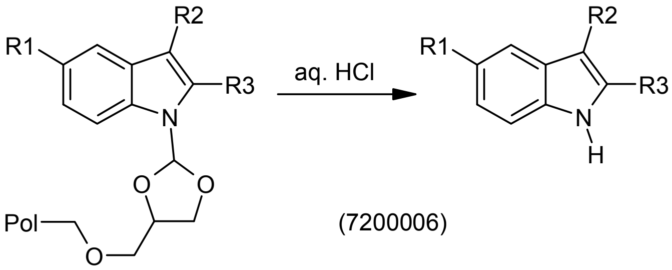
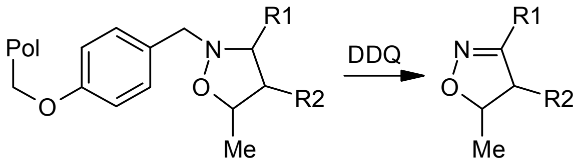


(6998023)

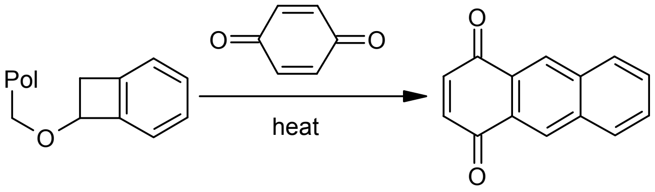
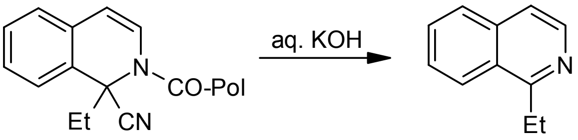
[also: traceless cleavage (new func. group)]

traceless cleavage (N-heterocycle)

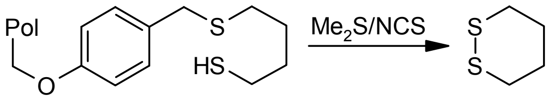
For the release of an existing N-heterocyclic system, linked to the support via its nitrogen atom, leading to the saturated (i. e. sec. amine) or unsaturated/aromatic heterocycle.

 (7200006)	 (6998283)

traceless cleavage (aromatization)
For cleavage reactions proceeding with concurrent aromatization to give arenes or hetarenes.

 (6998319)	 (6996148) *[also: traceless cleavage (N-heterocycle)]*

traceless cleavage (heterocyclization)
For various cleavage reactions proceeding via generation of a heterocyclic ring, excluding reactions where a carbonyl group of the ligand linkage is incorporated in the product (e. g. in lactam/lactone-type compounds; cf. the comments given above). – When used in reaction queries, this keyphrase may be especially useful in conjunction with other "traceless cleavage" terms.



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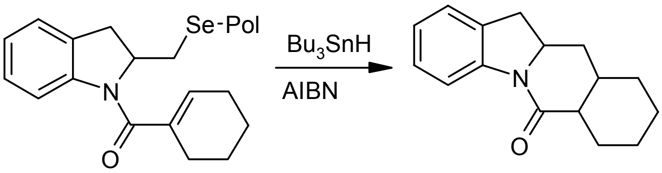
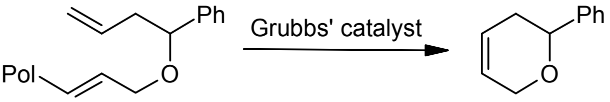
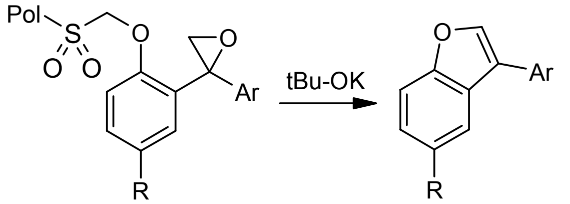


(7200033) *[also: traceless cleavage (C-C)]*



(6997196) *[also: traceless cleavage (olefin)]*



(7200032) *[also: traceless cleavage (aromatization)]*

B) GENERAL TERMS:

analytical method For reactions where the application of an analytical method, which is relevant to solid-phase methodology, is described in the TOPICS field. Accordingly, the keyphrase should not be assigned to reactions where the product is characterized by standard solution-phase procedures (NMR, IR, GLC etc.) following cleavage of the product from the support.

IR, single-bead IR, gel-phase NMR, MAS NMR For reactions where the application of the particular solid-phase analysis is described in the TOPICS field. *Additional keyphrase: "analytical method".*

asymmetric synthesis For reactions with the stereoselective formation of a new stereocenter with specific absolute configuration.

carbohydrate synthesis For reactions where the non-polymeric parts of the reactants and/or products are saccharides or contain sugar moieties as substructures.

click chemistry Concept by Sharpless et al. applied to selective and fast reactions leading to heteroatom links; usually employed for the synthesis of triazole systems by Cu-catalyzed 1,3-dipolar cycloadditon reactions of azides with alkynes. *Additional keyphrases: usually ”ring closure”, ”1,3-dipolar cycloaddition”, ”5-membered heterocycle formation”.*

collective abstract Assigned to one reaction (usually with detailed information in the TOPICS datafield) of an abstract which comprises several publications on a common topic, often by different authors, e. g. on general synthetic methodology, analytical methods, or the synthesis of certain macromolecules.

colorimetric test Description of a new colorimetric test for functional groups etc. or detailed study of a known colorimetric method (in the TOPICS datafield); not for standard reaction monitoring (by, e. g., the Kaiser ninhydrin test).

compound library Assigned to one representatitive product when a group of similar compounds has been synthesized, usually -but not necessarily - when the author of the publication uses the term "library". In most cases, just one reaction of an abstract will have this keyphrase; library size, yield/purity ranges etc. should be described in the TOPICS field of this reaction.

ion exchangers For reactions where the reactants and/or products are attached to ion-exchange resins such as Dowex ..., Amberlite ..., Amberlyst ... etc.

multicomponent reaction For reactions in which a target structure is assembled from at least three different carbon-contributing components in a single reaction step.

Additional keyphrases: possibly a name reaction such as ""Ugi condensation", "Petasis reaction", "Strecker synthesis" etc.

no conversion For reactions where all products have a yield of 0%.

nucleoside synthesis For syntheses of nucleoside derivatives (including analogues and natural products containing a nucleoside scaffold), but not for the preparation of the non-phosphorylated starting materials of RNA/DNA synthesis.

nucleotide synthesis For syntheses of oligo(deoxy/ribo)nucleotides and analogues, including the preparation of non-phosphorylated starting materials.

organometal complex formation Formation of organometallic coordination compounds (as opposed to "C-metalation", cf. Chapter C7). This keyword is also assigned if the formation of complexes is only described in the TOPICS field.

decomplexation Removal of an organic ligand from a metal complex, with the free ligand being the product of the reaction (the keyphrase is not assigned to organometal-promoted reactions proceeding with loss of the metal complex, e.g. reactions of metal carbene comlexes).

peptide synthesis For reactions where the reactant and/or product contains at least 2 (natural or unnatural) amino acids linked by an amide bond, and where the major part of the ligand is a peptide.

peptidomimetic synthesis For the synthesis of di- or oligomers considered as peptide analogs (usually formed by replacing the amide linkage with other functional groups).

pharmacological study For reactions in which results of pharmacological assays or SAR studies are described in the TOPICS datafield.

racemization For reactions involving the racemization of a substrate.

stability test For reactions with identical reactants and products, usually describing the stability of a support-ligand system towards certain reaction conditions.

steroid synthesis For reactions of steroidal reactants/products (including vitamin D_2 derivatives).

C) STRUCTURE AND FUNCTIONAL GROUPS:

C1) C-C Formation/Cleavage

C-acylation For the formation of a C—CO-R or C—CS-R bond ("R" can be any atom).

C-alkylation For the formation of a C—alkyl bond, excluding ring-forming reactions.

C-arylation For the formation of a C—aryl bond.

Additional keyphrases to these 3 terms: Depending on the mechanism (e.g. "nucleophilic substitution", "Suzuki coupling") and on the other coupling partner (thus, a Friedel-Crafts acylation will always be "C-acylation" + "C-arylation"); keyphrases of chapter C6 may apply to "C-alkylation" reactions.

olefination For any coupling reaction with formation of one new non-aromatic C=C double bond.
Additional keyphrases: Usually a "Wittig..." reaction, or a (aldol, Knoevenagel) "condensation", or a "metathesis" reaction.

C-C cleavage For any cleavage of a C-C single bond.
Additional keyphrases: Possibly "decarboxylation".

C=C cleavage For any cleavage of a non-aromatic C=C double bond.
Additional keyphrases: Possibly "ozonolysis".

alkyne cleavage For any cleavage of a CC triple bond.
Additional keyphrases: Possibly "oxidation (alkyne)".

C2) C-N Formation/Cleavage ("C" not carbonyl)

N-alkylation For (single-bond) alkylations of any nitrogen atom of a reactant (i. e. excluding reagents such as ammonia, hydrazine etc.); excluding cyclizations with C-N bond formation.
Additional keyphrases: Usually "nucleophilic substitution" and "amination" (if the N-containing compound is an amine); possibly keyphrases of chapter C6.

N-arylation For arylations of any nitrogen atom of a reactant.
Additional keyphrases: Usually "aromatic/heteroaromatic substitution" and "amination" (if the N-compound is an amine); possibly keyphrases of chapter C6.

amination For reactions of an alkyl/aryl substrate (not a carboxylic acid derivative) with ammonia or an amine (not an amide, hydrazine etc.) to give a C-N bond.
Additional keyphrases: Usually "N-alkylation" (not for reagents, e. g. ammonia).

[aziridine formation: cf. chapter C8, Ring Systems]

imine formation For C=N formation in products of type $R_2C=N-R'$ (R: H, alkyl, aryl; R': H, OR, alkyl, aryl). No special keyphrases are provided for hydrazones, diimides, and other analogs.
Additional keyphrases: Usually "condensation" (not "N-alkylation").

guanylation For the formation of a guanidine functionality, usually by reaction of an amine with a carbodiimide, a thiourea derivative, or a special guanylation reagent. Also for the synthesis of heterocyclic non-aromatic guanidines if typical guanylation conditions are used.
Additional keyphrases: Possibly "amination" (generally not: "N-alkylation").

hydrazone formation For the generation of a hydrazone functionality (N-N=C) or more highly functionalized analogues (e.g., sulfonylhydrazones or semicarbazones) via formation of the C=N bond; not used for the synthesis of heterocyclic scaffolds.
Additional keyphrases: Usually "condensation".

hydroaminomethylation A tandem hydroformylation/reductive amination reaction of olefins with amines and CO/H_2, which leads to the saturated aminomethylated products.
Additional keyphrases: "hydroformylation", "hydrogenation", "formylation", "reductive amination", "reductive alkylation", "reduction (imine)", "high-pressure reaction", "C-alkylation", "amination", "N-alkylation".

reductive alkylation For C-N formation via reduction of an imine intermediate.
Additional keyphrases: "reductive amination", "reduction (imine)", usually "amination" and "N-alkylation" ("imine formation" only for 2 consecutive reactions).

reductive amination For C-N formation via reduction of an imine intermediate.
Additional keyphrases: "reductive alkylation", "reduction (imine)", usually "amination" and "N-alkylation" ("imine formation" only for 2 consecutive reactions).

diazotation For the formation of diazo or diazonium compounds.
Additional keyphrases: -

diazo coupling For the coupling of a diazonium compound to give the azo product (or the tautomeric hydrazone), usually with C-N bond formation, or the

triazene product in reactions with amines.
Additional keyphrases: Possibly N-alkylation.

C-N cleavage For all cleavages of N-alkyl (or N-aryl) single bonds; this includes, e.g., cleavages of N-substituted amides to give the free amide R-CO-NH_2 (as in the resin cleavage of Rink resin supported amides; cf. the "amide cleavage" definition in chapter C4), but not the cleavage of a CO-N bond.
Additional keyphrases: -

C=N cleavage For all C=N cleavages (e.g., of imines or hydrazones), with the exception of diazo compounds (e. g. diazomethane).
Additional keyphrases: -

C3) C-O Formation/Cleavage ("C" not carbonyl)

hydroxylation For the introduction of an aryl/alkyl-OH group.
Additional keyphrases: Possibly "hydroboration", "addition", or "nucleophilic substitution".

O-alkylation For alkylations of any oxygen atom (in most cases an OH group) of a reactant (i. e. excluding water, NaOH, etc.); excluding cyclizations with C-O bond formation. This definition includes alkylations of alcohols/phenols (giving ethers), carboxylic acids (e.g. with MeI or diazomethane; i. e. esterifications which are not "O-acylations"), and sulfonic or phosphonic acids.
Additional keyphrases: Possibly "nucleophilic substitution", "etherification", or "esterification", or keyphrases of chapter C6.

O-arylation For arylations of any oxygen atom (usually an OH group) of a reactant.
Additional keyphrases: Possibly "aromatic/heteroaromatic substitution", "etherification", or keyphrases of chapter C6.

etherification For formation of compounds of type R-O-R' with R and R' = alkyl or aryl; not for the formation of heterocycles or acetals.
Additional keyphrases: Usually "O-alkylation", possibly "nucleophilic substitution", "Mitsunobu reaction" or "Williamson ether synthesis".

acetalization Formation of cyclic or acyclic acetals/ketals or thioacetals/thioketals; not for glycosylations.
Additional keyphrases: "dehydration", possibly "ring closure", "annelation".

[epoxidation: cf. chapter C8, Ring Systems]

acetal cleavage For all cleavages of cyclic or acyclic acetals/ketals or thioacetals/thioketals, often with regeneration of a carbonyl group; excluding

functional group transformations at the anomeric carbon of sugars.
Additional keyphrases: Possibly "C-O cleavage", "ring cleavage", or "carbonyl deprotection".

C-O cleavage For all cleavages of O-alkyl (or O-aryl) single bonds; this includes cleavages of ethers, of esters CO-O-R at the O-R bond (as in the cleavage of Wang resin esters to the free carboxylic acid; cf. the "ester cleavage" definition in chapter C4), and of the O-R bond in sulfonates and phosphates.
Additional keyphrases: -

dehydration For reactions involving loss of water, e.g. by elimination or acetal formation, excluding "condensation" reactions (this term already implies dehydration).
Additional keyphrases: Possibly "elimination", or "acetalization".

C4) Carboxylic Acid Derivatives

N-acylation General term for all coupling reactions leading to cyclic or acyclic N-CO or N-CS bonds (excluding reactions of reagents, e.g. ammonia); the particular group formed is described by the more specific keyphrases, e. .g. "amidation" (for some less frequent groups, e.g. hydrazides or hydroxamates, there are no special keyphrases).
Additional keyphrases: Possibly "amidation", or "peptide coupling", or "carbamate formation" or "urea formation".

O-acylation General term for all coupling reactions leading to cyclic or acyclic O-CO or O-CS bonds (excluding reactions of reagents, e.g. water or NaOH); the particular group formed is described by the more specific keyphrases, e. g. "esterification" (for some less frequent groups, e.g. acid anhydrides, there are no special keyphrases).
Additional keyphrases: Possibly "esterification" or "carbamate formation".

S-acylation General term for all coupling reactions leading to cyclic or acyclic S-CO or S-CS bonds (excluding reactions of reagents, e.g. NaSH); the particular group formed is described by the more specific keyphrases, e. g. "esterification".
Additional keyphrases: Possibly "esterification".

amidation For coupling reactions leading to cyclic or acyclic products of type R_2N-CX-R' (R: H, alkyl, aryl, OR; X: O, S; R': H, alkyl, aryl, halogen)

with formation of the N-CX or CX-R' bond.
Additional keyphrases: "N-acylation"; possibly "lactam formation".

[lactam formation: cf. chapter C8, Ring Systems]

peptide coupling For coupling reactions of two α-amino acids or peptides via an amide bond.
Additional keyphrases: "amidation", "N-acylation".

carbamate formation For coupling reactions leading to cyclic or acyclic products of type R_2N-CX-X-R' (R: any atom but nitrogen; X: O, S; R': alkyl, aryl) with formation of either the N-CX or the CX-X bond.
Additional keyphrases: "N-acylation" (N-CX formation) or "O-acylation".

carbonate formation For coupling reactions leading to cyclic or acyclic products of type R-X-CX-X-R (R: H, alkyl, aryl, amine; X: O, S) with formation of the CX-X bond.
Additional keyphrases: "O-acylation" or "S-acylation".

[carboxylation: cf. chapter C6, Special C-Groups]

[decarboxylation: cf. chapter C6, Special C-Groups]

[guanylation: cf. chapter C2, C-N Bond Formation/Cleavage]

hydrazide formation For coupling reactions leading to cyclic or acyclic products with N-N-CX-R groups (R: alkyl, aryl; X: O, S) with formation of the N-CX bond, where the two N-atoms may carry additional functionalities such as carbonyl groups but no further nitrogen substitutents (thus excluding triazene derivatives).
Additional keyphrases: Usually "N-acylation" or "hydrazinolysis".

esterification For coupling reactions leading to cyclic or acyclic products of type R-CX-Y-R' (R: H, alkyl, aryl, halogen; X, Y: O, S; R': alkyl, aryl, N of “active esters“) with formation of either the CX-Y or the Y-R' bond. This definition implies that the formation of inorganic esters, i.e. phosphates, phosphonates, sulfonates etc., is not classified as "esterification"; similarly, the formation of carbonates is not included.
Additional keyphrases: "O/S-acylation" (CX-Y formation) or "O/S-alkylation" (Y-R' formation); possibly "transesterification", "lactonization".

transesterification For esterifications (cf. the above definition) where the (thio)alcohol moiety of an ester substrate is replaced by a different (thio)alcohol.
Additional keyphrases: "esterification", "ester cleavage", "O/S-acylation".

[lactone formation: cf. chapter C8, Ring Systems]

urea formation For coupling reactions leading to cyclic or acyclic products of type R_2N-CX-NR_2 (R: anything but nitrogen or acyl; X: O, S) or close analogs [e.g. RN=C(SR)-NR_2].
Additional keyphrases: "N-acylation"; possibly "addition" (for reactions with iso[thio]cyanates).

amide cleavage For the cleavage of the cyclic or acyclic N-CX bond in reactants of type R_2N-CX-R' (R: H, alkyl, aryl, OR; X: O, S; R': H, alkyl, aryl, halogen). A different keyphrase is assigned to the frequent solid-phase cleavage of one of the R_2N bonds (cf. "C-N cleavage" and explanations there).
Additional keyphrases: -

carbamate cleavage For the cleavage of one of the cyclic or acyclic N-CX or CX-X bonds in reactants of type R_2N-CX-X-R' (R: any atom but nitrogen; X: O, S; R': alkyl, aryl).
Additional keyphrases: -

carbonate cleavage For the cleavage of one of the cyclic or acyclic X-CX bonds in reactants of type R-X-CX-X-R (R: H, alkyl, aryl, amine; X: O, S).
Additional keyphrases: -

ester cleavage For the cleavage of the cyclic or acyclic CX-Y bond in reactants of type R-CX-Y-R' (R: H, alkyl, aryl, halogen; X, Y: O, S; R': alkyl, aryl, N of “active esters“); excluding ester reductions. A different keyphrase is assigned to the frequent solid-phase cleavage of the Y-R' bond (cf. "C-O cleavage" and explanations there).
Additional keyphrases: -

hydrazide cleavage For the cleavage of the (cyclic or acyclic) N-CX bond in reactants with N-N-CX-R functionalities (R: alkyl or aryl; X: O, S).
Additional keyphrases: -

urea cleavage For the cleavage of a (cyclic or acyclic) CX-N bond in reactants of type R_2N-CX-NR_2 (R: anything but nitrogen or acyl; X: O, S).
Additional keyphrases: -

C5) S/SO/SO2 Functionalities

[For thiocarbonyl-related keyphrases: cf. chapter C4]

S-alkylation For alkylations of any sulfur atom of a reactant (i. e. excluding inorganic S-containing salts, SO_2, etc.); excluding cyclizations with C-S bond formation. This definition includes alkylations of alkyl or aryl thiols to give

sulfides (thioethers), or of sulfides to give sulfonium salts, or of thiocarboxylic acids to give thioesters.
Additional keyphrases: Possibly "nucleophilic substitution", "sulfuration", or "esterification", or keyphrases of chapter C6.

S-arylation For arylations of any sulfur atom of a reactant.
Additional keyphrases: Possibly "aromatic/heteroaromatic substitution", "etherification", or keyphrases of chapter C6.

[S-oxidation: cf. chapter D, Mechanism]

sulfonamidation For coupling reactions involving the formation of a cyclic or acyclic N-SO_2 bond.
Additional keyphrases: -

sulfonamide cleavage For the cleavage of the S-N bond in compounds of type R2N-SO2-R‘ or C=NR-SO2-R‘ [R, R‘: H, C].
Additional keyphrases: -

sulfonate formation For reactions leading to the formation of cyclic or acyclic products with a C-SO2-[O/S]-R group (R: H, C, negative charge).
Additional keyphrases: -

sulfone formation For coupling reactions involving the formation of a cyclic or acyclic C-SO2-C group.
Additional keyphrases: -

sulfuration For the introduction of sulfur, mercapto groups, or aryl/alkylmercapto moieties to any atom to give, e. g., thiocarbonyl compounds, thiols, or sulfides.
Additional keyphrases: Possibly "S-alkylation".

C-S cleavage For all cleavages of S-alkyl/aryl single bonds in sulfides, sulfones, sulfonium salts, S-alkyl-thioesters etc..
Additional keyphrases: -

desulfuration For the removal of sulfur, mercapto groups, or aryl/alkylmercapto moieties from any atom; excluding cleavages of thioesters.
Additional keyphrases: -.

C6) Addition/Cleavage of Special C-Groups to any Atom

alkynylation For the introduction of any alkyne at the triple-bond-carbon.
Additional keyphrases: Possibly "C/N/O/S-alkylation".

allylation For the introduction of an open-chain allyl group $-CR_2-CR=CR_2$ (R: H, alkyl, aryl, halogen; $CR_2 \neq$ double bond).
Additional keyphrases: Possibly "C/N/O/S-alkylation".

vinylation For the introduction of an open-chain vinyl group $-CR=CR_2$ (R: H, alkyl, aryl, halogen).
Additional keyphrases: Possibly "C/N/O/S-alkylation".

carbonylation For the introduction of a CO or CS group.
Additional keyphrases: Possibly "C/N/O/S-acylation".

carboxylation For the introduction of a COOH/CSSH/COSH group.
Additional keyphrases: Possibly "C/N/O/S-acylation".

decarboxylation For the removal of a COOH group
Additional keyphrases: Usually "C-C cleavage".

cyanation For the introduction of a cyano (-CN) group.
Additional keyphrases: Possibly "C-alkylation".

formylation For the introduction of a CHO group.
Additional keyphrases: Possibly "C/N/O/S-acylation".

hydroformylation Addition of a hydrogen atom and a CHO group to an unsaturated system (usually with H_2 and CO)..
Additional keyphrases: "formylation", "C-acylation", "C-alkylation", "hydrogenation".

glycosylation For coupling reactions with a sugar at the anomeric carbon.
Additional keyphrases: Possibly "C/N/O/S-alkylation".

C7) Other Functional Groups

azidation For the introduction of an azido (N_3) group..
Additional keyphrases: Possibly "nucleophilic substitution".

bromination Introduction of a Br atom.

chlorination Introduction of a Cl atom.

fluorination Introduction of a F atom.

iodination Introduction of a I atom.

dehalogenation Reductive removal of a halogen atom (i.e. H/halogen exchange).

hydroboration For the addition of boranes to olefins, usually as the first step of a hydroxylation procedure.
Additional keyphrases: Usually "hydroxylation".

hydrostannation Addition of a hydrogen atom and a stannyl group to an unsaturated system (alkene, alkyne, ketone).
Additional keyphrases: “C-metalation", “addition“.

C-metalation Only for carbon metalations, usually leading to organolithium or Grignard compounds or analogs, if the metalated compound is given as the product of a reaction or reaction step (i.e. not for intermediates); another keyphrase ("organometal complex formation") is assigned to metal complexes with coordinative ligands.

nitration For the derivatization of any atom with an NO_2 group.

nitrosation For the derivatization of any atom with an NO group.

phosphination For the synthesis of phosphines (usually from R_2PX), and for attachment of phosphines to atoms other than O/S, excluding phosphonium salt formations (vide infra).

phosphitylation For coupling reactions giving compounds of type $P(X\text{-}R)_3$... (R: H, alkyl, aryl; X: O, S, N).

phosphonation For the synthesis of phosphonic acids or phosphonates $R\text{-}PX(XR)_2$ (R: H, alkyl, aryl; X: O, S) with formation of the R-P, P-XR or X-R bond.

phosphonium salt formation For the synthesis of phosphonium salts R_4P^+

phosphorylation For coupling reactions giving compounds of type $PX(X\text{-}R)_3$... (R: H, alkyl, aryl; X: O, S, N).

C-selenation For the formation of C-Se bonds.

C-deselenation For the cleavage of C-Se bonds.

C-silylation For the silylation of any C-atom of a reactant.

N-silylation For the silylation of any N-atom of a reactant.

O-silylation For the silylation of any O-atom of a reactant.

desilylation For the removal of a silyl group from any C-, N- or O-atom of a reactant.

hydrosilylation Addition of a hydrogen atom and a silyl group to an unsaturated system (alkene, alkyne, ketone).
Additional keyphrases: “C-“ or "O-silylation", “addition“.

C8) Ring Systems

ring closure For any ring closing reaction (cyclizations, cycloadditions) leading to carbo- or heterocycles.
Additional keyphrases: Possibly "annelation", or "4/5/6/7-membered heterocycle formation", or "... cycloaddition", or "Diels-Alder reaction", or "cyclocondensation", etc.

[acetalization: cf. chapter C3, C-O Formation/Cleavage]
[cycloaddition: cf. chapter D, Mechanism]
[1,3-dipolar cycloaddition: cf. chapter D, Mechanism]
[cyclocondensation: cf. chapter D, Mechanism]
[radical cyclization: cf. chapter D, Mechanism]

annelation For reactions involving the fusion of an additional ring to an existing carbo- or heterocyclic system.
Additional keyphrases: ring closure.

aziridine formation For cyclizations leading to aziridines.
Additional keyphrases: "ring closure", possibly "annelation".

ring cleavage For cleavages of any carbo- or heterocyclic systems.
Additional keyphrases: -

[acetal cleavage: cf. chapter C3, C-O Formation/Cleavage]
[cyclorelease: cf. chapter A, Special Terms]

epoxidation For the formation of epoxides (oxiranes), usually from olefins.
Additional keyphrases: "ring closure", "oxidation (alkene)", possibly "annelation".

lactam formation For the synthesis of cyclic amides by any type of ring closure reaction. The ring system may contain other heteroatoms, which, however, must not be adjacent to the carbonyl group or nitrogen atom (thus excluding cyclic ureas, carbamates and hydrazides); another carbonyl group must not be adjacent to the nitrogen atom (which excludes cyclic imides).
Additional keyphrases: "ring closure", probably "4/5/6/7-membered heterocycle formation"), possibly "amidation", "N-acylation".

lactone formation For the synthesis of cyclic esters by any type of ring closure reaction. The ring system may contain other heteroatoms, which, however, must not be adjacent to the carbonyl group or ring oxygen (thus excluding cyclic carbonates, carbamates and peroxy esters); another carbonyl group must not be adjacent to the ring oxygen (which excludes cyclic anhydrides).
Additional keyphrases: "ring closure", probably "4/5/6/7-membered heterocycle formation", possibly "esterification", "O-acylation".

macrocycle formation For ring closure reactions leading to carbo- or heterocyclic systems containing at least 8 ring members – excluding fused ring systems (e.g., decalin), macrocyclic acetals, metal-containing rings, and certain highly bridged systems.

Additional keyphrases: "ring closure", possibly "annelation" or "lactone formation" or "lactam formation" etc.

4-membered heterocycle formation For the formation of any 4-membered heterocycle (excluding acetals) containing only O-, N-, or S-heteroatoms. *Additional keyphrases: "ring closure", possibly "annelation" or "lactone formation" or "lactam formation".*

5-membered heterocycle formation For the formation of any 5-membered heterocycle (excluding acetals) containing only O-, N-, or S-heteroatoms. *Additional keyphrases: "ring closure", possibly "annelation" or "lactone formation" or "lactam formation."*

6-membered heterocycle formation For the formation of any 6-membered heterocycle (excluding acetals) containing only O-, N-, or S-heteroatoms. *Additional keyphrases: "ring closure", possibly "annelation" or "lactone formation" or "lactam formation".*

7-membered heterocycle formation For the formation of any 7-membered heterocycle (excluding acetals) containing only O-, N-, or S-heteroatoms. *Additional keyphrases: "ring closure", possibly "annelation" or "lactone formation" or "lactam formation".*

D) MECHANISM AND REACTION CONDITIONS:

addition Addition reactions to double or triple bonds between carbon and/or hetero atoms which are neither "conjugate additions" (i.e., they are usually 1,2-additions) nor "cycloadditions".
Additional keyphrases: possibly "free-radical addition".

conjugate addition 1,4-(or 1,6 etc.)-Addition reactions to systems of type C=C-Z (Z= CO..., CN, NO_2, SO2..., etc.).
Additional keyphrases: “Michael addition", possibly "C-alkylation".

free-radical addition Addition of free radicals to unsaturated bonds (only for unambiguous cases, such as AIBN-mediated reactions; not for transformations where possible radical intermediates are discussed). Not assigned to reactions with the keyphrase "radical cyclization".
Additional keyphrases: "addition"; possibly also: "free-radical substitution".

aldol addition For coupling reactions of a carbonyl compound or analogue (e. g. the enol; or CN, NO2, SO, SO2 derivatives) with a second carbonyl compound to produce the β-hydroxy carbonyl compound (or analogue).
Additional keyphrases: "C-alkylation”, “addition“.

aldol condensation For coupling reactions of a carbonyl compound or analogue (e. g., CN, NO2, SO, SO2 derivatives) with a second carbonyl compound to afford the α,β-unsaturated product; excluding Knoevenagel condensations.
Additional keyphrases: “olefination“.

biocatalyzed reaction Reaction carried out in the presence of an enzyme, fungus, bacterium etc.
Additional keyphrases: -

cycloaddition For all (inter- or intramolecular) reactions between two unsaturated systems leading to a cyclic product, excluding 1,3-dipolar cycloadditions.
Additional keyphrases: "ring closure", possibly "Diels-Alder reaction" or "annelation".

1,3-dipolar cycloaddition For the (inter- or intramolecular) reaction between an unsaturated system with a 1,3-dipolar compound (e.g. an azide or nitrile oxide) leading to a cyclic product.
Additional keyphrases: "ring closure", probably "5-membered heterocycle formation", possibly "annelation".

cycloreversion Ring cleavage leading to the substrate(s) [i. e. diene + dienophile]of a cycloaddition reaction.
Additional keyphrases: "ring cleavage", possibly "C-C cleavage".

carbene reaction For reactions proceeding via carbene intermediates.
Additional keyphrases: -

condensation For condensation reactions (i.e. coupling reactions proceeding with loss of another molecule, usually water or alcohol) to which another, more specific keyphrase (e.g. aldol condensation, cyclocondensation, Claisen condensation, Ugi condensation etc.) cannot be assigned. The keyphrase is also omitted in standard transformations of carboxylic acid derivatives (esterifications, amidations).
Additional keyphrases: Often "imine formation"

cyclocondensation For the formation of a cyclic system by a condensation reaction for which a Name Reaction keyphrase does not exist.
Additional keyphrases: "ring closure" and other appropriate keyphrases of chapter C8 (Ring Systems).

[dehydration: cf. chapter C3, C-O Formation/Cleavage]

electrolysis For electrochemical reactions
Additional keyphrases: -

elimination Only for β-eliminations (or analogous conjugate eliminations), i.e. the elimination of two atoms/groups from adjacent atoms with concurrent formation of a double or triple bond.
Additional keyphrases: Possibly "dehalogenation".

ene-reaction For coupling reactions of olefins with unsaturated compounds (enophiles) involving H-migration to the enophile and an allylic shift of the ene double bond.
Additional keyphrases: Possibly "C-alkylation".

haloform reaction Cleavage of methyl ketones by treatment with halogen (Br_2, Cl_2, I_2) and a base, or of trihalomethyl ketones by reactions with nucleophiles.
Additional keyphrases: "C-C cleavage".

high-pressure reaction Reaction carried out at a higher than normal pressure (> 1 atm).
Additional keyphrases: -

hydrazinolysis For cleavage reactions (usually of CO-O, CO-N bonds) effected by hydrazine.
Additional keyphrases: -

hydrogenation For all hydrogenation reactions using either H_2 or catalytic

transfer hydrogenation (e.g. with ammonium formate or cyclohexadiene), and for all reductions of a CC triple to a double, or of a CC double to a single bond.
Additional keyphrases: -

hydrolysis Only for those hydrolytic reactions where water is actually present in the reaction conditions.
Additional keyphrases: Possibly "ester cleavage".

insertion For reactions of the general type A-B + C → A-C-B
Additional keyphrases: Possibly "C-alkylation".

ionic liquids For reactions employing ionic liquids, such as [bmim]BF_4, as solvent or co-solvent.
Additional keyphrases: -

isomerization Only for stereo-isomerizations (E/Z-isomerization or epimerization; not for "racemization"), or for tautomerizations of unsaturated systems with concurrent proton migation (a migration of other groups would be classified as "rearrangement"). The term is not assigned to reactions where the isomerization is only an integral part of a more complex reaction mechanism (e.g. in ene reactions, or aldol reactions via the enol).
Additional keyphrases: -

metathesis For all metathesis reactions, i.e. the catalyzed cross-coupling of two unsaturated systems.
Additional keyphrases: "olefination", "C=C cleavage".

microwaves For all reactions carried out under microwave irradiation
Additional keyphrases: -

organocopper chenistry For reactions performed with aryl-/alkylcopper reagents used directly or formed in situ (i.e., not including reactions using a copper catalyst or copper salts)..
Additional keyphrases: Often "C-alkylation" or "C-arylation".

oxidation For oxidations which cannot be described by the following more specific terms, usually relating to the oxidized functionality.

oxidation (prim. alcohol)

oxidation (sec. alcohol)

oxidation (1,2-diol)	*Additional keyphrases: Usually "C-C cleavage"*
oxidation (lactol)	
oxidation (hydroquinone)	
oxidation (aldehyde)	
oxidation (ketone)	*Additional keyphrases: Possibly "Baeyer-Villiger oxidation" etc.*
oxidation (acetal)	*Additional keyphrases: "C-O cleavage", "acetal cleavage"; possibly "ring cleavage"*
oxidation (thioacetal)	*Additional keyphrases: "C-S cleavage", "acetal cleavage"; possibly "ring cleavage", "desulfuration"*
oxidation (hydrazide)	Usually the first step of a safety-catch cleavage operation.
oxidation (acylcarbamate)	Often employed for the removal of chiral auxiliaries of the oxazolidinone type. *Additional keyphrases: "hydrolysis"*
oxidation (alkene)	For oxidative cleavage reactions or bis-O-additions; usually ozonolyses, epoxidations or dihydroxylations.
oxidation (alkyne)	Oxidative conversions of alkyne functionalities (excluding, e.g., simple addition or hydration reactions).
oxidation (furan)	
oxidation (aromatization)	Including oxidations leading to the keto tautomers of aromatic systems.
oxidation (benzylic carbon)	For the oxidation of benzylic functionalities to carbonyl-containing groups, and for the oxidative cleavage of Wang-type linkers or benzylic protecting groups.
B-oxidation	Usually for the oxidative work-up step after hydroborations or boron-based asymmetric aldol reactions.
I-oxidation	For oxidations of iodine atoms.
N-oxidation	For oxidations of aliphatic or aromatic amines.

P-oxidation	For P-oxidations not involving the following groups.
P-oxidation (phosphine)	
P-oxidation (phosphite)	
P-oxidation (phosphoramidite)	

S-oxidation	For S-oxidations not involving the following groups.
S-oxidation (thiol)	Excluding disulfide formations.
S-oxidation (sulfide)	Excluding disulfide formations.
S-oxidation (sulfoxide)	
S-oxidation (to disulfide)	For oxidations of thiols or sulfides to disulfides.

Se-oxidation	*Additional keyphrases: often "C-deselenation"*

ozonolysis For reactions with ozone, usually for olefin cleavages.
Additional keyphrases: "oxidation (alkene)"; usually "C=C cleavage".

photoreaction For all reactions carried out under irradiation with light.
Additional keyphrases: -

radical cyclization For ring closure reactions proceeding via radical intermediates, initiated by a radical promoter. Additional "free-radical"-terms (free-radical addition, free-radical substitution) are not assigned to these reactions.
Additional keyphrases: "ring closure"; possibly “C-arylation“, “aromatic/heteroaromatic substitution“, keyphrases of chapter C8 (Ring Systems).

[free-radical addition: cf. "addition"]
[free-radical substitution: cf. "substitution"]

rearrangement For the migration of non-H atoms or groups (cf. "isomerization" for H-migration), including the rearrangement of cyclic systems.
Additional keyphrases: -

reduction	For reductions (excluding "hydrogenation"s) which cannot be described by the following more specific terms relating to the reduced functionality.
reduction (arene)	Including hydrogenations; often for the reduction of heterocyclic arenes.
reduction (alkyl halide)	*Additional keyphrases: "dehalogenation"*
reduction (aryl halide)	*Additional keyphrases: "dehalogenation"*
reduction (alcohol)	
reduction (aldehyde)	Including thioaldehydes.
reduction (ketone)	Including thioketones.
reduction (acid)	Only for carboxylic acids, including thioacids.
reduction (acid halide)	Including thioacid halides.
reduction (anhydride)	Including anhydrides of thioacids.
reduction (ester)	Including thioesters.
reduction (amide)	Including imides and thioamides/imides.
reduction (Weinreb amide)	
reduction (carbamate)	Including thiocarbamates.
reduction (cyanide)	
reduction (azide)	*Additional keyphrases: possibly "Staudinger reaction"*
reduction (imine)	*Add. keyphrases: possibly "reductive amination" etc.*
reduction (hydrazone)	
reduction (nitro group)	
reduction (phosphine oxide)	
reduction (sulfonamide)	
reduction (sulfonate)	
reduction (sulfone)	
reduction (sulfoxide)	
reduction (sulfide)	
reduction (disulfide)	
reduction (selenide)	

reduction (ozonide)

sonication For all reactions carried out under ultrasound.
Additional keyphrases: -

aromatic substitution For all replacement reactions at an aromatic carbon where a non-H substituent is substituted by another atom or group (including hydrogen), excluding reactions of aromatic organolithium or Grignard compounds and analogs (i. e. Ar-M, with M = alkali, Mg, Zn, Cd, Hg) and excluding reactions at a heteroaromatic ring (see below).
Additional keyphrases: Possibly "C-arylation".

heteroaromatic substitution A type of “aromatic substitution” reaction (see above) where the substitution occurs in a heteroatom-containing aromatic ring (note: heteroatoms in a neighboring fused ring are not covered by this definition; thus, substitutions in the indole system at positions 2 and 3 are considered as “heteroaromatic” while reactions at positions 4-7 are “aromatic”).
Additional keyphrases: Possibly "C-arylation".

nucleophilic substitution Only for nucleophilic substitution reactions at saturated (non-carbonyl) carbons [Note: Substitutions at a carbonyl are accessible by keyphrases of chapter C4].
Additional keyphrases: Possibly "C/O/N/S-alkylation".

free-radical substitution For reactions, where heteroatoms (usually halogen, S, or Se) are displaced by other groups (usually hydrogen or alkyl groups) under radical conditions (often involving the presence of AIBN). Not assigned to reactions with the keyphrase "radical cyclization".
Additional keyphrases: Possibly also "free-radical addition".

E) NAME REACTIONS:

NOTE: The following definitions describe the basic features of the reactions; the keyphrases may also be assigned, however, to reactions where the structures or reaction conditions differ from the "standard procedures".

aza-Achmatowicz rearrangement Oxidative rearrangement of 2-aminomethyl-substituted furan derivatives (as latent 1,4-dicarbonyl compounds) to piperidin-3-one derivatives.
Additional keyphrases: "oxidation", "rearrangement", "ring cleavage", "ring closure", "6-membered heterocycle formation", "C-O cleavage".

Arbuzov-Michaelis synthesis Synthesis of $R\text{-}PO(OR')_2$ from an alkyl halide and the $P(OR')_3$ phosphite, or analogous reactions (e. g. $Ph_2P\text{-}O\text{-}R'$ -> $Ph_2PO\text{-}R$)
Additional keyphrases: "phosphonation".

Arndt-Eistert homologation For the Wolff rearrangement of a diazo ketone (usually in the presence of Ag_2O or Ph-COOAg) as the key step of the homolation sequence starting from a carboxylic acid or acyl halide.
Additional keyphrases: "rearrangement", "carbene reaction", "C-C cleavage", "C-alkylation".

Baeyer-Villiger oxidation Oxidation of ketones to esters or lactones with peracids.
Additional keyphrases: "oxidation (ketone)", "insertion", "esterification" ,"C-C cleavage", "rearrangement"; possibly "ring cleavage", "lactone formation" and "...-membered heterocycle formation".

Barbier reaction One-step synthesis of alcohols from aldehydes/ketones, an organic halide and a metal (e.g. Mg, Li, Zn, Pb); including reactions using pre-formed organometal halides (e.g., Grignard reagents).
Additional keyphrases: Usually "C-alkylation" or "C-arylation", "addition", possibly "Grignard reaction".

Bartoli indole synthesis Synthesis of indoles from nitroarenes and vinyl Grignard reagents.
Additional keyphrases: "ring closure", "5-membered heterocycle formation", "annelation", "reduction (nitro group)".

Barton decarboxylation Photochemical fragmentation of O-acyl-thiohydroxamates (often N-hydroxythiopyridone esters) with formation of an alkyl radical and CO_2.
Additional keyphrases: "photoreaction", "decarboxylation", "C-C cleavage".

Baylis-Hillman reaction Reaction of α,β-unsaturated systems with aldehydes to the α-hydroxyalkylated product in the presence of DABCO or similar catalysts.
Additional keyphrases: "addition", "C-alkylation".

aza-Baylis-Hillman reaction Reaction of α,β-unsaturated systems with imines, generated in situ from (generally sulfonyl-protected) amines and aldehydes, to give the α-aminoalkylated derivatives.
Additional keyphrases: "N-alkylation", "C-alkylation"; possibly "multicomponent reaction".

Beckmann rearrangement Rearrangement of oximes to amides or lactams, or fragmentation to nitriles.
Additional keyphrases: "C-C cleavage", "rearrangement".

Biginelli reaction Synthesis of tetrahydropyrimidinones from an aldehyde, a β-keto ester and urea.
Additional keyphrases: "ring closure", "6-membered heterocycle formation", "cyclocondensation"; possibly "multicomponent reaction".

Birch reduction Reduction of aromatic systems with alkali metal in liq. ammonia, and related reactions.
Additional keyphrases: Possibly "reduction (…)".

Bischler-Napieralski synthesis Ring closure of $Ar-(CH_2)_2-NH-CO-R$ to the 3,4-dihydroisoquinoline.
Additional keyphrases: "ring closure", "6-membered heterocycle formation", "annelation", "C-arylation".

Boekelheide reaction Conversion of 2-methylpyridine N-oxide to 2-hydroxymethylpyridine by treatment with acylating agents such as Ac_2O or TFAA..
Additional keyphrases: "hydroxylation".

Buchner ring enlargement Synthesis of cycloheptatrienes via reaction of a benzene ring with a diazo compound to give a cyclopropane-fused system, followed by ring enlargement.
Additional keyphrases: "ring cleavage", "ring closure", "carbene reaction", "insertion", "rearrangement".

Buchwald-Hartwig amination Synthesis of arylamines by Pd-catalyzed cross-coupling reactions of prim. or sec. amines with aryl halides or pseudohalides in the presence of a base.
Additional keyphrases: "amination", "N-arylation", "aromatic/heteroaromatic substitution".

Cadiot-Chodkiewicz coupling Coupling of a terminal alkyne with a haloalkyne in the presence of a Cu(I) salt.
Additional keyphrases: "C-alkylation", "alkynylation".

Chan-Lam coupling Formation of a carbon-heteroatom bond by $Cu(OAc)_2$-mediated oxidative coupling of a boronic acid with an amine, alcohol or thiol.
Additional keyphrases: "aromatic/heteroaromatic substitution", "N-/O-/S-arylation", possibly "amination/etherification/sulfuration".

Claisen condensation Base-catalyzed reaction of two esters (at least one with an α-H) to a β-keto ester (cf. "Dieckmann cyclization"), or reaction of an ester with a ketone to a β-diketone.
Additional keyphrases: "C-acylation", "C-alkylation".

Claisen-Schmidt condensation Base-catalyzed condensation of an aromatic aldehyde with an aliphatic aldehyde/ketone to the α,β-unsaturated product.
Additional keyphrases: "olefination", "aldol condensation".

Claisen rearrangement [3,3]-Sigmatropic rearrangement of allyl vinyl (or aryl) ethers to γ,δ-unsaturated carbonyl compounds (or 2-allylphenols).
Additional keyphrases: "rearrangement", "C-O cleavage", "C-alkylation"; possibly "allylation", or "C-arylation".

Clemmensen reduction Reduction of aldehydes or ketones to the methylene compounds with Zn/HCl.
Additional keyphrases: "reduction (aldehyde)" or "reduction (ketone)".

Cope elimination Thermolysis of an amine oxide to give the hydroxylamine and an olefin.
Additional keyphrases: "elimination", "C-N cleavage".

Corey-Kim oxidation Oxidation of prim. and sec. alcohols to aldehydes/ketones with NCS/Me_2S and a base (NEt_3).
Additional keyphrases: "oxidation (prim. alcohol)" or "oxidation (sec. alcohol)".

Curtius rearrangement Thermal decomposition of acyl azides to isocyanates.
Additional keyphrases: "rearrangement", "C-C cleavage".

Dakin-West reaction Reaction of an α-amino acid with an anhydride in the presence of a base resulting in the replacement of the carboxyl group by an acyl group (via an oxazolone intermediate).
Additional keyphrases: "C-C cleavage" " C-acylation", "C-alkylation".

Darzens condensation Reaction of aldehydes or ketones with α-haloacid esters (or analogues) to give the α,β-epoxy derivatives.
Additional keyphrases: "epoxidation", "ring closure".

Dieckmann cyclization Base-catalyzed reaction of a diester to a cyclic β-keto ester (cf. "Claisen cyclization").
Additional keyphrases: "ring closure".

Diels-Alder reaction [4+2]-Cycloaddition reaction; both the diene and the dienophile may contain heteroatoms.
Additional keyphrases: "ring closure", "cycloaddition", possibly "annelation".

Doebner reaction Synthesis of quinoline derivatives (cinchoninic acids) from an aromatic amine, an aromatic aldehyde, and pyruvic acid.
Additional keyphrases: "ring closure", "annelation", "6-membered heterocycle formation", possibly ”multicomponent reaction”.

Doetz reaction Benzannulation of aromatic Fischer carbene complexes with alkynes to produce 1,4-naphthols.
Additional keyphrases: "ring closure", "annelation", “carbene reaction”.

Eschweiler-Clarke methylation The reductive methylation of primary or secondary amines by reaction with formaldehyde and formic acid.
Additional keyphrases: "N-alkylation", "amination", “reductive amination”, “reductive alkylation”.

Ferrier rearrangement Synthesis of 2,3-unsaturated glycosides from glycals via nucleophilic substitution/allylic shift reactions.
Additional keyphrases: "rearrangement", "elimination", "carbohydrate synthesis", possibly "C-O cleavage".

Fischer indole synthesis Acid-catalyzed formation of indoles from N-arylhydrazones.
Additional keyphrases: "ring closure", "annelation", "5-membered heterocycle formation", "C-arylation".

Friedel-Crafts acylation Lewis acid catalyzed acylation of aromatic compounds.
Additional keyphrases: "C-arylation", "C-acylation".

Friedel-Crafts alkylation Lewis acid catalyzed alkylation of aromatic compounds.
Additional keyphrases: "C-arylation", "C-alkylation".

Friedlaender synthesis Synthesis of quinolines from o-aminobenzaldehydes (or their imine derivatives in the Borsche modification) and ketones.
Additional keyphrases: "ring closure", "6-membered heterocycle formation", "annelation", "cyclocondensation".

Fries rearrangement Rearrangement of phenol esters to o/p-acylphenols.
Additional keyphrases: "ester cleavage", "C-acylation", "C-arylation".

Gabriel-Cromwell reaction Synthesis of aziridines from α-bromoacrylates and amines.
Additional keyphrases: Usually "ring closure", "amination", "Michael addition", "conjugate addition", "nucleophilic substitution".

Gassman indole synthesis One-pot synthesis of the indole scaffold via sequential reaction of anilines and thiomethylcarbonyl compounds with tBuOCl and then with a base such as Et_3N.
Additional keyphrases: Usually "ring closure", "annelation", "5-membered heterocycle formation", "C-arylation", "N-acylation", "amidation", "lactam formation".

Gewald thiophene synthesis Multicomponent condensation of activated nitriles with carbonyl compounds and sulfur in the presence of a base to give thiophenes.
Additional keyphrases: "ring closure", "5-membered heterocycle formation", "cyclocondensation", "sulfuration".

Grignard reaction Reaction of RMgX with an electrophilic compound.
Additional keyphrases: Usually "C-alkylation" or "C-arylation", "addition", possibly "Barbier reaction".

Hantzsch pyridine synthesis Synthesis of dihydropyridines from a β-dicarbonyl compound, an aldehyde, and ammonia, as well as related procedures.
Additional keyphrases: "ring closure", "6-membered heterocycle formation", "cyclocondensation"; possibly "multicomponent reaction".

Hantzsch pyrrole synthesis Synthesis of pyrroles from a β-keto ester, a halomethyl ketone, and ammonia or an amine, as well as related procedures.
Additional keyphrases: "ring closure", "5-membered heterocycle formation", "cyclocondensation"; possibly "multicomponent reaction".

Hantzsch thiazole synthesis Synthesis of thiazoles from an α-haloketone and a thiourea.
Additional keyphrases: "ring closure", "5-membered heterocycle formation", "cyclocondensation".

Heck reaction Pd-catalyzed coupling of alkenes/alkynes with aryl/alkenyl/benzyl halides, triflates etc.
Additional keyphrases: Usually (alkene + aryl halide) "C-arylation", "aromatic/heteroaromatic substitution", "C-alkylation".

Henry reaction Aldol reaction of nitroalkanes with aldehydes or ketones to the nitro alcohol or nitroalkene.
Additional keyphrases: either "aldol condensation",“olefination“ or ”aldol addition”, “addition“, “C-alkylation“.

Hinsberg thiophene synthesis Synthesis of thiophenes from α-diketones and thiodiacetyl compounds.
Additional keyphrases: "5-membered heterocycle formation",“ring closure“, “cyclocondensation“.

Hofmann rearrangement Conversion of a prim. carboxylic amide to the amine with extrusion of CO via an isocyanate intermediate.
Additional keyphrases: "amide cleavage".

Hofmann elimination Elimination of an amino group following exhaustive methylation.
Additional keyphrases: "C-N cleavage", "elimination".

Jones oxidation Oxidation with the Jones reagent ($CrO_3/H_2SO_4/H_2O$).
*Additional keyphrases: "oxidation (*oxidized functional group*)".*

Julia olefination Synthesis of (predominantly) (E)-olefins by reactions of aldehydes with aryl sulfones in the presence of a base.
Additional keyphrases: "olefination", ”C-S cleavage”.

Julia-Lythgoe coupling Reaction of an arylsulfone carbanion with an aldehyde to a β-sulfonylalkoxide; in situ acylation affords β-acyloxysulfones required for the Julia-Lythgoe olefination.
Additional keyphrases: "C-alkylation", "addition", "aldol addition".

Julia-Lythgoe olefination Olefin formation by reductive elimination of β-acyloxysulfones (generated by the Julia-Lythgoe coupling) using Na-Hg or SmI_2.
Additional keyphrases: "olefination", "reduction (sulfone)", "C-O cleavage", "C-S cleavage".

Knoevenagel condensation Condensation of aldehydes or ketones with active methylene compounds (usually of type $Z-CH_2-Z$, Z: CO..., CN, NO2 etc.).
Additional keyphrases: Usually "olefination".

Kroehnke pyridine synthesis Synthesis of pyridines from α-pyridinium methyl ketones, α,β-unsaturated ketones, and NH_4OAc.
<u>Additional keyphrases</u>: "ring closure", "cyclocondensation", "6-membered heterocycle formation".

Kroehnke-King-Ortoleva reaction Conversion of bromoacetophenone-derived pyridinium intermediates to arenecarboxylic acids by treatment with hydroxides.
<u>Additional keyphrases</u>: "C-C cleavage", "oxidation (ketone)".

Kumada coupling Pd- or Ni-catalyzed cross-coupling reaction of Grignard reagents with vinyl or aryl halides or pseudohalides.
<u>Additional keyphrases</u>: "Grignard reaction", possibly "C-arylation", "aromatic/heteroaromatic substitution".

Liebeskind-Srogl coupling Coupling reaction of a boronic acid with a thiol ester (or analogue) to form ketones (or analogues) in the presence of Cu(I) thiophenecarboxylate as mediator.
<u>Additional keyphrases</u>: Possibly "C-arylation", "aromatic/heteroaromatic substitution".

Luche reduction Reduction of carbonyl compounds with the NaBH4/$CeCl_3$ reagent system, e.g. for the selective 1,2-reduction of α,β-unsaturated enones to allylic alcohols or the chemoselective reduction of ketones in the presence of aldehydes.
<u>Additional keyphrases</u>: Usually "reduction (ketone)".

Madelung indole synthesis Synthesis of indoles by intramolecular cyclization of N-acylated ortho-alkylanilines with strong base at high temperature or (in a modified form of the method) by cyclization of anilines carrying an electro-withdrawing group on the ortho-alkyl substituent under milder conditions.
<u>Additional keyphrases</u>: "cyclocondensation", "5-membered heterocycle formation", "ring closure", "annelation".

Mannich reaction Reaction of an active hydrogen compound with an aldehyde and an amine/ammonia to the aminomethylated analog.
<u>Additional keyphrases</u>: Usually "C-alkylation", "amination", "N-alkylation".

Michael addition Conjugate addition of a nucleophile to an α,β-unsaturated system (= conjugate addition).
<u>Additional keyphrases</u>: "conjugate addition", possibly "C-alkylation".

Mitsunobu reaction Reaction of an alcohol with an active hydrogen compound (e.g. phenol, carboxylic acid) in the presence of DEAD/PPh_3, and analogous reactions.
<u>Additional keyphrases</u>: Often "etherification", "O-alkylation".

Negishi coupling Pd-catalyzed cross-coupling reaction of aryl/vinyl halides with organozinc reagents.
<u>Additional keyphrases</u>: Usually "C-arylation", "aromatic/heteroaromatic substitution".

Nenitzescu indole synthesis Preparation of indoles from p-benzoquinones and β-acyl-enamines.
<u>Additional keyphrases</u>: "cyclocondensation", "5-membered heterocycle formation", "ring closure", "annelation".

Nicholas reaction Reaction of the stabilized cation generated from $Co_2(CO)_6$ complexes of propargylic alcohol derivatives with nucleophiles to give propargylated products after demetalation.
<u>Additional keyphrases</u>: "decomplexation", possibly "O-alkylation"/"etherification" or "C-alkylation".

Nozaki-Hiyama reaction Coupling reaction of aldehydes with vinyl or allyl halides in the presence of Cr reagents to afford the corresponding unsaturated secondary alcohols.
<u>Additional keyphrases</u>: "C-alkylation", "addition", "elimination", possibly "allylation".

Paal-Knorr pyrrole synthesis Preparation of pyrroles by heating 1,4-dicarbonyl compounds with ammonia or primary amines.
<u>Additional keyphrases</u>: "cyclocondensation", "5-membered heterocycle formation", "ring closure".

Passerini reaction Three-component reaction of an isocyanide with a carboxylic acid and an aldehyde/ketone to afford an α-acyloxy carboxamide.
<u>Additional keyphrases</u>: Usually "C-acylation", "O-acylation", "amidation", "esterification", "C-alkylation"´, ”multicomponent reaction”.

Pauson-Khand cycloaddition Reaction of an alkyne with an alkene and CO and $Co_2(CO)_8$ to a cyclopentenone.
<u>Additional keyphrases</u>: "ring closure", "carbonylation", "cycloaddition", "C-acylation"; possibly ”multicomponent reaction”.

Petasis reaction A boronic acid Mannich reaction, i. e. a 3-component reaction of an activated carbonyl, an amine, and a boronic acid to the C-substituted aminomethyl derivative.
<u>Additional keyphrases</u>: "N-alkylation", "C-alkylation", "condensation", "amination"; probably “C-arylation“, “aromatic/heteroaromatic substitution“, ”multicomponent reaction”.

Peterson olefination Reaction of a carbonyl compound with an α-silyl carbanion to give an olefin.
Additional keyphrases: "olefination", "addition", "desilylation".

Pictet-Spengler synthesis Reaction of Ar-$(CH_2)_2$-NH_2 with a carbonyl compound to the tetrahydroisoquinoline.
Additional keyphrases: "ring closure", "annelation", "6-membered heterocycle formation", "cyclocondensation","C-arylation".

Piloty-Robinson pyrrole synthesis Formation of pyrroles by acid-catalyzed ring closure of azines derived from enolizable ketones.
Additional keyphrases: "ring closure", "5-membered heterocycle formation", "cyclocondensation", possibly "annelation".

Pfitzner-Moffat oxidation Oxidation of prim. and sec. alcohols to aldehydes and ketones via alkoxysulfonium ylides, generated by treatment with DMSO and DCC in the presence of an acid.
Additional keyphrases: "oxidation (prim. alcohol)" or "oxidation (sec. alcohol)".

Prins reaction Acid-catalyzed reaction of alkenes with formaldehyde (or other aldehydes) to give 1,3-diols, or their acetals, or the allylic alcohols.
Additional keyphrases: "addition", "C-alkylation", ”hydroxylation”.

Pummerer rearrangement Rearrangement of sulfoxides in the presence of acyclic anhydrides to give α-acyloxythioethers, or related reactions of the sulfonium ion intermediate with nucleophiles.
Additional keyphrases: Usually "rearrangement", "O-alkylation", "esterification", "acetalization".

Ramberg-Baecklund reaction Formation of alkenes by SO_2 extrusion upon treatment of α–halo sulfones (possibly generated in situ) with strong bases.
Additional keyphrases: "olefination", "C-S cleavage", "rearrangement".

Reformatsky reaction Reaction of the organozinc derivative of an α-halo ester with a carbonyl compound to give a β-hydroxy ester.
Additional keyphrases: "addition", "C-alkylation".

chromium-Reformatsky reaction Analogous reactions with organochromium compounds.
Additional keyphrases: "addition", "C-alkylation".

Robinson annulation Synthesis of cyclic enones (usually decalin derivatives) from cyclohexanones and methyl vinyl ketones by a Michael addition/intramolecular aldol condensation sequence.
Additional keyphrases: "ring closure", "annelation", "Michael addition", "conjugate addition".

Robinson-Gabriel oxazole synthesis Synthesis of oxazoles by cyclocondensation of α-acylamino ketones.
Additional keyphrases: "ring closure", "cyclocondensation", "5-membered heterocycle formation".

Robinson-Schoepf reaction Reaction of acetonedicarboxylic acid with methylamine and a dialdehyde to a tropinone.
Additional keyphrases: "ring closure", "cyclocondensation", "5-" and "6-membered heterocycle formation", "C-C cleavage", "decarboxylation", "multicomponent reaction".

Sakurai reaction Lewis acid-catalyzed allylic substitution of a silyl group in the reaction of allylsilanes with carbon nucleophiles.
Additional keyphrases: Usually "C-alkylation", "desilylation", "allylation".

Schmidt rearrangement While the term "Schmidt reaction" comprises various reactions of carbonyl compounds with hydrazoic acids, the keyphrase "Schmidt rearrangement" is only used for the acid-promoted one-carbon degradation of benzylic azides to the corresponding anilines (via a methyleneiminium ion intermediate).
Additional keyphrases: "rearrangement", "C-C cleavage", "C-N cleavage", "N-arylation".

Sharpless epoxidation Asymmetric epoxidation with a hydroperoxide (e.g. tBu-OOH), a Ti catalyst (e.g. $Ti(O\text{-}iPr)_4$), and and a chiral tartrate.
Additional keyphrases: "ring closure", "epoxidation", "oxidation (alkene)", "asymmetric synthesis".

Sharpless dihydroxylation Os-catalyzed asymmetric cis-dihydroxylation of an olefin with, e.g., $K_2OsO_2(OH)_4$, K_2CO_3, $K_3Fe(CN)_6$, and $(DHQD)_2$-PHAL or an analog.
Additional keyphrases: "oxidation (alkene)", "hydroxylation", "asymmetric synthesis".

Sonogashira reaction Reaction of aryl halides with terminal alkynes to arylacetylenes in the presence of Cu and Pd catalysts [usually Cu(I) and Pd(0) reagents].
Additional keyphrases: "Heck reaction", "C-alkylation", "C-arylation", "alkynylation", "aromatic/heteroaromatic substitution".

Staudinger cycloaddition Synthesis of β-lactams by [2+2] cycloaddition reactions of imines with ketenes (usually generated from acetyl chlorides).
Additional keyphrases: "ring closure", "4-membered heterocycle formation", "cycloaddition", "lactam formation", "amidation", "N-acylation".

Staudinger reaction Reaction of a tert. phosphine with an azide R'-N_3 to give products of type R_3P=N-R'; used, e.g., for the reduction of azides to amines.
Additional keyphrases: possibly "phosphination" or "reduction (azide)".

Stetter reaction Addition of (often aromatic) aldehydes to Michael acceptors in the presence of a base and a cyanide or thiazolium salt catalyst to afford 1,4-dicarbonyl compounds.
Additional keyphrases: "Michael addition", "conjugate addition", "C-alkylation", usually also "C-arylation".

Stille coupling Pd-catalyzed coupling of an organostannane with a halide, or acetate, or tosylate etc.
Additional keyphrases: Usually "C-arylation", "aromatic/heteroaromatic substitution".

Strecker synthesis Synthesis of α-amino nitriles (precursors of α-amino acids) by reaction of aldehydes with cyanides and amines (or ammonia equivalents).
Additional keyphrases: "amination", "N-alkylation", "C-alkylation", "cyanation", "addition", "condensation", "multicomponent reaction".

Suzuki coupling Pd-catalyzed coupling of an organoboron compound with a halide, or tosylate etc.
Additional keyphrases: Usually "C-arylation", "aromatic/heteroaromatic substitution".

Swern oxidation Oxidation of prim./sec. alcohols to aldehydes/ketones with oxalyl chloride (or, in a modified procedure, $SO_3 \cdot Py$), DMSO, and an amine.
Additional keyphrases: "oxidation (prim. alcohol)" or "oxidation (sec. alcohol)".

Tamao-Fleming oxidation Oxidation of a C-Si bond with formation of the alcohol.
Additional keyphrases: "oxidation", ”desilylation”.

Tebbe olefination Transformation of a carbonyl compound to the alkene with a terminal methylene group using the Tebbe reagent [$TiCl(Cp)_2$-CH_2-$AlMe_2$].
Additional keyphrases: "olefination".

Tsuge reaction Preparation of isoxazole-fused tetrahydroindolizines by cycloaddition of olefinic dipolarophiles to pyridinium methylides, followed by reaction with nitrile oxides.
Additional keyphrases: "1,3-dipolar cycloaddition", "ring closure", "annelation", "5-membered heterocycle formation".

Ugi condensation A four-component condensation (4CC) reaction of an amine, an aldehyde, a carboxylic acid, and an isocyanide.
Additional keyphrases: Usually "N-acylation", "C-alkylation", "amidation", "N-alkylation", "C-acylation", "multicomponent reaction"; possibly "4/5/6/7-membered heterocycle formation".

Ullmann reaction Copper-mediated formation of aryl ethers from aryl halides and aryl oxides (or alkoxides), and analogous reactions or amines with aryl halides.
Additional keyphrases: "aromatic/heteroaromatic substitution", and usually either "etherification"/"O-arylation" or "amination"/"N-arylation".

Vilsmeier-Haack reaction Formylation with disubstituted formamides and POCl3, usually in reactions with activated aromatic substrates.
Additional keyphrases: "formylation", "C-acylation", "C-arylation".

von Braun reaction Reaction of tert. amines with BrCN to give cyanamides (and an alkyl bromide).
Additional keyphrases: "C-N cleavage", "cyanation".

von Pechmann reaction Synthesis of coumarins from phenols and β-keto esters.
Additional keyphrases: "ring closure", "cyclocondensation", "annelation", "6-membered heterocycle formation", "C-arylation", "ester cleavage", "esterification", "transesterification", "O-acylation", "lactone formation".

von Richter cinnoline synthesis Formation of cinnoline derivatives by diazotation of o-aminoaryl-acetylenes, followed by hydration/cyclization.
Additional keyphrases: "ring closure", "6-membered heterocycle formation", "annelation ".

Wacker oxidation Oxidation of terminal alkenes to methyl ketones with $PdCl_2$, oxygen, and a co-oxidant (usually $CuCl_2$).
Additional keyphrases: "oxidation (alkene)".

Westphal reaction Preparation of cycloimmonium salts by base-catalyzed reactions of azinium or azolium salts with 1,2-diketones.
Additional keyphrases: "ring closure", "6-membered heterocycle formation", "annelation", "cyclocondensation".

Williamson ether synthesis Only for Williamson-type etherifications under classical conditions, i.e. for reactions of alkyl halides or pseudohalides with sodium alkoxides/aryloxides generated from the alcohol and Na, NaH, or NaOH.
Additional keyphrases: "etherification", "nucleophilic substitution", "O-alkylation".

Wittig olefin synthesis Reaction of a carbonyl compound with a phosphonium ylide (e.g. $R_2C=PPh_3$) to the olefin.
Additional keyphrases: "olefination".

Wittig-Horner olefination (Also known as "Horner-Emmons-Wadsworth reaction") Reaction of a carbonyl compound with the anion of a phosphonate (e.g. $R-PO(O-R')_2$).
Additional keyphrases: "olefination".

aza-Wittig reaction Reaction of an iminophosphorane with a carbonyl compound.
Additional keyphrases: Usually "imine formation".

Zincke reaction Synthesis of pyridinium salts from a primary amine, replacing the nitrogen atom of an N-(2,4-dinitrophenyl)-substituted pyridinium salt.
Additional keyphrases: "ring cleavage", "ring closure", "6-membered heterocycle formation".