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Review

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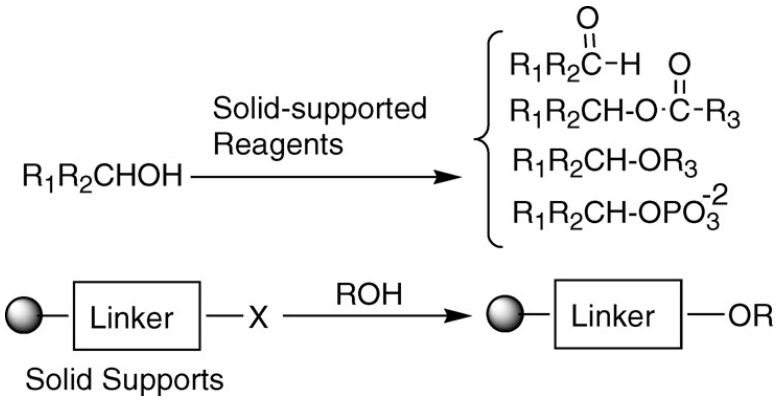

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Reviews

Reactions of Solid-Supported Reagents and Solid Supports with Alcohols and Phenols through Their Hydroxyl Functional Group

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Alcohols and phenols are involved in several solid-phase organic reactions. The success of solid phase reactions with hydroxyl functional group in alcohols and phenols has generated a tremendous interest in expanding the field of solid-phase organic synthesis. This Review summarizes reactions of alcohol and phenols through their hydroxyl functional group with solid-supported reagents and solid supports. The aim of this Review is to give the reader a well-structured and extensive collection of these reactions from literature published from 1964 to June 2002. The reaction conditions, resins and solvents used, and yields are given in table format. References need to be consulted for more detailed information about a specific reaction. These tables document the rapidly expanding number of traditional solution-phase reactions that have been successfully adapted to solid-phase synthesis over the past 38 years. Our goal for the review of the overviewed reactions is to assist the solid-phase organic chemist in selecting the ideal resin, experimental conditions, and reactions to design and to implement successful synthetic strategies involving alcohols and phenols. The reaction classification will facilitate the data access and presentation. Several reactions may overlap in different categories. This Review does not include solid-phase reaction of resins having hydroxyl functional group with compounds other than alcohols or phenols.

Two categories of reaction are discussed here: (I) reactions of solid-supported reagents with alcohols and phenols and (II) reactions of solid supports with alcohols and phenols (anchoring of alcohols and phenols to solid supports through their hydroxyl functional group). Reactions are specifically focused on the modification or anchoring of hydroxyl functional groups in these compounds. The subject has been organized according to the type of solid supports and reactions, respectively.

I. Reactions of Solid-Supported Reagents with Alcohols and Phenols

These reactions are classified according to the following list: (I.1) solid-supported oxidizing reagents (solid-supported oxidants); (I.2) solid-supported acylating reagents; (I.3) solid-supported reagents for the synthesis of ethers and phase-transfer catalytic reagents; (I.4) solid-supported coupling reagents; and (I.5) solid-supported phosphines.

Solid-supported reagents have been used for decades and have been proven to be useful for a wide variety of chemical modifications. These reagents offer the advantages of both solution-phase chemistry and solid-phase organic synthesis.

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Monitoring the progress of the reactions is easy by applying thin-layer chromatography, NMR, or LC/MS techniques. The use of an excess of reagent is also allowed without the need for additional purification steps. Solid-supported reagents provide a very efficient method to avoid the presence of impurities, coupling reagents, or tertiary amines in the solution, since several of these reagents are attached to solid supports. For the purpose of this Review, we will focus on solid-supported reagents that are involved in modification of hydroxyl functional groups in alcohols and phenols. The on-resin modification of alcohols and phenols is a useful synthetic strategy, since it leads to a wide range of compounds of interest for combinatorial chemistry. Many of these solid-supported reagents offer some advantages over traditional solution-phase chemistry in modification of alcohols and phenols.

II. Reactions of Solid Supports with Alcohols and Phenols (Anchoring of Alcohols and Phenols to Solid Supports through Their Hydroxyl Functional Group)

The attachment of alcohols and phenols to polymer supports has been intensively investigated, in particular with regard to the solid-phase synthesis of ethers and esters. Solid support reactions with alcohols and phenols include (1) attachment as ethers (O-alkylation or O-arylation), (2) attachment as esters (esterification), and (3) miscellaneous reactions (attachment through other functional groups or linkers).

II.1. Attachment as Ethers (O-Alkylation and O-Arylation). Alcohols or phenols (ROH, ArOH) can be immobilized on resins (R′X, X = leaving group, R′ = resin or resin-attached linker; linker functionality is part of the base polymer or has been attached to a base polymer) through a variety of synthetic strategies.

The tabulated reactions illustrate a wide variety of resins and linkers developed for anchoring of alcohols and phenols as ethers according to the following list:

(II.1.1) Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds): (II.1.1.1) reactions on Merrifield resin; (II.1.1.2) reactions on trityl resins; (II.1.1.3) reactions on Wang resin; (II.1.1.4) reactions on Rink resin; (II.1.1.5) reactions on other resins; (II.1.1.6) the synthesis of polymer-supported chiral auxiliary compounds; (II.1.1.7) monoprotection of diols (monoether attachment); (II.1.1.8) diprotection of diols (diether attachment); (II.1.1.9) synthesis of solid-supported reagents; (II.1.1.10) synthesis of solid supports with acetal linkers; (II.1.1.11) reactions with polymer-bound DHP (linker based on the dihydropyranyl group); (II.1.1.12) attachment through a boronic acid linker (reactions with polymer-bound boronic acid); (II.1.1.13) silyl linker for the attachment of alcohols; (II.1.1.14) thiocarbonate-functionalized resins for the attachment of phenols; and (II.1.1.15) attachment through miscellaneous linkers;

(II.1.2) Mitsunobu reaction: (II.1.2.1) Mitsunobu reaction to immobilize hydroxyl functional group as phenol ethers; (II.1.2.2) Mitsunobu reaction on amino functional groups (attachment as amines); and (II.1.2.3) Mitsunobu reaction for immobilization of hydroxyl functional group of other compounds;

(II.1.3) Carbohydrate reactions: (II.1.3.1) immobilization and protection of carbohydrates; (II.1.3.2) the synthesis of disaccharides and polysaccharides (glycosylation reactions); and (II.1.3.3) enzymatic glycosylation; and

(II.1.4) Oligonucleotide synthesis.

II.1.1. Attachment to Resins (Immobilization of Hydroxyl Functional Group and Synthesis of Miscellaneous Compounds). Hydroxyl functions have been anchored to several solid supports through many linkers. The linker strategies most commonly used are attachment as ethers, silyl ethers, and acetals. Mitsunobu and glycosylation reactions, nucleoside immobilization, and nucleotide synthesis on solid supports are commonly used for attachment of alcohols as ethers on solid supports.

The attachment of alcohols as ethers is more synthetically challenged than esterification and might require the use of harsher reagents and conditions, such as strong bases (Williamson ether synthesis in the case of Merrifield and trityl resins) or acids (in the case of Wang resin), high temperatures, and long reaction times, to achieve complete conversions. Strong bases, such as alkali metal hydrides, are required to deprotonate the hydroxyl group of aliphatic alcohols. THF, DMF, or diglyme are commonly suitable solvents used for the conversion reactions of Merrifield and related resins into alkyl benzyl ethers.

Many resins have been used in attachment reactions. Almost all reported solid-phase syntheses of ethers are O-alkylation or O-arylation of alcohols, which differ only in the type of alkylating agent used and in the precise reaction conditions. For example, cross-linked chloromethyl polystyrene (Merrifield resin) has frequently been used to O-alkylate aliphatic alcoholates, mainly for attaching linkers, ligands, or various synthetic auxiliaries to the support.[93,94] Phenols can be etherified by nucleophilic substitution of resin-bound benzyl halides[95,96] or sulfonyl chloride.[97−99]

Trityl-substituted cross-linked polystyrene has been used to anchor alcohols and phenols in a variety of reactions. Attachment of alcohols and phenols to trityl linkers is usually carried out by treating trityl chloride resin with the alcohol in the presence of a base. Modified trityl resins, such as 2-chlorotrityl resin have been used for linking alcohols to the solid phase to facilitate the attachment and ultimate cleavage of alcohols.[100−102]

Wang resin can also be etherified with aliphatic alcohols under acidic reaction conditions by conversion of polystyrene-bound alcohol into a trichloroacetamidate[103] or thiocarbonate.[104] Support-bound aryldiazomethanes also react with alcohols in the presence of Lewis acids to yield benzyl ethers.[105] Resin-bound benzylic thiocarbonates react with aliphatic alcohols in the presence of silver(I) salts to yield resin-bound benzyl ethers.[104,106]

Other support-bound electrophiles that react with aliphatic alcohols to yield ethers are epoxides[107,108] and rhodium carbenoids generated from diazocarbonyl compounds and rhodium(II) acetate.[109] The latter strategies enable the

preparation of dialkyl ethers under essentially neutral reaction conditions and, thus, the etherification of base- or acid-labile alcohols.

Many other linkers are used for attachment of alcohols to solid supports. Acetals are a further functional group suitable for linking alcohols to insoluble supports. Resin-bound diols and amino alcohol, which reversibly form cyclic acetals with aldehydes and ketones, have been used as linkers for attachment of carbonyl compounds as acetals. A frequently used linker of this class is resin-bound dihydropyran, which forms mixed acetals (tetrahydropyranyl ethers) with aliphatic or aromatic primary alcohols, secondary alcohols, and hydroxylamines upon acid catalysis (e.g., 95% TFA−water or PPTS in DCE). Acetals formed are stable to strong nucleophiles and basic conditions.[110,111,112]

Alcohols can be attached to solid supports by a boronic acid linker. This is a useful strategy for the protection of diols.[113,114] Alcohols can be also linked to insoluble supports as silyl ethers. Polymer-bound silyl ethers can be prepared by the treatment of support-bound silyl chlorides or silyl trifluoroacetates with alcohols in the presence of a base (imidazole, DIEA, or DMAP in DCM).[115−119] Alternatively, silyl ethers can be prepared by heating resin-bound silanes R_3SiH[115] with aromatic or aliphatic alcohols in the presence of catalytic amounts of a rhodium complex [$(PPh_3)_3RhCl$, rhodium(II) perfluorobutyrate].[119]

II.1.2. Mitsunobu Reaction. Phenols can be etherified with resin-bound benzyl alcohols by the Mitsunobu reaction. A review of the tables shows the important role of the Mitsunobu reaction. Mitsunobu reactions can be performed in the presence of coupling reagents, such as DEAD, DIAD, ADDP, or TMAD and either PPh_3 or PBu_3. Sterically hindered secondary alcohols also work well in these conditions. The mild reaction condition of the Mitsunobu reaction allows alcohols containing base-sensitive groups to be incorporated. Furthermore, phenol groups have also been attached to hydroxymethyl-*p*-alkoxybenzyl resins (HMPP resins) by a Mitsunobu reaction.[275−279]

II.1.3. Carbohydrate Reactions. Carbohydrates are frequently attached to solid-phase support as ethers. Further glycosylation technologies for oligomer growth on solid phase that use different functionalities are available, and among them, other choices exist according to the needs of the specific synthesis: for example, the glycal,[329] the sulfoxide,[330] the trichloroacetamidate,[331] and the enzyme-based technology[332] have all been successfully employed. Our focus is on the solid-phase reactions that apply free hydroxyl functional groups of carbohydrates in solution, such as glycal and enzyme glycosylation.

II.1.4. Oligonucleotide Synthesis. Oligonucleotides (ONs) are the other major class of important biopolymers that are readily adaptable to automated synthesis on solid phase using phosphotriester, phosphonate, and phosphoramidite approaches. It is not the purpose of this Review to discuss solid-phase synthesis of oligonucleotides. Our focus is only on the reaction of solid supports with nucleosides. Derivatized support carrying a nucleoside with a free 5′-hydroxyl group is treated with a phosphorylating reagent to yield a nucleoside phosphomonochloridite attached to a support. Further treatment of the immobilized nucleoside phosphomonochloridite at room temperature with a second protected nucleoside followed by oxidation with iodine yield a fully protected dimer.[381−383]

II.2. Attachment as Esters. Parts II.2.1, II.2.2, and II.2.3 of Table 2 illustrate a wide variety of resins and linkers developed for anchoring of alcohols and phenols as esters according to the following list: (II.2.1) immobilization of hydroxyl functional group and synthesis of miscellaneous compounds; (II.2.2) monoprotection of symmetrical diols; and (II.2.3) carbonate synthesis.

Both aliphatic alcohols and phenols have been immobilized as esters of support-bound carboxylic acids. The esterification can be achieved by treatment of resin-bound acids with alcohols and a carbodiimide[398,399] or by acylation of alcohols with support-bound acyl halides.[400] Valuable alcohols can be esterified quantitatively with excess support-bound acylating agent.[147] The excess of acylating agent can be capped by treatment of the support with methanol.

Alcohols can be attached to support-bound alcohol linkers as carbonates.[401] Carbonates are generally more resistant toward nucleophilic cleavage than esters. The reaction of *N*,*N*′-disuccinimidyl carbonate (DSC) with 4-hydroxymethyl-PS-resin and 4-hydroxymethyl-Nbb-PS-resin affords the corresponding active carbonates, which can react smoothly with compounds containing hydroxyl functions (e.g., Boc-*O*-benzyl threoninol [Boc-Thr(Bzl)-OH], Boc-Ser-OAllyl, and BOC-Tyr-OAllyl).[401]

II.3. Attachment by Other Strategies (Miscellaneous Reactions). Additional tables have listed many other strategies for the attachment of alcohols and phenols to solid supports.

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Abbreviations

9-BBN	9-borabicyclo[3.3.1]nonane
Ac	acetyl
Ac_2O	acetic anhydride
ACC-SiO_2	ammonium chlorochromate
ACN	acetonitrile
ADDP	azodicarboxylic acid dipiperidide
aq	aqueous
Argogel	PEG-grafted cross-linked polystyrene
BAL	backbone amide linker
BHA	benzhydrylamine resin
Bn	benzyl
BOBA	*para*-benzyloxybenzylamine
Boc	*tert*-butyloxycarbonyl
BTSC	bis(trimethylsilyl)chromate
BSA	*N*,*O*-bis(trimethylsilyl)acetamide
BSP	sulfobromophthalein sodium
Bu	butyl
Bz	benzoyl
CDI	*N*,*N*-carbonyl diimidazole
CPG	controlled pore glass
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-diazobicyclo[5.4.0]undec-5-ene
DCC	*N*,*N*′-dicyclohexylcarbodiimide
DCE	dichloroethane
DCM	dichloromethane

DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DEAD	diethyl azodicarboxylate
DHP	2,3-dihydro-4*H*-pyran
DIAD	diisopropyl azodicarboxylate
DIC	diisopropylcarbodiimide
DIPEA	diisopropylethylamine
DMA	*N*,*N*-dimethylacetamide
DMAC	*N*,*N*-dimethylacetamide
DMAD	dimethyl acetylenedicarboxylate
DMAP	4-(dimethylamino)pyridine
DMDO	dimethyldioxirane
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
DMT	4,4′-dimethoxytrityl
DMTSB	dimethylthiosulfonium tetrafluoroborate
DMTST	dimethylthiosulfonium triflate
DSC	*N*,*N*′-disuccinimidyl carbonate
DTBP	2,6-di-*tert*-butyl pyridine
DTT	dithiothreitol
DVB	divinylbenzene (mixture of regioisomers)
EDC	1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride
EGDMA	ethyleneglycol dimethacrylate
Et	ethyl
EtOAc	ethyl acetate
Fmoc	9-fluorene methyloxycarbonyl
Fuc	L-fucose
GalNAc	*N*-acetyl-D-galactosamine
GalT	galactosyltransferase
GlcNAc	*N*-acetyl-D-glucosamine
glycan	synonym of polysaccharide
HMBA	4-hydroxymethylbenzoic acid linker
HMPB	4-hydroxymethyl-3-methoxyphenoxybutyric acid
HOBt	hydroxybenzotriazole
IBX	1-hydroxy-1,2-benziodoxol-3(1H)-one-1-oxide
MALDRE	2-methoxy-4-benzyloxypolystyrene aldehyde resin
MBHA	4-methylbenzhydramine
*m*CPBA	*meta*-chloroperoxybenzoic acid
Me	methyl
MeOPEG	poly(ethylene glycol) monomethyl ether
Merrifield resin	partially chloromethylated, cross-linked polystyrene
Mmt	monomethoxytrityl
MPEG	polymer poly(ethylene glycol) monomethyl ether
MS	molecular sieve
MSNT	1-(mesitylene-2-sulfonyl)-3-nitro-1,2,4-triazole
Multipin	polymer crowns grafted with various supports
NaHMDS	sodium hexamethyldisilazane
NBS	*N*-bromosuccinimide
NCPS	non-cross-linked polystyrene
NeuAc	*N*-acetyl-neuraminic acid
NIS	*N*-iodosuccinimide
NMI	*N*-methylimidazole
NMM	*N*-methylmorpholine
NMO	4-methylmorpholine *N*-oxide
NMP	*N*-methylpyrrolidinone
NPG	*n*-pentenyl glycosides
Ns	4-nitrobenzenesulfonyl
PAL	peptide amide linker; 5-(4-aminomethyl-3,5-dimethoxyphenoxy)valeric acid linker
PAM	4-(hydroxymethyl)phenylacetic acid linker
PAN	poly(arylamide)-poly(*N*-acryloxysuccinimide)
PBu_3	tributylphosphine
PDC	pyridinium dichromate
PDDM	polymeric diphenyldiazomethane
PE	polyethylene
PEG	poly(ethylene glycol)
(PEG)	PEG with linker or spacer
PEGA	poly(ethylene glycol)−polyacrylamide copolymer
PEG−PS	poly(ethylene glycol)−polystyrene
Ph	phenyl
Phth	phthaloyl
PIN	polyethylene pin
Piv	pivaloyl
PMM	poly(methyl metacrylate)
$PolyTPPI_2$	polymer-bound triphenylphosphine diiodide
PPh_3	triphenylphosphine
PPTS	pyridinium tosylate
PS	cross-linked polystyrene
PS-DES	polystyryl-diethylsilyl
PS-DIEA	*N*,*N*-(diisopropyl)aminomethylpolystyrene resins
PS−DVB	polystyrene−divinylbenzene copolymer
PS−PEG	polystyrene−poly(ethylene glycol) graft polymer
P-TBD	polystyrene-supported 1,5,7-triazabicylco[4.4.0]-dec-5-ene
PTSA	*para*-toluenesulfonic acid
PVPDC	poly(vinylpyridinium dichromate)
$(Pyz\text{-}CrO_5)_n$	pyrazine-based polymeric complex of oxidoperoxochromimum (VI)
R	alkyl
RAM	Rink amide linker, (2,4-dimethoxyphenyl)(4-alkoxyphenyl)methylamine
r.t.	room temperature
Sasrin	cross-linked polystyrene with 4-alkoxy-2-methoxybenzyl alcohol linker (super acid sensitive resin)
Sephadex	dextran; a branched glycan consisting of 1,6-α-linked glucopyranose
Sepharose	agarose; an unbranched glycan consisting of D-galactose and 3,6-anhydro-L-galactose
SG	silica gel
S-Le	sialyl-Lewis
TBAF	tetrabutylammonium fluoride
TBAI	tetrabutylammonium iodide
TBDPS	*tert*-butyldiphenylsilyl
TBDMSCl	*tert*-butyldimethylsilyl chloride
TBS	*tert*-butyldimethylsilyl
TBTU	3-[(dimethyliminium)dimethylamino)methyl]-1,2,3-benzotriazol-1-ium-1-olate tetrafluoroborate
t-Bu	*tert*-butyl
TCA	trichloroacetic acid
TEA	triethylamine
TEMPO	4-alkoxy-2,2,6,6-tetramethylpiperidine-1-oxide
Tentagel	PEG-grafted cross-linked polystyrene
Tentagel-PHB	PEG-grafted cross-linked polystyrene functionalized with a Wang linker
TES	triethylsilyl
Tf	triflate (trifluoromethanesulfonyl)
TFA	trifluoroacetic acid
TFE (TfOH)	trifluoroethanol
TFAA	trifluoroacetic anhydride
TG	PEG-grafted polystyrene (e.g., Tentagel)
(TG)	TG with linker or spacer
THF	tetrahydrofurane
THP	2-tetrahydropyranyl
TIS, TIPS	triisopropylsilyl
TMAD	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
TMS	trimethylsilyl
TMSOTf	trimethylsilyl trifluoromethanesulfonate
TPAP	tetrapropylammonium perruthenate, $[Pr_4N][RuO_4]$
TPP	triphenyl phosphine
Tr	trityl, triphenylmethyl
UDP−Gal	uridine 5′-diphosphogalactose
Wang resin	cross-linked polystyrene with 4-benzyloxybenzyl alcohol linker
Z	cbz, benzyloxycarbonyl

Table 1. Solid-Support Reagents

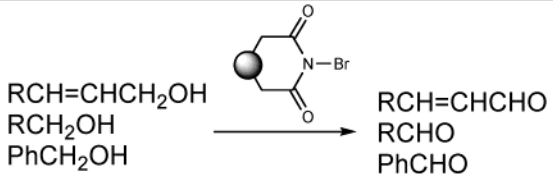
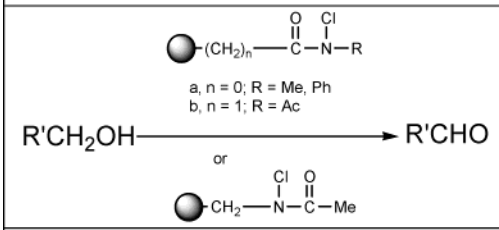
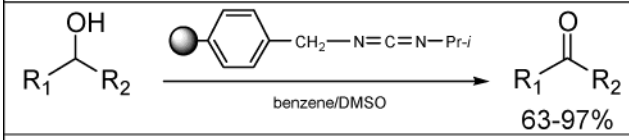
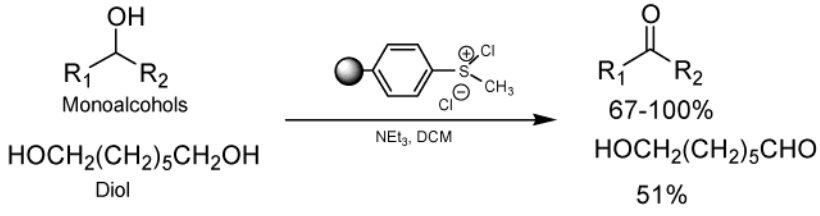
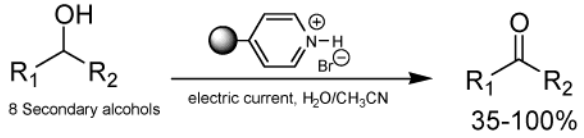
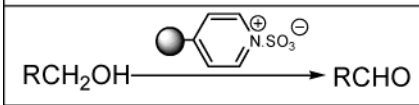
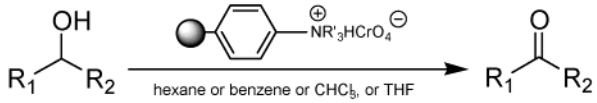
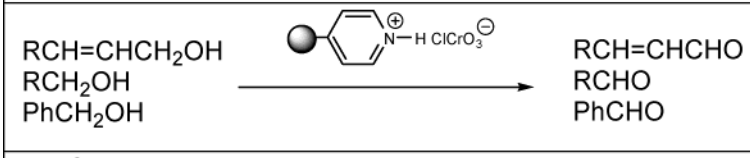
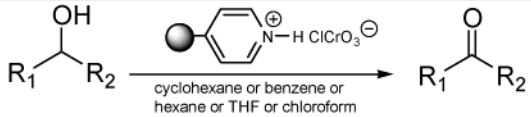
I. Solid-supported Reagents	
I.1. Solid-supported oxidizing reagents (solid-supported oxidants)	**Comments and References**
	**Polymeric supported *N*-bromoimides** - Oxidation of primary, allylic, and benzylic alcohols to aldehydes[1]
	***N*-Chloroamide polystyrene resins** - Prepared from treating Nylon 66 with *t*-butyl hypochlorite and chlorine oxide in CCl_4 - Oxidation of alcohols[2]
	**Polystyrene isopropylcarbodiimide derived from aminomethyl polystyrene** - Moffatt oxidation of primary, secondary and benzylic alcohols - Six examples, yields 63-97%[3]
	**Polymeric thioanisole dichloride (polystyrene) prepared from poly(*p*-bromostyrene)-poly(*p*-methylmercaptostyrene)** - Oxidation of primary and secondary alcohols - Five examples - Monooxidation of diols (heptanediol, pentanediol) - Oxidation of sensitive compounds like prostaglandin intermediate[4]
	**Poly-4-vinylpyridinium hydrobromide derived from polystyrene** - Catalyzes the electrochemical oxidation of secondary alcohols to ketones - Oxidation of secondary alcohols in preference to the primary alcohols[5,6]
	**Sulfur trioxide pyridine complex polymer bound** - Suggested to be applied in DMSO oxidation of alcohols[7]
	**Polymer-supported chromate** - Prepared from treating commercial Amberlyst A-26 (Cl^-) resin with CrO_3/H_2O - Oxidation of primary, secondary, allylic, and benzylic alcohols to aldehydes or ketones - Fifteen examples, yields 73-98%[8,9]
	**Polyvinylpyridinium chlorochromate** prepared from treating crosslinked poly(vinylpyridine) with CrO_3, aq. HCl - Oxidation of primary, secondary, allylic, and benzylic alcohols to aldehydes and ketones[10,11]
	**Polyvinylpyridinium chlorochromate** - Prepared from treating crosslinked poly(4-vinylpyridine) with CrO_3, aq. HCl - Polymer-supported acid chromate prepared from treating chloride form of acroporous resin with aqueous chromium trioxide - Oxidizing the alcohol groups directly

Table 1 (Continued)

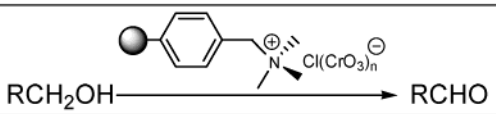
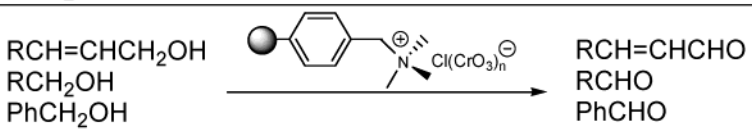
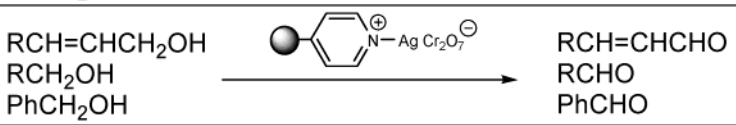
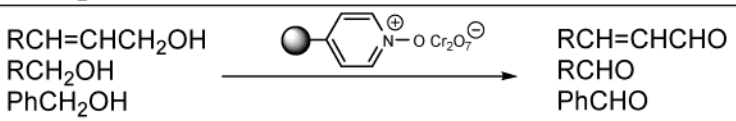
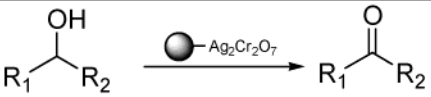
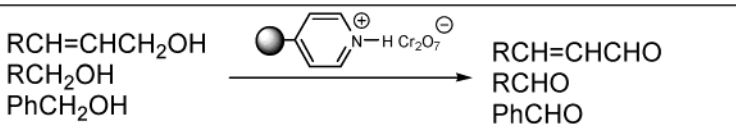
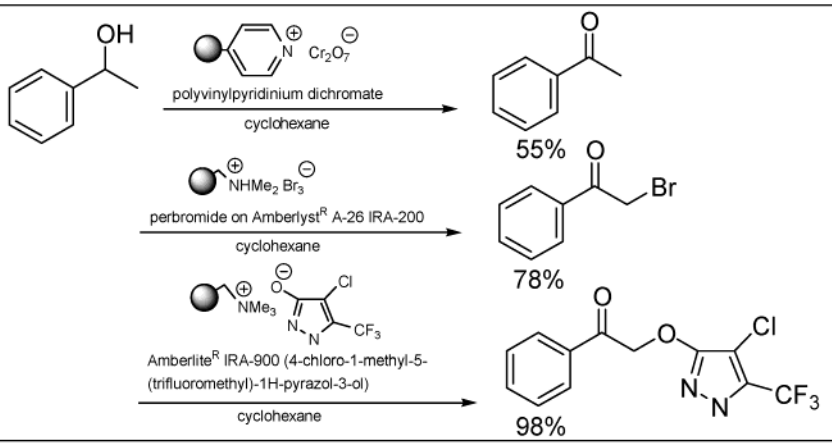
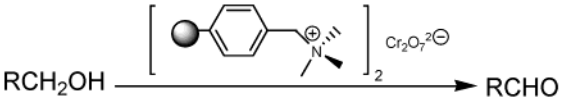
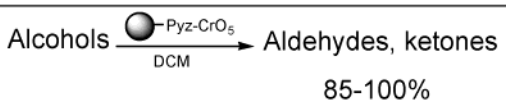
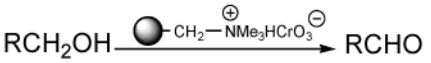
	attached to the ring structure - Nine examples, 73-100%[9,10]
	**Polymer-supported chlorochromate** - Prepared from Amberlyst^R A-26 (Cl^-) - Oxidation of primary and secondary alcohols[11]
	**Polymer-supported chlorochromate** - Prepared from Amberlyst^R A-26 (Cl^-) - Oxidation of primary and secondary alcohols[11]
	**Polyvinylpyridine-supported silver dichromate** - Oxidation of primary, allylic, and benzylic alcohols to aldehydes[12]
	**Polyvinylpyridine *N*-oxide-supported dichromate** - Oxidation of primary, allylic, and benzylic alcohols to aldehydes[13]
	**Polyethyleneimine-supported silver dichromate** - A stable, mild, and efficient oxidizing agent for the conversion of alcohols to carbonyl compounds[14]
	**Polyvinylpyridinium dichromate** - Prepared from treating crosslinked poly(vinylpyridine) with CrO_3/H_2O - Oxidation of primary, secondary, benzylic and allylic alcohols to aldehydes and ketones - Recyclable oxidant - Yields usually more than 90%[15-17]
	**Polyvinylpyridinium dichromate** - One-pot, multistep synthesis of a pyrazole derivative employing three different polymeric reagents simultaneously - Oxidation, bromination and alkylation - 48% overall yield for one-pot synthesis, compared with 42% overall yield when each of the three steps was performed separately[18,19]
	**Polymer-supported quaternary ammonium perchromate** - Converts allylic alcohols to α,β-unsaturated aldehydes but does not oxidize saturated alcohols - Yields 75-89%[20]
	**Pyrazine-based polymeric complex of oxidoperoxochromium (VI) compound $(Pyz\text{-}CrO_5)_n$** - Benzyl alcohols, α,β-unsaturated alcohols, primary and secondary alcohols, α-hydroxyketones, hydroquinone, catechol, 1,4-dihydroxynaphthalene - Thirty examples of alcohols[19]
	**Polymeric chromate derived from polystyrene** - Oxidation of alcohols and alkyl halides to carbonyl compounds

Table 1 (Continued)

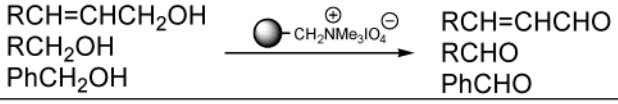
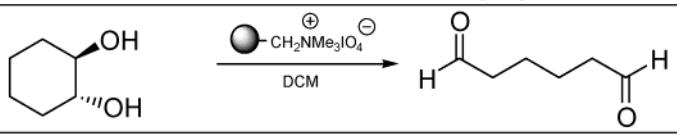
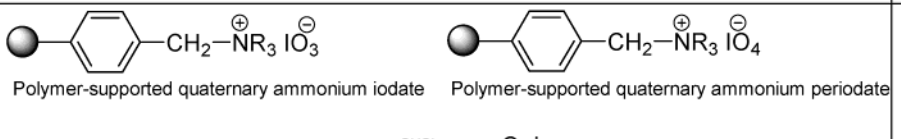
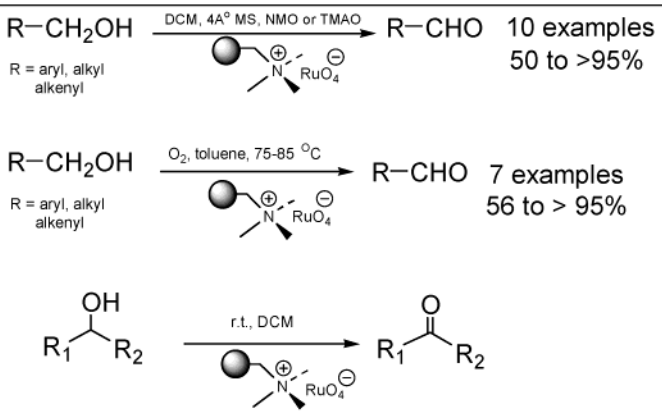
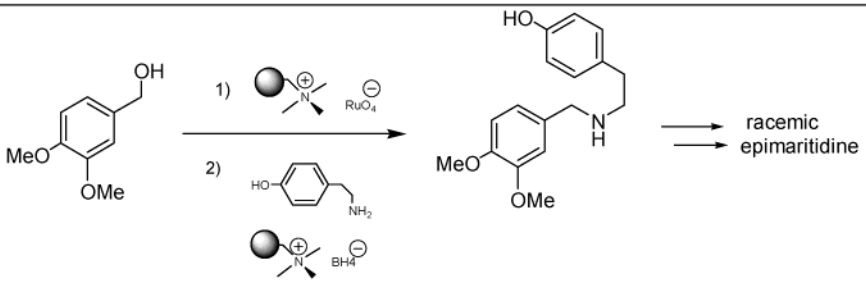
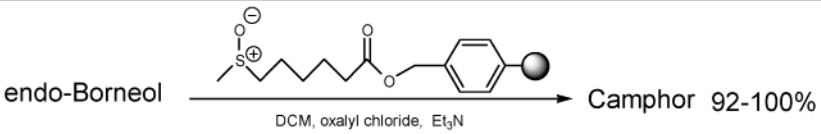
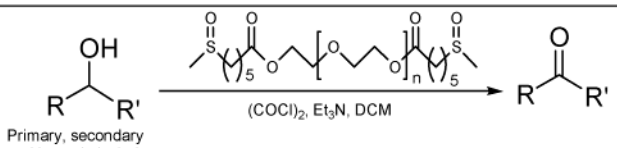
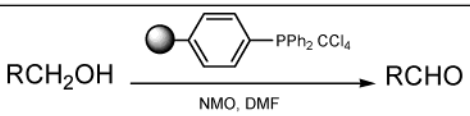
	- Oxidizing the alcohol groups directly attached to a ring structure[21,22]
	**(Polystyrylmethyl)trimethylammonium metaperiodate** - Polymer-supported metaperiodate - Oxidation of alcohols[2]
	**(Polystyrylmethyl)trimethylammonium metaperiodate** - Oxidative cleavage of 1,2-diols[2]
	**Polymer-supported quaternary ammonium iodate or periodate** - Prepared from treating Amberlyst^R A-26 OH^- with aq. HIO_4 or from treating Amberlite^R IRA 904 Cl^- with $NaIO_4$ solution - Oxidation of quinols, catechols and glycols (eleven examples) - Cleavage of 1,2-diols to the corresponding carbonyl compounds[23,24]
	**(Polystyrylmethyl)trimethylammonium perruthenate or polymer (Amberlyst^R A-26)-supported perruthenate** - Prepared from treating Amberlyst^R IR27 with aq. $KRuO_4$ - Polymer supported perruthenate (PSP) - Oxidation of primary and secondary alcohols - Remarkable selectivity for primary versus secondary alcohols - The oxidation of activated primary alcohols, such as benzylic or α,β-unsaturated alcohols using the reagent stoichiometrically or catalytically in conjunction with a cooxidant such as air, oxygen, or amine *N*-oxides (*N*-methylmorpholine oxide or trimethylamine oxide)[25-29]
	**(Polystyrylmethyl)trimethylammonium perruthenate or polymer (Amberlyst^R A-26)-supported perruthenate** - Synthesis of the alkaloids (+/-)-epimaritidine and (+/-)-epimaritidine using an orchestrated multi-step sequence of polymer supported reagents[30]
	**6-(Methylsulfinyl)hexanoylmethyl polystyrene (Merrifield resin derived polymeric supported sulfoxide oxidizing agent)** - Recyclable solid-phase sulfoxide reagent for Swern oxidation of primary alcohols to aldehydes - Modified Swern oxidation[31]
	**PEG2000 bound sulfoxide** - Derived from poly(ethylene glycol) (PEG) - Soluble polymer-supported sulfoxide - The reagent is removed from the reaction mixture by precipitation with cold diethyl ether and filtration. - Modified Swern oxidation - Seven examples, yields 95-99%[32]
	**Derived from Wang resin and Rink acid** - TPAP-catalytic oxidation of primary, benzylic (Wang resin), and secondary (Rink acid) alcohols[33]

Table 1 (Continued)

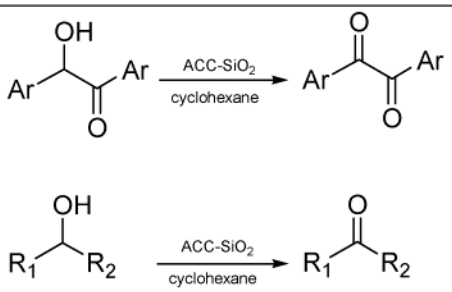
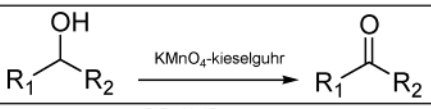
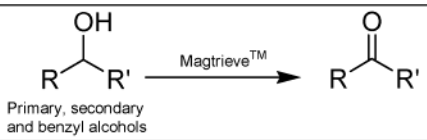
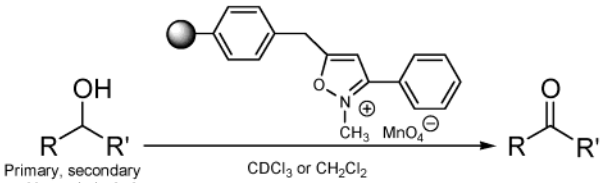
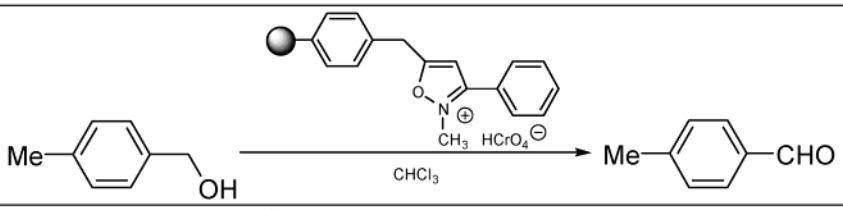
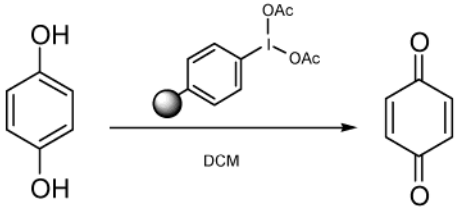
Alcohols $\xrightarrow{BTSC/SiO_2}$ Carbonyls Primary and secondary alcohols (1-octanol, 2-cyclohexylethanol, phenylethanol, 1-indanol, menthol, *o*-methoxy benzyl alcohol, *p*-bromo-benzyl alcohol, *m*-nitro-benzyl alcohol)	**Silica gel supported bis(trimethylsilyl)chromate (BTSC)** - Oxidizes various types of alcohols to carbonyls, reaction times are short, and over oxidation to carboxylic acids is not observed. - Yields 94-99% - Oxidation of aryl substituted unsaturated alcohols is not satisfactory[34,35]
	**Ammonium chlorochromate adsorbed on silica gel (ACC-SiO_2)** - Prepared by adding silica gel to a solution of ammonium chlorochromate in water, and evaporation to dryness - Benzoins are converted cleanly to benzils (five examples, yields 79-95%). - Primary, secondary and allylic alcohols (seven examples, yields 65-91%) - Unlike the oxidation with BTSC on silica, cinnamyl alcohol is cleanly converted to cinnamalydehyde.[36]
	**$KMnO_4$ supported on silica gel** - Five examples, yields 82-97%[37]
1,2-Diols $\xrightarrow[DCM]{SiO_2\text{-}NaIO_4}$ Aldehydes	**Silica gel supported metaperiodate** - Oxidative cleavage of 1,2-diols - The reaction can be performed in DCM, and the reagent can thus be used for reactants not soluble in THF or water - Yields 90-99%[38]
	**Magtrieve™, a magnetically retrievable oxidant based on tetravalent chromium dioxide (CrO_2)** - Six examples; 61-95%[39]
	**Derived from styrene-DVB or styrene-ethyleneglycol dimethacrylate (EGDMA) (2%) crosslinked polymer** - A crosslinked polystyrene-supported solid phase analog of isoxazolinium permanganate - Oxidizes alcoholic groups attached to an alicyclic ring structure contrary to poly(4-vinylpyridinium permanganate) resin - Quantitative yield - The polymer can be regenerated and reused several times - Ten examples; yields 80-88%[40]
	**Derived from poly(methyl metacrylate) (PMM) with 2% ethyleneglycol demethacrylate** - PMM-isoxazolinium Cr(VI) - Yield 73-82%[41]
	**Polymer-supported phenyliodine (III) diacetate** - Yield 63%[42]

Table 1 (Continued)

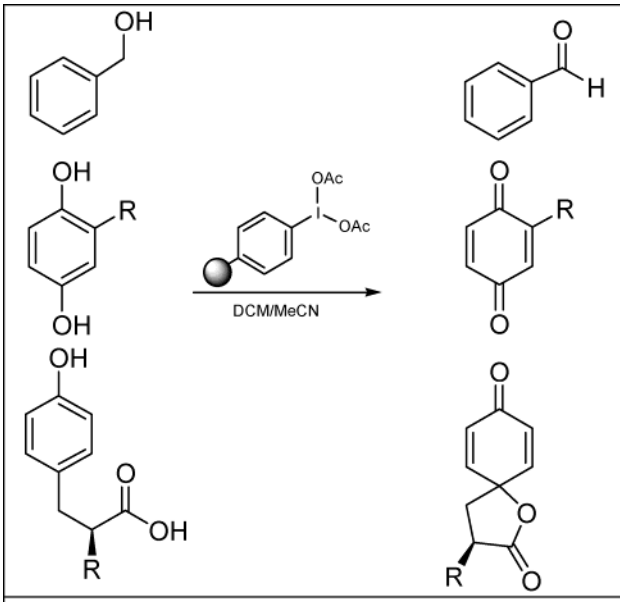
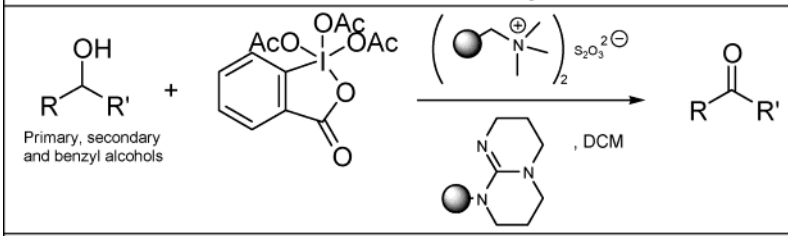
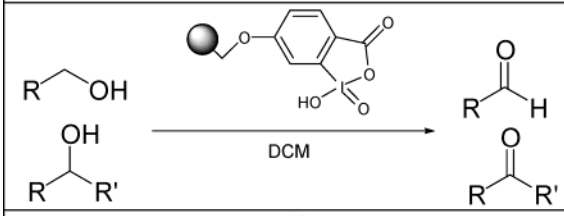
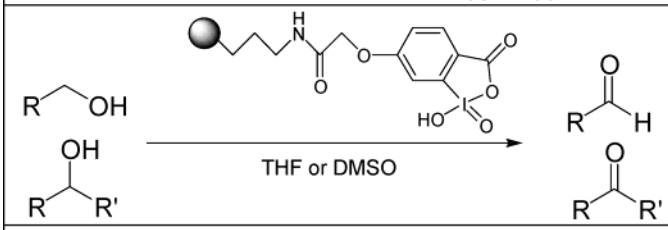
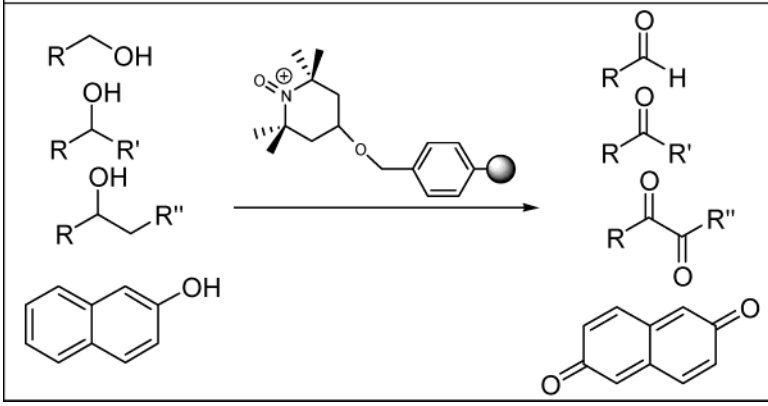
	**Polymer-supported phenyliodine (III) diacetate** - Polymer-supported bis(acetoxy)iodobenzene reagent promotes the oxidation of benzylic alcohols to the corresponding aldehydes - This reagent also affects the conversion of substituted 1,4-dihydro aromatics to the corresponding quinone systems - Yield 75-100%[43,44]
	**Amberlyst^R A-26 thiosulfate resin** - Reduces the I(V) and I(III) periodinate species to the I(I) species - Nine examples, yields 68-97%[45]
	**Polymer-supported periodinane reagent** - Derived from polystyrene resin - Oxidation of benzylic, allylic, primary as well as secondary alcohols - Twenty examples, yields 26 to >95%[46]
	**Polymer-supported periodinane reagent** - Derived from aminopropylsilica gel - Primary and secondary alcohols - Ten examples, yields 82-100%[47]
	**4-Alkoxy-2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO) polystyrene** - Oxidation of TEMP polystyrene with *N*-chlorosuccinimide yields the corresponding polymer-bound oxoammonium salt (TEMPO) - Oxidation of primary and secondary alcohols - Yields 65-95%[48,49]

Table 1 (Continued)

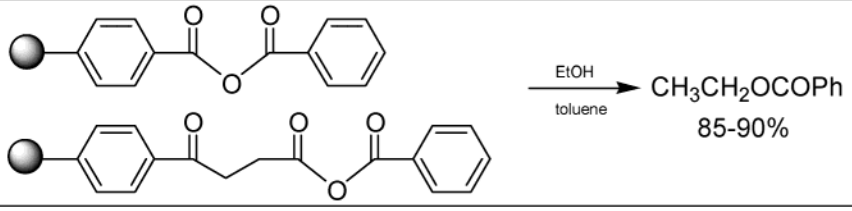
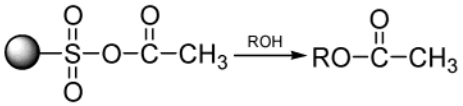
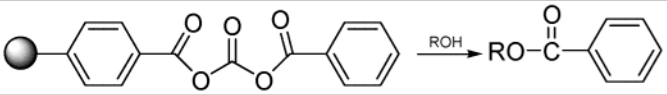
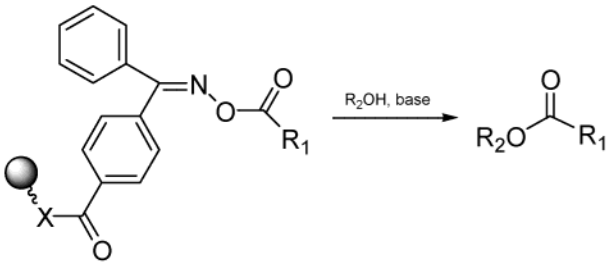
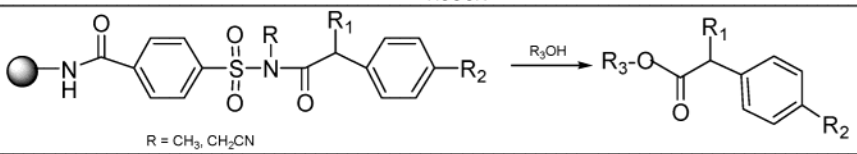
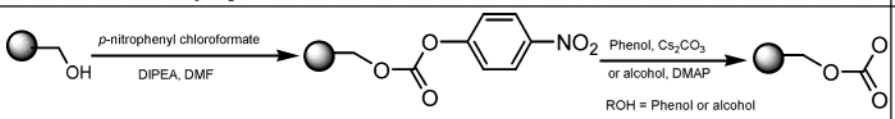
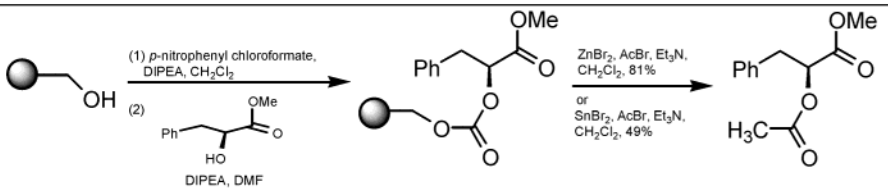
I. Solid-supported Reagents	
I.2. Solid-supported acylating reagents	**Comments and References**
	**Popcorn polystyrene derived from polystyrene bearing carboxylic acid** - Acylation of alcohols - Conversion of alcohols to esters[50]
	**Polystyrene-DVB acylating agent** - Yield 100% - Ten examples[51]
	**Copolystyrene-DVB vinylbenzoic acid** - Benzoylation of alcohols[52,53]
	**Polymer-bound oxime esters** - Derivatized Rink linker - Used for esterification and peptide synthesis[54]
	Polystyrene-DVB-supported acylating agents - Acylation reaction by the DMAP polymer as an acyl-transfer - Two examples, yields 82-100%[55]
	**Polystyrene-DVB 1%** - Safety catch linker - Utilized for esterification[56-58]
	**Hydroxymethyl resin derived from Merrifield resin** - Used for the preparation of esters on Merrifield resin-bound equivalent[59]
	**Wang resin** - One pot-formation of esters - Yields: 10-97% final products[60]
	Amberlite^R IRA-68 - Basic ion exchange resin - Acylation of alcohols with acid chlorides - Products in >97% purity - Nine examples, yields 84-100%[61]

Table 1 (Continued)

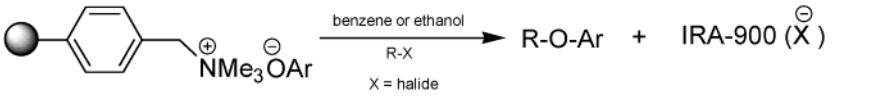
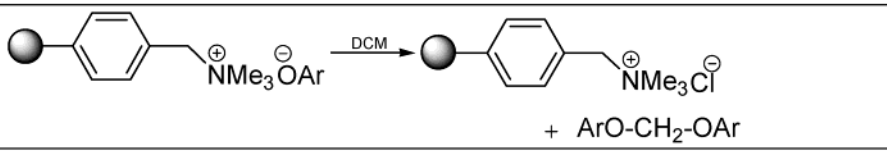
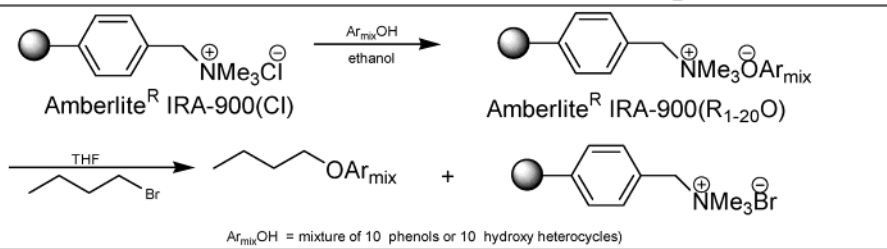
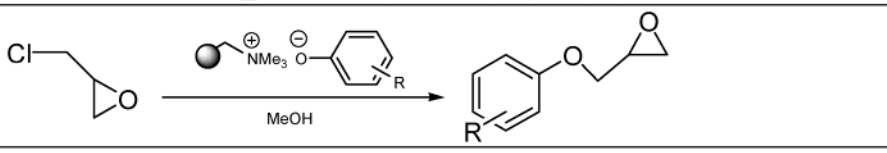
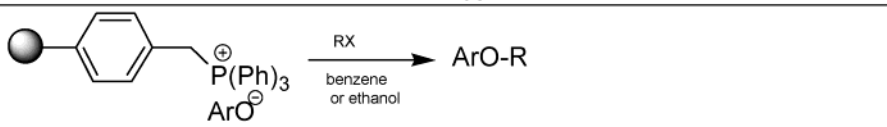
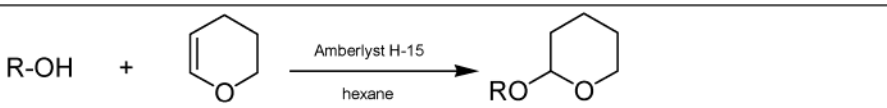
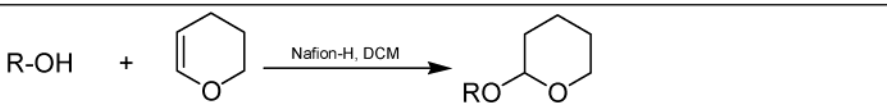
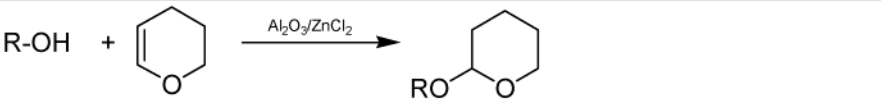
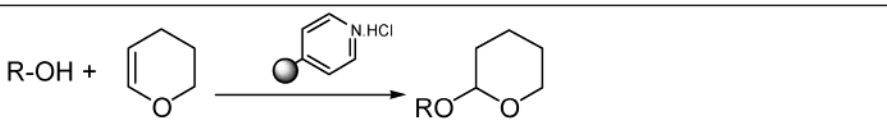
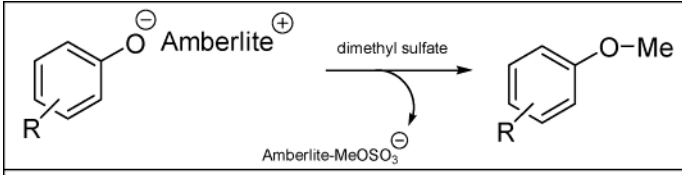
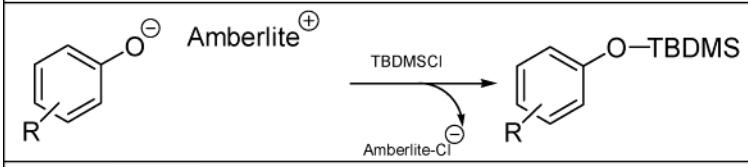
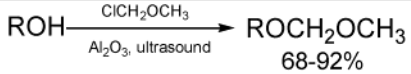
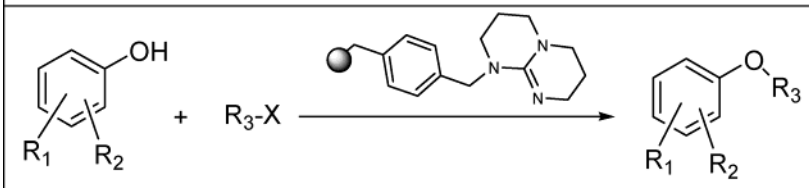
I. Solid-supported Reagents	
I.3. Solid-supported reagents for the synthesis of ethers and phase transfer catalytic reagents	**Comments and References**
	Cross-linked polystyrene resin-DVB 2% - Triphase catalysis - Synthesis of ethers by alkoxide or phenoxide displacement[62]
	**Anion exchange resin derived from treating Amberlite^R IRA-900 (Cl^-) with NaOH and ArOH in EtOH** - Synthesis of aryl alkyl ethers and heteroaryl alkyl ethers from alkyl halides - Sixteen examples, yields 10-100% - Primary alkyl derivatives are the most reactive alkyl halides[63,64]
	**Derived from treating Amberlite^R IRA-400 (Cl^-) with ArONa solution** - Synthesis of diaryloxymethanes from dichloromethane - Fifteen examples, yields 90-95%[65]
	**Amberlite^R IRA-900(ArO^-) anion exchange resin** - Used to generate phenoxides and heteroaryl oxides from a mixture of phenols or heteroaryl equivalents[18,64]
	**Amberlite^R IRA-400** - Polymer-supported phenoxides - Attachment of phenols to epichlorohydrin described[66]
	**Poly(vinylbenzyltriphenylphosphonium)-bound nucleophilic reagent** - Derived from Merrifield resin - Used for the synthesis of ethers - Yields 50-90%[67]
	**Amberlyst^R H-15** - Tetrahydropyranylation of alcohols and phenols - Thirteen examples, yields 90-98% - Primary, secondary, tertiary alcohols, and phenols[68]
	**Polymeric perfluorinated resin sulfonic acid (Nafion-H)** - Nine examples, yields 89-98% - Preparation of *O*-THP derivatives of alcohols - Primary, secondary and allylic alcohols[69]
	**Alumina impregnated with zinc chloride** - Tetrahydropyranylation of alcohols on a solid phase of alumina impregnated with zinc chloride - Protection of alcohols - Fifteen examples, yields 75-90%[70]
	**Poly(4-vinylpyridine) resin** - Protecting alcohols and phenols - Nine examples, yields 84-98%[71]

Table 1 (Continued)

	**Resin-bound phenoxides** - Synthesis of methyl ethers by action of dimethyl sulfate - Eight examples, yields 75-98%[72]
	**Resin-bound phenoxides** - Supported phenoxide ions can be protected with *t*-butyldimethylsilyl (TBDMS) - Seven examples, yields 65-96%[73]
	**Alumina** - Methoxymethylation of alcohols with methoxymethyl chloride on the surface of alumina - Inert to tertiary alcohols - Protection of primary and secondary hydroxyl groups in presence of tertiary ones[74]
	**Polymer-supported 1,5,7-triazabicyclo[4.4.0]dec-5-ene (PTBD)** - Polymer-supported bicyclic guanidine base - Used to deprotonate and support a variety of phenols, which can then be *O*-alkylated with a variety of alkyl halides - Used for the formation of aryl ethers from suitable phenols and alkyl halides - The ability to use tertiary halides and phenols with electron-donating or withdrawing groups - Yields 32-98%[75]

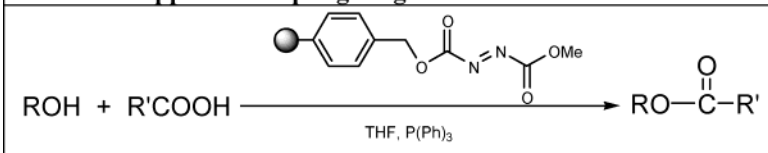
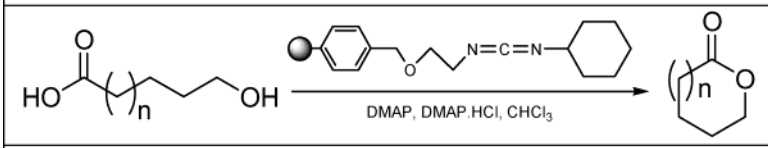
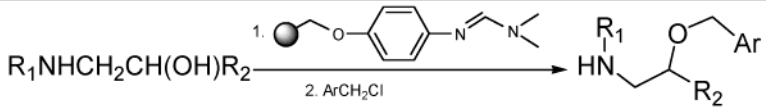
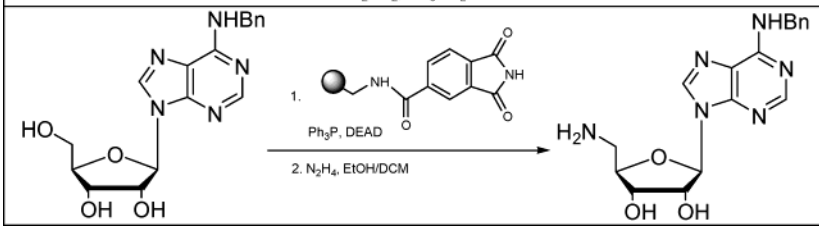
I. Solid-supported Reagents	
I.4. Solid-supported coupling reagents	**Comments and References**
	**Ethoxycarbonyl azocarboxymethyl polystyrene** -.Prepared from treating hydroxymethyl polystyrene with $COCl_2$, H_2NNHCO_2Me and NBS or Cl_2 - Mitsunobu reactions - Esters from carboxylic acids and alcohols, lactones from hydroxyl acids - 56-88% conversion rate[76]
	**Polystyrene-carbodiimide resin** - Used for the synthesis of macrolactones from hydroxyl acids[77]
	***p*-Diazoniumphenyl substituted Wang resin** - Immobilization of alcohols[78]
	**Derived aminomethyl resin** - A phthalimide containing resin - Conversion of a hydroxyl group to the corresponding amine under Mitsunobu conditions[79]

Table 1 (Continued)

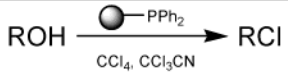
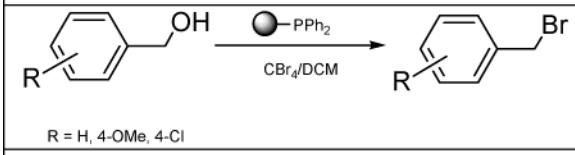
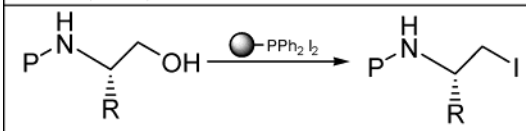
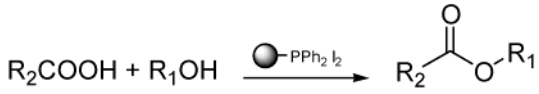
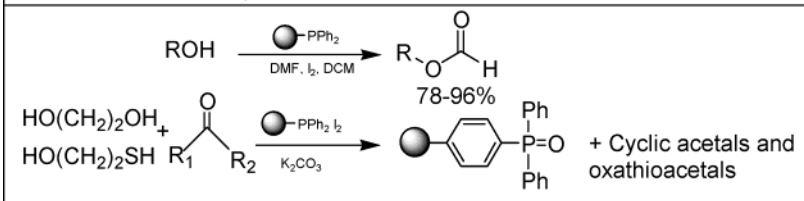
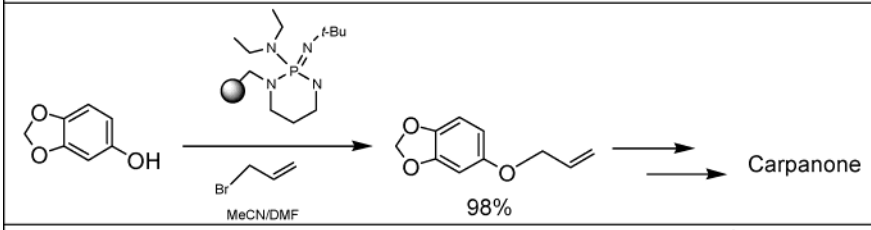
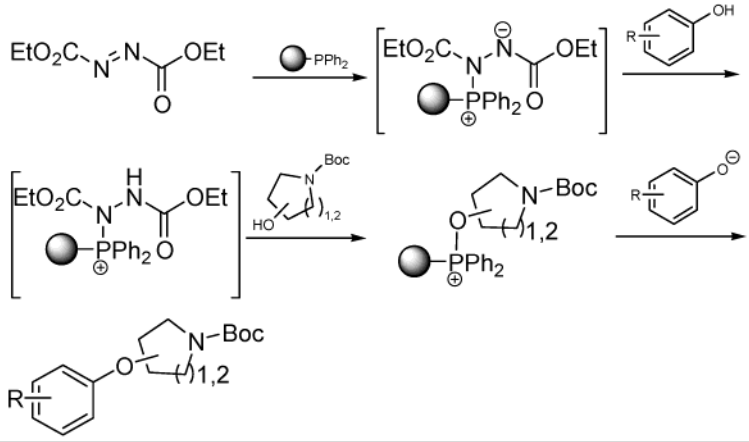
I. Solid-supported Reagents	
I.5. Solid-supported phosphines	**Comments and References**
	**Triphenylphosphine polystyrene** - Used for the conversion of alcohols to alkyl chlorides - No HCl is released and the conditions are neutral.[80-82]
	**Triphenylphosphine polystyrene** - Bromination of alcohols[83]
	**Polymer-bound (polystyryl) triphenylphosphine diiodide** - Generated *in situ* with I_2 - Used to convert alcohols to iodides - Used to prepare *N*-protected β-amino iodides[81,84,85]
	**Polymer-bound (polystyryl) triphenylphosphine diiodide** - Carboxylic acids can be esterified with a variety of alcohols[86]
	**Polymer-bound (polystyryl) triphenylphosphine diiodide** - The reagent in DMF also converts primary and secondary alcohols to their corresponding formate esters - A range of primary and secondary alcohols were employed with yields from 78 to 96%. - Under the same conditions, tertiary alcohols are converted to the corresponding iodide derivatives. - Converting a range of carbonyl compounds into acetals, cyclic acetals, and oxathioacetals (84-92%)[87]
	**Polystyrene phosphoramidate** - *O*-Alkylation catalysis[88]
	**Triphenylphosphine polystyrene** - Synthesis of aryl ethers from amino alcohols[89]

Table 2 (Continued)

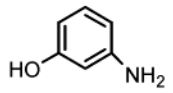
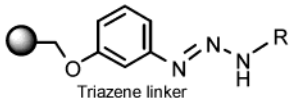
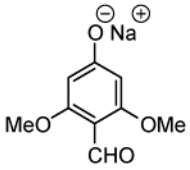
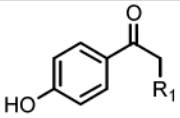
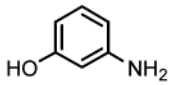
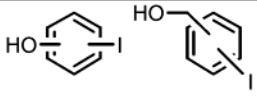
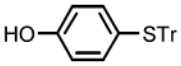
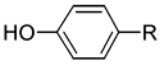
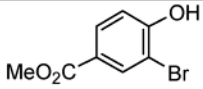
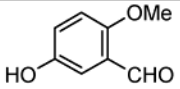
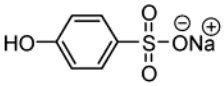
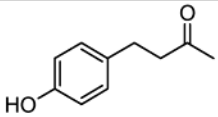
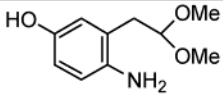
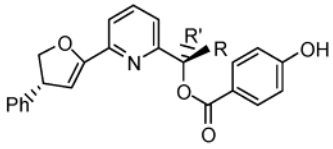
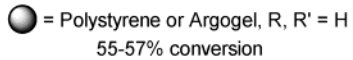
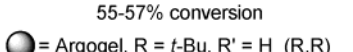
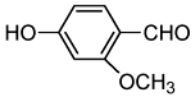
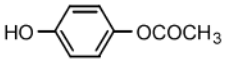
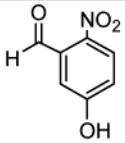
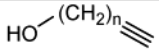
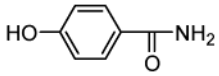
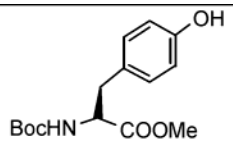
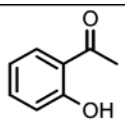
 - NaH, DMF - Triazene linker developed from Merrifield resin  Triazene linker - Used for the synthesis of amide and urea libraries[133]	 - DMF - Immobilization of phenols[134]	 - NaH, DMF -. Immobilization of phenols - Syntheses of tetrasubstituted pyrazoles described - 12-membered library[135]
 - NaH, *n*-Bu_4NI - Subsequent reaction with amines to give diazonium salts used for synthesis of 3-alkoxy-4-aryl piperidines as aspartic peptidase inhibitors[136]	 - NaH, THF or MeONa, DMF - Subsequent reactions leading to butenolides described[94]	 - Thiohydroxamic acid as a photolabile "traceless" linker developed - NaH, DMF - Yields for attachment and detachment reactions (85 and 55%, respectively)[137]
 R = CH_2OH, COOMe - NaOMe, DMA - Immobilization of phenols described[95]	 - NaOMe, DMA - Used for the synthesis of resin-bound sulfonamide – Monitoring reaction with spin echo magic angle proton NMR[138]	 - NaOMe, DMF - 2-Methoxy-4-benzyloxypolystyrene aldehyde resin (MALDRE) derived from Merrifield resin - Synthesis of secondary amides[139]
 - NaOMe, DMA - One example - Synthesis of arginine-containing peptides by guanidine attachment to a sulfonyl linker - Overall yield reported[97]	 - NaOMe, DMF - Further modifications on carbonyl group - Used in peptide synthesis[140]	 - DMF, NaOMe, $(Bu)_4NI$, 81% - To synthesize a novel safety-catch linker for synthesis of amides and esters[141]
ROK - DMF, 18-crown-6 - Immobilization of alcohols[142-144]	  = Polystyrene or Argogel, R, R' = H 55-57% conversion  = Argogel, R = *t*-Bu, R' = H (R,R) or R = H , R' = *t*-Bu (R,S) 40% conversion - **Merrifield resin or ArgoGel™-Wang-Cl** - DMF, K_2CO_3 - Preparation of polymeric ligands to assess in the palladium-catalyzed allylic alkylation[145]	 - *t*-BuOK, DMSO or DMA - Synthesis of SASRIN™ resin[146]
 - K_2CO_3, DMF, $LiAlH_4$ - Synthesis of photodetachable arylsilane polymer linkage[96]		
 - *n*-Bu_4NI, DMF, Cs_2CO_3 - Construction of dodecasaccharide[147]	 - Pyridine - New linker used for synthesis of isoxazole-based amino acids[93]	 - NaOH, DMSO - Preparation of *p*-benzyloxybenzylamine (BOBA) resin after reduction with $BH_3.SMe_2$ (94% yield for this resin)[148]

Table 2 (Continued)

 - Coupling yield more than 25%[149,150]	 **Wang and Merrifield resins** - Synthetic equivalents of 3-formylchromone and chromone reported[151]

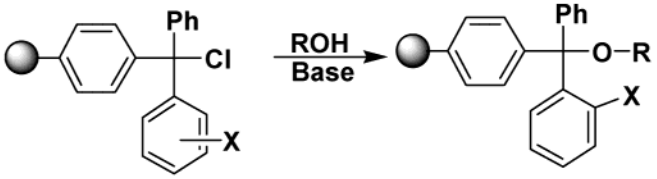
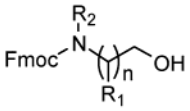
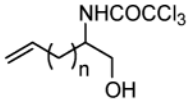
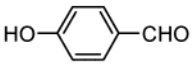
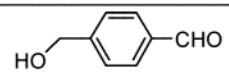
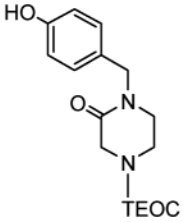
II. Solid supports reactions with alcohols and phenols		
II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)		
II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)		
II.1.1.2. Reactions on trityl resins  **X = H, 2-Cl, CH_3, 4-CH_3O**		
ROH **Conditions** **Comments and References**		
 **Trityl chloride resin** - Piperidine - Tentagel resin derivatized with either Rink or trityl linker - Eight symmetrical diamines and amino alcohols - Synthesis of diverse perhydro-1,4-diazepine-2,5-diones[152]	 n = 0-2 **Trityl chloride resin** -.Synthesis of 6-, 7- and 8-membered azacycles via olefin metathesis - Yield for cleavage products 85-89%[153]	 **Trityl chloride resin** - Pyridine, THF - Used for the anchoring of phenols - Solid phase synthesis of isoxazolines[154]
ROH **2-Chlorotrityl chloride-substituted polystyrene** - Fmoc-hydroxylamine, 2 aminobutanol, 3-aminopropane-1-ol, phenylalanilol, 4-aminobutanol, 1,3-diaminopropan-2-ol, ethyleneglycol, 2-(2-aminoethoxy)ethanol, *N*-methyl-2-aminoethanol, 4-aminomethyl benzyl alcohol, glycinol, pyrolinol - Synthesis of hydroxamic acids[155,156]	 **Trityl chloride resin** - Sym-collidone, Bu_4NI, DCM - Used in streocontrolled synthesis of polyketide libraries - Yield for cleaved product 60%[157]	ROH **Trityl chloride resin, NovaSyn^R dichlorotrityl, 2-chlorotrityl chloride NovaSyn^R TGT** - Pyridine - Chlorodiphenylmethyl benzoylamidomethyl polystyrene[100,101,150,154]
ROH = Different primary alcohols **Trityl resin (X = 4-CH_3O, 4-CH_3, 2-Cl)** - Etherification of various alcohols with resins of the trityl type - Yield 25-50%[102]	 TEOC = trimethylsilylethoxycarbamide **2-Chlorotrityl resin** - DIEA, DCM - Modification of 2-ketopiperazine with solid phase *C*-alkylation and *N*-acylations[158]	

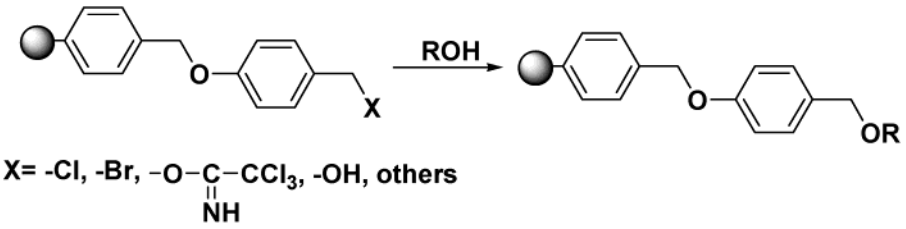
Table 2 (Continued)

II. Solid supports reactions with alcohols and phenols

II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)

II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)

II.1.1.3. Reactions on Wang resin



X= -Cl, -Br, $-O-\overset{\overset{NH}{\|}}{C}-CCl_3$, -OH, others

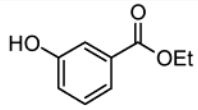
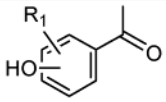
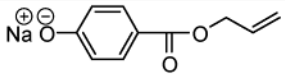
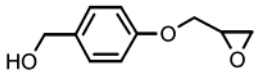
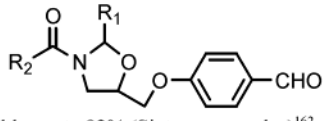
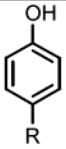
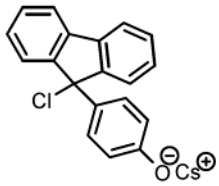
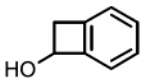
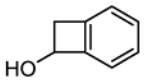
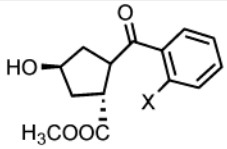
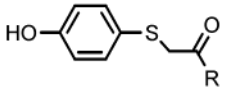
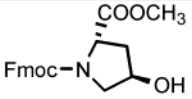
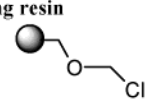
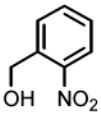
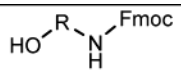
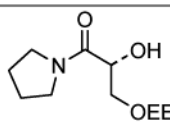
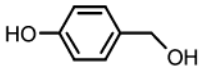
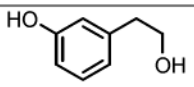
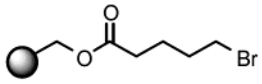
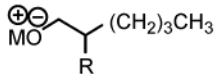
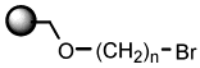
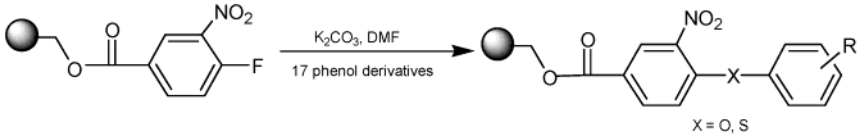
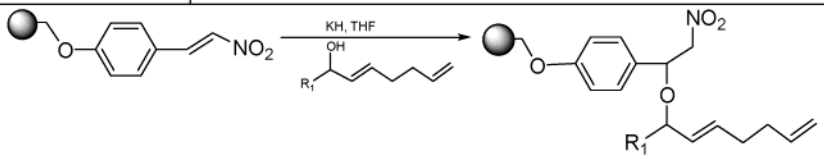
ROH Conditions Comments and References		
 **Wang chloride resin** - KO*t*-Bu - Immobilization of phenols[159]	 **Wang chloride resin** - Cs_2CO_3, NaI, DMF - Phenol attachment - Synthesis of 2,4,6-trisubstituted pyridines[160]	 **Wang chloride resin** - DMF - Synthesis of hexahydroisoindoles[161]
 **Wang chloride resin** - NaH, DMF - Solid-phase synthesis of 1,3-oxazolidines  - Yields: up to 92% (Sixteen examples)[162]	 **Wang chloride resin** - Used for immobilization of phenol - NaOMe, DMA - Conditions for attachment and detachment were investigated.[163]	 **Wang chloride resin** - New phenylfluorenyl based linkers developed from Wang resin and 1% cross linked aminomethyl polystyrene, respectively - DMF, 20% AcCl/DCM - Cleavage conditions: 10% TFA, DCM, 1 h. - An example of immobilization of an amine compound gave high yields (>80%)[164]
 **Wang trichloroacetamidate resin** - TfOH, DCM/hexane - Used for synthesis of benzoannelated nitrogen heterocycles[165]	ROH **Wang or Tentagel trichloroacetamidate resin** - Polymer-bound *p*-alkoxybenzyl trichloroacetamidate used for protection of alcohols as benzyl ethers - $BF_3.OET_2$, DCM - Coupling yields 70-98% - Monobenzylation of symmetrical diols - ROH = primary, secondary and tertiary diols, alcohols of different classes, fourteen examples[103]	 **Wang trichloroacetamidate resin** - TfOH, DCM, hexane - Traceless linker - Homo- and hetero-Diels-Alder reactions of *O*-quinodimethanes - Synthesis of tetrahydroisoquinolines - Total yields: 10-47%[166]
 **Wang trichloroacetamidate resin** - TfOH, DCM - Synthesis of pyrrolo[2,1-c][1,4]benzodiazepine-5,11-diones[167]	 **Wang trichloroacetamidate resin** - A new alkoxyphenyl-sulfinyl type linker developed - Used for the diastereoselective preparation of hydroxyl derivatives[168]	 **Wang trichloroacetamidate resin** - Used for immobilization of alcohols - $BF_3.OET_2$ or CF_3SO_3H, DCM - Synthesis of pyrrolo[2,1-c][1,4]benzodiazepines described[169]

Table 2 (Continued)

ROH **Modified Wang resin**  - Immobilization of alcohols and phenols[170]	 **Wang or NovaSyn^R TGA trichloroacetamidate resins** - $BF_3.Et_2O$, THF/DCM[171]	 **Wang or NovaSyn^R TGA trichloroacetamidate resins** - $BF_3.Et_2O$, THF/DCM[171]
 **Wang bromide resin** - NaH, Bu_4NI, THF, 18-crown-6 - Synthesis of aspartyl protease inhibitor libraries - 84% loading efficiency[172]	 **Wang resin** - Used for immobilization of 1,4-benzenedimethanol. - 1. Cl_3CCN, DBU, DCM; 2. $BF_3.OEt_2$, THF/DCM - Synthesis of polyethers using cyclic sulfates described. - Five examples; yields: 41-66%[173]	 **Modified Wang resin**  - Used for synthesis of benzoannelated nitrogen heterocycles[165]
 **Modified Wang resin** - Prepared from the reaction of bromo alcohols with Wang trichloroacetamidate resin  - Williamson ether synthesis developed on solid support - Eleven examples[174]	 **Modified Wang resin** - Synthesis of functionalized biaryl ethers - Theoretical yields based on Wang resin 40-58%[175]	
 **Modified substituted Wang resin** - 20-50% overall yields for final products - Synthesis of cyclic ethers[176]		

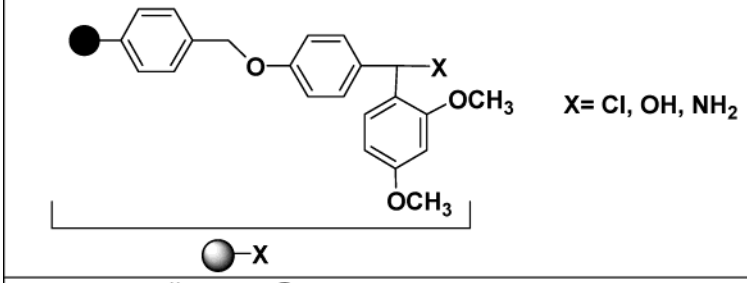
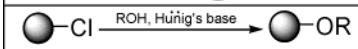
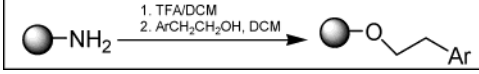
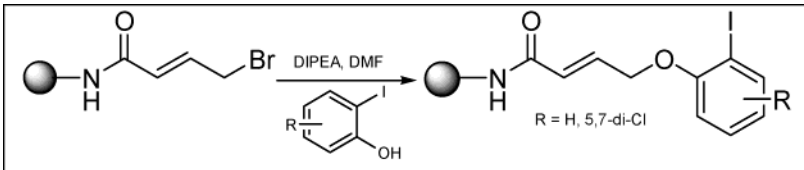
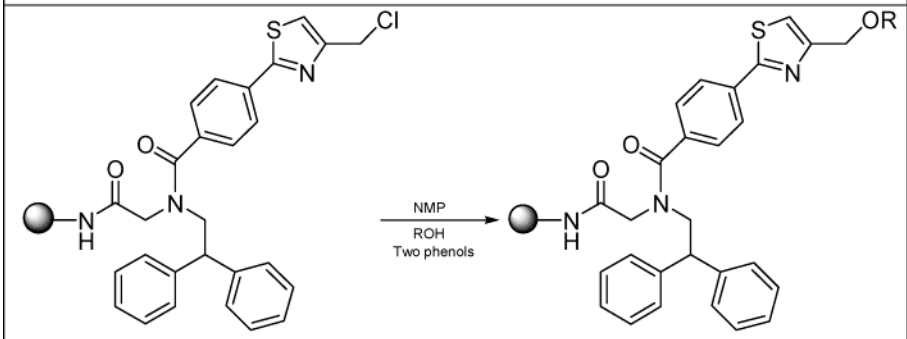
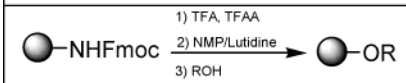
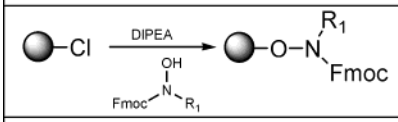
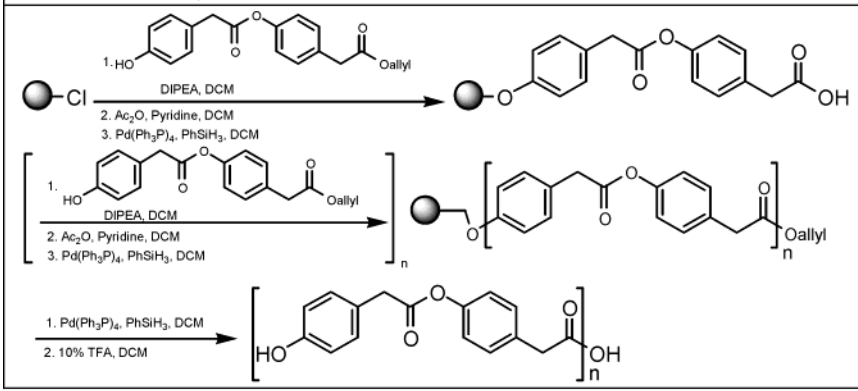
II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)	
II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)	
II.1.1.4. Reactions on Rink resin	**Comments and References**
	
	**Rink chloride resin** - Four examples, Yields 85-96%[177]
	**Rink amide resin polystyrene crown** - Nine examples; yields: 33-90%[178]

Table 2 (Continued)

	**Derived from Rink amide resin** - Two examples - *O*-alkylation - Construction of indole and benzofuran systems - Purified yields for final compounds 81-83%[179]
	**Derived from Rink amide resin** - The preparation of 2,4-disubstituted thiazoles - Yield for final compounds after cleavage 63-70%[180]
	**Derived from Rink resin** - Immobilization of nucleophiles on polystyrene supports - Three examples, quantitative or decomposition[181]
	**Rink chloride resin** - Synthesis of hydroxamic acids - Twelve examples - Yields: 58-95%[155]
	***JandaJe*l-Rink resin** - Synthesis of oligoesters - Yields: 54-79% (n = 0-12)[182]

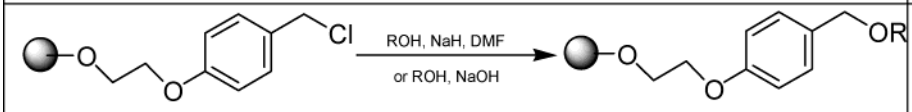
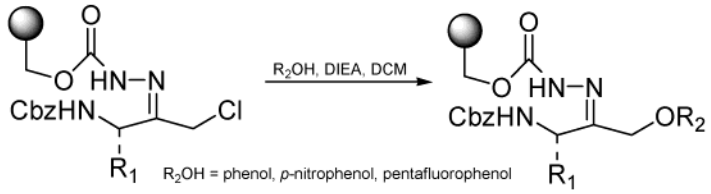
II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (*O*-Alkylation or *O*-arylation)	
II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)	
II.1.1.5. Reactions on other resins	**Comments and References**
	**Derived from ArgoGel-Wang resin** - Immobilization of alcohols - Five examples; overall yield reported[183]
	**Derived from ArgoGel-OH** - Used for the preparation of cystein protease inhibitors - Yield for cleaved products 31-37%[184]

Table 2 (Continued)

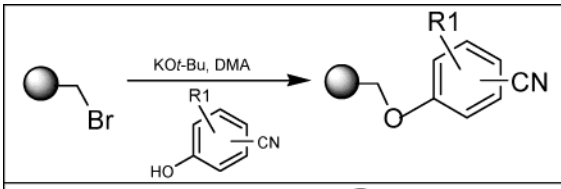
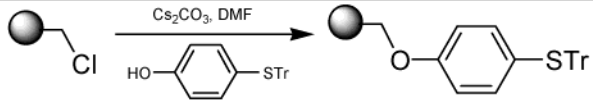
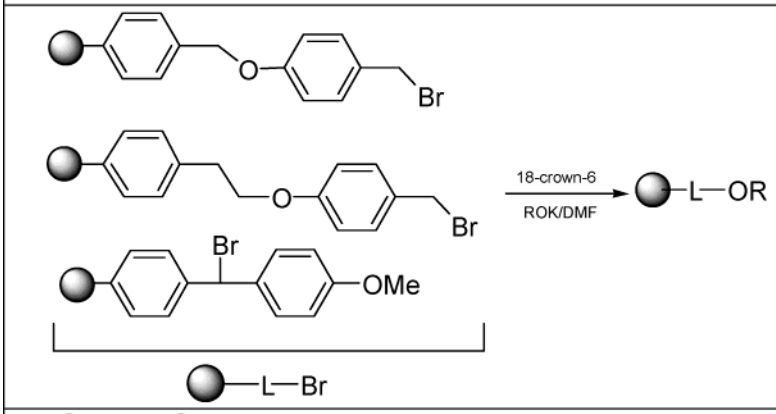
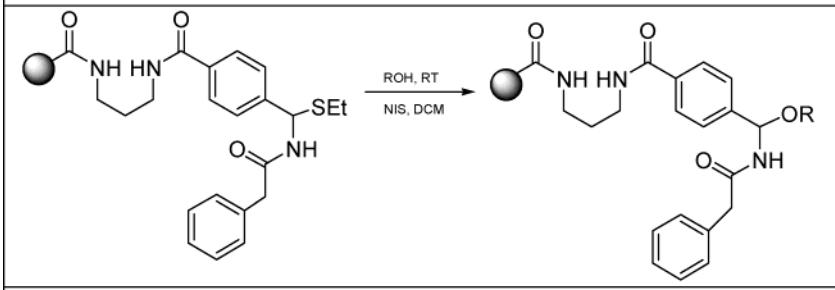
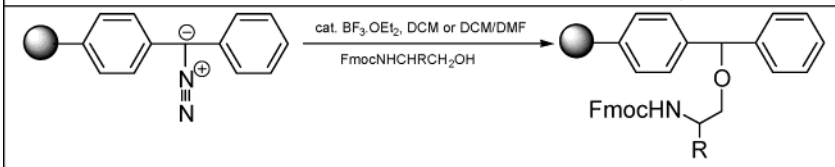
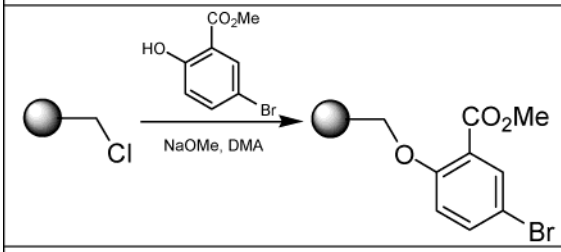
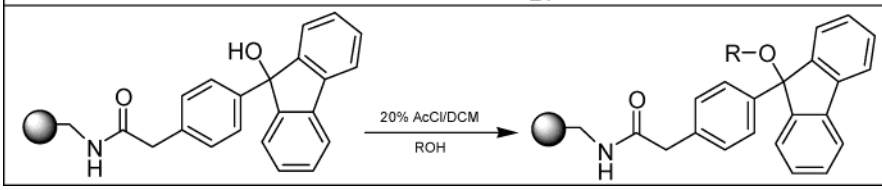
	***p*-Alkoxybenzyl bromide resin** - Synthesis of oxadiazoles[185]
	**Benzhydrylamine resin (BHA resin)** - Use of thioester resins described[186]
	**4-(Bromomethyl)phenoxymethyl polystyrene** **4-(Bromomethyl)phenoxyethyl polystyrene** **4-Bromo-(4-methoxyphenyl)methyl polystyrene** - Immobilization of alcohols[142-144]
	**Derived from Polystyrene or Tentagel resin** - Immobilization and cleavage of alcohols on solid support under much milder conditions than methodology based on dihydropyran functionalized resins - Final product yields 62-80% (coupling and cleavage)[187]
	**Polymeric diphenyldiazomethane (PDDM) (the diphenyldiazomethane derivative of crosslinked polystyrene)** - Side-chain anchoring of hydroxy amino acid derivatives - Synthesis of fully protected alcohols - Eleven examples; yields: 42-90%[105]
	**PEG crosslinked polystyrene disk** - Synthesis of biphenyls using Suzuki coupling reaction described[188]
	**Derived from aminomethyl polystyrene resin or TentaGel-S-NH_2 resin** - Immobilization of nucleophiles like alcohols[189]

Table 2 (Continued)

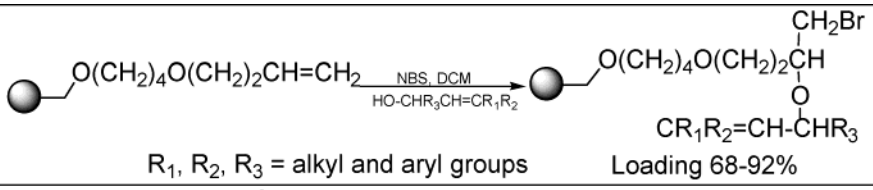
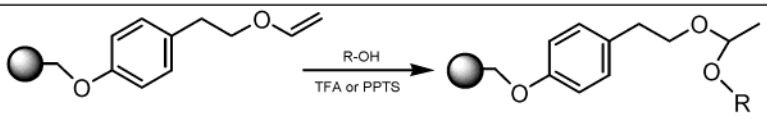
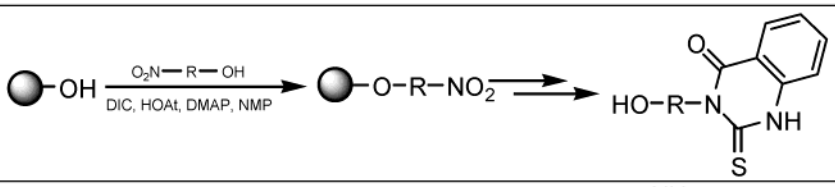
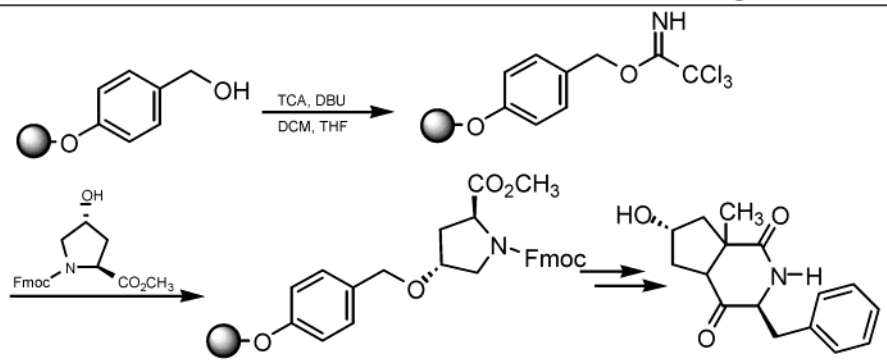
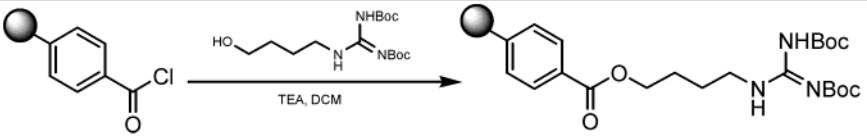
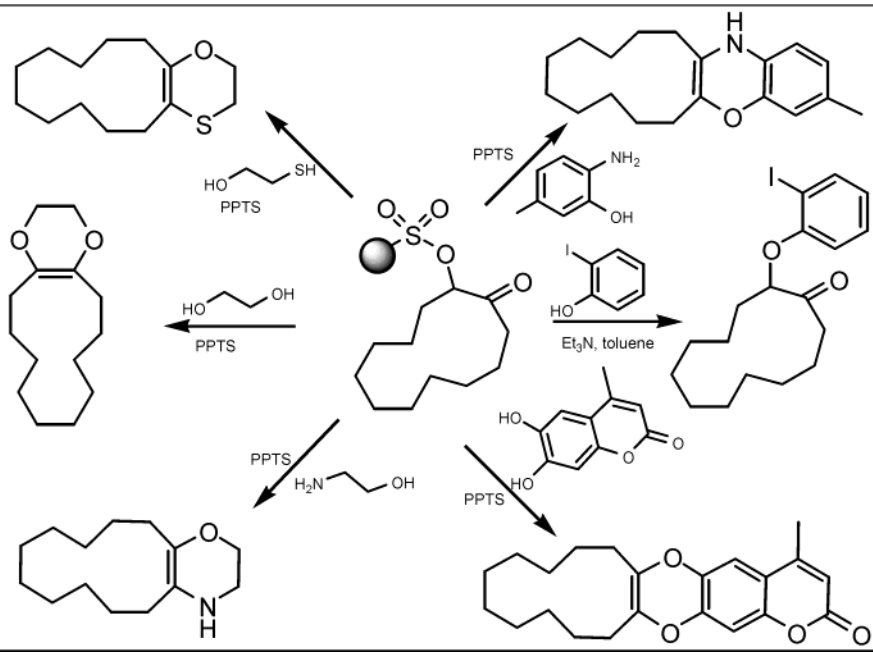
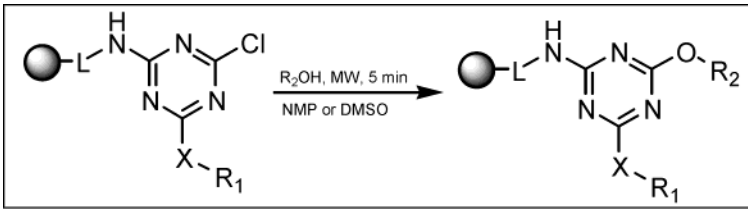
	**Derived from Merrifield resin** - Synthesis of γ-butyrolactones - Six examples[121]
	**Derived from Merrifield resin** - A vinyl ether type linker - Used for immobilization of alcohols, imidazoles, and tetrazoles - Subsequent Suzuki coupling reactions were investigated.[190]
	**SynPhase™ lantern resin (long-chain HMP)** - Synthesis of quinazolines-2-thioxo-4-ones - Five examples; moderate yields[191]
	**Four different resin types including Wang resin, Ellman resin, polystyrene-polyoxyethylene NovaSyn® resin, and polyoxyethylene-polyoxypropylene (POEPOP)** - 2,5-Diketopiperazines solid-phase synthesis[192]
	**Derived Merrifield resin** - A novel resin (loading capacity, 0.6 mmol/g) developed - Used to synthesize a 2,5,6-trisubstituted-4(3*H*)-pyrimidinones targeting HIV-1 reverse transcriptase[193]
	**Novel polystyrene sulfonic-ketone resin** - Employed for construction of a variety of heterocyclic compounds[194]

Table 2 (Continued)

	**Pyrimidine scaffold attached to cellulose membrane through L linker** - Subsequent reaction with alcohols assisted by microwave[195]

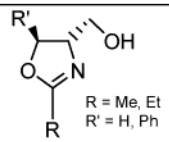
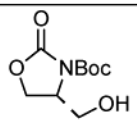
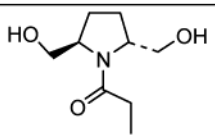
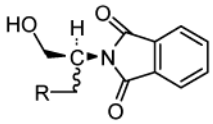
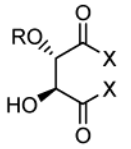
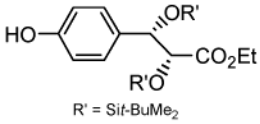
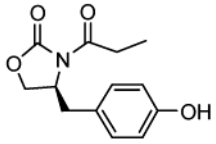
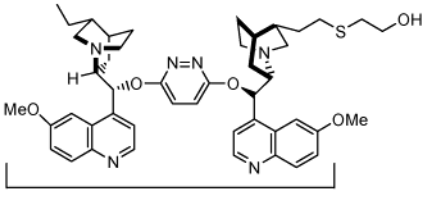
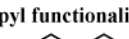
II. Solid supports reactions with alcohols and phenols		
II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)		
II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)		
II.1.1.6. The synthesis of polymer-supported chiral auxiliary compounds 		
ROH **Conditions** **Comments and References**		
 **Merrifield resin** - NaH, THF - Polymer-supported oxazoline chiral auxiliary - Preparation of nonracemic α-alkyl-carboxylic acid using polymer-bound oxazolines - Three examples[196]	 **Merrifield resin** - KH, DMF, 18-crown-6 - Polymer-supported oxazolidinone - Polymer-supported chiral auxiliary - Chiral oxazolidinone on Merrifield resin - Synthesis of chiral carboxylic acid (42% yield with enantiomeric excess of 96%)[197]	 **Merrifield resin** - Polymer-supported chiral auxiliary - Preparation of non-racemic 3,5-disubstituted-δ-butyrolactones - Lactones isolated in 34% overall yield[198]
 **Merrifield resin** - KH, 18-crown-6, THF - Polymer supported enantioselective reactions - α-Methylation of cyclohexanone[156]	 X = OCH_3 or $N(CH_3)_2$ R= Bn **Merrifield resin** - NaH, 18-crown-6, CsF, dioxane, *n*-BuNI - Chiral polymers - Derived from L-tartaric acid[199]	 R' = Si*t*-$BuMe_2$ **Merrifield resin** - K_2CO_3, DMF - Chiral polymers via asymmetric epoxidation and dihydroxylation - A polymer bearing a chiral diol pendant[200]
 **Merrifield, Wang or Tentagel-PHB resins** - Polymer-bound chiral auxiliaries - Polymer-bound Evans oxazolidinones - Synthesis of chiral primary alcohols - Aldol reactions[197,201,202]	 L **Chloropropyl functionalized silica gel**  - NaH, THF - Silica gel supported *Cinchona* alkaloid (chiral auxiliary immobilized on silica support) - Catalytic asymmetric dihydroxylation of alkenes[203]	

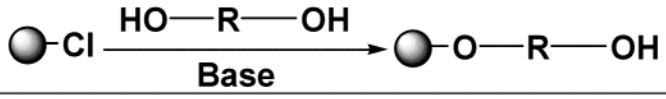
Table 2 (Continued)

II. Solid supports reactions with alcohols and phenols

II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)

II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)

II.1.1.7. Monoprotection of diols (monoether attachment)



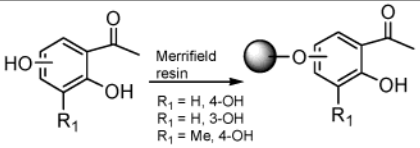
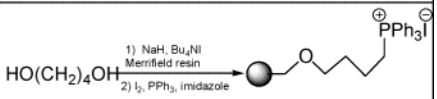
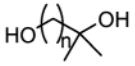
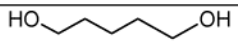
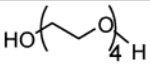
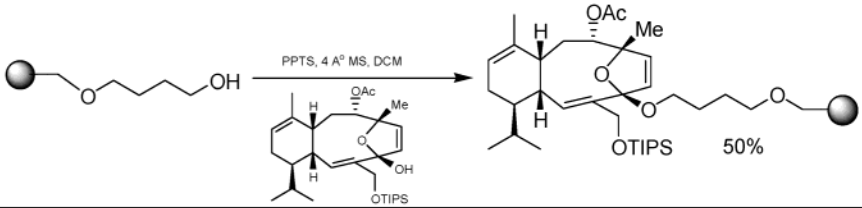
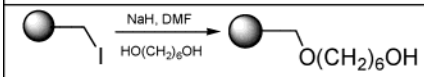
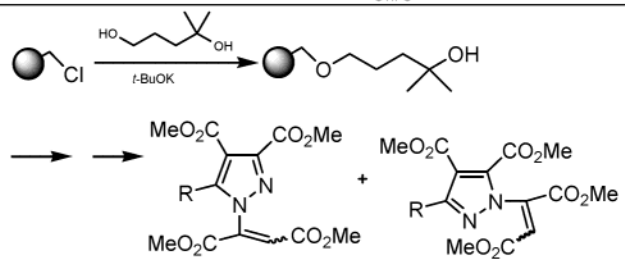
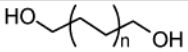
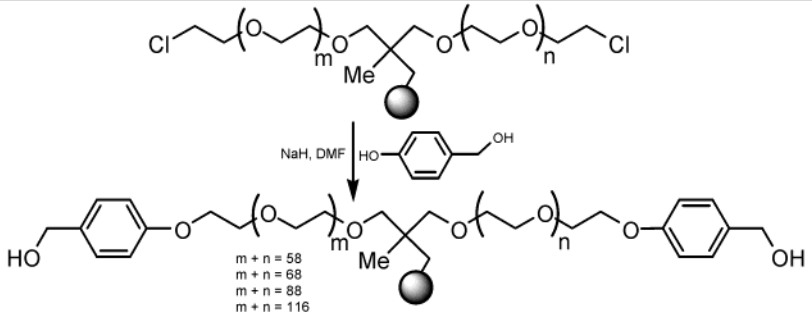
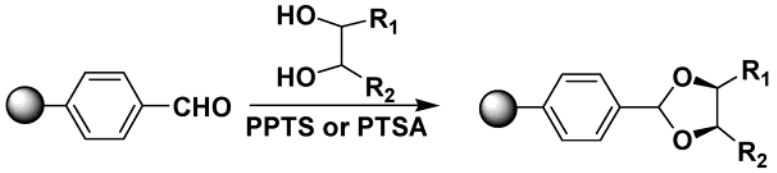
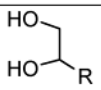
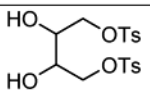
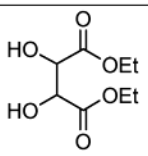
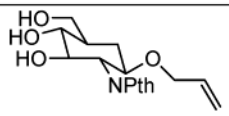
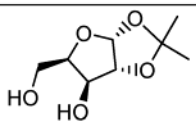
HO-R-OH **Conditions** **Comments and References**		
 **Merrifield resin** - Immobilization of alcohols[204]	 **Merrifield resin** -Synthesis of cyclopentane derivatives[205] **Merrifield resin** - Designing epothilones - One example - Overall yield reported - *O*-Alkylation[206]	 **Merrifield resin** - Synthesis of epothilones A and B[206]
 Polymer-bound 4,4'-dimethyltrityl chloride or trityl chloride - Pyridine - Preparation of monoacetates of symmetrical diols[207]	 **Merrifield resin** - KO*t*-Bu, THF - Solid support-bound tertiary alkyl alcohol - Four examples - The linker is stable towards strongly alkaline conditions as well as strong nucleophiles - Overall yield reported - *O*-Alkylation - Preparation of solid-supported *t*-alkoxycarbonylation reagents for anchoring of amines[208]	 **Merrifield resin** - Polymer-supported oligosaccharides via *n*-pentenyl glycosides (NPG) - Used in glycosidation[209]
 **Merrifield resin** - NaH, DMA - Monoprotection of diols[210]	 **Merrifield resin** - NaH, *n*-Bu_4NI, DMF, 99% - Solid-phase synthesis of combinatorial sarcodictyin libraries[147]  	
 **Merrifield resin** - Preparation of chiral lithium amides on solid support to apply in enantioselective deprotonation of cyclic ketones - Yield for amines was typically 40%.[211]	 **Several resins (imidazole, carbamate, and α-silylnitrosocarbamate) developed from Merrifield resin** - Traceless synthesis of pyrazole derivatives - Yields: 11-70% last four steps[212]	

Table 2 (Continued)

 **Trityl resin (PS-DVB)** - Pyridine, THF - Bifunctionalized resins - Immobilization of diols - Modification on unbound OH like oxidation and Wittig reaction, esterification - Coupling yields 75-90% - Preparation of β-mercaptoketones - Monoprotection of symmetrical diols, triols and tetraols, preparation of monoacetates of symmetrical diols - Reactions like oxidation, esterification on unbound hydroxyl group[142,143,213-228]	 **New poly(styrene-oxyethylene) graft copolymer resin** - Loading: 0.32-050 mmol/g[229]

II. Solid supports reactions with alcohols and phenols		
II.1 Attachment as ethers (*O*-alkylation or *O*-arylation)		
II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)		
II.1.1.8. Diprotection of diols (diether attachment)		
		
ROH **Conditions** **Comments and References**		
 **Polystyrene derivatized** - Protection of diols[230,231]	 **Derived from Merrifield resin** - PTSA, toluene - Used in synthesis of polymer-supported active phase transfer catalysis[232]	 **Derived from Merrifield resin** - PTSA, benzene - Polystyrene resins with chiral fragments derived from tartaric acid[199]
 **Wang aldehyde resin** - Camphorsulfonic acids , molecular sieves, CH_3CN - Protection of diols[233]	 **Wang aldehyde resin** - PPTS, DCM - Protection of diols[234]	

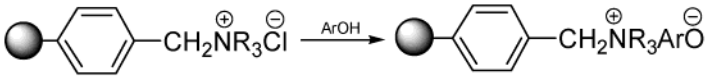
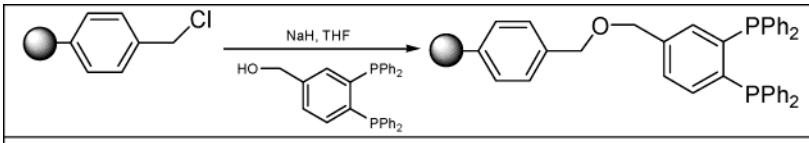
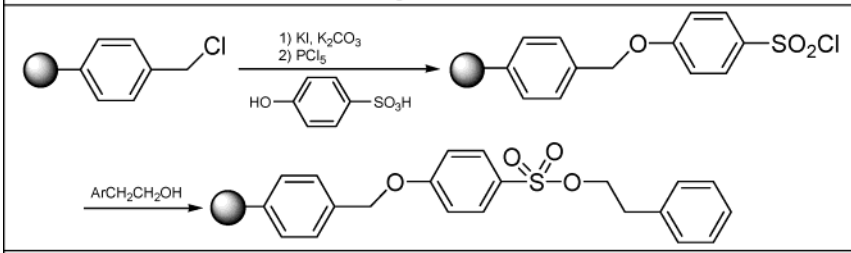
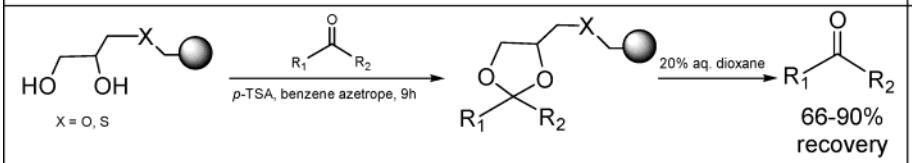
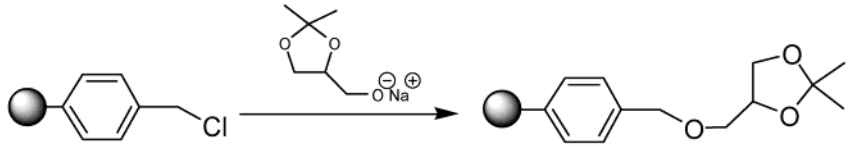
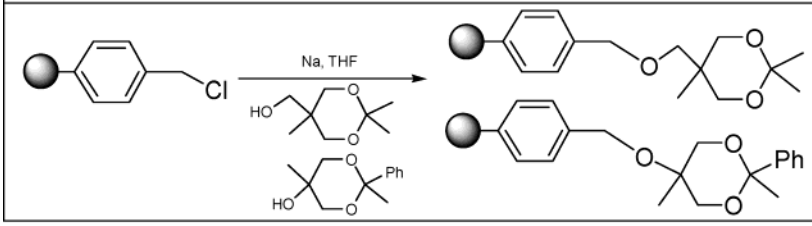
II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)	
II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)	
II.1.1.9. Synthesis of solid-supported reagents	Comments and References
	**Polystyrene derivatized** - Polymer-supported ionic reagents - Chloride form of Amberlite^R IRA-900 - Used in alkylation of alkyl halides[64,235,236]

Table 2 (Continued)

	**Merrifield resin** - Synthesis of polymer-supported diphosphine - Polymer-supported *O*-phenylene(diphosphine) ligands - Forming complexes with a range of metals[237]
	**Merrifield resin** - Anchoring the side chain of guanidine - Resin bound sulfonates[97-99]
	Polystyrene supported 1,5,7-triazabicyclo [4.4.0] dec-5-ene (PTBD) - Synthesis of aryl ethers from phenols and alkyl halides and aryl halides - Yield for final products 32-99%[75]
	**A polymer supported diol** - Used in isolating aldehydes and ketones from mixtures and as a protecting group for aldehyde and ketones - Eleven examples - Catch and release purification involving a covalent process[238]

II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)	
II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)	
II.1.1.10. Synthesis of solid supports with acetal linkers	**Comments and References**
	**Merrifield resin** - Supports containing 1,2-diol function used for protection of aldehydes and ketones - Acetal linkers for the preparation of aldehydes - Monoprotection of symmetrical aromatic diols and symmetrical diols - Further transformations such as Wittig reaction, aldol or benzoin condensation or Grignard addition[95,219,239-243]
	**Merrifield resin** - Polymer-bound 1,3-diols as monoblocking agents of symmetrical dialdehydes[219]

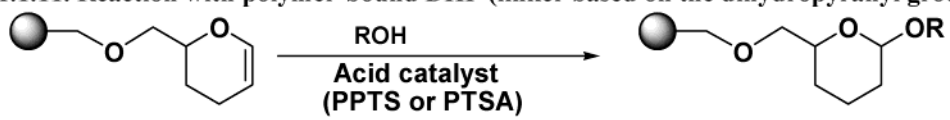
II. Solid supports reactions with alcohols and phenols
II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)
II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)
II.1.1.11. Reaction with polymer-bound DHP (linker based on the dihydropyranyl group)


Table 2 (Continued)

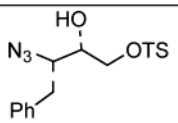
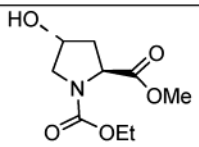
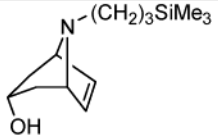
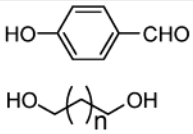
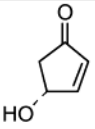
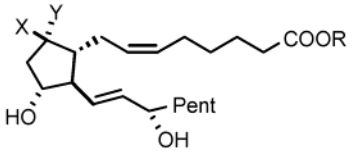
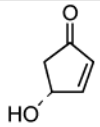
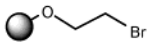
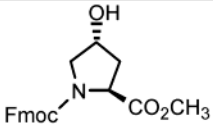
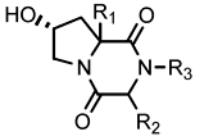
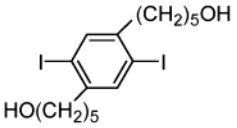
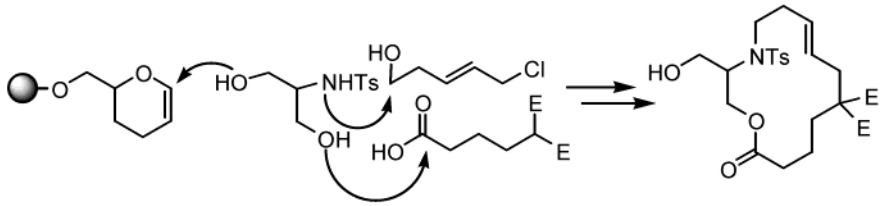
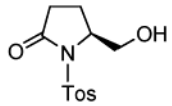
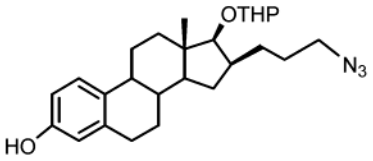
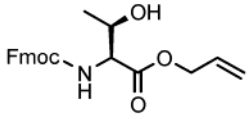
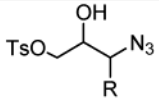
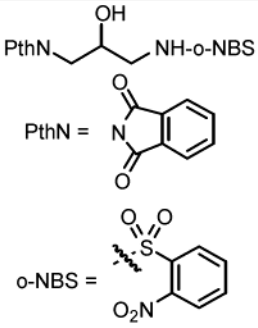
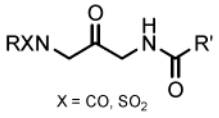
ROH (alcohols or phenols) Conditions Comments and References		
 **DHP-linked Merrifield resin** - Core unit linked to resin via THP protected alcohol - Synthesis of aspartic protease inhibitors - Yield for final products (different protease inhibitors) 47-86%; 20-50% in the diol series; 30-70% for the monoalcohol diamine derivatives[110,111,244,245]	 **DHP-functionalized polystyrene support** - Solid-phase synthesis strategy for the preparation of 2-pyrrolidinemethanol ligands[112]	$HO(CH_2)_nOH$ **DHP-linked Wang resin** - Alcohol to aldehyde conversion[112,245-249]
 **DHP-functionalized polystyrene support** - Solid-phase synthesis of atropane derivatives - Yield for final products 50-73%[249]	 (n = 4, 6, 12) **Derived from Merrifield resin** - Synthesis of pyrrolidines - Overall yields 32-50%[246]	 **THP linker attached to non-cross-linked polystyrene** - Used for immobilization of alcohols - Synthetic approach for prostaglandins and derivatives reported[250]  **DHP-linked Merrifield resin** - Primary and secondary alcohols - Tertiary alcohols show very poor loading efficiencies. - Synthesis of prostaglandins[110,111]
 **Non-cross linked polystyrene (NCPS) a soluble copolymer support** - Synthesis of prostaglandin F2α on a non-cross-linked polystyrene support (NCPS) - The overall isolated yield is about 30% after 10 chemical steps[251] **Tentagel-S (bromide)** - Poly(styrene)block (polyethylenglycol) resin  - Prostaglandin synthesis[111]	 **DHP-linked Wang resin** - Solid phase synthesis of a new class of 2,5-diketopiperazines[252] 	 **DHP-linked Merrifield resin** - 49% loading - Solid-phase synthesis of oligo(1,4-phenyleneethylene) by a divergent convergent tripling strategy[253]
 **DHP-linked Wang resin** - Used for immobilization of hydroxyl containing compounds - Used for the synthesis of macroheterocycles. - Yields high[254,255]		

Table 2 (Continued)

 **DHP-linked Merrifield resin** - Synthesis of amino alcohols[256]	 **DHP-HM resin** - Steroid derivatization on solid support[257]	 **DHP resin** - Used for immobilization of threonine - Synthesis of Tyr[13]-octreotate described[258]
 Derived from Merrifield resin - Simple glucal-based linker developed from Merrifield resin - Used for immobilization of alcohols (primary, secondary, tertiary) on the solid support. - Seven examples, yields: 32-92%[259]	 **Merrifield resin with dihydropyran linker** - Immobilization of alcohols and further synthesis of heterocycles[260]	 **DHP linked Wang resin** - Used for immobilization of hydroxyl containing synthon - Applied for synthesis of 1,3-diaminoketones  - Five examples; 25-60% overall yields[261]

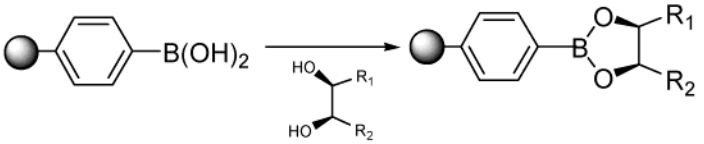
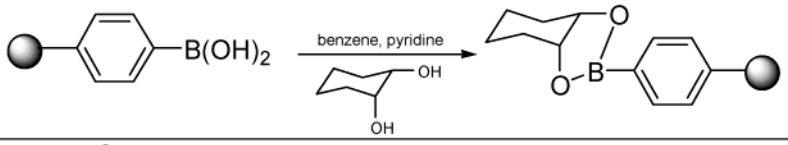
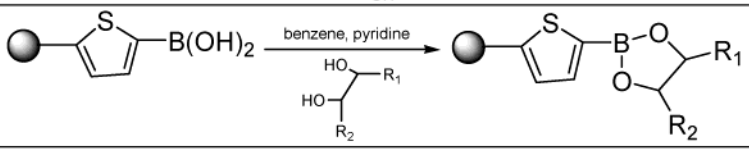
II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)	
II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)	
II.1.1.12. Attachment through a boronic acid linker (reactions with polymer-bound boronic acid)	**Comments and References**
 	**Polystyrene/boronic acid** - Solid-phase separation of *cis-trans* diol mixtures - Only *cis*-diols are bound. - Protecting group of diols[10,226,262-264]
	**Polystyrene/boronic acid** - Protection of diols[113,114]

Table 2 (Continued)

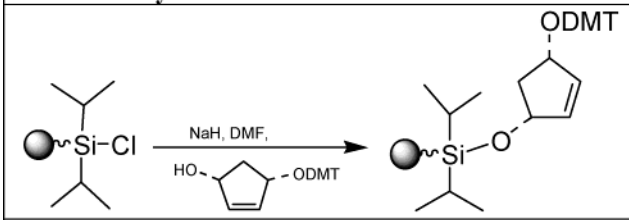
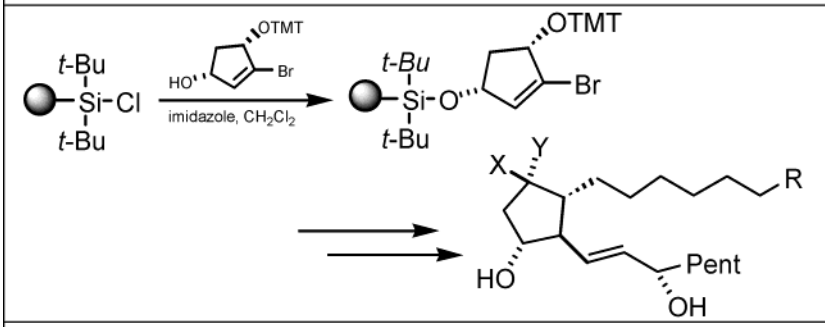
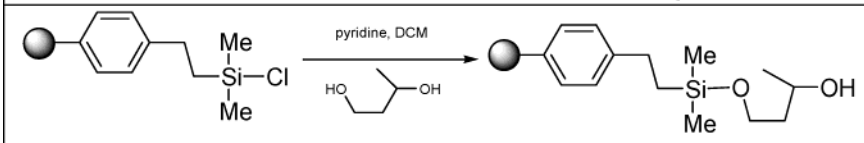
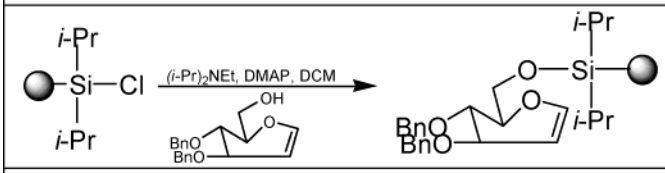
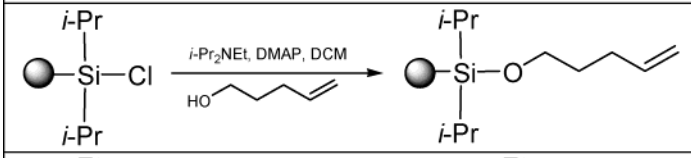
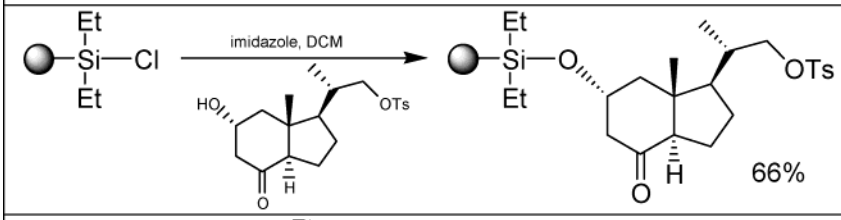
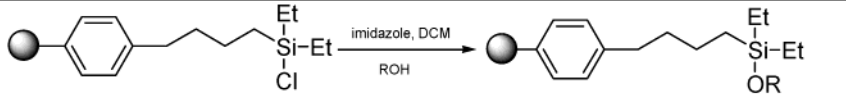
II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (O-alkylation or O-arylation)	
II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)	
II.1.1.13. Silyl linker for the attachment of alcohols	**Comments and References**
	**Resin-bound hydroxycyclopentenone** - Macroporous resin - Solid-phase synthesis of prostaglandins - Final yield for prostaglandin 50%[265-267]
	**Chlorodibutylsilyl polystyrene resin** - Used for attachment of alcohols - Synthetic approach for prostaglandins developed[268]
	**Silyl chloride bound to a cross-linked polystyrene matrix through stable dimethylene spacers** - Polymer-supported organosilicon protecting groups to protect and immobilize hydroxyl-containing free molecules - Selective protection of primary hydroxyls in the presence of secondary, and secondary over tertiary - Final product yield after further reactions and cleavage 90%[118]
	**Silylated polystyrene polymer resin (polystyrene diisopropylsilyl chloride)** - Construction of β-linked oligosaccharides by coupling of glycal derived thioethyl glycosyl donors[117]
	**Polystyrene diisopropylsilyl chloride** - Prepared from polystyrene by lithiation and reaction with dichlorodiisopropylsilane - Used for stereocontrolled synthesis of polyketide libraries - Yield for final cleavage reaction 85%[158]
	**Chlorinated polystyrene-diethylsilane resin (diethylsilyl chloride resin) (PS-DES)** - Solid-phase synthesis of vitamin D3 system[269]
 ROH = 1-(2-methoxybenzoyl)-2-pyrrolidinemethanol, 2-(1-naphthyl)ethanol, *N*-Fmoc-ethanolamine, 1-(4-methoxyphenoxy)-2-propanol, *trans*-2-phenylcyclohexanol, epiandrosterone	**Butyldiethylsilane polystyrene (PS-DES) resin** - Polymer-supported trialkylsilanes for direct attachment of oxygen-based functional groups such as primary and secondary alcohols - Overall loading yields 60-91% (from precursor resin without chlorine)[115]

Table 2 (Continued)

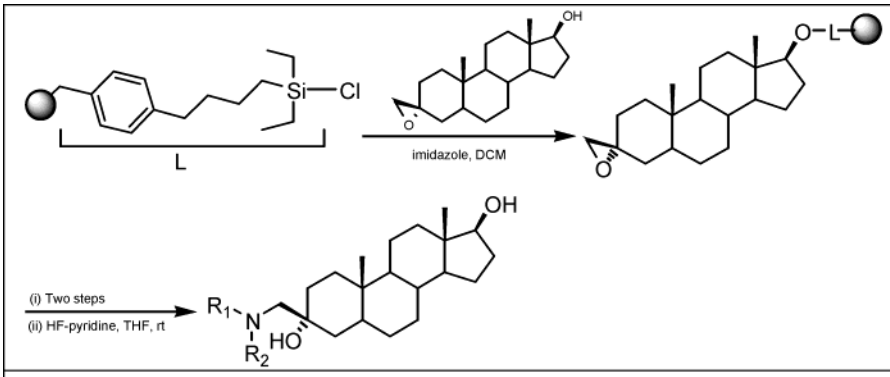
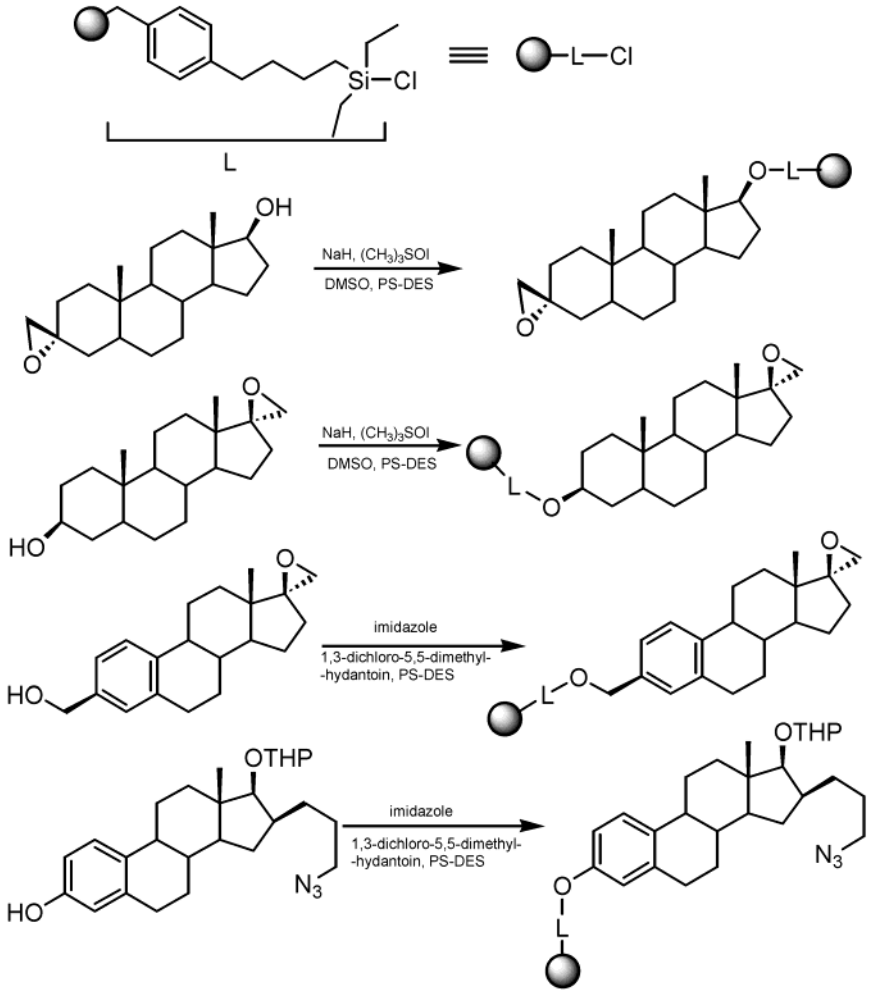
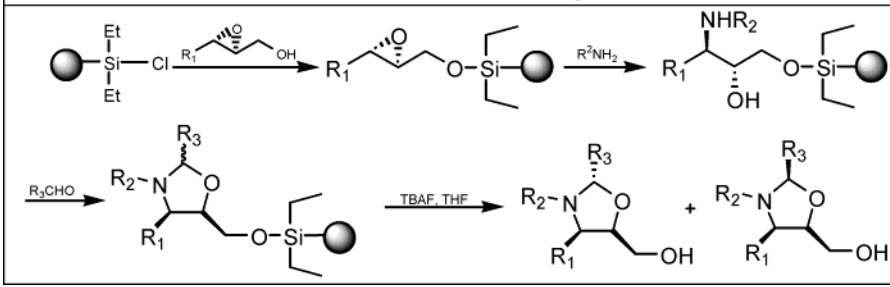
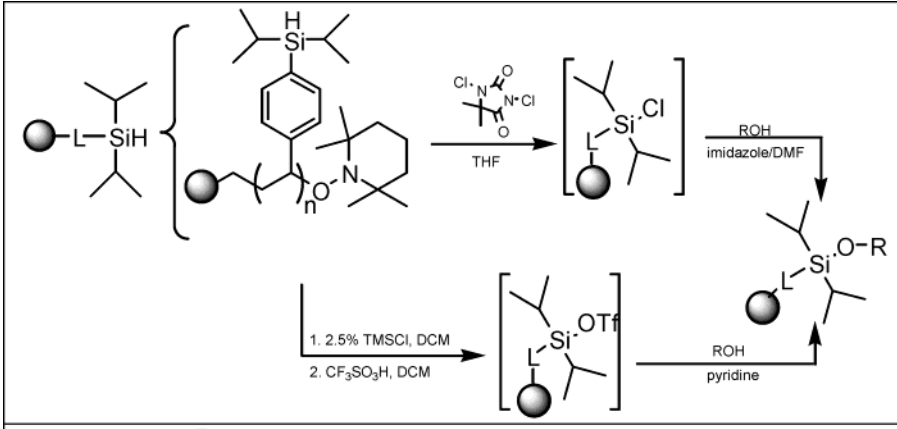
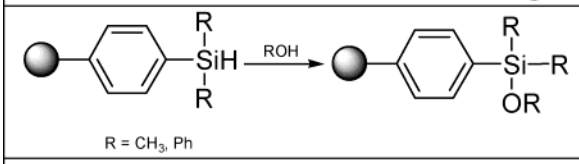
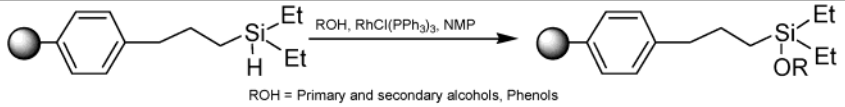
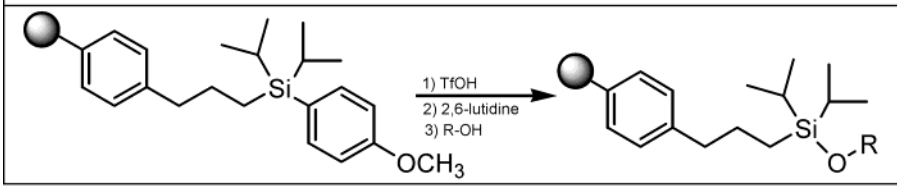
	**Butyldiethylsilane polystyrene (PS-DES) resin** - The steroid substrates can be diverse. - Used to build steroid libraries - HF must be used for resin cleavage.[270]
	**Butyldiethylsilane polystyrene (PS-DES)** - Used for immobilization of four different types of steroid alcohols and phenols - Subsequent reactions on solid support were investigated.[270]
	**Chlorinated polystyrene-diethylsilane resin (diethylsilyl chloride resin) (PS-DES)** - Used for immobilization of alcohols. - Synthesis of several 1,3-oxazoline libraries - Mild cleaving conditions - Synthesis of a library of highly substituted chiral 1,3-oxazolidines - Yields: 59-99% (based on the resin)[271]

Table 2 (Continued)

	**Polystyrene silyl resin 1** - synthesized from polystyrene resin - Used for anchoring of alcohols on solid support - Seven examples; yields: 63-88%[272]
	**Polystyrene-diethylsilane resin** - Used for immobilization of alcohols[273]
	**Polymer-supported trialkylsilane** - Gel-type resin - Alcoholysis and carbonyl hydrosilylation - Yield 50-87% for two steps (loading and cleavage) - Dimethylsilyl polystyrene is commercially available for immobilization of alcohols[119]
	**Alkylsilyl-tethered resin** - Used for immobilization of alcohols described[274]

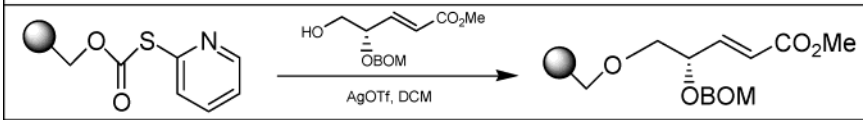
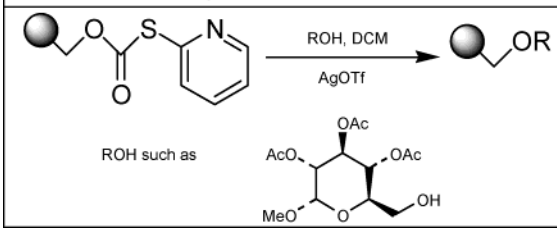
II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)	
II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)	
II.1.1.14. Thiocarbonate functionalized resins for the attachment of alcohols	**Comments and References**
	**Thiopyridine carbonyl Wang resin** - Yield 90%[104]
	**2-Pyridinyl thiocarbonate Wang resin** - Six examples, yields 80-98%[106]

Table 2 (Continued)

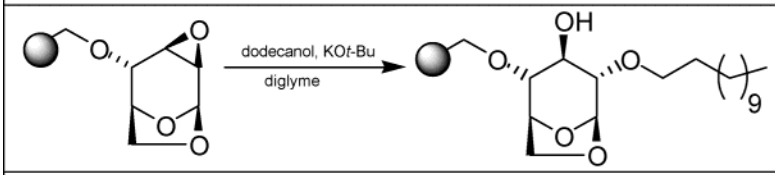
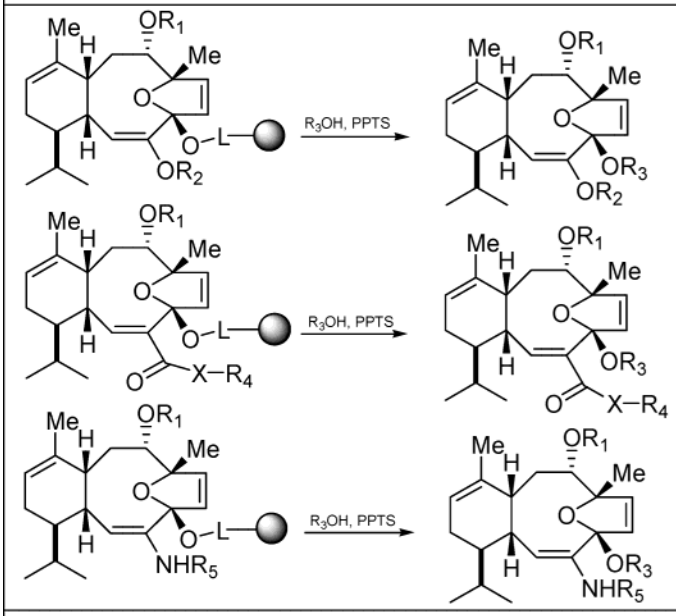
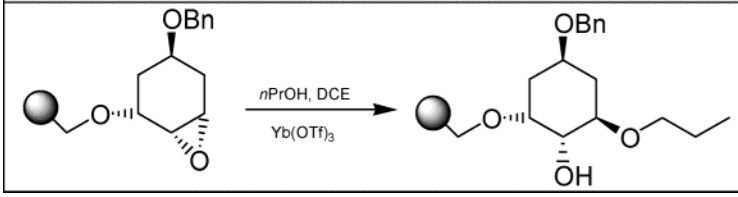
II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (*O*-Alkylation or *O*-arylation)	
II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)	
II.1.1.15. Attachment through miscellaneous linkers	**Comments and References**
	Polystyrene-based support with *p*-alkoxybenzyl linker (Wang resin) - Immobilization of alcohols[109]
	**Wang resin** - Attachment of dodecanol and subsequent synthesis reported[107]
	**Wang resin** - Synthesis of Sarcodictyins[147]
	**Merrifield resin** - Yield 100%[108]

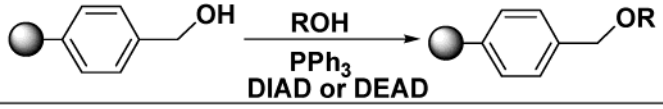
Table 2 (Continued)

II. Solid supports reactions with alcohols and phenols

II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)

II.1.2. Mitsunobu reaction

II.1.2.1. Mitsunobu reaction to immobilize hydroxyl functional group as phenol ethers



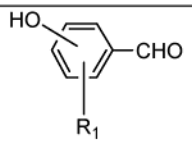
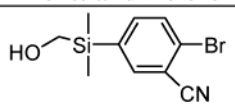
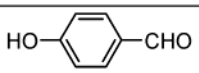
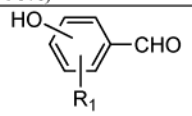
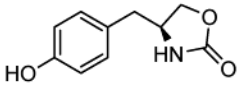
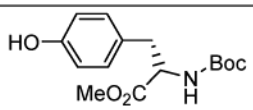
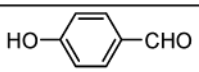
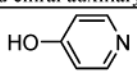
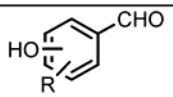
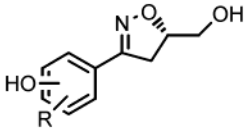
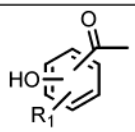
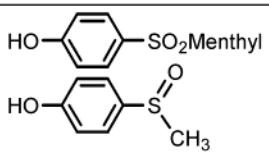
ROH, Conditions Comments and References		
 **Wang resin** - PPh_3, THF, DEAD - Hydroxybenzaldehydes attached to Wang resin - Loading ranging from 0.24 to 0.89 meq/g - Phenols immobilization - Solid-phase synthesis of proline analogs - Solid-phase synthesis of 2,3-dihydro-4-pyridones (eight examples, yields for final products 60-90%)[275-277,280]	 **Wang resin** - PPh_3, DIAD, NMM - Photodettachable aryl silane polymer linkage for use in solid phase organic synthesis[96]	 **Wang resin** - NMM, DIAD, PPh_3 - Synthesis of imidazole or 2,3-dihydro-4-pyridines (using DEAD and TPP)[280,281]
 **Wang resin** - PPh_3, DEAD, THF - Synthesizing proline derivatives[276]	 **Wang resin** - DEAD, NMM, PPh_3 - Synthesis of chiral α-substituted β-hydroxy acid derivatives - Solid supported chiral auxillary[201]	 **Wang resin or Merrifield resin** - DEAD, PPh_3, NMM - Attachment of the alcohol functional group in amino acid; yield > 80%[282]
 **Wang resin** - PPh_3, DEAD, NMM - Immobilization of aldehydes and olefins in the synthesis of tetrahydroquinolines[283]	 **Wang resin** - PPh_3, DEAD, DMF, THF - Synthesis of *N*-acyl-2-substituted dihydro-4-pyridones[284]	 **Wang resin** - PPh_3, DIAD, THF - Synthesis of isoxazolines described.  - Seven examples; yields: 38-78%[285]
 **Wang resin** - Solid-phase bound chalcones used for synthesis of 2,4,6-trisubstituted pyrimidines. - Three examples; yields 79-93%[286]	 **Wang resin** - Used for immobilization of *p*-hydroxyphenyl menthyl sulfinate - PPh_3, DIEA, DEAD, toluene, THF - Subsequent Grignard reactions investigated[287]	

Table 2 (Continued)

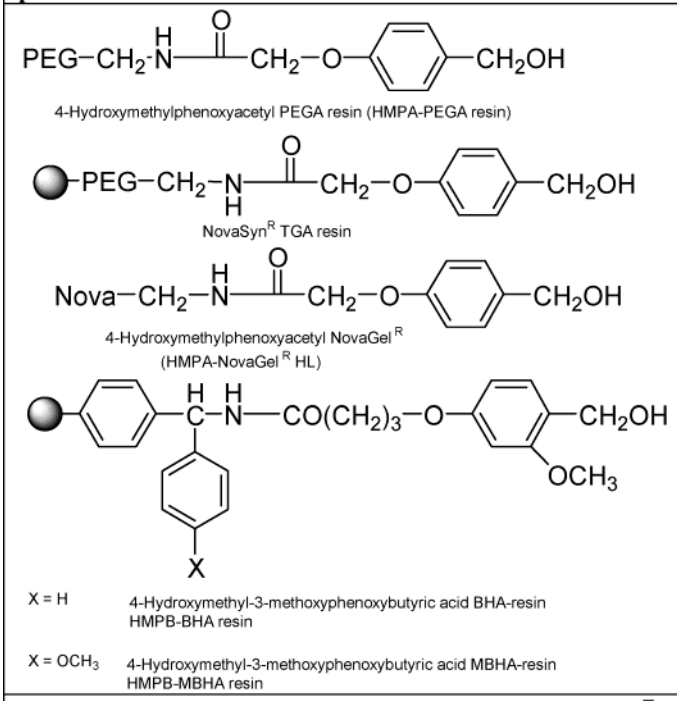
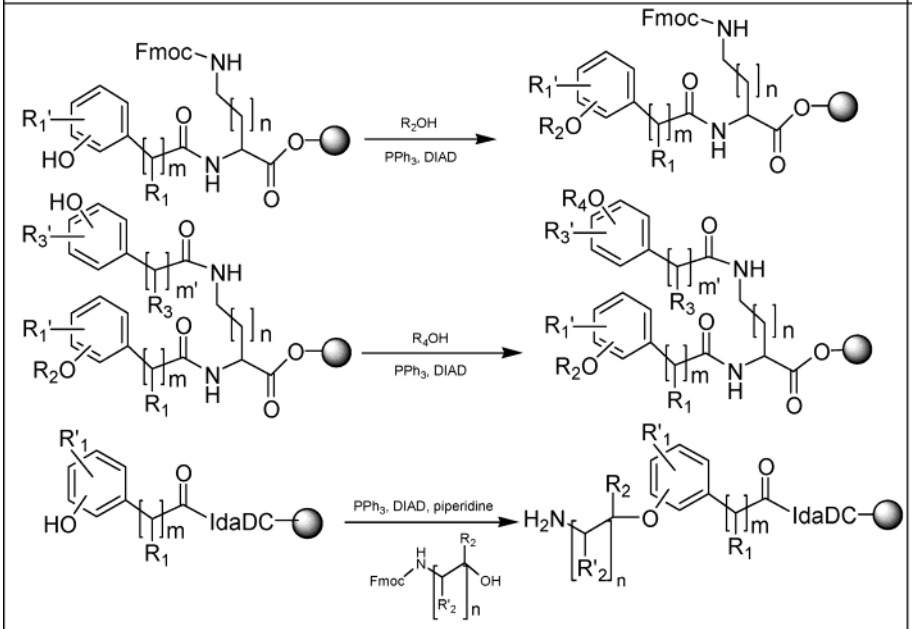
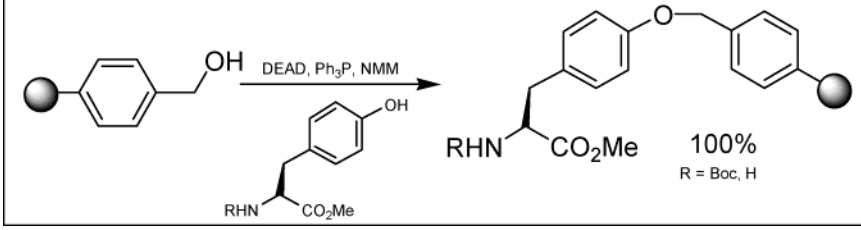
II.1.2.1. Mitsunobu reaction to immobilize hydroxyl functional group as phenol ethers	Comments and References
	**4-Hydroxymethylphenoxyacetyl PEGA resin (HMPA-PEGA resin)** **NovaSyn^R TGA resin,** **4-Hydroxymethylphenoxyacetyl NovaGel^R (HMPA-NovaGel^R HL)** **4-Hydroxymethyl-3-methoxyphenoxybutyric acid BHA-resin (HMPB-BHA resin)** **4-Hydroxymethyl-3 methoxyphenoxybutyric acid MBHA-resin (HMPB-MBHA resin)** - Resins for immobilization of phenols using the Mitsunobu reaction[275,277]
	**Derived from polystyrene resin** - Library of *N*,*N*-bis-(alkoxy acyl)diaminoacids - Library of *N*-acyl amino ethers - 600 phenolic compounds were isolated.[278]
	**Hydroxymethyl polystyrene resin** - Substitution level 0.03-0.9 meq/g in different solvents[275]

Table 2 (Continued)

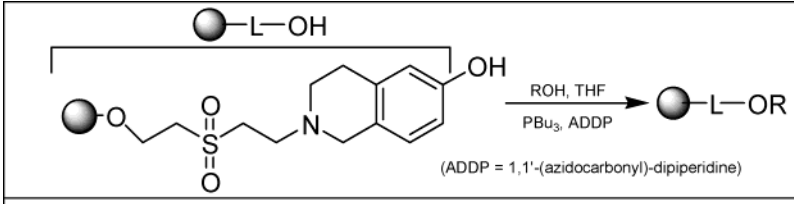
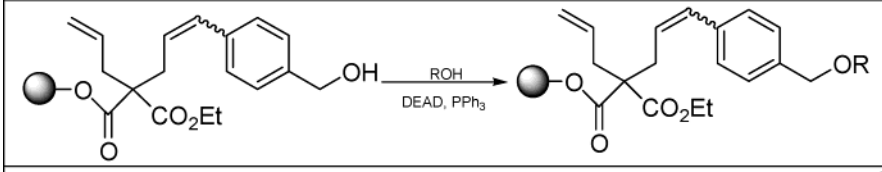
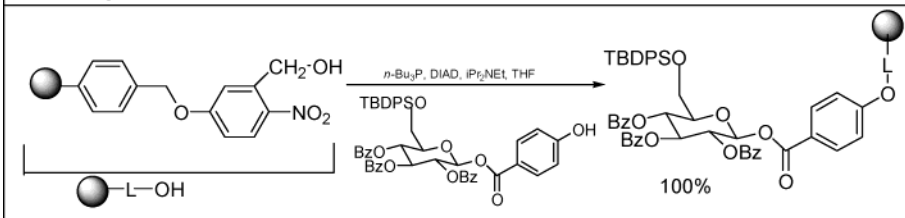
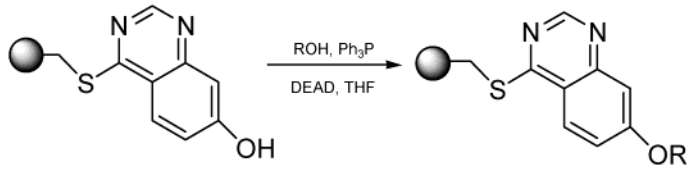
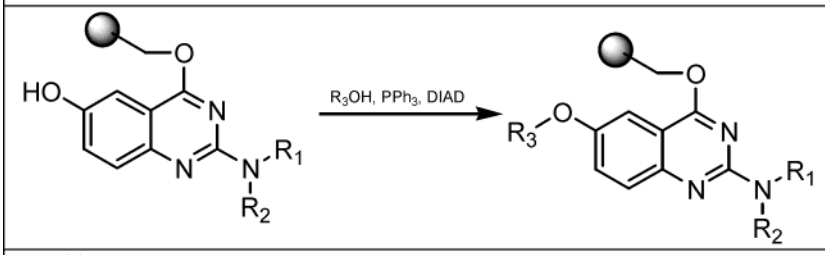
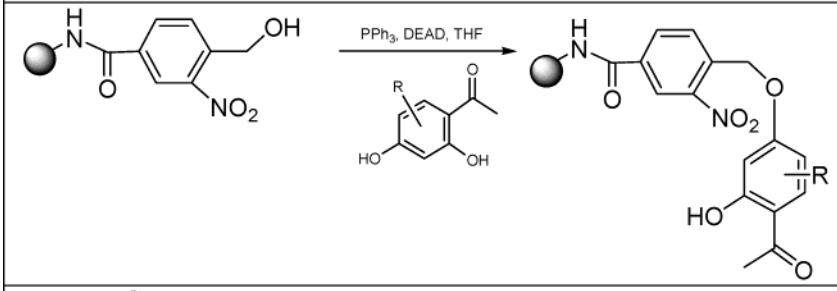
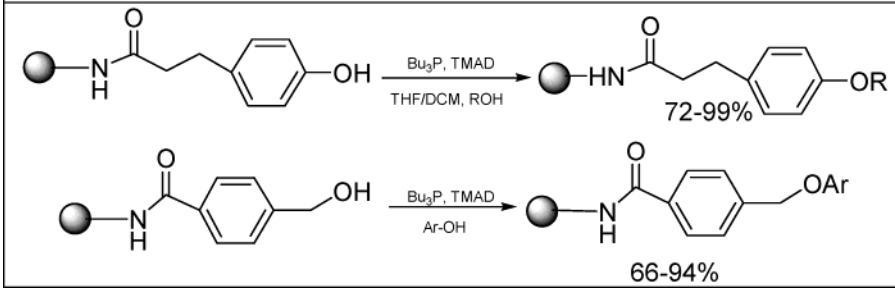
	**Derived from hydroxymethylene resin** - Preparation of derivatives of tetrahydroisoquinolines - Ten examples; overall yields reported 80-90%[288]
	**Derived from Merrifield resin** - One example - Overall yield reported[289]
	**Derived from Merrifield resin** - Construction of a dodecasaccharide[290]
	**Derived from Merrifield resin** - Synthesis of oxindole quinazolines using solid phase multiparallel chemistry[291]
	**Derived from Wang resin** - Novel synthesis of 2,6-disubstituted 4(3*H*)-quinazolinones reported[292]
	**Derived from TG resin** - Dihydropyrans synthesis[204]
	**Derived from TentaGel resin-supported benzyl alcohol** - Solid-phase synthesis of aryl ethers via the Mitsunobu reaction[275,277,279,293]

Table 2 (Continued)

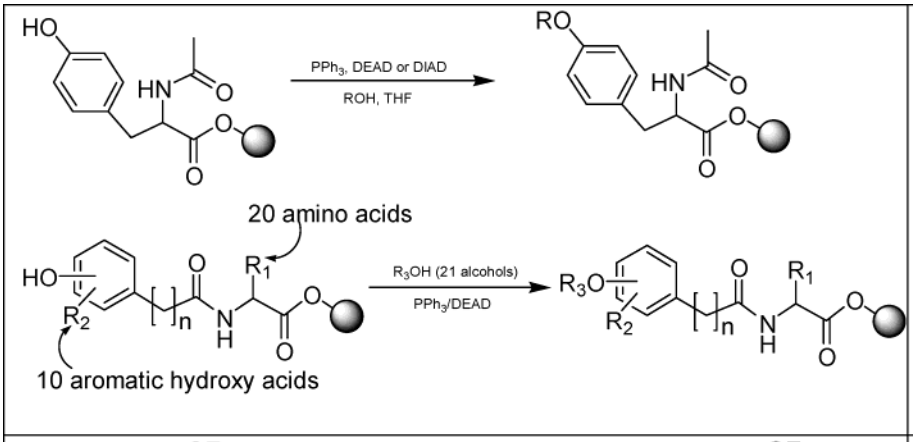
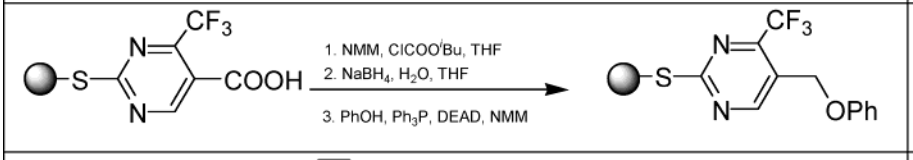
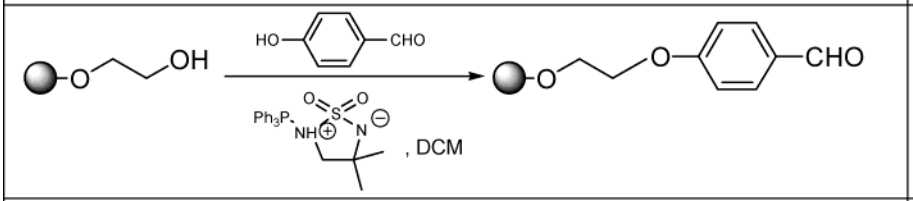
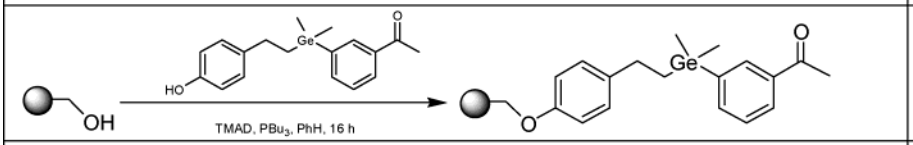
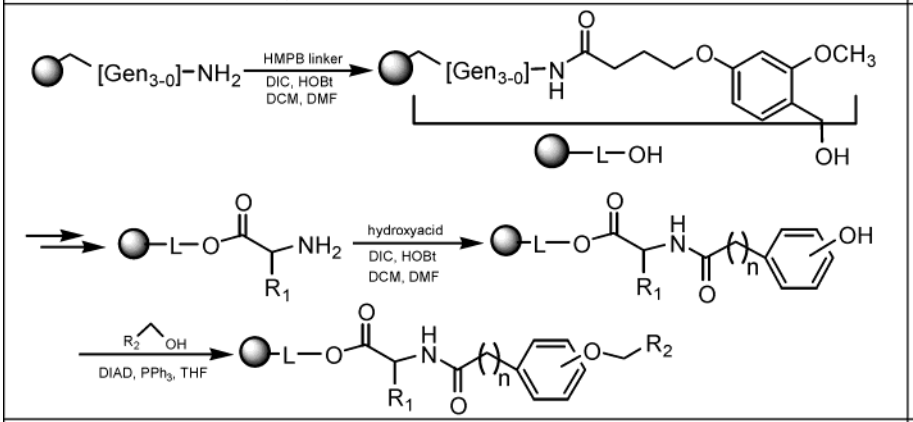
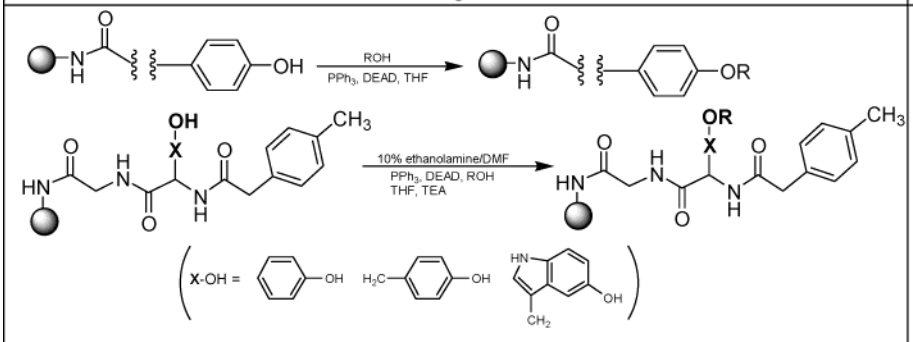
	***N*-acetylated tyrosine on polyethyleneglycol grafted PS-1% DVB** - Polymer-supported Mitsunobu ether formation on phenolic hydroxy groups of resin bound Ac-Tyr - *O*-alkylated *N*-acetyl tyrosine for different primary alcohols (39-99%) - Library containing 4200 compounds, 21 alcohols (aromatic, aliphatic and heteroaromatic alcohols as well as diols and *N*-protected amino alcohols), 20 natural amino acids, 10 aromatic hydroxy acids - Yield 60-95% when R = CH_3 (glycine)[294]
	**NovaSyn^R TG thiol resin (TentaGel SH resin)** - Traceless linker - Safety-catch thioether - Sulfur-based linker for attachment of small heterocycles[295]
	**Derived from ArgoGel^{TM} resin** - Preparation of secondary amide-based linkers - Preparation of ureas, sulfonamides, aryl amides, and alkyl amides - Overall yield reported[296]
	**ArgoGel^{TM}** - New germanium-based linker for solid phase synthesis of pyrazole library[297]
	**High loading dendrimer resin** - Used for synthesis of aryl ethers. - Five examples; yields 67-100%. - Better than normal TentaGel resin[298]
	**PIN = [Polyethylene Pin]-[MA/DMA]-HMD-$COCH_2NH$-(Rink handle)$_{16}$** - Alkylation of pin-bound phenols[299]

Table 2 (Continued)

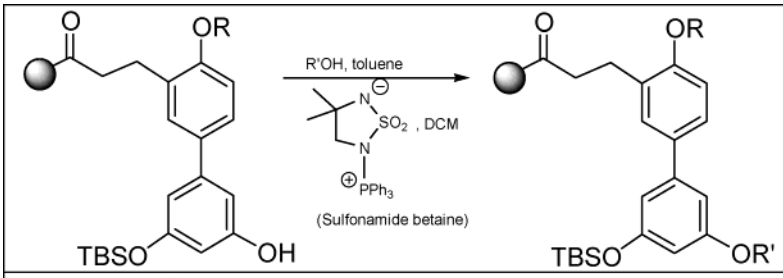
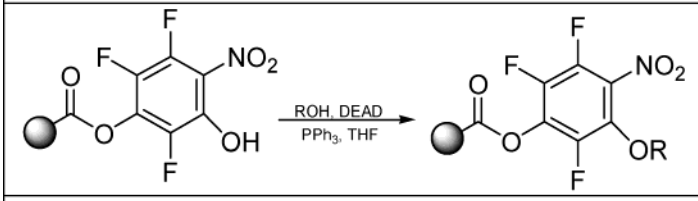
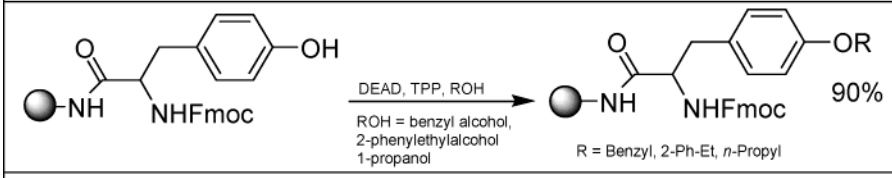
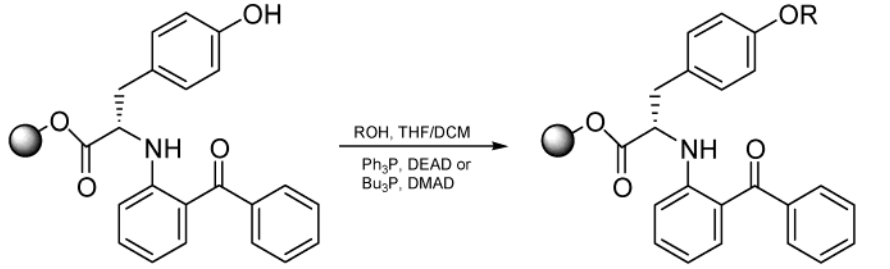
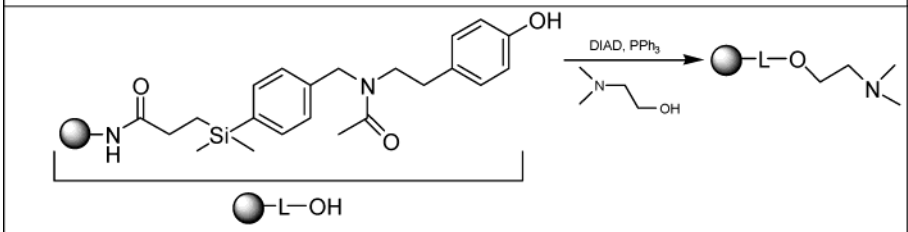
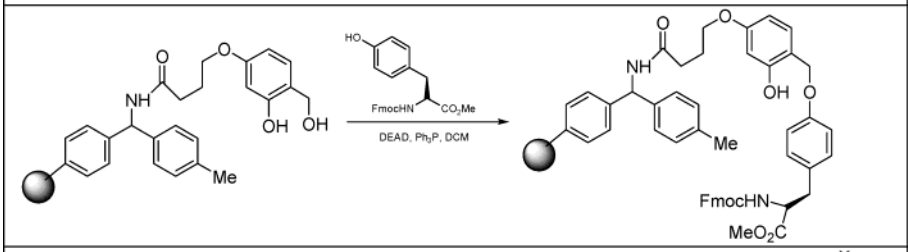
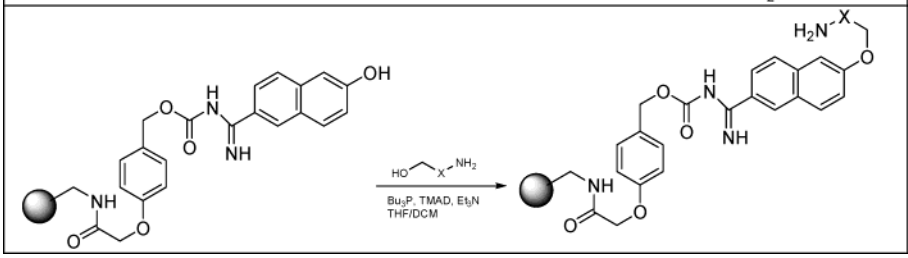
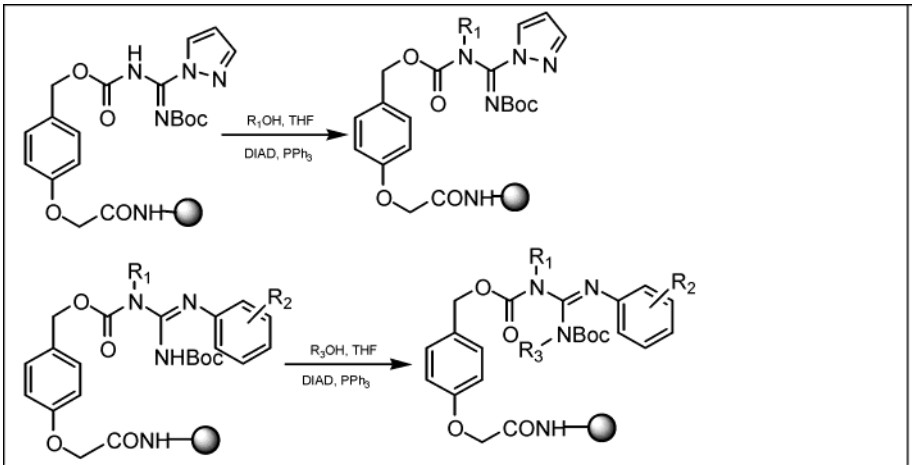
	**Biphenyl phenol linker from polystyrene carboxylic resin** - Mitsunobu functionalization of biphenyl phenols[300]
	**Derived from carboxypolystyrene** - Synthesis of farnesyl transferase inhibitors[301]
	**Fmoc-tyrosine coupled to deprotected Rink Amide resin** - Mitsunobu *O*-alkylation[302]
	**Derived from trityl chloride resin** - Synthesis of *N*-(2-benzoylphenyl)-L-tyrosine PPAR gamma agonists[303]
	**Derived from BHA resin** - Simple silyl linker for the synthesis of aryl-containing molecules - *O*-Alkylation[304]
	**Derived from HMPA-MBHA resin** - Phenol attachment - Synthesis of tyrosine-containing cyclic peptides[305]
	**Derived from HMPA carbonate resin** - Immobilization of aminoalcohols[306]

Table 2 (Continued)

	**Derived from polystyrene amine resin** - Acid-labile linker - Mitsunobu alkylation of a resin-bound bis-carbamoyl pyrazole followed by displacement of the pyrazole by anilines, and a second Mitsunobu alkylation to yield the trisubstituted guanidine after cleavage. - Used for synthesis of a library of substituted guanidines[323]
	Derived from aminomethyl polystyrene resin - A straightforward synthesis of substituted sulfamides described[324]

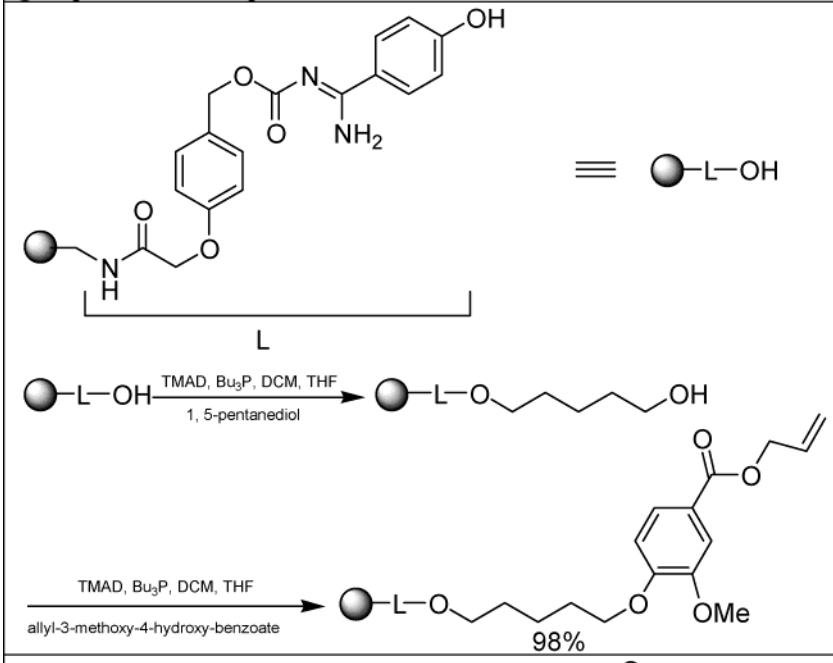
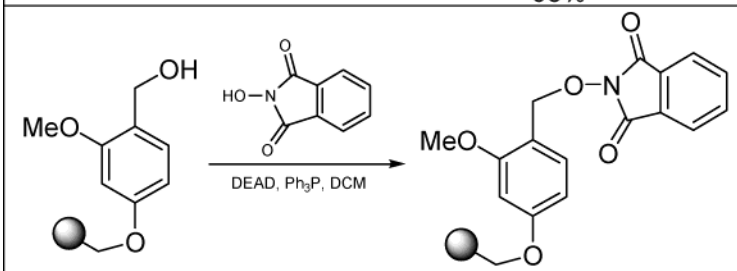
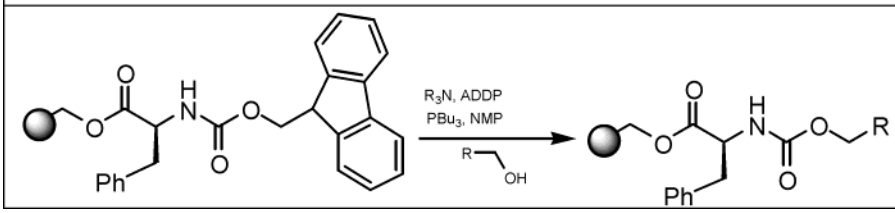
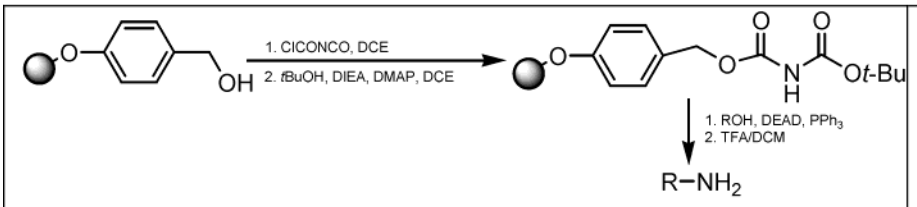
II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)	
II.1.2. Mitsunobu reaction	
II.1.2.3. Mitsunobu reaction for immobilization of hydroxyl functional groups of other compounds	**Comments and References**
	**Derived from aminomethyl polystyrene resin** - A linker for amidines[325]
	**Derived from Sasrin resin** - Solid-phase synthesis of hydroxamic acid based TNF-α convertase inhibitors[326]
	**Substituted Wang resin** - Used for synthesis of carbamates - Yields: 40-82% (eight examples)[327]

Table 2 (Continued)

	**Polymer bound iminodicarbonate resin** - Used for Mitsunobu reaction to synthesize primary amines - Nine examples; yields 0-85%[328]

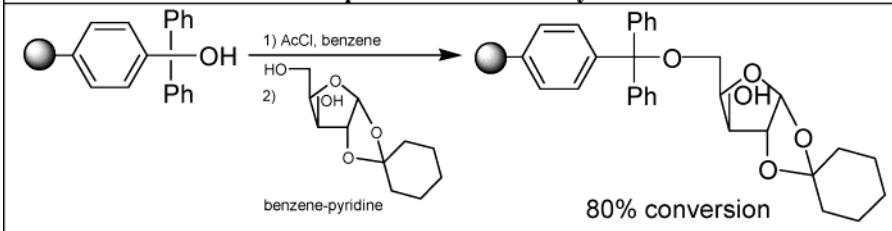
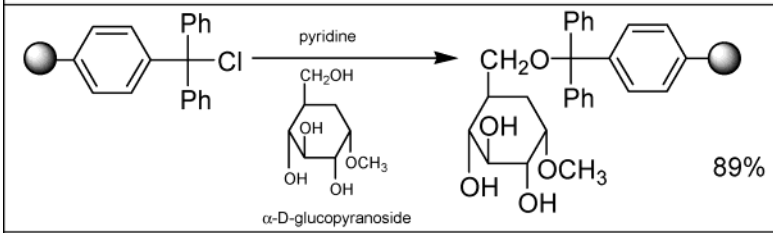
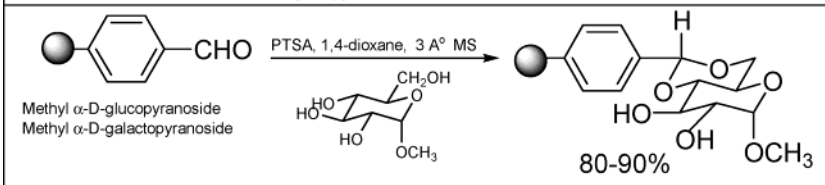
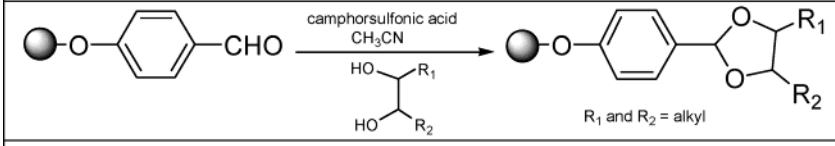
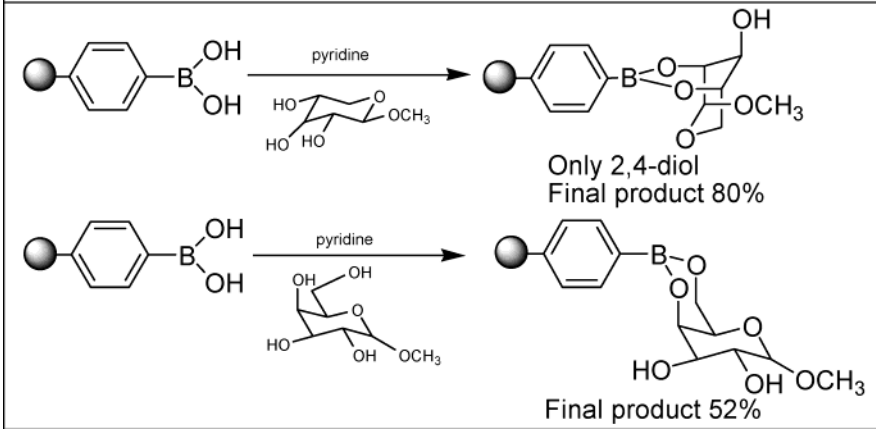
II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)	
II.1.3. Carbohydrate reactions	
II.1.3.1. Immobilization and protection of carbohydrates	**Comments and References**
	**Tritylated polymer (styrene-2%-DVB)** - Copolystyrene-DVB incorporating a chiral group (1,2-*O*-cyclohexylidine-D-xylofuranose) - Used in asymmetric synthesis of atrolactiv acid - 80-87% yields for resin - Asymmetric synthesis (synthesis of α-hydroxy acids on insoluble polymer supports) - D or L obtained in 73-87% yields[333]
	**Polystyrene trityl chloride resin** - Use of polymers as protecting groups of primary alcohol functional groups - Glycoside synthesis - Final product overall yield 86%[224]
	**Derived from Merrifield resin** - Crosslinked microreticular resin and polystyrene-DVB 1% - Attachment of various carbohydrates in the form of benzylidene acetals to a Merrifield type of resin - Applications of organic polymers as supports and protecting groups - Glycoside synthesis - Resin-bound aldehyde as protective group for carbohydrates - Protection of diols - Preparation of partially substituted derivatives of D-glucose - Polymer containing vinylbenzaldehyde used as a protecting group in the synthesis of partially substituted derivatives of methyl α-D-glucopyranoside[224,225,231,334]
	**Wang aldehyde resin** - Formation of *p*-alkoxybenzylidene acetals on solid support - Six examples; yield of products after acetal formation and cleavage 70-92%[106]
	**Polystyrylboronic acid (copolystyrne-DVB incorporating a boronic acid)** - Diol protection in carbohydrate synthesis - Application of polystyrylboronic acid to the one-pot synthesis of acylated carbohydrate derivatives - Glycoside synthesis - Partial acylation of cyclic polyols[262,263,335]

Table 2 (Continued)

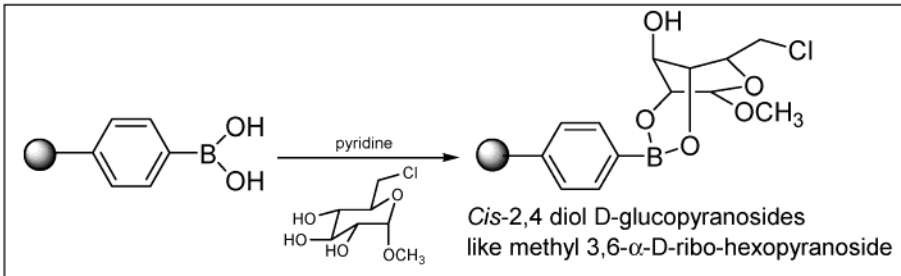
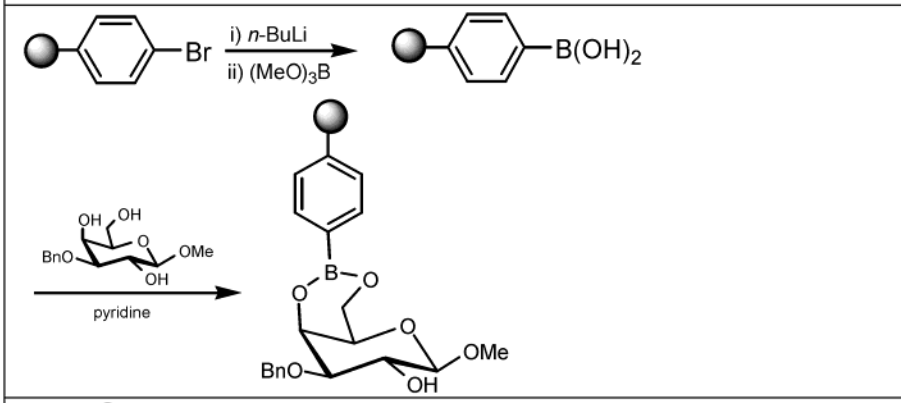
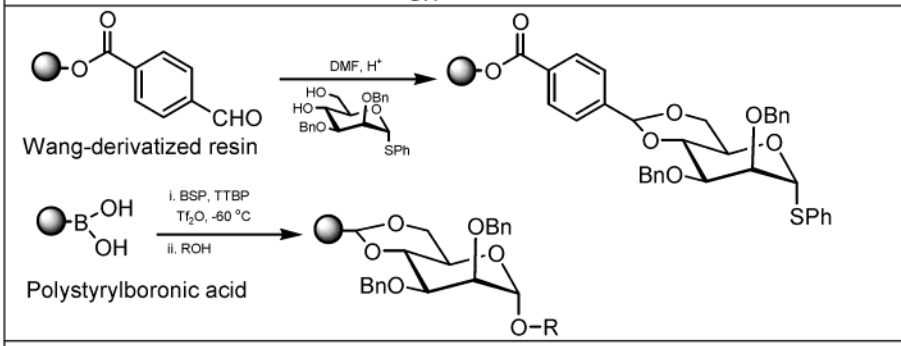
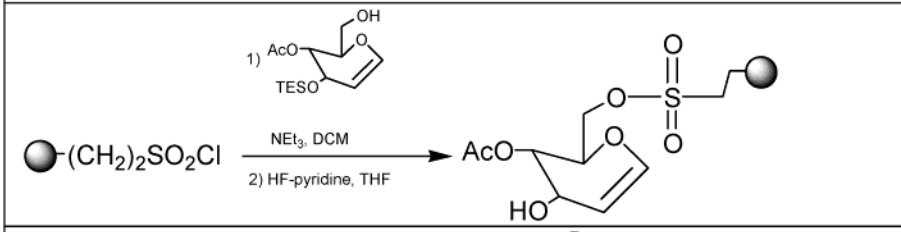
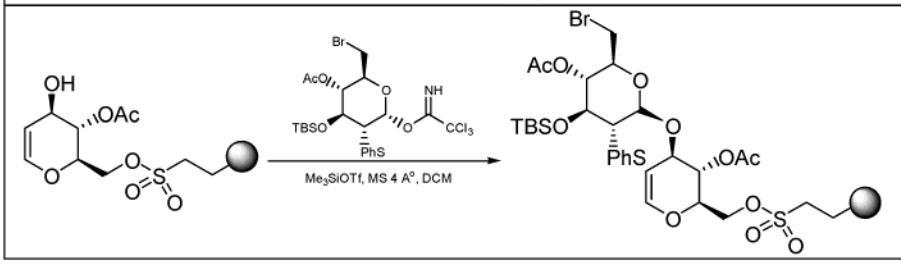
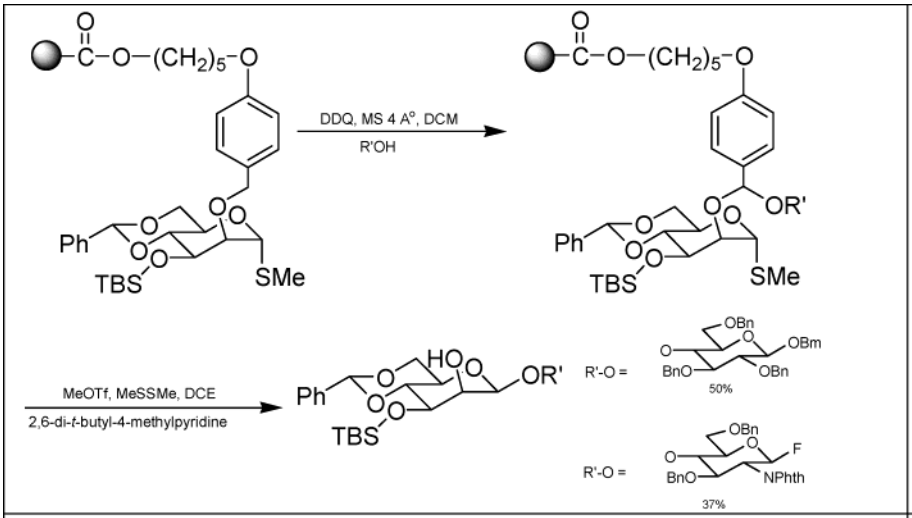
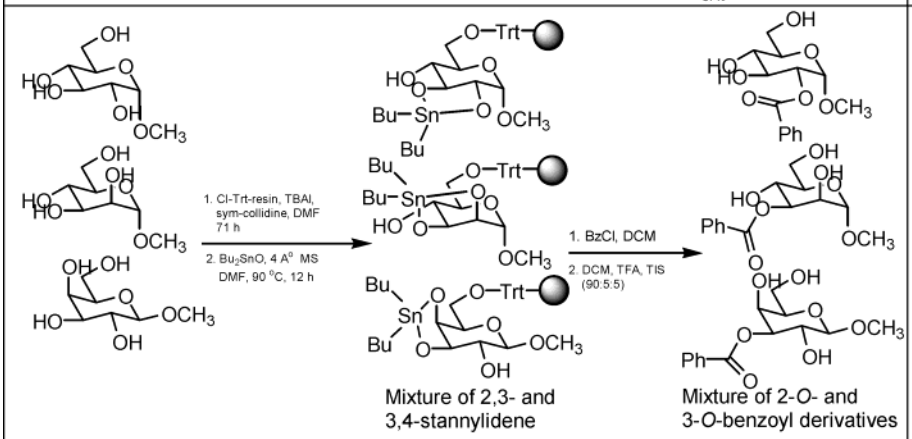
	**Polystyrylboronic acid** - Preparation of a deoxy-sugar[262]
	**Polystyrylboronic acid** - A reusable polymeric support for oligosaccharide synthesis prepared[336]
	**Wang-derivatized and polystyrylboronic acid resins** - Six examples; yields: 73-84%[337]
	**Derived from Merrifield resin** - Solid-phase synthesis of 6-deoxyoligosaccharide - 67% isolated yield for final product - Also methyl 4-*O*-acetyl-2,3-di-*O*-benzyl-α-D-glucopyranoside couples with resin in 93-97% yields[338]
	**Derived from Merrifield resin** - Glycosidation of support-bound alcohols with trichloroacetamides[338]

Table 2 (Continued)

	**Derived from PEG resin** - Protecting group strategy for oligosaccharides - Axial 2-OH group direct the aglycon in the glycosylation reaction to the β face - Synthesis of β-mannosides[339]
	**Derived from chlorotrityl resin** - Used for the immobilization of carbohydrates - Subsequent tin-mediated regioselective acylation. - Carbohydrate unprotected. - Regioselectivity > 98% - Yields: 60-98%[340]

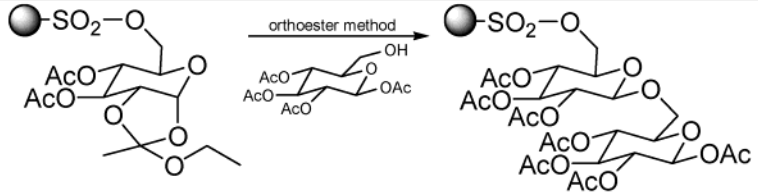
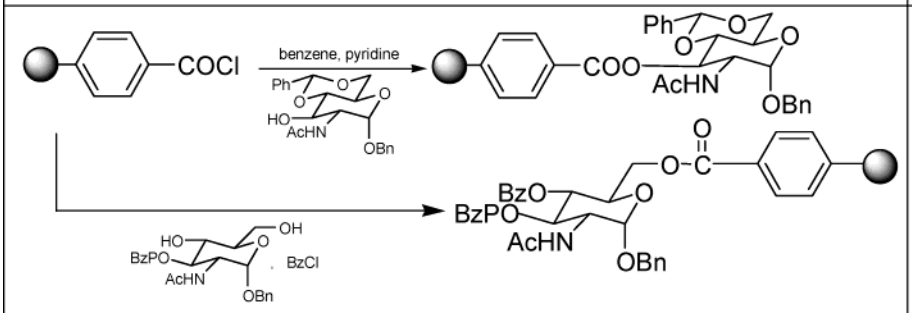
II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)	
II.1.3. Carbohydrate reactions	
II.1.3.2. The synthesis of disaccharides and polysaccharides (glycosylation reactions)	**Comments and References**
	**Derived from free radical polymerization of 1,2,3,4-tetra-*O*-acetyl-6-*O*-(*p*-vinylphenylsulphonyl)-β-D-glucopyranose with styrene to yield a copolymer containing 6% of the substituted styrene units** - Transorthoesterification followed by rearrangement - Octaacetate of gentiobiose in 42% yield[341,342]
	**Derived from crosslinked styrene-DVB popcorn polyamide** - Esterification using benzyl-2-acetamido-2-deoxy-4,6-*O*-benzylidene-α-D-glucopyranoside - Solid-phase synthesis of 2-acetamido-6-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-2-deoxy-D-glucose - Preparation of β-(1-3)-linked aminosugar disaccharide (51% overall yield)[343,344]

Table 2 (Continued)

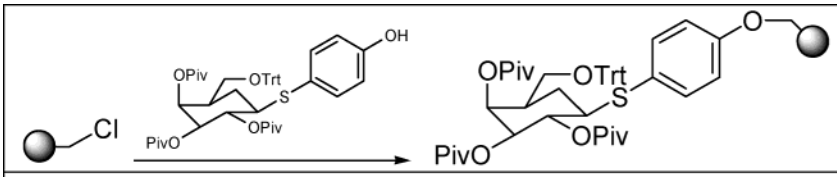
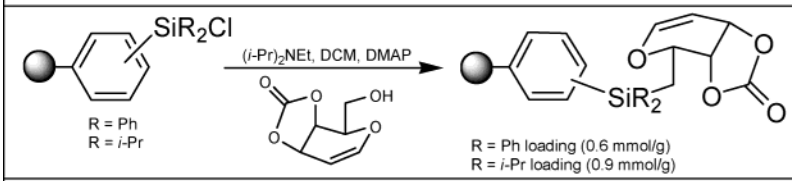
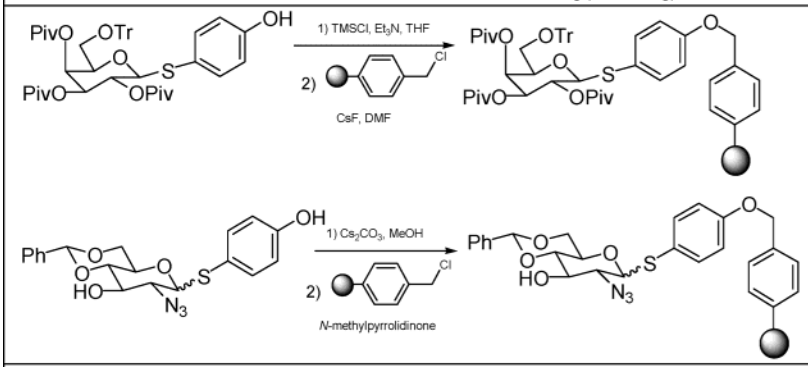
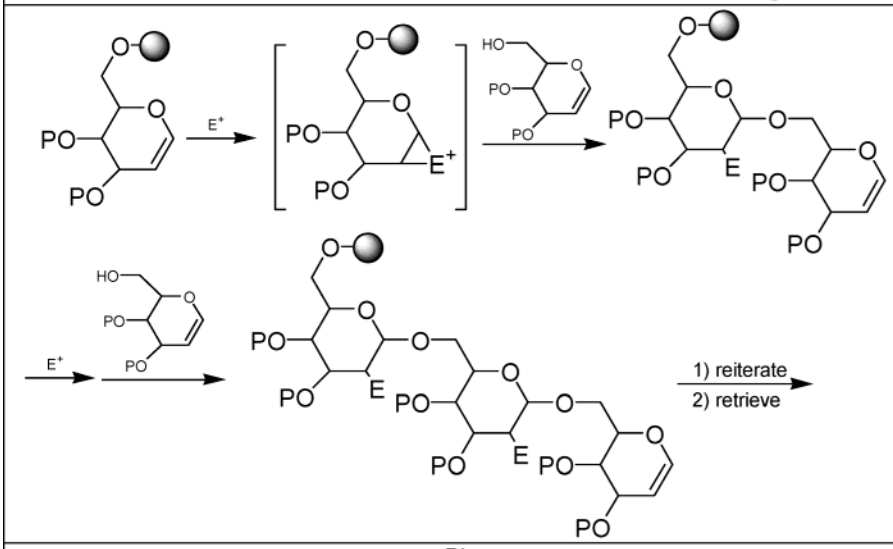
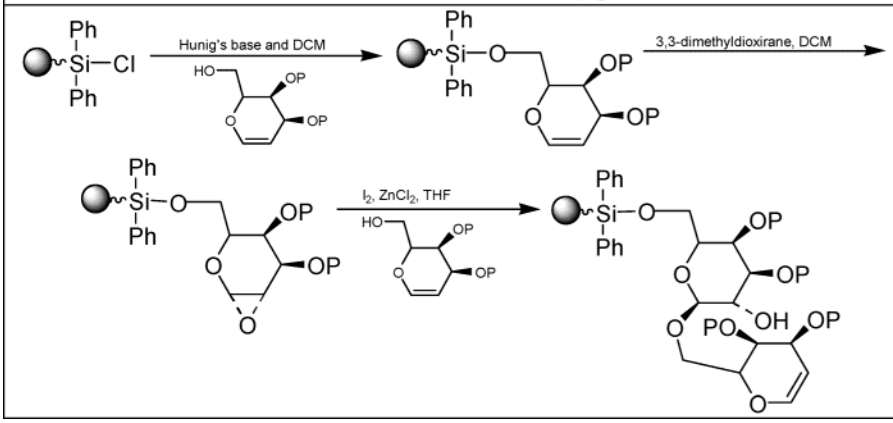
	**Merrifield resin** - Glycosyl oxazoline donor chemistry- α-(1-6)-linked disaccharide[344]
	**Derived from polystyrene-DVB (1%)** - Preparation of a polymer-linked glycal - For preparation of β-(1-6)-linked oligosaccharides[345]
	**Merrifield resin** - Attaching of a monosaccharide to Merrifield resin via a *p*-hydroxythiophenyl linkage - Overall yield of 52% for trisaccharide - Glycosylation using anomeric sulfoxides[330]
	**Derived from Wang resin** - Solid-phase carbohydrate synthesis employing glycals - Glycal assembly method[346-348]
	**Derived from polystyrene-DVB copolymer** - Applicable to synthesizing glycopeptide and glycosylated proteins as well as oligosaccharides - Synthesis of oligosaccharides from glycals - The average yield per coupling cycle consisting of epoxidation and glycosidation: 70%[329,347,349]

Table 2 (Continued)

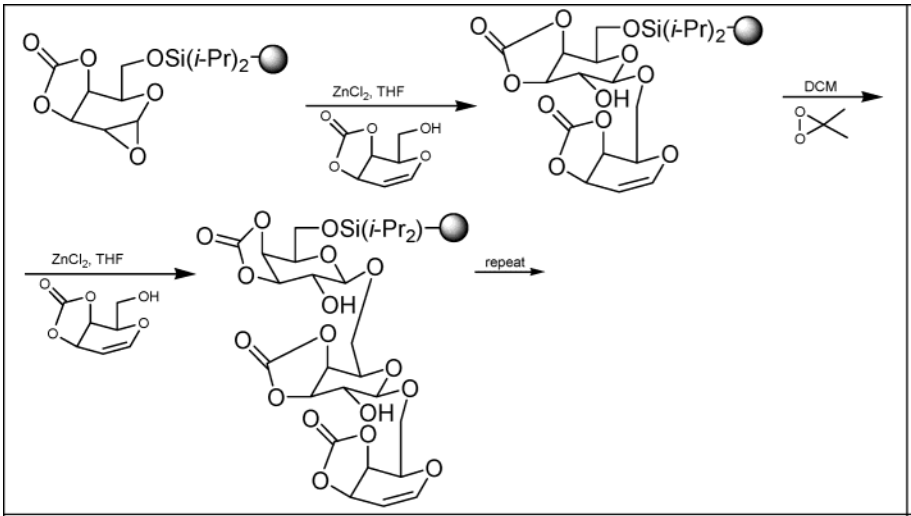
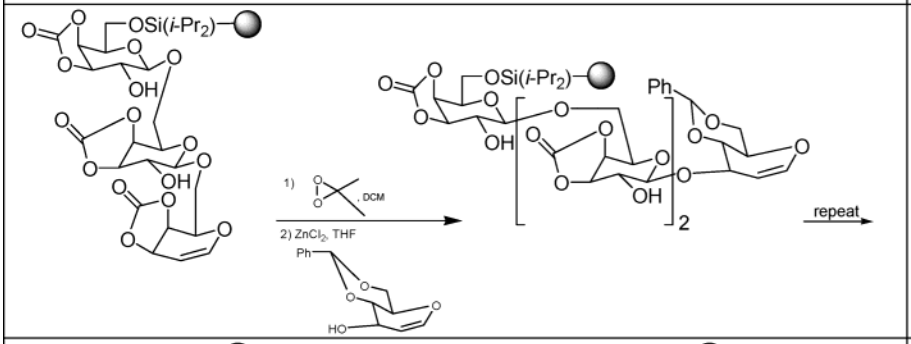
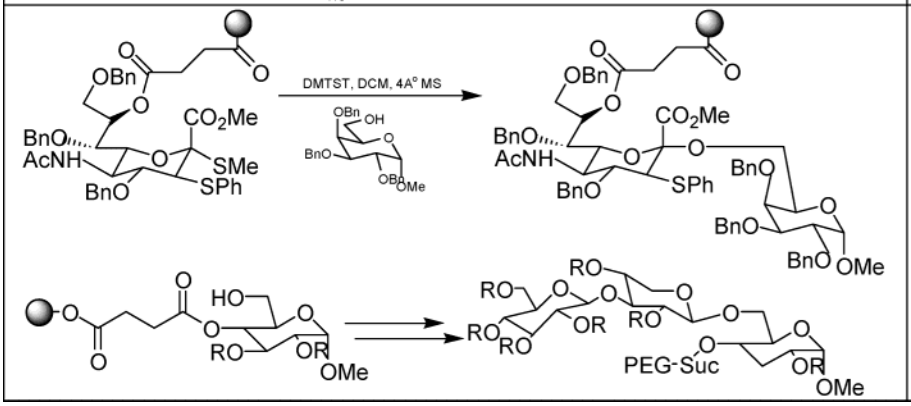
	**Derived from polystyrene-DVB copolymer** - Solid-phase synthesis of oligosaccharides using glycal-based donor technology - Solid-phase synthesis of 1,6-linked polysaccharide residues - 90% two-step coupling stage - 74% overall yield - Using Ph instead of *i*-Pr: overall yields 32% and 70% per two step coupling stage - Synthesis of Lewis β antigen[329,347,349-351]
	**Derived from polystyrene-DVB copolymer** - Coupling yield 80% - Solid-phase synthesis of hexasaccharide (29% overall yield)[347,351]
	**Succinylated polyethylene glycol monomethyl ether (MPEG)** - Soluble polymeric reagents - Sialic acid glycosyl donor supported on MeO-PEG - For use in glycosylation of galactose analogues to give α-linked disaccharides - Stereoselective glycosylation - Yields for cleaved disaccharides: 65-70%[352,353]

Table 2 (Continued)

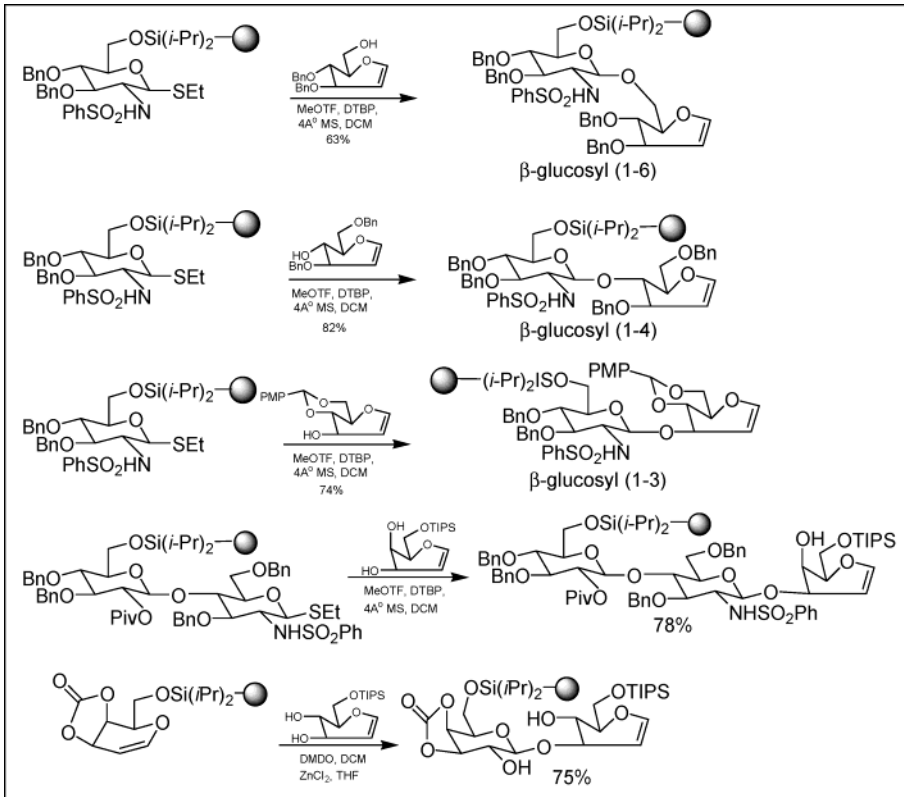
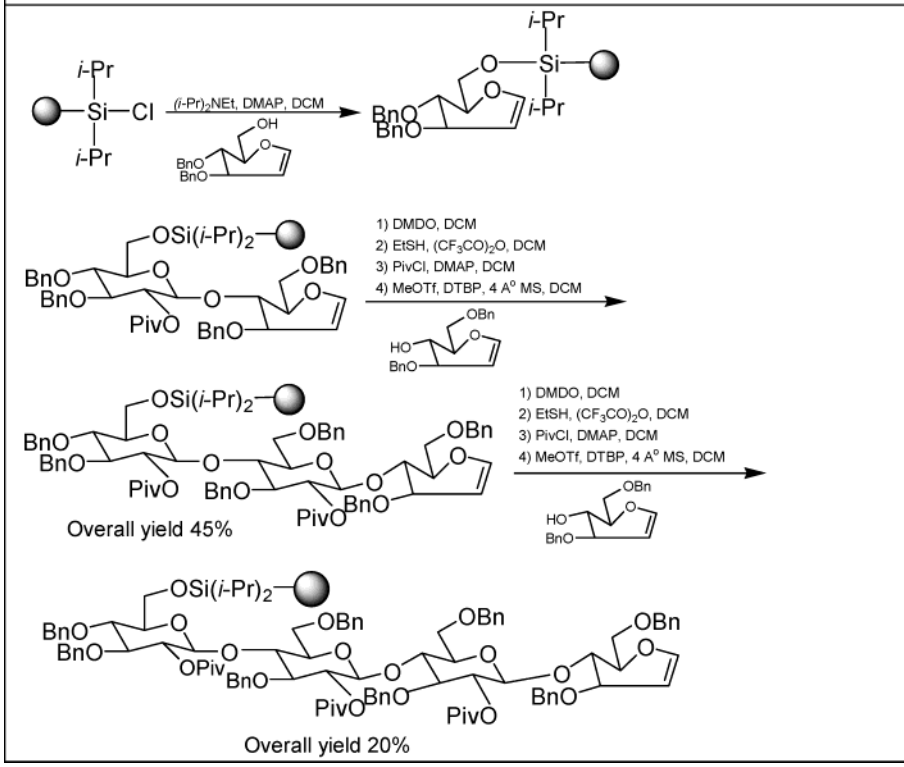
	**Polymer-bound ethylsulfanyl-2-amidoglucosyl** - Polymer-bound glycal - Synthesis of oligosaccharides from glycals - Construction of α-linked oligosaccharides by coupling of glycal derived thioethyl glycosyl donors - Complete solid-phase synthesis of the oligosaccharide domain of the Lewis β blood group determinant[116]
	**Silylated polystyrene polymer resin** - Polymer-bound thioethyl glucosyl donor - Polymer-bound glycal - Construction of β-linked oligosaccharides by coupling of glycal derived thioethyl glycosyl donors - Solid-phase synthesis of β(1-4) linked glucosides[117]

Table 2 (Continued)

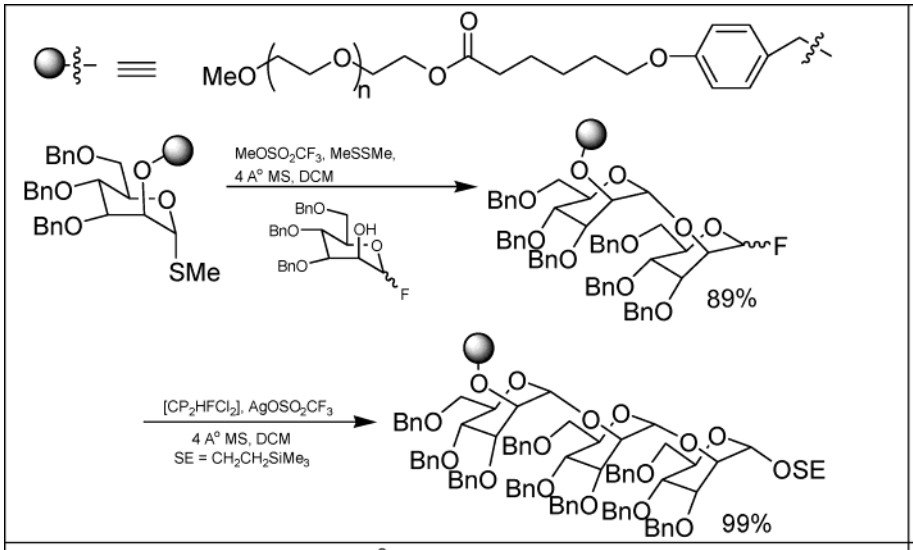
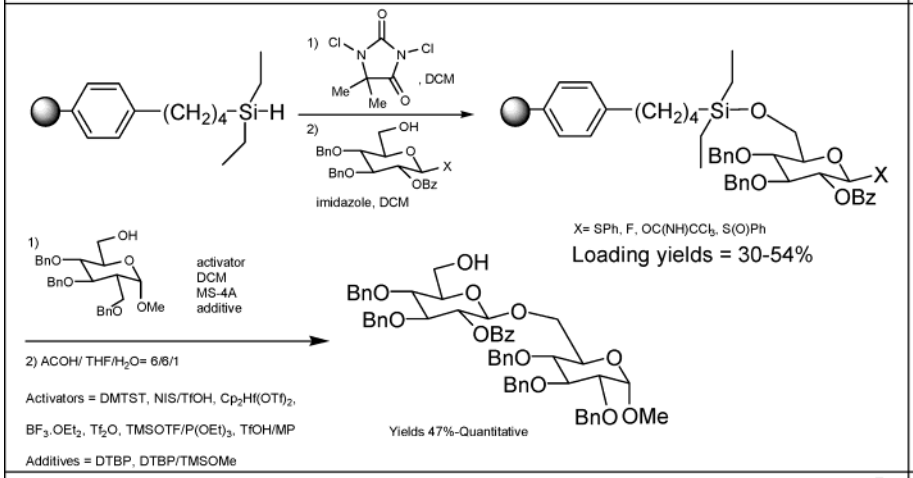
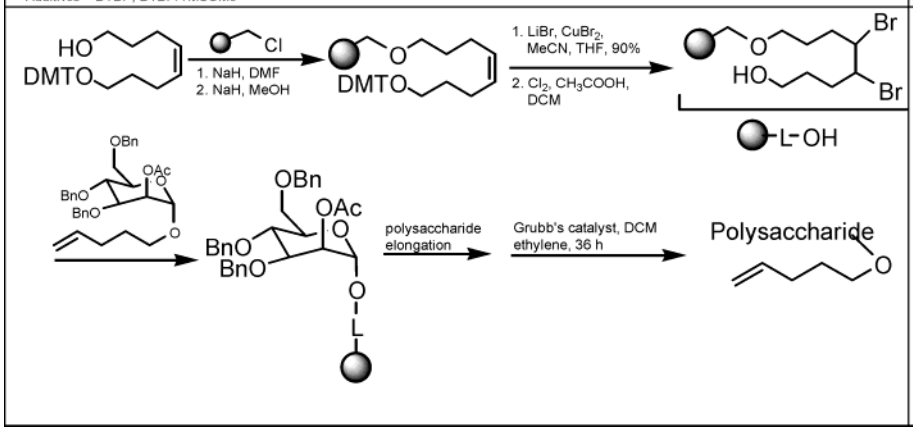
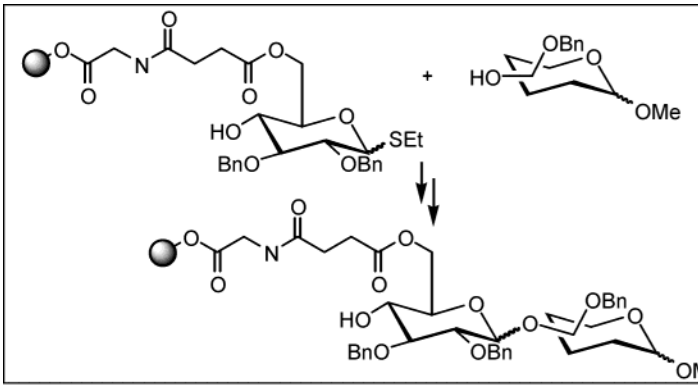
	**PEG monomethyl ether soluble monoether** - Orthogonal glycosylation strategy for rapid assembly of oligosaccharides on a polymer support[354]
	**PS-DES resin** - Glycosylation of solid-supported glycosyl donors tethered by a trialkylsilane linker[355]
	**Derived from Merrifield resin** - A 4,5-dibromo-1,8-diol linker - Used for the synthesis of polysaccharides[356]

Table 2 (Continued)

	**Derived from Wang resin** - Review of the role of combinatorial chemistry toward understanding the function of carbohydrates and carbohydrate conjugates[357]

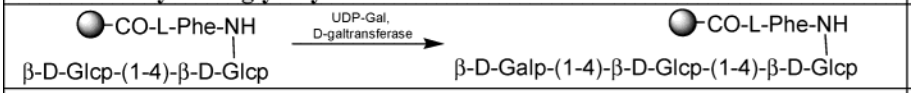
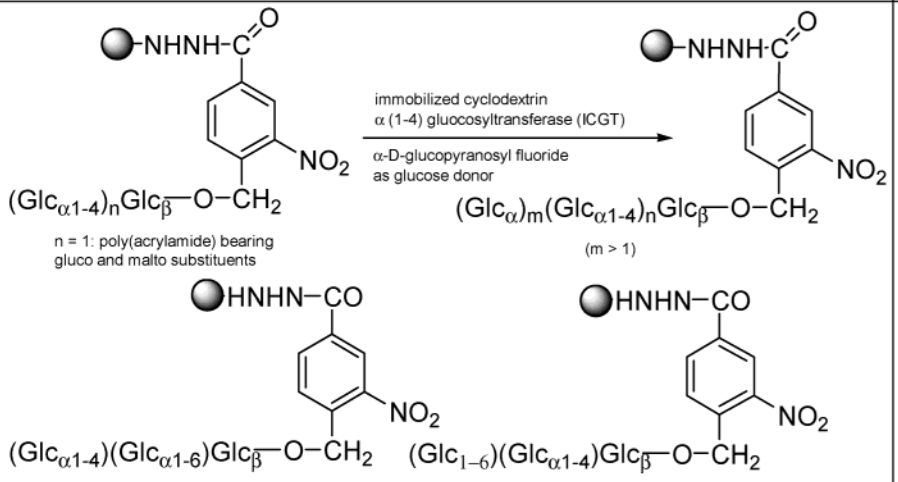
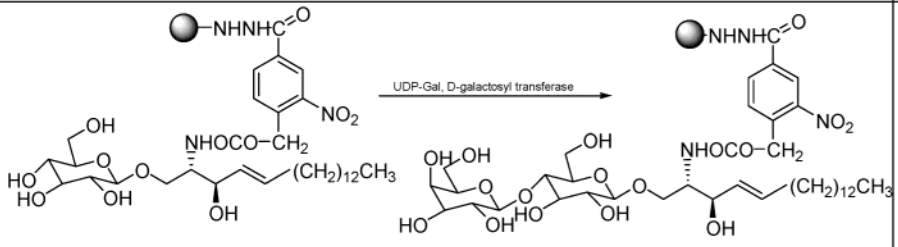
II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)	
II.1.3. Carbohydrate reactions	
II.1.3.3. Enzymatic glycosylation	**Comments and References**
	**Poly(acrylamide)-poly(*N*-acryloxysuccinimide) (PAN)** - Enzymatic synthesis of oligosaccharides[358,359]
	**Aminoethyl-substituted polyacrylamide gel beads** - Highest transfer (4.2%) for the polymer bearing maltotriose groups - Glycogen synthase reaction with polymer-bound oligosaccharides[360]
	**Poly(acrylamide)-poly (*N*-acryloxysuccinimide)(PAN)** - Synthesis of oligosaccharides (glysphinolipids) on solid supports - 36% transfer yield - Final product yield after cleavage 54% - Catalysed incorporation of D-glucose into acceptor polymers[361,362]

Table 2 (Continued)

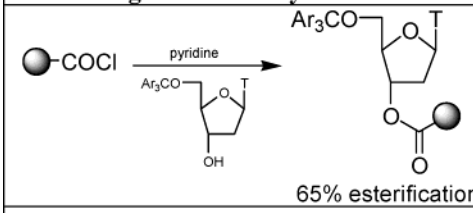
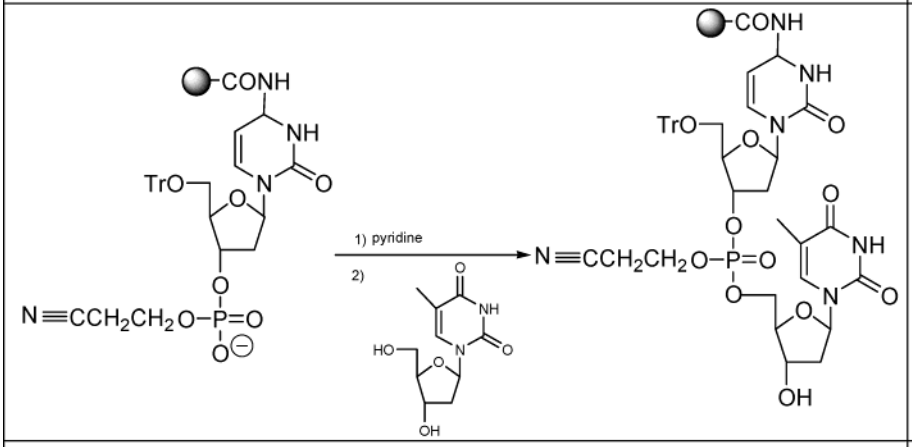
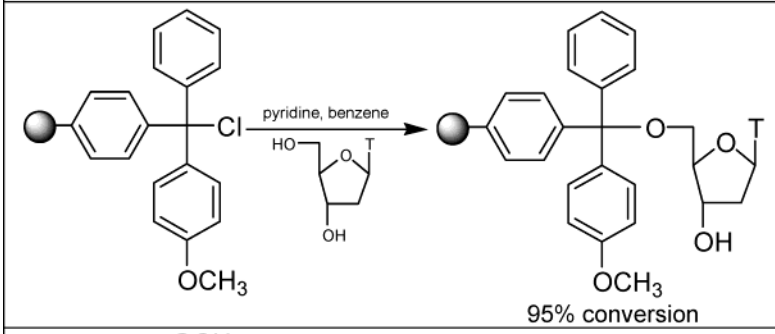
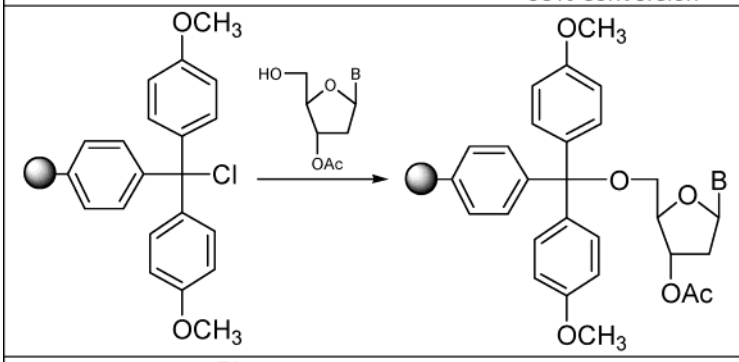
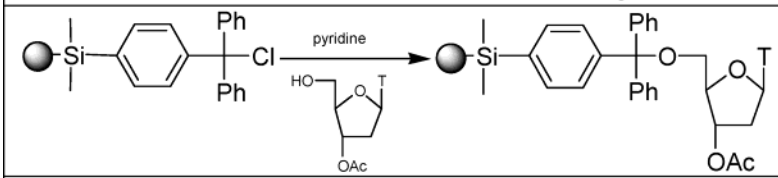
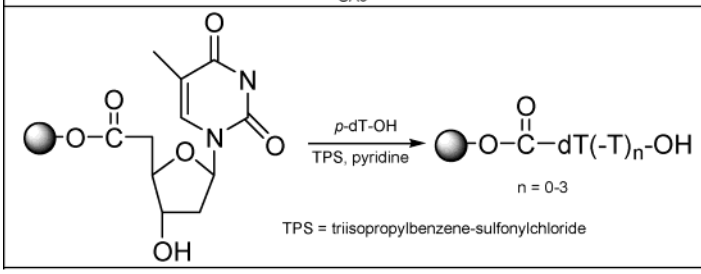
II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)	
II.1.4. Oligonucleotide synthesis	**Comments and References**
	**Derived from carboxylated styrene popcorn polymer** - Synthesis of thymidylylthymidylylthymidine[384,385]
	**Derived from popcorn polymer of styrene, *p*-vinylbenzoic acid and divinylbenzene** - Synthesis of oligodeoxyribonucleotides - Yield for TrdCPT 61% based on the amount of trityldeoxycytidine bound to the support[386]
	**Derived from crosslinked polystyrene with monomethoxytrityl chloride groups (polymer-supported *p*-methoxytrityl chloride)** - Used in oligonucleotide synthesis - Stepwise synthesis of trithymidine diphosphate - Thymidylyl-(3'-5')-thymidylyl-(3'-5')-thymidine isolated in 38% conversion based on polymer-bound dinucleoside phosphate[387]
	**Polymeric dimethoxytrityl chloride** - Coupling yields 50-60%[388]
	**Silica-bound trityl group** - Oligonucleotide synthesis - Yield for dTpdT(Ac) 54%[389]
	***N*-Vinylpyrrolidone-vinylacetate copolymer** - Oligonucleotide synthesis[390]

Table 2 (Continued)

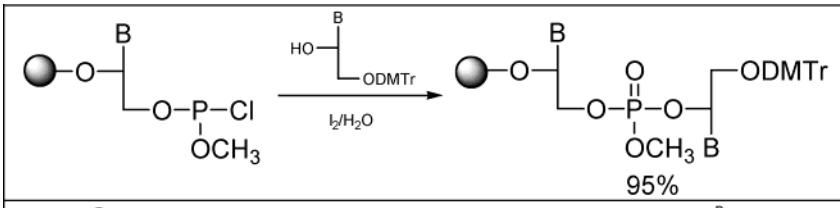
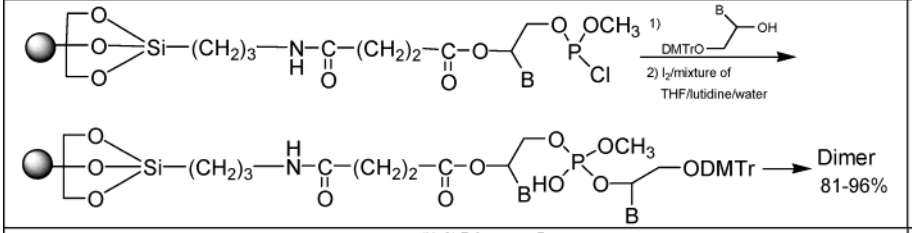
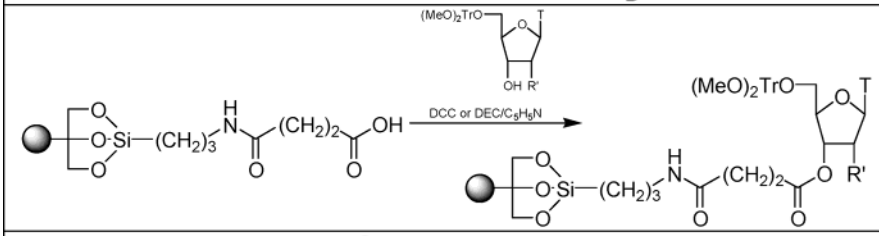
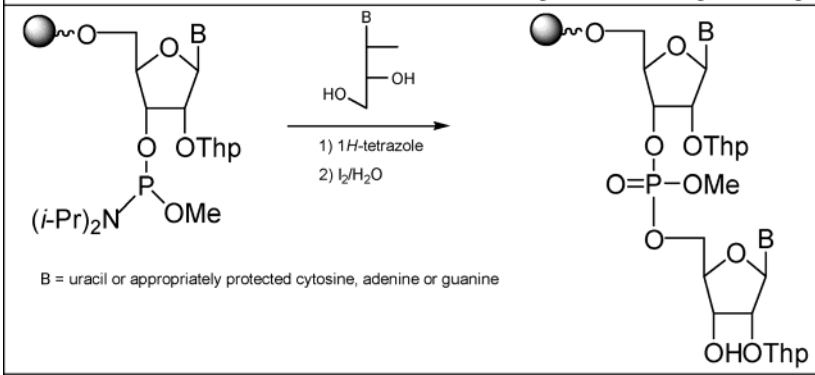
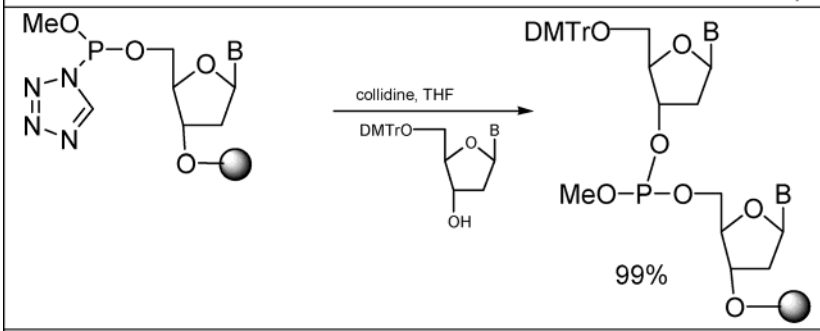
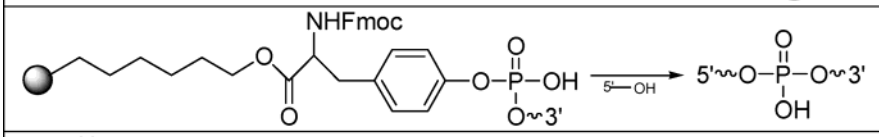
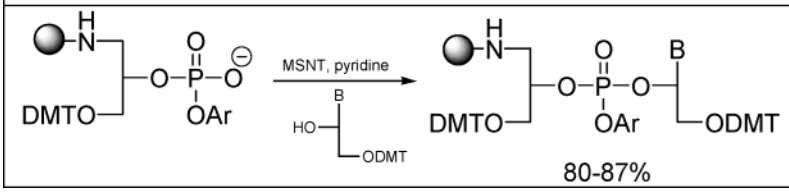
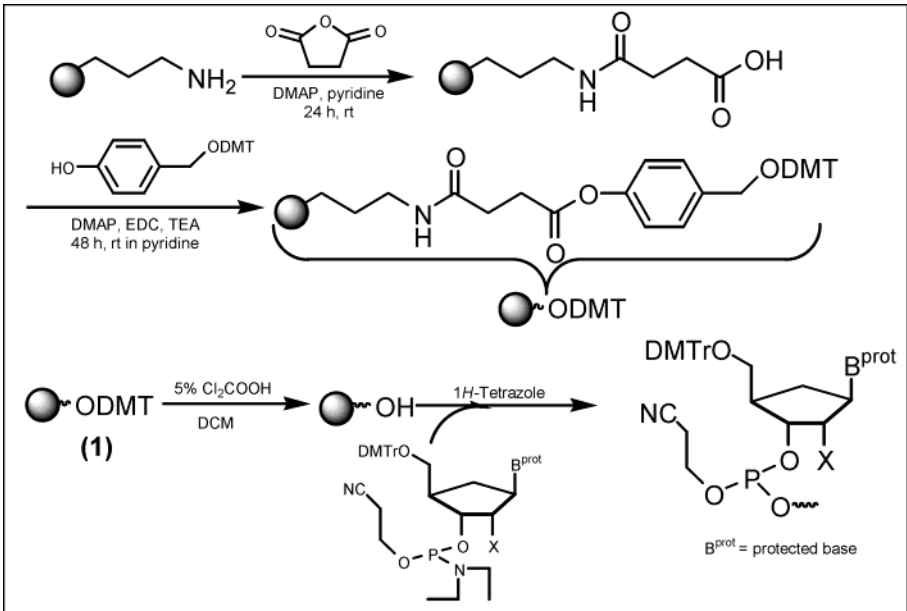
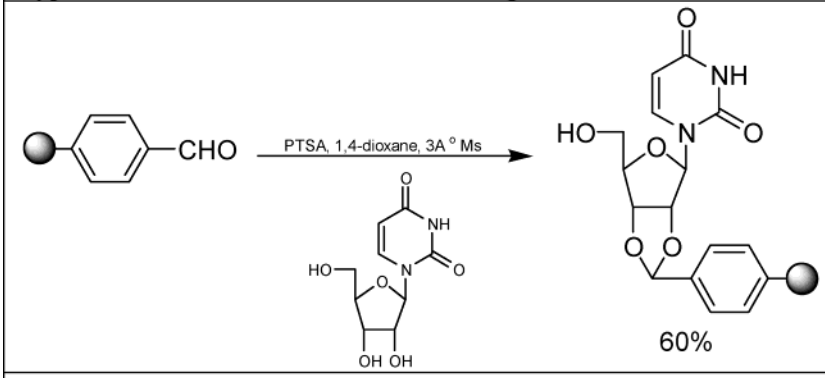
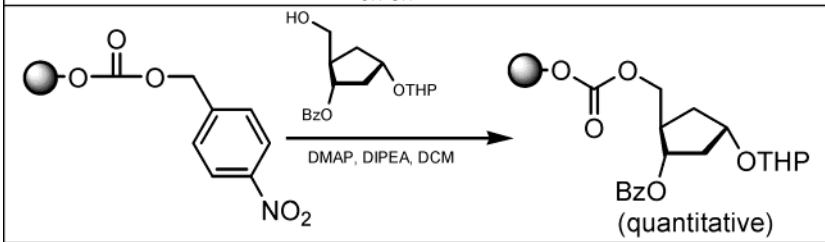
	**Derived from silica support** - Solid-phase synthesis of oligodeoxyribonucleotides via phosphodichloridite approach[391]
	**Derived from silica support** - Synthesis of oligonucleotides - Six examples, Isolated yield 81-96%[391,392]
	**Polymer supported silica gel** - Oligonucleotide synthesis on solid supports[392]
	**Derived from silica gel or CPG** - Regioselective formation of the (3'-5')-dinucleoside phosphotriesters[382,383]
	- The resin is not specified. - Tetranucleotide synthesized in an overall yield of 94%[393]
	**Derived from CPG Tentagel** - Synthesis of oligonucleotide-amino acid conjugates using Tentagel and CPG matrices - Synthesis of 3'-phosphoryltyrosine-terminated oligonucleotides[394]
	**Derived from Tentagel resin** - 3',3'-Internucleoside phosphodiester linkage - Final products C-3'-P-3'-C and C-3'-P-3'-T (90%)[395]

Table 2 (Continued)

	**Derived from CPG solid support** - Used to develop a resin-attached ODMT for the synthesis of a library of 3'-thiophosphorylated dinucleotides. - A 64-membered library[396]
Type of Reaction: Other reactions involving nucleosides	**Comments and References**
	**Derivatized from Merrifield resin** - Immobilization of nucleosides as acetals - 5'-Phosphorylation[231]
	***p*-Nitrophenyl carbonate resin** - A sugar moiety is immobilized on the solid support. - Used for the synthesis of nucleosides[397]

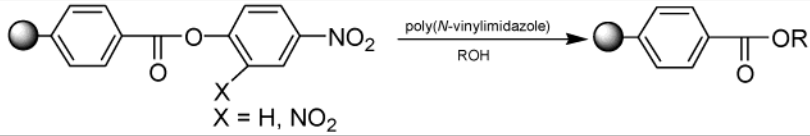
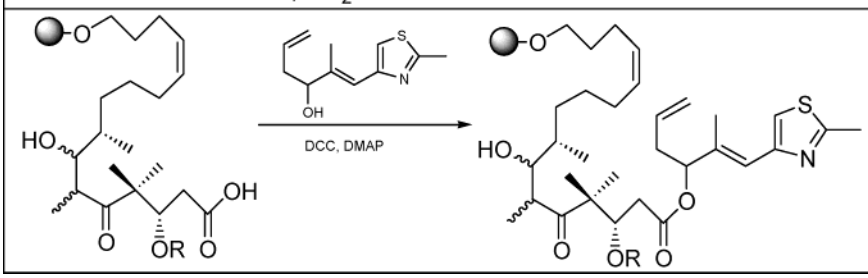
II. Solid supports reactions with alcohols and phenols	
II.2. Attachment as esters	
II.2.1. Immobilization of hydroxyl functional group and synthesis of miscellaneous compounds	**Comments and References**
	**Copolymers of acrylic acid and *p*-nitrophenyl *p*-vinylbenzoate or 2,4-dinitrophenyl *p*-vinylbenzoate** - Kinetic study[402]
	**Derived from Merrifield resin** - Designing epothilones - One example - Part of total synthesis - Six examples of different alcohols with yield ~85%[206]

Table 2 (Continued)

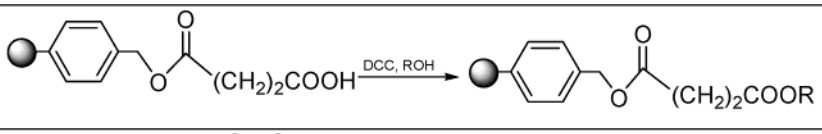
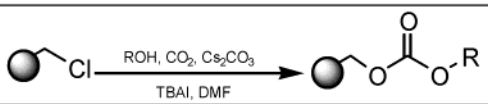
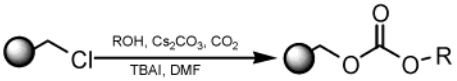
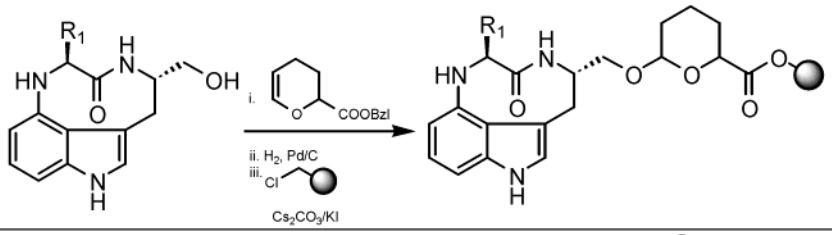
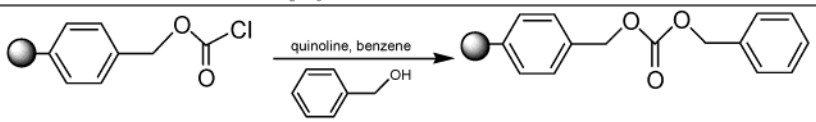
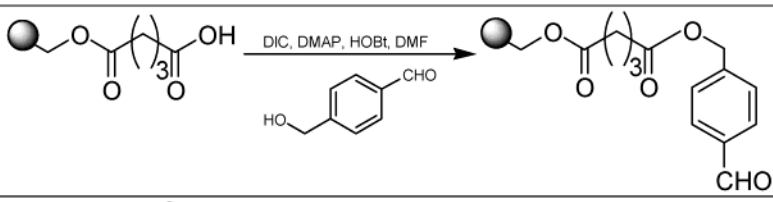
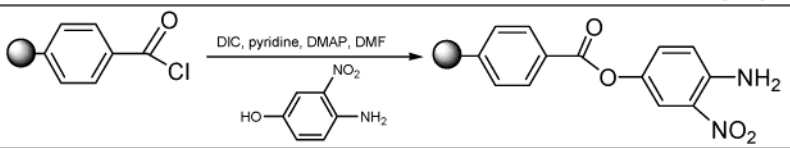
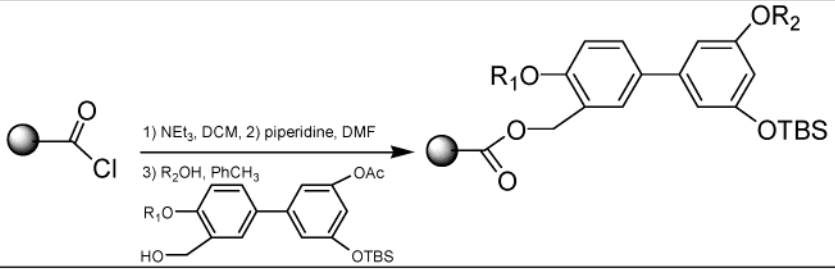
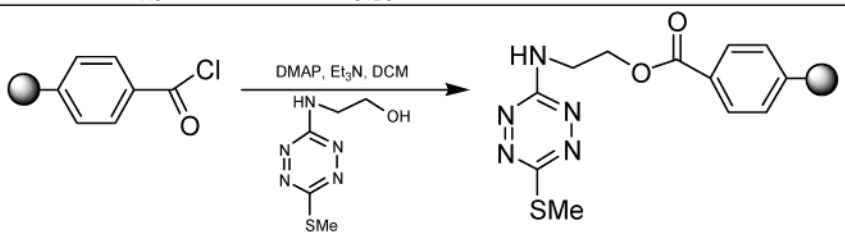
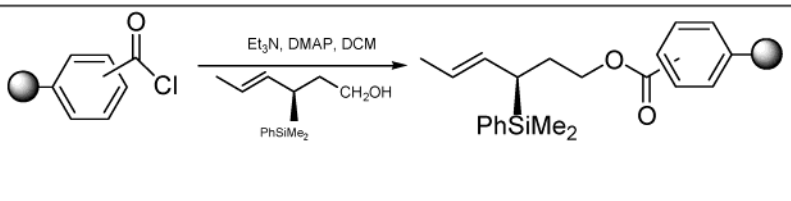
	**Derived from Merrifield resin** - ROH = L-tyrosine, L-mentol - Hemi-succinate-linkers - Compatible with Fmoc and Boc chemistries - Attaching yield: 95%[398]
	Derived from Merrifield resin - Knoevenagel condensation of unsymmetrical malonamic esters and malonates on solid support[403]
	**Merrifield resin** - Both primary and secondary alcohols are applicable - Nine entries; yields: 58-98%[404]
	**Merrifield resin** - Cesium carbonate investigated for solid phase synthesis of carbonates and carbamates[405]
	**Merrifield resin** - Synthesis of natural-like chiral derivatives[406]
	**Derived from Merrifield resin** - Polymer-bound carboxylic anhydride function[407]
	**Derived from polystyrene-DVB 1%** - Used in stereocontrolled synthesis of polyketide libraries - Yield for cleaved final product 64%[158]
	**Derived from carboxylated polystyrene (polystyrene acid chloride)** - Synthesis of phenolic libraries - 600 Compounds, yields 15-45%[278]
	**Derived from carboxylated polystyrene (polystyrene acid chloride)** - Immobilization of alcohols[408]
	**Derived from carboxylated polystyrene (polystyrene acid chloride)** - Polymer-supported 1,2,4,5-tetrazines -.Used for inverse Diels-Alder reaction - Synthesis of aromatic 1,2-diazines by inverse Diels-Alder reaction - Loading yield more than 90% - Overall yield of final products 22-82% based on the initial loading level of carboxylic acid[223,409]
	**Derived from carboxylated polystyrene (polystyrene acid chloride)** - >90% loading yield - Asymmetric crotylation reactions on solid support - Synthesis of stereochemically well-defined polypropionate-like subunits - Overall yield 37%[409]

Table 2 (Continued)

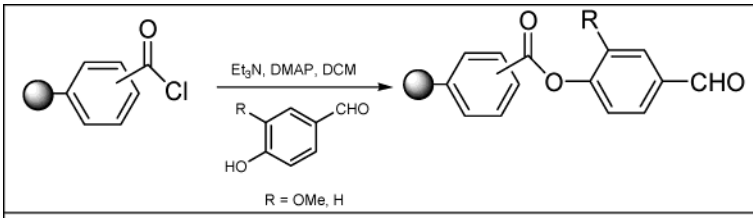
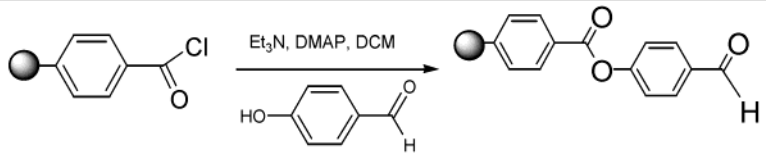
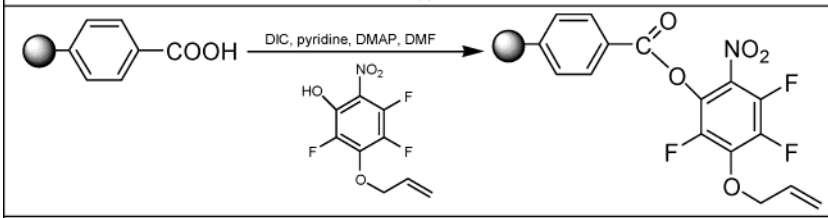
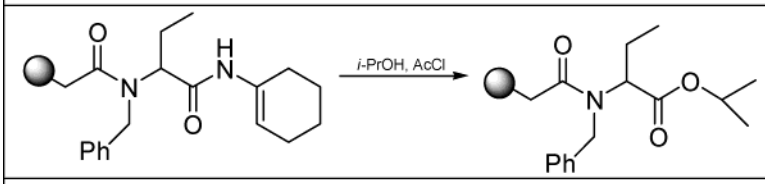
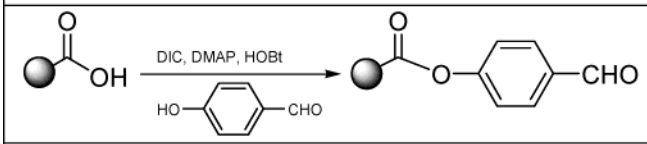
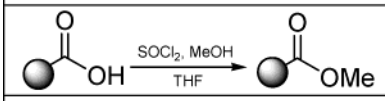
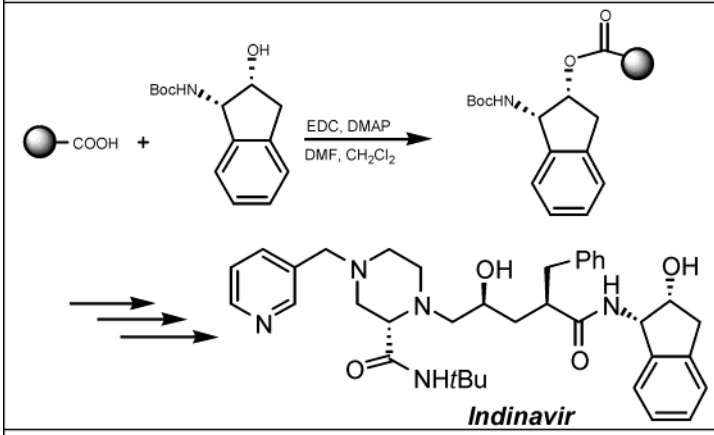
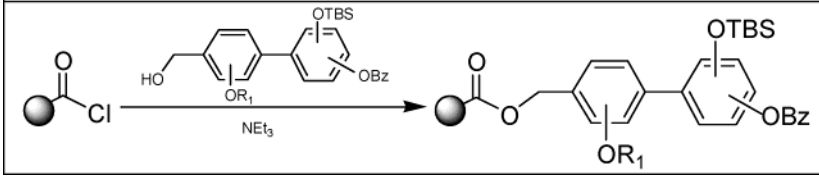
	
	**Derived from carboxylated polystyrene (polystyrene acid chloride)** - 80% yield[91]
	**Carboxypolystyrene resin** - Synthesis of inhibitors of farnesyl transferase - Phenol attachment[410]
	**Derived from carboxypolystyrene resin** - Synthesis of acylaminoesters and pyrroles via Ugi reaction on solid support[411]
	**Carboxypolystyrene** - Used in stereocontrolled synthesis of polyketide libraries - Yield for cleavage final product 50%[158]
	**Carboxypolystyrene** - Synthesis of pyrazolones described[412]
	**Carboxypolystyrene** - Synthesis of indinavir described - 12 other analogues of indinavir synthesized; yields: 81-95%[413]
	**Derived from multipin solid support** - Utilized for esterification[299,300]

Table 2 (Continued)

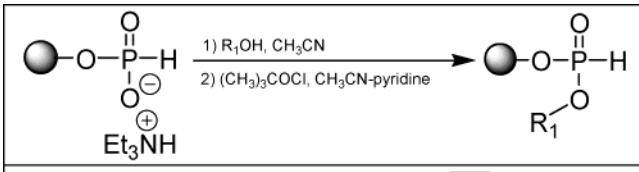
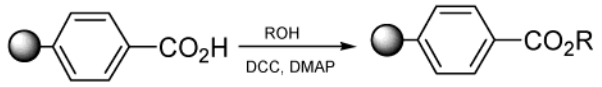
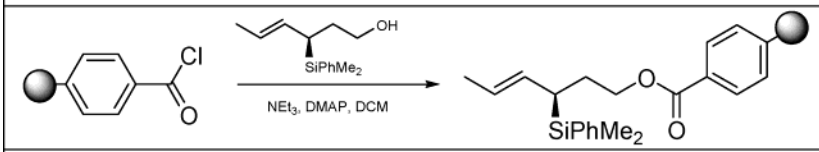
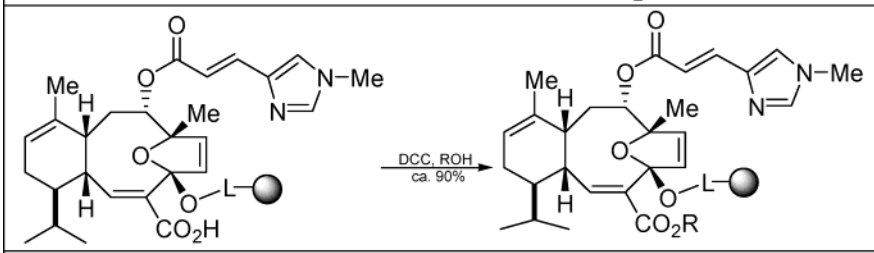
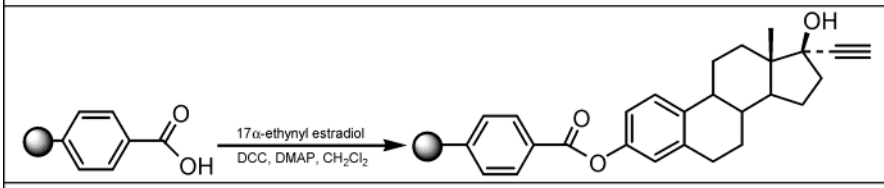
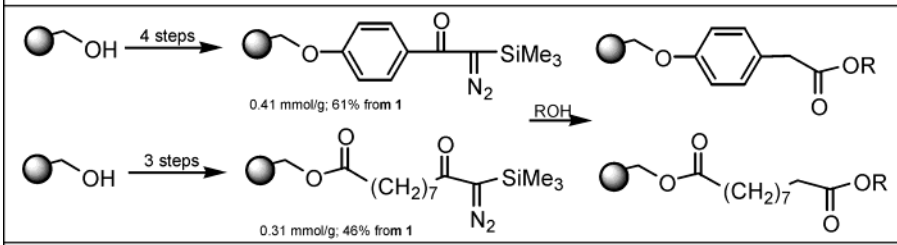
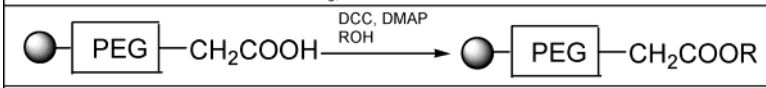
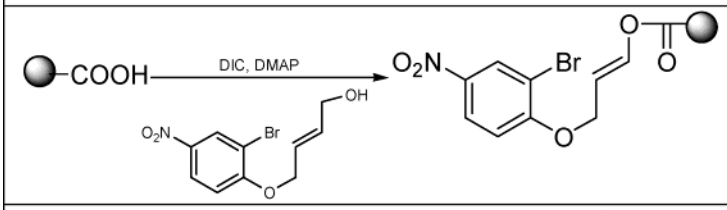
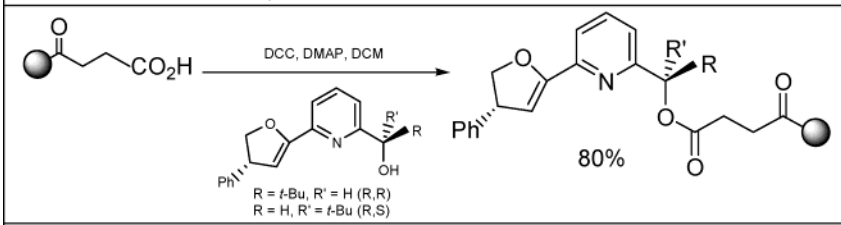
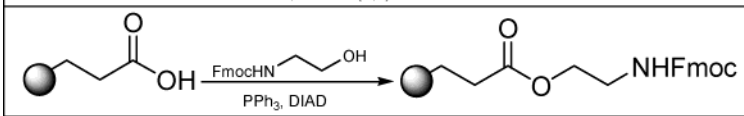
	**Derived from Wang resin** - Solid-phase synthesis of α-amino phosphonates (25-99%), phosphonic acid and α-hydroxy phosphonates (72-92%) - Loading yield 60%[414,415]
	**Derived from Wang resin** - Immobilization of alcohols[416-418]
	**Polystyrene carboxylic resin derived from Wang resin** - Synthesis of stereochemically well-defined propionate-like compounds[419]
	**Derived from Wang resin** - Synthesis of Sarcodictyins[147]
	**Derived from carboxylated resin (obtained from Wang resin by oxidation)** - Subsequent Stille couplings succeeded - Used for synthesis of estradiol derivatives[420]
	**Two types of resin-bound α-TMS diazoketones developed from Wang resin** - Used for immobilization of alcohols, thiols, and amines. - Employed for subsequent syntheses of oxazoles[421]
	**NovaSyn^R TG carboxy resin** - Immobilized alcohols via esterification reaction[399]
	**Derived from carboxylated styrene-DVB copolymer resin and carboxylated Tentagel** - Synthesis of furane rings - Yield for the final products, 63-80%[399]
	**Derived from Tentagel resin** - Preparation of polymeric ligands to assess in the palladium-catalyzed allylic alkylation[145]
	**Derived from Tentagel resin** - Synthesis of *N*-(alkoxy-acyl)amino alcohols[152]

Table 2 (Continued)

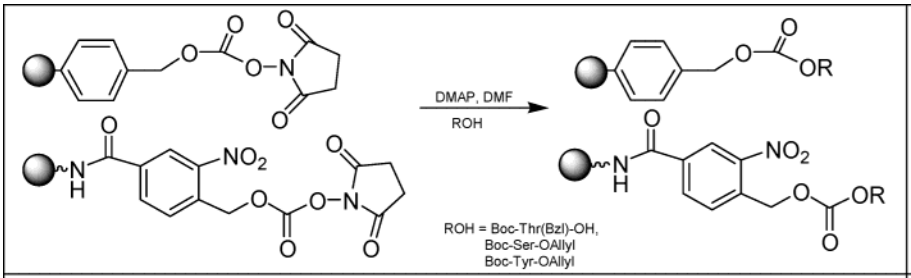
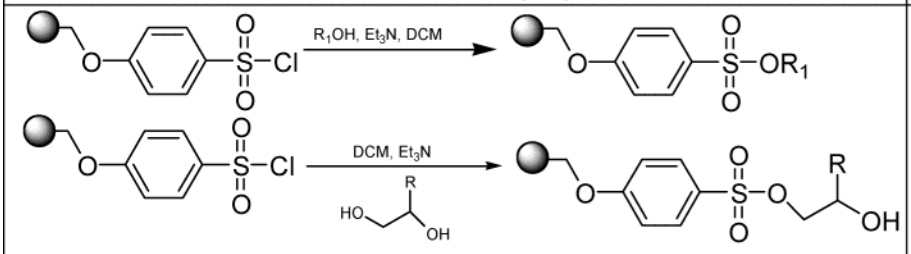
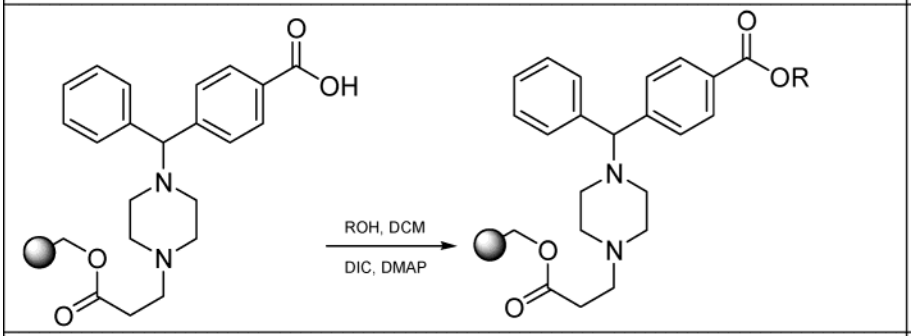
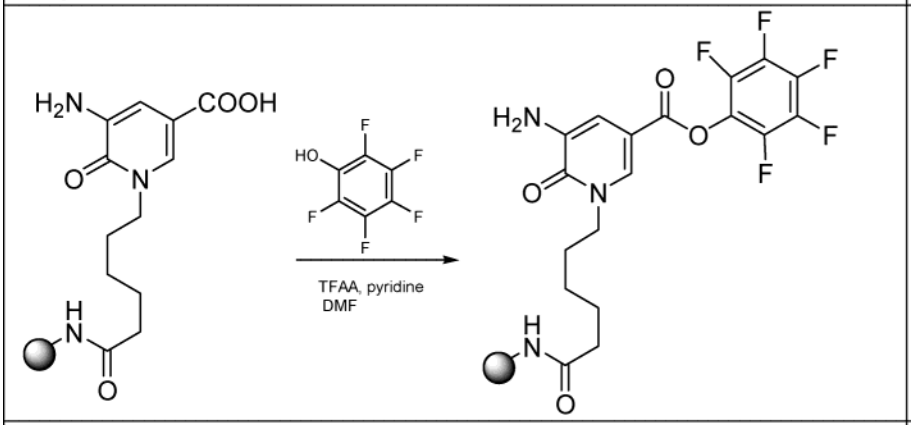
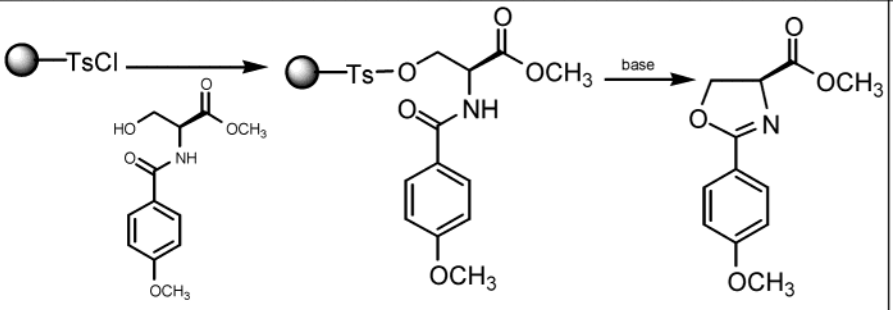
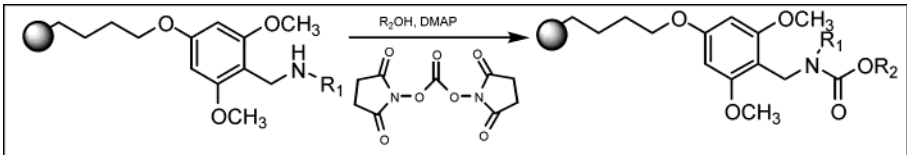
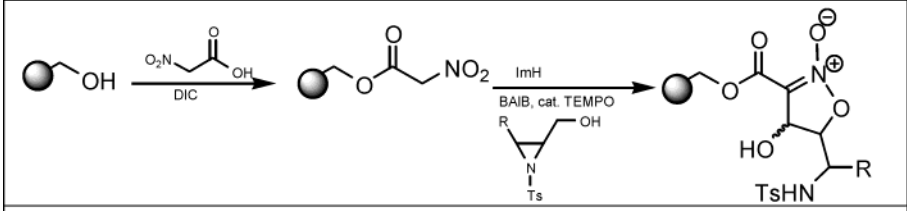
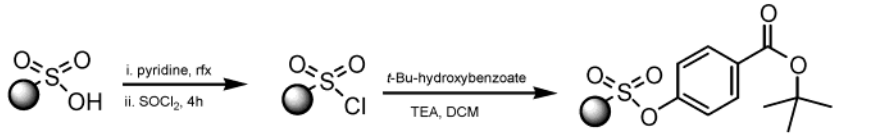
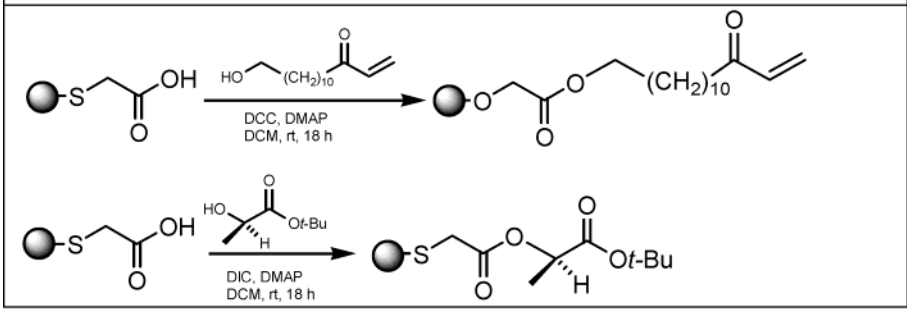
	**Active carbonate resins synthesized from the corresponding hydroxymethyl resins (polystyrene) with *N*, *N*'-disuccinimidyl carbonate (DSC)** - Anchoring of a hydroxyl function - Synthesis of cyclic (head-to-tail) and alcohol peptides - Yield: 42%[401]
	**Sulfonyl chloride polystyrene derived from Merrifield resin** - Catch and release strategy in reaction with alcohols to generate polymer-supported tosylates, which can be cleaved with nucleophiles to generate secondary and tertiary amines, thioethers and *N*-alkylimidazoles - Using of aryl sulfonate esters in solid phase synthesis and their cleavage with amines, thiolate and imidazole - To prepare oxazolidinones by a cyclative cleavage strategy[99,422-424]
	**Derived from REM resin** - Synthesis of novel analogs of δ opioid ligand SNC-80 described[425]
	**Macrocrowns with knorr linker** - Solid phase synthesis of 1,3,5-trisubstituted pyridin-2-ones[426]
	**Polymer-bound tosyl chloride used for the synthesis of oxazolines from hydroxyamides.** - Twenty eight examples; yields, 32-75%[427]

Table 2 (Continued)

	**Derived from BAL-resin** - Synthesis of *N*-substituted carbamates reported[428]
	**Derived from hydroxylated resin** - One-pot nitroaldol-cyclization procedure reported - Synthesis of 4-hydroxy-4,5-dihydroisoxazoles described[429]
	**Various resins including phenol, tetrahydropyranyl, sulfonic and chloromethyl polystyrenes** - Review of solid phase heterocycle chemistry - Used for construction of heterocycles[308]
	**Derived from ArgoGel resin** - Subsequent synthesis of macrolactones described[430]

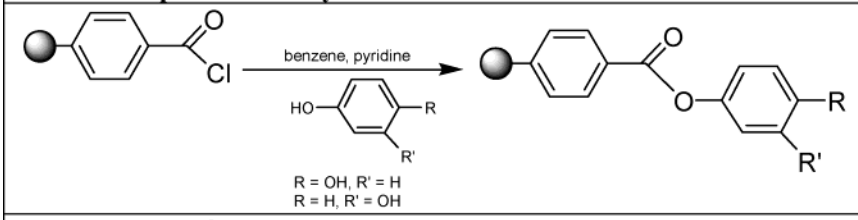
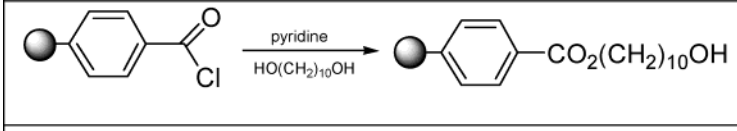
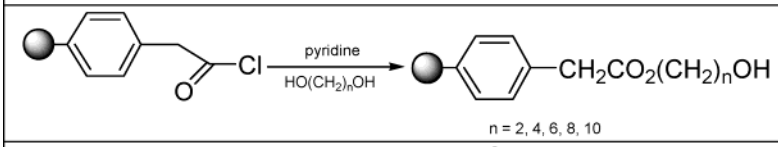
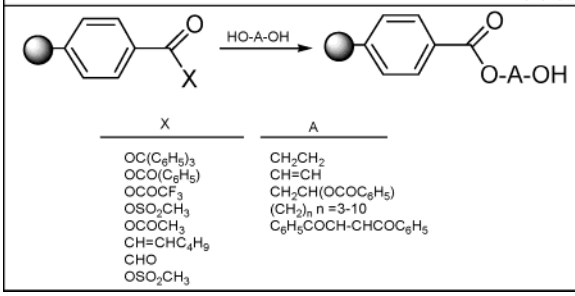
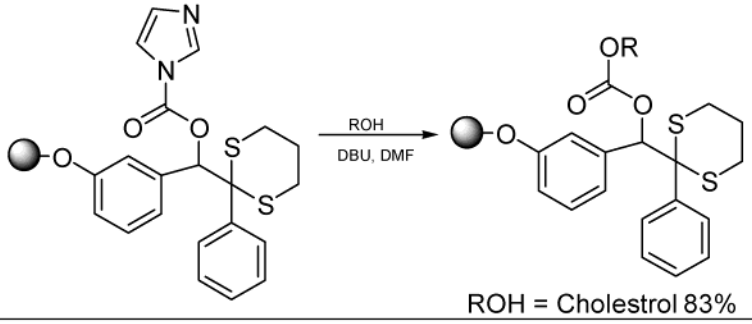
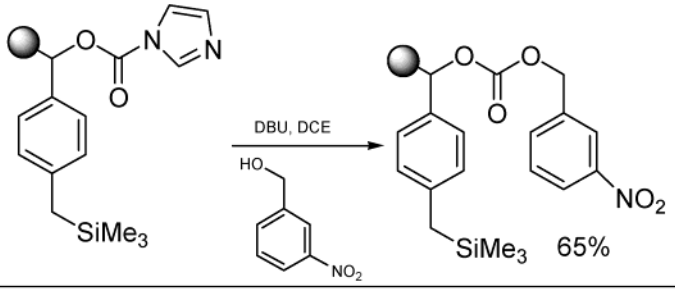
II. Solid supports reactions with alcohols and phenols	
II.2. Attachment as esters	
II.2.2. Monoprotection of symmetrical diols	**Comments and References**
	**Derived from carboxylated polystyrene (polystyrene acid chloride)** - Symmetrical dihydroxy compounds such as hydroquinone, resorcinol, 1,5-naphthalenediol, and 2,7-naphthalenediol - Final products yields 22-74%, conversion 29-95%[221,222,334]
	**Derived from carboxylated polystyrene (polystyrene acid chloride)** - Monoprotection of symmetrical diols - Immobilization of aromatic diols (resorcinol, 7-hydroxy-2-naphtol, 22-74%)[214,215,221,222,418]
	**Derived from polystyrene-DVB 2%** - The synthesis of monoethers of symmetrical diols - Monoprotection of symmetrical diols - Synthesis of monotrityl ethers (37-51%)[221,230]
	**Derived from Wang resin** - Conditions for each X group described - Yields of the final products after cleavage: 22-83%[207,217,226]

Table 2 (Continued)

II. Solid supports reactions with alcohols and phenols	
II.2. Attachment as esters	
II.2.3. Carbonate synthesis	**Comments and References**
	**Derived from Merrifield resin** - Addition of alcohols to solid-supported imidazocarbonates results in the generation of carbonates. - Synthesis of a carbonate - One example - Yield: 83%[128]
	**Derived from Merrifield resin** - Synthesis of silyl linkers[127]

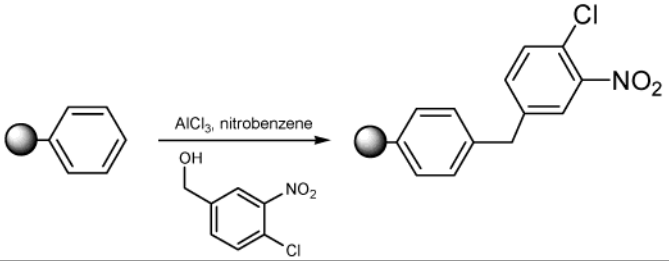
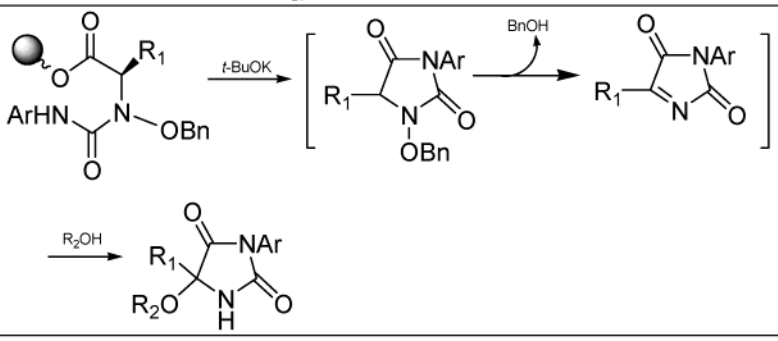
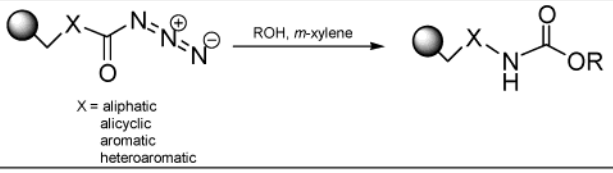
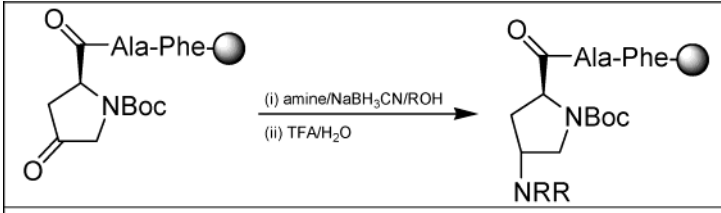
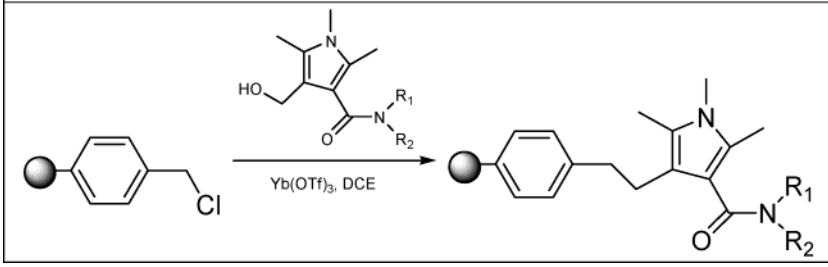
II. Solid supports reactions with alcohols and phenols	
II.3. Attachment by other strategies (miscellaneous reactions)	**Comments and References**
	**Derived from macroporous polystyrene** - Friedel Craft alkylation[431]
	**Derived from Wang resin** - Solid phase synthesis of 5-alkoxyhydantoin libraries[432]
	**Derived from Wang resin** - Curtius rearrangement - Synthesis of Fmoc protected amines - Seven examples; yields 34-78%[159]

Table 2 (Continued)

	**Derived from multipin solid supports** - The library synthesis of 4-aminoproline analogs[433]
	**Merrifield resin** - Synthesis of heterocycles - Carbon-carbon coupling[434]

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