

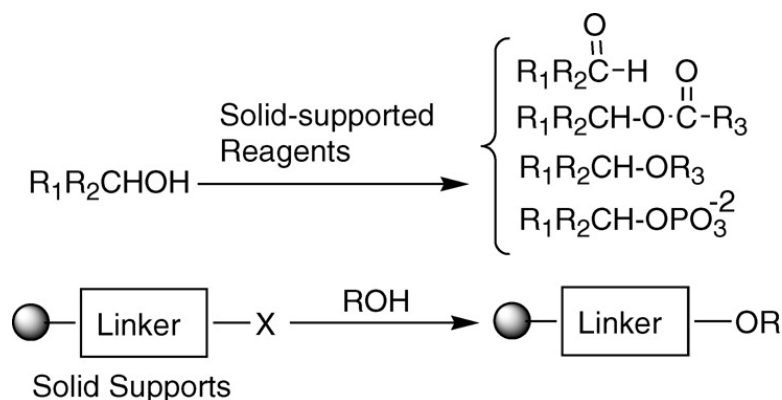
Review

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

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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 dihydropyranil 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 trichloroacetamidate¹⁰³ 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 R₃SiH¹¹⁵ with aromatic or aliphatic alcohols in the presence of catalytic amounts of a rhodium complex [(PPh₃)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 PPh₃ or PBu₃. 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 trichloroacetamide,³³¹ and the enzyme-based technology³³² 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 treat-

ment 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 ₂ O	acetic anhydride
ACC-SiO ₂	ammonium chlorochromate
ACN	acetonitrile
ADDP	azodicarboxylic acid dipiperidide
aq	aqueous
Argogel	PEG-grafted cross-linked polystyrene backbone amide linker
BAL	backbone amide linker
BHA	benzhydramine resin
Bn	benzyl
BOBA	<i>para</i> -benzyloxybenzylamine
Boc	<i>tert</i> -butyloxycarbonyl
BTSC	bis(trimethylsilyl)chromate
BSA	<i>N,O</i> -bis(trimethylsilyl)acetamide
BSP	sulfobromophthalein sodium
Bu	butyl
Bz	benzoyl
CDI	<i>N,N</i> -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	<i>N,N'</i> -dicyclohexylcarbodiimide
DCE	dichloroethane
DCM	dichloromethane

DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone	PEG-PS	poly(ethylene glycol)-polystyrene
DEAD	diethyl azodicarboxylate	Ph	phenyl
DHP	2,3-dihydro-4 <i>H</i> -pyran	Phth	phthaloyl
DIAD	diisopropyl azodicarboxylate	PIN	polyethylene pin
DIC	diisopropylcarbodiimide	Piv	pivaloyl
DIPEA	diisopropylethylamine	PMM	poly(methyl methacrylate)
DMA	<i>N,N</i> -dimethylacetamide	PolyTPPI ₂	polymer-bound triphenylphosphine diiodide
DMAC	<i>N,N</i> -dimethylacetamide	PPh ₃	triphenylphosphine
DMAD	dimethyl acetylenedicarboxylate	PPTS	pyridinium tosylate
DMAP	4-(dimethylamino)pyridine	PS	cross-linked polystyrene
DMDO	dimethyldioxirane	PS-DES	polystyryl-diethylsilyl
DMF	<i>N,N</i> -dimethylformamide	PS-DIEA	<i>N,N</i> -(diisopropyl)aminomethylpolystyrene resins
DMSO	dimethyl sulfoxide	PS-DVB	polystyrene-divinylbenzene copolymer
DMT	4,4'-dimethoxytrityl	PS-PEG	polystyrene-poly(ethylene glycol) graft polymer
DMTSB	dimethylthiosulfonium tetrafluoroborate	P-TBD	polystyrene-supported 1,5,7-triazabicyclo[4.4.0]-dec-5-ene
DMTST	dimethylthiosulfonium triflate	PTSA	<i>para</i> -toluenesulfonic acid
DSC	<i>N,N'</i> -disuccinimidyl carbonate	PVPDC	poly(vinylpyridinium dichromate)
DTBP	2,6-di- <i>tert</i> -butyl pyridine	(Pyz-CrO ₅) _n	pyrazine-based polymeric complex of oxidoperoxochromium (VI)
DTT	dithiothreitol	R	alkyl
DVB	divinylbenzene (mixture of regioisomers)	RAM	Rink amide linker, (2,4-dimethoxyphenyl)(4-alkoxyphenyl)methylamine
EDC	1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride	r.t.	room temperature
EGDMA	ethyleneglycol dimethacrylate	Sasrin	cross-linked polystyrene with 4-alkoxy-2-methoxybenzyl alcohol linker (super acid sensitive resin)
Et	ethyl	Sephadex	dextran; a branched glycan consisting of 1,6- α -linked glucopyranose
EtOAc	ethyl acetate	Sepharose	agarose; an unbranched glycan consisting of D-galactose and 3,6-anhydro-L-galactose
Fmoc	9-fluorene methyloxycarbonyl	SG	silica gel
Fuc	L-fucose	S-Le	sialyl-Lewis
GalNAc	<i>N</i> -acetyl-D-galactosamine	TBAF	tetrabutylammonium fluoride
GalT	galactosyltransferase	TBAI	tetrabutylammonium iodide
GlcNAc	<i>N</i> -acetyl-D-glucosamine	TBDPS	<i>tert</i> -butyldiphenylsilyl
glycan	synonym of polysaccharide	TBDMSCI	<i>tert</i> -butyldimethylsilyl chloride
HMBA	4-hydroxymethylbenzoic acid linker	TBS	<i>tert</i> -butyldimethylsilyl
HMPB	4-hydroxymethyl-3-methoxyphenoxybutyric acid	TBTU	3-[(dimethyliminium)dimethylamino)methyl]-1,2,3-benzotriazol-1-ium-1-olate tetrafluoroborate
HOBt	hydroxybenzotriazole	<i>t</i> -Bu	<i>tert</i> -butyl
IBX	1-hydroxy-1,2-benziodoxol-3(1 <i>H</i>)-one-1-oxide	TCA	trichloroacetic acid
MALDRE	2-methoxy-4-benzyloxypolystyrene aldehyde resin	TEA	triethylamine
MBHA	4-methylbenzhydramine	TEMPO	4-alkoxy-2,2,6,6-tetramethylpiperidine-1-oxide
<i>m</i> CPBA	<i>meta</i> -chloroperoxybenzoic acid	Tentagel	PEG-grafted cross-linked polystyrene
Me	methyl	Tentagel-PHB	PEG-grafted cross-linked polystyrene functionalized with a Wang linker
MeOPEG	poly(ethylene glycol) monomethyl ether	TES	triethylsilyl
Merrifield resin	partially chloromethylated, cross-linked polystyrene	Tf	triflate (trifluoromethanesulfonyl)
Mmt	monomethoxytrityl	TFA	trifluoroacetic acid
MPEG	polymer poly(ethylene glycol) monomethyl ether	TFE (TFOH)	trifluoroethanol
MS	molecular sieve	TFAA	trifluoroacetic anhydride
MSNT	1-(mesitylene-2-sulfonyl)-3-nitro-1,2,4-triazole	TG	PEG-grafted polystyrene (e.g., Tentagel)
Multipin	polymer crowns grafted with various supports	(TG)	TG with linker or spacer
NaHMDS	sodium hexamethyldisilazane	THF	tetrahydrofuran
NBS	<i>N</i> -bromosuccinimide	THP	2-tetrahydropyranyl
NCPS	non-cross-linked polystyrene	TIS, TIPS	triisopropylsilyl
NeuAc	<i>N</i> -acetyl-neuraminic acid	TMAD	<i>N,N,N',N'</i> -tetramethylethylenediamine
NIS	<i>N</i> -iodosuccinimide	TMS	trimethylsilyl
NMI	<i>N</i> -methylimidazole	TMSOTf	trimethylsilyl trifluoromethanesulfonate
NMM	<i>N</i> -methylmorpholine	TPAP	tetrapropylammonium perruthenate, [Pr ₄ N][RuO ₄]
NMO	4-methylmorpholine <i>N</i> -oxide	TPP	triphenyl phosphine
NMP	<i>N</i> -methylpyrrolidinone	Tr	trityl, triphenylmethyl
NPG	<i>n</i> -pentenyl glycosides	UDP-Gal	uridine 5'-diphosphogalactose
Ns	4-nitrobenzenesulfonyl	Wang resin	cross-linked polystyrene with 4-benzyloxybenzyl alcohol linker
PAL	peptide amide linker; 5-(4-aminomethyl-3,5-dimethoxyphenoxy)valeric acid linker	Z	cbz, benzyloxycarbonyl
PAM	4-(hydroxymethyl)phenylacetic acid linker		
PAN	poly(arylamide)-poly(<i>N</i> -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		

Table 1. Solid-Support Reagents

I. Solid-supported Reagents		
I.1. Solid-supported oxidizing reagents (solid-supported oxidants)		Comments and References
$\begin{array}{l} \text{RCH=CHCH}_2\text{OH} \\ \text{RCH}_2\text{OH} \\ \text{PhCH}_2\text{OH} \end{array} \xrightarrow{\text{Polymer-} \begin{array}{c} \text{O} \\ \parallel \\ \text{N-Br} \\ \parallel \\ \text{O} \end{array}} \begin{array}{l} \text{RCH=CHCHO} \\ \text{RCHO} \\ \text{PhCHO} \end{array}$		Polymeric supported <i>N</i>-bromimides - Oxidation of primary, allylic, and benzylic alcohols to aldehydes ¹
$\text{R}'\text{CH}_2\text{OH} \xrightarrow{\text{Polymer-} \begin{array}{c} \text{O} \quad \text{Cl} \\ \parallel \quad \\ \text{C} \quad \text{N-R} \end{array}} \text{R}'\text{CHO}$ <p style="text-align: center;">a, n = 0; R = Me, Ph b, n = 1; R = Ac</p> <p style="text-align: center;">or</p> $\text{Polymer-} \begin{array}{c} \text{Cl} \quad \text{O} \\ \quad \parallel \\ \text{CH}_2 \quad \text{N} \quad \text{C} \quad \text{Me} \end{array}$		<i>N</i>-Chloroamide polystyrene resins - Prepared from treating Nylon 66 with <i>t</i> -butyl hypochlorite and chlorine oxide in CCl ₄ - Oxidation of alcohols ²
$\text{R}_1\text{CH(OH)R}_2 \xrightarrow[\text{benzene/DMSO}]{\text{Polymer-} \begin{array}{c} \text{CH}_2\text{-N=C=N-Pr-i} \end{array}} \text{R}_1\text{C(=O)R}_2$ <p style="text-align: center;">63-97%</p>		Polystyrene isopropylcarbodiimide derived from aminomethyl polystyrene - Moffatt oxidation of primary, secondary and benzylic alcohols - Six examples, yields 63-97% ³
$\begin{array}{l} \text{R}_1\text{CH(OH)R}_2 \\ \text{Monoalcohols} \\ \text{HOCH}_2(\text{CH}_2)_5\text{CH}_2\text{OH} \\ \text{Diol} \end{array} \xrightarrow[\text{NEt}_3, \text{DCM}]{\text{Polymer-} \begin{array}{c} \text{Cl} \\ \\ \text{S}^+ \\ \quad \\ \text{Cl} \quad \text{CH}_3 \end{array}} \begin{array}{l} \text{R}_1\text{C(=O)R}_2 \\ \text{67-100\%} \\ \text{HOCH}_2(\text{CH}_2)_5\text{CHO} \\ \text{51\%} \end{array}$		Polymeric thioanisole dichloride (polystyrene) prepared from poly(<i>p</i>-bromostyrene)-poly(<i>p</i>-methylmercaptostyrene) - Oxidation of primary and secondary alcohols - Five examples - Monooxidation of diols (heptanediol, pentanediol) - Oxidation of sensitive compounds like prostaglandin intermediate ⁴
$\text{R}_1\text{CH(OH)R}_2 \xrightarrow[\text{electric current, H}_2\text{O/CH}_3\text{CN}]{\text{Polymer-} \begin{array}{c} \text{N}^+\text{-H} \\ \\ \text{Br}^- \end{array}} \text{R}_1\text{C(=O)R}_2$ <p style="text-align: center;">8 Secondary alcohols 35-100%</p>		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}
$\text{RCH}_2\text{OH} \xrightarrow{\text{Polymer-} \begin{array}{c} \text{N}^+\text{SO}_3^- \end{array}} \text{RCHO}$		Sulfur trioxide pyridine complex polymer bound - Suggested to be applied in DMSO oxidation of alcohols ⁷
$\text{R}_1\text{CH(OH)R}_2 \xrightarrow[\text{hexane or benzene or CHCl}_3, \text{ or THF}]{\text{Polymer-} \begin{array}{c} \text{NR}_3^+\text{HCrO}_4^- \end{array}} \text{R}_1\text{C(=O)R}_2$		Polymer-supported chromate - Prepared from treating commercial Amberlyst A-26 (Cl ⁻) resin with CrO ₃ /H ₂ O - Oxidation of primary, secondary, allylic, and benzylic alcohols to aldehydes or ketones - Fifteen examples, yields 73-98% ^{8,9}
$\begin{array}{l} \text{RCH=CHCH}_2\text{OH} \\ \text{RCH}_2\text{OH} \\ \text{PhCH}_2\text{OH} \end{array} \xrightarrow{\text{Polymer-} \begin{array}{c} \text{N}^+\text{-H ClCrO}_3^- \end{array}} \begin{array}{l} \text{RCH=CHCHO} \\ \text{RCHO} \\ \text{PhCHO} \end{array}$		Polyvinylpyridinium chlorochromate prepared from treating crosslinked poly(vinylpyridine) with CrO₃, aq. HCl - Oxidation of primary, secondary, allylic, and benzylic alcohols to aldehydes and ketones ^{10,11}
$\text{R}_1\text{CH(OH)R}_2 \xrightarrow[\text{cyclohexane or benzene or hexane or THF or chloroform}]{\text{Polymer-} \begin{array}{c} \text{N}^+\text{-H ClCrO}_3^- \end{array}} \text{R}_1\text{C(=O)R}_2$		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)

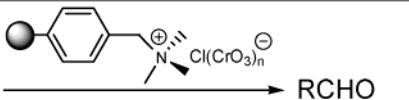
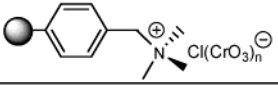
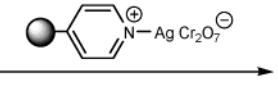
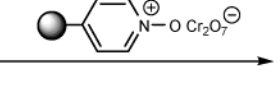
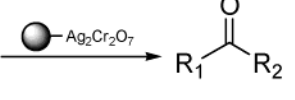
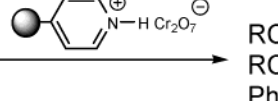
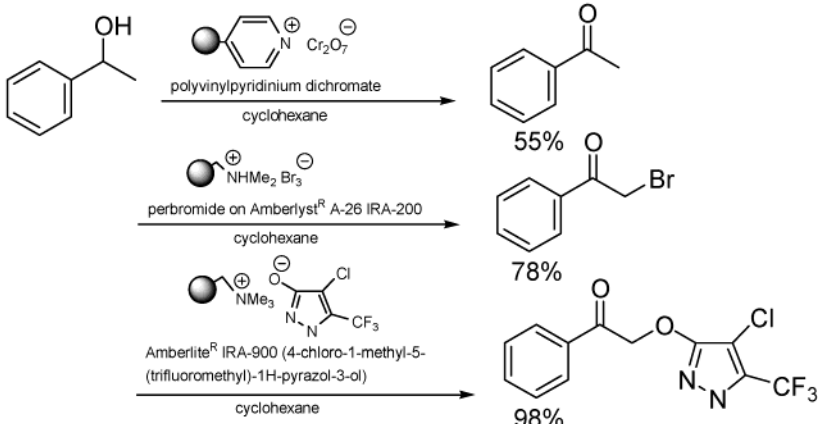
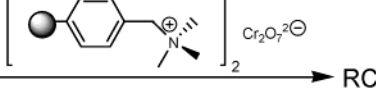

		attached to the ring structure - Nine examples, 73-100% ^{9,10}
$RCH_2OH \xrightarrow{\text{polymer-supported reagent}} RCHO$		Polymer-supported chlorochromate - Prepared from Amberlyst [®] A-26 (Cl) - Oxidation of primary and secondary alcohols ¹¹
$RCH=CHCH_2OH$ RCH_2OH $PhCH_2OH$		$RCH=CHCHO$ $RCHO$ $PhCHO$ Polymer-supported chlorochromate - Prepared from Amberlyst [®] A-26 (Cl) - Oxidation of primary and secondary alcohols ¹¹
$RCH=CHCH_2OH$ RCH_2OH $PhCH_2OH$		$RCH=CHCHO$ $RCHO$ $PhCHO$ Polyvinylpyridine-supported silver dichromate - Oxidation of primary, allylic, and benzylic alcohols to aldehydes ¹²
$RCH=CHCH_2OH$ RCH_2OH $PhCH_2OH$		$RCH=CHCHO$ $RCHO$ $PhCHO$ Polyvinylpyridine N-oxide-supported dichromate - Oxidation of primary, allylic, and benzylic alcohols to aldehydes ¹³
$R_1-CH(OH)-R_2 \xrightarrow{\text{Ag}_2\text{Cr}_2\text{O}_7} R_1-C(=O)-R_2$		Polyethyleneimine-supported silver dichromate - A stable, mild, and efficient oxidizing agent for the conversion of alcohols to carbonyl compounds ¹⁴
$RCH=CHCH_2OH$ RCH_2OH $PhCH_2OH$		$RCH=CHCHO$ $RCHO$ $PhCHO$ Polyvinylpyridinium dichromate - Prepared from treating crosslinked poly(vinylpyridine) with CrO ₃ /H ₂ O - 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}	
$RCH_2OH \xrightarrow{\left[\text{polymer-supported reagent} \right]_2} RCHO$		Polymer-supported quaternary ammonium perchromate - Converts allylic alcohols to α,β -unsaturated aldehydes but does not oxidize saturated alcohols - Yields 75-89% ²⁰
Alcohols $\xrightarrow[\text{DCM}]{\text{Pyz-CrO}_5}$ Aldehydes, ketones 85-100%		Pyrazine-based polymeric complex of oxidoperochromium (VI) compound (Pyz-CrO₅)_n - Benzyl alcohols, α,β -unsaturated alcohols, primary and secondary alcohols, α -hydroxyketones, hydroquinone, catechol, 1,4-dihydroxynaphthalene - Thirty examples of alcohols ¹⁹
$RCH_2OH \xrightarrow{\text{polymer-supported reagent}} RCHO$		Polymeric chromate derived from polystyrene - Oxidation of alcohols and alkyl halides to carbonyl compounds

Table 1 (Continued)

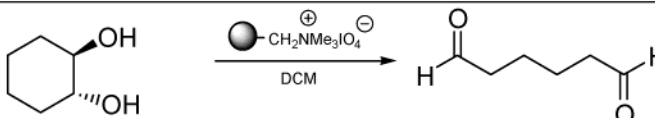

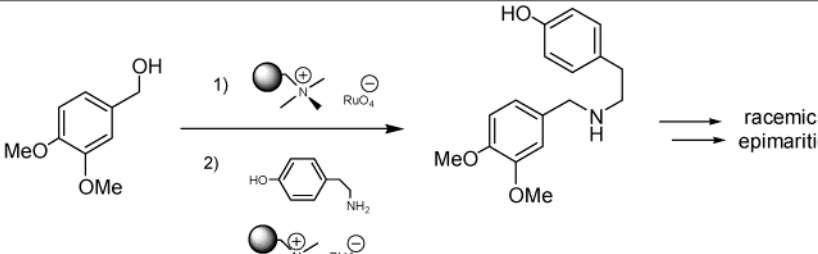
$\begin{array}{l} \text{RCH=CHCH}_2\text{OH} \\ \text{RCH}_2\text{OH} \\ \text{PhCH}_2\text{OH} \end{array} \xrightarrow{\text{CH}_2\text{NMe}_3\text{IO}_4^-} \begin{array}{l} \text{RCH=CHCHO} \\ \text{RCHO} \\ \text{PhCHO} \end{array}$	<ul style="list-style-type: none"> - Oxidizing the alcohol groups directly attached to a ring structure^{21,22} <p>(Polystyrylmethyl)trimethylammonium metaperiodate</p> <ul style="list-style-type: none"> - Polymer-supported metaperiodate - Oxidation of alcohols²
	<p>(Polystyrylmethyl)trimethylammonium metaperiodate</p> <ul style="list-style-type: none"> - Oxidative cleavage of 1,2-diols²
 <p>Polymer-supported quaternary ammonium iodate Polymer-supported quaternary ammonium periodate</p> <p>Quinols and Catechols $\xrightarrow[\text{resin}]{\text{CHCl}_3}$ Quinones</p> <p>0-100%</p>	<p>Polymer-supported quaternary ammonium iodate or periodate</p> <ul style="list-style-type: none"> - Prepared from treating Amberlyst[®] A-26 OH⁻ with aq. HIO₄ or from treating Amberlite[®] IRA 904 Cl⁻ with NaIO₄ solution - Oxidation of quinols, catechols and glycols (eleven examples) - Cleavage of 1,2-diols to the corresponding carbonyl compounds^{23,24}
$\text{R-CH}_2\text{OH} \xrightarrow[\text{resin}]{\text{DCM, 4A}^\circ\text{MS, NMO or TMAO}} \text{R-CHO}$ <p>R = aryl, alkyl, alkenyl</p> <p>10 examples 50 to >95%</p>	<p>(Polystyrylmethyl)trimethylammonium perruthenate or polymer (Amberlyst[®] A-26)-supported perruthenate</p> <ul style="list-style-type: none"> - Prepared from treating Amberlyst[®] IR27 with aq. KRuO₄ - 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 <i>N</i>-oxides (<i>N</i>-methylmorpholine oxide or trimethylamine oxide)²⁵⁻²⁹
$\text{R-CH}_2\text{OH} \xrightarrow[\text{resin}]{\text{O}_2, \text{toluene, 75-85 }^\circ\text{C}} \text{R-CHO}$ <p>R = aryl, alkyl, alkenyl</p> <p>7 examples 56 to > 95%</p>	
$\text{R}_1\text{CH(OH)R}_2 \xrightarrow[\text{resin}]{\text{r.t., DCM}} \text{R}_1\text{C(=O)R}_2$	
	<p>(Polystyrylmethyl)trimethylammonium perruthenate or polymer (Amberlyst[®] A-26)-supported perruthenate</p> <ul style="list-style-type: none"> - Synthesis of the alkaloids (+/-)-epimaritidine and (+/-)-epimaritidine using an orchestrated multi-step sequence of polymer supported reagents³⁰
$\text{endo-Borneol} \xrightarrow[\text{DCM, Et}_3\text{N}]{\text{oxalyl chloride}} \text{Camphor}$ <p>92-100%</p>	<p>6-(Methylsulfinyl)hexanoylmethyl polystyrene (Merrifield resin derived polymeric supported sulfoxide oxidizing agent)</p> <ul style="list-style-type: none"> - Recyclable solid-phase sulfoxide reagent for Swern oxidation of primary alcohols to aldehydes - Modified Swern oxidation³¹
$\text{R-CH(OH)R}' \xrightarrow[\text{DCM}]{(\text{COCl})_2, \text{Et}_3\text{N}}$ <p>Primary, secondary and benzyl alcohols</p>	<p>PEG2000 bound sulfoxide</p> <ul style="list-style-type: none"> - 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
$\text{RCH}_2\text{OH} \xrightarrow[\text{DMF}]{\text{NMO, PPh}_2\text{CCl}_4} \text{RCHO}$	<p>Derived from Wang resin and Rink acid</p> <ul style="list-style-type: none"> - TPAP-catalytic oxidation of primary, benzylic (Wang resin), and secondary (Rink acid) alcohols³³

Table 1 (Continued)


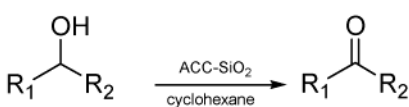
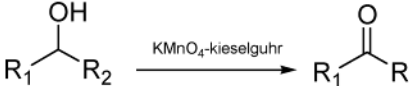

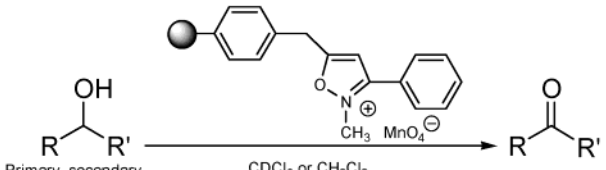
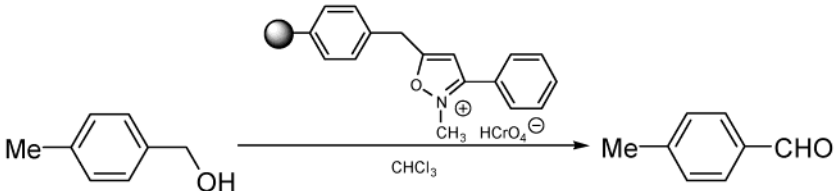
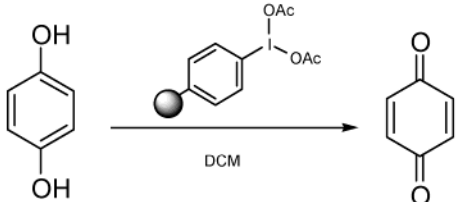
<p>Alcohols $\xrightarrow{\text{BTSC/SiO}_2}$ Carbonyls</p> <p>Primary and secondary alcohols (1-octanol, 2-cyclohexylethanol, phenylethanol, 1-indanol, menthol, <i>o</i>-methoxy benzyl alcohol, <i>p</i>-bromo-benzyl alcohol, <i>m</i>-nitro-benzyl alcohol)</p>	<p>Silica gel supported bis(trimethylsilyl)chromate (BTSC)</p> <ul style="list-style-type: none"> - 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}
 	<p>Ammonium chlorochromate adsorbed on silica gel (ACC-SiO₂)</p> <ul style="list-style-type: none"> - Prepared by adding silica gel to a solution of ammonium chlorochromate in water, and evaporation to dryness - Benzoin is converted cleanly to benzil (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 cinnamaldehyde.³⁶
	<p>KMnO₄ supported on silica gel</p> <ul style="list-style-type: none"> - Five examples, yields 82-97%³⁷
<p>1,2-Diols $\xrightarrow[\text{DCM}]{\text{SiO}_2\text{-NaIO}_4}$ Aldehydes</p>	<p>Silica gel supported metaperiodate</p> <ul style="list-style-type: none"> - 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
 <p>Primary, secondary and benzyl alcohols</p>	<p>MagtrieveTM, a magnetically retrievable oxidant based on tetravalent chromium dioxide (CrO₂)</p> <ul style="list-style-type: none"> - Six examples; 61-95%³⁹
 <p>Primary, secondary and benzyl alcohols</p>	<p>Derived from styrene-DVB or styrene-ethyleneglycol dimethacrylate (EGDMA) (2%) crosslinked polymer</p> <ul style="list-style-type: none"> - 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
	<p>Derived from poly(methyl methacrylate) (PMM) with 2% ethyleneglycol demethacrylate</p> <ul style="list-style-type: none"> - PMM-isoxazolinium Cr(VI) - Yield 73-82%⁴¹
	<p>Polymer-supported phenyliodine (III) diacetate</p> <ul style="list-style-type: none"> - Yield 63%⁴²

Table 1 (Continued)

	<p>Polymer-supported phenyliodine (III) diacetate</p> <ul style="list-style-type: none"> - 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}
<p>Primary, secondary and benzyl alcohols</p>	<p>Amberlyst[®] A-26 thiosulfate resin</p> <ul style="list-style-type: none"> - Reduces the I(V) and I(III) periodinate species to the I(I) species - Nine examples, yields 68-97%⁴⁵
	<p>Polymer-supported periodinane reagent</p> <ul style="list-style-type: none"> - Derived from polystyrene resin - Oxidation of benzylic, allylic, primary as well as secondary alcohols - Twenty examples, yields 26 to >95%⁴⁶
	<p>Polymer-supported periodinane reagent</p> <ul style="list-style-type: none"> - Derived from aminopropylsilica gel - Primary and secondary alcohols - Ten examples, yields 82-100%⁴⁷
	<p>4-Alkoxy-2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO) polystyrene</p> <ul style="list-style-type: none"> - Oxidation of TEMPO polystyrene with <i>N</i>-chlorosuccinimide yields the corresponding polymer-bound oxoammonium salt (TEMPO) - Oxidation of primary and secondary alcohols - Yields 65-95%^{48,49}

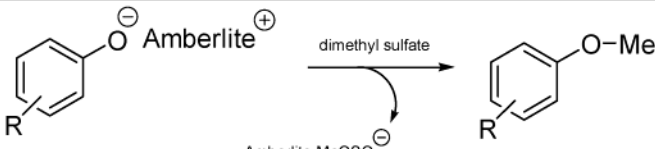
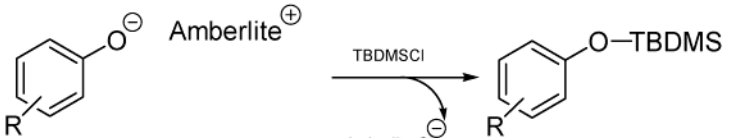
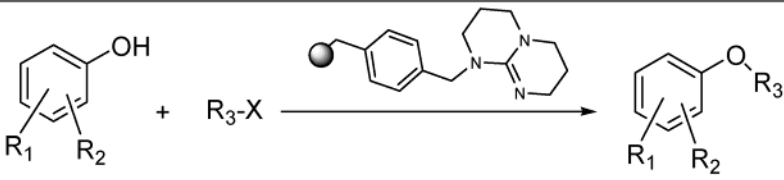
Table 1 (Continued)

I. Solid-supported Reagents		
I.2. Solid-supported acylating reagents		Comments and References
	<p>Popcorn polystyrene derived from polystyrene bearing carboxylic acid</p> <ul style="list-style-type: none"> - Acylation of alcohols - Conversion of alcohols to esters⁵⁰ 	
	<p>Polystyrene-DVB acylating agent</p> <ul style="list-style-type: none"> - Yield 100% - Ten examples⁵¹ 	
	<p>Copolystyrene-DVB vinylbenzoic acid</p> <ul style="list-style-type: none"> - Benzoylation of alcohols^{52,53} 	
	<p>Polymer-bound oxime esters</p> <ul style="list-style-type: none"> - Derivatized Rink linker - Used for esterification and peptide synthesis⁵⁴ 	
	<p>Polystyrene-DVB-supported acylating agents</p> <ul style="list-style-type: none"> - Acylation reaction by the DMAP polymer as an acyl-transfer - Two examples, yields 82-100%⁵⁵ 	
	<p>Polystyrene-DVB 1%</p> <ul style="list-style-type: none"> - Safety catch linker - Utilized for esterification⁵⁶⁻⁵⁸ 	
	<p>Hydroxymethyl resin derived from Merrifield resin</p> <ul style="list-style-type: none"> - Used for the preparation of esters on Merrifield resin-bound equivalent⁵⁹ 	
	<p>Wang resin</p> <ul style="list-style-type: none"> - One pot-formation of esters - Yields: 10-97% final products⁶⁰ 	
$\text{RCOCl} + \text{R}'\text{OH} \xrightarrow[\text{EtOAc}]{\text{Amberlite}^{\text{R}} \text{IRA-68}} \text{RCOOR}'$	<p>Amberlite[®] IRA-68</p> <ul style="list-style-type: none"> - 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[®] 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[®] IRA-400 (Cl) with ArONa solution - Synthesis of diaryloxymethanes from dichloromethane - Fifteen examples, yields 90-95% ⁶⁵
<p style="text-align: center;"><small>Ar_{mix}OH = mixture of 10 phenols or 10 hydroxy heterocycles)</small></p>		Amberlite[®] IRA-900(ArO) anion exchange resin - Used to generate phenoxides and heteroaryl oxides from a mixture of phenols or heteroaryl equivalents ^{18,64}
		Amberlite[®] 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[®] H-15 - Tetrahydropyranlation 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 - Tetrahydropyranlation 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)

	<p>Resin-bound phenoxides</p> <ul style="list-style-type: none"> - Synthesis of methyl ethers by action of dimethyl sulfate - Eight examples, yields 75-98%⁷²
	<p>Resin-bound phenoxides</p> <ul style="list-style-type: none"> - Supported phenoxide ions can be protected with <i>t</i>-butyldimethylsilyl (TBDMS) - Seven examples, yields 65-96%⁷³
<p>ROH $\xrightarrow[\text{Al}_2\text{O}_3, \text{ultrasound}]{\text{ClCH}_2\text{OCH}_3}$ ROCH₂OCH₃ 68-92%</p>	<p>Alumina</p> <ul style="list-style-type: none"> - 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 ones⁷⁴
	<p>Polymer-supported 1,5,7-triazabicyclo[4.4.0]dec-5-ene (PTBD)</p> <ul style="list-style-type: none"> - Polymer-supported bicyclic guanidine base - Used to deprotonate and support a variety of phenols, which can then be <i>O</i>-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
<p>ROH + R'COOH $\xrightarrow[\text{THF, P(Ph)}_3]{\text{resin-CH}_2\text{O-CO-N=N-CO-OMe}}$ RO-C(=O)-R'</p>	<p>Ethoxycarbonyl azocarboxymethyl polystyrene</p> <ul style="list-style-type: none"> - Prepared from treating hydroxymethyl polystyrene with COCl₂, H₂NNHCO₂Me and NBS or Cl₂ - Mitsunobu reactions - Esters from carboxylic acids and alcohols, lactones from hydroxyl acids - 56-88% conversion rate⁷⁶
<p>HO-(CH₂)_n-OH $\xrightarrow[\text{DMAP, DMAP.HCl, CHCl}_3]{\text{resin-CH}_2\text{O-CH}_2\text{CH}_2\text{N=C=N-cyclohexane}}$ (CH₂)_n-O</p>	<p>Polystyrene-carbodiimide resin</p> <ul style="list-style-type: none"> - Used for the synthesis of macrolactones from hydroxyl acids⁷⁷
<p>R₁NHCH₂CH(OH)R₂ $\xrightarrow[\text{2. ArCH}_2\text{Cl, 3. NH}_2\text{NH}_2, \text{CH}_3\text{CO}_2\text{H}]{\text{1. resin-CH}_2\text{O-C}_6\text{H}_4\text{-N=N-CH}_2\text{NMe}_2}$ R₁NHCH₂CH(OAr)R₂</p>	<p><i>p</i>-Diazoniumphenyl substituted Wang resin</p> <ul style="list-style-type: none"> - Immobilization of alcohols⁷⁸
<p>HO-C6H2(OH)-NHBn $\xrightarrow[\text{2. N}_2\text{H}_4, \text{EtOH/DCM}]{\text{1. resin-CH}_2\text{O-NH-CO-C}_6\text{H}_3\text{(NH)-CO-NHBn}}$ H₂N-C6H2(OH)-NHBn</p>	<p>Derived aminomethyl resin</p> <ul style="list-style-type: none"> - A phthalimide containing resin - Conversion of a hydroxyl group to the corresponding amine under Mitsunobu conditions⁷⁹

Table 1 (Continued)

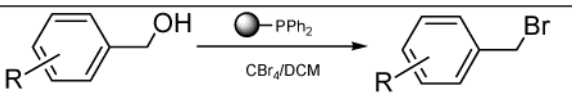
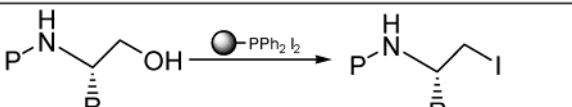
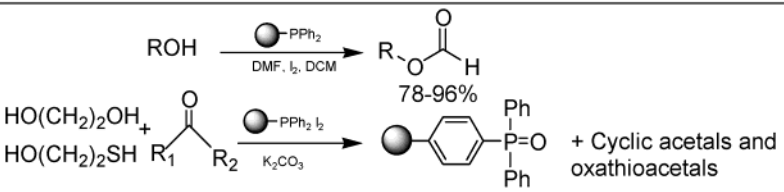
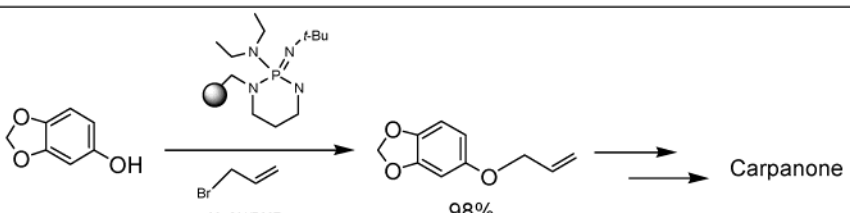
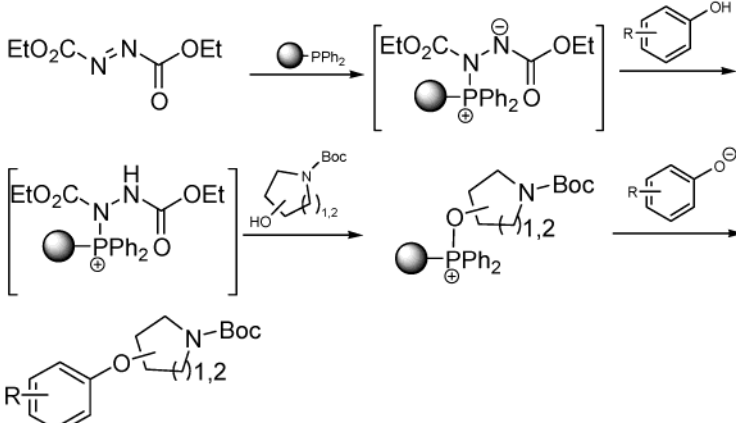
I. Solid-supported Reagents		Comments and References
I.5. Solid-supported phosphines $\text{ROH} \xrightarrow[\text{CCl}_4, \text{CCl}_3\text{CN}]{\text{PPh}_2} \text{RCI}$		Triphenylphosphine polystyrene - Used for the conversion of alcohols to alkyl chlorides - No HCl is released and the conditions are neutral. ⁸⁰⁻⁸²
 $\text{R-CH}_2\text{OH} \xrightarrow[\text{CBr}_4/\text{DCM}]{\text{PPh}_2} \text{R-CH}_2\text{Br}$ <p>R = H, 4-OMe, 4-Cl</p>		Triphenylphosphine polystyrene - Bromination of alcohols ⁸³
 $\text{P-NH-CH}_2\text{-CH}_2\text{-OH} \xrightarrow{\text{PPh}_2 \text{ I}_2} \text{P-NH-CH}_2\text{-CH}_2\text{-I}$ <p>P = Cbz, Fmoc, Boc R = Side chain of Ala, Abu, Val, Phe, Phg, Asp(OBn), Asp(OtBu)</p>		Polymer-bound (polystyryl) triphenylphosphine diiodide - Generated <i>in situ</i> with I ₂ - Used to convert alcohols to iodides - Used to prepare <i>N</i> -protected β-amino iodides ^{81,84,85}
$\text{R}_2\text{COOH} + \text{R}_1\text{OH} \xrightarrow{\text{PPh}_2 \text{ I}_2} \text{R}_2\text{COOR}_1$ <p>benzoic acid + MeOH: 90% conversion octanoic acid + 5α-cholestan-3β-ol: 93% conversion</p>		Polymer-bound (polystyryl) triphenylphosphine diiodide - Carboxylic acids can be esterified with a variety of alcohols ⁸⁶
 $\text{ROH} \xrightarrow[\text{DMF, I}_2, \text{DCM}]{\text{PPh}_2} \text{R-O-CO-H}$ <p>78-96%</p> $\text{HO(CH}_2)_2\text{OH} + \text{R}_1\text{C(=O)R}_2 \xrightarrow[\text{K}_2\text{CO}_3]{\text{PPh}_2 \text{ I}_2} \text{Cyclic acetal} + \text{Cyclic oxathioacetal}$ <p>+ Cyclic acetals and oxathioacetals</p>		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
 <p>98% Carpanone</p>		Polystyrene phosphoramidate - <i>O</i> -Alkylation catalysis ⁸⁸
 $\text{EtO}_2\text{C-NH-NH-CO-OEt} \xrightarrow{\text{PPh}_2} [\text{EtO}_2\text{C-N}^-\text{N}^+\text{CO-OEt}] \xrightarrow{\text{R-OH}} \text{R-O-NH-NH-CO-OEt}$		Triphenylphosphine polystyrene - Synthesis of aryl ethers from amino alcohols ⁸⁹

Table 1 (Continued)

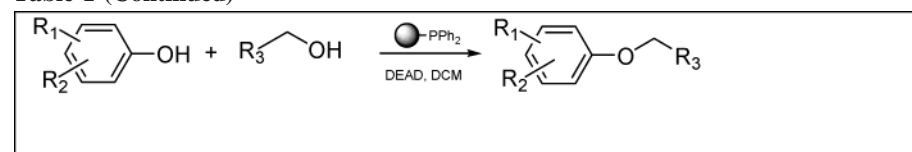
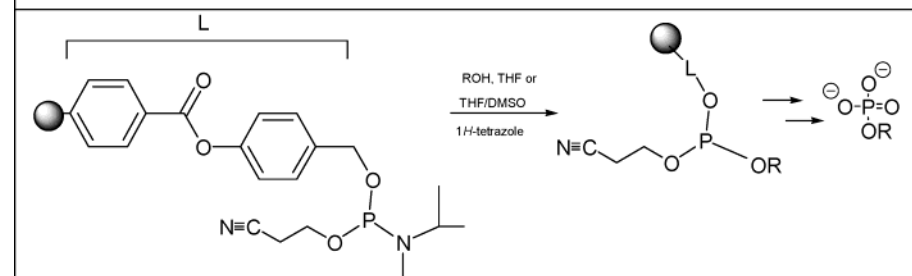
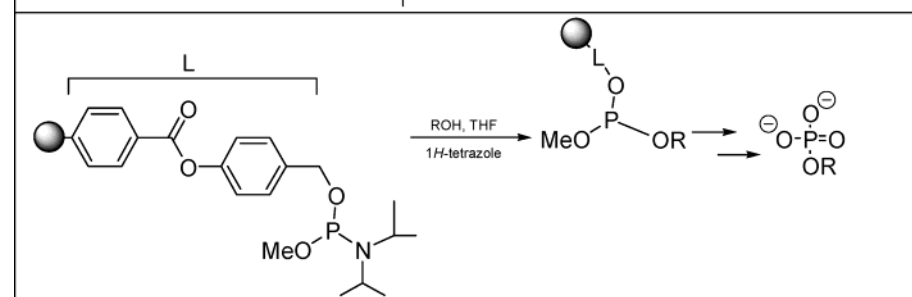
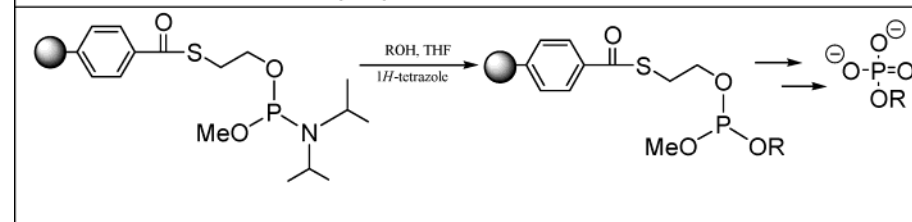
 <p>Reaction scheme showing the synthesis of aryl ethers from phenols and alcohols using a polymer-bound triphenylphosphine reagent. The starting materials are a phenol with substituents R₁ and R₂ and an alcohol R₃-OH. The reaction conditions are DEAD and DCM. The product is an aryl ether where the phenol oxygen is linked to the R₃ group.</p>	<p>Triphenylphosphine polystyrene</p> <ul style="list-style-type: none"> - A traceless reagent for Mitsunobu reactions - Synthesis of aryl ethers from phenols and alcohol - Aryl ether library (15-members) from five phenols and three alcohols, yields 59-94%⁹⁰
 <p>Reaction scheme showing the synthesis of a polymer-bound cyanoethoxy <i>N,N</i>-diisopropylamine phosphine. The starting material is a polymer-bound phosphine with a cyanoethoxy group. The reaction conditions are ROH, THF or THF/DMSO, and 1<i>H</i>-tetrazole. The product is a polymer-bound phosphine with a cyanoethoxy group and an OR group.</p>	<p>Polymer-bound cyanoethoxy <i>N,N</i>-diisopropylamine phosphine</p> <ul style="list-style-type: none"> - Polystyryl derivative - Preparation of carbohydrate and nucleoside monophosphates - Three examples, yields 67-79% for final products⁹¹
 <p>Reaction scheme showing the synthesis of a polymer-bound methoxy <i>N,N</i>-diisopropylamine phosphine. The starting material is a polymer-bound phosphine with a methoxy group. The reaction conditions are ROH, THF, and 1<i>H</i>-tetrazole. The product is a polymer-bound phosphine with a methoxy group and an OR group.</p>	<p>Polymer-bound methoxy <i>N,N</i>-diisopropylamine phosphine</p> <ul style="list-style-type: none"> - Polystyryl derivative - Preparation of carbohydrate monophosphates - Two examples, 39-56% coupling yields⁹²
 <p>Reaction scheme showing the synthesis of a polymer-bound methoxy <i>N,N</i>-diisopropylamine phosphine with a sulfonate group. The starting material is a polymer-bound phosphine with a methoxy group and a sulfonate group. The reaction conditions are ROH, THF, and 1<i>H</i>-tetrazole. The product is a polymer-bound phosphine with a methoxy group and an OR group.</p>	<p>Polymer-bound methoxy <i>N,N</i>-diisopropylamine phosphine</p> <ul style="list-style-type: none"> - Polystyryl derivative - Preparation of carbohydrate methylphosphates - Two examples, 52-63% coupling yields⁹²

Table 2. Solid Supports Reactions with Alcohols and Phenols

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.1.1.1. Reactions on Merrifield resin		
ROH, Conditions Comments and References		
<ul style="list-style-type: none"> - NaH, 15-crown-5 - Glycosylation on an alkyl thiol polymer - Total yield for disaccharide 54%¹²⁰ 	<ul style="list-style-type: none"> - NaH, THF - Loading 84% - Synthesis of γ-butyrolactones - Six examples¹²¹ 	<ul style="list-style-type: none"> - NaH, THF - Synthesis of photodetachable arylsilane polymer linkage⁹⁶
<ul style="list-style-type: none"> - Linker based on the dihydropyranyl (DHP) group - Coupling of alcohols to solid supports¹¹⁰ - DMA - Subsequent reactions leading to butenolides described⁹⁴ 	<ul style="list-style-type: none"> - KI, acetone, NaH, DMF - New linkers used for diverse solid phase syntheses¹²² 	<ul style="list-style-type: none"> - NaH, THF - Synthesis of oligo(1,4-phenyleneethylene) of defined lengths (oligomers)¹²³
<ul style="list-style-type: none"> - NaH, 15-crown-5 - A formamidine linker for use in solid-phase synthesis of amino ethers - Eight examples - Yield for final products 80-95%⁷⁸ 	<ul style="list-style-type: none"> - NaH, DMF - Immobilization of glycidol derivatives¹²⁴ 	<p>Loading 96% Loading 40%</p> <ul style="list-style-type: none"> - NaH, TBAI, THF - Polymer-supported benzotriazole as a traceless linker - Used in the synthesis of small library of homogenated secondary and tertiary amine products (final products yields 0-77%)¹²⁵
<p>Derived from Merrifield resin</p> <ul style="list-style-type: none"> - NaH, NMP - Synthesis of seven-membered lactams - Loading yield 84% - Ring-closing metathesis described¹²⁶ 	<ul style="list-style-type: none"> - NaH, DMF - Used for the synthesis of silyl linkers^{127,128} 	<ul style="list-style-type: none"> - NaH, DMF - Synthesis of 1,4-benzodiazepine-2,5-diones - Final products yields 40-92%¹²⁹
<p>Merrifield resin or Wang-chloride resin</p> <ul style="list-style-type: none"> - DMA - Polymer-supported preparation of substituted phenols (isolated yields for final twelve compounds 52-85%)¹³⁰ 	<ul style="list-style-type: none"> - NaH, THF, DMA - Used for ketalisation with 3,5-cyclohexadiene-1,2-diols¹³¹ 	<p>X = H, OMe</p> <p>Merrifield resin or bromomethyl Tentagel resin</p> <ul style="list-style-type: none"> - NaH, DMF - Used in the synthesis of dithiane-protected photolabile safety catch linker¹³²

Table 2 (Continued)

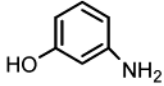
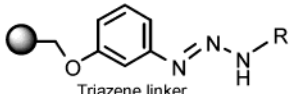
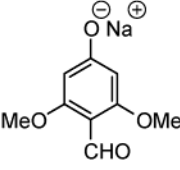
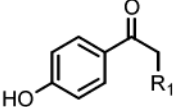
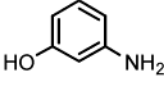
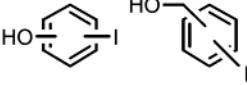
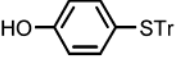
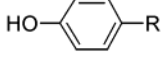
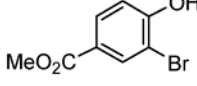
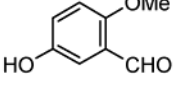
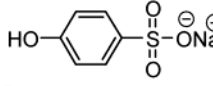
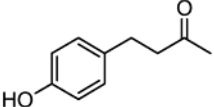
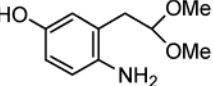
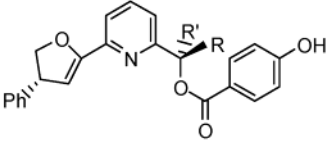
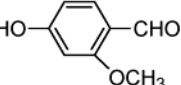
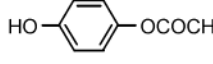
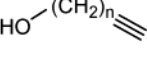
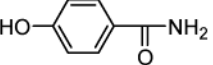
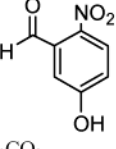
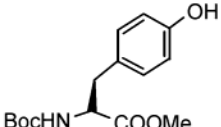
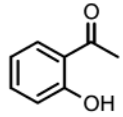
 <p>- NaH, DMF - Triazene linker developed from Merrifield resin</p>  <p>Triazene linker - Used for the synthesis of amide and urea libraries¹³³</p>	 <p>- DMF - Immobilization of phenols¹³⁴</p>	 <p>- NaH, DMF - Immobilization of phenols - Syntheses of tetrasubstituted pyrazoles described - 12-membered library¹³⁵</p>
 <p>- NaH, <i>n</i>-Bu₄NI - Subsequent reaction with amines to give diazonium salts used for synthesis of 3-alkoxy-4-aryl piperidines as aspartic peptidase inhibitors¹³⁶</p>	 <p>- NaH, THF or MeONa, DMF - Subsequent reactions leading to butenolides described¹³⁴</p>	 <p>- Thiohydroxamic acid as a photolabile "traceless" linker developed - NaH, DMF - Yields for attachment and detachment reactions (85 and 55%, respectively)¹³⁷</p>
 <p>R = CH₂OH, COOMe - NaOMe, DMA - Immobilization of phenols described⁹⁵</p>	 <p>- NaOMe, DMA - Used for the synthesis of resin-bound sulfonamide - Monitoring reaction with spin echo magic angle proton NMR¹³⁸</p>	 <p>- NaOMe, DMF - 2-Methoxy-4-benzyloxypolystyrene aldehyde resin (MALDRE) derived from Merrifield resin - Synthesis of secondary amides¹³⁹</p>
 <p>- NaOMe, DMA - One example - Synthesis of arginine-containing peptides by guanidine attachment to a sulfonyl linker - Overall yield reported⁹⁷</p>	 <p>- NaOMe, DMF - Further modifications on carbonyl group - Used in peptide synthesis¹⁴⁰</p>	 <p>- DMF, NaOMe, (Bu)₄NI, 81% - To synthesize a novel safety-catch linker for synthesis of amides and esters¹⁴¹</p>
<p>ROK - DMF, 18-crown-6 - Immobilization of alcohols¹⁴²⁻¹⁴⁴</p>	 <p>● = Polystyrene or Argogel, R, R' = H 55-57% conversion ● = Argogel, R = <i>t</i>-Bu, R' = H (R,R) or R = H, R' = <i>t</i>-Bu (R,S) 40% conversion - Merrifield resin or ArgoGel™-Wang-Cl - DMF, K₂CO₃ - Preparation of polymeric ligands to assess in the palladium-catalyzed allylic alkylation¹⁴⁵</p>	 <p>- <i>t</i>-BuOK, DMSO or DMA - Synthesis of SASRIN™ resin¹⁴⁶</p>
 <p>- K₂CO₃, DMF, LiAlH₄ - Synthesis of photodetachable arylsilane polymer linkage⁹⁶</p>	 <p>- Pyridine - New linker used for synthesis of isoxazole-based amino acids⁹³</p>	 <p>- NaOH, DMSO - Preparation of <i>p</i>-benzyloxybenzylamine (BOBA) resin after reduction with BH₃.SMe₂ (94% yield for this resin)¹⁴⁸</p>
 <p>- <i>n</i>-Bu₄NI, DMF, Cs₂CO₃ - Construction of dodecasaccharide¹⁴⁷</p>		

Table 2 (Continued)

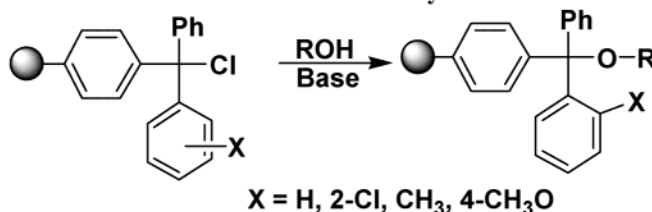
 <p>BocHN-CH(CH₂-C₆H₄-OH)-COOMe - Coupling yield more than 25%^{149,150}</p>	 <p>Wang and Merrifield resins - Synthetic equivalents of 3-formylchromone and chromone reported¹⁵¹</p>	
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II. Solid supports reactions with alcohols and phenols

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



ROH

Conditions

Comments and References

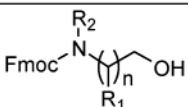
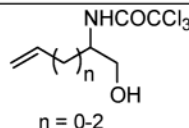
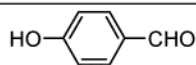
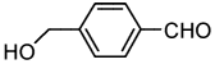
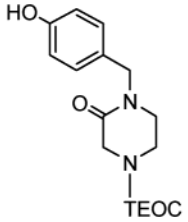
 <p>Trityl chloride resin - Piperidine - Tentagel resin derivatized with either Rink or trityl linker - Eight symmetrical diamines and amino alcohols - Synthesis of diverse perhydro-1,4-diazepine-2,5-diones¹⁵²</p>	 <p>n = 0-2 Trityl chloride resin - Synthesis of 6-, 7- and 8-membered azacycles via olefin metathesis - Yield for cleavage products 85-89%¹⁵³</p>	 <p>Trityl chloride resin - Pyridine, THF - Used for the anchoring of phenols - Solid phase synthesis of isoxazolines¹⁵⁴</p>
<p>ROH 2-Chlorotrityl chloride-substituted polystyrene - Fmoc-hydroxylamine, 2 aminobutanol, 3-aminopropane-1-ol, phenylalaninol, 4-aminobutanol, 1,3-diaminopropan-2-ol, ethyleneglycol, 2-(2-aminoethoxy)ethanol, <i>N</i>-methyl-2-aminoethanol, 4-aminomethyl benzyl alcohol, glycinol, pyrrolinol - Synthesis of hydroxamic acids^{155,156}</p>	 <p>Trityl chloride resin - Sym-collidone, Bu₄NI, DCM - Used in stereocontrolled synthesis of polyketide libraries - Yield for cleaved product 60%¹⁵⁷</p>	<p>ROH Trityl chloride resin, NovaSyn^R dichlorotrityl, 2-chlorotrityl chloride NovaSyn^R TGT - Pyridine - Chlorodiphenylmethyl benzoylamidomethyl polystyrene^{100,101,150,154}</p>
<p>ROH = Different primary alcohols Trityl resin (X = 4-CH₃O, 4-CH₃, 2-Cl) - Etherification of various alcohols with resins of the trityl type - Yield 25-50%¹⁰²</p>	 <p>TEOC = trimethylsilyloxyethyl carbamate 2-Chlorotrityl resin - DIEA, DCM - Modification of 2-ketopiperazine with solid phase <i>C</i>-alkylation and <i>N</i>-acylations¹⁵⁸</p>	

Table 2 (Continued)

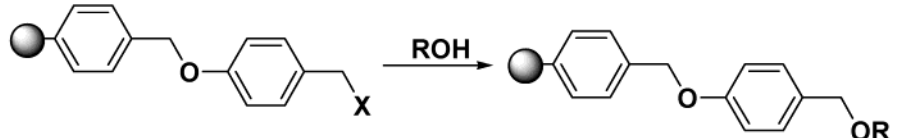
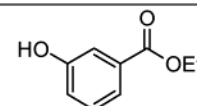
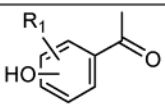
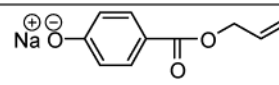
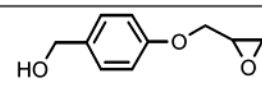
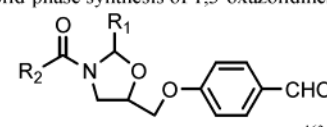
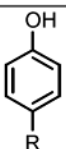
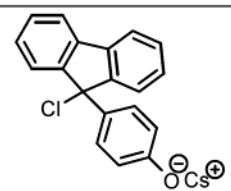
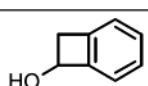
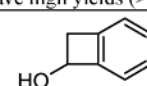
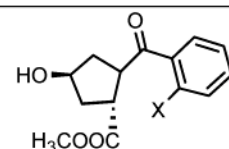
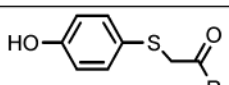
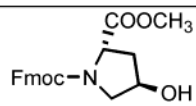
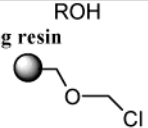
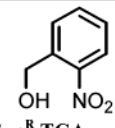
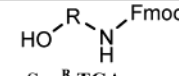
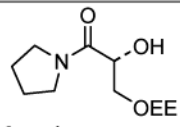
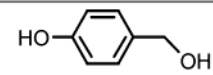
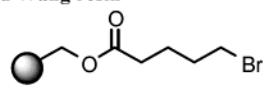
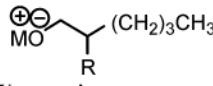
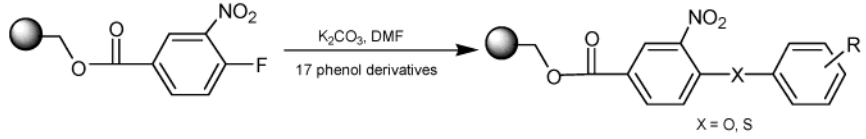
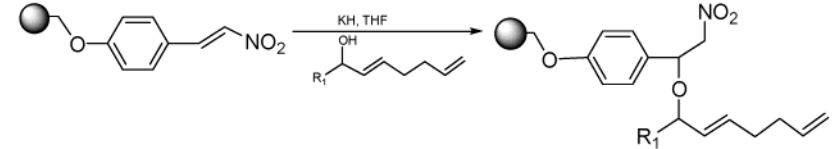
II. Solid supports reactions with alcohols and phenols		
II.1. Attachment as ethers (<i>O</i> -alkylation or <i>O</i> -arylation)		
II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)		
II.1.1.3. Reactions on Wang resin		
 <p>X = -Cl, -Br, -O-C(=O)-CCl₃, -OH, others</p>		
ROH Conditions Comments and References		
 <p>Wang chloride resin - KO^tBu - Immobilization of phenols¹⁵⁹</p>	 <p>Wang chloride resin - Cs₂CO₃, NaI, DMF - Phenol attachment - Synthesis of 2,4,6-trisubstituted pyridines¹⁶⁰</p>	 <p>Wang chloride resin - DMF - Synthesis of hexahydroisindoles¹⁶¹</p>
 <p>Wang chloride resin - NaH, DMF - Solid-phase synthesis of 1,3-oxazolidines</p>  <p>- Yields: up to 92% (Sixteen examples)¹⁶²</p>	 <p>Wang chloride resin - Used for immobilization of phenol - NaOMe, DMA - Conditions for attachment and detachment were investigated.¹⁶³</p>	 <p>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</p>
 <p>Wang trichloroacetamidate resin - TfOH, DCM/hexane - Used for synthesis of benzoannulated nitrogen heterocycles¹⁶⁵</p>	<p>ROH</p> <p>Wang or Tentagel trichloroacetamidate resin - Polymer-bound <i>p</i>-alkoxybenzyl trichloroacetamidate used for protection of alcohols as benzyl ethers - BF₃·OEt₂, DCM - Coupling yields 70-98% - Monobenylation of symmetrical diols - ROH = primary, secondary and tertiary diols, alcohols of different classes, fourteen examples¹⁰³</p>	 <p>Wang trichloroacetamidate resin - TfOH, DCM, hexane - Traceless linker - Homo- and hetero-Diels-Alder reactions of <i>O</i>-quinodimethanes - Synthesis of tetrahydroisoquinolines - Total yields: 10-47%¹⁶⁶</p>
 <p>Wang trichloroacetamidate resin - TfOH, DCM - Synthesis of pyrrolo[2,1-<i>c</i>][1,4]benzodiazepine-5,11-diones¹⁶⁷</p>	 <p>Wang trichloroacetamidate resin - A new alkoxyphenyl-sulfonyl type linker developed - Used for the diastereoselective preparation of hydroxyl derivatives¹⁶⁸</p>	 <p>Wang trichloroacetamidate resin - Used for immobilization of alcohols - BF₃·OEt₂ or CF₃SO₃H, DCM - Synthesis of pyrrolo[2,1-<i>c</i>][1,4]benzodiazepines described¹⁶⁹</p>

Table 2 (Continued)

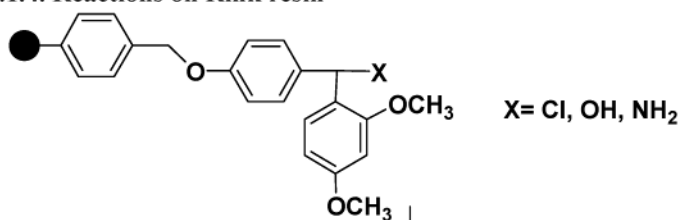
<p>Modified Wang resin</p>  <p>- Immobilization of alcohols and phenols¹⁷⁰</p>	<p>Wang or NovaSyn[®] TGA trichloroacetamide resins</p>  <p>- BF₃·Et₂O, THF/DCM¹⁷¹</p>	<p>Wang or NovaSyn[®] TGA trichloroacetamide resins</p>  <p>- BF₃·Et₂O, THF/DCM¹⁷¹</p>
<p>Wang bromide resin</p>  <p>- NaH, Bu₄NI, THF, 18-crown-6 - Synthesis of aspartyl protease inhibitor libraries - 84% loading efficiency¹⁷²</p>	<p>Wang resin</p>  <p>- Used for immobilization of 1,4-benzenedimethanol. - 1. Cl₃CCN, DBU, DCM; 2. BF₃·OEt₂, THF/DCM - Synthesis of polyethers using cyclic sulfates described. - Five examples; yields: 41-66%¹⁷³</p>	<p>Modified Wang resin</p>  <p>- Used for synthesis of benzoannulated nitrogen heterocycles¹⁶⁵</p>
<p>Modified Wang resin</p>  <p>- Prepared from the reaction of bromo alcohols with Wang trichloroacetamide resin - Williamson ether synthesis developed on solid support - Eleven examples¹⁷⁴</p>	<p>Modified Wang resin</p>  <p>- Synthesis of functionalized biaryl ethers - Theoretical yields based on Wang resin 40-58%¹⁷⁵</p>	
<p>Modified substituted Wang resin</p>  <p>- 20-50% overall yields for final products - Synthesis of cyclic ethers¹⁷⁶</p>		

II. Solid supports reactions with alcohols and phenols

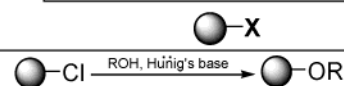
II.1. Attachment as ethers (*O*-alkylation or *O*-arylation)

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

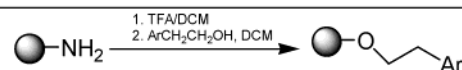
II.1.1.4. Reactions on Rink resin



Comments and References

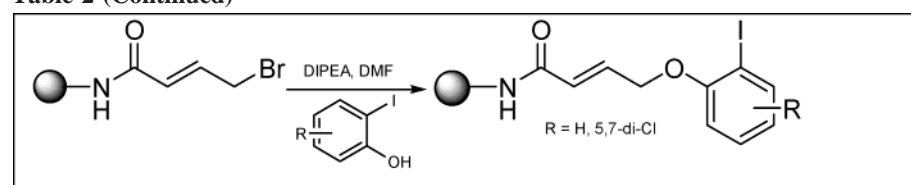
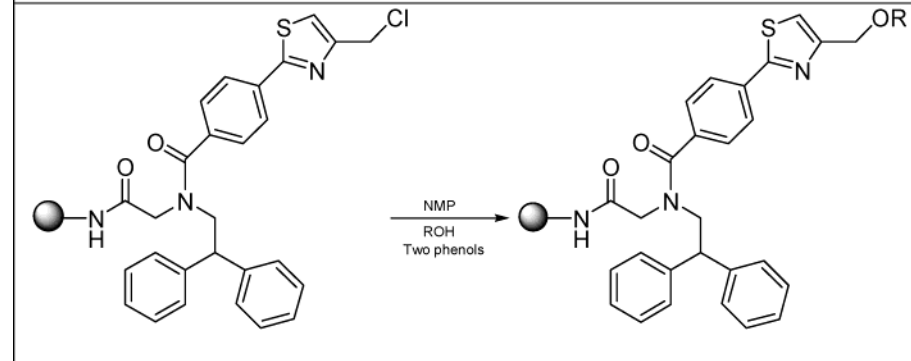
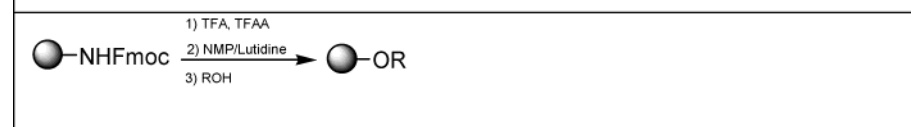
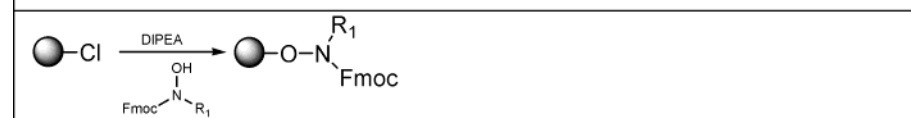
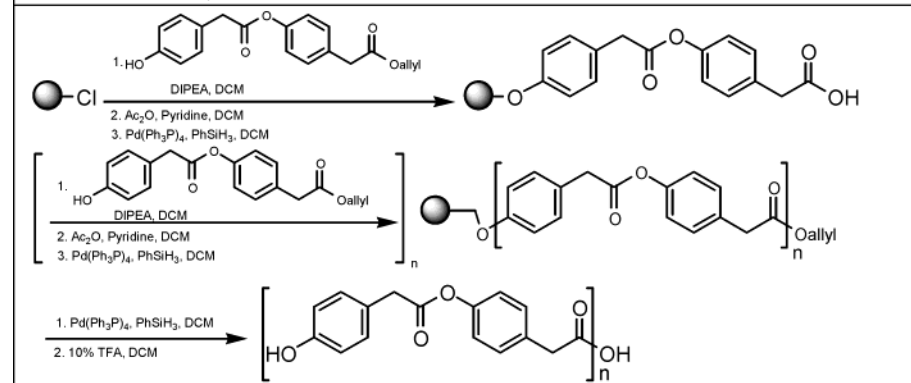


Rink chloride resin
- Four examples, Yields 85-96%¹⁷⁷



Rink amide resin polystyrene crown
- Nine examples; yields: 33-90%¹⁷⁸

Table 2 (Continued)

	<p>Derived from Rink amide resin</p> <ul style="list-style-type: none"> - Two examples - <i>O</i>-alkylation - Construction of indole and benzofuran systems - Purified yields for final compounds 81-83%¹⁷⁹
	<p>Derived from Rink amide resin</p> <ul style="list-style-type: none"> - The preparation of 2,4-disubstituted thiazoles - Yield for final compounds after cleavage 63-70%¹⁸⁰
	<p>Derived from Rink resin</p> <ul style="list-style-type: none"> - Immobilization of nucleophiles on polystyrene supports - Three examples, quantitative or decomposition¹⁸¹
	<p>Rink chloride resin</p> <ul style="list-style-type: none"> - Synthesis of hydroxamic acids - Twelve examples - Yields: 58-95%¹⁵⁵
	<p>JandaJel-Rink resin</p> <ul style="list-style-type: none"> - 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

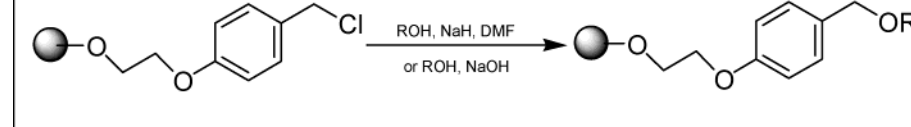
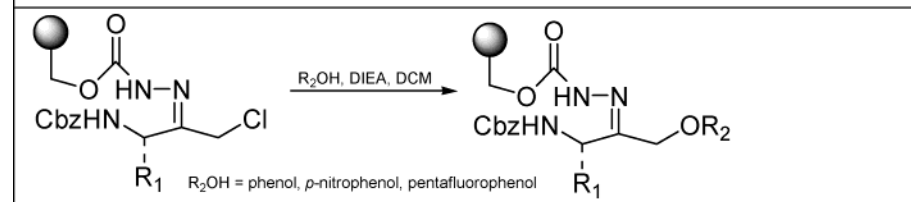
	Comments and References
	<p>Derived from ArgoGel-Wang resin</p> <ul style="list-style-type: none"> - Immobilization of alcohols - Five examples; overall yield reported¹⁸³
	<p>Derived from ArgoGel-OH</p> <ul style="list-style-type: none"> - Used for the preparation of cysteine protease inhibitors - Yield for cleaved products 31-37%¹⁸⁴

Table 2 (Continued)

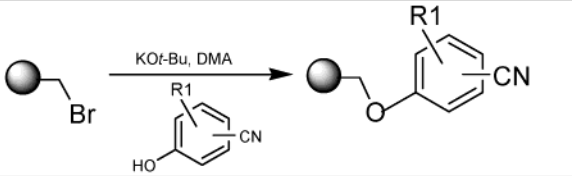
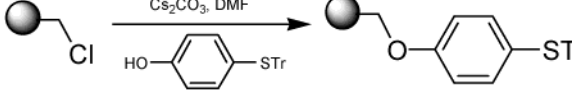
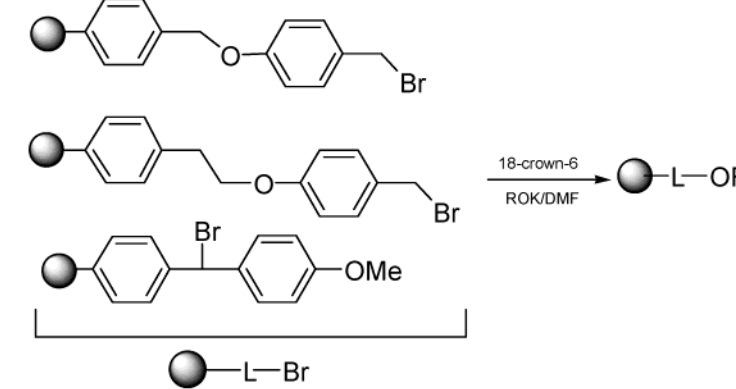
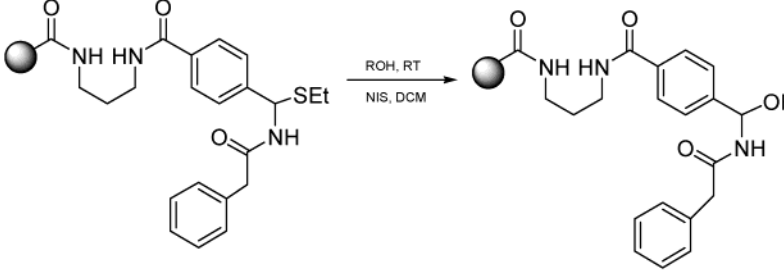
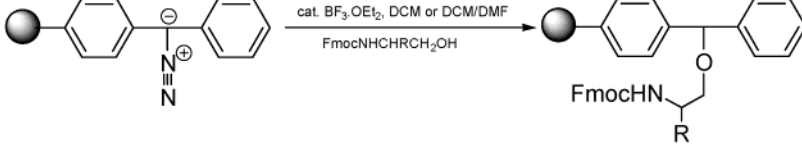
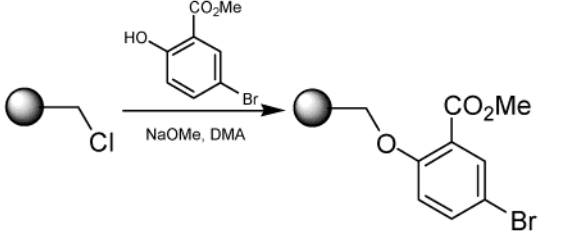
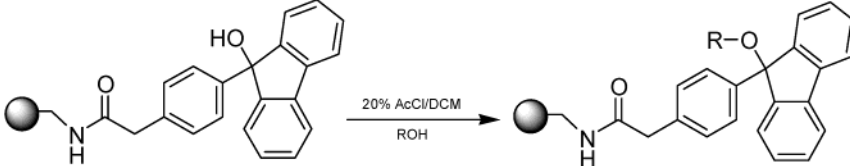
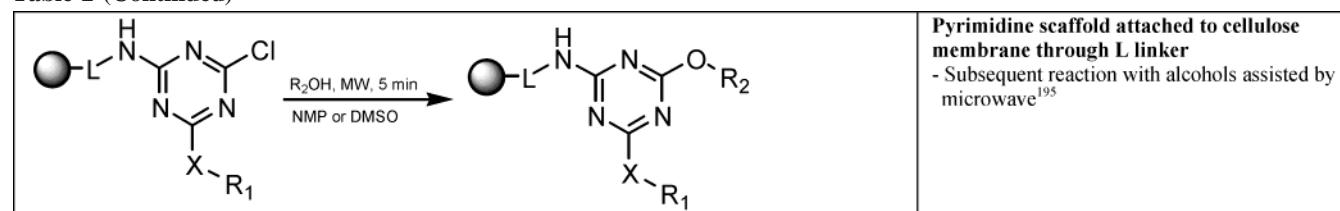
	<p><i>p</i>-Alkoxybenzyl bromide resin - Synthesis of oxadiazoles¹⁸⁵</p>
	<p>Benzhydrylamine resin (BHA resin) - Use of thioester resins described¹⁸⁶</p>
	<p>4-(Bromomethyl)phenoxyethyl polystyrene 4-(Bromomethyl)phenoxyethyl polystyrene 4-Bromo-(4-methoxyphenyl)methyl polystyrene - Immobilization of alcohols¹⁴²⁻¹⁴⁴</p>
	<p>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</p>
	<p>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</p>
	<p>PEG crosslinked polystyrene disk - Synthesis of biphenyls using Suzuki coupling reaction described¹⁸⁸</p>
	<p>Derived from aminomethyl polystyrene resin or TentaGel-S-NH2 resin - Immobilization of nucleophiles like alcohols¹⁸⁹</p>

Table 2 (Continued)

<p>$R_1, R_2, R_3 = \text{alkyl and aryl groups}$ Loading 68-92%</p>	<p>Derived from Merrifield resin</p> <ul style="list-style-type: none"> - Synthesis of γ-butyrolactones - Six examples¹²¹
	<p>Derived from Merrifield resin</p> <ul style="list-style-type: none"> - A vinyl ether type linker - Used for immobilization of alcohols, imidazoles, and tetrazoles - Subsequent Suzuki coupling reactions were investigated.¹⁹⁰
	<p>SynPhase™ lantern resin (long-chain HMP)</p> <ul style="list-style-type: none"> - Synthesis of quinazolines-2-thioxo-4-ones - Five examples; moderate yields¹⁹¹
	<p>Four different resin types including Wang resin, Ellman resin, polystyrene-polyoxyethylene NovaSyn[®] resin, and polyoxyethylene-polyoxypropylene (POEPOP)</p> <ul style="list-style-type: none"> - 2,5-Diketopiperazines solid-phase synthesis¹⁹²
	<p>Derived Merrifield resin</p> <ul style="list-style-type: none"> - A novel resin (loading capacity, 0.6 mmol/g) developed - Used to synthesize a 2,5,6-trisubstituted-4(3<i>H</i>)-pyrimidinones targeting HIV-1 reverse transcriptase¹⁹³
	<p>Novel polystyrene sulfonic-ketone resin</p> <ul style="list-style-type: none"> - Employed for construction of a variety of heterocyclic compounds¹⁹⁴

Table 2 (Continued)

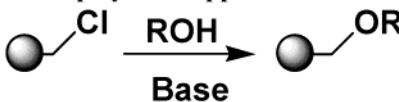


II. Solid supports reactions with alcohols and phenols

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.1.1.6. The synthesis of polymer-supported chiral auxiliary compounds



ROH Conditions Comments and References

<p>Merrifield resin</p> <ul style="list-style-type: none"> - NaH, THF - Polymer-supported oxazoline chiral auxiliary - Preparation of nonracemic α-alkyl-carboxylic acid using polymer-bound oxazolines - Three examples¹⁹⁶ 	<p>Merrifield resin</p> <ul style="list-style-type: none"> - 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 	<p>Merrifield resin</p> <ul style="list-style-type: none"> - Polymer-supported chiral auxiliary - Preparation of non-racemic 3,5-disubstituted-δ-butyrolactones - Lactones isolated in 34% overall yield¹⁹⁸
<p>Merrifield resin</p> <ul style="list-style-type: none"> - KH, 18-crown-6, THF - Polymer supported enantioselective reactions - α-Methylation of cyclohexanone¹⁵⁶ 	<p>Merrifield resin</p> <ul style="list-style-type: none"> - NaH, 18-crown-6, CsF, dioxane, <i>n</i>-BuNI - Chiral polymers - Derived from L-tartaric acid¹⁹⁹ 	<p>Merrifield resin</p> <ul style="list-style-type: none"> - K₂CO₃, DMF - Chiral polymers via asymmetric epoxidation and dihydroxylation - A polymer bearing a chiral diol pendant²⁰⁰
<p>Merrifield, Wang or Tentagel-PHB resins</p> <ul style="list-style-type: none"> - Polymer-bound chiral auxiliaries - Polymer-bound Evans oxazolidinones - Synthesis of chiral primary alcohols - Aldol reactions^{197,201,202} 	<p>Chloropropyl functionalized silica gel</p> <ul style="list-style-type: none"> - NaH, THF - Silica gel supported <i>Cinchona</i> alkaloid (chiral auxiliary immobilized on silica support) - Catalytic asymmetric dihydroxylation of alkenes²⁰³ 	

Table 2 (Continued)

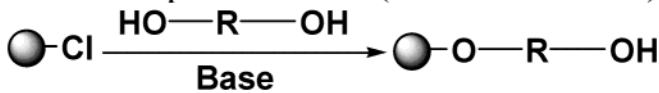
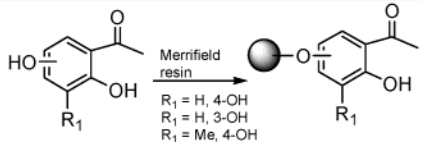
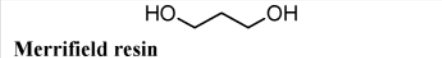
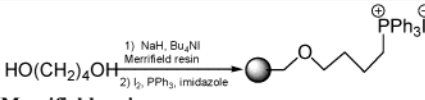
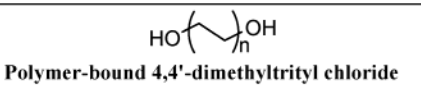
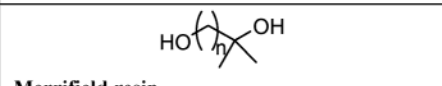
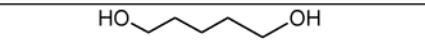
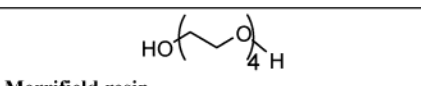
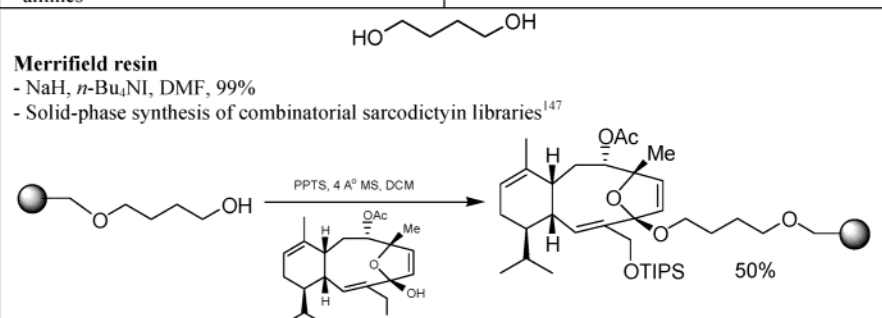
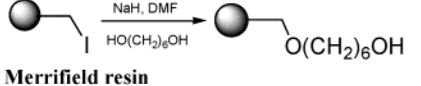
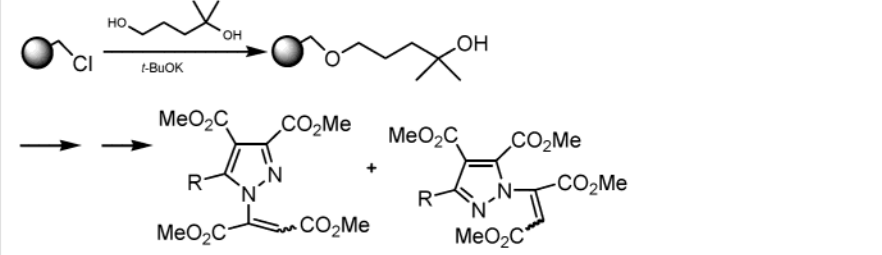
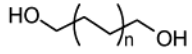
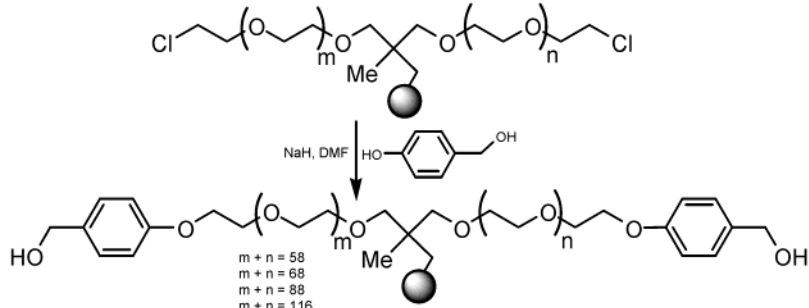
II. Solid supports reactions with alcohols and phenols		
II.1. Attachment as ethers (<i>O</i>-alkylation or <i>O</i>-arylation)		
II.1.1. Attachment to resins (immobilization of hydroxyl functional group and synthesis of miscellaneous compounds)		
II.1.1.7. Monoprotection of diols (monoether attachment)		
		
HO-R-OH		
Conditions		
Comments and References		
 <p>Merrifield resin $R_1 = \text{H}, 4\text{-OH}$ $R_1 = \text{H}, 3\text{-OH}$ $R_1 = \text{Me}, 4\text{-OH}$</p> <p>Merrifield resin - Immobilization of alcohols²⁰⁴</p>	 <p>Merrifield resin - Synthesis of cyclopentane derivatives²⁰⁵</p> <p>Merrifield resin - Designing eptitholones - One example - Overall yield reported - <i>O</i>-Alkylation²⁰⁶</p>	 <p>1) NaH, Bu₄Ni Merrifield resin 2) PPh₃, imidazole</p> <p>Merrifield resin - Synthesis of eptitholones A and B²⁰⁶</p>
 <p>Polymer-bound 4,4'-dimethyltrityl chloride or trityl chloride - Pyridine - Preparation of monoacetates of symmetrical diols²⁰⁷</p>	 <p>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 - <i>O</i>-Alkylation - Preparation of solid-supported <i>t</i>-alkoxycarbonylation reagents for anchoring of amines²⁰⁸</p>	 <p>Merrifield resin - Polymer-supported oligosaccharides via <i>n</i>-pentenyl glycosides (NPG) - Used in glycosidation²⁰⁹</p>
 <p>Merrifield resin - NaH, DMA - Monoprotection of diols²¹⁰</p>	 <p>Merrifield resin - NaH, <i>n</i>-Bu₄NI, DMF, 99% - Solid-phase synthesis of combinatorial sarcodictyin libraries¹⁴⁷</p> <p>50%</p>	
 <p>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</p>	 <p>Several resins (imidazole, carbamate, and α-silylnitrosocarbamate) developed from Merrifield resin - Traceless synthesis of pyrazole derivatives - Yields: 11-70% last four steps²¹²</p>	

Table 2 (Continued)

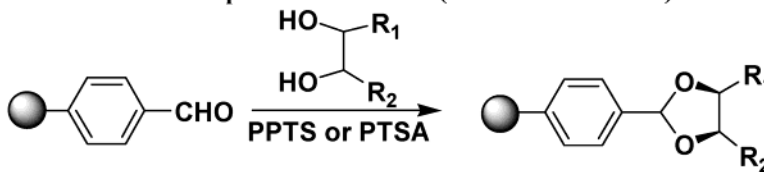
 <p>Trityl resin (PS-DVB)</p> <ul style="list-style-type: none"> - Pyridine, THF - Bifunctionalized resins - Immobilization of diols - Modification on unbound OH like oxidation and Wittig reaction, esterification - Coupling yields 75-90% - Preparation of β-mercaptoketones - Monoprotection of symmetrical diols, triols and tetraols, preparation of monoacetates of symmetrical diols - Reactions like oxidation, esterification on unbound hydroxyl group^{142,143,213-228} 	 <p>New poly(styrene-oxyethylene) graft copolymer resin</p> <ul style="list-style-type: none"> - Loading: 0.32-050 mmol/g²²⁹ <p>$m+n=58$ $m+n=68$ $m+n=88$ $m+n=116$</p>
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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)

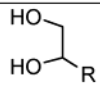
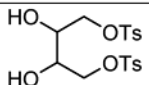
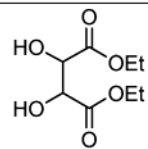
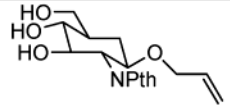
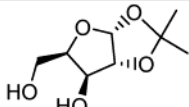
II.1.1.8. Diprotection of diols (diether attachment)



ROH

Conditions

Comments and References

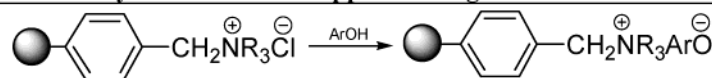
 <p>Polystyrene derivatized</p> <ul style="list-style-type: none"> - Protection of diols^{230,231} 	 <p>Derived from Merrifield resin</p> <ul style="list-style-type: none"> - PTSA, toluene - Used in synthesis of polymer-supported active phase transfer catalysis²⁵² 	 <p>Derived from Merrifield resin</p> <ul style="list-style-type: none"> - PTSA, benzene - Polystyrene resins with chiral fragments derived from tartaric acid¹⁹⁹
 <p>Wang aldehyde resin</p> <ul style="list-style-type: none"> - Camphorsulfonic acids, molecular sieves, CH₃CN - Protection of diols²³³ 	 <p>Wang aldehyde resin</p> <ul style="list-style-type: none"> - PPTS, DCM - Protection of diols²³⁴ 	

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[®] IRA-900
- Used in alkylation of alkyl halides^{64,235,236}

Table 2 (Continued)

	Merrifield resin - Synthesis of polymer-supported diphosphine - Polymer-supported <i>O</i> -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)

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Table 2 (Continued)

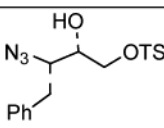
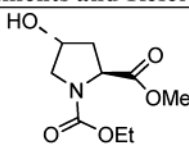
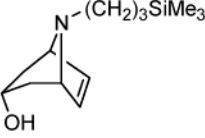
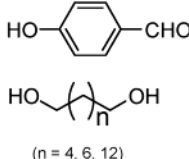
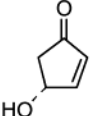
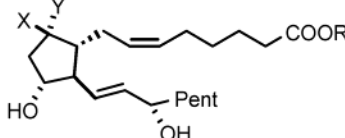
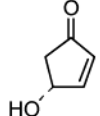
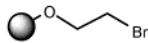
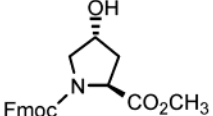
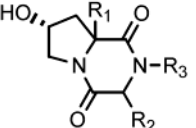
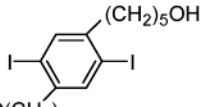
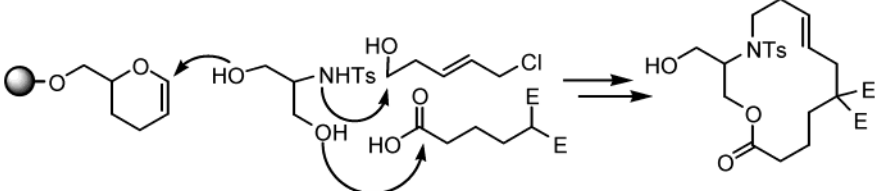
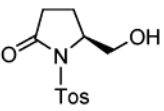
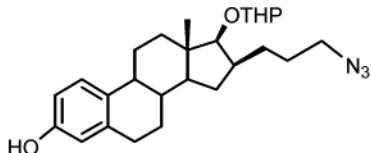
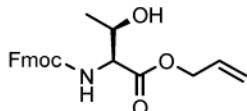
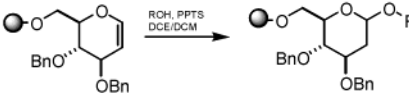
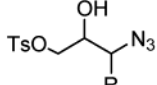
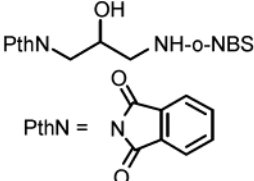
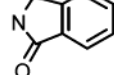
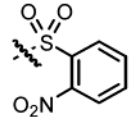
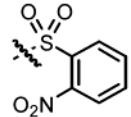
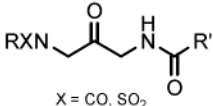
ROH (alcohols or phenols)		
Conditions		
Comments and References		
 <p>DHP-linked Merrifield resin</p> <ul style="list-style-type: none"> - Core unit linked to resin via THP protected alcohol - Synthesis of aspartic protease inhibitors - Yield for final products (different protease inhibitors) 47-86%; 20-50% in the diol series; 30-70% for the monoalcohol diamine derivatives^{110,111,244,245} 	 <p>DHP-functionalized polystyrene support</p> <ul style="list-style-type: none"> - Solid-phase synthesis strategy for the preparation of 2-pyrrolidinemethanol ligands¹¹² 	<p>$\text{HO}(\text{CH}_2)_n\text{OH}$</p> <p>DHP-linked Wang resin</p> <ul style="list-style-type: none"> - Alcohol to aldehyde conversion^{112,245-249}
 <p>DHP-functionalized polystyrene support</p> <ul style="list-style-type: none"> - Solid-phase synthesis of atropane derivatives - Yield for final products 50-73%²⁴⁹ 	 <p>Derived from Merrifield resin</p> <ul style="list-style-type: none"> - Synthesis of pyrrolidines - Overall yields 32-50%²⁴⁶ 	 <p>THP linker attached to non-cross-linked polystyrene</p> <ul style="list-style-type: none"> - Used for immobilization of alcohols - Synthetic approach for prostaglandins and derivatives reported²⁵⁰  <p>DHP-linked Merrifield resin</p> <ul style="list-style-type: none"> - Primary and secondary alcohols - Tertiary alcohols show very poor loading efficiencies. - Synthesis of prostaglandins^{110,111}
 <p>Non-cross linked polystyrene (NCPS) a soluble copolymer support</p> <ul style="list-style-type: none"> - Synthesis of prostaglandin F2α on a non-cross-linked polystyrene support (NCPS) - The overall isolated yield is about 30% after 10 chemical steps²⁵¹ <p>Tentagel-S (bromide)</p> <ul style="list-style-type: none"> - Poly(styrene)block (polyethyleneglycol) resin  <ul style="list-style-type: none"> - Prostaglandin synthesis¹¹¹ 	 <p>DHP-linked Wang resin</p> <ul style="list-style-type: none"> - Solid phase synthesis of a new class of 2,5-diketopiperazines²⁵² 	 <p>DHP-linked Merrifield resin</p> <ul style="list-style-type: none"> - 49% loading - Solid-phase synthesis of oligo(1,4-phenyleneethylene) by a divergent convergent tripling strategy²⁵³
 <p>DHP-linked Wang resin</p> <ul style="list-style-type: none"> - Used for immobilization of hydroxyl containing compounds - Used for the synthesis of macroheterocycles. - Yields high^{254,255} 		

Table 2 (Continued)

 <p>DHP-linked Merrifield resin - Synthesis of amino alcohols²⁵⁶</p>	 <p>DHP-HM resin - Steroid derivatization on solid support²⁵⁷</p>	 <p>DHP resin - Used for immobilization of threonine - Synthesis of Tyr¹³-octreotate described²⁵⁸</p>
 <p>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</p>	 <p>Merrifield resin with dihydroxy acetal linker - Immobilization of alcohols and further synthesis of heterocycles²⁶⁰</p>	 <p>PthN = </p>  <p>o-NBS = </p> <p>DHP linked Wang resin - Used for immobilization of hydroxyl containing synthon - Applied for synthesis of 1,3-diaminoketones</p>  <p>X = CO, SO₂</p> <p>- Five examples; 25-60% overall yields²⁶¹</p>

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)

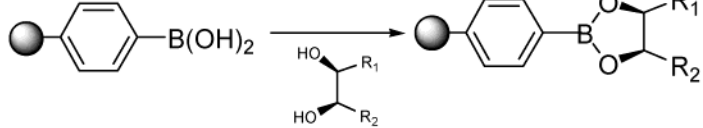
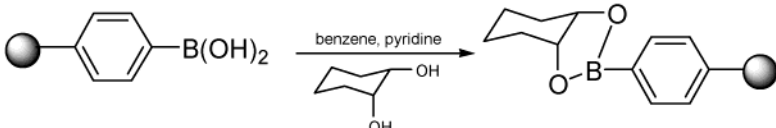
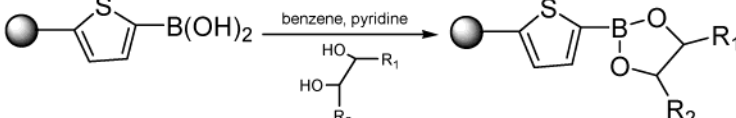
II.1.1.12. Attachment through a boronic acid linker (reactions with polymer-bound boronic acid)	Comments and References
 	<p>Polystyrene/boronic acid - Solid-phase separation of <i>cis-trans</i> diol mixtures - Only <i>cis</i>-diols are bound. - Protecting group of diols^{10,226,262-264}</p>
	<p>Polystyrene/boronic acid - Protection of diols^{113,114}</p>

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 glycol derived thioethyl glycosyl donors ¹¹⁷
	Polystyrene diisopropylsilyl chloride - Prepared from polystyrene by lithiation and reaction with dichlorodisopropylsilane - 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
<p>ROH = 1-(2-methoxybenzoyl)-2-pyrrolidinemethanol, 2-(1-naphthyl)ethanol, <i>N</i>-Fmoc-ethanolamine, 1-(4-methoxyphenoxy)-2-propanol, <i>trans</i>-2-phenylcyclohexanol, epiandrosterone</p>	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)

<p>(i) Two steps (ii) HF-pyridine, THF, rt</p>	<p>Butyldiethylsilane polystyrene (PS-DES) resin</p> <ul style="list-style-type: none"> - The steroid substrates can be diverse. - Used to build steroid libraries - HF must be used for resin cleavage.²⁷⁰
	<p>Butyldiethylsilane polystyrene (PS-DES) resin</p> <ul style="list-style-type: none"> - Used for immobilization of four different types of steroid alcohols and phenols - Subsequent reactions on solid support were investigated.²⁷⁰
	<p>Chlorinated polystyrene-diethylsilane resin (diethylsilyl chloride resin) (PS-DES)</p> <ul style="list-style-type: none"> - 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-oxazolines - Yields: 59-99% (based on the resin)²⁷¹

Table 2 (Continued)

	<p>Polystyrene silyl resin 1</p> <ul style="list-style-type: none"> - synthesized from polystyrene resin - Used for anchoring of alcohols on solid support - Seven examples; yields: 63-88%²⁷²
	<p>Polystyrene-diethylsilane resin</p> <ul style="list-style-type: none"> - Used for immobilization of alcohols²⁷³
	<p>Polymer-supported trialkylsilane</p> <ul style="list-style-type: none"> - Gel-type resin - Alcoholysis and carbonyl hydrosilylation - Yield 50-87% for two steps (loading and cleavage) - Dimethylsilyl polystyrene is commercially available for immobilization of alcohols¹¹⁹
	<p>Alkylsilyl-tethered resin</p> <ul style="list-style-type: none"> - Used for immobilization of alcohols described²⁷⁴

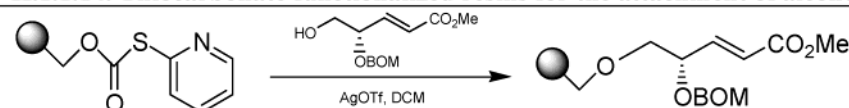
II. Solid supports reactions with alcohols and phenols

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)

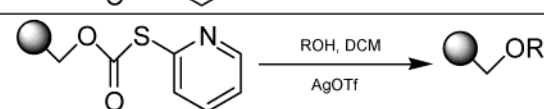
II.1.1.14. Thiocarbonate functionalized resins for the attachment of alcohols

Comments and References



Thiopyridine carbonyl Wang resin

- Yield 90%¹⁰⁴



2-Pyridinyl thiocarbonate Wang resin

- Six examples, yields 80-98%¹⁰⁶

ROH such as

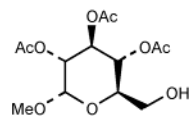


Table 2 (Continued)

II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (<i>O</i>-Alkylation or <i>O</i>-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 <i>p</i>-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)

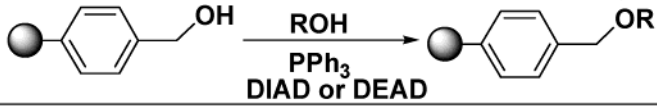
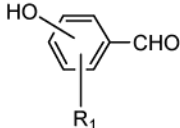
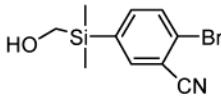
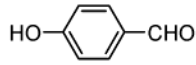
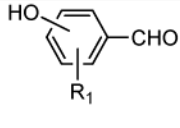
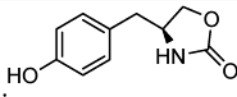
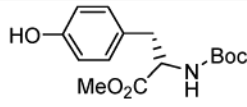
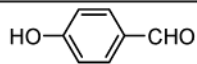
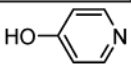
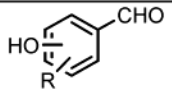
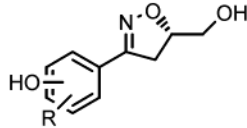
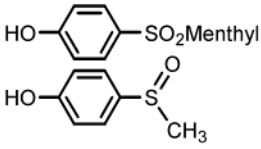
II. Solid supports reactions with alcohols and phenols		
II.1. Attachment as ethers (<i>O</i> -alkylation or <i>O</i> -arylation)		
II.1.2. Mitsunobu reaction		
II.1.2.1. Mitsunobu reaction to immobilize hydroxyl functional group as phenol ethers		
		
ROH, Conditions Comments and References		
		
Wang 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 - Photodetachable 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 auxiliary 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 <i>N</i> -acyl-2-substituted dihydro-4-pyridones ²⁸⁴	Wang resin - PPh ₃ , DIAD, THF - Synthesis of isoxazolines described. 
Wang resin - Solid-phase bound chalcones used for synthesis of 2,4,6-trisubstituted pyrimidines. - Three examples; yields 79-93% ²⁸⁶		- Seven examples; yields: 38-78% ²⁸⁵
	Wang resin - Used for immobilization of <i>p</i> -hydroxyphenyl menthyl sulfinate - PPh ₃ , DIEA, DEAD, toluene, THF - Subsequent Grignard reactions investigated ²⁸⁷	

Table 2 (Continued)

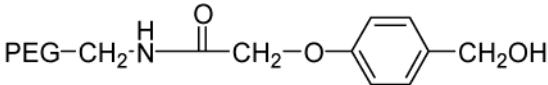
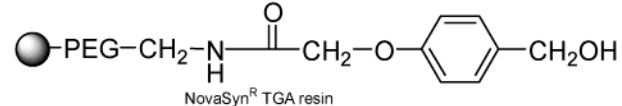
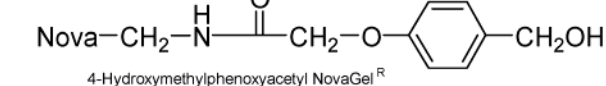
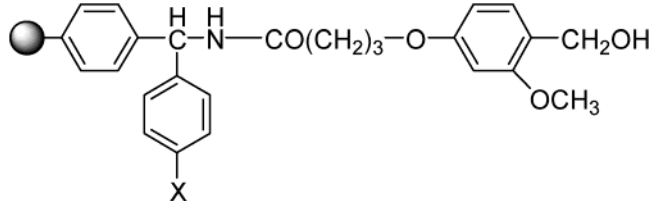
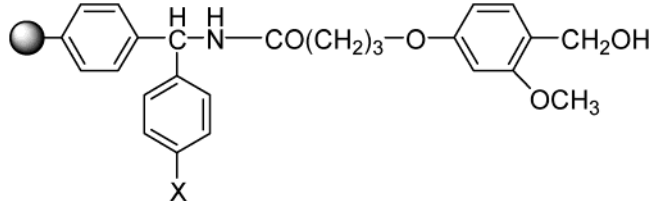
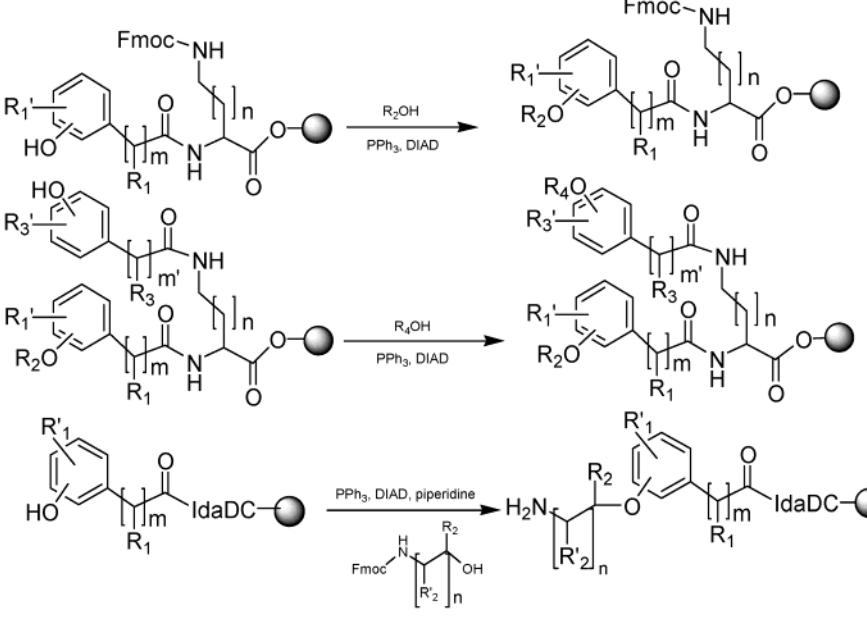
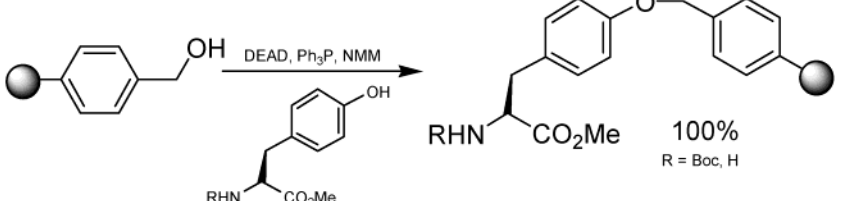
II.1.2.1. Mitsunobu reaction to immobilize hydroxyl functional group as phenol ethers	Comments and References
<p>  4-Hydroxymethylphenoxyacetyl PEGA resin (HMPA-PEGA resin) </p> <p>  NovaSyn[®] TGA resin </p> <p>  4-Hydroxymethylphenoxyacetyl NovaGel[®] (HMPA-NovaGel[®] HL) </p> <p>  X = H 4-Hydroxymethyl-3-methoxyphenoxybutyric acid BHA-resin HMPB-BHA resin </p> <p>  X = OCH₃ 4-Hydroxymethyl-3-methoxyphenoxybutyric acid MBHA-resin HMPB-MBHA resin </p>	<p> 4-Hydroxymethylphenoxyacetyl PEGA resin (HMPA-PEGA resin) NovaSyn[®] TGA resin, 4-Hydroxymethylphenoxyacetyl NovaGel[®] (HMPA-NovaGel[®] 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} </p>
<p>  </p>	<p> Derived from polystyrene resin - Library of <i>N,N</i>-bis-(alkoxy acyl)diaminoacids - Library of <i>N</i>-acyl amino ethers - 600 phenolic compounds were isolated.²⁷⁸ </p>
<p>  </p>	<p> Hydroxymethyl polystyrene resin - Substitution level 0.03-0.9 meq/g in different solvents²⁷⁵ </p>

Table 2 (Continued)

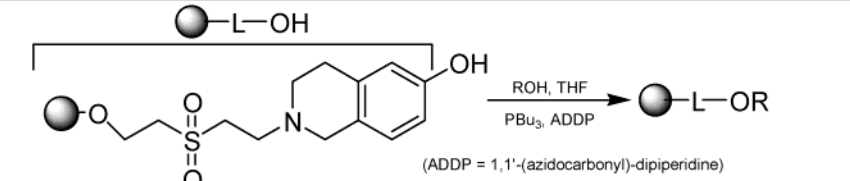
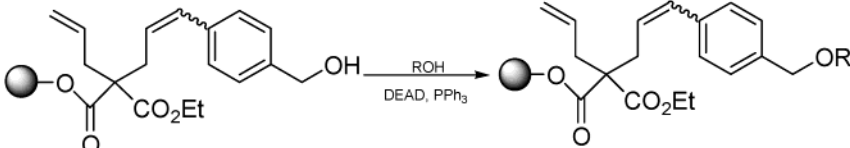
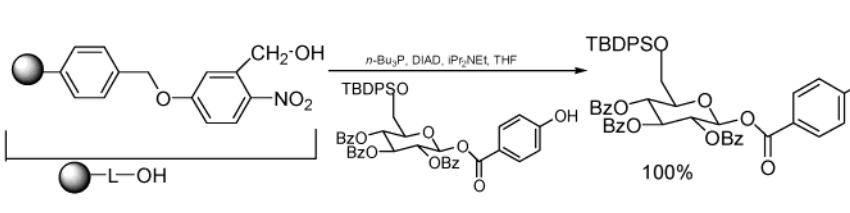
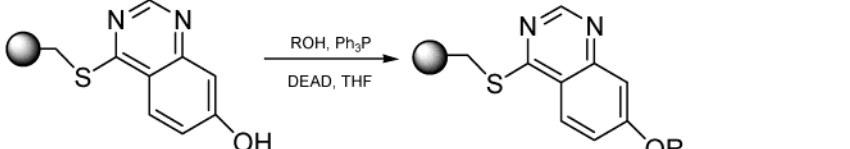
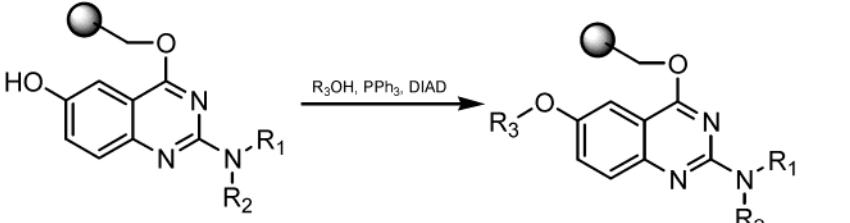
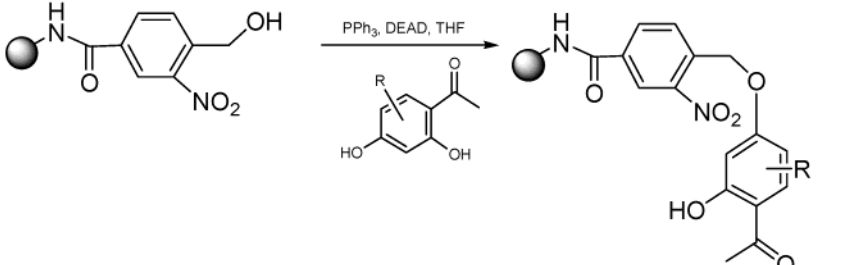
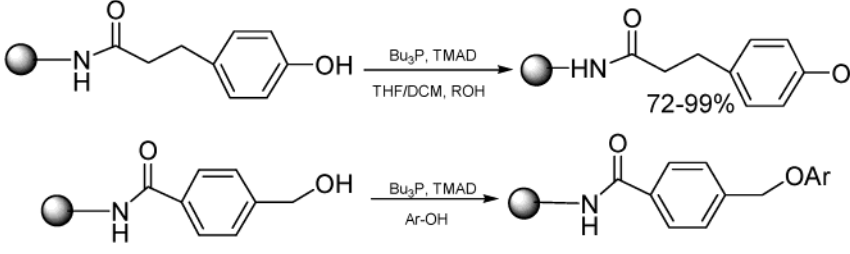
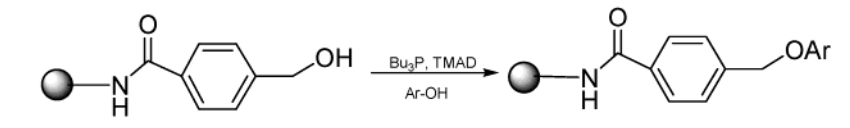
 <p style="text-align: center;">(ADDP = 1,1'-(azidocarbonyl)-dipiperidine)</p>	<p>Derived from hydroxymethylene resin</p> <ul style="list-style-type: none"> - Preparation of derivatives of tetrahydroisoquinolines - Ten examples; overall yields reported 80-90%²⁸⁸
	<p>Derived from Merrifield resin</p> <ul style="list-style-type: none"> - One example - Overall yield reported²⁸⁹
 <p style="text-align: center;">100%</p>	<p>Derived from Merrifield resin</p> <ul style="list-style-type: none"> - Construction of a dodecasaccharide²⁹⁰
	<p>Derived from Merrifield resin</p> <ul style="list-style-type: none"> - Synthesis of oxindole quinazolines using solid phase multiparallel chemistry²⁹¹
	<p>Derived from Wang resin</p> <ul style="list-style-type: none"> - Novel synthesis of 2,6-disubstituted 4(3H)-quinazolinones reported²⁹²
	<p>Derived from TG resin</p> <ul style="list-style-type: none"> - Dihydropyrans synthesis²⁰⁴
 <p style="text-align: center;">72-99%</p>  <p style="text-align: center;">66-94%</p>	<p>Derived from TentaGel resin-supported benzyl alcohol</p> <ul style="list-style-type: none"> - Solid-phase synthesis of aryl ethers via the Mitsunobu reaction^{275,277,279,293}

Table 2 (Continued)

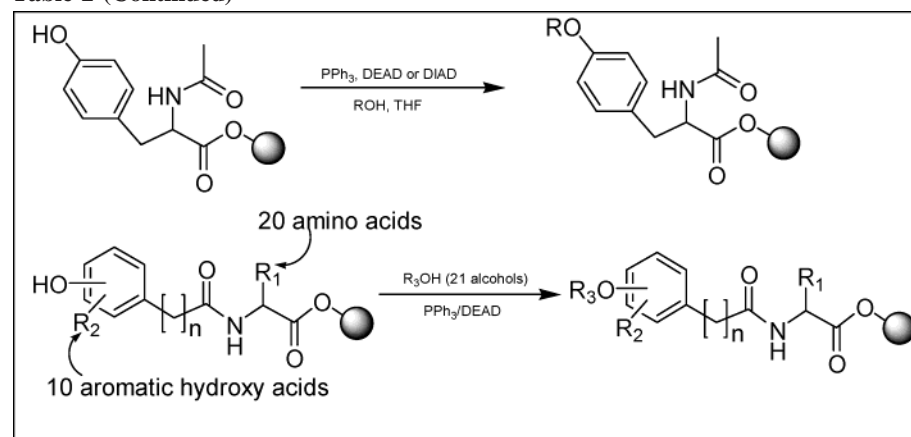
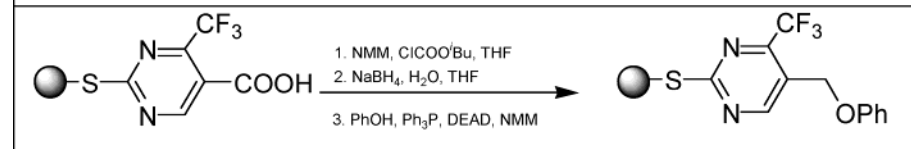
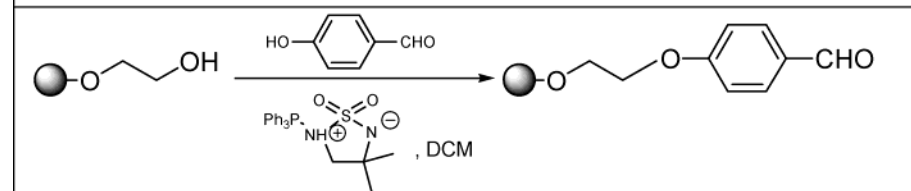
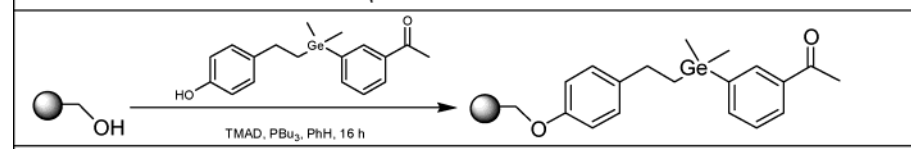
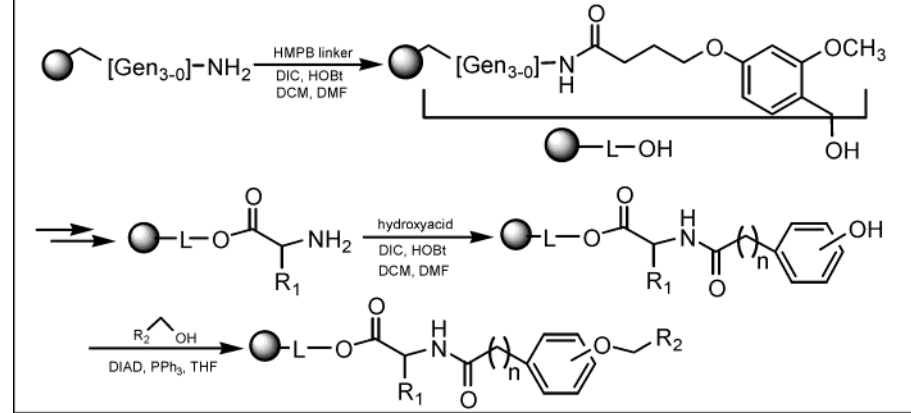
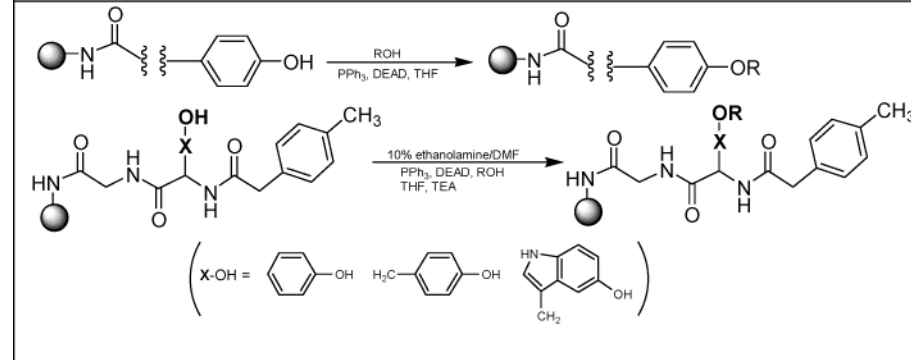
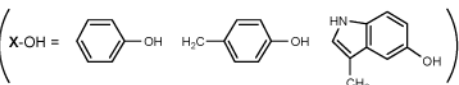
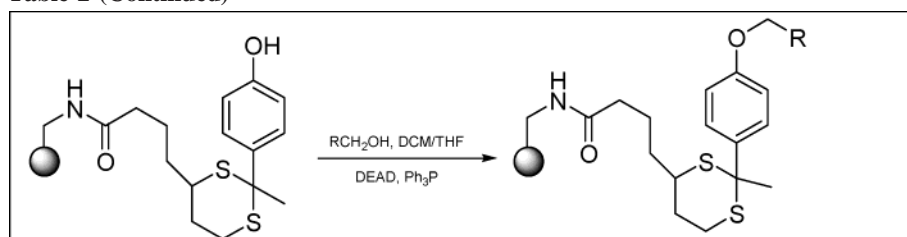
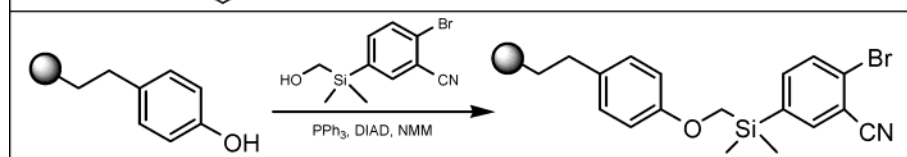
 <p>Reaction 1: N-acetylated tyrosine derivative on a resin support reacts with PPh_3, DEAD or DIAD in ROH, THF to form an N-alkylated product.</p> <p>Reaction 2: A resin-bound amino acid with a hydroxy acid side chain (R₂) reacts with 21 alcohols (R₃OH) and PPh_3/DEAD to form an N-alkylated product with a different alcohol side chain (R₃).</p> <p>Labels: 20 amino acids, 10 aromatic hydroxy acids.</p>	<p>N-acetylated tyrosine on polyethyleneglycol grafted PS-1% DVB</p> <ul style="list-style-type: none"> - 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 = CH₃ (glycine)²⁹⁴
 <p>Reaction: NovaSyn[®] TG thiol resin (TentaGel SH resin) reacts with 1. NMM, ClCOO^tBu, THF; 2. NaBH₄, H₂O, THF; 3. PhOH, Ph₃P, DEAD, NMM to form a resin-bound phenyl thioether.</p>	<p>NovaSyn[®] TG thiol resin (TentaGel SH resin)</p> <ul style="list-style-type: none"> - Traceless linker - Safety-catch thioether - Sulfur-based linker for attachment of small heterocycles²⁹⁵
 <p>Reaction: ArgoGel[™] resin (hydroxyethyl ether) reacts with 4-hydroxybenzaldehyde and a phosphonium salt (Ph₃P⁺, N⁻, DCM) to form a resin-bound secondary amide-based linker.</p>	<p>Derived from ArgoGel[™] resin</p> <ul style="list-style-type: none"> - Preparation of secondary amide-based linkers - Preparation of ureas, sulfonamides, aryl amides, and alkyl amides - Overall yield reported²⁹⁶
 <p>Reaction: ArgoGel[™] resin reacts with a germanium-based linker (TMAD, PBU₃, PhH, 16 h) to form a resin-bound germanium-based linker.</p>	<p>ArgoGel[™]</p> <ul style="list-style-type: none"> - New germanium-based linker for solid phase synthesis of pyrazole library²⁹⁷
 <p>Reaction 1: A resin-bound dendrimer resin ([Gen₃₋₀]-NH₂) reacts with an HMP linker (DIC, HOBT, DCM, DMF) to form a resin-bound dendrimer resin with a hydroxy acid side chain.</p> <p>Reaction 2: The resin-bound dendrimer resin with a hydroxy acid side chain reacts with a hydroxy acid (DIC, HOBT, DCM, DMF) to form a resin-bound dendrimer resin with a hydroxy acid side chain.</p> <p>Reaction 3: The resin-bound dendrimer resin with a hydroxy acid side chain reacts with an alcohol (R₂-OH, DIAD, PPh₃, THF) to form a resin-bound dendrimer resin with an ether side chain.</p>	<p>High loading dendrimer resin</p> <ul style="list-style-type: none"> - Used for synthesis of aryl ethers. - Five examples; yields 67-100%. - Better than normal TentaGel resin²⁹⁸
 <p>Reaction 1: A resin-bound PIN resin (polyethylene pin) reacts with an alcohol (ROH, PPh₃, DEAD, THF) to form a resin-bound PIN resin with an ether side chain.</p> <p>Reaction 2: A resin-bound PIN resin with a hydroxy acid side chain reacts with 10% ethanolamine/DMF (PPh₃, DEAD, ROH, THF, TEA) to form a resin-bound PIN resin with an ether side chain.</p> <p>Labels: X-OH = </p>	<p>PIN = [Polyethylene Pin]-[MA/DMA]-HMD-COCH₂NH-(Rink handle)₁₆</p> <ul style="list-style-type: none"> - Alkylation of pin-bound phenols²⁹⁹

Table 2 (Continued)

<p style="text-align: center;">(Sulfonamide betaine)</p>	<p>Biphenyl phenol linker from polystyrene carboxylic resin - Mitsunobu functionalization of biphenyl phenols³⁰⁰</p>
	<p>Derived from carboxypolystyrene - Synthesis of farnesyl transferase inhibitors³⁰¹</p>
<p style="text-align: center;">R = Benzyl, 2-Ph-Et, <i>n</i>-Propyl</p>	<p>Fmoc-tyrosine coupled to deprotected Rink Amide resin - Mitsunobu <i>O</i>-alkylation³⁰²</p>
	<p>Derived from trityl chloride resin - Synthesis of <i>N</i>-(2-benzoylphenyl)-L-tyrosine PPAR gamma agonists³⁰³</p>
	<p>Derived from BHA resin - Simple silyl linker for the synthesis of aryl-containing molecules - <i>O</i>-Alkylation³⁰⁴</p>
	<p>Derived from HMPA-MBHA resin - Phenol attachment - Synthesis of tyrosine-containing cyclic peptides³⁰⁵</p>
	<p>Derived from HMPA carbonate resin - Immobilization of aminoalcohols³⁰⁶</p>

Table 2 (Continued)

	<p>Derived from aminomethyl resin - Novel thioacetal linker developed and used for immobilization of alcohol via Mitsunobu reaction³⁰⁷</p>
	<p>Various resins including phenol, tetrahydropyranyl, sulfonic and chloromethyl polystyrenes - Used for construction of heterocycles³⁰⁸</p>

II. Solid supports reactions with alcohols and phenols

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

II.1.2. Mitsunobu reaction

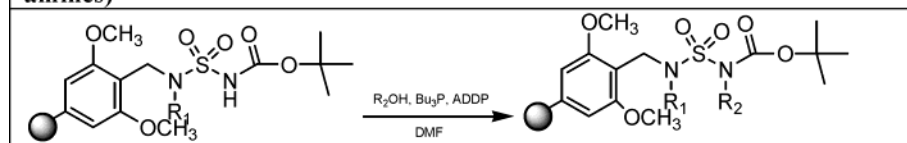
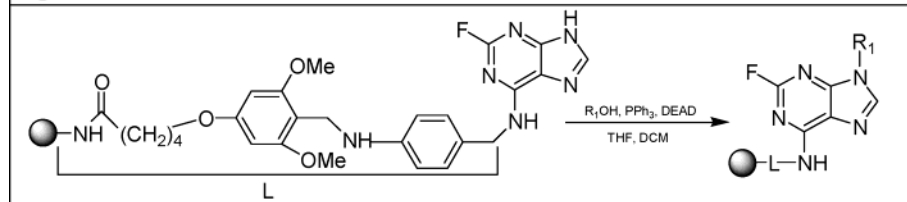
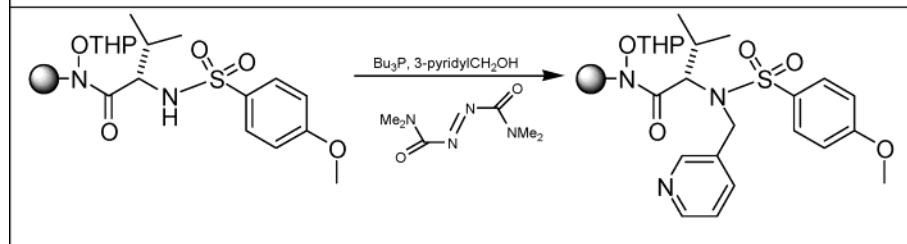
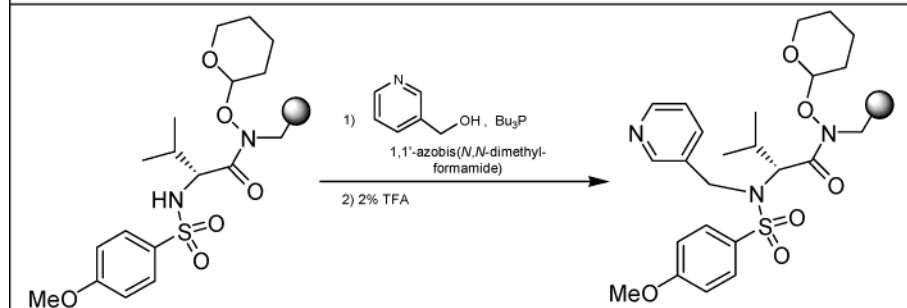
II.1.2.2. Mitsunobu reaction on amino functional groups (attachment as amines)	Comments and References
	<p>Polystyrene resin - Synthesis of bound <i>O</i>-hydroxylamine (0.68 mmol/g)³⁰⁹</p>
	<p>PAL derivatized MBHA resin (amine derivatized crowns) - Selective <i>N</i>-9 alkylation - Nine examples - Synthesis of 2,9-substituted purines - Yield 73-88% - <i>N</i>-Alkylation³¹⁰</p>
	<p>Derived from Tentagel NH₂ resin - <i>N</i>-Alkylation³¹¹</p>
	<p>Derived from Tentagel resin - Protection of the hydroxamate oxygen as a THP ether - Synthesis of stromelysin inhibitor³¹¹</p>

Table 2 (Continued)

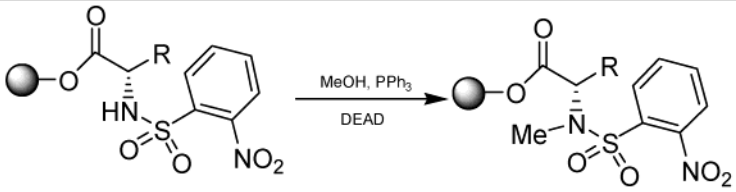
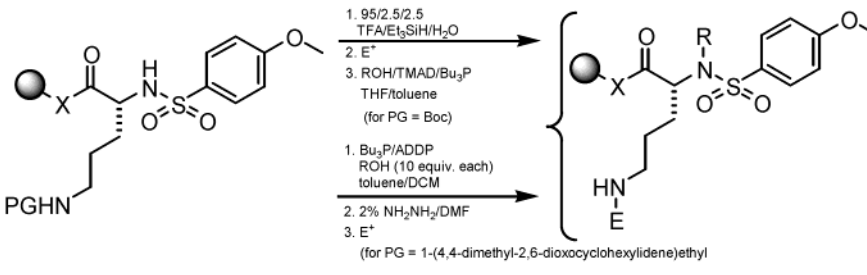
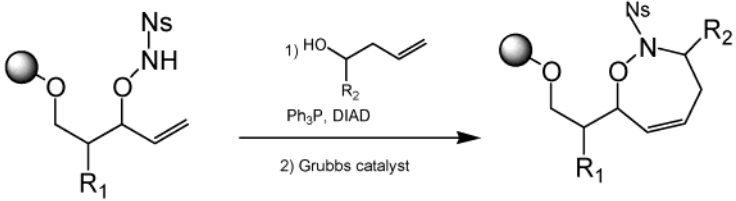
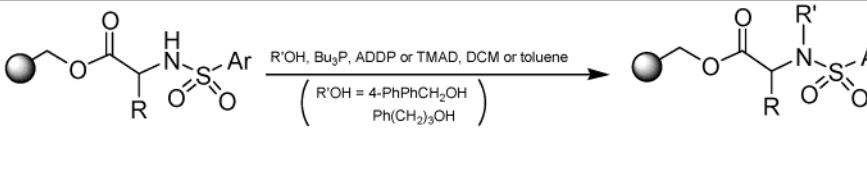
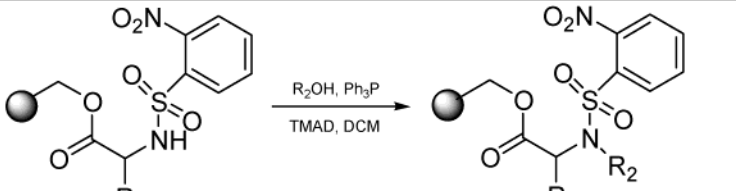
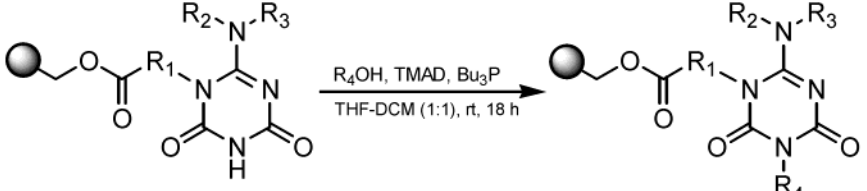
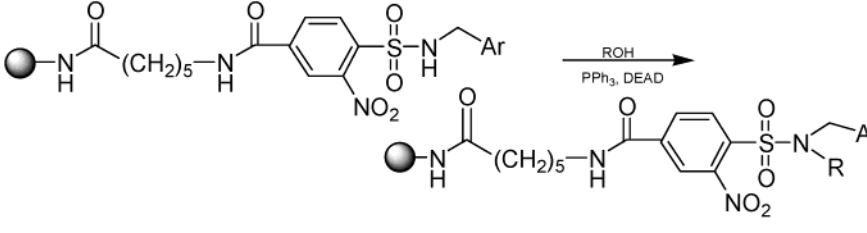
	<p>2-Chlorotrityl resin</p> <ul style="list-style-type: none"> - Eight examples; yields: 80-100% over 4 steps - <i>N</i>-Alkylation (sulfonamide)³¹²
	<p>Derived from PS-2-Cl-Trityl-ONHFmoc resin or ArgoGel-OH resin</p> <ul style="list-style-type: none"> - For each resin and E⁺, conditions indicated - Nearly 200 compounds prepared³¹³
	<p>Derived from Trityl resin</p> <ul style="list-style-type: none"> - Ring closing metathesis used in the synthesis of tetrahydrooxazepines - Three-hundred twenty examples, 60-80% purity³¹⁴
	<p>Derived from ArgoGel (Wang), Wang and Sasrin resins</p> <ul style="list-style-type: none"> - Solid-phase synthesis of <i>N</i>-alkyl sulfonamides - Forty five examples; yields: 0-100% - Higher purity observed with ArgoGel (Wang) resin - <i>N</i>-Alkylation (sulfonamide) - Yield 66-100% (final products)³¹⁵
	<p>Derived from Wang resin</p> <ul style="list-style-type: none"> - Synthesis of trisubstituted hydantoins³¹⁶
	<p>Derived from Wang resin</p> <ul style="list-style-type: none"> - Used for the synthesis of 6-amino-2,4-dioxo-3,4-dihydro-1,3,5-triazine derivatives described. - Fourteen examples; yields: 62-78%³¹⁷
	<p>Derived from BHA resin</p> <ul style="list-style-type: none"> - Preparation of secondary amine by the Mitsunobu reaction of a resin bound sulfonamide with alcohols - Ten examples; yields 0-100%³¹⁸

Table 2 (Continued)

	<p>Derived from polystyrene-based acid-labile Sasrin resin</p> <ul style="list-style-type: none"> - Synthesis of quinazoline-2,4-diones - Nineteen examples - Final products yields 84-98%³¹⁹
	<p>Resin-bound O-NBS-amino acids</p> <ul style="list-style-type: none"> - Mitsunobu reaction³²⁰
	<p>N,N-Di-Boc-isothiourea methyl polystyrene</p> <ul style="list-style-type: none"> - Prepared from Merrifield resin with excess of thiourea - Solid-supported thiourea - Used in the synthesis of a polymer-bound N-alkyl-N,N'-bis-Boc-thiopseudourea - Used in the synthesis of various Boc-protected guanidines. - Seven examples, purified yields 85-100% for final products³²¹
	<p>Prepared from Merrifield resin</p> <ul style="list-style-type: none"> - DHP-bound resin - Attachment of alcohols; yield 81%²⁵⁵
	<p>Derived from Rink resin</p> <ul style="list-style-type: none"> - Synthesis of triazolopyridazines³²²
	<p>Derived from Merrifield resin</p> <ul style="list-style-type: none"> - Solid-phase synthesis of BRL 49653 - Modified Mitsunobu condition¹³⁴

Table 2 (Continued)

	<p>Derived from polystyrene amine resin</p> <ul style="list-style-type: none"> - 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 guanidines³²³
	<p>Derived from aminomethyl polystyrene resin</p> <ul style="list-style-type: none"> - A straightforward synthesis of substituted sulfamides described³²⁴
II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (O-alkylation or O-arylation)	
II.1.2. Mitsunobu reaction	
<p>II.1.2.3. Mitsunobu reaction for immobilization of hydroxyl functional groups of other compounds</p>	<p>Comments and References</p>
	<p>Derived from aminomethyl polystyrene resin</p> <ul style="list-style-type: none"> - A linker for amidines³²⁵
	<p>Derived from Sasrin resin</p> <ul style="list-style-type: none"> - Solid-phase synthesis of hydroxamic acid based TNF-α convertase inhibitors³²⁶
	<p>Substituted Wang resin</p> <ul style="list-style-type: none"> - Used for synthesis of carbamates - Yields: 40-82% (eight examples)³²⁷

Table 2 (Continued)

	<p>Polymer bound iminodiphenylmethanol resin</p> <ul style="list-style-type: none"> - Used for Mitsunobu reaction to synthesize primary amines - Nine examples; yields 0-85%³²⁸
<p>II. Solid supports reactions with alcohols and phenols</p> <p>II.1. Attachment as ethers (<i>O</i>-alkylation or <i>O</i>-arylation)</p>	
<p>II.1.3. Carbohydrate reactions</p>	
<p>II.1.3.1. Immobilization and protection of carbohydrates</p>	<p>Comments and References</p>
	<p>Tritylated polymer (styrene-2%-DVB)</p> <ul style="list-style-type: none"> - Copolystyrene-DVB incorporating a chiral group (1,2-<i>O</i>-cyclohexylidene-D-xylofuranose) - Used in asymmetric synthesis of atrolactic acid - 80-87% yields for resin - Asymmetric synthesis (synthesis of α-hydroxy acids on insoluble polymer supports) - D or L obtained in 73-87% yields³³³
	<p>Polystyrene trityl chloride resin</p> <ul style="list-style-type: none"> - Use of polymers as protecting groups of primary alcohol functional groups - Glycoside synthesis - Final product overall yield 86%²²⁴
	<p>Derived from Merrifield resin</p> <ul style="list-style-type: none"> - 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}
	<p>Wang aldehyde resin</p> <ul style="list-style-type: none"> - Formation of <i>p</i>-alkoxybenzylidene acetals on solid support - Six examples; yield of products after acetal formation and cleavage 70-92%¹⁰⁶
	<p>Polystyrylboronic acid (copolystyrene-DVB incorporating a boronic acid)</p> <ul style="list-style-type: none"> - 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)

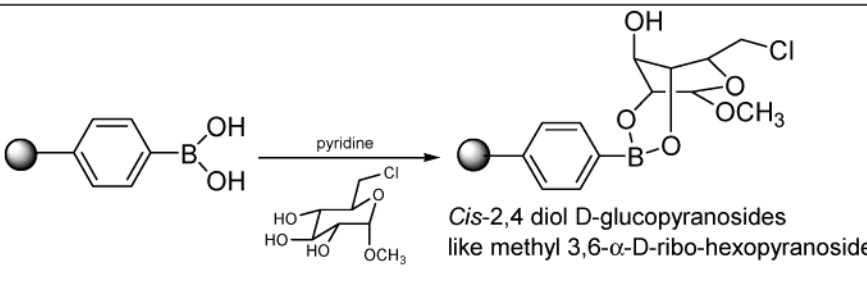
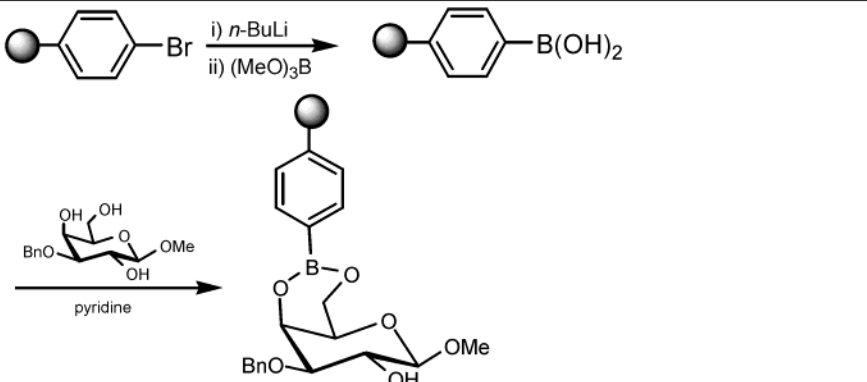
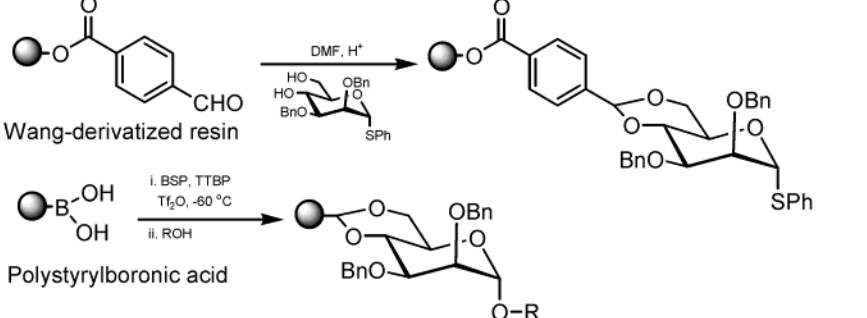
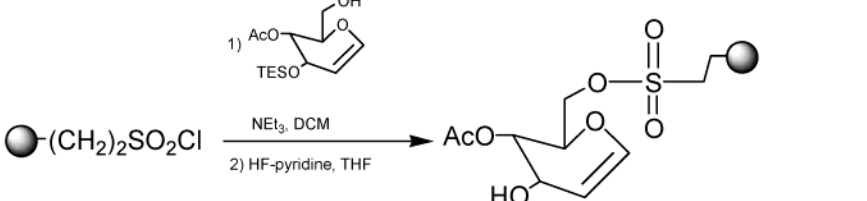
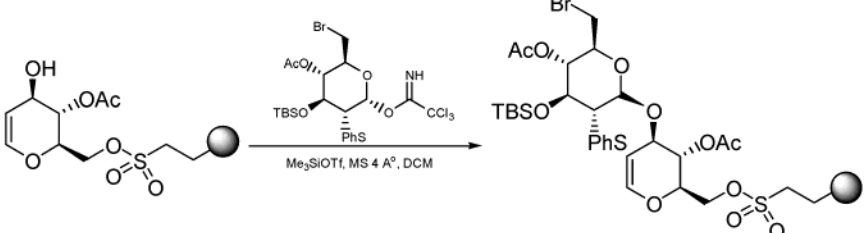
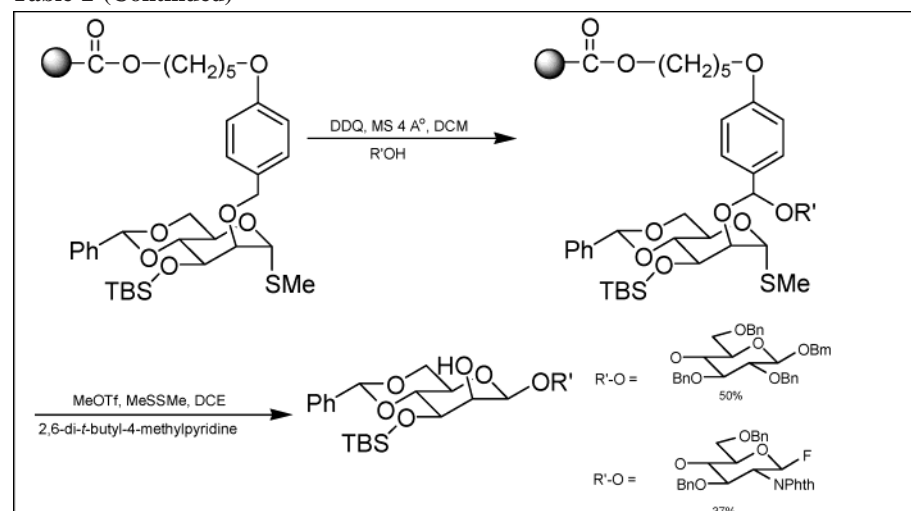
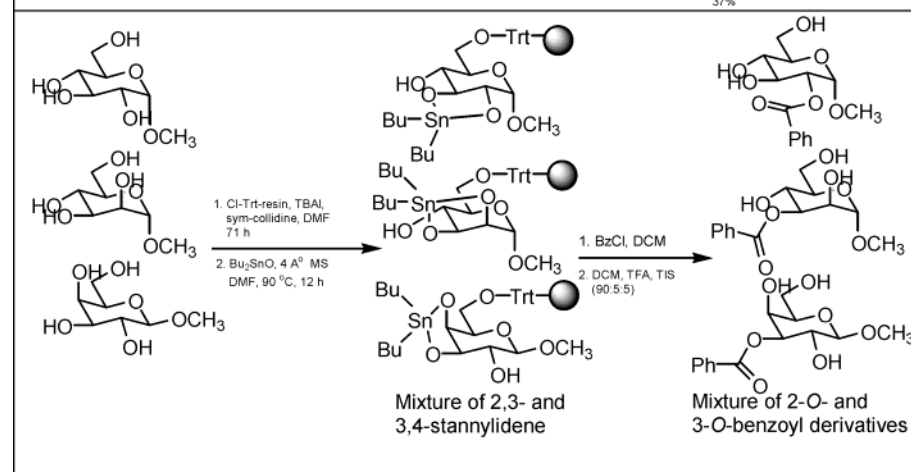
 <p>Polystyrylboronic acid - Preparation of a deoxy-sugar²⁶²</p> <p><i>Cis</i>-2,4 diol D-glucopyranosides like methyl 3,6-α-D-ribo-hexopyranoside</p>	
 <p>Polystyrylboronic acid - A reusable polymeric support for oligosaccharide synthesis prepared³³⁶</p>	
 <p>Wang-derivatized resin</p> <p>Polystyrylboronic acid</p> <p>Wang-derivatized and polystyrylboronic acid resins - Six examples; yields: 73-84%³³⁷</p>	
 <p>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% yields³³⁸</p>	
 <p>Derived from Merrifield resin - Glycosidation of support-bound alcohols with trichloroacetamides³³⁸</p>	

Table 2 (Continued)

	<p>Derived from PEG resin</p> <ul style="list-style-type: none"> - Protecting group strategy for oligosaccharides - Axial 2-OH group direct the aglycon in the glycosylation reaction to the β face - Synthesis of β-mannosides³³⁹
	<p>Derived from chlorotriptyl resin</p> <ul style="list-style-type: none"> - 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

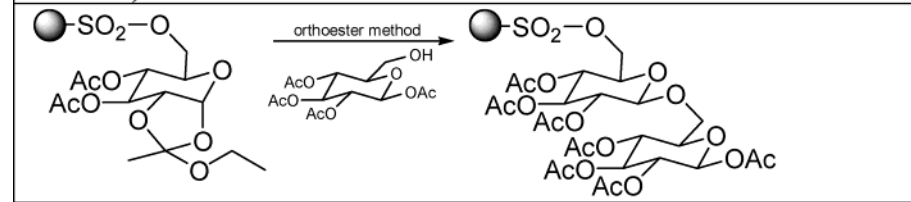
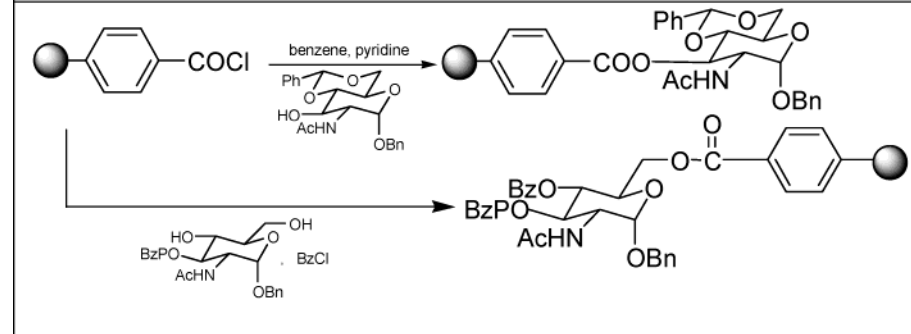
II.1.3.2. The synthesis of disaccharides and polysaccharides (glycosylation reactions)	Comments and References
	<p>Derived from free radical polymerization of 1,2,3,4-tetra-<i>O</i>-acetyl-6-<i>O</i>-(<i>p</i>-vinylphenylsulfonyl)-β-D-glucopyranose with styrene to yield a copolymer containing 6% of the substituted styrene units</p> <ul style="list-style-type: none"> - Transorthoesterification followed by rearrangement - Octaacetate of gentiobiose in 42% yield^{341,342}
	<p>Derived from crosslinked styrene-DVB popcorn polyamide</p> <ul style="list-style-type: none"> - Esterification using benzyl-2-acetamido-2-deoxy-4,6-<i>O</i>-benzylidene-α-D-glucopyranoside - Solid-phase synthesis of 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)

	<p>Merrifield resin</p> <ul style="list-style-type: none"> - Glycosyl oxazoline donor chemistry- α-(1-6)-linked disaccharide³⁴⁴
<p>R = Ph R = <i>i</i>-Pr</p> <p>R = Ph loading (0.6 mmol/g) R = <i>i</i>-Pr loading (0.9 mmol/g)</p>	<p>Derived from polystyrene-DVB (1%)</p> <ul style="list-style-type: none"> - Preparation of a polymer-linked glycal - For preparation of β-(1-6)-linked oligosaccharides³⁴⁵
<p>1) TMSCl, Et₃N, THF</p> <p>2) CsF, DMF</p>	<p>Merrifield resin</p> <ul style="list-style-type: none"> - Attaching of a monosaccharide to Merrifield resin via a <i>p</i>-hydroxythiophenyl linkage - Overall yield of 52% for trisaccharide - Glycosylation using anomeric sulfoxides³³⁰
<p>1) reiterate 2) retrieve</p>	<p>Derived from Wang resin</p> <ul style="list-style-type: none"> - Solid-phase carbohydrate synthesis employing glycals - Glycal assembly method³⁴⁶⁻³⁴⁸
<p>Hunig's base and DCM</p> <p>3,3-dimethyldioxirane, DCM</p> <p>I₂, ZnCl₂, THF</p>	<p>Derived from polystyrene-DVB copolymer</p> <ul style="list-style-type: none"> - 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)

<p>Reaction scheme showing the synthesis of oligosaccharides on a solid support. A glycal-based donor with a dimethylsilyloxy group on the anomeric carbon is coupled to a glycal-based acceptor with a dimethylsilyloxy group on the anomeric carbon. The reaction is catalyzed by $ZnCl_2$ in THF. The product is a disaccharide with a dimethylsilyloxy group on the anomeric carbon of the second sugar. This process is repeated to form longer oligosaccharides.</p>	<p>Derived from polystyrene-DVB copolymer</p> <ul style="list-style-type: none"> - 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>i</i>-Pr: overall yields 32% and 70% per two step coupling stage - Synthesis of Lewis β antigen^{329,347,349-351}
<p>Reaction scheme showing the synthesis of a hexasaccharide on a solid support. A glycal-based donor with a dimethylsilyloxy group on the anomeric carbon is coupled to a glycal-based acceptor with a dimethylsilyloxy group on the anomeric carbon. The reaction is catalyzed by $ZnCl_2$ in THF. The product is a disaccharide with a dimethylsilyloxy group on the anomeric carbon of the second sugar. This process is repeated to form longer oligosaccharides.</p>	<p>Derived from polystyrene-DVB copolymer</p> <ul style="list-style-type: none"> - Coupling yield 80% - Solid-phase synthesis of hexasaccharide (29% overall yield)^{347,351}
<p>Reaction scheme showing the synthesis of disaccharides on a succinylated polyethylene glycol monomethyl ether (MPEG) support. A glycal-based donor with a succinyl group on the anomeric carbon is coupled to a glycal-based acceptor with a succinyl group on the anomeric carbon. The reaction is catalyzed by DMTST in DCM, followed by 4A MS. The product is a disaccharide with a succinyl group on the anomeric carbon of the second sugar. This process is repeated to form longer oligosaccharides.</p>	<p>Succinylated polyethylene glycol monomethyl ether (MPEG)</p> <ul style="list-style-type: none"> - 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}

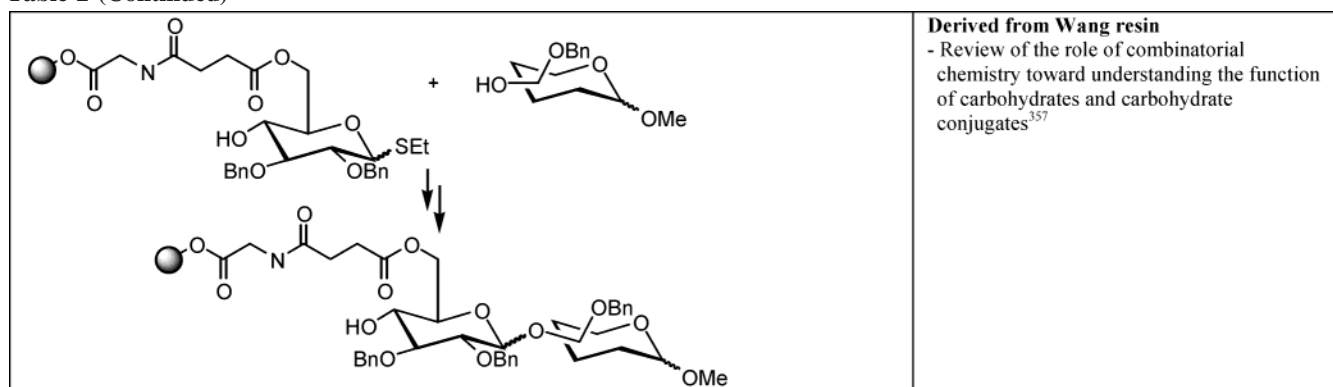
Table 2 (Continued)

<p> $\text{BnO-BnO-OSi}(i\text{-Pr})_2\text{-SEt-PhSO}_2\text{HN} + \text{BnO-BnO-OH} \xrightarrow{\text{MeOTf, DTBP, 4A}^\circ\text{MS, DCM}}$ $\beta\text{-glucosyl (1-6)}$ (63%) </p> <p> $\text{BnO-BnO-OSi}(i\text{-Pr})_2\text{-SEt-PhSO}_2\text{HN} + \text{BnO-BnO-OBn-OH} \xrightarrow{\text{MeOTf, DTBP, 4A}^\circ\text{MS, DCM}}$ $\beta\text{-glucosyl (1-4)}$ (82%) </p> <p> $\text{BnO-BnO-OSi}(i\text{-Pr})_2\text{-SEt-PhSO}_2\text{HN} + \text{PMP-OH} \xrightarrow{\text{MeOTf, DTBP, 4A}^\circ\text{MS, DCM}}$ $\beta\text{-glucosyl (1-3)}$ (74%) </p> <p> $\text{BnO-BnO-OSi}(i\text{-Pr})_2\text{-PivO-NHSO}_2\text{Ph} + \text{BnO-OBn-OH-OTIPS} \xrightarrow{\text{MeOTf, DTBP, 4A}^\circ\text{MS, DCM}}$ (78%) </p> <p> $\text{OSi}(i\text{-Pr})_2\text{-OH-OTIPS} + \text{HO-OH} \xrightarrow{\text{DMDO, DCM, ZnCl}_2, \text{THF}}$ (75%) </p>	<p>Polymer-bound ethylsulfanyl-2-amidoglucosyl</p> <ul style="list-style-type: none"> - 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 determinant¹¹⁶
<p> $\text{Si-Cl}_2 + \text{BnO-BnO-OH} \xrightarrow{(i\text{-Pr})_2\text{NEt, DMAP, DCM}}$ $\text{BnO-BnO-O-Si}(i\text{-Pr})_2$ </p> <p> $\text{BnO-BnO-OSi}(i\text{-Pr})_2\text{-PivO-OBn} + \text{BnO-BnO-OH} \xrightarrow{\text{1) DMDO, DCM; 2) EISH, (CF}_3\text{CO)}_2\text{O, DCM; 3) PivCl, DMAP, DCM; 4) MeOTf, DTBP, 4 A}^\circ\text{MS, DCM}}$ (Overall yield 45%) </p> <p> $\text{BnO-BnO-OSi}(i\text{-Pr})_2\text{-PivO-OBn} + \text{BnO-BnO-OH} \xrightarrow{\text{1) DMDO, DCM; 2) EISH, (CF}_3\text{CO)}_2\text{O, DCM; 3) PivCl, DMAP, DCM; 4) MeOTf, DTBP, 4 A}^\circ\text{MS, DCM}}$ (Overall yield 20%) </p>	<p>Silylated polystyrene polymer resin</p> <ul style="list-style-type: none"> - Polymer-bound thioethyl glycosyl 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 glucosides¹¹⁷

Table 2 (Continued)

<p> $\text{MeO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{CO}(\text{CH}_2)_4\text{O}-\text{Ph}-\text{Support}$ Reagents: $\text{MeOSO}_2\text{CF}_3$, MeSSMe, 4 \AA MS, DCM Yield: 89% Reagents: $[\text{CP}_2\text{HFCl}_2]$, $\text{AgOSO}_2\text{CF}_3$, 4 \AA MS, DCM, $\text{SE} = \text{CH}_2\text{CH}_2\text{SiMe}_3$ Yield: 99% </p>	<p>PEG monomethyl ether soluble monoether - Orthogonal glycosylation strategy for rapid assembly of oligosaccharides on a polymer support³⁵⁴</p>
<p> $\text{Ph}-(\text{CH}_2)_4\text{Si}-\text{H}$ 1) $\text{Cl}-\text{N}(\text{Me})_2$, DCM 2) Glycosyl donor, imidazole, DCM $\text{X} = \text{SPh}, \text{F}, \text{OC}(\text{NH})\text{CCl}_3, \text{S}(\text{O})\text{Ph}$ Loading yields = 30-54% 1) Glycosyl acceptor, activator (DCM, MS-4A, additive) 2) $\text{ACOH}/\text{THF}/\text{H}_2\text{O} = 6/6/1$ Activators = DMTST, NIS/TIOH, $\text{Cp}_2\text{H}(\text{OTf})_2$ $\text{BF}_3 \cdot \text{OEt}_2$, Tf_2O, $\text{TMSOTf}/\text{P}(\text{OEt})_3$, TIOH/MP Additives = DTBP, $\text{DTBP}/\text{TMSOMe}$ Yields 47%-Quantitative </p>	<p>PS-DES resin - Glycosylation of solid-supported glycosyl donors tethered by a trialkylsilane linker³⁵⁵</p>
<p> $\text{HO}-(\text{CH}_2)_4\text{O}-\text{DMTO}$ 1. NaH, DMF 2. NaH, MeOH Yield: 90% 2. Cl_2, CH_3COOH, DCM L-OH polysaccharide elongation Grubb's catalyst, DCM, ethylene, 36 h Polysaccharide </p>	<p>Derived from Merrifield resin - A 4,5-dibromo-1,8-diol linker - Used for the synthesis of polysaccharides³⁵⁶</p>

Table 2 (Continued)



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
	<p>Poly(acrylamide)-poly(<i>N</i>-acryloxysuccinimide) (PAN)</p> <ul style="list-style-type: none"> - Enzymatic synthesis of oligosaccharides^{358,359}
<p>$n = 1$: poly(acrylamide) bearing gluco and malto substituents</p> <p>$(m > 1)$</p> <p>Crosslinked poly(acrylamide) beads carrying both $\alpha(1-4)$ and $\alpha(1-6)$ glycosyl residue</p>	<p>Aminoethyl-substituted polyacrylamide gel beads</p> <ul style="list-style-type: none"> - Highest transfer (4.2%) for the polymer bearing maltotriose groups - Glycogen synthase reaction with polymer-bound oligosaccharides³⁶⁰
	<p>Poly(acrylamide)-poly(<i>N</i>-acryloxysuccinimide)(PAN)</p> <ul style="list-style-type: none"> - Synthesis of oligosaccharides (glysphingolipids) 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)

	<p>Cross-linked polyacrylamide gel beads (Bio-Gel P-100, 100-200, 300 mesh)</p> <ul style="list-style-type: none"> - Using <i>in situ</i> generation of UDP-D-galactose - Polymer-supported enzymatic synthesis on a preparative scale - Acceptor sugar is bound via a 2-nitrobenzoyl group as aglycon to a modified polymeric acrylamide - Enzymatic synthesis of oligosaccharides on a polymer support: light-sensitive substituted polyacrylamide beads - 0.4-24.1% enzymatic incorporation of galactose - 51% overall yield for final compound^{359,360,363-368}
	<p>Aminoethyl-substituted poly(acrylamide) gel beads</p> <ul style="list-style-type: none"> - Light-sensitive polymers linked to saccharides - Polymers having (1-4)- and (1-6)-linked α-D-glucopyranosyl groups as acceptors in the glycogen synthase reaction - Four examples^{365,366}
	<p>Derived from aminopropylsilica resin</p> <ul style="list-style-type: none"> - Solid-phase supported chemical-enzymatic synthesis of a Sialyl Lewis X glycopeptide and oligosaccharides - Solid-phase synthesis of glycopeptides using enzyme-based glycosylation technology^{332,369-374}
	<p>Derived from copolymers of acrylamide</p> <ul style="list-style-type: none"> - A water soluble polymer pendant GlcNAc - Water soluble polyacrylamide having 3'-sialyl <i>N</i>-acetyl-lactosamine - Chemoenzymatic oligosaccharide synthesis on a soluble polymeric carrier - Chemoenzymatic preparation of a glycoconjugate polymer having a sialyloligosaccharide: L Neu5Ac-α(2-3)Gal-β(1-)GlcNAc³⁷⁵⁻³⁷⁶

Table 2 (Continued)

	<p>Derived from controlled pore glass</p> <ul style="list-style-type: none"> - Synthesis of polysaccharides described - Synthesis of oligosaccharides related to sialyl Lewis X antigen mediated by β-1,4-galactosyltransferase and α-2,3-sialyltransferase³⁷⁷
	<p>Copolymer of 6-acrylamidocaproic acid as a water-soluble having pendant GlcNAc residues</p> <ul style="list-style-type: none"> - Synthesis of sialoglycoconjugates on a peptidase-sensitive polymer support - Synthesis of 6-aminoglycoside of sialooligosaccharide³⁷⁸
	<p>PEGA (polymerization of a mixture of mono- and di-acryloylated polyethylene glycol (diamino-PEG) with acrylamide or <i>N,N</i>-dimethyl acrylamide</p> <ul style="list-style-type: none"> - 90% conversion³⁷¹

Table 2 (Continued)

<p style="text-align: center;">Sephrose-linker-S</p>	<p>Derived from epoxy Sepharose 6B and thiopyridyl Sepharose 6B</p> <ul style="list-style-type: none"> - Solid-phase enzymatic synthesis of a sialyl lewis X tetrasaccharide on a sepharose matrix using β-1,4-galactosyltransferase, α-2,3-sialyltransferase, and fucosyltransferase - Enzymatic gal transfer 70-98% - Total yield 52%³⁷⁹
	<p>Activated thiopropyl-sepharose</p> <ul style="list-style-type: none"> - Synthesis of Lewis A trisaccharide - Coupling yield 68%³⁷⁹
	<p>Derived from homogeneously soluble PEG polymer used</p> <ul style="list-style-type: none"> - Chemo-enzymatic synthesis of the Galili epitope Galα(1\rightarrow3)Galβ(1\rightarrow4)GalNAc was described.³⁸⁰

Table 2 (Continued)

II. Solid supports reactions with alcohols and phenols	
II.1. Attachment as ethers (<i>O</i>-alkylation or <i>O</i>-arylation)	
II.1.4. Oligonucleotide synthesis	Comments and References
<p style="text-align: center;">65% esterification</p>	<p>Derived from carboxylated styrene popcorn polymer</p> <ul style="list-style-type: none"> - Synthesis of thymidylthymidylthymidine^{384,385}
	<p>Derived from popcorn polymer of styrene, <i>p</i>-vinylbenzoic acid and divinylbenzene</p> <ul style="list-style-type: none"> - Synthesis of oligodeoxyribonucleotides - Yield for TrdCPT 61% based on the amount of trityldeoxycytidine bound to the support³⁸⁶
<p style="text-align: center;">95% conversion</p>	<p>Derived from crosslinked polystyrene with monomethoxytrityl chloride groups (polymer-supported <i>p</i>-methoxytrityl chloride)</p> <ul style="list-style-type: none"> - Used in oligonucleotide synthesis - Stepwise synthesis of trithymidine diphosphate - Thymidyl-(3'-5')-thymidyl-(3'-5')-thymidine isolated in 38% conversion based on polymer-bound dinucleoside phosphate³⁸⁷
	<p>Polymeric dimethoxytrityl chloride</p> <ul style="list-style-type: none"> - Coupling yields 50-60%³⁸⁸
	<p>Silica-bound trityl group</p> <ul style="list-style-type: none"> - Oligonucleotide synthesis - Yield for dTpT(Ac) 54%³⁸⁹
<p style="text-align: center;">n = 0-3</p> <p style="text-align: center;">TPS = triisopropylbenzene-sulfonylchloride</p>	<p><i>N</i>-Vinylpyrrolidone-vinylacetate copolymer</p> <ul style="list-style-type: none"> - Oligonucleotide synthesis³⁹⁰

Table 2 (Continued)

<p style="text-align: center;">95%</p>	<p>Derived from silica support</p> <ul style="list-style-type: none"> - Solid-phase synthesis of oligodeoxyribonucleotides via phosphodichloridite approach³⁹¹
<p style="text-align: right;">Dimer 81-96%</p>	<p>Derived from silica support</p> <ul style="list-style-type: none"> - Synthesis of oligonucleotides - Six examples, Isolated yield 81-96%^{391,392}
	<p>Polymer supported silica gel</p> <ul style="list-style-type: none"> - Oligonucleotide synthesis on solid supports³⁹²
<p>B = uracil or appropriately protected cytosine, adenine or guanine</p>	<p>Derived from silica gel or CPG</p> <ul style="list-style-type: none"> - Regioselective formation of the (3'-5')-dinucleoside phosphotriesters^{382,383}
<p style="text-align: center;">99%</p>	<ul style="list-style-type: none"> - The resin is not specified. - Tetranucleotide synthesized in an overall yield of 94%³⁹³
	<p>Derived from CPG Tentagel</p> <ul style="list-style-type: none"> - Synthesis of oligonucleotide-amino acid conjugates using Tentagel and CPG matrices - Synthesis of 3'-phosphoryltyrosine-terminated oligonucleotides³⁹⁴
<p style="text-align: center;">80-87%</p>	<p>Derived from Tentagel resin</p> <ul style="list-style-type: none"> - 3',3'-Internucleoside phosphodiester linkage - Final products C-3'-P-3'-C and C-3'-P-3'-T (90%)³⁹⁵

Table 2 (Continued)

<p>DMAP, pyridine 24 h, rt</p> <p>DMAP, EDC, TEA 48 h, rt in pyridine</p> <p>5% Cl₂COOH DCM</p> <p>1H-Tetrazole</p> <p>DMTrO</p> <p>NC</p> <p>B^{prot}</p> <p>B^{prot} = protected base</p>	<p>Derived from CPG solid support</p> <ul style="list-style-type: none"> - Used to develop a resin-attached ODMT for the synthesis of a library of 3'-thiophosphorylated dinucleotides. - A 64-membered library³⁹⁶
<p>Type of Reaction: Other reactions involving nucleosides</p>	
<p>PTSA, 1,4-dioxane, 3A ° Ms</p> <p>60%</p>	<p>Derivatized from Merrifield resin</p> <ul style="list-style-type: none"> - Immobilization of nucleosides as acetals - 5'-Phosphorylation²³¹
<p>BzO</p> <p>DMAP, DIPEA, DCM</p> <p>BzO</p> <p>(quantitative)</p>	<p>p-Nitrophenyl carbonate resin</p> <ul style="list-style-type: none"> - A sugar moiety is immobilized on the solid support. - Used for the synthesis of nucleosides³⁹⁷
<p>II. Solid supports reactions with alcohols and phenols</p>	
<p>II.2. Attachment as esters</p>	
<p>II.2.1. Immobilization of hydroxyl functional group and synthesis of miscellaneous compounds</p> <p>poly(N-vinylimidazole)</p> <p>ROH</p> <p>X = H, NO₂</p>	<p>Comments and References</p> <ul style="list-style-type: none"> - Copolymers of acrylic acid and p-nitrophenyl p-vinylbenzoate or 2,4-dinitrophenyl p-vinylbenzoate - Kinetic study⁴⁰²
<p>DCC, DMAP</p>	<p>Derived from Merrifield resin</p> <ul style="list-style-type: none"> - Designing eptitholones - 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 ^{1223,409}
	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)

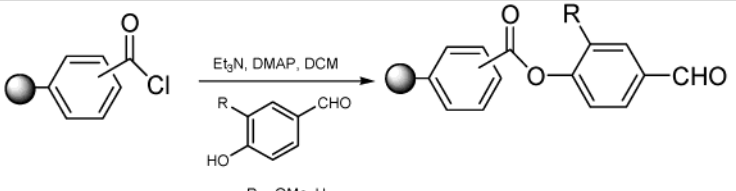
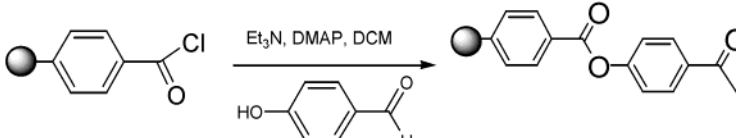
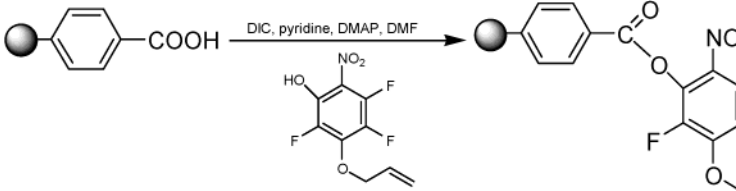
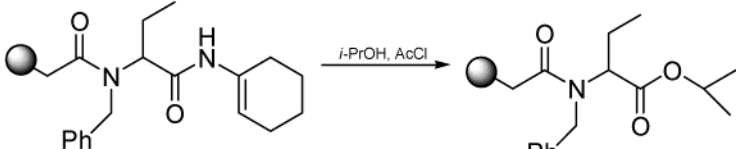
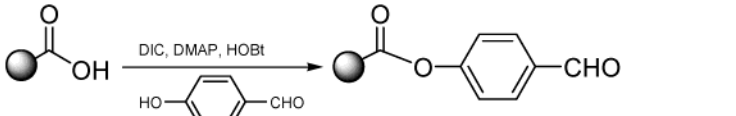

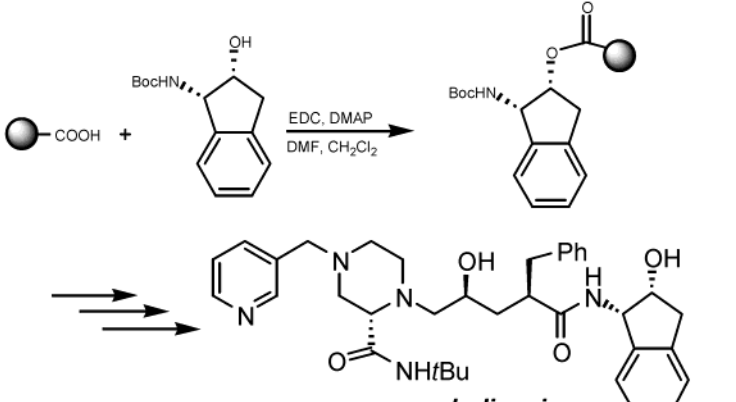
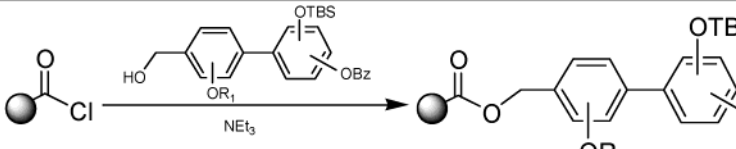
 <p style="text-align: center;">R = OMe, H</p>	
	Derived from carboxylated polystyrene (polystyrene acid chloride) - 80% yield ⁹¹
	Carboxypolystyrene resin - Synthesis of inhibitors of farnesyl transferase - Phenol attachment ⁴¹⁰
	Derived from carboxypolystyrene resin - Synthesis of acylaminoesters and 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
 <p style="text-align: center;">Indinavir</p>	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)

	<p>Derived from Wang resin</p> <ul style="list-style-type: none"> - Solid-phase synthesis of α-amino phosphonates (25-99%), phosphonic acid and α-hydroxy phosphonates (72-92%) - Loading yield 60%^{414,415}
	<p>Derived from Wang resin</p> <ul style="list-style-type: none"> - Immobilization of alcohols⁴¹⁶⁻⁴¹⁸
	<p>Polystyrene carboxylic resin derived from Wang resin</p> <ul style="list-style-type: none"> - Synthesis of stereochemically well-defined propionate-like compounds⁴¹⁹
	<p>Derived from Wang resin</p> <ul style="list-style-type: none"> - Synthesis of Sarcodictyins¹⁴⁷
	<p>Derived from carboxylated resin (obtained from Wang resin by oxidation)</p> <ul style="list-style-type: none"> - Subsequent Stille couplings succeeded - Used for synthesis of estradiol derivatives⁴²⁰
	<p>Two types of resin-bound α-TMS diazoketones developed from Wang resin</p> <ul style="list-style-type: none"> - Used for immobilization of alcohols, thiols, and amines. - Employed for subsequent syntheses of oxazoles⁴²¹
	<p>NovaSyn[®] TG carboxy resin</p> <ul style="list-style-type: none"> - Immobilization alcohols via esterification reaction³⁹⁹
	<p>Derived from carboxylated styrene-DVB copolymer resin and carboxylated Tentagel</p> <ul style="list-style-type: none"> - Synthesis of furane rings - Yield for the final products, 63-80%³⁹⁹
	<p>Derived from Tentagel resin</p> <ul style="list-style-type: none"> - Preparation of polymeric ligands to assess in the palladium-catalyzed allylic alkylation¹⁴⁵
	<p>Derived from Tentagel resin</p> <ul style="list-style-type: none"> - Synthesis of <i>N</i>-(alkoxy-acyl)amino alcohols¹⁵²

Table 2 (Continued)

<p>ROH = Boc-Thr(Bzl)-OH, Boc-Ser-OAllyl Boc-Tyr-OAllyl</p>	<p>Active carbonate resins synthesized from the corresponding hydroxymethyl resins (polystyrene) with <i>N,N'</i>-disuccinimidyl carbonate (DSC)</p> <ul style="list-style-type: none"> - Anchoring of a hydroxyl function - Synthesis of cyclic (head-to-tail) and alcohol peptides - Yield: 42%⁴⁰¹
	<p>Sulfonyl chloride polystyrene derived from Merrifield resin</p> <ul style="list-style-type: none"> - 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 <i>N</i>-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}
	<p>Derived from REM resin</p> <ul style="list-style-type: none"> - Synthesis of novel analogs of δ opioid ligand SNC-80 described⁴²⁵
	<p>Macrocrowns with knorr linker</p> <ul style="list-style-type: none"> - Solid phase synthesis of 1,3,5-trisubstituted pyridin-2-ones⁴²⁶
	<p>Polymer-bound tosyl chloride used for the synthesis of oxazolines from hydroxyamides.</p> <ul style="list-style-type: none"> - Twenty eight examples; yields, 32-75%⁴²⁷

Table 2 (Continued)

	Derived from BAL-resin - Synthesis of <i>N</i> -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				
<p>R = OH, R' = H R = H, R' = OH</p>	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-naphthol, 22-74%) ^{214,215,221,222,418}				
<p>n = 2, 4, 6, 8, 10</p>	Derived from polystyrene-DVB 2% - The synthesis of monoethers of symmetrical diols - Monoprotection of symmetrical diols - Synthesis of monotrityl ethers (37-51%) ^{221,230}				
<table border="0" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center; border-bottom: 1px solid black;">X</th> <th style="text-align: center; border-bottom: 1px solid black;">A</th> </tr> </thead> <tbody> <tr> <td style="vertical-align: top;"> OC(C₆H₅)₃ OC(C₆H₅) OCOCF₃ OSO₂CH₃ COCH₃ CH=CHC₄H₉ CHO OSO₂CH₃ </td> <td style="vertical-align: top;"> CH₂CH₂ CH=CH CH₂CH(OCOC₆H₅) (CH₂)_n, n = 3-10 C₆H₅COCH-CHCOC₆H₅ </td> </tr> </tbody> </table>	X	A	OC(C ₆ H ₅) ₃ OC(C ₆ H ₅) OCOCF ₃ OSO ₂ CH ₃ COCH ₃ CH=CHC ₄ H ₉ CHO OSO ₂ CH ₃	CH ₂ CH ₂ CH=CH CH ₂ CH(OCOC ₆ H ₅) (CH ₂) _n , n = 3-10 C ₆ H ₅ COCH-CHCOC ₆ H ₅	Derived from Wang resin - Conditions for each X group described - Yields of the final products after cleavage: 22-83% ^{207,217,226}
X	A				
OC(C ₆ H ₅) ₃ OC(C ₆ H ₅) OCOCF ₃ OSO ₂ CH ₃ COCH ₃ CH=CHC ₄ H ₉ CHO OSO ₂ CH ₃	CH ₂ CH ₂ CH=CH CH ₂ CH(OCOC ₆ H ₅) (CH ₂) _n , n = 3-10 C ₆ H ₅ COCH-CHCOC ₆ H ₅				

Table 2 (Continued)

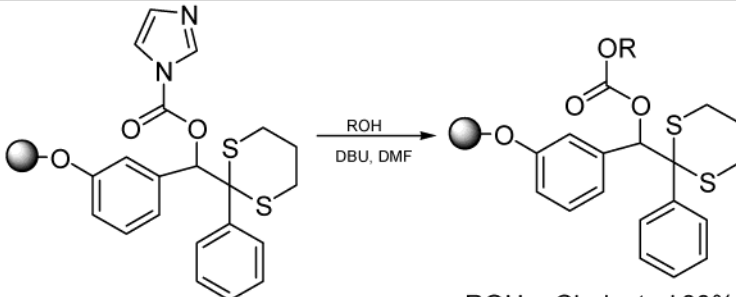
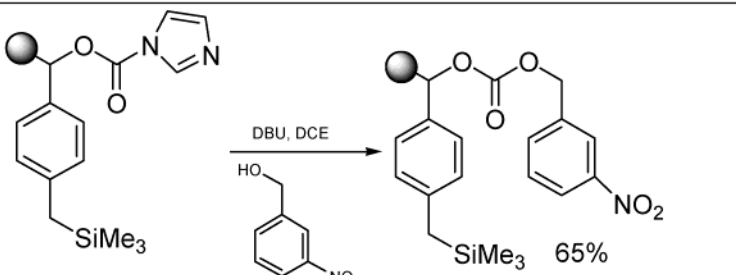
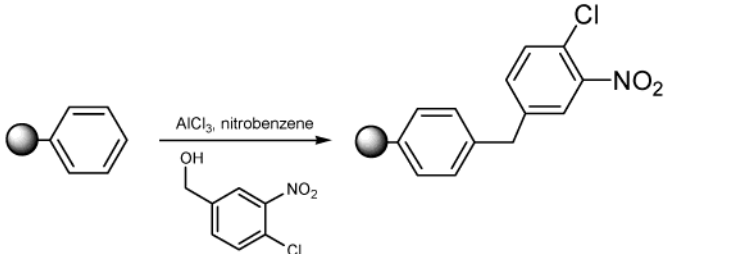
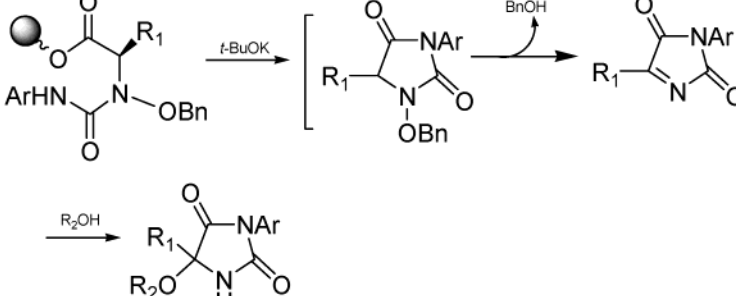

II. Solid supports reactions with alcohols and phenols	
II.2. Attachment as esters	
II.2.3. Carbonate synthesis	Comments and References
 <p style="text-align: center;">ROH = Cholesterol 83%</p>	<p>Derived from Merrifield resin</p> <ul style="list-style-type: none"> - Addition of alcohols to solid-supported imidazocarbonates results in the generation of carbonates. - Synthesis of a carbonate - One example - Yield: 83%¹²⁸
 <p style="text-align: center;">65%</p>	<p>Derived from Merrifield resin</p> <ul style="list-style-type: none"> - Synthesis of silyl linkers¹²⁷
II. Solid supports reactions with alcohols and phenols	
II.3. Attachment by other strategies (miscellaneous reactions)	Comments and References
	<p>Derived from macroporous polystyrene</p> <ul style="list-style-type: none"> - Friedel Craft alkylation⁴³¹
	<p>Derived from Wang resin</p> <ul style="list-style-type: none"> - Solid phase synthesis of 5-alkoxyhydantoin libraries⁴³²
 <p>X = aliphatic alicyclic aromatic heteroaromatic</p>	<p>Derived from Wang resin</p> <ul style="list-style-type: none"> - Curtius rearrangement - Synthesis of Fmoc protected amines - Seven examples; yields 34-78%¹⁵⁹

Table 2 (Continued)

	<p>Derived from multipin solid supports</p> <ul style="list-style-type: none"> - The library synthesis of 4-aminoproline analogs⁴³³
	<p>Merrifield resin</p> <ul style="list-style-type: none"> - Synthesis of heterocycles - Carbon-carbon coupling⁴³⁴

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