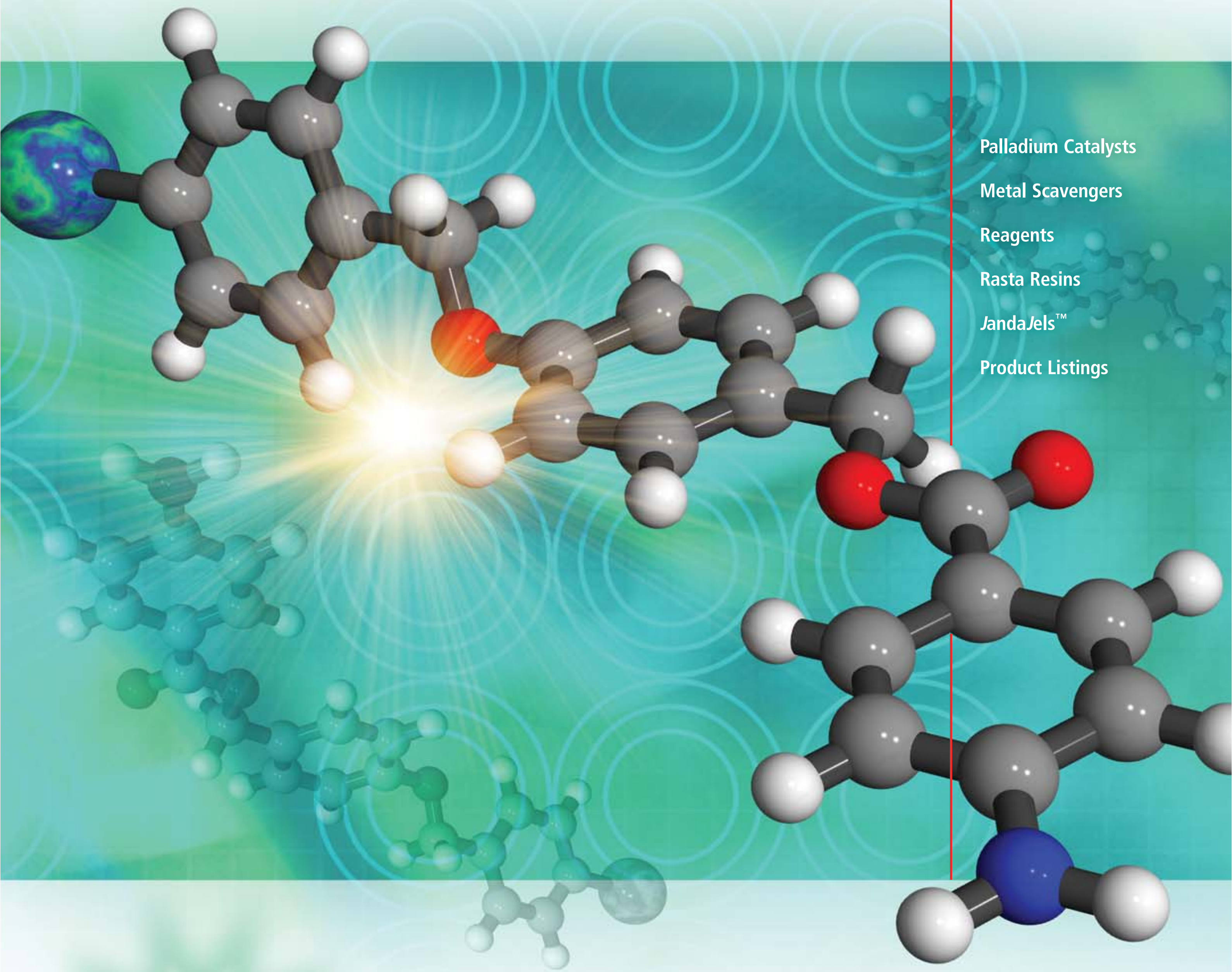
ChemFiles

Vol. 5 No. 11

Polymer-Supported Catalysts and Reagents



- Palladium Catalysts
- Metal Scavengers
- Reagents
- Rasta Resins
- JandaJels™
- Product Listings

See pages 4 and 6

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Introduction

Solid-supported reagents have been utilized in a variety of ways to facilitate combinatorial synthesis. They are also being used in solution-phase parallel syntheses and in multi-step organic syntheses as scavengers to ease reaction workup and product purification.

Polymer-supported reagents have several advantages over their homogenous equivalents. These include the following:

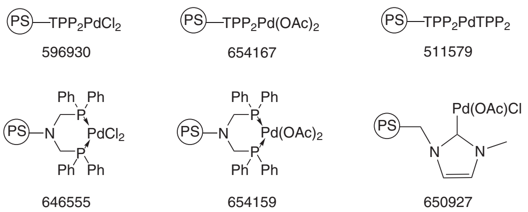
- Reagents are separated from the final product by simple filtration.
- Large excess of reagents can be used.
- High concentrations of reagents allow slower reactions to be driven to completion.
- Washing and filtration steps can be automated.
- It is easier to dispense reagents in library syntheses.
- Supported analogs of toxic, explosive, or odorous reagents are safer and more convenient to handle than the corresponding soluble compound.

Sigma-Aldrich has developed a variety of scavenger resins and polymer-bound reagents useful for a wide range of solution-based synthetic reactions. For the complete listing of polymer-supported reagents, please visit sigma-aldrich.com/drugdiscovery. If you do not see a particular reagent or scavenger you need, please contact your local Sigma-Aldrich office (see back cover), or visit www.sigma-aldrich.com.

Palladium Catalysts on Solid Support

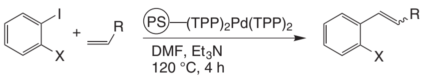
Palladium has become one of the most commonly used catalysts in organic chemistry. The range of transformations involving palladium include: Heck reactions; Suzuki, Negishi, Sonagashira, and Stille coupling reactions; Buchwald amidations; carbonylation reactions; and hydrogenations. There are many synthetic drawbacks to using homogeneous palladium catalysts that can be overcome by attaching the palladium to a functionalized polystyrene resin. The advantages of solid-supported palladium reagents include:

- Easy workup of the reaction by filtration of the solid-supported palladium reagent
- Low residual Pd levels in the crude final product
- Recyclability of the solid-supported palladium reagent



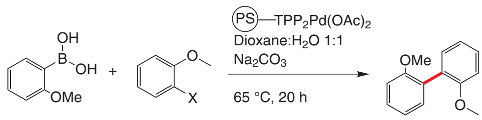
Applications of Solid-Supported Palladium Reagents

Heck Reaction Mini-Library

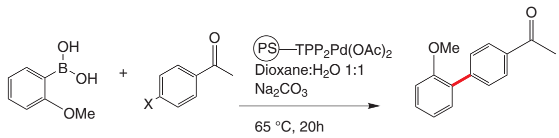


	X	R	Yield
1	OCH_3	CN	72%
2	OCH_3	CO_2Me	76%
3	OCH_3	Ph	99%
4	OCH_3	4-pyridyl	99%
5	H	CN	98%
6	H	CO_2Me	88%
7	H	Ph	92%
8	H	4-pyridyl	84%

Suzuki Reaction

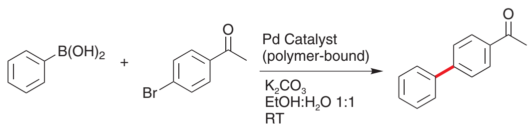


Aryl Halide	Yield
I	96%
Br	71%
Cl	11%



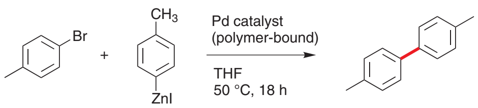
Aryl Halide	Yield
I	85%
Br	83%
Cl	8%

Suzuki Reaction Recycle the Catalyst

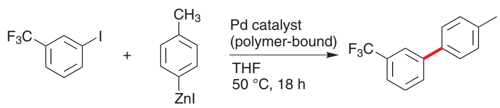


Pd Catalyst	Cycle 1 Yield	Cycle 2 Yield	Cycle 3 Yield	Cycle 4 Yield
596930	99%	99%	99%	99%
654167	99%	99%	99%	99%
646555	99%	99%	99%	99%
654159	99%	99%	99%	99%

Negishi Reaction



Pd Catalyst	Product Yield
596930	82%
654167	85%
646555	81%
654159	83%

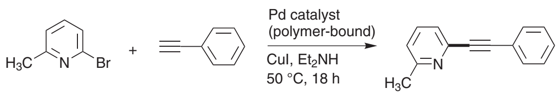


Pd Catalyst	Product Yield	Byproduct Yield[a]
596930	83%	4%
654167	84%	5%
646555	86%	4%
654159	81%	5%

[a] 4,4-dimethylbiphenyl

Sonogashira Coupling Catalyzed by Palladium on Polymer Supports

Supported palladium catalysts are widely used in the Suzuki, Heck, and Sonogashira cross-coupling reactions. The advantages to using supported catalysts in organic synthesis include reagent stability, suitability for automation, ease of workup, recyclability, and lower Pd contamination in the final product. Here, we describe the application of four commercially available polymer-supported palladium reagents as catalysts in the Sonogashira coupling.



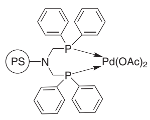
Typical Experimental Procedure

The palladium catalyst (0.01 mmol Pd) is charged into the reaction vessel. Diethylamine (6 mL), followed by 2-bromo-6-methylpyridine (1.0 g, 5.8 mmol), phenylacetylene (1.2 g, 11.8 mmol), and copper(I) iodide (2.8 mg, 0.0145 mmol) is added to the reaction vessel. The resulting mixture is stirred at 55–60 °C for 18 h, cooled, and then filtered. The resin is washed with THF (2 × 3 mL), the THF filtrates combined and evaporated to yield a dark colored oil. The oil is dissolved in ether (30 mL), extracted twice with water (10 mL) and twice with brine (10 mL), dried with anhydrous sodium sulfate, filtered and evaporated to yield a dark colored oil. The crude oil thus obtained is purified by flash chromatography on silica gel using ethyl acetate: hexane (9:1). The purified product, 6-methyl-2-(phenylethynyl)pyridine, is isolated as a yellow oil. (See the table below for yields.)

Cat. No.	Catalyst Name	Coupling Yield
596930	Dichlorobis(triphenylphosphine)palladium(II), polymer-bound	92%
654167	Diacetobis(triphenylphosphine)palladium(II), polymer-bound	91%
646555	Bis[(diphosphanyl)methyl]laminepalladium(II) dichloride, polymer-bound	88%
654159	Bis[(diphenylphosphanyl)methyl]amine-palladium(II) diacetate, polymer-bound	80%

Bis[(diphenylphosphanyl)methyl]aminepalladium(II) diacetate, polymer-bound

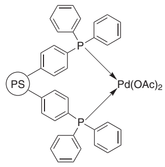
70–90 mesh
0.5–1.0 mmol/g Pd
1% DVB



654159-1G	1 g
654159-5G	5 g

Diacetobis(triphenylphosphine)palladium(II), polymer-bound

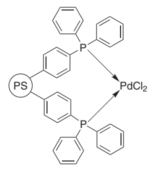
200–400 mesh
1.0–1.5 mmol/g Pd
1% DVB



654167-5G	5 g
654167-25G	25 g

Dichlorobis(triphenylphosphine)palladium(II), polymer-bound

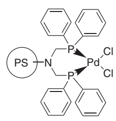
200–400 mesh
1.0–2.0 mmol/g
2% DVB



596930-1G	1 g
596930-5G	5 g

Bis[(diphosphanyl)methyl]laminepalladium(II) dichloride, polymer-bound

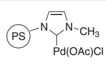
70–90 mesh
0.5–1.5 mmol/g N
2% DVB



646555-1G	1 g
646555-5G	5 g

***N*-Methylimidazolium palladium (II), polymer-bound**

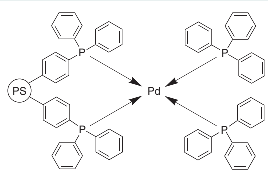
50–100 mesh
0.5–1.5 mmol/g Pd
1% DVB



650927-5G	5 g
650927-25G	25 g

Tetrakis(triphenylphosphine)palladium(0), polymer-bound

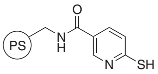
200–400 mesh
0.5–0.9 mmol/g
2% DVB



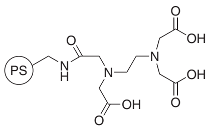
511579-1G	1 g
511579-5G	5 g

Metal Scavengers

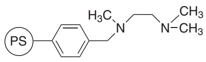
Metal compounds are widely used in organic and medicinal chemistry as either reactants or catalysts. Since most metal ions have physiological activities, reducing residual metal levels has become a key step in syntheses of bioactive compounds.[1] Application of resin scavengers is an efficient method to remove metal ions during post-synthesis purification.[2] Sigma-Aldrich has developed several different functionalized resin scavengers to remove metals in a variety of organic syntheses.



6-Thiolnicotinamide, polymer-bound, 643904



Ethylenediaminetriacetic acid acetamide, polymer-bound, 656844



N,N,N'-Trimethylethylenediamine, polymer-bound, 656836

Typical Procedure of Removal Metals

Add 3–5 eq. of resin scavenger to an organic solution of crude product containing metal ion. The resulting mixture is stirred for 4–16 h at room temperature to allow the scavenger to fully bind to the metal ions. In some cases, the addition of a few drops of water to the solution is necessary to increase the binding rate. The scavenger is then removed by filtration.

Maximum Binding Capacity of Scavengers

The maximum binding capacity of the scavenger was determined by stirring a mixture of a scavenger (1 eq.) and a metal salt (2.5–4 eq.) in an organic solvent (THF, MeOH, EtOH, dichloromethane) or a mixture of two solvents overnight. The resin was filtered and washed with solvent, dried, and then analyzed for metal content by microanalysis.

Metal	6-Thionicotin-amide, Polymer-Bound (643904)	Ethylenediamine-triacetic Acid Acetamide, Polymer-Bound (656844)	*N,N,N'*-Trimethyl-ethylenediamine, Polymer-Bound (656836)
Ag(I)	1.45 mmol/g	Not tested	Not tested
Cd(II)	1.07 mmol/g	1.28 mmol/g	Not tested
Co(II)	1.11 mmol/g	0.89 mmol/g	1.41 mmol/g
Cu(I)	Not tested	1.48 mmol/g	1.49 mmol/g
Cu(II)	1.00 mmol/g	1.57 mmol/g	1.10 mmol/g
Hg(II)	0.67 mmol/g	Not tested	Not tested
Ni(II)	0.35 mmol/g	0.47 mmol/g	1.15 mmol/g
Pd(II)	0.79 mmol/g	0.47 mmol/g	1.41 mmol/g
Zn(II)	1.07 mmol/g	1.48 mmol/g	1.27 mmol/g

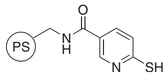
References

(1) Welch, C. J. et al. *Org. Process Res. Dev.* **2005**, *9*, 198.

(2) Urawa, Y.; Miyazawa, M.; Ozeki, N.; Ogura, K. *Org. Process Res. Dev.* **2003**, *7*, 191.

6-Thionicotinamide, polymer-bound

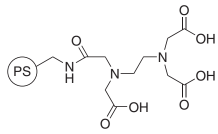
70–90 mesh
2.0–3.0 mmol/g N
1% DVB



643904-5G	5 g
643904-25G	25 g

Ethylenediaminetriacetic acid acetamide, polymer-bound

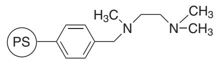
50–100 mesh
3.5–4.0 mmol/g N
1% DVB



656844-5G	5 g
656844-25G	25 g
656844-100G	100 g

N,N,N'-Trimethylethylenediamine, polymer-bound

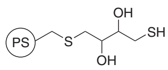
100–200 mesh
2.5–3.0 mmol/g N
1% DVB



656836-5G	5 g
656836-25G	25 g
656836-100G	100 g

DL-Dithiothreitol, polymer-bound

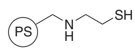
100-200 mesh
2.0-3.0 mmol/g S
1% DVB



641944-5G	5 g
641944-25G	25 g

2-Mercaptoethylamine, polymer-bound

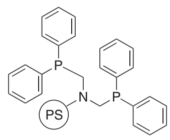
70–90 mesh
1.0–1.5 mmol/g
1% DVB



641022-5G	5 g
641022-25G	25 g

Bis[(diphenylphosphanyl)methyl]amine, polymer-bound

70–90 mesh
1.0–2.0 mmol/g N
1% DVB



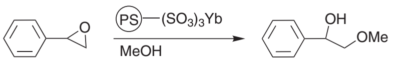
643955-5G	5 g
643955-25G	25 g

Polymer-Bound Lewis Acids

Lewis acids are important catalysts for many types of transformations in organic chemistry. Lanthanide salts serve as mild alternatives to traditional hard Lewis acids. Reactions catalyzed by the polymer-bound lanthanide Lewis acids include acetalization, aldol reaction and allylation of aldehydes, nucleophilic addition to imines, aza-Diels–Alder reactions, and ring opening of epoxides.[1] Polymer-bound reagents react the same as the solution-phase equivalent and have the added advantage of ease of handling, simplified reaction workup and, in some cases, recyclability.

Ytterbium(III) Polystyrenesulfonate

Typical Experimental Procedure for Ring Opening of Epoxides

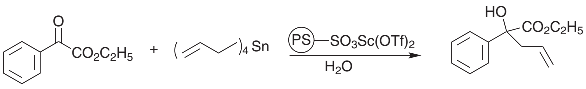


Styrene oxide (0.12 mL, 1 mmol) and ytterbium(III) polystyrene-sulfonate polymer-bound (100 mg, 0.056 mmol) were mixed in methanol (1 mL), and stirred at room temperature overnight (16 h). TLC showed that the reaction went to completion. The reaction was filtered and the resin washed with methanol (2 × 1 mL). The combined solution phases were evaporated to give 2-methoxy-1-phenylethanol a colorless oil (151 mg, 100%).

Scandium(III) Bis(trifluoromethanesulfonate), Polymer-Bound

One of the important transition metal Lewis acid catalysts is scandium(III) bis(trifluoromethanesulfonate), which is widely used in carbon–carbon bond and carbon–heteroatom bond formation.[2]

Typical Experimental Procedure for Addition of Allyl Group to Esters



Ethyl benzoylformate (178 mg, 1 mmol), tetraallyltin (282 mg, 1 mmol) and scandium bis(trifluoromethanesulfonate), polymer-bound (10 mg, 0.0068 mmol) were mixed in water (6 mL). The mixture very quickly became cloudy and was stirred at room temperature overnight. Then ether (20 mL) was added and the mixture was passed through a silica gel pad. The organic layer was separated, dried, and evaporated to afford a white solid (205 mg, 95% yield). The structure was confirmed by ^{1}H NMR.

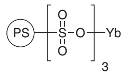
References

(1) Dondoni, A.; Massi, A. *Tetrahedron Lett.* **2001**, *42*, 7975. Yu, L.; Chen, D.; Li, J.; Wang, P. G. *J. Org. Chem.* **1997**, *62*, 3575.

(2) Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W. L. *Chem. Rev.* **2002**, *102*, 2227. Kobayashi, S.; Kitagawa, H.; Matsubara, R. *J. Comb. Chem.* **2001**, *3*, 401.

Ytterbium(III) polystyrenesulfonate

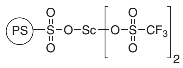
30–60 mesh
0.5–1.5 mmol/g
macroporous



641030-5G	5 g
641030-25G	25 g

Scandium(III) bis(trifluoromethanesulfonate), polymer-bound

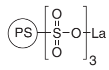
30–60 mesh
0.5–1.5 mmol/g
macroporous



590312-1G	1 g
590312-5G	5 g
590312-25G	25 g

Lanthanum(III) polystyrenesulfonate

16–50 mesh
0.25–0.5 mmol/g
macroporous



643718-25G	25 g
643718-100G	100 g

NEW Solid-Supported Reagents for Efficient, Facile Amide Bond Formations

N-Acylation reactions are ubiquitous transformations in organic synthesis. The strong demand of peptide chemistry for efficient, selective activators of the carboxyl group to form a peptide bond lead to a large number of different coupling reagents. Complementary to the emerging interest in polymer-supported reagents, numerous immobilized derivatives of the most popular coupling reagents have been reported in recent years. Examples are polymer-bound hydroxybenzotriazole (HOBt, Cat. No. **09656**) and polymer-bound carbodiimides (Cat. No. **00787**), which are both widely used.

Sigma-Aldrich is now expanding the portfolio for polymer-supported N-acylations with new *N*-hydroxysuccinimidyl- and 2-nitrophenol resins—precursors for polymer-bound active esters[1,2] and a new polymer-supported HBTU reagent.

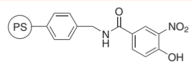
References

(1) Lee, J. W.; Louie, Y. Q.; Walsh, D., P.; Chang, Y.-T. *J. Comb. Chem.* **2003**, *5*, 330.

(2) Shao, H.; Zhang, Q.; Goodnow, R.; Chen, L.; Tam, S. *Tetrahedron Lett.* **2000**, *41*, 4257.

2-Nitrophenol, polymer bound

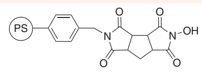
200–400 mesh
~1,3 mmol/g



50598-1G	1 g
50598-5G	5 g

***N*-Hydroxysuccinimide, polymer-bound**

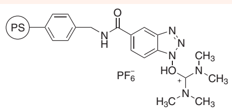
200–400 mesh
~1,1 mmol/g



71346-5G	5 g

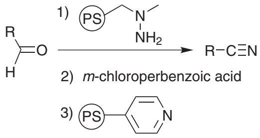
***O*-Benzotriazol-1-yl-*N*,*N*,*N'*,*N'*-tetramethyluronium hexafluorophosphate, polymer bound**

100–300 mesh
~1 mmol/g

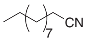
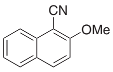
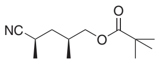
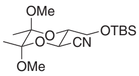


39898-1G	1 g
39898-5G	5 g

One-Pot Conversion of Aldehydes to Nitriles Using Polymer-Supported Reagents[1]



Nitriles[a] Prepared from their Corresponding Aldehyde Using a Solid-Supported Hydrazine

Entry	Nitrile	Yield[b]
1		100%
2		77%
3		90%
4		100%

[a] All new compounds were fully characterized.
[b] Yields are isolated yields; purity greater than 95% by ^{1}H NMR

References

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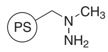
N-Methylhydrazine, polymer-bound

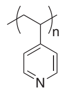
100–200 mesh
2.0–3.0 mmol/g
1% DVB



640344-5G	5 g
640344-25G	25 g

Poly(4-vinylpyridine)

2% cross-linker

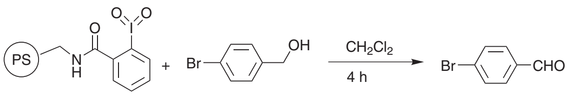


226963-10G	10 g
226963-50G	50 g
226963-250G	250 g

2-Iodylbenzamide, Polymer-Bound for Oxidation

Hypervalent iodine reagents have been extensively used in many chemical transformations, especially for mild and safe oxidation of alcohols to carbonyl compounds.[1] Polymer-supported hypervalent iodine is more stable than the soluble analog, suitable for automation, and ease of reaction workup. 2-Iodylbenzamide, polymer-bound, has demonstrated reactivity for oxidations similar to polymer-bound IBX, of which it is an analogue.[2,3]

Typical Experimental Procedure



2-Iodylbenzamide, polymer-bound (300 mg, 0.2 mmol) and bromobenzyl alcohol (18 mg, 0.1 mmol) are mixed and stirred in CH_2Cl_2 (1 mL) at room temperature for 4 h. The reaction was filtered and the resin washed with CH_2Cl_2 (3 × 1 mL). The combined reaction solution and washings were evaporated to dryness to give a white solid (18 mg, 100%). ^{1}H NMR confirmed that all of the alcohol was converted to the aldehyde.

References

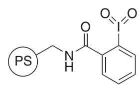
(1) Varvoglis, A. *Tetrahedron*, **1997**, 53. Tohma, H.; Kita, Y. *Adv. Synth. Catal*. **2004**, *346*, 111.

(2) Mubaier, M.; Giannis, A. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 4393. Sorg, G.; Mengel, A.; Jung, G.; Rademann, *J. Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 4395. Reed, N. N.; Delgado, M.; Hereford, K.; Clapham, B.; Janda, K. D. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 204. Lei, Z.; Denecker, C.; Jegasothy, S.; Sherrington, D. C.; Slater, N. K. H.; Sutherland, A. J. *Tetrahedron Lett.* **2003**, *44*, 1635.

(3) Chung, W.-J.; Kim, D.-K.; Lee, Y.-S. *Tetrahedron Lett.* **2003**, *44*, 9251.

2-Iodylbenzamide, polymer-bound

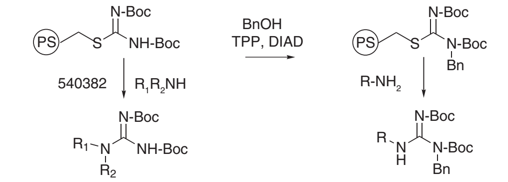
50–100 mesh
0.5–1.0 mmol/g
1% DVB



654175-5G	5 g
654175-25G	25 g

Guanylation of Amines by Bis(*tert*-butoxycarbonyl)thiopseudourea, Polymer-Bound

The synthesis of guanidine-containing bioactive molecules is of great interest in medicinal chemistry. The guanidine moiety is fully protonated under physiological conditions due to its strong basicity.[1] Introduction of a guanidinyl group can be achieved by the reaction of substituted amines with various guanylation reagents.[2,3,4] One such guanylating reagent is bis(*tert*-butoxycarbonyl)thiopseudourea, polymer-bound.



R_1R_2NH: propylamine, piperidine
Monosubstituted derivatives

R: H, propyl, phenethyl
Disubstituted derivatives

Typical Experimental Procedure

Synthesis of *N,N* Disubstituted- *N*′,*N*″-bis(*tert*-butoxycarbonyl) Guanidine

The amine (1 mmol) and bis(*tert*-butoxycarbonyl)thiopseudourea, polymer-bound (5 mmol) are mixed in THF (5 mL) and stirred for 40 h at room temperature. The mixture is filtered and the resin washed with THF (2 × 3 mL). The combined washings are evaporated to dryness to give a pure monosubstituted guanidine. The structures are confirmed by ^{1}H NMR and mass spectrometry.

N,N Disubstituted-N′,N″-bis(tert-butoxycarbonyl) Guanidine

Amine	Yield
propylamine	100%
piperidine	100%

Synthesis of *N,N*′ Disubstituted-*N*′,*N*″-bis(*tert*-butoxycarbonyl) Guanidine

Polymer-bound bis(*tert*-butoxycarbonyl)thiopseudourea (200 mg, 0.2 mmol) and triphenylphosphine (313 mg, 1.2 mmol) were added to a fritted reaction vessel. A solution of benzyl alcohol (108 mg, 1.0 mmol) in THF (3 mL) was added. The mixture was stirred for 20 min, followed by dropwise addition of diisopropyl azodicarboxylate (0.196 mL, 1.0 mmol). The resulting mixture was stirred overnight at room temperature. The reaction solution was drained and the resin washed with several portions of THF and methanol. Ammonia (2 mmol) or amine (0.6 mmol) in THF (2.5 mL) was added to the reaction vessel. The mixture was agitated overnight at room temperature. The reaction mixture was filtered and the solution collected. The resin was washed with several portions of THF and methanol. The combined reaction solution and washings were evaporated to dryness. The residue was purified by flash chromatography (silica gel, column size: 1.5 × 20 cm). The structures of the isolated products were confirmed by ^{1}H NMR and mass spectrometry. The BOC group can be removed using standard deprotection methods to yield the desired unprotected substituted guanidine.

N,N′ Disubstituted-N′,N″-bis(tert-butoxycarbonyl) Guanidine

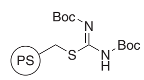
Alcohol	Amine	Yield
benzyl alcohol	ammonia	81%
benzyl alcohol	propylamine	93%
benzyl alcohol	phenethylamine	89%

References

(1) Goodman, M. et al. *J. Org. Chem.* **1998**, *63*, 8432.
(2) Dodd, D. S.; Wallace, O. B. *Tetrahedron Lett.* **1988**, *39*, 5701.
(3) Acton, J. J.; Jones, A. B. *Tetrahedron Lett.* **1999**, *37*, 4319.
(4) Dodd, D. S.; Kozikowski, A. P. *Tetrahedron Lett.* **1994**, *35*, 977.

Bis-Boc-thiopseudourea, polymer-bound

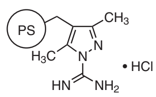
100–200 mesh
1.0 mmol/g S
1% DVB



540382-5G	5 g
540382-25G	25 g

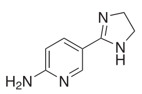
3,5-Dimethyl-1*H*-pyrazole-1-carboxamidine hydrochloride, polymer-bound

100–200 mesh
1.0–2.0 mmol/g
2% DVB



633429-1G	1 g
633429-5G	5 g

NEW Heterocyclic Building Blocks from Sigma-Aldrich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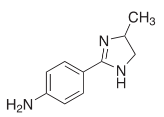
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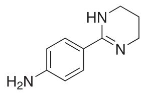
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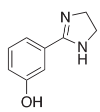
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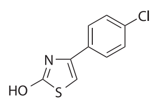
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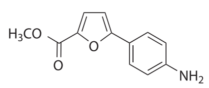
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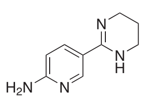
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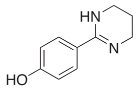
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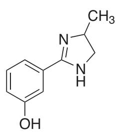
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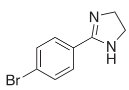
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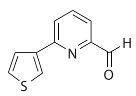
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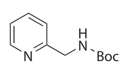
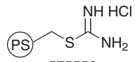
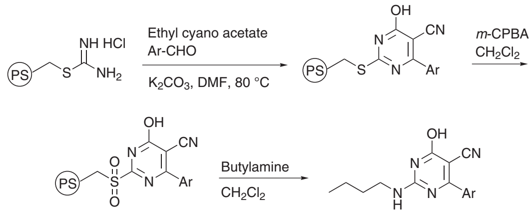

L480347

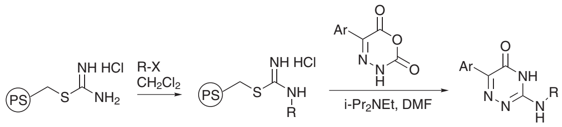
Synthesis of Heterocyclic Compounds Using Thiopseudourea Hydrochloride, Polymer-Bound

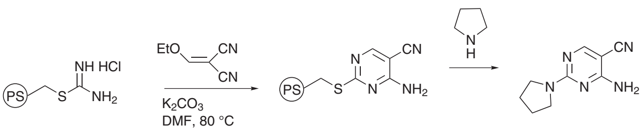
Heterocyclic compounds are common scaffolds in drug discovery.[1] Many different types of heterocyclic compounds can be prepared using new synthetic methods that have been developed based on supported reagents.[2] Thiopseudourea hydrochloride, polymer-bound is a polymer reagent useful for synthesis of different types of 6-membered heterocycles, for example pyrimidines[3] and 1,2,4-triazin-5-ones.[1,3,4]



575550







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(2) Franzen, R. G. *J. Comb. Chem.* **2000**, *2*, 195.

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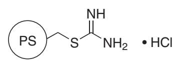
Thiopseudourea hydrochloride, polymer-bound

100–200 mesh
2.2 mmol/g S
1% DVB



575550-5G	5 g
575550-25G	25 g
575550-100G	100 g

Polyaniline-Supported Vanadyl Acetylacetonate for Oxidation of Alcohols

The oxidation of alcohols to aldehydes and ketones is one of the most important and frequently used transformations in organic chemistry.[1] Most oxidizing reagents that have been developed require stoichiometric quantities and laborious workup. To improve the atom economy of such reactions, the development of catalytic systems with molecular oxygen as the primary oxidant in the presence of transition metal catalysts have been in focus in recent years.

Polyaniline-supported $VO(acac)_2$ has been described to catalyze efficiently the oxidation of alcohols to aldehydes and ketones in high yields with molecular oxygen in toluene at ca. 100 °C.[2] The protocol does not require base and the catalyst can be recycled without loss of activity.

References

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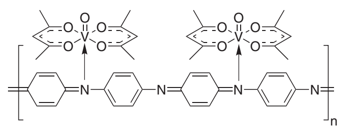
Vanadyl acetylacetonate bound to polyaniline

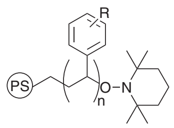
200–400 mesh
~1 mmol/g



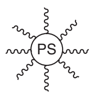
69052-1G	1 g
69052-5G	5 g

Rasta Resins

Rasta Resins are produced by a unique living free radical polymerization process (**Structure 1**).[1] The unique polymer structure of the Rasta Resin consists of a polystyrene core with long, linear polymer chains that contain the desired reagent, catalyst, or scavenger (**Structure 2**). Rasta Resins have higher loading than typical polymer-bound reagents. This increased loading is advantageous in that less polymer material is required to achieve the same synthetic results.[2] Isocyanate on Rasta Resin can be utilized to scavenge excess primary and secondary amines from crude reactions.[1] Chloromethyl on Rasta Resin can be used in the same manner as Merrifield resin to produce a wide range of organic compounds.[3,4]



Structure 1



Structure 2

References

(1) Hodges, J.; L. Harikrishnan, L.; Ault-Justus, S. *J. Comb. Chem*. **2000**, *2*, 80.

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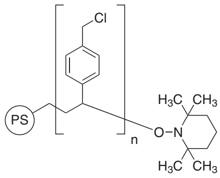
Chloromethyl on Rasta Resin

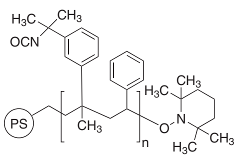
50–100 mesh
4.0–5.0 mmol/g Cl
1% DVB



643661-5G	5 g
643661-25G	25 g

Isocyanate on Rasta Resin

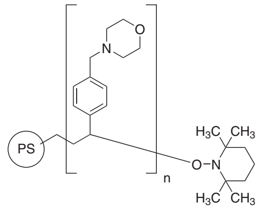
100–200 mesh
2.0 mmol/g
1% DVB



569666-5G	5 g
569666-25G	25 g

Morpholine on Rasta Resin

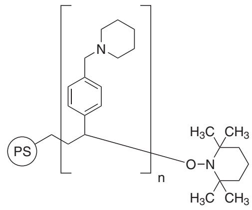
50–100 mesh
4.0–5.0 mmol/g
1% DVB



643599-5G	5 g
643599-25G	25 g

Piperidine on Rasta Resin

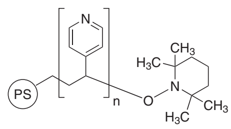
50–100 mesh
3.0–5.0 mmol/g
1% DVB



643602-5G	5 g
643602-25G	25 g

Pyridine on Rasta Resin

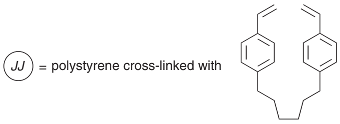
50–100 mesh
6.5–7.5 mmol/g N
1% DVB



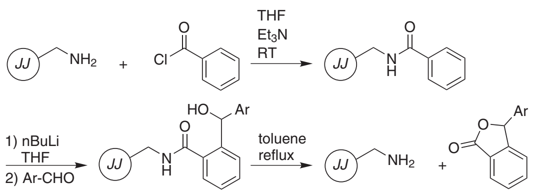
655457-5G	5 g
655457-25G	25 g

JandaJels™

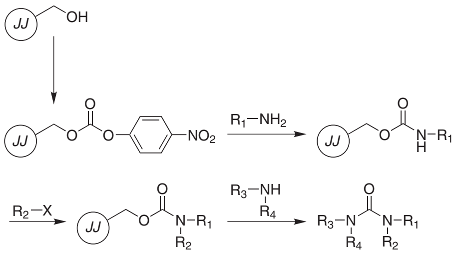
JandaJels are designed to create a "solvent-like organic microenvironment to catalyze organic reactions".[1] The flexible tetrahydrofuran-like cross-linker gives the JandaJels increased swelling and solvation characteristics as compared to polystyrene resins cross-linked with divinylbenzene.[2,3] The increased swelling results in better site accessibility as compared to highly cross-linked polymers.[4] JandaJels have been used for solid-supported organic synthesis (SPOS)[5–8] as well as polymer-bound reagents in a wide variety of synthetic transformations,[9–11] catalysis,[12,13] chiral catalysis,[14–17] and in small library synthesis.[18–23]



Synthesis of a Phthalimide Library[18]



Synthesis of a Di-, Tri-, and Tetra-substituted Urea Library[19]



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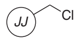
JandaJel™-Cl

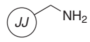
100–200 mesh
0.5–1.0 mmol/g
2% cross-linker



524549-5G	5 g
524549-50G	50 g
524549-100G	100 g

JandaJel™-NH_2

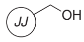
100–200 mesh
1.0 mmol/g N
2% cross-linker



524611-1G	1 g
524611-5G	5 g
524611-50G	50 g
524611-100G	100 g

JandaJel™-OH

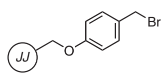
200–400 mesh
1.0 mmol/g OH
2% cross-linker



524581-1G	1 g
524581-5G	5 g

JandaJel™4-benzyloxybenzyl bromide

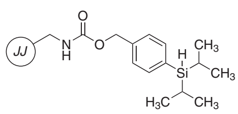
50–100 mesh
0.8–1.2 mmol/g
1% cross-linker



632880-5G	5 g
632880-25G	25 g

JandaJel™-carbamic acid 4-diisopropylsilanybenzyl ester

50–100 mesh
0.5–1.5 mmol/g Si
1% cross-linker

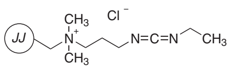


646067-5G	5 g

To order: Contact your local Sigma-Aldrich office (see back cover), or visit sigma-aldrich.com.

JandaJel™-1,(3-dimethylaminopropyl-3-Ethyl

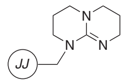
50–100 mesh
1.5–2.0 mmol/g
2% cross-linker



567248-1G	1 g
567248-5G	5 g

JandaJel™-1,3,4,6,7,8-hexahydro-2*H*-pyrimido-[1,2-*a*]pyrimidine

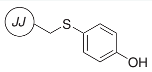
100–200 mesh
2.3 mmol/g
1% cross-linker



570494-5G	5 g
570494-25G	25 g

JandaJel™-4-mercaptophenol

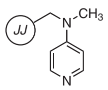
100–200 mesh
0.8 mmol/g S
1% cross-linker



569674-5G	5 g
569674-25G	25 g

JandaJel™-4-methylaminopyridine

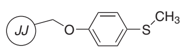
50–100 mesh
1.5 mmol/g N
1% cross-linker



635170-5G	5 g
635170-25G	25 g

JandaJel™-4-(methylthio)phenol

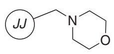
50–100 mesh
0.5–1.0 mmol/g S
1% cross-linker



656879-5G	5 g
656879-25G	25 g

JandaJel™-morpholine

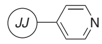
100–200 mesh
3.6 mmol/g N
1% cross-linker



578819-5G	5 g
578819-25G	25 g

JandaJel™-polypyridine

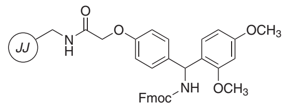
100–200 mesh
8.0 mmol/g
1% cross-linker



576387-5G	5 g
576387-25G	25 g

JandaJel™-rink amide

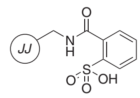
100–200 mesh
0.5 mmol/g
1% cross-linker



570508-5G	5 g
570508-25G	25 g

JandaJel™-sulfonic acid

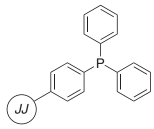
50–100 mesh
1.20 mmol/g S
1% cross-linker



658790-5G	5 g
658790-25G	25 g
658790-100G	100 g

JandaJel™-triphenylphosphine

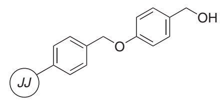
50–100 mesh
3.0 mmol/g P
2% cross-linker



533416-1G	1 g
533416-5G	5 g

JandaJel™-Wang

50–100 mesh
1.0 mmol/g
2% cross-linker



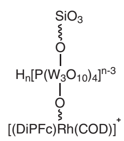
524646-1G	1 g
524646-5G	5 g

Additional Products

Catalysts

1,1′-Bis(diisopropylphosphino)ferrocene(COD) Rh-phosphotungstic acid on alumox

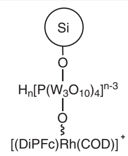
150 mesh
0.028 mmol/g Rh



636665-1G	1 g
636665-5G	5 g

1,1′-Bis(diisopropylphosphino)ferrocene(COD) Rh-phosphotungstic acid on silica gel

100–200 mesh
0.02 mmol/g Rh

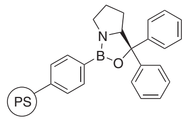


634344-1G	1 g
634344-5G	5 g

Additional Products

3,3-Diphenyltetrahydropyrrold[1,2-c][1,3,2]oxazaborolidine polymer-bound

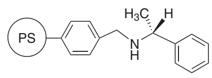
70–90 mesh
0.5–1.5 mmol/g N
1% DVB



643947-5G	5 g
643947-25G	25 g

(*R*)-α-Methylbenzylamine, polymer-bound

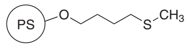
100–200 mesh
2.0 mmol/g N
1% DVB



576395-5G	5 g
576395-25G	25 g

4-(Methylthio)-1-butanol, polymer-bound

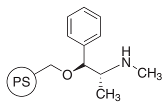
100–200 mesh
1.0–2.0 mmol/g
1% DVB



589268-5G	5 g
589268-25G	25 g

1*R*,2*R*-Pseudoephedrine, polymer-bound

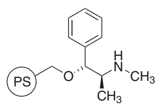
50–100 mesh
1.0–2.0 mmol/g
1% DVB



651508-5G	5 g
651508-25G	25 g

1*S*,2*S*-Pseudoephedrine, polymer-bound

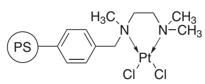
50–100 mesh
1.0–2.0 mmol/g
1% DVB



649031-5G	5 g
649031-25G	25 g

Platinum dichoride complexed to trimethylethylene diamine, polymer-bound

50–100 mesh
0.5–1.5 mmol/g Pt
1% DVB

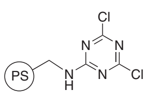


660965-500MG	500 mg
660965-1G	1 g

Coupling Reagent

4,6-Dichloro-1,3,5-triazene, polymer-bound

100–200 mesh
1.0–2.0 mmol/g
1% DVB

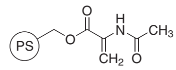


579297-5G	5 g
579297-25G	25 g

Linkers

N-Acetamidoacrylic acid, polymer-bound

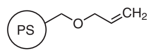
100–200 mesh
1.0–1.5 mmol/g
1% DVB



641448-5G	5 g
641448-25G	25 g

Allyl alcohol, polymer-bound

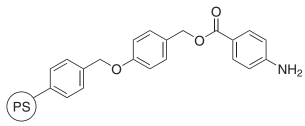
100–200 mesh
1.5–2.0 mmol/g O
1% DVB



637270-5G	5 g
637270-25G	25 g

4-Aminobenzoate, polymer-bound on Wang

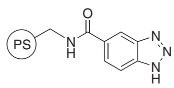
100–200 mesh
0.5–1.5 mmol/g N
1% DVB



650307-5G	5 g
650307-25G	25 g

Benzotriazole, polymer-bound

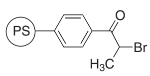
50–100 mesh
1.0–1.5 mmol/g
1% DVB



589047-5G	5 g
589047-25G	25 g

4-Benzyloxybenzyl bromide, polymer-bound

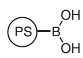
100–200 mesh
0.5–1.0 mmol/g Br
1% DVB



534854-5G	5 g
534854-25G	25 g

Boronic acid, polymer-bound

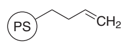
50–100 mesh
1.0–2.0 mmol/g
1% DVB



632627-1G	1 g
632627-5G	5 g

Butene, polymer-bound

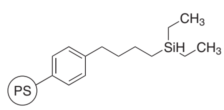
50–100 mesh
1.0–2.0 mmol/g



649775-5G	5 g
649775-25G	25 g

Butyldiethylsilane, polymer-bound

100–200 mesh
1.1–1.6 mmol/g
1% DVB

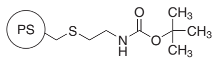


522309-1G	1 g
522309-5G	5 g

To order: Contact your local Sigma-Aldrich office (see back cover), or visit sigma-aldrich.com.

tert-Butyl *N*-(2-mercaptoethyl)carbamate, polymer-bound

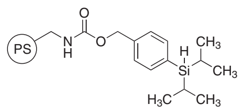
100–200 mesh
2.0 mmol/g S
1% DVB



579378-5G	5 g
579378-25G	25 g

Carbamic acid 4-diisopropylsilanyl-benzyl ester, polymer-bound

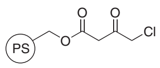
50–100 mesh
0.5–1.5 mmol/g Si
1% DVB



644307-5G	5 g
644307-25G	25 g

4-Chloroacetoacetate, polymer-bound

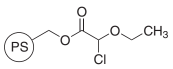
50–100 mesh
0.5–1.5 mmol/g Cl
1% DVB



641235-5G	5 g
641235-25G	25 g

2-Chloro-2-ethoxyacetate, polymer-bound

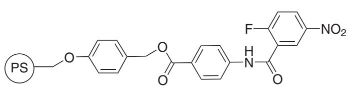
50–100 mesh
0.5–1.5 mmol/g
1% DVB



640433-5G	5 g
640433-25G	25 g

4-(2-Fluoro-5-nitro-benzoylamino)benzoate on Wang resin

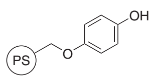
100–200 mesh
0.5–1.5 mmol/g F
1% DVB



659150-5G	5 g
659150-25G	25 g

4-Hydroxyphenol, polymer-bound

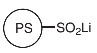
50–100 mesh
0.5–1.5 mmol/g OH
1% DVB



650382-5G	5 g
650382-25G	25 g

Lithium sulfinate, polymer-bound

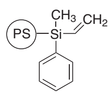
100–200 mesh
1.5–2.5 mmol/g Li
1% DVB



633402-5G	5 g
633402-25G	25 g

Methylphenylvinylsilane, polymer-bound

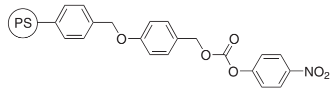
50–100 mesh
1.0–1.5 mmol/g Si
1% DVB



655473-5G	5 g
655473-25G	25 g
655473-100G	100 g

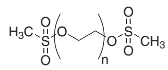
4-Nitrophenylcarbonate, polymer-bound

100–200 mesh
0.5–1.1 mmol/g
1% DVB



538485-1G	1 g
538485-10G	10 g
538485-50G	50 g

Poly(ethylene glycol) mesylate

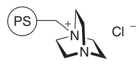


528188-1G	1 g
528188-5G	5 g

Reagents

1,4-Diazabicyclo(2.2.2)octane hydrochloride, polymer-bound

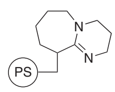
100–200 mesh
2.0 mmol/g N
1% DVB



578282-25G	25 g

1,8-Diazabicyclo[5.4.0]undec-7-ene, polymer-bound

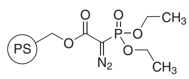
50–100 mesh
1.0–1.5 mmol/g N
1% DVB



595128-1G	1 g
595128-5G	5 g

α-Diazophosphonoacetate, polymer-bound

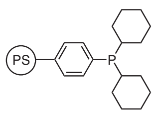
50–100 mesh
1.0 mmol/g
1% DVB



640409-5G	5 g
640409-25G	25 g

Dicyclohexylphenylphosphine, polymer-bound

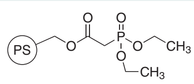
50–100 mesh
1.0–2.0 mmol/g P
1% DVB



632120-5G	5 g
632120-25G	25 g

Diethylphosphonoacetate, polymer-bound

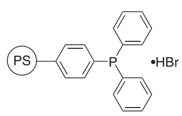
70–90 mesh
0.5–1.5 mmol/g P
1% DVB



596167-1G	1 g
596167-5G	5 g

Diphenylphosphane hydrobromide, polymer-bound

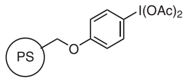
200–400 mesh
2.5–3.0 mmol/g Br
2% DVB



657034-5G	5 g
657034-25G	25 g

4-Hydroxyiodobenzene diacetate, polymer-bound

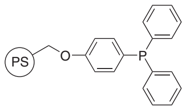
100–200 mesh
0.5–1.5 mmol/g I
1% DVB



634778-5G	5 g
634778-25G	25 g
634778-100G	100 g

(4-Hydroxphenyl)diphenylphosphine, polymer-bound

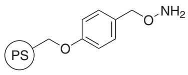
50–100 mesh
1.5–2.0 mmol/g P
1% DVB



596736-5G	5 g
596736-25G	25 g

Hydroxylamine, polymer-bound on Wang

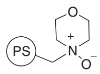
100–200 mesh
1.0–1.5 mmol/g
1% DVB



641014-5G	5 g
641014-25G	25 g

Morpholine *N*-oxide, polymer-bound

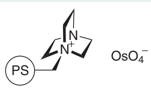
50–100 mesh
2.0–3.0 mmol/g
1% DVB



589683-5G	5 g
589683-25G	25 g

Osmium tetroxide, polymer-bound

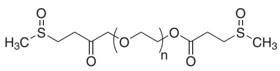
100–200 mesh
1.0–2.0 mmol/g N
1% DVB



589969-5G	5 g
589969-25G	25 g

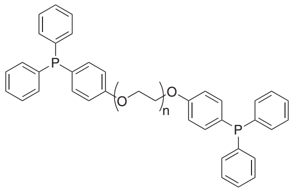
Poly(ethylene glycol) bis(3-methylsulfinyl)propionate

0.5–1.0 mmol/g S



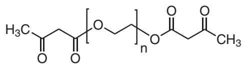
649589-5G	5 g

Poly(ethylene glycol) di-(4-hydroxyphenyl)diphenylphosphine



532649-1G	1 g
532649-5G	5 g

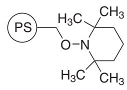
Poly(ethylene glycol) diacetoacetate



632562-5G	5 g
632562-25G	25 g

TEMPO, polymer-bound

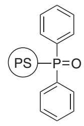
100–200 mesh
1.0 mmol/g
1% DVB



566098-1G	1 g
566098-5G	5 g

Triphenylphosphine oxide, polymer-bound

200–400 mesh
2.5–3.0 mmol/g P
2% DVB

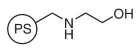


655430-5G	5 g
655430-25G	25 g

Scavengers

Ethanolamine, polymer-bound

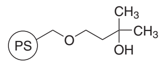
100–200 mesh
1.0–2.0 mmol/g
1% DVB



634387-5G	5 g
634387-25G	25 g

1-Hydroxy-1,1-dimethylpropyloxymethyl, polymer-bound

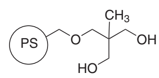
50–100 mesh
2.0–3.0 mmol/g OH
1% DVB



648353-5G	5 g
648353-25G	25 g

2-Hydroxymethyl-1,3-propanediol, polymer-bound

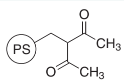
50–100 mesh
2.5–3.5 mmol/g
1% DVB



634328-1G	1 g
634328-5G	5 g

2,4-Pentanedione, polymer-bound

100–200 mesh
2.5–3.5 mmol/g O
2% DVB



648639-5G	5 g
648639-25G	25 g

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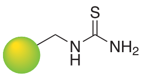
Functionalized Resins Solving Your Problems with Metal Contamination

The QuadraPure™ functionalized macroporous and microporous resins are designed to solve problems associated with the metal contamination that occurs during pharmaceutical or fine chemical processing from laboratory scale through to manufacturing. The very low levels of extractable impurities make QuadraPure™ products particularly suitable for use in GMP-compliant applications. QuadraPure™ Metal Scavengers are available in 5-g, 25-g, and 100-g units, as well as larger quantities.

Macroporous Resins

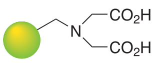


QuadraPure™ TU
655422
400–600 µm

Typical Experimental Capacity	Effective in Acid/Base
0.19 mmol/g (based on $Pd(OAc)_2$ in CH_2Cl_2)	Y/Y

Metals Removed
Pd, Pt, Ru, Au, Ag, Cu, Ni, Zn, Hg, Pb, and Cd

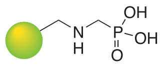
[a] pH < 2 gives poor scavenging.



QuadraPure™ IDA
657026
350–750 µm

Typical Experimental Capacity	Effective in Acid/Base
0.16 mmol/g (based on $Cu(acac)_2$ in CH_2Cl_2)	Y[a]/Y

Metals Removed
Fe, Al, Ga, In, Cu, V, Pb, Ni, Zn, Cd, Be, Mn, Ca, Mg, Sr, and Ba

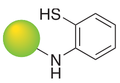


QuadraPure™ AMPA
657611
350–750 µm

Typical Experimental Capacity	Effective in Acid/Base
0.17 mmol/g (based on $Ni(acac)_2$ in CH_2Cl_2)	Y[a]/Y

Metals Removed
Fe, Cu, Ni, Pb, V, Al, Sn, Zn, Cd, Co, Pd, Ca, Mg, Sr, and Ba

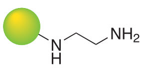
Microporous Resins



QuadraPure™ MPA
657662
100–400 µm

Typical Experimental Capacity	Effective in Acid/Base
0.15 mmol/g	Y/Y

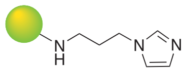
Metals Removed
Pd, Ru, Rh, Hg, Au, Ag, Cu, Pb, Ir, Pt, Cd, Co, and Sn



QuadraPure™ AEA
657646
100–400 µm

Typical Experimental Capacity	Effective in Acid/Base
0.13 mmol/g	N/Y

Metals Removed
Pd, Sn, Ru, Pt, Ni, Cu, Zn, and Co



QuadraPure™ IMDAZ
657654
100–400 µm

Typical Experimental Capacity	Effective in Acid/Base
0.15 mmol/g	N/Y

Metals Removed
Ni, Pd, Os, Rh, Co, V, Fe, Cu, and Sn

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