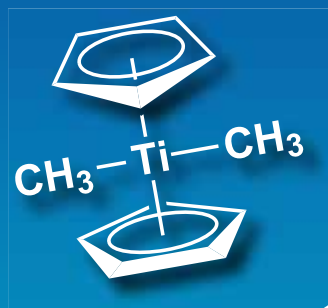
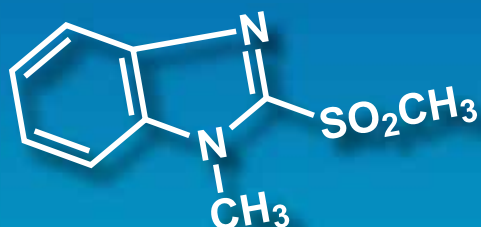
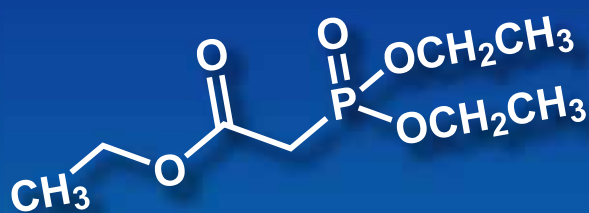
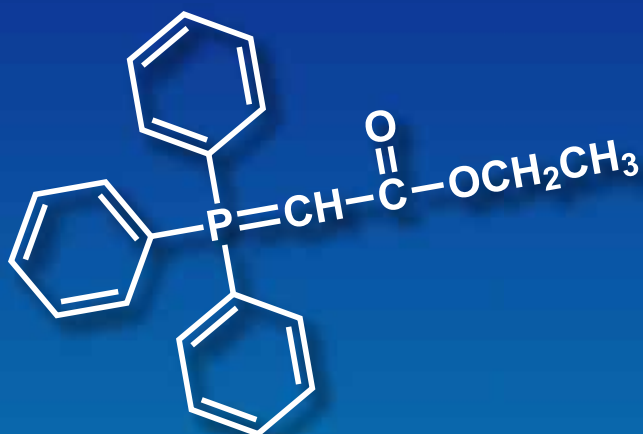


烯炔化反应

Olefination



Wittig试剂

Horner-Wadsworth-Emmons试剂

Z选择的Horner-Wadsworth-Emmons试剂

Peterson 反应试剂

Julia-Kocienski烯炔化试剂

钛试剂

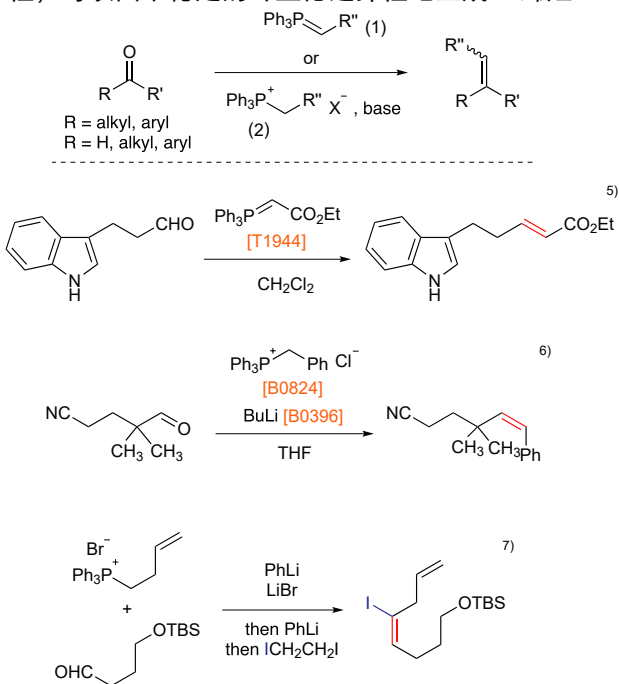
烯炔化反应

羰基烯炔化自发现以来已成为有机合成中最基础的转化之一，目前已经开发出一系列丰富多样的合成方法。特别是，该合成方法使用第三主族元素，其中磷，硅和硫原子最受关注，也最为成功。许多这种转化都是经典的人名反应。简单举例：Peterson 烯炔化（硅），Julia和Julia型 (-Kocienski, -Lythgoe)（硫），以及Horner-Wadsworth-Emmons（HWE）（磷）。其中最著名的羰基烯炔化反应Witting反应，是这种合成方法中最具有代表性的。经过几年的发展，一些改进的方法和类似的HWE反应由于其实用性被发展出来。一些新的方法具有更简单的操作方法以及增加的*E/Z*选择性¹⁾。此外，有机钛化合物可以转变为酯和酰胺（再烯炔化反应中不具有反应活性）可以让烯炔反应更加丰富和具有多样性²⁾。

这本手册介绍大量用于根据反应类型排列的烯炔化反应的反应砌块。

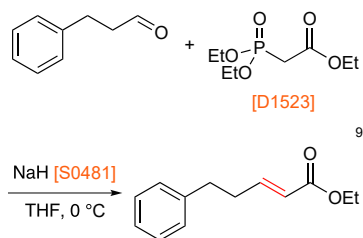
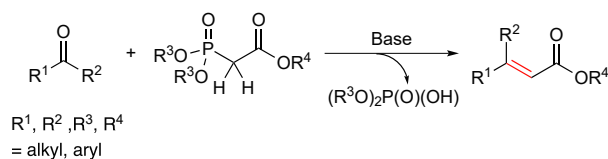
● Wittig试剂

Wittig反应是有机反应中通过母体醛或酮构建烯炔基团的经典方法³⁾。该反应由磷叶立德（1）引发，磷叶立德可以是稳定的物质或者由盐（2）和碱原位生成。Wittig反应经常生成*Z*-烯炔作为单一产品，但是不同的反应条件可以生成*E*-烯炔产物^{4,7)}。例如，通过高温下添加苯基锂进行Schlosser改性，可以由不稳定的叶立德选择性地生成*E*-烯炔。



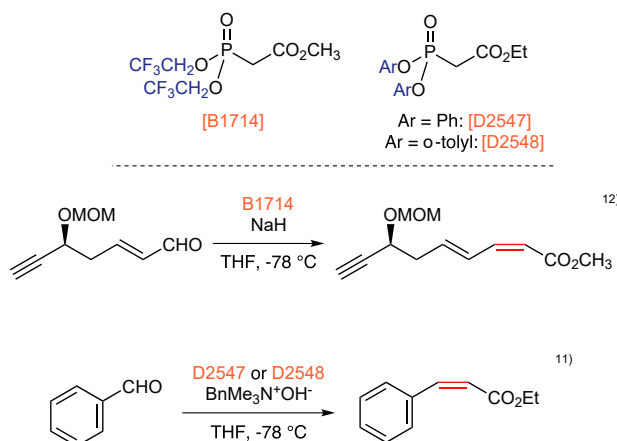
● Horner-Wadsworth-Emmons反应

Horner-Wadsworth-Emmons (HWE) 反应经常应用于以醛和酮为原料合成取代（二和三取代）烯炔产物⁸⁾。*E*-烯炔通常优于*Z*-烯炔。磷酸酯可以特征性的与强碱反应。这些可以生成活性的和稳定性的磷阴离子，可以与醛和酮直接反应。这些磷酸盐副产物可以通过萃取分离简单去除。



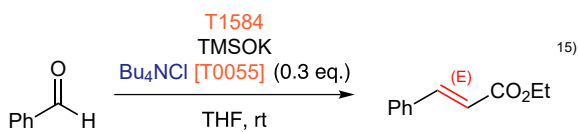
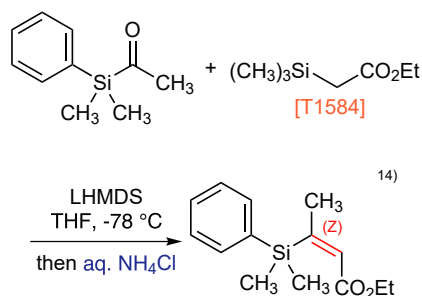
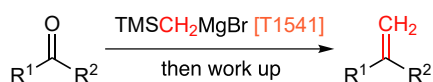
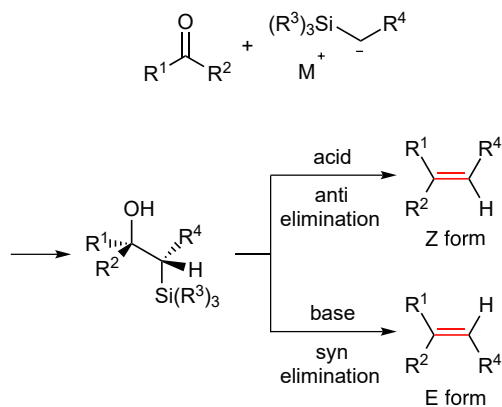
● Z-Horner-Wadsworth-Emmons反应

HWE反应可以优先的得到*E*-烯炔，结果是经过修饰后可以得到*Z*-烯炔。Gennari和Still报道了首例*Z*选择的HWE反应使用双(2,2,2-三氟乙基)(甲氧羰基甲基)磷酸酯[B1714]¹⁰⁾。后来，Ando开发了二芳基磷酸酯如D2547和D2548，可以高选择性的获得*Z*- α,β -不饱和酯¹¹⁾。这种方法使用季铵盐氢氧化物或DBU作为碱，不需要使用特殊的实验设备/技术。



Peterson反应

Peterson反应是通过在醛和酮中加入 α -硅烷基碳负离子和用酸或碱作后续处理生成烯一种合成方法¹³⁾。该反应具有的优点是可以通过加入酸或碱来调整已知烯烃的立体化学。当将酸添加到加合物中时硅烷醇通过反消除而得到 Z -烯烃。但是，当加入碱时则进行顺位消除得到 E -烯烃。

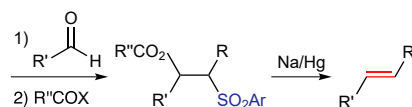
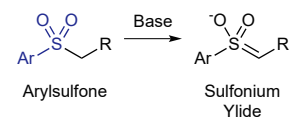


Julia-Lythgoe反应

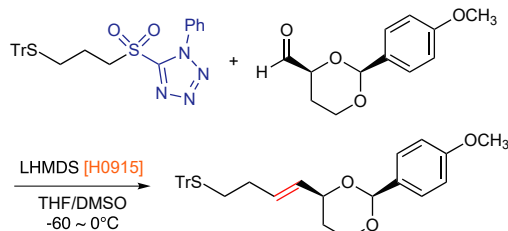
Julia-Lythgoe反应及其多种子形式是使用芳基砜将醛转化为烯烃的非常有用合成方法¹⁶⁾。该反应以逐步方式发生合成 E -烯烃；(1)将磺酰胺加至醛中；(2)所得羟基的酰化；(3)用Na(Hg)还原。后来，S. A. Julia 和 Kocienski的小组优化了这一转变，使用杂芳族砜部分在一锅中进行^{17,18)}，即所谓的Modified Julia's。该方法对于连接两个复杂片段时特别有用。

此外，Ando等报道了使用M2860在Julia-Kocienski型亚甲基化的应用¹⁹⁾。

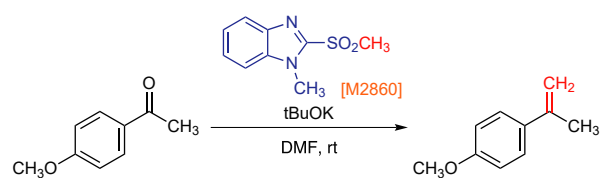
Standard Julia-Lythgoe Reaction ¹⁶⁾



Julia-Kocienski Reaction ²⁰⁾

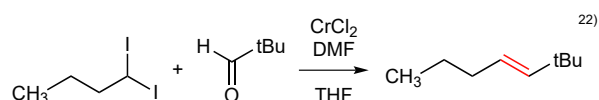
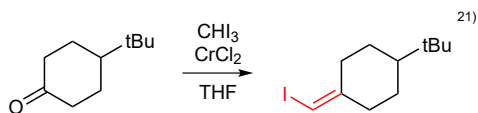
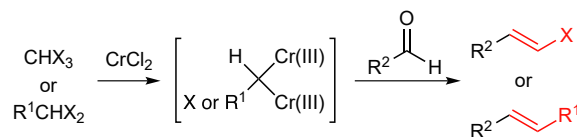


Julia-Kocienski Type Methylenylation ¹⁹⁾



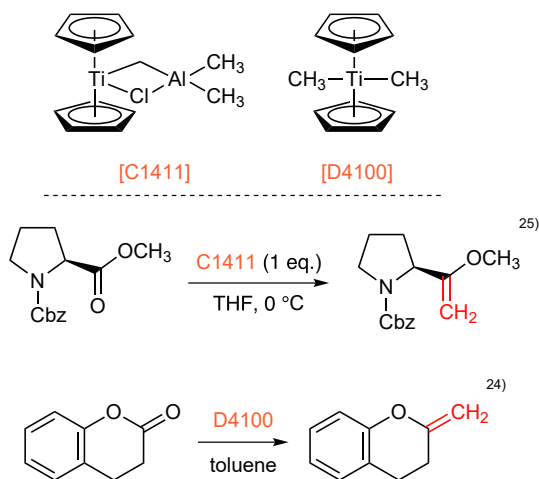
Takai-Utimoto反应

Takai和Utimoto曾报道过一种由卤仿和氯化铬(II)反应制备的偕位-二铬试剂与醛类反应生成卤代烯烃²¹⁾。本方法适用于1,1-二卤化物²²⁾，可用于延长烷基链和构建含有其它官能团结构的烯烃。卤代烯烃和官能化烯烃是特别有用的底物，例如可用于交叉偶联反应中。



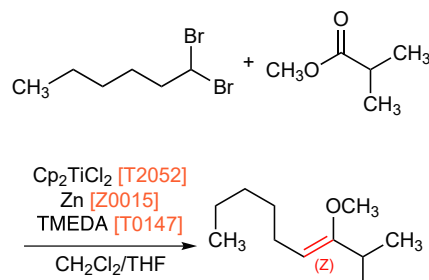
● 使用钛试剂的烯烃化反应

Tebbe²³⁾和Petasis²⁴⁾试剂是典型的应用于羰基烯烃化的有机钛试剂，以及许多羰基化合物的亚甲基化反应。与其他的亚甲基化反应只能与醛和酮反应不同的是，有机钛试剂可以与非活性的羰基如酯和酰胺基团反应。

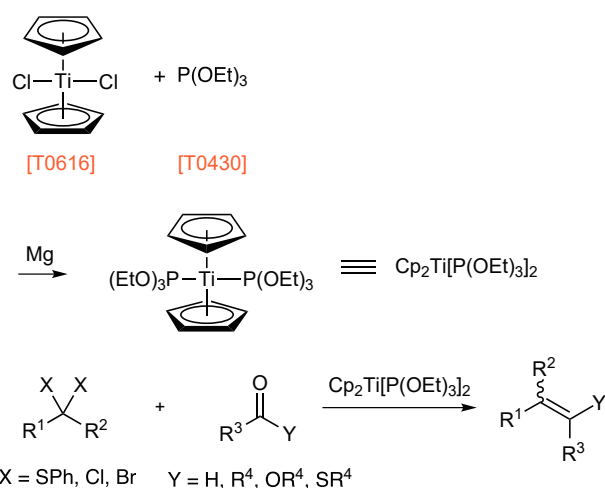


除了上述的钛化合物，Takai和Utimoto报道了烯烃RCHX₂-TiCl₄-Zn体系可以应用于羰基²⁶⁾。在这个反应中，可以选择性得到Z-烯烃。Takeda课题组同样报道了羰基化合物的普通烯烃化反应通过与硫缩醛和偕二卤代和二茂钛(II)化合物Cp₂Ti[P(OEt)₃]₂²⁷⁾。

Takai-Utimoto's Olefination System ²⁶⁾

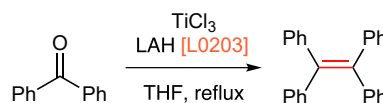


Takeda's Olefination System ²⁷⁾

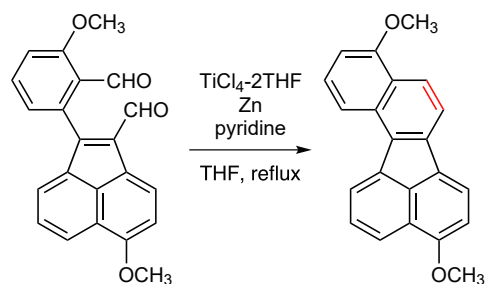


McMurry偶联是另一种著名的使用钛试剂的烯化方法²⁸⁾。该反应可用于杂耦合和分子内烯化以及同构耦合和构建大中型结构²⁹⁾。使用有机钛化合物进行烯化反应具有独特的特征和反应活性，并已使用多年。

Original McMurry Coupling ^{g28)}



McMurry Type Ring Closure ²⁹⁾



参考文献

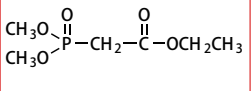
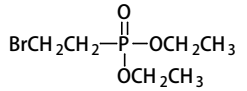
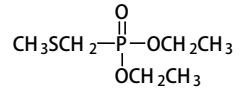
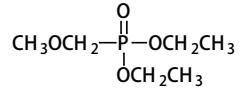
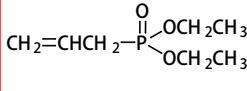
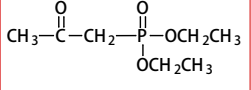
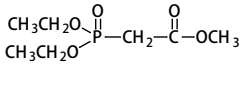
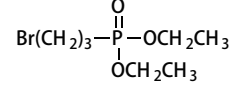
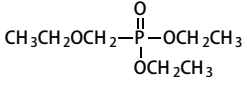
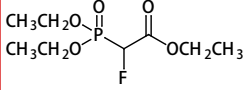
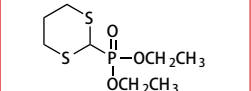
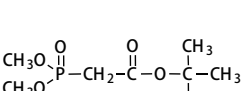
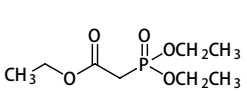
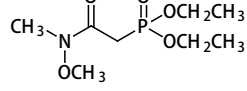
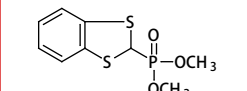
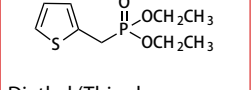
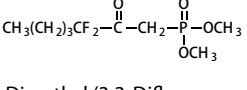
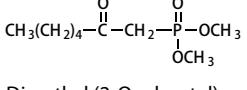
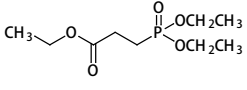
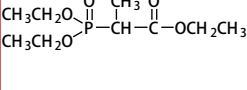
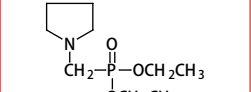
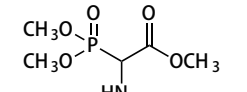
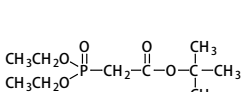
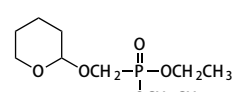
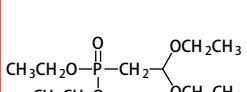
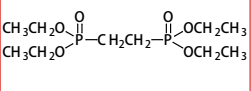
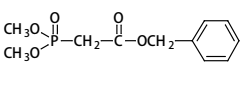
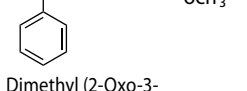
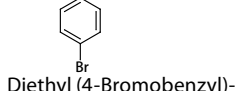
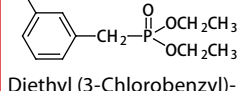
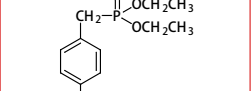
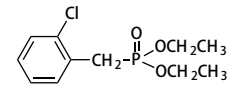
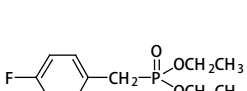
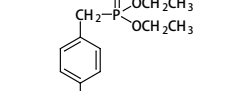
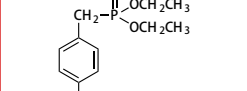
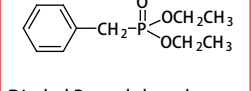
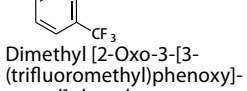
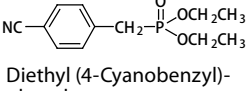
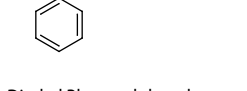
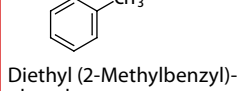
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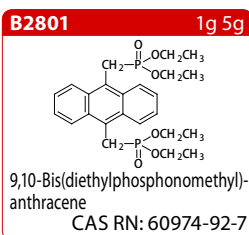
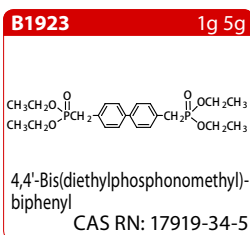
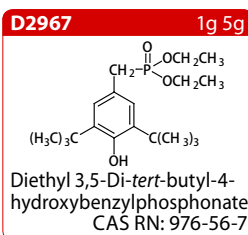
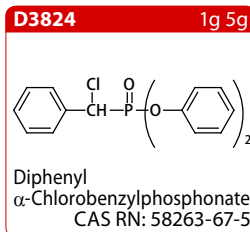
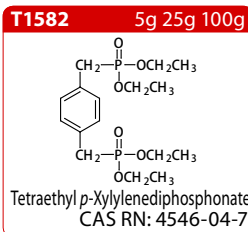
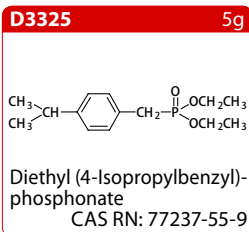
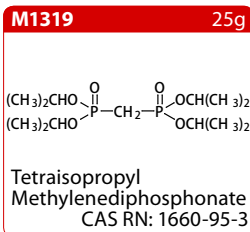
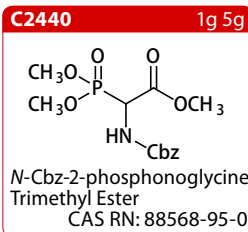
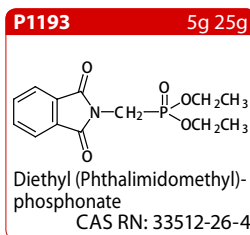
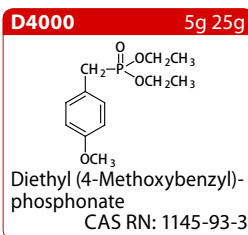
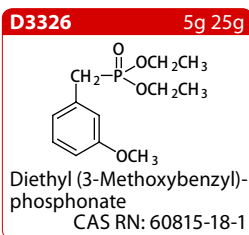
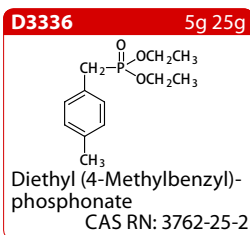
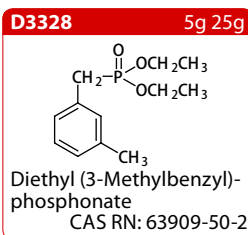
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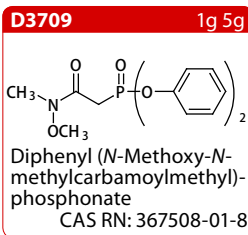
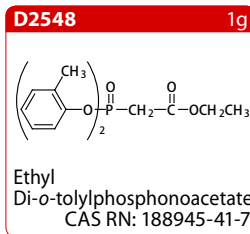
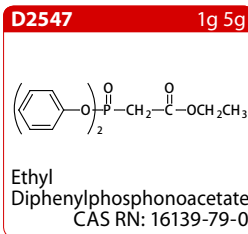
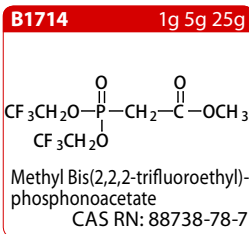
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<p>C1009 5g 25g</p> <p>(Chloromethyl)-triphenylphosphonium Chloride CAS RN: 5293-84-5</p>	<p>M0779 25g 100g 500g</p> <p>Methyltriphenylphosphonium Bromide CAS RN: 1779-49-3</p>	<p>M2702 5g 25g</p> <p>Methyltriphenylphosphonium Chloride CAS RN: 1031-15-8</p>	<p>M0253 25g 100g 500g</p> <p>Methyltriphenylphosphonium Iodide CAS RN: 2065-66-9</p>	<p>T2565 1g 5g</p> <p>Bestmann Ylide CAS RN: 15596-07-3</p>
<p>T1958 5g 25g</p> <p>(Triphenylphosphoranylidene)-acetonitrile CAS RN: 16640-68-9</p>	<p>C1739 25g 100g</p> <p>(Cyanomethyl)-triphenylphosphonium Chloride CAS RN: 4336-70-3</p>	<p>T2001 5g 25g</p> <p>(Triphenylphosphoranylidene)-acetaldehyde CAS RN: 2136-75-6</p>	<p>F0331 5g 25g</p> <p>(Formylmethyl)-triphenylphosphonium Chloride CAS RN: 62942-43-2</p>	<p>E0382 25g 100g 500g</p> <p>Ethyltriphenylphosphonium Bromide CAS RN: 1530-32-1</p>
<p>M0828 25g 100g 500g</p> <p>(Methoxymethyl)-triphenylphosphonium Chloride CAS RN: 4009-98-7</p>	<p>E1336 25g 100g</p> <p>Ethyltriphenylphosphonium Chloride CAS RN: 896-33-3</p>	<p>E0549 25g 250g</p> <p>Ethyltriphenylphosphonium Iodide CAS RN: 4736-60-1</p>	<p>P1438 5g 25g</p> <p>Triphenylpropargylphosphonium Bromide CAS RN: 2091-46-5</p>	<p>T1363 25g 100g</p> <p>Methyl (Triphenylphosphoranylidene)acetate CAS RN: 2605-67-6</p>
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<p>T1944 25g 250g</p> <p>Ethyl (Triphenylphosphoranylidene)acetate CAS RN: 1099-45-2</p>	<p>D2164 5g 25g</p> <p>(1,3-Dioxolan-2-yl)methyltriphenylphosphonium Bromide CAS RN: 52509-14-5</p>	<p>C1635 25g</p> <p>(3-Carboxypropyl)-triphenylphosphonium Bromide CAS RN: 17857-14-6</p>	<p>E0407 25g 250g</p> <p>Carbomethoxymethyl(triphenyl)-phosphonium Bromide CAS RN: 1530-45-6</p>	<p>B0970 25g 250g</p> <p>Butyltriphenylphosphonium Bromide CAS RN: 1779-51-7</p>
<p>B5730 25g</p> <p>Butyltriphenylphosphonium Chloride CAS RN: 13371-17-0</p>	<p>D1654 5g 25g</p> <p>2-Dimethylaminoethyltriphenylphosphonium Bromide CAS RN: 21331-80-6</p>	<p>T3159 1g</p> <p>Triphenyl(2-thienylmethyl)-phosphonium Bromide CAS RN: 23259-98-5</p>	<p>C1641 5g</p> <p>Ethyl 2-(Triphenylphosphoranylidene)propionate CAS RN: 5717-37-3</p>	<p>C1061 25g 250g</p> <p>4-(Carboxybutyl)-triphenylphosphonium Bromide CAS RN: 17814-85-6</p>

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D1655 5g 25g 2-(1,3-Dioxan-2-yl)-ethyltriphenylphosphonium Bromide CAS RN: 69891-92-5	T1498 1g 5g (3-Trimethylsilyl-2-propynyl)-triphenylphosphonium Bromide CAS RN: 42134-49-6	H0540 25g 100g 500g Hexyltriphenylphosphonium Bromide CAS RN: 4762-26-9	T1458 5g 25g SEM-triphenylphosphonium Chloride CAS RN: 82495-75-8	D2907 5g 25g (2,4-Dichlorobenzyl)-triphenylphosphonium Chloride CAS RN: 2492-23-1
B5241 5g 25g (4-Bromobenzyl)-triphenylphosphonium Bromide CAS RN: 51044-13-4	N0701 25g (4-Nitrobenzyl)-triphenylphosphonium Bromide CAS RN: 2767-70-6	C1581 5g 25g (4-Chlorobenzyl)-triphenylphosphonium Chloride CAS RN: 1530-39-8	C1759 25g (2-Chlorobenzyl)-triphenylphosphonium Chloride CAS RN: 18583-55-6	B4486 1g 5g [(1H-Benzotriazol-1-yl)methyl]-triphenylphosphonium Chloride CAS RN: 111198-09-5
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P1182 25g Phenacetyltriphenylphosphonium Bromide CAS RN: 6048-29-9	M2463 1g 5g (3-Methoxybenzyl)-triphenylphosphonium Chloride CAS RN: 18880-05-2	C1286 25g Cinnamyltriphenylphosphonium Bromide CAS RN: 7310-74-9	D4072 5g (3,4-Dimethoxybenzyl)-triphenylphosphonium Bromide CAS RN: 70219-09-9	E0421 5g 4-Ethoxybenzyltriphenylphosphonium Bromide CAS RN: 82105-88-2
N0700 5g 25g (1-Naphthylmethyl)-triphenylphosphonium Chloride CAS RN: 23277-00-1	T1506 25g Triphenyl(tetradecyl)-phosphonium Bromide CAS RN: 25791-20-2	B2286 5g trans-2-Butene-1,4-bis(triphenylphosphonium Chloride) CAS RN: 106423-29-4		
Horner-Wadsworth-Emmons Reagents 试剂 Horner-Wadsworth-Emmons Reagents		H0779 5g 25g Dimethyl (2-Hydroxyethyl)-phosphonate CAS RN: 54731-72-5	D3981 1g 5g Dimethyl 2-(1,3-Dithiole)-phosphonate CAS RN: 133113-76-5	D4607 5g 25g Diethyl (Trichloromethyl)-phosphonate CAS RN: 866-23-9
O0208 5g 25g Dimethyl (2-Oxopropyl)-phosphonate CAS RN: 4202-14-6	P1265 25g 250g Trimethyl Phosphonoacetate CAS RN: 5927-18-4	D4588 1g 5g Diethyl (3-Bromopropyl)-phosphonate CAS RN: 1186-10-3	D3813 25g 100g Diethyl (Hydroxymethyl)-phosphonate CAS RN: 3084-40-0	C1430 5g 25g Diethyl Cyanomethylphosphonate CAS RN: 2537-48-6

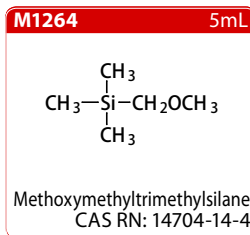
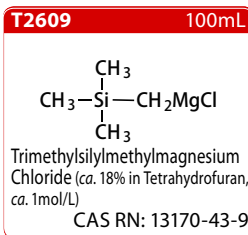
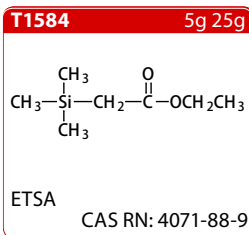
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<p>D5644 1g 5g</p>  <p>Diethyl (Thiophen-2-ylmethyl)phosphonate CAS RN: 2026-42-8</p>	<p>D5176 200mg 1g</p>  <p>Dimethyl (3,3-Difluoro-2-oxoheptyl)phosphonate CAS RN: 50889-46-8</p>	<p>D4244 1g 5g</p>  <p>Dimethyl (2-Oxoheptyl)-phosphonate CAS RN: 36969-89-8</p>	<p>D1524 25g 250g</p>  <p>Triethyl 3-Phosphonopropionate CAS RN: 3699-67-0</p>	<p>T2135 5g 25g</p>  <p>Triethyl 2-Phosphonopropionate CAS RN: 3699-66-9</p>
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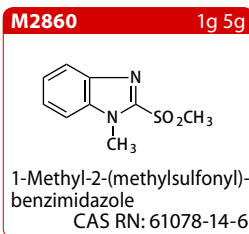
Z-Selective Horner-Wadsworth-Emmons 试剂
Z-Selective Horner-Wadsworth-Emmons Reagents



Peterson反应试剂
Peterson Reaction Reagents



Julia-Kocienski 烯炔化试剂
Julia-Kocienski Olefination Reagents



Titanium 试剂

Titanium Reagents

T0616 5g 25g



Titanocene Dichloride
CAS RN: 1271-19-8

T2052 100mL 500mL



Titanium(IV) Chloride (14% in
Dichloromethane, ca. 1.0mol/L)
CAS RN: 7550-45-0



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