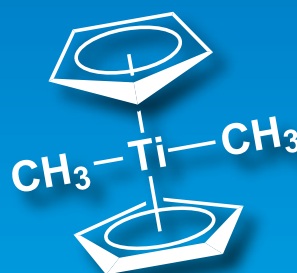
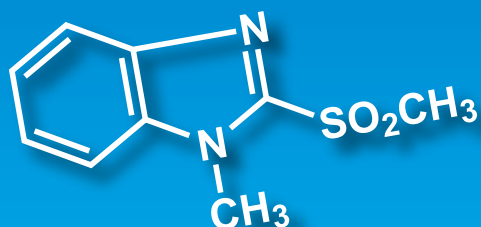
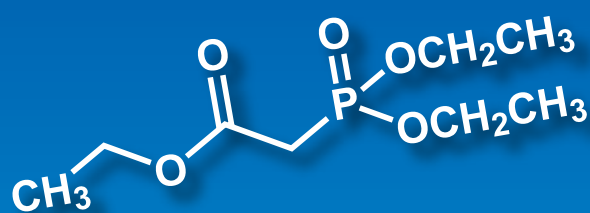
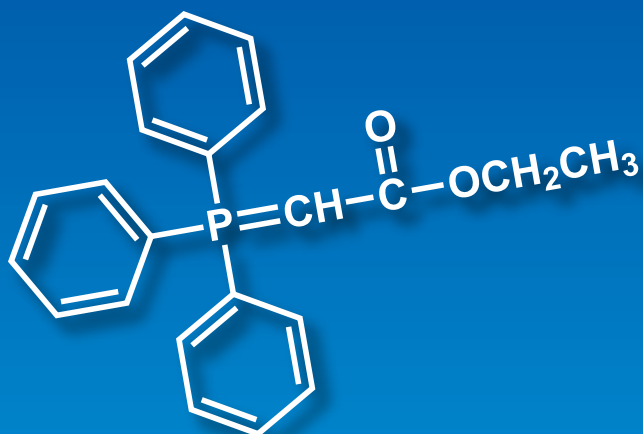


Olefination



Wittig Reagents

Horner-Wadsworth-Emmons Reagents

Z-Selective Horner-Wadsworth-Emmons Reagents

Peterson Reaction Reagents

Julia-Kocienski Olefination Reagents

Titanium Reagents

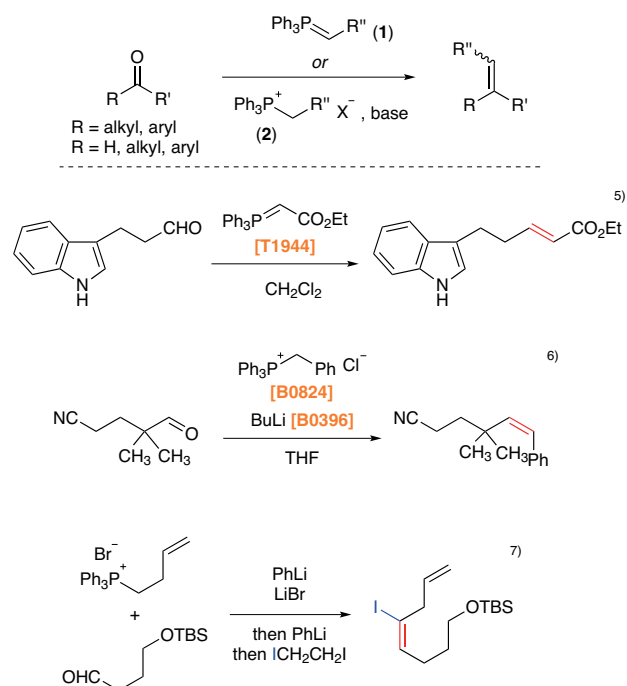
Olefination

Carbonyl olefination is one of the most fundamental conversions in organic synthesis and since the initial discovery, a wide variety of synthetic methods have been developed. In particular, synthetic methods that utilize 3rd row elements like phosphorus, silicon and sulfur atoms had received the most attention and success. Many of these transformations are classic named reactions; Peterson olefination (silicon), Julia and Julia-type (-Kocienski, -Lythgoe) (sulfur), and Horner-Wadsworth-Emmons (HWE) (phosphorus) to name a few. The most well-known carbonyl olefination reaction, The Wittig reaction, is also the most representative of the general synthetic method. A number of improved methods for it and the similar HWE reaction have been developed over the years due to their usefulness. Some of the new methods have easier work-up procedures and increased *E/Z* selectivity.¹⁾ Furthermore, it is known that organotitanium compounds can convert esters and amides (which are typically unreactive under olefination conditions) which brought wider diversity and utility to olefinations.²⁾

This brochure introduces a variety of building blocks for olefinations, sorted by their reactions.

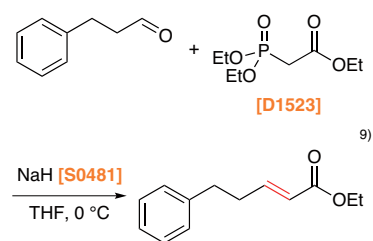
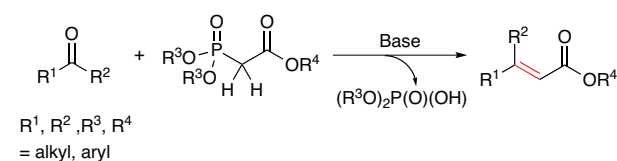
● Wittig reaction

The Wittig reaction is the classical way to install an olefin group from a parent aldehyde or ketone and is frequently utilized in organic synthesis.³⁾ This reaction is incurred using a phosphonium ylide (1), which can exist as a stable compound, or can be generated from the salt form (2) *in situ* by treatment with base. Wittig reactions often provide the *Z*-olefin as the exclusive product, but varied conditions can provide the *E*-olefin product. For instance, Schlosser modification via adding phenyllithium at elevated temperatures can provide *E*-olefins selectively from unstabilized ylides.^{4,7)}



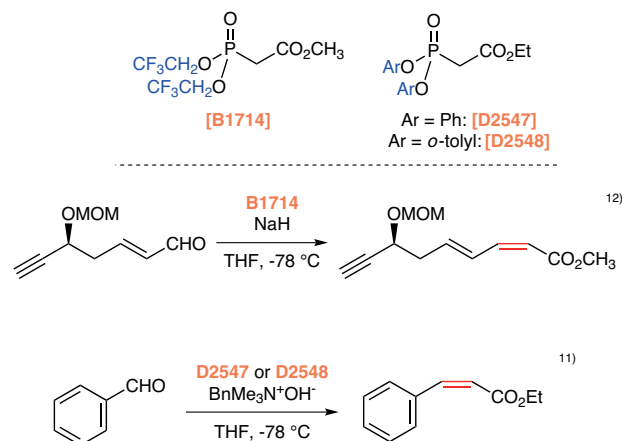
● Horner-Wadsworth-Emmons reaction

The Horner-Wadsworth-Emmons (HWE) reaction is a frequently used synthetic method to obtain substituted (di- and tri-) olefin products from aldehydes and ketones.⁸⁾ *E*-olefins are generally preferred over *Z*-olefins. Phosphonate esters are typically used with strong bases. These produce reactive and stabilized phosphonium anions, which readily react with aldehydes and ketones. The given phosphonate byproducts are easily removed by extraction.



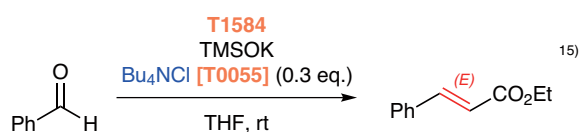
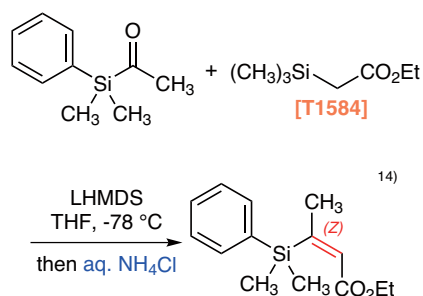
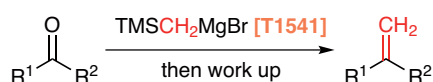
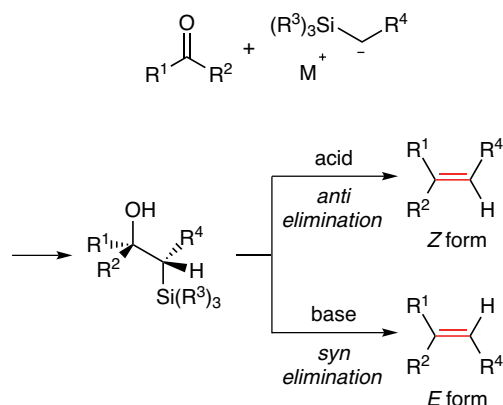
● Z-Selective Horner-Wadsworth-Emmons reaction

The HWE reaction preferably gives *E*-olefins. As a result modifications have been developed to obtain *Z*-olefins. Gennari and Still have reported the first *Z*-selective HWE reaction using bis(2,2,2-trifluoroethyl) (methoxycarbonylmethyl)phosphonate [B1714].¹⁰⁾ Later, Ando developed diaryl phosphonoacetates such as D2547 and D2548 which are able to provide *Z*- α,β -unsaturated esters in high stereoselectivity.¹¹⁾ This method uses quaternary ammonium hydroxides or DBU as the base, and it does not require any special experimental-equipment/-technique to conduct.



Peterson reaction

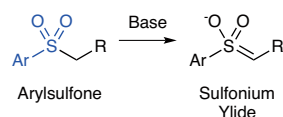
The Peterson reaction is a synthetic method that affords olefins by the addition of a α -silyl carbanion to aldehydes and ketones and successive treatment with acid or base.¹³ This reaction has the advantage that a given olefin's stereochemistry can be adjusted by adding acid or base. When an acid is added to the adduct, the *Z*-olefin is given via *anti*-elimination of a silanol. However, when base is added, *syn*-elimination proceeds to provide *E*-olefins.



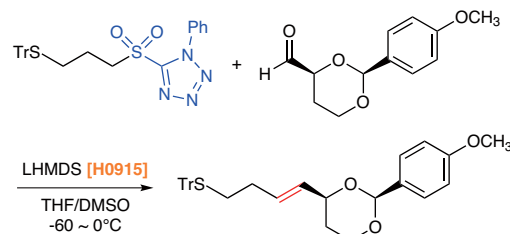
Julia-Lythgoe reaction

The Julia-Lythgoe reaction and its various sub-forms are useful synthetic methods to convert aldehydes to olefins using arylsulfones.¹⁶ This reaction occurs in a stepwise manner to provide *E*-olefins; (1) addition of a sulfonamide to an aldehyde; (2) acylation of resulting hydroxyl group; (3) reduction with Na(Hg). Later, S. A. Julia and Kocienski's group refined the transformation to be conducted in one pot by using heteroaromatic sulfone moieties,^{17,18} which are known as Modified Julia's. This method can be particularly useful in joining two complex fragments. Furthermore, Ando have reported the utility of M2860 in Julia-Kocienski type methylenations.¹⁹

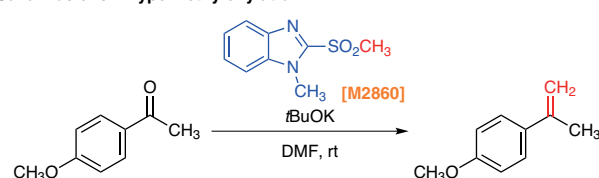
Standard Julia-Lythgoe Reaction¹⁶



Julia-Kocienski Reaction²⁰

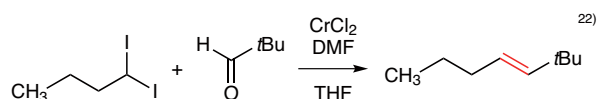
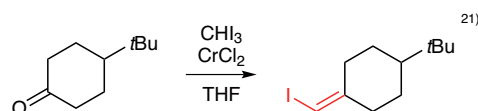
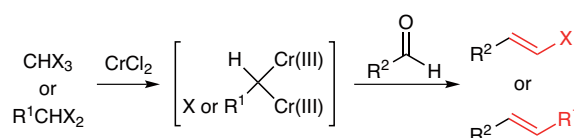


Julia-Kocienski Type Methylenation¹⁹



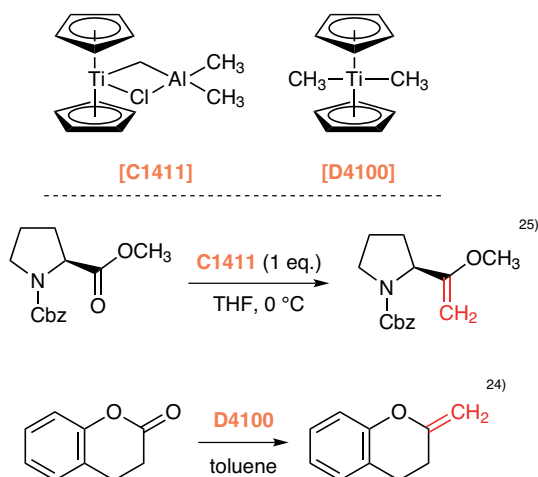
Takai-Utimoto reaction

Takai and Utimoto have reported that a *gem*-dichromium reagent prepared from a haloform and chromium(II) chloride reacts with aldehydes to provide haloolefins.²¹ This method is applicable to 1,1-dihalides²² and utilized in elongation of alkyl chains and the construction of olefins with other functional groups. The haloolefins and functionalized olefins are particularly useful substrates, such as in cross-coupling reactions.



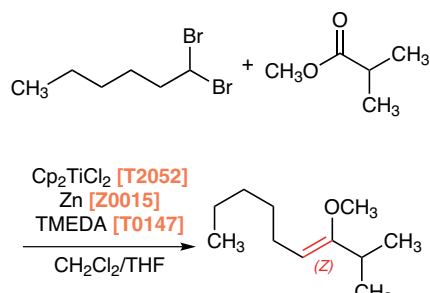
● Olefination reactions using titanium reagents

Tebbe²³⁾ and Petasis²⁴⁾ reagents are representative organotitanium reagents used in carbonyl olefination which have been used for methylenation of various carbonyl compounds. Unlike other methylenation reagents which react with only aldehydes and ketones, organotitanium reagents can react with relatively inactive carbonyl groups such as esters and amides.

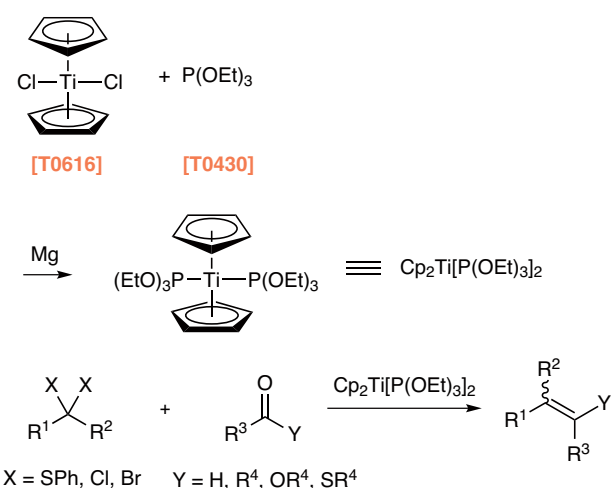


Besides the titanium compounds stated above, olefination utilizing the $RCHX_2$ - $TiCl_4$ -Zn system reported by Takai and Utimoto can also be used on carbonyl groups.²⁶⁾ In this reaction, Z-olefins are given preferentially. Takeda's group have also reported more general olefinations of carbonyl compounds by the treatment of thioacetals or *gem*-dihalides and a titanocene(II) compound $Cp_2Ti[P(OEt)_3]_2$.²⁷⁾

Takai-Utimoto's Olefination System²⁶⁾



Takeda's Olefination System²⁷⁾

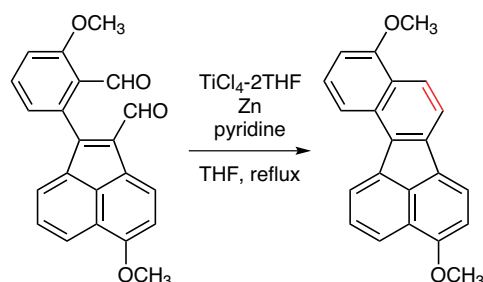


The McMurry coupling is another well-known olefination method using titanium reagents.²⁸⁾ This reaction can be applied to heterocoupling and an intramolecular olefination as well as homocoupling and the construction of medium and large sized rings utilizing.²⁹⁾ Olefinations using organotitanium compounds have unique features and reactivity, and have been used for many years.

Original McMurry Coupling²⁸⁾



McMurry Type Ring Closure²⁹⁾

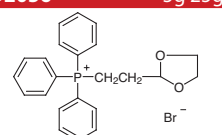
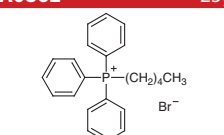
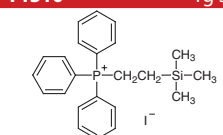
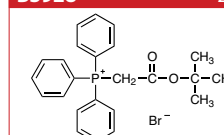
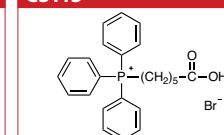
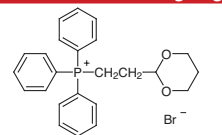
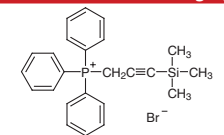
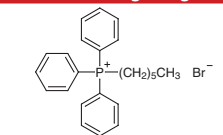
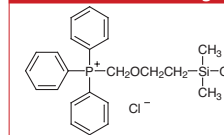
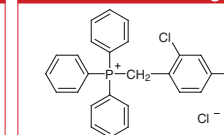
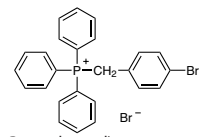
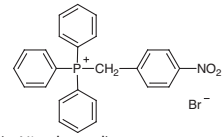
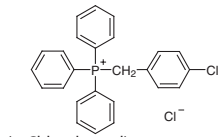
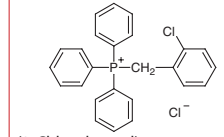
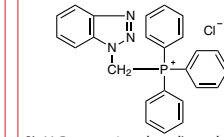
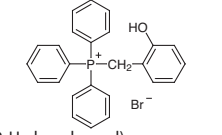
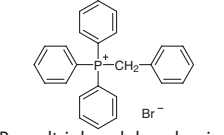
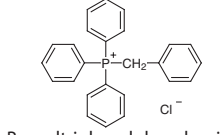
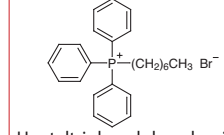
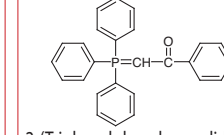
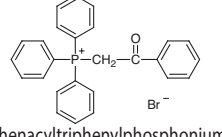
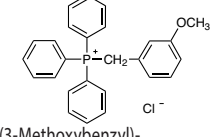
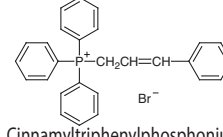
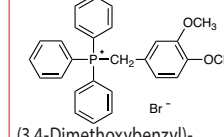
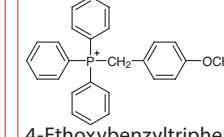
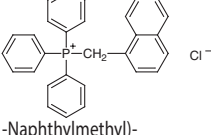
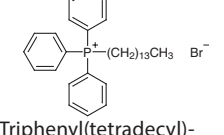
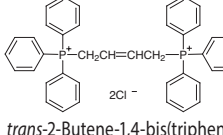


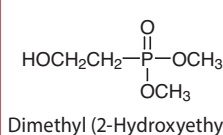
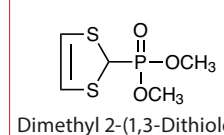
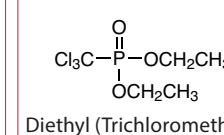
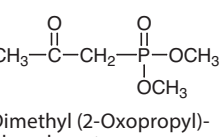
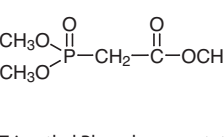
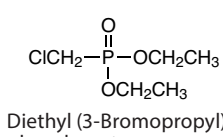


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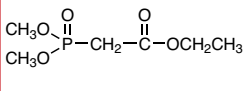
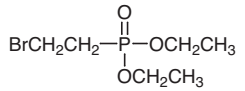
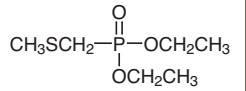
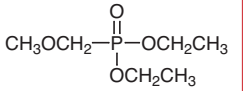
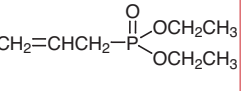
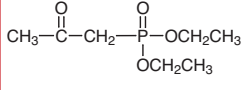
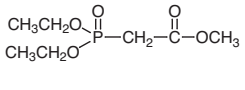
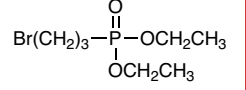
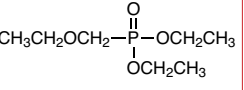
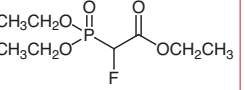
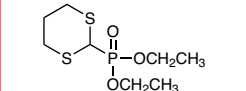
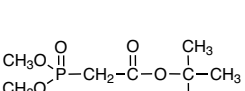
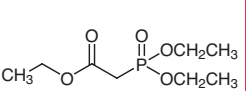
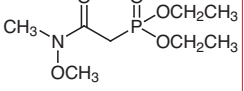
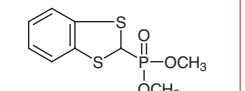
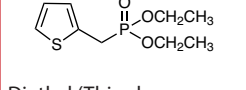
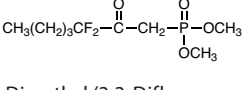
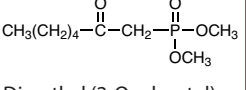
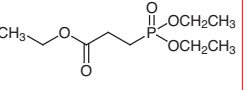
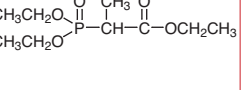
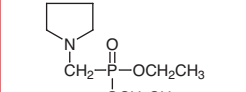
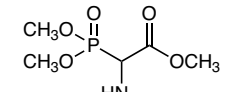
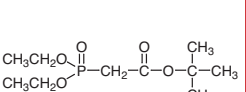
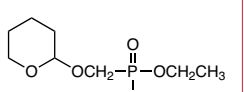
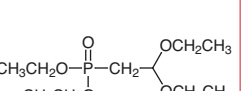
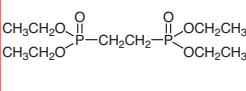
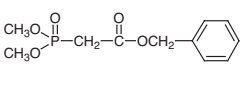
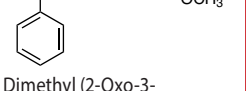
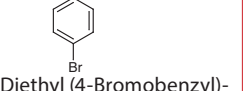
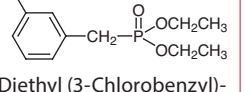
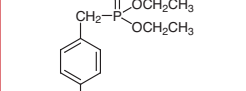
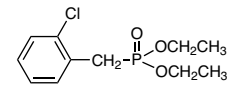
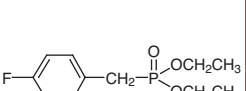
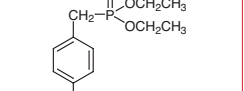
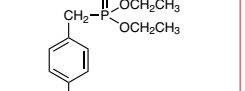
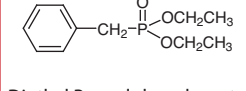
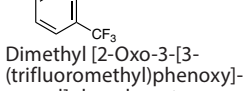
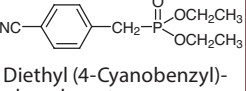
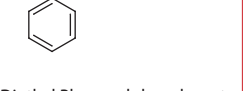
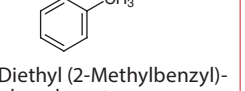
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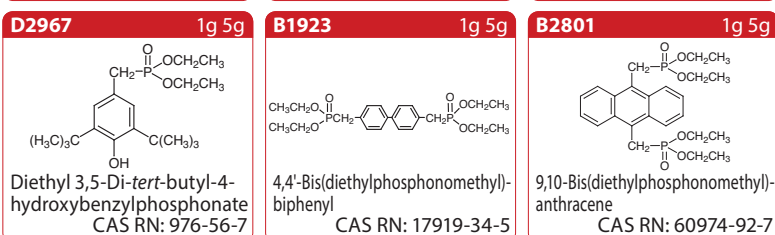
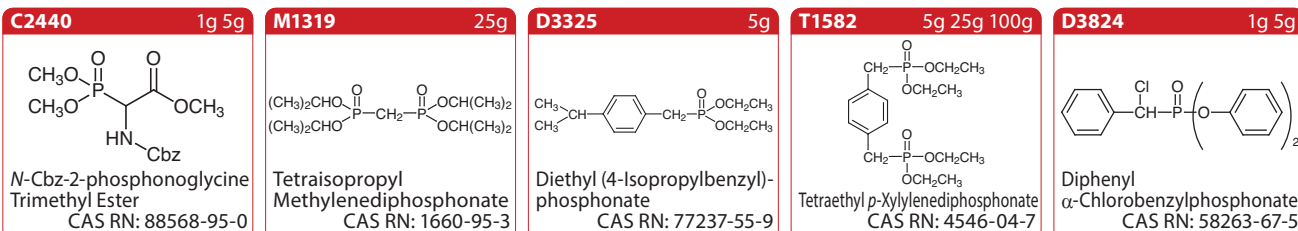
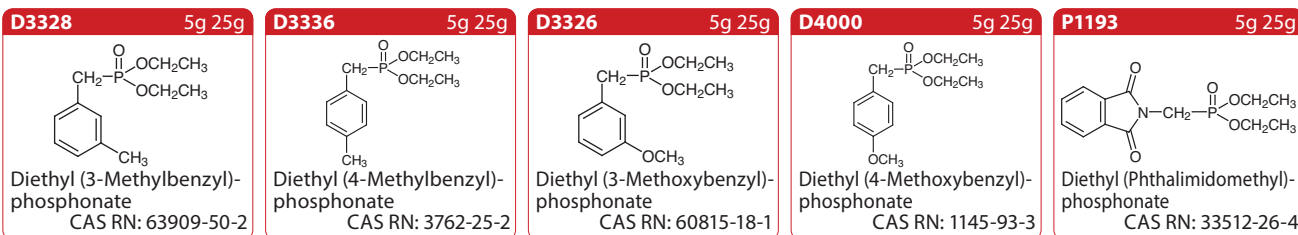
Wittig Reagents

<p>Wittig Reagents</p>	<p>C1442 10g 25g</p> <p>Tributyl(cyanomethyl)- phosphonium Chloride CAS RN: 82358-61-0</p>	<p>T2718 5g</p> <p>Tributyl(1,3-dioxolan-2-ylmethyl)- phosphonium Bromide CAS RN: 115754-62-6</p>	<p>B1206 5g 25g</p> <p>(Bromomethyl)- triphenylphosphonium Bromide CAS RN: 1034-49-7</p>	
<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 (Triphenyl- phosphoranylidene)acetate CAS RN: 2605-67-6</p>
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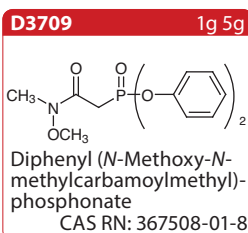
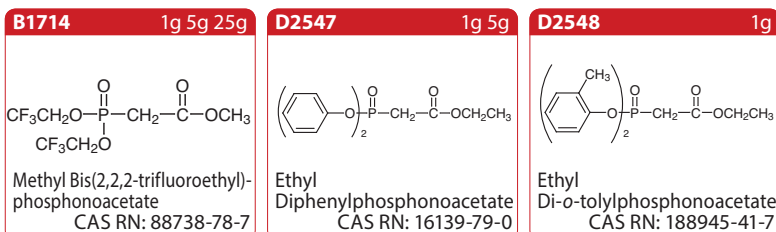
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<p>B5241 5g 25g</p>  <p>(4-Bromobenzyl)-triphenylphosphonium Bromide CAS RN: 51044-13-4</p>	<p>N0701 25g</p>  <p>(4-Nitrobenzyl)-triphenylphosphonium Bromide CAS RN: 2767-70-6</p>	<p>C1581 5g 25g</p>  <p>(4-Chlorobenzyl)-triphenylphosphonium Chloride CAS RN: 1530-39-8</p>	<p>C1759 25g</p>  <p>(2-Chlorobenzyl)-triphenylphosphonium Chloride CAS RN: 18583-55-6</p>	<p>B4486 1g 5g</p>  <p>[(1<i>H</i>-Benzotriazol-1-yl)methyl]-triphenylphosphonium Chloride CAS RN: 111198-09-5</p>
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<p>P1182 25g</p>  <p>Phenyltriphenylphosphonium Bromide CAS RN: 6048-29-9</p>	<p>M2463 1g 5g</p>  <p>(3-Methoxybenzyl)-triphenylphosphonium Chloride CAS RN: 18880-05-2</p>	<p>C1286 25g</p>  <p>Cinnamyltriphenylphosphonium Bromide CAS RN: 7310-74-9</p>	<p>D4072 5g</p>  <p>(3,4-Dimethoxybenzyl)-triphenylphosphonium Bromide CAS RN: 70219-09-9</p>	<p>E0421 5g</p>  <p>4-Ethoxybenzyltriphenylphosphonium Bromide CAS RN: 82105-88-2</p>
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<p>Horner-Wadsworth-Emmons Reagents</p>				
<p>O0208 5g 25g</p>  <p>Dimethyl (2-Oxopropyl)-phosphonate CAS RN: 4202-14-6</p>	<p>P1265 25g 250g</p>  <p>Trimethyl Phosphonoacetate CAS RN: 5927-18-4</p>	<p>H0779 5g 25g</p>  <p>Dimethyl (2-Hydroxyethyl)-phosphonate CAS RN: 54731-72-5</p>	<p>D3981 1g 5g</p>  <p>Dimethyl 2-(1,3-Dithiole)-phosphonate CAS RN: 133113-76-5</p>	<p>D4607 5g 25g</p>  <p>Diethyl (Trichloromethyl)-phosphonate CAS RN: 866-23-9</p>
<p>D4588 1g 5g</p>  <p>Diethyl (3-Bromopropyl)-phosphonate CAS RN: 1186-10-3</p>	<p>D3813 25g 100g</p>  <p>Diethyl (Hydroxymethyl)-phosphonate CAS RN: 3084-40-0</p>	<p>C1430 5g 25g</p>  <p>Diethyl Cyanomethylphosphonate CAS RN: 2537-48-6</p>		

Olefination

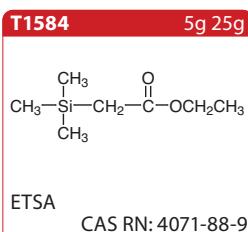
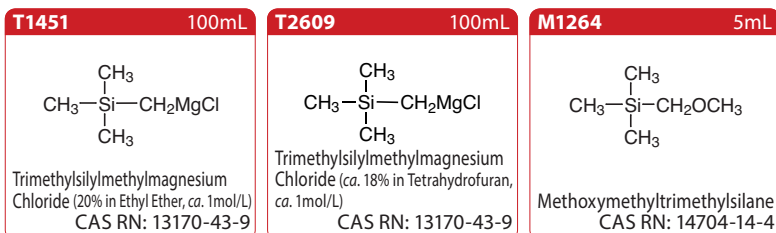
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D3174 5g 25g  Diethyl (2-Oxopropyl)phosphonate CAS RN: 1067-71-6	D2873 5g 25g  Methyl Diethylphosphonoacetate CAS RN: 1067-74-9	D4434 1g 5g  Diethyl (3-Bromopropyl)phosphonate CAS RN: 1186-10-3	D5095 5g 25g  Diethyl (Ethoxymethyl)phosphonate CAS RN: 10419-80-4	F0340 1g 5g  Triethyl 2-Fluoro-2-phosphonoacetate CAS RN: 2356-16-3
D4074 5g  Diethyl (1,3-Dithian-2-yl)phosphonate CAS RN: 62999-73-9	B5094 5g 25g  tert-Butyl Dimethylphosphonoacetate CAS RN: 62327-21-3	D1523 25g 100g 500g  Triethyl Phosphonoacetate CAS RN: 867-13-0	D3708 1g 5g  Diethyl (N-Methoxy-N-methylcarbamoylmethyl)phosphonate CAS RN: 124931-12-0	D3992 1g  Dimethyl 1,3-Benzodithiol-2-ylphosphonate CAS RN: 62217-35-0
D5644 1g 5g  Diethyl (Thiophen-2-ylmethyl)phosphonate CAS RN: 2026-42-8	D5176 200mg 1g  Dimethyl (3,3-Difluoro-2-oxoheptyl)phosphonate CAS RN: 50889-46-8	D4244 1g 5g  Dimethyl (2-Oxoheptyl)phosphonate CAS RN: 36969-89-8	D1524 25g 250g  Triethyl 3-Phosphonopropionate CAS RN: 3699-67-0	T2135 5g 25g  Triethyl 2-Phosphonopropionate CAS RN: 3699-66-9
P1258 5g  Diethyl 1-Pyrrolidinemethylphosphonate CAS RN: 51868-96-3	B4011 1g 5g  N-Boc-2-phosphonoglycine Trimethyl Ester CAS RN: 89524-98-1	B2814 1g 5g  tert-Butyl Diethylphosphonoacetate CAS RN: 27784-76-5	D4611 200mg 1g  Diethyl [(Tetrahydropyran-2-yl)oxy]methylphosphonate CAS RN: 71885-51-3	D2423 5g 25g  Diethyl 2,2-Diethoxyethylphosphonate CAS RN: 7598-61-0
T2294 1g 5g  Tetraethyl Ethylenediphosphonate CAS RN: 995-32-4	B2815 1g 5g  Benzyl Dimethylphosphonoacetate CAS RN: 57443-18-2	D4408 200mg 1g  Dimethyl (2-Oxo-3-phenoxypropyl)phosphonate CAS RN: 40665-68-7	D3688 5g 25g  Diethyl (4-Bromobenzyl)phosphonate CAS RN: 38186-51-5	C1595 1g 5g  Diethyl (3-Chlorobenzyl)phosphonate CAS RN: 78055-64-8
D3335 5g 25g  Diethyl (4-Chlorobenzyl)phosphonate CAS RN: 39225-17-7	D5265 1g 5g  Diethyl (2-Chlorobenzyl)phosphonate CAS RN: 29074-98-4	D3324 5g 25g  Diethyl (4-Fluorobenzyl)phosphonate CAS RN: 63909-58-0	D3689 5g 25g  Diethyl (4-Iodobenzyl)phosphonate CAS RN: 173443-43-1	D5208 5g  Diethyl (4-Nitrobenzyl)phosphonate CAS RN: 2609-49-6
B1795 25g  Diethyl Benzylphosphonate CAS RN: 1080-32-6	D4397 1g  Dimethyl [2-Oxo-3-[3-(trifluoromethyl)phenoxy]propyl]phosphonate CAS RN: 54094-19-8	D3323 5g 25g  Diethyl (4-Cyanobenzyl)phosphonate CAS RN: 1552-41-6	D3339 1g 5g  Diethyl Phenacylphosphonate CAS RN: 3453-00-7	D3327 5g 25g  Diethyl (2-Methylbenzyl)phosphonate CAS RN: 62778-16-9



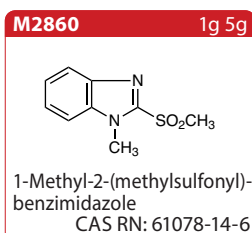
Z-Selective Horner-Wadsworth-Emmons Reagents



Peterson Reaction Reagents



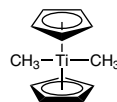
Julia-Kocienski Olefination Reagents

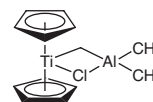


Titanium Reagents

T0616 5g 25g

 Titanocene Dichloride
 CAS RN: 1271-19-8

D4100 25g 100g

 Petasis Reagent
 (5% in Tetrahydrofuran/Toluene)
 CAS RN: 1271-66-5

C1411 25mL

 Tebbe Reagent
 (ca. 0.5mol/L in Toluene)
 CAS RN: 67719-69-1

T2052 100mL 500mL

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

T3238 100mL 500mL

 Titanium(IV) Chloride
 (ca. 19% in Toluene, ca. 1.0mol/L)
 CAS RN: 7550-45-0

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