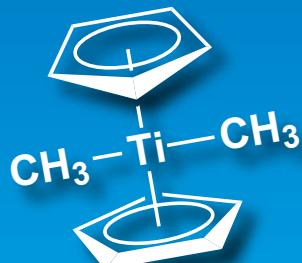
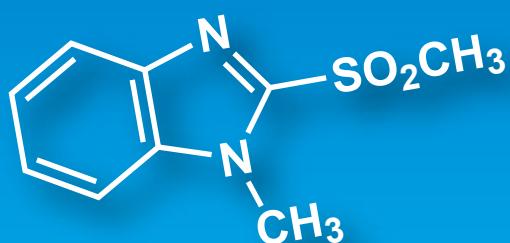
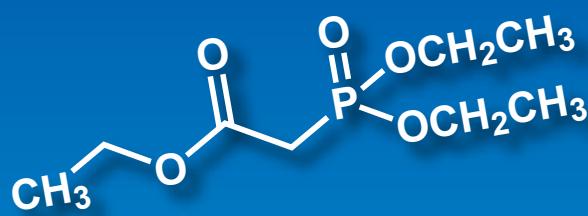
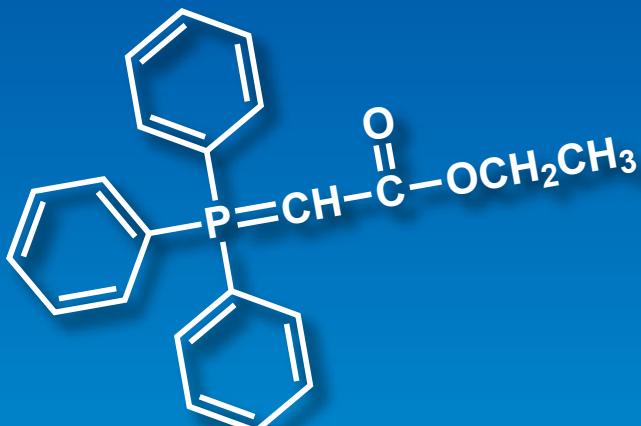


# Olefination



**Wittig Reagents**

**Horner-Wadsworth-Emmons Reagents**

**Z-Selective Horner-Wadsworth-Emmons Reagents**

**Peterson Reaction Reagents**

**Julia-Kocienski Olefination Reagents**

**Titanium Reagents**

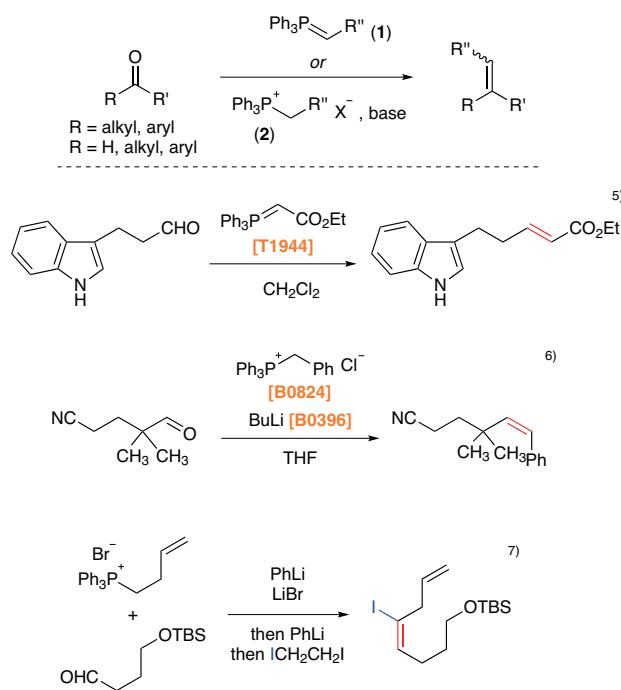
# Olefination

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 3<sup>rd</sup> 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.<sup>1)</sup> 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 olefinaitons.<sup>2)</sup>

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

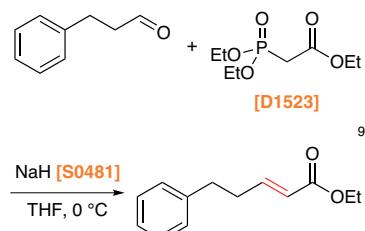
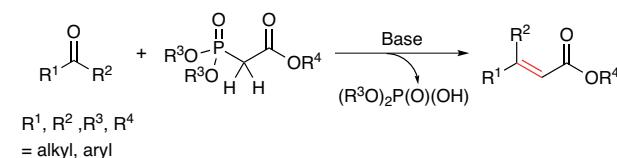
## ● Wittig reaction

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.<sup>3)</sup> 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.<sup>4,7)</sup>



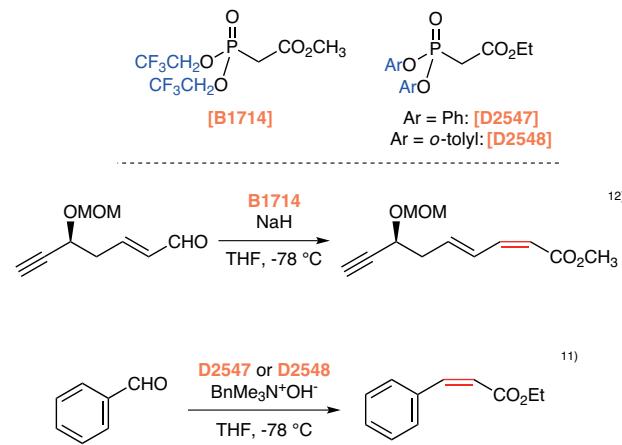
## ● Horner-Wadsworth-Emmons reaction

The Horner-Wadsworth-Emmons (HWE) reaction is a frequently used synthetic method to obtain substituted (di- and tri-) olefin products from aldehydes and ketones.<sup>8)</sup> *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.



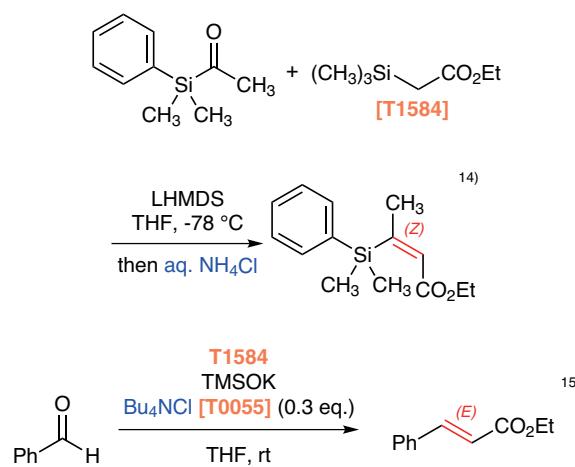
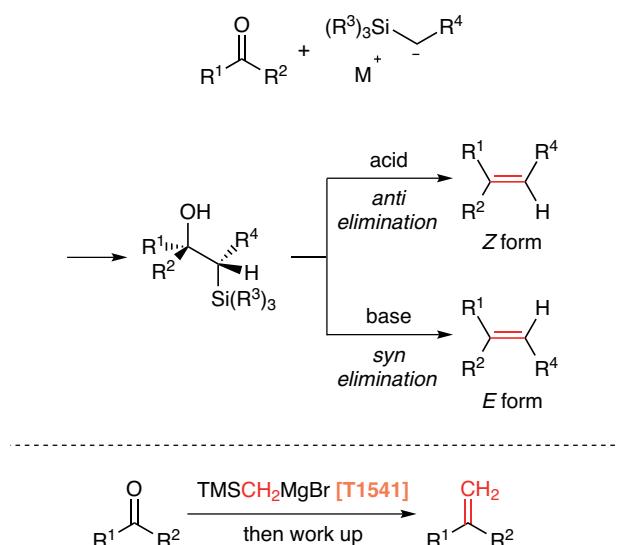
## ● Z-Selective Horner-Wadsworth-Emmons reaction

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]**).<sup>10)</sup> Later, Ando developed diaryl phosphonoacetates such as **D2547** and **D2548** which are able to provide *Z*- $\alpha,\beta$ -unsaturated esters in high stereoselectivity.<sup>11)</sup> 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

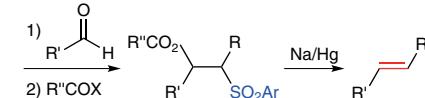
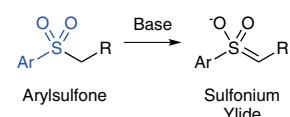
The Peterson reaction is a synthetic method that affords olefins by the addition of a  $\alpha$ -silyl carbanion to aldehydes and ketones and successive treatment with acid or base.<sup>13)</sup> This reaction has the advantage that a given olefin's stereochemistry can be adjusted by adding acid or base. 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.



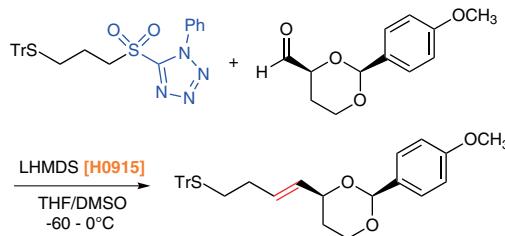
### Julia-Lythgoe reaction

The Julia-Lythgoe reaction and its various sub-forms are useful synthetic methods to convert aldehydes to olefins using arylsulfones.<sup>16)</sup> 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,<sup>17,18)</sup> 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.<sup>19)</sup>

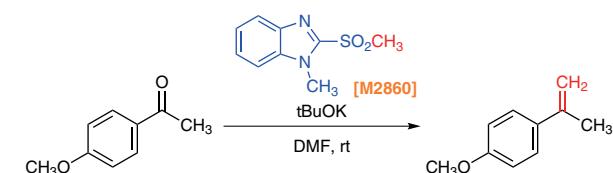
### Standard Julia-Lythgoe Reaction<sup>16)</sup>



### Julia-Kocienski Reaction<sup>20)</sup>

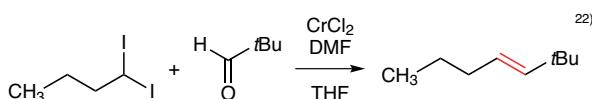
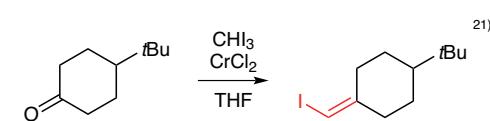
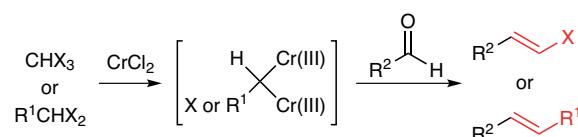


### Julia-Kocienski Type Methylenation<sup>19)</sup>



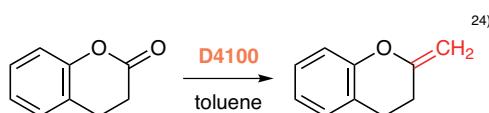
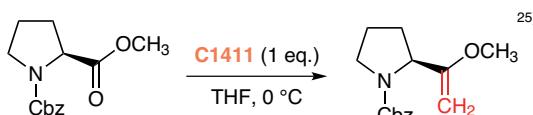
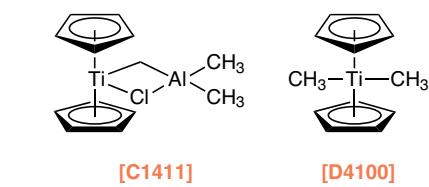
### Takai-Utimoto reaction

Takai and Utimoto have reported that a *gem*-dichromium reagent prepared from a haloform and chromium(II) chloride reacts with aldehydes to provide haloolefins.<sup>21)</sup> This method is applicable to 1,1-dihalides<sup>22)</sup> 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.



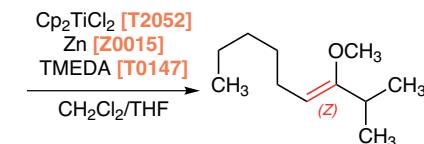
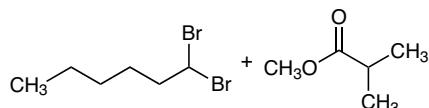
### ● Olefination reactions using titanium reagents

Tebbe<sup>23)</sup> and Petasis<sup>24)</sup> 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.

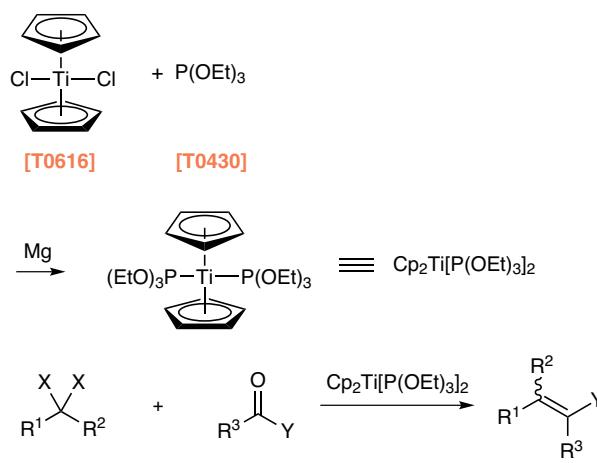


Besides the titanium compounds stated above, olefination utilizing the  $\text{RCHX}_2\text{-TiCl}_4\text{-Zn}$  system reported by Takai and Utimoto can also be used on carbonyl groups.<sup>26)</sup> In this reaction, Z-olefins are given preferentially. Takeda's group have also reported more general olefinations of carbonyl compounds by the treatment of thioacetals or *gem*-dihalides and a titanocene(II) compound  $\text{Cp}_2\text{Ti}[\text{P}(\text{OEt})_3]_2$ .<sup>27)</sup>

### Takai-Utimoto's Olefination System<sup>26)</sup>

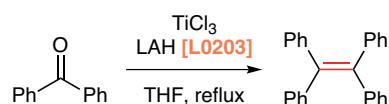


### Takeda's Olefination System<sup>27)</sup>

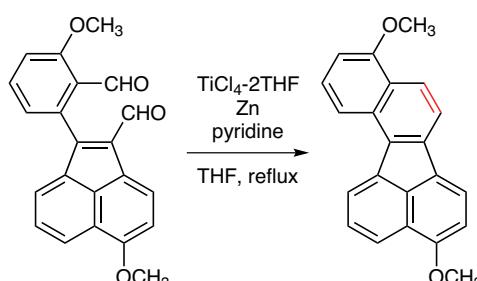


The McMurry coupling is another well-known olefination method using titanium reagents.<sup>28)</sup> This reaction can be applied to heterocoupling and an intramolecular olefination as well as homocoupling and the construction of medium and large sized rings utilizing.<sup>29)</sup> Olefinations using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

### Original McMurry Coupling<sup>28)</sup>



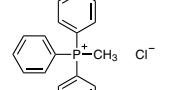
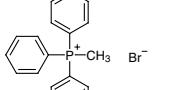
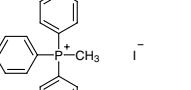
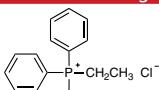
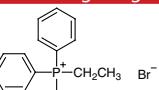
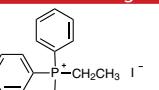
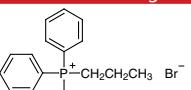
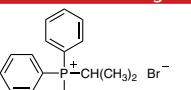
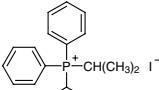
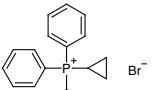
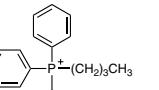
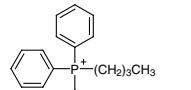
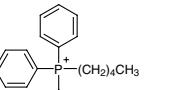
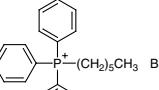
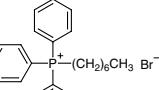
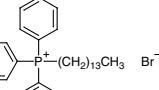
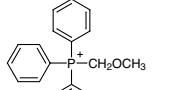
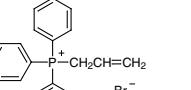
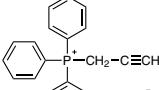
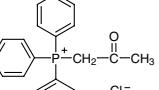
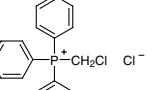
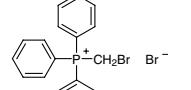
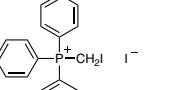
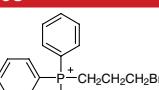
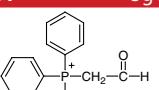
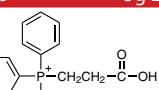
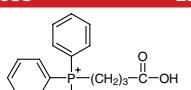
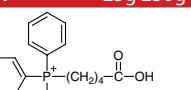
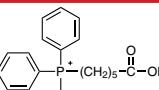
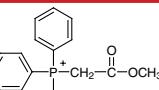
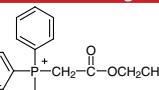
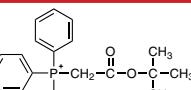
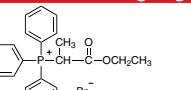
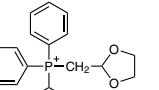
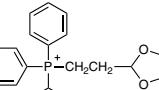
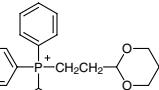
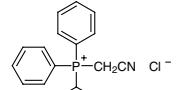
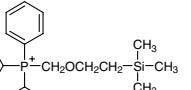
### McMurry Type Ring Closure<sup>29)</sup>



## References

- 1) review: B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* **1989**, *89*, 863.
- 2) F. N. Tebbe, G. W. Parshall, and G. S. Reddy, *J. Am. Chem. Soc.* **1978**, *100*, 3619.
- 3) a) G. Wittig, U. Schöllkopf, *Chem. Ber.* **1954**, *87*, 1318.  
b) G. Wittig, W. Haag, *Chem. Ber.* **1955**, *88*, 1654.
- 4) M. Schlosser, K. F. Christmann, *Angew. Chem. Int. Ed.* **1966**, *5*, 126.
- 5) D. H. Dethé, V. K. Boda, A. Mandal, *Eur. J. Org. Chem.* **2018**, *39*, 5417.
- 6) T. Shu, S. Li, X-Y. Chen, Q. Liu, C. von Essen, K. Rissanen, D. Enders, *Chem. Commun.* **2018**, *55*, 7661.
- 7) M. Brandstätter, M. Freis, N. Huwyler, E. M. Carreira, *Angew. Chem. Int. Ed.* **2019**, *58*, 2490.
- 8) a) L. Horner, H. Hoffmann, H. G. Wippel, *Chem. Ber.* **1958**, *91*, 61.  
b) W. S. Wadsworth, W. D. Emmons, *J. Am. Chem. Soc.* **1961**, *83*, 1733.
- 9) Y.-G. Chen, B. Shuai, C. Ma, X.-J. Zhang, P. Fang, T.-S. Mei, *Org. Lett.* **2017**, *19*, 2969.
- 10) W. C. Still, C. Gennari, *Tetrahedron Lett.* **1983**, *24*, 4405.
- 11) a) K. Ando, *Tetrahedron Lett.* **1995**, *36*, 4105.  
b) K. Ando, *J. Org. Chem.* **1997**, *62*, 1934.
- 12) R. Sayini, P. Srihari, *Synthesis* **2018**, *50*, 663.
- 13) D. J. Peterson, *J. Org. Chem.* **1968**, *33*, 780.
- 14) B. H. Lipshutz, N. Tanaka, B. R. Taft, C.-T. Lee, *Org. Lett.* **2006**, *8*, 1963.
- 15) M. Das, A. Manvar, I. Fox, D. J. Roberts, D. F. O'Shea, *Synlett* **2017**, *28*, 2401.
- 16) a) M. Julia, J-M. Paris, *Tetrahedron Lett.* **1973**, *14*, 4833.  
b) P. J. Kocienski, B. Lythgoe, I. Waterhouse, *J. Chem. Soc., Perkin Trans. 1* **1980**, *1045*.
- 17) J. B. Baudin, G. Hareau, S. A. Julia, O. Ruel, *Tetrahedron Lett.* **1991**, *32*, 1175.
- 18) P. R. Blakemore, W. J. Cole, P. J. Kocienski, A. Morley, *Synlett* **1998**, *26*.
- 19) K. Ando, T. Kobayashi, N. Uchida, *Org. Lett.* **2015**, *17*, 2554.
- 20) T. Takizawa, K. Watanabe, K. Narita, K. Kudo, T. Oguchi, H. Abe, T. Katoh, *Heterocycles* **2008**, *76*, 275.
- 21) K. Takai, K. Nitta, K. Utimoto, *J. Am. Chem. Soc.* **1986**, *108*, 7408.
- 22) T. Okazoe, K. Takai, K. Utimoto, *J. Am. Chem. Soc.* **1987**, *109*, 951.
- 23) F. N. Tebbe, G. W. Parshall, G. S. Reddy, *J. Am. Chem. Soc.* **1978**, *100*, 3611.
- 24) N. A. Petasis, E. I. Bzowej, *J. Am. Chem. Soc.* **1990**, *112*, 6392.
- 25) A. G. M. Barrett, F. Damiani, *J. Org. Chem.* **1999**, *64*, 1410.
- 26) T. Okazoe, K. Takai, K. Oshima, K. Utimoto, *J. Org. Chem.* **1987**, *52*, 4410.
- 27) a) Y. Horikawa, M. Watanabe, T. Fujiwara, T. Takeda, *J. Am. Chem. Soc.* **1997**, *119*, 1127.  
b) T. Takeda, R. Sasaki, T. Fujiwara, *J. Org. Chem.* **1998**, *63*, 7286.
- 28) J. E. McMurry, M. P. Fleming, *J. Am. Chem. Soc.* **1974**, *96*, 4708.
- 29) S. Lahore, U. Narkhede, L. Merlini, S. Dallavalle, *J. Org. Chem.* **2013**, *78*, 10860.

## Wittig Reagents

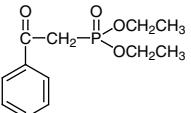
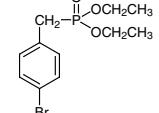
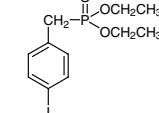
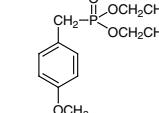
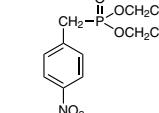
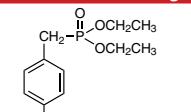
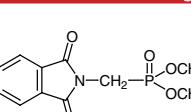
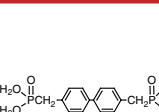
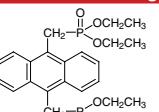
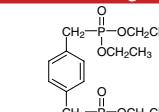
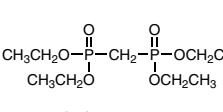
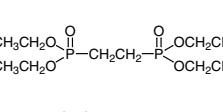
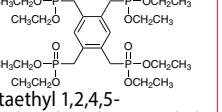
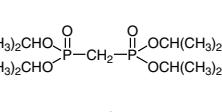
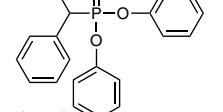
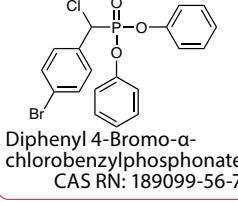
<b>M2702</b> 5g 25g	<b>M0779</b> 25g 100g 500g	<b>M0253</b> 25g 100g 500g
 Methyltriphenylphosphonium Chloride CAS RN: 1031-15-8	 Methyltriphenylphosphonium Bromide CAS RN: 1779-49-3	 Methyltriphenylphosphonium Iodide CAS RN: 2065-66-9
<b>E1336</b> 25g 100g	<b>E0382</b> 25g 100g 500g	<b>E0549</b> 25g 250g
 Ethyltriphenylphosphonium Chloride CAS RN: 896-33-3	 Ethyltriphenylphosphonium Bromide CAS RN: 1530-32-1	 Ethyltriphenylphosphonium Iodide CAS RN: 4736-60-1
<b>P1200</b> 25g 500g	<b>I1289</b> 5g 25g	
 Triphenylpropylphosphonium Bromide CAS RN: 6228-47-3	 Isopropyltriphenylphosphonium Bromide CAS RN: 1530-33-2	
<b>I0552</b> 5g 25g	<b>C1378</b> 5g	<b>B5730</b> 25g
 Isopropyltriphenylphosphonium Iodide CAS RN: 24470-78-8	 Cyclopropyltriphenylphosphonium Bromide CAS RN: 14114-05-7	 Butyltriphenylphosphonium Chloride CAS RN: 13371-17-0
<b>B0970</b> 25g 250g	<b>A0862</b> 25g	
 Butyltriphenylphosphonium Bromide CAS RN: 1779-51-7	 Amyltriphenylphosphonium Bromide CAS RN: 21406-61-1	
<b>H0540</b> 25g 100g 500g	<b>H0545</b> 25g 500g	<b>T1506</b> 25g
 Hexyltriphenylphosphonium Bromide CAS RN: 4762-26-9	 Heptyltriphenylphosphonium Bromide CAS RN: 13423-48-8	 Triphenyl(tetradecyl)phosphonium Bromide CAS RN: 25791-20-2
<b>M0828</b> 25g 100g 500g	<b>A1007</b> 25g	
 (Methoxymethyl)triphenylphosphonium Chloride CAS RN: 4009-98-7	 Allyltriphenylphosphonium Bromide CAS RN: 1560-54-9	
<b>P1438</b> 5g 25g	<b>A1305</b> 25g	<b>C1009</b> 5g 25g
 Triphenylpropargylphosphonium Bromide CAS RN: 2091-46-5	 Acetyltriphenylphosphonium Chloride CAS RN: 1235-21-8	 (Chloromethyl)triphenylphosphonium Chloride CAS RN: 5293-84-5
<b>B1206</b> 5g 25g	<b>I1179</b> 1g 5g	
 (Bromomethyl)triphenylphosphonium Bromide CAS RN: 1034-49-7	 (Iodomethyl)triphenylphosphonium Iodide CAS RN: 3020-28-8	
<b>B1208</b> 25g	<b>F0331</b> 5g 25g	<b>C3309</b> 5g 25g
 3-Bromopropyltriphenylphosphonium Bromide CAS RN: 3607-17-8	 (Formylmethyl)triphenylphosphonium Chloride CAS RN: 62942-43-2	 (2-Carboxyethyl)triphenylphosphonium Bromide CAS RN: 51114-94-4
<b>C1635</b> 25g	<b>C1061</b> 25g 250g	
 (3-Carboxypropyl)triphenylphosphonium Bromide CAS RN: 17857-14-6	 4-(Carboxybutyl)triphenylphosphonium Bromide CAS RN: 17814-85-6	
<b>C3113</b> 5g	<b>M1326</b> 25g	<b>E0407</b> 25g 250g
 (5-Carboxypentyl)triphenylphosphonium Bromide CAS RN: 50889-29-7	 Carbamethoxymethyl(triphenylphosphonium Bromide CAS RN: 1779-58-4	 Carbethoxymethyl(triphenylphosphonium Bromide CAS RN: 1530-45-6
<b>B3928</b> 25g	<b>E1300</b> 5g 25g	
 (tert-Butoxycarbonylmethyl)triphenylphosphonium Bromide CAS RN: 59159-39-6	 (1-Ethoxy-1-oxopropan-2-yl)triphenylphosphonium Bromide CAS RN: 30018-16-7	
<b>D2164</b> 5g 25g	<b>D2056</b> 5g 25g	<b>D1655</b> 5g 25g
 (1,3-Dioxolan-2-yl)methyltriphenylphosphonium Bromide CAS RN: 52509-14-5	 2-(1,3-Dioxolan-2-yl)ethyltriphenylphosphonium Bromide CAS RN: 86608-70-0	 2-(1,3-Dioxolan-2-yl)ethyltriphenylphosphonium Bromide CAS RN: 69891-92-5
<b>C1739</b> 25g 100g	<b>T1458</b> 5g 25g	
 (Cyanomethyl)triphenylphosphonium Chloride CAS RN: 4336-70-3	 SEM-triphenylphosphonium Chloride CAS RN: 82495-75-8	

<b>T1510</b>  1g 5g <chem>[Ph2P+]CH2CH2Si(CH3)3I</chem> (2-Trimethylsilylethyl)-triphenylphosphonium Iodide CAS RN: 63922-84-9	<b>T1498</b>  1g 5g <chem>[Ph2P+]CH2C#C[Si](CH3)2Br</chem> (3-Trimethylsilyl-2-propynyl)-triphenylphosphonium Bromide CAS RN: 42134-49-6	<b>B0824</b>  25g 500g <chem>[Ph2P+]CH2C6H5Cl</chem> Benzyltriphenyl-phosphonium Chloride CAS RN: 1100-88-5	<b>B2025</b>  25g <chem>[Ph2P+]CH2C6H5Br</chem> Benzyltriphenyl-phosphonium Bromide CAS RN: 1449-46-3	<b>C1581</b>  5g 25g <chem>[Ph2P+]CH2C6H4Cl</chem> (4-Chlorobenzyl)triphenyl-phosphonium Chloride CAS RN: 1530-39-8
<b>B5241</b>  5g 25g <chem>[Ph2P+]CH2C6H4Br</chem> (4-Bromobenzyl)triphenyl-phosphonium Bromide CAS RN: 51044-13-4	<b>D2907</b>  5g 25g <chem>[Ph2P+]CH2C6H3(Cl)2</chem> (2,4-Dichlorobenzyl)triphenyl-phosphonium Chloride CAS RN: 2492-23-1	<b>C1759</b>  25g <chem>[Ph2P+]CH2C6H4Cl</chem> (2-Chlorobenzyl)triphenyl-phosphonium Chloride CAS RN: 18583-55-6	<b>H1240</b>  5g <chem>[Ph2P+]CH2C6H4OH</chem> (2-Hydroxybenzyl)triphenyl-phosphonium Bromide CAS RN: 70340-04-4	<b>M2463</b>  1g 5g <chem>[Ph2P+]CH2C6H3OCH3</chem> (3-Methoxybenzyl)triphenyl-phosphonium Chloride CAS RN: 18880-05-2
<b>D4072</b>  5g <chem>[Ph2P+]CH2C6H3OCH3</chem> (3,4-Dimethoxybenzyl)-triphenylphosphonium Bromide CAS RN: 70219-09-9	<b>N0701</b>  25g <chem>[Ph2P+]CH2C6H3NO2</chem> (4-Nitrobenzyl)triphenyl-phosphonium Bromide CAS RN: 2767-70-6	<b>N0700</b>  5g 25g <chem>[Ph2P+]CH2C1=CC=CC=C1</chem> (1-Naphthylmethyl)triphenyl-phosphonium Chloride CAS RN: 23277-00-1	<b>P1182</b>  25g <chem>[Ph2P+]CH2C(=O)c6ccccc6</chem> Phenacyltriphenyl-phosphonium Bromide CAS RN: 6048-29-9	<b>C1286</b>  25g <chem>[Ph2P+]CH2CH=CHC6H5</chem> Cinnamyltriphenyl-phosphonium Bromide CAS RN: 7310-74-9
<b>B4486</b>  1g 5g <chem>[Ph2P+]CH2C1=NN=C1</chem> [(1H-Benzotriazol-1-yl)methyl]-triphenylphosphonium Chloride CAS RN: 111198-09-5	<b>B2286</b>  5g <chem>[Ph2P+]CH=CHCH2CH=CH[Ph2P+]</chem> trans-2-Butene-1,4-bis(triphenyl-phosphonium Chloride) CAS RN: 106423-29-4	<b>C1442</b>  10g 25g <chem>CH3(CH2)3P+(CH2)3CH3CH2CN</chem> Tributyl(cyanomethyl)-phosphonium Chloride CAS RN: 82358-61-0	<b>T2718</b>  5g <chem>CH2=C1CO1P+(CH2)3CH3CH2Br</chem> Tributyl(1,3-dioxolan-2-ylmethyl)phosphonium Bromide CAS RN: 115754-62-6	<b>A1439</b>  25g <chem>[Ph2P=CHC(=O)CH3]Br</chem> (Acetylethylene)-triphenylphosphorane CAS RN: 1439-36-7
<b>T2001</b>  5g 25g <chem>[Ph2P=CHC(=O)H]Br</chem> (Triphenylphosphoranylidene)-acetaldehyde CAS RN: 2136-75-6	<b>T4314</b>  1g <chem>[Ph2P=CHC(=O)CH3]Br</chem> 2-(Triphenyl-phosphoranylidene)propanal CAS RN: 24720-64-7	<b>T1363</b>  25g 100g <chem>[Ph2P=CHC(=O)OC2=CC=C(C=C2)C3=CC=CC=C3]Br</chem> Methyl (Triphenyl-phosphoranylidene)acetate CAS RN: 2605-67-6	<b>T1944</b>  25g 250g <chem>[Ph2P=CHC(=O)OC2=CC=C(C=C2)C3=CC=CC=C3]Br</chem> Ethyl (Triphenyl-phosphoranylidene)acetate CAS RN: 1099-45-2	<b>B3877</b>  5g 25g <chem>[Ph2P=CHC(=O)OC2=CC=C(C=C2)C3=CC=CC=C3]Br</chem> tert-Butyl (Triphenyl-phosphoranylidene)acetate CAS RN: 35000-38-5
<b>P2980</b>  5g 25g <chem>[Ph2P=CHC(=O)OC2=CC=C(C=C2)C3=CC=CC=C3]Br</chem> Benzyl (Triphenyl-phosphoranylidene)acetate CAS RN: 15097-38-8	<b>C1641</b>  5g <chem>[Ph2P=CHC(=O)OC2=CC=C(C=C2)C3=CC=CC=C3]Br</chem> Ethyl 2-(Triphenyl-phosphoranylidene)propionate CAS RN: 5717-37-3	<b>T1958</b>  5g 25g <chem>[Ph2P=CHC#N]Br</chem> (Triphenylphosphoranylidene)-acetonitrile CAS RN: 16640-68-9	<b>T2565</b>  1g 5g <chem>[Ph2P=CHC=O]Br</chem> Bestmann Ylide CAS RN: 15596-07-3	<b>T2002</b>  1g 5g <chem>[Ph2P=CHC(=O)C6H5]Br</chem> 2-(Triphenylphosphoranylidene)-acetophenone CAS RN: 859-65-4
<b>H0779</b>  5g <chem>HOCH2CH2P(=O)(OCH3)2</chem> Dimethyl (2-Hydroxyethyl)-phosphonate CAS RN: 54731-72-5	<b>O0208</b>  5g 25g <chem>CH3C(=O)CH2P(=O)(OCH3)2</chem> Dimethyl (2-Oxopropyl)-phosphonate CAS RN: 4202-14-6	<b>P1265</b>  25g 250g <chem>CH3OCH2P(=O)(OCH3)2CH2C(=O)OCH3</chem> Diethyl Carboxymethylphosphonate CAS RN: 5927-18-4		
<b>B5094</b>  5g 25g <chem>CH3OCH2P(=O)(OCH3)2CH2C(=O)OCH2CH3</chem> tert-Butyl Dimethylphosphonoacetate CAS RN: 62327-21-3	<b>E1160</b>  25g <chem>CH3OCH2P(=O)(OCH3)2CH2C(=O)OCH2CH3</chem> Ethyl Dimethyl-phosphonoacetate CAS RN: 311-46-6	<b>B2815</b>  1g 5g <chem>CH3OCH2P(=O)(OCH3)2CH2C(=O)OCH2C6H5</chem> Benzyl Dimethyl-phosphonoacetate CAS RN: 57443-18-2	<b>D5176</b>  200mg 1g <chem>CH3(CH2)3CF2CH2P(=O)(OCH3)2CH2C(=O)OCH3</chem> Dimethyl (3,3-Difluoro-2-oxoheptyl)phosphonate CAS RN: 50889-46-8	<b>D4397</b>  1g <chem>CH3OCH2C(=O)CH2P(=O)(OCH3)2C6H2(C(F)(F)F)CO</chem> Dimethyl [2-Oxo-3-[3-(trifluoromethyl)phenoxy]-propyl]phosphonate CAS RN: 54094-19-8

## Horner-Wadsworth-Emmons Reagents

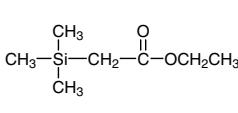
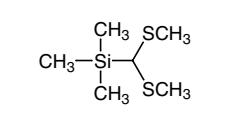
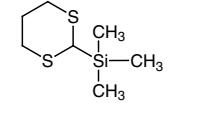
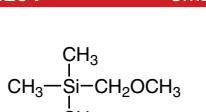
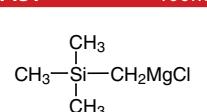
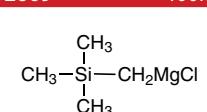
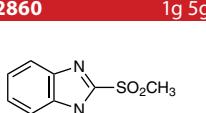
## Olefination

<b>B4011</b>  1g 5g N-Boc-2-phosphonoglycine Trimethyl Ester CAS RN: 89524-98-1	<b>C2440</b>  1g 5g N-Cbz-2-phosphonoglycine Trimethyl Ester CAS RN: 88568-95-0	<b>D3981</b>  1g 5g Dimethyl 2-(1,3-Dithiole)-phosphonate CAS RN: 133113-76-5	<b>D3992</b>  1g Dimethyl 1,3-Benzodithiol-2-ylphosphonate CAS RN: 62217-35-0	<b>D3813</b>  25g 100g Diethyl (Hydroxymethyl)-phosphonate CAS RN: 3084-40-0
<b>D3873</b>  5g 25g Diethyl (Methoxymethyl)-phosphonate CAS RN: 32806-04-5	<b>D4588</b>  1g 5g Diethyl (3-Bromopropyl)-phosphonate CAS RN: 3167-63-3	<b>D4607</b>  5g 25g Diethyl (Trichloromethyl)-phosphonate CAS RN: 866-23-9	<b>D5095</b>  5g 25g Diethyl (Ethoxymethyl)-phosphonate CAS RN: 10419-80-4	<b>M1208</b>  5g 25g Diethyl (Methylthiomethyl)-phosphonate CAS RN: 28460-01-7
<b>B1781</b>  5g 25g Diethyl 2-Bromoethylphosphonate CAS RN: 5324-30-1	<b>D4434</b>  1g 5g Diethyl (3-Bromopropyl)-phosphonate CAS RN: 1186-10-3	<b>D6296</b>  1g 5g Diethyl (4-Bromobutyl)-phosphonate CAS RN: 63075-66-1	<b>D3080</b>  5g 25g 2-(Diethoxyphosphoryl)-acetic Acid CAS RN: 3095-95-2	<b>D2873</b>  5g 25g Methyl Diethyl-phosphonoacetate CAS RN: 1067-74-9
<b>B2814</b>  1g 5g tert-Butyl Diethylphosphonoacetate CAS RN: 27784-76-5	<b>C1430</b>  5g 25g Diethyl Cyanomethyl-phosphonate CAS RN: 2537-48-6	<b>D1523</b>  25g 100g 500g Triethyl Phosphonoacetate CAS RN: 867-13-0	<b>D1524</b>  25g 250g Triethyl 3-Phosphonopropionate CAS RN: 3699-67-0	<b>D2423</b>  5g 25g Diethyl 2,2-Diethoxyethyl-phosphonate CAS RN: 7598-61-0
<b>T2135</b>  5g 25g Triethyl 2-Phosphonopropionate CAS RN: 3699-66-9	<b>D3708</b>  1g 5g Diethyl (N-Methoxy-N-methylcarbamoylmethyl)-phosphonate CAS RN: 124931-12-0	<b>F0340</b>  1g 5g Triethyl 2-Fluoro-2-phosphonoacetate CAS RN: 2356-16-3	<b>D4611</b>  200mg 1g Diethyl [(Tetrahydropyran-2-yloxy)methyl]phosphonate CAS RN: 71885-51-3	<b>D4074</b>  5g Diethyl (1,3-Dithian-2-yl)-phosphonate CAS RN: 62999-73-9
<b>P1258</b>  5g Diethyl 1-Pyrrolidinemethyl-phosphonate CAS RN: 51868-96-3	<b>D3069</b>  1g 5g Diethyl Allylphosphonate CAS RN: 1067-87-4	<b>D3174</b>  5g 25g Diethyl (2-Oxopropyl)-phosphonate CAS RN: 1067-71-6	<b>D4968</b>  25g Diethyl (p-Toluenesulfonyloxymethyl)phosphonate CAS RN: 31618-90-3	<b>B1795</b>  25g Diethyl Benzylphosphonate CAS RN: 1080-32-6
<b>C1595</b>  1g 5g Diethyl (3-Chlorobenzyl)-phosphonate CAS RN: 78055-64-8	<b>D5265</b>  1g 5g Diethyl (2-Chlorobenzyl)-phosphonate CAS RN: 29074-98-4	<b>D2967</b>  1g 5g Diethyl 3,5-Di-tert-butyl-4-hydroxybenzylphosphonate CAS RN: 976-56-7	<b>D3323</b>  5g 25g Diethyl (4-Cyanobenzyl)-phosphonate CAS RN: 1552-41-6	<b>D3324</b>  5g 25g Diethyl (4-Fluorobenzyl)-phosphonate CAS RN: 63909-58-0
<b>D3326</b>  5g 25g Diethyl (3-Methoxybenzyl)-phosphonate CAS RN: 60815-18-1	<b>D3327</b>  5g 25g Diethyl (2-Methylbenzyl)-phosphonate CAS RN: 62778-16-9	<b>D3328</b>  5g 25g Diethyl (3-Methylbenzyl)-phosphonate CAS RN: 63909-50-2	<b>D3335</b>  5g 25g Diethyl (4-Chlorobenzyl)-phosphonate CAS RN: 39225-17-7	<b>D3336</b>  5g 25g Diethyl (4-Methylbenzyl)-phosphonate CAS RN: 3762-25-2

<b>D3339</b>  1g 5g Diethyl Phenacylphosphonate CAS RN: 3453-00-7	<b>D3688</b>  5g 25g Diethyl (4-Bromobenzyl)-phosphonate CAS RN: 38186-51-5	<b>D3689</b>  5g 25g Diethyl (4-Iodobenzyl)-phosphonate CAS RN: 173443-43-1	<b>D4000</b>  5g 25g Diethyl (4-Methoxybenzyl)-phosphonate CAS RN: 1145-93-3	<b>D5208</b>  5g Diethyl (4-Nitrobenzyl)-phosphonate CAS RN: 2609-49-6
<b>D5900</b>  1g 5g Diethyl [4-(Trifluoromethyl)-benzyl]phosphonate CAS RN: 99578-68-4	<b>P1193</b>  5g 25g Diethyl (Phthalimidomethyl)-phosphonate CAS RN: 33512-26-4	<b>B1923</b>  1g 5g 4,4'-Bis(diethyl-phosphonomethyl)biphenyl CAS RN: 17919-34-5	<b>B2801</b>  1g 5g 9,10-Bis(diethyl-phosphonomethyl)anthracene CAS RN: 60974-92-7	<b>T1582</b>  5g 25g 100g Tetraethyl p-Xylenediphosphonate CAS RN: 4546-04-7
<b>T2329</b>  5g 25g Tetraethyl Methylenediphosphonate CAS RN: 1660-94-2	<b>T2294</b>  1g 5g Tetraethyl Ethylenediphosphonate CAS RN: 995-32-4	<b>T3904</b>  1g 5g Octaethyl 1,2,4,5-Tetrakis(phosphonomethyl)-benzene CAS RN: 136455-49-7	<b>M1319</b>  25g Tetraisopropyl Methylenediphosphonate CAS RN: 1660-95-3	<b>D3824</b>  1g 5g Diphenyl α-Chlorobenzylphosphonate CAS RN: 58263-67-5
<b>D3875</b>  5g 25g Diphenyl 4-Bromo-α-chlorobenzylphosphonate CAS RN: 189099-56-7				

## Z-Selective Horner-Wadsworth-Emmons Reagents

## Peterson Reaction Reagents

<b>T1584</b>  5g 25g Ethyl (Trimethylsilyl)-acetate CAS RN: 4071-88-9	<b>B2004</b>  1g Bis(methylthio)-(trimethylsilyl)methane CAS RN: 37891-79-5	<b>T1514</b>  5g 25g 2-Trimethylsilyl-1,3-dithiane CAS RN: 13411-42-2	<b>M1264</b>  5mL Methoxymethyl-trimethylsilane CAS RN: 14704-14-4	<b>T1451</b>  100mL Trimethylsilylmethyl-magnesium Chloride (20% in Ethyl Ether, ca. 1mol/L) CAS RN: 13170-43-9	<b>T2609</b>  100mL Trimethylsilylmethyl-magnesium Chloride (ca. 18% in Tetrahydrofuran, ca. 1mol/L) CAS RN: 13170-43-9
		<b>M2860</b>  1g 5g 1-Methyl-2-(methylsulfonyl)-benzimidazole CAS RN: 61078-14-6			

## Julia-Kocienski Olefination Reagents

## Titanium Reagents

**T2052** 20mL 100mL 500mL

TiCl<sub>4</sub>

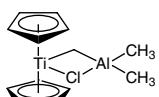
Titanium(IV) Chloride (14% in  
Dichloromethane, ca. 1.0mol/L)  
CAS RN: 7550-45-0

**T3238** 20mL 100mL 500mL

TiCl<sub>4</sub>

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

**C1411** 25mL



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

**D4100** 25g 100g



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

**T0616** 5g 25g



Titanocene Dichloride  
CAS RN: 1271-19-8



---

## **Ordering and Customer Service**

### **TCI AMERICA**

Tel : 800-423-8616 / 503-283-1681  
Fax : 888-520-1075 / 503-283-1987  
E-mail : Sales-US@TCIchemicals.com

### **TCI EUROPE N.V.**

Tel : +32 (0)3 735 07 00  
Fax : +32 (0)3 735 07 01  
E-mail : Sales-EU@TCIchemicals.com

### **TCI Deutschland GmbH**

Tel : +49 (0)6196 64053-00  
Fax : +49 (0)6196 64053-01  
E-mail : Sales-DE@TCIchemicals.com

### **Tokyo Chemical Industry UK Ltd.**

Tel : +44 (0)1865 78 45 60  
E-mail : Sales-UK@TCIchemicals.com

### **梯希爱(上海)化成工业发展有限公司**

Tel : 800-988-0390 / 021-67121386  
Fax : 021-6712-1385  
E-mail : Sales-CN@TCIchemicals.com

### **Tokyo Chemical Industry (India) Pvt. Ltd.**

Tel : 1800 425 7889 / 044-2262 0909  
E-mail : Sales-IN@TCIchemicals.com

### **TOKYO CHEMICAL INDUSTRY CO., LTD.**

Tel : +81 (0)3-5640-8878  
E-mail : globalbusiness@TCIchemicals.com

• Chemicals itemized in this brochure are for research and testing use only. Please avoid use other than by chemically knowledgeable professionals. • Information such as listed products and its specifications and so on are subject to change without prior notice. • The contents may not be reproduced or duplicated in whole or in part without permission of Tokyo Chemical Industry Co., Ltd.