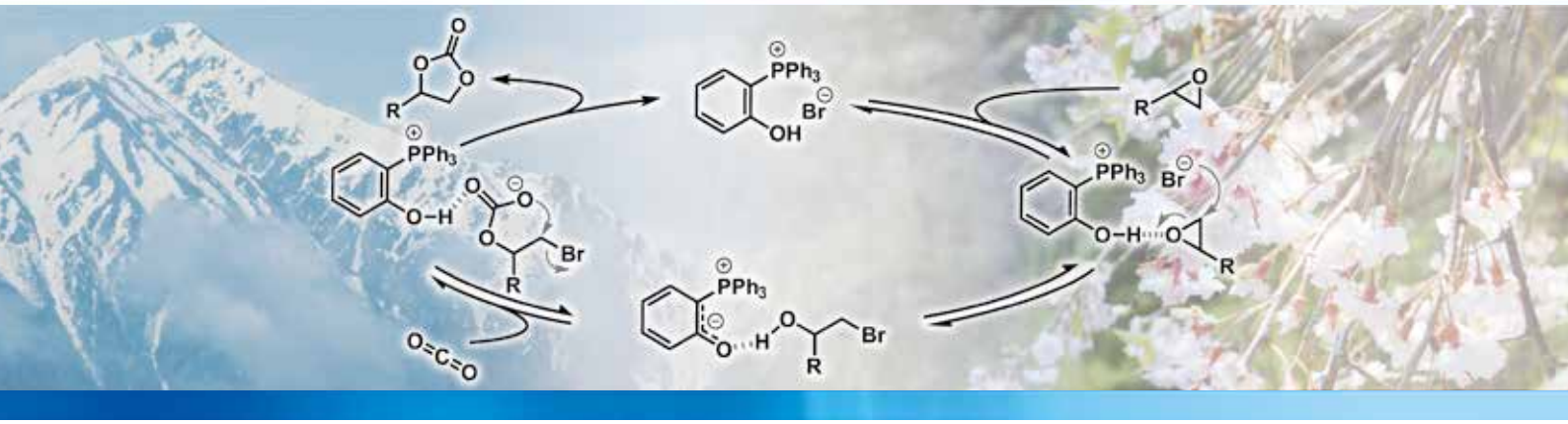
TCIMAIL

No. 183 I SPRING 2020



Contents

ISSN 1349-4848 CODEN:TCIMDW

Research Article

Design of Bifunctional Tetraarylphosphonium Salt Catalysts

Yasunori Toda and Hiroyuki Suga

Department of Materials Chemistry, Faculty of Engineering, Shinshu University: Wakasato, Nagano-shi, Nagano 380-8553, Japan
E-mail: ytoda@shinshu-u.ac.jp; sugahio@shinshu-u.ac.jp

Abstract: The [3+2] reactions between epoxides and carbon dioxide proceeded effectively in the presence of bifunctional tetraarylphosphonium salt catalysts, affording the corresponding cyclic carbonates in high yields. The use of isocyanates instead of carbon dioxide was found to be efficient for the synthesis of oxazolidinones from epoxides. In addition, we have successfully developed a novel phosphonium ylide as a nucleophilic catalyst for selective acylation of primary alcohols.

Keywords: organocatalyst, bifunctional catalysis, phosphonium salt, [3+2] reaction, acylation

1. Introduction

Environmentally-friendly chemical syntheses are desired for creating a sustainable society. In the field of catalysis development, organocatalysts have emerged as green catalysts and great progress in their use has been made over the past two decades. Most organocatalysts have been designed to achieve stereocontrol, especially enantiocontrol, in asymmetric reactions, whereas there are relatively limited numbers of reports on catalysts that enable the control of chemoselectivity intentionally in non-asymmetric reactions. Our group focused on tetraarylphosphonium salts (TAPS), which bear four aryl groups on the phosphorus atom, and has been exploring their catalytic functions. We herein describe the design of bifunctional TAPS catalysts and TAPS-catalyzed [3+2] reactions between epoxides and heterocumulenes. The reactions using a bifunctional TAPS-derived phosphonium ylide as a novel nucleophilic catalyst are also reported.

2. Bifunctional TAPS catalysis

2-1. Catalyst design challenges

Phosphonium salts are phosphorus(V) compounds widely used in organic synthesis as precursors of Wittig reagents, phase transfer catalysts, ionic liquids, and other applications.[1] Tetraarylphosphonium salts (TAPS), which are stereoelectronically tunable, are attractive scaffolds for organocatalysts.[2] As shown in **Figure 1**, it is expected that TAPS bearing a hydroxyl group on an aromatic ring might serve as a bifunctional catalyst composed of a Brønsted acidic site (a phenolic hydroxy group) and a nucleophilic site (a halide ion). However, the catalytic ability of TAPS has remained unexploited.[3] Therefore, we reasoned that the exploration of TAPS functions for catalysis would be fruitful from the viewpoint of developing new molecular technology.

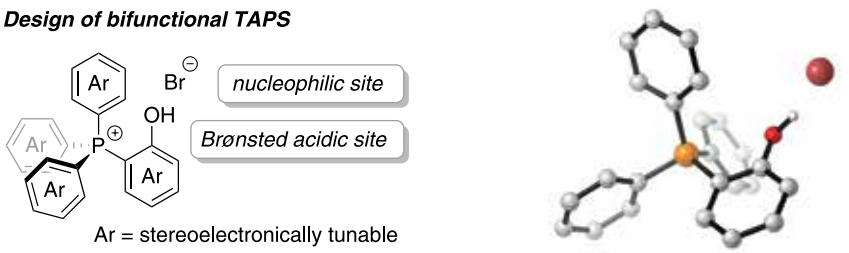
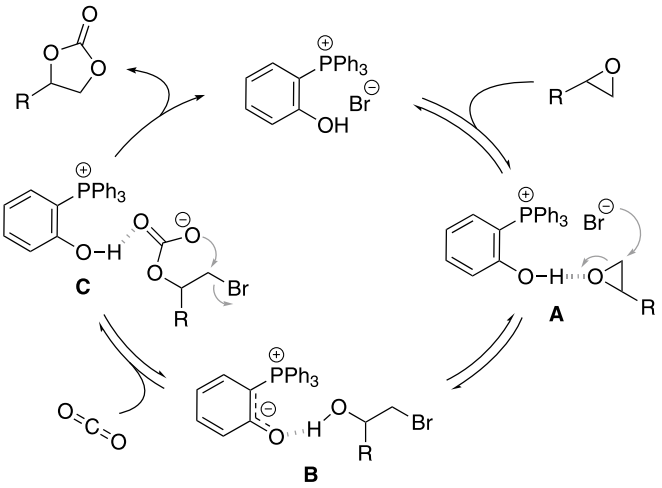


Figure 1. Design of bifunctional TAPS and an optimized structure by DFT calculations (M06-2X/6-31G(d) for C, H, O, and P, M06-2X/LanL2DZ for Br, IEFPCM=PhCl)

2-2. [3+2] Reactions of epoxides with carbon dioxide

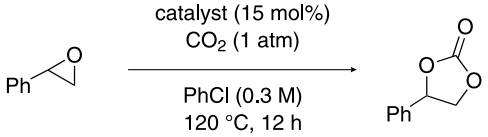
The role of carbon dioxide (CO_2) as a C1 building block of valuable compounds, namely CO_2 fixation, has been recognized as crucial in organic synthesis.[4] One of the most well-known methods is the reaction between epoxides and CO_2 to produce five-membered cyclic carbonates, and several catalytic systems including onium salt catalysis have been reported to date.[5] Thus, we expected that bifunctional TAPS might efficiently promote the epoxide-CO_2 reaction for the following reasons (**Scheme 1**): (i) Brønsted acid activation of the epoxide could accelerate the epoxide ring-opening step by the halide ion (**A**); (ii) the TAPS-derived phosphonium ylide could serve as a Brønsted base to facilitate CO_2 insertion into the halohydrin intermediate **B**. Notably, there are only a few reports of CO_2 fixation using bifunctional phosphonium salt catalysts.[6]

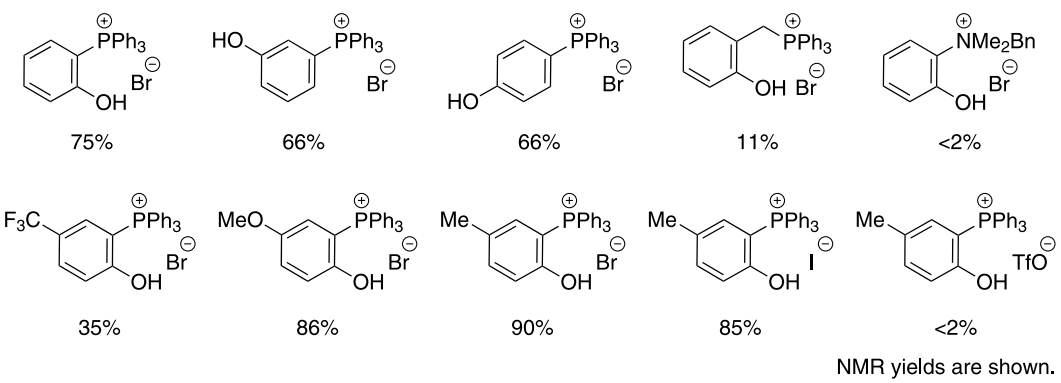


Scheme 1. Working hypothesis of the bifunctional TAPS-catalyzed CO_2 fixation

At the outset of our studies, the screening of TAPS was performed using styrene oxide with 15 mol% of catalyst and a balloon of CO_2 in 0.3 M chlorobenzene at 120 °C for 12 h (**Table 1**). We discovered that a bifunctional TAPS catalyst possessing a phenolic hydroxy group at the *ortho*-position could facilitate the present reaction, affording the corresponding carbonate in moderate yield. Interestingly, the use of different but similar types of onium salts resulted in lower yields. The substituents on the phenol moiety were further investigated, and methyl-substituted TAPS (**MeTAPS-Br**) was found to give the highest yield under the reaction conditions.[7] Switching the bromide ion to a less nucleophilic counterion such as triflate led to no formation of the products, while TAPS having an iodide ion (**MeTAPS-I**) showed comparable reactivity.

Table 1. Catalyst screening in CO_2 fixation

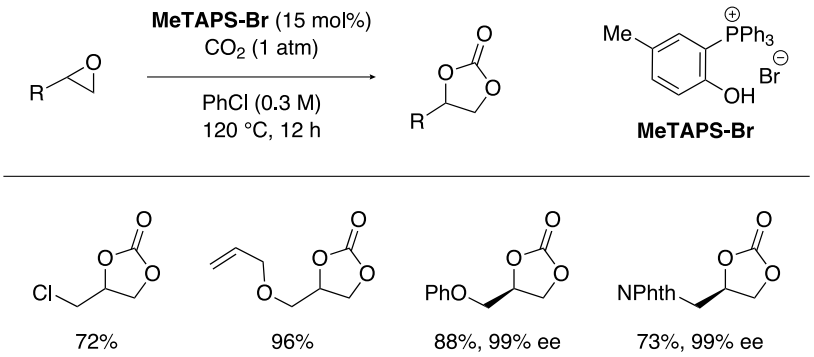




NMR yields are shown.

The scope of epoxides is summarized in **Table 2**. Commercially available terminal epoxides such as epichlorohydrin and allyl glycidyl ether provided the products in good yields. Moreover, enantiopure (*S*)-phenyl glycidyl ether and (*R*)-*N*-glycidylphthalimide underwent the CO_2 fixation in a stereoretentive manner with high enantiomeric excess.

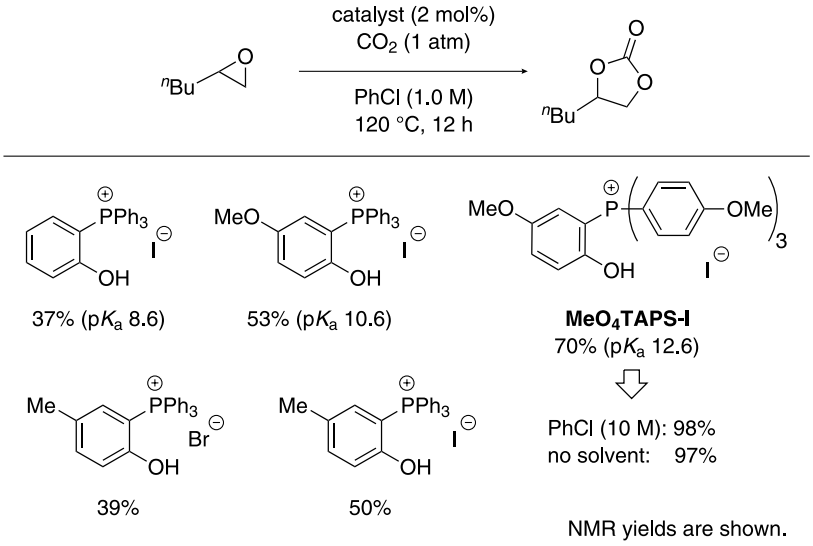
Table 2. Scope of epoxides in CO_2 fixation



2-3. Development of 2nd generation TAPS

Although **MeTAPS-Br** can catalyze the epoxide-CO_2 reaction under atmospheric pressure of CO_2, some issues remained to be addressed, including the amount of the catalyst (15 mol%) and the reaction temperature (120 °C). Thus, we devoted our efforts to the development of highly active bifunctional TAPS in the cyclic carbonate synthesis by scrutinizing electronically-tuned TAPS. It was surprising that less-acidic TAPS bearing methoxy group(s) produced cyclic carbonates in higher yields. Finally, we disclosed that 2 mol% of **MeO$_4$TAPS-I** was able to catalyze the reaction at 60 °C, leading to high yields in 10 M chlorobenzene or solvent-free conditions (**Table 3**).[8] Furthermore, mechanistic studies by DFT calculations revealed that the enhanced catalytic activity by introduction of the methoxy groups on TAPS was attributed to the stabilization of carbonate intermediate **C** in **Scheme 1**.

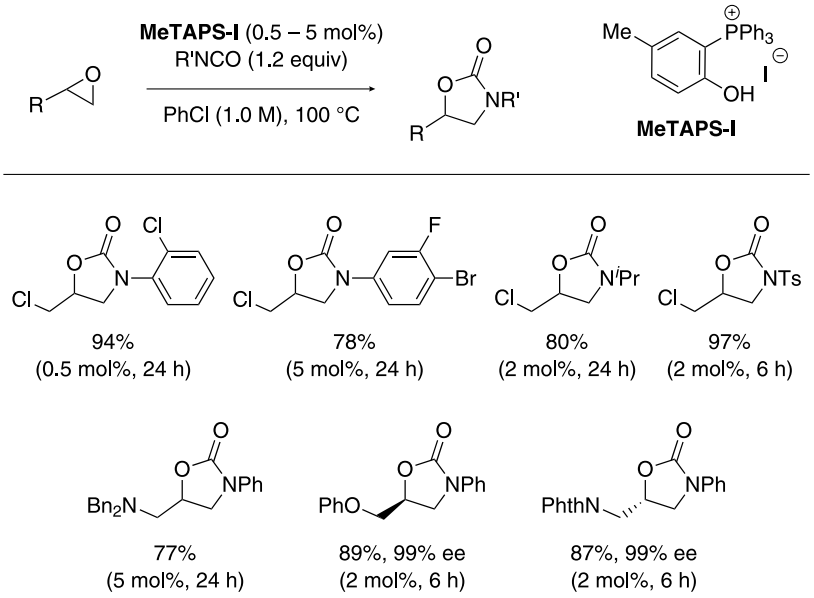
Table 3. Correlation between the acidity and activity of TAPS



2-4. [3+2] Reactions of epoxides with isocyanates

We next focused on the synthesis of oxazolidinones which represent an important class of nitrogen and oxygen containing heterocyclic compounds. It is known that isocyanates, isoelectronic compounds of CO_2, undergo [3+2] reactions with epoxides in the presence of catalysts such as quaternary ammonium salts to form oxazolidinones.[9] However, conventional catalysis would not be applicable to a practical synthesis because harsh reaction conditions or complicated experimental procedures are often required. These problems have some recent modernized solutions using metal (salen) complexes,[10] but the scope of isocyanates has been limited. We hence envisioned that our bifunctional TAPS catalysis might overcome the issues of the epoxide-isocyanate reaction. To our delight, the reaction using 0.5–5 mol% of **MeTAPS-I** efficiently yielded the desired oxazolidinones in 1.0 M chlorobenzene at 100 °C (**Table 4**).[11] It should be emphasized that our catalysis tolerated electron-deficient aryl isocyanates and aliphatic isocyanates, which led to poor yields in most previous reports.

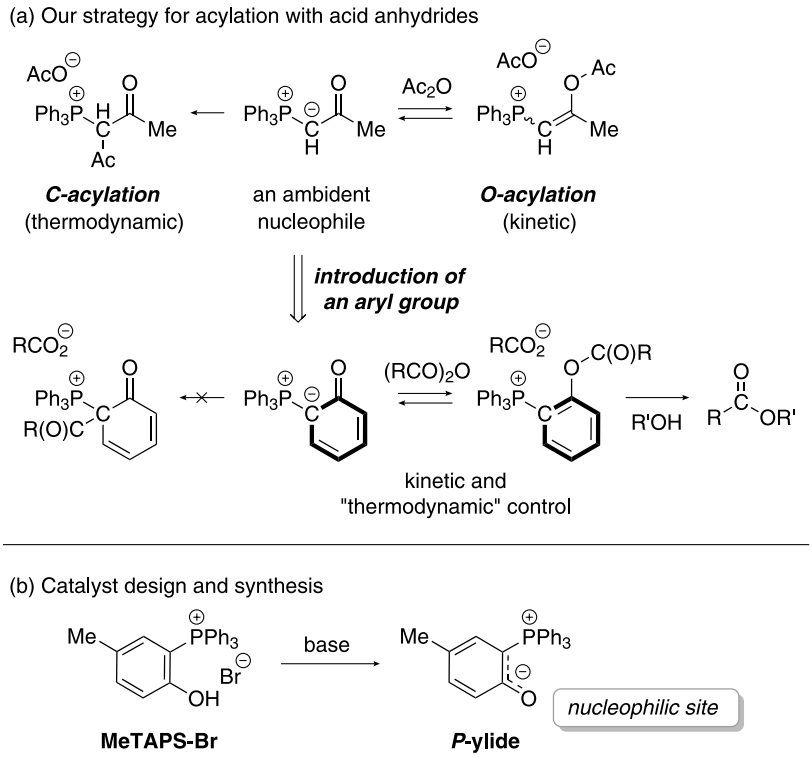
Table 4. Bifunctional TAPS-catalyzed synthesis of oxazolidinones



3. Phosphonium ylide catalysis

3-1. Catalyst design challenges

Carbonyl-stabilized phosphonium ylides (*P*-ylides) are known as ambident nucleophiles.[12] A recent report on the mechanism of this type of *P*-ylide with acetic anhydride suggested that *O*-acylation of the ylides is kinetically favored (**Scheme 2a**).[13] It has also been shown that the *C*-acylated, thermodynamically favored product was obtained exclusively in the same reaction, in which irreversible acyl-transfer from an *O*-acylated ylide to a *C*-acylated ylide occurred. Therefore, it could be feasible to establish nucleophilic catalysis by *P*-ylides if the *O*-acylated intermediate is allowed to undergo acyl-transfer to external nucleophiles. For this investigation, we designed a bifunctional TAPS-derived *P*-ylide (**Scheme 2b**). The aryl group introduced into the ylide carbon moiety is expected to block undesired *C*-acylation, because *O*-acylation gives not only a kinetically stable product but also a thermodynamically stable product due to the aromatic stabilization.

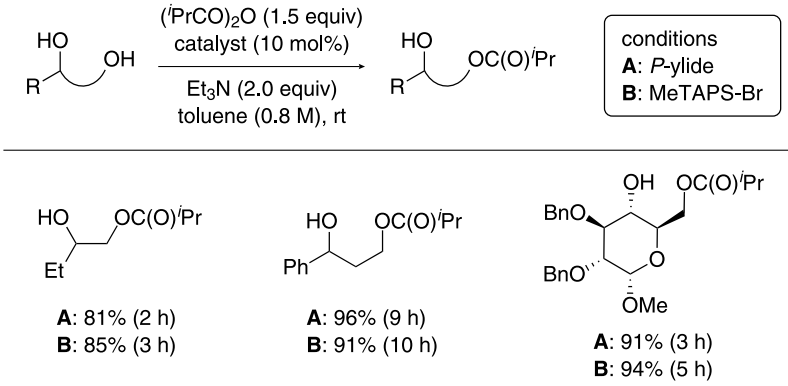


Scheme 2. Design of nucleophilic catalysis by a phosphonium ylide

3-2. Selective acylation of primary alcohols

Selective acylation of a primary alcohol in the presence of secondary alcohol(s) affords great utility in organic synthesis. Several methods such as reagent-control systems[14] and metal catalysis[15] have been developed to date. In contrast, few organocatalysts have been applied to selective acylation,[16] and thus we sought to use the TAPS-derived *P*-ylide as a nucleophilic catalyst for this purpose. The reactions were carried out using 1.5 equiv of isobutyric anhydride, 10 mol% of *P*-ylide (conditions A) or **MeTAPS-Br** (conditions B), and 2.0 equiv of triethylamine in toluene (0.8 M) at room temperature, leading to highly selective acylation of mixed 1,n-diols (**Table 5**).[17] The catalysis can also achieve base-free acylation and acetylation with acetic anhydride.

Table 5. Primary alcohol selective acylation of 1,n-diols



4. Conclusion

TAPS-catalyzed [3+2] reactions between epoxides and heterocumulenes, including CO_2 and isocyanates, are described. The catalytic ability of bifunctional TAPS was proved to catalyze CO_2 fixation under atmospheric pressure of CO_2. This TAPS catalysis is also applicable to the reaction of epoxides with isocyanates, where the scope of isocyanates has been expanded. In addition, a TAPS-derived phosphonium ylide was successfully developed, enabling selective acylation of primary alcohols. We have identified the importance of our catalyst design to exhibit unique behavior. Further synthetic applications would empower TAPS as a fascinating catalyst.

References

(1) (a) B. E. Maryanoff, A. B. Reitz, *Chem. Rev*. **1989**, *89*, 863. (b) R. W. Hoffmann, *Angew. Chem., Int. Ed*. **2001**, *40*, 1411. (c) J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev*. **2002**, *102*, 3667. (d) T. Werner, *Adv. Synth. Catal*. **2009**, *351*, 1469.

(2) (a) D. Marcoux, A. B. Charette, *J. Org. Chem*. **2008**, *73*, 590. (b) D. Marcoux, A. B. Charette, *Adv. Synth. Catal*. **2008**, *350*, 2967.

(3) (a) K. Manabe, *Tetrahedron Lett*. **1998**, *39*, 5807. (b) K. Manabe, *Tetrahedron* **1998**, *54*, 14465.

(4) J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow, W. Leitner, *Chem. Rev*. **2018**, *118*, 434.

(5) (a) T. Sakakura, K. Kohno, *Chem. Commun*. **2009**, 1312. (b) M. North, R. Pasquale, C. Young, *Green Chem*. **2010**, *12*, 1514. (c) R. R. Shaikh, S. Pornpraprom, V. D'Elia, *ACS Catal*. **2018**, *8*, 419.

(6) (a) T. Werner, H. Büttner, *ChemSusChem* **2014**, *7*, 3268. (b) H. Büttner, J. Steinbauer, T. Werner, *ChemSusChem* **2015**, *8*, 2655. (c) J. Großeheilmann, H. Büttner, C. Kohrt, U. Kragl, T. Werner, *ACS Sustainable Chem. Eng*. **2015**, *3*, 2817. (d) D. Wei-Li, J. Bi, L. Sheng-Lian, L. Xu-Biao, T. Xin-Man, A. Chak-Tong, *Appl. Catal., A* **2014**, *470*, 183. (e) S. Liu, N. Suematsu, K. Maruoka, S. Shirakawa, *Green Chem*. **2016**, *18*, 4611.

(7) Y. Toda, Y. Komiyama, A. Kikuchi, H. Suga, *ACS Catal*. **2016**, *6*, 6906.

(8) Y. Toda, Y. Komiyama, H. Esaki, K. Fukushima, H. Suga, *J. Org. Chem*. **2019**, *84*, 15578.

(9) (a) G. P. Speranza, W. J. Peppel, *J. Org. Chem*. **1958**, *23*, 1922. (b) J. E. Herweh, T. A. Foglia, D. Swern, *J. Org. Chem*. **1968**, *33*, 4029. (c) I. Shibata, A. Baba, H. Iwasaki, H. Matsuda, *J. Org. Chem*. **1986**, *51*, 2177. (d) C. Qian, D. Zhu, *Synlett* **1994**, 129. (e) X. Zhang, W. Chen, *Chem. Lett*. **2010**, *39*, 527.

(10) (a) T. Baronsky, C. Beattie, R. W. Harrington, R. Irfan, M. North, J. G. Osende, C. Young, *ACS Catal*. **2013**, *3*, 790. (b) R. L. Paddock, D. Adhikari, R. L. Lord, M.-H. Baik, S. T. Nguyen, *Chem. Commun*. **2014**, *50*, 15187. (c) P. Wang, J. Qin, D. Yuan, Y. Wang, Y. Yao, *ChemCatChem* **2015**, *7*, 1145.

(11) Y. Toda, S. Gomyou, S. Tanaka, Y. Komiyama, A. Kikuchi, H. Suga, *Org. Lett*. **2017**, *19*, 5786.

(12) A. W. Johnson, *Ylides and Imines of Phosphorus*; Wiley: New York, 1993.

(13) P. A. Byrne, K. Karaghiosoff, H. Mayr, *J. Am. Chem. Soc*. **2016**, *138*, 11272.

(14) (a) T. W. Greene, P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 4th Edition; John Wiley & Sons: New York, 2007. (b) S. Yamada, *J. Org. Chem*. **1992**, *57*, 1591. (c) K. Ishihara, H. Kurihara, H. Yamamoto, *J. Org. Chem*. **1993**, *58*, 3791.

(15) (a) G. W. Breton, *J. Org. Chem*. **1997**, *62*, 8952. (b) P. A. Procopiou, S. P. D. Baugh, S. S. Flack, G. G. A. Inglis, *J. Org. Chem*. **1998**, *63*, 2342. (c) A. Orita, A. Mitsutome, J. Otera, *J. Org. Chem*. **1998**, *63*, 2420. (d) M.-H. Lin, T. V. RajanBabu, *Org. Lett*. **2000**, *2*, 997.

(16) (a) P. Ilankumaran, J. G. Verkade, *J. Org. Chem*. **1999**, *64*, 9063. (b) G. A. Grasa, T. Güveli, R. Singh, S. P. Nolan, *J. Org. Chem*. **2003**, *68*, 2812. (c) K. Ibe, Y. Hasegawa, M. Shibuno, T. Shishido, Y. Sakai, Y. Kosaki, K. Susa, S. Okamoto, *Tetrahedron Lett*. **2014**, *55*, 7039.

(17) Y. Toda, T. Sakamoto, Y. Komiyama, A. Kikuchi, H. Suga, *ACS Catal*. **2017**, *7*, 6150.

Author Information

Assistant Prof. **Yasunori Toda**
(Department of Materials Chemistry, Faculty of Engineering, Shinshu University)
Yasunori Toda received his B.S. Chemistry degree from Tohoku University (2008). He obtained his Ph.D. from Tohoku University under the supervision of Prof. Masahiro Terada (2013). He joined the group of Prof. Jeffrey Johnston at Vanderbilt University in June 2013, and then he began a position as Assistant Prof. of Chemistry at Shinshu University in April 2015.

Prof. **Hiroyuki Suga**
(Department of Materials Chemistry, Faculty of Engineering, Shinshu University)
Hiroyuki Suga obtained his Ph.D. from Kyushu University (1988). In 1988, he moved to Osaka University as a research assistant. In 1998, he moved to Shinshu University, and then he began a position as Associate Prof. of Chemistry. He promoted to a full professor in Apr 2006.

Related Products

(2-Hydroxy-5-methylphenyl)triphenylphosphonium Bromide (= MeTAPS-Br)	1g	5g	H1748
(2-Hydroxy-5-methylphenyl)triphenylphosphonium Iodide (= MeTAPS-I)	1g	5g	H1749
Styrene Oxide	25mL	500mL	E0013
Epichlorohydrin	25g	500g	E0012
Allyl Glycidyl Ether	25mL	500mL	A0221
(*S*)-Glycidyl Phenyl Ether	1g	5g	G0410
(*R*)-*N*-Glycidylphthalimide	5g	25g	G0327
Isobutyric Anhydride	25mL	500mL	I0111

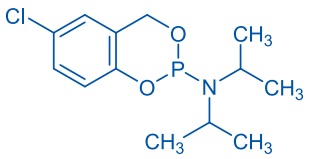
New Product Information

New Reagents for the Synthesis of Triphosphate

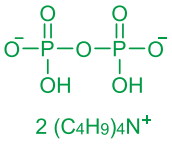
5-Chlorosaligenyl-*N*,*N*-diisopropylphosphoramidite (1) Product Number: **C3326**
200mg 1g

Bis(tetrabutylammonium) Dihydrogen Pyrophosphate (2) Product Number: **B5440**
200mg 1g

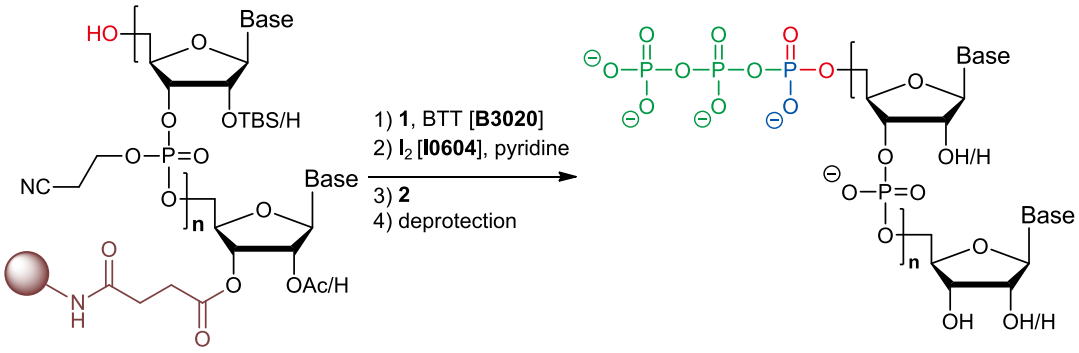
5-Chloro-saligenyl-*N*,*N*-diisopropylphosphoramidite (**1**) and bis(tetrabutylammonium) dihydrogen pyrophosphate (**2**) are useful reagents for introducing a triphosphate group onto the 5'-end of oligonucleotides. These reagents are applicable to both solid phase synthesis and a standard oligonucleitide synthesizer, and are anticipated to be powerful tools in chemical and biochemical research.



1



2



Reference

1) I. Sarac, C. Meier, *Curr. Protoc. Nucleic Acid Chem.* **2016**, 64:4.67.1.

Related Products

5-(Benzylthio)-1*H*-tetrazole (= BTT)			25g	B3020
Iodine		25g	500g	I0604
Tetrabutylammonium Fluoride (*ca.* 1mol/L in Tetrahydrofuran)	25mL	100mL	500mL	T1338

Dipeptides Degradable by Enzyme in Lysosome

Val-Cit-PAB-OH (1) Product Number: **V0155**
25mg 100mg

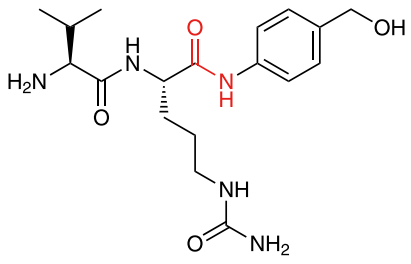
Fmoc-Val-Cit-PAB-OH (2) Product Number: **F1223**
25mg 100mg

Fmoc-Val-Cit-PAB-PNP (3) Product Number: **F1114**
100mg 500mg

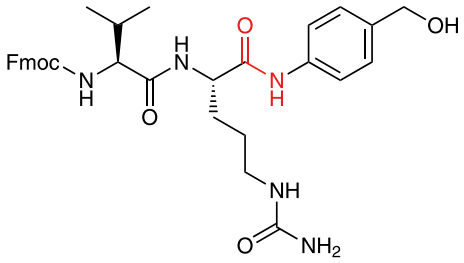
Alloc-Val-Cit-PAB-OH (4) Product Number: **A3348**
250mg 1g

MC-Val-Cit-PAB-OH (5) Product Number: **M3224**
250mg 1g

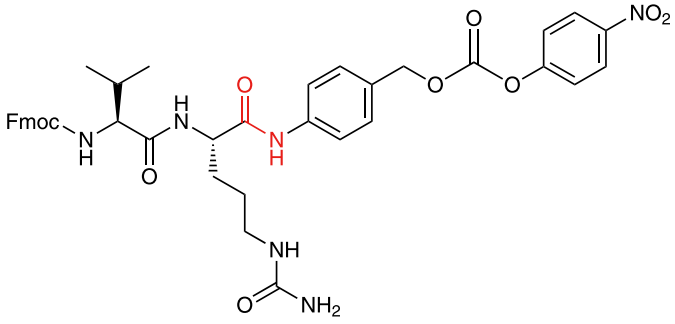
1, **2**, **3**, **4**, and **5** are dipeptides containing valine (Val)-citrulline (Cit) and *p*-aminobenzylalcohol (PAB) moieties. It has been reported that Cathepsin B in the lysosome degrades the peptide bond between Cit-PAB.[1] Therefore, a drug conjugate bound covalently with carbamate bonds between PAB and the drug can be synthesized by using the dipeptide as a linker. The drug can be then released by hydrolysis after cleavage of the peptide bond between Cit-PAB. Antibody-drug conjugates (ADCs) in which the *N*-terminus of Val is bound to an antibody have been developed.[2]



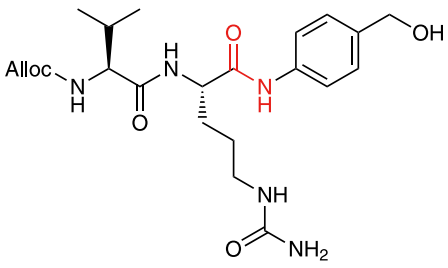
1



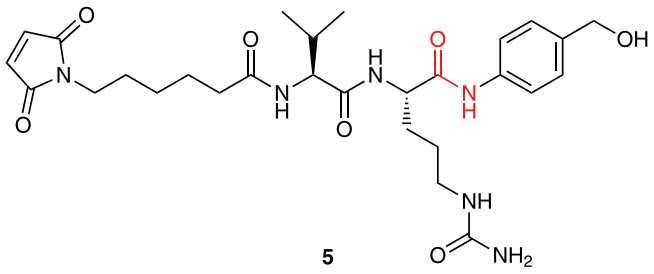
2



3



4



5

References

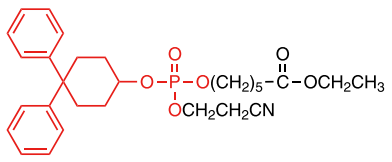
1) G. M. Dubowchik, R. A. Firestone, L. Padilla, D. Willner, S. J. Hofstead, K. Mosure, J. O. Knipe, S. J. Lasch, P. A. Trail, *Bioconjugate Chem*. **2002**, *13*, 855.
2) M. Dorywalska, P. Strop, J. A. Melton-Witt, A. Hasa-Moreno, S. E. Farias, M. G. Casas, K. Delaria, V. Lui, K. Poulsen, C. Loo, S. Krimm, G. Bolton, L. Moine, R. Dushin, T.–T. Tran, S.-H. Liu, M. Rickert, D. Foletti, D. L. Shelton, J. Pons, A. Rajpal, *Bioconjugate Chem*. **2015**, *26*, 650.

Diphenylcyclohexane Derivatives for Research on the Optimization of Pharmacokinetics in Blood

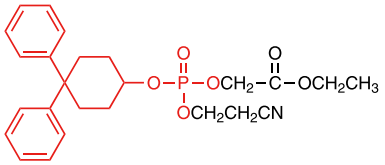
Ethyl 6-[(2-Cyanoethoxy)(4,4-diphenylcyclohexyloxy)phosphoryloxy]hexanoate (1) Product Number: **E1313**
100mg 500mg

Ethyl 2-[(2-Cyanoethoxy)(4,4-diphenylcyclohexyloxy)phosphoryloxy]acetate (2) Product Number: **E1268**
100mg 500mg

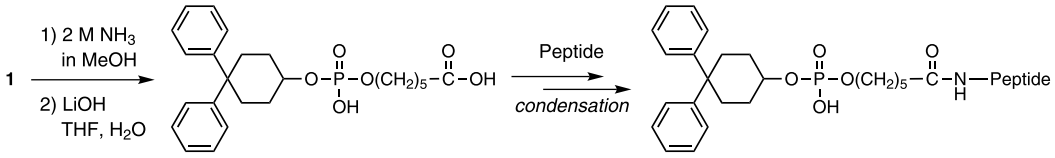
Ethyl 6-[(2-cyanoethoxy)(4,4-diphenylcyclohexyloxy)phosphoryloxy]hexanoate (**1**) is utilized for the improvement of peptide half-life *in vivo*.[1] Zobel *et al*. have found that a peptide modified with **1** has about 50-fold longer half-life time in plasma compared to a non-modified peptide. This idea is based on the notion that diphenylcyclohexyl phosphate moiety of **1** has high affinity to serum albumin.[2] Furthermore, ethyl 2-[(2-cyanoethoxy)-(4,4-diphenylcyclohexyloxy)phosphoryloxy]acetate (**2**), whose alkyl chain length is different from **1**, is also available as a building block to introduce similar moiety in order to optimize pharmacokinetics of peptides in blood.



1
[E1313]



2
[E1268]



References

1) K. Zobel, M. F. T. Koehler, M. H. Beresini, L. D. Caris, D. Comb, *Bioorg. Med. Chem. Lett*. **2003**, *13*, 1513.
2) R. B. Lauffer, D. J. Parmelees, S. U. Dunham, H. S. Ouellet, R. P. Dolan, S. Witte, T. J. McMurry, R. C. Walovitch, *Radiology* **1998**, *207*, 529.

Related Products

4,4-Diphenylcyclohexanol	1g	5g	D4973
Dansylamide [for Albumin binding assay]	25mg	100mg	D5405
Dansylglycine [for Albumin binding assay]	25mg	100mg	D5406
BD140 [for Albumin binding assay]	25mg	100mg	D4898

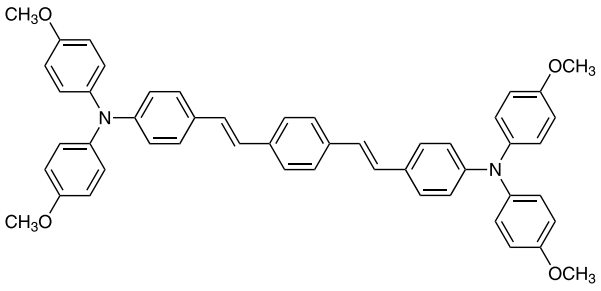
TOP-HTM: New Hole Transporting Materials for Perovskite Solar Cells with High Device Stability

TOP-HTM-α1 (1) Product Number: **B5672**
1g 5g 25g

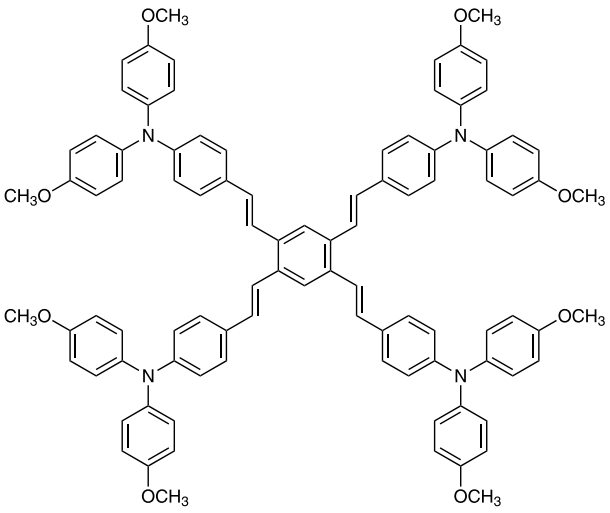
TOP-HTM-α2 (2) Product Number: **T3722**
1g 5g 25g

Perovskite solar cells (PSCs), in which lead halide perovskite is used as a light absorber, have received increasing attention since Miyasaka's first report in 2009.[1] In recent years, the practical development of these PSCs has been conducted around the world because of their high power conversion efficiency (PCE) and the capability to fabricate them on a large scale by solution processes.

Carrier transport materials are key for achieving high PCE and high device stability in PSCs. Spiro-OMeTAD is most widely used as a standard hole transporting material (HTM) in conventional structure PSCs. However, Spiro-OMeTAD is too expensive for the mass production of PSCs. In addition, some additives such as LiTFSI, TBP, and Co(III) complexes, which are necessary to increase PCEs in Spiro-OMeTAD-based PSCs, may promote deterioration of the resulting devices. Therefore, cost-effective and additive-free HTMs are required for the practical development of PSCs. Given these issues, TOP-HTM-α1 (**1**) and TOP-HTM-α2 (**2**) have been developed as new HTMs.[2] They are more cost-effective than conventional HTMs and work without any additives. The $CH_3NH_3PbI_3$ PSCs based on **1** and **2** gave high PCEs of 15.0% and 16.6%, respectively. Furthermore, these devices exhibited higher stability than devices based on Spiro-OMeTAD under continuous 1 sun illumination (**Figure 1**).



1



2

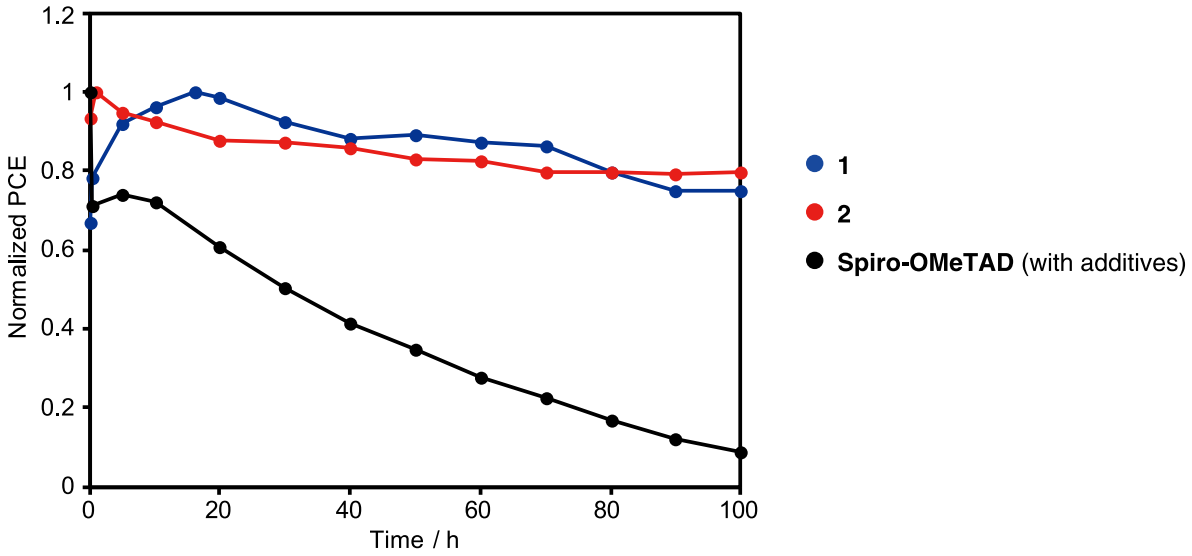


Figure 1. Device stability

1 and **2** were developed in collaboration with Prof. Atsushi Wakamiya, Kyoto University.

References

1) Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells
A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, *131*, 6050.
2) H. Nishimura, I. Okada, T. Tanabe, A. Wakamiya, Pending Patent Application PCT/JP2019/030162.

Related Products

1,4-Bis[4-(di-*p*-tolylamino)styryl]benzene		1g	B2080
4,4'-Bis[4-(di-*p*-tolylamino)styryl]biphenyl		200mg	B4682
V886	1g	5g	V0146
4,4'-(2,3-Dihydrothieno[3,4-*b*][1,4]dioxine-5,7-diyl)bis[*N*,*N*-bis(4-methoxyphenyl)aniline]		200mg	D5155

Tetrahedral Building Blocks for the Synthesis of 3D Covalent Organic Frameworks (COFs) and Porous Polymers

Tetrakis(4-aminophenyl)methane (1) Product Number: **T2947**
200mg 1g

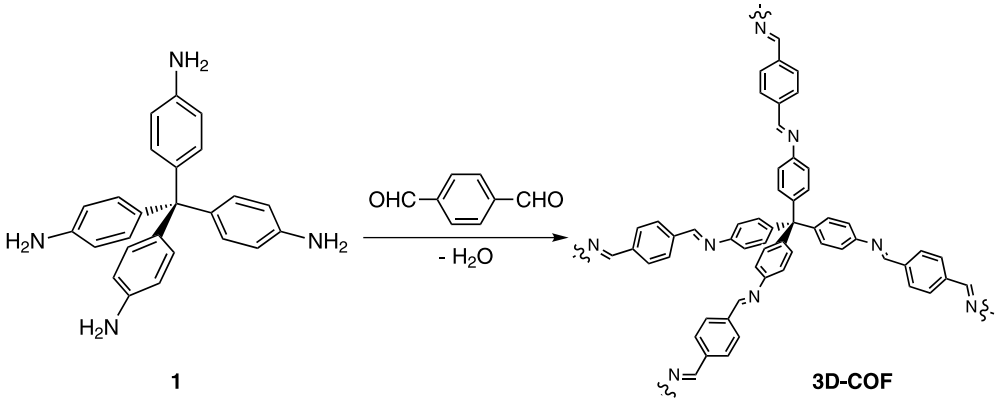
Tetrakis(4-ethynylphenyl)methane (2) Product Number: **T3151**
100mg 1g

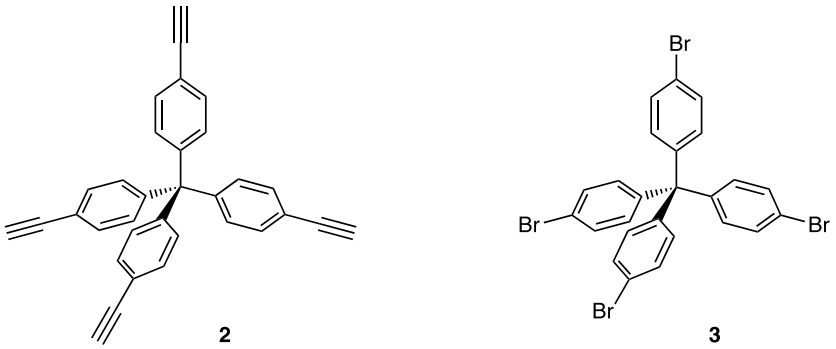
Tetrakis(4-bromophenyl)methane (3) Product Number: **T2960**
1g 5g

Three-dimensional (3D) covalent organic frameworks (COFs) and porous polymers are anticipated to be applicable for gas storage and separation, and as catalysts because of their high specific surface area and thermal stability. COFs are 2D or 3D covalently extended crystalline materials composed of light atoms.[1,2]

Yaghi *et al*. synthesized a 3D-COF by dehydration condensation of tetrakis(4-aminophenyl)methane (**1**) and terephthalaldehyde.[3] The resultant COF was reported to have a diamond-like structure owing to the tetrahedral structure of **1**.

Furthermore, building blocks with tetrahedral centers such as tetrakis(4-ethynylphenyl)methane (**2**) and tetrakis-(4-bromophenyl)methane (**3**) are useful for producing porous polymers. Synthesis of porous polymers by click reactions[4,5] and coupling reactions[4,6] using **2** or **3** have been already reported.





References

1) P. J. Waller, F. Gándara, O. M. Yaghi, *Acc. Chem. Res*. **2015**, *48*, 3053.
2) S. Kandambeth, K. Dey, R. Banerjee, *J. Am. Chem. Soc*. **2019**, *141*, 1807.
3) F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klöck, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc*. **2009**, *131*, 4570.
4) J. R. Holst, E. Stöckel, D. J. Adams, A. I. Cooper, *Macromolecules* **2010**, *43*, 8531.
5) P. Pandey, O. K. Farha, A. M. Spokoyny, C. A. Mirkin, M. G. Kanatzidis, J. T. Hupp, S. T. Nguyen, *J. Mater. Chem*. **2011**, *21*, 1700.
6) T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu, G. Zhu, *Angew. Chem. Int. Ed*. **2009**, *48*, 9457.

Related Product

Terephthalaldehyde	25g	100g	500g	T0010

Phytohormone Mimics for the Study of *Striga*

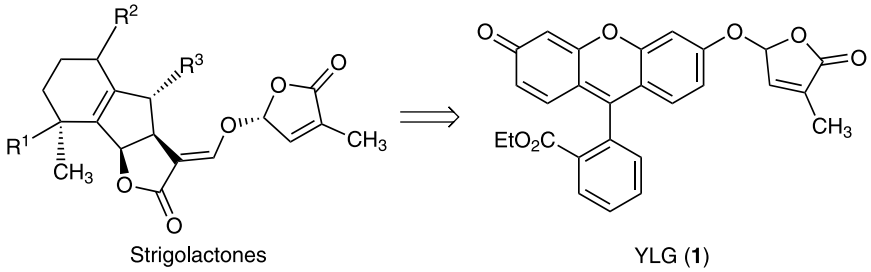
Yoshimulactone Green (YLG) (1)

Product Number: **E1238**
1mg 10mg

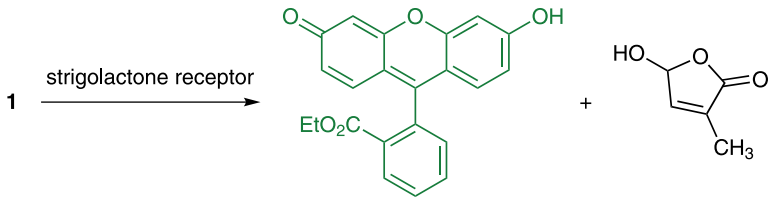
Sphynolactone-7 (2)

Product Number: **P2745**
5mg 25mg

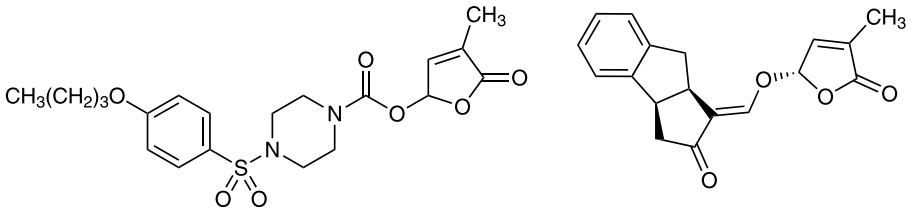
Striga is a parasitic plant called “witchweed” that has been significantly reducing the amount of grains yield especially in Africa.[1] *Striga* germinates by detecting strigolactone, a plant hormone produced from a host plant but the strigolactone receptor had not been identified and the detailed mechanism had not been revealed. Then Hagiwara *et al*. developed Yoshimulactone Green (YLG, **1**),[2] a fluorescent agonist which act on strigolactone receptor. **1** binds to a protein ShHTL which is a strigolactone receptor, and strong green fluorescent products are generated after being hydrolyzed by ShHTL.



Strigolactones YLG (**1**)



Tsuchiya *et al*. established an assay to measure IC_{50} of YLG against ShHTL, and they explored and screened compounds which strongly binds to ShHTL. Finally they discovered Sphynolactone-7 (SPL7, **2**), a strigolactone mimic which binds very strongly to ShHTL7, and they found that it can force *Striga* to germinate and wither in soil without the host plant as a nutrient source.[3] The activity of SPL7 against *Striga* germination is extremely high compared with other existing strigolactone analogs like GR24,[4] but SPL7 binds specifically to the strigolactone receptor of *Striga*. Furthermore, SPL7’s bioactivity as other plants’ hormone is very weak. So it is expected to be used as a revolutionary control method against *Striga*.



SPL7 (**2**) GR24

References

1) G. Ejeta, *Integrating New Technologies for Striga Control*, World Scientific Publishing, **2007**, 3.
2) Y. Tsuchiya, M. Yoshimura, Y. Sato, K. Kuwata, S. Toh, D. Holbrook-Smith, H. Zhang, P. McCourt, K. Itami, T. Kinoshita, S. Hagihara, *Science* **2015**, *349*, 864.
3) D. Uraguchi, K. Kuwata, Y. Hijikata, R. Yamaguchi, H. Imaizumi, S. Am, C. Rakers, N. Mori, K. Akiyama, S. Irle, P. McCourt, T. Kinoshita, T. Ooi, Y. Tsuchiya, *Science* **2018**, *362*, 1301.
4) E. M. Mangnus, F. J. Dommerholt, R. L. P. De Jong, B. Zwanenburg, *J. Agr. Food Chem*. **1997**, *45*, 1409.

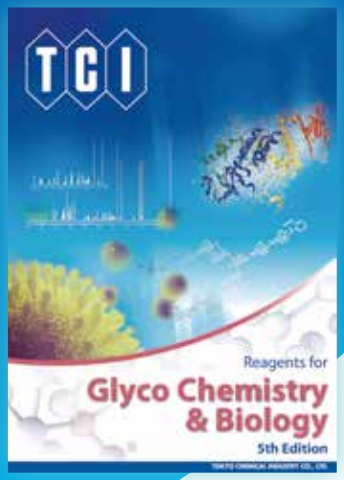
TCIMAIL
SPRING 2020 I No. 183

Reagents for Glyco Chemistry & Biology 5th Edition

<Published on July 2017>

Total of 900 products including 200 new products

- Newly-launched *N*-glycan (synthetic)
- Many oligosaccharides applicable to sugar-conjugation
- ^{1}H NMR spectral data of 250 products
- Categorized and description of products for easy to understand



Useful variety reagent for Glycotechnology research

Request Your Copy Online

www.TCIchemicals.com/g-catalog5/

www.TCIchemicals.com

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 784560
Fax : +44 (0)1865 784561
E-mail : Sales-UK@TCIchemicals.com

TCI Chemicals (India) Pvt. Ltd.
Tel : 1800 425 7889 / 044-2262 0909
Fax : 044-2262 8902
E-mail : Sales-IN@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 CO., LTD.
Tel : +81 (0)3-5640-8878
Fax : +81 (0)3-5640-8902
E-mail : globalbusiness@TCIchemicals.com

TOKYO CHEMICAL INDUSTRY

Printed in Japan