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# Air-Stable tris-(stilbene)Ni(0) Complexes

by Dr. Josep Cornella and Rakan Saeb

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#### **USA Office**

Strem 7 Mulliken Way Newburyport, MA 01950

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USA

Tel: (978) 499-1600 Fax: (978) 465-3104

Prof. Eric Rivard, University of Alberta Prof. Dwight Seferos, University of Toronto

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Tel: (800) 647-8736 Fax: (800) 517-8736

Email: info@ascensusspecialties.com

#### **European Offices**

 Strem
 Tel: +33 (0) 3 88 62 52 60

 15, rue de l'Atome
 Fax: +33 (0) 3 88 62 26 81

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Zone Industrielle Email: info-europe@ascensusspecialties.com F-67800 BISCHHEIM, France

Strem Chemicals UK, Ltd.
An Independent Distributor of Strem Products

Newton Hall Town Street, Newton

Cambridge, CB22 7ZE UK

Tel: +44 (0)1223 873 028 Fax: +44 (0)1223 870 207 Email: enquiries@strem.co.uk

#### Ascensus Specialties Global Headquarters

 Ascensus Specialties
 Tel: (425) 448 1679 / TF

 Global Headquarters
 Tel: (888) 797 9362

 2821 Northup Way, Suite 275
 Email: eat/@acceptains.

Email: ask@ascensusspecialties.com www.ascensusspecialties.com

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## **Glossary of Terms**

[α] <sub>n</sub>	 Specific rotation
AAS	 Atomic Absorption Standard
ACS	 Conforms to American Chemical Society specifications
air sensitive	 Product may chemically react with atmospheric oxygen or carbon dioxide
	at ambient conditions. Handle and store under an inert atmosphere of
	nitrogen or argon.
amp	 Ampouled
b.p.	 Boiling point in °C at 760mm of Hg (Torr), unless otherwise noted
d.	 Density
	 Decomposes
elec. gr.	 Electronic Grade, suitable for electronic applications
f.p.	 Flash point in °F
J .	 Granular
heat sensitive	 Product may chemically degrade if stored for prolonged periods of time at
h.,	ambient temperatures or higher. Store at 5°C or lower.
hydrate	Unspecified water content which may vary slightly from lot to lot Product may absorb water if exposed to the atmosphere for prolonged
hygroscopic	 periods of time (dependent on humidity and temperature). Handle and
	store under an inert atmosphere of nitrogen or argon.
light sensitive	 Product may chemically degrade if exposed to light
liq.	 Liquid
m.p.	 Melting point in °C
moisture sensitive	 Product may chemically react with water. Handle and store under an inert
	atmosphere of nitrogen or argon.
NMR grade	Suitable as a Nuclear Magnetic Resonance reference standard
optical grade	 For optical applications
pwdr.	 Powder
primary standard	 Used to prepare reference standards and standardize volumetric solutions
PURATREM	 Product has a minimum purity of 99.99% (metals basis)
purified	 A grade higher than technical, often used where there are no official
	standards
	 Pore volume
pyrophoric	 Product may spontaneously ignite if exposed to air at ambient conditions
reagent	 High purity material, generally used in the laboratory for detecting,
BEO	measuring, examining or analyzing other substances
REO	 Rare Earth Oxides. Purity of a specific rare-earth metal expressed as a percentage of total rare-earths oxides.
C A	 Surface area
store cold	Product should be stored at -18°C or 4°C, unless otherwise noted (see
Store Colu	 product details)
subl.	 Sublimes
superconductor grade	 A high purity, analyzed grade, suitable for preparing superconductors
tech. gr.	 Technical grade for general industrial use
TLC	 Suitable for Thin Layer Chromotography
	 Vapor pressure mm of Hg (Torr)
xtl.	 Crystalline
	•

### **About Purity**

Chemical purity	 is reported after the chemical name, e.g. Ruthenium carbonyl, 99%
Metals purity	 is reported in parentheses with the respective element, e.g. Gallium (III)
	bromide, anhydrous, granular (99.999%-Ga) PURATREM where
	100% minus the metal purity is equal to the maximum allowable
	percentage of trace metal impurity

#### **Biographical Sketches**



#### Dr. Josep Cornella

Josep Cornella (Pep) was born in La Bisbal del Penedès, a small town in south Catalunya. He graduated in chemistry in 2008 from the University of Barcelona and carried MSc studies in the Department of Organic Chemistry studying the chemistry of allylboron reagents. After completing his masters thesis, he moved to the United Kingdom to pursue doctoral studies in the group of Prof. Igor Larrosa (QMUL). In early 2012, he earned his PhD working on the use of aromatic carboxylic acids as aryl donors in metal-catalyzed decarboxylative reactions. He then moved back to Catalunya, where he joined the group of Prof. Ruben Martin (ICIQ) with a COFUND Fellowship

and later as Marie Curie Postdoctoral Fellow. There, he developed novel transformations involving Ni-catalyzed C–O bond activation and carbon dioxide insertion into organic molecules. In 2015, Pep obtained a Beatriu de Pinós Fellowship to carry out further postdoctoral studies in the group of Prof. Phil S. Baran at The Scripps Research Institute, California, USA. During this time, he worked on the discovery and implementation of new transformations based on the concept of "redox-active esters" as practical and readily available partners for Ni- and Fe-catalyzed C–C bond forming reactions. In summer 2017, he was selected as Max Planck Research Group Leader (MPRGL) to create and lead the Laboratory for Sustainable Catalysis at the Max-Planck-Institut für Kohlenforschung (Germany). His work focuses on the development of sustainable catalytic strategies based on the design of ligands, reagents and catalysts to streamline organic synthesis.



#### Rakan Saeb

Rakan grew up in Munich and studied Chemistry at the Ludwig Maximilian University of Munich (LMU Munich). He carried out undergraduate research in the group of Dr. Oliver Thorn-Seshold, working on the synthesis of novel topoisomerase inhibitors, as well as in the group of Prof. Paul Knochel, studying the chemistry of organolithium species. During his undergraduate studies Rakan worked in the biotech company 4SC AG, synthesizing potential drug candidates for cancer treatment. Driven by his interest in organometallic chemistry and catalysis, he joined Dr. Josep Cornella at the Max-Planck-Institut für Kohlenforschung, focusing on studies on Ni(0)-olefin complexes. In 2021 he graduated from LMU Munich, obtaining a M.Sc. in chemistry and

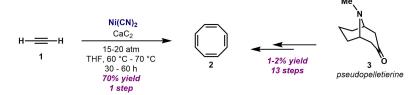
is currently pursuing PhD studies with Dr. Cornella, further investigating the chemistry of Ni(0)-olefin complexes.

#### Air-Stable tris-(stilbene)Ni(0) Complexes<sup>1</sup>

Dr. Josep Cornella and Rakan Saeb Max-Planck-Institut für Kohlenforschung Kaiser-Wilhelm-Platz, 1 45470 Mülheim an der Ruhr Germany

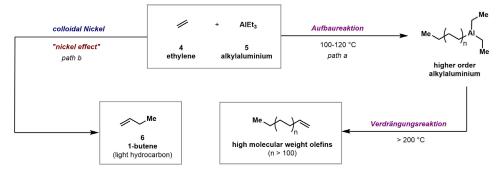
#### Ni-olefin chemistry: a brief historical perspective

In 1897, Sabatier and Senderens reported on the gas-phase hydrogenolysis<sup>2</sup> and hydrogenation<sup>3</sup> of substances aided by nickel (Ni) salts, a feature considered as the beginning of Ni catalysis. Despite the power of this seminal milestone, the application of Ni in the context of organic molecules remained underexplored for several years. In a remarkable example, Reppe reported on the tri- and tetramerization of acetylene (1) to generate benzene<sup>4</sup> and COT (cyclooctatetraene, 2),<sup>5</sup> respectively. Up until then, the synthesis of tetraene 2 had been limited to the modification of *pseudopelletierine* (3), a naturally occurring compound obtained from the root-bark of the pomegranate tree. At that time, the synthesis of COT required a 13-step sequence, affording an overall yield of 1-2%.<sup>6</sup> Yet, the application of Ni(CN)<sub>2</sub> on simple acetylene (1), led to the synthesis of COT in an outstanding 70% yield in one catalytic step (Scheme 1).<sup>5,7</sup> This example illustrates the power of catalysis and highlights the paradigm shift in the construction of organic molecules.



Scheme 1: The power of catalysis: catalytic preparation of COT vs. traditional synthetic route.

Although the work of Reppe truly epitomizes the remarkable synergy between alkynes and Ni, the studies on the interactions between Ni and unsaturated compounds by Prof. Karl Ziegler and Prof. Günther Wilke laid the foundations of modern organonickel chemistry and industrial applications thereof. Yet, these contributions initiated with an unexpected and serendipitous observation during the study of the catalytic synthesis of higher molecular weight olefins from simple ethylene (4). The process under investigation at that time at the Max-Planck-Institut für Kohlenforschung was the "Aufbaureaktion" (addition reaction), where triethylaluminum (5) adds into terminal olefins to generate higher order alkylaluminum compounds (Scheme 2). At that time, this process received a lot of attention as it permitted the rapid synthesis of surfactants. Raising the reaction temperature leads to further addition of the alkylaluminium reagent into ethylene ("Verdrängungsreaktion", displacement reaction) which, after elimination resulted in the formation of high order α olefins (Scheme 2, path a).8 In a routine experiment in 1952, Erhard Holzkamp, a researcher working with Ziegler, did not obtain the expected polymerized olefins when heating 100 atm of ethylene with triethylaluminum to 100 °C. Instead, the reaction yielded mainly 1-butene (6). This unexpected outcome was systematically repeated by Holzkamp and led to a focused investigation into what were the critical factors that changed the outcome of the well-established "Verdrängungsreaktion".9 Scientists concluded that traces of metallic particles, formed after exhaustive acidic washings of the reactor walls, were responsible for catalyzing the formation of 1-butene. This hypothesis led scientists to examine all elements of the periodic table to identify which element was responsible for the observed reactivity. Finally, it was found that Ni salts were the catalysts responsible for the formation of 1-butene, and this reactivity became known as the "nickel effect" (Scheme 2, path b).9 It is important to mention that the exhaustive scrutiny of a plethora of salts of different elements led to the discovery that titanium/aluminum catalysts efficiently catalyze the polymerization of olefins under mild conditions,9 an achievement that led Karl Ziegler together with Giulio Natta to be awarded with the Nobel Prize in Chemistry in 1963.10



Scheme 2: The "Aufbaureaktion", the "Verdrängungsreaktion", and the "nickel effect".

The discovery of the "nickel effect" opened up a new field of research and spurred a myriad of programs studying the interaction and reactivity of unsaturated hydrocarbons with nickel compounds.7, 11-13 Reed reported that Reppe catalysts based on Ni(CO), were able to catalyze the dimerization of butadiene (7) to generate COD (1,5-cyclooctadiene, 8) in 30% – 40% yield. 14 However, treatment of other Ni(II) salts with organometallic reagents would lead to the precipitation of metallic nickel with poor catalytic reactivity.<sup>15</sup> Nevertheless, Wilke and co-workers studied further the "nickel effect" responsible for the abovementioned dimerization. Hence, when Ni(acac), was mixed with phenylacetylene (9) (as stabilizer) and reduced with organoaluminum compounds. 24% COD and 63% t.t.t-CDT (trans.trans.trans.trans.1.5.9cyclododecatriene, 10) were obtained (Scheme 3A). 15-16 By altering the compound that stabilizes the reduced nickel, Wilke was capable of shifting the course of the reaction, thus favoring either the trimerization or the dimerization products (Scheme 3B). 15, 17-18 This procedure was of high industrial relevance at that time, as CDT could be used as a starting material for the synthesis of dodecandioic acid and azacyclotridecan-2-one; precursors in the production of polyesters and super polyamides. 19 To the best of our knowledge, this is one of the first examples in which, by changing the "stabilizer" that affects the Ni center, a completely different reaction outcome is obtained. 15, 17-18 We currently understand this as the effect of the ligand on the Ni, which influences the energy of transition states, leading to different reaction pathways.

A. Wilke's reaction of butadiene with Ni and aluminium reagents

B. Wilke's reaction of butadiene with Ni and aluminium reagents with different ligands

Scheme 3: (A) Dimerization of butadiene by employing the "nickel effect". (B) By altering the stabilizer, t,t,t-CDT and 1.5-COD could be generated with high selectivity and excellent yields. 15, 17-18

Studies on the mechanism of the cyclooligomerization of butadiene led to the synthesis, isolation and characterization of the 16-electron complex (*trans,trans,trans*-cyclododeca-1,5,9-triene)nickel(0) (Ni(*t*-CDT), **13**), which represents an early example of *homoleptic metal-olefin complexes*. <sup>15-16, 20-21</sup> Addition of 1,5-cyclooctadiene (COD) led to displacement of CDT from the nickel center and concomitant formation of the 18-electron bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)<sub>2</sub>, **14**). Both complexes turned out to be applicable in the catalytic trimerization of butadiene, <sup>15</sup> and can be easily prepared from Ni(acac)<sub>2</sub> and AIR<sub>2</sub> (Scheme 4). <sup>16, 21</sup>

Scheme 4: Synthesis of the first homoleptic Ni(0)-olefin complexes. 15-16, 20-21

The facile access to Ni(COD), (Strem 28-0010) and Ni(t-CDT) laid the foundations for the development of other Ni(0)-olefin complexes and accelerated the research on organonickel chemistry. Since then, the 18-electron Ni(COD), has reigned sovereign as a source of Ni(0) due to its relative stability compared to other Ni(0) precursors, and facile exchange of its COD ligands. Despite the vast utility, both, Ni(t-CDT) and Ni(COD), suffer from instability towards air, thus decomposing rapidly to Ni black when exposed to traces of oxygen. The lability of the COD and t,t,t-CDT ligands provides great reactivity for ligand exchange; nevertheless, this property is tightly connected to thermal instability, requiring storage of these compounds under cryogenic conditions to avoid decomposition.<sup>22</sup> Despite the great success of Ni(COD)<sub>a</sub> as a Ni(0) source, efforts have been placed in developing alternative Ni(0) sources to circumvent such practical caveats. Over the years, other 18-, 16-, and even 14-electron Ni(0)-olefin complexes were developed. The latter, represent extremely sensitive compounds which have been shown to be highly pyrophoric. 11-12 A solution to their stability is the addition of external σ-donating phosphines<sup>12</sup> or NHC ligands, thus turning an unstable 14-electron Ni(0)-olefin complexes into stable heteroleptic 16-electron complexes.<sup>23</sup> This strategy was recently applied by Montgomery and Hazari, showing that such complexes can be applied as synthons for other bis-olefin-Ni(0) complexes as well as some air-stable pre-catalysts. <sup>24-27</sup> In addition, Ni(II) pre-catalysts bearing various σ-donating ligands, <sup>28-32</sup> NHC-Ni(0)-olefin complexes, <sup>24-27</sup> as well as encapsulation of Ni(COD), with paraffin<sup>33</sup> have been developed and represent only a few examples of providing practical access to Ni(0) for catalysis. Some of these pre-catalysts are indeed extremely useful and are now commercially available in the Strem catalog. While being extremely valuable solutions for specific problems, different issues associated with such complexes still exist. For example, these complexes usually lack modularity, and thus restrict extensive ligand survey. Additionally, the necessity of reducing Ni(II) complexes via ligand exchange/reduction/ disproportionation pathways in order to release a Ni(0) species can result in undefined ligand to metal ratios and formation of undesired salt byproducts.34 Therefore, a modular Ni(0) source that enables rapid and broad ligand screening and would not suffer from the issues connected to Ni(COD), was still highly coveted.

Afundamental discovery in the area of Ni(0)-olefin complexes was reported by Steigerwald and Nuckolls. While searching for a stable tetraalkyl Ni(IV) complex, the authors synthesized a unique 16-electron Ni(0)-olefin complex bearing three (5*Z*,11*E*)-dibenzo[*a*,*e*][8]annulene molecules as ligands (15). The authors obtained crystallographic evidence for its connectivity and pointed out a rather exceptional stability towards oxidation under air; however, no catalytic application was reported (Figure 1).<sup>35</sup>



Nuckolls' and Steigerwalds complex

Figure 1: Air-stable 16-electron Ni(0)-olefin complex.35

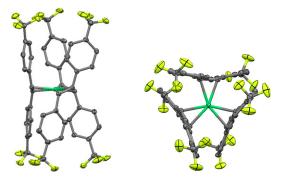
Despite this isolated precedent, Ni(COD)<sub>2</sub> still dominates the field of organonickel chemistry for 60 years as Ni(0) precursor. Recently, Schrauzer's air-stable Ni(0)-olefin complex Ni(COD)(DQ) (<u>Strem 28-0040</u>) (DQ = duroquinone, **16**)<sup>36</sup> was reported by Engle to be catalytically active in certain catalytic domains where a strongly nucleophilic ligand is present.<sup>37</sup>

#### Ni(4-CF3 stb) 2 - 1st generation of air-stable Ni(0)-olefin pre-catalysts

During our investigations on the mechanism of a low-temperature Ni-olefin-Li-catalyzed Kumada-Corriu cross-coupling, the preparation of various 16-electron Ni(0)-olefin complexes was of great interest.  $^{36-39}$  We turned our attention to a rather forgotten complex reported by Wilke in a patent: Ni(t-stb) $_3$  (tris-(trans-stilbene)Ni(0), 17). This complex was originally prepared by an olefin exchange reaction, using Ni(t-CDT) and trans-stilbene. $^{21}$  Similar to Steigerwald and Nuckolls' complex (15), $^{35}$  17 exhibited certain stability when exposed to air (6 hours at 25 °C or 3 days at 0 °C without decomposition). Yet, Ni(t-stb) $_3$  was temperature sensitive and slow ligand dissociation eventually led to decomposition (<1 week). $^{22}$  When trifluoromethyl groups were introduced at the para-position of the stilbene (trans-1,2-bis(4-trifluoromethyl)phenyl)ethene,  $^{4$ -CF3}stb, 18), Ni( $^{4$ -CF3}stb) $_3$  (19) was obtained in 70% yield (Scheme 5, left). $^{22}$  Surprisingly, Ni( $^{4$ -CF3}stb) $_3$  exhibited a remarkable air-stability for several months when kept in a freezer at  $^{-1}$ 8 °C, and could be manipulated at ambient temperature on a benchtop setting for several days before decomposition was observed. $^{22}$ 

Scheme 5: Syntheses of 19.

X-ray analysis revealed that, similarly to **15** and **13**, Ni( $^{4\text{-}\text{CF}3}$ stb) $_3$  consists of three olefin ligands wrapped around the Ni center in a propeller-like arrangement, thus rendering a slightly distorted trigonal-planar coordination geometry (Figure 2). Donation of electron density from the Ni center towards the olefin  $\pi^*$  orbitals results in an elongation of the stilbene olefin bond lengths (average of 1.389 Å), which coincides with Nuckolls' and Steigerwald's complex (**15**) (average of 1.39 Å) $^{35}$  and with Ni(COD) $_2$  (average of 1.39 Å). $^{22,40}$  It is noteworthy to point out that Ni( $^{4\text{-CF}3}$ stb) $_3$  is chiral, resulting in a racemate in the unit cell. With the goal of facilitating the synthesis of **19**, a practical method was developed utilizing the traditional Wilke recipe: reduction of Ni(acac) $_2$  with AlEt $_3$  in the presence of **18** generated 23 g of the complex in high yields in a single run (95%, Scheme 5, right). Besides the X-ray analysis, additional information on the 1:3 metal:ligand ratio of **19** was obtained by elemental analysis, coordination with external ligands as well as by degradation studies. However, no conclusive NMR analysis was obtained for this complex and thus, it could not be discarded that the powder form of the complex consists of alternative coordination modes around the Ni center. Studies toward fully elucidating the structural features of **19** are currently ongoing in our laboratory.



**Figure 2:** ORTEP diagram of complex **19**. Ar = p-CF $_3$ -C $_r$ - $_t$ - $_t$ - $_t$ -Crystallized from toluene. Two molecules of toluene are present in the unit cell (omitted for clarity). Colors: Green: Ni; Black: C; Yellow: F. Hydrogen atoms were omitted for clarity. Left: side view. Right: top view along the principal axis.

#### Ligand exchange studies

In order to evaluate the potential of  $\mathrm{Ni}(^{4\text{-}\mathrm{CF3}}\mathrm{stb})_3$  as a viable  $\mathrm{Ni}(0)$  source for catalysis, its ligand exchange abilities were explored. Hence,  $\mathrm{Ni}(^{4\text{-}\mathrm{CF3}}\mathrm{stb})_3$  was mixed with a set of different ligands commonly applied in nickel catalysis, namely phosphines and diamines. Interestingly, complex **19** underwent smooth ligand exchange with bidentate phosphines such as dppf (1,1)-bis-(diphenylphosphino)ferrocene, **20**),  $^{41\text{-}42}$  monodentate triphenyl phosphine (PPh $_3$ , **21**) and amines such as 2,2'-bipyridine (bipy, **22**) (Scheme 6). $^{43\text{-}44}$  In all cases, 16-electron complexes were formed bearing one  $^{4\text{-}\mathrm{CF3}}\mathrm{stb}$  unit. The products formed were characterized by crystallographic and spectroscopic techniques, and identified as (dppf)  $\mathrm{Ni}(^{4\text{-}\mathrm{CF3}}\mathrm{stb})$  (**23**),  $\mathrm{(PPh}_3)_2\mathrm{Ni}(^{4\text{-}\mathrm{CF3}}\mathrm{stb})$  (**24**) and (bipy) $\mathrm{Ni}(^{4\text{-}\mathrm{CF3}}\mathrm{stb})$  (**25**) respectively. $^{22}$  The latter example exhibits similar features as Nuckolls' and Steigerwald's complex, when two ligands in **15** are displaced by bipy. $^{35}$ 

Scheme 6: Ligand exchange reactions investigated for Ni(4-CF3stb), with dppf, PPh, bipy and THF.

As shown in Scheme 6, ligand exchange with complex **19** is highly facile for a variety of mono-and bidentate ligands. Yet, such facile ligand exchange turned out to be its Achilles heel: when dissolved in THF at room temperature in the absence of any supporting ligand such as diamine, phosphine or NHC, **19** would rapidly decompose into Ni black. Attempts to intercept intermediates of this decomposition resulted in the isolation of the extremely sensitive compound  $Ni(^{4-CF3}stb)_2(THF)$  (**26**) at a very low temperature, which corresponds to the substitution of one  $^{4-CF3}stb$  for a THF molecule. Although still speculative, formation of **26** suggests that decomposition of **19** in THF solutions proceeds via ligand dissociation facilitated by the nucleophilic ethereal solvent. Decomposition of tris-Ni(0)-olefin complexes in ethereal solvents has been noted in the case of the 16-electron complex ( $\mu\eta^2,\eta^2C_7H_{12}$ ) [ $Ni(\eta^2,\eta^2C_7H_{12})I_2$ ]. While no evidence was provided, ligand displacement by THF at 20 °C was believed to be the reason for decomposition. Due to that rapid exchange of ligands in solution, complete characterization of the  $Ni(^{4-CF3}stb)_3$  in solution still poses severe challenges.

#### Catalytic transformations

The facile ligand exchange in **19** observed in solution immediately revealed that this behavior should be of high value in catalytic contexts. Moreover, complex **19** has been shown to deliver well-defined Ni(0):L ratios, thus permitting a control over the species at the onset of the reaction. In order to explore the catalytic abilities of **19**, a survey of important catalytic transformations, which utilize Ni as catalyst was performed. The results were benchmarked with the yields reported using either Ni(COD)<sub>2</sub> or an alternative Ni(II) precursor.

Hartwig and co-workers reported that Ni(COD)<sub>2</sub> was inefficient in the formation of heterobiaryls, making the application of a Ni(II) species essential for a successful coupling.<sup>28</sup> Ni(<sup>4</sup> <sup>CF3</sup>stb)<sub>3</sub> turned out to be a good pre-catalyst in this catalytic transformation, resulting in the generation of high yields (>99%) of the coupling product (27). When Ni(<sup>4-CF3</sup>stb)<sub>3</sub> was stored for more than 180 days in a freezer under air, an 82% yield was obtained (Scheme 7Å).<sup>22</sup> Good yields were also observed in the aryl coupling with acetals developed by Doyle (Scheme 7B).<sup>22,46</sup> Furthermore, 19 demonstrated to be also applicable in C(sp²)–C(sp²) Negishi cross-coupling reactions between an aryl bromide and a vinyl zinc reagent (Scheme 7C).<sup>22,47</sup> In the context of alkyl-alkyl Negishi coupling, 19 also performed well although higher temperatures where required (Scheme 7D).<sup>22,48</sup> The requirement of higher temperature might indicate that differences between Ni(COD)<sub>2</sub> and Ni(<sup>4-CF3</sup>stb)<sub>3</sub> might exist in generating the catalytically active species (*vide infra*). Heck coupling also were amenable and 19 afforded good yields of the C–C product 31 (Scheme 7E).<sup>22,49</sup>

Scheme 7: C–C bond forming reactions catalyzed by 19. (A) Heteroaryl Suzuki cross-coupling. (B) C–O arylation of acetals. (C) Aryl-vinyl Negishi cross-coupling. (D) Alkyl-Alkyl Negishi cross-coupling. (E) A Heck-type reaction. <sup>a</sup>This reaction was performed with a batch of 19 that was stored in a freezer at –18 °C under air for >180 d. <sup>b</sup>The yield was determined by gas chromatography with a flame ionization detector using an internal standard. <sup>a</sup>C5 °C. <sup>b</sup>Using a catalyst stored under air at 25 °C for 14 d.

The cycloaddition of benzonitrile with 2,3-dimethylbuta-1,3-diene, using catalytic amounts of  $PCy_3$  and  $Ni(COD)_2$ , was reported to generate the pyridine derivative **32** in 88% yield.<sup>50</sup> When  $Ni(^{4-CF3}stb)_3$  was employed, a yield of 84% was achieved. Additionally, when displacing the air-sensitive ligand by its protonated air-stable counterpart  $PCy_3 \bullet HBF_4$  together with amounts of  $K_3PO_4$ , equimolar to the ligand, an only slightly reduced yield (77%) was obtained, permitting the performance of this catalytic transformation without the need of a glovebox (Scheme 8A).<sup>22</sup>

**Scheme 8**: Additional examples of Ni(0)- catalysis. (A) Oxidative cyclization. (B) C–H activation. (C) Buchwald-Hartwig C–N bond formation with alkylamines. (D) C–SMe reduction with silanes. <sup>a</sup>This reaction was performed using PCy<sub>a</sub>. <sup>b</sup>The yield was determined by gas chromatography with a flame ionization detector using an internal standard.

While first examples of C(sp²)–H bond activation were already reported in 1963,<sup>51</sup> it was not until recently that Ni-catalyzed C–H activation became a routinely explored strategy. Following a recent protocol by Chatani,<sup>52</sup> isoquinolone derivative **33** (Scheme 8B) could be generated in an excellent yield of 94% (86% with Ni(COD)<sub>2</sub>).<sup>22,52</sup> Another cross-coupling reaction of paramount importance is the Buchwald-Hartwig amination reaction to forge C(sp²)–N bonds.<sup>53</sup> Amination of 4-chlorobenzotrifluoride with morpholine proceeded smoothly with the aid of SIPr as the ligand for Ni (91%, Scheme 8C, **34**).<sup>22,32</sup> Ni(0)-olefin complexes were demonstrated to be a valuable source for the formation of heterogeneous Ni(0) nanoparticles by Martin and co-workers. Reduction of 2-(methylthio)naphthalene with silanes afforded 91% yield of **35** (Scheme 8D).<sup>22,54</sup>

Finally, we demonstrated that  $Ni(^{4-CF3}stb)_3$  was able to have orthogonal reactivity to that of  $Ni(COD)_2$ . For example, in the C–H activation of electron-poor arenes, the use of  $Ni(COD)_2$  results in the formation of catalytically inactive species as a result of hydrometalation of the COD. Yet, the electron-deficient nature of the double bond in  $^{4-CF3}stb$  prevents such hydrometalation in the ligand, and permits the hydrometalation to occur in the triple bond, thus generating **36** in excellent yields (Scheme 9).<sup>22, 26</sup>

Scheme 9: Ni(\*CF3stb)<sub>3</sub> prevents detrimental deactivation pathways associated to the COD in Ni(COD)<sub>2</sub>. <sup>a</sup>Yield determined by <sup>19</sup>F NMR.

#### Shortcomings of the Ni(4-CF3 stb), pre-catalyst

Although Ni(<sup>4-CF3</sup>stb)<sub>3</sub> is applicable to a variety of Ni-catalyzed organic transformations, several limitations still prevailed and required further detailed analysis. For example, Ni(<sup>4-CF3</sup>stb)<sub>3</sub> is unstable at high temperatures when heated in the solid state. Moreover, the complex decomposes within a week when exposed to air at room temperature. More importantly, Ni(<sup>4-CF3</sup>stb)<sub>3</sub> is also unstable in solution without supporting ligands, which prevents the preparation of stock solutions or its use in certain homogenous "ligand-less" reactions. Finally, the electron-deficient nature of the <sup>4-CF3</sup>stb ligand affects elementary steps in certain catalytic domains, thus requiring harsher conditions (Figure 3).<sup>22</sup>

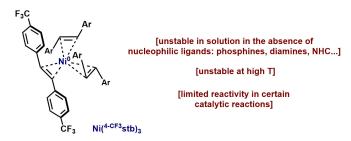


Figure 3: Drawbacks of the air-stable Ni(4-CF3 stb) 2.

These limitations have consequences when attempting certain catalytic reactions (Scheme 10). For example, the Buchwald-Hartwig amination using anilines required slightly elevated reaction temperatures (130 °C) to generate **37** in 90% yield (Scheme 10A). When performing the reaction at 100 °C, as reported for Ni(COD)<sub>2</sub>, traces of product were observed. A similar behavior was observed in the Ni-catalyzed ester formation from amides reported by Garg. While ester **38** was generated in a yield of 85% when using Ni(COD)<sub>2</sub> at 100 °C, 60 only 39% was obtained when using Ni(4-CF3 stb)<sub>3</sub>. Heating up the reaction to 130 °C led to an increase in yield up to 65% (Scheme 10B). We believe that in these cases, the high energetic cost to dissociate the stilbene ligand from L-Ni(0)-stilbene complexes might affect the energetic profile of the reaction (*vide infra*).

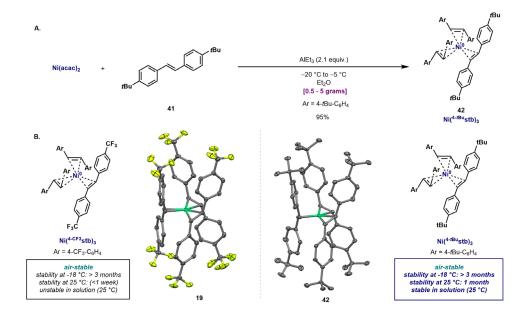
A. [Ni] (2 mol%) Ni(COD)2: 96% dppf (4 mol%) Ni(<sup>4-CF3</sup>stb)<sub>3</sub>: <5% (90% at 130 °C) NaOtBu toluene, 100 °C 37 B. [Ni] (10 mol%) terpy (10 mol%) Ni(COD)2: 85% Ni(4-CF3stb)3: 39% (65% at 130 °C) toluene Вос 100 °C 38

Scheme 10: Limitations in the catalytic reactivity of Ni(<sup>4-CF3</sup>stb)<sub>3</sub>. (A) Buchwald-Hartwig C–N bond formation with arylamines. (B) Ester formation through C–N bond activation of amides. (C) Alkyl-alkyl Kumada cross-coupling. (D) Conversion of vinyl triflates into vinyl iodides.

Examples of the instability of Ni(<sup>4-CF3</sup>stb)<sub>3</sub> in solution can be found when attempting the Kambe coupling<sup>57</sup> or the Reisman triflate-iodide exchange.<sup>58</sup> In both cases Ni(<sup>4-CF3</sup>stb)<sub>3</sub> does not survive the time required to generate the active species, thus decomposing without catalyzing the reaction (Scheme 10C and D).<sup>22</sup>

#### Ni(4-tBu stb) 3 - 2nd generation of air-stable pre-catalysts

In order to tackle the problematics associated with Ni(4-CF3 stb)<sub>3</sub>, various Ni(0) stilbene complexes bearing different substituents in the stilbene unit were synthesized, isolated and characterized.59 Eventually, solid-state analysis led us to hypothesize that in addition to its electronic influence, the CF2-moiety also exerted a severe steric constraint at the edges of the complexes. We then envisaged that in order to discriminate between electronics and steric effects in the stability toward oxidation, the CF, group could be replaced by the isostere 'Bu group. Indeed, a complex bearing three p-'Bu-stilbene ligands (41) was successfully synthesized following the optimized protocol for 19 (Scheme 11A). This orange complex (42, Ni(4-fBustb)<sub>2</sub>) was found to be remarkably air stable when compared to all the previously synthesized complexes, including 19. A direct comparison of the physical properties between 19 and 42 is highlighted in Scheme 11B. It is clear that 42 exhibits both an increased stability in solid state as well as in solution.<sup>59</sup> While **19** suffers from decomposition in solution at ambient temperature when no external ligand is added, 42 does not suffer from these drawbacks, and the Ni species remain stable in solution in various solvents. Although both complexes are stable for at least 3 months in the freezer (-18 °C), 42 did not show signs of decomposition for one month at room temperature. 59 Once again, the composition of this complex as well as its structure was determined by elemental analysis, X-ray crystallography, XPS, titration and degradation studies. Yet, complete structural analysis by NMR was prevented due to the exchange of the ligands in solution.59



Scheme 11: (A) Preparation of Ni(4-18ustb)<sub>3</sub>. (B) Comparison between 19 and 42 and ORTEP structures of these complexes compared to each other. Colors: Green: Ni, Black: C, Yellow: F. Hydrogen atoms are omitted for clarity.

#### **Catalytic transformations**

The different stabilities in solution between **19** and **42** suggested that different ligand exchange rates occur, which could dramatically affect the catalytic properties of each complex. An example of such differences was noted in the Buchwald-Hartwig amination reaction with anilines (*vide supra*).<sup>55</sup> When the reaction profile was monitored by NMR, severe differences were encountered. While complex **19** was inefficient at the reported temperature (100 °C), the newly prepared complex **42** catalyzed the reaction smoothly (Figure 4).<sup>59</sup>

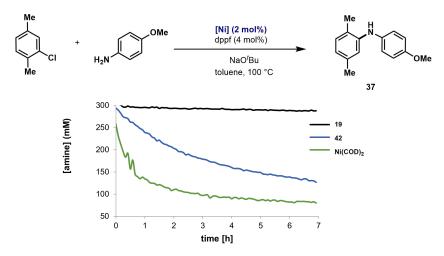


Figure 4: Kinetic profiles of the consumption of the aryl chloride in the Buchwald-Hartwig amination.

The differences in reactivity observed, led us to hypothesize that Ni(<sup>4-IBu</sup>stb)<sub>3</sub> could be amenable in transformations where Ni(<sup>4-IBu</sup>stb)<sub>3</sub> failed to react. Therefore, reactions in Scheme 10 were repeated using Ni(<sup>4-IBu</sup>stb)<sub>3</sub> instead (Scheme 12). As shown, the Buchwald-Hartwig amination (Scheme 12A),<sup>55, 59</sup> the activation of amides (Scheme 12B).<sup>56, 59</sup> Kambe's alkyl-alkyl cross-coupling using isoprene as ligand (Scheme 12C),<sup>57</sup> as well as the catalytic conversion of vinyl triflates into vinyl iodides (Scheme 12D),<sup>58</sup> recovered the reactivity when using Ni(<sup>4-IBu</sup>stb)<sub>3</sub>, affording similar yields as seen with Ni(COD)<sub>2</sub>.<sup>59</sup>

Scheme 12: Catalytic transformations performed. (A) Buchwald-Hartwig C–N bond formation with arylamines. (B) Ester formation through C–N bond activation of amides. (C) Alkyl-alkyl Kumada cross-coupling. (D) Conversion of vinyl triflates into vinyl iodides.

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The differences in reactivity between different stilbene ligands are certainly of great interest, as tuning the electronics on the olefin should now be considered as an additional parameter when optimizing Ni-catalyzed transformations. Investigations on the physical properties, catalytic activity, stereoelectronic effects and structural differences rendered by the simple change of substituents in the stilbene unit in Ni(0) complexes are currently ongoing in our laboratory.

#### Summary

In summary, complexes Ni(<sup>4-CF3</sup>stb)<sub>3</sub> (Strem 28-0060) and Ni(<sup>4-EBu</sup>stb)<sub>3</sub> (Strem 28-0070) represent more air-stable alternatives to the current Ni(0) sources, which allows practical incorporation of Ni(0) into routine experimentation. These two complexes permit the practitioner to perform a plethora of various catalytic transformations commonly applied in organic synthesis without the need of using gloveboxes or complex Schlenk techniques. It has been shown that Ni(<sup>4-CF3</sup>stb)<sub>3</sub> can be as catalytically competent as Ni(COD)<sub>2</sub>, and in some instances, surpasses its catalytic activity. The instability of Ni(<sup>4-CF3</sup>stb)<sub>3</sub> in solution without the addition of external ligands together with the decomposition after prolonged exposure to air, led to the design and synthesis of Ni(<sup>4-EBu</sup>stb)<sub>3</sub>. This last complex represents a robust source of Ni(0), with broader scope of reactivity which approaches the levels of Ni(COD)<sub>2</sub>.

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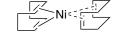
- This article has been elaborated utilizing parts of the masters thesis of Mr. Rakan Saeb (Ludwig Maximilian University of Munich, Germany, 2021), Doctoral Dissertation from Dr. Lukas Nattmann (Ruhr Universität Bochum, Germany, 2020) as well as the two articles in references 22 and 59.
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28-0010 Bis(1,5-cyclooctadiene)nickel (0), 98+% (1295-35-8)

HAZ (C<sub>8</sub>H<sub>12</sub>)<sub>2</sub>Ni; FW: 275.08; yellow xtl.; m.p. 60° dec. (under N<sub>2</sub>) air sensitive, (store cold)



2g

10g

#### Technical Notes:

- 1. Pre-catalyst for the coupling of benzoxazole with N-tosylhydrazone.
- Catalyst precursor for heterogeneously nickel-catalysed hydrogenolysis of aryl ethers without arene hydrogenation.
- 3. Pre-catalyst for reductive cleavage of C-OMe bonds with silanes as reducing agents.
- 4. Pre-catalyst for the cross-coupling reactions of benzylic pivalates with arylboroxines.
- 5. Pre-catalyst for the cross-coupling of benzylic carbamates with arylboronic esters.
- 6. Pre-catalyst for the direct arylation of C(sp³)-H Bonds in aliphatic amides via bidentate-chelation.
- Pre-catalyst for the cross-coupling reactions of potassium alkoxyalkyl- and benzyltrifluoroborates with an array of aryl bromides and co-catalyzed by iridium photoredox catalyst under visible light at ambient temperature.
- 8. Pre-catalyst for highly regioselective indoline synthesis, co-catalyzed by Ruthenium photoredox catalyst.
- 9. Catalyst for conversion of amides to esters via the activation of amide C-N bonds.
- 10. Catalyst for borylation of aryl fluorides via C-F cleavage.
- 11. Catalyst for Suzuki-Miyaura coupling of amides.
- 12. Catalyst for the cross-coupling reaction of the aryl methyl ether alkylation.

$$R^{1} \stackrel{\text{find} Ni(COD)_{2}}{\text{ID mol}\% \ PCy_{3}} \rightarrow R^{1} \stackrel{\text{find} Ni(COD)_{2}}{\text{ITMDSO, Toluene, } 110^{\circ}\text{C}} \rightarrow R^{1} \stackrel{\text{find}}{\text{II}} \rightarrow Ref. \ \textbf{(3)}$$

28-0010 (continued)

Bis(1,5-cyclooctadiene)nickel (0), 98+% (1295-35-8)

$$(Het)Ar \xrightarrow{N_1 \text{Me or Bn}} + (pin)B - (Het)Ar \xrightarrow{Ni(COD)_2: SIPr} (Het)Ar \xrightarrow{Ni(CD)_2: SIPr} (Het)Ar \xrightarrow{NI(CD)_2:$$

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# 28-0040 (1,5-Cyclooctadiene)(duroquinone) nickel(0), min. 98% (40759-64-6) C<sub>18</sub>H<sub>24</sub>NiO<sub>2</sub>; FW: 331.08; orange to red solid; m.p. 227(dec) 1g

#### Technical Notes:

- 1. Catalyst for C-CN bond activation in late-stage carbon isotope exchange of aryl nitriles.1
- Air stable Nickel(0)-olefin precatalyst for a variety of synthetic methods including Suzuki-Miyaura cross coupling reactions and amination of aryl chlorides.<sup>2</sup>

28-0040 (1,5-Cyclooctadiene)(duroquinone) nickel(0), min. 98% (40759-64-6) (continued)

(Y = CH or N)

of <sup>13</sup>CN and <sup>14</sup>CN labels Late-stage incorporation First carbon isotope exchange method for nitriles Over 30 examples, with 10 complex pharmaceuticals and alkenyl nitriles Aryl, heteroaryl,

51% exchange, 72% yield

Tech. Note (1) Ref. (1)

References:

- 1. J. Am. Chem. Soc. 2021, 143, 4817.
- Angew. Chem. Int. Ed. 2020, 59, 7409.

#### 28-0070 Tris(trans-1,2-bis(4-tert-butylphenyl)ethene)nickel(0), min. 97% (2468315-70-8) C<sub>66</sub>H<sub>84</sub>Ni; FW: 936.07; red-orange pwdr.

NEW

(store cold) Note: Prolonged storage under inert atmosphere

recommended. Patents: EP19189236.3, DE 102019214138.2. Product

sold under, use subject to, terms and conditions of Limited Use License found at www.strem.com/sgk1

Ar
$$Ar = \rho^{-1}Bu-C_{6}H_{4}$$
tBu

tBu

Technical Note:

Temperature and air-stable Ni(0) source. Applications include a fast kinetic profile in Buchwald-Hartwig amination reactions. Other uses include various catalytic transformations with and without external ligands, and many other industrially relevant transformations.

1g

5g

28-0070 Tris(trans-1,2-bis(4-tert-butylphenyl)ethene)nickel(0), min. 97% (2468315-70-8) (continued)

#### References:

Organometallics, 2020, 39, 3295-3300.

 $\begin{array}{lll} \textbf{NEW} & \textbf{Tris(trans-1,2-bis(4-(trifluoromethyl)phenyl)ethene)} \\ & \textbf{nickel(0), min. 97\% (2413906-36-0)} \\ & \textbf{C}_{48}\textbf{H}_{30}\textbf{F}_{18}\textbf{Ni; FW: }1007.41; \text{ red solid} \\ & \textit{(store cold)} \\ \end{array}$ 

Note: Prolonged storage under inert atmosphere recommended.

Patents: EP19189236.3, DE 102019214138.2. Product sold under, use subject to, terms and conditions of Limited Use License found at www.strem.com/sgk1

$$CF_3$$
 Ar  $f_5$   $f_5$   $f_6$   $f_6$   $f_7$   $f_8$   $f_8$ 

#### Technical Notes:

- Air-stable Ni(0) source. Catalyst can be weighed out in air. Decomposition of the catalyst occurs at 25 °C eventually under air after ca. 1 week.
- 2. Applications include various catalytic transformations.
- 3. Electron-deficient stilbene prevents ligand hydrometallation.

28-0060 Tris(trans-1,2-bis(4-(trifluoromethyl)phenyl)ethene)nickel(0), min. 97% (2413906-36-0) (continued)

28-0060 Tris(trans-1,2-bis(4-(trifluoromethyl)phenyl)ethene)nickel(0), min. 97% (2413906-36-0) (continued)

References:

1. Nat. Catal. 2020, 3, 6-13.

#### **BERYLLIUM (Compounds)**

04-4000 Beryllium(II) acetylacetonate min. 97%

NEW (10210-64-7)

Be(CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>2</sub>; FW: 207.22; white

pwdr.; m.p. 108; d. 1.116 moisture sensitive

Note: sublimes at 90 °C at 0.2 Torr

## Me Me Me

500mg 2g

2g

10q

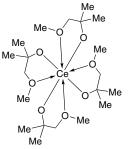
#### **CERIUM (Compounds)**

58-5500 Tetrakis[1-(methoxy)-2-methyl-2-propanolato] cerium, [Ce(mmp)4], 98% (1262520-82-0)

C<sub>20</sub>H<sub>44</sub>CeO<sub>8</sub>; FW: 552.68; light yellow to orange

pwdr.

air sensitive. moisture sensitive



#### Technical Note:

 CVD and ALD alkoxide precursor for preparation of cerium thin films:

Film	Reactants/Conditions	Substrate/Temperature	Ref	
CeO <sub>2</sub>	[Ce(mmp)4] in toluene; 1 mbar; Oxidants: O <sub>2</sub> (MOCVD) or H <sub>2</sub> O (ALD)	Si(100); 250-600°C (MOCVD); 150-350°C (ALD)	[1-3]	
CeAlO <sub>3</sub>	[Ce(mmp)4] in toluene; 1 mbar; Oxidant: O <sub>2</sub> (MOCVD); Et <sub>2</sub> Al(OEt)	Si(100), Si(100)//TiN; 400-450°C	[4]	
Pt@CeO <sub>2</sub>	[Ce(mmp)4] in cyclohexane; 10 hPa Oxidant: O <sub>2</sub> (MOCVD); [MeCpPtMe <sub>3</sub> ]	Si(100); 400°C	[5]	
CeO <sub>2</sub>	[Ce(mmp)4] in cyclohexane;10 mbar Oxidant: O <sub>2</sub> (MOCVD)	Si(100), Carbon foil; 400 °C	[6]	
CeO <sub>2</sub>	[Ce(mmp)4] in toluene; 1 mbar Oxidant: O <sub>2</sub> (ALD)	Si(100), Si(100)//TiN; 250°C	[7]	

#### Thermal behavior

- Under atmospheric pressure [Ce(mmp)4] shows a continual, gradual loss of mass over the temperature range 25-180°C,
  - followed by rapid loss of mass at 180-250°C. Mass loss is complete at 300°C with remaining residue of 16.5% (probably CeO<sub>2</sub>).
- [Ce(mmp)4] sublimes intact at 120°C without deposition of residues at low pressure (0.8 Torr).
- Thermal decomposition at ~275 °C [1].
- TGA data is available in [1] and [2].

#### References:

- 1. Chem. Vap. Deposition 2009, 15, 259.
- 2. Inorg. Chem. 2011, 50, 11644.
- 3. Nanoscale Res. Lett. 2013, 8, 456.
- Thin Solid Films 2013, 536, 68.
- Thin Solid Films 2015, 589, 246.
- 6. Surf. Coat. Tech. 2015, 280, 148.
- Beilstein J. Nanotechnol. 2018, 9, 890.

#### CHROMIUM (Compounds)

24-0600 Methylbenzoate chromium tricarbonyl, min.

98% (12125-87-0)

C<sub>11</sub>H<sub>8</sub>CrO<sub>5</sub>; FW: 272.18; orange solid;

HAZ m.p. 95-96°C

air sensitive, moisture sensitive



#### Technical Note:

1. Chromium carbonyl based catalyst for the hydrogenation of conjugated dienes<sup>2,3</sup> and alkynes.<sup>1</sup>

$$\text{Me}^{\text{CO}_2 R} + \text{H}_2 \qquad \qquad \text{24-0600} \qquad \text{Me} \qquad \text{Tech. Note (1)}$$

#### References:

- 1. Synthesis 1993, 7, 643.
- 2. Russ. Chem. Bull. 2002, 51, 1341.
- 3. Russ. Chem. Bull. 2018, 67, 923.

#### **ELECTROPOLISHED STAINLESS STEEL BUBBLERS (Vertical)**

95-1050 NEW Stainless steel bubbler, 600ml, vertical, electropolished with fill-port, pneumatic actuator valves, DOT 4B



1cyl

1 kit

500mg

2g

#### **GADOLINIUM (Compounds)**

 64-4250
 Gadolinium(III) bromide, anhydrous (99.99%-Gd) (REO) PURATREM
 5g

 NEW
 (13818-75-2)
 25g

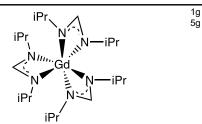
 GdBr<sub>s</sub>; FW: 396.96; white xtl.; m.p. 770

air sensitive, moisture sensitive, hygroscopic

64-3575 NEW Tris(N,N'-di-i-propylformamidinato)gadolinium(III), (99.999+%-Gd) PURATREM Gd-FMD  $C_{21}H_{45}GdN_8$ ; FW: 538.87; white to off-white pwdr.

air sensitive, moisture sensitive Note: Product sold under, use subject to, terms

and conditions of label license at www.strem.com/harvard2.



#### KITS (Compounds)

96-0280 Chromalite® SpectraChrom Kit

NEW

Sold in collaboration with Purolite for research purposes only.

Contains 25ml of the following:

Chromalite MIDA/M/Ni Chromalite MIDA/M/Co Chromalite MIDA/M/Zn Chromalite MIDA/M/Cu Chromalite MIDA/M/Fe

Chromalite MIDA/M

#### **METALS SCAVENGING AGENTS (Compounds)** 10g 08-4225 Glucamine Alkyl Silica, borate scavenger но он vellow-white pwdr. 50g NEW moisture sensitive Note: Particle size 37-200 um OH Sold in collaboration with Si-Novation for research purposes only. Patent: PCT/ "OH CN2016/092663. HO 16-0800 Imidazole Sulfide Mercapto Alkyl Silica, 10g metals and organic impurity scavenger 50g NEW vellow-white pwdr. moisture sensitive Note: Particle size 37-200 um Sold in collaboration with Si-Novation for research purposes only. Patent: PCT/ CN2016/092663. 16-0805 Octadecyl Sulfide Propyl Silica, non-polar 10g impurity scavenger 50g NEW yellow-white pwdr. moisture sensitive Note: Particle size 37-200 µm C3H6SC18H37 Sold in collaboration with Si-Novation for research purposes only. Patent: PCT/ CN2016/092663. 08-4230 Poly Carboxylic Acid Alkyl Silica, metals and 10g 50g organic impurity scavenger NEW yellow-white pwdr. moisture sensitive Note: Particle size 37-200 um Sold in collaboration with Si-Novation for OH research purposes only. Patent: PCT/ CN2016/092663. 16-0815 Poly Mercaptoalkyl Silica, metals and organic 10g impurity scavenger 50g NEW yellow-white pwdr. moisture sensitive Note: Particle size 20-200 um Sold in collaboration with Si-Novation for research purposes only. Patent: PCT/ CN2016/092663. 07-9255 Poly Quaternary Ammonium Alkyl Silica, 10q ⊝ Cl metals and organic impurity scavenger 50q NEW yellow-white pwdr. moisture sensitive Note: Particle size 37-200 µm Sold in collaboration with Si-Novation for research purposes only. Patent: PCT/ CN2016/092663

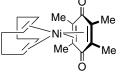
#### **METALS SCAVENGING AGENTS (Compounds)** 16-0810 Polyamine Sulfide Alkyl Silica, metals and 10g organic impurity scavenger 50a NEW yellow-white pwdr. moisture sensitive SH Note: Particle size 37-200 µm Sold in collaboration with Si-Novation for SR research purposes only. Patent: PCT/ CN2016/092663. 16-0820 Tetraamine Sulfide Alkyl Silica, metals and 10a organic impurity scavenger 50q NEW yellow-white pwdr. moisture sensitive SH Note: Particle size 37-200 um Sold in collaboration with Si-Novation for H<sub>2</sub>N research purposes only. Patent: PCT/ CN2016/092663. 16-0825 Thiourea Sulfide Mercapto Silica, metals and 10a organic impurity scavenger 50a NEW yellow-white pwdr. moisture sensitive Ĥ Note: Particle size 37-200 um Sold in collaboration with Si-Novation for SH research purposes only. Patent: PCT/ CN2016/092663. MOFS AND LIGANDS FOR MOF SYNTHESIS (Compounds) Copper benzene-1,3,5-tricarboxylate MOF (HKUST-1(Cu))/PVDF membrane 29-3150 1x1cm (35/65 wt.%) (51937-85-0) NEW blue membrane: SA: BET 500 m<sup>2</sup>/a moisture sensitive 40-1125 Zirconium 1,4-dicarboxybenzene MOF (UiO-66)/PVDF membrane (60/40 1x1cm wt.%) (1072413-89-8) NEW white membrane; SA: BET 650-700 m<sup>2</sup>/g moisture sensitive **NICKEL** (Compounds) 28-0040 (1,5-Cyclooctadiene)(duroquinone) nickel(0), 250mg 1a

min. 98% (40759-64-6)

NEW

C<sub>18</sub>H<sub>24</sub>NiO<sub>2</sub>; FW: 331.08; orange to red solid;

m.p. 227(dec)



#### Technical Notes:

- 1. Catalyst for C-CN bond activation in late-stage carbon isotope exchange of aryl nitriles.1
- Air stable Nickel(0)-olefin precatalyst for a variety of synthetic methods including Suzuki-Miyaura cross coupling reactions and amination of aryl chlorides.2

28-0040 (1,5-Cyclooctadiene)(duroquinone) nickel(0), min. 98% (40759-64-6) (continued)

(Y = CH or N)

Late-stage incorporation of <sup>13</sup>CN and <sup>14</sup>CN labels First carbon isotope exchange method for nitriles Over 30 examples, with 10 complex pharmaceuticals Aryl, heteroaryl, and alkenyl nitriles

#### References:

- 1. J. Am. Chem. Soc. 2021, 143, 12, 4817-4823.
- 2. Angew. Chem. Int. Ed. 2020, 59, 7409.

#### 28-0070 Tris(trans-1,2-bis(4-tert-butylphenyl)ethene) 1g nickel(0), min. 97% (2468315-70-8) 5g tBu NEW C<sub>66</sub>H<sub>84</sub>Ni; FW: 936.07; red-orange pwdr. (store cold) Note: Prolonged storage under inert atmosphere recommended. Patents: EP19189236.3, DE 102019214138.2. Product sold under, use subject to, terms and conditions of Limited Use License found at $Ar = p^{-t}Bu-C_6H_4$ www.strem.com/sqk1

#### Technical Note:

Temperature and air-stable Ni(0) source. Applications include
a fast kinetic profile in Buchwald-Hartwig amination reactions.
Other uses include various catalytic transformations with and without external ligands, and many other industrially relevant transformations.

28-0070 Tris(trans-1,2-bis(4-tert-butylphenyl)ethene)nickel(0), min. 97% (2468315-70-8) (continued)

References:

(60 bar)

1. Organometallics, 2020, 39, 3295-3300.

#### NITROGEN (Compounds) 07-1070 (1Z,3Z)-1,3-Bis[[(4S)-4,5-dihydro-4-phenyl-2-25mg Me Me oxazolyl]methylene]-2,3-dihydro-5,6-dimeth-100mg NEW yl-1H-isoindole, 95% (1358991-79-3) C<sub>30</sub>H<sub>27</sub>N<sub>3</sub>O<sub>2</sub>; FW: 461.6; light yellow to yellow pwdr. moisture sensitive, (store cold) Note: Sold in collaboration with Daicel for research purposes only Ph

690 mg C6-C24 n = 1 to 9 Ref. (1)

ligand mix (1:1)

07-1070 (1Z,3Z)-1,3-Bis[[(4S)-4,5-dihydro-4-phenyl-2-oxazolyl]methylene]-2,3-dihydro-5,6-dimeth-(continued) yl-1H-isoindole, 95% (1358991-79-3)

#### Technical Notes:

- 1. Ligand for the Ni-catalzyed enantioselective fluorination of oxindoles.
- 2. Ligand used in Nozaki-Hiyama-Kishi reaction.
- 3. Ligand for the highly enantioselective Cu-catalyzed alkylation of β-ketoesters with benzyl and allylic alcohols.
- Ligand for the highly enantioselective Cu-catalyzed electrophilic trifluoromethylation and trifluoromethylthiolations
  of β-ketoesters.

BnOH or 
$$CO_2R^3$$
 +  $R'''$   $R'''$ 

#### References:

- 1. Chem. Eur. J. 2011, 17, 14922.
- 2. J. Am. Chem. Soc. 2012, 134, 2946.
- 3. J. Am. Chem. Soc. 2012, 134, 10769.
- 4. Chem. Eur. J. 2014, 20, 93.

# 07-1065 (1Z,3Z)-1,3-Bis[[(4R)-4,5-dihydro-4-phenyl-2-oxazolyl]methylene]-2,3-dihydro-1H-isoindole, 95% (1429056-54-1) C<sub>28</sub>H<sub>28</sub>N<sub>3</sub>O<sub>2</sub>; FW: 433.5; light yellow to yellow pwdr. moisture sensitive, (store cold) Note: Sold in collaboration with Daicel for research purposes only.

#### Technical Notes:

- 1. Ligand for the enantioselective Fe-catalyzed azidation of β-ketoesters and oxindoles.
- Ligand for the enantioselective Fe-catalyzed hydrosilylation of ketones.
- 3. Ligand for the enantioselective Zn-catalyzed allylation of oxindole derivatives with allyl bromide.
- Ligand for the Zn-catalyzed asymmetric electrophilic cyanation of 3-substituted oxindoles.
- 5. Ligand for the α-selective Co-catalyzed hydroborations of alkynes.

07-1065 (1Z,3Z)-1,3-Bis[[(4R)-4,5-dihydro-4-phenyl-2-oxazolyl]methylene]-2,3-dihydro-1H-isoindole, (continued) 95% (1429056-54-1)

$$\begin{array}{c|c} O & [Fe] \ Ligand \\ \hline R^1 & CO_2R^3 & \hline N_3\text{-transfer reagent} \\ \hline P^-NO_2C_6H_4CO_2Ag & \hline R^1 & CO_2R^3 \\ \hline P^-NO_2C_6H_4CO_2Ag & \hline R^2 & \hline N_1 & N_2 \\ \hline R^2 & \hline N_2 & \hline N_1 & N_2 \\ \hline R^2 & \hline N_2 & \hline N_1 & N_2 \\ \hline R^2 & \hline N_2 & \hline N_1 & N_2 \\ \hline R^2 & \hline N_2 & \hline N_2 & \hline N_3 & \hline$$

Tech. Note (1) Ref. (1)

Tech. Note (2) Ref. (2)

$$\begin{array}{c} R^2 \\ N \\ N \\ R^3 \end{array} + \begin{array}{c} Br \\ \hline \\ K_2CO_3, CHCl_3, rt, 18h \\ \hline \\ R^3 \end{array} + \begin{array}{c} R^1 \\ N \\ R^3 \end{array}$$

Tech. Note (3) Ref. (3)

Tech. Note (4) Ref. (4)

R | Co] Ligand/CH<sub>2</sub>SiMe<sub>3</sub> | BPin | Tech. Note (5) | Ref. (5)

#### References:

- 1. J. Am. Chem. Soc. 2013, 135, 5356.
- 2. J. Am. Chem. Soc. 2015, 137, 2456.
- 3. Angew. Chem. Int. Ed. 2016, 55, 7852.
- 4. Org. Lett. 2017, 19, 4018.
- Angew. Chem. Int. Ed. 2020, 59, 23010.

#### 07-1068 NEW

(1Z,3Z)-1,3-Bis[[(4S)-4,5-dihydro-4-(tert-butyl)-2-oxazolyl]methylene]-2,3-dihydro-1H-isoin-dole, 98% (1361563-41-8)

 $C_{24}H_{31}N_3O_2$ ; FW: 393.5; light yellow to yellow

Pwdr.

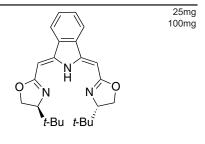
moisture sensitive, (store cold)

Note: Sold in collaboration with Daicel for

research purposes only.

#### Technical Notes:

- Ligand for the Ni-catalzyed enantioselective fluorination of oxindoles.
- Ligand used in Nozaki-Hiyama-Kishi reaction.



07-1068 (continued) (1Z,3Z)-1,3-Bis[[(4S)-4,5-dihydro-4-(tert-butyl)-2-oxazolyl]methylene]-2,3-dihydro-1H-isoin-dole, 98% (1361563-41-8)

$$\begin{array}{c} R^2 & H & R^1 \\ \hline & & \\ N & \\ Boc & \\ \end{array} \begin{array}{c} [Ni] \text{ Ligand/NFSI} \\ 4A \text{ MS, Et}_2O, \text{ rt, 6h} \\ \end{array} \begin{array}{c} R^2 & F_{\text{N}} & R^1 \\ \hline & \\ N & \\ Boc & \\ \end{array}$$

#### References:

1. Chem. Eur. J. 2011, 17, 14922.

3,6-Bis(dimethylamino)-9-(2,6-dimethyl-phenyl)-10-methylacridin-10-ium bromide, min. 95% (2380163-04-0)

C<sub>28</sub>H<sub>30</sub>BrN<sub>3</sub>, FW: 464.45; orange to red to dark red solid

air sensitive
Note: Sold in collaboration with Solvias for research purposes only.

#### Technical Notes:

- 1. Organophotoredox catalyst used in Ni-assisted C-C cross-coupling without C-O bond formation.
- 2. Acridinium catalysts used for photoredox deuteration of clomipramine.

$$\begin{array}{c} \text{N} \quad \text{CO}_2\text{H} + \\ \text{Boc} \end{array} \begin{array}{c} \text{[Ni]/[Photocat]-} h_{\text{In}} \\ \hline 2,2'\text{-bipy, } \text{Cs}_2\text{CO}_3, \text{DMF}} \end{array} \begin{array}{c} \text{Tech. Note (1)} \\ \text{Ref. (1, 3)} \end{array}$$

#### References:

- 1. Angew. Chem. Int. Ed. 2018, 57, 2436.
- Synthesis 2019, 51, 4359.
- ACS Catal. 2020, 10, 210.

# 3,6-Bis(dimethylamino)-9-mesityl-10-methylacridin-10-ium bromide, min. 95% (2180894-90-8) C<sub>27</sub>H<sub>32</sub>BrN<sub>3</sub>; FW: 478.48; orange to red to dark red solid air sensitive Note: Sold in collaboration with Solvias for research purposes only.

Me

#### Technical Note:

1. See 07-8230 (page 29)

07-1058 NEW **2,2-Bis[(4R)-4-tert-butyl-2-oxazolin-2-yl] propane, 98%, (99% ee)** *(131833-97-1)* C<sub>17</sub>H<sub>30</sub>N<sub>3</sub>O<sub>2</sub>; FW: 294.4; off white to light yellow pwdr.

moisture sensitive, (store cold)
Note: Sold in collaboration with Daicel for

research purposes only.

### Me Me O N N Bu t-Bu

100ma

#### Technical Notes:

- 1. Ligand for the enantioselective H-atom transfer Reactions to generate β2-amino acids.
- Ligand for the Cu-catalyzed asymmetric alkylation of β-keto esters with xanthydrols.
- Ligand used in Zn-catalyzed asymmetric hetero-Diels-Alder reaction of trans-1-methoxy-3-trimethylsilyloxy-buta-1,3-diene.

#### References:

- 1. Angew. Chem. Int. Ed. 2004, 43, 1235.
- 2. Adv. Synth. Catal. 2013, 355, 2815.
- 3. Eur. J. Org. Chem. 2020, 5388.

# 07-1076 (4R,4'R,5S,5'S)-2,2'-Cyclobutylidenebis[4,5-dihydro-4,5-diphenyloxazole], 98% C<sub>34</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>; FW: 498.6; off white to light yellow pwdr. moisture sensitive, (store cold) Note: Sold in collaboration with Daicel for research purposes only 07-1079 (4S,4'S)-2,2'-Cyclobutylidenebis[4,5-dihydro-4-tert-butyloxazole], min. 95% (298693-02-4)

(45,4'S)-2,2'-Cyclobutylidenebis[4,5-dihy-dro-4-tert-butyloxazole], min. 95% (298693-02-4) C<sub>18</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>: FW: 306.4; off white to light yellow pwdr. moisture sensitive, (store cold)
Note: Sold in collaboration with Daicel for

Note: Sold in collaboration with Daicel for research purposes only

#### Technical Note:

Ligand used in the enantioselective organolithium additions to imines.

#### References:

1. Adv. Synth. Catal. 2008, 350, 1023.

07-1062

(4S,4'S)-2,2'-Cyclopropylidenebis[4-tert-butyl-

NEW

**4,5-dihydrooxazole], 95%** (195379-09-0)  $C_{17}H_{28}N_2O_2$ ; FW: 292.4; off white to light yellow pwdr. moisture sensitive, (store cold)

Note: Sold in collaboration with Daicel for research purposes only.

t-Bu

25mg

100mg

Technical Notes:

- Ligand for the highly enantioselective Cu-catalyzed Friedel-Crafts alkylations of pyrroles and indoles with α'-hydroxy enones.
- Ligand used in Lewis acid catalyzed Aldol reactions to generate optically active pyridine derivatives from prochiral pyridine-N-oxides.
- 3. Ligand used in Cu-catalyzed tandem Nazarov cyclization/Wagner-Meerwein rearrangement to synthesize Enokipodin B.
- 4. Ligand used in enantioselective Cu-catalyzed oxy-alkynylation of diazo compounds.
- 5. Ligand used in Cu-catalyzed oxyvinylation of diazo compounds.

#### References:

- 1. J. Am. Chem. Soc. 2005, 127, 4154.
- 2. Chem. Eur. J. 2006, 12, 3472.
- 3. Chem. Eur. J. 2013, 19, 4835.
- 4. J. Am. Chem. Soc. 2017, 139, 8420.
- 5. Org. Lett. 2020, 22, 3884.

07-1073 NEW (4S,4'S)-2,2'-(4,6-Dibenzofurandiyl)bis[4,5-dihydro-4-phenyloxazole], 98% (246040-77-7)  $C_{30}H_{22}N_2O_3$ ; FW: 458.5; off white to light yellow pwdr.

moisture sensitive, (store cold)

Note: Sold in collaboration with Daicel for

research purposes only

Ph Ph

25mg

100mg

#### Technical Notes:

- Ligand for the Ni-catalyzed enantioselective addition of nitrones to activated cyclopropanes.
- 2. Ligand for the Zn-catalyzed Friedel-Crafts alkylation with α-substituted acrylates.
- 3. Ligand for the Lewis acid mediated enantioselective intramolecular redox reactions to generate ring-fused tetrahydroquinolines.
- 4. Ligand for the Lews acid-catalyzed highly enantioselective α-cyanation with 4-acetylphenyl cyanate.
- Ligand for the Ni-catalyzed asymmetric 1,3-dipolar cycloaddition of β-fluoroalkylated α,β-Unsaturated 2-pyridylsulfones with nitrones to generate chiral fluoroalkylated isoxazolidines and γ-amino alcohols.

$$R \downarrow O \downarrow O \uparrow R + \frac{\bar{O}}{R^2} \uparrow R^1 \qquad [Ni] \text{ Ligand} \qquad R \downarrow O \downarrow O \uparrow R \qquad \text{Tech. Note (1)}$$

$$R \downarrow O \downarrow O \uparrow R + \frac{\bar{O}}{R^2} \uparrow R^1 \qquad Ref. (1)$$

#### References:

- 1. J. Am. Chem. Soc. 2005, 127, 5764.
- 2. Angew. Chem. Int. Ed. 2008, 47, 9913.
- 3. J. Am. Chem. Soc. 2009, 131, 13226.
- 4. Chem. Eur. J. 2017, 23, 1775.
- 5. Angew. Chem. Int. Ed. 2017, 56, 1510.

07-1085

NEW

(4R,4'R,5S,5'S)-2,2'-(1,3-Dihydro-2H-inden-2ylidene)bis[4,5-dihydro-4,5-diphenyloxazole], 98% (1656253-81-4)

C<sub>39</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>; FW: 560.7; off white to light yellow pwdr.

moisture sensitive, (store cold)

Note: Sold in collaboration with Daicel for research purposes only

25mg

100mg

#### Technical Note:

1. Ligand used in Cu(II)-catalyzed enantioselective intramolecular cyclization of N-alkenylureas.

#### References:

1. Org. Lett. 2015, 17, 1018.

07-1434 (NEW)	(4R,4'R)-2,2'-(1,3-Dihydro-2H-inden-2-ylidene) bis[4,5-dihydro-4-isopropyloxazole], 98%, (99% ee) C <sub>21</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub> ; FW: 340.5; off white to light yellow pwdr. moisture sensitive, (store cold) Note: Sold in collaboration with Daicel for research purposes only	i-Pr	100mg
07-1435 NEW	(4S,4'S)-2,2'-(1,3-Dihydro-2H-inden-2-ylidene) bis[4,5-dihydro-4-isopropyloxazole], 98%, (99% ee)  C <sub>21</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub> ; FW: 340.5; off white to light yellow pwdr.  moisture sensitive, (store cold)  Note: Sold in collaboration with Daicel for research purposes only	i-Pr N N in i-Pr	100mg
07-1082 (NEW)	(4R,4'R)-2,2'-(1,3-Dihydro-2H-inden-2-ylidene) bis[4,5-dihydro-4-tert-butyloxazole], 98%, (99% ee) C <sub>23</sub> H <sub>32</sub> N <sub>2</sub> O <sub>2</sub> ; FW: 368.5; off white to light yellow pwdr. moisture sensitive, (store cold) Note: Sold in collaboration with Daicel for research purposes only	t-Bu t-Bu	100mg
07-1049 NEW	2-[(4R)-4,5-Dihydro-4-isopropyl-2-oxazolyl] pyridine, 98% (99% ee) (132187-16-7) C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O; FW: 190.2; light yellow to yellow pwdr. moisture sensitive, (store cold) Note: Sold in collaboration with Daicel for research purposes only.	O N N-Pr	100mg

#### Technical Note:

Ligand for the Pd-catalyzed enantioselective diene cyclization/hydrosilylation.

#### References:

1. J. Org. Chem. 2000, 65, 3836.

07-1048 NEW

2-[(4S)-4,5-Dihydro-4-isopropyl-2-oxazolyl]

pyridine, 98%, (99% ee) (108915-04-4) C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O; FW: 190.2; off white to light yellow pwdr.

moisture sensitive, (store cold) Note: Sold in collaboration with Daicel for research

purposes only.

100mg

#### Technical Notes:

- Ligand used in the Pd-catalyzed asymmetric aerobic Aza-Wacker-Type cyclization. 1.
- Ligand used in Pd-catalyzed conjugate addition of arylboronic acids to β-substituted cyclic enones. 2.
- 3. Ligand for enantioselective Ir-catalyzed silylation of aromatic C-H bonds.
- 4. Ligand for the Co-catalyzed enantioselective Markovnikov 1,2-hydrosilylation of conjugated dienes.
- 5. Ligand used for the Ni-catalyzed intramolecular desymmetrization addition of aryl halides to 1,3-diketones.

- 1. Angew. Chem. Int. Ed. 2012, 51, 9141.
- 2. J. Am. Chem. Soc. 2013, 135, 14996.
- 3. Angew. Chem. Int. Ed. 2017, 56, 1092.
- ACS Catal. 2019, 9, 1612. 4.
- 5. Chem. Commun., 2020, 56, 8194.

#### 07-1340 Dodecabenzylbambus[6]uril, Bn-BU[6]

(1308315-95-8)NEW

C<sub>114</sub>H<sub>108</sub>N<sub>24</sub>O<sub>12</sub>; FW: 2006.23; white pwdr. Note: Patents: CZ302710B6, EP2501699B1,

US8779120, WO2011057590A1,



- Exhibits exceptionally strong binding of anions with different sizes in chloroform.
- 2. Macrocycle used in the real-time analysis of anion mixtures by NMR methods.
- 3. Used as a transmembrane CI-/HCO3- antiporter.
- Used as a carrier in tailor-made liquid membranes for highly selective electromembrane extractions of inorganic anions.
- 5. Used for anion complexation in the study of the influence of counterions on the [N-I-N]+ halogen bond in solution, in the solid state and in silico.



- ChemPlusChem., 2015, 80, 1601-1606. 1.
- 2. Chem. Commun., 2015, 51, 4666.
- 3. Chem, 2019, 5, 429-444.
- Anal. Chim. Acta, 2017, 950, 49-56.
- 5. Chem. Sci., 2015, 6, 3746-3756.

#### 07-1342 Dodecamethylbambus[6]uril hydrate, BU[6] (1227292-62-7)NEW

 $C_{42}H_{60}N_{24}O_{12}\cdot XH_2O$ ; FW: 1093.08; white pwdr. Note: Patents: CZ302710B6, EP2501699B1, US8779120, WO2011057590A1,

#### Technical Note:

A new macrocyclic compound which is able to bind anions with high affinity and selectivity.

#### References:

- Chem. Eur. J., 2011, 17, 5605-5612.
- Org. Lett., 2011, 13(15), 4000.

100mg

100ma

#### 07-1041 2-[(4S)-4-Isobutyl-4,5-dihydro-2-oxazolyl]-5-(trifluoromethyl)pyridine, 98%, (99% NEW

C<sub>13</sub>H<sub>15</sub>F<sub>3</sub>N<sub>2</sub>O; FW: 272.3; off white to light yellow pwdr.

moisture sensitive, (store cold) Note: Sold in collaboration with Daicel for

research purposes only

#### 07-7059 2-[(4S)-4-Isopropyl-4,5-dihydro-2-oxazolyl]-5-(trifluoromethyl)pyridine, 98%, (99% NEW ee)

C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>N<sub>2</sub>O; FW: 258.2; off white to light yellow

moisture sensitive, (store cold)

Note: Sold in collaboration with Daicel for

research purposes only.

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07-1088 NEW (4R,4'R)-2,2'-(1-Phenylpropane-2,2-diyl) bis(4,5,5-triphenyl-4,5-dihydrooxazole), 98% (2409652-69-1)

 $C_{51}H_{42}N_2O_2$ ; FW: 714.9; off white to light yellow pwdr.

moisture sensitive, (store cold)

Note: Sold in collaboration with Daicel for research purposes only

#### Technical Note:

 Ligand for the Ni-catalyzed enantioconvergent reductive hydroalkylation of olefins with α-heteroatom phosphorus alkyl electrophiles.

References:

1. J. Am. Chem. Soc. 2020, 142, 214.

07-1055

1-[(4R)-4-tert-Butyl-4,5-dihydro-2-oxazolyl]
isoquinoline, 98%, (99% ee) (1402851-53-9)

C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O; FW: 254.3; off white to light yellow pwdr.
moisture sensitive, (store cold)

Note: Sold in collaboration with Daicel for research
purposes only.

t-Bu 25mg 100mg

#### Technical Note:

 Ligand for the Ni-catalyzed asymmetric cross-coupling of secondary electrophiles with secondary nucleophiles, specifically, stereoconvergent Negishi reactions of racemic benzylic bromides with achiral cycloalkylzinc reagents.

$$R = \begin{bmatrix} Br \\ Csl \text{ or } Mgl_2, Solvent \end{bmatrix}$$

$$R = \begin{bmatrix} R^1 \\ R^1 \end{bmatrix}$$

References:

1. J. Am. Chem. Soc. 2012, 134, 17003.

07-1045
NEW

2-[(4R)-4-tert-Butyl-4,5-dihydro-2-oxazolyl]
pyridine, 95%, (99% ee) (242482-28-6)
C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O; FW: 204.3; off white to light yellow pwdr.
moisture sensitive, (store cold)
Note: Sold in collaboration with Daicel for research
purposes only

25mg
100mg

#### Technical Notes:

- 1. Ligand for asymmetric Pd-catalyzed directed intermolecular fluoroarylation of styrenes.
- Ligand used in Ir visible light photoredox/Ni-catalyzed cross-coupling of acyl chlorides with potassium alkoxymethyltrifluoroborates.
- 3. Ligand for Ni-catalyzed asymmetric intramolecular reductive Heck reaction of unactivated alkenes.
- 4. Ligand used in Au(III)-catalyzed intramolecular alkoxycyclization of a 1,6-enyne.
- 5. Ligand for the Ni-catalyzed asymmetric reductive arylbenzylation of unactivated alkene.

07-1045 2-[(4R)-4-tert-Butyl-4,5-dihydro-2-oxazolyl]pyridine, 95%, (99% ee) (242482-28-6) (continued)

R<sub>3</sub>= H or D; X=CH<sub>2</sub>, O, NTs

X=CH<sub>2</sub>, O, NTs

- 1. J. Am. Chem. Soc. 2014, 136, 4101.
- 2. Org. Lett. 2016, 18, 732.
- 3. Org. Lett. 2019, 21, 6989.
- 4. J. Am. Chem. Soc. 2019, 141, 18221.
- 5. Org. Lett. 2020, 22, 2724.

07-1044 2-[(4S)-4-tert-Butyl-4,5-dihydro-2-oxazolyl]

pyridine, 98%, (99% ee) (117408-98-7)
C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O; FW: 204.3; off white to light yellow pwdr.

moisture sensitive, (store cold)
Note: Sold in collaboration with Daicel for research

Note: Sold in collaboration with Daicel for research purposes only

### O N t-Bu

100mg

#### Technical Notes:

- 1. Ligand used in Pd-catalyzed conjugate addition of arylboronic acids to β-substituted cyclic enones.
- Ligand for the enantioselective Pd-catalyzed oxidative β,β-fluoroarylation of α,β-unsaturated carbonyl derivatives.
- Ligand for the Pd-catalyzed asymmetric Aza-Wacker-Type cyclization of N-Ts hydrazine-tethered tetrasubstituted olefins.
- 4. Ligand for the Co-catalyzed enantioselective Markovnikov 1,2-hydrosilylation of conjugated dienes.
- 5. Ligand for the Pd-catalyzed enantioselective desymmetrization of polycyclic cyclohexenediones.

EWG 
$$f$$
 [Pd] Ligand/Ar-B(OH)<sub>2</sub> FWG  $f$  Tech. Note (2) Ref. (2)

 $\mathsf{EWG} = \mathsf{COR},\, \mathsf{CO}_2\mathsf{R},\, \mathsf{CONR}_1\mathsf{R}_2,\, \mathsf{CO}_2\mathsf{H},\, \mathsf{CH}_2\mathsf{CN},\, \mathsf{CHO}$ 

- 1. J. Am. Chem. Soc. 2013, 135, 14996.
- 2. Angew. Chem. Int. Ed. 2016, 55, 9045
- 3. J. Am. Chem. Soc. 2018, 140, 7587.
- 4. ACS Catal. 2019, 9, 1612.
- 5. Org. Lett. 2019, 21, 8689.

07-1050 NEW 2-[(4S)-4-tert-Butyl-4,5-dihydro-2-oxazolyl]-4-(tri-fluoromethyl)pyridine, 98% (1257527-14-2)

 $C_{13}H_{15}F_3N_2O$ ; FW: 272.3; off white to light yellow pwdr.

moisture sensitive, (store cold)

Note: Sold in collaboration with Daicel for research purposes only.

CF<sub>3</sub> 100mg

t-Bu

#### Technical Notes:

- 1. Ligand used in enantioselective Pd-catalyzed alkene difunctionalization reaction.
- 2. Ligand used in enantioselective Heck arylations of acyclic alkenyl alcohols.
- 3. Ligand for enantioselectiv Pd-catalyzed conjugate addition of arylboronic acids to β-substituted cyclic enones.

#### References:

- 1. J. Am. Chem. Soc. 2010, 132, 17471.
- 2. Science 2012, 338, 1455.
- 3. J. Am. Chem. Soc. 2013. 135. 14996.

#### **PHOSPHORUS (Compounds)**

15-8406 NEW [S(R)]-N-((1R)-(Adamantan-1-yl)(5-(diphenyl-phosphanyl)-9,9-dimethyl-9H-

xanthen-4-yl)methyl)-2-methyl-2-propanesulfinamide, 95% (2162939-91-3)

 $\rm C_{42}H_{48}NO_2PS;$  FW: 661.9; white to off-white pwdr. air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

PPh<sub>2</sub> HN Ad

Me Me

#### Technical Note:

 Ligand for the Pd-catalyzed enantioselective arylation of general sulfenate anions.

References:

1. J. Am. Chem. Soc. 2018, 140, 3467.

25ma

15-8404 [S(R)]-N-((1S)-(Adamantan-1-yl)(5-(diphenylphosphanyl)-9,9-dimethyl-9H-

xanthen-4-yl)methyl)-2-methyl-2-propanesulfinamide, 95% (2183514-08-9) C<sub>40</sub>H<sub>48</sub>NO<sub>2</sub>PS; FW: 661.9; white to off-white pwdr.

air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

Technical Note: See 15-8406 (page 39) 1

NEW

[S(R)]-N-[(1S)-1-[2-(9-Anthracenyl) 15-8370

phenyl]-2-(diphenylphosphino)ethyl]-2-meth-NEW yl-2-propanesulfinamide, 95% (1936438-22-0) C38H36NOPS; FW: 585.7

air sensitive, moisture sensitive, (store cold) Note: Sold in collaboration with Daicel for research purposes only.

Ph<sub>2</sub>P

50mg

50mg

#### Technical Notes:

- 1. Organocatalyst used in enantioselective intermolecular cross Rauhut-Currier reactions of activated alkenes with acrolein.
- 2. Used in phosphine-catalyzed asymmetric umpolung addition of trifluoromethyl ketimines to Morita-Baylis-Hillman carbonates.
- 3. Used in the enantioselective phosphine-catalyzed allylic alkylations of mix-indene with MBH carbonates.
- Used in phosphine-catalyzed asymmetric synthesis of α-quaternary amine via umpolung γ-addition of ketimines to allenoates.
- 5. Ligand for the direct Pd-catalyzed cross-coupling reaction of easily accessible secondary phosphine oxides and aryl bromides, which provides rapid access to P-chiral phosphine oxides.

Ar OBoc Peng-Phos Toluene, rt 
$$CO_2^t$$
Bu Peng-Phos Toluene, rt  $CO_2^t$ Bu  $CO_2^t$ Bu  $CO_2^t$ Bu  $CO_2^t$ Bu

$$R^{1}$$
 OBoc Peng-Phos Toluene, rt  $R^{1}$   $R^{2}$  Tech. Note (3) Ref. (3)

$$\begin{array}{c} \text{Ar} \\ \text{N} \\ \text{R} \end{array} + \begin{array}{c} \begin{array}{c} \text{Peng-Phos} \\ \text{CO}_2\text{R'} \end{array} \end{array} \begin{array}{c} \text{Ar} \\ \text{Toluene, rt} \end{array} \begin{array}{c} \text{Ar} \\ \text{R} \end{array} \begin{array}{c} \text{EWG} \\ \text{Ref. (4)} \end{array}$$

EWG = CF3, ester

Me O R<sup>1</sup>
H + 
$$R^2 \frac{I}{I}$$
Br [Pd] Peng-Phos
 $Cs_2CO_3$ , anisole, 35°C
 $R^2$ 
Tech. Note (5)

15-8370 (continued) [S(R)]-N-[(1S)-1-[2-(9-Anthracenyl)phenyl]-2-(diphenylphosphino)ethyl]-2-methyl-2-propanesulfinamide, 95% (1936438-22-0)

#### References:

- Chem. Commun., 2016, 52, 7612. 1
- 2. Angew. Chem. Int. Ed. 2016, 55, 13316.
- 3 Org. Lett. 2017, 19, 6080.
- Org. Lett. 2017, 19, 6550. 4
- J. Am. Chem. Soc. 2019, 141, 20556.

15-8380 NEW

[S(R)]-N-[(1S)-1-[2-(9-Anthracenyl) phenyl]-2-(diphenylphosphino)ethyl]-N,2-dimethyl-2-propanesulfinamide, 95%

C<sub>39</sub>H<sub>38</sub>NOPS; FW: 599.8; white to off-white pwdr. air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

Ph<sub>2</sub>P 0-5 ′tBu 50mg

15-8478 NEW

[S(R)]-N-[(S)-[(3-(Benzyloxy)-2-(dicyclohexylphosphino)phenyl]-(1,1'-biphenyl)methyl]-N,2-dimethyl-2-propanesulfinamide, 95%

C<sub>43</sub>H<sub>54</sub>NO<sub>2</sub>PS; FW: 679.9; white to off-white pwdr. air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

25mg Ph ″tBu Me PCy<sub>2</sub> OBn

15-8482 NEW

[S(R)]-N-[(S)-[3-(Benzyloxy)-2-(dicyclohexylphosphino)phenyl]-(2-naphthalenyl)methyl]-N,2-dimethyl-2-propanesulfinamide, 95%

C<sub>41</sub>H<sub>52</sub>NO<sub>2</sub>PS; FW: 653.9; white to off-white pwdr. air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

25mg "tBu PCy<sub>2</sub> OBn

15-8480 NEW

[S(R)]-N-[(S)-[3-(Benzyloxy)-2-(dicyclohexylphosphino)phenyl]-(2-naphthalenyl)methvI1-2-methyl-2-propanesulfinamide, 95%

C<sub>40</sub>H<sub>50</sub>NO<sub>2</sub>PS; FW: 639.9; white to off-white pwdr. air sensitive moisture sensitive Note: Sold in collaboration with Daicel for

research purposes only.

25mg "tBu PCy<sub>2</sub> OBn

15-8476

NEW

[S(R)]-N-[(R)-[(3-(Benzyloxy)-2-(dicyclohexylphosphino)phenyl)phenylmethyl]-N,2-dimethyl-2-propanesulfinamide, 95%

C<sub>37</sub>H<sub>50</sub>NO<sub>2</sub>PS; FW: 603.8; white to off-white pwdr. air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

25mg Ph tBu PCy<sub>2</sub> OBn

#### PHOSPHORUS (Compounds) 15-8474 [S(R)]-N-[(S)-[(3-(Benzyloxy)-2-(dicyclohexyl-25mg phosphino)phenyl)phenylmethyl]-N,2-dimeth-NEW yl-2-propanesulfinamide, 95% C<sub>37</sub>H<sub>50</sub>NO<sub>2</sub>PS; FW: 603.8; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only. ÓBn 15-8472 [S(R)]-N-[(R)-[(3-(Benzyloxy)-2-(dicyclohex-25mg ylphosphino)phenyl)phenylmethyl]-2-meth-NEW yl-2-propanesulfinamide, 95% C<sub>36</sub>H<sub>48</sub>NO<sub>2</sub>PS; FW: 589.8; white to off-white pwdr. air sensitive, moisture sensitive PCy<sub>2</sub> Note: Sold in collaboration with Daicel for research purposes only. ÓBn 15-8470 [S(R)]-N-[(S)-[(3-(Benzyloxy)-2-(dicyclohexylphosphino)phenyl)phenylmeth-25mg yl]-2-methyl-2-propanesulfinamide, 95% NEW C<sub>36</sub>H<sub>48</sub>NO<sub>2</sub>PS; FW: 589.8; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only. N-[(1S)-1-[1,1'-Biphenyl]-2-yl-2-(diphenyl-15-8506 50mg Ph<sub>2</sub>P phosphino)ethyl]-3,5-bis(trifluoromethyl)-ben-NEW zamide, 95% (2089424-10-0) C<sub>35</sub>H<sub>26</sub>F<sub>6</sub>NOP; FW: 621.6; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.

#### Technical Notes:

- 1. Organocatalyst used in aza-[4+2] cycloaddition of N-sulfonyl-1-aza-1,3-dienes with vinyl ketones.
- Catalyst for the enantioselective [3+2] cycloadditions of γ-substituted allenoates with β-perfluoroalkyl enones.
- Catalyst for asymmetric intermolecular cross Rauhut-Currier reaction of β-perfluoroalkyl-substituted enones and vinyl ketones.

NSO<sub>2</sub>R<sup>2</sup>

$$R^3$$
 $R^3$ 
 $R^4$ 
 $R^4$ 

- 1. Org. Lett. 2017, 19, 1710.
- 2. Chem. Sci., 2017, 8, 4660.
- 3. Adv. Synth. Catal. 2017, 359, 3347.

15-8368 NEW [S(R)]-N-[(1S)-1-[1,1'-Biphenyl]-2-yl-2-(diphenylphosphino)ethyl]-2-methyl-2-propanesulfinamide, 95% (1936438-14-0)

 $C_{30}H_{32}$ NOPS; FW: 485.6; white to off-white pwdr. air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

100mg

#### Technical Notes:

- Organocatalyst used in enantioselective intermolecular cross Rauhut-Currier reactions of activated alkenes with acrolein.
- 2. Organocatalyst used in aza-[4+2] cycloaddition of N-sulfonyl-1-aza-1,3-dienes with vinyl ketones.
- 3. Catalyst for the enantioselective [3+2] cycloadditions of  $\gamma$ -substituted allenoates with  $\beta$ -perfluoroalkyl enones.
- Ligand for the direct Pd-catalyzed cross-coupling reaction of easily accessible secondary phosphine oxides and aryl bromides, which provides rapid access to P-chiral phosphine oxides.

$$R_1 \xrightarrow{\text{CO}_2\text{Et}} \xrightarrow{\text{CO}_2\text{Et}} \xrightarrow{\text{EtO}_2\text{C}} R_f \xrightarrow{\text{Ref. (3)}} R_f \xrightarrow{\text{Tech. Note (3)}} R_f \xrightarrow{\text{Ref. (3)}} R_f \xrightarrow{\text{Re$$

$$\begin{array}{c} \text{Me O} \\ \text{P} \\ \text{H} \end{array} + R^2 \\ \hline \begin{array}{c} \text{I} \\ \\ \hline \end{array} \end{array} \begin{array}{c} \text{Br} \\ \hline \\ \text{Cs}_2 \text{CO}_3, \text{ anisole, } 35^{\circ}\text{C} \end{array} \begin{array}{c} \text{Me O} \\ \\ \text{P} \\ \end{array} \begin{array}{c} \text{R}^1 \\ \\ \text{Ref. (4)} \end{array}$$

- 1. Chem. Commun., 2016, 52, 7612.
- 2. Org. Lett. 2017, 19, 1710.
- Chem. Sci., 2017, 8, 4660.
- J. Am. Chem. Soc. 2019, 141, 20556.

15-8520 NEW

(11bR)-2,6-Bis[4-(9-anthracenyl)-2,6-bis(isopropyl)phenyl]-4-hydroxy-4-oxide-dinaphtho[2,1d:1',2'-f][1,3,2]dioxaphosphepin, 95%, (99% ee) (1236191-19-7)

10mg 25mg

C<sub>70</sub>H<sub>61</sub>O<sub>4</sub>P; FW: 1021.2; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research

purposes only.

Technical Notes:

1. Organocatalyst for enantioselective Friedel-Crafts alkylation reaction of indoles with  $\alpha,\beta$ -unsaturated acyl phosphonates.

Used in the Lewis base/chiral Brønsted acid catalyzed enantioselective bromocycloetherification.

Chiral phosphoric acid catalyst for the kinetic resolution of indolines based on a self-redox reaction.

$$R^{\text{JOC}}OH \xrightarrow{\text{NBS-CPA}} OH \xrightarrow{\text{NBS-CPA}} R^{\text{Br}}Or \xrightarrow{\text{Ref. (2)}} R^{\text{Er. (2)}}$$

References:

Chem. Commun. 2010, 46, 4112. 1.

Org. Lett., 2012, 14, 256.

Angew. Chem. Int. Ed. 2016, 55, 3148.

15-8521 (11bS)-2,6-Bis[4-(9-anthracenyl)-2,6-bis(isopropyl)phenyl]-4-hydroxy-4-oxide-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 95%, (99% ee) NEW (1051435-82-5)

10mg 25mg

C<sub>72</sub>H<sub>61</sub>O<sub>4</sub>P; FW: 1021.2; off white to light yellow pwdr.

Note: Sold in collaboration with Daicel for research purposes only.

Technical Notes:

1. Used in direct Brønsted acid catalyzed asymmetric three-component Kabachnik-Fields reaction.

2. Used in direct catalytic asymmetric synthesis of cyclic aminals from aldehydes.

3. Brønsted acid catalyst for asymmetric acetalization of aliphatic aldehydes.

15-8521 (continued)

(11bS)-2,6-Bis[4-(9-anthracenyl)-2,6-bis(isopropyl)phenyl]-4-hydroxy-4-oxide-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 95%, (99% ee) (1051435-82-5)

#### References:

- 1. Angew. Chem. Int. Ed. 2013, 52, 4474.
- 2. J. Am. Chem. Soc. 2008, 130, 15786.
- 3. Angew. Chem. Int. Ed. 2008, 47, 5079.

15-0564 NEW (11aS)-3,7-Bis[3,5-bis[3,5-bis(trifluoromethyl) phenyl]phenyl]-10,11,12,13-tetrahydro-5-hydroxy-diindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocin, 98%, (99% ee)

 $C_{61}H_{31}F_{24}O_4P$ ; FW: 1314.8; off white to light yellow pwdr.

Note: Sold in collaboration with Daicel for research purposes only.

15-8588 NEW (11aR)-3,7-Bis[3,5-bis(tert-butyl)-4-methoxyphenyl]-10,11,12,13-tetrahydro-10,10,13,13tetramethyl-5-hydroxy[7,1-de:1',7'-fg][1,3,2] dioxaphosphocin, 98%, (99% ee)

C<sub>51</sub>H<sub>67</sub>O<sub>6</sub>P; FW: 807; off white to light yellow pwdr.

Note: Sold in collaboration with Daicel for research purposes only.

15-8589 NEW (11aS)-3,7-Bis[3,5-bis(tert-butyl)-4-methoxyphenyl]-10,11,12,13-tetrahydro-10,10,13,13-tetramethyl-5-hydroxy-5-oxide-diindeno[7,1-de:1',7'-fg][1,3,2] dioxaphosphocin, 98%, (99% ee)

 $C_{51}H_{67}O_6P$ ; FW: 807; off white to light yellow pwdr.

Note: Sold in collaboration with Daicel for research purposes only.

25mg

100mg

#### PHOSPHORUS (Compounds) 15-0578 (11aS)-3,7-Bis[3,5-bis(tert-butyl)phenyl]-25mg t-Bu 10,11,12,13-tetrahydro-5-hydroxy-5-oxide-diin-NEW deno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocin, 98%, (99% ee) C<sub>45</sub>H<sub>55</sub>O<sub>4</sub>P; FW: 690.9; off white to light yellow t-Bu pwdr. O.PEOH Note: Sold in collaboration with Daicel for research purposes only. t-Bu t-Bu 15-8592 (11aR)-3,7-Bis[3,5-bis(tert-butyl)phenyl]-25mg t-Bu 10,11,12,13-tetrahydro-10,10,13,13-tetrameth-100mg NEW yl-5-hydroxy-5-oxide-diindeno[7,1-de:1',7'-fg] [1,3,2]dioxaphosphocin, 98%, (99% ee) Me t-Bu C<sub>40</sub>H<sub>63</sub>O<sub>4</sub>P; FW: 747; off white to light yellow Mρ 0 pwdr. O. OH. Note: Sold in collaboration with Daicel for Me t-Bu research purposes only. t-Bu 15-8593 (11aS)-3,7-Bis[3,5-bis(tert-butyl)phenyl]-10,11,12,13-tetrahydro-10,10,13,13-25mg tetramethyl-5-hydroxy-5-oxide-diindeno[7,1-de:1',7'-fg][1,3,2]dioxaphos-100mg NEW phocin, 98%, (99% ee) C<sub>40</sub>H<sub>63</sub>O<sub>4</sub>P; FW: 747; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only. 15-8575 (11aR)-3.7-Bis(4-chlorophenyl)-10.11.12.13-25ma tetrahydro-10,10,13,13-tetramethyl-5-hydroxy-100ma Me NEW diindeno[7,1-de:1',7'-fg][1,3,2]dioxaphospho-.<sub>P</sub>=0 cin, 98% $\cap$ HO C<sub>33</sub>H<sub>29</sub>Cl<sub>2</sub>O<sub>4</sub>P; FW: 591.5; off white to light yellow Me nwdr Note: Sold in collaboration with Daicel for research purposes only. 15-3360 1-[2,6-Bis(cyclohexyloxy)phenyl]-2-(di-tert-100ma butylphosphaneyl)-1H-imidazole, min. 95% tBu 500mg NEW (2179272-79-6) $C_{29}H_{45}N_2O_2P$ ; FW: 484.66; white to off-white to tBu pale vellow solid air sensitive Note: Sold in collaboration with Solvias for research purposes only. Patents: EP 1625133, US 2007/0123707.

#### Technical Notes:

- Ligand for the Pd-catalyzed Barbier-Negishi coupling of secondary alkyl bromides with aryl and alkenyl triflates and nonaflates.
- Used in Pd-catalyzed enantioselective synthesis of β2- and β3- amino acids via asymmetric and regiodivergent C-H Functionalization of Boc-1,3-oxazinanes.

$$R^{1} \xrightarrow{R^{2}} + R^{3} - X \xrightarrow{\text{[Pd] Ligand}} R_{1} \xrightarrow{\text{Mg, LiCl, ZnCl}_{2}; THF} R^{1} \xrightarrow{R^{2}} R^{3} \xrightarrow{\text{Tech. Note (1)}} Ref. (1)$$

15-3360 1-[2,6-Bis(cyclohexyloxy)phenyl]-2-(di-tertbutylphosphaneyl)-1H-imidazole, min. 95% (continued) (2179272-79-6)

#### References:

- 1. Angew. Chem. Int. Ed. 2018, 57, 1982.
- 2. Nat. Catal. 2019, 2, 882.

#### Technical Notes:

- . Organocatalyst used in aza-[4+2] cycloaddition of N-sulfonyl-1-aza-1,3-dienes with vinyl ketones.
- Catalyst for the enantioselective [3+2] cycloadditions of γ-substituted allenoates with β-perfluoroalkyl
  enones.
- Phosphine catalyst for difunctionalization of β-fluoroalkyl α, β-Enones to generate β-amino α-diazo carbonyl compounds.

$$\begin{array}{c}
O \\
R_1
\end{array}
+ Ar$$

$$\begin{array}{c}
CO_2Et \\
\end{array}$$

$$\begin{array}{c}
Phosphine \\
toluene, -20^{\circ}C
\end{array}$$

$$\begin{array}{c}
EtO_2C \\
Ar
\end{array}$$

$$\begin{array}{c}
R_1 \\
Ar
\end{array}$$

$$\begin{array}{c}
Ref. (2)
\end{array}$$
Tech. Note (2)

$$\begin{array}{c} O & R'' \\ R' & + R_1R_2R_3SiN_3 & \underline{Phosphine} \\ o\text{-xylene, rt, N}_2 & R' & R_f \end{array}$$

$$\begin{array}{c} NH_2 \\ R_f & Ref. (3) \end{array}$$

- Org. Lett. 2017, 19, 1710.
- 2. Chem. Sci., 2017, 8, 4660
- 3. Angew. Chem. Int. Ed. 2018, 57, 15787.

15-8372 NEW [S(R)]-N-[(1S)-1-[3',5'-Bis(1,1-dimethylethyl)-4'-methoxy[1,1'-biphenyl]-2-yl]-2-(diphenyl-phosphino)ethyl]-2-methyl-2-propanesulfinamide, 95% (1936438-26-4)

C<sub>39</sub>H<sub>50</sub>NO<sub>2</sub>PS; FW: 627.9; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for N.S.

OMe

t-Bu

Me

t-Bu

'tBu

OMe

Ph<sub>2</sub>P

Technical Notes:

 Organocatalyst used in enantioselective intermolecular cross Rauhut-Currier reactions of activated alkenes with acrolein.

research purposes only.

- Used in phosphine-catalyzed asymmetric umpolung addition of trifluoromethyl ketimines to Morita-Baylis-Hillman carbonates.
- 3. Organocatalyst for [4+2] anulation of electron-deficient dienes and vinyl ketones.

Ar OBoc 
$$N + CO_2^tBu \xrightarrow{Peng-Phos} Toluene, rt$$
  $N CF_3 Ref. (2)$  Ref. (2)

References:

- 1. Chem. Commun., 2016, 52, 7612.
- 2. Angew. Chem. Int. Ed. 2016, 55, 13316.
- 3. Adv. Synth. Catal. 2018, 360, 682.

15-8438 NEW [S(R)]-N-[(R)-[3,5-Bis(1,1-dimethylethyl)-4-methoxyphenyl][2-(dicyclohexylphosphino) phenyl]methyl]-N,2-dimethyl-2-propanesulfinamide. 95%

 $C_{30}H_{62}NO_2PS$ ; FW: 640.0; white to off-white pwdr. air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

Technical Notes:

 Ligand for the Pd-catalyzed enantioselective reductive Heck reactions to generate 3.3-disubstituted 2.3-dihydrobenzofuran.

2. Ligand for the Pd-catalyzed enantioselective carboiodination of olefin-tethered aryl iodides.

Ligand for the Pd-catalyzed enantioselective dicarbofunctionalization of unactivated alkenes via Heck-Suzuki coupling reaction.

50mg

50mg

15-8438 [S(R)]-N-[(R)-[3,5-Bis(1,1-dimethylethyl)-4-methoxyphenyl][2-(dicyclohexylphosphino) (continued) phenyl]methyl]-N,2-dimethyl-2-propanesulfinamide, 95%

$$R^{1} \stackrel{\text{II}}{ | | |} X \stackrel{\text{II}}{ | |} X_{2} \stackrel{\text{II}}{ | |} X_{2} \stackrel{\text{II}}{ | |} X_{2} \stackrel{\text{II}}{ | |} X_{3} \stackrel{\text{II}}{ | |} X_{4} \stackrel{\text{II}}{ |} X$$

X = O: N-Boc

$$R^{1} \stackrel{\text{I}}{\underset{\text{II}}{|I|}} X \stackrel{\text{I}}{\underset{\text{II}}{|I|}} R^{2} \stackrel{\text{[Pd] XuPhos}}{\underset{\text{R-B(OH)}_{2}}{|I|}} R^{1} \stackrel{\text{II}}{\underset{\text{II}}{|I|}} X^{1} \stackrel{\text{II}}{\underset{\text{II}$$

X = C, O, N; R = Aryl, Alkyl, Vinyl

#### References:

- Angew. Chem. Int. Ed. 2018, 57, 10373. 1.
- 2. J. Am. Chem. Soc. 2019, 141, 8110.
- Angew. Chem. Int. Ed. 2019, 58, 14653.
- Angew. Chem. Int. Ed. 2020, 59, 2769.

#### 15-8436 [S(R)]-N-[(S)-[3,5-Bis(1,1-dimethylethyl)-4-methoxyphenyl][2-(dicyclohexylphosphino)phenyl]methyl]-N,2-dimethyl-2-propanesulfinamide, 95%

50mg

50mg

50mg

NEW

C<sub>39</sub>H<sub>62</sub>NO<sub>2</sub>PS; FW: 640.0; white to off-white pwdr. air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

#### Technical Note:

See 15-8438 (page 48) 1.

#### 15-8434 NEW

[S(R)]-N-[(R)-[3,5-Bis(1,1-dimethylethyl)-4-methoxyphenyl][2-(dicyclohexylphosphino) phenyl]methyl]-2-methyl-2-propanesulfinamide, 95%

C<sub>38</sub>H<sub>60</sub>NO<sub>2</sub>PS; FW: 625.9; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for

0 "tBu PCy<sub>2</sub>

t-Bu

OMe

t-Bu

#### 15-8320 NEW

[S(R)]-N-[(R)-[3,5-Bis(1,1-dimethylethyl)-4-methoxyphenyl][2-(diphenylphosphino)phenyl] methyl]-2-methyl-2-propanesulfinamide, 95% (1616688-64-2)

C<sub>38</sub>H<sub>48</sub>NO<sub>2</sub>PS; FW: 613.80; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for

t-Ru t-Bu tBu PPh<sub>2</sub>

OMe

#### Technical Note"

Ligand for the enantioselective Au-catalyzed [3+3] cycloaddition reaction of 2-(1-alkynyl)-alk-2-en-1-ones with nitrones.

research purposes only.

research purposes only.

#### References:

Angew. Chem. Int. Ed. 2014, 53, 4350.

PHOSPHOR	US (Compounds)		
15-8318 NEW	[S(R)]-N-[(S)-[3,5-Bis(1,1-dimethylethyl)-4-methylphosphino)phenyl]methyl]-2-methyl-2-propa (1616688-63-1) C <sub>38</sub> H <sub>48</sub> NO <sub>2</sub> PS; FW: 613.80; white to off-white pwd air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research	nesulfinamide, 95% r.	50mg
Technical Note: 1. See 15-	8320 (page 49)		
15-8464 NEW	[S(R)]-N-[(S)-3,5-Bis(dimethylethyl)phenyl] [2-(dicyclohexylphosphanyl)phenyl]-N,2-dimethyl-2-propanesulfinamide, 95% C <sub>38</sub> H <sub>60</sub> NOPS; FW: 607.9; light-yellow to yellow pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	t-Bu t-Bu  N.S. "tBu  Me	50mg
15-8462 NEW	[S(R)]-N-[(S)-3,5-Bis(dimethylethyl)phenyl] [2-(dicyclohexylphosphanyl)phenyl]-2-meth- yl-2-propanesulfinamide, 95% C <sub>37</sub> H <sub>58</sub> NOPS; FW: 595.9; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	PCy <sub>2</sub> t-Bu  O  N  S  "tBu  PCy <sub>2</sub> t-Bu  PCy <sub>2</sub> t-Bu	50mg
15-8578 NEW	(11aR)-3,7-Bis((4-(1,1-dimethylethyl)phenyl)-10,11,12,13-tetrahydro-10,10,13,13-tetramethyl-5-hydroxy-diindeno[7,1-de:1',7'-fg][1,3,2] dioxaphosphocin, 98%, (99% ee) C <sub>41</sub> H <sub>47</sub> O <sub>4</sub> P; FW: 634.8; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	Me O P O H Me P Bu	25mg 100mg
15-8562 NEW	(11aR)-3,7-Bis(3,5-dimethylphenyl)- 10,11,12,13-tetrahydro-10,10,13,13-tetrameth- yl-5-hydroxy-5-oxide-diindeno[7,1-de:1',7'-fg] [1,3,2]dioxaphosphocin, 98%, (99% ee) C <sub>37</sub> H <sub>39</sub> O <sub>4</sub> P; FW: 578.7; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	Me	25mg 100mg
15-8563 NEW	(11aS)-3,7-Bis(3,5-dimethylphenyl)- 10,11,12,13-tetrahydro-10,10,13,13-tetrameth- yl-5-hydroxy-5-oxide-diindeno[7,1-de:1',7'-fg] [1,3,2]dioxaphosphocin, 98%, (99% ee) $C_{37}H_{39}O_4P$ ; FW: 578.7; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	Me Me Me Me Me Me Me Me	25mg 100mg

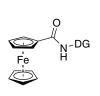
15-0165 NEW

(2R,3R)-(+)-Bis(diphenylphosphino)butane, min.98%,(R,R)-CHIRAPHOS (74839-84-2) (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>; FW: 426.48; white xtl.; m.p. 104-109 °C air sensitive

PPh<sub>2</sub> P̄Ph₂

Technical Notes:

- 1. A bidentate chiral phosphine ligand used in chiral catalysis.1-2
- Also used in metal catalysis chemistry.3 2.



Tech. Note (1) Ref. (1)

250mg

1g

5g

1g

DG = directing group, chiral ligand 15-0165, up to 46% ee

R = alkyl, aryl,up to 94% yield.

#### References:

- Organometallics, 2017, 4979-4989. 1.
- J. Am. Chem. Soc. 1996, 118, 4723-4724.
- J. Am. Chem. Soc. 2008, 130, 12874-12875.

15-8250 NEW

Bis(3,5-di-tert-butylphenyl)cyclohexylphosphine, min. 98% CyTyrannoPhos (2097604-67-4) C<sub>34</sub>H<sub>53</sub>P; FW: 492.76; white to off-white solid air sensitive, moisture sensitive

250mg tBu tBu

tBu

amp

#### Technical Note:

Ligand used for Ni-catalysed Suzuki coupling of reactions of benzylic acetals.

OR 
$$(\rho\text{-F-Ar}^1\text{BO})_3$$
 or  $(\rho\text{-F-Ar}^1\text{BO})_3$  OR OR OR  $(\rho\text{-F-Ar}^1\text{BO})_3$  Toluene, 70 °C, 16 h  $(\rho\text{-F-Ar}^1\text{BO})_3$  Ref. (1)

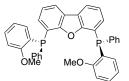
#### References:

Nat. Chem., 2017, 9, 779.

15-1269 NEW

(-)-4,6-Bis((S)-(2-methoxyphenyl)(phenyl) phosphinyl)dibenzo[b,d]furan, min. 97% (2119686-75-6)

C<sub>38</sub>H<sub>30</sub>O<sub>3</sub>P<sub>2</sub>; FW: 596.60; white to off-white solid air sensitive, moisture sensitive, (store cold) Note: Sold under license of WO2017/191310 for research purposes only.



25mg 100mg

#### Technical Note:

P-Chirogenic Xantphos ligand used for the synthesis and application in Rhodium-catalyzed asymmetric hydrogenation.



Rh(CO)<sub>2</sub>(acac), 1.2 eq. Ligand 40° C. 50 bar





Tech. Note (1) Ref. (1)

#### References:

ACS Catal., 2017, 7, 6162-6169.

#### PHOSPHORUS (Compounds) 15-8524 (11bR)-2,6-Bis[2-methoxyphenyl-5-(tert-bu-25mg MeO tyl)]-4-hydroxy-4-oxide-dinaphtho[2,1-d:1',2'-f] 100mg NEW [1,3,2]dioxaphosphepin, 98%, (99% ee) C<sub>42</sub>H<sub>41</sub>O<sub>6</sub>P; FW: 672.7; off white to light yellow t-Bu pwdr. Note: Sold in collaboration with Daicel for research purposes only. t-Bu MeO 25mg 15-8525 (11bS)-2,6-Bis[2-methoxyphenyl-5-(tert-butyl)]-4-hydroxy-4-oxide-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 98%, (99% ee) 100mg NEW C<sub>42</sub>H<sub>41</sub>O<sub>6</sub>P; FW: 672.7; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only. 2-[Bis(1-methylethyl)phosphino]-1-phenyl-1H-pyrrole, 100mg 15-3365 min. 95% (1257847-61-2) 500mg NEW C<sub>16</sub>H<sub>22</sub>NP; FW: 259.33; white to off-white to pale yellow solid air sensitive Note: Sold in collaboration with Solvias for research purposes only. Patents: EP 1625133, US 2007/0123707. Technical Notes: 1. Ligand for the Ru-catalyzed direct amination of secondary alcohols using ammonia. Ligand for the Pd-catalyzed $\alpha$ - and $\beta$ -arylation of acyclic N-Boc amines. 2. Used in Pd-catalyzed enantioselective synthesis of β²- and β³- amino acids via asymmetric and regiodivergent C-H Functionalization of Boc-1,3-oxazinanes. OH [Ru] Ligand R1 NH<sub>2</sub> NH<sub>3</sub>; Cyclohexane, 140°C Tech. Note (1) Ref. (1)

- 1. Angew. Chem. Int. Ed. 2010, 49, 8130.
- 2. Angew. Chem. Int. Ed. 2014, 53, 2678.
- Nat. Catal. 2019, 2, 882. 3.

15-1285 NEW

1,3-Bis[(1R)-1-(1-naphthalenyl)ethyl]-2,3-dihydro-1H-1,3,2-diazaphosphol-2-yl trifluoromethanesulfonate, min. 98% (2377935-66-3) C<sub>27</sub>F<sub>3</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>PS; FW: 544.53; light beige solid moisture sensitive

O S O CF<sub>3</sub>

> 98% conversion

50mg

250mg

Technical Notes:

- 1. Asymmetric Imine Hydroboration Catalyzed by Chiral Diazaphospholenes.
- Enantioselective Imine Reduction Catalyzed by Phosphenium Ions. 2.

Note: Patents: PCT #CA2018/051078

grams of catalyst in 3 steps!

#### References:

asymmetric imine reduction

- Angew. Chem. Int. Ed. 2017, 56, 16660. 1.
- J. Am. Chem. Soc. 2019, 141, 36, 14083-14088. 2.



Technical Note:

Used as an organocatalyst for enantioselective imine reduction.



1. J. AIII.	Sileili. 300. <b>2013</b> , 141, 14003.		
15-8585 NEW	(11aS)-3,7-Bis(4-nitrophenyl)-10,11,12,13-tetrahydro-10,10,13,13-tetramethyl-5-hydroxy-5-oxide-diindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocin, 95%, (99% ee) $C_{33}M_{29}N_2O_8P$ ; FW: 612.6; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	Me NO <sub>2</sub> Me NO <sub>2</sub> Me NO <sub>2</sub>	25mg 100mg
15-8584	(11aR)-3,7-Bis(4-nitrophenyl)-10,11,12,13-tetrahy	ydro-10,10,13,13-tetrameth-	25mg
NEW	yl-5-hydroxy-5-oxide-diindeno[7,1-de:1',7'-fg][1, (99% ee) C <sub>33</sub> H <sub>29</sub> N <sub>2</sub> O <sub>8</sub> P; FW: 612.6; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research		100mg

#### **PHOSPHORUS (Compounds)** 15-8460 [S(R)]-N-[(R)-3,5-Bis(trifluoromethyl)phenyl] 50mg [2-(dicyclohexylphosphanyl)phenyl]-N,2-di-NEW methyl-2-propanesulfinamide, 95% C<sub>32</sub>H<sub>42</sub>F<sub>6</sub>NOPS; FW: 633.7; gray pwdr. air sensitive, moisture sensitive ″tBu Note: Sold in collaboration with Daicel for Me research purposes only. [S(R)]-N-[(S)-[3,5-Bis(trifluoromethyl)phenyl] 15-8516 50ma CF<sub>3</sub> [2- (diphenylphosphino)phenyl]meth-NEW yl]-2-methyl-2-propanesulfinamide, 95% 0 (2262535-73-7) .Š.<sub>″tBu</sub> C<sub>31</sub>H<sub>28</sub>F<sub>6</sub>NOPS; FW: 607.6; white to off-white pwdr. air sensitive, moisture sensitive PPh<sub>2</sub> Note: Sold in collaboration with Daicel for research purposes only.

#### Technical Note:

Phosphine ligand for the Ag(I)-catalyzed enantioselective [3+2] cycloaddition of azomethine ylides.

#### References:

Ora Riomal Chem 2019 17 1395

15-8581 NEW	(11aS)-3,7-Bis(4-(trifluoromethyl)phenyl)-10,11,12,13-tetrahydro-10,10,13,13-tetramethyl-5-hydroxy-5-oxide-diindeno[7,1-de:1',7'-fg] [1,3,2]dioxaphosphocin, 95%, (99% ee) $C_{36}F_{29}F_{6}O_4P$ ; FW: 658.6; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	Me O OH Me CF <sub>3</sub>	25mg 100mg
15-7555	Bis(2,4,4-trimethylpentyl)phosphinic acid, min. 85%, CYTOP® 501 ( $83411$ - $71$ - $6$ ) $C_{16}H_{35}O_2P$ ; FW: 290.42; Yellow liq.; f.p. >2226 °F; d. 0.92 Note: Sold in collaboration with Solvay.	Me Me O Me Me	100g
NEW		Me OH Me	500g

PHOSPHORU	JS (Compounds)	
15-8486 NEW	[S(R)]-N-[(R)-[2-(Diadamantanphosphino) phenyl]phenylmethyl]-N,2-dimethyl-2-propanesulfinamide, 95%  C <sub>38</sub> H <sub>52</sub> NOPS; FW: 601.9; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	50mg
15-8484 NEW	[S(R)]-N-[(S)-[2-(Diadamantanphosphino)phenyl]phenylmethyl]-N,2-dimethyl-2-propanesulfinamide, 95% $C_{38}H_{52}NOPS; FW: 601.9; white to off-white pwdr. \\ \textit{air sensitive, moisture sensitive} \\ Note: Sold in collaboration with Daicel for research purposes only. $	50mg
15-8488 NEW	[S(R)]-N-[(R)-[2-(Diadamantanphosphino) phenyl]phenylmethyl]-2-methyl-2-propanesulfinamide, 95%  C <sub>37</sub> H <sub>50</sub> NOPS; FW: 587.8; white to off-white pwdr. air sensitive, moisture sensitive  Note: Sold in collaboration with Daicel for research purposes only.	50mg
15-8490 NEW	[S(R)]-N-[(S)-[2-(Diadamantanphosphino)phenyl]phenylmethyl]-2-meth-yl-2-propanesulfinamide, 95%  C <sub>37</sub> H <sub>50</sub> NOPS; FW: 587.8; white to off-white pwdr. air sensitive, moisture sensitive  Note: Sold in collaboration with Daicel for research purposes only.	50mg
15-8570 (NEW)	(11aS)-3,7-Di-9-anthracenyl-10,11,12,13-tetrahydro-10,10,13,13-tetramethyl-5-hydroxy-5-oxide-diindeno[7,1-de:1',7'-fg][1,3,2]dioxaphos-phocin, 95%, (99% ee) $C_{49}H_{39}O_4P$ ; FW: 722.8; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	25mg 100mg
15-1044 NEW	Di-t-butylphosphine (50% in Toluene) (819-19-2) [(CH <sub>3</sub> ) <sub>3</sub> C] <sub>2</sub> PH; FW: 146.22; colorless liq.; d. 0.79 air sensitive	25g 100g
15-8454 NEW	[S(R)]-N-[(1S)-1-[2-(Dicyclohexylphosphanyl) phenyl]-cyclohexyl]-2-methyl-2-propanesulfinamide, 95%  C <sub>29</sub> H <sub>48</sub> NOPS; FW: 489.7; white to off-white pwdr. air sensitive, moisture sensitive  Note: Sold in collaboration with Daicel for research purposes only.	50mg
15-8452 NEW	[S(R)]-N-[(1S)-1-[2-(Dicyclohexylphosphanyl) phenyl]-2,2-dimethylpropyl]-2-methyl-2-propanesulfinamide, 95%  C <sub>27</sub> H <sub>46</sub> NOPS; FW: 463.7; white to off-white pwdr. air sensitive, moisture sensitive  Note: Sold in collaboration with Daicel for research purposes only.	50mg

PHOSPHOR	US (Compounds)		
15-8450 NEW	[S(R)]-N-[(R)-[2-(Dicyclohexylphosphanyl) phenyl](4-methoxyphenyl)methyl]-N,2-dimethyl-2-propanesulfinamide, 95% C <sub>31</sub> H <sub>46</sub> NO <sub>2</sub> PS; FW: 511.7; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	OMe O N.S. (tBu Me PCy <sub>2</sub>	50mg
15-8448 NEW	[S(R)]-N-[(S)-[2-(Dicyclohexylphosphanyl)phen yl]-N,2-dimethyl-2-propanesulfinamide, 95% C <sub>31</sub> H <sub>46</sub> NO <sub>2</sub> PS; FW: 511.7; yellow air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research		50mg
15-8458 NEW	[S(R)]-N-[(R)-[2-(Dicyclohexylphosphanyl) phenyl](4-(tert-butyl)phenyl)methyl]-N,2-dimethyl-2-propanesulfinamide, 95% C <sub>34</sub> H <sub>52</sub> NOPS; FW: 553.8; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	O U U U U U U U U U U U U U U U U U U U	50mg
15-8432 NEW	[S(R)]-N-[(S)-1-[2-(Dicyclohexylphosphino) phenyl]-(1,1'-biphenyl)methyl]-2-methyl-2-propanesulfinamide, 95% C <sub>35</sub> H <sub>46</sub> NOPS; FW: 559.8; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	Ph O N S V tBu PCy <sub>2</sub>	50mg
15-8444 NEW	[S(R)]-N-[(R)-[2-(Dicyclohexylphosphino) phenyl]-2-naphthalenylmethyl]-N,2-dimethyl-2-propanesulfinamide, 95% C <sub>34</sub> H <sub>46</sub> NOPS; FW: 547.8; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	O N.S., tBu Me PCy <sub>2</sub>	50mg
15-8446 NEW	[S(R)]-N-[(R)-[2-(Dicyclohexylphosphino) phenyl]-2-naphthalenylmethyl]-2-dimethyl-2-propanesulfinamide, 95% C <sub>33</sub> H <sub>44</sub> NOPS; FW: 533.7; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	O N S., tBu PCy <sub>2</sub>	50mg

15-8440 NEW

[S(R)]-N-[(S)-[2-(Dicyclohexylphosphino) phenyl]-1-naphthalenylmethyl]-N,2-dimethyl-2-propanesulfinamide, 95% (2241598-33-2) C<sub>34</sub>H<sub>46</sub>NOPS; FW: 547.8; pink pwdr.

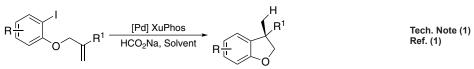
air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

50mg

#### Technical Note:

1. Ligand for the Pd-catalyzed enantioselective reductive Heck reactions to generate 3,3-disubstituted 2,3-dihydrobenzofuran.



#### References:

1. Angew. 15-8442 NEW	Chem. Int. Ed. 2018, 57, 10373.  [S(R)]-N-[(S)-[2-(Dicyclohexylphosphino)phenyl]-2-naphthalenylmeth- yl]-N,2-dimethyl-2-propanesulfinamide, 95%  C <sub>34</sub> H <sub>46</sub> NOPS; FW: 547.8; light-yellow to yellow pwdr. air sensitive, moisture sensitive	50mg
15-8430	Note: Sold in collaboration with Daicel for research purposes only.  [S(R)]-N-[(R)-[2-(Dicyclohexylphosphino) phenyl]phenylmethyl]-N,2-dimethyl-2-propanesulfinamide, 95% C <sub>30</sub> H <sub>44</sub> NOPS; FW: 497.7; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	50mg
15-8428	[S(R)]-N-[(S)-[2-(Dicyclohexylphosphino)phenyl]phenylmethyl]-N,2-dimeth-	50mg

yl-2-propanesulfinamide, 95% (2241598-32-1) NEW

C<sub>30</sub>H<sub>44</sub>NOPS; FW: 497.7; white to off-white pwdr. air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

Technical Note:

See 15-8440 (page 57)

15-8424 [S(R)]-N-[(S)-[2-(Dicyclohexylphosphino)phenyl]phenylmethyl]-2-methyl-2-propanesulfinamide, 95% (1595319-99-5) NEW

C<sub>29</sub>H<sub>42</sub>NOPS; FW: 483.7; white to off-white pwdr.

air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.

Technical Note:

1. See 15-8426 (page 58) 50mg

15-8426 NEW [S(R)]-N-[(R)-[2-(Dicyclohexylphosphino)phenyl] phenylmethyl]-2-methyl-2-propanesulfinamide, 95%

C<sub>29</sub>H<sub>42</sub>NOPS; FW: 483.7; white to off-white pwdr. air sensitive. moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

Ph O 50mg
N S 11th

#### Technical Notes:

- Ligand for the Pd-catalyzed enantioselective reductive Heck reactions to generate 3,3-disubstituted 2,3-dihydrobenzofuran.
- 2. Ligand for the Pd-catalyzed enantioselective Heck reaction of aryl triflates and alkynes.

$$R^{1} \stackrel{\text{II}}{=} X + R^{2} = R^{3} \stackrel{\text{[Pd] XuPhos}}{=} R^{3} \stackrel{\text{R}^{1}}{=} R^{3}$$

$$R^{1} \stackrel{\text{Tech. Note (2)}}{=} R^{3}$$

$$R^{2} \stackrel{\text{Ref. (2)}}{=} R^{3}$$

#### References:

- 1. Angew. Chem. Int. Ed. 2018, 57, 10373.
- J. Am. Chem. Soc. 2019, 141, 19246.

NEW

[5(K)]-N-[(K)-[4-(,),1-Dimetriylethyl)phenyi] [5-(diphenylphosphino)-9,9-dimethyl-9H-xanthen-4-yl]methyl]-2-methyl-2-propanesulfinamide, 95% (2160535-58-8)

C<sub>42</sub>H<sub>46</sub>NO<sub>2</sub>PS; FW: 659.9; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.

#### Technical Note:

 Ligand for the Au-catalyzed asymmetric intramolecular cyclization of N-allenamides for the synthesis of chiral tetrahydrocarbolines.

15-8410 [S(R)]-N-[(R)-[4-(1,1-Dimethylethyl)phenyl][5-(diphenylphosphino)-9,9-dimethyl-9H-xanthen-4-yl]methyl]-2-methyl-2-propanesulfinamide, 95% (2160535-58-8) (continued)

#### References:

1. Angew. Chem. Int. Ed. 2017, 56, 15905.

15-8408 [S(R)]-N-[(S)-[4-(1,1-Dimethylethyl)phenyl][5-(diphenylphosphino)-9,9-dimethyl-9H-xanthen-4-yl]methyl]-2-methyl-2-propanesulfinamide, 95%

50ma

NEW

C<sub>42</sub>H<sub>46</sub>NO<sub>2</sub>PS; FW: 659.9; white to off-white pwdr.

air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

#### Technical Notes:

- 1. Ligand for the Au-catalyzed asymmetric intramolecular cyclization of N-allenamides for the synthesis of chiral tetrahydrocarbolines.
- 2. Ligand for the Pd-catalyzed enantioselective intermolecular denitrogenative cyclization of benzotriazoles with allenes and N-allenamides.

#### References:

- 1. Angew. Chem. Int. Ed. 2017, 56, 15905.
- Angew. Chem. Int. Ed. 2019, 58, 11444.

#### 15-4665 NEW

2-[(1,1-Dimethylethyl)thio]-N-[2-(diphenylphosphino)ethyl]-ethanamine (1883429-96-6)

C<sub>20</sub>H<sub>28</sub>NPS; FW: 345.48; yellow oil air sensitive

Note: Patents: US20170088571A1; U.S. Provisional

Patent Application No. 62/827,627.

# 50mg

#### Technical Note:

SNP ligand used in Ru-catalyzed selective ester hydrogenation.

#### References:

Org. Process Res. Dev. 2020, 24, 415. 1.

#### 15-4670 2-[(1,1-Dimethylethyl)thio]-N-[2-(diphenylphosphinyl)ethyl]-ethanamine

C<sub>20</sub>H<sub>28</sub>NOPS; FW: 361.48; yellow oil

Note: Patents: US20170088571A1; U.S. Provisional

Patent Application No. 62/827,627.

## Ph P N-H

250mg

25q

100a

500a

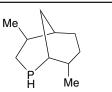
#### Technical Note:

1. See 15-4665 (page 59)

## 15-7605 4,8-Dimethyl-2-phosphabicyclo[3.3.1]nonane, min. 90%, CYTOP® 170 (328952-85-8)

 $C_{10}H_{19}P$ ; FW: 170.2; Colorless to pale yellow liq.; m.p. -22 °C; b.p. 120 °C; f.p. 221 °F; d. 0.95

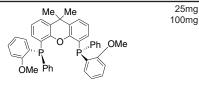
air sensitive, moisture sensitive Note: Sold in collaboration with Solvay.



#### 15-1239 NEW

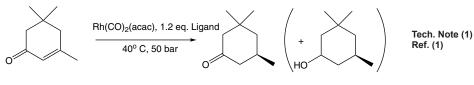
## (9,9-Dimethyl-9H-xanthene-4,5-diyl)bis[(o-methoxyphenyl)phenylphosphine], min. 97% (2119686-35-8)

 $C_{41}H_{36}O_3P_2$ ; FW: 638.67; white to off-white solid air sensitive, moisture sensitive, (store cold) Note: Sold under license of WO2017/191310 for research purposes only.



#### Technical Notes:

- P-Chirogenic Xantphos ligand used for the synthesis and application in Rhodium-catalyzed asymmetric hydrogenation.
- 2. Diastereo- and enantioselective copper catalyzed hydroallylation of disubstituted cyclopropenes.



#### References:

- 1. ACS Catal., 2017, 7, 6162-6169
- 2. Chem. Sci., 2018, 9, 6503-6508.

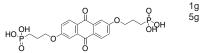
#### 15-8245 NEW

#### (((9,10-Dioxo-9,10-dihydroanthracene-2,6-diyl) bis(oxy))bis(propane-3,1-diyl))bis(phosphonic acid), 98%, 2.6-DPPEAQ

C<sub>20</sub>H<sub>22</sub>O<sub>10</sub>P<sub>2</sub>; FW: 484.33; light yellow to beige pwdr.

Note: U.S. Patents: 62/628,599, 62/740,526. Patent Application: PCT/US19/17479. Product sold under, use subject to, terms and conditions

of Limited Use License at www.strem.com/harvard5



#### Technical Note:

 A highly stable phosphonate-functionalized anthraquinone used as a redox-active material in a negative potential electrolyte (negolyte) for aqueous redox flow batteries operating at nearly neutral pH.

- Adv. Energy Mater. 2019, 9(12), 1900039.
- 2. Joule, 2018, 2(9), 1894–1906.

#### PHOSPHORUS (Compounds) 15-8396 [S(R)]-N-[(1S)-2-(Diphenylphosphino)-1-[2-(di-50mg Ph<sub>2</sub>P adamantanphosphanyl)phenyl]ethyl]-2-meth-NEW yl-2-propanesulfinamide, 95% C<sub>44</sub>H<sub>57</sub>NOP<sub>2</sub>S; FW: 709.9; white to off-white pwdr. air sensitive, moisture sensitive PAd<sub>2</sub> Note: Sold in collaboration with Daicel for research purposes only. 15-8394 [S(R)]-N-[(1S)-2-(Diphenylphosphino)-1-[2-(di-50mg Ph<sub>2</sub>P cyclohexylphosphanyl)phenyl]ethyl]-2-meth-0 NEW yl-2-propanesulfinamide, 95% C<sub>36</sub>H<sub>49</sub>NOP<sub>2</sub>S; FW: 605.8; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only. 15-8398 [S(R)]-N-[(1S)-2-(Diphenylphosphino)-1-[2-(di-50mg phenylphosphino)-4,5-dimethoxyphenyl] NEW ethyl]-2-methyl-2-propanesulfinamide, 95% MeC $C_{38}H_{41}NO_3P_2S$ ; FW: 653.8; white to off-white pwdr. PPh<sub>2</sub> MeC air sensitive. moisture sensitive Note: Sold in collaboration with Daicel for research purposes only. 15-8392 [S(R)]-N-[(1S)-2-(Diphenylphosphino)-1-[2-(di-50mg Ph<sub>2</sub>P phenylphosphino)phenyl]ethyl]-2-meth-NEW yl-2-propanesulfinamide, 95% (1824731-39-6) C<sub>36</sub>H<sub>37</sub>NOP<sub>2</sub>S; FW: 593.7; white to off-white pwdr. air sensitive, moisture sensitive PPh<sub>2</sub> Note: Sold in collaboration with Daicel for research purposes only.

#### Technical Notes:

- Chiral sulfinamide bisphosphine catalysts for highly enantioselective intermolecular cross-Rauhut-Currier reactions.
- Used in phosphine-catalyzed asymmetric intermolecular cross-vinylogous Rauhut-Currier Reactions of vinyl Ketones with para-quinone methides.
- 3. Used in the enantioselective phosphine-catalyzed allylic alkylations of mix-indene with MBH carbonates.
- Ligand for the Pd-catalyzed fast and living polymerizations of various diazoacetate monomers under mild conditions.
- Ligand for the direct Pd-catalyzed cross-coupling reaction of easily accessible secondary phosphine oxides and aryl bromides, which provides rapid access to P-chiral phosphine oxides.

$$R^{1} \xrightarrow{\text{COR}^{2}} \xrightarrow{\text{R}} \xrightarrow{\text{Solvent, } \text{t}^{\circ}\text{C}} \xrightarrow{\text{R}} \text{Solvent, } \text{R}^{\circ}\text{COR}^{2}$$

$$R^{1} \xrightarrow{\text{R}} \xrightarrow{\text{R}} \text{R}^{2} \xrightarrow{\text{R}} \text{Solvent, } \text{R}^{\circ}\text{COR}^{2}$$

$$R^{1} \xrightarrow{\text{R}} \xrightarrow{\text{R}} \text{COR}^{2}$$

$$R^{2} \xrightarrow{\text{CO}_{2}\text{R}^{3}} \xrightarrow{\text{CO}_{2}\text{R}^{3}} \text{Tech. Note (2)}$$

$$R^{1} \xrightarrow{\text{R}} \xrightarrow{\text{R}} \text{CO}_{2}\text{R}^{3}$$

15-8392 [S(R)]-N-[(1S)-2-(Diphenylphosphino)-1-[2-(diphenylphosphino)phenyl]ethyl]-2-meth-(continued) yl-2-propanesulfinamide, 95% (1824731-39-6)

$$R^{1} \stackrel{\stackrel{\textstyle | I |}{ }}{ } + \stackrel{\textstyle OBoc}{ } \stackrel{\textstyle Xiao\text{-Phos}}{ } \stackrel{\textstyle Toluene, \ rt}{ } R^{1} \stackrel{\stackrel{\textstyle | I |}{ }}{ } \stackrel{\textstyle I |}{ } \stackrel{$$

$$\begin{array}{c|c} N_2 \\ H & OR \\ \hline OR & \hline Pd] Xiao-Phos \\ \hline THF, rt, air & OOR \\ \hline \end{array}$$

R = Alkyl or Aryl

- 1. Angew. Chem. Int. Ed. 2015, 54, 14853.
- 2. ACS Catal. 2017, 7, 2805.
- 3. Org. Lett. 2017, 19, 6080.
- 4. J. Am. Chem. Soc. 2018, 140, 17773.

5. J. Am. (	Chem. Soc. <b>2019</b> , <i>141</i> , 20556.	
15-8358 NEW	[S(R)]-N-[(R)-[6-(Diphenylphosphino)benzo[d] [1,3]dioxol-5-yl]-1-naphthalenylmethyl]-N,2-dimethyl-2-propanesulfinamide, 95%  C <sub>35</sub> H <sub>34</sub> NO <sub>3</sub> PS; FW: 579.7; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	50mg
15-8354 NEW	[S(R)]-N-[(R)-[6-(Diphenylphosphino)benzo[d] [1,3]dioxol-5-yl]-1-naphthalenylmeth- yl]-2-methyl-2-propanesulfinamide, 95% C <sub>34</sub> H <sub>32</sub> NO <sub>3</sub> PS; FW: 565.7; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	50mg
15-8356 NEW	[S(R)]-N-[(S)-[6-(Diphenylphosphino)benzo[d][1,3]dioxol-5-yl]-1-naphtha- lenylmethyl]-2-methyl-2-propanesulfinamide, 95% C <sub>34</sub> H <sub>32</sub> NO <sub>3</sub> PS; FW: 565.7; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	50mg
15-8352 NEW	[S(R)]-N-[(R)-[6-(Diphenylphosphino)benzo[d] [1,3]dioxol-5-yl]phenylmethyl]-2-methyl-2-propanesulfinamide, 95%  C <sub>30</sub> H <sub>30</sub> NO <sub>3</sub> PS; FW: 515.6; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	50mg

#### PHOSPHORUS (Compounds) 15-8350 [S(R)]-N-[(S)-[6-(Diphenylphosphino)benzo[d][1,3]dioxol-5-yl]phenylmeth-50mg vI1-2-methyl-2-propanesulfinamide, 95% NEW C<sub>30</sub>H<sub>30</sub>NO<sub>3</sub>PS; FW: 515.6; white to off-white pwdr. air sensitive, light sensitive Note: Sold in collaboration with Daicel for research purposes only. 15-8360 [S(R)]-N-[(S)-[2-(Diphenylphosphino)-4.5-di-50ma OMe methoxyphenyl)](4-methoxyphenyl)meth-NEW yl]-N,2-dimethyl-2-propanesulfinamide, 95% C<sub>33</sub>H<sub>38</sub>NO<sub>4</sub>PS; FW: 575.7; light-yellow to yellow pwdr. air sensitive, moisture sensitive MeO 'tBu Note: Sold in collaboration with Daicel for research purposes only. Me MeO 15-8422 [S(R)]-N-[(1R)-1-[5-(Diphenylphosphi-25mg Me Me no)-9,9-dimethyl-9H-xanthen-4-yl]-2,2-dimeth-NEW ylpropyl]-2-methyl-2-propanesulfinamide, 95% (2162939-92-4)C<sub>36</sub>H<sub>42</sub>NO<sub>2</sub>PS; FW: 583.8; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for tBu research purposes only. Technical Note: Ligand for the Pd-catalyzed enantioselective arylation of general sulfenate anions. Tech. Note (1) Cs<sub>2</sub>CO<sub>3</sub>, Mesitylene Ref. (1)

R<sup>1</sup> = Alkyl, Aryl References:

J. Am. Chem. Soc. 2018, 140, 3467.

X = I. Br

15-8420 [S(R)]-N-[(1S)-1-[5-(Diphenylphosphino)-9,9-dimethyl-9H-xan-then-4-yl]-2,2-dimethylpropyl]-2-methyl-2-propanesulfinamide, 95% (2162939-89-9)

C<sub>36</sub>H<sub>42</sub>NO<sub>2</sub>PS; FW: 583.8; white to off-white pwdr.

air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

Technical Note:

1. See 15-8422 (page 63)

15-8400 [S(R)]-N-[(R)-[5-(Diphenylphosphino)-9,9-dimethyl-9H-xanthen-4-yl](4-methoxyphenyl)
methyl]-2-methyl-2-propanesulfinamide, 95%
(2160535-56-6)
C<sub>39</sub>H<sub>40</sub>NO<sub>3</sub>PS; FW: 633.8; white to off-white pwdr.
air sensitive, moisture sensitive
Note: Sold in collaboration with Daicel for research purposes only.

Technical Note:

 Ligand for the Au-catalyzed asymmetric intramolecular cyclization of N-allenamides for the synthesis of chiral tetrahydrocarbolines.

15-8400 [S(R)]-N-[(R)-[5-(Diphenylphosphino)-9,9-dimethyl-9H-xanthen-4-yl](4-methoxyphenyl) methyl]-2-methyl-2-propanesulfinamide, 95% (2160535-56-6) (continued)

#### References:

Angew. Chem. Int. Ed. 2017, 56, 15905.

15-8402 [S(R)]-N-[(S)-[5-(Diphenylphosphino)-9,9-dimethyl-9H-xanthen-4-yl](4-methoxyphenyl)methyl]-2-methyl-2-propanesulfinamide, 95% (2160535-57-7) NEW

C<sub>39</sub>H<sub>40</sub>NO<sub>3</sub>PS; FW: 633.8; white to off-white pwdr. air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

Technical Note:

See 15-8400 (page 63)

15-8418 [S(R)]-N-[(S)-(phenyl)[5-(Diphenylphosphino)-9,9-dimethyl-9H-xanthen-4-yl](phenyl) NEW methyl]-2-methyl-2-propanesulfinamide, 95%

research purposes only.

C<sub>0</sub>H<sub>0</sub>NO<sub>0</sub>PS; FW: 603.8; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for

Me Me PPh₂ tBu'

50mg

50mg

50ma

15-8512 NEW

N-[(1S)-2-(Diphenylphosphino)-1-(2-(diphenylphosphino)phenyl)ethyl]-3,5-bis(trifluoromethyl)-benzamide, 95%

C<sub>41</sub>H<sub>31</sub>F<sub>6</sub>NOP<sub>2</sub>; FW: 729.6; white to off-white pwdr.

air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

CF<sub>2</sub>

Ph<sub>2</sub>P

15-4645 NEW

N-[2-(Diphenylphosphino)ethyl]-2-[(4-methylphenyl)thio]-ethanamine (1883429-99-9)

C23H26NPS; FW: 379.50; yellow oil air sensitive

Note: Patents: US20170088571A1: U.S. Provisional Patent Application No. 62/827,627.

100mg

#### Technical Note:

SNP ligand used in Ru-catalyzed selective ester hydrogenation.

Tech. Note (1) Ref. (1)

100mg

#### References:

Ora, Process Res. Dev. 2020, 24, 415.

15-4625 NEW

N-[2-(Diphenylphosphino)ethyl]-2-(methylthio)-ethanamine (1802182-42-8) C<sub>17</sub>H<sub>22</sub>NPS; FW: 303.40; yellow oil

air sensitive

Note: Patents: US20170088571A1; U.S. Provisional Patent Application No. 62/827,627.

50mg

#### Technical Note:

1. See 15-4645 (page 65)

15-8378 NEW

[S(R)]-N-[(1S)-1-[(Diphenylphosphino)methyl]-2,2-dimethylpropyl]-2-methyl-2-propanesulfinamide. 95% (1853342-54-7)

C<sub>22</sub>H<sub>32</sub>NOPS; FW: 389.5; white to off-white pwdr. air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

#### Technical Notes:

- Used in phosphine-catalyzed asymmetric intermolecular cross-vinylogous Rauhut-Currier Reactions of vinyl Ketones with para-quinone methides.
- Used in the enantioselective phosphine-catalyzed allylic alkylations of mix-indene with MBH carbonates.

15-8378 [S(R)]-N-[(1S)-1-[(Diphenylphosphino)methyl]-2,2-dimethylpropyl]-2-methyl-2-propanesulfi-(continued) namide, 95% (1853342-54-7)

$$R^{1} \stackrel{\textstyle \bigcap}{\stackrel{\textstyle \square}{\parallel}} + \stackrel{\textstyle \bigcap}{\longleftarrow} OBoc \\ + \stackrel{\textstyle \longleftarrow}{\longleftarrow} OBoc \\ \hline - CO_{2}R^{3} \\ \hline$$

#### References:

- ACS Catal. 2017, 7, 2805. 1.
- Org. Lett. 2017, 19, 6080.

15-8376 [S(R)]-N-[(1S)-1-[(Diphenylphosphino)methyl]-2-methylpropyl]-2-methyl-2-Propanesulfin-NEW amide, 95% (1803239-46-4)

C<sub>21</sub>H<sub>30</sub>NOPS; FW: 375.5; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.

50mg Ph<sub>2</sub>P

#### Technical Notes:

- Sulfinamide phosphine organocatalyst for the enantioselective intramolecular Rauhut-Currier reaction. 1.
- 2. Used in phosphine-catalyzed asymmetric intermolecular cross-vinylogous Rauhut-Currier Reactions of vinyl Ketones with para-quinone methides.
- 3. Used in the enantioselective phosphine-catalyzed allylic alkylations of mix-indene with MBH carbonates.

**EWG** 

Toluene.

- 2. ACS Catal. 2017, 7, 2805.
- 3. Org. Lett. 2017, 19, 6080.

15-8326 NEW [S(R)]-N-[(S)-[2-(Diphenylphosphino) phenyl]-(1,1'-biphenyl)methyl]-2-methyl-2-propanesulfinamide, 95%

C<sub>35</sub>H<sub>34</sub>NOPS; FW: 547.7; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for

research purposes only.

Ph O N.S. tBu PPh<sub>2</sub> 100mg

50ma

#### Technical Note:

 Ligand for the enantioselective Au-catalyzed [3+3] cycloaddition reaction of 2-(1-alkynyl)-alk-2-en-1-ones with nitrones.

#### References:

Angew. Chem. Int. Ed. 2014, 53, 4350.

15-8348 NEW [S(R)]-N-[(1R)-1-[2-(Diphenylphosphino) phenyl]-2,2-dimethylpropyl]-N,2-dimethyl-2-propanesulfinamide, 95% (2049042-08-0)  $C_{28}H_{36}NOPS$ ; FW: 465.6; white to off-white pwdr. moisture sensitive

N S TEBU

#### Technical Note:

 Ligand used in the Copper(I)-catalyzed asymmetric intermolecular [3+2] cycloaddition of azomethine ylides with α Trifluoromethyl α,β-unsaturated esters.

#### References:

1. ACS Catal. 2017, 7, 210.

15-8330 NEW [S(R)]-N-[(1R)-1-[2-(Diphenylphosphino) phenyl]-2,2-dimethylpropyl]-2-methyl-2-propanesulfinamide, 95% (1906918-20-4) C<sub>27</sub>H<sub>34</sub>NOPS; FW: 451.6; white to off-white pwdr. air sensitive, moisture sensitive
Note: Sold in collaboration with Daicel for

research purposes only.

tBu O N S.,,tBu H PPh<sub>2</sub>

#### Technical Notes:

- Ligand used for diastereo- and enantioselective Cu(I)-catalyzed intermolecular [3+2] cycloaddition of azomethine ylides with β-trifluoromethyl β, β-Disubstituted enones.
- Ligand used in the Copper(I)-catalyzed asymmetric intermolecular [3+2] cycloaddition of azomethine ylides with α-Trifluoromethyl α,β-unsaturated esters.
- Ligand used for Ag(I)-catalyzed enantioselective [3+2] cycloaddition of azomethine ylides.

$$\begin{array}{c|c} R & N & CO_2Me \\ \hline R^1 & Ar \\ \hline F_3C & O \end{array} \qquad \begin{array}{c} [Cu^l] \ \text{Ming-Phos} \\ \hline Cs_2CO_3; \ THF/MTBE, \ -50^{\circ}C \end{array} \qquad \begin{array}{c} Ar & P^1 \\ \hline R & CO_2Me \end{array} \qquad \begin{array}{c} \text{Tech. Note (1)} \\ \hline Ref. \ (1) \end{array}$$

15-8330 [S(R)]-N-[(1R)-1-[2-(Diphenylphosphino)phenyl]-2,2-dimethylpropyl]-2-methyl-2-propane-continued) sulfinamide, 95% (1906918-20-4)

$$\begin{array}{c|c} EtO_2C \\ \hline F_3C & R \end{array} + R^1 \stackrel{\frown}{\nearrow} N \stackrel{\frown}{\nearrow} CO_2Me \xrightarrow{CS_2CO_3; \ THF, \ -60^{\circ}C} \xrightarrow{EtO_2C} \stackrel{CF_3}{\longrightarrow} \stackrel{R}{\nearrow} R \\ \hline R^1 & N \stackrel{\frown}{\nearrow} CO_2Me \end{array}$$

#### References:

- 1. Angew. Chem. Int. Ed. 2016, 55, 6324.
- 2. ACS Catal. 2017, 7, 210.
- Org. Biomol. Chem., 2019, 17, 1395.

research purposes only.

15-8514 NEW N-[(1S)-2-(Diphenylphosphino)-1-phenylethyl]-3,5-bis(trifluoromethyl)-benzamide, 95% (1853342-57-0)

C<sub>29</sub>H<sub>22</sub>F<sub>8</sub>NOP; FW: 545.5; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for

Ph<sub>2</sub>P O 50mg

#### Technical Notes:

- 1. Organocatalyst used in aza-[4+2] cycloaddition of N-sulfonyl-1-aza-1,3-dienes with vinyl ketones.
- Catalyst for the enantioselective [3+2] cycloadditions of γ-substituted allenoates with β-perfluoroalkyl
  enones.
- 3. Organocatalyst used in effective asymmetric vinylogous Mannich reaction of isatin imines with  $\alpha, \alpha$ -dicyanoolefins.
- Chiral phosphine catalyzed α-functionalization of 2-vinylpyridines via enantioselective cross Rauhut-Currier reaction.

$$\begin{array}{c} NSO_2R^2 \\ R^1 \end{array} + \begin{array}{c} O \\ R \end{array} \xrightarrow{Phosphine} \\ R \xrightarrow{Acetone, \ rt} \\ \end{array} \begin{array}{c} R^3 \\ N \\ SO_2R^2 \end{array}$$
 Tech. Note (1)

15-8514 N-[(1S)-2-(Diphenylphosphino)-1-phenylethyl]-3,5-bis(trifluoromethyl)-benzamide, 95% (2001) (1853342-57-0)

### References:

- 1. Org. Lett. 2017, 19, 1710.
- Chem. Sci., 2017, 8, 4660.
- 3. Org. Chem. Front., 2017, 4, 101.
- Org. Lett. 2018, 20, 1304.

### 15-8366 [S(R)]-N-[(1S)-2-(Diphenylphosphi-no)-1-phenylethyl]-2-methyl-2-propanesulfinamide, 95% (1803239-44-2) C<sub>24</sub>H<sub>28</sub>NOPS; FW: 409.5; white to off-white pwdr. air sensitive, moisture sensitive

research purposes only.

### Technical Notes:

- 1. Sulfinamide phosphine organocatalyst for the enantioselective intramolecular Rauhut-Currier reaction.
- 2. Organocatalyst used in aza-[4+2] cycloaddition of N-sulfonyl-1-aza-1,3-dienes with vinyl ketones.

Note: Sold in collaboration with Daicel for

- 3. Used in the enantioselective phosphine-catalyzed allylic alkylations of mix-indene with MBH carbonates.
- Ligand for the direct Pd-catalyzed cross-coupling reaction of easily accessible secondary phosphine oxides and aryl bromides, which provides rapid access to P-chiral phosphine oxides.

$$\begin{array}{c} NSO_2R^2 \\ R^1 \\ \hline \\ R^3 \\ \end{array} \begin{array}{c} O \\ \hline \\ R \\ \hline \\ \end{array} \begin{array}{c} Xiao\text{-Phos} \\ \hline \\ Acetone, \ rt \\ \hline \\ \\ R^1 \\ \hline \\ \\ N \\ SO_2R^2 \\ \end{array} \begin{array}{c} Tech. \ Note \ (2) \\ Ref. \ (2) \\ \end{array}$$

$$R^{1}$$
  $\stackrel{|I|}{=}$   $+$   $\stackrel{|I$ 

15-8366 [S(R)]-N-[(1S)-2-(Diphenylphosphino)-1-phenylethyl]-2-methyl-2-propanesulfinamide, 95% (continued) (1803239-44-2)

Me Q R<sup>1</sup> 
$$R^2$$
  $R^2$   $R^2$ 

### References:

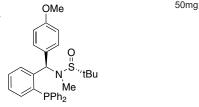
- 1. Angew. Chem. Int. Ed. 2015, 54, 6874.
- 2. Org. Lett. 2017, 19, 1710.
- 3. Org. Lett. 2017, 19, 6080.
- J. Am. Chem. Soc. 2019, 141, 20556.

### 15-8338 NEW

[S(R)]-N-[(R)-[2-(Diphenylphosphino)phenyl] (4-methoxyphenyl)methyl]-N,2-dimethyl-2-propanesulfinamide, 95%

C<sub>31</sub>H<sub>34</sub>NO<sub>2</sub>PS; FW: 515.6; white to off-white pwdr. air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.



50mg

100ma

15-8336 [S(R)]-N-[(S)-[2-(Diphenylphosphino)phenyl](4-methoxyphenyl)meth-

yl]-N,2-dimethyl-2-propanesulfinamide, 95% C<sub>31</sub>H<sub>34</sub>NO<sub>2</sub>PS; FW: 515.6; white to off-white pwdr.

air sensitive. moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

15-8314 NEW [S(R)]-N-[(S)-[2-(Diphenylphosphino)phenyl](4-methoxyphenyl)methyl]-2-methyl-2-propanesulfinamide, 95% (1616688-62-0)

C<sub>30</sub>H<sub>30</sub>NO<sub>2</sub>PS; FW: 501.60; white to off-white pwdr.

air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

### Technical Notes:

- Ligand for the enantioselective Au-catalyzed [3+3] cycloaddition reaction of 2-(1-alkynyl)-alk-2-en-1-ones with nitrones.
- Ligand used for Ag(I)-catalyzed enantioselective [3+2] cycloaddition of azomethine ylides.

- 1. Angew. Chem. Int. Ed. 2014, 53, 4350.
- 2. Org. Biomol. Chem., 2019, 17, 1395.

15-8316 NEW [S(R)]-N-[(R)-[2-(Diphenylphosphino)phenyl] (4-methoxyphenyl)methyl]-2-methyl-2-propanesulfinamide, 95% (1595319-96-2) C<sub>90</sub>H<sub>32</sub>NO<sub>9</sub>PS; FW: 501.60; white to off-white

pwdr.

air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for

research purposes only.

## OMe OMS N S N H PPh<sub>2</sub>

### Technical Notes:

- Ligand for the enantioselective Au-catalyzed [3+3] cycloaddition reaction of 2-(1-alkynyl)-alk-2-en-1-ones with nitrones.
- 2. Used in enantioselective Au-catalyzed synthesis of indolyl-substituted cyclopenta[c]furans.
- Used in the Au-catalyzed enantioselective synthesis of polycyclic indoline skeletons and enantiomerically enriched β-substituted tryptamine-allenes by kinetic resolution.

$$R^{1} \longrightarrow R^{3} + R^{5} \longrightarrow R^{4} \longrightarrow R^{4$$

### References:

- 1. Angew. Chem. Int. Ed. 2014, 53, 4350.
- 2. Org. Lett. 2018, 20, 6403.
- 3. Chem. Commun., 2019, 55, 4210.

15-8346 NEW [S(R)]-N-[(S)-[3,5-Bis(trifluoromethyl)phenyl] [2-(diphenylphosphino)phenyl]methyl]-N,2-dimethyl-2-propanesulfinamide, 95%

C<sub>32</sub>H<sub>30</sub>F<sub>6</sub>NOPS; FW: 621.6; light-yellow to yellow pwdr.

air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

CF<sub>3</sub> CF<sub>3</sub> 50mg

### PHOSPHORUS (Compounds) 15-8342 [S(R)]-N-[(R)-[2-(Diphenylphosphino) 50mg phenyl]-1-naphthalenylmethyl]-N,2-dimeth-NEW yl-2-propanesulfinamide, 95% C<sub>34</sub>H<sub>34</sub>NOPS; FW: 535.7; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for ′tBu research purposes only. 15-8344 [S(R)]-N-[(S)-[3,5-Bis(1,1-dimethylethyl)-4-me-50mg OMe thoxyphenyl][2-(diphenylphosphino)phenyl] NEW t-Bu t-Bu methyl]-N,2-dimethyl-2-propanesulfinamide, 95% C<sub>30</sub>H<sub>50</sub>NO<sub>2</sub>PS; FW: 535.7; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for tBu research purposes only. 15-8340 50mg [S(R)]-N-[(S)-[2-(Diphenylphosphino)phenyl]-1-naphthalenylmethyl]-N,2-dimethyl-2-propanesulfinamide, 95% NEW C<sub>34</sub>H<sub>34</sub>NOPS; FW: 535.7; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.

15-8322 [S(R)]-N-[(S)-[2-(Diphenylphosphino)phenyl]-1-naphthalenylmethyl]-2-methyl-2-propanesulfinamide, 95% (1595319-95-1)

100mg

C<sub>33</sub>H<sub>32</sub>NOPS; FW: 521.7; white to off-white pwdr. air sensitive, moisture sensitive

Note: Sold in collaboration with Daicel for research purposes only.

1. Ligand for the enantioselective Au-catalyzed [3+3] cycloaddition reaction of 2-(1-alkynyl)-alk-2-en-1-ones

- 2. Used in enantioselective Au-catalyzed synthesis of indolyl-substituted cyclopenta[c]furans.
- Ligand for the enantioselective Au-catalyzed intermolecular exo [4+3]-cycloaddition to generate chiral oxa-bridged benzocycloheptanes.

$$R^{1} = R^{3} + R^{5} = R^{4} = R^{4$$

Technical Notes:

15-8322 [S(R)]-N-[(S)-[2-(Diphenylphosphino)phenyl]-1-naphthalenylmethyl]-2-methyl-2-propane-(continued) sulfinamide, 95% (1595319-95-1)

### References:

- 1. Angew. Chem. Int. Ed. 2014, 53, 4350.
- 2. Org. Lett. 2018, 20, 6403.

<ol><li>Org. Let</li></ol>	t. <b>2019</b> , <i>21</i> , 3018.	
15-8334 NEW	[S(R)]-N-[(R)-[2-(Diphenylphosphino)phenyl] phenylmethyl]-N,2-dimethyl-2-propanesulfinamide, 95% C <sub>30</sub> H <sub>32</sub> NOPS; FW: 485.6; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	50mg
15-8332 NEW	[S(R)]-N-[(S)-[2-(Diphenylphosphino)phenyl]phenylmethyl]-N,2-dimethyl-2-propanesulfinamide, 95%  C <sub>30</sub> H <sub>32</sub> NOPS; FW: 485.6; light-yellow to yellow pwdr. air sensitive, moisture sensitive  Note: Sold in collaboration with Daicel for research purposes only.	50mg
15-8312 NEW	[S(R)]-N-[(R)-[2-(Diphenylphosphino)phenyl] phenylmethyl]-2-methyl-2-propanesulfin- amide, 95% (1616688-59-5) C <sub>29</sub> H <sub>30</sub> NOPS; FW: 471-60; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	100mg

### Technical Notes:

- Ligand for the enantioselective Au-catalyzed [3+3] cycloaddition reaction of 2-(1-alkynyl)-alk-2-en-1-ones with nitrones.
- Ligand used for Ag(I)-catalyzed enantioselective [3+2] cycloaddition of azomethine ylides.

- Angew. Chem. Int. Ed. 2014, 53, 4350.
- Org. Biomol. Chem., 2019, 17, 1395. 2.

### New Products Since Chemiker XXXI (November 2019) PHOSPHORUS (Compounds) 15-8310 [S(R)]-N-[(S)-[2-(Diphenylphosphino)phenyl]phenylmethyl]-2-methyl-2-pro-100mg panesulfinamide, 95% (1595319-97-3) NEW C<sub>29</sub>H<sub>30</sub>NOPS; FW: 471.60; white to off-white pwdr air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only. Technical Note: 1. See 15-8312 (page 73) 15-4660 N-[2-(Diphenylphosphinyl)ethyl]-2-[tritylth-250mg io]-ethanamine NEW C<sub>35</sub>H<sub>34</sub>NOPS; FW: 547.70; waxy solid Note: Patents: US20170088571A1; U.S. Provisional Patent Application No. 62/827,627. Technical Note: SNP(O) ligand used in Ru-catalyzed selective ester hydrogenation. $_{R_{1}}^{1} + _{R_{2}}^{1} = \frac{\text{[Ru] SNP(O) Ligand}}{\text{KO-}^{1}\text{C}_{4}\text{H}_{9}, 40^{\circ}\text{C}} \xrightarrow{R} ^{OH} + R_{1}\text{OH}$ Tech. Note (1) Ref. (1) References: Org. Process Res. Dev. 2020, 24, 415. N-[2-(Diphenylphosphinyl)ethyl]-2-[(4-methylphe-15-4640 250mg nyl)thio]-ethanamine NEW C<sub>23</sub>H<sub>26</sub>NOPS; FW: 395.50; white solid Note: Patents: US20170088571A1: U.S. Provisional Patent Application No. 62/827,627. Technical Note: See 15-4660 (page 74) 15-4620 N-[2-(Diphenylphosphinyl)ethyl]-2-(methylth-250ma io)-ethanamine (1839552-30-5) NEW C<sub>17</sub>H<sub>22</sub>NOPS; FW: 319.4; white solid Note: Patents: US20170088571A1: U.S. Provisional Patent Application No 62/827,627. Technical Note: 1. See 15-4660 (page 74) Me-S15-4630 N-[2-(Diphenylphosphinyl)ethyl]-2-(phenylth-100mg io)-ethanamine NEW C<sub>22</sub>H<sub>24</sub>NOPS; FW: 381.47; white solid Note: Patents: US20170088571A1; U.S. Provisional

Patent Application No. 62/827,627.

Technical Note:

See 15-4660 (page 74)

### PHOSPHORUS (Compounds) 15-8364 [S(R)]-N-[(R)-(3,5-Di-tert-butyl-4-methoxyphe-50mg OMe nyl)[2-(diphenylphosphino)-4,5-dimethoxy-NEW t-Bu t-Bu phenyl]-2-methyl-2-propanesulfinamide, 95% C<sub>40</sub>H<sub>53</sub>NO<sub>4</sub>PS; FW: 673.9; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for .ڬ.<sub>//tBu</sub> research purposes only. MeO PPh<sub>2</sub> MeO 15-8412 [S(R)]-N-[(R)-[3.5-Di-tert-butyl-4-methoxy-50ma Me Me phenyl][5-(diphenylphosphino)-9,9-dimeth-NEW yl-9H-xanthen-4-yl]methyl]-2-methyl-2-propanesulfinamide, 95% C<sub>47</sub>H<sub>56</sub>NO<sub>3</sub>PS; FW: 746.0; white to off-white pwdr. air sensitive, moisture sensitive PPh<sub>2</sub> tBu Note: Sold in collaboration with Daicel for HN research purposes only. tBu' OMe tBu 50mg 15-8414 [S(R)]-N-[(S)-[3,5-Di-tert-butyl-4-methoxyphenyl][5-(diphenylphosphino)-9,9-dimethyl-9H-xanthen-4-yl]methyl]-2-methyl-2-propanesulfinamide, NEW 95% C<sub>47</sub>H<sub>56</sub>NO<sub>3</sub>PS; FW: 746.0; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only. 15-8496 [S(R)]-N-[(S)-(3.5-Di-tert-butyl-4-methoxyphe-25ma OMe nyl)[2-(di-tert-butylphosphino)phenyl]meth-NEW yl]-2-methyl-2-propanesulfinamide, 95% t-Bu t-Bu C<sub>34</sub>H<sub>56</sub>NO<sub>2</sub>PS; FW: 573.9; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only. P~tBu tBú 15-8468 [S(R)]-N-[(S)-[3,5-Di-tert-butyl-4-methoxyphe-25ma OMe nyl][(3-benzyloxy-2-(dicyclohexylphosphino) NEW phenyl)methyl]-N,2-dimethyl-2-propanesulfint-Bu t-Bu amide, 95% $C_{46}H_{68}NO_3PS$ ; FW: 746.1; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only. 'tBu

PCy<sub>2</sub>

OBn

PHOSPHORU	JS (Compounds)		
15-8466 (NEW)	[S(R)]-N-[(S)-[3,5-Di-tert-butyl-4-methoxyphenyl][(3-benzyloxy-2-(dicyclohexylphosphino) phenyl)methyl]-2-methyl-2-propanesulfinamide, 95% C <sub>45</sub> H <sub>66</sub> NO <sub>3</sub> PS; FW: 732.1; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	OMe t-Bu t-Bu O S V TBu PCy <sub>2</sub>	25mg
15-8504 NEW	[S(R)]-N-[(1S)-1-[2-(Di-tert-butylphosphanyl) phenyl]-2,2-dimethylpropyl]-2-methyl-2-propanesulfinamide, 95%  C <sub>23</sub> H <sub>42</sub> NOPS; FW: 411.6; white to off-white pwdr. air sensitive, moisture sensitive  Note: Sold in collaboration with Daicel for research purposes only.	tBu O N S TBu H P tBu tBu	25mg
15-8502 (NEW)	[S(R)]-N-[(1R)-1-[2-(Di-tert-butylphosphanyl) phenyl]phenylmethyl]-2-methyl-2-propanesul-finamide, 95%  C <sub>25</sub> H <sub>38</sub> NOPS; FW: 431.6; white to off-white pwdr. air sensitive, moisture sensitive  Note: Sold in collaboration with Daicel for research purposes only.	Ph O S YtBu P TBu	25mg
15-8500 NEW	[S(R)]-N-[(1S)-1-[2-(Di-tert-butylphosphanyl)phyl-2-propanesulfinamide, 95%  C <sub>25</sub> H <sub>38</sub> NOPS; FW: 431.6; white to off-white pwdr. air sensitive, moisture sensitive  Note: Sold in collaboration with Daicel for research		25mg
15-8492 <u>NEW</u>	[S(R)]-N-[(S)-[2-(Di-tert-butylphosphino) phenyl]-adamantylmethyl]-2-methyl-2-propanesulfinamide, 95% C <sub>28</sub> H <sub>48</sub> NOPS; FW: 489.7; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	Ad O S S S T T T T T T T T T T T T T T T T	25mg
15-8494 NEW	[S(R)]-N-[(S)-[2-(Di-tert-butylphosphino) phenyl[(2-naphthalenyl)methyl]-2-methyl-2-propanesulfinamide, 95% C <sub>25</sub> H <sub>40</sub> NOPS; FW: 481.7; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	O S NH P tBu tBu	25mg

	New Products Since Chemiker XXX	I (November 2019)	
PHOSPHORU	JS (Compounds)		
15-1840 NEW	<b>n-Dodecylphosphonic acid, min. 90%</b> (5137-70-CH $_3$ (CH $_2$ ) $_{11}$ P(O)(OH) $_2$ ; FW: 250.31; white waxy sol		1g 5g 25g
15-8510 NEW	N-[(1S)-(1-Ferrocenyl)-2-(diphenylphosphino) ethyl)]-3,5-bis(trifluoromethyl)-benzamide, 95% (2131816-17-4) C <sub>33</sub> H <sub>26</sub> F <sub>6</sub> FeNOP; FW: 653.4; yellow pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	CF <sub>3</sub> CF <sub>3</sub>	50mg
	ne derived bifunctional phosphine catalyst for tric oxa- $[4+2]$ cycloaddition of $\alpha$ -ubstituted allenones nes.		
R <sup>1</sup> R <sup>2</sup>	$R^3 + \longrightarrow \begin{array}{c} COR^5 & Phosphine \\ \hline R^4 & Toluene, rt \end{array}$	COR <sup>5</sup> R <sup>1</sup> O R <sup>4</sup> R <sup>3</sup>	Tech. Note (1) Ref. (1)
	$R^2 = CN$ , H, Alkyl; $R^3 = R_f$ , Ar; $R^4 = Alkyl$ , $R^5 = Ar$ ,	alkyl	
References: 1. Chem. E	Eur. J. <b>2017</b> , 23, 13587.		
15-8386 NEW	[S(R)]-N-[(1S)-1-Ferrocenylethyl-2-(diphenyl-phosphino)ethyl]-2-methyl-2-propanesulfinamide, 95%  C <sub>28</sub> H <sub>32</sub> FeNOPS; FW: 517.4; white to off-white pwdr.  air sensitive, moisture sensitive  Note: Sold in collaboration with Daicel for research purposes only.	Ph <sub>2</sub> P O N S Fe H tBu	100mg
15-8540 NEW	(11bR)-4-Hydroxy-2,6-bis(adamantan-1-yl)-4-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepinoxide, 95% $C_{40}H_{41}O_4P; \ \text{off white to light yellow pwdr.}$ Note: Sold in collaboration with Daicel for research purposes only.	Ad O P OH Ad	25mg 100mg
15-8544 NEW	(11bR)-4-Hydroxy-2,6-bis(2,6-dimethoxy-phenyl)-4-oxide-dinaphtho[2,1-d:1',2'-f][1,3,2] dioxaphosphepin, 98% $C_{36}H_{29}O_8P$ ; FW: 620.6; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	MeO OMe OMe OMe OMe	25mg 100mg

15-8534 NEW

(11bR)-4-Hydroxy-2,6-bis(5'-phenyl[1,1':3',1"terphenyl]-2'-yl)-4-dinaphtho[2,1-d:1',2'-f] [1,3,2]dioxaphosphepinoxide, 98%, (99% ee) C<sub>68</sub>H<sub>45</sub>O<sub>4</sub>P; FW: 957.1; off white to light yellow pwdr.

Note: Sold in collaboration with Daicel for research purposes only.

25mg Ph 100mg OH Ph Ph Ph

25mg

25ma

100mg

15-8535 NEW

(11bS)-4-Hydroxy-2,6-bis(5'-phenyl[1,1':3',1"-terphenyl]-2'-yl)-4-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepinoxide, 98%, (99% ee)

(1639447-03-2) C<sub>68</sub>H<sub>45</sub>O<sub>4</sub>P; off white to light yellow pwdr.

Note: Sold in collaboration with Daicel for research purposes only.

Technical Note:

Used in the Lewis base/chiral Brønsted acid catalyzed enantioselective bromocycloetherification.

$$R \xrightarrow{\text{NBS-CPA}} OH \xrightarrow{\text{NBS-CPA}} Ph_3P=S, PhMe, 0^{\circ}C \xrightarrow{\text{R}} R \xrightarrow{\text{Er}} Or \xrightarrow{\text{E}} O$$

$$(Z) \text{-alkene} (E) \text{-alkene}$$

$$(E) \text{-alkene}$$

### References:

Chirality, 2014, 26, 344.

15-8530 NEW

(4R)-4-Hydroxy-2,6-bis(3,3",5,5"-tetrakis(tertbutyl)-[1,1':3',1"-terphenyl]-5'-yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-oxide, 98%

C<sub>88</sub>H<sub>101</sub>O<sub>4</sub>P; FW: 1253.7; off white to light yellow pwdr.

Note: Sold in collaboration with Daicel for research purposes only.

t-Bu t-Bu 100mg t-Bu t-Bu t-Bu OH t-Bu t-Bu t-Bu

15-8548 NEW

(11bR)-4-Hydroxy-2,6-bis(2,4,6-trimethoxyphenyl)-4-oxide-dinaphtho[2,1-d:1',2'-f][1,3,2] dioxaphosphepin, 98%

C<sub>38</sub>H<sub>33</sub>O<sub>10</sub>P; FW: 680.6; off white to light yellow pwdr.

Note: Sold in collaboration with Daicel for research purposes only.

25mg OMe MeO 100mg OMe PO OMe MeO OMe

15-8550 NEW (11bR)-4-Hydroxy-9,14-dinitro-2,6-bis[2,4,6-tris(1-methylethyl)phenyl]-4-oxide-Dinaph-tho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 98% (1535206-22-4)

 $\rm C_{50}H_{55}N_2O_8P;\,FW:\,848;$  off white to light yellow pwdr.

Note: Sold in collaboration with Daicel for research purposes only.

i-Pr i-Pr 10mg 25mg 25mg 25mg

25mg

79

100mg

### Technical Notes:

1. Organocatalyst used for the kinetic resolution of secondary alcohols.

- Catalyst used in the kinetic resolution of β-amino alcohols via asymmetric substitutions at sp3-hybridized carbon atoms.
- 3. Brønsted acid catalyst used for asymmetric desymmetrization of α-symmetric acid anhydrides.

### References:

- 1. Angew. Chem. Int. Ed. 2013, 52, 10227.
- Angew. Chem. Int. Ed. 2016, 55, 13137.
- Tetrahedron Lett., 2016, 57, 4098.

### 15-8558 NEW

(6aR)-14-Hydroxy-6,7-diphenyl-14-oxide-dinaphtho[1,2-d:2',1'-f][1,3,2]dioxaphosphepin, 98%, (99% ee) (956610-76-7)

C<sub>32</sub>H<sub>21</sub>O<sub>4</sub>P; FW: 500.5; off white to light yellow pwdr.

Note: Sold in collaboration with Daicel for research purposes only.

### Technical Notes:

1. Organocatalyst for desymmetrization of meso-aziridines.

 Used in the enantioselective Pd/Brønsted acid-catalyzed carbonylative carbocyclization of enallenes via cross-dehydrogenative coupling with terminal alkynes.

Ph

15-8558 (6aR)-14-Hydroxy-6,7-diphenyl-14-oxide-dinaphtho[1,2-d:2',1'-f][1,3,2]dioxaphosphepin, (continued) 98%, (99% ee) (956610-76-7)

$$R^{1} + CO_{(1 \text{ atm})} + R = R$$

$$R^{1} + R^{2} + CO_{(1 \text{ atm})} + R = R$$

$$R^{1} + R^{2} + R$$

$$R^{1} + R^{2} + R$$

$$R^{1} + R^{2} + R^{2} + R$$

$$R^{2} + R^{2} + R^{2}$$

### References:

- 1. J. Am. Chem. Soc. 2007, 129, 12084.
- 2. Angew. Chem. Int. Ed. 2017, 56, 4535.

### 15-8559 NEW

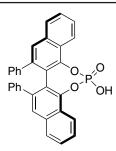
(6aS)-14-Hydroxy-6,7-diphenyl-14-oxide-dinaphtho[1,2-d:2',1'-f][1,3,2]dioxaphosphepin, 98%, (99% ee) (175223-61-7)

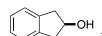
C<sub>32</sub>H<sub>21</sub>O<sub>4</sub>P; FW: 500.5; off white to light yellow pwdr.

Note: Sold in collaboration with Daicel for research purposes only.

### Technical Note:

 Used in the enantioselective racemic resolution of a range of 1,2-amino via liquid-liquid extraction of alcohols.





Tech. Note (1) Ref. (1)

25ma

100ma

### References:

1. ChemSusChem 2018, 11, 178.

### 15-8554 NEW

(8aR)-18-Hydroxy-8,9-diphenyl-18-oxide-diphenanthro[4,3-d:3',4'-f][1,3,2]dioxaphosphepin, 98%, (99% ee) (877130-18-6)  $C_{40}H_{25}O_4P$ ; FW: 600.6; off white to light yellow pwdr

Note: Sold in collaboration with Daicel for research purposes only.

### Technical Notes:

- 1. Organocatalyst for amidation of imines.
- Organocatalyst for desymmetrization of meso-aziridines.
- Chiral Brønsted acid used in catalytic asymmetric aza-Darzens aziridine synthesis.
- Organocalalyst for the remote α-C-H bond activation of alcohols or amines triggered by the radical trifluoromethylation of alkenes.
- Used in the enantioselective Pd/Brønsted acid-catalyzed carbonylative carbocyclization of enallenes via cross-dehydrogenative coupling with terminal alkynes.
- Used in the enantioselective synthesis of tropanes via Brønsted acid catalyzed pseudotransannular desymmetrization.
- Cu-catalyst used in Cu/achiral pyridine ligand catalyzed enantioselective radical oxytrifluoromethylation of alkenes with alcohols.

 $\begin{array}{lll} \textbf{15-8554} & \textbf{(8aR)-18-Hydroxy-8,9-diphenyl-18-oxide-diphenanthro[4,3-d:3',4'-f][1,3,2]dioxaphosphepin,} \\ \textbf{(continued)} & \textbf{98\%, (99\% ee)} & \textbf{(871130-18-6)} \end{array}$ 

$$\begin{array}{c} XH \\ R^{1} \\ H \end{array}$$

$$XH \\ X = O, Ar; Solvent, 80°C \\ R^{2} \\ X = O, Ar; Solvent, 80°C \\ X = O, Ar$$

- 1. J. Am. Chem. Soc. 2005, 127, 15696.
- 2. J. Am. Chem. Soc. 2007, 129, 12084.
- 3. Org. Lett. 2011, 13, 2188.
- 4. Org. Chem. Front., 2017, 4, 2139.
- Angew. Chem. Int. Ed. 2017, 56, 4535.
- Angew. Chem. Int. Ed. 2017, 56, 8883.
- 7. Angew. Chem. Int. Ed. 2020, 59, 6780.

15-8555 NEW

(8aS)-18-Hydroxy-8,9-diphenyl-18-oxide-diphenanthro[4,3-d:3',4'-f][1,3,2]dioxaphosphepin, 98%, (99% ee)

(871130-17-5) C<sub>40</sub>H<sub>25</sub>O<sub>4</sub>P; FW: 600.6; light yellow to yellow pwdr

Note: Sold in collaboration with Daicel for research purposes only.

25mg 100mg

### Technical Notes:

- Organocatalyst for amidation of imines. 1.
- Organocatalyst for asymmetric reduction of α-imino esters to generate 2. α-amino esters.
- 3. Organocatalyst for desymmetrization of meso-aziridines.
- 4. Organocatalyst for the highly enantioselective addition of indoles to N-acyl imines.
- Organocatalyst for the enantioselective Friedel-Crafts reaction of pyrrole derivatives with imines. 5.
- Organocatalyst for the desymmetrization of meso-aziridines with functionalized mercaptans. 6.
- 7. Organocatalyst for highly enantioselective benzoyloxylation of 3-aryloxindoles.

Tech. Note (6) Ref. (7)

15-8555 (8aS)-18-Hydroxy-8,9-diphenyl-18-oxide-diphenanthro[4,3-d:3',4'-f][1,3,2]dioxaphosphepin, 98%, (99% ee) (871130-17-5) (continued)

- 1. J. Am. Chem. Soc. 2005, 127, 15696.
- 2. Chem. Commun., 2007, 4477.
- 3. J. Am. Chem. Soc. 2007, 129, 5830.
- J. Am. Chem. Soc. 2007, 129, 12084. 4.
- Org. Lett. 2007, 9, 2609. 5.
- Org. Lett. 2007, 9, 4065. 6.
- 7. Org. Lett. 2009, 11, 5186.

	Chem. Int. Ed. <b>2011</b> , <i>50</i> , 1135. hem. Soc. <b>2011</b> , <i>133</i> , 3339.		
15-7560 NEW	Isobutylphosphine, min. 95%, CYTOP® 141 (4023-52-3) C <sub>4</sub> H <sub>9</sub> PH <sub>2</sub> ; FW: 90.11; Colorless liquid; b.p. 78 °C; of air sensitive, moisture sensitive, pyrophoric Note: Sold in collaboration with Solvay.	Me d. 0.77 H <sub>2</sub> P Me	25g 100g
15-8498 NEW	[S(R)]-N-[(S)-(4-Methoxyphenyl)[2-(di-tert-butylphosphino)phenyl]methyl]-2-methyl-2-propanesulfinamide, 95% $C_{26}H_{40}NO_2PS; \ FW: \ 461.6; \ white to off-white pwdr. \ air sensitive, moisture sensitive \ Note: Sold in collaboration with Daicel for research purposes only.$	OMe O O O O O O O O O O O O O O O O O O O	25mg
15-8416 (NEW)	[S(R)]-N-[(S)-(1-naphthalenyl)]5-(diphenyl-phosphino)-9,9-dimethyl-9H-xanthen-4-yl] methyl]-2-methyl-2-propanesulfinamide, 95% $C_{42}H_{40}NO_2PS$ ; FW: 653.8; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	Me Me PPh <sub>2</sub> HN tBu S	50mg

	New Products Since Chemiker XXXI	(November 2019)	
PHOSPHORU	IS (Compounds)		
15-0558 NEW	(11bS)-8,9,10,11,12,13,14,15-Octahydro-4-hydror fluoromethyl)phenyl]phenyl]-4-oxide-dinaphtholophosphepin, 98%, (99% ee) $C_{64}H_{39}F_{24}O_4P; FW: 1358.9; off white to light yellow protest of the collaboration with Daicel for research$	[2,1-d:1',2'-f][1,3,2]dioxa- owdr.	25mg 100mg
15-1279 NEW  Technical Notes:  1. P-Chirog hydroger	(1S,1'S)-(-)-(Oxybis(2,1-phenylen))bis((2-methoxyphenyl)(phenyl)phosphine), min. 97% (2119686-55-2) C <sub>38</sub> H <sub>32</sub> O <sub>3</sub> P <sub>2</sub> ; FW: 598.61; white to off-white solid air sensitive, moisture sensitive, (store cold) Note: Sold under license of WO2017/191310 for research purposes only.	OMe Ph	25mg 100mg Me symmetric
	Rh(CO) <sub>2</sub> (acac), 1.2 eq. Ligand  40° C, 50 bar	/	ech. Note (1) Ref. (1)
	Cul (5 mol%) Ligand (6 molton) Ligand (6 molton) LiO <sup>t</sup> Bu, (MeO) <sub>2</sub> Si(Me)H, TH		ech. Note (2) Ref. (2)
15-7535 NEW	9-Phosphabicyclononanes in toluene, mixture of isomers, CYTOP® 282T (13887-02-0) C <sub>8</sub> H <sub>15</sub> P; FW: 142.17; Colorless to pale yellow liq.; f.p. 41 °F; d. 0.94 air sensitive, moisture sensitive Note: Sold in collaboration with Solvay.	PH	100g 500g
15-8362 NEW	[S(R)]-N-[(S)-[2-(Diphenylphosphino)-4,5-dimethoxyphenyl]-1-naphthalenylmethyl]-2-methyl-2-propanesulfinamide, 95% C <sub>35</sub> H <sub>36</sub> NO <sub>3</sub> PS; FW: 581.7; white to off-white pwdr. <i>air sensitive</i> , <i>moisture sensitive</i> Note: Sold in collaboration with Daicel for research purposes only.	MeO N S "tE	50mg Bu
15-3035 NEW	(3-(Tert-butoxy)-2',6'-diisopropyl-6-methoxy- [1,1'-biphenyl]-2-yl)dicyclohexylphosphane GPhos, 98% (2489243-29-8) C <sub>35</sub> H <sub>35</sub> O <sub>2</sub> P; FW: 536.78; white xtl.; m.p. 240 Note: Patents: US 6,395,916, US 6,307,087	OtBu  MeO PCy <sub>2</sub> iPr	50mg 250mg

15-3035 (3-(Tert-butoxy)-2',6'-diisopropyl-6-methoxy-[1,1'-biphenyl]-2-yl)dicyclohexylphosphane (continued) GPhos, 98% (2489243-29-8)

### Technical Note:

1. Novel mono-phosphine Buchwald ligand that supports a catalyst of improved stability. The GPhos-derived catalyst exhibits improved performance for room temperature C–N cross coupling reactions between a broad scope of primary amines and aryl halides.¹ The ligand is designed to promote C–N cross coupling across a wide range of substrate classes with low catalyst loadings. It shows an improved relative rate of productive catalysis versus catalyst deactivation compared to previous catalysts. The GPhos-supported catalyst exhibits better reactivity than previous catalysts both under ambient conditions and at elevated temperatures. Its use allows for the coupling of a variety of primary amine and aniline nucleophiles, including (1) unhindered, (2) five-membered-ring N-heterocycle-containing, and (3) α-tertiary primary amines, each of which previously required a different catalyst to achieve optimal results. The GPhos-supported catalyst is also well suited for coupling electron-deficient anilines as well as N-heterocycle-containing aryl halides and amines.

### References:

J. Am. Chem. Soc., 2020, 142, 35, 15027.

15-6910 2-((2R,3R)-3-(tert-Butyl)-4-(3,5-dicyclopen-25mg Me. tyl-2,6-dimethoxyphenyl)-2,3-dihydrobenzo[d] 100mg NEW [1,3]oxaphosphol-2-yl)propan-2-ol, min. 97%, 500mg OH (99% ee) (2R,3R)-Baryphos (2416226-97-4) ″t-Bu C22H45O4P: FW: 524.68: white solid MeO OMe Note: Sold under license from Zejun for research purposes only. Patents: ZL2013105048267, CN104558038.

### Technical Note:

1. Ligand/palladium catalyst for asymmetric Suzuki-Miyaura cross-coupling reactions.

### References:

1. J. Am. Chem. Soc. 2020, 142, 8036-8043

25mg 15-6911 2-((2S,3S)-3-(tert-Butyl)-4-(3,5-dicyclopentyl-2,6-dimethoxyphenyl)-2,3-dihydrobenzo[d] 100mg NEW [1,3]oxaphosphol-2-yl)propan-2-ol, min. 97%, 500mg (99% ee) (2S,3S)-Baryphos (2416226-68-9) tBu C<sub>32</sub>H<sub>45</sub>O<sub>4</sub>P; FW: 524.68; white solid MeO OMe Note: Sold under license from Zejun for research purposes only. Patents: ZL2013105048267, CN104558038.

### Technical Note:

1. See 15-6910 (page 85)

PHOSPHORI	US (Compounds)	
15-8390 NEW	[S(R)]-N-[(1R)-1-[2-((tert-Butyldiphenylsilyl)oxy) phenyl)]-2-yl-2-(diphenylphosphino)ethyl]-2-methyl-2-propanesulfinamide, 95% C <sub>40</sub> H <sub>4e</sub> NO <sub>2</sub> PSSi; FW: 663.9; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	50mg
15-8388 NEW	[S(R)]-N-[(1S)-1-[2-((tert-Butyldiphenylsilyl)oxy)phenyl)]-2-yl-2-(diphenyl-phosphino)ethyl]-2-methyl-2-propanesulfinamide, 95% C <sub>40</sub> H <sub>46</sub> NO <sub>2</sub> PSSi; FW: 663.9; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	50mg
15-7620 NEW	Tetrabutylphosphonium chloride (68-72 wt% solution in methanol) (2304-30-5)  C <sub>16</sub> H <sub>36</sub> CIP; FW: 294.88; Pale yellow liq.; f.p. 52 °F; d. 0.9  "Bu  P+ CI "Bu	100g 500g
15-7625 NEW	Tetrabutylphosphonium chloride (49-51 wt% solution in toluene) (2304-30-5) C <sub>16</sub> H <sub>36</sub> CIP; FW: 294.88; Pale yellow liq.; f.p. 43 °F	100g 500g
15-1579 NEW	Tetrabutyphosphonium bromide (75% in water) (3115-68-2) (C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> P+Br-; FW: 339.35; colorless to light brown liq.; f.p. >2200 °F; d. 1.06	100g 500g
15-8596 NEW	(11aR)-10,11,12,13-Tetrahydro-5-hydroxy-3,7-bis[2,4,6-tricyclohexylphenyl]-5-oxide-diinde-no[7,1-de:1¹,7²-fg][1,3,2]dioxaphosphocin, 98% C <sub>ss</sub> H <sub>ss</sub> O <sub>4</sub> P; FW: 959.3; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	10mg 25mg
15-8612 NEW	(3aR,8aR)-Tetrahydro-6-hydroxy-2,2-dimeth-yl-4,4,8,8-tetrakis(3,5-diisopropyl-4-methoxy-phenyl)-6-oxide-[1,3]dioxolo[4,5-e][1,3,2] dioxaphosphepine, 98% C <sub>so</sub> H <sub>8s</sub> O <sub>10</sub> P; FW: 985.3; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	25mg 100mg
15-8613 NEW	(3aS,8aS)-Tetrahydro-6-hydroxy-2,2-dimethyl-4,4,8,8-tetrakis(3,5-diisopropyl-4-methoxyphenyl)-6-oxide-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine, 98%  C <sub>56</sub> H <sub>86</sub> O <sub>10</sub> P; FW: 985.3; off white to light yellow pwdr.  Note: Sold in collaboration with Daicel for research purposes only.	25mg 100mg

	Trow I roudete office offermer 755	(110101111001 2010)	
PHOSPHORE	JS (Compounds)		
15-8617 NEW	(3aR,8aR)-Tetrahydro-6-hydroxy-2,2-dimethyl-4,4,8,8-tetrakis(3,5-di-tert-butylphenyl)-6-oxide-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine, 98%, (99% ee) 98%, (99% ee) $C_{ss}H_{ss}O_{s}P$ ; FW: 977.4; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	t-Bu t-Bu t-Bu t-Bu t-Bu t-Bu t-Bu	
15-8618 NEW	(3aS,8aS)-Tetrahydro-6-hydroxy-2,2-dimethyl-tylphenyl)-6-oxide-[1,3]dioxolo[4,5-e][1,3,2]dioxc $C_{63}H_{93}O_6P$ ; FW: 977.4; off white to light yellow pw. Note: Sold in collaboration with Daicel for research	aphosphepine, 98%, (99% ee) rdr.	- 25mg 100mg
15-8608 NEW	(3aR,8aR)-Tetrahydro-6-hydroxy-2,2-dimethyl-4,4,8,8-tetrakis(4-(tert-butyl)phenyl)-6-oxide-[1,3]dioxolo[4,5-e][1,3,2]dioxaphos-phepine, 98%, (99% ee) C <sub>47</sub> H <sub>61</sub> O <sub>6</sub> P; FW: 753; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	t-Bu  Me  O  P  OH  t-Bu  t-Bu	100mg
15-8609 NEW	(3aS,8aS)-Tetrahydro-6-hydroxy-2,2-dimethyl-phenyl)-6-oxide-[1,3]dioxolo[4,5-e][1,3,2]dioxolo $_{47}H_{81}O_{6}P$ ; FW: 753; off white to light yellow pwdi Note: Sold in collaboration with Daicel for research	phosphepine, 98%, (99% ee)	25mg 100mg
	(3aR,8aR)-Tetrahydro-6-hydroxy-2,2-dimeth-yl-4,4,8,8-tetra-2-naphthalenyl-6-oxide-1,3-di-oxolo[4,5-e][1,3,2]dioxaphosphepin, 98%, (99% ee) (952649-50-2) C <sub>47</sub> H <sub>37</sub> O <sub>6</sub> P; FW: 728.8; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.  or the Zn-catalyzed asymmetric Simmons-Smith panation of both functionalized and unfunctionalized	Me O P O H O O H O O O O O O O O O O O O O	25mg 100mg
$\stackrel{R^2}{\searrow} \stackrel{R^3}{-} \stackrel{-}{}$	$ \begin{array}{c} \text{[Zn]-TADDOL} \\ \text{DCE, -15°C to } T \end{array} $		Tech. Note (1) Ref. (1)

### References:

1. Adv. Synth. Catal. 2006, 348, 2363.

15-8603 NEW	(3aS,8aS)-Tetrahydro-6-hydroxy-2,2-dimethyl-4,4,8,8-tetra-2-naphthale-nyl-6-oxide-1,3-dioxolo[4,5-e][1,3,2]dioxaphosphepin, 98%, (99% ee)	25mg 100mg
	$C_{47}H_{37}O_6P$ ; FW: 728.8; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	
15-8566 NEW	(11aR)-10,11,12,13-Tetrahydro-10,10,13,13-tetramethyl-5-hydroxy-3,7-di-2-naphthale-nyl-5-oxide-diindeno[7,1-de:1',7'-fg][1,3,2] dioxaphosphocin, 98%, (99% ee) C <sub>4</sub> ,H <sub>3s</sub> O <sub>4</sub> P; FW: 622.7; off white to light yellow pwdr.  Note: Sold in collaboration with Daicel for research purposes only.	25ო <u>დ</u> 100ოდ
15-8567 NEW	(11aS)-10,11,12,13-Tetrahydro-10,10,13,13-tetramethyl-5-hydroxy-3,7-di-2-naphtha lenyl-5-oxide-diindeno[7,1-de:1¹,7¹-fg][1,3,2]dioxaphosphocin, 98%, (99% ee) $C_{41}H_{36}O_4P$ ; FW: 622.7; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	- 25mg 100mg
15-8572 NEW	(11aR)-10,11,12,13-Tetrahydro-10,10,13,13-tetramethyl-5-hydroxy-3,7-di-9-phenanthre-nyl-5-oxide-diindeno[7,1-de:1',7'-fg][1,3,2] dioxaphosphocin, 98%, (99% ee) C <sub>49</sub> H <sub>39</sub> O <sub>4</sub> P; FW: 722.8; off white to light yellow pwdr.  Note: Sold in collaboration with Daicel for research purposes only.	25mg 100mg
15-8573 NEW	(11aS)-10,11,12,13-Tetrahydro-10,10,13,13-tetramethyl-5-hydroxy-3,7-di-9-phenan-threnyl-5-oxide-diindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocin, 98%, (99% ee) $C_{40}H_{30}O_4P$ ; FW: 722.8; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	25mg 100mg
15-8629 NEW	(3aR,8aR)-4,4,8,8-Tetrakis(3,5-di-tert-butyl-phenyl)-2,2-bis(4-chlorophenyl)-6-hydroxy-tetrahydro-6-oxide-[1,3]dioxolo[4,5-e][1,3,2] dioxaphosphepine, 95%, (99% ee)  C <sub>73</sub> H <sub>95</sub> Cl <sub>2</sub> O <sub>6</sub> P; FW: 1170.4; off white to light yellow pwdr.  Note: Sold in collaboration with Daicel for research purposes only.	25mg 100mg
15-8630 NEW	(3aS,8aS)-4,4,8,8-Tetrakis(3,5-di-tert-butylphenyl)-2,2-bis(4-chlorophenyl)-6-hydroxy-tetrahydro-6-oxide-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine, 95%, (99% eego <sub>73</sub> H <sub>95</sub> Cl <sub>2</sub> O <sub>6</sub> P; FW: 1170.4; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	25mg ) 100mg

PHOSPHOR	US (Compounds)		
15-8625 (NEW)	(3aR,8aR)-4,4,8,8-Tetrakis(3,5-di-tert-butylphenyl)-2,2-bis(4-fluorophenyl)-6-hydroxytetrahydro-6-oxide-[1,3]dioxolo[4,5-e][1,3,2] dioxaphosphepine, 98%, (99% ee) $C_{75}H_{96}F_2O_6P$ ; FW: 1137.5; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	t-Bu t-Bu t-Bu t-Bu t-Bu t-Bu t-Bu t-Bu	25mg 100mg
15-8626 NEW	(3aS,8aS)-4,4,8,8-Tetrakis(3,5-di-tert-butylpher 6-hydroxy-tetrahydro-6-oxide-[1,3]dioxolo[4,5- 98%		25mg 100mg
	C <sub>73</sub> H <sub>95</sub> F <sub>2</sub> O <sub>6</sub> P; FW: 1137.5; off white to light yellow Note: Sold in collaboration with Daicel for research		
15-8634 NEW	(3aR,8aR)-4,4,8,8-Tetrakis(3,5-di-tert-butyl-phenyl)-6-hydroxy-2,2-bis(4-(trifluoromethyl) phenyl)tetrahydro-6-oxide-[1,3]dioxolo[4,5-e] [1,3,2]dioxaphosphepine, 98% $C_{76}H_{96}F_6O_6P$ ; FW: 1237.5; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for research purposes only.	F <sub>3</sub> C t-Bu t-Bu t-Bu t-Bu t-Bu	25mg 100mg
15-8635 NEW	(3aS,8aS)-4,4,8,8-Tetrakis(3,5-di-tert-butylpher fluoromethyl)phenyl)tetrahydro-6-oxide-[1,3]d sphepine, 98% C <sub>7s</sub> H <sub>9s</sub> F <sub>6</sub> O <sub>8</sub> P; FW: 1237.5; off white to light yellow Note: Sold in collaboration with Daicel for research	ioxolo[4,5-e][1,3,2]dioxapho- pwdr.	25mg 100mg
15-8638 NEW	(3aR,8aR)-4,4,8,8-Tetrakis(3,5-di-tert-butyl-phenyl)-6-hydroxy-2,2-di-p-tolyltetrahydro-6-oxide-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine, 98%, (99% ee) $C_{76}H_{101}O_6P$ ; FW: 1129.6; off white to light yellow pwdr. Note: Sold in collaboration with Daicel for esearch purposes only.	t-Bu t-Bu t-Bu t-Bu t-Bu t-Bu t-Bu t-Bu	25mg 100mg
15-8639 NEW	(3aS,8aS)-4,4,8,8-Tetrakis(3,5-di-tert-butylpher yltetrahydro-6-oxide-[1,3]dioxolo[4,5-e][1,3,2]cee) $C_{75}H_{101}O_9P$ ; FW: 1129.6; off white to light yellow p Note: Sold in collaboration with Daicel for research	lioxaphosphepine, 98%, (99% wdr.	25mg 100mg

15-8621 NEW (3a'R,8a'R)-4',4',8',8'-Tetrakis(3,5-di-tert -butylphenyl)-6'-hydroxy-tetrahydrospiro[cyclohexane-1,2'-6'-ox[1,3]dioxolo[4,5-e][1,3,2] dioxaphosphepine, 98%, (99% ee)

 $C_{66}H_{97}O_6P$ ; FW: 1017.4; off white to light yellow pwdr.

Note: Sold in collaboration with Daicel for research purposes only.

t-Bu t-Bu	25mg 100mg
t-Bu t-Bu	
O P OH	
t-Bu t-Bu	
t-Bu t-Bu	

25mg

100mg

100g 500g

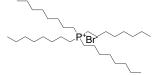
15-8622 (3a'S,8a'S)-4',4',8',8'-Tetrakis(3,5-di-tert-butylphenyl)-6'-hydroxy-tetrahy-drospiro[cyclohexane-1,2'-6'-ox[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine, 98%, (99% ee)

C<sub>66</sub>H<sub>97</sub>O<sub>6</sub>P; FW: 1017.4; off white to light yellow pwdr.

Note: Sold in collaboration with Daicel for research purposes only.

15-7630 Tetraoctylphosphonium bromide (45-55 wt% in toluene) (23906-97-0)

C<sub>32</sub>H<sub>e8</sub>BrP; FW: 563.76; Colorless to pale yellow liq.; f.p. 43 °F *hygroscopic* 



### Technical Notes:

- Thermally stable, soluble quaternary phosphonium derivative used in metal separation¹ and lubricant additive applications².
- Catalyst for the oxidation of alkyl aromatic compounds<sup>3</sup> and preparation of mononitrated aromatic compounds<sup>4</sup>.

### References:

- Green Chemistry, 2012, 14, 1657-1665.
- US20150232777A1.
- 3. US9932287B2.
- 4. WO2012156540A3.

15-7580 NEW Tributyl(ethyl)phosphonium bromide, min. 95% (45-55% in water), CYPHOS® IL 676W (7392-50-9) C<sub>14</sub>H<sub>32</sub>BrP; FW: 311.29; Colorless to pale yellow liq. Note: Sold in collaboration with Solvay.

"Bu 100g Et-P-"Bu Br 500g

### Technical Notes:

- 1. CYPHOS® IL 676W has been used in phase transfer catalysis [1].
- 2. CYPHOS® IL 676W is an effective in aluminum electroplating [2].
- 3. CYPHOS® IL 676W has also been exploited in organic transformations as a cocatalyst [3].
- 4. CYPHOS® IL 676W has been observed to increase the SN2 reactions rate of sulfonate esters with bromide ion [5].
- 5. CYPHOS® IL 676W has been demonstrated effective at capturing SO2 from flue gas [5].

$$O_2N$$
  $\longrightarrow$   $O_3$  + Br  $\longrightarrow$   $O_2N$   $\longrightarrow$   $O_3$  + MeBr  $\longrightarrow$  Ref. (4)

15-7580 Tributyl(ethyl)phosphonium bromide, min. 95% (45-55% in water), CYPHOS® IL 676W (continued) (7392-50-9)

- 1. JP Patent 02304061, Dec. 17, 1990.
- 2. JP Patent 04021794, Jan. 24, 1992.
- 3. Tetrahedron Lett. 2004, 45, 7359.
- 4. J. Phys. Org. Chem. 2006, 19, 281.
- 5. AIChE, 2015, 6, 2028.

15-7570 (NEW)	TributyImethyIphosphonium p-toluenesulfonate, min. 95% (45-55% in water), CYPHOS® IL 120W (55767-12-9)  C <sub>13</sub> H <sub>30</sub> P(C <sub>7</sub> H <sub>7</sub> O <sub>3</sub> S); FW: 388.55; Colorless to pale yellow liq.  Note: Sold in collaboration with Solvay.	100g 500g
15-7575 NEW	TributyI(octyI)phosphonium chloride, min. 93%, CYPHOS® IL 253 (56315-19-6) C <sub>20</sub> H <sub>44</sub> CIP; FW: 351.00; Colorless to pale yellow viscous liq.; b.p. >2200 °C; f.p. 306 °F; d. 0.92 Note: Sold in collaboration with Solvay.	100g 500g
15-7615 NEW	Tributylphosphine sulfide/tributylphosphine (50:50 mixture), CYTOP® 506 (3084-50-2)  C12H27PS/C12H27P; Colorless to amber liq.; f.p. >2212 °F in Bu line liquid in Solvay.	25g 100g 500g
15-7585 NEW	TributyItetradecyl phosphonium chloride, (ca. 50% in water), CYPHOS® 4345W (81741-28-8) C <sub>26</sub> H <sub>56</sub> CIP; FW: 435.16; Yellow green viscous liq.; d. 0.95 Note: Sold in collaboration with Solvay.	100g 500g
15-7565 NEW	Triethyl(octyl)phosphonium chloride (45-55% solution), CYPHOS® IL 541W (482647-71-2)  C <sub>14</sub> H <sub>32</sub> CIP; FW: 266.83; Colorless to pale yellow liq. Note: Sold in collaboration with Solvay.	100g 500g
15-7590 NEW	Trihexyl(octyl)phosphonium chloride, min. 95%, CYPHOS® IL 356 (850134-85-9)  C <sub>26</sub> H <sub>56</sub> CIP; FW: 435.16; Colorless to pale yellow liq.; f.p. >230 °F  Note: Sold in collaboration with Solvay.	100g 500g

	New Products Since Chemiker XXX	(I (November 2019)	
PHOSPHOR	JS (Compounds)		
15-8374 NEW	[S(R)]-N-[(1S)-1-(2',4',6'-Triisopropyl)-(1,1'-bi-phenyl)-2-yl-2-(diphenylphosphino)eth-yl]-2-methyl-2-propanesulfinamide, 95% C <sub>39</sub> H <sub>50</sub> NOPS; FW: 611.9; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	Ph <sub>2</sub> P N S tBu	50mg
15-8456 NEW	[S(R)]-N-[(R)-[2,4,6-(Triisopropylphenyl)) methyl]-4-methoxyphenyl][2-(dicyclohexyl- phosphino)phenyl]methyl]-2-methyl-2-pro- panesulfinamide, 95% C <sub>38</sub> H <sub>60</sub> NOPS; FW: 609.9; white to off-white pwdr. air sensitive, moisture sensitive Note: Sold in collaboration with Daicel for research purposes only.	i-Pr O N S VtBu PCy <sub>2</sub>	50mg
quantum 2. A Gener. Convers 3. Raw ma for II-VI: and IV-V References: 1. Physika 2. Chem. M	sed in the manufacture of nanocrystals, specifically		100g 500g
15-6659 NEW	Trioctylphosphine selenide min. 80% (20612-73 (C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> PSe; FW: 449.59; colorless to pale yellow f.p. >230 °F; d. 0.9 <i>STENCH</i>		25g 100g 500g
15-7550 NEW	Trioctylphosphine sulfide, CYTOP® 505 (2551-53-3) C <sub>24</sub> H <sub>51</sub> PS; FW: 402.71; colorless to pale yellow liq f.p. 230 °F; d. 0.89 Note: Sold in collaboration with Solvay.	n-Oct n-Oct—P=S n-Oct	25g 100g 500g
15-7610 NEW amp	Tripropylphosphine, min. 98%, CYTOP® 330 (2234-97-1) C <sub>9</sub> H <sub>21</sub> P; FW: 160.24; Colorless liq.; d. 0.8 air sensitive, moisture sensitive, pyrophoric	nPr	50g 250g

air sensitive, moisture sensitive, pyrophoric Note: Sold in collaboration with Solvay.

PHOTOCHEM	IICAL EQUIPMENT (Other)	
98-7850	EvoluChem™ Light proofing upgrade	1 ea
NEW	Note: This item is compatible with the EvoluChem™ PhotoRedOx Box (98-7500	
09 7075	& 98-7550). Sold in collaboration with HepatoChem.	1 ea
98-7975	EvoluChem™ PhotoRedOx Box Light Source - Electric Power PAR20-18W, LG, Wavelength 380nm, 25 degrees,	i ea
NEW	100-240V AC	
	Note: This item is compatible with the EvoluChem™ PhotoRedOx	
	Box (98-7500 & 98-7550). A light source is required for use of the PhotoRedOx Box. For related products, see www.strem.com/	
	evoluchem. Sold in collaboration with HepatoChem.	
98-7950	EvoluChem™ PhotoRedOx Box Light Source -	1ea
NEW	Wavelength 365nm, Electric Power 18W	
_	Note: This item is compatible with the EvoluChem PhotoRedOx Box (98-7500 & 98-7550). A light source is required for use of	
	the PhotoRedOx Box. For related products see www.strem.	
	com/evoluchem. Sold in collaboration with HepatoChem.	
98-7780	EvoluChem™ PhotoRedOx Box Photochemistry Holder - 2 x 20 ml vials	1ea
NEW	Note: This item is compatible with the EvoluChem PhotoRedOx Box (98-7500 & 98-7550). A photochemistry holder is required for use of the PhotoRedOx Box.	
	For additional holder options, please see www.strem.com/evoluchem . Sold in	
	collaboration with HepatoChem.	
98-7790	EvoluChem™ PhotoRedOx Box Photochemistry Holder - 8 x 4 ml vials	1 ea
NEW	Note: This item is compatible with the EvoluChem™ PhotoRedOx Box (98-7500 &	
_	98-7550). A photochemistry holder is required for use of the PhotoRedOx Box. For additional holder options, please see www.strem.com/evoluchem.	ı
	Sold in collaboration with HepatoChem.	
98-7550	EvoluChem™ PhotoRedOx Box (Temperature controlled)	1 ea
NEW	Note: Sold in collaboration with HepatoChem.	
RHENIUM (Co	• •	
75-4200	Trimethylsilyl perrhenate, 98% (99.999%-Re) PURATREM (16687-12-0)  Me	250mg 1g
NEW	ReO <sub>3</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> ; FW: 323.39; white solid; m.p. 79.5-80.5	19 5g
	ReO <sub>3</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> ; FW: 323.39; white solid; m.p. 79.5-80.5 air sensitive, light sensitive, moisture sensitive, hygroscopic	-3
	Ó WIE	
RUTHENIUM	(Compounds)	
44-3210	Dichloro[N-[2-(diphenylphosphino-κP)ethyl]-	50mg
NEW	2-(methylthio-kS)ethanamine-kNj(triphenyl-	
_	phosphine) ruthenium  C <sub>35</sub> H <sub>37</sub> Cl <sub>2</sub> NP <sub>2</sub> RuS; FW: 737.67; yellow solid  Ph—P—Ru—S	
Technical Note:	I I (il Ma	
	for selective ester hydrogenation.  Ph PPh <sub>3</sub>	
O	+ H <sub>2</sub> [Ru] SNP(O) Ligand (50 bar) + R <sub>1</sub> OH	T I. N
↓ <sub>.R</sub> 1 ·	$+ H_2 \xrightarrow{\text{I. a.j. o. i. (a) 2.3 gains}} + R_1OH$	Tech. Note (1) Ref. (1)
R´ `O´''	(50 bar) R	
References.		
	cess Res. Dev. <b>2020</b> , 24, 415.	
44-3245	Dichloro[rel-[N(S)]-N-[2-(diphenylphos-	50mg
NEW	phinyl-kO)ethyl]-2-[(R)-benzylthio-kS]ethana- mine-kN](triphenylphosphine) ruthenium	
	C <sub>41</sub> H <sub>41</sub> Cl <sub>2</sub> NOP <sub>2</sub> RuS; FW: 829.76; magenta pwdr.	
	air sensitive Cl Bn	
	Note: Patents: US20170088571A1; Ph PPh <sub>3</sub>	
	U.U. I TUVISIUTIAI FAICITI AUDITUALIUTI INU. UZ/OZ I .UZ I .	

1. See 44-3210 (page 93)

### **RUTHENIUM (Compounds)** 44-3230 Dichloro[rel-[N(S)]-N-[2-(diphenylphos-100mg phinyl-kO)ethyl]-2-[(R)-methylthio-kS]ethan-NEW amine-kN](triphenylphosphine) ruthenium (1839552-42-9) C<sub>35</sub>H<sub>37</sub>Cl<sub>2</sub>NOP<sub>2</sub>RuS; FW: 753.66; brick red solid moisture sensitive Note: Patents: US20170088571A1; U.S. Provisional Patent Application No. 62/827.627. Technical Note: See 44-3210 (page 93) 44-3240 Dichloro[rel-[N(S)]-N-[2-(diphenylphos-50mg phinyl-κO)ethyl]-2-[(R)-phenylthio-κS]ethana-NEW mine-κN](triphenylphosphine) ruthenium C<sub>40</sub>H<sub>39</sub>Cl<sub>2</sub>NOP<sub>2</sub>RuS; FW: 815.74; dark red xtl. air sensitive Note: Patents: US20170088571A1; U.S. Provisional Patent Application No. 62/827,627. Technical Note: See 44-3210 (page 93) 44-3235 Dichloro[rel-[N(S)]-N-[2-(diphenylphos-100ma phinyl-κO)ethyl]-2-[(R)-tert-butylthio-κS]ethan-NEW amine-kN](triphenylphosphine) ruthenium

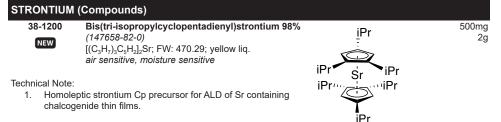
C<sub>38</sub>H<sub>43</sub>Cl<sub>2</sub>NOP<sub>2</sub>RuS; FW: 795.75; black brown solid

Note: Patents: US20170088571A1; U.S. Provisional Patent Application No. 62/827,627.

Technical Note:

1. See 44-3210 (page 93)

air sensitive



### STRONTIUM (Compounds)

38-1200 Bis(tri-isopropylcyclopentadienyl)strontium 98% (147658-82-0) (continued)

Target Deposit	Deposition Technique	Delivery Temperature	Pressure	Co-reactants	Deposition Temperature	Ref.
SrO	ALD	100 °C	7.5 Torr	H <sub>2</sub> O	250 °C	[1]
SrO	ALD	140-145 °C	1 Torr	H <sub>2</sub> O	150-390 °C	[7]
SrTiO <sub>3</sub>	ALD	100 °C	7.5 Torr	H <sub>2</sub> O, Ti(O <sup>i</sup> Pr) <sub>4</sub>	250-325 °C	[1]
SrTiO <sub>3</sub>	ALD	150 °C	0.2 Torr	H <sub>2</sub> O, Ti(NMe <sub>2</sub> ) <sub>4</sub>	120-330 °C	[10]
SrTiO <sub>3</sub>	ALD	90 °C	0.7 Torr	O <sub>3</sub> , H <sub>2</sub> O, Ti(Me <sub>5</sub> Cp)(OMe) <sub>3</sub>	370 °C	[6]
SrTiO <sub>3</sub>	ALD	90 °C	0.7 Torr	O <sub>3</sub> , H <sub>2</sub> O, Ti(O <sup>i</sup> Pr) <sub>2</sub> (tmhd) <sub>2</sub>	370 °C	[6]
SrTiO <sub>3</sub>	ALD	130 °C		O <sub>3</sub> , Ti(NEtMe) <sub>4</sub>	300 °C	[4]
SrTiO <sub>3</sub>	PEALD	120 °C		O <sub>2</sub> plasma, Ti(O <sup>1</sup> Pr) <sub>2</sub> (tmhd) <sub>2</sub>	250 °C	[5]
La <sub>x</sub> Sr <sub>1-</sub> <sub>x</sub> TiO <sub>3</sub>	ALD	130 °C	1 Torr	H <sub>2</sub> O, Ti(O <sup>i</sup> Pr) <sub>4</sub> , La(fmd) <sub>3</sub>	225 °C	[9]
SrSnO <sub>3</sub>	ALD	130 °C	1 Torr	Sn(NMe <sub>2</sub> ) <sub>4</sub> , H <sub>2</sub> O	180 °C	[12]
SrZrO <sub>3</sub>	ALD	130 °C	1 Torr	H <sub>2</sub> O, Zr(Nme <sub>2</sub> ) <sub>4</sub>	225 °C	[11]
SrRuO <sub>3</sub>	CVD/ALD			O <sub>2</sub> , RuO <sub>4</sub>	230 °C	[8]
SrS	ALD	100 °C	7.5 Torr	H <sub>2</sub> S	120-460 °C	[2]
M:SrS (M=Cu, Pb, Ce, Mn, Eu)	ALD	100 °C	7.5 Torr	H <sub>2</sub> S, Cu(Cp)(PEt <sub>3</sub> ), Pb('Bu <sub>3</sub> Cp) <sub>2</sub> , Ce(Cp) <sub>3</sub> , Mn(thmd) <sub>3</sub> , Eu(thmd) <sub>3</sub>	120-380 °C	[3]

### Thermal Behavior:

- TGA available in [2]
- Decomposition in process ~250 °C [1, 7]
- Vapor pressure ~0.5 Torr at 120 °C [5]

- 1. Chem. Vap. Deposition 2001, 7, 75.
- 2. Chem. Mater. 2002, 14, 1937.
- 3. J. Electrochem. Soc. 2004, 151, H221.
- 4. J. Appl. Phys. **2011**, 109, 094101.
- 5. J. Electrochem. Soc. 2011, 158, G34.
- 6. Chem. Mater. 2013, 25, 953.
- 7. J. Phys. Chem. C 2013, 117, 11578.
- 8. ECS Trans. 2013, 58, 171.
- 9. J. Appl. Phys. 2014, 115, 224108.
- 10. Thin Solid Films **2014**, 550, 53.
- 11. J. Appl. Phys. 2018, 124, 044102.
- 12. J. Vac. Sci. Technol. A, 2019, 37, 050902.

	Ascensus Legacy Froducts	
BORON (Cor	mpounds)	
<b>05-0110</b> HAZ	CALLERY™ Dimethylsulfide borane, min. 93% (13292-87-0) (CH <sub>3</sub> ) <sub>2</sub> S:BH <sub>3</sub> ; FW: 75.97; colorless to slightly yellow liq.; m.p40°; f.p. 65°F; d. 0.801	Me 25g 100g
	moisture sensitive, (store cold)	3
	Note: Product and trademark of Ascensus Specialties LLC	
<b>05-1000</b> HAZ	CALLERY™ (R)-Methyl oxazaborolidine, 1M in toluene (112022-83-0) C <sub>18</sub> H <sub>20</sub> BNO; FW: 277.17; colorless to amber liq.; f.p. 40°F (toluene); d. 0.925 moisture sensitive Note: Product and trademark of Ascensus Specialties LLC	10ml Ph 50ml
<b>05-1001</b> HAZ	CALLERY™ (S)-Methyl oxazaborolidine, 1M in toluene (112022-81-8) C <sub>18</sub> H <sub>20</sub> BNO; FW: 277.17; colorless to amber liq.; f.p. 40°F (toluene); d. 0.925 moisture sensitive Note: Product and trademark of Ascensus Specialties LLC	10ml 50ml
93-0540 HAZ	CALLERY™ Triethylborane, min 99.8% (97-94-9) B(C₂H₅)₃; FW: 98.00; clear to slightly amber liq.; m.p92.9°; b.p. 95°; f.p. 32.8°F; d. 0.6961 (23°) pyrophoric Note: Product and trademark of Ascensus Specialties LLC	100g <b>Ξ</b> t
LITHIUM (C	ompounds)	
03-1275 NEW HAZ	CALLERY™ Lithium hexamethyldisilazane, 24% solution in tetrahydrofuran (4039-32-1)  C <sub>6</sub> H <sub>18</sub> LiNSi <sub>2</sub> ; FW: 167.33; yellow to amber; f.p6.16; d. 0.867 moisture sensitive  Note: Product and trademark of Ascensus Specialties LLC  Me—Si  Me—Me  Me—Me	100g 500g 2.5kg Li <sup>†</sup>
POTASSIUI	M (Elemental Forms)	
<b>19-1990</b> amp HAZ	CALLERY™ Potassium Metal, min. 99% (breakseal ampoule) (7440-09-7) K; FW: 39.09; under argon; m.p. 63.7°; b.p. 760°; d. 0.86 air sensitive, moisture sensitive Note: Product and trademark of Ascensus Specialties LLC	1g 5g
93-1990	CALLERY™ Potassium Metal, min. 99% (prescored ampoule) (7440-09-7)	1g
amp HAZ	K; FW: 39.09; under argon; m.p. 63.7°; b.p. 760°; d. 0.86 air sensitive, moisture sensitive Note: Product and trademark of Ascensus Specialties LLC	5g 25g
<b>19-1910</b> amp HAZ	CALLERY™ Sodium-Potassium Alloy 22:78 (min. 99%) (11135-81-2) NaK; liq.; 78% K, 22% Na (under argon); m.p12.6°; b.p. 785°; d. 0.855 air sensitive, moisture sensitive	1g 5g 25g
	Note: Product and trademark of Ascensus Specialties LLC	50g
POTASSIUI	M (Compounds)	
19-1045 NEW HAZ	CALLERY™ Potassium hexamethyldisilazane, 15% in toluene (40949-94-8) [(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> NK; FW: 199.49; colorless to amber liquid; f.p6.88; d. 0.879 air sensitive, moisture sensitive, STENCH Note: Product and trademark of Ascensus Specialties LLC	100g le 500g le <sup>2.5kg</sup>
19-1000 NEW HAZ	CALLERY™ Potassium tert-amylate, 25% solution in toluene (41233-93-6) C₅H₁₁KO; FW: 126.24; clear to amber; f.p. 39.92 air sensitive, heat sensitive, moisture sensitive Note: Product and trademark of Ascensus Specialties LLC	250g 1kg 5kg

19-1020	CALLERY™ Potassium tert-butoxide, 20% solution in tetra-	100
NEW	hydrofuran (865-47-4)	500
	C <sub>4</sub> H <sub>9</sub> KO; FW: 112.21; colorless to amber; f.p. 0.14; d. 0.906	2.5k
HAZ	air sensitive, heat sensitive, moisture sensitive	
	Note: Product and trademark of Ascensus Specialties LLC Me	
93-1910	CALLERY™ Potassium tert-butoxide, min. 99% (865-47-4) K+	100
HAZ	KOC(CH <sub>3</sub> ) <sub>3</sub> ; FW: 112.21; white to off-white pwdr.; m.p. 256° dec.	500
	moisture sensitive Me——Me	2.5
	Note: Product and trademark of Ascensus Specialties LLC Me	
DIUM (C	ompounds)	
11-1275	CALLERY™ Sodium hexamethyldisilazane, 40%	100
	solution in tetrahydrofuran (1070-89-9)	500
NEW	C <sub>6</sub> H <sub>18</sub> NNaSi <sub>2</sub> ; FW: 183.38; yellow to brown; f.p23.98 Me—Si	2.5k
HAZ	air sensitive, heat sensitive, moisture sensitive	
	Note: Product and trademark of Ascensus Specialties	
	LLC Me—Si	
	Me Me	
14 4000		500
11-1630	CALLERY™ Sodium tert-amylate, 35% in tetrahydrofuran (14593-46-5)  Me	500 2.5k
NEW	(C.H.)(CH.) CONa: FW: 110.13: vellow to amber liquid:	2.50
HAZ	f.p6.16	
	air sensitive, heat sensitive, moisture sensitive Me Et	
	Note: Product and trademark of Ascensus Specialties LLC	
93-1022	CALLERY™ Sodium tert-butoxide, min. 98% (865-48-5) Na <sup>+</sup>	100
HAZ	C <sub>4</sub> H <sub>9</sub> ONa; FW: 96.11; White to light yellow pwdr.	500
	moisture sensitive	
	Note: Product and trademark of Ascensus Specialties LLC <sup>t</sup> Bu	
11-0595	CALSELECT™ Sodium triacetoxyborohydride, O	25
HAZ	min. 97% (56553-60-7)	100
	Na(OOCCH <sub>3</sub> ) <sub>3</sub> BH; FW: 211.94; white pwdr.; m.p. 106 °C	500
	all Sensitive, moisture Sensitive, (store cold)	2.5k
	Note: Product and trademark of Ascensus Specialties LLC	
	O O Me	
	Na <sup>+</sup>	
	Me	
11-1117	VENPURE™ AF CAPLETS (sodium borohydride), min. 99% (16940-66-2)	50
NEW	NaBH <sub>4</sub> ; FW: 37.83; White caplets; m.p. > 360 °C	250
HAZ	air sensitive, moisture sensitive	1k
	Note: Product and trademark of Ascensus Specialties LLC	
11-1120	VENPURE™ AF GRANULE (sodium borohydride), min. 99% (16940-66-2)	50
NEW	NaBH <sub>4</sub> ; FW: 37.83; White granules; m.p. > 360 °C	250
HAZ	air sensitive, moisture sensitive	1k
	Note: Product and trademark of Ascensus Specialties LLC	
11-1119	VENPURE™ SF GRANULE (sodium borohydride), min. 98.5% (16940-66-2)	50
NEW	NaBH <sub>4</sub> ; FW: 37.83; White granules; m.p. > 360 °C	250
HAZ	air sensitive, moisture sensitive Note: Product and trademark of Ascensus Specialties LLC	14
	<u>'</u>	
93-1118	VENPURE™ SF POWDER (sodium borohydride), min. 98.5% (16940-66-2)	50
HAZ	NaBH <sub>4</sub> ; FW: 37.83; white pwdr.; m.p. > 360 °C; d. 1.074	250
	moisture sensitive Note: Product and trademark of Ascensus Specialties LLC	1k
14 4404		F00
11-1121	VENPURE™ SOLUTION (sodium borohydride 12%; sodium hydroxide 40%)	500
NEW	in water (16940-66-2)	2.5k
HAZ	NaBH <sub>4</sub> ; FW: 37.83; Clear colorless; b.p. 130-135 °C; d. 1.4 air sensitive, moisture sensitive	
	Note: Product and trademark of Ascensus Specialties LLC	

Coming S	oon	
05-1785	CALLERY™ 9-Borabicyclo-[3.3.1]-nonane in tetrahydrofuran 0.5M (rep.monomer) (280-64-8)	ВН
05-0175	CALLERY™ Borane tetrahydrofuran, 1M in tetrahydrofuran (14044-65-6)	O BH <sub>3</sub>
05-0156	CALLERY™ (+)-Diisopinocampheylchloroborane, 60-65% solution in hexanes ((+)-DPC) (112246-73-8)	Me Me Me Me Me Me Me
05-0155	CALLERY™ (-)-Diisopinocampheylchloroborane, 60-65% solution in heptanes ((-)-DPC) (85116-37-6)	Me Me Me Me Me
05-0130	CALLERY™ 5-Ethyl-2-methylpyridine borane, min. 93% (1014979-56-6)	Me BH <sub>3</sub>
05-1655	CALLERY™ Isopropyl Pinacol Borate, min. 98% (61676-62-8)	Me Me O B O Pr
03-1430	CALLERY™ Lithium tert-Butoxide, 20% solution in tetrahydro- furan (1907-33-1)	Li <sup>+</sup> O· <sup>†</sup> Bu
03-1410	CALSELECT™ Lithium triethylborohydride, 1M in tetrahydrofuran (22560-16-3)	Et   BH <sup>-</sup> Et Li <sup>+</sup>
03-1400	CALSELECT™ Lithium tri-sec-butylborohydride, 1M in tetrahydrofuran (38721-52-7)	Et Me  Et BH-Et  Me Me  Li+
03-4870	CALSELECT™ Lithium Tri-tert-butoxy Aluminum Hydride, 1M in tetrahydrofuran (17476-04-9)	<sup>t</sup> Bu `O H⁻ Li⁺ O Al `O tBu tBu
05-1750	CALLERY™ Methoxydiethylborane, 50% in tetrahydrofuran (7397-46-8)	Me O Et B Et
05-1700	CALLERY™ Methoxydiethylborane, min. 97% (7397-46-8)	Me O
05-1635	CALLERY™ Methyl Boronic Acid, min. 96.5% (13061-96-6)	OH Me <sup>∕ B</sup> \OH

Coming S	oon		
05-1780	CALLERY™ N,N-Diethylaniline borane, min. 97% (13289-97-9)	BH <sub>3</sub>	
05-0145	CALLERY™ Pinacolborane with 1% triethylamine, min. 97.5% (25015-63-8)	Me Et N Et Me 1%	
19-1035	CALLERY™ Potassium ethoxide, 24% in ethanol (DN w/ 5% toluene) (917-58-8)	Et <sub>\O</sub> . K <sup>+</sup>	
19-1090	CALLERY™ Potassium hexamethyldisilazane, 20% solution in tetrahydrofuran (40949-94-8)	Me Me Me I Me Me Si N Si Me K <sup>+</sup>	
19-1040	CALLERY™ Potassium isopropoxide, 19% in isopropanol (6831-82-9)	Me Me Me I Me Si N. Si Me K+	
19-1095	CALLERY™ Potassium Methoxide, 25% solution in Methanol (865-33-8)	K <sup>+O</sup> `Me	
19-1070	CALLERY™ Potassium tert-amylate, 5% solution in cyclohexane (41233-93-6)	K <sup>+</sup> Me Et	
19-1060	CALLERY™ Potassium tert-amylate, 15% solution in cyclohexane (41233-93-6)	K <sup>+</sup> Me Et	
19-1085	CALLERY™ Potassium tert-amylate, 15% solution in hexanes (41233-93-6)	K+ Me Et	
19-1080	CALLERY™ Potassium tert-butoxide, 12% solution in tetrahydrofuran (865-47-4)	K <sup>+</sup> O <sup>-</sup> Me — Me	
19-1030	CALLERY™ Potassium 3,7-Dimethyl-3-octylate, 50% in n-heptane (263148-42-1)	Me K+-O Me Me	
11-1615	CALLERY™ Sodium mentholate, 50% in hexanes (19321-38-1)	HO O Na <sup>+</sup>	
11-1725	CALLERY™ Sodium n-butoxide, 20% solution in n-Butanol (2372-45-4)	TO Na <sup>+</sup>	

Coming S	oon		
11-1625	CALLERY™ Sodium tert-amylate (14593-46-5)	Me	
		Na <sup>+</sup>	
		Me Et	
11-1740	CALLERY™ Sodium tert-amylate, 25% in Cyclohexane (14593-46-5)	Me O	
		Na <sup>+</sup> Et	
11-1635	CALLERY™ Sodium tert-amylate, 25% in Toluene (14593-46-5)	Me -O.	
		Na <sup>+</sup>	
11-1735	CALLERY™ Sodium tert-butoxide, 20% solution in tetrahydrofuran	Me´ `Et Na+	
	(865-48-5)	O-	
		<sup>t</sup> Bu	
05-0565	CALLERY™ Tri-n-butylborane-3-methoxypropylamine, min. 98% (345269-15-0)	ı	
		<sup>n</sup> Bu <sup>/B</sup> <sup>n</sup> Bu	
		H <sub>2</sub> N O Me	
05-0140	CALLERY™ Triethylamine borane, min. 95% (1722-26-5)	Et BH3	
		Et N Et	
05-0550	CALLERY™ Triethylborane, 14% in tetrahydrofuran (97-94-9)	Et	
		Et´ <sup>B</sup> `Et	
05-1665	CALLERY™ Triethylborane (85%); Triethyaluminum (15%)	Et Et	
	(97-93-8; 97-94-9)	Et Et Al Et	
		85% 15%	
05-0555	CALLERY™ Triethylborane-1,3-diaminopropane, min. 97% (148861-07-8)	<u> </u>	
	(14000) 07 07	Et <sup>_B</sup> `Et	
		$H_2N$ $NH_2$	
05-0560	CALLERY™ Triethylborane-diethylenetriamine, min. 97%	Et	
	(1187733-83-0)	Et B\Et	
		н	
		$H_2N$ $NH_2$	
05-1675	CALLERY™ Trimethyl Borate Azeotrope, 72% in Methanol (121-43-7; 67-56-1)	Me <sub>`O</sub>	
	(127 40 7, 07 00 1)	Me O B O Me	
05-1645	CALLERY™ Trimethylboroxin, 50% solution in tetrahydrofuran (823-96-1)	Me B O B Me	
	(020 00 1)	0\0	
		B	
		Me	

Coming S	oon	
11-1600	CALSELECT™ Sodium tri-sec-butylborohydride, 1M in tetrahydrofuran <i>(67276-04-4)</i>	EtMe
		Et BH- Et
		∥ ∥ Me Me
		Na <sup>+</sup>
03-1450	VENPURE™ Lithium borohydride 10%, in tetrahydrofuran (169	949-15-8)
11-1122	VENPURE™ 930 Solution (sodium borohydride 9%; sodium hy	droxide 30%) (16940-66-2)



### **cGMP & Custom Synthesis**Providing reliable solutions for over 30 years

Ascensus delivers consistent quality and expertise in cGMP and custom synthesis production. All chemists at the Newburyport site are regularly trained on GMP standards and participate in GMP production to provide customers with reliable products and services.

### **cGMP Production**

Custom synthesis services and process development are conducted under the strictest confidence. A broad range of chemical transformations are possible at our Newburyport facility. For pharmaceutical applications, manufacturing is conducted under current Good Manufacturing Practices (cGMP) in kilo-lab suites. This capability has been available at the Newburyport site since 1988. Complete documentation is provided, including validation and stability studies. Both Active Pharmaceutical Ingredients (APIs) and late stage raw materials for APIs are manufactured. Active Drug Master Files (DMFs) are also maintained in North America and Europe. Quality agreements are in place with major US and International drug companies.

### **Site Capabilities**

### GMP Suites & Facilities

- 3 ISO Class 7 rooms
- 2 controlled, non-classified GMP rooms
- Dedicated glassware
- Dedicated production suite
- Verified Line Clearance prior to project change-over

### ▲ Analytical Support

- Method Development
- Methods Transfer
- Methods Verification/ Validation
- Data Integrity
- Release and Stability Testing

### Equipment & Scale

- Kilo-lab production
- Up to 22L dedicated glassware
- Capable of 50-75L
- Expansion capacity (150L)
- 10s to few 100s of kilos of API
- Cryogenic (down to -78°C)
- Max temperature 265°C

### O Cleaning

- Dedicated glassware
- Cleaning SOPs
  - Rinse release
    - Depyrogenated
  - Swab-released
- Cleaning Validation

### **Current APIs**

- Cisplatin
- Carboplatin
- Dexmedetomidine HCI\*
- Isoproterenol HCI\*
- Selenious Acid\*\*
- Cupric Sulfate Pentahydrate
- Chromic Chloride
- Pamidronic Acid\*
- Sodium Sulfide Nonahydrate

### **Available Booklets**











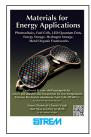












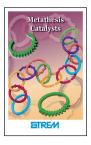


















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**Ascensus Specialties** 

Strem Chemicals, Inc. 7 Mulliken Way Newburyport, MA 01950-4098 U.S.A.

Tel.: (978) 499-1600 Fax: (978) 465-3104

(Toll-free numbers below US & Canada only) Tel.: (800) 647-8736 Fax: (800) 517-8736

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