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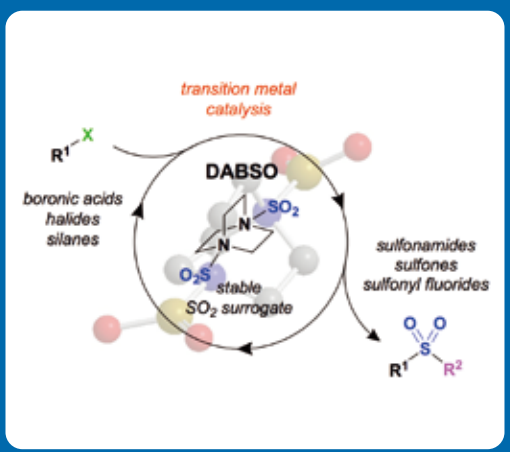

目次

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年頭に寄せて

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寄稿論文

DABCO-*bis*(sulfur dioxide), DABSO, as a Source of Sulfur Dioxide in Transition Metal-Catalyzed Reactions

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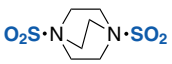
Abstract: The *bis*-adduct of DABCO with sulfur dioxide, DABSO, has been shown to function as an effective surrogate for gaseous sulfur dioxide. DABSO is a stable, solid reagent. The use of DABSO has allowed the first efficient transition metal-catalyzed cross-coupling type reactions of sulfur dioxide to be achieved. Early reactions employed palladium catalysts in combination with aryl iodides and *N*,*N*-dialkyl hydrazines, to deliver *N*-aminosulfonamides as products. More recently, alternative aryl substrates such as aryl bromides and aryl boronic acids have been employed, and products such as sulfones and sulfonyl fluorides can now be prepared in an efficient manner. In addition to palladium, reactions have been reported that use copper, cobalt and iridium catalysts. This review considers the catalytic reactions that have been developed using DABSO as a reagent, and is structured by type of catalyst used, and further by the type of product obtained.

Keywords: sulfur dioxide, catalysis, sulfonamide, sulfone, transition metal

1 Introduction

Sulfur dioxide has a long history of use in organic synthesis as both a reagent and solvent. Pericyclic reactions, including cheletropic additions and ene reactions, as well as the combination with preformed organometallic reagents such as organolithiums and Grignard reagents, are two examples of the transformations for which sulfur dioxide is well known.[1] Despite an extensive literature covering these and related reactions, there were very few examples in the literature of sulfur dioxide being used as a reagent in combination with transition metal catalysts.[2] Notwithstanding the lack of literature precedent, we were interested in the development of cross-coupling type reactions in which sulfur dioxide would be incorporated. Our key breakthrough was the discovery that the *bis*-adduct of DABCO with sulfur dioxide, which we have named DABSO, functions as an effective surrogate[3] reagent for sulfur dioxide gas (Figure 1).[4] DABSO is a colorless crystalline solid that decomposes at 200 °C (DSC). DABSO is air stable and easily handled. It is usually stored under inert gas at room temperature.[5] Although we have shown that DABSO can function as a SO_2-surrogate in combination with preformed organometallics,[6] the focus of this review is the use of DABSO in transition metal catalysis.



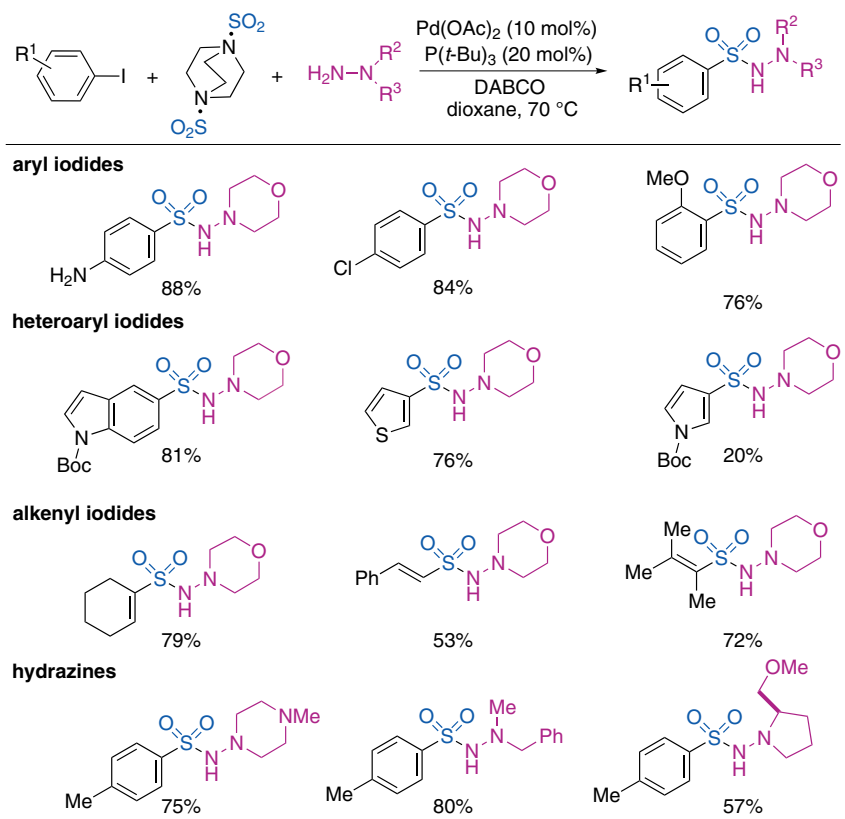
(**DABSO**) DSC 200 °C
DABCO-*bis*-(sulfur dioxide)

Figure 1.

2 Palladium-Catalyzed Reactions

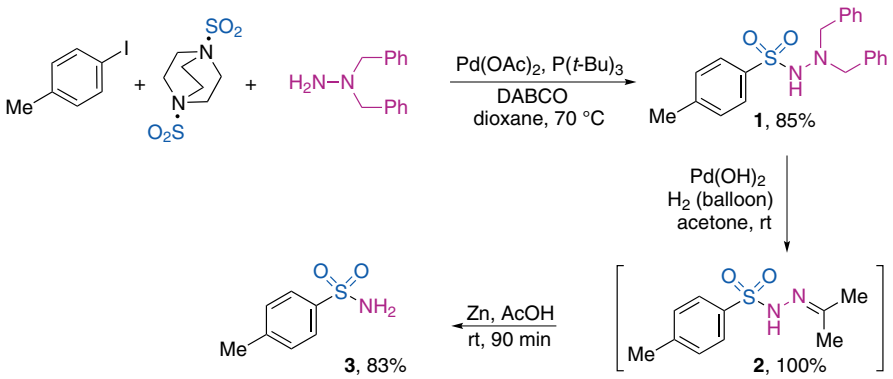
2-1. Sulfonamide Synthesis

The sulfonamide functional group features in a wide range of pharmaceuticals and agrochemicals, and as such these important motifs were the first class of compounds that we targeted. The successful chemistry allowed the union of aryl iodides, sulfur dioxide (provided from the reagent DABSO) and *N*,*N*-dialkylhydrazines, using a palladium(0) catalyst, to provide *N*-aminosulfonamides as the products.[7] Selected examples are shown in Scheme 1; variation of the aryl iodide component was readily achieved, and a broad range of functional groups could be tolerated. Heteroaryl iodides were also competent substrates, as were alkenyl iodides. The *N*-nucleophile was limited to *N*,*N*-dialkylhydrazines, but variation of the alkyl substituents of the hydrazine was possible. All of the reactions were achieved using a catalyst generated from P(*t*-Bu)$_3$ (used as its HBF_4 salt)[8] and $Pd(OAc)_2$. The majority of reactions required only 0.6 equivalents of DABSO, demonstrating the excellent uptake of SO_2 during these reactions. Although this chemistry is limited in the scope of *N*-nucleophiles that can be employed, it does represent the first example of an efficient three-component cross-coupling type reaction that employs sulfur dioxide.



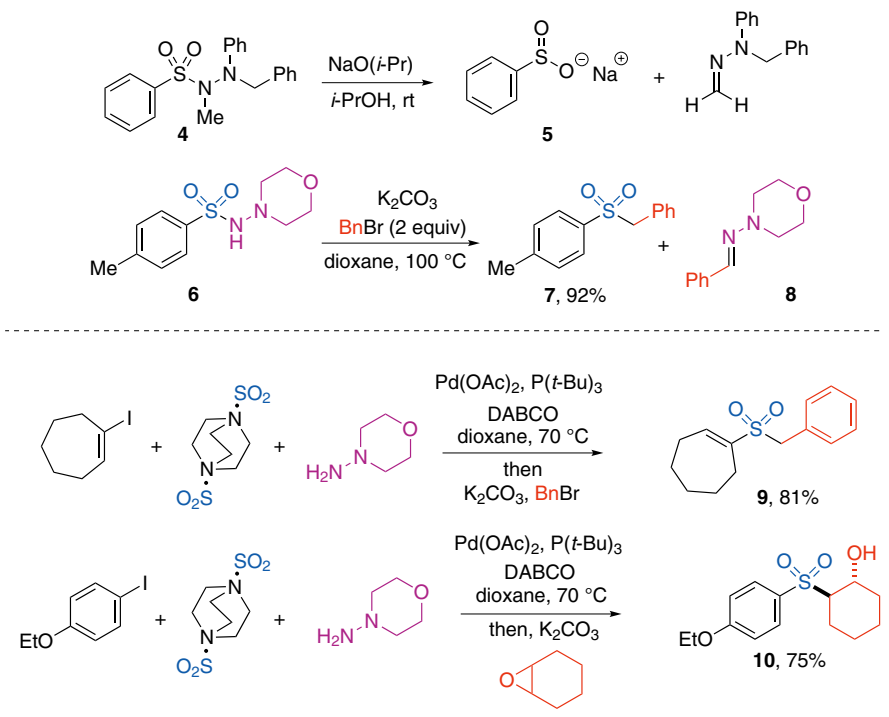
Scheme 1. Palladium-catalyzed *N*-aminosulfonamide synthesis from aryl iodides, DABSO and *N*,*N*-dialkylhydrazines

Access to the parent sulfonamides using this chemistry was possible if *N*,*N*-dibenzylhydrazine was used as the *N*-nucleophile. The initially formed *N*-aminosulfonamide **1** was treated with hydrogen gas over a $Pd(OH)_2$ catalyst in acetone as solvent. The *in situ* generated hydrazone **2** was then treated with zinc in acetic acid to provide the parent sulfonamide **3**.[7b]



Scheme 2. Parent sulfonamide synthesis using *N*,*N*-dibenzylhydrazine as the nucleophile

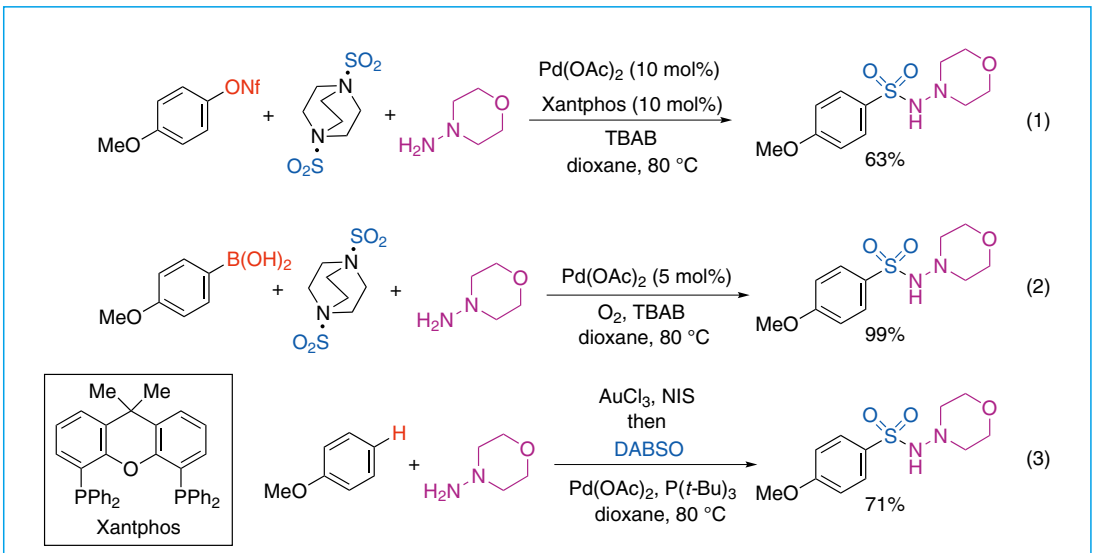
Literature dating from 1957 had shown that *N*-aminosulfonamides can function as precursors to sulfinate salts. For example, when *N*,*N*,*N*-trialkylaminosulfonamide **4** was treated with an alkoxide base in isopropanol, sulfinate **5** was generated in good yield (Scheme 3).[9]



Scheme 3. Exploiting *N*-aminosulfonamides synthesis for sulfone preparation

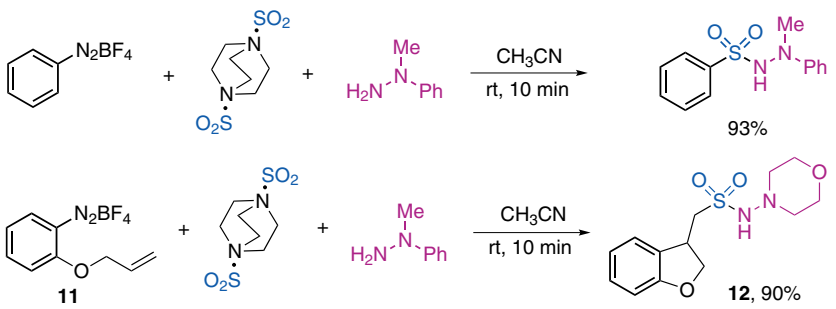
We were able to develop a version of this process that was applicable to the type of aminosulfonamides produced in Scheme 2. For example, following treatment of aminosulfonamide **6** with K_2CO_3 and two equivalents of BnBr, sulfone **7** was obtained in 92% yield.[10] The reactions proceed by initial alkylation of the aminosulfonamide *N*-atom, followed by deprotonation and elimination to generate an intermediate sulfinate and hydrazone byproduct **8**; the sulfinate salt reacts with the excess benzyl bromide to provide the desired sulfone. This protocol could be extended to a one-pot process whereby the palladium-catalysed aminosulfonamide synthesis was combined with sulfinate formation/arylation. For example, an alkenyl iodide substrate provided sulfone **9**, while an aryl iodide substrate, in combination with an epoxide electrophile for the second step, provide β-hydroxysulfone **10**.

The Wu group at Fudan University has made significant contributions to the use of DABSO in synthesis. One of their first contributions was to show that aryl nonaflates (perfluorobutanesulfonates) could be used as substrates in place of aryl iodides in the synthesis *N*-aminosulfonamides.[11] The reactions used a modified catalyst system in which Xantphos was employed as the supporting ligand (Scheme 4, eq 1). This is an important extension as it allows phenols to be considered as substrates for these reactions. The same group also demonstrated that aryl boronic acids could be employed as substrates (Scheme 4, eq 2).[12] This change to boronic acid substrates required the use of a Pd(II) catalyst and an oxidant, which was provided by an oxygen atmosphere. No phosphine ligand was required for these transformations. The Wu group demonstrated that an initial gold-catalyzed iodination, generating the iodoarene *in situ*, could be combined with the palladium-catayzed aminosufonylation, allowing simple arenes to function as the starting materials (Scheme 4, eq 3).[13] It should be noted that this is a two-step, one-pot process. All three of the transformations shown in Scheme 3, in which the arene starting material is varied, are still limited to the use of *N*,*N*-dialkylhydrazines as the *N*-nucleophiles. The Wu group has also introduced the use of potassium metabisulfate ($K_2S_2O_5$) as an alternative sulfur dioxide surrogate.[14] In their original report, aryl iodides were combined with $K_2S_2O_5$ and *N*,*N*-dialkylhydrazines using Pd(0) catalysis, to provide the expected *N*-aminosulfonamides.



Scheme 4. Variation of the arene starting material in the palladium-catalyzed synthesis of *N*-aminosulfonamides

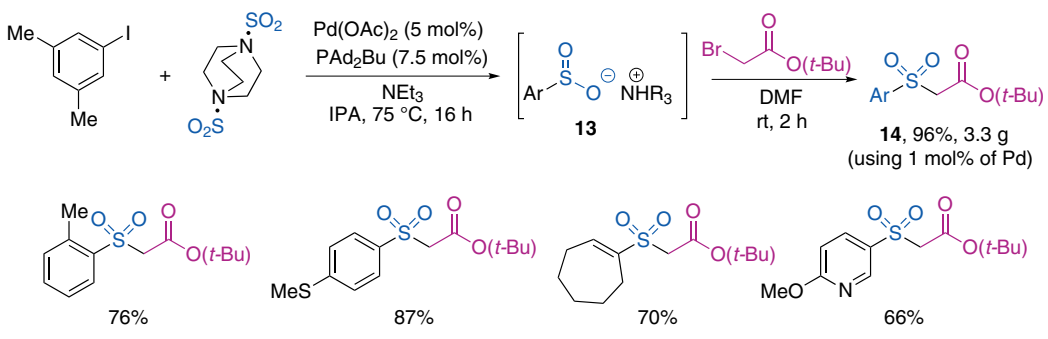
The Wu group have been pioneers of the use of DABSO as a source of sulfur dioxide in radical-based processes, often under metal-free conditions. Although these reactions are beyond the scope of this review, their lead publication in this area is shown in Scheme 5.[15] The reactions employ aryl diazonium salts as aryl radical precursors, which can be combined with DABSO and an *N*,*N*-dialkylhydrazine to deliver *N*-aminosulfonamides as products. Importantly, these reactions are conducted at room temperature. A control reaction, using a substrate that features a tethered alkene (**11**), proceeded *via* cyclisation, ultimately providing *N*-aminosulfonamide **12** as the product, thus confirming the presence of radical intermediates.



Scheme 5. Radical based routes to *N*-aminosulfonamides

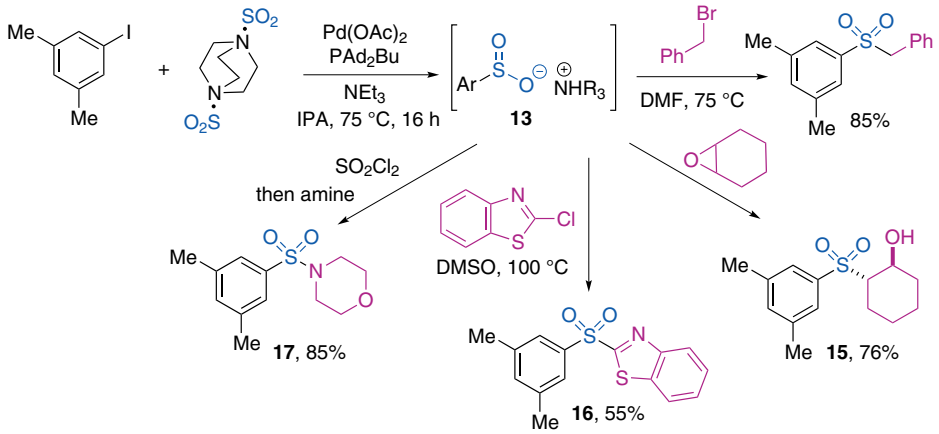
2-2. Sulfinate Formation

The palladium-catalyzed preparation of *N*-aminosulfonamides, introduced in Scheme 2, established that SO_2 could be introduced in cross-coupling type reactions. However, the limitations with respect to the *N*-nucleophile result in the formation of specialized, not generally useful, products. In order to deliver a reaction of more utility we targeted the direct formation of sulfinate salts. This was achieved by replacing the *N*-nucleophile used in Scheme 2 with a hydride source, with the use of isopropanol being most effective; the general process is shown in Scheme 6.[16] Aryl iodides are combined with DABSO in isopropanol (this serves as both solvent and hydride source) using a Pd(0) catalyst generated from $Pd(OAc)_2$ and PAd_2Bu, with triethylamine as a base. The resulting sulfinates (**13**), can then be combined with a broad range of electrophiles, for example an alkyl halide, to provide the corresponding sulfone (**14**). When performed on gram scale the catalyst loading could be reduced to 1 mol%. Good variation of the aryl iodide substrate was possible, and alkenyl as well as heteroaryl variants could also be used (Scheme 6). A related reaction, which uses $K_2S_2O_5$ as the SO_2 source and sodium formate as the reductant, has been reported by scientists at Pfizer in the US.[17]



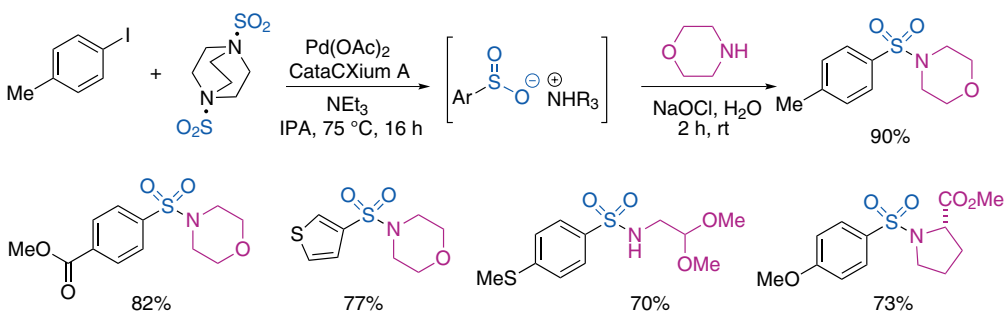
Scheme 6. Palladium-catalyzed sulfinate formation

The utility of sulfinate salts is that they can be combined with a variety of alternative electrophiles to provide a correspondingly broad range of products. Selected examples of this approach, using sulfinate **13**, are shown in Scheme 7; the use of an epoxide provides β-hydroxy sulfone **15**, nucleophilic aromatic substitution delivers aryl-heteroaryl sulfone **16**, and chlorination followed by amine addition provides sulfonamide **17**.[16]



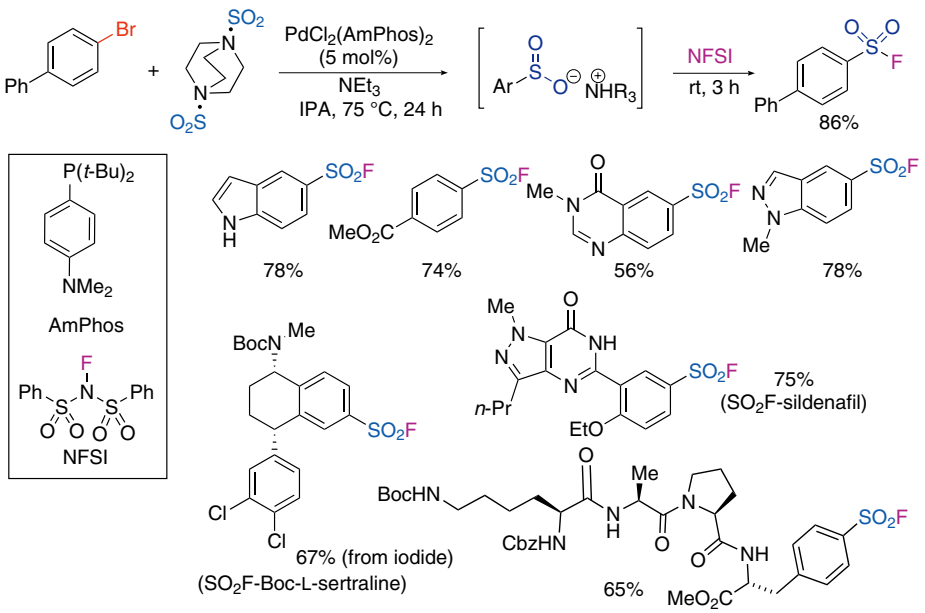
Scheme 7. Catalytically generated sulfinates as versatile intermediates in synthesis

Given the prevalence of sulfonamides in medicinal and agrochemistry, we wanted to adapt the sulfinate synthesis described above to provide a simple and efficient entry to these important functional groups. Accordingly, we adapted our earlier chemistry based on the use of pre-formed organometallic reagents,[6d] and were able to show that treatment of the *in situ* catalytically generated sulfinate intermediates with an aqueous solution of the relevant amine and bleach (NaOCl), provides the corresponding sulfonamides in high yield (Scheme 8).[18] The reactions proceed *via in situ* formation of the *N*-chloroamines. Broad variation of both the aryl iodide and amine component was possible, including the use of heteroaryl iodides, and well as amines bearing acid-sensitive functional groups. Amino acids could also be employed, and the corresponding sulfonamides were obtained with no erosion of enantiomeric excess.



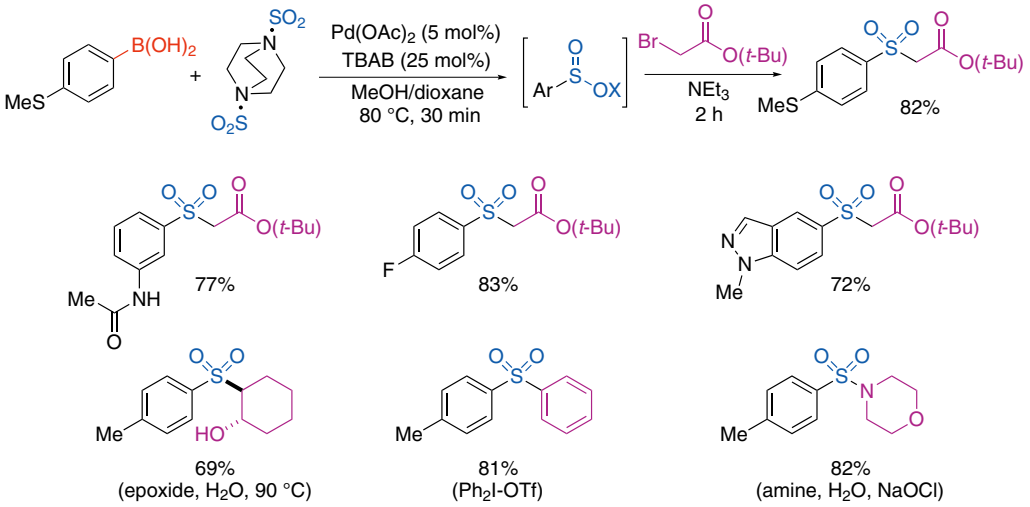
Scheme 8. Sulfonamide synthesis using *in situ* generated *N*-chloroamines

The sulfinate syntheses shown in Schemes 6, 7, and 8 all employ (hetero)aryl iodide substrates. A re-evaluation of phosphine ligands allowed a new catalyst system, this time featuring the ligand AmPhos, to be used in combination with (hetero)aryl bromide substrates.[19] In a collaboration with scientists at Pfizer, this chemistry was showcased in the synthesis of a range of sulfonyl fluorides (Scheme 9). The *in situ* generated sulfinates are treated with NFSI, which is a source of F^+, and delivered the corresponding sulfonyl fluorides in good yields. Good variation of the aryl bromide was possible. Sulfonyl fluorides are important molecules for the design of covalent inhibitors, and as probe reagents in chemical biology applications; Scheme 9 also shows the preparation of several sulfonyl fluorides from halogenated pharmaceuticals, or pharmaceutical fragments that were prepared using this methodology.



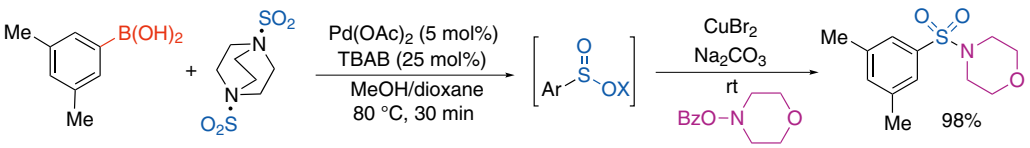
Scheme 9. The palladium-catalyzed preparation of sulfonyl fluorides from aryl halides

To complement the Pd(0)-catalyzed sulfonylation procedures described above, we have also developed a Pd(II)-catalyzed protocol that employs aryl boronic acids as the substrates (Scheme 10).[20] The reaction conditions consist of $Pd(OAc)_2$ with tetrabutylammonium bromide (TBAB) in a methanol/dioxane solvent mixture at 80 °C. No phosphine ligands were required in the reactions. Complete conversion to sulfinate was achieved after just 30 minutes, at which point an electrophile could be added. As shown in Scheme 10, good variation of the starting aryl boronic acid, including heterocyclic variants was possible, and a variety of electrophiles could be introduced in the second step, allowing access to various sulfones as well as sulfonamides. A related transformation, which uses $K_2S_2O_5$ as the SO_2 source, has been reported by scientists at Pfizer in the US.[21]



Scheme 10. The palladium(II)-catalyzed preparation of sulfinates from aryl boronic acids, and onwards reactivity

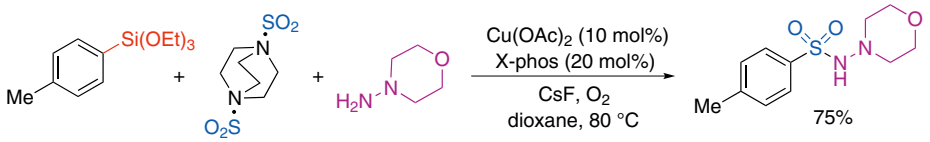
The sulfonamide shown in Scheme 10 was prepared by the addition of an aqueous solution of the amine and NaOCl to the *in situ* generated sulfinate. The reaction proceeds *via* the *in situ* formation of the *N*-chloroamine which functions as an electrophilic amine component. Similar reactivity has been reported by Tu and co-workers, who used preformed *N*-benzoyloxyamines as electrophilic amine components in combination with a Cu(II) catalyst (Scheme 11).[22]



Scheme 11. The palladium(II)-catalyzed preparation of sulfinates and onwards to sulfonamides using *N*-benzoyloxyamines

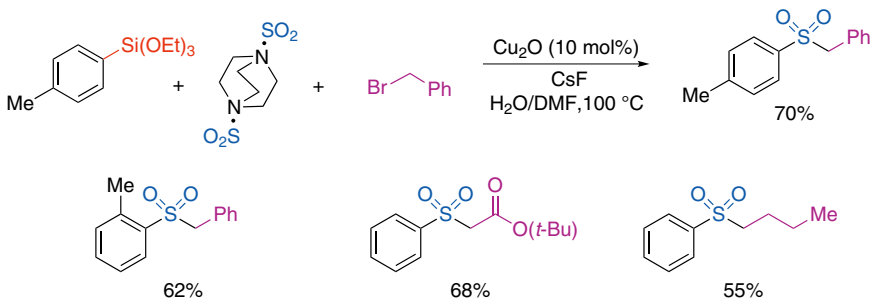
3 Copper-Catalyzed Reactions

The Wang group were the first to report a copper-catalyzed process involving DABSO. They developed a variant of the aminosulfonamide synthesis shown in Scheme 1, but employed aryl triethoxysilanes as the substrates in combination with a Cu(II)-catalyst (Scheme 12).[23] $Cu(OAc)_2$ was employed as the catalyst, along with an oxygen atmosphere. The reactions were tolerant of a broad range of silanes, but the commercial availability of these reagents is limited. As with the related palladium-catalyzed reactions, the *N*-nucleophile is again limited to *N*,*N*-dialkylhydrazines.



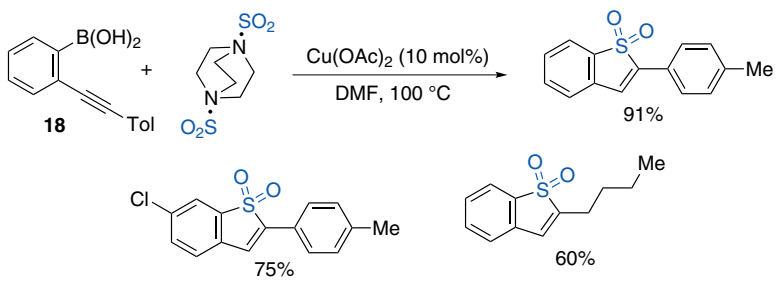
Scheme 12. The copper(II)-catalyzed preparation of *N*-aminosulfonamides using aryl triethoxysilanes

The Wu group employed the same class of aryl substrate in a copper-catalyzed sulfone synthesis.[24] Their method involved the combination of aryl triethoxysilanes, DABSO, and an alkyl halide using Cu_2O as catalyst (Scheme 13).



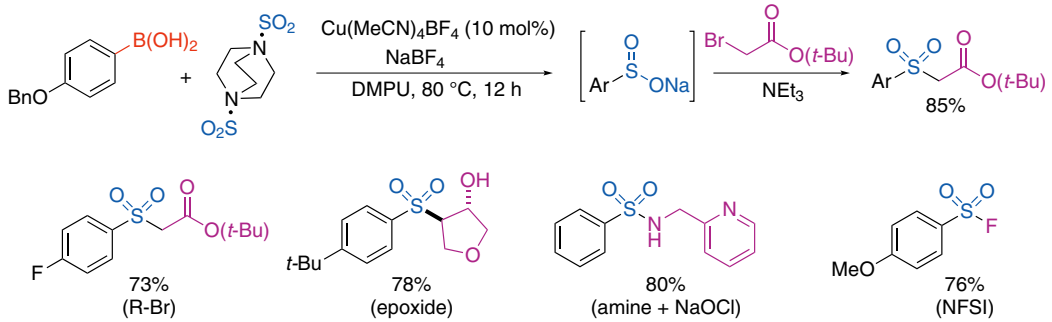
Scheme 13. The copper-catalyzed preparation of sulfones using aryl triethoxysilanes

The same group reported a copper-catalyzed preparation of benzothiophene-1,1-dioxides (Scheme 14). The chemistry involved the combination of *o*-alkynylboronic acids (**18**), with DABSO and a Cu(II) catalyst.[25] Reasonable variation of the substrate was possible, delivering the expected heterocycles in moderate to good yields.



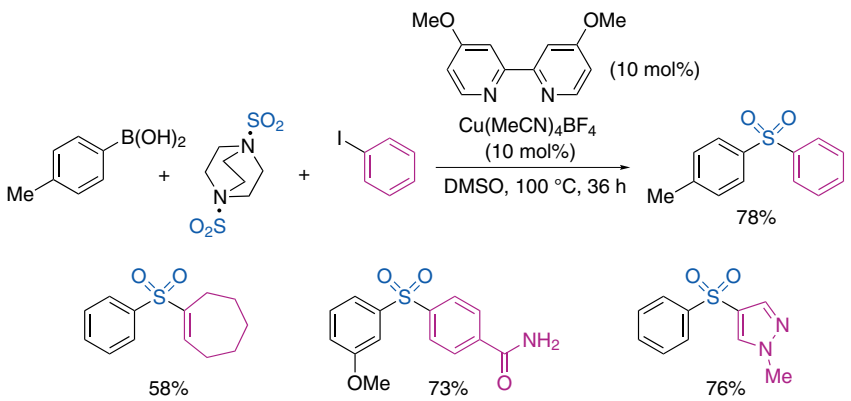
Scheme 14. The copper-catalyzed synthesis of benzothiophene-1,1-dioxides

Our laboratory has reported a Cu(I)-catalyzed synthesis of aryl sulfinates using aryl boronic acids as substrates (Scheme 15).[26] The chemistry employs the commercially available copper catalyst $Cu(MeCN)_4BF_4$ and relies on a 12 hour reaction to achieve complete sulfinate formation. Addition of a variety of electrophiles is possible, trapping the sulfinate, and providing sulfones, sulfonamides, and sulfonyl fluorides. This chemistry provides a copper variant of the palladium-catalyzed reactions presented in Scheme 10.



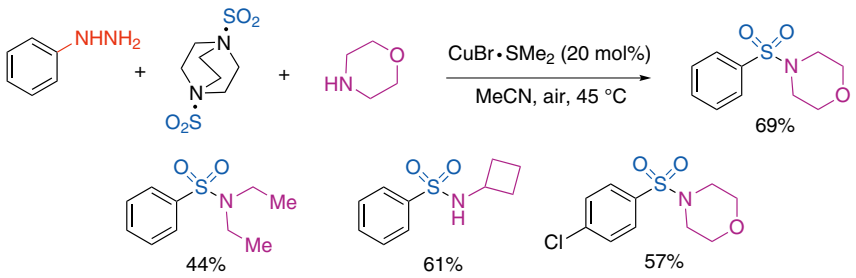
Scheme 15. The copper(I)-catalyzed sulfinate formation, and onwards to sulfones, sulfonamides and sulfonyl fluorides

Our laboratory was also able to exploit copper-catalysis in developing the first examples of a sulfonylative Suzuki-Miyaura cross-coupling (Scheme 16).[26] The reactions allowed the direct combination of aryl boronic acids, aryl halides and sulfur dioxide (provided from DABSO), and employ the same commercial copper catalyst, this time partnered with the indicated bipyridine ligand. Good variation of both the aryl iodide and aryl boronic acid was possible, including the use of heteroaryl variants, as well as alkenyl examples. This chemistry represents the first sulfonylative variant of any classic cross-coupling process.



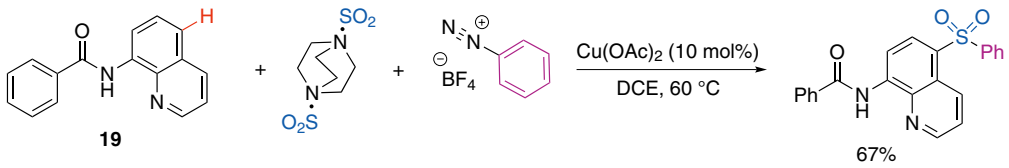
Scheme 16. The copper(I)-catalyzed sulfonylative Suzuki-Miyaura cross-coupling

A copper-catalyzed direct sulfonamide synthesis has also been reported, and involves the coupling of aryl hydrazines, sulfur dioxide (from DABSO), and amines, using a CuBr catalyst and an air atmosphere (Scheme 17).[27] The chemistry involves the oxidative conversion of the aryl hydrazines to aryl radicals. This is a rare example of a direct sulfonamide synthesis, but is limited by the need to employ aryl hydrazines as the substrates.



Scheme 17. The copper(I)-catalyzed sulfonamide synthesis employing aryl hydrazine substrates

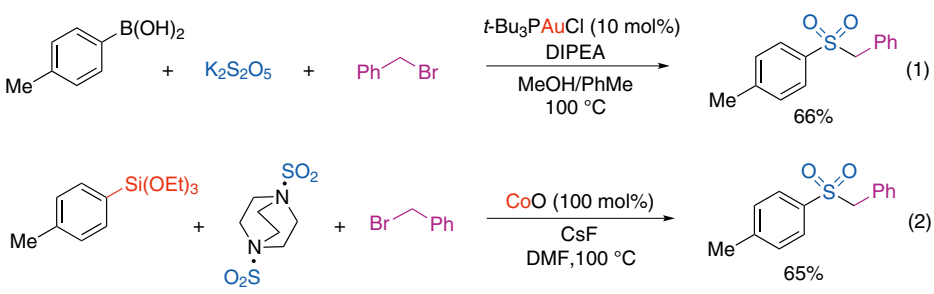
The final copper-catalyzed DABSO-based reaction we will consider is a recent report from the Wu group, and involves the sulfonylation of an aryl C-H bond (Scheme 18).[28] The chemistry is radical based, and involves the coupling of a quinolinyl-derived amide (**19**) with DABSO and an aryl diazonium salt using a Cu(II) catalyst. The targeted C-H functionalization products, diaryl sulfones, are obtained in moderate yields.



Scheme 18. The copper(II)-catalyzed C-H sulfonylation of 8-aminoquinoline amides

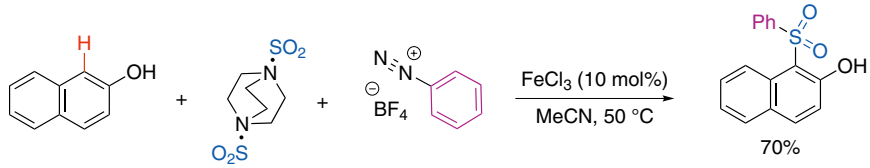
4 Miscellaneous Metal Catalysts

Although palladium and copper catalysts provide the majority of examples of DABSO, and alternative SO_2-surrogates, use in synthesis, there are a handful of reports that employ different metal catalysts. For example, The Toste group, in collaboration with scientists at Pfizer, have demonstrated that Au(I) complexes are effective catalysts for the addition of sulfur dioxide to aryl boronic acids.[29] They utilized this reactivity in a one-pot sulfone synthesis (Scheme 19, eq 1). Note, $K_2S_2O_5$ is used as the SO_2-source. Recently, a Au(I)-carbene complex has also been used in a closely related system.[30] The same overall transformation can also be promoted using a cobalt complex.[31] In this case, cobalt oxide is used in stoichiometric amounts, and promotes the union of aryl triethoxysilanes, DABSO and an alkyl halide (Scheme 19, eq 2).

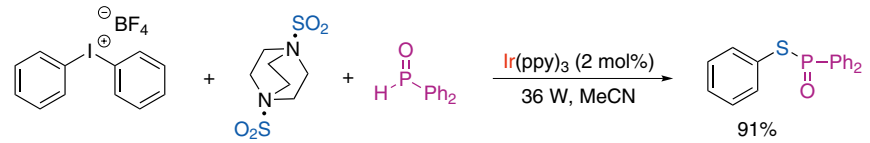


Scheme 19. Gold and cobalt mediated sulfone syntheses

The Wu group has reported a second aryl C-H sulfonylation protocol, this time employing an iron catalyst (Scheme 20).[32] This radical process combines 2-napthols, DABSO, and aryl diazoniums salts, and delivers diaryl sulfone products in good yields. A simple $FeCl_3$ catalyst is employed. The final transformation we will consider is a recent report from the Wu group concerning thiophosphate synthesis. Aryl iodonium salts are used as the substrates and are combined with DABSO and diphenylphosphine oxide, in the presence of an iridium photocatalyst (Scheme 21).[33] Irradiation with visible light results in formation of the thiophosphonate **20**. This is an unusual example of DABSO use in which the SO_2 is reduced during the transformations.



Scheme 20. Iron-catalyzed naphthol sulfonylation



Scheme 21. Iridium-catalyzed thiophosphonate synthesis

5 Conclusions

The advent of DABSO (and other reagents) as an effective surrogate for sulfur dioxide gas has allowed the development of a range of transition metal catalyzed reactions that result in sulfur dioxide incorporation. Although early examples deliver rather esoteric products, more recent reactions deliver synthetically useful products. Palladium and copper based catalysts dominate the reactions that have been reported, but recent advances suggest that alternative metals could provide useful, and different, reactivity.

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執筆者紹介

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Michael Willis is a Professor of Chemistry at the University of Oxford. He received his undergraduate education at Imperial College London, and his Ph.D. from the University of Cambridge working with Prof. Steven Ley. After a postdoctoral stay with Prof. David Evans at Harvard University, he was appointed to a lectureship at the University of Bath in November 1997. In January 2007 he moved to the University of Oxford, where he is now a Professor of Chemistry and a Fellow of Lincoln College. His group's research interests are based on the development and application of new catalytic processes for organic synthesis, with a particular interest in transition metal catalysis. His work has been recognized by the award of recent prizes, including the Royal Society of Chemistry's 2014 Catalysis in Organic Chemistry Award, and the 2015 Pfizer, AstraZeneca, Syngenta, Process Chemistry Research Award.

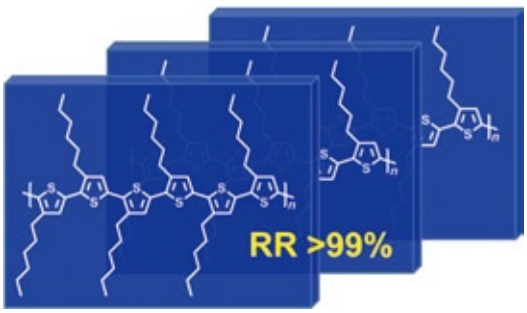
TCI 関連製品

B3960	DABSO [= Bis(sulfur Dioxide)-1,4-diazabicyclo[2.2.2]octane Adduct]			1g	4,200 円	5g	14,500 円
D0134	DABCO [= 1,4-Diazabicyclo[2.2.2]octane]	25g	2,200 円	100g	6,600 円	500g	14,200 円
P2480	Potassium Disulfite			25g	1,700 円	500g	2,900 円
T0054	TBAB (= Tetrabutylammonium Bromide)	25g	1,900 円	100g	5,000 円	500g	12,600 円
F0335	NFSI [= *N*-Fluorobenzenesulfonimide] [Fluorinating Reagent]			5g	8,300 円	25g	29,000 円
C2204	Cesium Fluoride			25g	5,700 円	100g	14,800 円
A1424	Palladium(II) Acetate			1g	8,600 円	5g	28,600 円
P2161	Palladium(II) Acetate (Purified)					1g	13,500 円
T2666	Tetrakis(acetonitrile)copper(I) Tetrafluoroborate	1g	3,200 円	5g	9,400 円	25g	32,900 円
C2346	Copper(II) Acetate Monohydrate			25g	1,800 円	500g	4,300 円
T1912	Tri-*tert*-butylphosphine					5g	35,800 円
B2709	Xantphos [= 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene]	1g	5,000 円	5g	17,500 円	25g	60,000 円
D4531	Amphos [= (4-Dimethylaminophenyl)di-*tert*-butylphosphine]			1g	9,800 円	5g	34,800 円
D5038	XPhos (= 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl)			1g	9,400 円	5g	33,000 円
D3886	4,4'-Dimethoxy-2,2'-bipyridyl			1g	7,200 円	5g	20,500 円
T1946	$Ir(ppy)_3$ [= Tris(2-phenylpyridinato)iridium(III)] (purified by sublimation)					200mg	43,500 円
P1528	Pearlman's Catalyst [= Palladium Hydroxide (contains Pd, PdO) on Carbon] (wetted with *ca.* 50% Water)			10g	19,100 円	50g	69,900 円

高位置規則性有機半導体ポリマー：P3HT

P2513 Poly(3-hexylthiophene-2,5-diyl) (Mn.=*ca.* 40,000) (regioregular) (1)
100mg 16,800円 500mg 58,800円

ポリ(3-ヘキシルチオフェン)（P3HT，**1**）は溶解性に優れた代表的な有機半導体ポリマーであり，有機エレクトロニクス分野で広く研究されています。エレクトロニクス材料のパフォーマンスはその材料の品質に大変敏感であり，中でもポリマーの純度や分子量は重要なファクターとなります。直接アリール化重合（DArP）[1,2]により合成された**1**は，位置規則性が高く，高純度で平均分子量・分子量分布の品質が安定している特徴があります。また，**1**は溶解性に優れており，塗布工程による有機薄膜太陽電池[3,4]，ペロブスカイト太陽電池[5]ならびに有機トランジスタ[6]の研究に有用です。



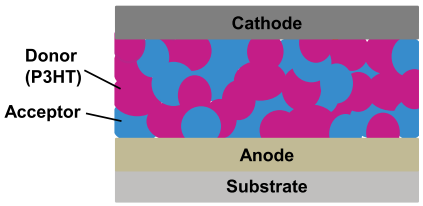


図1. 有機薄膜太陽電池（OPV）

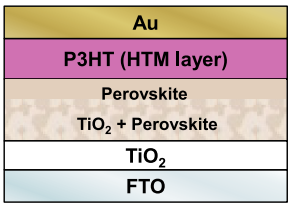


図2. ペロブスカイト太陽電池（PSC）

図3. 有機トランジスタ（OFET）

本製品は，京都大学化学研究所小澤文幸教授との共同開発により試薬化されました。

文献

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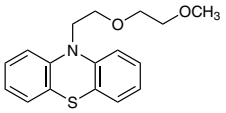
高い電流密度をもつ非水系レドックスフロー電池材料：MEEPT

M3068 10-[2-(2-Methoxyethoxy)ethyl]-10*H*-phenothiazine (1)　10g 19,500円



MEEPT (**1**)

Odom らが開発した 10-[2-(2-メトキシエトキシ)エチル]-10*H*-フェノチアジン（MEEPT，**1**）は，酸化還元活性部位としてフェノチアジン骨格と，溶解性を高めるアルコキシ基をもつことから，非水系レドックスフロー電池（RFB）の正極材料として注目されています。**1** は有機溶媒と任意の比率で混和し，高濃度の電解液を与えます。さらに，高い電流密度，長いサイクル特性を示すことが報告されており，非水系 RFB デバイスの開発に有用です[1]。

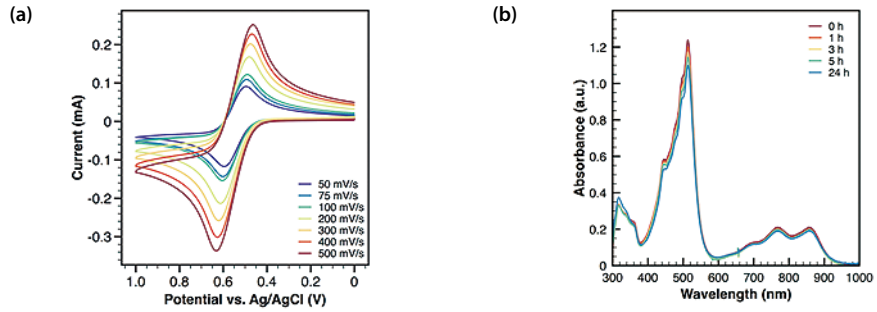


図 1. MEEPT/MEEPT$^+$ の電気化学的，分光学的性質

(a) Cyclic voltammogram of MEEPT at 10 mM in 0.1 M $TBAPF_6$ in DCM recorded at scan rates from 10 to 500 mV/s. (b) UV-vis spectra of MEEPT-$SbCl_6$ at 0.15 mM in acetonitrile for up to 24 h after dissolution. (These graphical materials were provided by Prof. Odom.)

文献

1) High current density, long duration cycling of soluble organic active species for non-aqueous redox flow batteries
J. D. Milshtein, A. P. Kaur, M. D. Casselman, J. A. Kowalski, S. Modekrutti, P. L. Zhang, N. H. Attanayake, C. F. Elliott, S. R. Parkin, C. Risko, F. R. Brushett, S. A. Odom, *Energy Environ. Sci.* **2016**, *9*, 3531.

関連製品

M1531	4-Methacryloyloxy-2,2,6,6-tetramethylpiperidine 1-Oxyl Free Radical	1g 6,400円	5g 22,100円
H0865	4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-Oxyl Free Radical (= TEMPOL)	5g 7,900円	25g 26,800円
B5642	Bis(2,2,6,6-tetramethyl-4-piperidyl-1-oxyl) Sebacate	1g 7,200円	5g 24,900円
A1343	4-Amino-2,2,6,6-tetramethylpiperidine 1-Oxyl Free Radical	1g 9,200円	5g 30,600円
V0137	2,2'-(2-Vinylanthracene-9,10-diylidene)dimalononitrile	1g 10,700円	5g 36,500円
V0136	2,2'-(2-Vinylanthracene-9,10-diylidene)bis(1,3-dithiole)	100mg 13,500円	500mg 47,100円

用語解説：レドックスフロー電池

レドックスフロー電池（RFB）は，充放電による劣化が少なく長寿命ですが，リチウムイオン電池に比べるとエネルギー密度が低く，小型化には向いていないため，大規模な設置型の蓄電池としての応用が検討されています。RFB 分野ではバナジウムイオンや水溶性の有機活物質を用いた水系 RFB の開発が盛んに行われています[1,2]。一方，溶媒を水から有機溶媒（アセトニトリル，カーボネートなど）に置き換えることで有機活物質の溶解度が上がり，エネルギー密度が上がるものと期待されています[3]。

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無水条件でペロブスカイト形成を可能にする酢酸鉛

L0315 Lead(II) Acetate [for Perovskite precursor] (1) 1g 2,200円 5g 5,500円 25g 16,500円

ペロブスカイト太陽電池は，高効率で低コストに作製可能な次世代の太陽電池として盛んに研究されています。この太陽電池の光吸収層は鉛ペロブスカイトであり，高品質なペロブスカイト前駆体を用いることで太陽電池の効率が上がり，再現性が得られることが知られています[1)]。最近，酢酸鉛をペロブスカイト前駆体に用いる例が報告されています。一般に，酢酸鉛三水和物が市販されていますが，極めて水分を低減した酢酸鉛（無水）（**1**）を用いることで無水条件でのペロブスカイト形成が可能です。また，酢酸鉛を用いることで，ペロブスカイトの速い結晶成長と，超平滑でピンホールフリーのペロブスカイト膜を形成することができます[2-7)]。

Scheme 1. 酢酸鉛から $CH_3NH_3PbI_3$ への生成機構[2)]

文献

1) Reproducible fabrication of efficient perovskite-based solar cells: X-ray crystallographic studies on the formation of $CH_3NH_3PbI_3$ layers
A. Wakamiya, M. Endo, T. Sasamori, N. Tokitoh, Y. Ogomi, S. Hayase, Y. Murata, *Chem. Lett.* **2014**, *43*, 711.
2) PCE >10%: Effect of different lead precursors on perovskite solar cell performance and stability
F. K. Aldibaja, L. Badia, E. Mas-Marzá, R. S. Sánchez, E. M. Barea, I. Mora-Sero, *J. Mater. Chem. A* **2015**, *3*, 9194.
3) PCE >17%: High performance perovskite solar cell *via* multi-cycle low temperature processing of lead acetate precursor solutions
T. Singh, T. Miyasaka, *Chem. Commun.* **2016**, *52*, 4784.
4) PCE 14%: Ultrasmooth organic–inorganic perovskite thin-film formation and crystallization for efficient planar heterojunction solar cells
W. Zhang, M. Saliba, D. T. Moore, S. K. Pathak, M. T. Hörantner, T. Stergiopoulos, S. D. Stranks, G. E. Eperon, J. A. Alexander-Webber, A. Abate, A. Sadhanala, S. Yao, Y. Chen, R. H. Friend, L. A. Estroff, U. Wiesner, H. J. Snaith, *Nat. Commun.* **2015**, *6*, 6142.
5) PCE >18%: High-performance inverted planar heterojunction perovskite solar cells based on lead acetate precursor with efficiency exceeding 18%
L. Zhao, D. Luo, J. Wu, Q. Hu, W. Zhang, K. Chen, T. Liu, Y. Liu, Y. Zhang, F. Liu, T. P. Russell, H. J. Snaith, R. Zhu, Q. Gong, *Adv. Funct. Mater.* **2016**, *26*, 3508.
6) PCE >13%: Pinhole-free perovskite films for efficient solar modules
W. Qiu, T. Merckx, M. Jaysankar, C. Masse de la Huerta, L. Rakocevic, W. Zhang, U. W. Paetzold, R. Gehlhaar, L. Froyen, J. Poortmans, D. Cheyns, H. J. Snaith, P. Heremans, *Energy Environ. Sci.* **2016**, *9*, 484.
7) PCE >14%: Chlorine incorporation for enhanced performance of planar perovskite solar cell based on lead acetate precursor
J. Qing, H.-T. Chandran, Y.-H. Cheng, X.-K. Liu, H.-W. Li, S.-W. Tsang, M.-F. Lo, C.-S. Lee, *ACS Appl. Mater. Interfaces* **2015**, *7*, 23110.

関連製品

L0279	Lead(II) Iodide (99.99%, trace metals basis) [for Perovskite precursor]	1g	2,200円	5g	5,500円	25g	12,500円	100g	35,000円	1kg	250,000円
L0288	Lead(II) Bromide [for Perovskite precursor]	1g	2,800円	5g	9,500円	25g	35,100円				
L0291	Lead(II) Chloride (purified by sublimation) [for Perovskite precursor]	1g	8,000円	5g	28,000円						
L0292	Lead(II) Chloride [for Perovskite precursor]	1g	2,800円	5g	8,500円	25g	29,500円				
M2556	Methylamine Hydroiodide (MAI), (Water <100 ppm) [for Perovskite precursor]	1g	3,400円	5g	8,500円	25g	21,300円	100g	57,500円		
F0974	Formamidine Hydroiodide (FAI), (Water <100 ppm) [for Perovskite precursor]	1g	8,400円	5g	29,500円	25g	98,000円				

ELISA 用調製済み基質溶液

N1109 4-Nitrophenyl Phosphate (Ready-to-use solution) [for ELISA] (1)

100mL 10,000 円

1 は, リン酸4-ニトロフェニル(pNPP)を含む ELISA 用調製済み溶液です。**1** をアルカリフォスファターゼと反応させると可溶性の黄色物質を生じます。これにより，反応を水酸化ナトリウム水溶液で停止した後，生成物を 405 nm の吸光度で測定することが可能です。

使用方法：96 ウェルプレートを用いた方法を示します。

1. **1** を室温に戻し，軽く混ぜる。
2. **1** を各ウェルに 100 μL ずつ加える。
3. 室温で 30 分間反応させる。
4. 100 μL の 1 mol/L 水酸化ナトリウム水溶液を加え反応を停止させる。
5. 反応停止から 1 時間以内に 405 nm の吸光度を測定する。

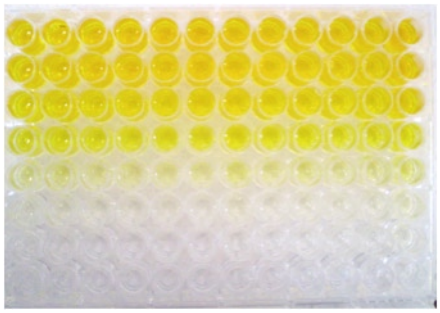

図 1. 96 ウェルプレートを用いた使用例

文献
1) A. Voller, D. E. Bidwell, A. Bartlett, *Bull. World Health Organ.* **1976**, *53*, 55.

関連製品

D4005 Disodium 4-Nitrophenyl Phosphate Hexahydrate [for Biochemical Research] 1g 2,500 円 5g 7,500 円
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αGal エピトープ（Galα1-3Gal）を検出可能な抗 αGal ポリクローナル抗体

A3123 Anti-αGal Polyclonal Antibody (Chicken) (1) 1vial 50,000 円

ヒト生体内には自然抗体として抗αGal 抗体（anti-αGal antibody）が存在します。この抗体がブタ移植片細胞表面等に発現している αGal 抗原（αGal エピトープ）を認識し，反応することが異種移植片生着の大きな障壁になっていることがわかっています。近年，再生医療用の細胞加工品や抗体医薬品にこの αGal エピトープが含まれることが課題となっており，αGal エピトープの存在を迅速に検出することは非常に重要なテクノロジーとなっています。

抗αGal ポリクローナル抗体（**1**）は，抗αGal モノクローナル抗体と同程度の高い特異性を持ち，α1-3Gal 構造を特異的に認識します（図 1）。

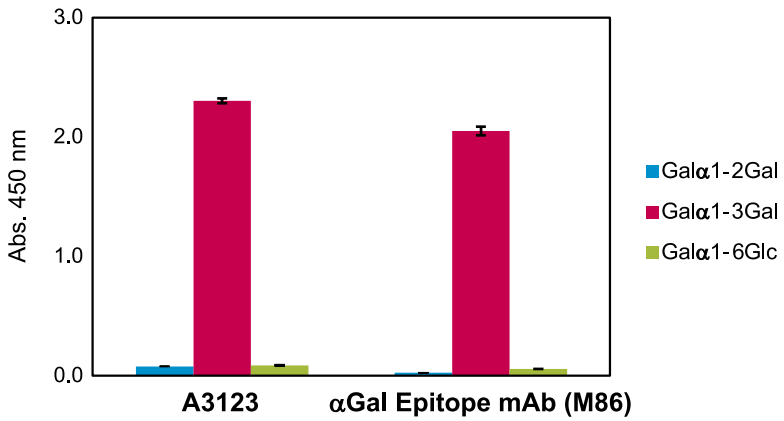

図 1. 抗αGal ポリクローナル抗体による α1-3Gal 構造の特異的な認識
ELISA プレートに各糖鎖をコートし，抗αGal 抗体を反応させた後，二次抗体を用いて検出を行った。

本製品は試薬であり，試験・研究用のみにご利用ください。

関連製品

A3144	Anti-αGal Polyclonal Antibody Biotin Conjugate	1vial 75,000 円
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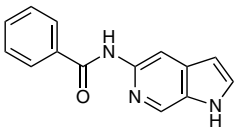
O0490 OAC1 (1) 10mg 20,000 円 50mg 60,000 円



1

OAC1（**1**）は，小分子ライブラリーのハイスループットスクリーニングにより OCT4 活性化化合物として同定されました[1]。**1** は人工多能性幹細胞（iPS 細胞）のリプログラムを増強します。さらに **1** は，マウス繊維芽細胞の機能性アストロサイトへの直接的なリプログラムに使用されました[2]。

1 はまた，ヒト臍帯血由来造血幹細胞と前駆細胞の *ex vivo* の増幅も増強します[3]。**1** による増幅にはホメオボックスタンパク質 HOXB4 が必須の成分です。

本製品は試薬であり，試験・研究用のみにご利用ください。

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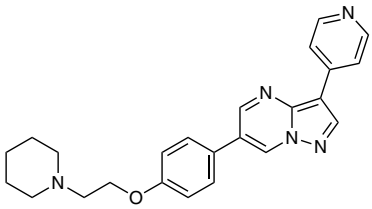
1) W. Li, E. Tian, Z.-X. Chen, G. Sun, P. Ye, S. Yang, D. Lu, J. Xie, T.-V. Ho, W. M. Tsark, C. Wang, D. A. Horne, A. D. Riggs, M. L. R. Yip, Y. Shi, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 20853.
2) E. Tian, G. Sun, G. Sun, J. Chao, P. Ye, C. Warden, A. D. Riggs, Y. Shi, *Cell Rep.* **2016**, *16*, 781.
3) X. Huang, M.-R. Lee, S. Cooper, G. Hangoc, K.-S. Hong, H.-M. Chung, H. E. Broxmeyer, *Leukemia* **2016**, *30*, 144.

AMP 活性化プロテインキナーゼ（AMPK）阻害剤

D5394 Dorsomorphin (1) 10mg 10,300 円 50mg 35,900 円



1

ドルソモルヒン（**1**）は AMP 活性化プロテインキナーゼ（AMPK）の阻害剤です[1]。AMPK は Ki = 109 nM で **1** によって阻害されます。一方，**1** は構造的に関連したキナーゼである脾臓チロシンキナーゼ（SYK）やゼータ鎖関連プロテインキナーゼ（ZAPK），プロテインキナーゼ A（PKA），プロテインキナーゼ Cθ（PKCθ），ヤーヌスキナーゼ（JAK）に対し，有意な阻害を示しません。

1 はまた，骨形成タンパク質（BMP）シグナルを阻害します[2]。**1** はヒト胚性幹細胞（hESCs）の自己複製を促進します[3]。興味深いことに，**1** はこの自己複製を長期にわたり（5 回以上の継代）維持します。

本製品は試薬であり，試験・研究用のみにご利用ください。

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1) G. Zhou, R. Myers, Y. Li, Y. Chen, X. Shen, J. Fenyk-Melody, M. Wu, J. Ventre, T. Doebber, N. Fujii, N. Musi, M. F. Hirshman, L. J. Goodyear, D. E. Moller, *J. Clin. Invest.* **2001**, *108*, 1167.
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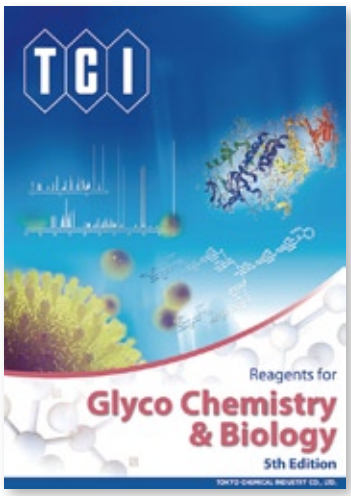

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