Homogeneous Catalysis

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Diaryl Sulfoxides from Aryl Benzyl Sulfoxides: A Single Palladium-Catalyzed Triple Relay Process**

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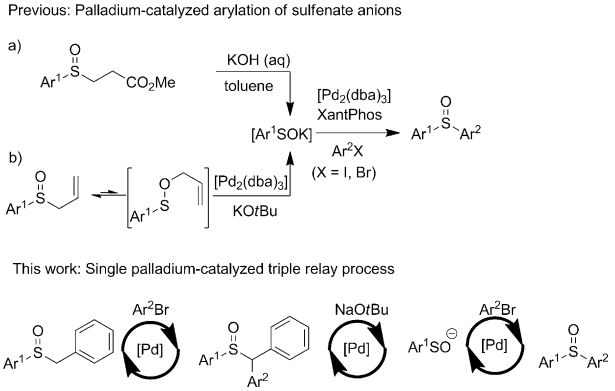
Abstract: *A novel approach to produce diaryl sulfoxides from aryl benzyl sulfoxides is reported. Optimization of the reaction conditions was performed using high-throughput experimentation techniques. The [Pd(dba)$_2$]/NiXantPhos catalyst system successfully promotes a triple relay process involving sulfoxide α-arylation, C–S bond cleavage, and C–S bond formation. The byproduct benzophenone is formed by an additional palladium-catalyzed process. It is noteworthy that palladium-catalyzed benzylative C–S bond cleavage of sulfoxides is unprecedented. A wide range of aryl benzyl sulfoxides, as well as alkyl benzyl sulfoxides with various (hetero)aryl bromides were employed in the triple relay process in good to excellent yields (85–99%). Moreover, aryl methyl sulfoxides, dibenzyl sulfoxides, and dimethylsulfoxide could be utilized to generate diaryl sulfoxides involving multiple catalytic cycles by a single catalyst.*



Scheme 1. Synthetic approaches to diaryl sulfoxides. dba = dibenzylideneacetone.

Sulfoxides are widely occurring in natural products,[1] synthetic bioactive compounds,[2] and materials.[3] They are also very important structural motifs in marketed therapeutics, such as Nexium for heartburn and esophagitis,[4a] and Provigil for narcolepsy.[4b] Furthermore, in recent years, sulfoxides have attracted attention as ligands in catalysis.[5] Despite the importance of sulfoxides, rapid syntheses of diversified diaryl sulfoxides remains challenging.

Two classic methods to generate diaryl sulfoxides are the oxidation of sulfides[6] and the nucleophilic substitution of electrophilic sulfoxide derivatives.[7] Madec, Poli, and coworkers reported the preparation of aryl sulfoxides by the palladium-catalyzed arylation of sulfenate anions with aryl iodides and bromides (Scheme 1 a,b).[8] In the presence of 20 equivalents of KOH, sulfenate anions could be generated from the retro-Michael reaction of β-sulfinyl esters (Scheme 1 a).[8a,b] In a second report, a palladium-catalyzed C–O bond cleavage of allylic sulfenate esters by a Mislow–Braverman–Evans rearrangement of the allylic sulfoxides was described (Scheme 1 b).[8c] Subsequently, the sulfenate anions were arylated with aryl iodides or bromides to yield diaryl sulfoxides. The substrate scope of these reactions is narrow.

Herein, we report a general, high-yielding method for the synthesis of diaryl sulfoxides. Remarkably, mechanistic studies reveal that a single palladium catalyst promotes at least three distinct reactions in this transformation (Scheme 1).[9]

We recently reported the palladium-catalyzed functionalization of weakly acidic sp^3-hybridized C–H bonds (pK_a values 28–35 in DMSO) by a deprotonative cross-coupling process (DCCP). Using this approach, we developed coupling protocols for diarylmethanes,[10] sulfoxides,[11] sulfones,[12] amides,[13] and chromium-activated benzylic amines (to produce enantioenriched diarylmethylamines).[14] During our study on the α-arylation of sulfoxides using the ligand **L1**,[15] we noticed that a diaryl sulfoxide by-product (**3a**) was generated in up to 20% yield from benzyl phenyl sulfoxide (**1a**) with 4-*tert*-butyl bromobenzene (**2a**) [10 mol% Pd(OAc)$_2$, 15 mol% **L1**, 3 equiv LiO*t*Bu, in cyclopentyl methyl ether (CPME) at 110°C for 12 h; Table 1, entry 1]. We initiated the optimization by performing a ligand screen using the reaction conditions described in Table 1. Of the 112 sterically and electronically diverse mono- and bidentate phosphines examined, two classic ligands [SPhos (**L2**) and DavePhos (**L3**)] along with NiXantPhos (**L4**)[16] outperformed **L1** (Table 1). On a laboratory scale, the yields of **3a** with SPhos, DavePhos, and NiXantPhos were 25%, 33%, and 22%, respectively (Table 1, entry 1 versus entries 2–4). Because the role of the base is crucial to DCCP reactions,

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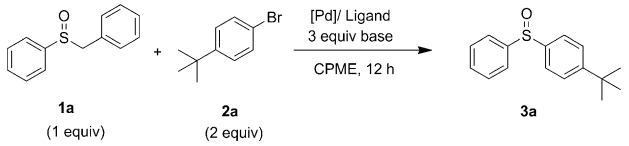
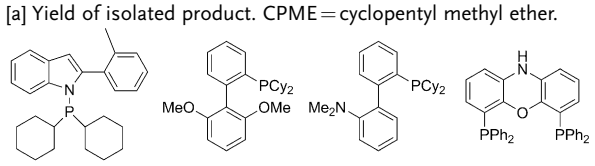
Table 1: Optimization of diaryl sulfoxide formation by cross-coupling of benzyl phenyl sulfoxide (**1a**) with 4-*tert*-butylbromobenzene (**2a**).



1a (1 equiv) + **2a** (2 equiv) → **3a**

Entry	Catalyst	Ligand	Catalyst/ligand (mol%)	*T* [°C]	Base	Yield [%][a]
1	$Pd(OAc)_2$	**L1**	10:15	110	LiO*t*Bu	20
2	$Pd(OAc)_2$	**L2**	10:15	110	LiO*t*Bu	25
3	$Pd(OAc)_2$	**L3**	10:15	110	LiO*t*Bu	33
4	$Pd(OAc)_2$	**L4**	10:15	110	LiO*t*Bu	22
5	$Pd(OAc)_2$	**L4**	10:15	110	NaO*t*Bu	83
6	$Pd(OAc)_2$	**L4**	10:15	80	NaO*t*Bu	85
7	$[Pd_2(dba)_3]$	**L4**	10:15	80	NaO*t*Bu	55
8	$[Pd_2(dba)_3]$	**L4**	10:15	80	NaO*t*Bu	91
9	$[Pd_2(dba)_3]$	**L4**	5:7.5	80	NaO*t*Bu	91
10	$[Pd_2(dba)_3]$	**L4**	2.5:3.8	80	NaO*t*Bu	68
11	$[Pd_2(dba)_3]$	**L4**	5:7.5	55	NaO*t*Bu	28

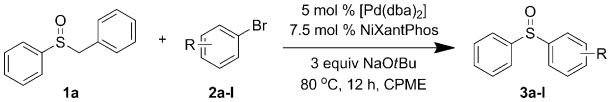
[a] Yield of isolated product. CPME = cyclopentyl methyl ether.



Kwong's ligand (**L1**) SPhos (**L2**) DavePhos (**L3**) NiXantPhos (**L4**)

we next examined 12 bases and four solvents using the ligands SPhos (**L2**), DavePhos (**L3**), and NiXantPhos (**L4**; see the Supporting Information). The highest yield was with 15 mol% NiXantPhos (**L4**), 10 mol% $Pd(OAc)_2$, and NaO*t*Bu in CPME (Table 1, entry 5). Forging ahead with NiXantPhos, a similar yield was obtained when the temperature was reduced to 80°C (entry 6). Examination of four palladium sources $[Pd(OAc)_2]$, $[Pd(cod)Cl_2]$, $[Pd(NCCH_3)_2Cl_2]$, and $[Pd_2(dba)_3]$] in six solvents was undertaken using NiXantPhos (**L4**) and NaO*t*Bu at 80°C for 12 hours. Among the variables examined, $[Pd_2(dba)_3]$ in CPME rendered the highest assay yield on microscale. Unfortunately, we were unable to translate these conditions to lab scale, and only 55% yield of **3a** was obtained. We hypothesized that contamination of commercial $[Pd_2(dba)_3]$ with nanoparticles was a potential problem (Table 1, entry 7).[17] Changing to $[Pd(dba)_2]$ overcame this issue, thus generating **3a** in 91% yield (Table 1, entry 8). We were able to decrease the Pd/ligand loading from 10:15 mol% to 5:7.5 mol% while maintaining the high yield (Table 1, entry 9). Reduction to 2.5:3.8 mol%, however, resulted in lower yield (entry 10). Therefore, 5 mol% $[Pd(dba)_2]$ and 7.5 mol% NiXantPhos were employed. Decreasing the temperature to 55°C led to only 28% yield of **3a** (entry 11). Further optimization of the loading of NaO*t*Bu and the ratios of **1a** and **2a** revealed that 3 equivalents of NaO*t*Bu and a 1:2 ratio of **1a**/**2a** was optimal (see the Supporting Information). Thus, our best reaction conditions were 5 mol% $[Pd(dba)_2]$, 7.5 mol% NiXantPhos (**L4**), **1a** (as the limiting reagent), 2 equivalents of **2a**, and 3 equivalents NaO*t*Bu in CPME at 80°C for 12 hours.

Table 2: Substrate scope of aryl bromides in palladium-catalyzed formation of diaryl sulfoxides with **1a**.



1a + **2a-l** → **3a-l**

R	Product	Yield [%][a]	R	Product	Yield [%][a]
4-*t*Bu	**3a**	91	2-Me	**3g**	90[b]
4-NMe_2	**3b**	91[b]	1-naphthyl	**3h**	93
4-F	**3c**	95	3-OMe	**3i**	93
4-Cl	**3d**	93	2-pyridyl	**3j**	89[d]
4-CF_3	**3e**	85[c]	3-pyridyl	**3k**	94[b,c] (86[e])
4-NO_2	**3f**	94	4-pyridyl	**3l**	85[b,c]

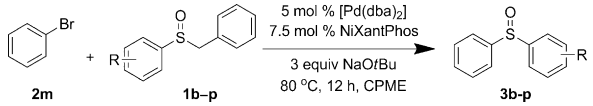
[a] Yield of isolated product. [b] 110°C. [c] 24 h. [d] 6 h. [e] **1a** (5 mmol), **2k** (10 mmol), CPME (50 mL), 36 h.

The reaction conditions identified for the formation of **3a** were evaluated for a series of aryl bromides with **1a** (Table 2). Electron-donating groups on the aryl bromides, such as 4-*tert*-butyl and 4-*N,N*-dimethylamino, were well tolerated, thus providing **3a** and **3b**, respectively, in 91% yield. The cross-coupling reactions proceeded smoothly with **1a** and various aryl bromides bearing electron-withdrawing groups, including 4-fluoro (**2c**), 4-chloro (**2d**), 4-trifluoromethyl (**2e**), and 4-nitro (**2f**), thus providing **3c**–**f** in 85–95% yield. Excellent chemoselectivity in coupling at bromide over the chloride was achieved with 4-chloro bromobenzene (**2d**). The sterically more demanding 2-bromotoluene (**2g**) and 1-bromonaphthalene (**2h**) furnished the products **3g** (90%) and **3h** (93%), respectively. 3-Bromoanisole generated the coupling product **3i** in 93% yield.

Bioactive sulfoxides often contain heterocycles.[18] Our protocol is effective for the synthesis of heterocyclic sulfoxides, as demonstrated with couplings to yield 2-, 3-, and 4-pyridyl phenyl sulfoxides (**3j–l**) in 89, 94, and 85% yield, respectively. To achieve these yields, higher reaction temperatures (110°C) and longer reaction times (24 h) were needed. It is noteworthy that **3j** is the key motif for an anti-inflammatory agent[18a] and **3l** is derived from a hair papilla cell proliferation agent.[18b] To show the scalability of our method, we performed the reaction using 5 mmol benzyl phenyl sulfoxide (**1a**) and 10 mmol 3-bromopyridine (**2k**). The product, **3k** was isolated in 86% yield.

We next turned our attention to the substrate scope of aryl benzyl sulfoxides in coupling reactions with bromobenzene (**2m**) to generate diaryl sulfoxides. Electron-donating 4-methyl and 4-*N,N*-dimethylamino groups were well tolerated, thus giving **3m** and **3b** in 99 and 92% yield, respectively. Substrates bearing the electron-withdrawing 4-F (**1c**), 4-Cl (**1d**), and 4-CF_3 (**1e**) groups furnished the products in 86–92% yield. The congested 2-tolyl and 1-naphthyl benzyl sulfoxides **1g** and **1h** afforded **3g** (93%) and **3h** (91%), respectively. Aryl heteroaryl sulfoxides were provided from heteroaryl benzylsulfoxides in excellent yields under slightly modified reaction conditions (see Table 3 for details). 3-Pyridyl (**3k**), 2-furanyl (**3n**), and 2-thienyl (**3m**) phenyl sulfoxides were thus prepared. The compound **3n** could be utilized as a key motif for an antituberculotic reagent.[18c] Alkyl aryl sulfoxides could also be prepared, as demonstrated

Table 3: Substrate scope of aryl benzyl sulfoxides in palladium-catalyzed formation of diaryl sulfoxides with bromobenzene (**2m**).



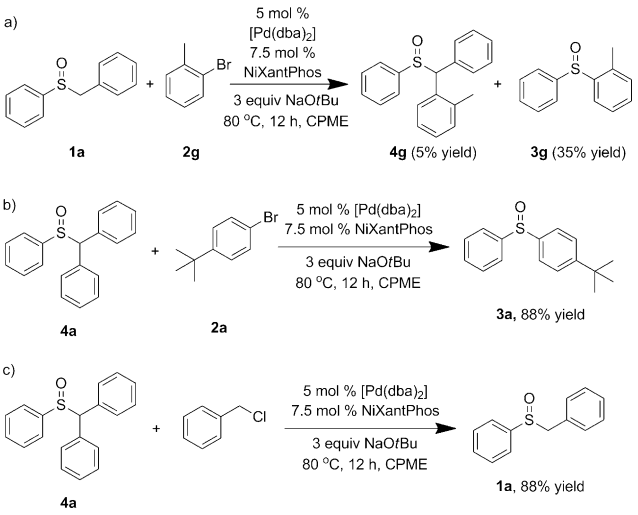
R	Product	Yield [%][a]	R	Product	Yield [%][a]
4-Me	**3m**	99	1-naphthyl	**3h**	91
4-NMe_2	**3b**	92	3-pyridyl	**3k**	89[c]
4-F	**3c**	92	2-furanyl	**3n**	90
4-Cl	**3d**	91[b]	2-thienyl	**3o**	85[c]
4-CF_3	**3e**	86	cyclohexyl	**3p**	90[c]
2-Me	**3g**	93[c]			

[a] Yield of isolated product. [b] 24 h. [c] 110 °C.

by generation of cyclohexyl phenyl sulfoxide (**3p**) in 90% yield.

To generate diaryl sulfoxides, the Pd/NiXantPhos catalyst must promote multiple distinct reactions, including cleavage and formation of C–S bonds. Based on experiments discussed below, a tricatalytic cycle is proposed in Figure 1. The first cycle (A), is the α-arylation of aryl benzyl sulfoxides. We recently reported a similar catalytic arylation of methyl phenyl sulfoxides in up to 95% yield and one example of the arylation of a benzyl phenyl sulfoxide (80% yield).[11] Support for cycle A was gained when the temperature was decreased from 110 °C to 80 °C (Scheme 2a) in the reaction of **1a** with 2-tolyl bromide (**2g**). We isolated the diarylmethyl sulfoxide **4g** (intermediate **E**; Figure 1) in 5% yield along with the 35% of the diaryl sulfoxide **3g** (Scheme 2a). These results support the proposed α-arylation cycle A. Subsequently, diphenylmethyl phenyl sulfoxide (**4a**) was synthesized independently and subjected to the optimized reaction conditions with 4-*tert*-butyl bromobenzene (Scheme 2b). The diaryl sulfoxide product **3a** was generated in 88% yield.

In the second catalytic cycle (B) a novel cleavage of the C–S bond occurs (Figure 1). Arene coordination of the aryl diarylmethyl sulfoxide moiety (**F**) to palladium is followed by formation of a π-benzyl intermediate (**G**) and expulsion of aryl sulfenate (**H**). The intermediate **G** is attacked by the



Scheme 2. Generation of **4g** and α-arylation and benzylation of **4a**.

NaO*t*Bu base, thus generating a diarylmethyl *tert*-butyl ether (**J**), which we have isolated from the reaction mixture. The yield of this byproduct is always significantly lower than expected based on the reaction stoichiometry. Further studies demonstrated that the Ar_2CH-O-*t*Bu undergoes a base-induced E2 elimination to generate Ar_2CH-ONa, which is oxidized by palladium in a fourth catalytic cycle. When 3 equivalents of 4-nitro bromobenzene are employed, nitrobenzene is isolated in 76% yield. If 2 equivalents of the aryl bromide is used, we propose the eliminated isobutylene is reduced to isobutane (see the Supporting Information for details).

Palladium π-benzyl intermediates were pioneered by Fiaud and Kuwano,[19] who have developed them into useful synthetic intermediates. We are not aware, however, of previous observation of sulfenates as leaving groups in π-benzylation reactions. The sulfenate generated in cycle B undergoes palladium-catalyzed cross-coupling with aryl bromides in cycle C and produces the diaryl sulfoxide. As further support of the intermediacy of aryl sulfenate (**H**), we added benzyl chloride in the standard catalysis conditions with

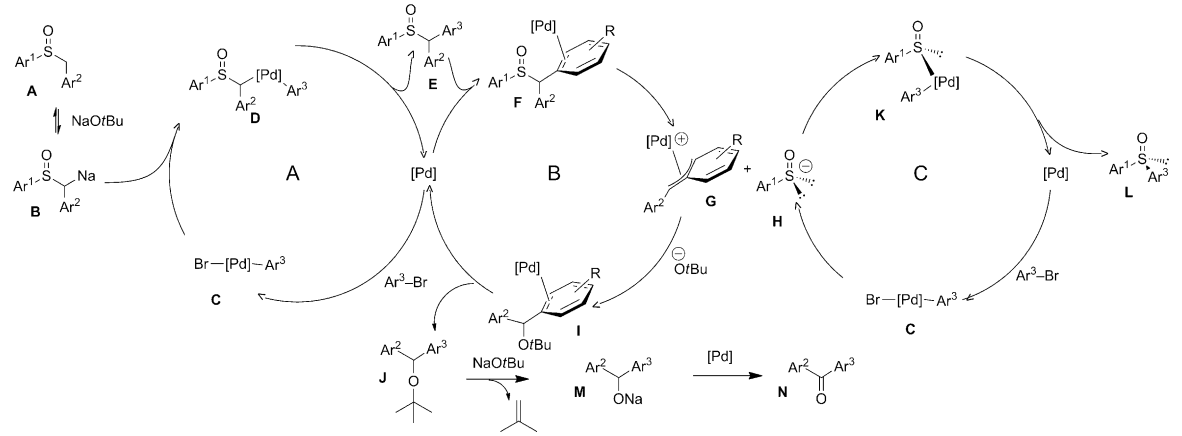
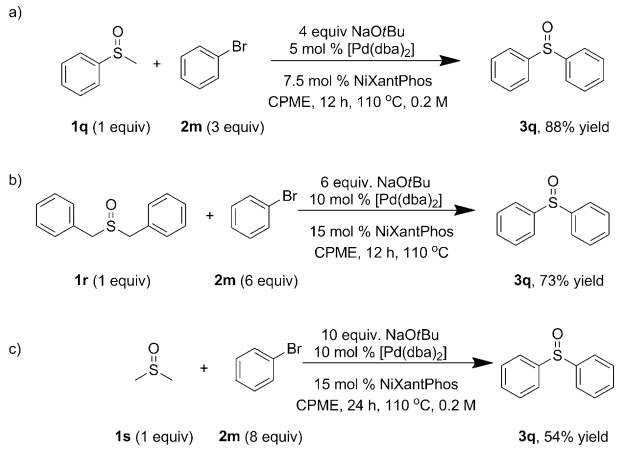


Figure 1. Proposed mechanism of the palladium-catalyzed triple relay process.

diphenylmethyl phenyl sulfoxide (**4a**, Scheme 2c). Benzyl phenyl sulfoxide (**1a**) was isolated in 88% yield.

As mentioned, we recently reported the first palladium-catalyzed α-arylation of methyl sulfoxides with aryl halides.[11] The products generated from this α-arylation are aryl benzyl sulfoxides, which are the starting materials in Tables 1–3. Thus, we were interested in exploring the synthesis of diaryl sulfoxides directly from aryl methyl sulfoxides.[20] The pK_a of methyl aryl sulfoxides is significantly higher than that of benzyl aryl sulfoxides, however. Fortunately, the $[Pd(dba)_2]$/NiXantPhos system proved to be suitable for this transformation (Scheme 3a). Thus, starting with methyl phenyl



Scheme 3. Tandem palladium-catalyzed synthesis of diphenyl sulfoxide (**3q**) from methyl phenyl sulfoxide (**1q**), dibenzyl sulfoxide (**1r**), and dimethyl sulfoxide (DMSO; **1s**).

sulfoxide (**1q**) diphenyl sulfoxide (**3q**) was generated directly in 88% yield using a 0.2 M concentration. This tandem route broadens the substrate scope. We next sought to generate diphenyl sulfoxide starting from dibenzyl sulfoxide (**1r**, Scheme 3b). The desired product **3q** was provided in 73% yield from **1r** upon increasing the catalyst/ligand loading to 10:15 mol%. Interestingly, dimethyl sulfoxide (DMSO), a common solvent, could also be utilized. DMSO underwent dual α-arylation to generate **3q** in 54% yield (Scheme 3c). Considering this reaction involves four α-arylations and two S-arylations, the yield is reasonable.

In summary, we report a novel triple relay process to generate diaryl sulfoxides directly from aryl benzyl sulfoxides and aryl bromides. $[Pd(dba)_2]$/NiXantPhos efficiently catalyzed the reactions, and a variety of diaryl sulfoxides, as well as alkyl aryl sulfoxides, were produced in good to excellent yields. Mechanistic studies indicate three distinct core catalytic cycles: sulfoxide α-arylation, C–S bond cleavage, and C–S bond formation. The byproduct benzophenone is formed by an additional palladium-catalyzed process. The palladium-catalyzed benzylative C–S bond cleavage of sulfoxides is unprecedented.

Experimental Section

General procedure for catalysis: $[Pd(dba)_2]$ (2.88 mg, 0.005 mmol) and ligand **L4** (4.14 mg, 0.0075 mmol) were added to an oven-dried microwave vial equipped with a stirbar under a nitrogen atmosphere, and 1.0 mL dry CPME was then added. After the catalyst/ligand solution was stirred for 2 h at 24 °C, NaO*t*Bu (28.8 mg, 0.30 mmol, 3 equiv) was added to the reaction vial followed by benzyl phenyl sulfoxide (21.6 mg, 0.10 mmol, 1.0 equiv). The microwave vial was sealed and 4-*tert*-butyl bromobenzene (34.6 μL, 0.20 mmol, 2.0 equiv) was added by syringe under a nitrogen atmosphere. Note that if the benzyl sulfoxide or aryl bromide is a solid, it was added to the reaction vial before NaO*t*Bu. The reaction mixture was heated to 80 °C by oil bath and stirred for 12 h. The sealed vial was cooled to room temperature, opened to air, and the reaction mixture was passed through a short pad of silica gel. The pad was then rinsed with 10:1 dichloromethane/methanol. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (eluted with EtOAc/hexanes 1:4) to give the product (23.5 mg, 91% yield) as a white solid.

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[1] a) K. Suwanborirux, K. Charupant, S. Amnuoypol, S. Pummangura, A. Kubo, N. Saito, *J. Nat. Prod.* **2002**, *65*, 935; b) S. Kim, R. Kubec, R. A. Musah, *J. Ethnopharmacol.* **2006**, *104*, 188; c) I. Dini, G. C. Tenore, A. Dini, *J. Nat. Prod.* **2008**, *71*, 2036; d) M. El-Aasr, Y. Fujiwara, T. Takeya, S. Tsukamoto, M. Ono, D. Nakamo, M. Okawa, J. Kinjo, H. Yoshimitsu, T. Nohara, *J. Nat. Prod.* **2010**, *73*, 1306.

[2] a) K. L. Rinehart, R. Sakai, US2004/59112A1, **2004**; b) Amira Pharmaceuticals Inc., US/2010/4331A1, **2010**; c) J. H. Hutchinson, T. J. Seiders, J. M. Arruda, J. R. Roppe, (Amira Pharmaceuticals Inc.), WO2010/42652A2, **2010**; d) Combinatorx (Singapore) Pte. Ltd., US2010/9970A1, **2010**; e) Achaogen Inc., WO2009/137130A2, **2009**.

[3] a) T. Oyama, K. Naka, Y. Chujo, *Macromolecules* **1999**, *32*, 5240; b) M. Numata, Y. Aoyagi, Y. Tsuda, T. Yarita, A. Takatsu, *Anal. Chem.* **2008**, *80*, 509.

[4] a) Astra Aktiebolag, US5877192A, **1998**; b) Laboratoire L. Lafon, US4927855A, **1990**.

[5] For reviews, see a) M. Mellah, A. Voituriez, E. Schulz, *Chem. Rev.* **2007**, *107*, 5133, and references therein; some recent examples: b) C. Jiang, D. J. Covell, A. F. Stepan, M. S. Plummer, M. C. White, *Org. Lett.* **2012**, *14*, 1386; c) E. M. Stang, M. C. White, *J. Am. Chem. Soc.* **2011**, *133*, 14892; d) P. K. Dornan, P. L. Leung, V. M. Dong, *Tetrahedron* **2011**, *67*, 4378; e) J. Chen, F. Lang, X. Zhang, L. Cun, J. Zhu, J. Deng, J. Liao, *J. Am. Chem. Soc.* **2010**, *132*, 4552; f) R. Mariz, X. Luan, M. Gatti, A. Linden, R. Dorta, *J. Am. Chem. Soc.* **2008**, *130*, 2172.

[6] a) E. Wojaczyńska, J. Wojaczyński, *Chem. Rev.* **2010**, *110*, 4303; b) G. E. O'Mahony, P. Kelly, S. E. Lawrence, A. R. Maguire, *ARKIVOC (Gainesville, FL, U.S.)* **2011**, *2011*, 1; c) C. Bolm, *Coord. Chem. Rev.* **2003**, *237*, 245.

[7] a) Z. Han, D. Krishnamerthy, P. Grover, K. Fang, X. Su, H. S. Wilkinson, Z.-H. Lu, D. Magiera, C. H. Senanayake, *Tetrahedron* **2005**, *61*, 6386; b) K. Hiroi, F. Kato, *Tetrahedron* **2001**, *57*, 1543; c) F. Xue, D. Wang, X. Li, B. Wan, *J. Org. Chem.* **2012**, *77*, 3071; d) N. Furukawa, S. Ogawa, K. Matsumur, H. Fujihara, *J. Org. Chem.* **1991**, *56*, 6341.

[8] a) G. Maitro, S. Vogel, G. Prestat, D. Madec, G. Poli, *Org. Lett.* **2006**, *8*, 5951; b) G. Maitro, S. Vogel, M. Sadaoui, G. Prestat, D. Madec, G. Poli, *Org. Lett.* **2007**, *9*, 5493; c) E. Bernoud, G. Le Duc, X. Bantreil, G. Prestat, D. Madec, G. Poli, *Org. Lett.* **2010**, *12*, 320.

[9] For recent examples of palladium-catalyzed tandem transformations, see a) Y. Shang, X. Jie, J. Zhou, S. Huang, W. Wei, *Angew. Chem.* **2013**, *125*, 1337; *Angew. Chem. Int. Ed.* **2013**, *52*, 1299; b) M. Zhang, P. Hu, J. Zhou, S. Huang, S. Wei, *Org. Lett.* **2013**, *15*, 1718.

[10] a) J. Zhang, A. Bellomo, A. D. Creamer, S. D. Dreher, P. J. Walsh, *J. Am. Chem. Soc.* **2012**, *134*, 13765; b) A. Bellomo, J. Zhang, N. Trongsiriwat, P. J. Walsh, *Chem. Sci.* **2013**, *4*, 849.

[11] T. Jia, A. Bellomo, K. EL Baina, S. D. Dreher, P. J. Walsh, *J. Am. Chem. Soc.* **2013**, *135*, 3740.

[12] B. Zheng, T. Jia, P. J. Walsh, *Org. Lett.* **2013**, *15*, 1690.

[13] B. Zheng, T. Jia, P. J. Walsh, *Org. Lett.* **2013**, *15*, 4190.

[14] a) G. I. McGrew, J. Temaismithi, P. J. Carroll, P. J. Walsh, *Angew. Chem.* **2010**, *122*, 5673; *Angew. Chem. Int. Ed.* **2010**, *49*, 5541; b) J. Zhang, C. Stanciu, B. Wang, M. M. Hussain, C.-S. Da, P. J. Carroll, S. D. Dreher, P. J. Walsh, *J. Am. Chem. Soc.* **2011**, *133*, 20552; c) G. I. McGrew, C. Stanciu, J. Zhang, P. J. Carroll, S. D. Dreher, P. J. Walsh, *Angew. Chem.* **2012**, *124*, 11678; *Angew. Chem. Int. Ed.* **2012**, *51*, 11510.

[15] C. M. So, C. P. Lau, F. Y. Kwong, *Org. Lett.* **2007**, *9*, 2795.

[16] a) L. A. van der Veen, P. H. Keeven, G. C. Schoemaker, J. N. H. Reek, P. C. Kamer, P. W. N. M. van Leeuwen, M. Lutz, A. L. Spek, *Organometallics* **2000**, *19*, 872; b) P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Acc. Chem. Res.* **2001**, *34*, 895.

[17] S. S. Zalesskiy, V. P. Ananikov, *Organometallics* **2012**, *31*, 2302.

[18] a) Actelion Pharmaceuticals Ltd, K. Hilpert, F. Hubler, WO2012/114268A1, **2012**; b) Taisho Pharmaceutical Co. Ltd., JP2005/41871A, **2005**; c) The University of Tennessee Research Foundation, Colorado State University Research Foundation, WO2005/7625A2, **2005**; d) J. Weinstock, J. Wu, P. Cao, W. D. Kingbury, J. L. McDermott, M. P. Kodrasov, D. M. McKelvey, K. G. Suresh, S. J. Goldenberg, M. R. Mattern, B. Nicholson, *ACS Med. Chem. Lett.* **2012**, *3*, 789.

[19] a) J.-Y. Legros, J.-C. Fiaud, *Tetrahedron Lett.* **1992**, *33*, 2509; b) R. Kuwano, Y. Kondo, Y. Matsuyama, *J. Am. Chem. Soc.* **2003**, *125*, 12104; c) R. Kuwano, Y. Kondo, *Org. Lett.* **2004**, *6*, 3545.

[20] After submission of this work, Nolan and co-workers reported a synthesis of diaryl sulfoxides from aryl methyl sulfoxides: F. Izquierdo, A. Chartoire, S. P. Nolan, *ACS Catal.* **2013**, *3*, 2190.

