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Palladium Catalyzed Aryl C–H Amination with O_2 via In Situ Formation of Peroxide-Based Oxidant(s) from Dioxane

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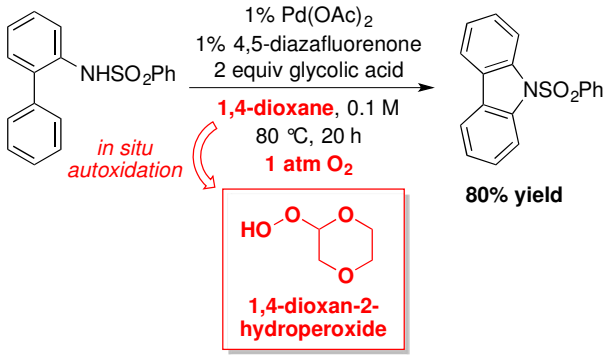
Abstract: (DAF)Pd(OAc)$_2$ (DAF = 4,5-diazafluorenone) catalyzes aerobic intramolecular aryl C–H amination with *N*-benzenesulfonyl-2-aminobiphenyl in dioxane to afford the corresponding carbazole product. Mechanistic studies show that the reaction involves *in situ* generation of peroxide species from 1,4-dioxane and O_2, and the reaction further benefits from the presence of glycolic acid, an oxidative decomposition product of dioxane. An induction period observed for the formation of the carbazole product correlates with the formation of 1,4-dioxan-2-hydroperoxide via autoxidation of 1,4-dioxane, and the in situ-generated peroxide is proposed to serve as the reactive oxidant in the reaction. These findings have important implications for the palladium-catalyzed aerobic oxidation reactions conducted in ethereal solvents.

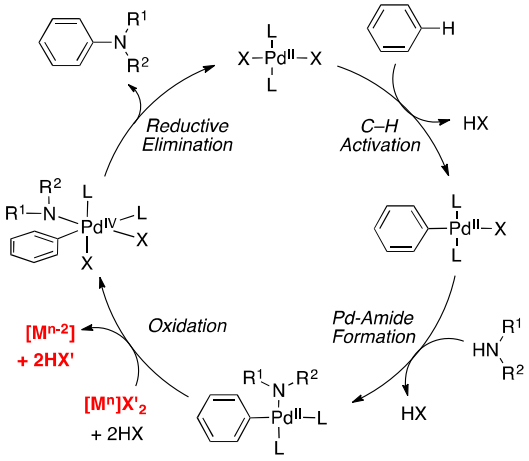
TOC Graphic:



Introduction

Palladium-catalyzed oxidation reactions that form aryl C–N bonds from aryl C–H bonds and amines could have significant value in organic synthesis, and such transformations could complement other widely used C–N bond-forming reactions, such as Ullmann-type and Buchwald-Hartwig cross-coupling reactions.[1] Palladium-catalyzed C–H amination methods typically require strong stoichiometric oxidants, such as diacetoxyiodobenzene,[2] oxone,[3] or [F^+] sources.[4,5] A common reaction pathway associated with these reactions involves oxidation of an aryl-Pd^{II} intermediate to a high-valent Pd^{III} or Pd^{IV} species,[6] which then undergoes facile reductive elimination of the C–N bond and circumvents the intermediacy of an unstable Pd^0 species (Scheme 1).[7,8]

Scheme 1. Aryl C–H amination via Pd^{II}/Pd^{IV} catalysis.



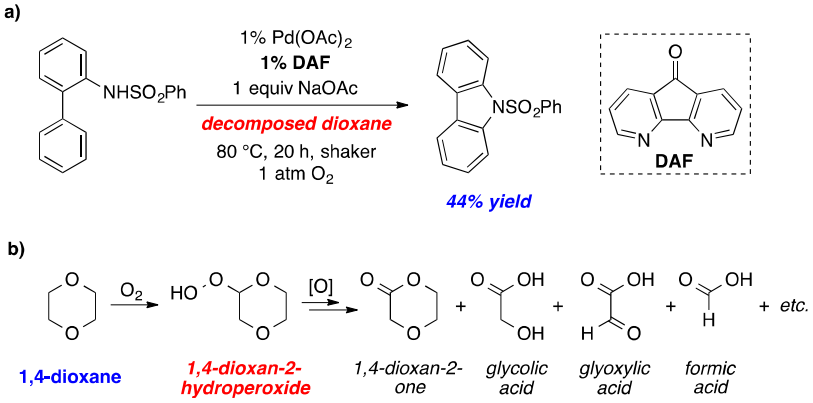
The requirement for strong stoichiometric oxidants impacts the appeal of the reactions, because the advantage of direct C–H functionalization in terms of step economy are partially offset by reduced overall atom economy. To address this deficiency, we have been interested in the development of C–H amination methods compatible with molecular oxygen as the

oxidant.[9,10,11] Here, we report the identification of a unique mechanistic pathway to achieve aerobic aryl C–H amination in the conversion of *N*-benzenesulfonyl-2-aminobiphenyl to *N*-benzenesulfonylcarbazole. The reaction involves in situ generation of a peroxide-based oxidant from O_2 and the solvent, 1,4-dioxane, and mechanistic insight into in situ generation of the peroxide-based oxidant is provided.[12,13]

Results

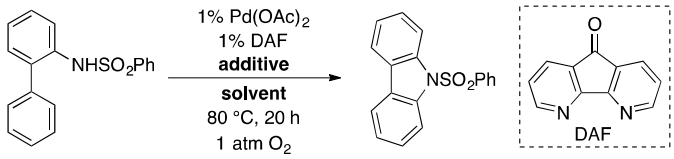
In an effort to discover mild conditions for aryl C–H amination reactions, we evaluated the various ligand-supported palladium catalysts for the transformation of *N*-benzenesulfonyl-2-aminobiphenyl into the corresponding carbazole with molecular oxygen as the sole oxidant. This reaction was selected based on the ease of product analysis as well as the precedence for this reaction to be compatible with aerobic catalytic turnover (albeit at high temperature, 120 °C, and with limited scope).[7a,b] During the course of screening studies, 44 turnovers were achieved with a 4,5-diazafluorenone (DAF)-ligated $Pd(OAc)_2$ catalyst in 1,4-dioxane at 80 °C under 1 atm O_2 (Scheme 2a). Inspection of the crude ^{1}H NMR spectrum of the reaction mixture, however, revealed the presence of numerous byproducts, which were eventually traced to the use of an aged bottle of dioxane that had been used in the experiments. Significant quantities of 1,4-dioxan-2-hydroperoxide were detected in the bottle of dioxane by ^{1}H NMR spectroscopic analysis of a partially concentrated sample of the solvent, and the same hydroperoxide and various oxidative fragmentation products were identified in the crude ^{1}H NMR spectrum of the completed catalytic reaction (Scheme 2b).

Scheme 2. a) Discovery of a positive effect of peroxide species in carbazole synthesis. b) Dioxane decomposition by autoxidation.



When the reaction was repeated with a fresh bottle of 1,4-dioxane, no carbazole product was obtained (Table 1, entry 1). This result prompted us to carry out a number of control experiments to probe the origin of successful reactivity with the old bottle of dioxane depicted in Scheme 2. Upon changing the solvent to toluene and adding *tert*-butylhydroperoxide (TBHP), a yield comparable to that obtained with the decomposed dioxane was observed (45%, entry 2). Addition of a more activated peroxide oxidant, *tert*-butylperoxybenzoate (TBPB), provided an even higher yield of carbazole (82%, entry 3). These results implicate the involvement of 1,4-dioxan-2-hydroperoxide as an oxidant in the reaction, and they resemble previous observations of Alper[14] and Sigman[15] in their studies of Wacker oxidations of alkenes in tetrahydrofuran (THF). In these reactions, oxidative decomposition of THF was observed, and TBHP was found to be effective as an oxidant.

Table 1. Investigation of additive effects on aerobic carbazole synthesis with a (DAF)$Pd(OAc)_2$ catalyst system.



Entry	Additive (equiv)	Solvent (0.1 M)	% Yield	dioxane decomposition?
1	none	dioxane	0	no
2	*t*-butylhydroperoxide (1.1)	toluene	45	n/a
3	*t*-butylperoxybenzoate (1.1)	toluene	82	n/a
4	glycolic acid (0.1)	dioxane	10	trace
5	glycolic acid (1)	dioxane	43	yes[a]
6	glycolic acid (2)	dioxane	80	yes[a]
7	glycolic acid (2)	toluene	0	n/a
8	glyoxylic acid (2)	dioxane	0	no
9	oxalic acid (2)	dioxane	0	no
10	methyl glycolate (2)	dioxane	4	trace
11	ethylene glycol (2)	dioxane	0	no[b]
12	1-propanol (2)	dioxane	0	no[b]

[a] 1,4-Dioxan-2-hydroperoxide, 1,4-dioxan-2-one and unidentified formate species were detected in the ^{1}H NMR spectrum of the reaction mixture. [b] Co-solvent quantities (4:1 dioxane:alcohol) were also ineffective.

Additional control experiments showed that successful catalytic turnover could be achieved in fresh dioxane if specific additives were included in the reaction mixture. The reaction of *N*-benzenesulfonyl-2-aminobiphenyl was performed using fresh dioxane in the presence of 1-2 equiv of glycolic acid, glyoxylic acid and oxalic acid (cf. Scheme 2b) (Table 1, entries 4-9). Of these additives, glycolic acid promotes the reaction. An 80% yield of carbazole was obtained when two equivalents of glycolic acid were included in the reaction mixture (entry 6). In contrast, no product was observed from reactions performed in the presence of glyoxylic acid and oxalic acid (entries 8 and 9), nor was product formed in the presence of glycolic acid when

toluene was used as the solvent (entry 7). Analysis of the reaction mixtures after 20 h showed that dioxane decomposition products, similar to those observed when the reaction was performed with aged dioxane, were observed in the successful reactions that contained glycolic acid (entries 5 and 6). Dioxane decomposition was not observed in the unsuccessful reactions containing glyoxylic acid or oxalic acid. Inclusion of methyl glycolate provided only trace reactivity (entry 10), while ethylene glycol and propanol were completely ineffective (entries 11-12). In none of the latter three reactions was dioxane decomposition observed. To summarize, successful formation of carbazole product correlates with the oxidative decomposition of dioxane. 1,4-Dioxan-2-hydroperoxide and 1,4-dioxan-2-one were isolated from the successful reaction mixtures, and several unidentified formate species were evident in the ^{1}H NMR spectrum of the crude reaction mixtures (see the electronic supplementary information for details).

The reaction of *N*-benzenesulfonyl-2-aminobiphenyl in the presence of 2 equiv of glycolic acid in dioxane was monitored by ^{1}H NMR spectroscopy, and the results reveal a significant induction period for product formation. As shown in Figure 1a, the appearance of carbazole product correlates with the appearance of dioxane oxidation products 1,4-dioxan-2-hydroperoxide and 1,4-dioxan-2-one. The transformation of glycolic acid into oxidized products was not monitored, but glycolic acid was consumed by the end of the reaction. This time course may be compared with a time course for the same reaction, using *tert*-butylperoxybenzoate (TBPB) in toluene (Figure 1b), which exhibits a negligible induction period but proceeds in similar yield.

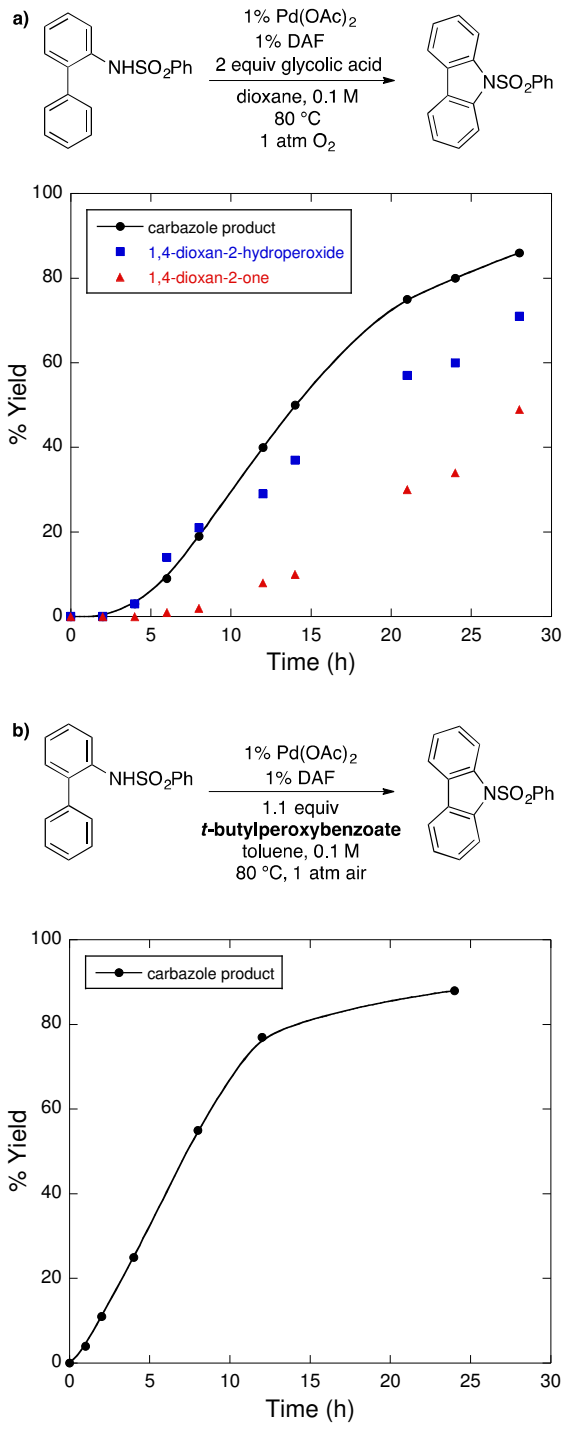
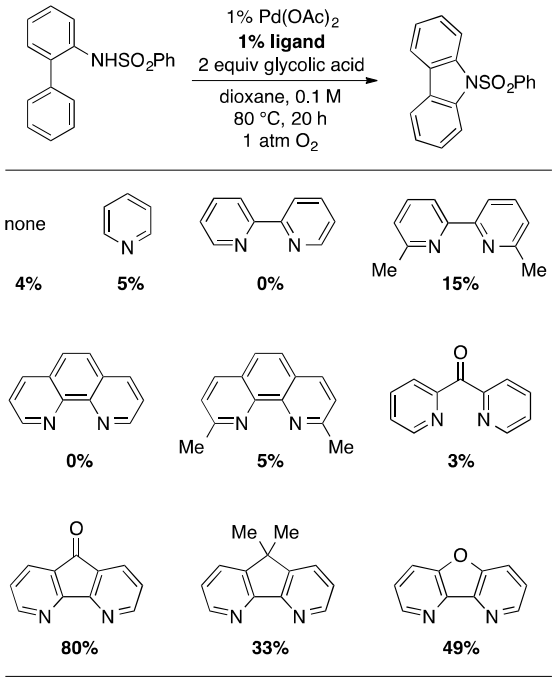


Figure 1. a) Reaction time course: (DAF)Pd(OAc)$_2$ catalyst with glycolic acid in dioxane and b) Reaction time course: (DAF)Pd(OAc)$_2$ catalyst with *t*-butylperoxybenzoate in toluene. Yields were calculated with respect to 0.05 mmol of starting substrate and were determined by ^{1}H NMR spectroscopic analysis using phenyltrimethylsilane as the internal standard. DAF = 4,5-diazafluorenone.

A screen of common (bi)pyridyl ligand derivatives in the presence of glycolic acid revealed that DAF is especially effective as a ligand for the reaction (Chart 1).[16] Simple pyridine, bipyridine, and phenanthroline derivatives did not promote the reaction, and a control experiment in which no ligand was added gave only trace carbazole product. Different diazafluorene derivatives and 6,6'-dimethylbipyridine also promoted the reaction, but not as effectively as DAF.

Chart 1. Comparison of neutral donor ligands for the $Pd(OAc)_2$ / glycolic acid mediated carbazole synthesis in dioxane.



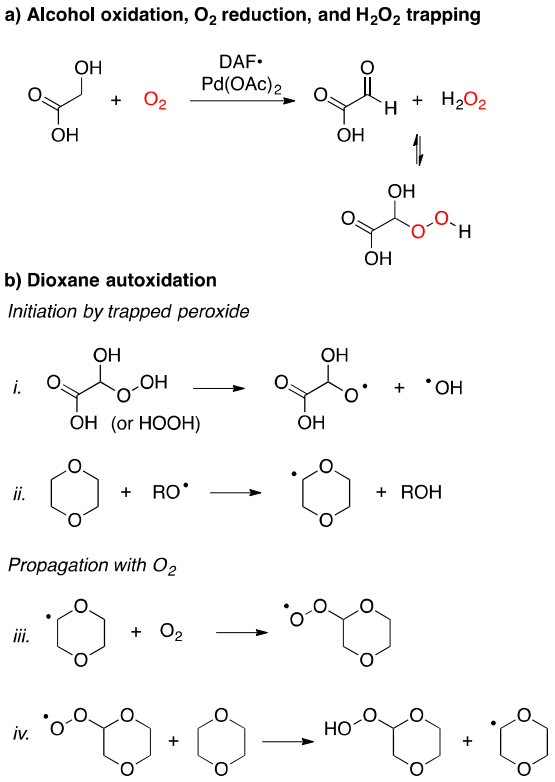
Discussion

The results described above suggest that in situ formation of alkyl peroxides from 1,4-dioxane solvent enable Pd-catalyzed C–H oxidation with O_2 as the terminal oxidant. The principal observations described above may be summarized as follows: (1) 1,4-dioxan-2-hydroperoxide is directly observed in the reaction mixture, (2) product formation is observed in

dioxane only when solvent oxidative decomposition products are also observed, (3) formation of 1,4-dioxan-2-hydroperoxide (and other dioxane-based decomposition products) temporally correlates with the formation of the carbazole product, (4) glycolic acid promotes the oxidative decomposition of fresh dioxane under the catalytic conditions, and (5) the reaction carried out with dioxane and glycolic acid exceeds the performance of reactions that employ simple alkylperoxide-based oxidants.

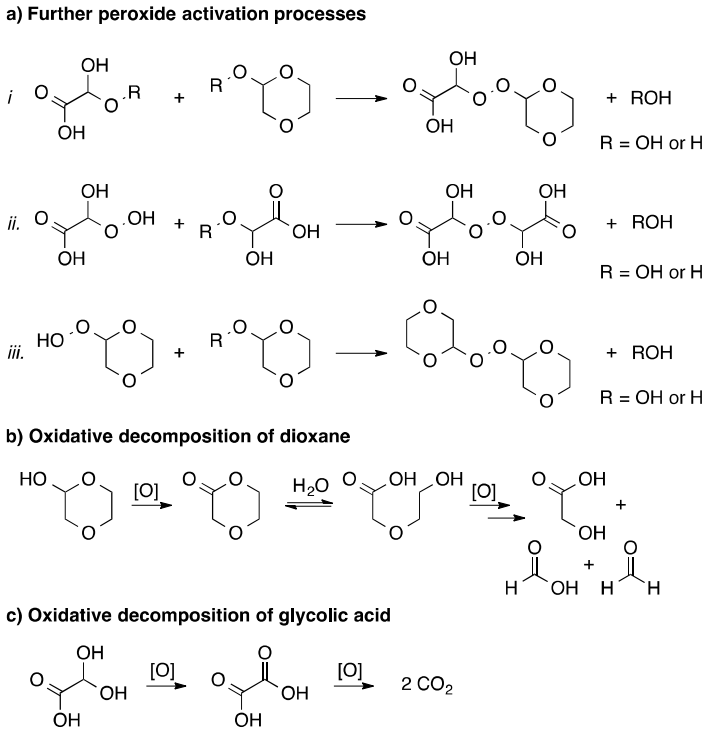
Although various mechanistic aspects of these reactions are not fully understood, a number of reasonable hypotheses can be offered to explain the experimental observations (Schemes 3, 4 and 5). The disappearance of glycolic acid under the catalytic conditions is best explained by (DAF)Pd$(OAc)_2$-mediated oxidation of the primary alcohol to afford glyoxylic acid via aerobic Pd^{II}/Pd^0 catalysis. Aerobic alcohol oxidation by Pd^{II} generates hydrogen peroxide,[17] which could form an adduct with glyoxylic acid (the aldehyde generated from glycolic acid oxidation; Scheme 3a). Either hydrogen peroxide or the corresponding glyoxylic acid adduct could serve as an initiator for autoxidation of dioxane via a radical chain pathway (Scheme 3b). Trapping of alkyl radicals by O_2 eventually affords 1,4-dioxan-2-hydroperoxide and other associated oxidative decomposition products.[18]

Scheme 3. a) Generation of activated peroxide by reduction of O_2 and *in situ* trapping. b) Proposed mechanism for autoxidation of dioxane.



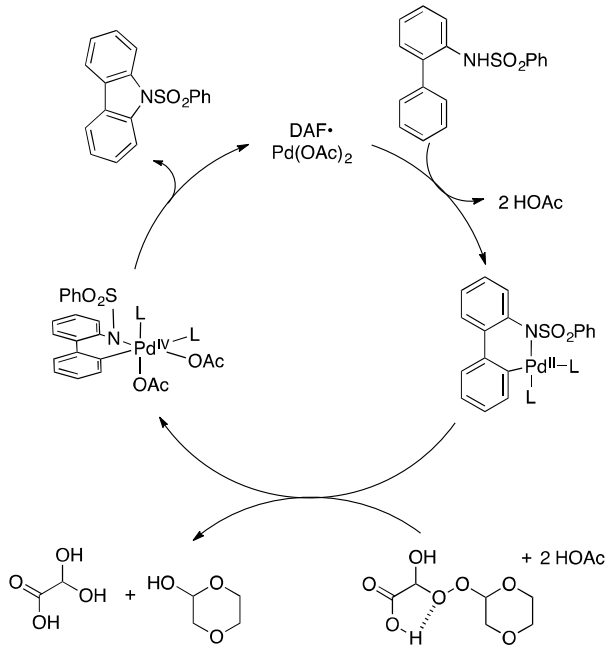
Our results suggested that 1,4-dioxan-2-hydroperoxide and TBHP are capable of promoting the aryl C–H amination reaction, but the more activated peroxide TBPB gave a higher yield, comparable to that obtained when glycolic acid was used in dioxane (cf. Table 1). The 1,4-dioxan-2-hydroperoxide species generated from the autoxidation of dioxane accumulates during the reaction (cf. Figure 1a), and various options exist to generate a more reactive peroxide (Scheme 4a). Any of the activated peroxide species could potentially contribute to the catalytic aryl C–H amination reaction, and these oxidants also could be consumed in the oxidative decomposition of dioxane (Scheme 4b) and glycolic acid (Scheme 4c).

Scheme 4. Mechanistic pathways for a) peroxide activation b) decomposition of dioxane and c) decomposition of glycolic acid.



These mechanistic considerations provide a rationale for the role of glycolic acid in the generation of a strong peroxide oxidant under Pd-catalyzed aerobic oxidation conditions in dioxane. A hypothetical Pd^{II}/Pd^{IV} catalytic cycle that incorporates a peroxide-based oxidant in intramolecular aryl C–H amination is shown in Scheme 5. In 2013, Jiao and coworkers described the use of *N*-hydroxyphthalimide to mediate autoxidation of toluene to generate a reactive oxidant in chelate-directed Pd-catalyzed arene hydroxylation.[19] Although certain details of their proposed mechanism differ from Scheme 5, both reactions exploit autoxidation of a weak C–H bond in the solvent to generate an O_2-derived peroxide capable of oxidizing an arylpalladium(II) intermediate to a higher oxidation state, resulting in facile carbon-heteroatom bond formation. Overall, this concept represents an unusual, but valuable strategy to use O_2 as a stoichiometric oxidant in Pd-catalyzed oxidation reactions.[20]

Scheme 5. Proposed mechanism for substrate oxidation via high-valent Pd^{II}/Pd^{IV} catalysis with an *in situ* generated peroxide as the oxidant.



Conclusions

In summary, we have identified a palladium catalyst system that takes advantage of glycolic acid as a primary alcohol additive and 1,4-dioxane as a solvent for in situ generation of strong peroxide oxidants that promote efficient Pd-catalyzed intramolecular aryl C–H amination of a 2-aminobiphenyl derivative. Monitoring of the reaction time course demonstrates a direct correlation between generation of the reactive hydroperoxide and formation of the C–H amination product. These observation highlight a valuable strategy to use O_2 as a stoichiometric oxidant in challenging C–H oxidation reactions, but also highlight potential complexities that could arise when performing aerobic oxidation reactions in the presence of solvents that have weak C–H bonds.

Experimental

General considerations

All commercially available compounds were purchased and used as received, unless otherwise noted. Anhydrous 1,4-dioxane in 100 ml sure-seal bottles was purchased from Aldrich. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 MHz or 500 MHz spectrometers and chemical shifts are given in parts per million relative to internal tetramethylsilane (0.00 ppm for ^{1}H) or $CDCl_3$ (77.16 ppm for ^{13}C). Flash chromatography was carried out with SiliaFlash® P60 (Silicycle, particle size 40-63 um, 230-400 mesh) or by using a CombiFlash Rf® automated chromatography system with reusable high performance silica columns (RediSep® Rf Gold Silica, 20-40 µm spherical particles).

CAUTION: Although no explosions or other safety incidents were encountered in the course of this work, the experiments described here involve the formation of potentially explosive peroxide intermediates. All reactions were performed on small scale behind a blast shield. Appropriate safety measures should be taken into consideration in the reproduction or extension of this work.

General procedure for reactions set up in a custom parallel reactor

A heavy wall 13x100 mm culture tube was charged with *N*-benzenesulfonyl-2-aminobiphenyl (15.5 mg, 0.05 mmol) and other solid additives, such as glycolic acid, as desired. Separate stock solutions of $Pd(OAc)_2$ and ligand were prepared such that the correct quantity of each (0.01 equiv) could be delivered and the total volume would reach 0.5 ml (0.1 M). The culture tube was loaded onto a custom 48-well parallel reactor that allows for heating under a reflux condenser and 1 atm of O_2 with orbital shaking in the absence of ambient light. The reaction vessel was

purged with O_2 after being loaded onto the shaker apparatus. The reaction mixtures were heated to 80 °C and allowed to shake vigorously. At the desired time point, the reaction mixtures were allowed to cool to room temperature, removed from the parallel reactor and concentrated to oil. The mixtures were analyzed by ^{1}H NMR spectroscopy using $CDCl_3$ containing phenyltrimethylsilane as the internal standard.

General procedure for reactions employing peroxide additives

A 6 ml vial was charged with *N*-benzenesulfonyl-2-aminobiphenyl (15.5 mg, 0.05 mmol). Stock solutions of peroxide additive (*t*-butylhydroperoxide or *t*-butylperoxybenzoate) in toluene were prepared such that the correct quantity (1.1 equiv) could be added via syringe. Separate stock solutions of $Pd(OAc)_2$ and ligand were prepared such that the correct quantity of each (0.01 equiv) could be delivered and the total volume would reach 0.5 ml (0.1 M). The vial was sealed with a Teflon cap and loaded into a heating block on a shaker table, allowing for orbital shaking. The reaction mixture was heated to 80 °C and allowed to shake vigorously. At the desired time point, the reaction mixture was allowed to cool to room temperature and concentrated to oil. The mixture was analyzed by ^{1}H NMR spectroscopy using $CDCl_3$ containing with phenyltrimethylsilane as the internal standard.

Notes

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Electronic Supplementary Information (ESI) is available. See DOI: 10.1039/xxxxxxxxx

Acknowledgements

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