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Functionalization of [60]Fullerene via Palladium-Catalyzed C–H Bond Activation

Guan-Wu Wang

Abstract The palladium-catalyzed C–H bond activation strategy has been successfully applied to fullerene chemistry, and several types of [60]fullerene-fused heterocycles and carbocycles have been obtained. The synthesis of [60]fullerene-fused indolines, isoquinolinones, azepines, tetrahydroisoquinolines, tetrahydrobenzazepines, sultones, tetrahydrobenzooxepines/isochromans, and dihydrophenanthrenes has been achieved by the palladium-catalyzed reactions of [60]fullerene with anilides, benzamides, *N*-sulfonyl-2-aminobiaryls, *N*-benzyl sulfonamides, *N*-(2-arylethyl) sulfonamides, arylsulfonic acids, 2-phenylethyl/benzyl alcohols, and 2-arylbenzoic acids, respectively.

Keywords [60]Fullerene · Annulation · Carbocycle · C–H activation · Heterocycle · Palladium catalyst

Contents

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Abbreviations

BQ	*p*-Benzoquinone
Bs	Benzenesulfonyl
Cs	4-Chlorobenzenesulfonyl
equiv.	Equivalent(s)
Et	Ethyl
h	Hour(s)
Me	Methyl
MeCN	Acetonitrile
mL	Mililiter(s)
mol	Mole(s)
Ms	Methanesulfonyl
ODCB	*ortho*-Dichlorobenzene
Ph	Phenyl
Piv	Pivaloyl
PTSA	*p*-Toluenesulfonic acid
rt	Room temperature
TFA	Trifluoroacetic acid
Ts	*p*-Toluenesulfonyl

1 Introduction

Functionalization of fullerenes can not only retain the unique characteristics of pristine fullerenes but also modulate their properties by attaching different organic addends. Over the past two decades, various types of reactions have been developed to provide a diversity of fullerene derivatives [1]. Among them, transition-metal-mediated or -catalyzed reactions of [60]fullerene (C_{60}) have attracted increasing attention [2–4]. The functionalized fullerenes have huge potential applications in materials science, biology, and nanotechnology [5, 6]. On the other hand, the palladium-catalyzed C–H bond activation has emerged as one of the most important methodologies to construct C–C and C–X bonds in organic synthesis [7–9]. C–H bond activation enables the late-stage diversification of various kinds of organic scaffolds, ranging from relatively small molecules like drug candidates, luminescent compounds for optical applications, and photochromic molecules to complex polydisperse organic compounds such as metal–organic frameworks (MOFs) and polymers [10–12]. Recently, we have been interested in the functional group-

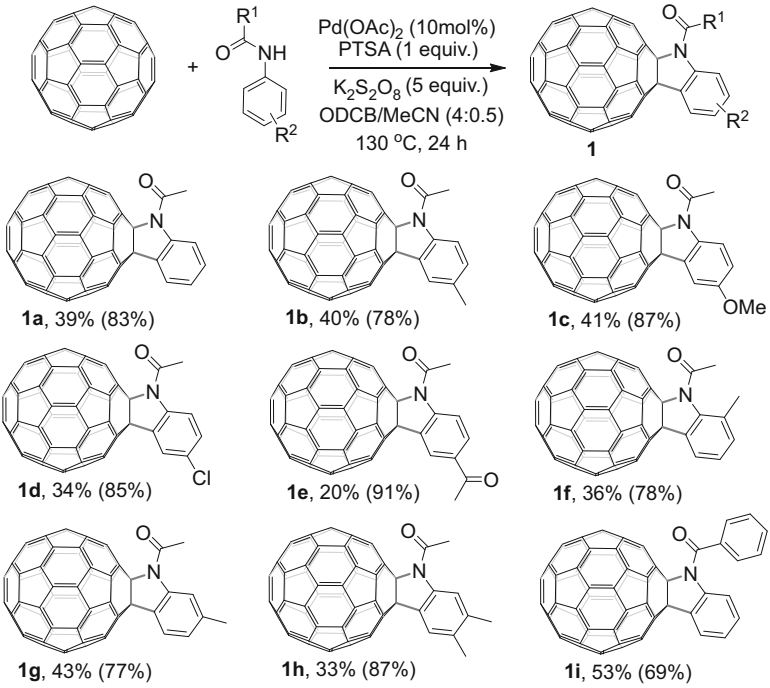
directed sp^2 C–H activations. By employing $NHCOCH_3$, $CONHOCH_3$, $CONH_2$, and N=NAr as the directing groups, we have achieved the *ortho*-acetoxylation [13] and *ortho*-alkoxylation [14] of anilides, *ortho*-alkoxylation of *N*-methoxybenzamides [15], synthesis of phenanthridinones from *N*-methoxybenzamides and aryl iodides [16], synthesis of isoindolinones from *N*-methoxybenzamides and alkenes [17], *ortho*-arylation of benzamides [18], decarboxylative *ortho*-acylation of *O*-methyl ketoximes [19], and decarboxylative *ortho*-acylation of azobenzenes [20]. We have also successfully extended the palladium-catalyzed C–H bond activation strategy to fullerene chemistry. It is known that palladium-catalyzed reactions via non-C–H activation routes have been used for the functionalization of C_{60} [21–27]. Luh and coworkers first developed the palladium-catalyzed [3+2] cycloaddition of C_{60} [21, 22]. The Itami group then reported the palladium-catalyzed hydroarylation of C_{60} with boronic acids and subsequent cleavage of organo(hydro)fullerenes [23, 24], as well as the regioselective unsymmetrical tetraallylation of C_{60} [25, 26]. In this review article, we will focus on the progress in functionalization of C_{60} by the palladium-catalyzed and ligand-directed C–H activation protocols to construct C_{60}-fused heterocycles and carbocycles.

2 Palladium-Catalyzed Formation of [60]Fullerene-Fused Heterocycles

The functionalization of C_{60} via the Pd-catalyzed C–H bond activation usually requires a directing group to achieve high regioselectivity and efficiency. When the directing group contains a heteroatom, it would take part in the formation of palladacycle and the subsequent insertion of C_{60} to give a larger palladacycle intermediate. Reductive elimination of the intermediate generates the C_{60}-fused heterocycle. In this section, we will describe several Pd-catalyzed reactions of C_{60} with different substrates bearing directing groups with a nitrogen or oxygen atom, which involves the formation of the C–N or C–O bond in the C_{60}-fused heterocycles.

2.1 Palladium-Catalyzed Reaction of [60]Fullerene with Anilides

In 2009, the synthesis of [60]fulleroindolines through the Pd-catalyzed heteroannulation of C_{60} with *o*-iodoanilines was reported [28]. Nevertheless, halide by-products were generated, and a large number of *o*-iodoanilines were expensive or difficult to be prepared, thus limiting further application of the present reaction. We had investigated the *ortho*-acetoxylation [13] of anilides via the palladium-

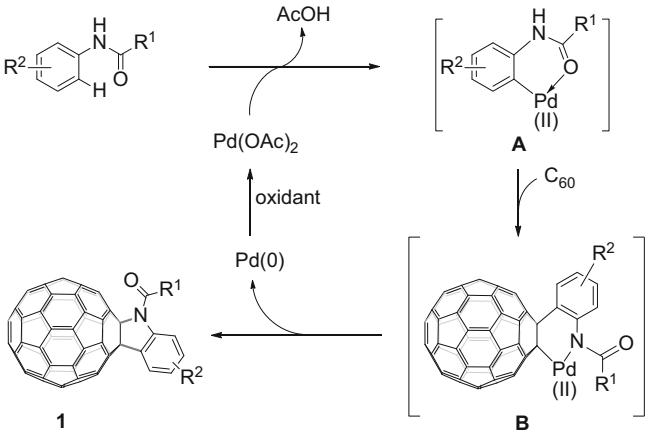


Scheme 1 Pd-catalyzed reaction of C_{60} with anilides

catalyzed C–H activation at that time. It is obvious that it would be highly desirable to utilize anilides instead of *o*-iodoanilines as starting material to functionalize C_{60} (Scheme 1) [29].

With the commercially available acetanilide as the model substrate to react with C_{60}, $K_2S_2O_8$ was found to be a better oxidant than Oxone, $Cu(OAc)_2$, and *p*-benzoquinone (BQ), and *p*-toluenesulfonic acid (PTSA) played a critical role for the success of current heteroannulation of C_{60}. It was noteworthy that a mixture of *ortho*-dichlorobenzene (ODCB, 4 mL) and acetonitrile (MeCN, 0.5 mL) was employed as the solvents. MeCN was added to increase the solubility of the employed inorganic salts.

As shown in Scheme 1, acetanilide and other acetanilides bearing electron-donating groups and weak electron-withdrawing group on the *para* position of the phenyl ring afforded products **1a–d** in 34–41% yields (78–87% yields based on consumed C_{60}). It should be pointed out that the yields in the parentheses of products **1a–d** as well as other products were calculated on the basis of consumed C_{60}. However, substrates with an electron-withdrawing ketone group and the *ortho*-substituent on the phenyl ring retarded the reaction obviously, giving the corresponding products **1e** and **1f** only in 20% and 36% yield, respectively, even by increasing the $Pd(OAc)_2$ loading to 50 mol% in pure ODCB. When anilides were substituted at the *meta* position, products **1g** and **1h** resulting from the reactions at



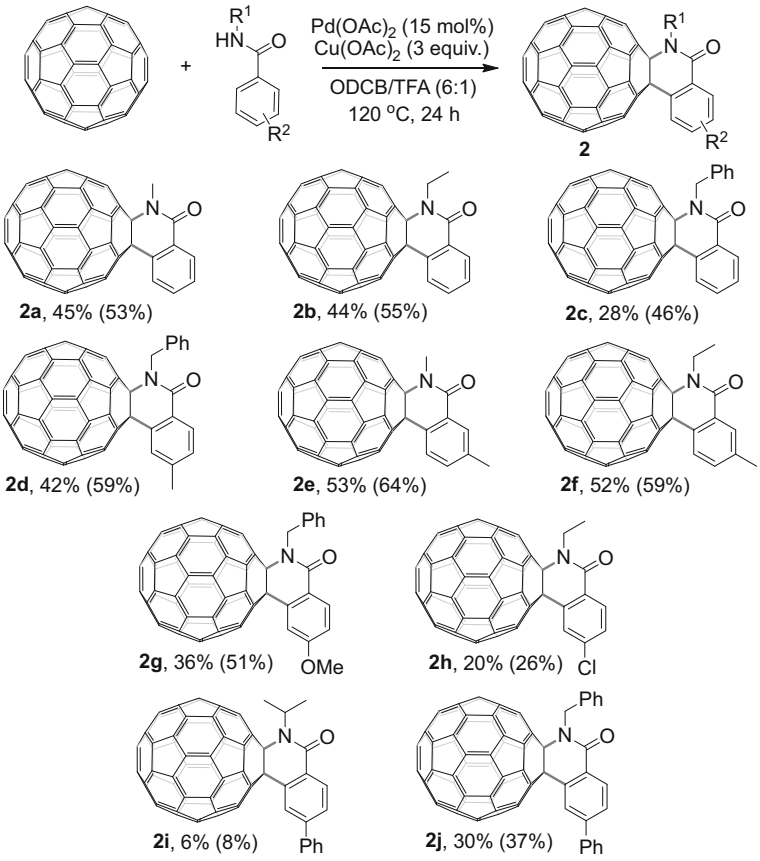
Scheme 2 Proposed reaction mechanism for the Pd-catalyzed reaction of C_{60} with anilides

the less sterically hindered positions were obtained regioselectively in good yields (33–43%). Intriguingly, *N*-benzoylated aniline was found to be the most effective substrate and provided product **1i** in 53% yield.

A plausible mechanism was proposed and is shown in Scheme 2 [29]. The reaction was supposed to be initiated by an amide-directed C–H deprotonation by AcO^- with the help of a Pd(II) species to give the intermediate **A**, followed by insertion of C_{60} into the arylpalladium bond to afford the intermediate **B**. Subsequent reductive elimination of the intermediate **B** produced fulleroindolines and Pd (0). The Pd(0) species was reoxidized to a Pd(II) species by the oxidant $K_2S_2O_8$ to complete the catalytic cycle. All the other annulation reactions of C_{60} to give [60] fullerene-fused heterocycles (vide infra) proceeded via a similar pathway and will not be described in details.

2.2 *Palladium-Catalyzed Reaction of [60]Fullerene with Benzamides*

In the early 2010, the palladium-catalyzed *ortho*-alkoxylation of *N*-methoxybenzamides was realized by using the CONHOMe group as a directing group [15]. Subsequently, the same directing group was utilized for the palladium-catalyzed synthesis of phenanthridinones from *N*-methoxybenzamides and aryl iodides [16] and the palladium-catalyzed synthesis of isoindolinones from *N*-methoxybenzamides and alkenes [17]. The simple amide $CONH_2$ group as the ligand was later also employed to direct the palladium-catalyzed *ortho*-arylation of benzamides [18]. Therefore, it was natural that the amide-directed C–H activation protocol was extended to fullerene chemistry. During our work on the palladium-catalyzed annulation of benzamides to C_{60}, Chuang and coworkers



Scheme 3 Pd-catalyzed reaction of C_{60} with benzamides

independently discovered the same reaction. Thus, we jointly published these results (Scheme 3) [30].

Systematic screening of a range of oxidants and solvents for the Pd-catalyzed heteroannulation of C_{60} with *N*-methyl benzamide revealed that $Cu(OAc)_2$ and ODCB/TFA (6:1) performed best, giving fulleroisoquinolinone **2a** in 45% yield. Then a variety of substrates with either electron-donating or electron-withdrawing groups on their benzamide aryl rings were examined, and fulleroisoquinolinones **2b–j** were isolated in 6–53% yields (8–64% yield based on converted C_{60}). Substrates containing electron-donating groups generally afforded the corresponding fulleroisoquinolinones **2d–g** in good yields (36–53%). In addition, substrates with a *meta* substituent underwent regioselective C–H activations at their less hindered positions. In contrast, substrates bearing electron-withdrawing groups such as the chloro and phenyl units provided products **2h–j** in only moderate yields (6–30%). It should be noted that under the standard conditions, the reactions of amides bearing *N*-benzyl substituent with C_{60} yielded debenzylated products. Therefore, only

0.2 mL of TFA was used for these substrates to give the desired products **2c**, **2d**, **2g**, and **2j** in 28, 42, 36, and 30% yields, respectively. The extremely low yield of **2i** may be attributed to the bulkiness of the isopropyl group that made the formation of palladacycle difficult.

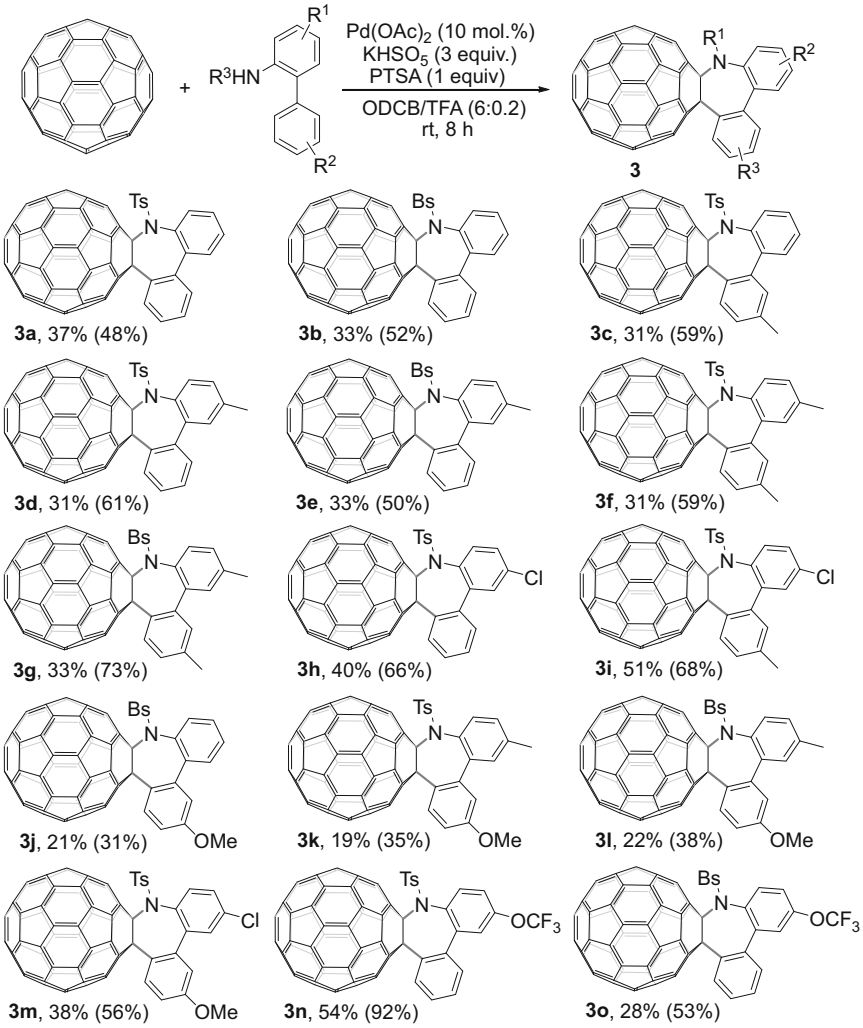
Similar to our previous conditions [29], we found that the combination of $K_2S_2O_8$ and mesitylenesulfonic acid (MesSA) was also applicable to the palladium-catalyzed reaction of C_{60} with benzamides.

2.3 Palladium-Catalyzed Reaction of [60]Fullerene with N-Sulfonyl-2-aminobiaryls

2-Aminobiaryls have been utilized to construct different sizable heterocycles. The Pd(II)-catalyzed cross-coupling of *N*-sulfonyl-2-aminobiaryls with alkenes to afford phenanthridine derivatives [31] and C–H bond activation/intramolecular amidation to synthesize carbazoles from 2-acetaminobiphenyls [32] have been demonstrated. Chuang and coworkers then developed the Pd(II)-catalyzed synthesis of [60]fulleroazepines from the reaction of C_{60} and *N*-sulfonyl-2-aminobiaryls through C–H bond activation and sequential C–C and C–N bond formation at room temperature (Scheme 4) [33].

Screening the Pd-catalyzed reaction of C_{60} with *N*-tosyl-2-aminobiphenyl showed that 10 mol% of $Pd(OAc)_2$, 3 equiv. of $KHSO_5$, and 1 equiv. of PSTA in 6.2 mL of ODCB/TFA (6:0.2) at ambient temperature were the optimal conditions. It was found that the new system using hybrid acids of PTSA and TFA was important for synthesis of the 7-membered-ring heterocycle under very mild conditions. This success was believed to be the unusual stability made by the hybrid acid system that stabilized the eight-membered palladacycle intermediates.

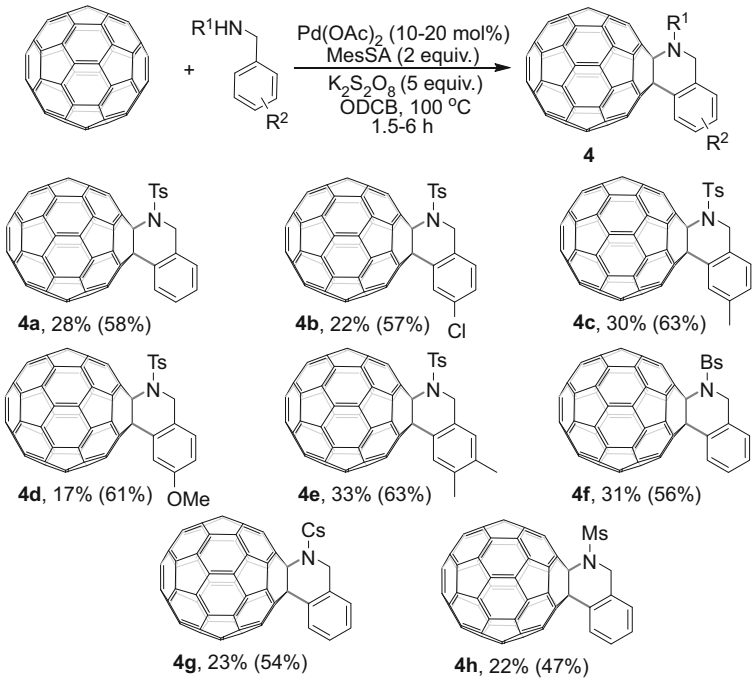
With the optimized results in hand, the scope and generality of the reaction by employing a variety of substrates containing electron-donating and electron-withdrawing groups on both the aromatic rings of 2-aminobiaryls were next investigated. The *N*-sulfonyl-2-aminobiaryls without substituent on any aryl rings underwent reaction with C_{60} smoothly to give **3a** and **3b** in 37% and 33% isolated yields, respectively. Substrates with electron-donating methyl groups on the aryl rings afforded **3c–g** in 31–33% yields. It was also observed that C–H activations occurred regioselectively at the less hindered and more electron-rich *para* positions relative to the methyl substituents to give **3c**, **3f**, and **3g**. Surprisingly, substrates bearing electron-withdrawing chloro group gave products **3h** and **3i** in excellent yields (40% and 51%). Products **3j–l** were isolated in lower chemical yields (19–22%) due to the formation of bis- and multi-addition products. It was suggested that the presence of an electron-donating methoxy group made the substrates more reactive. However, a relatively good yield (38%) could be obtained for **3m** with the additional presence of an electron-pulling chloro group. Substrates with a trifluoromethoxy (OCF_3) group afforded **3n–o** in 28–54% yields.



Scheme 4 Pd-catalyzed reaction of C_{60} with *N*-sulfonyl-2-aminobiaryls

2.4 Palladium-Catalyzed Reaction of [60]Fullerene with N-Benzyl Sulfonamides

It was previously reported that the amide-directed *ortho* C–H bond activation occurred selectively at the benzamide phenyl ring rather than at the phenyl ring of the *N*-benzyl moiety for the Pd-catalyzed reaction of C_{60} with *N*-benzyl benzamides [30]. Intriguingly, in efforts to extend *N*-benzyl benzamides to other substrates, we found that the usage of *N*-benzyl sulfonamides changed the site

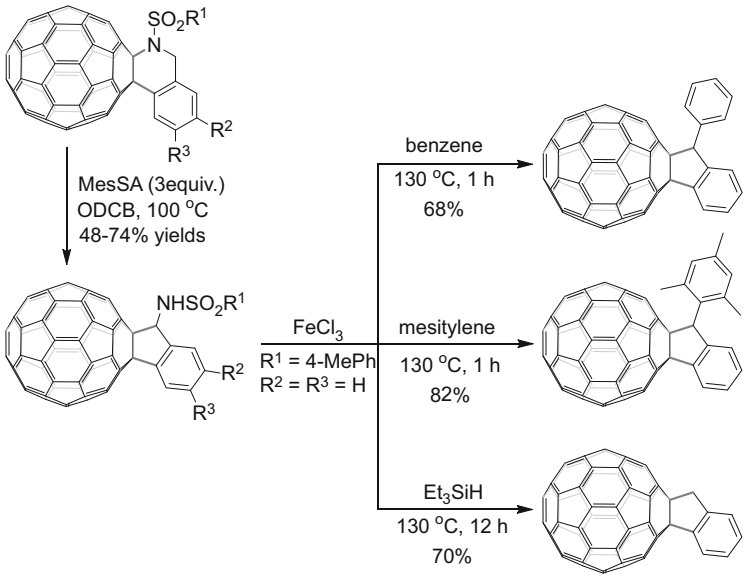


Scheme 5 Pd-catalyzed reaction of C_{60} with *N*-benzyl sulfonamides

selectivity of the *ortho* C–H activation to the phenyl ring of the *N*-benzyl moiety, which provided C_{60}-fused tetrahydroisoquinolines (Scheme 5) [34].

Initially, the Pd-catalyzed reaction of C_{60} with *N*-benzyl-4-toluenesulfonamide was selected as the model reaction for optimization study. It was found that $K_2S_2O_8$ was the best oxidant for the reaction at 100°C. Although both TFA (0.5 mL) and MesSA (2 equiv.) were effective additives to promote the reaction, MesSA was superior to TFA in terms of both the amount of the used acid and product yield based on converted C_{60}. A wide variety of *N*-benzyl sulfonamides with electron-withdrawing group (4-Cl) and electron-donating groups (4-Me, 4-MeO, 3,4-$(Me)_2$) on the benzylamine moiety could be used to afford products **4b–e** in 17–33% yields. It should be noted that the substrate with a 4-MeO group tended to generate more by-products under the employed standard conditions. As a result, the reaction temperature and the amount of MesSA were lowered to 70°C and 1 equiv., respectively, and the desired product **4d** could be obtained in 17% yield. Product **4e** was formed regioselectively from *N*-(3,4-dimethylbenzyl)-4-toluenesulfonamide in 33% yield due to steric hindrance. In addition, different functional groups attached to the nitrogen atom such as benzenesulfonyl (Bs), 4-chlorobenzenesulfonyl (Cs), and methanesulfonyl (Ms) worked well, and the corresponding products **4f–h** were obtained in 22–31% yields.

Intriguingly, the obtained C_{60}-fused tetrahydroisoquinolines could be transformed to C_{60}-fused indanes through a MesSA-promoted rearrangement.



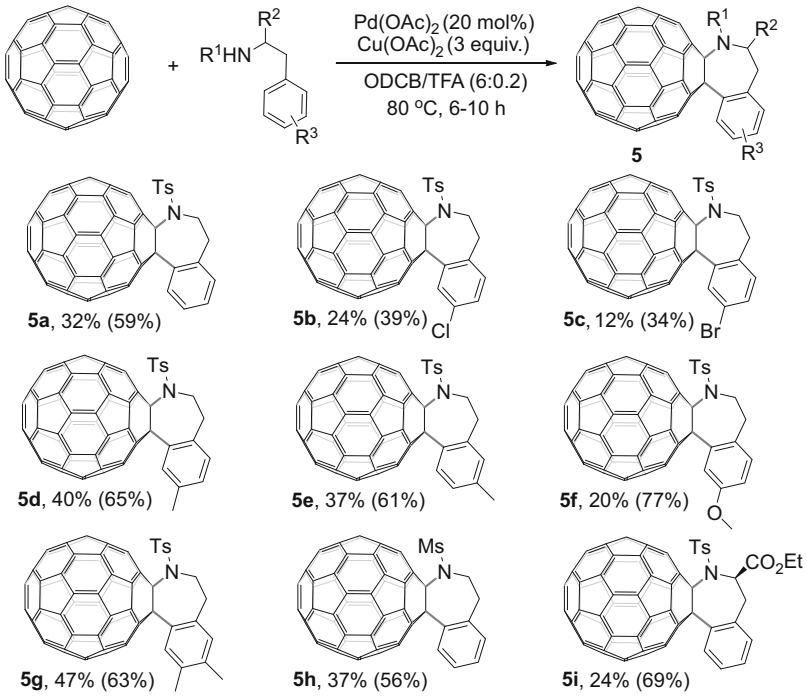
Scheme 6 MesSA-promoted rearrangement of C_{60}-fused tetrahydroisoquinolines to C_{60}-fused indanes and subsequent $FeCl_3$-promoted reactions

Furthermore, the sulfonamide group in C_{60}-fused indanes could be removed or replaced with an aryl group by the $FeCl_3$-promoted reduction and Friedel–Crafts-type reaction (Scheme 6) [34].

2.5 *Palladium-Catalyzed Reaction of [60]Fullerene with N-(2-Arylethyl) Sulfonamides*

2-Arylethylamines have been exploited to construct heterocycles via C–H activation reactions. Orito et al. reported the Pd-catalyzed direct aromatic carbonylation of 2-arylethylamines [35]. The Yu group developed the Pd-catalyzed intramolecular C–H aminations to prepare indolines from 2-arylethyl triflamides and 2-arylethyl 2-pyridylsulfonamides [36–38]. However, using 2-arylethylmine derivatives to construct seven-membered tetrahydrobenzazepines via C–H activation protocol had not been reported yet. We succeeded in the heteroannulation of C_{60} with various *N*-(2-arylethyl) sulfonamides to give the rare C_{60}-fused tetrahydrobenzazepines through the Pd-catalyzed C–H activation protocol (Scheme 7) [39].

The reaction of C_{60} with *N*-phenethyl-*p*-toluenesulfonamide as the model reaction was initially chosen to screen the optimal conditions. By employing the similar conditions for the Pd-catalyzed reaction of C_{60} with *N*-benzyl sulfonamides [34], that is, a combination of $K_2S_2O_8$ and MesSA, the model reaction gave a yield of only 6%. Further optimization revealed that $Cu(OAc)_2$ as the oxidant and ODCB/



Scheme 7 Pd-catalyzed reaction of C_{60} with *N*-(2-arylethyl) sulfonamides

TFA (6.2 mL, v/v = 30:1) as the solvent were the optimal reaction conditions to provide product **5a** in 32% yield.

N-Phenethyl-*p*-toluenesulfonamide and other substrates with either electron-withdrawing or electron-donating groups on the 2-arylethylamine ring worked well and gave the desired products **5a**–**g** in 12–47% yields. Among them, substrates with an electron-withdrawing chloro or bromo group at the *para* position of the phenyl ring gave **5b** and **5c** in lower yields based on consumed C_{60} because they tended to generate some fullerene by-products. Furthermore, 2-phenethylamine with the Ms group attached to the nitrogen atom was also effective and gave **5h** in 37% yield. Interestingly, the tosylamide of L-phenylalanine was also reactive under our optimal conditions, and the novel C_{60}-fused amino acid derivative **5i** was obtained in 24% yield.

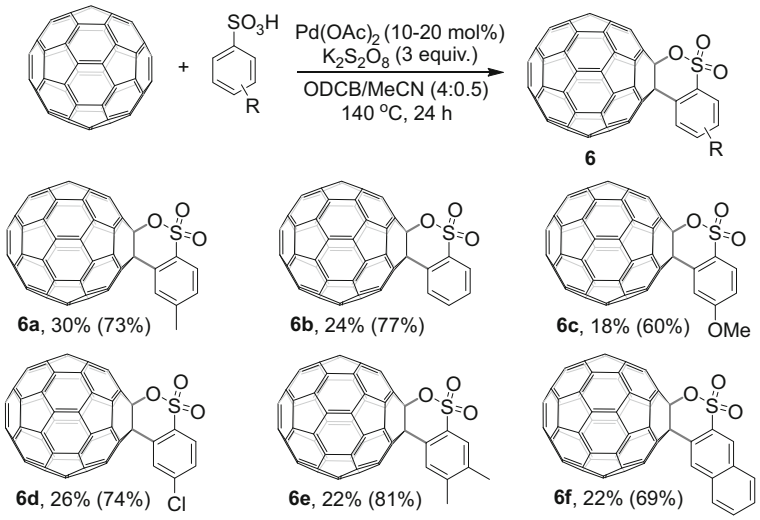
It is noteworthy that the synthesis of [60]fulleroazepines from rigid *N*-sulfonyl-2-aminobiaryls required a hybrid acid system (PTSA/TFA) [33]. In the present work, flexible *N*-(2-arylethyl) sulfonamides incorporating an alkyl chain, even the chiral amino acid moiety, were utilized as the substrates, and only TFA was required as the acid additive. In addition, $Pd(OAc)_2/Cu(OAc)_2$ in ODCB-TFA (7 mL, v/v = 6 : 1), which was similar to our system, was totally inert in Chuang's work. The rare C_{60}-fused seven-membered ring products were supposed to be

generated by C–H activation via a hard-to-form eight-membered-ring palladacycle intermediate, which still remains as a great challenge.

2.6 *Palladium-Catalyzed Reaction of [60]Fullerene with Arylsulfonic Acids*

Carboxylic acids have been utilized to direct C–H bond activations, and C–H halogenation, arylation, alkylation, olefination, hydroxylation, and carboxylation reactions have been successfully realized. PTSA has been frequently added to promote Pd-catalyzed C–H activation reactions by increasing the electrophilicity of the Pd(II) center [29, 33, 40]. Just like carboxylic acids, it is possible that arylsulfonic acids can be functionalized via sulfonic acid group-directed C–H activation. However, such arylsulfonic acid derivatives had not been reported in the aforementioned reactions involving PTSA [29, 33, 40]. The electron-deficient aryl ring of arylsulfonic acids is less prone to the C–H activation step compared to that of aryl carboxylic acids. Nevertheless, we successfully achieved the synthesis of C_{60}-fused sultones by the Pd-catalyzed reaction of arylsulfonic acids with C_{60} via unprecedented sulfonic acid group-directed C–H bond activation (Scheme 8) [41].

Screening the reaction conditions showed that $K_2S_2O_8$ as the oxidant and ODCB (4 mL)/MeCN (0.5 mL) as the solvent at 140 °C for 24 h were the optimal conditions, similar to those for the previously reported Pd-catalyzed reaction of C_{60} with anilides [29].



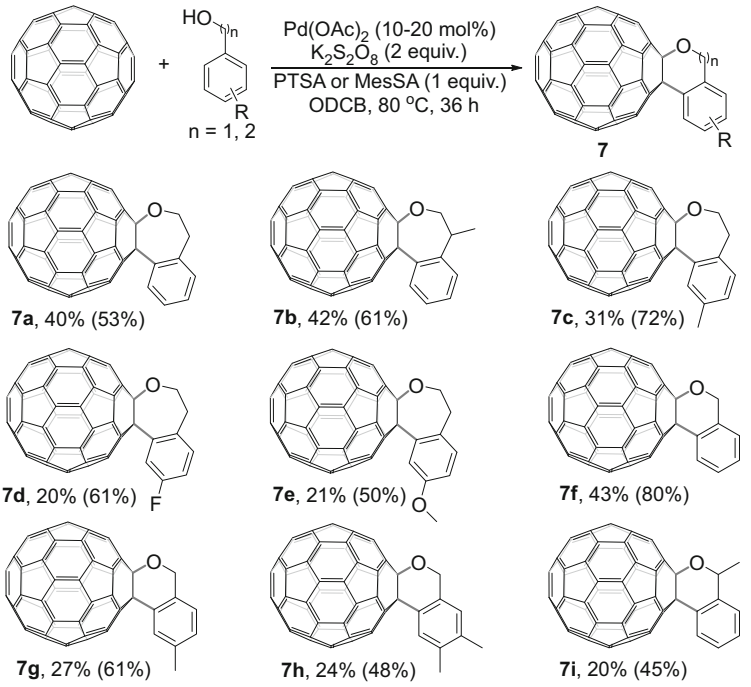
Scheme 8 Pd-catalyzed reaction of C_{60} with arylsulfonic acids

Arylsulfonic acids with both electron-donating and electron-withdrawing substituents on the phenyl ring could be smoothly transformed into the desired products **6a–e** in 18–30% yields. β-Naphthylsulfonic acid could also be employed and provided sultone **6f** in 22% yield. Although C_{60} could be successfully utilized in the Pd-catalyzed C–H activation of arylsulfonic acids, the attempts to functionalized PTSA with other olefins such as acrylates and styrenes failed under conditions previously employed for aromatic carboxylic acids or other combinations of $Pd(OAc)_2$, oxidants, and solvents, reflecting the unique property of C_{60}.

2.7 Palladium-Catalyzed Reaction of [60]Fullerene with 2-Phenylethyl/Benzyl Alcohols

The Pd-catalyzed hydroxyl-directed C–H activation reactions remain difficult to perform due to the possible oxidation, β-hydride elimination, and weak coordination of alcohols with Pd(II) [42–44]. Only three works on the Pd-catalyzed olefination [42], intramolecular cyclization [43], and carbonylation [44] of phenethyl alcohols had been reported before we investigated their application in fullerene chemistry. We recently achieved the hydroxyl-directed C–H activation/C–O cyclization reactions of phenethyl alcohols and benzyl alcohols with C_{60} to afford C_{60}-fused tetrahydrobenzooxepine and isochroman derivatives (Scheme 9) [45]. It should be noted that the Pd-catalyzed C–H activation of benzyl alcohols had no precedent.

Screening the $Pd(OAc)_2$-catalyzed reaction of representative 2-phenylethanol with C_{60} indicated that oxidant $K_2S_2O_8$ performed best and arylsulfonic acids such as PTSA and MesSA played critical role in the reaction. Unlike the previous Pd-catalyzed hydroxyl-directed C–H activations [26–28], our protocol does not require extra base additives as well as amino acid ligands. As shown in Scheme 9, phenylethyl alcohol gave the desired C_{60}-fused tetrahydrobenzooxepine **7a** in 40% yield. The methyl substituent at the benzylic position did not affect the reaction, and product **7b** was obtained in 42% yield. Substrates containing either an electron-donating group or electron-withdrawing group on the phenyl ring could also be used and provided products **7c–e** in 20–31% yields. In addition, it was found that benzyl alcohols were also compatible with the present reaction. Benzyl alcohol provided C_{60}-fused isochroman **7f** in 43% yield, showing a high efficiency of this C–H activation/C–O cyclization protocol. Nevertheless, 4-methylbenzyl alcohol and 3,4-dimethylbenzyl alcohol gave inferior results and afforded products **2g** and **2h** in 27% and 24% yields, respectively. A secondary alcohol could also be employed, and product **2i** was isolated in 20% yield.

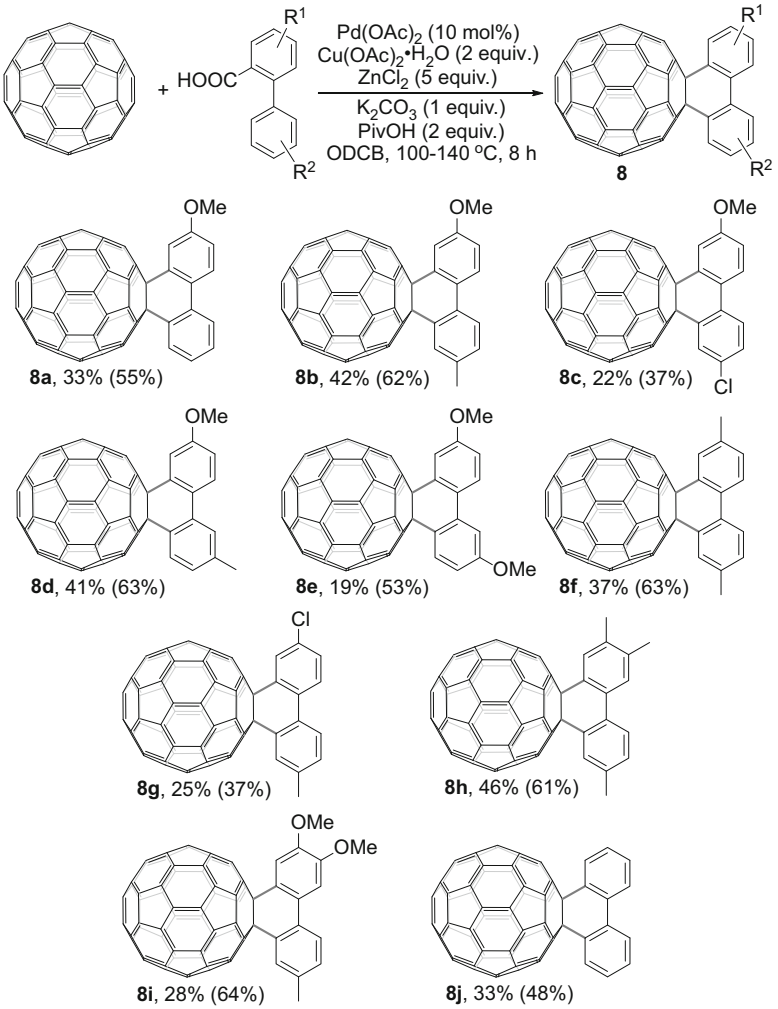


Scheme 9 Pd-catalyzed reaction of C_{60} with phenethyl and benzyl alcohols

3 Palladium-Catalyzed Reaction of [60]Fullerene with 2-Arylbenzoic Acids

The abovementioned palladium-catalyzed reactions of C_{60} via C–H activation involved directing groups with a nitrogen or oxygen atom, which participated in the formation of palladacycle intermediates and C_{60}-fused heterocycles. The attached heteroatoms in C_{60}-fused heterocycles would lower the LUMO energy levels of fullerene derivatives and thus are not beneficial to the improvement of open-circuit voltage (V_{oc}), a key factor for organic photovoltaic devices. Therefore, it is desirable to synthesize fullerene derivatives with two carbon atoms directly attached to the fullerene skeleton in order to achieve higher V_{oc}. The recent synthesis of phenanthrenes from 2-phenylbenzoic acids with alkynes through a decarboxylation/C–H activation sequence prompted us to investigate the palladium-catalyzed decarboxylative coupling of 2-arylbenzoic acids with C_{60} to obtain C_{60}-fused carbocycles (Scheme 10) [46].

Optimization of the reaction conditions revealed that $Cu(OAc)_2$ was the best oxidant and Lewis acid $ZnCl_2$ was crucial for the success of this formal [4+2] annulation reaction. It was believed that $ZnCl_2$ may facilitate the process of decarboxylation. Furthermore, the addition of K_2CO_3 and PivOH could improve the reaction efficiency.



Scheme 10 Pd-catalyzed reaction of C_{60} with 2-arylbenzoic acids

4-Methoxy biphenyl-2-carboxylic acid with an electron-donating methyl group at the 4′-position exhibited good reactivity to afford **8b** in 42% yield. In comparison, only 22% yield was obtained for **8c** with an electron-withdrawing chloro group at the 4′-position. Similarly, the electronic effect was also very obvious when different substituent groups were situated at the 3′-position. The methyl group performed far better than the methoxy group, and products **8d** and **8e** were isolated in 41% and 19% yields, respectively. Furthermore, 4′-methyl-biphenyl-2-carboxylic acids with both electron-donating and electron-withdrawing substituents at the 4-position could be smoothly transformed into the desired products **8f–i** in 25–46% yields.

Finally, the simplest 2-phenylbenzoic acid could also be used to produce **8j** in 33% yield.

The cyclic voltammetry of **8a–j** showed that they had similar first reduction potentials to that of 6,6-phenyl-C_{61}-butyric acid methyl ester (PCBM), which has been widely used as an acceptor in organic photovoltaics. The LUMO levels of fullerene compounds are estimated by their onset reduction potentials (LUMO = $(E_1 + 4.8)$ eV). The high LUMO levels of the obtained C_{60}-fused carbocycles are expected to result in high V_{oc}, and thus, they may have potential application as acceptors in organic photovoltaic devices.

4 Conclusion

In summary, the palladium-catalyzed C–H bond activation protocols have been successfully exploited in the functionalization of C_{60}. Several types of substrates containing directing groups with a nitrogen or oxygen atom have been employed to form C_{60}-fused heterocycles. Anilides, benzamides, *N*-sulfonyl-2-aminobiaryls, *N*-benzyl sulfonamides, *N*-(2-arylethyl) sulfonamides, arylsulfonic acids, and 2-phenylethyl/benzyl alcohols have been employed to react with C_{60} to synthesize C_{60}-fused heterocycles. These C–H activation reactions involve palladacycle intermediates, of which ring size ranges from a 6-membered ring to a hard-to-form 8-memebered ring. The palladium-catalyzed decarboxylative coupling of 2-arylbenzoic acids with C_{60} to generate C_{60}-fused carbocycles has also been disclosed recently. It is expected that continual exploration of the C–H bond activation strategy to functionalize fullerenes will widen the substrate scope and produce more novel fullerene derivatives with different heterocycles and carbocycles.

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