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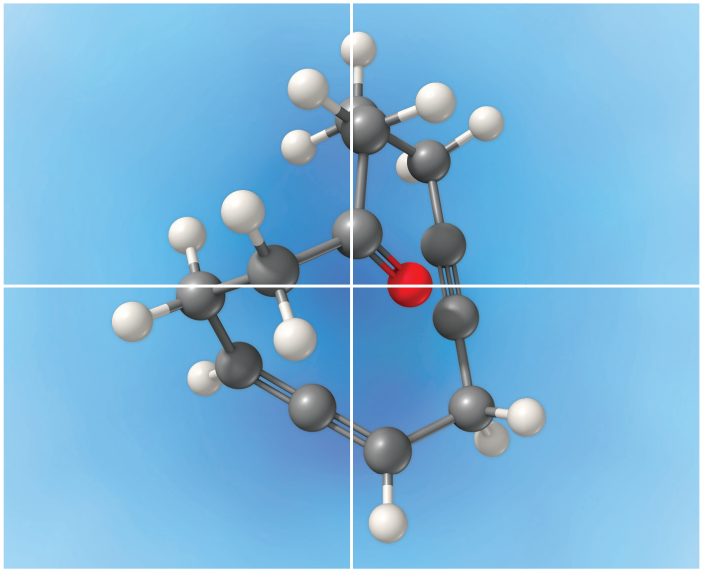

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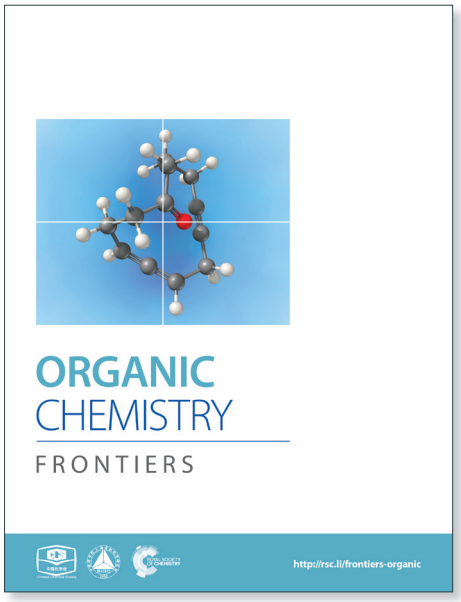

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Research Article

Palladium-catalyzed heteroannulation of [60]fullerene with *N*-(2-arylethyl) sulfonamides via C–H bond activation

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Palladium-catalyzed heteroannulation of [60]fullerene with various *N*-(2-arylethyl) sulfonamides afforded a variety of [60]fullerene-fused tetrahydrobenzazepines. These reactions were initiated by C–H bond activation and followed by cyclization. In addition, further transformation and electrochemistry of the obtained [60]fullerene-fused tetrahydrobenzazepines were investigated.

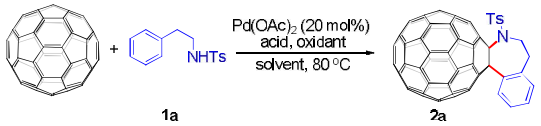
Due to immense potential applications in materials science and biological science, fullerenes and their derivatives have attracted significant attentions.[1] A vast number of chemical reactions have been discovered to functionalize fullerenes over the past two decades.[2] Among them transition-metal-mediated or -catalyzed reactions of [60]fullerene (C_{60}) have attracted increasing attention.[3] Recently, our group has investigated reactions of C_{60} mediated by transition metal salts such as $Mn(OAc)_3$,[3a,c] $Fe(ClO_4)_3$,[4] $Cu(OAc)_2$,[5] $Pb(OAc)_4$[6] and Ag_2CO_3[7] to obtain a variety of novel fullerene products. Functionalization of C_{60} through Pd-catalyzed C–H bond activation strategy has also been disclosed. However, this protocol is relatively underdeveloped and limited to a few Pd-catalyzed heteroannulations of C_{60} with anilides,[8a] benzamides,[8b] arylsulfonic acids,[8c] *N*-benzyl sulfonamides,[8d] phenylethyl/benzyl alcohols[8e] and *N*-sulfonyl-2-aminobiaryls.[9] Therefore, there is still a demand to prepare more fullerene compounds with different appended moieties through Pd-catalyzed C–H bond activation.

On the other hand, Pd-catalyzed ligand-directed C–H bond activation has emerged as one of the most powerful tools to construct C–C and C–X (X = heteroatom) bonds in organic synthesis.[10] 2-Arylethylamines have been applied to construct heterocycles via C–H activation reactions.[11] Orito *et al* reported the Pd-catalyzed direct aromatic carbonylation of 2-arylethylamines.[11a] The Yu group developed the Pd-catalyzed intramolecular C–H aminations to prepare indolines from 2-arylethyl triflamides and 2-arylethyl 2-pyridylsulfonamides.[11b-d] However, using 2-arylethylmine derivatives to construct seven-membered tetrahydrobenzoazepine via C–H activation strategy is unknown until now.

As the formation of C_{60}-fused seven-membered-ring compounds through Pd-catalyzed C–H bond activation presumably proceeds through a relatively scarce eight-membered palladacycle intermediate, the synthesis of C_{60}-fused seven-membered-ring compounds remains a great challenge.[8e,9] In continuation of our Pd-catalyzed reactions of C_{60},[8] herein we report the novel heteroannulation of C_{60} with various *N*-(2-arylethyl) sulfonamides to give the rare C_{60}-fused tetrahydrobenzazepines through Pd-catalyzed C–H activation protocol. Furthermore, these C_{60}-fused tetrahydrobenzazepines were found to undergo TfOH-promoted rearrangements.

We chose the reaction of C_{60} with *N*-phenethyl-*p*-toluenesulfonamide (**1a**) as the model reaction to screen the optimal conditions. At the onset, C_{60} (36 mg, 0.05 mmol) was allowed to react with 3 equiv of **1a** in the presence of 3 equiv of $K_2S_2O_8$, 1 equiv of mesitylenesulfonic acid dihydrdate (MesSA) and 20 mol% of $Pd(OAc)_2$ in 6 mL of *o*-dichlorobenzene (ODCB) at 80 °C for 10 h. To our satisfaction, the desired fullerotetrahydrobenzazepine **2a** was obtained in 6% yield (Table 1, entry 1). Replacing MesSA with *p*-toluenesulfonic acid (PTSA)

Table 1 Screening conditions for the reaction of C_{60} with 1a[a]



1a 2a

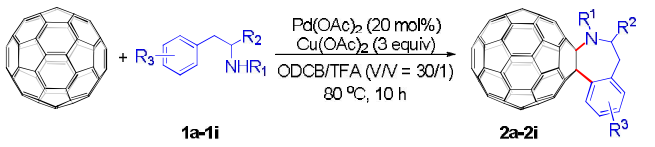
Entry	Acid	Oxidant	Solvent (mL)	Yield of **2a** (%)[b]
1[c]	MesSA	$K_2S_2O_8$	ODCB (6)	6 (30)
2[c]	PTSA	$K_2S_2O_8$	ODCB (6)	14 (50)
3[c]	PTSA/TFA	$K_2S_2O_8$	ODCB (6)	18 (36)
4	TFA	$K_2S_2O_8$	ODCB (6)	18 (60)
5[d]	AcOH	$K_2S_2O_8$	ODCB (6)	trace
6[e]	PivOH	$K_2S_2O_8$	ODCB (6)	trace
7	TFA	Oxone	ODCB (6)	8 (36)
8	TFA	AgOAc	ODCB (6)	< 3%
9	TFA	BQ	ODCB (6)	7 (58)
10	TFA	$Cu(OAc)_2$	ODCB (6)	30 (55)
11[c]	PTSA	$Cu(OAc)_2$	ODCB (6)	trace
12	TFA	$Cu(OAc)_2$	ODCB/DMSO (5:1)	0
13	TFA	$Cu(OAc)_2$	ODCB/CH_3CN (5:1)	0
14	TFA	$Cu(OAc)_2$	ODCB/DMF (5:1)	0
15[f]	TFA	$Cu(OAc)_2$	ODCB (6)	17 (49)
16[g]	TFA	$Cu(OAc)_2$	ODCB (6)	32 (59)

[a]Unless otherwise specified, all reactions were performed with 0.05 mmol of C_{60}, 0.15 mmol of **1a**, 20 mol% of $Pd(OAc)_2$, 0.15 mmol of oxidant and 0.3 mL of acid in 6 mL of ODCB at 80 °C for 10 h. [b]Isolated yield, that in parentheses was based on consumed C_{60}. [c]1 equiv of the solid acid was used. [d]0.3 mL of AcOH was used. [e]193 mg of PivOH was used. [f]10 mol% of $Pd(OAc)_2$ was used, and the reaction time was 18 h. [g]0.2 mL of TFA was used. Ts = *p*-toluenesulfonyl, DMSO = dimethyl sulfoxide, DMF = *N*,*N*-dimethylformamide.

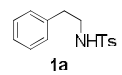
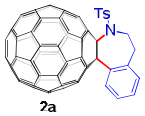
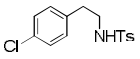
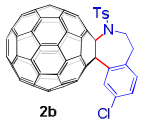
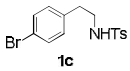
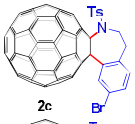
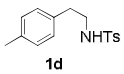
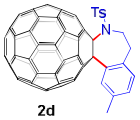
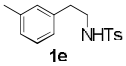
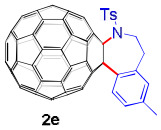
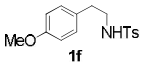
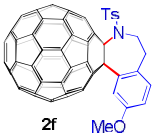
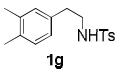
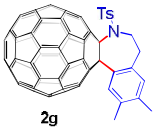
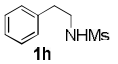
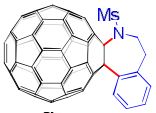
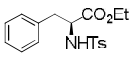
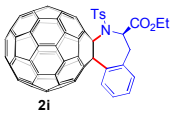
led to **2a** in 14% yield (Table 1, entry 2). When the reaction was performed in a mixture of PTSA (1 equiv) and trifluroacetic acid (TFA, 0.3 mL),[9] the product yield could be further improved to 18% yield (Table 1, entry 3). However, TFA itself also provided a comparative yield with much more recovered C_{60} (Table 1, entry 4 vs entry 3). The use of acetic acid (AcOH) or pivalic acid (PivOH) to replace TFA was unsuccessful (Table 1, entries 5 and 6). All these results suggested that TFA was more suitable for this reaction. The critical role played by TFA was believed to participate in the in situ formation of a more reactive $Pd(TFA)_2$ species from the $Pd(OAc)_2$ precatalyst,[12] thus promoting the current heteroannulation of C_{60}. After the acid was selected, several oxidants were screened. Compared to $K_2S_2O_8$, Oxone, AgOAc and *p*-benzoquinone (BQ), $Cu(OAc)_2$ afforded the best result with a yield of 30% (Table 1, entry 10 vs entries 4 and 7-9). Notably, the fruitless attempt to replace TFA with PTSA further confirmed that TFA was the best acid for this reaction (Table 1, entry 11). In addition, the desired reaction did not take place in the presence of DMSO, CH_3CN or DMF (Table 1, entries 12−14). Reducing the $Pd(OAc)_2$ loading decreased the product yield dramatically (Table 1, entry 15 vs entry 10). Gratifyingly, decreasing the amount of TFA from 0.3 mL to 0.2 mL could give a slightly better yield (32%) (Table 1, entry 16 vs entry 10). Therefore, 0.05 mmol of C_{60}, 20 mol% of $Pd(OAc)_2$, 3 equiv of **1a**, 3 equiv of $Cu(OAc)_2$ with ODCB/TFA (6.2 mL, v/v = 30:1) as the solvent at 80 °C were selected as the optimal reaction conditions.

With the optimal conditions in hand, the scope of this annulation was explored by using a variety of substrates as illustrated in Table 2. We were pleased to find that all of the examined *N*-(2-arylethyl) sulfonamides **1a-1i** could be applied to furnish the desired C_{60}-fused tetrahydrobenzazepines **2a-2i** in synthetically valuable yields. Substrates bearing either an electron-withdrawing group or electron-donating group on the 2-arylethylamine ring worked well and gave the desired products **2b-2g** in 12-47% yields (Table 2, entries 2-7). The substrate with an electron-withdrawing chloro or bromo group at the para position of the phenyl ring (**1b, 1c**) gave a lower yield based on consumed C_{60} because it tended to generate some fullerene byproducts, which were most probably formed from the reaction of C_{60} with bulk ODCB (Table 2, entries 2 and 3). The efforts to increase the product yields and inhibit the formation of byproducts by adjusting the reaction temperature and reaction time proved fruitless. Substrate **1d** with a methyl group at the para position of the phenyl ring provided **2d** in 40% yield (Table 2, entry 4), while substrate **1f** with a strong electron-donating methoxy group at the para position of the phenyl ring resulted in a decreased yield (Table 2, entry 6). When substrates were substituted at the meta position (**1e**, **1g**), products resulting from the reactions at the less sterically hindered positions were regioselectively obtained in 37% and 47% yields, respectively (Table 2, entries 5 and 7). In addition, 2-phenethylamine with the methanesulfonyl (Ms) group attached to the nitrogen atom **(1h)** gave a comparable product yield to that of **1a** (Table 2, entry 8 vs entry 1). It is of interest to note that the tosylamide of L-phenylalanine (**1i**) was also reactive under our optimal conditions, and a novel C_{60}-fused amino acid derivative was isolated in 24% yield (Table 2, entry 9).

Table 2 Pd-catalyzed heteroannulation of C_{60} with *N*-(2-arylethyl) sulfonamides **1a-1i**[a]



1a-1i **2a-2i**

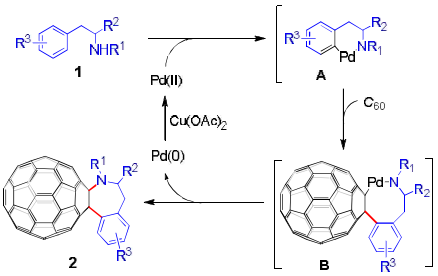
Entry	Substrate **1**	Product **2**	Yield (%)[b]	Recovered C_{60} (%)
1	 **1a**	 **2a**	32 (59)	46
2	 **1b**	 **2b**	24 (39)	38
3	 **1c**	 **2c**	12 (34)	65
4	 **1d**	 **2d**	40 (65)	38
5	 **1e**	 **2e**	37 (61)	39
6	 **1f**	 **2f**	20 (77)	74
7[c]	 **1g**	 **2g**	47 (63)	25
8	 **1h**	 **2h**	37 (56)	34
9	 **1i**	 **2i**	24 (69)	65

[a]Unless otherwise specified, all reactions were performed with 0.05 mmol of C_{60}, 0.15 mmol of **1a-1i**, 0.01 mmol of $Pd(OAc)_2$, 0.15 mmol of $Cu(OAc)_2$ and 0.2 mL of TFA in 6 mL of ODCB at 80 °C for 10 h. [b]Isolated yield, that in parentheses was based on consumed C_{60}. [c]The reaction was performed for 6 h.

All products **2a-2i** were unambiguously characterized by HRMS, ^{1}H NMR, ^{13}C NMR, FT-IR and UV-vis spectra. The ESI mass spectra of **2a-2i** gave the correct molecular ion peaks. In their ^{13}C NMR spectra, the observation of at least 51 lines in the range of 133-156 ppm for the sp^2-carbons of the C_{60} skeleton, and two

peaks at 78-80 ppm and 70-72 ppm for the two sp^3-carbons of the fullerene cage, consistent with the C_1 symmetry of their molecular structures. The IR spectra of **2a-2i** showed two strong absorptions at 1330-1350 cm^{-1} and 1140-1160 cm^{-1} due to the sulfonamide group. Furthermore, their UV-vis spectra displayed a characteristic peak at 433-437 nm, which is the diagnostic absorption for the 1,2-adduct of C_{60}.[7,9]

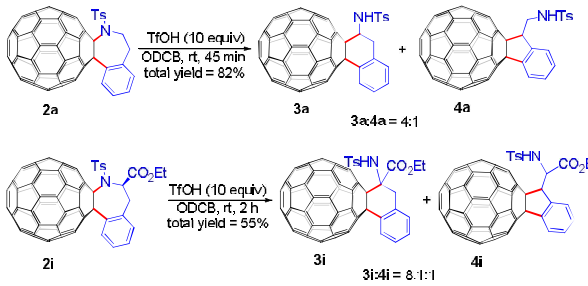
Based on our experimental results and previously suggested mechanisms in the literature,[8,9] a plausible mechanism for the formation of the C_{60}-fused tetrahydrobenzazepines is shown in Scheme 1. Initially, *N*-(2-arylethyl) sulfonamide **1** is coordinated to the Pd(II) species, followed by ortho C–H activation to produce intermediate **A**. Insertion of C_{60} into the arylpalladium bond in **A** yields intermediate **B**. Subsequent reductive elimination of intermediate **B** generates C_{60}-fused tetrahydrobenzazepine **2** and Pd(0). The latter is reoxidized to a Pd (II) species by $Cu(OAc)_2$ to complete the catalytic cycle.



Scheme 1 Proposed reaction mechanism for the formation of C_{60}-fused tetrahydrobenzazepines **2**

The alternative possible five-membered-ring [60]fulleroindanes resulted from annulation at the benzylic position and the ortho position of *N*-(2-arylethyl) sulfonamides were not observed, indicating the preference of the ligand-directed C–H activation pathway. It should be noted that the formation of [60]fulleroazepines via Pd-catalyzed C–H bond activation has been reported.[9] However, only rigid *N*-sulfonyl-2-aminobiaryls were used as the substrates, and a hybrid acids system (PTSA/TFA) was crucial for the efficient formation of the seven-membered-ring products.[9] In our present work, flexible *N*-(2-arylethyl) sulfonamides incorporating an alkyl chain, even chiral amino acid moiety, were employed as the substrates, and only TFA was required as the acid additive (Table 1, Entry 3 vs Entry 4). 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.[9] A related work on C_{60}-fused tetrahydroazepinones and -azepinonimines formed from the $Cu(OAc)_2$-promoted heteroannulations of C_{60} with *N*-sulfonylated *o*-amino-aromatic methyl ketones or *O*-alkyl oximes was recently disclosed.[13] Besides the sulfonamide group, another functional group such as ketone or oxime group was required to facilitate the radical pathway.

The further transformations of representative C_{60}-fused tetrahydrobenzazepines **2a** and **2i** were also investigated. Intriguingly, treatment of C_{60}-fused tetrahydrobenzazepine **2a** with 10 equiv of trifluoromethanesulfonic acid (TfOH) at ambient temperature for 45 min afforded a mixture of fullerotetrahydronaphthalene **3a** and fulleroindane **4a** (4:1) in a total yield of 82%. The attempt to obtain **3a** and **4a** directly from the Pd-catalyzed reaction of C_{60} with **1a** (Table 1, entry 16) by adding 10 equiv of TfOH led to a yield of only 5% along with 79% of recovered C_{60}, showing extremely low efficiency of the direct transformation. Similarly, treatment of C_{60}-fused tetrahydrobenzazepine **2i** with 10 equiv of TfOH for 2 h afforded an 8.1:1 mixture of **3i** and **4i** in 55% yield. Both **3i** and **4i** bearing a phenylalanine moiety which is a biologically active motif, hinting potential application of **3i** and **4i** in biomedical sciences. In addition, the preparation of C_{60}-fused tetrahydronaphthalene[14] and indane[8d,14,15] derivatives are still limited, this method provides a new route to synthesize these two types of compounds.



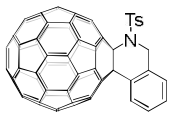
Scheme 2 Transformation of C_{60}-fused tetrahydrobenzazepines **2a** and **2i**

The half-wave reduction potentials of **2a-2i** along with **5** (Fig. 1) and C_{60} were measured by cyclic voltammetry and are summarized in Table 3. We noted that the reduction potentials of C_{60}-fused tetrahydrobenzazepines were dependent on the substituents on the 2-arylethylamine moiety. Products bearing an electron-withdrawing group are reduced more easily, whereas products with electron-donating groups give more negative first redox reduction potentials (**2b-2c** vs **2d-2g**). Compound **2h** bearing the mesyl group has a more positive first redox reduction potential than that substituted by the tosyl group (**2h** vs **2a**). Compared with the seven-membered-ring compound **2a**, the first reduction potential of its six-membered-ring analogue **5** shows a positive shift (–1.120 V for **5** vs –1.133 V for **2a**), exhibiting an effect of the C_{60}-fused ring size. In addition, the first reduction potentials of **2a-2i** and **5** are 40-73 mV negatively shifted compared to that of C_{60}. In consideration of their high solubility in common solvents such as CS_2, $CHCl_3$, chlorobenzene and *o*-dichlorobenzene, C_{60}-fused tetrahydrobenzazepines may have potential application in organic photovoltaic devices when combined with suitable polymer donors.[16,17] Close examination of the cyclic voltammograms indicated that the first two redoxes of **2a-2i** were reversible, while their third redoxes were irreversible. Therefore, this unique electrochemical property may be exploited to generate ring-opened trianions of **2a-2i** by controlled potential electrolysis (CPE), and then undergo nucleophilic reactions with various electrophiles to give other diversified fullerene derivatives.[18]

Table 3 Half-wave reduction potentials (V) of **2a**-**2i**, **5** and C_{60}[a]

compound	E_1	E_2	E_3
2a	–1.133	–1.533	–2.004
2b	–1.128	–1.532	–2.041
2c	–1.124	–1.528	–2.013
2d	–1.135	–1.522	–2.008
2e	–1.132	–1.517	–1.997
2g	–1.140	–1.535	–2.043
2g	–1.149	–1.545	–2.048
2h	–1.118	–1.509	–1.992
2i[b]	–1.122	–1.515	–1.964
5	–1.120	–1.514	–2.000
C_{60}	–1.076	–1.460	–1.925

[a]Potential values versus Fc/Fc^+ reference electrode. Conditions: ca 1 mM of the title compound and 0.1 mM of *n*-Bu_4NClO_4 in anhydrous ODCB; reference electrode: SCE; working electrode: Pt; auxiliary electrode: Pt wire; scanning rate: 20 mV s^{-1}. [b]Saturated solution of **2i**.



5

Fig. 1 Structure of compound **5**.

In summary, we have successfully synthesized the C_{60}-fused tetrahydrobenzazepines by the Pd-catalyzed heteroannulation of [60]fullerene with various *N*-(2-arylethyl) sulfonamides via C–H bond activation strategy. The rare seven-membered products are supposed to be generated via a hard-to-form eight-membered palladacycle intermediate. In the presence of TfOH, the C_{60}-fused tetrahydrobenzazepines could be converted to the C_{60}-fused tetrahydronaphthalene and indane derivatives.

Acknowledgment

We are grateful for financial support from the National Natural Science Foundation of China (No. 21132007) and Specialized Research Fund for the Doctoral Program of Higher Education (20123402130011).

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures and characterization data. See DOI: 10.1039/b000000x/

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