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Synthesis of Fullerotetrahydroquinolines via [4+2] Cycloaddition Reaction of [60]Fullerene with in Situ Generated Aza-*o*-quinone Methides

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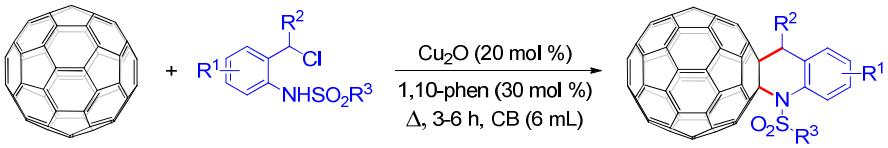
ABSTRACT



An efficient [4+2] cycloaddition reaction of [60]fullerene with the in situ generated aza-*o*-quinone methides from *N*-(*ortho*-chloromethyl)aryl sulfonamides with the assistance of Cu_2O has been developed to afford a series of fullerotetrahydroquinolines. This strategy exhibits a broad substrate scope and

excellent functional group tolerance. A tentative reaction pathway for the formation of fullerotetrahydroquinolines is proposed on the basis of the experimental results.

INTRODUCTION

As a consequence of the huge potential applications in materials, biology, and nanoscience, fullerene derivatives have continued to capture the interest of chemists worldwide.[1] As a result, numerous efforts have been devoted to the efficient construction of various organofullerenes during the past two decades. Among them, [4+2] cycloaddition is one of the most commonly used methods to synthesize [60]fullerene (C_{60})-fused six-membered carbocyclic derivatives.[2] However, reports on the formation of C_{60}-fused six-membered heterocyclic derivatives via [4+2] cycloaddition are relatively limited.[3] In the early 1990s, Eguchi and co-workers reported hetero-Diels-Alder reactions of C_{60} yielding C_{60}-fused dihydropyran and dihydrothiopyran derivatives through the C–O and C–S bond formation, respectively.[3a–c] In 1998, the Martin group realized the first synthesis of nitrogen-bonded C_{60} derivatives via hetero-Diels-Alder reaction of C_{60} with *o*-aminobenzyl alcohols, which were prepared by the reaction of aldehydes with *N*-methylanilinochlorophenylborane in refluxing *o*-dichlorobenzene for 5 h.[3e] Since then, there has been no report on the hetero-Diels-Alder reaction of C_{60}. Therefore, the development of a more straightforward, reliable, and practical method for the

synthesis of diverse C_{60}-fused six-membered heterocyclic derivatives through [4+2] cycloaddition is desirable and challenging.

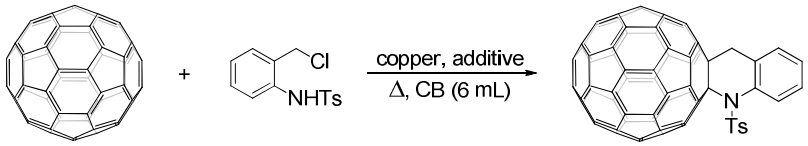
On the other hand, *ortho*-quinone methides (oQMs) are versatile intermediates and have been found extensive applications in organic chemistry due to their highly polarized and quite reactive properties.[4] The cycloaddition reaction of oQMs with various dienophiles provides a facile and efficient method for the construction of heterocyclic compounds. Compared to the well-developed oQMs, the related reports on analogous aza-*o*-quinone methides (aoQMs) as reactive intermediates in the cycloaddition are much less investigated. To date, several methods have been developed for the formation of aoQMs by photolysis,[5] pyrolysis,[6] fluoride-induced elimination,[7] and base-promoted elimination.[8] To the best of our knowledge, the in situ formation of aoQMs assisted by a metal oxide has never been reported. Additionally, it is well recognized that C_{60} behaves as an electron-deficient olefin and undergoes various types of cycloaddition reactions.[2,3] We envisioned that C_{60} should react with the in situ generated aoQMs to form nitrogen-bearing six-membered organofullerenes. In view of our continuing interest in fullerene chemistry,[9,10] herein we report the synthesis of fullerotetrahydroquinolines through hetero-Diels-Alder reaction of C_{60} with the in situ generated aoQMs from *N*-(*ortho*-chloromethyl)aryl sulfonamides with the assistance of Cu_2O.

RESULTS AND DISCUSSION

We initiated our study with the model reaction of C_{60} (0.05 mmol) and *N*-(2-(chloromethyl)phenyl)-4-methylbenzenesulfonamide **1a** (2.0 equiv) in anhydrous chlorobenzene (CB) at 120 °C under an open-air atmosphere (Table 1). The anticipated product **2a** could be isolated in 3% yield without any additive (entry 1). It was reported that aoQMs could be efficiently generated in situ under basic conditions.[8] Therefore, we conducted the reaction in the presence of Na_2CO_3 (2.0 equiv), and the yield of **2a** was increased to 13% (entry 2). The yield could be further improved to 21% when K_2CO_3 was used (entry 3). To our disappointment, Cs_2CO_3, which was frequently employed as the base for the in situ generation of aoQMs from *N*-(*ortho*-chloromethyl)aryl amides,[8a-c,e-h] could hardly promote the formation of **2a** (entry 4). In continuing our interest in copper-involved functionalizations of C_{60},[10] when Cu_2O (2.0 equiv) was utilized to replace K_2CO_3, a better yield of 33% was obtained (entry 5 vs entry 3). To further improve the practicability of the reaction, a catalytic amount (0.2 equiv) of Cu_2O was used. Unfortunately, the yield of **2a** dropped dramatically to 19% (entry 6). To our delight, the yield was increased to 25% when 0.2 equiv of 1,10-phenanthroline (1,10-phen) was added as a ligand to the reaction (entry 7), and the yield was further improved to 33% when 0.3 equiv of 1,10-phen was employed (entry 8). Nevertheless, increasing the amount of 1,10-phen to 0.4 equiv led to a slight decrease of the product yield to 26% (entry 9). It was not beneficial to the formation of **2a** when the amount of Cu_2O was decreased from 0.2 equiv to 0.1 equiv, giving **2a** in only 17% yield (entry 10). Increasing the loading of Cu_2O to 0.3 equiv did not afford a better result (entry 11 vs entry 8). Next,

2,2-bipyridyl (bpy) was employed as the ligand, the yield was decreased slightly to 28%, whereas the yield dropped obviously by replacing with triphenylphosphine (PPh_3), providing **2a** in only 15% yield (entries 12 and 13 vs entry 8). Different copper salts were subsequently evaluated and attempted to further enhance the product yield. To our disappointment, Cu(I) salts such as CuCN, CuSCN, CuCl, CuBr, and CuI could not facilitate the reaction (entries 14–18 vs entry 1). Similar poor results were obtained when CuO, $Cu(OTf)_2$, $Cu(OAc)_2 \cdot H_2O$, and $CuCl_2$ were employed (entries 19–22). The decrease or increase of the loading of substrate **1a** was not beneficial to the improvement of the yield, giving **2a** in 27% and 28% yields, respectively (entries 23 and 24). Reducing or elevating the temperature both decreased the reaction efficiency, providing **2a** in 24% and 27% yields, respectively (entries 25 and 26). In addition, the variation of the reaction time was also investigated, and the results demonstrated that the reaction time of 3.0 h was the best (entries 27 and 28 vs entry 8). Carrying out the reaction under a dry air atmosphere led to a slightly reduced yield of 28% (Table 1, entry 29 vs entry 8). Similarly, the desired product **2a** was isolated in 28% yield under an oxygen atmosphere (Table 1, entry 30 vs entry 8). It is noteworthy that a decreased yield of 25% was obtained under a nitrogen atmosphere, indicating that the open-air atmosphere had certain beneficial influence on the reaction efficiency (Table 1, entry 31 vs entry 8). Thus, the optimal reaction conditions were a molar ratio of 1/2/0.2/0.3 for the reagents C_{60}, **1a**, Cu_2O, and 1,10-phen, and a temperature of 120 ℃ for 3 h in anhydrous chlorobenzene (6 mL) under an open-air atmosphere.

Table 1. Optimization of Reaction Conditions[a]



1a **2a**

entry	copper/additive	molar ratio[b]	yield (%)[c]
1	/	1:2:0:0	3 (75)
2	Na_2CO_3	1:2:0:2	13 (57)
3	K_2CO_3	1:2:0:2	21 (75)
4	Cs_2CO_3	1:2:0:2	3 (43)
5	Cu_2O	1:2:2:0	33 (77)
6	Cu_2O	1:2:0.2:0	19 (70)
7	Cu_2O/1,10-phen	1:2:0.2:0.2	25 (74)
8	**Cu_2O/1,10-phen**	**1:2:0.2:0.3**	**33 (83)**
9	Cu_2O/1,10-phen	1:2:0.2:0.4	26 (74)
10	Cu_2O/1,10-phen	1:2:0.1:0.15	17 (68)
11	Cu_2O/1,10-phen	1:2:0.3:0.45	33 (73)
12	Cu_2O/bpy	1:2:0.2:0.3	28 (72)
13	Cu_2O/PPh_3	1:2:0.2:0.3	15 (71)
14	CuCN/1,10-phen	1:2:0.2:0.3	6 (67)

15	CuSCN/1,10-phen	1:2:0.2:0.3	4 (67)
16	CuCl/1,10-phen	1:2:0.2:0.3	3 (33)
17	CuBr/1,10-phen	1:2:0.2:0.3	4 (67)
18	CuI/1,10-phen	1:2:0.2:0.3	3 (50)
19	CuO/1,10-phen	1:2:0.2:0.3	14 (74)
20	$Cu(OTf)_2$/1,10-phen	1:2:0.2:0.3	3 (75)
21	$Cu(OAc)_2 \cdot H_2O$/1,10-phen	1:2:0.2:0.3	3 (75)
22	$CuCl_2$/1,10-phen	1:2:0.2:0.3	3 (99)
23	Cu_2O/1,10-phen	1:1.5:0.2:0.3	27 (75)
24	Cu_2O/1,10-phen	1:2.5:0.2:0.3	28 (61)
25[d]	Cu_2O/1,10-phen	1:2:0.2:0.3	24 (83)
26[e]	Cu_2O/1,10-phen	1:2:0.2:0.3	27 (64)
27[f]	Cu_2O/1,10-phen	1:2:0.2:0.3	25 (68)
28[g]	Cu_2O/1,10-phen	1:2:0.2:0.3	27 (84)
29[h]	Cu_2O/1,10-phen	1:2:0.2:0.3	28 (88)
30[i]	Cu_2O/1,10-phen	1:2:0.2:0.3	28 (85)
31[j]	Cu_2O/1,10-phen	1:2:0.2:0.3	25 (71)

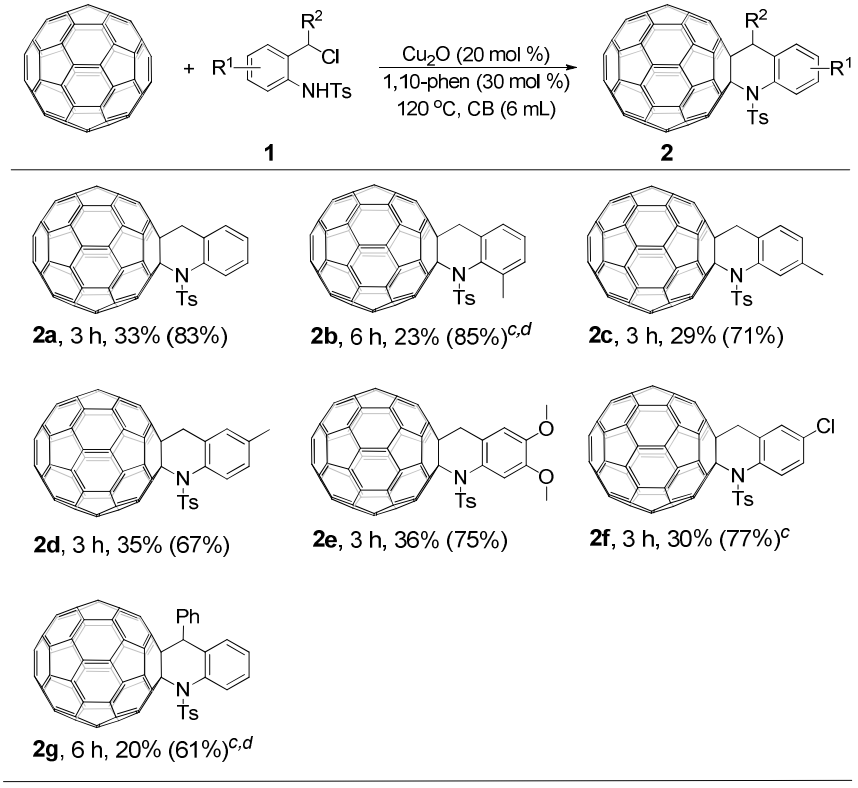
[a]Unless otherwise noted, the reactions were performed in anhydrous chlorobenzene (6 mL) at 120°C under an open-air atmosphere for 3.0 h. [b]Molar ratio referred to C_{60}/**1a**/copper/additive. [c]Isolated yields. Values in parentheses were based on the

consumed C_{60}. [d]The reaction was performed at 110 °C. [e]The reaction was performed at 130 °C. [f]The reaction time was 4.0 h. [g]The reaction time was 2.0 h. [h]The reaction was performed under a dry air atmosphere. [i]The reaction was performed under an oxygen atmosphere. [j]The reaction was performed under a nitrogen atmosphere.

The substrate scope of this transformation was then investigated under the optimized reaction conditions, and the results are presented in Table 2. At first, the reaction of C_{60} with *N*-(2-(chloromethyl)aryl)-4-methylbenzenesulfonamides **1** bearing different substituents on the aromatic ring was examined. The reaction showed good tolerance for diverse electron-donating or electron-withdrawing groups at different positions on the aromatic ring of substrates **1**, giving the corresponding products **2b**–**f** in 23–36% yields. The substrates with electron-donating substituents (**1c**–**e**) generally exhibited higher reactivity than that with an electron-withdrawing group (**1f**), probably because the electron-donating substituents would make the aoQMs more electron-rich and thus facilitated the subsequent cycloaddition with electron-deficient C_{60}. In addition, the influence of the substituents at different positions of the aromatic ring was not obvious except for the substituent at the *ortho*-position of the sulfonamide moiety due to steric effect. For example, a higher reaction temperature of 140 °C was essential for **1b** to achieve the synthetically valuable product yield. It is worth noting that the disubstituted *N*-(2-(chloromethyl)aryl)-4-methylbenzenesulfonamide **1e** with two strong electron-donating methoxy groups efficiently afforded cycloadduct **2e** in 36% yield.

The chloro atom on the phenyl ring could be tolerated under the optimal reaction conditions, and can be utilized for further functionalizations at a later stage using cross-coupling protocols. Moreover, substrate **1g** with a phenyl substituent at the benzylic position also proceeded well to produce the corresponding product **2g**, albeit in a relatively lower yield.

Table 2. Results for the [4+2] Cycloaddition Reaction of C_{60} with 1a–g[a,b]

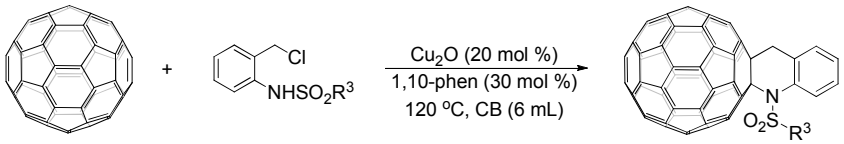


[a]Unless otherwise noted, the reactions were performed with C_{60} (0.05 mmol), **1** (0.10 mmol), Cu_2O (0.01 mmol), and 1,10-phen (0.015 mmol) in anhydrous chlorobenzene (6 mL) at 120 °C under an open-air atmosphere. [b]Isolated yields. Values in

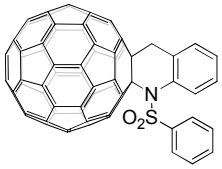
parentheses were based on the consumed C_{60}. [c]The reaction was performed at 140 °C. [d]Molar ratio of C_{60}/**1**/Cu_2O/1,10-phen is 1/2/0.5/0.75.

To further expand the scope of this transformation, *N*-(2-(chloromethyl)phenyl) sulfonamides **1** with a wide range of different sulfonamide moieties were then examined, and the results are shown in Table 3. The substrates **1h**–**p** with both electron-rich and electron-deficient sulfonamide groups underwent effective transformations, giving the corresponding products **2h**–**p** in 26–34% yields. The *o*- and *m*-methyl substituted substrates (**1i** and **1j**) proceeded well with good yields of 32% and 31%, respectively, which were nearly the same as that (33%) of product **2a**, suggesting that the steric effect of the substituents on the aromatic ring of the sulfonamide moiety was negligible. Nevertheless, the electronic nature of the substituents on the phenyl ring of the sulfonamide moiety had an obvious influence on the reaction. For example, substrates **1k** and **1m** bearing either a strong electron-donating or electron-withdrawing group at the 4-position decreased the reaction conversion and required a higher reaction temperature of 140 °C to produce **2k** and **2m** in 26% and 28% yields, respectively. Electron-rich heterocycle-containing sulfonamide **1n** was also a suitable substrate for this transformation, affording **2n** in 33% yield. When the arylsulfonamide group of the substrates was changed to an alkylsulfonamide moiety as in the cases of **1o** and **1p**, the transformations also proceeded well, providing the corresponding products **2o** and **2p** in 29% and 31% yields, respectively.

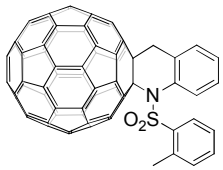
Table 3. Results for the [4+2] Cycloaddition Reaction of C_{60} with 1h–p[a,b]



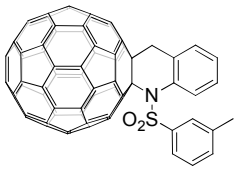
1 **2**



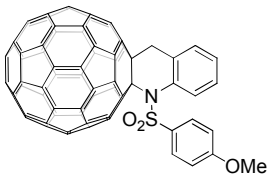
2h, 3 h, 34% (72%)



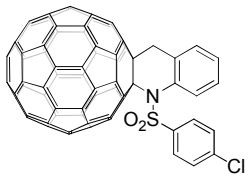
2i, 3 h, 32% (80%)



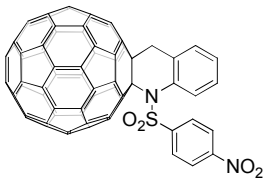
2j, 3 h, 31% (79%)



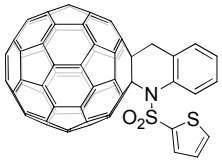
2k, 5 h, 26% (76%)[c]



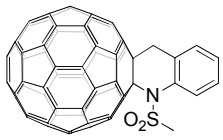
2l, 3 h, 30% (91%)



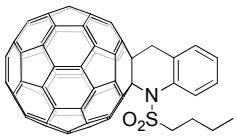
2m, 5 h, 28% (74%)[c]



2n, 3 h, 33% (89%)[c]



2o, 3 h, 29% (85%)



2p, 3 h, 31% (78%)

[a]Unless otherwise noted, the reactions were performed with C_{60} (0.05 mmol), **1** (0.10 mmol), Cu_2O (0.01 mmol), and 1,10-phen (0.015 mmol) in anhydrous chlorobenzene (6 mL) at 120 °C under an open-air atmosphere. [b]Isolated yields. Values in parentheses were based on the consumed C_{60}. [c]The reaction was performed at 140 °C.

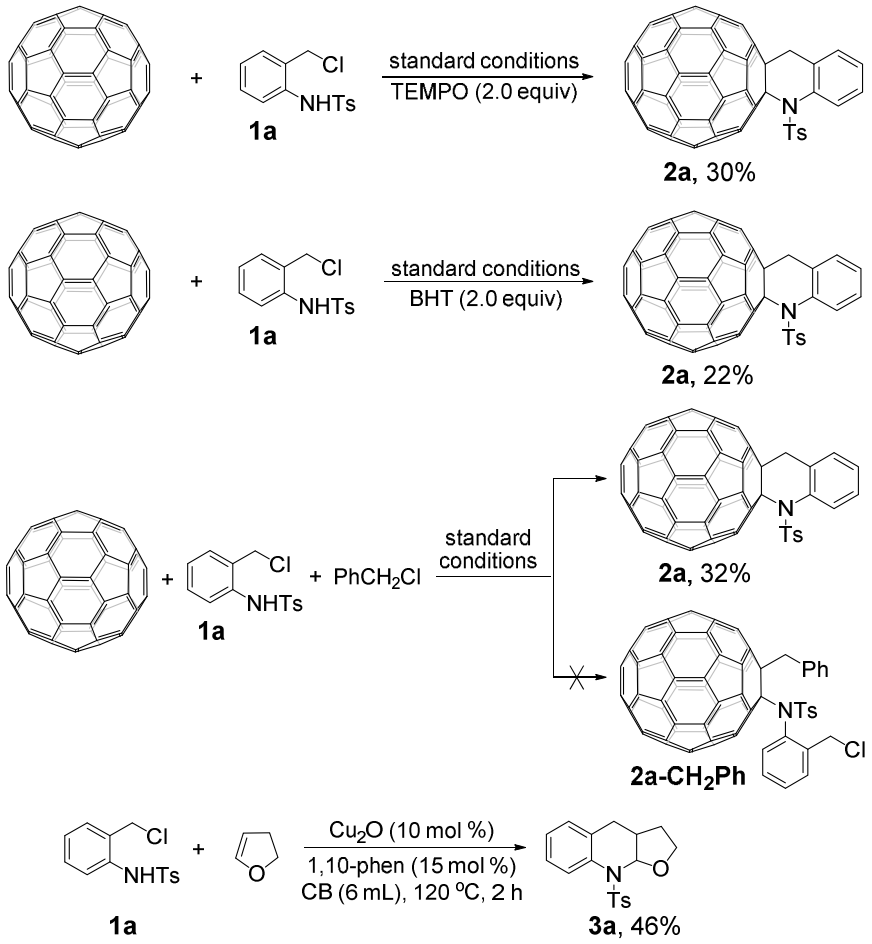
The structures of products **2a**–**p** were unambiguously characterized by using HRMS (MALDI-TOF), ^{1}H NMR, ^{13}C NMR, FT-IR, and UV-vis spectra. All HRMS of

these products exhibited the correct $[M]^+$ peaks. Their ^1H NMR spectra displayed the expected chemical shifts as well as the splitting patterns for all protons. The ^{13}C NMR spectra of **2a**–**p** exhibited more than 49 peaks in the range of 157–133 ppm for the 58 sp^2-carbons of the fullerene cage and two peaks at 82–67 ppm for the two sp^3-carbons of the fullerene skeleton, consistent with the C_1 symmetry of their molecular structures. To further confirm the structure, the HSQC and HMBC spectra were carried out using **2c** as a representative example. The HSQC spectrum of **2c** displayed that the protons at 4.80 ppm and 4.05 ppm had correlations with the carbon at 42.2 ppm. The HMBC spectrum of **2c** showed that the protons at 4.80 ppm and 4.05 ppm were correlated with the two sp^3-carbons of C_{60} at 80.3 ppm and 67.9 ppm. These 2D-NMR results were fully consistent with that **2c** had a structure of fullerotetrahydroquinoline. The UV-vis spectra of **2a**–**p** exhibited a peak at 433–434 nm, which is the characteristic absorption for 1,2-adducts of C_{60}.

To gain insight for the reaction mechanism of this transformation, some control experiments were conducted (Scheme 1). Addition of the well-known radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 2.0 equiv) to the reaction mixture had nearly negligible effect on the transformation, giving **2a** in 30% yield. Additionally, when 2,6-ditertbutyl-4-methyiphenol (BHT, 2.0 equiv) was used as the radical scavenger, the formation of **2a** could not be prohibited significantly either, and **2a** was isolated in 22% yield. The above observations indicated that radical species may be not involved in this transformation. Previous work has shown that C_{60} is an excellent electrophile and reacts with a variety of nucleophilic reagents. The acidic N–

H proton could be deprotonated under basic conditions to give the sulfonamide anion, which may undergo nucleophilic attack to C_{60} to afford the fullerotetrahydroquinolines. To test this hypothesis, we did the following control experiments. The reaction of C_{60} with **1a** in the presence of benzyl chloride (2 equiv) was performed under the standard conditions, and nearly the same yield (32%) of **2a** as that (33%) in the absence of benzyl chloride was obtained. The possible benzylated product **2a-CH$_2$Ph**, which would be formed by the initial nucleophilic attack of the sulfonamide anion to C_{60} followed by intramolecular SN2 reaction to benzyl chloride, could not be identified. Furthermore, the reaction of C_{60} with *N*-phenyl *para*-toluenesulfonylamine in the presence/absence of benzyl chloride were conducted under otherwise the same conditions, and no fullerene product could be isolated. On the other hand, treatment of **1a** with 2,3-dihydrofuran under the optimal reaction conditions could deliver the [4+2] cycloaddition product **3a** in 46% yield (Scheme 1). Considering the electro-rich nature of 2,3-dihydrofuran, the possibility through nucleophilic addition of **1a** to 2,3-dihydrofuran to give **3a** was negligible. The above results suggested that a stepwise reaction mechanism involving the initial nucleophilic attack of the sulfonamide anion to C_{60} could be excluded, and thus the formation of **2** should proceed most likely via a hetero-Diels-Alder process.

Scheme 1. Control Experiments

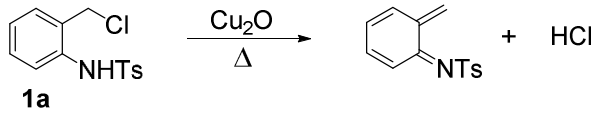


Furthermore, after the reaction was completed, we observed a green copper precipitate, which was the same as that formed from the control reaction of **1a** with Cu_2O and 1,10-phen at 120 °C for 3 h in CB. The electron paramagnetic resonance (EPR) experiment of the green solid in DMSO suggested that a Cu(II) species existed.[11] The X-Ray diffraction experiment further confirmed that the single crystal **4** grown from the green copper solid was a complex of 1,10-phen and $CuCl_2$ (see the Supporting Information).[12] To gain deep insight into the mechanism, X-ray photoelectron spectroscopy (XPS) was used to investigate the oxidation state of the

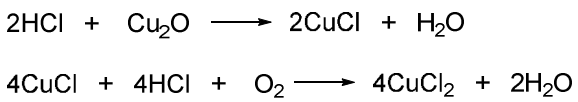
copper solid obtained from the reaction mixture. The binding energy (BE) peak at ~934 eV was assigned to a Cu^{2+} species.[13] The BE peak at ~931.5 eV suggested the presence of a Cu^{+} or Cu^{0} species.[13] Because Cu $2p_{3/2}$ XPS could not differentiate Cu^{+} from Cu^{0}, Auger Cu LMM spectrum was used to confirm the presence of Cu^{+} at BE ~ 571 eV, and no Cu^{0} species was present in our system because there was no BE peak at ~568 eV in the Auger Cu LMM spectrum (see the Supporting Information).[14] Thus, the copper solid obtained from the reaction mixture should consist of Cu(phen)Cl_2 and Cu_2O. The XPS experiment was also employed to study the oxidation state of the copper species for the reaction under a nitrogen atmosphere. The results indicated that no Cu^{0} species was generated and Cu_2O, CuCl, and Cu(phen)Cl_2 were observed (see the Supporting Information).

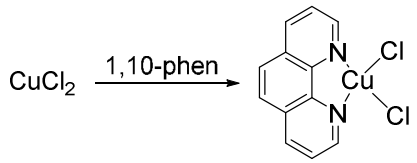
The possible pathway for the formation of aoQM and **4** is shown in Scheme 2. The removal of HCl from substrate **1a** generates the aoQM intermediate, likely with the assistance of Cu_2O. The reaction of Cu_2O and HCl provides CuCl, which is converted to $CuCl_2$ in the presence of HCl and O_2. Then **4** is produced when $CuCl_2$ is coordinated with 1,10-phen (Scheme 2).

Scheme 2. Formation of aoQM and Complex 4



1a

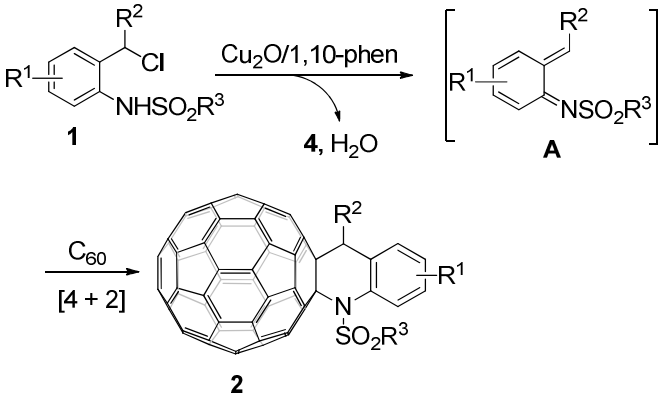




4

On the basis of the above experimental results and literature precedents,[8] a plausible reaction mechanism of this transformation is presented in Scheme 3. First, the aoQM intermediate **A** could be generated in situ from *N*-(*ortho*-chloromethyl)aryl sulfonamide **1** with the assistance of Cu_2O and 1,10-phen, accompanied by the simultaneous release of complex **4** and H_2O. Although the exact role played by Cu_2O is not very clear, it may behave as a base for the removal of HCl from **1**, and also consumes the generated HCl to generate CuCl and eventually complex **4** in the presence of O_2 and 1,10-phen. Intermediate **A** then undergoes the hetero-Diels-Alder reaction with C_{60} to provide the desired product **2**.

Scheme 3. Proposed Reaction Mechanism for the Formation of 2



CONCLUSION

In summary, we have successfully developed an efficient and convenient method for the synthesis of fullerotetrahydroquinolines from the hetero-Diels-Alder reaction of C_{60} with the in situ generated aza-*o*-quinone methides from *N*-(*ortho*-chloromethyl)aryl sulfonamides with the assistance of catalytic amounts of Cu_2O and 1,10-phenanthroline, which are more efficient than the commonly used inorganic bases such as Cs_2CO_3, Na_2CO_3, and K_2CO_3. This is the first example of the metal oxide-induced in situ formation of aza-*o*-quinone methides. The present method features a broad substrate scope and good functional group tolerance.

EXPERIMENTAL SECTION

General Methods. ^{1}H NMR spectra were referenced to residual DMSO at 2.50 ppm or TMS at 0.00 ppm, while ^{13}C NMR spectra were referenced to residual DMSO at 39.50 ppm, $CHCl_2CHCl_2$ at 72.80 ppm, or $CHCl_3$ at 77.16 ppm. High-resolution mass spectra (HRMS) were obtained by MALDI-TOF in a positive mode or ESI-FT-ICR in a positive mode.

General Procedure for the Synthesis of 2a–p from the Reaction of C_{60} with 1a–p. A mixture of C_{60} (0.05 mmol), *N*-(2-(chloromethyl)aryl)-sulfonamide **1** (0.10 mmol), Cu_2O (0.01 mmol), and 1,10-phenanthroline (1,10-phen) (0.015 mmol) was dissolved in anhydrous chlorobenzene (6 mL). Then the solution was vigorously stirred at the desired temperature and stopped at the designated time. The resulting solution was evaporated in *vacuo*, and the residue was then separated on a silica gel column. The recovered C_{60} was firstly collected with CS_2 as the eluent. Then the eluent was changed to CS_2/CH_2Cl_2 (15:1 v/v unless specified) to separate out the desired product **2**.

*Fullerotetrahydroquinoline **2a***. By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with *N*-(2-(chloromethyl)phenyl)-4-methylbenzenesulfonamide **1a** (29.7 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (3.0 mg, 0.015 mmol) at 120 ^oC for 3.0 h afforded recovered C_{60} (21.5 mg, 60%) and **2a** (16.0 mg, 33%): amorphous brown solid; ^1H NMR (400 MHz, CS_2 with DMSO-d_6 as the external reference) δ 7.64 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 7.6 Hz, 1H), 7.41–7.30 (m, 3H), 7.04 (d, J = 8.2 Hz, 2H), 4.35 (d, J = 13.6 Hz, 1H), 3.75 (d, J = 13.6 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, CS_2 with DMSO-d_6 as the external reference) δ 156.0, 153.9, 151.8, 147.5, 146.9, 146.7, 145.94, 145.91, 145.8, 145.7, 145.53, 145.48, 145.46, 145.3, 145.04, 145.03, 145.0, 144.9, 144.69, 144.68, 144.65, 144.61, 144.58, 144.4, 144.1, 143.87, 143.85, 143.84, 143.1, 143.0, 142.8, 142.4, 142.1, 142.0, 141.94, 141.88, 141.8, 141.7, 141.6, 141.5, 141.3, 141.02, 140.98, 140.94, 140.8, 140.5, 140.3, 139.8, 139.2, 138.94,

138.89, 138.3, 137.4, 137.3, 136.6, 135.8, 135.4, 134.4, 129.8, 128.9, 128.2, 128.0, 127.74, 127.69, 80.7 (sp^3-*C* of C_{60}), 68.4 (sp^3-*C* of C_{60}), 43.0, 21.2; FT-IR ν/cm^{-1} (KBr) 1333 (*S*=*O*), 1159 (*S*=*O*), 814 (*N*–*S*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.05), 317 (4.60), 434 (3.43), 697 (2.65); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{74}H_{13}NO_2S$ $[M]^+$ 979.0662, found 979.0653.

Fullerotetrahydroquinoline ***2b***. By following the general procedure, the reaction of C_{60} (35.8 mg, 0.05 mmol) with *N*-(2-(chloromethyl)-6-methylphenyl)-4-methylbenzenesulfonamide **1b** (30.7 mg, 0.10 mmol), Cu_2O (3.7 mg, 0.025 mmol), and 1,10-phen (7.3 mg, 0.0375 mmol) at 140 ^oC for 6.0 h afforded recovered C_{60} (26.1 mg, 73%) and **2b** (11.4 mg, 23%): amorphous brown solid; ^1H NMR (400 MHz, CS_2 with DMSO-d_6 as the external reference) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.49–7.41 (m, 3H), 7.24 (d, *J* = 8.2 Hz, 2H), 5.14 (d, *J* = 13.7 Hz, 1H), 3.99 (d, *J* = 13.7 Hz, 1H), 2.71 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CS_2 with DMSO-d_6 as the external reference) δ 156.4, 154.3, 151.6, 147.5, 146.9, 146.5, 146.00, 145.96, 145.8, 145.7, 145.55, 145.53, 145.48, 145.4, 145.2, 145.02, 144.96, 144.9, 144.74, 144.71, 144.66, 144.5, 144.2, 144.0, 143.84, 143.81, 143.3, 143.0, 142.9, 142.5, 142.15, 142.06, 142.05, 142.02, 141.9, 141.8, 141.63, 141.62, 141.60, 141.4, 141.1, 141.02, 140.96, 140.9, 140.5, 140.1, 139.9, 139.3, 139.1, 138.6, 138.52, 138.47, 137.9, 137.41, 137.36, 136.0, 135.6, 134.3, 130.1, 128.8, 128.6, 128.4, 126.0, 81.0 (sp^3-*C* of C_{60}), 67.7 (sp^3-*C* of C_{60}), 43.6, 21.3, 19.0; FT-IR ν/cm^{-1} (KBr) 1335 (*S*=*O*), 1158 (*S*=*O*), 809 (*N*–*S*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.12), 318 (4.67), 434 (3.50), 696 (2.70); HRMS (MALDI-TOF) *m*/*z*

calcd for $C_{75}H_{15}NO_2S$ $[M]^+$ 993.0818, found 993.0807.

Fullerotetrahydroquinoline ***2c***. By following the general procedure, the reaction of C_{60} (35.8 mg, 0.05 mmol) with *N*-(2-(chloromethyl)-5-methylphenyl)-4-methylbenzenesulfonamide **1c** (31.0 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (2.9 mg, 0.015 mmol) at 120 ^oC for 3.0 h afforded recovered C_{60} (21.1 mg, 59%) and **2c** (14.5 mg, 29%): amorphous brown solid; ^1H NMR (400 MHz, $CDCl_2CDCl_2$) δ 7.93 (d, J = 8.2 Hz, 2H), 7.68 (s, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.25 (d, J = 8.2 Hz, 2H), 4.80 (d, J = 13.7 Hz, 1H), 4.05 (d, J = 13.7 Hz, 1H), 2.55 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$) δ 155.6, 153.5, 151.0, 147.0, 146.4, 145.47, 145.45, 145.42, 145.3, 145.1, 145.04, 144.99, 144.98, 144.94, 144.85, 144.44, 144.41, 144.34, 144.32, 144.23, 144.19, 144.15, 144.11, 143.8, 143.6, 143.45, 143.42, 143.3, 143.2, 142.7, 142.4, 141.9, 141.6, 141.5, 141.45, 141.43, 141.36, 141.3, 141.14, 141.11, 141.0, 140.8, 140.47, 140.43, 140.37, 140.3, 140.1, 139.6, 139.3, 138.7, 138.3, 137.85, 137.81, 137.5, 137.0, 136.5, 135.1, 135.0, 133.7, 133.1, 129.4, 129.0, 128.7, 127.4, 127.3, 80.3 (sp^3-*C* of C_{60}), 67.9 (sp^3-*C* of C_{60}), 42.2, 20.7, 20.6; FT-IR ν/cm^{-1} (KBr) 1337 (*S*=*O*), 1158 (*S*=*O*), 809 (*N*–*S*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.09), 317 (4.65), 434 (3.52), 694 (2.70); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{75}H_{15}NO_2S$ $[M]^+$ 993.0818, found 993.0811.

Fullerotetrahydroquinoline ***2d***. By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with *N*-(2-(chloromethyl)-4-methylphenyl)-4-methylbenzenesulfonamide **1d** (30.8 mg,

0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (3.0 mg, 0.015 mmol) at 120 ^oC for 3.0 h afforded recovered C_{60} (17.4 mg, 48%) and **2d** (17.1 mg, 35%): amorphous brown solid; ^1H NMR (400 MHz, $CDCl_2CDCl_2$) δ 7.91 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.5 Hz, 1H), 7.46–7.37 (m, 2H), 7.25 (d, J = 8.2 Hz, 2H), 4.75 (d, J = 13.7 Hz, 1H), 4.01 (d, J = 13.7 Hz, 1H), 2.52 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$) δ 155.6, 153.6, 151.2, 147.1, 146.4, 145.6, 145.49, 145.45, 145.4, 145.2, 145.1, 145.04, 145.02, 144.99, 144.9, 144.49, 144.46, 144.43, 144.39, 144.24, 144.19, 144.16, 143.8, 143.7, 143.5, 143.44, 143.36, 143.3, 142.8, 142.4, 141.9, 141.6, 141.54, 141.50, 141.47, 141.4, 141.3, 141.2, 141.10, 141.09, 140.8, 140.52, 140.48, 140.44, 140.3, 140.1, 139.7, 139.4, 138.7, 138.44, 138.38, 137.3, 137.0, 136.6, 136.0, 135.3, 135.1, 135.0, 133.8, 128.8, 128.7, 128.5, 128.4, 127.3, 80.4 (sp^3-*C* of C_{60}), 67.8 (sp^3-*C* of C_{60}), 42.6, 20.7; FT-IR ν/cm^{-1} (KBr) 1333 (*S*=*O*), 1159 (*S*=*O*), 814 (*N*–*S*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.10), 317 (4.66), 434 (3.55), 694 (2.65); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{75}H_{15}NO_2S$ $[M]^+$ 993.0818, found 993.0809.

*Fullerotetrahydroquinoline **2e***. By following the general procedure, the reaction of C_{60} (35.7 mg, 0.05 mmol) with *N*-(2-(chloromethyl)-4,5-dimethoxyphenyl)-4-methylbenzenesulfonamide **1e** (35.5 mg, 0.10 mmol), Cu_2O (1.6 mg, 0.01 mmol), and 1,10-phen (3.0 mg, 0.015 mmol) at 120 ^oC for 3.0 h afforded recovered C_{60} (18.4 mg, 52%) and **2e** (18.7 mg, 36%) with CS_2/CH_2Cl_2 (10:1, v/v) as the eluent for silica gel column purification: amorphous brown solid; ^1H NMR (400 MHz, $CDCl_2CDCl_2$) δ 7.91 (d, J = 8.2 Hz, 2H), 7.34 (s, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.05 (s, 1H), 4.50 (d, J = 13.8 Hz, 1H), 4.00 (s, 3H),

3.98 (s, 3H), 3.94 (d, J = 13.8 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$) δ 155.5, 153.5, 151.2, 148.5, 147.8, 147.1, 146.4, 145.8, 145.5, 145.4, 145.2, 145.1, 145.05, 145.02, 144.9, 144.5, 144.44, 144.38, 144.3, 144.2, 143.9, 143.64, 143.57, 143.44, 143.38, 143.3, 142.8, 142.5, 141.9, 141.7, 141.6, 141.48, 141.45, 141.4, 141.3, 141.25, 141.15, 141.1, 140.8, 140.55, 140.48, 140.3, 140.2, 139.9, 139.3, 138.7, 138.4, 136.9, 136.8, 136.6, 135.1, 135.0, 133.9, 130.3, 128.9, 128.8, 127.3, 112.6, 109.8, 80.7 (sp^3-*C* of C_{60}), 68.1 (sp^3-*C* of C_{60}), 55.5, 55.3, 42.3, 20.8; FT-IR ν/cm^{-1} (KBr) 1329 (*S*=*O*), 1160 (*S*=*O*), 810 (*N*–*S*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.09), 318 (4.62), 433 (3.51), 696 (2.65); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{76}H_{17}NO_4S$ $[M]^+$ 1039.0873, found 1039.0862.

Fullerotetrahydroquinoline ***2f***. By following the general procedure, the reaction of C_{60} (35.8 mg, 0.05 mmol) with *N*-(4-chloro-2-(chloromethyl)phenyl)-4-methylbenzenesulfonamide **1f** (33.2 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (3.1 mg, 0.015 mmol) at 140 ^{o}C for 3.0 h afforded recovered C_{60} (21.9 mg, 61%) and **2f** (14.9 mg, 30%): amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 7.90 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.2 Hz, 1H), 7.66–7.57 (m, 2H), 7.27 (d, J = 8.0 Hz, 2H), 4.66 (d, J = 13.8 Hz, 1H), 4.02 (d, J = 13.8 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$) δ 154.8, 153.0, 150.7, 147.1, 146.5, 145.52, 145.50, 145.4, 145.2, 145.15, 145.12, 145.08, 145.05, 144.9, 144.50, 144.49, 144.4, 144.3, 144.24, 144.20, 144.19, 144.0, 143.9, 143.8, 143.6, 143.4, 143.34, 143.28, 142.5, 142.2, 141.9, 141.65, 141.57, 141.55, 141.51, 141.45, 141.25, 141.19, 141.17, 141.12, 141.07, 140.9, 140.55, 140.52,

140.48, 140.3, 140.1, 139.7, 139.4, 138.8, 138.5, 138.0, 137.2, 136.70, 136.68, 136.6, 134.97, 134.95, 133.8, 133.6, 130.6, 128.9, 128.0, 127.8, 127.3, 80.4 (sp^3-*C* of C_{60}), 67.6 (sp^3-*C* of C_{60}), 42.3, 20.8; FT-IR ν/cm^{-1} (KBr) 1334 (*S*=*O*), 1158 (*S*=*O*)816 (*N*–*S*), 662 (*C*–*Cl*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.09), 318 (4.64), 433 (3.45), 691 (2.70); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{74}H_{12}NO_2S^{35}Cl$ $[M]^+$ 1013.0272, found 1013.0259.

Fullerotetrahydroquinoline ***2g***. By following the general procedure, the reaction of C_{60} (35.6 mg, 0.05 mmol) with *N*-(2-(chloro(phenyl)methyl)phenyl)-4-methylbenzenesulfonamide **1g** (37.2 mg, 0.10 mmol), Cu_2O (3.6 mg, 0.025 mmol), and 1,10-phen (7.3 mg, 0.0375 mmol) at 140 ^{o}C for 6.0 h afforded recovered C_{60} (24.0 mg, 67%) and **2g** (10.5 mg, 20%): amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.38–7.19 (m, 7H), 5.80 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$) δ 152.1, 151.3, 151.1, 146.9, 146.4, 146.3, 145.5, 145.45, 145.43, 145.37, 145.3, 145.02, 144.98, 144.9, 144.7, 144.45, 144.44, 144.40, 144.3, 144.24, 144.17, 144.14, 144.09, 144.06, 144.0, 143.7, 143.4, 143.33, 143.27, 143.24, 142.4, 141.8, 141.6, 141.48, 141.46, 141.4, 141.3, 141.2, 141.1, 140.9, 140.8, 140.7, 140.5, 140.2, 140.0, 139.9, 139.7, 138.7, 137.9, 137.6, 137.5, 137.0, 136.5, 136.0, 134.8, 134.6, 134.0, 132.8, 129.5, 129.0, 127.8, 127.5, 127.3, 127.2, 126.5, 81.4 (sp^3-*C* of C_{60}), 73.2 (sp^3-*C* of C_{60}), 54.7, 20.6; FT-IR ν/cm^{-1} (KBr) 1339 (*S*=*O*), 1162 (*S*=*O*), 810 (*N*–*S*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.12), 319 (4.71), 434 (3.49), 694

(2.65); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{80}H_{17}NO_2S$ $[M]^+$ 1055.0975, found 1055.0992.

Fullerotetrahydroquinoline ***2h***. By following the general procedure, the reaction of C_{60} (35.6 mg, 0.05 mmol) with *N*-(2-(chloromethyl)phenyl)benzenesulfonamide **1h** (28.4 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (2.9 mg, 0.015 mmol) at 120 °C for 3.0 h afforded recovered C_{60} (18.9 mg, 53%) and **2h** (16.1 mg, 34%): amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 8.05 (d, J = 7.3 Hz, 2H), 7.88 (d, J = 7.5 Hz, 1H), 7.66–7.56 (m, 3H), 7.55–7.43 (m, 3H), 4.82 (d, J = 13.7 Hz, 1H), 4.08 (d, J = 13.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$) δ 155.2, 153.3, 150.8, 147.0, 146.3, 145.43, 145.37, 145.3, 145.2, 145.1, 144.99, 144.95, 144.93, 144.92, 144.8, 144.41, 144.37, 144.35, 144.14, 144.10, 144.06, 143.8, 143.6, 143.4, 143.22, 143.15, 142.6, 142.2, 141.8, 141.54, 141.47, 141.44, 141.40, 141.3, 141.2, 141.06, 141.02, 141.00, 140.7, 140.43, 140.40, 140.32, 140.26, 139.9, 139.5, 139.3, 138.7, 138.3, 137.9, 137.5, 136.6, 136.3, 135.0, 134.9, 133.6, 132.2, 128.9, 128.2, 128.1, 127.74, 127.72, 127.2, 80.3 (sp^3-*C* of C_{60}), 67.8 (sp^3-*C* of C_{60}), 42.5; FT-IR ν/cm^{-1} (KBr) 1328 (*S*=*O*), 1156 (*S*=*O*), 820 (*N*–*S*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.13), 318 (4.69), 433 (3.50), 696 (2.70); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{73}H_{11}NO_2S$ $[M]^+$ 965.0505, found 965.0516.

Fullerotetrahydroquinoline ***2i***. By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with *N*-(2-(chloromethyl)phenyl)-2-methylbenzenesulfonamide **1i** (30.0 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (2.9 mg, 0.015 mmol) at 120 °C for 3.0 h

afforded recovered C_{60} (21.5 mg, 60%) and **2i** (15.8 mg, 32%): amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 8.17 (d, J = 7.5 Hz, 1H), 7.95–7.89 (m, 1H), 7.70–7.66 (m, 1H), 7.65–7.57 (m, 2H), 7.36 (t, J = 7.5 Hz, 1H), 7.26–7.18 (m, 2H), 5.44 (d, J = 13.8 Hz, 1H), 4.17 (d, J = 13.8 Hz, 1H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$) δ 155.7, 153.5, 151.0, 147.1, 146.4, 145.5, 145.4, 145.3, 145.1, 145.04, 145.02, 144.98, 144.95, 144.5, 144.4, 144.22, 144.18, 144.1, 143.8, 143.72, 143.66, 143.5, 143.3, 143.2, 142.7, 142.1, 141.8, 141.6, 141.51, 141.46, 141.44, 141.38, 141.2, 141.15, 141.06, 141.03, 141.00, 140.8, 140.5, 140.3, 140.0, 139.42, 139.37, 138.7, 138.34, 138.26, 137.9, 137.7, 137.4, 137.1, 136.6, 135.1, 135.0, 133.6, 132.7, 131.8, 131.2, 129.0, 128.3, 128.2, 127.7, 125.3, 80.5 (sp^3-*C* of C_{60}), 67.5 (sp^3-*C* of C_{60}), 42.7, 20.1; FT-IR ν/cm^{-1} (KBr) 1328 (*S*=*O*), 1157 (*S*=*O*), 822 (*N*–*S*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.05), 318 (4.62), 434 (3.45), 697 (2.65); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{74}H_{13}NO_2S$ $[M]^+$ 979.0662, found 979.0646.

*Fullerotetrahydroquinoline **2j***. By following the general procedure, the reaction of C_{60} (35.8 mg, 0.05 mmol) with *N*-(2-(chloromethyl)phenyl)-3-methylbenzenesulfonamide **1j** (29.4 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (2.9 mg, 0.015 mmol) at 120 ^{o}C for 3.0 h afforded recovered C_{60} (21.7 mg, 61%) and **2j** (15.3 mg, 31%): amorphous brown solid; ^{1}H NMR (400 MHz, CS_2 with DMSO-d_6 as the external reference) δ 7.62–7.55 (m, 3H), 7.43–7.29 (m, 3H), 7.18–7.07 (m, 2H), 4.43 (d, J = 13.6 Hz, 1H), 3.77 (d, J = 13.6 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, CS_2 with DMSO-d_6 as the external reference) δ 156.0, 154.0, 151.8, 147.5, 146.9, 146.5, 145.99, 145.96, 145.9, 145.7,

145.6, 145.52, 145.50, 145.3, 145.1, 145.02, 145.00, 144.9, 144.73, 144.72, 144.67, 144.66, 144.5, 144.1, 143.93, 143.88, 143.86, 143.2, 143.0, 142.5, 142.13, 142.11, 142.05, 142.0, 141.9, 141.8, 141.73, 141.68, 141.6, 141.3, 141.1, 141.0, 140.9, 140.5, 140.3, 139.9, 139.3, 138.94, 138.88, 138.4, 137.7, 137.2, 136.7, 135.8, 135.5, 134.4, 132.8, 129.8, 128.5, 128.35, 128.28, 128.1, 127.8, 124.9, 80.6 (sp^3-*C* of C_{60}), 68.4 (sp^3-*C* of C_{60}), 43.0, 21.0; FT-IR ν/cm^{-1} (KBr) 1339 (*S*=*O*), 1162 (*S*=*O*), 818 (*N*–*S*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.02), 318 (4.57), 434 (3.39), 696 (2.60); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{74}H_{13}NO_2S$ $[M]^+$ 979.0662, found 979.0651.

Fullerotetrahydroquinoline ***2k***. By following the general procedure, the reaction of C_{60} (35.7 mg, 0.05 mmol) with *N*-(2-(chloromethyl)phenyl)-4-methoxybenzenesulfonamide **1k** (31.0 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (3.0 mg, 0.015 mmol) at 140 °C for 5.0 h afforded recovered C_{60} (23.5 mg, 66%) and **2k** (12.6 mg, 26%) with CS_2/CH_2Cl_2 (10:1, v/v) as the eluent for silica gel column purification: amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 7.97 (d, J = 9.0 Hz, 2H), 7.90–7.85 (m, 1H), 7.66–7.55 (m, 3H), 6.92 (d, J = 9.0 Hz, 2H), 4.84 (d, J = 13.7 Hz, 1H), 4.09 (d, J = 13.7 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$) δ 162.2, 155.5, 153.4, 151.1, 147.1, 146.4, 145.54, 145.47, 145.4, 145.3, 145.2, 145.1, 145.01, 145.00, 144.97, 144.8, 144.44, 144.40, 144.39, 144.3, 144.22, 144.20, 144.1, 143.8, 143.6, 143.4, 143.31, 143.25, 142.7, 142.4, 141.9, 141.6, 141.52, 141.49, 141.45, 141.40, 141.3, 141.13, 141.08, 141.05, 140.8, 140.51, 140.45, 140.4, 140.3, 140.1, 139.7, 139.4, 138.7, 138.4, 138.2, 137.2, 136.7, 136.2, 135.0, 133.7, 131.4, 129.5, 129.1, 128.2,

127.80, 127.76, 113.4, 80.3 (sp^3-*C* of C_{60}), 67.9 (sp^3-*C* of C_{60}), 54.9, 42.5; FT-IR ν/cm^{-1} (KBr) 1327 (*S*=*O*), 1152 (*S*=*O*), 828 (*N*–*S*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.13), 318 (4.66), 434 (3.50), 697 (2.70); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{74}H_{13}NO_3S$ $[M]^+$ 995.0611, found 995.0601.

Fullerotetrahydroquinoline ***2l***. By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with 4-chloro-*N*-(2-(chloromethyl)phenyl)benzenesulfonamide **1l** (31.4 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (3.0 mg, 0.015 mmol) at 120 °C for 3.0 h afforded recovered C_{60} (23.9 mg, 67%) and **2l** (15.1 mg, 30%): amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.72–7.61 (m, 3H), 7.50 (d, *J* = 8.6 Hz, 2H), 4.82 (d, *J* = 13.8 Hz, 1H), 4.15 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$) δ 155.1, 153.2, 150.6, 147.0, 146.4, 145.5, 145.4, 145.3, 145.13, 145.09, 145.03, 144.99, 144.97, 144.9, 144.5, 144.41, 144.39, 144.3, 144.18, 144.15, 144.09, 144.07, 144.0, 143.8, 143.6, 143.4, 143.24, 143.18, 142.5, 142.1, 141.9, 141.6, 141.52, 141.48, 141.45, 141.38, 141.2, 141.1, 141.04, 141.02, 140.8, 140.5, 140.44, 140.43, 140.3, 139.9, 139.6, 139.4, 138.8, 138.7, 138.6, 138.4, 137.8, 137.4, 136.7, 136.2, 135.1, 134.9, 133.6, 128.9, 128.5, 128.3, 127.8, 127.7, 80.5 (sp^3-*C* of C_{60}), 67.8 (sp^3-*C* of C_{60}), 42.6; FT-IR ν/cm^{-1} (KBr) 1346 (*S*=*O*), 1163 (*S*=*O*), 820 (*N*–*S*), 740 (*C*–*Cl*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.09), 318 (4.64), 433 (3.46), 697 (2.74); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{73}H_{10}NO_2S^{35}Cl$ $[M]^+$ 999.0115, found 999.0107.

Fullerotetrahydroquinoline ***2m***. By following the general procedure, the reaction of

C_{60} (35.8 mg, 0.05 mmol) with *N*-(2-(chloromethyl)phenyl)-4-nitrobenzenesulfonamide **1m** (32.5 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (3.0 mg, 0.015 mmol) at 140 ^oC for 5.0 h afforded recovered C_{60} (22.1 mg, 62%) and **2m** (13.9 mg, 28%) with CS_2/CH_2Cl_2 (10:1, v/v) as the eluent for silica gel column purification: amorphous brown solid; ^1H NMR (400 MHz, $CDCl_2CDCl_2$) δ 8.31 (d, J = 8.9 Hz, 2H), 8.26 (d, J = 8.9 Hz, 2H), 7.91–7.86 (m, 1H), 7.71–7.60 (m, 3H), 4.78 (d, J = 13.8 Hz, 1H), 4.15 (d, J = 13.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$) δ 154.8, 153.1, 150.1, 148.9, 147.1, 146.4, 145.9, 145.6, 145.5, 145.3, 145.2, 145.10, 145.08, 145.06, 145.02, 144.53, 144.47, 144.44, 144.30, 144.26, 144.13, 144.06, 144.0, 143.9, 143.8, 143.7, 143.5, 143.3, 143.1, 142.5, 141.9, 141.8, 141.7, 141.6, 141.54, 141.52, 141.47, 141.2, 141.14, 141.08, 141.0, 140.9, 140.6, 140.50, 140.49, 140.3, 140.0, 139.5, 138.8, 138.5, 137.9, 137.3, 136.6, 136.3, 135.3, 134.7, 133.5, 128.8, 128.7, 128.5, 128.13, 128.11, 123.3, 80.9 (sp^3-*C* of C_{60}), 67.7 (sp^3-*C* of C_{60}), 42.6; FT-IR ν/cm^{-1} (KBr) 1514 (*NO_2*), 1336 (*S=O*), 1164 (*S=O*), 826 (*N–S*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.01), 318 (4.56), 434 (3.33), 695 (2.65); HRMS (MALDI-TOF) *m/z* calcd for $C_{73}H_{10}N_2O_4S$ $[M]^+$ 1010.0356, found 1010.0342.

*Fullerotetrahydroquinoline **2n***. By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with *N*-(2-(chloromethyl)phenyl)thiophene-2-sulfonamide **1n** (28.9 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (3.1 mg, 0.015 mmol) at 140 ^oC for 3.0 h afforded recovered C_{60} (22.6 mg, 63%) and **2n** (16.2 mg, 33%): amorphous brown solid; ^1H NMR (400 MHz, $CDCl_2CDCl_2$) δ 7.87 (d, J = 7.4

Hz, 1H), 7.75–7.70 (m, 1H), 7.69–7.55 (m, 4H), 7.03 (t, J = 4.4 Hz, 1H), 4.66 (d, J = 13.8 Hz, 1H), 4.10 (d, J = 13.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$) δ 155.2, 153.3, 150.6, 147.1, 146.4, 145.5, 145.4, 145.3, 145.2, 145.07, 145.05, 145.02, 144.99, 144.9, 144.5, 144.44, 144.39, 144.23, 144.17, 144.15, 144.13, 144.11, 143.8, 143.6, 143.4, 143.30, 143.26, 142.7, 142.5, 141.9, 141.6, 141.53, 141.46, 141.4, 141.3, 141.2, 141.1, 141.0, 140.9, 140.8, 140.54, 140.45, 140.44, 140.3, 140.0, 139.7, 139.3, 138.7, 138.3, 137.9, 137.3, 136.8, 135.9, 135.08, 135.07, 133.64, 133.57, 133.2, 129.2, 128.4, 127.9, 127.8, 126.7, 80.7 (sp^3-*C* of C_{60}), 67.9 (sp^3-*C* of C_{60}), 42.4; FT-IR ν/cm^{-1} (KBr) 1346 (*S*=*O*), 1159 (*S*=*O*), 821 (*N*–*S*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.06), 318 (4.61), 433 (3.41), 695 (2.60); HRMS (MALDI-TOF) m/z calcd for $C_{71}H_9NO_2S_2$ $[M]^+$ 971.0069, found 971.0056.

Fullerotetrahydroquinoline ***2o***. By following the general procedure, the reaction of C_{60} (35.6 mg, 0.05 mmol) with *N*-(2-(chloromethyl)phenyl)methanesulfonamide **1o** (21.8 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (3.0 mg, 0.015 mmol) at 120 ^{o}C for 3.0 h afforded recovered C_{60} (23.6 mg, 66%) and **2o** (13.1 mg, 29%): amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 7.72–7.63 (m, 2H), 7.62–7.53 (m, 2H), 5.09 (d, J = 13.7 Hz, 1H), 4.23 (d, J = 13.7 Hz, 1H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$) δ 155.0, 153.2, 150.9, 147.1, 146.5, 145.6, 145.5, 145.4, 145.2, 145.12, 145.08, 145.04, 144.9, 144.6, 144.5, 144.44, 144.42, 144.3, 144.22, 144.15, 144.1, 143.92, 143.87, 143.8, 143.5, 143.34, 143.26, 142.7, 142.2, 142.0, 141.7, 141.6, 141.52, 141.45, 141.22, 141.20, 141.15, 141.1, 140.9, 140.7, 140.6, 140.40, 140.36, 140.1, 140.0, 139.4, 138.9, 138.7, 138.6, 138.5, 137.7,

136.4, 135.2, 133.6, 128.1, 128.0, 127.9, 127.8, 80.9 (sp^3-*C* of C_{60}), 68.0 (sp^3-*C* of C_{60}), 45.1, 42.9; FT-IR ν/cm^{-1} (KBr) 1341 (*S*=*O*), 1156 (*S*=*O*), 825 (*N*–*S*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.05), 318 (4.59), 433 (3.41), 696 (2.60); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{68}H_9NO_2S$ $[M]^+$ 903.0349, found 903.0333.

Fullerotetrahydroquinoline ***2p***. By following the general procedure, the reaction of C_{60} (35.7 mg, 0.05 mmol) with *N*-(2-(chloromethyl)phenyl)butane-1-sulfonamide **1p** (25.7 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (2.9 mg, 0.015 mmol) at 120 °C for 3.0 h afforded recovered C_{60} (21.3 mg, 60%) and **2p** (14.6 mg, 31%): amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 7.68–7.64 (m, 1H), 7.63–7.53 (m, 3H), 5.21 (d, *J* = 13.7 Hz, 1H), 4.21 (d, *J* = 13.7 Hz, 1H), 3.66–3.57 (m, 1H), 3.55–3.45 (m, 1H), 2.18–2.06 (m, 2H), 1.54–1.37 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$) δ 155.2, 153.3, 151.1, 147.1, 146.5, 145.6, 145.5, 145.3, 145.2, 145.12, 145.06, 145.02, 144.97, 144.9, 144.6, 144.5, 144.4, 144.30, 144.27, 144.22, 144.17, 144.16, 143.84, 143.80, 143.7, 143.6, 143.3, 143.2, 142.7, 142.1, 142.0, 141.7, 141.6, 141.5, 141.4, 141.21, 141.18, 141.14, 141.0, 140.9, 140.7, 140.6, 140.4, 140.1, 139.9, 139.4, 139.2, 139.1, 138.7, 138.6, 137.5, 137.1, 135.4, 135.3, 133.5, 128.1, 128.0, 127.9, 127.8, 80.9 (sp^3-*C* of C_{60}), 67.7 (sp^3-*C* of C_{60}), 56.1, 42.9, 25.2, 20.3, 12.6; FT-IR ν/cm^{-1} (KBr) 1334 (*S*=*O*), 1145 (*S*=*O*), 828 (*N*–*S*); UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.01), 317 (4.54), 433 (3.37), 697 (2.60); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{71}H_{15}NO_2S$ $[M]^+$ 945.0818, found 945.0808.

Attempted Radical Scavenging Experiments.

A mixture of C_{60} (35.7 mg, 0.05 mmol),

N-(2-(chloromethyl)phenyl)-4-methylbenzenesulfonamide **1a** (29.1 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), 1,10-phen (3.0 mg, 0.015 mmol), and TEMPO (15.6 mg, 0.10 mmol) was dissolved in anhydrous chlorobenzene (6 mL). Then the solution was vigorously stirred at 120 ^oC for 2 h. The resulting solution was evaporated in *vacuo*, and the residue was then separated on a silica gel column with CS_2 as the eluent to give the recovered C_{60} (20.3 mg, 57%) and then **2a** (14.5 mg, 30%) with CS_2/CH_2Cl_2 (15:1 v/v) as the eluent.

A mixture of C_{60} (35.9 mg, 0.05 mmol), *N*-(2-(chloromethyl)phenyl)-4-methylbenzenesulfonamide **1a** (29.4 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), 1,10-phen (3.1 mg, 0.015 mmol), and BHT (21.9 mg, 0.10 mmol) was dissolved in anhydrous chlorobenzene (6 mL). Then the solution was vigorously stirred at 120 ^oC for 2 h. The resulting solution was evaporated in *vacuo*, and the residue was then separated on a silica gel column with CS_2 as the eluent to give the recovered C_{60} (26.3 mg, 73%) and then **2a** (10.8 mg, 22%) with CS_2/CH_2Cl_2 (15:1 v/v) as the eluent.

Reaction of C_{60} with 1a in the Presence of Benzyl Chloride.

By following the general procedure, the reaction of C_{60} (35.7 mg, 0.05 mmol) with *N*-(2-(chloromethyl)phenyl)-4-methylbenzenesulfonamide **1a** (29.5 mg, 0.10 mmol), benzyl chloride (11.5 μL, 0.10 mmol), Cu_2O (1.6 mg, 0.01 mmol), and 1,10-phen (3.1 mg, 0.015 mmol) at 120 ^oC for 3.0 h afforded recovered C_{60} (23.2 mg, 65%) and **2a** (15.3 mg, 32%).

Reaction of C_{60} with *N*-Phenyl *para*-Toluenesulfonylamine in the

Presence/Absence of Benzyl Chloride.

A mixture of C_{60} (35.8 mg, 0.05 mmol), *N*-phenyl *para*-toluenesulfonylam (24.7 mg, 0.10 mmol), benzyl chloride (11.5 μL, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (3.0 mg, 0.015 mmol) was dissolved in anhydrous chlorobenzene (6 mL). Then the solution was vigorously stirred at 120 ^oC for 3 h. No fullerene products could be identified.

A mixture of C_{60} (35.9 mg, 0.05 mmol), *N*-phenyl *para*-toluenesulfonylam (24.8 mg, 0.10 mmol), Cu_2O (1.5 mg, 0.01 mmol), and 1,10-phen (3.1 mg, 0.015 mmol) was dissolved in anhydrous chlorobenzene (6 mL). Then the solution was vigorously stirred at 120 ^oC for 3 h. No fullerene products could be identified.

Preparation of 3a. A mixture of *N*-(2-(chloromethyl)phenyl)-4-methylbenzenesulfonamide **1a** (89.0 mg, 0.30 mmol), 2,3-dihydro-furan (226.8 μL, 3.0 mmol), Cu_2O (4.3 mg, 0.03 mmol), and 1,10-phen (8.9 mg, 0.045 mmol) in anhydrous chlorobenzene (6 mL) was heated at 120 ^oC for 2 h. The reaction mixture was cooled to room temperature and most of the solvent was evaporated in *vacuo*. The residue was purified by column chromatography (SiO_2, PE/EtOAc = 10:1) to afford **3a**[8a] as white solid (45.6 mg, 46%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 7.7 Hz, 1H), 7.23 (d, J = 8.2 Hz, 2H), 7.19 (dd, J = 7.7, 0.8 Hz, 1H), 7.11 (td, J = 7.4, 1.0 Hz, 1H), 7.05 (d, J = 7.3 Hz, 1H), 6.18 (d, J = 8.4 Hz, 1H), 3.64–3.54 (m, 2H), 3.08–2.98 (m, 1H), 2.40 (s, 3H), 2.36 (dd, J = 14.7, 2.1 Hz, 1H), 2.15 (dd, J = 14.7, 4.9 Hz, 1H), 1.91–1.82 (m, 1H), 1.37–1.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 138.5, 136.2, 132.6, 129.8, 128.9,

127.5, 127.0, 126.2, 125.7, 89.4, 67.6, 41.1, 29.3, 29.2, 21.6; HRMS (ESI-FT-ICR) *m*/*z* calcd for $C_{18}H_{20}NO_3S$ $[M+H]^+$ 330.1158, found 330.1164.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

NMR spectra of products **2a**–**p** and **3a**, EPR spectrum and XPS spectra of the copper species from reaction mixtures (PDF)

X-ray crystallographic data for **4** (CIF)

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Notes

The authors declare no competing financial interest.

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