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# Evolution of Late Transition-Metal-Catalyzed Intermolecular Reductive Coupling Reaction of [60]Fullerene and *N*-Sulfonylaldimines: Competing Formation of Hydrobenzylated [60]Fullerenes and 1,2-Dihydrofullerene

**Venkatachalam Rajeshkumar**[a] **and Shih-Ching Chuang***[a]

**Keywords:** Fullerenes / Transition metals / C–C coupling / Reductive coupling

A system based on late transition-metal halides, phosphanes, water, and reducing agents in 1,2-dichlorobenzene can efficiently catalyze the intermolecular reductive coupling of [60]fullerene with *N*-sulfonylaldimines to afford novel 1,2-hydrobenzylated [60]fullerene derivatives. We found that both group VIIB metals (cobalt, rhodium, iridium) and group VIIIB metals (nickel, palladium, platinum) perform this coupling reaction. A control experiment in the absence of aldimines produced $C_{60}H_2$, which showed that the reaction might proceed via a [60]fullerene metal complex [M($\eta^2$-$C_{60}$)(ligand)]. An isotope labeling experiment with $D_2O$ as deuterium source resulted in deuterioaryzilation with deuterium bonded to the sp$^3$-carbon of $C_{60}$, providing evidence of a five-membered azametallacycle intermediate. Evaluation of the scope of reductive coupling reaction with versatile aldimines gave access to the hydroaryzilation products. All the reductive coupling products were completely characterized by IR and NMR spectroscopy and ESI mass spectrometry. A possible reaction mechanism based on these results is proposed. This discovery of the formation of reductive coupling compounds and metal-catalyzed formation of $C_{60}H_2$ are both new to metal catalysis and fullerene chemistry.

## Introduction

Functionalized fullerenes[1] have attracted great attention because of their potential applications in the fields of biological and material sciences.[2] In this context, a number of chemical reactions have been extensively developed, and some of the [60]fullerene derivatives have shown considerable potential for applications in organic photovoltaics.[2g–2p] Although a large variety of chemical reactions have been discovered to derivatize fullerenes, transition-metal-catalyzed reactions of fullerenes are comparatively less developed. The relatively unexplored nature of metal-mediated reactions with fullerenes might be the consequence of the ease of formation of insoluble complexes, low-yields of products, and difficulties in characterization. Previous studies have recognized that some transition metals, such as palladium,[3a–3e] rhodium,[3f–3j] cobalt,[3k–3m] manganese,[3n–3q] iron,[3r,3s] and copper,[3t–3v] can mediate functionalization of the fullerene sphere. In this context, we have recently also reported annulations of benzamides with [60]fullerene through palladium(II)-catalyzed C–H bond activation[4] to afford fullero-isoquinolinones. In 1998, Cheng et al. first reported a nickel-catalyzed [2+2+2] cycloaddition between $C_{60}$ and a tethered diyne mediated by stoichiometric amounts of nickel complexes;[5] this study is to date the only example of [60]fullerene functionalization mediated by nickel complexes. More recently, Jin and Yamamoto et al. established that cobalt catalysts, with Mn as a reductant and $H_2O$ as a proton source, can efficiently provide monohydroalkylated fullerenes from $C_{60}$ and alkyl bromides at ambient temperature through a radical mechanism.[3l]

On the other hand, transition-metal-catalyzed reductive couplings of two organic π-frameworks, such as alkyne/alkene,[6] alkyne/carbonyl,[7] alkyne/imine,[8] or alkene/imine[9] coupling reactions, constitute a convenient method for the construction of C–C bonds in organic synthesis. Of these reactions, reductive couplings of an alkyne with an aldehyde or imine in particular afforded access to synthetically important allylic alcohols and allylic amines, respectively. To the best of our knowledge, reductive coupling of two π-components usually gives products in low yields when $C_{60}$ is used as a coupling partner, such as in the case of the synthesis of $C_{120}$.[1n] On the other hand, metal-catalyzed coupling has not been applied successfully in fullerene chemistry. Such coupling with fullerenes might be hampered by the highly reversible coordination processes of fullerenes with transition metals.

Our continuing efforts in exploring the chemistry of metal-catalyzed reactions of [60]fullerene promoted us to investigate direct reductive coupling reactions between [60]fullerene and imines for potential applications. Here we disclose new late transition-metal-catalyzed coupling reactions between [60]fullerene and *N*-sulfonylaldimines with

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[a] Department of Applied Chemistry, National Chiao Tung University,
Hsinchu, Taiwan 30010, R.O.C.
Fax: +886-35723764
E-mail: jscchuang@faculty.nctu.edu.tw

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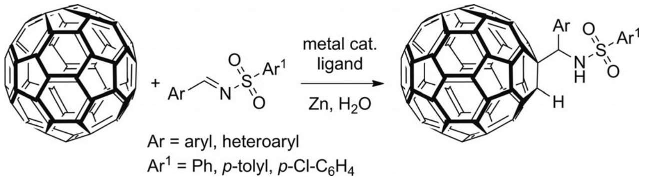
water as proton source, to afford hydrobenzylated [60]fullerene derivatives incorporating sulfonyl-protected amino groups (Scheme 1). These reductive coupling reactions offer a previously inaccessible methodology that opens up a new route to a new class of fullerene derivatives, as well as a metal-catalyzed method for the formation of $C_{60}H_2$.

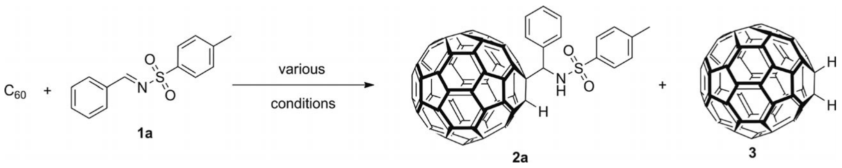


Scheme 1. Reductive coupling of [60]fullerene and *N*-sulfonyl aldimines.

## Results and Discussion

To develop this interesting methodology and to broaden its scope, we first produced variously substituted *N*-sulfonyl aldimines **1a**–**y** by reported procedures[10] and selected imine **1a** (Table 1) as a model substrate for screening of reaction conditions. We then carried out the reaction between $C_{60}$ (36 mg, 0.050 mmol) and aldimine **1a** (65 mg, 0.25 mmol) in the presence of nickel complex [Ni(dppe)$Br_2$] (20 mol-%), containing a bidentate ligand, Zn as reducing agent, and water as proton source in anhydrous *o*-dichlorobenzene (*o*-DCB, 6 mL) under $N_2$ in a sealed tube at 120 °C for 24 h. We found (Entry 1, Table 1) that reductive coupling product **2a** was isolated in a low yield (9%), together with $C_{60}H_2$ (6%). The initial results encouraged us to focus on developing efficient conditions for this reaction by surveying different nickel complexes. Fortuitously, when we changed the catalyst to $NiBr_2$ with $PPh_3$ as a ligand, we obtained **2a** in an improved yield (16%) together with $C_{60}H_2$ in 30% yield (Table 1, Entry 2). In view of the above results, we switched to a reaction with another prepared nickel complex, $NiCl_2(PPh_3)_2$; as expected, the reductive coupling product **2a** was obtained in a slightly higher yield of 19% (22% based on converted $C_{60}$, Entry 3). We then examined other nickel complexes such as $NiBr_2(PPh_3)_2$ or $NiBr_2[P(p\text{-tolyl})_3]_2$ for this coupling reaction. Surprisingly, when the reactions were performed with these complexes under the standard conditions described above, the coupling product **2a** was isolated in slightly better yields [22 and 21%, respectively (29% and 27% based on converted $C_{60}$), Entries 4–5]. Under the standard conditions, we found that $NiBr_2$(phen) (phen = 1,10-phenanthroline) also promoted this coupling reaction, to afford **2a** in 13% yield together with a 26% yield of $C_{60}H_2$ (Entry 6). However, we

Table 1. Formation of **2a** under various conditions.[a]



| Entry | Catalysts (20%), ligand | Reducing agent | Proton source | Solvents, temperature [°C] | Yield of **2a** [%][b] | Yield of **3** [%][c] | Recovered $C_{60}$ [%][c] |
|---|---|---|---|---|---|---|---|
| 1 | $NiBr_2$(dppe) | Zn | $H_2O$ | *o*-DCB (120) | 9 (26) [31] | 6 (17) | 64 |
| 2[d] | $NiBr_2$, $PPh_3$ | Zn | $H_2O$ | *o*-DCB (120) | 16 (23) [40] | 30 (42) | 29 |
| 3 | $NiCl_2(PPh_3)_2$ | Zn | $H_2O$ | *o*-DCB (120) | 19 (22) [32] | 27 (30) | 12 |
| 4 | $NiBr_2(PPh_3)_2$ | Zn | $H_2O$ | *o*-DCB (120) | 22 (29) [37] | 17 (22) | 25 |
| 5 | $NiBr_2[P(p\text{-tolyl})_3]_2$ | Zn | $H_2O$ | *o*-DCB (120) | 21 (27) [35] | 17 (22) | 24 |
| 6 | Ni(Phen)$Br_2$ | Zn | $H_2O$ | *o*-DCB (120) | 13 (16) [24] | 26 (33) | 20 |
| 7 | $NiBr_2(PCy_3)_2$ | Zn | $H_2O$ | *o*-DCB (120) | 0 | 0 | 85 |
| 8 | none | Zn | $H_2O$ | *o*-DCB (120) | 0 | 0 | 92 |
| 9 | $NiBr_2(PPh_3)_2$ | none | $H_2O$ | *o*-DCB (120) | 0 | 0 | 95 |
| 10[e] | $NiBr_2(PPh_3)_2$ | Zn | $H_2O$ | *o*-DCB (120) | 0 | 0 | 97 |
| 11 | $NiBr_2(PPh_3)_2$ | Zn | $H_2O$ | *o*-DCB (100) | 9 (17) [24] | 14 (26) | 50 |
| 12 | $NiBr_2(PPh_3)_2$ | Zn | $H_2O$ | toluene (120) | 0 | 0 | 89 |
| 13 | $NiBr_2(PPh_3)_2$ | Zn | $H_2O$ | 1-Cl-naphthalene (120) | trace | 24 (33) | 29 |
| 14[f] | $NiBr_2(PPh_3)_2$ | Zn | $CH_3COOH$ | *o*-DCB (120) | 13 (18) [34] | 32 (45) | 29 |
| 15[g] | $NiBr_2(PPh_3)_2$ | Zn | none | *o*-DCB (120) | 0 | 0 | 45 |
| 16[h] | $NiBr_2(PPh_3)_2$ | Zn | $H_2O$ | *o*-DCB (120) | 0 | 0 | 0 |
| 17[i] | none | Zn | $H_2O$ | *o*-DCB (120) | 0 | 0 | 96 |
| 18 | $NiBr_2(PPh_3)_2$ | Fe | $H_2O$ | *o*-DCB (120) | 0 | 0 | 98 |
| 19 | $NiBr_2(PPh_3)_2$ | Mn | $H_2O$ | *o*-DCB (120) | trace | 0 | 81 |

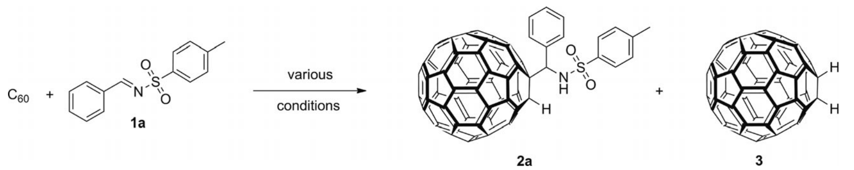
[a] Unless otherwise specified, all reactions were carried out with $C_{60}$ (0.050 mmol), imine (0.25 mmol), catalyst (0.010 mmol, 20 mol-%), Zn (0.25 mmol), and $H_2O$ (0.10 mmol) in dry *o*-DCB (6 mL) at 120 °C for 24 h under $N_2$ in a sealed tube. [b] Isolated yields after column chromatography. Values in parentheses are based on consumed $C_{60}$. Values in square brackets are based on $C_{60}$ involved in the catalytic cycle, excluding that used in forming $C_{60}H_2$. [c] Yields were measured by HPLC analysis. [d] $PPh_3$ (0.5 equiv.). [e] Reaction carried out without purging with nitrogen gas. [f] Performed with acetic acid (2 equiv.). [g] Carried out with $NiBr_2(PPh_3)_2$ (1.2 equiv.) and molecular sieves (4 Å, 100 mg) at 120 °C for 24 h and then addition of excess $H_2O$. [h] Reaction carried out in the absence of $C_{60}$. [i] Reaction performed in the absence of imine.

observed that $NiBr_2(PCy_3)_2$ displayed no catalytic activity for this reaction, likely due to the greater bulkiness of its ligand (Entry 7). Importantly, the reaction also did not take place in the absence either of Ni complexes or of zinc (Entries 8–9). It is also noteworthy that the coupling product **2a** was not observed without purging of the reaction mixture with nitrogen gas (Entry 10).

Furthermore, we tested this catalytic reaction with different solvents, temperatures, and proton sources. We found that lowering the reaction temperature diminished the reaction yields (Entry 11) and observed that toluene was ineffective as a solvent for this coupling reaction; neither **2a** nor $C_{60}H_2$ was observed (Entry 12). We noted that use of 1-chloronaphthalene as solvent brought about a deterioration in the reaction performance, with only trace amounts of **2a** being obtained (Entry 13). The coupling product **2a** was obtained in 13% yield when acetic acid was employed as proton source (Entry 14). A control experiment showed that **2a** was not obtained when the reaction was performed with a stoichiometric amount of catalyst under anhydrous conditions in the presence of 4 Å molecular sieves (Entry 15); this confirmed the necessity of the proton source at the initial stage. Another control experiment performed without $C_{60}$ gave the expected hydrolysis products of the aldimine (Entry 16). Treatment of $C_{60}$ with $H_2O$ in the presence of zinc gave no products (Entry 17), demonstrating the necessity of nickel catalysts. Other reductants, such as Fe or Mn, hampered the reaction (Entries 18–19). Overall, the overall reaction yields with **2a** and $C_{60}H_2$ point to a monofunctionalized fullerene reaction yield in the 30–60% range. The isolated yields of **2a** based on $C_{60}$ involved in the catalytic cycle, excluding that used in forming $C_{60}H_2$, are mostly in the 30–40% range.

Because the reductive coupling reaction had been successful with Ni complexes, we further evaluated the performances of other transition metals of groups VII B and VIII B in this coupling reaction. Separate loading of palladium acetate (20 mol-%) with $PPh_3$ as ligand proved totally ineffective for this coupling reaction (Table 2, Entry 1). However, $PdCl_2(PPh_3)_2$ yielded the coupling product **2a** (15%, Entry 2). To our surprise, we observed only a limited amount of **2a** (5%) when the reaction was performed with $PtCl_2(PPh_3)_2$ at 120 °C (Entry 3); formation of stable green-colored $C_{60}$ complexes $Pt(\eta^2\text{-}C_{60})(PPh_3)_2$ (26%)[15] dominated this reaction. We observed no improvements in the reaction yields on raising the reaction temperature to 150 °C (Entry 4). The group VII B transition metals (Co and Ir) also displayed comparable reactivity in this coupling reaction. While we performed the reaction with $CoI_2$ and $(PPh_3)_2$ as a catalyst,[6c] we isolated product **2a** in 18% yield (Entry 5), comparable with results achieved with Ni and Pd. The prepared catalyst $CoI_2(PPh_3)_2$ provided **2a** in a low yield (8%) and produced $C_{60}H_2$ in 55% yield (Entry 6). Further, we found that Wilkinson's catalyst was ineffective for this reductive coupling and afforded only $C_{60}H_2$ in 35% yield (Entry 7). Because Wilkinson's catalyst afforded only $C_{60}H_2$, we examined the catalytic activity of another form of rhodium, $RhCl_3$, in the presence of $PPh_3$ (20 and 40 mol-%) as ligand. We found that its coupling ability was limited; only trace amounts of **2a** were observed upon addition of 20 mol-% of ligand (Entry 8). Increasing the molar percentages of ligands produced no **2a**, but more $C_{60}H_2$ was isolated (Entry 9). However, use of another chloro-bridged Rh catalyst, $[Cp^*RhCl_2]_2$, afforded coupling product **2a** in a 13% yield (Entry 10). It was interesting to find that the analogous iridium complex $[Cp^*IrCl_2]_2$ showed comparable

Table 2. Evaluation of catalytic activities of other group VII and VIII B metals in the formation of **2a**.[a]



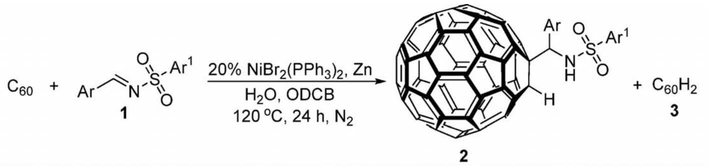
| Entry | Catalyst (20%), ligand | Reducing agent | Proton source | Solvent (temperature) [°C] | Yield of **2a** [%][b] | Yield of **3** [%][c] | Recovered $C_{60}$ [%][c] |
|---|---|---|---|---|---|---|---|
| 1[e] | $Pd(OAc)_2$, $PPh_3$ | none | $H_2O$ | *o*-DCB (120) | 0 | 0 | 99 |
| 2 | $PdCl_2(PPh_3)_2$ | Zn | $H_2O$ | *o*-DCB (120) | 15 (17) [24] | 27 (30) | 11 |
| 3 | $PtCl_2(PPh_3)_2$ | Zn | $H_2O$ | *o*-DCB (120) | 5 (26) | 0 | 74 (2)[d] |
| 4 | $PtCl_2(PPh_3)_2$ | Zn | $H_2O$ | *o*-DCB (150) | 0 | 0 | 27 (11)[d] |
| 5[e] | $CoI_2$, $PPh_3$ | Zn | $H_2O$ | *o*-DCB (120) | 18 (24) [44] | 34 (45) | 25 |
| 6 | $CoI_2(PPh_3)_2$ | Zn | $H_2O$ | *o*-DCB (120) | 8 (9) [22] | 55 (60) | 9 |
| 7 | $RhCl(PPh_3)_3$ | Zn | $H_2O$ | *o*-DCB (120) | 0 | 35 (64) | 46 |
| 8 | $RhCl_3$, $PPh_3$ (1:1) | Zn | $H_2O$ | *o*-DCB (120) | 5 (40) | 0 | 87 |
| 9 | $RhCl_3$, $PPh_3$ (1:2) | Zn | $H_2O$ | *o*-DCB (120) | 0 | 45 (74) | 40 |
| 10 | $[Cp^*RhCl_2]_2$ | Zn | $H_2O$ | *o*-DCB (120) | 13 (14) [21] | 32 (33) | 5 |
| 11 | $[Cp^*IrCl_2]_2$ | Zn | $H_2O$ | *o*-DCB (120) | 17 | 35 | 0 |
| 12[e] | $IrCl_3$, $PPh_3$ | Zn | $H_2O$ | *o*-DCB (120) | 0 | 17 (69) | 76 |

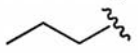
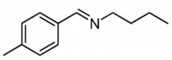
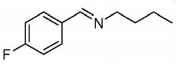
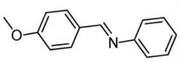
[a] Unless otherwise specified, all reactions were carried out with $C_{60}$ (0.050 mmol), imine (0.25 mmol), catalyst (0.010 mmol, 20 mol-%), Zn (0.25 mmol), and $H_2O$ (0.10 mmol) in dry *o*-DCB (6 mL) at 120 °C for 24 h under $N_2$ in a sealed tube. [b] Isolated yields after column chromatography. Values in parentheses are based on consumed $C_{60}$. Values in square brackets are based on $C_{60}$ involved in the catalytic cycle, excluding that used in forming $C_{60}H_2$. [c] Yields were determined by HPLC analysis. [d] Values in parentheses are yields of $Pt(\eta^2\text{-}C_{60})(PPh_3)_2$. [e] $PPh_3$ (0.5 equiv.).

catalytic activity (Entry 11) whereas $IrCl_3$ with $PPh_3$ as ligand was ineffective (Entry 12) in this reductive coupling reaction. After a series of screenings of the reaction conditions and metal complexes, we decided to choose the optimal conditions given in Entry 4 in Table 1 for further exploration of the scope of this reductive coupling reaction on the basis of catalyst efficiency and direct availability.

With the optimized reaction conditions to hand, the scope and reactivity of different *N*-sulfonylaldimine derivatives was investigated. The reactions of aldimines **1a**, **1b**, and **1c** with [60]fullerene proceeded smoothly to give **2a**–**c** in moderate yields [22, 27, and 21% (29, 47, and 30% based on converted $C_{60}$), respectively] under the selected conditions (Table 3, Entries 1–3). We observed that aldimines **1d**–**h** showed lower reactivities in this coupling reaction [11–16% (12–29% based on converted $C_{60}$), Entries 4–8]. Under the optimal reaction condition, aldimines **1i** and **1j**, with the electron-donating *tert*-butyl group on the phenyl ring, provided their corresponding coupling products **2i** and **2j** in 21 and 22% isolated yields (Entries 9 and 10). Extremely low yields were observed in the reactions of imines such as **1k** and **1l** featuring the dimethylamino or the electron-withdrawing cyano group (5% and 8% respectively, Entries 11 and 12). This lower reactivity is probably attributable to coordination of nitrogen to the nickel complexes, reducing the catalytic activity. Under similar reaction conditions, imines derived from naphthaldehydes such as **1m**–**q** underwent the reductive coupling reaction effectively, providing their corresponding products **2m**–**q** in moderate yields (10–22%; Entries 13–17). It is worth mentioning that these naphthalene derivatives had excellent solubilities in common organic solvents such as chloroform, toluene, *o*-dichlorobenzene, and carbon disulfide. Interestingly, the heteroarylaldimines **1r**–**u** also exhibited good reactivity towards this coupling under the standard conditions, affording reductive coupling products **2r**–**u** in 21, 27, 21, and 28% isolated yields (42, 35, 27, and 41% based on converted $C_{60}$), respectively (Entries 18–21). The reductive coupling was limited only to substrates of aryl *N*-sulfonylaldimines. We observed that aliphatic imine **1v** did not provide

Table 3. Nickel-catalyzed reductive coupling of [60]fullerene with a variety of *N*-sulfonylaldimines and *N*-alkyl or -aryl imines.[a]



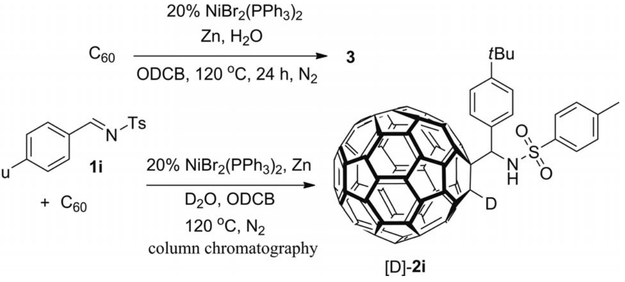
| Entry | Aldimine **1** | | Product **2** | Yield of **2** (%)[b] | Yield of **3** (%)[c] | Recovered |
|---|---|---|---|---|---|---|
| | Ar | Ar$^1$ | | | | $C_{60}$ (%)[c] |
| 1 | $C_6H_5$ | 4-Me-$C_6H_4$ (**1a**) | **2a** | 22(29) [37] | 17(22) | 25 |
| 2 | $C_6H_5$ | $C_6H_5$ (**1b**) | **2b** | 27(47) [62] | 14(25) | 44 |
| 3 | 4-Me-$C_6H_4$ | 4-Me-$C_6H_4$ (**1c**) | **2c** | 21(30) [44] | 22(31) | 31 |
| 4[d] | 4-Me-$C_6H_4$ | $C_6H_5$ (**1d**) | **2d** | 12(13) [21] | 40(40) | 2 |
| 5[d] | 4-Me-$C_6H_4$ | 4-Cl-$C_6H_4$ (**1e**) | **2e** | 16(21) [32] | 26(34) | 24 |
| 6 | 4-OMe-$C_6H_4$ | 4-Me-$C_6H_4$ (**1f**) | **2f** | 12(29) [38] | 11(25) | 58 |
| 7 | 4-OMe-$C_6H_4$ | $C_6H_5$ (**1g**) | **2g** | 12(13) [31] | 57(60) | 4 |
| 8 | 4-OMe-$C_6H_4$ | 4-Cl-$C_6H_4$ (**1h**) | **2h** | 11(12) [21] | 35(39) | 10 |
| 9[d] | 4-*t*Bu-$C_6H_4$ | 4-Me-$C_6H_4$ (**1i**) | **2i** | 21(31) [42] | 17(25) | 32 |
| 10 | 4-*t*Bu-$C_6H_4$ | $C_6H_5$ (**1j**) | **2j** | 22(30) [37] | 14(20) | 28 |
| 11 | 4-$NMe_2$-$C_6H_4$ | 4-Cl-$C_6H_4$ (**1k**) | **2k** | 5(7) [25] | 58(73) | 22 |
| 12 | 4-CN-$C_6H_4$ | $C_6H_5$ (**1l**) | **2l** | 8(11) [13] | 12(15) | 24 |
| 13 | 1-naphthyl | 4-Me-$C_6H_4$ (**1m**) | **2m** | 10(13) [23] | 36(45) | 21 |
| 14 | 2-naphthyl | 4-Me-$C_6H_4$ (**1n**) | **2n** | 20(24) [32] | 20(24) | 19 |
| 15 | 2-naphthyl | $C_6H_5$ (**1o**) | **2o** | 19(28) [32] | 9(13) | 31 |
| 16 | 2-OMe-1-naphthyl | 4-Me-$C_6H_4$ (**1p**) | **2p** | 22(28) [45] | 30 (38) | 21 |
| 17 | 2-OMe-1-naphthyl | $C_6H_5$ (**1q**) | **2q** | 20(44) [48] | 4(8) | 56 |
| 18 | 2-furyl | 4-Me-$C_6H_4$ (**1r**) | **2r** | 21(42) [47] | 4 (9) | 52 |
| 19[d] | 2-thienyl | 4-Me-$C_6H_4$ (**1s**) | **2s** | 27(35) [39] | 9(12) | 21 |
| 20 | 2-thienyl | $C_6H_5$ (**1t**) | **2t** | 21(27) [33] | 19(23) | 19 |
| 21[d] | 3-thienyl | 4-Me-$C_6H_4$ (**1u**) | **2u** | 28(41) [55] | 17(24) | 31 |
| 22 |  | 4-Me-$C_6H_4$ (**1v**) | **2v** | 0 | 16(60) | 74 |
| | | | | 0 | trace[e] | 97 |
| 23 |  **1w** | | **2w** | 0 | 13(49) | 74 |
| 24 |  **1x** | | **2x** | 0 | 44(51) | 16 |
| 25 |  **1y** | | **2y** | 0 | 5(26) | 79 |

[a] Unless otherwise specified, all reactions were carried out with $C_{60}$ (0.050 mmol), an aldimine (0.25 mmol), $NiBr_2(PPh)_2$ (0.010 mmol, 20 mol-%), Zn (0.25 mmol, 5 equiv.), and $H_2O$ (0.10 mmol) in anhydrous *o*-DCB (6 mL) at 120 °C under $N_2$ over 24 h. [b] Isolated yields after column chromatography. Values in parentheses are based on converted $C_{60}$. Values in square brackets are based on $C_{60}$ involved in the catalytic cycle, excluding that used in formation of $C_{60}H_2$. [c] Yields were measured by HPLC analysis. [d] Reactions were performed with $H_2O$ (0.20 mmol) for 48 h. [e] Reaction was performed at room temp.

the corresponding coupling product, but that $C_{60}H_2$ was produced, probably due to the instability[11] of imine **1v** (Entry 22). Neither *N*-alkyl aldimines **1w** and **1x**, nor *N*-aryl aldimine **1y** gave their corresponding products (Entries 23–25); with these substrates only $C_{60}H_2$ was observed. This suggested that the interaction of oxygen from the sulfonyl group (–$SO_2$–) with the nickel center in the intermediate might be essential for the formation of these reductive coupling products **2a**–**u**, which is consistent with Ogoshi's observations.[15] In short, the observed reductive coupling is highly chemoselective for aryl *N*-sulfonylaldimine substrates, providing coupling products in 0–28% yields (0–47% based on converted $C_{60}$) and $C_{60}H_2$ in 0–58% (0–73% based on converted $C_{60}$) yields. The yields based on $C_{60}$ involved in the catalytic cycle, excluding that used in forming $C_{60}H_2$, are mostly in the 30 to 50% range but can be up to 62% (Entry 2). The developed methodology should be useful for functionalization of fullerenes in one-pot catalysis as long as starting materials equipped with aryl aldimine functionalities are available.

To investigate the mechanistic pathway of the reaction further, controlled experiments were conducted. We heated a solution of $C_{60}$ (36 mg, 0.05 mmol) with $NiBr_2(PPh_3)_2$ (7.3 mg, 0.010 mmol, 20 mol-%), Zn (16 mg, 0.25 mmol), and $H_2O$ (9 µL, 0.50 mmol) in anhydrous *o*-DCB (6 mL) under nitrogen for 24 h at 120 °C in a sealed tube. HPLC analysis[12] showed a peak corresponding to $C_{60}H_2$[13] at a retention time ($R_t$) of 7.7 min (Buckyprep column, flow rate: 1 mL min$^{-1}$) in 48% yield.

Meier et al. observed that treatment of $C_{60}$ with zinc (excess) at room temperature followed by quenching with water produced $C_{60}H_2$ in 50% yield.[13f] Under our standard reaction conditions, however, we did not observe the formation of $C_{60}H_2$ in the absence of a nickel catalyst, due to the limited amount of zinc (5 equiv.) in the system. Replacement of $H_2O$ by $D_2O$ (4 µL, 0.20 mmol) in the reaction between aldimine **1i** and $C_{60}$ resulted in incorporation of deuterium at the sp$^3$-carbon of $C_{60}$ to afford [D]-**2i** in 19% isolated yield (Scheme 2), thereby providing solid support for our proposed mechanism. However, we did not observe a deuterated amine group because of deuterium/hydrogen exchange[14] during column chromatography (Figure 1; see the Supporting Information for detailed isotope exchange experiments).



Scheme 2. Evidence for the proposed mechanism.

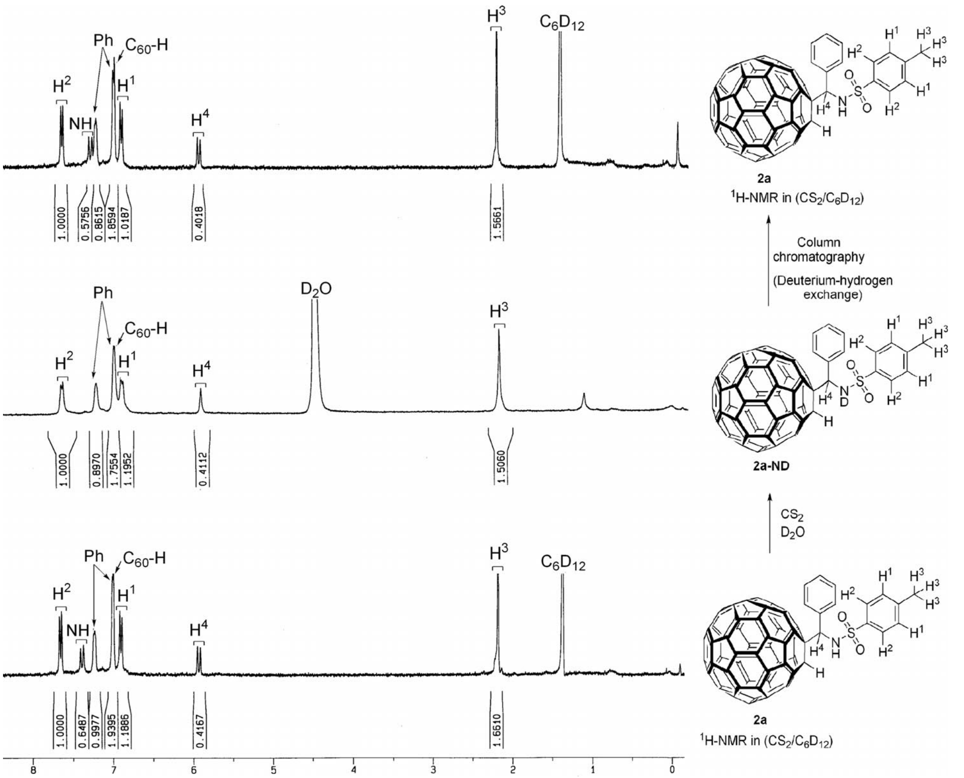
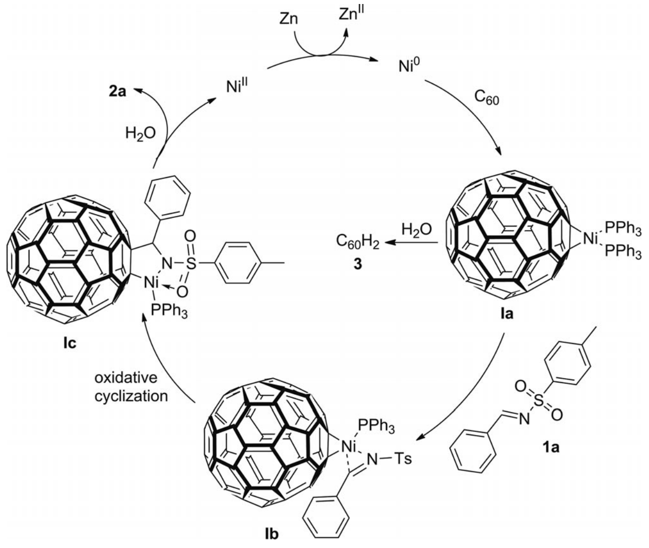


Figure 1. Deuterium/hydrogen exchange in **2a**.

A plausible mechanism for the formation of **2a**–**u** based on the controlled experiments is proposed (Scheme 3). The reaction could be initiated by the reduction of $Ni^{II}$ to $Ni^0$ by zinc, followed by coordination to a [6,6]-ring junction of $C_{60}$ to generate the intermediate nickel complex $Ni(\eta^2\text{-}C_{60})(PPh_3)_2$ (**Ia**). The proposed intermediate complex is equivalent to those described by Fagan and Balch et al., who reported that $C_{60}$ binds to transition metals, such as Ni, Pd, Pt, Ir, and Rh complexes, in an η$^2$-fashion and forms $\eta^2\text{-}C_{60}$ metal complexes.[15] We find that complexation of **Ia** with aldimine **1a** competes with hydrolysis of **Ia**. If the complex **Ia** exists long enough without hydrolysis by $H_2O$, displacement of a $PPh_3$ by an aldimine **1a** and sequential oxidative cyclization through **Ib** could form the five-membered-ring azanickelacycle intermediate **Ic**. Evidence for the formation of five-membered azanickelacycles from imines and alkynes was recently provided by Ogoshi et al.[16] Similarly, five-membered nickelacycles containing nitrogen or oxygen have been observed or proposed as intermediates in small molecules.[9,16,17] From the isolated yields of **2** and $C_{60}H_2$ (**3**) in Table 3, we conclude that hydrolysis is highly dependent on the coordination capabilities of aldimine substrates **1**. The hydrolysis rate of **Ia** can be as fast as nearly twelve times that of complexation rate of **Ia** with **1**, as shown for the 4-(dimethylamino)phenyl 4-chlorophenyl aldimine **1k** (Entry 11) and as slow as one-fifth, exemplified by the 2-methoxynaphthyl phenyl aldimine **1q** (Entry 17). Finally, intermediate **Ic** could then undergo hydrolysis to give derivative **2a** and $Ni^{II}$ species. Again $Ni^{II}$ could be reduced by zinc, regenerating $Ni^0$ for the next cycle.



Scheme 3. Plausible reaction pathway.

We characterized all these reductive coupling products **2a**–**u** by IR and $^1H$ and $^{13}C$ NMR spectroscopy and by electron-spray time-of-flight (ESI-TOF) mass spectrometry (see the Supporting Information). In their IR spectra, S=O stretching bands appeared at 1162 and 1331 cm$^{-1}$. The ESI-TOF mass spectra of **2a**–**u** gave all corresponding *m*/*z* [M – 1] base peaks. The $^1H$ NMR spectrum of **2a** displayed a singlet at $\delta = 7.02$ ppm for the proton bonded to the fullerene sp$^3$ carbon. The protons on the benzylic carbon and nitrogen atoms in **2a** are coupled to each other with a coupling constant of 11.0 Hz and these observations are consistent with known results.[18] In the $^{13}C$ NMR spectra of **2a**, excluding addend carbons, there were at least 46 peaks observed in the 133–155 ppm range for the 58 sp$^2$-carbons of the $C_{60}$ skeleton and two peaks at $\delta = 59.09$ and 70.30 ppm

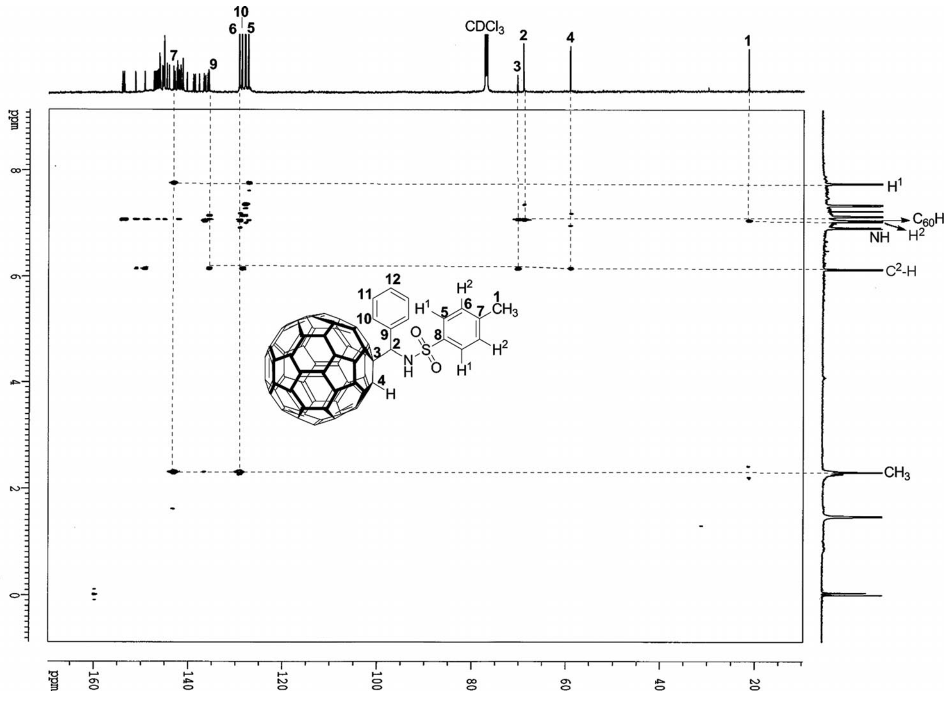


Figure 2. 2D-HMBC spectrum of compound **2a**.

for the two sp$^3$-carbons of the $C_{60}$. The numbers of sp$^2$-carbon atoms in the $^{13}$C NMR spectra of **2a**–**u** revealed that these structures lack any planes of symmetry.

Figure 2 displays a 2D-HMBC spectrum of compound **2a**. We carried out structural elucidation on the basis of one-bond (2D-HMQC) and two- or three-bond (2D-HMBC) correlation spectra.[19] The signals of carbon atoms C2 and C4 are easily predicted by one-bond correlation (HMQC). HMBC data show that the sp$^3$-carbon C3 in the fullerene skeleton correlates with the protons on C2 and C4 through two-bond coupling. The carbon C2 correlates with the proton on C4, which is three bonds away (Figure 2). Lastly, the UV/Vis spectra each displayed a characteristic peak at 429 nm, which corresponds to the electronic absorption for the 1,2 adduct of $C_{60}$.

## Conclusions

In conclusion, we have for the first time successfully demonstrated a late transition-metal-catalyzed [60]fullerene/aldimine reductive coupling reaction leading to the synthesis of 1,2-hydrobenzylated [60]fullerene derivatives. In addition, our control experiments implied that the reaction proceeds through a competing [60]fullerene-nickel complex intermediate, as evidenced by the formation of $C_{60}H_2$. Furthermore, an isotope-labeling experiment in the presence of $D_2O$ afforded the fullerene derivative incorporating deuterium on the sp$^3$-carbon, which provides support for intermediacy of the five-membered azanickelacycle. The developed π–π reductive coupling involving fullerene and aided by metal catalysis should complement another methodology based on [2+2] cycloadditions;[20] these discoveries of the reductive formation of coupling compounds and metal-catalyzed routes to $C_{60}H_2$ are both new to fullerene chemistry. Further applications of these reductive coupling products in materials sciences are under investigation in our laboratory.

## Experimental Section

**Typical Procedure for Synthesis of Reductive Coupling Products 2a–u:** Dry *o*-dichlorobenzene (6 mL) and a stirrer bar were placed in a flame-dried thick-walled high-pressure glass tube containing $C_{60}$ (36 mg, 0.050 mmol), an imine **1** (0.25 mmol), $NiBr_2(PPh_3)_2$ (7.3 mg, 0.010 mmol), Zn (16 mg, 0.25 mmol), and $H_2O$ (1.8–3.6 µL, 2–4 equiv.). The tube was then purged with nitrogen, sealed quickly with a screw-type cap under a stream of nitrogen, and placed in an oil bath at 120 °C. After having been stirred for 24 h, the reaction mixture was allowed to cool to room temperature and then subjected to flash column chromatography with toluene as eluent to recover unreacted $C_{60}$ and $C_{60}H_2$. Continued elution with toluene then gave the reductive coupling product **2**. Spectral data for compounds **2a**–**u** follow.

**Compound 2a:** Yield 0.0106 g. $R_f$ = 0.39 (toluene). $^1$H NMR (300 MHz, $CS_2/CDCl_3$ 1:2): δ = 2.30 (s, 3 H, C*H*$_3$), 6.12 (d, *J* = 11.0 Hz, 1 H, C*H*NH), 6.87 (d, *J* = 11.0 Hz, 1 H, N*H*), 7.02 (s, 1 H, $C_{60}$-*H*), 7.05 (s, 2 H, C*H*), 7.12 (t, *J* = 2.7 Hz, 3 H, C*H*), 7.33 (dd, *J* = 3.5, 6.6 Hz, 2 H, C*H*), 7.73 (d, *J* = 8.2 Hz, 2 H, C*H*) ppm. $^{13}$C NMR (150 MHz, $CS_2/CDCl_3$ 1:2): δ = 21.4 (*C*H$_3$), 59.1 (sp$^3$-*C*–H in $C_{60}$), 69.0 (*C*HNH), 70.3 (other sp$^3$ carbon in $C_{60}$), 127.3, 128.0, 128.02, 128.7, 129.3, 135.7, 135.8, 135.9, 136.4, 136.8, 137.8, 138.7, 139.0, 140.3, 140.4, 141.2, 141.23, 141.3, 141.65, 141.7, 141.8, 141.82, 142.0, 142.04, 142.2, 142.24, 142.39, 142.4, 142.5, 142.54, 142.9, 143.0, 143.2, 146.0, 146.03, 146.08, 146.1, 146.2, 146.3, 146.4, 146.5, 146.7, 146.8, 147.0, 147.1, 147.3, 149.3, 151.3, 153.6, 154.0 ppm. FT-IR (KBr): ṽ = 526, 551, 700, 809, 1056, 1087, 1162, 1330, 1428, 2921, 3255 cm$^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for $C_{74}H_{14}NO_2S$ $[M - H]^-$ 980.0745; found 980.0769.

**Compound 2b:** Yield 0.0128 g. $R_f$ = 0.41 (toluene). $^1$H NMR (300 MHz, $CS_2/CDCl_3$ 1:2): δ = 5.97 (d, *J* = 10.8 Hz, 1 H, C*H*NH), 6.98 (s, 1 H, $C_{60}$-*H*), 7.00 (d, *J* = 3.3 Hz, 3 H, C*H*), 7.12–7.25 (m, 6 H, C*H*, N*H*), 7.77 (d, *J* = 7.4 Hz, 2 H, C*H*) ppm. $^{13}$C NMR (150 MHz, $CS_2/C_6D_{12}$): δ = 60.6 (sp$^3$-*C*–H in $C_{60}$), 70.6 (*C*HNH), 71.9 (other sp$^3$ carbon in $C_{60}$), 129.0, 129.7, 130.2, 133.8, 137.2, 137.6, 137.9, 139.5, 140.3, 141.4, 141.9, 142.8, 143.2, 143.4, 143.6, 143.7, 143.8, 143.9, 144.1, 144.5, 145.7, 146.2, 146.7, 146.9, 147.1, 147.6, 147.7, 147.9, 148.1, 148.3, 148.4, 148.5, 148.7, 148.8, 150.8, 152.9, 155.2, 155.6 ppm. FT-IR (KBr): ṽ = 526, 544, 576, 687, 725, 749, 875, 903, 960, 1046, 1089, 1166, 1325, 1459, 1510 cm$^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for $C_{73}H_{12}NO_2S$ $[M - H]^-$ 966.0588; found 966.0625.

**Compound 2c:** Yield 0.0104 g. $R_f$ = 0.43 (toluene). $^1$H NMR (300 MHz, $CS_2/C_6D_{12}$): δ = 2.15 (s, 3 H, C*H*$_3$), 2.20 (s, 3 H, C*H*$_3$), 5.88 (d, *J* = 11 Hz, 1 H, C*H*NH), 6.80 (d, *J* = 7.7 Hz, 2 H, C*H*), 6.91 (d, *J* = 8.1 Hz, 2 H, C*H*), 6.96 (s, 1 H, $C_{60}$-*H*), 7.11 (d, *J* = 8.0 Hz, 2 H, C*H*), 7.32 (d, *J* = 11.1 Hz, 1 H, N*H*), 7.64 (d, *J* = 8.2 Hz, 2 H, C*H*) ppm. $^{13}$C NMR [150.7 MHz, $CS_2/C_6D_{12}$, with $Cr(acac)_3$ as relaxation reagent]: δ = 22.8 (*C*H$_3$), 23.0 (*C*H$_3$), 60.4 (sp$^3$-*C*–H in $C_{60}$), 70.2 (*C*HNH), 71.9 (other sp$^3$ carbon in $C_{60}$), 128.9, 130.1, 130.6, 134.4, 137.1, 137.5, 137.7, 138.6, 138.9, 139.2, 140.1, 140.4, 141.7, 142.6, 142.61, 142.63, 142.7, 143.0, 143.02, 143.17, 143.2, 143.36, 143.4, 143.6, 143.61, 143.7, 143.77, 143.8, 143.9, 144.0, 144.2, 144.4, 145.5, 146.0, 146.4, 146.48, 146.49, 146.5, 146.6, 146.7, 146.71, 146.9, 147.3, 147.4, 147.42, 147.5, 147.7, 148.1, 148.2, 148.3, 148.6, 151.0, 153.0, 155.2, 155.5 ppm. FT-IR (KBr): ṽ = 526, 567, 665, 754, 810, 1161, 1328, 1429, 2854, 2921, 3025, 3259 cm$^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for $C_{75}H_{16}NO_2S$ $[M - H]^-$ 994.0901; found 994.0956.

**Compound 2d:** Yield 0.006 g. $R_f$ = 0.43 (toluene). $^1$H NMR (300 MHz, $CS_2/C_6D_{12}$): δ = 2.13 (s, 3 H, C*H*$_3$), 5.92 (d, *J* = 10.9 Hz, 1 H, C*H*NH), 6.79 (d, *J* = 8.0 Hz, 2 H, C*H*), 6.95 (s, 1 H, $C_{60}$-*H*), 7.08–7.24 (m, 6 H, C*H*, N*H*), 7.76 (d, *J* = 7.7 Hz, 2 H, C*H*) ppm. $^{13}$C NMR (150 MHz, $CS_2/C_6D_{12}$): δ = 23.0 (*C*H$_3$), 60.6 (sp$^3$-*C*–H in $C_{60}$), 70.4 (*C*HNH), 72.0 (other sp$^3$ carbon in $C_{60}$), 129.0, 130.2, 130.4, 133.6, 134.5, 137.3, 137.6, 137.9, 139.2, 139.4, 140.3, 140.6, 141.6, 141.85, 141.9, 142.8, 143.2, 143.4, 143.6, 143.7, 143.8, 143.9, 144.1, 144.5, 144.6, 145.7, 146.2, 146.67, 146.7, 146.9, 147.1, 147.5, 147.6, 147.7, 147.9, 148.3, 148.4, 148.5, 148.7, 151.1, 153.1, 155.3, 155.6 ppm. FT-IR (KBr): ṽ = 525, 545, 606, 684, 723, 748, 763, 876, 901, 960, 1092, 1166, 1325, 1431, 1511, 2359 cm$^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for $C_{74}H_{14}NO_2S$ $[M - H]^-$ 980.0745; found 980.0789.

**Compound 2e:** Yield 0.008 g. $R_f$ = 0.54 (toluene). $^1$H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 3 H, C*H*$_3$), 6.16 (d, *J* = 11.0 Hz, 1 H, C*H*NH), 6.60 (d, *J* = 10.7 Hz, 1 H, N*H*), 6.98 (d, *J* = 7.9 Hz, 2 H, C*H*), 7.02 (s, 1 H, $C_{60}$-*H*), 7.19–7.25 (m, 4 H, C*H*), 7.75 (d, *J* = 8.5 Hz, 2 H, C*H*) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$): δ = 21.0 (*C*H$_3$), 59.2 (sp$^3$-*C*–H in $C_{60}$), 69.0 (*C*HNH), 70.2 (other sp$^3$ carbon in $C_{60}$), 128.66, 128.7, 128.9, 129.0, 132.3, 135.7, 135.8, 136.6, 137.7, 138.2, 138.5, 138.9, 139.17, 139.2, 140.4, 140.5, 141.25, 141.3, 141.4, 141.7, 141.8, 141.85, 141.9, 142.1, 142.2, 142.3, 142.5, 142.6, 143.05, 143.1, 144.16, 144.2, 144.69, 144.7, 145.2, 145.3, 145.35, 145.4, 145.45, 145.5, 145.59, 145.6, 145.7, 146.09, 146.1, 146.19, 146.2, 146.29, 146.3, 146.45, 146.5, 146.66, 146.7, 146.9, 147.1, 147.3, 147.5, 149.3, 151.1, 153.5, 153.9 ppm. FT-IR (KBr): $\tilde{\nu}$ = 526, 627, 754, 1035, 1057, 1087, 1163, 1339, 1509, 2851, 2920, 2955, 3257 $\text{cm}^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for $C_{74}H_{13}ClNO_2S$ $[M - H]^-$ 1014.0355; found 1014.0388.

**Compound 2f:** Yield 0.0061 g. $R_f$ = 0.24 (toluene). $^1$H NMR (300 MHz, $CS_2/CDCl_3$ 1:2): $\delta$ = 2.34 (s, 3 H, $CH_3$), 3.73 (s, 3 H, $OCH_3$), 6.13 (d, $J$ = 10.7 Hz, 1 H, C*H*NH), 6.56 (d, $J$ = 10.7 Hz, 1 H, N*H*), 6.67 (d, $J$ = 8.2 Hz, 2 H, C*H*), 7.02 (s, 1 H, $C_{60}$-*H*), 7.10 (d, $J$ = 8.0 Hz, 2 H, C*H*), 7.27 (d, $J$ = 6.7 Hz, 2 H, C*H*), 7.74 (d, $J$ = 7.6 Hz, 2 H, C*H*) ppm. $^{13}$C NMR [150.7 MHz, $CS_2/CDCl_3$ 1:2, with Cr(acac)$_3$ as relaxation reagent]: $\delta$ = 21.4 ($CH_3$), 55.1 ($OCH_3$), 59.1 (sp$^3$-*C*–H in $C_{60}$), 68.5 (*C*HNH), 70.6 (other sp$^3$ carbon in $C_{60}$), 133.5, 127.3, 127.9, 129.3, 129.8, 135.7, 135.9, 136.5, 136.8, 137.7, 138.8, 139.1, 140.3, 140.4, 141.2, 141.28, 141.3, 141.67, 141.7, 141.8, 141.84, 142.1, 142.2, 142.3, 142.4, 142.5, 142.6, 143.0, 143.02, 143.3, 144.1, 144.14, 144.6, 144.7, 145.2, 145.22, 145.24, 145.3, 145.4, 145.41, 145.5, 145.58, 145.6, 146.01, 146.1, 146.12, 146.14, 146.2, 146.24, 146.4, 146.42, 146.7, 146.72, 146.9, 147.0, 147.2, 147.4, 149.6, 151.4, 153.7, 154.0, 159.2 ppm. FT-IR (KBr): $\tilde{\nu}$ = 526, 545, 671, 810, 1036, 1161, 1243, 1328, 1516, 2921, 3240 $\text{cm}^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for $C_{75}H_{16}NO_3S$ $[M - H]^-$ 1010.0850; found 1010.0900.

**Compound 2g:** Yield 0.006 g. $R_f$ = 0.23 (toluene). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.73 (s, 3 H, $OCH_3$), 6.17 (d, $J$ = 10.8 Hz, 1 H, C*H*NH), 6.59 (d, $J$ = 11.0 Hz, 1 H, N*H*), 6.67 (d, $J$ = 8.6 Hz, 2 H, C*H*), 7.03 (s, 1 H, $C_{60}$-*H*), 7.26 (d, $J$ = 8.4 Hz, 2 H, C*H*), 7.34 (d, $J$ = 8.0 Hz, 2 H, C*H*), 7.42 (d, $J$ = 7.6 Hz, 1 H, C*H*), 7.88 (d, $J$ = 7.5 Hz, 2 H, C*H*) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 55.2 ($OCH_3$), 59.2 (sp$^3$-*C*–H in $C_{60}$), 68.6 (*C*HNH), 70.7 (other sp$^3$ carbon in $C_{60}$), 113.7, 127.4, 128.9, 129.9, 132.7, 135.8, 136.0, 136.6, 136.61, 137.8, 138.9, 139.3, 139.8, 140.4, 140.5, 141.4, 141.42, 141.5, 141.8, 141.83, 142.0, 142.2, 142.3, 142.4, 142.6, 142.68, 142.7, 143.09, 143.1, 143.16, 144.2, 144.3, 144.78, 144.8, 145.3, 145.37, 145.4, 145.49, 145.5, 145.6, 145.7, 145.72, 145.8, 146.16, 146.2, 146.27, 146.3, 146.37, 146.4, 146.5, 146.6, 146.8, 147.0, 147.2, 147.4, 147.5, 149.6, 151.4, 153.8, 154.2, 159.4 ppm. FT-IR (KBr): $\tilde{\nu}$ = 525, 544, 605, 686, 749, 875, 1035, 1162, 1250, 1325, 1433, 1451, 1511 $\text{cm}^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for $C_{74}H_{14}NO_3S$ $[M - H]^-$ 996.0694; found 996.0739.

**Compound 2h:** Yield 0.0058 g. $R_f$ = 0.36 (toluene). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.76 (s, 3 H, $OCH_3$), 6.15 (d, $J$ = 10.9 Hz, 1 H, C*H*NH), 6.67 (d, $J$ = 10.8 Hz, 1 H, N*H*), 6.70 (d, $J$ = 8.7 Hz, 2 H, C*H*), 7.01 (s, 1 H, $C_{60}$-*H*), 7.24–7.28 (m, 4 H, C*H*), 7.77 (d, $J$ = 8.6 Hz, 2 H, C*H*) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 55.4 ($OCH_3$), 59.3 (sp$^3$-*C*–H in $C_{60}$), 68.8 (*C*HNH), 70.5 (other sp$^3$ carbon in $C_{60}$), 113.8, 127.6, 128.8, 129.1, 130.0, 135.8, 135.9, 136.7, 137.8, 138.4, 139.0, 139.3, 139.33, 140.5, 140.6, 141.3, 141.4, 141.47, 141.5, 141.8, 141.9, 141.96, 142.0, 142.2, 142.3, 142.4, 142.6, 142.7, 142.73, 143.16, 143.2, 144.26, 144.3, 144.8, 144.83, 145.3, 145.4, 145.5, 145.52, 145.56, 145.6, 145.68, 145.7, 145.8, 146.2, 146.23, 146.3, 146.32, 146.4, 146.42, 146.55, 146.6, 146.8, 147.0, 147.2, 147.3, 147.6, 149.4, 151.2, 153.6, 154.0, 159.6 ppm. FT-IR (KBr): $\tilde{\nu}$ = 526, 545, 575, 754, 824, 1031, 1088, 1163, 1214, 1253, 1338, 1458, 2853, 2924, 2956 $\text{cm}^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for $C_{74}H_{13}ClNO_3S$ $[M - H]^-$ 1030.0304; found 1030.0314.

**Compound 2i:** Yield 0.011 g. $R_f$ = 0.5 (toluene). $^1$H NMR (300 MHz, $CS_2/C_6D_{12}$): $\delta$ = 1.13 [s, 9 H, $C(CH_3)_3$], 2.15 (s, 3 H, $CH_3$), 5.87 (d, $J$ = 11.1 Hz, 1 H, C*H*NH), 6.86 (d, $J$ = 8.0 Hz, 2 H, C*H*), 6.95 (s, 1 H, $C_{60}$-*H*), 6.98 (d, $J$ = 8.4 Hz, 2 H, C*H*), 7.12 (d, $J$ = 8.4 Hz, 2 H, C*H*), 7.26 (d, $J$ = 11.1 Hz, 1 H, N*H*), 7.59 (d, $J$ = 8.2 Hz, 2 H, C*H*) ppm. $^{13}$C NMR [150.7 MHz, $CS_2/C_6D_{12}$, with Cr(acac)$_3$ as relaxation reagent]: $\delta$ = 21.3 ($CH_3$), 31.0 [$C(CH_3)_3$], 34.1 [$C(CH_3)_3$], 59.1 (sp$^3$-*C*–H in $C_{60}$), 68.7 (*C*HNH), 70.2 (other sp$^3$ carbon in $C_{60}$), 124.8, 127.3, 128.3, 129.0, 132.7, 135.6, 135.9, 136.4, 136.7, 137.6, 138.7, 139.0, 140.2, 140.23, 141.1, 141.2, 141.55, 141.6, 141.7, 141.72, 141.9, 141.94, 142.1, 142.14, 142.3, 142.4, 142.43, 142.7, 142.8, 142.9, 144.0, 144.5, 144.53, 145.0, 145.1, 145.2, 145.24, 145.3, 145.4, 145.5, 145.9, 145.92, 145.98, 146.0, 146.1, 146.2, 146.3, 146.6, 146.63, 146.8, 146.9, 147.2, 147.22, 149.6, 150.8, 151.3, 153.6, 153.9 ppm. FT-IR (KBr): $\tilde{\nu}$ = 525, 574, 664, 729, 903 1161, 1323, 1650, 2960, 3254 $\text{cm}^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for $C_{78}H_{22}NO_2S$ $[M - H]^-$ 1036.1371; found 1036.1422.

**Compound 2j:** Yield 0.0111 g. $R_f$ = 0.5 (toluene). $^1$H NMR (300 MHz, $CS_2/C_6D_{12}$): $\delta$ = 1.12 [s, 9 H, $C(CH_3)_3$], 5.91 (d, $J$ = 11.0 Hz, 1 H, C*H*NH), 6.96–7.00 (m, 3 H, C*H*), 7.06–7.17 (m, 5 H, C*H*), 7.24 (d, $J$ = 11.1 Hz, 1 H, N*H*), 7.71–7.74 (m, 2 H, C*H*) ppm. $^{13}$C NMR (150 MHz, $CS_2/C_6D_{12}$): $\delta$ = 32.5 [$C(CH_3)_3$], 35.3 [$C(CH_3)_3$], 60.6 (sp$^3$-*C*–H in $C_{60}$), 70.3 (*C*HNH), 71.7 (other sp$^3$ carbon in $C_{60}$), 126.4, 128.8, 129.9, 133.3, 134.1, 137.1, 137.4, 137.8, 139.2, 140.2, 140.5, 141.3, 141.6, 141.7, 142.6, 142.64, 142.96, 143.0, 143.1, 143.4, 143.5, 143.6, 143.7, 143.8, 144.26, 144.3, 145.5, 145.9, 146.5, 146.6, 146.65, 146.7, 146.9, 147.3, 147.33, 147.4, 147.5, 147.7, 148.1, 148.2, 148.3, 148.6, 151.0, 151.8, 155.0, 155.4 ppm. FT-IR (KBr): $\tilde{\nu}$ = 526, 565, 603, 685, 732, 749, 902, 1165, 1263, 1324, 1429, 1427, 2960, 3263 $\text{cm}^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for $C_{77}H_{20}NO_2S$ $[M - H]^-$ 1022.1214; found 1022.1257.

**Compound 2k:** Yield 0.0027 g. $R_f$ = 0.29 (toluene). $^1$H NMR (300 MHz, $CS_2/C_6D_{12}$): $\delta$ = 2.80 [s, 6 H, $N(CH_3)_2$], 5.84 (d, $J$ = 11.2 Hz, 1 H, C*H*NH), 6.26 (d, $J$ = 8.6 Hz, 2 H, C*H*), 6.91 (s, 1 H, $C_{60}$-*H*), 6.99 (d, $J$ = 8.6 Hz, 2 H, C*H*), 7.03 (d, $J$ = 8.4 Hz, 2 H, C*H*), 7.17 (d, $J$ = 10.6 Hz, 1 H, N*H*), 7.64 (d, $J$ = 8.6 Hz, 2 H, C*H*) ppm. $^{13}$C NMR (150 MHz, $CS_2/C_6D_{12}$): $\delta$ = 41.6 [$N(CH_3)_2$], 60.7 (sp$^3$-*C*–H in $C_{60}$), 70.5 (*C*HNH), 72.5 (other sp$^3$ carbon in $C_{60}$), 113.1, 124.3, 130.3, 130.5, 131.1, 137.3, 137.6, 137.9, 139.2, 140.1, 140.2, 140.4, 140.8, 141.8, 141.9, 142.8, 142.85, 142.90, 143.2, 143.3, 143.4, 143.6, 143.8, 143.96, 144.0, 144.07, 144.1, 144.14, 144.5, 144.6, 145.7, 146.17, 146.2, 146.7, 146.72, 146.76, 146.78, 146.8, 146.9, 147.0, 147.1, 147.5, 147.57, 147.6, 147.7, 147.8, 147.89, 147.9, 148.3, 148.4, 148.55, 148.6, 148.8, 149.0, 151.0, 151.5, 153.2, 155.4, 155.6 ppm. FT-IR (KBr): $\tilde{\nu}$ = 526, 575, 625, 713, 755, 823, 877, 1028, 1098, 1161, 1339, 2850, 2917, 2956, 3223 $\text{cm}^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for $C_{75}H_{16}ClN_2O_2S$ $[M - H]^-$ 1043.0621; found 1043.0702.

**Compound 2l:** Yield 0.0041 g. $R_f$ = 0.11 (toluene). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 6.28 (d, $J$ = 10.7 Hz, 1 H, C*H*NH), 6.96 (d, $J$ = 10.1 Hz,1 H, N*H*), 7.02 (s, 1 H, $C_{60}$-*H*), 7.37 (d, $J$ = 7.7 Hz, 2 H, C*H*), 7.44–7.53 (m, 5 H, C*H*), 7.91 (d, $J$ = 7.4 Hz, 2 H, C*H*) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 59.2 (sp$^3$-*C*–H in $C_{60}$), 68.5 (*C*HNH), 69.6 (other sp$^3$ carbon in $C_{60}$), 112.3, 117.9, 127.2, 129.1, 129.4, 131.7, 133.2, 135.5, 135.6, 136.7, 138.1, 139.0, 139.2, 139.4, 140.5, 140.6, 140.9, 141.1, 141.2, 141.4, 141.79, 141.8, 142.1, 142.2, 142.3, 142.6, 142.7, 143.0, 143.1, 143.14, 144.05, 144.1, 144.7, 144.8, 145.28, 145.3, 145.4, 145.5, 145.54, 145.6, 145.8, 145.83, 146.1, 146.2, 146.24, 146.27, 146.3, 146.4, 146.5, 146.6, 146.7, 147.1, 147.5, 147.8, 150.0, 153.0, 153.5 ppm. FT-IR (KBr): $\tilde{\nu}$ = 526, 560, 603, 687, 753, 1079, 1164, 1214, 1340, 1429, 1448, 2921, 3240 $\text{cm}^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for $C_{74}H_{11}N_2O_2S$ $[M - H]^-$ 991.0541; found 991.0591.

**Compound 2m:** Yield 0.0053 g. $R_f$ = 0.45 (toluene). $^1$H NMR (300 MHz, CS$_2$/C$_6$D$_{12}$): $\delta$ = 1.92 (s, 3 H, C$H_3$), 6.47 (d, $J$ = 8.1 Hz, 2 H, C$H$), 6.84 (d, $J$ = 11.4 Hz, 1 H, C$H$NH), 7.17 (t, $J$ = 8.9 Hz, 2 H, C$H$), 7.30 (t, $J$ = 7.4 Hz, 1 H, C$H$), 7.43–7.63 (m. 7 H, C$H$, N$H$ ), 8.35 (d, $J$ = 8.6 Hz, 1 H, C$H$) ppm. $^{13}$C NMR [150.7 MHz, CS$_2$/C$_6$D$_{12}$, with Cr(acac)$_3$ as relaxation reagent]: $\delta$ = 22.7 ($C$H$_3$), 61.1 (sp$^3$-$C$–H in C$_{60}$), 64.0 ($C$HNH), 71.8 (other sp$^3$ carbon in C$_{60}$), 124.2, 126.3, 127.2, 128.1, 128.3, 128.6, 129.9, 130.0, 130.1, 132.7, 133.8, 134.5, 137.1, 137.6, 137.7, 139.4, 139.9, 140.5, 141.7, 142.4, 142.5, 142.53, 142.6, 143.0, 143.1, 143.4, 143.45, 143.5, 143.6, 143.64, 143.68, 143.7, 143.86, 143.9, 144.2, 144.3, 145.4, 145.5, 146.0, 146.39, 146.4, 146.5, 146.6, 146.63, 146.8, 146.9, 147.0, 147.3, 147.4, 147.55, 147.6, 147.7, 148.1, 148.14, 148.3, 148.6, 148.9, 151.0, 152.6, 154.9, 155.7 ppm. FT-IR (KBr): ṽ = 527, 671, 773, 1088, 1160, 1380, 1429, 1508 cm$^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for C$_{78}$H$_{16}$NO$_2$S [M – H]$^-$ 1030.0901; found 1030.0955.

**Compound 2n:** Yield 0.0102 g. $R_f$ = 0.44 (toluene). $^1$H NMR (300 MHz, CS$_2$/CDCl$_3$ 1:2): $\delta$ = 1.92 (s, 3 H, C$H_3$), 6.33 (d, $J$ = 11.0 Hz, 1 H, C$H$NH), 6.78 (d, $J$ = 8.1 Hz, 2 H, C$H$), 6.97 (d, $J$ = 11.1 Hz, 1 H, N$H$), 7.13 (s, 1 H, C$_{60}$-$H$), 7.42–7.47 (m, 2 H, C$H$), 7.55 (d, $J$ = 8.9 Hz, 1 H, C$H$), 7.64–7.79 (m, 6 H, C$H$) ppm. $^{13}$C NMR [150.7 MHz, CS$_2$/CDCl$_3$ 1:2, with Cr(acac)$_3$ as relaxation reagent]: $\delta$ = 21.0 ($C$H$_3$), 59.3 (sp$^3$-$C$–H in C$_{60}$), 69.4 ($C$HNH), 70.3 (other sp$^3$ carbon in C$_{60}$), 125.9, 126.3, 126.4, 127.2, 127.5, 127.9, 128.1, 128.7, 129.1, 132.4, 132.6, 132.9, 135.7, 136.0, 136.4, 136.5, 137.8, 138.8, 139.2, 140.3, 140.4, 141.27, 141.3, 141.67, 141.7, 141.8, 141.83, 142.05, 142.1, 142.2, 142.3, 142.4, 142.5, 142.6, 143.0, 143.02, 143.5, 144.1, 144.6, 144.7, 145.18, 145.2, 145.37, 145.4, 145.43, 145.55, 145.6, 145.7, 146.0, 146.1, 146.12, 146.15, 146.2, 146.36, 146.4, 146.6, 146.7, 146.9, 147.0, 147.2, 147.4, 149.5, 151.2, 153.6, 154.0 ppm. FT-IR (KBr): ṽ = 526, 566, 672, 784, 808, 900, 1059, 1079, 1161, 1324, 1428, 15132884, 2918, 3053, 3258 cm$^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for C$_{78}$H$_{16}$NO$_2$S [M – H]$^-$ 1030.0901; found 1030.0948.

**Compound 2o:** Yield 0.0097 g. $R_f$ = 0.43 (toluene). $^1$H NMR (300 MHz, CS$_2$/C$_6$D$_{12}$): $\delta$ = 6.13 (d, $J$ = 11.2 Hz, 1 H, C$H$NH), 6.88 (d, $J$ = 2.4 Hz, 3 H, C$H$), 7.04 (s, 1 H, C$_{60}$-$H$), 7.25 (dd, $J$ = 3.2, 6.1 Hz, 2 H), 7.43 (t, $J$ = 1.6 Hz, 2 H), 7.51 (dd, $J$ = 3.4, 5.9 Hz, 2 H), 7.63 (s, 1 H), 7.78–7.81 (m, 3 H) ppm. $^{13}$C NMR [150.7 MHz, CS$_2$/CDCl$_3$, with Cr(acac)$_3$ as relaxation reagent]: $\delta$ = 60.6 (sp$^3$-$C$–H in C$_{60}$), 70.7 ($C$HNH), 71.8 (other sp$^3$ carbon in C$_{60}$), 127.3, 128.0, 128.2, 128.7, 129.1, 129.4, 129.5, 129.86, 129.9, 133.5, 133.7, 134.0, 134.5, 134.8, 137.2, 137.5, 137.8, 139.3, 140.2, 140.6, 141.3, 141.7, 141.8, 142.7, 142.74, 142.9, 143.1, 143.11, 143.2, 143.23, 143.4, 143.5, 143.6, 143.7, 143.78, 143.8, 143.9, 144.0, 144.3, 144.4, 145.5, 146.0, 146.5, 146.56, 146.6, 146.7, 146.75, 146.8, 146.9, 146.96, 147.0, 147.4, 147.43, 147.47, 147.5, 147.6, 147.7, 147.9, 148.2, 148.24, 148.4, 148.5, 148.7, 150.8, 152.7, 155.1, 155.4 ppm. FT-IR (KBr): ṽ = 527, 602, 727, 749, 896, 1059, 1079, 1163, 1328, 1423, 2850, 2919, 3257 cm$^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for C$_{77}$H$_{14}$NO$_2$S [M – H]$^-$ 1016.0745; found 1016.0821.

**Compound 2p:** Yield 0.0117 g. $R_f$ = 0.41 (toluene). $^1$H NMR (300 MHz, CS$_2$/C$_6$D$_{12}$): $\delta$ = 1.95 (s, 3 H, C$H_3$), 3.62 (s, 3 H, OC$H_3$), 6.44 (d, $J$ = 8.1 Hz, 2 H, C$H$), 6.73 (d, $J$ = 11.1 Hz, 1 H, C$H$NH), 6.84 (d, $J$ = 9.1 Hz, 1 H, C$H$), 7.20 (d, $J$ = 7.4 Hz, 1 H, C$H$), 7.24 (s, 1 H, C$_{60}$-$H$), 7.30 (d, $J$ = 8.2 Hz, 2 H, C$H$), 7.46–7.52 (m, 3 H, C$H$), 7.63 (d, $J$ = 10.5 Hz, 1 H, N$H$), 8.28 (d, $J$ = 9.2 Hz, 1 H, C$H$) ppm. $^{13}$C NMR [150.7 MHz, CS$_2$/C$_6$D$_{12}$, with Cr(acac)$_3$ as relaxation reagent]: $\delta$ = 22.6 ($C$H$_3$), 56.5 (O$C$H$_3$), 61.0 (sp$^3$-$C$–H in C$_{60}$), 64.3 ($C$HNH), 71.7 (other sp$^3$ carbon in C$_{60}$), 114.1, 118.2, 124.1, 125.4, 128.1, 129.0, 129.7, 129.8, 130.3, 132.1, 133.8, 137.7, 137.9, 138.4, 139.9, 140.3, 141.7, 142.4, 142.5, 143.0, 143.1, 143.14, 143.2, 143.3, 143.5, 143.54, 143.6, 143.8, 143.84, 143.9, 144.3, 144.5, 145.3, 145.6, 145.9, 145.94, 146.1, 146.45, 146.5, 146.54, 146.7, 146.8, 147.0, 147.2, 147.22, 147.3, 147.5, 147.7, 148.1, 148.2, 148.3, 148.5, 148.6, 153.0, 154.5, 156.0, 156.03, 156.1 ppm. FT-IR (KBr): ṽ = 526, 800, 1019, 1078, 1160, 1246, 1320, 1507, 2850, 2922 cm$^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for C$_{79}$H$_{18}$NO$_3$S [M – H]$^-$ 1060.1007; found 1060.1063.

**Compound 2q:** Yield 0.0103 g. $R_f$ = 0.43 (toluene). $^1$H NMR (300 MHz, CS$_2$/CDCl$_3$ 1:2): $\delta$ = 3.70 (s, 3 H, OC$H_3$), 6.83–6.94 (m, 3 H), 7.01–7.06 (m, 2 H), 7.33–7.40 (m, 2 H), 7.60–7.67 (m, 5 H), 7.95 (d, $J$ = 20.0 Hz, 1 H), 8.47 (d, $J$ = 9.18 Hz, 1 H) ppm. $^{13}$C NMR (150 MHz, CS$_2$/CDCl$_3$ 1:2): $\delta$ = 55.4 (O$C$H$_3$), 59.7 (sp$^3$-$C$–H in C$_{60}$), 63.4 ($C$HNH), 70.5 (other sp$^3$ carbon in C$_{60}$), 112.7, 115.9, 122.6, 124.0, 126.6, 127.8, 128.0, 128.5, 129.0, 131.4, 132.1, 132.5, 135.6, 135.7, 136.4, 136.6, 138.7, 138.9, 139.2, 140.4, 141.1, 141.3, 141.7, 141.8, 142.1, 142.2, 142.4, 142.5, 142.59, 142.6, 143.0, 143.2, 144.0, 144.3, 144.6, 144.8, 145.2, 145.28, 145.3, 145.4, 145.6, 145.9, 146.0, 146.1, 146.3, 146.4, 146.8, 146.96, 147.0, 147.3, 147.4, 151.6, 153.0, 154.7, 154.75, 154.8 ppm. FT-IR (KBr): ṽ = 527, 577, 596, 639, 686, 750, 804, 871, 912, 960, 1022, 1082, 1166, 1215, 1249, 1340, 1428, 1460, 1515, 1597 cm$^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for C$_{78}$H$_{16}$NO$_3$S [M – H]$^-$ 1046.0850; found 1046.0879.

**Compound 2r:** Yield 0.01 g. $R_f$ = 0.13 (toluene). $^1$H NMR (300 MHz, CS$_2$/C$_6$D$_{12}$): $\delta$ = 2.29 (s, 3 H, C$H_3$), 6.0–6.05 (m, 1 H), 6.17 (d, $J$ = 2.7 Hz, 1 H) 6.61 (d, $J$ = 10.8 Hz, 1 H, N$H$), 6.84 (s, 1 H, C$_{60}$-$H$), 7.09 (t, $J$ = 4.5 Hz, 4 H, C$H$), 7.68 (d, $J$ = 7.8 Hz, 2 H, C$H$) ppm. $^{13}$C NMR [150.7 MHz, CS$_2$/C$_6$D$_{12}$, with Cr(acac)$_3$ as relaxation reagent]: $\delta$ = 23.2 ($C$H$_3$), 59.6 (sp$^3$-$C$–H in C$_{60}$), 63.8 ($C$HNH), 71.2 (other sp$^3$ carbon in C$_{60}$), 111.8, 111.9, 128.8, 130.9, 137.2, 137.5, 138.1, 138.8, 139.0, 140.5, 140.7, 141.7, 141.8, 142.7, 142.8, 143.1, 143.3, 143.4, 143.6, 143.7, 143.9, 143.94, 144.0, 144.3, 144.4, 144.41, 145.6, 146.0, 146.1, 146.6, 146.63, 146.67, 146.7, 146.8, 146.9, 146.92, 146.95, 147.0, 147.4, 147.5, 147.6, 147.8, 147.9, 148.2, 148.24, 148.3, 148.4, 148.8, 151.1, 151.7, 152.6, 155.0, 155.1 ppm. FT-IR (KBr): ṽ = 526, 595, 665, 785, 812, 902, 1085, 1162, 1331, 1422, 1509 cm$^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for C$_{72}$H$_{12}$NO$_3$S [M – H]$^-$ 970.0537; found 970.0561.

**Compound 2s:** Yield 0.0134 g. $R_f$ = 0.35 (toluene). $^1$H NMR (300 MHz, CS$_2$/C$_6$D$_{12}$): $\delta$ = 2.26 (s, 3 H, C$H_3$), 6.23 (d, $J$ = 10.7 Hz, 1 H, C$H$NH), 6.71–6.73 (m, 2 H, C$H$, N$H$), 6.84 (s, 1 H, C$_{60}$-$H$), 7.02 (t, $J$ = 7.6 Hz, 4 H, C$H$), 7.66 (d, $J$ = 8.2 Hz, 2 H, C$H$) ppm. $^{13}$C NMR [150.7 MHz, CS$_2$/C$_6$D$_{12}$, with Cr(acac)$_3$ as relaxation reagent]: $\delta$ = 23.2 ($C$H$_3$), 60.0 (sp$^3$-$C$–H in C$_{60}$), 65.8 ($C$HNH), 72.1 (other sp$^3$ carbon in C$_{60}$), 127.3, 128.0, 128.9, 129.6, 130.8, 137.2, 137.4, 138.2, 138.7, 139.3, 140.2, 140.7, 141.2, 141.7, 141.8, 142.56, 142.6, 142.7, 142.8, 143.1, 143.27, 143.3, 143.5, 143.6, 143.64, 143.8, 143.9, 143.94, 144.0, 144.3, 144.31, 144.4, 145.6, 146.0, 146.6, 146.7, 146.9, 147.1, 147.4, 147.42, 147.5, 147.6, 147.8, 148.1, 148.14, 148.4, 148.7, 148.8, 150.9, 152.4, 154.8, 155.2 ppm. FT-IR (KBr): ṽ = 526, 669, 700, 809, 901, 1031, 1159, 1263, 1326, 1420, 1507, 1559 cm$^{-1}$. HRMS (ESI-TOF, negative): *m*/*z* calcd. for C$_{72}$H$_{12}$NO$_2$S$_2$ [M – H]$^-$ 986.0309; found 986.0343.

**Compound 2t:** Yield 0.0101 g. $R_f$ = 0.37 (toluene). $^1$H NMR (300 MHz, CS$_2$/CDCl$_3$ 1:2): $\delta$ = 6.15 (d, $J$ = 10.8 Hz, 1 H, C$H$NH), 6.48 (d, $J$ = 10.5 Hz, 1 H, N$H$), 6.84 (dd, $J$ = 3.7, 5.0 Hz, 1 H, C$H$), 6.92 (s, 1 H, C$_{60}$-$H$), 7.09 (d, $J$ = 3.7 Hz, 1 H, C$H$), 7.18 (d, $J$ = 5.1 Hz, 1 H, C$H$), 7.39 (t, $J$ = 7.2 Hz, 2 H, C$H$), 7.49 (t, $J$ = 7.5 Hz, 1 H, C$H$), 7.89 (d, $J$ = 7.5 Hz, 2 H, C$H$) ppm. $^{13}$C NMR [150.7 MHz, CS$_2$/C$_6$D$_{12}$, with Cr(acac)$_3$ as relaxation reagent]: $\delta$ = 60.0 (sp$^3$-$C$–H in C$_{60}$), 65.8 ($C$HNH), 72.0 (other sp$^3$ carbon in

C$_{60}$), 127.5, 128.1, 128.7, 128.8, 129.7, 130.1, 130.2, 133.7, 133.9, 137.3, 137.4, 138.2, 139.3, 140.2, 140.7, 140.8, 141.4, 141.8, 141.81, 142.1, 142.2, 142.24, 142.6, 142.61, 142.7, 142.9, 143.1, 143.3, 143.32, 143.5, 143.6, 143.7, 143.86, 143.9, 144.0, 144.3, 144.4, 144.7, 145.1, 145.2, 145.6, 146.1, 146.6, 146.63, 146.8, 146.9, 147.1, 147.4, 147.44, 147.5, 147.7, 147.8, 147.9, 148.1, 148.12, 148.2, 148.4, 148.8, 148.9, 149.1, 150.8, 152.4, 154.8, 155.2 ppm. FT-IR (KBr): $\tilde{\nu}$ = 526, 595, 686, 899, 1059, 1163, 1329, 1447, 1513 cm$^{-1}$. HRMS (ESI-TOF, negative): *m/z* calcd. for $C_{71}H_{10}NO_2S_2$ [M – H]$^-$ 972.0152; found 972.0190.

**Compound 2u:** Yield 0.014 g. $R_f$ = 0.39 (toluene). $^1$H NMR (300 MHz, $CS_2/C_6D_{12}$): $\delta$ = 2.23 (s, 1 H, C$H_3$), 6.01 (d, $J$ = 10.8 Hz, 1 H, C*H*NH), 6.92 (s, 1 H, C$_{60}$-*H*), 6.96–7.06 (m, 5 H, C*H*), 7.47 (d, $J$ = 11.2 Hz, 1 H, N*H*), 7.69 (d, $J$ = 8.2 Hz, 2 H, C*H*) ppm. $^{13}$C NMR [150.7 MHz, $CS_2/C_6D_{12}$, with Cr(acac)$_3$ as relaxation reagent]: $\delta$ = 23.1 (*C*H$_3$), 60.1 (sp$^3$-*C*–H in C$_{60}$), 66.1 (*C*HNH), 71.7 (other sp$^3$ carbon in C$_{60}$), 126.3, 127.4, 128.3, 128.4, 128.6, 128.8, 128.9, 137.1, 137.5, 137.8, 138.3, 138.9, 139.2, 140.2, 140.6, 141.7, 145.6, 146.0, 146.4, 146.5, 146.54, 146.6, 146.7, 146.71, 146.8, 146.85, 146.9, 146.93, 147.3, 147.4, 147.5, 147.56, 147.6, 147.7, 147.73, 148.1, 148.13, 148.2, 148.4, 148.5, 148.7, 151.2, 152.9, 155.1, 155.3 ppm. FT-IR (KBr): $\tilde{\nu}$ = 526, 672, 905, 1059, 1079, 1159, 1330, 2850, 2918, 3235 cm$^{-1}$. HRMS (ESI-TOF, negative): *m/z* calcd. for $C_{72}H_{12}NO_2S_2$ [M – H]$^-$ 986.0309; found 986.0363.

**Supporting Information** (see footnote on the first page of this article): Detailed experimental procedures and full spectroscopic data for all new compounds are given, as well as copies of $^1$H and $^{13}$C NMR spectra and HRESI mass spectra.

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