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Palladium-Catalyzed and Hybrid Acids-Assisted Synthesis of [60]Fulleroazepines in One Pot under Mild Conditions: Annulation of *N*-Sulfonyl-2-aminobiaryls with [60]Fullerene through Sequential C-H Bond Activation, C-C and C-N Bond Formation

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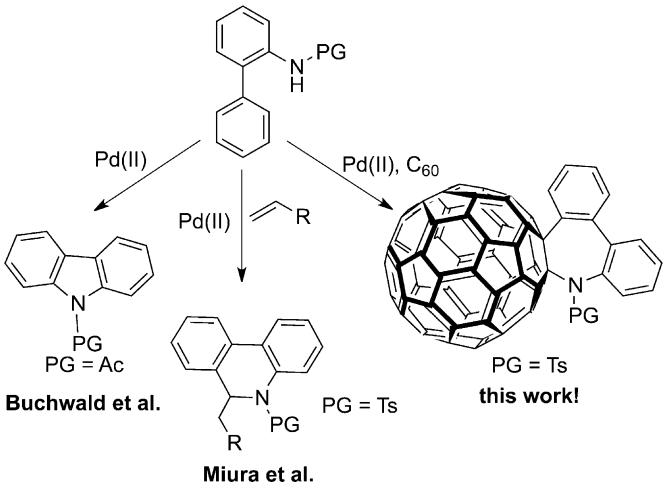
Abstract: An extraordinarily efficient hybrid acids-assisted, palladium-catalyzed and chelating-group-assisted C–H bond activation of *N*-sulfonyl-2-aminobiaryls and their annulations with [60]fullerene *via* sequential C–C and C–N bond formation at room temperature to afford [60]fulleroazepines is demonstrated. The formation of [60]fulleroazepines is highly regioselective and tolerant to both electron-withdrawing and electron-donating groups on the aryl moiety and the reaction gives monofunctionalized fullerenes in good yields (up to 54% isolated yield and 92% based on converted C_{60}).

Keywords: C–C, C–N bond formation; C–H activation; fullerenes; hybrid acids; palladium

Introduction

Fullerenes and their derivatives have attracted much attention for more than two decades because they have displayed promising applications in the field of materials science.[1] Traditionally, functionalized fullerenes were mostly prepared by common organic reactions.[2] Recently, the transition metal-mediated methodology has emerged as another potential tool for the functionalization of fullerenes[3] since functionalizing fullerenes by metal catalysis provides both efficient and greener synthetic features. In this context, palladium-mediated reactions of small molecules with fullerenes have been relatively more explored.[3a–e] With the greener C–H bond activation methodology, we recently have achieved the annulation of benzamides with [60]fullerene through palladium(II)-catalyzed C–H bond activation and prepared fulleroisoquinolinones[4] for their applications as n-type materials in highly-efficient organic photovoltaics (OPVs).[1e] On the other hand, the recent progress in palladium-catalyzed C–H bond activation has made it one of the most powerful tools to construct C–C, C–O, and C–N bonds, and its synthetic applications have been elegantly demonstrated in the synthesis of valuable pharmaceutical and natural products.[5] Generally, a directing group is needed for selective activation of a C–H bond. A number of directing groups such as carbonyl-based, nitrogen-containing groups or an allyl moiety have been utilized.[6] We noticed that the utility of 2-aminobiaryls to construct different sizable heterocycles has also been developed;[7] for example, Miura et al. reported the cross-coupling of *N*-sulfonyl-2-aminobiaryls with alkenes to afford phenanthridine derivatives[8] (six-membered rings). In 2005, Buchwald and co-workers demonstrated a highly efficient Pd(II)-catalyzed C–H bond activation/intramolecular amidation for the synthesis of carbazoles[9] (five-membered rings) from 2-acetaminobiphenyls. However, to the best of our knowledge, the use of *N*-protected-2-aminobiaryls to construct seven-membered ring azepine compounds through Pd-catalyzed C–H bond activation has not been reported to date. Previously developed synthetic methodology for azepine syntheses involved rhodium-catalyzed hetero-[5+2]cycloaddition of cyclopropylimines and alkynes,[10] palladium-catalyzed intramolecular Heck reaction of *o*-iodo-*N*-protected aniline with α-(*o*-bromophenyl)acrylate followed by intramolecular amination,[11] gold-catalyzed intermolecular [4+3]annulation of α,β-unsaturated imines and alkynes,[12] palladium-catalyzed, ligand controlled cyclization of 2-chloro-*N*-(2-vinyl)aniline,[13] and a very recent Pd-catalyzed reaction of aryl iodides with *o*-bromoani-



Scheme 1. Synthesis of heterocyclic compounds with different ring sizes from *N*-protected 2-aminobiaryls (PG: protecting group).

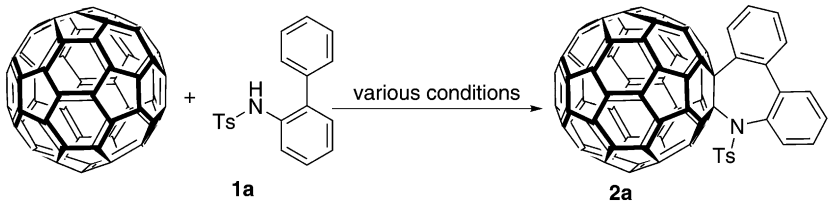
lines and norbornene/norbornadiene.[14] Herein, we wish to disclose that the synthesis of seven-membered-ring azepines couplled to [60]fulleroazepines, have been achieved through C–H bond activation of *N*-sulfonyl-2-aminobiaryls, involving C–C and C–N bond formation with C_{60} under palladium-catalysis with hybrid acids at room temperature whereby [60]fullerene participates as the incorporated π-component (Scheme 1). The success of the formation of a seven-membered-ring azepine lies in the lack of eliminable β-hydrogens as featured in the all-carbon C_{60} and the use of a hybrid acids system that enables stabilization of eight-membered palladacycle intermediates.[6z]

Results and Discussion

To disclose the success of this work, we first delineate our search for the best conditions. The reaction conditions were optimized with *N*-tosyl-2-aminobiphenyl (**1a**) as a model substrate and the results are summarized in Table 1. Initially, we attempted the present reaction with our previously reported conditions[4] using $Cu(OAc)_2$ as an oxidant in *o*-dichlorobenzene (ODCB)/trifluoroacetic acid (TFA) solvent (6:1) at 120 °C; unfortunately, no desired product **2a** was observed (Table 1, entry 1). Neither was **2a** observed without TFA in control experiments (entries 2 and 3). Gratifyingly, the product **2a** was isolated in 19% yield when the reaction was performed at 50 °C in a hybrid acid system where *p*-TsOH played the role as an additive (1 equiv.) in ODCB/TFA (6/1 mL, entry 4). Encouraged by these preliminary results, we then screened to find optimal conditions for this reaction under milder conditions. We found that metal oxidizing agents, such as $Cu(OAc)_2$, CH_3COOAg or Ag_2O, were not efficient for this catalytic reaction (entries 5–7). We did not find the desired product **2a** when the reaction was performed with benzoquinone (BQ) as oxidants (entry 8). Interestingly, when the reaction was performed with 10 mol% of $Pd(OAc)_2$, 3 equiv. of $KHSO_5$ as oxidants and 1 equiv. of *p*-TsOH in 6.2 mL of ODCB/TFA (6:0.2) at ambient temperature, the desired monofunctionalized fullerene product **2a** was isolated in good chemical yield (37%; 48% based on converted C_{60}, entry 9). $K_2S_2O_8$ was also an effective oxidant for this functionalization when compared to other metal oxidizing agents (entry 10 *vs.* entries 4–8). We noted that increasing reaction temperature or time did not improve reaction yields (entries 11–15). Lower reaction yields were observed when the reaction was carried out in the absence of either oxidants or *p*-TsOH (entries 16 and 17). In addition, we also tested the present reaction with different sulfonic acids as additives, but the resulting functionalization was relatively less efficient (entries 18 and 19). We further found that increasing stoichiometric amounts of *p*-TsOH (2 equiv.) did not result in any obvious improvement of yields (entry 20). Other tested solvent combinations, including AcOH, CH_3CN or toluene, were not effective for this reaction (entries 21–23). It is noteworthy that the amount of TFA is significant for the success of the studied reaction – increasing the volume ratio of TFA led to lower yield of **2a** (entries 24 and 25). Finally, we did not observe an improvement of reaction yield with a loading of 15 mol% of $Pd(OAc)_2$ (entry 26). The previously investigated catalytic system for the formation of fulleroindolines (5-membered rings)[1e,3e] and fulleroisoquinolinones (6-membered rings)[4] relied on conditions at higher temperature (120 °C) with palladium(II) catalysts in the presence of *p*-TsOH or TFA. However, these conditions are not applicable for the preparation of fulleroazepines (7-membered rings). The new system that uses hybrid acids of *p*-TsOH and TFA made the synthesis of the 7-membered-ring system successful under very mild conditions. This success may be due to the unusual stability made by the hybrid acid system[6z] that stabilizes the eight-membered palladacycle intermediates, although this intermediancy remains to be explored.

With the optimized results in hand, we next investigated the scope and generality of the reaction by employing a variety of substrates **1b–v** (Table 2) featuring electron-donating and electron-withdrawing groups on both the aromatic rings of 2-aminobiaryls. We built up a series of substituted 2-aminobiaryls **1** *via* Suzuki–Miyaura coupling of 2-bromoanilines with arylboronic acids (see the Supporting Information for the synthesis of **1b–v**).[15] In general, the investigated reactions with all substrates **1b–v** afforded good yields of the corresponding fulleroazepines **2b–v**

Table 1. Optimization of reaction conditions.[a]



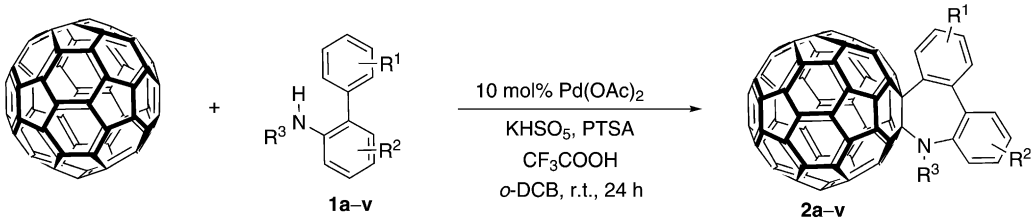
1a **2a**

Entry	Oxidant	Additive	Solvents (v/v; mL)	Temp [°C], time [h]	Yield [%][b]	Yield [%][c]	Recovered C_{60}
1	$Cu(OAc)_2$	none	*o*-DCB/TFA (6:1)	120, 24 h	0	0	quant.
2	$KHSO_5$	*p*-TsOH	*o*-DCB(6)	r.t., 24 h	0	0	97
3	$KHSO_5$	*p*-TsOH	*o*-DCB(6)	120, 24 h	2 (15)	4 (31)	86
4	$Cu(OAc)_2$	*p*-TsOH	*o*-DCB/TFA (6:1)	50, 24 h	19 (81)	20 (88)	77
5	$Cu(OAc)_2$	*p*-TsOH	*o*-DCB/TFA (6:0.2)	r.t., 24 h	15 (77)	13 (67)	80
6	CH_3COOAg	*p*-TsOH	*o*-DCB/TFA (6:0.2)	r.t., 24 h	3 (15)	6 (32)	82
7	Ag_2O	*p*-TsOH	*o*-DCB/TFA (6:0.2)	r.t., 24 h	4 (64)	5 (75)	93
8	BQ	*p*-TsOH	*o*-DCB/TFA (6:0.2)	r.t., 24 h	0	0	78
9	$KHSO_5$	*p*-TsOH	*o*-DCB/TFA(6:0.2)	r.t., 24 h	37 (48)	39 (51)	23
10	$K_2S_2O_8$	*p*-TsOH	*o*-DCB/TFA (6:0.2)	r.t., 24 h	30 (52)	35 (60)	42
11	$KHSO_5$	*p*-TsOH	*o*-DCB/TFA(6:0.2)	50, 15 h	35 (51)	43 (61)	31
12	$KHSO_5$	*p*-TsOH	*o*-DCB/TFA(6:0.2)	50, 18 h	33 (51)	38 (58)	35
13	$KHSO_5$	*p*-TsOH	*o*-DCB/TFA(6:0.2)	50, 24 h	30 (47)	33 (52)	37
14	$KHSO_5$	*p*-TsOH	*o*-DCB/TFA (6:0.2)	80, 8 h	27 (45)	28 (47)	41
15	$K_2S_2O_8$	*p*-TsOH	*o*-DCB/TFA (6:0.2)	r.t., 36 h	31 (47)	33 (49)	34
16	none	*p*-TsOH	*o*-DCB/TFA(6:0.2)	r.t., 24 h	5 (48)	8 (67)	89
17	$KHSO_5$	none	*o*-DCB/TFA (6:0.2)	r.t., 24 h	24 (59)	22 (55)	60
18	$KHSO_5$	*p*-EBSA[d]	*o*-DCB/TFA(6:0.2)	r.t., 24 h	29 (38)	24 (33)	25
19	$KHSO_5$	BSA[e]	*o*-DCB/TFA(6:0.2)	r.t., 24 h	19 (34)	15 (26)	45
20[f]	$KHSO_5$	*p*-TsOH	*o*-DCB/TFA (6:0.2)	r.t., 24 h	29 (45)	32 (49)	34
21	$KHSO_5$	*p*-TsOH	*o*-DCB/AcOH(6:0.2)	r.t., 24 h	0	0	86
22	$KHSO_5$	*p*-TsOH	*o*-DCB/CH_3CN (6:0.2)	r.t., 24 h	0	0	92
23	$KHSO_5$	*p*-TsOH	Toluene/TFA(15:0.2)	r.t., 24 h	12 (48)	8 (33)	75
24	$KHSO_5$	*p*-TsOH	*o*-DCB/TFA (6:0.3)	r.t., 24 h	21 (42)	16 (34)	51
25	$K_2S_2O_8$	*p*-TsOH	*o*-DCB/TFA (6:0.5)	r.t., 24 h	16 (20)	17 (21)	21
26[g]	$KHSO_5$	*p*-TsOH	*o*-DCB/TFA(6:0.2)	r.t., 24 h	31 (48)	27 (42)	35

[a] All reactions were performed with 0.050 mmol of C_{60}, 0.15 mmol of **1a**, 0.15 mmol of oxidant, 0.050 mmol of sulfonic acid as additives, and 0.005 mmol of $Pd(OAc)_2$ in the listed amounts of solvents at ambient temperature for 24 h unless otherwise noted.
[b] Isolated yields after column chromatography. Values in parentheses are based on consumed C_{60}.
[c] Yields were measured by ^1H NMR spectroscopy, using mesitylene as an internal standard.
[d] 4-Ethylbenzenesulfonic acid.
[e] Benzenesulfonic acid.
[f] Employing 2 equiv. of *p*-TsOH as additive.
[g] Reaction performed with a 15 mol% loading of $Pd(OAc)_2$.

with high regioselectivity and all the products **2a–v** showed good solubility in common organic solvents used for fullerene derivatives, such as $CHCl_3$, CH_2Cl_2, ODCB, CS_2 and toluene. We determined all the isolated yields by weighing and by using ^1H NMR spectroscopic methods, with mesitylene as an internal standard. In our investigation, substrate **1b**, without substituents on any aryl rings, underwent reaction with C_{60} smoothly to give **2b** in good isolated yield (33%; 52% based on converted C_{60}, entry 2). In the same manner, substrates **1c–g** featuring electron-donating methyl groups on the aryl rings afforded the corresponding products in yields in the ranges 31–33% and 50–73% based on isolated and converted C_{60} yields respectively (entries 3–7). We observed that substrates **1c**, **1f** and **1g** underwent regioselective C–H activations at their less hindered and more electron-rich *para*-positions relative to their methyl substituents. To our surprise, substrates bearing electron-withdrawing chloro groups, **1h** and **1i**, produced their products **2h** and **2i** in excellent isolated yields (40 and 51%; 66 and 68% based on converted C_{60}; entries 8 and 9). We isolated the monofunctionalized products **2j–l** in lower chemical yields (19–22%) due to the formation of bis- and multi-addition products (entries 10–12); this notion was ascribed to the presence

Table 2. Palladium-catalyzed syntheses of the [60]fulleroazepines **2a–v**.[a]



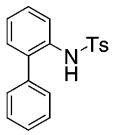
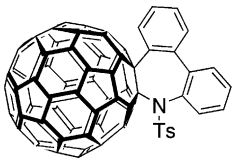
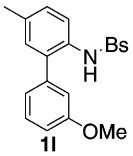
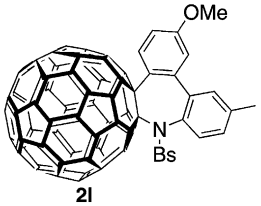
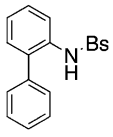
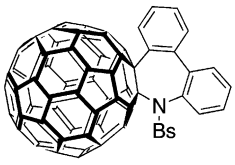
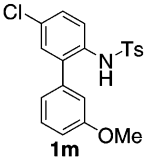
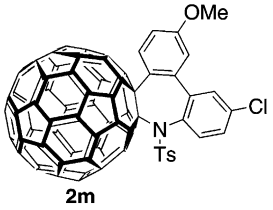
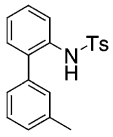
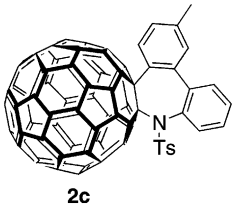
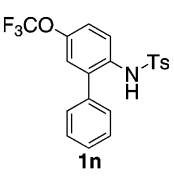
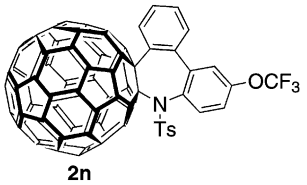
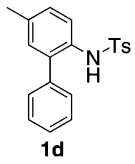
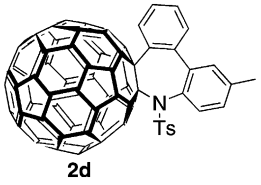
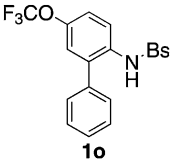
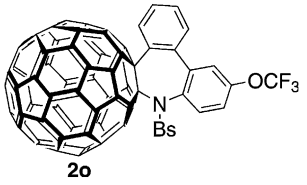
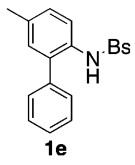
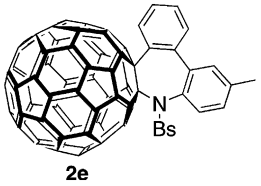
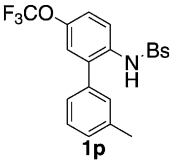
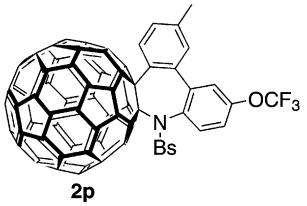
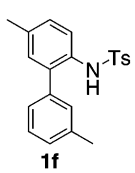
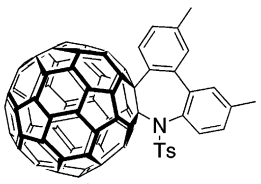
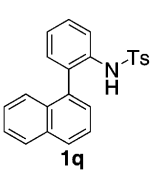
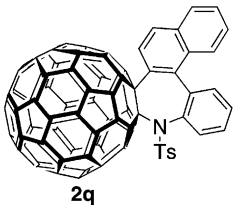
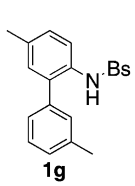
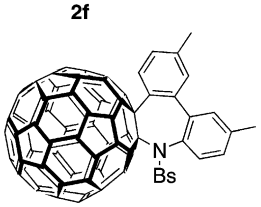
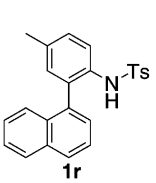
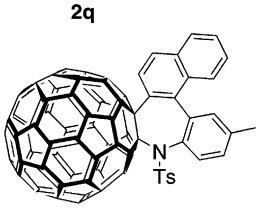
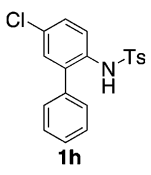
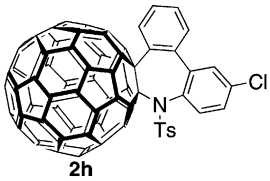
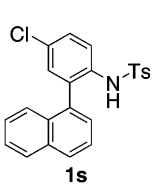
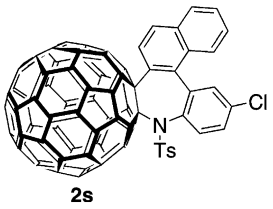
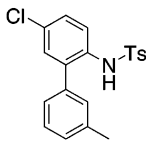
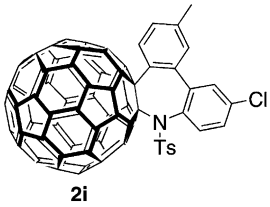
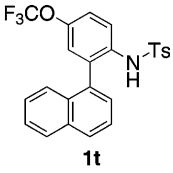
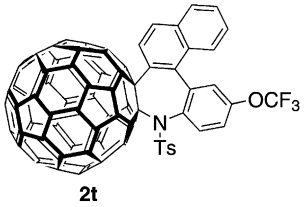
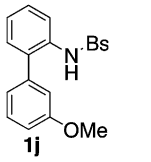
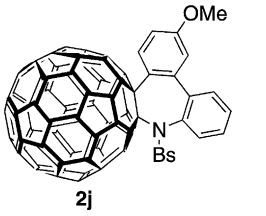
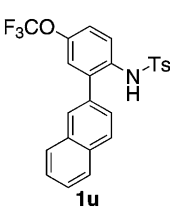
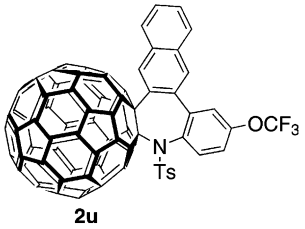
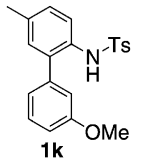
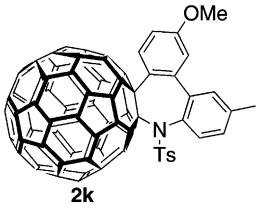
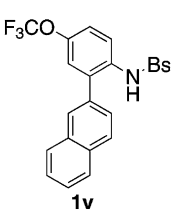
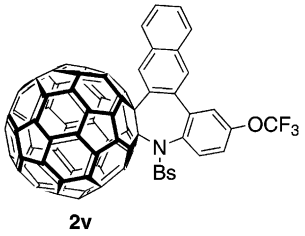
Entry	Substrate **1**	Product **2**	Yield [%]	C_{60} [%][e]	Entry	Substrate **1**	Product **2**	Yield [%]	C_{60} [%][e]
1	 **1a**	 **2a**	37 (48)[b] 39 (51)[c] 44 (53)[b,d]	23 17[d]	12	 **1l**	 **2l**	22 (38)[b] 22 (37)[c]	41
2	 **1b**	 **2b**	33 (52)[b] 34 (54)[c]	36	13	 **1m**	 **2m**	38 (56)[b] 39 (57)[c]	33
3	 **1c**	 **2c**	31 (59)[b] 30 (57)[c]	47	14	 **1n**	 **2n**	54 (92)[b] 53 (91)[c]	42
4	 **1d**	 **2d**	31 (61)[b] 31 (62)[c]	50	15	 **1o**	 **2o**	28 (53)[b] 35 (66)[c]	47
5	 **1e**	 **2e**	33 (50)[b] 40 (61)[c]	34	16	 **1p**	 **2p**	47 (68)[b] 58 (84)[c]	31
6	 **1f**	 **2f**	31 (59)[b] 33 (61)[c]	47	17	 **1q**	 **2q**	29 (72)[b] 35 (84)[c]	59
7	 **1g**	 **2g**	33 (73)[b] 28 (61)[c]	54	18	 **1r**	 **2r**	31 (79)[b] 32 (80)[c]	61

Table 2. (Continued)

Entry	Substrate **1**	Product **2**	Yield [%]	C_{60} [%][e]	Entry	Substrate **1**	Product **2**	Yield [%]	C_{60} [%][e]
8	 **1h**	 **2h**	40 (66)[b] 42 (68)[c]	38	19	 **1s**	 **2s**	38 (78)[b] 42 (87)[c]	51
9	 **1i**	 **2i**	51 (68)[b] 52 (69)[c]	24	20	 **1t**	 **2t**	32 (85)[b] 33 (89)[c]	63
10	 **1j**	 **2j**	21 (31)[b] 21 (31)[c]	33	21	 **1u**	 **2u**	26 (76)[b] 30 (88)[c]	66
11	 **1k**	 **2k**	19 (35)[b] 19 (35)[c]	45	22	 **1v**	 **2v**	25 (50)[b] 33 (64)[c]	49

[a] All reactions were performed using 0.050 mmol of C_{60}, 0.15 mmol of substrate **1**, 0.15 mmol of $KHSO_5$, 0.050 mmol of PTSA and 0.0050 mmol of $Pd(OAc)_2$ in 6.2 mL of ODCB/TFA (6:0.2, v/v, mL) at 25 °C for 24 h unless otherwise mentioned.
[b] Isolated yields after column chromatography; values in parentheses are based on converted C_{60}.
[c] Yields were measured by ^1H NMR spectroscopy, using mesitylene as an internal standard.
[d] Yields were obtained from the reaction of C_{60} (500 mg, 0.690 mmol) with substrate **1a** using the optimal conditions.
[e] Yields of recovered C_{60}.

of an electron-donating methoxy group that made the substrates more reactive. However, the additional presence of a more electron-pulling group, a chloro moiety, provided relatively good yields (entry 13). It was noteworthy that substrates equipped with trifluoromethoxy (OCF_3) group (**1n–p**) provided their corresponding products **2n–p** in moderate to excellent isolated yields of 54, 28 and 47%, respectively (entries 14–16). In addition, we extended the generality of the present reaction to substrates with a naphthalene moiety such as in **1q–t**; these substrates afforded the desired products in good yields (29–38%; >72% based on converted C_{60}, entries 17–20). Finally, the reaction of substrates **1u** and **1v** having an OCF_3 group with C_{60} resulted in the formation of single regioisomers **2u** and **2v** in moderate yields (26 and 25%, entries 21 and 22). Furthermore, we scaled up the present reaction (13.9-fold) under the optimized conditions using the substrate **1a** with C_{60} (500 mg, 0.690 mmol) and this afforded the product **2a** in 44% isolated yield and 53% based on converted C_{60} (entry 1). This result has demonstrated that this methodology provides an efficient access to [60]fulleroazepines on a larger scale.

Furthermore, we characterized the [60]fulleroazepines **2a–v** using infrared (IR), ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, atmospheric-pressure chemical ionization (APCI) mass spectrometry (MS), and X-ray crystallography (compound **2a**).[16] In the IR spectrum of **2a**, S=O stretching bands appeared at 1164 and 1355 cm^{-1}. All APCI-MS data corresponded to the expected formulae of the isolated [60]fulleroazepines. In the ^{13}C NMR spectra of **2a–v**, excluding the addend carbons, there were at

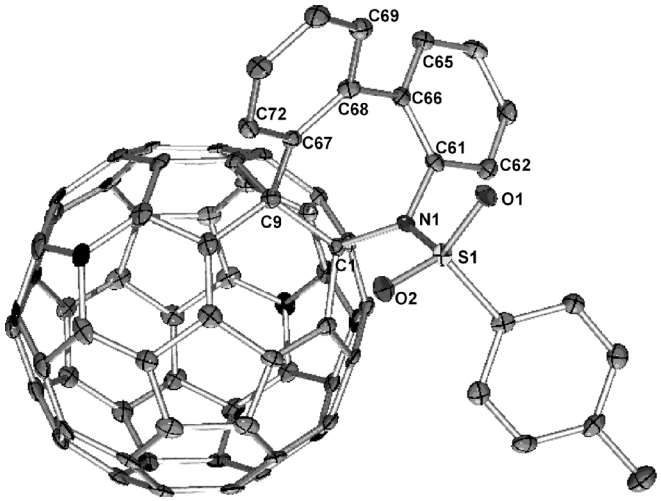
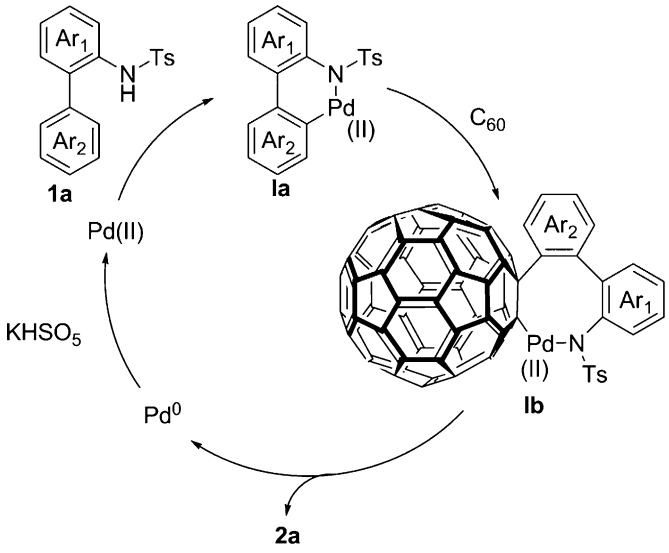


Figure 1. X-ray crystal structure of compound **2a**. Two toluene (solvent) molecules were omitted for clarity.



Scheme 2. Proposed reaction mechanism.

least 56 peaks observed in the range of 130–157 ppm for the 58 sp^2-carbons of the C_{60} skeleton and another two peaks in the range of 70–72 and 87–90 ppm, respectively, for the two sp^3-carbons of the monofunctionalized C_{60}. The number of sp^2-carbons of **2a–v** in ^{13}C NMR spectra revealed that these structures lack a plane of symmetry due to non-planar azepine rings. Figure 1 presents the thermal ellipsoid structure of compound **2a** determined using X-ray diffraction analysis.[17] The annelated seven-membered-ring appears to be a boat-like structure with tosyl and one of the benzene rings located on the same side with respect to the azepine ring.

The selected bond angles associated with azepine ring, ∢C68–C66–C61, ∢C66–C61–N1, ∢C61–N1–C1, ∢N1–C1–C9, ∢C1–C9–C67, ∢C9–C67–C68, and ∢C67–C68–C66, are 119.0(4), 117.2(4), 113.9(3), 111.4(3), 113.4(3), 122.7(4) and 124.7 (4) degrees, respectively. To the best of our knowledge, the currently obtained fulleroazepine structure appears to be the first crystal structure of a C_{60} derivative derivative with an exo-hedrally functionalized seven-membered ring.

Based upon the experimental results and known metal-catalyzed, directing group-assisted C–H bond activation reactions,[7b,8,9a,b] we propose a mechanism for the present palladium-catalyzed formation of [60]fulleroazepines (Scheme 2). Initially the coordination of substrate **1a** with $Pd(OAc)_2$, followed by activation of the *ortho* C–H bond in aryl ring Ar_2, results in the formation of six-membered ring palladacycle **Ia**. Subsequent coordination and insertion of C_{60} to intermediate **Ia** generates an eight-membered palladacycle intermediate **Ib**. Finally, reductive elimination affords the [60]fulleroazepine **2a** and Pd(0) species. The Pd(0) species are reoxidized to Pd(II) by $KHSO_5$ to finish the catalytic cycle. It is noteworthy that previous examples of seven-membered-ring C_{60} derivatives were synthesized through metal-free [5+2] cycloadditions.[18]

Conclusions

In summary, we have successfully demonstrated the synthesis of [60]fulleroazepines from the reaction of C_{60} and *N*-sulfonyl-2-aminobiaryls under palladium(II) catalysis through C–H bond activation and sequential C–C and C–N bond formation at room temperature. The formation of [60]fulleroazepines is highly regioselective and this catalysis tolerates the presence of a variety of substituents on both aromatic rings. The new system using hybrid acids of *p*-TsOH and TFA made the synthesis of 7-membered-ring system successful under very mild conditions. This hybrid protocol may provide a novel system for syntheses of other higher-membered ring systems that are presently inapplicable with simple catalytic system. Furthermore, studies on applications of these [60]fulleroazepine derivatives in organic photovoltaics are underway in our laboratory.

Experimental Section

General Procedure for Synthesis of [60]Fulleroazepines 2a–v

To a reaction tube containing C_{60} (36 mg, 0.050 mmol), *N*-sulfonyl-2-aminobiaryls **1** (0.15 mmol), $Pd(OAc)_2$ (1.1 mg, 0.0050 mmol), $KHSO_5$ (22.8 mg, 0.15 mmol) and *p*-toluenesulfonic acid (8.6 mg, 0.050 mmol) were added 6 mL of dry *o*-dichlorobenzene, 0.2 mL of trifluoroacetic acid (TFA), and a stir bar. The tube was closed with screw type cap and

the mixture allowed to stir vigorously (1000 rpm) for 24 h at room temperature. After completion of the reaction, the reaction mixture was subjected to column chromatography using toluene as an eluent for recovery of the unreacted C_{60}. Continuing elution with toluene gave [60]fulleroazepine **2**. Spectral data of compounds **2a–v** are given below.

Spectral data of compound (2a): $R_f = 0.48$ (toluene); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.38$ (s, 3H), 7.21 (d, $J =$ 8.1 Hz, 2H), 7.40 (d, $J = 7.8$ Hz, 1H), 7.47 (t, $J = 7.3$ Hz, 1H), 7.59–7.64 (m, 1H), 7.70–7.74 (m, 3H), 7.81 (d, $J =$ 8.2 Hz, 2H), 8.06 (d, $J = 7.7$ Hz, 1H), 8.49 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR [150 MHz, $CDCl_3$, with $Cr(acac)_3$ as relaxation reagent]: $\delta = 21.5$, 71.5, 88.8, 127.5, 129.1, 129.2, 129.4, 129.42, 129.6, 129.62, 130.8, 130.84, 133.0, 133.3, 136.1, 136.12, 139.0, 139.1, 139.6, 139.7, 139.8, 140.1, 140.4, 140.5, 141.1, 141.2, 141.3, 141.7, 141.72, 142.2, 142.25, 142.3, 142.4, 142.41, 142.5, 142.55, 142.6, 142.65, 142.7, 142.71, 142.87, 142.9, 143.2, 143.3, 144.4, 144.5, 144.54, 144.6, 145.1, 145.2, 145.26, 145.3, 145.32, 145.4, 145.5, 145.54, 145.6, 145.7, 146.0, 146.16, 146.18, 146.2, 146.25, 146.3, 146.6, 146.7, 146.72, 147.9, 148.4, 149.7, 152.1, 153.6, 157.0; FT-IR (KBr): $\nu = 527$, 671, 756, 1057, 1090, 1164, 1355, 1433, 2924, 2959, 3024 cm^{-1}; HR-MS (APCI$^-$): $m/z = 1041.0827$, calcd. for $C_{79}H_{15}NO_2S$ [M$^-$]: 1041.0823.

Spectral data of compound (2b): $R_f = 0.51$ (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3 = 1{:}2$): $\delta = 7.36$–7.49 (m, 5H), 7.58–7.62 (m, 1H), 7.69–7.74 (m, 3H), 7.90 (d, $J =$ 6.8 Hz, 2H), 8.04 (dd, $J = 1.3$, 7.7 Hz, 1H), 8.46 (d, $J =$ 7.9 Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3 = 1{:}2$, with $Cr(acac)_3$ as relaxation reagent]: $\delta = 71.3$, 88.6, 127.3, 128.7, 129.0, 129.1, 129.3, 129.5, 130.5, 130.7, 132.3, 132.8, 133.2, 135.9, 136.0, 138.9, 139.0, 139.4, 139.6, 139.7, 140.1, 140.3, 141.0, 141.06, 141.1, 141.5, 141.6, 142.0, 142.04, 142.1, 142.2, 142.27, 142.3, 142.4, 142.43, 142.5, 142.53, 142.6, 142.7, 142.9, 143.1, 144.2, 144.3, 144.4, 144.5, 145.0, 145.05, 145.1, 145.12, 145.2, 145.3, 145.4, 145.5, 145.8, 146.0, 146.05, 146.1, 146.12, 146.4, 146.5, 146.6, 147.8, 148.2, 149.4, 151.8, 153.4, 156.7; FT-IR (KBr): $\nu = 527$, 757, 1057, 1090, 1164, 1215, 1355, 2855, 2926, 2961, 3020 cm^{-1}; HR-MS (APCI$^-$): $m/z =$ 1027.0655, calcd. for $C_{78}H_{13}NO_2S$ [M$^-$]: 1027.0667.

Spectral data of compound (2c): $R_f = 0.55$ (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3 = 1{:}2$): $\delta = 2.39$ (s, 3H), 2.57 (s, 3H), 7.17 (d, $J = 8.3$ Hz, 2H), 7.35 (td, $J = 1.2$, 7.9 Hz, 2H), 7.42 (td, $J = 1.4$, 7.4 Hz, 1H), 7.47 (s, 1H), 7.68 (td, $J =$ 1.3, 7.5 Hz, 1H), 7.74 (d, $J = 8.3$ Hz, 2H), 8.0 (dd, $J = 1.2$, 7.7 Hz, 1H), 8.28 (d, $J = 9.2$ Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3 = 1{:}2$, with $Cr(acac)_3$ as relaxation reagent]: $\delta =$ 21.1, 21.4, 70.9, 88.3, 127.3, 128.7, 129.2, 129.21, 129.3, 129.5, 130.4, 130.5, 132.6, 133.8, 135.86, 135.9, 138.7, 138.86, 138.9, 139.3, 139.32, 139.5, 139.6, 139.8, 140.1, 140.2, 140.9, 141.0, 141.02, 141.4, 141.5, 141.8, 142.0, 142.01, 142.1, 142.17, 142.2, 142.3, 142.4, 142.44, 142.5, 142.6, 142.7, 142.72, 142.8, 143.0, 144.1, 144.3, 144.32, 144.4, 144.9, 145.0, 145.01, 145.1, 145.2, 145.3, 145.32, 145.4, 145.7, 145.9, 146.0, 146.01, 146.2, 146.4, 146.5, 147.6, 148.1, 149.5, 152.0, 153.5, 157.0; FT-IR (KBr): $\nu = 527$, 572, 668, 757, 969, 1081, 1165, 1215, 1359, 1494, 2871, 2926, 2963 cm^{-1}; HR-MS (APCI$^-$): $m/z = 1055.0972$, calcd. for $C_{80}H_{17}NO_2S$ [M$^-$]: 1055.0980.

Spectral data of compound (2d): $R_f = 0.51$ (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3 = 1{:}2$): $\delta = 2.38$ (s, 3H), 2.60 (s, 3H), 7.17 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 2.9$ Hz, 3H), 7.53–7.58 (m, 1H), 7.68 (dd, $J = 1.3$, 5.3 Hz, 2H), 7.74 (d, $J =$ 7.5 Hz, 1H), 7.82 (d, $J = 0.8$ Hz, 1H), 8.43 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3 = 1{:}2$, with $Cr(acac)_3$ as relaxation reagent] $\delta = 21.4$, 21.7, 71.3, 88.5, 127.3, 128.8, 129.1, 129.2, 129.3, 129.6, 129.9, 130.2, 132.9, 133.0, 135.9, 136.0, 138.8, 138.9, 139.0, 139.3, 139.5, 139.6, 140.2, 140.3, 140.5, 140.9, 141.0, 141.1, 141.5, 141.9, 142.0, 142.04, 142.14, 142.2, 142.35, 142.36, 142.4, 142.5, 142.6, 142.7, 142.74, 143.0, 144.2, 144.3, 144.31, 144.4, 144.9, 145.0, 145.01, 145.04, 145.1, 145.13, 145.2, 145.3, 145.32, 145.4, 145.7, 145.9, 146.0, 146.03, 146.3, 146.4, 146.5, 147.7, 148.2, 149.6, 152.0, 153.4, 156.8; FT-IR (KBr): $\nu = 527$, 587, 669, 754, 966, 1081, 1163, 1359, 2852, 2923, 2957 cm^{-1}; HR-MS (APCI$^-$): $m/z = 1055.0958$, calcd. for $C_{80}H_{17}NO_2S$ [M$^-$]: 1055.0980.

Spectral data of compound (2e): $R_f = 0.38$ (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3 = 1{:}2$): $\delta = 2.60$ (s, 3H), 7.24–7.27 (m, 2H), 7.38–7.51 (m, 3H), 7.56–7.61 (m, 3H), 7.85 (s, 1H), 7.91 (d, $J = 7.8$ Hz, 2H), 8.46 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (150 MHz, $CS_2/CDCl_3 = 1{:}2$): $\delta = 21.8$, 71.5, 88.8, 127.4, 128.9, 129.1, 129.4, 129.5, 129.9, 130.1, 130.3, 132.4, 133.1, 133.2, 136.0, 136.2, 138.95, 139.0, 139.1, 139.5, 139.7, 139.8, 140.3, 140.5, 140.9, 141.0, 141.16, 141.2, 141.7, 142.1, 142.2, 142.24, 142.3, 142.4, 142.42, 142.5, 142.6, 142.63, 142.64, 142.7, 142.8, 143.0, 143.2, 144.3, 144.4, 144.5, 144.6, 145.05, 145.1, 145.14, 145.18, 145.2, 145.3, 145.34, 145.4, 145.5, 145.52, 145.6, 145.9, 146.1, 146.13, 146.15, 146.2, 146.21, 146.23, 146.5, 146.6, 146.7, 147.9, 148.4, 149.6, 152.0, 153.6, 156.9; FT-IR (KBr): ν = 527, 633, 737, 754, 1164, 1355, 2850, 2919 cm^{-1}; HR-MS (APCI$^-$): $m/z = 1041.0807$, calcd. for $C_{79}H_{15}NO_2S$ [M$^-$]: 1041.0823.

Spectral data of compound (2f): $R_f = 0.57$ (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3 = 1{:}2$): $\delta = 2.38$ (s, 3H), 2.57 (s, 3H), 2.59 (s, 3H), 7.17 (d, $J = 8.1$ Hz, 2H), 7.24 (s, 2H), 7.36 (dd, $J = 1.3$, 8.1 Hz, 1H), 7.51 (d, $J = 1.5$ Hz, 1H), 7.76 (d, $J = 8.3$ Hz, 2H), 7.82 (s, 1H), 8.30 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3 = 1{:}2$, with $Cr(acac)_3$ as relaxation reagent]: $\delta = 21.1$, 21.5, 21.7, 71.1, 88.4, 127.4, 129.2, 129.3, 129.5, 129.6, 129.9, 130.3, 132.8, 133.8, 135.9, 136.1, 138.8, 138.9, 139.0, 139.3, 139.5, 139.7, 140.0, 140.2, 140.4, 140.5, 140.9, 141.0, 141.1, 141.5, 141.9, 141.07, 141.1, 142.2, 142.24, 142.3, 142.4, 142.47, 142.5, 142.6, 142.7, 142.8, 143.1, 144.2, 144.3, 144.4, 144.5, 144.9, 145.05, 145.1, 145.12, 145.2, 145.3, 145.4, 145.42, 145.44, 145.8, 146.0, 146.04, 146.05, 146.1, 146.3, 146.5, 146.53, 147.7, 148.2, 149.7, 152.2, 153.7, 157.1; FT-IR (KBr): $\nu = 527$, 667, 757, 814, 1091, 1164, 1355, 1494, 2855, 2924, 2960, 3022 cm^{-1}; HR-MS (APCI$^-$): $m/z =$ 1069.1129, calcd. for $C_{81}H_{19}NO_2S$ [M$^-$]: 1069.1136.

Spectral data of compound (2g): $R_f = 0.55$ (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3 = 1{:}2$): $\delta = 2.57$ (s, 3H), 2.60 (s, 3H), 7.24 (d, $J = 5.2$ Hz, 2H), 7.38 (t, $J = 7.8$ Hz, 3H), 7.46 (d, $J = 7.2$ Hz, 1H), 7.50 (s, 1H), 7.81 (s, 1H), 7.88 (d, $J = 7.9$ Hz, 2H), 8.30 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3 = 1{:}2$, with $Cr(acac)_3$ as relaxation reagent]: $\delta = 21.7$, 22.3, 71.7, 89.1, 128.0, 129.2, 130.0, 130.3, 130.6, 130.9, 132.8, 133.4, 134.42, 136.5, 136.7, 139.4, 139.5, 139.6, 139.62, 140.0, 140.1, 140.2, 140.3, 140.5, 141.0, 141.2, 141.5, 141.7, 141.74, 142.2, 142.6, 142.7, 142.74, 142.8, 142.9, 142.91, 143.0, 143.04, 143.1, 143.12, 143.16, 143.2, 143.3, 143.6, 143.7, 144.8, 145.0, 145.03, 145.1, 145.6, 145.66, 145.7, 145.72, 145.8, 145.84, 145.9, 146.0, 146.03, 146.1, 146.4, 146.6, 146.64, 146.68, 146.7, 146.72, 147.0, 147.1, 147.2, 148.4, 148.9, 150.1, 152.7, 154.3, 157.7; FT-IR (KBr): $\nu = 527$, 589, 632, 756, 1056, 1091, 1166, 1215, 1356, 1446, 1495, 2856, 2924,

2961, 3022 cm^{-1}; HR-MS (APCI$^-$): m/z = 1055.0992, calcd. for $C_{80}H_{17}NO_2S$ [M$^-$]: 1055.0980.

Spectral data of compound (2h): R_f = 0.63 (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ = 1:2): δ = 2.39 (s, 3H), 7.21 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.4 Hz, 1H), 7.43 (dd, J = 2.4, 8.4 Hz, 1H), 7.60–7.66 (m, 1H), 7.72–7.75 (m, 3H), 7.78 (s, 1H), 8.04 (d, J = 2.4 Hz, 1H), 8.49 (d, J = 7.8 Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3$ = 1:2, with $Cr(acac)_3$ as relaxation reagent]: δ = 21.5, 71.3, 88.7, 127.3, 129.1, 129.4, 129.42, 129.5, 129.54, 131.9, 132.7, 133.1, 135.9, 136.1, 136.4, 138.9, 139.0, 139.02, 139.5, 139.6, 139.7, 139.8, 140.1, 140.4, 141.0, 141.1, 141.12, 141.6, 142.0, 142.1, 142.2, 142.22, 142.3, 142.33, 142.4, 142.5, 142.54, 142.57, 142.6, 142.8, 143.1, 143.3, 144.1, 144.3, 144.35, 144.4, 144.5, 144.9, 145.0, 145.07, 145.1, 145.2, 145.22, 145.24, 145.4, 145.5, 145.6, 145.8, 146.0, 146.07, 146.1, 146.14, 146.2, 146.4, 146.5, 146.6, 151.5, 153.1, 156.6; FT-IR (KBr): ν = 526, 572, 669, 808, 1020, 1042, 1087, 1162, 1260, 1353, 2850, 2918 cm^{-1}; HR-MS (APCI$^-$): m/z = 1075.0407, calcd. for $C_{79}H_{14}ClNO_2S$ [M$^-$]: 1075.0434.

Spectral data of compound (2i): R_f = 0.71 (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ = 1:2): δ = 2.39 (s, 3H), 2.58 (s, 3H), 7.18 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 8.2 Hz, 2H), 7.48 (s, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.99 (d, J = 2.1 Hz, 1H), 8.31 (d, J = 8.1 Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3$ = 1:2, with $Cr(acac)_3$ as relaxation reagent]: δ = 21.1, 21.5, 70.9, 88.4, 127.3, 128.8, 129.3, 129.33, 129.5, 130.2, 131.8, 132.5, 133.7, 135.8, 136.0, 136.4, 138.6, 138.8, 138.9, 139.2, 139.4, 139.5, 139.54, 139.8, 139.81, 140.0, 140.4, 140.9, 141.1, 141.5, 141.9, 142.0, 142.1, 142.2, 142.3, 142.4, 142.43, 142.48, 142.5, 142.51, 142.7, 143.06, 143.1, 144.0, 144.3, 144.4, 144.43, 144.9, 145.0, 145.03, 145.1, 145.15, 145.2, 145.24, 145.3, 145.4, 145.5, 145.7, 146.0, 146.06, 146.1, 146.4, 146.5, 146.53, 147.7, 148.2, 149.3, 151.7, 153.2, 156.8; FT-IR (KBr): ν = 527, 577, 660, 757, 813, 1088, 1164, 1215, 1357, 1487, 1596, 2855, 2925, 2959, 3023 cm^{-1}; HR-MS (APCI$^-$): m/z = 1089.0586, calcd. for $C_{80}H_{16}ClNO_2S$ [M$^-$]: 1089.0590.

Spectral data of compound (2j): R_f = 0.25 (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ = 1:2): δ = 3.99 (s, 3H), 7.12 (dd, J = 2.9, 8.8 Hz, 1H), 7.26 (s, 1H), 7.41–7.54 (m, 5H), 7.74 (td, J = 1.9, 9.0 Hz, 1H), 7.95 (d, J = 7.3 Hz, 2H), 8.05 (d, J = 7.2 Hz, 1H), 8.37 (d, J = 8.8 Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3$ = 1:2]: δ = 55.3, 70.7, 88.3, 113.8, 118.8, 127.4, 128.7, 129.1, 129.5, 130.6, 130.75, 130.8, 132.3, 132.6, 134.5, 135.9, 136.0, 138.9, 139.0, 139.4, 139.6, 139.8, 140.4, 141.0, 141.1, 141.14, 141.3, 141.4, 141.6, 142.0, 142.1, 142.2, 142.28, 142.3, 142.33, 142.47, 142.5, 142.56, 142.6, 142.7, 142.8, 142.9, 143.1, 144.2, 144.4, 144.5, 144.53, 145.0, 145.03, 145.07, 145.1, 145.15, 145.2, 145.24, 145.3, 145.4, 145.44, 145.5, 145.8, 146.0, 146.05, 146.1, 146.13, 146.2, 147.8, 148.3, 149.4, 152.0, 153.6, 157.2, 160.2; FT-IR (KBr): ν = 526, 576, 728, 906, 1056, 1080, 1166, 1232, 1355, 1445, 1483, 1601, 2819, 2959, 3064 cm^{-1}; HR-MS (APCI$^+$): m/z = 1058.0809, calcd. for $C_{79}H_{16}NO_3S$ [M+1]: 1058.0851.

Spectral data of compound (2k): R_f = 0.28 (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ = 1:2): δ = 2.38 (s, 3H), 2.60 (s, 3H), 3.97 (s, 3H), 7.06 (dd, J = 2.9, 5.9 Hz, 1H), 7.16–7.26 (m, 5H), 7.75 (d, J = 8.3 Hz, 2H), 7.80 (s, 1H), 8.31 (d, J = 8.8 Hz, 1H); ^{13}C NMR (150 MHz, $CS_2/CDCl_3$ = 1:2): δ = 21.4, 21.6, 55.2, 70.6, 88.2, 113.5, 118.6, 127.3, 129.2, 129.8, 129.9, 130.4, 130.5, 132.6, 134.5, 135.8, 136.0, 138.76, 138.8, 138.9, 139.2, 139.4, 139.6, 140.0, 140.3, 140.6, 140.8, 141.0, 141.1, 141.4, 141.5, 141.9, 142.0, 142.04, 142.1, 142.16, 142.2, 142.3, 142.4, 142.44, 142.5, 142.6, 142.8, 143.0, 144.1, 144.3, 144.4, 144.42, 144.8, 144.9, 145.0, 145.03, 145.05, 145.1, 145.2, 145.21, 145.3, 145.31, 145.4, 145.7, 145.9, 145.92, 145.96, 146.0, 146.02, 146.3, 146.4, 146.5, 147.7, 148.2, 149.6,152.2, 153.6, 157.2, 160.0; FT-IR (KBr): ν = 527, 668, 755, 1057, 1165, 1232, 1354, 1463, 1495, 1570, 1601, 2850, 2919 cm^{-1}; HR-MS (APCI$^-$): m/z = 1085.1069, calcd. for $C_{81}H_{19}NO_3S$ [M$^-$]: 1085.1086.

Spectral data of compound (2l): R_f = 0.37 (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ = 1:2): δ = 2.60 (s, 3H), 3.97 (s, 3H), 7.05 (dd, J = 2.9, 8.8 Hz, 1H), 7.19 (d, J = 2.8 Hz, 1H), 7.26 (d, J = 0.9 Hz, 2H), 7.36–7.50 (m, 3H), 7.80 (s, 1H), 7.88 (d, J = 7.5 Hz, 2H), 8.31 (d, J = 8.8 Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3$ = 1:2, with $Cr(acac)_3$ as relaxation reagent]: δ = 21.6, 55.1, 70.6, 88.2, 113.6, 118.6, 127.3, 128.6, 129.8, 129.9, 130.4, 130.6, 132.1, 132.6, 134.4, 135.8, 136.0, 138.7, 138.9, 139.2, 139.5, 139.7, 140.3, 140.6, 140.8, 141.0, 141.03, 141.3, 142.5, 141.8, 142.0, 142.03, 142.15, 142.2, 142.3, 142.4, 142.5, 142.6, 142.9, 143.0, 144.1, 144.3, 144.4, 144.42, 144.9, 145.0, 145.01, 145.1, 145.12, 145.2, 145.3, 145.4, 145.7, 145.9, 145.93, 145.96, 146.0, 146.02, 146.3, 146.4, 146.5, 147.7, 148.2, 149.4, 152.1, 153.6, 157.1, 160.0; FT-IR (KBr): ν = 527, 589, 755, 969, 1082, 1165, 1218, 1355, 1494, 1569, 2852, 2924, 2961, 3011 cm^{-1}; HR-MS (APCI$^-$): m/z = 1071.0927, calcd. for $C_{80}H_{17}NO_3S$ [M$^-$]: 1071.0929.

Spectral data of compound (2m): R_f = 0.53 (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ = 1:2): δ = 2.39 (s, 3H), 3.97 (s, 3H), 7.06 (dd, J = 2.8, 8.8 Hz, 1H), 7.13 (d, J = 2.8 Hz, 1H), 7.16 (s, 1H), 7.29 (s, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.40 (dd, J = 2.4, 8.5 Hz, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.96 (d, J = 2.4 Hz, 1H), 8.3 (d, J = 8.7 Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3$ = 1:2, with $Cr(acac)_3$ as relaxation reagent]: δ = 21.4, 55.1, 70.4, 88.2, 114.1, 118.6, 127.3, 128.9, 129.2, 129.24, 130.7, 131.9, 132.3, 134.3, 135.7, 135.9, 136.4, 138.8, 138.9, 139.3, 139.4, 139.7, 139.8, 139.9, 139.93, 140.3, 140.8, 141.0, 141.5, 141.8, 141.9, 142.0, 142.1, 142.2, 142.3, 142.4, 142.42, 142.7, 142.9, 143.0, 143.9, 144.1, 144.3, 144.31, 144.4, 144.8, 144.9, 145.0, 145.02, 145.07, 145.1, 145.2, 145.3, 145.4, 145.7, 145.9, 145.92, 146.0, 146.03, 146.3, 146.4, 146.5, 147.7, 148.1, 149.2, 151.7, 153.2, 156.9, 160.1; FT-IR (KBr): ν = 527, 694, 729, 759, 1045, 1082, 1164, 1218, 1356, 1462, 1495, 1604, 2858, 2925, 2957, 3027 cm^{-1}; HR-MS (APCI$^-$): m/z = 1105.0545, calcd for $C_{80}H_{16}ClNO_3S$ [M$^-$]: 1105.0539.

Spectral data of compound (2n): R_f = 0.5 (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ = 1:2): δ = 2.39 (s, 3H), 7.21 (d, J = 8.1 Hz, 2H), 7.29 (dd, J = 1.7, 4.2 Hz, 1H), 7.40 (d, J = 8.6 Hz, 1H), 7.60–7.74 (m, 3H), 7.77 (d, J = 8.3 Hz, 2H), 7.89 (d, J = 1.8 Hz, 1H), 8.48 (d, J = 7.6 Hz, 1H); ^{13}C NMR (150 MHz, $CS_2/CDCl_3$ = 1:2): δ = 21.6, 71.3, 88.9, 120.4 (q, J = 257.9 Hz), 121.0, 121.5, 127.4, 129.5, 129.6, 129.61, 129.8, 132.3, 132.7, 133.14, 136.0, 136.02, 139.0, 139.2, 139.6, 139.7, 139.8, 139.9, 140.1, 140.4, 141.1, 141.2, 141.21, 141.7, 142.1, 142.2, 142.3, 142.4, 142.42, 142.5, 142.6, 142.66, 142.7, 142.88, 142.9, 143.2, 143.5, 144.1, 144.4, 144.5, 144.6, 144.8, 145.0, 145.2, 145.27, 145.3, 145.34, 145.5, 145.6, 145.64, 145.9, 146.15, 146.2, 146.21, 146.24, 146.3, 146.6, 146.66, 146.7, 147.9, 148.4, 149.3, 150.5, 151.6, 153.1, 156.7; FT-IR (KBr): ν = 529, 667, ,732, 755, 1164, 1232, 1354, 2850, 2919 cm^{-1}; HR-MS (APCI$^-$): m/z = 1125.0659, calcd. for $C_{80}H_{14}F_3NO_3S$ [M$^-$]: 1125.0646.

Spectral data of compound (2o): R_f = 0.5 (toluene); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (d, J = 7.8 Hz, 1H), 7.42–7.79 (m, 7H), 7.92–7.94 (m, 3H), 8.51 (d, J = 7.7 Hz, 1H); ^{13}C NMR [150 MHz, $CDCl_3$, with $Cr(acac)_3$ as relaxation reagent]: δ = 71.3, 88.8, 120.4 (q, J = 257.3 Hz), 121.1, 121.6, 127.4, 129.0, 129.57, 129.6, 129.9, 132.3, 132.7, 132.74, 133.1, 135.9, 136.0, 138.9, 139.0, 139.2, 139.6, 139.7, 139.9, 140.0, 140.3, 141.1, 141.12, 141.2, 141.6, 142.1, 142.11, 142.2, 142.27, 142.3, 142.36, 142.4, 142.5, 142.52, 142.56, 142.6, 142.64, 142.7, 142.86, 142.9, 143.2, 144.1, 144.4, 144.5, 144.52, 144.7, 144.9, 145.2, 145.23, 145.26, 145.3, 145.32, 145.4, 145.5, 145.6, 145.8, 146.1, 146.15, 146.2, 146.22, 146.23, 146.3, 146.6, 146.64, 146.7, 147.9, 148.48, 149.05, 150.5, 151.4, 153.0; FT-IR (KBr): ν = 527, 577, 757, 1056, 1091, 1167, 1214, 1253, 1359, 1484, 2855, 2925, 2958 cm^{-1}; HR-MS (APCI$^+$): m/z = 1112.0541, calcd. for $C_{79}H_{13}F_3NO_3S$ [M + 1]: 1112.0568.

Spectral data of compound (2p): R_f = 0.69 (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ = 1:2): δ = 2.59 (s, 3H), 7.29 (d, J = 8.2 Hz, 1H), 7.42 (dd, J = 3.5, 8.1 Hz, 4H), 7.51 (t, J = 7.6 Hz, 2H), 7.87 (dd, J = 2.5, 4.2 Hz, 2H), 7.91 (s, 1H), 8.34 (d, J = 8.1 Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3$ = 1:2, with $Cr(acac)_3$ as relaxation reagent]: δ = 21.0, 70.9, 88.5, 120.3 (q, J = 258.9 Hz), 120.7, 121.4, 127.3, 128.8, 129.5, 130.4, 132.2, 132.4, 132.5, 133.7, 135.8, 135.9, 138.5, 138.9, 139.0, 139.37, 139.4, 139.42, 139.5, 139.6, 139.8, 140.2, 140.9, 141.0, 141.5, 142.0, 142.02, 142.1, 142.2, 142.22, 142.3, 142.4, 142.5, 142.54, 142.76, 142.8, 143.1, 144.0, 144.3, 144.4, 144.41, 144.7, 144.8, 145.0, 145.05, 145.1, 145.2, 145.21, 145.3, 145.4, 145.5, 145.7, 146.0, 146.1, 146.13, 146.2, 146.4, 146.5, 147.7, 148.3, 149.0, 150.3, 151.5, 153.1, 156.7; FT-IR (KBr): ν = 527, 589, 755.6, 1054, 1091, 1168, 1217, 1253, 1358, 1493, 2919, 3026 cm^{-1}; HR-MS (APCI$^-$): m/z = 1125.0700, calcd. for $C_{80}H_{14}F_3NO_3S$ [M$^-$]: 1125.0646.

Spectral data of compound (2q): R_f = 0.5 (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ = 1:2): δ = 2.35 (s, 3H), 7.05 (d, J = 8.0 Hz, 2H), 7.57–7.71 (m, 6H), 7.81 (td, J = 1.4, 8.3 Hz, 1H), 8.01–8.13 (m, 4H), 8.58 (d, J = 8.8 Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3$ = 1:2, with $Cr(acac)_3$ as relaxation reagent]: δ = 21.4, 70.8, 88.9, 125.8, 126.4, 126.7, 126.8, 127.1, 128.1, 128.8, 128.9, 129.1, 129.5, 131.8, 133.0, 133.3, 133.6, 133.7, 135.2, 135.4, 136.9, 138.7, 138.8, 138.9, 139.0, 139.1, 139.3, 139.5, 139.6, 140.1, 140.8, 141.0, 141.2, 141.6, 141.9, 141.91, 142.1, 142.2, 142.3, 142.4, 142.5, 142.6, 142.7, 142.73, 143.1, 144.25, 144.3, 144.5, 144.6, 144.9, 145.0, 145.1, 145.17, 145.2, 145.21, 145.23, 145.4, 145.41, 145.8, 145.9, 146.0, 146.1, 146.3, 146.5, 146.53, 147.7, 148.2, 149.8, 152.1, 153.9, 156.3; FT-IR (KBr): ν = 526, 675, 755, 815, 1048, 1087, 1165, 1355, 1595, 2850, 2918 cm^{-1}; HR-MS (APCI$^-$): m/z = 1091.0955, calcd. for $C_{83}H_{17}NO_2S$ [M$^-$]: 1091.0980.

Spectral data of compound (2r): R_f = 0.58 (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ = 1:2): δ = 2.29 (s, 3H), 2.64 (s, 3H), 6.98 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 1H), 7.50 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 8.3 Hz, 2H), 7.79 (s, 1H), 7.95 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 8.9 Hz, 1H), 8.09 (d, J = 8.2 Hz, 1H), 8.51 (d, J = 8.7 Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3$ = 1:2, with $Cr(acac)_3$ as relaxation reagent]: δ = 21.4, 21.7, 70.8, 88.9, 125.9, 126.4, 126.7, 126.8, 127.1, 128.0, 129.0, 129.4, 129.6, 131.6, 133.0, 133.4, 133.7, 134.0, 135.2, 135.4, 137.0, 138.4, 138.6, 138.7, 138.87, 138.9, 139.0, 139.3, 139.6, 140.1, 140.14, 140.8, 141.0, 141.2, 141.6, 141.8, 141.9, 142.1, 142.2, 142.3, 142.32, 142.34, 142.5, 142.54, 142.6, 142.66, 142.7, 143.1, 144.2, 144.3, 144.5, 144.6, 144.8, 145.0, 145.02, 145.1, 145.2, 145.35, 145.4, 145.8, 145.9, 146.0, 146.02, 146.2, 146.4, 146.5, 147.7, 148.2, 150.0, 152.3, 154.0, 156.3; FT-IR (KBr): ν = 526, 667, 694, 730, 759, 1047, 1084, 1163, 1218, 1354, 1463, 1495, 1604, 2871, 2924, 2957, 3026 cm^{-1}; HR-MS (APCI$^-$): m/z = 1105.1141, calcd. for $C_{84}H_{19}NO_2S$ [M$^-$]: 1105.1136.

Spectral data of compound (2s): R_f = 0.66 (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ = 1:2): δ = 2.29 (s, 3H), 7.0 (d, J = 8.1 Hz, 2H), 7.51–7.64 (m, 6H), 7.99 (d, J = 2.3 Hz, 2H), 8.09 (d, J = 9.1 Hz, 2H), 8.54 (d, J = 8.8 Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3$ = 1:2, with $Cr(acac)_3$ as relaxation reagent]: δ = 21.4, 70.8, 89.2, 125.3, 126.7, 126.8, 127.2, 127.4, 128.3, 129.1, 129.2, 130.1, 132.8, 133.2, 133.4, 133.7, 134.9, 135.3, 135.4, 135.6, 138.9, 139.0, 139.04, 139.2, 139.5, 139.8, 140.2, 140.4, 140.9, 141.1, 141.3, 141.7, 141.9, 142.1, 142.2, 142.3, 142.33, 142.4, 142.5, 142.6, 142.7, 142.8, 143.1, 143.2, 144.3, 144.35, 144.4, 144.6, 145.0, 145.1, 145.14, 145.2, 145.4, 145.5, 145.6, 145.8, 146.1, 146.13, 146.2, 146.4, 146.6, 146.64, 147.9, 148.3, 149.7, 151.9, 153.7, 156.1; FT-IR (KBr): ν = 527, 573, 672, 757, 1046, 1086, 1164, 1216, 1356, 1595, 2857, 2927, 2962, 3019 cm^{-1}; HR-MS (APCI$^-$): m/z = 1125.0571, calcd. for $C_{83}H_{16}ClNO_2S$ [M$^-$]: 1125.0590.

Spectral data of compound (2t): R_f = 0.67 (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ = 1:2): δ = 2.31 (s, 3H), 7.01 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 6.5 Hz, 1H), 7.56–7.67 (m, 5H), 7.86 (s, 1H), 7.97–8.1 (m, 3H), 8.52 (d, J = 8.8 Hz, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3$ = 1:2, with $Cr(acac)_3$ as relaxation reagent]: δ = 21.4, 70.6, 89.0, 120.3 (q, J = 261.2 Hz), 121.2, 124.9, 125.8, 126.6, 127.0, 127.3, 128.2, 129.1, 130.1, 132.6, 132.9, 133.3, 133.5, 135.0, 135.3, 138.8, 138.9, 139.0, 139.2, 139.3, 139.6, 139.9, 140.6, 140.8, 140.9, 141.1, 141.3, 141.6, 141.7, 141.9, 141.92, 142.0, 142.1, 142.2, 142.4, 142.43, 142.5, 142.7, 142.72, 142.8, 142.9, 143.0, 144.17, 144.2, 144.23, 144.4, 144.9, 144.94, 144.98, 145.0, 145.01, 145.04, 145.1, 145.15, 145.2, 145.3, 145.4, 145.7, 145.9, 146.0, 146.02, 146.3, 146.4, 146.46, 146.5, 147.7, 148.1, 148.7, 149.4, 151.6, 153.4, 155.9; FT-IR (KBr): ν = 527, 573, 675, 756, 812, 920, 968, 1045, 1085, 1165, 1254, 1357, 1486, 1595, 2853, 2922, 2958 cm^{-1}; HR-MS (APCI$^-$): m/z = 1175.0793, calcd. for $C_{84}H_{16}F_3NO_3S$ [M$^-$]: 1175.0803.

Spectral data of compound (2u): R_f = 0.72 (toluene); ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ = 1:2): δ = 2.29 (s, 3H), 6.97 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.6 Hz, 1H), 7.48 (d, J = 8.6 Hz, 1H), 7.56–7.64 (m, 4H), 7.93 (d, J = 7.8 Hz, 1H), 8.0 (dd, J = 1.8, 9.8 Hz, 2H), 8.04 (s, 1H), 8.76 (s, 1H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3$ = 1:2, with $Cr(acac)_3$ as relaxation reagent]: δ = 21.4, 71.2, 87.4, 120.2 (q, J = 258.0 Hz), 120.6, 121.0, 127.2, 127.4, 127.7, 128.2, 128.9, 129.2, 132.6, 132.97, 133.0, 133.3, 135.5, 135.8, 136.1, 138.8, 138.9, 139.0, 139.01, 139.5, 139.54, 139.7, 140.1, 140.8, 141.1, 141.2, 141.5, 141.9, 142.0, 142.1, 142.15, 142.18, 142.19, 142.2, 142.3, 142.4, 142.5, 142.7, 142.8, 143.0, 143.1, 144.0, 144.1, 144.2, 144.3, 144.4, 144.8, 145.0, 145.03, 145.1, 145.13, 145.17, 145.2, 145.24, 145.4, 145.41, 145.7, 145.96, 145.98, 146.0, 146.03, 146.05, 146.1, 146.4, 146.5, 146.53, 147.7, 148.2, 149.6, 150.2, 151.6, 152.9, 156.4; FT-IR (KBr): ν = 527, 675, 754, 1048, 1090, 1166, 1215, 1253, 1356, 1489, 2850, 2919, 3030 cm^{-1}; HR-MS (APCI$^-$): m/z = 1175.0800, calcd. for $C_{84}H_{16}F_3NO_3S$ [M$^-$]: 1175.0803.

Spectral data of compound (2v): R_f = 0.55 (toluene); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21–7.41 (m, 4H), 7.55 (d,

$J=8.6$ Hz, 1H), 7.60–7.68 (m, 2H), 7.82 (d, $J=7.6$ Hz, 2H), 7.97–8.05 (m, 3H), 8.12 (s, 1H), 8.84 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=71.6$, 87.7, 120.5 (q, $J=257.6$ Hz), 121.1, 121.5, 127.4, 127.44, 127.6, 128.0, 128.6, 128.8, 129.1, 132.7, 132.9, 133.1, 133.2, 133.3, 133.5, 135.8, 136.0, 136.2, 139.1, 139.2, 139.3, 139.7, 139.9, 139.92, 140.3, 141.1, 141.3, 141.4, 141.7, 141.9, 142.2, 142.25, 142.3, 142.33, 142.4, 142.43, 142.5, 142.7, 142.8, 142.9, 143.3, 144.3, 144.4, 144.5, 144.6, 145.0, 145.2, 145.27, 145.3, 145.32, 145.34, 145.4, 145.5, 145.6, 145.7, 145.9, 146.2, 146.3, 146.32, 146.6, 146.7, 146.8, 147.9, 148.4, 149.5, 150.6, 151.7, 153.2, 156.6; FT-IR (KBr): $\nu=528$, 593, 733, 754, 1054, 1091,1169, 1216, 1253, 1357, 1494, 2850, 2920, 2955 cm^{-1}; HR-MS (APCI$^+$): $m/z=1162.0700$, calcd. for $C_{83}H_{15}F_3NO_3S$ [M+1]: 1162.0725.

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[16] See the Supporting Information for detailed characterization.

[17] X-ray crystallographic data for compound **2a**: black bricks; crystal size: $0.30\times0.02\times0.01\ mm^3$ grown from toluene; formula: $C_{93}H_{31}NO_2S$; crystal system: monoclinic; space group P 1 21/n 1; $d=1.534\ mg\,m^{-3}$, $V=5308.3(13)\ Å^3$; $a=22.324(3)$ Å; $b=9.8454(12)$ Å; $c=24.400(4)$ Å; $\beta=98.192(4)°$; $R_1=0.0612$; $R_w=0.1253$. CCDC 881206 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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