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Annulation of Benzamides with [60]Fullerene through Palladium(II)-Catalyzed C−H Bond Activation

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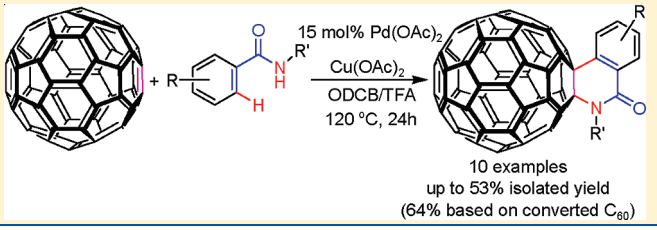
Supporting Information

ABSTRACT: Palladium-catalyzed heteroannulation of *N*-substituted benzamides with [60]fullerene, which proceeds through direct sp^2 C−H bond activation to form 7-membered ring pallada-intermediate with C_{60}, led to formation of [60]fulleroisoquinolinones in moderate to good yields (8−64% based on recovered C_{60}). A plausible reaction pathway is proposed.



INTRODUCTION

Fullerene derivatives have an extensive range of applications.[1] Although the functionalization of [60]fullerene using organic methodologies is well established,[2] studies of metal-catalyzed methodologies for fullerene functionalization remain relatively unexplored.[3] Transition-metal catalysis is an efficient tool in organic synthesis, enabling many diverse chemical transformations that are otherwise difficult to achieve using traditional methods.[4] Although C−H activation methodologies are well established in common organic synthesis,[5] their transfer to fullerene chemistry is relatively poorly developed. Recently, Wang et al. reported the Pd-catalyzed heteroannulations of [60]fullerene with *o*-iodoanilines[6] and anilides,[7] initiated through oxidative addition of aryl iodides to Pd(0) and C−H bond activation, respectively. This methodology provides fulleroindolines (five-membered rings) efficiently. Our research program on application of transition-metal catalysis for functionalizing C_{60} led us to study C−H activation of electron-poor aromatics with fullerenes. We assume that benzamides could be assembled with [60]fullerene to form fulleroisoquinolinones (six-membered rings) using the recently reported conditions.[7] However, these substrates are less reactive toward C−H activation under the described conditions because of the low electron density on the phenyl ring. Herein, we report the efficient Pd-catalyzed syntheses of the fulleroisoquinolinones **2** through C−H bond activation of benzamides under relatively mild conditions (Scheme 1).

RESULTS AND DISCUSSION

First, we synthesized the *N*-alkylated benzamides **1a**−**j** according to conventional methods.[8] We used *N*-methylbenzamide (**1a**) as a model substrate for our optimization studies. Initially, we evaluated the reaction of C_{60} (36 mg, 0.050 mmol) with **1a** (20 mg, 0.15 mmol) in the presence of $Pd(OAc)_2$ (1.68 mg, 0.0075 mmol, 15 mol %) and Oxone (22 mg, 0.15 mmol) in *o*-DCB/TFA (6:1, v/v; 7 mL) at 120 °C in a sealed tube for 24 h; we obtained the desired C_{60}-fused isoquinolinone **2a** in 10% isolated yield (14% based on recovered C_{60}) (Table 1, entry 1). Thus, the formation of fulleroisoquinolinone was relatively poor under these conditions; we explored reactions using other oxidizing reagents and solvents in a quest for better yields. The corresponding reactions performed using the common oxidants $Cu(OAc)_2$,[4c,12,13] CH_3COOAg,[9] and Ag_2O,[10] under the standard conditions described above, improved the yields of **2a** to 45, 26, and 23%, respectively (Table 1, entries 2−4). Next, we tested the catalytic reaction using AcOH,[11] DMSO,[12] CH_3CN,[13] and 1-chloronaphthalene as cosolvents, but the resulting transformations were relatively less efficient (entries 5−8). The reactions performed in chlorobenzene/TFA (10:1) gave **2a** in 10% yield with only a trace amount of recovered C_{60} (entry 9). The addition of 1 equiv of water deteriorated the reaction performance (entry 10). When reactions were carried out with 10 and 20 mol % of $Pd(OAc)_2$, **2a** was produced in 27 and 50% yield, respectively (entries 11 and 12). It is noteworthy that increasing the loading of $Pd(OAc)_2$ from 10 to 50 mol % did not result in obvious improvement of yields (entry 2 vs entries 11−14). This was attributed to formation of higher adducts; we isolated isomeric mixtures of bisadducts in 19 and 37% yields for 30 and 50 mol % loadings of $Pd(OAc)_2$, respectively (entries 13 and 14). Without the presence of $Cu(OAc)_2$ or excess loadings of $Cu(OAc)_2$, the yields were not improved; we only isolated 19 and 34% yields of **2a** for 0 and 6 equiv loadings of $Cu(OAc)_2$ (entries 15 and 16). Other organic reoxidizing reagent such as benzoquinone did not give the desired product, but gave mostly recovered C_{60} (entry 17).

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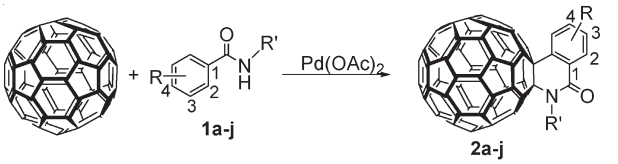
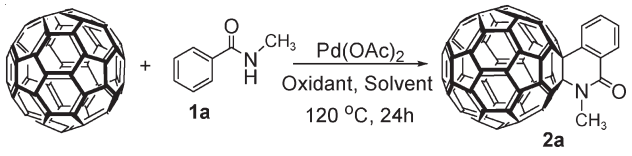
Scheme 1. Heteroannulation of [60]Fullerene with *N*-Substituted Benzamides



1a: R = H; R' = Me. **1b**: R = H; R' = Et
1c: R = H; R' = Bn. **1d**: R = 4-Me; R' = Bn
1e: R = 3-Me; R' = Me. **1f**: R = 3-Me; R' = Et
1g: R = 4-OMe; R' = Bn. **1h**: R = 4-Cl; R' = Et
1i: R = 4-Ph; R' = i-Pr. **1j**: R = 4-Ph; R' = Bn

Table 1. Reactions of C_{60} with 1a under Various Conditions[a]

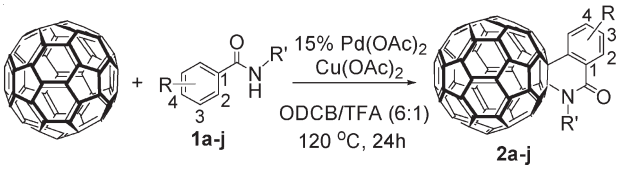


entry	oxidant	solvents (mL)	yield[b] (%)
1	Oxone	*o*-DCB/TFA (6:1)	10 (14)
2	$Cu(OAc)_2$	*o*-DCB/TFA (6:1)	45 (53)
3	CH_3COOAg	*o*-DCB/TFA (6:1)	26 (37)
4	Ag_2O	*o*-DCB/TFA (6:1)	23 (35)
5	$Cu(OAc)_2$	*o*-DCB/AcOH (6:1)	4 (10)
6	Cu(OAc)	*o*-DCB/DMSO (6:1)	<3
7	$Cu(OAc)_2$	*o*-DCB/CH_3CN (6:1)	<3
8	$Cu(OAc)_2$	1-Cl-naphthalene/TFA (6:1)	14 (86)
9	$Cu(OAc)_2$	PhCl/TFA(10:1)	10 (15)
10[c]	$Cu(OAc)_2$	*o*-DCB/TFA (6:1)	21
11[d]	$Cu(OAc)_2$	*o*-DCB/TFA (6:1)	27 (84)
12[d]	$Cu(OAc)_2$	*o*-DCB/TFA (6:1)	50 (61)
13[d]	$Cu(OAc)_2$	*o*-DCB/TFA (6:1)	37 (43)[g]
14[d]	$Cu(OAc)_2$	*o*-DCB/TFA (6:1)	0[h]
15	none	*o*-DCB/TFA (6:1)	19 (54)
16	$Cu(OAc)_2$[e]	*o*-DCB/TFA (6:1)	34 (40)
17	benzoquinone[f]	*o*-DCB/TFA (6:1)	0[i]

[a] All reactions were performed with 0.050 mmol of C_{60}, 0.15 mmol of **1a**, 0.15 mmol of oxidant, and 0.0075 mmol of $Pd(OAc)_2$ in the listed solvent at 120 °C for 24 h unless otherwise noted. [b] Isolated yields after column chromatography. Values in parentheses are based on consumed C_{60}. [c] Reaction performed with 1 equiv of H_2O added. [d] Entries 11, 12, 13, and 14 were carried out with 10, 20, 30, and 50 mol % of $Pd(OAc)_2$, respectively. [e] 6 equiv of $Cu(OAc)_2$ was loaded. [f] 3 equiv of benzoquinone. [g] 19% bisadducts were isolated. [h] 37% bisadducts were isolated. [i] 98% C_{60} was recovered.

Therefore, our systematic screening of a range of oxidants and solvents revealed that the heteroannulation of [60]fullerene with the *N*-substituted benzamide **1a** was optimized when performed in the presence of $Cu(OAc)_2$ in ODCB/TFA (6:1), giving the fulleroisoquinolinone **2a** in good yield (45%; Table 1, entry 2). Notably, TFA has been used as a solvent in organic syntheses for the sp^2 C−H bond activation of amides[9] and oxime ethers.[10] Since the reaction incorporated TFA as a cosolvent (bp 72.4 °C), the reaction carried out at 120 °C required good sealing for prevention of TFA loss. We observed that TFA loss during the reaction caused lower yielding results.

Table 2. Palladium-Catalyzed Syntheses of the Fulleroisoquinolinones 2a−j[a]



entry	R	R′	amides	product	yield[b] (%)	yield[c] (%)	recovered C_{60} (%)
1	H	Me	**1a**	**2a**	45 (53)	44 (51)	14
2	H	Et	**1b**	**2b**	44 (55)	47 (58)	19
3[d]	H	Bn	**1c**	**2c**	28 (46)	19 (32)	39
4[d]	4-Me	Bn	**1d**	**2d**	42 (59)	40 (56)	28
5	3-Me	Me	**1e**	**2e**	53 (64)	57 (69)	17
6	3-Me	Et	**1f**	**2f**	52(59)	60 (67)	11
7[d]	4-OMe	Bn	**1g**	**2g**	36 (51)	34 (48)	32
8	4-Cl	Et	**1h**	**2h**	20 (26)	21 (27)	22
9	4-Ph	*i*-Pr	**1i**	**2i**	6 (8)	5 (6)	22
10[d]	4-Ph	Bn	**1j**	**2j**	30 (37)	29 (36)	19

[a] All reactions were performed using 0.050 mmol of C_{60}, 0.15 mmol of the amide, 0.15 mmol of $Cu(OAc)_2$, and 0.0075 mmol of $Pd(OAc)_2$ in ODCB/TFA (6:1, v/v; 7 mL) at 120 °C 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, using mesitylene as an internal standard. [d] Reaction was performed using only 0.2 mL of TFA.

With the optimal conditions in hand, we evaluated the catalytic scope of this system by employing a variety of substrates **1b**−**j** (Table 2) featuring either electron-donating and -withdrawing groups on their benzamide aryl rings. In general, substrates equipped with electron-donating groups afforded their corresponding fulleroisoquinolinones in good yields (Table 2, entries 4−7). Substrates **1e** and **1f** underwent regioselective C−H activations[7] at their less hindered and more electron-rich para positions (relative to their Me substituents) to afford **2e** and **2f** in excellent yields of 53 and 52%, respectively (Table 2, entries 5 and 6). Substrates bearing electron-withdrawing groups, such as the chloro and phenyl units of **1h**−**j**, provided their products in only moderate yields (Table 2, entries 8−10). Under the standard conditions, the reactions of amides bearing *N*-benzyl substituents (**1c**, **1d**, **1g**, and **1j**) yielded debenzylated products. To overcome this problem, we performed these experiments using only 0.2 mL of TFA to obtain the desired products in moderate yields (Table 2, entries 3, 4, 7, and 10). The extremely low yield of **2i** may be attributed to the bulkiness of the isopropyl group that makes formation of pallada-intermediate poor (entry 9). We further surveyed the reaction yields using 10, 15, and 20 mol % of $Pd(OAc)_2$ catalysts under optimal conditions and summarized the isolated yields measured by the weighing method in Figure 1. We found that the yields obtained from 10 mol % of $Pd(OAc)_2$ are relatively lower and those from 15 and 20 mol % of $Pd(OAc)_2$ catalysts are higher and comparable (see the Supporting Information for plots of yields on the basis of recovered C_{60}).

We characterized the fulleroisoquinolinones **2a**−**j** using infrared (IR) and ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, fast atom bombardment mass spectrometry (FAB MS), and X-ray crystallography. All MS data corresponded to the expected formulas of the isolated fulleroisoquinolinones. Because each of these compounds possesses a symmetrical plane, its ^{13}C NMR spectrum exhibits 30 peaks for the sp^2-hybridized carbon atoms on the C_{60} cage. In their IR spectra, C═O stretching bands appear at ca. 1650 cm^{-1}. Figure 2 displays a 2D-HMBC spectrum of the selected compound **2f**. We made partial peak assignments on the basis of one- (2D-HMQC) and three-bond (2D-HMBC) correlation spectra. For example, the signals of the protons on the C6, C7, C9, C10, C11, and C12 atoms of **2f** were readily assignable in terms of their one-bond couplings, according to the 2D-HMQC data (see the Supporting Information). The sp^3-hybridized carbon atoms of the C_{60} moiety of **2f** appear as two signals at 62.60 (C1) and 79.29 (C2) ppm; C1 and C2 correlate with the protons on C6 and C11, respectively, through three-bond couplings. The C═O carbon atom C3 correlates with the protons on both C9 and C11, which are three bonds away. We unambiguously assigned the quaternary sp^2-hybridized carbon atoms C4, C5, and C8 through their three-bond correlations with the protons on the C6, C7/C9, and C6 atoms, respectively. Notably, all of the signals of the sp^2-hybridized aryl protons of the fulleroisoquinolinones appear downfield away from $CHCl_3$ (7.26 ppm). Figure 3 presents the structure of compound **2d** determined using X-ray diffraction analysis.[14]

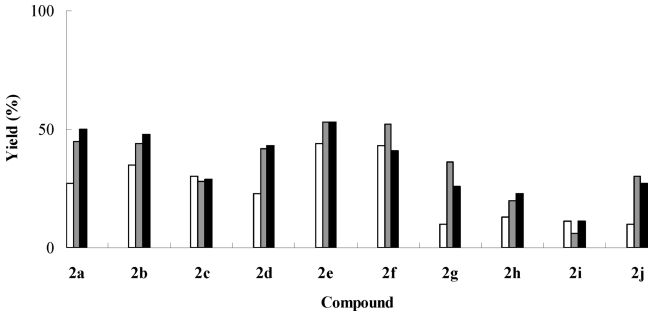


Figure 1. Summary of reaction yields using 10 (white), 15 (gray), and 20 mol % (black) $Pd(OAc)_2$ catalysts under optimal conditions.

Scheme 2 presents a plausible mechanism for the formation of the fulleroisoquinolinones. Complexation of Pd(II) with the nitrogen atom in amides **1a**−**j**, followed by ortho C−H activation, results in the formation of a five-membered-ring palladacyle **Ia**.[15] Subsequent insertion of C_{60} to intermediate **Ia** generates intermediate **Ib**. Finally, reductive elimination affords the fulleroisoquinolinones **2a**−**j** and Pd(0), which is oxidized to Pd(II) by $Cu(OAc)_2$ to complete the catalytic cycle.

Next, we compared the electrochemical and UV−vis spectroscopic properties of the structurally similar six- (fulleroisoquinolinones) and five-membered-ring (fulleroindolines) compounds. Table 3 summarizes the half-wave reduction potentials of the isomeric compounds **2a** and **3a**.[7] To our surprise, the fulleroisoquinolinone **2a** exhibits its first reduction potential at −1.14 V, which is only 10 mV more negative than that of C_{60}; we observed similar trends in the values of its second (−1.52 V) and third (−1.99 V) reduction potentials, suggesting that attachment of the electronegative nitrogen atom to the sp^3-hybridized carbon atom of the fullerene cage compensates for the reduced potentials typically imparted after monofunctionalization. In contrast, the five-membered-ring fulleroindoline **3a** underwent an inherently lower first reduction at −1.17 V, consistent with the observations of Suzuki et al., who found that five-membered-ring fullerene derivatives generally exhibit more-negative potentials.[16] Again, this behavior is consistent with the notion

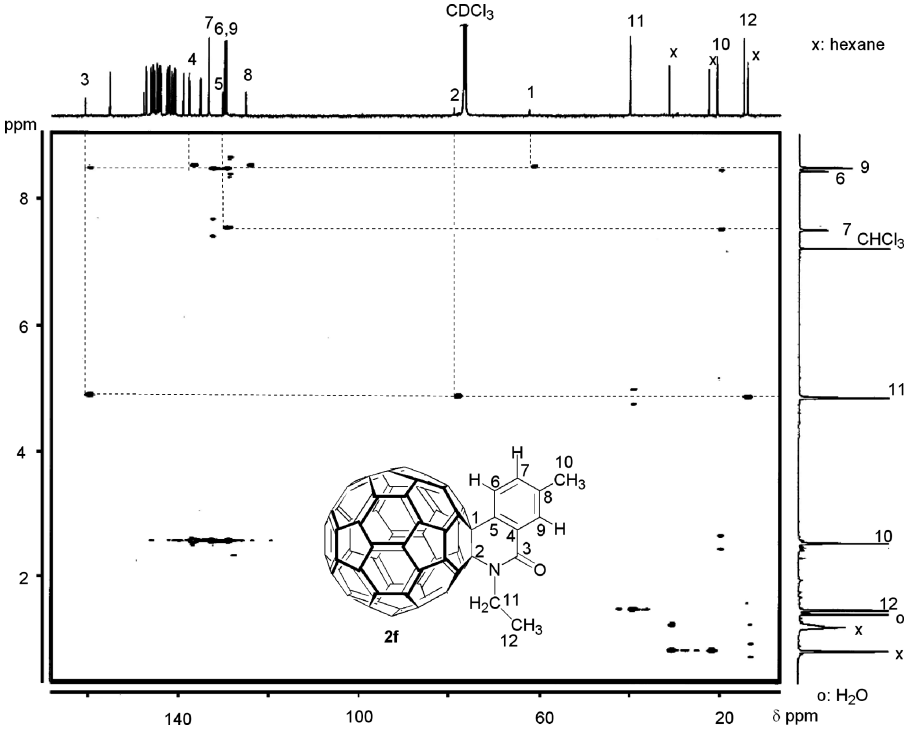


Figure 2. 2D-HMBC spectrum of compound **2f**.

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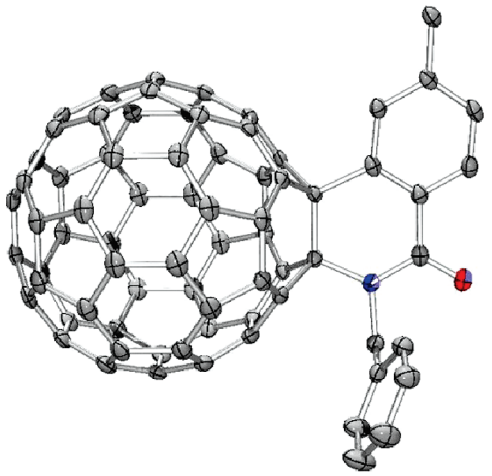


Figure 3. X-ray crystal structure of compound **2d**.

Scheme 2. Proposed Reaction Pathway

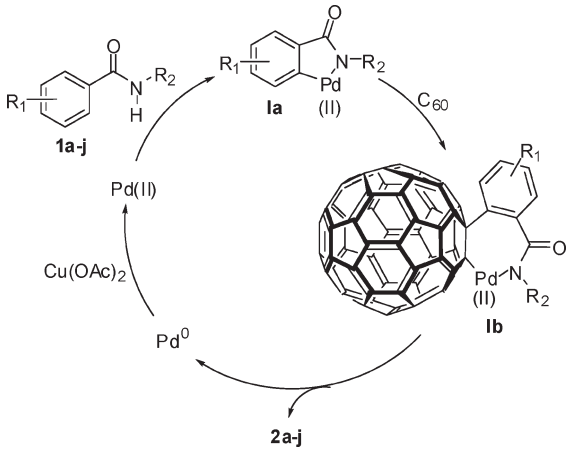
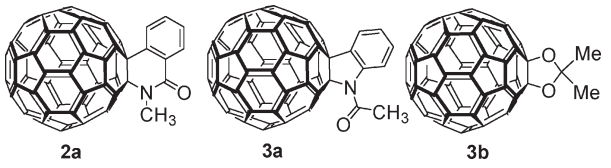


Table 3. Half-Wave Reduction Potentials (V)[a] of C_{60}, 2a, 3a, and 3b

compd	E^1	E^2	E^3
C_{60}	−1.13	−1.52	−1.98
2a	−1.14	−1.52	−1.99
3a	−1.17	−1.54	−1.92
3b[16]	−1.13	−1.50	−1.99

[a] Versus ferrocene/ferrocenium. Conditions: ca. 0.50 mM of C_{60}, **2a**, or **3a** and 0.050 mM Bu_4NPF_6 in anhydrous *o*-DCB; reference electrode: Ag/0.01 M $AgNO_3$ and 0.050 mM *n*-Bu_4NClO_4 in anhydrous acetonitrile; working electrode: glassy carbon; auxiliary electrode: Pt; scanning rate: 20 mV s^{-1}.

that attachment of a heteroatom to an sp^3-hybridized carbon atom of a C_{60} cage shifts the reductive waves anodically (cf. values for **3b** in Table 3). Notably, we observed similar reduction potentials when analyzing these compounds using differential pulse voltammetry and Osteryoung square wave voltammetry.[8] Furthermore, the first reduction potential of the monoadducts is nearly the same as that of C_{60}, indicating that they should have nearly the same reactivity toward further functionalization. However, the products would become relatively unreactive under the cosolvent of trifluoroacetic acid due to protonation. This manner will retard them for further being functionlized to form higher adducts. Finally, the electronic absorptions of **2a** and **3a** in their UV−vis spectra were nearly identical; they both feature typical absorptions at 426 nm and extended absorption at 688 nm, consistent with those of corresponding fullerene monoadducts.[7]



In conclusion, fulleroisoquinolinones can be prepared efficiently from heteroannulations of [60]fullerene with *N*-alkylbenzamides through C−H bond activation under Pd(II) catalysis. We used trifluoroacetic acid as a key cosolvent for improving the reaction performance. The isolated fulleroisoquinolinones are easier to be reduced as compared to their 5-membered-ring isomers according to electrochemical studies. Extensions of this study to the syntheses of isoquinolinones using alkynes are underway.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of [60]Fulleroisoquinolinone 2. To a pressure-affordable thick-wall glass tube containing C_{60} (36 mg, 0.05 mmol), benzamide **1** (0.15 mmol), $Pd(OAc)_2$ (1.68 mg, 0.0075 mmol), and $Cu(OAc)_2$ (27 mg, 0.15 mmol) were added 6 mL of dry *o*-dichlorobenzene, 1 mL of TFA, and a stir bar. The tube was sealed with an O-ring and Teflon cap. After the tube was stirred at 120 °C without loss of TFA (bp 72.4 °C) for 24 h, the reaction mixture was cooled to room temperature and then subjected to column chromatography using toluene as a starting eluent for recovery of the unreacted C_{60}. Subsequent elution with 2% ethyl acetate in toluene afforded fulleroisoquinolinone **2**. Spectral data of compound **2a**−**j** follow.

Spectral data of compound 2a: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$ = 1:2) δ 4.11 (s, 3H), 7.63 (dt, J = 7.3, 1.0 Hz, 1H), 7.74 (dt, J = 1.7 Hz, 7.2 Hz, 1H), 8.65 (dd, J = 1.6 Hz, 8.1 Hz, 2H); ^{13}C NMR (176.0 MHz, CS_2/$CDCl_3$ = 1:2, with $Cr(acac)_3$ as relaxation reagent) 33.5, 62.1, 79.5, 125.8, 128.0, 128.4, 130.0, 132.8, 133.63, 134.1, 135.4, 138.1, 139.3, 140.9, 141.17, 141.23, 141.7, 142.2, 142.3, 142.6, 142.7, 143.0, 144.3, 144.5, 144.9, 145.0, 145.1, 145.2, 145.7, 145.8, 146.0, 146.1, 146.4, 146.5, 146.8, 147.6, 148.1, 155.4, 161.9; FT-IR (KBr) ν (cm^{-1}) 526, 554, 728, 901, 1374, 1465, 1653; HRMS (FAB^+) calcd for $C_{68}H_8NO$ (M + 1) 854.0606 found 854.0620.

Spectral data of compound 2b: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$ = 1:2) δ 1.52 (t, J = 6.9 Hz, 3H), 4.87 (q, J = 6.9 Hz, 2H), 7.62 (dt, J = 1.1 Hz, 8.1 Hz, 1H), 7.73 (dt, J = 1.8 Hz, 8.0 Hz, 1H), 8.66 (d, J = 8.2 Hz, 2H); ^{13}C NMR (176.0 MHz, CS_2/$CDCl_3$ = 1:2, with $Cr(acac)_3$ as relaxation reagent) 15.0, 40.2, 62.6, 79.1, 125.7, 127.8, 129.6, 130.0, 132.5, 133.2, 133.6, 135.3, 138.0, 139.1, 140.9, 141.1, 141.3, 141.6, 142.17, 142.19, 142.5, 142.6, 142.9, 144.3, 144.3, 144.5, 144.7, 144.9, 144.99, 145.02, 145.6, 145.8, 145.9, 146.0, 146.3, 146.4, 147.4, 147.5, 148.0, 155.3, 160.2; FT-IR (KBr) ν (cm^{-1}) 526, 738, 830, 1199, 1310, 1398,

1462, 1514, 1653; HRMS (FAB$^+$) calcd for $C_{69}H_{10}NO$ (M + 1) 868.0762 found 868.0760.

Spectral data of compound 2c: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$ = 1:2) δ 6.07 (s, 2H), 7.08−7.19 (m, 3H), 7.31 (d, J = 7.4 Hz, 2H), 7.66 (t, J = 7.3 Hz, 1H), 7.77 (dt, J = 1.5 Hz, 7.7 Hz, 1H), 8.69 (dd, J = 1.8 Hz, 8.1 Hz, 2H); ^{13}C NMR (150.7 MHz, CS_2/$CDCl_3$ = 1:2) 48.39, 63.1, 79.7, 125.8, 126.9, 127.2, 128.2, 128.4, 129.8, 130.6, 133.2, 133.9, 134.4, 135.4, 139.4, 141.1, 141.4, 141.8, 142.39, 142.42, 142.8, 142.9, 143.1, 144.5, 144.5, 144.7, 145.0, 145.2, 145.3, 145.8, 146.0, 146.1, 146.2, 146.56, 146.63, 147.5, 147.8, 148.3, 155.5, 162.5; FT-IR (KBr) ν (cm^{-1}) 526, 736, 970, 1030, 1321, 1393, 1451, 1513, 1541, 1651; HRMS (FAB$^+$) calcd for $C_{74}H_{12}NO$ (M + 1) 930.0919 found 930.0933.

Spectral data of compound 2d: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$ = 1:2) δ 2.54 (s, 3H), 6.09 (s, 2H), 7.08−7.23 (m, 3H), 7.31 (d, J = 7.4 Hz, 2H), 7.46 (d, J = 8.0 Hz, 1H), 8.43 (s, 1H), 8.58 (d, J = 8.0 Hz, 1H); ^{13}C NMR (176.0 MHz, CS_2/$CDCl_3$ = 1:2, with Cr(acac)$_3$ as relaxation reagent) 21.9, 47.8, 62.7, 79.3, 123.2, 126.6, 126.9, 128.1, 129.0, 129.9, 130.7, 133.6, 133.7, 135.1, 137.6, 137.8, 139.1, 140.8, 141.08, 141.10, 141.6, 142.10, 142.14, 142.5, 142.6, 142.7, 142.8, 143.5, 144.18, 144.23, 144.4, 144.7, 144.8, 144.9, 145.1, 145.5, 145.7, 145.8, 145.9, 146.26, 146.30, 147.5, 147.9, 155.3, 161.8; FT-IR (KBr) ν (cm^{-1}) 527, 6943, 973, 1122, 1183, 1379, 1414, 1513, 1540, 1651; HRMS (FAB$^+$) calcd for $C_{75}H_{14}NO$ (M + 1) 944.1075 found 944.1066.

Spectral data of compound 2e: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$ = 1:2) δ 2.59 (s, 3H), 4.11 (s, 3H), 7.55 (dd, J = 1.5 Hz, J = 8.3 Hz, 1H), 8.45 (s, 1H), 8.52 (d, J = 8.2 Hz, 1H); ^{13}C NMR (150.7 MHz, CS_2/$CDCl_3$ = 1:2, with Cr(acac)$_3$ as relaxation reagent) 20.8, 33.5, 61.9, 79.5, 125.6, 129.5, 130.2, 131.1, 133.5, 133.6, 135.5, 137.8, 138.1, 139.3, 140.9, 141.15, 141.23, 141.8, 142.17, 142.23, 142.5, 142.6, 142.9, 144.3, 144.5, 144.8, 144.9, 145.1, 145.2, 145.71, 145.74, 145.9, 146.0, 146.3, 146.4, 146.9, 147.6, 148.1, 155.5, 161.7; FT-IR (KBr) ν (cm^{-1}) 526, 578, 594, 761, 1061, 1362, 1424, 1465, 1513, 1541, 1655; HRMS (FAB$^+$), calcd for $C_{69}H_{10}NO$ (M + 1) 868.0762 found 868.0764.

Spectral data of compound 2f: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$ = 1:2) δ 1.51 (t, J = 6.9 Hz, 3H), 2.59 (s, 3H), 4.83 (q, J = 6.8 Hz, 2H), 7.52 (d, J = 8.3 Hz, 1H), 8.43 (s, 1H), 8.50 (d, J = 8.3 Hz, 1H); ^{13}C NMR (150.7 MHz, CS_2/$CDCl_3$ = 1:2, with Cr(acac)$_3$ as relaxation reagent) 15.0, 20.8, 40.1, 62.3, 79.0, 125.5, 129.6, 130.19, 130.23, 133.3, 133.4, 135.3, 137.5, 137.9, 139.1, 140.8, 141.0, 141.3, 141.6, 142.10, 142.13, 142. 5, 142.6, 142.9, 144.2, 144.3, 144.4, 144.6, 144.8, 144.9, 145.0, 145.5, 145.7, 145.8, 145.9, 146.2, 146.3, 147.4, 147.5, 147.9, 155.4, 160.1; FT-IR (KBr) ν (cm^{-1}) 526, 578, 766, 1069, 1185, 1319, 1380, 1425, 1462, 1513, 1650; HRMS (FAB$^+$) calcd for $C_{70}H_{12}NO$ (M + 1) 882.0919, found 882.0910.

Spectral data of compound 2g: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$ = 1:2) δ 3.92 (s, 3H), 6.06 (s, 2H), 7.10−7.23 (m, 4H), 7.33 (d, J = 7.4 Hz, 2H), 8.13 (d, J = 1.9 Hz, 1H), 8.67 (d, J = 8.6 Hz, 1H); ^{13}C NMR (150.7 MHz, CS_2/$CDCl_3$ = 1:2) 48.1, 55.5, 63.1, 79.7, 113.4, 116.3, 118.9, 126.8, 127.2, 128.4, 133.0, 133.9, 135.3, 136.3, 138.0, 138.1, 139.5, 141.1, 141.4, 141.8, 142.39, 142.42, 142.7, 142.8, 143.0, 143.1, 144.5, 144.5, 144.7, 145.0, 145.16, 145.21, 145.3, 145.8, 146.0, 146.1, 146.2, 146.56, 146.60, 147.8, 147.9, 148.3, 155.5, 162.4, 163.5; FT-IR (KBr) ν (cm^{-1}) 527, 576, 754, 1029, 1106, 1183, 1250, 1280, 1387, 1434, 1603, 1646; HRMS (FAB$^+$) calcd for $C_{75}H_{14}NO_2$ (M + 1) 960.1025 found 960.1007.

Spectral data of compound 2h. ^{1}H NMR (300 MHz, CS_2/$CDCl_3$ = 1:2) δ 1.51 (t, J = 6.9, 3H), 4.85 (q, J = 6.9 Hz, 2H), 7.59 (dd, J = 1.9, 8.4 Hz, 1H), 8.59 (s, 1H), 8.62 (s, 1H); ^{13}C NMR (176.0 MHz, CS_2/$CDCl_3$ = 1:2, with Cr(acac)$_3$ as relaxation reagent) 14.7, 40.3, 62.2, 79.3, 124.1, 128.4, 129.6, 131.5, 133.8, 135.2, 135.3, 138.0, 139.39, 139.5, 141.0, 141.1, 141.3, 141.5, 142.19, 142.22, 142.6, 142.7, 143.0, 144.2, 144.3, 144.5, 144.6, 144.9, 144.98, 145.04, 145.6, 145.8, 145.9, 146.0, 146.38, 146.44, 147.1, 147.6, 148.1, 154.7, 159.9; FT-IR (KBr) ν (cm^{-1}) 526, 766, 1064, 1150, 1308, 1418, 1457, 1512, 1540, 165; HRMS (FAB$^+$), calcd for $C_{69}H_9ClNO$ (M + 1) 902.0373 found 902.0361.

Spectral data of compound 2i: ^{1}H NMR (600 MHz, CS_2/$CDCl_3$ = 1:2) δ 1.83 (d, J = 6.6 Hz, 6H), 5.85 (septet, 1H), 7.35 (m, 3H), 7.54 (dd, J = 1.0 Hz, 7.9 Hz, 2H), 7.79 (dd, J = 1.6 Hz, 8.2 Hz, 1H), 8.67 (d, J = 8.2 Hz, 1H), 8.76 (d, J = 1.5 Hz, 1H) ; ^{13}C NMR (150.7 MHz, CS_2/$CDCl_3$ = 1:2, with Cr(acac)$_3$ as relaxation reagent) 20.7, 51.3, 63.7, 80.5, 125.7, 126.9, 127.2, 128.2, 128.6, 129.0, 130.3, 133.8, 133.9, 135.7, 137.8, 139.5, 139.8, 141.2, 141.3, 141.5, 141.8, 142.5, 142.8, 142.9, 143.2, 144.5, 144.76, 144.79, 144.9, 145.1, 145.2, 145.8, 146.1, 146.3, 146.6, 146.7, 147.6, 147.8, 148.3, 155.7, 161.7; FT-IR (KBr) ν (cm^{-1}) 527, 695, 749, 851, 1031, 1072, 1200, 1340, 1375, 1433, 1515, 1541, 1653; HRMS (FAB$^+$) calcd for $C_{76}H_{16}NO$ (M + 1) 958.1232 found 958.1217.

Spectral data of compound 2j: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$ = 1:2) δ 6.10 (s, 2H), 7.09−7.26 (m, 2H), 7.35−7.46 (m, 6H), 7.60 (td, J = 1.5 Hz, 7.4 Hz, 2H), 7.87 (dd, J = 1.6 Hz, 8.2 Hz, 1H), 8.79 (d, J = 8.2 Hz, 1H), 8.87 (d, J = 1.5 Hz, 1H); ^{13}C NMR (150.7 MHz, CS_2/$CDCl_3$ = 1:2) 48.2, 63.1, 79.7, 124.5, 126.8, 127.0, 127.1, 127.2, 128.4, 128.5, 128.9, 129.0, 131.3, 133.9, 134.7, 137.7, 138.0, 139.5, 139.6, 141.1, 141.3, 141.8, 142.3, 142.4, 142.7, 142.8, 143.0, 144.4, 144.6, 145.0, 145.06, 145.10, 145.2, 145.7, 145.9, 146.07, 146.10, 146.2, 146.49, 146.54, 147.5, 147.7, 148.2, 155.4, 162.2; FT-IR (KBr) ν (cm^{-1}) 527, 545, 695, 752, 972, 1031, 1122, 1215, 1384, 1408, 1436, 1606, 1650; HRMS (FAB$^+$) calcd for $C_{80}H_{16}NO$ (M + 1) 1006.1232, found 1006.1255.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and full spectroscopic/spectrometric data (IR; ^{1}H and ^{13}C NMR) for all new compounds; X-ray crystallographic data for compound **2d** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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