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On the Thermal Stability of [60]Fullerene Cycloadducts: Retro-Cycloaddition Reaction of 2-Pyrazolino[4,5:1,2][60]fullerenes

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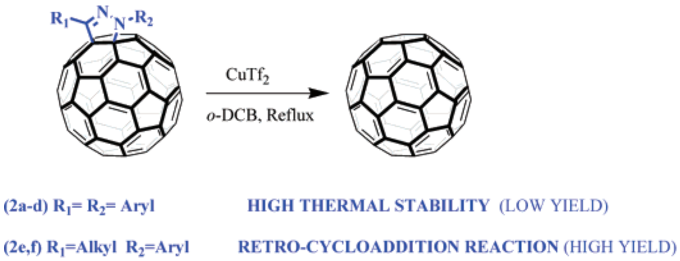

2-Pyrazolino[4,5:1,2][60]fullerenes undergo a thermally induced retro-cycloaddition process whose efficiency is influenced by the nature of the *C*-substituent. *C*-Aryl-*N*-Aryl-2-pyrazolino[60]fullerenes (**2a−d**) poorly undergo a thermal retro-cycloaddition reaction even in the presence of a strong dipolarophile or a metal Lewis acid which, in contrast to other fullerene derivatives, shows their remarkable thermal stability. *C*-Alkyl-*N*-Aryl-2-pyrazolino[60]fullerenes (**2e−f**) show a different behavior, being more vulnerable to the presence of copper triflate and leading to the retro-cycloaddition product (pristine C_{60}) in good yield.

Introduction

Since the discovery of fullerenes[1] and other nanoforms of carbon,[2] an enormous effort has been dedicated to their chemical functionalization.[3] However, despite the belief that the chemistry of fullerenes is well established, their singular electronic and geometrical features with reactive double bonds forming a convex surface is a unique scenario still being tested in a wide variety of new reactions.[4] Among the many well-known exohedral reactions developed on the fullerene sphere, 1,3-dipolar cycloadditions have played a prominent role[5] with applications in fields such as medicinal chemistry[6] and materials science.[7] Although pyrrolidino[3,4:1,2][60]fullerenes have been by far the most studied derivatives obtained from 1,3-dipolar cyclo-

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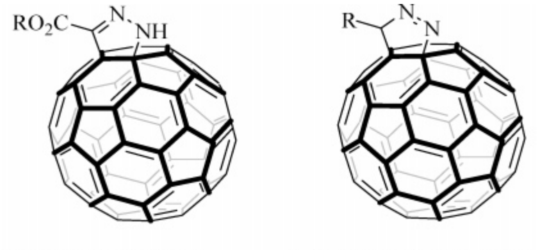
additions,[8] other fullerene-fused pentagonal heterocyclic rings, like pyrazolino[60]fullerenes, also display interesting chemical, electrochemical, and photophysical properties.[9] Pyrazolino[60]fullerenes have been obtained by addition of nitrile imines to [60]fullerene in good yields.[10] Nitrile imines are efficiently prepared by dehydrohalogenation of halohydrazones, obtained in turn by chlorination or bromination of the corresponding hydrazones. Despite the huge amount of work devoted to the preparation of fullerene cycloadducts, much less is known however on their chemical and thermal stability. The thermal stability of chemically modified fullerenes is a fundamental aspect in order to determine the best candidates to prepare functional C_{60}-based materials able to withstand the ambient conditions to maintain their efficiency, thus preventing any further chemical or thermal degradation. This issue is particularly important in those photoelectronic devices, such us photovoltaic cells, where oxygen, water, and extreme temperatures represent the main agents affecting the stability and performance of organic sollar cells.[11] Some of us have recently reported the thermally induced transition metal-catalyzed quantitative retro-cycloaddition reaction of pyrrolidino[3,4:1,2]-fullerenes[12] as well as isoxazolino[3,4:1,2]fullerenes[13] and proved its utility as a new and useful protection-deprotection protocol.[12] In a very recent paper, this methodology has been successfully applied to induce the retro-cycloaddition process in pyrrolidino-SWCNTs (SWCNT: Single-wall Carbon Nanotube) derivatives, thus demonstrating the suitability of this protocol to afford highly pure SWCNTs.[14] Here, we report the study carried out on the thermal stability of a series of 2-pyrazolino[60]fullerenes bearing different substituents, (*C*-aryl-*N*-aryl or *C*-alkyl-*N*-aryl) under the same experimental conditions used previously for fulleropyrrolidines, which afforded pristine C_{60} quantitatively. The results indicates that C-substitution on the pyrazole ring plays an important role in the course of this reaction, being that l,3-diaryl-2-pyrazolino[60]fullerenes are thermally stable compounds which are less susceptible to undergo the retro-cycloaddition reaction under these conditions and forming C_{60} in very low yields. In contrast, 1-aryl-3-alkyl-2-pyrazolino derivatives are more vulnerable to these experimental conditions, undergoing an efficient thermally induced transition metal-catalyzed retro-cycloaddition reaction. Related 1-pyrazolino-fused fullerenes are known to decompose easily in refluxing toluene, affording a mixture of methanofullerenes.[15] Recently, 2-pyrazolino[60]fullerenes (**1**) were obtained via isomerization of 1-pyrazolines which, in turn, were synthesized by 1,3-dipolar cycloadditions from alkyl diazoacetates (Figure 1).[16] Thermal stability studies of these nitrogen-unsubstituted 2-pyrazolino[60]fullerenes showed decomposition in refluxing *o*-dichlorobenzene, affording a mixture of methanofullerenes through the loss of N_2. However, no evidence of retro-cycloaddition reaction was reported under these conditions.



1 R= Et or $(CH_2)_7CH_3$ 1-pyrazolino[60]fullerenes

FIGURE 1. 2-Pyrazolino[60]fullerenes (**1**) and the isomer 1-pyrazolino-[60]fullerenes.

Herein we describe the unprecedented retro-cycloaddition reaction of ***N***-substitued 2-pyrazolino[60]fullerenes under thermal or microwave assisted conditions to yield the parent [60]-fullerene.

Results and Discussion

In order to determine if the experimental conditions previously used for the retro-cycloaddition reaction of fulleropyrrolidines,[12] and fulleroisoxazolines[13] were suitable for 2-pyrazolino[60]-fullerenes, we have followed the same protocol: excess of dipolarophile (maleic anhydride) as well as the use of copper triflate ($CuTf_2$) to coordinate the metal to the nitrogen atoms and, therefore, facilitate the retro-cycloaddition process. For this purpose, we have synthesized a series of 2-pyrazolino[60]-fullerenes bearing different substituents (Figure 2). Compounds **2a**,[17] **2b**,[10c] **2c**,[10d] and **2e**[10a] have previously been described by some of us and were prepared according to the procedure described in their respective literature.

2-Pyrazolino[60]fullerene derivatives **2d** and **2f** had not been previously reported and were synthesized by 1,3-dipolar cycloaddition of the corresponding nitrile imines, which were generated in situ from the corresponding hydrazones (see experimental section).

The compounds to study were first heated at reflux in *o*-DCB for 48 h, and small amounts (0.5 mL) of each reaction were collected every 24 h, diluted, and submitted to HPLC analysis (Table 1, *o*-DCB-24h and *o*-DCB-48 h). The results of these experiments showed that pristine C_{60} was obtained in different amounts, although the efficiency of the process in *C*-Aryl-*N*-Aryl-2-pyrazolino[60]fullerenes was not very high (1−23%). The same experiments perfomerd on *C*-Alkyl-*N*-Aryl-2-

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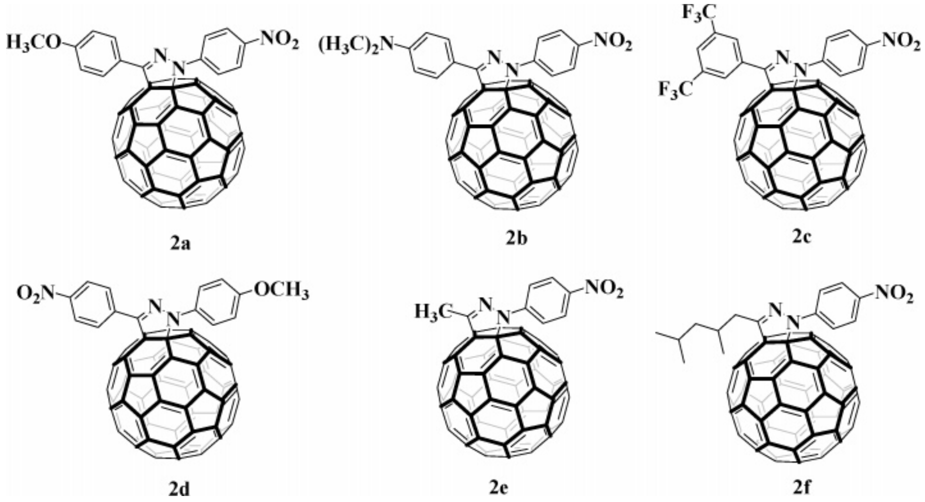

FIGURE 2. 2-Pyrazolino[60]fullerenes investigated for the thermal retro-cycloaddition reaction.

TABLE 1. Experimental Conditions Used for the Retro-Cycloaddition Reaction of 2-pyrazolino[60]Fullerenes[a] and Formation of Pristine C_{60} (%) Determined by HPLC

experiment	2a	2b	2c	2d	2e	2f
o-DCB-24h.	11	4	1	12	10	26
o-DCB-48 h.	23	8	2	17	14	29
MA-24h.	15	6	0	13	7	33
MA-48 h.	15	16	1	22	15	44
$CuTf_2$-24 h.	10	*b*	2	8	48	28
$CuTf_2$-48 h.	10	*b*	3	11	48	*c*
MA-$CuTf_2$-24 h.	6	*b*	1	7	54	18
MA-$CuTf_2$-48 h.	7	*b*	4	11	72	*c*

[a] All the reactions were performed in *o*-DCB at reflux; MA = 30 equiv of maleic anhydride; $CuTf_2$ = 1 equiv of copper triflate. [b] These reactions formed an insoluble precipitate; therefore, analysis of % of conversion could not be performed. [c] Reactions were completed after 24 h.

pyrazolino[60]fullerenes showed a better performance, and C_{60} was obtained from low to moderate yields (10−29%).

In order to increase the efficiency of the retrocycloaddition process, we carried out the same experiments in the presence of a big excess (30 equiv) of maleic anhydride as a strong dipolarophile (Table 1, MA-24h, and MA-48 h). Analysis of each reaction by HPLC showed that pristine C_{60} was obtained in small amounts for *C*-Aryl-*N*-Aryl-2-pyrazolino[60]fullerenes (0−22%). Therefore the presence of a strong dipolarofile like maleic anhydride does not produce an important improvement over the retrocycloaddition process in these compounds. Concerning *C*-Alkyl-*N*-Aryl-2-pyrazolino[60]fullerenes, the results were moderately better (7−44%), but this improvement is not remarkable compared to the yields obtained by thermally induced retrocycloadition; therefore, maleic anhydride does not play an important role in the retro-cycloaddition reaction, contrary to trends previously observed for other fullerene-fused derivatives like pyrrolidinofullerenes[9] and isoxazolinofullerenes.[10]

Considering the scarce influence of the presence of an excess of dipolarophile on the reaction outcome, we decided to introduce in our scheme a metal Lewis acid, in order to determine if a possible coordination with the nitrogen atoms could activate the retro-cycloaddition reaction. For this purpose, we carried out the same reactions in the presence of 1 equiv of copper triflate (Table 1, $CuTf_2$-24 h, and $CuTf_2$-48 h). The observed trend for *C*-Aryl-*N*-Aryl-2-pyrazolino[60]fullerenes (**2a**−**d**) was similar to that previously obtained with maleic anhydride, indicating the low reactivity of these compounds to undergo a retro-cycloaddition under these experimental conditions. *C*-Alkyl-*N*-Aryl-2-pyrazolino[60]fullerenes derivatives (**2e**,**f**) showed, in contrast, a remarkable improvement (28−48%) of retro-cycloaddition reaction, thus pointing out that copper triflate plays an important role in the process. Essays performed both in the presence of maleic anhydride (30 equiv) and copper triflate (1 equiv) gave the best results for *C*-Alkyl-*N*-Aryl-2-pyrazolino[60]fullerene **2e** (72%), demonstrating the suitability and broad scope of the methodology previously developed for pyrrolidinofullerenes[12] and isoxazolinofullerenes.[13] Interestingly, and in contrast to that observed for compound **2e**, the amount of pristine C_{60} resulting from the retro-cycloaddition process from **2f** was relatively low (18%), being completed after 24 h. Careful investigation of chromatograms for compounds **2e** and **2f** in the presence of copper triflate or copper triflate and maleic anhydride revealed the formation of additional extra peaks (16.5 min), thus accounting for the obtained low yield of pristine C_{60} (Figure 3). UV−vis spectroscopy, used as a detection system in our HPLC experiments, allowed us to record the UV−vis spectra of these new compounds which showed the typical absorption spectrum of a fullerene-based compound.[18] Further investigations are currently underway in order to determine the nature of these unexpected products which will shed light on and improve the understanding of these retro-cycloaddition reactions.

Microwave irradiation is a means of rapidly introducing energy into a chemical reaction and has shown to be particularly useful in those reactions requiring harsh conditions as high temperatures and long reaction times;[19] particularly interesting is the application of this source of energy in cycloaddition reactions[20] as well as in fullerene chemistry.[21] In order to test the chemical and thermal stability of *C*-Aryl-*N*-Aryl-2- pyrazolino-[60]fullerenes (**2a**−**d**), we carried out assays under microwave irradiation as the energy source instead of classical heating. For

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(18) Preliminary results for **2f** reveal the presence of a new fullerene derivative with loss of mass (M.S.: 911), this finding indicates the existence of an additional chemical process, thus completing the retro-cycloaddition reaction in a shorter time than that observed for 1,3-diaril-2-pyrazolines.

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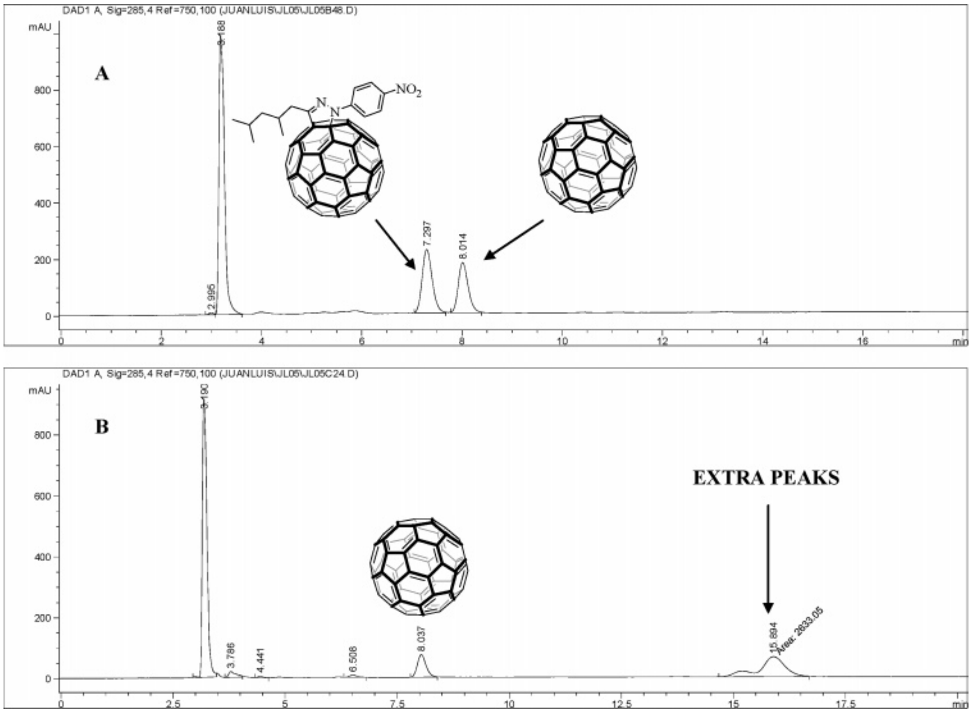

FIGURE 3. (A) Chromatogram of the thermal retrocycloaddition of **2f** in the presence of maleic anhydride (48 h). (B) Chromatogram of the reaction of **2f** with copper triflate (24 h).

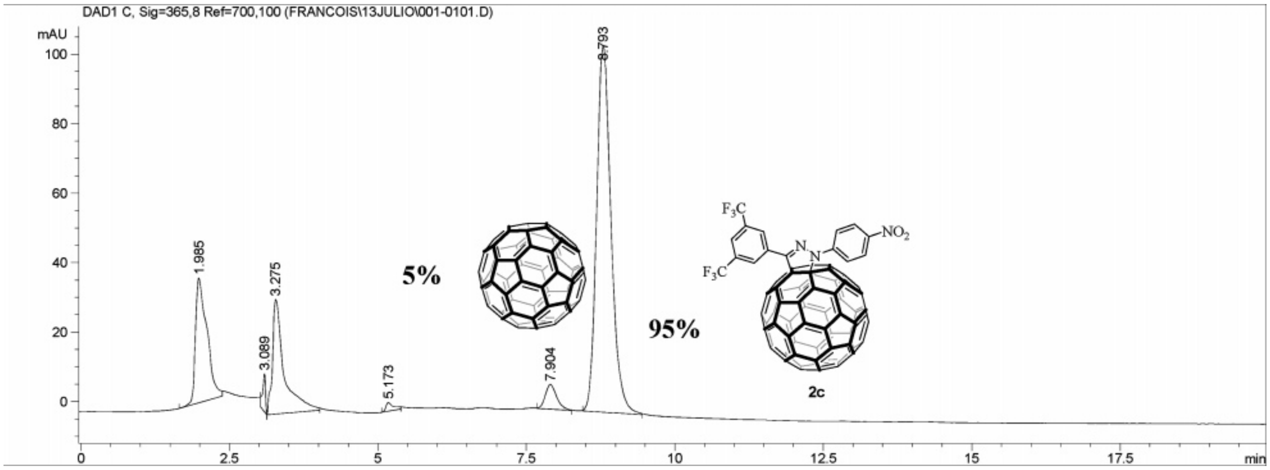

FIGURE 4. Chromatogram of the reaction of **2c** with MA and $CuTf_2$, in trichlorobenzene under pressure, after 12 h of microwave irradiation.

this purpose, we decided to use **2c**, which resulted in being the less susceptible molecule to undergo the retro-cycloaddition process by classical heating. Copper(II) triflate (1 equiv), maleic anhydride (30 equiv), and **2c** in *o*-DCB (20 mL) were irradiated during 12 h (4 cycles of 3 h) at 150 W under pressure (6 psi) with a temperature profile of 196 °C. A small amount of the solution was diluted and submitted to HPLC analysis. The results showed that the rate of retro-cycloaddition reaction is very similar (1.4%) to that observed by classical heating (1%). In an attempt to increase the strength of the conditions, we decided to use a higher boiling point solvent, 1,2,4-tricholorobenzene (temperature profile of 204 °C, pressure 7 psi). The chromatogram of this reaction (Figure 4) showed that, even after 12 h of irradiation at 200 W, only 5% of [60]fullerene was formed, indicating that these *C*-Aryl-*N*-Aryl-2-pyrazolino[60]fullerenes are highly stable fullerene derivatives under thermal conditions.

In summary, we have studied the thermal retro-cycloaddition reaction in a series of 2-pyrazolino[60]fullerene derivatives (**2a−f**). According to the experimental findings, *C*-Aryl-*N*-Aryl-2-pyrazolino[60]fullerenes (**2a−d**) do not undergo an efficient retro-cycloaddition process under a variety of experimental conditions, which reveals that these compounds are thermally stable fullerene derivatives. In contrast, the presence of an alkyl chain in the carbon atom of the pyrazole ring results in an easier cleavage of the 1,3 dipole, leading to pristine C_{60} in good yield (72%). However, in this case a new and additional reaction takes place affording unexpected fullerene derivatives. Work is currently in progress to determine the nature of these compounds. These results show the importance of the thermal stability in order to prepare new C_{60}-based materials as well as the strong impact that the nature of the substituents (alkyl or aryl) has on the thermal stability of the prepared cycloadducts, in particular in those devices such as photovolaic cells, where longer periods of time under sun light exposure results in a temperature increase of the photo- and electroactive materials.

Experimental Section

Chemical shifts in the NMR spectra are reported in ppm downfield from tetramethylsilane (TMS). FT-IR spectra were recorded as KBr pellets. Mass spectrometry experiments were realized using a MALDI-TOF technique, using dithranol [1,8-dihydroxy-9(10*H*)-anthracenone] as matrix.

Microwave irradiations were performed with a CEM Discover microwave oven, under pressure when indicated, equipped with a temperaure detection system through a optic fiber device and control of the irradiation power.

Compound 2d. 152 mg (0.21 mmol) of fullerene C_{60} were dissolved in 150 mL of toluene and stirred during 30 min at room temperature. (*E*)-1-(4-Methoxyphenyl)-2-(4-nitrobenzylidene)hydrazone was then added to the solution (143 mg, 0.53 mmol). Iodine (768 mg, 3.15 mmol) and, after 1 min, 0.16 mL (160 mg, 1.05 mmol) of DBU were then added. The reaction mixture was stirred overnight at room temperature, then filtrated over SiO_2 (filter was washed thoroughly with CH_2Cl_2), and evaporated. The residue was purified over column chromatography (SiO_2, eluent hexane/toluene 9/1 to eliminate the remaining C_{60}, then toluene).

Yield: 81 mg were obtained, 39%. Mp > 200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, $J = 8.4$ Hz, 2H), 8.35 (d, $J = 8.4$ Hz, 2H), 7.82 (d, $J = 8.4$ Hz, 2H), 7.04 (d, $J = 8.4$ Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 147.6, 147.4, 147.3, 146.4, 146.3, 146.0, 145.9, 145.8, 145.7, 145.5, 145.3, 145.2, 145.1, 144.9, 144.8, 144.3, 144.2, 143.2, 143.1, 142.9, 142.8, 142.4, 142.3, 142.2, 142.1, 141.8, 140.3, 140.1, 140.0, 139.1, 136.7, 136.1, 129.0, 128.7, 128.2, 126.9, 124.1, 114.7, 93.2, 80.2, 55.5. FT-IR (KBr): 2921, 2851, 2359, 1594, 1540, 1504, 1461, 1332, 1242, 1105, 1031, 960, 904, 880, 849, 829, 728, 689, 647 cm^{-1}. UV−vis λ (ϵ) 321 (68 200), 256 (235 200). MS *m/z* 989.0489 (M$^-$). Calculated for $C_{71}H_{11}N_3O_3$: 989.0800.

Compound 2f. 50 mg (0.18 mmol) of (*E*)-1-(*p*-nitrophenyl)-2-(3,5,5-trimethylhexylidene)hydrazone[22] were mixed with 48.2 mg (0.36 mmol) of *N*-chlorosuccinimide and 10 μL of pyridine (9.8 mg, 0.12 mmol). Chloroform was evaporated under reduced pressure, the residue disolved in toluene, and triethylamine in excess (2 mL, 14 mmol) and C_{60} (129 mg, 0.18 mmol) were added. The reaction was then stirred for 30 min, toluene was removed under reduced pressure, and the residue was purified by CC (toluene/hexane 1:1), while further purification of the solid was accomplished by washing and centrifugation with MeOH and pentane.

Yield: 43.8 mg (24%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, $J = 9.6$ Hz, 2H), 8.18 (d, $J = 9.2$ Hz, 2H), 3.16 (dd, $J = 6$ and 16 Hz, 1H), 3.02 (dd, $J = 8$ and 16 Hz, 1H), 2.55 (m, 1H), 1.66 (dd, $J = 3.6$ and 14 Hz, 1H), 1.40 (dd, $J = 6.6$ and 14 Hz, 1H), 1.36 (d, $J = 6.4$ Hz, 3H), 1.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 148.9, 147.7, 147.2, 146.5, 146.4, 146.3, 146.2, 146.1, 145.9, 145.4, 145.4, 145.3, 145.2, 145.1, 144.7, 144.7, 144.4, 144.1, 144.1, 143.6, 143.2, 142.9, 142.8, 142.4, 142.4, 142.4, 142.23, 142.3, 142.05, 142.00, 141.7, 141.0, 140.9, 139.3, 139.2, 136.98, 136.95, 136.0, 135.9, 129.0, 128.2, 125.5, 125.3, 118.5, 88.65, 84.0, 51.3, 39.1, 31.3, 30.2, 28.4, 23.1. MS *m/z* 995.1922 (M$^-$). Calculated for $C_{75}H_{21}N_3O_2$: 995.1634.

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Supporting Information Available: Characterization details for the new compounds described in this paper and a typical profile for microwave reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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