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Rapid microwave-assisted synthesis of *N*-benzyl fulleropyrrolidines under solvent free conditions

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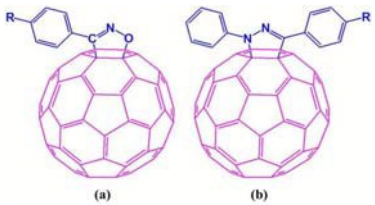
A series of new *N*-benzyl fulleropyrrolidines were synthesized in one-pot of C_{60} with the dibenzylamine and aldehyde derivatives using microwave irradiation under solvent-free conditions in good yield. This method provides several advantages involving high yields and rates, decrease of the extent of decomposition of the substrates as well as environmental friendliness compared to the conventional methods.

1. Introduction

Since the historic article of Kroto *et al.*[1] was reported, the chemistry of fullerene derivatives has become one of the most developing fields of organic chemistry because of their potential applications in many fields such as medicinal chemistry, material science and organic photovoltaics.[2] Extensive investigation on the chemical functionalization of fullerenes have been made for further research on their properties and applications involving varietal radical additions, nuclophilic additions, cycloadditions, and multiadditions.[3,4] Cycloaddition reaction of fullerene has been intensively disscussed because of the electron-withdrawing nature of each pyracyclene unit in fullerene which makes it an ideal dienophile and dipolarphile. 1,3-Dipolar cycloaddition reaction is one of the most effective and convenient methods for the synthesis of functionalized fullerenes.[5] Among the wide variety of synthesized organofullerene compounds, the family of fulleropyrrolidines has played a prominent role.[6] After Prato's method[7] for the preparation of these compounds from C_{60}, methyl glycine and formaldehyde, other various pathways were considered, intensively[8-10].

Microwave irradiation is a clean method for introducing energy into the reactions. This nonconventional energy source is able to improve reaction times and yields, and in some cases can lead to various results from those obtained with conventional methods.[11] Under these singular reaction conditions, dielectric properties, energy transfer, and penetration depth are completely different from those in conventional heating, so enhancement of the chemo-, regio- and stereoselectivity can be observed. The synthetic utility of microwave irradiation in organic synthesis has increased considerably in the recent years. This method can be considered as environmentally friendly, mainly because solvent-free reactions using solid supports are especially suited to microwave conditions.[12] Microwave technology has been successfully used to carry out difficult cycloadditions and to obtain temperature sensitive compounds, particularly interesting 1,3-dipolar cycloaddition. The effectiveness of microwave method in generating 1,3-dipoles *in situ* and in promotion of the subsequent cycloadditions[13] especially in combination with solvent free method[14a,14b] has been demonstrated. The combination of solvent-free conditions and microwave irradiation considerably reduced reaction time, enhanced yields and presented hopeful environmental advantages. In this regard, recently several worth researches have been considered for the synthesis of organic compounds. There are various advantages of performing synthesis in dry media such as short reaction times, increased safety and economic advantages due to the elimination of solvent. In addition, solvent free microwave methods are also clean and efficient. According to the previous literature, a number of organic reactions using microwaves in solvent free conditions reported by De la Hoz *et al.*[14a] and Font *et al.*[14b] in the context of synthesis of several heterocyclic compounds and fulleropyrrolidines, respectively. In fact, solvent free reactions under microwave irradiation confirmed more suitable and successful progresses such as short reaction times, high yields of products and eco-friendly nature.[14,17]

Recently during our studies on the application of various techniques in organic reactions, we have successfully demonstrated the synthesis of fullerene derivatives by 1,3-dipolar cycloaddition reactions. (Scheme 1)[13e, 15]

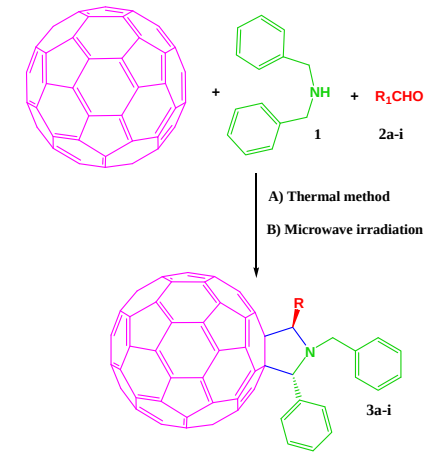


Scheme 1. The chemical structures of fulleroisoxazoline (a) and fulleropyrazoline (b)

In this context, the main aims of this research are demonstration of the synthetic utility of environmentally benign techniques (microwave irradiation and solvent-free conditions) in organic synthesis in order to illustrate the synergy between them and simplification of the experimental procedure for the preparation of *N*-benzyl fulleropyrrolidines. For these reasons we focused our attempt on developing a rapid, microwave-assisted 1,3-dipolar cycloaddition of dibenzylamine and aldehyde derivatives with C_{60}.

2. Results and discussion

In this research, cycloaddition reactions of C_{60}, dibenzylamine and substituted aldehydes under conventional conditions and microwave irradiation occurred to prepare the corresponding *N*-benzyl fulleropyrrolidines as described in Scheme 2.



R1: C_6H_5 **(2a)**, 4-$NO_2C_6H_4$ **(2b),** 4-$OCH_3C_6H_4$, **(2c)** 4-$N(CH_3)_2C_6H_4$ **(2d)**, 4-$CH_3C_6H_4$, **(2e)** 4-ClC_6H_4 **(2f)**, 2-pyridine **(2g),** 2-thiophen **(2h),** 2-furan **(2i)**

Scheme 2. Synthesis of *N*-benzyl fulleropyrrolidines under conventional method and microwave- promoted solvent free conditions.

In our study, synthesis of *N*-benzyl fulleropyrrolidines under solvent free microwave conditions is discussed as an efficient and green procedure to promote 1, 3-dipolar cycloaddition reactions with good yields and short reaction times. In our initial study, the effects and the amount of substrates, microwave irradiation power and time on the efficiency and yield were discussed in detail. First, the ratio of starting materials in one-pot three-component reaction was briefly investigated. Reaction of C_{60} with 1 equiv. of dibenzylamine and 1 equiv. of benzaldehyde took place gently in toluene under reflux condition for 6 h. The desired fulleropyrrolidine **3a** could be isolated by chromatography on silica gel with a comparatively moderate yield (entry 1, Table 1). As shown in Table 1, different ratio of starting material was examinated to increase the yields. When the amounts of dibenzylamine and benzaldehyde were reached up to 2 equiv., the yields of desired products were considerably increased (entry 2, Table 1). In the next step, when increasing the amount of dibenzylamine and benzaldehyde to 3 equiv, the yield of the reaction did not significantly change. However, by comparison, reaction of C_{60} with excess of dibenzylamine (5 equiv.) and benzaldehyde (4 equiv.) did not improve the yields drastically, whereas it caused to produce by-products and trouble in separation. The reaction conditions and results are presented in Table 1.

Table 1. Effect of substrate molar ratio on the synthesis of *N*-benzyl fulleropyrrolidine **3a** *via* conventional heating method

Entry	Dibenzylamine	Benzaldehyde	C_{60}	Yield (%)[a]
1	1	1	1	10
2	**2**	**2**	**1**	**51**
3	3	3	1	53
4	5	4	1	45

[a]isolated yields

For the examination of influence of green procedure in this reaction, it was investigated under promoted microwave solvent free conditions (powers 200 to 800 W). For convenience, the reaction of dibenzyamine, benzaldehyde **2a** and C_{60} was chosen as a model reaction. It was found that with a suitable molar ratio, microwave irradiation power and irradiation time could influence on the product yields. Various range of irradiation powers (200 to 800) were studied and the results were summarized in Table 2.

Table 2. Effects of microwave irradiation power on the reaction of benzaldehyde, dibenzylamine and C_{60}[a]

Entry	**Microwave power (W)**	**Time (min.)**	**Yield (%)[b]**
1	200	10	NR[c]
2	300	10	NR
3	400	10	NR
4	500	10	20
5	600	10	35
6	**700**	**10**	**63**
7	800	10	64

[a]Benzaldehyde : Dibenzylamine : C_{60} : 2 : 2 : 1.
[b]Isolated yields.
[C]No reaction.

As shown in Table 2, (entry 1-3) when the irradiation power was 200, 300 and 400 W, no reaction occurred within 10 minutes. However, the reaction could not progress and control well in the irradiation power of 800 W (Table 2, entry 7). Finally 700 W was selected as the accurate irradiation power. Then other various irradiation times was studied under 700 W. It was found with increasing the reaction time from 2-10 min, the yields were also increased (Table 3, entry 1–5). With increasing the irradiation time from 10-20 min, not only the product yields did not improve but also the amount of side products increased (Table 3, entry 6–7).

Table 3. Effects of microwave irradiation time on the reaction of benzaldehyde, dibenzylamine and C_{60}[a]

Entry	Microwave power (W)	Time (min.)	Yield (%)[b]
1	700	2	NR[c]
2	700	4	10
3	700	6	22
4	700	8	40
5	**700**	**10**	**63**
6	700	12	63
7	700	20	65

[a] Benzaldehyde : Dibenzylamine : C_{60} : 2 : 2 : 1.
[b] Isolated yields.
[C] No reaction.

Thus, all effective factors in the microwave-promoted reaction were optimized. After optimization of the conditions, we accomplished the reactions using different types of aldehyde derivatives under the same conditions. The desired *N*-substituted fulleropyrrolidines have been synthesized with *trans* stereochemistry similar to the reported research by Troshin *et al*.[16] Under microwave irradiation and solvent-free conditions, the new *N*-benzyl fulleropyrrolidines were obtained in good yields and the reaction results were summarized in Table 4.

Table 4. Synthesis of *N*-benzyl fulleropyrrolidines under conventional and microwave conditions

Entry	Aldehyde	Products	Time (h)[a]	Yields (%)[c]	Time (min)[b]	Yields (%)[c]
1	2a	3a	6	51	10	63
2	2b	3b	5	52	10	64
3	2c	3c	4	26	12	45
4	2d	3d	6	20	15	38
5	2e	3e	6	15	15	32
6	2f	3f	3	41	10	54
7	2g	3g	2	22	12	36
8	2h	3h	5	54	10	65
9	2i	3i	2	27	10	38

[a]Reflux time of toluene.
[b]Microwave irradiation time.
[C]Isolated yields.

By comparison with the conventional reaction, the same reaction occurred within 2-6 h at 110 ºC and afforded the desired *N*-benzyl fulleropyrrolidines in moderate yields. According to Table 4, it is clear that the reaction rates and yields were considerably increased in solvent free conditions under microwave irradiation without any significant amounts of undesirable side products. Under conventional conditions, long reaction times and high temperatures resulted in partial or total decomposition of substrates and products in the reaction mixture. These problems can be completely resolved by using microwave irradiation.[13a]

However, it is clear that microwave irradiation is an efficient, easy, green and appropriate technique for the constructing pyrrolidine cycle on fullerene through 1,3-dipolar cycloaddition reaction. Considering all the experiments, the results showed great acceleration, short reaction times and high yields under microwave irradiation compared to conventional conditions (Fig.1.).

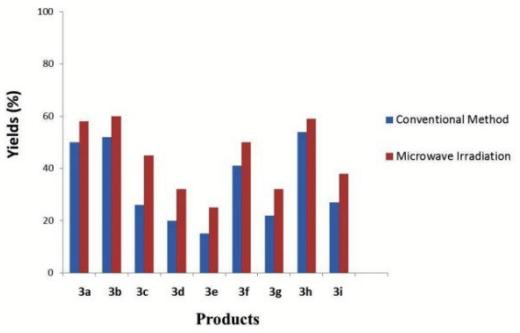
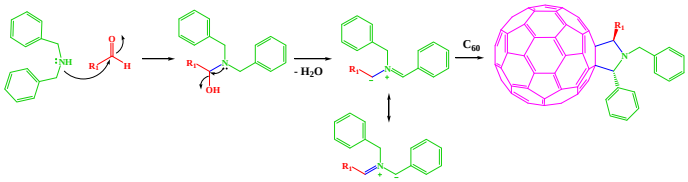


Fig. 1. Comparison of the isolated yields of the final products in Table 4

According to the previous literature about synthesis of *N*-alkylpyrrolidino[60]fullerenes[14b], various hetrocyclic compounds[13,14a] and the present data in Table 4 about the synthesis of *N*-benzyl fulleropyrrolidines, it is demonstrated that under microwave irradiation along with solvent free conditions, the times and yields of the reactions are surprisingly improved compared to the conventional methods. Thus application of microwave irradiation in combination with solvent free method[14] for improvement of the reactions is more efficient and convenient than that of conventional methods.

Avoiding solvent usage in the case of microwave technique, environmental contamination can be reduced in the synthesis process with appropriate improvement compared to solvent-based syntheses. In fact solvent-free condition is especially suitable for microwave activation and has several advantages including environmental safety, the economic viewpoint, high yields of the products and short reaction times.[14,17]

The Plausible mechanism for the synthesis of *N*-benzyl fulleropyrrolidines was proposed (Scheme 3). At first azomethine ylides as the key intermediates were generated *in situ* from dibenzylamine and aldehyde derivatives. Then the cycloadducts were prepared by 1,3-dipolar cycloadditions between these dipoles and fullerene. In all cases, under microwave irradiation excellent accelerations and great improvements in the yields and reaction conditions are observed. Under these conditions, azomethine ylides as very reactive chemical intermediates are produced very fast, thus facilitating 1,3-dipolar cycloadditions.



Scheme 3. Plausible mechanism for the synthesis of *N*-benzyl fulleropyrrolidines

The structures of isolated new products (**3a-i**) were identified by spectroscopic data such as: MS, ^{1}H NMR, ^{13}C NMR and FT-IR analyses. As the example (**3a**), in the IR spectra, the stretching

vibration of C-N in pyrrolidine cycle was appeared in the region between ν = 1000-1350 cm^{-1}. The stretching frequency of aromatic C=C is appeared in the region between m = 1450–1610 cm^{-1}. The stretching frequency of C–H in the aromatic cycles was assigned at m = 3024 cm^{-1} (Fig. 2).

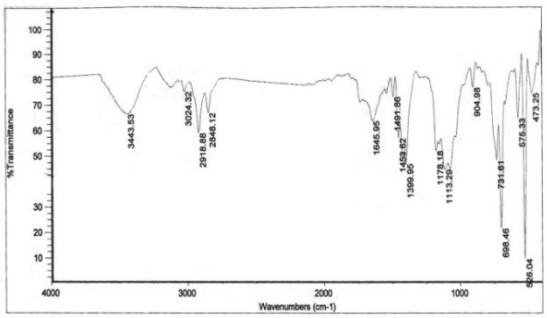


Fig. 2. IR spectrum of *N*-(benzyl)- 2,5-diphenyl- 3,4-fulleropyrrolidine (**3a**)

In the mass spectrum (EI, 70 eV), the peak at m/z 91 and 720 is related to benzyl and C_{60} ions, respectively. In the ^{1}H NMR spectra in $CDCl_3$-CS_2 was shown the two doublet signals around δ= 3.5-5.0 corresponding to CH_2 related to benzyl group. The signals about δ= 6.0 and δ= 7.0-8.2 are assigned by protons of CH of pyrrolidine and aromatic rings, respectively (Fig. 3).

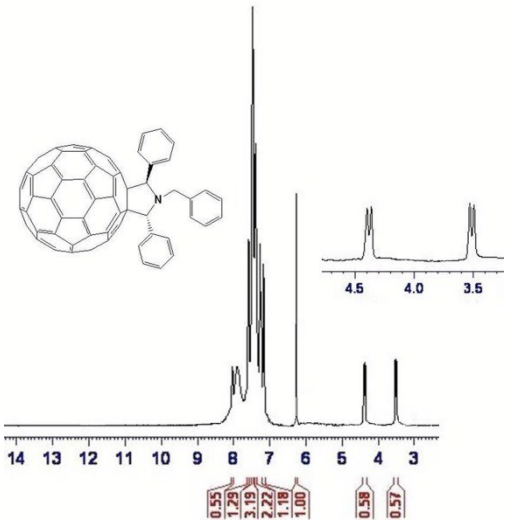


Fig. 3. ^{1}H NMR spectrum of N-(benzyl)- 2,5-diphenyl- 3,4-fulleropyrrolidine (**3a**)

In summary, under the thermal conditions or microwave irradiations, a series of new *N*-benzyl fulleropyrrolidines were synthesized *via* 1,3-dipolar cycloadditions of C_{60} with 1,3-dipoles derived in situ from corresponding dibenzylamine and aldehyde derivatives. Microwave irradiation in combination with solvent free conditions provides a convenient route to prepare C_{60}-derivatives bearing five-membered heterocycles with high yields and short reaction times.

3. Conclusions

The present study provides a simple, efficient and eco-friendly approach for the synthesis of *N*-benzyl fulleropyrrolidines in solvent free under microwave conditions. Compared with the conventional methods, this technique has main advantages including mild and clean reaction conditions, decrease of the extent of decomposition of the substrates and the products, high yields, enhanced reaction rates and environmental friendliness. Combination of microwave irradiation and solvent-free conditions establishes a method towards the green chemistry general concept.

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4. Experimental

4.1. Chemicals and Instruments

Crystalline C_{60} powder used in this work was over 99.5% purity from Aldrich. All solvents and chemical reagents were purchased from Aldrich and Fluka and used without further purification. The IR spectra were recorded on FT-IR Magna 550 apparatus using with KBr plates. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400 MHz spectrometers in the presence of tetramethylsilane as internal standard. EIMS (70 eV) was performed by Finnigan-MAT-8430 mass spectrometer in m/z. Microwave irradiation was carried out using a Litres Solo Microwave Oven ME3410W apparatus.

4.2. General procedure for the synthesis of *N*-benzyl fulleropyrrolidines under reflux conditions (Method A)

A mixture of C_{60} (36.0 mg, 0.05 mmol), dibenzyl amine (0.05 mmol), and aldehyde (0.05 mmol) were dissolved in 20 mL of toluene and refluxed under nitrogen atmosphere for the desired time. The course of the reaction was monitored by TLC with toluene as an eluent. At the end of reaction, the solvent was evaporated in vacuo, and the residue was separated on a silica gel column using toluene to afford cycloadducts.

4.3. General procedure for microwave-promoted for the synthesis of *N*-benzyl fulleropyrrolidines under microwave irradiation (Method B)

A mixture of C_{60} (36.0 mg, 0.05 mmol), dibenzyl amine (0.05 mmol), and aldehyde (0.05 mmol) were subjected to microwave irradiation (700 W) under ambient pressure for an optimized time listed in Table 3. The reaction was monitored by TLC. After irradiation, the mixture was cooled to room temperature and then dissolved in toluene-CS_2 (1:1 v/v) followed by filtration. After removal of the solvent, the product was further purified by column chromatography with toluene as an eluent to afford the *N*-benzyl

fulleropyrrolidine derivatives.

Representative spectral data for different cycloadducts reported in Table 4

***N*-(benzyl)- 2,5-diphenyl- 3,4-fulleropyrrolidine (3a):** Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$- CS_2): δ (ppm) 3.50 (d, 1H, CH), 4.39 (d, 1H, CH), 6.27 (s, 2H, CH), 7.17 (d, 2H, ArH), 7.40 (m, 4H, ArH), 7.47 (m, 6H, ArH), 7.59 (d, 2H, ArH), 8.03 (d, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$- CS_2): δ (ppm) 60, 88.21, 95.14, 105.18, 114.82, 127.27, 128.59, 128.64, 128.66, 128.70, 129.02, 129.08, 130.12, 130.26, 130.34, 130.48, 130.64, 135.88, 136.84, 136.92, 137.70, 137.78, 138.08, 138.54, 139.66, 140.11, 140.28, 141.74, 142.00, 142.11, 142.15, 144.58, 144.99, 145.15, 145.34, 145.53, 146.05, 146.25, 146.30, 146.31, 147.39, 154.02, 155.14, 155.83;. FT-IR (KBr): 3024, 2918, 1645, 1491, 1453, 1399, 1178, 1113, 731, 698, 526 cm^{-1}; MS (EI, 70 eV): m/z (%) = 1006 (M^+, 6), 720 (10), 285 (5), 91 (100), 77 (57)**.**

***N*-(benzyl)- 2- (4′ -nitrophenyl)- 5-phenyl- 3,4-fulleropyrrolidine (3b):** Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$- CS_2): δ (ppm) 4.2 (d, 1H, CH), 5.6 (d, 1H, CH), 5.9 (d, 1H, CH), 6.2 (d, 1H, CH), 7.40 (m, 10H, ArH), 8.51 (dd, 4H, ArH); FT-IR (KBr): 3100, 2921, 1707, 1601, 1522, 1454, 1400, 1344, 1105, 744, 699, 526 cm^{-1}; MS (EI, 70 eV): m/z (%) = 1050 (M^+, 4), 330 (5), 285 (5), 239 (5), 149 (9), 91 (92), 77 (32), 57 (100)**.**

***N*-(benzyl)- 2- (4′ -methoxyphenyl)- 5-phenyl- 3,4-fulleropyrrolidine (3c):** Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$- CS_2): δ (ppm) 3.6 (d, 1H, CH), 3.9 (s, 3H, OCH_3); 4.3 (d, 1H, CH), 5.30 (d, 1H, CH), 6.21 (d, 1H, CH), 6.99 (d, 2H, ArH), 7.15 (d, 1H, ArH), 7.25 (d, 1H, ArH), 7.38 (m, 4H, ArH), 7.50 (m, 4H, ArH), 7.60 (d, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$- CS_2): δ (ppm) 70.50, 88.19, 88.75, 102.87, 108.69, 113.39, 119.33, 128.28, 128.58, 128.92, 130.27, 132.37, 135.60, 138.13, 140.47, 144.58, 145.20, 151.30, 152.95, 153.70, 154.54, 155.18, 156.05, 157.13, 158.86, 159.52, 160.64, 161.13, 162.08 , FT-IR (KBr): 3127, 2918, 1607, 1507, 1425, 1246, 1178, 1106, 1033, 728, 699, 525 cm^{-1}; MS (EI, 70 eV): m/z (%) = 1035 (M^+, 2), 315 (5), 224 (12), 208 (10), 107 (10), 91 (100), 77 (30), 57 (60)**.**

***N*-(benzyl)- 2- (4′ -*N*,*N*-dimethylaminophenyl)- 5-phenyl- 3,4-fulleropyrrolidine (3d):** Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$- CS_2): δ (ppm); 3.04 (s, 6H, NMe_2), 3.31 (d, 1H, CH), 4.36 (d, 1H, CH), 5.25 (d, 1H, CH), 6.75 (d, 1H, CH), 6.91 (d, 1H, ArH), 7.06 (d, 2H, ArH), 7.35 (m, 3H, ArH), 7.44 (m, 3H, ArH), 7.61 (m, 3H, ArH), 8.19 (d, 1H, ArH), 8.31 (d, 1H, ArH), FT-IR (KBr): 3110, 2917, 1609, 1425, 1179, 1099, 900, 727, 574, 525 cm^{-1}; MS (EI, 70 eV): m/z (%) = 1048 (M^+, 5), 237 (10), 253 (5), 91 (100), 77 (40), 57 (72)**.**

***N*-(benzyl)- 2- (4′ -methylphenyl)- 5-phenyl- 3,4-fulleropyrrolidine (3e):** Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$- CS_2): δ (ppm) 7.60 (d, 2H, ArH), 7.46 (d, 2H, ArH), 7.39 (m, 7H, ArH), 7.17 (m, 3H, ArH), 6.24 (d, 1H, CH), 4.38 (d, 1H, CH), 4.23 (d, 1H, CH), 3.50 (d, 1H, CH), 2.42 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$- CS_2): δ (ppm) 35.14, 84.17, 86.48, 89.25, 91.42, 99.12, 100.32, 101.59, 102.23, 103.87, 106.63, 108.44, 109.89, 112.35, 114.77, 117.18, 120.09, 123.57, 127.05, 128.19, 128.31, 128.58, 129.40, 130.42, 132.13, 134.84, 135.25, 138.86, 141.72, 143.11, 144.51, 145.23, 146.24, 150.42, 153.20, 155.69, 158.40, 161.08, 162.17, 167.23; FT-IR (KBr): 3024, 2916, 1599, 1492, 1451, 1371, 1292, 1175, 1072, 1026, 732, 697, 574, 525 cm-1; MS (EI, 70 eV): m/z (%) = 1019 (M^+, 5), 208 (10), 91 (100), 77 (22), 57 (71), 52 (9)**.**

***N*-(benzyl)- 2- (4′ -chlorophenyl)- 5-phenyl- 3,4-fulleropyrrolidine (3f):** Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$- CS_2): δ (ppm); 3.50 (d, 1H, CH); 4.35 (d, 1H, CH), 4.81 (d, 1H, CH), 6.24 (d, 1H, CH), 7.40 (m, 3H, ArH), 7.07 (d, 1H, ArH), 7.18 (d, 2H, ArH), 7.47 (m, 4H, ArH), 7.57 (d, 2H, ArH), 7.84 (m, 2H, ArH), δ (ppm) 83.75, 87.22, 93.71, 101.02, 107.22, 109.85, 116.38, 117.55, 119.93, 128.01, 128.17, 128.26, 128.51, 128.59, 128.66, 128.69, 128.75, 129.06, 129.08, 129.46, 130.05, 130.42, 131.51, 131.65, 141.72, 142.11, 143.13, 143.19, 145.37, 145.52, 146.31; FT-IR (KBr): 3165, 2921, 1630, 1488, 1400, 1178, 729, 699, 525 cm^{-1}; MS (EI, 70 eV): m/z (%) = 1039 (M^+, 5), 319 (4), 228 (7), 111 (9), 91 (100), 77 (33)**.**

***N*-(benzyl)- 2- phenyl- 5- (2′ - pyrimidyl)- 3,4-fulleropyrrolidine (3g):** Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$- CS_2): δ (ppm) 3.59 (d, 1H, CH); 4.22 (d, 1H, CH), 4.40 (d, 1H, CH), 6.00 (d, 1H, CH), 7.46 (dd, 1H, ArH), 7.40 (m, 10H, ArH), 7.68 (d, 1H, ArH), 8.01 (d, 1H, ArH), 9.24 (d, 1H, ArH), FT-IR (KBr): 3100, 2916, 1631, 1425, 1179, 900, 726, 574, 524 cm^{-1}; MS (EI, 70 eV): m/z (%) = 1006 (M^+, 3), 285 (5), 193 (35), 192 (17), 91 (63), 78 (17), 77 (60), 57 (100)**.**

***N*-(benzyl)- 2- phenyl- 5- (2′ - thienyl)- 3,4-fulleropyrrolidine (3h):** Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$- CS_2): δ (ppm) 3.67 (d, 1H, CH), 4.41 (d, 1H, CH), 6.34 (s, 1H, CH), 6.44 (s, 1H, CH), 7.15 (dd, 3H, ArH), 7.22 (d, 2H, ArH), 7.37 (dd, 2H, ArH),7.46 (m, 3H, ArH), 7.53 (d, 1H, ArH), 7.62 (d, 2H, ArH), ^{13}C NMR (100 MHz, CDCl3- CS2): δ (ppm) 82.48, 90.85, 93.45, 94.29, 99.97, 101.60, 102.14, 103.59, 109.64, 117.23, 118.16, 119.47, 126.53, 126.58, 126.80, 127.83, 128.44, 128.54, 129.13, 129.45, 129.54, 129.89, 129.92, 130.22, 130.97, 131.57, 132.24, 136.14, 136.62, 138.31, 138.81, 140.08, 140.62, 141.32, 142.22, 142.78, 143.36, 143.80, 145.64, 145.86, 146.21, 146.44, 146.64, 146.73, 147.13, 147.44, 148.14, 148.32, 148.55, 149.92, 150.78, 151.33, 151.70, 152.77, 152.94, 153.31, 153.70, 154.19, 154.36, 155.40, 156.58, 157.27, 157.67, 157.95, 158.36, 158.77, 159.95, 161.09, 161.33, 161.95, 162.17, 164.15; FT-IR (KBr): 3120, 2916, 1634, 1491, 1425, 1178, 733, 697, 574, 525 cm^{-1}; MS (EI, 70 eV): m/z (%) = 1011 (M^+, 6), 213 (5), 200 (12), 91 (100), 83 (65), 77 (38), 57 (62)**.**

***N*-(benzyl)- 2- phenyl- 5- (2′ - furanoyl)- 3,4-fulleropyrrolidine (3i):** Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$- CS_2): δ (ppm) 7.89 (d, 1H, ArH), 7.81 (d, 2H, ArH), 7.66 (m, 4H, ArH), 7.45 (m, 3H, ArH), 7.27 (d, 1H, ArH), 7.17 (d, 2H, ArH), 6.51 (d, 1H, CH), 6.48 (d, 1H, CH), 4.39 (d, 1H, CH), 3.49 (d, 1H, CH); ^{13}C NMR (100 MHz, CDCl3- CS2): δ (ppm) 104.99, 105.93, 107.63, 110.65, 123.50, 124.90, 127.12, 128.31, 129.09, 133.44, 136.89, 140.33, 141.32, 141.58, 144.71, 146.10, 149.68, 157.70, 169.79; FT-IR (KBr): 3130, 2916, 1637, 1491, 1400, 1177, 1073, 729, 697, 574, 525 cm^{-1}; MS (EI, 70 eV): m/z (%) = 995 (M^+, 3), 275 (5), 208 (2), 184 (5), 91 (100), 83 (21), 77 (91), 67 (35)**.**

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