Regioselective ring-opening of epoxides by carbazole: a direct preparation of novel *N*-(β-hydroxyalkyl)carbazoles

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The influence of various parameters including solvent, base and temperature on the reaction between carbazole and epoxides was studied. This led to the development of a regioselective ring-opening of epoxides by the potassium salt of carbazole in DMSO at 100 °C which is a straightforward way to prepare new *N*-(β-hydroxyalkyl)carbazoles in good to excellent yields. Fifteen new compounds are described.

Keywords: carbazole, carbazole potasium salt, epoxide, *N*-alkylation, *N*-(β-hydroxyalkyl)carbazole

Introduction

Carbazole and its substituted derivatives have an undeniable role in human life science,[1] and are an important class of nitrogen-containing heterocyclic compounds widely found in nature mainly as naturally-occurring carbazole alkaloids.[2] In addition, naturally-occurring carbazole alkaloids as well as other synthetic carbazole derivatives are well known for exhibiting many types of pharmacological activity including anti-inflammatory, antibacterial, anti-tumour, anticonvulsant, antipsychotic, anti-diabetic, anti-malarial, anticancer, and anti-Alzheimer properties.[3] Also carbazole and its substituted derivatives have found widespread applications in various industries,[4] such as electroluminescent materials for fabrication of organic light emitting devices (OLEDs),[5] carbazole-based polymers for solid-state organic dye-sensitised solar cells,[6] in electrochemistry[7] and as pigments.[8]

Despite the importance of carbazole, however, this compound has rarely found an application in its parental form. The majority of carbazole scaffolds described above have diverse organic functionalities either on the aryl residues or the N-atom.[9] The functionalisation of the N-atom in carbazole and its derivatives is mostly achieved through C–N bond formation. To accomplish this, a very weakly basic N-atom of carbazole is activated to react with certain carbon electrophiles such as alkyl halides *via* S_N2-type reactions either under conventional[10] or microwave assisted[11] conditions, aryl halides using Cu-catalysed S_NAr-type reactions (Ullmann-type reactions) under microwave irradiation[12] and alcohols using Mitsunobu condition.[13] However, to the best of our knowledge, among the carbon electrophiles used to react with carbazole, no report has yet appeared for C–N bond formation *via* ring-opening of epoxides with carbazole.

Recently, the *N*-(3-phenylamino-2-hydroxypropyl) carbazole P7C3 and related analogues were reported as new neuroprotective and pro-neurogenic agents (Fig. 1).[14] In the search for new chemotherapeutic agents, having structural features resembling P7C3, and also in continuation of our interest in the design and synthesis of new β-adrenoceptor blocking agents[15–19] like carazolol,[20] herein we describe the regioselective ring-opening of epoxides with carbazole as a straightforward way to prepare new *N*-(β-hydroxyalkyl) carbazoles (Fig. 1).

Results and discussion

Our planned method of preparation of *N*-(β-hydroxyalkyl) carbazoles **3** was by heating a variety of epoxides **2** with carbazole **1** in a solvent in the presence of a base, as shown in Scheme 1.

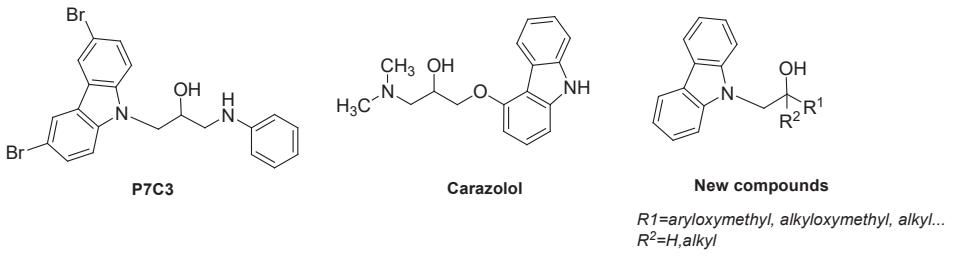
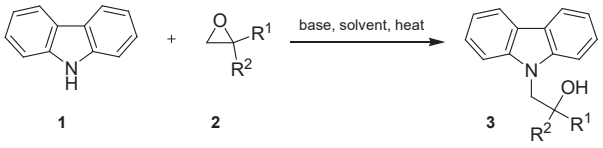


Fig. 1 The structure of P7C3, carazolol and general structure of synthesised compounds.



3a: R^1= $PhOCH_2$, R^2= H
3b: R^1= 4-MeO-$C_6H_4OCH_2$, R^2= H
3c: R^1= 4-Et-$C_6H_4OCH_2$, R^2= H
3d: R^1= 4-Me_2CH-$C_6H_4OCH_2$, R^2= H
3e: R^1= 3,4-Me_2-$C_6H_3OCH_2$, R^2= H
3f: R^1= 3-Me-4-Cl-$C_6H_3OCH_2$, R^2= H
3g: R^1= 4-Cl-$C_6H_4OCH_2$, R^2= H
3h: R^1= 2,4-Cl_2-$C_6H_3OCH_2$, R^2= H
3i: R^1= $BuOCH_2$, R^2= H
3j: R^1= Me_2CHOCH_2, R^2= H
3k: R^1= $MeC(=CH_2)CO_2CH_2$, R^2= H
3l: R^1= Me, R^2= H
3m: R^1= Et, R^2= H
3n: R^1= Me, R^2= Me
3o:

Scheme 1

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Table 1 Effects of various bases, temperature and duration of reaction on the yields of *N*-(2-hydroxycyclohexyl) carbazole **3o** prepared by reaction of carbazole **1** and cyclohexene oxide (Scheme 1)[a]

Entry	Solvent	Base	Temperature/°C	Time/h	Yield/%[b]
1	H_2O	KOH	Reflux	72	18
2	EtOH	KOH	Reflux	72	25
3	MeOH	KOH	Reflux	72	21
4	PEG200	KOH	100	72	27
5	DMF	KOH	100	15	46
6	DMSO	KOH	100	10	52
7	NMP	KOH	100	24	43
8	MeCN	KOH	Reflux	48	35
9	acetone	KOH	Reflux	48	12
10	THF	KOH	Reflux	48	28
11	Toluene	KOH	Reflux	36	NR[c]
12	DMSO	KOH	110	10	54
13	DMSO	KOH	120	9	56
14	DMSO	KOH	130	8	58
15	DMSO	KOH	140	8	60
16	DMSO	KOH	150	10	61
17	DMSO	–	100	72	NR
18	DMSO	Et_3N	100	24	30
19	DMSO	DBU	100	12	36
20	DMSO	DMAP	100	15	28
21	DMSO	DABCO	100	14	32
22	DMSO	K_2CO_3	100	11	45
23	DMSO	Cs_2CO_3	100	11	49
24	DMSO	MgO	100	48	10
25	DMSO	Basic Al_2O_3	100	48	14
26	DMF	NaH	100	14	65

[a]Reaction conditions: carbazole (0.01 mol), epoxide (0.015 mol), base (0.01 mol) and solvent (20 mL).
[b]Isolated yield.
[c]No reaction.

First we wished to establish the optimum conditions for the reaction. For this purpose, the reaction of carbazole **1** with cyclohexene oxide which affords **3o**, regioselectively, was selected as a test reaction. The influence of various parameters including solvent, base and temperature was evaluated. The results obtained are shown in Table 1. The choice of an appropriate solvent is of great importance for the efficient progress of the reaction, so we examined the effect of a variety of protic and aprotic solvents in the presence of KOH as a base (entries 1–11). In water, a low yield (18%) of **3o** was obtained after refluxing for 72 h. Other protic solvents were not much better (entries 2–4). However, applying polar aprotic solvents somewhat improved the yield (entries 5–10). DMSO gave the best result (52%) (entry 6) and it was assigned as the solvent of choice. With DMSO as the selected solvent, we tested the effect of various temperatures on the yield of the reaction (entries 6, 12–16). As can be seen, by increasing the temperature up to 150 °C, an improvement in yield was observed; however, the yields obtained were still moderate. As mentioned previously, the N-atom of carbazole is an extremely weak base and requires to be activated by an efficient base. In the absence of a base the reaction, unsurprisingly, could not be achieved at all (entry 17). We then screened the effect of some organic and inorganic bases at 100 °C, but none of them were very effective (entries 18–26), but using NaH as base was the most successful with a yield of 65%. The low yields obtained for products are attributed to the fact that the N–H bond of carbazole has a weakly acidic nature and thus exhibits low nucleophilic power at the N-atom.

Table 2 Effects of solvent and temperature on the yields of *N*-(2-hydroxycyclohexyl)carbazole **3o** prepared by reaction of the potassium salt of carbazole (**1**; **K** for **H**) and cyclohexene oxide (Scheme 1)[a]

Entry	Solvent	Temperature/°C	Time/h	Yield/%[b]
1	H_2O	Reflux	48	62
2	DMF	100	10	83
3	DMSO	100	7	91
4	NMP	100	14	75
5	MeCN	Reflux	36	47
6	Acetone	Reflux	48	34
7	[bmim][BF_4]	100	24	51
8	[bmim][Br]	100	24	55
9	TBAC	100	24	42
10	THF	Reflux	36	42
11	Toluene	Reflux	48	NR[c]
12	DMSO	r.t.	72	10
13	DMSO	50	48	26
14	DMSO	80	18	56
15	DMSO	90	12	86
16	DMSO	110	7	91
17	DMSO	130	7	92
18	DMSO	150	6	92

[a]Reaction conditions: Potassium carbazol-9-ide (0.01 mol), epoxide (0.015 mol) and solvent (20 mL).
[b]Isolated yield.
[c]No reaction.

To enhance the reaction yield, we then changed the procedure and used the potassium salt of carbazole instead of a carbazole-base combination in the reaction. We decided to pre-prepare the potassium salt of carbazole by dissolving carbazole in a refluxing ethanolic solution of KOH followed by evaporation of solvent and recrystallisation from hot MeOH. Having prepared the potassium salt of carbazole (**1**; **K** for **H**), we investigated the effect of solvent and temperature on the ring-opening of cyclohexene oxide with the potassium salt of carbazole (Table 2). As can be seen among the studied solvents (entries 1–11), DMSO was the best solvent for progress of reaction giving a yield of 91%. Thus, DMSO was selected for all subsequent reactions (entry 3). Because of the ionic nature of the potassium salt of carbazole, we also examined the influence of some ionic liquids[21] as solvents on the sample reaction but contrary to our expectations no superiority over traditional organic solvents was observed (entries 7–9). Other solvents used in this experiment afforded **3o** in low to moderate yields, and the use of toluene failed to generate **3o** (entry 11).

We then investigated the influence of temperature on the sample reaction (entries 3, 12–18). Performing the reaction at room temperature resulted in a low yield of **3o** even if the reaction time was prolonged. An incremental rise in temperature improved the reaction yields up to 100 °C, but no improvement in yield was seen between 100–150 °C.

Having obtained the optimised reaction conditions, the generality and the scope of this method was investigated by applying the optimised reaction conditions to a variety of structurally diverse epoxides (Table 3).

As shown in Table 3, 14 terminal epoxides containing alkyl, alkoxy and aryloxy substituents were used to prepare the corresponding *N*-(β-hydroxyalkyl)carbazoles **3a**–**n** in yields of 75–91%. In all reactions, the ring-openings of epoxides were achieved regioselectively, the result of nucleophilic carbazole

Table 3 Yields and duration of reaction for the preparation of *N*-(β-hydroxyalkyl)carbazoles **3a–o** by reaction of the potassium salt of carbazole (**1**; **K** for **H**) with various epoxides **1a–n** (Scheme 1)[a]

Entry	Product[b]	Time/h	Yield/%[c]
1	**3a**	12	87
2	**3b**	13	90
3	**3c**	15	89
4	**3d**	15	85
5	**3e**	14	87
6	**3f**	15	84
7	**3g**	13	86
8	**3h**	14	83
9	**3i**	9	92
10	**3j**	9	90
11	**3k**	8	75
12	**3l**	8	81
13	**3m**	7	89
14	**3n**	7	88
15	**3o**	7	91

[a]Reaction conditions: Potassium carbazol-9-ide (0.01 mol), epoxide (0.015 mol) and DMSO (20 mL) at 100 °C.

[b]All products were characterised by ^{1}H NMR and ^{13}C NMR, IR, CHN, and MS analysis.

[c]Isolated yield.

anion attacks predominantly at the less hindered side. Indeed, in some cases, small amounts of isomers were also obtained as indicated by GC-analysis (< 5–9%). All the reactions were completed in 7–15 as indicated by a TLC check. The reaction of the potassium salt of carbazole with 2-aryloxymethyl-oxiranes is interesting since the obtained products **3a–h** have a close resemblance to a general structure known to be present in β-adrenoceptor blocking agents (*i.e.* $R^1R^2NCH_2CH(OH)CH_2OAr$).[22]

The biological activities of the title compounds are currently under investigation and will be reported in due course.

Experimental

All chemical reagents were purchased from Merck, Fluka or Sigma-Aldrich companies. The aryloxy glycidyl ethers were either purchased or synthesised *via* coupling of appropriate phenols and epibromohydrin according to the reported procedure.[23,24] Solvents were purified by standard procedures, and stored over 3Å molecular sieves. Reactions were followed by TLC using SILG/UV 254 silica-gel plates. Column chromatography was performed on silica gel 60 (0.063–0.200 mm, 70–230 mesh; ASTM). Melting points were determined using an Electrothermal IA 9000 melting point apparatus in open capillary tubes and are uncorrected. IR spectra were obtained using a Shimadzu FTIR-8300 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Brüker Avance-DPX-250 spectrometer operating at 250 and 62.5 MHz, respectively. Chemical shifts are given in δ relative to tetramethylsilane (TMS) as an internal standard, coupling constants *J* are given in Hz. Abbreviations used for ^{1}H NMR signals are: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. GC/MS was performed on a Shimadzu GC/MS-QP 1000-EX apparatus (m/z; rel.%). Elemental analyses were performed on a Perkin–Elmer 240-B micro-analyser.

Synthesis of potassium carbazol-9-ide (**1**; **K** *for* **H**)*; general procedure*

In a round-bottomed flask (100 mL), a mixture of 9*H*-carbazole (1.67 g, 0.01 mol) and KOH (0.67 g, 0.012 mol) in EtOH (40 mL) was heated at reflux for 4 h (TLC control). The solvent was then evaporated and dried to afford crude carbazole potassium salt (**1**; **K** for **H**), which was recrystallised from hot methanol (50 mL) to give a bright yellow-brown solid (1.95 g, 95%). An alternative method for preparation of carbazole potassium salt was also reported in which 9*H*-carbazole and KOH was heated in xylene.[25]

Synthesis of aryloxy glycidyl ethers (**2c–f** *and* **2h**)*; general procedure*

In a round-bottomed flask (100 mL), a mixture of the appropriate phenol (0.01 mol), epibromohydrin (2.05 g, 0.015 mol) and K_2CO_3 (1.38 g, 0.01 mol) in anhydrous MeCN (40 mL) was heated at reflux for 12–24 h (TLC control). After completion of the reaction, the solvent was evaporated *in vacuo*. The foam obtained was dissolved in $CHCl_3$ (100 mL) and subsequently washed with water (2 × 100 mL). The organic layer was dried over anhydrous sodium sulphate and evaporated. The crude aryloxy glycidyl ether was purified by short-column chromatography on silica gel eluting with *n*-hexane.

Synthesis of **3a–o***; general procedure*

In a round bottom flask (50 mL), a mixture of potassium carbazol-9-ide (0.01 mol) and the appropriate epoxide (0.015 mol) in DMSO (20 mL) was heated at 100 °C until TLC monitoring indicated no further improvement in the reaction (7–15 h). After completion of the reaction, the solvent was evaporated *in vacuo*. The foam obtained was dissolved in $CHCl_3$ (100 mL) and subsequently washed with water (2 × 100 mL). The organic layer was dried over anhydrous sodium sulphate and evaporated. The crude product was purified by short-column chromatography on silica gel eluting with *n*-hexane:EtOAc.

*1-(9*H*-Carbazol-9-yl)-3-phenoxypropan-2-ol* **3a**: Yellow oil (87%); IR (ν_{max}): 3375, 3049, 2969, 1455, 1297, 1210 cm^{-1}; ^{1}H NMR: δ 3.79–3.82 (m, 1H, C*H*OH), 3.99 (s, 1H, OH, exchangeable with D_2O), 4.20–4.24 (m, 2H, NCH_2), 4.40–4.46 (m, 2H, OCH_2), 6.78–6.84 (m, 2H, aryl), 7.18–7.49 (m, 11H, aryl); ^{13}C NMR: δ 56.8, 65.1, 71.6, 112.0, 116.2, 117.9, 118.2, 119.8, 120.9, 121.7, 129.8, 132.4, 159.5; MS (EI) m/z (%): 317 (23.7) (M^+); Anal. calcd for: $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41; found: C, 79.40; H, 6.12; N, 4.56%.

*1-(9*H*-Carbazol-9-yl)-3-(4-methoxyphenoxy)propan-2-ol* **3b**: White prisms (90%); m.p. 85–87 °C; IR (ν_{max}): 3370, 3068, 2940, 1474, 1269, 1218 cm^{-1}; ^{1}H NMR: δ 2.16 (s, 3H, OCH_3), 3.95 (dd, *J* = 4.9, 11.2 Hz, 2H, NCH_2), 4.18 (s, 1H, OH, exchangeable with D_2O), 4.37–4.41 (m, 3H, OCH_2, C*H*OH), 6.79–6.85 (m, 4H, aryl), 7.20–7.24 (m, 6H, aryl), 7.46–7.51 (m, 2H, aryl); ^{13}C NMR: δ 57.5, 59.4, 65.0, 71.9, 112.0, 115.8, 117.0, 118.7, 120.2, 121.8, 124.1, 133.0, 151.5, 158.6; MS (EI) m/z (%): 347 (11.3) (M^+); Anal. calcd for: $C_{22}H_{21}NO_3$: C, 76.06; H, 6.09; N, 4.03; found: C, 75.94; H, 6.17; N, 3.90%.

*1-(9*H*-Carbazol-9-yl)-3-(4-ethylphenoxy)propan-2-ol* **3c**: White prisms (89%); m.p. 89–91 °C; IR (ν_{max}): 3400, 3077, 2965, 1485, 1273, 1230 cm^{-1}; ^{1}H NMR: δ 1.43 (t, *J* = 7.3 Hz, 3H, CH_3), 2.60 (q, *J* = 7.3 Hz, 2H, CH_2CH_3), 3.92–3.97 (m, 3H, NCH_2CH), 4.17 (s, 1H, OH, exchangeable with D_2O), 4.52–4.61 (m, 2H, OCH_2), 6.95 (d, *J* = 8.0 Hz, 2H, aryl), 7.38–7.46 (m, 10H, aryl); ^{13}C NMR: δ 16.0, 34.1, 59.7, 65.8, 71.9, 112.8, 117.5, 119.8, 120.6, 122.0, 123.9, 129.1, 130.9, 131.6, 152.0; MS (EI) m/z (%): 345 (22.9) (M^+); Anal. calcd for: $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71; N, 4.05; found: C, 80.06; H, 6.80; N, 3.94%.

*1-(9*H*-Carbazol-9-yl)-3-(4-isopropylphenoxy)propan-2-ol* **3d**: White cubes (85%); m.p. 64–66 °C; IR (ν_{max}): 3340, 3025, 2990, 1468, 1280, 1209 cm^{-1}; ^{1}H NMR: δ 1.64 (d, *J* = 7.5 Hz, 6H, $2CH_3$), 2.98–3.05 (m, 1H, $CH(CH_3)_2$), 3.91–3.95 (m, 2H, NCH_2), 4.13 (s, 1H, OH, exchangeable with D_2O), 4.45–4.52 (m, 3H, OCH_2CH), 6.98–7.09 (m, 4H, aryl), 7.26–7.47 (m, 8H, aryl); ^{13}C NMR: δ 23.9, 37.0, 59.7, 65.6, 71.5, 112.4, 117.8, 119.0, 120.7, 122.0, 124.1, 129.0, 131.0, 132.7, 153.9; MS (EI) m/z (%): 359 (9.4) (M^+); Anal. calcd for: $C_{24}H_{25}NO_2$: C, 80.19; H, 7.01; N, 3.90; found: C, 80.26; H, 7.09; N, 3.95%.

*1-(9*H*-Carbazol-9-yl)-3-(3,4-dimethylphenoxy)propan-2-ol* **3e**: White needles (87%); m.p. 83–85 °C; IR (ν_{max}): 3425, 3041, 2938, 1467, 1289, 1251 cm^{-1}; ^{1}H NMR: δ 2.29 (s, 3H, CH_3), 3.04 (s, 3H, CH_3), 3.68–3.77 (m, 3H, NCH_2CH), 4.01 (s, 1H, OH, exchangeable with D_2O), 4.16 (dd, *J* = 6.9, 13.5 Hz, 1H, OCH_AH_B), 4.43 (dd, *J* = 3.1, 13.5 Hz, 1H, OCH_AH_B), 6.78–6.85 (m, 4H, aryl), 6.98–7.12 (m, 7H, aryl); ^{13}C NMR: δ 24.1, 25.0, 59.3, 65.0, 72.3, 111.9, 112.7, 116.9, 118.7, 119.3, 120.9, 123.0, 129.8, 131.2, 132.9, 138.0, 159.1; MS (EI) m/z (%): 345 (15.7) (M^+); Anal. calcd for: $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71; N, 4.05; found: C, 80.04; H, 6.79; N, 3.92%.

1-(9H-Carbazol-9-yl)-3-(4-chloro-3-methylphenoxy)propan-2-ol **3f**: Yellow oil (84%); IR (ν_{max}): 3364, 3100, 2950, 1469, 1304, 1227, 758 cm^{-1}; ^1H NMR: δ 2.37 (s, 3H, CH_3), 3.98–4.03 (m, 2H, NCH_2), 4.29 (s, 1H, OH, exchangeable with D_2O), 4.56–4.70 (m, 3H, OCH_2, C*H*OH), 6.80–6.85 (m, 3H, aryl), 7.18–7.43 (m, 8H, aryl); ^{13}C NMR: δ 21.9, 59.4, 65.0, 71.2, 112.0, 113.9, 118.1, 119.5, 120.3, 121.9, 122.3, 126.7, 130.9, 132.0, 138.1, 158.3; MS (EI) m/z (%): 365 (16.6) (M^+); Anal. calcd for: $C_{22}H_{20}ClNO_2$: C, 72.22; H, 5.51; N, 3.83; found: C, 72.35; H, 5.65; N, 3.89%.

1-(9H-Carbazol-9-yl)-3-(4-chlorophenoxy)propan-2-ol **3g**: Yellow oil (86%); IR (ν_{max}): 3395, 3050, 2977, 1483, 1275, 1213, 760 cm^{-1}; ^1H NMR: δ 3.47 (d, *J* = 6.8 Hz, 1H, NCH_AH_B), 3.70 (s, 1H, OH, exchangeable with D_2O), 3.82 (d, *J* = 6.8 Hz, 1H, NCH_AH_B), 4.09 (dd, *J* = 6.4, 16.2 Hz, 2H, OCH_2), 4.28–4.33 (m, 1H, C*H*OH), 6.52–6.61 (m, 4H, aryl), 7.05–7.25 (m, 8H, aryl); ^{13}C NMR: δ 58.8, 64.9, 73.0, 112.7, 117.0, 118.2, 119.6, 121.9, 123.2, 127.1, 130.5, 132.9, 159.1; MS (EI) m/z (%): 351 (18.9) (M^+); Anal. calcd for: $C_{21}H_{18}ClNO_2$: C, 71.69; H, 5.16; N, 3.98, found: C, 71.58; H, 5.23; N, 4.06%.

1-(9H-Carbazol-9-yl)-3-(2,4-dichlorophenoxy)propan-2-ol **3h**: White prisms (83%); m.p. 113–115 °C; IR (ν_{max}): 3412, 3100, 2985, 1462, 1309, 1226, 820, 750 cm^{-1}; ^1H NMR: δ 3.62 (s, 1H, OH, exchangeable with D_2O), 3.94–3.97 (m, 2H, NCH_2), 4.17–4.31 (m, 3H, OCH_2CH), 6.67–7.29 (m, 9H, aryl), 7.90 (d, *J* = 8.1 Hz, 2H, aryl); ^{13}C NMR: δ 57.9, 63.8, 71.3, 113.0, 118.1, 119.6, 120.5, 121.9, 122.4, 124.0, 127.9, 129.1, 131.9, 133.5, 152.7; MS (EI) m/z (%): 385 (21.6) (M^+); Anal. calcd for: $C_{21}H_{17}Cl_2NO_2$: C, 65.30; H, 4.44; N, 3.63; found: C, 65.19; H, 4.51; N, 3.67%.

1-Butoxy-3-(9H-carbazol-9-yl)propan-2-ol **3i**: White needles (92%); m.p. 111–113 °C; IR (ν_{max}): 3350, 3100, 2985, 1473, 1295, 1217 cm^{-1}; ^1H NMR: δ 0.93 (t, *J* = 7.5 Hz, 3H, CH_3), 1.34–1.41 (m, 2H, CH_2CH_3), 1.54–1.59 (m, 2H, OCH_2CH_2), 2.54 (s, 1H, OH, exchangeable with D_2O), 3.25–3.40 (m, 4H, CH_2OCH_2), 4.20–4.22 (m, 1H, C*H*OH), 4.33–4.40 (m, 2H, NCH_2), 7.18–7.24 (m, 2H, aryl), 7.43–7.48 (m, 4H, aryl), 8.04 (d, *J* = 7.8 Hz, 2H, aryl); ^{13}C NMR: δ 13.9, 20.8, 33.7, 59.0, 64.1, 72.9, 75.4, 112.5, 119.1, 120.9, 121.6, 122.3, 132.4; MS (EI) m/z (%): 297 (20.1) (M^+); Anal. calcd for: $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80; N, 4.71; found: C, 76.61; H, 7.73; N, 4.79%.

1-(9H-Carbazol-9-yl)-3-isopropoxypropan-2-ol **3j**: Yellow oil (90%); IR (ν_{max}): 3400, 3050, 2956, 1479, 1297, 1225 cm^{-1}; ^1H NMR: δ 0.94 (d, *J* = 7.3 Hz, 6H, $2CH_3$), 3.15 (dd, *J* = 4.1, 10.5 Hz, 2H, OCH_2), 3.32–3.37 (m, 1H, $CH(CH_3)_2$), 3.49–3.54 (m, 1H, C*H*OH), 3.79 (s, 1H, OH, exchangeable with D_2O), 4.12 (dd, *J* = 6.5, 12.7 Hz, 1H, NCH_AH_B), 4.46 (dd, *J* = 3.4, 13.8 Hz, 1H, NCH_AH_B), 7.20–7.27 (m, 4H, aryl), 7.45–7.56 (m, 4H, aryl); ^{13}C NMR: δ 24.1, 59.7, 65.6, 68.0, 74.1, 112.8, 118.6, 119.8, 121.0, 122.9, 133.5; MS (EI) m/z (%): 283 (18.2) (M^+); Anal. calcd for: $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47; N, 4.94; found: C, 76.37; H, 7.40; N, 5.02%.

3-(9H-Carbazol-9-yl)-2-hydroxypropyl methacrylate **3k**: Green prisms (75%); m.p. 114–116 °C; IR (ν_{max}): 3370, 3100, 2982, 1740, 1459, 1310, 1240 cm^{-1}; ^1H NMR: δ 2.68 (s, 3H, CH_3), 3.31–3.39 (m, 3H, NCH_2CH), 3.86 (s, 1H, OH, exchangeable with D_2O), 4.05 (dd, *J* = 6.8, 13.5 Hz, 1H, OCH_AH_B), 4.56 (dd, *J* = 3.4, 13.6 Hz, 1H, OCH_AH_B), 4.91 (s, 1H, $=CH_AH_B$), 5.27 (s, 1H, $=CH_AH_B$), 7.26–7.34 (m, 2H, aryl), 7.50–7.58 (m, 2H, aryl), 7.83–7.89 (d, *J* = 8.0 Hz, 2H, aryl), 8.21 (d, *J* = 8.0 Hz, 2H, aryl); ^{13}C NMR: δ 20.6, 59.8, 65.3, 70.1, 111.8, 118.6, 119.9, 120.7, 122.9, 124.2, 133.7, 137.1, 170.2; MS (EI) m/z (%): 309 (16.9) (M^+); Anal. calcd for: $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53; found: C, 73.85; H, 6.12; N, 4.67%.

1-(9H-Carbazol-9-yl)propan-2-ol **3l**: Creamy needle crystals (81%); m.p. 103–105 °C; IR (ν_{max}): 3410, 3020, 2946, 1460, 1315 cm^{-1}; ^1H NMR: δ 1.21–1.31 (m, 3H, CH_3), 2.44 (s, 1H, OH, exchangeable with D_2O), 4.31–4.40 (m, 2H, NCH_2), 4.69–4.77 (m, 1H, C*H*OH), 7.22–7.28 (m, 4H, aryl), 7.47–7.49 (m, 4H, aryl); ^{13}C NMR: δ 25.8, 65.0, 68.9, 112.0, 118.3, 119.1, 120.9, 123.1, 132.8; MS (EI) m/z (%): 225 (12.5) (M^+); Anal. calcd for: $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22; found: C, 80.05; H, 7.78; N, 6.34%.

1-(9H-Carbazol-9-yl)butan-2-ol **3m**: White prisms (89%); m.p. 113–115 °C; IR (ν_{max}): 3400, 3087, 2938, 1450, 1284 cm^{-1}; ^1H NMR: δ 0.91 (t, *J* = 7.4 Hz, 3H, CH_3), 1.41–1.45 (m, 2H, CH_2CH_3), 3.01 (s, 1H, OH, exchangeable with D_2O), 3.62–3.65 (m, 1H, C*H*OH), 3.89–3.96 (m, 1H, NCH_AH_B), 4.15 (dd, *J* = 2.9, 12.8 Hz, 1H, NCH_AH_B), 7.28–7.50 (m, 8H, aryl); ^{13}C NMR: δ 9.8, 28.5, 63.7, 72.0, 112.3, 119.8, 121.4, 122.1, 123.9, 132.7; MS (EI) m/z (%): 239 (18.9) (M^+); Anal. calcd for: $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85; found: C, 80.35; H, 7.24; N, 5.93%.

1-(9H-Carbazol-9-yl)-2-methylpropan-2-ol **3n**: White cubes (88%); m.p. 107–109 °C; IR (ν_{max}): 3510, 3074, 2953, 1480, 1289, 1250 cm^{-1}; ^1H NMR: δ 0.95 (s, 6H, $2CH_3$), 2.94 (s, 1H, OH, exchangeable with D_2O), 3.81 (s, 2H, NCH_2), 7.18–7.24 (m, 4H, aryl), 7.40–7.48 (m, 4H, aryl); ^{13}C NMR: δ 27.1, 66.2, 70.8, 112.6, 118.5, 120.3, 121.9, 122.8, 132.6; MS (EI) m/z (%): 239 (15.3) (M^+); Anal. calcd for: $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85; found: C, 80.43; H, 7.25; N, 5.80%.

2-(9H-Carbazol-9-yl)cyclohexanol **3o**: Yellow oil (91%); IR (ν_{max}): 3389, 3065, 2948, 1471, 1302 cm^{-1}; ^1H NMR: δ 1.31–1.37 (m, 4H, $2CH_2$), 1.69–1.78 (m, 4H, $2CH_2$), 2.97 (s, 1H, OH, exchangeable with D_2O), 3.82–3.90 (m, 2H, NC*H*C*H*OH), 7.26–7.54 (m, 8H, aryl); ^{13}C NMR: δ 21.9, 25.2, 28.0, 32.9, 59.9, 70.1, 112.9, 118.6, 120.3, 121.4, 123.7, 132.8; MS (EI) m/z (%): 265 (19.8) (M^+); Anal. calcd for: $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28; found: C, 81.58; H, 7.14; N, 5.37%.

The authors wish to thank Shiraz University of Technology research council for partial support of this work.

Received 29 November 2015; accepted 29 December 2015
Paper 1503745 doi: 10.3184/174751916X14538054606043
Published online: 8 February 2016

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