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^{1}H and ^{13}C NMR spectral assignments of some novel 2,4,6,8-tetraaryl-3,7-diazabicyclo[3.3.1]nonan-9-one derivatives

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The ^{1}H and ^{13}C NMR spectra of 2,4,6,8-tetraaryl-3,7-diazabicyclo[3.3.1]nonan-9-ones (1–2), oximes (3–8) and *O*-benzyl oximes (9–12) were recorded. The chemical shifts were unambiguously assigned using 1D and 2D NMR spectral data. The results clearly indicate that the compounds exist in chair-boat conformation with equatorial and axial orientation of the aryl groups in the chair and boat forms, respectively. Since the molecules are flexible and dynamic in solution, the chair and boat forms are mutually interconvertible. In 3–12, because of the effect of oximation/oximination, all the protons in the heterobicyclic systems gave distinct signals except the benzylic protons of the boat form. In all synthesized compounds, the aryl group protons at C-6,8 are shielded by the aryl groups at C-2,4 and therefore appear in the lower frequency region than the aryl groups at C-2,4.

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Keywords: NMR; ^{1}H NMR; ^{13}C NMR; 2D NMR; bispidines; diazabicyclo[3.3.1]nonan-9-ones; oximes; *O*-benzyloximes

Introduction

In recent years, bispidines have attracted increased attention owing to their aesthetically pleasing crystal structures, stereochemistry, intramolecular interactions, formation from 1,3-diaza adamantanes and conversion to diazaadamantanes.[1–4] The synthesis and stereochemistry of 3,7-diazabicyclo[3.3.1]nonane-9-ones[5–7] and their derivatives are of much interest because of their diverse biological activities,[8–10] such as antibacterial, antifungal, antiarrhythmic, antiphologistic, antithrombic, calcium antagonistic, hypotensive and neuroleptic, and also because of their presence in naturally occurring lupin alkaloids.[11–14]

In continuation with our earlier work on the NMR spectral studies of some mono heterocycles,[15,16] herein we report NMR spectral studies of a few new 2,4,6,8-tetraaryl-3,7-diazabicyclo[3.3.1]nonan-9-ones (**1–2**), novel 2,4,6,8-tetraaryl-3,7-diazabicyclo[3.3.1]nonan-9-one oximes (**3–8**) and *O*-benzyloximes (**9–12**) (Scheme 1) synthesized in our laboratory. The assignments and stereochemistry were established on the basis of 1D and 2D NMR spectroscopic techniques and from literature evidences.[6,7,17–19]

Results and Discussion

All the synthesized compounds were characterized by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR and mass spectral studies. Compound **12** is taken as representative compound, and for this the ^{1}H–^{1}H COSY, HSQC, HMBC and NOESY spectra were recorded. The ^{1}H and ^{13}C NMR chemical shift values of all the synthesized compounds are represented in Tables 1 and 3, respectively. The 2D ^{1}H and ^{13}C correlations of compound **12** are shown in Tables 2 and 4. Analytical, IR and mass spectral data of all the synthesized compounds are given as supplementary material.

Proton chemical shifts

In compound **12**, the singlets at 4.20 (1H) and 4.08 (1H) ppm have cross-peaks with the signals at 2.78 (1H) and 3.84 (7H) ppm, respectively. Moreover, the 4.20 and 4.08 ppm signals show correlation with the doublet at 7.47 (4H) ppm, which is due to the *ortho* protons of the phenyl groups in the chair form, and the reason for its downfield shift is the interaction with the nitrogen lone pair. These correlations suggest that the 4.20 and 4.08 ppm resonances are due to the benzylic protons H-2 and H-4 in the chair form. Probably, another singlet at 4.27 (2H) ppm is due to the benzylic protons H-6 and H-8 in the boat form. The

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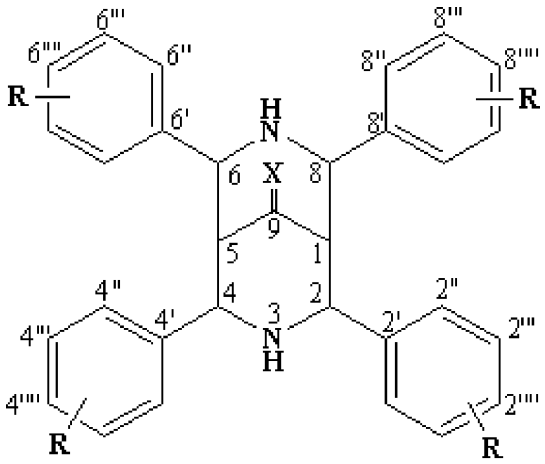


Compound	X	R
1	O	3-F
2	O	4-F
3	NOH	H
4	NOH	4-Cl
5	NOH	4-CH_3
6	NOH	4-OCH_3
7	NOH	3-F
8	NOH	4-F
9	NOBn	H
10	NOBn	4-Cl
11	NOBn	4-CH_3
12	NOBn	4-OCH_3

Scheme 1. Structure and numberings for compounds **1–12**.

strong correlation between 2.78/4.20 and between 3.84/4.08 ppm suggests that the benzylic protons are in axial orientation in the chair form. The higher frequency shift in one of the bridgehead proton is due to the interaction of that proton with the N–O bond. Owing to this $A^{1,3}$ interaction, the *syn* α-proton is deshielded by about 1 ppm and therefore the doublet at 3.84 (7H) ppm is assigned to H-5 proton (which is an overlapped signal with the doublet of the methoxy protons at C-2′′′′ and C-4′′′′). This is confirmed by its cross-peak with H-2′′′ and H-4′′′ at 6.92 (4H) ppm. Likewise, an intense signal at 3.69 (6H) ppm has strong correlation with the triplet at 6.55 ppm, which clearly suggests that the sharp singlet is certainly due to the methoxy protons at C-6′′′′ and C-8′′′′. Therefore, the 2.78, 3.84, 4.20 and 4.08 ppm signals are unambiguously assigned to the H-1, H-5, H-2 and H-4 protons, respectively. Furthermore, the singlet at 4.27 (2H) ppm shows a strong cross-peak with the bridgehead protons and hence unambiguously assigned to the H-6 and H-8 protons (i.e. benzylic protons in the boat form).

In the NOESY spectrum of **12**, a cross-peak is observed between the two broad NH singlets at 1.84 and 1.49 ppm, which suggests that these two protons undergo exchange in $CDCl_3$.

The doublets at 5.18 (1H, J = 12.5 Hz) and 5.26 (1H, J = 12.5 Hz) ppm have strong correlation between them and both doublets have proximity with *ortho* protons of phenyl group in the *O*-benzyl moiety, which suggests that these two doublets can be ascribed to the methylene protons in the *O*-benzyl moiety, which are diastereotopic in nature.

On the basis of the observed chemical shifts, long-range couplings and nOes, we suggest that the synthesized bicyclic oxime ether exists in chair-boat conformation, which are dynamic and mutually interconvertible in the solution phase, with equatorial and axial disposition of all the aryl substitutions in chair and boat forms, respectively. Moreover, the lower frequency resonance of the aryl protons in the boat form is presumably due to the shielding by the aryl groups in the chair form, i.e. the phenyl groups of the boat form may reasonably lie in the shielding region of the phenyl groups in chair form. One more striking fact is that, when compared with the benzylic protons chemical shift of the oximes **3–6** and their corresponding *O*-benzyloximes **9–12**, the benzylic protons of the oxime ethers **9–12** are slightly more shielded. This may be due to the influence of the phenyl group of the *O*-benzyl moiety (Scheme 2).

Similarly, the ^{1}H NMR signals of other bicyclic oxime ethers and oximes have been assigned and are summarized in Table 1.

Carbon chemical shifts

The carbon signals are unambiguously assigned using HSQC and HMBC spectra recorded for the representative compound **12**. All other carbon signals of the synthesized oximes/oxime ethers (except compound **8**, ^{13}C NMR for this compound could not be recorded owing to poor solubility) are assigned by comparison with those of compound **12** and summarized in Table 3. The observed HSQC and HMBC correlations of **12** are listed in Table 4.

Experimental

Synthesis of 2,4,6,8-tetraaryl-3,7-diazabicyclo[3.3.1]nonan-9-ones (1,2)

A mixture of acetone, the respective substituted benzaldehyde and ammonium acetate in 1 : 4 : 2, ratio in ethanol was warmed and kept overnight. The formed bicyclic compounds were filtered and washed with a diethyl ether–ethanol (5 : 1) mixture. Then the crude ketones were recrystallized from ethanol to afford the pure compounds.

Synthesis of 2,4,6,8-tetraaryl-3,7-diazabicyclo[3.3.1]nonan-9-one oximes (3–8)

Method A

To the respective ketone (1 equiv.) in ethanol/chloroform (1 : 1) mixture, hydroxylamine hydrochloride (1.2 equiv.) and sodium acetate trihydrate (3 equiv.) were added and refluxed for about 30–40 h. After completion of the reaction, which was concentrated and the crude product was poured into cold water and then subjected to column chromatography.

Table 1. Proton chemical shift values of compounds **1 – 12** [δ (ppm)]

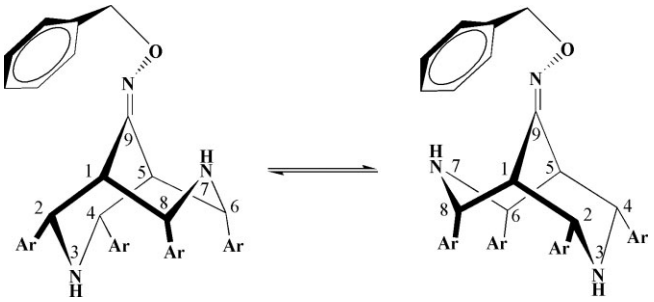
Compound	H-1	H-2	H-4	H-5	H-6 and H-8	NH-3	NH-7	Aryl group protons attached at C-2,4,6 and 8: H-2″ and H-4″	H-2‴ and H-4‴	H-2⁗ and H-4⁗	H-6″ and H-8″	H-6‴ and H-8‴	H-6⁗ and H-8⁗	Phenyl protons in *O*-Bn: *meta*	*ortho/para*	OH[a]/O–CH_2–Ph	CH_3/OCH_3
1	2.83 s	4.37 s	4.37 s	2.83 s	4.67 s	2.15 s	1.57 bs	7.31 d	7.39 t	7.09 t	6.45 dd	7.03 dd	6.79 t	–	–	–	–
2	2.79 s	4.34 s	4.34 s	2.79 s	4.63 s	2.09 s	1.49 s	7.49 t	7.07 t	–	6.64 t	6.71 t	–	–	–	–	–
3	2.88 d $J = 1.7$	4.33 s	4.26 d $J = 1.1$	4.01 d $J = 1.8$	4.42 d $J = 2.8$	2.01 bs	1.63 bs	7.61 t	7.40 t	7.33 dd	6.74 dd	7.04 m		–	–	7.61[b]	–
4	2.77 d $J = 1.3$	4.27 s	4.19 s	3.89 d $J = 1.9$	4.29 d $J = 2.5$	1.94 s	1.58 bs	7.51 t	7.39 dd	–	6.68 dd	7.05 dd	–	–	–	8.07 bs	–
5	2.96 s	4.23 s	4.14 s	4.01 s	4.30 s	1.87 s	1.51 bs	7.44 t	7.16 d	–	6.63 t	6.81 t	–	–	–	8.01 bs	2.124, 2.142 (C-2‴, C-4‴) 2.333 (C-6‴, C-8‴)
6	2.80 s	4.23 s	4.16 s	3.93 s	4.35 s	1.90 bs	1.64 bs	7.49 t	6.87 dd	–	6.69 d	6.59 t	–	–	–	7.49[b]	3.804, 3.840 (C-2‴, C-4‴) 3.781, 3.794 (C-6‴, C-8‴)
7	2.85 d $J = 2.0$	4.30 d $J = 1.2$	4.23 s	3.95 d $J = 2.0$	4.35 s	1.98 s	1.43 bs	7.34 m		7.06 ddd	[c]	6.99 dqn	6.75 ddd	–	–	8.55 bs	–
8	2.71 s	4.22 s	4.15 s	3.85 s	4.25 d $J = 3.2$	1.89 s	1.53 bs	7.49 dd	7.04 dt	–	6.70 d	6.66 t	–	–	–	8.51 bs	–
9	2.88 s	4.28 s	4.17 s	3.93 s	4.35 s	1.96 bs	1.55 bs	7.58 d	7.41 m	7.38 m	6.62 d	7.01 m		7.46 t	7.38–7.41[d] m	5.15, d [$J = 12.5$] 5.27, d [$J = 12.5$]	–
10	2.68 s	4.14 s	4.03 s	3.72 s	4.14 s	1.81 s	1.49 s	7.41 d	7.30 t	–	6.48 dd	6.93 dd	–	7.33–7.37 m		5.08, d [$J = 12.5$] 5.17, d [$J = 12.5$]	–
11	2.75 s	4.15 s	4.04 s	3.81 s	4.25 s	1.81 bs	1.46 bs	7.38 d	7.12 dd	–	6.47 dd	6.74 dd	–	7.33 t	7.29 m	5.09, d [$J = 12.6$] 5.18, d [$J = 12.6$]	2.131, 2.139 (C-2‴, C-4‴) 2.321 (C-6‴, C-8‴)
12	2.78 s	4.20 s	4.08 s	3.84 s	4.27 s	1.84 bs	1.49 bs	7.47 d	6.92 dd	–	6.61 d	6.55 t	–	7.45[e] t	7.40[f] t	5.18, d [$J = 12.5$] 5.26, d [$J = 12.5$]	3.836, 3.842 (C-2‴, C-4‴) 3.695 (C-6‴, C-8‴)

[a] OH and NH protons of the oximes are identified by D_2O exchange.
[b] Merged wih H-2″ and H-4″.
[c] 6.59 (td), 6.52 (td), 6.47 (d), 6.41 (d).
[d] Overlapped with H-2‴, H-4‴ and H-2⁗, H-4⁗.
[e] *Meta* and *para* protons of *O*-Bn.
[f] *Ortho* protons of *O*-Bn.

Table 2. Correlations in the HOMOCOSY and NOESY spectra of **12** [δ (ppm)]

Signal	Correlations in HOMOCOSY	Correlations in NOESY
7.47 (d, 4H, H-2″ and H-4″)	6.92	4.27, 4.20, 4.08, 3.84, 2.78
7.45 (3H, *meta, para* protons of *O*-Bn)	7.40	5.26, 5.18
7.40 (t, 2H, *ortho* protons of *O*-Bn)	7.45	–
6.92 (dd, 4H, H-2‴ and H-4‴)	7.40	3.84
6.61 (d, 4H, H-6″ and H-8″)	6.55	4.27(s), 3.69
6.55 (t, 4H, H-6‴ and H-8‴)	6.61	4.27(w), 3.69
5.26 (d, 1H, $-O-CH_2-Ph$)	5.18	7.45
5.18 (d, 1H, $-O-CH_2-Ph$)	5.26	7.45
4.27 (s, 2H, H-6 and H-8)	3.84, 2.78	7.47, 6.61, 3.84(w), 2.78(w), 1.49(w)
4.20 (s, 1H, H-2)	2.78	7.47, 2.78
4.08 (s, 1H, H-4)	3.84	7.47, 6.61(w), 6.55(w), 3.84
3.84 (d, 7H, H-5, OCH_3 at C-2⁗ and C-4⁗)	4.27, 4.08, 2.78(w)	7.47, 6.92, 6.61(w)
3.69 (s, 6H, OCH_3 at C-6⁗ and C-8⁗)	–	6.61(w), 6.55
2.78 (s, 1H, H-1)	4.27, 4.20, 3.84(w)	7.47, 6.61, 6.55(w), 4.27, 4.20
1.84 (bs, 1H, NH-3)	–	1.49
1.49 (bs, 1H, NH-7)	–	6.61, 4.27, 1.84

s: Strong correlation; w: weak correlation.



Scheme 2. Conformational interconversion.

Method B

The appropriate ketone (1 equiv.) and hydroxylamine hydrochloride (1.2 equiv.) were refluxed for about 5–6 h in presence of pyridine catalyst in ethanol/chloroform (1 : 1). After completion of the reaction, the excess solvent was distilled off, washed with a large excess of water and column-chromatographed.

Synthesis of 2,4,6,8-tetraaryl-3,7-diazabicyclo[3.3.1]nonan-9-one *O*-benzyloximes (9–12)

To a boiling solution of bicyclic ketone (1 equiv.) in ethanolic chloroform (1 : 1), *O*-benzylhydroxylamine hydrochloride (1.2 equiv.) and sodium acetate trihydrate (3 equiv.) were added and refluxed for about 30–40 h. After the usual workup, the solid was separated and purified by column chromatography.

Recording of spectra

All the 1D NMR spectra of compounds **1–2** were recorded on a JEOL GSX 400 spectrometer at 298 K and those of **3–9** and **11** were recorded on a Bruker AMX 400 NMR spectrometer, whereas the spectra of **10** and **12** were recorded on a Bruker DRX 500 NMR instrument. The ^1H and ^{13}C NMR spectra were measured, respectively, in 0.03 and 0.05 M solutions in $CDCl_3$ with tetramethylsilane (TMS) as internal reference in 5 mm NMR tubes. All the 2D NMR spectra were recorded on the DRX 500 instrument using standard parameters. For recording 2D spectra, 0.05 M solution in $CDCl_3$ with TMS was used in 5 mm NMR tubes. All the spectra of compounds **3–12** were measured at a temperature of 300 K.

The pulse conditions were as follows: for compounds **1** and **2**, ^1H NMR spectra: SF 399.65 MHz, AQ 2.05 s, NS 64, P1 7.5 μs, RG 24, DR 0.49 Hz; ^{13}C NMR spectra: SF 100.40 MHz, AQ 0.65 s, NS 2048, P1 4 μs, RG 28, DR 1.53 Hz; for compounds **3–9** and **11**, ^1H NMR spectra: SF 400.13 MHz, AQ 1.95 s, NS 16, DS 0, SW 8389.2 Hz, P1 11.0 μs, RG 50.8, DR 0.51 Hz, DW 59.6 μs, DE 6.0 μs; ^{13}C NMR spectra: SF 100.61 MHz, AQ 1.30 s, NS 512, DS 2, SW 25125.6 Hz, P1 11.0 μs, RG 1149.4, DR 0.76 Hz, DW 19.9 μs, DE 6.0 μs; for compounds **10** and **12**, ^1H NMR spectra: SF 500.03 MHz, AQ 0.99 s, NS 64, DS 0, SW 4960.3 Hz, P1 9.0 μs, RG 16, DR 1.0 Hz, DW 100.8 μs, DE 119.04 μs; ^{13}C NMR spectra: SF 125.73 MHz, AQ 0.52 s, NS 2048, DS 0, SW 31446.5 Hz, P1 16.5 μs, RG 16384, DR 1.91 Hz, DW 15.9 μs, DE 6.0 μs; for the COSY 45° spectrum: SF 500.03 MHz, AQ 0.21 s, NS 16, DS 16, SW 4960.3 Hz, P1 9.0 μs, RG 32, DW 100.8 μs, DE 6.0 μs; for the NOESY experiments: SF 500.03 MHz, AQ 0.21 s, NS 64, DS 16, SW 4960.3 Hz, P1 9.0 μs, RG 32, DW 100.8 μs, DE 119.04 μs; for the HSQC spectrum: SF 500.03 (^1H)/125.74(^{13}C) MHz, AQ 0.21 s, NS 16, DS 16, SW 4960.3 Hz, P1 9.0 μs, P2 18.0 μs, RG 8192, DW 100.8 μs, DE 6.0 μs; for the HMBC spectrum: SF 500.03(^1H)/125.74(^{13}C) MHz, AQ 0.21 s, NS 16, DS 16, SW 4960.3 Hz, P1 9.0 μs, P2 18.0 μs, RG 4096, DW 100.8 μs, DE 6.0 μs.

^1H and ^{13}C chemical shift values are given in δ scale (ppm) and are referred to TMS via the solvent signals (^1H, residual $CHCl_3$ at 7.26 ppm; ^{13}C, $CDCl_3$ at 77.16 ppm). Coupling constants *J* are reported in hertz (Hz). The expansions for the abbreviations used are s: singlet, bs: broad singlet, d: doublet, dd: doublet of doublet, ddd: doublet of doublet of doublet; dqn: doublet of quintet, m: multiplet, t: triplet, SF: spectrometer frequency, AQ: acquisition time, NS: number of transients, DS: dummy scans, SW: spectral width, RG: receiver gain, DR: digital resolution, DW: dwell time, DE: pre scan delay.

Table 3. Carbon chemical shift values of compounds **1–7** and **9–12** [δ (ppm)]

								Ipso carbons									
Compound	C-1	C-2	C-4	C-5	C-6	C-8	C-9	C-2′	C-4′	C-2‴′ and C-4‴′	C-6′	C-8′	C-6‴′ and C-8‴′	*O*-Bn *ipso* carbon	*O*-CH_2-Ph	CH_3/OCH_3	Other aryl carbons
1	61.24	62.69	62.69	61.24	58.28	58.28	209.60	147.42	147.34	164.57 164.09	142.84	142.77	162.12 161.65	–	–	–	130.79, 130.55, 130.47, 129.94, 129.86, 122.27, 121.67, 115.08, 114.87, 114.21, 113.65, 113.43, 113.27, 113.05
2	61.50	62.53	62.53	61.50	58.07	58.07	209.56	135.91	135.91	163.55	135.91	135.91	161.09	–	–	–	128.74, 128.12, 128.03, 127.97, 127.85, 116.21, 115.31, 115.09, 114.79
3	51.33	64.19	62.04	44.66	57.45	57.54	161.29	146.12	146.02	–	141.44	141.31	–	–	–	–	128.59, 128.10, 127.57, 126.94, 126.71, 126.42, 126.14
4	50.94	63.40	61.29	44.21	56.86	56.99	159.86	144.51	144.36	132.85	139.55	139.67	133.70	–	–	–	128.85, 128.50, 128.14, 127.98, 127.71
5	51.17	63.91	61.75	45.67	56.68	57.05	161.32	143.31	143.29	135.69	138.01	137.32	136.17	–	–	21.09, 21.16 (C-2‴′,C4‴′); 20.96, 20.95 (C-6‴′, C-8‴′)	129.64, 129.28, 128.97, 128.79, 127.36, 126.66, 126.52
6	51.31	63.52	61.39	44.69	56.76	56.95	161.36	133.47	133.32	158.94	139.11	139.11	158.30	–	–	55.26 (C-2‴′, C-4‴′) 55.07 (C-6‴′, C-8‴′)	128.16, 127.82, 127.49, 113.92, 113.76, 113.45
7	51.03	63.41	61.29	44.41	57.00	57.11	159.54	148.17	148.17	164.57 164.08	143.67	143.61	162.06 161.64	–	–	–	130.41, 130.39, 130.33, 129.83, 129.80, 129.75, 128.48, 122.69, 122.16, 121.90, 121.87, 113.99, 113.73, 113.51, 113.46
9	51.16	64.06	62.00	45.69	57.34	57.53	160.95	146.28	146.13	–	141.35	141.35	–	138.63	75.57	–	128.52, 128.25, 128.01, 127.51, 126.91, 126.65, 126.40
10	50.67	63.09	61.09	45.10	56.64	56.83	159.32	144.22	144.04	132.57	139.33	139.44	133.40	138.20	75.70	–	128.73, 128.59, 128.29, 128.08, 127.88, 127.62
11	51.20	63.89	61.82	45.79	56.85	57.04	161.44	143.49	143.38	135.88	138.39	138.54	136.99	138.65	75.37	21.09 (C-2‴′, C-4‴′) 20.98 (C-6‴′, C-8‴′)	129.06, 128.59, 128.41, 128.18, 127.56, 126.76, 126.46, 126.21
12	51.30	63.47	61.44	45.86	56.63	56.83	161.47	133.72	133.56	158.19	138.79	138.79	158.11	138.64	75.42	55.42 (C-2‴′, C-4‴′) 55.09 (C-6‴′, C-8‴′)	128.42, 128.21, 127.83, 127.66, 127.41, 114.13, 113.85, 113.36, 113.30

Table 4. Correlations in the HSQC and HMBC spectra of **12** [δ (ppm)]

Signal	Correlations in HSQC	Correlations in HMBC
7.47 (d, 4H, H-2″ and H-4″)	128.42–113.30	63.47(β), 61.44(β)
7.45 (3H, *meta, para* protons of *O*-Bn)	128.42–113.30	75.42(β)
7.40 (t, 2H, *ortho* protons of *O*-Bn)	128.42–113.30	138.64(β), 75.42(γ)
6.92 (dd, 4H, H-2‴ and H-4‴)	128.42–113.30	133.72(β), 133.56(β), 114.13–113.30
6.61 (d, 4H, H-6″ and H-8″)	128.42–113.30	138.79(α), 56.83(β), 56.63(β)
6.55 (t, 4H, H-6‴ and H-8‴)	128.42–113.30	138.79(β), 114.13–113.30
5.26 (d, 1H, $-O-CH_2-Ph$)	75.24	138.64(α)
5.18 (d, 1H, $-O-CH_2-Ph$)	75.24	138.64(α)
4.27 (s, 2H, H-6 and H-8)	56.83	138.79(α)
4.20 (s, 1H, H-2)	63.47	133.56(α)
4.08 (s, 1H, H-4)	61.44	133.72(α)
3.84 (d, 7H, H-5, OCH_3 at C-2⁗ and C-4⁗)	45.86, 55.42	161.47(α), 158.91(α)
3.69 (s, 6H, OCH_3 at C-6⁗ and C-8⁗)	55.09	158.19(α)
2.78 (s, 1H, H-1)	51.30	161.47(α)
1.84 (bs, 1H, NH-3)	–	–
1.49 (bs, 1H, NH-7)	–	–

α: α-Correlation; β: β-correlation; γ: γ-correlation.

Supplementary material

Supplementary electronic material for this paper is available in Wiley InterScience at http://www.interscience.wiley.com/jpages/0749-1581/suppmat/

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