



# GREEN CHEMICAL SYNTHESIS OF DIVERSE IMINOSACCHARIDES OF SUBSTITUTED PYRAZOLE USING IONIC LIQUID

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An efficient and mild synthesis of some diverse iminosaccharides of pyrazole has been carried out. Compounds (**8a-b**) have been synthesized by the treatment of isoniazide with chalcones (**6a-b**) using [bbim][BF<sub>4</sub>] ionic liquid as a solvent under microwave irradiation. Compounds (**8a-b**) on reaction with various aldoses afforded corresponding iminosaccharides compounds containing pyrazole moiety (**9a-l**) in presence of ionic liquid under microwaves. The products have been isolated, purified and characterized by different spectral methods i.e. IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and Mass spectra. The potent antimicrobial effects (MIC) of the synthesized compounds were investigated.

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and chiral catalysts in asymmetric catalysis.<sup>13</sup> Carbohydrates also possess antibacterial, antiviral, antineoplastic, antiprotozoal and antifungal activities.<sup>14,15</sup> In carbohydrate chemistry, a large number of imines have been reported, both by reaction of sugar aldehydes with amines and by reaction of aminosugars with aldehydes.<sup>16-18</sup> Rawal *et al.*<sup>19</sup> reported the synthesis of quinoxaline and its iminosugar derivatives by using sodium zeolite catalyst under microwave irradiation.

## Introduction

To improve chemical process and to reduce environmental pollution has become an urgent task for chemical researchers these days. Microwave-assisted synthesis using ionic liquid as a solvent and catalyst shows distinct advantages over the traditional process, such as energy conservation, short reaction time and elimination of volatile organic solvent. Ionic liquids, the molten salts with melting points at or below ambient temperature, have attracted intense focus due to their remarkable chemical and physical properties such as high thermal stability,<sup>1,2</sup> negligible vapor pressure<sup>3</sup> and high ionic conductivity.<sup>4</sup> They have been used as an alternative to volatile organic solvents for organic synthesis in homogeneous as well as biphasic processes.<sup>5</sup>

Pyrazoles and its derivatives have been found to possess biological activities such as antimicrobial,<sup>6</sup> antihistaminic,<sup>7</sup> anticancer,<sup>8</sup> anticonvulsant<sup>9</sup> and anti-inflammatory<sup>10</sup> activity. Schiff base (also known as imine and azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine group. They are used as pigments, dyes, catalyst, intermediate in organic synthesis and polymer stabilizer.<sup>11</sup> Schiff bases also show a broad range of biological activities, including anti-inflammatory, antiviral, antimalarial, antipyretic and antimicrobial properties.<sup>12</sup>

Recently, carbohydrates and their derivatives have emerged as an important tool for stereoselective synthesis and as a chiral pool for the design of chiral ligands. They are used as chiral building blocks, precursors for drug synthesis

Looking at the role of pyrazole, Schiff base and carbohydrate in medicinal chemistry and the impact of ionic liquid and microwave irradiation in green chemistry, it was planned to synthesis some diverse iminosaccharide of pyrazole using ionic liquid under microwave irradiation.

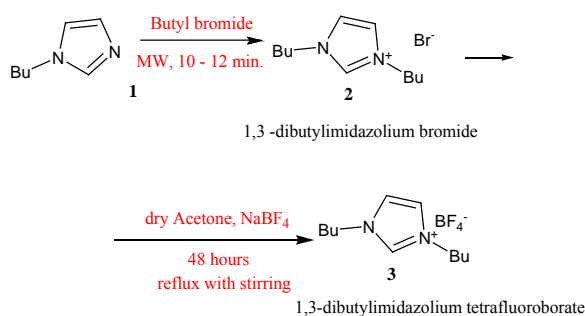
## Experimental

All the reactions were carried out in a domestic microwave oven (Kenstar, Model No. OM-26 EGO). TLC was carried out on silica plates precoated with silica (0.2 mm), and visualization was accomplished by iodine vapours. NMR spectra were taken on a Bruker Avance II 400 NMR Spectrometer using TMS as internal standard and chemical shift were expressed in δ ppm. The FT-IR spectra were recorded on Bruker FT-IR spectrometer. Melting points were determined in open capillaries and are uncorrected. Solvents and reagents were obtained from commercial sources and were used without further purification.

### Synthesis of ionic liquid 1,3-dibutylimidazolium tetrafluoroborate [bbim][BF<sub>4</sub>] (3)

1,3-Dibutylimidazolium bromide (0.1 mol), (**2**) was dissolved in dry acetone and sodium tetrafluoroborate (0.1 mol) was added to it. The reaction mixture was refluxed with stirring for 48 hours. After reflux, the solvent was evaporated under reduced pressure and dichloromethane

was added. Then it was again stirred for 2-3 hours. Filtration of the solution by silica filter 8-10 times afforded a viscous yellow liquid as a final product. Progress of the reaction was monitored by silver nitrate test.



IR (KBr  $\text{cm}^{-1}$ ): 1645 (C=C str.), 3049 (C-H str. in olefin), 1070 (C-N str.), 2960 (C-H str. in  $\text{CH}_3\text{-CH}_2$ ) and 1600 (C=N str.);  $^1\text{H NMR}$ :  $\delta$  ppm: 0.5 (t, 6H,  $\text{CH}_3$ ), 1.20-1.30 (m, 4H,  $\text{CH}_2$ ), 1.95 (m, 4H,  $\text{CH}_2$ ), 2.5 (t, 2H,  $\text{CH}_2$ ), 3.40 (t, 2H,  $\text{CH}_2$ ), 4.6-4.7 (d, 2H, CH) and 10.41 (s, 1H, CH);  $^{13}\text{C NMR}$ :  $\delta$  ppm: 12.5, 20.0, 30.1, 57.6, 132, 121.2 and 124.

#### Synthesis of substituted 1-(4-aminophenyl)-3-phenylprop-2-en-1-one (6a-b)

*p*-Aminoacetophenone (0.01 mol), (4) was dissolved in ethanol and benzaldehyde/*p*-chlorobenzaldehyde (0.01 mol), (5a/5b) and 10% NaOH was added to it. The reaction mixture was irradiated under microwave irradiation for 6 to 8 min at 300 W. After completion of reaction, the viscous mass formed was poured into ice cold water with vigorous stirring and left for complete precipitation. The crude product was dried and purified by recrystallization from ethanol.

#### 1-(4-Aminophenyl)-3-phenylprop-2-en-1-one (6a)

Yield 70 %, M.P. 160-165  $^\circ\text{C}$ ;  $\text{C}_{15}\text{H}_{13}\text{NO}$ ; IR (KBr)  $\text{cm}^{-1}$ : 1630 (C=C str.), 3450 (N-H str.), 1680 ( $\alpha,\beta$ -unsaturated C=O str.), 1600, 1550 and 1450 (C-C str. in aromatic ring), 3000 (=C-H str.);  $^1\text{H NMR}$  (ppm): 6.55-7.40 (Ar-H, 5H, m), 7.90 (CH, d, 1H), 7.60 (CH, d, 1H) and 4.00 (NH, 2H);  $^{13}\text{C-NMR}$  (ppm): 115.4 (2C), 122.0, 125.5 (2C), 126.7, 127.2, 129.4 (2C), 130.0 (2C), 134.5, 142.5, 151.5 and 184.5 (unsaturated C=O); Mass (m/z): 223 [M] $^+$

#### 1-(4-Aminophenyl)-3-(4-chlorophenyl)prop-2-en-1-one (6b)

Yield 70 %, M.P. 140-142  $^\circ\text{C}$ ;  $\text{C}_{15}\text{H}_{12}\text{ClNO}$ ; IR (KBr)  $\text{cm}^{-1}$ : 1630 (C=C str.), 3400 (N-H str.), 1685 ( $\alpha,\beta$ -unsaturated C=O str.), 1600, 1550 and 1450 (C-C str. in aromatic ring), 3040 (=C-H str.) and 840 (p-substituent in aromatic ring);  $^1\text{H NMR}$  (ppm): 6.50-7.55 (Ar-H, 8H, m), 8.05 (CH, d, 1H), 7.60 (CH, d, 1H) and 4.10 (NH, 2H);  $^{13}\text{C-NMR}$  (ppm): 115.0 (2C), 123.5, 125.5 (2C), 126.7, 127.6 (2C), 129.5 (2C), 131.4, 133.0 (Ar-Cl), 142.5, 151.5 and 180.5 (unsaturated C=O); Mass (m/z): 257 [M] $^+$ , 259 [M+2]

#### Synthesis of substituted [5-(4-aminophenyl)-3-phenyl-4,5-dihydro-1H-pyrazol-1-yl](pyridin-4-yl)methanone (8a-b)

Compound (6a/6b) (0.01 mol), isoniazide (0.01 mol), (7) and few drops of acetic acid were dissolved in ionic liquid (10 mL) (3). The reaction mixture was irradiated under microwave irradiation for 10-12 min. The reaction mixture was poured into ice cold water and stirred for few minutes to afford final product. The solid product was filtered and it was purified by recrystallization from ethanol.

#### [5-(4-Aminophenyl)-3-phenyl-4,5-dihydro-1H-pyrazol-1-yl](pyridin-4-yl)methanone (8a)

Yield 75 %, M.P. 120-122  $^\circ\text{C}$ ;  $\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}$ ; IR (KBr)  $\text{cm}^{-1}$ : 3450 (N-H str.), 1650 (C=O str. amide), 1600, 1500 and 1450 (C-C str. in aromatic ring);  $^1\text{H NMR}$  (ppm): 6.0-9.06 (Ar-H, 13H, m), 2.00 ( $\text{CH}_2$  d, 2H) and 4.00 (CH, t, 1H, weak);  $^{13}\text{C-NMR}$  (ppm): 38.5, 42.5, 114.5 (2C), 122.5 (2C), 126.5 (2C), 128.5 (2C), 130.0, 129.6 (2C), 131.0, 132.5, 142.5, 146.5, 150.5 (2C), 154.5 and 160.0 (C=O).

#### [5-(4-Aminophenyl)-3-(4-chlorophenyl)-4,5-dihydro-1H-pyrazol-1-yl](pyridin-4-yl)methanone (8b)

Yield 65 %, M.P. 110-112  $^\circ\text{C}$ ;  $\text{C}_{21}\text{H}_{17}\text{ClN}_4\text{O}$ ; IR (KBr)  $\text{cm}^{-1}$ : 3400 (N-H str.), 1690 (C=O str. amide), 1600, 1550, 1450 (C-C str. in aromatic ring) and 840 (p-substituent in aromatic ring);  $^1\text{H NMR}$  (ppm): 6.0-9.06 (Ar-H, 12H, m), 2.5 ( $\text{CH}_2$  d, 2H) and 4.0 (CH, t, 1H, weak);  $^{13}\text{C-NMR}$  (ppm): 38.0, 44.5, 115.5 (2C), 123.5 (2C), 127.5 (2C), 129.0, 129.6 (2C), 130.0 (2C), 132.5, 136.6 (C-Cl), 142.5, 146.5, 150.5 (2C), 154.5 and 167.0 (C=O); Mass (m/z): 376 [M] $^+$ , 378 [M+2]

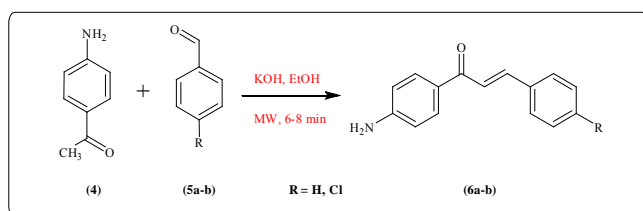
#### Synthesis of iminosaccharides (9a-l)

Compound (7) (0.01 mol) and sugar was dissolved in ionic liquid (10 mL), (3). Few drops of acetic acid were added to it. The reaction mixture was irradiated under microwave irradiation for 12 min at 720 W. On completion of reaction, the resultant mass was poured into ice cold water with vigorous stirring. The solid product was filtered, washed and dried. The product was recrystallized by ethanol.

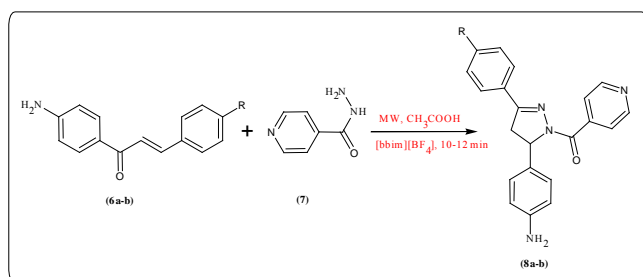
IR (KBr)  $\text{cm}^{-1}$ : 1590 (cyclic C=N str.), 1070 (C-N str.), 1680 (C=O str.), 1620, 1550, 1450 (C-C str. in aromatic ring), 1640 (open C=N str.) and 3400 (OH str.);  $^1\text{H NMR}$  (ppm): 7.5 (d, 1H, CH=N), 6.0-9.06 (Ar-H, 12H, m), 2.5 ( $\text{CH}_2$  doublet, 2H), 4.0 (CH, triplet, 1H), 4.44 - 3.67 (sugar proton) and 5.04 (OH, 1H, s).  $^{13}\text{C-NMR}$  (ppm): 38.5, 41.5, 114.5 (2C), 122.8 (2C), 127.5 (2C), 128.5 (2C), 129.6 (2C), 130.5, 131.0, 132.5, 141.5, 146.9, 150.8 (2C), 154.6, 160.0 (C=O), 163.7 (C=N), 70.5, 73.0, 72.5, 74.0 and 65.0. Mass (m/z): 504 (9a), 474 (9b), 474 (9c), 504 (9d), 444 (9e), 474 (9f), 538 (9g), 508 (9h), 508 (9i), 538 (9j), 478 (9k) and 508 (9l).

## Results and Discussion

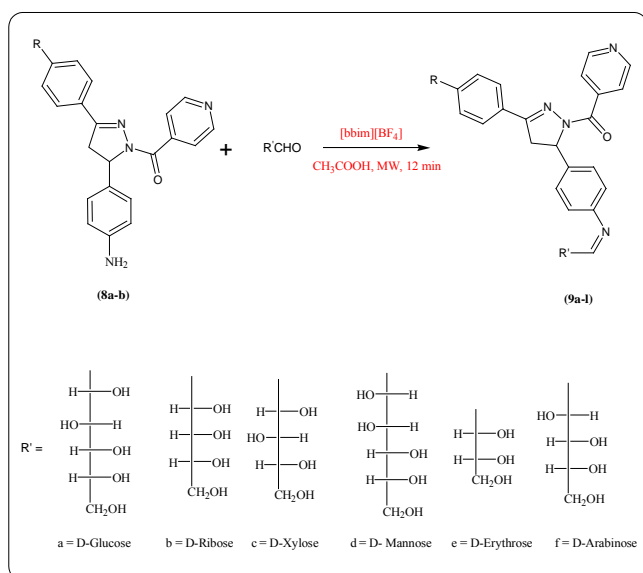
Reaction between p-aminoacetophenone with benzaldehyde/p-chlorobenzaldehyde afforded chalcones (**6a** and **6b**). The structures of the chalcones were established on the basis of their spectral data. Appearance of IR bands at  $1644\text{ cm}^{-1}$  for C=C,  $1685\text{ cm}^{-1}$  for  $\alpha,\beta$ -unsaturated carbonyl group and  $3050\text{ cm}^{-1}$  for =C-H bond confirms the synthesis of chalcone. Appearance of a doublet for =C-H at  $\delta\ 7.9$  ppm further confirms the structure of product. The products **6a** or **6b** were confirmed by a signal at 184.5 for unsaturated carbonyl group in  $^{13}\text{C}$  NMR. These compounds showed molecular ion (m/z) peaks at 233 and 257 and 259 (M+2).



**Scheme 2a.** Synthesis of chalcone **6a-b**



**Scheme 2b.** Synthesis of pyrazole derivative **8a-b**



**Scheme 2c.** Synthesis of iminosaccharide derivative **9a-l**

The structures of compound (**8a-b**) were confirmed by the appearance of IR band at  $2220$  and  $1650\text{ cm}^{-1}$  for C=N and C-N stretching frequency, respectively and disappearance of a band due to  $\alpha,\beta$ -unsaturated C=O stretching frequency at  $1685\text{ cm}^{-1}$ . In proton NMR a doublet for  $\text{CH}_2$  and a triplet for C-H at  $\delta\ 2.5$  and  $\delta\ 4.0$  ppm, respectively also support the

formation of product. In  $^{13}\text{C}$  NMR, signals for cyclic C=N at  $155.5$  ppm and cyclic C-N at  $46.0$  ppm also support the formation of product (**8a-b**). According to mass spectral data compounds (**8a-b**) showed molecular ion peaks at 342 and 376 and 378 (M+2) respectively, supporting the formation of product.

Reaction of substituted pyrazole derivatives (**8a-b**) with various aldoses sugars in ethanol using acetic acid as a catalyst afforded iminosaccharide (Schiff bases) with azomethine linkage (**9a-l**). 10-12 hours of reflux was required for this process. When the same reaction was carried out in microwaves the reaction time was reduced from hours to minutes and the yield of products was also increased. But in this process, ethanol is still used, which is a pollutant and difficult to use. When imino sugars were synthesized using ionic liquid as a solvent under microwave irradiation, reaction time was reduced and the yield of product was also increased.

The structures of the final products were established on the basis of their spectral data. Disappearance of two bands at  $3400$  and  $3250\text{ cm}^{-1}$  due to  $-\text{NH}_2$  stretching (symmetric and asymmetric) and appearance of bands in the region of  $3400\text{-}3450\text{ cm}^{-1}$  for OH stretching and  $1630\text{-}1640\text{ cm}^{-1}$  corresponding to C=N stretching confirmed the assigned structure of iminosaccharides. In  $^1\text{H}$  NMR spectrum, the absence of signal at  $\delta\ 5.80\text{-}5.86$  due to proton of  $\text{NH}_2$  and presence of a doublet for imino protons (CH=N) at  $\delta\ 8.52$  and a singlet for OH proton at  $\delta\ 5.04$  favoured the formation of final product (**9a-l**). Signal of proton of sugar chain were congregated with the solvent absorption in a broad signal at  $\delta\ 4.45\text{-}3.64$ . The final products were also confirmed by  $^{13}\text{C}$  NMR, where appearance of signal at  $163.5$  ppm for imine and  $65\text{-}72.0$  ppm for C-OH supported the proposed structures. Further, mass spectrum also in favour of the structure of iminosaccharides by the molecular ion peak (m/z) at 504, 474, 444, 538 and 508. Physical data of all synthesized compound have been given in Table 1.

**Table 1.** Physical data of synthesized compounds

Com-pounds	Molecular formula	Molecular weight	Yield, %	Melting point, °C
<b>6a</b>	$\text{C}_{15}\text{H}_{13}\text{NO}$	233	70	160-165
<b>6b</b>	$\text{C}_{15}\text{H}_{12}\text{ClNO}$	257	70	140-142
<b>8a</b>	$\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}$	342	75	120-122
<b>8b</b>	$\text{C}_{21}\text{H}_{17}\text{N}_4\text{OCl}$	376	65	110-112
<b>9a</b>	$\text{C}_{27}\text{H}_{28}\text{N}_4\text{O}_6$	504	80	100-102
<b>9b</b>	$\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_5$	474	75	150-152
<b>9c</b>	$\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_5$	474	82	140-142
<b>9d</b>	$\text{C}_{27}\text{H}_{28}\text{N}_4\text{O}_6$	504	70	165-168
<b>9e</b>	$\text{C}_{25}\text{H}_{24}\text{N}_4\text{O}_4$	444	82	200-210
<b>9f</b>	$\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_5$	474	75	185-188
<b>9g</b>	$\text{C}_{27}\text{H}_{27}\text{N}_4\text{O}_6\text{Cl}$	538	80	170-172
<b>9h</b>	$\text{C}_{26}\text{H}_{25}\text{N}_4\text{O}_5\text{Cl}$	508	75	180-182
<b>9i</b>	$\text{C}_{26}\text{H}_{25}\text{N}_4\text{O}_5\text{Cl}$	508	79	130-132
<b>9j</b>	$\text{C}_{27}\text{H}_{27}\text{N}_4\text{O}_6\text{Cl}$	538	85	260-262
<b>9k</b>	$\text{C}_{25}\text{H}_{23}\text{N}_4\text{O}_4\text{Cl}$	478	80	120-122
<b>9l</b>	$\text{C}_{26}\text{H}_{25}\text{N}_4\text{O}_5\text{Cl}$	508	80	190-192

**Table 2.** Microbial activity of synthesized compound (minimum inhibition concentration) (mg mL<sup>-1</sup>)

Com- poun ds	R/R'	Bacteria (MIC) (mg mL <sup>-1</sup> )				Fungi (MIC) (mg mL <sup>-1</sup> )		
		<i>E. coli</i>	<i>P. aeruginosa</i>	<i>S. aureus</i>	<i>S. pyogenus</i>	<i>C. albicans</i>	<i>A. niger</i>	<i>A. clavatus</i>
<b>8<sup>a</sup></b>	R=H	250	200	250	200	500	1000	1000
<b>8<sup>b</sup></b>	R=Cl	125	200	250	125	500	500	1000
<b>9<sup>a</sup></b>	D-Glucose	200	125	200	250	250	1000	500
<b>9<sup>b</sup></b>	D-Ribose	100	200	125	200	1000	>1000	1000
<b>9<sup>c</sup></b>	D-Xylose	100	250	250	200	>1000	1000	500
<b>9<sup>d</sup></b>	D- Mannose	100	200	250	125	1000	1000	500
<b>9<sup>e</sup></b>	D-Erythrose	100	200	200	250	500	500	500
<b>9<sup>f</sup></b>	D-Arabinose	125	125	200	125	1000	>1000	1000
<b>9<sup>g</sup></b>	D-Glucose	100	250	100	200	250	500	1000
<b>9<sup>h</sup></b>	D-Ribose	100	125	200	125	500	1000	1000
<b>9<sup>i</sup></b>	D-Xylose	62.5	250	200	250	1000	1000	1000
<b>9<sup>j</sup></b>	D- Mannose	200	125	200	100	1000	500	500
<b>9<sup>k</sup></b>	D-Erythrose	100	125	250	100	250	500	1000
<b>9<sup>l</sup></b>	D-Arabinose	125	100	125	125	500	1000	1000
<i>Standards</i>								
<b>1</b>	Ampicillin	100	----	250	100	-	-	-
<b>2</b>	Greseofulvin	-	-	-	-	500	100	100

### Biological activities

Representative synthesized compounds were screened *in vitro* for their antimicrobial activities against Gram-negative bacteria *E. coli* and *P. aeruginosa* and Gram-positive bacteria *S. aureus* and *S. pyogenus*. The synthesized compounds were also screened against three strains of fungi (*A. niger*, *C. albicans* and *A. clavatus*). Antibacterial activity was evaluated by agar cup plate method and antifungal assay was carried out by disc diffusion method using Ampicillin (antibacterial) and Greseofulvin (antifungal) as standard drugs respectively.

The synthesized iminosugars have excellent antibacterial, but relatively poor antifungal activity. Compound (**9i**) shows excellent antimicrobial activity against *E.coli* bacteria strain and also good activity against other bacteria strain. Compounds (**9a**), (**9g**) and (**9k**) show good fungicidal activities against *C. albicans*. Compounds (**9j**), (**9d**) and (**9e**) show moderate activity against all the three fungi strain. Almost all the titled compounds exhibited weak, moderate or high antimicrobial activity and moderate to weak antifungal activity (Table 2)

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### References

- Rogers, R. D., Seddon, K. R., *Science*, **2003**, 302, 792.
- Sheldon, R., *Green Chem.*, **2005**, 7, 267.
- Earle, M. J., Esperanc, J. M. S. S., Gilea, M. A., Lopes, J. N. C., Rebelo, L. P. N., Magee, J. W., Seddon, K. R., Widegren, J. A., *Nature*, **2006**, 439, 831.
- Sakaebe, H., Matsumoto, H., *Electrochem. Commun.*, **2003**, 5, 594.
- Plechkova, N. V., Seddon, K. R., *Chem. Soc. Rev.*, **2008**, 37, 123.
- Pimerova, E. V., Voronina, E. V., *Pharm. Chem. J.*, **2001**, 35, 18.
- Michon, V., Du Penhoat, C. H., Tombret, F., Gillardin, J. M., Lepagez, F., Berthon, L., *Eur. J. Med. Chem.*, **1995**, 30, 147.
- Park, H. J., Lee, K., Park, S., Ahn, B., Lee, J. C., Cho, H. Y., Lee, K. I., *Bioorg. Med. Chem. Lett.*, **2005**, 15, 3307.
- Bouabdallah, I., Barret, L. A., Zyad, A., Ramadan, A., Zidane, I., Melhaoui, A., *Nat. Prod. Res.*, **2006**, 20, 1024.
- Tewari, A. K., Mishra, A., *Bioorg. Med. Chem.*, **2001**, 9, 715.
- Dhar, D. N., Taploo, C. L., *J. Sci. Ind. Res.*, **1982**, 41, 501.
- da Silva, C. M., da Silva, D. L., Modolo, L. V., Alves, R. B., de Resende, M. A., Martins, C. V. B., de Fatima, A., *J. Adv. Res.*, **2011**, 2, 1.
- Dieguez M., Pomies O., Ruiz A., Diaz V., Castillon, S., Claver, C., *Coord. Chem. Rev.*, **2004**, 248, 2165.

- <sup>14</sup>Nogueira, C. M., Parmanhan, B. R., Farias, P. P., Correa, A. G., *Rev. Virtual Quim.*, **2009**, *1*(2), 149.
- <sup>15</sup>Wong, C. H., Ed., Carbohydrate-based Drug Discovery, Wiley VCH, Weinheim, Germany, **2003**.
- <sup>16</sup>Costamagna I, Barroso N, D Matsuhira, B., Villagran, M., *Inorg. Chim. Acta.*, **1998**, *273*, 191.
- <sup>17</sup>Costamagna I, Lillo I, F Matsuhira, B, Noseda, M. D., Villagran, M., *Carbohydr. Res.*, **2003**, *338*, 1535.
- <sup>18</sup>Perez, E. M. S., Ávalos, M., Babiano, R., *Carbohydr. Res.*, **2010**, *345*, 23.
- <sup>19</sup>Rawal, M. K., Tiwari, U., Parashar, B., Ameta, R., Punjabi, P. B., *Indian J. Chem.*, **2011**, *50B*, 734.

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