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ONE-POT SYNTHESIS OF BENZOTRIAZOLES AND BENZOTRIAZOLE 1-OXIDES BY REDUCTIVE CYCLIZATION OF *o*-NITROPHENYLAZO COMPOUNDS WITH BENZYL ALCOHOL

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Abstract - Reductive cyclization of 2-[(2-nitrophenyl)azophenols **1** with benzyl alcohol and sodium hydroxide afforded 2-(2*H*-benzotriazol- 2-yl)phenols **3** and their 1-oxide **2** in good to excellent yields.

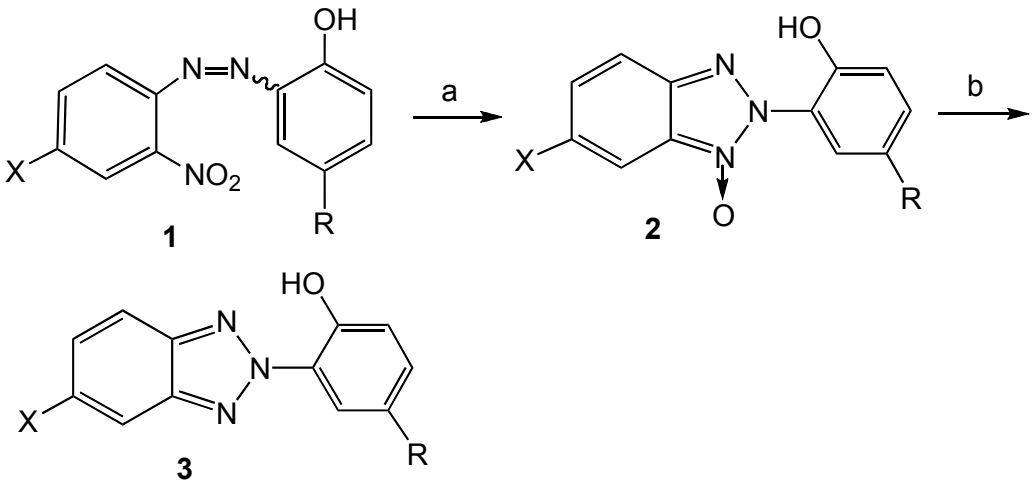
Benzotriazole derivatives serve as important precursor for the construction of heterocyclic ring systems.[1-6] Many of them have significant pharmaceutical activities.[7-9] The others have been used as building block for the preparation of UV light absorbers.[10-14]

For the preparation of benzotriazole derivatives, the most frequently used method is the reductive cyclization of *o*-nitroazobenzene derivatives (Scheme 1). The following reducing agents have been used: powdered zinc and NaOH in an aqueous MeOH,[15] hydrazine hydrate in the presence of NaOH,[16,17] catalytic hydrogenation over palladium on charcoal[18-21] or platinum sulfide on carbon[22] or on modified Raney Nickel,[23,24] with electrolytic reduction at a mercury electrode,[25] and formamidine sulfinic acid, and baker's yeast.[27]

The corresponding *N*-oxide **2** was an intermediate of the above reaction and could be prepared by the reduction of *o*-nitroazobenzene with glucose in alcoholic NaOH,[28] or with a mixture of sodium hydrosulfide and NaOH in toluene and water,[29] or with hydrazine hydrate in aqueous MeOH containing 2,3-dichloro-1,4-naphthoquinone.[30] The method using baker's yeast is also applicable for the preparation of *N*-oxide.[27]

In the course of developing novel scaffolds for medicinal and light absorbers application, we found that 2-aryl-2*H*-benzotriazoles **2, 3** could be prepared from *o*-nitroazobenzene **1** without using any of the above listed reducing agents. Here we report in full experimental details of the new procedure and the related spectral data.

Our preparations of compounds **2** and **3** were based on the reducing properties of benzyl alcohol under basic condition. Treatment of a solution of azo compound **1a** in benzyl alcohol with NaOH at 80 °C afforded rather fast formation of the corresponding *N*-oxide **2a** and after 1.5 h this compound was isolated in good yield (Table 1, entry 1). However, when the reaction was performed at 150 °C, the initially formed *N*-oxide was transformed into benzotriazole **3a** which was then isolated in excellent yield (entry 2).



Scheme 1. *Reagents*: (a) benzyl alcohol, NaOH, t < 100°C;
(b) benzyl alcohol, NaOH, t > 120°C

To explore the scope and versatility of this method the effect of various substituents on the benzotriazole skeleton and on the phenyl group were investigated.

As it can be seen in Table 1, neither the substitution of the benzotriazole (entries 7-12 and 13-16), nor the substituent of the phenyl group (entries 3-6, 9-12, and 13-16) affected significantly the yield of the reductive cyclization. In all cases, we got good or excellent yields.

In the above reactions benzyl alcohol acts as reducing agent. Namely, the process starts with single electron transfer from the oxygen to the nitro group and then proceeds according to the known reduction reactions of this group.

In summary, we have demonstrated that 2-aryl-2*H*-benzotriazoles can be prepared conveniently from readily available *o*-nitroazobenzene without using expensive reducing agents. This new method has the potential to be used in the synthesis of many other derivatives of benzotriazoles.

Table 1 Compounds Prepared by the Reduction of **1a-h**

Entry	Substrate	Product	X	R	Temp (°C)	Time (h)	TLC R_f	Mp (°C)	Yield[a] (%)
1	**1a**	**2a**	H	Me	80	1.5	0.45	143-45	90
2	**1a**	**3a**	H	Me	150	1	0.79	126-28	95
3	**1b**	**2b**	H	Ph	80	1.5	0.38	169-70	81
4	**1b**	**3b**	H	Ph	185	4	0.70	153-55	98
5	**1c**	**2c**	H	cyclohexyl	120	15	0.42	149-51	80
6	**1c**	**3c**	H	cyclohexyl	150	0.5	0.85	134-36	81
7	**1d**	**2d**	Cl	Me	80	2.5	0.51	173-75	52
8	**1d**	**3d**	Cl	Me	150	1	0.80	146-48	87
9	**1e**	**2e**	Cl	Ph	80	1.5	0.47	176-78	61
10	**1e**	**3e**	Cl	Ph	150	1	0.73	136-39	74
11	**1f**	**2f**	Cl	cyclohexyl	80	1.5	0.50	131-33	75
12	**1f**	**3f**	Cl	cyclohexyl	150	1.5	0.88	117-18	79
13	**1g**	**2g**	MeO	Me	80	1.5	0.33	133-35	69
14	**1g**	**3g**	MeO	Me	150	1	0.75	126-27	57
15	**1h**	**2h**	MeO	Ph	120	1.5	0.43	178-80	75
16	**1h**	**3h**	MeO	Ph	140	1.5	0.66	118-24	80

[a]Isolated and unoptimized yields.

EXPERIMENTAL

Mps were determined on a Büchi apparatus and are uncorrected. IR spectra were recorded on Bruker Alpha FT Spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX-500 spectrometer. All NMR spectra are reported in ppm relative to TMS. Merck precoated silica gel 60 F_{254}

plates were used for TLC and Kieselgel 60 for column chromatography. A hexane-acetone 5:2 (v/v) mixture was used for TLC.

Preparation of *N*-oxides 2; General Procedure

To a stirred solution of **1** (16 mmol) in freshly distilled benzyl alcohol (60 mL) was added pulverized NaOH (0.7 g, 18 mmol) and the resulting mixture was heated with stirring at the temperature and for the time given in Table 1. After cooling, water was added (25 mL), the mixture was acidified by the addition of 2N aqueous HCl and then extracted with CH_2Cl_2 (3x25 mL). The combined organic layers were dried ($MgSO_4$), concentrated in vacuum and the residue was dried under IR lamp.

Preparation of Benzotriazoles 3; General Procedure

To a stirred solution of **1** (20 mmol) in freshly distilled benzyl alcohol (60 mL) was added NaOH powder (1.4 g, 35 mmol) and the resultant mixture was heated with stirring at the temperature and for the time given in Table 1. Evaporation of benzyl alcohol under reduced pressure provided a residue which was treated with water. The solids were collected by filtration and then washed successively with water and EtOH.

2-(2*H*-1,2,3-Benzotriazol-2-yl)-4-methylphenol (2a)[31]

IR (KBr): 3442 (OH), 1520, 1454, 1360, 1233, 1113 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.38 (s, 3H, CH_3), 7.13 (d, *J*= 8.5 Hz, 1H, C_6-H), 7.30 (dd, *J*= 8.5 and 1 Hz, 1H, C_5-H), 7.47 (t, *J*= 8 Hz, 1H, $C_{6'}$-H), 7.52 (t, *J*= 8 Hz, 1H, $C_{5'}$-H), 7.57 (br. s, 1H, C_3-H), 7.82 (d, *J*= 8.5 Hz, 1H, $C_{7'}$-H), 7.84 (d, *J*= 8.5 Hz, 1H, $C_{4'}$-H), 9.77 (s, 1H, OH).

^{13}C NMR ($CDCl_3$): δ = 20.37 (CH_3), 113.27 (C-7'), 119.25 (C-4'), 121.17 (C-6), 124.95 (C-2), 126.09 (C-3), 126.48 (C-7a'), 127.94 (C-6), 129.26 (C-5'), 131.01 (C-4), 133.61 (C-5), 142.20 (C-3a'), 149.82 (C-1).

3-(1-Oxido-2*H*-1,2,3-benzotriazol-2-yl)-3-biphenylol (2b)

IR (KBr): 3441 (OH), 1615, 1520, 1449, 1381, 1298, 1114 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.31 (d, *J*= 8.5 Hz, 1H, C_5-H), 7.35 (t, *J*= 7.5 Hz, 1H, C_{10}-H), 7.44 (t, *J*= 7.5 Hz, 2H, C_9-H and C_{11}-H), 7.50 (t, *J*= 8 Hz, 1H, $C_{6'}$-H), 7.54 (m-t, *J*= 8 Hz, 1H, $C_{5'}$-H), 7.60 (d, *J*= 7.5 Hz, 2H, C_8-H and C_{12}-H), 7.74 (d, *J*= 8.5 Hz, 1H, C_6-H), 7.85 (d, *J*= 8.3 Hz, 1H, $C_{7'}$-H), 7.87 (d, *J*= 8.6 Hz, 1H, $C_{4'}$-H), 8.01 (s, 1H, C_2-H), 10.12 (s, 1H, OH).

^{13}C NMR ($CDCl_3$): δ = 113.30 (C-7'), 119.35 (C-4'), 121.81 (C-5), 124.66 (C-2), 125.63 (C-3), 126.59 (C-7a'), 126.86 (C-8 and C-12), 127.46 (C-10), 128.51 (C-6'), 128.91 (C-9 and C-11), 129.41 (C-5'), 131.39 (C-6), 134.78 (C-1), 139.28 (C-7), 142.36 (C-3a'), 151.43 (C-4).

Anal. Calcd for $C_{18}H_{13}N_3O_2$: C, 71.28; H, 4.32; N, 13.85. Found: C, 71.04; H, 4.55; N, 13.67.

4-Cyclohexyl-2-(1-oxido-2*H*-1,2,3-benzotriazol-2yl)phenol (2c)

IR (KBr): 3442 (OH), 1614, 1505, 1457, 1388, 1254, 1105 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.26 (m, 1H, $C_{4''}$-H), 1.41 (m, 2H, $C_{3''}$-H and $C_{5''}$-H), 1.43 (m, 2H, $C_{2''}$-H and $C_{6''}$-H), 1.75 (m, 1H, $C_{4''}$-H), 1.85 (m, 2H, $C_{3''}$-H and $C_{5''}$-H), 1.92 (m, 2H, $C_{2''}$-H and $C_{6''}$-H), 2.56 (m, 1H, $C_{1''}$-H), 7.00 (br.s, 1H, OH), 7.16 (d, *J*= 8.4 Hz, 1H, C_6-H), 7.36 (d, *J*= 8.4 Hz, 1H, C_5-H), 7.49 (t, *J*= 8.0 Hz, 1H, $C_{6'}$-H), 7.53 (t, *J*= 8.0 Hz, 1H, $C_{5'}$-H), 7.60 (s, 1H, C_3-H), 7.84 (d, *J*= 8.6 Hz, 1H, $C_{7'}$-H), 7.87 (d, *J*= 8.8 Hz, 1H, $C_{4'}$-H).

^{13}C NMR ($CDCl_3$): δ = 26.03 (C-4"), 26.79 (C-3" and C-5"), 34.51 (C-2" and C-6"), 43.56 (C-1"), 113.30 (C-7'), 119.29(C-4'), 121.21 (C-6), 124.11 (C-3), 125.04 (C-2), 126.53 (C-7a'), 127.94 (C-6'), 129.23 (C-5'), 131.49 (C-5), 141.49 (C-4), 142.22 (C-3a'), 149.98 (C-1).

Anal. Calcd for $C_{18}H_{19}N_3O_2$: C, 69.88; H, 6.19; N, 13.58. Found: C, 70.11; H, 6.34, N, 13.36.

2-(6-Chloro-1-oxido-2*H*-1,2,3-benzotriazol-2-yl)-4-methylphenol (2d)[28]

IR (KBr): 3441 (OH), 1616, 1509, 1498, 1362, 1254, 1123 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.38 (s, 3H, CH_3), 7.13 (d, *J*= 8.4 Hz, 1H, C_6-H), 7.32 (dd, *J*= 8.4 and 1.0 Hz, 1H, C_5-H), 7.46 (dd, *J*= 8.4 and 1.5 Hz, 1H, $C_{5'}$-H), 7.54 (br. s, 1H, C_3-H), 7.80 (d, *J*= 9.2 Hz, 1H, $C_{4'}$-H), 7.84 (br. s, 1H, $C_{7'}$-H), 9.26 (br. s, 1H, OH).

^{13}C NMR ($CDCl_3$): δ = 20.38 (CH_3), 112.47 (C-7'), 120.53 (C-4'), 121.31 (C-6), 124.81 (C-2), 126.01 (C-3), 126.58 (C-7a'), 131.10 (C-5'), 131.19 (C-4), 133.81 (C-5), 134.28 (C-6'), 140.58 (C-3a'), 149.79 (C-1).

3-(6-Chloro-1-oxido-2*H*-1,2,3-benzotriazol-2-yl)-4-biphenylol (2e)

IR (KBr): 3440 (OH), 1500, 1447, 1358, 1233, 1121 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.31 (d, *J*= 8.6 Hz, 1H, C_5-H), 7.36 (t, *J*= 7.2 Hz, 1H, C_{10}-H), 7.45 (t, *J*= 7.2 Hz, 2H, C_9-H and C_{11}-H), 7.47 (d, *J*= 7.9 Hz, 1H, $C_{5'}$-H), 7.60 (dd, *J*= 8.5 and 1 Hz, 2H, C_8-H and C_{12}-H), 7.76 (dd, *J*= 8.5 and 2 Hz, 1H, C_5-H), 7.82 (d, *J*= 9.1 Hz, 1H, $C_{4'}$-H), 7.88 (br. s, 1H, $C_{7'}$-H), 7.98 (d, *J*= 2 Hz, 1H, C_2-H), 9.89 (s, 1H, OH).

^{13}C NMR ($CDCl_3$): δ = 112.49 (C-7'), 120.62 (C-4'), 121.94 (C-5), 124.58 (C-2), 125.49 (C-3), 126.70 (C-7a'), 126.88 (C-8 and C-12), 127.57 (C-10), 128.96 (C-9 and C-11), 131.28 (C-5'), 131.67 (C-6), 134.56 (C-6), 134.98 (C-1), 139.18 (C-7), 140.74 (C-3a'), 151.38 (C-4).

Anal. Calcd for $C_{18}H_{12}ClN_3O_2$: C, 64.01; H, 3.58; N, 12.44. Found: C, 63.92; H, 3.77, N, 12.21.

2-(6-Chloro-1-oxido-2*H*-1,2,3-benzotriazol-2-yl)-4-cyclohexylphenol (2f)

IR (KBr): 3440 (OH), 1500, 1447, 1358, 1233, 1121 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.26 (m, 1H, $C_{4''}$-H), 1.40 (m, 2H, $C_{3''}$-H and $C_{5''}$-H), 1.42 (m, 2H, $C_{2''}$-H and $C_{6''}$-H), 1.75 (m, 2H, $C_{4''}$-H), 1.86 (m, 2H, $C_{3''}$-H and $C_{5''}$-H), 1.91 (m, 2H, $C_{2''}$-H and $C_{6''}$-H), 2.55 (m, 1H, $C_{1''}$-H), 7.15 (d, *J*= 8.5 Hz, 1H, C_6-H), 7.37 (d, *J*= 8.2 Hz, 1H, C_5-H), 7.46 (d, *J*= 9.1 Hz, 1H, $C_{5'}$-H), 7.56

s, 1H, C_3-H), 7.81 (d, *J*= 9.1 Hz, 1H, $C_{4'}$-H), 7.85 (s, 1H, C_7'-H), 8,0 (br. s, 1H, OH).

^{13}C NMR ($CDCl_3$): δ = 26.41 (C-4"), 27.17 (C-3" and C-5"), 34.90 (C-2" and C-6"), 43.93 (C-1"), 112.87 (C-7'), 120.94 (C-4'), 121.71 (C-6), 124.41 (C-3), 125.28 (C-2), 127.00 (C-7a'), 131.45 (C-5'), 132.17 (C-5), 134.65 (C-6'), 140.96 (C-3a'), 142.03 (C-4), 150.36 (C-1).

Anal. Calcd for $C_{18}H_{18}ClN_3O_2$: C, 62.88; H, 5.28; N, 12.22. Found: C, 62.59; H, 5.02; N, 12.49.

2-(6-Methoxy-1-oxido-2*H*-1,2,3-benzotriazol-2-yl)-4-methylphenol (2g)

IR (KBr): 3441 (OH), 1632, 1529, 1511, 1469, 1341, 1275, 1225, 1114 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 3H, CH_3), 3.94 (s, 3H, OCH_3), 6.98 (d, *J*= 1.7 Hz, 1H, $C_{7'}$-H), 7.12 (d, *J*= 8.4 Hz, 1H, C_6-H), 7.19 (dd, *J*= 9.4 and 2.2 Hz, 1H, $C_{5'}$-H), 7.29 ((d, *J*= 8.5 Hz, 1H, C_5-H), 7.52 (s, 1H, C_3-H), 7.71 (d, *J*= 9.4 Hz, 1H, $C_{4'}$-H), 10.00 (br. s, 1H, OH).

^{13}C NMR ($CDCl_3$): δ = 20.39 (CH_3), 56.14 (OCH_3), 89.71 (C-7'), 120.28 (C-4'), 121.14 (C-6), 124.93 (C-5'), 125.23 (C-2), 125.91 (C-3), 127.27 (C-7a'), 130.89 (C-4), 133.29 (C-5), 138.89 (C-3a'), 149.74 (C-1), 160.15 (C-6').

Anal. Calcd for $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.83; N, 15.49. Found: C, 62.21; H, 4.63; N, 15.25.

3-(6-Methoxy-1-oxydo-2*H*-1,2,3-benzotriazol-2-yl)-4-biphenylol (2h)

IR (KBr): 3440 (OH), 1632, 1620, 1526, 1488, 1378, 1285, 1224, 1014 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3. 59 (s, 3H, OCH_3), 6.99 (s, 1H, $C_{7'}$-H), 7.19 (dd, *J*= 9.4 and 1.7 Hz, 1H, $C_{5'}$-H), 7.29 (d, *J*= 8.5 Hz, 1H, C_5-H), 7.35 (t, *J*= 7.4 Hz, 1H, C_{10}-H), 7.44 (t, *J*= 7.5 Hz, 2H, C_9-H and C_{11}-H), 7.60 (d, *J*= 7.7 Hz, 2H, C_8-H and C_{12}-H), 7.71 (dd, *J*= 8.4 and 1.6 Hz, 1H, C_6-H), 7.73 (d, *J*= 9.4, 1H, $C_{4'}$-H), 7.95 (s, 1H, C_2-H), 8.00 (br. s, 1H, OH).

^{13}C NMR ($CDCl_3$): δ = 56.16 (OCH_3), 89.63 (C-7'), 120.34 (C-4'), 121.72 (C-5), 124.47 (C-2), 125.08 (C-5'), 125.86 (C-3), 126.85 (C-8 and C-12), 127.40 (C-7a'), 128.90 (C-9 and C-11),131.05 (6), 134.63 (C-1), 139.02 (C-3a'), 139.37 (C-7), 151.36 (C-4), 160.30 (C-6').

Anal. Calcd for $C_{19}H_{15}N_3O_3$: C, 68.46; H, 4.54; N, 12.61. Found: C, 68.52; H, 4.43; N, 12. 82.

2-(2*H*-1,2,3-Benzotriazol-2-yl)-4-methoxyphenol (3a)[31]

IR (KBr): 3441 (OH), 1615, 1599, 1514, 1473, 1348, 1304, 1251, 1131 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.41 (s, 3H, CH_3), 7.09 (d, *J*= 8.4 Hz, 1H, C_6-H), 7.16 (d, *J*= 8.4 Hz, 1H, C_5-H), 7.49 (dd, *J*= 8.4 and 3.0 Hz, 2H, $C_{5'}$-H and $C_{6'}$-H), 7.94 (dd, *J*= 6.6 and 3.0 Hz, 2H, $C_{4'}$-H and $C_{7'}$-H), 8.22 (s, 1H, C_3-H), 11.11 (s, 1H, OH).

3-(2*H*-1,2,3-Benzotriazol-2-yl)-4-biphenylol (3b)[11]

IR (KBr): 3441 (OH), 1615, 1596, 1484, 1355, 1225, 1133 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.27 (d, *J*= 8.5 Hz, 1H, C_5-H), 7.35 (t, *J*= 7.3 Hz, 1H, C_{10}-H), 7.46 (t, *J*= 7.5 Hz, 2H, C_9-H and C_{11}-H), 7.49 (dd, *J*= 6.5 and 3.0 Hz, 2H, $C_{5'}$-H and $C_{6'}$-H), 7.59 (d, *J*= 8.5 Hz, 1H, C_5-H), 7.66 (d, *J*= 7.5 Hz, 2H, C_8-H and C_{12}-H), 7.93 (dd, *J*= 6.5 and 3.0 Hz, 2H, $C_{4'}$-H and $C_{7'}$-H), 8.65 (d, *J*=

1.8 Hz, 1H, C_2-H), 11.37 (s, 1H, OH).

^{13}C NMR ($CDCl_3$): δ = 117.71 (C-4' and C-7'), 119.42 (C-5), 119.48 (C-2), 125.44 (C-3), 126.79 (C-8), 127.24 (C-10), 127.81 (C-5' and C-6'), 128.86 (C-9 and C-11), 129.04 (C-6), 133.48 (C-1), 139.72 (C-7), 142.87 (C-3a' and C-7a'), 149.17 (C-4).

2-(2*H*-1,2,3-Benzotriazol-2-yl)-4-cyclohexylphenol (3c)[11]

IR (KBr): 3442 (OH), 1616, 1595, 1515, 1448, 1351, 1254, 1220, 1132 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.29 (m, 1H, $C_{4''}$-H), 1.43 (m, 2H, $C_{3''}$-H and $C_{5''}$-H), 1.47 (m, 2H, $C_{2''}$-H and $C_{6''}$-H), 1.76 (d, *J*= 12.5 Hz, 1H, $C_{4''}$-H), 1.86 (d, *J*= 12.5 Hz, 2H, $C_{3''}$-H and $C_{5''}$-H), 1.94 (d, *J*= 12.5 Hz, 2H, $C_{2''}$-H and $C_{6''}$-H), 2.57 (m, 1H, $C_{1''}$-H), 7.12 (d, *J*= 8.5 Hz, 1H, C_6-H), 7.20 (dd, *J*= 8.5 and 0.9 Hz, 1H, C_5-H), 7.47 (dd, *J*= 6.5 and 2.9 Hz, 2H, $C_{5'}$-H and $C_{6'}$-H), 7.93 (dd, *J*= 6.5 and 2.9 Hz, 2H, $C_{4'}$-H and $C_{7'}$-H), 8.24 (d, *J*= 0.8 Hz, 1H, C_3-H), 11.13 (s, 1H, OH).

^{13}C NMR ($CDCl_3$): δ = 26.09 (C-4''), 26.88 (C-3'' and C-5''), 34.58 (C-2'' and C-6''), 43.74 (C-1''), 117.67 (C-4' and C-7'), 118.75 (C-6), 119.03 (C-3), 124.95 (C-2), 127.61 (C-5' and C-6'), 129.12 (C-5), 140.20 (C-4), 142.81 (C-3a' and C-7a'), 147.75 (C-1).

2-(5-Chloro-2*H*-1,2,3-benzotriazol-2-yl)-4-methylphenol (3d)[28]

IR (KBr): 3442 (OH), 1618, 1596, 1516, 1383,1236,1053 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 3H, CH_3), 7.07 (d, *J*= 8.3 Hz, 1H, C_6-H), 7.14 (d, *J*= 8.3 Hz, 1H, C_5-H), 7.40 (dd, *J*= 8.1 and 0.9 Hz, 1H, $C_{5'}$-H), 7.84 (d, *J*= 8.8 Hz, 1H, $C_{4'}$-H), 7.88 (s, 1H, $C_{7'}$-H), 8.12 (s, 1H, C_3-H), 10.83 (s, 1H, OH).

^{13}C NMR ($CDCl_3$): δ = 20.53 (CH_3), 116.65 (C-7'), 118.77 (C-4'), 118.85 (C-6), 121.09 (C-3), 124.60 (C-2), 129.18 (C-5'), 129.77 (C-4), 131.62 (C-5), 133.53 (C-6'), 141.29 (C-3$^{a'}$), 143.12 (C-7$^{a'}$), 147.48 (C-1).

3-(5-Chloro-2*H*-1,2,3-benzotriazol-2-yl)-4-biphenylol (3e)

IR (KBr): 3442 (OH), 1613, 1593, 1482, 1391, 1242, 1057 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.26 (d, *J*= 8.1 Hz, 1H, C_5-H), 7.36 (d, *J*= 7.5 Hz, 1H, C_{10}-H), 7.43 (dd, *J*= 9.0 and 1.0 Hz, 1H, $C_{6'}$-H), 7.46 (t, *J*= 8.0 Hz, 2H, C_9-H and C_{11}-H), 7.60 (dd, *J*= 8.5 and 2.0 Hz, 1H, C_6-H), 7.65 (d, *J*= 7.6 Hz, 2H, C_8-H and C_{12}-H), 7.88 (d, *J*= 9.1 Hz, 1H, $C_{7'}$-H), 7.93 (d, *J*= 1.0 Hz, 1H, $C_{4'}$-H), 8.61 (d, *J*= 2.0 Hz, 1H, C_2-H), 11.10 (s, 1H, OH).

^{13}C NMR ($CDCl_3$): δ = 116.73 (C-4'), 118.87 (C-7'), 119.50 (C-5), 119.54 (C-2), 125.24 (C-3), 126.78 (C-8 and C-12), 127.33 (C-10), 128.90 (C-9 and C-11), 129.40 (C-6 and C-6'), 133.62 (C-1), 133.75 (C-5'), 139.59 (C-7), 141.39 (C-7a'), 143.22 (C-3a'), 149.12 (C-4).

Anal. Calcd for $C_{18}H_{12}ClN_3O$: C, 67.19; H, 3.76; N, 13.06. Found: C, 67.02; H, 3.58; N, 13.01.

2-(5-Chloro-2*H*-1,2,3-benzotriazol-2-yl)-4-cyclohexylphenol (3f)

IR (KBr): 3440 (OH), 1618, 1596, 1449, 1348, 1253, 1048 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.28 (m, 1H, $C_{4''}$-H), 1.43 (m, 2H, $C_{3''}$-H and $C_{5''}$-H), 1.47 (m, 2H, $C_{2''}$-H and $C_{6''}$-H), 1.77 (m, 1H, $C_{4''}$-H), 1.87 (m, 2H, $C_{3''}$-H and $C_{5''}$-H), 1.93 (m, 2H, $C_{2''}$-H and $C_{6''}$-H),2.57 (m, 1H, $C_{1''}$-H), 7.11 (d, *J*= 8.4 Hz, 1H, $C_{6'}$-H), 7.21 (d, *J*= 8.0 Hz, 1H, C_5-H), 7.42 (d, *J*= 9.0 Hz, 1H, $C_{5'}$-H), 7.87 (d, *J*= 9.0 Hz, 1H, $C_{4''}$-H), 7.93 (s, 1H, $C_{7'}$-H), 8.20 (s, 1H, C_3-H), 10.88 (br. s, 1H, OH).

^{13}C NMR ($CDCl_3$): δ = 26.07 (C-4"), 26.85 (C-3" and C-5"), 34.56 (C-2" and C-6"), 43.71 (C-1"), 116.69 (C-7'), 118.83 (C-4'), 118.87 (C-6), 119.04 (C-3), 124.76 (C-2), 129.19 (C-5'), 129.52 (C-5), 133.53 (C-6'), 140.36 (4), 141.34 (C-3a'), 143.17 (C-7a'), 147.72 (C-1).

Anal. Calcd for $C_{18}H_{18}ClN_3O$: C, 65.95; H, 5.53; N, 12.82. Found: C, 66.13; H, 5.32; N, 12.59.

2-(5-Methoxy-2*H*-1,2,3-benzotriazol-2-yl)-4-methylphenol (3g)[11]

IR (KBr): 3441 (OH), 1630, 1521, 1437, 1302, 1228, 1123, 1026 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.31 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 7.05 (d, *J*= 8.0 Hz, 1H, C_6-H), 7.17 (d, *J*= 9.0 Hz, 1H, $C_{6'}$-H), 7.19 (d, *J*= 9.0 Hz, 1H, C_5-H), 7.33 (s, 1H, $C_{4'}$-H), 7.67 (s, 1H, C_3-H), 7.91 (d, *J*= 9.0 Hz, 1H, $C_{7'}$-H), 10.40 (br. s, 1H, OH).

^{13}C NMR ($CDCl_3$): δ = 20.07 (CH_3), 55.88 (OCH_3), 95.06 (C-4'), 118.10 (C-6), 118.96 (C-7'), 122.28 (C-6'), 124.24 (C-3), 126.58(C-2), 128.50 (C-4), 131.28 (C-5), 139.61 (C-7a'), 144.58 (C-3a'), 148.2 (C-1), 159.10 (C-5').

3-(5-Methoxy-2*H*-1,2,3-benzotriazol-2-yl)-4-biphenylol (3h)

IR (KBr): 3450 (OH), 1624, 1614, 1500, 1310, 1140 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.89 (s, 3H, OCH_3), 7.10 (s, 1H, $C_{4'}$-H), 7.13 (d, *J*= 9.2 Hz, 1H, $C_{6'}$-H), 7.23 (d, *J*= 8.6 Hz, 1H, C_5-H), 7.34 (t, *J*= 7.3 Hz, 1H, C_{10}-H), 7.44 (t, *J*= 7.5 Hz, 2H, C_9-H and C_{11}-H), 7.54 (d, *J*= 8.6 Hz, 1H, C_6-H), 7.65 (d, *J*= 7.5 Hz, 2H, C_8-H and C_{12}-H), 7.77 (d, *J*= 9.2 Hz, 1H, $C_{7'}$-H), 8.56 (s, 1H, C_2-H), 11.31 (s, 1H, OH).

^{13}C NMR ($CDCl_3$): δ = 55.64 (OCH_3), 94.17 (C-4'), 118.46 (C-7'), 118.99 (C-2), 119.25 (C-5), 122.98 (C-6'), 125.53 (C-3), 126.76 (C-8 and C-12), 127.15 (C-10), 128.40 (C-6), 128.82 (C-9 and C-11), 133.33 (C-1), 139.02 (C-7a'), 139.81 (C-7), 143.94 (C-3a'), 148.74 (C-4), 159.81 (C-5').

Anal. Calcd for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.70; H, 4.55; N, 13.31.

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