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RESEARCH ARTICLE

Synthesis of new potential UV-filters

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Abstract

Three new silylated 2-(2'-hydroxyphenyl)benzotriazole derivatives were prepared. Starting with the easily available simple 2-(2'-hydroxyphenyl)benzotriazole, the target compounds were synthesized by a stepwise synthetic protocol, namely alkylation, thermal rearrangement and silylation.

Keywords

Benzotriazoles · rearrangement · silyl derivatives · UV-filters

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1 Introduction

As a result of the thinning of the protective ozone layer, the exposure to ultraviolet light (UV) is increasing worldwide. UV light, which is approximately 90% of this radiation, can pass through window glass, penetrates into the dermis, and may cause tanning, wrinkling, and skin cancer. Malignant melanoma is the most harmful of all skin cancers. It has been increasing faster than any other cancer and regarding the number of cases it has more than doubled in the last 5 years. Therefore, protection against the UV light has been growing and is of crucial significance [1]-[7].

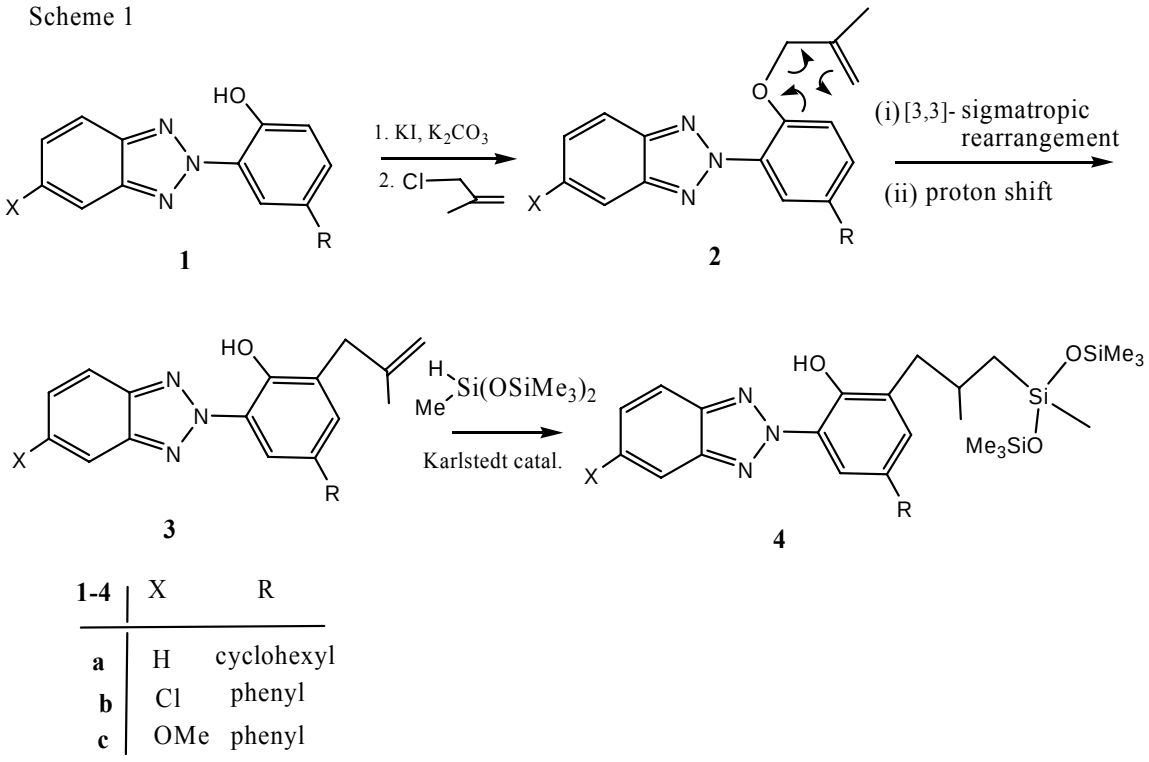
A number of molecules are employed as UV light protecting agents. Among them compounds having intramolecular H-bond are strong UV absorbers and show proper photostability. 2-(2'-Hydroxyphenyl)benzotriazole derivatives (e.g. Mexoryl XL) are widely used as UV stabilizers. In these molecules the photoinduced excited state returns to the ground state by a proton transfer and rapid non-radiative dissipation of the harmful UV energy ($S_1 \rightarrow S_1^{'} \rightarrow S_0^{'} \rightarrow S_0$) [8]-[13].

Recently, we have described papers about the synthesis of new silylated hydroxyphenyl-benzotriazole derivatives. Some of them had excellent UVA-filter activity and high photostability [14]. Following this research, we have prepared three new hydroxyphenyl-benzotriazole derivatives with substituents on the benzotriazole moiety and/or on the phenyl group. The synthesis followed is shown in the Fig. 1.

2 Results and discussion

Earlier we had elaborated a new and economical method for the synthesis of 2-(2'-hydroxyphenyl)benzotriazole derivatives (Fig. 1) and here we used its potential for the preparation of these starting materials [15, 16]. Compound **1a** was then treated with 2-(chloromethyl)prop-1-ene in the presence of KI and K_2CO_3 to afford ether **2a**, in good yield. The ^{1}H and ^{13}C NMR spectra of **2a** showed the typical pattern of a benzo[*d*][1,2,3]triazole skeleton where two pairs of ortho-coupled aromatic protons at ($\delta_{7.42}$ and $\delta_{7.96}$) were assignable to C_4-H and C_5-H, (or C_6-H and C_7-H), respectively. Furthermore, the ^{1}H NMR spectrum revealed the presence of a 2-

Scheme 1



1-4	X	R
a	H	cyclohexyl
b	Cl	phenyl
c	OMe	phenyl

Fig. 1.

methyl-2-propenyloxy group ($\delta_{4.47}$,$\delta_{4.86}$, and $\delta_{4.95}$), and a cyclohexylphenyl moiety. Thermal rearrangement of compounds **2a** in boiling *N*,*N*-diethylbenzeneamine afforded the wanted intermediate **3a**, in excellent yield. In the ^{1}H spectrum the signal at ($\delta_{11.42}$, OH) together with the other part of spectra justified the structure of **3a**. This compound was then silylated with heptamethyltrisiloxane in the presence of Karlstedt catalyst [17] to furnish the target compounds **4a**, in good yield. The structure of compound **4a** was also justified by its spectra. For instance, both ^{1}H and ^{13}C NMR spectra showed the characteristic signals of the benzotriazole and cyclohexylphenyl skeleton, the hydroxyl group ($\delta_{11.34}$), and the heptamethyl-disiloxanyl moiety [$\delta_{0.08}$(Si-CH_3) and $\delta_{0,11}$ (18 H, 6 CH_3)].

The reaction of the chloro compound **1b** with 2-(chloromethyl)prop-1-ene gave the ether **2b**, which was thermally rearranged. The product **3b** was then silylated with heptamethyltrisiloxane in the presence of Karlstedt catalyst to afford compound **4b**, in an overall yield 44.3%.

Likewise, the methoxy analog **4c** was prepared with the alkylation of **1c** followed by rearrangement and silylation. Here, the overall yield of the three steps was lower (15.6%).

3 Conclusion

We have elaborated a straightforward method for the preparation of three potential UV-filters. The synthesis of these compounds **4a-c** was achieved in three steps starting with the easily available benzotriazole derivatives **1a-c**, in good or acceptable overall yield. The UV absorption and photostability of these new compounds will be published in due course.

4 Experimental

All solvents were used as received from commercial vendors and no further attempts were made to purify or dry them. Melting points were determined on a Büchi apparatus and are uncorrected. IR spectra were recorded on a Bruker Alpha FT Spectrophotometer. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker DRX-500 spectrometer operating at 500 MHz and 125 MHz, respectively. All NMR spectra are reported in ppm relative to TMS, used as an internal standard. The ^{1}H and ^{13}C NMR signals were assigned on the bases of ATP, COSY, HMQC, and HMBC experiences. Merck precoated silica gel 60 F_{254} plates were used for TLC and Kieselgel 60 for column chromatography using a solution of hexane-EtOAc (5:0.2) as eluent. Elemental analyses for C, H, N agreed favorably with calculated values.

4.1 General procedure for the preparation of compounds 2a-c

Compound **1** (23.6 mmol), KI (3.9 g, 23.6 mmol), and K_2CO_3 (3.2 g, 23.6 mmol) were mixed in butan-2-one (100 ml) and after adding 2-(chloromethyl)prop-1-ene (5.0 g, 5.6 ml, 23.8 mmol) the resulting mixture was heated under reflux for 4 h. After cooling, the precipitate was filtered off and the solvent was evaporated in vacuo. The residue was purified by column chromatography.

The following products were thus prepared:

2-[2-(2-Methylallyloxy)-5-cyclohexylphenyl)-2*H*-benzo[*d*][1,2,3]triazole (**2a**)

Yield: 60%, yellow oil; TLC: R_f = 0.74 (hexane-acetone 5:2); IR (KBr): 2950, 1520, 1475, 1413, 1255 cm^{-1}; ^{1}H-NMR

($CDCl_3$): 1.24 (m, 1H, C_4"-H), 1.35 (m, 2H, C_3"-H and C_5"-H), 1.42 (m, 2H, C_2"-H and C_6"-H), 1.67 (s, 3H, CH_3), 1.72 (m, 1H, C_4"-H), 1.83 (m, 2H, C_3"-H and C_5"-H), 1.91 (m, 2H, C_2"-H and C_6"-H), 2.53 (m, 1H, C_1"-H), 4.47 (s, 2H, OCH_2), 4.86 (s, 1H, $=CH_2$), 4.95 (s, 1H, $=CH_2$), 7.04 (d, J= 8.6 Hz, C_3'-H), 7.29 (dd, J= 8.6 and 1.9 Hz, 1H, C_4'-H), 7.42 (dd, J= 6.6 and 3.0 Hz, 2H, C_5-H and C_6-H), 7.52 (d, J= 1.9 Hz, 1H, C_6'-H), 7.96 (dd, J= 6.6 and 3.0 Hz, 2H, C_4-H and C_7-H); ^{13}C-NMR ($CDCl_3$): 19.17 CH_3, 26.05 (C-4"),26.80 (C-3" and C-5"), 34.48 (C-2" and C-6"), 43.55 (C-1"), 72.84 (OCH_2), 112.66 (=C), 114.41 (C-3'), 118.40 (C-4 and C-7), 125.69 (C-6'), 126.65 (C-5 and C-6), 129.18 (C-4'), 130.44 (C-1'), 140.17 (C=), 141.04 (C-3'), 144.75 (C-7a), 150.69 (C-3a). Anal. Calcd for $C_{22}H_{25}N_3O$: C, 76.05; H, 7.25; N, 12.09. Found: C,76.17; H, 7.02; N, 11.94.

5-Chloro-2-{4-[2-methyl-2-propen-1-yl]-3-biphenylyl}-2*H*-1,2,3-benzotriazole (**2b**).

Yield: 74%, light yellow crystals; m.p.: 107-108 ^{o}C; TLC: R_f =0.65 (hexane-acetone 5:2); IR (KBr): 1489, 1290, 12.61, 909 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 1.71 (s, 3H, CH_3), 4.55 (s, 2H, OCH_2), 4.91 (s, 1H, $=CH_2$), 5.00 (s, 1H, $=CH_2$), 7.19 (d, J= 8.7 Hz, 1H, C_5'-H), 7.34 (t, J= 7.5 Hz, C_{10}'-H), 7.39 (dd, J= 9.1 and 1.5 Hz, 1H, C_6-H), 7.43 (t, J= 7.5 Hz, 2H, C_9'-H and C_{11}'-H), 7.59 (d, J= 8.1 Hz, 2H, C_8'-H and C_{12}'-H), 7.70 (dd, J= 8.7 and 2.1 Hz, 1H, C_6'-H), 7.92 (d, J= 9.1 Hz, 1H, C_7-H), 7.93 (s, 1H, C_2'-H), 7.97 (s, 1H C_4-H); ^{13}C-NMR ($CDCl_3$): 19.17 (CH_3), 72.78 (OCH_2), 112.99 (=C), 114.71 (C-5'), 117.43 (C-4), 119.67 (C-7), 125.98 (C-2'), 126.81 (C-8' and C-12'), 127.44 (C-10'), 128.46 (C-6), 128.90 (C-9' and C-11'), 129.51 (C-6'), 130.61 (C-3'), 132.67 (C-5), 134.36 (C-1'), 139.22 (C-7'), 139.80 (C=), 143.32 (C-7a), 145.13 (C-3a), 151.90 (C-4'). Anal. Calcd for $C_{22}H_{18}ClN_3O$: C, 70.30; H, 4.83; N, 11.18. Found: C, 70.12; H, 5.04; N, 10.96.

5-Methoxy-2-{ 4-[2-methyl-2-propen-1-yl]-3-biphenylyl} -2*H*-1,2,3-benzotriazole (**2c**).

Yield: 70%, light yellow crystals; m.p.: 115-116 ^{o}C; TLC: R_f =0.44 (hexane-EtOAc 4:1); ^{1}H-NMR ($CDCl_3$): 1.71 (s, 3H, CH_3), 3.91 (s, 3H, OCH_3), 4.55 (s, 2H, OCH_2), 4.91 (s, 1H, $=CH_2$), 5.01 (s, 1H, $=CH_2$), 7.34 (t, J= 7.5 Hz, 1H, C_{10}'-H), 7.39 (dd, J= 9.1 and 1.5 Hz, 1H, C_6-H), 7.43 (t, J= 7.5 Hz, 2H, C_9'-H and C_{11}'-H), 7.59 (d, J= 8.1 Hz, 2H, C_8'-H and C_{12}'-H), 7.70 (dd, J= 8.7 and 2.1 Hz, 1H, C_6'-H),7.92 (d, J= 9.1 Hz, 1H, C_7-H), 7.93 (s, 1H, C_3'-H), 7.97 (s, 1H, C_4-H); ^{13}C-NMR ($CDCl_3$): 19.17 (CH_3), 55.54 (OCH_3), 72.76 (OCH_2), 112.99 (=C), 117.43 (C-4), 119.67 (C-7), 125.98 (C-2'), 126.81 (C-8' and C-12'), 127.44 (C-10'), 128.90 (C-9' and C-11'),129.51 (C-6'), 130.61 (C-3'), 133.62 (C-1'), 134.36 (C-5'), 139.22 (C-7'), 139.80 (C=), 143.32 (C-7a), 145.13 (C-3a), 151.90 (C-4'). Anal. Calcd for $C_{23}H_{21}N_3O_2$: C, 74.37; H, 5.70; N, 11.31. Found: C, 74.21; H, 5.50; N, 11.11,

4.2 General procedure for the synthesis of **3a-c** by thermal rearrangement

A solution of compound **3** (30 mmol) in *N*,*N*-diethylbenzeneamine (50 ml) was heated under reflux for 4 h. After cooling, the mixture was treated with aqueous HCl (15 %, 50 ml) and then extracted three times with CH_2Cl_2 (50 ml each). The combined organic extracts were dried ($MgSO_4$), and concentrated to give a solid residue which was crystallized from hexane.

The following products were thus prepared:

2-(2*H*-1,2,3 benzotriazol-2-yl)-4-cyclohexyl-6-(2-methyl-2-propen-1-yl)phenol (**3a**).

Yield: 94%, white crystals; m.p.: 125-127^{o}C; TLC: R_f =0.9 (hexane-acetone 5:2); ^{1}H-NMR ($CDCl_3$): 1.29 (m, 1H, C_4"-H), 1.40 (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), 2.55 (m, 1H, C_1"-H), 3.49 (s, 2H, CH_2), 4.74 (s, 1H, $=CH_2$), 4.86 (s, 1H, $=CH_2$), 7.09 (d, J= 1.7 Hz, 1H, C_5-H), 7.46 (dd, J= 6.5 and 3.0 Hz, 2H, C_5'-H and C_6'-H), 7.92 (dd, J= 6.5 and 3.0 Hz, 2H, C_4'-H and C_7'-H), 8.13 (d, J= 1.9 Hz, 1H, C_3-H), 11.42 (s, 1H, OH); ^{13}C-NMR ($CDCl_3$): 22.55 (CH_3), 26.11 (C-4"), 26.90 (C-3" and C-5"), 34.60 (C-2" and C-6"), 38.05 (CH_2), 43.78 (C-1"), 111.58 (=C), 117.19 (C-3), 117.61 (C-4' and C-7'), 124.88 (C-2), 127.53 (C-5' and C-6'), 129.26 (C-6), 130.24 (C-5), 139.39 (C-4), 142.75 (C-3a' and C-7a'), 144.56 (C=), 146.04 (C-1). Anal. Calcd for $C_{22}H_{25}N_3O$: C, 76.05; H, 7.25; N, 12.09. Found: C,75.93; H, 7.14; N, 11.96.

3-(5-Chloro-2*H*-1,2,3-benzotriazol-2-yl)-5-(2-methyl-2-propen-1-yl)-4-biphenylol (**3b**).

Yield: 88%, light yellow crystals; m.p.: 138-139 ^{o}C; TLC: R_f =0.87 (hexane-acetone 5:2); ^{1}H-NMR ($CDCl_3$): 1.83 (s, 3H, CH_3), 3.56 (s, 2H, CH_2), 4.79 (s, 1H, $=CH_2$), 4.89 ((s, 1H, $=CH_2$), 7.35 (t, J= 7.4 Hz, 1H, C_{10}-H), 7.42 (dd, J= 9.2 and 1.6 Hz, 1H, C_6'-H), 7.44 (t, J= 7.5 Hz, 2H, C_9-H and C_{11}-H), 7.50 (d, J= 1.8 Hz, 1H, C_6-H), 7.65 (d, J= 7.5 Hz, 2H, C_8-H and C_{12}-H), 7.87 (d, J= 9.0 Hz, 1H, C_7'-H), 7.91 (d, J= 1.2 Hz, 1H, C_4'-H), 8.51 (d, J= 2.2 Hz, 1H, C_2-H), 11.40 (s, 1H, OH); ^{13}C-NMR ($CDCl_3$): 22.56 (CH_3), 38.04 (CH_2), 111.98 (=C), 116.67 (C-4'), 117.76 (C-2), 118.82 (C-7'), 125.20 (C-3), 126.80 (C-8 and C-12), 127.22 (C-10), 128.85 (C-9 and C-11), 129.32 (C-3), 130.23 (C-5), 130.33 (C-6), 132.80 (C-1), 133.67 (C-5'), 139.81 (C-7), 141.33 (C-7a'), 143.15 (C-3a'), 144.15 (C=), 147.46 (C-4). Anal. Calcd for $C_{22}H_{18}ClN_3O$: C, 70.30; H, 4.83; N, 11.18. Found: C, 70.08; H, 4.64; N, 11.06.

3-(5-Methoxy-2*H*-1,2,3-benzotriazol-2-yl)-5-(2-methyl-2-propen-1-yl)-4-biphenylol (**3c**).

Yield: 50%, yellow crystals; m.p.: 125-126 ^{o}C; TLC: R_f =0.75 (hexane-EtOAc 4:1); ^{1}H-NMR ($CDCl_3$): 1.84 (s, 3H, CH_3), 3.56 (s, 2H, CH_2), 3.91 (s, 3H, OCH_3), 4.80 (s, 1H, $=CH_2$), 4.88 (s, 1H, $=CH_2$), 7.11 (C_4'-H), 7.14 (d, J= 9.2 Hz, 1H, C_6'-H), 7.34 (t, J= 7.5 Hz, 1H, C_{10}-H), 7.43 (t, J= 7.8 Hz, 2H, C_9-H and C_{11}-H), 7.46 (s, 1H, C_6-H), 7.66 (d, J=

7.5 Hz, 2H, C_8-H and C_{12}-H), 7.77 (d, J= 9.2 Hz, 1H, C_7'-H), 8.48 (s, 1H, C_2-H), 11.60 (s, 1H, OH); ^{13}C-NMR ($CDCl_3$): 22.57 (CH_3), 38.07 (CH_2), 55.67 (OCH_3), 94.21 (C-4'), 111.88 (=C), 117.33 (C-2), 118.45 (C-7'), 122.91 (C-6'), 126.82 (C-8 and C-12), 127.07 (C-10), 128.79 (C-9 and C-11), 129.41 (C-6), 129.94 (C-5), 132.57 (C-1), 139.00 (C-7a'), 140.08 (C-7), 143.92 (C-3a'), 144.33 (C=), 147.12 (C-4), 159.81 (C-5'). Anal. Calcd for $C_{23}H_{21}N_3O_2$: C, 74.37; H, 5.70; N, 11.31. Found: C, 74.11; H, 5.53; N, 11.15.

4.3 General procedure for the synthesis of compounds **4**

To a stirred solution of compound **3** (3 mmol) in xylene (20 ml) were added 1,1,1,3.5,5,5-heptamethyltrisiloxane (1 g, 4.5 mmol) and Karlstedt catalyst (10 drops), and the resulting mixture was heated at 100 ^{o}C for 8 h. After cooling, the solvent was evaporated in vacuo and the residue was purified by column chromatography.

The following products were thus prepared:

2-(2*H*-1,2,3-Benzotriazol-2-yl)-4-cyclohexyl-6-(2-methyl-3-{1,3,3,3-tetramethyl-1-[trimethylsilyl-oxy]disiloxanyl)propyl}phenol (**4a**).

Yield: 66%, yellow oil; TLC: R_f =0.78 (hexane-acetone 5:0.1); IR (KBr): 1471, 1250, 1142, 1037 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 0.08 (s, 3H, CH_3), 0.11 (s, 18H, 6 CH_3), 0.51 (dd, J= 14.8 and 9.3 Hz, 1H, C_3'''-H), 0.74 (dd, J= 14.8 and 4.5 Hz, 1H, C_3'''-H), 1.02 (d, J= 6.6 Hz, 3H, C_3''-H), 1.33 (m, 1H, C_4''-H), 1.44 (m, 2H, C_3''-H and C_5''-H), 1.52 (m, 2H, C_2''-H and C_6''-H), 1.80 (m-d, J= 12.5 Hz, 2H, C_4''-H), 1.90 (m-d, J= 12.5 Hz, 2H, C_3''-H), 1.97 (m-d, J= 12.5 Hz, 2H, C_2''-H and C_6''-H), 2.16 (m, 1H, C_2'''-H), 2.58 (m, 1H, C_1''-H), 2.65 (dd, J= 13.1 and 7.9 Hz, 1H, C_1'''-H), 2.78 (dd, J= 13.1 and 6.3 Hz, 1H, C_1'''-H), 7.07 (d, J= 1.6 Hz, 1H, C_5-H), 7.49 (dd, J= 6.6 and 3.0 Hz, 2H, C_5'-H), 7.96 (dd, J= 6.6 and 3.0 Hz, 2H, C_4'-H and C_7'-H), 8.13 (d, J= 1.6 Hz, 1H, C_3-H), 11.34 (s, 1H, OH); ^{13}C-NMR ($CDCl_3$): 0.82 (CH_3), 1.86 (CH_3), 22.51 (CH_3), 26.04 (C-3'''), 26.12 (C-4''), 26.90 (C-5''), 29.26 (C-2''), 34.62 (C-2'' and C-6''), 41.22 (C-1'''), 43.78 (C-1''), 116.78 (C-3), 117.60 (C-4' and C-7'), 124.79 (C-2), 127.41 (C-5' and C-6'), 130.77 (C-5), 131.34 (C-6), 138.96 (C-4), 142.72 (C-3a and C-7a), 146.15 (C-1). Anal. Calcd for $C_{29}H_{47}N_3O_3Si_3$: C, 61.00; H, 8.31; N, 7.37. Found: C, 59.89; H, 8.22; N, 7.16.

3-(5-Chloro-2*H*-1,2,3-benzotriazol-2-yl)-5-(2-methyl-3-{1,3,3,3-tetramethyl-1-[trimethylsilyl oxy]-disiloxanyl}propyl)-4-biphenylol (**4b**).

Yield: 68%, yellow oil; TLC: R_f =0.62 (hexane-acetone 5:0.1); IR (KBr): 1475, 1255, 1033, 849 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 0.10 (s, 9H, 3 CH_3), 0.14 (s, 3H, CH_3), 0.15 (s, 3H, CH_3), 0.58 (dd, J= 14.8 and 9.2 Hz, 1H, C_3''-H), 0.81 (dd, J= 14.8 and 4.6 Hz, 1H, C_3''-H), 1.08 (d, J= 6.9 Hz, 3H, CH_3), 2.25 (m, 1H, C_2''-H), 2.73 (dd, J= 13.2 and 8.3 Hz, 1H, C_1''-H), 2.90 (dd, J= 13.2 and 6.2 Hz, 1H, C_1''-H), 7.40 (t, J= 7.3, 1H, C_{10}-H), 7.44 (dd, J= 9.0 and 1.1 Hz,1H, C_6'-H), 7.50 (m, 3H, C_6-H, C_9-H, and C_{11}-H), 7.70 (d, J= 7.6 Hz, 2H, C_8-H and C_{12}-H), 7.89 (d, J= 9.0 Hz, 1H, C_7'-H), 7.95 (s,1H, C_4'-H), 8.51 (d, J= 1.8 Hz, 1H, C_2-H), 11.61 (s, 1H, OH); ^{13}C-NMR ($CDCl_3$): 0.87 (CH_3), 1.88 (CH_3), 22.48 (CH_3), 26.16 (C-3''), 29.27 (C-2''), 41.26 (C-1''), 117.34 (C-2), , 118.75 (C-7'), 125.09 (C-3), 126.76 (C-8 and C-12), 127.09 (C-10), 128.78 (C-9 and C-11), 129.14 (C-6'), 130.85 (C-6), 132.24 (C-5), 132.42 (C-1), 133.51 (C-5'), 139.96 (C-7), 141.25 (C-7a'), 143.08 (C-3a'), 147.59 (C-4). Anal. Calcd for $C_{29}H_{40}ClN_3O_3Si_3$: C, 58.21; H, 6.74; N, 7.02. Found: C, 57.94; H, 6.52; N, 7.15.

3-(5-Methoxy-2*H*-1,2,3-benzotriazol-2-yl)-5-(2-methyl-3-{1,3,3,3-tetramethyl-1-[trimethylsilyl oxy]disiloxanyl}propyl)-4-biphenylol (**4c**).

Yield: 45%, yellow crystals; m.p.: 56-59 ^{o}C; TLC: R_f =0.52 (hexane-EtOAc 5:2); ^{1}H-NMR ($CDCl_3$): 0.11 (s, 3H, CH_3), 0.12 (s, 9H, 3 CH_3), 0.13 (s, 9H, 3 CH_3), 0.57 (dd, J= 14.8 and 9.2 Hz, 1H, C_3''-H), 0.80 (dd, J= 14.8 and 4.6 Hz, 1H, C_3''-H), 1.06 (d, J= 6.5 Hz, 3H, CH_3), 2.24 (m,1H, C_2''-H), 2.72 (dd, J= 13.2 and 8.2 Hz, 1H, C_1''-H), 2.90 (dd, J= 13.2 and 6.2 Hz, 1H, C_1''-H), 3.96 (s, 3H, OCH_3), 7.18 (dd, J= 8.9 and 1.6 Hz, 1H, C_6'-H), 7.38 (t, J= 7.3, 1H, C_{10}-H), 7.45 (s, 1H, C_6-H), 7.49 (m, 2H, C_9-H and C_{11}-H), 7.71 (d, J= 7.5 Hz, 2H, C_8-H and C_{12}-H), 7.83 (d, J= 9.1 Hz, 1H, C_7'-H), 8.49 (d, J= 2.0 Hz, 1H, C_2-H), 11.54 (s, 1H, OH); ^{13}C-NMR ($CDCl_3$): 0.84 (CH_3),, 1.87 (6 CH_3), 22.49 (CH_3), 26.18 (C-3''), 29.28 (C-2''), 41.27 (C-1''), 94.22 (C-4'), 116.96 (C-2), 118.43 (C-7'), 122.76 (C-6'), 126.81 (C-8 and C-12), 128.73 (C-9 and C-11), 131.96 (C-5), 132.23 (C-1), 138.96 (C-7a'), 140.24 (C-7), 143.88 (C-3a'), 147.26 (C-4), 159.72 (C-5). Anal. Calcd for $C_{30}H_{43}N_3O_4Si_3$: C, 60.67; H, 7.30; N, 7.07. Found: C, 60.89; H, 7.02; N, 7.18.

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