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A General Synthesis of 1-(1-Alkenyl)benzotriazoles

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Abstract: 1-Methyl, 1-(alkoxymethyl) and 1-(trimethylsilylmethyl)benzotriazoles are metallated at the α-carbon. Trapping of the resulting metallated species with chlorotrimethylsilane gives compounds which undergo Peterson olefination even with hindered ketones. In some cases, metallation at the 4-position of the benzotriazole is observed. An exhaustive metallation/silylation sequence gives 4-trimethylsilyl substituted 1-benzotriazoles in good yields. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Benzotriazoles; Metallation; Olefination; Silicon and compounds.

INTRODUCTION

1-(1-Alkenyl)benzotriazoles have been widely used in the preparation of important structural templates such as pyrrolo[2,3-d]pyrimidines[1] (found in various nucleoside antibiotics isolated from strains of *Streptomyces*), carbazoles[2,3] and indoles.[4-6] This versatility has also made them key intermediates in the synthesis of natural products.[7-9] The photo-induced conversion of 1-(1-alkenyl)benzotriazoles to indoles, reported by Wender,[6] provides a recent example of this approach. This conversion was of particular interest to us because a necessary key step in our synthesis of gelsemine[8,9] was the conversion of a ketone to a spiro oxindole. A variety of methods had been tried but with no success, possibly because of the severe steric congestion at the reaction centre. It was noted that a possible variation of Wender's indole synthesis might lead to the formation of oxindoles after chemical manipulation of the product obtained from the photolysis of carefully designed 1-(1-substituted-1-alkenyl)benzotriazoles. However, a search of the literature for methods of synthesising the substrates required, showed that despite their many applications, there was no general synthesis of 1-(1-alkenyl)benzotriazoles. The first route to 1-(1-alkenyl)benzotriazoles was developed by Rees and Storr[10] and involved the dehydrohalogenation of the product from the reaction of 1-chlorobenzotriazole and an olefin. However, this mild and simple approach yielded a mixture of 1-(1-alkenyl)- and 2-(1-alkenyl)benzotriazoles in which the latter predominated. Later, Märky *et al.*[11] developed an alternative route which comprised the preparation of 1-allylbenzotriazoles and the subsequent base-catalysed isomerisation to 1-(1-alkenyl)benzotriazoles. The scope of this methodology is limited by the range of allyl halides available and furthermore leads to a mixture of *E*- and *Z*-isomers. A markedly improved approach to 1-(1-

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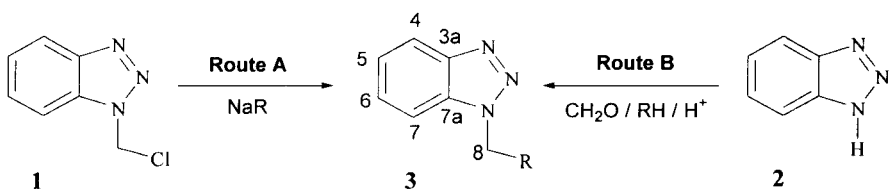
alkenyl)benzotriazoles reported by Katritzky *et al.*[12-14] involved a Wittig reaction between the triphenylphosphonium salt derived from 1-chloromethylbenzotriazole and a range of aldehydes. The stereoselectivity of this route (*trans* adduct isolated exclusively) was offset by the modest yields obtained in all but one case. More recently, Katritzky *et al.*[15] developed a methodology for the transformations of aldehydes and ketones to one-carbon homologated carboxylic acids based upon 1-(1-alkenyl)benzotriazoles. A few years ago, we reported[16] an efficient preparation of 1-adamantylidenemethyl-1*H*-benzotriazole by means of a Peterson reaction. It was found that this compound is easily lithiated and that the lithio derivative reacts with a wide range of electrophiles to give new 1-(1-alkenyl)benzotriazoles. This method is particularly efficient for preparing 1-(1-alkenyl)benzotriazoles with alkylthio- and other heteroatom substituents, which were difficult to prepare by conventional methods. We now wish to report in detail the results of our more general exploration of the Peterson olefination route to 1-(1-alkenyl)benzotriazoles.

RESULTS AND DISCUSSION

This route was established independently by our group[17] and Katritzky and co-workers.[12,18] The synthesis of 1-(1-alkenyl)benzotriazoles was achieved by means of a Peterson reaction of a ketone with the lithio derivatives of suitably functionalised benzotriazolyl compounds, such as **4** and **8**. Such compounds were obtained by two different routes. 1-Alkoxymethyl-1*H*-benzotriazoles and 1-aryloxymethyl-1*H*-benzotriazoles made from primary alcohols and phenols were synthesised by a method devised by Burckhalter and co-workers,[19] which involves the nucleophilic substitution reaction of 1-chloromethylbenzotriazole **1** with an alkoxide or aryloxide anion (route A, Scheme 1).

A different procedure (route B), originally reported by Katritzky and co-workers,[20] was used in the case of secondary and tertiary alcohols since the original method gave poor yields probably because of the reduced nucleophilicity and greater basicity of the more hindered alkoxide anions. Both routes yielded **3** in average to good yields (Table 1).



Scheme 1

In order to prepare the silyl precursors required for the Peterson reaction, we were greatly helped by the property of the benzotriazolyl moiety to strongly stabilise a negative charge on the adjacent carbon atom.[12,17,21,22] In an attempted preparation of **3j** from sodium benzotriazolate and trimethylsilylmethylchloride, 1-methyl-1*H*-benzotriazole and 2-methyl-2*H*-benzotriazole were also isolated. It was thought that these by-products had

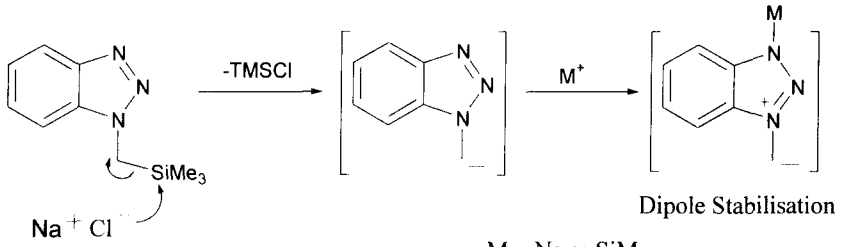
Table 1

Preparation of 1-alkoxy- and 1-aryloxymethyl-1H-benzotriazoles **3**

Entry	Route	R	Yield (%)	Entry	Route	R	Yield (%)
3a	A	OCH_3	90	**3g**	B	O^tBu	76
3b	A	OCD_3	51	**3h**	B	O^iPr	80
3c	A	OC_6H_5	85	**3i**	B	OC_6H_{11}	73
3d	A	$C_7H_7O_2$ [a]	69	**3j**	--	TMS	53
3e	A	OC_9H_{11} [b]	77	**3k**	B	OC_2H_5	77
3f	A	S^tBu	95				

[a] $C_7H_7O_2$ = 4-$MeOC_6H_4O$; [b] OC_9H_{11} = 2,4,6-$(CH_3)_3C_6H_2O$

arisen by chloride ion-induced desilylation, as shown in Scheme 2.



M = Na or $SiMe_3$

Scheme 2

The facility of this process suggests that the benzotriazolyl moiety is stabilising the carbanion formed, perhaps through dipole stabilisation as depicted in Scheme 2. Further experimentation showed that methylene or methine groups at the 8-position (see structure **3** for numbering) can be readily metallated by LDA or *n*-butyllithium and that the metallated species can be trapped with electrophiles, thus providing direct evidence for this stabilisation. For example, on addition of **3** to LDA at -78°C in THF, the anion was readily formed as indicated by the deep blue colour of the solution. Subsequent trapping of the carbanion with TMSCl at -78°C afforded **4** in moderate to good yields, with the yields decreasing with greater steric bulk in the alkoxy group (Scheme 3, Table 2).

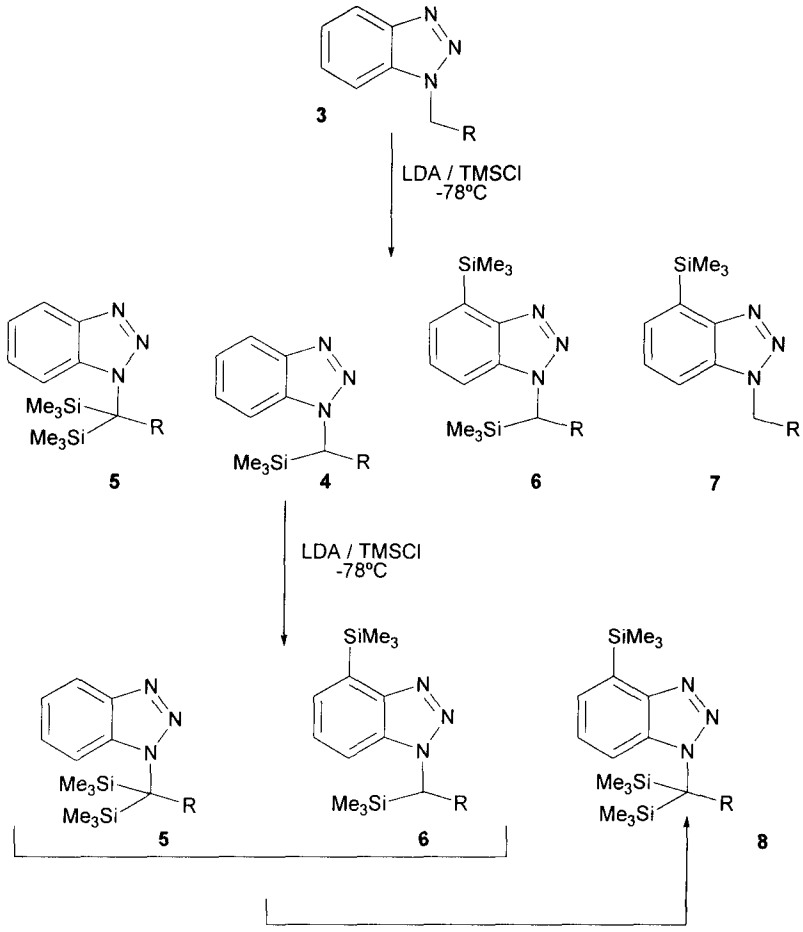
Interestingly, in the cases of R= OCH_3 and R= OCD_3, di-silylated products **5** were isolated, showing that the remaining methine proton on the carbon adjacent to the benzotriazolyl moiety is fairly acidic. However, when the steric bulk increases around this position, the *gem* di-silylation process did not take place and instead products silylated at the 4-position such as **6** and **7**, were formed. It had been anticipated that metallation might occur at the 7-position because of the directing effect of the oxygen atom of the alkoxy group. However, interpretation of the aromatic region of the NMR spectra, assisted by studies reported by Rondeau *et al.*[23] suggested that lithiation and subsequent silylation had occurred at the 4-position. Later, an X-ray structure of a

Table 2
Silylation experiments.

Entry	R	4(%)	5(%)	6(%)	7(%)	8(%)	Entry	R	4(%)	5(%)	6(%)	7(%)	8(%)
3a	OCH_3	79	4	2	--	--	**3l**	OC_2D_5	81	--	--	--	--
3b	OCD_3	81	3	2	--	--	**4a**	OCH_3	21	76[c]	--	--	10
3c	OC_6H_5	86	--	3	--	--	**4b**	OCD_3	17	46	18	--	10
3d	$C_7H_7O_2$[a]	69	--	--	--	--	**4c**	OC_6H_5	20	36	2	--	1
3e	OC_9H_{11}[b]	44	--	8	--	--	**5a,6a**[d]	OCH_3	--	--	--	--	78
3f	S^tBu	80	--	10	--	--	**5b**[d]	OCD_3	--	--	--	--	86
3g	O^tBu	46	--	5	12	--	**5c**[d]	OC_6H_5	--	--	--	--	68
3h	O^iPr	54	--	6	2	--	**4g**[d]	O^tBu	--	--	91	--	--
3i	OC_6H_{11}	34	--	6	2	--	**4j**[d]	TMS	--	44	--	--	41
3j	TMS	83	--	3	--	--	**5j**[d]	TMS	--	--	--	--	84
3k	OC_2H_5	44	--	--	--	--							

[a] $C_7H_7O_2$ = 4-$MeOC_6H_4O$; [b] OC_9H_{11} = 2,4,6-$(CH_3)_3C_6H_2O$; [c] combined yield of **5a** and **6a**; [d] exhaustive metallation/silylation process.

product obtained from the photolysis of **10a**[24,25] provided irrefutable evidence that metallation takes place at the 4-position rather than the 7-position. There have been few reports of such metallation of the benzenoid ring of a fused heterocyclic system directed by a nitrogen atom of the adjacent heteroaromatic ring.[26,27] Intrigued by the formation of 4-TMS substituted benzotriazolyl derivatives and the possibility previously noted by Barrett and co-workers[28] that 4-TMS indoles could be intermediates in the synthesis of ergot alkaloids, we decided to explore ways of preparing such compounds in an efficient manner. A single stage metallation/silylation of **4** was initially conducted, leading to a mixture of di-silylated and tri-silylated products (Scheme 3, Table 2). Although an acidic proton remains on the methine carbon at the 8-position, it was thought that metallation at the 4-position would be favoured owing to the steric hindrance at the 8-position caused by the presence of the TMS group. In practice, very little 4-TMS substituted product was formed from **4a**, **4b** or **4c**. It seems that the congestion at the 8-position is not as great as was supposed. This result can also be interpreted as a measure of the lower acidity of the proton at the 4-position in comparison with the one at the 8-position. In order to maximise silylation at the 4-position, it was decided to conduct exhaustive metallation/silylation reactions *i.e.* a one-pot method comprising three successive additions of *n*-butyllithium and TMSCl to substrates **5** and diisopropylamine (Scheme 3). As shown in Table 2, excellent yields of product **8** were obtained. The method devised to prepare **8** from **4** is high yielding, since the partially silylated products generated *en route* , such as **5**



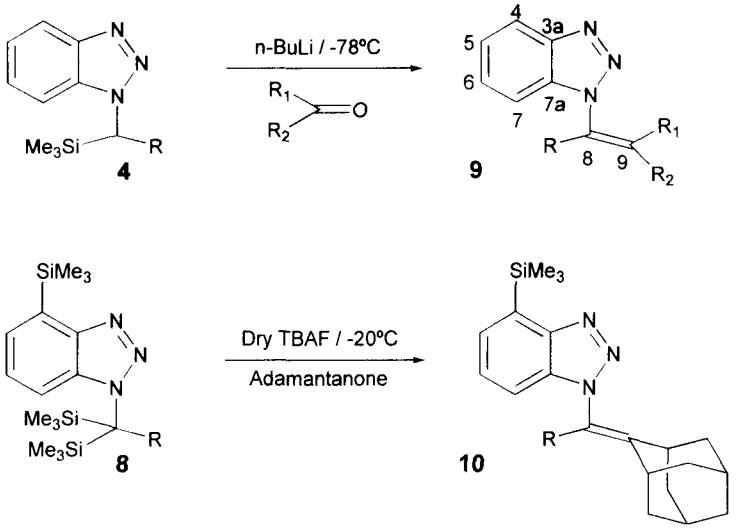
SCHEME 3

Scheme 3

and **6**, are further silylated in subsequent repetitions. In this manner, **8a** and **8b** were prepared in overall yields of 63% (87% based on recovered starting material) and 70% (83% based on recovered starting material) respectively from the corresponding starting materials **4a** and **4b**. The exhaustive silylation of **4g** afforded **6g** in the excellent yield of 91%, probably due to the steric bulk of the *tert*-butyl group prohibiting a second silylation at the 8-position. One astonishing result was the preparation of the tetrakis-trimethylsilyl compound **8j** in an overall yield of 78% from **4j**, *via* compound **5j**.

Having developed a high-yielding route to the substrates required, we carried out an investigation into the preparation of 1-(1-alkenyl)benzotriazoles by the Peterson reaction. Initially, the use of LDA as the base to initiate the Peterson olefination reaction gave unclean reactions with only moderate yields of alkenes. The use

of *n*-butyllithium proved crucial and in most cases afforded alkenes in excellent yields from adamantanone and



Scheme 4

Table 3
Peterson olefination reaction experiments.

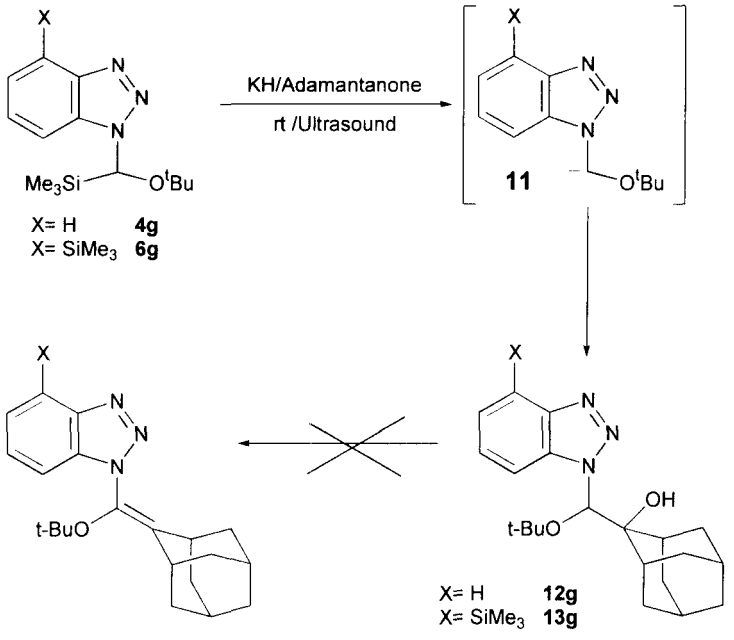
Entry	R	Ketone	Product	Yield (%)	Entry	R	Ketone	Cpd	Yield (%)
4a	OCH_3	Ad	**9a**	80[d]	**4k**	OC_2H_5	Ad	**9k**	89[c]
4b	OCD_3	Ad	**9b**	95[c]	**4l**	OC_2D_5	Ad	**9l**	85[c]
4c	OC_6H_5	Ad	**9c**	69[c]	**4a**	OCH_3	C	**9m**	86[c]
4d	$C_7H_7O_2$[a]	Ad	**9d**	45[c]	**4a**	OCH_3	B	**9n**	49[c]
4e	OC_9H_{11}[b]	Ad	**9e**	--	**4a**	OCH_3	Acp	**9o**	78[c]
4f	S^tBu	Ad	**9f**	--	**8a**	OCH_3	Ad	**10a**	72[e]
4g	O^tBu	Ad	**9g**	--	**8b**	OCD_3	Ad	**10b**	71[e]
4h	O^iPr	Ad	**9h**	66[c]	**8c**	OC_6H_5	Ad	**10c**	46[e]

[a] $C_7H_7O_2$ = 4-$MeOC_6H_4O$; [b] OC_9H_{11} = 2,4,6-$(CH_3)_3C_6H_2O$; [c] use of *n*-butyllithium as the base; [d] use of LDA as the base; [e] use of TBAF.
Ad = adamantanone; Acp = acetophenone; B = benzophenone; C = cyclohexanone.

various other ketones (Scheme 4, Table 3).

Unfortunately, sterically hindered substrates such as **4e**, **4f** and **4g** did not give any of the corresponding alkenes by this method. The use of potassium hydride as a replacement for *n*-butyllithium yielded the alcohols **12g** and **13g** (from **4g** and **6g** respectively) (Scheme 5). In all our attempts, no compounds silylated at the 8-position were isolated, indicating that the first step of this protocol (formation of intermediate **11**) does take place. In the case of **4g**, the desilylated starting material **3g** was obtained alongside **12g**, suggesting that the

formation of the latter proceeds *via* the carbanion intermediate **11** (Scheme 5), generated by nucleophilic attack



Scheme 5

on the TMS group. Attempts to dehydrate **13g** by a wide variety of dehydrating methods, such as dry DMSO at 180°C,[29] *p*-toluenesulphonic acid supported on silica gel in benzene at 80°C,[30] the Burgess reagent[31-33] and treatment with triflic anhydride in the conditions reported by Ikegami and co-workers[34] were unsuccessful. After considerable effort, the syntheses of **9g** was and other sterically hindered olefins such as **9f** were achieved by reaction of 1-(adamantylidenemethyl)-1*H*-benzotriazole and the appropriate electrophile in the presence of $MgBr_2$ and *n*-butyllithium.[16]

In order to prepare 4-TMS substituted 1-(1-alkenyl)benzotriazoles, the method previously described needed to be modified. Since no hydrogens were present at the position adjacent to the benzotriazolyl group, the anion required to induce the Peterson olefination reaction could not be generated in the usual way. A search of the literature revealed that Ogata and Shimizu[35] had achieved a high yielding fluoride-catalysed Peterson reaction of 1-[bis(trimethylsilyl)methyl]-1,2,4-triazole with various carbonyl compounds. Our initial attempts following this protocol were conducted with **5a** and **5c** and adamantanone in the presence of a catalytic amount of TBAF. The olefins **9a** and **9c** were isolated in yields of 64% and 26% respectively, along with substantial amounts of **3a** and **3c** respectively. These yields were considerably lower than those recorded for these substrates by our original method. These disappointing results were attributed to the fact that TBAF, purchased from Aldrich as a 1.0 M solution in THF, has a water content of approximately 5%. We therefore decided to use an 'anhydrous' source of fluoride, obtained by drying TBAF according to the procedure described by Cox and co-workers.[36] The use of TBAF 'freshly dried' by this method afforded alkenes **10** in average to good yields, with small

amounts of side-products **7** (Scheme 4, Table 3).

CONCLUSION

We have devised a general route to 1-(1alkenyl)benzotriazoles involving the transformation of silylated substrates into olefins according to a Peterson olefination process. The silylated reagents were obtained by metallation/silylation of compounds **3**. This was rendered possible by the property of the benzotriazolyl moiety to stabilise a negative charge adjacent to it, probably by dipole-stabilisation as illustrated in Scheme 2. Interestingly, the silylation of substrates **3** bearing small R groups (such as **3a** and **3b**) yielded a *gem* di-silylated side-product **5** as well as the main product **4** and one other di-silylated compound **6**, with a TMS group attached at the 4-position. In the presence of bulky R groups, **6** was the only di-silylated product isolated alongside **4**. The efficiency of the repetitive metallation/silylation process introduces a TMS group at the 4-position of the benzenoid ring. This opens these substrates to a whole range of useful and important chemical manipulations.[37]

EXPERIMENTAL

Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded on GE QE-300 MHz and Bruker WP4W 400MHz spectrometers unless otherwise indicated. Chemical shifts are reported in part per million (δ) relative to TMS (δ 0.0 ppm) in ^{1}H NMR and $CDCl_3$ (middle peak of triplet δ 77.0 ppm) in ^{13}C NMR. The structures **3** and **9** carry the numbering system referred to in ^{1}H and ^{13}C data. Infrared (IR) spectra were recorded on a Philips PU 9706 instrument as solutions in dichloromethane. Ultraviolet (UV) spectra were recorded on a PYE Unicam PU 8800. Mass spectra and accurate masses were obtained on a 70 eV VG Autospec mass spectrometer. Microanalyses were determined by using a Carlo Erba Elemental Analyser MOD 1106. All the melting points were measured on a Kofler hot stage microscope. Two varieties of silica gel were used in column chromatography purifications: Merck Kieselgel Silica gel 60G and Merck Flash Silica (230-400 mesh). The light petroleum used for column chromatography has a boiling range of 40-60°C. Trimethylsilylchloride and diisopropylamine were distilled from calcium hydride, *N,N*-dimethylformamide was distilled from and stored over 4Å molecular sieves. The purity of *n*-butyllithium was estimated by titration using diphenylacetic acid.[38] 1-Chloromethyl-1*H*-benzotriazole **1** was prepared according to the procedure reported by Burckhalter *et al.*[19] The following compounds were obtained according to procedures previously reported: 1-Methoxy-1*H*-benzotriazole (3a),[39] 1-Trimethylsilylmethyl-1*H*-benzotriazole (3j).[12,16]

***1-Trideuteriomethoxymethyl-1H-benzotriazole* (3b).** Route A. D_4-methanol (10 g, 11.26 ml) was introduced into a dry flask, under a dry nitrogen atmosphere. Sodium (3 g) was added and then dry DMF (80 ml). The reaction mixture was stirred overnight, at 50°C, under nitrogen atmosphere before **1** (4.36 g, 26 mmol) was added and the reaction mixture was stirred at 50°C for 4 h. After cooling, water (300 ml) and ether (100 ml) were added. The aqueous layer was extracted with ether (3x70 ml) and the combined ethereal extracts washed with water (5x50 ml), brine (2x50 ml), dried with $MgSO_4$ and filtered. Removal of the solvent under reduced

pressure gave an oil. Purification by column chromatography, using flash silica and elution with 50/50 ether/light petroleum gave **3b** (2.2g, 51%); microcrystals; mp 30-32°C; ^{1}H NMR (90 MHz; $CDCl_3$) 7.97 (1H, d, J = 8 Hz, H-4), 7.66-7.16 (3H, m, H-5, H-6, H-7), 5.82 (2H, s, H-8); ^{13}C NMR (22.5 MHz; $CDCl_3$) 146.02 (C-3a), 132.42 (C-7a), 127.57 (C-6), 124.00 (C-5), 119.55 (C-4), 109.50 (C-7), 74.82 (C-8); ν_{max} (dichloromethane)/cm^{-1} 2270, 2230 and 2080 (C-D), 1190, 1165, 1130, 1025, 870, 780; Anal. Calcd. for $C_8H_6D_3N_3O$: C, 57.8; H/D, 5.7; N, 25.3. Found: C, 57.75; H/D, 5.45; N, 25.5.

***1-Phenoxymethyl-1H-benzotriazole* (3c).**[39] Route A. Phenol (13 g, 13.8 mmol) was dissolved in dry DMF (10 ml) under a dry nitrogen atmosphere and sodium hydride (2.6 g of a 55% dispersion in mineral oil, 60 mmol) was added. The reaction mixture was stirred at 60°C for 4 h before **1** (1 g, 5.97 mmol) was added and the stirring was further continued at 60°C for 20 h. After cooling to room temperature, water (100 ml) was added, the reaction mixture was extracted with dichloromethane (3x100 ml) and the combined dichloromethane extracts were successively washed with a 2M NaOH solution (3x100 ml), water (3x50 ml), brine (2x50 ml), dried with $MgSO_4$ and filtered. Removal of the solvent under reduced pressure gave a light brown solid. Purification by column chromatography, using flash silica and elution with 50/50 ether/light petroleum gave **3c** (1.15 g, 85%); mp 67.0-69.5°C (lit.[39] mp 64°C). ^{1}H NMR and ^{13}C NMR data were identical to the ones reported.

***1-(4-Methoxyphenoxy)-methyl-1H-benzotriazole* (3d).**[39] Route A. Same procedure as the one used to prepare **3c** using 4-methoxyphenol (12 g, 10.3 mmol), dry DMF (10 ml), sodium hydride (2.5 g of a 55% dispersion in mineral oil, 57.3 mmol) and **1** (1 g, 5.97 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using flash silica and elution with 50/50 ether/light petroleum gave **3d** (1.06 g, 69%); microcrystals; mp 95.4-97.4°C (lit.[39] mp 96°C). ^{1}H NMR and ^{13}C NMR data were identical to the ones reported.

***1-(2,4,6-Trimethylphenoxy)-methyl-1H-benzotriazole* (3e).** Route A. Same procedure as the one used to prepare **3c** using 2,4,6-trimethylphenol (10 g, 10.3 mmol), dry DMF (15 ml), sodium hydride (2.0 g of a 55% dispersion in mineral oil, 45.8 mmol) and **1** (1 g, 5.97 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using flash silica and elution with 20/80 ether/light petroleum gave **3e** (1.24 g, 77%); microcrystals; mp 82.7-84.0°C; ^{1}H NMR (90 MHz; $CDCl_3$) 8.08 (1H, d, J = 9 Hz, H-4), 7.51-7.30 (3H, m, H-5, H-6, H-7), 6.77 (2H, s, *m*-H), 6.29 (2H, s, H-8), 2.26 (3H, s, *p*-Me), 1.95 (6H, s, *o*-Me); ^{13}C NMR (22.5 MHz, $CDCl_3$) 155.44 (*ipso*-C), 145.99 (C-3a), 134.29 (*p*-C), 133.01 (C-7a), 130.10 (*o*-C), 129.58 (*m*-C), 127.83 (C-6), 124.15 (C-5), 119.78 (C-4), 109.23 (C-7), 77.12 (C-8), 20.50 (*p*-Me), 15.86 (*o*-Me); ν_{max} (dichloromethane)/cm^{-1} 1495, 1460, 1220, 1170, 1150, 1135, 1040, 1000, 990; Anal. Calcd. for $C_{16}H_{17}N_3O$: C, 71.9; H, 6.4; N, 15.7. Found: C, 72.1; H, 6.45; N, 16.0.

***1-Tert-butylthiomethyl-1H-benzotriazole* (3f).** Route A. 2-Methyl-propane-2-thiol (31 ml, 28.0 mmol) was dissolved in dry DMF (25 ml), under a dry nitrogen atmosphere and sodium hydride (4.6 g of a 60% dispersion in mineral oil, 115 mmol) was added. The reaction mixture was stirred for 1 h at room temperature before **1** (2 g, 12 mmol) was added and then stirred for a further 6 h at 80°C. After cooling to room temperature, water

(100 ml) was added, the reaction mixture was extracted with dichloromethane (3x100 ml) and the combined dichloromethane extracts were successively washed with a 2M NaOH solution (3x100 ml), water (3x50 ml), brine (2x50 ml), dried with $MgSO_4$ and filtered. Removal of the solvent under reduced pressure gave a yellow oil. Purification by column chromatography, using flash silica and elution with 30/70 ether/light petroleum gave **3f** (2.5 g, 95%); Oil; ^{1}H NMR (300 MHz; $CDCl_3$) 8.05 (1H, d, J = 8 Hz, H-4), 7.75 (1H, d, J = 8 Hz, H-7), 7.50 (1H, t, J = 8 Hz), 7.40 (1H, t, J = 8 Hz) (H-5, H-6), 5.85 (2H, s, H-8), 1.25 (9H, s, *tert*-butyl); ^{13}C NMR (75 MHz; $CDCl_3$) 146.50 (C-3a), 132.03 (C-7a), 127.06 (C-6), 123.90 (C-5), 119.84 (C-4), 110.66 (C-7), 47.34 (C-8), 44.18 ($\underline{C}(CH_3)_3$), 30.55 ($3xCH_3$, (*tert*-butyl); ν_{max} (dichloromethane)/cm^{-1} 2960, 2900, 2860, 1450, 1365, 1220, 1150, 1070; Anal. Calcd. for $C_{11}H_{15}N_3S$: C, 59.70; H, 6.83; N, 18.99; S, 14.48. Found: C, 59.95; H, 6.95; N, 19.05; S 14.55.

***1-Tert-butoxymethyl-1H-benzotriazole* (3g).**[39] Route B. Formaldehyde gas, obtained upon the heating of paraformaldehyde (6 g), was bubbled through *tert*-butanol (20 ml) for 25 min, under a dry nitrogen atmosphere. To the then resulting cloudy solution, *tert*-butanol (10 ml), benzotriazole (5.95 g, 50 mmol), benzene (60 ml) and conc. sulphuric acid (5 drops) were added and the mixture was then heated under reflux using a Dean-Stark apparatus for 4 h. After cooling, the mixture was poured onto ice/water (100 ml) and made basic using a 2M NaOH solution, followed by extraction with ether (3x100 ml). The combined ethereal extracts were washed with brine (100 ml), dried with $MgSO_4$ and filtered. Removal of the solvent under reduced pressure gave a colourless oil. Purification by column chromatography, using flash silica and elution with 20/80 ether/light petroleum gave **3g** (7.83 g, 76%); Oil ; ^{1}H NMR (90 MHz; $CDCl_3$) 7.90 (1H, d, J = 8 Hz, H-4), 7.57 (1H, d, J = 8 Hz, H-7), 7.08 (2H, m, H-5, H-6), 5.90 (2H, s, C-8), 1.06 (9H, s, *tert*-butyl); ^{13}C NMR (22.5 MHz, $CDCl_3$) 145.50 (C-3a), 132.07 (C-7a), 126.88 (C-6), 123.24 (C-5), 118.77 (C-4), 109.69 (C-7), 75.16 ($O\underline{C}(CH_3)_3$), 71.07 (C-8), 26.97 ($3xCH_3$, (*tert*-butyl); ν_{max} (dichloromethane)/cm^{-1} 1615, 1500, 1450, 1395, 1370, 1320, 1240, 1190, 1145, 1130, 1090, 885, 785; HRMS Calcd. for $C_{11}H_{15}N_3O$: 205.1215(M^+). Found 205.1214.

***1-(2-propanoxy)-methyl-1H-benzotriazole* (3h).** Route B. Same procedure as the one used to prepare **3g** using 2-propanol (4 ml and 2 ml), benzotriazole (1.19 g, 10 mmol), benzene (12 ml) and conc. sulphuric acid (1 drop). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography using flash silica and elution with 20/80 ether/light petroleum gave **3h** (1.52 g, 80%); microcrystals; mp 73.5 - 74.5°C; ^{1}H NMR (90 MHz; $CDCl_3$) 7.95 (1H, d, J = 8 Hz, H-4), 7.69-7.15 (3H, m, H-5, H-6, H-7), 5.92 (2H, s, H-8), 3.65 (1H, m, isopropyl), 1.01 (6H, d, J 8, isopropyl); ^{13}C NMR (22.5 MHz, $CDCl_3$) 146.18 (C-3a), 132.55 (C-7a), 127.54 (C-6), 124.02 (C-5), 119.66 (C-4), 109.91 (C-7), 74.82 (C-8), 70.31 ($\underline{C}H(CH_3)_2$), 21.63 (($CH(\underline{C}H_3)_2$); ν_{max} (dichloromethane)/cm^{-1} 1385, 1375, 1180, 1170, 1150, 1125, 1080, 1000; Anal. Calcd. for $C_{10}H_{13}N_3O$: C, 62.8; H, 6.8; N, 22.0. Found: C, 62.9; H, 6.85; N, 22.2.

***1-Cyclohexanoxymethyl-1H-benzotriazole* (3i).** Route B. Same procedure as the one used to prepare **3g** using cyclohexanol (4 ml and 2.5 ml), benzotriazole (1.19 g, 10 mmol), benzene (12 ml) and conc. sulphuric acid (1

drop). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography using flash silica and elution with 20/80 ether/light petroleum gave **3i** (1.68 g, 73%); microcrystals; mp 62 - 64°C; ^{1}H NMR (90 MHz; $CDCl_3$) 7.90 (1H, d, J = 8 Hz, H-4), 7.56 (1H, d, J = 8 Hz, H-7), 7.41-7.07(2H, m, H-5, H-6), 5.88 (2H, s, H-8), 3.27 (1H, m, *ipso*-H), 1.73-0.84 (10H, m, cyclohexyl); ^{13}C NMR (22.5 MHz, $CDCl_3$) 145.91 (C-3a), 132.34 (C-7a), 127.22 (C-6), 123.75 (C-5), 119.34 (C-4), 109.72 (C-7), 75.75 (*ipso*-C), 74.48 (C-8), 31.39, 23.23, 24.97 (cyclohexyl); ν_{max} (dichloromethane)/cm^{-1} 1455, 1170, 1150, 1125, 1090, 1015, 1000, 775; Anal. Calcd. for $C_{13}H_{17}N_3O$: C, 67.5; H, 7.35; N, 18.2. Found: C, 67.45; H, 7.4; N, 18.2.

***1-(Methoxy-trimethylsilyl-methyl)-1H-benzotriazole* (4a).**[40] Dry diisopropylamine (1.54 ml, 11 mmol) was dissolved in dry THF (10 ml), under a dry nitrogen atmosphere and cooled to -78°C. *n*-BuLi (7.24 ml of a 1.45M solution in hexanes, 10.5 mmol) was added dropwise with stirring and the mixture was stirred at -78°C for 15 min, before **3a** (1.63 g, 10 mmol) in dry THF (2 ml) was added dropwise. The resulting reaction mixture was stirred for 55 min and TMSCl (6.35 ml, 50 mmol), in dry THF (6.35 ml, 1:1 mixture), was added. The reaction mixture was stirred for 10 min at -78°C and was then allowed to warm to room temperature and stirred until the colour was discharged. Ether (50 ml) and a saturated NH_4Cl solution (30 ml) were added. The organic layer was successively washed with a saturated NH_4Cl solution (2x30 ml), brine (30 ml) dried with $MgSO_4$ and filtered. Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using flash silica and elution with 20/80 ether/light petroleum gave several products **4a**, **5a**, **6a**. **4a** (1.16 g, 79%); microcrystals; mp 77.4 - 78°C (lit.[40] mp 77-78°C); ν_{max} (dichloromethane)/cm^{-1} 1610, 1490, 1450, 1320, 1250, 1240, 1180, 1150, 1130, 1090, 1050, 1000, 950, 870, 850, 810; ^{1}H and ^{13}C NMR data were identical to the ones reported.

***1-(Methoxy-bistrimethylsilyl-methyl)-1H-benzotriazole* (5a).** (111 mg, 4%); microcrystals; mp 109.7-110.7°C; ^{1}H NMR (300 MHz; $CDCl_3$) 8.05 (1H, d, J = 8 Hz, H-4), 7.80 (1H, d, J = 8 Hz, H-7), 7.30 - 7.45 (2H, m, H-5, H-6), 3.40 (3H, s, OMe), 0.20 (18H, s, 2xTMS); ^{13}C NMR (75 MHz, $CDCl_3$) 146.11 (C-3a), 133.14 (C-7a), 126.35 (C-6), 123.67 (C-5), 119.55 (C-4), 113.94 (C-7), 94.27 (C-8), 56.14 (OMe), -0.21 (2xTMS); ν_{max} (dichloromethane)/cm^{-1} 3060, 2990, 2300, 1450, 1260, 890-850; Anal. Calcd. for $C_{14}H_{25}N_3OSi_2$ C 54.73, H 8.14, N 13.68. Found: C 54.95, H 8.35, N 13.70.

***1-(Methoxy-trimethylsilyl-methyl)-4-trimethylsilyl-1H-benzotriazole* (6a).** (65 mg, 2%); microcrystals; mp 69.2-71.6°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.65 (1H, d, J = 8 Hz, H-7), 7.40-7.50 (2H, m, H-5, H-6), 5.60 (1H, s, H-8), 3.40 (3H, s, OMe), 0.50 (9H, s, aryl TMS), 0.20 (18H, s, 2xTMS); ^{13}C NMR (75 MHz, $CDCl_3$) 149.98 (C-3a), 133.66 (C-7a), 132.28 (C-4), 129.39 (C-6), 126.54 (C-5), 111.06 (C-7), 87.52 (C-8), 59.29 (OMe), -0.70 (aryl TMS), -3.07 (2xTMS); ν_{max} (dichloromethane)/cm^{-1} 3060, 2995, 2300, 1425, 1265, 900; Anal. Calcd. for $C_{14}H_{25}N_3OSi_2$ C 54.73, H 8.14, N 13.68. Found: C 54.55, H 8.30, N 13.90.

***1-(Trideuteriomethoxy-trimethylsilyl-methyl)-1H-benzotriazole* (4b).** Same procedure as the one used to prepare **4a** using **3b** (1.25 g, 7.56 mmol), dry diisopropylamine (1.17 ml, 8.32 mmol), *n*-BuLi (5.12 ml of a

1.55M solution in hexanes, 7.94 mmol) and TMSCl (4.80 ml, 37.80 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using Kieselgel and elution with 20/80 ether/light petroleum gave several products **4b**, **5b**, **6b**. **4b** (1.45 g, 81%); microcrystals; mp 77.4 - 78.2°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.91 (1H, d, J = 8 Hz, H-4), 7.60 (1H, d, J = 8 Hz, H-7), 7.49-7.1 (2H, m, H-5, H-6), 5.52 (1H, s, H-8), 0.2 (9H, s, TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 145.72 (C-3a), 133.1 (C-7a), 126.95 (C-6), 123.59 (C-5), 119.47 (C-4), 110.31 (C-7), 87.46 (C-8), -3.55 (TMS); ν_{max} (dichloromethane)/cm^{-1} 2260, 2220, 2080 (C-D), 1250, 1240, 1115, 1055, 895, 845, 805; Anal. Calcd. for $C_{11}H_{14}D_3N_3OSi$: C, 55.5; H/D, 7.3; N, 17.65. Found: C, 55.4; H/D, 7.05; N, 17.65.

***1-(Trideuteriomethoxy-bistrimethylsilyl-methyl)-1H-benzotriazole* (5b).** (73 mg, 3%); microcrystals; mp 112.7-114.5°C; ^{1}H NMR (300 MHz; $CDCl_3$) 8.05 (1H, d, J = 8 Hz, H-4), 7.80 (1H, d, J = 8 Hz, H-7), 7.40 (1H, t, J = 8 Hz) and 7.30 (1H, t, J = 8 Hz) (H-5 or H-6), 0.20 (18H, s, 2xTMS); ^{13}C NMR (75 MHz, $CDCl_3$) 146.06 (C-3a), 133.43 (C-7a), 126.33 (C-6), 123.65 (C-5), 119.51 (C-4), 113.91 (C-7), 94.06 (C-8), 55.45 (weak multiplet, OCD_3), -0.27 (2xTMS); ν_{max} (dichloromethane)/cm^{-1} 2980, 2920, 1110, 1080, 860; Anal. Calcd. for $C_{14}H_{22}N_3D_3OSi_2$: C, 54.14; H/D, 8.2; N, 13.53. Found: C, 54.40; H/D, 8.25; N, 13.35

***1-(Trideuteriomethoxy-trimethylsilyl-methyl)-4-trimethylsilyl-1H-benzotriazole* (6b).** (44 mg, 2%); microcrystals; mp 76.3-76.9°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.70 (1H, d, J = 8 Hz, H-7), 7.50 (2H, m, H-5, H-6), 5.60 (1H, s, H-8), 0.50 (9H, s, aryl TMS), 0.20 (9H, s, TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 149.96 (C-3a), 133.63 (C-7a), 132.26 (C-4), 129.39 (C-6), 126.54 (C-5), 111.05 (C-7), 87.40 (C-8), -0.70 (aryl TMS), -3.07 (TMS); ν_{max} (dichloromethane)/cm^{-1} 2040, 2960, 1260, 740; Anal. Calcd. for $C_{14}H_{22}D_3N_3OSi_2$: C, 54.19; H/D, 8.2; N, 13.55. Found: C, 54.35; H/D, 8.30; N, 13.35

***1-(Phenoxy-trimethylsilyl-methyl)-1H-benzotriazole* (4c).** Same procedure as the one used to prepare **4a** using **3c** (1.0 g, 4.44 mmol), dry diisopropylamine (0.69 ml, 4.89 mmol), *n*-BuLi (2.92 ml of a 1.6M solution in hexanes, 4.67 mmol) and TMSCl (2.82 ml, 22.22 mmol). Removal of the solvent under reduced pressure gave a brown oil. Purification by column chromatography, using flash silica and elution with 20/80 ether/light petroleum gave two products **4c** and **5c**. **4c** (1.11 g, 86%); microcrystals; mp 95.4 - 96.8°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.93 (1H, d, J = 8 Hz, H-4), 7.43 (1H, d, J = 8 Hz, H-7), 7.34 -7.19 (2H, m, H-5, H-6), 7.12 (2H, t, J = 8 Hz, *m*-H), 6.97-6.85 (3H, m, *o, p*-H), 6.5 (1H, s, H-8), 0.2 (9H, s, TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 158.5 (*ipso*-C), 145.5 (C-3a), 132.1 (C-7a), 129.1 and 116.4 (*o* - and *m*-C), 127.3 (C-6), 123.6 (C-5), 122.4 (*p*-C), 119.4 (C-4), 110.6 (C-7), 83.9 (C-8), -3.9 (TMS); ν_{max} (dichloromethane)/cm^{-1} 1590, 1490, 1450, 1210, 850, 820; Anal. Calcd. for $C_{16}H_{19}N_3OSi$: C, 64.6; H, 6.4; N, 14.1. Found: C, 64.9; H, 6.5; N, 14.35

***1-(Phenoxy-bistrimethylsilyl-methyl)-1H-benzotriazole* (5c).** Same procedure as the one used to prepare **4a** using **4c** (1.1 g, 3.70 mmol), dry diisopropylamine (0.57 ml, 4.07 mmol), *n*-BuLi (2.43 ml of a 1.6M solution in hexanes, 3.89 mmol) and TMSCl (2.35 ml, 18.52 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using flash silica and elution with 20/80 ether/light petroleum

gave several compounds **5c**, **6c**, **8c**. **5c** (487 mg, 36%); microcrystals; mp 137.4-138.8°C; ^{1}H NMR (300 MHz; $CDCl_3$) 8.10 (1H, d, J = 8 Hz, H-4), 7.75 (1H, d, J = 8 Hz, H-7), 7.35 (2H, m, H-5, H-6), 7.10 (2H, t, J = 8 Hz, *m*-H), 6.95 (1H, t, J = 8 Hz, *p*-H), 6.60 (2H, d, J = 8 Hz, *o*-H), 0.20 (18H, s, 2xTMS); ^{13}C NMR (75 MHz, $CDCl_3$) 158.89 (*ipso*-C), 146.15 (C-3a), 133.69 (C-7a), 129.01 (*o*-C), 126.60 (C-5), 123.96 and 122.94 (C-6, *p*-C), 119.51 (*m*-C), 119.41 (C-4), 114.46 (C-7), 94.97 (C-8), 0.27 (2xTMS); ν_{max} (dichloromethane)/cm^{-1} 3040, 2960, 2900, 1595, 1495, 1210, 850; Anal. Calcd. for $C_{19}H_{27}N_3OSi_2$: C, 61.74; H, 7.36; N, 11.36. Found: C, 62.00; H, 7.45; N, 11.35

***1-(Phenoxy-bistrimethylsilyl-methyl)-4-trimethylsilyl-1H-benzotriazole* (8c).** (15 mg, 1%); microcrystals; mp 136.1-136.9°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.70 (1H, d, J = 8 Hz, H-7), 7.45 (1H, d, J = 8 Hz) and 7.25 (1H, t, J = 8 Hz) (H-5, H-6), 7.10 (2H, t, J = 8 Hz, *m*-H), 6.95 (1H, t, J = 8 Hz, *p*-H), 6.65 (2H, d, J = 8 Hz, *o*-H), 0.55 (9H, s, aryl TMS), 0.20 (18H, s, 2xTMS); ^{13}C NMR (75 MHz, $CDCl_3$) 158.96 (*ipso*-C), 149.88 (C-3a), 132.61 and 132.51 (*p*-C, C-7a), 129.56 (C-6), 128.98 and 119.49 (*o*-C, *m*-C), 125.82 (C-5), 122.83 (C-4), 115.06 (C-7), 94.88 (C-8), 0.29 (2xTMS), -0.65 (aryl TMS); ν_{max} (dichloromethane)/cm^{-1} 3040, 2960, 2900, 1600, 1490, 1210, 1110; Anal. Calcd. for $C_{22}H_{35}N_3OSi_3$: C, 59.81; H, 7.99; N, 9.51. Found: C, 59.80; H, 8.00; N, 9.60.

***1-(2,4,6-Trimethylphenoxy-trimethylsilyl-methyl)-1H-benzotriazole* (4e).** Same procedure as the one used to prepare **4a** using **3e** (1.06 g, 3.96 mmol), dry diisopropylamine (0.61 ml, 4.36 mmol), *n*-BuLi (2.91 ml of a 1.45M solution in hexanes, 4.22 mmol) and TMSCl (2.50 ml, 19.70 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using flash silica and elution with 40/60 ether/light petroleum gave two products **4e** and **6e**. **4e** (591 mg, 44%); microcrystals; mp 119.0-120.5°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.94 (1H, d, J = 8 Hz, H-4), 7.2-7.08 (2H, m, H-5, H-6), 6.57 (2H, s, *m*-H), 6.4 (1H, d, J = 8 Hz, H-7), 5.81 (1H, s, H-8), 2.13.(3H, s, *p*-Me), 1.78 (6H, s, *o*-Me), 0.45 (9H, s, TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 152.34 (*ipso*-C), 144.99 (C-3a), 134.58 (*p*-C), 133.56 (C-7a), 130.16 (*o*-C), 129.29 (*m*-C), 126.77.(C-6), 123.40 (C-5), 119.00 (C-4), 109.01 (C-7), 82.63 (C-8), 20.32 (*p*-Me), 15.68 (*o*-Me), -2.52 (TMS); ν_{max} (dichloromethane)/cm^{-1} 1215, 895, 865, 830; Anal. Calcd. for $C_{19}H_{25}N_3OSi$: C, 67.25; H, 7.4; N, 12.4. Found: C, 67.50; H, 7.60; N, 12.60.

***1-(Tert-butylthio-trimethylsilyl-methyl)-1H-Benzotriazole* (4f).** Same procedure as the one followed to prepare **4a** using **3f** (2.44 g, 11.02 mmol), dry diisopropylamine (1.62 ml, 11.57 mmol), *n*-BuLi (8.66 ml of a 1.40M solution in hexanes, 12.12 mmol) and TMSCl (7.0 ml, 55.11 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using flash silica and elution with 15/85 ether/light petroleum gave two products **4f** and **6f**. **4f** (2.6 g, 80%); microcrystals; mp 128.8-130.1°C; ^{1}H NMR (300 MHz; $CDCl_3$) 8.05 (1H, d, J = 8 Hz, H-4), 7.85 (1H, d, J = 8 Hz, H-7); 7.45 (1H, t, J = 8 Hz) and 7.35 (1H, t, J = 8 Hz) (H-5, H-6), 5.90 (1H, s, H-8), 1.15 (9H, s, *tert*-butyl), 0.10 (9H, s, TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 146.74 (C-3a), 132.08 (C-7a), 126.39 (C-6), 123.58 (C-5), 120.01 (C-4), 112.07 (C-7), 52.98 (C-8), 45.05 ($\underline{C}(CH_3)_3$), 30.34 (CH_3, *tert*-butyl), -2.46 (TMS); ν_{max} (dichloromethane)/cm^{-1} 2970, 2900, 2860, 1450,

1370, 1240, 1160, 1070, 850; Anal. Calcd. for $C_{14}H_{23}N_3SSi$: C, 57.3; H, 7.90; N, 14.3; S, 10.9. Found: C, 57.1; H, 7.95; N, 14.1; S, 11.1.

***1-(Tert-butylthio-trimethylsilyl-methyl)-4-trimethylsilyl-1H-benzotriazole* (6f).** (399 mg, 10%); microcrystals; mp 113.3-114.0°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.85 (1H, d, J = 8 Hz, H-7), 7.45 (2H, m, H-5, H-6), 5.85 (1H, s, H-8), 1.20 (9H, s, *tert*-butyl), 0.50 (9H, s, aryl TMS), 0.10 (9H, s, TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 150.66 (C-3a), 132.88 and 132.68 (C-7a, C-4), 129.08 (C-6), 125.64 (C-5), 112.51 (C-7), 52.70 (C-8), 44.92 ($\underline{C}(CH_3)_3$), 30.45 (CH_3, *tert*-butyl), -0.65 (aryl TMS), -2.36 (TMS); ν_{max} (dichloromethane)/cm^{-1} 2960, 1400, 1370, 1250, 1080, 960, 840; Anal. Calcd. for $C_{17}H_{31}N_3SSi_2$: C, 55.84; H, 8.54; N, 11.49; S, 8.77. Found: C, 56.05; H, 8.65; N, 11.50; S, 8.90

***1-(Tert-butoxy-trimethylsilyl-methyl)-1H-Benzotriazole* (4g).** Same procedure as the one used to prepare **4a** using **3g** (7.88 g, 38.4 mmol), dry diisopropylamine (10.76 ml, 76.8 mmol), *n*-BuLi (26.48 ml of a 1.45M solution in hexanes, 38.4 mmol) and TMSCl (24.37 ml, 192 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using flash silica and elution with 15/85 ether/light petroleum gave several products **4g**, **6g**, **7g**. **4g** (4.84 g, 46%); microcrystals; mp 111.6 - 113.6°C(hexane); ^{1}H NMR (300 MHz; $CDCl_3$) 7.99 (1H, d, J = 8 Hz, H-4), 7.76 (1H, d, J = 8 Hz, H-7), 7.49-7.18 (2H, m, H-5, H-6), 6.21 (1H, s, H-8), 1.05 (9H, s, *tert*-butyl), 0.05 (9H, s, TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 146.50 (C-3a), 132.58 (C-7a), 126.49 (C-6), 123.67 (C-5), 119.64 (C-4), 112.43 (C-7), 81.33 (C-8), 77.27 ($\underline{C}(CH_3)_3$), 27.49 ($C(\underline{C}H_3)_3$), -3.52 (TMS); ν_{max} (dichloromethane)/cm^{-1} 1085, 870, 855, 815; Anal. Calcd. for $C_{14}H_{23}N_3OSi$: C, 60.65; H, 8.3; N, 15.2. Found: C, 60.35; H, 8.25; H, 15.1.

***1-(Tert-butoxy-trimethylsilyl-methyl)-4-trimethylsilyl-1H-Benzotriazole* (6g).** (700 mg, 5%); microcrystals; mp 67.9-70.0°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.80 (1H, d, J = 8 Hz, H-7), 7.40 (2H, m, H-5, H-6), 6.20 (1H, s, H-8), 1.10 (9H, s, *tert*-butyl), 0.50 (9H, s, aryl TMS), 0.10 (9H, s, TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 150.41 (C-3a), 133.07 (C-7a), 131.32 (C-4), 129.12 (C-6), 125.68 (C-5), 113.02 (C-7), 80.99 (C-8), 77.06 ($\underline{C}(CH_3)_3$), 27.55 (CH_3, *tert*-butyl)), -0.65 (aryl TMS), -3.43 (TMS); ν_{max} (dichloromethane)/cm^{-1} 3040, 2980, 2850, 1440, 1375, 1260, 1105, 890; Anal. Calcd. for $C_{17}H_{31}N_3OSi_2$: C, 58.40; H, 12.02; N, 8.94. Found: C, 58.30; H, 11.75; N, 8.95.

***1-(2-Propanoxy-trimethylsilyl-methyl)-1H-benzotriazole* (4h).** Same procedure as the one used to prepare **4a** using **3h** (478 mg, 2.5 mmol), dry diisopropylamine (0.39 ml, 2.75 mmol), *n*-BuLi (2.2 ml of a 1.20M solution in hexanes, 2.64 mmol) and TMSCl (1.60 ml, 12.60 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using flash silica and elution with 75/25 ether/light petroleum gave several products **4h**, **6h**, **7h**. **4h** (355 mg, 54%); microcrystals; mp 115-117°C; ^{1}H NMR (90 MHz; $CDCl_3$) 8.00 (1H, d, J = 8 Hz, H-4), 7.71 (1H, d, J = 8 Hz, H-7), 7.40 (1H, t, J = 8 Hz) and 7.29 (1H, t, J = 8 Hz) (H-5, H-6), 5.94 (1H, s, H-8), 3.47 (1H, m, isopropyl), 1.18 (3H, d, J 8) (isopropyl), 0.9 (3H, d, J 8) (isopropyl), 0.10.(9H, s, TMS); ^{13}C NMR (22.5 MHz, $CDCl_3$) 146.05 (C-3a), 132.61 (C-7a), 126.54 (C-6),

123.48 (C-5), 119.42 (C-4), 111.1 (C-7), 83.99 (C-8), 71.53 ($\underline{C}H(CH_3)_2$), 22.39 and 20.42 (CH_3, isopropyl), -3.69 (TMS); ν_{max} (dichloromethane)/cm^{-1} 1070, 1030, 870, 840, 800; Anal. Calcd. for $C_{13}H_{21}N_3OSi$: C, 59.3; H, 8.0; N, 16.0. Found: C, 59.1; H, 7.95; N, 15.9.

***1-(Cyclohexanoxy-trimethylsilyl-methyl)-1H-benzotriazole* (4i).** Same procedure as the one used to prepare **4a** using **3i** (578 mg, 2.5 mmol), dry diisopropylamine (0.39 ml, 2.75 mmol), *n*-BuLi (2.2 ml of a 1.20M solution in hexanes, 2.64 mmol) and TMSCl (1.60 ml, 12.60 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using flash silica and elution with 15/85 ether/light petroleum gave several products **4i**, **6i**, **7i**. **4i** (259 mg, 34%); microcrystals; mp 93-94°C; ^{1}H NMR (300 MHz; $CDCl_3$) 8.04 (1H, d, J = 8 Hz, H-4), 7.76 (1H, d, J = 8 Hz, H-7), 7.53-7.3 (2H, m, H-5, H-6), 6.05 (1H, s, H-8), 3.26 (1H, m, *ipso*-H), 1.95 (1H, br.s) and 1.85-1.00 (9H, m) (cyclohexyl), 0.11 (9H, s, TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 146.02 (C-3a), 132.55 (C-7a), 126.41 (C-6), 123.37 (C-5), 119.33 (C-4), 111.13 (C-7), 83.64 (C-8), 76.81(*ipso*-C), 32.28, 30.06, 25.13, 23.18 and 23.07 (cyclohexyl), -3.69 (TMS); ν_{max} (dichloromethane)/cm^{-1} 1090, 880, 860, 825; Anal. Calcd. for $C_{16}H_{25}N_3OSi$: C, 63.4; H, 8.25; N, 13.9. Found: C, 63.5; H, 8.35; N, 13.95

***1-Bistrimethylsilylmethyl-1H-Benzotriazole* (4j).**[12] Same procedure as the one used to prepare **4a** using **3j** (2.35 g, 11.46 mmol), dry diisopropylamine (1.77 ml, 13.0 mmol), *n*-BuLi (8.02 ml of a 1.50M solution in hexanes, 12.0 mmol) and TMSCl (7.27 ml, 57.0 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using flash silica and elution with 10/90 ether/light petroleum gave two products **4j** and **6j**. **4j** (2.62 g, 83%); microcrystals; mp 140.4-141.6°C (lit.[12] mp 144-145°C); ^{1}H NMR (300 MHz; $CDCl_3$) 8.05 (1H, d, J = 8 Hz, H-4), 7.45 (2H, d, J = 8 Hz, H-7 and H-5 or H-6), 7.35 (1H, m, H-5 or H-6), 3.70 (1H, s, H-8), 0.15 (18H, s, 2xTMS); ^{13}C NMR (75 MHz, $CDCl_3$) 145.23 (C-3a), 133.84 (C-7a), 126.22 (C-6), 123.21 (C-5), 119.77 (C-4),109.66 (C-7), 43.37 (C-8), -0.71 (2xTMS); ν_{max} (dichloromethane)/cm^{-1} 2970, 1225, 1015, 850 Anal. Calcd. for $C_{13}H_{23}N_3Si_2$: C, 56.27; H, 8.35; N, 15.14. Found: C, 56.10; H, 8.20; N, 15.05

***1-(Bistrimethylsilyl-methyl)-4-trimethylsilyl-1H-benzotriazole* (6j).** (105 mg, 3%); microcrystals; mp 54.5-56.1°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.55 (3H, m, H-5, H-6, H-7), 3.80 (1H, s, H-8), 0.62 (9H, s, aryl TMS), 0.22 (18H, s, 2xTMS); ^{13}C NMR (75 MHz, $CDCl_3$) 148.99 (C-3a), 133.18 (C-7a), 132.52 (C-4), 128.79 (C-6), 125.59 (C-5), 110.22 (C-7), 43.08 (C-8), -0.67 (aryl TMS and 2xTMS); ν_{max} (dichloromethane)/cm^{-1} 2980, 2950, 1400, 1245, 1015, 850 Anal. Calcd. for $C_{16}H_{31}N_3Si_3$: C, 54.96; H, 8.93; N, 12.02. Found: C, 54.90; H, 9.10; N, 11.80.

***1-(Ethoxy-trimethylsilyl-methyl)-1H-benzotriazole* (4k).** Same procedure as the one used to prepare **4a** using **3k** (994 mg, 5.62 mmol), dry diisopropylamine (0.87 ml, 6.18 mmol), *n*-BuLi (3.69 ml of a 1.60M solution in hexanes, 5.90 mmol) and TMSCl (3.6 ml, 28.22 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using flash silica and elution with 20/80 ether/light petroleum

gave **4k** (612 mg, 44%); microcrystals; mp 66.5-67.7°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.96 (1H, d, J = 8 Hz, H-4), 7.63 (1H, d, J = 8 Hz, H-7), 7.37 (1H, t, J = 8 Hz) and 7.24 (1H, t, J = 8 Hz) (H-5, H-6), 5.71 (1H, s, H-8), 3.38 (2H, q, J = 8 Hz, OEt), 1.04 (3H, t, J = 8 Hz, OEt), 0.05 (9H, s, TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 145.89 (C-3a), 132.98 (C-7a), 126.86 (C-6), 123.61 (C-5), 119.54 (C-4), 110.65 (C-7), 86.07 (C-8), 66.81 ($O\underline{C}H_2CH_3$), 14.50 ($OCH_2\underline{C}H_3$), -3.51 (TMS); ν_{max} (dichloromethane)/cm^{-1} 1100, 1055, 880, 855; Anal. Calcd. for $C_{12}H_{19}N_3OSi$: C, 57.8; H, 7.6; N, 16.9. Found: C, 58.1; H, 7.8; N, 17.05.

***1-(Methoxy-bistrimethylsilyl-methyl)-4-trimethylsilyl-1H-benzotriazole* (8a).** Dry diisopropylamine (0.64 ml, 4.21 mmol) was dissolved in dry THF (15 ml), under a dry nitrogen atmosphere and cooled to -78°C. *n*-BuLi (0.64 ml of a 1.54M solution in hexanes, 3.85 mmol) was added dropwise with stirring and the mixture was stirred at -78°C for 15 min. A mixture of **5a** and **6a** (1.29 g, 4.21 mmol) in dry THF (2 ml) was added dropwise with stirring to the LDA solution (the solution turned blue instantly) and the reaction mixture was stirred at -78°C for 60 min. TMSCl (0.59 ml, 4.64 mmol) in dry THF (0.59 ml, 1:1 mixture), was added and the reaction mixture was stirred at -78°C for 15 min before it was allowed to warm to room temperature. It was cooled to -78°C over 30 min and *n*-BuLi (1.50 ml of a 1.54M solution in hexanes, 9.02 mmol) was added dropwise. This time, the solution took a lighter blue colour and was stirred at -78°C for 60 min. TMSCl (0.45 ml) in dry THF (0.45 ml) was added and the reaction mixture was stirred at -78°C for 15 min before it was allowed to warm to room temperature. It was cooled to -78°C over 30 min, *n*-BuLi (0.90 ml of a 1.54M solution in hexanes, 5.70 mmol) was added dropwise and the mixture was stirred at -78°C for 60 min. TMSCl (0.45 ml) in dry THF (0.45 ml), was added and the reaction mixture was stirred at -78°C for 15 min before it was allowed to warm to room temperature. Ether (50 ml) and saturated NH_4Cl solution (30 ml) were added. The organic layer was successively washed with saturated NH_4Cl solution (2x30 ml), brine (30 ml), dried with $MgSO_4$ and filtered. Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using Kieselgel and elution with 5/95 ether/light petroleum gave **8a** (1.24 g, 78%); microcrystals; mp 151.0-152.8°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.80 (1H, d, J = 8 Hz, H-7), 7.30-7.45 (2H, m, H-5, H-6), 3.40 (3H, s, OMe), 0.50 (9H, s, aryl TMS), 0.20 (18H, s, 2xTMS); ^{13}C NMR (75 MHz, $CDCl_3$) 149.86 (C-3a), 132.84 (C-7a), 132.28 (C-4), 129.29 (C-6), 125.66 (C-5), 114.62 (C-7), 94.00 (C-8), 56.10 (OMe), -0.16 (2xTMS), -0.66 (aryl TMS); ν_{max} (dichloromethane)/cm^{-1} 3060, 2995, 2300, 1425, 1260, 900, 850; Anal. Calcd. for $C_{17}H_{33}N_3OSi_3$: C, 53.83; H, 8.71; N, 11.08. Found: C, 53.95; H, 8.95; N, 11.00.

***1-(Trideuteriomethoxy-bistrimethylsilyl-methyl)-4-trimethylsilyl-1H-benzotriazole* (8b).** Same procedure as the one used to prepare **8a** using **5b** (938 mg, 3.02mmol), dry diisopropylamine (0.45 ml, 3.18 mmol), *n*-BuLi (respectively 2.15 ml, 1.15 ml, 0.65 ml of a 1.55M solution in hexanes) and TMSCl (respectively 0.42 ml, 0.30 ml, 1.92 ml). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using Kieselgel and elution with 5/95 ether/light petroleum gave **8b** (988 mg, 86%); microcrystals; mp 150.5-152.8°C, ^{1}H NMR (300 MHz; $CDCl_3$) 7.80 (1H, d, J = 8 Hz, H-7), 7.45 (1H, d, J = 8 Hz, H-5), 7.35 (1H, t, J = 8 Hz, H-6), 0.50 (9H, s, aryl TMS), 0.20 (18H, s, 2xTMS); ^{13}C NMR (75 MHz,

$CDCl_3$) 149.70 (C-3a), 132.72 (C-7a), 132.12 (C-4), 129.26 (C-6), 125.65 (C-5), 114.61 (C-7), 93.94 (C-8), -0.21 (2xTMS), -0.61 (aryl TMS); ν_{max} (dichloromethane)/cm^{-1} 3040, 2960, 1390, 1245, 1110, 1075, 850; Anal. Calcd. for $C_{17}H_{30}D_3N_3OSi_3$: C, 53.40; H/D, 8.78; N, 11.00. Found: C, 53.60; H/D, 8.80; N, 11.25.

***1-(Tristrimethylsilyl-methyl)-1H-benzotriazole* (5j).** Same procedure as the one used to prepare **8a** using **4j** (1.0 g, 3.61 mmol), dry diisopropylamine (0.53 ml, 3.79 mmol), *n*-BuLi (respectively 2.84 ml, 1.50 ml, 0.80 ml of a 1.4M solution in hexanes) and TMSCl (respectively 0.50 ml, 0.30 ml, 2.3 ml). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using Kieselgel and elution with 5/95 ether/light petroleum gave two products **5j** and **8j**. **5j** (547 mg, 44%); microcrystals; mp 85.5-86.5°C; ^1H NMR (300 MHz; $CDCl_3$) 8.05 (1H, d, J = 8 Hz, H-4), 7.75 (1H, d, J = 8 Hz, H-7), 7.40-7.25 (2H, m, H-5, H-6), 0.35 (27H, s, 3xTMS); ^{13}C NMR (75 MHz, $CDCl_3$) 146.21 (C-3a), 134.62 (C-7a), 125.07 (C-6), 123.00 (C-5), 119.97 (C-4), 113.58 (C-7), 46.56 (C-8), 4.33 (3xTMS); ν_{max} (dichloromethane)/cm^{-1} 2950, 2895, 1250, 1090, 850; Anal. Calcd. for $C_{19}H_{39}N_3Si_4$: C, 54.96; H, 8.93; N, 12.02. Found: C, 54.70; H, 8.90; N, 11.75.

***4-Trimethylsilyl-1-(tristrimethylsilyl-methyl)-1H-benzotriazole* (8j).** (623 mg, 41%); microcrystals; mp 131.6-132.6°C; ^1H NMR (300 MHz; $CDCl_3$) 7.75 (1H, d, J = 8 Hz, H-7), 7.30-7.45 (2H, m, H-5, H-6), 0.50 (9H, s, aryl TMS), 0.35 (27H, s, 3xTMS); ^{13}C NMR (75 MHz, $CDCl_3$) 150.50 (C-3a), 133.46 and 133.34 (C-4, C-7a), 128.60 (C-6), 124.27 (C-5), 114.22 (C-7), 46.0 (C-8), 4.47 (3xTMS), -0.58 (aryl TMS); ν_{max} (dichloromethane)/cm^{-1} 2960, 2900, 1395, 1245, 1090, 930, 850; Anal. Calcd. for $C_{19}H_{39}N_3Si_4$: C, 54.09; H, 9.32; N, 9.96. Found: C, 53.85; H, 9.40; N, 9.80

***1-(Adamantylidene-methoxy-methyl)-1H-benzotriazole* (9a).** Dry diisopropylamine (0.160 ml, 1.14 mmol) was dissolved in dry THF (5 ml) under a dry nitrogen atmosphere and was cooled to -78°C. After 10 min, *n*-BuLi (0.92 ml of a 1.19M solution in hexanes, 1.09 mmol) was added dropwise and the mixture was stirred at -78°C for 15 min. **4a** (244 mg, 1.04 mmol) in THF (0.5 ml) was added dropwise and the mixture was stirred at -78°C for 45 min. *n*-BuLi (0.875 ml of a 1.19M solution in hexanes, 1.04 mmol) was added dropwise and after 15 min, adamantanone (78 mg, 0.52 mmol) in dry THF (0.5 ml) was added, the mixture was stirred at -78°C for 15 minutes and allowed to warm to room temperature over 1 hour. Ether (30 ml) and a saturated NH_4Cl solution (30ml) were added. The organic layer was successively washed with a saturated a NH_4Cl solution (3x20 ml), brine (20 ml), dried with $MgSO_4$ and filtered. Removal of solvent under reduced pressure gave an brown oil. Purification by column chromatography, using flash silica and elution with 40/60 ether/light petroleum gave **9a** (121 mg, 80%); microcrystals; mp 85-86°C; ^1H NMR (90 MHz; $CDCl_3$) 8.05 (1H, d, J 8, H-4), 7.6-7.2 (3H, m, H-5, H-6, H-7), 3.3 (3H, s, OMe), 3.25 (1H, s) and 2.4-2.0 (13H, m, adamantyl); ^{13}C NMR (22.5 MHz, $CDCl_3$) 145 (C-3a), 134 and 133 (C-8, C-9), 132 (C-7a), 128 (C-6), 124 (C-5), 119 (C-4), 110 (C-7), 58 (OMe), 39.6, 39.3, 36 (CH_2 adamantyl), 31, 30, 27 (CH adamantyl); ν_{max} (dichloromethane)/cm^{-1} 1685 (C=C), 1600, 1480, 1450, 1380, 1350, 1200, 1160, 1100, 1060, 1020, 1000, 950, 800; λ_{max} (EtOH)/nm 220, 255, 285; Anal. Calcd. for $C_{18}H_{21}N_3O$: C, 73.0; H, 7.1; N, 14.2. Found: C, 73.1; H, 7.1; N, 14.2.

***1-(Adamantylidene-trideuteriomethoxy-methyl)-1H-benzotriazole* (9b).** Dry **4b** (85 mg, 0.355 mmol) was dissolved in dry THF (5 ml) under a dry nitrogen atmosphere and cooled to -78°C. *n*-BuLi (0.23 ml of a 1.45M solution in hexanes, 0.34 mmol) was added dropwise and the reaction stirred at -78°C for 45 minutes. Adamantanone (46 mg, 0.30 mmol) in dry THF (0.5ml) was added dropwise and the reaction mixture was stirred at -78°C for 15 minutes before it was allowed to warm to room temperature over 1 hour. Ether (30 ml) and a saturated NH_4Cl solution (30ml) were added. The organic layer was successively washed with a saturated NH_4Cl solution (3x20 ml), brine (20 ml), dried with $MgSO_4$ and filtered. Removal of solvent under reduced pressure gave an brown oil. Purification by column chromatography, using Kieselgel and elution with 15/85 ether/light petroleum gave **9b** (86 mg, 95%); microcrystals; mp 82.5 - 84.5°C; ^{1}H NMR (300 MHz; $CDCl_3$) 8.09 (1H, d, J = 8 Hz, H-4), 7.59 (1H, d, J = 8 Hz, H-7), 7.51 (1H, t, J = 8 Hz) and 7.39 (1H, t, J = 8 Hz) (H-5, H-6), 3.29 (1H, s) and 2.15-1.68 (13H, m) (adamantyl); ^{13}C NMR (75 MHz, $CDCl_3$) 145.03 (C-3a), 133.0 (C-9), 132.85 (C-7a), 132.5 (C-8), 127.94 (C-6), 124.02 (C-5), 119.67 (C-4), 110.06 (C-7), 38.76, 38.67, 36.53 (CH_2 adamantyl), 31.35, 30.58, 27.75 (CH adamantyl); ν_{max} (dichloromethane)/cm^{-1} 2050 (C-D), 1690 (C=C), 1450, 1180, 1100, 1060; λ_{max} (EtOH)/nm 221, 256, 285; Anal. Calcd. for $C_{18}H_{18}D_3N_3O$: C, 72.5; H/D, 7.2; N, 14.1. Found: C, 72.7; H/D, 7.15; N, 14.3.

***1-(Adamantylidene-phenoxy-methyl)-1H-benzotriazole* (9c).** Same procedure as the one used to prepare **9b** using **4c** (121 mg, 0.41 mmol), *n*-BuLi (0.27 ml of a 1.45M solution in hexanes, 0.39 mmol) and adamantanone (59 mg, 0.39 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using Kieselgel and elution with 10/10/80 ether/ dichloromethane /light petroleum gave (95 mg, 69%); microcrystals; mp 163.7 - 164.4°C; ^{1}H NMR (90 MHz; $CDCl_3$) 7.80 (1H, d, J = 8 Hz, H-4), 7.75 (1H, d, J = 8 Hz, H-7), 7.6-6.8 (7H, m, H-5, H-6, OPh), 3.38 (1H, br.s), 2.4.(1H, br.s) and 2.12-1.74 (12H, m, adamantyl); ^{13}C NMR (22.5 MHz, $CDCl_3$) 155.5 (*ipso*-C), 145.0 (C-3a), 137.0 (C-9), 132.7 (C-7a), 129.4, 115.5 (*o*-, *m*-C), 128.5 (C-6), 128.1 (C-8), 123.9 (C-5), 122.7 (*p*-C), 119.4 (C-4), 110.3 (C-7), 38.5, 38.4, 36.4 (CH_2 adamantyl), 31.5, 30.9 , 27.3 (CH adamantyl); ν_{max} (dichloromethane)/cm^{-1} 1720, 1700 (C=C), 1600, 1500, 1460, 1220, 1185, 1085; λ_{max} (EtOH)/nm 223, 260, 266 (shoulder), 273, 287; Anal. Calcd. for $C_{23}H_{23}N_3O$: C, 77.3; H, 6.4; N, 11.8. Found: C, 77.15; H, 6.4; N, 11.7.

***1-(Adamantylidene-4-methoxyphenoxy-methyl)-1H-benzotriazole* (9d).** Same procedure followed as the one to prepare **9b** using **4d** (67 mg, 0.21 mmol), *n*-BuLi (0.13 ml of a 1.45M solution in hexanes, 0.19 mmol) and adamantanone (29 mg, 0.19 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using Kieselgel and elution with 10/10/80 ether/dicholoromethane/light petroleum gave **9d** (33 mg, 45%); microcrystals; mp 166.6 - 168°C; ^{1}H NMR (90 MHz; $CDCl_3$) 7.97 (1H, d, J = 8 Hz, H-4), 7.72 (1H, d, J = 8 Hz, H-7), 7.57-7.16 (2H, m, H-5, H-6), 7.00 (2H, d, J = 10 Hz) and 6.70 (2H, d, J = 10 Hz) (*o*-, *m*-H), 3.62 (3H, s, OMe), 3.23 (1H, br.s), 2.34 (1H, br.s) and 2.12-1.69 (12H, m, adamantyl); ^{13}C NMR (22.5 MHz, $CDCl_3$) 155.5 (*ipso*-C), 149.21 (*p*-C), 145.02 (C-3a), 136.43 (C-9), 133.02 (C-7a), 128.33 (C-8), 127.95 (C-6), 123.99 (C-5), 119.66 (C-4), 116.79, 114.46 (*o*-, *m*-C), 110.45 (C-7), 53.39 (OMe), 38.92, 38.75,

36.53 (CH_2 adamantyl) 31.71, 30.93, 27.76 (CH adamantyl); ν_{max} (dichloromethane)/cm^{-1} 1695 (C=C), 1525, 1465, 1220, 1195, 1090; λ_{max} (EtOH)/nm 227, 260, 285; Anal. Calcd. for $C_{24}H_{25}N_3O_2$: C, 74.4; H, 6.45; N, 10.85. Found: C, 74.25; H, 6.4; N, 10.8.

***1-(Adamantylidene-2-propanoxy-methyl)-1H-benzotriazole* (9h).** Same procedure as the one used to prepare **9b** using **4h** (58 mg, 0.22 mmol), *n*-BuLi (0.13 ml of a 1.6M solution in hexanes, 0.21 mmol) and adamantanone (31 mg, 0.21 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using Kieselgel and elution with 10/90 ether/light petroleum gave **9h** (44 mg, 66%); Oil; ^{1}H NMR (300 MHz; $CDCl_3$) 8.06 (1H, d, *J* = 8 Hz, H-4), 7.61 (1H, d, *J* = 8 Hz, H-7), 7.47 (1H, t, *J* = 8 Hz) and 7.37 (1H, t, *J* = 8 Hz) (H-5, H-6), 3.47 (1H, m, isopropyl), 3.26 (1H, br.s), 2.0-1.9 (7H, m) and 1.86-1.70 (6H, m) (adamantyl), 1.14 (6H, d, *J* 6, isopropyl); ^{13}C NMR (75 MHz, $CDCl_3$) 145.22 (C-3a), 133.41 (C-9), 133.15 (C-7a), 130.33 (C-8), 127.84 (C-6), 124.03 (C-5), 119.74 (C-4), 110.44(C-7), 71.25 ($O\underline{C}H(CH_3)_2$), 38.98, 38.64, 36.77 (CH_2 adamantyl), 31.65, 30.90, 27.97 (CH adamantyl), 21.76 (CH_3, isopropyl); ν_{max} (dichloromethane)/cm^{-1} 1680 (C=C), 1440, 1370, 1175, 1110, 1090; λ_{max} (EtOH)/nm 220, 255, 285; HRMS Calcd. for $C_{20}H_{26}N_3O$: 324.2076 (M^+). Found 324.2076.

***1-(Adamantylidene-ethoxy-methyl)-1H-benzotriazole* (9k).** Same procedure as the one used to prepare **9b** using **4k** (212 mg, 0.85 mmol), *n*-BuLi (0.54 ml of a 1.45M solution in hexanes, 0.78 mmol) and adamantanone (114 mg, 0.76 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using Kieselgel and elution with 15/85 ether/light petroleum gave **9k** (209 mg, 89%); microcrystals; mp 112 - 114°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.95 (1H, d, *J* = 8 Hz, H-4), 7,50 (1H, d, *J* = 8 Hz, H-7), 7.37 (1H, t, *J* = 8 Hz) and 7.24 (1H, t, *J* = 8 Hz) (H-5, H-6), 3.38 (2H, q, *J* = 8 Hz, OEt), 3.16 (1H, br.s), 1.85 (7H, br.s) and 1.69-1.56 (6H, m, adamantyl), 1.06 (3H, t, *J* = 8 Hz, OEt); ^{13}C NMR (75 MHz, $CDCl_3$) 144.90 (C-3a), 133.21 (C-9), 132.98 (C-7a), 130.99 (C-8), 127.70, (C-6), 123.82 (C-5), 119.47 (C-4), 110.04 (C-7), 65.54 ($O\underline{C}H_2CH_3$), 38.64, 38.48, 36.42 (CH_2 adamantyl), 31.30, 30.58, 27.65 (CH adamantyl), 14.36 ($OCH_2\underline{C}H_3$); ν_{max} (dichloromethane)/cm^{-1} 1705 (C=C), 1465, 1200, 1115, 1100, 930; λ_{max} (EtOH)/nm 216, 256, 285; Anal. Calcd. for $C_{19}H_{23}N_3O$: C, 73.8; H, 7.4; N, 13.6. C, 73.55; H, 7.5; N, 13.5.

***1-(Adamantylidene-deuteroethoxy-methyl)-1H-benzotriazole* (9l).** Same procedure as the one used to prepare **9b** using **4l** (140 mg, 0.55 mmol)), *n*-BuLi (0.33 ml of a 1.6M solution in hexanes, 0.53 mmol) and adamantanone (79 mg, 0.53 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using Kieselgel and elution with 15/85 ether/light gave **9l** (740 mg, 85%); microcrystals; mp 114 - 116°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.99 (1H, d, *J* = 8 Hz, H-4), 7.54 (1H, d, *J* = 8 Hz, H-7), 7.43 (1H, t, *J* = 8 Hz) and 7.3 (1H, t, *J* = 8 Hz) (H-5, H-6), 3.21 (1H, br.s), 1.96-1.79 (7H, m) and 1.75-1.62 (6H, m) (adamantyl); ^{13}C NMR (75 MHz, $CDCl_3$) 144.99 (C-3a), 133.29, 133.03 and 131.07 (C-7a, C-8, C-9), 127.76 (C-6), 123.89 (C-5), 119.55 (C-4), 110.11 (C-7), 38.73, 38.56 , 36.51 (CH_2 adamantyl), 31.39, 30.66, 27.74 (CH adamantyl); ν_{max} (dichloromethane)/cm^{-1} 2210 and 2080 (C-D), 1680 (C=C), 1440, 1175,

1140, 1120, 1095, 1050, 995;); λ_{max} (EtOH)/nm 213, 255, 286; Anal. Calcd. for $C_{19}H_{18}D_5N_3O$: C, 72.6; H/D, 8.9; N, 13.4. Found: C, 73.0; H/D, 7.6; N, 13.4.

***1-(Cyclohexylidene-methoxy-methyl)-1H-benzotriazole* (9m).** Same procedure as the one used to prepare **9b** using **4a** (99 mg, 0.42 mmol)), *n*-BuLi (0.28 ml of a 1.45M solution in hexanes, 0.41 mmol) and cyclohexanone (39 mg, 0.40 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using Kieselgel and elution with 15/85 ether/light gave **9m** (84 mg, 86%); Oil; ^{1}H NMR (300 MHz; $CDCl_3$) 8.1 (1H, d, J = 8 Hz, H-4), 7.6-7.44 (2H, m) and 7.37 (1H, td, J = 8 Hz and J = 1 Hz) (H-5, H-6, H-7), 3.33 (3H, s, OMe), 2.48 (2H, br.t, J = 8 Hz), 1.79-1.61 (4H, br.m) and 1.61-1.38 (4H, br.m) (cyclohexyl); ^{13}C NMR (75 MHz, $CDCl_3$) 145.12 (C-3a), 135.70 (C-9), 133.45 (C-7a), 128.09 (C-6), 124.81 (C-8), 124.16 (C-5), 119.82 (C-4), 110.26 (C-7), 57.77 (OMe), 28.29, 27.48, 27.40, 27.35, 26.16 (CH_2 cyclohexyl); ν_{max} (dichloromethane)/cm^{-1} 1685 (C=C), 1440, 1230, 1200, 1160, 1125, 1070; λ_{max} (EtOH)/nm 220, 255, 285; Anal. Calcd. for $C_{14}H_{17}N_3O$: C, 69.1; H, 7.0; N, 17.3. Found: C, 69.35; H, 7.2; N, 17.4.

***1-(Diphenylidene-methoxy-methyl)-1H-benzotriazole* (9n).** Same procedure as the one used to prepare **9b** using **4a** (113 mg, 0.48 mmol), *n*-BuLi (0.27 ml of a 1.45M solution in hexanes, 0.40 mmol) and benzophenone (68 mg, 0.38 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using Kieselgel and elution with dichloromethane gave **9n** (60 mg, 49%); microcrystals; mp 160.1-161.7°C; ^{1}H NMR (300 MHz; $CDCl_3$) 8.03 (1H, d, J = 8 Hz, H-4), 7.67-7.3 (8H, m), 7.11-6.88 (5H, m, aromatic H), 3.52 (3H, s, OMe); ^{13}C NMR (75 MHz, $CDCl_3$) 145.00 (C-3a), 140.68 (C-9), 137.86 and 137.56 (*ipso*-C), 132.92 (C-7a), 129.70, 129.21 and 128.27, 127.96 (*o*-, *m*-C), 128.27 and 127.20 (*p*-C), 127.78 (C-6), 124.25 (C-5), 123.71 (C-8), 119.92 (C-4), 110.11 (C-7), 57.84 (OMe); ν_{max} (dichloromethane)/cm^{-1} 1665 (C=C), 1500, 1470, 1245, 1090; λ_{max} (EtOH)/nm 210, 233, 258; Anal. Calcd. for $C_{21}H_{17}N_3O$: C, 77.1; H, 5.2; N, 12.8. Found: C, 77.2; H, 5.2; N, 13.05.

***1-Benzotriazolyl-1-methoxy-2-phenyl-propene* (9o).**[15] Same procedure as the one used to prepare **9b** using **4a** (86 mg, 0.37 mmol), *n*-BuLi (0.25 ml of a 1.45M solution in hexanes, 0.36 mmol) and acetophenone (44 mg, 0.37 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using Kieselgel and elution with 60/40% dichloromethane/light petroleum gave **9o** as a mixture of isomers (76 mg, 78%); microcrystals; mp 97.0 - 99.5°C (lit.[15] mp 101-102°C for *trans* isomer); ^{1}H NMR (300 MHz; $CDCl_3$) mixture of isomers (1.2 : 1) 8.15 (1H, d, J = 8 Hz), 8.0 (1H, d, J = 8 Hz), 7.8-7.3 (9H, m), 7.1-6.9 (9H, m), 3.48 (3H, br.s, OMe), 3.34 (3H, br.s, OMe), 2.37 (3H, br.s, Me), 1.87 (3H, br.s, Me); ν_{max} (dichloromethane)/cm^{-1} 1680 (C=C), 1460, 1225, 1180, 1160, 1085; λ_{max} (EtOH)/nm 216, 251, 288 (shoulder); Anal. Calcd. for $C_{16}H_{15}N_3O$: C, 72.5; H, 5.7; N, 15.8. Found: C, 72.35; H, 5.65; N, 15.85.

***1-(Adamantylidene-methoxy-methyl)-4-trimethylsilyl-1H-benzotriazole* (10a).** To a stirred solution of adamantanone (100 mg, 0.66 mmol) and **8a** (300 mg, 0.79 mmol) in dry THF (1 ml) under argon atmosphere, at -20°C, was added freshly dried TBAF (0.02 mg, 0.07 mmol). The mixture was stirred at -20°C for 2 h and then

allowed to warm to room temperature over 1 h. The reaction mixture was poured into ice water and extracted with ether. The organic layer was washed with water, brine, dried with $MgSO_4$ and filtered. Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using Kieselgel and elution with 5/95 ether/light petroleum gave two products **7a** and **10a**. **10a** (173 mg, 72%); microcrystals; mp 105.3-106.5°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.60 (1H, m, H-7), 7.50 (2H, m, H-5, H-6), 3.40 (3H, s, OMe), 3.30 (1H, br.s) and 2.10-1.70 (13H, m) (adamantyl), 0.50 (9H, s, aryl TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 149.14 (C-3a), 133.55, 132.93, 132.49, 132.21 (C-4, C-7a, C-8, C-9), 129.56 (C-6), 127.26 (C-5), 110.85 (C-7), 58.15 (OMe), 38.94, 38.86, 36.74 (CH_2 adamantyl), 31.41, 30.73, 27.93 (CH adamantyl), -0.71 (aryl TMS); ν_{max} (dichloromethane)/cm^{-1} 2920, 2850, 1690, 1400, 1100, 840, 860; λ_{max} (EtOH)/nm 207, 250; Anal. Calcd. for $C_{21}H_{29}N_3OSi$: C, 68.66; H, 7.92; N, 11.43. Found: C, 68.30; H, 8.05; N, 11.25

***1-(Methoxymethyl)-4-trimethysilyl-1H-benzotriazole* (7a).** (58 mg); oil; ^{1}H NMR (300 MHz; $CDCl_3$) 7.65 (1H, m, H-7), 7.50 (2H, m, H-5, H-6), 5.93 (2H, s, H-8), 3.34 (3H, s, OMe), 0.50 (9H, s, aryl TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 150.42 (C-3a), 133.85, 131.54 (C-4, C-7a), 129.67 (C-6), 127.11 (C-5), 110.24 (C-7), 78.31 (C-8), 56.81 (OMe), -0.79 (aryl TMS); ν_{max} (dichloromethane)/cm^{-1} 2980, 2950, 1400, 1160, 1090, 850; Anal. Calcd. for $C_{11}H_{17}N_3OSi$: C, 56.2; H, 7.3; N, 17.9. Found: C, 55.90; H, 7.10; N, 17.75.

***1-(Adamantylidene-trideuteriomethoxy-methyl)-4-trimethylsilyl-1H-benzotriazole* (10b).** Same procedure as the one used to prepare **10a** using adamantanone (96 mg, 0.64 mmol), **8b** (294 mg, 0.77 mmol) and freshly dried TBAF (0.02 mg, 0.07 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by column chromatography, using flash silica and elution with 5/95 ether/light petroleum gave two products **7b** and **10b**. **10b** (168 mg, 71%); microcrystals; mp 111.6-112.9°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.60 (1H, m, H-7), 7.50 (2H, m, H-5, H-6), 3.30 (1H, br.s) and 2.10-1.70 (13H, m) (adamantyl), 0.55 (9H, s, aryl TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 149.11 (C-3a), 133.49, 133.03, 132.37 and 132.19 (C-4, C-7a, C-8, C-9), 129.54 (C-6), 127.23 (C-5), 110.78 (C-7), 38.91, 38.82, 36.71 (CH_2 adamantyl), 31.39, 30.69, 27.91 (CH adamantyl), -0.74 (aryl TMS); ν_{max} (dichloromethane)/cm^{-1} 2910, 2840, 2050 (C-D), 1685, 1395, 1180, 1090, 835; λ_{max} (EtOH)/nm 204, 256; Anal. Calcd. for $C_{21}H_{26}D_3N_3OSi$: C. 68.06; H/D. 8.0; N, 11.34. Found: C, 68.00; H/D, 7.90; N, 11.25.

***1-(Trideuteriomethoxymethyl)-4-trimethysilyl-1H-benzotriazole* (7b).** (61 mg); Oil; ^{1}H NMR (300 MHz; $CDCl_3$) 7.65 (1H, m, H-7), 7.50 (2H, m, H-5, H-6), 5.95 (2H, s, H-8), 0.50 (9H, s, aryl TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 150.46 (C-3a), 133.90 (C-7a), 131.55 (C-4), 129.69 (C-6), 127.13 (C-5), 110.26 (C-7), 78.30 (C-8), 56 (CD_3, weak multiplet), -0.77 (aryl TMS); ν_{max} (dichloromethane)/cm^{-1} 2950, 2310, 2060, 1600, 1400, 1240, 1115, 860; HRMS Calcd. for $C_{11}H_{14}D_3N_3OSi$: 238.1321 (M^+). Found 238.1329.

***1-(Adamantylidene-phenoxy-methyl)-4-trimethylsilyl-1H-benzotriazole* (10c).** Same procedure as the one used to prepare **10a** using adamantanone (139 mg, 0.92 mmol), **8c** (488 mg, 1.11 mmol) and freshly dried TBAF (0.29 mg, 0.11 mmol). Removal of the solvent under reduced pressure gave an oil. Purification by

column chromatography, using flash silica and elution with 10/90 ether/light petroleum gave two products **7c** and **10c**. **10c** (219 mg, 46%); microcrystals; mp 175.5-177.5°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.75 (1H, m, H-7), 7.45 (2H, m, H-5, H-6), 7.20 (4H, m, *o*-, *m*-H), 6.90 (1H, m, *p*-H), 3.15 (1H, br.s), 2.45 (1H, br.s) and 2.05-1.80 (12H, m) (adamantyl), 0.45 (9H, s, aryl TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 155.72 (*ipso* C), 148.78 (C-3a), 136.84 (C-2), 133.21 (C-7a), 131.54 (C-4), 129.32 (C-6), 120.23, 115.24 (*o*-, *m*-C), 127.88 (C-8), 127.02 (C-5), 110.87 (C-7), 38.77, 38.52, 36.35 (CH_2 adamantyl), 31.50, 30.77, 27.56 (CH adamantyl), -1.00 (aryl TMS); ν_{max} (dichloromethane)/cm^{-1} 2930, 2860, 1580, 1480, 1205, 1060, 860, 840; λ_{max} (EtOH)/nm 210, 260; Anal. Calcd. for $C_{26}H_{31}N_3OSi$: C, 72.69; H, 7.27; N, 9.72. Found: C, 72.55; H, 7.20; N, 9.70.

***1-(Phenoxymethyl)-4-trimethysilyl-1H-benzotriazole* (7c)** (68 mg); microcrystals; mp 54.2-55.5°C; ^{1}H NMR (300 MHz; $CDCl_3$) 7.70 (1H, m, H-7), 7.50 (2H, m, H-5, H-6), 7.25 (2H, t, J = 8 Hz, *m*-H), 7.15 (2H, d, J = 8 Hz, *o*-H), 7.00 (1H, t, J = 8 Hz, *p*-H), 6.55 (2H, s, H-8), 0.50 (9H, s, aryl TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 156.43 (*ipso* C), 150.61 (C-3a), 134.08 (C-7a), 131.67 (C-4), 129.87 (C-6), 120.73, 116.16 (*o*-, *m*-C), 127.40 (C-5), 122.87 (*p*-C), 110.27 (C-7), 74.69 (C-8), -0.77 (aryl TMS); ν_{max} (dichloromethane)/cm^{-1} 3070, 2990, 1435, 1270, 905, 740; Anal. Calcd. for $C_{16}H_{19}N_3OSi$: C, 64.61; H, 6.44; N, 14.13. Found: C, 64.65; H, 6.55; N, 13.90.

***2-(Benzotriazol-1-yl-tert-butoxy-methyl)-adamantan-2-ol* (12g).** To a stirred solution of potassium hydride (160 mg of a 35% solution in mineral oil, 1.40 mmol) in dry THF (3 ml), under a dry atmosphere of argon was added **4g** (106 mg, 0.38 mmol) and adamantanone (54 mg, 0.38 mmol). The mixture was stirred for 5 min and subsequently subjected to ultrasound for 2.25 h. Ether (20 ml) and a saturated NH_4Cl solution (20 ml) were added. The organic layer was washed successively with a saturated NH_4Cl solution (2x10 ml), brine (15 ml) dried with $MgSO_4$ and filtered. Removal of the solvent under reduced pressure gave a yellow oil. Purification by column chromatography, using flash silica and elution with 40/60 ether/light gave **12g** (82 mg, 61%); microcrystals; mp 203.7-205.7°C; ^{1}H NMR (300 MHz; $CDCl_3$) 8.00 (1H, d, J = 8 Hz, H-4), 7.95 (1H, d, J = 8 Hz, H-7), 7.45 (1H, t, J = 8 Hz) and 7.30 (1H, t, J = 8 Hz) (H-5, H-6), 6.85 (1H, s, H-8), 2.70-1.20 (adamantyl), 1.05 (9H, s, *tert*-butyl); ^{13}C NMR (75 MHz, $CDCl_3$) 146.51 (C-3a), 132.61 (C-7a), 127.00 (C-6), 123.73 (C-5), 119.33 (C-4), 114.49 (C-7), 85.77 (C-8), 77.70, 77.23 ($\underline{C}(CH_3)_3$, C-9), 37.37, 34.05, 32.53, 32.25, 32.16 (CH_2 adamantyl), 34.42, 32.11, 26.45, 26.32 (CH adamantyl), 27.75 (CH_3, *tert*-butyl); *m/z* 298, 205 (7), 150 (100), 104 (20), 93 (42), 92 (13), 79 (88), 67 (31), 41 (50); ν_{max} (dichloromethane)/cm^{-1} 3600, 2940, 1380, 1110; Anal. Calcd. for $C_{21}H_{29}N_3O_2$: C, 70.75; H, 8.48; N, 11.79. Found: C, 70.35; H, 8.25; N, 11.60.

***2-[Tert-butoxy-(4-trimethylsilyl-benzotriazol-1-yl)-methyl]-adamantan-2-ol* (13g)** Same procedure as the one used to prepare **12g** using **6g** (100 mg, 0.29 mmol), potassium hydride (122 mg of a 35% solution in mineral oil, 1.06 mmol) and adamantanone (52 mg, 0.34 mmol). Removal of the solvent under reduced pressure gave a yellow oil. Purification by column chromatography, using flash silica and elution with 5/5/90 ether/ethyl acetate/light petroleum gave **12g** (64 mg, 52%); microcrystals; mp 169.8-170.9°C; ^{1}H NMR (300 MHz; $CDCl_3$)

7.95 (1H, d, J = 8 Hz, H-7), 7.42 (2H, m, H-5, H-6), 6.85 (1H, s, H-8), 1.60-1.20 (14H, m, adamantyl), 1.10 (9H, s, *tert*-butyl), 0.50 (9H, s aryl TMS); ^{13}C NMR (75 MHz, $CDCl_3$) 150.61 (C-3a), 133.03 (C-7a), 131.81 (C-4), 129.30 (C-6), 126.22 (C-5), 115.11 (C-7), 85.80 (C-8), 77.79 (C-9 and $\underline{C}(CH_3)_3$), 37.96, 34.60, 33.19, 32.82, 32.69 (CH_2 adamantyl), 34.95, 32.66, 27.02, 26.92 (CH adamantyl), 27.84 (CH_3, *tert*-butyl), -0.60 (aryl TMS; ν_{max} (dichloromethane)/cm^{-1} 3520, 2890, 1080; Anal. Calcd. for $C_{24}H_{37}N_3O_2Si$: C, 67.40; H, 8.70; N, 9.80. Found: C, 67.50; H, 8.85; N, 9.60.

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