N-[α-(*o*- and *p*-Methoxyaryl)alkyl]benzotriazoles: Preparation and Use in Synthesis

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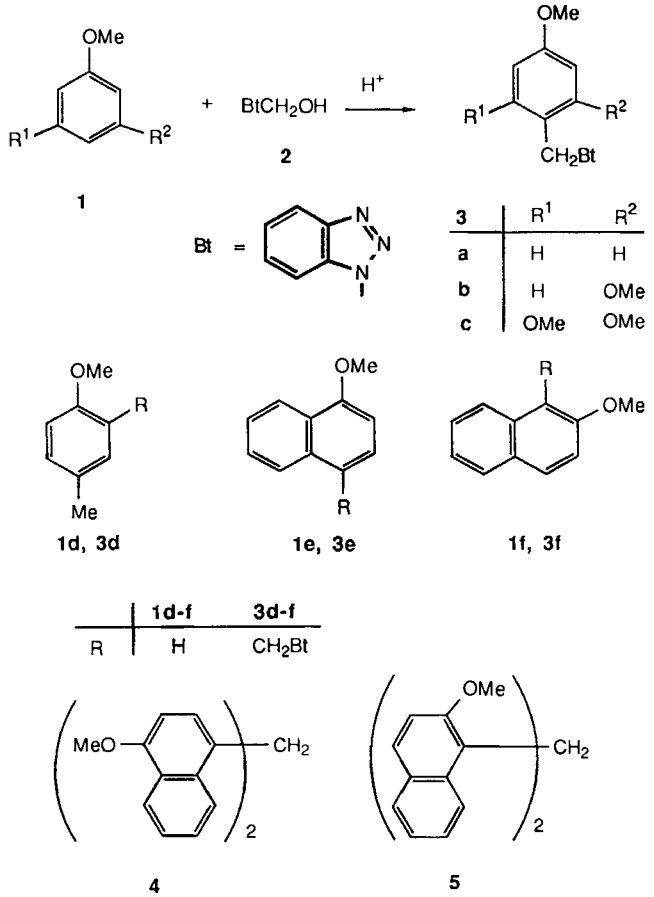
Methoxybenzenes and -naphthalenes are benzotriazolylmethylated in the *para*-position or if this is blocked in an *ortho*-position. The methylene groups in the products are readily substituted by electrophiles via the lithiated derivatives. Displacement of the benzotriazole group can be effected by organometallic reagents or by electron-rich benzoid compounds to afford a versatile method for the synthesis of substituted aryl ethers.

The preceding paper[1] demonstrates a convenient synthesis for substituted phenols, utilizing benzotriazole as a synthetic auxiliary. Many important natural products and other synthetic targets possess phenol ether fragments[2], and we have therefore examined the use of benzotriazole in the synthesis of phenol ethers. We speculated that the activation of an aromatic ring by a methoxy group could assist the electrophilic alkylation with 1-(hydroxymethyl)-1*H*-benzotriazole and that subsequent elaboration of the derivatives/and displacement of the benzotriazole group would enable the synthesis of substituted phenol ethers. We now report the results.

Scheme 1

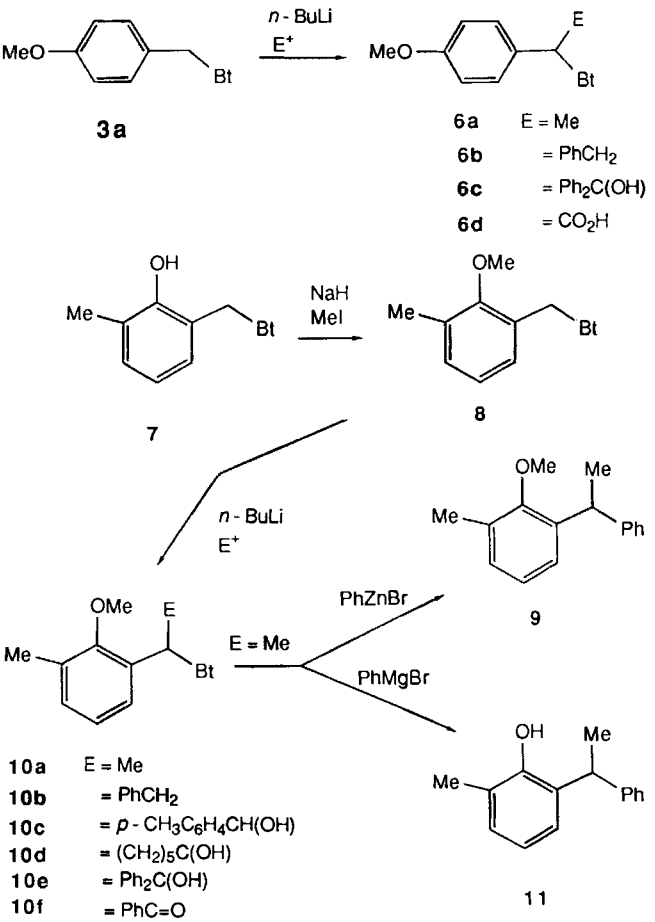


Results and Discussion

Synthesis of (1*H*-Benzotriazol-1-ylmethyl)phenyl Methyl Ethers

(i) *By Direct Alkylation of the Corresponding Methoxybenzenes*: Anisole, 1,3-dimethoxybenzene, and 1,3,5-trimethoxybenzene, on heating with 1-(hydroxymethyl)-1*H*-benzotriazole (**2**) in acetic acid alone, or in the presence of *p*-toluenesulfonic acid in toluene, gave the corresponding al-

Scheme 2



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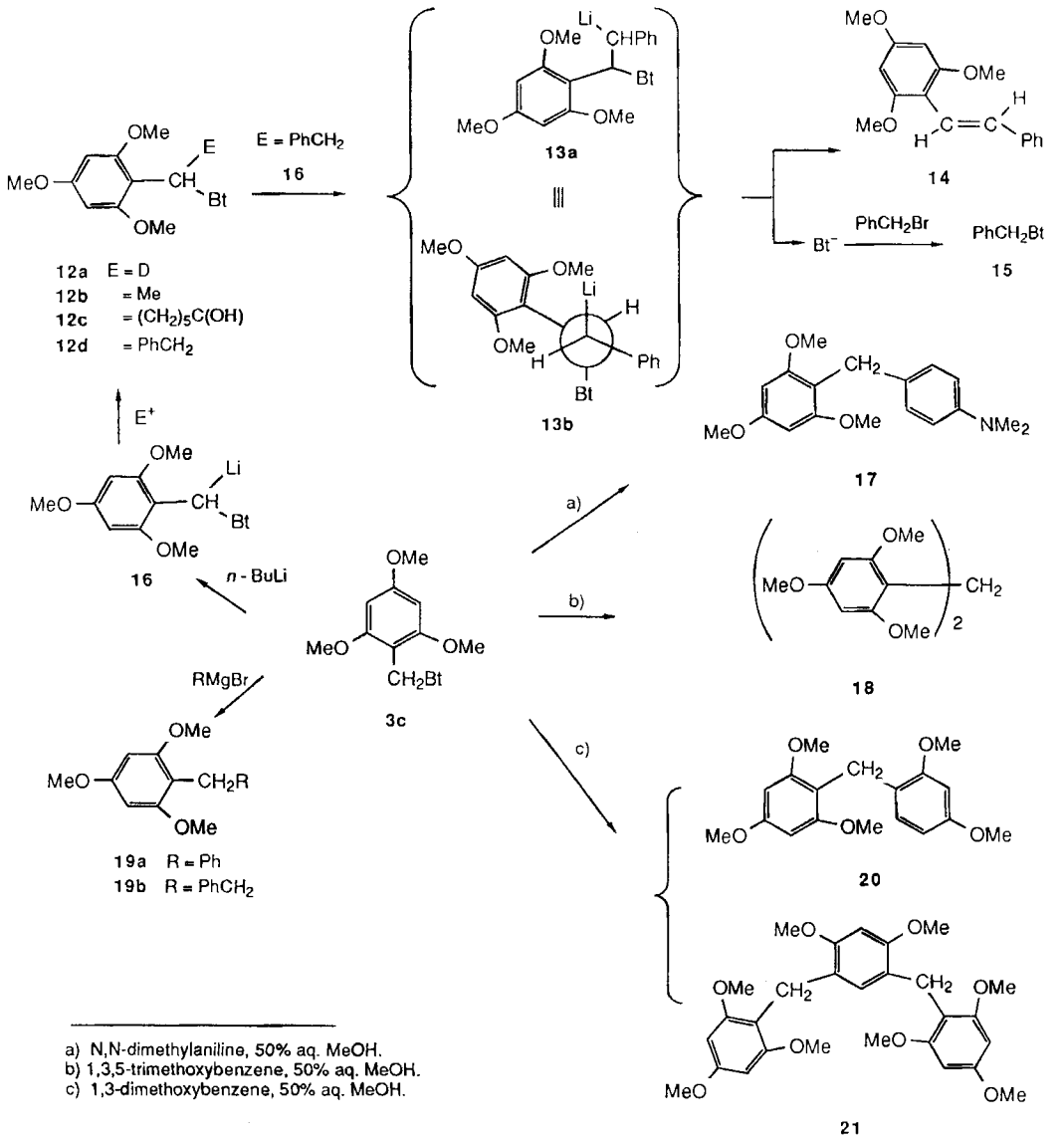
kylated products **3a–c**. The alkylation occurs at the position *para* to a methoxy group. When the *para*-position is occupied, the benzotriazolylmethylation occurs *ortho* to the methoxy group as shown in the alkylation of *p*-methylanisole (**1d**) to give **3d** in a yield of 24%. The same pattern is found in the benzotriazolylmethylation of 1- and 2-methoxynaphthalenes. For 1-methoxynaphthalene where a *para*-position is available, the alkylation occurs at the 4-position. However, for 2-methoxynaphthalene where a *para*-position is not available, the alkylation occurs at the most reactive *ortho*-, i.e. the 1-position, to give **3f**. In the reactions of 1- and 2-methoxynaphthalenes with **2**, byproducts **4** and **5** are also obtained in yields of 46 and 18%, respectively. Obviously **4** and **5** are formed by further reactions of **3e** and **3f** with more methoxynaphthalenes (**4** and **5** were previously prepared directly from the methoxynaphthalenes with formaldehyde[3,4]). This is confirmed by the formation of **5** in a yield of 73% from the reaction of **3f** with 2-methoxynaphthalene in refluxing toluene in the presence of *p*-toluenesulfonic acid. Analogous reactions are described below.

(ii) *By Conversion of the Corresponding Phenol to Its Methyl Ether:* The preparations of the *o*-(benzotriazolylmethyl)phenols **7** and **22** are described in the preceding paper[1]. Treatment of **7** and **22** with sodium hydride in DMSO, followed by addition of methyl iodide, afforded the corresponding methyl ethers **8** (97%) and **3f** (90%), respectively.

Lithiation of (Benzotriazol-1-ylmethyl)phenyl Methyl Ethers

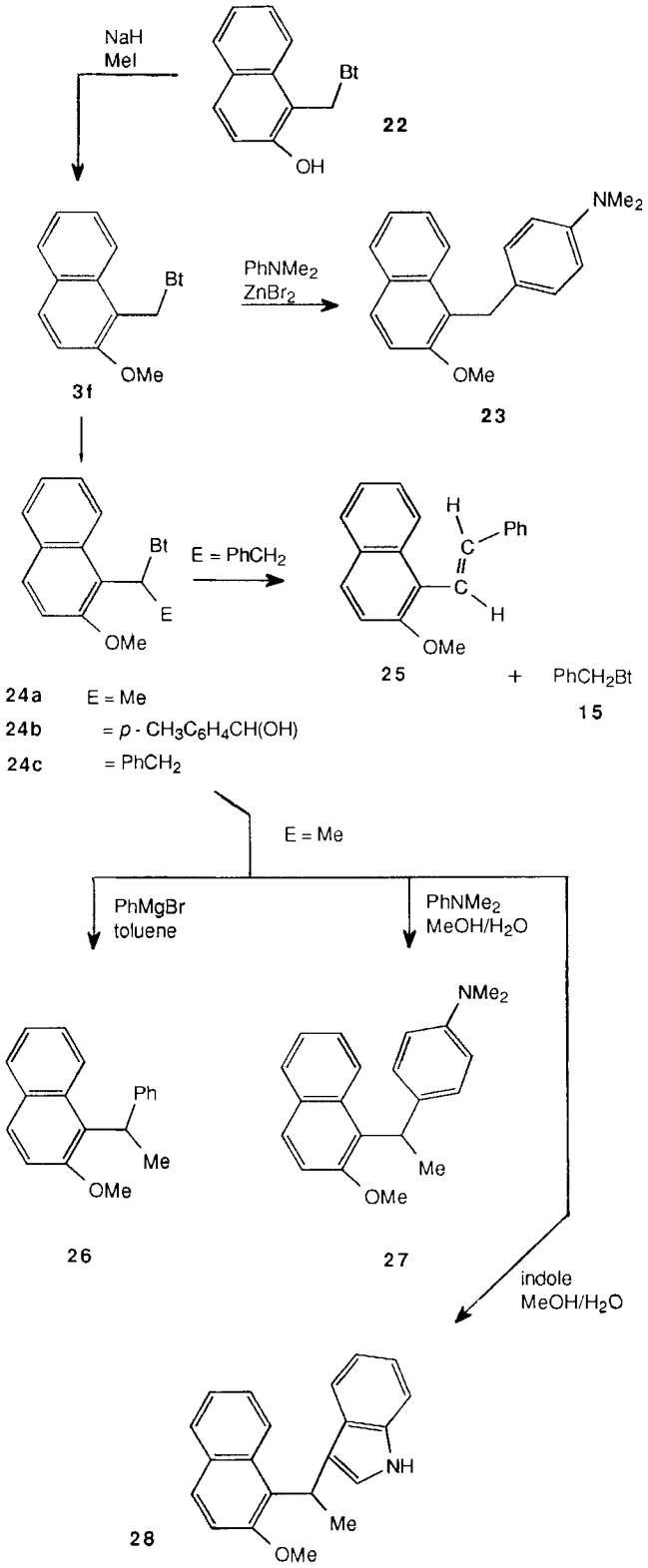
The phenol ether derivatives **3** and **8** possess relatively acidic methylene groups, which are benzylic and are also attached to an electron-withdrawing benzotriazole group. These methylene groups are indeed capable of ready deprotonation. Treatment of the ethers **3a** and **8** with *n*BuLi, followed by trapping the resulting anions with a variety of electrophiles, gave the expected products **6a–d** and **10a–f**, respectively in good yields (see Table 2). With substrate **3c**, in which the methylene group is more hindered, reactions of the anion with deuterium oxide, methyl iodide, or cy-

Scheme 3



clohexanone gave the desired products **12a–c**. However, with benzyl bromide, the desired product **12d** was accompanied by *trans*-1-phenyl-2-(2,4,6-trimethoxyphenyl)ethene (**14**) and 1-benzyl-1*H*-benzotriazole (**15**). Evidently, **12d** was in part deprotonated by the co-existing lithio salt **16** to give **13** (the methine proton while more acidic, is more hindered). *anti*-Elimination of the benzotriazole anion from **13** releases the strain energy to give the *trans*-alkene **14**. Subsequent attack of the benzotriazole anion on benzyl bromide affords **15**. The same phenomenon was observed with substrate **3f** which reacted with benzyl bromide to give a low yield of the expected product **24c** along with compounds **15** and **25**.

Scheme 4



Displacement of the Benzotriazole Group

(i) *By Grignard Reagents:* No reaction of **3c** occurred with phenylmagnesium bromide in refluxing THF. However, in refluxing toluene[5] **3c** reacted with phenyl- and benzylmagnesium bromide to give the desired products **19a** and **19b** in yields of 56 and 13%, respectively.

The naphthyl derivative **3f** did not react with phenylmagnesium bromide in THF at room temperature, or under reflux, or in toluene under reflux for 2 days. However, the introduction of a substituent at the methylene carbon enhanced the reactivity. Thus compound **24a** and phenylmagnesium bromide in refluxing toluene gave the desired product **26** in a yield of 69% (Scheme 4). Similarly, while compound **8** was unaffected by Grignard reagents, its methyl derivative **10a** reacted quite readily (Scheme 2). With phenylmagnesium bromide, product **11** was obtained in which benzotriazole has been displaced and the methoxy group simultaneously demethylated. The use of the milder reagent phenylzinc bromide avoided the demethylation and gave compound **9** in a yield of 75%.

(ii) *By Electron-Rich Aromatic and Heteroaromatic Compounds:* For 4-(benzotriazol-1-ylmethyl)-*N,N*-dialkylanilines, we have demonstrated[6] that the benzotriazole group can be displaced by electron-rich aromatic nucleophiles including anilines, 1,3-dimethoxybenzene, 1,3,5-trimethoxybenzene, pyrroles, and indoles. These same nucleophiles are now found similarly to displace the benzotriazole groups in the present compounds. Thus, **3c** was found to give products **17** and **18** when treated with *N,N*-dimethylaniline and 1,3,5-trimethoxybenzene, respectively (Scheme 3). With 1,3-dimethoxybenzene, in addition to the monosubstituted product **20** (38%), the disubstituted analogue **21** (48%) was also obtained.

While the reaction between **3f** and *N,N*-dimethylaniline required forced conditions in refluxing toluene in the presence of anhydrous zinc bromide to give **23**, the presence of a substituent at the methylene carbon again enhanced the reactivity. Thus, **24a** with *N,N*-dimethylaniline and indole under much milder conditions in refluxing 50% aqueous methanol solution gave the desired products **27** and **28**, respectively (Scheme 4). With indole, 2-methoxynaphthalene was also isolated, it was the major product in the reaction of **24a** with 1,3-dimethoxybenzene, and the only product with 1,3,5-trimethoxybenzene. Heating **24a** alone under the same reaction conditions also gave 2-methoxynaphthalene. In another experiment, when a mixutre of **24a**, indole, and zinc bromide was heated to 140°C for 5 h, 2-methoxynaphthalene was again obtained. It may thus be concluded that due to steric crowding, compound **24a** is not stable under vigorous reaction conditions, and dissociates to 2-methoxy-

naphthalene. It is reported[7] that 1,1'-benzylidenebis(2-methoxynaphthalene) is readily hydrolyzed under acidic conditions with the cleavage of the C–C bond to yield benzaldehyde and 2-methoxynaphthalene.

Experimental

General: See preceding paper[1].

General Procedure for the Alkylation of Phenol Ethers: A mixture of 1.49 g (10 mmol) of 1-(hydroxymethyl)-1*H*-benzotriazole, the appropriate phenol ether (10 mmol), and 1.90 g of *p*-toluenesulfonic acid (10 mmol) in 60 ml of toluene (THF was used as the solvent for **1b**, acetic acid was used both as the solvent and the acid catalyst for **1c**) was heated under reflux for the appropriate time (see Table 1). The solvent was then removed under reduced pressure, and to the residue was added sodium hydrogen carbonate solution (10%, 30 ml). The product was extracted with diethyl ether (3 × 30 ml), the combined extract washed with water and dried with $MgSO_4$. The solvent was removed in vacuo and the residue triturated with the appropriate solvent or chromatographed, as indicated below, to give the pure product.

Table 1. Preparation of (benzotriazol-1-ylmethyl)phenyl ethers **3** and **8**

No.	React. time [h]	Yield (%)	Crystal form[a] M.p. [°C]	Molecular formula (Mol. mass)	Calcd. / Found C	H	N
3a	48	30	microcryst. 78–80	$C_{14}H_{13}N_3O$ (239.3)	70.28 / 70.02	5.48 / 5.47	17.56 / 17.81
3b	25[b]	37	prisms[c] 68–70	$C_{15}H_{15}N_3O_2$ (269.3)	66.90 / 66.67	5.61 / 5.59	15.60 / 15.65
3c	48[d]	52	microcryst.[e] 159–161	$C_{16}H_{17}N_3O_3$ (299.3)	64.20 / 64.01	5.72 / 5.84	14.04 / 13.78
3d	48	24	plates 97–99	$C_{15}H_{15}N_3O$ (253.3)	71.13 / 71.48	5.97 / 6.04	16.59 / 16.70
3e	1	38	microcryst.[f] 168–170	$C_{18}H_{15}N_3O$ (289.3)	74.72 / 74.60	5.23 / 5.23	14.52 / 14.67
3f	5	50[g]	microcryst. 171–173	$C_{18}H_{15}N_3O$ (289.3)	74.72 / 74.85	5.23 / 5.26	14.52 / 14.78
8	–	97	plates 64–66	$C_{15}H_{15}N_3O$ (253.3)	71.13 / 71.38	5.97 / 6.00	16.59 / 16.38

[a] Recrystallization solvent: hexane/benzene except where stated otherwise. – [b] THF was used as the solvent. – [c] Recrystallization solvent: hexane. – [d] Acetic acid was used both as the solvent and as the acid catalyst. – [e] Recrystallization solvent: EtOH/H_2O. – [f] Recrystallization solvent: chloroform. – [g] Compound **3f** was also obtained from **22** in a yield of 90%.

4-(1H-Benzotriazol-1-ylmethyl)anisole (**3a**): The crude product was chromatographed with petroleum ether (40–60°C)/ethyl acetate (7:1). – ^{1}H NMR: δ = 3.74 (s, 3H), 5.75 (s, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.3–7.4 (m, 3H), 8.03 (d, *J* = 8.1 Hz, 1H). – ^{13}C NMR: δ = 51.7, 55.1, 109.7, 114.2, 119.8, 123.7, 126.7, 127.2, 129.0, 132.6, 146.2, 159.5.

1-(1H-Benzotriazol-1-ylmethyl)-2,4-dimethoxybenzene (**3b**): The crude product was chromatographed with petroleum ether (40 to 60°C)/ethyl acetate (4:1). – ^{1}H NMR: δ = 3.69 (s, 3H), 3.75 (s, 3H), 5.72 (s, 2H), 6.3–6.4 (m, 2H), 7.06 (d, *J* = 8.3 Hz, 1H), 7.25–7.40 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H). – ^{13}C NMR: δ = 46.1, 54.9, 55.0, 98.1, 104.2, 109.9, 115.2, 119.2, 123.3, 126.6, 130.2, 132.6, 145.6, 157.7, 160.9.

2-(1H-Benzotriazol-1-ylmethyl)-1,3,5-trimethoxybenzene (**3c**): The crude product was triturated with water and diethyl ether. – ^{1}H NMR: δ = 3.77 (s, 3H), 3.79 (s, 6H), 5.81 (s, 2H), 6.11 (s, 2H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H). – ^{13}C NMR: δ = 41.0, 55.2, 55.6, 90.3, 103.4, 110.4, 119.2, 123.1, 126.3, 132.8, 145.6, 159.6, 161.8.

2-(1H-Benzotriazol-1-ylmethyl)-4-methylanisole (**3d**): The crude product was chromatographed with petroleum ether (40–60°C)/ethyl acetate (10:1). – ^{1}H NMR (200 MHz): δ = 2.16 (s, 3H), 3.81 (s, 3H), 5.79 (s, 2H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.92 (s, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 7.26–7.52 (m, 3H), 8.02 (dd, *J* = 9.0, 1.0 Hz, 1H). – ^{13}C NMR (50 MHz): δ = 20.2, 46.4, 55.3, 110.0, 110.4, 119.6, 122.7, 123.5, 126.9, 129.2, 130.0, 132.9, 145.9, 154.6.

Reaction of 1-Methoxynaphthalene (**1e**) *with* **2**: The crude product was chromatographed with petroleum ether (40–60°C)/ethyl acetate (10:1) to give **3e** in a yield of 30% and **4** in a yield of 46%.

1-(1H-Benzotriazol-1-ylmethyl)-4-methoxynaphthalene (**3e**): ^{1}H NMR (200 MHz): δ = 3.96 (s, 3H), 6.18 (s, 2H), 6.73 (d, *J* = 7.9 Hz, 1H), 7.2–7.35 (m, 4H), 7.42–7.55 (m, 2H), 7.95–8.15 (m, 2H), 8.25–8.32 (m, 1H). – ^{13}C NMR (50 MHz): δ = 51.0, 55.5, 102.7, 110.1, 119.9, 121.7, 122.7, 122.8, 123.7, 125.5, 125.9, 127.1, 127.4, 127.6, 132.1, 133.0, 146.3, 156.3.

Bis(4-methoxynaphthalen-1-yl)methane (**4**): ^{1}H NMR (200 MHz): δ = 3.86 (s, 6H), 4.63 (s, 2H), 6.56 (d, *J* = 7.9 Hz, 2H), 6.89 (d, *J* = 7.9 Hz, 2H), 7.4–7.5 (m, 4H), 7.9–8.0 (m, 2H), 8.3–8.4 (m, 2H). – ^{13}C NMR (50 MHz): δ = 34.7, 55.3, 103.4, 122.5, 123.8, 124.9, 125.8, 126.4, 126.8, 128.2, 133.0, 154.3.

Reaction of 2-Methoxynaphthalene (**1f**) *with* **2**: The crude product was chromatographed with petroleum ether (40–60°C)/ethyl acetate (10:1) to give **3f** in a yield of 50% and **5** in a yield of 18%.

1-(1H-Benzotriazol-1-ylmethyl)-2-methoxynaphthalene (**3f**): ^{1}H NMR: δ = 4.08 (s, 3H), 6.33 (s, 2H), 7.2–7.3 (m, 4H), 7.46–7.54 (m, 2H), 7.72–7.76 (m, 1H), 7.86 (d, *J* = 9.2 Hz, 1H), 7.95 (dt, *J* = 8.0, 1.3 Hz, 1H), 8.37 (dd, *J* = 8.6, 0.8 Hz, 1H). – ^{13}C NMR: δ = 43.0, 56.5, 110.4, 112.5, 114.4, 119.6, 123.1, 123.5, 123.9, 126.8, 127.6, 128.4, 129.1, 131.4, 132.8, 133.2, 146.0, 155.2.

Bis(2-methoxynaphthalen-1-yl)methane (**5**): ^{1}H NMR (200 MHz): δ = 3.79 (s, 6H), 4.89 (s, 2H), 7.1–7.3 (m, 6H), 7.6–7.7 (m, 4H), 8.17 (d, *J* = 8.4 Hz, 2H). – ^{13}C NMR (50 MHz): δ = 21.6, 56.6, 113.8, 123.0, 123.7, 124.4, 125.7, 127.9, 128.2, 129.4, 133.7, 154.5.

General Procedure for the Conversion of the Phenol Derivatives **7** *and* **22** *into the Corresponding Methyl Ethers* **8** *and* **3f**: To a solution of the appropriate phenol derivative (10 mmol) in 20 ml of dimethyl sulfoxide was added 0.48 g of sodium hydride (60% in mineral oil; 12 mmol). The solution was stirred at room temp. for 30 min, and 1.25 ml of methyl iodide (20 mmol) was added. The solution was stirred for an additional 10 min, poured into 40 ml of ice/water, and extracted with diethyl ether (3 × 50 ml). The combined extract was washed four times with water, dried ($MgSO_4$) and the solvent evaporated to give the essentially pure product.

2-(1H-Benzotriazol-1-ylmethyl)-6-methylanisole (**8**): ^{1}H NMR: δ = 2.30 (s, 3H), 3.72 (s, 3H), 5.86 (s, 2H), 6.90 (d, *J* = 5.2 Hz, 2H), 7.05–7.15 (m, 1H), 7.25–7.50 (m, 3H), 8.02 (dt, *J* = 8.3, 1.1 Hz, 1H). – ^{13}C NMR: δ = 15.9, 47.0, 60.6, 109.8, 119.6, 123.6, 124.2, 126.9, 127.1, 127.6, 131.2, 131.7, 132.7, 145.9, 156.2.

1-(1H-Benzotriazol-1-ylmethyl)-2-methoxynaphthalene (**3f**) was obtained from **22** in a yield of 90% and is identical in all respects to that prepared as described above.

General Procedure for the Lithiation of **3** *and* **8**: To a solution of the appropriate substrate (1.0 mmol) in 20 ml of THF at –78°C

was added 0.4 ml of *n*BuLi (2.5 M in hexane; 1 mmol). The resulting solution was stirred at −78°C for 2 h, then an electrophile (1.0 mmol) in 3 ml of THF was added. After allowing to reach room temp., stirring was continued overnight, and the solution was diluted with water and extracted with diethyl ether (3 × 30 ml). The combined extract was washed with water and dried ($MgSO_4$). The solvent was removed in vacuo and the residue recrystallized or chromatographed as indicated below to afford the pure product. Results are compiled in Table 2.

Table 2. Lithiation of (benzotriazol-1-ylmethyl)phenyl ethers **3** and **8**

Substrate	Electrophile Product	Yield (%)	Recryst. solvent M.p. [°C]	Molecular formula (Mol. mass)	Calcd. Found C	H	N
3a	MeI	80	hex./C_6H_6	$C_{15}H_{15}N_3O$	71.13	5.97	16.59
	6a		83–85[a]	(253.3)	70.96	5.98	16.49
3a	$PhCH_2Br$	85	hex./C_6H_6	$C_{21}H_{19}N_3O$	76.57	5.81	12.76
	6b		134–136[b]	(329.4)	76.42	5.82	12.63
3a	$Ph_2C=O$	80	hex./C_6H_6	$C_{27}H_{23}N_3O_2$	76.94	5.50	9.97
	6c		200–202[a]	(421.5)	76.86	5.53	9.94
3a	CO_2	78	MeOH/EtOAc	$C_{15}H_{13}N_3O_3$	63.60	4.63	14.83
	6d		192–194[a]	(283.3)	63.33	4.63	14.77
8	**MeI**	90	**hex./C_6H_6**	$C_{16}H_{17}N_3O$	71.89	6.41	15.71
	10a		95–97[a]	(267.3)	72.03	6.46	15.70
8	$PhCH_2Br$	70	hex./C_6H_6	$C_{22}H_{21}N_3O$	76.94	6.16	12.24
	10b		102–104[c]	(343.4)	77.03	6.26	12.33
8	[d]	87[f]	hex./EtOAc	$C_{23}H_{23}N_3O_2$	73.97	6.21	11.25
	10c[e]		200–202[a]	(373.5)	74.10	6.32	11.29
8	[d]	87[h]	hex./EtOAc	$C_{23}H_{23}N_3O_2$	73.97	6.21	11.25
	10c[g]		152–154[a]	(373.5)	74.10	6.32	11.29
8	[i]	80	hex./EtOAc	$C_{21}H_{25}N_3O_2$	71.77	7.17	11.96
	10d		147–149[c]	(351.4)	71.90	7.33	12.06
8	$Ph_2C=O$	75	**MeOH/EtOAc**	$C_{28}H_{25}N_3O_2$	77.22	5.79	9.65
	10e		195–197[c]	(435.5)	77.51	5.85	9.71
8	$PhCO_2Et$	76	hex./C_6H_6	$C_{22}H_{19}N_3O_2$	73.93	5.36	11.76
	10f		102–104[a]	(357.4)	73.71	5.31	11.70
3c	D_2O	95	MeOH	$C_{16}H_{16}DN_3O_3$	[k]		
	12a		160–162[j]				
3c	MeI	85	hex./C_6H_6	$C_{17}H_{19}N_3O_3$	65.16	6.11	13.41
	12b		117–119[c]	(313.4)	65.09	6.15	13.42
3c	[i]	72	**hex./C_6H_6**	$C_{22}H_{27}N_3O_4$	66.48	6.85	10.57
	12c		116–118[a]	(397.5)	66.23	6.84	10.91
3c	$PhCH_2Br$	64	**hex./C_6H_6**	$C_{23}H_{23}N_3O_3$	70.93	5.95	10.79
	12d		124–126[c]	(389.5)	70.64	5.96	10.68
3f	MeI	98	hex./EtOAc	$C_{19}H_{17}N_3O$	75.23	5.65	13.85
	24a		131–133[a]	(303.4)	75.10	5.57	14.01
3f	[d]	60	hex./EtOAc	$C_{26}H_{23}N_3O_2$	76.26	5.66	10.26
	24b		213–215[a]	(409.5)	75.96	5.56	10.20
3f	$PhCH_2Br$	16[l]	hex./C_6H_6	$C_{25}H_{21}N_3O$	79.13	5.58	11.07
	24c		124–126[a]	(379.5)	78.80	5.50	11.11

[a] Microcrystals. — [b] Prisms. — [c] Plates. — [d] *p*-$CH_3C_6H_4CHO$. — [e] Isomer I. — [f] The isolated yield of the pure isomer I is 25%. — [g] Isomer II. — [h] The isolated yield of the pure isomer II is 36%. — [i] Cyclohexanone. — [j] Needles. — [k] Calcd. 300.1333, found 300.1336 (MS). — [l] 1-Benzyl-1*H*-benzotriazole was isolated in a yield of 14%.

4-[1-(1H-Benzotriazol-1-yl)ethyl]anisole (**6a**): The crude product was chromatographed with petroleum ether (40–60°C)/ethyl acetate (7:1). — ^{1}H NMR: δ = 2.11 (d, *J* = 7.1 Hz, 3H), 3.73 (s, 3H), 6.00 (q, *J* = 7.1 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 7.2–7.3 (m, 5H), 8.0–8.1 (m, 1H). — ^{13}C NMR: δ = 20.9, 55.0, 58.4, 110.1, 114.0, 119.7, 123.6, 126.8, 127.4, 131.9, 132.2, 146.2, 159.2.

4-[1-(1H-Benzotriazol-1-yl)-2-phenylethyl]anisole (**6b**): The crude product was recrystallized from hexane/benzene. — ^{1}H NMR (200 MHz): δ = 3.71 (dd, *J* = 13.8, 6.8 Hz, 1H), 3.73 (s, 3H), 4.08 (dd, *J* = 13.8, 8.7 Hz, 1H), 5.91 (dd, *J* = 8.7, 6.8 Hz, 1H), 6.75–6.85 (m, 2H), 7.0–7.4 (m, 10H), 7.95–8.05 (m, 1H). — ^{13}C NMR (50 MHz): δ = 41.4, 55.1, 64.7, 109.6, 114.1, 119.8, 123.7, 126.7, 126.9, 128.2, 128.3, 129.0, 130.8, 132.8, 137.2, 146.0, 159.4.

2-(1H-Benzotriazol-1-yl)-2-(4-methoxyphenyl)-1,1-diphenylethanol (**6c**): The crude product was recrystallized from hexane/benzene. — ^{1}H NMR (200 MHz): δ = 3.66 (s, 3H), 5.83 (s, 1H), 6.59 (d, *J* = 8.3 Hz, 3H), 6.9–7.5 (m, 14H), 7.98 (d, *J* = 8.2 Hz, 1H). — ^{13}C NMR (50 MHz): δ = 55.0, 68.0, 81.2, 109.3, 113.0, 120.2, 124.4, 125.4, 126.4, 126.8, 126.9, 127.1, 127.7, 128.0, 128.2, 130.1, 133.2, 143.1, 144.8, 145.4, 159.2.

2-(1H-Benzotriazol-1-yl)-2-(4-methoxyphenyl)acetic acid (**6d**): The crude product was recrystallized from methanol/ethyl acetate. — ^{1}H NMR (200 MHz): δ = 3.76 (s, 3H), 7.00 (d, *J* = 8.1 Hz, 2H), 7.15 (s, 1H), 7.35–7.74 (m, 5H), 8.07 (d, *J* = 8.0 Hz, 1H). — ^{13}C NMR (50 MHz): δ = 55.2, 63.7, 111.0, 114.1, 119.2, 124.0, 125.9, 127.5, 130.6, 132.8, 145.2, 159.5, 169.5.

2-[1-(1H-Benzotriazol-1-yl)ethyl]-6-methylanisole (**10a**): Evaporation of the solvent gave an essentially pure product. — ^{1}H NMR: δ = 2.16 (d, *J* = 7.0 Hz, 3H), 2.32 (s, 3H), 3.73 (s, 3H), 6.40 (q, *J* = 7.0 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.24–7.44 (m, 3H), 8.02 (d, *J* = 8.3 Hz, 1H). — ^{13}C NMR: δ = 16.3, 21.2, 52.5, 60.9, 110.1, 119.8, 123.7, 124.5, 125.0, 126.9, 131.1, 131.5, 132.6, 133.1, 146.1, 155.6.

2-[1-(Benzotriazol-1-yl)-2-phenylethyl]-6-methylanisole (**10b**): The crude product was chromatographed with petroleum ether (40–60°C)/ethyl acetate (8:1). — ^{1}H NMR: δ = 2.25 (s, 3H), 3.46 (s, 3H), 3.72 (dd, *J* = 14.0, 6.4 Hz, 1H), 4.09 (dd, *J* = 14.0, 8.9 Hz, 1H), 6.40 (dd, *J* = 8.9, 6.4 Hz, 1H), 6.9–7.3 (m, 9H), 7.40 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.94 (dd, *J* = 8.0, 1.0 Hz, 1H). — ^{13}C NMR: δ = 16.3, 41.2, 58.1, 60.6, 109.6, 119.4, 123.6, 124.4, 125.6, 126.6, 126.8, 128.3, 129.1, 130.8, 131.6, 133.1, 137.5, 145.6, 155.7.

Reaction of **8** *with p-Tolualdehyde:* The crude product was chromatographed with petroleum ether (40–60°C)/ethyl acetate (3:1) to give the pure isomer I in a yield of 25%, the pure isomer II in a yield of 36%, and a mixture of both isomers in a yield of 26%. The total yield was 87%.

2-(1H-Benzotriazol-1-yl)-2-(2-methoxy-3-methylphenyl)-1-(4-methylphenyl)ethanol (**10c**)

Isomer I: ^{1}H NMR: δ = 2.19 (s, 3H), 2.28 (s, 3H), 3.36 (d, *J* = 2.7 Hz, 1H), 3.53 (s, 3H), 5.98 (dd, *J* = 7.4, 2.7 Hz, 1H), 6.34 (d, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.1–7.4 (m, 6H), 7.80 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H). — ^{13}C NMR: δ = 16.5, 21.0, 60.7, 60.8, 75.2, 109.7, 119.5, 123.8, 124.4, 126.7, 127.0, 127.2, 128.6, 128.9, 130.8, 132.0, 133.1, 137.1, 137.9, 145.0, 156.9.

Isomer II: ^{1}H NMR: δ = 2.16 (s, 3H), 2.23 (s, 3H), 3.20 (s, 3H), 4.22 (d, *J* = 4.9 Hz, 1H), 6.05 (dd, *J* = 8.8, 4.9 Hz, 1H), 6.32 (d, *J* = 8.8 Hz, 1H), 6.92 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 3H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.25 (td, *J* = 8.1, 1.3 Hz, 1H), 7.34 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.46 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H). — ^{13}C NMR: δ = 16.5, 21.0, 60.3, 62.8, 75.1, 110.1, 119.4, 124.0, 124.1, 126.6, 126.9, 127.3, 128.7, 129.0, 130.7, 131.8, 133.6, 136.9, 137.4, 145.2, 156.0.

1-[(1H-Benzotriazol-1-yl)(2-methoxy-3-methylphenyl)methyl]-cyclohexanol (**10d**): The crude product was washed with hexane. — ^{1}H NMR: δ = 1.1–1.7 (m, 10H), 2.33 (s, 3H), 3.75 (d, *J* = 1.5 Hz, 1H), 3.90 (s, 3H), 6.25 (s, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 7.10 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.35 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.48 (dt, *J* = 6.9, 0.9 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.92 (dd, *J* = 7.8, 1.4 Hz,

1H), 8.05 (td, J = 8.4, 0.9 Hz, 1H). – ^{13}C NMR: δ = 16.9, 21.2, 21.5, 34.6, 36.3, 61.1, 62.7, 74.6, 109.8, 120.0, 124.0, 124.1, 127.6, 128.0, 128.7, 130.0, 131.7, 134.0, 144.9, 156.5.

2-(1H-Benzotriazol-1-yl)-2-(2-methoxy-3-methylphenyl)-1,1-diphenylethanol (**10e**): The crude product was chromatographed with petroleum ether (40–60°C)/ethyl acetate (5:1). – ^{1}H NMR: δ = 2.15 (s, 3H), 3.07 (s, 3H), 5.93 (s, 1H), 6.9–7.5 (m, 15H), 7.67 (td, J = 8.4, 1.1 Hz, 1H), 7.90 (td, J = 8.4, 0.9 Hz, 1H), 7.95 (dd, J = 7.8, 1.5 Hz, 1H). – ^{13}C NMR: δ = 17.1, 59.9, 60.3, 81.7, 109.8, 119.9, 123.6, 124.2, 125.8, 127.1, 127.2, 127.5, 127.6, 127.8, 128.1, 128.5, 128.8, 129.6, 132.0, 133.3, 143.0, 144.5, 145.2, 156.3.

ω-(1H-Benzotriazol-1-yl)-ω-(2-methoxy-3-methylphenyl)acetophenone (**10f**): The crude product was chromatographed with petroleum ether (40–60°C)/ethyl acetate (3:1). – ^{1}H NMR: δ = 2.30 (s, 3H), 3.43 (s, 3H), 6.99 (t, J = 7.7 Hz, 1H), 7.20 (t, J = 8.0 Hz, 2H), 7.25–7.52 (m, 6H), 7.95–8.05 (m, 3H), 8.16 (s, 1H). – ^{13}C NMR: δ = 16.3, 60.5, 62.8, 110.8, 119.9, 123.7, 124.1, 126.0, 127.4, 127.7, 128.6, 128.7, 131.9, 133.2, 133.8, 134.1, 146.2, 156.6, 192.4.

(1H-Benzotriazol-1-yl)deuterio(2,4,6-trimethoxyphenyl)methane (**12a**): Evaporation of solvent gave the essentially pure product. – ^{1}H NMR: δ = 3.76 (s, 3H), 3.78 (s, 6H), 5.79 (s, 1H), 6.11 (s, 2H), 7.25 (t, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H). – ^{13}C NMR: δ = 40.8, 55.1, 55.5, 90.3, 103.3, 110.4, 119.2, 123.0, 126.3, 132.8, 145.6, 159.5, 161.7.

2-[1-(1H-Benzotriazol-1-yl)ethyl]-1,3,5-trimethoxybenzene (**12b**): The crude product was chromatographed with petroleum ether (40–60°C)/ethyl acetate (12:1). – ^{1}H NMR (200 MHz): δ = 2.24 (d, J = 7.1 Hz, 3H), 3.67 (s, 6H), 3.77 (s, 3H), 6.09 (s, 2H), 6.42 (q, J = 7.1 Hz, 1H), 7.2–7.3 (m, 3H), 7.95–8.05 (m, 1H). – ^{13}C NMR (50 MHz): δ = 17.9, 50.5, 55.2, 55.6, 90.8, 108.7, 110.5, 119.3, 123.0, 126.0, 132.9, 145.9, 159.0, 161.1.

1-[1-(1H-Benzotriazol-1-yl)(2,4,6-trimethoxyphenyl)methyl]cyclohexanol (**12c**): The crude product was chromatographed with petroleum ether (40–60°C)/ethyl acetate (10:1). – ^{1}H NMR (200 MHz): δ = 1.2–2.1 (m, 10H), 3.75 (s, 6H), 3.81 (s, 3H), 4.85 (s, 1H), 6.1–6.2 (broad, 2H), 6.33 (s, 1H), 7.25–7.40 (m, 3H), 7.95–8.05 (m, 1H). – ^{13}C NMR (50 MHz): δ = 21.5, 21.8, 25.9, 34.8, 36.4, 55.2, 55.8, 62.2, 74.5, 90.5, 105.5, 119.4, 123.4, 126.7, 133.9, 144.5, 159.0, 161.1.

Reaction of **3c** *with Benzyl Bromide:* The crude product was chromatographed with petroleum ether (40–60°C)/ethyl acetate (10:1) to give **12d**, **14**, and **15** in yields of 64%, 10%, and 12%, respectively.

2-[1-(1H-Benzotriazol-1-yl)-2-phenylethyl]-1,3,5-trimethoxybenzene (**12d**): ^{1}H NMR: δ = 3.58 (s, 6H), 3.73 (s, 3H), 3.98 (dd, J = 13.5, 8.8 Hz, 1H), 4.31 (dd, J = 13.5, 6.6 Hz, 1H), 6.00 (s, 2H), 6.50 (dd, J = 8.8, 6.6 Hz, 1H), 7.1–7.3 (m, 8H), 7.95–8.05 (m, 1H). – ^{13}C NMR: δ = 37.6, 55.1, 55.7, 56.1, 90.9, 107.2, 110.4, 119.3, 123.1, 126.1, 127.9, 129.4, 133.1, 138.6, 145.8, 159.4, 161.2.

1,3,5-Trimethoxy-2-(trans-2-phenylethenyl)benzene (**14**): M.p. 58 to 59°C (ref.[11] 58–59°C). – ^{1}H NMR: δ = 3.78 (s, 3H), 3.83 (s, 6H), 6.13 (s, 2H), 7.12–7.22 (m, 1H), 7.30 (t, J = 7.9 Hz, 2H), 7.43 (d, J = 7.3 Hz, 2H), 7.50 (d, J = 7.3 Hz, 2H). – ^{13}C NMR: δ = 55.1, 55.6, 90.7, 108.0, 119.8, 126.0, 126.4, 128.3, 129.7, 139.6, 159.4, 160.1.

1-Benzyl-1H-benzotriazole (**15**): M.p. 115–117°C (ref.[12] 115–116°C). – ^{1}H NMR: δ = 5.83 (s, 2H), 7.2–7.4 (m, 8H), 8.05 (dt, J = 8.0, 1.0 Hz, 1H). – ^{13}C NMR: δ = 52.1, 109.6, 119.9, 123.8, 127.3, 127.5, 128.5, 128.9, 132.7, 134.7, 146.2.

1-[1-(1H-Benzotriazol-1-yl)ethyl]-2-methoxynaphthalene (**24a**): Evaporation of solvent gave the essentially pure product. – ^{1}H NMR: δ = 2.45 (d, J = 7.2 Hz, 3H), 3.94 (s, 3H), 6.92 (q, J = 7.2 Hz, 1H), 7.0–7.3 (m, 6H), 7.71 (dd, J = 8.0, 1.4 Hz, 1H), 7.81 (d, J = 9.0 Hz, 1H), 7.97 (dt, J = 7.8, 1.4 Hz, 1H), 8.02 (d, J = 9.0 Hz, 1H). – ^{13}C NMR: δ = 18.7, 52.0, 56.5, 110.3, 112.9, 119.5, 119.7, 122.5, 123.5, 123.6, 126.5, 127.1, 128.9, 129.4, 130.8, 131.6, 133.2, 146.3, 154.3.

2-(1H-Benzotriazol-1-yl)-2-(2-methoxynaphthalen-1-yl)-1-(4-methylphenyl)ethanol (**24b**): The crude product was triturated with diethyl ether. – ^{1}H NMR: δ = 2.17 (s, 3H), 3.58 (s, 3H), 4.57 (d, J = 2.5 Hz, 1H), 6.6–6.7 (m, 1H), 6.8–7.4 (m, 11H), 7.67 (t, J = 9.0 Hz, 2H), 8.00 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 9.0 Hz, 1H). – ^{13}C NMR: δ = 21.0, 56.5, 63.5, 73.4, 110.5, 112.9, 116.1, 119.6, 122.6, 123.5, 124.1, 126.7, 127.2, 127.3, 128.1, 128.8, 129.2, 131.2, 132.1, 133.6, 135.7, 137.3, 145.7, 155.2.

Reaction of **3f** *with Benzyl Bromide:* The crude product was chromatographed with dichloromethane to give **15**, **24c**, and **25** in yields of 14, 16, and 20%, respectively.

1-[1-(1H-Benzotriazol-2-phenylethyl]-2-methoxynaphthalene (**24c**): ^{1}H NMR: δ = 3.63 (s, 3H), 4.16 (dd, J = 13.6, 9.0 Hz, 1H), 4.60 (dd, J = 13.6, 6.0 Hz, 1H), 7.0–7.4 (m, 12H), 7.68 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.9–8.0 (m, 1H), 8.23 (d, J = 9.0 Hz, 1H). – ^{13}C NMR: δ = 38.4, 56.7, 57.6, 110.3, 113.2, 118.2, 119.4, 122.9, 123.6, 126.4, 126.6, 127.1, 127.9, 128.8, 129.4, 129.5, 131.0, 131.9, 133.3, 137.9, 146.0, 155.0.

2-Methoxy-1-(trans-2-phenylethenyl)naphthalene (**25**): Oil. – Calcd. for $C_{19}H_{16}O$ 260.1201, found 260.1200 (MS). – ^{1}H NMR: δ = 3.92 (s, 3H), 7.1–7.5 (m, 8H), 7.58 (d, J = 6.8 Hz, 2H), 7.75 (t, J = 6.8 Hz, 2H), 8.25 (d, J = 6.8 Hz, 1H). – ^{13}C NMR: δ = 56.3, 113.1, 120.5, 122.2, 123.5, 124.3, 126.4, 126.5, 127.4, 128.3, 128.6, 128.7, 129.3, 132.6, 134.8, 138.1, 154.7.

Procedure for the Reaction of **10a** *with Phenylzinc Bromide, Preparation of 2-Methyl-6-(1-phenylethyl)anisole* (**9**): To 8.0 ml of phenylmagnesium bromide (1 mmol/ml in diethyl ether; 8 mmol) was added a solution of 3.6 g of zinc bromide (16 mmol) in 12 ml of THF to give a white precipitate. To the mixture was added 0.27 g (1.0 mmol) of **10a**. Toluene (20 ml) was then added, and the diethyl ether and THF were removed by distillation until the temp. reached the boiling point of toluene. The resulting solution was then heated under reflux for 3 d (until TLC indicated that the starting material had been consumed), cooled, poured into ice/water, acidified with 2 N HCl and the mixture extracted with diethyl ether (3 × 30 ml). The combined extract was dried with $MgSO_4$, the solvent removed in vacuo and the residue chromatographed with petroleum ether (40–60°C)/ethyl acetate (40:1) to give the pure product. – ^{1}H NMR: δ = 1.58 (d, J = 7.3 Hz, 3H), 2.28 (s, 3H), 3.57 (s, 3H), 4.56 (q, J = 7.3 Hz, 1H), 6.9–7.3 (m, 8H). – ^{13}C NMR: δ = 16.3, 22.0, 37.6, 60.4, 123.9, 125.8, 125.9, 127.5, 128.2, 129.2, 130.9, 139.1, 146.7, 156.2.

General Procedure for the Displacement of Benzotriazole by Grignard Reagents: To a solution of the appropriate benzotriazole derivative (1.0 mmol) in 20 ml of toluene at room temp. was added the corresponding Grignard reagent (12 mmol) in diethyl ether (see Table 3). The solvent was distilled off until the temp. reached the boiling point of toluene, and the resulting solution was refluxed for the appropriate time until TLC indicated that the starting material had been consumed (see Table 3). The mixture was poured into 20 ml of ice/water, acidified with 2 N HCl, the mixture extracted with diethyl ether (3 × 30 ml) and the combined extract dried with $MgSO_4$. The solvent was removed in vacuo and the residue chromatographed with petroleum ether (40–60)/ethyl acetate to give the pure product (see Table 3).

Table 3. Displacement of benzotriazole in the (benzotriazolylalkyl)phenyl ethers by Grignard reagents and aromatic nucleophiles

Substrate	Reagent[a]	React. time [h]	Product	Yield (%)	M.p. [°C]	Purif. solvent[b]	Crystal form	Molecular formula (Mol. mass)	C	Calcd. / Found H	N
3e	1-MN	1	**4**	46	151–153[c]	10:1	plates	–		–	
3f	2-MN	5	**5**	73[d]	145–147[e]	10:1	microcryst.	–		–	
10a	PhZnBr	72	**9**	75	oil	40:1	–	$C_{16}H_{18}O$		[f]	
10a	PhMgBr	48	**11**	38	oil[g]	12:1	–	–		–	
3c	DMA	23	**17**	70	89–90[h]	[i]	plates	–		–	
3c	TMB	30	**18**	40	116–117[j]	9:1	microcryst.	–		–	
3c	PhMgBr	8	**19a**	56	93–95[k]	20:1	microcryst.	–		–	
3c	$PhCH_2MgBr$	8	**19b**	13	oil	[l]	–	$C_{17}H_{20}O_3$	74.97	7.40	–
								(272.3)	75.01	7.41	–
3c	DMB	24	**20**	38	146–148	9:1	plates	$C_{18}H_{22}O_5$	67.91	6.97	–
								(318.4)	67.96	7.07	–
3c	DMB	24	**21**	48	157–159	9:1	microcryst.	$C_{28}H_{34}O_8$	67.45	6.87	–
								(485.5)	67.15	6.96	–
3f	DMA	12	**23**	83	107–109	8:1	plates	$C_{20}H_{21}NO$	82.44	7.26	4.81
									82.38	7.34	4.66
24a	PhMgBr	24	**26**	69	70–72	hexane	microcryst.	$C_{19}H_{18}O$	86.99	6.92	–
								(262.4)	86.69	7.01	–
24a	DMA	72	**27**	52	oil	10:1	–	$C_{21}H_{23}NO$		[m]	
24a	Indole	24	**28**	43	45–47	10:1	microcryst.	$C_{21}H_{19}NO$	83.69	6.35	4.65
								(301.4)	83.54	6.48	4.55

[a] MN = methoxynaphthalene; DMA = *N,N*-dimethylaniline; TMB = 1,3,5-trimethoxybenzene; DMB = 1,3-dimethoxybenzene. – [b] The ratio indicates that of petroleum ether (40–60°C)/ethyl acetate which is the solvent system used for chromatography. – [c] Ref.[3] m.p. 150.5–152°C. – [d] Compound **5** was also obtained as a byproduct in a yield of 18% in the reaction of 2-MN with **2**. – [e] Ref.[8] m.p. 146–147°C. – [f] Calcd. 226.1357, found 226.1359 (MS). – [g] Ref.[9] b.p. 166°C/10 Torr. – [h] Ref.[6] m.p. 89 to 90°C. – [i] The crude product was recrystallized from hexane. – [j] Ref.[2a] m.p. 116–117°C. – [k] Ref.[10] m.p. 92–94°C. – [l] The eluent for the chromatography is hexane/CH_2Cl_2 (1:2). – [m] Calcd. 305.1764, found 305.1768 (MS).

2-Methyl-6-(1-phenylethyl)phenol (**11**): ^{1}H NMR: δ = 1.59 (d, *J* = 7.2 Hz, 3H), 2.13 (s, 3H), 4.30 (q, *J* = 7.2 Hz, 1H), 4.59 (s, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.98 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.1–7.3 (m, 6H). – ^{13}C NMR: δ = 15.8, 21.2, 39.0, 120.3, 124.0, 125.5, 126.4, 127.4, 128.7, 128.9, 131.3, 145.3, 151.6.

2-Benzyl-1,3,5-trimethoxybenezene (**19a**): ^{1}H NMR: δ = 3.69 (s, 6H), 3.71 (s, 3H), 3.93 (s, 2H), 6.10 (s, 2H), 7.0–7.2 (m, 5H). – ^{13}C NMR: δ = 28.2, 55.1, 55.4, 90.4, 110.0, 125.1, 127.8, 128.3, 142.1, 158.7, 159.6.

1,3,5-Trimethoxy-2-phenethylbenzene (**19b**): ^{1}H NMR: δ = 2.69 to 2.76 (m, 2H), 2.84–2.90 (m, 2H), 3.72 (s, 6H), 3.77 (s, 3H), 6.11 (s, 2H), 7.0–7.3 (m, 5H). – ^{13}C NMR: δ = 24.7, 35.7, 55.2, 55.5, 90.4, 110.9, 125.4, 127.9, 128.5, 143.1, 158.7, 159.2.

2-Methoxy-1-(1-phenylethyl)naphthalene (**26**): ^{1}H NMR: δ = 1.80 (d, *J* = 7.3 Hz, 3H), 3.70 (s, 3H), 5.26 (q, *J* = 7.3 Hz, 1H), 7.1–7.3 (m, 8H), 7.68–7.75 (m, 2H), 7.84 (d, *J* = 8.0 Hz, 1H). – ^{13}C NMR: δ = 18.0, 34.4, 56.7, 114.6, 123.1, 124.4, 125.1, 125.8, 127.0, 127.9, 128.0, 128.4, 128.6, 129.9, 132.5, 146.0, 154.8.

Procedure for the Reaction of **3f** *with 2-Methoxynaphthalene, Preparation of Bis(2-methoxynaphthalen-1-yl)methane* (**5**): A mixture of 0.58 g of **3f** (2 mmol), 0.63 g of 2-methoxynaphthalene (4 mmol), and 0.38 g of *p*-toluenesulfonic acid (2 mmol) in 30 ml of toluene was heated under reflux for 46 h. The toluene was then removed under reduced pressure, to the residue was added 30 ml of 10% NaOH solution, and the mixture was extracted with CH_2Cl_2. The combined extract was dried with $MgSO_4$, the solvent removed in vacuo and the residue chromatographed with petroleum ether (40–60°C)/ethyl acetate (60:1) to give **5** (0.48 g, 73%). This compound is identical in all respects to that prepared as described above.

Procedure for the Reaction of **3f** *with N,N-Dimethylaniline, Preparation of 1-[4-(Dimethylamino)phenylmethyl]-2-methoxynaphthalene* (**23**): To a solution of 0.48 g of **3f** (2 mmol) and 0.48 g of *N,N*-dimethylaniline (4 mmol) in 20 ml of dry toluene under nitrogen was added 0.90 g of anhydrous zinc bromide (4 mmol). The whole was heated under reflux for 12 h, then poured into ice/water. The solution was extracted with Et_2O (3 × 30 ml), the combined extract dried with MgSO, the solvent removed in vacuo and the residue chromatographed with petroleum ether (40–60°C)/ethyl acetate (8:1) to give **23** (0.48 g, 83%). – ^{1}H NMR: δ = 2.73 (s, 6H), 3.79 (s, 3H), 4.38 (s, 2H), 6.55 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.9 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 9.5 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 1H). – ^{13}C NMR: δ = 29.4, 40.6, 56.4, 112.8, 113.4, 122.3, 123.0, 123.8, 126.2, 127.9, 128.2, 128.7, 129.21, 129.24, 133.3, 148.7, 154.6.

General Procedure for the Displacement of Benzotriazole by Electron-Rich Aromatic Compounds: To a solution of the substrate (1.0 mmol) in 20 ml of MeOH under reflux was added a solution of the appropriate aromatic nucleophile (1.0 mmol) and 0.5 ml of conc. hydrochloric acid in water (20 ml). The whole was then heated under reflux for the appropriate time (see Table 3) followed by addition of an aqueous KOH solution (1 M; 30 ml) and subsequently cooled. The mixture was extracted with diethyl ether (3 × 30 ml), the combined extract dried with $MgSO_4$, the solvent removed in vacuo and the residue recrystallized or chromatographed (see Table 3).

2-[4-(Dimethylamino)phenylmethyl]-1,3,5-trimethoxybenzene (**17**): ^{1}H NMR: δ = 2.85 (s, 6H), 3.76 (s, 6H), 3.77 (s, 3H), 3.83 (s, 2H), 6.12 (s, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H). – ^{13}C NMR: δ = 27.1, 41.0, 55.2, 55.6, 90.6, 111.0, 112.9, 128.8, 130.7, 148.7, 158.7, 159.3.

1,1'-Methylenebis(2,4,6-trimethoxybenzene) (**18**): ^{1}H NMR: δ = 3.68 (s, 12H), 3.75 (s, 6H), 3.84 (s, 2H), 6.08 (s, 4H). – ^{13}C NMR: δ = 16.5, 55.0, 55.9, 91.0, 111.8, 158.6, 159.1.

2-(2,4-Dimethoxyphenylmethyl)-1,3,5-trimethoxybenzene (**20**): ^{1}H NMR: δ = 3.70 (s, 6H), 3.71 (s, 3H), 3.80 (s, 3H), 3.82–3.83 (m, 5H), 6.17 (s, 2H), 6.27 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.43 (d, *J* = 2.5 Hz, 1H), 6.55 (d, *J* = 8.3 Hz, 1H). – ^{13}C NMR: δ = 21.4, 55.10, 55.13, 55.20, 55.6, 90.5, 98.0, 103.4, 108.7, 122.0, 127.8, 158.0, 158.5, 159.2, 159.6.

1,5-Dimethoxy-2,4-bis(2,4,6-trimethoxyphenylmethyl)benzene (**21**): ^{1}H NMR: δ = 3.50 (s, 12H), 3.70 (s, 4H), 3.80 (s, 6H), 3.83 (s, 6H), 5.94 (s, 1H), 6.02 (s, 4H), 6.42 (s, 1H). – ^{13}C NMR: δ = 21.0, 55.1, 55.3, 55.7, 90.2, 95.1, 109.3, 120.4, 127.8, 155.5, 158.9, 159.2.

1-{1-[4-(Dimethylamino)phenyl]ethyl}-2-methoxynaphthalene (**27**): ^{1}H NMR: δ = 1.78 (d, *J* = 7.3 Hz, 3H), 2.82 (s, 6H), 3.76 (s, 3H), 5.20 (q, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.8 Hz, 2H), 7.1–7.3 (m, 5H), 7.66–7.74 (m, 2H), 7.86–7.92 (m, 1H). – ^{13}C NMR: δ = 18.4, 33.5, 40.8, 56.9, 112.7, 114.7, 123.0, 124.7, 125.6, 127.5, 128.1, 128.4, 128.5, 129.9, 132.5, 134.2, 148.4, 154.8.

3-[1-(2-Methoxynaphthalen-1-yl)ethyl]indole (**28**): – ^{1}H NMR: δ = 1.89 (d, *J* = 7.2 Hz, 3H), 3.79 (s, 3H), 5.46 (q, *J* = 7.2 Hz, 1H), 6.78–6.86 (m, 1H), 6.9–7.3 (m, 7H), 7.6–7.8 (m, 3H) 8.18 to 8.22 (m, 1H). – ^{13}C NMR: δ = 19.3, 28.0, 56.9, 110.8, 114.5, 118.8, 119.6, 121.0, 121.2, 121.5, 123.0, 124.4, 125.5, 127.19, 127.22, 128.2, 128.6, 129.9, 132.9, 136.4, 154.5.

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