# Hartwig–Buchwald Amination on Solid Supports: a Novel Access to a Diverse Set of 1*H*-Benzotriazoles

Viktor Zimmermann and Stefan Bräse*

*Institut für Organische Chemie, Universität Karlsruhe (TH), Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany*

*Received June 27, 2007*

Hartwig–Buchwald amination reactions of bromo- and chloroarenes were performed on solid supports with triazene-linked arenes. Immobilized 2-haloarenes were treated with diverse primary amines and anilines at 100 °C under palladium catalysis to yield *N*-substituted 2-aminoarenes. The latter were alternatively formed through reaction of bromo- and chloroarenes with immobilized primary 2-aminobenzenes. Subsequent acidic cleavage furnished 1*H*-benzotriazoles in high purities. The two described routes allow a broad range of the substitution pattern of *N*-substituted 1*H*-benzotriazoles.

Hartwig–Buchwald amination is a powerful technique to convert arylhalides into the corresponding anilines.[1] Since this reaction tolerates diverse amines and is compatible with various functional groups, this reaction ought to be particularly suitable for combinatorial syntheses. However, the examples described in the literature are limited.[2] To our knowledge, a systematic variation of immobilization of both the nucleophile and the halide is lacking.

Recently, we disclosed a straightforward solid-phase synthesis of 1-alkyl 1*H*-benzotriazoles via nucleophilic displacement.[3] However, the structural diversity was limited due to the fact that only 1-alkyl-5-nitro-substituted 1*H*-benzotriazoles can be obtained. Since the benzotriazolyl moiety is shown to be an important—but still underdeveloped—pharmacophore,[4] an alternative entry to this class was investigated.

In this manuscript, we report on a versatile route to 1-alkyl- and 1-aryl-1*H*-benzotriazoles[4,5] (see Table 1).

The required *ortho*-halo arene and *ortho*-nitro arene triazene resins **3**–**6** were synthesized via optimized procedures from anilines and benzylaminomethyl polystyrene (**1**), which is available from chloromethylated polystyrene (1–2% cross-linked).[6,7] The anilines[8] were immobilized on Merrifield resin under standard conditions via their diazonium salts **2a**–**d** (Scheme 1).[9] The loadings were determined by elemental analysis. The amino resins **7** and **8** were synthesized by reduction of the corresponding nitro resins **5** and **6**.[10]

The Hartwig–Buchwald amination of triazene-linked 2-bromobenzene **3** was performed under various conditions (Scheme 2). Catalyst systems based on $Pd_2(dba)_3$ or $Pd(OAc)_2$ as palladium sources and *rac*-BINAP or BiPheP-$(Cy)_2$[11] as ligands in toluene proved most suitable. After considerable experimentation, we found that reaction conditions involving an excess of the amine, 2–5 equiv KO$^t$Bu, and 0.11–0.27 equiv catalyst provide optimal conditions for a clean conversion. Subsequently, resin **3** was treated for 6–7 days with diverse primary amines and anilines **9** at 100 °C under palladium catalysis to yield triazene-linked *N*-substituted 2-anilines **10**.

In general, both primary alkyl amines and anilines are good substrates for the Hartwig–Buchwald reaction. Fluoride atoms and etheral oxygen groups are tolerated. Electron withdrawing groups (as in amines **9s**–**u**) as well as electron donating groups (as in amine **9v**) are well suited. With benzylamine (**9h**), no reaction took place and the starting material was recovered. The reaction failed presumably due to destruction of the amino reagent via a palladium-promoted benzylic C–N scission. Even chloroarene triazenes are suitable: the reaction was exemplary applied to resin **4** to yield the *N*-substituted resin **11**.

In order to introduce chloro and bromo groups, we reversed the order in the Hartwig–Buchwald reaction and used the immobilized aniline resins **7** and **8**. The same optimized conditions were used for the coupling of chloro- and bromoarenes **12** to these resins (Scheme 3).

Gratifyingly, in particular, electron-poor and electron-rich arenes are suitable substrates. In addition, dihaloarenes can be used, whereby only with dibromoarenes does considerable double arylation takes place. 1-Bromo-4-chlorobenzene (**12g**) reacts with **7** exclusively via the bromo position yielding the 4-chlorobenzene *N*-substituted resin **13g**.

2-Halogenated pyridine and quinolines are also suitable precursors.

Mild acidic cleavage (5 mol % TFA in dichloromethane, rt, 5 min) of the triazene linker provided *ortho*-amino-substituted arene diazonium salts, which immediately cyclize to give corresponding 1*H*-benzotriazoles **18** in excellent purities and moderate overall yields (Scheme 4). The reduced yields in some cases were attributed to preliminary N–N cleavage from the resin, which does not influence the overall purity. In the case of the nitro-substituted compound **18y**

* E-mail: braese@ioc.uka.de. Fax: +49 721 608 8581.

10.1021/cc700105p CCC: $37.00 © 2007 American Chemical Society
Published on Web 10/26/2007

**Table 1.** 1*H*-Benzotriazoles Prepared

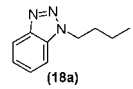
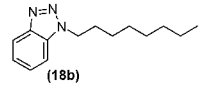
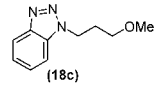
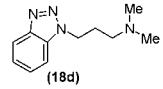
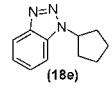
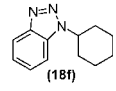
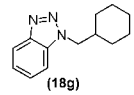
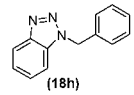
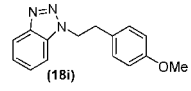
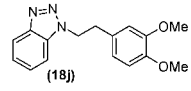
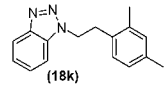
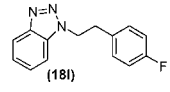
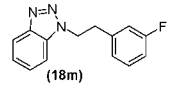
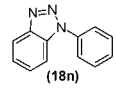
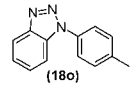
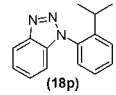
| Entry | Resin | Amine/ Arene | Benzotriazole | Purity (%)[a] | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | **3** | **9a** |  (18a) | 97 | 66 |
| 2 | **3** | **9b** |  (18b) | 95 | 36 |
| 3 | **3** | **9c** |  (18c) | 97 | 69 |
| 4 | **3** | **9d** |  (18d) | 85 | 72 |
| 5 | **3** | **9e** |  (18e) | 86 | 40 |
| 6 | **3** | **9f** |  (18f) | 98 | 43 |
| 7 | **3** | **9g** |  (18g) | 99 | 88 |
| 8 | **3** | **9h** |  (18h) | n.r.[c] | --[d] |
| 9 | **3** | **9i** |  (18i) | 92 | 40 |
| 10 | **3** | **9j** |  (18j) | 99 | 83 |
| 11 | **3** | **9k** |  (18k) | 97 | 71 |
| 12 | **3** | **9l** |  (18l) | 99 | 18 |
| 13 | **3** | **9m** |  (18m) | 78 | 6 |
| 14 | **3** | **9n** |  (18n) | 99 | 16 |
| 15 | **3** | **9o** |  (18o) | 99 | 37 |
| 16 | **3** | **9p** |  (18p) | 99 | 48 |

**Table 1.** Continued

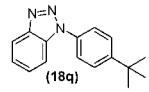
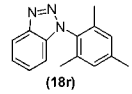
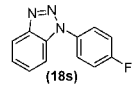
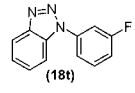
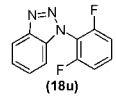
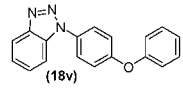
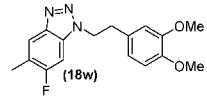
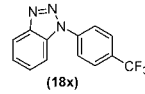
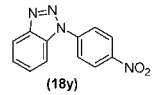
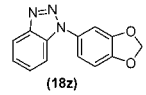
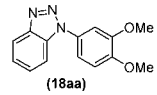
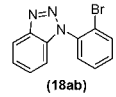
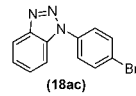
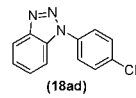
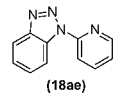
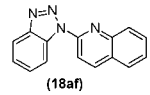
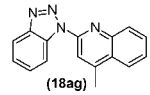
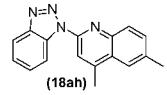
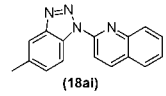
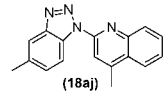
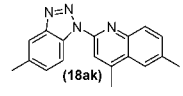
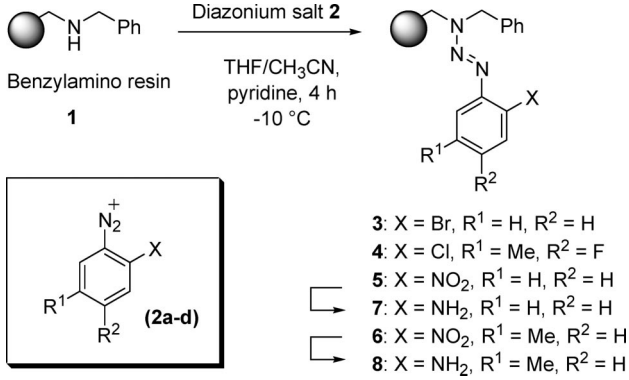
| Entry | Resin | Amine/ Arene | Benzotriazole | Purity (%)[a] | Yield (%)[b] |
|---|---|---|---|---|---|
| 17 | **3** | **9q** |  (18q) | 94 | 23 |
| 18 | **3** | **9r** |  (18r) | 99 | 38 |
| 19 | **3** | **9s** |  (18s) | 96 | 17 |
| 20 | **3** | **9t** |  (18t) | 99 | 19 |
| 21 | **3** | **9u** |  (18u) | 98 | 15 |
| 22 | **3** | **9v** |  (18v) | 97 | 27 |
| 23 | **4** | **9j** |  (18w) | 99 | 83 |
| 24 | **7** | **12a** |  (18x) | 88 | 37 |
| 25 | **7** | **12b** |  (18y) | 95 | 1 |
| 26 | **7** | **12c** |  (18z) | 99 | 37 |
| 27 | **7** | **12d** |  (18aa) | 95 | 51 |
| 28 | **7** | **12e** |  (18ab) | 60 | 22 |
| 29 | **7** | **12f** |  (18ac) | 86 | 28 |
| 30 | **7** | **12g** |  (18ad) | 95 | 53 |
| 31 | **7** | **12h** |  (18ae) | 95 | 42 |

**Table 1.** Continued

| Entry | Resin | Amine/ Arene | Benzotriazole | Purity (%)[a] | Yield (%)[b] |
|---|---|---|---|---|---|
| 32 | **7** | **12i** |  (18af) | 99 | 39 |
| 33 | **7** | **12j** |  (18ag) | 99 | 38 |
| 34 | **7** | **12k** |  (18ah) | 99 | 35 |
| 35 | **8** | **12i** |  (18ai) | 89 | 16 |
| 36 | **8** | **12j** |  (18aj) | 80 | 64 |
| 37 | **8** | **12k** |  (18ak) | 99 | 66 |

[a] Purity of the water-washed product mixture. [b] Isolated yield of, based on the loading of the triazene resin used. [c] No reaction. [d] Not calculated.

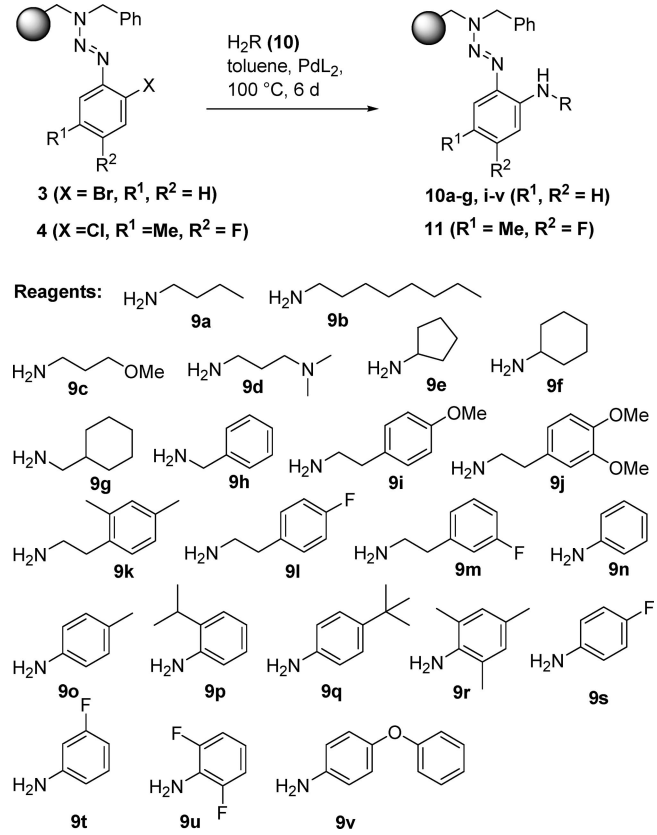
**Scheme 1.** Attachment of Diazonium Ions To Solid Supports




(entry 25), the exceptionally low yield might be explained by the higher solubility in water during the standard workup procedure.

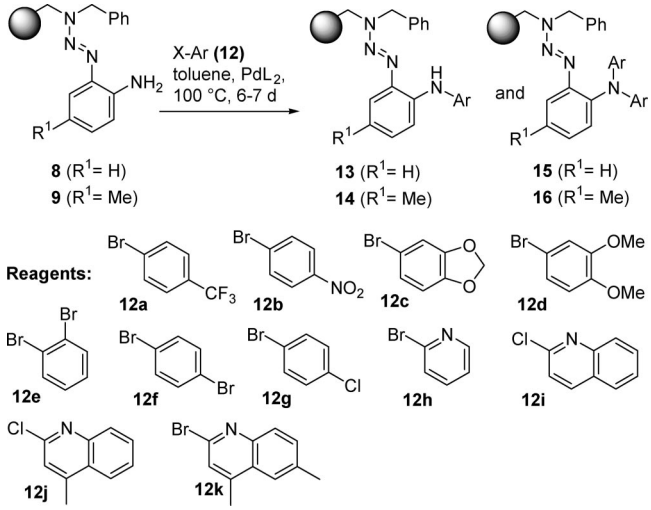
If the cleavage is performed in the presence of trimethylsilyl azide, substrates with non-nucleophilic *ortho*-substituents lead to the generation of aryl azides[12] which are stable at room temperature in contrast to the diazonium salts. Under the same conditions, primary and secondary *ortho*-amino (nucleophilic) substituents result in quantitative formation of benzotriazoles (**18**) due to the quick cyclization reaction. Thus, this cleavage protocol is suitable for analytical purposes for example by rapid gas-chromatographic analysis. The resulting purities of the desired benzotriazoles actually reflect the turnover of the Hartwig–Buchwald reaction on the solid support.

**Scheme 2.** Hartwig–Buchwald Reactions (Method A)

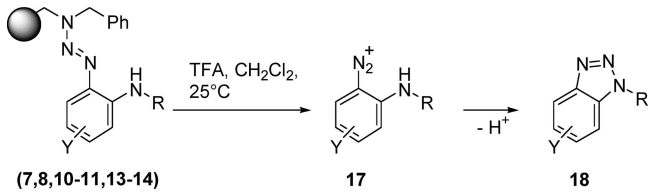



In conclusion, the solid-phase synthesis of diverse *N*-substituted benzotriazoles using the Hartwig–Buchwald reac-

**Scheme 3.** "Inverse" Hartwig–Buchwald Reactions (Method B)




**Scheme 4.** Cleavage to Yield 1*H*-Benzotriazoles




tion starting from readily available compounds is presented. The products were obtained in high purities and moderate overall yields. The presented work substantially extends the chemical transformations to be carried out on solid supports to give the desired benzotriazoles. The two alternative routes to the immobilized *N*-substituted 2-anilines allow a larger set of substitution pattern of the *N*-substituent and give a prospect on a straightforward synthesis of novel 1*H*-benzotriazoles.

Additionally, the solid-phase synthesis reported here results exclusively in $N^1$ substitution on the benzotriazole moiety, while most conventional synthesis strategies usually provide mixtures of *N*-isomers.[13]

## Experimental Procedures

**General Remarks.** $^1$H NMR: Bruker DP 300 (300 MHz), Bruker DP 400 (400 MHz); $\delta$ = 7.26 ppm for $CHCl_3$. Description of signals: s = singlet, bs = broad singlet, d = doublet, *t* = triplet, q = quartet, m = multiplet, mc = centered multiplet, dd = doublet of doublets, ddd = doublet of dd, dt = doublet of triplets, dq = doublet of quartets, tt = triplet of triplets. The spectra were analyzed according to first order. All coupling constants are absolute values. Abbreviations for signals: Ar-H = Aryl-H. $^{13}$C NMR: Bruker DP 300 (75 MHz), Bruker DP 400 (100 MHz); $\delta$ = 77.0 ppm for deuterochloroform. The signal structure was analyzed by DEPT and described as follows: + = primary or tertiary C-atom (positive signal), – = secondary C-atom (negative signal), q = quaternary C-atom (no signal). IR (infrared-spectroscopy): Perkin Elmer FT-IR 1750. The substances were dissolved in distilled dichloromethane. The resins were measured as KBr pellets on a Bruker IFS88 IR. ps = polystyrene. MS (mass spectroscopy): EI-HRMS (electronic ionization–high resolution mass spectroscopy); Kratos MS 50 (70 eV) and Thermo Quest Finnigan MAT 95 XL (70 eV). GC (gas chromatography) analytical: Hewlett-Packard HP 5890 Series II 12 m × 0.25 mm capillary column HP I (carrier gas $N_2$). TLC (Thin-layer chromatography): Silica gel coated aluminum plates (Merck, silica gel 60, F254). Detection under UV-light at 254 nm, displayed with molybdato phosphate (5% phosphomolybdic acid in ethanol, dipping solution), potassium permanganate (0.45 g potassium permanganate and 2.35 g of sodium carbonate in 90 mL of water, dipping solution). Elemental analysis: elementar vario EL at the Mikroanalytisches Labor des Instituts für Organische Chemie der Universität Bonn. Descriptions without nominated temperature were done at room temperature (rt). Solid materials (except resins) were powdered. Chemicals, solvents, reagents, and chemicals were purchased from Aldrich, Fluka, Janssen, and Merck. Merrifield resin (1–2% cross-linked, 200–400 mesh) was obtained from CalBioChem-NovaBioChem with loading = 1.06 $g \cdot mol^{-1}$. In order to get the molecular mass of the resin and to calculate the elemental analysis, the following calculation has to be performed:

$$\text{molar mass}_{\text{new}} = \frac{1000}{\text{loading}_{\text{old}}} - (\text{molar mass}_{\text{sub}} - \text{molar mass}_{\text{add}})$$

**Formula 1. Formula for the Calculation of the Molar Mass of a Derivatized Resin.** Solvents for reactions for organometallic and other sensitive materials (benzene, ether, tetrahydrofuran, dichloromethane) were distilled under argon. All resins were washed sequentially by using a vacuum reservoir connected to a sintered glass frit. Cleavage was conducted using Teflon tubes with a frit connected to a vacuum line or with a glass pipette filled with glass wool or paper filter. Evaporation of the solvent was achieved using a rotary evaporator and/or high vacuum (ca. 0.1 mbar).

**Equipment.** Reactions with small resin samples (0.60 g) were performed either in 15 mL polypropylene syringes with a plastic frit insert or in 20 mL of glass vials. The vessels were placed on a temperated aluminum block mounted on a wrist-shaker. The reaction vessels were closed with rubber septa for the duration of the experiment; in the initial phase of increasing temperature (15 min), the equation of overpressure was achieved by inserting a cannula into the gas phase through the septum.

Reactions with larger resin samples (> 1.5 g) and reactions with the Bartra reagent were performed in glass flasks. Acidic cleavages with trifluoroacetic acid were performed in 10 mL of glass syringes with a glass frit insert. Plastic syringes with a plastic frit insert are not suitable. Reactions mixtures containing resins were either stirred with an overhead stirrer or shaken on a wrist-shaker. Stirring with a magnetic stirrer was avoided to prevent destruction of the resin beads. The reduction procedures described in this paper (with exception of the reduction with Bartra reagent[14]) are suitable for automated synthesis.

**General Procedures. 1. General Procedure for the Synthesis of *N*-Benzylaminomethylpolystyrene (1, benzylamine resin).** In a three-necked flask equipped with a reflux cooler and an overhead stirrer, 10 g of Merrifield resin is dispersed in 150 mL of DMF, and then, 15 equiv of benzyl amine and 1.2 equiv of potassium iodide are added. The mixture is stirred at 80 °C for 48 h, and then, the resin is filtered on a glass frit and washed following the general washing procedure, then dried in high vacuum for 1–2 d. The resin is of white color. Quantitative turnover and new loading are calculated from the elementary analysis as described above.

**2. General Procedure for the Synthesis of Triazene $T_1$ Resins via Loading *N*-Benzylaminomethylpolystyrene (1) with Nitroarene Diazonium Salts 2.** For 10 g of benzylamine resin, 3.0 equiv of aniline are dissolved in 60 mL of THF at room temperature, 7.0 equiv of $BF_3 \cdot OEt_2$ are added and the solution is cooled at −15 °C. Then, 4.0 equiv of *iso*-pentyl nitrite are added dropwise and the reaction mixture is stirred at −15 °C for 30 min. Some diazonium salts precipitate immediately, and some require longer reaction times. Then, 120 mL of cold (−15 °C) pentane (or diethyl ether) are added and the reaction mixture is cooled to −50 °C. The precipitated solid diazonium salt **2** is given then on a glass frit and washed 3 times with 50 mL of cold (−50 °C) pentane (or diethyl ether); thereafter, it is dissolved at −25 °C in 160 mL of acetonitrile. In a separate flask, the benzylamine resin (**1**) is suspended in 140 mL of THF and 25 equiv of pyridine are added; the mixture is then cooled down at −15 °C. The diazonium salt solution is then given portionwise to the benzylamine suspension at −15 °C, and the reaction mixture is slowly (within 2 h) allowed to warm up to room temperature. The resin is filtered on a glass frit, washed following the general washing procedure, and then dried in high vacuum for 1–2 days. Turnover and new loading is calculated from the elementary analysis as described above.

**3. General Washing Procedure for Resins.** The resin is washed on a glass or plastic frit with various solvents (25 mL of solvent per 1 g of resin is added, and 5 min later the vacuum applied) in the following sequence:

Prewash: DMF, MeOH, THF, THF/Water (1:1), Water, THF, MeOH; 1 time

1. wash: DMF (5 min), MeOH (5 min); 2 times
2. wash: THF (5 min), pentane; 2 times
3. wash: $CH_2Cl_2$, pentane; 3 times

The last wash is an additional wash with pentane.

**4. General Procedure for Catalytic Reduction of Nitroarene Resins 4 with Sodium Sulfide.**[10] The reaction vessel is charged with 0.60 g of nitroarene resin **5** or **6**, 10 equiv of $Na_2S$, and 10 equiv of $K_2CO_3$, and 0.10 equiv of catalyst **19** in 15 mL of solvent (DMF/water 9:1) is added. The reaction vessel is closed with a septum and shaken with a wrist-shaker at 80 °C for 4 days. The resin is washed on a plastic frit following the general washing procedure and then dried in high vacuum for 1–2 days. The reaction turnover is determined through analysis of cleavage products; new loading is calculated from the elementary analysis as described above.

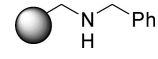
**5. General Procedure for Hartwig–Buchwald (HB) Reactions on the Triazen-$T_1$-Linker. a. "Direct" HB Reaction (Support-Bound Haloarene Reacts with Free Amine).** The reaction vessel is charged with 0.60 g of 2-haloarene resin **3** or **4** and 4 equiv of potassium *tert*-butanolate. A 2 mL portion of toluene (extra dry) and 5 equiv amine are added. A solution of Pd catalyst, prepared through dissolution of 0.055–0.135 equiv $Pd_2(dba)_3$ and 0.110–0.270 equiv *rac*-BINAP {alternatively, 0.075 equiv $Pd_2(dba)_3$ and 0.300 equiv of 2-(dicyclohexylphosphino)biphenyl, BipheP-$(Cx)_2$} in 15 mL toluene (extra dry) at 100 °C, is cooled down to 80 °C and added. The reaction vessel is closed with a septum and is shaken with a wrist-shaker at 100 °C for 6–7 days. The resin is washed on a plastic frit following the general washing procedure and then dried in high vacuum for 1–2 days. The reaction turnover is determined through analysis of cleavage products; new loading is calculated from the elementary analysis as described above.

**b. "Inverse" HB Reaction (Support-Bound Amine Reacts with Free Haloarene).** The reaction vessel is charged with 0.60 g of 2-aminoarene resin **7** or **8** and 4 equiv of potassium *tert*-butanolate. A 2 mL portion of toluene (extra dry) and 5 equiv haloarene are added. A solution of Pd catalyst, prepared through dissolution of 0.075 equiv $Pd_2(dba)_3$ and 0.150 equiv *rac*-BINAP {alternatively, 0.075 equiv $Pd_2(dba)_3$ and 0.300 equiv of 2-(dicyclohexylphosphino)biphenyl, BipheP$(Cx)_2$} in 15 mL toluene (extra dry) at 100 °C, is cooled down to 80 °C and added. The reaction vessel is closed with a septum and is shaken with a wrist-shaker at 100 °C for 6–7 days. The resin is washed on a plastic frit following the general washing procedure and then dried in high vacuum for 1–2 days. The reaction turnover is determined through analysis of cleavage products; new loading is calculated from the elementary analysis as described above.

**6. Cleavage Protocol.**[11,15] **a.** A 0.50 g portion of resin is suspended in 6 mL of methylene chloride, and then, 0.15 mL of trimethylsilyl azide and 0.10 mL of trifluoroacetic acid are added and shaken for 5 min at room temperature. The filtrate is collected, and the resin is washed twice with 4 mL methylene chloride. Subsequently, the united filtrate is washed with water (2 × 6 mL). The organic solvent is then stripped off, and the product is dried in vacuum.

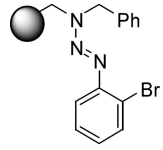
**b.** A 0.50 g portion of resin is suspended in 6 mL of methylene chloride, then 0.15 mL of trimethylsilyl azide and 0.10 mL of trifluoroacetic acid are added and shaken for 5 min at room temperature. The filtrate is collected, and the resin is washed twice with 4 mL methylene chloride. Subsequently, the united filtrate is washed with a 1 M KOH solution (2 × 6 mL), whereby the lower phase (organic) is slowly stirred with magnetic stirrer (not shaken!). Subsequently, the water phase is disposed of and the organic phase is washed with water (2 × 6 mL). The organic solvent is then stripped off, and the product is dried in vacuum.

**7. Compounds. *N*-Benzylaminomethylpolystyrene (1).** Preparation as described in the General Procedures 1 section.



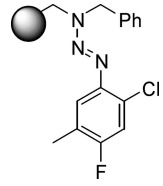
The product resin is of white color. IR (KBr): $\nu$ = 3650 (m), 3442 (m), 3339 (m), 3162 (m), 3082 (vs), 3059 (vs), 3024 (vs), 2915 (vs), 2849 (vs), 2311 (m), 1944 (s), 1871 (m), 1803 (m), 1746 (m), 1721 (m), 1677 (m), 1601 (vs), 1583 (s), 1543 (w), 1510 (s), 1492 (vs), 1450 (vs), 1421 (s), 1362 (s), 1330 (s), 1181 (s), 1155 (s), 1106 (s), 1067 (s), 1027 (s), 980 (s), 965 (s), 943 (m), 908 (s), 843 (s), 822 (s), 748 (vs), 697 (vs), 620 (s), 535 (vs) $cm^{-1}$. A typical batch gives the following: $C_{110}H_{11}N_1$ (1447 g/mol) calc C 91.30, H 7.73, N 0.97; found C 90.52, H 8.22, N 0.96. Loading: 0.691 mmol/g.

**[*N*-Benzyl-*N*-(2-bromophenyldiazenyl)aminomethyl]polystyrene (3).** Preparation as described in the General



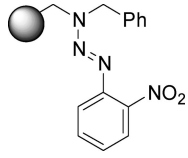

Procedures 2 section. The product resin is of beige color. A typical batch gives the following: $C_{103}H_{101}N_3Br_1$ calc C 84.69, H 6.97, N 2.88; found C 83.81, H 7.30, N 2.85. Loading: 0.685 mmol/g.

**[*N*-Benzyl-*N*-(2-chloro-4-fluoro-5-methylphenyldiazenyl)aminomethyl]polystyrene (4).** Obtained from Bayer AG.



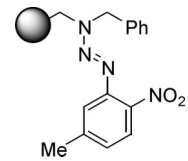

Loading: 0.889 mmol/g.

**[*N*-Benzyl-*N*-(2-nitrophenyldiazenyl)aminomethyl]polystyrene (5).** Preparation as described in the General



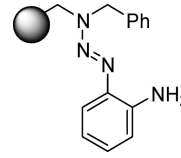

Procedures 2 section. The product resin is of yellow color. IR (KBr): $\nu$ = 3648 (w), 3617 (w), 3587 (w), 3446 (vw), 3156 (m), 3082 (vs), 3060 (vs), 3026 (vs), 3001 (vs), 2923 (br., vs), 2851 (vs), 2632 (m), 2604 (m), 2578 (m), 2337 (m), 2312 (m), 1944 (s), 1871 (s), 1804 (s), 1776 (w), 1748 (m), 1720 (s), 1700 (m), 1680 (m), 1671 (m), 1653 (w), 1602 (vs), 1583 (s), 1524 (vs), 1494 (vs), 1474 (vs), 1455 (vs), 1419 (vs), 1355 (vs), 1323 (vs), 1270 (s), 1179 (s), 1154 (s), 1135 (s), 1113 (s), 1076 (s), 1029 (s), 1001 (s), 985 (s), 946 (s), 907 (s), 857 (s), 841 (s), 755 (vs), 703 (vs), 650 (m), 620 (m) $cm^{-1}$. A typical batch gives the following: $C_{106}H_{104}N_4O_2$ calc C 86.85, H 7.15, N 3.82; found C 86.05, H 7.276, N 3.773. Loading: 0.682 mmol/g.

**[*N*-Benzyl-*N*-{5-methyl-2-nitro-phenyldiazenyl}-aminomethyl]polystyrene (6).** Preparation as described in the General Procedures 2 section. The product resin is of bright brown color. IR (KBr): $\nu$ = 3649 (w), 3616 (w), 3442 (vw), 3155 (m), 3081 (vs), 3060 (vs), 3026 (vs), 3003 (vs),



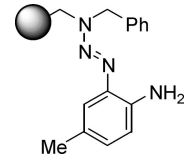

2924 (vs), 2912 (vs), 2849 (vs), 2631 (m), 2601 (m), 2337 (m), 2311 (m), 1944 (s), 1872 (s), 1803 (s), 1769 (m), 1750 (m), 1719 (m), 1700 (m), 1675 (m), 1601 (vs), 1583 (vs), 1522 (vs), 1494 (vs), 1454 (vs), 1414 (vs), 1345 (vs), 1176 (vs), 1141 (vs), 1124 (vs), 1112 (vs), 1076 (s), 1028 (vs), 983 (vs), 940 (s), 906 (s), 883 (s), 862 (s), 843 (vs), 818 (vs), 758 (vs), 701 (vs), 672 (s), 632 (vs) $cm^{-1}$. A typical batch gives the following: $C_{82}H_{81}N_4O_2$ calc C 85.30, H 7.07, N 4.85; found C 85.02, H 7.33, N 4.83. Loading: 0.866 mmol/g.

**[*N*-Benzyl-*N*-(2-aminophenyldiazenyl)aminomethyl]polystyrene (7).** Preparation as described in the General




Procedures 4 section. The product resin is of yellow color. IR (KBr): $\nu$ = 3646 (w), 3581 (w), 3479 (s, N–H), 3377 (s, N–H), 3222 (m), 3082 (vs), 3059 (vs), 3027 (vs), 3000 (vs), 2912 (br., vs), 2847 (vs), 2629 (m), 2602 (m), 2579 (m), 2359 (w), 2337 (m), 2312 (m), 2259 (w), 1944 (s), 1873 (s), 1803 (s), 1775 (m), 1748 (m), 1722 (m), 1673 (m), 1602 (s), 1542 (m), 1494 (vs), 1453 (s), 1350 (s), 1317 (s), 1147 (s), 1075 (m), 1029 (m), 1000 (m), 947 (w), 906 (m), 844 (m), 763 (s), 706 (s), 668 (s) $cm^{-1}$. A typical batch gives the following: $C_{92}H_{92}N_4$ calc C 88.14, H 7.40, N 4.47; found C 85.33, H 7.82, N 4.34. Loading: 0.798 mmol/g.

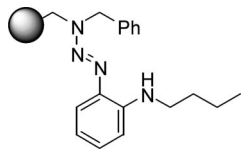
**[*N*-Benzyl-*N*-{2-amino-5-methyl-phenyldiazenyl}-aminomethyl]-polystyrene (8).** Preparation as described in




the General Procedures 4 section. The product resin is of brown color. IR (KBr): $\nu$ = 3648 (w), 3475 (s, N–H), 3366 (s, N–H), 3163 (w), 3082 (vs), 3059 (vs), 3026 (vs), 3000 (vs), 2916 (br., vs), 2849 (vs), 2729 (m), 2631 (m), 2600 (m), 2337 (m), 2311 (m), 2256 (m), 1945 (s), 1871 (s), 1802 (s), 1780 (m), 1750 (s), 1720 (m), 1675 (m), 1614 (s), 1601 (s), 1583 (s), 1539 (m), 1507 (vs), 1494 (vs), 1453 (vs), 1421 (s), 1350 (s), 1149 (s), 1128 (s), 1074 (m), 1029 (m), 1008 (m), 949 (m), 906 (m), 881 (m), 845 (m), 809 (s), 761 (s), 704 (s), 670 (s), 625 (m) $cm^{-1}$.

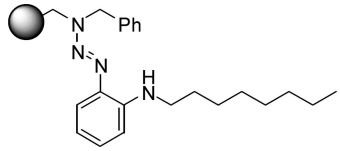
A typical batch gives the following: $C_{92}H_{93}N_4$ calc C 87.58, H 7.44, N 4.98; found C 83.37, H 7.67, N 5.19. Loading: 0.889 mmol/g.

**[*N*-Benzyl-*N*-{2-(butylamino)-phenyldiazenyl}-aminomethyl]polystyrene (10a).** Preparation as described in the General Procedures 5a section from 2-bromo resin



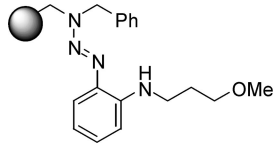
(**3**) and *n*-butyl amine (**9a**). The product resin is of brown color. A typical batch gives the following: $C_{159}H_{163}N_4$ calc C 89.66, H 7.71, N 2.63; found C 87.58, H 7.16, N 2.57. Turnover: 97%. Loading: 0.469 mmol/g.

**[*N*-Benzyl-*N*-{2-(*n*-octylamino)-phenyldiazenyl}-aminomethyl]polystyrene (10b).** Preparation as described



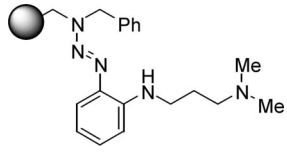
in the General Procedures 5a section from 2-bromo resin (**3**) and *n*-octyl amine (**9b**). The product resin is of brown color. IR $\nu$ = 3644 (m), 3400 (m, NH), 3081 (vs), 3060 (vs), 3026 (vs), 2922 (vs), 2849 (vs), 2631 (m), 2601 (m), 2337 (m), 2312 (m), 1944 (s), 1873 (s), 1804 (s), 1746 (m), 1666 (s), 1643 (s), 1601 (vs), 1548 (s), 1493 (vs), 1452 (vs), 1348 (vs), 1321 (vs), 1181 (s), 1152 (s), 1109 (s), 1072 (s), 1028 (s), 979 (s), 948 (s), 907 (vs), 841 (s), 761 (vs), 703 (vs), 620 (s) $cm^{-1}$. A typical batch gives the following: $C_{137}H_{145}N_4$ EA calc C 89.06, H 7.91, N 3.03; found C 87.92, H 7.25, N 3.00. Turnover: 95%. Loading: 0.541 mmol/g.

**[*N*-Benzyl-*N*-{2-(3-methoxypropylamino)-phenyldiazenyl}-aminomethyl]polystyrene (10c).** Preparation as described



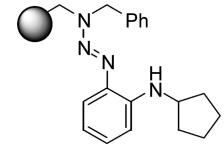
in the General Procedures 5a section from 2-bromo resin (**3**) and 3-methoxypropyl amine (**9c**). The product resin is of brown color. IR $\nu$ = 3646 (w), 3398 (s, NH), 3083 (vs), 3060 (vs), 3026 (vs), 3000 (vs), 2921 (vs), 2850 (vs), 2632 (m), 2603 (m), 2337 (m), 2312 (m), 1944 (s), 1872 (s), 1804 (s), 1746 (m), 1672 (m), 1601 (vs), 1547 (m), 1493 (vs), 1452 (vs), 1350 (s), 1182 (s), 1155 (s), 1117 (s), 1072 (s), 1029 (s), 983 (s), 907 (s), 842 (m), 762 (s), 704 (s), 621 (m) $cm^{-1}$. A typical batch gives the following: $C_{174}H_{178}N_4O_1$ calc C 89.36, H 7.66, N 2.39; found C 87.49, H 7.44, N 2.34. Turnover: 97%. Loading: 0.427 mmol/g.

**[*N*-Benzyl-*N*-{2-(3′-(dimethylaminopropyl)amino)-phenyldiazenyl}aminomethyl]polystyrene (10d).** Prepara-



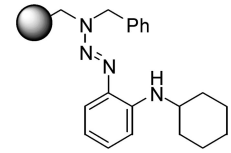
tion as described in the General Procedures 5a section from 2-bromo resin (**3**) and 3-(*N*,*N*-dimethylamino)-propyl amine (**9d**). The product resin is of brown color. IR $\nu$ = 3645 (w), 3398 (m, NH), 3082 (vs), 3060 (vs), 3026 (vs), 3000 (vs), 2927 (vs), 2850 (vs), 2819 (vs), 2774 (vs), 2718 (s), 2632 (m), 2604 (m), 2337 (m), 2312 (m), 1944 (s), 1872 (s), 1804 (s), 1746 (s), 1678 (s), 1601 (vs), 1545 (s), 1493 (vs), 1452 (vs), 1351 (s), 1320 (s), 1177 (s), 1154 (s), 1072 (s), 1029 (s), 983 (s), 907 (s), 842 (s), 764 (s), 705 (s), 621 (m) $cm^{-1}$. A typical batch gives the following: $C_{166}H_{172}N_5$ calc C 89.12, H 7.75, N 3.13; found C 87.01, H 7.42, N 3.05. Turnover: 85%. Loading: 0.447 mmol/g.

**[*N*-Benzyl-*N*-(2-cyclopentylaminophenyldiazenyl)-aminomethyl]polystyrene (10e).** Preparation as described



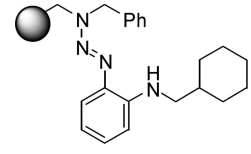
in the General Procedures 5a section from 2-bromo resin (**3**) and cyclopentyl amine (**9e**). The product resin is of brown color. IR $\nu$ = 3646 (w), 3398 (s, NH), 3082 (vs), 3060 (vs), 3026 (vs), 3000 (vs), 2926 (vs), 2848 (vs), 2632 (m), 2603 (m), 2337 (m), 2311 (m), 1944 (s), 1873 (s), 1804 (s), 1744 (s), 1678 (s), 1645 (s), 1602 (vs), 1554 (s), 1494 (vs), 1453 (vs), 1358 (s), 1180 (s), 1154 (s), 1071 (s), 1029 (s), 983 (s), 907 (s), 843 (s), 765 (s), 705 (s), 621 (m) $cm^{-1}$. A typical batch gives the following: $C_{198}H_{201}N_4$ calc C 90.19, H 7.68, N 2.12; found C 87.09, H 7.29, N 2.05. Turnover: 86%. Loading: 0.379 mmol/g.

**[*N*-Benzyl-*N*-{2-cyclohexylamino-phenyldiazenyl}-aminomethyl]-polystyrene. (10f).** Preparation as described



in the General Procedures 5a section from 2-bromo resin (**3**) and cyclohexyl amine (**9f**). The product resin is of brown color. IR $\nu$ = 3652 (w), 3622 (w), 3390 (m, NH), 3082 (vs), 3061 (vs), 3027 (vs), 2928 (vs), 2853 (vs), 2628 (m), 2596 (m), 2337 (m), 2311 (m), 1944 (s), 1873 (s), 1804 (s), 1747 (m), 1719 (m), 1678 (s), 1601 (vs), 1494 (vs), 1452 (vs), 1350 (vs), 1317 (vs), 1179 (s), 1154 (s), 1111 (s), 1074 (s), 1029 (s), 982 (s), 907 (s), 843 (s), 819 (s), 761 (vs), 704 (vs), 622 (m) $cm^{-1}$. A typical batch gives the following: $C_{199}H_{203}N_4$ calc C 90.17, H 7.72, N 2.11; found C 87.45, H 7.37, N 2.05. Turnover: 98%. Loading: 0.377 mmol/g.

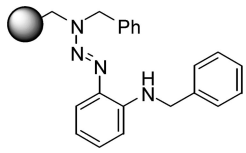
**[*N*-Benzyl-*N*-(2-cyclohexymethylaminophenyldiazenyl)-aminomethyl]-polystyrene (10g).** Preparation as described



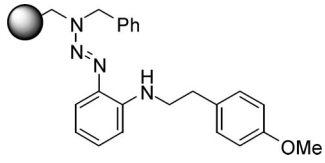
in the General Procedures 5a section from 2-bromo resin (**3**) and cyclohexylmethyl amine (**9g**). The product resin is of brown color. IR $\nu$ = 3644 (w), 3410 (m, NH), 3082 (vs), 3060 (vs), 3026 (vs), 3014 (vs), 2923 (vs), 2849 (vs), 2337 (m), 2311 (m), 1944 (s), 1873 (s), 1804 (s), 1745 (m), 1669

(s), 1601 (vs), 1493 (vs), 1452 (vs), 1350 (s), 1320 (s), 1177 (s), 1154 (s), 1072 (s), 1029 (s), 983 (m), 907 (s), 842 (m), 758 (vs), 700 (vs) $cm^{-1}$. A typical batch gives the following: $C_{149}H_{154}N_4$ calc C 89.44, H 7.76, N 2.80; found C 86.02, H 7.41, N 2.70. Turnover: 99%. Loading: 0.500 mmol/g.

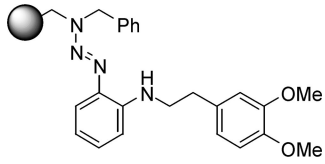
**Attempted Synthesis of [*N*-Benzyl-*N*-{2-(benzylamino)-phenyldiazenyl}aminomethyl]polystyrene (10h).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and benzyl amine (**9h**). The product resin is of brown color. No reaction was determined.



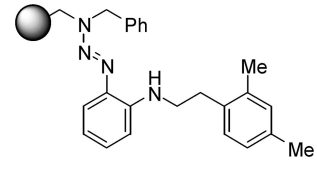
**[*N*-Benzyl-*N*-{2-(4′-methoxy-phenethylamino)-phenyldiazenyl}aminomethyl]polystyrene (10i).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 4-methoxyphenethyl amine (**9i**). The product resin is of brown color. A typical batch gives the following: $C_{178}H_{179}N_4O_1$ calc C 89.44, H 7.55, N 2.34; found C 87.85, H 7.29, N 2.30. Turnover: 92%. Loading: 0.418 mmol/g.



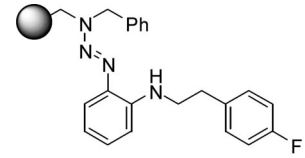
**[*N*-Benzyl-*N*-{2-(3′,4′-dimethoxyphenethylamino)-phenyldiazenyl}aminomethyl]polystyrene (10j).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 3,4-dimethoxyphenethyl amine (**9j**). The product resin is of brown color. IR $\nu$ = 3646 (w), 3615 (w), 3398 (m, NH), 3081 (vs), 3060 (vs), 3026 (vs), 2999 (vs), 2915 (vs), 2849 (vs), 2633 (m), 2603 (m), 2337 (w), 2311 (w), 1945 (m), 1873 (m), 1804 (m), 1747 (m), 1673 (m), 1601 (s), 1510 (s), 1494 (s), 1452 (s), 1348 (s), 1264 (s), 1238 (s), 1177 (m), 1157 (s), 1071 (s), 1030 (s), 989 (m), 943 (m), 907 (m), 844 (m), 761 (s), 702 (s), 622 (w) $cm^{-1}$. A typical batch gives the following: $C_{149}H_{151}N_4O_2$ calc C 88.17, H 7.50, N 2.76; found C 86.27, H 7.28, N 2.70. Turnover: 99%. Loading: 0.493 mmol/g.



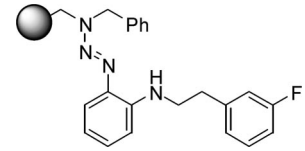
**[*N*-Benzyl-*N*-{2-(2′,4′-dimethyl-phenethylamino)-phenyldiazenyl}aminomethyl]polystyrene (10k).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 2,4-dimethylphenethyl amine (**9k**). The product resin is of brown color. IR $\nu$ = 3650 (w), 3397 (m, NH), 3082 (vs), 3060 (vs), 3027 (vs), 3000 (vs), 2924 (vs), 2843 (vs), 2727 (m), 2631 (m), 2603 (m), 2336 (w), 2312 (w), 1944 (s), 1872 (s), 1804 (s), 1746 (m), 1671 (s), 1644 (s), 1601 (vs), 1494 (vs), 1452 (s), 1326 (vs), 1181 (s), 1153 (s), 1073 (s), 1029 (s), 981 (s), 908 (s), 842 (s), 818 (s), 755 (vs), 704 (vs) $cm^{-1}$. A typical batch gives the following: $C_{133}H_{135}N_4$ calc C 89.27, H 7.60, N 3.13; found C 87.34, H 7.40, N 3.06. Turnover: 97%. Loading: 0.559 mmol/g.



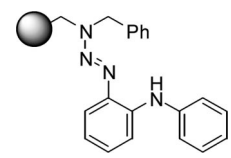
**[*N*-Benzyl-*N*-{2-(4′-fluorophenethylamino)-phenyldiazenyl}-aminomethyl]polystyrene (10l).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 4-fluorophenethyl amine (**9l**). The product resin is of brown color. IR $\nu$ = 3645 (w), 3398 (m, NH), 3081 (vs), 3060 (vs), 3026 (vs), 2923 (vs), 2849 (vs), 2631 (m), 2603 (m), 2337 (m), 2311 (m), 1944 (s), 1873 (s), 1804 (s), 1746 (m), 1675 (s), 1644 (s), 1601 (vs), 1547 (s), 1510 (vs), 1493 (vs), 1452 (vs), 1349 (vs), 1328 (vs), 1224 (s), 1182 (s), 1155 (s), 1112 (s), 1073 (s), 1029 (s), 981 (s), 940 (s), 907 (s), 841 (s), 760 (vs), 704 (vs), 620 (s) $cm^{-1}$. A typical batch gives the following: $C_{122}H_{121}N_4F$ calc C 88.15, H 7.34, N 3.37; found C 87.94, H 7.41, N 3.36. Turnover: 99%. Loading: 0.602 mmol/g.



**[*N*-Benzyl-*N*-{2-(3′-fluorphenethylamino)-phenyldiazenyl}-aminomethyl]polystyrene (10m).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 3-fluorophenethyl amine (**9m**). The product resin is of brown color. IR $\nu$ = 3651 (w), 3390 (s, NH), 3161 (m), 3082 (vs), 3061 (vs), 3027 (vs), 2915 (vs), 2849 (vs), 2631 (m), 2603 (m), 2337 (m), 2311 (m), 1944 (s), 1873 (s), 1804 (s), 1746 (m), 1663 (s), 1644 (s), 1601 (vs), 1546 (s), 1494 (vs), 1452 (vs), 1351 (vs), 1319 (vs), 1254 (s), 1151 (s), 1110 (s), 1074 (s), 1029 (s), 984 (s), 942 (m), 907 (s), 842 (m), 760 (s), 703 (s), 621 (s) $cm^{-1}$. A typical batch gives the following: $C_{128}H_{127}N_4F$ calc C 88.33, H 7.35, N 3.22; found C 87.09, H 7.25, N 3.18. Turnover: 78%. Loading: 0.575 mmol/g.

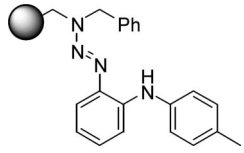


**[*N*-Benzyl-*N*-{2-(phenylamino)-phenyldiazenyl}-aminomethyl]polystyrene (10n).** Preparation as described in the General Procedures 5a section from 2-bromo resin

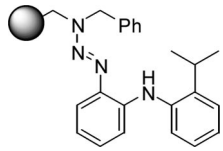


(**3**) and aniline (**9n**). The product resin is of brown color. IR $\nu$ = 3645 (w), 3375 (m, NH), 3083 (vs), 3061 (vs), 3028 (vs), 2931 (br., vs), 2848 (vs), 2631 (m), 2604 (m), 2337 (m), 2311 (m), 1944 (s), 1872 (s), 1804 (s), 1746 (s), 1674 (s), 1602 (vs), 1495 (vs), 1452 (vs), 1346 (vs), 1321 (vs), 1181 (s), 1151 (s), 1108 (s), 1072 (s), 1028 (s), 1000 (s), 981 (s), 964 (s), 937 (s), 907 (vs), 842 (vs), 765 (vs), 707 (vs), 617 (s) $cm^{-1}$. A typical batch gives the following: $C_{145}H_{143}N_4$ calc C 89.69, H 7.42, N 2.88; found C 88.00, H 7.56, N 2.83. Turnover: 99%. Loading: 0.515 mmol/g.

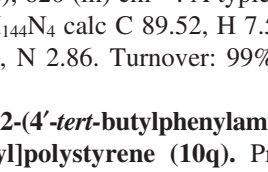
**[*N*-Benzyl-*N*-{2-(4′-methylphenylamino)-phenyldiazenyl}aminomethyl]polystyrene (10o).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 4-methyl aniline (**9o**). The product resin is of brown color. IR $\nu$ = 3645 (w), 3377 (s, NH), 3082 (vs), 3060 (vs), 3026 (vs), 2923 (vs), 2850 (vs), 2631 (m), 2604 (m), 2337 (w), 2312 (w), 1943 (s), 1873 (s), 1804 (s), 1746 (m), 1678 (s), 1600 (vs), 1518 (vs), 1494 (vs), 1452 (vs), 1348 (vs), 1321 (vs), 1178 (s), 1150 (vs), 1100 (s), 1074 (s), 1029 (s), 984 (s), 907 (s), 841 (m), 806 (s), 759 (vs), 702 (vs), 621 (m) $cm^{-1}$. A typical batch gives the following: $C_{142}H_{141}N_4$ calc C 89.59, H 7.47, N 2.94; found C 87.45, H 7.61, N 2.88. Turnover: 99%. Loading: 0.525 mmol/g.




**[*N*-Benzyl-*N*-{2-(2′-isopropylphenylamino)-phenyldiazenyl}-aminomethyl]polystyrene (10p).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 2-isopropyl aniline (**9p**). The product resin is of brown color. IR $\nu$ = 3649 (w), 3391 (m, NH), 3081 (vs), 3060 (vs), 3026 (vs), 2924 (vs), 2849 (vs), 2632 (m), 2603 (m), 2337 (w), 2311 (w), 1943 (s), 1869 (s), 1802 (s), 1773 (w), 1749 (m), 1717 (w), 1684 (m), 1653 (m), 1636 (m), 1602 (s), 1559 (s), 1541 (s), 1507 (vs), 1494 (vs), 1455 (vs), 1419 (s), 1362 (s), 1243 (w), 1178 (m), 1152 (s), 1100 (m), 1072 (m), 1029 (m), 981 (m), 937 (w), 907 (m), 842 (m), 759 (vs), 700 (vs), 620 (m) $cm^{-1}$. A typical batch gives the following: $C_{143}H_{144}N_4$ calc C 89.52, H 7.56, N 2.92; found C 87.54, H 7.69, N 2.86. Turnover: 99%. Loading: 0.521 mmol/g.

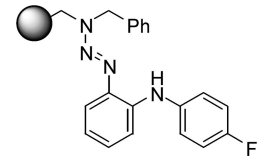



**[*N*-Benzyl-*N*-{2-(4′-*tert*-butylphenylamino)-phenyldiazenyl}aminomethyl]polystyrene (10q).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 4-*tert*-butyl aniline (**9q**). The product resin is of brown color. IR $\nu$ = 3647 (m), 3378 (s, NH), 3082 (vs), 3062 (vs), 3027 (vs), 2910 (br., vs), 2850 (vs), 2631 (m), 2603 (m), 2337 (m), 2311 (m), 1944 (s), 1871 (s), 1803 (s), 1748 (s), 1671 (s), 1602 (vs), 1520 (vs), 1495 (vs), 1455 (vs), 1348 (vs), 1181 (s), 1154 (s), 1101 (s), 1095 (s), 1073 (s), 1029 (s), 982 (s), 941 (s), 907 (s), 841 (s), 762 (s), 705 (vs), 620 (s) $cm^{-1}$. A typical batch gives the following: $C_{130}H_{132}N_4$ calc C 89.20, H 7.60, N 3.20; found C 88.14, H 7.68, N 3.15. Turnover: 94%. Loading: 0.571 mmol/g.

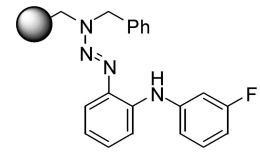



**[*N*-Benzyl-*N*-{2-(2′,4′,6′-trimethylphenylamino)-phenyldiazenyl}aminomethyl]polystyrene (10r).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 2,4,6-trimethyl aniline (**9r**). The product resin is of brown color. IR $\nu$ = 3645 (w), 3378 (s, NH), 3157 (m), 3081 (vs), 3059 (vs), 3028 (vs), 2913 (vs), 2850 (vs), 2730 (m), 2632 (m), 2601 (m), 2337 (m), 2312 (m), 1944 (s), 1873 (s), 1804 (s), 1746 (s), 1679 (s), 1637 (s), 1601 (vs), 1547 (s), 1495 (vs), 1453 (vs), 1375 (vs), 1351 (vs), 1315 (vs), 1242 (s), 1179 (s), 1149 (s), 1099 (s), 1074 (s), 1029 (s), 985 (s), 942 (s), 907 (s), 854 (m), 764 (s), 706 (s), 622 (w) $cm^{-1}$. A typical batch gives the following: $C_{143}H_{144}N_4$ calc C 89.52, H 7.56, N 2.92; found C 87.41, H 7.69, N 2.86. Turnover: 99%. Loading: 0.521 mmol/g.

**[*N*-Benzyl-*N*-{2-(4′-fluorophenylamino)-phenyldiazenyl}-aminomethyl]-polystyrene (10s).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 4-fluoro aniline (**9s**). The product resin is of brown color. IR $\nu$ = 3645 (w), 3378 (m, NH), 3081 (vs), 3060 (vs), 3027 (vs), 2908 (br., vs), 2848 (vs), 2632 (m), 2604 (m), 2337 (m), 2311 (m), 2255 (w), 1944 (s), 1872 (s), 1804 (s), 1747 (s), 1601 (vs), 1510 (vs), 1494 (vs), 1452 (vs), 1347 (vs), 1218 (s), 1181 (s), 1146 (s), 1100 (s), 1072 (s), 1028 (s), 980 (s), 944 (s), 907 (vs), 841 (vs), 816 (vs), 760 (vs), 706 (vs), 615 (s) $cm^{-1}$. A typical batch gives the following: $C_{115}H_{112}N_4F_1$ calc C 88.02, H 7.19, N 3.57; found C 87.83, H 7.85, N 3.55. Turnover: 96%. Loading: 0.637 mmol/g.

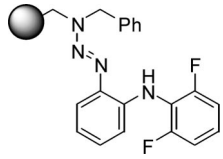



**[*N*-Benzyl-*N*-{2-(3′-fluorophenylamino)-phenyldiazenyl}-aminomethyl]polystyrene (10t).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 3-fluoro aniline (**9t**). The product resin is of brown



color. IR $\nu$ = 3648 (w), 3389 (m, NH), 3082 (vs), 3061 (vs), 3027 (vs), 2924 (br., vs), 2848 (vs), 2631 (m), 2604 (m), 2337 (m), 2311 (m), 1943 (s), 1871 (s), 1804 (s), 1747 (s), 1602 (vs), 1539 (s), 1494 (vs), 1454 (vs), 1347 (vs), 1181 (s), 1154 (s), 1108 (s), 1072 (s), 1029 (s), 1001 (s), 980 (s), 937 (s), 907 (s), 842 (s), 765 (vs), 705 (vs), 620 (s) $cm^{-1}$. A typical batch gives the following: $C_{135}H_{132}N_4F_1$ calc C 88.63, H 7.27, N 3.06; found C 88.30, H 7.72, N 3.05. Turnover: 99%. Loading: 0.547 mmol/g.

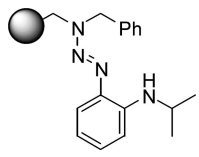
**[*N*-Benzyl-*N*-{2-(2′,6′-difluorophenylamino)-phenyldiazenyl}aminomethyl]polystyrene (10u).** Preparation as



described in the General Procedures 5a section from 2-bromo resin (**3**) and 2,6-difluoro aniline (**9u**). The product resin is of brown color. A typical batch gives the following: $C_{117}H_{113}N_4F_2$ calc C 87.11, H 7.06, N 3.47; found C 85.07, H 7.21, N 3.40. Turnover: 98%. Loading: 0.620 mmol/g.

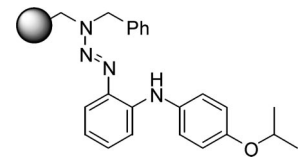
**[*N*-Benzyl-*N*-{2-(4′-phenoxyphenylamino)-phenyldiazenyl}aminomethyl]polystyrene (10v).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 4-phenoxy aniline (**9v**). The product resin is of brown color. IR $\nu$ = 3646 (w), 3373 (s, NH), 3083 (vs), 3060 (vs), 3026 (vs), 2917 (vs), 2849 (vs), 2632 (m), 2603 (m), 2337 (w), 2312 (w), 1943 (s), 1872 (s), 1804 (s), 1747 (m), 1645 (s), 1601 (vs), 1507 (vs), 1492 (vs), 1452 (vs), 1352 (vs), 1325 (vs), 1236 (vs), 1172 (s), 1154 (s), 1101 (s), 1071 (s), 1029 (s), 983 (s), 937 (m), 907 (s), 869 (s), 842 (s), 759 (vs), 701 (vs), 621 (w) $cm^{-1}$. A typical batch gives the following: $C_{163}H_{159}N_4O$ calc C 89.39, H 7.32, N 2.56; found C 87.84, H 7.53, N 2.51. Turnover: 97%. Loading: 0.457 mmol/g.

**[*N*-Benzyl-*N*-{2-(*iso*-propylamino)-phenyldiazenyl}aminomethyl]polystyrene (10w).** Preparation as described in



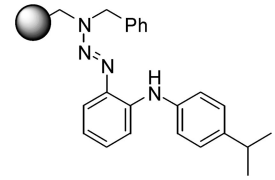
the General Procedures 5a section from 2-bromo resin (**3**) and *iso*-propyl amine (**9w**). The product resin is of brown color. A typical batch gives the following: Turnover: 79%.

**[*N*-Benzyl-*N*-{2-(4′-*iso*-propoxyphenylamino)-phenyldiazenyl}aminomethyl]-polystyrene (10x).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 4-*iso*-propoxy aniline (**9x**). The product resin

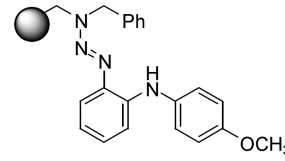


is of brown color. A typical batch gives the following: Turnover: 94%.

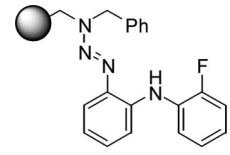
**[*N*-Benzyl-*N*-{2-(4′-isopropylphenylamino)-phenyldiazenyl}aminomethyl]polystyrene (10y).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 4-isopropyl aniline (**9y**). The product resin is of brown color. A typical batch gives the following: Turnover: 96%.



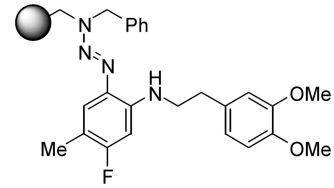
**[*N*-Benzyl-*N*-{2-(4-methoxyphenylamino)-phenyldiazenyl}aminomethyl]polystyrene (10z).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 4-methoxy aniline (**9z**). The product resin is of brown color. A typical batch gives the following: $C_{143}H_{142}N_4O_1$ calc C 88.87, H 7.41, N 2.90; found C 87.19, H 7.27, N 2.85. Turnover: 99%. Loading: 0.517 mmol/g.



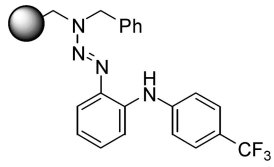
**[*N*-Benzyl-*N*-{2-(2′-fluorophenylamino)-phenyldiazenyl}-aminomethyl]polystyrene (10aa).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**3**) and 2-fluoro aniline (**9aa**). The product resin is of brown color. A typical batch gives the following: Turnover: 98%.



**[*N*-Benzyl-*N*-{4-fluoro-5-methyl-2-(3′,4′-dimethoxyphenethylamino)-phenyl-diazenyl}-aminomethyl]polystyrene (11).** Preparation as described in the General Procedures 5a section from 2-bromo resin (**4**) and 3,4-dimethoxyphenethyl amine (**9j**). The product resin is of brown color. A typical batch gives the following: Turnover: 95%. Loading: 0.79 mmol/g (calc from precursor resin).

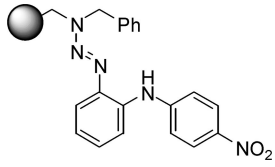


**[*N*-Benzyl-*N*-{2-(4′-trifluormethylbenzeneamino)phenyldiazenyl}aminomethyl]polystyrene (13a).** Preparation as



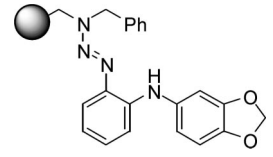
described in the General Procedures 5b section from 2-amino resin (**7**) and 1-bromo-4-trifluoromethyl benzene (**12a**). The product resin is of brown color.IR $\nu$ = 3650 (w), 3622 (w), 3480 (m, NH), 3375 (s, NH), 3162 (w), 3083 (vs), 3061 (vs), 3029 (vs), 2911 (vs), 2853 (vs), 2633 (m), 2604 (m), 2338 (w), 2313 (w), 1945 (s), 1876 (s), 1804 (s), 1748 (m), 1668 (s), 1602 (s), 1494 (s), 1453 (s), 1327 (s), 1164 (s), 1119 (s), 1068 (s), 1029 (s), 984 (s), 942 (s), 907 (s), 841 (s), 760 (s), 705 (s) $cm^{-1}$. A typical batch gives the following: $C_{98}H_{94}N_4F_3$ calc C 85.00, H 6.84, N 4.04; found C 82.78, H 7.29, N 3.94. Turnover: 88%. Loading: 0.722 mmol/g.

**[*N*-Benzyl-*N*-{2-(4′-nitrobenzeneamino)phenyldiazenyl}-aminomethyl]-polystyrene (13b).** Preparation as described



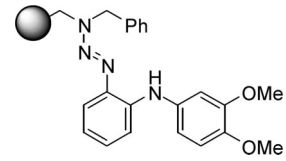
in the General Procedures 5b section from 2-amino resin (**7**) and 1-bromo-4-nitro benzene (**12b**). The product resin is of brown color. IR $\nu$ = 3650 (w), 3622 (w), 3480 (m, NH), 3376 (s, NH), 3162 (w), 3083 (vs), 3060 (vs), 3029 (vs), 2911 (vs), 2850 (vs), 2632 (m), 2605 (m), 2437 (w), 2337 (w), 2312 (w), 1945 (s), 1875 (s), 1805 (s), 1749 (m), 1722 (m), 1673 (m), 1604 (vs), 1583 (vs), 1494 (vs), 1453 (s), 1329 (vs), 1181 (s), 1154 (s), 1113 (s), 1076 (s), 1030 (s), 984 (s), 938 (s), 908 (s), 843 (s), 811 (s), 764 (vs), 706 (vs) $cm^{-1}$. A typical batch gives the following: $C_{122}H_{119}N_5O_2$ calc C 86.84, H 7.11, N 4.15; found C 85.87, H 7.61, N 4.09. Turnover: 95%. Loading: 0.593 mmol/g.

**[*N*-Benzyl-*N*-{2-(3′,4′-methylendioxybenzeneamino)-phenyldiazenyl}aminomethyl]polystyrene (13c).** Prepara-



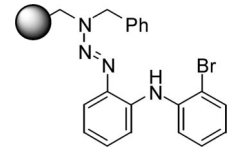
tion as described in the General Procedures 5b section from 2-amino resin (**7**) and 1-bromo-3,4-methylenedioxy benzene (**12c**). The product resin is of brown color. IR $\nu$ = 3483 (s, NH), 3377 (vs, NH), 3082 (vs), 3062 (vs), 3029 (vs), 2911 (vs), 2852 (vs), 2632 (m), 2604 (m), 2337 (w), 2311 (w), 1946 (s), 1875 (s), 1805 (s), 1751 (m), 1603 (s), 1494 (s), 1451 (s), 1349 (s), 1237 (s), 1185 (s), 1153 (s), 1106 (s), 1076 (s), 1040 (s), 987 (s), 936 (s), 908 (s), 842 (s), 820 (s), 758 (s), 704 (s), 663 (m) $cm^{-1}$. A typical batch gives the following: $C_{101}H_{98}N_4O_2$ calc C 86.66, H 7.06, N 4.00; found C 85.00, H 7.27, N 3.94. Turnover: 99%. Loading: 0.714 mmol/g.

**[*N*-Benzyl-*N*-{2-(3′,4′-dimethoxyphenylamino)phenyldiazenyl}-aminomethyl]-polystyrene (13d).** Preparation as described



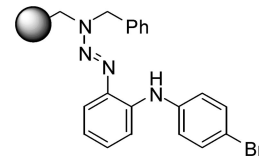
in the General Procedures 5b section from 2-amino resin (**7**) and 1-bromo-3,4-dimethoxy benzene (**12d**). The product resin is of brown color. IR $\nu$ = 3650 (w), 3620 (w), 3481 (m, NH), 3378 (s, NH), 3163 (w), 3084 (vs), 3060 (vs), 3028 (vs), 2915 (vs), 2851 (vs), 2632 (m), 2604 (m), 2338 (w), 2312 (w), 1945 (s), 1876 (s), 1805 (s), 1750 (m), 1646 (s), 1602 (vs), 1514 (vs), 1495 (vs), 1454 (vs), 1348 (s), 1253 (s), 1235 (s), 1184 (s), 1155 (s), 1075 (s), 1030 (s), 967 (s), 941 (s), 908 (s), 842 (s), 763 (vs), 705 (vs), 612 (s) $cm^{-1}$. A typical batch gives the following: $C_{117}H_{117}N_4O_2$ calc C 87.22, H 7.32, N 3.48; found C 84.93, H 7.23, N 3.35. Turnover: 95%. Loading: 0.621 mmol/g.

**[*N*-Benzyl-*N*-{2-(2′-bromobenzeneamino)phenyldiazenyl}-aminomethyl]-polystyrene (13e).** Preparation as described



in the General Procedures 5b section from 2-amino resin (**7**) and 1,2-dibromo benzene (**12e**). The product resin is of brown color. IR $\nu$ = 3644 (w), 3622 (w), 3380 (m, NH), 3375 (m, NH), 3164 (w), 3081 (s), 3060 (s), 3028 (s), 2914 (s), 2851 (s), 2632 (w), 2604 (w), 2337 (w), 2312 (w), 1945 (m), 1875 (m), 1805 (m), 1749 (w), 1643 (m), 1603 (s), 1511 (s), 1494 (s), 1452 (s), 1390 (m), 1349 (s), 1179 (m), 1153 (m), 1107 (m), 1075 (m), 1029 (m), 982 (m), 941 (m), 908 (m), 842 (m), 813 (m), 761 (s), 702 (s), 615 (m) $cm^{-1}$. A typical batch gives the following: $C_{117}H_{114}N_4Br$ calc C 84.85, H 6.94, N 3.38; found C 84.94, H 7.35, N 3.38. Turnover: 60% (+22% product of double arylation). Loading: 0.604 mmol/g.

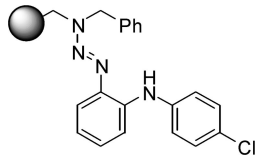
**[*N*-Benzyl-*N*-{2-(4′-brombezeneamino)phenyldiazenyl}-aminomethyl]-polystyrene (13f).** Preparation as described



in the General Procedures 5b section from 2-amino resin (**7**) and 1,2-dibromo benzene (**12f**). The product resin is of brown color. IR $\nu$ = 3651 (w), 3622 (w), 3375 (s, NH), 3163 (w), 3081 (vs), 3060 (vs), 3029 (vs), 2910 (vs), 2850 (vs), 2632 (m), 2604 (m), 2338 (w), 2313 (w), 1945 (s), 1876 (s), 1805 (s), 1751 (m), 1643 (s), 1602 (s), 1500 (s), 1451 (s), 1391 (s), 1347 (s), 1180 (s), 1155 (s), 1108 (s), 1075 (s), 1029 (s), 1004 (s), 941 (m), 908 (s), 838 (s), 817 (s), 765 (s), 706 (s), 620 (m) $cm^{-1}$. A typical batch gives the following:

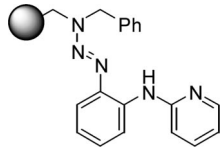
$C_{115}H_{112}N_4Br$ calc C 84.74, H 6.93, N 3.44; found C 83.74, H 7.11, N 3.38. Turnover: 86% (+14% product of double arylation). Loading: 0.613 mmol/g.

**[*N*-Benzyl-*N*-{2-(4′-chlorbenzeneamino)phenyldiazenyl}-aminomethyl]-polystyrene (13g).** Preparation as described



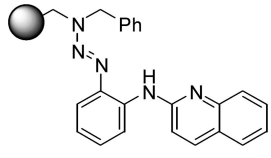
in the General Procedures 5b section from 2-amino resin (**7**) and 1-bromo-4-chloro benzene (**12g**). The product resin is of brown color. IR $\nu$ = 3649 (w), 3622 (w), 3375 (s, NH), 3163 (w), 3083 (vs), 3060 (vs), 3027 (vs), 2912 (vs), 2853 (vs), 2632 (m), 2604 (m), 2338 (w), 2312 (w), 1945 (s), 1875 (s), 1804 (s), 1749 (m), 1646 (s), 1601 (vs), 1495 (vs), 1454 (vs), 1391 (s), 1327 (vs), 1235 (s), 1179 (vs), 1153 (vs), 1094 (s), 1075 (s), 1029 (s), 979 (s), 941 (s), 908 (s), 820 (s), 762 (vs), 704 (vs), 621 (s) $cm^{-1}$. A typical batch gives the following: $C_{118}H_{115}N_4Cl$ calc C 87.24, H 7.13, N 3.45; found C 84.57, H 7.22, N 3.35. Turnover: 95%. Loading: 0.616 mmol/g.

**[*N*-Benzyl-*N*-{2-(pyridin-2′-yl-amino)phenyldiazenyl}-aminomethyl]-polystyrene (13h).** Preparation as described



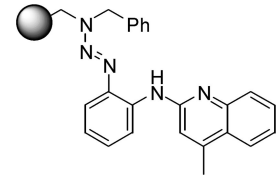
in the General Procedures 5b section from 2-amino resin (**7**) and 2-bromo pyridine (**12h**). IR $\nu$ = 3650 (w), 3622 (w), 3482 (m, NH), 3376 (s, NH), 3163 (m), 3081 (vs), 3061 (vs), 3028 (vs), 2911 (vs), 2852 (vs), 2632 (m), 2605 (m), 2337 (w), 2312 (w), 1945 (s), 1876 (s), 1805 (s), 1749 (m), 1603 (vs), 1514 (vs), 1494 (vs), 1454 (vs), 1340 (vs), 1183 (s), 1154 (s), 1108 (s), 1076 (s), 1030 (s), 989 (s), 940 (s), 908 (s), 844 (s), 818 (s), 770 (vs), 705 (vs), 617 (s) $cm^{-1}$. A typical batch gives the following: $C_{99}H_{97}N_5$ calc C 87.66, H 7.21, N 5.16; found C 85.45, H 7.20, N 5.02. Turnover: 95%. Loading: 0.737 mmol/g.

**[*N*-Benzyl-*N*-{2-(quinolin-2′-yl-amino)-phenyldiazenyl}-aminomethyl]polystyrene (13i).** Preparation as described



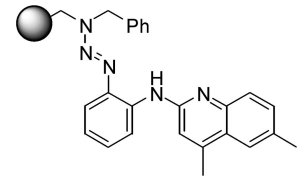
in the General Procedures 5b section from 2-amino resin (**7**) and 2-chloro quinoline (**12i**). The product resin is of brown color. IR $\nu$ = 3651 (w), 3622 (w), 3479 (m, NH), 3374 (s, NH), 3163 (w), 3081 (vs), 3060 (vs), 3028 (vs), 2912 (vs), 2852 (vs), 2632 (m), 2605 (m), 2338 (w), 2312 (w), 1945 (s), 1876 (s), 1805 (s), 1752 (m), 1599 (s), 1529 (s), 1494 (s), 1452 (s), 1346 (s), 1244 (s), 1154 (s), 1076 (s), 1029 (s), 982 (s), 941 (s), 908 (s), 819 (s), 758 (s), 705 (s), 644 (s) $cm^{-1}$. A typical batch gives the following: $C_{118}H_{114}N_5$ calc C 88.46, H 7.17, N 4.37; found C 84.99, H 7.12, N 4.20. Turnover: 99%. Loading: 0.624 mmol/g.

**[*N*-Benzyl-*N*-{2-(4′-methylquinolin-2′-yl-amino)-phenyldiazenyl}aminomethyl]-polystyrene (13j).** Preparation as



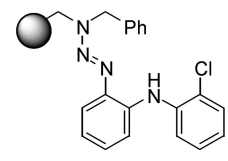
described in the General Procedures 5b section from 2-amino resin (**7**) and 2-chloro-4-methyl quinoline (**12j**). The product resin is of brown color. IR $\nu$ = 3650 (w), 3622 (w), 3481 (w, NH), 3370 (s, NH), 3163 (w), 3083 (vs), 3061 (vs), 3028 (vs), 2913 (vs), 2852 (vs), 2632 (m), 2604 (m), 2337 (w), 2312 (w), 1945 (s), 1880 (s), 1805 (s), 1750 (m), 1599 (s), 1569 (s), 1524 (s), 1507 (s), 1494 (s), 1452 (s), 1389 (s), 1357 (s), 1245 (s), 1214 (s), 1182 (s), 1154 (s), 1076 (s), 1030 (s), 988 (s), 943 (s), 907 (s), 852 (s), 762 (s), 704 (s), 620 (s) $cm^{-1}$. A typical batch gives the following: $C_{101}H_{98}N_5$ calc C 87.78, H 7.15, N 5.07; found C 82.16, H 6.87, N 4.72. Turnover: 99%. Loading: 0.724 mmol/g.

**[*N*-Benzyl-*N*-{2-(4′,6′-dimethylquinolin-2′-yl-amino)-phenyldiazenyl}aminomethyl]-polystyrene (13k).** Prepara-



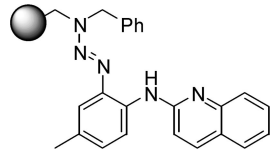
tion as described in the General Procedures 5b section from 2-amino resin (**7**) and 2-bromo-4,6-dimethyl quinoline (**12k**). The product resin is of brown color. IR $\nu$ = 3649 (w), 3621 (w), 3481 (w, NH), 3371 (vs, NH), 3163 (w), 3081 (vs), 3060 (vs), 3029 (vs), 2911 (vs), 2852 (vs), 2632 (m), 2604 (m), 2358 (m), 2338 (m), 2313 (m), 1944 (s), 1874 (s), 1804 (s), 1749 (s), 1671 (s), 1600 (vs), 1565 (vs), 1519 (vs), 1495 (vs), 1455 (vs), 1388 (vs), 1356 (vs), 1320 (vs), 1245 (vs), 1178 (vs), 1154 (vs), 1105 (vs), 1075 (vs), 1030 (vs), 989 (vs), 941 (vs), 907 (vs), 847 (vs), 825 (vs), 760 (vs), 705 (vs) $cm^{-1}$. A typical batch gives the following: $C_{117}H_{115}N_5$ calc C 88.31, H 7.28, N 4.40; found C 86.26, H 7.36, N 4.30. Turnover: 99%. Loading: 0.628 mmol/g.

**[*N*-Benzyl-*N*-{2-(2-chlorophenylamino)phenyldiazenyl}-aminomethyl]polystyrene (13l).** Preparation as described



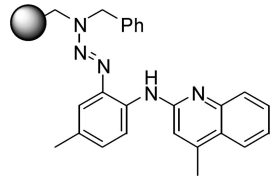
in the General Procedures 5b section from 2-amino resin (**7**) and 1,2-dichlorobenzene (**12l**). The product resin is of brown color. A typical batch gives the following: $C_{106}H_{103}N_4Cl_1$ calc C 86.70, H 7.07, N 3.81; found C 73.81, H 6.683, N 3.251. Turnover: 87%. Loading: 0.681 mmol/g.

**[*N*-Benzyl-*N*-{2-(quinolin-2′-yl-amino)-5-methyl-phenyldiazenyl}aminomethyl]-polystyrene (14i).** Preparation as



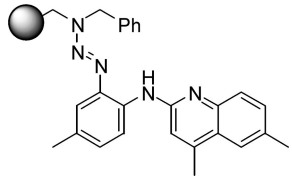
described in the General Procedures 5b section from 2-amino-5-methyl resin (**8**) and 2-chloro quinoline (**12i**). The product resin is of brown color. A typical batch gives the following: $C_{152}H_{149}N_5$ calc C 89.24, H 7.34, N 3.42; found C 81.23, H 7.01, N 3.11. Turnover: 98%. Loading: 0.489 mmol/g.

**[*N*-Benzyl-*N*-{2-(4′-methylquinolin-2′-yl-amino)-5-methyl-phenyldiazenyl}aminomethyl]-polystyrene (14j).** Prepara-



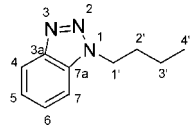
tion as described in the General Procedures 5b section from 2-amino-5-methyl resin (**8**) and 2-chloro-4-methyl quinoline (**12j**). The product resin is of brown color. A typical batch gives the following: Turnover: 80%. Loading: 0.79 mmol/g (calc from precursor resin).

**[*N*-Benzyl-*N*-{2-(4′,6′-dimethylquinolin-2′-yl-amino)-5-methyl-phenyldiazenyl}aminomethyl]-polystyrene (14k).** Preparation as described in the General Procedures 5b section



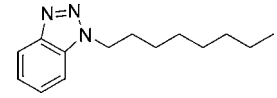
from 2-amino-5-methyl resin (**8**) and 2-bromo-4,6-dimethyl quinoline (**12k**). The product resin is of brown color. IR $\nu$ = 3651 (w), 3374 (s, NH), 3086 (vs), 3060 (vs), 3027 (vs), 2915 (vs), 2337 (w), 2311 (w), 1944 (m), 1873 (m), 1804 (m), 1747 (m), 1666 (m), 1603 (s), 1494 (s), 1453 (s), 1349 (s), 1156 (m), 1074 (m), 1029 (m), 907 (m), 877 (m), 824 (m), 764 (m), 705 (m), 620 (m) $cm^{-1}$. A typical batch gives the following: $C_{130}H_{129}N_5$ EA calc C 88.64, H 7.38, N 3.97; found C 85.03, H 7.44, N 3.81. Turnover: 99%. Loading: 0.567 mmol/g.

**1-Butyl-1*H*-benzotriazole (18a).** Cleavage from **10a** as



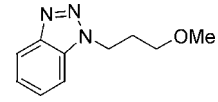
described in the General Procedures 6a section. Yield: 66%. Purity: 97% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.94 (t, $^3J$ = 7.39 Hz, 3 H, $CH_3$), 1.35 (tq, $^3J$ = 7.65, $^3J$ = 7.39 Hz, 2 H, 3′-$CH_2$), 1.98 (tt, $^3J$ = 7.65, $^3J$ = 7.14 Hz, 2 H, 2′-$CH_2$), 4.64 (t, $^3J$ = 7.14 Hz, 2 H, 1′-$CH_2$), 7.37 (ddd, $^3J$ = 8.34, $^3J$ = 6.70, $^4J$ = 1.27 Hz, 1 H, 5-H), 7.48 (ddd, $^3J$ = 8.33, $^3J$ = 6.70, $^4J$ = 0.89 Hz, 1 H, 6-H), 7.53 (ddd, $^3J$ = 8.33, $^4J$ = 1.27, $^5J$ = 0.88 Hz, 1 H, 7-H), 8.06 (ddd, $^3J$ = 8.34, $^4J$ = 0.89, $^5J$ = 0.88 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 13.48 (+, $CH_3$), 19.92 (–, 3′-$CH_2$), 31.64 (–, 2′-$CH_2$), 48.09 (–, 1′-$CH_2$), 109.40 (+, C-Ar), 119.80 (+, C-Ar), 124.09 (+, C-Ar), 127.29 (+, C-Ar), 132.95 (quart, 7a-$NC_q$), 145.47 (quart, 3a-$NC_q$) ppm. MS ($C_{10}H_{13}N_3$) *m*/*z* (%RA): 175 (54) [$M^+$], 147 (4) [$C_{10}H_{13}N_1^+$], 146 (4), 133 (8), 132 (11), 118 (10), 104 (18), 91 (100) [$C_6H_5N^+$], 77 (33) [$C_6H_5^+$]. HRMS ($C_{10}H_{13}N_3$) calc 175.1110; found 175.1109.

**1-(*n*-Octyl)-1*H*-benzotriazole (18b).** Cleavage from **10b**



as described in the General Procedures 6a section. Yield: 36%. Purity: 95% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.85 (t, $^3J$ = 7.1 Hz, 3 H, $CH_3$), 1.20–1.35 (m, 10 H, 3′,4′,5′,6′,7′-H), 2.00 (tt, $^3J$ = 7.2, $^3J$ = 7.0 Hz, 2 H, 2′-H), 4.62 (t, $^3J$ = 7.2 Hz, 2 H, 1′-H), 7.36 (ddd, $^3J$ = 8.3, $^3J$ = 6.7, $^4J$ = 1.0 Hz, 1 H, 5-H), 7.47 (ddd, $^3J$ = 8.2, $^3J$ = 6.7, $^4J$ = 0.6 Hz, 1 H, 6-H), 7.52 (br.d, $^3J$ = 8.2 Hz, 1 H, 7-H), 8.05 (br.d, $^3J$ = 8.3 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.00 (+, $CH_3$), 22.55 (–, $CH_2$), 26.70 (–, $CH_2$), 28.96 (–, $CH_2$), 29.00 (–, $CH_2$), 29.64 (–, $CH_2$), 31.67 (–, $CH_2$), 48.36 (–, $NCH_2$), 109.37 (+, C-Ar), 119.89 (+, C-Ar), 123.98 (+, C-Ar), 127.23 (+, C-Ar), 132.98 (quart, C-7a), 145.65 (quart, C-3a) ppm. MS ($C_{14}H_{21}N_3$) *m*/*z* (%RA): 231 (47) [$M^+$], 203 (4) [$M^+$–$N_2$, $C_{14}H_{21}N^+$], 202 (7) [$M^+$–$N_2$–H, $C_{14}H_{20}N^+$], 188 (11) [$M^+$–$N_2$–$CH_3$, $C_{13}H_{18}N^+$], 174 (22) [$M^+$–$N_2$–$C_2H_5$, $C_{12}H_{16}N^+$], 160 (14) [$M^+$–$N_2$–$C_3H_7$, $C_{11}H_{14}N^+$], 146 (45) [$M^+$–$N_2$–$C_4H_9$, $C_{10}H_{12}N^+$], 132 (77) [$M^+$–$N_2$–$C_5H_{11}$, $C_9H_{10}N^+$], 119 (26) [$C_6H_5N_3^+$], 106 (97), 91 (100) [$C_6H_5N^+$], 77 (49), 71 (11), 57 (22).

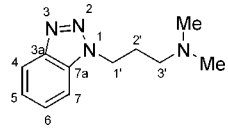
**1-(3′-Methoxypropyl)-1*H*-benzotriazole (18c).** Cleavage



from **10c** as described in the General Procedures 6a section. Yield: 69%. Purity: 97% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$= 8.03 (ddd, $^3J$ = 8.4, $^4J$ = 1.0, $^5J$ = 0.9 Hz, 1 H, 4-H), 7.54 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^5J$ = 0.9 Hz, 1 H, 7-H), 7.46 (ddd, $^3J$ = 8.3, $^3J$ = 6.8, $^4J$ = 1.0 Hz, 1 H, 6-H), 7.34 (ddd, $^3J$ = 8.4, $^3J$ = 6.8, $^4J$ = 1.0 Hz, 1 H, 5-H), 4.72 (t, $^3J$ = 6.8 Hz, 2 H, 1′-$NCH_2$), 3.30 (t, $^3J$ = 5.7 Hz, 2 H, 3′-$OCH_2$), 3.29 (s, 3 H, $OCH_3$), 2.24 (tt, $^3J$ = 6.8 Hz, 5.7 Hz, 2 H, 2′-$CH_2$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 30.0 (–, 2′-$CH_2$), 44.7 (–, 3′-$OCH_2$), 58.7 (+, $OCH_3$), 68.4 (–, 1′-$NCH_2$), 109.3 (+, C-Ar), 119.9 (+, C-Ar), 123.7 (+, C-Ar), 127.2 (+, C-Ar), 133.3 (quart, 7a-$NC_q$), 145.9 (quart, 3a-$NC_q$) ppm. IR $\nu$ = 3470 (w), 3063 (w), 2928 (s), 2876 (s), 2832 (m), 1682 (w), 1615 (m), 1496 (s), 1481 (m), 1455 (s), 1391 (m), 1352 (m), 1316 (m), 1274 (s), 1227 (s), 1194 (s), 1161 (s), 1117 (vs), 1081 (s), 1043 (s), 1018 (m), 1001

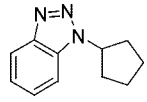
(m), 925 (m), 900 (w), 884 (w), 779 (s), 769 (s), 748 (vs), 704 (m), 666 (w) $cm^{-1}$. MS ($C_{10}H_{13}N_3O_1$) *m/z* (%RA): 191 (100) [$M^+$], 176 (24) [$M^+$–$CH_3$, $C_9H_{10}N_3O_1^+$], 165 (7), 161 (7), 133 (47) [$M^+$–$N_2$–$OCH_2$, $C_9H_{11}N^+$], 132 (38) [$M^+$–$N_2$–$OCH_3$, $C_9H_{10}N^+$], 130 (20), 118 (20), 105 (20), 104 (39), 91 (17) [$C_6H_5N_1^+$], 77 (39) [$C_6H_5^+$]. HRMS calc 191.1059; found 191.1061.

**1-{3′-(Dimethylamino)-propyl}-1*H*-benzotriazole (18d).** Cleavage from **10d** as described in the General Procedures



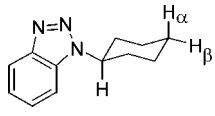

6a section. Yield: 72%. Purity: 85% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.42 (tt, $^3J$ = 7.6, 6.7 Hz, 2 H, 2′-$CH_2$), 2.59 (s, 6 H, $NCH_3$), 2.86 (t, $^3J$ = 7.6 Hz, 2 H, 3′-$CH_2$), 4.72 (t, $^3J$ = 6.7 Hz, 2 H, 1′-$CH_2$), 7.36 (ddd, $^3J$ = 8.5, $^3J$ = 6.8, $^4J$ = 1.0 Hz, 1 H, 5-H), 7.49 (ddd, $^3J$ = 8.3, $^3J$ = 6.8, $^4J$ = 1.0 Hz, 1 H, 6-H), 7.56 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^5J$ = 0.9 Hz, 1 H, 7-H), 8.03 (ddd, $^3J$ = 8.5, $^4J$ = 1.0, $^5J$ = 0.9 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 25.6 (–, 2′-$CH_2$), 43.7 (+, 2C, $NCH_3$), 45.2 (–, 3′-$CH_2$), 55.7 (–, 1′-$CH_2$), 109.2 (+, C-Ar), 120.0 (+, C-Ar), 124.2 (+, C-Ar), 127.7 (+, C-Ar), 133.0 (quart, 7a-$NC_q$), 145.9 (quart, 3a-$NC_q$) ppm. MS ($C_{11}H_{16}N_4$) *m/z* (%RA): 204 (6) [$M^+$], 159 (3) [$C_9H_9N_3^+$], 132 (12%) [$C_9H_{10}N_1^+$], 104 (5), 85 (5), 84 (8), 77 (9), 72 (6), 70 (6), 58 (100).

**1-Cyclopentyl-1*H*-benzotriazole (18e).** Cleavage from



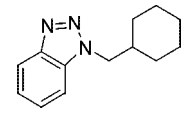

**10e** as described in the General Procedures 6a section. Yield: 40%. Purity: 86% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.80 ($m_c$, 2 H, 3′$_\alpha$*(4′$_\alpha$*)-H), 2.02 ($m_c$, 2 H, 3′$_\beta$*(4′$_\beta$*)-H), 2.30 ($m_c$, 4 H, 2′(5′)-H), 5.15 (quin, $^3J$ = 7.0 Hz, 1 H, 1′-H), 7.34 (ddd, $^3J$ = 8.3, $^3J$ = 6.9, $^4J$ = 1.0 Hz, 1 H, 5-H), 7.44 (ddd, $^3J$ = 8.3, $^3J$ = 6.9, $^4J$ = 0.9 Hz, 1 H, 6-H), 7.54 (br.d, $^3J$ = 8.3 Hz, 1 H, 7-H), 8.04 (br.d, $^3J$ = 8.3 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 24.5 (–, 2 C, $CH_2$-3′(4′)), 32.4 (–, 2 C, $CH_2$-2′(5′)), 60.2 (+, CH-1′), 109.8 (+, C-Ar), 120.0 (+, C-Ar), 123.8 (+, C-Ar), 126.8 (+, C-Ar), 132.6 (quart, C-7a), 146.2 (quart, C-3a) ppm. IR $\nu$ = 3061 (m), 2958 (s), 2873 (s), 1689 (s), 1597 (s), 1493 (s), 1454 (s), 1358 (m), 1272 (s), 1200 (vs), 1137 (s), 1071 (s), 1001 (s), 944 (s), 845 (s), 783 (s), 747 (vs), 718 (s), 701 (s) $cm^{-1}$. MS ($C_{11}H_{13}N_3$) *m/z* (%RA): 187 (100) [$M^+$], 158 (42) [$M^+$–H–$N_2$, $C_{11}H_{12}N^+$], 144 (15), 130 (45) [$M^+$–H–$N_2$–$C_2N_4$, $C_9H_8N^+$], 117 (15), 104 (29), 91 (51) [$C_6H_5N^+$], 77 (25) [$C_6H_5^+$], 67 (10).

**1-Cyclohexyl-1*H*-benzotriazole (18f).** Cleavage from **10f**



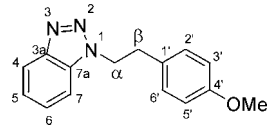

as described in the General Procedures 6a section. Yield: 43%. Purity: 98% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.39 (dtt, $^2J$ = 12.5, $^3J$ = 12.4, $^3J$ = 3.2 Hz, 1 H, 4′$_\alpha$-H), 1.45–1.58 (m, 2 H, 3′$_\beta$(5′$_\beta$)-H), 1.81 (br.dt, $^2J$ = 12.5, $^3J$ = 3.2 Hz, 1 H, 4′$_\beta$-H), 1.99 (br.ddd, $^2J$ = 13.9, $^3J$ = 3.5 Hz, $^3J$ = 3.2 Hz, 2 H, 3′$_\alpha$(5′$_\alpha$)-H), 2.09–2.22 (m, 4 H, 2′(6′)-H), 4.64 (tt, $^3J$ = 10.5, $^3J$ = 5.3 Hz, 1 H, 1′-H), 7.33 (ddd, $^3J$ = 8.3, $^3J$ = 6.8, $^4J$ = 1.0 Hz, 1 H, 5-H), 7.43 (ddd, $^3J$ = 8.3, $^3J$ = 6.8, $^4J$ = 1.0 Hz, 1 H, 6-H), 7.55 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^4J$ = 0.9 Hz, 1 H, 7-H), 8.04 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^4J$ = 0.9 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 25.3 (–, $CH_2$-4′), 25.6 (–, 2 C, $CH_2$-3′(5′)), 32.6 (–, 2 C, $CH_2$-2′(6′)), 59.1 (+, CH-1′), 109.7 (+, C-Ar), 120.1 (+, C-Ar), 123.7 (+, C-Ar), 126.7 (+, C-Ar), 132.2 (quart, C-7a), 146.1 (quart, C-3a) ppm. IR $\nu$ = 3061 (m), 2935 (vs), 2858 (vs), 1689 (m), 1613 (s), 1599 (s), 1490 (s), 1453 (vs), 1396 (m), 1366 (m), 1351 (m), 1324 (m), 1293 (s), 1273 (s), 1235 (s), 1197 (m), 1159 (vs), 1137 (m), 1117 (m), 1067 (s), 1051 (m), 999 (s), 925 (m), 894 (m), 846 (w), 818 (m), 784 (s), 769 (s), 747 (vs), 701 (m), 670 (w) $cm^{-1}$. MS ($C_{12}H_{15}N_3$) *m/z* (%RA): 201 (100) [$M^+$], 182 (21), 172 (22) [$M^+$–H–$N_2$, $C_{12}H_{14}N^+$], 166 (32), 165 (38), 158 (25), 144 (33) [$M^+$–H–$N_2$–$C_2N_4$, $C_{10}H_{10}N^+$], 130 (31) [$M^+$–H–$N_2$–$C_3N_6$, $C_9H_8N^+$], 119 (15) [$M^+$–$C_6N_{10}$, $C_6H_5N_3^+$], 105 (18), 104 (23), 91 (54) [$C_6H_5N^+$], 77 (31) [$C_6H_5^+$]. HRMS ($C_{12}H_{15}N_3$) calc 201.1266; found 201.1264.

**1-Cyclohexylmethyl-1*H*-benzotriazole (18g).** Cleavage



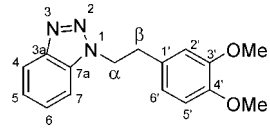

from **10 g** as described in the General Procedures 6a section. Yield: 88%. Purity: 99% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.99–1.25 (m, 6 H, 3′,4′,5′-H), 1.56–1.76 (m, 4 H, 2′(6′)-H), 2.04 (ttt, $^3J$ = 11.1, $^3J$ = 7.2, $^3J$ = 3.5 Hz, 1 H, 1′-H), 4.43 (d, $^3J$ = 7.2 Hz, 2 H, $NCH_2$), 7.33 (ddd, $^3J$ = 8.3, $^3J$ = 6.6, $^4J$ = 1.3 Hz, 1 H, 5-H), 7.45 (ddd, $^3J$ = 8.3, $^3J$ = 6.6, $^4J$ = 1.0 Hz, 1 H, 6-H), 7.49 (ddd, $^3J$ = 8.3, $^4J$ = 1.3, $^4J$ = 0.9 Hz, 1 H, 7-H), 8.04 (br.d, $^3J$ = 8.3 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 25.5 (–, 2 C, $CH_2$-3′(5′)), 26.0 (–, $CH_2$-4′), 30.8 (–, 2 C, $CH_2$-2′(6′)), 38.6 (+, CH-1′), 54.3 (–, 2 C, $NCH_2$), 109.5 (+, C-Ar), 119.9 (+, C-Ar), 123.7 (+, C-Ar), 127.1 (+, C-Ar), 133.4 (quart, C-7a), 145.8 (quart, C-3a) ppm. IR $\nu$ = 3068 (s), 2934 (vs), 2851 (vs), 2661 (m), 1935 (m), 1902 (m), 1780 (m), 1681 (s), 1616 (m), 1592 (s), 1496 (s), 1450 (s), 1370 (s), 1348 (s), 1322 (s), 1305 (s), 1263 (s), 1219 (s), 1186 (s), 1161 (s), 1133 (s), 1095 (s), 1078 (m), 1061 (s), 1051 (s), 1030 (m), 1001 (m), 963 (m), 950 (m), 936 (m), 894 (m), 843 (m), 782 (s), 741 (vs), 703 (m), 668 (m), 618 (m) $cm^{-1}$. MS ($C_{13}H_{17}N_3$) *m/z* (%RA): 215 (37) [$M^+$], 202 (28), 188 (21), 182 (15), 166 (63), 165 (70), 152 (20), 133 (19), 132 (38), 105 (53), 104 (41), 94 (100) [$M^+$–$C_6H_5N_3$–$H_2$, $C_7H_{10}^+$], 91 (23) [$C_6H_5N^+$], 83 (16), 77 (51) [$C_6H_5^+$], 65 (17), 55 (32). HRMS ($C_{13}H_{17}N_3$) calc 215.1422; found 215.1417.

**1-(4′-Methoxy-phenethyl)-1*H*-benzotriazole (18i).** Cleavage from **10i** as described in the General Procedures 6a section. Yield: 40%. Purity: 92% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.24 (t, $^3J$ = 7.33 Hz, 2 H, $CH_2$), 3.74 (s, 3 H, $OCH_3$), 4.80 (t, $^3J$ = 7.33 Hz, 2 H, $NCH_2$), 6.75 (br.d, $^3J$ =



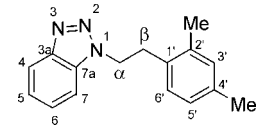
8.72 Hz, 2 H, 2′(6′)-H), 6.98 (br.d, $^3J$ = 8.72 Hz, 2 H, 3′(5′)-H), 7.26 (ddd, $^3J$ = 8.15, $^4J$ = 1.14, $^5J$ = 0.89 Hz, 1 H, 7-H), 7.33 (ddd, $^3J$ = 8.27,$^3J$ = 6.95, $^4J$ = 1.14 Hz, 1 H, 5-H), 7.40 (ddd, $^3J$ = 8.15,$^3J$ = 6.95, $^4J$ = 1.01 Hz, 1 H, 6-H), 8.04 (ddd, $^3J$ = 8.27, $^4J$ = 1.01, $^5J$ = 0.89 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 35.4 (–, $CH_2$), 50.1 (–, $NCH_2$), 55.2 (+, $OCH_3$), 109.3 (+, C-Ar), 114.2 (+, 2 C, 2′(6′)-C-Ar), 119.6 (+, C-Ar), 124.1 (+, C-Ar), 127.4 (+, C-Ar), 129.2 (quart, 1′-$C_q$), 129.7 (+, 2 C, 3′(5′)-C-Ar), 133.1 (quart, 7a-$NC_q$), 145.2 (quart, 3a-$NC_q$), 158.6 (quart, 4′-$OC_q$) ppm. MS ($C_{15}H_{15}N_3O_1$) *m*/*z* (%RA): 253 (1) [$M^+$], 204 (15), 202 (43), 167 (36), 166 (100) [$C_{10}H_{16}N_1O_1^+$], 165 (96) [$C_{10}H_{15}N_1O_1^+$], 152 (10), 139 (7), 121 (14), 94 (40).

**1-(3′,4′-Dimethoxyphenethyl)-1*H*-benzotriazole (18j).** Cleavage from **10j** as described in the General Procedures



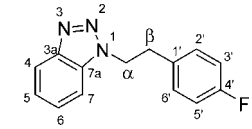
6a section. Yield: 83%. Purity: 99% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.20 (t, $^3J$ = 7.1 Hz, 2 H, $\beta$-$CH_2$), 3.62 (s, 3 H, $OCH_3$), 3.78 (s, 3 H, $OCH_3$), 4.79 (t, $^3J$ = 7.1 Hz, 2 H, α-$NCH_2$), 6.38 (d, $^4J$ = 2.0 Hz, 1 H, 2′-H), 6.62 (dd, $^3J$ = 8.2, $^4J$ = 2.0 Hz, 1 H, 6′-H), 6.70 (d, $^3J$ = 8.2 Hz, 1 H, 5′-H), 7.18 (ddd, $^3J$ = 8.2, $^4J$ = 1.1, $^5J$ = 0.7 Hz, 1 H, 7-H), 7.28 (ddd, $^3J$ = 8.2, $^3J$ = 7.0, $^4J$ = 1.1 Hz, 1 H, 5-H), 7.34 (ddd, $^3J$ = 8.2, $^3J$ = 7.0, $^4J$ = 1.1 Hz, 1 H, 6-H), 7.99 (ddd, $^3J$ = 8.2, $^4J$ = 1.1, $^5J$ = 0.7 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 35.9 (–, $CH_2$), 49.8 (–, $NCH_2$), 55.7 (+, $OCH_3$), 55.9 (+, $OCH_3$), 109.2 (+, C-Ar), 111.5 (+, C-Ar′), 112.0 (+, C-Ar′), 119.8 (+, C-Ar), 120.6 (+, C-Ar′), 123.7 (+, C-Ar), 127.1 (+, C-Ar), 129.9 (quart, $C_q$-Ar′), 133.2 (quart, 7a-$NC_q$), 145.7 (quart, 3a-$NC_q$), 148.0 (quart, $C_q$-Ar′), 149.0 (quart, $C_q$-Ar′) ppm. IR $\nu$ = 3862 (w), 3094 (s), 3069 (s), 3035 (s), 2997 (s), 2964 (s), 2839 (s), 2706 (m), 2596 (m), 2274 (m), 2177 (w), 2053 (m), 1977 (m), 1933 (m), 1887 (w), 1838 (m), 1792 (m), 1704 (m), 1606 (s), 1590 (s), 1516 (vs), 1498 (s), 1455 (vs), 1419 (s), 1338 (s), 1309 (s), 1262 (vs), 1232 (vs), 1208 (vs), 1191 (s), 1143 (vs), 1114 (s), 1092 (s), 1028 (vs), 944 (s), 917 (m), 855 (s), 817 (s), 788 (s), 768 (vs), 756 (vs), 716 (s), 667 (m), 629 (s) cm$^{-1}$. MS ($C_{16}H_{17}N_3O_2$) *m*/*z* (%RA): 283 (29) [$M^+$], 279 (8), 219 (5), 191 (7), 191 (7), 182 (10), 167 (19), 165 (14) [$C_{10}H_{13}O_2^+$], 164 (66) [$C_{10}H_{12}O_2^+$], 151 (100) [$C_9H_{11}O_2^+$], 149 (41) [$C_9H_9O_2^+$], 132 (10), 107 (6), 104 (13), 91 (15), 77 (26), 71 (9), 57 (12). HRMS ($C_{16}H_{17}N_3O_2$) calc 283.1321; found 283.1321.

**1-(2′,4′-Dimethyl-phenethyl)-1*H*-benzotriazole (18k).** Cleavage from **10k** as described in the General Procedures 6a section. Yield: 71%. Purity: 97% (GC). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.21 (s, 3 H, $CH_3$), 2.26 (s, 3 H, $CH_3$), 3.25 (t, $^3J$ = 7.44 Hz, 2 H, $\beta$-$CH_2$), 4.80 (t, $^3J$ = 7.44 Hz, 2 H, α-$CH_2$), 6.85–6.96 (complex, 3 H, Ar′-H), 7.28 (dd, $^3J$ =



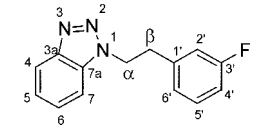
7.91, $^4J$ = 1.32 Hz, 1 H, 7-H), 7.39 (ddd, $^3J$ = 8.10, $^3J$ = 6.97, $^4J$ = 1.32 Hz, 1 H, 5-H), 7.44 (ddd, $^3J$ = 7.91, $^3J$ = 6.97, $^4J$ = 1.32 Hz, 1 H, 6-H), 8.10 (dd, $^3J$ = 8.10, $^4J$ = 1.32 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 19.0 (+, $CH_3$), 20.9 (+, $CH_3$), 33.3 (–, $\beta$-$CH_2$), 49.3 (–, α-$NCH_2$), 109.5 (+, C-Ar), 119.1 (+, C-Ar), 125.1 (+, C-Ar), 127.1 (+, C-Ar), 127.8 (+, C-Ar′), 129.3 (+, C-Ar′), 131.5 (+, C-Ar′), 132.0 (quart, $C_q$-Ar′), 133.2 (quart, 7a-$NC_q$), 135.9 (quart, $C_q$-Ar′), 137.0 (quart, $C_q$-Ar′), 144.0 (quart, 3a-$NC_q$) ppm. IR $\nu$ = 3065 (s), 3035 (s), 3005 (s), 2946 (s), 2922 (s), 2869 (s), 2733 (m), 2363 (m), 1907 (m), 1776 (s), 1745 (s), 1616 (s), 1590 (s), 1505 (s), 1496 (s), 1455 (vs), 1399 (s), 1379 (s), 1361 (s), 1340 (s), 1308 (s), 1269 (s), 1209 (vs), 1159 (vs), 1081 (s), 1002 (s), 955 (s), 920 (m), 900 (m), 878 (m), 836 (s), 815 (s), 781 (vs), 768 (s), 747 (vs), 706 (s), 667 (m), 613 (w) cm$^{-1}$. MS ($C_{16}H_{17}N_3$) *m*/*z* (%RA): 251 (11) [$M^+$], 222 (4), 208 (6), 180 (6), 167 (9), 132 (100) [$C_{10}H_{12}^+$], 119 (62) [$C_6H_5N_3^+$], 104 (27), 91 (11), 77 (32), 69 (26), 51 (10). HRMS calc 251.1422; found 251.1431.

**1-(4′-Fluorophenethyl)-1*H*-benzotriazole (18l).** Cleavage



from **10l** as described in the General Procedures 6a section. Yield: 18%. Purity: 99% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.28 (t, $^3J$ = 7.2 Hz, 2 H, $\beta$-$CH_2$), 4.81 (t, $^3J$ = 7.2 Hz, 2 H, α-$CH_2$), 6.89 ($m_c$, 2 H, 3′(5′)-H), 7.00 ($m_c$, 2 H, 2′(6′)-H), 7.22 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^5J$ = 0.8 Hz, 1 H, 7-H), 7.32 (ddd, $^3J$ = 8.3, $^3J$ = 7.0, $^4J$ = 1.0 Hz, 1 H, 5-H*), 7.38 (ddd, $^3J$ = 8.3, $^3J$ = 7.0, $^4J$ = 1.0 Hz, 1 H, 6-H*), 8.03 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^5J$ = 0.8 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 35.5 (–, $CH_2$-$\beta$), 49.6 (–, d, $^6J_{CF}$ = 1 Hz, $CH_2$-α), 109.0 (+, C-Ar), 115.6 (+, d, $^2J_{CF}$ = 21 Hz, 2 C, C-3′(5′)), 120.0 (+, C-Ar), 123.9 (+, C-Ar), 127.3 (+, C-Ar), 130.2 (+, d, $^2J_{CF}$ = 8 Hz, 2 C, C-2′(6′)), 133.0 (quart, C-7a), 133.1 (quart, d, $^4J_{CF}$ = 3 Hz, C-1′), 145.7 (quart, C-3a), 161.9 (quart, d, $^1J_{CF}$ = 245 Hz, C-4′) ppm. MS ($C_{14}H_{12}N_3F$) *m*/*z* (%RA): 241 (26) [$M^+$], 213 (5) [$M^+$–$N_2$, $C_{14}H_{12}NF^+$], 212 (22) [$M^+$–$N_2$–H, $C_{14}H_{11}NF^+$], 198 (3), 183 (8), 167 (9), 152 (3), 132 (100) [$M^+$–$C_7H_6F$, $C_7H_6N_3^+$], 122 (61) [$M^+$–$C_6H_5N_3$, $C_8H_7F^+$], 109 (83) [$M^+$–$C_7H_6N_3$, $C_7H_6F^+$], 104 (39), 103 (22), 83 (7), 77 (61), 63 (3), 51 (7). HRMS calc 241.1015; found 241.1024.

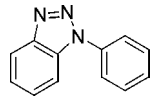
**1-(3′-Fluorophenethyl)-1*H*-benzotriazole (18m).** Cleav-



age from **10m** as described in the General Procedures 6a section. Yield: 6%. Purity: 78% (GC). $^1$H NMR (400 MHz,

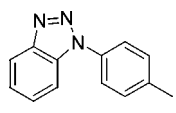
$CDCl_3$): $\delta = 3.31$ (t, $^3J = 7.3$ Hz, 2 H, $\beta$-$CH_2$), 4.84 (t, $^3J = 7.3$ Hz, 2 H, α-$CH_2$), 6.79–6.85 (m, 2 H, Ar′-H), 6.88 (dddd, $^3J_{HF} = 8.6$ Hz, $^3J = 8.3$, $^4J = 2.5$, $^5J = 0.9$, 1 H, 4′-H), 7.17 (ddd, $^3J = 8.3$, $^3J = 7.8$, $^4J_{HF} = 6.0$ Hz, 1 H, 5′-H), 7.25 (ddd, $^3J = 8.1$, $^4J = 1.1$, $^5J = 0.8$ Hz, 1 H, 7-H), 7.32 (ddd, $^3J = 8.2$, $^3J = 7.0$, $^4J = 1.1$ Hz, 1 H, 5-H), 7.39 (ddd, $^3J = 8.1$, $^3J = 7.0$, $^4J = 1.1$ Hz, 1 H, 6-H), 8.03 (ddd, $^3J = 8.2$, $^4J = 1.1$, $^5J = 0.8$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 36.0$ (–, d, $^4J_{CF} = 1.8$ Hz, $\beta$-$CH_2$), 49.2 (–, α-$CH_2$), 108.9 (+, C-Ar), 114.0 (+, d, $^2J_{CF} = 21$ Hz, C-2′*), 115.6 (+, d, $^2J_{CF} = 21$ Hz, C-4′*), 120.1 (+, C-Ar), 123.8 (+, C-Ar), 124.4 (+, d, $^4J_{CF} = 3$ Hz, C-6′), 127.3 (+, C-Ar), 130.3 (+, d, $^3J_{CF} = 8$ Hz, C-5′), 133.0 (quart, C-7a), 139.6 (quart, d, $^3J_{CF} = 7$ Hz, C-1′), 145.9 (quart, C-3a), 163.0 (quart, d, $^1J_{CF} = 247$ Hz, C-3′), ppm. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta = -113$ ppm. IR $\nu = 3439$ (w), 3063 (m), 2933 (m), 1946 (w), 1691 (w), 1615 (s), 1590 (vs), 1521 (m), 1490 (vs), 1479 (s), 1454 (vs), 1397 (w), 1362 (w), 1270 (s), 1256 (s), 1211 (m), 1160 (s), 1143 (s), 1097 (s), 1070 (m), 1011 (s), 973 (w), 940 (m), 918 (w), 890 (m), 867 (w), 779 (vs), 769 (s), 747 (vs), 731 (m), 705 (m), 692 (s), 667 (w), 617 (w) $cm^{-1}$.

**1-Phenyl-1*H*-benzotriazole (18n).**[16] Cleavage from **10n**



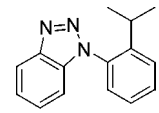
as described in the General Procedures 6a section. Yield: 16%. Purity: 99% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.43 (ddd, $^3J = 8.4$, $^3J = 6.9$, $^4J = 1.0$ Hz, 1 H, 5-H), 7.50 (tt, $^3J = 6.7$, $^4J = 1.2$ Hz, 1 H, 4′-H), ($m_c$, 2 H, AA′-part of an AA′BB′-system, 3′(5′)-H), 7.55 (ddd, $^3J = 8.4$, $^3J = 6.9$, $^4J = 1.0$ Hz, 1 H, 6-H), 7.61 ($m_c$, 2 H, 3′(5′)-H), 7.74 (ddd, $^3J = 8.4$, $^4J = 1.0$, $^5J = 0.8$ Hz, 1 H, 7-H), 7.78 ($m_c$, 2 H, 2′(6′)-H), 8.14 (ddd, $^3J = 8.4$, $^4J = 1.0$, $^5J = 0.8$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 110.4$ (+, C-Ar), 120.3 (+, C-Ar), 122.9 (+, 2 C, C-Ar′), 124.4 (+, C-Ar), 128.2 (+, C-Ar), 128.7 (+, C-4′), 129.9 (+, 2 C, C-Ar′), 132.4 (quart, C-7a), 137.1 (quart, C-1′), 146.5 (quart, C-3a) ppm. MS ($C_{12}H_9N_3$) *m/z* (%RA): 195 (28) [$M^+$], 167 (100) [$M^+$–$N_2$, $C_{12}H_9N^+$], 166 (26), 139 (8), 77 (21), 51 (8). HRMS ($C_{15}H_{15}N_3$) calc 195.0796; found 195.0801. IR $\nu = 3433$ (w), 3058 (s), 2928 (w), 2338 (w), 1969 (w), 1917 (w), 1822 (w), 1785 (w), 1692 (m), 1597 (vs), 1502 (vs), 1460 (s), 1449 (s), 1394 (m), 1328 (w), 1291 (s), 1277 (s), 1245 (m), 1188 (s), 1145 (m), 1126 (m), 1092 (vs), 1060 (vs), 1012 (vs), 943 (w), 925 (m), 849 (w), 785 (s), 762 (vs), 750 (vs), 710 (s), 698 (vs), 662 (s), 623 (w) $cm^{-1}$.

**1-(4′-Methylphenyl)-1*H*-benzotriazole (18o).**[17] Cleavage



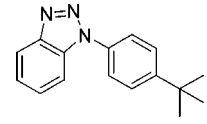
from **10o** as described in the General Procedures 6a section. Yield: 37%. Purity: 99% (GC). $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 2.46$ (s, 3 H, $CH_3$), 7.36–7.44 (m, 3 H, 6,2′(6′)-H), 7.52 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.1$ Hz, 1 H, 5-H*), 7.64 ($m_c$, 2 H, BB′-part of an AA′BB′-system, 3′(5′)-H), 7.70 (ddd, $^3J = 8.3$, $^4J = 1.1$, $^5J = 0.6$ Hz, 1 H, 7-H), 8.12 (ddd, $^3J = 8.3$, $^4J = 1.1$, $^5J = 0.6$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 21.2$ (+, $CH_3$), 110.4 (+, C-Ar), 120.3 (+, C-Ar), 122.9 (+, 2 C, C-Ar′), 124.2 (+, C-Ar), 128.0 (+, C-Ar), 130.4 (+, 2 C, C-Ar′), 132.4 (quart, C-7a), 134.6 (quart, C-4′), 138.8 (quart, C-1′), 146.5 (quart, C-3a) ppm. MS ($C_{13}H_{11}N_3$) *m/z* (%RA): 209 (22) [$M^+$], 181 (52) [$M^+$–$N_2$, $C_{13}H_{11}N^+$], 180 (100) [$M^+$–$N_2$–H, $C_{13}H_{10}N^+$], 166 (11), 152 (4), 140 (3), 91 (21) [$C_6H_5N^+$], 77 (3), 65 (17), 51 (3). HRMS ($C_{13}H_{11}N_3$) calc 209.0953; found 209.0961. IR $\nu = 3879$ (w), 3096 (s), 3077 (s), 3062 (s), 3035 (s), 2972 (s), 2952 (s), 2933 (s), 2865 (s), 2740 (m), 2680 (m), 2553 (m), 2447 (w), 2315 (m), 2124 (w), 2059 (w), 1937 (m), 1906 (s), 1868 (m), 1803 (m), 1776 (s), 1732 (m), 1673 (s), 1613 (s), 1578 (s), 1518 (vs), 1487 (vs), 1454 (vs), 1416 (s), 1392 (s), 1378 (s), 1316 (s), 1294 (vs), 1278 (vs), 1248 (vs), 1188 (vs), 1148 (s), 1127 (vs), 1113 (vs), 1068 (vs), 1009 (vs), 970 (s), 944 (m), 920 (m), 820 (vs), 784 (s), 762 (s), 738 (vs), 707 (s), 662 (s) $cm^{-1}$.

**1-(2′-Isopropylphenyl)-1*H*-benzotriazole (18p).** Cleav-



age from **10p** as described in the General Procedures 6a section. Yield: 48%. Purity: 99% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.11$ (d, $^3J = 6.8$ Hz, 6 H, $CH_3$), 2.59 (sep, $^3J = 6.8$ Hz, 1 H, CH), 7.29 (ddd, $^3J = 7.8$, $^4J = 1.0$, $^4J = 1.0$ Hz, 1 H, Ar′-H), 7.30 (ddd, $^3J = 8.2$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 7-H), 7.35 (ddd, $^3J = 7.8$, $^3J = 5.3$, $^4J = 3.5$ Hz, 1 H, Ar′-H), 7.40 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 5-H), 7.47 (ddd, $^3J = 8.2$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 6-H), 7.54–7.57 (m, 2 H, Ar′-H), 8.13 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 23.8$ (+, 2 C, $CH_3$), 28.1 (+, CH), 109.9 (+, C-Ar), 120.0 (+, C-Ar), 124.1 (+, C-Ar), 126.7 (+, C-Ar′), 127.2 (+, C-Ar′), 127.4 (+, C-Ar′), 128.0 (+, C-Ar), 130.6 (+, C-Ar′), 133.8 (quart, C-7a), 134.6 (quart, C-2′), 145.5 (quart, C-1′), 146.4 (quart, C-3a) ppm. MS ($C_{15}H_{15}N_3$) *m/z* (%RA): 237 (21) [$M^+$], 208 (6) [$M^+$–$N_2$–H, $C_{15}H_{14}N^+$], 194 (40) [$M^+$–$C_3H_7$, $C_{12}H_8N_3^+$], 167 (100) [$M^+$–$N_2$–$C_3H_6$, $C_{12}H_9N^+$], 152 (2), 140 (2), 130 (2), 115 (2), 91 (8) [$C_6H_5N^+$], 77 (7), 65 (2), 51 (2). HRMS ($C_{15}H_{15}N_3$) calc 237.1266; found 237.1268. IR $\nu = 3471$ (w), 3065 (m), 2966 (vs), 2929 (s), 2870 (s), 2335 (w), 1930 (w), 1820 (w), 1694 (w), 1614 (m), 1602 (m), 1499 (vs), 1458 (vs), 1448 (s), 1385 (m), 1365 (m), 1350 (w), 1297 (m), 1274 (vs), 1244 (s), 1212 (m), 1185 (s), 1164 (w), 1144 (w), 1123 (m), 1094 (s), 1061 (vs), 1034 (s), 1007 (vs), 949 (w), 917 (w), 891 (w), 871 (w), 849 (w), 787 (vs), 749 (vs), 691 (m), 669 (m), 626 (m) $cm^{-1}$.

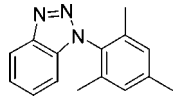
**1-(4′-tert-Butylphenyl)-1*H*-benzotriazole (18q).** Cleav-



age from **10q** as described in the General Procedures 6a section. Yield: 23%. Purity: 94% (GC). $^1$H NMR (400 MHz,

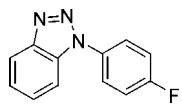
$CDCl_3$): $\delta = 1.39$ (s, 9 H, $CH_3$), 7.41 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 5-H), 7.52 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 6-H), 7.61 ($m_c$, 2 H, AA′-part of an AA′BB′-system, 3′(5′)-H), 7.69 ($m_c$, 2 H, BB′-part of an AA′BB′-system, 2′(6′)-H), 7.74 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.8$ Hz, 1 H, 7-H), 8.12 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.8$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 31.3$ (+, 3 C, $CH_3$), 34.9 (quart, $C_q$), 110.4 (+, C-Ar), 120.3 (+, C-Ar), 122.6 (+, 2 C, C-Ar′), 124.2 (+, C-Ar), 126.7 (+, 2 C, C-Ar′), 128.0 (+, C-Ar), 132.4 (quart, C-7a), 134.5 (quart, C-4′), 146.5 (quart, C-3a), 152.0 (quart, C-1′) ppm. MS ($C_{16}H_{17}N_3$) *m*/*z* (%RA): 251 (26) [$M^+$], 223 (4) [$M^+$–$N_2$, $C_{16}H_{17}N^+$], 208 (14) [$M^+$–$N_2$–$CH_3$, $C_{15}H_{14}N^+$], 193 (11), 180 (6), 167 (100) [$M^+$–$N_2$–$C_4H_8$, $C_{12}H_9N^+$], 117 (4), 103 (2), 90 (14) [$C_6H_4N^+$], 77 (5), 57 (17) [$C_4H_9^+$]. HRMS ($C_{16}H_{17}N_3$) calc 251.1427; found 251.1427. IR $\nu = 3071$ (s), 3058 (s), 2960 (vs), 2904 (vs), 2868 (s), 2675 (w), 2547 (w), 2343 (w), 2314 (w), 2121 (w), 1953 (w), 1922 (m), 1897 (w), 1798 (w), 1697 (m), 1605 (s), 1515 (vs), 1488 (s), 1476 (s), 1464 (s), 1451 (vs), 1416 (s), 1396 (s), 1362 (s), 1317 (m), 1293 (s), 1274 (vs), 1247 (s), 1205 (vs), 1179 (m), 1148 (s), 1126 (s), 1117 (s), 1068 (vs), 1027 (s), 1006 (vs), 977 (m), 951 (w), 919 (m), 844 (vs), 825 (s), 783 (s), 767 (s), 750 (vs), 668 (m), 650 (w), 636 (w) $cm^{-1}$.

**1-(2′,4′,6′-Trimethylphenyl)-1*H*-benzotriazole (18r).**[18] Cleavage from **10r** as described in the General Procedures



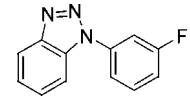
6a section. Yield: 38%. Purity: 99% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.85$ (s, 6 H, 2′(6′)-$CH_3$), 2.38 (s, 3 H, 4′-$CH_3$), 7.04 ($m_c$, 2 H, 3′(5′)-H), 7.18 (ddd, $^3J = 8.1$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 7-H), 7.39 (ddd, $^3J = 8.2$, $^3J = 7.0$, $^4J = 1.1$ Hz, 1 H, 5-H), 7.45 (ddd, $^3J = 8.1$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 6-H), 8.14 (ddd, $^3J = 8.2$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 17.3$ (+, 2 C, $CH_3$-2′(6′)), 21.2 (+, $CH_3$-4′), 109.7 (+, C-Ar), 120.1 (+, C-Ar), 123.9 (+, C-Ar), 127.9 (+, C-Ar), 129.3 (+, 2 C, C-3′(5′)), 131.7 (quart, C-7a), 133.9 (quart, C-4′), 136.2 (quart, 2 C, C-2′(6′)), 140.2 (quart, C-1′), 145.5 (quart, C-3a) ppm. MS ($C_{15}H_{15}N_3$) *m*/*z* (%RA): 237 (44) [$M^+$], 209 (31) [$M^+$–$N_2$, $C_{15}H_{15}N^+$], 208 (91) [$M^+$–$N_2$–H, $C_{15}H_{14}N^+$], 194 (100) [$M^+$–$N_2$–$CH_3$, $C_{14}H_{12}N^+$], 179 (3), 167 (4), 152 (2), 115 (3), 91 (10), 77 (9), 65 (3), 51 (2). IR $\nu = 3418$ (w), 3090 (m), 3063 (m), 3030 (m), 2978 (s), 2956 (m), 2921 (s), 2858 (m), 2738 (w), 2352 (w), 1965 (w), 1927 (w), 1795 (w), 1732 (w), 1613 (s), 1498 (vs), 1453 (s), 1377 (m), 1293 (m), 1272 (vs), 1244 (m), 1193 (s), 1162 (m), 1144 (m), 1082 (vs), 1039 (m), 1005 (s), 948 (m), 884 (w), 852 (vs), 784 (s), 768 (m), 748 (vs), 675 (m) $cm^{-1}$.

**1-(4′-Fluorophenyl)-1*H*-benzotriazole (18s).** Cleavage



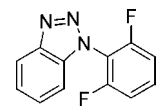
from **10s** as described in the General Procedures 6a section. Yield: 17%. Purity: 96% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.30$ ($m_c$, 2 H, AA′-part of an AA′BB′-system, 3′(5′)-H), 7.43 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 5-H), 7.54 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 6-H), 7.67 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 7-H), 7.74 ($m_c$, 2 H, 2′(6′)-H), 8.14 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 110.0$ (+, C-Ar), 116.9 (+, d, $^2J_{CF} = 23$ Hz, 2 C, C-3′(5′)), 120.4 (+, C-Ar), 124.5 (+, C-Ar), 124.9 (+, d, $^3J_{CF} = 9$ Hz, 2 C, C-2′(6′)), 128.4 (+, C-Ar), 132.4 (quart, C-7a), 133.1 (quart, d, $^4J_{CF} = 3$ Hz, C-1′), 146.5 (quart, C-3a), 162.4 (quart, d, $^1J_{CF} = 249$ Hz, C-4′) ppm. MS ($C_{12}H_8N_3F$) *m*/*z* (%RA): 213 (25) [$M^+$], 185 (100) [$M^+$–$N_2$, $C_{12}H_8NF^+$], 164 (3), 157 (8), 95 (14), 75 (10), 63 (2). HRMS ($C_{12}H_8N_3F$) calc 213.0702; found 213.0705. IR $\nu = 3432$ (w), 3061 (m), 2930 (m), 2855 (w), 1956 (w), 1919 (w), 1879 (m), 1792 (w), 1688 (w), 1607 (m), 1589 (m), 1516 (vs), 1454 (s), 1424 (m), 1276 (s), 1235 (vs), 1189 (s), 1155 (m), 1127 (m), 1100 (s), 1070 (vs), 1011 (m), 941 (w), 918 (w), 850 (s), 830 (vs), 819 (s), 784 (s), 769 (s), 742 (vs), 705 (w), 671 (m), 664 (m), 632 (w) $cm^{-1}$.

**1-(3′-Fluorphenyl)-1*H*-benzotriazole (18t).** Cleavage from



**10t** as described in the General Procedures 6a section. Yield: 19%. Purity: 99% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.20$ (ddd, $^3J = 8.3$, $^3J = 8.1$, $^4J_{HF} = 2.4$, $^5J = 1.3$ Hz, 1 H, 5′-H), 7.45 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 5-H), 7.54–7.64 (m, 4 H, 1′,4′,6′,6-H), 7.76 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.8$ Hz, 1 H, 7-H), 8.15 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.8$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 110.2$ (C-Ar), 110.4 (d, $^2J_{CF} = 25$ Hz, C-4′), 115.5 (d, $^2J_{CF} = 21$ Hz, C-2′), 118.1 (d, $^4J_{CF} = 3$ Hz, C-6′), 120.6 (C-Ar), 124.6 (C-Ar), 128.6 (C-Ar), 131.2 (d, $^3J_{CF} = 9$ Hz, C-5′), 132.1 (C-7a), 139.5 (d, $^3J_{CF} = 7$ Hz, C-1′), 146.7 (C-3a), 163.2 (d, $^1J_{CF} = 249$ Hz, C-3′) ppm. MS ($C_{12}H_8N_3F$) *m*/*z* (%RA): 213 (31) [$M^+$], 185 (100) [$M^+$–$N_2$, $C_{12}H_8NF^+$], 164 (4), 157 (8), 133 (2), 95 (18), 75 (11), 63 (2). HRMS ($C_{12}H_8N_3F$) calc 213.0702; found 213.0704. IR $\nu = 3438$ (w), 3075 (m), 3028 (m), 2929 (m), 2856 (m), 1955 (w), 1797 (w), 1610 (vs), 1502 (vs), 1462 (s), 1324 (w), 1291 (s), 1268 (m), 1250 (s), 1226 (s), 1172 (s), 1156 (m), 1137 (m), 1087 (s), 1063 (s), 1004 (m), 932 (s), 866 (s), 852 (s), 788 (s), 768 (s), 743 (vs), 683 (s), 660 (m) $cm^{-1}$.

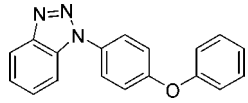
**1-(2′,6′-Difluorphenyl)-1*H*-benzotriazole (18u).** Cleavage



from **10u** as described in the General Procedures 6a section. Yield: 15%. Purity: 98% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.20$ (dddd, $^3J_{HF} = 10.6$, $^3J = 8.7$, $^4J = 1.5$, $^5J_{HF} = 1.5$ Hz, 2 H, 3′(5′)-H), 7.37 (ddd, $^3J = 8.2$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 7-H), 7.44 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 5-H), 7.50–7.59 (m, 2 H, 6,4′-H), 8.16 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 109.73$ (+, t, $^5J_{CF} = 1.5$ Hz, C-7), 112.63 (+,

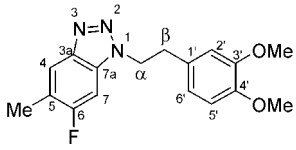
dd, $^2J_{CF}$ = 21, $^2J_{CF}$ = 4 Hz, C-3′*), 112.66 (+, dd, $^2J_{CF}$ = 21, $^2J_{CF}$ = 4 Hz, C-5′*), 120.31 (+, C-Ar), 124.42 (+, C-Ar), 128.61 (+, C-Ar), 131.56 (+, t, $^3J_{CF}$ = 10 Hz, C-4′), 134.03 (quart, C-7a), 145.44 (quart, C-3a), 157.86 (quart, dd, $^1J_{CF}$ = 257, $^3J_{CF}$ = 3 Hz, 2 C, C-2′(6′)) ppm. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ = −118 ppm. MS ($C_{12}H_7N_3F_2$) *m*/*z* (%RA): 231 (26) [$M^+$], 203 (100) [$M^+$–$N_2$, $C_{12}H_7NF_2^+$], 202 (36) [$M^+$–$N_2$–H, $C_{12}H_6NF_2^+$], 183 (11), 164 (7), 140 (2), 113 (5), 63 (14). HRMS ($C_{12}H_7N_3F_2$) calc 231.0608; found 231.0612. IR $\nu$ = 3071 (m), 2961 (m), 2926 (m), 2854 (w), 2530 (w), 2356 (w), 1949 (w), 1684 (w), 1625 (s), 1615 (s), 1600 (vs), 1570 (m), 1521 (vs), 1478 (vs), 1450 (s), 1384 (m), 1292 (vs), 1246 (vs), 1200 (m), 1190 (m), 1156 (m), 1146 (m), 1123 (m), 1061 (vs), 1011 (vs), 990 (m), 917 (w), 883 (w), 848 (w), 790 (vs), 782 (vs), 767 (s), 747 (vs), 721 (s), 701 (w), 660 (m) $cm^{-1}$.

**1-(4′-Phenoxyphenyl)-1*H*-benzotriazole (18v).** Cleavage



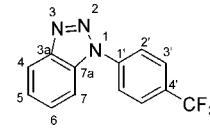
from **10v** as described in the General Procedures 6a section. Yield: 27%. Purity: 97% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.07–7.11 (m, 2 H, Ar-H), 7.14–7.22 (m, 3 H, Ar-H), 7.36–7.44 (m, 3 H, Ar-H), 7.53 (ddd, $^3J$ = 8.3, $^3J$ = 7.0, $^4J$ = 1.0 Hz, 1 H, 6-H), 7.67–7.72 (m, 3 H, Ar-H), 8.13 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^5J$ = 0.8 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 110.2 (+, C-Ar), 119.4 (+, 2 C, C-Ar′), 119.5 (+, 2 C, C-Ar′), 120.3 (+, C-Ar), 124.2 (+, C-Ar), 124.3 (+, C-Ar′), 124.6 (+, 2 C, C-Ar′), 128.2 (+, C-Ar), 130.0 (+, 2 C, C-Ar′), 131.9 (quart, C-1′), 132.9 (quart, C-7a), 146.4 (quart, C-3a), 156.4 (quart, C-OAr), 157.9 (quart, C-OAr) ppm. MS ($C_{18}H_{13}N_3O$) *m*/*z* (%RA): 287 (18) [$M^+$], 259 (25) [$M^+$–$N_2$, $C_{18}H_{13}NO^+$], 230 (6), 203 (3), 182 (20) [$M^+$–$N_2$–$C_6H_5$, $C_{12}H_8N_1O^+$], 166 (100) [$M^+$–$N_2$–$C_6H_5O$, $C_{12}H_{18}N^+$], 154 (9), 139 (6), 115 (7), 77 (11), 51 (3). HRMS ($C_{18}H_{13}N_3O$) calc 287.1059; found 287.1059. IR $\nu$ = 3416 (w), 3075 (m), 2926 (w), 2439 (w), 1887 (w), 1784 (w), 1624 (m), 1588 (s), 1510 (vs), 1490 (vs), 1453 (m), 1425 (m), 1313 (m), 1291 (s), 1244 (vs), 1200 (s), 1190 (s), 1160 (m), 1126 (m), 1105 (s), 1068 (vs), 1020 (m), 1006 (m), 955 (w), 914 (m), 874 (s), 837 (vs), 799 (m), 783 (s), 762 (s), 745 (vs), 714 (w), 698 (s), 676 (m), 667 (w) $cm^{-1}$.

**6-Fluor-5-methyl-1-(3′,4′-dimetoxyphenethyl)-1*H*-benzotriazole (18w).** Cleavage from **11** as described in the



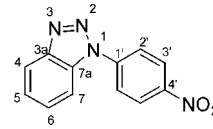
General Procedures 6a section. Yield: 64%. Purity: >95% ($^1$H NMR). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.36 (d, $^4J_{HF}$ = 2.8 Hz, 3 H, 5-$CH_3$), 3.21 (t, $^3J$ = 7.2 Hz, 2 H, $\beta$-$CH_2$), 3.67 (s, 3 H, $OCH_3$), 3.80 (s, 3 H, $OCH_3$), 4.75 (t, $^3J$ = 7.2 Hz, 2 H, α-$NCH_2$), 6.40 (d, $^4J$ = 2.0 Hz, 1 H, 2′-H), 6.61 (dd, $^3J$ = 9.2, $^4J$ = 2.0 Hz, 1 H, 6′-H), 6.72 (d, $^3J$ = 9.2 Hz, 1 H, 5′-H), 6.83 (d, $^3J_{HF}$ = 9.7 Hz, 1 H, 7-H), 7.83 (d, $^4J_{HF}$ = 6.0 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (62 MHz, $CDCl_3$): $\delta$ = 15.5 (d, $^3J_{CF}$ = 29 Hz, $CH_3$), 35.5 ($CH_2$), 50.5 ($NCH_2$), 55.7 ($OCH_3$), 55.9 ($OCH_3$), 94.8 (d, $^2J_{CF}$ = 32 Hz, 7-C), 111.7 (C-Ar′), 112.0 (C-Ar′), 120.2 (4-C), 120.9 (C-Ar′), 125.5 (d, $^2J_{CF}$ = 24 Hz, 5-$C_q$), 129.4 (1′-$C_q$), 133.5 (d, $^3J_{CF}$ = 8 Hz, 7a-$NC_q$), 148.2 ($C_q$-Ar′), 149.1 ($C_q$-Ar′), 161.6 (d, $^1J_{CF}$ = 254 Hz, 6-$C_q$) ppm. $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = −114 ppm. GCMS ($C_{17}H_{18}FN_3O_2$) *m*/*z* (%RA): 277 (100) [$M^+$–HF–$H_2O$, $C_{17}H_{15}N_3O^+$], 201 (19), 199 (17), 183 (13), 152 (10) [$M^+$–$C_8H_6FN_3$, $C_9H_{12}O_2^+$], 124 (3), 77 (13), 51 (9).

**1-(4′-Trifluormethylbenzene)-1*H*-benzotriazole (18x).** Cleavage from **13a** as described in the General Procedures



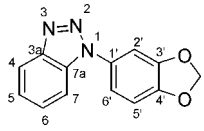
6a section. Yield: 19%. Purity: 81% (GC). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.47 (ddd, $^3J$ = 8.3,$^3J$ = 7.0, $^4J$ = 0.9 Hz, 1 H, 5-H), 7.60 (ddd, $^3J$ = 8.5,$^3J$ = 7.0, $^4J$ = 1.0 Hz, 1 H, 6-H), 7.77 (ddd, $^3J$ = 8.5, $^4J$ = 0.9, $^5J$ = 0.8 Hz, 1 H, 7-H), 7.88 (br.d, $^3J$ = 8.5 Hz, 2 H, Ar′-H), 7.98 (br.d, $^3J$ = 8.5 Hz, 2 H, Ar′-H), 8.17 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^5J$ = 0.8 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 110.1 (+, C-Ar), 120.7 (+, C-Ar), 122.6 (+, 2 C, C-2′(6′)), 123.7 (quart, q, $^1J_{CF}$ = 272 Hz, $CF_3$), 124.8 (+, C-Ar), 127.2 (+, q, $^4J_{CF}$ = 4 Hz, 2 C, C-3′(5′)), 128.9 (+, C-Ar), 130.5 (quart, q, $^3J_{CF}$ = 33 Hz, C-4′), 132.0 (quart, C-7a), 139.9 (quart, C-1′), 146.8 (quart, C-3a) ppm. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ = −63 ppm. MS ($C_{13}H_8N_3F_3$) *m*/*z* (%RA): 263 (31) [$M^+$], 235 (100) [$M^+$–$N_2$, $C_{13}H_8N_1F_3^+$], 216 (23), 185 (10), 167 (11), 166 (21), 145 (31), 125 (5), 95 (7). HRMS ($C_{13}H_8N_3F_3$) calc 263.0670; found 263.0674.

**1-(4′-Nitrophenyl)-1*H*-benzotriazole (18y).** Cleavage from



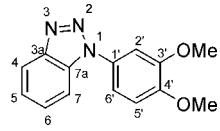
**13b** as described in the General Procedures 6a section. Purity: 95% ($^1$H-NMR). $^1$H NMR (400 MHz, DMSO): $\delta$ = 7.50 (ddd, $^3J$ = 8.4, $^3J$ = 7.0, $^4J$ = 0.9 Hz, 1 H, 5-H), 7.67 (ddd, $^3J$ = 8.4, $^3J$ = 7.0, $^4J$ = 1.0 Hz, 1 H, 6-H), 8.02 (ddd, $^3J$ = 8.4, $^4J$ = 0.9, $^5J$ = 0.9 Hz, 1 H, 7-H), 8.17 (ddd, $^3J$ = 8.4, $^4J$ = 1.0, $^5J$ = 0.9 Hz, 1 H, 3-H), 8.18 ($m_c$, AA′-part of an AA′BB′-system, 2 H, Ar′-H), 8.44 ($m_c$, BB′-part of an AA′BB′-system, 2 H, Ar′-H) ppm. $^{13}$C NMR (100 MHz, DMSO): $\delta$ = 111.2 (+, C-Ar), 120.0 (+, C-Ar), 122.8 (+, 2 C, C-Ar′), 125.2 (+, C-Ar), 125.5 (+, 2 C, C-Ar′), 129.4 (+, C-Ar), 131.4 (quart, C-7a), 141.2 (quart, C-1′), 146.0 (quart, C-4′*), 146.8 (quart, C-3a*) ppm. MS ($C_{12}H_8N_4O_2$) *m*/*z* (%RA): 240 (37) [$M^+$], 212 (16) [$M^+$–$N_2$, $C_{12}H_8N_2O_2^+$], 195 (13), 182 (4), 166 (100) [$M^+$–$N_2$–$NO_2$, $C_{12}H_8N^+$], 149 (4), 140 (14), 139 (12), 119 (4) [$C_6H_5N_3^+$], 91 (3), 76 (14), 63 (4).

**1-(3′,4′-Methylendioxybenzene)-1*H*-benzotriazole (18z).** Cleavage from **13c** as described in the General Procedures 6a section. Yield: 32%. Purity: 95% (GC). $^1$H NMR (400



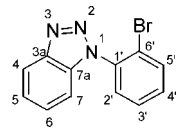
MHz, $CDCl_3$): $\delta = 6.09$ (s, 2 H, $CH_2$), 6.98 (d, $^3J = 8.2$ Hz, 1 H, 5′-H), 7.19 (dd, $^3J = 8.2$, $^4J = 2.2$ Hz, 1 H, 6′-H), 7.22 (d, $^4J = 2.2$ Hz, 1 H, 2′-H), 7.40 (ddd, $^3J = 8.3$,$^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 5-H), 7.52 (ddd, $^3J = 8.3$,$^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 6-H), 7.66 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 7-H), 8.11 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$, DEPT): $\delta = 102.1$ (–, $CH_2$), 104.9 (+, C-Ar), 108.7 (+, C-Ar), 110.2 (+, C-Ar), 116.7 (+, C-Ar), 120.3 (+, C-Ar), 124.3 (+, C-Ar), 128.1 (+, C-Ar), 131.0 (quart, C-1′), 133.0 (quart, C-7a), 146.3 (quart, C-3a), 148.0 (quart, $C_q$-Ar), 148.7 (quart, $C_q$-Ar) ppm. MS ($C_{13}H_9N_3O_2$) *m*/*z* (%RA): 239 (65) [$M^+$], 222 (16), 211 (62) [$C_{13}H_9N_1O_2^+$], 181 (31) [$C_{12}H_7N_1O_1^+$], 153 (100), 132 (17), 126 (18), 105 (16), 77 (35). HRMS calc 239.0695; found 239.0696.

***N*-(3′,4′-Dimethoxyphenyl)-1*H*-benzotriazole (18aa).** Cleav-



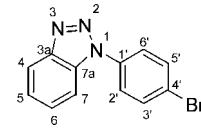
age from **13d** as described in the General Procedures 6a section. Yield: 51%. Purity: 95% ($^1$H NMR). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 3.92$ (s, 3 H, OMe), 3.94 (s, 3 H, OMe), 7.02 (br.d, $^3J = 8.2$ Hz, 1 H, 6′-H), 7.21–7.25 (m, 2 H, 2′,5′-H), 7.43 (ddd, $^3J = 8.3$, $^3J = 6.9$, $^4J = 1.0$ Hz, 1 H, 5-H), 7.53 (ddd, $^3J = 8.3$, $^3J = 6.9$, $^4J = 1.0$ Hz, 1 H, 6-H), 7.68 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.7$ Hz, 1 H, 7-H), 8.12 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.7$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 56.19$ (+, $OCH_3$), 56.22 (+, $OCH_3$), 107.42 (+, C-Ar′), 110.56 (+, C-Ar), 111.42 (+, C-Ar′), 115.26 (+, C-Ar′), 119.56 (+, C-Ar), 125.11 (+, C-Ar), 128.50 (+, C-Ar), 129.61 (quart, $C_{1'}$), 132.68 (quart, $C_{7a}$), 144.99 (quart, $C_{3a}$), 149.76 (quart, $OC_{q'}$), 149.99 (quart, $OC_{q'}$) ppm. MS ($C_{14}H_{13}N_3O_2$) *m*/*z* (%RA): 255 (14) [$M^+$], 227 (2) [$M^+$–$N_2$, $C_{14}H_{13}NO_2^+$], 212 (13) [$M^+$–$N_2$–$CH_3$, $C_{13}H_{10}NO_2^+$], 196 (7) [$M^+$–$N_2$–$OCH_3$, $C_{13}H_{10}NO^+$], 184 (6), 169 (10), 149 (9), 119 (87) [$C_6H_5N_3^+$], 106 (16) [$M^+$–$C_6H_4N_3$–$OCH_3$, $C_7H_6O^+$], 91 (51), 77 (10), 73 (12), 69 (100), 64 (21), 51 (35). HRMS calc 255.1008; found 255.1010.

***N*-(2′-Bromophenyl)-1*H*-benzotriazole (18ab).** Cleavage



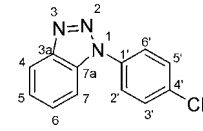
from **13e** as described in the General Procedures 6a section. Yield: 22%. Purity: 60% ($^1$H NMR). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.35$ (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 7-H), 7.43 (m, 2 H), 7.52 (ddd, $^3J = 8.3$, $^3J = 6.8$, $^4J = 1.0$ Hz, 2 H, 5(6)-H), 7.82 (m, 1 H, Ar′-H), 7.87 (dd, $^3J = 5.8$, $^4J = 2.7$ Hz, 1 H, Ar′-H), 8.15 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 4-H) ppm.

***N*-(4′-Bromophenyl)-1*H*-benzotriazole (18ac).** Cleavage



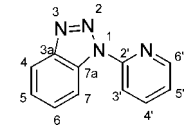
from **13f** as described in the General Procedures 6a section. Yield: 28%. Purity: 86% ($^1$H NMR). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.42$ (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 0.9$ Hz, 1 H, 5-H), 7.54 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 6-H), 7.65 ($m_c$, AA′-part of an AA′BB′-system, 2 H, Ar′-H), 7.69 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 7-H), 7.71 ($m_c$, BB′-part of an AA′BB′-system, 2 H, Ar′-H), 8.12 (ddd, $^3J = 8.3$, $^4J = 0.9$, $^5J = 0.9$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 110.1$ (+, C-Ar), 120.4 (+, C-Ar), 122.3 (quart, $C_{4'}$), 124.1 (+, 2 C, C-Ar′), 124.6 (+, C-Ar), 128.5 (+, C-Ar), 132.0 (quart, $C_{7a}$), 133.0 (+, 2 C, C-Ar′), 136.0 (quart, $C_{1'}$), 146.5 (quart, $C_{3a}$) ppm. MS ($C_{12}H_8BrN_3$) *m*/*z* (%RA): 273/275 (14/14) [$M^+$], 245/247 (9/9) [$M^+$–$N_2$, $C_{12}H_8BrN^+$], 166 (100) [$M^+$–$N_2$–Br, $C_{12}H_8N^+$], 149 (32), 140 (10) [$M^+$–$N_2$–Br–$C_2H_2$, $C_{10}H_6N^+$], 76 (10). HRMS calc 272.9902; found 272.9907.

***N*-(4′-Chlorophenyl)-1*H*-benzotriazole (18ad).**[19] Cleav-



age from **13g** as described in the General Procedures 6a section. Yield: 53%. Purity: 95% ($^1$H NMR). $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.42$ (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 5-H), 7.54 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 6-H), 7.56 ($m_c$, AA′-part of an AA′BB′-system, 2 H, Ar′-H), 7.68 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 7-H), 7.72 ($m_c$, BB′-part of an AA′BB′-system, 2 H, Ar′-H), 8.12 (ddd, $^3J = 8.3$, $^4J = 1.0$, $^5J = 0.9$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 110.0$ (+, C-Ar), 120.4 (+, C-Ar), 123.9 (+, 2 C, C-Ar′), 124.5 (+, C-Ar), 128.5 (+, C-Ar), 130.0 (+, 2 C, C-Ar′), 132.1 (quart, C-7a), 134.4 (quart, C-Ar′), 135.5 (quart, C-Ar′), 146.5 (quart, C-3a) ppm. MS ($C_{12}H_8ClN_3$) *m*/*z* (%RA): 229/231 (35/14) [$M^+$], 201/203 (100/34) [$M^+$–$N_2$, $C_{12}H_8ClN^+$], 167 (24), 140 (18) [$M^+$–$N_2$–Cl–$C_2H_2$, $C_{10}H_6N^+$], 139 (15), 111 (35), 75 (37).

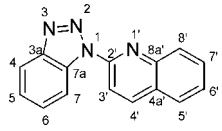
***N*-(Pyridin-2′-yl)-1*H*-benzotriazole (18ae).**[20] Cleavage



from **13h** as described in the General Procedures 6b section. Yield: 42%. Purity: 95% (GC). $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.31$ (ddd, $^3J = 7.4$, $^3J = 4.9$, $^4J = 1.0$ Hz, 1 H, 5′-H), 7.44 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.1$ Hz, 1 H, 5*-H), 7.59 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.1$ Hz, 1 H, 6*-H), 7.93 (ddd, $^3J = 8.3$, $^3J = 7.4$, $^4J = 1.9$ Hz, 1 H, 4′-H), 8.11 (ddd, $^3J = 8.3$, $^4J = 1.1$, $^5J = 0.9$ Hz, 1 H, 7-H), 8.30 (ddd, $^3J = 8.3$, $^4J = 1.1$, $^5J = 0.9$ Hz, 1 H, 4-H), 8.61 (ddd, $^3J = 4.9$, $^4J = 1.9$, $^5J = 0.9$ Hz, 1 H, 6′-H), 8.65 (ddd, $^3J = 8.3$, $^4J =$

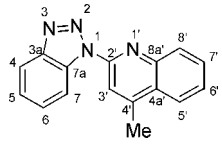
1.0, $^5J = 0.9$ Hz, 1 H, 3′-H) ppm. MS ($C_{11}H_8N_4$) *m/z* (%RA): 196 (30) [$M^+$], 168 (100) [$M^+$–$N_2$, $C_{11}H_8N_2^+$], 142 (7), 140 (7), 117 (4), 84 (4), 78 (59), 51 (12). HRMS calc 196.0749; found 196.0753.

***N*-(Quinolin-2′-yl)-1*H*-benzotriazole (18af).**[21] Cleavage



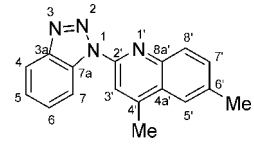
from **13i** as described in the General Procedures 6b section. Yield: 39%. Purity: 99% ($^1$H NMR). $^1$H NMR: $\delta = 7.48$ (ddd, $^3J = 8.4$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 6-H), 7.57 (ddd, $^3J = 8.1$, $^3J = 7.0$, $^4J = 1.1$ Hz, 1 H, 6′-H), 7.66 (ddd, $^3J = 8.4$, $^3J = 7.0$, $^4J = 1.1$ Hz, 1 H, 5-H), 7.78 (ddd, $^3J = 8.5$, $^3J = 7.0$, $^4J = 1.5$ Hz, 1 H, 7′-H), 7.88 (br.dd, $^3J = 8.1$, $^4J = 1.5$ Hz, 1 H, 5′-H), 8.12–8.17 (m, 2 H, 4,8′-H), 8.36 (d, $^3J = 9.0$ Hz, 1 H, 4′-H), 8.48 (d, $^3J = 9.0$ Hz, 1 H, 3′-H), 8.95 (ddd, $^3J = 8.4$, $^4J = 1.1$,$^5J = 0.9$ Hz, 1 H, 7-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 113.4$ (+, C-Ar′), 115.4 (+, C-Ar), 119.9 (+, C-Ar), 125.2 (+, C-Ar), 126.7 (+, C-Ar′), 127.1 (quart, C-4′a), 127.8 (+, C-Ar′), 128.8 (+, C-Ar), 129.0 (+, C-Ar′), 130.5 (+, C-Ar′), 131.7 (quart, C-7a), 139.2 (+, C-4′), 146.6 (quart, C-2′), 146.9 (quart, C-3a), 150.5 (quart, C-8′a) ppm. MS ($C_{15}H_{10}N_4$) *m/z* (%RA): 246 (27) [$M^+$], 218 (100) [$M^+$–$N_2$, $C_{15}H_{10}N_2^+$], 174 (25), 146 (5), 128 (63) [$M^+$–$C_6H_4N_3$, $C_9H_6N^+$], 119 (4) [$C_6H_5N_3^+$], 105 (8), 101 (15), 91 (10) [$C_6H_5N^+$], 77 (11), 51 (3). HRMS calc 246.0905; found 246.0920.

***N*-(4′-Methylquinolin-2′-yl)-1*H*-benzotriazole (18ag).** Cleav-



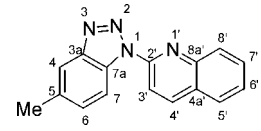
age from **13j** as described in the General Procedures 6b section. Yield: 38%. Purity: 99% ($^1$H NMR). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 2.79$ (d, $^4J = 0.9$ Hz, 3 H, 4′-$CH_3$), 7.46 (ddd, $^3J = 8.4$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 6-H), 7.55 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.2$ Hz, 1 H, 7′-H), 7.63 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.1$ Hz, 1 H, 5-H), 7.74 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.4$ Hz, 1 H, 6′-H), 7.99 (br.dd, $^3J = 8.3$, $^4J = 1.2$ Hz, 1 H, 5′-H), 8.11 (ddd, $^3J = 8.3$, $^4J = 1.4$, $^5J = 0.5$ Hz, 1 H, 8′-H), 8.12 (ddd, $^3J = 8.3$ Hz, $^4J = 1.0$ Hz, $^5J = 0.8$ Hz, 1 H, 4-H), 8.30 (q, $^4J = 0.9$ Hz, 1 H, 3′-H), 8.92 (ddd, $^3J = 8.4$ Hz, $^4J = 1.1$ Hz, $^5J = 0.8$ Hz, 1 H, 7-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 19.1$ (+, $CH_3$-6′), 113.5 (+, C-Ar′), 115.5 (+, C-Ar), 119.6 (+, C-Ar), 123.9 (+, C-Ar′), 125.0 (+, C-Ar), 126.4 (+, C-Ar′), 127.2 (quart, C-4′a), 128.8 (+, C-Ar), 129.4 (+, C-Ar′), 130.1 (+, C-Ar′), 131.7 (quart, C-7a), 146.4 (quart, C-2′), 146.9 (quart, C-3a), 147.9 (quart, C-4′), 150.2 (quart, C-8′a) ppm. MS ($C_{16}H_{12}N_4$) *m/z* (%RA): 260 (28) [$M^+$], 232 (100) [$M^+$–$N_2$, $C_{16}H_{12}N_2^+$], 204 (4), 142 (41) [$M^+$–$C_6H_4N_3$, $C_{10}H_8N^+$], 140 (13), 116 (21), 115 (23), 89 (4), 77 (5). HRMS calc 260.1062; found 260.1068.

***N*-(4′,6′-Dimethylquinolin-2′-yl)-1*H*-benzotriazole (18ah).** Cleavage from **13k** as described in the General Procedures 6b section. Yield: 35%. Purity: 99% ($^1$H NMR). $^1$H NMR



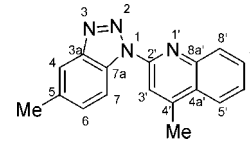
(400 MHz, $CDCl_3$): $\delta = 2.56$ (s, 3 H, 6′-$CH_3$), 2.76 (d, $^4J = 0.9$ Hz, 3 H, 4′-$CH_3$), 7.46 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 6-H), 7.56 (dd, $^3J = 8.6$, $^4J = 1.9$ Hz, 1 H, 7′-H), 7.62 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.0$ Hz, 1 H, 5-H), 7.74 ($m_c$, 1 H, 5′-H), 8.00 (d, $^3J = 8.6$ Hz, 1 H, 8′-H), 8.12 (ddd, $^3J = 8.3$ Hz, $^4J = 1.0$ Hz, $^5J = 0.8$ Hz, 1 H, 4-H), 8.24 (q, $^4J = 0.9$ Hz, 1 H, 3′-H), 8.90 (ddd, $^3J = 8.3$ Hz, $^4J = 1.0$ Hz, $^5J = 0.8$ Hz, 1 H, 7-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 19.1$ (+, $CH_3$-6′), 21.8 (+, $CH_3$-4′), 113.5 (+, C-Ar′), 115.5 (+, C-Ar), 119.6 (+, C-Ar), 123.0 (+, C-Ar′), 125.0 (+, C-Ar), 127.2 (quart, C-4′a), 128.8 (+, C-Ar), 129.1 (+, C-Ar′), 131.7 (quart, C-7a), 132.3 (+, C-Ar′), 136.8 (quart, C-6′), 144.8 (quart, C-Ar′), 146.7 (quart, C-3a), 147.2 (quart, C-Ar′), 149.6 (quart, C-8′a) ppm. MS ($C_{17}H_{14}N_4$) *m/z* (%RA): 274 (33) [$M^+$], 246 (100) [$M^+$–$N_2$, $C_{17}H_{14}N_2^+$], 231 (7) [$M^+$–$N_2$–$CH_3$, $C_{16}H_{11}N_2^+$], 208 (4), 179 (4), 156 (41) [$M^+$–$C_6H_4N_3$, $C_{11}H_{10}N^+$], 141 (10), 128 (8), 119 (16) [$C_6H_5N_3^+$], 116 (8), 105 (3), 91 (11), 77 (5), 69 (8), 51 (3). HRMS calc 274.1218; found 274.1220.

***N*-(Quinolin-2′-yl)-5-methyl-1*H*-benzotriazole (18ai).** Cleav-



age from **14i** as described in the General Procedures 6b section. Yield: 16%. Purity: 98% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 2.57$ (br.s, 3 H, 5-$CH_3$), 7.49 (ddd, $^3J = 8.2$, $^4J = 1.6$, $^5J = 0.9$ Hz, 1 H, 8′-H), 7.57 (ddd, $^3J = 8.2$, $^3J = 7.0$, $^4J = 1.3$ Hz, 1 H, 7′-H), 7.77 (ddd, $^3J = 8.3$, $^3J = 7.0$, $^4J = 1.6$ Hz, 1 H, 6′-H), 7.88 (dd, $^3J = 8.5$, $^4J = 1.1$ Hz, 1 H, 6-H), 7.90 (m, 1 H, 4-H), 8.15 (m, 1 H, 5′-H), 8.36 (br.d, $^3J = 8.9$ Hz, 1 H, 4′-H), 8.48 (d, $^3J = 8.9$ Hz, 1 H, 3′-H), 8.82 (d, $^3J = 8.5$ Hz, 1 H, 7-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 21.5$ (+, $CH_3$), 113.4 (+, C-Ar), 114.9 (+, C-Ar), 118.9 (+, C-Ar′), 126.6 (+, C-Ar′), 127.8 (+, C-Ar′), 128.8 (+, C-Ar′), 130.5 (+, C-Ar), 131.0 (+, C-Ar), 135.3 (quart, $C_q$), 136.8 (quart, $C_q$), 137.6 (quart, $C_q$′), 139.1 (+, C-Ar), 146.6 (quart, $C_q$′), 147.5 (quart, $C_q$′), 150.5 (quart, $C_q$) ppm.

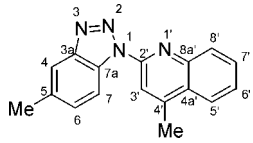
***N*-(4′-Methylquinolin-2′-yl)-5-methyl-1*H*-benzotriazole (18aj).** Cleavage from **14j** as described in the General



Procedures 6b section. Yield: 64%. Purity: 80% ($^1$H NMR). $^1$H NMR (250 MHz, $CDCl_3$): $\delta = 2.51$ (s, 3 H, 5-$CH_3$), 2.74 (s, 3 H, 4′-$CH_3$), 7.43 (d, $^3J = 8.8$ Hz, 1 H, 6-H), 7.55 (dd, $^3J = 8.1$, $^3J = 7.2$ Hz, 1 H, 6′-H), 7.72 (dd, $^3J = 9.0$, $^3J = 8.1$ Hz, 1 H, 7′-H), 7.81 (s, 1 H, 4-H), 7.95 (d, $^3J =$

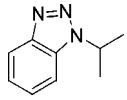
7.2 Hz, 1 H, 5′-H), 8.05 (d, $^3J$ = 9.0 Hz, 1 H, 8′-H), 8.13 (br.s, 3′-H), 8.70 (d, $^3J$ = 8.8 Hz, 1 H, 7-H) ppm.

***N*-(4′,6′-Dimethylquinolin-2′-yl)-5-methyl-1*H*-benzotriazole (18ak).**[22] Cleavage from **14k** as described in the General



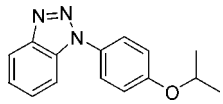
Procedures 6b section. Yield: 66%. Purity: 99% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.56 (br.s, 3 H, 6′-$CH_3$), 2.58 (br.s, 3 H, 5-$CH_3$), 2.79 (d, $^4J$ = 0.9 Hz, 3 H, 4′-$CH_3$), 7.46 (dd, $^3J$ = 8.5, $^4J$ = 1.1 Hz, 1 H, 6-H), 7.59 (dd, $^3J$ = 8.6, $^4J$ = 1.9 Hz, 1 H, 7′-H), 7.78 (m, 1 H, 5′-H), 7.88 (m, 1 H, 4-H), 8.03 (d, $^3J$ = 8.6 Hz, 1 H, 8′-H), 8.28 (quart, $^4J$ = 0.9 Hz, 1 H, 3′-H), 8.78 (d, $^3J$ = 8.5 Hz, 1 H, 7-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 19.1 (+, $CH_3$-6′), 21.5 (+, $CH_3$-5), 21.9 (+, $CH_3$-4′), 113.6 (+, C-Ar), 114.9 (+, C-Ar), 118.8 (+, C-Ar), 123.1 (+, C-Ar), 127.2 (quart, $C_q$), 129.1 (+, C-Ar), 130.2 (quart, $C_q$), 130.8 (+, C-Ar), 132.2 (+, C-Ar), 135.1 (quart, $C_q$), 136.3 (quart, $C_q$), 144.9 (quart, $C_q$), 147.1 (quart, $C_q$), 147.5 (quart, $C_q$), 149.7 (quart, $C_q$) ppm. $C_{18}H_{16}N_4$MS *m/z* (%RA): 288 (30) [$M^+$], 261 (23), 260 (100) [$M^+$–$N_2$, $C_{18}H_{16}N_2^+$], 259 (78), 245 (7), 236 (10), 207 (7), 156 (43), 141 (10) 140 (9), 130 (12), 129 (11), 128 (10), 116 (9), 104 (8), 91 (4). HRMS calc 288.1375; found 288.1372.

**1-Isopropyl-1*H*-benzotriazole (18al).** Cleavage from **10w**



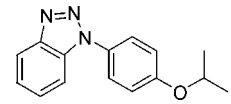
as described in the General Procedures 6a section. Purity: 79% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.73 (d, $^3J$ = 6.8 Hz, 6 H, $CH_3$), 5.08 (sep, $^3J$ = 6.8 Hz, 1 H, NCH), 7.34 (ddd, $^3J$ = 8.3, $^3J$ = 7.0, $^4J$ = 1.0 Hz, 1 H, 5-H), 7.45 (ddd, $^3J$ = 8.3, $^3J$ = 7.0, $^4J$ = 1.0 Hz, 1 H, 6-H), 7.56 (br.d, $^3J$ = 8.3 Hz, 1 H, 7-H), 8.05 (br.d, $^3J$ = 8.3 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 22.2 ($CH_3$), 51.6 (NCH), 109.6 (C-Ar), 120.1 (C-Ar), 123.7 (C-Ar), 126.8 (C-Ar), 131.1 (C-7a), 145.8 (C-3a) ppm. GCMS ($C_9H_{11}N_3$) *m/z* (%RA): 161 (21) [$M^+$], 146 (1) [$M^+$–$CH_3$, $C_8H_8N_3^+$], 132 (6) [$M^+$–$N_2$–H, $C_9H_{10}N^+$], 118 (12) [$M^+$–$C_3H_7$, $C_6H_4N_3^+$], 105 (2), 91 (100) [$M^+$–$N_2$–$C_3H_6$, $C_6H_5N^+$], 77 (24), 63 (34), 50 (23).

**1-(4′-Isopropoxyphenyl)-1*H*-benzotriazole (18am).** Cleav-



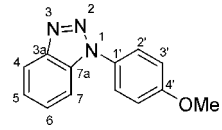
age from 0.50 g **10x** as described in the General Procedures 6a section. Yield: 21.6 mg (0.0853 mmol). Purity: 94% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.38 (d, $^3J$ = 6.0 Hz, 6 H, $CH_3$), 4.62 (sep, $^3J$ = 6.0 Hz, 1 H, OCH), 7.07 ($m_c$, 2 H, AA′-part of an AA′BB′-system, 3′(5′)-H), 7.40 (ddd, $^3J$ = 8.3, $^3J$ = 7.0, $^4J$ = 1.0 Hz, 1 H, 5-H), 7.50 (ddd, $^3J$ = 8.3, $^3J$ = 7.0, $^4J$ = 1.0 Hz, 1 H, 6-H), 7.62 ($m_c$, 2 H, BB′-part of an AA′BB′-system, 2′(6′)-H), 7.66 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^5J$ = 0.8 Hz, 1 H, 7-H), 8.12 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^5J$ = 0.8 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 22.0 (+, $CH_3$), 70.5 (+, OCH), 110.3 (+, C-Ar), 116.7 (+, 2 C, C-Ar′), 120.1 (+, C-Ar), 124.2 (+, C-Ar), 124.6 (+, 2 C, C-Ar′), 128.0 (+, C-Ar), 129.6 (quart, C-1′), 132.7 (quart, C-7a), 146.2 (quart, C-3a), 158.3 (quart, C-4′) ppm. MS ($C_{15}H_{15}N_3O_1$) *m/z* (%RA): 253 (13) [$M^+$], 220 (4), 205 (9), 202 (27), 183 (77) [$M^+$–$N_2$–$C_3H_6$, $C_{12}H_9NO^+$], 168 (81), 166 (90) [$M^+$–$N_2$–$C_3H_7O$, $C_{12}H_8N^+$], 165 (100) [$M^+$–$N_2$–$C_3H_8O$, $C_{12}H_7N^+$], 154 (56), 152 (37), 139 (12), 115 (11), 105 (11), 94 (40), 91 (11) [$C_6H_5N^+$], 77 (24), 65 (10), 51 (9). HRMS ($C_{15}H_{15}N_3O_1$) calc 253.1215; found 253.1219.

**1-(4′-Isopropylphenyl)-1*H*-benzotriazole (18an).** Cleav-



age from 0.50 g **10y** as described in the General Procedures 6a section. Yield: 28.7 mg (0.121 mmol). Purity: 96% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.32 (d, $^3J$ = 6.9 Hz, 6 H, $CH_3$), 3.02 (sep, $^3J$ = 6.9 Hz, 1 H, OCH), 7.40 (ddd, $^3J$ = 8.3, $^3J$ = 7.0, $^4J$ = 1.0 Hz, 1 H, 5-H), 7.44 ($m_c$, 2 H, AA′-part of an AA′BB′-system, 3′(5′)-H), 7.52 (ddd, $^3J$ = 8.3, $^3J$ = 7.0, $^4J$ = 1.0 Hz, 1 H, 6-H), 7.67 ($m_c$, 2 H, BB′-part of an AA′BB′-system, 2′(6′)-H), 7.72 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^5J$ = 0.8 Hz, 1 H, 7-H), 8.12 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^5J$ = 0.8 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 23.9 (+, $CH_3$), 34.0 (+, CH), 110.4 (+, C-Ar), 120.3 (+, C-Ar), 123.0 (+, 2 C, C-Ar′), 124.3 (+, C-Ar), 127.8 (+, 2 C, C-Ar′), 128.1 (+, C-Ar), 132.6 (quart, C-7a), 134.8 (quart, C-4′), 146.4 (quart, C-3a), 149.8 (quart, C-1′) ppm. MS ($C_{15}H_{15}N_3$) *m/z* (%RA): 237 (25) [$M^+$], 209 (6) [$M^+$–$N_2$, $C_{15}H_{15}N^+$], 194 (46) [$M^+$–$N_2$–$CH_3$, $C_{14}H_{12}N^+$], 180 (3), 167 (100) [$M^+$–$N_2$–$C_3H_6$, $C_{12}H_9N^+$], 152 (2), 139 (2), 103 (5), 91 (6) [$C_6H_5N^+$], 77 (7), 63 (2), 51 (2). HRMS ($C_{15}H_{15}N_3$) calc 237.1266; found 237.1279.

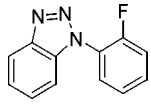
**1-(4′-Methoxyphenyl)-1*H*-benzotriazole (18ao).** Cleav-



age from **10z** as described in the General Procedures 6a section. Purity: 99% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.89 (s, 3 H, $OCH_3$), 7.09 ($m_c$, AA′-part of an AA′BB′-system, 2 H, 3′(5′)-H), 7.40 (ddd, $^3J$ = 8.3, $^3J$ = 7.0, $^4J$ = 1.0 Hz, 1 H, 5-H), 7.51 (ddd, $^3J$ = 8.3, $^3J$ = 7.0, $^4J$ = 1.0 Hz, 1 H, 6-H), 7.63–7.67 (m, 3 H, 7, 2′(6′)-H), 8.12 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^5J$ = 0.9 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 55.7 (+, $OCH_3$), 110.2 (+, C-Ar), 115.0 (+, 2 C, C-Ar), 120.2 (+, C-Ar), 124.2 (+, C-Ar), 124.6 (+, 2 C, C-Ar), 128.0 (+, C-Ar), 130.0 (quart, $C_q$-1′), 132.7 (quart, $C_q$-7a), 146.3 (quart, $C_q$-3a), 159.9 (quart, $C_q$-4′), ppm. MS ($C_{13}H_{11}N_3O_1$) *m/z* (%RA): 225 (36) [$M^+$], 197 (11) [$M^+$–$N_2$, $C_{13}H_{11}NO^+$], 184 (47), 182 (100) [$M^+$–$N_2$–$CH_3$, $C_{12}H_8NO^+$], 167 (18), 154 (62) [$M^+$–$N_2$–$CH_3$–CO,

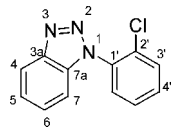
$C_{11}H_8N^+$], 128 (17), 127 (13), 105 (8), 92 (10), 77 (18). IR $\nu$ = 3061 (vs), 3032 (s), 3003 (vs), 2973 (s), 2938 (s), 2843 (s), 2672 (m), 2598 (m), 2556 (m), 2496 (m), 2341 (w), 2312 (w), 2200 (w), 2102 (w), 2047 (m), 1952 (m), 1920 (m), 1886 (s), 1795 (m), 1687 (s), 1650 (s), 1611 (vs), 1519 (vs), 1451 (vs), 1370 (s), 1317 (s), 1283 (vs), 1254 (vs), 1185 (vs), 1144 (s), 1129 (s), 1116 (vs), 1061 (vs), 1030 (vs), 1014 (vs), 948 (m), 918 (m), 829 (vs), 810 (s), 798 (s), 784 (s), 766 (s), 748 (vs), 701 (m), 671 (s), 662 (s), 636 (m) $cm^{-1}$.

**1-(2′-Fluorophenyl)-1*H*-benzotriazole (18ap).** Cleavage



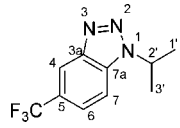
from **10aa** as described in the General Procedures 6a section. Yield: 14.8 mg (0.0694 mmol). Purity: 98% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.34–7.41 (m, 2 H, Ar-H*), 7.43 (ddd, $^3J$ = 8.3, $^4J_{HF}$ = 6.7, $^4J$ = 1.3 Hz, 1 H, 6′-H), 7.47–7.57 (m, 3 H, Ar-H*), 7.70 (ddd, $^3J_{HF}$ = 8.4, $^3J$ = 7.0, $^4J$ = 1.8 Hz, 1 H, 3′-H), 8.14 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^5J$ = 0.8 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 110.5 (d, $^XJ_{CF}$ = 5 Hz, C-Ar), 117.2 (d, $^2J_{CF}$ = 19 Hz, C-3′), 120.2 (C-Ar), 124.3 (C-Ar), 125.2 (d, $^4J_{CF}$ = 4 Hz, C-4′), 127.7 (C-Ar), 128.9 (d, $^4J_{CF}$ = 2 Hz, C-5′), 131.0 (d, $^3J_{CF}$ = 8 Hz, C-6′), 133.5 (C-7a), 145.9 (C-3a), 155.6 (d, $^1J_{CF}$ = 254 Hz, C-2′) ppm. MS ($C_{12}H_8N_3F$) *m/z* (%RA): 213 (29) [$M^+$], 185 (100) [$M^+$–$N_2$, $C_{12}H_8NF^+$], 164 (10), 157 (7), 138 (4), 95 (7), 75 (9), 63 (5). HRMS ($C_{12}H_8N_3F$) calc 213.0702; found 213.0706.

**1-(2′-Chlorophenyl)-1*H*-benzotriazole (18aq).** Cleavage



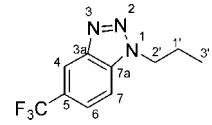
from **13l** as described in the General Procedures 6a section. Purity: 82% (GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.37 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^5J$ = 0.9 Hz, 1 H, 7-H), 7.43 (ddd, $^3J$ = 8.3, $^3J$ = 7.1, $^4J$ = 0.1 Hz, 1 H, Ar-H), 7.47–7.57 (m, 4 H), 7.65 (ddd, $^3J$ = 7.7, $^4J$ = 1.5, $^5J$ = 0.5 Hz, 1 H, Ar′-H), 8.16 (ddd, $^3J$ = 8.3, $^4J$ = 1.0, $^4J$ = 0.9 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 110.6 (+, C-Ar), 120.2 (+, C-Ar), 124.3 (+, C-Ar), 128.0 (+, C-Ar), 128.2 (+, C-Ar), 129.2 (+, C-Ar), 130.9 (+, C-Ar), 131.1 (quart, $C_q$), 131.2 (+, C-Ar), 134.2 (quart, $C_q$), 134.4 (quart, $C_q$), 145.6 (quart, 4-$NC_q$), ppm. MS ($C_{12}H_8ClN_3$) *m/z* (%RA): 229/231 (22/8) [$M^+$], 201/203 (45/16) [$M^+$–$N_2$, $C_{12}H_8ClN^+$], 166 (100) [$M^+$–$N_2$–Cl, $C_{12}H_8N^+$], 140 (21), 111/113 (19/7) [$M^+$–$C_6H_4N_3$, $C_6H_4Cl^+$], 75 (44), 50 (20).

**1-Isopropyl-5-trifluoromethyl-1*H*-benzotriazole (18ar).** Cleavage from **21** as described in the General Procedures



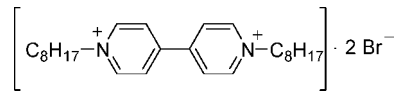
6a section. Purity: 83% (GC). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.75 (d, $^3J$ = 7.5 Hz, 6 H, 1′(3′)-H), 5.11 (sep, $^3J$ = 7.5 Hz, 1 H, 2′-H), 7.65–7.68 (m, 2 H, 6,7-H), 8.37 (br.s, 1 H, 4-H) ppm. GCMS ($C_{10}H_{10}F_3N_3$) *m/z* (%RA): 229 (30) [$M^+$], 210 (8) [$M^+$–F, $C_{10}H_{10}F_2N_3^+$], 200 (20) [$M^+$–$N_2$–H, $C_{10}H_9F_3N^+$], 186 (16), 166 (41), 159 (100) [$M^+$–$N_2$–$C_3H_6$, $C_7H_4F_3N^+$], 145 (66) [$C_7H_4F_3^+$], 140 (47), 138 (19), 132 (32), 125 (6), 117 (34), 108 (23), 100 (11), 94 (13), 88 (29), 75 (41), 69 (82), 63 (37).

**1-Propyl-5-trifluoromethyl-1*H*-benzotriazole (18as).** Cleav-



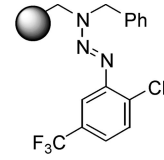
age from **22** as described in the General Procedures 6a section. Purity: 87% (GC). GCMS ($C_{10}H_{10}F_3N_3$) *m/z* (%RA): 229 (35) [$M^+$], 200 (41) [$M^+$–$N_2$–H, $C_{10}H_9F_3N^+$], 173 (48), 166 (24), 159 (100) [$M^+$–$N_2$–$C_3H_6$, $C_7H_4F_3N^+$], 156 (24), 145 (80) [$C_7H_4F_3^+$], 140 (40), 132 (31), 122 (20), 110 (22), 100 (29), 94 (23), 69 (84), 51 (26).

***N*,*N*-Dioctyl-4,4-bipyridinium dibromide (19).** 1.00 g



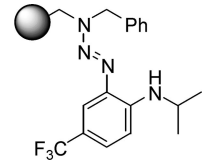
(6.28 mmol) of 4,4′-bipyridyl were solved in 100 mL of DMF, and then subsequently, 1.45 g (7.49 mmol, 1.19 equiv) of 1-bromoctane and 0.500 g (3.01 mmol, 0.480 equiv) of potassium iodide were added. The solution was heated to 100 °C and then allowed to cool down. The resulting dark solution of the catalyst (0.0628 mmol/mL) was used (diluted as necessary) for reduction reactions.

**[*N*-Benzyl-*N*-(2-chloro-5-(trifluoromethyl)phenyldiazenyl)aminomethyl]polystyrene (20).** Loading: 0.667



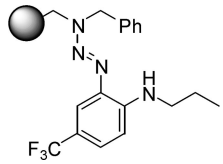
mmol/g.

**[*N*-Benzyl-*N*-{2-(isopropylamino)-5-trifluoromethylphenyldiazenyl}aminomethyl]polystyrene (21).** Prepara-



tion as described in the General Procedures 5a section from 2-chloro-5-trifluoromethyl resin (**20**) and *iso*-propyl amine (**9w**). The product resin is of brown color. Turnover: 83%.

**[*N*-Benzyl-*N*-{2-(propylamino)-5-trifluoromethylphenyldiazenyl}aminomethyl]polystyrene (22).** Preparation as described in the General Procedures 5a section from 2-chloro-5-trifluoromethyl resin (**20**) and *n*-propyl amine (**9ab**). The product resin is of brown color. Turnover: 87%.




**Acknowledgment.** Our work was supported by the Deutsche Forschungsgemeinschaft (BR1750-2, Graduiertenkolleg 804) and Fonds der Chemischen Industrie. We also thank Bayer CropScience AG for the donation of chemicals.

## References and Notes

(1) Wolfe, J. P.; Tomori, H.; Sadighi, J. P.; Yin, J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1158–1174.
(2) (a) For an early example of Hartwig–Buchwald reactions on solid supports, see: Ketcha, D. M.; Wilson, L. J.; Portlock, D. E. *Tetrahedron Lett.* **2000**, *41*, 6253–6257. (b) Further examples: Weigand, K.; Pelka, S. *Org. Lett.* **2002**, *4*, 4689–4692. (c) Further examples: Weigand, K.; Pelka, S. *Mol. Diversity* **2003**, *7*, 181–184.
(3) Lormann, M. E. P.; Walker, C. H.; Es-Sayed, M.; Bräse, S. *Chem. Commun.* **2002**, 1296–1297.
(4) Katritzky, A. R.; Lan, X.; Yang, J. Z.; Denisko, O. V *Chem. Rev.* **1998**, *98*, 409–548.
(5) A preliminary example has been presented in an account without any details: Bräse, S. *Acc. Chem. Res.* **2004**, *37*, 805–815.
(6) Merrifield resin (0.93 mmol/g) was obtained from Polymer Laboratories.
(7) Dahmen, S.; Bräse, S. In *Handbook of Combinatorial Chemistry*; Nicolaou, K. C., Hanko, R., Hartwig W., Eds.; VCH, Weinheim, 2002; Chapter 4.
(8) The haloarenes, amines, and anilines used are commercially available from Aldrich. For **2b** (giving rise to resin **4**): Kleiderer, E. C.; Adams, R. *J. Am. Chem. Soc.* **1933**, *55*, 4219–4225.
(9) All new nonpolymeric compounds were characterized by NMR, IR, MS, and HRMS. The purity was determined using GC, GC-MS, and NMR techniques. Polymeric compounds were characterized using IR and elemental analysis (CHN) (see the Experimental Procedures section).
(10) Zimmermann, V.; Avemaria, F.; Bräse, S. *J. Comb. Chem.* **2007**, *9*, 200–203.
(11) Wolfe, J. P.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 2413–2416.
(12) (a) Avemaria, F.; Zimmermann, V.; Bräse, S. *Synlett* **2004**, 1163–1166. (b) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem.* **2005**, *117*, 5320–5374. (c) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 5188–5240.
(13) Kaczmarek, L.; Luniewski, W.; Zagrodzki, B.; Godlewska, J.; Osiadacz, J.; Wietrzyk, J.; Opolski, A.; Peczynska-Czoch, W. *Acta Pol. Pharm.* **2002**, *59* (3), 199–207.
(14) Bartra, M.; Romea, P.; Urpí, F.; Vilarrasa, J. *Tetrahedron* **1990**, *46*, 587–594.
(15) Trimethylsilyl azide is a commercially available combustible liquid, which has no explosive properties. However, long contact to $CH_2Cl_2$ results in formation of highly explosive methylene azides. See ref 12b.
(16) Schoepff, M. *Chem. Calc.* **1890**, *23*, 1843.
(17) Borsche, W.; Feise, M. *Chem. Calc.* **1907**, *40*, 384.
(18) Kulagowski, J. J.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2725–2732.
(19) Lambert, P.-H.; Bertin, S.; Lacoste, J.-M.; Volland, J.-P.; Krick, A.; Furet, E.; Botrel, A.; Guenot, P. *J. Mass. Spectrom.* **1998**, *33*, 242–249.
(20) Lawson; Perkin; Robinson, *J. Chem. Soc. [London]* **1924**, 653.
(21) Holt, S. J.; Petrow, V. *J. Chem. Soc. [London]* **1948**, 922.
(22) Peczynska-Czoch, W.; Pognan, F.; Kaczmarek, L.; Boratynski, J. *J. Med. Chem.* **1994**, *37*, 3503–3510.

CC700105P