A Novel Method for the Synthesis of 2,3-Benzo-1,3a,6a-triazapentalenes through Pummerer-Type Reactions of γ-(Benzotriazol-1-yl)allylic Sulfoxides

Taehoon Kim,[a] Kyongtae Kim,*[a] and Yung Ja Park*[b]

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Treatment of 1-(arylmethyl)benzotriazoles **1** with *n*BuLi in THF at –78 °C, followed by addition of 1-aryl-2-chloroethanones, gave diastereomeric mixtures of 1-[(aryl)(benzotriazol-1-yl)methyl]oxiranes **2**. Treatment of **2** with *n*BuLi in THF at –78 °C, followed by acidification, afforded a mixture of (*E*)- and (*Z*)-allylic alcohols **3**, which were converted into 1,2-disubstituted 2-(alkyl- or aryl)-1-(benzotriazol-1-yl)-3-sulfanylpropenes **5** via the corresponding allylic chlorides **4**. Oxidation of sulfides **5** by *m*CPBA in CH_2Cl_2 at room temperature, followed by treatment with trifluoroacetic anhydride (TFAA) at room temperature, gave the title compounds in good yields. It was found that treatment of the title compounds with Raney-Ni in EtOH under hydrogen at reflux gave 2-(pyrazol-1-yl)aniline derivatives in excellent yields.

Introduction

Heteropentalenes belonging to class B in Ramsden's classification[1] have received considerable attention from the point of view of their electronic structure and potential synthetic utility.[2] This class of mesomeric betaines has basically been synthesized by two different methods. The first method, which has been most widely used, involves treatment of 1-(*o*-nitroaryl)pyrazoles[3] or 1-(*o*-nitroaryl)indazoles[4] with triethyl phosphite. Similarly, treatment of 2-benzoyl-2′-nitroazobenzene with triethylphosphite gave triazapentalenes.[5] The second method involves photolysis of 1-(*o*-azidoaryl)indazoles and pyrazoles.[4a,6] Thermally or photochemically generated free nitrenes or nitrenoid-like species may be involved as intermediates. In addition, alkylation of pyrazoles, followed by cyclodehydration with aqueous alkali,[7] and *N*-amination of 1-phenacylpyrazole with *o*-mesitylenesulfonylhydroxylamine[8] have been reported to give triazapentalenes.

In connection with our ongoing project exploring the potential utility of benzotriazole as a synthetic auxiliary,[9] thionium ions generated from benzotriazoles bearing tethered sulfoxides under Pummerer conditions were intended to be utilized as electrophiles, affording triazapentalenes. This should occur if internal trapping of the Pummerer thionium ion by the N-2 atom of the benzotriazole moiety takes place at the γ-position of an allyl sulfoxide, followed by application of Pummerer-type conditions.

[a] School of Chemistry and Molecular Engineering, Seoul National University,
Seoul 151-742, Korea
Fax: (internat.) + 82-2/874-8858
E-mail: kkim@plaza.snu.ac.kr
[b] Department of Chemistry, Sook Myung Women's University, Seoul 140-742, Korea

Results and Discussion

We prepared a diastereomeric mixture of [(aryl)(benzotriazol-1-yl)methyl]oxiranes **2** by treatment of 1-(arylmethyl)-benzotriazoles **1** with *n*BuLi in THF at −78 °C, followed by addition of 1-aryl-2-chloroethanones, and assigned the configurations of the stereocenters according to a reported procedure[9] (Scheme 1). Upon treatment of **2** with *n*BuLi (1.5 equiv.) in THF at −78 °C, followed by acidification, a mixture of (*E*)- and (*Z*)-allylic alcohols **3** was obtained. The mixture was separated by column chromatography. The stereochemistry of (*E*)- and (*Z*)-**3** was determined by NOE investigations. For example, compound (*E*)-**3g** (Ar = 4-FC_6H_4, R^1 = 2,5-$Me_2C_6H_3$), with a singlet at δ = 4.63 (600 MHz, $CDCl_3$) assignable to the allylic protons, displayed NOE effects between two *ortho* protons (δ = 7.45−7.47) of the 4-FC_6H_4 group and one *ortho* proton (δ = 6.93) of the 2,5-$Me_2C_6H_3$ group, whereas compound (*Z*)-**3g** had NOE effects arising from the allylic protons (δ = 4.19) and a single *ortho* proton (δ = 7.11) of the 2,5-$Me_2C_6H_3$ group. Similar NOE effects were observed for the other allylic alcohols (*E*)- and (*Z*)-**3**. Consequently, one can readily determine the ratio of (*E*)- and (*Z*)-**3** from the chemical shifts of the allylic protons of **3**, without separation of the stereoisomers. The allylic alcohols were converted into allylic chlorides **4** with $SOCl_2$ (3 equiv.) in THF at room temperature.

Unexpectedly, the conversion of **3** into **4** was accompanied by isomerization, and so their ratio in a mixture of (*E*)- and (*Z*)-**4** would be different from that in a mixture of the

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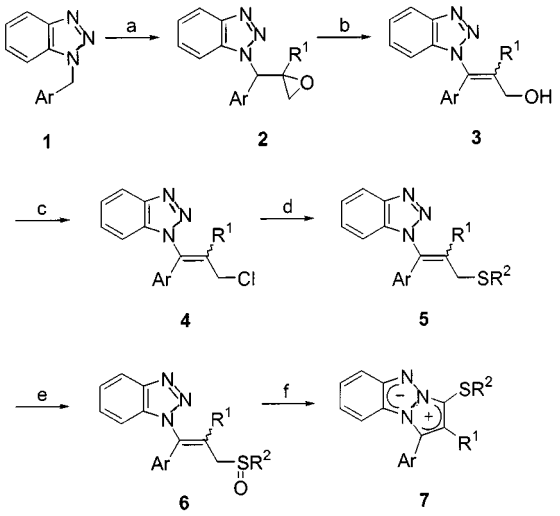


Scheme 1. Synthesis of 2,3-benzo-1,3a,6a-triazapentalenes **7**: a) ref.[9]; b) *n*BuLi, THF, −78 °C, 0.5 h; c) $SOCl_2$, THF, 25 °C, 1 h; d) R^2SH, NaOEt, THF, 25 °C, 5 h; e) *m*-CPBA, CH_2Cl_2, 25 °C, 10 min; f) TFAA, THF, 25 °C, 1 h

corresponding stereoisomer **3**. The chlorides **4** were converted into sulfides **5** by treatment with thiols (5 equiv.) in the presence of NaOEt in THF at room temperature. The stereochemistry of **4** was retained during the formation of **5**. The *m*CPBA-mediated (1 equiv.) oxidation of a mixture of (*E*)- and (*Z*)-**5** gave a mixture of (*E*)- and (*Z*)-sulfoxides **6**, which were separable by chromatography. The stereochemistry was judged with the aid of the ^1H NMR spectra of compounds **6** prepared from pure (*E*)-**5** and from pure (*Z*)-**5** to be retained during these oxidations. The ratios of the stereoisomers of compounds **2**−**6** were determined on the basis of the allylic proton absorptions, in which (*E*) isomers showed absorptions downfield from those of (*Z*) isomers. Yields of compounds **2**−**6** and the ratios of the stereoisomers of each compound are summarized in Table 1.

Treatment of compounds **6**, irrespective of their stereochemistry, with trifluoroacetic anhydride (TFAA) (5 equiv.) in THF for 1 h at room temperature gave triazapentalenes **7** in good yields (Table 2).

Table 2. Yields of triazapentalenes **7**

Product	Ar	R^1	R^2	Yield [%][a]
7a	Ph	Ph	Ph	85
7b	Ph	4-MeC_6H_4	Ph	79
7c	Ph	*t*Bu	Ph	88
7d	Ph	Ph	CH_2CH_2OH	34
7e	4-FC_6H_4	Ph	Ph	82
7f	4-FC_6H_4	Me	Ph	79
7g	4-FC_6H_4	2,5-$Me_2C_6H_3$	Ph	82
7h	4-FC_6H_4	2,5-$Me_2C_6H_3$	4-$MeOC_6H_4$	76
7i	4-FC_6H_4	Me	*n*Pr	85
7j	4-$MeOC_6H_4$	Ph	Ph	91
7k	4-$MeOC_6H_4$	4-MeC_6H_4	Ph	80

[a] Isolated yields.

The structures of compounds **7** were determined from spectroscopic and analytical data. In particular, the ^1H and ^{13}C NMR spectroscopic data were informative regarding the structures of **7**, since compounds **7a**, **7e**, and **7j** do not exhibit any ^1H NMR absorptions corresponding to aliphatic protons or ^{13}C NMR absorptions at fields above δ = 100, indicating the absence of even a quaternary carbon atom.[10] These spectroscopic properties, coupled with the X-ray single-crystal structure of **7f**, clearly indicate that compounds **7** have planar triazapentalene skeletons (Fig-

Table 1. Yields of products **2**−**6** and ratios of the stereoisomers

Product	Ar	R^1	R^2	Yield (%)[a]				
				2 (*R*,*R*)/(*S*,*S*); (*R*,*S*)/(*S*,*R*)	**3** (*E*)/(*Z*)	**4** (*E*)/(*Z*)	**5** (*E*)/(*Z*)	**6** (*E*)/(*Z*)
a	Ph	Ph	Ph	50 (2.22:1)	87 (1.84:1)	86 (3.11:1)	71 (2.98:1)	88 (3.05:1)
b	Ph	4-MeC_6H_4	Ph	28 (1.48:1)	80 (1.31:1)	83 (2.51:1)	67 (2.46:1)	85 (2.38:1)
c	Ph	*t*Bu	Ph	23[b]	75[c]	87 (1.57:1)	70 (1.54:1)	86 (1.48:1)
d	Ph	Ph	CH_2CH_2OH	50 (2.22:1)	87 (1.84:1)	86 (3.11:1)	86[d]	90[e]
e	4-FC_6H_4	Ph	Ph	37 (1.22:1)	84 (1.19:1)	87 (4.84:1)[f]	83 (5.54:1)	92 (5.42:1)
f	4-FC_6H_4	Me	Ph	55 (1.17:1)	75 (1.41:1)	78 (7.05:1)	81 (7.00:1)	91 (6.94:1)
g	4-FC_6H_4	2,5-$Me_2C_6H_3$	Ph	42 (1.09:1)	85 (1.18:1)	91 (2.78:1)[g]	82 (2.81:1)	62 (2.71:1)
h	4-FC_6H_4	2,5-$Me_2C_6H_3$	4-$MeOC_6H_4$	42 (1.09:1)	85 (1.18:1)	91 (2.78:1)	69 (1.12:1)[h]	86 (1.02:1)
i	4-FC_6H_4	Me	*n*Pr	55 (1.17:1)	75 (1.41:1)	79 (5.19:1)[i]	64 (5.41:1)	89[j]
j	4-$MeOC_6H_4$	Ph	Ph	50 (1.31:1)	83[k]	84 (1:1.88)	89 (1:1.91)	94 (1:1.85)
k	4-$MeOC_6H_4$	4-MeC_6H_4	Ph	61 (1.48:1)	90[l]	84 (1:2.04)	69 (1:2.06)	93 (1:2.02)

[a] Isolated yields. The ratios of the stereoisomers were determined from the ^1H NMR (300 MHz, $CDCl_3$) spectroscopic data. Each compound was prepared from the precursor, the ratio of stereoisomers of which was specified otherwise stated. [b] Yield of (*R*,*R*)-**2c**. (*R*,*S*)-**2c**: negligible on the basis of the ^1H NMR spectrum. [c] Yield of (*E*)-**3c**. [d] Yield of (*E*)-**5d** obtained from treatment of pure (*E*)-**4d**. [e] Yield of (*E*)-**6d** obtained from treatment of pure (*E*)-**5d**. [f] The (*E*)/(*Z*) ratio was obtained from treatment of **3e** [(*E*)/(*Z*) = 0.96:1], recovered from the repeated chromatography of **3e** [(*E*)/(*Z*) = 1.19:1] for the separation of the stereoisomers. [g] The (*E*)/(*Z*) ratio was obtained from treatment of pure (*E*)-**3g**. [h] The (*E*)/(*Z*) ratio was obtained from treatment of **4h** [(*E*)/(*Z*) = 1.14:1], recovered from the repeated chromatography of **4h** [(*E*)/(*Z*) = 2.78:1]. [i] The (*E*)/(*Z*) ratio was obtained from treatment of **3i** [(*E*)/(*Z*) = 0.84:1], recovered from the repeated chromatography of **3i** [(*E*)/(*Z*) = 1.41:1]. [j] Yield of (*E*)-**6i** obtained from treatment of pure (*E*)-**5i**. [k] Yield of (*Z*)-**3j** obtained from treatment of pure (*R*,*S*)-**2j**. [l] Yield of (*Z*)-**3k** obtained from treatment of pure (*R*,*S*)-**2k**.

ure 1). The X-ray crystal structure of **7f**[11] shows that the N1−N2 and N2−N3 bond lengths are 1.3775(58) and 1.3417(59) Å, respectively, values which are close to each other. In addition, the C7−C8 and C8−C10 bond lengths are 1.3801(71) and 1.3993(77) Å, respectively, indicating the absence of a localized double bond.

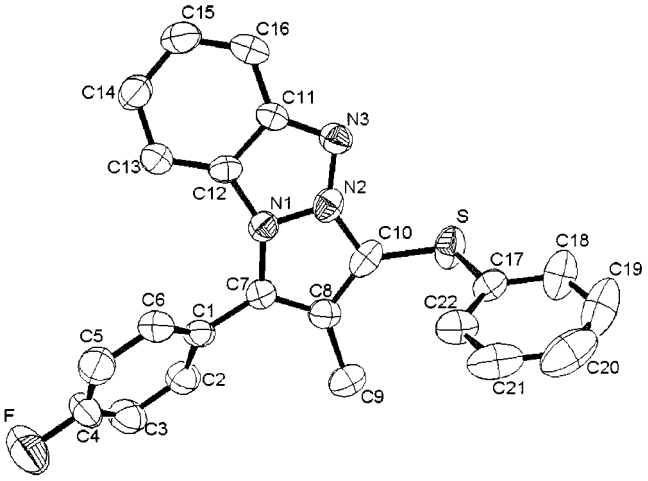
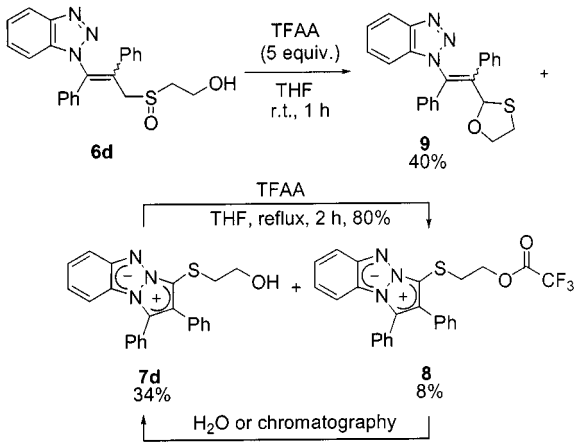


Figure 1. ORTEP drawing of the molecular structure of **7f**; the thermal ellipsoids are set at the 50% probability level; the hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: N1−C7 1.3807(65), C7−C8 1.3801(71), C8−C10 1.3993(77), N2−C10 1.3673(69), N1−N2 1.3775(58), N2−N3 1.3417(59); C12−N1−N2 105.85(0.39), N1−N2−N3 113.64(0.39), N2−N3−C11 103.46(0.39), C7−N1−N2 108.88(0.39), N1−N2−C10 108.22(0.44), N1−C7−C8 107.08(0.43), C7−C8−C10 108.23(0.46), C8−C10−N2 107.57(0.47), C9−C8−C10 124.20(0.53), N2−C10−S 119.60(0.45), C8−C10−S 132.83(0.42), C1−C7−C8 131.23(0.47), C7−C8−C9 127.43(0.52)

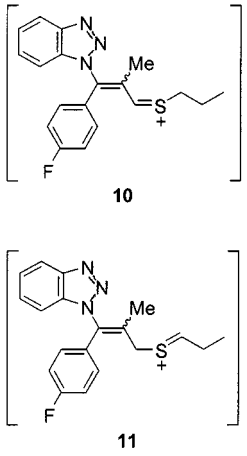
Apart from the cases of compounds **6** bearing an alkyl- or arylthio group, treatment of (*E*)-**6d** (Ar = R^1 = Ph, R^2 = CH_2CH_2OH) with TFAA under the same conditions gave a mixture exhibiting two spots (R_f = 0.58, 0.47; EtOAc/*n*-hexane, 1:5) on TLC. However, the spot with the higher R_f value slowly faded out concomitantly with the appearance of a new spot (R_f = 0.18). Chromatography (silica gel, 70−230 mesh; EtOAc/*n*-hexane, 1:5) of the reaction mixture gave three compounds. The first was a small amount of an unknown compound (R_f = 0.58), subsequently identified as trifluoroacetate **8** (8%) (Scheme 2), showing an IR (neat) band at 1777 cm^{-1} (C=O) and ^{13}C NMR (75 MHz, $CDCl_3$) absorptions at δ = 157.4 (C=O, J_{C-CF3} = 42.1 Hz, quadruplet), and a quadruplet at δ = 114.6 (CF_3, J_{C-F} = 282.4 Hz). The ^{19}F NMR spectrum (470 MHz, $CDCl_3$) showed an absorption at δ = −75.4. Compound **7d** (R_f = 0.18) and (*E*)-**9** (R_f = 0.47) were also isolated, in 34 and 40% yields, respectively. Treatment of **7d** with TFAA in THF at reflux gave compound **8**. Compound **9** is believed to be competitively formed by an alternative intramolecular trapping of a hydroxy group by 2-hydroxyethylthionium ion.

Treatment of **6i** (Ar = 4-FC_6H_4, R^1 = Me, R^2 = *n*Pr) under the same conditions gave only a single mesomeric betaine **7i** (85%). This result indicates that the loss of a proton to give a thionium ion occurs regioselectively in favor

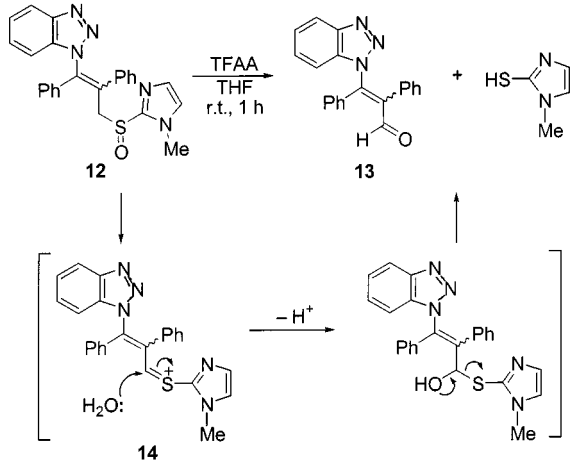


Scheme 2. Reaction of **6d** with TFAA

of a more stable conjugated thionium ion **10** rather than a nonconjugated ion **11**.



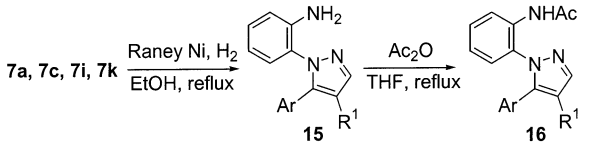
Interestingly, treatment of sulfoxide **12** [(*E*)/(*Z*) = 2.78:1] (Scheme 3), prepared in three steps from **4a** and 1-methyl-2-mercaptoimidazole, under the same conditions gave aldehyde **13** [(*E*)/(*Z*) = 1.56:1] in 70% yield. The formation of **13** may be explained by hydrolysis of the thionium interme-



Scheme 3. Synthesis of β-(benzotriazol-1-yl)allylic aldehyde **13**

diate **14**, which rapidly undergoes hydrolysis rather than intramolecular cyclization, yielding **13** when the hetarylthio group acts as a good stable leaving group.

In order to remove the alkyl- or arylthio groups from **7**, selected compounds **7a**, **7c**, **7i**, and **7k** were treated with Raney-Ni in EtOH under hydrogen at reflux[12] (Scheme 4). However, reductive ring-cleavage occurred to give the corresponding 2-(4,5-disubstituted pyrazol-1-yl)anilines **15a**, **15c**, **15i**, and **15k** in excellent yields.



Scheme 4. Synthesis of 2-(pyrazol-1-yl)aniline derivatives **16**

Compounds **15a**, **15c**, **15i**, and **15k** were viscous liquids and were converted into the corresponding acetamido derivatives **16** for analysis. Yields of **15** and **16**, together with reaction times yielding **15**, are summarized in Table 3.

Table 3. Yields of products **15** and **16**

Starting compound **7**	Ar	R^1	R^2	Time [h]	Products yield [%][a] **15**	**16**
a	Ph	Ph	Ph	15[b]	89	94
c	Ph	*t*Bu	Ph	3	86	91
i	4-FC_6H_4	Me	*n*Pr	5	89	95
k	4-$MeOC_6H_4$	4-MeC_6H_4	Ph	3	92	92

Solvent: THF.

Conclusions

A novel method has been developed for the synthesis of triazapentalene derivatives by treatment of γ-(benzotriazol-1-yl)allylic sulfoxides with trifluoroacetic anhydride in THF at room temperature Mesomeric betaines bearing alkyl- or arylthio groups have been found to be good precursors for 2-(4,5-disubstituted pyrazol-1-yl)anilines, which were previously difficult to obtain.

Experimental Section

General: The ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$ solution containing Me_4Si as an internal standard, with a Bruker-Spectrospin spectrometer. Complete assignment was achieved by NOE and 2D NMR correlation experiments. The ^{19}F NMR spectra were recorded at 470 MHz in $CDCl_3$ solution containing $CFCl_3$ as an external standard. IR spectra were obtained in KBr or as thin films on KBr plates with a Shimadzu IR-470 infrared spectrophotometer. All reactions were monitored for completion by thin layer chromatography (TLC), which was performed on precoated silica gel plates (Merck 60 F_{254}) and detection was achieved with the aid of UV light. Column chromatography was performed on silica gel (70−230 mesh) with EtOAc/*n*-hexane solvent mixtures. Melting points were measured with a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were carried out by the Korea Basic Science Institute. For the synthesis of the 1-(alkyl or aryl)-1-[(aryl)(benzotriazol-1-yl)methyl]oxiranes **2**, see ref.[9]

General Procedure for the Synthesis of 3: *n*BuLi (0.39−0.92 mmol) was added at −78 °C to a solution of **2** (0.26−0.61 mmol) in THF (30 mL). The mixture was stirred for 30 min, followed by addition of 0.1 N HCl (50 mL), and extracted with CH_2Cl_2 (30 mL × 3). The extracts were dried with $MgSO_4$. Removal of the solvent in vacuo gave a residue, which was chromatographed on a silica gel column (3 × 10 cm; EtOAc/*n*-hexane, 1:1) to give compound **3**.

(*E*)-3-(Benzotriazol-1-yl)-2,3-diphenyl-2-propenol {(*E*)-3a [or (*E*)-3d]}: M.p. 148−150 °C (MeOH). IR (KBr): ṽ = 3340, 3048, 2920, 1478, 1440, 1232, 1073, 1020, 761, 740, 705 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.10 (br. s, 1 H, CH_2OH), 4.76 (d, *J* = 6.1 Hz, 2 H, CH_2OH), 7.05−7.12 (m, 6 H, ArH), 7.20−7.31 (m, 2 H, ArH), 7.35−7.43 (m, 5 H, ArH), 7.90 (d, *J* = 7.6 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 64.1, 110.7, 120.2, 124.2, 128.1, 128.3, 128.6, 129.0, 129.2, 129.3, 130.0, 133.7, 134.7, 135.7, 137.2, 140.5, 145.7. $C_{21}H_{17}N_3O$ (327.38): calcd. C 77.04, H 5.23, N 12.84; found C 77.10, H 5.13, N 12.91.

(*Z*)-3-(Benzotriazol-1-yl)-2,3-diphenyl-2-propenol {(*Z*)-3a [or (*Z*)-3d]}: M.p. 151−153 °C (MeOH). IR (KBr): ṽ = 3312, 3048, 2896, 1480, 1441, 1265, 1097, 1076, 740, 694 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.89 (br. s, 1 H, CH_2OH), 4.26 (d, *J* = 7.2 Hz, 2 H, CH_2OH), 6.88−6.93 (m, 3 H, ArH), 7.11−7.40 (m, 10 H, ArH), 8.12 (d, *J* = 7.9 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 64.3, 111.7, 120.6, 124.9, 128.4, 128.6, 128.8, 129.0, 129.2, 129.3, 130.1, 133.5, 134.6, 135.0, 138.5, 140.8, 146.3. $C_{21}H_{17}N_3O$ (327.38): calcd. C 77.04, H 5.23, N 12.84; found C 77.08, H 5.10, N 12.88.

3-(Benzotriazol-1-yl)-3-phenyl-2-(4-tolyl)-2-propenol (3b): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1.31:1. IR (neat): ṽ = 3360, 3040, 2912, 1601, 1483, 1441, 1377, 1267, 1232, 1152, 1062, 1022, 816, 742, 699 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.19 (s, 3 H, CH_3, *E*), 2.33 (s, 3 H, CH_3, *Z*), 2.34 (s, 1 H, CH_2OH, *E*), 2.86 (t, *J* = 7.1 Hz, 1 H, CH_2OH, *Z*), 4.25 (d, *J* = 7.1 Hz, 2 H, CH_2OH, *Z*), 4.78 (s, 2 H, CH_2OH, *E*), 6.81−7.50 (m, 12 H, ArH, *E* and *Z*), 7.95 (d, *J* = 7.2 Hz, 1 H, ArH, *E*), 8.13 (d, *J* = 7.9 Hz, 1 H, ArH, *Z*).

3-(Benzotriazol-1-yl)-2-(*tert*-butyl)-3-phenyl-2-propenol [(*E*)-3c]: M.p. 153−155 °C (MeOH). IR (KBr): ṽ = 3312, 3048, 2950, 1595, 1480, 1435, 1363, 1265, 1230, 1080, 741, 691 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.03 [s, 9 H, $C(CH_3)_3$], 2.31 (s, 1 H, CH_2OH), 4.37 (s, 2 H, CH_2OH), 7.19−7.42 (m, 8 H, ArH), 8.03 (d, *J* = 7.6 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 30.5, 37.5, 62.2, 111.1, 120.1, 124.4, 128.3, 128.9, 129.2, 129.3, 134.4, 135.2, 137.8, 146.1, 150.0. $C_{19}H_{21}N_3O$ (307.39): calcd. C 74.24, H 6.89, N 13.67; found C 74.31, H 6.91, N 13.59.

3-(Benzotriazol-1-yl)-3-(4-fluorophenyl)-2-phenyl-2-propenol (3e): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1.19:1. IR (neat): ṽ = 3360, 3048, 2920, 1600, 1511, 1448, 1370, 1265, 1231, 1079, 746, 694 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.77 (t, *J* = 5.7 Hz, 1 H, CH_2OH, *E*), 2.96 (t, *J* = 7.0 Hz, 1 H, CH_2OH, *Z*), 4.23 (d, *J* = 6.9 Hz, 2 H, CH_2OH, *Z*), 4.73 (d, *J* = 5.4 Hz, 2 H, CH_2OH, *E*), 6.73−7.51 (m, 12 H, ArH, *E* and *Z*), 7.89 (d, *J* = 8.0 Hz, 1 H, ArH, *E*), 8.05−8.14 (m, 1 H, ArH, *Z*).

3-(Benzotriazol-1-yl)-3-(4-fluorophenyl)-2-methyl-2-propenol [3f (or 3i)]: Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1.41:1. IR (neat): ṽ = 3368,

3042, 2912, 1595, 1505, 1441, 1371, 1267, 1227, 1156, 1089, 1008, 904, 745, 520 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.82 (s, 3 H, CH_3, *E*), 2.21 (s, 3 H, CH_3, *Z*), 3.07 (s, 1 H, CH_2OH, *E*), 3.10 (s, 1 H, CH_2OH, *Z*), 3.93 (s, 2 H, CH_2OH, *Z*), 4.46 (s, 2 H, CH_2OH, *E*), 6.88−7.45 (m, 7 H, ArH, *E* and *Z*), 8.04−8.12 (m, 1 H, ArH, *E* and *Z*).

3-(Benzotriazol-1-yl)-2-(2,5-dimethylphenyl)-3-(4-fluorophenyl)-2-propenol [3g (or 3h)]: Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1.18:1. IR (neat): $\tilde{\nu}$ = 3360, 3040, 2920, 1593, 1497, 1443, 1374, 1265, 1225, 1155, 841, 740, 526 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.12 (s, 3 H, CH_3, *E*), 2.20 (s, 3 H, CH_3, *Z*), 2.22 (s, 3 H, CH_3, *E*), 2.33 (t, *J* = 5.8 Hz, 1 H, CH_2OH, *E*), 2.34 (s, 3 H, CH_3, *Z*), 2.87 (t, *J* = 7.2 Hz, 1 H, CH_2OH, *Z*), 4.09−4.24 (m, 2 H, CH_2OH, *Z*), 4.48−4.68 (m, 2 H, CH_2OH, *E*), 6.72−7.53 (m, 10 H, ArH, *E* and *Z*), 7.86 (d, *J* = 8.2 Hz, 1 H, ArH, *E*), 8.12−8.19 (m, 1 H, ArH, *Z*).

3-(Benzotriazol-1-yl)-3-(4-methoxyphenyl)-2-phenyl-2-propenol (3j): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1.19:1. IR (neat): $\tilde{\nu}$ = 3362, 3024, 2912, 1601, 1503, 1444, 1370, 1230, 1065, 756, 526 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.62 (s, 1 H, CH_2OH, *E*), 3.01 (s, 1 H, CH_2OH, *Z*), 3.72 (s, 3 H, OCH_3, *Z*), 3.80 (s, 3 H, OCH_3, *E*), 4.22 (s, 2 H, CH_2OH, *Z*), 4.75 (s, 2 H, CH_2OH, *E*), 6.54−7.47 (m, 12 H, ArH, *E* and *Z*), 7.89 (d, *J* = 7.6 Hz, 1 H, ArH, *E*), 8.12 (d, J = 7.92, 1 H, ArH, *Z*).

(*Z*)-3-(Benzotriazol-1-yl)-3-(4-methoxyphenyl)-2-(4-tolyl)-2-propenol [(*Z*)-3k]: M.p. 156−158 °C (MeOH). IR (KBr): $\tilde{\nu}$ = 3368, 3042, 2920, 1595, 1499, 1441, 1374, 1236, 1081, 748, 520 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.33 (s, 3 H, CH_3), 2.86 (t, *J* = 6.96 Hz, 1 H, CH_2OH), 3.71 (s, 3 H, OCH_3), 4.20 (d, *J* = 6.8 Hz, 2 H, CH_2OH), 6.63 (d, *J* = 7.8 Hz, 2 H, ArH), 6.84 (d, *J* = 7.2 Hz, 2 H, ArH), 6.94 (d, *J* = 7.1 Hz, 1 H, ArH), 7.11 (d, *J* = 8.0 Hz, 2 H, ArH), 7.24 (d, *J* = 8.1 Hz, 2 H, ArH), 8.06−8.13 (m, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 21.6, 55.5, 64.2, 111.8, 114.2, 120.5, 124.7, 127.5, 128.4, 129.8, 130.0, 131.5, 133.6, 133.8, 135.6, 138.0, 139.4, 146.3, 160.1. $C_{22}H_{18}FN_3O$ (359.40): calcd. C 73.52, H 5.05, N 11.69; found C 73.45, H 5.01, N 11.77.

General Procedure for the Synthesis of 4: $SOCl_2$ (0.60−1.59 mmol) was added at room temperature to a solution of **3** (0.20−0.53 mmol) in THF (30 mL). The mixture was stirred for 1 h, followed by addition of water (50 mL) and extraction with CH_2Cl_2 (30 mL × 3). The extracts were dried with $MgSO_4$. Removal of the solvent in vacuo gave a residue, which was chromatographed on a silica gel column (3 × 10 cm; EtOAc/*n*-hexane, 1:5) to give compound **4**.

(*E*)-1-(3-Chloro-1,2-diphenylpropenyl)-1*H*-benzotriazole {(*E*)-4a [or (*E*)-4d]}: M.p. 137−139 °C (MeOH). IR (KBr): $\tilde{\nu}$ = 3048, 2910, 1480, 1436, 1376, 1259, 1038, 760, 739, 692 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 4.63 (s, 2 H, CH_2Cl), 6.98−7.42 (m, 13 H, ArH), 7.85 (d, *J* = 7.1, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 46.6, 110.6, 120.3, 124.3, 128.1, 128.3, 128.8, 128.9, 129.0, 129.5, 130.4, 133.6, 135.4, 135.8, 136.7, 137.6, 145.8. $C_{21}H_{16}ClN_3$ (345.82): calcd. C 72.93, H 4.66, N 12.15; found C 72.85, H 4.73, N 12.05.

(*Z*)-1-(3-Chloro-1,2-diphenylpropenyl)-1*H*-benzotriazole {(*Z*)-4a [or (*Z*)-4d]}: M.p. 142−144 °C (MeOH). IR (KBr): $\tilde{\nu}$ = 3048, 2928, 1478, 1438, 1377, 1270, 1048, 756, 745, 699 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 4.26 (s, 2 H, CH_2Cl), 6.83−7.35 (m, 13 H, ArH), 8.03−8.12 (m, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 45.2, 111.2, 120.5, 124.8, 126.3, 128.6, 128.7, 128.9, 129.0, 129.1, 129.4, 129.8, 130.0, 135.3, 137.7, 138.2, 146.2. $C_{21}H_{16}ClN_3$ (345.82): calcd. C 72.93, H 4.66, N 12.15; found C 72.87, H 4.77, N 12.13.

1-[3-Chloro-1-phenyl-2-(4-tolyl)propenyl]-1*H*-benzotriazole (4b): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 2.51:1. IR (neat): $\tilde{\nu}$ = 3040, 2920, 1479, 1440, 1375, 1252, 1040, 756, 696 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.20 (s, 3 H, CH_3, *E*), 2.36 (s, 3 H, CH_3, *Z*), 4.32 (s, 2 H, CH_2Cl, *Z*), 4.72 (s, 2 H, CH_2Cl, *E*), 6.77−7.60 (m, 12 H, ArH, *E* and *Z*), 7.97 (d, *J* = 7.1 Hz, 1 H, ArH, *E*), 8.13 −8.21 (m, 1 H, ArH, *Z*).

1-(2-Chloromethyl-3,3-dimethyl-1-phenylbut-1-enyl)-1*H*-benzotriazole (4c): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1.57:1. IR (neat): $\tilde{\nu}$ = 3048, 2928, 1477, 1438, 1377, 1238, 1038, 760, 691 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.09 [s, 9 H, $C(CH_3)_3$, *E*], 1.28 [s, 9 H, $C(CH_3)_3$, *Z*], 4.04 (s, 2 H, CH_2Cl, *Z*), 4.28 (s, 2 H, CH_2Cl, *E*), 7.26−7.55 (m, 8 H, ArH, *E* and *Z*), 8.01−8.10 (m, 1 H, ArH, *E* and *Z*).

1-[3-Chloro-1-(4-fluorophenyl)-2-phenylpropenyl]-1*H*-benzotriazole (4e): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 4.84:1. IR (neat): $\tilde{\nu}$ = 3048, 2912, 1488, 1436, 1377, 1240, 1052, 742, 699, 521 cm^{-1}. *E*/*Z* ($CDCl_3$) = 4.84:1. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 4.33 (s, 2 H, CH_2Cl, *Z*), 4.69 (s, 2 H, CH_2Cl, *E*), 6.73−7.54 (m, 12 H, ArH, *E* and *Z*), 7.95 (d, *J* = 8.1 Hz, 1 H, ArH, *E*), 8.12−8.19 (m, 1 H, ArH, *Z*).

1-[3-Chloro-1-(4-fluorophenyl)-2-methylpropenyl]-1*H*-benzotriazole 4f (or 4i): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 7.05:1. IR (neat): $\tilde{\nu}$ = 3044, 2920, 1480, 1441, 1370, 1265, 1081, 760, 694, 516 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.87 (s, 3 H, CH_3, *E*), 2.23 (s, 3 H, CH_3, *Z*), 4.03 (s, 2 H, CH_2Cl, *Z*), 4.32 (s, 2 H, CH_2Cl, *E*), 6.98−7.47 (m, 7 H, ArH, *E* and *Z*), 8.07−8.16 (m, 1 H, ArH, *E* and *Z*).

1-[3-Chloro-1-(4-fluorophenyl)-2-(2,5-dimethylphenyl)propenyl]-1*H*-benzotriazole [4g (or 4h)]: Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 2.78:1. IR (neat): $\tilde{\nu}$ = 3040, 2928, 1501, 1477, 1368, 1268, 1077, 756, 691 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.18 (s, 3 H, CH_3, *E*), 2.19 (s, 3 H, CH_3, *E*), 2.25 (s, 3 H, CH_3, *Z*), 2.39 (s, 3 H, CH_3, *Z*), 4.11 (d, *J* = 11.4 Hz, 1 H of CH_2Cl, *Z*), 4.36 (d, *J* = 11.4 Hz, 1 H of CH_2Cl, *Z*), 4.57 (d, *J* = 11.0 Hz, 1 H of CH_2Cl, *E*), 4.65 (d, *J* = 11.0 Hz, 1 H of CH_2Cl, *E*), 6.67−7.64 (m, 10 H, ArH, *E* and *Z*), 7.91 (d, *J* = 7.9 Hz, 1 H, ArH, *E*), 8.13−8.21 (m, 1 H, ArH, *Z*).

1-[3-Chloro-1-(4-methoxyphenyl)-2-phenylpropenyl]-1*H*-benzotriazole (4j): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1:1.88. IR (neat): $\tilde{\nu}$ = 3048, 2912, 1511, 1444, 1388, 1236, 1046, 745, 696 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 3.68 (s, 3 H, OCH_3, *Z*), 3.82 (s, 3 H, OCH_3, *E*), 4.30 (s, 2 H, CH_2Cl, *Z*), 4.73 (s, 2 H, CH_2Cl, *E*), 6.52−7.49 (m, 12 H, ArH, *E* and *Z*), 7.90 (d, *J* = 7.4 Hz, 1 H, ArH, *E*), 8.10−8.17 (m, 1 H, ArH, *Z*).

1-[3-Chloro-1-(4-methoxyphenyl)-2-(4-tolyl)propenyl]-1*H*-benzotriazole (4k): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1:2.04. IR (neat): $\tilde{\nu}$ = 3048, 2920, 1512, 1442, 1370, 1254, 1038, 926, 742, 691 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.18 (s, 3 H, CH_3, *E*), 2.36 (s, 3 H, CH_3, *Z*), 3.70 (s, 3 H, OCH_3, *Z*), 3.84 (s, 3 H, OCH_3, *E*), 4.29 (s, 2 H, CH_2Cl, *Z*), 4.73 (s, 2 H, CH_2Cl, *E*), 6.57−7.48 (m, 11 H, ArH, *E* and *Z*), 7.95 (d, *J* = 8.1 Hz, 1 H, ArH, *E*), 8.09−8.17 (m, 1 H, ArH, *Z*).

General Procedure for the Synthesis of 5: Sodium (0.51−1.38 mmol) was placed in absolute EtOH (15 mL), followed by addition of thiol (0.51−1.38 mmol). The mixture was stirred for 5 min, followed by

addition of a solution of **4** (0.17−0.46 mmol) in THF (30 mL) at room temperature. The mixture was additionally stirred for 2−5 h, followed by addition of water (50 mL) and extraction with CH_2Cl_2 (30 mL × 3). The extracts were dried with $MgSO_4$. Removal of the solvent in vacuo gave a residue, which was chromatographed on a silica gel column (3 × 10 cm; EtOAc/*n*-hexane, 1:5) to give compound **5**.

(*E*)-1-[1,2-Diphenyl-3-(phenylsulfanyl)propenyl]-1*H*-benzotriazole [(*E*)-5a]: M.p. 136−138 °C (MeOH). IR (KBr): $\tilde{\nu}$ = 3048, 2910, 1473, 1436, 1374, 1152, 1084, 736, 696 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 4.26 (s, 2 H, CH_2S), 7.04−7.41 (m, 18 H, ArH), 7.91 (d, *J* = 8.1 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 40.3, 110.6, 120.2, 124.2, 127.4, 128.5, 128.6, 128.7, 128.9, 129.1, 129.2, 129.5, 129.8, 130.6, 131.4, 133.7, 135.8, 135.9, 137.8, 138.5, 145.6. $C_{27}H_{21}N_3S$ (419.54): calcd. C 77.30, H 5.05, N 10.02, S, 7.64; found C 77.19, H 5.11, N 10.08, S, 7.61.

(*Z*)-1-[1,2-Diphenyl-3-(phenylsulfanyl)propenyl]-1*H*-benzotriazole [(*Z*)-5a]: M.p. 175−178 °C (CH_2Cl_2/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3040, 2915, 1472, 1435, 1377, 1268, 1212, 1049, 755, 692 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 3.90 (s, 2 H, CH_2S), 6.78−7.38 (m, 18 H, ArH), 7.98−8.03 (m, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 40.2, 111.4, 120.3, 124.5, 127.2, 128.3, 128.5, 128.6, 128.8, 129.0, 129.1, 130.0, 131.4, 133.9, 135.8, 136.0, 138.7, 139.1, 146.2 (signals of two aromatic C atoms not visible). $C_{27}H_{21}N_3S$ (419.54): calcd. C 77.30, H 5.05, N 10.02, S 7.64; found C 77.24, H 5.12, N 10.10, S 7.69.

1-[1-Phenyl-3-phenylsulfanyl-2-(4-tolyl)propenyl]-1*H*-benzotriazole (5b): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 2.46:1. IR (neat): $\tilde{\nu}$ = 3042, 2920, 1480, 1433, 1382, 1245, 1087, 744, 691 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.18 (s, 3 H, CH_3, *E*), 2.34 (s, 3 H, CH_3, *Z*), 3.96 (s, 2 H, CH_2S, *Z*), 4.29 (s, 2 H, CH_2S, *E*), 6.83−7.49 (m, 17 H, ArH, *E* and *Z*), 7.95 (d, *J* = 7.3 Hz, 1 H, ArH, *E*), 8.09 (d, *J* = 7.2 Hz, 1 H, ArH, *Z*).

1-[3,3-Dimethyl-1-phenyl-2-(phenylsulfanylmethyl)but-1-enyl]-1*H*-benzotriazole (5c): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1.54:1. IR (neat): $\tilde{\nu}$ = 3048, 2912, 1475, 1435, 1376, 1250, 1226, 1154, 1072, 746, 694 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.10 [s, 9 H, $C(CH_3)_3$, *E*], 1.27 [s, 9 H, $C(CH_3)_3$, *Z*], 3.68 (s, 2 H, CH_2S, *Z*), 3.89 (s, 2 H, CH_2S, *E*), 6.85−7.48 (m, 13 H, ArH, *E* and *Z*), 7.96 (d, *J* = 8.3 Hz, 1 H, ArH, *E*), 8.02 (d, *J* = 8.3 Hz, 1 H, ArH, *Z*).

(*E*)-2-{[3-(Benzotriazol-1-yl)-2,3-diphenylallyl]sulfanyl}ethanol [(*E*)-5d]: M.p. 141−143 °C (CH_2Cl_2/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3392, 3048, 2912, 1601, 1481, 1440, 1376, 1268, 1224, 1153, 1067, 744, 698 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.85 (s, 1 H, CH_2CH_2OH), 2.65 (t, *J* = 5.9, 2 H, CH_2CH_2OH), 3.48−3.60 (m, 2 H, CH_2CH_2OH), 3.90 (s, 2 H, CH_2S), 7.03−7.56 (m, 13 H, ArH), 7.93 (d, *J* = 8.0 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 35.7, 60.9, 111.1, 120.5, 124.8, 128.5, 128.6, 128.7, 128.9, 129.0, 129.9, 133.4, 134.0, 135.7, 138.6, 140.1, 146.2. $C_{23}H_{21}N_3OS$ (387.50): calcd. C 71.29, H 5.46, N 10.84, S 8.28; found C 71.38, H 5.50, N 10.77, S 8.20.

1-[1-(4-Fluorophenyl)-2-phenyl-3-(phenylsulfanyl)propenyl]-1*H*-benzotriazole (5e): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 5.54:1. IR (neat): $\tilde{\nu}$ = 3040, 2918, 1489, 1421, 1382, 1266, 1221, 1065, 754, 691 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 3.99 (s, 2 H, CH_2S, *Z*), 4.26 (s, 2 H, CH_2S, *E*), 6.70−7.51 (m, 17 H, ArH, *E* and *Z*), 7.93 (d, *J* = 8.2 Hz, 1 H, ArH, *E*), 8.11−8.18 (m, 1 H, ArH, *Z*).

1-[1-(4-Fluorophenyl)-2-methyl-3-(phenylsulfanyl)propenyl]-1*H*-benzotriazole (5f): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 7.00:1. IR (neat): $\tilde{\nu}$ = 3038, 2912, 1571, 1512, 1488, 1294, 1210, 1085, 745, 692 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.83 (s, 3 H, CH_3, *E*), 2.20 (s, 3 H, CH_3, *Z*), 3.65 (s, 2 H, CH_2S, *Z*), 3.89 (s, 2 H, CH_2S, *E*), 6.64−7.38 (m, 12 H, ArH, *E* and *Z*), 8.01−8.11 (m, 1 H, ArH, *E* and *Z*).

1-[2-(2,5-Dimethylphenyl)-1-(4-fluorophenyl)-3-(phenylsulfanyl)-propenyl]-1*H*-benzotriazole (5g): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 2.81:1. IR (neat): $\tilde{\nu}$ = 3042, 2924, 1594, 1476, 1242, 1080, 904, 746, 694 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.14 (s, 3 H, CH_3, *E*), 2.22 (s, 3 H, CH_3, *Z*), 2.24 (s, 3 H, CH_3, *E*), 2.35 (s, 3 H, CH_3, *Z*), 3.64 (d, *J* = 12.9 Hz, 1 H of CH_2S, *Z*), 4.08 (d, *J* = 12.9 Hz, 1 H of CH_2S, *Z*), 4.10 (d, *J* = 11.8 Hz, 1 H of CH_2S, *E*), 4.30 (d, *J* = 11.8 Hz, 1 H of CH_2S, *E*), 6.69−7.51 (m, 15 H, ArH, *E* and *Z*), 7.90 (d, *J* = 8.1 Hz, 1 H, ArH, *E*), 8.12−8.19 (m, 1 H, ArH, *Z*).

1-[2-(2,5-Dimethylphenyl)-1-(4-fluorophenyl)-3-(4-methoxyphenylsulfanyl)propenyl]-1*H*-benzotriazole (5h): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1.12:1. IR (neat): $\tilde{\nu}$ = 3040, 2912, 1597, 1488, 1426, 1226, 1135, 1082, 744, 696 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.15 (s, 3 H, CH_3, *E*), 2.21 (s, 3 H, CH_3, *Z*), 2.24 (s, 3 H, CH_3, *E*), 2.36 (s, 3 H, CH_3, *Z*), 3.53 (d, *J* = 13.1 Hz, 1 H of CH_2S, *Z*), 3.69 (s, 3 H, OCH_3, *Z*), 3.78 (s, 3 H, OCH_3, *E*), 3.97 (d, *J* = 12.2 Hz, 1 H of CH_2S, *E*), 4.07 (d, *J* = 13.1 Hz, 1 H of CH_2S, *Z*), (d, *J* = 12.2 Hz, 1 H of CH_2S, *E*), 6.49−7.50 (m, 14 H, ArH, *E* and *Z*), 7.89 (d, *J* = 8.2 Hz, 1 H, ArH, *E*), 8.10−8.19 (m, 1 H, ArH, *Z*).

(*E*)-1-[1-(4-Fluorophenyl)-2-methyl-3-(propylsulfanyl)propenyl]-1*H*-benzotriazole [(*E*)-5i]: M.p. 136−138 °C (CH_2Cl_2/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3040, 2912, 1575, 1502, 1490, 1294, 1208, 1087, 746, 691 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 0.96 (t, *J* = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 1.44−1.59 (m, 2 H, $CH_2CH_2CH_3$), 1.82 (s, 3 H, CH_3), 2.55 (t, *J* = 7.3 Hz, 2 H, $CH_2CH_2CH_3$), 3.49 (s, 2 H, CH_2S), 7.03 (t, *J* = 8.7 Hz, 2 H, ArH), 7.20 (d, *J* = 8.0 Hz, 1 H, ArH), 7.29−7.42 (m, 4 H, ArH), 8.09 (d, *J* = 8.1 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 13.8, 18.7, 23.2, 34.9, 36.3, 110.6, 116.1 ($^2J_{C-F}$ = 21.7 Hz), 120.5, 124.4, 128.3, 131.3 ($^3J_{C-F}$ = 8.3 Hz), 131.4, 131.9 ($^4J_{C-F}$ = 3.4 Hz), 133.5, 136.9, 146.0, 163.1 ($^1J_{C-F}$ = 248.2 Hz). $C_{19}H_{20}FN_3S$ (341.45): calcd. C 66.83, H 5.90, N 12.31, S 9.39; found C 66.88, H 5.83, N 12.39, S 9.30.

1-[1-(4-Methoxyphenyl)-2-phenyl-3-(phenylsulfanyl)propenyl]-1*H*-benzotriazole (5j): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1:1.91. IR (neat): $\tilde{\nu}$ = 3040, 2912, 1601, 1488, 1450, 1280, 1156, 1088, 746, 692, 516 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 3.69 (s, 3 H, OCH_3, *Z*), 3.81 (s, 3 H, OCH_3, *E*), 3.98 (s, 2 H, CH_2S, *Z*), 4.31 (s, 2 H, CH_2Cl, *E*), 6.53−7.51 (m, 17 H, ArH, *E* and *Z*), 7.92 (d, *J* = 7.4 Hz, 1 H, ArH, *E*), 8.06−8.14 (m, 1 H, ArH, *Z*).

1-[1-(4-Methoxyphenyl)-3-phenylsulfanyl-2-(4-tolyl)propenyl]-1*H*-benzotriazole (5k): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1:2.06. IR (neat): $\tilde{\nu}$ = 3042, 2920, 1599, 1487, 1444, 1276, 1215, 1078, 742, 694, 518 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.17 (s, 3 H, CH_3, *E*), 2.35 (s, 3 H, CH_3, *Z*), 3.70 (s, 3 H, OCH_3, *Z*), 3.81 (s, 3 H, OCH_3, *E*), 3.94 (s, 2 H, CH_2S, *Z*), 4.30 (s, 2 H, CH_2S, *E*), 6.55−7.40 (m, 16 H, ArH, *E* and *Z*), 7.94 (d, *J* = 8.0 Hz, 1 H, ArH, *E*), 8.06−8.14 (m, 1 H, ArH, *Z*).

General Procedure for the Synthesis of 6 and 12: *m*CPBA (0.12−0.35 mmol) was added at room temperature to a solution of **5** (0.12−0.35 mmol) in CH_2Cl_2 (25 mL). The mixture was stirred

for 5 min, followed by addition of aqueous $NaHCO_3$ (10%) and extraction with CH_2Cl_2 (30 mL × 3). The combined extracts were dried with $MgSO_4$. After removal of the solvent in vacuo, the residue was chromatographed on a silica gel column (2 × 10 cm; EtOAc/*n*-hexane, 1:1) to give compound **6**.

(*E*)-1-(3-Benzenesulfinyl-1,2-diphenylpropenyl)-1*H*-benzotriazole [(*E*)-6a]: M.p. 148−150 °C (CH_2Cl_2/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3040, 2896, 1476, 1438, 1270, 1225, 1073, 1043, 740, 699, 478 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 4.10 (d, *J* = 13.0 Hz, 1 H of CH_2S), 4.43 (d, *J* = 13.0 Hz, 1 H of CH_2S), 6.99−7.56 (m, 18 H, ArH) 7.82−7.88 (m, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 64.4, 110.9, 120.2, 124.3, 124.4, 128.2, 128.3, 128.8, 129.1, 129.3, 129.8, 130.1, 130.2, 131.8, 133.2, 133.7, 134.9, 137.4, 137.9, 144.3, 145.7. $C_{27}H_{21}N_3OS$ (435.54): calcd. C 74.46, H 4.86, N 9.65, S 7.36; found C 74.54, H 4.90, N 9.59, S 7.33.

(*Z*)-1-(3-Benzenesulfinyl-1,2-diphenylpropenyl)-1*H*-benzotriazole [(*Z*)-6a]: M.p. 155−157 °C (CH_2Cl_2/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3040, 2912, 1475, 1438, 1374, 1270, 1212, 1080, 1044, 742, 692, 492 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 3.96 (d, *J* = 13.6 Hz, 1 H of CH_2S), 4.30 (d, *J* = 13.6 Hz, 1 H of CH_2S), 6.87−7.39 (m, 18 H, ArH) 8.02−8.09 (m, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 65.6, 112.0, 120.3, 124.1, 124.9, 128.5, 128.7, 128.8, 129.1, 129.4, 129.6, 130.1, 130.2, 131.6, 133.0, 134.0, 135.3, 136.6, 139.1, 144.3, 146.3. $C_{27}H_{21}N_3OS$ (435.54): calcd. C 74.46, H 4.86, N 9.65, S 7.36; found C 74.40, H 4.91, N 9.57, S 7.40.

1-[3-Benzenesulfinyl-1-phenyl-2-(4-tolyl)propenyl]-1*H*-benzotriazole (6b): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 2.38:1. IR (neat): $\tilde{\nu}$ = 3040, 2942, 1588, 1476, 1433, 1351, 1263, 1071, 861, 749, 516 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.18 (s, 3 H, CH_3, *E*), 2.31 (s, 3 H, CH_3, *Z*), 3.93 (d, *J* = 12.9 Hz, 1 H of CH_2S, *Z*), 4.10 (d, *J* = 13.0 Hz, 1 H of CH_2S, *E*), 4.22 (d, *J* = 12.9 Hz, 1 H of CH_2S, *Z*), 4.41 (d, *J* = 13.0 Hz, 1 H of CH_2S, *E*), 6.86−7.68 (m, 17 H, ArH, *E* and *Z*), 7.93 (d, *J* = 7.2 Hz, 1 H, ArH, *E*), 8.12 (d, *J* = 7.2 Hz, 1 H, ArH, *Z*).

1-(2-Benzenesulfinylmethyl-3,3-dimethyl-1-phenylbut-1-enyl)-1*H*-benzotriazole (6c): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1.48:1. IR (neat): $\tilde{\nu}$ = 3048, 2952, 1603, 1473, 1436, 1363, 1265, 1232, 1078, 1043, 740, 686 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.14 [s, 9 H, $C(CH_3)_3$, *E*], 1.23 [s, 9 H, $C(CH_3)_3$, *Z*], 3.71 (d, *J* = 13.9 Hz, 1 H of CH_2S, *Z*), 3.83 (d, *J* = 13.9 Hz, 1 H of CH_2S, *Z*), 4.12 (s, 2 H, CH_2S, *E*), 6.98−7.57 (m, 13 H, ArH, *E* and *Z*), 7.96−8.07 (m, 1 H, ArH, *E* and *Z*).

(*E*)-2-[3-(Benzotriazol-1-yl)-2,3-diphenylprop-2-ene-1-sulfinyl]-ethanol [(*E*)-6d]: M.p. 120−122 °C (CH_2Cl_2/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3380, 3040, 2912, 1600, 1480, 1441, 1280, 1226, 1080, 1038, 744, 696 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.73−2.98 (m, 2 H, CH_2CH_2OH), 3.05 (s, 1 H, CH_2CH_2OH), 4.01−4.19 (m, 2 H, CH_2CH_2OH), 4.12 (d, *J* = 12.9 Hz, 1 H of CH_2S), 4.47 (d, *J* = 12.9 Hz, 1 H of CH_2S), 7.05−7.67 (m, 13 H, ArH), 7.92 (d, *J* = 7.9 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 53.8, 57.3, 60.1, 111.7, 120.4, 125.0, 128.7, 128.8, 128.9, 129.3, 129.4, 130.0, 130.1, 132.9, 133.9, 135.1, 136.5, 138.5, 146.3. $C_{23}H_{21}N_3O_2S$ (403.50): calcd. C 68.46, H 5.25, N 10.41, S 7.95; found C 68.51, H 5.22, N 10.49, S 7.90.

1-[3-Benzenesulfinyl-1-(4-fluorophenyl)-2-phenylpropenyl]-1*H*-benzotriazole (6e): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 5.42:1. IR (neat): $\tilde{\nu}$ = 3042, 2928, 1592, 1447, 1288, 1236, 1080, 869, 744, 517 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 3.94 (d, *J* = 13.5 Hz, 1 H of CH_2S, *Z*), 4.07 (d, *J* = 13.0 Hz, 1 H of CH_2S, *E*), 4.25 (d, *J* = 13.5 Hz, 1 H of CH_2S, *Z*), 4.37 (d, *J* = 13.0 Hz, 1 H of CH_2S, *E*), 6.71−7.75 (m, 17 H, ArH, *E* and *Z*), 7.92 (d, *J* = 8.1 Hz, 1 H, ArH, *E*), 8.10−8.18 (m, 1 H, ArH, *Z*).

1-[3-Benzenesulfinyl-1-(4-fluorophenyl)-2-methylpropenyl]-1*H*-benzotriazole (6f): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 6.94:1. IR (neat): $\tilde{\nu}$ = 3040, 2920, 1588, 1445, 1226, 1165, 1052, 878, 742, 521 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.85 (s, 3 H, CH_3, *E*), 2.21 (s, 3 H, CH_3, *Z*), 3.85 (d, *J* = 12.8 Hz, 1 H of CH_2S, *Z*), 4.01 (d, *J* = 13.0 Hz, 1 H of CH_2S, *E*), 4.20 (d, *J* = 12.8 Hz, 1 H of CH_2S, *Z*), 4.32(d, *J* = 13.0 Hz, 1 H of CH_2S, *E*), 6.65−7.41 (m, 12 H, ArH, *E* and *Z*), 8.02−8.11 (m, 1 H, ArH, *E* and *Z*).

1-[3-Benzenesulfinyl-2-(2,5-dimethylphenyl)-1-(4-fluorophenyl)-propenyl]-1*H*-benzotriazole (6g): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 2.71:1. IR (neat): $\tilde{\nu}$ = 3048, 2920, 1598, 1443, 1228, 1181, 1074, 872, 746, 520 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.00 (s, 3 H, CH_3, *E*), 2.06 (s, 3 H, CH_3, *E*), 2.34 (s, 3 H, CH_3, *Z*), 2.45 (s, 3 H, CH_3, *Z*), 3.65 (d, *J* = 12.6 Hz, 1 H of CH_2S, *Z*), 3.92 (d, *J* = 12.8 Hz, 1 H of CH_2S, *E*), 4.38 (d, *J* = 12.8 Hz, 1 H of CH_2S, *E*), 4.39 (d, *J* = 12.6 Hz, 1 H of CH_2S, *Z*), 6.75−7.99 (m, 16 H, ArH, *E* and *Z*).

(*E*)-1-[2-(2,5-Dimethylphenyl)-1-(4-fluorophenyl)-3-(4-methoxybenzenesulfinyl)propenyl]-1*H*-benzotriazole [(*E*)-6h]: M.p. 97−99 °C (CH_2Cl_2/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3040, 2912, 1700, 1587, 1486, 1444, 1294, 1248, 1156, 1048, 828, 740, 520 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.99 (s, 3 H, CH_3 of major), 2.07 (s, 3 H, CH_3 of minor), 2.31 (s, 3 H, CH_3 of minor), 2.42 (s, 3 H, CH_3 of major), 3.62 (d, *J* = 12.6 Hz, 1 H, CH_2S of major), 3.83 (s, 3 H, OCH_3 of major and minor), 3.93 (d, *J* = 12.7 Hz, 1 H, CH_2S of minor), 4.34 (d, *J* = 12.7 Hz, 1 H, CH_2S of minor), 4.38 (d, *J* = 12.6 Hz, 1 H, CH_2S of major), 6.72−7.95 (m, 15 H, ArH of major and minor). $C_{30}H_{26}FN_3O_2S$ (511.61): calcd. C 70.43, H 5.12, N 8.21, S 6.27; found C 70.48, H 5.21, N 8.18, S 6.35.

(*Z*)-1-[2-(2,5-Dimethylphenyl)-1-(4-fluorophenyl)-3-(4-methoxybenzenesulfinyl)propenyl]-1*H*-benzotriazole [(*Z*)-6h]: M.p. 152−154 °C (CH_2Cl_2/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3040, 2920, 1704, 1588, 1488, 1444, 1294, 1248, 1160, 1081, 1041, 827, 744, 518 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.10 (s, 3 H, CH_3 of major), 2.22 (s, 3 H, CH_3 of minor), 2.33 (s, 3 H, CH_3 of minor), 2.42 (s, 3 H, CH_3 of major), 3.54 (d, *J* = 12.9 Hz, 1 H, CH_2S of minor), 3.77 (d, *J* = 12.8 Hz, 1 H, CH_2S of major), 3.75 (s, 3 H, OCH_3 of major), 3.80 (s, 3 H, OCH_3 of minor), 4.03 (d, *J* = 12.9 Hz, 1 H, CH_2S of minor), 4.39 (d, *J* = 12.8 Hz, 1 H, CH_2S of major), 6.69−7.56 (m, 14 H, ArH of major and minor), 8.07−8.16 (m, 1 H, ArH of major and minor). $C_{30}H_{26}FN_3O_2S$ (511.61): calcd. C 70.43, H 5.12, N 8.21, S 6.27; found C 70.39, H 5.17, N 8.25, S 6.24.

(*E*)-1-[1-(4-Fluorophenyl)-2-methyl-3-(propanesulfinyl)propenyl]-1*H*-benzotriazole [(*E*)-6i]: M.p. 128−130 °C (CH_2Cl_2/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3040, 2912, 1601, 1490, 1448, 1290, 1242, 1180, 1040, 841, 746 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.10 (t, *J* = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 1.72−1.90 (m, 2 H, $CH_2CH_2CH_3$), 1.91 (s, 3 H, CH_3), 2.63−2.82 (m, 2 H, $CH_2CH_2CH_3$), 3.55 (d, *J* = 12.5 Hz, 1 H of CH_2S), 3.94 (d, *J* = 12.5 Hz, 1 H of CH_2S), 7.03 (t, *J* = 8.4 Hz, 2 H, ArH), 7.17−7.58 (m, 5 H, ArH), 8.06 (d, *J* = 8.0 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 13.7, 16.6, 19.6, 55.3, 58.4, 110.9, 116.3 ($^2J_{C-F}$ = 21.7 Hz), 120.3, 124.6, 128.6, 130.6, 130.9 ($^4J_{C-F}$ = 3.5 Hz), 132.1 ($^3J_{C-F}$ = 8.3 Hz), 133.4, 135.5, 145.3, 163.4 ($^1J_{C-F}$ = 248.6 Hz). $C_{19}H_{20}FN_3OS$ (357.45): C 63.84, H 5.64, N 11.76, S 8.97; C 63.90, H 5.61, N 11.72, S 9.02.

1-[3-Benzenesulfinyl-1-(4-methoxyphenyl)-2-phenylpropenyl]-1*H*-benzotriazole (6j): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1:1.85. IR (neat): $\tilde{\nu}$ =3048, 2912, 1603, 1490, 1454, 1284, 1218, 1142, 841, 725 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 3.69 (s, 3 H, OCH_3, *Z*), 3.80 (s, 3 H, OCH_3, *E*), 3.92 (d, *J* = 13.5 Hz, 1 H of CH_2S, *Z*), 4.11 (d, *J* = 13.0 Hz, 1 H of CH_2S, *E*), 4.25 (d, *J* = 13.5 Hz, 1 H of CH_2S, *Z*), 4.43 (d, *J* = 13.0 Hz, 1 H of CH_2S, *E*), 6.55−7.66 (m, 17 H, ArH, *E* and *Z*), 7.91 (d, *J* = 7.4 Hz, 1 H, ArH, *E*), 8.10−8.18 (m, 1 H, ArH, *Z*).

1-[3-Benzenesulfinyl-1-(4-methoxyphenyl)-2-(4-tolyl)propenyl]-1*H*-benzotriazole (6k): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 1:2.02. IR (neat): $\tilde{\nu}$ = 3042, 2920, 1596, 1480, 1448, 1275, 1211, 1088, 825, 740, 516 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.19 (s, 3 H, CH_3, *E*), 2.33 (s, 3 H, CH_3, *Z*), 3.72 (s, 3 H, OCH_3, *Z*), 3.81 (s, 3 H, OCH_3, *E*), 3.91 (d, *J* = 13.5 Hz, 1 H of CH_2S, *Z*), 4.09 (d, *J* = 13.0 Hz, 1 H of CH_2S, *E*), 4.19 (d, *J* = 13.5 Hz, 1 H of CH_2S, *Z*), 4.42 (d, *J* = 13.0 Hz, 1 H of CH_2S, *E*), 6.57−7.68 (m, 16 H, ArH, *E* and *Z*), 7.93 (d, *J* = 8.0 Hz, 1 H, ArH, *E*), 8.08−8.17 (m, 1 H, ArH, *Z*).

1-[3-(1-Methyl-1*H*-imidazole-2-sulfinyl)-1,2-diphenylpropenyl]-1*H*-benzotriazole (12): Viscous liquid; (*E*)/(*Z*) ($CDCl_3$) = 2.79:1. IR (neat): $\tilde{\nu}$ = 3056, 2928, 1601, 1486, 1441, 1396, 1270, 1209, 1155, 1048, 907, 745, 518 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 3.53 (s, 3 H, CH_3, *Z*), 3.73 (s, 3 H, CH_3, *E*), 4.59 (d, *J* = 4.7 Hz, 2 H, CH_2S, *Z*), 4.65 (d, *J* = 13.2 Hz, 1 H of CH_2S, *E*), 5.10 (d, *J* = 13.2 Hz, 1 H of CH_2S, *E*), 6.73−7.62 (m, 15 H, ArH and =CH, *E* and *Z*), 7.93 (d, *J* = 8.0 Hz, 1 H, ArH, *E*), 8.08−8.14 (m, 1 H, ArH, *Z*).

General Procedure for the Synthesis of 7, 9, and 13: TFAA (0.55−1.60 mmol) was added at room temperature to a solution of **6** (0.11−0.32 mmol) in THF (20 mL). The mixture was stirred for 1 h at room temperature, followed by addition of aqueous $NaHCO_3$ (10%) and extraction with CH_2Cl_2 (20 mL × 3). The combined extracts were dried with $MgSO_4$. After removal of the solvent in vacuo, the residue was chromatographed on a silica gel column (70−230 mesh, 3 × 10 cm; EtOAc/*n*-hexane, 1:5) to give compound **7**.

4,5-Diphenyl-6-(phenylsulfanyl)-2,3-benzo-1,3a,6a-triazapentalene (7a): M.p. 177−179 °C (MeOH). IR (KBr): $\tilde{\nu}$ = 3048, 1595, 1571, 1492, 1464, 1368, 1294, 1193, 864, 718, 696 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.91 (t, *J* = 7.8 Hz, 1 H, ArH), 7.15−7.55 (m, 17 H, ArH), 7.68 (d, *J* = 8.4 Hz, 1 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 103.5, 111.7, 114.9, 117.9, 119.2, 121.3, 126.7, 126.8, 127.6, 128.2, 128.3, 128.7, 129.3, 129.4, 129.5, 129.7, 130.3, 131.1, 131.2, 136.1, 147.0 (signals of two aromatic C atoms not visible). $C_{27}H_{19}N_3S$ (417.53): calcd. C 77.67, H 4.59, N 10.06, S 7.68; found C 77.23, H 4.59, N 10.12, S, 7.85.

4-Phenyl-6-(phenylsulfanyl)-5-(4-tolyl)-2,3-benzo-1,3a,6a-triazapentalene (7b): M.p. 190−192 °C (MeOH). IR (KBr): $\tilde{\nu}$ = 3048, 2904, 1595, 1571, 1491, 1464, 1368, 1294, 1190, 1088, 864, 819, 734, 694, 513 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.36 (s, 3 H, CH_3), 6.92 (t, *J* = 7.5 Hz, 1 H, ArH), 7.10−7.29 (m, 9 H, ArH), 7.35−7.58 (m, 7 H, ArH), 7.68 (d, *J* = 8.4 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 21.7, 103.4, 111.7, 114.9, 117.8, 119.1, 121.3, 126.6, 126.7, 127.5, 128.2, 128.3, 128.4, 129.3, 129.4, 129.5, 129.7, 130.3, 130.9, 136.2, 138.1, 147.0. $C_{28}H_{21}N_3S$ (431.55): calcd. C 77.93, H 4.90, N 9.74, S 7.43; found C 78.05, H 4.89, N 9.70, S 7.31.

5-(*tert*-Butyl)-4-phenyl-6-(phenylsulfanyl)-2,3-benzo-1,3a,6a-triazapentalene (7c): M.p. 185−187 °C (MeOH). IR (KBr): $\tilde{\nu}$ = 3046, 2944, 1572, 1492, 1460, 1430, 1369, 1214, 1121, 1003, 873, 778, 728, 688 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.39 [s, 9 H, $(CH_3)_3C$], 6.40 (d, *J* = 8.2 Hz, 1 H, ArH), 6.73 (t, *J* = 7.7 Hz, 1 H, ArH), 7.08−7.19 (m, 3 H, ArH), 7.21−7.31 (m, 3 H, ArH), 7.52−7.66 (m, 6 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 32.5, 34.1, 101.7, 110.8, 114.3, 117.6, 118.0, 121.5, 126.1, 126.2, 126.3, 129.4, 129.6, 130.2, 131.5, 132.5, 134.9, 136.4, 146.6. $C_{25}H_{23}N_3S$ (397.54): calcd. C 75.53, H 5.83, N 10.57, S 8.07; found C 75.68, H 5.86, N 10.55, S 8.00.

6-(2-Hydroxyethylsulfanyl)-4,5-diphenyl-2,3-benzo-1,3a,6a-triazapentalene (7d): M.p. 162−164 °C (EtOAc/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3368, 3048, 2922, 1595, 1494, 1369, 1297, 1196, 1062, 905, 862, 718, 520 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.98 (t, *J* = 5.1 Hz, 2 H, CH_2CH_2OH), 3.72 (t, *J* = 5.1 Hz, 2 H, CH_2CH_2OH), 4.76 (s, 1 H, CH_2CH_2OH), 6.90 (t, *J* = 7.9 Hz, 1 H, ArH), 7.32−7.43 (m, 12 H, ArH), 7.65 (d, *J* = 8.5 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 41.4, 60.9, 106.0, 111.7, 114.4, 118.0, 119.9, 121.4, 127.0, 127.9, 128.0, 128.4, 128.8, 129.4, 129.5, 130.2, 131.1, 131.2, 146.6. $C_{23}H_{19}N_3OS$ (385.48): calcd. C 71.66, H 4.97, N 10.90, S 8.32; found C 71.62, H 4.94, N 10.95, S 8.31.

4-(4-Fluorophenyl)-5-phenyl-6-(phenylsulfanyl)-2,3-benzo-1,3a,6a-triazapentalene (7e): M.p. 197−199 °C (MeOH). IR (KBr): $\tilde{\nu}$ = 3048, 2928, 1596, 1571, 1499, 1465, 1369, 1296, 1217, 1153, 883, 732, 696 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 6.94 (t, *J* = 7.8 Hz, 1 H, ArH), 7.14−7.27 (m, 7 H, ArH), 7.31−7.43 (m, 7 H, ArH), 7.47−7.54 (m, 2 H, ArH), 7.68 (d, *J* = 8.7 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 103.7, 111.4, 115.0, 116.7 ($^2J_{C-F}$ = 21.8 Hz), 118.0, 121.2, 124.4 ($^4J_{C-F}$ = 3.5 Hz), 126.8, 126.9, 127.8, 128.4, 128.8, 130.0, 131.0, 131.1, 132.3 ($^3J_{C-F}$ = 8.4 Hz), 136.0, 147.0, 163.3 ($^1J_{C-F}$ = 248.4 Hz) (signals of two aromatic C atoms not visible). $C_{27}H_{18}FN_3S$ (435.52): calcd. C 74.46, H 4.17, N 9.65, S 7.36; found C 74.41, H 4.15, N 9.68, S 7.32.

4-(4-Fluorophenyl)-5-methyl-6-(phenylsulfanyl)-2,3-benzo-1,3a,6a-triazapentalene (7f): M.p. 173−175 °C (MeOH). IR (KBr): $\tilde{\nu}$ = 3038, 2912, 1571, 1524, 1486, 1371, 1291, 1217, 1192, 1150, 828, 736, 508 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.38 (s, 3 H, 9-H) 6.91 (t, *J* = 7.8 Hz, 1 H, 13-H), 7.13−7.41 (m, 9 H, 3, 5, 14, 15, 18, 19, 20, 21, 22-H), 7.58−7.68 (m, 3 H, 2, 6, 16-H). ^{13}C NMR ($CDCl_3$, 150 MHz, 25 °C, TMS): δ = 9.7 (C-9), 104.0 (C-10), 110.6 (C-14), 114.3 (C-16), 116.2 (*J* = 21.7 Hz; C-3, 5), 117.2 (C-13), 118.1 (C-7), 120.6 (C-12), 123.1 (C-8), 124.2 (*J* = 3.4 Hz; C-1), 126.0 (C-15), 126.3 (C-20), 127.1 (C-19, 21), 129.2 (C-18, 22), 131.0 (*J* = 8.3 Hz; C-2, 6), 135.4 (C-17), 146.3 (C-11), 162.7 (*J* = 248.3 Hz; C-4). $C_{22}H_{16}FN_3S$ (373.45): calcd. C 70.76, H 4.32, N 11.25, S 8.59; found C 70.76, H 4.36, N 11.04, S 8.23. Refer to Figure 1 for numbering the position for the NMR data.

5-(2,5-Dimethylphenyl)-4-(4-fluorophenyl)-6-(phenylsulfanyl)-2,3-benzo-1,3a,6a-triazapentalene (7g): M.p. 153−155 °C (MeOH). IR (KBr): $\tilde{\nu}$ = 3040, 2904, 1595, 1571, 1491, 1465, 1366, 1296, 1219, 1152, 1081, 838, 804, 727, 688 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.88 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 6.92−7.02 (m, 2 H, ArH), 7.05−7.26 (m, 9 H, ArH), 7.36−7.47 (m, 3 H, ArH), 7.54 (d, *J* = 8.3 Hz, 1 H, ArH), 7.71 (d, *J* = 8.5 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 125 MHz, 25 °C, TMS): δ = 19.4, 20.9, 104.8, 110.9, 114.5, 116.0 ($^2J_{C-F}$ = 21.5 Hz), 117.3, 118.3, 120.7, 124.3 ($^4J_{C-F}$ = 3.1 Hz), 126.3, 126.6, 127.9, 128.4, 128.9, 129.4, 129.8, 129.9, 130.4 ($^3J_{C-F}$ = 8.4 Hz), 132.4, 134.3, 134.9, 135.1, 146.5, 162.5 ($^1J_{C-F}$ = 248.1 Hz). $C_{29}H_{22}FN_3S$ (463.57): calcd. C 75.14, H 4.78, N 9.06, S 6.92; found C 74.84, H 4.82, N 8.97, S 6.93.

5-(2,5-Dimethylphenyl)-4-(4-fluorophenyl)-6-(4-methoxyphenylsulfanyl)-2,3-benzo-1,3a,6a-triazapentalene (7h): M.p. 146−148 °C (MeOH). IR (KBr): $\tilde{\nu}$ = 3042, 2920, 1584, 1483, 1368, 1291, 1236, 1171, 1081, 1027, 822, 734, 628, 521 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.83 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 3.75 (s, 3 H, OCH_3), 6.71−6.79 (m, 2 H, ArH), 6.89−7.01 (m, 2 H, ArH), 7.05−7.16 (m, 4 H, ArH), 7.25−7.32 (m, 2 H, ArH), 7.34−7.45 (m, 3 H, ArH), 7.50 (d, J = 8.3 Hz, 1 H, ArH), 7.71 (d, J = 8.4 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 19.9, 21.4, 55.7, 107.3, 111.4, 114.7, 114.9, 116.5 ($^2J_{C-F}$ = 21.8 Hz), 117.5, 118.6, 121.1, 124.8 ($^4J_{C-F}$ = 3.5 Hz), 125.7, 126.7, 127.7, 129.8, 130.3, 130.4, 130.8 ($^3J_{C-F}$ = 8.1 Hz), 132.9, 133.0, 143.9, 135.3, 147.0, 159.7, 162.9 ($^1J_{C-F}$ = 247.7 Hz). $C_{30}H_{24}FN_3OS$ (493.60): calcd. C 73.00, H 4.90, N 8.51, S 6.50; found C 72.88, H 4.92, N 8.43, S 6.58.

4-(4-Fluorophenyl)-5-methyl-6-(propylsulfanyl)-2,3-benzo-1,3a,6a-triazapentalene (7i): M.p. 137−139 °C (MeOH). IR (KBr): $\tilde{\nu}$ = 3040, 2944, 1588, 1526, 1486, 1464, 1376, 1296, 1214, 1148, 828, 739, 614 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.04 (t, J = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 1.59−1.67 (m, 2 H, $CH_2CH_2CH_3$), 2.36 (s, 3 H, CH_3) 2.92 (t, J = 7.3 Hz, 2 H, $CH_2CH_2CH_3$), 6.85 (t, J = 8.1 Hz, 1 H, ArH), 7.25−7.39 (m, 4 H, ArH), 7.56−7.66 (m, 3 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 10.3, 13.6, 23.7, 36.0, 107.1, 110.9, 114.3, 116.6 ($^2J_{C-F}$ = 21.8 Hz), 117.0, 118.2, 121.0, 122.7, 124.9 ($^4J_{C-F}$ = 3.5 Hz), 126.3, 131.4 ($^3J_{C-F}$ = 8.1 Hz), 147.0, 163.1 ($^1J_{C-F}$ = 247.8 Hz). $C_{19}H_{18}FN_3S$ (339.43): calcd. C 67.23, H 5.35, N 12.38, S 9.45; found C 67.27, H 5.32, N 12.45, S 9.45.

4-(4-Methoxyphenyl)-5-phenyl-6-(phenylsulfanyl)-2,3-benzo-1,3a,6a-triazapentalene (7j): M.p. 166−168 °C (MeOH). IR (KBr): $\tilde{\nu}$ = 3048, 2920, 1600, 1499, 1465, 1369, 1291, 1248, 1177, 1024, 832, 732, 692 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 3.90 (s, 3 H, OCH_3), 6.92 (t, J = 7.7 Hz, 1 H, ArH), 6.97−7.06 (m, 2 H, ArH), 7.12−7.49 (m, 14 H, ArH), 7.66 (d, J = 8.5 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 55.8, 103.4, 111.5, 114.7, 114.9, 117.7, 119.2, 120.4, 121.3, 126.6, 126.7, 127.7, 127.8, 128.2, 128.6, 129.6, 131.0, 131.4, 131.8, 136.2, 147.0, 160.5. $C_{28}H_{21}N_3OS$ (447.55): calcd. C 75.14, H 4.73, N 9.39, S 7.16; found C 75.03, H 4.70, N 9.33, S 7.16.

4-(4-Methoxyphenyl)-6-phenylsulfanyl-5-(4-tolyl)-2,3-benzo-1,3a,6a-triazapentalene (7k): M.p. 175−177 °C (MeOH). IR (KBr): $\tilde{\nu}$ = 3048, 2920, 1601, 1568, 1464, 1371, 1291, 1248, 1176, 1024, 864, 820, 734, 684 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.36 (s, 3 H, CH_3), 3.90 (s, 3 H, OCH_3), 6.91 (t, J = 8.0 Hz, 1 H, ArH), 6.98−7.05 (m, 2 H, ArH), 7.09−7.29 (m, 9 H, ArH), 7.33−7.48 (m, 4 H, ArH), 7.66 (d, J = 8.4 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 21.7, 55.8, 103.1, 111.5, 114.7, 114.9, 117.6, 119.1, 120.5, 121.3, 126.6, 126.7, 127.4, 127.9, 128.3, 129.5, 129.6, 130.8, 131.8, 136.3, 138.0, 147.0, 160.4. $C_{29}H_{23}N_3OS$ (461.58): calcd. C 75.46, H 5.02, N 9.10, S 6.95; found C 75.33, H 5.01, N 9.02, S 6.82.

4,5-Diphenyl-6-(2-trifluoroacetoxyethylsulfanyl)-2,3-benzo-1,3a,6a-triazapentalene (8): Viscous liquid. IR (neat): $\tilde{\nu}$ = 3048, 2920, 1777, 1595, 1494, 1464, 1272, 1359, 1297, 1216, 1156, 905, 864, 715 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 3.23 (t, J = 6.6 Hz, 2 H, SCH_2), 4.36 (t, J = 6.6 Hz, 2 H, OCH_2), 6.93 (t, J = 7.7 Hz, 1 H, ArH), 7.27−7.56 (m, 12 H, ArH), 7.86 (d, J = 8.4 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 31.6, 66.8, 103.9, 111.7, 114.5, 114.6 (CF_3, J_{C-F} = 282.4 Hz), 117.9, 119.4, 121.2, 126.9, 127.0, 127.7, 128.0, 128.4, 128.7, 129.4, 130.2, 130.9, 131.1, 147.0, 157.4 (C=O, J_{C-CF3} = 42.1 Hz).

(*E*)-1-(Benzotriazol-1-yl)-2-(1,3-oxathiolan-2-yl)stilbene [(*E*)-9]: M.p. 158−160 °C (EtOAc/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3048, 2928, 1601, 1481, 1438, 1380, 1265, 1208, 1150, 1054, 905, 739, 697 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.66−2.78 (m, 1 H, 1 H of SCH_2), 2.95−3.08 (m, 1 H, 1 H of SCH_2), 3.77−3.88 (m, 1 H, 1 H of OCH_2), 4.13−4.25 (m, 1 H, 1 H of OCH_2), 6.29 (s, 1 H, CH), 7.00−7.09 (m, 3 H, ArH), 7.18−7.54 (m, 10 H, ArH), 7.88 (d, J = 8.3 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 34.6, 73.3, 84.4, 110.6, 120.1, 124.1, 127.6, 127.9, 128.1, 129.2, 129.7, 130.0, 130.6, 133.5, 134.2, 134.7, 134.9, 141.4, 145.5. $C_{23}H_{19}N_3OS$ (385.48): calcd. C 71.66, H 4.97, N 10.90, S 8.32; found C 71.49, H 5.01, N 10.99, S 8.39.

(*E*)-(Benzotriazol-1-yl)-2,3-diphenylacrolein [(*E*)-13]: M.p. 122 −124 °C (EtOAc/*n*-hexane). IR (neat): $\tilde{\nu}$ = 3048, 2848, 1670, 1592, 1480, 1441, 1387, 1316, 1278, 1227, 1072, 1035, 905, 715, 695 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 6.89 (d, J = 7.1 Hz, 1 H, ArH), 6.96−7.01 (m, 2 H, ArH), 7.09−7.18 (m, 3 H, ArH), 7.25−7.43 (m, 4 H, ArH), 7.49−7.57 (m, 2 H, ArH), 7.60−7.68 (m, 1 H, ArH), 8.01 (d, J = 8.0 Hz, 1 H, ArH), 9.97 (s, 1 H, O=CH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 111.1, 120.7, 125.0, 128.8, 128.9, 129.0, 129.2, 129.6, 130.0, 130.6, 131.8, 132.6, 133.5, 136.8, 146.2, 150.1, 192.3. $C_{21}H_{15}N_3O$ (325.36): calcd. C 77.52, H 4.65, N 12.91; found C 77.98, H 4.59, N 12.88.

General Procedure for the Synthesis of 15: A mixture of **7** (0.10−0.15 mmol) and Raney-Ni (50 mg) in THF (20 mL) was heated for 15 h at reflux under hydrogen. Removal of the insoluble materials by filtration followed by evaporation of the solvent, gave a residue, which was chromatographed on a silica gel column (2 × 10 cm; EtOAc/*n*-hexane, 1:3) to give compound **15**.

2-(4,5-Diphenylpyrazol-1-yl)aniline (15a): Viscous liquid. IR (neat): $\tilde{\nu}$ = 3448, 3344, 3040, 1611, 1500, 1372, 1307, 952, 905, 764, 692 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.16 (s, 2 H, NH_2), 6.57 (t, J = 8.1 Hz, 1 H, ArH), 6.73−6.86 (m, 2 H, ArH), 7.07−7.34 (m, 11 H, ArH), 7.99 (s, 1 H, N=CH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 117.0, 118.3, 121.8, 126.2, 126.3, 126.8, 128.4, 128.7, 128.8, 128.9, 129.7, 130.1, 130.5, 133.2, 140.5, 140.9, 143.7.

2-(4-*tert*-Butyl-5-phenylpyrazol-1-yl)aniline (15c): Viscous liquid. IR (neat): $\tilde{\nu}$ = 3440, 3336, 3048, 2944, 1614, 1497, 1456, 1433, 1369, 1305, 1219, 960, 763, 744, 696 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.23 (s, 9 H, $C(CH_3)_3$], 4.14 (s, 2 H, NH_2), 6.44−6.52 (m, 1 H, ArH), 6.70 (dd, J = 8.0, 1.2 Hz, 1 H, ArH), 6.76 (dd, J = 7.8, 1.4 Hz, 1 H, ArH), 6.96−7.04 (m, 1 H, ArH), 7.22−7.32 (m, 5 H, ArH), 7.71 (s, 1 H, N=CH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 30.9, 32.3, 116.7, 118.0, 126.5, 128.1, 128.6, 128.7, 129.4, 130.3, 131.3, 132.6, 138.8, 141.1, 143.9.

2-[5-(4-Fluorophenyl)-4-methylpyrazol-1-yl]aniline (15i): Viscous liquid. IR (neat): $\tilde{\nu}$ = 3448, 3336, 3040, 2920, 1614, 1504, 1454, 1372, 1305, 1220, 1153, 961, 833, 747 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.16 (s, 3 H, CH_3), 4.23 (s, 2 H, NH_2), 6.53−6.62 (m, 1 H, ArH), 6.70 (dd, J = 7.9, 1.5 Hz, 1 H, ArH), 6.81 (dd, J = 8.1, 1.2 Hz, 1 H, ArH), 6.96−7.05 (m, 2 H, ArH), 7.06−7.20 (m, 3 H, ArH), 7.65 (s, 1 H, N=CH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 9.7, 115.5, 115.8 ($^2J_{C-F}$ = 21.4 Hz), 117.1, 118.4, 126.3, 126.5 ($^4J_{C-F}$ = 3.5 Hz), 128.3, 129.5, 131.6 ($^3J_{C-F}$ = 8.0 Hz), 140.5, 141.8, 143.5, 162.7 ($^1J_{C-F}$ = 246.8 Hz).

2-[5-(4-Methoxyphenyl)-4-(*p*-tolyl)pyrazol-1-yl]aniline (15k): Viscous liquid. IR (neat): $\tilde{\nu}$ = 3448, 3352, 3032, 2928, 1608, 1515, 1496, 1446, 1248, 1176, 950, 814, 747, 728 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.35 (s, 3 H, CH_3), 3.78 (s, 3 H,

OCH_3), 4.13 (s, 2 H, NH_2), 6.54−6.63 (m, 1 H, ArH), 6.73−6.85 (m, 4 H, ArH), 7.04−7.23 (m, 7 H, ArH), 7.93 (s, 1 H, N=CH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 21.6, 55.5, 114.3, 117.0, 118.4, 121.4, 122.4, 126.3, 128.2, 128.7, 129.6, 130.4, 131.7, 136.4, 140.4, 140.5, 143.7, 159.8 (signal of one aromatic C atom not visible).

General Procedure for the Synthesis of 16: Acetic anhydride (0.10−0.15 mmol) was added at room temperature to a solution of **15** (0.09−0.14 mmol) in THF (10 mL). The mixture was heated at reflux for 7 h, followed by addition of a aqueous $NaHCO_3$ (10%) and extraction with CH_2Cl_2 (10 mL × 2). The combined organic extracts were dried with $MgSO_4$. After removal of the solvent in vacuo, the residue was chromatographed on a silica gel column (2 × 10 cm; EtOAc/*n*-hexane, 1:1) to give compound **16**.

1-(2-Acetamidophenyl)-4,5-diphenylpyrazole (16a): M.p. 117−119 °C (EtOAc/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3320, 3040, 2912, 1686, 1590, 1513, 1444, 1366, 1294, 763, 692 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.15 (s, 3 H, CH_3), 6.75 (d, *J* = 2.7 Hz, 1 H, ArH), 6.87 (t, *J* = 7.7 Hz, 1 H, ArH), 7.05−7.12 (m, 2 H, ArH), 7.21−7.46 (m, 9 H, ArH), 8.02 (s, 1 H, N=CH), 8.37 (d, *J* = 8.2 Hz, 1 H, ArH), 8.93 (s, 1 H, NH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.4, 122.5, 123.2, 123.9, 126.3, 127.2, 127.6, 128.4, 129.0, 129.10, 129.16, 129.19, 129.6, 130.6, 132.6, 134.1, 141.1, 141.4, 168.9. $C_{23}H_{19}N_3O$ (353.42): calcd. C 78.16, H 5.42, N 11.89; found C 78.21, H 5.46, N 11.90.

1-(2-Acetamidophenyl)-4-*tert*-butyl-5-phenylpyrazole (16c): M.p. 141−143 °C (EtOAc/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3312, 3048, 2952, 1688, 1590, 1516, 1441, 1360, 1294, 1225, 961, 764, 696 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 1.24 [s, 9 H, $C(CH_3)_3$], 2.14 (s, 3 H, CH_3), 6.74−6.83 (m, 2 H, ArH), 7.13−7.23 (m, 3 H, ArH), 7.24−7.35 (m, 3 H, ArH), 7.76 (s, 1 H, N=CH), 8.27 (d, *J* = 8.2 Hz, 1 H, ArH), 8.79 = (s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 25.4, 30.9, 32.2, 122.5, 123.5, 126.3, 127.4, 128.5, 128.8, 129.1, 131.2, 131.4, 132.0, 134.4, 139.4, 141.7, 168.7. $C_{21}H_{23}N_3O$ (333.43): calcd. C 75.65, H 6.95, N 12.60; found C 75.52, 6.97, N 12.54.

1-(2-Acetamidophenyl)-5-(4-fluorophenyl)-4-methylpyrazole (16i): M.p. 161−163 °C (EtOAc/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3216, 3000, 2912, 1681, 1590, 1536, 1505, 1451, 1361, 1297, 1217, 1153, 836, 811, 752 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.14 (s, 3 H, $COCH_3$), 2.18 (s, 3 H, CH_3), 6.67 (d, *J* = 7.8 Hz, 1 H, ArH), 6.87 (t, *J* = 7.5 Hz, 1 H, ArH), 6.97−7.14 (m, 4 H, ArH), 7.25−7.34 (m, 1 H, ArH), 7.71 (s, 1 H, N=CH), 8.37 (d, *J* = 8.2 Hz, 1 H, ArH), 9.10 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 9.7, 25.4, 116.2 ($^2J_{C-F}$ = 21.6 Hz), 116.4, 123.2, 123.9, 126.0 ($^4J_{C-F}$ = 3.2 Hz), 127.1, 128.9, 129.1, 131.8 ($^3J_{C-F}$ = 8.4 Hz), 133.9, 141.1, 142.4, 162.9 ($^1J_{C-F}$ = 247.7 Hz), 168.8. $C_{18}H_{16}FN_3O$ (309.34): calcd. C 69.89, H 5.21, N 13.58; found C 69.94, H 5.18, N 13.63.

1-(2-Acetamidophenyl)-5-(4-methoxyphenyl)-4-(*p*-tolyl)pyrazole (16k): M.p. 108−110 °C (EtOAc/*n*-hexane). IR (KBr): $\tilde{\nu}$ = 3258, 3008, 1687, 1601, 1515, 1496, 1440, 1364, 1286, 1243, 1179, 950, 760, 726 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): δ = 2.15 (s, 3 H, $COCH_3$), 2.33 (s, 3 H, CH_3), 3.80 (s, 3 H, OCH_3), 6.76−6.90 (m, 2 H, ArH), 7.03−7.26 (m, 7 H, ArH), 7.30−7.43 (m, 2 H, ArH), 7.97 (s, 1 H, N=CH), 8.38 (d, *J* = 8.2 Hz, 1 H, ArH), 8.94 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): δ = 21.5, 27.3, 55.5, 114.4, 121.7, 122.2, 128.2, 128.8, 128.9, 129.2, 129.6, 130.2, 131.3, 132.1, 136.2, 136.5, 137.3, 140.2, 140.4, 160.0, 173.8. $C_{25}H_{23}N_3O_2$ (397.47): calcd. C 75.54, H 5.83, N 10.57; found C 75.49, H 5.88, N 10.61.

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[11] The X-ray diffraction data were collected at 293 K with an Enraf−Nonius CAD 4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71070 Å). Crystal data for **7f**: $C_{22}H_{16}FN_3S$, triclinic, $P\bar{1}$, *a* = 9.534(9), *b* = 9.721(9), *c* = 10.832(9) Å, α = 69.17(8), β = 72.98(9), γ = 88.83(9)°, *V* = 893.2(14) $Å^3$, *Z* = 2, $\rho_{calcd.}$ = 1.388 gcm^{-3}, *F*(000) = 388, θ = 2.11−21.99°, 2188 measured reflections, 1613 [*R*(int) = 0.0422] independent reflections, $R(F) = 0.0610$ [$F > I\sigma(F)$], $wR = 0.2023$, *GOF* = 1.053. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-167576. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21 EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
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