Synthesis of Substituted α,β-Unsaturated Ketones, Pyrazoles, Isoxazoles and 2,4,6-Triarylpyrylium Chlorophosphates via β-Lithiation of Benzotriazolylvinyl Ethyl Ether

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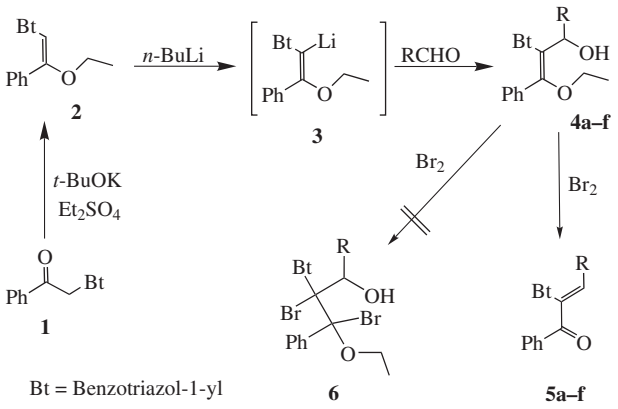
Abstract: Quenching the β-lithiated benzotriazolylvinyl ethyl ether **2** with aldehydes, acid chlorides and chalcones provided the corresponding β-hydroxyalkyl derivatives **4a–f**, β-keto vinyl ethers **7a**,**b**, and Michael adducts **8a**,**b**, respectively. The alkylated product **4** was converted into α,β-unsaturated ketones **5a–f** upon treatment with bromine. β-Keto vinyl ethers **7a**,**b** cyclocondensed with hydrazines to afford pyrazoles **9a–d**, and with hydroxylamine hydrochloride to give isoxazoles **10a**,**b**. Treatment of **8** with phosphorus pentachloride resulted in the formation of 2,4,6-triarylpyrylium chlorophosphates **12**.

Key words: heteroatom, β-lithiation, vinyl ethyl ether, benzotriazole, electrophile

Heteroatom-assisted metalations are important tool for the functionalization of carbocyclic-aromatic and heteroaromatic compounds, and regioselective *ortho*-lithiation at an sp^2-hybridized ring carbon directed by heteroatom bearing substituent.[1] Recently, the generation and reaction of sp^2 carbanionic centers in the proximity of heterocyclic nitrogen atom have been reported.[2] The metalation without the assistance of an activating group is often difficult to achieve due to charge repulsion of the heteroatom lone pair, and low acidity of the hydrogen to be abstracted. Repulsion between the lone pair of nitrogen atom and negative charge considerably reduces the thermodynamic stability.

Regioselective metalation of vinyl ethers has received considerable attention. McDougal and Rico reported the β-lithiation by *sec*-butyllithium of methoxymethyl vinyl ether, which was then reacted with a variety of electrophiles.[3,4] *cis*-2-Ethoxyvinyl lithium has been synthesized by transmetalation from the corresponding tin derivative.[5,6] Lithiation of vinyl ethers is known to proceed smoothly at the α-position upon treatment with organolithium compounds at low temperature,[7,8] and the pressure of additional directing groups such as halogens or thioaryl groups generally assist and stabilize the lithiation product by intramolecular interaction.

Benzotriazole is a good activating group for α-lithiations,[9–12] serving as both a strong electron-withdrawing and coordinative group during the lithiation. These two properties can facilitate metalation. We report herein the β-lithiation of benzotriazolylvinyl ethyl ether **2** and the subsequent reactions with various electrophiles provide a method of producing substituted derivatives (e.g. α,β-unsaturated ketones, pyrazoles, and isoxazoles) and 2,4,6-triarylpyrylium chlorophosphates (Schemes 1 and 2).



For designation of R in **4** and **5** see Table 1

Scheme 1

α-Benzotriazolyl-substituted ketones have been used as a precursor for the synthesis of various useful organic compounds.[13–15] Thus, simply mixing benzotriazol-1-ylacetophenone (**1**) with diethyl sulfate in dimethyl sulfoxide in the presence of *t*-BuOK at room temperature afforded α-phenyl-β-benzotriazolylvinyl ethyl ether (**2**) in excellent yield (Scheme 1). The ^{1}H NMR spectrum showed a characteristic signal at approximately 7.10 ppm, which was assigned to the proton attached to the double bond. The *cis* orientation of the ethoxy group and the vinylic proton was established by NOE: irradiation of the vinylic proton of **2** at 7.10 ppm showed NOE effects on the methylene protons at 3.68 ppm.

Compound **2** was used to study the effect of the nitrogen atom in the assisted β-lithiation of vinyl ether. Treatment of compound **2** with 1.3 equivalents of *n*-butyllithium at –78 °C followed by quenching with a variety of electrophiles such as aldehydes, acid chlorides and chalcones gave the corresponding β-hydroxyalkyl derivatives **4a–f**, β-keto vinyl ethers **7a**,**b**, and Michael adducts **8a**,**b**, respectively, in good yields. The structures of the alkyated product **4**, **7** and **8** were confirmed on the basis of their

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spectral data as summarized in the experimental section. The alkylated products **4** were subsequently treated with bromine in CH_2Cl_2 at 0–25 °C to give only the corresponding α,β-unsaturated ketones **5a–f** in 62–76% instead of the expected products of type **6** (Scheme 1, Table 1). The reactivity of the β-keto vinyl ether **7** towards certain nitrogen nucleophiles was also investigated. Thus, treatment of compound **7** with hydrazines, and hydroxylamine hydrochloride in refluxing ethanol provided pyrazoles **9a–d**, and isoxazoles **10a**,**b**, respectively, in good yields (Scheme 2, Table 1).

An alternative route for the synthesis of 2,4,6-triarylpyrylium salts utilizing enol ethers **8** was investigated for R = Ph. Thus, treatment with perchloric acid at 70–90 °C or heating with *p*-TsOH in boiling toluene for 24 hours gave the diketone **11**, whereas heating in toluene with 3 equivalents of phosphorus pentachloride at 80–100 °C gave the pyrylium salts **12a**,**b** in good yields (Scheme 2, Table 1).

In summary, α-phenyl-β-benzotriazolylvinyl ethyl ether underwent facile β-lithiation, most likely due to coordination of nitrogen of the benzotriazole moiety towards lithium via a four-membered ring complex. Quenching the β-lithiated vinyl ethyl ether **3** with a variety of electrophiles provided the corresponding alkylated products, which were used as precursors for the synthesis of various useful organic compounds.

All mps are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini (300 MHz) spectrometer in $CDCl_3$ with TMS as the internal standard. Microanalyses were performed on a Carlo Erba 1106 elemental analyzer.

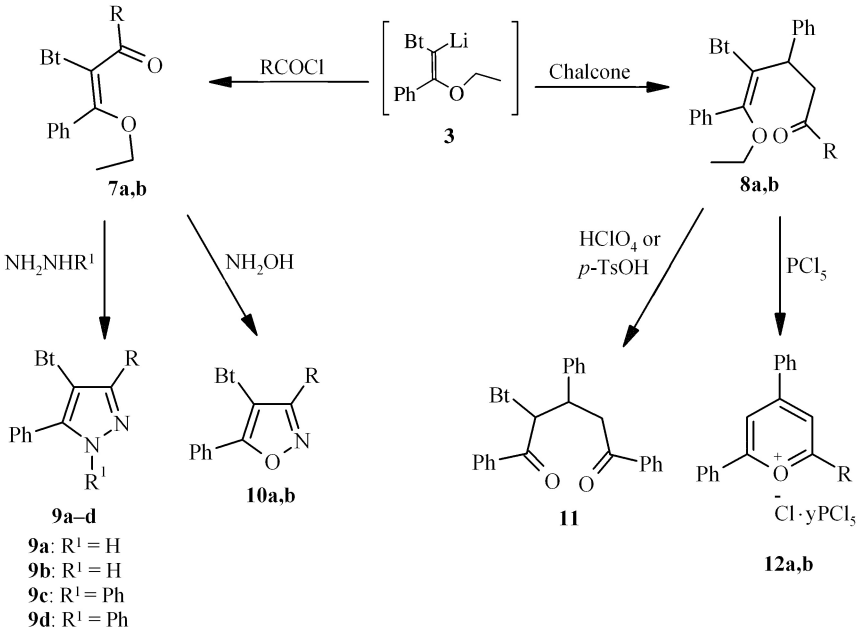
Table 1 Synthesis of Novel Benzotriazole Derivatives **4**,**5**,**7–10**, and Pyrylium Salts **12**

Entry	R	Yield (%)	Entry	R	Yield (%)
4a	4-$CH_3C_6H_4$	69	**7a**	C_6H_5	83
4b	4-$CH_3OC_6H_4$	82	**7b**	4-$CH_3C_6H_4$	72
4c	4-ClC_6H_4	65	**8a**	C_6H_5	78
4d	pyridin-4-yl	71	**8b**	4-$CH_3C_6H_4$	65
4e	$(CH_3)_2CH$	65	**9a**	C_6H_5	77
4f	C_2H_5	60	**9b**	4-$CH_3C_6H_4$	84
5a	4-$CH_3C_6H_4$	76	**9c**	C_6H_5	82
5b	4-$CH_3OC_6H_4$	71	**9d**	4-$CH_3C_6H_4$	79
5c	4-ClC_6H_4	75	**10a**	C_6H_5	82
5d	pyridin-4-yl	62	**10b**	4-$CH_3C_6H_4$	75
5e	$(CH_3)_2CH$	67	**12a**	C_6H_5	77[a]
5f	C_2H_5	73	**12b**	4-$CH_3C_6H_4$	71

[a] Lit.[16] yield = 36%.

2-Benzotriazol-1-yl-1-ethoxy-1-phenylethene (2)

A mixture of α-benzotriazol-1-ylacetophenone (**1**; 3.6 g, 15 mmol), diethyl sulfate (4.6 g, 30 mmol) and *t*-BuOK (3.4 g, 30 mmol) was stirred in DMSO (20 mL) at r.t. for 3 h. The mixture was poured into ice water (50 mL) and extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed several times with H_2O and dried ($MgSO_4$, 5 g). The solvent was removed in vacuo and the resulting oil was purified by column chromatography (silica gel,



For designation of R in **7–10** and **12** see Table 1

Scheme 2

CH_2Cl_2–hexanes, 2:1) to afford **2**; yield: 3.82 g (96%); mp 67–69 °C.

^{1}H NMR: δ = 8.07 (d, *J* = 8.4 Hz, 1 H), 7.69–7.55 (m, 8 H), 7.10 (s, 1 H), 3.68 (q, *J* = 7.0 Hz, 2 H), 1.07 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR: δ = 153.1, 145.2, 133.2, 133.1, 129.6, 128.6, 127.3, 126.7, 123.8, 119.5, 111.5, 106.3, 67.2, 14.9.

Anal. Calcd for $C_{16}H_{15}N_3O$ (265.32): C, 72.43; H, 5.70. Found C, 72.65; H, 6.01.

Reaction of Lithiated 2-Benzotriazol-1-yl-1-ethoxy-1-phenylethene (2) with Electrophiles; Compounds 4, 7, and 8; General Procedure

To a solution of **2** (1.3 g, 5 mmol) in anhyd THF (20 mL) was added a 1.6 M solution of *n*-BuLi in pentane (1.3 equiv, 4 mL, 6.5 mmol) at –78 °C. The mixture was stirred at –78 °C for 2 h, and a solution of the electrophile (7 mmol, 1.4 equiv) in THF (5 mL) was added. The reaction mixture was then stirred at –78 °C for 4 h and further 12 h at r.t. The mixture was then poured into aq sat. NH_4Cl solution and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with H_2O (25 mL), dried ($MgSO_4$) and concentrated in vacuo. The products were isolated by column chromatography (eluent: EtOAc–hexanes, 1:30, then 1:10).

(*E*)-2-(Benzotriazol-1-yl)-3-ethoxy-1-(4-methylphenyl)-3-phenylprop-2-en-1-ol (4a)

Yield: 1.32 g (69%); mp 87–89 °C.

^{1}H NMR: δ = 8.00 (d, *J* = 8.2 Hz, 1 H), 7.67 (d, *J* = 8.0 Hz, 1 H), 7.58–7.12 (m, 11 H), 6.18 (d, *J* = 10.1 Hz, 1 H), 4.56 (d, *J* = 10.1 Hz, 1 H), 3.55 (q, *J* = 7.2 Hz, 2 H), 2.17 (s, 3 H), 0.93 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR: δ = 145.1, 140.5, 136.7, 132.9, 132.7, 128.6, 128.5, 128.4 (2 C), 128.3, 127.9, 124.7, 123.9, 119.7, 110.2, 108.0, 70.4, 66.3, 20.4, 14.6.

Anal. Calcd for $C_{24}H_{23}N_3O_2$ (385.47): C, 74.78; H, 6.01; N, 10.90. Found: C, 74.55; H, 6.24; N, 10.63.

(*E*)-2-(Benzotriazol-1-yl)-3-ethoxy-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-ol (4b)

Yield: 1.65 g (82%); mp 93–95 °C.

^{1}H NMR: δ = 8.03 (d, *J* = 8.2 Hz, 1 H), 7.62 (d, *J* = 8.2 Hz, 1 H), 7.51 –7.08 (m, 11 H), 6.13 (d, *J* = 5.8 Hz, 1 H), 4.62 (d, *J* = 5.8 Hz, 1 H), 3.84 (s, 3 H), 3.61 (q, *J* = 7.2 Hz, 2 H), 0.93 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR: δ = 159.8, 146.1, 136.2, 132.9, 132.7, 130.0, 128.6, 128.5, 128.2 (2 C), 127.8, 124.9, 124.0, 120.2, 113.8, 109.9, 70.6, 65.9, 55.7, 14.3.

Anal. Calcd for $C_{24}H_{23}N_3O_3$ (401.47): C, 71.80; H, 5.77; N, 10.47. Found: C, 72.03; H, 5.49; N, 10.36.

(*E*)-2-(Benzotriazol-1-yl)-1-(4-chlorophenyl)-3-ethoxy-3-phenylprop-2-en-1-ol (4c)

Yield: 1.32 g (65%); mp 112–114 °C.

^{1}H NMR: δ = 8.10 (d, *J* = 8.2 Hz, 1 H), 7.70 (d, *J* = 8.2 Hz, 1 H), 7.61–7.15 (m, 11 H), 5.40 (s, 1 H), 4.09 (s, 1 H), 4.03 (q, *J* = 7.2 Hz, 2 H), 1.39 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR: δ = 149.9, 145.6, 139.9, 133.8, 132.7, 132.5, 129.9, 129.6, 128.2, 127.6, 126.3, 125.1, 124.2, 119.8, 113.4, 110.0, 70.1, 65.4, 14.3.

Anal. Calcd for $C_{23}H_{20}ClN_3O_2$ (405.89): C, 68.06; H, 4.97. Found: C, 67.88; H, 5.17.

(*E*)-2-(Benzotriazol-1-yl)-3-ethoxy-3-phenyl-1-pyridin-4-yl-prop-2-en-1-ol (4d)

Yield: 1.32 g (71%); mp 91–93 °C.

^{1}H NMR: δ = 7.92 (d, *J* = 8.5 Hz, 1 H), 7.77–7.19 (m, 7 H), 6.89 (d, *J* = 8.5 Hz, 2 H), 6.49 (d, *J* = 8.7 Hz, 2 H), 5.64 (d, *J* = 7.9 Hz, 1 H), 4.37 (d, *J* = 7.9 Hz, 2 H), 3.49–3.38 (m, 2 H), 0.77 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR: δ = 158.3, 154.8, 144.3, 134.5, 132.6, 131.2, 129.4, 128.7, 127.0, 126.1, 123.4, 119.2, 119.2, 113.1, 111.3, 71.7, 65.6, 14.6.

Anal. Calcd for $C_{22}H_{20}N_4O_2$ (372.43): C, 70.95; H, 5.41; N, 15.04. Found: C, 71.14; H, 5.49; N, 15.32.

(*E*)-2-(Benzotriazol-1-yl)-1-ethoxy-4-methyl-1-phenylpent-1-en-3-ol (4e)

Yield: 1.10 g (65%); oil.

^{1}H NMR: δ = 8.10 (d, *J* = 8.5 Hz, 1 H), 7.68–7.30 (m, 8 H), 3.97 (dd, *J* = 9.6, 9.9 Hz, 1 H), 3.71 (d, *J* = 9.9 Hz, 1 H), 3.58–3.31 (m, 2 H), 1.13–1.04 (m, 1 H), 0.85 (d, *J* = 6.4 Hz, 3 H), 0.78 (t, *J* = 7.0 Hz, 3 H), 0.66 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR: δ = 154.1, 144.6, 134.3, 131.6, 129.8, 129.6, 128.7, 127.3, 123.7, 119.6, 118.8, 112.3, 76.9, 65.4, 32.1, 19.4, 19.1, 14.7.

Anal. Calcd for $C_{20}H_{23}N_3O_2$ (337.43): N, 12.45. Found: N, 12.13.

(*E*)-2-(Benzotriazol-1-yl)-1-ethoxy-1-phenylpent-1-en-3-ol (4f)

Yield: 0.97 g (60%); oil.

^{1}H NMR: δ = 8.10 (d, *J* = 8.5 Hz, 1 H), 7.68–7.37 (m, 8 H), 4.36 (d, *J* = 8.7 Hz, 1 H), 3.64–3.34 (m, 3 H), 1.33–1.07 (m, 2 H), 0.82 (t, *J* = 7.0 Hz, 3 H), 0.73 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR: δ = 153.3, 144.8, 134.6, 130.9, 129.9, 129.2, 128.7, 127.3, 124.1, 120.4, 119.0, 109.7, 72.5, 65.8, 28.0, 14.7, 10.6.

Anal. Calcd for $C_{19}H_{21}N_3O_2$ (323.40): C, 70.57; H, 6.55; N, 12.99. Found: C, 70.28; H, 6.23; N, 12.75.

(*E*)-2-(Benzotriazol-1-yl)-3-ethoxy-1,3-diphenylpropenone (7a)

Yield: 1.53 g (83%); mp 143–145 °C.

^{1}H NMR: δ = 8.08 (d, *J* = 8.2 Hz, 1 H), 7.65 (d, *J* = 7.4 Hz, 2 H), 7.51–7.11 (m, 11 H), 3.76 (q, *J* = 7.0 Hz, 2 H), 1.09 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR: δ = 191.0, 166.1, 145.4, 137.7, 134.0, 132.3, 131.7, 131.0, 129.8, 128.7 (2 C), 128.0, 127.9, 123.9, 120.1, 1165.8, 109.9, 67.9, 15.1.

Anal. Calcd for $C_{23}H_{19}N_3O_2$ (369.43): C, 74.78; H, 5.18; N, 11.37. Found: C, 75.02; H, 4.97; N, 11.15.

(*E*)-2-(Benzotriazol-1-yl)-3-ethoxy-1-(4-methylphenyl)-3-phenylpropenone (7b)

Yield: 1.38 g (72%); mp 158–160 °C.

^{1}H NMR: δ = 8.03 (d, *J* = 8.2 Hz, 1 H), 7.69–7.14 (m, 12 H), 3.81 (q, *J* = 7.0 Hz, 2 H), 2.37 (s, 3 H), 1.03 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR: δ = 190.5, 161.2, 144.6, 136.2, 133.8, 132.0, 131.6, 130.4, 130.0, 128.8, 128.5, 127.9, 127.4, 124.6, 120.3, 118.0, 109.8, 67.6, 21.4, 14.6.

Anal. Calcd for $C_{24}H_{21}N_3O_2$ (383.45): C, 75.18; H, 5.52; N, 10.96. Found: C, 75.22; H, 5.19; N, 10.75.

(*E*)-4-(Benzotriazol-1-yl)-5-ethoxy-1,3,5-triphenylpent-4-en-1-one (8a)

Yield: 1.85 g (78%); mp 152–154 °C.

^{1}H NMR: δ = 7.97 (d, *J* = 8.2 Hz, 1 H), 7.88 (d, *J* = 7.3 Hz, 2 H), 7.68 (d, *J* = 5.8 Hz, 2 H), 7.57–6.77 (m, 14 H), 4.83 (t, *J* = 7.3 Hz,

1 H), 3.76 (q, J = 6.9 Hz, 2 H), 3.36 (dd, $^2J_{AB}$ = 7.0 Hz, ^3J = 3.0 Hz, 1 H, A part of AB system), 3.32 (dd, $^2J_{AB}$ = 6.8 Hz, ^3J = 2.5 Hz, 1 H, B part of AB system), 0.69 (t, J = 6.9 Hz, 3 H).

^{13}C NMR: δ = 197.6, 154.1, 144.7, 141.1, 136.8, 135.2, 133.0, 132.3, 129.8, 129.7, 128.9, 128.4, 128.3, 128.0, 127.3, 126.8, 126.6, 123.2, 119.7, 119.1, 110.9, 65.3, 41.4, 41.3, 14.7.

Anal. Calcd for $C_{31}H_{27}N_3O_2$ (473.58): C, 78.62; H, 5.75. Found: C, 78.94; H, 5.61.

(*E*)-4-(Benzotriazol-1-yl)-5-ethoxy-1-(4-methylphenyl)-3,5-diphenylpent-4-en-1-one (8b)
Yield: 1.59 g (65%); mp 136–138 °C.

^{1}H NMR: δ = 8.08 (d, J = 8.2 Hz, 1 H), 7.78 (d, J = 7.2 Hz, 2 H), 7.62–7.30 (m, 11 H), 7.29 (d, J = 7.7 Hz, 2 H), 7.03 (d, J = 8.3 Hz, 2 H), 4.79 (t, J = 7.3 Hz, 1 H), 3.89 (q, J = 6.9 Hz, 2 H), 3.43 (dd, $^2J_{AB}$ = 7.2 Hz, ^3J = 2.8 Hz, 1 H, A part of AB system), 3.43 (dd, $^2J_{AB}$ = 6.8 Hz, ^3J = 2.3 Hz, 1 H, B part of AB system), 2.44 (s, 3 H), 0.86 (t, J = 6.9 Hz, 3 H).

^{13}C NMR: δ = 198.1, 156.2, 145.0, 140.8, 136.5, 135.0, 133.8, 132.1, 130.1, 129.9, 128.8, 128.2, 128.0, 127.6, 126.9, 126.7, 124.0, 123.6, 119.8, 118.6, 110.4, 66.2, 42.2, 41.9, 24.0, 15.1.

Anal. Calcd for $C_{32}H_{29}N_3O_2$ (487.61): C, 78.83; H, 5.99; N, 8.62. Found: C, 78.46; H, 5.95; N, 8.85.

Substituted α,β-Unsaturated Ketones 5a–f; General Procedure
A mixture of compound **4** (3 mmol) and Br_2 (0.3 mL, 6 mmol) in CH_2Cl_2 (15 mL) was stirred for 30 min at 0 °C. The resultant mixture was allowed to attain r.t. and stirred for an additional 3 h. Then the solvent was evaporated in vacuo. The residue was subjected to column chromatography on silica gel, and eluted with a mixture of EtOAc–hexanes (1:10, then 1: 5) to give the desired product **5**.

(*E*)-2-Benzotriazol-1-yl-3-(4-methylphenyl)-1-phenylpropenone (5a)
Yield: 0.77 g (76%); mp 158–160 °C.

^{1}H NMR: δ = 8.10 (d, J = 8.5 Hz, 1 H), 7.83–7.18 (m, 13 H), 2.37 (s, 3 H), 2.17 (s, 3 H).

^{13}C NMR: δ = 189.9, 154.3, 146.0, 145.6, 133.8, 132.0, 131.5, 129.7, 128.9, 128.3, 127.9 127.6, 124.1, 119.9, 118.5, 111.7, 109.6, 21.0.

Anal. Calcd for $C_{22}H_{17}N_3O$ (339.40): C, 77.86; H, 5.05; N, 12.38. Found: C, 78.08; H, 5.13; N, 12.47.

(*E*)-2-Benzotriazol-1-yl-3-(4-methoxyphenyl)-1-phenylpropenone (5b)
Yield: 0.76 g (71%); mp 175–177 °C.

^{1}H NMR: δ = 8.11–8.06 (m, 3 H), 7.55–7.12 (m, 9 H), 7.03 (d, J = 8.8 Hz, 2 H), 3.93 (s, 3 H).

^{13}C NMR: δ = 190.3, 156.1, 145.9, 133.8, 132.5, 131.7, 130.6, 129.7, 128.6, 128.3, 127.9, 127.0, 124.1, 120.6, 119.4, 114.2, 110.1, 55.0.

Anal. Calcd for $C_{22}H_{17}N_3O_2$ (355.40): C, 74.35; H, 4.82. Found: C, 74.02; H, 4.73.

(*E*)-2-Benzotriazol-1-yl-3-(4-chlorophenyl)-1-phenylpropenone (5c)
Yield: 0.81 g (75%); mp 189–191 °C.

^{1}H NMR: δ = 8.11 (dd, J = 2.1, 7.3 Hz, 1 H), 7.80–7.18 (m, 9 H), 7.13 (d, J = 7.1 Hz, 2 H), 6.77 (d, J = 7.0 Hz, 2 H).

^{13}C NMR: δ = 190.7, 145.6, 140.1, 137.2, 136.3, 132.9 (2C), 131.5, 131.2, 129.6, 129.1, 129.0, 128.6, 128.5, 124.4, 120.1, 109.8.

Anal. Calcd for $C_{21}H_{14}ClN_3O$ (359.82): C, 70.10; H, 3.92; N, 11.68. Found: C, 70.43; H, 4.22; N, 11.41.

(*E*)-2-Benzotriazol-1-yl-1-phenyl-3-pyridin-4-yl-propenone (5d)
Yield: 0.61 g (62%); mp 138–140 °C.

^{1}H NMR: δ = 8.10 (d, J = 8.5 Hz, 1 H), 8.05 (d, J = 8.3 Hz, 1 H), 7.92–7.35 (m, 11 H).

^{13}C NMR: δ = 192.0, 151.0, 149.2, 145.8, 137.2, 133.8, 131.7, 129.1, 128.9, 127.8, 126.4, 123.6, 119.8, 118.5, 114.0, 110.2.

Anal. Calcd for $C_{20}H_{14}N_4O$ (326.36): C, 73.61; H, 4.32; N, 17.17. Found: C, 73.54; H, 4.08; N, 16.96.

(*E*)-2-Benzotriazol-1-yl-4-methyl-1-phenylpent-2-en-1-one (5e)
Yield: 0.59 g (67%); mp 110–112 °C.

^{1}H NMR: δ = 8.01 (d, J = 8.5 Hz, 1 H), 7.70 (d, J = 7.3 Hz, 2 H), 7.50–7.19 (m, 6 H), 6.83 (d, J = 10.5 Hz, 1 H), 2.41–2.31 (m, 1 H), 1.03 (d, J = 6.7 Hz, 6 H).

^{13}C NMR: δ = 190.4, 154.3, 145.3, 136.5, 133.9, 132.8, 132.0, 129.1, 128.5, 128.1, 124.0, 120.0, 109.7, 28.4, 22.1.

Anal. Calcd for $C_{18}H_{17}N_3O$ (291.36): C, 74.21; H, 5.88. Found: C, 73.93; H, 5.74.

(*E*)-2-Benzotriazol-1-yl-1-phenylpent-2-en-1-one (5f)
Yield: 0.61 g (73%); colorless microcrystals; mp 105–107 °C.

^{1}H NMR: δ = 8.02 (d, J = 8.5 Hz, 1 H), 7.67–7.21 (m, 8 H), 6.73 (t, J = 7.9 Hz, 1 H), 2.13–1.99 (m, 2 H), 0.96 (t, J = 7.0 Hz, 3 H).

^{13}C NMR: δ = 191.2, 154.1, 144.8, 136.1, 133.5, 132.4, 131.3, 129.6, 129.0, 128.2, 123.6, 119.7, 110.1, 24.8, 17.3.

Anal. Calcd for $C_{17}H_{15}N_3O$ (277.33): C, 73.63; H, 5.45; N, 15.15. Found: C, 73.42; H, 5.68; N, 15.02.

3-Substituted 1-(5-Phenylpyrazol-4-yl)benzotriazoles 9; General Procedure
To a solution of β-keto vinyl ethers **7** (3 mmol) in EtOH (20 mL) was added hydrazine hydrate or phenyl hydrazine (3.6 mmol). After refluxing the mixture until the complete conversion of the starting material (TLC control), it was concentrated under vacuum. The obtained residue was purified by column chromatography on silica gel (hexanes–EtOAc) to give **9a–d** as pure products.

1-(3,5-Diphenyl-1*H*-pyrazol-4-yl)-1*H*-benzotriazole (9a)
Yield: 0.78 g (77%); mp 154–156 °C.

^{1}H NMR: δ = 12.33 (br s, 1 H), 7.99 (d, J = 8.2 Hz, 1 H), 7.75 (d, J = 8.2 Hz, 1 H), 7.57–7.18 (m, 12 H).

^{13}C NMR: δ = 155.4, 149.3, 146.0, 140.2, 133.4, 132.7, 130.3, 130.1, 129.2, 128.4 (2 C), 128.0, 127.5, 123.9, 123.2, 119.8, 109.8.

Anal. Calcd for $C_{21}H_{15}N_5$ (337.39): C, 74.76; H, 4.48. Found: C, 74.66; H, 4.57.

1-[3-(4-Methylphenyl)-5-phenyl-1*H*-pyrazol-4-yl]-1*H*-benzotriazole (9b)
Yield: 0.89 g (84%); mp 147–149 °C.

^{1}H NMR: δ = 11.98 (br s, 1 H), 8.05 (d, J = 8.2 Hz, 1 H), 7.87 (d, J = 8.2 Hz, 1 H), 7.47–7.33 (m, 5 H), 7.29 (d, J = 7.5 Hz, 2 H), 7.18 (d, J = 8.2 Hz, 2 H), 7.08 (d, J = 8.0 Hz, 2 H), 2.27 (s, 3 H).

^{13}C NMR: δ = 162.0, 156.6, 155.5, 146.3, 140.1, 133.3, 131.1, 129.9, 129.1, 128.5, 128.0, 127.6, 126.7, 124.2, 123.6, 119.8, 110.5, 21.2.

Anal. Calcd for $C_{22}H_{17}N_5$ (351.41): C, 75.19; H, 4.88; N, 19.93. Found: C, 74.98; H, 4.52; N, 19.76.

1-(1,3,5-Triphenyl-1*H*-pyrazol-4-yl)-1*H*-benzotriazole (9c)
Yield: 1.02 g (82%); mp 168–170 °C.

^{1}H NMR: δ = 8.11 (d, *J* = 8.5 Hz, 1 H), 7.89 (d, *J* = 8.5 Hz, 1 H), 7.80–7.18 (m, 17 H).

^{13}C NMR: δ = 165.4, 163.8, 152.2, 146.3, 144.3, 141.0, 133.7, 129.1, 128.9, 128.2 (2 C), 127.8, 127.4 (2 C), 126.9, 126.1, 124.3, 123.9, 120.1, 118.3, 109.8.

Anal. Calcd for $C_{27}H_{19}N_5$ (413.49): C, 78.43; H, 4.63; N, 16.94. Found: C, 78.79; H, 4.46; N, 16.81.

1-[3-(4-Methylphenyl)-1,5-diphenyl)-1*H*-pyrazol-4-yl]-1*H*-benzotriazole (9d)
Yield: 1.01 g (79%); mp 177–179 °C.

^{1}H NMR: δ = 8.06 (d, *J* = 8.5 Hz, 1 H), 7.57–7.13 (m, 17 H), 2.29 (s, 3 H).

^{13}C NMR: δ = 161.1, 158.4, 153.6, 146.8, 141.9, 133.6, 132.1, 131.5, 129.9 (2 C), 129.3, 129.0, 128.2 (2 C), 127.7, 127.0, 126.7, 124.0, 123.6, 119.6, 111.0, 21.7.

Anal. Calcd for $C_{28}H_{21}N_5$ (427.51): C, 78.67; H, 4.95; N, 16.38. Found: C, 78.35; H, 4.67; N, 16.51.

3-Substituted-1-(5-Phenylisoxazol-4-yl)benzotriazoles 10; General Procedure
A mixture of β-keto vinyl ether **7** (3 mmol) and hydroxylamine hydrochloride (0.2 g, 3 mmol) in EtOH (20 mL) was stirred for 16 h at 65–80 °C and left to cool down to r.t. The product was precipitated by addition of H_2O (10 mL), the precipitate was filtered off, washed with toluene and recrystallized from benzene.

1-(3,5-Diphenylisoxazol-4-yl)-1*H*-benzotriazole (10a)
Yield: 0.83 g (82%); mp 156–158 °C.

^{1}H NMR: δ = 8.22 (d, *J* = 8.2 Hz, 1 H), 7.63–7.18 (m, 13 H).

^{13}C NMR: δ = 168.0, 155.1, 148.3, 144.8, 138.1, 133.6, 132.4, 131.8, 129.9, 129.1, 128.0, 127.8, 127.3, 126.6, 124.1, 120.3, 109.8.

Anal. Calcd for $C_{21}H_{14}N_4O$ (338.37): C, 74.54; H, 4.17; N, 16.56. Found: C, 74.67; H, 4.22; N, 16.43.

1-[3-(4-Methylphenyl)-5-diphenylisoxazol-4-yl]-1*H*-benzotriazole (10b)
Yield: 0.79 g (75%); mp 139–141 °C.

^{1}H NMR: δ = 8.14 (d, *J* = 8.5 Hz, 1 H), 7.75–7.36 (m, 8 H), 7.31 (d, *J* = 7.5 Hz, 2 H), 7.11 (d, *J* = 7.5 Hz, 2 H), 2.21 (s, 3 H).

^{13}C NMR: δ = 166.1, 156.3, 151.0, 146.2, 137.6, 133.2, 132.7, 131.4, 130.1, 129.0, 128.3, 127.9, 127.0, 126.9, 123.8, 119.6, 109.9, 22.3.

Anal. Calcd for $C_{22}H_{16}N_4O$ (352.40): C, 74.98; H, 4.58; N, 15.90. Found: C, 75.21; H, 4.81; N, 15.66.

2-Benzotriazol-1-yl-1,3,5-triphenylpenta-1,5-dione (11)
Compound **8a** (0.95 g, 2 mmol) was heated with either 57% $HClO_4$ (10 mL) at 70–90 °C for 1.5 h or refluxed in toluene with *p*-TsOH (0.52 g, 3 mmol) for 5 h. The mixture was cooled, and the crystals of pentadione derivative **11** was filtered off, washed with EtOH (3 × 10 mL) and recrystallized from hexanes; yield: 0.83 g (93%); mp 176–178 °C (Lit.[16] mp 177–179 °C).

^{1}H NMR: δ = 8.12 (d, *J* = 7.7 Hz, 1 H), 7.90 (d, *J* = 7.8 Hz, 2 H), 7.84 (d, *J* = 8.5 Hz, 1 H), 7.54–7.10 (m, 11 H), 6.98 (s, 5 H), 4.87 (q, *J* = 6.5 Hz, 1 H), 3.61 (d, *J* = 6.5 Hz, 2 H).

^{13}C NMR: δ = 197.5, 192.6, 146.0, 138.1, 136.6, 135.0, 134.2, 133.3, 132.2, 129.0, 128.9, 128.6, 128.5, 128.3, 128.2, 127.6, 127.4, 123.8, 119.8, 111.0, 66.5, 41.7, 41.2.

2,4,6-Triarylpyrylium Chlorophosphates 12; General Procedure
A solution of 4-benzotriazol-1-yl-5-ethoxy-1,3,5-triarylpent-4-en-1-one (**8**; 0.95 g, 2 mmol) and PCl_5 (1.25 g, 6 mmol) in anhyd toluene (50 mL) was stirred for 3 h at 80–100 °C. On cooling reaction mixture to r.t., yellow crystals were precipitated. The crystals were collected by filtration, washed with anhyd Et_2O (3 × 10 mL), and dried in vacuo over P_2O_5. Compounds **12a**,**b** are extremely hygroscopic.

2,4,6-Triphenylpyrylium Chlorophosphate (12a)
Yield: 0.69 g (77% calculated assuming y = 0.5); mp 214–218 °C (dec.) (Lit.[16] mp 210–215 °C).

^{1}H NMR: δ = 9.20 (s, 2 H), 8.82–8.68 (m, 6 H), 7.75 (s, 6 H), 7.44 (s, 3 H).

^{13}C NMR: δ = 169.9, 165.9, 135.4, 135.3, 131.8, 131.4, 130.3, 129.9, 129.2, 128.7, 115.7.

2-(4-Methylphenyl)-4,6-diphenylpyrylium Chlorophosphate (12b)
Yield: 0.66 g (71% calculated assuming y = 0.5); mp 190–194 °C (dec.).

^{1}H NMR: δ = 8.92 (s, 2 H), 8.65–8.45 (m, 6 H), 7.85 (s, 6 H), 7.54 (s, 3 H), 2.45 (s, 3 H).

^{13}C NMR: δ = 168.6, 166.2, 137.8, 135.9, 133.7, 132.6, 132.4, 132.0, 131.5, 131.0, 130.3, 129.9, 129.6, 129.0, 128.7, 128.5, 128.1,127.7, 127.3, 115.7, 23.9.

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