New Synthetic Routes to Furans and Dihydrofurans from 1-Propargylbenzotriazole

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Base-assisted cyclizations of 1-[3-[hydroxy(substituted methyl)]propargyl]benzotriazoles, derived from lithiated 1-propargylbenzotriazole (1) and aromatic aldehydes or ketones, gave 2-arylfurans **5** or 1-(5,5-diaryl-2,5-dihydrofuran-2-yl)benzotriazoles **7**, respectively, in high yields. Compounds **7** with Grignard reagents yielded trisubstituted 2,5-dihydrofurans **9**.

Furans constitute one of the most important classes of heteroaromatic compounds. The furan ring is common to many naturally occurring compounds, such as terpenoids, lipids, steroids, ionophores, and aflatoxines.[1,2] The role of furans and their hydrogenated derivatives is also significant because of the presence of the furan nucleus in the structures of a variety of commercially important pharmaceuticals, and flavor and fragrance compounds,[1,3] as well as in diverse synthetic intermediates (see a recent review[4]). Numerous synthetic approaches to furans and dihydrofurans are known (for recently reported procedures see[3,5-11] and references therein), but the most important methods all involve C–O bond formation at the key step of the heterocyclic ring construction.

Recently, efficient [3 + 2] annulations of allenylsilanes with aldehydes in the presence of $TiCl_4$,[6] of allenylsilanes with acylium ions,[3] and of the dienolate anion of ethyl 2-bromo-4-[(*tert*-butyldimethylsilyl)oxy]crotonate with aldehydes[10] have been described for the synthesis of substituted furans[3] and 2,3-dihydrofurans.[6,10] These methods, however, are limited by the relatively low availability of the starting compounds: thus, 2-bromo-4-[(*tert*-butyldimethylsilyl)oxy]crotonate has been synthesized in three steps from ethyl 4-hydroxycrotonate, *tert*-butyldimethylsilyl chloride, and imidazole with an overall 38% yield.[12] An improved four-step preparation from (bromomagnesio)(trimethylsilyl)acetylide via *N*-[3-(trimethylsilyl)-2-propynylidene]-4-methylbenzenesulfonohydrazide gave a 40% yield of (trimethylsilyl)allene.[13] Moreover, attempted annulations of allenylsilanes employing ketones did not give satisfactory results,[6] and no analogous transformations using aromatic aldehydes have been reported.

We now report a new and simple synthetic route to substituted furans and dihydrofurans using readily available 1-propargylbenzotriazole (**1**) as a three-carbon annulation unit. Recently, we described the preparation of 1-propargylbenzotriazole and some regioselective reactions of its mono- and dianions with electrophiles, which can be directed to occur on either the sp- or the sp^3-hybridized carbon atom or at both of these centers.[14] The reactions of 1-(3-lithiopropargyl)benzotriazole (generated in situ from **1** and BuLi in THF) with aromatic aldehydes or ketones yielded the addition products **2** in high yields[14] (Scheme I). These transformations have now been further developed to provide new routes to furans and to 2,5-dihydrofurans.

Compounds **2** derived from 1-propargylbenzotriazole (**1**) and aromatic aldehydes upon heating with ethanolic NaOH cyclized with the elimination of benzotriazole to give the corresponding 2-substituted furans **5** in 53–81% yield (Scheme I, Table I). This reaction is closely related to the previously reported preparations of furans from 4-(tetrahydropyran-2-yloxy)-2-butynolates[17] or allenylaluminum reagents[18] with aldehydes. Evidently, the mechanism of the presently described process (Scheme I) also includes an intermediate formation of α-allenyl alkoxides **3** (derived from the isomerization of the acetylenes **2**) followed by their intramolecular cyclization into 2,5-dihydrofurans **4**. The latter are readily aromatized under the reaction conditions with elimination of the benzotriazolyl anion to yield furans **5** (for a review of benzotriazole as a leaving group see ref 19). Significantly, the cycloeliminations of compounds **2** to furans **5** do not require treatment of the intermediate 2,5-dihydrofurans **4** with acids, which is essential for prior procedures.[17,18] Interestingly, in contrast to our reaction, **1** → **5** (Scheme I), [3 + 2] annulation of the lithio derivative of methoxyallene with ketones and aldehydes occurred via an attack of C-1 of the reagent on the carbonyl group of substrates and yielded 3-methoxy-2,5-dihydrofurans or, depending on steric factors, vinyl epoxides.[5] The feasibility of the acetylene–allene isomerization of **2** into **3** is

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Scheme I

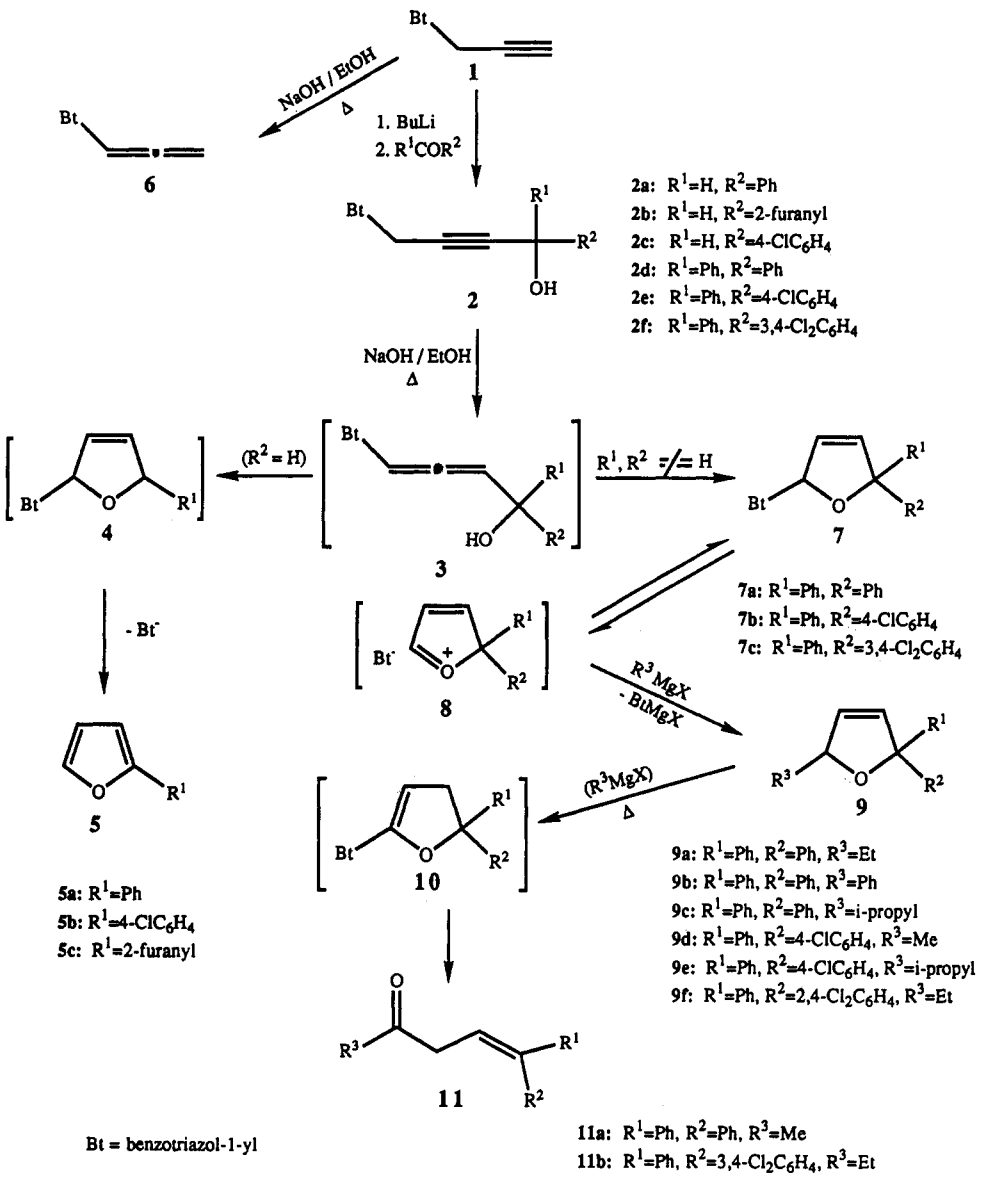

Table I. Preparation of Compounds 5a–c, 7a–c, 9a–f, 11a–b

compd. no.	isolated yield (%)	mp (°C) or bp (°C)	crystal form	Anal. found (%)			Anal. calcd (%)			molecular formula	HRMS found (%)	HRMS calcd (%)
				C	H	N	C	H	N			
5a	81	94–96/10 Torr[a]	oil							$C_{10}H_8O$	144.0567	144.0575
5b	62	75–76[b]	needles[c]							$C_{10}H_7O$		
5c	53	*d*	oil							$C_{10}H_7O$	134.0378	134.0368
7a	77	169–170	needles[c]	78.04	5.05	12.43	77.86	5.05	12.43	$C_{22}H_{17}N_3O$		
7b	68	151–152	needles[c]	70.67	4.24	11.24	70.68	4.31	11.24	$C_{22}H_{16}ClN_3O$		
7c	90	56–57	needles[c]	64.67	3.65	10.22	64.72	3.70	10.29	$C_{22}H_{15}Cl_2N_3O$		
9a	95		oil							$C_{18}H_{18}O$	250.1356	250.1358
9b	86		oil							$C_{22}H_{18}O$	298.1361	298.1358
9c	84		oil							$C_{19}H_{20}O$	264.1514	264.1514
9d	87		oil							$C_{17}H_{15}ClO$	270.0811	270.0811
9e	82		oil							$C_{19}H_{19}ClO$	298.1148	298.1124
9f	90		oil	67.34	4.92		67.72	5.05		$C_{18}H_{16}Cl_2O$		
11a	89		oil							$C_{17}H_{16}O$	236.1200	236.1201
11b	42		oil	67.57	4.87		67.72	5.05		$C_{18}H_{16}Cl_2O$		

[a] Reference 15, bp 92–95 °C/10 Torr. [b] Reference 15, mp 74–75 °C. [c] From ethanol. [d] Reference 16, oil.

demonstrated by the easy transformation of 1-propargylbenzotriazole (1) into 1-allenylbenzotriazole (6) under the reaction conditions (Scheme I).

An analogous [3 + 2] annulation of 1 with aromatic ketones resulted in the formation of 1-(5,5-diaryl-2,5-dihydrofuran-2-yl)benzotriazoles 7 in 68–90% yield (Scheme I). 2,5-Dihydrofurans **7b,c** have been isolated as mixtures of two diastereomers in ratios of ca. 1:1.3 and 1:1.5, respectively (by ^1H and ^{13}C NMR spectra). By contrast to the analogous intermediates 4 derived from 1 and aldehydes, compounds 7 were found to be relatively stable under basic conditions.

Previous papers from this laboratory demonstrated that benzotriazole-derived aminals reversibly ionize to yield

the benzotriazolyl anion and iminium cations, as shown by the structure–reactivity dependence observed, crossover experiments, and the conductivity of these compounds in solutions (for a review see ref 19). Due to such ionization, aminals of this type were able to undergo the replacement of the benzotriazole auxiliary group by Grignard and other organometallic reagents resulting in the introduction of various carbon substituents.[19,20] In view of the similar reactivity of benzotriazole-derived *N,O*- and *N,S*-acetals, an analogous S_N1 mechanism is also assumed for similar transformations in the sulfur[21] and oxygen series.[22] The reactivity of these compounds toward Grignard reagents increases in a parallel with the degree of a substitution at the acetal carbon atom, in agreement with S_N1 but not with the alternative S_N2 mechanism (cf. ref:[21] the displacement of benzotriazolate anion in *N*-[(alkylthio)-dialkylmethyl]benzotriazoles occurs smoothly, but fails for *sec*-alkyl *N,S*-acetals of this type[21]).

We have now found that 2,5-dihydrofurans of type **7** bearing a (benzotriazol-1-yl) substituent in the 2 position of the heterocyclic ring can also serve as substrates in transformations of this type. Thus, compounds **7** upon heating with Grignard reagents in toluene yielded 2,5,5-trisubstituted 2,5-dihydrofurans **9** in 82–95% yields (Scheme I). Analogously to the previously reported transformations of benzotriazole-derived animals, and of *N,O*- and *N,S*-acetals,[19,21,22] our new reaction **7** → **9** probably also occurs by a S_N1 mechanism involving ionization of the N–C bond of the *N,O*-acetal fragment of the 2,5-dihydrofurans **7** to generate cationic species **8** which then couples with the Grignard reagent to yield the product **9** (Scheme I).

Interestingly, a prolonged heating of compounds **7** with an excess of Grignard reagent in toluene (Scheme I) resulted in the formation of β,γ-unsaturated ketones **11** (Scheme I). The formation of compounds **11** probably involved a base-assisted isomerization of initially formed 2,5-dihydrofurans **9** to 2,3-dihydrofuran derivatives **10**, followed by the ring cleavage in dihydrofurans **10** to give ketones **11**. The latter process probably occurred via a deprotonation of the allylic position in compounds **10**. Previously, conversion of 2,5-dihydrofurans into their thermodynamically more stable 2,3-dihydro isomers was achieved by heating then with t-BuOK in t-BuOH.[23] Base-induced cleavage of the tetrahydrofuran ring has also been reported.[24]

In conclusion, 1-propargylbenzotriazole (**1**) has been shown to be a useful reagent for new and potentially quite general synthetic routes to furan and 2,5-dihydrofuran derivatives. The presence of the benzotriazol-1-yl substituent in the compounds of type **7** enables additional functionalizations of these 2,5-dihydrofurans (cf. with ref 19). Further studies are under way in our group to extend the presently described strategy to the synthesis of other types of heteroaromatic compounds.

Experimental Section

General. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded in $CHCl_3$. NMR spectra were taken in $CDCl_3$ except for compounds **7** which were recorded in $(CD_3)_2SO$, with tetramethylsilane as internal standard for ^1H (300 MHz) or solvent as internal standard for ^{13}C (75 MHz). Assignments for ^{13}C NMR spectra in neccessary cases were confirmed by APT experiments. Tetrahydrofuran was distilled under nitrogen immediately before use from sodium/benzophenone. All reactions with air-sensitive compounds were carried out in atmospheres of argon or nitrogen. Column chromatography was conducted with silica gel grade 60–200 mesh. Compounds **1** and **2a–f** were prepared analogously to literature procedures.[14] Analytical data for new compounds **2c,e,f** are given below.

1-Hydroxy-4-(benzotriazol-1-yl)-1-(4-chlorophenyl)but-2-yne (2c): needles, yield 75%; mp 164–15 °C (from ethanol); IR 3370 cm^{-1} (OH); ^1H NMR δ 5.41 (s, 1 H, CH), 5.59 (s, 2 H, CH_2), 7.29 (d, J = 8.5 Hz, 2 H, Ar), 7.39–7.44 (m, 3 H, Bt and Ar, overlapped), 7.52 (dd, J = 8.3 and 6.9 Hz, 1 H, Bt), 7.75 (d, J = 8.3 Hz, 1 H, Bt); ^{13}C NMR δ 37.2 (CH_2), 61.5 (CHOH), 76.4 ($CH_2C{\equiv}C$), 86.2 ($C{\equiv}C$), 109.2 (Bt), 118.6 (Bt), 123.2 (Bt), 126.6 (Bt), 127.0 (2 C, Ar), 127.3 (2 C, Ar), 131.4 (Ar), 132.2 (Bt), 138.9 (Ar), 144.9 (Bt), Anal. Calcd for $C_{16}H_{12}ClN_3O$: C, 64.54; H, 4.06; N, 14.11. Found: C, 64.63; H, 4.14; N, 14.21.

1-Hydroxy-4-(benzotriazol-1-yl)-1-(4-chlorophenyl)-1-phenylbut-2-yne (2e): needles, yield 80%; mp 130–1 °C (from ethanol); IR 3331 cm^{-1} (OH); ^1H NMR δ 5.52 (s, 2 H, CH_2), 7.21–7.50 (m, 11 H, Bt and Ar overlapped), 7.56 (d, J = 8.4 Hz, 1 H, Bt), 7.93 (d, J = 8.4 Hz, 1 H, Bt); ^{13}C NMR δ 38.4 (CH_2), 73.7 (COH), 78.8 ($CH_2C{\equiv}C$), 89.2 ($C{\equiv}C$), 109.7 (Bt), 119.7 (Bt), 124.2 (Bt), 125.9 (C, Ar), 127.4 (2 C, Ar), 127.5 (Bt), 128.0 (2 C, Ar), 128.3 (4 C, Ar), 132.2 (Bt), 133.6 (Ar), 143.0 (Ar), 143.9 (Ar), 145.7 (Bt). Anal. Calcd for $C_{22}H_{16}ClN_3O$: C, 70.68; H, 4.31; N, 11.24. Found: C, 70.63; H, 4.26; N, 11.17.

1-Hydroxy-4-(benzotriazol-1-yl)-1-(3,4-dichlorophenyl)-1-phenylbut-2-yne (2f): needles; mp 137–8 °C (from ethanol); IR 3373 cm^{-1} (OH); ^1H NMR δ 5.95 (s, 2 H, CH_2), 7.16 (s, 1 H, OH), 7.25–7.64 (m, 9 H, Bt and Ar), 8.00 (d, J = 8.5 Hz, 1 H, Bt), 8.10 (d, J = 8.3 Hz, 1 H, Bt); ^{13}C NMR δ 37.7 (CH_2), 72.0 (CHO), 80.1 ($CH_2C{\equiv}C$), 87.9 ($C{\equiv}C$), 110.7 (Bt), 119.3 (Bt), 124.3 (Bt), 125.5 (2 C, Ar), 126.0 (Ar), 127.3 (Bt), 127.6 (2 C, Ar), 128.2 (2 C, Ar), 130.0 (Ar), 130.4 (Ar), 130.8 (Ar), 132.4 (Bt), 144.7 (Ar), 145.3 (Bt), 146.9 (Ar). Anal. Calcd for $C_{22}H_{15}Cl_2N_3O$: C, 64.72; H, 3.70; N, 10.29. Found: C, 64.94; H, 3.68; N, 10.27.

General Procedure for the Preparation of 2-Substituted Furans (5a,b). A mixture of the appropriate alcohol **2a–c** (5 mmol) and sodium hydroxide (0.4 g, 10 mmol) in ethanol (50 mL) was refluxed for 12 h. Water (30 mL) and ethyl ether (50 mL) were added. The organic phase was separated, washed with water (3 × 30 mL) and dried ($MgSO_4$). Solvent was distilled in vacuo and the crude product purified by column chromatography or by recrystallization.

2-Phenylfuran (5a). Purified by column chromatography (chloroform): ^1H NMR ($CDCl_3$) δ 6.41 (dd, J = 2.1 and 1.5 Hz, 1 H, H-4 of furan), 6.60 (d, J = 3.6 Hz, 1 H, H-3 of furan), 7.23 (d, J = 7.8 Hz, 1 H, Ph), 7.34 (dd, J = 8.1 and 7.5 Hz, 2 H, Ph), 7.42 (d, J = 1.8 Hz, 1 H, H-5 of furan), 7.65 (d, J = 8.1 Hz, 2 H, Ph); ^{13}C NMR ($CDCl_3$) δ 104.9 (C-4 of furan), 111.6 (C-3 of furan), 123.7 (2 C, Ph), 127.3 (Ph), 128.6 (2 C, Ph), 130.8 (Ph), 142.0 (C-5 of furan), 153.9 (C-2 of furan).

2-(4-Chlorophenyl)furan (5b). Purified by recrystallization from ethanol: ^1H NMR ($CDCl_3$) δ 6.46 (dd, J = 3.3 and 1.8 Hz, 1 H, H-4 of furan), 6.63 (d, J = 3.4 Hz, 1 H, H-3 of furan), 7.34 (d, J = 9.0 Hz, 2 H, Ar), 7.45 (d, J = 1.8 Hz, 1 H, H-5 of furan), 7.58 (d, J = 8.8 Hz, 2 H, Ar); ^{13}C NMR δ 105.4 (C-4 of furan), 111.7 (C-3 of furan), 125.0 (2 C, Ar), 128.8 (2 C, Ar), 129.3 (Ar), 132.9 (Ar), 142.3 (C-5 of furan), 152.9 (C-2 of furan).

2,2′-Bifuryl (5c). Purified by column chromatography (chloroform–hexane 1:2): ^1H NMR ($CDCl_3$) δ 6.44 (dd, J = 3.4 and 1.8 Hz, 2 H, H-4 of furan), 6.54 (d, J = 3.4 Hz, 2 H, H-3 of furan), 7.40 (d, J = 1.8 Hz, 2 H, H-5 of furan); ^{13}C NMR δ 105.0 (C-4), 111.3 (C-3), 141.7 (5-C), 146.6 (C-2).

1-Allenylbenzotriazole (6). A mixture of 1-propargylbenzotriazole (**1**) (0.1 mol, 15.7 g) and sodium hydroxide (0.1 mol, 4.0 g) in ethanol (50 mL) was stirred at 25 °C for 10 h. Water (100 mL) was added and the mixture was extracted with diethyl ether (100 mL), washed with water (3 × 50 mL), and dried ($MgSO_4$). Solvent was evaporated in vacuo to give a crude oily

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product which was purified by recrystallization from cold diethyl ether: needles, yield 9.42 g (60%); mp 45–46 °C; ^{1}H NMR ($CDCl_3$) δ 5.79 (d, J = 6.6 Hz, 2 H, CH_2), 7.34–7.47 (m, 2 H, Bt), 7.78 (m, 2 H, CH and Bt, overlapped), 8.04 (d, J = 8.4 Hz, 1 H, Bt); ^{13}C NMR δ 88.6 (CH_2), 97.7 (CH), 110.8 (Bt), 119.8 (Bt), 124.3 (Bt), 127.6 (Bt), 131.3 (Bt), 146.2 (Bt), 201.5 (C). Anal. Calcd for $C_9H_7N_3$: C, 68.78; H, 4.49; N, 26.73. Found: C, 68.71; H, 4.47; N, 27.15.

General Procedure for the Preparation of 2-(Benzotriazol-1-yl)-5,5-diaryl-2,5-dihydrofurans (7a–c). A mixture of the appropriate alcohol **2d–f** (10 mmol) and sodium hydroxide (0.40 g, 10 mmol) in ethanol (50 mL) was stirred at 60–80 °C for 12 h. Water (50 mL) and ethyl ether (100 mL) were added. The organic phase was separated, washed with water (80 mL × 3), and dried ($MgSO_4$). Solvent was evaporated in vacuo and the crude product recrystallized from ethanol.

2-(Benzotriazol-1-yl)-5,5-diphenyl-2,5-dihydrofuran (7a): ^{1}H NMR δ 6.30 (dd, J = 5.9 and 1.4 Hz, 1 H, H-2 of furan), 7.02 (dd, J = 5.9 and 2.1 Hz, 1 H, H-3 of furan), 7.17–7.42 (m, 13 H, Bt and Ph, overlapped), 7.55 (dd, J = 2.1 and 1.4 Hz, H-4 of furan), 8.02 (d, J = 8.3 Hz, 1 H, Bt); ^{13}C NMR δ 92.9 (C-2 of furan), 98.2 (C-5 of furan), 110.9 (Bt), 119.8 (Bt), 123.4 (C-3 of furan), 124.0 (Bt), 126.2 (4 C, Ph), 127.2 (Bt), 127.6 (Ph), 127.8 (Ph), 128.2 (2 C, Ph), 128.4 (2 C, Ph), 132.0 (Bt), 139.1 (C-4 of furan), 142.5 (Ph), 143.6 (Ph), 146.7 (Bt).

2-(Benzotriazo-1-yl)-5-(4-chlorophenyl)-5-phenyl-2,5-dihydrofuran (7b). A mixture of two diastereomers in a ratio of 1:1.3: ^{1}H NMR δ 6.35 (m, 1 H, H-2 of furan), 6.98 (m 1 H, H-3 of furan), 7.16–7.38 (m, 1 H, Bt and Ar, overlapped), 7.53 (d, J = 7.3 Hz, 1 H, H-4 of furan), 8.05 (m, 1 H, Bt); ^{13}C NMR δ 92.3 (0.6 C, C-2 of furan), 92.5 (0.4 C, C-2 of furan), 95.4 (C-5 of furan), 110.3 (0.6 C, Bt), 110.5 (0.4 C, Bt), 119.3 (0.6 C, Bt), 119.4 (0.4 C, Bt), 123.4 (C-3 of furan), 123.8 (Bt), 127.0 (Bt), 125.7, 125.9, 127.1, 127.2, 127.3, 127.4, 127.6, 128.0, 128.1, 128.2 (9 C, Ar), 131.6 (0.6 C, Ph), 131.7 (0.4 C, Ph), 133.0 (0.6 C, Bt), 133.2 (0.4 C, Bt), 138.3 (C-4 of furan), 141.0 (0.6 C, Ar), 141.8 (0.4 C, Ar), 142.0 (0.4 C, Ar), 142.8 (0.6 C, Ar), 146.1 (0.6 C, Bt), 146.2 (0.4 C, Bt).

2-(Benzotriazol-1-yl)-5-(3,4-dichlorophenyl)-5-phenyl-2,5-dihydrofuran (7c). A mixture of two diastereomers in a ratio of 1:1.5: ^{1}H NMR δ 6.25 (m, 1 H, H-2 of furan), 6.85 (m, 1 H, H-3 of furan), 6.92–7.42 (m, 1 H, H-4 of furan), 6.92–7.42 (m, 12 H, Ar), 7.92 (m, 1 H, Bt); ^{13}C NMR ($CDCl_3$) δ 92.4 (0.6 C, C-2 of furan), 92.7 (0.4 C, C-2 of furan), 95.1 (0.6 C, C-5 of furan), 95.2 (0.4 C, C-5 of furan), 110.3 (0.6 C, Bt), 110.6 (0.4 C, Bt), 119.8 (0.4 C, Bt), 119.9 (0.6 C, Bt), 124.1 (0.4 C, Bt), 124.2 (0.6 C, Bt), 125.9 (C-3 of furan), 127.4 (0.4 C, Bt), 127.6 (0.6 C, Bt), 125.5, 125.7, 125.8, 126.1, 127.9, 128.2, 128.3, 128.4, 128.5, 128.6 (6 C, Ar), 130.2 (0.6 C, Ar), 132.3 (0.6 C, Ar), 132.5 (0.4 C, Ar), 138.1 (C-4 of furan), 141.5 (0.4 C, Ar), 142.4 (0.6 C, Ar), 142.9 (0.6 C, Ar), 143.9 (0.4 C, Ar), 146.5 (Bt).

General Procedure for the Preparation of 2,2,5-Trisubstituted 2,5-Dihydrofurans (9). 1.0 M Grignard reagent in diethyl ether (4 mmol) was added dropwise at 25 °C with stirring to a solution of the appropriate compound **7a–c** (2 mmol) in toluene (20 mL). The mixture was refluxed for 2 h and cooled to 25 °C. Water (50 mL) was added, followed by extraction with diethyl ether (40 mL). The organic phase was washed with water (3 × 30 mL) and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue subjected to column chromatography (chloroform) to afford pure product.

2,2-Diphenyl-5-ethyl-2,5-dihydrofuran (9a): ^{1}H NMR ($CDCl_3$) δ 0.82 (t, J = 7.4 Hz, 3 H, CH_3), 1.55 (dq, J = 13.5 and 7.4 Hz, 2 H, CH_3), 4.82 (m, 1 H, H-5 of furan), 5.81 (dd, J = 5.9 and 1.3 Hz, 1 H, H-3 of furan), 6.16 (dd, J = 5.9 and 2.2 Hz, 1 H, H-4 of furan), 7.08–7.26 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) δ 9.73 (CH_3), 28.7 (CH_2), 87.2 (C-5 of furan), 94.0 (C-2 of furan), 126.2, 126.5, 126.9, 128.0 (10 C, Ph), 129.5 (C-3 of furan), 132.8 (C-4 of furan), 145.6 (Ph), 145.8 (Ph).

2,2,5-Triphenyl-2,5-dihydrofuran (9b): ^{1}H NMR ($CDCl_3$) δ 5.94 (dd, J = 2.4 and 1.5 Hz, 1 H, H-5 of furan), 6.00 (dd, J = 5.9 and 1.5 Hz, 1 H, H-4 of furan), 6.44 (dd, J = 5.9 and 2.4 Hz, 1 H, H-3 of furan), 7.17–7.44 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$) δ 87.9 (C-5 of furan), 95.0 (C-2 of furan), 126.2, 126.8, 127.1, 127.2, 127.9, 128.1, 128.2, 128.4, 128.7 (15 C, Ph), 130.2 (C-4 of furan), 132.8 (C-3 of furan), 140.8 (Ph), 145.2 (Ph), 145.3 (Ph).

2,2-Diphenyl-5-isopropyl-2,5-dihydrofuran (9c): ^{1}H NMR ($CDCl_3$) δ 0.77 (d, J = 6.8 Hz, 3 H, CH_3), 0.87 (d, J = 6.8 Hz, 3 H, CH_3), 1.73 (dq, J = 6.8 and 13.4 Hz, 1 H, CH), 4.56 (m, 1 H, H-5 of furan), 5.86 (dd, J = 6.0 and 1.4 Hz, 1 H, H-4 of furan), 6.23 (dd, J = 6.0 and 2.1 Hz, 1 H, H-3 of furan), 7.07–7.29 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) δ 18.3 (CH_3), 18.9 (CH_3), 33.2 (CH), 91.4 (C-5 of furan), 93.9 (C-2 of furan), 126.2 (2 C, Ph), 126.9 (2 C, Ph), 127.9 (C-4 of furan), 128.0 (2 C, Ph), 128.3 (2 C, Ph), 133.3 (C-3 of furan), 145.7 (Ph), 145.8 (Ph).

2-(4-Chlorophenyl)-2-phenyl-5-methyl-2,5-dihydrofuran (9d). A mixture of two diastereomers in a ratio of 1:1: ^{1}H NMR ($CDCl_3$) δ 1.33 (dd, J = 6.4 and 6.5 Hz, 3 H, CH_3), 5.05 (m, 1 H, H-5 of furan), 6.18 (dd, J = 5.9 and 2.3 Hz, 1 H, H-3 of furan), 7.15–7.33 (m, 9 H, Ar); ^{13}C NMR ($CDCl_3$) δ 21.7 (CH_3), 81.9 (0.5 C, C-5 of furan), 82.0 (0.5 C, C-5 of furan), 93.8 (0.5 C, C-2 of furan), 93.9 (0.5 C, C-2 of furan), 126.2, 126.4 (2 C, Ar), 127.1 (0.5 C, Ph), 127.2 (0.5 C, Ph), 127.8, 127.9, 128.0, 128.1 (6 C, Ar), 131.4 (C-4 of furan), 131.9 (C-3 of furan), 132.8 (Ph), 144.0 (0.5 C, Ar), 144.6 (0.5 C, Ar), 144.8 (0.5 C, Ar), 145.4 (0.5 C, Ar).

2-Phenyl-2-(4-chlorophenyl)-5-isopropyl-2,5-dihydrofuran (9e). A mixture of diastereomers in a ratio of 1:1: ^{1}H NMR ($CDCl_3$) δ 0.75 (d, J = 6.7 Hz, 3 H, CH_3), 0.84 (dd, J = 6.8 and 6.8 Hz, 3 H, CH_3), 1.68 (m, 1 H, CH), 4.63 (m, 1 H, H-5 of furan), 5.84 (m, 1 H, H-4 of furan), 6.16 (m, 1 H, 3-H of furan), 7.04–7.24 (m, 9 H, Ar); ^{13}C NMR ($CDCl_3$) δ 18.2 (0.5 C, CH_3), 18.3 (0.5 C, CH_3), 18.8 (CH_3), 33.1 (CH), 91.5 (C-5 of furan), 93.4 (0.5 C, C-2 of furan), 93.5 (0.5 C, C-2 of furan), 126.0 (Ar), 126.2 (Ar), 126.5 (2 C, Ar), 127.6 (Ar), 127.8 (Ar), 128.0 (Ar), 128.1 (2 C, Ar), 128.7 (C-4 of furan), 132.7 (Ph), 132.8 (C-3 of furan), 144.3 (0.5 C, Ar), 144.5 (0.5 C, Ar), 145.2 (0.5 C, Ar), 145.3 (0.5 C, Ar).

2-(3,4-Dichlorophenyl)-2-phenyl-5-ethyl-2,5-dihydrofuran (9f). A mixture of diastereomers in a ratio of 1:1: ^{1}H NMR ($CDCl_3$) δ 0.82 (m, 3 H, CH_3), 1.53 (m, 2 H, CH_2), 4.81 (m, 1 H, H-5 of furan), 5.86 (dd, J = 6.0 and 1.2 Hz, H-4 of furan), 6.12 (dd, J = 6.0 and 2.2 Hz, 1 H, H-3 of furan), 7.00–7.30 (m, 7 H, Ar), 7.38 (s, 1 H, Ar); ^{13}C NMR ($CDCl_3$) δ 9.7 (0.5 C, CH_3), 9.8 (0.5 C, CH_3), 28.7 (CH_2), 87.5 (C-5 of furan), 93.2 (C-2 of furan), 125.7, 125.9, 126.0, 126.1, 126.2, 126.3, 127.2, 127.3, 128.1, 128.2, 128.3, 128.4, 128.6, 129.9 (8 C, Ar), 130.4 (C-4 of furan), 130.8 (Ph), 131.7 (C-3 of furan), 132.0 (0.5 C, Ar), 132.1 (0.5 C, Ar), 144.4 (0.5 C, Ar), 144.6 (0.5 C, Ar), 146.0 (0.5 C, Ar), 146.3 (0.5 C, Ar).

General Procedure for the Preparation of β,γ-Unsaturated Ketones (11a,b). 1.0 M Grignard reagent in diethyl ether (4 mmol) was added dropwise at 25 °C with stirring to a solution of the appropriate compound **7a,c** (2 mmol) in toluene (20 mL). The mixture was refluxed for 48 h and cooled to 25 °C. Water (50 mL) was added, followed by extraction with diethyl ether (40 mL). The organic phase was washed with water (3 × 30 mL) and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue subjected to column chromatography (chloroform–hexanes 1:1) to afford pure product as the major fraction.

5,5-Diphenylpent-4-en-2-one (11a): IR 1712 cm^{-1} (OH); ^{1}H NMR δ 2.09 (s, 3 H, CH_3), 3.25 (d, J = 7.3 Hz, 2 H, CH_2), 6.28 (t, J = 7.3 Hz, 1 H, CH=), 7.11–7.40 (m, 10 H, Ph); ^{13}C NMR δ 29.7 (CH_3), 44.5 (CH_2), 120.4 (CH=), 127.2 (2 C, Ph), 128.0 (2 C, Ph), 128.2 (2 C, Ph), 128.3 (2 C, Ph), 129.5 (2 C, Ph), 139.3 (Ph), 141.7 (Ph), 144.6 (>C=), 206.4 (CO).

6-(3,4-Dichlorophenyl)-6-phenylhex-5-en-3-one (11b). A mixture of two geometric isomers in a ratio of ca. 1.5:1: IR 1708 cm^{-1} (CO); ^{1}H NMR δ 0.95 (dd, J = 7.3 and 7.2 Hz, 3 H, CH_3), 2.31 (m, 2 H, CH_2CO), 3.14 (m, 2 H, CH_2), 6.23 (m, 1 H, CH=), 6.92–7.39 (m, 8 H, Ar); ^{13}C NMR δ 17.8 (CH_3), 36.1 (CH_2), 43.2 (CH_2CO), 122.0 (0.4 C, CH=, minor isomer), 122.5 (0.6 C, CH=, major isomer), 126.5, 127.2, 127.6, 127.7, 128.2, 128.5, 129.0, 129.1, 129.4, 129.5, 129.9, 130.3, 131.1, 131.4, 131.5, 132.2, 132.5, 138.2, 139.4, 140.8, 141.9 (12 C, Ar), 142.3 (0.4 C, >C=, minor isomer), 142.4 (0.6 C, >C=, major isomer), 208.6 (CO).