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Synthesis and Stereochemistry of ω-Azolylalkenes [1]

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ABSTRACT

ω-Azolylalkenes **3**, **4**, *and* **5** *were synthesized by N-alkylation or C-alkylation of ω-bromoalkenes* **2**, *which were obtained either by phase transfer Wittig reactions of ω-bromoalkylphosphonium salts* **1** *with aldehydes or by Wittig reactions of ω-hydroxyalkylphosphonium salts* **6** *with aldehydes and subsequent bromination. ω-Azolylalkenes* **3** *were also directly prepared by the Wittig reaction of ω-azolylalkyltriphenylphosphonium salts* **8** *with aromatic aldehydes. The stereochemistry of these Wittig reactions was studied. © 1997 John Wiley & Sons, Inc.*

INTRODUCTION

The synthesis of biologically active azole compounds has been of continuing interest to us over many years [2–4]. Many N-vinyl azoles were found to be effective fungicides and plant growth regulators, such as diniconazole (S-3308L) and uniconazole (S-3307). Recently, we became interested in stereoselective syntheses of ω-azolylalkenes, some of them having shown potential fungicidal activities [5,6]. Here we wish to report in detail the preparation of ω-azolylalkenes **3**, **4**, and **5** by different synthetic routes.

The most convenient synthetic approach to ω-azolylalkenes **3**, **4**, and **5** is by N-alkylation or C-alkylation of ω-bromoalkenes **2**, which were easily obtained by phase transfer Wittig reactions of ω-bromoalkylphosphonium salts **1** with aldehydes, as depicted in Scheme 1.

The key ω-bromoalkenes **2** were also synthesized by bromination of ω-hydroxyalkenes **7**, which were obtained via the Wittig reaction of ω-hydroxyalkylphosphonium salts **6** with aromatic aldehydes (Scheme 2) according to a literature report [7]. However, the synthesis of **2** via this method suffers somewhat by the fact that the ω-hydroxyalkylphosphonium salts **6** could be prepared only in low to moderate yields, especially when $n = 4$ and 5; however, this method provides a synthetic approach to ω-bromoalkenes with high *E*-stereoselectivity.

Finally, the ω-azolylalkenes **3** were also prepared by the direct Wittig reaction of ω-azolylalkyltriphenylphosphonium bromides **8** with aromatic aldehydes (Scheme 3). Since the phosphonium salts **8** were obtained via a facile solid/liquid N-alkylation of ω-bromoalkylphosphonium salts **1** with 1H-1,2,4-triazole or imidazole, this synthetic approach supplies another convenient route to ω-azolylalkenes **3**.

Dedicated to Professor W. E. McEwen on the occasion of his 75th birthday.

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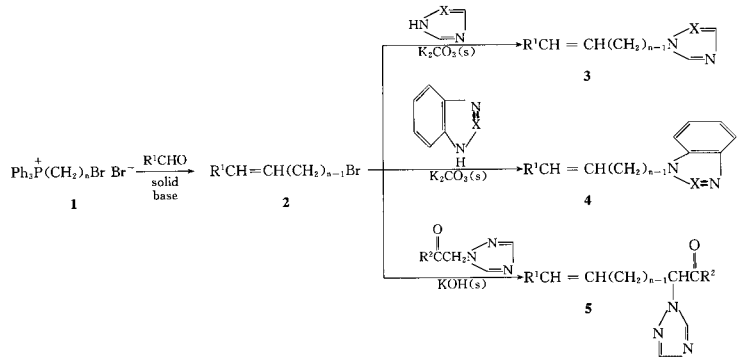

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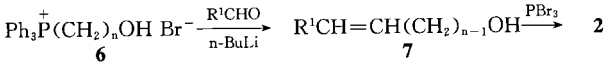

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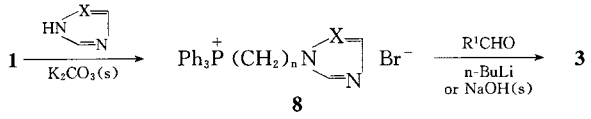

SCHEME 3

RESULTS AND DISCUSSION

Preparation of the ω-Bromoalkenes 2

ω-Bromoalkenes are important intermediates in the preparation of some pharmaceutical compositions, pheromones or other natural products [8–11]. They were usually obtained after multistep reactions [11,12]. The Wittig reaction of the easily accessible ω-bromoalkyltriphenylphosphonium salts **1** with aldehydes might be an attractive method to ω-bromoalkenes **2**; however, an early study on this reaction using RONa as base resulted in a complex mixture of the alkenes [13]. These can be due to partial elimination of HBr or to cyclization. The instability of the bromides **2** in the presence of strong base limited the application of the direct Wittig reaction of **1** in organic synthesis. However, when the Wittig reactions were carried out under mild phase transfer conditions, we found that the reactions took place smoothly and ω-bromoalkenes **2** were obtained in satisfactory yields [14]. No other by-products were found by gas chromatography–mass spectra (GC-MS) detection.

This process proved to be efficient with different aldehydes and with different carbon chain lengths of the phosphonium salts; however, different reaction conditions had to be employed with various kinds of aldehydes. When a benzaldehyde substituted with an electron-withdrawing group was used, a good yield of 2 was obtained by employing solid NaOH as base. When there was an electron-releasing substituent on the benzaldehyde, the use of solid KOH resulted in a better yield. The K_2CO_3 (s)/dioxane system was found to be effective when aliphatic aldehydes were used. The results and spectral data of some new ω-bromoalkenes are listed in Tables 1 and 2.

The stereochemistry of this reaction is obviously related to the solvent used. When tetrahydrofuran or dioxane is used, the reaction is *Z*-selective; however, when methylene dichloride is employed, the *Z*-selectivity of alkene formation is much lowered, this being similar to the solvent effect reported by Le Bigot and co-workers [15,16]. The polarity of the solvent might play an important role in the different stereoselectivity.

We also prepared **2** by employing the Wittig reaction of ω-hydroxylalkylphosphonium salt **6** with aldehydes and subsequent bromination with PBr_3. Although this method to prepare **2** required a multistep sequence, the ω-bromoalkenes could be obtained in one-pot reactions with anomalous *E*-stereoselectivity [7] (see Table 1).

Preparation of ω-Azolylalkenes, **3**, **4**, *and* **5** *via N-Alkylation or C-Alkylation of* **2**

Synthesis of ω-azolylalkenes **3** and **4** was easily accomplished by phase transfer N-alkylation of **2** with various azoles in the presence of PEG-600 and K_2CO_3(s). The yields are higher than 74%, as shown in Table 3. The spectral data of some new ω-azolylalkenes are listed in Table 4.

TABLE 1 Preparation of ω-Unsaturated Bromides **2**

Alkene	*R*[a]	*R*[1]	*n*	*Method*[b]	*Solvent*	*E/Z*[c]	*Yield (%)*[d]
2a	4-NO_2		4	A	CH_2Cl_2	46/54	75
					THF	15/85	78
2b	3-NO_2		4	A	CH_2Cl_2	43/57	82
					THF	16/84	81
2c	4-Cl		4	A	CH_2Cl_2	53/47	85
					THF	12/88	83
2d	2,4-2Cl		4	A	CH_2Cl_2	43/57	89
					THF	12/88	82
2e	H		4	A	CH_2Cl_2	49/51	79
					THF	12/88	82
2f	3-Br		4	A	CH_2Cl_2	47/53	86
					THF	13/87	89
2g	2-Cl		4	A	CH_2Cl_2	48/52	82
2h	3,4-2Cl		4	A	CH_2Cl_2	61/39	91
2i	4-OCH_3		4	B	CH_2Cl_2	37/63	58
2j			4	C	Dioxane	12/88	46
2k			4	C	Dioxane	11/89	48
2l	4-Cl		6	A	THF	13/87	81
2m	4-Cl		8	A	THF	11/89	78
2n	4-Cl		10	A	THF	9/91	72
2o	H		5	D	THF	89/11	49
2p	4-F		5	D	THF	91/9	45
2q	3-F		5	D	THF	72/28	47
2r	4-Cl		5	D	THF	88/12	50
2s	3-Cl		5	D	THF	77/23	48
2t	2-Cl		5	D	THF	57/43	45
2u	3-Br		5	D	THF	80/20	49
2v	4-NO_2		5	D	THF	83/17	54
2w	3-NO_2		5	D	THF	86/14	51
2x	4-CH_3		5	D	THF	89/11	53
2y	4-OCH_3		5	D	THF	93/7	41
2z	2,4-2Cl		5	D	THF	68/32	52

[a] R^1 =  .

[b] A: 1 + R^1CHO, NaOH(s), reflux, 8–10 hours. B: 1 + R^1CHO, KOH(s), reflux, 8–10 hours. C: 1 + R^1CHO, K_2CO_3(s), 95°C, 10–12 hours. D: 6 + R^1CHO, BuLi; then PBr_3.

[c] *E*/*Z* ratios were determined by GC and checked by ^{1}H-NMR.

[d] Isolated yields based on phosphonium salts used.

The ω-azolylalkenes **5** were also synthesized by phase transfer C-alkylations of **2** with α-triazolylketones. The best results were obtained when the KOH(s)/CH_3CN/PEG-800 system was employed. The amount of α-triazolylketone used must be in excess so as to minimize the formation of dialkylated byproducts. The results and spectral data of some compounds **5** are listed in Tables 3 and 4.

Preparation of ω-Azolylalkenes **3** *by Direct Wittig Reactions of* **8** *with Aromatic Aldehydes*

ω-Bromoalkylphosphonium salts **1** reacted with 1H-1,2,4-triazole or imidazole under phase-transfer conditions to give ω-azolylalkyltriphenylphosphonium bromides **8**. The Wittig reactions of **8** with aromatic aldehydes directly led to ω-azolylalkenes **3**. When *n*-BuLi was used as the base, the reaction showed mainly *E*-selectivity: the electron-donating substituents on the benzaldehyde led to good *E*-selectivity, whereas both the presence of a strong electron-withdrawing substituent (NO_2) and ortho substitution on the benzaldehyde resulted in low selectivity. This anomalous *E*-selectivity is perhaps due to the presence of a lithium salt and the azolyl group in the ylide chain [17]. When the reaction was carried out under phase-transfer conditions (solid NaOH), either more *Z*-alkene or a nearly equal amount of isomers of **3** was obtained. The results are listed in Table 5.

In summary, we present here several synthetic methods to various ω-azolylalkenes. The different

TABLE 2 IR, MS, and ^{1}H-NMR Data of Some New Compounds **2**

Number	*IR* (cm^{-1})	*MS* (*m/z*)	^{1}*H-NMR* ($CDCl_3$, δ)
2a	1642, 1340, 970, 860, 742	269, 271 (M^+, 1:1) 190, 162, 116	2.0–2.7 (m, 4H), 3.46 (t, 2H, J = 6.6 Hz), 5.85 (dt, 1H, J = 11.8, 6.8 Hz), 6.48 (d, 1H, J = 11.8 Hz), 7.3–8.3 (m, 4H)
2b	1655, 1350, 900, 800, 732, 675	269, 271 (M^+, 1:1) 190, 162, 116	2.0–2.7 (m, 4H), 3.46 (t, 2H, J = 6.8 Hz), 5.80 (dt, 1H, Cis, J = 11.8, 7.2 Hz), 6.58 (d, 1H, cis, J = 11.8 Hz), 7.4–8.3 (m, 4H)
2c	1640, 1440, 840, 680	260 (M^+), 223, 179	1.9–2.5 (m, 4H), 3.36 (t, 2H, J = 6.8 Hz), 5.60 (dt, 1H, cis, J = 11.2, 7.0 Hz), 6.38 (d, 1H, cis, J = 11.2 Hz), 7.1–7.3 (m, 4H)
2d	1650, 1470, 868, 730	294 (M^+), 214, 185, 150	1.9–2.5 (m, 4H), 3.38 (t, 2H, J = 6.6 Hz), 5.76 (dt, 1H, cis, J = 11.4, 7.0 Hz), 6.49 (d, 1H, cis, J = 11.4 Hz), 7.1–7.5 (m, 3H)
2f	1650, 1450, 860, 800, 680	304 (M^+), 225, 197, 171, 169	1.9–2.5 (m, 4H), 3.37 (t, 2H, J = 6.8 Hz), 6.36 (t, 2H, cis, J = 11.4 Hz), 5.58 (dt, 1H, cis, J = 11.4, 6.8 Hz), 7.2–8.1 (m, 4H)
2n	1640, 1440, 835, 680	344 (M^+), 307, 263	1.9–2.6 (m, 16H), 3.38 (t, 2H, J = 6.8 Hz), 5.4–6.6 (m, 2H), 7.1–7.3 (m, 4H)
2p	1645, 1450, 980, 820	258 (M^+), 177, 135	1.64–2.57 (m, 6H), 3.41–3.82 (t, 2H), 5.52–6.57 (m, 2H), 7.19–7.52 (m, 4H)
2r	1640, 1450, 840, 730	274 (M^+), 193, 151	1.65–2.53 (m, 6H), 3.32–3.78 (t, 2H), 5.58–6.59 (m, 2H), 7.22–7.58 (m, 4H)
2u	1650, 1450, 970, 805	318 (M^+), 237, 195, 117	1.73–2.49 (m, 6H), 3.36–3.71 (t, 2H), 5.51–6.58 (m, 2H), 7.23–7.52 (m, 4H)
2v	1650, 1350, 960, 850	285 (M^+), 204, 162	1.89–2.62 (m, 6H), 3.45–4.81 (t, 2H), 5.82–6.59 (m, 2H), 7.41–8.19 (m, 4H)
2x	1650, 970, 850	254 (M^+), 173, 131	1.98–2.52 (m, 9H), 3.40–3.62 (t, 2H), 5.52–6.52 (m, 2H), 7.12–7.52 (m, 4H)
2z	1660, 965, 830	308 (M^+), 227, 185	1.87–2.57 (m, 6H), 3.32–3.49 (t, 2H), 5.65–6.81 (m, 2H), 7.24–7.48 (m, 3H)

stereochemistry of the Wittig reactions and reaction conditions were also explored. ω-Azolylalkenes with different isomer ratios can be obtained by employing one or another of the synthetic approaches, as needed.

EXPERIMENTAL

Melting points were uncorrected. ^{1}H-NMR spectra were recorded on a Varian XL-200 MHz spectrometer. Mass spectra were measured on an HP 5988A spectrometer. Infrared spectra were recorded on a Shimadzu IR-408 infrared spectrometer. Gas chromatographic analyses were performed on an HP 5988A GC-MS instrument employing a 12 m capillary column and HP-5 as the liquid phase. All solvents and materials were reagent grade and purified as required. The phosphonium salts **1** were prepared from Ph_3P and the corresponding dibromides in 72–95% yields, according to published procedure [18]. The phosphonium salts **6** were obtained by reacting Ph_3P with ω-hydroxyalkyl bromides in the presence of K_2CO_3(s) [7]. The phosphonium salts **8** were synthesized from **1** in 45–85% yields as we reported previously [17].

Preparation of ω-Bromoalkenes **2**

Method A: A mixture of **1** (0.044 mol), a substituted benzaldehyde (0.04 mol), sodium hydroxide powder (2 g, 0.05 mol), several drops of water when necessary, and an organic solvent (100 mL) was stirred at reflux for 8–10 hours, filtered, and the products separated by short column chromatography on silica gel. The *E* and *Z* alkenes that showed two peaks in their GC-MS spectra were identified by analyzing their mass spectral data. The *E*/*Z* ratio of the alkene was then determined from the peak areas, with confirmation based on ^{1}H-NMR spectral analyses.

Method B: A mixture of **1** (0.044 mol), a substituted benzaldehyde (0.04 mol), potassium hydroxide powder (2.8 g, 0.05 mol), and CH_2Cl_2 (100 mL) was stirred at reflux for 8–10 hours. After workup, **2** was obtained.

Method C: A mixture of **1** (0.044 mol), an aliphatic aldehyde (0.04 mol), potassium carbonate powder (6.9 g, 0.05 mol), and several drops of water in dioxane was stirred at 95°C for 10–12 hours. After filtration, the solvent was removed and the residue was eluted with petroleum ether through a short silica gel column to give **2**.

Method D: At − 15°C, a solution of *n*-BuLi in ether (0.04 mol) was added dropwise to a suspension of 6 (0.02 mol) in THF (30 mL) under N_2. After the mixture had been stirred for 30 minutes, a solution

TABLE 3 Preparation of x-Azolylalkenes **3**, **4**, and **5** from **2**

Compounds	*R*[a]	*R*[2]	*X*	*n*	*Formula*	*Method*[b]	*Yield (%)*[c]
3a	4-NO_2		N	4	$C_{13}H_{14}N_4O$	A	76
3b	3-NO_2		N	4	$C_{13}H_{14}N_4O$	A	81
3c	4-Cl		N	4	$C_{13}H_{14}ClN_3$	A	83
3d	2,4-2Cl		N	4	$C_{13}H_{13}Cl_2N_3$	A	78
3e	3,4-2Cl		N	4	$C_{13}H_{13}Cl_2N_3$	A	82
3f	3-Br		N	4	$C_{13}H_{14}BrN_3$	A	85
3g	2-Cl		N	4	$C_{13}H_{14}ClN_3$	A	80
3h	H		N	4	$C_{13}H_{15}N_3$	A	86
3i	H		N	5	$C_{14}H_{17}N_3$	A	76
3j	4-F		N	5	$C_{14}H_{16}FN_3$	A	82
3k	3-F		N	5	$C_{14}H_{16}FN_3$	A	75
3l	4-Cl		N	5	$C_{14}H_{16}ClN_3$	A	85
3m	3-Cl		N	5	$C_{14}H_{16}ClN_3$	A	76
3n	2-Cl		N	5	$C_{14}H_{16}ClN_3$	A	81
3o	3-Br		N	5	$C_{14}H_{16}BrN_3$	A	78
3p	4-NO_2		N	5	$C_{14}H_{16}N_4O$	A	79
3q	3-NO_2		N	5	$C_{14}H_{16}N_4O$	A	80
3r	4-CH_3		N	5	$C_{15}H_{19}N_3$	A	78
3s	4-OCH_3		N	5	$C_{15}H_{19}N_3O$	A	81
3t	2,4-2Cl		N	5	$C_{14}H_{15}Cl_2N_3$	A	85
3u	2-Cl		CH	4	$C_{14}H_{15}ClN_2$	A	74
3v	4-Cl		CH	4	$C_{14}H_{15}ClN_2$	A	78
3w	3,4-2Cl		CH	4	$C_{14}H_{14}Cl_2N_2$	A	76
3x	3-Br		CH	4	$C_{14}H_{15}BrN_2$	A	80
4a	H		CH	4	$C_{18}H_{18}N_2$	A	81
4b	2-Cl		CH	4	$C_{18}H_{17}ClN_2$	A	75
4c	4-Cl		CH	4	$C_{18}H_{17}ClN_2$	A	79
4d	H		N	4	$C_{17}H_{17}N_3$	A	85
4e	4-F		N	4	$C_{17}H_{16}FN_3$	A	82
4f	4-Cl		N	4	$C_{17}H_{16}ClN_3$	A	81
4g	2-Cl		N	4	$C_{17}H_{16}ClN_3$	A	83
5a	2-Cl	*t*-Bu		4	$C_{19}H_{24}ClN_3O$	B	85
5b	3-Br	*t*-Bu		4	$C_{19}H_{24}BrN_3O$	B	88
5c	4-F	*t*-Bu		4	$C_{19}H_{24}FN_3O$	B	90
5d	2-Cl	Ph		4	$C_{21}H_{20}ClN_3O$	B	74
5e	H	Ph		4	$C_{21}H_{21}N_3O$	B	78
5f	4-Cl	Ph		4	$C_{21}H_{20}ClN_3O$	B	82
5g	3-Br	Ph		4	$C_{21}H_{20}BrN_3O$	B	81
5h	3,4-2Cl	Ph		4	$C_{21}H_{19}Cl_2N_3O$	B	85
5i	4-F	Ph		4	$C_{21}H_{20}FN_3O$	B	81

[a] $R^1 =$  .

[b] A: K_2CO_3(s), acetone, PEG-600, Δ, 6–8 hours. B: KOH(s), CH_3CN, PEG-800, 60°C, 1–2 hours.
[c] Isolated yields based on x-bromoalkenes **2**.

of an aromatic aldehyde (0.024 mol) in THF (30 mL) was added dropwise, and the mixture was then stirred for 1 hour at room temperature. The mixture was washed with saturated sodium chloride solution (40 mL), and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic layer was dried with anhydrous magnesium sulfate. The solvent was removed to give crude 7. Then 30 mL of ether was added, and an ether solution of PBr_3 (0.007 mol, 1.90 g) was dropped very slowly into the ether solution containing 7 and 0.5 mL of pyridine with cooling by an ice bath. The mixture was maintained at room temperature for 12 hours. The mixture was washed with saturated sodium chloride solution (30 mL), and, after the usual workup, 2 was obtained.

Preparation of x*-Azolylalkenes* 3 *and* 4 *by N-Alkylation of* 2

A mixture of 2 (0.02 mol), 1H-1,2,4-triazole (0.02 mol, 1.38 g) or benzimidazole (0.02 mol, 2.36 g) or benzotriazole (0.02 mol, 2.38 g) or imidazole (0.02

TABLE 5 Preparation of x-Azolylalkenes **3** by Direct Wittig Reactions of **8** with Aromatic Aldehydes

Alkenes	*X*	*n*	*R*[a]	*Condition*[b]	*E/Z*[c]	*Yield (%)*[d]
3c	N	4	4-Cl	A	81/19	85
3d			2,4-2Cl	A	57/43	81
3e			3,4-2Cl	A	75/25	86
3f			3-Br	A	84/16	83
3g			2-Cl	A	55/45	75
3h			H	A	88/12	74
3a′			3-Cl	A	67/33	83
3b′			4-F	A	86/14	88
3c′			4-CH_3	A	77/23	82
3d′			4-OCH_3	A	88/12	70
3e′			4-$N(CH_3)_2$	A	95/5	78
3f′	CH	4	H	A	68/32	75
3g′	N	3	H	A	71/29	79
				B	23/77	64
3h′			2-Cl	A	45/55	82
				B	31/69	65
3i′			3-Cl	A	64/36	83
				B	26/74	70
3j′			4-Cl	A	64/36	86
				B	28/72	72
3k′			2-Br	A	59/41	81
				B	33/67	71
3l′			4-F	A	72/28	91
				B	31/69	75
3m′			4-CH_3	A	70/30	81
3n′			4-OCH_3	A	86/14	72
3o′			4-$N(CH_3)_2$	A	88/12	74
3p′			4-NO_2	A	49/51	76
3q′			3-Br	B	32/68	67
3r′			3-F	B	33/67	71
3s′			2,4-2Cl	B	47/53	75
3t′	CH	3	H	A	68/32	85
3u′			4-$N(CH_3)_2$	A	97/3	75
3v′			4-F	A	75/25	70
3w′			4-NO_2	A	40/60	68

[a] $R^1 =$  .

[b] A: BuLi, THF, −15 °C. B: NaOH(s), CH_2Cl_2, 40 °C, 4–6 hours.

[c] *E*/*Z* was determinated by GC and checked by ^{1}H-NMR.

[d] Isolated yields based on phosphonium salts **8**.

slowly. After 5 minutes, the reaction mixture was warmed slowly and stirred at room temperature for 12 hours. Then two volumes of petroleum ether were added to precipitate most of the phosphine oxide. After filtration, the solvent was removed and the residue was separated with acetone/ether (1:1) by being passed through a short silica gel column. The solvent was removed to give 3. Its *E*/*Z* ratio was determinated by GC and checked by ^{1}H-NMR.

Method B: A mixture of 8 (0.022 mol), an aromatic aldehyde (0.02 mol), and sodium hydroxide powder (1g, 0.025 mol) in CH_2Cl_2 (40 mL) was stirred at reflux for 4–6 hours. After the usual workup, 3 was obtained.

ACKNOWLEDGMENT

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TABLE 4 IR, MS, and ^{1}H-NMR Data of Some New Compounds **3**, **4**, and **5**

Number	*IR* (cm^{-1})	*MS* (*m/z*)	^{1}*H-NMR* ($CDCl_3$, δ)
3a	1640, 1278, 1140, 860	258 (M^+), 241, 189, 143	2.0–2.5 (m, 4H), 4.1–4.3 (m, 2H), 5.8–6.6 (m, 2H), 7.3–8.3 (m, 4H), 8.11 (s, 1H), 7.98 (s, 1H)
3c	1650, 1140, 1012, 848	247 (M^+), 180, 143	2.0–2.4 (m, 4H), 4.1–4.4 (m, 2H), 5.6–6.5 (m, 2H), 7.1–7.4 (m, 4H), 8.15 (s, 1H), 8.02 (s, 1H)
3d	1650, 1440, 1140, 960	281 (M^+), 177	1.9–2.3 (m, 4H), 4.23 (t, 2H, J = 7.4 Hz), 5.6–6.7 (m, 2H), 7.0–7.5 (m, 3H), 7.98 (s, 1H), 8.11 (s, 1H)
3f	1590, 1275, 965, 880	293 (M^+), 222, 207, 143	2.0–2.2 (m, 4H), 3.9–4.1 (m, 2H), 6.0–6.5 (m, 2H), 6.9–7.4 (m, 2H), 7.85–8.15 (m, 2H)
3j	1645, 1380, 970, 850	244 (M^+), 176, 147, 133	1.99–2.48 (m, 6H), 4.11–4.29 (t, 2H), 5.53–6.52 (m, 2H), 7.25–7.65 (m, 4H), 8.03 (s, 1H), 8.35 (s, 1H)
3l	1640, 1380, 970, 840	261 (M^+), 192, 151, 129	1.92–2.50 (m, 6H), 4.10–4.13 (t, 2H), 5.61–6.42 (m, 2H), 7.23–7.65 (m, 4H), 8.00 (s, 1H), 8.35 (s, 1H)
3p	1640, 1385, 970, 860	272 (M^+), 203, 162, 129	2.01–2.49 (m, 6H), 4.11–4.32 (t, 2H), 5.53–6.47 (m, 2H), 7.42–8.15 (m, 4H), 8.05 (s, 1H), 8.31 (s, 1H)
3r	1650, 1300, 970, 850	241 (M^+), 172, 129, 117	1.9–2.45 (m, 6H), 2.71 (s, 3H), 4.00–4.36 (t, 2H), 5.61–6.32 (m, 2H), 7.21–7.53 (m, 4H), 8.01 (s, 1H), 8.34 (s, 1H)
3t	1640, 1385, 970, 830	295 (M^+), 260, 185, 163	1.93–2.48 (m, 6H), 4.01–4.32 (t, 2H), 5.71–6.32 (m, 2H), 7.25–7.53 (m, 4H), 8.05 (s, 1H), 8.35 (s, 1H)
3v	1590, 1450, 850	248 (M^+), 151, 143, 121	1.9–2.5 (m, 4H), 4.0–4.2 (m, 2H), 5.6–6.7 (m, 2H), 7.0–7.5 (m, 4H), 7.4–7.7 (m, 2H), 7.8–7.9 (s, 1H)
3x	1590, 1475, 800, 605	292 (M^+), 263, 211, 171	1.8–2.5 (m, 4H), 3.8–4.0 (t, 2H), 6.0–6.2 (m, 2H), 6.6–7.3 (m, 4H), 7.2–7.3 (dd, 2H), 8.9 (s, 1H)
4a	1600, 1360, 970, 745	262 (M^+), 171, 144, 131	1.8–2.4 (m, 4H), 4.0–4.3 (m, 2H), 5.5–6.6 (m, 2H), 7.1–7.8 (m, 9H), 7.7–8.0 (s, 1H)
4c	1615, 1490, 970, 850	298 (M^+), 171, 131, 115	1.90–2.35 (m, 4H), 4.02–4.20 (m, 2H), 5.5–6.5 (m, 2H), 7.0–7.8 (m, 9H)
4e	1645, 1500, 1275	281 (M^+), 253, 224, 157	1.90–2.66 (m, 4H), 4.30–4.66 (m, 2H), 5.56–6.68 (m, 2H), 7.10–8.12 (m, 8H)
4f	1650, 1490, 1140	297 (M^+), 268, 240, 233	2.02–2.64 (m, 4H), 4.35–4.68 (m, 2H), 5.62–6.54 (m, 4H), 7.12–8.18 (m, 8H)
5a	1710, 1650, 1500	345 (M^+), 260, 57	1.10–1.20 (d, 9H), 1.25–2.32 (m, 6H), 5.54–6.80 (m, 2H), 5.48 (t, 1H), 7.10–7.50 (m, 4H), 7.85–8.35 (m, 2H)
5b	1705, 1650, 1505	391 (M^+), 57	1.05–1.20 (d, 9H), 1.25–2.35 (m, 6H), 5.44–6.52 (m, 3H), 6.90–7.35 (m, 4H), 7.85–8.35 (m, 2H)
5c	1710, 1670, 1505	329 (M^+), 242, 57	1.05–1.20 (d, 9H), 1.25–2.40 (m, 6H), 5.45–6.48 (m, 3H), 6.90–7.30 (m, 4H), 7.80–8.35 (m, 2H)
5d	1720, 1670, 1500	365 (M^+), 296, 105	1.25–2.45 (m, 6H), 5.50–6.55 (m, 3H), 6.90–7.62 (m, 9H), 7.90–8.15 (m, 2H)
5g	1720, 1660, 1525	411 (M^+), 105	1.20–2.52 (m, 6H), 5.42–6.55 (m, 3H), 7.05–7.60 (m, 9H), 7.84–8.20 (m, 2H)
5i	1710, 1670, 1510	349 (M^+), 280, 105	1.25–2.52 (m, 6H), 5.42–6.48 (m, 3H), 7.25–7.60 (m, 9H), 7.80–8.40 (m, 2H)

mol, 1.36 g), potassium carbonate powder (0.06 mol, 8.28 g), and PEG-600 (0.5 g) dissolved in acetone (80 mL) was stirred under reflux for 6–8 hours. The mixture was filtered, the solvent removed from the filtrate, and the residue chromatographed and eluted with ether and ethyl acetate through a short silica gel column to give **3** and **4**.

Preparation of **5** *by C-Alkylation of* **2**

A mixture of **2** (0.027 mol), an α-triazolylketone (0.04 mol), potassium hydroxide powder (0.054 mol, 3.02 g), and PEG-800 (0.5 g) dissolved in CH_3CN (100 mL) was stirred at 60°C for 1–2 hours. After filtration, the solvent was removed and the residue was passed through a short silica gel column to give **5**.

Preparation of ω*-Azolylalkenes* **3** *by Direct Wittig Reactions of* **8** *with Aromatic Aldehydes*

Method A: A solution of *n*-BuLi (0.002 mol) in ether was added dropwise to a suspension of dry phosphonium salt **8** (0.002 mol) in anhydrous THF (20 mL) at -15°C under N_2. The mixture was stirred for 30 minutes to give a red solution. A solution of aromatic aldehyde (0.002 mol) in THF was added