PENTENOLIDE ANALOGUES OF ANTIFUNGAL BUTENOLIDES: STRATEGIES TOWARDS 3,6-DISUBSTITUTED PYRANONES AND UNEXPECTED LOSS OF BIOLOGICAL EFFECT

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Pentenolide analogues of antifungal 3,5-disubstituted butenolides were prepared by oxidative cyclization of 2-(substituted aryl)hex-5-enoic acids as the key step. Given the limitations of the methodology, another approach to the title compounds based on the Pd-catalyzed carbonylative lactonization of 4-iodo-3-en-1-ols was developed, and the carbonylation conditions were optimized. While the former sequence allows only the introduction of a substituted methyl at C6, pyranones bearing a range of various C-substituents at C6 can be prepared by the latter. Somewhat surprisingly, unlike the corresponding butenolides with the same substitution pattern, the title pentenolides possess no antifungal or cytostatic activity.

Keywords: Pentenolides; Lactones; Electrophilic cyclization; Carbonylation; Stereoselective hydroalumination; Pd catalysis; Biological Activity.

Naturally occurring pentenolides, i.e. 5,6-dihydro-2*H*-pyran-2-ones display interesting biological properties, including phytotoxicity, cytotoxicity against tumour cells, antifungal and/or antimicrobial activity[1]. In terms of the relationship between activity and substitution pattern, most biologically active pentenolides can be found among 6-substituted 5,6-dihydro-2*H*-pyran-2-ones. Fostriecin[2] possessing significant antitumour activity via inhibition of protein phosphatase A is probably the most notable example. In addition, a few natural products comprising a variously substituted unsaturated δ-lactone unit as the crucial structural feature, such as podolactones[3] and CR 377[4] (**1**), have shown significant antifungal effects. Hence, having identified 3-(halophenyl)-5-[(acyloxy)methyl]-2,5-dihydrofuran-2-ones (**2**; Chart 1) as an emerging class of novel antifungal and cytotoxic agents[5], comparable with amphotericin B in antifungal potency,

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we were naturally attracted to exploring the synthesis and properties of the corresponding pyranones. Since the unsaturated lactone moiety has been proposed[6] as the crucial feature of the pharmacophore of antifungal activity, the relationship between the size of the lactone ring and the biological effect of the compounds was an important issue to be addressed.

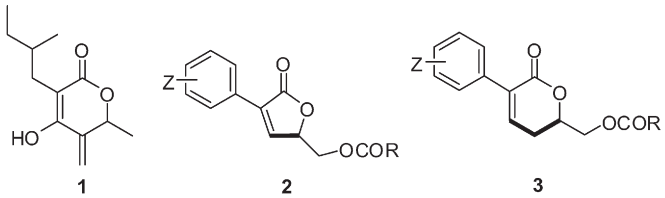


CHART 1

Following the structure of furanones **2** and the suggestion of the pharmacophore, analogous pentenolides can be logically designed by simple ring expansion into pentenolides **3** with the (acyloxy)methyl moiety being located at C6. In this paper, we wish to report the synthesis and biological evaluation of a series of 3,6-disubstituted pyranone analogues of antifungally active 3,5-disubstituted furanones.

RESULTS AND DISCUSSION

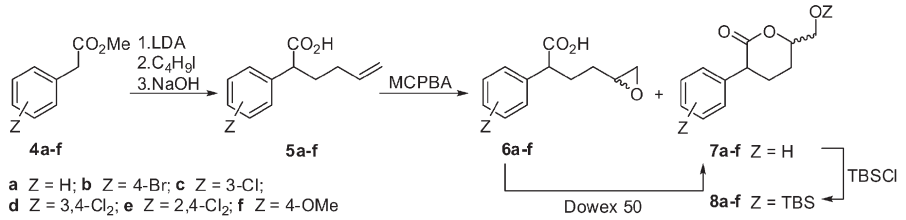
Chemistry

Since majority of biologically active pentenolides are 6-substituted pyranones[1] (vide supra) with no substitution at C3, a number of strategies leading to this class of compounds have been developed. Apart from the probably most usual cyclization of suitably substituted δ-hydroxy acids and countless modifications of this method[7–10], more recent strategies[11] involve e.g. hetero Diels–Alder reaction, Mukaiyama reactions, cyclocarbonylation of unsaturated alcohols, ring closing metathesis processes and others. On the other hand, α-arylated pyranones received little attention. However, even using the above-mentioned range of methods enabling access to 6-substituted pyranones, the preparation of target compounds **3** would involve several steps.

Thus, considering commercial availability of substituted phenylacetic acids, we resorted to classical cyclization strategy[5a,12], employed in the construction of the 3,5-disubstituted furanone unit from the $-CH_2CO_2R$ group of their methyl esters. Following the introduction of but-3-en-1-yl chain

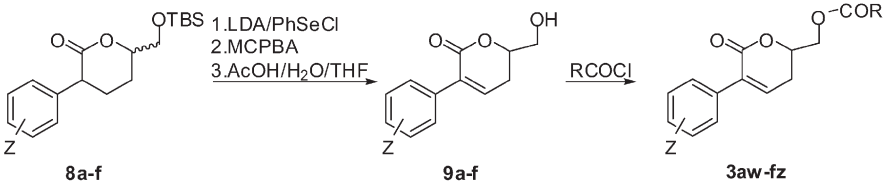
into α-position to the ester group, electrophilic cyclization in the next step would deliver C6-substituted pyranones (Scheme 1).

In the event, enolization and alkylation of methyl esters **4** with 4-iodobut-1-ene furnished the corresponding alkenyl esters, in which the carboxylic group was liberated by hydrolysis, and the resultant 2-arylhex-5-enoic acids **5** were treated with m-chloroperoxybenzoic acid. Surprisingly, unlike the corresponding pent-4-enoic acids leading to furanones[5a,12], the intermediate epoxides did not undergo spontaneous cyclization. Based on the analysis of NMR spectra, the crude reaction mixtures contained substantial amounts of unreacted epoxy acids **6** together with (hydroxymethyl)-pyranones **7**.



SCHEME 1

Since the cyclization could not be driven to completion even after prolonged heating under the reaction conditions, the mixtures were exposed to various acidic conditions, including e.g. TFA/CH_2Cl_2 [13], TsOH/$CHCl_3$, in the attempt to achieve maximum yield of pyranones **7** in one transformation. While all experiments resulted in unsatisfactory yields or even destruction of the starting material, literature search revealed several reports[14] on smooth cyclization of 5,6-dihydroxyhexanoic acids on an acid resin (Amberlyst 15) under heterogeneous conditions. Thus, exposure of the mixture of **6** and **7** to Dowex 50 in MeCN gave 61–72% yields of diastereomeric mixtures (*trans*:*cis* 2:1 by NMR) of pyranones **7**. Hence, following the epoxidation step, the solvent was replaced with MeCN, a weight equivalent of Dowex 50 was added, and the reaction sequence performed in one pot. Since the saturated lactones **7** with a free primary hydroxy group were extremely prone to ring opening, the hydroxy group was immediately protected as a TBS ether to afford silyloxy derivatives **8**. The endocyclic double bond was then introduced in a usual fashion[5a,12], i.e. via phenylselanylation/selenoxide elimination/deprotection (Scheme 2) furnishing (hydroxymethyl)-pentenolides **9**, which were esterified to yield the target 6-[(acyloxy)methyl]-pyranones **3**.



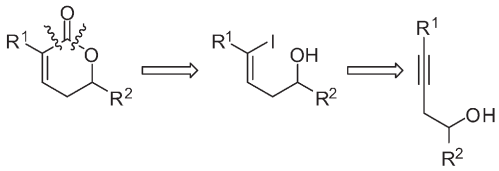
a Z = H; **b** Z = 4-Br; **c** Z = 3-Cl;
d Z = 3,4-Cl_2; **e** Z = 2,4-Cl_2; **f** Z = 4-OMe

w R = 4-ClC_6H_4; **x** R = styryl;
y R = *t*-Bu; **z** R = Me

SCHEME 2

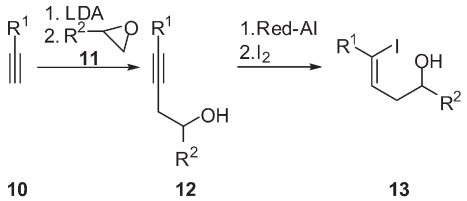
This methodology can be viewed as general with regard to substitution at C3 (the pyranone unit can be, in principle, constructed in all esters bearing the $–CH_2CO_2R$ moiety), and, if a need arises, the introduction of chirality at C6 via some of the available AE or AD procedures should also be possible. Substitution at C6, however, is limited by the range of available electrophiles, and further transformations would be needed in order to attach a C-substituent other than a substituted methyl.

In view of this limitation, we attempted to develop a more general methodology, which would allow functionalization of C6 with a wide range of C-substituents. In this regard, disconnection based on Pd-catalyzed carbonylative lactonization of suitable homoallylic alcohols appeared advantageous since the starting materials can be, in turn, prepared by hydrometallation/halogenation of easily available homopropargylic alcohols (Scheme 3). While this sequence has been used[15–17] in the synthesis of substituted butenolides from propargylic alcohols, examples of preparation of pentenolides via cyclocarbonylation processes are much less frequent, with Ru-mediated cyclocarbonylation of allenyl alcohols described by Takahashi[18] being probably the most notable example. This process, however, is not applicable to the synthesis of α-arylated compounds. Formation of pentenolides via Pd-mediated carbonylative lactonization has also been used as the terminating step of carbopalladation cascades[15b,16,19] or, again, employs allenyl alcohols as the starting materials[20].



SCHEME 3

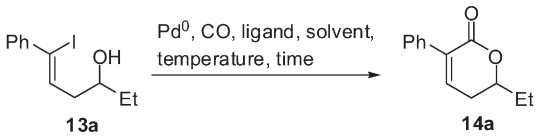
Homopropargylic alcohols **12** were prepared by nucleophilic ring-opening[21] of a range of epoxides with substituted acetylide anions, and further treated with Red-Al[22] (Scheme 4). However, it has been well established[23] that hydroalumination of homopropargylic alcohols proceeds much slower (several hours at reflux) than that of their propargylic counterparts (less than 2 h at 0 °C). In fact, in the case of R^1 = alkyl, not even a trace of the products was detected or identified after reflux for more than 6 h. Various modifications of the aluminum hydrometallating reagent, such as replacement of the alkoxy ligands on the metal by other alkoxy groups (methoxy, 2-(dimethylamino)ethoxy, ethylendioxy, ethylsulfanyl) and attempts to increase the electrophilicity of aluminum by attachment of fluorophenoxy groups gave either results comparable to Red-Al or no reaction at all.



SCHEME 4

Hence, as the hydroalumination of **12** required several hours at reflux to proceed to completion, the reaction was applicable only to homopropargylic alcohols, in which R^1 was a stable aryl moiety. The organometallic intermediates were then quenched with I_2 or *N*-iodosuccinimide to afford homoallylic alcohols **13**. An overview of the substances prepared by this sequence is shown in Table I.

Finally, alcohols **13** were subjected to cyclocarbonylation reaction, the conditions of which were optimized using **13a** as a model substrate (Scheme 5, Table II).



SCHEME 5

Somewhat surprisingly, using a common catalyst, $[PdCl_2(PPh_3)_2]$ at 60 °C, little or no progress was detected in DMF, MeCN and benzene, while notable conversions were obtained in MeOH. In DMF, which was the solvent of

TABLE I
Overview of compounds **10**–**13**

10	**11**	**12** and **13**					
R^1	R^2	**12**	R^1	R^2	Yield %	**13**	Yield %
Ph	Ph	**12a**	Ph	Et	92	**13a**	70
3F-C_6H_4	but-3-en-1-yl	**12b**	Ph	but-3-en-1-yl	76	**13b**	64
pyridin-3-yl	$PhOCH_2$	**12c**	Ph	$PhOCH_2$	64	**13c**	57
1-$C_{10}H_7$	(*S*)-Ph	**12d**	Ph	(*S*)-Ph	42	**13d**	72
	Bu	**12e**	Ph	Bu	85	**13e**	70
		12f	pyridin-3-yl	$PhOCH_2$	77	**13f**	69
		12g	pyridin-3-yl	Ph	41	**13g**	43
		12h	pyridin-3-yl	but-3-en-1-yl	50	**13h**	47
		12i	3F-Ph	Bu	88	**13i**	65
		12j	3F-Ph	$PhOCH_2$	74	**13j**	63
		12k	3F-Ph	Ph	53	**13k**	72
		12l	1-$C_{10}H_7$	Bu	75	**13l**	83
		12m	1-$C_{10}H_7$	$PhOCH_2$	62	**13m**	80
		12n	1-$C_{10}H_7$	Et	87	**13n**	82
		12o	1-$C_{10}H_7$	but-3-en-1-yl	85	**13o**	83

TABLE II
Reaction conditions for cyclocarbonylation of model substrate **13a**

Solvent	Temp., °C	Time, h	Catalyst	Yield of **14a**, %
DMF	60	3	$[PdCl_2(PPh_3)_2]$	trace
MeCN	60	3	$[PdCl_2(PPh_3)_2]$	0
Benzene	60	3	$[PdCl_2(PPh_3)_2]$	trace
MeOH	100	24	$[PdCl_2(PPh_3)_2]$	1/8[a]
DMF	70	21	$[PdCl_2(PPh_3)_2]$	66
EtOH	70	18	$[PdCl_2(PPh_3)_2]$	1/25[a]
EtOH	70	18	$[Pd_2(dba)_3\{2\text{-furyl})_3P\}]$	1/25[a]
Benzene	70	18	$[PdCl_2(PPh_3)_2]$	2/3[a]
MeCN	70	18	$[PdCl_2(PPh_3)_2]$	1/4[a]
EtOH	70	9	(biphenyl-2-yl)$Cy_2P[Pd_2(dba)_3]$	90

[a] Ratio starting material/product determined by NMR.

choice for the carbonylative lactonization of the related 3-iodoalken-1-ols leading to the corresponding butenolides[16], the reaction required 100 °C/21 h to give a 66% isolated yield of pentenolide **14a**. At 70 °C, substantial degrees of conversion were observed in all solvents, and the reaction was fastest in EtOH, even though it did not reach completion. Switching to the (biphenyl-2-yl)dicyclohexylphosphane ligand[24] led to a complete conversion in approximately 9 h, and a high isolated yield of the pentenolide product. These results are, to some extent, in line with our earlier observations[16] that the carbonylation of the above mentioned 3-iodoalken-1-ols required DMF as solvent because of the formation of relatively stable, five-membered chelates (**15**, Chart 2), while there was no or little difference between MeOH and DMF when the complexation was prevented by changing OH into a non-participating group. Apparently, possible formation of six-membered complexes **16** is negligible, if it occurs at all.

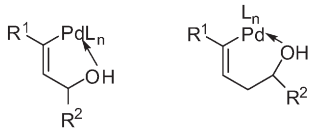
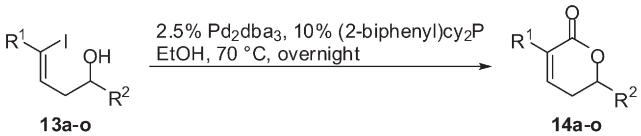


CHART 2

The remaining precursors **13b**–**13o** were subjected to the optimized conditions (Scheme 6) to give the corresponding pyranones **14b**–**14o** in good to excellent isolated yields, as shown in Table III.



SCHEME 6

As a whole, the outlined reaction sequence provides a short and easy access to 3,6-disubstituted pentenolides with a variety of substituents at C6 including enantiomerically pure substrates (**14d**). In contrast to the above described classical cyclization approach, however, substitution at C3 is limited to the stable aryl groups that (i) enable hydroalumination with Red-Al and (ii) survive several hours of reflux with this reagent.

TABLE III
Overview of isolated yields of pyranones **14a**–**14o**

Starting material	R^1	R^2	Product	Yield, %
13a	Ph	Et	**14a**	90
13b	Ph	but-3-en-1-yl	**14b**	89
13c	Ph	$PhOCH_2$	**14c**	89
13d	Ph	(*S*)-Ph	**14d**	82
13e	Ph	Bu	**14e**	86
13f	pyridin-3-yl	$PhOCH_2$	**14f**	70
13g	pyridin-3-yl	Ph	**14g**	72
13h	pyridin-3-yl	but-3-en-1-yl	**14h**	68
13i	3F-Ph	Bu	**14i**	87
13j	3F-Ph	$PhOCH_2$	**14j**	88
13k	3F-Ph	Ph	**14k**	85
13l	1-$C_{10}H_7$	Bu	**14l**	90
13m	1-$C_{10}H_7$	$PhOCH_2$	**14m**	91
13n	1-$C_{10}H_7$	Et	**14n**	86
13o	1-$C_{10}H_7$	but-3-en-1-yl	**14o**	87

Biological Activity

All target compounds **3aw**–**3fz** and **14a**–**14o** were subjected to screening for antifungal activity[5] against a panel of potentially pathogenic yeasts (*Candida albicans* ATCC 44859, *Candida krusei* E28, *Candida tropicalis* 156, *Candida glabrata* 20/I, *Trichosporon beigelii* 1188) and filamentous fungi (*Aspergillus fumigatus* 231, *Absidia corymbifera* 272, *Trichophyton mentagrophytes* 445), and to the evaluation of cytostatic activity[25] on mouse lymphocytic leukemia L1210 cells (ATCC CCL 219), CCRF-CEM T lymphoblastoid cells (human acute lymphoblastic leukemia, ATCC CCL 119), human promyelocytic leukemia HL-60 cells (ATCC CCL 240) and human cervix carcinoma HeLa S3 cells (ATCC CCL 2.2). In all cases, no significant activity was detected at relevant concentrations.

CONCLUSION

We have extended the cyclization methodology developed[5] in the preparation of 3,5-disubstituted butenolides to 3,6-disubstituted pentenolides, and explored the conversion of easy-to-make homopropargylic alcohols

into 3,6-disubstituted pentenolides via the hydroalumination/iodination/carbonylative lactonization sequence. While the C6 substituent is limited to a substituted methyl group using the former method, the limitations and relatively harsh conditions needed in the hydrometallation of the starting homopropargylic alcohols is a major drawback of the latter. Complete loss of biological activity is also noteworthy since this means that the pharmacophore of antifungal activity is restricted to a five-membered (butenolide) ring. As both butenolides and pentenolides are in principle capable of conjugate addition, these results also bring further evidence that the mechanism of antifungal action of 3,5-disubstituted butenolides does not result from a Michael addition of an intercellular nucleophile[6] (we have also recently shown[26] that 3-(substituted aryl)-5-[(acyloxy)methyl]-2,5-dihydrofuran-2-ones act by damaging fungal cell membranes in *Candida albicans*). Being small molecules, the pyranones described in this paper are likely to be able to penetrate inside the cells by passive transport processes (simple diffusion). Thus, it appears that they have no target structure(s) on the fungal cell membrane as well as inside the cell.

EXPERIMENTAL

Substituted phenylacetic acids, alkynes **10** and epoxides **11** were purchased from Sigma–Aldrich and used as received. The acids were converted to the corresponding methyl esters **4** as described previously[6]. THF was freshly distilled from sodium benzophenone ketyl. DMF was dried over 3 Å molecular sieves. Melting points were determined on a Kofler block and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded of $CDCl_3$ solutions at ambient temperature on a Varian Mercury-Vx BB 300 spectrometer operating at 300 MHz for ^{1}H. Chemical shifts were recorded as δ values in ppm and were indirectly referenced to tetramethylsilane (TMS) via the solvent signal (7.26 for ^{1}H, 77.0 for ^{13}C in $CDCl_3$). Coupling constants (*J*) are given in Hz. Where NMR spectra of mixtures were recorded, only those data which could be determined unequivocally were given. In case of mixtures of diastereomers, the isomers are referred to as A and B. Infrared spectra (wavenumbers in cm^{-1}) were recorded either in $CDCl_3$ (oily substances) or in KBr (crystalline substances) on a Nicolet Impact 400 spectrophotometer. Low-resolution mass spectra were measured on a Magnum Finnigan Mat apparatus. Elemental analysis was carried out on a CHNS-OCE FISONS EA 1110 instrument. Analytical thin-layer chromatography (TLC) was conducted on Merck TLC plates (silica gel 60 F254, aluminium back), and the plates were visualized under UV light and in iodine vapors. Silica gel 60 (230–400 mesh) for column chromatography was purchased from Merck.

Preparation of 2-Arylhex-5-enoic Acids

1.6 M BuLi in hexanes (10.4 ml, 16.54 mmol) and diisopropylamine (2.2 ml, 15.73 mmol) were added to dry THF (100 ml) at –10 °C under Ar and the solution was stirred at 0 °C for 10 min. The resultant LDA solution was then cooled to –60 °C, and a solution of methyl

ester **4** (15.00 mmol) in THF (5 ml) was added. The temperature was maintained at –60 °C for 30 min, and a solution of 4-iodobut-1-ene (18.00 mmol) in THF (5 ml) was added. The reaction mixture was slowly allowed to warm to room temperature (over 1 h), and then stirred for 12 h. The mixture was diluted with ethyl acetate, washed with saturated aqueous NH_4Cl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (petroleum ether).

Methyl 2-phenylhex-5-enoate. Yield 82%, yellowish oil. ^{1}H NMR: 7.36–7.22 m, 5 H (Ar); 5.86–5.70 m, 1 H (H5); 5.04–4.96 m, 2 H (H6); 3.65 s 3 H ($COOCH_3$); 3.62–3.53 m, 1 H (H2); 2.23–2.11 m, 1 H (H4); 1.94–1.81 m, 1 H (H4′); 1.67–1.49 m, 1 H (H3); 1.40–1.21 m, 1 H (H3′). ^{13}C NMR: 174.4, 138.9, 137.5, 128.6, 127.9, 127.2, 115.4, 51.9, 50.7, 32.5, 31.5. IR: 2956 (w), 2934 (w), 2360 (w), 1731 (s), 1455 (m), 1436 (m). LRMS: 205 (M^+ + H, 4), 197 (5), 177 (12), 159 (6), 149 (100), 135 (12), 121 (11), 115 (12), 105 (31), 95 (25), 91 (42), 77 (33), 67 (45), 55 (72), 51 (20).

Methyl 2-(4-bromophenyl)hex-4-enoate. Yield 90%, yellowish oil. ^{1}H NMR: 7.48–7.40 m, 2 H (AA′BB′, Ar); 7.21–7.14 m, 2 H (AA′BB′, Ar); 5.84–5.68 m, 1 H (H5); 5.04–4.99 m, 1 H (H6); 4.99–4.94 m, 1 H (H6′); 3.65 s, 3 H ($COOCH_3$); 3.54 t, 1 H, J = 7.6 (H2); 2.23–2.05 m, 1 H (H4); 2.05–1.92 m, 2 H (H3 + H4′); 1.92–1.75 m, 1 H (H3′). ^{13}C NMR: 173.9, 137.8, 137.2, 131.7, 129.7, 121.2, 115.6, 52.1, 50.1, 32.3, 31.3. IR: 3019 (m), 2953 (w), 1732 (s), 1489 (m). LRMS: 283 (M^+, 9), 275 (1), 263 (1), 242 (3), 230 (100), 209 (14), 196 (20), 183 (3), 169 (22), 142 (6), 128 (11), 115 (12), 103 (18), 89 (18), 77 (6), 63 (7), 51 (6).

Methyl 2-(3-chlorophenyl)hex-4-enoate. Yield 95%, yellowish oil. ^{1}H NMR: 7.33–7.28 m, 1 H (Ar); 7.25–7.14 m, 3 H (Ar); 5.85–5.67 m, 1 H (H5); 5.05–5.00 m, 1 H (H6); 5.00–4.95 m, 1 H (H6′); 3.66 s, 3 H ($COOCH_3$); 3.55 t, 1 H, J = 7.6 (H2); 2.26–2.07 m, 1 H (H4); 2.07–1.93 m, 2 H (H3 + H4′); 1.93–1.75 m, 1 H (H3′). ^{13}C NMR: 173.8, 140.8, 137.2, 134.4, 129.8, 128.1, 127.5, 126.2, 115.6, 52.1, 50.3, 32.3, 31.3. IR: 2954 (m), 2259 (w), 1731 (s), 1434 (m). LRMS: 238 (M^+, 70), 233 (10), 221 (12), 207 (10), 197 (100), 191 (20), 177 (45), 165 (68), 155 (23), 137 (62), 125 (52), 115 (50), 102 (27), 89 (22), 69 (58), 55 (38).

Methyl 2-(3,4-dichlorophenyl)hex-5-enoate. Yield 91%, yellowish oil. ^{1}H NMR: 7.40 d, 1 H, J = 2.0 (ArH2); 7.39 d, 1 H, J = 8.2 (ArH5); 7.14 dd, 1 H, J_1 = 8.2, J_2 = 2.0 (ArH6); 5.83–5.66 m, 1 H (H5); 5.83–5.00 m, 1 H (H6); 5.00–4.94 m, 1 H (H6′); 3.67 s, 3 H ($COOCH_3$); 3.53 t, 1 H, J = 7.7 (H2); 2.23–2.08 m, 1 H (H4); 2.05–1.94 m, 2 H (H3 + H4′); 1.90–1.76 m, 1 H (H3′). ^{13}C NMR: 173.5, 138.9, 137.0, 132.6, 131.4, 130.5, 130.0, 127.4, 115.8, 52.2, 49.8, 32.3, 31.3. IR: 3020 (m), 2954 (m), 1732 (s), 1474 (m). LRMS: 273 (M^+, 5), 272 (8), 255 (2), 230 (5), 218 (100), 199 (12), 186 (42), 172 (9), 159 (37), 137 (9), 115 (10), 102 (13), 89 (8), 75 (9), 67 (8), 55 (13).

Methyl 2-(2,4-dichlorophenyl)hex-5-enoate. Yield 83%, yellowish oil. ^{1}H NMR: 7.40 d, 1 H, J = 2.2 (ArH3); 7.36–7.28 m, 1 H (ArH6); 7.23 dd, 1 H, J_1 = 8.4, J_2 = 2.1 (ArH5); 5.87–5.69 m, 1 H (H5); 5.07–4.95 m, 2 H (H6); 4.20–4.04 m, 1 H (H2); 3.67 s, 3 H ($COOCH_3$); 2.24–2.09 m, 1 H (H4); 2.09–1.93 m, 2 H (H3 + H4′); 1.93–1.74 m, 1 H (H3′). ^{13}C NMR: 173.5, 137.1, 135.4, 134.7, 133.5, 129.7, 129.4, 127.5, 115.6, 52.2, 46.1, 31.9, 31.3. IR: 2953 (m), 1732 (s), 1474 (m), 1254 (m). LRMS: 273 (M^+, 12), 272 (16), 255 (1), 239 (9), 218 (100), 199 (15), 186 (25), 172 (17), 159 (50), 137 (10), 115 (11), 102 (12), 89 (7), 75 (7), 63 (7), 55 (11).

Methyl 2-(4-methoxyphenyl)hex-4-enoate. Yield 76%, yellowish oil. ^{1}H NMR: 7.25–7.18 m, 2 H (AA′BB′, Ar); 6.91–6.81 m, 2 H (AA′BB′, Ar); 5.86–5.69 m, 1 H (H5); 5.05–4.93 m, 2 H (H6); 3.79 s, 3 H (OCH_3); 3.65 s, 3 H ($COOCH_3$); 3.52 t, 1 H, J = 7.6 (H2); 2.22–2.06 m, 1 H (H4); 2.05–1.93 m, 2 H (H3 + H4′); 1.91–1.76 m, 1 H (H3′). ^{13}C NMR: 174.7, 158.7, 137.6,

131.0, 128.9, 115.3, 144.0, 55.2, 52.0, 49.8, 32.5, 31.4. IR: 2953 (m), 2258 (w), 1730 (s), 1512 (s), 1437 (m). LRMS: 180 (M^+, 70), 175 (85), 151 (19), 121 (100), 91 (5).

Hydrolysis. General Procedure

A methyl 2-(substituted phenyl)hex-5-enoate (8.60 mmol) was dissolved in a mixture of MeOH/H_2O (3:1, 25 ml), NaOH (17 mmol) was added to the solution, and the reaction mixture heated to reflux for 2 h. Methanol was removed on a rotary evaporator, the mixture diluted with H_2O, acidified with concentrated HCl to pH 1, then diluted with a saturated aqueous NaCl, and extracted with ethyl acetate (3×). The combined extracts were dried over anhydrous Na_2SO_4 and the solvent evaporated to afford the corresponding acid. The crude product was purified by column chromatography (petroleum ether, petroleum ether/ethyl acetate 9:1 then 8:2).

2-Phenylhex-5-enoic acid (**5a**). Quantitative yield, yellowish oil. ^{1}H NMR: 7.37–7.27 m, 5 H (Ar); 5.85–5.69 m, 1 H (H5); 5.05–5.02 m, 1 H (H6); 5.02–5.00 m, 1 H (H6′); 3.59 t, 1 H, J = 7.6 (H2); 2.27–2.11 m, 1 H (H4); 2.11–1.97 m, 2 H (H3 + H4′); 1.97–1.81 m, 1 H (H3′).

2-(4-Bromophenyl)hex-4-enoic acid (**5b**). Quantitative yield, yellowish oil. ^{1}H NMR: 7.50–7.39 m, 2 H (AA′BB′, Ar); 7.23–7.11 m, 2 H (AA′BB′, Ar); 5.84–5.64 m, 1 H (H5); 5.06–4.93 m, 2 H (H6); 3.54 t, 1 H, J = 7.6 (H2); 2.24–2.06 m, 1 H (H4); 2.06–1.93 m, 2 H (H3 + H4′); 1.93–1.76 m, 1 H (H3′).

2-(3-Chlorophenyl)hex-4-enoic acid (**5c**). Quantitative yield, yellowish oil. ^{1}H NMR: 7.36–7.30 m, 1 H (Ar); 7.30–7.17 m, 3 H (Ar); 5.85–5.68 m, 1 H (H5); 5.07–5.01 m, 1 H (H6); 5.01–4.97 m, 1 H (H6′); 3.57 t, 1 H, J = 7.6 (H2); 2.27–1.96 m, 3 H (H3 + H4); 1.96–1.75 m, 1 H (H3′).

2-(3,4-Dichlorophenyl)hex-5-enoic acid (**5d**). Quantitative yield, yellowish oil. ^{1}H NMR: 7.41 d, 1 H, J = 1.8 (ArH2); 7.40 d, 1 H, J = 8.3 (ArH5); 7.15 dd, 1 H, J_1 = 8.3, J_2 = 1.8 (ArH6); 5.85–5.64 m, 1 H (H5); 5.07–5.01 m, 1 H (H6); 5.01–4.94 m, 1 H (H6′); 3.55 t, 1 H, J = 7.6 (H2); 2.25–2.08 m, 1 H (H4); 2.08–1.94 m, 2 H (H3 + H4′); 1.94–1.77 m, 1 H (H3′).

2-(2,4-Dichlorophenyl)hex-5-enoic acid (**5e**). Quantitative yield, yellowish oil. ^{1}H NMR: 7.41 d, 1 H, J = 2.2 (ArH3); 7.35–7.27 m, 1 H (ArH6); 7.23 dd, 1 H, J_1 = 2.1, J_2 = 8.4 (ArH5); 5.86–5.64 m, 1 H (H5); 4.09–5.93 m, 2 H (H6); 4.25–4.02 m, 1 H (H2); 2.26–2.10 m, 1 H (H4); 2.10–1.95 m, 2 H (H3 + H4′); 1.95–1.77 m, 1 H (H3′).

2-(4-Methoxyphenyl)hex-4-enoic acid (**5f**). Quantitative yield, white crystalline substance, m.p. 58–60 °C. ^{1}H NMR: 7.25–7.18 m, 2 H (AA′BB′, Ar); 6.90–6.81 m, 2 H (AA′BB′, Ar); 5.84–5.68 m, 1 H (H5); 5.04–4.94 m, 2 H (H6); 3.79 s, 3 H (OCH_3); 3.53 t, 1 H, J = 7.6 (H2); 2.22–2.07 m, 1 H (H4); 2.07–1.95 m, 2 H (H3 + H4′); 1.92–1.78 m, 1 H (H3′).

Preparation of Tetrahydropyranones **8**

MCPBA (5.98 mmol, purity 50%) was added to a solution of acid **5** (2.39 mmol) in $CHCl_3$ (25 ml), and the mixture was heated under reflux for 4 h. The reaction mixture was then concentrated, and the crude product redissolved in MeCN (25 ml). Dowex 50 (1.0 g) was added, the resultant mixture stirred at ambient temperature for 24 h, and filtered through sintered glass. The resin was washed with ethyl acetate and methanol, the combined extracts were concentrated, and the product chromatographed on silica gel, pretreated with acetic acid (petroleum ether/ethyl acetate 8:2–1:1, 1% AcOH). The saturated lactone **7** (1.5 mmol) was dissolved in dry DMF (2 ml), and imidazole (1.8 mmol) with TBDMSCl (1.65 mmol) was added to the solution. After 12 h at room temperature, the reaction mix-

ture was diluted with ethyl acetate, washed with saturated NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (petroleum ether/ethyl acetate 8:2).

6-{[(tert-Butyldimethylsilyl)oxy]methyl}-3-phenyltetrahydropyran-2-one (**8a**). Yield 66%, yellowish oil, mixture of diastereomers. ^{1}H NMR: 7.39–7.20 m, m, 5 H (Ar, A + B); 4.56–4.45 m, 1 H (H6, A + B); 3.86–3.76 m, 2 H (CH_2O, A + B); 3.70–3.61 m, 1 H (H3, A + B); 2.34–2.19 m, 1 H (H4, A + B); 2.16–1.81 m, 3 H (H4 + H5, A + B); 0.91 s, 9 H (CCH_3, A); 0.87 s, 9 H (CCH_3, B); 0.096 s, 6 H ($SiCH_3$, A); 0.05 s, 3 H ($SiCH_3$, B); 0.034 s, 3 H ($SiCH_3$, B). ^{13}C NMR: 172.7, 171.9, 138.4, 139.0, 128.7, 128.1, 127.2, 81.2, 79.6, 65.2, 64.9, 48.3, 46.0, 28.5, 26.6, 25.8, 25.0, 22.2, 18.2, –3.6, –5.4. IR: 2930 (m), 2858 (m), 1728 (m), 1256 (m). LRMS: 321 (M^+, 6), 315 (60), 239 (18), 221 (52), 195 (82), 182 (12), 142 (43), 116 (100), 103 (35), 89 (35), 75 (95), 59 (35).

3-(4-Bromophenyl)-6-{[(tert-butyldimethylsilyl)oxy]methyl}tetrahydropyran-2-one (**8b**). Yield 63%, diastereoisomer A, white crystalline substance, m.p. 79–80 °C, diastereoisomer B, white crystalline substance, m.p. 92–94 °C. ^{1}H NMR: isomer A 7.50–7.43 m, 2 H (AA′BB′, Ar); 7.15–7.07 m, 2 H (AA′BB′, Ar); 4.54–4.44 m, 1 H (H6); 3.78 d, 2 H, J = 4.4 (CH_2O); 3.60 dd, 1 H, J_1 = 11.1, J_2 = 6.0 (H3); 2.31–2.15 m, 1 H (H4); 2.15–1.83 m, 3 H (H4′ + H5); 0.91 s, 9 H (CCH_3); 0.09 s, 6 H ($SiCH_3$); isomer B 7.49–7.43 m, 2 H (AA′BB′, Ar); 7.15–7.08 m, 2 H (AA′BB′, Ar); 4.55–4.43 m, 1 H (H6); 3.81 d, 2 H, J = 4.7 (CH_2O); 3.76 t, 1 H, J = 7.8 (H3); 2.33–2.15 m, 1 H (H4); 2.13–1.89 m, 3 H (H4′ + H5); 0.90 s, 9 H (CCH_3); 0.10 s, 1 H ($SiCH_3$). ^{13}C NMR: isomer A: 171.3, 138.3, 131.8, 129.9, 121.2, 81.3, 65.1, 47.9, 28.4, 25.8, 25.0, 18.3, –5.39, –5.44; isomer B: 172.3, 137.8, 131.7, 130.1, 121.3, 79.4, 64.8, 45.3, 26.4, 25.8, 22.3, 18.3, –5.38, –5.43. IR: isomer A: 2931 (m), 2858 (m), 2250 (w), 1727 (s), 1258 (m); isomer B: 2930 (m), 2858 (m), 2250 (w), 1738 (m), 1254 (m). LRMS: isomer A 399 (M^+, 18) 383 (8), 341 (10), 313 (83), 297 (9), 239 (17), 221 (35), 197 (20), 171 (12), 142 (62), 116 (100), 103 (32), 89 (20), 75 (25), 59 (15); isomer B 399 (M^+, 16), 383 (10), 355 (10), 343 (22), 325 (38), 315 (100), 241 (42), 221 (58), 195 (58), 142 (100), 116 (100), 103 (58), 89 (42), 75 (70), 59 (40).

6-{[(tert-Butyldimethylsilyl)oxy]methyl}-3-(3-chlorophenyl)tetrahydropyran-2-one (**8c**). Yield 68%, yellowish oil, mixture of diastereomers. ^{1}H NMR: 7.34–7.08 m, 4 H (Ar, A + B); 4.55–4.45 m, 1 H (H6, A + B); 3.83–3.73 m, 3 H (2 CH_2OA + 1 H3B); 3.67–3.52 m, 3 H (2 CH_2B + 1 H3A); 2.32–1.88 m, 4 H (H4 + H5, A + B); 0.91 s, 9 H (CCH_3, A); 0.87 s, 9 H (CCH_3, B); 0.99 s, 3 H ($SiCH_3$, A); 0.093 s, 3 H ($SiCH_3$, A); 0.049 s, 3 H ($SiCH_3$, B); 0.041 s, 3 H ($SiCH_3$, B). ^{13}C NMR: 172.2, 171.3, 141.2, 140.7, 134.5, 129.8, 128.5, 127.5, 126.6, 81.3, 79.5, 67.0, 64.8, 48.1, 45.6, 29.2, 28.4, 26.4, 25.8, 25.0, 22.4, 18.2, –3.6, –5.4. IR: 2930 (m), 2360 (w), 1731 (m), 1712 (m), 1257 (m) LRMS: 355 (M^+, 12), 297 (38), 269 (58), 195 (58), 177 (72), 151 (100), 115 (63), 75 (82), 59 (38).

6-{[(tert-Butyldimethylsilyl)oxy]methyl}-3-(3,4-dichlorophenyl)tetrahydropyran-2-one (**8d**). Yield 57%, yellowish oil, mixture of diastereomers. ^{1}H NMR: 7.44–7.32 m, 2 H (Ar, A + B); 7.17–7.05 m, 1 H (Ar, A + B); 4.55–4.45 m, 1 H (H6, A + B); 3.83–3.45 m, 3 H (CH_2O + H3, A + B); 2.32–1.70 m, 4 H (H4 + H5, A + B); 0.91 s, 3 H (CCH_3, A); 0.91 s, 3 H (CCH_3, B); 0.88 s, 3 H (CCH_3, A); 0.88 s, 3 H (CCH_3, B); 0.85 s, 3 H (CCH_3, A); 0.85 s, 3 H (CCH_3, B); 0.098 s, 3 H ($SiCH_3$, A); 0.092 s, 3 H ($SiCH_3$, B); 0.053 s, 3 H ($SiCH_3$, A); 0.045 s, 3 H ($SiCH_3$, B). ^{13}C NMR: 173.1, 170.9, 139.5, 138.8, 132.5, 131.2, 130.4, 127.9, 127.5, 81.4, 79.3, 67.1, 65.1, 47.6, 45.0, 29.1, 28.3, 25.8, 25.4, 25.0, 22.6, 18.2, 17.6, –4.9, –5.4. IR: 2956 (m), 2931 (m), 2859 (m), 1713 (m), 1472 (m). MS: 389 (M^+, 15), 370 (15), 348 (2), 345 (5), 337 (22), 315 (24), 311 (2), 271 (1), 229 (100), 201 (10), 176 (4), 159 (15).

6-{[(tert-Butyldimethylsilyl)oxy]methyl}-3-(2,4-dichlorophenyl)tetrahydropyran-2-one (**8e**). Yield 51%, yellowish oil, mixture of diastereomers. ^{1}H NMR: 7.43–7.39 m, 1 H (Ar, A + B); 7.27–7.15 m, 2 H (Ar, A + B); 4.60–4.48 m, 1 H (H6, A + B); 4.21 t, 1 H, *J* = 8.1 (H3, B); 3.94–3.75 m, 3 H (H3A + CH_2O, A + B); 2.29–1.82 m, 4 H (H4 + H5, A + B); 0.91 s, 9 H (CCH_3, A); 0.90 s, 9 H (CCH_3, B); 0.11 s, 3 H ($SiCH_3$, A); 0.10 s, 3 H ($SiCH_3$, B); 0.096 s, 6 H ($SiCH_3$, A + B). ^{13}C NMR: 171.7, 170.6, 136.5, 135.5, 134.7, 134.2, 134.1, 134.0, 131.6, 131.0, 130.1, 129.8, 127.8, 127.6, 81.6, 79.7, 65.4, 64.9, 46.6, 43.0, 27.5, 25.9, 25.5, 25.1, 26.10, 26.09, 18.6, 18.5, –5.1, –5.2. IR: 2956 (m), 2930 (m), 1728 (m), 1476 (m). LRMS: 389 (M^+, 7), 371 (5), 345 (6), 331 (40), 303 (100), 285 (18), 229 (25), 211 (20), 185 (78), 159 (18), 143 (18), 115 (35), 105 (30), 89 (25), 75 (75), 59 (57).

6-{[(tert-Butyldimethylsilyl)oxy]methyl}-3-(4-methoxyphenyl)tetrahydropyran-2-one (**8f**). Yield 65%, yellowish oil, mixture of diastereomers. ^{1}H NMR: 7.18–7.12 m, 2 H (AA′BB′, Ar, A + B); 6.91–6.85 m, 2 H (AA′BB′, Ar, A + B); 4.54–4.44 m, 1 H (H6, A + B); 3.83–3.73 m, 2 H (CH_2O, A + B); 3.79 s, 3 H (OCH_3, overlapped); 3.64–3.55 m, 1 H (H3, A + B); 2.30–1.86 m, 4 H (H4 + H5, A + B); 0.91 s, 9 H (CCH_3, A + B); 0.097 s, 6 H ($SiCH_3$, A); 0.087 s, 6 H ($SiCH_3$, B). ^{13}C NMR: 173.1, 172.2, 158.7, 131.4, 130.9, 129.3, 129.1, 114.1, 114.0, 81.1, 79.4, 65.3, 64.9, 55.2, 47.6, 45.0, 28.4, 26.6, 25.9, 25.1, 22.4, 18.33, 18.29, –5.38, –5.41. IR: 2956 (m), 2931 (m), 2253 (m), 1731 (m), 1515 (m), 1464 (m), 1251 (m). LRMS: 350 (M^+, 20), 315 (11), 254 (100), 241 (38), 226 (61), 178 (31), 149 (81), 115 (42), 63 (17).

Preparation of Pentenolides **9**. General Procedure

Diisopropylamine (0.18 ml 1.27 mmol), 1.6 M BuLi in hexane (0.83 ml 1.33 mmol) and dry THF (20 ml) were placed in a dry Schlenk tube under Ar and stirred at –10 °C for 10 min. The LDA solution was cooled to –60 °C, and a solution of a TBS-protected lactone **7** (1.2 mmol) in dry THF (2 ml) was added. Phenylselanyl bromide (1.8 mmol) in dry THF (2 ml) was added after 30 min, and the resultant mixture was slowly allowed to warm to room temperature, stirred for additional 4 h, diluted with ethyl acetate, washed with a saturated aqueous NH_4Cl, dried over anhydrous Na_2SO_4, and concentrated. The crude product was rapidly purified by column chromatography, and redissolved in $CHCl_3$ (20 ml). MCPBA (1.79 mmol) was added to the solution, and the reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was then washed with 5% aqueous Na_2CO_3, extracted with ethyl acetate (3×), dried over anhydrous Na_2SO_4, and the solvent evaporated. The crude product was purified by column chromatography (petroleum ether, petroleum ether/Et_2O 97:3 then 9:1).

The pure TBS-protected lactone (1.00 mmol) was dissolved in a mixture of CH_3COOH/H_2O/THF (3:1:1, 5 ml), and the solution was stirred at room temperature for 15 h. The reaction mixture was then diluted with ethyl acetate, washed with saturated NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The product was purified by column chromatography (petroleum ether, petroleum ether/ethyl acetate 6:4), to afford the desired pyranones **9**.

6-(Hydroxymethyl)-3-phenyl-5,6-dihydro-2H-pyran-2-one (**9a**). Yield 58%, white crystalline substance, m.p. 105–107 °C. ^{1}H NMR: 7.51–7.42 m, 2 H (Ar); 7.40–7.26 m, 3 H (Ar); 7.12 dd, 1 H, J_1 = 6.3, J_2 = 3.0 (H4); 4.64–4.53 m, 1 H (H6); 4.17 t, 1 H, *J* = 6.2 (OH); 3.86–3.69 m, 2 H (CH_2O); 2.78–2.51 m, 2 H (H5). ^{13}C NMR: 164.1, 142.6, 137.1, 133.0, 129.2, 128.7, 128.6, 79.2, 64.0, 26.9. IR: 3298 (m) 1708 (s), 1204 (s), 1028 (m), 792 (m). LRMS: 205 (M^+ + H, 11), 186 (11), 173 (90), 157 (16), 145 (28), 127 (25), 115 (100), 102 (11), 91 (18), 77 (10), 63 (15), 51 (12).

3-(4-Bromophenyl)-6-(hydroxymethyl)-5,6-dihydro-2H-pyran-2-one (**9b**). Yield 62%, white crystalline substance, m.p. 118–120 °C. ^{1}H NMR: 7.56–7.50 m, 2 H (AA′BB′, Ar); 7.47–7.41 m, 2 H (AA′BB′, Ar); 7.19 dd, 1 H, J_1 = 6.1, J_2 = 3.0 (H4); 4.65–4.54 m, 1 H (H6); 4.18 t, 1 H, J = 6.0 (OH); 3.85–3.69 m, 2 H (CH_2O); 2.76–2.53 m, 2 H (H5). ^{13}C NMR: 164.0, 143.4, 136.3, 131.9, 131.8, 131.2, 122.2, 79.2, 64.0, 26.9. IR: 3390 (s), 1706 (s), 1489 (m), 1208 (m), 1012 (m). LRMS: 282 (M^+ – H, 8), 264 (8), 254 (5), 237 (12), 222 (11), 196 (8), 172 (6), 157 (7), 144 (60), 128 (10), 115 (100), 101 (8), 89 (17), 75 (11), 63 (18), 50 (11).

3-(3-Chlorophenyl)-6-(hydroxymethyl)-5,6-dihydro-2H-pyran-2-one (**9c**). Yield 52%, white crystalline substance, m.p. 85–88 °C. ^{1}H NMR: 7.56–7.52 m, 1 H (Ar); 7.47–7.31 m, 3 H (Ar); 7.22 dd, 1 H, J_1 = 6.3, J_2 = 3.0 (H4); 4.66–4.55 m, 1 H (H6); 3.85–3.69 m, 2 H (CH_2O); 2.79–2.55 m, 2 H (H5). ^{13}C NMR: 163.9, 144.0, 139.1, 134.0, 131.7, 130.4, 129.2, 128.5, 127.7, 79.2, 63.9, 29.9. IR: 3397 (s), 1708 (s), 1200 (m), 1098 (m), 794 (m). LRMS: 239 (M^+ + H, 18), 220 (8), 207 (69), 191 (12), 179 (15), 163 (6), 151 (12), 144 (35), 129 (5), 115 (100), 101 (8), 89 (12), 75 (11), 63 (15), 50 (9).

3-(3,4-Dichlorophenyl)-6-(hydroxymethyl)-5,6-dihydro-2H-pyran-2-one (**9d**). Yield 55%, white crystalline substance, m.p. 161–164 °C. ^{1}H NMR: 7.72 d, 1 H, J = 2.2 (ArH2); 7.56 d, 1 H, J = 8.5 (ArH5); 7.48 dd, 1 H, J_1 = 8.5, J_2 = 2.2 (ArH6); 7.28 dd, 1 H, J = 6.0, 3.0 (H4); 4.70–4.54 m, 1 H (H6); 4.20 t, 1 H, J = 6.2 (OH); 3.87–3.68 m, 2 H (CH_2O); 2.80–2.55 m, 2 H (H5). ^{13}C NMR: 163.8, 144.6, 137.6, 132.1, 132.0, 131.2, 130.9, 130.7, 129.2, 79.2, 63.9, 26.9. IR: 3462 (s), 2929 (w), 1709 (s), 1473 (m), 1201 (s). LRMS: 273 (M^+, 2), 239 (4), 207 (33), 185 (90), 159 (23), 137 (20), 129 (16), 115 (35), 105 (28), 89 (38), 75 (100), 59 (53).

3-(2,4-Dichlorophenyl)-6-(hydroxymethyl)-5,6-dihydro-2H-pyran-2-one (**9e**). Yield 65%, white crystalline substance, m.p. 120–123 °C. ^{1}H NMR: 7.52 dd, 1 H, J_1 = 1.9, J_2 = 0.6 (ArH3); 7.40 dd, 1 H, J_1 = 8.2, J_2 = 1.9 (ArH5); 7.36 dd, 1 H, J_1 = 8.2, J_2 = 0.6 (ArH6); 7.06 dd, 1 H, J_1 = 6.0, J_2 = 3.0 (H4); 4.70–4.58 m, 1 H (H6); 4.21 t, 1 H, J = 6.2 (OH); 3.89–3.68 m, 2 H (CH_2O); 2.81–2.56 m, 2 H (H5). ^{13}C NMR: 162.4, 145.0, 135.0, 134.4, 134.3, 132.7, 130.9, 129.0, 127.4, 79.0, 63.2, 26.1. IR: 3466 (s), 1698 (s), 1477 (m), 1209 (m), 1066 (m). LRMS: 273 (M^+, 8), 270 (10), 253 (10), 237 (100), 219 (13), 209 (23), 193 (43), 178 (65), 167 (13), 149 (78), 135 (11), 123 (8), 115 (41), 99 (10), 87 (12), 73 (18), 63 (19), 50 (13).

6-(Hydroxymethyl)-3-(4-methoxyphenyl)-5,6-dihydro-2H-pyran-2-one (**9f**). Yield 58%, white crystalline substance, m.p. 103–106 °C. ^{1}H NMR: 7.46–7.39 m, 2 H (AA′BB′, Ar); 7.04 dd, 1 H, J_1 = 6.0, J_2 = 3.0 (H4); 6.93–6.86 m, 2 H (AA′BB′, Ar); 4.60–4.50 m, 1 H (H6); 4.15 s, 1 H (OH); 3.79 s, 3 H (OCH_3); 3.81–3.71 m, 2 H (CH_2O); 2.72–2.49 m, 2 H (H5). ^{13}C NMR: 164.4, 160.4, 141.0, 132.4, 130.3, 129.4, 114.1, 79.1, 64.0, 55.5, 26.9. IR: 3397 (s), 1709 (s), 1514 (m), 1250 (m), 1177 (m), 1031 (m). LRMS: 234 (M^+, 100), 216 (27), 203 (80), 188 (18), 172 (39), 159 (48), 146 (22), 131 (53), 115 (42), 103 (88), 91 (45), 77 (55), 63 (30), 51 (29).

Preparation of Esters **3**. General Procedure

Dry pyridine (0.30 mmol), and acyl chloride were added dropwise to a solution of alcohol **8** (0.20 mmol) in dry CH_2Cl_2 (1 ml) at 0 °C under Ar. The reaction mixture was maintained at 0 °C for 12 h and then diluted with ethyl acetate, washed with saturated NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The ester was purified by TLC chromatography with UV detection (254 nm) (petroleum ether/ethyl acetate 1:1). The yields of the esters were in the range 85–90%.

6-{[(4-Chlorobenzoyl)oxy]methyl}-3-phenyl-5,6-dihydro-2H-pyran-2-one (**3aw**). Yellowish oil. ^{1}H NMR: 8.06–7.97 m, 2 H (AA′BB′, Ar); 7.51–7.33 m, 7 H (Ar + AA′BB′, Ar); 6.99 dd, 1 H,

J_1 = 6.2, J_2 = 3.0 (H4); 4.95–4.84 m, 1 H (H6); 4.59 d, 2 H, J = 4.4 (H7); 2.80–2.52 m, 2 H (H5). ^{13}C NMR: 165.4, 163.3, 139.9, 139.8, 135.0, 133.3, 131.2, 128.8, 128.4, 128.3, 128.2, 127.8, 75.1, 65.3, 26.6. IR: 3027 (m), 3014 (m), 2954 (m), 2359 (w), 1724 (s), 1596 (s), 1459 (s), 1272 (s). LRMS: 343 (M^+, 10), 281 (5), 225 (6), 186 (41), 139 (100), 115 (39), 105 (25), 91 (10), 75 (18), 63 (9), 50 (13).

6-{[(2,2-Dimethylpropanoyl)oxy]methyl}-3-phenyl-5,6-dihydro-2H-pyran-2-one (**3ay**). White crystalline substance, m.p. 69–71 °C. For $C_{16}H_{20}O_4$ (276.2) calculated: 70.81% C, 6.99% H; found: 70.65% C, 7.11% H. ^{1}H NMR: 7.50–7.31 m, 5 H (Ar); 6.97 dd, 1 H, J_1 = 6.0, J_2 = 3.0 (H4); 4.81–4.70 m, 1 H (H6); 4.33 d, 2 H, J = 4.9 (CH_2O); 2.72–2.46 m, 2 H (H5); 1.24 s, 9 H (CH_3). ^{13}C NMR: 178.2, 163.4, 140.0, 135.1, 133.2, 128.4, 128.2, 77.2, 75.1, 64.5, 38.9, 27.1, 26.6. IR: 3019 (m), 2976 (m), 2360 (w), 2340 (w), 1724 (s), 1480 (m), 1282 (m). MS: 289 (M^+, 74), 244 (2), 237 (2), 227 (1), 205 (100), 187 (40), 169 (5), 159 (2), 143 (4), 131 (2), 115 (2), 85 (1).

6-[(Acetyloxy)methyl]-3-phenyl-5,6-dihydro-2H-pyran-2-one (**3az**). White crystalline substance, m.p. 104–106 °C. For $C_{14}H_{14}O_4$ (246.2) calculated: 68.28% C, 5.73% H; found: 67.97% C, 5.98% H. ^{1}H NMR: 7.49–7.32 m, 5 H (Ar); 6.97 dd, 1 H, J_1 = 6.2, J_2 = 2.9 (H4); 4.82–4.71 m, 1 H (H6); 4.39–4.28 m, 2 H (CH_2O); 2.73–2.48 m, 2 H (H5); 2.13 s, 3 H (CH_3COO). ^{13}C NMR: 170.7, 163.3, 139.8, 135.1, 133.2, 128.4, 128.3, 128.2, 75.0, 64.7, 26.6, 20.8. IR: 3019 (s), 2951 (m), 2360 (w), 1728 (s), 1369 (m). LRMS: 247 (M^+ + H, 100), 205 (3), 186 (28), 173 (8), 168 (4), 158 (20), 141 (10), 129 (12), 115 (43), 102 (5), 91 (5), 76 (4), 63 (5), 51 (4).

6-{[(4-Chlorobenzoyl)oxy]methyl}-3-(4-bromophenyl)-5,6-dihydro-2H-pyran-2-one (**3bw**). Colorless oil. ^{1}H NMR: 8.04–7.98 m, 2 H (AA′BB′, Ar); 7.54–7.48 m, 2 H (AA′BB′, Ar); 7.46–7.40 m, 2 H (AA′BB′, Ar); 7.37–7.31 m, 2 H (AA′BB′, Ar); 7.0 dd, 1 H, J_1 = 6.2, J_2 = 3.2 (H4); 4.95–4.85 m, 1 H (H6); 4.59 d, 2 H, J = 4.7 (CH_2O); 2.80–2.57 m, 2 H (H5). ^{13}C NMR: 165.4, 163.0, 140.2, 140.0, 133.8, 132.3, 131.5, 131.2, 129.9, 128.9, 127.7, 122.8, 77.2, 75.2, 65.2, 29.7, 26.7. IR: 2927 (w), 2359 (w), 2341 (w), 1724 (s), 1596 (m), 1489 (m). LRMS: 266 (M^+ – (chlorobenzoyl)oxy, 5), 236 (3), 222 (18), 209 (5), 194 (8), 185 (69), 162 (2), 157 (12), 139 (8), 129 (100), 115 (10), 101 (53), 91 (19), 75 (40), 63 (12), 55 (33).

3-(4-Bromophenyl)-6-{[(2,2-dimethylpropanoyl)oxy]methyl}-5,6-dihydro-2H-pyran-2-one (**3by**). Colorless oil. ^{1}H NMR: 7.53–7.45 m, 2 H (AA′BB′, Ar); 7.37–7.30 m, 2 H (AA′BB′, Ar); 6.97 dd, 1 H, J_1 = 6.0, J_2 = 3.0 (H4); 4.81–4.69 m, 1 H (H6); 4.33 d, 2 H, J = 4.7 (CH_2O); 2.71–2.45 m, 2 H (H5); 1.23 s, 9 H (CH_3). ^{13}C NMR: 178.1, 163.0, 140.3, 133.9, 132.2, 131.4, 129.9, 122.7, 75.2, 64.4, 38.9, 27.1, 26.6. IR: 3027 (m), 2976 (m), 2936 (m), 2360 (w), 1724 (s), 1489 (s), 1202 (s). LRMS: 367 (M^+, 45), 283 (7), 264 (35), 253 (2), 222 (11), 209 (5), 185 (6), 157 (6), 144 (10), 128 (10), 115 (48), 89 (6), 69 (6), 57 (100).

6-[(Acetyloxy)methyl]-3-(4-bromophenyl)-5,6-dihydro-2H-pyran-2-one (**3bz**). Colorless oil. ^{1}H NMR: 7.54–7.45 m, 2 H (AA′BB′, Ar); 7.38–7.29 m, 2 H (AA′BB′, Ar); 6.97 dd, 1 H, J_1 = 6.3, J_2 = 3.0 (H4); 4.83–4.70 m, 1 H (H6); 4.39–4.27 m, 2 H (CH_2O); 2.72–2.48 m, 2 H (H5); 2.12 s, 3 H (CH_3COO). ^{13}C NMR: 170.7, 163.0, 140.2, 133.9, 132.2, 131.4, 129.9, 75.0, 64.6, 26.6, 20.7. IR: 3028 (m), 2926 (m), 2358 (w), 1727 (s), 1589 (w), 1490 (m), 1369 (m). MS: 325 (M^+, 90), 323 (100), 321 (8), 278 (5), 254 (5), 215 (4), 207 (2), 138 (3), 97 (2).

6-{[(4-Chlorobenzoyl)oxy]methyl}-3-(3-chlorophenyl)-5,6-dihydro-2H-pyran-2-one (**3cw**). Colorless oil. ^{1}H NMR: 8.03–7.98 m, 2 H (AA′BB′, Ar); 7.47–7.39 m, 3 H (Ar + AA′BB′, Ar); 7.38–7.29 m, 3 H (Ar); 7.01 dd, 1 H, J_1 = 6.0, J_2 = 3.0 (H4); 4.95–4.85 m, 1 H (H6); 4.59 d, 2 H, J = 4.7 (CH_2O); 2.81–2.58 m, 2 H (H5). ^{13}C NMR: 165.3, 162.9, 140.8, 140.0, 136.6, 134.1, 132.2, 131.2, 129.5, 128.9, 128.6, 128.4, 127.7, 126.5, 75.2, 65.2, 26.6. IR: 2927 (w),

2359 (w), 1724 (s), 1596 (m), 1271 (s). LRMS: 377 (M^+, 2), 220 (83), 192 (23), 139 (100), 115 (82), 75 (42), 63 (10), 50 (18).

3-(3-Chlorophenyl)-6-{[(2,2-dimethylpropanoyl)oxy]methyl}-5,6-dihydropyran-2H-pyran-2-one (**3cy**). Colorless oil. ^{1}H NMR: 7.47–7.43 m, 1 H (Ar); 7.38–7.28 m, 3 H (Ar); 6.99 dd, 1 H, J_1 = 6.2, J_2 = 2.9 (H4); 4.81–4.69 m, 1 H (H6); 4.33 d, 2 H, J = 4.7 (CH_2O); 2.72–2.48 m, 2 H (H5); 1.24 s, 9 H (CH_3). ^{13}C NMR: 178.1, 162.9, 140.9, 136.7, 134.1, 132.1, 129.5, 128.5, 128.4, 126.5, 75.2, 64.4, 38.9, 27.1, 26.6. IR: 3023 (m), 2976 (m), 2935 (m), 2874 (m), 2438 (w), 1728 (s), 1567 (m), 1480 (s), 1282 (s). LRMS: 323 (M^+, 17), 281 (3), 267 (2), 254 (2), 239 (8), 220 (77), 207 (19), 192 (25), 178 (10), 163 (10), 144 (12), 128 (10), 115 (62), 101 (8), 89 (9), 69 (15), 57 (100).

6-[(Acetyloxy)methyl]-3-(3-chlorophenyl)-5,6-dihydro-2H-pyran-2-one (**3cz**). Yellowish oil. ^{1}H NMR: 7.47–7.42 m, 1 H (Ar); 7.38–7.28 m, 3 H (Ar); 6.99 dd, 1 H, J_1 = 6.0, J_2 = 3.0 (H4); 4.82–4.71 m, 1 H (H6); 4.39–4.27 m, 2 H (CH_2O); 2.74–2.50 m, 2 H (H5); 2.13 s, 3 H (CH_3COO). ^{13}C NMR: 170.7, 162.9, 140.9, 136.7, 134.1, 132.1, 129.5, 128.5, 128.4, 126.5, 75.0, 64.6, 26.5, 20.8. IR: 3019 (s), 2927 (m), 2359 (w), 1740 (s), 1369 (m). LRMS: 281 (M^+, 27), 220 (53), 192 (31), 163 (18), 144 (23), 115 (100), 89 (12), 75 (18), 63 (12), 51 (7).

6-{[(4-Chlorobenzoyl)oxy]methyl}-3-(3,4-dichlorophenyl)-5,6-dihydro-2H-pyran-2-one (**3dw**). Colorless oil. ^{1}H NMR: 8.03–7.97 m, 2 H (AA′BB′, Ar); 7.57 d, 1 H, J = 1.9 (ArH2); 7.47–7.40 m, 3 H (AA′BB′, Ar + ArH5); 7.32 dd, 1 H, J_1 = 8.4, J_2 = 2.1 (ArH6); 7.02 dd, 1 H, J_1 = 6.0, J_2 = 3.0 (H4); 4.95–4.84 m, 1 H (H6); 4.59 d, 2 H, J = 4.7 (CH_2O); 2.82–2.59 m, 1 H (H5). ^{13}C NMR: 165.3, 162.6, 141.0, 140.0, 134.8, 132.7, 132.4, 131.3, 131.2, 130.23, 130.17, 128.9, 127.6, 77.4, 75.2, 65.1, 26.6. IR: 2926 (w), 2257 (w), 1724 (m), 1596 (w), 1473 (w), 1271 (m). LRMS: 341 (M^+ – 2 Cl, 2), 289 (5), 205 (3), 186 (68), 173 (18), 158 (28), 142 (10), 129 (15), 115 (42), 91 (8), 77 (6), 57 (100).

3-(3,4-Dichlorophenyl)-6-{[(3-phenylpropenoyl)oxy]methyl}-5,6-dihydro-2H-pyran-2-one (**3dx**). Yellowish oil. ^{1}H NMR: 7.75 d, 1 H, J = 16.2 (CH-Ar); 7.62–7.28 m, 8 H (Ar); 7.02 dd, 1 H, J_1 = 6.0, J_2 = 3.0 (H4); 6.48 d, 1 H, J = 15.9 (CH); 4.90–4.79 m, 1 H (H6); 4.49 d, 2 H, J = 4.4 (H7); 2.80–2.56 m, 2 H (H5). ^{13}C NMR: 166.5, 162.7, 146.1, 141.1, 134.9, 134.0, 132.7, 132.4, 131.2, 130.7, 130.21, 130.17, 129.0, 128.2, 127.7, 116.9, 75.3, 64.5, 26.6. IR: 3022 (m), 2927 (m), 2360 (w), 1720 (s), 1637 (s), 1473 (m), 1311 (m). LRMS: 326 (M^+ – phenyl, 8), 308 (1), 282 (3), 264 (78), 253 (18), 236 (43), 222 (20), 194 (12), 185 (19), 157 (18), 144 (30), 128 (25), 115 (100), 101 (10), 89 (17), 75 (12), 63 (18), 50 (11).

3-(3,4-Dichlorophenyl)-6-{[(2,2-dimethylpropanoyl)oxy]methyl}-5,6-dihydro-2H-pyran-2-one (**3dy**). Colorless oil. ^{1}H NMR: 7.58 d, 1 H, J = 2.2 (ArH2); 7.44 d, 1 H, J = 8.3 (ArH5); 7.33 dd, 1 H, J_1 = 8.4, J_2 = 2.1 (ArH6); 7.01 dd, 1 H, J = 6.1, 3.3 (H4); 4.81–4.70 m, 1 H (H6); 4.33 d, 2 H, J = 4.7 (CH_2O); 2.73–2.50 m, 2 H (H5); 1.24 s, 9 H (CH_3). ^{13}C NMR: 178.2, 162.7, 141.1, 134.9, 132.7, 132.4, 131.3, 130.2, 130.18, 127.7, 75.2, 64.4, 38.9, 27.1, 26.6. IR: 3027 (m), 2975 (m), 2934 (m), 2338 (w), 1727 (s), 1474 (m), 1283 (m). LRMS: 357 (M^+, 8), 273 (2), 254 (12), 241 (3), 226 (10), 178 (5), 162 (3), 149 (12), 128 (2), 115 (8), 85 (3), 69 (5), 57 (100).

6-[(Acetyloxy)methyl]-3-(3,4-dichlorophenyl)-5,6-dihydro-2H-pyran-2-one (**3dz**). Colorless oil. ^{1}H NMR: 7.57 d, 1 H, J = 2.0 (ArH2); 7.44 d, 1 H, J = 8.5 (ArH5); 7.32 dd, 1 H, J_1 = 8.5, J_2 = 2.0 (ArH6); 7.0 dd, 1 H, J_1 = 6.0, J_2 = 3.0 (H4); 4.82–4.71 m, 1 H (H6); 4.39–4.27 m, 2 H (CH_2O); 2.75–2.51 m, 2 H (H5); 2.13 s, 3 H (CH_3COO). ^{13}C NMR: 170.7, 162.6, 141.1, 134.9, 132.7, 132.4, 131.2, 130.2, 130.1, 127.6, 75.1, 64.5, 26.5, 20.7. IR: 2927 (w), 2257 (w), 1728 (s), 1473 (m), 1368 (m). LRMS: 315 (M^+, 40), 254 (100), 226 (52), 212 (20), 178 (27), 149 (68), 115 (35), 63 (11).

6-{[(4-Chlorobenzoyl)oxy]methyl}-3-(2,4-dichlorophenyl)-5,6-dihydro-2H-pyran-2-one (**3ew**). Colorless oil. ^{1}H NMR: 8.05–7.99 m, 2 H (AA′BB′, Ar); 7.47–7.39 m, 3 H (Ar + AA′BB′, Ar); 7.31–7.18 m, 2 H (Ar); 6.92 dd, 1 H, J_1 = 5.9, J_2 = 2.9 (H4); 5.02–4.93 m 1 H (H6); 4.62 d, 2 H, J = 4.7 (CH_2O); 2.81–2.59 m, 2 H (H5). ^{13}C NMR: 165.3, 162.2, 142.8, 140.0, 135.2, 134.1, 132.8, 131.7,131.5, 131.3, 129.5, 128.9, 127.7, 127.2, 75.4, 65.0, 26.6. IR: 2957 (w), 2927 (w), 2259 (w), 1725 (s), 1595 (m), 1271 (s). MS: 411 (M^+, 1), 408 (85), 402 (1), 253 (34), 155 (100).

3-(2,4-Dichlorophenyl)-6-{[(3-phenylpropenoyl)oxy]methyl}-5,6-dihydro-2H-pyran-2-one (**3ex**). Yellowish oil. ^{1}H NMR: 7.76 d, 1 H, J = 15.9 (CH-Ar); 7.61–7.49 m, 2 H (Ar); 7.47–7.35 m, 3 H (Ar); 7.31–7.17 m, 3 H (Ar); 6.91 dd, 1 H, J_1 = 5.9, J_2 = 2.9 (H4); 6.50 d, 1 H, J = 16.2 (CH); 4.99–4.87 m, 1 H (H6); 4.51 d, 2 H, J = 4.7 (CH_2O); 2.80–2.57 m, 2 H (H5). ^{13}C NMR: 166.5, 162.2, 146.0, 143.0, 135.1, 134.2, 134.1, 132.9, 131.7, 131.4, 130.6, 129.5, 128.9, 128.2, 127.2, 117.0, 75.5, 64.5, 26.5. IR: 2948 (w), 2928 (w), 2359 (w), 1724 (s), 1637 (m), 1476 (m). LRMS: 403 (M^+, 2), 341 (12), 315 (70), 223 (45), 197 (100), 142 (40), 116 (100), 89 (38), 75 (95), 59 (40).

3-(2,4-Dichlorophenyl)-6-{[(2,2-dimethylpropanoyl)oxy]methyl}-5,6-dihydro-2H-pyran-2-one (**3ey**). White crystalline substance, m.p. 125–127 °C. For $C_{17}H_{18}Cl_2O_4$ (357.2) calculated: 57.16% C, 5.08% H; found: 57.05% C, 5.20% H. ^{1}H NMR: 7.44 d, 1 H, J = 2.1 (ArH3); 7.28 dd, 1 H, J_1 = 8.2, J_2 = 2.1 (ArH5); 7.21 d, 1 H, J = 8.2 (ArH6); 6.89 dd, 1 H, J_1 = 5.9, J_2 = 2.9 (H4); 4.89–4.78 m, 1 H (H6); 4.36 d, 2 H, J = 4.7 (CH_2O); 2.74–5.50 m, 2 H (H5); 1.25 s, 9 H (CH_3). ^{13}C NMR: 178.4, 162.5, 143.2, 135.3, 134.4, 133.2, 132.0, 131.7, 129.7, 127.5, 75.6, 64.5, 39.2, 27.4, 26.8. IR: (2975 (w), 2358 (w), 1727 (s), 1588 (m), 1479 (m). LRMS: 357 (M^+, 40), 273 (10), 254 (60), 219 (10), 178 (12), 149 (25), 115 (11), 69 (7).

6-[(Acetyloxy)methyl]-3-(2,4-dichlorophenyl)-5,6-dihydro-2H-pyran-2-one (**3ez**). Colorless oil. ^{1}H NMR: 7.44 d, 1 H, J = 1.9 (ArH3); 7.32–7.27 m, 1 H (ArH5); 7.20 d, 1 H, J = 8.2 (ArH6); 6.89 dd, 1 H, J_1 = 5.9, J_2 = 2.9 (H4); 4.91–4.79 m, 1 H (H6); 4.41–4.29 m, 2 H (CH_2O); 2.75–2.50 m, 2 H (H5); 2.14 s, 3 H (CH_3COO). ^{13}C NMR: 170.7, 162.2, 143.0, 135.1, 134.1, 132.9, 131.7, 131.4, 129.5, 127.2, 75.3, 64.5, 26.4, 20.8. IR: 2953 (w), 2928 (w), 2257 (w), 1728 (s), 1476 (m). MS: 315 (M^+, 20), 310 (2), 296 (2), 279 (1), 273 (85), 255 (100), 253 (1), 237 (15), 227 (2), 212 (1), 211 (10), 209 (2), 203 (1), 176 (3).

6-{[(4-Chlorobenzoyl)oxy]methyl}-3-(4-methoxyphenyl)-5,6-dihydro-2H-pyran-2-one (**3fw**). White crystalline substance, m.p. 102–104 °C. For $C_{20}H_{17}ClO_5$ (372.8) calculated: 64.44% C, 4.60% H; found: 64.69% C, 4.82% H. ^{1}H NMR: 8.01 m, 2 H (AA′BB′, Ar), 7.46–7.37 m, 4 H (Ar); 6.95–6.87 m, 3 H (Ar + H4); 4.94–4.82 m, 1 H (H6); 4.58 d, 2 H, J = 4.8 (CH_2O); 3.82 s, 3 H (OCH_3); 2.78–2.53 m, 2 H (H5). ^{13}C NMR: 165.4, 163.6, 159.8, 139.9, 138.3, 132.6, 131.2, 129.5, 128.8, 127.8, 127.5, 113.7, 75.1, 65.3, 55.3, 26.6. IR: (2936 (w), 1723 (s), 1608 (m), 1513 (m), 1271 (s). LRMS: 373 (M^+, 18), 235 (5), 216 (100), 207 (42), 188 (50), 172 (86), 159 (33), 145 (22), 131 (25), 115 (28), 103 (46), 91 (15), 77 (28), 51 (22).

6-{[(2,2-Dimethylpropanoyl)oxy]methyl}-3-(4-methoxyphenyl)-5,6-dihydro-2H-pyran-2-one (**3fy**). White crystalline substance, m.p. 88–91 °C. For $C_{18}H_{22}O_5$ (318.4) calculated: 67.91% C, 6.97% H; found: 67.68% C, 7.21% H. ^{1}H NMR: 7.45–7.36 m, 2 H (AA′BB′, Ar); 6.94–6.85 m, 3 H (AA′BB′, Ar + H4); 4.79–4.68 m, 1 H (H6); 4.33 d, 2 H, J = 4.7 (CH_2O); 3.82 s, 3 H (OCH_3); 2.69–2.43 m, 2 H (H5); 1.24 s, 9 H (CH_3). ^{13}C NMR: 178.2, 163.6, 157.7, 138.4, 132.6, 129.5, 127.6, 113.7, 75.1, 64.6, 55.3, 38.9, 27.2, 26.6. IR: 2973 (w), 2257 (w), 1724 (s), 1609 (m), 1513 (m). LRMS: 318 (M^+, 12), 300 (10), 281 (5), 235 (5), 216 (62), 203 (17), 188 (52), 172 (95), 159 (27), 145 (20), 131 (22), 115 (30), 103 (38), 91 (18), 77 (25), 57 (100).

6-[(Acetyloxy)methyl]-3-(4-methoxyphenyl)-5,6-dihydro-2H-pyran-2-one (**3fz**). White crystalline substance, m.p. 69–72 °C. For $C_{15}H_{16}O_5$ (276.3) calculated 65.21% C, 5.84% H; found: 65.02% C, 5.80% H. ^{1}H NMR: 7.45–7.36 m, 2 H (AA′BB′, Ar); 6.95–6.86 m, 3 H (AA′BB′, Ar + H4); 4.81–4.69 m, 1 H (H6); 4.35–4.30 m, 2 H (CH_2O); 3.82 s, 3 H (OCH_3); 2.71–2.45 m, 2 H (H5); 2.12 s, 3 H (CH_3COO). ^{13}C NMR: 170.7, 163.5, 159.7, 138.3, 132.6, 129.5, 127.6, 113.7, 75.0, 64.7, 55.3, 26.5, 20.8. IR: 2937 (w), 1726 (m), 1609 (m), 1513 (m), 1368 (w). LRMS: 276 (M^+, 35), 267 (6), 216 (100), 207 (40), 188 (52), 172 (80), 159 (55), 147 (40), 131 (42), 115 (35), 103 (67), 91 (35), 77 (47), 63 (22), 51 (20).

Preparation of Homopropargylic Alcohols **12** (except **12f**, **12g**, **12h**). General Procedure

A solution of 1.6 M butyllithium in hexanes (1.6 ml, 2.6 mmol) was added dropwise to a solution of a terminal alkyne (2 mmol) in dry THF (15 ml) at –78 °C under Ar. After stirring for 50 min, a terminal epoxide (3 mmol) and $BF_3{\cdot}Et_2O$ (0.37 ml, 3 mmol) were added dropwise at –78 °C. The resultant mixture was stirred at –78 °C for 60 min, then slowly allowed to warm to room temperature, and diluted with ethyl acetate (20 ml). The solution was washed with a saturated aqueous solution of NH_4Cl, dried over anhydrous Na_2SO_4 and concentrated in vacuo to yield the crude product, which was purified by column chromatography (hexane/ethyl acetate 9:1).

6-Phenylhex-5-yn-3-ol (**12a**). Yield 3.52 g (92%), colorless oil. ^{1}H NMR: 7.46-7.38 m, 2 H (H2″, H6″), 7.35–7.22 m, 3 H (H3″, H4″, H5″); 3.82–3.69 m, 1 H (H3); 2.71–2.49 m, 2 H (H4); 1.76–1.58 m, 2 H (H2); 1.03 t, 3 H, J = 7.3 (H1). ^{13}C NMR: 131.6, 128.2, 127.9, 123.3, 86.1, 82.9, 71.5, 29.2, 27.9, 10.0. MS, *m/z* (%): 175 ($M^{\bullet+}$, 5), 133 (7), 115 (100), 105 (11), 89 (15), 59 (18).

1-Phenyloct-7-en-1-yn-4-ol (**12b**). Yield 1.2 g (76%), yellowish oil. ^{1}H NMR: 7.46–7.36 m, 2 H (H2′, H6′); 7.33–7.25 m, 3 H (H3′, H4′, H5′); 5.94–5.78 m, 1 H (H7); 5.13–4.96 m, 2 H (H8); 3.92–3.81 m, 1 H (H4); 2.67 dd, 1 H, J_1 = 16.8, J_2 = 5.0 (H3A); 2.57 dd, 1 H, J_1 = 16.8, J_2 = 6.6 (H3B); 2.34–2.11 m, 2 H (H5); 2.08–1.99 bs (OH); 1.76–1.64 m, 2 H (H6). ^{13}C NMR: 138.1, 131.6, 128.2, 127.93, 123.3, 115.0, 86.0, 83.1, 69.6, 35.3, 29.9, 28.4. IR ($CDCl_3$), ν_{max}: 3658 (w), 2937 (w), 2852 (w), 2248 (w), 1727 (w), 1641 (w), 1477 (w), 1409 (w). MS, *m/z* (%): 200 (22), 182 (100), 116 (54), 104 (18).

1-Phenoxy-5-phenylpent-4-yn-2-ol (**12c**). Yield 0.31 g (64%), yellowish oil. ^{1}H NMR: 7.44–7.37 m, 2 H (H2″, H6″); 7.34–7.25 m, 5 H (H3′, H5′, H3″, H4″, H5″); 7.03–6.90 m, 3 H (H2′, H4′, H6′); 4.31–4.22 m, 1 H (H2); 4.20–4.04 m, 2 H (H1); 2.82 d, 2 H, J = 6.3 (H3); 2.57–2.52 bs, 1 H (OH). ^{13}C NMR: 158.4, 131.6, 129.5, 128.2, 128.0, 123.1, 121.2, 114.6, 85.0, 83.1, 70.5, 68.7, 24.5. IR ($CDCl_3$), ν_{max}: 3340 (m), 3059 (m), 2921 (s), 1603 (s), 1496 (s), 1242 (s), 1168 (s). MS, *m/z* (%): 253 ($M^{\bullet+}$, 24), 235 (20), 142 (52), 115 (100), 77 (34).

(S)-1,4-Diphenylbut-3-yn-1-ol (**12d**). Yield 0.31 g (42%), colorless oil. ^{1}H NMR: 7.48–7.25 m, 10 H (Ar); 4.96 t, 1 H, J = 6.3 (H1); 2.87 d, 2 H, J = 6.3 (H2). ^{13}C NMR: 142.6, 131.6, 128.4, 128.2, 128.0, 127.9, 125.8, 123.2, 85.9, 83.2, 72.6, 30.6. IR ($CDCl_3$), ν_{max}: 3387 (m), 3031 (m), 2905 (m), 1598 (m), 1490 (m), 1454 (m), 1049 (m). MS, *m/z* (%): 222 (22), 207 (5), 105 (100), 77 (52), 51 (26).

1-Phenyloct-1-yn-4-ol (**12e**). Yield 0.42 g (85%), colorless oil. ^{1}H NMR: 7.44–7.38 m, 2 H (H2′, H6′); 7.32–7.25 m, 3 H (H3′, H4′, H5′); 3.88–3.78 m, 1 H (H4); 2.71–2.49 m, 2 H (H3); 1.90 s (OH); 1.67–1.54 m, 2 H (H5); 1.50–1.23 m, 4 H (H6, H7); 0.97–0.86 m, 3 H (H8). ^{13}C NMR: 131.6, 128.2, 127.9, 123.4, 86.2, 83.0, 70.2, 36.1, 28.4, 27.8, 22.6, 14.0. IR

($CDCl_3$), ν_{max}: 3582 (w), 3012 (w), 2933 (m), 2861 (w), 1727 (w), 1490 (w). MS, *m/z* (%): 203 ($M^{\bullet+}$, 29), 185 (97), 145 (54), 143 (73), 133 (66), 129 (100), 105 (87).

1-(3-Fluorophenyl)oct-1-yn-4-ol (**12i**). Yield 0.50 g (88%), colorless oil. ^{1}H NMR: 7.29–7.16 m, 2 H (Ar); 7.13–7.07 m, 1 H (Ar); 7.03–6.95 m, 1 H (Ar); 3.89–3.78 m, 1 H (H4); 2.70–2.49 m, 2 H (H3); 1.97 d, *J* = 4.9 (OH); 1.68–1.55 m, 2 H (H5); 1.52–1.28 m, 4 H (H6, H7); 0.97–0.89 m, 3 H (H8). ^{13}C NMR: 162.3 (d, *J* = 246.2), 129.8 (d, *J* = 8.6), 127.5 (d, *J* = 2.9), 125.2 (d, *J* = 9.4), 118.5 (d, *J* = 22.6), 115.2 (d, *J* = 21.2), 87.4, 81.8, 70.1, 36.1, 28.3, 27.8, 22.6, 14.0. IR ($CDCl_3$), ν_{max}: 3603 (w), 3019 (w), 2933 (m), 2861 (w), 1610 (w), 1581 (m), 1487 (w). MS, *m/z* (%): 221 ($M^{\bullet+}$, 100), 203 (18), 177 (10), 123 (16), 89 (90).

5-(3-Fluorophenyl)-1-phenoxypent-4-yn-2-ol (**12j**). Yield 0.50 g (74%), colorless oil. ^{1}H NMR: 7.34–7.16 m, 4 H (Ar); 7.16–7.07 m, 1 H (Ar); 7.04–6.93 m, 4 H (Ar); 4.31–4.21 m, 1 H (H2); 4.19–4.03 m, 2 H (H1); 2.81 d, 2 H, *J* = 6.3 (H3). ^{13}C NMR: 162.3 (d, *J* = 246.5), 158.4, 129.8, 129.5 (d, *J* = 8.5), 127.5 (d, *J* = 3.1), 125.0 (d, *J* = 9.4), 121.3, 118.5 (d, *J* = 22.6), 115.4 (d, *J* = 21.2), 114.5, 86.2, 81.9, 70.5, 68.7, 24.5. IR ($CDCl_3$), ν_{max}: 3407 (s), 3069 (s), 2927 (s), 2234 (m), 1608 (s), 1496 (s), 1405 (s), 1244 (s), 1172 (s). MS, *m/z* (%): 270 (32), 252 (12), 159 (41), 133 (100), 119 (72), 107 (31), 43 (28).

4-(3-Fluorophenyl)-1-phenylbut-3-yn-1-ol (**12k**). Yield 0.21 g (53%), colorless oil. ^{1}H NMR: 7.48–6.96 m, 9 H (Ar); 4.96 t, 1 H, *J* = 6.3 (H4); 2.87 d, 2 H, *J* = 6.3 (H6); 2.47 bs, 1 H (OH). ^{13}C NMR: 162.3 (d, *J* = 246.2), 142.6, 129.8 (d, *J* = 8.6), 128.5, 128.0, 127.5 (d, *J* = 3.2), 125.8, 125.1 (d, *J* = 9.4), 118.4 (d, *J* = 22.9), 115.3 (d, *J* = 21.1), 87.1, 81.9, 72.5, 30.4. IR ($CDCl_3$), ν_{max}: 3393 (m), 3066 (m), 2908 (m), 2234 (w), 1949 (w), 1693 (w), 1580 (s), 1487 (s), 1263 (m), 1151 (m), 1048 (m). MS, *m/z* (%): 240 (3), 223 (7), 134 (43), 107 (80), 79 (100).

1-(1-Naphthyl)oct-1-yn-4-ol (**12l**). Yield 0.37 g (75%), yellowish oil. ^{1}H NMR: 8.36–8.29 m, 1 H (Ar); 7.87–7.77 m, 2 H (Ar); 7.68–7.62 m, 1 H (Ar); 7.60–7.47 m, 2 H (Ar); 7.45–7.37 m, 1 H (Ar); 3.99–3.89 m, 1 H (H4); 2.87–2.67 m, 2 H (H3); 1.99–1.92 bs, 1 H (OH); 1.77–1.61 m, 2 H (H5); 1.57–1.24 m, 4 H (H6, H7); 0.99–0.92 m, 3 H (H8). ^{13}C NMR: 133.4, 133.1, 130.3, 128.3, 128.2, 126.6, 126.3, 126.1, 125.2, 121.0, 91.2, 81.0, 70.3, 36.2, 28.7, 27.8, 22.7, 14.0. IR ($CDCl_3$), ν_{max}: 3585 (s), 3058 (m), 2964 (s), 2876 (m), 2229 (w), 1585 (m), 1396 (s), 1110 (m). MS, *m/z* (%): 253 ($M^{\bullet+}$, 46), 235 (20), 183 (23), 155 (100), 141 (40).

5-(1-Naphthyl)-1-phenoxypent-4-yn-2-ol (**12m**). Yield 0.33 g (62%), yellowish oil. ^{1}H NMR: 8.34–8.28 m, 1 H (Ar); 7.87–7.78 m, 2 H (Ar); 7.68–7.63 m, 1 H (Ar); 7.56–7.48 m, 2 H (Ar); 7.45–7.24 m, 3 H (Ar); 7.04–6.96 m, 3 H (Ar); 4.42–4.33 m, 1 H (H2); 4.29–4.13 m, 2 H (H1); 2.99–1.92 d, 2 H, *J* = 6.3 (H3); 2.39 bs, 1 H (OH). ^{13}C NMR: 158.4, 133.4, 133.1, 130.3, 129.6, 128.4, 128.2, 126.7, 126.3, 126.0, 125.1, 121.3, 120.8, 114.6, 90.0, 81.2, 70.6, 68.9, 24.9. IR ($CDCl_3$), ν_{max}: 3583 (w), 3062 (w), 3012 (w), 2934 (w), 1599 (w), 1497 (m), 1396 (w). MS, *m/z* (%): 302 (40), 281 (10), 207 (34), 180 (28), 165 (24), 77 (43), 44 (100).

6-(1-Naphthyl)hex-5-yn-3-ol (**12n**). Yield 0.39 g (87%), yellowish oil. ^{1}H NMR: 8.36–8.30 m, 1 H (Ar); 7.87–7.78 m, 2 H (Ar); 7.68–7.36 m, 4 H (Ar); 3.92–3.83 m, 1 H (H3); 2.88–2.67 m, 2 H (H4); 1.81–1.63 m, 2 H (H2); 1.05 t, 3 H, *J* = 7.4 (H1). ^{13}C NMR: 133.4, 133.1, 130.3, 128.3, 128.2, 126.6, 126.3, 126.1, 125.2, 121.0, 91.2, 80.9, 71.6, 29.3, 28.2, 10.0. IR ($CDCl_3$), ν_{max}: 3405 (m), 3058 (m), 2964 (m), 2229 (w), 1585 (m), 1462 (m), 1396 (m), 1113 (m). MS, *m/z* (%): 225 ($M^{\bullet+}$, 100), 155 (33).

1-(1-Naphthyl)oct-7-en-1-yn-4-ol (**12o**). Yield 0.38 g (55%), yellowish oil. ^{1}H NMR: 8.12–8.07 m, 1 H (Ar); 7.90–7.77 m, 2 H (Ar); 7.60–7.39 m, 4 H (Ar); 5.97–5.82 m, 1 H (H7); 5.16–5.00 m, 2 H (H8); 4.01–3.90 m, 1 H (H4); 2.68–2.59 m, 2 H (H3); 2.36–2.19 m, 2 H (H6); 1.78–1.66 m, 2 H (H5). ^{13}C NMR (75 MHz, $CDCl_3$): 138.1, 133.4, 133.1, 130.3, 128.4,

128.2, 126.7, 126.3, 126.1, 125.2, 121.0, 115.1, 91.0, 81.1, 69.8, 35.5, 29.9, 28.7. IR ($CDCl_3$), ν_{max}: 3388 (m), 3059 (m), 2934 (m), 2223 (w), 1640 (m), 1585 (m), 1396 (m). MS, *m/z* (%): 251 ($M^{\bullet+}$, 3), 233 (100), 209 (12), 195 (32), 155 (79).

Preparation of Homopropargylic Alcohols **12f**, **12g**, **12h**. General Procedure

A solution of 1.6 M butyllithium in hexanes (1.25 ml, 2.0 mmol) was added dropwise to a solution of a terminal alkyne (2.0 mmol) in dry THF (15 ml) at 0 °C under Ar. After stirring for 10 min a terminal epoxide (1.3 mmol) and a solution of $LiClO_4$ (207 mg, 2.0 mmol) in THF (5 ml) were added dropwise at 0 °C. The resultant mixture was stirred at room temperature for 36 h, and then diluted with ethyl acetate (20 ml). The solution was washed with a saturated aqueous solution of NH_4Cl, dried over anhydrous Na_2SO_4 and concentrated in vacuo to yield the crude product, which was purified by column chromatography (hexane/ethyl acetate 9:1).

1-Phenoxy-5-(pyridin-3-yl)pent-4-yn-2-ol (**12f**). Yield 0.39 g (77%), yellowish oil. ^{1}H NMR: 8.64 d, 1 H, J_1 = 1.4 (H2′); 8.50 dd, 1 H, J_1 = 4.9, J_2 = 1.6 (H6′); 7.68 dt, 1 H, J_1 = 8.0, J_2 = 1.9 (H4′); 7.34–7.18 m, 3 H (H5′, H3″, H5″); 7.02–6.91 m, 3 H (H2″, H4″, H6″); 4.33–4.23 m, 1 H (H2); 4.18–4.03 m, 2 H (H1); 3.06–3.00 bs (OH); 2.84 d, 2 H, *J* = 6.3 (H3). ^{13}C NMR: 158.4, 152.3, 148.3, 138.6, 129.6, 122.9, 121.3, 120.4, 114.5, 89.1, 79.6, 70.5, 68.5, 24.6. IR ($CDCl_3$), ν_{max}: 3587 (w), 2933 (w), 2247 (w), 1600 (m), 1589 (m), 1497 (s), 1410 (m). MS, *m/z* (%): 253 (40), 235 (12), 158 (52), 132 (100), 77 (22).

1-Phenyl-4-(pyridin-3-yl)but-3-yn-1-ol (**12g**). Yield 0.34 g (41%), yellowish oil. ^{1}H NMR: 8.58 s, 1 H (H2′); 8.48–8.44 m, 1 H (H6′); 7.67 dt, 1 H, J_1 = 7.7, J_2 = 1.9 (H4′); 7.46–7.19 m, 6 H (H5′, H2″, H3″, H4″, H5″, H6″); 4.98 t, 1 H, *J* = 6.3 (H1); 2.91–2.86 m, 2 H (H2). ^{13}C NMR: 151.8, 147.6, 142.7, 139.0, 128.5, 128.0, 125.8, 123.1, 120.8, 90.4, 79.4, 72.4, 30.4. IR ($CDCl_3$), ν_{max}: 3352 (m), 2924 (w), 2229 (w), 1565 (w), 1408 (m), 1328 (w), 1055 (m). MS, *m/z* (%): 224($M^{\bullet+}$, 12), 117 (100), 79 (46).

1-(Pyridin-3-yl)oct-7-en-1-yn-4-ol (**12h**). Yield 0.21 g (50%), yellowish oil. ^{1}H NMR: 8.62 d, 1 H, J_1 = 1.65 (H2′); 8.48 dd, 1 H, J_1 = 4.9, J_2 = 1.6 (H6′); 7.67 dt, 1 H, J_1 = 8.0, J_2 = 1.9 (H4′); 7.24–7.18 m, 1 H (H5′); 5.92–5.77 m, 1 H (H7); 5.11–4.92 m, 2 H (H8); 3.94–3.82 m, 1 H (H4); 2.66–2.54 m, 2 H (H3); 2.32–2.12 m, 2 H (H6); 1.75–1.66 m, 2 H (H5). ^{13}C NMR: 152.2, 148.1, 138.6, 138.0, 122.9, 120.6, 115.1, 90.1, 79.5, 69.4, 35.5, 29.9, 28.4. IR ($CDCl_3$), ν_{max}: 3374 (m), 2930 (m), 2227 (m), 1640 (m), 1409 (m), 1083 (m). MS, *m/z* (%): 202 (3), 202 (100), 185 (1).

Preparation of Iodo Alcohols **13** (Except **13f**, **13g**, **13h**). General Procedure

A 60% solution of Red-Al in toluene (1.25 ml, 4.5 mmol) was added to a solution of a homopropargylic alcohol **12** (1.5 mmol) in dry THF (20 ml) and the mixture was stirred at 80 °C for 2 h. Ethyl acetate was then added (0.6 ml, 6.75 mmol) to decompose residual Red-Al, the mixture was cooled down to –78 °C, and a solution of iodine (3.6 mmol) in THF (5 ml) was added dropwise. The resultant mixture was slowly allowed to warm to room temperature and diluted with ethyl acetate (20 ml). The solution was washed with a saturated aqueous solution of $NaHCO_3$ and $Na_2S_2O_3$, dried over anhydrous Na_2SO_4 and concentrated in vacuo to yield the crude iodo alcohol **13**, which was purified by column chromatography (hexane/ethyl acetate 9:1).

(Z)-6-Iodo-6-phenylhex-5-en-3-ol (**13a**). Yield 1.2 g (70%), colorless oil. ^{1}H NMR: 7.46–7.39 m, 2 H (H2″, H6″), 7.38–7.21 m, 3 H (H3″, H4″, H5″); 6.05 t, 1 H, *J* = 6.9 (H5); 3.85–3.71 m, 1 H

(H3); 2.61–2.40 m, 2 H (H4); 1.82 bs, 1 H (OH); 1.67–1.48 m, 2 H (H2); 1.01 t, 3 H, *J* = 7.3 (H1). MS, *m/z* (%): 302 (0), 285 (6), 244 (30), 175 (10), 133 (10), 117 (100), 59 (20).

(Z)-1-Iodo-1-phenylocta-1,7-dien-4-ol (**13b**). Yield 0.6 g (64%), yellowish oil. ^{1}H NMR: 7.50–7.40 m, 2 H (H2′, H6′); 7.34–7.22 m, 3 H (H3′, H4′, H5′); 6.04 t, 1 H, J_1 = 6.9 (H2); 5.94–5.78 m, 1 H (H7); 5.14–4.96 m, 2 H (H8); 3.95–3.82 m, 1 H (H4); 2.67–2.44 m, 2 H (H3); 2.34–2.11 m, 2 H (H6); 1.76–1.61 m, 3 H (H5 + OH). ^{13}C NMR: 143.0, 138.2, 135.0, 134.8, 128.5, 128.2, 115.1, 107.2, 70.7, 45.5, 36.2, 30.0. IR ($CDCl_3$), ν_{max}: 3567 (w), 3012 (w), 2861 (m), 1715 (m), 1630 (w), 1443 (m), 1394 (w). MS, *m/z* (%): 328 (3), 243 (12), 200 (37), 182 (69), 116 (100), 104 (20).

(Z)-5-Iodo-1-phenoxy-5-phenylpent-4-en-2-ol (**13c**). Yield 0.18 g (57%), yellowish oil. ^{1}H NMR: 7.51–7.41 m, 2 H (H2″, H6″); 7.35–7.21 m, 5 H (H3′, H5′, H3″, H4″, H5″); 7.03–6.88 m, 3 H (H2′, H4′, H6′); 6.15–6.04 m, 1 H (H4); 4.31–4.13 m, 1 H (H2); 4.11–3.87 m, 2 H (H1); 2.72–2.60 m, 2 H (H3). ^{13}C NMR: 158.6, 143.1, 134.4, 134.2, 129.9, 129.7, 128.8, 128.6, 128.5, 128.4, 121.7, 121.4, 108.1, 71.7, 69.7, 41.8. IR ($CDCl_3$), ν_{max}: 3410 (m), 2923 (m), 1602 (s), 1496 (s), 1240 (m), 1137 (m). MS, *m/z* (%): 380 (3), 269 (100), 244 (20), 133 (53), 115 (96), 105 (51), 91 (68), 77 (53).

(1S,3Z)-4-Iodo-1,4-diphenylbut-3-en-1-ol (**13d**). Yield 0.20 g (72%), yellowish oil. ^{1}H NMR: 7.45–7.24 m, 10 H (Ar); 6.00 t, 1 H, *J* = 6.9 (H3); 4.94 dd, 1 H, J_1 = 7.7, J_2 = 5.5 (H1); 2.90–2.71 m, 2 H (H2). ^{13}C NMR: 143.6, 143.0, 134.6, 128.58, 128.53, 128.47, 128.3, 128.2, 127.9, 126.1, 125.8, 107.5, 73.4, 47.1. IR ($CDCl_3$), ν_{max}: 3386 (m), 3027 (m), 2922 (m), 1599 (m), 1442 (m), 1628 (m). 1029 (m). MS, *m/z* (%): 332 (3), 244 (28), 205 (10), 117 (70), 107 (97), 79 (100).

(Z)-1-Iodo-1-phenyloct-1-en-4-ol (**13e**). Yield 0.29 g (70%), yellowish oil. ^{1}H NMR: 7.49–7.44 m, 2 H (H2′, H6′); 7.33–7.24 m, 3 H (H3′, H4′, H5′); 6.05 t, 1 H, *J* = 6.9 (H2); 3.91–3.81 m, 1 H (H4); 2.61–2.42 m, 2 H (H3); 1.63–1.48 m, 2 H (H5); 1.47–1.23 m, 4 H (H6, H7); 0.97–0.90 m, 3 H (H8). ^{13}C NMR: 143.1, 135.2, 128.5, 128.3, 128.2, 107.1, 71.1, 45.5, 37.0, 27.8, 22.7, 14.1. IR ($CDCl_3$), ν_{max}: 3374 (m), 3057 (w), 2955 (m), 1715 (m), 1595 (w), 1443 (m), 1219 (m), 1030 (m). MS, *m/z* (%): 331 ($M^{\bullet+}$, 18), 316 (18), 313 (100), 303 (96), 289 (42), 275 (30), 261 (50), 253 (34), 247 (85).

(Z)-1-(3-Fluorophenyl)-1-iodooct-1-en-4-ol (**13i**). Yield 0.38 g (65%), yellowish oil. ^{1}H NMR: 7.28–7.23 m, 2 H (Ar); 7.21–7.15 m, 1 H (Ar); 6.99–6.91 m, 1 H (Ar); 6.10 t, 1 H, *J* = 6.6 (H2); 3.91–3.80 m, 1 H (H4); 2.60–2.40 m, 2 H (H3); 1.61–1.48 m, 2 H (H5); 1.47–1.23 m, 4 H (H6, H7); 0.98–0.87 m, 3 H (H8). ^{13}C NMR: 162.3 (d, *J* = 246.2), 136.4, 129.5 (d, *J* = 8.6), 124.2 (d, *J* = 2.9), 115.7 (d, *J* = 22.9), 115.1 (d, *J* = 21.1), 104.9, 71.0, 45.5, 37.0, 27.8, 22.7, 14.1. IR ($CDCl_3$), ν_{max}: 3312 (w), 3065 (m), 2955 (m), 2929 (m), 2859 (m), 1608 (m), 1583 (m), 1429 (m), 1146 (m). MS, *m/z* (%): 349 ($M^{\bullet+}$, 6), 331 (8), 307 (100), 293 (5), 211 (34).

(Z)-5-(3-Fluorophenyl)-5-iodo-1-phenoxypent-4-en-2-ol (**13j**). Yield 0.45 g (63%), yellowish oil. ^{1}H NMR: 7.39–7.16 m, 5 H (Ar); 7.03–6.88 m, 4 H (Ar); 6.18 t, 1 H, *J* = 6.6 (H4); 4.30–4.20 m, 1 H (H2); 4.10–3.90 m, 2 H (H1); 2.67 t, 2 H, *J* = 6.9 (H3). ^{13}C NMR: 162.3 (d, *J* = 246.5), 158.3, 145.0 (d, *J* = 8.0), 135.2, 129.6, 129.4 (d, *J* = 8.6), 124.1 (d, *J* = 2.9), 121.3, 115.7 (d, *J* = 23.3), 115.2 (d, *J* = 21.2), 114.5, 105.6, 71.4, 69.2, 41.5, 19.0. IR ($CDCl_3$), ν_{max}: 3418 (m), 2924 (m), 1599 (m), 1496 (m), 1428 (m), 1244 (m), 1044 (m). MS, *m/z* (%): 398 (3), 287 (67), 262 (21), 160 (26), 133 (93), 119 (100), 94 (41), 77 (71).

(Z)-4-(3-Fluorophenyl)-4-iodo-1-phenylbut-3-en-1-ol (**13k**). Yield 0.17 g (72%), yellowish oil. ^{1}H NMR: 7.44–7.23 m, 8 H (Ar); 7.00–6.92 m, 1 H (Ar); 6.06 t, 1 H, *J* = 6.6 (H3); 4.92 dd, 1 H, J_1 = 7.7, J_2 = 5.5 (H1); 2.88–2.64 m, 2 H (H2); 2.17 bs, 1 H (OH). ^{13}C NMR: 162.2 (d, *J* = 246.2), 145.0 (d, *J* = 8.0), 143.5, 135.8, 129.5 (d, *J* = 8.6), 128.5, 127.9, 125.7, 124.1 (d, *J* =

2.9), 115.7 (d, *J* = 22.9), 115.0 (d, *J* = 21.5), 115.1, 105.2, 73.2, 46.9. IR ($CDCl_3$), ν_{max}: 3374 (s), 3030 (s), 2922 (s), 2358 (m), 1948 (m), 1608 (s), 1582 (s), 1428 (s), 1256 (s). MS, *m/z* (%): 368 (0), 351 (4), 262 (20), 223 (10), 133 (31), 107 (100), 79 (80).

(Z)-1-Iodo-1-(1-naphthyl)oct-1-en-4-ol (**13l**). Yield 0.47 g (83%), yellowish oil. ^{1}H NMR: 8.12–8.07 m, 1 H (Ar); 7.89–7.77 m, 2 H (Ar); 7.59–7.37 m, 4 H (Ar); 5.91 t, 1 H, *J* = 6.9 (H2); 3.97–3.87 m, 1 H (H4); 2.71–2.53 m, 2 H (H3); 1.69–1.32 m, 6 H (H5, H6, H7); 0.99–0.93 m, 3 H (H8). ^{13}C NMR: 141.8, 137.5, 133.7, 130.5, 128.5, 128.2, 126.2, 126.01, 125.99, 125.7, 125.2, 102.0, 71.1, 44.9, 37.0, 27.8, 22.7, 14.0. IR ($CDCl_3$), ν_{max}: 3335 (m), 3057 (m), 2929 (s), 2858 (s), 1927 (w), 1585 (m), 1465 (m), 1396 (m), 1014 (w). MS, *m/z* (%): 381 ($M^{\bullet+}$, 4), 321 (22), 309 (20), 268 (100), 246 (24), 145 (28).

(Z)-5-Iodo-5-(1-naphthyl)-1-phenoxypent-4-en-2-ol (**13m**). Yield 0.36 g (80%), yellowish oil. ^{1}H NMR: 8.11–8.05 m, 1 H (Ar); 7.89–7.78 m, 2 H (Ar); 7.57–7.24 m, 6 H (Ar); 7.03–6.94 m, 3 H (Ar); 5.98 t, 1 H, *J* = 6.6 (H4); 4.36–4.27 m, 1 H (H2); 4.18–3.98 m, 2 H (H1); 2.78 t, 2 H, *J* = 6.6 (H3). ^{13}C NMR: 158.4, 136.5, 133.7, 129.6, 128.7, 128.2, 126.2, 126.1, 126.0, 125.6, 125.2, 121.3, 114.6, 102.7, 71.4, 69.3, 41.0. IR ($CDCl_3$), ν_{max}: 3592 (w), 3011 (w), 2929 (w), 1599 (m), 1497 (m), 1322 (w). MS, *m/z* (%): 431 ($M^{\bullet+}$, 100), 413 (14), 367 (43).

(Z)-6-Iodo-6-(1-naphthyl)hex-5-en-3-ol (**13n**). Yield 0.42 g (82%), yellowish oil. ^{1}H NMR: 8.13–8.07 m, 1 H (Ar); 7.89–7.77 m, 2 H (Ar); 7.60–7.38 m, 4 H (Ar); 5.91 t, 1 H, *J* = 6.6 (H5); 3.90–3.81 m, 1 H (H3); 2.71–2.53 m, 2 H (H4); 1.76–1.53 m, 2 H (H2); 1.05 t, 3 H, *J* = 7.4 (H1). ^{13}C NMR: 141.8, 137.5, 133.7, 130.5, 128.6, 128.2, 126.2, 126.02, 126.00, 125.7, 125.2, 102.0, 72.4, 44.5, 30.1, 10.0. IR ($CDCl_3$), ν_{max}: 3374 (s), 3057 (s), 2961 (s), 2875 (s), 1640 (m), 1589 (m), 1504 (m), 1393 (s), 1230 (s). MS, *m/z* (%): 355 ($M^{\bullet+}$, 21), 239 (43), 225 (100), 209 (21).

(Z)-1-Iodo-1-(1-naphthyl)octa-1,7-dien-4-ol (**13o**). Yield 0.38 g (83%), yellowish oil. ^{1}H NMR: 8.12–8.07 m, 1 H (Ar); 7.90–7.77 m, 2 H (Ar); 7.59–7.38 m, 4 H (Ar); 5.97–5.82 m, 2 H (H2 + H7); 5.17–5.00 m, 2 H (H8); 4.01–3.91 m, 1 H (H4); 2.69–2.58 m, 2 H (H3); 2.35–2.19 m, 2 H (H6); 1.77–1.65 m, 2 H (H8 + OH). ^{13}C NMR: 141.8, 138.2, 137.3, 133.7, 130.5, 128.6, 128.2, 126.2, 126.02, 125.97, 125.7, 125.2, 115.1, 102.2, 70.6, 44.9, 36.2, 30.0. IR ($CDCl_3$), ν_{max}: 3373 (m), 2927 (m), 2852 (m), 1640 (m), 1505 (m), 1393 (m), 1230 (m). MS, *m/z* (%): 379 ($M^{\bullet+}$, 40), 364 (16), 251 (44), 233 (95), 195 (16), 155 (100).

Preparation of Iodo Alcohols **13f**, **13g**, **13h**. General Procedure

A 60% solution of Red-Al in toluene (1.25 ml, 4.5 mmol) was added to a solution of a homopropargylic alcohol (1.5 mmol) in dry THF (20 ml) and the mixture was stirred at 80 °C for 2 h. Ethyl acetate was added (0.6 ml, 6.75 mmol) to decompose residual Red-Al, the mixture was cooled down to –78 °C and a solution of NIS (3.6 mmol) in THF (5 ml) was added dropwise. The resultant mixture was slowly allowed to warm to room temperature, and diluted with ethyl acetate (20 ml). The solution was washed with a saturated aqueous solution of $NaHCO_3$ and $Na_2S_2O_3$, dried over anhydrous Na_2SO_4 and concentrated in vacuo to yield the crude iodo alcohol, which was purified by column chromatography (hexane/ethyl acetate 9:1).

(Z)-5-Iodo-1-phenoxy-5-(pyridin-3-yl)pent-4-en-2-ol (**13f**). Yield 0.16 g (69%), yellowish oil. ^{1}H NMR: 8.70 bs, 1 H (H2′); 8.49 bs, 1 H (H6′); 7.80 dt, 1 H, J_1 = 8.0, J_2 = 1.9 (H4′); 7.34–7.22 m, 3 H (H5′, H3″, H5″); 7.02–6.88 m, 3 H (H2″, H4″, H6″); 6.24 t, 1 H, *J* = 6.9 (H4); 4.32–4.22 m, 1 H (H2); 4.11–3.90 m, 2 H (H1); 2.68 t, 2 H, *J* = 6.3 (H3). ^{13}C NMR: 158.3, 148.8, 148.2, 139.2, 136.9, 136.6, 129.6, 123.2, 121.3, 114.5, 102.4, 71.4, 69.1, 41.7.

IR ($CDCl_3$), ν_{max}: 3587 (w), 3019 (w), 2874 (w), 2246 (w), 1599 (m), 1497 (m), 1412 (w), 1289 (w). MS, *m/z* (%): 381 (9), 288 (33), 254 (100), 236 (41), 133 (25).

(Z)-4-Iodo-1-phenyl-4-(pyridin-3-yl)but-3-en-1-ol (**13g**). Yield 0.15 g (43%), yellowish oil. ^{1}H NMR: 8.60–8.55 m, 1 H (H2′); 8.44–8.39 m, 1 H (H6′); 7.75–7.69 m, 1 H (H4′); 7.47–7.17 m, 6 H (H5′, H2″, H3″, H4″, H5″, H6″); 6.10 t, 1 H, *J* = 6.6 (H3); 5.00–4.91 m, 1 H (H1); 2.82–2.77 m, 2 H (H2). ^{13}C NMR: 152.2, 148.9, 143.6, 138.7, 137.0, 136.6, 128.6, 128.0, 125.8, 123.0, 102.2, 73.1, 29.6. IR ($CDCl_3$), ν_{max}: 3374 (s), 2952 (s), 1942 (m), 1602 (s), 1582 (s), 1420 (m), 1204 (s). MS, *m/z* (%): 352 ($M^{\bullet+}$, 4), 245 (100), 117 (67), 107 (45), 89 (28), 79 (100).

(Z)-1-Iodo-1-(pyridin-3-yl)octa-1,7-dien-4-ol (**13h**). Yield 0.12 g (47%), yellowish oil. ^{1}H NMR: 8.75–8.60 bs, 1 H (H2′); 8.51–8.41 bs, 1 H (H6′); 7.78 d, 1 H, J_1 = 8.0 (H4′); 7.30–7.21 m, 1 H (H5′); 6.17 t, 1 H, *J* = 8.0 (H2); 5.91–5.77 m, 1 H (H7); 5.12–4.94 m, 2 H (H8); 3.95–3.82 m, 1 H (H4); 2.58–2.44 m, 2 H (H3); 2.30–2.11 m, 2 H (H6); 1.71–1.60 m, 2 H (H5). ^{13}C NMR: 178.0, 148.6, 148.0, 138.1, 137.6, 136.9, 123.2, 115.1, 101.7, 70.2, 45.5, 36.2, 30.0, 29.6. IR ($CDCl_3$), ν_{max}: 3073 (m), 2927 (m), 2852 (m), 1640 (m), 1485 (m), 1392 (m). MS, *m/z* (%): 329 (8), 311 (15), 202 (71), 184 (100), 144 (52).

Preparation of 5,6-Dihydro-2*H*-pyran-2-ones **14**. General Procedure

Triethylamine (5.2 mmol), [$Pd_2(dba)_3$] (2.5 mole %) and bicyclohexylphosphine (10 mole %) were added to a solution of an iodo alcohol **13** (1.3 mmol) in dry ethanol (15 ml), and the reaction mixture was stirred under CO (ambient pressure) at 70 °C for 16 h. The solvent was then evaporated and the residue diluted with ethyl acetate (20 ml). The solution was washed with a saturated aqueous solution of NaCl, dried over anhydrous Na_2SO_4 and concentrated in vacuo to yield the crude pyranone **14**, which was purified by column chromatography (hexane/ethyl acetate 9:1).

6-Ethyl-3-phenyl-5,6-dihydro-2H-pyran-2-one (**14a**). Yield 0.22 g (92%), colorless crystals. ^{1}H NMR: 7.49–7.42 m, 2 H (H2″, H6″); 7.38–7.31 m, 3 H (H3″, H4″, H5″); 6.98–6.92 m, 1 H (H4); 4.51–4.39 m, 1 H (H6); 2.55–2.42 m, 2 H (H1′); 1.98–1.67 m, 2 H (H5); 1.07 t, 3 H, *J* = 7.4 (H2′). ^{13}C NMR: 164.5, 140.8, 135.5, 133.2, 128.2, 128.2, 128.1, 79.0, 29.6, 27.8, 9.3. IR (KBr), ν_{max}: 3055 (w), 2968 (m), 2879 (w), 1712 (s), 1666 (w), 1496 (m), 1364 (m), 1203 (s). MS, *m/z* (%): 202 (27), 173 (8), 144 (100), 115 (80), 102 (12).

6-(But-3-en-1-yl)-3-phenyl-5,6-dihydro-2H-pyran-2-one (**14b**). Yield 0.2 g (89%), white crystalline substance, m.p. 68–70 °C. ^{1}H NMR: 7.49–7.42 m, 2 H (H2″, H6″); 7.40–7.32 m, 3 H (H3″, H4″, H5″); 6.97–6.92 m, 1 H (H4); 5.92–5.75 m, 1 H (H3′); 5.16–4.98 m, 2 H (H4′); 4.60–4.47 m, 1 H (H6); 2.57–2.43 m, 2 H (H2′); 2.39–2.17 m, 2 H (H1′); 2.05–1.19 m, 1 H (H5A); 1.85–1.71 m, 1 H (H5B). ^{13}C NMR: 164.3, 140.6, 137.1, 135.4, 133.1, 131.7, 128.18, 128.13, 115.6, 100.1, 33.8, 30.0, 28.9. IR (KBr), ν_{max}: 3014 (m), 2944 (m), 2853 (w), 1716 (s), 1641 (w), 1446 (m), 188 (m), 1285 (w). MS, *m/z* (%): 230 (100), 212 (60), 184 (64), 146 (11), 85 (13).

6-(Phenoxymethyl)-3-phenyl-5,6-dihydro-2H-pyran-2-one (**14c**). Yield 0.07 g (89%), white crystalline substance, m.p. 104–105 °C. ^{1}H NMR: 7.52–7.45 m, 2 H (H2″, H6″); 7.42–7.26 m, 5 H (H3′, H5′, H3″, H4″, H5″); 7.05–6.92 m, 4 H (H4, H2′, H4′, H6′); 4.95–4.85 m, 1 H (H6); 4.30–4.18 m, 2 H (OCH_2); 2.90–2.65 m, 2 H (H5). ^{13}C NMR: 163.4, 158.1, 140.4, 135.2, 133.1, 129.6, 128.33, 128.26, 121.4, 114.5, 75.4, 68.4, 29.7, 27.0. IR (KBr), ν_{max}: 2922 (m), 1713 (s), 1602 (m), 1496 (m), 1252 (m), 1187 (m), 1086 (w). MS, *m/z* (%): 281 ($M^{\bullet+}$, 20), 187 (82), 169 (22), 143 (26), 115 (100), 77 (38).

(S)-3,6-Diphenyl-5,6-dihydro-2H-pyran-2-one (**14d**). Yield 0.11 g (82%), white crystalline substance, m.p. 161–163 °C, $[\alpha]_D$ –210 (*c* 0.53, $CHCl_3$). ^{1}H NMR: 7.54–7.34 m, 10 H (Ar); 7.04 dd, 1 H, J_1 = 5.8, J_2 = 3.0 (H4); 5.55 dd, 1 H, J_1 = 11.0, J_2 = 4.7 (H6); 2.92–2.71 m, 2 H (H5). ^{13}C NMR: 164.0, 140.5, 138.4, 135.3, 134.5, 128.7, 128.6, 128.3, 128.28, 128.26, 126.1, 79.1, 32.4. IR: 3401 (w), 2916 (w), 1709 (s), 1454 (m), 1363 (m), 1173 (m). IR (KBr), ν_{max}: 3392 (w), 3050 (m), 1711 (s), 1496 (m), 1364 (m), 1197 (s). MS, *m/z* (%): 251($M^{\bullet+}$, 7), 144 (100), 115 (49), 77 (10).

6-Butyl-3-phenyl-5,6-dihydro-2H-pyran-2-one (**14e**). Yield 0.11 g (86%), white crystalline substance, m.p. 96–97 °C. ^{1}H NMR: 7.48–7.43 m, 2 H (H2″, H6″); 7.33–7.23 m, 3 H (H3″, H4″, H5″); 6.98–6.95 t, 1 H, *J* = 6.0 (H4); 4.56–4.45 m, 1 H (H6); 2.54–2.45 m, 2 H (H5); 1.93–1.79 m, 1 H (H1′A); 1.76–1.63 m, 1 H (H1′B); 1.62–1.31 m, 4 H (H2′, H3′); 0.97–0.91 m, 3 H (H4′). ^{13}C NMR: 164.5, 140.7, 135.5, 133.2, 128.26, 128.21, 128.17, 77.9, 34.5, 30.1, 27.0, 22.5, 13.9. IR (KBr), ν_{max}: 3392 (m), 3056 (m), 2957 (s), 2891 (s), 1699 (s), 1366 (s), 1199 (s). MS, *m/z* (%): 231 ($M^{\bullet+}$, 6), 213 (100), 185 (48), 161 (17), 129 (13).

6-(Phenoxymethyl)-3-(pyridin-3-yl)-5,6-dihydro-2H-pyran-2-one (**14f**). Yield 0.10 g (70%), brown crystalline substance, m.p. 70–73 °C. ^{1}H NMR: 8.78–8.49 m, 2 H (H2′, H6′); 7.90 d, 1 H, J_1 = 8.0 (H4′); 7.51–7.18 m, 3 H (H5′, H3″, H5″); 7.09 dd, 1 H, J_1 = 6.0, J_2 = 2.8 (H4); 7.03–6.88 m, 3 H (H2″, H4″, H6″); 4.97–4.87 m, 1 H (H6); 4.24 dd, 2 H, J_1 = 4.4, J_2 = 2.2 (OCH_2); 2.95–2.69 m, 2 H (H5). ^{13}C NMR: 162.9, 158.0, 149.0, 148.3, 142.0, 136.4, 131.7, 130.0, 129.6, 123.1, 121.5, 114.5, 75.6, 68.3, 27.0. IR (KBr), ν_{max}: 2928 (w), 2249 (w), 1727 (s), 1600 (m), 1420 (m), 1300 (w). MS, *m/z* (%): 281 (22), 188 (100), 174 (31), 160 (12), 146 (50), 118 (76), 91 (31), 77 (59).

6-Phenyl-3-(pyridin-3-yl)-5,6-dihydro-2H-pyran-2-one (**14g**). Yield 0.09 g (72%), brown crystalline substance, m.p. 174–177 °C. ^{1}H NMR: 8.63–8.56 bs, 1 H (H2′); 8.52–8.44 bs, 1 H (H6′); 7.67 dt, 1 H, J_1 = 8.0, J_2 = 1.7 (H4′); 7.47–7.20 m, 7 H (H4, H5′, H2″, H3″, H4″, H5″, H6″); 4.98 t, 1 H, *J* = 6.1 (H6); 2.92–2.87 m, 2 H (H5). ^{13}C NMR: 151.8, 147.7, 142.7, 139.0, 128.5, 128.0, 125.8, 123.1, 90.3, 79.4, 72.5, 30.4, 29.7. IR (KBr), ν_{max}: 2960 (m), 1720 (s), 1601 (m), 1583 (w), 1432 (m), 1147 (m). MS, *m/z* (%): 252 ($M^{\bullet+}$, 17), 234 (10), 206 (14), 145 (100), 116 (49).

6-(But-3-en-1-yl)-3-(pyridin-3-yl)-5,6-dihydro-2H-pyran-2-one (**14h**). Yield 0.03 g (68%), brown crystalline substance, m.p. 74–77 °C. ^{1}H NMR: 8.68–8.61 bs, 1 H (H2″); 8.60–8.53 bs, 1 H (H6″); 7.88 dt, 1 H, J_1 = 8.0, J_2 = 1.9 (H4″); 7.30 dd, 1 H, J_1 = 8.0, J_2 = 4.7 (H5″); 7.05–7.00 m, 1 H (H4); 5.90–5.74 m, 1 H (H3′); 5.14–4.99 m, 2 H (H4′); 4.62–4.51 m, 1 H (H6); 2.59–2.51 m, 2 H (H5); 2.38–2.18 m, 2 H (H2′); 2.05–1.91 m, 1 H (H1′A); 1.85–1.72 m, 1 H (H1′B). ^{13}C NMR: 163.9, 149.3, 148.6, 142.0, 137.0, 136.1, 131.3, 130.3, 122.9, 115.8, 76.6, 33.8, 30.1, 28.6. IR (KBr), ν_{max}: 3019 (m), 2947 (m), 1716 (s), 1641 (m), 1478 (m), 1420 (m), 1326 (m). MS, *m/z* (%): 231 (25), 230 (78), 186 (26), 146 (100), 144 (27).

6-Butyl-3-(3-fluorophenyl)-5,6-dihydro-2H-pyran-2-one (**14i**). Yield 0.19 g (87%), white crystalline substance, m.p. 85–86 °C. ^{1}H NMR: 7.38–7.19 m, 3 H (Ar); 7.09–6.92 m, 2 H (Ar + H4); 4.56–4.45 m, 1 H (H6); 2.54–2.45 m, 2 H (H5); 1.93–1.79 m, 1 H (H4′A); 1.76–1.63 m, 1 H (H4′B); 1.62–1.31 m, 4 H (H2′, H3′); 0.97–0.91 m, 3 H (H4′). ^{13}C NMR: 164.1 (d, *J* = 245.3), 160.8, 141.6, 137.5 (d, *J* = 8.1), 132.5, 129.7 (d, *J* = 8.3), 123.9 (d, *J* = 2.9), 115.4 (d, *J* = 22.6), 115.1 (d, *J* = 20.9), 77.9, 34.5, 30.1, 26.9, 22.4, 13.9. IR (KBr), ν_{max}: 3390 (m), 2956 (s), 2934 (s), 2910 (m), 2870 (m), 1708 (s), 1613 (m), 1580 (s), 1435 (s), 1217 (s), 1162 (s), 1079 (s). MS, *m/z* (%): 249 ($M^{\bullet+}$, 29), 261 (98), 221 (100), 203 (19), 179 (17).

3-(3-Fluorophenyl)-6-(phenoxymethyl)-5,6-dihydro-2H-pyran-2-one (**14j**). Yield 0.25 g (88%), white crystalline substance, m.p. 100–103 °C. ^{1}H NMR: 7.38–7.19 m, 5 H (Ar); 7.08–6.90 m,

5 H (4 Ar + H4); 4.93–4.82 m, 1 H (H6); 4.28–4.17 m, 2 H (OCH_2); 2.90–2.65 m, 2 H (H5). ^{13}C NMR: 162.4 (d, *J* = 245.6), 163.0, 158.0, 141.3, 137.2 (d, *J* = 8.3), 132.0 (d, *J* = 2.3), 129.7 (d, *J* = 8.6), 129.6, 123.9, 121.4, 115.5 (d, *J* = 22.9), 115.2 (d, *J* = 21.1), 114.5, 75.4, 68.3, 26.9. IR (KBr), ν_{max}: 3393 (m), 2919 (m), 1705 (s), 1601 (m), 1498 (s), 1246 (s), 1175 (m). MS, *m/z* (%): 298 (22), 205 (56), 191 (48), 163 (27), 133 (100), 115 (34), 94 (59), 77 (62).

3-(3-Fluorophenyl)-6-phenyl-5,6-dihydro-2H-pyran-2-one (**14k**). Yield 0.09 g (85%), white crystalline substance, m.p. 111–113 °C. ^{1}H NMR: 7.49–7.23 m, 8 H (Ar); 7.09–7.02 m, 2 H (Ar + H4); 5.55 dd, 1 H, J_1 = 11.0, J_2 = 5.0 (H6); 2.93–2.72 m, 2 H (H5). ^{13}C NMR: 163.6, 162.5 (d, *J* = 245.7), 141.4, 138.1, 137.3 (d, *J* = 8.3), 132.4, 129.7 (d, *J* = 8.3), 128.7, 126.7, 124.0 (d, *J* = 2.9), 115.4 (d, *J* = 22.6), 115.2 (d, *J* = 21.2), 79.1, 32.3. IR (KBr), ν_{max}: 2956 (m), 1711 (s), 1611 (w), 1583 (m), 1435 (m), 1207 (s), 1149 (m). MS, *m/z* (%): 269 ($M^{\bullet+}$, 7), 251 (2), 223 (3), 202 (3), 162 (100), 133 (59), 77 (12).

6-Butyl-3-(1-naphthyl)-5,6-dihydro-2H-pyran-2-one (**14l**). Yield 0.31 g (90%), white crystalline substance, m.p. 58–59 °C. ^{1}H NMR: 7.90–7.82 m, 2 H (Ar); 7.77–7.70 m, 1 H (Ar); 7.51–7.43 m, 3 H (Ar); 7.39–7.33 m, 1 H (Ar); 6.97–6.93 m, 1 H (H4); 4.77–4.66 m, 1 H (H6); 2.63–2.56 m, 2 H (H5); 2.01–1.71 m, 2 H (H1′); 1.68–1.36 m, 4 H (H2′, H3′); 1.02–0.93 m, 3 H (H4′). ^{13}C NMR: 164.6, 143.7, 133.7, 133.5, 132.9, 131.7, 128.8, 128.4, 127.2, 126.1, 125.8, 125.2, 125.0, 78.3, 34.6, 30.1, 27.0, 22.5, 13.9. IR (KBr), ν_{max}: 3401 (w), 3061 (m), 3012 (s), 2959 (s), 2873 (s), 1926 (w), 1712 (s), 1593 (m), 1467 (m), 1396 (s), 1253 (m). MS, *m/z* (%): 281 ($M^{\bullet+}$, 18), 263 (100), 253 (63), 235 (55), 211 (21).

3-(1-Naphthyl)-6-(phenoxymethyl)-5,6-dihydro-2H-pyran-2-one (**14m**). Yield 0.20 g (91%), white crystalline substance, m.p. 97–100 °C. ^{1}H NMR: 7.91–7.85 m, 2 H (Ar); 7.80–7.73 m, 1 H (Ar); 7.53–7.45 m, 3 H (Ar); 7.41–7.30 m, 3 H (Ar); 7.07–6.95 m, 4 H (Ar + H4); 5.13–5.03 m, 1 H (H6); 4.36–4.22 m, 2 H (OCH_2); 3.00–2.72 m, 2 H (H5). ^{13}C NMR: 163.5, 158.1, 143.4, 133.5, 133.3, 132.8, 131.6, 129.6, 129.0, 128.4, 127.3, 126.3, 125.9, 125.2, 125.0, 121.5, 114.6, 75.8, 68.6, 27.0. IR (KBr), ν_{max}: 3062 (m), 3013 (s), 2932 (m), 1724 (s), 1600 (s), 1589 (s), 1497 (s), 1396 (m). MS, *m/z* (%): 330 (40), 237 (13), 219 (21), 191 (50), 178 (21), 165 (100), 152 (40), 77 (48).

6-Ethyl-3-(1-naphthyl)-5,6-dihydro-2H-pyran-2-one (**14n**). Yield 0.28 g (86%), white crystalline substance, m.p. 75–78 °C. ^{1}H NMR: 7.89–7.83 m, 2 H (Ar); 7.76–7.71 m, 1 H (Ar); 7.51–7.44 m, 3 H (Ar); 7.38–7.34 m, 1 H (Ar); 6.97–6.93 m, 1 H (H4); 4.71–4.59 m, 1 H (H6); 2.66–2.51 m, 2 H (H5); 2.03–1.76 m, 2 H (H1′); 1.13 t, 3 H, *J* = 7.4 (H2′). ^{13}C NMR: 164.6, 143.7, 133.7, 133.5, 132.9, 131.7, 128.8, 128.4, 127.2, 126.1, 125.8, 125.2, 125.0, 79.4, 29.6, 27.9, 9.4. IR (KBr), ν_{max}: 3062 (m), 3014 (s), 2971 (m), 2883 (m), 1716 (s), 1463 (m), 1395 (m). MS, *m/z* (%): 252 (30), 207 (11), 179 (31), 165 (100), 152 (21).

6-(But-3-en-1-yl)-3-(1-naphthyl)-5,6-dihydro-2H-pyran-2-one (**14o**). Yield 0.22 g (87%), white crystalline substance, m.p. 67–70 °C. ^{1}H NMR: 7.89–7.83 m, 2 H (Ar); 7.75–7.70 m, 1 H (Ar); 7.51–7.44 m, 3 H (Ar); 7.38–7.34 m, 1 H (Ar); 6.97–6.92 m, 1 H (H4); 5.96–5.80 m, 1 H (H3′); 5.19–5.04 m, 2 H (H4′); 4.78–4.67 m, 1 H (H6); 2.64–2.53 m, 2 H (H5); 2.44–2.28 m, 2 H (H2′); 2.12–1.98 m, 1 H (H1′A); 1.92–1.79 m, 1 H (H1′B). ^{13}C NMR: 164.4, 143.6, 137.2, 133.6, 133.5, 132.9, 131.6, 128.8, 128.4, 127.2, 126.2, 125.8, 125.2, 125.0, 115.7, 34.0, 30.1, 29.0. IR (KBr), ν_{max}: 3063 (w), 3012 (m), 2927 (m), 2854 (m), 1716 (s), 1641 (m), 1396 (m), 1329 (m). MS, *m/z* (%): 280 ($M^{\bullet 2+}$, 7), 261 (76), 251 (16), 233 (100), 219 (18), 191 (22), 179 (27).

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