Highly Efficient Intramolecular Cyclizations of 2'-Hydroxychalcones to 4-Chloro-2*H*-chromenes Under Vilsmeier Conditions

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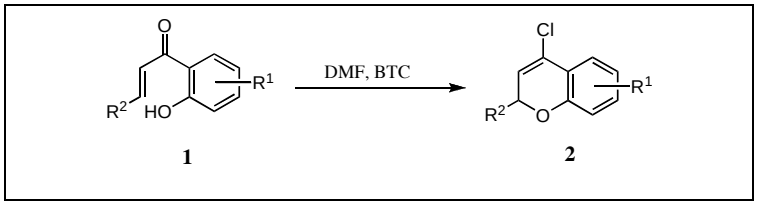

Highly efficient intramolecular cyclization and of 2'-hydroxychalcones to 4-chloro-2*H*-chromenes under Vilsmeier conditions have been developed. In comparison with the reported methods, studies carried out indicate that Vilsmeier reagent generated *in situ* from DMF and *bis*(trichloromethyl) carbonate (BTC) provides excellent chemselectivity, higher yields and avoids the formation of inorganic phosphorus salts.

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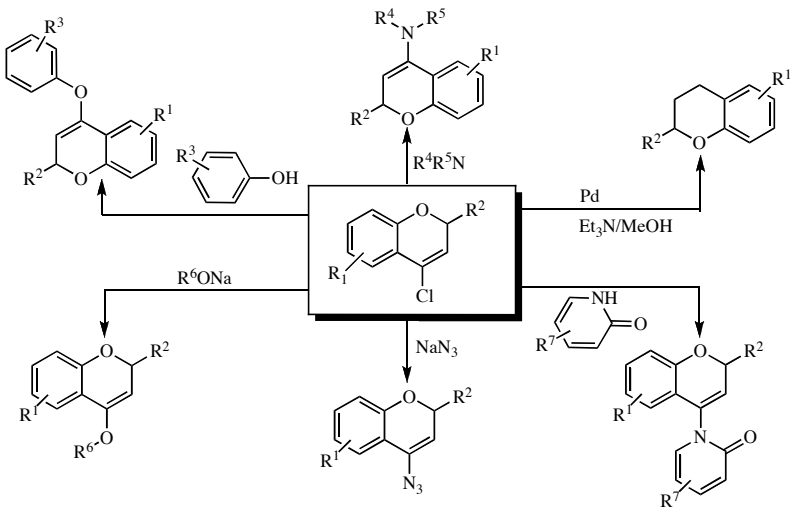
INTRODUCTION

The chromene system is widely distributed in nature, and some derivatives have been shown to exhibit significant pharmacological activity [1]. Functionalized chromenes have shown greater significance for their health promoting effects. As shown in Figure 1, 4-chloro-2*H*-chromene derivatives have been extensively used as versatile building blocks for the synthesis of many *O*-heterocyclic systems with potential bioactivity [2-8].

To the best of our knowledge, 4-chloro-2*H*-chromenes have been prepared by modification of the pre-constructed chromonone nucleus [9]. On the other hand, they could be synthesized through the construction of the 4-chlorochromene ring from γ-chloropropargyl aryl ethers which have involved tedious procedures [10]. Kumar provided a better way for the direct synthesis of substituted 4-chloro-2*H*-chromenes from the Vilsmeier reaction of 2'-hydroxychalcones in moderate yields [11]. Generally, most of these procedures often suffer from certain drawbacks such as long reaction time, unexpected side reactions and the unsatisfactory yields. In view of the potential bioactivity of these compounds, however, it is still of continued interest and attention to develop a new simple and efficient method for the synthesis of these compounds.

Scheme 1. Various applications of 4-Chloro-2*H*-chromenes



The Vilsmeier-Hack reaction was initially used for the formylation of activated aromatic substrates and carbonyl compounds. The reactions of aliphatic substrates, particularly carbonyl compounds with chloromethylene-iminium salts are highly versatile. They lead to multiple iminoalkylations in the presence of excess reagent and the resulting intermediates undergo cyclization to afford aromatic or heterocyclic compounds such as quinolines, indoles, quinozolines, and pyridines [12]. Following our recent success [13], in this paper, we wish to report a simple and efficient process for the synthesis of 4-chloro-2*H*-chromenes using a novel Vilsmeier-type reagent generated *in situ* from DMF and *bis*(trichloromethyl) carbonate (BTC). The easily accessible 2'-hydroxy-chalcones were used as starting materials. This work is the continuation of a program with the aim to extend the applications of BTC, especially those combinations of BTC with other reagents. BTC has proven to be a valuable synthon for the synthesis of a large number of organic compounds [14]. As a stable crystalline solid, it is safer and more convenient to handle, transport and store. Reactions with BTC usually proceed under mild conditions and afford good to excellent yields.

RESULTS AND DISCUSSION

Our first study is focused to determine the best ratio of DMF/BTC for 4-chloro-2*H*-chromenes. We studied the reaction of 2'-hydroxychalcone **1a** in the presence of various amounts of BTC and DMF (Table 1). This study demonstrated that the combination of 1 equivalent of BTC and 3 equivalents DMF is most suitable to convert one equivalent of substrate **1a** to 4-chloro-2*H*-chromene **2a**. Another important factor is reaction temperature, and 80 °C is sufficient to carry out the conversion. In comparison with reported methods using other reagents, our procedure can provide excellent selectivity and higher yields and is carried out under milder conditions. Besides, the solvent effect and reaction time were investigated. A series of solvents were tested to optimize the reaction conditions (Table 1, Entries 6-10). When CH_3CN, DMF, or THF was used, the reaction proceeded slowly and gave poor to moderate yields. Good yield was obtained in 1,2-dichloroethane or toluene, and 1,2-dichloroethane was found to be preferable (Table 1). The reaction was monitored by TLC [ethyl acetate/cyclohexane = 1:50], and the isolated yields of different reaction times are summarized in Table 1.

Table 1

Reaction of 2'-Hydroxychalcone with DMF/BTC

Entry	Ratio of **1a**:BTC:DMF	Temp. (°C)	Time (hours)	Yield [a] (%)
1	1:1/3:1	50	6	30 [b]
2	1:1/3:1	80	6	58 [b]
3	1:1:3	50	6	45 [b]
4	1:1:3	80	2	91 [b]
5	1:1:3	80	6	86 [b]
6	1:2:6	80	2	83 [b]
7	1:1:3	80	2	80 [c]
8	1:1:3	80	2	60 [d]
9	1:1:3	60	2	55 [e]
10	1:1:3	80	2	68 [f]

[a] Isolated yield [b] $ClCH_2CH_2Cl$ as solvent [c] Toluene as solvent [d] CH_3CN as solvent [e] THF as solvent [f] DMF as solvent

With respect to the scope and limitation of 4-chloro-2*H*-chromenes synthesis using our improved protocol, a wide range of substituted and structurally diverse 2'-hydroxychalcones were subjected to this reaction under similar conditions. As summarized in Table 2, a variety of substituted 4-chloro-2*H*-chromenes were obtained in good to excellent yields. The structures of the synthesized compounds were confirmed by ^{1}H NMR, IR and MS (new compounds were further confirmed by ^{13}C- NMR and elemental analysis).

Based on our research results, we wish to give a proposed mechanism for the formation of 4-chloro-2*H*-chromenes. The reaction seems to proceed through ring

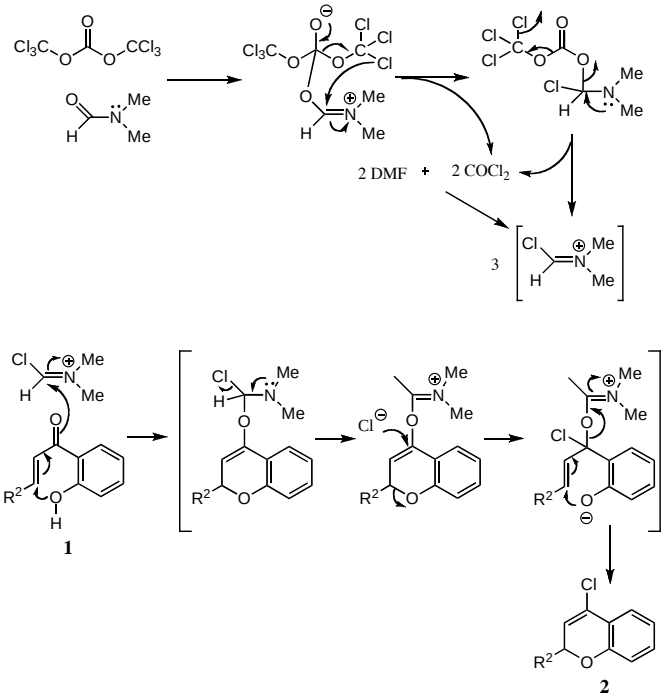
Table 2

Vilsmeier Cyclizations of 2'-Hydroxychalcones **1** to 4-Chloro-2*H*-chromenes **2**

Entry	Substrate			Product **2**	Time (hours)	Yield %	Molecular Formula
1	2'-Hydroxychalcones **1**						
2		**R^1**	**R^2**				
3	**1a**	H	C_6H_5	**2a**	2	93	$C_{15}H_{11}ClO$
4	**1b**	H	*p*-$(CH_3)C_6H_4$	**2b**	3	92	$C_{16}H_{13}ClO$
5	**1c**	H	*o*-ClC_6H_4	**2c**	2	89	$C_{15}H_{10}Cl_2O$
6	**1d**	H	*p*-ClC_6H_4	**2d**	2	90	$C_{15}H_{10}Cl_2O$
7	**1e**	H	*m*-ClC_6H_4	**2e**	2	89	$C_{15}H_{10}Cl_2O$
8	**1f**	H	*m*-$(MeO)C_6H_4$	**2f**	1	94	$C_{16}H_{13}ClO_2$
9	**1g**	H	*m*-$(NO_2)C_6H_4$	**2g**	3	84	$C_{15}H_{10}ClNO_3$
10	**1h**	H	*m*-FC_6H_4	**2h**	2	87	$C_{15}H_{10}ClFO$
11	**1i**	H	2-Chloro-6-Fluoro-C_6H_4	**2i**	2	88	$C_{15}H_{10}Cl_2FO$
12	**1j**	5-Methyl	C_6H_5	**2j**	3	86	$C_{16}H_{13}ClO$
13	**1k**	3,5-Dichloro	C_6H_5	**2k**	3	85	$C_{15}H_9Cl_3O$
14	**1l**	H		**2l**	3	84	$C_{13}H_9ClO_2$

closure to give the enolate intermediate, which further reacts with chloromethyleneiminium salts **I** and on hydrolysis yields the corresponding 4-chloro-2*H*-chromenes as represented in Scheme 2. The milder reaction conditions employed and the ready availability of the starting materials enticed us to adapt this useful methodology for the synthesis of 4-chloro-2*H*-chromenes.

Scheme 2. The proposed mechanism for the cyclization of 2'-hydroxychalcones to 4-Chloro-2*H*-chromenes



In summary, we have developed a highly efficient intramolecular cyclization of 2'-hydroxychalcones to 4-chloro-2*H*-chromenes under Vilsmeier conditions. In comparison with the reported methods, the Vilsmeier reagent generated *in situ* from DMF and *bis*(trichloromethyl) carbonate (BTC) provides excellent selectivity, higher yields and avoids the formation of inorganic phosphorus salts. We believe this procedure will bring a more practical alternative to the existing methods in the future.

EXPERIMENTAL

Infrared spectra were recorded on a Thermo Nicolet Avatar 370 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were measured on a Varian Mercur plus-400 spectrometer using $CDCl_3$ as the solvent. MS (EI) were recorded on a Finnigan Trace DSQ Mass spectrometer at an ionization potential of 75eV. Elemental analysis was determined on a Carlo-Erba 1108 instrument. The progress of the reaction was monitored by TLC. All solvents were of analytical grade without further purification. The starting materials 2'-hydroxychalcones **1** were synthesized by Claisen condensation of appropriately substituted *o*-hydroxyacetophenones and benzaldehydes in ethanol in the presence of 50% KOH [15].

General Procedure. BTC (0.9 g, 3 mmoles) in $ClCH_2CH_2Cl$ (10 mL) was added dropwise to a solution of DMF (0.9 mL, 9 mmoles) in $ClCH_2CH_2Cl$ (5 mL) immersed in an ice-water bath. The mixture was stirred for 20 minutes to obtain the Vilsmeier reagent. Then substituted 2'-hydroxychalcones **1** (3 mmoles) in $ClCH_2CH_2Cl$ (15 mL) was added dropwise to the mixture at 0-5 °C. The reaction mixture was stirred at room temperature for 30 minutes and maintained on an oil bath at 80 °C for 1-3 hours. After completion of the reaction (monitored by TLC [ethyl acetate/cyclohexane = 1:50]), the mixture was poured into ice-water. The organic layer was separated and the aqueous layer extracted with $ClCH_2CH_2Cl$ (10 mL × 2). The combined organic layer washed successively with brine (20 mL × 3) and dried over anhydrous magnesium sulfate. After filtrate and condensation, the residue was separated by column chromatography (silica gel-cyclohexane) to obtain the pure product.

4-Chloro-2-phenyl-2*H*-chromene (2a). Compound **2a**: Colorless oil [11]; IR (KBr, cm^{-1}): 1632 (C=C); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 5.90 (s, 2H, 2-, and 3-H), 6.80 (d, 1H, 8-H, J = 8.4 Hz), 6.90-6.94 (m, 1H, 6-H), 7.13-7.17 (m, 1H, 7-H), 7.29-7.47 (m, 6H, 5-, 2'-, 3'-, 4'-, 5'- , and 6'-H); MS: *m/s* (%) = 244 ([M + 2]$^+$, 21), 243 ([M + 1]$^+$, 27), 242 (M+, 57), 241 ([M - 1]$^+$, 61), 207 ([M - Cl]$^+$, 100).

4-Chloro-2-*p*-tolyl-2*H*-chromene (2b). Compound **2b**: Colorless oil [11]; IR (KBr, cm^{-1}): 1628 (C=C); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 2.28 (s, 3H, CH_3), 5.83 (d, 1H, 2-H, J = 3.6 Hz), 5.86 (d, 1H, 3-H, J = 4.0 Hz), 6.77 (d, 1H, 8-H, J = 8.0 Hz), 6.86-6.90 (m, 1H, 6-H), 7.10-7.13 (m, 3H, 7-, 3'-, and 5'-H), 7.26 (d, 2H, 2'-, and 6'-H, J = 8.0 Hz), 7.44 (dd, 1H, 5-H, J = 0.9, 1.6 Hz); MS: *m/s* (%) = 258 ([M + 2]$^+$, 23), 257 ([M + 1]$^+$, 26), 256 (M+, 64), 255 ([M - 1]$^+$, 50), 221 ([M - Cl]$^+$, 100).

4-Chloro-2-(2-chlorophenyl)-2*H*-chromene (2c). Compound **2c**: Colorless oil [11]; IR (KBr, cm^{-1}): 1629 (C=C); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 5.93 (d, 1H, 2-H, *J* = 3.2 Hz), 6.39 (d, 1H, 3-H, *J* = 3.6 Hz), 6.86 (dd, 1H, 8-H, *J* = 1.2, 1.2 Hz), 6.94-6.98 (m, 1H, 6-H), 7.18-7.26 (m, 3H, 7-, 3'-, and 5'-H), 7.37-7.39 (m, 1H, 4'-H), 7.46-7.48 (m, 1H, 6'-H), 7.56-7.58 (m, 1H, 5-H); MS: *m/s* (%) = 278 ([M + 2]$^+$, 30), 277 ([M + 1]$^+$, 23), 276 (M$^+$, 44), 275 ([M - 1]$^+$, 32), 241 ([M - Cl]$^+$, 100).

4-Chloro-2-(4-chlorophenyl)-2*H*-chromene (2d). Compound **2d**: Colorless oil [11]; IR (KBr, cm^{-1}): 1630 (C=C); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 5.88 (s, 2H, 2-, and 3-H), 6.80 (d, 1H, 8-H, *J* = 8.4 Hz), 6.92-6.96 (m, 1H, 6-H), 7.15-7.19 (m, 1H, 7-H), 7.29-7.47 (m, 5H, 5-, 2'-, 3'-, 5'- , and 6'-H); MS: *m/s* (%) = 278 ([M + 2]$^+$, 33), 277 ([M + 1]$^+$, 29), 276 (M$^+$, 49), 275 ([M - 1]$^+$, 33), 241 ([M - Cl]$^+$, 100).

4-Chloro-2-(3-chlorophenyl)-2*H*-chromene (2e). Compound **2e**: Colorless oil [11]; IR (KBr, cm^{-1}): 1630 (C=C); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 5.90 (s, 2H, 2-, and 3-H), 6.82 (d, 1H, 8-H, *J* = 8.0Hz), 6.94-6.98 (m, 1H, 6-H), 7.17-7.21 (m, 1H, 7-H), 7.25-7.46 (m, 5H, 5-, 2'-, 4'-, 5'- , and 6'-H); MS: *m/s* (%) = 278 ([M + 2]$^+$, 22), 277 ([M + 1]$^+$, 23), 276 (M$^+$, 35), 275 ([M - 1]$^+$, 33), 241 ([M - Cl]$^+$, 100).

4-Chloro-2-(3-methoxyphenyl)-2*H*-chromene (2f). Compound **2f**: Colorless oil [11]; IR (KBr, cm-1): 1627 (C=C); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 3.78 (s, 3H, OCH3), 5.89 (d, 1H, 2-H, J = 3.6 Hz), 5.93 (d, 1H, 3-H, J = 3.6 Hz), 6.78 (d, 1H, 8-H, J = 8.4 Hz), 6.87-6.96 (m, 3H, 6-, 2'-, and 4'-H), 7.15-7.19 (m, 1H, 6'-H), 7.34-7.48 (m, 3H, 5-, 7-, and 5'-H); MS: m/s (%) = 274 ([M + 2]$^+$, 11), 277 ([M + 1]$^+$, 25), 276 (M$^+$, 18), 275 ([M - 1]$^+$, 23), 237 ([M - Cl]$^+$, 100).

4-Chloro-2-(3-nitrophenyl)-2*H*-chromene (2g). Compound **2g**: Colorless oil [11]; IR (KBr, cm-1): 1633 (C=C); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 5.97 (d, 1H, 2-H, *J* = 4.0 Hz), 6.04 (d, 1H, 3-H, *J* = 3.6 Hz), 6.85 (d, 1H, 8-H, *J* = 8.0 Hz), 6.96-7.00 (m, 1H, 6-H), 7.20-7.24 (m, 1H, 5-H), 7.47-7.56 (m, 2H, 7-, and 5'-H), 7.77 (d, 1H, 6'-H, *J* = 3.6 Hz), 8.17 (dd, 1H, 2'-H, *J* = 0.8, 0.8 Hz), 8.29 (s, 1H, 4'-H); MS: m/s (%) = 289 ([M + 2]$^+$, 10), 288 ([M + 1]$^+$, 12), 287 (M$^+$, 30), 286 ([M - 1]$^+$, 23), 252 ([M - Cl]$^+$, 100).

4-Chloro-2-(3-fluorophenyl)-2*H*-chromene (2h). Compound **2h**: Colorless oil; IR (KBr, cm-1): 1645 (C=C); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 5.90 (s, 2H, 2-, and 3-H), 6.83 (d, 1H, 8-H, *J* = 8.0 Hz), 6.94-7.03 (m, 2H, 6-, and 4'-H), 7.13-7.21 (m, 3H,), 7.30-7.34 (m, 1H, 7-H), 7.46-7.47 (dd, 1H, 2'-H, *J* = 1.2, 1.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 77.3, 113.7, 115.4, 116.0, 120.0, 121.3, 122.3, 128.5, 130.2, 130.3, 142.0, 142.1, 153.1, 161.6, 164.0; MS: m/s (%) = 262 ([M + 2]$^+$, 15), 261 ([M + 1]$^+$, 16), 260 (M$^+$, 34), 259 ([M - 1]$^+$, 36), 225 ([M - Cl]$^+$,100); Calcd. for $C_{15}H_{10}ClFO$: C, 69.11; H, 3.87. Found: C, 69.18; H, 3.93.

4-Chloro-2-(2-chloro-6-fluorophenyl)-2*H*-chromene (2i). Compound **2i**: mp 97.8-99.2 °C; IR (KBr, cm-1): 1644 (C=C); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 5.82 (d, 1H, 2-H, *J* = 2.4 Hz), 6.67 (s, 1H, 3-H), 6.78 (d, 1H, 8-H, *J* = 8.4 Hz), 6.95-7.06 (m, 2H, 6-, and 3'-H), 7.19-7.31 (m, 3H, 7-, 4'-, and 5'-H), 7.49 (d, 1H, 5-H, *J* = 8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: ^{13}C NMR (100 MHz, $CDCl_3$): δ = 72.6, 115.1, 115.4, 119.5, 121.4, 124.6, 125.2, 126.0, 128.2, 130.6, 130.8, 134.5, 154.0, 161.1, 163.6; MS: m/s (%) = 296 ([M + 2]$^+$, 24), 295 ([M + 1]$^+$, 18), 294 (M$^+$, 37), 293 ([M - 1]$^+$, 25), 259 ([M - Cl]$^+$,100); *Anal.* Calcd. for $C_{15}H_9Cl_2FO$: C, 61.04; H, 3.07. Found: C, 61.15; H, 3.11.

4-Chloro-6-methyl-2-phenyl-2*H*-chromene (2j). Compound **2j**: Colorless oil; IR (KBr, cm-1): 1635 (C=C); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 2.30 (s, 3H, CH_3), 5.91(s, 1H, 2-H), 5.95 (s, 1H, 3-H), 6.72 (d, 1H, 8-H, *J* = 8.0 Hz), 6.98-7.01 (m, 1H, 5'-H), 7.25-7.35 (m, 4H, 7-, 5-, 3'-, and 4'-H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 20.6, 77.7, 115.7, 119.8, 121.8, 124.8, 126.0, 126.9, 128.2, 128.5, 128.6, 130.3, 130.6, 131.2, 139.6, 151.2; MS: m/s (%) = 258 ([M + 2]$^+$, 18), 257 ([M + 1]$^+$, 25), 256 (M$^+$, 55), 255 ([M - 1]$^+$, 60), 221 ([M - Cl]$^+$, 100); *Anal.* Calcd. for $C_{16}H_{13}ClO$: C, 74.85; H, 5.10. Found: C, 74.99; H, 5.13.

4,6,8-Trichloro-2-phenyl-2*H*-chromene (2k). Compound **2k**: mp 51.1-55.3 °C; IR (KBr, cm-1): 1641 (C=C); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 6.07 (d, 1H, 2-H, *J* = 4.0 Hz), 6.13 (d, 1H, 3-H, *J* = 4.0 Hz), 7.25 (d, 1H, 8-H, *J* = 8.0 Hz), 7.27-7.36 (6H, 5-, 2'-, 3'-, 4'-, 5'-, and 6'-H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 77.9, 122.0, 122.4, 122.9, 123.4, 124.5, 126.0, 126.4, 126.5, 128.7, 128.9, 130.5, 133.2, 138.5, 147.8; MS: m/s (%) = 313 ([M + 4]$^+$, 18), 311 ([M + 2]$^+$, 45), 310 ([M + 1]$^+$, 49), 309 (M$^+$, 51), 275 ([M + 1 - Cl]$^+$, 100); *Anal.* Calcd. for $C_{15}H_9Cl_3O$: C, 57.82; H, 2.91. Found: C, 57.93; H, 3.14.

4-Chloro-2-(furan-2-yl)-2*H*-chromene (2l). Compound **2l**: Colorless oil [11]; IR (KBr, cm-1): 1633 (C=C); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 5.95 (d, 1H, 2-H, *J* = 4.4 Hz), 5.98 (d, 1H, *J* = 4.4 Hz), 6.31-6.37 (m, 1H, 3'-H), 6.37 (d, 1H, 4'-H, *J* = 4.4 Hz), 6.94-6.98 (m, 1H, 8-H), 7.16-7.20 (m, 1H, 6-H), 7.41-7.42 (m, 1H, 5'-H), 7.49 (dd, 1H, 5-H, *J* = 1.6, 1.6 Hz); MS: m/s (%) = 234 ([M + 2]$^+$, 6), 233 ([M + 1]$^+$, 5), 232 (M$^+$, 16), 231 ([M – 1]$^+$, 9), 197 ([M - Cl]$^+$, 100);

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