A Novel Synthesis of Isoflavones *via* Copper(I)-Catalyzed Intramolecular Cyclization Reaction

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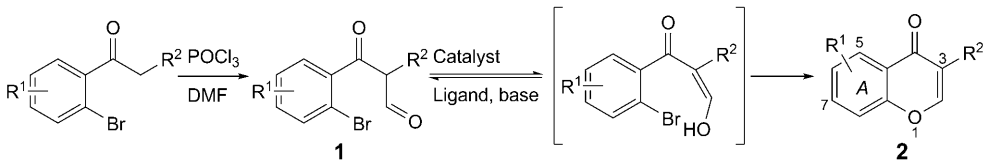
Isoflavone derivatives were synthesized *via* intramolecular cyclization of 3-(2-bromophenyl)-3-oxopropanal derivatives, using CuI as the catalyst, 2-picolinic acid (= pyridine-2-carboxylic acid) as the ligand, K_2CO_3 as the base, and DMF as the solvent, in up to 96% yield. The synthesis is functional group-tolerant.

Introduction. – Isoflavones are highly abundant in the legume family of plants and forage grasses, exhibiting numerous biological activities, such as antimicrobial [1], estrogenic [2], antioxidative, antihemolytic [3], and antigiardial effects [4]. These pharmacological activities have stimulated much interest in the synthesis of isoflavones [5] and 3-alkylbenzopyranones [6].

Some methodologies for the preparation of these isoflavones have been already developed [7–11]. However, the reported methods suffer from hazardous materials or harsh reaction conditions. Transition metal-catalyzed coupling reactions have emerged as a powerful tool for the formation of C–C [12] and C–X [13] (X = N, O, S) bonds. *Maiti* and *Buchwald* had successfully developed an efficient and complementary set of Cu- and Pd-based catalyst systems for the selective *O*- and *N*-arylation of unprotected amino phenols using aryl halides [14]. Together with our previous efforts [15] to construct heterocycles *via* CuI-catalyzed intramolecular cyclization reactions, these prompted us to investigate the feasibility of a synthesis strategy featuring a Cu-catalyzed cyclization reaction of the 3-(2-bromophenyl)-3-oxo-2-phenylpropanal derivatives (*Scheme*).

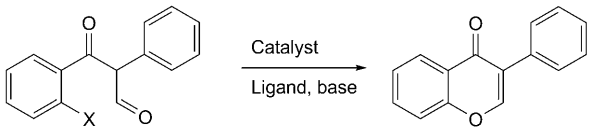
Scheme



Results and Discussion. – To investigate the feasibility of the intramolecular C–O bond formation, we first focused on optimization of the reaction conditions for the synthesis of 3-phenyl-4*H*-chromen-4-one (**2a**) from 3-(2-bromophenyl)-3-oxo-2-phe-

nylpropanal (**1a**; *Table 1*), which could be obtained through a modified procedure under mild conditions [16] from 1-(2-bromophenyl)-2-phenylethanone. ^{1}H-NMR Spectrum of **1** exhibited typical aldehydic H-atom signals at *ca.* 9.5 ppm except for **1m** which exists solely in enolic form as evidenced by a *doublet* (enolic OH signal) at 14.61 ppm in $CDCl_3$ and a broad *singlet* at 11.18 ppm in deuterated DMSO. As shown in *Table 1*, in the instance that no catalyst and ligand were introduced, the product was obtained in 37% yield (*Entry 10*). A satisfactory result was obtained with 10 mol-% CuI, 20 mol-% 2-picolinic acid (= pyridine-2-carboxylic acid) [17], and 200 mol-% K_2CO_3 in DMF at 135–140° under N_2. We subsequently tested other ligands, and only 1,10-phenanthroline provided comparable results (*Entries 1*, *2*, and *4*). Our investigation of bases revealed that K_2CO_3 was the optimal base, while stronger bases yielded only trace amounts of product (*Entries 3* and *4*). The solvent plays an important role in the reaction. No product was detected when 1,4-dioxane and toluene were utilized (*Entries 6–9*), and when DMSO was used, the yield was only 20% (*Entry 5*). When the substrate was 3-(2-chlorophenyl)-3-oxo-2-phenylpropanal (**1a′**), the product was obtained in slightly lower yield.

Table 1. *Optimization of the Reaction Conditions*[a])



1a X = Br
1a' X = Cl

2a

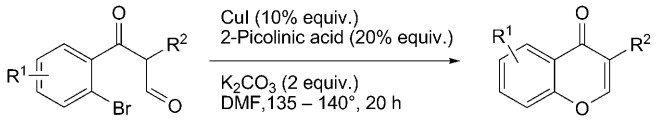
Entry	X	Catalyst	Ligand	Base	Solvent	Yield [%][b])
1	Br	CuI	1,10-Phenanthroline	K_2CO_3	DMF	82
2	Br	CuI	L-Proline	K_2CO_3	DMF	47
3	Br	CuI	2-Picolinic acid	Cs_2CO_3	DMF	18
4	Br	CuI	2-Picolinic acid	K_2CO_3	DMF	96
5	Br	CuI	2-Picolinic acid	K_2CO_3	DMSO[c])	20
6	Br	CuI	2-Picolinic acid	*t*-BuONa	Toluene[d])	–
7	Br	CuI	2-Picolinic acid	K_2CO_3	1,4-Dioxane[d])	–
8	Br	CuI	2-Picolinic acid	Cs_2CO_3	1,4-Dioxane[d])	–
9	Br	CuI	2-Picolinic acid	*t*-BuONa	1,4-Dioxane[d])	–
10	Br	–	–	K_2CO_3	DMF	37
11	Cl	CuI	2-Picolinic acid	K_2CO_3	DMF	86

[a]) All the reactions were run with **1** (0.5 mmol), in the presence of 10 mol-% of catalyst and 20 mol-% of ligand, and 200 mol-% of base at 135–140° under N_2 for 20 h. [b]) Yields after chromatography. [c]) At 70–80°. [d]) Under reflux.

With the optimal reaction conditions in hand, we then explored the scope and generality of the process. As shown in *Table 2*, the catalyst system was tolerant of a wide range of substituents. The yield was almost quantitative when R^1 was H, followed by when R^2 was 4-MeC_6H_4. As can be seen from *Entries 2*, *7*, *9*, *12*, and *13*, good yields were obtained with both electron-donating and -withdrawing substituents on R^2. However,

substituents on R^1, independent of electron-donating or -withdrawing character, decreased the yields significantly (*Entries 3*, *5*, *8*, and *11*). Steric hindrance caused a significant decrease in the yields (*Entries 4*, *6*, and *10*).

Table 2. *Intramolecular Cyclization of Isoflavones*[a])



1 **2**

Entry	Substrate	R^1	R^2	Product	Yield [%][b])
1	**1a**	H	Ph	**2a**	96
2	**1b**	H	4-Me–C_6H_4	**2b**	94
3	**1c**	4,5-OCH_2O	Ph	**2c**	64
4	**1d**	3-Me	Ph	**2d**	71
5	**1e**	5-F	Ph	**2e**	75
6	**1f**	H	2-Cl–C_6H_4	**2f**	34
7	**1g**	H	4-F–C_6H_4	**2g**	86
8	**1h**	5-MeO	Ph	**2h**	66
9	**1i**	H	4-Cl–C_6H_4	**2i**	84
10	**1j**	H	3,5-Me_2–C_6H_3	**2j**	56
11	**1k**	5-MOMO[c])	Ph	**2k**	64
12	**1l**	H	Naphthalen-2-yl	**2l**	72
13	**1m**	H	Me	**2m**	64

[a]) All the reactions were run under optimal reaction conditions. [b]) Yields after chromatography. [c]) MOMO = Methoxymethoxy.

Based on these results, a plausible reaction pathway for the conversion of aldehydes to corresponding isoflavones is depicted in the *Scheme*. In the presence of bases, the substrates undergo aldehyde–enol conversion, followed by Cu^I-catalyzed C–O bond-formation to give the target compounds.

Conclusions. – In summary, we have developed a novel method for the synthesis of isoflavones from 3-(2-bromophenyl)-3-oxopropanal derivatives *via* CuI-catalyzed intramolecular cyclization. This method offers several advantages including good yields, a simple workup procedure, and high substituent tolerance.

Experimental Part

General. Reagents and chemicals were purchased from commercial suppliers and used without further purification. Flash chromatography (FC): silica gel (SiO_2; 200–300 mesh) from *Qingdao Ocean Chemicals*, P. R. China. TLC: Silica-gel GF_{254} plates. M.p.: *XT5* Digital melting-point apparatus from *Beijing Keyi Elec-opti Instrument Factory*; uncorrected. IR: *ProStarLC240*; KBr pellets; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *UNITY INOVA* 400 and 101 MHz (^1H and ^{13}C, resp.), or 300 and 75 MHz (^1H and ^{13}C, resp.), $CDCl_3$ or deuterated DMSO soln., unless otherwise noted; δ in ppm and J in Hz. MS: *Micromass*.

General Procedure for the Synthesis of **1**. A soln. of substituted 1-(2-bromophenyl)ethanone (2 mmol) in DMF (3 ml) was added to a soln. of $POCl_3$ (3.5 equiv.) in DMF (2 ml) at 0° under N_2, and the

mixture was stirred at r.t. for 3 h, poured into H_2O, basified with $NaHCO_3$, heated at 80° for 0.5 h, and then separated between AcOEt and H_2O. The org. layer was dried (Na_2SO_4), filtered, evaporated, and subjected to CC to give **1**.

3-(2-Bromophenyl)-3-oxo-2-phenylpropanal (**1a**). White solid. M.p. 81–82°. IR: 3078, 3063, 3030, 3019, 2864, 2741, 1678, 1628, 1283, 1219, 1086, 756, 710. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.49 (*s*, 1 H); 7.73 (*d*, *J* = 8.0, 1 H); 7.56–7.41 (*m*, 6 H); 7.36 (*m*, 3 H). ^{13}C-NMR (101 MHz, $CDCl_3$): 188.8; 152.8; 141.7; 136.7; 133.5; 132.4; 131.7; 131.1; 129.7; 128.8; 128.4; 128.0; 123.1. HR-ESI-MS: 322.9664 ($[M+Na-2]^+$, $C_{15}H_9BrNaO_2^+$; calc. 322.9684).

3-(2-Chlorophenyl)-3-oxo-2-phenylpropanal (**1a′**). White solid. M.p. 101–102°. IR: 3078, 3054, 3028, 3017, 2846, 2742, 1679, 1624, 1224, 1054, 754, 710. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.51 (*s*, 1 H); 7.57–7.52 (*m*, 2 H); 7.52–7.41 (*m*, 5 H); 7.36 (*d*, *J* = 7.4, 2 H). ^{13}C-NMR (101 MHz, $CDCl_3$): 188.6; 151.0; 141.9; 134.6; 133.2; 132.3; 131.5; 131.0; 130.2; 129.6; 128.6; 128.2; 127.2. HR-ESI-MS: 279.0164 ($[M+Na-2]^+$, $C_{15}H_9ClNaO_2^+$; calc. 279.0189).

3-(2-Bromophenyl)-2-(4-methylphenyl)-3-oxopropanal (**1b**). White solid. M.p. 96–98°. IR: 3082, 3048, 3024, 2864, 2752, 1676, 1281, 1080, 762. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.47 (*s*, 1 H); 7.71 (*d*, *J* = 8.0, 1 H); 7.52 (*dd*, *J* = 7.6, 1.6, 1 H); 7.48–7.42 (*m*, 1 H); 7.35 (*td*, *J* = 8.0, 1.7, 1 H); 7.31–7.23 (*m*, 4 H); 2.40 (*s*, 3 H). ^{13}C-NMR (101 MHz, $CDCl_3$): 189.0; 152.5; 141.7; 138.7; 136.8; 133.5; 131.6; 131.1; 129.6; 129.4; 129.2; 128.0; 123.2; 21.6. HR-ESI-MS: 336.9813 ($[M+Na-2]^+$, $C_{16}H_{11}BrNaO_2^+$; calc. 336.9840).

3-(6-Bromo-1,3-benzodioxol-5-yl)-3-oxo-2-phenylpropanal (**1c**). White solid. M.p. 134–135°. IR: 3080, 3048, 2903, 2882, 2760, 1674, 1476, 1242, 1038, 714. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.54 (*s*, 1 H); 7.44 (*m*, 3 H); 7.32 (*d*, *J* = 7.0, 2 H); 7.12 (*s*, 1 H); 6.99 (*s*, 1 H); 6.07 (*d*, *J* = 1.9, 2 H). ^{13}C-NMR (101 MHz, $CDCl_3$): 188.9; 152.6; 150.1; 148.0; 142.0; 132.6; 129.7; 129.4; 128.8; 128.4; 114.9; 113.2; 110.4; 102.7. HR-ESI-MS: 366.9567 ($[M+Na-2]^+$, $C_{16}H_9BrNaO_4^+$; calc. 366.9582).

3-(2-Bromo-3-methylphenyl)-3-oxo-2-phenylpropanal (**1d**). White solid. M.p. 94–96°. IR: 3076, 3053, 2924, 2841, 2735, 1686, 1447, 1385, 1285, 1256, 1088, 1032, 781, 719, 712, 696. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.50 (*s*, 1 H); 7.52–7.40 (*m*, 3 H); 7.40–7.32 (*m*, 5 H); 2.52 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 189.0; 153.8; 141.4; 134.0; 137.2; 132.5; 132.4; 129.8; 128.7; 128.5; 128.4; 127.6; 125.3; 23.8. HR-ESI-MS: 336.9803 ($[M+Na-2]^+$, $C_{16}H_{11}BrNaO_2^+$; calc. 336.9840).

3-(2-Bromophenyl)-2-(2-chlorophenyl)-3-oxopropanal (**1f**). White solid. M.p. 126–128°. IR: 3056, 2843, 1688, 1279, 1086, 754. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.45 (*s*, 1 H); 7.73 (*d*, *J* = 7.8, 1 H); 7.66–7.27 (*m*, 7 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 201.3; 141.3; 133.7; 133.2; 132.0; 131.8; 131.2; 128.9; 128.7; 127.6; 118.8; 48.7. HR-ESI-MS: 356.9270 ($[M+Na-2]^+$, $C_{15}H_8BrClNaO_2^+$; calc. 356.9294).

3-(2-Bromophenyl)-2-(4-fluorophenyl)-3-oxopropanal (**1g**). White solid. M.p. 92–94°. IR: 3078, 2855, 2749, 1686, 1599, 1508, 1219, 764. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.47 (*d*, *J* = 0.9, 1 H); 7.72 (*d*, *J* = 8.1, 1 H); 7.56–7.43 (*m*, 2 H); 7.41–7.31 (*m*, 3 H); 7.16 (*t*, *J* = 8.0, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 188.7; 164.6; 161.3; 153.2; 140.9; 136.6; 133.6; 131.9; 131.8; 131.7; 131.0; 128.2; 128.0; 123.1; 115.7; 115.4. HR-ESI-MS: 340.9565 ($[M+Na-2]^+$, $C_{15}H_8BrFNaO_2^+$; calc. 340.9589).

3-(2-Bromo-5-methoxyphenyl)-3-oxo-2-phenylpropanal (**1h**). White solid. M.p. 89–90°. IR: 3081, 3046, 2901, 2880, 2755, 1674, 1476, 1242, 1038, 714. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.51 (*s*, 1 H); 7.58 (*d*, *J* = 8.9, 1 H); 7.50–7.41 (*m*, 3 H); 7.38–7.33 (*m*, 2 H); 7.05 (*d*, *J* = 3.0, 1 H); 6.91 (*dd*, *J* = 8.9, 3.0, 1 H); 3.85 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 188.9; 159.2; 152.5; 141.7; 137.3; 134.2; 132.4; 129.8; 128.8; 128.4; 117.8; 116.3; 113.4; 55.9. HR-ESI-MS: 352.9784 ($[M+Na-2]^+$, $C_{16}H_{11}BrNaO_3^+$; calc. 352.9789).

3-(2-Bromophenyl)-2-(4-chlorophenyl)-3-oxopropanal (**1i**). White solid. M.p. 83–85°. IR: 3070, 2864, 1686, 1590, 1219, 759, 741. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.45 (*s*, 1 H); 7.72 (*d*, *J* = 8.0, 1 H); 7.50 (*t*, *J* = 8.4, 1 H); 7.47–7.41 (*m*, 3 H); 7.36 (*t*, *J* = 7.7, 1 H); 7.30 (*s*, 1 H); 7.28 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 188.5; 153.3; 140.8; 136.5; 134.9; 133.6; 131.9; 131.3; 131.1; 130.8; 128.8; 128.1; 123.1. HR-ESI-MS: 352.9264 ($[M+Na-2]^+$, $C_{15}H_8BrClNaO_2^+$; calc. 356.9294).

3-(2-Bromophenyl)-2-(3,5-dimethylphenyl)-3-oxopropanal (**1j**). White solid. M.p. 114–116°. IR: 3075, 2918, 2855, 2735, 1682, 1605, 1427, 1221, 764. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.48 (*s*, 1 H); 7.73 (*d*, *J* = 7.9, 1 H); 7.53 (*d*, *J* = 6.9, 1 H); 7.46 (*t*, *J* = 7.4, 1 H); 7.36 (*t*, *J* = 7.4, 1 H); 7.06 (*s*, 1 H); 6.95 (*s*, 2 H); 2.39 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 189.0; 152.5; 142.1; 138.0; 136.9; 133.5; 132.4; 131.6; 131.1; 130.6; 128.0; 127.2; 123.2; 21.5. HR-ESI-MS: 350.9998 ($[M+Na-2]^+$, $C_{17}H_{13}BrNaO_2^+$; calc. 350.9997).

3-[2-Bromo-5-(methoxymethoxy)phenyl]-3-oxo-2-phenylpropanal (**1k**). Yellow oil. IR: 3081, 3056, 3024, 2908, 2853, 2769, 1663, 1575, 1239, 1089, 756, 710. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.52 (*s*, 1 H); 7.59 (*d*, *J* = 8.9, 1 H); 7.50–7.41 (*m*, 3 H); 7.36–7.32 (*m*, 2 H); 7.21 (*d*, *J* = 2.9, 1 H); 7.06 (*dd*, *J* = 8.9, 2.9, 1 H); 5.24 (*s*, 2 H); 3.50 (*s*, 3 H). ^{13}C-NMR (101 MHz, $CDCl_3$): 189.0; 157.0; 152.6; 141.8; 137.6; 134.4; 132.6; 129.9; 128.9; 128.5; 119.9; 118.8; 114.8; 94.9; 56.6. HR-ESI-MS: 382.9902 ($[M+Na-2]^+$, $C_{17}H_{13}BrNaO_4^+$; calc. 382.9895).

3-(2-Bromophenyl)-2-(naphthalen-2-yl)-3-oxopropanal (**1l**). White solid. M.p. 116–118°. IR: 3083, 3055, 2958, 2920, 2849, 2757, 1679, 1577, 1220, 1072, 758, 719. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.56 (*s*, 1 H); 7.93 (*d*, *J* = 8.5, 1 H); 7.91–7.87 (*m*, 2 H); 7.85 (*s*, 1 H); 7.75 (*d*, *J* = 8.1, 1 H); 7.57 (*d*, *J* = 7.7, 1 H); 7.53–7.51 (*m*, 2 H); 7.48–7.43 (*m*, 2 H); 7.41–7.35 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 189.0; 153.2; 141.9; 136.9; 133.7; 133.4; 133.3; 131.8; 131.3; 130.0; 129.6; 128.5; 128.1; 128.0; 127.2; 126.9; 126.5; 123.3. HR-ESI-MS: 372.9823 ($[M+Na-2]^+$, $C_{19}H_{13}BrNaO_4^+$; calc. 372.9840).

3-(2-Bromophenyl)-2-methyl-3-oxopropanal (**1m**). White solid. M.p. 162–163°. IR: 3071, 2924, 2598, 1647, 1562, 1346, 1233, 775. ^{1}H-NMR (400 MHz, $CDCl_3$): 14.62 (*d*, *J* = 6.0, 1 H); 8.35 (*d*, *J* = 5.4, 1 H); 7.62 (*d*, *J* = 7.9, 1 H); 7.39 (*d*, *J* = 7.5, 1 H); 7.33–7.22 (*m*, 2 H); 1.68 (*s*, 3 H). ^{1}H-NMR (400 MHz, (D_6)DMSO): 11.17 (*s*, 1 H); 7.65 (*d*, *J* = 7.9, 1 H); 7.42 (*t*, *J* = 7.3, 1 H); 7.35 (*t*, *J* = 6.9, 1 H); 7.29 (*d*, *J* = 6.9, 1 H); 7.04 (*s*, 1 H); 1.73 (*s*, 3 H). ^{13}C-NMR (101 MHz, (D_6)DMSO): 194.8; 184.2; 162.3; 132.6; 130.6; 128.8; 127.5; 118.9; 115.0; 7.5. HR-ESI-MS: 240.9868 (M^+, $C_{10}H_{10}BrO_2^+$; calc. 240.9864).

General Procedure for the Synthesis of **2**. A mixture of **1** (0.5 mmol), CuI (10 mg, 0.05 mmol), K_2CO_3 (138 mg, 1 mmol), 2-picolinic acid (12 mg, 0.01 mmol), and dry DMF (3 ml) in a flask filled with N_2 was stirred at 135–140° for 20 h. The mixture was separated between AcOEt (3 × 20 ml) and H_2O (30 ml). The org. layer was dried (Na_2SO_4), filtered, evaporated under vacuum, and purified by FC (hexane/AcOEt) to give product **2**. For anal. data of compounds **2a**, **2b**, **2g**, and **2h**, see [9]. For compounds **2e**, **2i**, **2l**, and **2m**, see [18–21], resp.

*7-Phenyl-8*H*-[1,3]dioxolo[4,5-*g*]chromen-8-one* (**2c**). White solid (85 mg, 64%). M.p. 152–153°. IR: 3091, 3040, 2901, 2780, 1636, 1611, 1260, 1037, 746, 703. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.93 (*s*, 1 H); 7.73–7.49 (*m*, 3 H); 7.42–7.37 (*m*, 3 H); 6.85 (*s*, 1 H); 6.09 (*s*, 2 H). ^{13}C-NMR (101 MHz, $CDCl_3$): 176.4; 154.7; 153.9; 153.6; 147.5; 133.1; 130.2; 129.7; 129.4; 125.9; 120.8; 104.0; 103.7; 99.1. HR-MS: 266.0580 (M^+, $C_{16}H_{10}O_4^+$; calc. 266.0579).

*8-Methyl-3-phenyl-4*H*-1-benzopyran-4-one* (**2d**). White solid (84 mg, 71%). M.p. 111–112°. IR: 3071, 3032, 2925, 2851, 2780, 1654, 1584, 1273, 1056, 770, 705. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.17 (*d*, *J* = 8.0, 1 H); 8.08 (*s*, 1 H); 7.62–7.55 (*m*, 2 H); 7.52 (*d*, *J* = 7.2, 1 H); 7.46 (*t*, *J* = 7.4, 2 H); 7.42–7.37 (*m*, 1 H); 7.32 (*t*, *J* = 7.6, 1 H); 2.51 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 176.6; 154.8; 153.0; 134.6; 132.1; 129.0; 128.6; 128.2; 127.6; 125.1; 124.9; 124.5; 124.0; 15.7. HR-MS: 236.0836 (M^+, $C_{16}H_{12}O_2^+$; calc. 236.0837).

*3-(2-Chlorophenyl)-4*H*-1-benzopyran-4-one* (**2f**). White solid (57 mg, 34%). M.p. 129–130°. IR: 3085, 3061, 3041, 3014, 2921, 2852, 1634, 1469, 1234, 1078, 746, 711. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.32 (*d*, *J* = 7.5, 1 H); 7.98 (*s*, 1 H); 7.71 (*d*, *J* = 7.2, 1 H); 7.54–7.49 (*m*, 2 H); 7.45 (*t*, *J* = 7.7, 1 H); 7.39–7.32 (*m*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 175.8; 163.1; 156.6; 154.6; 134.8; 134.0; 132.4; 131.1; 130.1; 127.3; 127.0; 126.7; 125.6; 124.4; 118.4. HR-MS: 256.0294 (M^+, $C_{15}H_9ClO_2^+$; calc. 256.0291).

*3-(3,5-Dimethylphenyl)-4*H*-1-benzopyran-4-one* (**2j**). White solid (70 mg, 56%). M.p. 86–87°. IR: 3072, 2918, 2852, 2731, 1651, 1467, 1307, 1188, 764, 692. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.32 (*d*, *J* = 7.9, 1 H); 8.00 (*s*, 1 H); 7.68 (*t*, *J* = 7.7, 1 H); 7.51–7.37 (*m*, 2 H); 7.18 (*s*, 2 H); 7.03 (*s*, 1 H); 2.37 (*s*, 6 H). ^{13}C-NMR (101 MHz, $CDCl_3$): 176.6; 156.4; 153.2; 138.3; 133.8; 131.9; 130.2; 127.0; 126.7; 125.9; 125.4; 124.8; 118.3; 21.6. HR-MS: 250.0994 (M^+, $C_{17}H_{14}O_2^+$; calc. 250.0994).

*6-(Methoxymethoxy)-3-phenyl-4*H*-chromen-4-one* (**2k**). White solid (90 mg, 64%). M.p. 113–114°. IR: 3067, 3040, 2958, 2902, 2861, 2825, 1648, 1489, 1279, 1068, 750, 699. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.03 (*s*, 1 H); 7.91 (*d*, *J* = 2.8, 1 H); 7.59 (*d*, *J* = 7.4, 2 H); 7.50–7.43 (*m*, 3 H); 7.43–7.37 (*m*, 2 H); 5.29 (*s*, 2 H); 3.53 (*s*, 3 H). ^{13}C-NMR (101 MHz, $CDCl_3$): 175.9; 169.9; 154.4; 153.0; 151.5; 131.9; 128.9; 128.5; 128.1; 124.6; 124.1; 119.4; 110.2; 94.8; 56.2. HR-MS: 282.0893 (M^+, $C_{17}H_{14}O_4^+$; calc. 282.0892).

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