Solvent-free synthesis of 5-oxo-5,6,7,8-tetrahydro-4*H*-benzo-[*b*]-pyran derivatives under microwave irradiation

Xue Yuan Hu, Xue Sen Fan, Xin Ying Zhang, Gui Rong Qu, and Yan Zhen Li

Abstract: Several benzo-[*b*]-pyran derivatives were prepared via microwave irradiation under solvent-free conditions in the presence of $InCl_3 \cdot 4H_2O$. The advantages of this method include simple operational process, environmental benignancy, and high efficiency. Moreover, the catalyst can be recovered and reused effectively for at least six times.

Key words: benzo-[*b*]-pyran derivatives, indium trichloride, microwave irradiation.

Résumé : On a préparé plusieurs dérivés du benzo[*b*]pyrane par irradiation à l'aide de micro-ondes, dans des conditions sans solvant et en présence de $InCl_3 \cdot 4H_2O$. Cette méthode présente l'avantage d'être écologique, très efficace et de comporter un processus opérationnel simple. De plus, le catalyseur peut être récupéré et réutilisé d'une façon efficace au moins six fois.

Mots clés : dérivés du benzo-[*b*]-pyrane, trichlorure d'indium, irradiation à l'aide de microonde.

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Introduction

Currently, research on the tetrahydropyran skeleton is of great interest in organic synthesis because the tetrahydropyran ring occurs in a number of natural products (1). Tetrahydropyran derivatives have also been extensively studied because they possess a wide range of biological activities and pharmacological properties, such as anticancer (2) and antihypertensive activities (3). Many procedures have been reported for the preparation of such compounds (4*a*); one of them is the condensation of α,β-unsaturated ketones with 5,5-dimethyl-1,3-cyclohexandione promoted by various catalysts. In this regard, anhydrous zinc chloride was recently utilized to catalyze this reaction to produce the substituted benzo-[*b*]-pyran derivatives. However, this method gives a low yield over a long reaction time (4*b*). A combination of glacial acetic acid and phosphoric anhydride could efficiently catalyze this reaction (4*c*), but the use of strongly acidic compounds is undesirable in view of green chemistry and may exclude some acid-sensitive substrates. Therefore, it is desirable to develop more efficient and greener synthetic methods for the preparation of benzo-[*b*]-pyran derivatives.

Recently, indium halides have emerged as mild Lewis acids imparting high regio- and chemo-selectivity in a variety of chemical transformations such as the Diels–Alder reaction (5), rearrangement reaction (6), Friedel–Crafts acylation reaction (7), Mukaiyama aldol reaction (8), Mannich-type reaction (9), and Biginelli reaction (10). Compared with conventional Lewis acids, indium halides possess advantages such as water stability, recyclability, and simplicity in operation. On the other hand, microwave-assisted organic syntheses have attracted considerable interests in recent years (11) because they offer several environmental and economic benefits, e.g., avoiding use of expensive and (or) toxic solvents, saving energy and time, and easier work-up after the reactions are completed. As part of our program aimed at developing environment-friendly methodologies for organic synthesis, we describe a simple, green, and efficient method for the synthesis of benzo-[*b*]-pyran derivatives. Treatments of chalcones (**1**) with 5,5-dimethyl-1,3-cyclohexandione (**2**) in the presence of $InCl_3 \cdot 4H_2O$ under microwave irradiation produced the corresponding 5-oxo-5,6,7,8-terahydro-4*H*-benzo-[*b*]-pyran derivatives (**3**) (Scheme 1) in excellent yields.

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Results and discussion

At the outset of this study, we examined the condensation process by employing 1,3-diphenyl-propenone **(1a)** (Scheme 2) and **2** as model substrates. A summary of the optimization experiments is provided in Table 1. When **1a** (1 mmol) was treated with **2** (1 mmol) in the presence of a catalytic amount of $InCl_3 \cdot 4H_2O$ (10 mol%) under the microwave irradiation power of 495 W for 10 min, the desired

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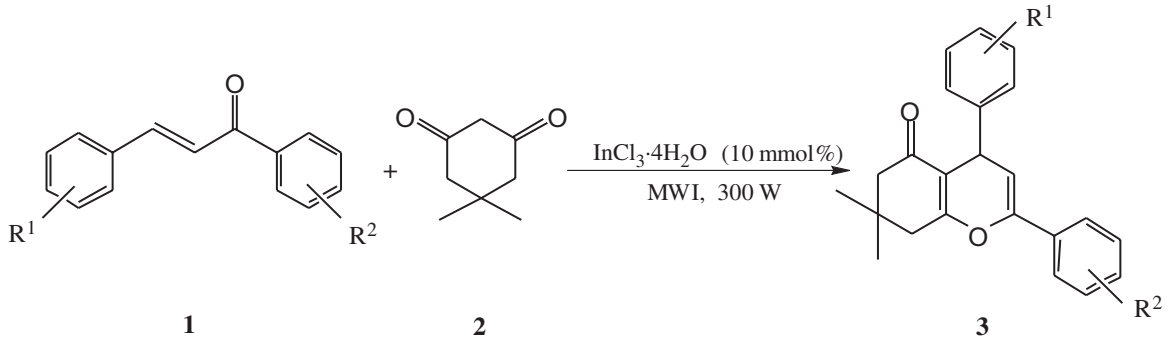
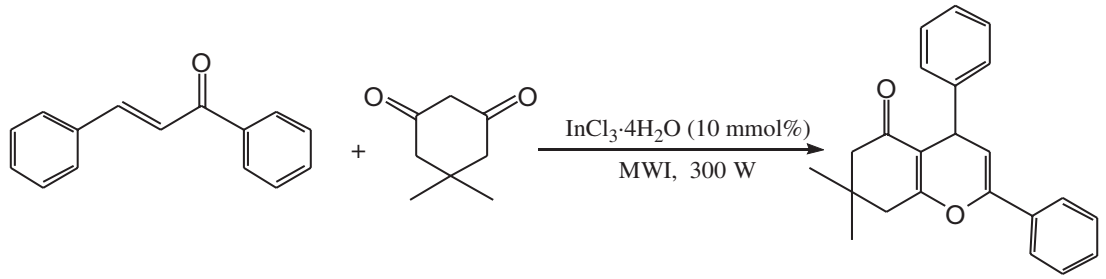
Scheme 1.



1 **2** **3**

Scheme 2.



1a **2** **3a**

Table 1. $InCl_3·4H_2O$-catalyzed synthesis of **3a** under different reaction conditions.

Entry	Microwave power (W)	Amount of $InCl_3·4H_2O$ (mol%)	Reaction time (min)	Isolated yields (%)
1	698	10	5	—
2	495	10	10	54
3	300	10	13	86
4	300	20	13	85
5	300	5	20	67
6	300	2.5	25	50
7	300	0	25	41

product **3a** was obtained with a moderate yield (54%), together with some unidentified by-products (Table 1, entry 2). However, no product could be obtained, and almost all the materials involved were carbonized when the reaction was carried out under a much higher irradiation power (698 W) (Table 1, entry 1). Under lower irradiation power (300 W), a much higher yield (86%) (Table 1, entry 3) was realized by treating the mixture of **1a** and **2** together with $InCl_3·4H_2O$ (10 mol%) for 13 min. On the other hand, the effect of the amount of $InCl_3·4H_2O$ on the output of this reaction was also investigated and the optimum concentration was determined to be 10 mol% (Table 1, entries 3–7). It should also be noted that the absence of $InCl_3·4H_2O$ would result in a much lower yield even over a longer reaction period (Table 1, entry 7).

With this exhilarating result, we extended this method to a variety of substituted chalcones to investigate its scope and generality.The results are listed in Table 2. A wide range of chalcones could react with **2** to give **3** with good yields (Table 2, entries 1–11). It is noted that the electronic property of the aromatic ring of chalcone affects the rate of this condensation process. In general, a shorter reaction time was needed with substrates bearing electron-withdrawing groups on the aromatic rings (Table 2, entries 2, 5–9). Substrates bearing electron-donating groups can also produce the corresponding products with satisfactory yields. However, a longer period was needed to complete the reaction (Table 2, entries 4, 10).

In view of green chemistry, recovery and reuse of the catalyst are highly preferable. To test this possibility, water was added to the reaction mixture upon completion of the reaction, and the product was extracted with ethyl acetate. The catalyst remaining in the aqueous phase was recovered by removing water under reduced pressure. Its reusability was investigated by using **1a** and **2** again as the model substrates. The corresponding product could be obtained with good yield even in the sixth round by using the catalyst recovered from the fifth round (Table 3, entry 6).

To compare conventional heating with solvent-free microwave irradiation for the synthesis of **3a**, a mixture of **1a** and **2** was dissolved in several organic solvents and the solution was refluxed using a classic heating method (oil bath in this case) in the presence of 10 mol% $InCl_3·4H_2O$. When the mixture of **1a** and **2** was refluxed in anhydrous ethanol for 5 h, no **3a** was formed (Table 4, entry 2). Although **3a** could be obtained with other solvents, a much longer reaction time was needed and the yield was much lower. Therefore, solvent-free microwave irradiation is more efficient compared with conventional heating in terms of reaction time and yield.

In conclusion, we have presented a new method for the preparation of benzo-[*b*]-pyran derivatives in the presence of $InCl_3·4H_2O$ under microwave irradiation. This simple and reproducible technique produces various benzo-[*b*]-pyran de-

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Table 2. Preparation of **3** promoted by $InCl_3·4H_2O$ under microwave irradiation.

Entry	R_1	R_2	Time (min)	Products	Isolated yields (%)
1	H	H	13	**3a**	86
2	H	*p*-Cl	10	**3b**	85
3	H	*p*-Br	15	**3c**	86
4	H	*p*-CH_3O	15	**3d**	83
5	H	*p*-NO_2	10	**3e**	80
6	*p*-NO_2	H	10	**3f**	92
7	*m*-NO_2	*p*-Cl	10	**3g**	91
8	*p*-Cl	*p*-NO_2	10	**3h**	93
9	*m*-NO_2	H	10	**3i**	90
10	*p*-CH_3	H	15	**3j**	83
11	*p*-Cl	H	10	**3k**	81

Note: Reactions performed in the presence of 10 mol% $InCl_3·4H_2O$ and irradiated at 300 W.

Table 3. Reusability of the catalyst.

Round	Catalyst recovered (%)	Isolated yields of **3a** (%)
1	99	86
2	99	85
3	98	85
4	99	84
5	97	83
6	98	83

Note: Reaction conditions: microwave power of 300 W and reaction time of 13 min.

rivatives in a few minutes with excellent yields without the involvement of toxic materials or the formation of undesirable side products. Moreover, the catalyst can be recovered conveniently and reused efficiently. With all these advantages, this method provides an attractive alternative for the preparation of benzo-[*b*]-pyran derivatives.

Experimental

Melting points were measured by a Kofler micromelting point apparatus and were uncorrected. Infrared spectra were recorded on a Bruker Vector 22 spectrometer in KBr with absorption in cm^{-1}. ^1H NMR spectra were determined on a Bruker AC 400 spectrometer as $CDCl_3$ or DMSO solutions. Chemical shifts (δ) were expressed in ppm downfield from the internal standard tetramethylsilane, and coupling constants *J* were given in Hz. Mass spectra were obtained by a HP5989B mass spectrometer.

General procedure for the preparation of 5-oxo-5,6,7,8-tetrahydro-4*H*-benzo-[*b*]- pyran derivatives

Chalcones **1** (1 mmol), 5,5-dimethyl-1,3-cyclo-hexanedione **2** (1 mmol), and $InCl_3·4H_2O$ (0.1 mmol) were mixed without solvent in a 10 mL open flask and placed in a domestic microwave oven. The mixture was irradiated at 300 W for a certain period of time, as required to complete the reaction (monitored by TLC). Upon completion, the reaction mixture was cooled down to room temperature. Water was added, and the mixture was extracted with ethyl acetate. After the organic layer was dried (Na_2SO_4) and concentrated, the residue was recrystallized from a mixture of ethyl acetate and hexane to give 3 (Table 2). All the products were fully characterized by IR, ^1H NMR, and MS. The catalyst remaining in the aqueous phase was recovered for reuse by removing water under reduced pressure.

Table 4. Comparison between the conventional heating and solvent-free microwave irradiation (MWI) for the synthesis of compound **3a**.

Entry	Solvents	Heating methods	Reaction time (min)	Isolated yields (%)
1	None	MWI	13	86
2	Ethanol	Reflux	300	—
3	Acetic acid	Reflux	480	70[a]
4	THF	Reflux	660	51[b]
5	Toluene	Reflux	480	64[b]
6	Ethyl acetate	Reflux	360	55[b]

[a]At completion, water was added to the mixture and the product was obtained by filtration and recrystallization with hexane – ethyl acetate (10:1).

[b]The products were obtained by preparative chromatography on silica gel using cyclohexane–EtOAc (5:1) as an eluent.

3a: mp 140–142 °C (lit. value (4c) mp 140 °C). IR (KBr, cm^{-1}): 3070, 3024, 2956, 2872, 1679, 1658, 1627, 1468, 1380, 1289, 1215, 1166, 1056, 975, 824, 769. ^1H NMR (400 MHz, $CDCl_3$, ppm): 1.06 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.23–2.59 (m, 4H, $2CH_2$), 4.49 (d, 1H, *J* = 4.8 Hz, CH), 5.70 (d, 1H, *J* = 4.8 Hz, =CH), 7.14–7.18 (m, 1H, ArH), 7.25–7.38 (m, 7H, ArH), 7.57–7.59 (m, 2H, ArH). MS (70 eV) *m*/*z* (%): 330 (M^+, 93.75), 253 (100), 197 (10.94), 141 (10.94), 105 (9.38), 77 (9.38).

3b: mp 172–174 °C (lit. value (4*b*) mp 175–176 °C). IR (KBr, cm^{-1}): 3078, 3042, 2955, 2868, 1680, 1658, 1626, 1490, 1380, 1273, 1215, 1166, 1057, 1015, 825, 765. ^1H NMR (400 MHz, $CDCl_3$, ppm): 1.09 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 2.22 –2.63 (m, 4H, 2 H_2), 4.51 (d, 1H, *J* = 4.8 Hz, CH), 5.74 (d, 1H, *J* = 4.8 Hz, =CH), 7.20–7.34 (m, 5H, ArH), 7.36 (d, 2H, *J* = 8.4 Hz, ArH), 7.53 (d, 2H, *J* = 8.4 Hz, ArH). MS (70 eV) *m*/*z* (%): 364 (M^+, 97.37), 287 (100), 231 (9.21), 202 (7.89), 175 (7.24), 139 (18.42), 111 (6.58), 83 (3.94).

3c: mp 180–182 °C. IR (KBr, cm^{-1}): 3078, 3024, 2956, 2869, 1679, 1659, 1627, 1489, 1453, 1382, 1311, 1299, 1265, 1212, 1169, 1125, 1054, 977, 831, 769. ^1H NMR (400 MHz, $CDCl_3$, ppm): 1.10 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.22–2.62 (m, 4H, $2CH_2$), 4.51 (d, 1H, *J* = 4.8 Hz, CH), 5.73 (d, 1H, *J* = 4.8 Hz, =CH), 7.19–7.22 (m, 1H, ArH), 7.29–7.34 (m, 4H, ArH), 7.46–7.53 (m, 4H, ArH). MS (70 eV) *m*/*z* (%): 409 (M^+, 100), 331 (92.96), 275 (8.45), 253 (7.04), 215 (14.08), 168 (14.08), 139 (8.45), 115 (7.04), 83 (5.63).

3d: mp 134–136 °C. IR (KBr, cm^{-1}): 3068, 3020, 2980, 2868, 1680, 1660, 1620, 1450, 1370, 1263, 1211, 1160, 1030, 973, 840, 762. ^1H NMR (400 MHz, DMSO, ppm): 1.06 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 2.18–2.58 (m, 4H, $2CH_2$), 3.81 (s, 3H, OCH_3), 4.47 (d, 1H, *J* = 4.8 Hz, CH), 5.57 (d, 1H, *J* = 4.8 Hz, =CH), 6.89 (d, 2H, *J* = 9.6 Hz, ArH), 7.14–7.18 (m, 1H, ArH), 7.25–7.33 (m, 4H, ArH),

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7.51 (d, 2H, *J* = 9.6 Hz, ArH). MS (70 eV) *m*/*z* (%): 360(M^+, 77.03), 283 (100), 171 (5.41), 135 (9.46) 115 (2.03), 77 (4.05).

3e: mp 148–150 °C. IR (KBr, cm^{-1}): 3078, 3024, 2955, 2863, 1674, 1658, 1625, 1594, 1514, 1381, 1346, 1285, 1212, 1168, 1123, 1053, 977, 849, 754. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.12 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 2.24–2.67 (m, 4H, $2CH_2$), 4.57 (d, 1H, *J* = 4.8 Hz, CH), 5.94 (d, 1H, *J* = 4.8 Hz, =CH), 7.22–7.33 (m, 5H, ArH), 7.77 (d, 2H, *J* = 8.4 Hz, ArH), 8.24 (d, 2H, *J* = 8.4 Hz, ArH). MS (70 eV) *m*/*z* (%): 374 (M^+, 75.18), 297 (100), 252 (96.38), 231 (8.74), 202 (5.98), 175 (5.86), 139 (13.43), 111 (4.95), 83 (4.93).

3f: mp 130–132 °C. IR (KBr, cm^{-1}): 3089, 3051, 2959, 2874, 1678, 1652, 1625, 1592, 1515, 1382, 1344, 1278, 1217, 1167, 1130, 1058, 975, 846, 767. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.09 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 2.22–2.61 (m, 4H, $2CH_2$), 4.65 (d, 1H, *J* = 4.8 Hz, CH), 5.67 (d, 1H, *J* = 4.8 Hz, =CH), 7.40–7.42 (m, 3H, ArH), 7.52 (d, 2H, *J* = 8.0 Hz, ArH), 7.61–7.62 (m, 2H, ArH), 8.17 (d, 2H, *J* = 8.0 Hz, ArH). MS (70 eV) *m*/*z* (%): 374 (M^+, 20.30), 358 (100), 328 (43.31), 253 (96.45), 197 (8.47), 141 (8.47), 105 (7.85), 77 (7.22).

3g: mp 194–196 °C. IR (KBr, cm^{-1}): 3073, 3062, 2960, 2868, 1680, 1662, 1631,1529, 1490, 1380, 1349, 1295, 1262, 1214, 1166, 1127, 1091, 1053, 976, 831, 743. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.11 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 2.23–2.66 (m, 4H, $2CH_2$), 4.65 (d, 1H, *J* = 4.8 Hz, CH), 5.67 (d, 1H, *J* = 4.8 Hz, =CH), 7.37 (d, 2H, *J* = 8.4 Hz, ArH), 7.48 (t, 1H, *J* = 8.0 Hz, ArH), 7.54 (d, 2H, *J* = 8.4 Hz, ArH), 7.70 (d, 1H, *J* = 7.6 Hz, ArH), 8.06 (d, 1H, *J* = 8.0 Hz, ArH), 8.17 (s, 1H, ArH). MS (70 eV) *m*/*z* (%): 409 (M^+, 22.86), 392 (100), 362 (40.00), 287 (85.71), 231 (9.52), 202 (5.71), 175 (9.05), 139 (20.00), 111 (6.67), 83 (4.76).

3h: mp 202–204 °C. IR (KBr, cm^{-1}): 3073, 3061, 2960, 2874, 1678, 1660, 1629, 1596, 1490, 1381, 1347, 1280, 1213, 1167, 1125, 1054, 977, 854, 755. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.10 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 2.23 – 2.60 (m, 4H, $2CH_2$), 4.54 (d, 1H, *J* = 4.8 Hz, CH), 5.89 (d, 1H, *J* = 4.8 Hz, =CH), 7.25–7.30 (m, 4H, ArH), 7.76 (d, 2H, *J* = 8.8 Hz, ArH), 8.25 (d, 2H, *J* = 8.8 Hz, ArH). MS (70 eV) *m*/*z* (%): 409 (M^+, 81.35), 374 (37.71), 358 (100), 329 (69.21), 253 (12.89), 197 (9.24), 141 (9.33) 105 (6.59), 77 (3.91).

3i: mp 138–140 °C. IR (KBr, cm^{-1}): 3094, 3070, 2953, 2874, 1683, 1658, 1629, 1527, 1494, 1382, 1348, 1318, 1275, 1217, 1169, 1125, 1056, 976, 874, 761. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.11 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 2.23–2.67 (m, 4H, $2CH_2$), 4.66 (d, 1H, *J* = 4.8 Hz, CH), 5.68 (d, 1H, *J* = 4.8 Hz, =CH), 7.37–7.49 (m, 4H, ArH), 7.62 (d, 2H, *J* = 7.6 Hz, ArH), 7.72 (d, 1H, *J* = 7.6 Hz, ArH), 8.07 (d, 1H, *J* = 8.4 Hz, ArH), 8.19 (s, 1H, ArH). MS (70 eV) *m*/*z* (%): 374 (M^+, 20.48), 358 (100), 328 (43.37), 253 (96.38), 197 (8.43), 141 (8.43), 105 (7.83), 77 (7.23).

3j: mp 84–86 °C. IR (KBr, cm^{-1}): 3051, 3024, 2956, 2871, 1678, 1656, 1627, 1512, 1449, 1380, 1272, 1214, 1165, 1125, 1056, 973, 854, 811, 769. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.06 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 2.18–2.58 (m, 7H, CH_3, $2CH_2$), 4.56 (d, 1H, *J* = 4.8 Hz, CH), 5.69 (d, 1H, *J* = 4.8 Hz, =CH), 7.08 (d, 2H, *J* = 7.6 Hz, ArH), 7.21 (d, 2H, *J* = 7.6 Hz, ArH), 7.30–7.37 (m, 3H, ArH), 7.58 (d, 2H, *J* = 8.0 Hz, ArH). MS (70 eV) *m*/*z* (%): 344 (M^+, 100), 329 (26.23), 253 (81.97), 197 (9.84), 141 (9.84), 105 (11.48), 77 (9.02).

3k: mp 108–110 °C. IR (KBr, cm^{-1}): 3078, 3040, 2890, 2868, 1679, 1658, 1627, 1490, 1380, 1273, 1215, 1167, 1057, 857, 721. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.08 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 2.22–2.58 (m, 4H, $2CH_2$), 4.51 (d, 1H, *J* = 4.8 Hz, CH), 5.70 (d, 1H, *J* = 4.8 Hz, =CH), 7.26–7.31 (m, 4H, ArH), 7.35–7.42 (m, 3H, ArH), 7.61(d, 2H, *J* = 7.6 Hz, ArH). MS (70 eV) *m*/*z* (%): 364 (M^+, 100), 287 (35.35), 253 (85.26), 202 (7.87), 197(9.80), 141 (9.80), 105 (11.37), 77 (11.02).

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