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SYNTHESIS OF 3-ARYLCOUMARINS BY $FeCL_3$-PROMOTED CYCLIZATION OF *orto*-METHOXY-SUBSTITUTED (*E*)-2,3-DIPHENYLPROPENOIC ACIDS OR THEIR METHYL ESTERS

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3-Arylcoumarins were conveniently synthesized in excellent yields by an iron(III) chloride-promoted tandem reaction using methoxy-substituted (E)-2,3-diphenylpropenoic acids or their methyl esters. The structure of 3-(4-methoxyphenyl)coumarin was established from X-ray crystallographic data.

Keywords: 3-arylcoumarin, iron(III) chloride, synthesis, tandem reaction.

Coumarins (2*H*-chromen-2-ones) are a large group of compounds found as natural products. They are also widely prepared synthetically because of their applications in medicine and the perfume and dye industries [1]. In particular, 3-aryl coumarins are used as fluorescent brightening agents, dispersed fluorescents, and laser dyes due to the stability of *trans*-stilbene skeleton under light irradiation [2].

The main synthetic strategy to construct 3-arylcoumarins is based on the ring-closure reaction of active methylene compounds and aryl aldehydes [3, 4], which suffers from drawbacks like the requirement of using activated phenols and expensive catalysts and has potential environmental issues as well. Although there are a few methods involving the use aryl methyl ethers to synthesize coumarins, the processes require harsh reaction conditions for ether bond cleavage in the cyclization step [5].

On the other hand, the direct functionalization of coumarins at the C-3 atom to construct 3-arylcoumarins is based on the Suzuki reaction of coumarinyl halides and boronic acids or esters, which still requires prefunctionalization of the coumarin moiety and suffers from a lack of step economy [6]. An alternative method is zincation of coumarin at the C-3 atom followed by a Negishi cross coupling [7]. Although a direct 3-arylation of coumarins *via* Pd-catalyzed coupling of coumarins and iodoarenes was recently discovered, the process was limited by its low functional group tolerance and low yields of the adducts [8].

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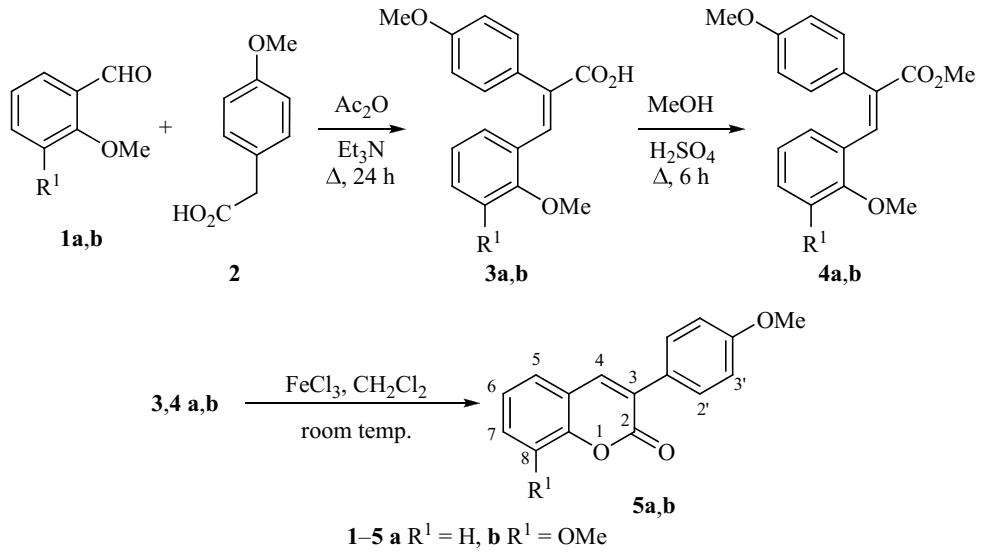
Different Lewis acids as reaction promoters or catalysts have been explored for coumarin synthesis in the ring-closure step, such as $ZnCl_2$, $TiCl_4$, and $NiCl_2$, etc. [9]. Outside of these contributions, there have been no focused efforts on using $FeCl_3$ as promoter. Recently, Maiti reported a reaction route synthesizing coumarin derivatives under dual catalysis with piperidine and $FeCl_3$ in refluxing toluene [10]; the presence of a secondary amine is essential for the success of this reaction.

To the best of our knowledge, no synthesis of coumarin using $FeCl_3$ as a sole promoter has been reported. In this study, we report a convenient method for the synthesis of 3-arylcoumarins at room temperature by an $FeCl_3$-promoted tandem reaction with methoxy-substituted (*E*)-2,3-diphenylpropenoic acids or their methyl esters as the starting materials.

Using appropriate methoxy-substituted benzaldehydes **1a**,**b** and phenylacetic acid **2** as starting materials, we prepared methoxy-substituted (*E*)-2,3-diphenylpropenoic acids **3a**,**b** by a modified Perkin condensation reaction [11, 12]. Previous studies have shown that such condensations invariably yield a mixture of *E*-isomer as the main product and *Z*-isomer as the minor product [11, 12], which can be separated by precipitation at different pH and recrystallization. The acids **3a**,**b** can be converted to their methyl esters **4a**,**b**.



Construction of coumarins **5a**,**b** from the methoxy-substituted 2,3-diphenylpropenoic acids **3a**,**b** or their methyl esters **4a**,**b** required the cleaving of the methyl ether bond. Various choices were available to effect the cleavage. The reagents usually employed are Brønsted acids, Lewis acids (those of the type BX_3 and AlX_3 most of all), alkaline reagents, nucleophiles, as well as oxidizing or reducing reagents. However, the cleavage of methyl ether, which has been extensively studied, is usually carried out under harsh conditions [13]. Reactions using $FeCl_3$ as a cleavage reagent need to be carried out in the presence of acyl chloride or acid anhydride, yielding esterified compounds [14]. The use of $FeCl_3$ as a sole cleavage reagent of methyl ethers has not so far been discussed. In this study, the cleavage capacity of $FeCl_3$ for aryl methyl ethers was tested by the investigation of model reactions using anisole and *o*-methoxybenzaldehyde as substrates (Table 1).

As shown in Table 1, the cleavage cannot proceed substantially at room temperature even with increased $FeCl_3$ dosage and prolonged reaction times. When we prolonged the reaction temperature, the yield slightly increased, but was still very low. When *o*-methoxybenzaldehyde was used as the substrate, the electron-withdrawing effect of *ortho*-aldehyde group causes the ether bond to be cleaved more easily [15]. Nevertheless, the yield was only slightly higher than using anisole.

TABLE 1. Effect of $FeCl_3$ on Ether Cleavage

Entry	$FeCl_3$, equiv.	Reaction conditions	Conversion, % (HPLC)
		Anisole	
1	0.1	room temp., CH_2Cl_2, 2 h	—
2	1	room temp., CH_2Cl_2, 2 h	Trace
3	1	room temp., CH_2Cl_2, 24 h	2
4	3	room temp., CH_2Cl_2, 24 h	3
5	3	80°C, 1,2-dichloroethane, 8 h	5
		o-Anisaldehyde	
6	0.1	room temp., CH_2Cl_2, 2 h	—
7	1	room temp., CH_2Cl_2, 2 h	Trace
8	1	room temp., CH_2Cl_2, 24 h	4
9	3	room temp., CH_2Cl_2, 24 h	5
10	3	80°C, 1,2-dichloroethane, 8 h	8

The synthesis of coumarins with active phenols as the starting materials and Lewis acids as catalysts, also called lactonization or ester exchange reaction, has been reported in a number of studies [1]. Construction of coumarins **5a**,**b** from methoxy-substituted 2,3-diphenylpropenoic acids **3a**,**b** or their methyl esters **4a**,**b** by a $FeCl_3$-promoted reaction was carried out for the first time; hence, as a starting point, we chose ester **4a** as the substrate to optimize the reaction conditions for the desired lactonization reaction (Table 2).

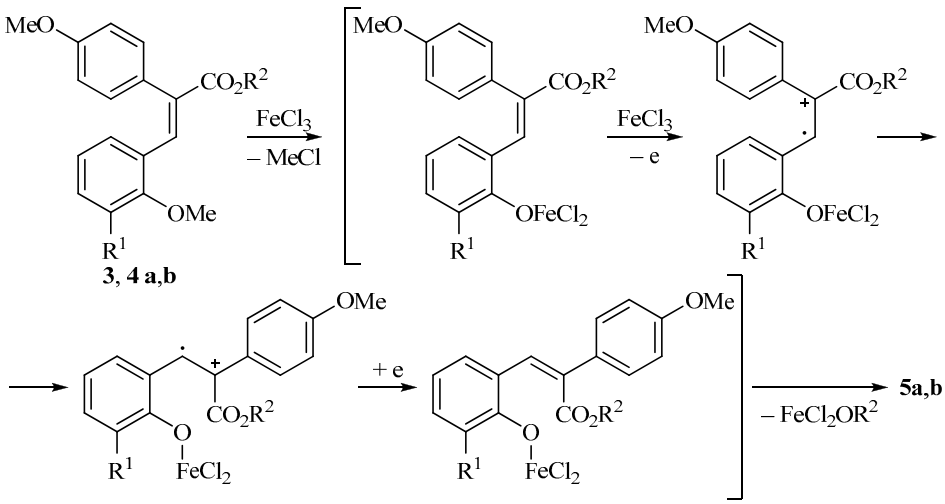
As shown in Table 2, by using 0.1 equiv. of $FeCl_3$ as the promoter, the reaction gave only a trace conversion (entry 1). With increased amount of $FeCl_3$ (entries 2-5), the conversion increased gradually, and a plateau of conversion was achieved when using $FeCl_3$ triple excess or more (entries 4-5), which implies that $FeCl_3$ may participate in the reaction as a stoichiometric reagent. The reaction conversion also increased with prolonged reaction times and reached its maximum after 8 h (entries 4, 6-7). The survey of solvents indicated that this reaction is sensitive to the solvent medium (entries 4, 8-10), and a comparably good conversion can be obtained in halogenated alkane solvents such as CH_2Cl_2, $CHCl_3$, and 1,2-dichloroethane. Various temperatures were tested for the reaction (entries 11-12), which shows that the reaction can be performed in a wide range of temperatures with good degree of conversion. For operational simplicity, the reactions were carried out at room temperature. A further investigation of the reaction mixture showed the presence of chloromethane [16], which further demonstrated that $FeCl_3$ participated in the ether cleavage reaction.

The acids **3a**,**b** and esters **4a**,**b** produced by Perkin condensation and esterification, respectively, were *E*-isomers [11], as indicated by ^{1}H NMR spectroscopy. Previous reports have shown that the chemical shifts of hydrogen on the double bond of (*E*)-2,3-diphenyl-substituted acrylic acids or esters are slightly downfield with respect to the *Z*-isomers. The *E*-isomers display a characteristic singlet resonance at about 8.0 ppm in the ^{1}H NMR spectrum; by contrast, the *Z*-isomers display a resonance at about 7.0 ppm [12]. In the current work, the chemical shifts of hydrogen on the double bond of acids **3a**,**b** and corresponding esters **4a**,**b** displayed a resonance at about 8.0 ppm. The double bond of the coumarin ring has *Z*-configuration, which requires the configuration inversion of the double bond upon the cyclization. In general, a double bond cannot freely rotate, so it must first be transformed to a single bond to accomplish the rotation.

Based on the previous studies [17] and the present experimental results, a coupling mechanism for the present tandem reaction was proposed. Firstly, $FeCl_3$ forms an oxonium salt complex, which assists in cleaving the ether bond. Secondly, one electron is abstracted by Fe^{3+} from the substrate to give a radical cationic species, which enables the configuration inversion. Finally, the cyclization occurs with the cleavage of the ester and release of $FeCl_2OR^2$ to give the corresponding coumarin ring.

TABLE 2. Effects of Reaction Conditions on the Lactonization Reaction of Ester **4a** into Coumarin **5a**

Entry	$FeCl_3$, equiv.	Solvent	Time, h	Temp., °C	Conversion, % (HPLC)
1	0.1	CH_2Cl_2	24	room temp.	5
2	1	CH_2Cl_2	8	room temp.	24
3	2	CH_2Cl_2	8	room temp.	58
4	3	CH_2Cl_2	8	room temp.	88
5	4	CH_2Cl_2	8	room temp.	90
6	3	CH_2Cl_2	4	room temp.	71
7	3	CH_2Cl_2	24	room temp.	90
8	3	$CHCl_3$	8	room temp.	87
9	3	1,2-Dichloroethane	8	room temp.	88
10	3	MeOH	8	room temp.	21
11	3	CH_2Cl_2	8	10	86
12	3	CH_2Cl_2	8	40	89



3, **4 a** R^1 = H, **b** R^1 = OMe; **3a**,**b** R^2 = H; **4a**,**b** R^2 = Me

To further confirm the structure of the obtained products, X-ray structural analysis of compound **5a** was performed (Fig. 1). Within the molecule, the C(7)−C(6), C(8)−C(10), and C(8)−C(9) bond lengths are 1.4306, 1.4830, and 1.4637 Å, respectively. These bonds are significantly shorter than the typical C−C single bond (1.53 Å), indicating a certain extent of conjugation involving the double bond, carbonyl group, and two benzene rings. The pyran ring is almost planar with the torsion angles C(7)−C(8)−C(9)−O(1), O(1)−C(1)−C(6)−C(7), and O(2)−C(9)−O(1)−C(1) being 0.34(18)°, -0.80(17)°, and 179.36(12)°, respectively.

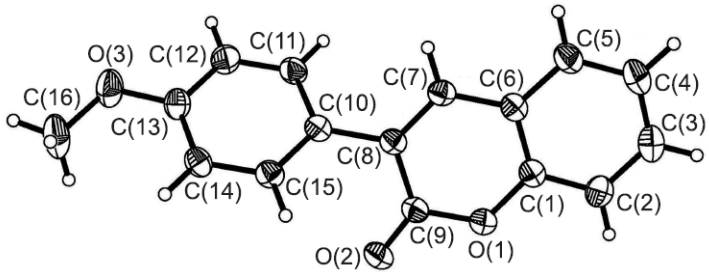


Fig. 1. Molecular structure of compound **5a** with atoms represented as thermal vibration ellipsoids at the 50% probability level.

In conclusion, a new and simple method of synthesizing 3-arylcoumarins in excellent yields by $FeCl_3$-promoted tandem reaction was developed. Although it is challenging to change to new substrate at this stage, the method still served as convenient and effective method for the synthesis of coumarin. The advantages include the use of easily available starting materials, mild reaction conditions, environmental friendliness, and simple operation. Thus, studies focused on further diversifying this moiety are currently under way in our laboratory.

EXPERIMENTAL

IR spectra were recorded on a Bruker Tensor 27 FTIR in KBr. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 and 100 MHz, respectively) with TMS as internal standard. Mass spectra were recorded on a QP2010 plus GC-MS instrument with chemical ionization. Elemental analyses were performed on a Perkin Elmer 2400 series elemental analyzer. Melting points were determined on a WPS-1B melting point apparatus and were uncorrected. The conversion was measured on a Shimadzu LC-10AVP HPLC system with a fluorescence detector (excitation wavelength 236 nm, emission wavelength 306 nm) using a Diamonsil C18 (250 × 4.6 mm, 5 μm) column; the mobile phase consisted of MeCN–0.05 M H_3PO_4, 40:60. Unless otherwise stated, all reactions were performed in an oven-dried vessel under nitrogen atmosphere. All anhydrous solvents were dried and purified by standard techniques prior to use. $FeCl_3$ was commercially obtained from Aladdin Chemical Co., Ltd (China) and used without further purification. Silica GF254 for TLC and silica gel (200-300 mesh) for column chromatography were purchased from Qingdao Marine Chemical Company (Qingdao, China).

Trace amounts of residual chloromethane in the reaction mixture were determined by a modified method [16] using an Agilent 6890 capillary gas chromatography system. The sample (0.3 ml) was dissolved in DMF–H_2O, 1:2 (5 ml) and separated on an Agilent DB-624 capillary column (30 m×0.32 mm×1.80 μm) in the headspace sampling mode with hydrogen flame ionization detector (FID). The column temperature was maintained at 60°C for 10 min, then raised to 180°C at the rate of 20°C·min^{-1} and maintained at 180°C for 2 min. The FID temperature was 250°C, and the injection port temperature was 200°C. The retention time of chloromethane was 4.1 min.

(*E*)-3-(2-Methoxyphenyl)-2-(4-methoxyphenyl)propenoic acid (3a). A mixture of 4-methoxyphenyl-acetic acid (**2**) (16.6 g, 0.1 mol), 2-methoxybenzaldehyde (**1a**) (13.6 g, 0.1 mol), Ac_2O (40 ml), and Et_3N (20 ml) was heated under reflux for 24 h. The red solution was allowed to cool to 60°C before water (10 ml) was added, and the mixture was stirred for 1 h at room temperature. The mixture was then poured into aqueous Na_2CO_3 solution (80 g in 300 ml of water) and stirred at 70°C until nearly all resinous material was dissolved. The solution was cooled to room temperature, extracted with Et_2O (3×100 ml), and carefully acidified with 6 M HCl to pH 3-4 with the precipitation of a yellow solid. The mixture was filtered, and the solid was washed with MeOH and recrystallized three times from MeOH. Yield 18.6 g (66%), light-yellow solid, mp 202-204°C (mp 202-203°C [18]). IR spectrum, ν, cm^{-1}: 1672 (C=O), 1599 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.75 (3H, s, CH_3); 3.84 (3H, s, CH_3); 6.61-6.67 (2H, m, H Ar); 6.88 (2H, d, *J* = 8.8, H Ar); 7.00-7.24 (4H, m, H Ar); 7.94 (1H, s, H-3); 12.61 (1H, s, COOH). Found, %: C 71.69; H 5.61. $C_{17}H_{16}O_4$. Calculated, %: C 71.82; H 5.67.

(*E*)-3-(2,3-Dimethoxyphenyl)-2-(4-methoxyphenyl)propenoic acid (3b) was obtained from compounds **1b** and **2** following the above procedure. Yield 63%, light-yellow solid, mp 172-174°C (mp 170-171°C [19]). IR spectrum, ν, cm^{-1}: 3422 (O–H), 1679 (C=O), 1612 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.75 (3H, s, CH_3); 3.79 (6H, s, $2CH_3$); 6.23 (1H, d, *J* = 7.8, H Ar); 6.73 (1H, t, *J* = 8.0, H Ar); 6.87 (2H, d, *J* = 8.6, H Ar); 6.91 (1H, d, *J* = 8.1, H Ar); 7.05 (2H, d, *J* = 8.6, H Ar); 7.89 (1H, s, H-3); 12.67 (1H, s, COOH). Found, %: C 68.59; H 5.71. $C_{18}H_{18}O_5$. Calculated, %: C 68.78; H 5.77.

Methyl (*E*)-3-(2-methoxyphenyl)-2-(4-methoxyphenyl)propenoate (4a). Concentrated sulfuric acid (10 ml) was added to a solution of acid **3a** (5.7 g, 0.02 mol) in MeOH (150 ml). Then the reaction mixture was heated under reflux for 6 h and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 ml) and subsequently washed with water (100 ml), aqueous Na_2CO_3 solution (10%, 2×100 ml), and brine. The organics were dried over Na_2SO_4, filtered, and concentrated in vacuum. The obtained crude product was recrystallized from MeOH. Yield 5.1 g (86%), colorless needles, mp 131-133°C. IR spectrum, ν, cm^{-1}: 1702 (C=O), 1601 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz). 3.80 (6H, s, $2CH_3$); 3.86 (3H, s, CH_3); 6.60 (1H, t, *J* = 7.5, H Ar); 6.74 (1H, d, *J* = 7.6, H Ar); 6.83-7.20 (6H, m, H Ar); 8.10 (1H, s, H-3). Mass spectrum, *m*/*z* (I_{rel}, %): 298 $[M]^+$ (100). Found, %: C 72.28; H 6.04. $C_{18}H_{18}O_4$. Calculated, %: C 72.47; H 6.08.

Methyl (*E*)-3-(2,3-dimethoxyphenyl)-2-(4-methoxyphenyl)propenoate (4b) was obtained from compound **3b** similarly to compound **4a**. Yield 87%, light-yellow solid, mp 96-98°C. IR spectrum, ν, cm^{-1}: 1705 (C=O), 1609 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.80 (3H, s, CH_3); 3.81 (3H, s, CH_3); 3.84 (3H, s, CH_3); 3.91 (3H, s, CH_3); 6.32 (1H, d, *J* = 7.8, H Ar); 6.69 (1H, t, *J* = 8.0, H Ar); 6.77 (1H, d, *J* = 7.7, H Ar); 6.85 (2H, d, *J* = 8.6, H Ar); 7.12 (2H, d, *J* = 8.6, H Ar); 8.06 (1H, s, H-3). Mass spectrum, *m*/*z* (I_{rel}, %): 328 $[M]^+$ (100). Found, %: C 69.24; H 6.09. $C_{19}H_{20}O_5$. Calculated, %: C 69.50; H 6.14.

3-(4-Methoxyphenyl)-2*H*-chromen-2-one (5a). Anhydrous $FeCl_3$ (4.9 g, 0.03 mol) was added to a solution of acid **3a** (2.8 g, 0.01 mol) or ester **4a** (3.0 g, 0.01 mol) in CH_2Cl_2 (200 ml). The black reaction mixture was stirred at room temperature for 6 to 8 h. The progress of the reaction was monitored by TLC. After the completion of reaction, the mixture was washed with HCl (1 mol/l, 3×200 ml). Then, the organic phase was sequentially washed with aqueous Na_2CO_3 solution (10%, 2×100 ml), water, and brine. The organics were dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel (CH_2Cl_2). Yield 2.0 g (78%, from compound **3a**) and 2.1 g (85%, from compound **4a**), light-yellow sheet crystals, mp 143-145°C (mp 140°C [4]). IR spectrum, ν, cm^{-1}: 3063 (=C–H); 1717 (C=O), 1608 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.85 (3H, s, CH_3); 6.97 (2H, d, *J* = 8.7, H-3',5'); 7.28-7.53 (4H, m, H-5,6,7,8); 7.68 (2H, d, *J* = 8.7, H-2',6'); 7.76 (1H, s, H-4). Mass spectrum, *m*/*z* (I_{rel}, %): 253 $[M+H]^+$ (18), 252 $[M]^+$ (100). Found, %: C 75.96; H 4.71. $C_{16}H_{12}O_3$. Calculated, %: C 76.18; H 4.79.

8-Methoxy-3-(4-methoxyphenyl)-2*H*-chromen-2-one (5b) was obtained following the above procedure. Yield 75% (from **3b**) and 79% (from **4b**), light-yellow needles, mp 148-150°C (mp 145°C [20]). IR spectrum, ν, cm^{-1}: 3072 (=C-H); 1704 (C=O), 1608 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.85 (3H, s, CH_3); 3.98 (3H, s, CH_3); 6.97 (2H, d, *J* = 8.7, H-3',5'); 7.06 (1H, d, *J* = 8.0, H-5); 7.10 (1H, d, *J* = 7.2, H-7); 7.21 (1H, dd, *J* = 8.0, *J* = 7.2, H-6); 7.69 (2H, d, *J* = 8.7, H-2',6'); 7.74 (1H, s, H-4). Mass spectrum, *m*/*z* (I_{rel}, %): 282 $[M]^+$ (100). Found, %: C 72.16; H 4.91. $C_{17}H_{14}O_4$. Calculated, %: C 72.33; H 5.00.

X-ray Structural Investigation of Compound 5a. Crystals of compound **5a** were obtained from the methanol solution by a slow evaporation process. A suitable single crystal of compound **5a** was selected for data collection performed on a Bruker APEX II spectrometer with graphite monochromator with MoKα radiation (λ = 0.71073 Å) using an ω–2θ scan mode at 296 K. Colorless crystal ($C_{16}H_{12}O_3$, *M* 252.26); at 296 K it was monoclinic, space group $P2_1/c$; *a* 6.1015(6), *b* 21.738(2), *c* 9.9137(10) Å; β 107.1310(10)°; *V* 1256.6(2) $Å^3$; *Z* 4; d_{calc} 1.333 g/cm^3. In a series of three scannings, 11262 reflections were selected. The structure was solved by direct method with SHELXS-97 and refined on F^2 by full-matrix least-square techniques with the SHELXS-97 program [21]. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms, isotropically refined with rider model position parameters, were located from different Fourier maps and added theoretically. Crystallographic data for compound **5a** have been deposited at the Cambridge Crystallographic Data Center (deposit CCDC 910488).

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