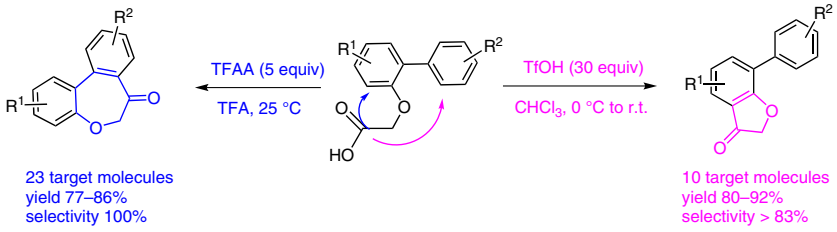
Synthesis J. Wang et al. Paper

Selective Friedel–Crafts Acylation Reactions of 2-Arylphenoxyacetic Acids: A Simple and Efficient Methodology to Synthesize Dibenzoxepine and Arylcoumaranone Derivatives

Jialin Wang[a,b]
Jiaqi Liu[a,b]
Hao Lan[a,b]
Wenyi Chu[*a,b]
Zhizhong Sun[*a,b]

[a] School of Chemistry and Materials Science, Heilongjiang University, 150080, Harbin, P. R. of China
[b] Key Laboratory of Chemical Engineering Process & Technology for High-Efficiency Conversion, College of Heilongjiang Province, 150080, Harbin, P. R. of China
wenyichu@hlju.edu.cn
Sunzz@hlju.edu.cn



Received: 10.03.2015
Accepted after revision: 17.04.2015
Published online: 19.06.2015
DOI: 10.1055/s-0034-1380211; Art ID: ss-2015-h0152-op

Abstract Intramolecular Friedel–Crafts acylation reactions of 2-arylphenoxyacetic acids are accomplished using trifluoroacetic anhydride or trifluoromethanesulfonic acid at 0 °C or room temperature. Depending on the reaction conditions, dibenzoxepines or arylcoumaranones are obtained in good yields and with high selectivities (83–100%). Plausible mechanistic pathways for the selective formation of the different reaction products are discussed.

Key words Friedel–Crafts acylations, 2-arylphenoxyacetic acids, dibenzoxepines, arylcoumaranones, regioselectivity

The synthesis of cycloketones represents an important area of research due to their wide spectrum of therapeutic applications.[1,2] Among them, dibenzoxepines and coumaranones are present in numerous therapeutic natural products. Dibenzoxepine derivatives have been described as extremely potent agonists of the TRPA1 receptor (**I**);[3] they are also effective against H-29 human colon adenocarcinoma and human breast cancer cells (**II**),[4] and are useful as nuclear hormone receptor modulators (**III**).[5] In addition, they are used extensively for the treatment of anxiety and depression (Figure 1).[6] Coumaranone derivatives are important intermediates for the synthesis of various bioactive compounds such as the heliquinomycin analogues (**IV**) and aurones (**V**) (Figure 1),[7] which have received significant attention in medicinal and pharmaceutical chemistry.[8] The therapeutic potential of coumaranones has been highlighted in recent studies reporting their anticancer, antimicrobial, antiparasitic, and antiviral activities.[9]

Owing to the diverse biological activities of compounds containing dibenzoxepine and coumaranone moieties, many different methods have been developed for the synthesis of these scaffolds. Examples include oxidative cyclization of *o*-acylphenols,[10] Pummerer rearrangement and intramolecular cyclization,[11] intramolecular etherification,[7b,12] nucleophilic substitution/cyclization,[13] polyphosphoric acid (PPA) promoted dehydration/cyclization,[14] etc. Most of these methods involve multistep procedures and relatively harsh reaction conditions, and deliver low yields and regioselectivities,[15] hence their applications have been somewhat constrained. Inter- and intramolecular Friedel–Crafts acylations of aromatic rings are considered to be the most fundamental methods for the synthesis of cycloketones.[16] However, acylating reagents such as acyl halides[17] and anhydrides[18] are unstable and sensitive to air. In con-

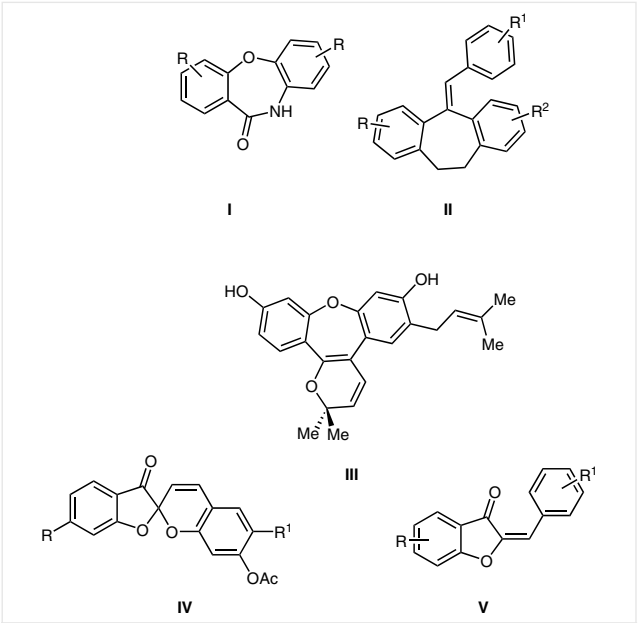
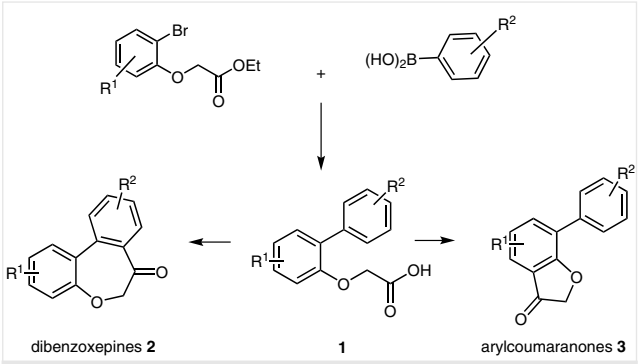


Figure 1 Examples of dibenzoxepine and coumaranone derivatives

trast, carboxylic acids[19] are cheap, readily available, and are stable to light and air, and can therefore be considered as good alternatives to other acylating reagents.

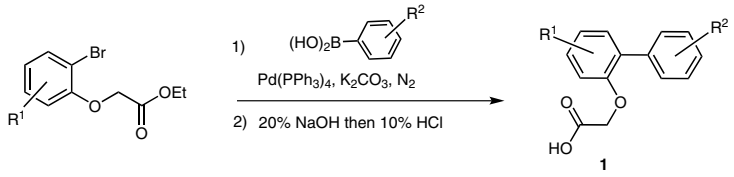
In our work, we found that the Friedel–Crafts acylation of 2-arylphenoxyacetic acids **1** occurred under different conditions to afford selectively compounds **2** and **3** in good yields and high regioselectivities (Scheme 1). The substrates **1** were obtained in good yields via Suzuki–Miyaura cross-coupling reactions (Table 1), but because of their low reactivity, their utilization in Friedel–Crafts reactions remains a challenging problem.



Scheme 1 Intramolecular selective Friedel–Crafts acylations proceeding via a carboxylic acid

Initially, we screened different catalysts and reagents for the selective acylation of (2-phenyl)phenoxyacetic acid (**1a**) (Table 2). No products were obtained from the reaction of compound **1a** with cyanuric chloride (TCT) in the presence of aluminum chloride ($AlCl_3$)[20] at room temperature (Table 2, entry 1). In addition, H-ZSM-5 (Zeolite Scony Mobile Number 5), hydrofluoric acid (HF), and sulfuric acid (H_2SO_4) were used in the acylation reaction,[21,22] but none of the desired products were observed (Table 2, entries 2–4). When polyphosphoric acid (PPA) or Eaton's reagent was used,[23,24] low yields of the corresponding dibenzoxepine product **2a** were obtained (Table 2, entries 5 and 6). With the aim of increasing the yield and regioselectivity of the reaction, organic superacid and acid anhydride catalyzed Friedel–Crafts acylation reactions[25] were examined. Treatment of **1a** with trifluoroacetic anhydride (TFAA) or methanesulfonic anhydride (MSAA) gave the corresponding product **2a** in 70% and 45% yields (Table 2, entries 7 and 8). We next examined the effects of strong acids (MSA, $ClSO_3H$, and TfOH) on the reaction. Methanesulfonic acid (MSA) and chlorosulfonic acid ($ClSO_3H$) were effective catalysts for the synthesis of dibenzoxepine **2a** in 33% and 37% yields (Table 2, entries 9 and 10), respectively. To our surprise, trifluoromethanesulfonic acid (TfOH) furnished **2a** in 17% yield and arylcoumaranone **3a** in 55% yield (Table 2, entry 11). According to these experimental results, trifluoroacetic anhydride and

Table 1 Synthesis of 2-Arylphenoxyacetic Acids **1** by Suzuki–Miyaura Cross-Coupling Reactions[a]

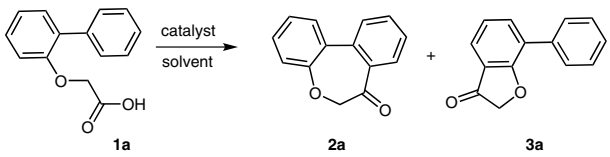


Entry	R^1	R^2	Product	Yield (%)[b]	Entry	R^1	R^2	Product	Yield (%)[b]
1	H	H	**1a**	85	13	*m*-Me	*m*-Cl	**1m**	85
2	*m*-Me	H	**1b**	87	14	*m*-Me	*m*-F	**1n**	84
3	H	*p*-Me	**1c**	85	15	*m*-F	H	**1o**	84
4	*m*-Me	*p*-Me	**1d**	88	16	*m*-F	*p*-Me	**1p**	89
5	*m*-Me	*m*-Me	**1e**	86	17	*m*-F	*m*,*p*-$(MeO)_2$	**1q**	84
6	*p*-MeO	H	**1f**	91	18	H	*p*-Ph	**1r**	80
7	*m*-MeO	H	**1g**	89	19	*m*-Me	*p*-Ph	**1s**	83
8	*m*-Me	*m*,*p*-$(MeO)_2$	**1h**	94	20	*p*-MeO	*p*-Ph	**1t**	83
9	*p*-MeO	*m*,*p*-$(MeO)_2$	**1i**	95	21	*m*-Ph	H	**1u**	82
10	*m*-MeO	*m*,*p*-$(MeO)_2$	**1j**	93	22	*m*-Me	Naphth	**1v**	84
11	H	*m*-Cl	**1k**	86	23	*p*-MeO	Naphth	**1w**	82
12	H	*m*-F	**1l**	89	24	*m*-Me	*o*-Cl	**1x**	74

[a] Reaction conditions: aryl bromide (10.0 mmol), arylboronic acid (12.0 mmol), K_2CO_3 (2.5 mmol), $Pd(PPh_3)_4$ (0.3 mmol), toluene (25 mL), 85 °C, N_2 atm, 12 h, then 20% NaOH solution, reflux, 3 h, then 10% HCl (ice–H_2O bath temperature), pH adjusted to 2–3.
[b] Yield of isolated product.

trifluoromethanesulfonic acid were effective reagents for the selective synthesis of compounds **2a** and **3a**, respectively.

Table 2 Effects of Different Reagents on the Selective Acylation Reaction of **1a**



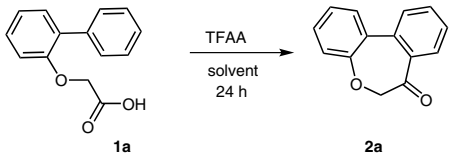
1a **2a** **3a**

Entry	Reagent (equiv)	Solvent	Temp (°C)	Time (h)	Product (Yield)[a]
1[b]	TCT/$AlCl_3$ (1.2)	$CHCl_3$	25	12	NR
2	H-ZSM-5 (0.5)	$PhNO_2$	160	12	NR
3	HF[c]	–	25	12	NR
4	H_2SO_4[c]	–	25	12	NR
5	PPA[c]	–	80	2	**2a** (22%)
6	Eaton's reagent[c,d]	–	80	2	**2a** (26%)
7	TFAA (5)	$CHCl_3$	25	24	**2a** (70%)
8	MSAA (1.3)	$PhNO_2$	80	12	**2a** (45%)
9	MSA (30)	$CHCl_3$	25	12	**2a** (33%)
10	$ClSO_3H$ (30)	$CHCl_3$	25	12	**2a** (37%), **3a** (trace)
11	TfOH (30)	$CHCl_3$	25	15	**2a** (17%), **3a** (55%)

[a] Yield of isolated product **2a** or **3a**. NR = no reaction.
[b] Cyanuric chloride (1.6 equiv) and pyridine (1 equiv) were used as additives.
[c] The reagent also serves as the solvent.
[d] Eaton's reagent is composed of a 1:10 solution by weight of P_2O_5 in MSA.

On the basis of these results, we next optimized the conditions for the selective acylation reaction of **1a** in the presence of trifluoroacetic anhydride to prepare compound **2a** (Table 3). Initially, the effect of the solvent was studied, and the results showed that trifluoroacetic acid (TFA) was superior to chloroform (Table 3, entries 1 and 2). Subsequently, the effects of temperature were examined; there was no change in the yield when the temperature was raised to 40 °C (Table 3, entries 2 and 3). Finally, the effect of the amount of trifluoroacetic anhydride was examined by varying the number of equivalents. Increasing the amount of trifluoroacetic anhydride from one to five equivalents resulted in an increased yield of the desired product from 64% to 82%, but increasing the amount of trifluoroacetic anhydride to 10 equivalents did not improve the yield further (Table 3, entries 2, 4 and 5). The optimum amount of trifluoroacetic anhydride was found to be five equivalents. It is important to note that the regioselectivity toward compound **2a** was 100%. The optimum reaction conditions for the synthesis of dibenzoxepine **2a** are as follows: (2-phenyl)phenoxyacetic acid (**1a**) (1 mmol), trifluoroacetic anhydride (5 equiv), trifluoroacetic acid (5 mL), 25 °C, 24 hours.

Table 3 Optimization of the Reaction Conditions for the Synthesis of **2a** in the Presence of Trifluoroacetic Anhydride (TFAA)



1a **2a**

Entry	TFAA (equiv)	Solvent	Temp (°C)	Yield[a,b]
1	5	$CHCl_3$	25	70%
2	**5**	**TFA**	**25**	**82%**
3	5	TFA	40	82%
4	1	TFA	25	64%
5	10	TFA	25	82%

[a] Yield of isolated product **2a**.
[b] Selectivity is 100%.

Having identified the optimum conditions for the reaction, we next studied the applicability of our protocol to various substrates. The results of these studies are summarized in Table 4. Substrates containing electron-donating groups (Table 4, entries 2–10) and/or electron-withdrawing groups (Table 4, entries 11–17) reacted smoothly, giving good yields of the expected products (82–86%) and excellent regioselectivities (100%). Besides these examples, we also examined the effects of phenyl and naphthyl substituents on the aryl rings of substrates **1**. The corresponding products **2** were obtained in good yields of 77–83% (Table 4, entries 18–23). This strategy showed an excellent tolerance toward a range of substituents (Me, MeO, F, Cl, Ph, etc.).

Following our preliminary investigations (Table 2), we next optimized the conditions for the selective acylation reaction of substrate **1a** in the presence of trifluoromethanesulfonic acid as the catalyst in order to synthesize arylcoumaranone **3a** (Table 5). It was clear from the results that the temperature played an important role in the reaction. When the reaction temperature was decreased from 35 °C to 0 °C, the yield of compound **3a** increased from a trace amount to 66%, and the yield of **2a** decreased from 67% to 8% (Table 5, entries 1–4). When the reaction temperature was slowly increased from 0 °C to room temperature, compound **3a** was obtained in an excellent yield of 85% (Table 5, entry 5). The amount of trifluoromethanesulfonic acid was also optimized by varying its number of equivalents from 10 to 40. When the amount of trifluoromethanesulfonic acid was increased from 10 to 30 equivalents, the yield of compound **3a** increased from 15% to 85% (Table 5, entries 5–7). A further increase in the amount of trifluoromethanesulfonic acid to 40 equivalents did not result in any signifi-

Table 4 Synthesis of Dibenzoxepines **2**[a]

1 **2**

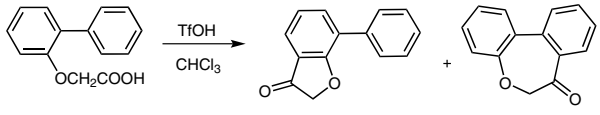
Entry	R^1	R^2	Product	Yield (%)[b]	Entry	R^1	R^2	Product	Yield (%)[b]
1	H	H	**2a**	82	13	*m*-Me	*m*-Cl	**2m**	83
2	*m*-Me	H	**2b**	84	14	*m*-Me	*m*-F	**2n**	81
3	H	*p*-Me	**2c**	83	15	*m*-F	H	**2o**	82
4	*m*-Me	*p*-Me	**2d**	82	16	*m*-F	*p*-Me	**2p**	84
5	*m*-Me	*m*-Me	**2e**	84	17	*m*-F	*m*,*p*-$(MeO)_2$	**2q**	85
6	*p*-MeO	H	**2f**	84	18	H	*p*-Ph	**2r**	80
7	*m*-MeO	H	**2g**	83	19	*m*-Me	*p*-Ph	**2s**	83
8	*m*-Me	*m*,*p*-$(MeO)_2$	**2h**	86	20	*p*-MeO	*p*-Ph	**2t**	81
9	*p*-MeO	*m*,*p*-$(MeO)_2$	**2i**	85	21	*m*-Ph	H	**2u**	80
10	*m*-MeO	*m*,*p*-$(MeO)_2$	**2j**	84	22	*m*-Me	Naphth	**2v**	79
11	H	*m*-Cl	**2k**	82	23	*p*-MeO	Naphth	**2w**	77
12	H	*m*-F	**2l**	80					

[a] Reaction conditions: **1** (1 mmol), TFAA (5 equiv), TFA (5 mL), 25 °C, 24 h.
[b] Yield of isolated product after purification by column chromatography. The selectivity in each case is 100%.

cant increase in the yield of **3a** (Table 5, entry 8). Hence the optimum amount of trifluoromethanesulfonic acid was 30 equivalents.

The optimum reaction conditions for the synthesis of arylcoumaranone **3a** are as follows: (2-phenyl)phenoxyacetic acid (**1a**) (1 mmol), $CHCl_3$ (3 mL), slow addition of trifluoromethanesulfonic acid (30 equiv) at 0 °C, then stirring at room temperature for 15 hours.

Table 5 Optimization of the Reaction Conditions for the Synthesis of **3a** in the Presence of Trifluoromethanesulfonic Acid (TfOH)



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

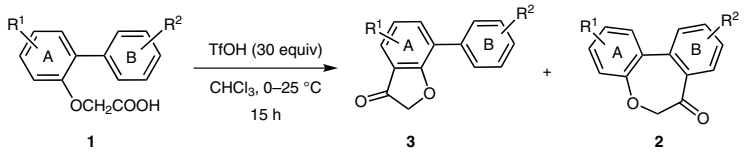
Entry	TfOH (equiv)	Temp (°C)	Time (h)	Product (yield)[a]
1	30	35	5	**3a** (trace), **2a** (67%)
2	30	25	9	**3a** (55%), **2a** (26%)
3	30	15	15	**3a** (62%), **2a** (17%)
4	30	0	15	**3a** (66%), **2a** (8%)
5	**30**	**0–25**[b]	**15**	**3a (85%), 2a (12%)**
6	10	0–25[b]	15	**3a** (15%), **2a** (61%)
7	20	0–25[b]	15	**3a** (34%), **2a** (32%)
8	40	0–25[b]	15	**3a** (85%), **2a** (12%)

[a] Yield of isolated product.
[b] TfOH was slowly added at 0 °C, and then the reaction mixture was stirred at room temperature for the appropriate amount of time.

Using the optimized conditions, the substrate scope of the Friedel–Crafts acylation reaction to synthesize arylcoumaranones **3**, selectively, was examined (Table 6). A substrate with an electron-donating group on the phenyl ring **A** gave a slightly higher yield of the corresponding product **3** than an example with an electron-donating substituent on the phenyl ring **B** (Table 6, entries 2 and 3). The presence of an electron-withdrawing group on the phenyl ring **B** did not affect the yield of the corresponding products **3** (Table 6, entries 4–7 and 11). In contrast, when an electron-withdrawing fluorine substituent was present on the phenyl ring **A** of substrate **1**, the corresponding product **3** was not obtained (Table 6, entry 8). When a phenyl group was located on the phenyl ring **B**, there was no obvious effect on the efficiency of the reactions and products **3** were furnished in similar yields (Table 6, entries 9 and 10).

Plausible reaction pathways for the selective Friedel–Crafts acylation reactions of substrate **1** are illustrated in Scheme 2. An intermediate carboxylic acid anhydride (**4**) is formed by the reaction of trifluoroacetic anhydride and substrate **1**. Steric effects present in intermediate **4** might improve the regioselectivity of the acylation and are beneficial for the formation of product **2**. Under the influence of the strong acid, trifluoromethanesulfonic acid, the intermediate sulfonic anhydride **5** is formed via elimination of water. As trifluoromethanesulfonate (TfO^-) is a good leaving group, intermediate **5** is transformed into ionic intermedi-

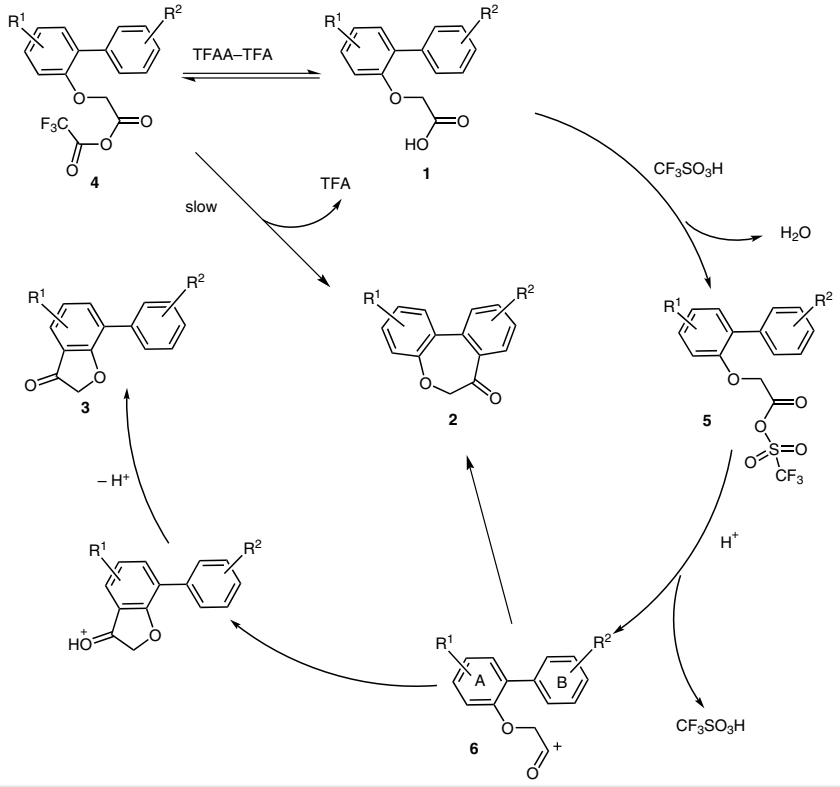
Table 6 Synthesis of Arylcoumaranones **3**[a]



1 3 2

Entry	Reactant	R^1	R^2	Yield of **3** (selectivity)[b]	Yield of **2** (selectivity)[b]
1	**1a**	H	H	85% (89%)	10% (11%)
2	**1b**	*m*-Me	H	89% (91%)	9% (9%)
3	**1c**	H	*p*-Me	80% (83%)	16% (17%)
4	**1k**	H	*m*-Cl	87% (91%)	9% (9%)
5	**1l**	H	*m*-F	88% (90%)	9% (10%)
6	**1m**	*m*-Me	*m*-Cl	90% (94%)	6% (6%)
7	**1n**	*m*-Me	*m*-F	92% (95%)	5% (5%)
8	**1o**	*m*-F	H	–	30% (100%)
9	**1r**	H	*p*-Ph	83% (85%)	15% (15%)
10	**1s**	*m*-Me	*p*-Ph	85% (89%)	10% (11%)
11	**1x**	*m*-Me	*o*-Cl	87% (100%)	–

[a] Reaction conditions: **1** (1 mmol), $CHCl_3$ (3 mL), TfOH (30 equiv), 0–25 °C, 15 h.
[b] Yield of isolated product after purification by column chromatography.



Scheme 2 Plausible mechanisms for the selective Friedel–Crafts acylation reactions

ate **6**, under acidic conditions, by removal of the trifluoromethanesulfonate group. As intermediate **6** exhibits less steric hindrance, the acylation products **2** and **3** can be obtained selectively under the appropriate conditions. The selectivity of the reaction was related to the nature of the substituents present on substrates **1**. The presence of electron-donating groups on the phenyl ring **A** facilitated the generation of products **3**. In contrast, the formation of products **2** was favored when an electron-donating group was located on the phenyl ring **B**. The selectivities were also related to the reaction temperature. A low temperature facilitated the formation of arylcoumaranones **3**, whilst higher temperatures resulted in moderate to good yields of dibenzoxepines **2**.

In conclusion, we have developed simple and efficient Friedel–Crafts acylations of acids **1** for the synthesis of cycloketones by using the simple reagents trifluoromethanesulfonic acid and trifluoroacetic anhydride at moderate temperatures. Depending on the reaction conditions, dibenzoxepine or arylcoumaranone derivatives are obtained in good yields and with high selectivities. The protocol is applicable to a variety of substrates **1** giving good to excellent yields of the corresponding products. In addition, plausible reaction mechanisms have been discussed.

Unless otherwise stated, all the reactions were carried out in air. Aryl bromides, Lewis acids, Brønsted acids, solid acid catalysts and arylboronic acids were purchased from Aladdin or Alfa, and were used without purification. Bases and solvents were purchased from Kermel Chemical Co. Ltd. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using Haiyang® Silica Gel 60 F254 plates (made by Branch of Qingdao Haiyang Chemical Co., Ltd of China), the plates were made visual by fluorescence quenching at 254 nm or 365 nm. Column chromatography was performed using Acros silica gel (60–200 μm, 60 Å). Petroleum ether (PE) refers to the fraction boiling in the 30–60 °C range. Melting points were measured with a Shenguang melting point apparatus. Infrared spectra (FT-IR) were recorded on a Perkin-Elmer Spectrum Two™ spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer (as $CDCl_3$ or DMSO-d_6 solutions) using TMS as an internal standard. High-resolution mass spectrometry (HRMS) was carried out using a Shimadzu LCMS-IT-TOF mass spectrometer. UV/Vis spectra were obtained using a Perkin-Elmer Lambda 950 spectrophotometer. Elemental analyses were obtained using a Perkin–Elmer 2400 Series II CHNS/O Analyzer.

Dibenzo[*b*,*d*]oxepin-7(6*H*)-ones 2; General Procedure

Biphenyl carboxylic acid **1** (1 mmol) was dissolved in dry TFA (5 mL) and treated with TFAA (5 equiv). The resulting mixture was stirred at 25 °C for 24 h and then quenched with ice–H_2O and extracted twice with $CHCl_3$. The combined organic layers were washed with H_2O and sat. Na_2CO_3 solution, dried over anhydrous $MgSO_4$, and concentrated under vacuum. Purification of the crude residue by column chromatography afforded dibenzo[*b*,*d*]oxepin-7(6*H*)-ones **2** as white solids.

Dibenzo[*b*,*d*]oxepin-7(6*H*)-one (2a)

Yield: 169 mg (82%); white solid; mp 77.3–80.0 °C; R_f = 0.42 (PE–EtOAc, 6:1).

FT-IR (KBr): 2920, 1679, 1446, 1210, 1052, 746, 719 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.78 (dd, *J* = 12.0, 4.5 Hz, 2 H), 7.72–7.65 (m, 2 H), 7.57 (td, *J* = 7.6, 1.1 Hz, 1 H), 7.47 (td, *J* = 7.7, 1.7 Hz, 1 H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1 H), 7.27 (dd, *J* = 7.9, 1.2 Hz, 1 H), 4.91 (s, 2 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 203.46, 156.35, 136.11, 135.90, 133.76, 132.54, 130.46, 130.21, 129.41, 128.91, 128.17, 126.08, 121.40, 82.58.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{11}O_2$: 211.0760; found: 211.0752.

UV/Vis (EtOH): λ_{max} = 309 nm.

Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.95; H, 4.81.

2-Methyldibenzo[*b*,*d*]oxepin-7(6*H*)-one (2b)

Yield: 188 mg (84%); white solid; mp 106.6–109.3 °C; R_f = 0.36 (PE–EtOAc, 6:1).

FT-IR (KBr): 2967, 2908, 1674, 1497, 1283, 1024, 830, 762, 691 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.77 (t, *J* = 7.4 Hz, 2 H), 7.66 (d, *J* = 7.4 Hz, 1 H), 7.55 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.48 (d, *J* = 1.7 Hz, 1 H), 7.25 (dd, *J* = 8.1, 1.6 Hz, 1 H), 7.14 (d, *J* = 8.1 Hz, 1 H), 4.86 (s, 2 H), 2.37 (s, 3 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 203.66, 154.19, 136.25, 135.96, 135.17, 133.65, 132.14, 130.84, 130.48, 129.29, 128.87, 128.05, 121.04, 82.57, 20.41.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}O_2$: 225.0916; found: 225.0920.

UV/Vis (EtOH): λ_{max} = 310 nm.

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.32; H, 5.40.

9-Methyldibenzo[*b*,*d*]oxepin-7(6*H*)-one (2c)

Yield: 186 mg (83%); white solid; mp 55.9–56.7 °C; R_f = 0.35 (PE–EtOAc, 6:1).

FT-IR (KBr): 2989, 2924, 1682, 1482, 1286, 1048, 811, 750, 679 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (s, 1 H), 7.56 (dd, *J* = 7.7, 1.7 Hz, 1 H), 7.49 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.45 (d, *J* = 8.0 Hz, 1 H), 7.37 (td, *J* = 7.6, 1.7 Hz, 1 H), 7.29 (td, *J* = 7.5, 1.4 Hz, 1 H), 7.21 (dd, *J* = 7.9, 1.3 Hz, 1 H), 4.82 (s, 2 H), 2.45 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 204.26, 157.00, 138.31, 136.06, 134.72, 134.52, 133.45, 130.30, 130.15, 130.04, 129.67, 126.14, 121.52, 82.95, 21.15.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}O_2$: 225.0916; found: 225.0918.

UV/Vis (EtOH): λ_{max} = 318 nm.

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.35; H, 5.39.

2,9-Dimethyldibenzo[*b*,*d*]oxepin-7(6*H*)-one (2d)

Yield: 196 mg (82%); white solid; mp 83.7–85.1 °C; R_f = 0.35 (PE–EtOAc, 6:1).

FT-IR (KBr): 3003, 2917, 1681, 1494, 1274, 1046, 824, 760 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 0.6 Hz, 1 H), 7.49–7.43 (m, 2 H), 7.34 (d, *J* = 1.7 Hz, 1 H), 7.16 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.09 (d, *J* = 8.1 Hz, 1 H), 4.78 (s, 2 H), 2.44 (s, 3 H), 2.39 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 204.64, 154.78, 138.17, 136.10, 135.62, 134.63, 134.60, 133.00, 130.68, 130.67, 129.98, 129.54, 121.16, 82.98, 21.18, 21.15.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}O_2$: 239.1073; found: 239.1068.

UV/Vis (EtOH): λ_{max} = 321 nm.

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.63; H, 5.93.

2,10-Dimethyldibenzo[*b*,*d*]oxepin-7(6*H*)-one (2e)

Yield: 200 mg (84%); white solid; mp 51.0–53.8 °C; R_f = 0.36 (PE–EtOAc, 6:1).

FT-IR (KBr): 2987, 2923, 1669, 1499, 1290, 1072, 815, 760 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.69 (d, *J* = 7.9 Hz, 1 H), 7.49 (d, *J* = 3.2 Hz, 2 H), 7.36 (d, *J* = 8.0 Hz, 1 H), 7.27–7.20 (m, 1 H), 7.12 (d, *J* = 8.1 Hz, 1 H), 4.81 (s, 2 H), 2.45 (s, 3 H), 2.37 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 203.93, 155.02, 144.49, 137.37, 135.61, 133.85, 133.13, 130.92, 130.83, 130.18, 129.90, 129.00, 121.21, 82.92, 21.94, 21.18.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}O_2$: 239.1073; found: 239.1070.

UV/Vis (EtOH): λ_{max} = 310 nm.

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.66; H, 5.93.

3-Methoxydibenzo[*b*,*d*]oxepin-7(6*H*)-one (2f)

Yield: 202 mg (84%); white solid; mp 113.4–115.7 °C; R_f = 0.38 (PE–EtOAc, 6:1).

FT-IR (KBr): 2997, 2926, 1678, 1438, 1281, 1038, 822, 761 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.78 (dd, *J* = 7.8, 1.3 Hz, 1 H), 7.74 (td, *J* = 7.7, 1.4 Hz, 1 H), 7.62 (d, *J* = 8.7 Hz, 1 H), 7.59 (d, *J* = 7.8 Hz, 1 H), 7.50 (td, *J* = 7.6, 1.1 Hz, 1 H), 6.96 (dd, *J* = 8.7, 2.6 Hz, 1 H), 6.84 (d, *J* = 2.6 Hz, 1 H), 4.89 (s, 2 H), 3.82 (s, 3 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 203.29, 160.89, 157.50, 136.32, 135.34, 133.77, 130.96, 129.05, 129.00, 127.39, 124.59, 112.23, 106.55, 82.32, 55.51.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}O_3$: 241.0865; found: 241.0860.

UV/Vis (EtOH): λ_{max} = 248 nm.

Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 74.97; H, 5.06.

2-Methoxydibenzo[*b*,*d*]oxepin-7(6*H*)-one (2g)

Yield: 199 mg (83%); white solid; mp 91.5–94.1 °C; R_f = 0.38 (PE–EtOAc, 6:1).

FT-IR (KBr): 2953, 2926, 1687, 1497, 1286, 1048, 829, 770 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.78 (ddd, *J* = 7.4, 3.8, 1.1 Hz, 2 H), 7.71 (dd, *J* = 8.2, 1.2 Hz, 1 H), 7.57 (td, *J* = 7.6, 1.3 Hz, 1 H), 7.19 (t, *J* = 5.6 Hz, 2 H), 7.00 (dd, *J* = 8.7, 3.1 Hz, 1 H), 4.86 (s, 2 H), 3.82 (s, 3 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 203.91, 156.89, 149.91, 136.15, 136.06, 133.64, 133.25, 129.36, 128.84, 128.26, 122.22, 115.72, 114.60, 82.76, 55.54.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}O_3$: 241.0865; found: 241.0864.

UV/Vis (EtOH): λ_{max} = 301 nm.

Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 74.98; H, 5.04.

9,10-Dimethoxy-2-methyldibenzo[*b*,*d*]oxepin-7(6*H*)-one (2h)

Yield: 245 mg (86%); white solid; mp 151.4–154.2 °C; R_f = 0.32 (PE–EtOAc, 6:1).

FT-IR (KBr): 3015, 2924, 2851, 1674, 1462, 1267, 1024, 821, 787, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 1.7 Hz, 1 H), 7.34 (s, 1 H), 7.20 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.14 (s, 1 H), 7.11 (d, *J* = 8.1 Hz, 1 H), 4.76 (s, 2 H), 3.97 (s, 3 H), 3.86 (s, 3 H), 2.38 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 202.31, 154.86, 153.56, 148.88, 135.42, 132.74, 131.97, 130.49, 130.39, 128.77, 121.10, 111.78, 111.73, 56.38, 56.26, 21.16.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}O_4$: 285.1128; found: 285.1130.

UV/Vis (EtOH): λ_{max} = 294 nm.

Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.84; H, 5.66.

3,9,10-Trimethoxydibenzo[*b*,*d*]oxepin-7(6*H*)-one (2i)

Yield: 256 mg (85%); white solid; mp 206.5–207.2 °C; R_f = 0.33 (PE–EtOAc, 6:1).

FT-IR (KBr): 2957, 2910, 1673, 1503, 1273, 1034, 833, 692 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (s, 1 H), 7.47 (d, *J* = 8.8 Hz, 1 H), 6.93 (s, 1 H), 6.86 (dd, *J* = 8.6, 2.4 Hz, 1 H), 6.76 (d, *J* = 2.4 Hz, 1 H), 4.77 (s, 2 H), 4.00 (s, 3 H), 3.97 (s, 3 H), 3.86 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 201.76, 161.13, 158.19, 153.78, 148.55, 132.24, 130.80, 128.12, 125.35, 112.39, 111.83, 111.56, 106.39, 82.23, 56.39, 56.35, 55.81.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}O_5$: 301.1077; found: 301.1079.

UV/Vis (EtOH): λ_{max} = 247, 295 nm.

Anal. Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37. Found: C, 67.97; H, 5.38.

2,9,10-Trimethoxydibenzo[*b*,*d*]oxepin-7(6*H*)-one (2j)

Yield: 252 mg (84%); white solid; mp 172.6–173.8 °C; R_f = 0.33 (PE–EtOAc, 6:1).

FT-IR (KBr): 3007, 2923, 2845, 1667, 1498, 1207, 1029, 865, 791, 694 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 1 H), 7.25 (d, *J* = 2.9 Hz, 1 H), 7.16 (t, *J* = 4.4 Hz, 2 H), 6.96 (dd, *J* = 8.7, 3.0 Hz, 1 H), 4.75 (s, 2 H), 3.97 (s, 3 H), 3.86 (s, 3 H), 3.82 (s, 3 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 201.73, 156.78, 153.12, 150.00, 148.46, 133.19, 130.64, 128.14, 121.86, 115.19, 114.69, 112.19, 111.14, 82.08, 55.97, 55.63, 55.59.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}O_5$: 301.1077; found: 301.1076.

UV/Vis (EtOH): λ_{max} = 257, 291 nm.

Anal. Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37. Found: C, 67.98; H, 5.38.

10-Chlorodibenzo[*b*,*d*]oxepin-7(6*H*)-one (2k)

Yield: 201 mg (82%); white solid; mp 170.1–172.0 °C; R_f = 0.40 (PE–EtOAc, 6:1).

FT-IR (KBr): 2910, 1682, 1439, 1288, 1069, 815, 763 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.4 Hz, 1 H), 7.56 (dd, *J* = 10.2, 1.9 Hz, 2 H), 7.43 (ddd, *J* = 9.4, 8.1, 1.9 Hz, 2 H), 7.35–7.31 (m, 1 H), 7.24 (d, *J* = 8.0 Hz, 1 H), 4.82 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 202.75, 157.17, 140.15, 138.88, 134.57, 132.25, 131.39, 131.18, 130.38, 129.57, 128.40, 126.41, 121.78, 82.81.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{10}ClO_2$: 245.0370; found: 245.0375.

UV/Vis (EtOH): λ_{max} = 269 nm.

Anal. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71; Cl, 14.49. Found: C, 68.71; H, 3.70; Cl, 14.50.

10-Fluorodibenzo[*b*,*d*]oxepin-7(6*H*)-one (2l)

Yield: 183 mg (80%); white solid; mp 133.1–134.9 °C; R_f = 0.39 (PE–EtOAc, 6:1).

FT-IR (KBr): 2937, 1685, 1491, 1263, 1043, 877, 761 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.89 (dd, *J* = 8.7, 6.2 Hz, 1 H), 7.75 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.55 (dd, *J* = 10.4, 2.6 Hz, 1 H), 7.50 (td, *J* = 7.7, 1.6 Hz, 1 H), 7.45–7.36 (m, 2 H), 7.28 (dd, *J* = 7.9, 1.2 Hz, 1 H), 4.91 (s, 2 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 201.92, 165.10 (d, *J* = 250 Hz), 156.36, 139.16 (d, *J* = 9 Hz), 132.55, 132.52, 131.99 (d, *J* = 110 Hz), 131.14, 130.50, 126.15, 121.53, 116.03 (d, *J* = 23 Hz), 115.43 (d, *J* = 24 Hz), 82.26.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{10}FO_2$: 229.0666; found: 229.0668.

UV/Vis (EtOH): λ_{max} = 267 nm.

Anal. Calcd for $C_{14}H_9FO_2$: C, 73.68; H, 3.97; F, 8.32. Found: C, 73.69; H, 3.99; F, 8.31.

10-Chloro-2-methyldibenzo[*b*,*d*]oxepin-7(6*H*)-one (2m)

Yield: 214 mg (83%); white solid; mp 109.8–112.2 °C; R_f = 0.40 (PE–EtOAc, 6:1).

FT-IR (KBr): 2923, 2854, 1685, 1498, 1292, 1045, 813, 793 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.4 Hz, 1 H), 7.54 (d, *J* = 2.0 Hz, 1 H), 7.43 (dd, *J* = 8.4, 2.1 Hz, 1 H), 7.35 (d, *J* = 1.6 Hz, 1 H), 7.21 (ddd, *J* = 8.1, 2.1, 0.6 Hz, 1 H), 7.11 (d, *J* = 8.1 Hz, 1 H), 4.78 (s, 2 H), 2.41 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 203.10, 154.98, 140.04, 139.02, 136.01, 134.65, 131.82, 131.71, 131.35, 130.73, 129.44, 128.27, 121.43, 82.86, 21.16.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}ClO_2$: 259.0527; found: 259.0529.

UV/Vis (EtOH): λ_{max} = 246 nm.

Anal. Calcd for $C_{15}H_{11}ClO_2$: C, 69.64; H, 4.29; Cl, 13.70. Found: C, 69.65; H, 4.28; Cl, 13.71.

10-Fluoro-2-methyldibenzo[*b*,*d*]oxepin-7(6*H*)-one (2n)

Yield: 196 mg (81%); white solid; mp 110.3–111.4 °C; R_f = 0.35 (PE–EtOAc, 6:1).

FT-IR (KBr): 2981, 2915, 1680, 1485, 1287, 1072, 872, 757 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.87 (dd, *J* = 8.7, 6.2 Hz, 1 H), 7.54 (dd, *J* = 10.2, 2.3 Hz, 2 H), 7.40 (td, *J* = 8.5, 2.6 Hz, 1 H), 7.28 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.15 (d, *J* = 8.1 Hz, 1 H), 4.85 (s, 2 H), 2.37 (s, 3 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 202.07, 165.07 (d, *J* = 250 Hz), 154.19, 139.32 (d, *J* = 9 Hz), 135.31, 132.31, 132.21, 131.77 (d, *J* = 155 Hz), 131.49, 130.75, 121.14, 115.86 (d, *J* = 23 Hz), 115.27 (d, *J* = 24 Hz), 82.22, 20.37.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}FO_2$: 243.0822; found: 243.0825.

UV/Vis (EtOH): λ_{max} = 246 nm.

Anal. Calcd for $C_{15}H_{11}FO_2$: C, 74.37; H, 4.58; F, 7.84;. Found: C, 74.39; H, 4.57; F, 7.82.

2-Fluorodibenzo[*b*,*d*]oxepin-7(6*H*)-one (2o)

Yield: 187 mg (82%); white solid; mp 131.6–132.2 °C; R_f = 0.38 (PE–EtOAc, 6:1).

FT-IR (KBr): 2924, 2854, 1693, 1496, 1268, 1048, 825, 773 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.79 (t, *J* = 7.3 Hz, 2 H), 7.70 (d, *J* = 7.3 Hz, 1 H), 7.58 (ddd, *J* = 13.2, 9.1, 1.8 Hz, 2 H), 7.30 (dd, *J* = 7.4, 2.5 Hz, 2 H), 4.91 (s, 2 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 203.26, 159.58 (d, *J* = 240 Hz), 152.60, 136.04, 134.95, 134.31 (d, *J* = 9 Hz), 133.83, 129.63, 129.04, 128.78, 123.27 (d, *J* = 9 Hz), 116.85 (d, *J* = 23 Hz), 116.42 (d, *J* = 24 Hz), 82.70.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{10}FO_2$: 229.0666; found: 229.0665.

UV/Vis (EtOH): λ_{max} = 289 nm.

Anal. Calcd for $C_{14}H_9FO_2$: C, 73.68; H, 3.97; F, 8.32. Found: C, 73.67; H, 3.98; F, 8.33.

2-Fluoro-9-methyldibenzo[*b*,*d*]oxepin-7(6*H*)-one (2p)

Yield: 204 mg (84%); white solid; mp 121.7–123.3 °C; R_f = 0.35 (PE–EtOAc, 6:1).

FT-IR (KBr): 3026, 2918, 1682, 1489, 1270, 1049, 824, 768 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.61 (s, 3 H), 7.54 (dd, *J* = 9.6, 2.2 Hz, 1 H), 7.31–7.24 (m, 2 H), 4.89 (s, 2 H), 2.42 (s, 3 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 203.21, 159.54 (d, *J* = 240 Hz), 152.50, 138.49, 135.76, 134.51, 134.28 (d, *J* = 9 Hz), 132.30, 129.66, 129.26, 123.16 (d, *J* = 9 Hz), 116.48 (d, *J* = 23 Hz), 116.19 (d, *J* = 24 Hz), 82.53, 20.48.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}FO_2$: 243.0822; found: 243.0824.

UV/Vis (EtOH): λ_{max} = 312 nm.

Anal. Calcd for $C_{15}H_{11}FO_2$: C, 74.37; H, 4.58; F, 7.84. Found: C, 74.38; H, 4.56; F, 7.83.

2-Fluoro-9,10-dimethoxydibenzo[*b*,*d*]oxepin-7(6*H*)-one (2q)

Yield: 246 mg (85%); white solid; mp 186.0–188.2 °C; R_f = 0.33 (PE–EtOAc, 6:1).

FT-IR (KBr): 2976, 2923, 2850, 1665, 1497, 1247, 1027, 825, 774 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.67 (dd, *J* = 10.0, 2.7 Hz, 1 H), 7.36 (s, 1 H), 7.29–7.21 (m, 2 H), 7.17 (s, 1 H), 4.82 (s, 2 H), 3.98 (s, 3 H), 3.87 (s, 3 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 200.91, 159.47 (d, *J* = 240 Hz), 153.15, 152.54, 148.72, 134.11 (d, *J* = 9 Hz), 129.48, 128.04, 122.79 (d, *J* = 9 Hz), 116.48 (d, *J* = 23 Hz), 116.06 (d, *J* = 24 Hz), 112.37, 111.21, 81.89, 56.00, 55.63.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{14}FO_4$: 289.0877; found: 289.0879.

UV/Vis (EtOH): λ_{max} = 247, 291 nm.

Anal. Calcd for $C_{16}H_{13}FO_4$: C, 66.66; H, 4.55; F, 6.59. Found: C, 66.68; H, 4.54; F, 6.58.

9-Phenyldibenzo[*b*,*d*]oxepin-7(6*H*)-one (2r)

Yield: 229 mg (80%); white solid; mp 121.0–122.8 °C; R_f = 0.38 (PE–EtOAc, 6:1).

FT-IR (KBr): 2918, 1677, 1477, 1234, 1055, 805, 754 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.09 (dd, *J* = 8.2, 2.1 Hz, 1 H), 8.04 (d, *J* = 2.0 Hz, 1 H), 7.82–7.73 (m, 4 H), 7.53 (t, *J* = 7.6 Hz, 2 H), 7.50–7.36 (m, 3 H), 7.29 (dd, *J* = 7.9, 1.1 Hz, 1 H), 4.95 (s, 2 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 203.29, 156.44, 139.72, 138.41, 136.37, 135.08, 132.13, 131.72, 130.55, 130.25, 130.12, 129.16, 128.15, 126.83, 126.66, 126.12, 121.46, 82.48.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{15}O_2$: 287.1073; found: 287.1072.

UV/Vis (EtOH): λ_{max} = 253, 281, 324 nm.

Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.92; H, 4.92.

2-Methyl-9-phenyldibenzo[*b*,*d*]oxepin-7(6*H*)-one (2s)

Yield: 249 mg (83%); white solid; mp 82.4–84.7 °C; R_f = 0.33 (PE–EtOAc, 6:1).

FT-IR (KBr): 3028, 2918, 1678, 1480, 1264, 1052, 829, 752 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.07 (dd, *J* = 8.2, 2.1 Hz, 1 H), 8.02 (d, *J* = 2.1 Hz, 1 H), 7.80–7.75 (m, 3 H), 7.53 (dd, *J* = 10.2, 4.8 Hz, 3 H), 7.44 (t, *J* = 7.3 Hz, 1 H), 7.27 (dd, *J* = 8.1, 1.6 Hz, 1 H), 7.16 (d, *J* = 8.1 Hz, 1 H), 4.90 (s, 2 H), 2.39 (s, 3 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 203.46, 154.28, 139.59, 138.43, 136.40, 135.20, 131.71, 131.59, 130.92, 130.36, 130.11, 129.12, 128.10, 126.80, 126.62, 121.09, 82.45, 20.44.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{17}O_2$: 301.1229; found: 301.1230.

UV/Vis (EtOH): λ_{max} = 284 nm.

Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.97; H, 5.36.

3-Methoxy-9-phenyldibenzo[*b*,*d*]oxepin-7(6*H*)-one (2t)

Yield: 256 mg (81%); white solid; mp 140.7–143.4 °C; R_f = 0.31 (PE–EtOAc, 6:1).

FT-IR (KBr): 2964, 2837, 1677, 1476, 1294, 1032, 815, 770 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 2.0 Hz, 1 H), 7.87 (dd, *J* = 8.1, 2.1 Hz, 1 H), 7.69–7.65 (m, 2 H), 7.55 (dd, *J* = 9.7, 8.6 Hz, 2 H), 7.47 (t, *J* = 7.5 Hz, 2 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 6.89 (dd, *J* = 8.7, 2.6 Hz, 1 H), 6.79 (d, *J* = 2.6 Hz, 1 H), 4.86 (s, 2 H), 3.86 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 203.51, 161.32, 158.00, 140.08, 139.42, 135.98, 135.77, 132.02, 130.84, 129.71, 128.94, 128.07, 127.87, 126.98, 125.02, 112.32, 106.42, 82.51, 55.58.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{17}O_3$: 317.1178; found: 317.1180.

UV/Vis (EtOH): λ_{max} = 288 nm.

Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.71; H, 5.11.

2-Phenyldibenzo[*b*,*d*]oxepin-7(6*H*)-one (2u)

Yield: 229 mg (80%); white solid; mp 132.5–134.6 °C; R_f = 0.35 (PE–EtOAc, 6:1).

FT-IR (KBr): 3029, 1689, 1480, 1268, 1054, 774, 757 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.93 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.77 (d, *J* = 2.2 Hz, 1 H), 7.72–7.67 (m, 1 H), 7.65–7.57 (m, 4 H), 7.49 (ddd, *J* = 22.8, 10.5, 4.5 Hz, 3 H), 7.40–7.35 (m, 1 H), 7.30 (d, *J* = 8.3 Hz, 1 H), 4.88 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 203.84, 156.23, 140.24, 139.31, 136.98, 136.21, 133.66, 133.51, 129.57, 129.46, 129.09, 128.97, 128.91, 128.20, 127.53, 127.09, 121.75, 82.88.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{15}O_2$: 287.1073; found: 287.1071.

UV/Vis (EtOH): λ_{max} = 306 nm.

Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.92; H, 4.92.

2-Methylbenzo[*b*]naphtho[2,3-*d*]oxepin-7(6*H*)-one (2v)

Yield: 217 mg (79%); white solid; mp 164.9–167.0 °C; R_f = 0.34 (PE–EtOAc, 6:1).

FT-IR (KBr): 2969, 2915, 2879, 1682, 1232, 1054, 757 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.25 (d, *J* = 8.6 Hz, 1 H), 8.05 (dd, *J* = 9.6, 6.7 Hz, 2 H), 7.71 (d, *J* = 8.6 Hz, 1 H), 7.67–7.60 (m, 2 H), 7.56 (d, *J* = 1.6 Hz, 1 H), 7.28 (dd, *J* = 8.1, 1.6 Hz, 1 H), 7.19 (d, *J* = 8.1 Hz, 1 H), 5.07 (s, 2 H), 2.39 (s, 3 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 206.15, 153.96, 135.46, 134.12, 133.69, 132.56, 132.31, 130.92, 130.76, 129.43, 128.19, 127.84, 126.72, 126.30, 125.63, 121.22, 86.22, 20.45.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{15}O_2$: 275.1073; found: 275.1076.

UV/Vis (EtOH): λ_{max} = 260 nm.

Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.20; H, 5.15.

3-Methoxybenzo[*b*]naphtho[2,3-*d*]oxepin-7(6*H*)-one (2w)

Yield: 224 mg (77%); white solid; mp 157.1–160.8 °C; R_f = 0.34 (PE–EtOAc, 6:1).

FT-IR (KBr): 2982, 2904, 1672, 1443, 1214, 1030, 802, 733 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.21 (d, *J* = 8.6 Hz, 1 H), 8.08–8.00 (m, 2 H), 7.64 (ddd, *J* = 21.1, 13.6, 7.8 Hz, 4 H), 7.01 (dd, *J* = 8.6, 2.2 Hz, 1 H), 6.90 (d, *J* = 2.2 Hz, 1 H), 5.12 (s, 2 H), 3.84 (s, 3 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 206.14, 160.85, 157.28, 134.22, 133.06, 132.35, 132.28, 131.35, 129.68, 128.16, 127.81, 126.48, 126.32, 125.60, 124.94, 112.38, 106.96, 86.00, 55.53.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{15}O_3$: 291.1022; found: 291.1025.

UV/Vis (EtOH): λ_{max} = 254, 273 nm.

Anal. Calcd for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found: C, 78.63; H, 4.85.

7-Phenylbenzofuran-3(2*H*)-ones 3; General Procedure

Biphenyl carboxylic acid **1** (1.0 mmol) was dissolved in dry $CHCl_3$ (3.0 mL), and TfOH (30 mmol, 2.64 mL) was added slowly at 0 °C under stirring. The resulting mixture was stirred at r.t. for 15 h, and then quenched with ice–H_2O and extracted twice with $CHCl_3$. The combined organic layers were washed with H_2O and sat. Na_2CO_3 solution, dried over anhydrous $MgSO_4$, and concentrated under vacuum. Purification of the crude residue by column chromatography afforded 7-phenylbenzofuran-3(2*H*)-ones **3** as yellow solids.

7-Phenylbenzofuran-3(2*H*)-one (3a)

Yield: 179 mg (85%); yellow solid; mp 89.1–92.4 °C; R_f = 0.40 (PE–EtOAc, 5:1).

FT-IR (KBr): 2924, 2854, 1737, 1424, 1261, 1025, 993, 762, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.63 (m, 4 H), 7.49 (t, *J* = 7.5 Hz, 2 H), 7.40 (t, *J* = 7.4 Hz, 1 H), 7.20 (t, *J* = 7.6 Hz, 1 H), 4.70 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.22, 171.35, 137.20, 135.10, 128.90, 128.65, 128.37, 127.76, 123.24, 122.78, 122.10, 74.89.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{11}O_2$: 211.0760; found: 211.0755.

UV/Vis (EtOH): λ_{max} = 245, 341 nm.

Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.96; H, 4.80.

5-Methyl-7-phenylbenzofuran-3(2*H*)-one (3b)

Yield: 199 mg (89%); yellow solid; mp 145.3–148.0 °C; R_f = 0.36 (PE–EtOAc, 5:1).

FT-IR (KBr): 2969, 2919, 1726, 1481, 1257, 1031, 879, 771 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73–7.68 (m, 2 H), 7.57 (d, *J* = 1.7 Hz, 1 H), 7.50–7.44 (m, 3 H), 7.39 (t, *J* = 7.4 Hz, 1 H), 4.68 (s, 2 H), 2.42 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.33, 169.87, 138.47, 135.22, 132.40, 128.86, 128.61, 128.28, 127.26, 122.69, 122.06, 75.15, 20.93.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}O_2$: 225.0916; found: 225.0918.

UV/Vis (EtOH): λ_{max} = 250, 349 nm.

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.31; H, 5.39.

7-(*p*-Tolyl)benzofuran-3(2*H*)-one (3c)

Yield: 180 mg (80%); yellow solid; mp 86.4–88.6 °C; R_f = 0.35 (PE–EtOAc, 5:1).

FT-IR (KBr): 2987, 2922, 1728, 1455, 1293, 1057, 998, 832, 793 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (dd, *J* = 7.4, 1.3 Hz, 1 H), 7.65 (dd, *J* = 7.7, 1.3 Hz, 1 H), 7.61 (d, *J* = 8.1 Hz, 2 H), 7.29 (d, *J* = 7.9 Hz, 2 H), 7.18 (t, *J* = 7.6 Hz, 1 H), 4.69 (s, 2 H), 2.41 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.34, 171.40, 138.32, 136.98, 132.16, 129.61, 128.50, 127.77, 122.90, 122.74, 122.02, 74.87, 21.46.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}O_2$: 225.0916; found: 225.0913.

UV/Vis (EtOH): λ_{max} = 253, 341 nm.

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.36; H, 5.38.

7-(3-Chlorophenyl)benzofuran-3(2*H*)-one (3k)

Yield: 212 mg (87%); yellow solid; mp 107.8–110.6 °C; R_f = 0.38 (PE–EtOAc, 5:1).

FT-IR (KBr): 2911, 1731, 1442, 1288, 1084, 990, 772, 684 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.66 (m, 3 H), 7.60 (d, *J* = 7.4 Hz, 1 H), 7.39 (ddd, *J* = 10.9, 8.1, 4.9 Hz, 2 H), 7.20 (t, *J* = 7.6 Hz, 1 H), 4.71 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.88, 171.12, 137.03, 136.84, 134.83, 130.12, 128.73, 128.40, 126.73, 126.24, 123.90, 122.85, 122.27, 74.96.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{10}ClO_2$: 245.0370; found: 245.0373.

UV/Vis (EtOH): λ_{max} = 242, 339 nm.

Anal. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71; Cl, 14.49. Found: C, 68.73; H, 3.69; Cl, 14.51.

7-(3-Fluorophenyl)benzofuran-3(2*H*)-one (3l)

Yield: 201 mg (88%); yellow solid; mp 102.1–104.7 °C; R_f = 0.35 (PE–EtOAc, 5:1).

FT-IR (KBr): 2922, 1726, 1480, 1258, 1191, 994, 840, 719 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 7.5 Hz, 1 H), 7.70 (d, *J* = 7.7 Hz, 1 H), 7.54–7.40 (m, 3 H), 7.20 (t, *J* = 7.6 Hz, 1 H), 7.10 (td, *J* = 8.1, 1.8 Hz, 1 H), 4.71 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.90, 171.13, 163.13 (d, *J* = 244 Hz), 137.16 (d, *J* = 8 Hz), 137.01, 130.38 (d, *J* = 8 Hz), 126.39, 124.22, 123.85, 122.84, 122.27, 115.68 (d, *J* = 22 Hz), 115.22 (d, *J* = 21 Hz), 74.94.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{10}FO_2$: 229.0666; found: 229.0664.

UV/Vis (EtOH): λ_{max} = 243, 341 nm.

Anal. Calcd for $C_{14}H_9FO_2$: C, 73.68; H, 3.97; F, 8.32. Found: C, 73.66; H, 3.98; F, 8.33.

7-(3-Chlorophenyl)-5-methylbenzofuran-3(2*H*)-one (3m)

Yield: 231 mg (90%); yellow solid; mp 143.9–146.7 °C; R_f = 0.35 (PE–EtOAc, 5:1).

FT-IR (KBr): 2983, 2928, 1734, 1473, 1255, 998, 876, 772, 694 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (t, *J* = 1.6 Hz, 1 H), 7.60 (dt, *J* = 7.4, 1.5 Hz, 1 H), 7.56 (d, *J* = 1.6 Hz, 1 H), 7.48 (d, *J* = 0.9 Hz, 1 H), 7.38 (tt, *J* = 4.7, 3.4 Hz, 2 H), 4.69 (s, 2 H), 2.43 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.01, 169.62, 138.24, 136.97, 134.80, 132.53, 130.07, 128.66, 128.28, 126.70, 125.72, 123.38, 122.24, 75.20, 20.90.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}ClO_2$: 259.0527; found: 259.0526.

UV/Vis (EtOH): λ_{max} = 242, 348 nm.

Anal. Calcd for $C_{15}H_{11}ClO_2$: C, 69.64; H, 4.29; Cl, 13.70. Found: C, 69.63; H, 4.27; Cl, 13.72.

7-(3-Fluorophenyl)-5-methylbenzofuran-3(2*H*)-one (3n)

Yield: 223 mg (92%); yellow solid; mp 126.4–127.7 °C; R_f = 0.33 (PE–EtOAc, 5:1).

FT-IR (KBr): 2991, 2923, 1734, 1475, 1274, 1190, 998, 780 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 1.6 Hz, 1 H), 7.46 (qd, *J* = 13.7, 7.8 Hz, 4 H), 7.09 (td, *J* = 8.4, 2.5 Hz, 1 H), 4.69 (s, 2 H), 2.43 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.05, 169.64, 163.13 (d, *J* = 244 Hz), 138.23, 137.30 (d, *J* = 8 Hz), 132.51, 130.33 (d, *J* = 8 Hz), 125.88, 124.17 (d, *J* = 3 Hz), 123.33, 122.24, 115.62 (d, *J* = 22 Hz), 115.11 (d, *J* = 21 Hz), 75.18, 20.90.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}FO_2$: 243.0822; found: 243.0824.

UV/Vis (EtOH): λ_{max} = 259, 348 nm.

Anal. Calcd for $C_{15}H_{11}FO_2$: C, 74.37; H, 4.58; F, 7.84. Found: C, 74.38; H, 4.59; F, 7.83.

7-([1,1′-Biphenyl]-4-yl)benzofuran-3(2*H*)-one (3r)

Yield: 238 mg (83%); yellow solid; mp 184.8–187.5 °C; R_f = 0.38 (PE–EtOAc, 5:1).

FT-IR (KBr): 2915, 1734, 1480, 1298, 1067, 997, 764 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.78 (m, 3 H), 7.74–7.70 (m, 2 H), 7.70–7.63 (m, 3 H), 7.47 (t, *J* = 7.5 Hz, 2 H), 7.41–7.36 (m, 1 H), 7.22 (t, *J* = 7.6 Hz, 1 H), 4.73 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.18, 171.40, 141.24, 140.76, 137.01, 134.01, 129.09, 129.01, 127.78, 127.63, 127.33, 123.28, 122.85, 122.15, 74.94.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{15}O_2$: 287.1073; found: 287.1075.

UV/Vis (EtOH): λ_{max} = 269, 344 nm.

Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.91; H, 4.95.

7-([1,1′-Biphenyl]-4-yl)-5-methylbenzofuran-3(2*H*)-one (3s)

Yield: 255 mg (85%); yellow solid; mp 152.8–154.4 °C; R_f = 0.34 (PE–EtOAc, 5:1).

FT-IR (KBr): 3034, 2923, 1719, 1480, 1257, 1029, 990, 842, 769 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.5 Hz, 2 H), 7.71 (d, *J* = 8.5 Hz, 2 H), 7.66–7.62 (m, 3 H), 7.47 (t, *J* = 7.5 Hz, 3 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 4.71 (s, 2 H), 2.44 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.30, 169.91, 141.11, 140.77, 138.25, 134.11, 132.46, 129.07, 128.96, 127.74, 127.58, 127.31, 126.79, 122.74, 122.11, 75.17, 20.95.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{17}O_2$: 301.1229; found: 301.1232.

UV/Vis (EtOH): λ_{max} = 274, 294, 343 nm.

Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.96; H, 5.38.

7-(2-Chlorophenyl)-5-methylbenzofuran-3(2*H*)-one (3x)

Yield: 225 mg (87%); yellow solid; mp 115.2–118.0 °C; R_f = 0.36 (PE–EtOAc, 5:1).

FT-IR (KBr): 2976, 2928, 1715, 1469, 1250, 1037, 996, 885, 764 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.49 (m, 2 H), 7.43 (d, *J* = 1.1 Hz, 1 H), 7.37 (ddd, *J* = 9.3, 5.8, 3.0 Hz, 3 H), 4.64 (s, 2 H), 2.42 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.13, 169.91, 140.10, 134.31, 133.74, 131.86, 131.76, 130.11, 129.81, 127.02, 125.31, 123.55, 121.60, 75.36, 20.85.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}ClO_2$: 259.0527; found: 259.0532.

UV/Vis (EtOH): λ_{max} = 343 nm.

Anal. Calcd for $C_{15}H_{11}ClO_2$: C, 69.64; H, 4.29; Cl, 13.70. Found: C, 69.67; H, 4.26; Cl, 13.73.

Acknowledgment

We are grateful for financial support from the Research Project of the Natural Science Foundation of Heilongjiang Province of China (No. B201208).

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380211.

References

(1) (a) Schoepfer, J.; Fretz, H.; Chaudhuri, B.; Muller, L.; Seeber, E.; Meijer, L.; Lozach, O.; Vangrevelinghe, E.; Furet, P. *J. Med. Chem.* **2002**, *45*, 1741. (b) Tehranchian, S.; Akbarzadeh, T.; Fazeli, R. M.; Jamalifar, H.; Shafiee, A. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 1023.

(2) (a) Bentley, W. K. In *The Isoquinoline Alkaloids*, Part 5, Vol. 1; Ravindranath, B., Ed.; Harwood Academic: Bangalore, **1998**, 93–106. (b) Castedo, L.; Suau, R. In *The Alkaloids*, Part 6, Vol. 29; Brossi, A., Ed.; Academic Press: Orlando, **1986**, 287–324.

(3) Gijsen, H. J. M.; Berthelot, D.; Zaja, M.; Brone, B.; Geuens, I.; Mercken, M. *J. Med. Chem.* **2010**, *53*, 7011.

(4) (a) Suau, R.; Lopez-Romero, J. M.; Rico, R.; Alonso, J. F.; Lobo, C. *Tetrahedron* **1996**, *52*, 11307. (b) Kithsiri Wijeratne, E. M.; Lesliebn Gunatilaka, A. A.; Kingston, D. G. I.; Haltiwanger, R. C.; Eggleston, D. S. *Tetrahedron* **1995**, *51*, 7877.

(5) Richey, N. R.; Yu, H. *Org. Process Res. Dev.* **2009**, *13*, 315.

(6) Olivera, R.; SanMartin, R.; Churruca, F.; Domínguez, E. *J. Org. Chem.* **2002**, *67*, 7215.

(7) (a) Zhou, G.; Zhu, J.; Xie, Z.; Li, Y. *Org. Lett.* **2008**, *10*, 721. (b) Hawkins, I.; Handy, S. T. *Tetrahedron* **2013**, *69*, 9200.

(8) (a) Hadj-esfandiari, N.; Navidpour, L.; Shadnia, H.; Amini, M.; Samadi, N.; Faramarzid, A. M.; Shafiee, A. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 6354. (b) Charrier, C.; Clarhaut, J.; Gesson, P. J.; Estiu, G.; Wiest, O.; Roche, J.; Bertrand, P. *J. Med. Chem.* **2009**, *52*, 3112.

(9) (a) Bandgar, R. B.; Patil, A. S.; Korbad, L. B.; Biradar, C. S.; Nile, N. S.; Khobragade, N. C. *Eur. J. Med. Chem.* **2010**, *45*, 3223. (b) Souard, F.; Okombi, S.; Beney, C.; Chevalley, S.; Valentin, A.; Boumendjel, A. *Bioorg. Med. Chem.* **2010**, *18*, 5724. (c) Haudecoeur, R.; Ahmed-Belkacem, A.; Yi, W.; Fortune, A.; Brillet, R.; Belle, C.; Nicolle, E.; Pallier, C.; Pawlotsky, M. J.; Boumendjel, A. *J. Med. Chem.* **2011**, *54*, 5395. (d) Shin, Y. S.; Shin, C. M.; Shin, S. J.; Lee, T. K.; Lee, S. Y. *Bioorg. Med. Chem. Lett.* **2011**, *21*, 4520. (e) Paduraru, P. M.; Wilson, D. P. *Org. Lett.* **2003**, *5*, 4911.

(10) (a) Moriarty, M. R.; Prakash, O.; Prakash, I. *J. Chem. Soc., Chem. Commun.* **1984**, 1342. (b) Fan, R.; Sun, Y.; Ye, Y. *Org. Lett.* **2009**, *11*, 5174.

(11) Amick, R. D. *J. Heterocycl. Chem.* **1975**, *12*, 1051.

(12) Alipour, M.; Khoobi, M.; Nadri, H.; Sakhteman, A.; Moradi, A.; Ghandi, M.; Shafiee, A. F. A. *Arch. Pharm.* **2013**, *346*, 577.

(13) Okombi, S.; Rival, D.; Bonnet, S.; Mariotte, M. A.; Perrier, E.; Boumendjel, A. *J. Med. Chem.* **2006**, *49*, 329.

(14) Amshumali, K. M.; Chavez, I.; Burgos, F.; Arancibia, V.; Manriquez, M. J.; Molins, E.; Roig, A. *J. Organomet. Chem.* **2005**, *690*, 1340.

(15) (a) Merour, Y. J.; Cossais, F. *J. Heterocycl. Chem.* **1991**, *28*, 1875. (b) Prakash, O.; Goyal, S. *Synthesis* **1992**, 629. (c) Khanna, S. M.; Garg, P. C.; Kapoor, P. R. *Synth. Commun.* **1992**, *22*, 2555. (d) Thakkar, K.; Cushman, M. *J. Org. Chem.* **1995**, *60*, 6499. (e) Beney, C.; Mariotte, M. A.; Boumendjel, A. *Heterocycles* **2001**, *55*, 967. (f) Diedrichs, N.; Ragot, P. J.; Thede, K. *Eur. J. Org. Chem.* **2005**, 1731.

(16) (a) Bandini, M.; Melloni, A.; Umani-Ronchi, A. *Angew. Chem. Int. Ed.* **2004**, *43*, 550; *Angew. Chem.* **2004**, *116*, 560. (b) Bandini, M.; Emer, E.; Tommasi, S.; Umani-Ronchi, A. *Eur. J. Org. Chem.* **2006**, 3527. (c) Gore, H. P. *Chem. Rev.* **1955**, *55*, 229.

(17) (a) Carmichael, D.; Floch, L. P.; Le Goff, X. F.; Piechaczyk, O.; Seeboth, N. *Chem. Eur. J.* **2010**, *16*, 14486. (b) Davis, C. M.; Groshens, J. T. *Synth. Commun.* **2011**, *41*, 255. (c) Kobayashi, S.; Iwamoto, S. *Tetrahedron Lett.* **1998**, *39*, 4697. (d) Murashige, R.; Hayashi, Y.; Ohmori, S.; Torii, A.; Aizu, Y.; Muto, Y.; Murai, Y.; Oda, Y.; Hashimoto, M. *Tetrahedron* **2011**, *67*, 641.

(18) (a) Pande, A. M.; Samant, D. S. *Synth. Commun.* **2011**, *41*, 754. (b) Bejblova, M.; Prochazkova, D.; Vlk, J. *Top. Catal.* **2009**, *52*, 178. (c) Selvin, R.; Hsu, L. H.; Her, M. T. *Catal. Commun.* **2008**, *10*, 169. (d) Derouane, G. E.; Schmidt, I.; Lachas, H.; Christensen, C. J. H. *Catal. Lett.* **2004**, *95*, 13.

(19) (a) Babu, A. S.; Yasuda, M.; Baba, A. *Org. Lett.* **2007**, *9*, 405. (b) Ranu, C. B.; Ghosh, K.; Jana, U. *J. Org. Chem.* **1996**, *61*, 9546. (c) Aiello, F.; Garofalo, A.; Grande, F. *Tetrahedron Lett.* **2010**, *51*, 6635. (d) Boroujeni, P. K.; Parvanak, K. *J. Serb. Chem. Soc.* **2011**, *76*, 155. (e) Li, J.; Jin, C.; Su, K. W. *Heterocycles* **2010**, *81*, 2555. (f) Boroujeni, P. K. *Chin. Chem. Lett.* **2010**, *21*, 1395.
(20) Kangani, C. O.; Day, W. B. *Org. Lett.* **2008**, *10*, 2645.
(21) Chassaing, S.; Kumarraja, M.; Pale, P.; Sommer, J. *Org. Lett.* **2007**, *9*, 3889.
(22) (a) Leng, W.; Zhou, X. S.; You, B.; Wu, M. L. *Langmuir* **2010**, *26*, 17836. (b) Usachev, A. S.; Usachev, I. B.; Sosnovskikh, Y. V. *Tetrahedron* **2014**, *70*, 60.
(23) Manjulatha, K.; Srinivas, S.; Mulakayala, N.; Rambabu, D.; Prabhakar, M.; Arunasree, M. K.; Alvala, M.; Basaveswara Rao, M. V. *Bioorg. Med. Chem. Lett.* **2012**, *22*, 6160.
(24) Zewge, D.; Chen, Y. C.; Deer, C.; Dormer, G. P.; Hughes, L. D. *J. Org. Chem.* **2007**, *72*, 4276.
(25) (a) Smyth, P. T.; Corby, W. B. *J. Org. Chem.* **1998**, *63*, 8946. (b) Wilkinson, C. M. *Org. Lett.* **2011**, *13*, 2232. (c) Yonezawa, N.; Hino, T.; Matsuda, K.; Matsuki, T.; Narushima, D.; Kobayashi, M.; Ikeda, T. *J. Org. Chem.* **2000**, *65*, 941. (d) Sharma, K. A.; Subramani, V. A.; Gorman, B. C. *Tetrahedron* **2007**, *63*, 389. (e) Surya Prakash, G. K.; Yan, P.; Torok, B.; Olah, G. A. *Catal. Lett.* **2003**, *87*, 109.