RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2014, **4**, 39020

Biomass-involved, facile and one-pot synthesis of *N*-aryl-2(3*H*)-benzoxazolones from methyl 3-dehydroshikimiate†

Ensheng Zhang,[ad] Xuejing Zhang,[b] Yuchen Cai,[b] Dejian Wang,[ad] Tianlong Xu,[ad] Jun Li,[c] Ming Yan[b] and Yong Zou*[ab]

Received 2nd July 2014
Accepted 14th August 2014

DOI: 10.1039/c4ra08233h

www.rsc.org/advances

A facile and one-pot method for the synthesis of *N*-aryl-2(3*H*)-benzoxazolones *via* microwave-assisted consecutive reactions between the biomass-derived methyl 3-dehydroshikimiate (3-MDHS), anilines and bis(trichloromethyl) carbonate (BTC) is reported. The protocol includes the efficient generation of the platform compounds *N*-arylated 2-aminophenols, followed by the smooth annulation reaction induced by BTC. This sequential process represents a metal-free, sustainable and functional group compatible method for the rapid construction of *N*-aryl-2(3*H*)-benzoxazolones.

Introduction

The 2(3*H*)-benzoxazolone scaffold represents an important privileged structure ubiquitously found in pharmaceuticals, agrochemicals and bioactive compounds. For example, the antipyretic analgesic chlorzoxazone,[1] the insecticide and acaricide phosalone,[2] the PPAR α/γ dual agonists[3] and the $P2X_3$ receptor antagonist[4] are all characterized by the 2(3*H*)-benzoxazolone core structure (Fig. 1). Accordingly, considerable efforts have been devoted to the preparation of 2(3*H*)-benzoxazolones and many effective methods have been reported.[5] Compared to the formation of *N*-unsubstituted 2(3*H*)-benzoxazolones, the construction of *N*-aryl-2(3*H*)-benzoxazolones is far less explored. Generally, method for the assembly of *N*-aryl-2(3*H*)-benzoxazolone motif involved the Diels–Alder reaction between exo-2-oxazolidinone dienes and acrolein followed by dehydrogenation using DDQ.[6] Chen's method based upon the Ullmann coupling reaction between 2(3*H*)-benzoxazolones and aryl halide was also effective and workable[4] (Scheme 1). However, these methods still suffer from multi-step sequences, harsh reaction conditions, long reaction times, as well as the necessity of transition metal-catalysts and the difficulty in obtaining starting materials in most cases. In addition, to the best of our knowledge, petroleum-based starting materials, but not biomass-derived substrates were used in the abovementioned methods. In this context, an alternative method that is facile, compatible and could make use of biomass-derived feedstock for the assembly of *N*-aryl-2(3*H*)-benzoxazolones would be genuinely attractive (Scheme 1).

In the past few years, cyclohexanones, cyclohexenones or polyhydroxylated cyclohexenones have been demonstrated to be intriguing precursors for the construction of various aromatics such as arylamines,[7] 2-aminobenzothiazoles,[8] protocatechuic acid,[9] hydroquinone,[10] catechol,[11] gallic acid,[12] and *N*-arylated amino acid derivatives.[13] This novel aliphatic to aromatic strategy is widely applicable due to the thermodynamically favourable and readily occurred dehydrogenation and/or dehydration process that lead to the formation of aromatics from cyclohexanone or polyhydroxylated cyclohexanone framework under mild conditions. Our previous studies have shown that the abundantly available bio-feedstock shikimic acid could be easily transformed into methyl 3-dehydroshikimiate (3-MDHS, **1**),

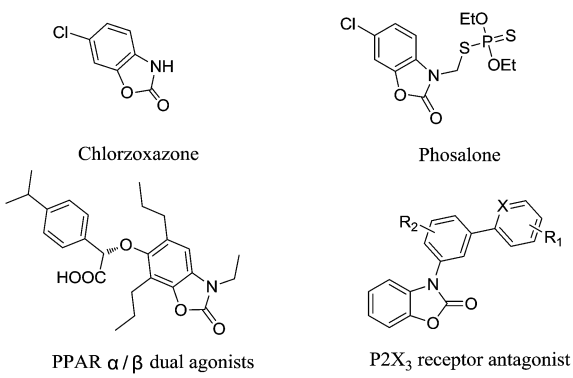


Fig. 1 Examples of biologically important 2(3*H*)-benzoxazolones.

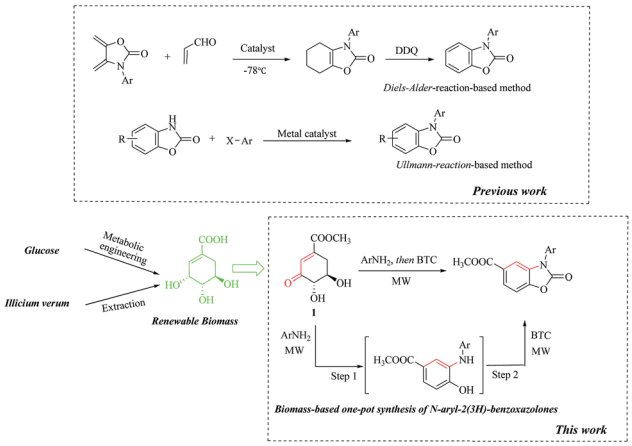
[a]*Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, P. R. China. E-mail: zou_jinan@163.com; Fax: +86 (20)85231119; Tel: +86 (20) 85231309*

[b]*School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou 510006, P. R. China. E-mail: zou_jinan@163.com*

[c]*Second Affiliated Hospital, College of Medicine, Zhejiang University, Zhejiang 310009, P. R. China*

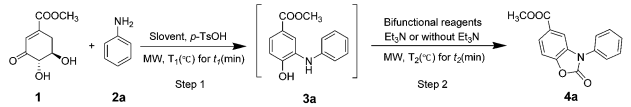
[d]*University of Chinese Academy of Sciences, Beijing 100039, P. R. China*

† Electronic supplementary information (ESI) available: See DOI: 10.1039/c4ra08233h



Scheme 1 Strategies for the construction of *N*-aryl-2(3*H*)-benzoxazolones.

Table 1 Screening of reaction conditions[a]



Entry	Solvent	Base	T_1/T_2 (°C)	t_1/t_2[b] (min)	Yield[c] (%)
1	CCl_4	Et_3N	76/rt	50/90	68
2	$CHCl_3$	Et_3N	60/rt	60/90	75
3	DMF	Et_3N	110/rt	6/120	Trace
4	DMSO	Et_3N	110/rt	6/120	Trace
5	NMP	Et_3N	110/rt	6/120	Trace
6	EtOH	Et_3N	78/rt	30/120	ND[d]
7	MeOH	Et_3N	65/rt	35/120	ND[d]
8	Dioxane	Et_3N	100/rt	20/120	78
9	CH_3CN	Et_3N	80/rt	15/90	89
10	CH_3CN	—	80/rt	15/90	Trace
11	CH_3CN	—	80/50	15/25	72
12	CH_3CN	—	80/80	15/5	92[e]
13	CH_3CN	Et_3N	80/80	15/5	78
14	CH_3CN	—	80/80	15/30	Trace[f]
15	CH_3CN	—	80/80	15/30	Trace[g]
16	CH_3CN	—	80/80	15/5	68[h]
17	CH_3CN	—	80/80	15/5	76[i]
18	CH_3CN	—	80/80	15/5	92[j]

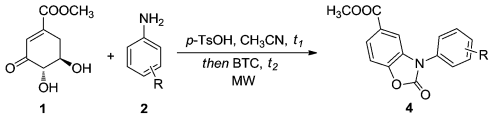
[a] Reaction conditions: **1** (0.19 g, 1.0 mmol), **2a** (1.0 mmol), *p*-TsOH (0.05 mmol), solvent (5.0 ml), BTC (1.5 mmol, added in step 2) with or without Et_3N (6.0 mmol). [b] The ramp time (0.5 min) is included as part of the reaction time. [c] Isolated yield. [d] Not detected, only intermediate **3a** was obtained. [e] Reaction conditions: **1** (0.19 g, 1.0 mmol), **2a** (1.0 mmol), *p*-TsOH (0.05 mmol), CH_3CN (5.0 ml) and BTC (1.5 mmol, added in step 2) under microwave condition. After completion, the reaction mixture was treated with aqueous Na_2CO_3 to afford the final product **4a**. [f] Urea was used as the bifunctional reagent for step 2. [g] Diethyl carbonate was used as the bifunctional reagent for step 2. [h] 0.5 mmol BTC was used. [i] 1.0 mmol BTC was used. [j] 2.0 mmol BTC was used.

subsequent consecutive reaction would then be conducted to afford *N*-arylated 2-aminophenols, a class of functionalized platform compounds with great potential for further transformation.[14] From green and sustainable chemistry perspective, the more protocols the biorenewable sources can be utilized and transformed, the less dependent on fossil-oil the human society will be.[15] And, the construction of a highly branched "family tree" is also very imperative for a certain platform compound.[16] Bearing this in mind and in continuation of our study for the development of new strategies and practical technologies for biomass conversion,[13,14] we herein describe a one-pot and metal-free protocol for the efficient and rapid synthesis of biologically important *N*-aryl-2(3*H*)-benzoxazolones from 3-MDHS, anilines and bis(trichloromethyl) carbonate (BTC).

Results and discussion

Initially, 3-MDHS (**1**), aniline (**2a**) and bis(trichloromethyl) carbonate (BTC, as the bifunctional reagent) were chosen as model substrates to screen the optimal reaction conditions in terms of solvent, catalyst and reaction temperature. Solvent screening was carried out by using *p*-TsOH as the catalyst for step 1 under microwave irradiation and Et_3N as the base for step 2 at room temperature (Table 1, entries 1–9). It would be evident from Table 1 that the identity of solvents was crucial for the overall yield of this consecutive reaction. For example, only moderate yields (68% and 75%, respectively) can be obtained when the reaction was carried out in nonpolar solvents such as CCl_4 and $CHCl_3$ (Table 1, entries 1 and 2), which can be contributed to the low conversion to **3a** in step 1 in these solvents (monitored by TLC). Polar solvents such as DMSO, DMF, NMP, ethanol, methanol, dioxane and CH_3CN were also screened. We have found that, although high conversion to intermediate **3a** was readily achieved in DMSO, DMF and NMP (monitored by TLC), only trace amount of the desired product **4a** was obtained in the final reaction step (Table 1, entries 3–5). To our delight, CH_3CN proved to be an excellent medium for both step 1 and step 2, affording **4a** in 89% isolated yield (Table 1, entry 9). Moreover, no desired product was detected when the consecutive reaction was carried out in protic solvents such as ethanol and methanol, although they have been previously shown to be excellent solvents for the preparation of intermediate **3a**.[14] This might be due to the competing side reaction between hydroxyl group and BTC (Table 1, entries 6 and 7). Subsequently, the effect of base and temperature on step 2 were also studied by using CH_3CN as the optimized solvent. The result showed that the desired product **4a** was obtained in an excellent yield (92%) when BTC (1.5 equiv) was added into the reaction mixture of step 1, and reacted in reflux in absence of Et_3N under microwave irradiation (Table 1, entry 12). It is noteworthy that, under this condition, the desired products **4a** could readily be obtained in pure form from the reaction mixture by simply treating with aqueous Na_2CO_3, thus leading to a more convenient procedure. Investigation on the different amounts of BTC revealed that 1.5 equiv was the most optimal for this reaction, whereas 0.5 equiv and 1.0 equiv of BTC afforded lower yields (68% and 76%, respectively, entries 16 and 17), and no significant improvement in the yield when increasing the amount of BTC to 2.0 equiv (Table 1, entry 18). In

Table 2 Scope of the reaction[a]



1 2 4

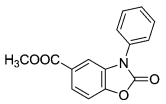
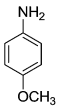
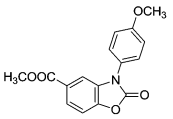
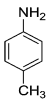
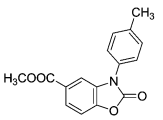
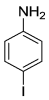
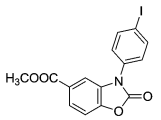
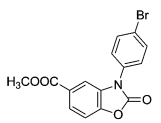
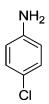
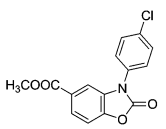
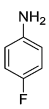
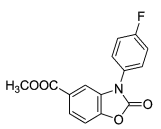
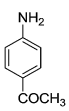
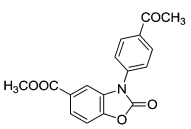
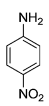
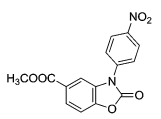
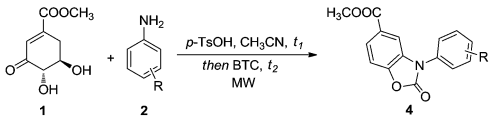
Entry	Arylamine	t_1/t_2[b] (min)	Product	Yield[c] (%)
1	 **2a**	15/5	 **4a**	92
2	 **2b**	13/3	 **4b**	95
3	 **2c**	12/3	 **4c**	93
4	 **2d**	15/5	 **4d**	87
5	 **2e**	20/6	 **4e**	87
6	 **2f**	20/6	 **4f**	85
7	 **2g**	20/10	 **4g**	79
8	 **2h**	20/8	 **4h**	83
9	 **2i**	20/10	 **4i**	80

Table 2 (*Contd.*)



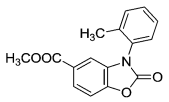
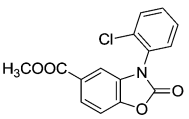
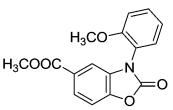
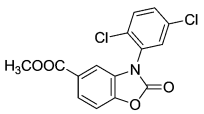
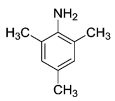
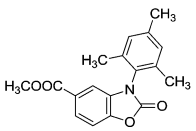
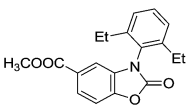
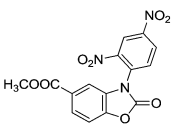
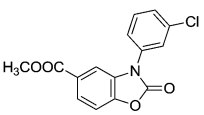
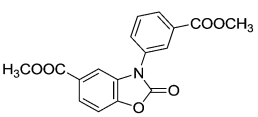
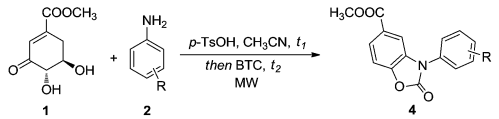
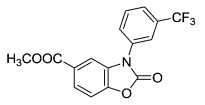
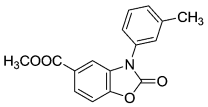
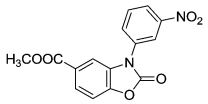
Entry	Arylamine	t_1/t_2[b] (min)	Product	Yield[c] (%)
10	 **2j**	15/10	 **4j**	89
11	 **2k**	20/10	 **4k**	76
12	 **2l**	20/10	 **4l**	90
13	 **2m**	20/10	 **4m**	69
14	 **2n**	25/10	 **4n**	67[d]
15	 **2o**	25/10	 **4o**	60[d]
16	 **2p**	—/—	 **4p**	ND[e]
17	 **2q**	20/8	 **4q**	84
18	 **2r**	25/10	 **4r**	76

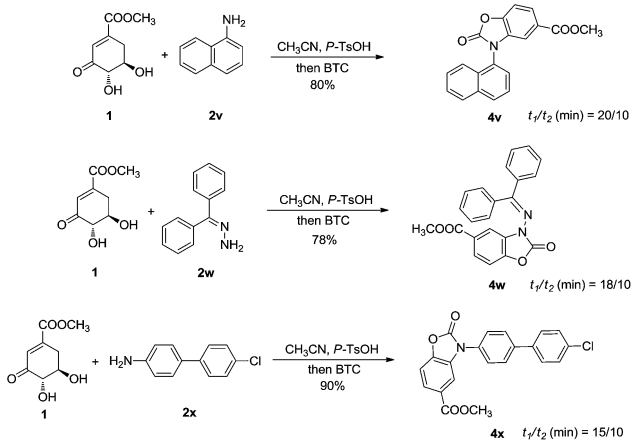
Table 2 (*Contd.*)



1 2 4

Entry	Arylamine	t_1/t_2[b] (min)	Product	Yield[c] (%)
19	 **2s**	25/10	 **4s**	75
20	 **2t**	15/5	 **4t**	93
21	 **2u**	20/10	 **4u**	82

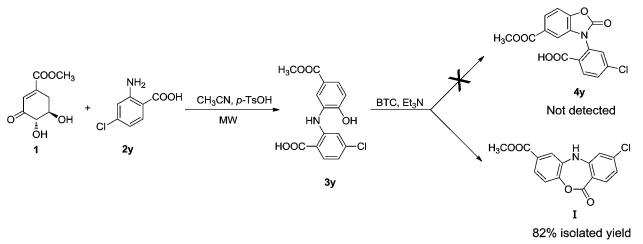
[a] Unless otherwise specified, all reactions were carried out using: 3-MDHS (0.19 g, 1.0 mmol), arylamine (1.0 mmol), *p*-TsOH (0.05 mmol), CH_3CN (5.0 ml), BTC (1.5 mmol) under microwave condition, after completion, the reaction mixture was treated with aqueous Na_2CO_3 to afford the final product **4**. [b] The ramp time (0.5 min) is included as part of the reaction time. [c] Isolated yield. [d] Purified by column chromatography (silica gel, 200–300 mesh). [e] ND: not detected.



Scheme 2 Consecutive reaction of 3-MDHS, BTC with 1-naphthylamine, 4-chloroxenylamine and benzophenone hydrazone (t_1 for step 1 and t_2 for step 2).

addition, other bifunctional carbonylic reagents such as urea and diethyl carbonate[17] were also tested in step 2, but only trace amount of the desired product was detected (Table 1, entries 14 and 15). Therefore, we considered that the optimized reaction conditions consist of: 3-MDHS (1.0 mmol), arylamine (1.0 mmol) in CH_3CN (5 ml) using *p*-TsOH (0.05 mmol) as the catalyst for step 1, and BTC (1.5 mmol) as the bifunctional reagent for step 2 both under microwave conditions with reflux (Table 1, entry 12).

Having established the optimized conditions, we examined the scope of the process using various substituted anilines which bear different electronic and steric properties. In general, moderate to excellent yields of *N*-aryl-2(3*H*)-benzoxazolones were readily obtained (Table 2). It is apparent that the reactivity of the anilines with an electron-donating group such as Me, OMe (Table 2, entries 2 and 3) is higher than anilines possessing an electron-withdrawing group such as COMe, NO_2, CO_2Me (Table 2, entries 8, 9 and 18). For example, the consecutive reaction of 4-methylaniline (**2c**), 3-MDHS and BTC in CH_3CN gave rise to the corresponding product **4c** in 93% isolated yield (Table 2, entry 3), whereas only a moderate yield (76%) of product **4r** was obtained when methyl 3-aminobenzoate (**2r**) was used as the substrate (Table 2, entry 18). In addition, neither the desired product nor the corresponding intermediate was detected when 2,4-dinitroaniline (**2p**) was used as the substrate (Table 2, entry 16), which may be due to the reduced nucleophilicity of the amino group. Halogen-substituted anilines were also subjected to the optimized reaction conditions and were found to be efficiently transformed into the corresponding *N*-aryl-2(3*H*)-benzo-xazolones (Table 2, entries 4–7, 11, 13 and 17). It could be concluded that the reactivity of 4-fluoroaniline (**2g**)



Scheme 3 BTC catalyzed facile synthesis of 3-chloro-7-methoxycarbonyl dibenz[*b*,*e*][1,4]oxazepin-11(5*H*)-one.

was slightly lower as compared with the 4-bromoaniline (**2e**) or 4-iodoaniline (**2d**) (Table 2, entries 4, 5 and 7). It is worth noting that all these halogen-substituted *N*-aryl-2(3*H*)-benzoxazolones can be easily functionalized or transformed, thus making them wonderful synthons for further transformation. Despite the steric hindrance of the *ortho*-substituent arylamines, the corresponding *N*-aryl-2(3*H*)-benzoxazolones could smoothly be obtained in moderate to good yields (Table 2, entries 10–15). For instance, products **4j**, **4k** were isolated in satisfying yields (89% and 76%, respectively) when 2-methylaniline (**2j**) and 2-cholroanilne (**2k**) were subjected to the optimized reaction conditions. To our delight, it has been demonstrated that this protocol was also applicable to polycyclic or pseudo arylamines. As shown in Scheme 2, 1-naphthylamine (**2v**), benzophenone hydrazone (**2w**) and 4-chloroxenylamine (**2x**) performed smoothly in this consecutive reaction to afford the corresponding *N*-aryl-2(3*H*)-benzoxazolones (**4v**, **4w** and **4x**, respectively) in good to excellent yields. It is worth mentioning that the compound **4x** may be regarded as a close analogue of the recently reported $P2X_3$ receptor antagonist.[4]

Notably, when 2-amino-4-chlorobenzoic acid (**2y**), 3-MDHS and BTC were subjected to this one-pot, two-step conditions, an unexpected but interesting result was obtained with the isolation of 3-chloro-7-methoxycarbonyl-dibenz[b,e][1,4]-oxazepin-11(5*H*)-one (**I**) as the sole product, but not 5-methoxycarbonyl-3-(5-chloro-2-carboxylphenyl)-2(3*H*)-benzox-azolone (**4y**). As shown in Scheme 3, the reaction of 2-amino-4-chlorobenzoic acid (**2y**) and 3-MDHS in step 1 gave a highly functionalized intermediate **3y**, which bears an adjacent carboxyl group as well as a phenolic hydroxyl group, thus facilitating the lactonization under the catalysis of BTC to afford 3-chloro-7-methoxycarbonyl-dibenz[b,e]-[1,4]-oxazepin-11(5*H*)-one (**I**) in 82% isolated yield.

Conclusion

In summary, a facile and efficient protocol for the one-pot construction of *N*-aryl-2(3*H*)-benzoxazolones from the biomass-derived substrate 3-MDHS (**1**) *via* the *N*-arylated 2-aminophenol intermediates under microwave condition has been established. A wide range of *N*-aryl-2(3*H*)-benzoxazolones have been smoothly synthesized in moderate to excellent yields *via* the sequential C–N bond-forming, aromatization and annulation reactions between 3-MDHS, anilines and BTC. The metal-free reaction conditions, the short reaction times, the operational simplicity, as well as the broad substrate scope are the attractive aspects of this methodology, thus representing an excellent alternative to the former Diels–Alder- or Ullmann-reaction-based methods. Besides, this consecutive reaction can also be extended to the synthesis of a novel dibenz[*b*,*e*][1,4]oxazepin-11-(5*H*)-one motif. Further investigations to develop this and our previously reported protocols into practical applications for the synthesis of various benzo-fused nitrogen-containing heterocycles from 3-MDHS are underway in our laboratory.

Experimental section

General

(−)-Methyl 3-dehydroshikimate was readily prepared from (−)-shikimic acid according to the ref. 14 (see the ESI† for details). Unless special notice, all the other reagents were obtained commercially and used without further purification. Reactions were monitored by TLC and column chromatography was performed on silica gel (200–300 mesh) using the EtOAc–PE system as eluent (PE, 60–90 °C). The reaction temperatures were detected in real time using an infrared thermometer and the ramp time (approximate 0.5 min) is included as part of the reaction time. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz) using CD_3COCD_3 or DMSO-d_6 as the solvent. Chemical shifts were reported in parts per million (ppm) and are calibrated using residual undeuterated solvent as an internal reference. HRMS spectra analyses were carried out on a LC-Q-TOF (ESI) apparatus. Mass spectrometry were measured on a Shimadzu GC-MS QP5050A in electron ionization mode. Melting points were measured on a Thiele apparatus and were uncorrected. All the microwave reactions were carried out in a monomode scientific microwave reactor with a condenser under atmosphere pressure.

General procedure for the syntheses of *N*-aryl-2(3*H*)-benzoxazolones (4a–4x)

To a solution of 3-MDHS (0.19 g, 1.0 mmol), arylamine (1.0 mmol) in CH_3CN (5 mL) was added *p*-TsOH (0.05 mmol). The flask was then placed into the microwave reactor and the mixture was irradiated (240 W) with stirring for indicated minutes (t_1). Then, BTC (1.5 mmol) was added and the result mixture was irradiated (240 W) for the indicated minutes (t_2). After completion (as monitored by TLC), the reaction mixture was poured into sodium carbonate solution (50 mL, 5%) and stirred vigorously, the resulting solid was filtered and dried to furnish the desired product in pure form. The isolated products could be further purified by recrystallization from EtOAc–PE or by column chromatography using EtOAc–PE as eluent if necessary.

5-Methoxycarbonyl-3-phenyl-2(3*H*)-benzoxazolone (4a). White flake crystal; yield: 0.25 g (92%); mp 138–140 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.85 (dd, J = 8.6, 1.6 Hz, 1H), 7.63 (d, J = 4.0 Hz, 4H), 7.57 (d, J = 8.4 Hz, 1H), 7.53 (m, 1H), 7.44 (d, J = 1.6 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C=O), 152.3 (C=O), 145.6, 132.8, 131.7, 129.9, 128.8, 125.8, 125.5, 124.9, 110.2, 109.2, 52.3; IR (KBr) ν_{max}/cm^{-1} 3050,

2988, 2950, 1777, 1709, 1620, 1596, 1505, 1467, 1380, 1284, 1246, 761, 691; MS (EI): *m*/*z* (%) = 269 ([M]$^+$, 100), 238 ([M − OCH_3]$^+$, 94), 210 ([M − $COOCH_3$]$^+$, 15), 194 (18), 166 (16); HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}NO_4$: 270.0761; found: 270.0763.

5-Methoxycarbonyl-3-(4-methoxyphenyl)-2(3*H*)-benzoxazolone (4b). White crystal; yield: 0.28 g (95%); mp 124–126 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.84 (dd, J = 8.4, 1.6 Hz, 1H), 7.54–7.57 (m, 3H), 7.36 (d, J = 1.6 Hz, 1H), 7.16 (dd, J = 6.8, 2.0 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.5 (C═O), 159.4 (C═O), 152.6, 145.5, 132.3, 127.6, 125.5, 125.1, 124.7, 115.1, 110.1, 109.1, 55.5, 52.3; MS (EI): *m*/*z* (%) = 299 ([M]$^+$, 100), 284 ([M − CH_3]$^+$, 7), 268 ([M − OCH_3]$^+$, 18), 240 ([M − $COOCH_3$]$^+$, 14), 196 (7); HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{14}NO_5$: 300.0866; found: 300.0874.

5-Methoxycarbonyl-3-(4-methylphenyl)-2(3*H*)-benzoxazolone (4c). White acicular crystal; yield: 0.26 g (93%); mp 147–149 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.85 (dd, J = 8.4, 1.6 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 1.6 Hz, 1H), 3.81 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C═O), 152.4 (C═O), 145.5, 138.6, 131.9, 130.3, 130.1, 125.7, 125.5, 124.8, 110.1, 109.2, 52.3, 20.7; IR (KBr) ν_{max}/cm^{-1} 3120, 3095, 3002, 2954, 2924, 1780, 1733, 1609, 1521, 1490, 1452, 1388, 1289, 1248, 835; MS (EI): *m*/*z* (%) = 283 ([M]$^+$, 100), 252 ([M − OCH_3]$^+$, 48), 224 ([M − $COOCH_3$]$^+$, 6), 180 (18), 152 (4); HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{14}NO_4$: 284.0917; found: 284.0921.

3-(4-Iodophenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (4d). Grey solid; yield: 0.34 g (87%); mp 169–171 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.00 (d, J = 8.4 Hz, 2H), 7.86 (dd, J = 8.4, 1.6 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 1.6 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C═O), 152.1 (C═O), 145.6, 138.7, 132.6, 131.3, 127.8, 125.5, 125.0, 110.2, 109.3, 94.7, 52.3; IR (KBr) ν_{max}/cm^{-1} 3112, 3083, 3059, 2964, 1776, 1713, 1618, 1497, 1458, 1422, 1382, 1290, 1250, 1199, 1004, 824; MS (EI): *m*/*z* (%) = 395 ([M]$^+$, 100), 364 ([M − OCH_3]$^+$, 38), 182 (16), 153 (13); HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}INO_4$: 395.9727; found: 395.9730.

3-(4-Bromophenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (4e). White solid; yield: 0.30 g (87%); mp 168–170 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.83–7.88 (m, 3H), 7.62 (dd, J = 6.8, 2.0 Hz, 2H), 7.58 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C═O), 152.1 (C═O), 145.5, 132.9, 132.1, 131.4, 127.9, 125.6, 125.0, 121.6, 110.2, 109.3, 52.3; IR (KBr) ν_{max}/cm^{-1} 3102, 3069, 2992, 2838, 1776, 1727, 1619, 1498, 1459, 1401, 1382, 1281, 1237, 1149, 1005, 829; MS (EI): *m*/*z* (%) = 349 ([M + 2]$^+$, 94), 347 ([M]$^+$, 100), 318 (53), 316 ([M − OCH_3]$^+$, 55); HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}Br^{79}NO_4$: 347.9866; found: 347.9862.

3-(4-Chlorophenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (4f). White acicular crystal; yield: 0.26 g (85%); mp 144–146 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.86 (dd, J = 8.4, 1.6 Hz, 1H), 7.66–7.72 (m, 4H), 7.57 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C═O), 152.1 (C═O), 145.5, 133.2, 131.7, 131.4, 129.9, 127.6, 125.5, 125.0, 110.2, 109.3, 52.3; IR (KBr) ν_{max}/cm^{-1} 3096, 3057, 2994, 2946, 2888, 2839, 1781, 1710, 1623, 1502, 1460, 1434, 1409, 1385, 1284, 1242, 1107, 1006, 837; MS(EI): *m*/*z* (%) = 305 ([M + 2]$^+$, 33), 303 ([M]$^+$, 100), 272 ([M − OCH_3]$^+$, 62), 244 ([M − $COOCH_3$]$^+$, 11); HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}Cl^{35}NO_4$: 304.0371; found: 304.0364.

3-(4-Fluorophenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (4g). White solid; yield: 0.23 g (79%); mp > 200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.86 (dd, J = 8.4, 1.6 Hz, 1H), 7.69–7.73 (m, 2H), 7.58 (d, J = 8.4 Hz, 1H), 7.46–7.50 (m, 2H), 7.41 (d, J = 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C═O), 162.8 (d, $^1J_{CF}$ = 244.7 Hz), 152.4, 145.5, 131.8, 129.0 (d, $^4J_{CF}$ = 2.6 Hz), 128.5 (d, $^3J_{CF}$ = 9.0 Hz), 125.5, 124.9, 116.9 (d, $^2J_{CF}$ = 23.0 Hz), 110.1, 109.1, 52.3; IR (KBr) ν_{max}/cm^{-1} 3064, 2997, 2953, 2845, 1782, 1707, 1624, 1514, 1459, 1420, 1384, 1285, 1249, 1103, 1008, 844, 765; MS (EI): *m*/*z* (%) = 287 ([M]$^+$, 100), 256 ([M − OCH_3]$^+$, 73), 228 ([M − $COOCH_3$]$^+$, 11), 212 (17); HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}FNO_4$: 288.0667; found: 288.0660.

3-(4-Acetylphenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (4h). Gray solid; yield: 0.26 g (83%); mp > 200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.19 (d, J = 8.4 Hz, 2H), 7.88 (dd, J = 8.4, 1.2 Hz, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 1.2 Hz, 1H), 3.82 (s, 3H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 197.1 (C═O), 165.4 (C═O), 152.0 (C═O), 145.6, 136.8, 136.4, 131.1, 129.8, 125.6, 125.4, 125.2, 110.3, 109.5, 52.4, 26.8; IR (KBr) ν_{max}/cm^{-1} 3012, 2961, 2857, 1778, 1711, 1678, 1600, 1514, 1490, 1451, 1380, 1294, 1264, 1091, 1006, 844, 766; MS (EI): *m*/*z* (%) = 311 ([M]$^+$, 54), 296 ([M − CH_3]$^+$, 100), 280 ([M − OCH_3]$^+$, 12); HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{14}NO_5$: 312.0866; found: 312.0864.

5-Methoxycarbonyl-3-(4-nitrophenyl)-2(3*H*)-benzoxazolone (4i). Yellow solid; yield: 0.25 g (80%); mp > 200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.48 (dd, J = 6.8, 2.0 Hz, 2H), 7.96 (dd, J = 6.8, 2.0 Hz, 2H), 7.90 (dd, J = 8.4, 1.6 Hz, 1H), 7.64 (d, J = 1.6 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C═O), 151.8 (C═O), 146.5, 145.7, 138.6, 130.7, 126.2, 125.7, 125.5, 125.2, 110.4, 109.7, 52.4; IR (KBr) ν_{max}/cm^{-1} 3122, 3084, 3062, 3003, 2950, 2840, 1788, 1727, 1596, 1523, 1503, 1455, 1380, 1314, 1288, 1263, 1148, 1006, 830, 761; MS (EI): *m*/*z* (%) = 314 ([M]$^+$, 100), 283 ([M − OCH_3]$^+$, 94), 255 ([M − $COOCH_3$]$^+$, 6); HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{10}N_2NaO_6$: 337.0431; found: 337.0432.

5-Methoxycarbonyl-3-(2-methylphenyl)-2(3*H*)-benzoxazolone (4j). White solid; yield: 0.25 g (89%); mp 138–140 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.86 (dd, J = 8.4, 1.6 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.50–7.55 (m, 3H), 7.42–7.46 (m, 1H), 7.13 (d, J = 1.6 Hz, 1H), 3.79 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C═O), 152.1 (C═O), 145.8, 136.0, 132.1, 131.6, 131.0, 130.1, 128.1, 127.6, 125.7, 124.9, 110.3, 109.1, 52.3, 17.0; IR (KBr) ν_{max}/cm^{-1} 3116, 3084, 3056, 3001, 2955, 1777, 1720, 1620, 1499, 1450, 1378, 1354, 1288, 1247, 1145, 1089, 998, 761; MS (EI): *m*/*z* (%) = 283 ([M]$^+$, 100), 252 ([M − OCH_3]$^+$, 32), 224 ([M − $COOCH_3$]$^+$, 5); HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{14}NO_4$: 284.0917; found: 284.0920.

3-(2-Chlorophenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (4k). White solid; yield: 0.23 g (76%); mp 152–154 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.88 (dd, J = 8.4, 1.6 Hz, 1H), 7.80–7.85 (m, 2H), 7.60–7.69 (m, 3H), 7.19 (d, J = 1.2 Hz, 1H), 3.79

(s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.3 (C═O), 151.8 (C═O), 145.6, 132.0, 131.6, 131.5, 130.8, 130.6, 129.6, 129.1, 125.8, 125.2, 110.5, 109.3, 52.3; IR (KBr) ν_{max}/cm^{-1} 3070, 2954, 1782, 1715, 1620, 1587, 1499, 1458, 1382, 1283, 1248, 1091, 1001, 956, 761; MS (EI): *m*/*z* (%) = 305 ([M + 2]$^+$, 33), 303 ([M]$^+$, 100), 272 ([M − OCH_3]$^+$, 80), 244 ([M − $COOCH_3$]$^+$, 12); HRMS: (ESI-TOF) *m*/*z* [M + H]$^+$ calcd. for $C_{15}H_{11}Cl^{35}NO_4$: 304.0371; found: 304.0364.

5-Methoxycarbonyl-3-(2-methoxyphenyl)-2(3*H*)-benzoxazolone (4l). White acicular crystal; yield: 0.27 g (90%); mp 164–166 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 7.84 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.56–7.60 (m, 3H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.14–7.19 (m, 2H), 3.79 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.7 (C═O), 155.1 (C═O), 152.6, 145.8, 132.3, 131.8, 129.5, 125.9, 125.1, 121.4, 120.4, 113.3, 110.4, 109.7, 56.2, 52.6; IR (KBr) ν_{max}/cm^{-1} 3139, 3081, 3023, 2979, 2956, 2834, 1781, 1731, 1618, 1599, 1510, 1490, 1380, 1289, 1250, 1095, 1019, 759, 743; MS (EI): *m*/*z* (%) = 299 ([M]$^+$, 100), 268 ([M − OCH_3]$^+$, 22), 240 ([M − $COOCH_3$]$^+$, 8); HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{14}NO_5$: 300.0866; found: 300.0872.

5-Methoxycarbonyl-3-(2,5-dichlorophenyl)-2(3*H*)-benzoxazolone (4m). White solid; yield: 0.23 g (69%); mp 182–184 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.04 (d, *J* = 2.4 Hz, 1H), 7.88 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.76 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 1.6 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.3 (C═O), 151.7 (C═O), 145.5, 132.8, 132.1, 132.0, 131.2, 130.9, 130.7, 130.6, 125.9, 125.4, 110.5, 109.7, 52.4; IR (KBr) ν_{max}/cm^{-1} 3121, 3095, 3036, 2997, 2953, 2846, 1770, 1722, 1617, 1568, 1492, 1453, 1409, 1362, 1287, 1253, 1196, 1150, 1100, 1006, 765, 717; MS (EI): *m*/*z* (%) = 341 ([M + 4]$^+$, 12), 339 ([M + 2]$^+$, 69), 337 ([M]$^+$, 100), 306 ([M − OCH_3]$^+$, 82), 278 ([M − $COOCH_3$]$^+$, 4); HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{10}Cl_2{}^{35}NO_4$: 337.9981; found: 337.9976.

5-Methoxycarbonyl-3-(2,4,6-trimethylphenyl)-2(3*H*)-benzoxazolone (4n). White solid; yield: 0.21 g (67%); mp 164–166 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.47 (d, *J* = 8.2 Hz, 1H) 7.25 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.98 (s, 2H), 6.60 (d, *J* = 2.0 Hz, 1H), 3.71 (s, 3H), 2.26 (s, 3H), 2.04 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.9 (C═O), 151.2 (C═O), 140.5, 139.5, 136.5, 135.7, 133.8, 129.6, 129.1, 122.9, 117.2, 112.1, 52.1, 20.6, 17.6; IR (KBr) ν_{max}/cm^{-1} 3012, 2951, 2918, 2856, 1781, 1728, 1697, 1612, 1520, 1483, 1444, 1377, 1299, 1207, 1160, 1001, 762; MS (EI): *m*/*z* (%) = 311 ([M]$^+$, 33), 285 (100); HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{17}NNaO_4$: 334.1050; found: 334.1048.

3-(2,6-Diethylphenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (4o). White solid; yield: 0.19 g (60%); mp 173–175 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.49 (d, *J* = 8.4 Hz, 2H) 7.21–7.28 (m, 3H), 6.63 (d, *J* = 1.6 Hz, 1H), 3.71 (s, 3H), 2.46–2.52 (m, 4H), 1.01 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.8 (C═O), 151.2 (C═O), 142.7, 140.3, 140.1, 135.3, 128.5, 127.4, 126.7, 122.9, 117.1, 112.4, 52.1, 23.9, 14.5; IR (KBr) ν_{max}/cm^{-1} 3067, 3030, 2963, 2875, 1781, 1731, 1693, 1611, 1520, 1444, 1373, 1209, 1160, 1115, 1000, 798, 762, 716; MS (EI): *m*/*z* (%) = 325 ([M]$^+$, 20), 299 (100), 294 ([M − OCH_3]$^+$, 8), 266 ([M − $COOCH_3$]$^+$, 10); HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{19}NNaO_4$: 348.1206; found: 348.1207.

3-(3-Chlorophenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (4q). White solid; yield: 0.25 g (84%); mp 145–147 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.86 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.79 (d, *J* = 1.6 Hz, 1H), 7.58–7.70 (m, 4H), 7.47 (d, *J* = 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C═O), 152.2 (C═O), 145.5, 134.1, 133.9, 131.5, 131.4, 128.9, 126.0, 125.6, 125.1, 124.6, 110.3, 109.3, 52.4; IR (KBr) ν_{max}/cm^{-1} 3125, 3093, 3063, 2959, 1798, 1725, 1623, 1594, 1496, 1459, 1437, 1383, 1293, 1265, 1149, 1094, 1008, 868, 783, 709; MS (EI): *m*/*z* (%) = 305 ([M + 2]$^+$, 33), 303 ([M]$^+$, 100), 272 ([M − OCH_3]$^+$, 84), 244 ([M − $COOCH_3$]$^+$, 11); HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd. for $C_{15}H_{11}Cl^{35}NO_4$: 304.0371; found: 304.0367.

5-Methoxycarbonyl-3-(3-(methoxycarbonyl)phenyl)-2(3*H*)-benzoxazolone (4r). White solid; yield: 0.25 g (76%); mp > 200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.21 (s, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 0.8 Hz, 1H), 7.87 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.79 (t, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 1.2 Hz, 1H), 3.89 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C═O), 165.3 (C═O), 152.3 (C═O), 145.6, 133.3, 131.6, 131.3, 130.5, 130.5, 129.3, 126.6, 125.5, 125.0, 110.2, 109.1, 52.5, 52.3; IR (KBr) ν_{max}/cm^{-1} 3095, 3077, 3060, 3005, 2958, 2845, 1779, 1713, 1623, 1587, 1492, 1349, 1281, 1243, 1110, 1016, 890, 755, 697; MS (EI): *m*/*z* (%) = 327 ([M]$^+$, 100), 296 ([M − OCH_3]$^+$, 82), 268 ([M − $COOCH_3$]$^+$, 4); HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{13}NaO_6$: 350.0635; found: 350.0640.

3-(3-(Trifluoromethyl)phenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (4s). White solid; yield: 0.25 g (75%); mp 128–130 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.08 (s, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.86–7.93 (m, 3H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C═O), 152.2 (C═O), 145.5, 133.7, 131.4, 131.2, 130.6 (q, $^2J_{CF}$ = 32.1 Hz), 130.0, 125.6, 125.5 (q, $^3J_{CF}$ = 3.4 Hz), 125.1, 123.0 (q, $^3J_{CF}$ = 3.4 Hz), 122.2 (q, $^1J_{CF}$ = 271.2 Hz), 110.2, 109.2, 52.3; IR (KBr) ν_{max}/cm^{-1} 3086, 3056, 3018, 2964, 1787, 1720, 1625, 1503, 1460, 1435, 1387, 1329, 1294, 1260, 1182, 1116, 882, 765, 700; MS (EI): *m*/*z* (%) = 337 ([M]$^+$, 90), 306 ([M − OCH_3]$^+$, 100), 278 ([M − $COOCH_3$]$^+$, 15); HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{10}F_3NNaO_4$: 360.0454; found: 360.0460.

5-Methoxycarbonyl-3-(3-methylphenyl)-2(3*H*)-benzoxazolone (4t). White solid; 0.26 g (93%); mp 114–116 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.84 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.40–7.44 (m, 3H), 7.35 (d, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C═O), 152.3 (C═O), 145.5, 139.6, 132.6, 131.7, 129.7, 129.5, 126.2, 125.5, 124.9, 122.8, 110.1, 109.2, 52.3, 20.8; IR (KBr) ν_{max}/cm^{-1} 3073, 3002, 2955, 2924, 2848, 1776, 1712, 1623, 1606, 1590, 1499, 1457, 1384, 1283, 1247, 1087, 999, 887, 763, 702; MS (EI): *m*/*z* (%) = 283 ([M]$^+$, 100), 252 ([M − OCH_3]$^+$, 54), 224 ([M − $COOCH_3$]$^+$, 7); HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{14}NO_4$: 284.0917; found: 284.0920.

3-(3-Nitrophenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (4u). Yellow solid; 0.26 g (82%); mp > 200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.53 (t, *J* = 2.0 Hz, 1H), 8.35–8.39 (m, 1H), 8.12–8.15 (m, 1H), 7.93 (t, *J* = 8.0 Hz, 1H), 7.88 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 1.6 Hz, 1H), 3.82 (s, 3H);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.7 (C═O), 152.4 (C═O), 148.7, 145.8, 134.1, 132.5, 131.6, 131.4, 125.8, 125.5, 123.7, 121.2, 110.5, 109.6, 52.6; IR (KBr) ν_{max}/cm^{-1} 3132, 3102, 2999, 2952, 1780, 1710, 1621, 1536, 1494, 1439, 1373, 1297, 1258, 1151, 1094, 885, 767, 701; MS (EI): m/z (%) = 314 ([M]$^+$, 100), 283 ([M − OCH_3]$^+$, 90), 255 ([M − $COOCH_3$]$^+$, 6); HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{15}H_{10}N_2NaO_6$: 337.0431; found: 337.0431.

5-Methoxycarbonyl-3-(naphthalen-1-yl)-2(3*H*)-benzoxazolone (4v). Yellow solid; 0.26 g (80%); mp 120–122 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.23 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.87–7.91 (m, 2H), 7.73–7.80 (m, 2H), 7.65–7.69 (m, 2H), 7.57–7.61 (m, 1H), 7.02 (d, J = 1.2 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.3 (C═O), 152.8 (C═O), 146.0, 134.1, 132.9, 130.4, 129.0, 128.7, 128.5, 127.7, 127.1, 126.8, 126.1, 125.6, 124.9, 122.2, 110.3, 109.1, 52.2; IR (KBr) ν_{max}/cm^{-1} 3058, 3000, 2953, 2846, 1790, 1723, 1621, 1599, 1511, 1492, 1455, 1373, 1291, 1247, 1148, 1047, 800, 773; HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{19}H_{14}NO_4$: 320.0917; found: 320.0922.

3-((Diphenylmethylene)amino)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (4w). White solid; 0.29 g (78%); mp 119–121 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.82 (dd, J = 8.4, 1.6 Hz, 1H), 7.66–7.74 (m, 4H), 7.53–7.57 (m, 2H), 7.40–7.57 (m, 4H), 7.29–7.31 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 178.6 (C═O), 165.4 (C═O), 147.7, 144.1, 135.3, 133.6, 132.6, 130.5, 130.2, 129.5, 128.7, 128.5, 127.7, 125.9, 124.9, 110.2, 109.7, 52.3; IR (KBr) ν_{max}/cm^{-1} 3056, 3032, 3007, 2957, 2848, 1787, 1717, 1620, 1560, 1490, 1460, 1366, 1288, 1244, 1093, 1003, 763, 695; MS (EI): m/z (%) = 372 ([M]$^+$, 28), 341 ([M − OCH_3]$^+$, 4), 180 (100); HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{22}H_{17}N_2O_4$: 373.1183; found: 373.1185.

3-(4′-Chloro-[1,1′-biphenyl]-4-yl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (4x). White solid; 0.34 g (90%); mp 187–189 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.94 (d, J = 8.4 Hz, 2H), 7.88 (dd, J = 8.4, 1.2 Hz, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 1.2 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 165.5 (C═O), 152.4 (C═O), 145.6, 139.1, 137.8, 132.9, 132.4, 131.6, 129.0, 128.7, 128.1, 126.3, 125.6, 125.0, 110.3, 109.3, 52.4; IR (KBr) ν_{max}/cm^{-1} 3042, 2960, 1786, 1719, 1620, 1522, 1490, 1459, 1383, 1286, 1241, 1092, 1007, 810, 762; HRMS: (ESI-TOF) m/z [M + H]$^+$ calcd. for $C_{21}H_{15}ClNO_4$: 380.0684; found: 380.0681.

3-Chloro-7-methoxycarbonyl-dibenz[b,e][1,4]oxazepin-11(5*H*)-one (I). Yellow solid; 0.25 g (82%); mp > 200 °C; ^{1}HNMR (400 MHz, DMSO-d_6): δ = 9.33 (s, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 2.4 Hz, 1H), 7.64 (dd, J = 8.8, 2.4 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H), 7.24 (d, J = 2.0 Hz, 1H), 6.99 (dd, J = 8.4, 2.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 165.1 (C═O), 163.3 (C═O), 149.6, 145.1, 139.8, 136.7, 136.3, 127.5, 125.1, 122.5, 121.2, 120.5, 118.4, 114.2, 52.3; IR (KBr) ν_{max}/cm^{-1} 3313, 3079, 3038, 3010, 2963, 2921, 1725, 1698, 1617, 1600, 1536, 1509, 1477, 1436, 1409, 1281, 1211, 1025, 1021, 766; MS (EI): m/z (%) = 303 ([M]$^+$, 16), 272 ([M − OCH_3]$^+$, 36), 244 ([M − $COOCH_3$]$^+$, 22); HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{15}H_{11}ClNO_4$: 304.0371; found: 304.0366.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21272280, 81201716, 81301890), Science & Technology Program of Guangdong Province and Guangzhou City (2011A081401002, 2014J4100224), Guang-dong Natural Science Foundation (S2013010014278), National Significant New Drugs Development (2011ZX09202-101-07). The authors are also grateful to Guangxi Wanshan Spice Co. Ltd. for giving high quality (−)-shikimic acid as a gift.

Notes and references

1 A. Porzelle, M. D. Woodrow and N. C. O. Tomkinson, *Org. Lett.*, 2010, **12**, 812.
2 A. Guardigl, W. Chow, P. m. Martwins and M. S. Lefar, *J. Agric. Food Chem.*, 1971, **19**, 742.
3 G. Q. Shi, J. F. Dropinski, B. M. McKeever, S. H. Xu, J. W. Becker, J. P. Berger, K. L. MacNaul, A. Elbrecht, G. C. Zhou, T. W. Doebber, P. R. Wang, Y. S. Chao, M. Forrest, J. V. Heck, D. E. Moller and A. B. Jones, *J. Med. Chem.*, 2005, **48**, 4457.
4 L. Chen, M. P. Dillon, L. C. Feng and M. M. Yang, US Patent 0324069, 2010.
5 (*a*) D. V. Dekhane, S. S. Pawar, S. V. Gupta, M. S. Shingare and S. N. Thore, *Lett. Org. Chem.*, 2011, **8**, 406; (*b*) B. Gabriele, R. Mancuso, G. Salerno and M. Costa, *J. Org. Chem.*, 2003, **68**, 601; (*c*) A. Noujima, T. Mitsudome, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Green Chem.*, 2013, **15**, 608; (*d*) L. Troisi, C. Granito, S. Perrone and F. Rosato, *Tetrahedron Lett.*, 2011, **52**, 4330; (*e*) X. F. Wang, G. Ling, Y. Xue and S. W. Lu, *Eur. J. Org. Chem.*, 2005, 1675.
6 (*a*) R. Bautista, A. Benavides, H. A. Jimenez-Vazquez and J. Tamariz, *Nat. Prod. Res.*, 2013, **27**, 1749; (*b*) P. Bernal and J. Tarnariz, *Helv. Chim. Acta*, 2007, **90**, 1449.
7 (*a*) M. T. Barros, S. S. Dey, C. D. Maycock and P. Rodrigues, *Chem. Commun.*, 2012, **48**, 10901; (*b*) J. Cossy and D. Belotti, *Org. Lett.*, 2002, **4**, 2557; (*c*) S. A. Girard, X. Hu, T. Knauber, F. Zhou, M. O. Simon, G. J. Deng and C. J. Li, *Org. Lett.*, 2012, **14**, 5606; (*d*) A. Hajra, Y. Wei and N. Yoshikai, *Org. Lett.*, 2012, **14**, 5488; (*e*) T. Ishikawa, E. Uedo, R. Tani and S. Saito, *J. Org. Chem.*, 2001, **66**, 186; (*f*) Y. J. Xie, S. W. Liu, Y. Liu, Y. Q. Wen and G. J. Deng, *Org. Lett.*, 2012, **14**, 1692.
8 J. W. Zhao, H. W. Huang, W. Q. Wu, H. J. Chen and H. F. Jiang, *Org. Lett.*, 2013, **15**, 2604.
9 J. E. Richman, Y. C. Chang, S. Kambourakis, K. M. Draths, E. Almy, K. D. Snell, G. M. Strasburg and J. W. Frost, *J. Am. Chem. Soc.*, 1996, **118**, 11587.
10 N. Q. Ran, D. R. Knop, K. M. Draths and J. W. Frost, *J. Am. Chem. Soc.*, 2001, **123**, 10927.
11 W. S. Li, D. M. Xie and J. W. Frost, *J. Am. Chem. Soc.*, 2005, **127**, 2874.
12 S. Kambourakis and J. W. Frost, *J. Org. Chem.*, 2000, **65**, 6904.
13 Y. Zou, E. S. Zhang, T. L. Xu, W. Wu, Y. Chen, M. Yuan, W. Wei and X. Zhang, *RSC Adv.*, 2013, **3**, 6545.

14 (*a*) W. Wu, Y. Zou, Y. Chen, J. Li, Z. L. Lv, W. Wei, T. K. Huang and X. K. Liu, *Green Chem.*, 2012, **14**, 363; (*b*) E. S. Zhang, T. L. Xu, D. J. Wang, T. K. Huang, M. Yuan, J. Li and Y. Zou, *RSC Adv.*, 2014, **4**, 10022; (*c*) E. S. Zhang, T. L. Xu, W. Wei, T. K. Huang, M. Yuan, W. Zeng and Y. Zou, *Synthesis*, 2014, **46**, 1167.

15 (*a*) E. Arceo, J. A. Ellman and R. G. Bergman, *ChemSusChem.*, 2010, **3**, 811; (*b*) F. Cherubini, *Energy Convers. Manage.*, 2010, **51**, 1412; (*c*) A. Uihlein and L. Schebek, *Biomass Bioenergy*, 2009, **33**, 793; (*d*) Y. G. Zheng, X. L. Chen and Y. C. Shen, *Chem. Rev.*, 2008, **108**, 5253; (*e*) T. R. Brown and R. C. Brown, *RSC Adv.*, 2013, **3**, 5758; (*f*) Z. Zhang, B. Du, L. J. Zhang, Y. X. Da, Z. J. Quan, L. J. Yang and X. C. Wang, *RSC Adv.*, 2013, **3**, 9201; (*g*) B. Wang, Y. Shen, J. K. Sun, F. Xu and R. C. Sun, *RSC Adv.*, 2014, **4**, 18917; (*h*) T. J. Schwartz, B. H. Shanks and J. A. Dumesic, *Green Chem.*, 2012, **14**, 1850; (*i*) B. Saha and M. M. Abu-Omar, *Green Chem.*, 2014, **16**, 24.

16 B. Kamm, *Angew Chem., Int. Ed.*, 2007, **46**, 5056.

17 (*a*) B. M. Bhanage, S. Fujita, Y. Ikushima and M. Arai, *Green Chem.*, 2004, **6**, 78; (*b*) S. Pulla, V. Unnikrishnan, P. Ramidi, S. Z. Sullivan, A. Ghosh, J. L. Dallas and P. Munshi, *J. Mol. Catal. A: Chem.*, 2011, **338**, 33.