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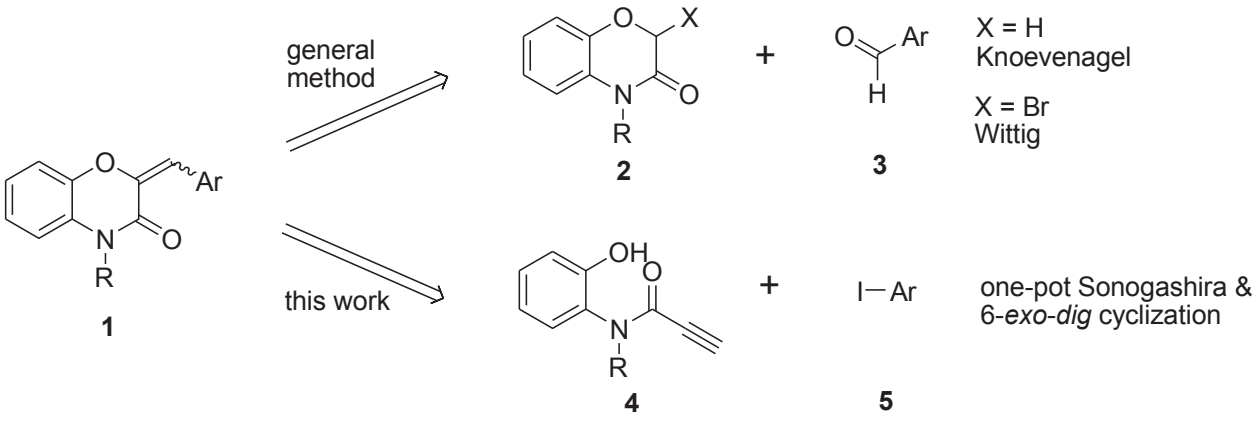
SYNTHESIS OF 2-(ARYLMETHYLENE)-1,4-BENZOXAZIN-3-ONE BY ONE-POT SONOGASHIRA AND 6-*EXO-DIG* CYCLIZATION

Dahye Lee,[1] Sunhwa Park,[1] Yosep Yu, Kye Jung Shin, and Jae Hong Seo*

Integrated Research Institute of Pharmaceutical Sciences, College of Pharmacy, The Catholic University of Korea, 43 Jibong-ro, Wonmi-gu, Bucheon, Gyeonggi-do 420-743, Republic of Korea; E-mail: jaehongseo@catholic.ac.kr

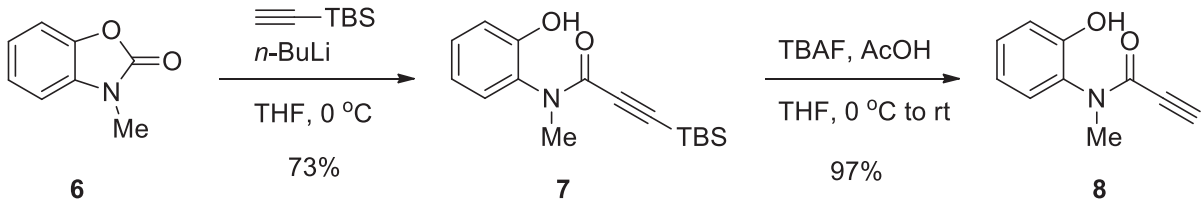
Abstract – A novel, efficient one-pot approach to synthesize 2-(arylmethylene)-1,4-benzoxazin-3-ones has been developed. This method effectively combined the Sonogashira reaction of electron-deficient propiolamide and successive 6-*exo-dig* cyclization to selectively provide (*Z*)-isomers of 2-(arylmethylene)-1,4-benzoxazin-3-ones in good yield.

1,4-Benzoxazin-3-ones have been found in numerous natural products and drugs, and show various biological activities.[2] Among them, 1,4-benzoxazin-3-ones with an arylmethylene group at the C2 position have been reported to have unique activities, such as neuroprotection and tyrosine kinase inhibition.[3] However, synthetic methods for 2-(arylmethylene)-1,4-benzoxazine have not been well-studied. Generally, 2-(arylmethylene)-1,4-benzoxazines **1** have been prepared by the condensation reaction between arylaldehyde **3** and proper nucleophilic derivatives of 1,4-benzoxazin-3-ones **2**, such as Knoevenagel (X = H)[3] and Wittig (X = Br)[2a] reactions (Scheme 1). Recently we reported a one-pot approach to synthesize 3-(arylmethylene)oxindoles combining Sonogashira, Heck and Suzuki-Miyaura reactions from the corresponding propiolamides.[4] The electron-deficient alkyne group of propiolamides has low reactivity toward general Sonogashira reactions, which hampers the development of a tandem reaction, including a Sonogashira reaction of propiolamides. As part of our ongoing efforts to develop novel synthetic methods for heterocycles by combining the Sonogashira reaction of electron-deficient alkyne substrate and other reactions, we describe a new, efficient approach for synthesizing 2-(arylmethylene)-1,4-benzoxazin-3-ones **1** from propiolamide **4** and aryl iodide **5**, connecting the Sonogashira reaction and successive 6-*exo-dig* cyclization.



Scheme 1. Synthetic methods for 2-arylmethylene-1,4-benzoxazin-3-ones

First, model substrate **8** was prepared from known benzoxazolone **6**[5] by modifying the procedure of Overman's group (Scheme 2).[6] The addition of TBS-acetylide to **6** yielded TBS-protected propiolamide **7**, in which the TBS group was deprotected by TBAF under AcOH-buffered conditions to provide the desired propiolamide **8** in 97% yield.

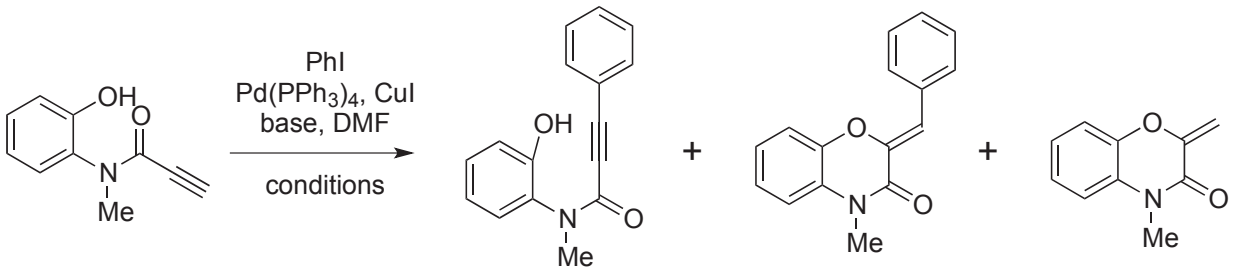


Scheme 2. Preparation of propiolamide **8**

Next, we tried to find optimal reaction conditions for a one-pot Sonogashira reaction and cyclization with propiolamide **8** (Table 1). Under Sonogashira reaction conditions of Zhu et al.,[7] which we used in our previous work, propiolamide **8** was successfully transformed into Sonogashira adduct **9** in 97% yield (entry 1). To facilitate cyclization, the reaction temperature was increased to 90 ºC after completion of the Sonogashira reaction. As expected, cyclized product **10** was formed at 90 ºC in 38% yield in combination with remaining intermediate **9** (20% yield) (entry 2). The stereochemistry of the olefin of **10** was determined to be *Z* configuration by comparing the known chemical shift of the vinyl proton (δ_H = 6.95 ppm for *Z* isomer, 6.75 ppm for *E* isomer).[8] To determine the effect of a base on the reaction, various bases were tested. Reactions with KOAc, Na_2CO_3 and K_2CO_3 were completed before increasing the temperature to 90 ºC. However, various unassignable by-products were also formed with the desired product **10** in low yield (26–27%) (entries 3-5). Using CsF and K_3PO_4 as a base helped to increase the yield of **10** to 35% and 33%, respectively. These reactions provide another cyclized product **11** in 8% and

28% yield, which was produced by direct cyclization of **8** before the Sonogashira reaction (entries 6 and 7). The best result was obtained with Cs_2CO_3, which gave **10** in 67% yield with a relatively small amount of **11** (3% yield) (entry 8). The reaction at room temperature with Cs_2CO_3 increased the amount of by-product **11** (22% yield) with moderate yield of **10** (50% yield) (entry 9). Increasing the reaction temperature to 90 ºC shortened the reaction time (0.5 h) but the yield of **10** was slightly lower than that of 60 ºC (57%, entry 10 vs 67%, entry 8). These results indicated that the reaction was strongly affected by the type of base and reaction temperature. With an optimal combination of base (Cs_2CO_3) and reaction temperature (60 ºC), the formation of by-product **11** was reduced, and the desired 1,4-benzoxazin-3-one **10** was obtained in good yield.

Table 1. Optimization of the reaction



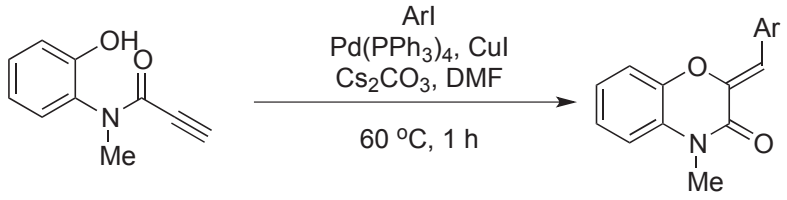
8 **9** **10** **11**

entry	base	conditions	yield (%)		
			9	**10**	**11**
1	NaOAc	60 °C, 2.5 h	97	-	-
2	NaOAc	60 °C, 3 h to 90 °C, 3 h	20	38	-
3	KOAc	60 °C, 2 h	-	26	-
4	Na_2CO_3	60 °C, 2 h	-	27	-
5	K_2CO_3	60 °C, 2 h	-	26	-
6	CsF	60 °C, 2 h	-	35	8
7	K_3PO_4	60 °C, 2 h	-	33	28
8	Cs_2CO_3	60 °C, 1 h	-	67	3
9	Cs_2CO_3	rt, 2 h	-	50	22
10	Cs_2CO_3	90 °C, 0.5 h	-	57	3

With the optimal reaction conditions, we next investigated the substrate scope of the reaction (Table 2). Aryl iodides with electron-withdrawing groups gave the desired products in good yield (entries 1-3). An electron-donating group (4-MeO) of aryl iodide decreased the yield to 42% (entry 4). This low yield is probably due to low reactivity of electronically-sufficient aryl iodide toward the Sonogashira reaction.

However, the reaction with aryl iodide bearing the 3-methoxy group proceeded smoothly to give **12e** in 67% yield (entry 5). The chemical shifts of the vinyl proton for all compounds (6.89~6.91 ppm) except **12c** (6.99 ppm) were similar to that of **10** (6.91 ppm), which supported the *Z* configuration of olefins. The olefin stereochemistry of **12c** was determined by measuring the coupling constant between the carbonyl carbon and vinyl proton ($^3J_{C\text{-}H}$ = 3.2 Hz) in non-decoupling ^{13}C NMR, which Honda et al. used to determine the olefin geometry of similar benzoxazin-3-one derivatives (*Z* isomer: $^3J_{C\text{-}H}$ = 3.1 Hz).[3a]

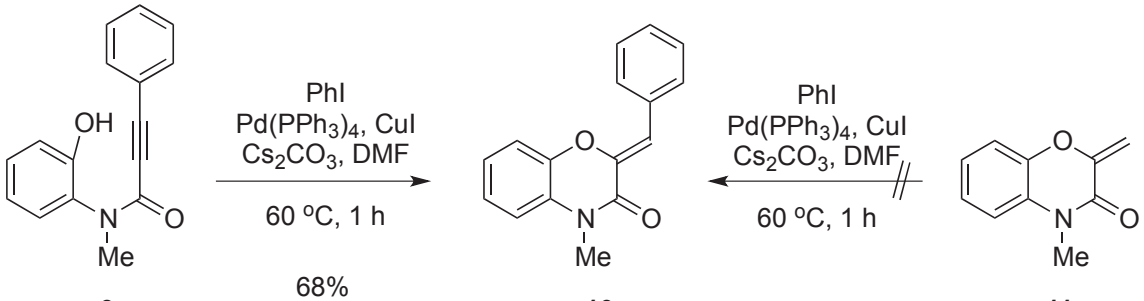
Table 2. Substrate scope of the reaction



8 **12**

entry	Ar	**12**	yield (%)
1	4-ClPh	**12a**	71
2	4-CF_3Ph	**12b**	61
3	4-NO_2Ph	**12c**	70
4	4-MeOPh	**12d**	42
5	3-MeOPh	**12e**	67

To support the intermediacy of Sonogashira adduct **9** in the reaction with Cs_2CO_3, **9** was exposed to the standard reaction conditions, which provide **10** in 68% yield. However, under the same reaction conditions, directly cyclized product **11** could not be transformed into **10** to be recovered quantitatively (Scheme 3). These results suggested that the reaction goes through a Sonogashira reaction followed by 6-*exo-dig* cyclization.[9]



9 **10** **11**

Scheme 3. Elucidation of intermediacy of **9** in the reaction

In conclusion, a novel, efficient synthetic method for 2-(arylmethylene)-1,4-benzoxazin-3-ones was developed by combining the Sonogashira reaction and 6-*exo*-*dig* cyclization, which provides the (*Z*)-isomer as the sole detectable isomer.

EXPERIMENTAL

All reactions were performed under an argon atmosphere with dry solvents, unless otherwise stated. All commercially available reagents were purchased and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) on silica gel plates (Merck TLC Silica Gel 60 F254) using UV light or PMA (an ethanolic solution of phosphomolybdic acid) as visualizing agent. Purification of products was conducted by column chromatography through silica gel 60 (0.060–0.200 mm). Melting points of all solid compounds were determined by Buchi M-565. NMR spectra were obtained on Bruker AVANCE III 500 MHz using residual undeuterated solvent as an internal reference. High-resolution mass spectra (HR-MS) were recorded on a JEOL JMS-700 using EI (electron impact).

Preparation of Propiolamide 8

3-(*tert*-Butyldimethylsilyl)-*N*-(2-hydroxyphenyl)-*N*-methylpropiolamide (7)

To a solution of (*tert*-butyldimethylsilyl)acetylene (0.22 mL, 1.2 mmol, 1.2 equiv) in THF (5 mL) was added *n*-BuLi (2.0 M in THF, 0.55 mL, 1.1 mmol, 1.1 equiv) at –78 °C. After 30 min a solution of *N*-methyl-2-benzoxazolinone (150 mg, 1.0 mmol, 1.0 equiv) in THF (5 mL) was added to the mixture, and the resulting solution was gradually warmed to 0 °C. After 5 h stirring at 0 °C, the mixture was diluted with sat. aq. NH_4Cl (1.0 mL), EtOAc (20 mL), and H_2O (10 mL) in order. Organic layer was separated, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, CH_2Cl_2) to yield TBS-propiolamide **7** (235 mg, 0.81 mmol, 81% yield) as a white solid. **7**: mp 152.2 °C; R_f = 0.50 (silica gel, CH_2Cl_2 : EtOAc 9 : 1); ^{1}H NMR (500 MHz, $CDCl_3$, 1.6:1 atropisomeric mixture): δ 7.25–7.21 (m, 1H, *major*), 7.16 (dd, *J* = 8.0, 1.7 Hz, 1H, *major*), 7.15 (dd, *J* = 8.3, 1.5 Hz, 1H, *minor*), 7.07 (dd, *J* = 8.3, 1.3 Hz, 1H, *minor*), 7.01–6.98 (m, 1H, *major and minor*), 6.96–6.93 (m, 1H, *minor*), 6.89 (td, *J* = 15.3, 1.3 Hz, 1H, *major*), 6.68 (s, 1H, *minor*), 5.97 (s, 1H, *major*), 3.67 (s, 3H, *minor*), 3.26 (s, 3H, *major*), 1.01 (s, 9H, *minor*), 0.69 (s, 9H, *major*), 0.24 (s, 6H, *minor*), –0.06 (d, *J* = 2.0 Hz, 6H, *major*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$, *major and minor*): δ 155.0, 154.2, 152.6, 151.1, 130.9, 130.3, 129.8, 129.2, 128.9, 124.2, 121.6, 121.1, 120.9, 117.3, 100.0, 97.3, 96.8, 96.6, 40.7, 35.7, 26.2, 25.9, 16.8, 16.3, –5.0, –5.3 ppm; HRMS (EI): calcd for $C_{16}H_{23}NO_2Si$ [M^+]: 289.1498, found 289.1498.

N-(2-Hydroxyphenyl)-*N*-methyl-3-phenylpropiolamide (8)

To a solution of TBS-propiolamide **7** (400 mg, 1.38 mmol, 1.0 equiv) in THF (15 mL) were added AcOH

(0.079 mL, 1.4 mmol, 1.0 equiv) and TBAF (1.0 M in THF, 1.5 mL, 1.5 mmol, 1.1 equiv) at 0 °C, and the resulting solution was stirred at 0 °C for 12 h. Then, the mixture was diluted with sat. aq. NH_4Cl (5 mL) and EtOAc (20 mL). Organic layer was separated, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexanes : EtOAc 2 : 1) to yield propiolamide **8** (234 mg, 1.34 mmol, 97% yield) as a white solid. **8**: mp 149.5 °C; R_f = 0.15 (silica gel, hexanes : EtOAc 2 : 1); ^{1}H NMR (500 MHz, $CDCl_3$, 1.6:1 atropisomeric mixture): δ 7.28–7.23 (m, 1H, *major and minor*), 7.19–7.15 (m, 1H, *major and minor*), 7.08 (dd, J = 8.3, 1.3 Hz, 1H, minor), 7.02–7.00 (m, 1H, *major and minor*), 6.94 (td, J = 15.3, 1.3 Hz, 1H, *major*), 6.44 (s, 1H, *minor*), 5.91 (s, 1H, *major*), 3.68 (s, 3H, *minor*), 3.37 (s, 1H, *minor*), 3.28 (s, 3H, *major*), 2.79 (s, 1H, *major*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$, *major and minor*): δ 154.6, 153.8, 152.7, 151.0, 130.54, 130.45, 129.3, 129.2, 124.6, 121.7, 121.0, 120.7, 117.6, 81.8, 79.6, 75.9, 75.8, 40.6, 35.9 ppm; HRMS (EI): calcd for $C_{10}H_9NO_2$ [M^+]: 175.0633, found 175.0634.

General Procedure for Sonogashira and 6-*exo-dig* Cyclization

To a stirred solution of propiolamide **8** (0.25 mmol, 1.0 equiv) in DMF (2.5 mL) were added the corresponding aryl iodide (0.28 mmol, 1.1 equiv), CuI (0.0013 mmol, 5 mol%), Cs_2CO_3 (0.75 mmol, 3.0 equiv) and $Pd(PPh_3)_4$ (0.025 mmol, 10 mol%) at 25 °C. The reaction mixture was stirred at 60 °C for 1 h. Then, the mixture was cooled to 25 °C and diluted with EtOAc (100 mL). Organic layer was washed with H_2O (15 mL X 3) and brine (15 mL), then dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude residue was purified by column chromatography (silica gel, CH_2Cl_2) to yield 1,4-benzoxazin-3-ones (**10**, **11**, **12a-e**) and/or phenylpropiolamide **9**.

***N*-(2-Hydroxyphenyl)-*N*-methyl-3-phenylpropiolamide (9)**

Yellow solid; mp 124.1 °C; R_f = 0.49 (silica gel, hexanes : EtOAc 1 : 1); ^{1}H NMR (500 MHz, $CDCl_3$, 5.3:1 atropisomeric mixture): δ 8.38 (s, 1H, *major*), 7.56–7.54 (m, 2H, *minor*), 7.41 (t, J = 7.5 Hz, 1H, *minor*), 7.33 (t, J = 7.5 Hz, 2H, *minor*), 7.28 (ddd, J = 8.1, 7.4, 1.6 Hz, 1H, *major*), 7.24 (t, J = 1.2 Hz, 1H, *minor*), 7.21 (dd, J = 8.0, 1.5 Hz, 2H, *major*), 7.19–7.17 (m, 2H, *minor*), 7.13 (dd, J = 8.3, 1.3 Hz, 1H, *major*), 7.09 (t, J = 7.8 Hz, 2H, *major*, 1H, *mionr*), 6.98 (dd, J = 8.3, 1.3 Hz, 2H, *major*), 6.95–6.93 (m, 1H, *minor*), 6.89 (td, J = 15.3, 1.5 Hz, 1H, *major*), 3.69 (s, 3H, *minor*), 3.35 (s, 3H, *major*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$, *major and minor*): δ 156.0, 155.2, 153.2, 151.2, 132.8, 130.9, 130.8, 130.3, 130.1, 129.9, 129.4, 129.0, 128.8, 128.3, 124.6, 121.6, 120.74, 120.68, 120.3, 120.0, 117.6, 93.6, 91.6, 82.1, 81.7, 40.7, 35.8 ppm; HRMS (EI): calcd for $C_{16}H_{13}NO_2$ [M^+]: 251.0946, found 251.0946.

(*Z*)-2-Benzylidene-4-methyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (10)

White solid; mp 155.1 °C [Lit.,[10] 155-156 °C]; R_f = 0.60 (silica gel, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, J = 7.5 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 7.20–7.18 (m, 1H),

7.10–7.07 (m, 2H), 7.02–7.00 (m, 1H), 6.96 (s, 1H), 3.48 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.4, 142.0, 141.2, 133.9, 130.1, 128.7, 128.3, 127.6, 123.9, 123.4, 116.1, 114.5, 113.0, 28.8 ppm; HRMS (EI): calcd for $C_{16}H_{13}NO_2$ [M^+]: 251.0946, found 251.0947.

4-Methyl-2-methylene-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (11)

White solid; mp 98.3 °C; R_f = 0.57 (silica gel, hexanes : EtOAc 3 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07–7.00 (m, 3H), 6.98–6.95 (m, 1H), 5.61 (d, J = 1.6 Hz, 1H), 5.06 (d, J = 1.6 Hz, 1H), 3.43 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.5, 147.9, 142.1, 127.3, 123.9, 122.9, 115.7, 114.3, 98.8, 28.4 ppm; HRMS (EI): calcd for $C_{10}H_9NO_2$ [M^+]: 175.0633, found 175.0627.

(*Z*)-2-(4-Chlorobenzylidene)-4-methyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (12a)

White solid; mp 214.9 °C; R_f = 0.47 (silica gel, hexanes : EtOAc 3 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.20–7.18 (m, 1H), 7.13–7.08 (m, 2H), 7.03–7.01 (m, 1H), 6.91 (s, 1H), 3.49 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.1, 141.8, 141.5, 133.9, 132.3, 131.3, 128.9, 127.5, 124.0, 123.6, 116.0, 114.5, 111.6, 28.9 ppm; HRMS (EI): calcd for $C_{16}H_{12}ClNO_2$ [M^+]: 285.0557, found 285.0560.

(*Z*)-4-Methyl-2-(4-(trifluoromethyl)benzylidene)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (12b)

Yellow solid; mp 171.1 °C; R_f = 0.45 (silica gel, hexanes : EtOAc 3 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.16–7.14 (m, 1H), 7.11–7.05 (m, 2H), 6.99–6.97 (m, 1H), 6.91 (s, 1H), 3.44 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.6, 142.5, 141.4, 137.2, 130.0, 129.5 (q, $^2J_{CF}$ = 32 Hz), 127.2, 125.5, 125.5 (q, $^3J_{CF}$ = 3.8 Hz), 124.2 (q, $^1J_{CF}$ = 270 Hz), 124.0, 123.7, 116.0, 114.5, 110.9, 28.8 ppm; HRMS (EI): calcd for $C_{17}H_{12}F_3NO_2$ [M^+]: 319.0820, found 319.0821.

(*Z*)-4-Methyl-2-(4-nitrobenzylidene)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (12c)

Yellow solid; mp 235.7 °C; R_f = 0.39 (silica gel, hexanes : EtOAc 3 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (d, J = 8.9 Hz, 2H), 7.97 (d, J = 8.9 Hz, 2H), 7.23 (dd, J = 7.5, 1.9 Hz, 1H), 7.18–7.12 (m, 2H), 7.06 (dd, J = 7.5, 1.9 Hz, 1H), 6.99 (s, 1H), 3.52 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.3, 146.7, 143.6, 141.3, 140.4, 130.3, 127.2, 124.3, 124.1, 123.9, 116.2, 114.7, 110.0, 29.0 ppm; HRMS (EI): calcd for $C_{16}H_{12}N_2O_4$ [M^+]: 296.0797, found 296.0794.

(*Z*)-2-(4-Methoxybenzylidene)-4-methyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (12d)

Yellow solid; mp 165.2 °C; R_f = 0.39 (silica gel, hexanes : EtOAc 3 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, J = 8.8 Hz, 2H), 7.17–7.14 (m, 1H), 7.10–7.03 (m, 2H), 6.99–6.97 (m, 1H), 6.94 (d, J = 8.9 Hz, 2H), 6.91 (s, 1H), 3.85 (s, 3H), 3.46 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 157.7, 142.1, 139.7, 131.7, 127.7, 126.6, 123.8, 123.2, 115.9, 114.4, 114.1, 112.9, 55.4, 28.7 ppm; HRMS (EI): calcd for $C_{17}H_{15}NO_3$ [M^+]: 281.1052, found 281.1055.

(*Z*)-2-(3-Methoxybenzylidene)-4-methyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (12e)

Yellow solid; mp 116.0 °C; R_f = 0.34 (silica gel, hexanes : EtOAc 3 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ

7.44 (s, 1H), 7.38 (d, J = 7.7 Hz, 1H), 7.30 (t, J = 7.9 Hz, 1H), 7.13–7.12 (m, 1H), 7.08–7.02 (m, 2H), 6.96–6.95 (m, 1H), 6.89 (s, 1H), 6.86 (dd, J = 8.2, 1.9 Hz, 1H), 3.85 (s, 3H), 3.43 (s, 3H);) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 157.1, 141.8, 141.2, 135.0, 129.4, 127.4, 123.8, 123.3, 122.8, 115.9, 115.0, 114.4, 114.2, 112.7, 55.3, 28.7 ppm; HRMS (EI): calcd for $C_{17}H_{15}NO_3$ [M^+]: 281.1052, found 281.1052.

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