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Electrochemical intramolecular dehydrogenative coupling of *N*-benzyl(thio)amides: a direct and facile synthesis of 4*H*- 1, 3-benzoxazines and 4*H*- 1, 3-benzothiazines

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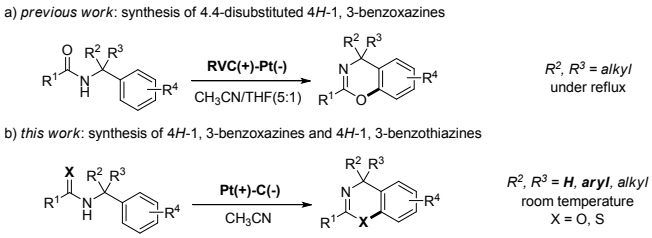
Keywords: Electrolysis / intramolecular dehydrogenative coupling / amides /4*H*- 1, 3-benzoxazines / 4*H*- 1, 3-benzothiazines /

The electrochemical dehydrogenative cyclization of *N*-benzylamides was investigated with Pt plate anode and graphite rod cathode in an undivided cell at room temperature. The oxidative degradation of the products was suppressed successfully and 4*H*- 1, 3-benzoxazines were obtained regardless of the substituents at the benzylic position. This method also allowed for the preparation of 4*H*- 1, 3-benzothiazines.

Introduction

In recent decades, as a novel and powerful approach to the construction of fused heterocyclic skeletons, the intramolecular dehydrogenative coupling (IDC) by utilizing the X-H (X = heteroatom) bond with a C-H bond has received considerable attention for its unique properties such as atom economy and high efficiency. [1] When amides and thioamides are used as substrates for this transformation, various *N*-heterocycle compounds could be prepared via intramolecular C-N, C-O or C-S bond formation process in an economically-favourable way. For example, via direct $sp^3(sp^2)$C−H aminative cyclization, *N*-arylisoindolinones [2] *N*-acyl indoline,[3] benzazetidine [4] or carbazoles [5] could be synthesized in good yields; *N*-aryl amide underwent oxidation to give benzoles by $Cu(OTf)_2$, [6] oxone, [7] or hypervalent iodine(III); [8] *N*-aryl thioamides could be transformed to benzothiazoles by direct oxidative coupling, [9] or under Pd catalysis oxidation, [10] photochemical cyclization, [11] and microwave irradiation conditions. [12] Although great progress has been achieved in this area, one drawback still exists in that stoichiometric oxidant or transition-metal catalyst is required in this type of reaction，which in some cases causes environmental problems and limits the application of this methodology in organic synthesis.

Compared with traditional thermochemical methods employing stoichiometric oxidant, organic electrosynthesis is more environmentally friendly for its avoidance of toxic or dangerous oxidizing reagents, and has attracted continuous interest as an alternative method of performing IDC reactions. [13] However, in some cases, this electrochemical process suffered from the oxidative degradation of the products for their lower oxidation potentials than their precursors, which would cause low yields and impurities. Thus, how to equilibrate the conversion of the start materials and the degradation of the products becomes a crucial issue in these reactions. Recently, Xu and co-workers reported a direct electrolysis of *N*-benzylamides to the efficient synthesis of substituted 4*H*-1, 3-benzoxazines, [14] but the substrate scope was limited to benzylic *gem*-dialkyl substituted *N*-benzylamides, and the yields was quite low or even no product was found in case of substrates with only one or no alkyl substituent at the benzylic position (Scheme 1a). [15] From the perspective of suppressing the degradation of the products, we speculate that this problem might be dissolved by employing milder electrolysis conditions. Herein, in connection with our interest to the synthesis of *N*-heterocycles by radical modification of amide derivatives, [16] we wish to report our result of electrochemical intramolecular aromatic C−H oxygenation of *N*-benzylamides [17] and C−H sulfurization of *N*-benzylthioamides [18] with 4*H*-1, 3-benzoxazines and 4*H*-1, 3-benzothiazines [19] obtained in moderate to good yields at room temperature (Scheme 1b).



Scheme 1. Electrochemical intramolecular dehydrogenative coupling of *N*-benzylamides and thioamides

Results and Discussion

Initially, *N*-benzylbenzamide **1a** was chosen as the model substrate to optimize the reaction conditions of

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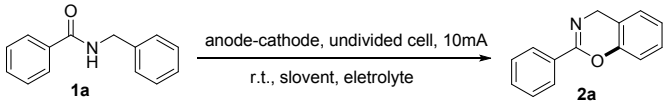
this elecreochemical intramolecular dehydrogenative coupling. The electrolysis of **1a** was firstly examined in an electrolyte solution of nBu$_4$NClO$_4$ (0.5 equiv) in

Table 1. Screening conditions[a]

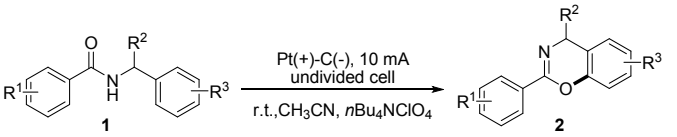


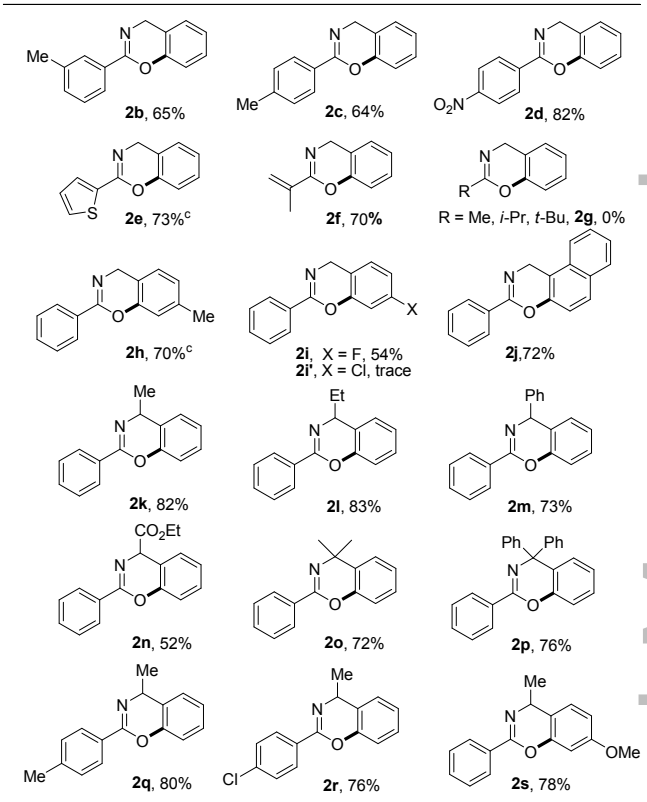
Entry	Anode-cathode	Solvent (10 mL)	Electrolyte (0.5 equiv)	Yield of **2a** (%)[b]
1	Pt(+)-Pt(-)	CH_3CN	nBu$_4$NClO$_4$	0
2	C(+)-Pt(-)	CH_3CN	nBu$_4$NClO$_4$	47
3	Pt(+)-C(-)	CH_3CN	nBu$_4$NClO$_4$	78(75)[c]
4	C(+)-C(-)	CH_3CN	nBu$_4$NClO$_4$	73
5	Pt(+)-C(-)	dioxane	nBu$_4$NClO$_4$	35
6	Pt(+)-C(-)	DMSO	nBu$_4$NClO$_4$	27
7	Pt(+)-C(-)	DMF	nBu$_4$NClO$_4$	21
8	Pt(+)-C(-)	THF	nBu$_4$NClO$_4$	trace
9	Pt(+)-C(-)	EtOAc	nBu$_4$NClO$_4$	0
10	Pt(+)-C(-)	CH_3CN/H_2O = 4:1, v/v	nBu$_4$NClO$_4$	61
11	Pt(+)-C(-)	CH_3CN	nBu$_4$NOAc	43
12	Pt(+)-C(-)	CH_3CN	nBu$_4$NBr	55
13	Pt(+)-C(-)	CH_3CN	Et$_4$BF$_4$	37
14	Pt(+)-C(-)	CH_3CN	Et$_4$NOTs	62
15	Pt(+)-C(-)	CH_3CN	nBu$_4$NClO$_4$	58[d]
16	Pt(+)-C(-)	CH_3CN	nBu$_4$NClO$_4$	63[e]

[a] Reaction conditions:The reaction was carried out on 0.2 mmol scale in undivided cell, constant current = 10 mA, RT, 2.0 h. [b] Isolated yield. [c] With RVC cathode. [d] constant current = 12 mA .[e] constant current = 8 mA.

CH_3CN at room temperature under air, and the results showed that the reaction was quite sensitive to the electrode materials. When Pt plate (1 cm × 1 cm) was used as both anode and cathode, no cyclic product chould be detected within 2 hours and all the start material decomposed after 4 hours (Table 1, entry 1). By changing the anode to graphite rod (Φ 6 mm × 65 mm), the generation of the cyclic product **2a** could be observed as monitored by TLC, but **2a** underwent decomposition gradually during the reaction. Finally, 2 hours later, all the start material disappeared and only 47% yield of **2a** was isolated (Table 1, entry 2). Interestingly, by the inversion of the electrode from C(+)-Pt(-) to Pt(+)-C(-), the decomposition of **2a** could be suppressed remarkably and the yield of **2a** was improved to 78%. When RVC anode was used instead of graphite rod, the yield of **2a** was 75% (Table 1, entry 3). A little lower yield of **2a** was achieved in case of C(+)-C(-), but the reaction needed longer reaction (4 hours) to complete (Table 1, entry 4). Changing CH_3CN to other polar solvent such as dioxane, DMSO, and DMF resulted in the formation of **2a** in only 21-35% yields (Table 1, entries 5–7). THF or EtOAc was not a suitable solvent for this reaction because of the poor solubility of eletrolyte (Table 1, entries 8-9). A mixture of CH_3CN and H_2O was also tested but led to lower yield of **2a** (Table 1, entry 10). Other commercial eletrolytes including nBu$_4$NOAc, nBu$_4$Br, Et$_4$BF$_4$, and Et$_4$OTs was also examined but nBu$_4$NClO$_4$ remained as the best one (Table 1, entries 11-14). Increasing the constant current to 12 mA or decreasing it to 8 mA caused lower yield of **2a** (Table 1, entries 15-16). On the basis of these results, entry 3 represents the best conditions.

Table 2. Synthesis of 4*H*-1, 3-benzoxazines [a, b]



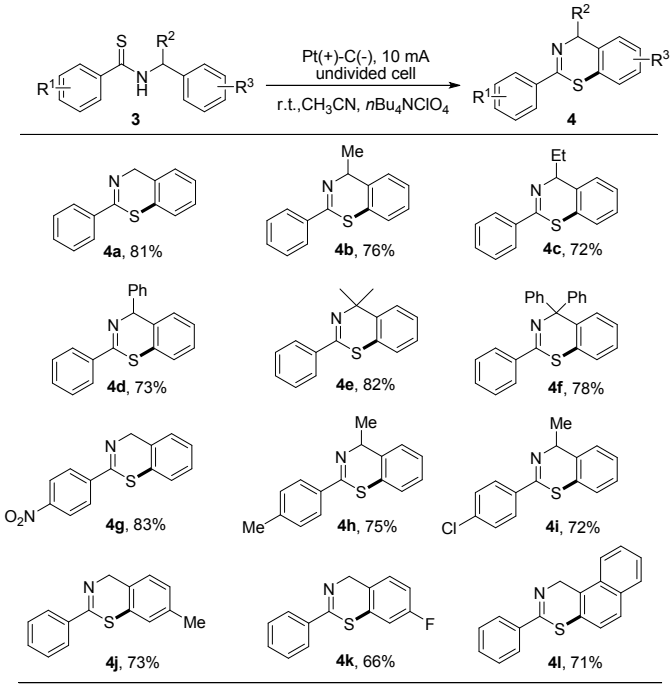


[a] Reaction conditions:The reaction was carried out on 0.2 mmol scale in undivided cell, Pt plate anode (1 cm × 1 cm), graphite rod cathode (Φ 6 mm × 65 mm), constant current = 10 mA, RT, 2.0 h .[b] Isolated yield. [c] With graphite rod anode and Pt plate cathode

Under the optimized reaction conditions, the scope of substrates was investigated with results summarized in Table 2. For substrates with electron-withdrawing or electron-donating group substituted on the benzoyl moiety of **1a**, the corresponding products were obtained in moderate to good yields (Table 2, **2b-d**). Furyl group was also tolerated in this reaction with the target product isolated in 73% yield in case of graphite rod anode and Pt plate cathode, and exchanging the two eletronodes caused only trace of the product (Table 2, **2e**). *N*-Benzyl methylacryloylamide substrate afforded the desired product in 70% yield (Table 2, **2f**). Aliphatic amides were not siutable substrates and the reaction led to complex mixture for the instability of the corresponding cylic products (Table 3, **2g**). For substrate with methyl group substituted on the benzyl moiety of **1a**, the reaction occurred smoothly to give the product in 70% yield in case of graphite rod anode and Pt plate cathode, and

exchanging the two eletronodes caused complex mixture (Table 2, **2h**). The fluoride substrate could also provide the desired product in moderate yield, but the chloride substrate failed (Table 2, **2i, 2i'**). This electrosynthetic method was also compatible for the synthesis of 1*H*-naphtho[1,2-*e*][1,3]oxazine, which represents the core structure of a serie of compounds exhibiting antifungal and antimicarobial activity (Table 3, **2j**). [20] Benzylic mono-substitued or gem-substitued *N*-benzyl amides also furnished the corresponding products in satisfied yields (Table 2, **2k-p**). Substrates with different substituents on the aryl rings of *N*-(1-phenylethyl)benzamide gave the corresponding products in good yields (Table 2, **2q-s**).

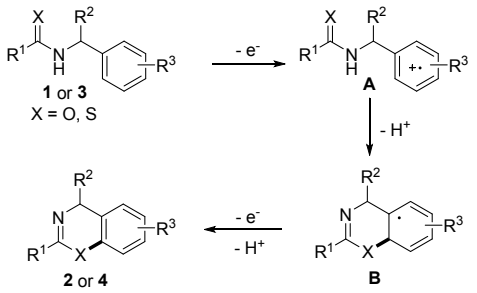
Table 3. Synthesis of 4*H*-1, 3-benzoxthiazines [a, b]



[a] Reaction conditions:The reaction was carried out on 0.2 mmol scale in undivided cell, Pt plate anode (1 cm × 1 cm), graphite rod cathode (*Φ* 6 mm × 65 mm), constant current = 10 mA, RT, 2.0 h .[b] Isolated yield.

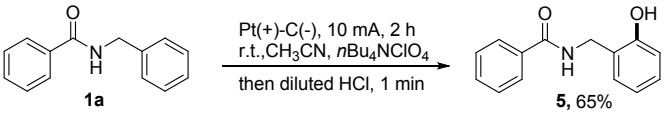
Subsequently, aiming at the synthesis of 4*H*-1, 3-benzothiazines, *N*-benzylbenzothioamide **3a** was examined under the optimized electrolytic conditions, and 2-phenyl- 4*H*-1, 3-benzothiazine **4a** was obtained in 81% yield as anticipated (Table 3, **4a**). Benzylic mono-substitued and gem-substitued *N*-benzylbenzothioamides readily cyclized to provide the corresponding products in good yields (Table 3, **4b-4f**). Substrates having 4-NO_2, 4-Me, 4-Cl substituents on the benzoyl moiety of **3a** also gave the desired products (Table 3, **4g-i**). Substrates with methyl group or F atom substituted on the benzyl moiety of **3a** gave the corresponding products in satisfied yields (Table 3, **4j-k**). Finally, 1*H*-naphtho[1,2-e][1,3]thiazine could also be prepared in good yield with this method (Table 3, **4l**).

Although the detailed reaction mechanism still remains to be clarified, a possible pathway is proposed according to the literature (Scheme 2). [15] Under the electrolysis conditions, the benzylic moeity of the substrate **1** or **3** was oxidized to generate the radical cation **A**, which underwent cyclization and deprotonation to give the intermediate radical **B**. Finnally, **B** was oxidized then underwent rearomatization to give rise to the cyclic product **2** or **4** (Scheme 2).



Scheme 2. Possible mechanism

To demonstrate the utility of our chemistry, a tandem electrolysis and hydrolysis reaction of **1a** was carried out as shown in Scheme 4. After eletrolyzed for 2 hours, the reaction solution of **1a** was added 2 mL diluted HCl (1.0 M) and 2 mL acetone. The cyclic product **2a** disappeared rapidly within 1 minute as monitored by TLC and *N*-(2-hydroxybenzyl) benzamide **5** was isolated as the product in 65% yield for two steps (Scheme 3). Compared with the reported methods for the synthesis of **5** with multiple steps and low total yields, [14b, 21] our method undoubtedly provides a convenient access to this kind of 1-amidoalkyl-2-phenol derivative.



Scheme 3. Tandem electrolysis and hydrolysis procedure

Conclusions

In conclusion, we have exploited a novel and facile approach to 4*H*-1, 3-benzoxazines and 4*H*-1, 3-benzothiazines by electrochemical IDC reaction of *N*-benzylamides and thioamides with moderate to good yields under mild conditions. To suppress the oxidative degradation and improve the yields of the products, the reactions were carried out with Pt plate anode and graphite rod cathode in an undivided cell at room temperature. Further investigation into the mechanism is currently underway in our laboratory.

Experimental Section

General Methods

Commercially available reagents were used as received without further purification unless otherwise indicated. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) using Silica Gel 60 F254 plates and were visualized by fluorescence quenching at 254 nm. For chromatographic purifications, analytically pure solvents were used and the silica gel 300-400 mesh was used as the solid support. ^{1}H NMR

and ^{13}C NMR chemical shifts were reported in δ units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in ^{1}H NMR and ^{13}C NMR spectra were set at 7.26 ppm and 77.0 ppm, respectively.

Typical experimental procedure for the synthesis of 4*H*- 1, 3-benzoxazines 2 and 4*H*- 1, 3-benzothiazines 4

In a 10 mL three-necked flask equipped with Pt plate anode (1 cm × 1 cm) and graphite rod cathode (*Φ* 6 mm × 65 mm), a solution of *N*-benzylbenzamide (42.2 mg, 0.2 mmol) and nBu_4NClO_4 (34.2 mg, 0.5 equiv) in CH_3CN (10 mL) was electrolyzed (constant current = 10 mA) at room temperature under air for 2-3 h. The reaction was stirred until starting material was completely consumed as monitored by TLC. Then the solvent was removed and the crude product was purified by flash chromatography on silica gel by gradient elution (ethyl acetate in petroleum ether, 8:1) to obtain the corresponding product. All the desired products were identified by full spectroscopic characterization and comparison with literature or analogous literature data.

2-phenyl-4*H*-benzo[e][1,3]oxazine [14a] **(2a)** Yellow liquid, 33 mg (78 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.06 (q, *J* = 8.4, 1.3 Hz, 2H), 7.48 – 7.47 (m, *J* = 5.0, 3.7 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 6.9 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 4.80 (s, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.84, 149.51, 132.28, 131.01, 128.26, 128.13, 127.32, 126.03, 124.77, 119.36, 115.55, 45.40.HRMS (ESI-TOF) m/z = 210.0913 $[M + H]^+$, calcd for $C_{14}H_{12}NO$: 210.0919

2-m-tolyl-4*H*-benzo[e][1,3]oxazine (2b) Yellow liquid, 29 mg (65 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.90 – 7.83 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 4.79 (s, 2H), 2.42 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.05, 149.57, 137.97, 132.19, 131.79, 128.15, 128.11, 127.91, 126.01, 124.73, 124.45, 119.39, 115.55, 45.40, 21.40.HRMS (ESI-TOF) m/z = 224.1070 $[M + H]^+$, calcd for $C_{15}H_{14}NO$: 224.1075

3-p-tolyl-4*H*-benzo[e][1,3]oxazine (2c) Yellow liquid, 29 mg (64 % yield);^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 8.1 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 3H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.04 – 7.01 (m, *J* = 15.2, 7.7 Hz, 2H), 4.78 (s, 2H), 2.41 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.94, 149.55, 141.28, 129.46, 128.97, 128.06, 127.26, 125.99, 124.65, 119.45, 115.51, 45.32, 21.50.HRMS (ESI-TOF) m/z = 224.1071 $[M + H]^+$, calcd for $C_{15}H_{14}NO$: 224.1075

3-(4-nitrophenyl)-4*H*-benzo[e][1,3]oxazine (2d) White solid, 42 mg (82 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 (q, *J* = 8.9 Hz, 4H), 7.27 (d, *J* = 6.2 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.05 – 7.02 (m, *J* = 15.8, 7.7 Hz, 2H), 4.84 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.02, 149.37, 149.02, 138.02, 128.40, 128.31, 126.11, 125.33,123.42, 118.67, 115.56, 45.60.HRMS (ESI-TOF) m/z = 255.0764 $[M + H]^+$, calcd for $C_{14}H_{11}N_2O_3$: 255.0770

2-(thiophen-2-yl)-4*H*-benzo[e][1,3]oxazine (2e) Yellow liquid, 32 mg (73 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 3.7 Hz, 1H), 7.43 (d, *J* = 5.0 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.14 – 7.08 (m, 2H), 7.05 (d, *J* = 6.8 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 4.75 (s, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 148.63, 148.24, 135.39, 128.25, 127.77, 127.12, 126.42, 125.07, 123.79, 118.22, 114.49, 44.20.HRMS (ESI-TOF) m/z = 216.0490 $[M + H]^+$, calcd for $C_{12}H_{10}NOS$: 216.0483

2-(prop-1-en-2-yl)-4*H*-benzo[e][1,3]oxazine (2f)Yellow liquid, 24 mg (70 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.19 (t, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 6.9 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.01 (s, 1H), 5.47 (s, 1H), 4.69 (s, 2H), 2.01 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 153.88, 149.52, 136.98, 128.04, 125.88, 124.48, 119.98, 119.20, 115.36, 45.48, 19.20.HRMS (ESI-TOF) m/z = 174.0934 $[M + H]^+$, calcd for $C_{11}H_{12}NO$: 174.0919

7-methyl-2-phenyl-4*H*-benzo[e][1,3]oxazine (2h) Yellow liquid, 31 mg (70 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.05 – 6.90 (m, 2H), 6.87 (s, 1H), 4.75 (s, 2H), 2.31 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.95, 147.33, 134.31, 130.93, 128.56, 128.24, 127.30, 126.33, 125.49, 118.92, 115.25, 45.43, 20.88.HRMS (ESI-TOF) m/z = 224.1070 $[M + H]^+$, calcd for $C_{15}H_{14}NO$: 224.1075

7-fluoro-2-phenyl-4*H*-benzo[e][1,3]oxazine (2i) Yellow liquid, 25 mg (54 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.53 – 7.46 (m, 1H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.04 – 6.99 (m, 1H), 6.83 (t, *J* = 9.6 Hz, 1H), 6.77 (d, *J* = 9.2 Hz, 1H), 4.76 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.34, 160.90, 152.11, 150.08, 131.85, 131.16, 128.30, 127.34, 114.98, 111.74 (d, J_{CF} = 21.6 Hz), 103.40 (d, J_{CF} = 25.2 Hz), 44.97. HRMS (ESI-TOF) m/z = 228.0829 $[M + H]^+$, calcd for $C_{14}H_{11}FNO$: 228.0825

3-phenyl-1*H*-naphtho[1,2-e][1,3]oxazine (2j) Yellow liquid, 37 mg (72 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.29 (d, *J* = 8.3 Hz, 1H), 8.20 (d, *J* = 7.0 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.55 – 7.48 (m, 4H), 7.14 (d, *J* = 8.3 Hz, 1H), 4.94 (s, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.66, 143.13, 132.47, 131.40, 130.07, 127.32, 126.79, 126.37, 125.32, 125.24, 123.16, 122.44, 122.17, 119.48, 112.40, 44.88.HRMS (ESI-TOF) m/z = 260.1066 $[M + H]^+$, calcd for $C_{18}H_{14}NO$: 260.1075

4-methyl-2-phenyl-4*H*-benzo[e][1,3]oxazine [14b] **(2k)** Yellow liquid, 31 mg (75 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 6.9 Hz, 2H), 7.52 – 7.41 (m, 3H), 7.23 – 7.14 (m, *J* = 8.3, 4.6 Hz, 1H), 7.13 (d, *J* = 4.4 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 4.83 (q, *J* = 6.9 Hz, 1H), 1.58 (d, *J* = 6.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.59, 148.85, 132.42, 130.91, 128.22, 127.90, 127.42, 125.98, 124.75, 124.71, 115.48, 50.03, 25.36.HRMS (ESI-TOF) m/z = 224.1073 $[M + H]^+$, calcd for $C_{15}H_{14}NO$: 224.1075

ethyl-2-phenyl-4*H*-benzo[e][1,3]oxazine (2l) Yellow liquid, 39 mg (83 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.23 – 8.03 (m, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.44 (t,

J = 7.3 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.17 – 7.07 (m, 2H), 7.04 (d, *J* = 8.1 Hz, 1H), 4.76 (t, *J* = 5.6 Hz, 1H), 1.99 – 1.91 (m, 1H), 1.90 – 1.83 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.97, 149.51, 132.42, 130.93, 128.25, 127.86, 127.45, 126.28, 124.62, 123.04, 115.37, 55.34, 31.74, 9.06.HRMS (ESI-TOF) m/z = 238.1247 [M + H] $^+$, calcd for $C_{16}H_{16}NO$: 238.1232

2, 4-diphenyl-4*H*-benzo[e][1,3]oxazine (2m) Yellow liquid, 42 mg (73 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 7.3 Hz, 2H), 7.47 (d, *J* = 7.1 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.33-7.26 (m, 4H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 5.85 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.08, 148.58, 144.16, 132.23, 131.15, 128.71, 128.25, 127.75, 127.68, 127.45, 127.41, 124.91, 122.73, 121.75, 115.68, 58.80.HRMS (ESI-TOF) m/z = 286.1220 [M + H] $^+$, calcd for $C_{20}H_{16}NO$: 286.1232

Ethyl 2-phenyl-4*H*-benzo[e][1,3]oxazine-4-carboxylate (2n) Yellow liquid, 29 mg (52 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 7.1 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 1H), 5.54 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.43, 153.92, 148.61, 131.86, 131.47, 129.34, 128.28, 127.82, 126.58, 125.11, 117.25, 116.05, 61.76, 58.20, 14.16.HRMS (ESI-TOF) m/z = 282.1114 [M + H] $^+$, calcd for $C_{17}H_{16}NO_3$: 282.1130

4, 4-dimethyl-2-phenyl-4*H*-benzo[e][1,3]oxazine (2o) Yellow liquid, 34 mg (72 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.26 (s, 1H), 7.23 – 7.22 (m, *J* = 12.2, 4.7 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 1.60 (s, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 150.03, 148.14, 132.62, 130.78, 128.62, 128.21, 127.70, 127.48, 125.32, 124.69, 115.45, 52.68, 32.54.HRMS (ESI-TOF) m/z = 238.1239 [M + H] $^+$, calcd for $C_{16}H_{16}NO$: 238.1232

2, 4, 4-triphenyl-4*H*-benzo[e][1,3]oxazine [14a] **(2p)** Yellow liquid, 55 mg (76 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.27 (m, 5H), 7.25 – 7.21 (m, 6H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 6.7 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.78, 149.03, 147.31, 132.26, 131.07, 129.30, 128.46, 128.34, 128.20, 127.84, 126.83, 125.62, 124.34, 115.70, 65.34.HRMS (ESI-TOF) m/z = 384.1370 [M + Na] $^+$, calcd for $C_{26}H_{19}NNaO$: 384.1364

4-methyl-2-p-tolyl-4*H*-benzo[e][1,3]oxazine (2q) Yellow liquid, 38 mg (80 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.21 (m, 3H), 7.12 (d, *J* = 4.2 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 4.81 (q, *J* = 6.9 Hz, 1H), 2.40 (s, 3H), 1.57 (d, *J* = 6.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.70, 148.91, 141.17, 129.63, 128.93, 127.84, 127.37, 125.95, 124.83, 124.64, 115.47, 49.96, 25.36, 21.50.HRMS (ESI-TOF) m/z = 238.1210 [M + H] $^+$, calcd for $C_{16}H_{16}NO$: 238.1232

2-(4-chlorophenyl)-4-methyl-4*H*-benzo[e][1,3]oxazine (2r) Yellow liquid, 39 mg (76 % yield);^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 – 8.05 (m, *J* = 25.8, 7.7 Hz, 2H), 7.41 (t, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.17 – 7.09 (m, 2H), 7.02 (d, *J* = 7.9 Hz, 1H), 4.81 (q, *J* = 6.8 Hz, 1H), 1.57 (d, *J* = 6.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.70, 148.65, 137.08, 133.38, 130.89, 128.79, 128.46, 127.97, 126.01, 124.91, 115.45, 50.03, 25.31.HRMS (ESI-TOF) m/z = 258.0678 [M +H] $^+$, calcd for $C_{15}H_{13}ClNO$: 258.0686

7-methoxy-4-methyl-2-phenyl-4*H*-benzo[e][1,3]oxazine (2s) Yellow liquid, 40 mg (78 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 7.1 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 1H), 6.78 (q, *J* = 8.8, 2.9 Hz, 1H), 6.65 (d, *J* = 2.9 Hz, 1H), 4.81 (q, *J* = 6.9 Hz, 1H), 3.80 (s, 3H), 1.58 (d, *J* = 6.9 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 156.53, 151.83, 142.74, 132.52, 130.87, 128.22, 127.39, 125.45, 116.31, 113.31, 110.66, 55.69, 50.39, 25.35.HRMS (ESI-TOF) m/z = 254.1183 [M +H] $^+$, calcd for $C_{16}H_{16}NO_2$: 254.1181

2-phenyl-4*H*-benzo[e][1,3]thiazine [19a] **(4a)**Yellow solid, 36 mg (81 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.40 – 7.38 (m, 1H), 7.33 – 7.29 (m, 3H), 4.79 (s, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 161.68, 136.98, 131.36, 131.16, 128.55, 127.94, 127.77, 127.56, 127.53, 126.90, 126.65, 56.78.HRMS (ESI-TOF) m/z = 226.0664 [M +H] $^+$, calcd for $C_{14}H_{12}NS$: 226.0690

4-methyl-2-phenyl-4*H*-benzo[e][1,3]thiazine (4b) Yellow solid, 36 mg (76 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 6.7 Hz, 2H), 7.44 (q, *J* = 11.2, 7.2 Hz, 3H), 7.39 – 7.27 (m, 4H), 4.55 (q, *J* = 6.9 Hz, 1H), 1.81 (d, *J* = 6.9 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.71, 137.22, 135.17, 131.03, 130.53, 128.52, 127.74, 127.62, 127.05, 126.72, 125.33, 60.06, 18.50.HRMS (ESI-TOF) m/z = 240.0857 [M +H] $^+$, calcd for $C_{15}H_{14}NS$: 240.0847

4-ethyl-2-phenyl-4*H*-benzo[e][1,3]thiazine (4c) Yellow solid, 36 mg (72 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 7.3 Hz, 2H), 7.49 – 7.45 (m, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.28 (m, *J* = 22.4, 7.5 Hz, 3H), 4.65 (t, *J* = 7.1 Hz, 1H), 2.07 – 2.03 (m, *J* = 22.8, 13.7, 7.0 Hz, 2H), 1.13 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.79, 137.45, 133.55, 131.01, 130.05, 128.51, 127.69, 127.33, 127.06, 126.79, 126.63, 66.27, 25.01, 11.31.HRMS (ESI-TOF) m/z = 254.1017 [M +H] $^+$, calcd for $C_{16}H_{16}NS$: 254.1003

2, 4-diphenyl-4*H*-benzo[e][1,3]thiazine (4d) Yellow solid, 44 mg (73 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.47 – 7.42 (m, 5H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.32 – 7.30 (m, *J* = 14.9, 7.7 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 5.38 (s, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 160.91, 140.39, 136.96, 135.38, 131.21, 130.93, 128.75, 128.56, 128.53, 128.41, 127.93, 127.48, 127.27, 127.03, 126.65, 69.01.HRMS (ESI-TOF) m/z = 302.1021 [M +H] $^+$, calcd for $C_{20}H_{16}NS$: 302.1003

4, 4-dimethyl-2-phenyl-4*H*-benzo[e][1,3]thiazine (4e) Yellow solid, 41 mg (82 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 7.4 Hz, 2H), 7.49 (d, *J* = 8.0 Hz,

1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.26 – 7.21 (m, 1H), 1.70 (s, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 155.99, 137.90, 137.43, 130.86, 128.88, 128.51, 127.89, 127.45, 126.90, 126.67, 124.77, 60.27, 27.32.HRMS (ESI-TOF) m/z = 254.1015 [M +H] $^+$, calcd for $C_{16}H_{16}NS$: 254.1003

2, 4, 4-triphenyl-4*H*-benzo[e][1,3]thiazine (4f) Yellow solid, 59 mg (78 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.10 (d, *J* = 7.1 Hz, 2H), 7.51 – 7.39 (m, 4H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.25 (m, *J* = 6.1, 4.0 Hz, 6H), 7.23 – 7.21 (m, 1H), 7.14 – 7.13 (m, *J* = 6.5, 3.2 Hz, 4H), 6.74 (d, *J* = 8.9 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.30, 145.60, 137.54, 136.73, 131.19, 130.71, 129.43, 129.27, 128.51, 127.82, 127.62, 127.40, 127.22, 126.98, 126.74, 74.30.HRMS (ESI-TOF) m/z = 378.1314 [M +H] $^+$, calcd for $C_{26}H_{20}NS$: 378.1316

3-(4-nitrophenyl)-4*H*-benzo[e][1,3]thiazine (4g) White solid, 45 mg (83 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.27 (d, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 6.1 Hz, 3H), 4.85 (s, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.81, 149.36, 142.38, 130.64, 129.98, 128.57, 128.02, 127.89, 127.08, 126.68, 123.73, 57.10.HRMS (ESI-TOF) m/z = 271.0518 [M +H] $^+$, calcd for $C_{14}H_{11}N_2O_2S$: 271.0541

4-methyl-2-p-tolyl-4*H*-benzo[e][1,3]thiazine (4h) Yellow solid, 38 mg (75 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 8.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 4.53 (q, *J* = 6.9 Hz, 1H), 2.38 (s, 3H), 1.80 (d, *J* = 6.9 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.60, 141.37, 135.35, 134.52, 130.68, 129.21, 127.70, 127.53, 126.99, 126.72, 125.29, 59.96, 21.45, 18.50.HRMS (ESI-TOF) m/z = 254.0997 [M +H] $^+$, calcd for $C_{16}H_{16}NS$: 254.1003

2-(4-chlorophenyl)-4-methyl-4*H*-benzo[e][1,3]thiazine (4i) Yellow solid, 39 mg (72 % yield);^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 8.5 Hz, 2H), 7.39 (s, 2H), 7.37 (d, *J* = 4.2 Hz, 2H), 7.35 (d, *J* = 6.5 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 4.51 (q, *J* = 6.9 Hz, 1H), 1.80 (d, *J* = 6.9 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.67, 135.08, 133.41, 130.19, 129.72, 129.03, 128.73, 127.77, 127.15, 126.74, 125.36, 60.12, 18.45.HRMS (ESI-TOF) m/z = 274.0447 [M +H] $^+$, calcd for $C_{15}H_{13}ClNS$: 274.0457

7-methyl-2-phenyl-4*H*-benzo[e][1,3]thiazine (4j) Yellow solid, 35 mg (73 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 7.4 Hz, 1H), 4.75 (s, 2H), 2.35 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 161.61, 137.46, 137.11, 131.08, 130.76, 128.52, 128.38, 128.32, 127.73, 127.00, 126.65, 56.40, 21.09.HRMS (ESI-TOF) m/z = 240.0833 [M +H] $^+$, calcd for $C_{15}H_{14}NS$: 240.0847

7-fluoro-2-phenyl-4*H*-benzo[e][1,3]thiazine (4k) Yellow solid, 32 mg (66 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 7.8 Hz, 2H), 7.50 – 7.47 (m, 1H),7.44 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.28 (m, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 10.8 Hz, 1H), 4.76 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 160.83 (d, J_{CF} = 247.2 Hz), 159.82, 135.57, 130.28, 128.32, 127.55, 126.95 (d, J_{CF} = 8.6 Hz), 126.71, 125.89, 113.53 (d, J_{CF} = 21.7 Hz), 112.58 (d, J_{CF} = 24.2 Hz), 54.97.HRMS (ESI-TOF) m/z = 244.0567 [M +H] $^+$, calcd for $C_{14}H_{11}FNS$: 244.0596

3-phenyl-1*H*-naphtho[1,2-e][1,3]thiazine (4l) Yellow solid, 39 mg (71 % yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.26 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.51 – 7.43 (m, 5H), 5.24 (s, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 161.56, 135.67, 132.09, 130.16, 129.45, 127.71, 127.54, 126.71, 126.62, 125.96, 125.16, 124.66, 123.51, 121.34, 50.80.HRMS (ESI-TOF) m/z = 276.0843 [M +H] $^+$, calcd for $C_{18}H_{14}NS$: 276.0847

Typical experimental procedure for the synthesis of *N*-(2-hydroxybenzyl)benzamide 5

In a 10 mL three-necked flask equipped with Pt plate anode (1 cm × 1 cm) and graphite rod cathode (*Φ* 6 mm × 65 mm), a solution of *N*-benzylbenzamide (42.2 mg, 0.2 mmol) and nBu_4NClO_4 (34.2 mg, 0.5 equiv) in CH_3CN (10 mL) was electrolyzed (constant current = 10 mA) at room temperature under air for 2-3 h. The reaction was stirred until starting material was completely consumed as monitored by TLC. Then 2 mL diluted HCl (1.0 M) and 2 mL acetone was added and the solution was stirred for 1 minute. The solvent was removed and the crude product was purified by flash chromatography on silica gel by gradient elution (ethyl acetate in petroleum ether, 6:1) to obtain the product.

***N*-(2-hydroxybenzyl)benzamide** [21a] **(5)** Yellow solid, (65% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.59 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.25 (s, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 4.55 (d, *J* = 6.5 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.68, 154.85, 131.77, 131.22, 129.88, 129.08, 127.66, 126.19, 123.12, 118.91, 116.89, 39.98.HRMS (ESI-TOF) m/z = 228.1042 [M +H] $^+$, calcd for $C_{14}H_{14}NO_2$: 228.1025

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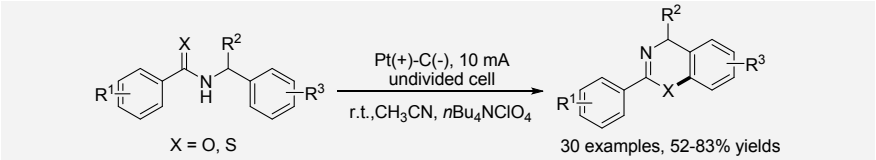

Intramolecular dehydrogenative coupling of *N*-benzylamides and thioamides was investigated under electrolysis condition and 4*H*-1, 3-benzoxazines and 4*H*- 1, 3-benzothiazine were obtained in moderate to good yields in CH_3CN at room temperature

((Organic electrosynthesis))

Hui Yu*, Mingdong Jiao, Ruohe Huang, Xiaowei Fang Page No. - Page No.

Electrochemical intramolecular dehydrogenative coupling of *N*-benzyl(thio)amides: a direct and facile synthesis of 4*H*- 1, 3-benzoxazines and 4*H*- 1, 3-benzothiazines

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