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Palladium-Catalyzed Carbonylation of *o*-Iodoanilines for Synthesis of Isatoic Anhydrides

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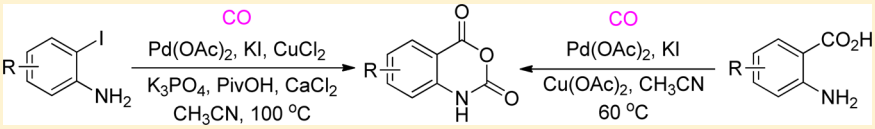
Supporting Information



ABSTRACT: A novel palladium-catalyzed oxidative double carbonylation of *o*-iodoanilines for the synthesis of isatoic anhydrides has been developed. The reaction employs readily available *o*-iodoanilines as the starting materials and proceeds under mild conditions. For extension, palladium-catalyzed oxidative carbonylation of anthranilic acids was developed for the synthesis of substituted isatoic anhydrides in high to excellent yields.

Over the past decades, transition-metal-catalyzed carbonylations with CO as a C1 source have been demonstrated as one of the most powerful tools for the synthesis of various of carbonyl compounds.[1] Especially, palladium-catalyzed carbonylation of aryl iodides or aryl bromides has been widely applied to synthesize aromatic esters, amides, and ketones in both academic and industrial communities.[2] Palladium-catalyzed carbonylation of challenging substrates such as aryl chlorides or aryl triflates has also been achieved by using electron-rich and bulky phosphine ligands.[3] Recently, carbonylation with a subsequent intramolecular cyclization reaction has been shown to be an efficient process for the straightforward synthesis of heterocycles.[4] The pioneering work of palladium-catalyzed carbonylation of *o*-iodoanilines, *o*-iodophenols, or *o*-iodothiophenols with a series of suitable coupling partners has been developed for the synthesis of valuable heterocycles by Alper and co-workers.[5] The group of Wu and Beller has developed a series of elegant palladium-catalyzed carbonylation of *o*-bromobenzaldehydes, *o*-hydroxyacetophenones, *o*-hydroxybenzaldehydes, and *o*-aminobenzamide with suitable coupling partners for the synthesis of pharmaceutical heterocycles.[6] However, the double carbonylation of *o*-iodoanilines for direct synthesis of isatoic anhydrides, which are a class of valuable chemicals and versatile building blocks, has not yet been realized.

Conventional methods for the synthesis of substituted isatoic anhydrides involve cyclization of anthranilic acid by highly toxic chloroformate or triphosgene.[7] The reaction is limited in substrate scope and proceeds under harsh conditions. New methods for the synthesis of substituted isatoic anhydrides that are compatible with various functional groups and proceed under mild conditions remain highly desirable. In 2012, we developed a palladium-catalyzed carbonylation of C−H bonds of *N*-alkyl anilines for the synthesis of isatoic anhydrides.[8] This reaction tolerates a wide range of functional groups and is a practical method for the rapid synthesis of substituted *N*-alkyl isatoic anhydrides under mild conditions. However, the intrinsic alkyl group on the nitrogen atom was hardly removable to produce the synthetically useful *N*-unsubstituted isatoic anhydrides. We hypothesized that palladium-catalyzed double carbonylation of readily available *o*-iodoanilines may be a straightforward route to synthesize of *N*-unsubstituted isatoic anhydrides. In this paper, we have developed a novel palladium-catalyzed oxidative double carbonylation of *o*-iodoanilines for the synthesis of *N*-unsubstituted isatoic anhydrides.

We began our study by investigating the palladium-catalyzed oxidative double carbonylation of *o*-iodoaniline **1a** in the presence of $CuCl_2$ and K_2CO_3 in CH_3CN. The desired isatoic anhydride **3a** was obtained in 21% yield under 3 atm of CO/O_2 (2:1) at 100 °C (Table 1, entry 1). However, no desired product was observed in the presence of $CuBr_2$, and 2-methyl-4*H*-benzo[*d*][1, 3]oxazin-4-one **4** was obtained in 14% yield when $Cu(OAc)_2$ was used as the oxidant (Table 1, entry 3). Screening of various bases and solvents revealed that K_3PO_4 and CH_3CN were the best choice for this carbonylation reaction (Table 1, entries 4−8). Then KI, which has been shown to improve the efficiency of palladium-catalyzed carbonylations, was added to the reaction.[2c,8,9] The yield of **3a** was slightly improved to 31% (Table 1, entry 9). To examine if the oxygen in the isatoic anhydride was coming from water in the solvent, 2.0 equiv of H_2O was added in the reaction. However, the reaction turned messy although a similar yield was obtained (Table 1, entry 10). Therefore, various dehydrating agents such as $CaCl_2$, 4 Å molecular sieves, $MgSO_4$, and Na_2SO_4, along with PivOH, which may provide oxygen, were screened to improve the reaction efficiency. We were pleased to find that the yield of isatoic anhydride **3a** was improved to 68% when KI, anhydrous $CaCl_2$, and PivOH were combined to be the additives (Table 1, entry 13). Changing the

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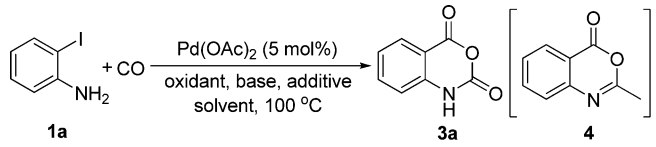
Table 1. Optimization of Conditions for Palladium-Catalyzed Oxidative Double Carbonylation of *o*-Iodoaniline[a]



1a 3a 4

entry	oxidant	base	additive (equiv)	solvent	yield (%)
1	$CuCl_2$	K_2CO_3		CH_3CN	21
2	$CuBr_2$	K_2CO_3		CH_3CN	0
3	$Cu(OAc)_2$	K_2CO_3		CH_3CN	0 (14)[b]
4	$CuCl_2$	Cs_2CO_3		CH_3CN	6
5	$CuCl_2$	*t*-BuOK		CH_3CN	25
6	$CuCl_2$	K_3PO_4		CH_3CN	26
7	$CuCl_2$	NEt_3		CH_3CN	24
8	$CuCl_2$	K_3PO_4		DMF	6
9	$CuCl_2$	K_3PO_4	KI (0.2)	CH_3CN	31
10	$CuCl_2$	K_3PO_4	KI (0.2)/H_2O (2.0)	CH_3CN	30
11	$CuCl_2$	K_3PO_4	KI (0.2)/$CaCl_2$ (2.0)	CH_3CN	35
12	$CuCl_2$	K_3PO_4	KI (0.2)/PivOH (3.0)	CH_3CN	40
13	**$CuCl_2$**	**K_3PO_4**	**KI (0.2)/$CaCl_2$ (2.0)/ PivOH (3.0)**	**CH_3CN**	**68**
14	$CuCl_2$	K_3PO_4	KI (0.2)/$CaCl_2$(2.0)/PivOH (1.0)	CH_3CN	57
15	$CuCl_2$	K_3PO_4	KI (0.2)/$CaCl_2$(2.0)/PivOH (5.0)	CH_3CN	58
16	$CuCl_2$	K_3PO_4	KI (0.2)/4 Å MS/PivOH (3.0)	CH_3CN	33[c]
17	$CuCl_2$	K_3PO_4	KI (0.2)/$MgSO_4$ (2.0)/PivOH (3.0)	CH_3CN	41
18	$CuCl_2$	K_3PO_4	KI (0.2)/Na_2SO_4 (2.0)/PivOH (3.0)	CH_3CN	42

[a]Reaction conditions: **1a** (0.2 mmol), $Pd(OAc)_2$ (5 mol %), oxidant (1.0 equiv), base (1.0 equiv), solvent (2 mL), CO/O_2 (2:1) 3 atm, at 100 °C for 24 h. [b]2-Methyl-4*H*-benzo[*d*][1,3]oxazin-4-one **4** (14%) was isolated. [c]4 Å MS (60 mg).

amount of PivOH resulted in no improvement (Table 1, entries 14 and 15), and 4 Å molecular sieves, $MgSO_4$, and Na_2SO_4 were less effective than $CaCl_2$ (Table 1, entries 16−18).

With the optimized reaction conditions in hand, a series of *o*-iodoanilines[10] were investigated. As shown in Table 2, this novel double carbonylation reaction displayed high functional group tolerance and proved to be a general method for the preparation of isatoic anhydrides. Halogen substituents such as fluoro, chloro, and bromo groups were tolerated under the conditions. Isatoic anhydrides **3b** and **3c** were obtained in 79−80% yields when 4-fluoro- or 4-chloro-substituted *o*-iodoanilines were used as the substrates (Table 2, entries 2 and 3). 5-Chloro- and 4-bromo-substituted *o*-iodoanilines gave the corresponding isatoic anhydrides **3d** and **3e** in 57% and 46% yields, respectively. Reactions with electron-withdrawing group substituted *o*-iodoanilines proceeded smoothly under the standard conditions. For example, ester-substituted isatoic anhydrides **3f** and **3g** were obtained in good yields (Table 2, entries 6 and 7). However, strong electron-withdrawing nitrile, acetyl and nitro substituted *o*-iodoanilines produced only the corresponding isatoic anhydrides **3h−3j** in 38−57% yields respectively (Table 2, entries 8−10). In contrast to electron-withdrawing group substituted substrates, electron-donating group substituted *o*-iodoanilines were less reactive and gave lower yields of isatoic anhydrides (Table 2, entries 11 and 12). In these reactions, several byproducts, such as *N*-(2-iodophenyl)pivalamide, 2-pivalamidobenzoic acid, and 1,3-bis(2-iodophenyl)urea, were observed. Notably, 1-iodonaphthalen-2-amine **1m** was tolerated under the conditions as well to afford 1*H*-naphtho[2,1-*d*][1,3]oxazine-1,3(4*H*)-dione **3m** in 56% yield (Table 2, entry 13). However, only 9% yield of *N*-methyl isatoic anhydride was obtained when *N*-methyl *o*-iodoaniline was used as the substrate.

In our previous palladium-catalyzed carbonylation of C−H bonds of *N*-alkyl anilines for the synthesis of isatoic anhydrides,[8] we assumed that anthranilic acid should be a key intermediate in the reaction. After a brief survey of reaction conditions (see Supporting Information), we found that palladium-catalyzed carbonylation of anthranilic acids proceeded smoothly to afford isatoic anhydrides in nearly quantitative yields under slightly modified conditions (Scheme 1).

On the basis of the aforementioned results and previous studies, a tentative mechanism for this carbonylation is proposed in Scheme 2. First, oxidative addition of *o*-iodoaniline to Pd(0) followed by insertion of carbon monoxide gives an acylpalladium intermediate **B**. Then, the intermediate **B** is transformed into intermediate **C**, assisted by K_3PO_4 and PivOH.[11] Reductive elimination of intermediate **C** affords Pd(0) species and intermediate **D**. Metathesis of intermediate **D** with PivOH provides anthranilic acid **E** by expulsion of $(Piv)_2O$.[12] Meanwhile, Pd(0) is oxidized by Cu(II) to generate the $Pd(II)X_2$ catalyst. Subsequently, metathesis of $Pd(II)X_2$ specie and **E** produces the intermediate **F**, which undergoes CO insertion to give intermediate **G**. Finally, reductive elimination of intermediate **G** in the presence of K_3PO_4 affords isatoic anhydride **3** and Pd(0).

In summary, we have developed a novel palladium-catalyzed oxidative double carbonylation of *o*-iodoanilines for the synthesis of *N*-unsubstituted isatoic anhydrides. The reaction employs readily available *o*-iodoanilines as the starting materials and tolerates a range of functional groups. A tentative mechanism of the reaction has been proposed. Palladium-catalyzed oxidative carbonylation of anthranilic acids has also been developed for the synthesis of substituted isatoic anhydrides in high to excellent yields. The carbonylation reactions provide straightforward routes for the synthesis of

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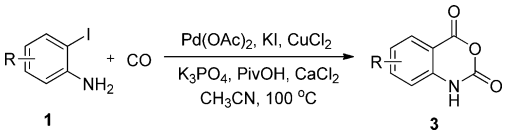
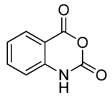
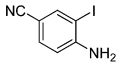
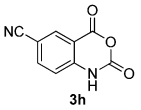
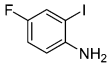
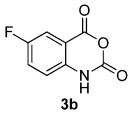
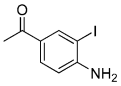
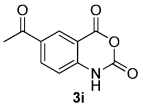
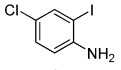
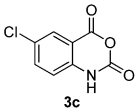
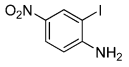
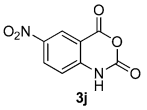
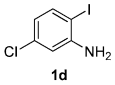
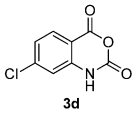
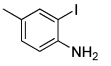
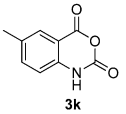
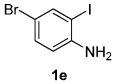
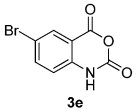
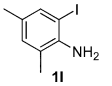
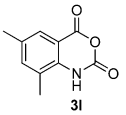
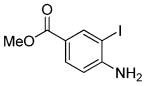
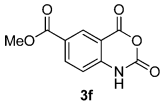
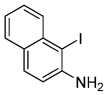
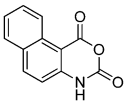
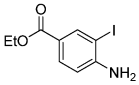
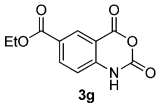
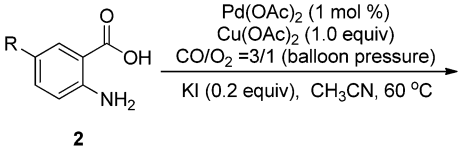
Table 2. Scope of Palladium-Catalyzed Carbonylation of *o*-Iodoanilines for the Synthesis of Isatoic Anhydrides[a]



entry	substrate	product	time (h)	yield (%)	entry	substrate	product	time (h)	yield (%)
1	 1a	 3a	24	68	8	 1h	 3h	84	57
2	 1b	 3b	36	79	9	 1i	 3i	48	48
3	 1c	 3c	60	80	10	 1j	 3j	96	38
4	 1d	 3d	48	57	11	 1k	 3k	24	51
5	 1e	 3e	60	46	12	 1l	 3l	36	44
6	 1f	 3f	72	68	13	 1m	 3m	72	56
7	 1g	 3g	72	70					

[a]Reaction conditions: **1** (0.2 mmol), $Pd(OAc)_2$ (5 mol %), $CuCl_2$ (1.0 equiv), K_3PO_4 (1.0 equiv), KI (0.2 equiv), $CaCl_2$ (2.0 equiv), PivOH (3.0 equiv), CO/O_2 (2:1) 3 atm, CH_3CN (2 mL), at 100 °C, 24–96 h.

Scheme 1. Palladium-Catalyzed Carbonylation of Anthranilic Acids for Synthesis of Isatoic Anhydrides



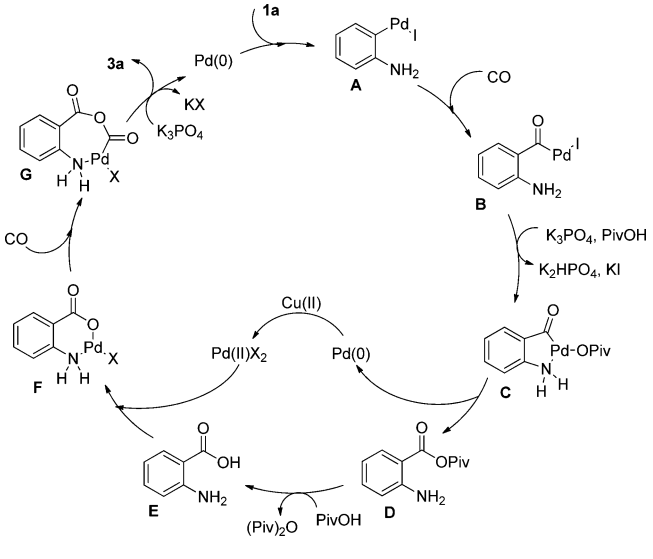
R=H, **3a,** 99% yield
R=F, **3b**, 85% yield
R=Cl, **3c,** 99% yield
R=Br, **3e,** 86% yield
R=Me, **3k,** 94% yield
R=OMe, **3n,** 91% yield

valuable *N*-unsubstituted isatoic anhydrides under mild conditions.

EXPERIMENTAL SECTION

General Information. ^1H NMR spectra were recorded at 400 MHz in DMSO-d_6, and ^{13}C NMR spectra were recorded at 100 MHz in DMSO-d_6. The following abbreviations are used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All products were further characterized by HRMS (ESI-TOF-Q); copies of their ^1H NMR and ^{13}C NMR spectra are provided

Scheme 2. Tentative Mechanism for Palladium-Catalyzed Carbonylation of *o*-Iodoanilines



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in Supporting Information. Infrared spectra were obtained by using FT-IR spectrometer. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. The *o*-iodoanilines **1a** and **1d** were prepared from the corresponding 2-nitroaniline according to the literature procedures.[10a] Others were prepared from the iodination of the corresponding substituted anilines in the presence of KI and H_2O_2 in acetic acid.[10b]

General Procedure for Palladium-Catalyzed Oxidative Double Carbonylation of *o*-Iodoanilines for the Synthesis of Isatoic Anhydrides. A mixture of *o*-iodoaniline **1** (0.2 mmol), $Pd(OAc)_2$ (5 mol %, 2.2 mg), $CuCl_2$ (0.2 mmol, 26.9 mg), KI (0.04 mmol, 6.6 mg), PivOH (0.6 mmol, 61.2 mg), K_3PO_4 (0.2 mmol, 42.4 mg), and $CaCl_2$ (0.4 mmol, 44.4 mg) was stirred in CH_3CN (2 mL) at 100 °C under 3 atm of CO/O_2 (2:1). After completion of the reaction (24−96 h), the reaction mixture was cooled to room temperature and vented to discharge the excess CO and O_2. The reaction was quenched with H_2O (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding isatoic anhydride **3** with hexanes/EtOAc (3/1) as the eluent.

General Procedure for Palladium-Catalyzed Carbonylation of Anthranilic Acids for the Synthesis of Isatoic Anhydrides. Anthranilic acid **2** (0.2 mmol), $Pd(OAc)_2$ (1 mol %, 0.4 mg), $Cu(OAc)_2$ (0.2 mmol, 36.3 mg), KI (0.04 mmol, 6.6 mg), and CH_3CN (2 mL) were charged in a 10 mL round-bottom flask. A balloon filled with CO/O_2 (3:1) was connected to the flask. Then, the flask was evacuated and backfilled (3 times, balloon) and stirred at 60 °C. When the reaction was completed (detected by TLC), the mixture was cooled to room temperature and vented to discharge the excess CO and O_2. The reaction was quenched with H_2O (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding isatoic anhydride **3** with hexanes/EtOAc (3/1) as the eluent.

1*H*-Benzo[*d*][1,3]oxazine-2,4-dione (3a). Yield: 68% (22.2 mg), white solid, mp 205−207 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.73 (s, 1 H), 7.90 (d, J = 7.6 Hz, 1 H), 7.73 (t, J = 7.6 Hz, 1 H), 7.24 (t, J = 7.2 Hz, 1 H), 7.14 (d, J = 8.0 Hz, 1 H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 159.9, 147.1, 141.4, 137.0, 128.9, 123.5, 115.3, 110.3. HRMS calcd (ESI) m/z for $C_8H_5NNaO_3$: $[M + Na]^+$ 186.0162, found 186.0167. MS m/z (relative intensity) 163 (38), 119 (100), 92 (70), 64 (30).

6-Fluoro-1*H*-benzo[*d*][1,3]oxazine-2,4-dione (3b). Yield: 79% (28.7 mg), white solid, mp 225−227 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.79 (s, 1 H), 7.64 (s, 2 H), 7.16 (d, J = 4.0 Hz, 1 H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 159.2, 157.6 (d, J_{CF} = 240.3 Hz), 146.8, 138.1, 124.8 (d, J_{CF} = 24 Hz), 117.6 (d, J_{CF} = 7.7 Hz), 114.0 (d, J_{CF} = 24.1 Hz), 111.5 (d, J_{CF} = 8.2 Hz). HRMS calcd (ESI) m/z for $C_8H_4FNNaO_3$: $[M + Na]^+$ 204.0067, found 204.0064. MS m/z (relative intensity) 181 (35), 137 (100), 109 (60), 82 (48).

6-Chloro-1*H*-benzo[*d*][1,3]oxazine-2,4-dione (3c). Yield: 80% (31.5 mg), white solid, mp 247−249 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.87 (s, 1 H), 7.84 (s, 1 H), 7.76 (d, J = 8.4 Hz, 1 H), 7.15 (d, J = 8.8 Hz, 1 H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 159.0, 146.8, 140.3, 136.7, 127.7, 127.2, 117.5, 112.0. HRMS calcd (ESI) m/z for $C_8H_4ClNNaO_3$: $[M + Na]^+$ 219.9772, found 219.9771. MS m/z (relative intensity) 197 (46), 153 (100), 125 (48), 63 (50).

7-Chloro-1*H*-benzo[*d*][1,3]oxazine-2,4-dione (3d). Yield: 57% (22.4 mg), white solid, mp 238−240 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.86 (s, 1 H), 7.90 (d, J = 8.4 Hz, 1 H), 7.28 (d, J = 8.0 Hz, 1 H), 7.13 (s, 1 H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 159.2, 147.0, 142.6, 141.2, 130.9, 123.7, 114.8, 109.5. HRMS calcd (ESI) m/z for $C_8H_4ClNNaO_3$: $[M + Na]^+$ 219.9772, found 219.9775. MS m/z (relative intensity) 197 (48), 153 (100), 126 (80), 63 (50).

6-Bromo-1*H*-benzo[*d*][1,3]oxazine-2,4-dione (3e). Yield: 46% (22.2 mg), white solid, mp 230−232 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.86 (s, 1 H), 7.97 (s, 1 H), 7.88 (d, J = 8.0 Hz, 1 H), 7.09 (d, J = 8.8 Hz, 1 H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 158.8, 146.7, 140.6, 139.3, 130.6, 117.7, 114.6, 112.4. HRMS calcd (ESI) m/z for $C_8H_4BrNNaO_3$: $[M + Na]^+$ 263.9267, found 263.9271. MS m/z (relative intensity) 241 (48), 197 (100), 171 (25), 90 (50), 63 (80).

Methyl 2,4-Dioxo-2,4-dihydro-1*H*-benzo[*d*][1,3]oxazine-6-carboxylate (3f). Yield: 68% (30.1 mg), white solid, mp 231−233 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 12.09 (s, 1 H), 8.37 (s, 1 H), 8.23 (d, J = 8.4 Hz, 1 H), 7.23 (d, J = 8.4 Hz, 1 H), 3.87 (s, 3 H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 164.7, 159.3, 146.8, 144.8, 136.9, 130.2, 124.4, 115.9, 110.7, 52.4. HRMS calcd (ESI) m/z for $C_{10}H_7NNaO_5$: $[M + Na]^+$ 244.0216, found 244.0221. MS m/z (relative intensity) 221 (30), 177 (100), 146 (60), 119 (35), 90 (25), 63 (30).

Ethyl 2,4-Dioxo-2,4-dihydro-1*H*-benzo[*d*][1,3]oxazine-6-carboxylate (3g). Yield: 70% (32.8 mg), white solid, mp 224−226 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 12.08 (s, 1 H), 8.37 (s, 1 H), 8.23 (d, J = 8.4 Hz, 1 H), 7.23 (d, J = 8.8 Hz, 1 H), 4.36−4.30 (m, 2 H), 1.34 (t, J = 7.2 Hz, 3 H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 164.2, 159.3, 146.8, 144.7, 136.8, 130.1, 124.7, 115.9, 110.5, 61.2, 14.1. HRMS calcd (ESI) m/z for $C_{11}H_9NNaO_5$: $[M + Na]^+$ 258.0373, found 258.0378. MS m/z (relative intensity) 235 (30), 191 (100), 163 (40), 146 (50), 90 (25), 63 (25).

2,4-Dioxo-2,4-dihydro-1*H*-benzo[*d*][1,3]oxazine-6-carbonitrile (3h). Yield: 57% (21.6 mg), yellow solid, mp 254−256 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 12.18 (s, 1 H), 8.36 (s, 1 H), 8.09 (d, J = 8.4 Hz, 1 H), 7.25 (d, J = 8.4 Hz, 1 H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 158.5, 146.6, 144.6, 139.4, 133.8, 117.7, 116.6, 111.6, 105.7. HRMS calcd (ESI) m/z for $C_9H_4N_2NaO_3$: $[M + Na]^+$ 211.0114, found 211.0114. MS m/z (relative intensity) 188 (35), 144 (100), 117 (70), 89 (25), 62 (25).

6-Acetyl-1*H*-benzo[*d*][1,3]oxazine-2,4-dione (3i). Yield: 48% (20.0 mg), yellow solid, mp 196−198 °C; IR (KBr, cm^{-1}): 3441, 2923, 1764, 1684, 1619, 1515, 1423. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 12.08 (s, 1 H), 8.41 (s, 1 H), 8.24 (d, J = 8.4 Hz, 1 H), 7.22 (d, J = 8.4 Hz, 1 H), 2.60 (s, 3 H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 195.8, 159.4, 146.9, 144.7, 136.0, 131.9, 129.6, 115.7, 110.4, 26.5. HRMS calcd (ESI) m/z for $C_{10}H_6NO_4$: $[M - H]^+$ 204.0302, found 204.0310. MS m/z (relative intensity) 205 (45), 190 (15), 161 (60), 146 (100), 90 (25), 63 (25).

6-Nitro-1*H*-benzo[*d*][1,3]oxazine-2,4-dione (3j). Yield: 38% (15.8 mg), yellow solid, mp 232−234 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 12.37 (s, 1 H), 8.56 (s, 1 H), 8.52 (d, J = 8.8 Hz, 1 H), 7.30 (d, J = 9.2 Hz, 1 H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 158.7, 146.6, 146.1, 142.4, 131.3, 124.6, 116.7, 111.2. HRMS calcd (ESI) m/z for $C_8H_4N_2NaO_5$: $[M + Na]^+$ 231.0012, found 231.0015. MS m/z (relative intensity) 208 (30), 182 (90), 164 (100), 134 (20), 106 (25), 90 (48), 63 (35).

6-Methyl-1*H*-benzo[*d*][1,3]oxazine-2,4-dione (3k). Yield: 51% (18.0 mg), white solid, mp 216−218 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.64 (s, 1 H), 7.68 (s, 1 H), 7.54 (d, J = 8.4 Hz, 1 H), 7.03 (d, J = 8.4 Hz, 1 H), 2.31 (s, 3 H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 159.9, 147.1, 139.2, 137.9, 133.0, 128.3, 115.3, 110.0, 20.1. HRMS calcd (ESI) m/z for $C_9H_7NNaO_3$: $[M + Na]^+$ 200.0318, found 200.0319. MS m/z (relative intensity) 177 (30), 133 (100), 104 (75), 78 (30), 51 (25).

6,8-Dimethyl-1*H*-benzo[*d*][1,3]oxazine-2,4-dione (3l). Yield: 44% (16.8 mg), white solid, mp 212−214 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 10.98 (s, 1 H), 7.57 (s, 1 H), 7.41 (s, 1 H), 2.29 (s, 6 H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 160.0, 147.3, 139.0, 137.6, 132.5, 126.1, 124.3, 110.2, 19.9, 16.9. HRMS calcd (ESI) m/z for $C_{10}H_9NNaO_3$: $[M + Na]^+$ 214.0475, found 214.0481. MS m/z (relative intensity) 191 (50), 147 (60), 119 (100), 104 (35), 91 (35), 66(20).

1*H*-Naphtho[2,1-*d*][1,3]oxazine-1,3(4*H*)-dione (3m). Yield: 56% (23.7 mg), brown solid, mp 265−267 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 12.07 (s, 1 H), 9.15 (d, J = 8.8 Hz, 1 H), 8.30 (d, J = 8.4 Hz, 1 H), 8.00 (d, J = 7.6 Hz, 1 H), 7.76 (t, J = 7.6 Hz, 1 H), 7.58 (t, J = 7.2 Hz, 1 H), 7.31 (d, J = 8.8 Hz, 1 H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 159.2, 147.5, 144.2, 138.6, 130.4, 130.1, 129.6, 129.3, 125.7, 123.8, 115.5, 101.6. HRMS calcd (ESI) m/z for $C_{12}H_7NNaO_3$:

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$[M + Na]^+$ 236.0318, found 236.0321. MS *m*/*z* (relative intensity) 213 (70), 169 (100), 141 (50), 114 (60), 88 (20), 71 (30).

6-Methoxy-1*H*-benzo[*d*][1,3]oxazine-2,4-dione (3n). Yield: 91% (35.0 mg), white solid, mp 206−208 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.61 (s, 1 H), 7.38 (d, J = 7.2 Hz, 1 H), 7.33 (s, 1 H), 7.10 (d, J = 8.8 Hz, 1 H), 3.80 (s, 3 H); HRMS calcd (ESI) *m*/*z* for $C_9H_7NNaO_4$: $[M + Na]^+$ 216.0267, found 216.0271. MS *m*/*z* (relative intensity) 193 (40), 148 (75), 121 (30), 106 (100), 79 (20), 51 (20).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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