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Electrochemically Enabled Selenium Catalytic Synthesis of 2,1-Benzoxazoles from *o*-Nitrophenylacetylenes

Lin-Wei Wang, Yu-Feng Feng, Hong-Min Lin, Hai-Tao Tang,* and Ying-Ming Pan*

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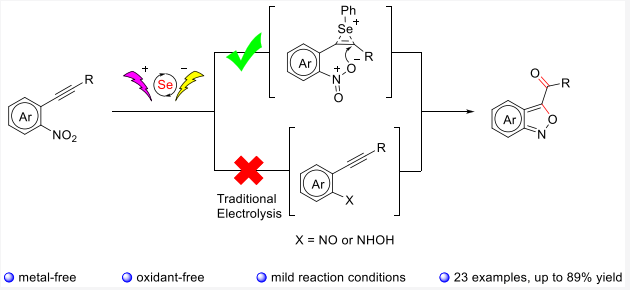
ABSTRACT: The study reported an electrochemically mediated method for the preparation of 2,1-benzoxazoles from *o*-nitrophenylacetylenes. Different from the traditional electrochemical reduction of nitro to nitroso, the nitro group directly underwent a cyclization reaction with the alkyne activated by selenium cation generated by the anodic oxidation of diphenyl diselenide and finally produced the desired products.



Organocatalysis has become the third major catalytic method after metal and enzyme catalysis due to its advantages of simple steps, low cost, and good compatibility of functional groups.[1] A series of organocatalysts, such as N-heterocyclic carbenes,[2] secondary amines,[3] and phosphine catalysts,[4] has been developed in the past few decades. After Sharpless initially reported the chlorination of alkenes catalyzed by an organoselenium catalyst in 1979,[5] selenium-catalyzed reactions have attracted extensive concern with continuous research on potential catalysts in organic synthesis.[6] Among them, diselenide combined with oxidants, such as PEROX,[7] high-valent iodine reagents,[8] N−F reagents,[9] and others,[10] for catalysis, has been widely reported in different reactions (Figure 1a). However, the use of these external oxidants usually suffers from substantial drawbacks such as increased reaction costs, unfavorable environmental effects, and formation of byproducts.

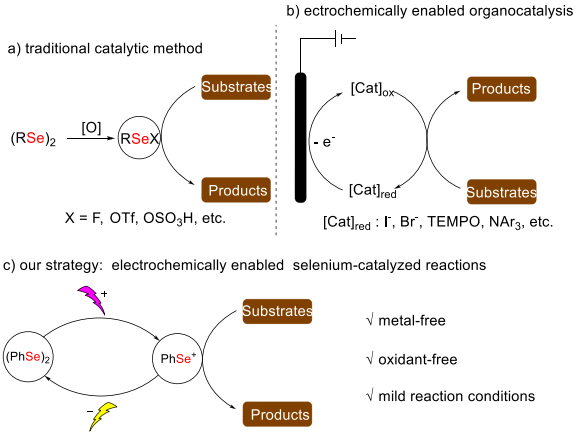


Figure 1. General catalytic modes.

The development of electrochemistry provides an efficient, mild, and controllable method for organic synthesis.[11] The electron transfer on the electrode surface could achieve redox reactions; thus, traditional oxidants could be avoided. In addition, the controllability of the current and potential indicates that the oxidation or reduction ability of the reaction system is operable. Therefore, electrochemically enabled organocatalysis is a promising metal- and oxidant-free catalytic method.[12] At the anode, the oxidation of organic catalysts could give intermediates with oxidizing properties. Then, the reactive intermediates react with the substrate to form the final product (Figure 1b). For example, Zeng's group reported a series of organic reactions with halogen catalysts under electrochemical conditions.[13] Xu's group utilized electrochemically enabled nitrogen-containing compounds (TEMPO or NAr3) as catalysts to synthesize structurally diverse heterocycles compounds.[14] The authors of the present study also reported a series of cross dehydrogenation coupling reactions catalyzed by halogen.[15] However, one shortcoming of the above-mentioned selenium catalysis is the use of excessive oxidants. The combination of organic electrosynthesis and selenium catalysis effectively avoids this shortcoming (Figure 1c). In 1981, Bannou reported a one-step preparation of allylic derivatives through electrochemical selenium catalysis of

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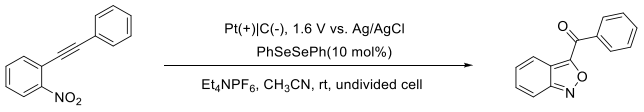
isoprenoids.[6d] Recently, Wirth and others also did some studies.[6e,f] To try more reactions in this area, this strategy was used with *o*-nitrophenylacetylenes as the substrate template, and the results obtained nucleophilic cyclization products of *o*-nitrophenylacetylenes catalyzed by diphenyl diselenide under the condition of constant potential in an undivided cell.

The reaction conditions were screened, as shown in Table 1, and the specific information on the other conditions is provided in Table S1. The optimal yield of product **2a** obtained a yield of 78% when the reaction was conducted in CH_3CN as a solvent at a constant potential of 1.6 V vs Ag/AgCl in the presence of Et_4NPF_6 (0.5 equiv) with diphenyl diselenide (PhSeSePh) as the catalyst (entry 1). Moreover, the necessity of electricity and PhSeSePh were verified through experiments. No desired product **2a** was detected under the conditions without electricity (entry 2) or PhSeSePh (entry 3). Reactions at 0 °C (entry 4) or 40 °C (entry 5) led to a decrease in yield. In comparison, only a trace yield of **2a** was obtained when DMF (entry 6) or DMSO (entry 7) were used as the solvent. When ^{n}Bu$_4$NI or ^{n}Bu$_4$NBF$_6$ was used instead of Et_4NPF_6 as the electrolyte, a decline in yield was obtained (entries 8 and 9). Exploration of the influence of voltage on the reaction showed that, when the voltage was reduced to 1.3 V (entry 10), the reaction did not occur. When the voltage was increased to 2.1 V (entry 11), the yield of **2a** decreased. The change in yield was also tested under constant current conditions, and the results showed that the reaction at a constant current of 5 mA (entry 12) would lead to a decrease in the yield of **2a**.

The tolerance of the substrate functional group was explored under the optimal conditions, and the results are shown in Figure 2. Various nitroalkynes with different aromatic groups containing electron-withdrawing (F, Cl, Br, CF_3, and CN) and electron-donating (Me, OMe, and *t*-Bu) groups reacted well, obtaining desired products **2b**−**2i** in moderate to medium yields (51%−78%). The desirable yields of 2,1-benzoxazoles also were obtained for the nitroalkynes containing Cl at its ortho- or meta-position on the aryl ring of R^1 (**2j**, **2k**). A notable detail is that **2k** had a longer reaction time but an improved yield than that of the other products. In addition, when R^1 was a fused ring or the heteroaryl group was tolerated, the corresponding product was isolated in 65% and 80% yields, respectively. Substrates bearing alkyl groups (R^1 = propyl, cyclopropyl) were also suitable for this transformation. Excitingly, **1p** could also achieve the target product **2p** with a yield of 33%. However, the corresponding products of unsubstituted terminal alkyne and TMS-substituted alkyne were not detected because the reaction of these two substrates would generate lots of byproducts. Next, the tolerance of R^2 on the benzene ring attached to the nitro group was explored. Among them, the electronic effect of R^2 demonstrated a little effect on the reaction, and both showed medium to good yields (**2s**−**2x**, 56%−89%). The yield of the electron-withdrawing groups was higher than that of the electron-donating groups. Moreover, 2-nitro-3-(phenylethynyl)pyridine obtained the target product in good yield (**2y**, 86%).

Several control experiments were performed to further clarify the reaction mechanism, as shown in Figure 3. When the reaction was carried out in the presence of 1,1-diphenylethene, a known free radical scavenger, **2a**, was obtained with an isolated yield of 68% under standard conditions (Figure 4a). This finding illustrated that the reaction was not carried out in a radical manner. Further experiments showed that **1a** could produce the target product in the presence of PhSeCl without electricity (Figure 4b). Meanwhile, the reaction could occur under anhydrous and oxygen-free conditions, and a good yield was obtained (Figure 4c). In addition, cyclic voltammetry (CV) experiments were conducted to further study the reaction mechanism (Figure

Table 1. Optimization of Reaction Conditions[a]



entry	variation from the standard reaction conditions	yield[b] (%)
1	none	78
2	no electricity	NR
3	no PhSeSePh	NR
4	reaction at 40 °C	59
5	reaction at 0 °C	36
6	DMF as a solvent	trace
7	DMSO as a solvent	trace
8	^{n}Bu$_4$NI (2.0 equiv) as an electrolyte	trace
9	^{n}Bu$_4$NBF$_6$ (2.0 equiv) as an electrolyte	30
10	constant potential: 1.3 V vs Ag/AgCl	NR
11	constant potential: 2.1 V vs Ag/AgCl	63
12[c]	constant current: 5 mA	72

[a]Reaction conditions: graphite rod cathode (Φ 6 mm), Pt plate anode (1 cm × 1 cm), undivided cell, constant potential = 1.6 V vs Ag/AgCl, **1a** (0.3 mmol), Et_4NPF_6 (0.5 equiv), catalyst (10 mol %), CH_3CN = 10 mL, rt. [b]Isolated yields. [c]0.4 F mol^{-1}. NR = no reaction

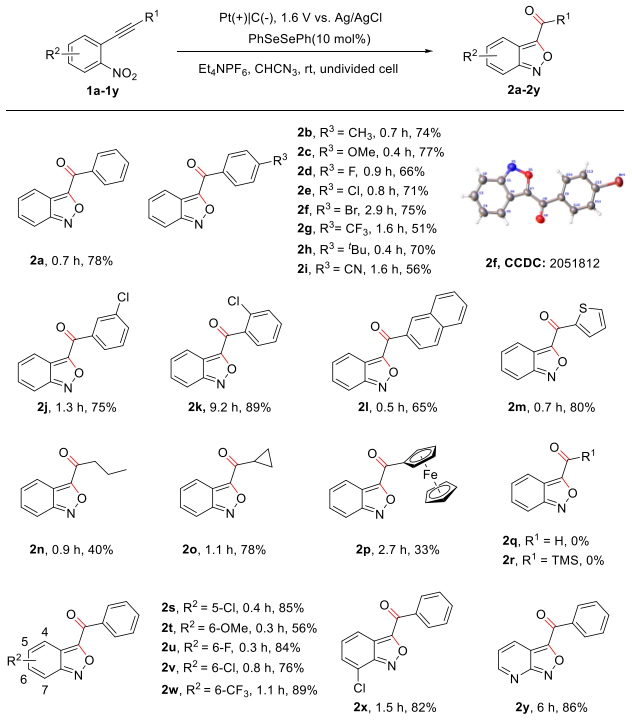


Figure 2. Substrate scope of nitroalkynes. Reaction conditions: graphite rod cathode (Φ 6 mm), Pt plate anode (1 cm × 1 cm), undivided cell, constant potential = 1.6 V vs Ag/AgCl, **1** (0.3 mmol), Et_4NPF_6 (0.5 equiv), PhSeSePh (10 mol %), CH_3CN = 10 mL, rt. Isolated yields.

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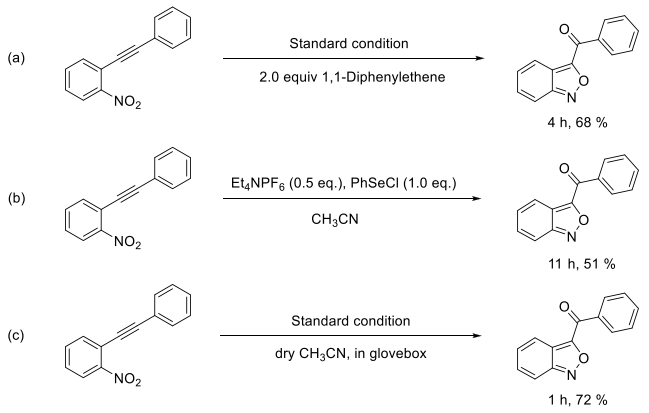


Figure 3. Control experiments.

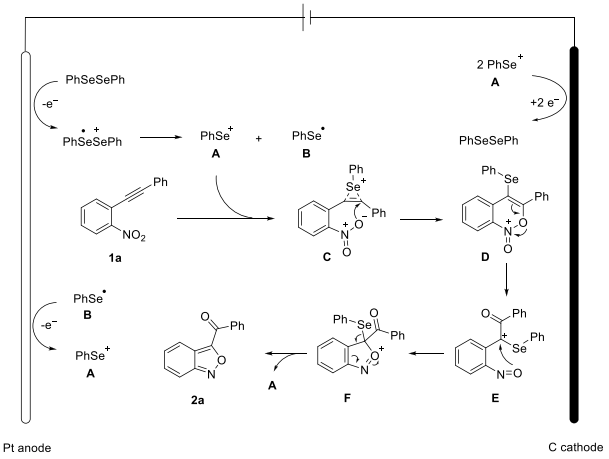


Figure 4. Proposed reaction mechanism.

S3). Obvious oxidation peaks of **1a** and **2a** could be observed at 2.00 V (curve b and curve e). Meanwhile, oxidation peaks of PhSeSePh were 1.25 and 1.45 V (curve c). These two oxidation peaks represent the oxidation activation of PhSeSePh, and phenyl selenium radical **B** generates selenium cation **A** by single electron transfer on the anode.[16] Therefore, our reaction condition was 1.6 V. CV curve d shows that the oxidation peak of **1a** disappeared, and the reduction peak appeared at 0.39 V. In accordance with the reported literature,[16] the former could be due to the combination of substrate **1a** with selenium cations produced by PhSeSePh, and the latter indicated that selenium cations were reduced at the cathode.

In accordance with the above control experiments and the reported literature,[16a,17] a possible mechanism for the electrochemical cyclization is proposed in Figure 4. The reaction starts with the formation of selenium cation **A** and phenyl selenium radical **B** by the activation of diphenyl diselenide in anodization. Phenyl selenium radical **B** could also generate selenium cation **A** by single electron transfer on the anode. The addition of **A** to substrate **1a** produces intermediate **C**. Then the oxygen on the nitro group of intermediate **C** undergoes an intramolecular nucleophilic cyclization to attack the alkyne activated by selenium cation to obtain intermediate **D**. The cleavage of the N−O bond generates intermediate **E**, which releases a selenium cation after the cyclization reaction to obtain the final target product **2a**. According to the switch experiment, part of the released selenium cation continued to participate in catalysis (Figure S2).

CONCLUSIONS

In summary, an electrochemical selenium catalytic system for nitroalkynes generation intramolecular nucleophilic cyclization was developed to construct 2,1-benzoxazoles in undivided cells. This strategy has a good reaction efficiency and a widened substrate range. In the reaction process, constant pressure is used to replace the external oxidant, thus avoiding the use of traditional oxidants and transition metals.

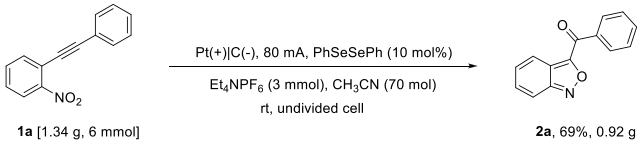
EXPERIMENTAL SECTION

Experimental Procedure. Without special instructions, all reagents and solvents were commercially available and were not further purified. Column chromatography was carried out using silica gel (300−400 mesh). NMR spectroscopy was performed on Bruker AV-400 or Bruker AV-600 instruments. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from TMS (δ 0.00) and relative to the signal of chloroform-*d* (δ 7.26, singlet) or DMSO-d_6 (δ 2.50, multiplet). ^{13}C NMR spectra were relative to the signal of $CDCl_3$ (77.0 ppm) or DMSO-d_6 (39.5 ppm). The abbreviations used to explain the multiplicities were as follows: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet; *J*, coupling constant in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from TMS (δ 0.00) and relative to the signal of chloroform-*d* (δ 77.00, triplet). The HRMS spectrum was measured by a micromass QTOF2 Quadrupole/Time of Flight Tandem mass spectrometer with electron spray ionization. Cyclic voltammograms were recorded on a CHI 660E potentiostat. Crystal measurement by XtaLAB Synergy-DS.

Synthesis of Starting Materials.[18] To a solution of 1-nitro-2-iodobenzene (3.0 mmol) in triethylamine (10 mL) at room temperature was added $PdCl_2(PPh_3)_2$ (0.0421 g, 0.06 mmol). The resultant suspension was stirred for 10 min, followed by the addition of alkynes (3.6 mmol) and then CuI (0.0114 g, 0.06 mmol). This mixture was then stirred for 6 h. The reaction mixture was washed with NH_4Cl (aq sat.) and brine and dry over Na_2SO_4. The solvent was removed, and the residue was subjected to silica gel column chromatography.

Procedures for the Electrolysis. A 25 mL three-necked round-bottomed flask was charged with nitroalkynes **1** (0.3 mmol, 1.0 equiv), diphenyl diselenide (0.03 mmol, 10 mol %), and Et_4NPF_6 (0.15 mmol, 0.5 equiv). The flask was equipped with a graphite rod (Φ 6 mm) cathode and a platinum plate (1 cm × 1 cm) anode. A Ag/AgCl electrode was used as the reference electrode. CH_3CN (10 mL) was added. Electrolysis was carried out at room temperature, which used a constant potential of 1.6 V vs Ag/AgCl until the substrate was completely consumed (monitored by TLC). After the reaction was completed, the solvent was concentrated under reduced pressure. Purification with silica gel column chromatography using petroleum ether/ethyl acetate to afford the desired products **2**.

To demonstrate our method's potential for application, we performed the reaction at a gram scale level in a beaker-type cell with the same electrode at room temperature for 12 h to afford corresponding products with satisfactory yields.



Crystal Preparation for 2f. A glass tube (Φ 8 mm) was charged with **2f** (30.1 mg). DMSO (1 mL) was added. Then 0.3 mL of H_2O was slowly added along the wall. Parafilm was used to seal the glass tube and make holes; then the tube was kept in a cool place for 3 days. Crystals precipitated in the glass tube.

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*Benzo[c]isoxazol-3-yl(phenyl)methanone (**2a**):* yellow solid; 78% yield, 52.2 mg; mp 91−92 °C; petroleum ether/ethyl acetate = 100:1−60:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32−8.27 (m, 2H), 8.16−8.10 (m, 1H), 7.78−7.73 (m, 1H), 7.71−7.64 (m, 1H), 7.61−7.54 (m, 2H), 7.45−7.39 (m, 1H), 7.32−7.26 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 181.5, 160.4, 157.3, 136.0, 133.8, 131.4, 130.1, 128.7, 128.5, 121.7, 121.6, 115.9; HR-MS (ESI) *m*/*z* calcd for $C_{14}H_{10}NO_2$ [M + H]$^+$ 224.0706, found 224.0707.

*Benzo[c]isoxazol-3-yl(p-tolyl)methanone (**2b**):* yellow solid; 74% yield, 52.6 mg; mp 100−101 °C; petroleum ether/ethyl acetate = 80:1−50:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14−8.09 (m, 2H), 8.05−8.00 (m, 1H), 7.67−7.62 (m, 1H), 7.34−7.25 (m, 3H), 7.20−7.14 (m, 1H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 181.0, 160.6, 157.2, 144.9, 133.4, 131.3, 130.2, 129.4, 128.2, 121.7, 121.5, 115.8, 21.8; HR-MS (ESI) *m*/*z* calcd for $C_{15}H_{12}NO_2$ [M + H]$^+$ 238.0863, found 238.0859.

*Benzo[c]isoxazol-3-yl(4-methoxyphenyl)methanone (**2c**):* yellow solid; 77% yield, 58.5 mg; mp 122−123 °C; petroleum ether/ethyl acetate = 80:1−40:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34−8.30 (m, 2H), 8.13−8.09 (m, 1H), 7.73−7.69 (m, 1H), 7.41−7.35 (m, 1H), 7.27−7.21 (m, 1H), 7.04−7.00 (m, 2H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 179.6, 164.2, 160.8, 157.1, 132.6, 131.2, 128.7, 128.0, 121.8, 121.4, 115.6, 114.0, 55.5; HR-MS (ESI) *m*/*z* calcd for $C_{15}H_{12}NO_3$ [M + H]$^+$ 254.0812, found 254.0829.

*Benzo[c]isoxazol-3-yl(4-fluorophenyl)methanone (**2d**):* yellow solid; 66% yield, 47.7 mg; mp 83−84 °C; petroleum ether/ethyl acetate = 100:1−60:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43−8.36 (m, 2H), 8.19−8.13 (m, 1H), 7.81−7.75 (m, 1H), 7.49−7.42 (m, 1H), 7.35−7.26 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 179.7, 166.1 (C−F, $^1J_{C-F}$ = 255.2 Hz), 160.2, 157.2, 132.9 (C−F, $^3J_{C-F}$ = 9.4 Hz), 132.3 (C−F, $^4J_{C-F}$ = 3.1 Hz), 131.4, 128.6, 121.7, 121.6, 116.0 (C−F, $^2J_{C-F}$ = 21.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −103.2; HR-MS (ESI) *m*/*z* calcd for $C_{14}H_9FNO_2$ [M + H]$^+$ 242.0612, found 242.0611.

*Benzo[c]isoxazol-3-yl(4-chlorophenyl)methanone (**2e**):* yellow solid; 71% yield, 54.7 mg; mp125−126 °C; petroleum ether/ethyl acetate = 120:1−70:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29−8.22 (m, 2H), 8.14−8.05 (m, 1H), 7.79−7.70 (m, 1H), 7.58−7.49 (m, 2H), 7.45−7.37 (m, 1H), 7.32−7.24 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 179.9, 160.0, 157.2, 140.4, 134.2, 131.5, 131.4, 129.1, 128.7, 121.8, 121.6, 115.9; HR-MS (ESI) *m*/*z* calcd for $C_{14}H_9ClNO_2$ [M + H]$^+$ 258.0316, found 258.0316.

*Benzo[c]isoxazol-3-yl(4-bromophenyl)methanone (**2f**):* yellow solid; 75% yield, 67.5 mg; mp 139−140 °C; petroleum ether/ethyl acetate = 100:1−50:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.04 (m, 2H), 8.02−7.97 (m, 1H), 7.67−7.57 (m, 3H), 7.34−7.28 (m, 1H), 7.21−7.16 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 180.0, 159.9, 157.2, 134.5, 132.0, 131.5, 131.4, 129.2, 128.7, 121.7, 121.5, 115.8; HR-MS (ESI) *m*/*z* calcd for $C_{14}H_9BrNO_2$ [M + H]$^+$ 301.9811, found 301.9802.

*Benzo[c]isoxazol-3-yl(4-(trifluoromethyl)phenyl)methanone (**2g**):* yellow solid; 51% yield, 44.5 mg; mp 107−108 °C; petroleum ether/ethyl acetate = 100:1−50:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34−8.30 (m, 2H), 8.03−7.97 (m, 3H), 7.93−7.87 (m, 1H), 7.60−7.55 (m, 1H), 7.47−7.41 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 180.4, 159.5, 156.9, 139.2, 132.9 (C−F, $^2J_{C-F}$ = 31.8 Hz), 132.2, 130.5, 129.5, 125.8 (C−F, $^3J_{C-F}$ = 3.7 Hz), 123.7 (C−F, $^1J_{C-F}$ = 271.2 Hz), 120.9, 120.8, 115.8; ^{19}F NMR (376 MHz, DMSO-d_6) δ −61.70; HR-MS (ESI) *m*/*z* calcd for $C_{15}H_9F_3NO_2$ [M + H]$^+$ 292.0580, found 292.0577.

*Benzo[c]isoxazol-3-yl(4-(tert-butyl)phenyl)methanone (**2h**):* yellow oil; 70% yield, 58.6 mg; petroleum ether/ethyl acetate = 100:1−60:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28−8.23 (m, 2H), 8.17−8.12 (m, 1H), 7.77−7.72 (m, 1H), 7.62−7.57 (m, 2H), 7.44−7.38 (m, 1H), 7.30−7.24 (m, 1H), 1.38 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 181.0, 160.6, 157.8, 157.2, 133.4, 131.3, 130.1, 128.3, 125.8, 121.8, 121.5, 115.8, 35.2, 31.0; HR-MS (ESI) *m*/*z* calcd for $C_{18}H_{18}NO_2$ [M + H]$^+$ 280.1332, found 280.1333.

*4-(Benzo[c]isoxazole-3-carbonyl)benzonitrile (**2i**):* yellow solid; 56% yield, 41.7 mg; mp 155−156 °C; petroleum ether/ethyl acetate = 70:1−20:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41−8.36 (m, 2H), 8.15−8.11 (m, 1H), 7.89−7.86 (m, 2H), 7.80−7.75 (m, 1H), 7.49−7.43 (m, 1H), 7.38−7.31 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 179.7, 159.4, 157.3, 139.0, 132.5, 131.6, 130.4, 129.4, 122.1, 121.3, 117.7, 116.8, 116.1; HR-MS (ESI) *m*/*z* calcd for $C_{15}H_8N_2NaO_2$ [M + Na]$^+$ 271.0478, found 271.0477.

*Benzo[c]isoxazol-3-yl(3-chlorophenyl)methanone (**2j**):* yellow solid; 75% yield, 57.8 mg; mp 89−90 °C; petroleum ether/ethyl acetate = 100:1−60:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.12−8.08 (m, 2H), 7.99−7.95 (m, 1H), 7.92−7.88 (m, 1H), 7.84−7.81 (m, 1H), 7.71−7.66 (m, 1H), 7.60−7.55 (m, 1H), 7.45−7.41 (m, 1H); ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 179.9, 159.5, 156.8, 137.6, 133.6, 133.5, 132.2, 130.9, 129.4, 129.2, 128.4, 120.9, 120.7, 115.8; HR-MS (ESI) *m*/*z* calcd for $C_{14}H_9ClNO_2$ [M + H]$^+$ 258.0316, found 258.0306.

*Benzo[c]isoxazol-3-yl(2-chlorophenyl)methanone (**2k**):* yellow solid; 89% yield, 68.6 mg; mp 54−55 °C; petroleum ether/ethyl acetate = 100:1−50:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93−7.88 (m, 1H), 7.84−7.80 (m, 1H), 7.72−7.66 (m, 2H), 7.67−7.63 (m, 1H), 7.63−7.54 (m, 2H), 7.46−7.40 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 181.4, 158.8, 157.2, 136.3, 133.2, 132.1, 130.4, 130.2, 130.0, 129.9, 127.7, 119.9, 119.8, 116.0; HR-MS (ESI) *m*/*z* calcd for $C_{14}H_9ClNO_2$ [M + H]$^+$ 258.0316, found 258.0310.

*Benzo[c]isoxazol-3-yl(naphthalen-2-yl)methanone (**2l**):* yellow solid; 65% yield, 53.2 mg; mp 114−115 °C; petroleum ether/ethyl acetate = 80:1−50:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.85−8.82 (m, 1H), 8.19−8.15 (m, 1H), 8.12−8.09 (m, 2H), 8.06−8.01 (m, 1H), 8.00−7.95 (m, 1H), 7.91−7.86 (m, 1H), 7.74−7.68 (m, 1H), 7.67−7.61 (m, 1H), 7.58−7.53 (m, 1H), 7.42−7.37 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 181.0, 160.1, 156.8, 135.3, 133.1, 132.1, 132.1, 131.9, 129.9, 129.3, 129.1, 128.7, 127.8, 127.3, 124.7, 121.0, 120.6, 115.7; HR-MS (ESI) *m*/*z* calcd for $C_{18}H_{12}NO_2$ [M + H]$^+$ 274.0863, found 274.0860.

*Benzo[c]isoxazol-3-yl(thiophen-2-yl)methanone (**2m**):* orange solid; 80% yield, 55.0 mg; mp 173−174 °C; petroleum ether/ethyl acetate = 100:1−60:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56−8.53 (m, 1H), 8.17−8.13 (m, 1H), 7.85−7.82 (m, 1H), 7.75−7.71 (m, 1H), 7.43−7.39 (m, 1H), 7.30−7.26 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 172.7, 159.5, 157.2, 142.0, 135.9, 135.5, 131.5, 128.9, 128.5, 121.6, 121.3, 115.8; HR-MS (ESI) *m*/*z* calcd for $C_{12}H_8NO_2S$ [M + H]$^+$ 230.0270, found 230.0269.

*1-(Benzo[c]isoxazol-3-yl)butan-1-one (**2n**):* colorless oil; 40% yield, 22.7 mg; petroleum ether/ethyl acetate = 120:1−70:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07−8.03 (m, 1H), 7.74−7.70 (m, 1H), 7.42−7.37 (m, 1H), 7.28−7.25 (m, 1H), 3.16 (t, *J* = 7.3 Hz, 2H), 1.90−1.82 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.3, 159.7, 157.5, 131.3, 128.4, 121.3, 119.1, 115.9, 42.0, 17.1, 13.7; HR-MS (ESI) *m*/*z* calcd for $C_{11}H_{12}NO_2$ [M + H]$^+$ 190.0863, found 190.0862.

*Benzo[c]isoxazol-3-yl(cyclopropyl)methanone (**2o**):* white solid; 78% yield, 43.8 mg; mp 73−74 °C; petroleum ether/ethyl acetate = 100:1−60:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.03−7.98 (m, 1H), 7.72−7.67 (m, 1H), 7.41−7.34 (m, 1H), 7.25−7.20 (m, 1H), 3.08−3.00 (m, 1H), 1.41−1.35 (m, 2H), 1.24−1.18 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.0, 160.0, 157.5, 131.2, 128.3, 121.3, 118.5, 115.7, 18.8, 12.7; HR-MS (ESI) *m*/*z* calcd for $C_{11}H_{10}NO_2$ [M + H]$^+$ 188.0706, found 188.0700.

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Benzo[c]isoxazol-3-yl(ferrocenylvinyl)methanone (**2p**): purple solid; 33% yield, 32.8 mg; mp 141−142 °C; petroleum ether/ethyl acetate = 100:1−60:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, J = 9.0 Hz, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.41−7.37 (m, 1H), 7.25−7.23 (m, 1H), 5.40 (t, J = 1.8 Hz, 2H), 4.76 (t, J = 2.4 Hz, 2H), 4.20 (s, 5H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 184.6, 161.1, 157.3, 131.4, 134.9, 127.8, 122.1, 120.1, 115.5, 73.9, 71.0, 70.5; HR-MS (ESI) m/z calcd for $C_{18}H_{14}FeNO_2$ [M + H]$^+$ 332.0368, found 332.0363.

(5-Chlorobenzo[c]isoxazol-3-yl)(phenyl)methanone (**2s**): orange solid; 85% yield, 65.5 mg; mp 80−81 °C; petroleum ether/ethyl acetate = 100:1−50:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29−8.25 (m, 2H), 8.15−8.12 (m, 1H), 7.71−7.64 (m, 2H), 7.59−7.54 (m, 2H), 7.35−7.30 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 180.9, 159.9, 155.6, 135.6, 134.7, 133.9, 133.3, 130.0, 128.7, 121.8, 120.1, 117.3; HR-MS (ESI) m/z calcd for $C_{14}H_9ClNO_2$ [M + H]$^+$ 258.0316, found 258.0308.

(6-Methoxybenzo[c]isoxazol-3-yl)(phenyl)methanone (**2t**): yellow solid; 56% yield, 42.5 mg; mp 173−174 °C; petroleum ether/ethyl acetate = 80:1−50:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29−8.25 (m, 2H), 7.97 (d, J = 9.3 Hz, 1H), 7.68−7.64 (m, 1H), 7.58−7.54 (m, 2H), 6.97−6.93 (m, 1H), 6.81 (d, J = 1.8 Hz, 1H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 181.5, 161.8, 159.5, 158.6, 135.9, 133.8, 130.1, 128.7, 125.6, 122.3, 118.7, 90.0, 55.5; HR-MS (ESI) m/z calcd for $C_{15}H_{12}NO_3$ [M + H]$^+$ 254.0812, found 254.0807.

(6-Fluorobenzo[c]isoxazol-3-yl)(phenyl)methanone (**2u**): yellow solid; 84% yield, 60.7 mg; mp 96−97 °C; petroleum ether/ethyl acetate = 100:1−60:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29−8.25 (m, 2H), 8.18−8.13 (m, 1H), 7.70−7.66 (m, 1H), 7.59−7.55 (m, 2H), 7.31−7.27 (m, 1H), 7.12−7.07 (m, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 181.1, 163.8 (C−F, $^1J_{C-F}$ = 254.1 Hz), 160.7 (C−F, $^4J_{C-F}$ = 1.8 Hz), 157.5 (C−F, $^3J_{C-F}$ = 12.9 Hz), 135.6, 134.0, 130.1, 128.8, 124.3 (C−F, $^3J_{C-F}$ = 10.5 Hz), 121.5 (C−F, $^2J_{C-F}$ = 30.3 Hz), 119.3, 98.2 (C−F, $^2J_{C-F}$ = 25.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −104.17; HR-MS (ESI) m/z calcd for $C_{14}H_9FNO_2$ [M + H]$^+$ 242.0612, found 242.0610.

(6-chloroBenzo[c]isoxazol-3-yl)(phenyl)methanone (**2v**): orange solid; 76% yield, 58.6 mg; mp 134−135 °C; petroleum ether/ethyl acetate = 100:1−60:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29−8.26 (m, 2H), 8.10−8.07 (m, 1H), 7.75−7.73 (m, 1H), 7.69−7.66 (m, 1H), 7.59−7.55 (m, 2H), 7.21−7.18 (m, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 181.0, 160.9, 157.3, 137.8, 135.5, 134.1, 130.3, 130.1, 128.8, 123.0, 120.0, 114.3; HR-MS (ESI) m/z calcd for $C_{14}H_9ClNO_2$ [M + H]$^+$ 258.0316, found 258.0311.

Phenyl(5-(trifluoromethyl)benzo[c]isoxazol-3-yl)methanone (**2w**): red solid; 89% yield, 75.1 mg; mp 109−110 °C; petroleum ether/ethyl acetate = 100:1−60:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31−8.25 (m, 3H), 8.12−8.09 (m, 1H), 7.71−7.67 (m, 1H), 7.60−7.56 (m, 2H), 7.42−7.39 (m, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 180.9, 161.4, 156.0, 135.4, 134.2, 133.5 (C−F, $^2J_{C-F}$ = 32.6 Hz), 130.1, 128.9, 123.9(C−F, $^3J_{C-F}$ = 2.7 Hz), 123.8, 123.0 (C−F, $^1J_{C-F}$ = 271.4 Hz), 121.7, 114.8 (C−F, $^3J_{C-F}$ = 5.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −64.51; HR-MS (ESI) m/z calcd for $C_{15}H_9F_3NO_2$ [M + H]$^+$ 292.0580, found 292.0591.

(7-Chlorobenzo[c]isoxazol-3-yl)(phenyl)methanone (**2x**): yellow solid; 82% yield, 63.2 mg; mp 110−111 °C; petroleum ether/ethyl acetate = 80:1−50:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30−8.23 (m, 2H), 8.07−8.01 (m, 1H), 7.71−7.64 (m, 1H), 7.60−7.54 (m, 2H), 7.45−7.39 (m, 1H), 7.23−7.16 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 181.0, 161.6, 155.7, 135.5, 134.1, 130.5, 130.1, 128.8, 128.7, 122.6, 122.0, 120.4; HR-MS (ESI) m/z calcd for $C_{14}H_9ClNO_2$ [M + H]$^+$ 258.0316, found 258.0307.

Isoxazolo[3,4-b]pyridin-3-yl(phenyl)methanone (**2y**): yellow solid; 86% yield, 57.8 mg; mp 140−142 °C; petroleum ether/ethyl acetate = 50:1−10:1 (v/v) as an eluent for column chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91−8.87 (m, 1H), 8.52−8.48 (m, 1H), 8.31−8.27 (m, 2H), 7.71−7.65 (m, 1H), 7.60−7.54 (m, 2H), 7.29−7.25 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 180.9, 165.4, 161.8, 158.6, 135.1, 134.3, 131.3, 130.2, 128.9, 123.8, 114.7; HR-MS (ESI) m/z calcd for $C_{13}H_9N_2O_2$ [M + H]$^+$ 225.0659, found 225.0657.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00012.

NMR spectra for compounds **2**, optimization of the reaction conditions, amperometric curve, on/off experiment, cyclic voltammetry studies, and crystal data (PDF)

Accession Codes

CCDC 2051812 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Hai-Tao Tang − *State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Sciences of Guangxi Normal University, Guilin 541004, People's Republic of China;* orcid.org/0000-0001-7531-0458; Email: httang@gxnu.edu.cn

Ying-Ming Pan − *State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Sciences of Guangxi Normal University, Guilin 541004, People's Republic of China;* orcid.org/0000-0002-3625-7647; Email: panym@mailbox.gxnu.edu.cn

Authors

Lin-Wei Wang − *State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Sciences of Guangxi Normal University, Guilin 541004, People's Republic of China*

Yu-Feng Feng − *State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Sciences of Guangxi Normal University, Guilin 541004, People's Republic of China*

Hong-Min Lin − *State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Sciences of Guangxi Normal University, Guilin 541004, People's Republic of China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.1c00012

Notes

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REFERENCES

(1) (a) MacMillan, D. W. C. The advent and development of organocatalysis. *Nature* **2008**, *455*, 304−308. (b) Dalko, P. I.; Moisan, L. In the Golden Age of Organocatalysis. *Angew. Chem., Int. Ed.* **2004**, *43*, 5138−5175. (c) Qin, Y.; Zhu, L.; Luo, S. Organocatalysis in Inert C-H Bond Functionalization. *Chem. Rev.* **2017**, *117*, 9433−9520.

(2) (a) Wang, M.; Huang, Z.; Xu, J.; Chi, Y. R. N-Heterocyclic Carbene-Catalyzed [3 + 4] Cycloaddition and Kinetic Resolution of Azomethine Imines. *J. Am. Chem. Soc.* **2014**, *136*, 1214−1217. (b) Zhu, T.; Mou, C.; Li, B.; Smetankova, M.; Song, B.-A.; Chi, Y. R. N-Heterocyclic Carbene-Catalyzed δ-Carbon LUMO Activation of Unsaturated Aldehydes. *J. Am. Chem. Soc.* **2015**, *137*, 5658−5661.

(3) Chauhan, P.; Mahajan, S.; Enders, D. Achieving Molecular Complexity via Stereoselective Multiple Domino Reactions Promoted by a Secondary Amine Organocatalyst. *Acc. Chem. Res.* **2017**, *50*, 2809−2821.

(4) (a) Feng, J.; Huang, Y. Phosphine-Catalyzed Remote 1,7-Addition for Synthesis of Diene Carboxylates. *ACS Catal.* **2020**, *10*, 3541−3547. (b) Xie, P.; Wang, L.; Yang, L.; Li, E.; Ma, J.; Huang, Y.; Chen, R. Domino Reaction for the Chemo- and Stereoselective Synthesis of *trans*-2,3-Dihydrobenzofurans from N-Thiophosphinyl Imines and Sulfur Ylides. *J. Org. Chem.* **2011**, *76*, 7699−7705.

(5) (a) Picard, J.-P.; Calas, R.; Dunogués, J.; Duffaut, N.; Gerval, J.; Lapouyade, P. Reductive Silylation of Benzoates: Convenient Synthesis of Aroylsilanes. *J. Org. Chem.* **1979**, *44*, 420−424. (b) Hori, T.; Sharpless, K. B. Selenium-catalyzed nonradical chlorination of olefins with N-chlorosuccinimide. *J. Org. Chem.* **1979**, *44*, 4204−4208.

(6) (a) Ortgies, S.; Breder, A. Oxidative Alkene Functionalizations *via* Selenium-π-Acid Catalysis. *ACS Catal.* **2017**, *7*, 5828−5840. (b) Singh, F. V.; Wirth, T. Selenium reagents as catalysts. *Catal. Sci. Technol.* **2019**, *9*, 1073−1091. (c) Shao, L.; Li, Y.; Lu, J.; Jiang, X. Recent progress in selenium-catalyzed organic reactions. *Org. Chem. Front.* **2019**, *6*, 2999−3041. (d) Torii, S.; Uneyama, K.; Ono, M.; Bannou, T. Generation and Recycle Use of Selenenylating Reagents in Electrochemical Oxyselenenylation-Deselenenylation of Olefins. *J. Am. Chem. Soc.* **1981**, *103*, 4606−4608. (e) Smith, D.S.; Winnick, J.; Ding, Y.; Bottomley, L. A. Electrosynthesis of a-keto acetals by a selenium-catalyzed transformation of aryl methyl ketones. *Electrochim. Acta* **1998**, *43*, 335−339. (f) Niyomura, O.; Cox, M.; Wirth, T. Electrochemical Generation and Use of Selenium Electrophiles. *Synlett* **2006**, *2*, 251−254.

(7) (a) Yu, L.; Ye, J.; Zhang, X.; Ding, Y.; Xu, Q. Recyclable $(PhSe)_2$-catalyzed selective oxidation of isatin by H_2O_2: a practical and waste-free access to isatoic anhydride under mild and neutral conditions. *Catal. Sci. Technol.* **2015**, *5*, 4830−4838. (b) Wang, X.; Wang, Q.; Xue, Y.; Sun, K.; Wu, L.; Zhang, B. An organoselenium-catalyzed N^1- and N^2-selective aza-Wacker reaction of alkenes with benzotriazoles. *Chem. Commun.* **2020**, *56*, 4436−4439. (c) Jing, X.; Yuan, D.; Yu, L. Green and Practical Oxidative Deoximation of Oximes to Ketones or Aldehydes with Hydrogen Peroxide/Air by Organoselenium Catalysis. *Adv. Synth. Catal.* **2017**, *359*, 1194−1201.

(8) (a) Browne, D. M.; Niyomura, O.; Wirth, T. Catalytic Use of Selenium Electrophiles in Cyclizations. *Org. Lett.* **2007**, *9*, 3169−3171. (b) Singh, F. V.; Wirth, T. Selenium-Catalyzed Regioselective Cyclization of Unsaturated Carboxylic Acids Using Hypervalent Iodine Oxidants. *Org. Lett.* **2011**, *13*, 6504−6507.

(9) (a) Ortgies, S.; Breder, A. Selenium-Catalyzed Oxidative C(sp^2)-H Amination of Alkenes Exemplified in the Expedient Synthesis of (Aza-)Indoles. *Org. Lett.* **2015**, *17*, 2748−2751. (b) Trenner, J.; Depken, C.; Weber, T.; Breder, A. Direct Oxidative Allylic and Vinylic Amination of Alkenes through Selenium Catalysis. *Angew. Chem., Int. Ed.* **2013**, *52*, 8952−8956. (c) Zhang, X.; Guo, R.; Zhao, X. Organoselenium-catalyzed synthesis of indoles through intramolecular C-H amination. *Org. Chem. Front.* **2015**, *2*, 1334−1337. (d) Kawamata, Y.; Hashimoto, T.; Maruoka, K. A Chiral Electrophilic Selenium Catalyst for Highly Enantioselective Oxidative Cyclization. *J. Am. Chem. Soc.* **2016**, *138*, 5206−5209.

(10) (a) Guo, R.; Huang, J.; Huang, H.; Zhao, X. Organoselenium-Catalyzed Synthesis of Oxygen- and Nitrogen-Containing Heterocycles. *Org. Lett.* **2016**, *18*, 504−507. (b) Liao, L.; Zhang, H.; Zhao, X. Selenium-π-Acid Catalyzed Oxidative Functionalization of Alkynes: Facile Access to Ynones and Multisubstituted Oxazoles. *ACS Catal.* **2018**, *8*, 6745−6750. (c) Cresswell, A. J.; Eey, S. T.-C.; Denmark, S. E. Catalytic, stereospecific *syn*-dichlorination of alkenes. *Nat. Chem.* **2015**, *7*, 146−152. (d) Yan, D.; Wang, G.; Xiong, F.; Sun, W.-Y.; Shi, Z.; Lu, Y.; Li, S.; Zhao, J. A selenium-catalysed *para*-amination of phenols. *Nat. Commun.* **2018**, *9*, 4293−4301.

(11) (a) Kingston, C.; Palkowitz, M. D.; Takahira, Y.; Vantourout, J. C.; Peters, B. K.; Kawamata, Y.; Baran, P. S. A Survival Guide for the "Electro-curious. *Acc. Chem. Res.* **2020**, *53*, 72−83. (b) Xiong, P.; Xu, H.-C. Chemistry with Electrochemically Generated N-Centered Radicals. *Acc. Chem. Res.* **2019**, *52*, 3339−3350. (c) Yuan, Y.; Lei, A. Electrochemical Oxidative Cross-Coupling with Hydrogen Evolution Reactions. *Acc. Chem. Res.* **2019**, *52*, 3309−3324. (d) Röckl, J. L.; Pollok, D.; Franke, R.; Waldvogel, S. R. A Decade of Electrochemical Dehydrogenative C,C-Coupling of Aryls. *Acc. Chem. Res.* **2020**, *53*, 45−61. (e) Moeller, K. D. Using Physical Organic Chemistry To Shape the Course of Electrochemical Reactions. *Chem. Rev.* **2018**, *118*, 4817−4833. (f) He, M.-X.; Mo, Z.-Y.; Wang, Z.-Q.; Cheng, S.-Y.; Xie, R.-R.; Tang, H.-T.; Pan, Y.-M. Electrochemical Synthesis of 1-Naphthols by Intermolecular Annulation of Alkynes with 1,3-Dicarbonyl Compounds. *Org. Lett.* **2020**, *22*, 724−728. (g) Jiang, Y.; Xu, K.; Zeng, C. Use of Electrochemistry in the Synthesis of Heterocyclic Structures. *Chem. Rev.* **2018**, *118*, 4485−4540. (h) Wang, P.; Gao, X.; Huang, P.; Lei, A. Recent Advances in Electrochemical Oxidative Cross-Coupling of Alkenes with H_2 Evolution. *ChemCatChem* **2020**, *12*, 27−40. (i) Hu, X.; Nie, L.; Zhang, G.; Lei, A. Electrochemical Oxidative [4 + 2] Annulation for the π-Extension of Unfunctionalized Heterobiaryl Compounds. *Angew. Chem., Int. Ed.* **2020**, *59*, 15238−15243.

(12) (a) Zhao, H.-B.; Hou, Z.-W.; Liu, Z.-J.; Zhou, Z.-F.; Song, J.; Xu, H.-C. Amidinyl Radical Formation through Anodic N-H Bond Cleavage and Its Application in Aromatic C-H Bond Functionalization. *Angew. Chem., Int. Ed.* **2017**, *56*, 587−590. (b) Mo, Z.-Y.; Zhang, Y.-Z.; Huang, G-b.; Wang, X.-Y.; Pan, Y-m.; Tang, H.-T. Electrochemical Sulfonylation of Alkynes with Sulfonyl Hydrazides: A Metal- and Oxidant-Free Protocol for the Synthesis of Alkynyl Sulfones. *Adv. Synth. Catal.* **2020**, *362*, 2160−2167. (c) Wang, X.-Y.; Zhong, Y.-F.; Mo, Z.-Y.; Wu, S.-H.; Xu, Y.-L.; Tang, H.-T.; Pan, Y.-M. Synthesis of Seleno Oxindoles *via* Electrochemical Cyclization of N-arylacrylamides with Diorganyl Diselenides. *Adv. Synth. Catal.* **2021**, *363*, 208.

(13) (a) Jiang, Y-y.; Wang, Q.-Q.; Liang, S.; Hu, L.-M.; Little, R. D.; Zeng, C.-C. Electrochemical Oxidative Amination of Sodium Sulfinates: Synthesis of Sulfonamides Mediated by NH_4I as a Redox Catalyst. *J. Org. Chem.* **2016**, *81*, 4713−4719. (b) Jiang, Y.-Y.; Liang, S.; Zeng, C.-C.; Hu, L.-M.; Sun, B.-G. Electrochemically initiated formation of sulfonyl radicals: synthesis of oxindoles *via* difunctionalization of acrylamides mediated by bromide ion. *Green Chem.* **2016**, *18*, 6311−6319.

(14) (a) Qian, X.-Y.; Li, S.-Q.; Song, J.; Xu, H.-C. TEMPO-Catalyzed Electrochemical C-H Thiolation: Synthesis of Benzothiazoles and Thiazolopyridines from Thioamides. *ACS Catal.* **2017**, *7*, 2730−2734. (b) Cai, C.-Y.; Xu, H.-C. Dehydrogenative reagent-free annulation of alkenes with diols for the synthesis of saturated O-heterocycles. *Nat. Commun.* **2018**, *9*, 3551−3557.

(15) (a) Zhang, Y.-Z.; Mo, Z.-Y.; Wang, H.-S.; Wen, X.-A.; Tang, H.-T.; Pan, Y.-M. Electrochemically enabled chemoselective sulfonylation hydrazination of indoles. *Green Chem.* **2019**, *21*, 3807−3811. (b) Zhong, P.-F.; Lin, H.-M.; Wang, L.-W.; Mo, Z.-Y.; Meng, X.-J.; Tang, H.-T.; Pan, Y.-M. Electrochemically enabled synthesis of sulphide imidazopyridines *via* a radical cyclization cascade. *Green*

https://dx.doi.org/10.1021/acs.joc.1c00012
J. Org. Chem. XXXX, XXX, XXX−XXX

Chem. **2020**, *22*, 6334−6339. (c) Meng, X.-J.; Zhong, P.-F.; Wang, Y.-M.; Wang, H-s.; Tang, H.-T.; Pan, Y-m. Electrochemical Difunctionalization of Olefines: Access to Selen omethyl-Substituted Cyclic Ethers or Lactones. *Adv. Synth. Catal.* **2020**, *362*, 506−511.

(16) (a) Mallick, S.; Baidya, M.; Mahanty, K.; Maiti, D.; Sarkar, S. D. Electrochemical Chalcogenation of *β*,*γ*-Unsaturated Amides and Oximes to Corresponding Oxazolines and Isoxazolines. *Adv. Synth. Catal.* **2020**, *362*, 1046−1052. (b) Wilken, M.; Ortgies, S.; Breder, A.; Siewert, I. Mechanistic Studies on the Anodic Functionalization of Alkenes Catalyzed by Diselenides. *ACS Catal.* **2018**, *8*, 10901−10912. (c) Hua, J.; Fang, Z.; Xu, J.; Bian, M.; Liu, C.; He, W.; Zhu, N.; Yang, Z.; Guo, K. Electrochemical oxidative cyclization of activated alkynes with diselenides or disulfides: access to functionalized coumarins or quinolinones. *Green Chem.* **2019**, *21*, 4706−4711.

(17) (a) Asao, N.; Sato, K.; Yamamoto, Y. $AuBr_3$-catalyzed cyclization of *o*-(alkynyl)nitrobenzenes. Efficient synthesis of isatogens and anthranils. *Tetrahedron Lett.* **2003**, *44*, 5675−5677.

(18) Fu, W.; Yang, K.; Chen, J.; Song, Q. Gold(I)-catalyzed synthesis of 2-substituted indoles from 2-alkynylnitroarenes with diboron as reductant. *Org. Biomol. Chem.* **2017**, *15*, 8354−8360.

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