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1,3-Dipolar Cycloaddition of Nitrile Imine with Carbon Dioxide: Access to 1,3,4-Oxadiazole-2(3*H*)-ones

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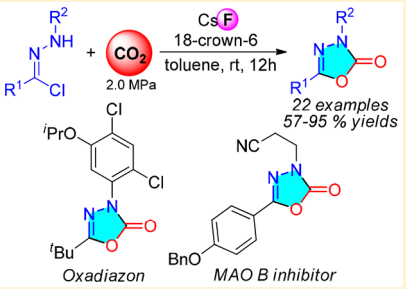
Supporting Information

ABSTRACT: Efficient synthesis of 1,3,4-oxadiazole-2(3*H*)-one was achieved by CsF/18-crown-6 mediated 1,3-dipolar cycloaddition of nitrile imine and 2.0 MPa of CO_2. CsF/18-crown-6 played a key role in enhancing the reactivity of CO_2 as a 1,3-dipolarophile. The practical utility of this transition-metal-free approach to 1,3,4-oxadiazole-2(3*H*)-one is highlighted by the convenient synthesis of a commercial herbicide Oxadiazon and a MAO B inhibitor.



The 1,3,4-oxadiazole-2(3*H*)-one core is a privileged scaffold frequently found in diverse compounds which show many biological and pharmaceutical activities (Figure 1). Oxadiazon

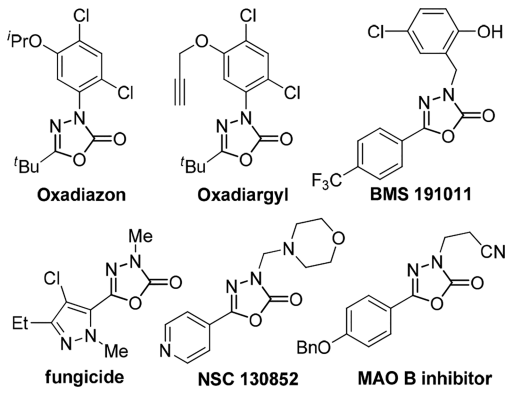


Figure 1. Structures of biologically important substituted 1,3,4-oxadiazole-2(3*H*)-ones.

and Oxadiargyl are commercial and environmentally benign herbicides and still used in agriculture widely. BMS 191011 has been established as an opener of the cloned large-conductance, Ca^{2+}-activated potassium channel.[1] NSC 130852 shows promising antimycobacterial activity.[2] Those compounds also serve as selective monoamine oxidase B (MAO B) inhibitors,[3] fungicides,[4] and a useful synthetic intermediate for other fine chemicals.[5] Although various methods for the construction of substituted 1,3,4-oxadiazole-2(3*H*)-one have been developed, most of these rely on laborious multistep procedures and use phosgene and benzotrichloride.[6] Recently, Chen[7a] and Jiang[7b] reported palladium-catalyzed oxidative carbonylation of acylhydrazines with carbon monoxide to synthesize 1,3,4-oxadiazole-2(3*H*)-ones. Although the use of phosgene was abandoned, this approach showed relatively limited substrate scope and employed expensive transition metal and equivalent metal oxidative reagents. Therefore, the development of more efficient and feasible methods to prepare diversely substituted 1,3,4-oxadiazole-2(3*H*)-ones is highly desirable.

Carbon dioxide (CO_2) as a C1 synthon for chemical synthesis has gained considerable attention because it is an abundant, low-cost, and nontoxic feedstock.[8] Except for using as an electrophile to react with various nucleophiles, CO_2 is also utilized as a cycloaddition partner to construct carbonyl-containing heterocycles. Although transition-metal catalyzed cycloaddition of CO_2 with unsaturated compounds[9] and epoxides[10] has been frequently reported in recent years, studies on 1,3-dipolar cycloaddition reactions[11,12] using CO_2 as a 1,3-dipolarophile have rarely been depicted probably due to the linear arrangement of two C═O bonds in carbon dioxide and its high thermodynamic stability and kinetic inertness. 1,3-Dipolar cycloaddition of nitrile imine with CO_2 was first observed in 1980 by Pfoertner and Foricher in the photoreaction of 3-methyl-4-phenylsydnone.[13] Another example involving nitrile imine and CO_2 was reported by Matsubara's group in 1996,[14] in which just two 1,3,4-oxadiazole-2(3*H*)-one products were synthesized in inapplicable yields (14%−25%) under harsh reaction conditions. The major challenge to make this reaction efficient and practical is the low reactivity of CO_2 toward 1,3-dipoles and fast dimerization of in situ formed nitrile imines.[15] Herein, we reported an efficient CsF/18-crown-6 mediated 1,3-dipolar cycloaddition reaction of nitrile imines with CO_2 to give various 1,3,4-oxadiazole-2(3*H*)-ones in good yield. CsF/18-crown-6 plays a key role in enhancing the reactivity of CO_2 as a 1,3-dipolarophile. The practical utility of this transition-metal-free[16] approach is

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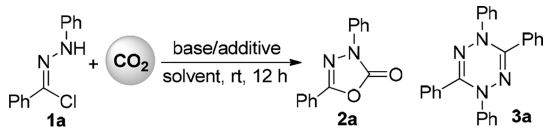
highlighted by the convenient synthesis of a commercial herbicide Oxadiazon and a MAO B inhibitor.

Our studies began by using hydrazonyl chloride as the nitrile imine precursor and subjecting **1a** to stoichiometric amounts of various bases in THF at 25 °C under a 2.0 MPa CO_2 pressure (Table 1). Organic bases used in Matsubara's reaction[13] are not suitable for the present reaction system (entries 1−3). The use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) led to the formation of the dimer **3a**, whereas no desired product **2a** was detected (entry 1). No transformation was observed in the presence of Et_3N (entry 2). 1,4-Diazabicyclo[2.2.2]octane (DABCO) gave very low yield of **2a** (entry 3). The use of Cs_2CO_3 and CsF bases resulted in a slightly improved yield of **2a** (entries 4 and 5). In light of previous reports by Moses[15a] and our group,[17] the combined use of crown ethers and inorganic bases in some base-mediated reactions not only enhances the solubility of the bases in organic solvents but also promotes the formation of reaction intermediates. Cs_2CO_3/18-crown-6 gave almost the same result as Cs_2CO_3 alone (entry 6), while the combination of CsF with 18-crown-6 led to a strikingly increased yield of **2a** (entry 7). The obvious difference between Cs_2CO_3/18-crown-6 and CsF/18-crown-6 implies that the fluorine anion probably accelerated the 1,3-dipolar cycloaddition with CO_2. It was reported by Arnold et al. that the fluorine anion could react with CO_2 to form the $(F-CO_2)^-$ anion, thereby significantly enhancing the reactivity of the C=O bond.[18] This phenomenon was also observed in some reactions involving CO_2.[19] It is noteworthy that the fluorine anion alone was not enough to facilitate this reaction since the combination of KF with 18-crown-6 only gave a 14% yield of **2a**. It is tentatively ascribed to the relatively low basicity of KF, difficultly promoting the formation of nitrile imine (entry 8).

A decrease of the CsF/18-crown-6 amount from 2.5 to 1.2 equiv shut down the reaction (entry 10). Interestingly, the decrease of 18-crown-6 loading alone did not affect the yield of **2a** (entry 11). Among a variety of solvents tested (see Supporting Information (SI)), toluene was revealed to be the optimal solvent (entry 13). Decreasing the temperature to 0 °C resulted in low conversion with a 22% yield of **2a** obtained (entry 14), whereas raising the temperature up to 70 °C gave a 30% yield of **2a** and other unidentified products (entry 15). Under a 1.0 atm CO_2 atmosphere, this reaction also proceeded but a strikingly decreased yield of **2a** was obtained (entry 16). The gram-scale reaction of **1a** gave a 67% yield of **2a**, which demonstrated the utility of this reaction system in preparative-scale syntheses (entry 17).

The substrate scope of 1,3-dipolar cycloaddition of nitrile imine and CO_2 under the optimized reaction conditions was investigated (Scheme 1). A series of hydrazonyl chlorides bearing electron-withdrawing (fluoro, chloro, bromo) and electron-donating (methyl, methoxyl, *tert*-butyl) substituents on the benzoyl chloride moiety were investigated for the cycloaddition with CO_2 and smoothly afforded the corresponding 1,3,4-oxadiazole-2(3*H*)-ones in good yields (**2b**−**2g**). The structural assignment for these products was further confirmed by a single-crystal X-ray analysis of **2f**.[20] *β*-Naphthyl, furan, and thiophene groups were also found to be compatible

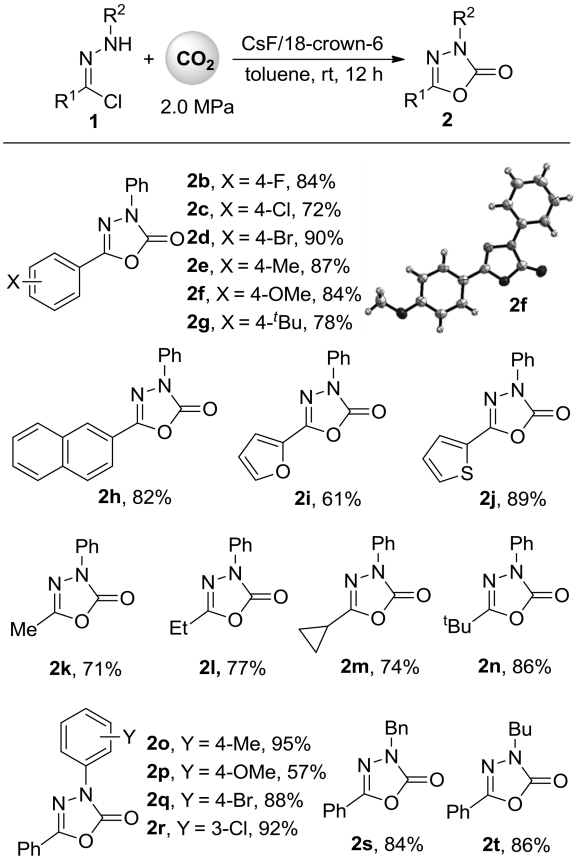
Table 1. Optimization of the Reaction Conditions[a]



entry	base/additive (equiv)	solvent	yield 2a	yield 3a
1	DBU (2.5)	THF	<1[b]	9
2	Et_3N (2.5)	THF	<1[b]	<1[b]
3	DABCO (2.5)	THF	3[b]	8
4	Cs_2CO_3 (2.5)	THF	25	13
5	CsF (2.5)	THF	20	10
6	Cs_2CO_3/18-crown-6 (2.5/2.5)	THF	27	7
7	CsF/18-crown-6 (2.5/2.5)	THF	85	12
8	KF/18-crown-6 (2.5/2.5)	THF	14	<1[b]
9	CsF/18-crown-6 (2.0/2.0)	THF	60	9
10	CsF/18-crown-6 (1.2/1.2)	THF	3[b]	<1[b]
11	CsF/18-crown-6 (2.5/1.2)	THF	85	12
12	CsF/18-crown-6 (2.5/0.4)	THF	70	10
13	CsF/18-crown-6 (2.5/1.2)	toluene	89	5
14[c]	CsF/18-crown-6 (2.5/1.2)	toluene	22	<1[b]
15[d]	CsF/18-crown-6 (2.5/1.2)	toluene	30	19
16[e]	CsF/18-crown-6 (2.5/1.2)	toluene	11	<1[b]
17[f]	CsF/18-crown-6 (2.5/1.2)	toluene	65	18

[a]Reaction conditions: **1a** (0.2 mmol), CO_2 (2.0 MPa), solvent (2 mL), 25 °C, 12 h. Isolated yield is given according to the average of two runs. [b]Yields were determined by NMR using 1,1,2,2-tetrachloroethane as an internal standard. [c]0 °C. [d]70 °C. [e]1.0 atm of CO_2. [f]**1a** (4.5 mmol, 1.04g), toluene (40 mL).

Scheme 1. Substrate Scope[a]



[a]**1** (0.2 mmol), CsF (0.5 mmol), 18-crown-6 (0.24 mmol), CO_2 (2.0 MPa), toluene (2 mL), 25 °C, 12 h. Isolated yield.

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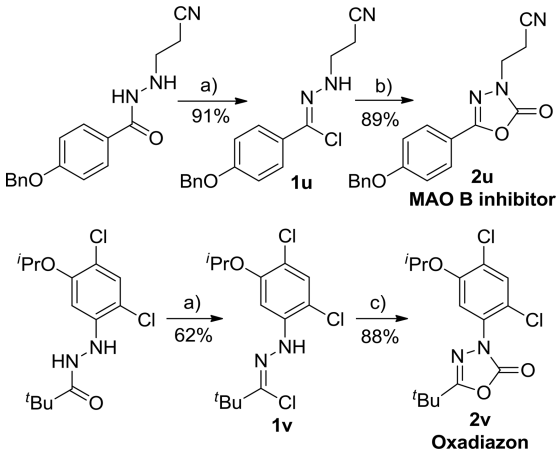
functionalities for this reaction (**2h**−**2j**). The methyl, ethyl, cyclopropyl, and even sterically hindered *tert*-butyl substituted hydrazonyl chloride also provided the corresponding products (**2k**−**2n**) in good yields. Hydrazonyl chlorides containing methyl, bromo, and chloro substituents on phenylhydrazone moiety participated in the reaction successfully to afford the desired products (**2o**, **2q**, **2r**) in excellent yields. Except for the arylhydrazones, substrates derived from benzylhydrazine (**1s**) and butylhydrazine (**1t**) were also suitable substrates for this reaction.

With easy accessibility of the raw material, broad substrate scope, and high efficiency, this reaction system would provide a concise and feasible access to valuable compounds containing the 1,3,4-oxadiazole-2(3*H*)-one skeleton. The reversible MAO B inhibitor **2u**,[3] which is considered as a potential drug applied to clinical therapy at the early stage of Parkinson's disease, was obtained in 89% isolated yield via 1,3-dipolar cycloaddition of **1u** and CO_2 (Scheme 2). The commercial herbicide Oxadiazon **2v** was also successfully synthesized through this efficient cycloaddition reaction system in 88% isolated yield (Scheme 2).

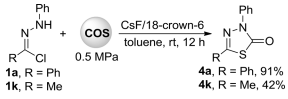
Scheme 2. Synthesis of MAO B Inhibitor 2u and Oxadiazon 2v



[a]PPh_3/CCl_4, MeCN, rt, 12 h. [b]Standand reaction conditions, 4 mL toluene. [c]Standand reaction conditions, 24 h.

Considering carbonyl sulfide (COS) is an analogue of carbon dioxide, the 1,3-dipolar cycloaddition of nitrile imine with COS was also carried out. Under the standard reaction conditions for CO_2, nitrile imine precursors **1a** and **1k** reacted with 0.5 MPa of COS smoothly to afford 1,3,4-thiadiazol-2(3*H*)-one compounds **4a** and **4k** respectively (Scheme 3).

Scheme 3. 1,3-Dipolar Cycloaddition of Nitrile Imine with Carbonyl Sulphide



To demonstrate the pivotal role of CsF and 18-crown-6 in promoting the 1,3-dipolar cycloaddition, some control experiments were carried out using the NMR method (see SI). When Cs_2CO_3 was added to the toluene-d_8 solution of **1k**, a signal for nitrile imine was observed and the dimer was immediately formed. When CsF was added to the toluene-d_8 solution of **1k**, no obvious signals for nitrile imine and the dimer were found. The addition of 18-crown-6 to the above-mentioned systems evidently enhanced the formation of nitrile imine and the dimer in the absence of CO_2. Both Cs_2CO_3/18-crown-6 and CsF/18-crown-6 systems could effectively produce the nitrile imine intermediate, but only CsF/18-crown-6 led to the high efficiency for the 1,3-dipolar cycloaddition reaction, suggesting that CsF/18-crown-6 played a key role in enhancing the reactivity of CO_2 as a 1,3-dipolarophile.

In summary, we have developed an efficient, transition-metal-free and practical access to a broad range of substituted 1,3,4-oxadiazole-2(3*H*)-ones via 1,3-dipolar cycloaddition of nitrile imine and CO_2. The key to the success of this transformation is the use of CsF as a base and 18-crown-6 as a pivotal additive to enhance the formation of a nitrile imine intermediate. CsF/18-crown-6 played a key role in enhancing the reactivity of CO_2 as a 1,3-dipolarophile. This approach was successfully applied in the convenient synthesis of a commercial herbicide Oxadiazon and a MAO B inhibitor.

EXPERIMENTAL SECTION

General Information. Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under a dry nitrogen or carbon dioxide atmosphere. DMF and DMAc were distilled under a N_2 atmosphere with CaH_2. CH_3CN and DCE were distilled with P_2O_5. THF, DME, Et_2O, 1, 4-dioxane, and toluene were distilled from sodium/benzophenone. All of the solvents were stored over 4 Å molecular sieves before use. Column chromatography was performed on silica gel (200−300 mesh). Thin layer chromatography was performed on 0.20 mm GF254 plates. Visualization was accomplished with UV light (254 nm). 18-crown-6 was recrystallized in CH_3CN. Unless otherwise indicated, carbon dioxide (99.999%) and carbonyl sulfide (99%) were used without further purification.

NMR spectra were recorded on a 400 or 500 M (^{1}H NMR, 400 or 500 MHz; ^{13}C NMR, 101 or 126 MHz) spectrometer in $CDCl_3$ at ambient temperature, and chemical shifts are expressed in parts per million (δ, ppm). Proton chemical shifts are referenced to 7.26 ppm ($CHCl_3$), and carbon chemical shifts are referenced to 77.0 ppm ($CDCl_3$). The data reported use the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; hept, heptet, and *J*, coupling constant in Hz. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry equipped with a Z-spray ionization source. Infrared spectra (IR) were measured using a Nicolet NEXUS FT-IR spectrophotometer.

Substrates **1** were prepared according to the reported procedures.[21]

General Procedure for the Reaction of Hydrazonyl Chloride with CO_2 or COS. A 20 mL oven-dried autoclave containing a stir bar was charged with hydrazonyl chloride **1** (0.20 mmol), 18-crown-6 (63.4 mg, 1.2 equiv), CsF (76.0 mg, 2.5 equiv), and 2.0 mL of toluene in a glovebox. After removal from the glovebox, the autoclave was purged with CO_2 (or COS) three times and then pressurized to 2.0 MPa CO_2 (or 0.5 MPa COS). The reaction mixture was stirred at room temperature (25 °C) for 12 h. Then the remaining gas was vented slowly. The reaction mixture was diluted with water (15 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, and evaporated under vacuum. The product was isolated by column chromatography on silica gel (petroleum ether−ethyl acetate = 40:1 to 1:1).

3,5-Diphenyl-1,3,4-oxadiazol-2(3H)-one (**2a**)[7] *[CAS 19226-10-9].* White solid (42.5 mg, 89% yield). R_f = 0.4 (EtOAc/petroleum ether = 1:30). Mp 109−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.95 (m, 4H), 7.56−7.46 (m, 5H), 7.29 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 150.7, 136.1, 131.9, 129.2 (2C), 129.1 (2C), 126.2, 126.0 (2C), 123.5, 118.4 (2C). IR (neat): ν 3422, 2912, 1779, 1355, 732, 679 cm^{-1}. HRMS (ESI, *m*/*z*): calculated for $C_{14}H_{10}N_2O_2Na$ [M + Na]$^+$, 261.0634; found, 261.0627.

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5-(4-Fluorophenyl)-3-phenyl-1,3,4-oxadiazol-2(3H)-one (**2b**)[7] *[CAS 1643432-85-2].* White solid (43.0 mg, 84%). R_f = 0.3 (EtOAc/petroleum ether = 1:40). Mp 139−140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.93 (m, 4H), 7.48 (dd, J = 8.0, 7.4 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 7.24−7.19 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 163.9, 151.7 (d, J = 284.5 Hz), 136.0, 129.2 (2C), 128.3 (d, J = 8.9 Hz) (2C), 126.2, 119.8 (d, J = 3.3 Hz), 118.3 (2C), 116.5 (d, J = 22.4 Hz) (2C). ^{19}F NMR (377 MHz, $CDCl_3$) δ −106.6 (s). IR (neat): ν 2921, 1783, 1357, 842, 741 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{14}H_{10}FN_2O_2$ [M + H] $^+$, 257.0721; found, 257.0726.

5-(4-Chlorophenyl)-3-phenyl-1,3,4-oxadiazol-2(3H)-one (**2c**)[7a] *[CAS 1643432-87-4].* White solid (39.2 mg, 72% yield). R_f = 0.3 (EtOAc/petroleum ether = 1:40). Mp 118−119 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.50−7.47 (m, 4H), 7.29 (t, J = 7.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 150.5, 138.3, 136.0, 129.5 (2C), 129.2 (2C), 127.2 (2C), 126.3, 122.0, 118.3 (2C). IR (neat): ν 2922, 1779, 1354, 830, 748 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{14}H_9ClN_2O_2Na$ [M + Na] $^+$, 295.0245; found, 295.0239.

5-(4-Bromophenyl)-3-phenyl-1,3,4-oxadiazol-2(3H)-one (**2d**)[7a] *[CAS 1643432-89-6].* White solid (57.0 mg, 90% yield). R_f = 0.3 (EtOAc/petroleum ether = 1:30). Mp 123−124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 7.48 (dd, J = 8.0, 7.4 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 150.5, 135.9, 132.5 (2C), 129.3 (2C), 127.4 (2C), 126.7, 126.3, 122.4, 118.4 (2C). IR (neat): ν 2917, 1770, 1404, 1355, 1070, 735 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{14}H_{10}BrN_2O_2$ [M + H] $^+$, 316.9920; found, 316.9928.

5-(4-Methylphenyl)-3-phenyl-1,3,4-oxadiazol-2(3H)-one (**2e**)[7] *[CAS 73634-97-6].* White solid (43.8 mg, 87% yield). R_f = 0.2 (EtOAc/petroleum ether = 1:30). Mp 155−156 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.47 (dd, J = 8.0, 7.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.27 (t, J = 7.4 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 150.8, 142.6, 136.2, 129.8 (2C), 129.2 (2C), 126.1, 126.0 (2C), 120.7, 118.3 (2C), 21.7. IR (neat): ν 3290, 1725, 1658, 1339, 742 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{15}H_{13}N_2O_2$ [M + H] $^+$, 253.0972; found, 253.0974.

5-(4-Methoxyphenyl)-3-phenyl-1,3,4-oxadiazol-2(3H)-one (**2f**)[7] *[CAS 1643432-84-1].* White solid (45.0 mg, 84% yield). R_f = 0.2 (EtOAc/petroleum ether = 1:30). Mp 131−133 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.7 Hz, 2H), 7.47 (dd, J = 8.0, 7.4 Hz, 2H), 7.27 (t, J = 7.4 Hz, 1H), 7.01 (d, J = 8.7 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5, 153.6, 150.8, 136.2, 129.2 (2C), 127.8 (2C), 126.0, 118.3 (2C), 115.9, 114.5 (2C), 55.5. IR (neat): ν 2919, 1769, 1356, 829, 741 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{15}H_{13}N_2O_3$ [M + H] $^+$, 269.0921; found, 269.0920.

5-(4-tert-Butylphenyl)-3-phenyl-1,3,4-oxadiazol-2(3H)-one (**2g**). Brown oil (45.9 mg, 78% yield). R_f = 0.4 (EtOAc/petroleum ether = 1:40). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.2 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.47 (dd, J = 8.2, 7.6 Hz, 2H), 7.28 (t, J = 7.6 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 153.8, 150.8, 136.2, 129.2 (2C), 126.1 (2C), 126.0, 125.9 (2C), 120.6, 118.4 (2C), 35.1, 31.1 (3C). IR (neat): ν 3429, 2964, 1784, 1592, 1371, 966, 751 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{18}H_{19}N_2O_2$ [M + H]$^+$, 295.1441; found, 295.1439.

5-(2-Naphthyl)-3-phenyl-1,3,4-oxadiazol-2(3H)-one (**2h**). White solid (47.3 mg, 82% yield). R_f = 0.2 (EtOAc/petroleum ether = 1:40). Mp 140−142 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.97−7.84 (m, 6H), 7.57−7.54 (m, 2H), 7.47 (dd, J = 7.8, 7.4 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.7, 150.7, 136.1, 134.7, 132.7, 129.2 (2C), 129.0, 128.9, 128.1, 128.0, 127.2, 126.8, 126.1, 121.8, 120.6, 118.3 (2C). IR (neat): ν 2922, 1775, 1498, 1263, 747 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{18}H_{13}N_2O_2$ [M + H] $^+$, 289.0972; found, 289.0971.

5-(2-Furyl)-3-phenyl-1,3,4-oxadiazol-2(3H)-one (**2i**) *[CAS 1628570-35-3].* Brown solid (27.8 mg, 61% yield). R_f = 0.3 (EtOAc/petroleum ether = 1:40). Mp 96−98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.58 (s, 1H), 7.39 (dd, J = 8.0, 7.6 Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 3.4 Hz, 1H), 6.54−6.53 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 147.0, 146.0, 138.7, 135.9, 129.2 (2C), 126.3, 118.4 (2C), 114.5, 112.1. IR (neat): ν 2922, 1773, 1497, 1368, 955, 763, 688 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{12}H_9N_2O_3$ [M + H] $^+$, 229.0608; found, 229.0603.

3-Phenyl-5-(2-thienyl)-1,3,4-oxadiazol-2(3H)-one (**2j**)[7a] *[CAS 1628570-34-2].* Brown solid (43.5 mg, 89% yield). R_f = 0.2 (EtOAc/petroleum ether = 1:40). Mp 135−137 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 3.6 Hz, 1H), 7.56 (d, J = 5.0 Hz, 1H), 7.46 (dd, J = 8.0, 7.6 Hz, 2H), 7.27 (t, J = 7.6 Hz, 1H), 7.16 (dd, J = 5.0, 3.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 150.1, 135.9, 130.2, 129.8, 129.2 (2C), 128.1, 126.2, 125.0, 118.3 (2C). IR (neat): ν 2922, 1789, 1471, 1090, 946, 752, 684 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{12}H_9N_2O_2S$ [M + H] $^+$, 245.0379; found, 245.0371.

5-Methyl-3-phenyl-1,3,4-oxadiazol-2(3H)-one (**2k**) *[CAS 28740-63-8].* Colorless solid (27.1 mg, 77% yield). R_f = 0.2 (EtOAc/petroleum ether = 1:40). Mp 73−75 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.43 (dd, J = 8.0, 7.6 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 151.1, 136.0, 129.1 (2C), 125.9, 118.1 (2C), 12.1. IR (neat): ν 2923, 1766, 1500, 1376, 1134, 954, 757, 686 cm^{-1}. HRMS (ESI, m/z): calculated for $C_9H_9N_2O_2$ [M + H] $^+$, 177.0659; found, 177.0656.

5-Ethyl-3-phenyl-1,3,4-oxadiazol-2(3H)-one (**2l**) *[CAS 28669-40-1].* White solid (27.0 mg, 71% yield). R_f = 0.4 (EtOAc/petroleum ether = 1:40). Mp 56−58 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 2H), 7.43 (dd, J = 8.0, 7.6 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 2.68 (q, J = 7.4 Hz, 2H), 1.34 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 151.2, 136.1, 129.1 (2C), 125.9, 118.1 (2C), 20.0, 9.6. IR (neat): ν 2960, 1783, 1501, 1015, 932, 748 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{10}H_{11}N_2O_2$ [M + H]$^+$, 191.0815; found, 191.0812.

5-Cyclopropyl-3-phenyl-1,3,4-oxadiazol-2(3H)-one (**2m**). Mp 78−79 °C, white solid (29.9 mg, 74% yield). R_f = 0.4 (EtOAc/petroleum ether = 1:40). Mp 78−79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.42 (dd, J = 8.0, 7.4 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 1.96−1.90 (m, 1H), 1.12−1.09 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 150.8, 136.1, 129.1 (2C), 125.8, 118.1 (2C), 7.1, 7.0 (2C). IR (neat): ν 2922, 1783, 1495, 1017, 729 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{11}H_{11}N_2O_2$ [M + H]$^+$, 203.0815; found, 203.0815.

5-tert-Butyl-3-phenyl-1,3,4-oxadiazol-2(3H)-one (**2n**)[14] *[CAS 1739-74-8].* Colorless oil (37.1 mg, 85% yield). R_f = 0.3 (EtOAc/petroleum ether = 1:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.8 Hz, 2H), 7.43 (dd, J = 7.8, 7.4 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8, 151.3, 136.1, 129.1 (2C), 125.8, 118.1 (2C), 32.8, 27.0 (3C). IR (neat): ν 2922, 1781, 1499, 1370, 1130, 966, 754 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{12}H_{15}N_2O_2$ [M + H]$^+$, 219.1128; found, 219.1124.

3-(4-Methylphenyl)-5-phenyl-1,3,4-oxadiazol-2(3H)-one (**2o**) *[CAS 528585-43-5].* White solid (28.7 mg, 57% yield). R_f = 0.2 (EtOAc/petroleum ether = 1:30). Mp 147−149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.92 (m, 2H), 7.81 (d, J = 8.2 Hz 2H), 7.54−7.47 (m, 3H), 7.26 (d, J = 8.2 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 150.8, 136.0, 133.7, 131.8, 129.7 (2C), 129.0 (2C), 125.9 (2C), 123.6, 118.4 (2C), 21.0. IR (neat): ν 2921, 1782, 1515, 1356, 813, 683 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{15}H_{13}N_2O_2$ [M + H]$^+$, 253.0972; found, 253.0970.

3-(4-Methoxyphenyl)-5-phenyl-1,3,4-oxadiazol-2(3H)-one (**2p**). White solid (50.9 mg, 95% yield). R_f = 0.2 (EtOAc/petroleum ether = 1:30). Mp 142−144 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.6 Hz, 2H), 7.83 (d, J = 9.0 Hz, 2H), 7.56−7.49 (m, 3H), 6.99 (d, J = 9.0 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 153.4, 150.9, 131.8, 129.4, 129.0 (2C), 125.9 (2C), 123.6, 120.3 (2C), 114.4 (2C), 55.6. IR (neat): ν 3420, 2919, 1768, 1513, 818 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{15}H_{13}N_2O_3$ [M + H]$^+$, 269.0921; found, 269.0915.

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*3-(4-Bromophenyl)-5-phenyl-1,3,4-oxadiazol-2(3H)-one (**2q**)*[7b] *[CAS 1778703-73-3].* Brown solid (55.8 mg, 88% yield). R_f = 0.4 (EtOAc/petroleum ether = 1:40). Mp 140−142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.8 Hz, 2H), 7.87−7.85 (m, 2H), 7.60−7.49 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 150.4, 135.2, 132.3 (2C), 132.2, 129.1 (2C), 126.0 (2C), 123.3, 119.7 (2C), 119.3. IR (neat): ν 2922, 1782, 1489, 1353, 733 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{14}H_{10}N_2O_2Br$ $[M + H]^+$, 316.9920; found, 316.9913.

*3-(3-Chlorophenyl)-5-phenyl-1,3,4-oxadiazol-2(3H)-one (**2r**).* White solid (50.2 mg, 92% yield). R_f = 0.3 (EtOAc/petroleum ether = 1:40). Mp 119−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, J = 2.0 Hz, 1H), 7.96−7.94 (m, 2H), 7.91−7.89 (m, 1H), 7.57−7.50 (m, 3H), 7.40 (t, J = 8.2 Hz, 1H), 7.27−7.24 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 150.4, 137.0, 135.1, 132.2, 130.3, 129.1 (2C), 126.13, 126.06 (2C), 123.2, 118.3, 116.0. IR (neat): ν 2921, 1779, 1353, 983, 731 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{14}H_9N_2O_2ClNa$ $[M + Na]^+$, 295.0245; found, 295.0244.

*3-Benzyl-5-phenyl-1,3,4-oxadiazol-2(3H)-one (**2s**)*[22] *[CAS 27643-12-5].* White solid (43.3 mg, 86% yield). R_f = 0.4 (EtOAc/petroleum ether = 1:10). Mp 118−119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.81 (m, 2H), 7.50−7.31 (m, 8H), 4.95 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 153.3, 134.9, 131.5, 128.9 (2C), 128.8 (2C), 128.34, 128.28 (2C), 125.7 (2C), 123.8, 49.7. IR (neat): ν 3309, 1766, 1355, 1018, 775, 731 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{15}H_{13}N_2O_2$ $[M + H]^+$, 253.0972; found, 253.0971.

*3-Butyl-5-phenyl-1,3,4-oxadiazol-2(3H)-one (**2t**)*[23] *[CAS 41125-98-8].* Colorless solid (36.6 mg, 84% yield). R_f = 0.4 (EtOAc/petroleum ether = 1:10). Mp 41−43 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 6.4 Hz, 2H), 7.52−7.44 (m, 3H), 3.80 (t, J = 7.2 Hz, 2H), 1.83−1.76 (m, 2H), 1.46−1.37 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 153.1, 131.4, 128.9 (2C), 125.5 (2C), 123.9, 45.7, 30.2, 19.6, 13.5. IR (neat): ν 2957, 2357, 1780, 1358, 1018, 739 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{12}H_{15}N_2O_2$ $[M + H]^+$, 219.1128; found, 219.1123.

*5-(4-Benzoxylphenyl)-3-(2-cyanoethyl)-1,3,4-oxadiazol-2(3H)-one (**2u**)*[3a] *[CAS 147807-20-3].* White solid (57.1 mg, 89% yield). R_f = 0.5 (EtOAc/petroleum ether = 1:1). Mp 151−153 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.9 Hz, 2H), 7.44−7.39 (m, 4H), 7.37−7.34 (m, 1H), 7.05 (d, J = 8.9 Hz, 2H), 5.13 (s, 2H), 4.09 (t, J = 6.9 Hz, 2H), 2.88 (t, J = 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7, 154.1, 153.0, 136.0, 128.7 (2C), 128.3 (2C), 127.7, 127.5 (2C), 116.2, 116.0, 115.4 (2C), 70.2, 41.5, 17.1. IR (neat): ν 3362, 2912, 2244, 1769, 1609, 1242, 998, 838, 743 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{18}H_{16}N_3O_3$ $[M + H]^+$, 322.1186; found, 322.1184.

*5-tert-Butyl-3-(2,4-dichloro-5-isopropoxyphenyl)-1,3,4-oxadiazol-2(3H)-one (**2v**) [CAS 19666-30-9].* White solid (60.9 mg, 88% yield). R_f = 0.3 (EtOAc/petroleum ether = 1:40). Mp 87−89 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.03 (s, 1H), 4.59−4.52 (m, 1H), 1.39 (d, J = 6.1 Hz, 6H), 1.37 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.5, 153.0, 152.2, 131.4, 131.3, 126.1, 123.1, 114.9, 73.0, 32.9, 27.0 (3C), 21.8 (2C). IR (neat): ν 2964, 1788, 1488, 1249, 1123, 1037, 748 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{15}H_{19}Cl_2N_2O_3$ $[M + H]^+$, 345.0767; found, 345.0773.

*3,5-Diphenyl-1,3,4-thiadiazol-2(3H)-one (**4a**) [CAS 62353-94-0].* White solid (46.2 mg, 91% yield). R_f = 0.4 (EtOAc/petroleum ether = 1:40). Mp 90−92 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 8.4 Hz, 2H), 7.77−7.75 (m, 2H), 7.49−7.46 (m, 5H), 7.33 (t, J = 7.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 150.5, 138.0, 131.1, 130.5, 129.03 (2C), 129.00 (2C), 127.0, 126.1 (2C), 121.8 (2C). IR (neat): ν 3360, 2921, 1685, 1487, 1261, 750, 685 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{14}H_{11}N_2OS$ $[M + H]^+$, 255.0587; found, 255.0586.

*5-Methyl-3-phenyl-1,3,4-thiadiazol-2(3H)-one (**4k**).* Colorless oil (16.1 mg, 42% yield). R_f = 0.4 (EtOAc/petroleum ether = 1:30). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.6 Hz, 2H), 7.43 (dd, J = 7.6, 7.4 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 149.0, 137.9, 129.0 (2C), 126.9, 121.7 (2C), 18.3. IR (neat): ν 3360, 2924, 1696, 1492, 1261, 801, 691 cm^{-1}. HRMS (ESI, m/z): calculated for $C_9H_9N_2OS$ $[M + H]^+$, 193.0430; found, 193.0431.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00963.

Control experiments using ^{1}H NMR; copies of ^{1}H and ^{13}NMR spectra of all products (PDF)

X-ray crystallographic data for compound **2f** (CIF)

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Notes

The authors declare no competing financial interest.

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