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Note

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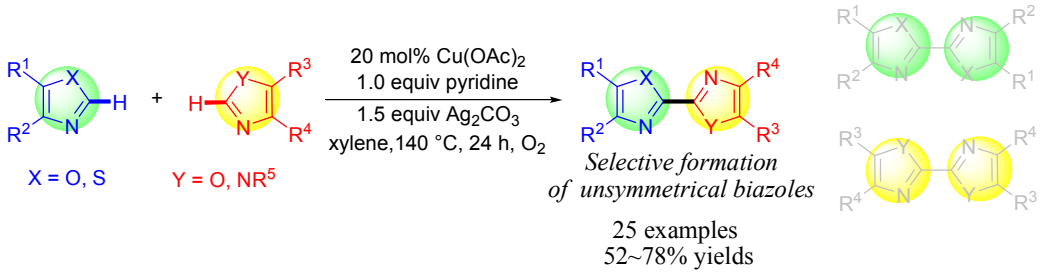


ABSTRACT: The copper(II)-catalyzed dehydrogenative coupling between two different azoles for the preparation of unsymmetrical biazoles has been developed. The current catalytic system can effectively control the chemoselectivity for hetero-coupling over homo-coupling.

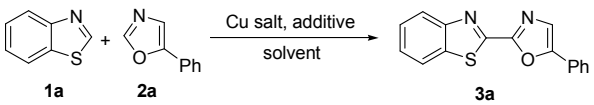
Transition metal-catalyzed cross-coupling reactions of nucleophiles (organometallic reagents and hydrocarbons) with electrophiles (organohalides or surrogates) are powerful synthetic tools to construct carbon-carbon (C–C) bonds and have made significant progress over the past decades.[1,2] However, from the viewpoint of synthetic simplicity and efficiency, atom economy and sustainable chemistry, direct dehydrogenative coupling through the cleavage of two C–H bonds would be one of the most ideal approaches for forming

(hetero)aryl–(hetero)aryl bonds, which avoids prefunctionalization of both of substrates prior to the coupling reaction.[3] In recent years, a number of examples of dehydrogenative cross-coupling, including between arene and arene,[4] between heteroarene and arene,[5] and between heteroarene and heteroarene,[6] have been reported. Nevertheless, some formidable challenges still remain to be overcome in this area, including a competition between cross-coupling and homo-coupling. In general, the three tactics may be used to achieve such a chemoselectivity: 1) the use of two (hetero)arenes with distinctly different electronic characteristics; 2) the chelation-directed strategy; and 3) the utilization of an excessive amount of one of the coupling components (up to 40–100 equivalents).

Imidazoles, oxazoles and thiazoles are a class of privileged structural motifs in bioactive natural products, pharmaceuticals, and organic functional materials, and their functionalization has recently attracted extensive attention. Ofial and co-workers developed the palladium(II)-catalyzed dehydrogenative cross-coupling of benzazoles with azoles by using 1.5 equiv of one of coupling components.[6d] Recently, we reported that the palladium(II)-catalytic system could give a high level of selectivity of cross-coupling between two structurally similar azoles even when the ratio of two partners is 1: 1.[6b] While the copper-catalytic systems effectively promote homo-coupling of azoles,[7] however, the copper-catalyzed cross-coupling reactions between two different azoles with high cross-coupling selectivity have not been reported yet. Herein, we describe for the first time a copper-catalytic dehydrogenative cross-coupling between two azoles with high chemoselectivity.

The dehydrogenative coupling reactions between two different azoles were carried out at a ratio of 1: 1. The investigation started with the coupling of benzothiazole and 5-phenyloxazole in the presence of $Cu(OAc)_2$ by using Ag_2CO_3 as the oxidant, and the cross-coupling product **3a** was obtained in 65% yield in xylene for 24 h at 140 °C (Table 1, entry 1). The negative effect was observed when an extra base such as Na_2CO_3 or *t*-BuOLi was employed (Table 1, entries 2-4). In controlled experiments, none or trace of cross-coupling product was observed in the absence of $Cu(OAc)_2$ or Ag_2CO_3 (Table 1, entries 5, 6). Further improvement of the reaction efficiency was achieved when pyridine (1.0 equiv) was introduced as an additive, and **3a** was obtained in 76% isolated yield (Table 1, entry 7). When 40 mol% of pyridine was used, the yield of **3a** decreased from 76% to 70% (Table 1, entry 8). Subsequently, other copper salts (i.e., $Cu(OTf)_2$, $CuCl_2$, and $Cu(acac)_2$) were found to lead to lower catalytic efficiency (Table 1, entries 9-11). After screening a series of solvents, xylene turned out to be the best choice (Table 1, entries 7, 12-15). In addtion, shortening reaction time, and decreasing reaction temperature could significantly diminish yields (Table 1, entries 17-18). Thus, the optimal reaction condition was obtained when 20 mol% of $Cu(OAc)_2$ was employed in combination with Ag_2CO_3 (1.5 equiv), pyridine (1.0 equiv) in xylene at 140 °C for 24 h under oxygen atmosphere.

Table 1. Optimization of the Dehydrogenative Cross-Coupling of Benzothiazole with 5-Phenyloxazole[a]



1a 2a 3a

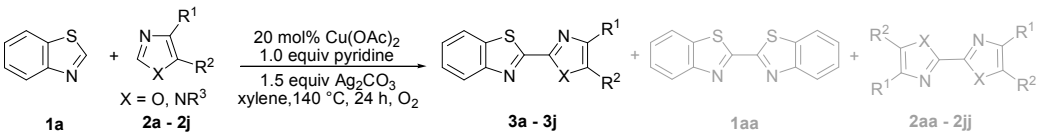
entry	Cu source	base	oxidant	additive	solvent	yield (%)[b]
1	$Cu(OAc)_2$	-	Ag_2CO_3	-	xylene	65
2	$Cu(OAc)_2$	*t*-BuOLi	-	-	xylene	42
3	$Cu(OAc)_2$	Na_2CO_3	-	-	xylene	trace
4	$Cu(OAc)_2$	*t*-BuOLi	Ag_2CO_3	-	xylene	47
5	$Cu(OAc)_2$	-	-	-	xylene	trace
6	-	-	Ag_2CO_3	-	xylene	n.d
7	$Cu(OAc)_2$	-	Ag_2CO_3	pyridine	xylene	76
8[c]	$Cu(OAc)_2$	-	Ag_2CO_3	pyridine	xylene	70
9	$Cu(OTf)_2$	-	Ag_2CO_3	pyridine	xylene	27
10	$CuCl_2$	-	Ag_2CO_3	pyridine	xylene	35
11	$Cu(acac)_2$	-	Ag_2CO_3	pyridine	xylene	46
12	$Cu(OAc)_2$	-	Ag_2CO_3	pyridine	toluene	70
13	$Cu(OAc)_2$	-	Ag_2CO_3	pyridine	dioxane	46
14	$Cu(OAc)_2$	-	Ag_2CO_3	pyridine	DCE	56
15	$Cu(OAc)_2$	-	Ag_2CO_3	pyridine	DMF	65
16	$Cu(OAc)_2$	-	Ag_2CO_3	PivOH	xylene	trace
17[d]	$Cu(OAc)_2$	-	Ag_2CO_3	pyridine	xylene	60
18[e]	$Cu(OAc)_2$	-	Ag_2CO_3	pyridine	xylene	55
19[f]	$Cu(OAc)_2$	-	Ag_2CO_3	pyridine	xylene	53
20[g]	$Cu(OAc)_2$	-	Ag_2CO_3	pyridine	xylene	56
21[h]	$Cu(OAc)_2$	-	Ag_2CO_3	pyridine + TEMPO	xylene	76

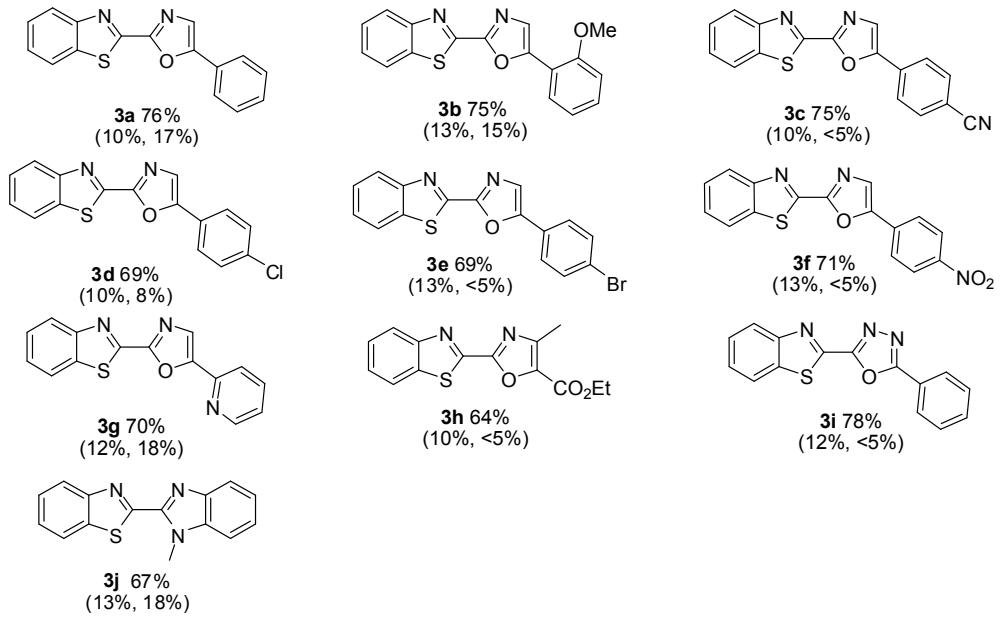
[a] Reactions were carried out using Cu salt (20 mol%), base (1.5 equiv), oxidant (1.5 equiv) additive (1.0 equiv), benzothiazole (0.25 mmol), 5-phenyloxazole (0.25 mmol) and solvent (1.0 mL) at 140 °C for 24 hours under oxygen atmosphere. [b] Yield of isolated product. [c] pyridine (40 mol%). [d] for 12 hours. [e] at 120 °C. [f] under air atmosphere. [g] under N_2 atmosphere. [h] TEMPO (1.0 equiv). DMF = dimethyl formamide. DCE = 1,2-dichloroethane. TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy.

Subsequently, the dehydrogenative cross-couplings of benzothiazole **1a** with various oxazoles were conducted under the optimized conditions (Table 2; for details, see Table S1). It was found that benzothiazole could react with a relatively broad range of oxazoles to afford the cross-coupling products with the C2/C2'-selectivity in satisfactory yields. The substituents on a benzene ring of aryl-substituted oxazoles **2** had a negligible effect on the cross-coupling reactions (Table 2, **3a-f**). Chloro and bromo substituents on the aromatic ring were tolerant

in this catalytic system, which could be subjected to further synthetic transformations (Table 2, **3d-e**). 5-(Pyridin-2-yl)-oxazole could undergo the coupling reaction to provide **3g** in 70% yield. In addition, the catalytic system was also suitable for other azoles (e.g., ethyl 4-methyloxazole-5-carboxylate, 2-phenyl-1,3,4-oxadiazole, and 1-methyl-1H-benzimidazole) (Table 2, **3h-j**).

Table 2. Selective Cross-Couplings of Benzothiazole with Azoles[a,b,c]



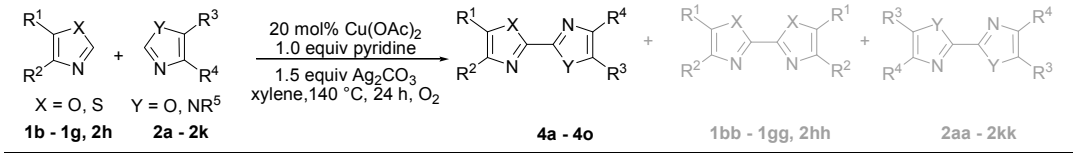


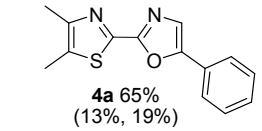
[a] Reactions were carried out using $Cu(OAc)_2$ (20 mol%), Ag_2CO_3 (1.5 equiv), pyridine (1.0 equiv), benzothiazole (0.5 mmol), and azole **2** (0.5 mmol) at 140 °C for 24 h under oxygen atmosphere. [b] Yields of isolated product. The yields in parentheses refer to the homocoupling products of benzothiazole (**1a**) and azole **2**, respectively. [c] For the detailed structure information of compounds, see Table S1.

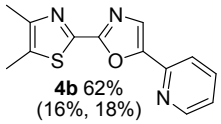
The optimized conditions could be further extended to the reactions between two non-benzofused azoles (Table 3; for details, see Table S2). A variety of thiazole, oxazole, imidazole derivatives were coupled to each other in acceptable yields. In comparison with the reactions between benzothiazole with azoles, the

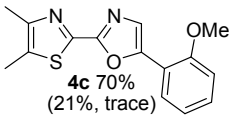
homo-coupling tendency between two non-benzofused azoles was slightly increased probably due to the least difference in π-electronic characteristics. As illustrated in Table 3, 4,5-dimethylthiazole could be coupled efficiently at the 2-position with various oxazoles, affording the corresponding cross-coupling products in 62~73% yields (Table 3, **4a-e**). Worthy of note was that some troublesome functional groups such as halide, ester, aldehyde, vinyl, and nitro could survive in the current catalytic system (Table 3, **4d-o**). The C4 unsubstituted thiazole was amenable to the dehydrogenative coupling at the C2 position in synthetically useful yields (Table 3, **4k** and **4l**). Furthermore, the both C4 and C5 unsubstituted thiazole also selectively underwent the cross-coupling at the C2 position (Table 3, **4m**; for the copy of HH-COSY spectrum of **4m**, see SI).

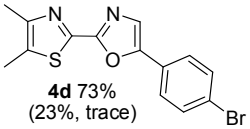
Table 3. Selective Cross-Couplings between Two Non-benzofused Azoles[a,b,c]

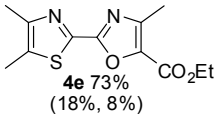


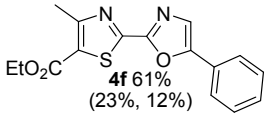

4a 65%
(13%, 19%)

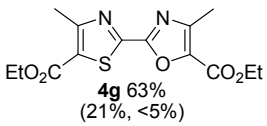

4b 62%
(16%, 18%)

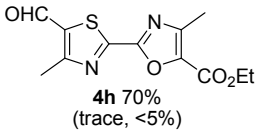

4c 70%
(21%, trace)

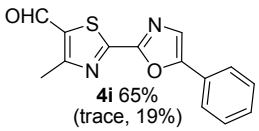

4d 73%
(23%, trace)

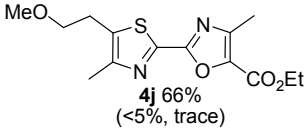

4e 73%
(18%, 8%)

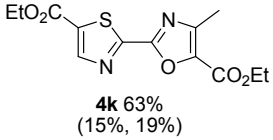

4f 61%
(23%, 12%)

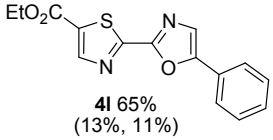

4g 63%
(21%, <5%)

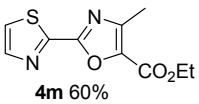

4h 70%
(trace, <5%)


4i 65%
(trace, 19%)

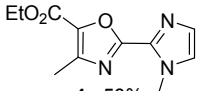

4j 66%
(<5%, trace)


4k 63%
(15%, 19%)

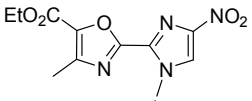

4l 65%
(13%, 11%)



4m 60%
(<5%, trace)



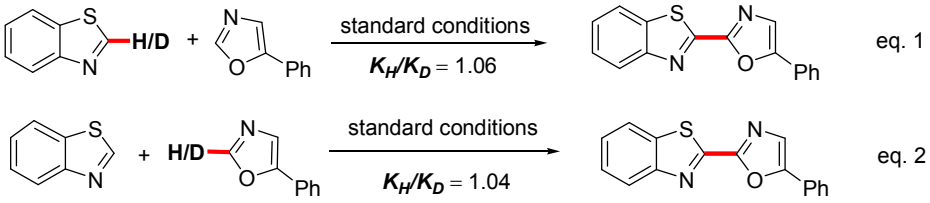
4n 58%
(<5%, n.d)



4o 52%[d]
(<5%, n.d)

[a] Reactions were carried out using $Cu(OAc)_2$ (20 mol%), Ag_2CO_3 (1.5 equiv), pyridine (1.0 equiv), azole **1** (0.5 mmol), and azole **2** (0.5 mmol) at 140 °C for 24 h under oxygen atmosphere. [b] Yields of isolated product. The yields in parentheses refer to the homocoupling products of azole **1** and azole **2**, respectively. [c] For the detailed structure information of compounds, see Table S2. [d] Oxazole **1** (0.5 mmol), and imidazole **2** (0.75 mmol).

Scheme 1. Kinetic Isotope Effect Study



Although the mechanism remains not completely clear at this stage, a plausible catalytic cycles could involve 1) C–H cupration of one azole to generate the organocopper species (Azole **1**)–CuL_n with a carbon–metal bond at the 2-position of azole,[7,8] 2) subsequent formation of the critical mixed bisheteroaryl–Cu intermediate (Azole **1**)–Cu–(Azole **2**), and 3) reductive elimination to afford the unsymmetrical 2,2′-bisazole. In order to gain mechanistic insights into the reaction, two control experiments were investigated. First, TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, 1.0 equiv) as a radical scavenger was observed to display a neglectable effect on the reaction of **1a** and **2a**, ruling out a radical pathway (Table 1, entry 21). Next, kinetic isotope effects (KIE) were studied with regard to the C-H/D bonds for both coupling partners.[9] The parallel (independent) reactions were performed by the use of 2-deuterio-benzothiazole and 2-deuterio-5-phenyloxazole under the optimized condition (Scheme 1). The

KIE values of 1.06 and 1.04 were observed for 2-deuterio-benzothiazole and 2-deuterio-5-phenyloxazole, respectively (Scheme 1, eq. 1 and eq. 2; for details, see SI). These results clearly indicated that the C2-H bond breaking of azole was not involved in the rate-determining step in the present reaction.

In summary, the Cu(II)-catalyzed dehydrogenative couplings between two different azoles have been developed. The current copper-catalytic system is not only suitable for a relatively wide range of azoles (e.g., thiazoles, oxazoles, imidazoles, and oxadiazoles), but also compatible with the presence of functional groups (e.g., halide, nitro, cyano, ester, aldehyde, and vinyl groups). We expect that insights gained from our present study are helpful for the understanding of transition metal-catalyzed dehydrogenative cross-couplings between two hereoarenes.

EXPERIMENTAL SECTION

General Procedure for Dehydrogenative Cross-Couplings between Two Azoles. A flame-dried Schlenk test tube with a magnetic stirring bar was charged with copper species (20 mol%), Ag_2CO_3 (0.75 mmol), pyridine (0.5 mmol), azole **1** (0.5 mmol), azole **2** (0.5 mmol), and xylene (1 mL) under 1 atm O_2 atmosphere. The resulting mixture was stirred for 10 min at room temperature, and then heated at 140 ºC for the indicated time. The mixture was cooled to room temperature, diluted with CH_2Cl_2 (20 mL), filtered through a Celite pad, and washed with CH_2Cl_2 (10-20 mL). The organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product and the homocoupling

products .

2-(5-Phenyloxazol-2-yl)-benzothiazole **(3a).** The crude residue was purified by flash column chromatography on silica gel to afford **3a** as a white solid (106 mg, 76%), **1aa** (7 mg, 10%) and **2aa** (12 mg, 17%) (petroleum/ethyl acetate = 15/1-8/1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (t, J = 7.2 Hz, 1H), 7.45-7.50 (m, 3H), 7.54-7.58 (m, 2H), 7.82 (d, J = 7.6 Hz, 2H), 7.95 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.9, 124.3, 124.4, 125.1, 126.7, 127.0, 127.1, 129.1, 129.5, 135.4, 153.6, 153.8, 154.5, 155.8 ppm. HRMS (ESI^+): calcd for $C_{16}H_{11}N_2OS$ $[M+H]^+$ 279.0592, found 279.0594.

2,2'-Bibenzothiazole (**1aa,** known compound)**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.71 (m, 4H), 7.92 (d, J = 7.6 Hz, 2H), 8.10-8.16 (m, 2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 122.2, 124.2, 126.8, 127.0, 127.7, 129.2, 136.0 ppm. HRMS (ESI^+): calcd for $C_{14}H_9N_2S_2$ $[M+H]^+$ 269.0207, found 269.0200.

5,5'-Diphenyl-2,2'-bioxazole (**2aa,** known compound). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (t, J = 7.2 Hz, 2H), 7.45 (t, J = 7.6 Hz, 4H), 7.57 (s, 2H), 7.79 (d, J = 7.6 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.0, 125.0, 127.1, 129.2, 129.5, 153.2 ppm.

2-(5-(2-Methoxyphenyl)oxazol-2-yl)benzothiazole (**3b**). The crude residue was purified by flash column chromatography on silica gel to afford **3b** as an off-white solid (116 mg, 75%), **1aa** (9 mg, 13%) and **2bb** (13 mg, 15%) (petroleum/ethyl acetate = 8/1-5/1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.00 (s, 3H), 6.99 (d, J = 8.4 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H),

7.53 (t, J = 7.6 Hz, 1H), 7.77 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 111.0, 116.3, 121.0, 121.9, 124.3, 126.5, 126.9, 127.0, 128.4, 130.2, 135.4, 150.2, 153.9, 154.7, 156.3 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{13}N_2O_2S$ $[M+H]^+$ 309.0698, found 309.0706.

5,5'-Di(2-methoxyphenyl)-2,2'-bioxazole (**2bb**, known compound). M.p.: 233-235 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.00 (s, 6H), 6.99 (d, J = 8.4 Hz, 2H), 7.06 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.76 (s, 2H), 8.00 (d, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 111.0, 111.7, 116.5, 121.1, 122.4, 126.8, 130.1, 135.2, 156.2 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{17}N_2O_4$ $[M+H]^+$ 349.1188, found 349.1179.

2-(5-(4-Cyanophenyl)oxazol-2-yl)benzothiazole (**3c**)**.** The crude residue was purified by flash column chromatography on silica gel to afford **3c** as an off-white solid (114 mg, 75%) and **1aa** (7 mg, 10%) (petroleum/ethyl acetate = 15/1-8/1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.70 (s, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 7.6 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.7, 118.4, 122.0, 124.6, 125.3, 126.8, 127.1, 127.3, 131.0, 133.0, 135.6, 151.5, 153.8, 153.8(4), 156.9 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{10}N_3OS$ $[M+H]^+$ 304.0545, found 304.0530.

2-(5-(4-Chlorophenyl)oxazol-2-yl)benzothiazole (**3d**)**.** The crude residue was purified by flash column chromatography on silica gel to afford **3d** as a white solid (108 mg, 69%), **1aa** (7 mg, 10%) and **2dd** (8 mg, 8%) (petroleum/ethyl acetate = 10/1-8/1 v/v).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.4 Hz, 2H), 7.47 (t, J = 7.6 Hz, 1H), 7.55-7.58 (m, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.0, 124.5, 124.6, 125.6, 126.3, 126.8, 127.1, 129.5, 135.4, 152.6, 153.8, 154.3, 156.0 ppm. HRMS (ESI^+): calcd for $C_{16}H_{10}ClN_2OS$ $[M+H]^+$ 313.0202, found 313.0208.

5,5'-Di(4-chlorophenyl)-2,2'-bioxazole (**2dd**). M.p.: 233-235 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.4 Hz, 4H), 7.56 (s, 2H), 7.72 (d, J = 8.4 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.4, 125.6, 126.2, 129.3, 129.6, 135.5 ppm. HRMS (ESI^+): calcd for $C_{18}H_{10}Cl_2N_2NaO_2$ $[M+Na]^+$ 379.0017, found 379.0047.

2-(5-(4-Bromophenyl)oxazol-2-yl)benzothiazole (**3e**, known compound)**.** The crude residue was purified by flash column chromatography on silica gel to afford **3e** as a white solid (123 mg, 69%), **1aa** (9 mg, 13%) (petroleum/ethyl acetate = 10/1-8/1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (t, J = 7.6 Hz, 1H), 7.53-7.57 (m, 3H), 7.59 (s, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.9, 123.6, 124.4, 124.6, 125.9, 126.4, 126.7, 127.0, 132.3, 135.4, 152.5, 153.7, 154.1, 155.9 ppm. HRMS (ESI^+): calcd for $C_{16}H_{10}BrN_2OS$ $[M+H]^+$ 356.9697, found 356.9702.

2-(5-(4-Nitrophenyl)oxazol-2-yl)benzothiazole (**3f**). The crude residue was purified by flash column chromatography on silica gel to afford **3f** as a yellow solid (115 mg, 71%) and **1aa** (9 mg, 13%) (petroleum/ethyl acetate = 3/1-2/1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.75 (s, 1H), 7.98 (d, J = 8.4 Hz, 3H), 8.22 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 8.8 Hz, 2H) ppm. ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 122.0, 124.6, 124.7, 125.0, 125.5, 127.2, 127.3, 132.8, 135.6, 147.9, 151.2, 153.8, 157.2 ppm. HRMS (ESI^+): calcd for $C_{16}H_{10}N_3O_3S$ $[M+H]^+$ 324.0443, found 324.0423.

2-(5-(Pyridin-2-yl)oxazol-2-yl)benzothiazole (**3g**)**.** The crude residue was purified by flash column chromatography on silica gel to afford **3g** as a white solid (98 mg, 70%), **1aa** (8 mg, 12%) and **2gg** (13 mg, 18%) (petroleum/ethyl acetate = 4/1-2/1 v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.28-7.29 (m, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.94-7.98 (m, 3H), 8.20 (d, J = 8.0 Hz, 1H), 8.66 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.2, 122.0, 123.8, 124.5, 126.9, 127.1, 127.6, 135.5, 137.1, 146.6, 150.2, 152.8, 153.8, 154.3, 156.4 ppm. HRMS (ESI^+): calcd for $C_{15}H_{10}N_3OS$ $[M+H]^+$ 280.0545, found 280.0542.

5,5'-Di(pyridin-2-yl)-2,2'-bioxazole (**2gg,** known compound). M.p.: 233-235 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.29 (t, J = 6.0 Hz, 2H), 7.81 (t, J = 7.6 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.95 (s, 2H), 8.68 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.0, 123.8, 127.4, 137.2, 146.6, 150.2, 150.9, 152.7 ppm. HRMS (ESI^+): calcd for $C_{16}H_{11}N_4O_2$ $[M+H]^+$ 291.0882, found 291.0875.

Ethyl 2-(benzothiazol-2-yl)-4-methyloxazole-5-carboxylate (**3h**). The crude residue was purified by flash column chromatography on silica gel to afford **3h** as an off-white solid (92 mg, 64%) and **1aa** (7 mg, 10%) (petroleum/ethyl acetate = 15/1-8/1 v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.41 (t, J = 7.0 Hz, 3H), 2.60 (s, 3H), 4.41 (q, J = 7.0 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5,

14.6, 61.6, 122.0, 125.0, 127.2, 127.3, 135.8, 139.0, 147.6, 153.3, 153.8, 156.2, 158.4 ppm. HRMS (ESI^+): calcd for $C_{14}H_{13}N_2O_3S$ $[M+H]^+$ 289.0647, found 289.0650.

Diethyl 4,4'-dimethyl-2,2'-bioxazole-5,5'-dicarboxylate (**2hh,** known compound). M.p.: 170-172 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.38 (t, J = 6.8 Hz, 6H), 2.56 (s, 6H), 4.38 (q, J = 6.8 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 14.4, 61.8, 139.3, 147.5, 150.1, 158.1 ppm. HRMS (ESI^+): calcd for $C_{14}H_{16}N_2O_6$ $[M+H]^+$ 309.1087, found 309.1091.

2-(5-Phenyl-1,3,4-oxadiazol-2-yl)benzothiazole (**3i**, known compound)**.** The crude residue was purified by flash column chromatography on silica gel to afford **3i** as an off-white solid (109 mg, 78%) and **1aa** (8 mg, 12%) (petroleum/ethyl acetate = 15/1-8/1 v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54-7.58 (m, 5H), 7.99 (d, J = 7.6 Hz, 1H), 8.23 (d, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.1, 123.1, 124.8, 127.4, 127.5, 127.7, 129.3, 132.6, 135.6, 150.9, 153.4, 160.3, 166.0 ppm. HRMS (ESI^+): calcd for $C_{15}H_{10}N_3OS$ $[M+H]^+$ 280.0545, found 280.0549.

2-(Benzothiazol-2-yl)-1-methyl-1H-benzoimidazole (**3j**, known compound)**.** The crude residue was purified by flash column chromatography on silica gel to afford **3j** as an off-white solid (89 mg, 67%), **1aa** (9 mg, 13%) and **2jj** (12 mg, 18%) (petroleum/ethyl acetate = 5/1-3/1 v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.42 (s, 3H), 7.33-7.41 (m, 2H), 7.44-7.48 (m, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.2, 110.2, 120.7, 121.9, 123.4, 124.0, 124.6, 126.3, 126.6, 135.5, 137.4, 142.9, 145.3, 154.2, 156.0 ppm. HRMS (ESI^+): calcd for $C_{15}H_{12}N_3S$ $[M+H]^+$

266.0752, found 266.0761.

1,1'-Dimethyl-2,2'-bibenzoimidazole (**2jj**, known compound)**.** M.p.: 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.34 (s, 6H), 7.35-7.43 (m, 4H), 7.49 (d, J = 7.6 Hz, 2H), 7.88 (d, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.6, 110.2, 120.5, 123.0, 124.1, 136.4, 142.7, 143.4 ppm. HRMS (ESI^+): calcd for $C_{16}H_{15}N_4$ $[M+H]^+$ 263.1297, found 263.1287.

2-(4,5-Dimethylthiazol-2-yl)-5-phenyloxazole (**4a**, known compound)**.** The crude residue was purified by flash column chromatography on silica gel to afford **4a** as an off-white solid (83 mg, 65%), **1bb** (7 mg, 13%) and **2aa** (14 mg, 19%) (petroleum/dichloromethane/ethyl acetate = 15/2/1-8/2/1 v/v). M.p.: 103-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 6H), 7.34 (t, J = 7.2 Hz, 1H), 7.42-7.45 (m, 3H), 7.76 (d, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.6, 14.9, 123.6, 124.7, 124.9, 127.3, 128.9, 130.0, 149.8, 150.7, 152.1, 155.9 ppm. HRMS (ESI^+): calcd for $C_{14}H_{13}N_2OS$ $[M+H]^+$ 257.0749, found 257.0745.

4,4',5,5'-Tetramethyl-2,2'-bithiazole (**1bb**, known compound). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 6H), 2.37 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.7, 14.9, 128.3, 149.6, 157.2 ppm.

2-(4,5-Dimethylthiazol-2-yl)-5-(pyridin-2-yl)oxazole (**4b**, known compound)**.** The crude residue was purified by flash column chromatography on silica gel to afford **4b** as a yellow solid (80 mg, 62%), **1bb** as a white solid (9 mg, 16%), and **2gg** as a white solid (13 mg, 18%) (petroleum/ethyl acetate = 5/1-2/1 v/v). M.p.: 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 6H), 7.22-7.25 (m, 1H), 7.74 (t, J = 7.6 Hz, 1H),

7.82 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 8.61-8.62 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.6, 13.9, 118.7, 122.2, 126.0, 135.9, 143.6, 145.8, 148.6, 148.9, 150.0, 150.5, 155.6 ppm. HRMS (ESI^+): calcd for $C_{13}H_{12}N_3OS$ $[M+H]^+$ 258.0701, found 258.0696.

2-(4,5-Dimethylthiazol-2-yl)-5-(2-methoxyphenyl)oxazole (**4c**, known compound)**.** The crude residue was purified by flash column chromatography on silica gel to afford **4c** as a pale yellow solid (100 mg, 70%), and **1bb** as a white solid (12 mg, 21%) (petroleum/ethyl acetate = 10/1-5/1 v/v). M.p.: 164-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 6H), 3.96 (s, 3H), 6.96 (d, J = 8.4 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.65 (s, 1H), 7.96 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 11.6, 15.0, 55.6, 110.8, 116.6, 120.9, 126.6, 127.8, 129.6, 129.8, 148.8, 150.1, 150.7, 154.9, 156.0 ppm. HRMS (ESI^+): calcd for $C_{15}H_{15}N_2O_2S$ $[M+H]^+$ 287.0854, found 287.0851.

5-(4-Bromophenyl)-2-(4,5-dimethylthiazol-2-yl)oxazole (**4d**, known compound)**.** The crude residue was purified by flash column chromatography on silica gel to afford **4d** as a yellow solid (122 mg, 73%), and **1bb** as a white solid (13 mg, 23%) (petroleum/dichloromethane/ethyl acetate = 10/2/1-6/2/1 v/v). M.p.: 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 6H), 7.44 (s, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.7, 15.0, 123.0, 124.2, 126.2, 126.3, 130.4, 132.2, 149.7, 150.9, 151.2, 156.2 ppm. HRMS (ESI^+): calcd for $C_{14}H_{12}BrN_2OS$ $[M+H]^+$ 334.9854, found 334.9852.

Ethyl 2-(4,5-dimethylthiazol-2-yl)-4-methyloxazole-5-carboxylate (**4e**, known

compound)**.** The crude residue was purified by flash column chromatography on silica gel to afford **4e** as a white solid (97 mg, 73%), **1bb** as a white solid (10 mg, 18%) and **2hh** as a white solid (6 mg, 8%) (petroleum/ethyl acetate = 10/1-5/1 v/v). M.p.: 95-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (t, J = 7.2 Hz, 3H), 2.42 (s, 3H), 2.44 (s, 3H), 2.53 (s, 3H), 4.36 (q, J = 7.2 Hz, 2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 11.8, 13.5, 14.4, 14.9, 61.4, 131.9, 137.8, 147.4, 148.4, 151.7, 156.5, 158.6 ppm. HRMS (ESI^+): calcd for $C_{12}H_{15}N_2O_3S$ $[M+H]^+$ 267.0803, found 267.0805.

Ethyl 4-methyl-2-(5-phenyloxazol-2-yl)thiazole-5-carboxylate (**4f**)**.** The crude residue was purified by flash column chromatography on silica gel to afford **4f** as a white solid (96 mg, 61%), **1cc** (20 mg, 23%) and **2aa** (9 mg, 12%) (petroleum/ethyl acetate = 15/1-8/1 v/v). mp: 123-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 (t, J = 8.0 Hz, 3H), 2.84 (s, 3H), 4.35 (q, J = 7.2 Hz, 2H), 7.37 (t, J = 7.0 Hz, 1H), 7.43 (t, J = 7.4 Hz, 2H), 7.52 (s, 1H), 7.77 (d, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 17.6, 61.8, 124.3, 125.0, 127.0, 129.2, 129.6, 130.2, 153.4, 155.2, 155.7, 161.6, 161.9 ppm. HRMS (ESI^+): calcd for $C_{16}H_{15}N_2O_3S$ $[M+H]^+$ 315.0803, found 315.0806.

Diethyl 4,4'-dimethyl-2,2'-bithiazole-5,5'-dicarboxylate (**1cc**, known compound)**.** M.p.: 184-186 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 (t, J = 7.2 Hz, 6H), 2.77 (s, 6H), 4.33 (q, J = 7.2 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 17.6, 61.7, 124.7, 161.4, 162.0 ppm. HRMS (ESI^+): calcd for $C_{14}H_{17}N_2O_4S_2$ $[M+H]^+$ 341.0630, found 341.0624.

Ethyl 2-(5-(ethoxycarbonyl)-4-methylthiazol-2-yl)-4-methyloxazole-5-carboxylate (**4g**,

known compound)**.** The crude residue was purified by flash column chromatography on silica gel to afford **4g** as a white solid (102 mg, 63%), and **1cc** as a pale yellow solid (18 mg, 21%) (petroleum/ethyl acetate = 10/1-7/1 v/v). M.p.: 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34-1.40 (m, 6H), 2.53 (s, 3H), 2.79 (s, 3H), 4.32-4.42 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4, 14.3, 14.4, 17.5, 61.6, 61.9, 125.5, 138.6, 147.5, 154.3, 155.5, 158.2, 161.5, 161.8 ppm. HRMS (ESI^+): calcd for $C_{14}H_{17}N_2O_5S$ $[M+H]^+$ 325.0858, found 325.0851.

Ethyl 2-(5-formyl-4-methylthiazol-2-yl)-4-methyloxazole-5-carboxylate (**4h**, known compound)**.** The crude residue was purified by flash column chromatography on silica gel to afford **4h** as an off-white solid (98 mg, 70%) (petroleum/ethyl acetate = 15/1-8/1 v/v). M.p.: 123-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (t, J = 7.2 Hz, 3H), 2.57 (s, 3H), 2.85 (s, 3H), 4.40 (q, J = 7.2 Hz, 2H), 10.16 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 14.4, 16.5, 61.8, 135.4, 139.1, 147.8, 155.3, 157.8, 158.2, 162.7, 182.2 ppm. HRMS (ESI^+): calcd for $C_{12}H_{13}N_2O_4S$ $[M+H]^+$ 281.0596, found 281.0599.

4-Methyl-2-(5-phenyloxazol-2-yl)thiazole-5-carbaldehyde (**4i**, known compound)**.** The crude residue was purified by flash column chromatography on silica gel to afford **4i** as a yellow solid (88 mg, 65%), and **2aa** as a white solid (14 mg, 19%) (petroleum/ethyl acetate = 10/1-5/1 v/v). M.p.: 152-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.85 (s, 3H), 7.39 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.2 Hz, 2H), 7.57 (s, 1H), 7.78 (d, J = 7.2 Hz, 2H), 10.15 (s, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 16.5, 124.8, 125.1, 126.8, 129.2, 129.8, 134.3, 153.9, 155.0, 159.0, 162.6, 182.3 ppm.

HRMS (ESI$^+$): calcd for $C_{14}H_{11}N_2O_2S$ $[M+H]^+$ 271.0541, found 271.0544.

Ethyl 2-(5-(2-methoxyethyl)-4-methylthiazol-2-yl)-4-methyloxazole-5-carboxylate (**4j**, known compound)**.** The crude residue was purified by flash column chromatography on silica gel to afford **4j** as an off-white solid (102 mg, 66%) (petroleum/ethyl acetate = 7/1-4/1 v/v). M.p.: 64-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (t, J = 7.2 Hz, 3H), 2.45 (s, 3H), 2.53 (s, 3H), 3.03 (t, J = 6.2 Hz, 2H), 3.36 (s, 3H), 3.57 (t, J = 6.0 Hz, 2H), 4.36 (q, J = 7.2 Hz, 2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.5, 14.4, 15.3, 27.5, 58.9, 61.3, 71.9, 134.0, 137.8, 147.4, 149.7, 151.7, 156.6, 158.6 ppm. HRMS (ESI$^+$): calcd for $C_{14}H_{19}N_2O_4S$ $[M+H]^+$ 311.1066, found 311.1065.

Ethyl 2-(5-(ethoxycarbonyl)thiazol-2-yl)-4-methyloxazole-5-carboxylate (**4k**, known compound)**.** The crude residue was purified by flash column chromatography on silica gel to afford **4k** as a white solid (98 mg, 63%), **1ff** as a pale yellow solid (12 mg, 15%), and **2hh** as a white solid (15 mg, 19%) (petroleum/ethyl acetate = 10/1-7/1 v/v). M.p.: 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39-1.42 (m, 6H), 2.57 (s, 3H), 4.38-4.44 (m, 4H), 8.52 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4, 14.3, 14.4, 61.6, 62.3, 132.8, 138.8, 147.5, 149.7, 155.3, 157.6, 158.2, 160.6 ppm. HRMS (ESI$^+$): calcd for $C_{13}H_{15}N_2O_5S$ $[M+H]^+$ 311.0702, found 311.0703.

Diethyl 2,2'-bithiazole-5,5'-dicarboxylate (**1ff,** known compound)**.** M.p.: 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (t, J = 7.2 Hz, 6H), 4.38 (q, J = 7.2 Hz, 4H), 8.45 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 62.2, 132.2, 149.4, 161.0 165.1 ppm. HRMS (ESI$^+$): calcd for $C_{12}H_{13}N_2O_4S_2$ $[M+H]^+$ 313.0317, found 313.0317.

Ethyl 2-(5-phenyloxazol-2-yl)thiazole-5-carboxylate (**4l**, known compound)**.** The crude residue was purified by flash column chromatography on silica gel to afford **4l** as a yellow solid (97 mg, 65%), **1ff** as a pale yellow solid (10 mg, 13%) and **2aa** as a white solid (8 mg, 11%) (petroleum/ethyl acetate = 10/1-7/1 v/v). M.p.: 104-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (t, J = 7.2 Hz, 3H), 4.39 (q, J = 7.2 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.2 Hz, 2H), 7.53 (s, 1H), 7.77 (d, J = 7.6 Hz, 2H), 8.51 (s, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.4, 62.2, 124.4, 125.0, 126.9, 129.2, 129.6, 131.5, 149.5, 153.5, 155.1, 158.9, 161.0 ppm. HRMS (ESI^+): calcd for $C_{15}H_{12}N_2O_3S$ $[M+H]^+$ 301.0647, found 301.0652.

Ethyl 4-methyl-2-(thiazol-2-yl)oxazole-5-carboxylate (**4m**, known compound). The crude residue was purified by flash column chromatography on silica gel to afford **4m** as a pale yellow solid (71 mg, 60%) (petroleum/ethyl acetate = 10/1-5/1 v/v). M.p.: 106-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (t, J = 7.2 Hz, 3H), 2.56 (s, 3H), 4.38 (q, J = 7.2 Hz, 2H), 7.57 (d, J = 2.4 Hz, 1H), 8.03 (d, J = 2.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4, 14.4, 61.5, 123.0, 138.3, 145.3, 147.4, 153.8, 156.2, 158.5 ppm. HRMS (ESI^+): calcd for $C_{10}H_{11}N_2O_3S$ $[M+H]^+$ 239.0490, found 239.0495.

Ethyl 4-methyl-2-(1-vinyl-1H-imidazol-2-yl)oxazole-5-carboxylate (**4n**, known compound). The crude residue was purified by flash column chromatography on silica gel to afford **4n** as a white solid (72 mg, 58%) (petroleum/ethyl acetate = 4/1-2/1 v/v). M.p.: 151-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 (t, J = 7.2 Hz, 3H), 2.54 (s, 3H), 4.36 (q, J = 7.2 Hz, 2H), 5.07 (d, J = 8.8 Hz, 1H), 5.36 (d, J = 15.6 Hz, 1H), 7.26

(s, 1H), 7.45 (s, 1H), 8.14 (dd, J = 15.6 Hz, J = 8.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4, 14.4, 61.3, 104.1, 118.8, 130.5, 131.4, 134.2, 137.3, 146.7, 153.4, 158.6 ppm. HRMS (ESI^+): calcd for $C_{12}H_{14}N_3O_3$ $[M+H]^+$ 248.1035, found 248.1034.

Ethyl 4-methyl-2-(1-methyl-4-nitro-1H-imidazol-2-yl)oxazole-5-carboxylate (**4o**, known compound). The crude residue was purified by flash column chromatography on silica gel to afford **4o** as a white solid (73 mg, 52%) (petroleum/ethyl acetate = 2/1-1/1 v/v). M.p.: 155-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 (t, J = 7.2 Hz, 3H), 2.53 (s, 3H), 4.22 (s, 3H), 4.35 (q, J = 7.2 Hz, 2H), 7.92 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl3): δ = 13.4, 14.4, 37.2, 61.6, 124.0, 133.8, 138.2, 146.7, 151.9, 158.3 ppm. HRMS (ESI^+): calcd for $C_{11}H_{13}N_4O_5$ $[M+H]^+$ 281.0886, found 281.0890.

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Supporting Information. Data and copies of NMR for compounds, and detailed hetero-couplings and homo-couplings. This material is available free of charge via the Internet at http://pubs.acs.org.

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