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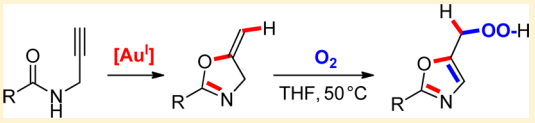
From Propargylic Amides to Functionalized Oxazoles: Domino Gold Catalysis/Oxidation by Dioxygen

A. Stephen K. Hashmi,* Maria Camila Blanco Jaimes, Andreas M. Schuster, and Frank Rominger

Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

Supporting Information

ABSTRACT: A new, highly efficient, and atom-economic access to a series of functionalized 2,5-disubstituted oxazoles from propargylic amides is reported. A series of propargylic amides were transformed to the corresponding alkylideneoxazolines by a gold(I) catalyst. The next step was an autoxidation to hydroperoxides bearing the heteroaromatic oxazoles. Experiments addressing the reaction mechanism reveal a radical pathway for this autoxidation process. The hydroperoxides could conveniently be converted to the corresponding alcohols by reduction with sodium borohydride.



INTRODUCTION

Propargylic amides have been widely studied as effective and versatile substrates for the synthesis of oxazoles,[1−4] which occur in different natural and non-natural compounds with biological and pharmaceutical properties.[5] This reaction can either be promoted by harsh basic conditions[2] or be catalyzed under much milder conditions by palladium[3] or gold.[4] Gold has emerged in the field of organic chemistry as a powerful tool and due to the high selectivity as well as mild reaction conditions has become one of the major topics in catalysis research.[6] The mild conditions of gold(I) catalysis provided the first access to alkylideneoxazolines **2**, the latter now for the first time can be investigated as building blocks for synthesis.

Overall, there are only a few reports where oxidizing agents are used to synthesize functionalized oxazoles.[8,9] Saito and co-workers[8] described the oxidative cycloisomerization of propargylic amides mediated by phenyliodine(III) diacetate (PIDA); and recently, Zhang and co-workers[9] reported the synthesis of 2,5-disubstituted oxazoles via gold-catalyzed alkyne oxidation using pyridine/quinoline *N*-oxides as oxidizing agents. While in heterogeneous gold catalysis oxidation by dioxygen is a dominating topic, in homogeneous gold catalysis only a handful of homogeneous gold-catalyzed reactions have been reported.

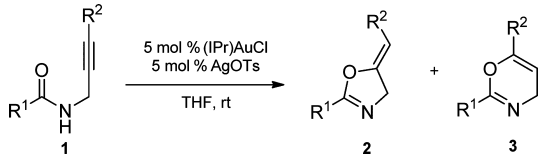
The direct oxidation with dioxygen in the context of homogeneous gold catalysis has only been reported in two cases, the oxidation of alcohols to aldehydes[10] and the oxidative cleavage of C−C double bonds after a 5-*exo*-*dig* cyclization (the latter quite similar to the formation of **2**).[11]

We wanted to study the new building blocks **2** in combination with dioxygen in order to obtain functionalized oxazoles from the combination gold(I) catalysis and oxidation rather than methyloxazoles[4a] from gold(III) catalysis.

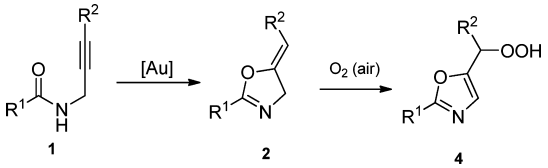
RESULTS AND DISCUSSION

We have recently reported the gold-catalyzed cycloisomerization of nonterminal propargylic amides **1** to the corresponding alkylideneoxazolines **2** and oxazines **3** (Scheme 1).[7] When, after completion of the catalysis, the reaction mixture was exposed to air, the initial product was converted to a different product. This new product turned out to be the corresponding hydroperoxymethyl oxazole **4**, which is formed as a result of a spontaneous oxidation mediated by the oxygen present in the air (Scheme 2). This is the first time such hydroperoxides are obtained from gold-catalyzed reactions, which usually are famous for tolerating both water and air.[12] Related autoxidations are only reported in the literature in the presence of different metals or radical initiators[13] and none of these had been used for the synthesis of oxazoles.

Scheme 1. Gold-Catalyzed Cycloisomerization of Nonterminal Propargylic Amides[7]



Scheme 2. Gold Catalysis Followed by Autoxidation of the Alkylideneoxazoline 2



As mentioned above, the starting point of our investigation was the unexpected product obtained in the gold-catalyzed reaction of propargylic amides **1**. The reaction was carried out in dry tetrahydrofuran (THF) at room temperature. As soon as the catalysis reaction was complete, the reaction flask was opened and stirred in air. After 30 min, the only product

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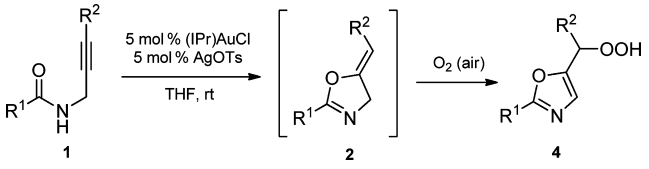
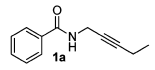
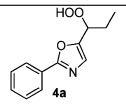
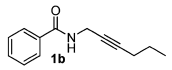
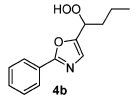
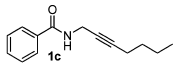
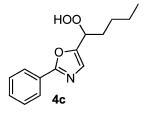
isolated corresponded to the hydroperoxymethyloxazole **4**. The results obtained with this procedure are summarized in Table 1.

Table 1. Preparation of 2,5-Disubstituted Oxazoles 4



Entry	Starting Material	Product	Yield (%)
1			32
2			47
3			52

In order to study the reaction scope and to identify the reaction pathway, we decided to work first with the terminal propargylic amide **5a** and to isolate its corresponding cycloisomerizated product, the methyleneoxazoline **6a**. The compound **6a** was then subjected to an atmosphere of dioxygen in THF in the presence or absence of gold and stirred overnight at 50 °C. Interestingly, in both cases the same product was isolated (Scheme 3) and the reaction rate was identical. Therefore, it was clear that gold played no role in the second part of the conversion, the oxidation reaction of the alkylideneoxazolines.

To explore the reaction scope, different electron-withdrawing (EWG) and electron-donating groups (EDG) in the benzene ring were investigated. The propargylic amides **5** were obtained in high yields using known procedures.[4] The gold-catalyzed cycloisomerization of compounds **5** in most of the cases took place at room temperature in the presence of 2 mol % of $Ph_3PAuNTf_2$ (Table 2, entries 1–4, 6–10, 12, 13, and 15). Only the formation of the 3,4,5-trimethoxy-substituted **6e** (entry 5), 3,5-dibromo-substituted **6k** (entry 11), and 3-nitro-subtituted **6n** (entry 14) needed heating to 35 °C. Most of the methyleneoxazolines **6** could be obtained in high yields; only the derivative **6e** gave a moderate yield (entry 5, 59%, characterized by an X-ray crystal structure analysis[14]). The highest yield was obtained with the derivative 3,5-dichloro-substituted **6l** (entry 12, 91%), whereas the 4-*n*-butoxy-substituted **6b** (entry 2, 78%) showed the fastest transformation.

With the methyleneoxazolines **6** we could now investigate the autoxidation process. First the conditions for the formation of the hydroperoxymethyloxazole were optimized for substrate **6a** (Table 3). Different solvents, substrate concentrations, and temperatures were tested. When the reaction was performed in THF at 50 °C (entries 1–4), it was possible to observe an increase of the conversion with the concentration of the substrate in the reaction mixture. When the reaction was performed at room temperature no conversion was observed at all (entry 5), suggesting that the initiation stage requires a relative high energy of activation. We then decided to change the solvent in order to investigate if the THF was directly initiating the oxidation process by its capability to form peroxides in the presence of oxygen.[15] In $CHCl_3$ (entry 6) and CCl_4 0.5 M at 50 °C (entry 8) the yields are comparable but the conversion is slower than in THF. Interestingly, the reaction also took place in absence of solvent (entry 10), indicating that molecular oxygen is the main oxidizing agent that promotes the conversion, although the presence of THF peroxide seems to accelerate the formation of the hydroperoxide **7**.

Additional mechanistic experiments are shown in Table 4. The first experiment (entry 1) in the absence of oxygen confirms that the latter is the oxidizing agent of the process. Even in the presence of molecular oxygen the oxidation does not take place in the presence of the well-known radical inhibitor *tert*-butylhydroxytoluene (BHT)[16] (entry 2). On the other hand, the reaction is accelerated by the presence of the radical initiator azobisisobutyronitrile (AIBN)[17] (entry 3). In this case, 85% of conversion was observed after only 8 h, in contrast to the 24 h needed to obtain 95% of conversion without the AIBN (Table 3, entry 4). From these results it is possible to conclude that the oxidation of methyleneoxazolines **6** follows a radical pathway, probably triggered by the combination of high temperature and light and promoted by the presence of oxygen and THF peroxides in the reaction flask.[18]

Scheme 4 depicts a possible pathway for the oxidation of methyleneoxazolines **6** to peroxides **7**. The first step would correspond to the activation of methyleneoxazoline **6** by loss of an H-radical, leading to the formation of the radical species **A** which is a resonance structure of **B**. When the reaction is carried out in THF an alternative pathway to form **A**, involving

Scheme 3. Oxidation of Methyleneoxazoline 6a Occurs with and without the Gold Catalyst

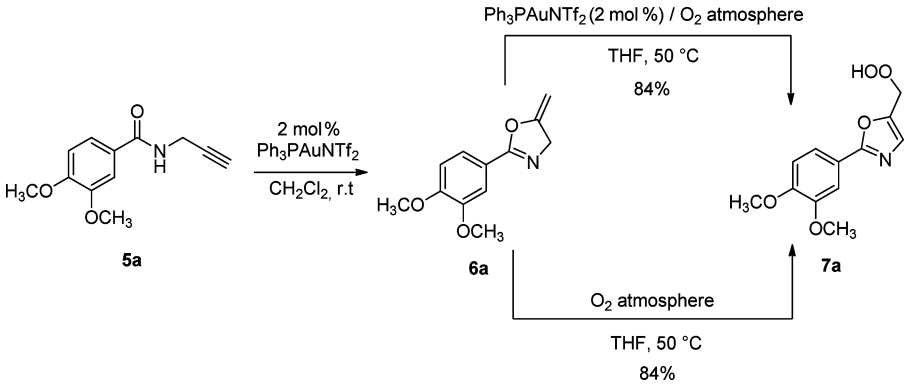


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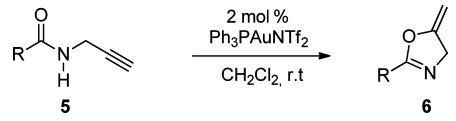
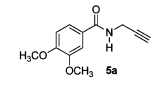
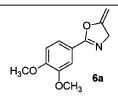
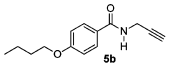
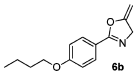
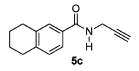
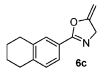
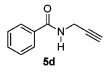
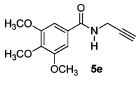
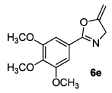
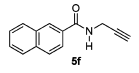
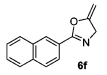
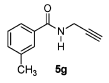
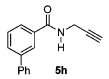
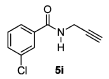
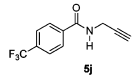
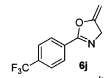
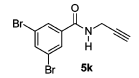
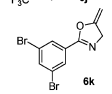
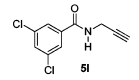
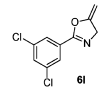
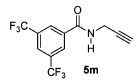
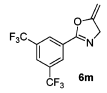
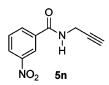
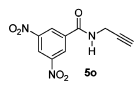
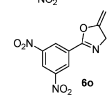
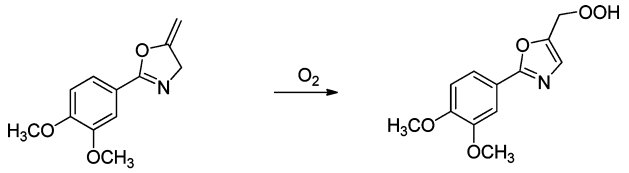
Table 2. Gold-Catalyzed Reaction of Propargylic Amides 5



Entry	Starting Material	Time	Product	Yield (%)[a]
1		20 h		83
2		6 h		78
3		12 h		80
4		12 h		91
5		48 h[b]		59
6		24 h		70
7		16 h		80
8		12 h		84
9		14 h		80
10		12 h		88
11		36 h[b]		81
12		12 h		91
13		12 h		88
14		48 h[b]		90
15		12 h		83

[a]Yields. [b]The reaction mixture was heated to 35 °C.

Table 3. Optimization of Reaction Conditions

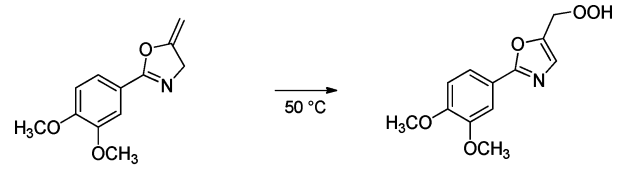


6a 7a

entry	solvent	temp (°C)	conc [6a]	reaction Time	yield by GC/MS (%)	yield[a] (%)
1	THF	50	0.01	20	5	
2	THF	50	0.10	20	58	85
3	THF	50	0.30	20	64	87
4	**THF**	**50**	**0.50**	**24**	**95**	**92**
5	THF	rt	0.50	48	0	
6	$CHCl_3$	50	0.50	24	56	87
7	CCl_4	50	0.05	60	47	85
8	CCl_4	50	0.50	48	93	90
9	CCl_4	rt	0.50	48	0	
10		rt		48	78	90

[a]Yield based on recovered starting material.

Table 4. Additional Control Experiments[a]

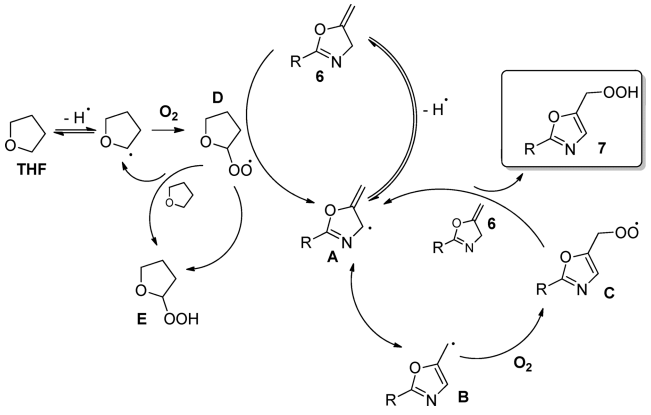


6a 7a

entry	external/oxidizing agent	solvent	time (h)	conv[b] (%)	yield[c] (%)
1		THF[d]	72	0	
2	BHT[e]/O_2	THF	72	0	
3	AIBN[f]/O_2	CCl_4	8	85	75

[a][6a] = 0.50 M, 50 °C. [b]Estimated by GC–MS analysis. [c]Yields. [d]Dry conditions, in absence of oxygen. [e]BHT: *tert*-butylhydroxytoluene, 10 mol %. [f]AIBN: azobisisobutyronitrile, 10 mol %.

Scheme 4. Proposed Pathway for the Oxidation of 6



the peroxyl radical of THF **D** as a radical initiator, could be operational. This pathway would explain the faster conversion of **6** under those conditions. Once the radical species **B** is formed, it would quickly react with O_2 to give rise to peroxyl radical **C**,[18] which in turn would react with a new molecule of methyleneoxazoline **6** removing its H-radical, thus forming the isolated peroxide **7** and a new radical species **A** to continue the oxidation process by achieving radical chain propagation.

With the proposed pathway of the oxidation (Scheme 4), the reaction conditions optimized (Table 3, entry 4), and methyleneoxazolines **6** synthesized (Table 2), we could now investigate the scope of the oxidation and explore one of the possible further transformations of peroxides **7**. Table 5 summarizes the results obtained with the different EWGs and EDGs in the benzene ring of **6**. In most of the cases, peroxides **7** were obtained in high yields (96–72%). The derivatives **7h** (entry 8)

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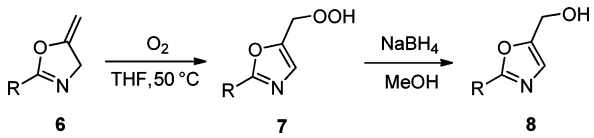
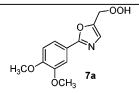
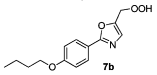
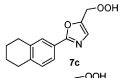
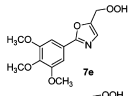
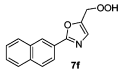
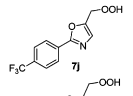
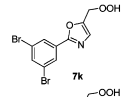
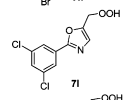
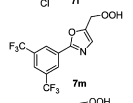
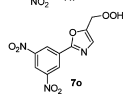
Table 5. Scope of the Reaction[a]



6 7 8

Entry	Product 7	σ[b]	Time[c]	Yield of 7[d]	Yield of 8[d]
1		-0.117	25 h	92%	81%
2		-0.320	30 h	96%	80%
3		-0.480	36 h	80%	80%
4		0.000	48 h	82%	96%
5		0.075	52 h	86%	83%
6		—	60 h	80%	88%
7		-0.070	60 h	80%	90%
8		0.060	60 h	64%	80%
9		0.370	64 h	72%	92%
10		0.540	66 h	92%	96%
11		0.720	104 h	73%	86%
12		0.746	168 h	80%	92%
13		0.830	8 d	37%	83%
14		0.710	8 d[e]	--	--
15		1.395	8 d[e]	--	--

[a][6] = 0.50 M. [b]Hammett constant associated with the substitution partner in the benzene ring.[19] [c]Reaction time needed to reach complete conversion of **6**. [d]Yields. [e]No product was formed, just the substrate was recovered.

and **7m** (entry 13) could only be obtained in moderate yields (64–37%). Nitro-substituted methyleneoxazoline **6n** (entry 14) and **6o** (entry 15) did not react under the employed conditions even after 8 days of reaction. In order to understand the behavior of the reaction as a function of the substituents in the benzene ring, we decided to associate this substitution pattern to the Hammett constants (σ) for *meta*- and *para*-substituted benzoic acids.[19] According to the proposed pathway (Scheme 4), the activation stage would depend on the stability and the ease to generate the delocalized radical (represented by the mesomers **A**/**B**) and thus exclusively depend on the electronic density of the R group. Hammett constants (σ) offer a valuable tool to quantify the electronic density associated to this part of the molecule. According to the results obtained, a consistent relationship between the σ values and the reaction time could be established. The derivatives **7a–d** (entries 1–4) possessed the smallest values of σ and presented the shortest reaction times (48–25 h) as well as the highest yields (96–80%), indicating that the oxidation process is accelerated by higher electronic density on the substrate. As expected, derivatives bearing EWG, namely **7i–l** (entries 9–12), showed larger reaction (168–64 h) times while retaining high yields (92–72%). The fact that nitro derivatives (entries 14–15) did not react could be explained by taking into account the big electron-withdrawing effect that nitro group perform in the molecule, increasing the activation energy needed to start the oxidation process. The derivative **7m** (entry 13), bearing two trifluoromethyl groups, could only be obtained after 8 days of reaction in moderate yield. Into the series of EWG and EDG investigated on the benzene ring in compounds **7**, the substitution pattern in presents **7m**, with an σ value of 0.83, constitutes the minimum electronic density needed to accomplish the oxidation process.

The structure of peroxides **7** was first elucidated by the ^{1}H NMR spectra, especially due to the presence of a broad peak between 9 and 11 ppm corresponding to the hydroperoxide proton. To unequivocally confirm the presence of the peroxide function, compounds **7** were reduced to their corresponding alcohol derivatives **8**. In all the cases, the reduction was performed in high yields using $NaBH_4$ as reducing agent in methanol (Table 5). The appearance of the characteristic peak for alcohols between 2 and 3 ppm in the ^{1}H NMR confirmed the structure of the reduced products and the peroxide precursor as well. The easy reduction to alcohols also illustrates the potential of the hydroperoxides **7** for organic synthesis.

Crystal structures were obtained for the peroxides **7f** and **7m** and for the alcohol derivatives **8a**, **8b** and **8e**.[14] In **7f**, the conformation of the hydroperoxide with a dihedral angle C–O–O–H of 92° resembles the conformation of hydrogen peroxide (90°). This still allows the formation of dimers by two intermolecular hydrogen bonds, each from the –OOH unit to the oxazole nitrogen atom of a second molecule of **7f** (Table 5). Compound **7m** shows a similar structural motive. By intermolecular hydrogen bonds between the –OH groups and the oxazole nitrogen atoms, the carbinol **8a** forms chains in the solid state. The same is true for **8b** and **8e**.

Experiments with **6a** applying both the gold catalyst and oxygen in THF at the same time gave only a reduced yield of 35% of the product **7a**. A control experiment with only the substrate and oxygen in THF shows that the substrate is slowly decomposing under these conditions by a radical pathway as well. On one hand, this demonstrates that gold catalysis and radical reactions in principle are compatible, on the other hand competing side-reactions cause problems.

■ CONCLUSIONS

This combination of a gold-catalyzed cycloisomerization to otherwise inaccessible building blocks and their in situ transformation to the corresponding hydroperoxides by a radical reaction pathway nicely demonstrates the compability of gold catalysis and radical reactions. The good yields obtained for a wide range of substrates with different EDGs and EWGs nicely

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underline the applicability in synthesis, although the established relationship between the electron-withdrawing/donating capability of the R group and the reaction rate revealed that the oxidation process has a limitation when strong EWG are present in the substrate. This methodology proved to be a novel access to 2,5-disubtituted oxazole derivatives in high yields and with high atom economy. For the formation of the hydroperoxides, the stepwise process is superior to the process applying oxygen during the gold-catalyzed cycloisomerization.

EXPERIMENTAL SECTION

General Methods. Chemicals were used without further purification. Dry dichloromethane and tetrahydrofuran were used. Chemical shifts were referenced to residual solvent protons. Signal multiplicity as follows: s (singlet), d (doublet), t (triplet), q (quartet), qu (quintet), hept (heptate), m (multiplet). ^{13}C assignment was achieved via HSQC, HMBC, and DEPT135 spectra. For HRMS with EI or FAB a magnetic sector field analyzer was used.

Compounds **1** and **2** are known and fully characterized.[7a]

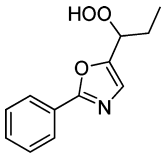
General Procedure 1 (GP 1): Gold-Catalyzed Cycloisomerization of Propargylic Amides 1 and Direct Conversion in Hydroperoxides 4. In a dry Schlenk flask, 5 mol % of the gold catalyst and 5 mol % AgOTs were dissolved in dry THF and stirred for 1 h. *N*-Propargylamide **1** (1 equiv) was added, and the reaction was stirred at room temperature for 16 h. After completion of the reaction, the reaction flask was opened and stirred in air for another 30 min. The crude product was absorbed on Celite by concentration of the reaction mixture with Celite 545 in vacuum. The reaction mixture was purified by column chromatography on silica.

General Procedure 2 (GP 2): Synthesis of Propargylic Amides 5.[4c,7a] Propargylamine (1.0 equiv with respect to the acid chloride) was dissolved in dry DCM, and 1 equiv of Et_3N and 2 mol % of DMAP were added. The reaction mixture was cooled to 0 °C, and 1 equiv of the acid chloride was added. The mixture was stirred for 15 min at 0 °C and then for 3 h at room temperature. After the reaction was completed, water was added and then the mixture extracted with DCM. The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The product was purified by column chromatography or by recrystallization.

General Procedure 3 (GP 3): Gold-Catalyzed Synthesis of Dihydrooxazoles 6.[4c,7a] The starting propargylic amide was dissolved in DCM, and then the gold catalyst (2 mol %) was added. The mixture was stirred for the denounced time. After the reaction was completed, the solvent was evaporated and the organic product purified by column chromatography or by recrystallization.

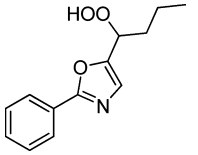
General Procedure 4 (GP 4): Oxidation of Dihydrooxazoles 6. A solution 0.5 M of the dihydrooxazole in THF was prepared and stirred for the prescribed time at 50 °C under O_2 atmosphere. After the reaction was completed, the solvent was evaporated and the organic product purified by column chromatography or by recrystallization.

General Procedure 5 (GP 5): Reduction of Peroxides 7. The corresponding peroxide was dissolved in methanol, and then $NaBH_4$ was added dropwise to the solution during 1 h. After the solution was stirred at room temperature for 2 h, water and a solution 1 M of chlorhydric acid were added, and the mixture was stirred for another 1 h. Finally, the reaction mixture was extracted with dichloromethane, the organic layer was dried over $MgSO_4$, and the solvent was evaporated. The organic product was purified by column chromatography or by recrystallization.



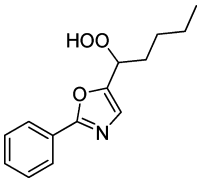
1-(2-Phenyl-1,3-oxazol-5-yl)propan-1-ol (4a). The reaction was carried out according to GP 1 with 93.6 mg of **1a** (500 μmol, 1 equiv), 15.5 mg of (IPr)AuCl (25.0 μmol, 5 mol %), and 6.97 mg of AgOTs (25.0 μmol, 5 mol %). Compound **4a** (30 mg) was obtained as a white solid (160 μmol, 32%). R_f = 0.62 (petroleum ether/ethyl acetate 2:1). Mp: 78.3−79.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.1 (br s, OOH), 7.68−7.76 (m, 2H), 7.27−7.46 (m, 3H), 7.00 (s, 1H), 4.85 (t, J = 7.3 Hz, 1H), 1.76−2.12 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 161.7 (s), 150.6 (s), 130.7 (d), 128.7 (d, 2C), 127.2 (d), 126.4 (d, 2 C), 126.4 (s), 80.1 (d), 23.8 (t), 10.3 (q). IR (neat): $\tilde{\nu}$ = 3160, 2972, 2936, 2879, 2850, 2253, 1685, 1548, 1485, 1450, 1376, 1334 cm^{-1}. HRMS (EI(+), 70 eV): $[C_{12}H_{13}O_2N]^+$ calcd 203.0946, found 203.0946.

1-(2-Phenyl-1,3-oxazol-5-yl)butan-1-ol (4b).



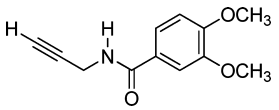
The reaction was carried out according to GP 1 with 101 mg of **1b** (500 μmol, 1 eq), 15.5 mg of (IPr)AuCl (25.0 μmol, 5 mol %), and 6.97 mg of AgOTs (25.0 μmol, 5 mol %) in 10 mL of dry THF. Compound **4b** (47 mg) was obtained as a white solid (233 μmol, 47%). R_f = 0.64 (petroleum ether/ethyl acetate 1:1). Mp: 64.7−66.1 °C. ^{1}HNMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ= 11.4 (br s, OOH), 7.68 (d, J = 7.5 Hz, 2H), 7.37 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 7.5 Hz, 2H), 6.97 (s, 1H), 4.92 (t, J = 7.3 Hz, 1H), 1.93−2.03 (m, 1H), 1.71−1.81 (m, 1H), 1.30−1.54 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ= 161.6 (s), 150.8 (s), 130.6 (d), 128.7 (d, 2C), 127.0 (d), 126.4 (d, 2C), 126.3 (s), 78.4 (d), 32.4 (t), 19.0 (t), 13.9 (q). IR (neat): $\tilde{\nu}$ = 3156, 2962, 2935, 2873, 2253, 1548, 1485, 1450, 1380, 1359, 1330, 1133, 1103, 1070. HRMS (EI (+), 70 eV): $[C_{13}H_{15}O_2N]^+$ calcd 217.1103, found 217.1102.

1-(2-Phenyl-1,3-oxazol-5-yl)pentan-1-ol (4c).



The reaction was carried out according to GP 1 with 108 mg of **1c** (500 μmol, 1 equiv), 15.5 mg of (IPr)AuCl (25.0 μmol, 5 mol %), and 6.97 mg of AgOTs (25.0 μmol, 5 mol %) in 10 mL of dry THF. Compound **4c** (52 mg) was obtained as a white solid (259 μmol, 52%). R_f = 0.66 (petroleum ether/ethyl acetate 1:1). Mp: 57.5−59.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.38 (br s, OOH), 7.64−7.72 (m, 2H), 7.34−7.42 (m, 1H), 7.26−7.33 (m, 2H), 6.97 (s, 1H), 4.90 (t, J = 7.3 Hz, 1H), 1.92− 2.07 (m, 1H), 1.72−1.88 (m, 1H), 1.24−1.48 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 161.6 (s), 150.8 (s), 130.6 (d), 128.7 (d, 2C), 127.0 (d), 126.4 (d, 2C), 126.3 (s), 78.7 (d), 30.0 (t), 27.9 (t), 22.5 (t), 14.0 (q). IR (neat): $\tilde{\nu}$ = 3160, 2958, 2932, 2871, 2253, 1547, 1485, 1466, 1450, 1380, 1333, 1133, 1071, 1026, 974. HRMS (EI (+), 70 eV): $[C_{14}H_{17}O_2N]^+$ calcd 231.1259, found 231.1251.

3,4-Dimethoxy-*N*-(prop-2-ynyl)benzamide (5a).



3,4-Dimethoxy-*N*-(prop-2-ynyl)benzamide was prepared according to GP 2. Propargylamine (0.066 g, 1.25 mmol), Et_3N (0.12 g, 1.25 mmol), DMAP (3 mg, 2 mol %), and 3,4-dimethoxybenzoyl chloride (0.25 g, 1.25 mmol) in 20 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 1:1) delivered 0.24 g (1.1 mmol, 88%) of **5a** as a white solid. R_f = 0.12 (petroleum ether/ethyl acetate 1:1). Mp: 147−148.5 °C. ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 7.95 (s, NH), 7.54 (dd, J = 6.9, 2.1 Hz, 1H), 7.52 (d, J = 2.2 Hz, 1H), 7.00 (d, J = 6.92 Hz, 1H), 4.17 (dd, J = 5.6, 2.5 Hz, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 2.64 (t, J = 2.5 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6, 25 °C, TMS): δ = 166.6 (s), 153.1 (s), 150.0

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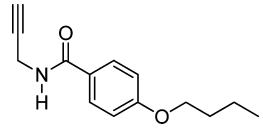
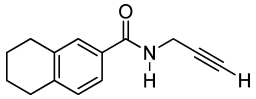
(s), 127.7 (s), 121.3 (s), 111.7 (s), 111.7 (s), 81.7 (s), 71.7 (s), 56.11 (s, 2C), 29.4 (s). IR (neat): $\tilde{\nu}$ = 1585, 1603, 1637, 3252, 3410 cm^{-1}. MS (70 eV): *m*/*z* 219 (63) [M^+], 188 (17) [$M^+ - CH_3O^\bullet$], 165 (100) [$M^+ - C_3H_4N^\bullet$]. HRMS (EI (+), 70 eV): [$C_{12}H_{13}NO_3$]$^+$ calcd 219.0895, found 219.0891.

4-Butoxy-*N*-(prop-2-ynyl)benzamide (5b).



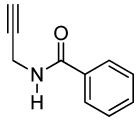
4-Butoxy-*N*-(prop-2-ynyl)benzamide was prepared according to GP 2. Propargylamine (0.28 g, 5 mmol), Et_3N (0.51 g, 5 mmol), DMAP (12 mg, 2 mol %), and 4-butoxybenzoyl chloride (1.06 g, 5 mmol) in 30 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 1.10 g (4.7 mmol, 94%) **5b** as a white solid. R_f = 0.26 (petroleum ether/ethyl acetate 2:1). Mp: 120.4−122.0 °C. ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 7.89 (dd, *J* = 9.3, 2.5 Hz, 2H), 6.99 (dd, *J* = 9.3, 2.5, 2H), 4.18 (dd, *J* = 5.6, 2.5 Hz, 2H), 4.08 (t, *J* = 6.5 Hz, 2H), 2.65 (t, *J* = 2.9 Hz, 1H), 1.78 (qu, *J* = 6.5 Hz, 2H), 1.52 (qt, *J* = 6.5, 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, acetone-d_6, 25 °C, TMS): δ = 166.4 (s), 162.7 (s), 129.9 (s, 2C), 127.3 (s), 114.9 (s, 2C), 81.6 (s), 71.7 (s), 68.5 (s), 32.0 (s), 29.9 (s), 19.9 (s), 14.1 (s). IR (neat): $\tilde{\nu}$ = 1639, 2953, 3301, 3320 cm^{-1}. MS (70 eV): *m*/*z* 231 (65) [M^+], 177 (56) [$M^+ - C_3H_4N^\bullet$], 121 (100) [$C_7H_4O_2^+$]. HRMS (EI (+), 70 eV): [$C_{14}H_{17}NO_2$]$^+$ calcd 231.1259, found 231.1265.

***N*-(Prop-2-yn-1-yl)-5,6,7,8-tetrahydronaphthalene-2-carboxamide (5c).**



N-(Prop-2-yn-1-yl)-5,6,7,8-tetrahydronaphthalene-2-carboxamide was prepared according to GP 2. 5,6,7,8-Tetrahydronaphthalene-2-carbonyl chloride was prepared by heating at reflux 5,6,7,8-tetrahydronaphthalene-2-carbonyl acid (0.352 g, 2.0 mmol) and $SOCl_2$ (4.72 g, 40 mmol); after 2 h, the excess of $SOCl_2$ was evaporated and the crude used in GP 2 without further purification. Propargylamine (0.11 g, 2.00 mmol), Et_3N (0.20 g, 2.00 mmol), DMAP (5 mg, 2 mol %), and the chloride (0.389 g, 2.00 mmol) in 20 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 0.36 g (1.70 mmol, 85%) **5c** as a white solid. R_f = 0.36 (petroleum ether/ethyl acetate 2:1). Mp: 113.3−114.7 °C. ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 7.95 (s, NH), 7.61 (d, *J* = 1.8 Hz, 1H), 7.61 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 4.17 (dd, *J* = 5.6, 2.5 Hz, 2H), 2.78 (t, *J* = 6.5 Hz, 4H), 2.63 (t, *J* = 2.5 Hz, 1H), 1.79 (qu, *J* = 6.5 Hz, 4H). ^{13}C NMR (75 MHz, acetone-d_6, 25 °C, TMS): δ = 167.1 (s), 141.5 (s), 137.8 (s), 132.5 (s), 129.9 (s), 128.9 (s), 125.2 (s), 81.7 (s), 71.7 (s), 29.9 (s), 29.3 (s, 2C), 23.7 (s, 2C). IR (neat): $\tilde{\nu}$ = 1535, 1571, 1612, 1641, 3309 cm^{-1}. MS (70 eV): *m*/*z* 213 (52) [M^+], 159 (100) [$M^+ - C_3H_4N^\bullet$]. HRMS (EI (+), 70 eV): [$C_{14}H_{15}NO$]$^+$ calcd 213.1154, found 213.1130.

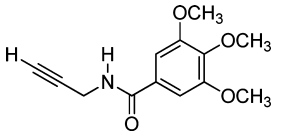
***N*-(Prop-2-yn-1-yl)benzamide (5d).**



N-(Prop-2-yn-1-yl)benzamide was prepared according to GP 2. Propargylamine (0.42 g, 3.0 mmol), Et_3N (0.16 g, 3.0 mmol), DMAP (6 mg, 2 mol %), and benzoyl chloride (0.36 g, 3.0 mmol) in 20 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 0.43 g (2.7 mmol, 90%) of **5d** as a white solid. R_f = 0.40 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 8.05 (s, NH), 7.92 (m, 2H), 7.50 (m, 3H), 4.20 (dd, *J* = 5.6, 2.6 Hz, 2H), 2.65 (t, *J* = 2.6 Hz, 1H).

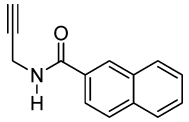
The ^{1}H NMR corresponds to that reported in the literature.[4c,7a]

3,4,5-Trimethoxy-*N*-(prop-2-ynyl)benzamide (5e).



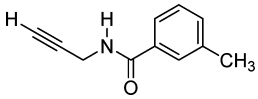
3,4,5-Trimethoxy-*N*-(prop-2-ynyl)benzamide was prepared according to the GP 2. Propargylamine (0.19 g, 3.53 mmol), Et_3N (0.36 g, 3.53 mmol), DMAP (9 mg, 2 mol %), and 3,4,5-trimethoxybenzoyl chloride (0.81 g, 3.53 mmol) in 20 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 1:1) delivered 0.8 g of (3.21 mmol, 91%) **5e** as a colorless solid. R_f = 0.3 (petroleum ether/ethyl acetate 1:1). Mp: 153.0−154.3 °C. ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 8.05 (s, NH), 7.26 (s, 2H), 4.17 (dd, *J* = 5.6, 2.5 Hz, 2H), 3.85 (s, 6H), 3.77 (s, 3H), 2.66 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6, 25 °C, TMS): δ = 165.5 (s), 154.2 (s, 2C), 142.0 (s), 130.4 (s), 105.1 (s, 2C), 81.6 (s), 71.9 (s), 56.5 (s, 2C), 60.6 (s), 29.5 (s). IR (neat): $\tilde{\nu}$ = 1588, 1638, 2943, 3289, 3388 cm^{-1}. MS (70 eV): *m*/*z* 249 (100) [M^+], 218 (9) [$M^+ - CH_3O^\bullet$], 195 (75) [$M^+ - C_3H_4N^\bullet$]. HRMS (EI (+), 70 eV): [$C_{13}H_{15}NO_4$]$^+$ calcd 249.1001, found 249.1001.

***N*-(Prop-2-ynyl)-2-naphthamide (5f).**



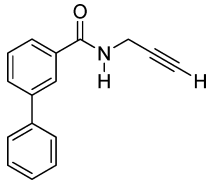
N-(Prop-2-ynyl)-2-naphthamide was prepared according to GP 2. of Propargylamine (0.40 g, 7.34 mmol), Et_3N (0.74 g, 7.34 mmol), DMAP (18 mg, 2 mol %), and naphthoyl chloride (1.40 g, 7.34 mmol) in 30 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 1:1) delivered 1.39 g (6.6 mmol, 90%) of **5f** as a white solid. R_f = 0.28 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 8.50 (s, 1H), 8.30 (s, NH), 7.99 (m, 4H), 7.59 (m, 2H), 4.27 (dd, *J* = 5.6, 2.5 Hz, 2H), 2.71 (t, *J* = 2.5 Hz, 1H). The ^{1}H NMR corresponds to that reported in the literature.[20]

3-Methyl-*N*-(prop-2-ynyl)benzamide (5g).



3-Methyl-*N*-(prop-2-ynyl)benzamide was prepared according to the GP 2. Propargylamine (0.11 g, 2.00 mmol), Et_3N (0.20 g, 2.00 mmol), DMAP (5 mg, 2 mol %), and 3-methylbenzoyl chloride (0.31 g, 2.00 mmol) in 20 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 0.32 g (1.85 mmol, 93%) of **5g** as a white solid. R_f = 0.30 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 8.01 (s, NH), 7.74 (s, 1H), 7.71 (m, 1H), 7.34 (m, 2H), 4.19 (dd, *J* = 5.5, 2.5 Hz, 2H), 2.65 (t, *J* = 2.5 Hz, 1H), 2.37 (s, 3H). The ^{1}H NMR corresponds to that reported in the literature.[21]

***N*-(Prop-2-yn-1-yl)biphenyl-3-carboxamide (5h).**



N-(Prop-2-yn-1-yl)biphenyl-3-carboxamide was prepared according to GP 2. Propargylamine (0.083 g, 1.50 mmol), Et_3N (0.15 g, 1.50 mmol), DMAP (3 mg, 2 mol %), and (1,1′-biphenyl)-3-carbonyl chloride (0.30 g, 1.50 mmol) in 20 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 3:1) delivered 0.32 g (1.36 mmol, 91%) of **5h** as a white solid. R_f = 0.29 (petroleum ether/ethyl acetate 3:1). Mp: 116.8−117.1 °C. ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 8.24 (s, NH), 8.20 (t, *J* = 1.8 Hz, 1H), 7.93 (ddd, *J* = 7.8, 1.8, 1.2 Hz, 1H), 7.83 (ddd, *J* = 7.8, 1.8, 1.2 Hz, 1H), 7.71 (dt, *J* = 7.5,

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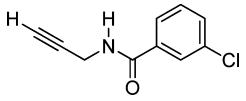
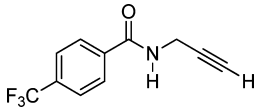
1.8 Hz, 2H), 7.57 (t, J = 7.8 Hz, 1H), 7.49 (td, J = 7.5, 1.8 Hz, 2H), 7.38 (tt, J = 7.5, 1.8 Hz, 1H), 4.23 (dd, J = 5.6, 2.5 Hz, 2H), 2.67 (t, J = 2.5 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6, 25 °C, TMS): δ = 166.9 (s), 142.1 (s), 141.1 (s), 140.0 (s), 130.6 (s), 129.9 (s), 129.8 (s, 2C), 128.6 (s), 127.9 (s, 2C), 127.2 (s), 126.5 (s), 81.5 (s), 71.9 (s), 29.5 (s). IR (neat): $\tilde{\nu}$ = 1583, 1604, 1645, 3286 cm^{-1}. MS (70 eV): m/z 235 (100) [M$^+$], 181 (89) [M$^+$ − $C_3H_4N^\bullet$]. HRMS (EI (+), 70 eV): $[C_{16}H_{13}NO]^+$ calcd 235.0997, found 235.0988.

3-Chloro-*N*-(prop-2-ynyl)benzamide (5i).



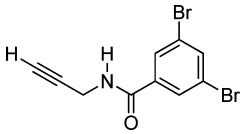
3-Chloro-*N*-(prop-2-ynyl)benzamide was prepared according to GP 2. Propargylamine (0.11 g, 2.00 mmol), Et_3N (0.20 g, 2.00 mmol), DMAP (5 mg, 2 mol %), and 3-chlorobenzoyl chloride (0.35 g, 2.00 mmol) in 20 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 0.35 g (1.80 mmol, 90%) of **5i** as a white solid. R_f = 0.44 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 8.20 (s, NH), 7.92 (s, 1H), 7.87 (d, J = 7.5 Hz, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 4.20 (dd, J = 5.5, 2.5 Hz, 2H), 2.68 (t, J = 2.5 Hz, 1H). The ^{1}H NMR corresponds to that reported in the literature.[22]

4-Trifluoromethyl-*N*-(prop-2-ynyl)benzamide (5j).



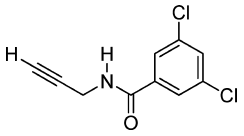
4-Trifluoromethyl-*N*-(prop-2-ynyl)benzamide was prepared according to GP 2. Propargylamine (0.11 g, 2.00 mmol), Et_3N (0.20 g, 2.00 mmol), DMAP (5 mg, 2 mol %), and 4-(trifluoromethyl)-benzoyl chloride (0.42 g, 2.00 mmol) in 20 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 3:1) delivered 0.40 g (1.76 mmol, 88%) of **5j** as a white solid. R_f = 0.38 (petroleum ether/ethyl acetate 3:1). Mp: 146.5−147.0 °C. ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 8.31 (s, NH), 8.12 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H), 4.22 (dd, J = 5.6, 2.5 Hz, 2H), 2.69 (t, J = 2.5 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6, 25 °C, TMS): δ = 165.8 (s), 133.4 (s), 133.0 (s), 131.7 (q, $^1J_{C,F}$ = 246.5 Hz), 129.0 (s, 2C), 126.3 (q, $^3J_{C,F}$ = 3.9 Hz, 2C), 81.1 (s), 72.2 (s), 29.7 (s). IR (neat): $\tilde{\nu}$ = 1547, 1580, 1642, 3309 cm^{-1}. MS (70 eV): m/z 227 (61) [M$^+$], 173 (100) [M$^+$ − $C_3H_4N^\bullet$], 145 (92) [M$^+$ − $C_4H_4NO^\bullet$]. HRMS (EI (+), 70 eV): $[C_{11}H_8F_3NO]^+$ calcd 227.0558, found 227.0555.

3,5-Dibromo-*N*-(prop-2-ynyl)benzamide (5k).



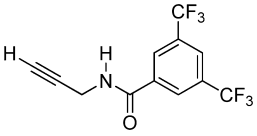
3,5-Dibromo-*N*-(prop-2-ynyl)benzamide was prepared according to GP 2. 3,5-Dibromobenzoyl chloride was prepared by heating at reflux 0.56 g (2.0 mmol) of 3,5-dibromobenzoic acid and 4.72 g (40 mmol) of $SOCl_2$ during 2 h, and the excess of $SOCl_2$ was evaporated and the crude used in GP 2 without further purification. Propargylamine (0.11 g, 2.00 mmol), Et_3N (0.20 g, 2.00 mmol), DMAP (5 mg, 2 mol %), and the chloride (0.597 g, 2.00 mmol) in 20 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 4:1) delivered 0.57 g (1.80 mmol, 90%) **5k** as a white solid. R_f = 0.52 (petroleum ether/ethyl acetate 4:1). Mp: 148−149.1 °C. ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 8.32 (s, NH), 8.06 (d, J = 1.8 Hz, 2H), 7.93 (t, J = 1.8 Hz, 1H), 4.20 (dd, J = 5.5, 2.6 Hz, 2H), 2.70 (t, J = 2.6 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6, 25 °C, TMS): δ = 164.2 (s), 138.8 (s), 137.3 (s, 2C), 130.3 (s, 2C), 123.6 (s), 80.8 (s), 72.4 (s), 29.8 (s). IR (neat): $\tilde{\nu}$ = 1543, 1555, 3277, 1586, 1634, 3064 cm^{-1}. MS (70 eV): m/z 317 (48) [M$^+$], 263 (100) [M$^+$ − $C_3H_4N^\bullet$], 235 (54) [$C_6H_3Br_2$]. HRMS (EI (+), 70 eV): $[C_{10}H_7NO^{79}Br_2]^+$ calcd 314.8894, found 314.8921.

3,5-Dichloro-*N*-(prop-2-ynyl)benzamide (5l).



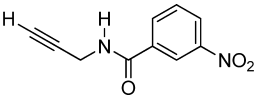
3,5-Dichloro-*N*-(prop-2-ynyl)benzamide was prepared according to GP 2. Propargylamine (0.14 g, 2.50 mmol), Et_3N (0.30 g, 2.50 mmol), DMAP (5 mg, 2 mol %), and 3,5-dichlorobenzoyl chloride (0.52 g, 2.50 mmol) in 20 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 3:1) delivered 0.45 g (2.00 mmol, 80%) **5l** as a white solid. R_f = 0.46 (petroleum ether/ethyl acetate 3:1). Mp: 140.6−142.0 °C. ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 8.31 (s, NH), 7.88 (d, J = 1.9 Hz, 2H), 7.66 (t, J = 1.9 Hz, 1H), 4.20 (dd, J = 5.5, 2.5 Hz, 2H), 2.71 (t, J = 2.5 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6, 25 °C, TMS): δ = 164.5 (s), 138.2 (s), 135.8 (s, 2C), 131.8 (s), 127.0 (s, 2C), 80.8 (s), 72.4 (s), 29.8 (s). IR (neat): $\tilde{\nu}$ = 1544, 1566, 1642, 3281 cm^{-1}. MS (70 eV): m/z 227 (41) [M$^+$], 173 (100) [M$^+$ − $C_3H_4N^\bullet$]. HRMS (EI (+), 70 eV): $[C_{10}H_7Cl_2NO]^+$ calcd 226.9905, found 226.9925.

3,5-Bis(trifluoromethyl)-*N*-(prop-2-ynyl)benzamide (5m).



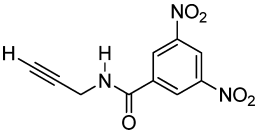
3,5-Bis(trifluoromethyl)-*N*-(prop-2-ynyl)benzamide was prepared according to GP 2. Propargylamine (0.11 g, 2.00 mmol), Et_3N (0.20 g, 2.00 mmol), DMAP (5 mg, 2 mol %), and the chloride (0.55 g, 2.00 mmol) in 20 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 4:1) delivered 0.52 g (1.76 mmol, 88%) of **5m** as a white solid. R_f = 0.64 (petroleum ether/ethyl acetate 4:1). Mp: 88.9−89.6 °C. ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 8.61 (s, NH), 8.55 (s, 2H), 8.26 (s, 1H), 4.29 (dd, J = 5.5, 2.6 Hz, 2H), 2.75 (t, J = 2.6 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6, 25 °C, TMS): δ = 164.3 (s), 137.5 (s), 132.4 (q, $^2J_{C,F}$ = 33.6 Hz, 2C), 125.8 (q, $^3J_{C,F}$ = 3.8 Hz, 2C), 125.7 (hept, $^3J_{C,F}$ = 3.9 Hz), 124.2 (q, $^1J_{C,F}$ = 272.2 Hz, 2C), 80.6 (s), 72.6 (s), 29.9 (s). IR (neat): $\tilde{\nu}$ = 1419, 1454, 1542, 1618, 1647, 3100, 3247 cm^{-1}. MS (70 eV): m/z 295 (66) [M$^+$], 241 (100) [M$^+$ − $C_3H_4N^\bullet$], 213 (68) [$C_8H_3F_6$]. HRMS (EI (+), 70 eV): $[C_{12}H_7NOF_6]^+$ calcd 295.0432, found 295.0409.

3-Nitro-*N*-(prop-2-ynyl)benzamide (5n).



3-Nitro-*N*-(prop-2-ynyl)benzamide was prepared according to GP 2. Propargylamine (0.14 g, 2.50 mmol), Et_3N (0.30 g, 2.50 mmol), DMAP (5 mg, 2 mol %), and the chloride (0.46 g, 2.50 mmol) in 20 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 0.41 g (2.00 mmol, 80%) of **5n** as a light yellow solid. R_f = 0.46 (petroleum ether/ethyl acetate 2:1). Mp: 146.5−147.9 °C. ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 8.74 (t, J = 1.8 Hz, 1H), 8.51 (s, NH), 8.40 (dt, J = 8.0, 1.8 Hz, 1H), 8.35 (dt, J = 8.0, 1.8 Hz, 1H), 7.81 (t, J = 8.0 Hz, 1H), 4.25 (dd, J = 5.5, 2.5 Hz, 2H), 2.72 (t, J = 2.5 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6, 25 °C, TMS): δ = 165.0 (s), 149.2 (s), 136.8 (s), 134.3 (s), 131.0 (s), 126.8 (s), 123.0 (s), 81.0 (s), 72.3 (s), 29.8 (s). IR (neat): $\tilde{\nu}$ = 1529, 1579, 1649, 3299 cm^{-1}. MS (70 eV): m/z 204 (61) [M$^+$], 150 (100) [M$^+$ − $C_3H_4N^\bullet$]. HRMS (EI (+), 70 eV): $[C_{10}H_8N_2O_3]^+$ calcd 204.0535, found 204.0523.

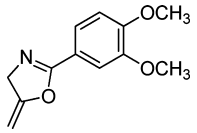
3,5-Dinitro-*N*-(prop-2-ynyl)benzamide (5o).



3,5-Dinitro-*N*-(prop-2-ynyl)benzamide was prepared according to GP 2. Propargylamine (0.11 g, 2.00 mmol), Et_3N (0.20 g, 2.00 mmol),

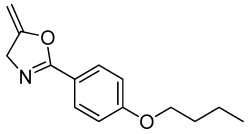
DMAP (4 mg, 2 mol %), and 3,5-dinitrobenzoylchloride (0.46 g, 2.00 mmol) in 20 mL of DCM were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 0.40 g (1.60 mmol, 80%) of **5o** as a light yellow solid. R_f = 0.50 (petroleum ether/ethyl acetate 2:1). Mp: 139.5−141.0 °C. ^{1}H NMR (300 MHz, acetone-d_6, 25 °C, TMS): δ = 9.12 (d, J = 1.9 Hz, 2H), 9.10 (t, J = 1.9 Hz, 1H), 8.85 (s, NH), 4.29 (dd, J = 5.4, 2.5 Hz, 2H), 2.76 (t, J = 2.5 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6, 25 °C, TMS): δ = 163.1 (s), 149.7 (s), 138.1 (s, 2C), 128.4 (s, 2C), 121.9 (s), 80.5 (s), 72.7 (s), 30.1 (s). IR (neat): $\tilde{\nu}$ = 1541, 1592, 1653, 3289 cm^{-1}. MS (70 eV): m/z 249 (100) [M$^+$], 195 (72) [M$^+$ − $C_3H_4N^\bullet$]. HRMS (EI (+), 70 eV): [$C_{10}H_7N_3O_5$]$^+$ calcd 249.0386, found 249.0382.

2-(3,4-Dimethoxyphenyl)-5-methylene-4,5-dihydrooxazole (6a).



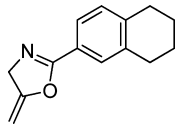
2-(3,4-Dimethoxyphenyl)-5-methylene-4,5-dihydrooxazole was prepared according to GP 3. Compound **5a** (0.24 g, 1.1 mmol) and PPh_3AuNTf_2 (16 mg, 2 mol %) were employed (reaction time 20 h). Flash chromatography on silica gel (PE/EA, 1:1) delivered 0.20 g (0.91 mmol, 83%) of **6a** as a white solid. R_f = 0.22 (petroleum ether/ethyl acetate 1:1); mp 93.7−95.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.56 (dd, J = 8.4, 1.8 Hz, 1H), 7.49 (d, J = 1.8 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 4.80 (q, J = 2.8 Hz, 1H), 4.63 (t, J = 2.8 Hz, 2H), 4.34 (q, J = 2.8, 1H), 3.93 (s, 3H), 3.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 163.7 (s), 159.1 (s), 152.2 (s), 149.0 (s), 121.8 (s), 119.5 (s), 110.6 (s), 110.5 (s), 83.7 (s), 57.8 (s), 56.2 (s), 56.1 (s). IR (neat): $\tilde{\nu}$ = 3085, 2965, 1649, 1605, 1514 cm^{-1}. MS (70 eV): m/z 219 (100) [M$^+$], 191 (53) [M$^+$ − CO], 177 (98) [M$^+$ − $C_2H_2O^\bullet$]. HRMS (EI (+), 70 eV): [$C_{12}H_{13}NO_3$]$^+$ calcd 219.0895, found 219.0882.

2-(4-Butoxyphenyl)-5-methylene-4,5-dihydrooxazole (6b).



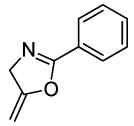
2-(4-Butoxyphenyl)-5-methylene-4,5-dihydrooxazole was prepared according to GP 3. Compound **5b** (0.46 g, 2.0 mmol) and PPh_3AuNTf_2 (15 mg, 1 mol %) were employed (reaction time 6 h). Flash chromatography on silica gel (PE/EA, 2:1) delivered 0.36 g (1.56 mmol, 78%) of **6b** as a white solid. R_f = 0.36 (petroleum ether/ethyl acetate 2:1). Mp: 36.0−36.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.90 (dd, J = 9.2, 2.3 Hz, 2H), 6.92 (dd, J = 9.3, 2.3 Hz, 2H), 4.78 (q, J = 2.8, 1H), 4.61 (t, J = 2.8 Hz, 2H), 4.33 (q, J = 2.8 Hz, 1H), 4.00 (t, J = 6.5 Hz, 2H), 1.78 (qu, J = 6.5 Hz, 2H), 1.50 (qt, J = 7.4, 6.5 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 163.6 (s), 162.1 (s), 159.1 (s), 129.7 (s, 2C), 118.9 (s), 114.4 (s, 2C), 83.3 (s), 67.9 (s), 57.7 (s), 31.2 (s), 19.2 (s), 13.8 (s). IR (neat): $\tilde{\nu}$ = 1609, 1652, 1691, 2872, 2936, 2960 cm^{-1}. MS (70 eV): m/z 231 (76) [M$^+$], 189 (100) [M$^+$ − $C_2H_2O^\bullet$], 175 (4) [M$^+$ − $C_4H_8^\bullet$], 133 (94) [$C_8H_7NO^+$]. HRMS (EI (+), 70 eV): [$C_{14}H_{17}NO_2$]$^+$ calcd 231.1259, found 231.1265.

5-Methylene-2-(5,6,7,8-tetrahydronaphthalen-2-yl)-4,5-dihydrooxazole (6c).



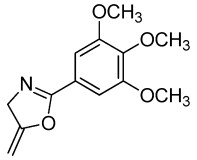
5-Methylene-2-(5,6,7,8-tetrahydronaphthalen-2-yl)-4,5-dihydrooxazole was prepared according to GP 3. Compound **5c** (0.25 g, 1.17 mmol) and PPh_3AuNTf_2 (16 mg, 2 mol %) were employed (reaction time 12 h). Flash chromatography on silica gel (PE/EA, 3:1) delivered 0.20 g (0.94 mmol, 80%) **6c** as a colorless viscous oil. R_f = 0.52 (petroleum ether/ethyl acetate 3:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.68 (d, J = 1.7 Hz, 1H), 7.66 (dd, J = 7.8, 1.7 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 4.79 (q, J = 2.6 Hz, 1H), 4.62 (t, J = 2.6 Hz, 2H), 4.34 (q, J = 2.6, 1H), 2.80 (t, J = 6.4 Hz, 4H), 1.81 (qu, J = 6.4 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 164.0 (s), 159.0 (s), 141.6 (s), 137.4 (s), 129.3 (s), 128.7 (s), 125.0 (s), 123.8 (s), 83.5 (s), 57.6 (s), 29.5 (s, 2C), 22.9 (s, 2C). IR (neat): $\tilde{\nu}$ = 1495, 1647, 1688, 2931 cm^{-1}. MS (70 eV): m/z 213 (100) [M$^+$], 185 (22) [M$^+$ − CO], 171 (66) [M$^+$ − $C_2H_2O^\bullet$]. HRMS (EI (+), 70 eV): [$C_{14}H_{15}NO$]$^+$ calcd 213.1154, found 213.1142.

5-Methylene-2-phenyl-4,5-dihydrooxazole (6d).



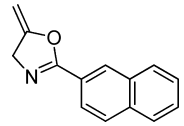
5-Methylene-2-phenyl-4,5-dihydrooxazole was prepared according to GP 3. Compound **5d** (0.30 g, 1.87 mmol) and PPh_3AuNTf_2 (27 mg, 2 mol %) were employed (reaction time 12 h). Flash chromatography on silica gel (PE/EA, 1:1) delivered 0.27 g (1.70 mmol, 91%) of **6d** as a light yellow viscous oil. R_f = 0.51 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.99 (m, 2H), 7.47 (m, 3H), 4.82 (q, J = 2.9 Hz, 1H), 4.65 (t, J = 2.9 Hz, 2H), 4.37 (q, J = 2.8, 1H). The ^{1}H NMR corresponds to that reported in the literature.[4c,7a]

5-Methylene-2-(3,4,5-trimethoxyphenyl)-4,5-dihydrooxazole (6e).



5-Methylene-2-(3,4,5-trimethoxyphenyl)-4,5-dihydrooxazole was prepared according to GP 3. Compound **5e** (0.43 g, 1.7 mmol) and PPh_3AuNTf_2 (25 mg, 2 mol %) were employed. The reaction was stirred at 35 °C during 48 h. Flash chromatography on silica gel (PE/EA, 1:1) delivered 0.25 g (1.0 mmol, 59%) of **6e** as a white solid. Crystals suitable for X-ray crystal structure analysis could be obtained.[14] R_f = 0.28 (petroleum ether/ethyl acetate 1:1). Mp: 70.0−71.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.22 (s, 2H), 4.82 (q, J = 2.8 Hz, 1H), 4.64 (t, J = 2.8 Hz, 2H), 4.36 (q, J = 2.8, 1H), 3.91 (s, 3H), 3.90 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 163.7 (s), 159.0 (s), 153.3 (s, 2C), 141.4 (s), 122.0 (s), 105.3 (s, 2C), 84.0 (s), 61.1 (s), 57.9 (s), 56.4 (s, 2C). IR (neat): $\tilde{\nu}$ = 1588, 1649, 1686, 2986, 3010 cm^{-1}. MS (70 eV): m/z 249 (100) [M$^+$], 221 (42) [M$^+$ − CO], 207 (66) [M$^+$ − $C_2H_2O^\bullet$]. HRMS (EI (+), 70 eV): [$C_{13}H_{15}NO_4$]$^+$ calcd 249.1001, found 249.1003.

5-Methylene-2-(naphthalen-2-yl)-4,5-dihydrooxazole (6f).



5-Methylene-2-(naphthalen-2-yl)-4,5-dihydrooxazole was prepared according to GP 3. Compound **5f** (0.418 g, 2.0 mmol) and PPh_3AuNTf_2 (37 mg, 2 mol %) were employed (reaction time 24 h). Flash chromatography on silica gel (PE/EA, 2:1) delivered 0.29 gr (1.39 mmol, 70%) **6f** as a white solid. R_f = 0.46 (petroleum ether/ethyl acetate 2:1). Mp: 53.7−54.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.48 (s, 1H), 8.06 (dd, J = 8.5, 1.7 Hz, 1H), 7.93 (dd, J = 6.9, 2.6, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.87 (dd, J = 6.9, 2.7 Hz, 1H), 7.57 (td, J = 6.9, 2.6 Hz, 1H), 7.53 (td, J = 6.9, 2.6 Hz, 1H), 4.88 (q, J = 2.8 Hz, 1H), 4.71 (t, J = 2.8 Hz, 2H), 4.40 (q, J = 2.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 163.9 (s), 158.9 (s), 134.9 (s), 132.7 (s), 128.9 (s), 128.8 (s), 128.4 (s), 127.8 (s), 127.9 (s), 126.7 (s), 124.2 (s), 124.0 (s), 83.8 (s), 57.9 (s). IR (neat): $\tilde{\nu}$ = 1650, 1686, 2834, 2926, 3051, 3436 cm^{-1}. MS (70 eV): m/z 209 (77) [M$^+$], 167 (100) [M$^+$ − $C_2H_2O^\bullet$], 127 (56) [$C_{10}H_7^+$]. HRMS (EI (+), 70 eV): [$C_{14}H_{11}NO$]$^+$ calcd 209.0841, found 209.0869.

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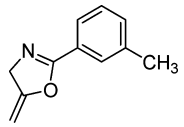
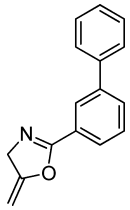
5-Methylene-2-(*m*-tolyl)-4,5-dihydrooxazole (6g).



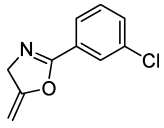
5-Methylene-2-(*m*-tolyl)-4,5-dihydrooxazole was prepared according to GP 3. Compound **5g** (0.25 g, 1.45 mmol) and PPh_3AuNTf_2 (21 mg, 2 mol %) were employed (reaction time 16 h). Flash chromatography on silica gel (PE/EA, 2:1) delivered 0.20 g (1.16 mmol, 80%) of **6g** as a pale yellow viscous oil. R_f = 0.44 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.80 (s, 1H), 7.77 (td, J = 4.1, 1.2 Hz, 1H), 7.31 (dd, J = 4.2, 1.1 Hz, 2H), 4.80 (q, J = 2.8 Hz, 1H), 4.63 (t, J = 2.8 Hz, 2H), 4.35 (q, J = 2.8, 1H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 164.0 (s), 159.0 (s), 138.4 (s), 132.7 (s), 128.7 (s), 128.5 (s), 126.7 (s), 125.2 (s), 83.8 (s), 57.8 (s), 21.4 (s). IR (neat): $\tilde{\nu}$ = 1588, 1647, 1689, 2920 cm^{-1}. MS (70 eV): m/z 173 (83) [M$^+$], 145 (32) [M$^+$ − CO], 131 (100) [M$^+$ − $C_2H_2O^\bullet$]. HRMS (EI (+), 70 eV): $[C_{11}H_{11}NO]^+$ calcd 173.0841, found 173.0835.

2-((1,1′-Biphenyl)-3-yl)-5-methylene-4,5-dihydrooxazole (6h).



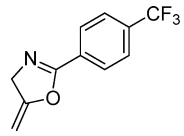
2-((1,1′-Biphenyl)-3-yl)-5-methylene-4,5-dihydrooxazole was prepared according to GP 3. Compound **5h** (0.25 g, 1.06 mmol) and PPh_3AuNTf_2 (16 mg, 2 mol %) were employed (reaction time 12 h). Flash chromatography on silica gel (PE/EA, 3:1) delivered 0.21 g (0.89 mmol, 84%) of **6h** as a white solid. R_f = 0.51 (petroleum ether/ethyl acetate 3:1). Mp: 67.7−68.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.22 (t, J = 1.8 Hz, 1H), 7.96 (dt, J = 7.7, 1.8 Hz, 1H), 7.75 (dt, J = 7.7, 1.8 Hz, 1H), 7.64 (dt, J = 7.5, 1.5 Hz, 2H), 7.52 (t, J = 7.7 Hz, 1H), 7.46 (td, J = 7.5, 1.5 Hz, 2H), 7.37 (tt, J = 7.5, 1.5 Hz, 1H), 4.84 (q, J = 2.8 Hz, 1H), 4.68 (t, J = 2.8 Hz, 2H), 4.38 (q, J = 2.8, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 163.9 (s), 159.0 (s), 141.7 (s), 140.3 (s), 130.6 (s), 129.1 (s), 129.0 (s, 2C), 127.9 (s), 127.4 (s), 127.3 (s, 2C), 126.9 (s), 126.8 (s), 84.0 (s), 57.9 (s). IR (neat): $\tilde{\nu}$ = 1586, 1601, 1654, 1688, 2851, 2905, 2919 cm^{-1}. MS (70 eV): m/z 235 (100) [M$^+$], 207 (60) [M$^+$ − CO], 193 (100) [M$^+$ − $C_2H_2O^\bullet$]. HRMS (EI (+), 70 eV): $[C_{16}H_{13}NO]^+$ calcd 235.0997, found 235.1010.

2-(3-Chlorophenyl)-5-methylene-4,5-dihydrooxazole (6i).



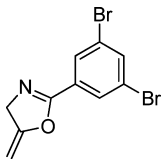
2-(3-Chlorophenyl)-5-methylene-4,5-dihydrooxazole was prepared according to GP 3. Compound **5i** (0.25 g, 1.29 mmol) and PPh_3AuNTf_2 (19 mg, 2 mol %) were employed (reaction time 14 h). Flash chromatography on silica gel (PE/EA, 3:1) delivered 0.20 g (1.03 mmol, 80%) of **6i** as a white solid. R_f = 0.6 (petroleum ether/ethyl acetate 3:1). Mp: 43.5−44.7 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.96 (t, J = 1.8 Hz, 1H), 7.85 (dt, J = 7.9, 1.8 Hz, 1H), 7.48 (dt, J = 7.9, 1.8 Hz, 1H), 4.82 (q, J = 2.8 Hz, 1H), 4.64 (t, J = 2.8 Hz, 2H), 4.38 (q, J = 2.8, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.7 (s), 158.7 (s), 134.8 (s), 132.0 (s), 129.9 (s), 128.6 (s), 128.2 (s), 126.2 (s), 84.4 (s), 57.9 (s). IR (neat): $\tilde{\nu}$ = 1598, 1651, 1691, 2913 cm^{-1}. MS (70 eV): m/z 193 (69) [M$^+$], 165 (13) [M$^+$ − CO], 151 (100) [M$^+$ − $C_2H_2O^\bullet$]. HRMS (EI (+), 70 eV): $[C_{10}H_8ClNO]^+$ calcd 193.0294, found 193.0280.

5-Methylene-2-(4-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (6j).



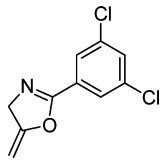
5-Methylene-2-(4-(trifluoromethyl)phenyl)-4,5-dihydrooxazole was prepared according to GP 3. Compound **5j** (0.25 g, 1.10 mmol) and PPh_3AuNTf_2 (16 mg, 2 mol %) were employed (reaction time 12 h). Flash chromatography on silica gel (PE/EA, 3:1) delivered 0.20 g (0.88 mmol, 88%) of **6j** as a white solid. R_f = 0.62 (petroleum ether/ethyl acetate 3:1). Mp: 48.1−49.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.10 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 4.85 (q, J = 2.8 Hz, 1H), 4.68 (t, J = 2.8 Hz, 2H), 4.41 (q, J = 2.8, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.6 (s), 158.5 (s), 133.4 (q, $^2J_{C,F}$ = 32.7 Hz), 131.7 (q, $^1J_{C,F}$ = 246.5 Hz), 128.4 (s, 2C), 125.5 (q, $^3J_{C,F}$ = 3.8 Hz, 2C), 121.9 (s), 84.5 (s), 57.9 (s). IR (neat): $\tilde{\nu}$ = 1618, 1649, 1674, 2921 cm^{-1}. MS (70 eV): m/z 227 (28) [M$^+$], 199 (27) [M$^+$ − CO], 185 (100) [M$^+$ − $C_2H_2O^\bullet$]. HRMS (EI (+), 70 eV): $[C_{11}H_8F_3NO]^+$ calcd 227.0558, found 227.0548.

2-(3,5-Dibromophenyl)-5-methylene-4,5-dihydrooxazole (6k). 2-(3,5-Dibromophenyl)-5-methylene-4,5-dihydrooxazole was



prepared according to GP 3. Compound **5k** (0.31 g, 0.98 mmol) and PPh_3AuNTf_2 (14.4 mg, 2 mol %) were employed. The reaction was stirred at 35 °C during 36 h. Flash chromatography on silica gel (PE/EA, 3:1) delivered 0.25 g (0.79 mmol, 81%) of **6k** as a white solid. R_f = 0.66 (petroleum ether/ethyl acetate 3:1). Mp: 85.4−86.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.06 (d, J = 1.7 Hz, 2H), 7.80 (t, J = 1.7 Hz, 1H), 4.84 (q, J = 2.8 Hz, 1H), 4.65 (t, J = 2.8 Hz, 2H), 4.40 (q, J = 2.8, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 161.3 (s), 158.3 (s), 137.1 (s), 130.0 (s, 2C), 129.7 (s, 2C), 127.5 (s), 84.7 (s), 57.8 (s). IR (neat): $\tilde{\nu}$ = 1557, 1645, 1694, 2913 cm^{-1}. MS (70 eV): m/z 317 (55) [M$^+$], 289 (47) [M$^+$ − CO], 275 (100) [M$^+$ − $C_2H_2O^\bullet$]. HRMS (EI (+), 70 eV): $[C_{10}H_7NO^{79}Br_2]^+$ calcd 314.8894, found 314.8880.

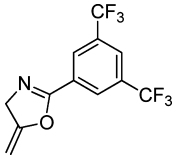
2-(3,5-Dichlorophenyl)-5-methylene-4,5-dihydrooxazole (6l). 2-(3,5-Dichlorophenyl)-5-methylene-4,5-dihydrooxazole was



prepared according to GP 3. Compound **5l** (0.25 g, 1.10 mmol) and PPh_3AuNTf_2 (16 mg, 2 mol %) were employed (reaction time 12 h). Flash chromatography on silica gel (PE/EA, 3:1) delivered 0.23 g (1.00 mmol, 91%) of **6l** as a white solid. R_f = 0.59 (petroleum ether/ethyl acetate 3:1). Mp: 71.0−72.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.86 (d, J = 1.8 Hz, 2H), 7.50 (t, J = 1.8 Hz, 1H), 4.84 (q, J = 2.8 Hz, 1H), 4.65 (t, J = 2.8 Hz, 2H), 4.40 (q, J = 2.8, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 161.6 (s), 158.3 (s), 135.4 (s, 2C), 131.7 (s), 129.5 (s), 126.4 (s, 2C), 84.7 (s), 57.8 (s). IR (neat): $\tilde{\nu}$ = 1592, 1654, 1689, 2922 cm^{-1}. MS (70 eV): m/z 227 (34) [M$^+$], 199 (29) [M$^+$ − CO], 185 (100) [M$^+$ − $C_2H_2O^\bullet$]. HRMS (EI (+), 70 eV): $[C_{10}H_7Cl_2NO]^+$ calcd 226.9905, found 226.9915.

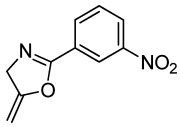
2-(3,5-Bis(trifluoromethyl)phenyl)-5-methylene-4,5-dihydrooxazole (6m). 2-(3,5-Bis(trifluoromethyl)phenyl)-5-methylene-4,5-dihydrooxazole was prepared according to GP 3. Compound **5m** (0.30 g, 1.0 mmol) and PPh_3AuNTf_2 (15.0 mg, 2 mol %) were employed (reaction time 12 h). Flash chromatography on silica gel

dx.doi.org/10.1021/jo301288w | J. Org. Chem. 2012, 77, 6394−6408



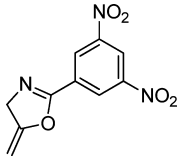
(PE/EA, 4:1) delivered 0.26 g (0.88 mmol, 88%) of **6m** as a white solid. R_f = 0.78 (petroleum ether/ethyl acetate 4:1). Mp: 36.8−37.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.44 (s, 2H), 8.02 (s, 1H), 4.91 (q, J = 2.8 Hz, 1H), 4.71 (t, J = 2.8 Hz, 2H), 4.46 (q, J = 2.8, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 161.3 (s), 158.1 (s), 132.2 (q, $^2J_{C,F}$ = 33.6 Hz, 2C), 129.0 (s), 128.2 (q, $^3J_{C,F}$ = 3.8 Hz, 2C), 125.1 (hept, $^3J_{C,F}$ = 3.8 Hz), 122.9 (q, $^1J_{C,F}$ = 272 Hz, 2C), 85.2 (s), 57.8 (s). IR (neat): $\tilde{\nu}$ = 1283, 1299, 1401, 1656, 1677 cm^{-1}. MS (70 eV): m/z 295 (27) [M$^+$], 267 (27) [M$^+$ − CO], 253 (100) [M$^+$ − $C_2H_2O^\bullet$]. HRMS (EI (+), 70 eV): [$C_{12}H_7NOF_6$]$^+$ calcd 295.0432, found 295.0431.

2-(3-Nitrophenyl)-5-methylene-4,5-dihydrooxazole (6n). 2-(3-Nitrophenyl)-5-methylene-4,5-dihydrooxazole was prepared according



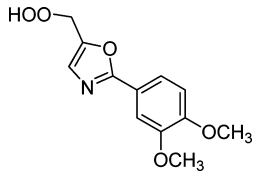
to GP 3. Compound **5n** (0.20 g, 0.98 mmol) and PPh_3AuNTf_2 (14 mg, 2 mol %) were employed. The reaction was stirred at 35 °C during 48 h. Flash chromatography on silica gel (PE/EA, 2:1) delivered 0.18 g (0.88 mmol, 90%) of **6n** as a light yellow solid. R_f = 0.44 (petroleum ether/ethyl acetate 2:1). Mp: 124.2−125.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.82 (dd, J = 2.0, 1.2 Hz, 1H), 8.37 (ddd, J = 8.0, 2.0, 1.2 Hz, 1H), 8.32 (dt, J = 8.0, 1.3 Hz, 1H), 7.65 (t, J = 8.0 Hz, 1H), 4.89 (q, J = 2.8 Hz, 1H), 4.70 (t, J = 2.8 Hz, 2H), 4.44 (q, J = 2.8, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 161.8 (s), 158.4 (s), 149.2 (s), 133.6 (s), 129.7 (s), 128.6 (s), 126.3 (s), 123.1 (s), 84.9 (s), 57.9 (s); IR (neat): $\tilde{\nu}$ = 1532, 1656, 1697, 2939 cm^{-1}. MS (70 eV): m/z 204 (49) [M$^+$], 176 (61) [M$^+$ − CO], 162 (100) [M$^+$ − $C_2H_2O^\bullet$]. HRMS (EI (+), 70 eV): [$C_{10}H_8N_2O_3$]$^+$ calcd 204.0535, found 204.0557.

2-(3,5-Dinitrophenyl)-5-methylene-4,5-dihydrooxazole (6o). 2-(3,5-Dinitrophenyl)-5-methylene-4,5-dihydrooxazole was prepared



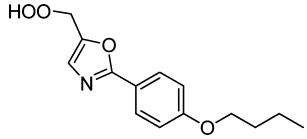
according to GP 3. Compound **5o** (0.28 g, 1.12 mmol) and PPh_3-$AuNTf_2$ (16 mg, 2 mol %) were employed (reaction time 12 h). Flash chromatography on silica gel (PE/EA, 3:1) delivered 0.23 g (0.924 mmol, 82.5%) of **6o** as a light yellow solid. R_f = 0.42 (petroleum ether/ethyl acetate 3:1). Mp: 131.2−132.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.18 (t, J = 2.0 Hz, 1H), 9.12 (d, J = 2.0 Hz, 2H), 4.96 (q, J = 2.8 Hz, 1H), 4.76 (t, J = 2.8 Hz, 2H), 4.51 (q, J = 2.8, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 160.1 (s), 157.9 (s), 148.7 (s), 130.5 (s, 2C), 127.9 (s, 2C), 121.2 (s), 86.0 (s), 58.1 (s). IR (neat): $\tilde{\nu}$ = 1541, 1653, 1674, 3091 cm^{-1}. MS (70 eV): m/z 249 (52) [M$^+$], 221 (74) [M$^+$ − CO], 207 (100) [M$^+$ − $C_2H_2O^\bullet$]. HRMS (EI (+), 70 eV): [$C_{10}H_7N_3O_5$]$^+$ calcd 249.0386, found 249.0377.

2-(3,4-Dimethoxyphenyl)-5-(hydroperoxymethyl)oxazole (7a). 2-(3,4-Dimethoxyphenyl)-5-(hydroperoxymethyl)oxazole was obtained according to GP 4 (reaction time 25 h). Dihydrooxazole (10.95 mg, 0.05 mmol) and 0.1 mL of THF were employed. Flash chromatography on silica gel (PE/EA, 1:1) delivered 10.0 mg (0.046 mmol, 92%) of **7a** as a white solid. R_f = 0.1 (petroleum ether/ethyl acetate 1:1). Mp: 118.0−118.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.78 (s, OOH), 7.37 (dd, J = 8.9, 1.9 Hz, 1H), 7.36



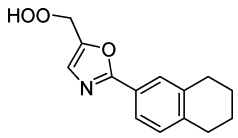
(d, J = 1.9 Hz, 1H), 7.08 (s, 1H), 6.82 (d, J = 8.9 Hz, 1H), 4.99 (s, 2H), 3.92 (s, 3H), 3.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 163.3 (s), 151.4 (s), 149.1 (s), 147.0 (s), 128.8 (s), 120.0 (s), 119.3 (s), 110.9 (s), 109.2 (s), 68.4 (s), 56.2 (s), 56.1 (s). IR (neat): $\tilde{\nu}$ = 1467, 1508, 1611, 2838, 2937, 3425 cm^{-1}. MS (70 eV): m/z 251 (1) [M$^+$], 233 (100) [M$^+$ − $H_2O^\bullet$], 204 (52) [M$^+$ − $CH_3O_2^\bullet$]. HRMS (EI (+), 70 eV): [$C_{12}H_{13}NO_5$]$^+$ calcd 251.0794, found 251.0810.

2-(4-Butoxyphenyl)-5-(hydroperoxymethyl)oxazole (7b).



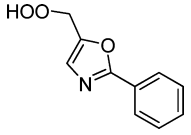
2-(4-Butoxyphenyl)-5-(hydroperoxymethyl)oxazole was obtained according to GP 4 (reaction time 30 h). Dihydrooxazole (5.78 mg, 0.025 mmol) and 0.05 mL of THF were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 5.50 mg (0.024 mmol, 96%) of **7b** as a white solid. R_f = 0.16 (petroleum ether/ehyl acetate 2:1). Mp: −119.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.75 (s, OOH), 7.72 (dd, J = 9.3, 2.3 Hz, 2H), 7.04 (s, 1H), 6.86 (dd, J = 9.3, 2.3 Hz, 2H), 4.96 (s, 2H), 4.01 (t, J = 6.5 Hz, 2H), 1.80 (qu, J = 6.5 Hz, 2H), 1.52 (qt, J = 7.4, 6.5 Hz, 2H), 1.00 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.6 (s), 161.3 (s), 145.8 (s), 128.4 (s), 128.2 (s, 2C), 118.9 (s), 114.6 (s, 2C), 68.2 (s), 67.9 (s), 31.2 (s), 19.2 (s), 13.8 (s). IR (neat): $\tilde{\nu}$ = 1497, 1611, 2872, 2933, 2956, 3131, 3437 cm^{-1}. MS (70 eV): m/z 263 (2) [M$^+$], 245 (61) [M$^+$ − $H_2O^\bullet$], 189 (85) [$C_{10}H_7NO_3^+$], 160 (100) [$C_9H_6NO_2^+$]. HRMS (FAB (+), NBA): [$C_{14}H_{17}NO_4$ + H]$^+$ calcd 264.1236, found 264.1225.

5-(Hydroperoxymethyl)-2-(5,6,7,8-tetrahydronaphthalen-2-yl)oxazole (7c).



5-(Hydroperoxymethyl)-2-(5,6,7,8-tetrahydronaphthalen-2-yl)oxazole was obtained according to GP 4 (reaction time 36 h). Dihydrooxazole (63.9 mg, 0.30 mmol) and 0.6 mL of THF were employed. Flash chromatography on silica gel (PE/EA, 3:1) delivered 60.0 mg (0.24 mmol, 80%) of **7c** as a viscous colorless oil. R_f = 0.24 (petroleum ether/ethyl acetate 3:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.78 (s, OOH), 7.60 (d, J = 8.3 Hz, 1H), 7.55 (s, 1H), 7.11 (s, 1H), 7.09 (d, J = 8.3 Hz, 1H), 5.00 (s, 2H), 2.77 (t, J = 6.5 Hz, 4H), 1.81 (qu, J = 6.5 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 163.1 (s), 146.8 (s), 140.4 (s), 137.6 (s), 129.5 (s), 128.7 (s), 127.2 (s), 123.7 (s), 123.6 (s), 68.3 (s), 29.5 (s, 2C). 23.0 (s, 2C). IR (neat): $\tilde{\nu}$ = 1484, 1549, 1682, 2932 cm^{-1}. MS (70 eV): m/z 245 (10) [M$^+$], 228 (15) [M$^+$ − OH$^\bullet$], 229 (100) [M$^+$ − H_2O], 198 (44) [M$^+$ − $CH_3O_2^\bullet$], 170 (41) [$C_{12}H_{12}N^\bullet$]. HRMS (EI (+), 70 eV): [$C_{14}H_{15}NO_3$]$^+$ calcd 245.1052, found 245.1039.

5-(Hydroperoxymethyl)-2-phenyloxazole (7d).



5-(Hydroperoxymethyl)-2-phenyloxazole was obtained according to GP 4 (reaction time 48 h). Dihydrooxazole (79.53 mg, 0.50 mmol) and 1.0 mL of THF were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 78.0 mg (0.41 mmol, 82%) of **7d** as a white

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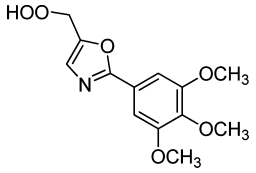
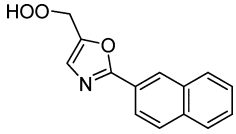
solid. R_f = 0.34 (petroleum ether/ethyl acetate 2:1). Mp: 87.0–88.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.81 (s, OOH), 7.84 (dd, J = 8.2, 1.5 Hz, 2H), 7.40 (m, 3H), 7.14 (s, 1H), 5.00 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.4 (s), 147.5 (s), 130.9 (s), 128.8 (s, 2C), 128.6 (s), 126.5 (s, 2C), 126.3 (s), 68.2 (s). IR (neat): $\tilde{\nu}$ = 1347, 1449, 1483, 1548, 2837, 2938, 3139 cm^{-1}. MS (70 eV): m/z 191 (14) [M^+], 174 (10) [$M^+ - OH^\bullet$], 173 (68) [$M^+ - H_2O$], 158 (91) [$M^+ - HO_2$], 144 (100) [$M^+ - CH_3O_2^\bullet$]. HRMS (EI (+), 70 eV): [$C_{10}H_9NO_3$]$^+$ calcd 191.0582, found 191.0570.

5-(Hydroperoxymethyl)-2-(3,4,5-trimethoxyphenyl)oxazole (7e). 5-(Hydroperoxymethyl)-2-(3,4,5-trimethoxyphenyl)oxazole was



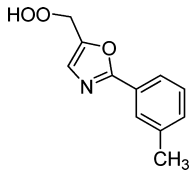
obtained according to GP 4 (reaction time 52 h). Dihydrooxazole (12.46 mg, 0.05 mmol) and 0.1 mL of THF were employed. Flash chromatography on silica gel (PE/EA, 1:1) delivered 12.0 mg (0.043 mmol, 86%) **7e** as a white solid. R_f = 0.22 (petroleum ether/ethyl acetate 1:1). Mp: 156.5–157.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.22 (s, OOH), 7.31 (s, 2H), 7.26 (s, 1H), 5.01 (s, 2H), 3.92 (s, 6H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 161.7 (s), 154.8 (s, 2C), 149.1 (s), 140.2 (s), 129.6 (s), 122.9 (s), 104.5 (s, 2C), 68.5 (s), 60.7 (s), 56.6 (s, 2C). IR (neat): $\tilde{\nu}$ = 1548, 1590, 2948, 3123, 3429 cm^{-1}. MS (70 eV): m/z 281 (2) [M^+], 266 (6)[$M^+ - CH_3^\bullet$], 264 (17) [$M^+ - OH^\bullet$], 263 (100) [$M^+ - H_2O$], 248 (35) [$M^+ - H_2O_2$]. HRMS (EI (+), 70 eV): [$C_{13}H_{15}NO_6$]$^+$ calcd 281.0899, found 281.0897.

5-(Hydroperoxymethyl)-2-(naphthalen-2-yl)oxazole (7f).



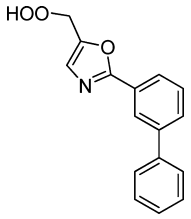
5-(Hydroperoxymethyl)-2-(naphthalen-2-yl)oxazole was obtained according to GP 4 (reaction time 60 h). Dihydrooxazole (10.45 mg, 0.05 mmol) and 0.1 mL of THF were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 25 mg (0.04 mmol, 80%) of **7f** as a white solid. Crystals suitable for X-ray crystal structure analysis could be obtained.[14] R_f = 0.2 (petroleum ether/ethyl acetate 2:1). Mp: 113.0–114.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.74 (s, OOH), 8.29 (s, 1H), 7.99 (dd, J = 8.6, 1.5 Hz, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 1H), 7.54 (td, J = 8.4, 1.1 Hz, 1H), 7.47 (td, J = 8.4, 1.2 Hz, 1H), 7.23 (s, 1H), 5.07 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 163.0 (s), 162.7 (s), 147.4 (s), 133.5 (s), 132.9 (s), 129.1 (s), 128.8 (s), 128.6 (s), 127.8 (s), 127.5 (s), 126.7 (s), 123.9 (s), 123.2 (s), 68.4 (s). IR (neat): $\tilde{\nu}$ = 1507, 1538, 1632, 3443 cm^{-1}. MS (70 eV): m/z 241 (8) [M^+], 223 (100) [$M^+ - H_2O^\bullet$], 194 (76) [$M^+ - CH_3O_2^\bullet$]. HRMS (EI (+), 70 eV): [$C_{14}H_{11}NO_3$]$^+$ calcd 241.0739, found 241.0728.

5-(Hydroperoxymethyl)-2-(*m*-tolyl)oxazole (7g).



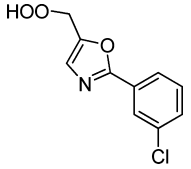
5-(Hydroperoxymethyl)-2-(*m*-tolyl)oxazole was obtained according to GP 4 (reaction time 60 h). Dihydrooxazole (51.9 mg, 0.3 mmol) and 0.6 mL of THF were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 49.0 mg (0.24 mmol, 80%) of **7g** as a pale yellow viscous oil. R_f = 0.26 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.80 (s, OOH), 7.66 (dt, J = 7.6, 1.5 Hz, 1H), 7.61 (s, 1H), 7.26 (m, 2H), 7.11 (s, 1H), 4.99 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.7 (s), 147.4 (s), 138.6 (s), 131.7 (s), 128.8 (s, 2C), 127.1 (s), 126.4 (s), 123.8 (s), 68.4 (s), 21.4 (s). IR (neat): $\tilde{\nu}$ = 1527, 1544, 2928, 2959, 3421 cm^{-1}. MS (70 eV): m/z 205 (2) [M^+], 187 (68) [$M^+ - H_2O$], 158 (90) [$M^+ - CH_3O_2$*], 130 (100) [$M^+ - C_2H_3O_3$*]. HRMS (EI (+), 70 eV): [$C_{11}H_{11}NO_3$]$^+$ calcd 205.0739, found 205.0741.

2-((1,1′-Biphenyl)-3-yl)-5-(hydroperoxymethyl)oxazole (7h).



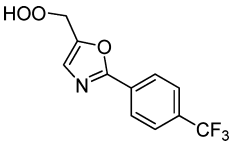
2-((1,1′-Biphenyl)-3-yl)-5-(hydroperoxymethyl)oxazole was obtained according to GP 4 (reaction time 60 h). Dihydrooxazole (58.8 mg, 0.25 mmol) and 0.5 mL of THF were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 43.0 mg (0.16 mmol, 64%) of **7h** as a viscous oil. R_f = 0.32 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.83 (s, OOH), 8.05 (t, J = 1.7 Hz, 1H), 7.78 (dt, J = 7.7, 1.7 Hz, 1H), 7.54 (m, 3H), 7.42 (m, 4H), 7.15 (s, 1H), 5.02 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.5 (s), 147.7 (s), 141.7 (s), 140.1 (s), 129.5 (s), 129.3 (s), 129.0 (s, 2C), 128.9 (s), 127.9 (s), 127.2 (s, 2C), 127.0 (s), 125.3 (s), 125.1 (s), 68.2 (s). IR (neat): $\tilde{\nu}$ = 1457, 1477, 1542, 1684, 3160 cm^{-1}. MS (70 eV): m/z 267 (5) [M^+], 250 (20) [$M^+ - OH^\bullet$], 249 (100) [$M^+ - H_2O$], 220 (84) [$M^+ - CH_3O_2^\bullet$], 192 (94) [$C_{14}H_{10}N^\bullet$]. HRMS (EI (+), 70 eV): [$C_{16}H_{13}NO_3$]$^+$ calcd 267.0895, found 267.0871.

2-(3-Chlorophenyl)-5-(hydroperoxymethyl)oxazole (7i).



2-(3-Chlorophenyl)-5-(hydroperoxymethyl)oxazole was obtained according to GP 4 (reaction time 64 h). Dihydrooxazole (48.38 mg, 0.25 mmol) and 0.5 mL of THF were employed. Flash chromatography on silica gel (PE/EA, 3:1) delivered 40.0 mg (0.18 mmol, 72%)of **7i** as a white solid. R_f = 0.24 (petroleum ether/ethyl acetate 3:1). Mp: 121.8–122.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.95 (s, OOH), 7.81 (t, J = 1.5 Hz, 1H), 7.79 (dt, J = 8.1, 1.5 Hz, 1H), 7.43 (dt, J = 8.1, 1.5 Hz, 1H), 7.36 (t, J = 8.1 Hz, 1H), 7.16 (s, 1H), 5.02 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 161.2 (s), 148.0 (s), 135.1 (s), 131.0 (s), 130.3 (s), 129.1 (s), 128.2 (s), 126.6 (s), 124.6 (s), 68.3 (s). IR (neat): $\tilde{\nu}$ = 1434, 1480, 1541, 1600, 3431 cm^{-1}. MS (70 eV): m/z 225 (3) [M^+], 208 (10) [$M^+ - OH^\bullet$], 207 (71) [$M^+ - H_2O$], 178 (100) [$M^+ - CH_3O_2^\bullet$], 150 (87) [C_8H_5ClN]$^+$. HRMS (EI (+), 70 eV): [$C_{10}H_8ClNO_3$]$^+$ calcd 225.0193, found 225.0167.

5-(Hydroperoxymethyl)-2-(4-(trifluoromethyl)phenyl)-oxazole (7j).



5-(Hydroperoxymethyl)-2-(4-(trifluoromethyl)phenyl)oxazole was obtained according to GP 4 (reaction time 66 h). Dihydrooxazole (56.75 mg, 0.25 mmol) and 0.5 mL of THF were employed. Flash chromatography on silica gel (PE/EA, 1:1) delivered 60.0 mg (0.23 mmol, 92%) of **7j** as a white solid. R_f = 0.22 (petroleum ether/ethyl acetate 1:1). Mp: 87.2–87.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 10.0 (s, OOH), 7.95 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.20 (s, 1H), 5.04 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 160.8 (s), 148.4 (s), 132.5 (s), 131.7 (q, $^1J_{C,F}$ =246.5 Hz), 129.0 (s), 126.6 (s, 2C), 125.8 (q, $^3J_{C,F}$ = 3.6 Hz, 2C), 121.7 (s), 68.1 (s). IR (neat): $\tilde{\nu}$ = 1330, 1554, 2925, 3431 cm^{-1}. MS (70 eV): m/z 259 (3)

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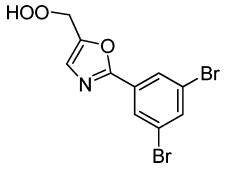
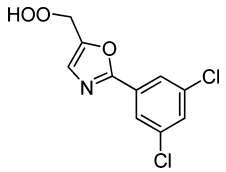
[M+], 242 (5) [M+ − OH•], 241 (27) [M+ − H_2O], 212 (53) [M+ − CH_3O_2•], 184 (100) [$C_9H_5F_3N$•]. HRMS (EI (+), 70 eV): [$C_{11}H_8F_3NO_3$]+ calcd 259.0456, found 259.0453.

2-(3,5-Dibromophenyl)-5-(hydroperoxymethyl)oxazole (7k).



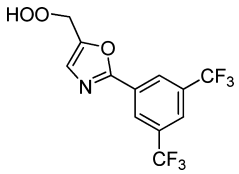
2-(3,5-Dibromophenyl)-5-(hydroperoxymethyl)oxazole was obtained according to GP 4 (reaction time 104 h). Dihydrooxazole (47.6 mg, 0.15 mmol) and 0.3 mL of THF were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 40.0 mg (0.11 mmol, 73%) of **7k** as a white solid. R_f = 0.58 (petroleum ether/ethyl acetate 2:1). Mp: 144.2−146.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.11 (s, OOH), 8.04 (d, J = 1.8 Hz, 2H), 7.75 (t, J = 1.8 Hz, 1H), 7.22 (s, 1H), 5.05 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 159.6 (s), 148.3 (s), 136.1 (s), 129.7 (s), 129.2 (s), 128.0 (s, 2C), 123.4 (s, 2C), 68.1 (s). IR (neat): $\tilde{\nu}$ = 1434, 1535, 1562, 1591, 2848, 3432 cm^{-1}. MS (70 eV): m/z 349 (12) [M+], 332 (11) [M+ − OH•], 331 (80) [M+ − H_2O], 316 (72) [M+ − HO_2], 302 (100) [M+ − CH_3O_2•]. HRMS (EI (+), 70 eV): [$C_{10}H_7{}^{81}Br_2NO_3$]+ calcd 350.8752, found 350.8747.

2-(3,5-Dichlorophenyl)-5-(hydroperoxymethyl)oxazole (7l).



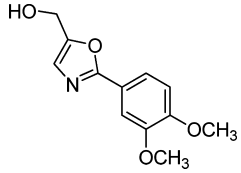
2-(3,5-Dichlorophenyl)-5-(hydroperoxymethyl)oxazole was obtained according to GP 4 (reaction time 168 h). Dihydrooxazole (68.4 mg, 0.30 mmol) and 0.6 mL of THF were employed. Flash chromatography on silica gel (PE/EA, 3:1) delivered 62.0 mg (0.24 mmol, 80%) of **7l** as a white solid. R_f = 0.46 (petroleum ether/ethyl acetate 3:1). Mp: 133.7−134.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.22 (s, OOH), 7.83 (d, J = 1.9 Hz, 2H), 7.44 (t, J = 1.9 Hz, 1H), 7.22 (s, 1H), 5.04 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 159.9 (s), 148.2 (s), 135.7 (s, 2C), 130.6 (s), 129.3 (s), 129.2 (s), 124.7 (s, 2C), 68.1 (s). IR (neat): $\tilde{\nu}$ = 1442, 1538, 1572, 1594, 2935 cm^{-1}. MS (70 eV): m/z 259 (11) [M+], 242 (4) [M+ − OH•], 241 (28) [M+ − H_2O], 226 (100) [M+ − HO_2•], 212 (50) [M+ − CH_3O_2•], 184 (63) [$C_8H_4Cl_2N$]. HRMS (EI (+), 70 eV): [$C_{10}H_7Cl_2NO_3$]+ calcd 258.9803, found 258.9792.

2-(3,5-Bis(trifluoromethyl)phenyl)-5-(hydroperoxymethyl)-oxazole (7m).



2-(3,5-Bis(trifluoromethyl)phenyl)-5-(hydroperoxymethyl)oxazole was obtained according to GP 4 (reaction time 192 h, 8 days). Dihydrooxazole (88.5 mg, 0.3 mmol) and 0.6 mL of THF were employed. Flash chromatography on silica gel (PE/EA, 3:1) delivered 37.0 mg (0.11 mmol, 37%) of **7m** as a white solid. Crystals suitable for X-ray crystal structure analysis could be obtained.[14] R_f = 0.48 (petroleum ether/ethyl acetate 3:1). Mp: 75.5−77.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.96 (s, OOH), 8.44 (s, 2H), 7.95 (s, 1H), 7.31 (s, 1H), 5.09 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 159.6 (s), 148.7 (s), 132.6 (q, $^2J_{C,F}$ = 34.1 Hz, 2C), 129.5 (s), 128.8 (s), 126.4 (q, $^3J_{C,F}$ =3.8 Hz, 2C), 123.9 (hept, $^3J_{C,F}$ = 3.8 Hz), 122.9 (q, $^1J_{C,F}$ = 272.9 Hz, 2C), 68.1 (s). IR (neat): $\tilde{\nu}$ = 1336, 1389, 1450, 1550, 3221 cm^{-1}. MS (70 eV): m/z 327 (6) [M+], 310 (5) [M+ − OH•], 309 (24) [M+ − H_2O], 294 (100) [M+ − HO_2], 280 (39) [M+ − CH_3O_2•], 252 (83) [$C_{10}H_4F_6N$•]. HRMS (EI (+), 70 eV): [$C_{12}H_7F_6NO_3$]+ calcd 327.0330, found 327.0316.

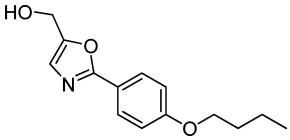
2-(3,4-Dimethoxyphenyl)-5-(hydroxymethyl)oxazole (8a).



2-(3,4-Dimethoxyphenyl)-5-(hydroxymethyl)oxazole was obtained according to GP 5. Compound **7a** (20 mg, 0.08 mmol), $NaBH_4$ (4.5 mg, 0.12 mmol), and MeOH (5 mL) were employed. Flash chromatography on silica gel (PE/EA, 1:2) delivered 15 mg (0.065 mmol, 81%) of **8a** as a white solid. Crystals suitable for X-ray crystal structure analysis could be obtained.[14]

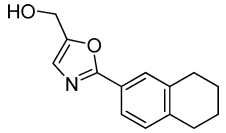
R_f = 0.11 (petroleum ether/ethyl acetate 1:2); mp 110.0−111.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.61 (dd, J = 8.4, 1.9 Hz, 1H), 7.54 (d, J = 1.9 Hz, 1H), 7.05 (s, 1H), 6.92 (d, J = 8.4 Hz, 1H), 4.73 (s, 2H), 3.93 (s, 3H), 3.96 (s, 3H), 2.28 (s, OH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.3 (s), 151.2 (s), 150.5 (s), 149.3 (s), 126.0 (s), 120.3 (s), 119.8 (s), 111.1 (s), 109.2 (s), 56.2 (s), 56.1 (s), 55.4 (s); IR (neat): $\tilde{\nu}$ = 1466, 1501, 1611, 2838, 2937, 3258, 3428 cm^{-1}; MS (70 eV): m/z 235 (100) [M+], 218 (25) [M+−OH•], 204 (21) [M+-CH_3O•]; HRMS (EI (+), 70 eV): [$C_{12}H_{13}NO_4$]+: calcd 235.0845, found 235.0861.

2-(4-butoxyphenyl)-5-(hydroxymethyl)oxazole 8b:



2-(4-butoxyphenyl)-5-(hydroxymethyl)oxazole was obtained according to GP 5. 40 mg (0.15 mmol) of **7b**, 8.5 mg (0.23 mmol) of $NaBH_4$ and 5 mL of MeOH were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 30 mg (0.12 mmol, 80%) **8b** as a white solid. Crystals suitable for X-ray crystal structure analysis could be obtained.[14] R_f = 0.1 (petroleum ether/ethyl acetate 2:1). Mp: 93.6−94.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.95 (dd, J = 9.3, 2.4 Hz, 2H), 7.05 (s, 1H), 6.94 (dd, J = 9.3, 2.4 Hz, 2H), 4.72 (s, 2H), 4.01 (t, J = 6.5 Hz, 2H), 2.07 (s, OH), 1.79 (qu, J = 6.5 Hz, 2H), 1.51 (qt, J = 7.4, 6.5 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.5 (s), 161.2 (s), 150.3 (s), 128.2 (s, 2C), 126.1 (s), 120.0 (s), 114.8 (s, 2C), 68.0 (s), 55.5 (s), 31.4 (s), 19.4 (s), 14.0 (s). IR (neat): $\tilde{\nu}$ = 1498, 1611, 2866, 2928, 2957, 3321 cm^{-1}. MS (70 eV): m/z 247 (89) [M+], 191 (100) [M+ − C_4H_8•], 160 (56) [$C_9H_6NO_2$+]. HRMS (EI (+), 70 eV): [$C_{14}H_{17}NO_3$]+ calcd 247.1208, found 247.1212.

2-(5,6,7,8-Tetrahydronaphthalen-2-yl)-5-(hydroxymethyl)-oxazole (8c).



2-(5,6,7,8-Tetrahydronaphthalen-2-yl)-5-(hydroxymethyl)oxazole was obtained according to GP 5. compound **7c** (20 mg, 0.082 mmol), $NaBH_4$ (4.6 mg, 0.12 mmol), and MeOH (5 mL) were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 15 mg (0.066 mmol, 80%) of **8c** as a viscous oil. R_f = 0.18 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.75 (s, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.14 (d, J = 7.8 Hz, 1H), 7.08 (s, 1H), 4.73 (s, 2H), 2.81 (m, 4H), 1.82 (m, 4H), 1.74 (s, OH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.6 (s), 150.3 (s), 140.2 (s), 137.6 (s), 129.6 (s), 127.1 (s), 125.9 (s), 124.5 (s), 123.5 (s), 55.4 (s), 29.5 (s, 2C), 23.0 (s, 2C). IR (neat): $\tilde{\nu}$ = 1496, 1551, 1618, 2854, 2925, 3198, 3413 cm^{-1}. MS (70 eV): m/z 229 (100) [M+], 198 (35) [M+ − CH_3O•], 170 (49) [$C_{12}H_{12}N$•]. HRMS (EI (+), 70 eV): [$C_{14}H_{15}NO_2$]+ calcd 229.1103, found 229.1113.

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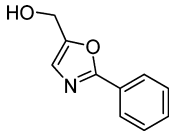
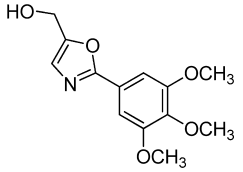
2-Phenyl-5-(hydroxymethyl)oxazole (8d).



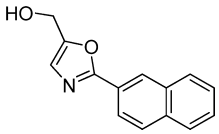
2-Phenyl-5-(hydroxymethyl)oxazole was obtained according to GP 5. Compound **7d** (45 mg (0.24 mmol), $NaBH_4$ (13.36 mg, 0.36 mmol), and MeOH (5 mL) were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 40 mg (0.23 mmol, 96%) of **8d** as a white solid. R_f = 0.20 (petroleum ether/ethyl acetate 2:1). Mp: 74.5–76.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.04 (m, 2H), 7.46 (m, 3H), 7.12 (s, 1H), 4.75 (s, 2H), 1.73 (s, OH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.4 (s), 150.9 (s), 130.7 (s), 128.9 (s, 2C), 127.6 (s), 126.5 (s, 2C), 126.3 (s), 68.2 (s). IR (neat): $\tilde{\nu}$ = 1450, 1483, 1547, 1614, 2852, 3110, 3285 cm^{-1}. MS (70 eV): *m*/*z* 175 (100) [M^+], 144 (67) [$M^+ - CH_3O^\bullet$], 116 (80) [$C_8H_6N^\bullet$]. HRMS (EI (+), 70 eV): $[C_{10}H_9NO_2]^+$ calcd 175.0633, found 175.0653.

2-(3,4,5-Trimethoxyphenyl)-5-(hydroxymethyl)oxazole (8e).



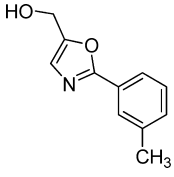
2-(3,4,5-Trimethoxyphenyl)-5-(hydroxymethyl)oxazole was obtained according to GP 5. Compound **7e** (50 mg, 0.18 mmol), $NaBH_4$ (10.2 mg, 0.27 mmol), and MeOH (5 mL) were employed. Flash chromatography on silica gel (PE/EA, 1:2) delivered 40 mg (0.15 mmol, 83%) of **8e** as a white solid. Crystals suitable for X-ray crystal structure analysis could be obtained.[14] R_f = 0.12 (petroleum ether/ethyl acetate 1:2). Mp: 175.6–176.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.24 (s, 2H), 7.08 (s, 1H), 4.73 (d, *J* = 4.6 Hz, 2H), 3.92 (s, 6H), 3.88 (s, 3H), 1.93 (t, *J* = 4.6 Hz, OH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.2 (s), 153.7 (s, 2C), 150.9 (s), 140.4 (s), 126.3 (s), 122.8 (s), 103.8 (s, 2C), 61.1 (s), 56.5 (s, 2C), 55.9 (s). IR (neat): $\tilde{\nu}$ = 1467, 1497, 1594, 2840, 2944, 3190, 3424 cm^{-1}. MS (70 eV): *m*/*z* 265 (100) [M^+], 250 (51) [$M^+ - CH_3^\bullet$], 248 (7) [$M^+ - OH^\bullet$], 206 (18) [$M^+ - C_2H_3O_2^\bullet$]. HRMS (EI (+), 70 eV): $[C_{13}H_{15}NO_5]^+$ calcd 265.0950, found 265.0942.

2-(Naphthalen-2-yl)-5-(hydroxymethyl)oxazole (8f).



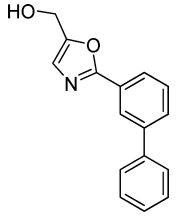
2-(Naphthalen-2-yl)-5-(hydroxymethyl)oxazole was obtained according to GP 5. Compound **7f** (10 mg, 0.04 mmol), $NaBH_4$ (3 mg, 0.06 mmol), and MeOH (2 mL) were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 8 mg (0.035 mmol, 88%) of **8f** as a white solid. R_f = 0.18 (petroleum ether/ethyl acetate 2:1). Mp: 98.6–99.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.53 (s, 1H), 8.11 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 2H), 7.85 (m, 1H), 7.53 (m, 2H), 7.16 (s, 1H), 4.79 (s, 2H), 2.77 (s, OH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.2 (s), 151.0 (s), 134.2 (s), 133.0 (s), 128.8 (s), 128.7 (s), 127.9 (s), 127.4 (s), 126.8 (s), 126.4 (s), 126.2 (s), 124.5 (s), 123.3 (s), 55.4 (s). IR (neat): $\tilde{\nu}$ = 1539, 1613, 1630, 3057, 3431 cm^{-1}. MS (70 eV): *m*/*z* 225 (100) [M^+], 194 (32) [$M^+ - CH_3O^\bullet$], 166 (55) [$C_{12}H_8N^+$]. HRMS (EI (+), 70 eV): $[C_{14}H_{11}NO_2]^+$ calcd 225.0790, found 225.0782.

2-(*m*-Tolyl)-5-(hydroxymethyl)oxazole (8g).



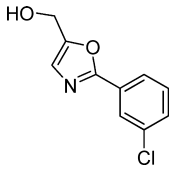
2-(*m*-Tolyl)-5-(hydroxymethyl)oxazole was obtained according to GP 5. Compound **7g** (44 mg, 0.21 mmol), $NaBH_4$ (11.9 mg, 0.32 mmol), and MeOH (5 mL) were employed. Flash chromatography on silica gel (PE/EA, 1:1) delivered 35 mg (0.19 mmol, 90%) of **8g** as a white solid. R_f = 0.16 (petroleum ether/ethyl acetate 1:1). Mp: 86.6–87.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.87 (s, 1H), 7.83 (d, *J* = 7.6, 1.4 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 4.74 (s, 2H), 2.41 (s, 3H), 1.93 (s, OH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.3 (s), 150.7 (s), 138.6 (s), 131.3 (s), 128.7 (s), 127.2 (s), 127.0 (s), 126.0 (s), 123.5 (s), 55.4 (s), 21.3 (s). IR (neat): $\tilde{\nu}$ = 1549, 1611, 2847, 2922, 3101, 3175 cm^{-1}. MS (70 eV): *m*/*z* 189 (84) [M^+], 158 (80) [$M^+ - CH_3O^\bullet$], 130 (100) [$C_9H_8N^\bullet$]. HRMS (EI (+), 70 eV): $[C_{11}H_{11}NO_2]^+$ calcd 189.0790, found 189.0787.

2-((1,1′-Biphenyl)-3-yl)-5-(hydroxymethyl)oxazole (8h).



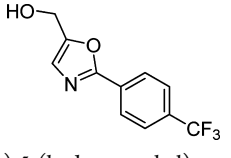
2-((1,1′-Biphenyl)-3-yl)-5-(hydroxymethyl)oxazole was obtained according to GP 5. Compound **7h** (26 mg, 0.10 mmol), $NaBH_4$ (5.7 mg, 0.15 mmol), and MeOH (5 mL) were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 20 mg (0.08 mmol, 80%) of **8h** as a very viscous oil. R_f = 0.35 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.28 (t, *J* = 1.7 Hz, 1H), 8.01 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.68 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.65 (dt, *J* = 7.5, 1.5 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 2H), 7.38 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.13 (s, 1H), 4.76 (s, 2H), 2.14 (s, OH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.1 (s), 150.9 (s), 141.9 (s), 140.2 (s), 129.3 (s), 129.2 (s), 128.9 (s, 2C), 127.7 (s), 127.2 (s, 2C), 126.1 (s), 125.2 (s), 125.1 (s), 55.4 (s, 2C). IR (neat): $\tilde{\nu}$ = 1477, 1543, 3034, 3143, 3210, 3276 cm^{-1}. MS (70 eV): *m*/*z* 251 (100) [M^+], 220 (39) [$M^+ - H_3O^\bullet$], 192 (69) [$C_{14}H_{10}N^\bullet$]. HRMS (EI (+), 70 eV): $[C_{16}H_{13}NO_2]^+$ calcd 251.0946, found 251.0923.

2-(3-Chlorophenyl)-5-(hydroxymethyl)oxazole (8i).



2-(3-Chlorophenyl)-5-(hydroxymethyl)oxazole was obtained according to GP 5. Compound **7i** (27 mg, 0.12 mmol), $NaBH_4$ (6.8 mg, 0.18 mmol), and MeOH (5 mL) were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 23 mg (0.11 mmol, 92%) of **8i** as a white solid. R_f = 0.24 (petroleum ether/ethyl acetate 2:1). Mp: 106.0–107.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.03 (t, *J* = 1.9 Hz, 1H), 7.92 (dt, *J* = 6.8, 1.9 Hz, 1H), 7.41 (m, 2H), 7.13 (s, 1H), 4.75 (s, 2H), 1.98 (s, OH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 160.7 (s), 151.3 (s), 134.9 (s), 130.5 (s), 130.1 (s), 128.9 (s), 126.5 (s), 126.2 (s), 124.4 (s), 55.3 (s). IR (neat): $\tilde{\nu}$ = 1477, 1544, 1601, 2917, 3103, 3222 cm^{-1}. MS (70 eV): *m*/*z* 209 (100) [M^+], 178 (84) [$M^+ - CH_3O^\bullet$], 150 (96) [$C_8H_5ClN^\bullet$]. HRMS (EI (+), 70 eV): $[C_{10}H_8ClNO_2]^+$ calcd 209.0244, found 209.0246.

2-(4-(Trifluoromethyl))-5-(hydroxymethyl)oxazole (8j).



2-(4-(Trifluoromethyl))-5-(hydroxymethyl)oxazole was obtained according to GP 5. Compound **7j** (20 mg, 0.077 mmol), $NaBH_4$ (4.4 mg, 0.12 mmol), and MeOH (5 mL) were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 18 mg (0.074 mmol, 96%) of **8j** as a white solid. R_f = 0.22 (petroleum ether/ethyl acetate 2:1). Mp:

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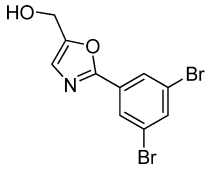
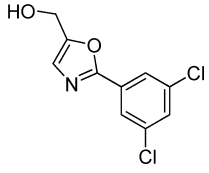
95.7−96.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.16 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.18 (s, 1H), 4.78 (s, 2H), 1.77 (s, OH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 160.8 (s), 148.0 (s), 132.5 (s), 131.7 (q, $^1J_{C,F}$ = 246.5 Hz), 129.0 (s), 126.6 (s, 2C), 125.8 (q, $^3J_{C,F}$ = 3.6 Hz, 2C), 121.7 (s), 55.3 (s). IR (neat): $\tilde{\nu}$ = 1328, 1418, 1554, 1624, 2934, 3273, 3422 cm^{-1}. MS (70 eV): m/z 243 (87) [M$^+$], 212 (55) [M$^+$ − $CH_3O^\bullet$], 184 (100) [$C_9H_5F_3N^\bullet$]. HRMS (EI (+), 70 eV): [$C_{11}H_8F_3NO_2$]$^+$ calcd 243.0507, found 243.0501.

2-(3,5-Dibromophenyl)-5-(hydroxymethyl)oxazole (8k).



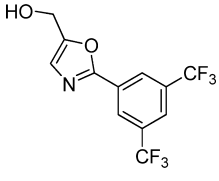
2-(3,5-Dibromophenyl)-5-(hydroxymethyl)oxazole was obtained according to GP 5. Compound **7k** (23 mg, 0.07 mmol), $NaBH_4$ (3.74 mg, 0.1 mmol), and MeOH (2 mL) were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 20 mg (0.06 mmol, 86%) of **8k** as a white solid. R_f = 0.29 (petroleum ether/ethyl acetate 2:1). Mp: 141.4−142.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.13 (d, J = 1.7 Hz, 2H), 7.74 (d, J = 1.7 Hz, 1H), 7.14 (s, 1H), 4.76 (s, 2H), 1.59 (s, OH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 159.0 (s), 151.4 (s), 135.5 (s), 130.1 (s), 127.7 (s, 2C), 126.2 (s), 123.1 (s, 2C), 55.0 (s). IR (neat): $\tilde{\nu}$ = 1262, 1405, 1536, 1590, 1636, 2963, 3421 cm^{-1}. MS (70 eV): m/z 333 (100) [M$^+$], 302 (64) [M$^+$ − $CH_3O^\bullet$], 274 (72) [$C_8H_4Br_2N^\bullet$]. HRMS (EI (+), 70 eV): [$C_{10}H_7{}^{79}Br_2NO_2$]$^+$ calcd 330.8844, found 330.8837.

2-(3,5-Dichlorophenyl)-5-(hydroxymethyl)oxazole (8l).



2-(3,5-Dichlorophenyl)-5-(hydroxymethyl)oxazole was obtained according to GP 5. Compound **7l** (34 mg, 0.13 mmol), $NaBH_4$ (7.38 mg, 0.2 mmol), and MeOH (5 mL) were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 30 mg (0.12 mmol, 92%) of **8l** as a white solid. R_f = 0.40 (petroleum ether/ethyl acetate 2:1). Mp: 115.3−116.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.92 (d, J = 1.8 Hz, 2H), 7.43 (t, J = 1.8 Hz, 1H), 7.14 (s, 1H), 4.76 (s, 2H), 2.03 (s, OH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 159.5 (s), 151.7 (s), 135.7 (s, 2C), 130.3 (s), 129.8 (s), 126.5 (s), 124.7 (s, 2C), 55.3 (s). IR (neat): $\tilde{\nu}$ = 1441, 1541, 1572, 1595, 3081, 3109, 3423 cm^{-1}. MS (70 eV): m/z 243 (86) [M$^+$], 212 (66) [M$^+$ − $CH_3O^\bullet$], 184 (100) [$C_8H_4Cl_2N\bullet$]. HRMS (EI (+), 70 eV): [$C_{10}H_7Cl_2NO_2$]$^+$ calcd 242.9854, found 242.9870.

2-(3,5-Bis(trifluoromethyl)phenyl)-5-(hydroxymethyl)-oxazole (8m).



2-(3,5-Bis(trifluoromethyl)phenyl)-5-(hydroxymethyl)oxazole was obtained according to GP 5. Compound **7m** (20 mg (0.06 mmol), $NaBH_4$ (3.47 mg, 0.09 mmol), and MeOH (2 mL) were employed. Flash chromatography on silica gel (PE/EA, 2:1) delivered 15 mg (0.05 mmol, 83%) of **8m** as a white solid. R_f = 0.33 (petroleum ether/ethyl acetate 2:1). Mp: 80.8−82.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.59 (s, 2H), 7.94 (s, 1H), 7.20 (s, 1H), 4.80 (s, 2H), 2.02 (s, OH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 159.2 (s), 152.4 (s), 132.5 (q, $^2J_{C,F}$ = 34 Hz, 2C), 129.2 (s), 126.7 (s), 126.3 (q, $^3J_{C,F}$ = 3.7 Hz, 2C), 123.7 (hept, $^3J_{C,F}$ = 3.7 Hz), 123.0 (q, $^1J_{C,F}$ = 273 Hz, 2C), 55.3 (s). IR (neat): $\tilde{\nu}$ = 1137, 1312, 1336, 1373, 1453, 1625, 3411 cm^{-1}. MS (70 eV): m/z 311 (58) [M$^+$], 280 (35) [M$^+$ − $CH_3O^\bullet$], 252 (100) [$C_{10}H_4F_6N^\bullet$]. HRMS (EI (+), 70 eV): [$C_{12}H_7F_6NO_2$]$^+$ calcd 311.0381, found 311.0373.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and ^{13}C NMR spectra for compounds **4a−c**, **5a−o**, **6a−o**, **7a−m**, and **8a−m** and X-ray data for compounds **6e**, **7f,m**, and **8a,b,e**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hashmi@hashmi.de.

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