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Spiro[indene-1,4'-oxa-zolidinones] Synthesis via Rh(III)-Catalyzed Coupling of 4-Phenyl-1,3-oxazol-2(3*H*)-ones with Alkynes: A Redox-Neutral Approach

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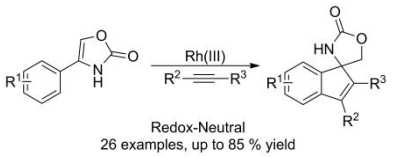
Supporting Information Placeholder

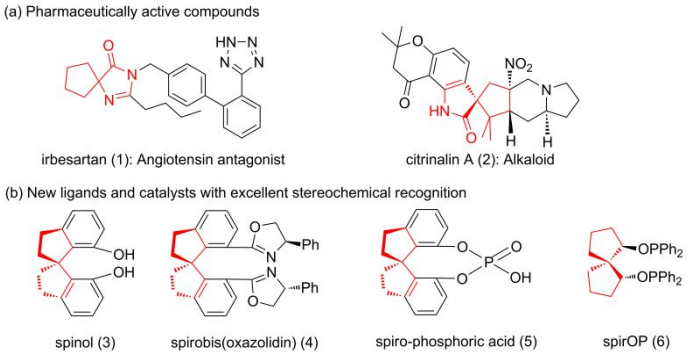


ABSTRACT: Transition metal-catalyzed C-H activation synthesis of heterocyclic spiro[4,4]nonanes has persistently witnessed the use of additional stoichiometric transition metal oxidant when employing C=C bond as the spiro ring closure site. Herein we have addressed the issue by reporting a redox-neutral strategy for spiro[indene-1,4'-oxa-zolidinones] synthesis via Rh(III)-catalyzed coupling of 4-phenyl-1,3-oxazol-2(3*H*)-ones with alkynes. The synthesis features a broad substrate scope and high regiospecificity.

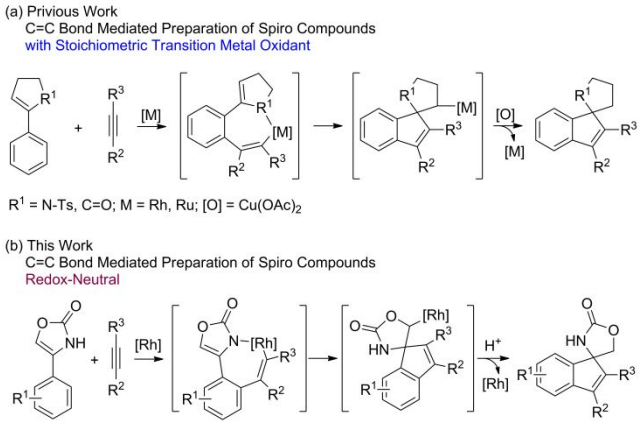
INTRODUCTION

Transition metal-catalyzed C-H functionalization has emerged as an important synthetic tool for building diverse organic compounds.[1] In this regard, an important class of synthetic targets are the ring structures.[2] A typical and substantially explored synthetic strategy involves an acyclic C-H activation directing group and an acyclic coupling partner, enabling the construction of relatively flat rings.[3] With the recent expansion of directing group to the cyclic architecture, the synthesis of spiro compounds has been rendered possible. In particular, heterocyclic spiro[4,4]nonanes have been the targets of intense interest due to the frequent use of these rigid structural scaffolds in pharmaceutically active compounds （Figure 1(a)), new ligands and catalysts（Figure 1(b)).[4]

Figure 1. Some application examples of spiro[4,4]nonanes



Scheme 1. Spiro Ring Formation Mediated by C-H Activation and Migratory Insertion at C=C Bond

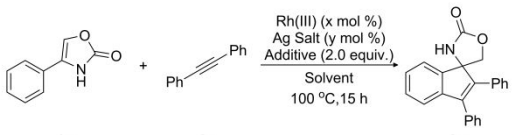


The documented C-H activation methods for heterocyclic spiro[4,4]nonanes can be divided into three categories. The first is the use of C=N bond as both the directing group and the migratory insertion site for spiro ring formation.[5] Due to, presumably, the high degree of polarization for metal-N bond (large difference in the electronegativity values between the metal and nitrogen atoms), facile proto-demetalation can occur and therefore the reaction can proceed in a redox-neutral fashion. The second exploits C=O bond as the directing group and α carbon as the reductive elimination site and spiro ring common atom.[6] The reductive elimination step in every catalytic cycle inevitably requires the use of a stoichiometric quantity of oxidant (e.g., $Cu(OAc)_2$) for converting metal catalyst from the catalytically incompetent low oxidation state back to the catalytically active high oxidation state. The third operates through a migratory insertion step at the C=C bond for the generation of spiro ring.[7] In the demonstrated synthetic protocols, a consistently observed phenomenon is the need for a stoichiometric quantity of $Cu(OAc)_2$. Although the exact role of $Cu(OAc)_2$ has yet to be unraveled, it has been suggested to serve as an oxidant (Scheme 1a). The difficulty for direct achievement of proto-demetalation and redox-neutral catalytic cycle should be caused by the low degree of polarization for metal-C bond (close electronegativity values between the metal and carbon atoms). This can be likened to the case of metal-H bond (when β hydride elimination occurs), for which an implementation of proto-demetalation pathway is extremely challenging (due to the even closer electronegativity values between the metal and hydrogen atoms), and therefore, a stoichiometric quantity of oxidant (e.g., $Cu(OAc)_2$) is generally required. We envisioned that a subtle adjustment of the atomic environment surrounding the C=C bond

could lead to a more polarized metal-C bond and the successful achievement of proto-demetalation process. Herein, we report the redox-neutral synthesis of spiro[indene-1,4'-oxa-zolidinones] via Rh(III)-catalyzed coupling of 4-aryl-1,3-oxazol-2(3*H*)-ones (abbreviated as oxazolones hereafter) and alkynes (Scheme 1b).

We have previously reported the synthesis of 1-aminoisoquinolines via Co(III)-catalyzed coupling of 3-aryl-1,2,4-oxadiazol-5(4*H*)-ones (abbreviated as oxadiazolones hereafter) with alkynes.[8] In that synthetic scenario, after the migratory insertion of alkynes, cyclization occurs at the nitrogen atom through reductive elimination; N-O bond then reacts as an internal oxidant; subsequent decarboxylation, protonation, and tautomerization afford the products. Herein, the replacement of C=N bond in oxadiazolones with C=C bond in oxazolones has completely altered the reaction pathway. The lack of internal oxidant (C-O bond is not sufficiently labile) makes it impossible to reinitiate the catalytic cycle if the reductive elimination cyclization occurs at the nitrogen atom. Instead, an alternative way of migratory insertion cyclization occurs at the carbon atom; this is followed by a proto-demetalation step to furnish the spiro ring products.

Table 1. Optimization of Rection Conditions[a,b]



1a **2a** **3a**

Entry	Rh(III) (x)	Ag Salt (y)	Additive	Solvent	Yield (%)
1	**[RhCp*Cl$_2$]$_2$ (5)**	**AgSbF$_6$ (20)**	**NaOAc**	**HFIP**	**85**
2	RhCp*(MeCN)$_3$(SbF$_6$)$_2$ (10)	--	NaOAc	HFIP	59
3	[Ru(*p*-cymene)Cl$_2$]$_2$ (5)	AgSbF$_6$ (20)	NaOAc	HFIP	33
4	[RuCp*Cl$_2$]$_n$ (5)	AgSbF$_6$ (20)	NaOAc	HFIP	8
5	[RhCp*Cl$_2$]$_2$ (5)	AgPF$_6$ (20)	NaOAc	HFIP	41
6	[RhCp*Cl$_2$]$_2$ (5)	AgOTf (20)	NaOAc	HFIP	32
7	[RhCp*Cl$_2$]$_2$ (5)	AgTFA (20)	NaOAc	HFIP	45
8	[RhCp*Cl$_2$]$_2$ (5)	AgSbF$_6$ (20)	LiOAc	HFIP	16
9	[RhCp*Cl$_2$]$_2$ (5)	AgSbF$_6$ (20)	KOAc	HFIP	56
10	[RhCp*Cl$_2$]$_2$ (5)	AgSbF$_6$ (20)	CsOAc	HFIP	46
11	[RhCp*Cl$_2$]$_2$ (5)	AgSbF$_6$ (20)	NaOAc	MeOH	Trace
12	[RhCp*Cl$_2$]$_2$ (5)	AgSbF$_6$ (20)	NaOAc	DCE	30
13	[RhCp*Cl$_2$]$_2$ (5)	AgSbF$_6$ (20)	NaOAc	MeCN	33
14	[RhCp*Cl$_2$]$_2$ (5)	AgSbF$_6$ (20)	NaOAc	DMF	7
15	[RhCp*Cl$_2$]$_2$ (5)	AgSbF$_6$ (20)	NaOAc	TFE	22

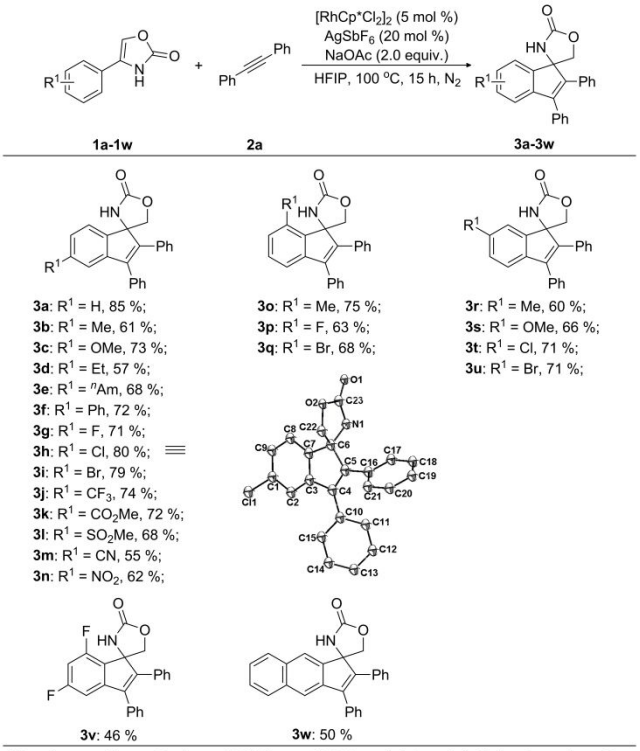
[a]Reaction Conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol, 1.5 equiv.), Solvent (1.5 mL), 100 °C, 15 h, N_2. [b]Isolated yields.

RESULTS AND DISCUSSION

We commenced our investigation by screening the reaction conditions for the coupling of 4-phenyl-1,3-oxazol-2(3*H*)-one (**1a**) with 1,2-diphenyl-acetylene (**2a**) (Table 1, Table S1 in Supporting Information). [RhCp*Cl$_2$]$_2$ was identified to be an effective catalyst precursor for the transformation. When 5 mol % of this catalytic species is combined with 20 mol % chloride abstraction reagent AgSbF$_6$ and 2.0 equiv. base NaOAc, the desired spiro ring product 2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3a**) can be obtained in 85 % yield after reaction at 100 °C in (CF$_3$)$_2$CHOH (HFIP) for 15 h (Table 1, Entry 1). The reaction can proceed directly under [RhCp*Cl$_2$]$_2$ catalysis (without AgSbF$_6$), albeit with a slightly lowered yield (Table S1, Entry 1). A change of the [RhCp*Cl$_2$]$_2$ quantity (2 mol % or 7 mol %) is not beneficial (Table S1, Entries 2,3). The base condition is required as only trace amount of **3a** can be observed under either acidic (HOAc) or neutral (no acid or base additive) conditions (Table S1, Entries 4,5). A

switching to either the cationic catalyst $[RhCp^*(MeCN)_3](SbF_6)_2$ (10 mol %) or the ruthenium catalytic system (5 mol % [Ru(*p*-cymene)$Cl_2]_2$ or $[RuCp^*Cl_2]_n$ / 20 mol % $AgSbF_6$ / 2.0 equiv. NaOAc) leads to an apparent reduction in the product yield (Table 1, Entries 2-4). The change of counterion of the chloride abstraction reagent from SbF_6^- to PF_6^-, OTf^-, or TFA^- exerts a negative impact on the reaction (Table 1, Entries 5-7). The base is also critical as LiOAc, KOAc, CsOAc, AgOAc, $Cu(OAc)_2$, Na_2CO_3, K_2CO_3, and HCOONa are not as effective as NaOAc (Table 1, Entries 8-10; Table S1, Entries 7-10). Reactions in other solvents (MeOH, DCE, MeCN, DMF, TFE, THF, ^{t}BuOH, ^{t}AmOH) all witness a pronounced drop in the product yield (Table 1, Entries 11-15; Table S1, Entries 11-13). No further improvement in the reaction outcome can be made with either the change of reaction temperature (60 °C, 80 °C, 120 °C, Table S1, Entries 14-16) or reaction time (5 h, 10 h, 20 h, Table S1, Entries 17-19).

Scheme 2. Substrate Scope for Oxazolones



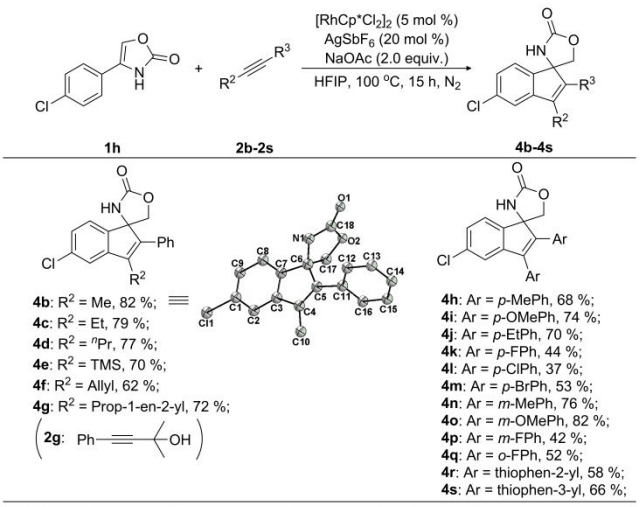
[a]Reaction conditions: 4-Aryloxazol-2(3*H*)-ones (**1**, 0.2 mmol, 1.0 equiv.), Diphenylacetylene (**2a**, 0.3 mmol, 1.5 equiv.), $[RhCp^*Cl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), NaOAc (0.4 mmol, 2.0 equiv.), HFIP (1.5 mL), 100 °C, 15h, N_2. [b]Isolated yield.

With the reaction conditions optimized, we next evaluated the substrate scope with respect to both oxazolones and alkynes (Scheme 2, 3). For oxazolones, a variety of electron-donating (Me, **1b**; OMe, **1c**; Et, **1d**; ^{n}Am, **1e**; Ph, **1f**) and electron-withdrawing (F, **1g**; Cl, **1h**; Br, **1i**; CF_3, **1j**; CO_2Me, **1k**; SO_2Me, **1l**; CN, **1m**; NO_2, **1n**) groups can be tolerated at the *para* position of phenyl ring. The spiro ring structure is unambiguously confirmed from the single-crystal structure of **3h**. The transformation is also tolerant of *ortho* substitution (Me, **1o**; F, **1p**; Br, **1q**); in these spiro ring products, oxazolone ring is orthogonal to the phenyl ring and therefore does not create unfavorable steric effect. For *meta*-substituted substrates (Me, **1r**; OMe, **1s**; Cl, **1t**; Br, **1u**), single regioisomers are formed at the sterically less hindered sites, regardless of the electronic character of the substituent. The di-

substitution (**1v**) is also compatible with the protocol developed herein. The change of phenyl group to naphthyl group leads to a less efficient reaction system (**1w**).

For alkynes reacting with **1h**, phenyl/alkyl unsymmetrical alkynes (Me, **2b**; Et, **2c**; ^{n}Pr, **2d**) can react smoothly with good yields and regioselectivity. Other unsymmetrical alkynes (TMS, **2e**; Allyl, **2f**) can also react smoothly with slightly lower yields. An infrequent used substrate, 2-methyl-4-phenylbut-3-yn-2-ol (**2g**) was also tried and the hydroxyl group has been removed to afford the prop-1-en-2-yl structure (**4g**).[9] The reactions for substituted symmetrical aryl/aryl alkynes are comparable in efficiency to **2a**. Electron-donating groups at the *para* and *meta* position of phenyl ring (*p*-Me, **2h**; *p*-OMe, **2i**; *p*-Et, **2j**; *m*-Me, **2n**; *m*-OMe, **2o**) seem more efficient than electron-withdrawing groups at the *para, meta* and *ortho* position (*p*-F, **2k**; *p*-Cl, **2l**; *p*-Br, **2m**; *m*-F, **2p**; *o*-F, **2q**). Heterocycle-substituted alkynes (thiophen-2-yl, **2r**; thiophen-3-yl, **2s**) are also viable substrates with moderate yields.

Scheme 3. Substrate Scope for Alkynes

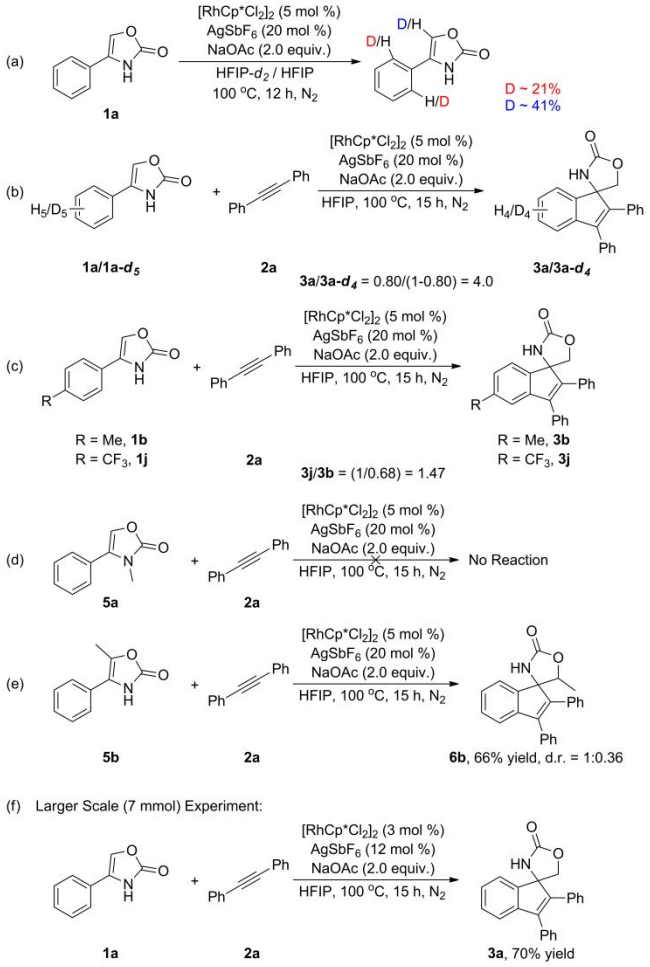


[a]Reaction conditions: 4-(4-chlorophenyl)oxazol-2(3*H*)-one (**1h**, 0.2 mmol, 1.0 equiv.), Alkynes (**2**, 0.3 mmol, 1.5 equiv.), $[RhCp^*Cl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), NaOAc (0.4 mmol, 2.0 equiv.), HFIP (1.5 mL), 100 °C, 15h, N_2. [b]Isolated yield.

With the substrate scope surveyed, we next proceeded to the establishment of reaction mechanism (Scheme 4). A H/D scrambling experiment performed for **1a** under otherwise standard conditions except with the replacement of HFIP with fully deuterated HFIP (HFIP-d_2) shows deuterium labeling on both the phenyl ring (ortho site with respect to the oxazolone group) and alkene group (Scheme 4a), supporting the ability to initiate the reaction by Rh(III)-catalyzed, oxazolone-directed ortho C-H activation on phenyl ring. Kinetic isotope effect (KIE) measurement on a reaction between **1a**/**1a**-d_5 and **2a** shows a high value of 4.0 (Scheme 4b), consistent with a turnover-limiting C-H activation step. An intermolecular competition reaction between **1b**/**1j** and **2a** slightly favors electron-deficient **1j** (Scheme 4c), suggesting a concerted metalation-deprotonation (CMD) C-H activation pathway. Further control experiments show that even deuteration can occur on both the phenyl ring and alkene group, only C-H activation on the phenyl ring proceeds to the completion of spiro ring production. Thus, *N*-methyl-4-phenyl-1,3-oxazol-2(3*H*)-one (**5a**) and 5-methyl-4-phenyl-1,3-oxazol-2(3*H*)-one (**5b**) are subjected to reaction with **2a**. No reaction is identified for **5a** (Scheme 4d) and 66% product yield is achieved for the reaction for **5b** (Scheme 4e). This observation also suggests the necessity of initial N-

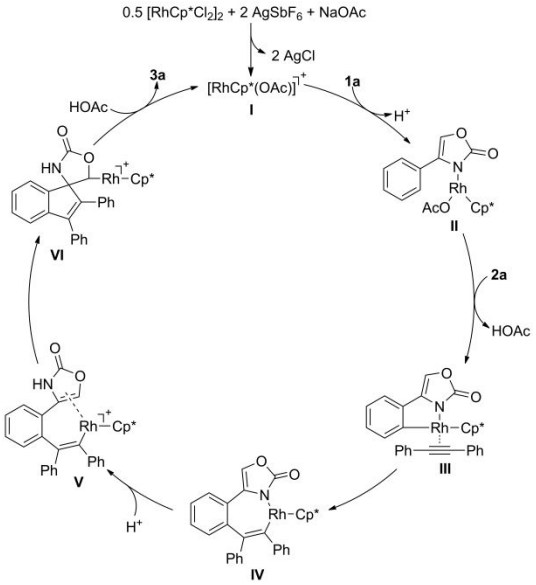
H deprotonation before the formation of Rh-N bond. A larger scale experiment is carried out between **1a** (1.13 g, 7.0 mmol) and **1b** under the optimized reaction conditions except slightly reduced amount of catalyst (3 mol % [Rh] and 12 mol % $AgSbF_6$). The product **3a** is obtained in 70 % yield (1.66 g) to demonstrate the practical utility of our method as a synthetic tool (Scheme 4f).

Scheme 4. Mechanistic Studies



Taken together, a two consecutive migratory insertion mechanism is proposed based on the above experimental evidence (Scheme 5): catalytically active $[RhCp^*(OAc)]^+$ (**I**) is first generated in situ from $[RhCp^*Cl_2]_2$, $AgSbF_6$, and NaOAc; **II** is then produced through N-H deprotonation of **1a** and Rh(III) coordination; *ortho* C-H activation occurs with the simultaneous formation of rhodacycle **III** (coordination of **2a** might assist the process); migratory insertion of alkyne generates **IV**; reprotonation of *N*- switches Rh(III) coordination to the alkene group as **V**; migratory insertion of alkene group furnishes **VI**; proto-demetalation generates product **3a** and releases **I** for the next catalytic cycle.[10]

Scheme 5. Proposed Reaction Pathway



CONCLUSION

In summary, we have developed a redox-neutral strategy for the synthesis of spiro[indene-1,4'-oxa-zolidinones] via Rh(III)-catalyzed coupling of 4-phenyl-1,3-oxazol-2(3*H*)-ones with alkynes. The strategy has fully addressed the stoich-iometric transition metal salt issue previously encountered when using an alkene group as the spiro ring closure site. The reaction features a broad substrate scope and high regio-specificity.

EXPERIMENTAL SECTION

All reactions are carried out under a dry nitrogen atmosphere using Schlenk techniques. The heat sources for reactions are ice-water bath (0 ^{o}C) and oil bath (higher than room temperature). All commercial reagents are used without additional purification, unless otherwise stated. Anhydrous solvents are purchased from commercial sources and transferred under an argon atmosphere. Alkynes are purchased from commercial sources or synthesized according to the procedure reported by Mikami and Lautens.[11] Analytical thin layer chromatography (TLC) is performed on precoated silica gel 60 GF254 plates. Flash column chromatography is performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC is achieved by use of UV light (254 nm) or iodine. NMR spectra are recorded on a Bruker DPX 400 or 500 spectrometer at 400 or 500 MHz for ^{1}H NMR, 101 or 126 MHz for ^{13}C NMR in $CDCl_3$ or DMSO-d_6 with tetramethylsilane (TMS) as an internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectrometric (HRMS) data are obtained using Thermo Fisher Scientific LTQ FTICR-MS, Waters Micromass GCT Premier, or Thermo Scientific Q Extractive HF Orbitrap-FTMS. Column conditions are reported in the experimental section below. Absolute configuration of product is determined by single-crystal X-ray analysis.

General Procedure for the Synthesis of Oxazolones.[12] To a stirred solution of the corresponding α-aryl ketones (32 mmol, 1.0 equiv.) and powdered potassium hydroxide (9.88 g, 176 mmol, 5.5 equiv.) in 80 mL methanol (MeOH) is added iodobenzene diacetate (11.34 g, 35.2 mmol, 1.1 equiv.) slowly at 0 °C. The reaction mixture is kept at room temperature (r.t.) until TLC indicates the total consumption of the α-aryl ketones. Then the whole reaction mixture is concentrated. The residue is shaken with water and ethyl acetate (EA). The combined organic layer is evaporated under reduced pressure. The residue is dissolved in a mixture of 20 mL MeOH and 20 mL 2 M aqueous hydrochloric acid and then stirred overnight at room temperature. If precipitate appears, the solid is filtered and washed with petroleum ether (PE). If oil appears, it can be extracted by EA and purified by flash column chromatography on silica gel with PE/EA (8:1-6:1) as the eluent. The obtained 1-aryl-2-hydroxypropan-1-ones (**1'**) are used directly for the next step without further purification and analysis by NMR and HRMS (for 1a, α-hydroxy ketones are commercially available).

To a stirred solution of **1'** (20 mmol, 1.0 equiv.) and potassium cyanate (KOCN, 3.24 g, 40 mmol, 2.0 equiv.) in 60 mL tetrahydrofuran (THF) is added acetic acid (HOAc, 2.88 g, 48 mmol, 2.4 equiv.) slowly at 50 °C. The reaction is further stirred until total consumption of **1'** indicated by TLC (generally overnight). The mixture is allowed to cool down to r.t., quenched with water (30 mL), extracted with EA (3 × 50 mL). The organic layers are combined, washed with saturated aqueous sodium bicarbonate (50 mL), dried over $MgSO_4$, concentrated in vacuo and purified by column chromatography on silica gel to give the desired products 4-aryl oxazol-2(3*H*)-ones (**1**) (30-92 % yield). (The ^1H and ^{13}C NMR spectra and HRMS of **1a-1d**, **1o**, **1r**, **1w** have been reported in the literature 12).

*4-phenyloxazol-2(3H)-one (**1a**)*[12]: Yellow solid, (2.77 g, 86 %). mp = 145-147 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.09 (s, 1H), 7.47 - 7.41 (m, 4H), 7.35 (t, J = 6.9 Hz, 2H), 7.14 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.2, 129.3, 129.0, 128.2, 126.2, 124.2, 123.9. **HRMS (EI)** TOF analyzer, Calcd. for $C_9H_7O_2N$: $[M]^+$, 161.0477. Found: m/z 161.0470.

*4-(p-tolyl)oxazol-2(3H)-one (**1b**)*[12]: Yellow solid, (2.80 g, 80 %). mp = 128-130 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.92 (s, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 1.5 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.2, 139.1, 129.9, 128.2, 125.4, 124.1, 123.4, 21.4. **HRMS (EI)** TOF analyzer, Calcd. for $C_{10}H_9O_2N$: $[M]^+$, 175.0633. Found: m/z 175.0628.

*4-(4-methoxyphenyl)oxazol-2(3H)-one (**1c**)*[12]: Yellow solid, (3.25 g, 85 %). mp = 176-178 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.84 (s, 1H), 7.37 (d, J = 8.8 Hz, 2H), 7.02 (s, 1H), 6.95 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H). **HRMS (EI)** TOF analyzer, Calcd. for $C_{10}H_9O_3N$: $[M]^+$, 191.0582. Found: m/z 191.0576.

*4-(4-ethylphenyl)oxazol-2(3H)-one (**1d**)*[12]: Yellow solid, (2.53 g, 67 %). mp = 181-183 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 11.10 (s, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.08 (s, 1H), 2.65 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.6 Hz, 3H).

*4-(4-pentylphenyl)oxazol-2(3H)-one (**1e**)*: Yellow solid, (2.87 g, 62 %). mp = 167-169 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.82 (d, J = 63.6 Hz, 1H), 7.35 (dd, J = 8.1, 1.4 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 1.3 Hz, 1H), 2.64 - 2.59 (m, 2H), 1.65 -

1.58 (m, 2H), 1.35 - 1.29 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3, 144.2, 129.3, 128.3, 124.2, 123.6, 123.4, 35.7, 31.4, 31.0, 22.5, 14.0. **HRMS (EI)** TOF analyzer, Calcd. for $C_{14}H_{17}O_2N$: $[M]^+$, 231.1259. Found: m/z 231.1266.

*4-([1,1'-biphenyl]-4-yl)oxazol-2(3H)-one (**1f**)*: mp = 211-214 °C. Yellow solid, (3.22 g, 68 %). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 10.63 (s, 1H), 7.67 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 7.3 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 7.3 Hz, 1H), 7.17 (d, J = 1.1 Hz, 1H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 158.0, 141.8, 140.0, 129.0, 127.91, 127.87, 127.8, 127.0, 125.1, 124.6, 124.0. **HRMS (EI)** TOF analyzer, Calcd. for $C_{15}H_{11}O_2N$: $[M]^+$, 237.0790. Found: m/z 237.0795.

*4-(4-fluorophenyl)oxazol-2(3H)-one (**1g**)*: mp = 267-269 °C. White solid, (2.54 g, 71 %). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 11.39 (s, 1H), 7.68 (d, J = 1.0 Hz, 1H), 7.64 - 7.59 (m, 2H), 7.34 - 7.27 (m, 2H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 162.3 (d, J = 246.1 Hz), 156.4, 126.8, 126.6 (d, J = 8.2 Hz), 125.0 (d, J = 2.3 Hz), 123.9 (d, J = 3.0 Hz), 116.4 (d, J = 22.0 Hz). **HRMS (EI)** TOF analyzer, Calcd. for $C_9H_6O_2NF$: $[M]^+$, 179.0383. Found: m/z 179.0379.

*4-(4-chlorophenyl)oxazol-2(3H)-one (**1h**)*: mp = 292-294 °C. Yellow solid, (3.35 g, 86 %). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 11.42 (s, 1H), 7.76 (d, J = 1.3 Hz, 1H), 7.60 - 7.56 (m, 2H), 7.55 - 7.48 (m, 2H). **^{13}C NMR (101 MHz, DMSO-d_6)** δ 155.9, 132.7, 129.0, 126.2, 125.8, 125.7, 125.3. **HRMS (EI)** TOF analyzer, Calcd. for $C_9H_6O_2NCl$: $[M]^+$, 195.0087. Found: m/z 195.0084.

*4-(4-bromophenyl)oxazol-2(3H)-one (**1i**)*: mp = 305-307 °C. Yellow solid, (3.82 g, 80 %). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 11.40 (s, 1H), 7.76 (s, 1H), 7.64 (dd, J = 7.0, 1.2 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H). **^{13}C NMR (101 MHz, DMSO-d_6)** δ 155.9, 131.9, 126.2, 126.1, 125.9, 125.3, 121.2. **HRMS (EI)** TOF analyzer, Calcd. for $C_9H_6O_2NBr$: $[M]^+$, 238.9582. Found: m/z 238.9585.

*4-(4-(trifluoromethyl)phenyl)oxazol-2(3H)-one (**1j**)*: mp = 288-290 °C. Yellow solid, (3.89 g, 85 %). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 11.56 (s, 1H), 7.91 (s, 1H), 7.82 (d, J = 8.6 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 156.3, 129.1, 128.7 (q, J = 32.0 Hz), 127.1, 126.5, 126.3 (q, J = 3.5 Hz), 124.9, 124.5 (q, J = 272.5 Hz). **HRMS (EI)** TOF analyzer, Calcd. for $C_{10}H_6O_2NF_3$: $[M]^+$, 229.0351. Found: m/z 229.0347.

*methyl 4-(2-oxo-2,3-dihydrooxazol-4-yl)benzoate (**1k**)*: mp = 145-147 °C. White solid, (1.31 g, 30 %). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 11.52 (s, 1H), 8.00 (d, J = 8.4 Hz, 2H), 7.88 (s, 1H), 7.70 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 166.2, 156.3, 131.8, 130.2, 129.4, 127.2, 126.9, 124.5, 52.7. **HRMS (ESI)** Orbitrap-FT analyzer, Calcd. for $C_{11}H_8O_4N$: $[M-H]^-$, 218.0459. Found: m/z 218.0455.

*4-(4-(methylsulfonyl)phenyl)oxazol-2(3H)-one (**1l**)*: mp = 266-268 °C. Yellow solid, (2.01 g, 42 %). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 11.59 (s, 1H), 7.98 (d, J = 8.6 Hz, 2H), 7.94 (s, 2H), 7.82 (d, J = 8.5 Hz, 2H), 3.25 (s, 3H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 156.2, 140.4, 132.2, 128.2, 127.7, 126.4, 124.9, 40.5. **HRMS (ESI)** FTICR analyzer, Calcd. for $C_{10}H_{10}O_4NS$: $[M+H]^+$, 240.0325. Found: m/z 240.0326.

*4-(2-oxo-2,3-dihydrooxazol-4-yl)benzonitrile (**1m**)*: mp = 301-303 °C. Yellow solid, (1.30 g, 35 %). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 11.58 (s, 1H), 8.16 - 7.82 (m, 3H), 7.74 (d, J = 7.9 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 156.2, 133.4, 131.7,

127.9, 126.4, 124.9, 119.1, 110.8. **HRMS (ESI)** Orbitrap-FT analyzer, Calcd. for $C_{10}H_5O_2N_2$: [M-H]$^-$, 185.0357. Found: m/z 185.0350.

*4-(4-nitrophenyl)oxazol-2(3H)-one (**1n**)*: mp = 322-324 °C. Red solid, (1.73 g, 33 %). **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 11.66 (s, 1H), 8.30 (d, *J* = 8.5 Hz, 2H), 8.01 (s, 1H), 7.82 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-d$_6$)** δ 156.1, 147.0, 133.7, 128.5, 126.2, 125.2, 124.8. **HRMS (ESI)** Orbitrap-FT analyzer, Calcd. for $C_9H_5O_4N_2$: [M-H]$^-$, 205.0255. Found: m/z 205.0251.

*4-(o-tolyl)oxazol-2(3H)-one **(1o)**[12]*: mp = 177-179 °C. Yellow solid, (1.93 g, 55 %). **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 11.13 (s, 1H), 7.44 - 7.40 (m, 1H), 7.35 (d, *J* = 1.3 Hz, 1H), 7.32 - 7.25 (m, 3H), 2.35 (s, 3H). **^{13}C NMR (101 MHz, DMSO-d$_6$)** δ 156.1, 135.9, 131.4, 128.9, 127.7, 126.8, 126.6, 126.5, 21.4. **HRMS (ESI)** FTICR analyzer, Calcd. for $C_{10}H_{10}O_2N$: [M+H]$^+$, 176.0706. Found: m/z 176.0706.

*4-(2-fluorophenyl)oxazol-2(3H)-one (**1p**)*: mp = 234-236 °C. White solid, (2.94 g, 82 %). **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 11.44 (s, 1H), 7.64 (td, *J* = 7.8, 1.5 Hz, 2H), 7.54 (d, *J* = 3.5 Hz, 2H), 7.45 - 7.39 (m, 1H), 7.38 - 7.29 (m, 2H). **^{13}C NMR (126 MHz, DMSO-d$_6$)** δ 159.1 (d, *J* = 249.8 Hz), 155.9, 130.3 (d, *J* = 8.6 Hz), 128.2 (d, *J* = 15.8 Hz), 126.7 (d, *J* = 2.9 Hz), 125.5 (d, *J* = 3.3 Hz), 121.9 (d, *J* = 1.9 Hz), 116.5 (d, *J* = 20.8 Hz), 115.3 (d, *J* = 12.9 Hz). **HRMS (EI)** TOF analyzer, Calcd. for $C_9H_6O_2NF$: [M]$^+$, 179.0383. Found: m/z 179.0377.

*4-(2-bromophenyl)oxazol-2(3H)-one (**1q**)*: mp = 267-270 °C. White solid, (3.01 g, 63 %). **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 11.24 (s, 1H), 7.76 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.59 (s, 1H), 7.53 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.49 (td, *J* = 7.6, 1.1 Hz, 1H), 7.38 - 7.32 (m, 3H). **^{13}C NMR (126 MHz, DMSO-d$_6$)** δ 155.8, 134.2, 130.9, 130.5, 128.5, 128.0, 127.6, 125.7, 121.3. **HRMS (EI)** TOF analyzer, Calcd. for $C_9H_6O_2NBr$: [M]$^+$, 238.9582. Found: m/z 238.9592.

*4-(m-totyl)oxazol-2(3H)-one (**1r**)*[12]: mp = 155-158 °C. Yellow solid, (2.10 g, 60 %). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 11.08 (s, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.28 (s, 2H), 7.18 (d, *J* = 6.5 Hz, 1H), 7.13 (s, 1H), 2.41 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 158.2, 139.0, 129.8, 129.2, 128.3, 126.1, 124.8, 123.8, 121.4, 21.4. **HRMS (EI)** TOF analyzer, Calcd. for $C_{10}H_9O_2N$: [M]$^+$, 175.0633. Found: m/z 175.0628.

*4-(3-methoxyphenyl)oxazol-2(3H)-one (**1s**)*: mp = 188-190 °C. Yellow solid, (2.22 g, 58 %). **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 11.36 (s, 1H), 7.73 (s, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.16 (t, *J* = 5.2 Hz, 2H), 6.91 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR (126 MHz, DMSO-d$_6$)** δ 160.1, 156.4, 130.5, 128.5, 127.5, 125.5, 116.7, 114.4, 109.9, 55.7. **HRMS (EI)** TOF analyzer, Calcd. for $C_{10}H_9O_3N$: [M]$^+$, 191.0582. Found: m/z 191.0579.

*4-(3-chrolophenyl)oxazol-2(3H)-one (**1t**)*: mp = 227-229 °C. White solid, (3.00 g, 77 %). **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 11.41 (s, 1H), 7.81 (s, 1H), 7.69 (t, *J* = 1.7 Hz, 1H), 7.53 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.42 - 7.37 (m, 1H). **^{13}C NMR (101 MHz, DMSO-d$_6$)** δ 156.3, 134.3, 131.3, 129.4, 128.5, 126.4, 124.1, 123.0, 96.0. **HRMS (EI)** TOF analyzer, Calcd. for $C_9H_6O_2NCl$: [M]$^+$, 195.0087. Found: m/z 195.0090.

*4-(3-bromophenyl)oxazol-2(3H)-one (**1u**)*: mp = 251-253 °C. White solid, (3.82 g, 80 %). **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 11.41 (s, 1H), 7.82 (d, *J* = 1.5 Hz, 1H), 7.81 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H). **^{13}C NMR (126 MHz, DMSO-d$_6$)** δ 156.2, 131.5, 131.4, 129.6, 126.9, 126.4, 126.3, 123.3, 122.8. **HRMS (EI)** TOF analyzer, Calcd. for $C_9H_6O_2NBr$: $[M]^+$, 238.9582. Found: m/z 238.9584.

*4-(2,4-difluorophenyl)oxazol-2(3H)-one (**1v**)*: mp = 168-170 °C. White solid, (2.44 g, 62 %). **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 11.44 (s, 1H), 7.66 (td, *J* = 8.7, 6.3 Hz, 1H), 7.52 (d, *J* = 3.4 Hz, 1H), 7.44 (ddd, *J* = 11.7, 9.2, 2.5 Hz, 1H), 7.25 (td, *J* = 8.5, 2.4 Hz, 1H). **^{13}C NMR (126 MHz, DMSO-d$_6$)** δ 162.1 (dd, *J* = 248.6, 12.7 Hz), 159.3 (dd, *J* = 252.7, 12.4 Hz), 155.9, 127.9 (dd, *J* = 26.2, 3.5 Hz), 127.8 (t, *J* = 2.9 Hz), 121.3 (d, *J* = 2.3 Hz), 112.7 (dd, *J* = 21.9, 3.5 Hz), 112.2 (dd, *J* = 13.2, 3.7 Hz), 105.4 (t, *J* = 25.9 Hz). **HRMS (EI)** TOF analyzer, Calcd. for $C_9H_5O_2NF_2$: $[M]^+$, 197.0288. Found: m/z 197.0284.

*4-(naphthalen-2-yl)oxazol-2(3H)-one (**1w**)*[12]: mp = 266-268 °C. Yellow solid, (3.04 g, 72 %). **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 11.53 (s, 1H), 8.07 (s, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.89 - 7.81 (m, 2H), 7.70 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.55 (pd, *J* = 6.9, 1.3 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-d$_6$)** δ 156.5, 133.3, 132.9, 129.0, 128.3, 128.2, 127.7, 127.4, 127.0, 126.0, 124.8, 122.9, 122.5. **HRMS (EI)** TOF analyzer, Calcd. for $C_{13}H_9O_2N$: $[M]^+$, 211.0633. Found: m/z 211.0637.

General Procedure for the Synthesis of 3a-3w and 4b-4s. To a 15 mL screwed tube equipped with magnetic stir bar and a PTFE screw plug are added 4-aryloxazol-2(3*H*)-ones (**1a-1w**, 0.2 mmol, 1.0 equiv.), alkynes **(2b-2s**, 0.3 mmol, 1.5 equiv.), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol %) and NaOAc (32.8 mg, 0.4 mmol, 2.0 equiv.). The screwed tube is transferred to a glovebox, and added with $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %) and HFIP (1.5 mL). After sealed with the screw plug, the screwed tube is taken out from the glovebox and the resulting solution is stirred at 100 °C for 15 h. The reaction mixture is concentrated in vacuo, and the residue is dissolved in DCM and purified by column chromatography (silica gel, PE/EA=3:1-1:1) to give the corresponding 2,3-disubstitutive spiro[indene-1,4'-oxazolidin]-2'-ones (**3a-3w**; **4b-4s**). The reaction products are subjected to ^{1}H/^{13}C NMR and HRMS measurements.

*2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3a**)*: mp = 229-232 °C. Yellow solid, (57.6 mg, 85 %). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.60 - 7.56 (m, 1H), 7.35 (dd, *J* = 3.7, 2.4 Hz, 1H), 7.33 (d, *J* = 1.8 Hz, 2H), 7.32 - 7.31 (m, 2H), 7.30 (dd, *J* = 4.8, 2.3 Hz, 2H), 7.28 - 7.27 (m, 2H), 7.27 - 7.25 (m, 3H), 7.24 (dd, *J* = 3.5, 1.3 Hz, 1H), 5.64 (s, 1H), 4.54 (d, *J* = 8.8 Hz, 1H), 4.47 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.6, 146.2, 142.4, 142.3, 142.3, 133.5, 133.2, 129.6, 129.5, 129.2, 128.7, 128.6, 128.2, 128.1, 127.5, 122.5, 121.5, 72.0, 70.4. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{23}H_{18}O_2N$ $[M+H]^+$ 340.1332, found 340.1329.

*5-methyl-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3b**)*: mp = 197-200 °C. Yellow solid, (43.3 mg, 61 %). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.45 (d, *J* = 7.5 Hz, 1H), 7.37 - 7.30 (m, 3H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 1.7 Hz, 1H), 7.24 (dt, *J* = 7.0, 2.7 Hz, 5H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 5.64 (s, 1H), 4.51 (d, *J* = 8.7 Hz, 1H), 4.45 (d, *J* = 8.7 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.8, 143.3, 142.8, 142.5, 142.2, 139.5, 133.7, 133.4, 129.6, 129.3, 128.7, 128.6, 128.1, 128.0, 127.9, 122.3, 122.2, 72.1, 70.2, 21.6. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{24}H_{20}O_2N$ $[M+H]^+$ 354.1489, found 354.1486.

*5-methoxy-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3c**)*: mp = 245-248 °C. Yellow solid, (54.0 mg, 73 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 (d, J = 8.0 Hz, 1H), 7.35 - 7.29 (m, 3H), 7.28 - 7.26 (m, 2H), 7.25 (d, J = 1.9 Hz, 3H), 7.24 (d, J = 0.9 Hz, 2H), 6.82 (dd, J = 6.8, 5.0 Hz, 2H), 5.87 (s, 1H), 4.50 (d, J = 8.7 Hz, 1H), 4.43 (d, J = 8.7 Hz, 1H), 3.78 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.1, 159.6, 144.0, 143.8, 141.9, 137.9, 133.4, 133.3, 129.5, 129.2, 128.7, 128.6, 128.2, 128.1, 123.2, 111.8, 108.2, 72.2, 70.0, 55.7. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{24}H_{20}O_3N$ $[M+H]^+$ 370.1438, found 370.1434.

*5-ethyl-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3d**)*: mp = 257-259 °C. Yellow solid, (41.6 mg, 57 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (d, J = 7.6 Hz, 1H), 7.32 (dd, J = 8.9, 6.1 Hz, 3H), 7.28 (dd, J = 7.6, 1.7 Hz, 2H), 7.27 - 7.22 (m, 5H), 7.15 (d, J = 7.6 Hz, 1H), 7.11 (s, 1H), 5.89 (s, 1H), 4.52 (d, J = 8.8 Hz, 1H), 4.44 (d, J = 8.7 Hz, 1H), 2.64 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.8, 146.1, 143.5, 142.8, 142.6, 142.3, 133.7, 133.4, 129.6, 129.3, 128.7, 128.6, 128.1, 128.0, 126.9, 122.4, 121.1, 72.2, 70.2, 29.1, 16.0. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{25}H_{22}O_2N$ $[M+H]^+$ 368.1645, found 368.1642.

*5-pentyl-2,3-triphenylspiro[indene-1,4' -oxazolidin]-2'-one (**3e**)*: mp = 232-234 °C. Yellow solid, (55.6 mg, 68 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 (d, J = 7.6 Hz, 1H), 7.37 - 7.33 (m, 1H), 7.32 (dd, J = 4.8, 2.8 Hz, 2H), 7.29 (d, J = 2.2 Hz, 1H), 7.28 - 7.26 (m, 1H), 7.26 - 7.24 (m, 4H), 7.22 (dd, J = 4.5, 2.1 Hz, 1H), 7.13 (dd, J = 7.6, 1.4 Hz, 1H), 7.09 (s, 1H), 5.76 (s, 1H), 4.52 (d, J = 8.7 Hz, 1H), 4.45 (d, J = 8.7 Hz, 1H), 2.64 - 2.54 (m, 2H), 1.63 - 1.54 (m, 2H), 1.36 - 1.27 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.7, 144.8, 143.5, 142.8, 142.5, 142.3, 133.7, 133.4, 129.6, 129.3, 128.7, 128.6, 128.1, 128.0, 127.4, 122.3, 121.6, 72.2, 70.2, 36.1, 31.53, 31.48, 22.5, 14.1. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{28}H_{28}O_2N$ $[M+H]^+$ 410.2115, found 410.2114.

*2,3,5-triphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3f**)*: mp = 266-268 °C. Yellow solid, (60.0 mg, 72 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 (d, J = 7.7 Hz, 1H), 7.54 - 7.50 (m, 3H), 7.47 (d, J = 1.2 Hz, 1H), 7.43 - 7.39 (m, 2H), 7.36 - 7.34 (m, 1H), 7.33 (t, J = 2.0 Hz, 1H), 7.32 (s, 1H), 7.32 (s, 2H), 7.31 (dd, J = 3.1, 1.3 Hz, 1H), 7.27 (s, 5H), 6.05 (s, 1H), 4.56 (d, J = 8.8 Hz, 1H), 4.48 (d, J = 8.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.8, 145.0, 143.2, 143.1, 143.0, 142.2, 140.9, 133.5, 133.2, 129.6, 129.3, 128.9, 128.7, 128.7, 128.23, 128.18, 127.7, 127.3, 126.5, 122.8, 120.4, 72.1, 70.3. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{29}H_{22}O_2N$ $[M+H]^+$ 416.1645, found 416.1642.

*5-fluoro-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3g**)*: mp = 252-255 °C. Yellow solid, (50.7 mg, 71 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 - 7.49 (m, 1H), 7.35 (dd, J = 4.6, 1.3 Hz, 1H), 7.34 - 7.31 (m, 2H), 7.28 (dd, J = 4.0, 1.9 Hz, 2H), 7.27 - 7.26 (m, 2H), 7.25 (d, J = 2.1 Hz, 2H), 7.24 - 7.21 (m, 1H), 7.03 - 6.97 (m, 2H), 5.86 (s, 1H), 4.52 (d, J = 8.8 Hz, 1H), 4.46 (d, J = 8.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.0 (d, J = 247.2 Hz), 159.5, 144.7 (d, J = 9.0 Hz), 144.3, 141.43, 141.41, 141.36, 132.9 (d, J = 5.0 Hz), 129.5, 129.1, 128.8, 128.7, 128.5, 128.4, 123.6 (d, J = 9.2 Hz), 113.8 (d, J = 23.3 Hz), 109.3 (d, J = 24.6 Hz), 72.0, 70.0. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{23}H_{17}O_2NF$ $[M+H]^+$ 358.1238, found 358.1234.

*5-chloro-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3h**)*: mp = 273-275 °C. Yellow solid, (59.9 mg, 80 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (d, J = 7.9 Hz, 1H), 7.37 - 7.31 (m, 3H), 7.31 - 7.28 (m, 1H), 7.28 - 7.27 (m, 2H), 7.27 - 7.26 (m, 3H), 7.25 - 7.22 (m, 3H), 6.12 (s, 1H), 4.49 (d, J = 8.8 Hz, 1H), 4.44 (d, J = 8.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.7, 144.4, 144.2, 143.96, 141.4, 135.6, 132.9, 132.8, 129.5, 129.1, 128.77, 128.76, 128.5, 128.4, 127.2, 123.4, 121.8, 71.8, 70.1. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{23}H_{17}O_2NCl$ $[M+H]^+$ 374.0937, found 374.0940.

*5-bromo-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3i**)*: mp = 288-290 °C. Yellow solid, (65.9 mg, 79 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 (dd, J = 7.9, 1.7 Hz, 1H), 7.42 - 7.39 (m, 2H), 7.36 - 7.31 (m, 3H), 7.27 (d, J = 2.1 Hz, 1H), 7.26 (dd, J = 5.3, 2.2 Hz, 3H), 7.24 (dd, J = 2.9, 1.4 Hz, 2H), 7.24 - 7.21 (m, 1H), 6.27 (s, 1H), 4.48 (d, J = 8.8 Hz, 1H), 4.43 (d, J = 8.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.8, 145.0, 144.5, 143.9, 141.3, 132.9, 132.8, 130.1, 129.5, 129.1, 128.8, 128.5, 128.4, 124.7, 123.8, 123.6, 71.8, 70.2. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{23}H_{17}O_2NBr$ $[M+H]^+$ 418.0437, found 418.0435.

*2,3-diphenyl-5-(trifluoromethyl)spiro[indene-1,4'-oxazolidin]-2'-one (**3j**)*: mp = 210-212 °C. Yellow solid, (60.3 mg, 74 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.52 (s, 1H), 7.37 (dd, J = 5.3, 3.7 Hz, 1H), 7.35 (q, J = 2.9 Hz, 2H), 7.31 (dd, J = 10.6, 2.2 Hz, 2H), 7.28 (d, J = 2.0 Hz, 2H), 7.27 - 7.26 (m, 2H), 7.24 (d, J = 3.7 Hz, 1H), 6.54 (s, 1H), 4.52 (d, J = 8.9 Hz, 1H), 4.46 (d, J = 8.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.9, 149.8 (d, J = 1.1 Hz), 144.1, 143.3, 141.4, 132.70, 132.67, 132.0 (q, J = 32.2 Hz), 129.5, 129.1, 128.9, 128.8, 128.6, 128.5, 124.5 (q, J = 3.8 Hz), 124.0 (q, J = 273.6 Hz), 122.7, 118.1 (q, J = 3.5 Hz), 71.6, 70.4. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{24}H_{17}O_2NF_3$ $[M+H]^+$ 408.1206, found 408.1204.

*Methyl-2'-oxo-2,3-diphenylspiro[indene-1,4'-oxazolidine]-5-carboxylate (**3k**)*: mp = 167-170 °C. Yellow solid, (57.2 mg, 72 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (dd, J = 7.8, 1.4 Hz, 1H), 7.93 (d, J = 1.1 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.36 (dt, J = 7.3, 2.2 Hz, 3H), 7.32 - 7.27 (m, 5H), 7.26 - 7.22 (m, 2H), 5.56 (s, 1H), 4.54 (d, J = 8.8 Hz, 1H), 4.48 (d, J = 8.8 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.7, 159.2, 150.9, 143.1, 142.7, 142.0, 141.8, 132.9, 132.8, 131.6, 129.5, 129.3, 129.1, 128.8, 128.5, 128.4, 122.32, 122.28, 71.7, 70.3, 52.4. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{25}H_{20}O_4N$ $[M+H]^+$ 398.1387, found 398.1387.

5-*(methylsulfonyl)-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3l**)*: mp = 283-285 °C. Yellow solid, (56.8 mg, 68 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (dd, J = 7.8, 1.6 Hz, 1H), 7.79 (d, J = 1.3 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.36 (dd, J = 5.1, 1.8 Hz, 3H), 7.33 - 7.29 (m, 3H), 7.28 - 7.25 (m, 4H), 6.37 (s, 1H), 4.52 (d, J = 8.9 Hz, 1H), 4.47 (d, J = 8.9 Hz, 1H), 3.04 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.5, 151.9, 144.7, 144.0, 142.1, 141.1, 132.4, 132.3, 129.5, 129.0, 129.0, 128.9, 128.8, 128.7, 126.9, 123.2, 119.8, 71.4, 70.3, 44.6. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{24}H_{20}O_4NS$ $[M+H]^+$ 418.1035, found 418.1038.

*2'-oxo-2,3-diphenylspiro[indene-1,4'-oxazolidine]-5-carbonitrile (**3m**)*: mp = 322-325 °C. Yellow solid, (40.0 mg, 55 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (dt, J = 7.7, 4.4 Hz, 2H), 7.57 (s, 1H), 7.41 - 7.35 (m, 3H), 7.33 - 7.28 (m, 3H), 7.26 - 7.23 (m, 4H), 5.47 (s, 1H), 4.54 (d, J = 8.9 Hz, 1H), 4.49 (d, J = 8.9 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.9, 150.8, 132.24, 132.19,

131.7, 129.4, 129.1, 129.0, 128.94, 128.86, 128.8, 124.7, 124.6, 123.5, 123.1, 118.53, 118.51, 113.6, 71.4, 70.4. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{24}H_{17}O_2N_2$ $[M+H]^+$ 365.1285, found 365.1286.

*5-nitro-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3n**)*: mp = 344-346 °C. Red solid, (47.6 mg, 62 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.23 (dd, J = 8.1, 2.0 Hz, 1H), 8.09 (d, J = 1.9 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.43 - 7.35 (m, 3H), 7.32 (dd, J = 4.6, 2.8 Hz, 2H), 7.30 - 7.27 (m, 4H), 7.26 (d, J = 4.6 Hz, 1H), 6.16 (s, 1H), 4.54 (d, J = 8.9 Hz, 1H), 4.49 (d, J = 8.9 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.3, 152.5, 149.5, 144.9, 144.2, 149.0, 132.22, 132.15, 129.4, 129.03, 128.97, 128.93, 128.87, 128.8, 123.0, 122.9, 116.3, 71.4, 70.2. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{23}H_{17}O_4N_2$ $[M+H]^+$ 385.1183, found 385.1181.

*7-methyl-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3o**)*: mp = 217-219 °C. Yellow solid, (53.0 mg, 75 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 - 7.28 (m, 3H), 7.28 - 7.24 (m, 5H), 7.24 - 7.20 (m, 3H), 7.11 (d, J = 7.2 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 5.74 (s, 1H), 4.65 (d, J = 9.0 Hz, 1H), 4.46 (d, J = 9.0 Hz, 1H), 2.50 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.5, 143.01, 143.00, 142.4, 142.0, 134.2, 133.6, 133.2, 130.0, 129.7, 129.4, 129.3, 128.7, 128.5, 128.1, 128.0, 119.3, 70.5, 69.5, 17.4. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{24}H_{20}O_2N$ $[M+H]^+$ 354.1489, found 354.1486.

*7-fluoro-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3p**)*: mp = 200-202 °C. Yellow solid, (45.0 mg, 63 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 - 7.32 (m, 2H), 7.32 - 7.30 (m, 2H), 7.30 - 7.28 (m, 2H), 7.27 (d, J = 1.5 Hz, 3H), 7.26 (d, J = 1.3 Hz, 2H), 7.09 (d, J = 7.5 Hz, 1H), 7.01 (dd, J = 13.0, 4.4 Hz, 1H), 6.18 (s, 1H), 4.68 (d, J = 8.8 Hz, 1H), 4.43 (d, J = 8.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.8, 159.0 (d, J = 251.2 Hz), 145.4 (d, J = 4.5 Hz), 143.3, 141.8, 133.2, 132.7, 131.6 (d, J = 7.4 Hz), 130.3 (d, J = 13.7 Hz), 129.7, 129.2, 128.7, 128.6, 128.4, 128.3, 117.6 (d, J = 2.4 Hz), 115.0 (d, J = 20.3 Hz), 69.9, 69.7. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{23}H_{17}O_2NF$ $[M+H]^+$ 358.1238, found 358.1235.

*7-bromo-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3q**)*: mp = 244-246 °C. Yellow solid, (56.7 mg, 68 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 (dd, J = 7.2, 1.7 Hz, 1H), 7.34 (dd, J = 4.9, 1.7 Hz, 1H), 7.31 (dd, J = 4.6, 1.8 Hz, 2H), 7.30 - 7.26 (m, 4H), 7.26 - 7.22 (m, 4H), 7.21 (d, J = 7.4 Hz, 1H), 5.84 (s, 1H), 4.83 (d, J = 8.9 Hz, 1H), 4.43 (d, J = 8.9 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.8, 145.7, 144.3, 142.3, 140.9, 133.0, 132.6, 131.5, 131.0, 129.6, 129.2, 128.8, 128.7, 128.5, 128.3, 120.5, 119.0, 71.1, 68.5. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{23}H_{17}O_2NBr$ $[M+H]^+$ 418.0437, found 418.0435.

*6-methyl-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3r**)*: mp = 172-174 °C. Yellow solid, (42.4 mg, 60 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 (s, 1H), 7.31 (dd, J = 8.5, 3.0 Hz, 3H), 7.28 (s, 1H), 7.27 - 7.26 (m, 1H), 7.25 (s, 1H), 7.24 (d, J = 1.1 Hz, 4H), 7.17 (d, J = 7.7 Hz, 1H), 7.12 (d, J = 7.7 Hz, 1H), 5.82 (s, 1H), 4.50 (d, J = 8.7 Hz, 1H), 4.43 (d, J = 8.7 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.8, 146.6, 142.2, 141.4, 139.6, 137.7, 133.7, 133.4, 129.9, 129.6, 129.2, 128.7, 128.5, 128.0, 123.4, 121.2, 72.1, 70.3, 21.5. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{24}H_{20}O_2N$ $[M+H]^+$ 354.1489, found 354.1486.

*6-methoxy-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3s**)*: mp = 201-203 °C. Yellow solid, (48.8 mg, 66 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 (d, J = 7.5 Hz, 1H), 7.35 (d, J = 5.7 Hz, 1H), 7.31 (d, J = 5.5 Hz, 2H), 7.28 (d, J = 2.2 Hz, 1H), 7.26 (d, J = 1.8 Hz, 1H), 7.25 (s, 4H), 7.22 (s, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.09 (s, 1H), 5.72 (s, 1H), 4.51 (d, J = 8.7 Hz, 1H), 4.45 (d, J =

8.7 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.7, 143.3, 142.7, 142.5, 142.3, 139.6, 133.6, 133.3, 129.6, 129.2, 128.7, 128.6, 128.11, 128.06, 127.9, 122.2, 72.2, 70.2, 21.6. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{24}H_{20}O_3N$ $[M+H]^+$ 370.1438, found 370.1436.

*6-chloro-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3t**)*: mp = 235-237 °C. Yellow solid, (53.0 mg, 71 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, J = 1.5 Hz, 1H), 7.32 (d, J = 6.3 Hz, 4H), 7.28 (dd, J = 6.3, 3.0 Hz, 4H), 7.23 (dd, J = 8.7, 5.0 Hz, 4H), 6.10 (s, 1H), 4.52 (d, J = 8.8 Hz, 1H), 4.46 (d, J = 8.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.6, 148.0, 142.7, 141.5, 140.8, 133.4, 133.1, 132.8, 129.5, 129.1, 128.8, 128.7, 128.4, 128.3, 123.1, 122.4, 71.8, 70.3. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{23}H_{17}O_2NCl$ $[M+H]^+$ 374.0942, found 374.0941.

*6-bromo-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3u**)*: mp = 271-273 °C. Yellow solid, (59.2 mg, 71 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, J = 1.6 Hz, 1H), 7.48 (dd, J = 8.1, 1.8 Hz, 1H), 7.36 - 7.30 (m, 3H), 7.30 - 7.26 (m, 3H), 7.26 - 7.24 (m, 3H), 7.24 - 7.22 (m, 1H), 7.18 - 7.15 (m, 1H), 6.14 (s, 1H), 4.52 (d, J = 8.8 Hz, 1H), 4.45 (d, J = 8.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.6, 148.2, 142.6, 141.6, 141.3, 133.0, 132.8, 132.5, 129.5, 129.1, 128.8, 128.7, 128.4, 128.3, 126.0, 122.8, 121.3, 71.7, 70.4. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{23}H_{17}O_2NBr$ $[M+H]^+$ 418.0437, found 418.0435.

*5,7-difluoro-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**3v**)*: mp = 188-191 °C. Yellow solid, (34.5 mg, 46 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 - 7.32 (m, 3H), 7.31 - 7.27 (m, 3H), 7.27 - 7.25 (m, 2H), 7.24 (dd, J = 7.3, 2.3 Hz, 2H), 6.84 (dd, J = 8.2, 1.9 Hz, 1H), 6.75 (td, J = 9.1, 1.9 Hz, 1H), 6.03 (s, 1H), 4.67 (d, J = 8.8 Hz, 1H), 4.43 (d, J = 8.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.5 (dd, J = 250.4, 10.7 Hz), 159.6, 158.6 (dd, J = 253.1, 13.1 Hz), 146.6 (dd, J = 10.2, 6.4 Hz), 145.0, 141.0, 132.6, 132.2, 129.6, 129.0, 128.80, 128.77, 128.7, 128.5, 105.8 (dd, J = 24.5, 3.2 Hz), 102.9, 102.7 (dd, J = 26.6, 24.5 Hz), 69.8, 69.4 (d, J = 1.7 Hz). **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{23}H_{16}O_2NF_2$ $[M+H]^+$ 376.1144, found 376.1141.

*2,3-diphenylspiro[cyclopenta[b]naphthalene-1,4'-oxazolidin]-2'-one (**3w**)*: mp = 284-286 °C. Yellow solid, (38.9 mg, 50 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (s, 1H), 7.89 - 7.85 (m, 1H), 7.80 - 7.77 (m, 1H), 7.65 (s, 1H), 7.50 (dd, J = 9.1, 4.9 Hz, 2H), 7.41 - 7.34 (m, 5H), 7.29 (s, 5H), 5.49 (s, 1H), 4.61 (d, J = 8.8 Hz, 1H), 4.53 (d, J = 8.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.3, 144.1, 143.0, 142.8, 140.2, 134.3, 133.5, 133.2, 132.8, 129.6, 129.3, 128.7, 128.4, 128.34, 128.32, 128.3, 126.9, 126.5, 121.9, 120.2, 73.0, 70.0. **HRMS (ESI)** FTICR analyzer, m/z calcd. for $C_{27}H_{20}O_2N$ $[M+H]^+$ 390.1489, found 390.1487.

*5-chloro-3-methyl-2-phenylspiro[indene-1,4'-oxazolidin]-2'-one (**4b**)*: mp = 257-259 °C. Yellow solid, (51.0 mg, 82 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.46 - 7.41 (m, 2H), 7.41 - 7.37 (m, 2H), 7.36 - 7.31 (m, 2H), 7.28 - 7.22 (m, 2H), 6.37 (s, 1H), 4.38 (d, J = 8.8 Hz, 1H), 4.33 (d, J = 8.8 Hz, 1H), 2.03 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.0, 145.3, 144.0, 143.3, 137.4, 135.5, 133.0, 129.3, 128.9, 128.5, 126.8, 122.9, 120.4, 71.6, 70.0, 11.6. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{18}H_{15}O_2NCl$ $[M+H]^+$ 312.0786, found 312.0786.

*5-chloro-3-ethyl-2-phenylspiro[indene-1,4'-oxazolidin]-2'-one (**4c**)*: mp = 224-226 °C. Yellow solid, (51.4 mg, 79 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.47 - 7.40 (m, 4H), 7.30 (t, J = 1.9 Hz, 1H), 7.29 (s, 2H), 7.26 (d, J = 2.3 Hz, 1H), 5.34 (s, 1H), 4.42 (d, J =

8.8 Hz, 1H), 4.37 (d, *J* = 8.8 Hz, 1H), 2.49 - 2.40 (m, 2H), 1.17 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.1, 144.3, 144.2, 143.2, 143.0, 135.5, 132.9, 129.1, 129.0, 128.6, 126.8, 123.2, 120.8, 71.4, 69.9, 19.3, 13.3. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{19}H_{17}O_2NCl$ $[M+H]^+$ 326.0942, found 326.0942.

*5-chloro-3-propyl-2-phenylspiro[indene-1,4'-oxazolidin]-2'-one (**4d**)*: mp = 245-247 °C. Yellow solid, (52.2 mg, 77 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.48 - 7.40 (m, 4H), 7.29 - 7.25 (m, 4H), 5.79 (s, 1H), 4.40 (d, *J* = 8.8 Hz, 1H), 4.36 (d, *J* = 8.8 Hz, 1H), 2.44 - 2.33 (m, 2H), 1.57 (dt, *J* = 14.3, 7.2 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.5, 144.6, 144.1, 143.8, 141.6, 135.5, 132.9, 129.3, 128.9, 128.5, 126.7, 123.1, 120.8, 71.4, 69.9, 28.0, 21.8, 14.3. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{20}H_{19}O_2NCl$ $[M+H]^+$ 340.1099, found 340.1098.

*5-chloro-3-(trimethylsilyl)-2-phenylspiro[indene-1,4'-oxazolidin]-2'-one (**4e**)*: mp = 301-303 °C. Yellow solid, (51.7 mg, 70 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.43 - 7.39 (m, 4H), 7.36 (d, *J* = 1.7 Hz, 1H), 7.25 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.21 - 7.17 (m, 2H), 5.94 (s, 1H), 4.39 (s, 2H), 0.04 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.1, 158.9, 147.4, 143.6, 141.9, 135.4, 134.7, 129.4, 128.8, 128.6, 126.3, 123.52, 123.47, 71.4, 71.3, 0.2. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{20}H_{21}O_2NClSi$ $[M+H]^+$ 370.1025, found 370.1025.

*5-chloro-3-allyl-2-phenylspiro[indene-1,4'-oxazolidin]-2'-one (**4f**)*: mp = 261-264 °C. Yellow solid, (41.8 mg, 62 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 - 7.43 (m, 4H), 7.38 - 7.34 (m, 2H), 7.29 (dd, *J* = 3.5, 2.5 Hz, 1H), 5.93 (ddt, *J* = 16.1, 10.2, 5.9 Hz, 1H), 5.47 (s, 1H), 5.14 (ddd, *J* = 18.7, 13.7, 1.5 Hz, 2H), 4.45 (d, *J* = 8.8 Hz, 1H), 4.40 (d, *J* = 8.8 Hz, 1H), 3.22 (d, *J* = 5.9 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.2, 144.7, 144.2, 144.0, 138.9, 135.5, 133.9, 132.5, 129.0, 128.9, 128.8, 126.9, 123.0, 121.4, 117.3, 71.6, 69.9, 30.6. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{20}H_{17}O_2NCl$ $[M+H]^+$ 338.0942, found 338.0942.

*5-chloro-3-(prop-1-en-2-yl)-2-phenylspiro[indene-1,4'-oxazolidin]-2'-one (**4g**)*: mp = 236-239 °C. Yellow solid, (48.5 mg, 72 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.48 - 7.45 (m, 1H), 7.45 - 7.44 (m, 1H), 7.44 - 7.40 (m, 2H), 7.38 (ddd, *J* = 5.7, 3.7, 1.4 Hz, 1H), 7.26 (dd, *J* = 5.9, 2.0 Hz, 1H), 7.12 (d, *J* = 1.8 Hz, 1H), 5.77 (s, 1H), 5.29 - 5.24 (m, 1H), 5.18 (s, 1H), 4.60 (d, *J* = 8.8 Hz, 1H), 4.50 (d, *J* = 8.8 Hz, 1H), 1.74 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.5, 145.3, 144.4, 144.1, 140.6, 137.4, 135.5, 133.5, 128.7, 128.6, 128.5, 127.1, 123.3, 121.6, 119.5, 72.0, 69.8, 24.0. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{20}H_{17}O_2NCl$ $[M+H]^+$ 338.0942, found 338.0942.

*5-chloro-2,3-di-p-tolylspiro[indene-1,4'-oxazolidin]-2'-one (**4h**)*: mp = 222-225 °C. Yellow solid, (54.6 mg, 68 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 (d, *J* = 7.8, 1H), 7.11 (d, *J* = 9.7, 2H), 7.07 - 7.00 (m, 6H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.53 (s, 1H), 4.31 (d, *J* = 8.8 Hz, 1H), 4.27 (d, *J* = 8.8 Hz, 1H), 2.23 (s, 3H), 2.18 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.2, 144.5, 144.4, 143.4, 140.9, 138.3, 138.2, 135.5, 130.0, 129.9, 129.51, 129.49, 129.2, 128.9, 127.0, 123.3, 121.7, 71.9, 69.6, 21.4, 21.3. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{25}H_{21}O_2NCl$ $[M+H]^+$ 402.1255, found 402.1256.

*5-chloro-2,3-bis(4-methoxyphenyl)spiro[indene-1,4'-oxazolidin]-2'-one (**4i**)*: mp = 287-290 °C. Yellow solid, (64.1 mg, 74 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 7.8 Hz, 1H), 7.29 - 7.26 (m, 2H), 7.23 - 7.17 (m, 6H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.81 (d,

J = 8.6 Hz, 2H), 5.64 (s, 1H), 4.48 (d, *J* = 8.8 Hz, 1H), 4.43 (d, *J* = 8.8 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** *δ* 159.5, 159.45, 159.38, 144.6, 144.4, 142.6, 140.1, 135.5, 130.7, 130.4, 126.9, 125.3, 125.2, 123.2, 121.6, 114.2, 72.1, 69.9, 55.3, 55.2. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{25}H_{21}O_4NCl$ $[M+H]^+$ 434.1154, found 434.1155.

*5-chloro-2,3-bis(4-ethylphenyl)spiro[indene-1,4'-oxazolidin]-2'-one (**4j**)*: mp = 259-262 °C. Yellow solid, (60.1 mg, 70 %). **^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 7.44 (d, *J* = 8.4 Hz, 1H), 7.25 (dt, *J* = 4.4, 2.2 Hz, 2H), 7.20 - 7.13 (m, 6H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.19 (s, 1H), 4.46 (d, *J* = 8.8 Hz, 1H), 4.41 (d, *J* = 8.8 Hz, 1H), 2.69 - 2.64 (m, 2H), 2.63 - 2.58 (m, 2H), 1.23 (dt, *J* = 15.3, 7.6 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 159.8, 144.6, 144.4, 143.5, 140.8, 135.4, 130.3, 130.2, 129.4, 129.0, 128.4, 128.2, 126.9, 123.3, 121.7, 71.9, 70.1, 28.7, 28.6, 15.2, 15.1. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{27}H_{25}O_2NCl$ $[M+H]^+$ 430.1568, found 430.1568.

*5-chloro-2,3-bis(4-fluorophenyl)spiro[indene-1,4'-oxazolidin]-2'-one (**4k**)*: mp = 298-300 °C. Yellow solid, (36.0 mg, 44 %). **^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 7.50 (d, *J* = 7.9 Hz, 1H), 7.34 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.22 (ddd, *J* = 8.4, 5.1, 2.7 Hz, 5H), 7.07 (t, *J* = 8.7 Hz, 2H), 7.00 (t, *J* = 8.7 Hz, 2H), 5.56 (s, 1H), 4.52 (d, *J* = 8.9 Hz, 1H), 4.42 (d, *J* = 8.9 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 162.7 (d, *J* = 249.8 Hz), 162.6 (d, *J* = 249.1 Hz), 159.2, 144.0, 143.8, 143.1, 140.7, 135.8, 131.3 (d, *J* = 8.1 Hz), 130.9 (d, *J* = 8.1 Hz), 128.6 (d, *J* = 3.5 Hz), 127.5, 123.5, 121.7, 116.14 (d, *J* = 21.5 Hz), 116.11 (d, *J* = 21.6 Hz), 71.8, 70.0. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{23}H_{15}O_2NF_2Cl$ $[M+H]^+$ 410.0754, found 410.0754.

*5-chloro-2,3-bis(4-chlorophenyl)spiro[indene-1,4'-oxazolidin]-2'-one (**4l**)*: mp = 316-319 °C. Yellow solid, (32.6 mg, 37 %). **^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 7.49 (d, *J* = 7.9 Hz, 1H), 7.38 - 7.32 (m, 3H), 7.29 - 7.26 (m, 2H), 7.25 - 7.14 (m, 5H), 5.93 (s, 1H), 4.51 (d, *J* = 8.9 Hz, 1H), 4.41 (d, *J* = 8.9 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 159.2, 144.0, 143.5, 143.2, 140.9, 135.9, 134.9, 134.7, 130.9, 130.9, 130.7, 130.4, 129.3, 129.0, 127.7, 123.6, 121.8, 71.7, 70.0. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{23}H_{15}O_2NCl_3$ $[M+H]^+$ 442.0163, found 442.0164.

*5-chloro-2,3-bis(4-bromophenyl)spiro[indene-1,4'-oxazolidin]-2'-one (**4m**)*: mp = 334-336 °C. Yellow solid, (56.1 mg, 53 %). **^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 7.50 (dd, *J* = 9.7, 8.2 Hz, 3H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.34 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.22 (d, *J* = 1.8 Hz, 1H), 7.14 - 7.08 (m, 4H), 5.99 (s, 1H), 4.50 (d, *J* = 8.9 Hz, 1H), 4.41 (d, *J* = 8.9 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 159.3, 144.0, 143.4, 143.2, 141.7, 140.9, 135.9, 133.2, 132.3, 131.4, 130.9, 130.6, 127.7, 123.6, 123.2, 122.9, 121.8, 71.7, 70.0. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{23}H_{15}O_2NClBr_2$ $[M+H]^+$ 529.9153, found 529.9155.

*5-chloro-2,3-di-m-tolylphenyl)spiro[indene-1,4'-oxazolidin]-2'-one (**4n**)*: mp = 178-181 °C. Yellow solid, (61.0 mg, 76 %). **^{1}H NMR (500 MHz, $CDCl_3$)** *δ* 7.47 (d, *J* = 7.9 Hz, 1H), 7.29 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.17 - 7.12 (m, 2H), 7.10 - 7.05 (m, 3H), 7.01 (dd, *J* = 9.9, 8.6 Hz, 2H), 5.65 (s, 1H), 4.49 (d, *J* = 8.8 Hz, 1H), 4.46 (d, *J* = 8.8 Hz, 1H), 2.31 (s, 3H), 2.25 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** *δ* 159.3, 144.4, 143.8, 141.4, 138.32, 138.26, 135.5, 132.9, 132.7, 129.9, 129.4, 129.2, 129.1, 128.6, 128.5, 127.1, 126.6, 126.2, 123.3, 121.8, 71.8, 70.1, 21.52, 21.49. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{25}H_{21}O_2NCl$ $[M+H]^+$ 402.1255, found 402.1256.

*5-chloro-2,3-bis(3-methoxyphenyl)spiro[indene-1,4'-oxazolidin]-2'-one (**4o**)*: mp = 205-208 °C. Yellow solid, (71.0 mg, 82 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 (d, J = 7.9 Hz, 1H), 7.34 - 7.24 (m, 4H), 7.20 (t, J = 8.0 Hz, 1H), 6.89 - 6.82 (m, 4H), 6.78 (s, 2H), 5.55 (s, 1H), 4.51 (d, J = 8.8 Hz, 1H), 4.48 (d, J = 8.8 Hz, 1H), 3.70 (s, 3H), 3.65 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.7, 159.6, 159.2, 144.3, 144.1, 143.7, 141.4, 135.7, 134.2, 133.9, 129.9, 129.8, 127.3, 123.4, 121.9, 121.6, 121.3, 114.7, 114.5, 114.4, 114.1, 71.8, 70.0, 55.2, 55.1. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{25}H_{21}O_4NCl$ $[M+H]^+$ 434.1154, found 434.1155.

*5-chloro-2,3-bis(3-fluorophenyl)spiro[indene-1,4'-oxazolidin]-2'-one (**4p**)*: mp = 236-239 °C. Yellow solid, (34.4 mg, 42 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (d, J = 7.9 Hz, 1H), 7.32 (ddt, J = 9.9, 7.9, 4.0 Hz, 3H), 7.24 (d, J = 1.8 Hz, 1H), 7.05 (pd, J = 8.7, 2.5 Hz, 4H), 6.99 - 6.93 (m, 2H), 6.08 (s, 1H), 4.52 (d, J = 8.9 Hz, 1H), 4.44 (d, J = 8.9 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.9 (d, J = 247.5 Hz), 162.7 (d, J = 247.5 Hz), 159.4, 144.0, 143.3, 141.1, 135.9, 134.51, 134.5 (d, J = 16.8 Hz), 130.7 (d, J = 8.1 Hz), 130.6 (d, J = 8.2 Hz), 127.8, 125.0 (d, J = 32.1 Hz), 124.9 (d, J = 32.0 Hz), 123.6, 121.9, 116.5 (d, J = 22.1 Hz), 116.0 (d, J = 4.5 Hz), 115.9, 115.8 (d, J = 2.9 Hz), 115.7, 71.6, 70.1. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{23}H_{15}O_2NF_2Cl$ $[M+H]^+$ 410.0754, found 410.0755.

*5-chloro-2,3-bis(2-fluorophenyl)spiro[indene-1,4'-oxazolidin]-2'-one (**4q**)*: mp = 213-215 °C. Yellow solid, (42.5 mg, 52 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, J = 8.0 Hz, 1H), 7.34 - 7.29 (m, 3H), 7.26 - 7.22 (m, 1H), 7.22 - 6.94 (m, 6H), 6.05 (s, 1H), 4.53 (d, J = 8.9 Hz, 1H), 4.48 (d, J = 8.9 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.1 (d, J = 246.4 Hz), 159.8 (d, J = 248.9 Hz), 159.4, 143.5, 143.4, 141.4, 135.7, 131.4, 130.94, 130.86, 130.7, 130.6, 127.5, 124.5 (d, J = 22.3 Hz), 124.4 (d, J = 22.2 Hz), 123.5, 122.1, 120.2 (d, J = 16.1 Hz), 120.0 (d, J = 16.4 Hz), 116.1 (d, J = 21.3 Hz), 116.0 (d, J = 22.4 Hz), 71.4, 70.6. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{23}H_{15}O_2NF_2Cl$ $[M+H]^+$ 410.0754, found 410.0754.

*5-chloro-2,3-di(thiophen-2-yl)spiro[indene-1,4'-oxazolidin]-2'-one (**4r**)*: mp = 187-189 °C. Yellow solid, (44.7 mg, 58 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.51 - 7.48 (m, 1H), 7.46 (d, J = 7.9 Hz, 1H), 7.34 (dd, J = 5.1, 0.9 Hz, 1H), 7.29 (dd, J = 7.9, 1.9 Hz, 1H), 7.26 (d, J = 1.6 Hz, 1H), 7.17 (d, J = 3.1 Hz, 3H), 7.02 (dd, J = 5.1, 3.7 Hz, 1H), 6.10 (s, 1H), 4.59 (d, J = 9.0 Hz, 1H), 4.50 (d, J = 9.0 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.2, 144.2, 144.0, 139.4, 135.9, 133.6, 133.5, 133.4, 133.1, 128.7, 128.3, 128.1, 127.9, 127.8, 127.5, 123.2, 121.7, 72.6, 69.6. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{19}H_{13}O_2NClS_2$ $[M+H]^+$ 386.0071, found 386.0070.

*5-chloro-2,3-di(thiophen-3-yl)spiro[indene-1,4'-oxazolidin]-2'-one (**4s**)*: mp = 175-178 °C. Yellow solid, (50.9 mg, 66 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.48 (d, J = 7.9 Hz, 1H), 7.46 - 7.39 (m, 2H), 7.38 (dd, J = 2.1, 1.2 Hz, 1H), 7.31 (dd, J = 7.9, 1.9 Hz, 1H), 7.27 - 7.26 (m, 2H), 6.99 (dd, J = 4.9, 1.2 Hz, 1H), 6.85 (dd, J = 5.1, 1.3 Hz, 1H), 5.37 (s, 1H), 4.54 (d, J = 8.9 Hz, 1H), 4.52 (d, J = 8.9 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.0, 144.3, 144.2, 138.9, 135.8, 135.5, 133.4, 132.8, 127.9, 127.7, 127.2, 126.6, 125.9, 125.0, 124.7, 123.2, 121.6, 72.5, 69.4. **HRMS (ESI)** Orbitrap-FT analyzer, m/z calcd. for $C_{19}H_{13}O_2NClS_2$ $[M+H]^+$ 386.0071, found 386.0070.

General Procedure for the H/D Scrambling Experiment. To a 15 mL screwed tube equipped with magnetic stir bar and a PTFE screw plug are added **1a** (32.2 mg, 0.20 mmol, 1equiv.), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol %) and NaOAc (32.8 mg, 2.0 equiv.). The screwed tube is transferred to a glovebox, and added with $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %), deuterated HFIP (0.6 mL) and HFIP (1 mL). After sealed with the screw plug, the screwed tube is taken out from the glovebox and the resulting solution is stirred at 100 °C for 15 h. The reaction mixture is cooled to r.t. and concentrated in vacuo, then the residue is dissolved in DCM and purified by column chromatography (silica gel, PE/EA=3:1)). The reaction product is subjected to ^1H NMR measurement.

General Procedure for the Synthesis of deuterated 4-phenyloxazol-2(3*H*)-one (1a-d_5) and the Kinetic Isotope Effect (KIE) Experiment.

1-(phenyl-d_5) ethan-1-one [13]: A solution of anhydrous carbon disulfide (CS_2, 10.0 mL) containing deuterated benzene (2.15 g, 25.6 mmol, 1.0 equiv.) and aluminum chloride ($AlCl_3$, 4.28 g, 32 mmol, 1.25 equiv.) are added to a 50 mL flask under N_2 atmosphere. To the mixture is dropwise added a solution of acetyl chloride (2.52 g, 32 mmol, 1.5 equiv.) in anhydrous CS_2 (10.0 mL) at 0 °C. The resulting mixture is allowed to warm up to r.t. and is stirred for 5 h. Then the mixture is heated to 50 °C for 3 h. After cooling to r.t., the resulting mixture is poured into ice water and extracted with DCM (3 × 50 mL). The organic layer is washed with saturated aqueous sodium carbonate (60 mL) and brine (40 mL), and then dried over Na_2SO_4. After concentration in vacuo, purified by column chromatography (silica gel, PE/EA=20:1) afforded *1-(phenyl-d_5) ethan-1-one* (2.59 g, 81%) as colorless oil.

4-(phenyl-d_5) oxazol-2(3H)-one [12]: To a stirred solution of 1-(phenyl-d_5) ethan-1-one (2.50 g, 20 mmol, 1.0 equiv.) and powdered potassium hydroxide (6.17 g, 110 mmol, 5.5 equiv.) in 50 mL methanol is added iodobenzene diacetate (7.73 g, 24 mmol, 1.2 equiv.) slowly at 0 °C. The reaction mixture is kept at room temperature until TLC indicated the total consumption of 1-(phenyl-d_5) ethan-1-one. After concentration of the reaction mixture, the residue is washed with water and extracted with EA (3 × 50 mL). The combined organic layer is evaporated under reduced pressure. The residue is dissolved in a mixture of 20 mL MeOH and 20 mL 2 M aqueous hydrochloric acid and then stirred overnight at r.t.. The product is collected with a glass dropper and then purified by column chromatography (silica gel, PE/EA=8:1) afforded 2-hydroxy-1-(phenyl-d_5) ethanone as a white solid which is used directly for the next step.

To a stirred solution of 2-hydroxy-1-(phenyl-d_5) ethanone (1.41 g, 10 mmol, 1equiv.) and KOCN (1.62 g, 20 mmol, 2.0 equiv.) in 60 mL THF is added HOAc (1.37 mL, 24 mmol, 2.4 equiv.) slowly at 50 °C. The reaction is further stirred at this temperature until TLC indicated the total consumption of 2-hydroxy-1-(phenyl-d_5) ethanone, and then poured into ice cooled H_2O and extracted with EA (3 × 50 mL). The organic layer is collected and concentrated in vacuo. Then the residue is purified by column chromatography (silica gel, PE/EA=3:1) to give 4-(phenyl-d_5)oxazol-2(3*H*)-one (1a-d_5) as a light yellow solid (1.26 g, 76% yield). mp = 166 - 169 °C. **^1H NMR (400 MHz, $CDCl_3$)** δ 10.67 (s, 1H), 7.14 (d, J = 1.5, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.4, 129.0, 128.7 -

128.2 (m), 128.2 - 128.0 (m), 126.0, 124.2 - 123.6 (m), 123.5. **HRMS (ESI)** TOF ananlyzer, m/z calcd. for $C_9H_3D_5O_2N$ $[M+H]^+$ 167.0863, found 167.0863.

To a 15 mL screwed tube equipped with magnetic stir bar and a PTFE screw plug are added **1a** (32.2 mg, 0.2 mmol, 1.0 equiv.), **1a-*d*$_5$** (33.2 mg, 0.2 mmol, 1.0 equiv.), **2a** (35.6 mg, 0.2 mmol, 1.0 equiv.), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol %) and NaOAc (32.8 mg, 0.4 mmol, 2.0 equiv.). The screwed tube is transferred to a glovebox, and added with $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %) and HFIP (1.5 mL). After sealed with the screw plug, the screwed tube is taken out from the glovebox and the resulting solution is stirred at 100 °C for 15 h. The reaction mixture is concentrated in vacuo, and the residue is dissolved in DCM and purified by column chromatography (silica gel, PE/EA=3:1). The reaction product is subjected to ^{1}H NMR measurement.

General Procedure for the Competition Experiment. To a 15 mL screwed tube equipped with magnetic stir bar and a PTFE screw plug are added **1b** (35.0 mg, 0.2 mmol, 1.0 equiv.), **1j** (45.8 mg, 0.2 mmol, 1.0 equiv.), **2a** (35.6 mg, 0.2 mmol, 1.0 equiv.), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol %) and NaOAc (32.8 mg, 0.4 mmol, 2.0 equiv.). The screwed tube is transferred to a glovebox, and added with $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %) and HFIP (1.5 mL). After sealed with the screw plug, the screwed tube is taken out from the glovebox and the resulting solution is stirred at 100 °C for 15 h. The reaction mixture is concentrated in vacuo, and the residue is dissolved in DCM and purified by column chromatography (silica gel, PE/EA=3:1). The reaction product is subjected to ^{1}H NMR measurement.

General Procedure for the Synthesis of 5a and 5b.

*3-Methyl-4-phenyloxazol-2(3H)-one (**5a**)*: Sodium hydride (96.0 mg, 60% w/w dispersion in mineral oil, 1.2 equiv.) is added portionwise to a solution of **1a** (322.1 mg, 2 mmol, 1.0 equiv.) in DMF (4 mL) at 0 °C and stirred for 45 min, then iodomethane (312.3 mg, 2.2 mmol, 1.1 equiv.) is added. The mixture is stirred at room temperature and indicated by TLC. After total consumption of **1a** (about 6 h), the reaction is quenched with water and extracted by EA. The organic layers are washed twice with 5 wt% aqueous LiCl solution to remove DMF. After additional washing with brine and drying over $MgSO_4$, the crude product is purified by column chromatography on silica gel (PE/EA=3:1). The title compound **5a** is obtained as a yellow solid in 90 % yield (315.1 mg).[14] mp = 89 - 92 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 - 7.45 (m, 3H), 7.39 - 7.35 (m, 2H), 6.84 (s, 1H), 3.24 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.4, 130.0, 129.5, 129.1, 128.1, 126.5, 123.7, 29.4. **HRMS (ESI)** FTICR analyzer, m/z Calcd. for $C_{10}H_{10}O_2N$: $[M+H]^+$, 176.0706. Found 176.0706.

*5-Methyl-4-phenyloxazol-2(3H)-one (**5b**)*: Propiophenone (2.68 g, 20 mmol, 1.0 equiv.), I_2 (1.02 g, 4 mmol, 20 mol%), and DMSO (20 mL) are stirred under air at 60 °C for 24 h as monitored by TLC. After cooling down to r.t., the solution is diluted with EA and washed with 0.1 mol/L $Na_2S_2O_3$ aqueous solution, extracted with EA three times, and evaporated under vacuum. The crude reaction mixture is purified by column chromatography on silica gel (eluent: PE/EA = 10:1) to get 2-hydroxy-1-phenylpropan-1-one (**5b'**) used for the next step immediately.[15] To a stirred solution of **5b'** (2.25 g, 15 mmol, 1.0 equiv.) and KOCN (2.43 g, 30 mmol, 2.0 equiv.) in 50 mL THF is added AcOH (2.16 g, 36 mmol, 2.4 equiv.) slowly at 50 °C. The reaction is further stirred until

total consumption of **5b'** indicated by TLC (generally overnight). The mixture is allowed to cool down to r.t., quenched with water (30 mL), extracted with EA (3 × 50 mL). The organic layers are combined, washed with saturated aqueous $NaHCO_3$ solution (50 mL), dried over $MgSO_4$, concentrated and purified by column chromatography on silica gel to give the desired products **5b** in 60% yield (1.58 g).[12] mp = 127 - 129 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 10.94 (s, 1H), 7.47 - 7.43 (m, 4H), 7.38 - 7.33 (m, 1H), 2.25 (s, 3H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 155.4, 133.0, 129.3, 128.2, 128.1, 126.3, 121.2, 11.7. **HRMS (ESI)** FTICR analyzer, m/z Calcd. for $C_{10}H_{10}O_2N$: $[M+H]^+$, 176.0706. Found 176.0706.

To a 15 mL screwed tube equipped with magnetic stir bar and a PTFE screw plug are added 3-Methyl-4-phenyloxazol-2(3*H*)-one (**5a**) or 5-Methyl-4-phenyloxazol-2(3*H*)-one (**5b**) (35.0 mg, 0.2 mmol, 1.0 equiv.), diphenylacetylene (**2a**, 53.5 mg, 0.3 mmol, 1.5 equiv.), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol %) and NaOAc (32.8 mg, 0.4 mmol, 2.0 equiv.). The screwed tube is transferred to a glovebox, and added with $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %) and HFIP (1.5 mL). After sealed with the screw plug, the screwed tube is taken out from the glovebox and the resulting solution is stirred at 100 °C for 15 h. The reaction mixture is concentrated in vacuo, and the residue is dissolved in DCM and purified by column chromatography (silica gel, PE/EA=3:1) to give 3'-methyl-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**6a**) or 5'-methyl-2,3-diphenylspiro[indene-1,4'-oxazolidin]-2'-one (**6b**). No **6a** is detected and **6b** is obtained as a yellow solid in 66 % yield (46.6 mg) with 1:0.36 as d.r. value for diastereoisomers. mp = 165 - 167 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 - 7.51 (m, 1H), 7.50 - 7.47 (m, 0.36H), 5.83 (s, 1H), 5.72 (s, 0.36H), 5.06 (q, J = 6.6 Hz, 1H), 4.65 (q, J = 6.4 Hz, 0.36H), 1.23 (d, J = 6.6 Hz, 3H), 1.05 (d, J = 6.4 Hz, 1.08H).

General Procedure for the Larger Scale Experiment. To a 50 mL screwed tube equipped with magnetic stir bar and a PTFE screw plug are added **1a** (1.13 g, 7.0 mmol, 1.0 equiv.), **2a** (1.87 g, 10.5 mmol, 1.5 equiv.), $[RhCp^*Cl_2]_2$ (129.8 mg, 0.21 mmol, 3 mol %) and NaOAc (1.15 g, 14.0 mmol, 2.0 equiv.). The screwed tube is transferred to a glovebox, and added with $AgSbF_6$ (288.5 mg, 0.84 mmol, 12 mol %) and HFIP (20 mL). After sealed with the screw plug, the screwed tube is taken out from the glovebox and the resulting solution is stirred at 100 °C for 15 h. The reaction mixture is concentrated in vacuo, and the residue is dissolved in DCM and purified by column chromatography (silica gel, PE/EA=3:1). The reaction product **3a** is obtained in 70 % yield (1.66 g, 4.9 mmol) as a yellow solid and further subjected to ^{1}H NMR measurement.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Crystallographic data and NMR spectra (PDF)

Crystallographic data of **3h** (CIF)

Crystallographic data of **4b** (CIF)

Sigle Crystal Information (CCDC)

3h: 1908968

4b: 1917788

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Notes

The authors declare no competing financial interest.

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