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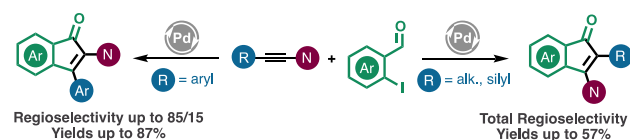
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Direct Access to 2,3-Disubstituted Amido-Indenones Through Annulation of 2-Iodobenzaldehydes with Ynamides.

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Supporting Information Placeholder



ABSTRACT: In this paper we report the annulation reaction between 2-iodobenzaldehyde derivatives and various ynamides. This palladium-catalyzed reaction leads to rare polysubstituted amino-indenones in good yields with a regioselectivity up to complete. Remarkably, a regiodivergent selectivity has been identified between aryl and alkyl or silyl ynamides, with the first leading mainly to 2-amido-indenones and the second to 3-amido-indenones.

1-Indenones and 1-indanones are valuable scaffolds found in many bioactive compounds (natural or synthetic) and for which various synthetic approaches are described (Figure 1).¹⁻⁴ However, when focusing on heteroatom-substituted indenones, it appears that far fewer methodologies are available, especially when different substituents are targeted in position 2 and 3.⁵ This is all the more true if one of the substituents is an amino group,^{6,7} which is quite surprising when you consider that nitrogen-based functionalities are ubiquitous in bioactive compounds. As illustration of these limitations, we can look at recent methods that have been reported for the synthesis of 2-amino-indenones (Figure 1 eq. A,^{7a} B^{7b} and C^{7c}). They often suffer a lack of versatility on the substituent of the nitrogen and/or the substituent in position 3. Thus, new routes to access these compounds (2- and 3-amino-indenones) which could particularly be modular at both positions (i.e. 2 and 3) remain desirable. Despite a great potential for the synthesis of 2,3-disubstituted indenone derivatives, annulations involving alkynes and 2-halo-benzaldehydes, first reported by Heck⁸ and then extended by Larock,⁹ remain moderately investigated and they are almost limited to carbon substituted, often symmetrical or with a strong dissymmetry in terms of steric hindrance (*t*-Bu vs primary alkyl for instance), internal alkynes. If we consider electron-rich alkynes bearing a heteroatom, a unique report including two examples with different yno ethers has been made by Zhu *et al.*¹⁰ In this context and based on our experience of carbonylation reactions applied to polarized alkynes,¹¹ we have decided to investigate this transformation using readily accessible ynamides¹² (*i.e.* alkynes substituted with an electron-depleted nitrogen) as this approach would represent a direct and versatile strategy to 2,3-disubstituted amido-indenones. However, while this reaction appeared to be mastered for non-polarized alkynes, some uncertainty remained with respect to its regioselectivity in the case of polarized C≡C triple bonds.

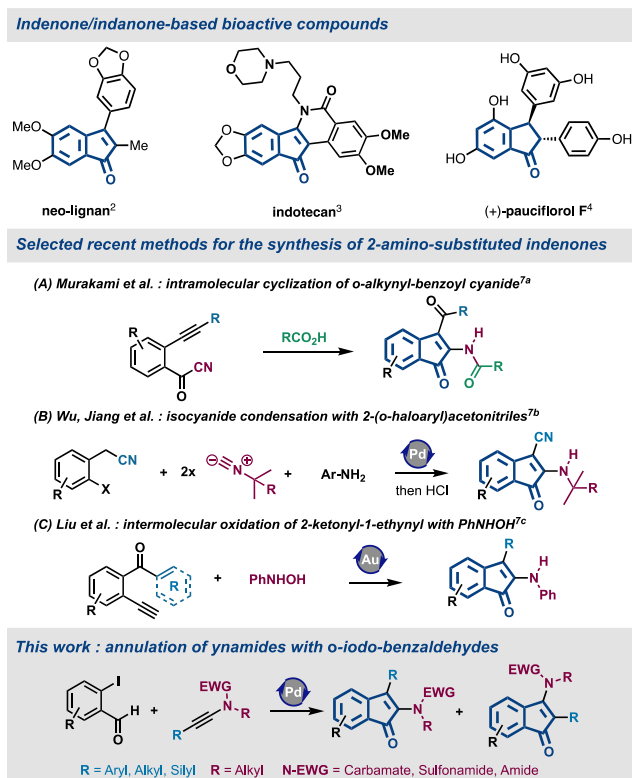
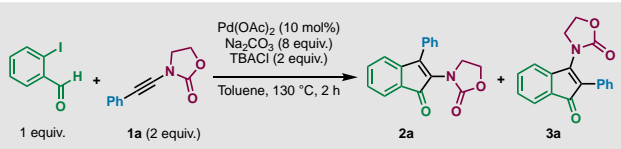


Figure 1 Selected examples of bioactive 2,3-disubstituted indenones and indanones, selected methods for the synthesis of 2-amino-indenones and our strategy.

To start our investigations, we focused our attention to ynamide **1a** bearing an oxazolidinone and a phenyl group. This substrate is readily available, robust and presents an interesting reactivity due to its electronic push-pull nature.

Inspired by Larock's report on palladium-catalyzed annulation of alkynes with *ortho*-halo-benzaldehydes⁹ and after optimization, our best reaction conditions were defined as follows: 1 equivalent of *ortho*-iodo-benzaldehyde, 2 equivalents of ynamide (0.1 M in toluene), 8 equivalents of Na₂CO₃, 2 equivalent of TBACl and 10 mol% of Pd(OAc)₂ at 130 °C for 2 h under argon atmosphere (**Table 1, Entry 1**). Under these conditions the reaction led to a mixture of the two regioisomers in 85% yield with an interesting **2a/3a** ratio of 70/30. The major isomer **2a** was determined by ¹H NMR NOESY experiments. Remarkably, this selectivity is opposite to the one described by Zhu for ymol ethers (*vide supra*) for which the 3-alkoxy compound was the only compound obtained. Control experiments showed that 1/ no reaction occurs in the absence of the catalyst (**Entry 2**), and 2/ both the conversion and the yield are lower when only 1 equivalent of **1a** is used (**Entry 3**). Then, in order to determine the effect of the catalyst on the yield or regioselectivity of the reaction, various Pd(II) based catalysts were tested but they led globally to similar results most of the time or to an erosion of either the selectivity or the yield.¹³ Notably, the direct use of various Pd(0) catalysts, such as tetrakis(triphenylphosphine) palladium, led to a complete degradation of the starting material (**Entry 4**). Notably, TBACl appeared to have an important role as conversion, selectivity and yield are negatively impacted in its absence (**Entry 5**). This can be explained by two potential effects: 1/ it is a phase transfer agent that can solubilize the inorganic base, 2/ it can play a stabilization role of the Pd(0) formed during the reaction after the reduction step of Pd(OAc)₂.¹⁴ Similarly, a lower amount of base (1 equivalent) or a lower temperature dramatically decreased the conversion of the reaction (**Entry 6 and 7** respectively).

Table 1 Optimized conditions and deviation effects^(a)



Deviations	Conv. [%] ^(b)	Ratio 2a/3a ^(b)	Yield [%] ^(c)
1 None	100	70/30	90
2 Without Pd(OAc) ₂	0	-	-
3 Only 1 equiv. of 1a	80	70/30	55
4 Pd(PPh ₃) ₄ as catalyst	100	n.d.	n.d. ^(d)
5 Without TBACl	80	60/40	58
6 2 equiv. of Na ₂ CO ₃	70	65/35	62
7 Reaction at 70 °C	85	50/50	66
8 NaOAc instead of Na ₂ CO ₃	100	60/40	54
9 Et ₃ N instead of Na ₂ CO ₃	100	n.d.	n.d. ^(d)
10 Acetonitrile as solvent	100	55/45	90
11 Dioxane as solvent	100	80/20	56

(a) See supporting information for details; (b) determined by ¹H NMR; (c) determined by ¹H NMR using CH₂BrCl as internal standard; (d) the reaction led to a complex mixture.

The change of base, inorganic or organic, (**Entry 8 and 9**) led to less good results both in terms of yield and selectivity than

our optimal conditions. Finally, the change of solvent gave interesting results. If acetonitrile led to an erosion of selectivity with a similar yield (**Entry 10**), the dioxane allowed to increase the **2a/3a** selectivity from 70/30 to 80/20 (**Entry 11**) but with a significantly lower yield of 56%. Of note, the change of halide on the aldehyde partner (*i.e.* *o*-bromo-benzaldehyde or *o*-chloro-benzaldehyde) led to a total inhibition of the reaction.

Once these optimized conditions were obtained, we decided to explore the scope and limitations of our methodology (**Figure 2**). First, keeping the oxazolidinone as the nitrogen moiety, we studied the effect of introducing various substituents on the aromatic ring. In general, all substitutions at various positions led to moderate to good results in terms of yields (47–85%) with **2/3** ratios from 60/40 to 85/15 (**2a/3a–2f/3f**). Remarkably, the introduction of a methyl group at the *ortho* position (**2f/3f**), significantly increasing the steric hindrance, led to the annulation compounds in a good 87% yield and a 65/35 **2f/3f** ratio.

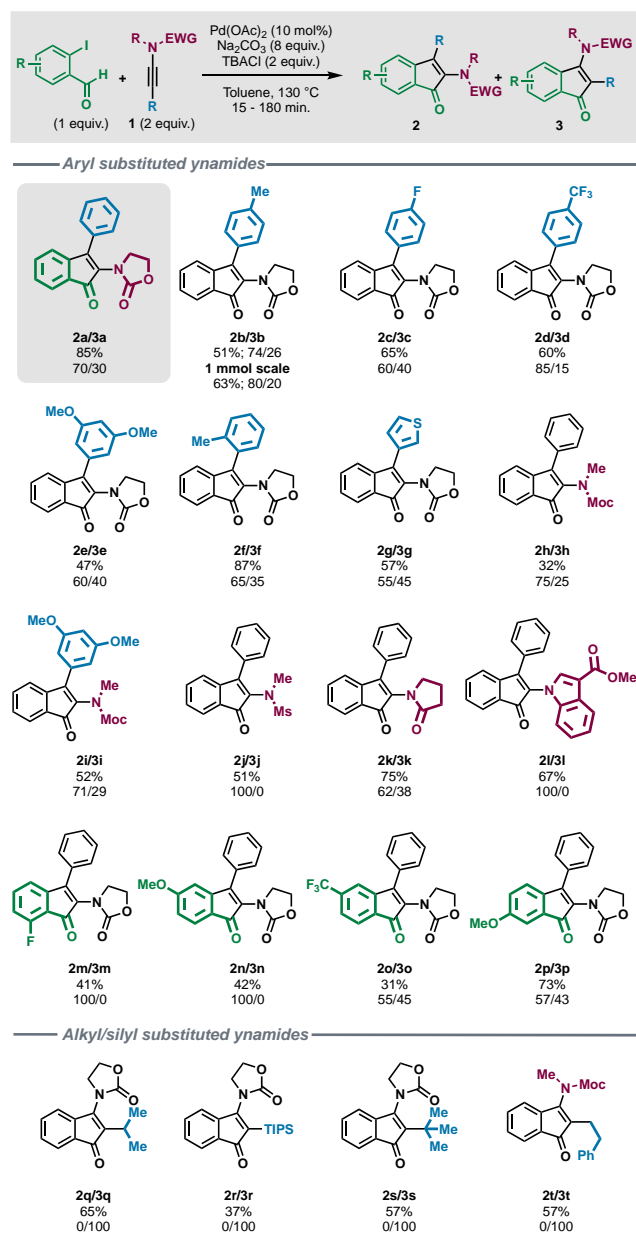


Figure 2 Scope of the reaction (isolated yields, **2/3** ratio determined by ¹H NMR, major isomer represented)

Nicely, an heteroaromatic such as a thiophene appeared to be compatible with this transformation and led to similar results as other aromatics (*i.e.*, 57% yield, **2g/3g** = 55/45). Then, we evaluated the effect of the substitutions on the nitrogen part of the ynamide. Pleasingly, substrates bearing an easily removable methyl carbamate (Moc) as electron-withdrawing group appeared compatible with this reaction (**2h** and **2i**). Ynamides substituted with sulfonamide, pyrrolidone or even indole led to good to very good regioselectivities in high yields (**2j/3j-2l/2l**). Then we looked at the influence of the iodo-benzaldehyde partner to the course of the reaction. Remarkably, electron-donating groups in *ortho* or *para* position to the aldehyde functionality led to a total regioselectivity to the corresponding products **2m** (*ortho*-fluoro) and **2n** (*para*-methoxy) (yields around 40%). At the opposite, an electron-withdrawing group on the *para* position such as a -CF₃ induced a significant decrease both in yield and regioselectivity. An electron-donating group, such as a methoxy, at the *meta* position induced a slight decrease in yield (73%) and a significant erosion of the selectivity (**2p/3p** = 57/43). Finally, we decided to look at ynamides bearing non-aromatic (alkyl or silyl) substituents on the alkyne and discovered surprisingly that, in all cases, the regioselectivity was complete for the 3-amido isomers (**3q**, **3r**, **3s**, **3t**) in yields from 37% to 65%.

Based on previous reports for this type of annulation,^{8,14} the mechanism of the reaction most likely involves a key carbopalladation step that directs the regioselectivity of the overall process (**Figure 3**). Our first idea was that the selectivity was potentially related to steric hindrance as reported by Larock. In this study, the most sterically demanding substituent is found in position 2 of resulting indenone. However, considering that compounds **2b/3b** (bearing a *p*-Me-Ph group) and **2f/3f** (*o*-Me-Ph), electronically equivalent but sterically very different, are obtained with similar ratios, this hypothesis could be dismissed. Thus, the difference in regioselectivity seems to be related to the polarization of the C≡C triple bond since the greater this character, the more selective the reaction is for isomer **2**. Indeed, when a simple phenyl is used as a substituent of the ynamide, leads to a selectivity **2a/3a** of 70/30. When the aromatic ring is electron-depleted (*p*-CF₃-Ph, **2d/3d**) the 2/3 ratio increases significantly to 85/15. On the other hand, when the ring is globally enriched (*p*-Me-Ph **2b/3b** or *p*-F-Ph **2c/3c** for example), the selectivity drops to a 2/3 ratio of 60/40. Equivalently, for the same aromatic substituent on the ynamide, when the nitrogen doublet is more available for conjugation with the C≡C triple bond, the selectivity increases. Thus, the **2j/3j** (sulfonamide) ratio is much higher than that obtained for **2a/3a** (carbamate) (100/0 and 70/30 respectively). Finally, when the C≡C appears weakly polarized, for instance in the case of ynamides bearing an alkyl or a silyl substituent, the selectivity is complete for the isomer **3** (**3q**, **3r**, **3s**, **3t**).

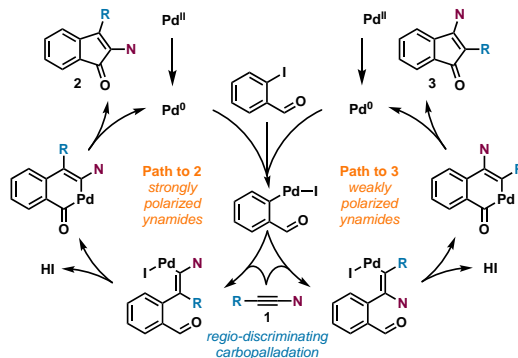


Figure 3 Proposed mechanisms for the formation of **2** and **3**

CONCLUSIONS

In conclusion, we have developed a direct access to 2,3-disubstituted amido-indenones thanks to a palladium-catalyzed annulation between various ynamides and *o*-iodobenzaldehydes. This reaction allows to reach unprecedented molecules in good to very good yields. In contrast to previous reports in the literature, the regioselectivity of the reaction, leading to 2 or 3 amido-indenones, seems to be mainly influenced by electronic parameters.

EXPERIMENTAL SECTION

General Experimental Consideration

Commercial reagents were used as received. All reactions were carried out under an atmosphere of argon in oven-dried sealed tubes. Toluene was freshly distilled over CaH₂ prior to use. Reaction progress was monitored by using thin-layer chromatography (TLC) with precoated silica on aluminium foils (0.25 mm thickness, Merck silica-gel (60-F₂₅₄)). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate. Flash column chromatography was performed on VWR silica gel (40–63 μm) using the indicated solvents, the solvent systems being indicated in v/v. Spectroscopic NMR and MS data were obtained using chromatographically homogeneous samples. ¹H NMR (400 or 500 MHz), ²⁹Si (80 or 99 MHz), ¹⁹F NMR (376 or 472 MHz) and ¹³C{¹H} NMR (101 or 126 MHz) spectra were recorded on Bruker Avance III HD 400 and 500 MHz instruments respectively in CDCl₃. All chemical shifts (δ) are reported in parts per million (ppm) and are referenced to residual solvent peaks in ¹H and ¹³C NMR experiments. Internal references of δ_H 7.26 and δ_C 77.16 were used for CDCl₃. ²⁹Si, ¹⁹F NMR spectra were referenced using the unified scale (derived from the ¹H spectrum) in agreement with IUPAC recommendations, and values were expressed against TMS, CFCl₃, and 85% H₃PO_{4(aq)} respectively. Infrared spectra were recorded using a PerkinElmer's Spectrum one™ spectrometer (ATR). Wavelengths (ν) are reported in cm⁻¹. High-resolution mass spectra (HRMS) were recorded with a TOF mass analyzer under ESI in positive ionization mode detection by the analytical facility at the Université de Strasbourg. Melting points were recorded on a Büchi Melting Point M-560.

General procedure for the annulation

2-iodobenzaldehyde (1 equiv., 0.2 mmol), ynamide **1** (2 equiv., 0.4 mmol), Na₂CO₃ (8 equiv., 1.6 mmol), tetrabutyl ammonium chloride (2 equiv., 0.4 mmol), palladium diacetate (10 mol%, 0.02 mmol) were placed in an oven-dried 5-mL sealed-tube (the use of sealed tube appeared to be critical in terms of yields). Then, freshly distilled toluene (4 mL) was added, and the vial was capped

under argon and heated at 130 °C until completion (monitoring by TLC). The reaction mixture was then filtered and concentrated under vacuum. The product was purified by flash column chromatography (see characterization for eluent) to obtain the targeted compounds **2** or **3**.

Product characterizations

3-(1-oxo-3-phenyl-1H-inden-2-yl)oxazolidin-2-one (2a) : Prepared following the General Procedure in 85% yield (0.21 mmol ; 61.9 mg) from 3-(2-phenylethynyl)-1,3-oxazolidin-2-one (0.5 mmol ; 93.6 mg) and 2-iodobenzaldehyde (0.25 mmol ; 58.0 mg). Dark red oil. Mixture of two isomers (72:28). **TLC** R_f : 0.30 (Cyclohexane/EtOAc = 60:40). **¹H NMR (400 MHz, CDCl₃)** δ 7.60 – 7.48 (m, 5H, α + β -isomer), 7.46 – 7.35 (m, 3H, α + β -isomer), 7.33 – 7.27 (m, 1H, α + β -isomer), 7.18 (dt, J = 7.2, 0.8 Hz, 1H, α -isomer), 4.46 (m, 2H, β -isomer), 4.42 (m, 2H α -isomer), 3.82 (m, 2H, α -isomer), 3.62 (m, 2H, β -isomer). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 192.7 (α -isomer), 156.4 (α -isomer), 154.1 (α -isomer), 142.8 (α -isomer), 140.4, 133.8 (α -isomer), 133.6 (β -isomer), 130.8 (β -isomer), 130.4 (α -isomer), 129.8 (α -isomer), 129.8 (β -isomer), 129.6 (α -isomer), 129.6 (β -isomer), 129.1 (x2 α -isomer), 129.0 (β -isomer), 128.8 (β -isomer), 128.6 (α -isomer), 128.3 (β -isomer), 127.7 (x2 α -isomer), 123.2 (α -isomer), 122.7 (β -isomer), 122.4 (β -isomer), 122.0 (α -isomer), 63.7 (β -isomer), 62.9 (α -isomer), 45.9 (α -isomer), 45.7 (β -isomer). β -isomer could not be fully characterized due to too low signals. **HRMS (ESI-TOF) m/z**: [M + Na]⁺ Calcd for C₁₈H₁₃NO₃Na 314.0788; Found 314.0790.

3-(1-oxo-3-(p-tolyl)-1H-inden-2-yl)oxazolidin-2-one (2b) : Prepared following the General Procedure in 51% yield (0.13 mmol ; 38.9 mg) from 3-[2-(4-methylphenyl)ethynyl]-1,3-oxazolidin-2-one (0.50 mmol ; 100.0 mg) and 2-iodobenzaldehyde (0.25 mmol ; 58.0 mg). Dark red oil. Mixture of two isomers (74:26). **TLC** R_f : 0.30 (Cyclohexane/EtOAc = 60:40). **¹H NMR (400 MHz, CDCl₃)** δ 7.50 (td, J = 9.2, 5.7 Hz, 3H, α + β -isomer), 7.44 – 7.27 (m, 3H, α + β -isomer), 7.25 – 7.16 (m, 1H, α + β -isomer), 7.17 – 7.00 (m, 1H, α + β -isomer), 4.44 (m, 2H, α + β -isomer), 3.80 (dd, J = 8.8, 7.1 Hz, 2H, α -isomer), 3.64 (t, J = 7.9 Hz, 2H, β -isomer), 2.43 (s, 3H, α -isomer), 2.39 (s, 3H, β -isomer). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 194.1 (β -isomer), 192.6 (α -isomer), 156.5 (α -isomer), 155.0 (β -isomer), 154.2 (α -isomer), 150.9 (β -isomer), 142.7 (α -isomer), 140.9 (α -isomer), 138.9 (α -isomer), 133.7 (α -isomer), 133.6 (β -isomer), 129.8 (x2, α -isomer), 129.6 (α -isomer), 129.5 (α -isomer), 129.4 (x2, β -isomer), 129.3 (α -isomer), 129.1 (x2, β -isomer), 128.9 (β -isomer), 127.8 (β -isomer), 127.7 (x2, α -isomer), 122.5 (β -isomer), 122.3 (β -isomer), 123.0 (α -isomer), 122.0 (α -isomer), 62.9 (α -isomer), 62.9 (β -isomer), 45.8 (α -isomer), 45.6 (β -isomer), 21.6 (α -isomer), 21.4 (β -isomer). β -isomer could not be fully characterized due to too low signals. **HRMS (ESI-TOF) m/z**: [M + Na]⁺ Calcd for C₁₉H₁₅NO₃Na 328.0944; Found 328.0941

3-(3-(4-fluorophenyl)-1-oxo-1H-inden-2-yl)oxazolidin-2-one (2c) : Prepared following the General Procedure in 65% yield (0.13 mmol ; 40.0 mg) from 3-[2-(4-fluorophenyl)ethynyl]-1,3-oxazolidin-2-one (0.40 mmol ; 82.1 mg) and 2-iodobenzaldehyde (0.20 mmol ; 46.4 mg). Orange oil. Mixture of two isomers (61:39). **TLC** R_f : 0.30 (Cyclohexane/EtOAc = 60:40). **¹H NMR (400 MHz, CDCl₃)** δ 7.63 – 7.54 (m, 1H, α + β -isomer), 7.54 – 7.48 (m, 1H, α + β -isomer), 7.45 – 7.34 (m, 2H, α + β -isomer), 7.30 (td, J = 7.0, 3.0 Hz, 1H, α + β -isomer), 7.21 (t, J = 8.6 Hz, 1H, α + β -isomer), 7.16 – 7.09 (m, 2H, α + β -isomer), 4.52 – 4.35 (m, 2H, α + β -isomer), 3.86 (dd, J = 8.8, 7.1 Hz, 2H, α -isomer), 3.64 (t, J = 7.8 Hz, 2H, β -isomer). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 193.8 (β -isomer), 192.6 (α -isomer), 163.7 (d, J = 251.7 Hz, α -isomer), 162.8 (d, J = 249.8 Hz, β -isomer), 156.3 (α -isomer),

154.9 (β -isomer), 153.0 (α -isomer), 151.5 (β -isomer), 142.6 (α -isomer), 140.2 (β -isomer), 133.9 (α -isomer), 133.7 (β -isomer), 131.6 (x2, d, J = 8.75 Hz, (β -isomer)), 130.4 (α -isomer), 129.9 (x2 d, J = 8.5 Hz α -isomer), 129.7 (α -isomer), 129.6 (β -isomer), 128.8 (α -isomer), 128.2 (β -isomer), 126.8 (d, J = 3.6 Hz, α -isomer), 125.7 (d, J = 3.4 Hz, β -isomer), 124.3 (β -isomer), 123.2 (α -isomer), 122.6 (β -isomer), 122.5 (β -isomer), 121.8 (α -isomer), 116.3 (x2, d, J = 21.7 Hz, α -isomer), 115.8 (x2, d, J = 21.7 Hz, β -isomer), 63.7 (β -isomer), 63.0 (α -isomer), 45.8 (α -isomer), 45.7 (β -isomer). **¹⁹F NMR (377 MHz, CDCl₃)** δ -108.9, (α -isomer) - 111.5 (β -isomer). **HRMS (ESI-TOF) m/z**: [M + Na]⁺ Calcd for C₁₈H₁₂FN₃Na 332.0693; Found 332.0690.

3-(1-oxo-3-(4-(trifluoromethyl)phenyl)-1H-inden-2-yl)oxazolidin-2-one (2d) : Prepared following the General Procedure in 60% yield (0.05 mmol ; 17.0 mg) from 3-{2-[4-(trifluoromethyl)phenyl]ethynyl}-1,3-oxazolidin-2-one (0.16 mmol ; 40.0 mg) and 2-iodobenzaldehyde (0.08 mmol ; 18.2 mg). Yellow-orange oil. Mixture of two isomers (85:15). **TLC** R_f : 0.28 (Cyclohexane/EtOAc = 60:40). **¹H NMR (400 MHz, CDCl₃)** δ 7.78 (d, J = 8.6 Hz, 2H), 7.73 – 7.64 (m, 2H), 7.53 (dt, J = 7.1, 0.9 Hz, 1H), 7.39 (td, J = 7.6, 1.3 Hz, 1H), 7.32 (ddd, J = 7.9, 7.0, 1.0 Hz, 1H), 7.13 – 7.06 (m, 1H), 4.50 – 4.41 (m, 2H), 4.00 – 3.92 (m, 2H). **¹³C{¹H} NMR (126 MHz, CDCl₃)** δ 192.6, 155.9, 151.7, 134.6, 134.17, 132.0, 131.7, 129.8 (x2), 128.9, 128.4, 128.1 (x2), 126.0 (q), 123.5, 121.7, 63.0, 45.8. *The ¹⁹F signal could not be detected.* **¹⁹F NMR (377 MHz, CDCl₃)** δ - 62.9. **HRMS (ESI-TOF) m/z**: [M + Na]⁺ Calcd for C₁₉H₁₂F₃NO₃Na 382.0661; Found 382.0656.

3-(3-(3,5-dimethoxyphenyl)-1-oxo-1H-inden-2-yl)oxazolidin-2-one (2e) : Prepared following the General Procedure in 47% yield (0.09 mmol ; 33.0 mg) from 3-[2-(3,5-dimethoxyphenyl)ethynyl]-1,3-oxazolidin-2-one (0.40 mmol ; 98.9 mg) and 2-iodobenzaldehyde (0.20 mmol ; 46.4 mg). Orange oil. Mixture of two isomers (74:26). **TLC** R_f : 0.30 (Cyclohexane/EtOAc = 60:40). **¹H NMR (400 MHz, CDCl₃)** δ 7.58 – 7.51 (m, 1H, α + β -isomer), 7.48 – 7.36 (m, 1H, α + β -isomer), 7.36 – 7.30 (m, 1H, α + β -isomer), 7.26 – 7.22 (m, 1H, α + β -isomer), 6.75 (d, J = 2.2 Hz, 2H, α -isomer), 6.60 (t, J = 2.3 Hz, 1H, α -isomer), 6.56 (d, J = 2.3 Hz, 2H, β -isomer), 6.51 (t, J = 2.3 Hz, 1H, β -isomer), 4.51 (dd, 2H, α -isomer), 4.46 (dd, 2H, β -isomer), 3.74 (dd, 2H, α + β -isomer) 3.85 (s, 6H, α -isomer), 3.83 (s, 6H, β -isomer). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 193.7 (β -isomer), 192.6 (α -isomer), 161.2 (x2 α -isomer), 160.8 (x2 β -isomer), 156.6 (α -isomer), 154.9 (β -isomer), 154.4 (α -isomer), 151.9 (β -isomer), 142.6 (α -isomer), 140.1 (β -isomer), 133.9 (α -isomer), 133.6 (β -isomer), 132.3 (α -isomer), 131.6 (β -isomer), 130.6 (β -isomer), 129.6 (α -isomer), 128.8 (α -isomer), 128.4 (β -isomer), 125.2 (α -isomer), 123.2 (α -isomer), 122.9 (β -isomer), 122.4 (β -isomer), 122.1 (α -isomer), 107.9 (x2 β -isomer), 105.7 (x2 α -isomer), 102.3 (α -isomer), 100.9 (β -isomer), 63.8 (β -isomer), 63.0 (α -isomer), 55.6 (x2 α -isomer), 55.5 (x2 β -isomer), 46.0 (α -isomer), 45.7 (β -isomer). **HRMS (ESI-TOF) m/z**: [M + Na]⁺ Calcd for C₂₀H₁₇NO₅Na 374.0999; Found 374.0994.

3-(1-oxo-3-(o-tolyl)-1H-inden-2-yl)oxazolidin-2-one (2f) : Prepared following the General Procedure in 87% yield (0.22 mmol ; 66.4 mg) from 3-[2-(2-methylphenyl)ethynyl]-1,3-oxazolidin-2-one (0.50 mmol ; 100.6 mg) and 2-iodobenzaldehyde (0.25 mmol ; 58.0 mg). Dark red oil. Mixture of two isomers (65:35). **TLC** R_f : 0.30 (Cyclohexane/EtOAc = 60:40). **¹H NMR (400 MHz, CDCl₃)** δ 7.50 – 7.38 (m, 1H), 7.31 – 7.15 (m, 6H), 6.73 (t, J = 6.6 Hz, 1H), 4.27 (t, J = 8.0 Hz, 2H), 3.68 (t, J = 7.9 Hz, 2H), 2.24 (s, 3H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 192.3, 155.4, 152.7, 143.7, 136.0, 134.1, 130.8, 130.8, 130.0, 129.6, 129.2, 128.4, 127.7, 126.1, 123.0, 121.6, 62.9, 45.4,

20.1. Only the α -isomer was isolated. **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{19}H_{15}NO_3Na$ 374.0944; Found 328.0941.

3-(1-oxo-3-(thiophen-3-yl)-1H-inden-2-yl)oxazolidin-2-one (2g): Prepared following the General Procedure in 57% yield (0.15 mmol ; 43.9 mg) from 3-[2-(thiophen-3-yl)ethynyl]-1,3-oxazolidin-2-one (0.52 mmol ; 100 mg) and 2-iodobenzaldehyde (0.26 mmol ; 60.0 mg). Red solid. Mixture of two isomers (55:45). **TLC** R_f : 0.30 (Cyclohexane/EtOAc = 60:40). **1H NMR (400 MHz, $CDCl_3$) δ** 7.88 (dd, $J = 2.9, 1.3$ Hz, 1H, α -isomer), 7.68 (dd, $J = 3.0, 1.2$ Hz, 1H, β -isomer), 7.56 – 7.45 (m, 2H, $\alpha + \beta$ -isomer), 7.40 (qdd, $J = 4.2, 2.8, 1.2$ Hz, 2H, $\alpha + \beta$ -isomer), 7.36 – 7.27 (m, 2H, $\alpha + \beta$ -isomer), 4.59 – 4.52 (m, 2H, β -isomer), 4.51 – 4.45 (m, 2H, α -isomer), 3.93 – 3.85 (m, 2H, α -isomer), 3.82 – 3.76 (m, 2H, β -isomer). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ** 193.9 (β -isomer), 192.6 (α -isomer), 156.7 (α -isomer), 155.1 (β -isomer), 149.7 (β -isomer), 149.4 (α -isomer), 142.4 (α -isomer), 140.7 (β -isomer), 133.8 (β -isomer), 133.8 (α -isomer), 131.2 (α -isomer), 130.5 (β -isomer), 129.7 (α -isomer), 129.4 (α -isomer), 129.4 (α -isomer), 129.2 (β -isomer), 128.1 (α -isomer), 127.7 (β -isomer), 127.4 (β -isomer), 127.0 (α -isomer), 126.9 (α -isomer), 126.8 (β -isomer), 125.9 (β -isomer), 123.0 (α -isomer), 122.6 (β -isomer), 122.1 (α -isomer), 122.0 (β -isomer), 63.7 (β -isomer), 63.0 (α -isomer), 45.9 (α -isomer), 45.3 (β -isomer). **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{16}H_{11}NO_3SNa$ 320.0352; Found 320.0333.

Methyl(1-oxo-3-phenyl-1H-inden-2-yl)carbamate (2h): Prepared following the general procedure in 32% yield (0.09 mmol ; 24.8 mg) from methyl *N*-methyl-*N*-(2-phenylethynyl)carbamate (0.53 mmol ; 100 mg) and 2-iodobenzaldehyde (0.26 mmol ; 61.3 mg). Orange solid. Mixture of two isomers (75:25). **TLC** R_f : 0.30 (Cyclohexane/EtOAc = 60:40). **1H NMR (400 MHz, $CDCl_3$) δ** 7.56 – 7.50 (m, 2H, $\alpha + \beta$ -isomer), 7.45 – 7.39 (m, 4H, $\alpha + \beta$ -isomer), 7.37 – 7.27 (m, 2H, $\alpha + \beta$ -isomer), 7.18 (d, $J = 7.3$ Hz, 1H, β -isomer), 7.04 (d, $J = 7.3$ Hz, 1H, α -isomer), 3.67 (s, 3H, α -isomer), 3.59 (s, 3H, β -isomer), 3.09 (s, 3H, α -isomer), 2.94 (s, 3H, β -isomer). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ** 194.6 (α -isomer), 192.8 (β -isomer), 156.2 (β -isomer), 155.1 (α -isomer), 143.0 (β -isomer), 142.1 (α -isomer), 133.6 (β -isomer), 133.4 (α -isomer), 131.0 (β -isomer), 129.2 (α -isomer), 129.2 (β -isomer), 129.0 (α -isomer), 128.9 (x2, α -isomer), 128.9 (β -isomer), 128.6 (x2, α -isomer), 128.6 (α -isomer), 128.5 (α -isomer), 127.6 (α -isomer), 123.1, (α -isomer) 122.4 (α -isomer), 120.2 (α -isomer), 53.4 (α -isomer), 53.1 (β -isomer), 36.0 (α -isomer) 29.7 (β -isomer). *β -isomer could not be completely identified due to too low signals.* **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{18}H_{15}NO_3Na$ 316.0944; Found 316.0943.

Methyl (3-(3,5-dimethoxyphenyl)-1-oxo-1H-inden-2-yl)methylcarbamate (2i): Prepared following the general procedure in 52% yield (0.42 mmol ; 147.3 mg) from methyl *N*-[2-(3,5-dimethoxyphenyl)ethynyl]-*N*-methylcarbamate (1.60 mmol ; 400.0 mg) and 2-iodobenzaldehyde (0.80 mmol ; 186.2 mg). Mixture of two isomers (71:29). **Isomer α (2i)**: 37% yield (0.30 mmol ; 104.9 mg) Orange oil. **TLC** R_f : 0.25 (Cyclohexane/EtOAc = 60:40). **IR (neat) ν_{max}** 2953, 2840, 1705, 1589, 1452, 1333, 1203, 1151, 1056, 766 cm^{-1} . **1H NMR (400 MHz, $CDCl_3$) δ** 7.46 (dt, $J = 7.1, 1.0$ Hz, 1H), 7.34 (td, $J = 7.5, 1.2$ Hz, 1H), 7.25 – 7.20 (m, 1H), 6.97 (d, $J = 7.3$ Hz, 1H), 6.54 (d, $J = 2.3$ Hz, 2H), 6.39 (t, $J = 2.3$ Hz, 1H), 3.73 (s, 6H), 3.61 (s, 6H), 3.05 (s, 3H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ** 194.4, 161.2, 160.7 (x2), 142.0, 133.4, 131.6, 130.6, 129.3, 126.5, 122.4, 120.2, 106.9 (x2), 105.6, 100.9, 55.5, 55.4 (x2), 53.4. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calcd for $C_{20}H_{20}NO_5$ 354.1335; Found 354.1342. **Isomer β (3i)**: 15% yield (0.12 mmol ; 42.5 mg) Orange oil. **TLC** R_f : 0.20 (Cyclohexane/EtOAc = 60:40). **1H NMR (500 MHz, $CDCl_3$) δ** 7.56 – 7.47 (m, 1H), 7.36 (td, $J = 7.5, 1.3$ Hz, 1H), 7.28

(d, $J = 7.9$ Hz, 1H), 7.21 (d, $J = 7.3$ Hz, 1H), 6.63 (d, $J = 2.3$ Hz, 2H), 6.56 (t, $J = 2.3$ Hz, 1H), 3.82 (s, 6H), 3.62 (s, 3H), 2.96 (s, 3H). **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ** 161.22, 142.7, 133.71, 132.73, 129.19, 123.09, 121.67, 105.64 (x2), 101.92, 55.52 (x2), 53.16, 29.74. *β -isomer could not be completely identified due to too low signals.*

***N*-methyl-*N*-(1-oxo-3-phenyl-1H-inden-2-yl)methanesulfonamide (2j)**: Prepared following the General Procedure in 51% yield (0.13 mmol ; 39.9 mg) from *N*-methyl-*N*-(2-phenylethynyl)methanesulfonamide (0.5 mmol ; 104 mg) and 2-iodobenzaldehyde (0.25 mmol ; 58 mg). Red oil. **TLC** R_f : 0.35 (Cyclohexane/EtOAc = 60:40). **IR (neat) ν_{max}** 2922, 2853, 1712, 1456, 1335, 1147, 958, 753 cm^{-1} . **1H NMR (400 MHz, $CDCl_3$) δ** 7.75 – 7.70 (m, 2H), 7.58 – 7.47 (m, 4H), 7.43 – 7.36 (m, 2H), 7.33 – 7.28 (m, 1H), 7.19 (dt, $J = 7.2, 0.9$ Hz, 1H), 3.23 (s, 3H), 2.98 (s, 3H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ** 194.7, 156.7, 143.1, 134.3, 132.9, 131.1, 130.7, 130.2, 129.4 (x2), 129.2, 128.5 (x2), 123.5, 122.8, 40.2, 37.5. **HRMS (ESI-TOF) m/z:** $[M + K]^+$ Calcd for $C_{17}H_{15}NO_3SK$ 352.0404; Found 352.0416.

1-(1-oxo-3-phenyl-1H-inden-2-yl)pyrrolidin-2-one (2k): Prepared following the General Procedure in 75% yield (0.19 mmol ; 54.2 mg) from 1-(2-phenylethynyl)pyrrolidin-2-one (0.50 mmol ; 92.6 mg) and 2-iodobenzaldehyde (0.25 mmol ; 58.0 mg). Mixture of two isomers (62:38). **Isomer α (2k)**: Prepared in 57% yield (0.14 mmol ; 45.8 mg) Orange oil. **TLC** R_f : 0.25 (Cyclohexane/EtOAc = 60:40). **1H NMR (400 MHz, $CDCl_3$) δ** 7.51 (ddt, $J = 15.5, 6.4, 1.9$ Hz, 6H), 7.43 – 7.29 (m, 2H), 7.17 (d, $J = 7.2$ Hz, 1H), 3.55 (t, $J = 7.0$ Hz, 2H), 2.45 (t, $J = 8.0$ Hz, 2H), 2.21 – 2.02 (m, 3H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ** 192.8, 175.5, 153.8, 143.0, 133.6, 131.2, 130.2, 129.3, 129.2, 128.9 (x2), 127.5 (x2), 123.1, 121.6, 48.7, 30.7, 29.7, 19.3. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calcd for $C_{19}H_{16}NO_2$ 290.1175; Found 290.1174. **Isomer β (3k)**: Prepared in 18% yield (0.05 mmol ; 8.4 mg) Orange oil. **TLC** R_f : 0.20 (Cyclohexane/EtOAc = 60:40). **1H NMR (400 MHz, $CDCl_3$) δ** 7.35 (dd, $J = 13.6, 6.3$ Hz, 2H), 7.21 (d, $J = 6.3$ Hz, 3H), 7.19 – 7.09 (m, 3H), 7.07 (d, $J = 7.4$ Hz, 1H), 3.28 (t, $J = 6.9$ Hz, 2H), 2.46 (t, $J = 7.9$ Hz, 2H), 2.05 – 1.96 (m, 2H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ** 194.3, 153.2, 141.0, 133.5, 130.6, 130.1, 129.4 (x2), 129.3, 128.6, 128.5 (x2), 128.2, 126.6, 122.4, 122.3, 48.7, 31.5, 20.1. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calcd for $C_{19}H_{16}NO_2$ 290.1175; Found 290.1174.

2-(3-acetyl-1H-indol-1-yl)-3-phenyl-1H-inden-1-one (2l): Prepared following the General Procedure in 67% yield (0.10 mmol ; 37.9 mg) from methyl 1-(2-phenylethynyl)-1H-indole-3-carboxylate (0.30 mmol ; 82.6 mg) and 2-iodobenzaldehyde (0.15 mmol ; 34.8 mg). Dark-red solid. **TLC** R_f : 0.30 (Cyclohexane/EtOAc = 85:15). **IR (neat) ν_{max}** 2919, 1704, 1537, 1537, 1453, 1198, 1151, 746 cm^{-1} . **1H NMR (400 MHz, $CDCl_3$) δ** 8.16 (dt, $J = 8.0, 1.0$ Hz, 1H), 7.80 (s, 1H), 7.71 – 7.60 (m, 1H), 7.53 – 7.45 (m, 1H), 7.42 – 7.28 (m, 7H), 7.25 – 7.13 (m, 1H), 7.03 (ddd, $J = 8.3, 7.1, 1.2$ Hz, 1H), 6.89 (dt, $J = 8.4, 0.9$ Hz, 1H), 3.91 (s, 3H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ** 191.5, 165.1, 151.1, 142.4, 136.0, 134.4, 134.1, 130.8, 130.1, 129.9, 129.2 (x2), 128.9, 128.7, 127.9 (x2), 126.6, 123.8, 123.2, 122.5, 122.5, 121.5, 111.9, 110.3, 51.2. **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{25}H_{17}NO_3Na$ 402.1101; Found 402.1117.

3-(7-fluoro-1-oxo-3-phenyl-1H-inden-2-yl)oxazolidin-2-one (2m): Prepared following the General Procedure in 41% yield (0.10 mmol ; 31.7 mg) from 3-(2-phenylethynyl)-1,3-oxazolidin-2-one (0.50 mmol ; 93.6 mg) and 2-fluoro-6-iodobenzaldehyde (0.25 mmol ; 62.5 mg). Dark-Red oil. **TLC** R_f : 0.25 (Cyclohexane/EtOAc = 60:40). **IR (neat) ν_{max}** 2921, 1751, 1712, 1620, 1468, 1408, 1225, 797, 698 cm^{-1} . **1H NMR (400 MHz, $CDCl_3$) δ** 7.58 – 7.46 (m, 5H), 7.37 (ddd, $J = 8.6, 7.3, 5.1$ Hz, 1H), 7.01 –

6.92 (m, 2H), 4.49 – 4.34 (m, 2H), 3.91 – 3.80 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 188.8, 157.7 (d, $J = 265.1$ Hz), 156.2, 153.0 (d, $J = 4.9$ Hz), 144.7 (d, $J = 3.7$ Hz), 136.3 (d, $J = 8.5$ Hz), 130.5, 130.5, 129.1 (x2), 127.7 (x2), 119.1, 118.9, 118.5 (d, $J = 2.4$ Hz), 114.0 (d, $J = 13.0$ Hz), 63.0, 45.8. ^{19}F NMR (376 MHz, CDCl_3) δ -112.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{13}\text{FNO}_3$ 310.0873; Found 310.0878.

3-(5-methoxy-1-oxo-3-phenyl-1H-inden-2-yl)oxazolidin-2-one (2n): Prepared following the General Procedure in 42% yield (0.07 mmol ; 22.6 mg) from 3-(2-phenylethynyl)-1,3-oxazolidin-2-one (0.34 mmol ; 64.2 mg) and 2-iodo-4-methoxybenzaldehyde (0.17 mmol ; 45 mg). Orange oil. TLC R_f : 0.30 (Cyclohexane/EtOAc = 60:40). IR (neat) ν_{max} 2922, 2852, 1753, 1706, 1594, 1474, 1220, 1092, 1027, 751 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.57 – 7.42 (m, 7H), 6.73 (d, $J = 2.2$ Hz, 1H), 6.66 (dd, $J = 8.0, 2.2$ Hz, 1H), 4.45 – 4.39 (m, 2H), 3.86 (d, $J = 2.7$ Hz, 1H), 3.83 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 191.2, 164.6, 156.3, 151.5, 145.5, 130.8, 130.2, 129.0 (x2), 128.6, 127.8 (x2), 125.3, 121.6, 111.6, 110.5, 63.0, 55.8, 45.9. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{16}\text{NO}_4$ 322.1073; Found 322.1069.

3-(1-oxo-3-phenyl-5-(trifluoromethyl)-1H-inden-2-yl)oxazolidin-2-one (2o): Prepared following the General Procedure in 31% yield (0.08 mmol ; 28 mg) from 3-(2-phenylethynyl)-1,3-oxazolidin-2-one (0.50 mmol ; 93.6 mg) and 2-iodo-4-(trifluoromethyl)benzaldehyde (0.25 mmol ; 75 mg). Orange oil. Mixture of two isomers (55:45). TLC R_f : 0.25 (Cyclohexane/EtOAc = 60:40). ^1H NMR (400 MHz, CDCl_3) δ 8.08 – 8.02 (β -isomer, m, 1H), 7.61 ($\alpha+\beta$ -isomer, 2H), 7.59 – 7.55 ($\alpha+\beta$ -isomer, m, 5H), 7.50 (α -isomer, 1H), 7.38 ($\alpha+\beta$ -isomer, s, 2H), 7.32 ($\alpha+\beta$ -isomer, m, 1H), 7.29 – 7.26 ($\alpha+\beta$ -isomer, m, 2H), 7.24 – 7.14 ($\alpha+\beta$ -isomer, m, 2H), 6.79 (α -isomer, 1H), 4.55 – 4.33 ($\alpha+\beta$ -isomer m, 4H), 4.11 – 3.99 (β -isomer m, 2H), 3.88 – 3.80 (α -isomer, m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 191.2 (α -isomer), 165.4 (α -isomer), 156.0 (α -isomer), 152.7 (β -isomer), 143.7 (α -isomer), 143.6 (β -isomer), 138.5 (α -isomer), 135.7 (α -isomer), 135.7 (β -isomer) 134.8 (α -isomer), 133.1 (β -isomer), 131.6 (β -isomer), 130.9 (β -isomer), 130.9 (α -isomer), 130.6 (β -isomer), 130.1 (α -isomer), 130.0 (x2, β -isomer), 129.8 (β -isomer), 129.5 (β -isomer), 129.4 (x2, α -isomer), 128.6 (β -isomer), 128.4 (x2, β -isomer), 128.3 (α -isomer), 128.3 (β -isomer), 127.6 (x2, α -isomer), 127.1 (α -isomer, q, $J = 4.3$ Hz), 124.3 (β -isomer, q, $J = 3.8$ Hz), 123.1 (α -isomer), 118.3 (α -isomer, q, $J = 3.5$ Hz), 100.0 (β -isomer), 67.8 (β -isomer), 63.1 (α -isomer), 55.7 (β -isomer), 45.7 (α -isomer). β -isomer could not be completely characterized due to too low signals. The CF_3 signal could not be detected. ^{19}F NMR (376 MHz, CDCl_3) δ -62.8, -63.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{12}\text{F}_3\text{NO}_3$ 360.0842; Found 360.0814.

3-(6-methoxy-1-oxo-3-phenyl-1H-inden-2-yl)oxazolidin-2-one (2p): Prepared following the General Procedure in 73% yield (0.18 mmol ; 58 mg) from 3-(2-phenylethynyl)-1,3-oxazolidin-2-one (0.50 mmol ; 93.6 mg) and 2-iodo-5-methoxybenzaldehyde (0.25 mmol ; 65.5 mg). Red oil. Mixture of two isomers (57:43). **Isomer α (2p)**: Prepared in 43% (0.10 mmol ; 33 mg). Red oil. TLC R_f : 0.28 (Cyclohexane/EtOAc = 60:40). ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 8.8$ Hz, 1H), 7.54 (s, 1H), 7.32 – 7.27 (m, 2H), 7.24 – 7.19 (m, 2H), 6.45 (dd, $J = 8.7, 3.0$ Hz, 1H), 6.27 (d, $J = 3.0$ Hz, 1H), 4.44 (t, $J = 9.5$ Hz, 2H), 4.04 (t, $J = 9.5$ Hz, 2H), 3.28 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 165.8, 159.0, 139.9, 139.8, 139.4, 135.7, 131.6, 130.0 (x2), 128.4 (x2), 127.9, 127.2, 117.4, 115.5, 89.6, 67.6, 55.7, 54.9. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{16}\text{NO}_4$ 322.1073; Found 322.1070. **Isomer β (3p)**: Prepared in 30% (0.08 mmol ; 25 mg). Orange oil. TLC R_f : 0.24 (Cyclohexane/EtOAc = 60:40). ^1H

NMR (400 MHz, CDCl_3) δ 7.61 – 7.55 (m, 2H), 7.51 (dtd, $J = 6.7, 4.8, 1.9$ Hz, 2H), 7.41 – 7.31 (m, 1H), 7.16 – 7.05 (m, 2H), 6.78 (dd, $J = 8.1, 2.5$ Hz, 1H), 4.54 – 4.36 (m, 2H), 3.84 (s, 3H), 3.78 (d, $J = 8.8$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 192.5, 161.5, 156.7, 155.9, 139.4, 134.1, 131.1, 130.9, 130.5, 129.0 (x2), 127.7 (x2), 123.2, 116.2, 111.2, 62.8, 55.8, 46.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{16}\text{NO}_4$ 322.1073; Found 322.1070.

3-(2-isopropyl-1-oxo-1H-inden-3-yl)oxazolidin-2-one (3q): Prepared following the General Procedure in 65% yield (0.16 mmol ; 41.8 mg) from 3-(3-methylbut-1-yn-1-yl)-1,3-oxazolidin-2-one (0.50 mmol ; 76.6 mg) and 2-iodobenzaldehyde (0.25 mmol ; 58.0 mg). Yellow oil. TLC R_f : 0.25 (Cyclohexane/EtOAc = 60:40). IR (neat) ν_{max} 2965, 2922, 1752, 1704, 1407, 1204, 1101, 1033, 764 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, $J = 7.1$ Hz, 1H), 7.34 (td, $J = 7.5, 1.2$ Hz, 1H), 7.22 (t, $J = 7.4$ Hz, 1H), 7.04 (d, $J = 7.3$ Hz, 1H), 4.61 (t, $J = 7.9$ Hz, 2H), 4.09 – 4.01 (m, 2H), 2.79 (p, $J = 6.9$ Hz, 1H), 1.29 (d, $J = 7.0$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 195.5, 155.2, 149.2, 140.8, 137.2, 133.4, 130.7, 128.9, 122.2, 119.7, 63.2, 46.7, 25.7, 20.6 (x2). HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{Na}$ 280.0944; Found 280.0939.

3-(1-oxo-2-(triisopropylsilyl)-1H-inden-3-yl)oxazolidin-2-one (3r): Prepared following the General Procedure in 37% yield (0.09 mmol ; 34.4 mg) from 3-[2-[tris(propan-2-yl)silyl]ethynyl]-1,3-oxazolidin-2-one (0.50 mmol ; 133.7 mg) and 2-iodobenzaldehyde (0.25 mmol ; 58.0 mg). Dark red oil. TLC R_f : 0.27 (Cyclohexane/EtOAc = 60:40). IR (neat) ν_{max} 2922, 2866, 1759, 1702, 1556, 1399, 1054, 715 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.50 (dt, $J = 7.1, 1.0$ Hz, 1H), 7.39 (td, $J = 7.5, 1.2$ Hz, 1H), 7.30 (td, $J = 7.4, 0.9$ Hz, 1H), 7.04 (dt, $J = 7.4, 0.9$ Hz, 1H), 4.59 (dd, $J = 8.4, 7.1$ Hz, 2H), 4.01 (dd, $J = 8.5, 7.1$ Hz, 2H), 1.49 (sept, $J = 7.5$ Hz, 3H), 1.12 (d, $J = 7.5$ Hz, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 199.7, 165.8, 155.9, 141.8, 133.5, 133.4, 132.4, 129.7, 122.8, 119.1, 63.1, 48.3, 19.1 (x6), 12.0 (x3). ^{29}Si NMR (80 MHz, CDCl_3) δ 2.60. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Li}]^+$ Calcd for $\text{C}_{21}\text{H}_{30}\text{NO}_3\text{SiLi}$ 377.2058; Found 372.2068.

3-(2-(tert-butyl)-1-oxo-1H-inden-3-yl)oxazolidin-2-one (3s): Prepared following the General Procedure in 57% yield (0.14 mmol ; 38.7 mg) from 3-(3,3-dimethylbut-1-yn-1-yl)-1,3-oxazolidin-2-one (0.5 mmol ; 83.6 mg) and 2-iodobenzaldehyde (0.25 mmol ; 58.0 mg). Yellow solid. TLC R_f : 0.30 (Cyclohexane/EtOAc = 60:40). IR (neat) ν_{max} 2958, 2920, 1748, 1706, 1604, 1412, 1071, 766 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.43 (dt, $J = 7.0, 0.9$ Hz, 1H), 7.39 – 7.30 (m, 1H), 7.22 (ddd, $J = 7.8, 7.1, 0.9$ Hz, 1H), 6.94 (dd, $J = 7.2, 0.8$ Hz, 1H), 4.67 – 4.51 (m, 2H), 4.09 (dt, $J = 9.3, 8.4$ Hz, 1H), 3.78 (td, $J = 8.8, 5.4$ Hz, 1H), 1.35 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 195.8, 155.9, 147.6, 142.8, 141.2, 133.8, 130.1, 129.0, 122.8, 118.2, 77.3, 62.8, 47.1, 33.7, 29.0 (x3). HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{Na}$ 294.1101; Found 294.1100.

Methyl methyl(1-oxo-2-phenethyl-1H-inden-3-yl)carbamate (3t): Prepared following the General Procedure in 57% yield (0.14 mmol ; 45.8 mg) from methyl *N*-methyl-*N*-(4-phenylbut-1-yn-1-yl)carbamate (0.50 mmol ; 108.6 mg) and 2-iodobenzaldehyde (0.25 mmol ; 58.0 mg). Red oil. TLC R_f : 0.40 (Cyclohexane/EtOAc = 60:40). IR (neat) ν_{max} 2971, 1702, 1451, 1340, 1154, 1047, 750 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.46 (dt, $J = 7.1, 0.9$ Hz, 1H), 7.36 – 7.26 (m, 2H), 7.25 – 7.13 (m, 5H), 6.88 (d, $J = 7.2$ Hz, 1H), 3.73 (d, $J = 1.5$ Hz, 3H), 3.02 (s, 3H), 2.83 (q, $J = 8.7$ Hz, 2H), 2.57 (t, $J = 7.7$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 196.3, 191.1, 156.5, 154.8, 142.3, 141.3, 133.3, 130.8, 130.2, 128.6, 128.5 (x4), 126.1, 122.2, 53.4,

35.8, 33.8, 25.4. **HRMS (ESI-TOF) m/z:** [M + H]⁺ Calcd for C₂₀H₂₀NO₃ 322.1438; Found 322.1417.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Optimization studies, experimental procedures, characterization data, and NMR spectra for all new compounds (PDF)

DATA AVAILABILITY STATEMENT

The data underlying this study are available in the published article and its online supplementary material.

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