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Stereodivergent Synthesis of Trisubstituted Enamides: Direct Access to Both Pure Geometrical Isomers.

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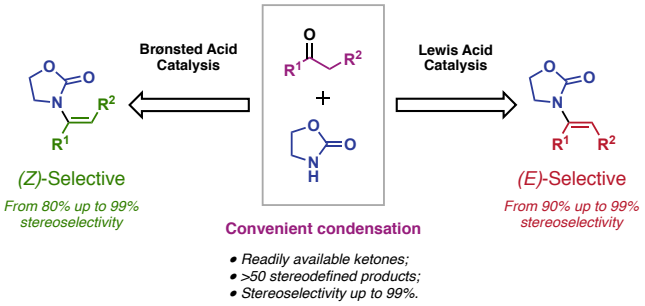


ABSTRACT: A stereodivergent strategy has been developed to access either *(E)*- or *(Z)*- isomers of trisubstituted enamides. Starting from an extensive range of ketones, it was possible to synthesize and isolate the desired pure isomer by switching the reaction conditions. Lewis Acid activation enables the formation of the *(E)*-isomers in high stereoselectivity (>90:10) and good yields. On the other hand, the use of a Brønsted acid allows the preparation of the *(Z)*-isomers, again in high selectivity (up to 99:1), with moderate yields.

Introduction

Enamides are a very versatile class of compounds in organic synthesis. [1] Their motif can be found in many bioactive and natural products [2] due to their high stability compared to the more unstable enamines.[3] The polarization of the double bond and the presence of the nitrogen atom confer them a reactivity that spans over a wide range; such as asymmetric hydrogenation via transition metal catalysis, cycloadditions, cyclopropanations and even nucleophilic additions. [4] The most widely applicable methodologies to synthesize enamides involve couplings with Cu and Pd in catalytic amount,[5] but other valuable methods have been recently developed using ynamides as substrates.[6] Coupling methodologies and other recent strategies for the synthesis of disubstituted enamides show in most of the cases good stereoselectivity. [7] For trisubstituted enamides instead, the access to pure isolated *(Z)*- or *(E)*-isomers becomes more challenging, especially for α,β substitutions. In the last few years, the Zhu group achieved remarkable results via a Pd-catalyzed arylation and alkynylation of ynamides. [8] Successively, a similar alkynylation and the carboxylation of ynamides were also successfully developed. [9] One of the latest methodology, reported by Maulide and co-workers, showed good results in the stereoselective synthesis of α,β-disubstituted enamides via formation of a keteniminium ion intermediate. [10]

However, in spite of the availability of different preparative methodologies, a general and simple method to obtain diasteromerically pure enamides is yet to be achieved. In contrast to the state of the art, an ideal approach would couple a carbonyl compound with an amide or a carbamate (the simplest retrosynthetic disconnection) avoiding the need for tailored substrates and elaborate synthetic pathways.

Since the 1980s, condensation reactions to synthesize enamides and derivatives have been extensively investigated, for example using Brønsted acids. [11] Among the most recent methodologies, the results obtained using titanium-based Lewis acids were notable. [12] The Touré group developed a synthesis of sterically hindered enamides obtaining high regio- and stereoselectivity.[13] Despite the promising results, this work was mainly limited to the condensation of the more reactive aldehydes and to access exclusively the geometrical *(E)*-isomers.

In this context, we wanted to extend the usefulness of condensation reactions to the less reactive ketones, tar-

geting a rapid access to the synthesis of both *(E)*- and *(Z)*-enamide isomers.

We herein demonstrate two simple strategies that allow the diastereoselective synthesis of either of the diastereomeric trisubstituted enamide by switching the reaction conditions starting from a common, readily available substrate. (Figure **1**)

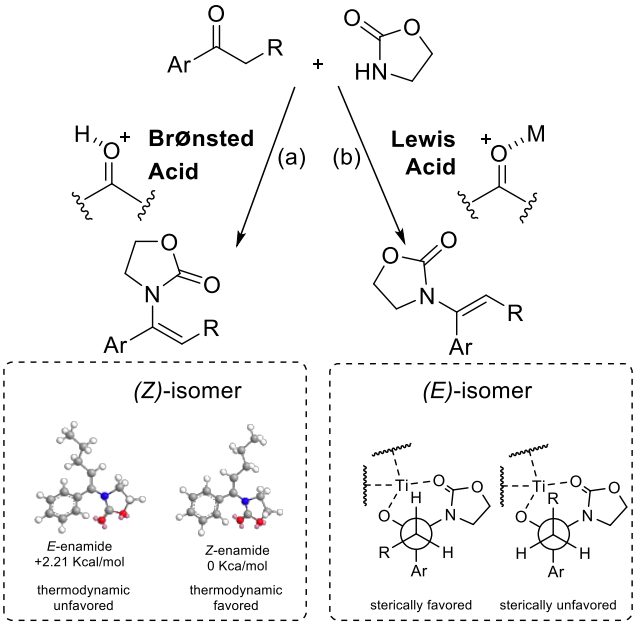
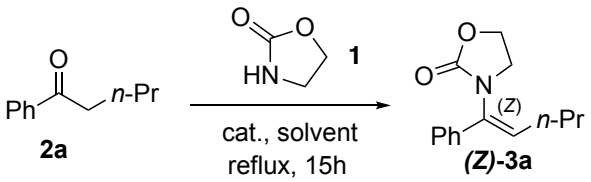


Figure 1. Condensation of ketones to the desired enamides isomer.

Results and Discussion

Preliminary screenings using oxazolidinone **1** and substrate **2a** were performed according to the existing literature procedures available for the condensation of aldehydes. [13-14] Carbonyl activation via Brønsted acid catalysis was used to synthesize the *(Z)*-isomer (Figure **1**, pathway **a**). This reaction is likely to follow the thermodynamic pathway and can be considered as an equilibrium process between a carbonyl compound and the corresponding enamide, which leads to the more stable (*Z*)-isomer of the product (for computational details see SI). On the other hand, a combination of $TiCl_4$ and Et_3N was employed to access to the *(E)*-isomer of the product (Figure **1**, pathway **b**). The Ti-NEt_3 adduct is assumed to first coordinate to the carbonyl oxygen activating the carbonyl group for reaction with oxazolidinone **1** to yield a Ti-coordinated carbinol amide. This intermediate then follows the E_2-elimination mechanism in the more sterically favored conformation affording the *E*-isomer of the enamide. For the first transformation, different solvents and Brønsted acids were screened under refluxing conditions (Table **1**). Benzene and 10 mol% of *p*-TSA gave the best results in terms of selectivity (11:89 *E/Z*) (entry 5), though toluene showed higher conversion (50%)(entry 6).

Table 1. Screening of Brønsted acid conditions for synthesis of (*Z*)-enamides.



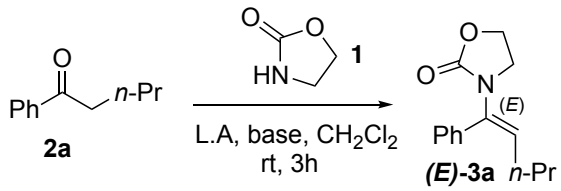
Entry	catalyst (mol%)	Oxazolidinone (equiv)	solvent	d.r. [*E:Z*]	conv. [%]
1	H_2SO_4(10)	2	toluene	22:78	4
2	CSA[a](10)	2	toluene	25:75	16
3	*p*-TSA[b](10)	2	toluene	15:85	40
4	*p*-TSA(10)	2	$PhCF_3$	21:79	35
5	*p*-TSA(10)	2	Benzene	11:89	30
6[c]	*p*-TSA(10)	3	toluene	15:85	50
7[d]	*p*-TSA(10)	3	toluene	-	nr

(a) CSA= Camphorsulfonic acid. (b) *p*-TSA = *para*-toluenesulfonic acid. (c) Reaction refluxed for 36 h. (d) Addition of molecular sieves 3Å.

We could observe significant amounts of unreacted starting material **2a** and oxazolidinone **1**, indicating the possibility of an equilibrium reaction. However, the addition of molecular sieves and other dehydrating agents was detrimental (entry 7 and SI). Meanwhile, the second method was also optimized (Table **2**). A screening of Lewis acid revealed that the combination of $TiCl_4$ and Et_3N was the more efficient catalytic couple (entry 3). [13] The initial conditions involved the use of the oxazolidinone **1** as the limiting reagent, giving 38% of conversion. Increasing the oxazolidinone amount to 2 equivalents, the conversion increased to 44% and with 3 equivalents it reached up to 55% (entries 4 and 5).

Also in this case the reaction resulted to be extremely selective (97:3 *E/Z*) and in the crude ^{1}H NMR only the signals of the starting ketone **2** and corresponding product **3** could be detected (see SI). A kinetic study revealed that the reaction rate was high at the beginning, reaching 40% of conversion in the first 10 minutes, and then drastically slowing down, reaching the final 55% of ketone consumption in the following hours. For this reason, different strategies of addition of the reagents were explored (see SI), but the results could not be significantly

Table 2. Screening of Lewis acid conditions for the synthesis of (*E*)-enamides.

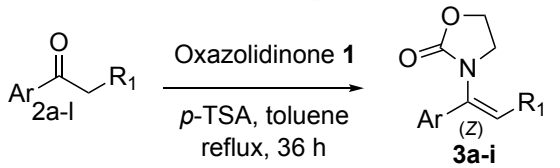


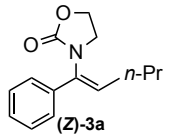
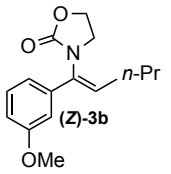
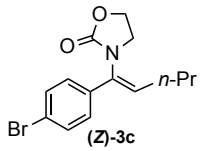
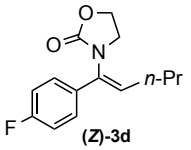
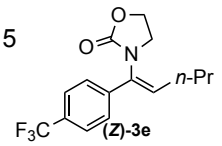
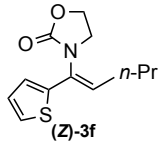
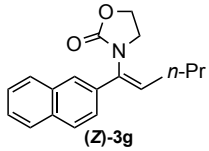
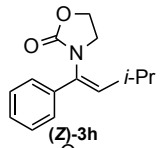
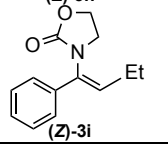
Entry	Oxazolidinone (equiv)	L.A. (equiv)	Base (equiv)	d.r. [*E:Z*]	conv. [%]
1	0.9	$AlCl_3$(1.2)	-	-	nr
2	0.9	$TiCl_4$(1.2)	-	-	nr
3	0.9	$TiCl_4$(1.2)	Et_3N(5)	98:2	38
4	2	$TiCl_4$(1.2)	Et_3N(5)	97:3	44
5	3	$TiCl_4$(1.2)	Et_3N(5)	97:3	55
6	3	$TiCl_4$(2.4)	Et_3N(10)	96:4	50
7[a]	3	$TiCl_4$(1.2)	Et_3N(5)	96:4	38

(a) Addition of molecular sieves 3Å.

improved. With the best conditions in hands, we started to explore the scope of these two stereoselective transformations. Firstly, ketones bearing an aryl group and an alkyl chain respectively in the α and β positions were investigated. Different substituents on the aryl were tested (Table 3, entries 2-5), showing comparable results for electron donating and electron withdrawing groups (for more examples see SI). The thiophene substituent was well tolerated (entry 6) and the naphthalene group gave impressive selectivity (entry 7, see SI). The alkyl chain on the β carbon was also varied, showing an increment of the diastereomeric ratio for the bulkier *i*-propyl substituent and a decrement for smaller groups (entries 8, 9 and more examples with d.r. in SI). Although the yields obtained in these reactions are not particularly high, the reactions are very clean and the unreacted starting material can easily be recovered. In most of the cases the untouched ketone can be recovered and corrected yields based on the real amount of reacted ketones are also reported (column 5, Table **3**). The same substrates were also tested under Lewis acid conditions (Table **4**). Noteworthy, this second pathway showed a perfect

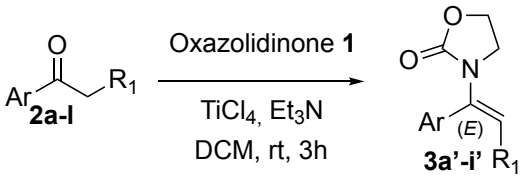
Table 3. Substrate scope for *(Z)*-enamides.

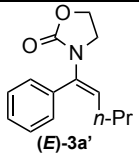
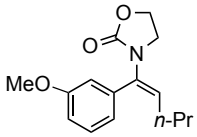
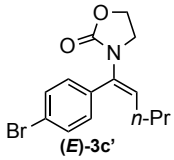
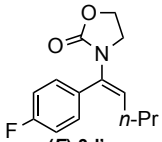
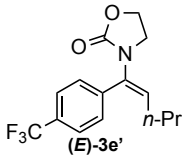
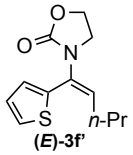
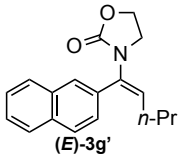
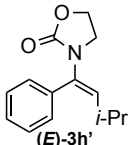
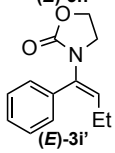


Entry	Enamide	Yield[a] [%]	Recovered s.m.[b][%]	Corrected Yield[c][%]
1	 (*Z*)-3a	33	49	65
2	 (*Z*)-3b	21	70	70
3	 (*Z*)-3c	18	64	50
4	 (*Z*)-3d	24	70	80
5	 (*Z*)-3e	20	70	67
6	 (*Z*)-3f	14	72	50
7	 (*Z*)-3g	20	61	51
8	 (*Z*)-3h	30	67	91
9	 (*Z*)-3i	30	44	54

(a) Isolated *(Z)*-enamide (>99:1). (b) Isolated amount of ketones after purification. (c) Yield based on recovered starting material.

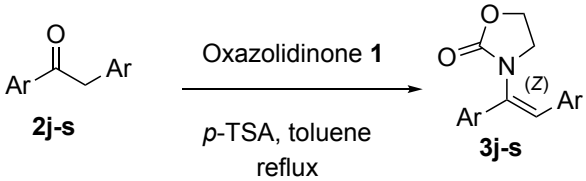
Table 4. Substrate scope for *(E)*-enamides.



Entry	Enamide	Yield[a] [%]	Recovered s.m.[b][%]	Corrected Yield[c][%]
1	 (*E*)-3a'	48	44	86
2	 (*E*)-3b'	20	67	60
3	 (*E*)-3c'	31	64	86
4	 (*E*)-3d'	33	43	58
5	 (*E*)-3e'	20	61	51
6	 (*E*)-3f'	24	34	37
7	 (*E*)-3g'	33	59	80
8	 (*E*)-3h'	30	69	97
9	 (*E*)-3i'	40	55	89

(a) Isolated *(E)*-enamide (>99:1). (b) Isolated amount of ketone after purification. (c) Yield based on recovered starting material.

Table 5. Substrate scope for α,β-diaryl (Z)-enamides.



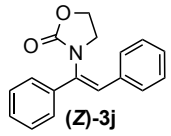
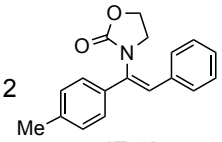
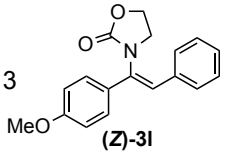
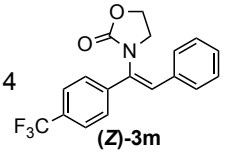
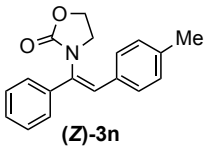
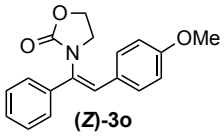
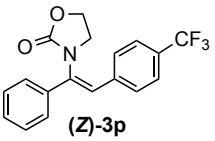
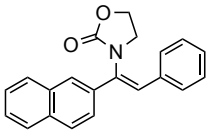
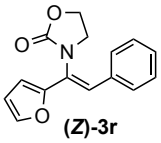
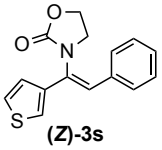
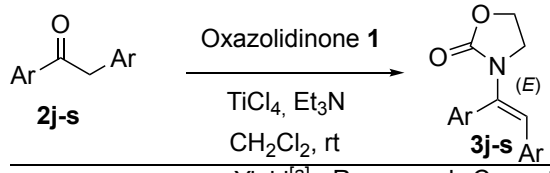
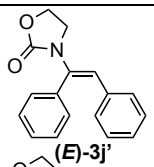
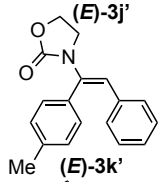
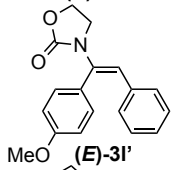
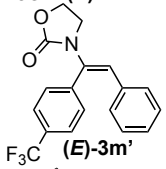
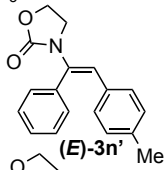
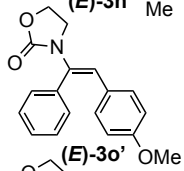
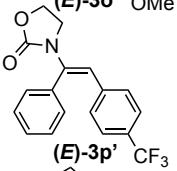
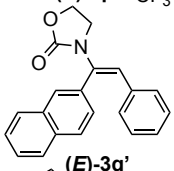
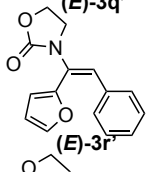
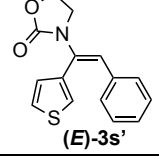
Entry	Enamide	Yield[a] [%]	Recovered s.m.[b][%]	Corrected Yield[c][%]
1	 (*Z*)-3j	10	85	67
2	 (*Z*)-3k	15	80	75
3	 (*Z*)-3l	18	74	69
4	 (*Z*)-3m	17	77	74
5	 (*Z*)-3n	16	80	80
6	 (*Z*)-3o	15	76	63
7	 (*Z*)-3p	14	84	88
8	 (*Z*)-3q	20	77	87
9	 (*Z*)-3r	16	68	50
10	 (*Z*)-3s	12	70	40

Table 6. Substrate scope for α,β-diaryl *(E)*-enamides.



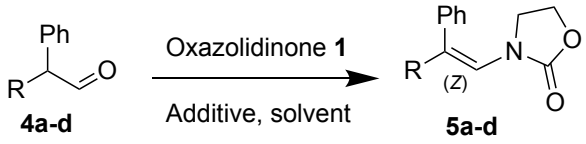
Entry	Enamide	Yield[a] [%]	Recovered s.m.[b][%]	Corrected Yield[c][%]
1	 (*E*)-3j'	30	68	94
2	 Me (*E*)-3k'	40	55	89
3	 MeO (*E*)-3l'	45	49	88
4	 F_3C (*E*)-3m'	38	56	86
5	 (*E*)-3n' Me	37	56	66
6	 (*E*)-3o' OMe	34	52	71
7	 (*E*)-3p' CF_3	32	78	73
8	 (*E*)-3q'	39	58	93
9	 (*E*)-3r'	30	50	60
10	 (*E*)-3s'	20	62	52

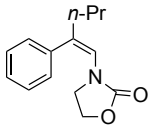
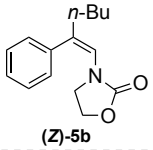
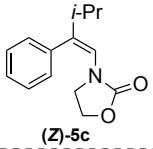
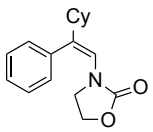
stereocontrol for most of the ketones with a benzene ring in the α position (entry 2-5 and 8-9, see SI). A somewhat lower selectivity was found both for the thiophene substituent and, conversely to the *p*-TSA methodology, the naphthalene moiety. In the same way as for the first pathway, it was possible to recover the starting material and both isolated and corrected yields are reported.

To further expand the scope of the reaction, other classes of unsymmetrical ketones were also included. Ketones with two aryl substituents were screened in both conditions, without any further optimization. The simplest biphenyl ketone (Table **5**, entry 1) gave a lower conversion and isolated yield compared to the previous class (Table **2**), but a similar selectivity in favor of the stable *(Z)*-isomer (see SI). Substituents on the α ring produced a slightly increment in terms of reactivity, with the same selectivity (entries 2-4). The same trend of reactivity was detected for ketones with a *para*-substituted β ring (entries 5-7). The naphthyl ring gave the best result (entry 8) and heteroaromatic compounds were again well tolerated.

The results obtained for the synthesis of the corresponding *(E)*-isomers were more successful, giving ex-

Table 7. Substrate scope for β,β-disubstituted *(Z)*-enamides.



Entry	Enamide	Method	d.r. [*E*:*Z*]	Yield[a] [%]
1	 (*Z*)-5a	$TiCl_4$	8:92	50
2		*p*-TSA	29:71	28
3	 (*Z*)-5b	$TiCl_4$	2:98	40
4		*p*-TSA	30:70	38
5	 (*Z*)-5c	$TiCl_4$	1:99	50
6		*p*-TSA	10:90	60
7	 (*Z*)-5d	$TiCl_4$	1:99	51
8		*p*-TSA	5:95	61

(a) Isolated yield of the pure major isomer (ratio >99:1).

cellent selectivity and even higher reactivity of the α aryl alkyl ketones, with an average yield of 35% (Table **6**, SI). In this case as well, all the starting materials **2** were recovered from the respective reactions, and the corrected yields (up to 94%) show the efficiency of these reactions, which minimize the waste of compounds.

Finally we tested the disubstituted aldehydes **4**, since previous results aiming to the *(E)*-isomers had shown bad selectivity. [13] However, for this class of substrates the two methodologies converged to give the *(Z)*-isomers (Table **7**, NOE experiments to verify the enamide geometry are reported in the SI). Increasing the bulkiness of the R group, $TiCl_4$ catalyzed reactions reached perfect level of selectivity, improving the previous results obtained with Brønsted acid catalysis.[14] In the cases of *n*-propyl and *n*- butyl groups the reactions also resulted in a higher isolated yield (entries 1 and 2, SI), but for *i*-propyl and cyclohexyl substituents the method with *p*-TSA was more effective (entries 3 and 4).

Experimental section

All reagents were used as supplied commercially without further purification. Chromatographic separations were performed on Kiesel gel 60 H silica gel (particle size: 0.063-0.100 mm) or Brockmann I, activated. Thin layer chromatography (TLC) was performed on aluminum plates coated with Kieselgel 60 (0.20 mm, UV254) and visualized under ultraviolet light (ν = 254 nm). ^{1}H NMR spectra were recorded on a Bruker 400 or 500 at 400/500 MHz in $CDCl_3$ and referenced internally to the residual $CHCl_3$ peak (7.26 ppm). ^{13}C NMR spectra were recorded at 75/125 MHz in $CDCl_3$ and referenced to the central peak of $CDCl_3$ (77.0 ppm). Chemical shifts are reported in ppm (δ scale). HRMS data were obtained using a Bruker MicroTOF-Q II instrument operation at ambient temperature.

General procedure for preparation of α-Aryl-alkyl Ketones 2b-h

Grignard reagent (15 mmol, 1.5 equiv.) was slowly added to a solution of cyano (-CN) (10 mmol, 1.0 equiv.) aromatic compounds in dry THF(30 mL) at 0°C. The reaction was allowed to stir at room temperature for 16 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution, and 1M HCl was added and the mixture was stirred for 1 h. The mixture was extracted with Et_2O (3x100 ml). The combined organic phases were combined and with washed brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to afford the crude products which then were purified by column chromatography on silica gel [pentane/ ethyl acetate (90:10)].

The chemical shifts of the compounds reflected the literature values.[15]

General procedure for preparation of α, β-DiAryl Ketones 2j-s

To a solution of aromatic acetic acid (15 mmol, 1.0 equiv.) and aromatic methyl ester (15 mmol, 1.0 equiv.) in DMF (45 mL) was added NaHMDS (2.0 M in THF) (30 mL, 60 mmol, 4.0 equiv.) at -10 over 1 min. The resulting mixture was stirred at -10 for 3.5 hours. To the resulting solution was then added saturated aqueous NH_4Cl solution. The resulting mixture was extracted with EtOAc (2x100 ml). The combined organic phase was washed with brine, dried over sodium sulfate and concentrated in vacuo. The residue was purified by silica gel column chromatography to give the desired product.

The chemical shifts of the compounds are in agreement with the literature values. [16]

Aldehydes **4a-d** were prepared from ethyl phenyl acetate and the corresponding bromide according to the literature.[17]

General procedure for the preparation of the α,β-enecarbamates 3a-s(*Z*-isomer)

A solution of the ketone (10 mmol, 1.0 equiv.), 2-oxazolidinone (30 mmol, 2.610g, 3 equiv.), and 10 mol% of *p*-toluenesulfonic acid (1 mmol, 190mg) in toluene (30 mL: 10 mmol ketone) was heated to reflux and the formed water was removed by azeotropic distillation over 36hrs. After cooling the solution to room temperature, it was washed with a saturated, aqueous solution of NH_4Cl (10 mL) and water (10 mL), and the combined organic layers were dried over Na_2SO_4. After evaporation of the organic solvent and purification by silica-gel flash chromatography (pentane/ ethyl acetate 80:20 to 70:30), the pure *E*- or Z-isomers of the enecarbamates were obtained.

(*Z*)-enecarbamates **3k, 3l, 3n, 3o, 3q, 3r** are in agreement with the reported datas.[8b]

*(Z)-3-(1-phenylpent-1-en-1-yl)oxazolidin-2-one (**3a**)*

Colorless oil, 0.726g (33% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.30 (m, 5H), 6.04 (t, *J* = 7.2 Hz, 1H), 4.55 – 4.42 (m, 2H), 3.73 – 3.65 (m, 2H), 2.24 (q, *J* = 7.3 Hz, 2H), 1.65 – 1.54 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.5, 135.8, 133.9, 130.6, 128.7, 128.2, 125.9, 62.3, 45.7, 30.3, 22.1, 14.1. HRMS (ESI-TOF) calcd for $C_{14}H_{17}NO_2Na$ $[M+Na]^+$: 254.1151, found: 254.1151.

A large scale for the synthesis of compound **3a** was carried out according to the general procedure for the preparation of the α,β-enecarbamates (*Z*-isomer). Ketone **2a**

(10g, 61.7mmol), oxazolidinone **1** (16g, 185.1mmol) and PTSA (1.18g, 6.17mmol) were refluxed in 100 ml toluene to afford product **3a** (4.53g, 32% yield).

(Z)-3-(1-(3-methoxyphenyl)pent-1-en-1-yl)oxazolidin-2-one (**3b**)

Colorless oil, 0.548g (21% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 15.9 Hz, 1H), 6.93 (ddd, *J* = 7.7, 1.7, 1.0 Hz, 1H), 6.88 – 6.86 (m, 1H), 6.84 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 6.01 (t, *J* = 7.2 Hz, 1H), 4.52 – 4.39 (m, 2H), 3.81 (s, 3H), 3.71 – 3.58 (m, 2H), 2.20 (q, *J* = 7.3 Hz, 2H), 1.54 (q, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 160.1, 156.5, 137.6, 133.8, 130.9, 129.9, 118.6, 113.5, 112.0, 62.4, 55.5, 45.9, 30.5, 22.2, 14.2. HRMS (ESI-TOF) calcd for $C_{15}H_{19}NO_3Na$ $[M+Na]^+$: 284.1257, found: 284.1256.

(Z)-3-(1-(4-bromophenyl)pent-1-en-1-yl)oxazolidin-2-one (**3c**)

Colorless oil, 0.556g (18% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.43 (m, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.01 (t, *J* = 7.2 Hz, 1H), 4.54 – 4.41 (m, 2H), 3.69 – 3.46 (m, 2H), 2.19 (q, *J* = 7.3 Hz, 2H), 1.54 (q, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.5, 135.1, 133.2, 132.0, 131.5, 127.6, 122.3, 62.4, 45.8, 30.5, 22.2, 14.2. HRMS (ESI-TOF) calcd for $C_{14}H_{16}BrNO_2Na$ $[M+Na]^+$: 332.0257, found: 332.0262.

(Z)-3-(1-(4-fluorophenyl)pent-1-en-1-yl)oxazolidin-2-one (**3d**)

Colorless oil, 0.598g (24% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.30 (m, 2H), 7.13 – 6.98 (m, 2H), 5.96 (t, J = 7.2 Hz, 1H), 4.56 – 4.43 (m, 2H), 3.71 – 3.58 (m, 2H), 2.21 (q, J = 7.3 Hz, 2H), 1.65 – 1.48 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-d) δ 162.6 (d, *J* = 270.4 Hz) 156.43, 133.00, 132.07 (d, *J* = 3.3 Hz), 130.49 (d, *J* = 1.4Hz), 127.65, 127.57, 115.74, 115.52, 62.27, 45.67, 30.28, 22.08, 14.02. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -113.7. HRMS (ESI-TOF) calcd for $C_{14}H_{16}FNO_2Na$ $[M+Na]^+$: 272.1057, found: 272.1059.

(Z)-3-(1-(4-(trifluoromethyl)phenyl)pent-1-en-1-yl)oxazolidin-2-one (**3e**)

Colorless oil, 0.598g (20% yield)**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (dt, *J* = 7.9, 0.8 Hz, 2H), 7.45 (dt, *J* = 7.9, 0.8 Hz, 2H), 6.12 (t, *J* = 7.2 Hz, 1H), 4.56 – 4.42 (m, 2H), 3.73 – 3.58 (m, 2H), 2.24 (q, *J* = 7.4 Hz, 2H), 1.62 – 1.49 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.5, 139.7, 133.3, 133.1, 130.3 (q, *J* = 32.5, 31.7 Hz), 126.2, 128.3 – 125.8 (m), 123.4 (q, *J* = 271.9 Hz), 62.4, 45.8, 30.6, 22.1, 14.2. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.7. HRMS (ESI-TOF) calcd for $C_{15}H_{16}F_3NO_2Na$ $[M+Na]^+$: 322.1035, found: 322.1025.

(Z)-3-(1-(thiophen-2-yl)pent-1-en-1-yl)oxazolidin-2-one (**3f**)

Brown oil, 0.332g (14% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.17 (m, 1H), 6.99 – 6.95 (m, 2H), 6.07 (t, *J* = 7.3 Hz, 1H), 4.53 – 4.47 (m, 2H), 3.82 – 3.76 (m, 2H), 2.17 (q, *J* = 7.4 Hz, 2H), 1.56 – 1.48 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 156.2, 140.4, 130.3, 128.8, 127.6, 124.8, 123.7, 62.4, 46.0, 30.0, 22.0, 14.0. HRMS (ESI-TOF) calcd for $C_{12}H_{15}NO_2SNa$ $[M+Na]^+$: 260.0716, found: 260.0738.

*(Z)-3-(1-(naphthalen-2-yl)pent-1-en-1-yl)oxazolidin-2-one (***3g***)*

Colorless oil, 0.562g (20% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 8.9, 4.4 Hz, 3H), 7.75 (s, 1H), 7.55 – 7.42 (m, 3H), 6.15 (t, *J* = 7.2 Hz, 1H), 4.58 – 4.45 (m, 2H), 3.77 – 3.65 (m, 2H), 2.27 (q, *J* = 7.3 Hz, 2H), 1.59 (h, *J* = 7.3 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 156.53, 133.91, 133.31, 133.24, 133.06, 131.14, 128.45, 128.10, 127.58, 126.43, 126.23, 124.78, 123.82, 62.27, 45.78, 30.40, 22.13, 14.06. HRMS (ESI-TOF) calcd for $C_{18}H_{19}NO_2Na$ $[M+Na]^+$: 304.1308, found: 304.1307.

(Z)-3-(3-methyl-1-phenylbut-1-en-1-yl)oxazolidin-2-one (**3h**)

Colorless oil, 0.693g (30% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.30 (m, 5H), 6.04 (t, *J* = 7.2 Hz, 1H), 4.55 – 4.42 (m, 2H), 3.73 – 3.65 (m, 2H), 2.24 (q, *J* = 7.3 Hz, 2H), 1.65 – 1.54 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.5, 135.8, 133.9, 130.6, 128.7, 128.2, 125.9, 62.3, 45.7, 30.3, 22.1, 14.1. HRMS (ESI-TOF) calcd for $C_{14}H_{17}NO_2Na$ $[M+Na]^+$: 254.1151, found: 254.1151.

(Z)-3-(1-phenylbut-1-en-1-yl)oxazolidin-2-one (**3i**)

Colorless oil, 0.651g (30% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.30 (m, 4H), 7.31 – 7.28 (m, 1H), 5.98 (t, *J* = 7.2 Hz, 1H), 4.52 – 4.38 (m, 2H), 3.72 – 3.59 (m, 2H), 2.24 (p, *J* = 7.5 Hz, 2H), 1.12 (t, *J* = 7.5 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.7 , 135.9 , 133.4 , 132.3 , 128.8 , 128.3 , 126.0 , 62.4 , 45.8 , 21.8 , 13.6 . HRMS (ESI-TOF) calcd for $C_{13}H_{15}NO_2Na$ $[M+Na]^+$: 240.0995, found: 240.0987.

(Z)-3-(1,2-diphenylvinyl)oxazolidin-2-one (**3j**) [8b]

White solid, mp 102.7−104.6 °C, 0.265g (10% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.26 (m, 10H), 6.90 (s, 1H), 4.53 – 4.40 (m, 2H), 3.77 – 3.63 (m, 2H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.4, 136.4, 135.3, 134.6, 128.9, 128.8, 128.3, 128.2, 127.0, 125.9, 62.6, 45.4. HRMS (ESI-TOF) calcd for $C_{17}H_{15}NO_2Na$ $[M+Na]^+$: 288.0995, found: 288.0990.

(Z)-3-(2-phenyl-1-(p-tolyl)vinyl)oxazolidin-2-one(**3K**)
0.418g (15% yield). The compound is in agreement with the reported datas.[8b]

(Z)-3-(1-(4-methoxyphenyl)-2-phenylvinyl)oxazolidin-2-one (**3l**)

0.531g (18% yield). The compound is in agreement with the reported datas.[8b]

(Z)-3-(2-phenyl-1-(4-(trifluoromethyl) phenyl) vinyl) oxazolidin-2-one (**3m**)

White solid, mp 80.8-81.2 °C, 0.566g (17% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.55 (m, 2H), 7.45 – 7.37 (m, 2H), 7.16 – 7.09 (m, 3H), 6.99 – 6.91 (m, 2H), 6.81 (s, 1H), 4.44 – 4.37 (m, 2H), 3.75 – 3.66 (m, 2H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.4, 140.3, 134.8, 133.6, 130.8 (q, J = 32.5 Hz), 129.0, 128.9, 128.8, 128.6, 126.3, 126.0 (q, J = 3.8 Hz), 124.1 (q, J = 272.6 Hz), 62.8, 45.3. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.7. HRMS (ESI-TOF) calcd for $C_{18}H_{14}F_3NO_2Na$ $[M+Na]^+$: 356.0874, found: 356.0884.

(Z)-3-(1-phenyl-2-(p-tolyl)vinyl)oxazolidin-2-one (**3n**)

0.446g (16% yield). The compound is in agreement with the reported datas.[8b]

(Z)-3-(2-(4-methoxyphenyl)-1-phenylvinyl)oxazolidin-2-one (**3o**)

0.443g (15% yield). The compound is in agreement with the reported datas.[8b]

(Z)-3-(1-phenyl-2-(4-(trifluoromethyl)phenyl)vinyl) oxazolidin-2-one (**3p**)

White solid, mp 127.1-129.7 °C, 0.466g (14% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.31 (m, 5H), 7.30 – 7.24 (m, 2H), 7.01 (d, J = 8.2 Hz, 2H), 6.88 (s, 1H), 4.40 – 4.33 (m, 2H), 3.65 – 3.59 (m, 2H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.1, 139.1, 136.7, 135.9, 129.9 (q, J = 32.7, 32.2 Hz), 129.6, 129.1, 128.6, 126.4, 125.9 (q, J = 3.8 Hz), 125.6, 122.8 (q, J = 273.1 Hz), 62.7, 45.7. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.6. HRMS (ESI-TOF) calcd for $C_{18}H_{14}F_3NO_2Na$ $[M+Na]^+$: 356.0874, found: 356.0882.

(Z)-3-(1-(naphthalen-2-yl)-2-phenylvinyl)oxazolidin-2-one (**3q**)

0.630g (20% yield). The compound is in agreement with the reported datas.[8b]

(Z)-3-(1-(furan-2-yl)-2-phenylvinyl)oxazolidin-2-one (**3r**)

0.408g (16% yield). The compound is in agreement with the reported datas.[8b]

(Z)-3-(2-phenyl-1-(thiophen-3-yl)vinyl)oxazolidin-2-one (**3s**)

Brown foams, 0.325g (12% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.39 (m, 3H), 7.39 – 7.34 (m, 2H), 7.34 – 7.27 (m, 2H), 7.27 – 7.23 (m, 1H), 6.93 (s, 1H), 4.48 – 4.39 (m, 2H), 3.73 – 3.64 (m, 2H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.7 , 138.7 , 134.9 , 130.4 , 128.9 , 128.4 , 128.3 , 127.0 , 126.7 , 125.3 , 122.2 , 62.7 , 45.4 . HRMS (ESI-TOF) calcd for $C_{15}H_{13}NO_2SNa$ $[M+Na]^+$: 294.0565, found: 294.0545.

General procedure for the preparation of the α,β-enecarbamates (*E*-isomer)

A nitrogen-flooded sealed vial containing corresponding ketones (10 mmol, 1.0 equiv.) in dry dichloromethane was cooled down to 0℃ before titanium tetrachloride (1.2 equiv.) was added dropwise. The resulting light yellow/orange solution was stirred at this temperature for 5 min. 2-oxazolidone (3.0 equiv.) pre-dissolved in dichloromethane (5 mL) was added slowly followed by dropwise addition of triethylamine (5 equiv.). The color of the reaction mixture turned black upon addition of the base, a color change that did not occur when using most other bases. The reaction mixture was allowed to warm up to r.t. and was stirred over 3 h with regular monitoring using thin layer chromatography plates. The crude mixture was cooled to 0°C, quenched by water (4 equiv.) and diluted with dichloromethane followed by portwise addition of Slica. The mixture was filtered by celite and the filtrate was washed with water. The layers were separated and the organic phase was extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel (ethyl ace-

tate/pentane, gradient from 1:4 to 1:2) to provide clean *E*-enamides.

(E)-3-(1-phenylpent-1-en-1-yl)oxazolidin-2-one (**3a'**)

White solid, mp 52.2-53.2 °C, 1.109g (48% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.28 (m, 3H), 7.27 – 7.22 (m, 2H), 5.83 (t, *J* = 7.7 Hz, 1H), 4.32 – 4.24 (m, 2H), 3.57 – 3.49 (m, 2H), 2.07 (td, *J* = 7.7, 6.5 Hz, 2H), 1.43 (h, *J* = 7.3 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.5 , 134.7 , 134.6 , 128.9 , 128.4 , 128.2 , 125.5 , 61.5 , 46.2 , 30.0 , 23.1 , 13.8 . HRMS (ESI-TOF) calcd for $C_{14}H_{17}NO_2Na$ $[M+Na]^+$: 254.1151, found: 254.1151.

A large scale for the synthesis of compound **3a'** was carried out according to the general procedure for the preparation of the α,β-enecarbamates (*E*-isomer). Ketone **2a** (8.0g, 49.4mmol), oxazolidinone **1** (12.9g, 148.1mmol) were treated with $TiCl_4$ (9.4g, 49.4mmol) and NEt_3 in 200ml DCM to afford product **3a'** (5.40g, 47% yield).

(E)-3-(1-(3-methoxyphenyl)pent-1-en-1-yl)oxazolidin-2-one (**3b'**)

Brown solid, mp 50.5-53.8 °C, 0.522mg (20% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 1H), 6.89 – 6.84 (m, 2H), 6.80 (dd, *J* = 2.6, 1.6 Hz, 1H), 5.87 (t, *J* = 7.8 Hz, 1H), 4.34 – 4.28 (m, 2H), 3.57 – 3.52 (m, 2H), 2.14 – 2.05 (m, 2H), 1.50 – 1.39 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 159.6, 156.5, 136.1, 134.3, 129.4, 125.7, 121.3, 114.5, 113.6, 61.5, 55.3, 46.1, 30.1, 23.1, 13.7. HRMS (ESI-TOF) calcd for $C_{15}H_{19}NO_3Na$ $[M+Na]^+$: 284.1257, found: 284.1275.

(E)-3-(1-(4-bromophenyl)pent-1-en-1-yl)oxazolidin-2-one (**3c'**)

Brown solid, mp 49.5-51.1 °C, 0.958g (31% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 2H), 7.18 – 7.12 (m, 2H), 5.80 (t, *J* = 7.8 Hz, 1H), 4.36 – 4.30 (m, 2H), 3.60 – 3.55 (m, 2H), 2.09 – 2.01 (m, 2H), 1.47 – 1.39 (m, 2H), 0.93 – 0.85 (m, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 156.3, 133.7, 133.6, 131.6, 130.5, 125.8, 122.3, 61.5, 46.1, 30.0, 23.0, 13.7. HRMS (ESI-TOF) calcd for $C_{14}H_{16}BrNO_2Na$ $[M+Na]^+$: 332.0257, found: 332.0265.

(E)-3-(1-(4-fluorophenyl)pent-1-en-1-yl)oxazolidin-2-one (**3d'**)

Colorless oil, 0.821g (33% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.25 (m, 2H), 7.13 – 7.06 (m, 2H), 5.83 (t, *J* = 7.7 Hz, 1H), 4.38 – 4.32 (m, 2H), 3.62 – 3.56 (m, 2H), 2.08 (q, *J* = 7.6 Hz, 2H), 1.46 (h, *J* = 7.3 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 162.4 (d, *J* = 247.9 Hz), 156.2, 133.7, 130.7, 130.6 (d, 8.1 Hz), 125.4, 115.4 (d, 21.6 Hz), 61.4, 46.1, 29.9, 23.0, 13.7. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -113.1. HRMS (ESI-TOF) calcd for $C_{14}H_{16}FNO_2Na$ $[M+Na]^+$: 272.1057, found: 272.1054.

(E)-3-(1-(4-(trifluoromethyl)phenyl)pent-1-en-1-yl)oxazolidin-2-one (**3e'**)

Brown oil, 0.598g (20% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 5.84 (t, *J* = 7.8 Hz, 1H), 4.38 – 4.32 (m, 2H), 3.65 – 3.57 (m, 2H), 2.06 (q, *J* = 7.5 Hz, 2H), 1.45 (h, *J* = 7.4 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.3, 138.6, 133.8, 130.4 (q, *J* = 32.6 Hz), 129.4, 126.5, 125.5 (q, *J* = 3.8 Hz), 122.8 (q, *J* = 272.8, 272.1, 271.2 Hz), 61.7, 46.3, 30.1, 23.1, 13.8. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.7. HRMS (ESI-TOF) calcd for $C_{15}H_{16}F_3NO_2Na$ $[M+Na]^+$: 322.1035, found: 322.1025.

(E)-3-(1-(thiophen-2-yl)pent-1-en-1-yl)oxazolidin-2-one (**3f'**)

Colorless oil, 0.569g (24% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 1H), 7.04 (d, *J* = 3.3 Hz, 2H), 5.92 (t, *J* = 7.6 Hz, 1H), 4.43 – 4.28 (m, 2H), 3.76 – 3.62 (m, 2H), 2.27 (q, *J* = 7.5 Hz, 2H), 1.56 – 1.44 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.6 , 137.0 , 129.7 , 128.4 , 127.7 , 127.2 , 126.3 , 61.8 , 46.7 , 30.7 , 23.0 , 13.9 . HRMS (ESI-TOF) calcd for $C_{12}H_{15}NO_2SNa$ $[M+Na]^+$: 260.0716, found: 260.0723.

(E)-3-(1-(naphthalen-2-yl)pent-1-en-1-yl)oxazolidin-2-one (**3g'**)

Colorless oil, 0.927g (33% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.81 (m, 3H), 7.80 – 7.72 (m, 1H), 7.55 – 7.47 (m, 2H), 7.38 (dd, *J* = 8.4, 1.7 Hz, 1H), 5.95 (t, *J* = 7.8 Hz, 1H), 4.37 – 4.27 (m, 2H), 3.61 – 3.51 (m, 2H), 2.15 (q, *J* = 7.6 Hz, 2H), 1.48 (h, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.6 , 134.5 , 133.1 , 133.0 , 132.2 , 128.3 , 128.2 , 128.1 , 127.7 , 126.5 , 126.4 , 126.4 , 126.2 , 61.5 , 46.2 , 30.1 , 23.1 , 13.8 . HRMS (ESI-TOF) calcd for $C_{18}H_{19}NO_2Na$ $[M+Na]^+$: 304.1308, found: 304.1291.

(E)-3-(3-methyl-1-phenylbut-1-en-1-yl)oxazolidin-2-one (**3h'**)

White solid, mp 98.2-102.1 °C, 0.693g (30% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.33 (m, 3H), 7.31 – 7.28 (m, 2H), 5.68 (d, *J* = 10.5 Hz, 1H), 4.35 – 4.29 (m, 2H), 3.59 – 3.54 (m, 2H), 2.46 (dp, *J* = 10.5, 6.6 Hz, 1H), 1.04 (d, *J* = 6.6 Hz, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 156.2, 135.0, 132.7, 132.11, 128.8, 128.4, 128.2, 61.4, 46.1, 27.4, 23.3. HRMS (ESI-TOF) calcd for $C_{14}H_{17}NO_2Na$ $[M+Na]^+$: 254.1151, found: 254.1151.

(E)-3-(1-phenylbut-1-en-1-yl)oxazolidin-2-one (**3i'**)

White solid, mp 62.5−64.3 °C, 0.868g (40% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.32 (m, 3H), 7.29 – 7.26 (m, 2H), 5.85 (t, *J* = 7.8 Hz, 1H), 4.38 – 4.24 (m, 2H), 3.63 – 3.46 (m, 2H), 2.12 (p, *J* = 7.5 Hz, 2H), 1.03 (t, *J* = 7.5 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.6 , 134.8 , 134.2 , 128.9 , 128.6 , 128.4 , 127.3 , 61.6 , 46.2 , 21.6 , 14.6 . HRMS (ESI-TOF) calcd for $C_{13}H_{15}NO_2Na$ $[M+Na]^+$: 240.0995, found: 240.1003.

(E)-3-(1,2-diphenylvinyl)oxazolidin-2-one (**3j'**)

White solid, mp 98.5−100.2 °C, 0.795g (30% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (ddd, *J* = 3.7, 3.2, 2.5 Hz, 3H), 7.31 – 7.27 (m, 2H), 7.14 – 7.06 (m, 3H), 6.99 – 6.94 (m, 2H), 6.83 (s, 1H), 4.39 – 4.33 (m, 2H), 3.65 – 3.59 (m, 2H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.2, 135.6, 135.5, 134.5, 129.6, 129.3, 129.0, 128.9, 128.1, 126.9, 122.9, 61.7, 46.1. HRMS (ESI-TOF) calcd for $C_{17}H_{15}NO_2Na$ $[M+Na]^+$: 288.0995, found: 288.1007.

(E)-3-(2-phenyl-1-(p-tolyl)vinyl)oxazolidin-2-one (**3k'**)

White foams, 1.116g (40% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.07 (m, 7H), 7.01 – 6.96 (m, 2H), 6.78 (s, 1H), 4.39 – 4.31 (m, 2H), 3.65 – 3.58 (m, 2H), 2.36 (s, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.3 , 138.9 , 135.7 , 135.6 , 131.4 , 129.7 , 129.5 , 129.3 , 128.1 , 126.8 , 122.6 , 61.7 , 46.1 , 21.5 . HRMS (ESI-TOF) calcd for $C_{18}H_{17}NO_2Na$ $[M+Na]^+$: 302.1157, found: 302.1150.

(E)-3-(1-(4-methoxyphenyl)-2-phenylvinyl)oxazolidin-2-one (**3l'**)

Colorless oil, 1.328g (45% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.18 (m, 2H), 7.14 – 7.05 (m, 3H), 7.01 – 6.96 (m, 2H), 6.88 – 6.82 (m, 2H), 6.74 (s, 1H), 4.40 – 4.31 (m, 2H), 3.82 (s, 3H), 3.67 – 3.58 (m, 2H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 160.0 , 156.2 , 135.8 , 135.3 , 130.9 , 129.3 , 128.1 , 126.7 , 126.6 , 122.3 , 114.4 , 61.7 , 55.4 , 46.1 . HRMS (ESI-TOF) calcd for $C_{18}H_{17}NO_3Na$ $[M+Na]^+$: 318.1106, found: 318.1102.

(E)-3-(2-phenyl-1-(4-(trifluoromethyl)phenyl)vinyl) oxazolidin-2-one (**3m'**)

White foams, 1.265g (38% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.55 (m, 2H), 7.42 (dt, *J* = 7.8, 0.9 Hz, 2H), 7.17 – 7.10 (m, 3H), 6.98 – 6.91 (m, 2H), 6.81 (s, 1H), 4.45 – 4.35 (m, 2H), 3.75 – 3.65 (m, 2H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.0, 138.2, 134.9, 134.5, 130.8 (q, *J* = 33.1, 32.7 Hz), 130.1, 129.3, 128.4, 127.4, 125.9 (q, *J* = 3.6 Hz), 123.9, 123.3 (q, *J* = 272.4 Hz), 61.8, 46.2. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.7. HRMS (ESI-TOF) calcd for $C_{18}H_{14}F_3NO_2Na$ $[M+Na]^+$: 356.0874, found: 356.0868.

(E)-3-(1-phenyl-2-(p-tolyl)vinyl)oxazolidin-2-one (**3n'**)

White solid, mp 105.6−107.4 °C, 1.032g (37% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 5H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.78 (s, 1H), 4.42 – 4.24 (m, 2H), 3.71 – 3.54 (m, 2H), 2.24 (s, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.3 , 136.7 , 134.8 , 134.7 , 132.5 , 129.6 , 129.2 , 129.0 , 128.8 , 128.8 , 123.2 , 61.7 , 46.1 , 21.3 . HRMS (ESI-TOF) calcd for $C_{18}H_{17}NO_2Na$ $[M+Na]^+$: 302.1157, found: 302.1154.

(E)-3-(2-(4-methoxyphenyl)-1-phenylvinyl)oxazolidin-2-one (**3o'**)

White solid, mp 111.8−113.1 °C, 0.443g (34% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 5H), 6.93 – 6.88 (m, 2H), 6.76 (s, 1H), 6.67 – 6.62 (m, 2H), 4.37 – 4.31 (m, 2H), 3.73 (s, 3H), 3.63 – 3.56 (m, 2H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 158.6 , 156.5 , 134.8 , 133.7 , 130.6 , 129.6 , 129.0 , 128.8 , 127.9 , 123.3 , 113.6 , 61.7 , 55.3 , 46.0 . HRMS (ESI-TOF) calcd for $C_{18}H_{17}NO_3Na$ $[M+Na]^+$: 318.1106, found: 318.1103.

(E)-3-(1-phenyl-2-(3-(trifluoromethyl)phenyl)vinyl) oxazolidin-2-one (**3p'**)

White solid, mp 85.8−87.5 °C, 1.066g (32% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.50 – 7.39 (m, 5H), 6.85 (s, 1H), 4.51 – 4.44 (m, 2H), 3.74 – 3.66 (m, 2H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 155.9, 139.5, 137.9, 133.9, 129.5, 129.4, 129.4, 129.2, 128.5 (q, *J* = 32.6, 32.2 Hz), 125.0 (q, *J* = 3.8 Hz), 122.9 (q, *J* = 273.6, 273.1 Hz), 120.2, 61.7, 46.0. ^{19}F NMR (377 MHz, Chloroform-

d) δ -62.6 . HRMS (ESI-TOF) calcd for $C_{18}H_{14}F_3NO_2Na$ $[M+Na]^+$: 356.0874, found: 356.0858.

(E)-3-(1-(naphthalen-2-yl)-2-phenylvinyl)oxazolidin-2-one (**3q'**)

White solid, mp 106.5−107.9 °C, 1.228g (39% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (td, *J* = 14.1, 13.3, 7.8 Hz, 4H), 7.50 (pd, *J* = 6.8, 1.5 Hz, 2H), 7.38 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.12 – 7.06 (m, 3H), 7.04 – 6.99 (m, 2H), 6.91 (s, 1H), 4.43 – 4.32 (m, 2H), 3.72 – 3.51 (m, 2H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.4 , 135.4 , 133.4 , 133.4 , 131.9 , 129.4 , 128.9 , 128.7 , 128.3 , 128.1 , 127.9 , 127.1 , 127.0 , 126.8 , 126.5 , 123.6 , 61.7 , 46.1 . HRMS (ESI-TOF) calcd for $C_{21}H_{17}NO_2Na$ $[M+Na]^+$: 338.1151, found: 338.1158.

(E)-3-(1-(furan-2-yl)-2-phenylvinyl)oxazolidin-2-one (**3r'**)

Brown oil, 0.765g (30% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.26 – 7.18 (m, 3H), 7.13 – 7.08 (m, 2H), 6.79 (s, 1H), 6.38 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.31 (dd, *J* = 3.4, 0.8 Hz, 1H), 4.45 – 4.39 (m, 2H), 3.83 – 3.76 (m, 2H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.3 , 147.4 , 142.8 , 135.3 , 128.9 , 128.3 , 127.6 , 126.0 , 125.5 , 112.0 , 111.5 , 61.9 , 46.4 . HRMS (ESI-TOF) calcd for $C_{15}H_{13}NO_3$ $[M+Na]^+$: 278.0793, found: 278.0798.

(E)-3-(2-phenyl-1-(thiophen-3-yl)vinyl)oxazolidin-2-one (**3s'**)

Brown solid, mp 87.9−91.6 °C, 0.542g (20% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.22 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.19 – 7.11 (m, 3H), 7.05 – 7.00 (m, 2H), 6.94 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.81 (s, 1H), 4.40 – 4.34 (m, 2H), 3.71 – 3.64 (m, 2H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.2 , 135.6 , 135.1 , 130.6 , 129.1 , 128.2 , 128.2 , 127.1 , 126.4 , 125.9 , 123.8 , 61.7 , 46.2 . HRMS (ESI-TOF) calcd for $C_{15}H_{13}NO_2SNa$ $[M+Na]^+$: 294.0565, found: 294.0539.

General procedure for the preparation of the β,β-enecarbamates 5a-d

The procedures follow the general methods for α,β-enecarbamates mentioned above.

(Z)-3-(2-phenylpent-1-en-1-yl)oxazolidin-2-one (**5a**)

Colorless oil, with $TiCl_4$: 1.155g (50% yield); with p-TSA: 0.647g (28% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 3H), 7.22 – 7.18 (m, 2H), 6.56 (s, 1H), 4.15 – 4.09 (m, 2H), 3.07 – 3.02 (m, 2H), 2.36 – 2.30 (m, 2H), 1.34 (h, *J* = 7.4 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C{1H} NMR (126 MHz, Chloroform-*d*) δ 157.3, 139.0, 129.1, 128.0, 127.3, 126.4, 120.5, 62.5, 45.1, 39.8, 21.2, 13.5. HRMS (ESI-TOF) calcd for $C_{14}H_{17}NO_2Na$ $[M+Na]^+$: 254.11551, found: 254.1149.

(Z)-3-(2-phenylhex-1-en-1-yl)oxazolidin-2-one (**5b**)

With $TiCl_4$: 0.980g (40% yield); with p-TSA: 0.931g (38% yield). The compound is in agreement with literature data.[6]

(Z)-3-(3-methyl-2-phenylbut-1-en-1-yl)oxazolidin-2-one (**5c**)

White solid, mp 77.2−79.2 °C, with $TiCl_4$: 1.155g (50% yield); with p-TSA: 1.386g (60% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.3 – 7.3 (m, 3H), 7.2 – 7.1 (m, 2H), 6.6 (d, J = 1.1 Hz, 1H), 4.1 – 4.0 (m, 2H), 3.0 – 2.9 (m, 2H), 2.6 (sd, J = 6.9, 1.1 Hz, 1H), 1.0 (d, J = 6.9 Hz, 6H). ^{13}C{1H} NMR (101 MHz, CDCl3) δ 157.3, 138.3, 132.0, 130.1, 127.8, 127.4, 119.7, 62.5, 45.2, 35.5, 22.0. HRMS (ESI-TOF) calcd for $C_{14}H_{17}NO_2Na$ $[M+Na]^+$: 254.11551, found: 254.1148.

*(Z)-3-(*2-Phenyl-2-cyclohexyl*)oxazolidin-2-one* (**5d**)

With $TiCl_4$: 1.382g (51% yield); with p-TSA: 1.409g (61% yield). The compound is in agreement with literature data.[18]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Additional conditions screening, additional analytical data and NMR spectra for the products (PDF)

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Notes

The authors declare no competing financial interest.

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