New Stannyl Enamides

Sébastien Naud, Jean-Christophe Cintrat

CEA/Saclay, Service de Marquage Moléculaire et Chimie Bio-organique, Bât. 547, Département de Biologie Joliot-Curie, 91191 Gif sur Yvette cedex, FRANCE
Fax +33(1)69087991; E-mail: jean-christophe.cintrat@cea.fr
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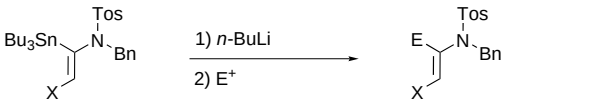
Abstract: New stannyl enamines derived from *N*-ethynyl oxazolidin-2-ones have been obtained. We describe for the first time the preparation of *N*-ethynyl oxazolidin-2-ones using trimethylsilylethynyl iodonium triflate. The first results of transmetallation and quenching experiments with prochiral carbonyl derivatives to give β-amino alcohols are also described.

Key words: enamide, hydrostannations, oxazolidinone, tin, ynamide

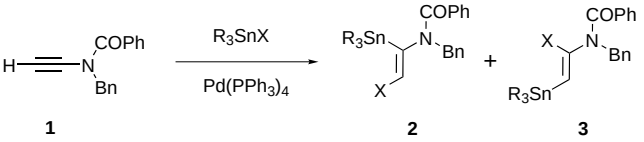
Recently, ynamides and enamides have attracted much attention in the literature due to their increased stability and easier preparation procedure compared to enamines and ynamines.[1] We are mainly interested in α-metallated enamides as 'umpolung' synthons for the synthesis of non-proteinogenic amino-acids, β-amino-alcohols and we have recently described the preparation[2] and palladium cross-coupling reactions of *N*-tosyl stannylated enamines.[3] With these compounds in hand, we next envisioned the use of the well-known transmetallation procedure with BuLi to obtain α-lithiated enamides, as shown in Scheme 1.



Scheme 1 Transmetallation of α-stannyl enamides.

Unfortunately, all attempts failed presumably due to β-elimination of TosLi. Therefore, we assumed that a chelating group (such as a CO group for instance) could be beneficial since the chelation could provide stabilization of the lithiated species as described with α-amino alkyltins.[4] Herein we describe the preparation of a range of newly protected stannylated enamines as well as our first results in the field of transmetallation of α-monostannyl enamides derived from oxazolidin-2-ones.

Our scheme for the synthesis of newly protected stannyl enamines was inspired from the approach we described previously, starting from *N*-benzoyl *N*-ethynyl benzylamine (**1**) prepared by Witulski.[5] Thus, addition of organotin derivatives to **1** was conducted in the presence of palladium tetrakis(triphenylphosphine) as shown in Scheme 2. The results are summarized in Table 1.



Scheme 2 Addition of organotin derivatives to ynamide **1**.

Table 1 Stannylation Reactions of Ynamide **1**

Entry	R	X	Product (ratio)	Yield (%)
1	Bu	H	**2a/3a** (85:15)	80[a]
2	Bu	Me_3Si	**2b/3b** (55:45)	49[a]
3	Me	Me_3Sn	**2c**	86

[a] Yield refers to purified α-stannyl isomers **2** only.

The addition of Bu_3SnH to **1** gives a mixture of α- and β-isomers however the α-stannylated compound was favoured and the desired product is obtained in very good yield (entry 1). The introduction of $Bu_3SnSiMe_3$ was also achieved in good yield although the regiochemical outcome of this reaction was quite disappointing (almost no regioselectivity was observed as seen in entry 2).[6] Finally, addition of hexamethylditin cleanly affords the distannylated compound in a stereospecific fashion since the *Z*-isomer was obtained as a single isomer (entry 3).

Although these results were quite stimulating, we must mention that the analysis of the products was complicated by the occurrence of rotamers in all the stannylated products **2** and **3**. Even when the NMR analyses were performed in THF at 323 K, broadening of the signals gave complicated spectra. To avoid this limitation we turned our attention to cyclic species and since many oxazolidin-2-ones are commercially available these cyclic carbamates appeared to be attractive starting materials. First attempts to obtain the protected ynamines **4** (Scheme 3) using BuLi in toluene, Cs_2CO_3 in DMF were unsatisfactory giving low yields (less than 20%) of the expected product. Changing the base to KHMDS greatly improved the yield and the ynamines were obtained in 50–60% yield.

Interestingly, this approach can be extended to chiral 4-substituted oxazolidinones and the results are summarized in Table 2.

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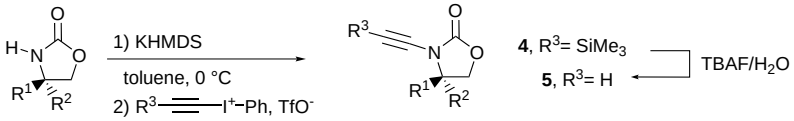


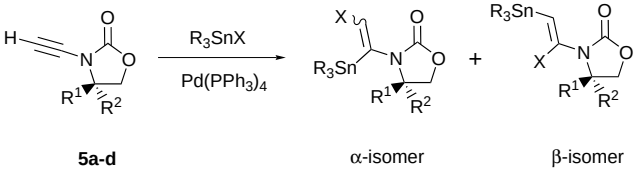
Scheme 3 Access to newly protected ethynyl amines.

Table 2 Synthesis of 3-Alkynyl Oxazolidinones

Entry	R^1	R^2	R^3	Product	Yield (%)
1	H	H	$SiMe_3$	**4a**	48
	H	H	H	**5a**	90
2	Ph	H	$SiMe_3$	**4b**	63
	Ph	H	H	**5b**	88
3	H	Bn	$SiMe_3$	**4c**	53
	H	Bn	H	**5c**	87
4	H	*i*-Pr	$SiMe_3$	**4d**	60
	H	*i*-Pr	H	**5d**	89

As described in Table 2, *N*-trimethylsilylethynylation of oxazolidin-2-ones is possible using KHMDS and trimethylsilylethynyl iodonium triflate and the presence of a substituent at C4 does not affect the yields (entries 2, 3, 4 compared to entry 1). Then the desilylation procedure gave excellent yields of the ethynyl parent compounds. It is noteworthy that the desilylation step can be performed on the purified compounds **4** or on the crude mixture without affecting the overall yield of compounds **5**.

The 3-ethynyl oxazolidin-2-ones **5** were used in stannylation procedures with palladium catalysis according to Scheme 4. The results are summarized in Table 3.



Scheme 4 Access to stannylated enamides derived from oxazolidinones.

From the results described in the above table, easy access to mono stannylated enamides derived from oxazolidinones is possible although a mixture of α- and β-isomers is always obtained (entries 1, 4, 7 and 10). Indeed, we expected a better selectivity at least with the 4-substituted oxazolidinones based on steric[7] or on electronic effects (CO···Sn intramolecular bond). Nevertheless the stereoselectivity of this reaction was very good since for the β-stannylated isomers only the compounds resulting from a *cis*-addition were detected in the NMR spectra of the crude reaction mixture. Addition of $Bu_3SnSiMe_3$ appeared to be more problematic since the yields were very low for all oxazolidin-2-ones and the regioselectivity was poor (entries 2, 5, 8 and 11).[6] Finally, reaction with distannylated compounds gave the desired products but, surprisingly, the stereochemical outcome was lower than expected since in some instances (entries 3 and 12) we ob-

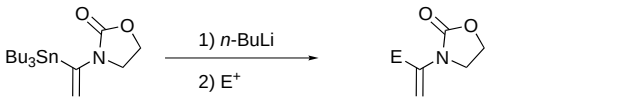
Table 3 Synthesis of Stannyl Enamides Derived from *N*-Ethynyl Oxazolidinones

Entry	Ynamine	R	R^1	R^2	X	Product (ratio)	Yield (%)
1	**5a**	Bu	H	H	H	**6α/6β** (70:30)	55[a]
2	**5a**	Bu	H	H	Me_3Si	**(*Z*)-7α/7β** (86:14)	11[a]
3	**5a**	Me	H	H	Me_3Sn	**8** (***Z***/***E***, 84:16)	63
4	**5b**	Bu	Ph	H	H	**9α/9β** (64:36)	46[a]
5	**5b**	Bu	Ph	H	Me_3Si	**(*Z*)-10α/10β** (78:22)	10[a]
6	**5b**	Bu	Ph	H	Bu_3Sn	**11**	35
7	**5c**	Bu	H	Bn	H	**12α/12β** (63:37)	38[a]
8	**5c**	Bu	H	Bn	Me_3Si	**(*Z*)-13α/13β** (89:11)	8[a]
9	**5c**	Bu	H	Bn	Bu_3Sn	**14**	43
10	**5d**	Bu	H	*i*-Pr	H	**15α/15β** (64:36)	57[a]
11	**5d**	Bu	H	*i*-Pr	Me_3Si	**(*Z*)-16α/16β** (87:13)	18[a]
12	**5d**	Me	H	*i*-Pr	Me_3Sn	**17** (***Z***/***E***, 76:24)	71

[a] Yield refers to purified α-stannyl isomer.

served a small amount of the *E*-isomer resulting from isomerization of the *Z*-isomer. The reaction appeared to be clean (based on TLC and ^{1}H NMR spectrum of the crude reaction mixture) although the yields are a bit low due to a very high sensitivity of the bis-stannylated enamides towards mild acidic conditions (even purification on silica gel using 2–5% of Et_3N resulted in extensive protodestannylation at the β-position).

With these stannyl enamides in hand, we then studied the transmetallation of the carbon–tin bond. Indeed, Hegedus[8] has reported the transmetallation of a similar compound but we wanted to check whether an asymmetric induction could be possible when using the enantiomerically pure compound and a prochiral electrophile. First, the experimental conditions were optimized with the achiral starting material. Thus, compound **6α** was subjected to BuLi and the α-lithiated product was then trapped with some electrophiles according to Scheme 5.



6α $E^+ = H_2O$ (**18**), D_2O, hexanal (**19**), methyl isopropyl ketone (**20**)

Scheme 5 Transmetallation/trapping of **6α**

Complete conversion of **6α** into the lithiated congener is only achieved using 2.4 equivalents[9] of *n*-BuLi and although trapping experiments with NH_2O (N = 1, 2) or an aldehyde gave good yields, 72% and 47%, of **18** and **19**, respectively, the yield dropped to 28% with a more sterically crowded ketone such as methyl isopropyl ketone.

Then, the same experiments were conducted starting from enantiomerically pure stannylated compound **12α** using identical prochiral carbonyl derivatives (Scheme 6).

Although moving to a 4-substituted oxazolidinone resulted in almost no change of the chemical yield (compared to **6α** in Scheme 5) either with an aldehyde or a ketone, no diastereoselectivity could be seen in the ^{1}H NMR spectrum analysis of the crude reaction mixture. This lack of asymmetric induction has also been observed with α-alkyl aminostannanes derived from oxazolidinones, which only display low diasteroselectivity.[10]

In conclusion, we have developed a new route to *N*-ethynyl oxazolidin-2-ones[11] starting from a readily available alkynyl iodonium triflate salt[12] and stannyl enamides derived either from amides or oxazolidin-2-ones. This strategy complements Hegedus approach in which only the α-isomer could be obtained.[8] Indeed, our synthetic scheme allows access to a wide range of mono-stannylated as well as bis-metallated enamides (Sn/Sn or Sn/Si) that appear to be promising tools for organic synthesis. Indeed, transmetallations of the α-(tin/carbon) bond and trapping with prochiral aldehydes or ketones affords β-amino alcohols but no assymetric induction could be obtained when starting from enantiopure oxazolidinones. We are currently working on the transmetallation or palladium catalyzed reactions of the bis metallated congener in order to introduce functionnal diversity at both Cα and Cβ positions.

All reactions were performed in flame-dried Schlenk tubes or flasks under an atmosphere of nitrogen. All commercially available compounds were purchased from Aldrich or Acros and used without further purification. THF was distilled under nitrogen from sodium benzophenone ketyl. All new compounds were fully characterized by spectroscopic methods (^{1}H NMR and ^{13}C NMR recorded on a Bruker AC 300 spectrometerin $CDCl_3$, MS, IR), HRMS and in the case of crystalline compounds melting point was recorded. Chromatography was preformed with pentane–Et_2O.

***N*-Benzyl-*N*-ethynyl-benzamide (1)**
FTIR (KBr): 3296, 2139, 1676 cm^{-1}.

^{1}H NMR: δ = 2.84 (s, 1 H), 4.92 (s, 2 H, CH_2), 7.29–7.63 (m, 8 H, Ar), 7.87 (m, 2 H, Ar).

^{13}C NMR: δ = 52.6, 61.7, 78.5, 127.7, 128.0, 128.5, 131.4, 133.2, 135.8, 170.5.

MS (ESI/TOF): *m*/*z* (%) = 258 (M + 23).

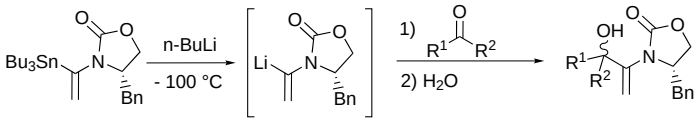
Stannylation of Ynamide 1; General Procedure
In a flame dried 100 mL flask, a catalytic amount of $Pd(PPh_3)_4$ (0.1%, 0.6 mg) is added to a solution of ynamide **1** (0.5 mmol) and R_3SnX (1.1 equiv, 0.55 mmol) in anhyd and degassed THF (25 mL). The resulting mixture is degassed, placed under nitrogen and warmed to 60 °C. The reaction was monitored by TLC. The mixture was then concentrated and the residue was purified by flash chromatography over silica gel.

***N*-Benzyl-*N*-[(*Z*)-1-(tributylstannyl)vinyl]benzamide (2a)**
FTIR (NaCl): 1632 cm^{-1}.

^{1}H NMR: δ = 0.87–1.90 (m, 27 H, 3 × Bu), 4.67 (s, 2 H, CH_2), 4.90 [s, 1 H, $^3J_{Sn–H(cis)}$ = 47.0 Hz], 5.20 [s, 1 H, $^3J_{Sn–H(trans)}$ = 105.0, 109.9 Hz], 6.89–7.17 (m, 8 H, Ar), 7.28–7.30 (m, 2 H, Ar).

^{13}C NMR: δ = 13.7 ($^1J_{C–Sn}$ = 356.4, 371.1 Hz), 13.9, 27.7 ($^3J_{C–Sn}$ = 58.6 Hz), 29.7 ($^2J_{C–Sn}$ = 19.5 Hz), 52.0, 110.4 ($^2J_{C–Sn}$ = 41.5 Hz), 126.4, 127.0, 127.2, 128.4, 128.8, 129.8, 136.9, 137.8, 150.7 ($^1J_{C–Sn}$ = 410.2–427.3 Hz), 171.9.

MS (CI): *m*/*z* (%) = 528 (M + 1, 100), 470 (M–57, 6).



12α

21 $R^1 = C_5H_{11}$, R^2 = H, yield = 57%
22 R^1 = *i*Pr, R^2 = Me, yield = 26%

Scheme 6 Trapping of enantiopure **12α** with prochiral carbonyl derivatives.

HRMS (FAB): *m*/*z* calcd for $C_{24}H_{32}NOSn$ $[M - Bu]^{+}\cdot$, 470.15059; found, 470.1508.

_N_-Benzyl-_N_-[(_Z_)-1-(tributylstannyl)2-(trimethylsilyl)vinyl]-benzamide (2b)

FTIR (NaCl): 1629 cm^{-1}.

^1H NMR: δ = 0.12 (s, 9 H, Me_3Si), 0.67–1.74 (m, 27 H, 3 × Bu), 4.77 (s, 2 H, CH_2), 6.15 (s, 1 H, $^3J_{Sn-H}$ = 123.9, 130.0 Hz), 6.90–7.80 (m, 10 H, Ar).

^{13}C NMR: δ = 0.3, 13.7 ($^1J_{C-Sn}$ = 332.0, 344.2 Hz), 28.2 ($^3J_{C-Sn}$ = 63.5 Hz), 29.5 ($^2J_{C-Sn}$ = 17.1 Hz), 52.7, 127.4, 128.1, 128.5, 128.7, 129.6, 137.8, 138.3, 163.7.

MS (ESI/TOF): *m*/*z* (%) = 600 (M + 1).

HRMS (FAB): *m*/*z* calcd for $C_{27}H_{40}NOSiSn$ $[M - Bu]^{+}\cdot$, 542.19012; found, 542.1903.

_N_-Benzyl-_N_-[(_Z_)-bis(trimethylstannyl)vinyl]benzamide (2c)

FTIR (NaCl): 1626 cm^{-1}.

^1H NMR: δ = 0.16 (s, 18 H, Me), 4.92 (s, 2 H, CH_2), 6.35 (s, 1 H, $^3J_{Sn-H}$ = 46.4, $^2J_{Sn-H}$ = 152.0 Hz), 7.02–7.46 (m, 5 H, Ar).

^{13}C NMR: δ = –7.4 ($^1J_{C-Sn}$ = 336.9, 356.4 Hz), –4.6 ($^1J_{C-Sn}$ = 346.7, 356.4 Hz), 52.8, 77.7, 127.4, 128.6, 129.7, 137.5, 138.3, 163.8, 170.5.

HRMS (FAB): *m*/*z* calcd for $C_{21}H_{28}NOSn_2$ $[M - Me]^{+}\cdot$, 550.02149; found, 550.0222.

Preparation of 'Ynamides'; Typical Procedure

In a flame dried 250 mL flask, oxazolidin-2-ones (11.5 mmol) are placed under vacuum for 15 min. The flask is then flushed with dry nitrogen and anhyd toluene (125 mL) is added. The resulting suspension is cooled to 0 °C and the resulting mixture degassed twice by the freeze-thaw process. KHMDS (1.2 equiv, 27.6 mL, 0.5 M/toluene) is added dropwise under nitrogen. The resulting mixture is warmed to r.t. over 3 h and phenyl(trimethylsilylethynyl)iodonium triflate (1.3 equiv, 6.71 g) is added portionwise. The resulting mixture was stirred at r.t. overnight and the reaction was monitored by TLC. The mixture was then filtered over a plug of silica gel (1 cm), rinsed with Et_2O (5 × 100 mL) and the solution was concentrated to give a residue that was purified by flash chromatography over silica gel.

The deprotection step using TBAF is performed according to literature procedure.[2,3,5]

3-[(Trimethylsilyl)ethynyl]-1,3-oxazolidin-2-one (4a)

White solid; mp 79.2–79.7 °C.

FTIR (KBr) : 2188, 1758 cm^{-1}.

^1H NMR: δ = 0.14 (s, 9 H, Me_3Si), 3.88 (dd, 2 H, CH_2N, ^3J = 6.7, 9.2 Hz), 4.38 (dd, 2 H, CH_2O, ^3J = 6.7, 9.2 Hz).

^{13}C NMR: δ = 0.1 ($^1J_{C-Si}$ = 58.6 Hz), 47.0, 63.2, 73.7, 91.5, 156.0.

MS (CI): *m*/*z* (%) = 184 (M + 1, 8), 201 (M + 18, 100).

HRMS (EI): *m*/*z* calcd for $C_8H_{13}NO_2Si$ $[M]^{+\cdot}$, 183.107156; found, 183.07182.

(_R_)-4-Phenyl-3-[(trimethylsilyl)ethynyl]-1,3-oxazolidin-2-one (4b)

White solid; mp 100.3–100.9 °C; $[\alpha]_D^{25}$ –191.7

FTIR (KBr): 2186, 1777, 1754 cm^{-1}.

^1H NMR: δ = 0.04 (s, 9 H, Me_3Si), 4.28 (dd, 1 H, CHO, ^3J = 7.3, ^2J = 9.2 Hz), 4.73 (dd, 1 H, CHO, ^3J = 8.5, ^2J = 9.2 Hz), 5.06 (dd, 1 H, CHN, ^3J = 7.3, 8.5 Hz), 7.30–7.47 (m, 5 H, Ar).

^{13}C NMR : δ = 0.0 ($^1J_{C-Si}$ = 58.6 Hz), 62.2, 70.7, 75.9, 90.6, 127.1, 129.3, 129.6, 136.0, 155.1.

MS (CI): *m*/*z* (%) = 260 (M + 1, 15), 277 (M + 18, 100).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{17}NO_2Si$ $[M]^{+}\cdot$, 259.10286; found, 259.10283.

(_S_)-4-Benzyl-3-[(trimethylsilyl)ethynyl]-1,3-oxazolidin-2-one (4c)

White solid; mp: 109.4–109.8 °C; $[\alpha]_D^{25}$ 96.2.

FTIR (KBr): 2148, 1764 cm^{-1}.

^1H NMR: δ = 0.22 (s, 9 H, Me_3Si), 2.93 (ddd, 1 H, Bn, ^4J = 2.4, ^3J = 7.9, ^2J = 14.0 Hz), 3.22 (dd, 1 H, Bn, ^3J = 3.6, ^2J = 14.0 Hz), 4.09 (m, 1 H, CHO), 4.22–4.33 (m, 2 H, CHO, CHN), 7.17–7.41 (m, 5 H, Ar).

^{13}C NMR: δ = –0.1 ($^1J_{C-Si}$ = 56.2 Hz), 37.5, 58.0, 67.1, 75.9, 90.2, 127.3, 128.8, 129.2, 134.0, 155.1

MS (CI): *m*/*z* (%) = 274 (M + 1, 91), 291 (M + 18, 100)

HRMS (EI): *m*/*z* calcd for $C_{15}H_{19}NO_2Si$ $[M]^{+}\cdot$, 273.11851; found, 273.11551.

(_S_)-4-Isopropyl-3-[(trimethylsilyl)ethynyl]-1,3-oxazolidin-2-one (4d)

White solid; mp 105.4–105.8 °C; $[\alpha]_D^{25}$ 39.8.

FTIR (KBr): 2187, 1769 cm^{-1}.

^1H NMR: δ = 0.13 (s, 9 H, Me_3Si), 0.92 (d, 3 H, CH_3, ^3J = 4.3 Hz), 0.94 (d, 3 H, CH_3, ^3J = 4.3 Hz), 2.13 (m, 1 H, CH), 3.92 (ddd, 1 H, CHN, ^3J = 8.5, 5.5, 4.3 Hz), 4.07 (dd, 1 H, CHO, ^3J = 5.5, ^2J = 9.2 Hz), 4.32 (dd, 1 H, CHO, ^3J = 8.5, ^2J = 9.2 Hz).

^{13}C NMR: δ = 0.1 ($^1J_{C-Si}$ = 56.2 Hz), 15.4, 17.2, 29.4, 61.9, 65.0, 74.9, 91.2, 156.0.

MS (CI): *m*/*z* (%) = 226 (M + 1, 78), 243 (M + 18, 100).

HRMS (EI): *m*/*z* calcd for $C_{11}H_{19}NO_2Si$ $[M]^{+}\cdot$, 225.11851; found, 225.11902.

3-Ethynyl-1,3-oxazolidin-2-one (5a)

Yellow solid; mp 55.8–56.0 °C.

FTIR (NaCl): 3289, 2154, 1769 cm^{-1}.

^1H NMR: δ = 2.83 (s, 1 H), 3.92 (dd, 2 H, CH_2N, ^3J = 9.2, 6.7 Hz), 4.43 (dd, 2 H, CH_2O, ^3J = 9.2, 6.7 Hz).

^{13}C NMR: δ = 46.6, 59.9, 63.4, 72.8, 156.4.

MS (CI): *m*/*z* (%): 112 (M + 1).

HRMS (EI): *m*/*z* calcd for $C_5H_5NO_2$ $[M]^{+}\cdot$, 111.03203; found, 111.03212.

(_R_)-3-Ethynyl-4-phenyl-1,3-oxazolidin-2-one (5b)

Yellow solid; mp 63.4–64.0 °C; $[\alpha]_D^{25}$ –199.9.

FTIR (NaCl): 3295, 2153, 1778 cm^{-1}.

^1H NMR: δ = 2.70 (s, 1 H), 4.23 (dd, 1 H, CHO, ^3J = 7.3, ^2J = 9.2 Hz), 4.73 (dd, 1 H, CHO, ^3J = 8.5, ^2J = 9.2 Hz), 5.07 (dd, 1 H, CHN, ^3J = 7.3, 8.5 Hz), 7.30–7.53 (m, 5 H, Ar)

^{13}C NMR: δ = 61.4, 61.8, 71.1, 71.8, 127.0, 129.5, 129.7, 135.9, 156.0

MS (CI): *m*/*z* (%) = 205 (M + 18).

HR-MS (EI): *m*/*z* calcd for $C_{11}H_9NO_2$ $[M]^{+}\cdot$, 187.06333; found, 187.06303.

(*S*)-4-Benzyl-3-ethynyl-1,3-oxazolidin-2-one (5c)
Yellow solid; mp 61.5–62.3 °C; $[\alpha]_D^{25}$ 104.9.

FTIR (KBr): 2184, 1753 cm^{-1}.

^1H NMR: δ = 2.90 (dd, 1 H, CH_2, ^3J = 7.0, ^2J = 14.0 Hz), 2.98 (s, 1 H), 3.12 (dd, 1 H, CH_2, ^3J = 3.0, ^2J = 14.0 Hz), 4.06 (dd, 1 H, CHO, ^3J = 9.2, ^2J = 12.8 Hz), 4.24 (m, 2 H, CHO, CHN), 7.13–7.34 (m, 5 H, Ar).

^{13}C NMR: δ = 37.4, 57.9, 61.9, 67.5, 71.9, 127.5, 129.0, 129.5, 134.0, 155.8.

MS (CI): *m*/*z* (%) = 202 (M + 1, 95), 219 (M + 18, 100)

HRMS (EI): *m*/*z* calcd for $C_{12}H_{11}NO_2$ $[M]^{+}\cdot$, 201.07898; found, 201.07949.

(*S*)-4-Isopropyl-3-ethynyl-1,3-oxazolidin-2-one (5d)
$[\alpha]_D^{25}$ 50.6 (*c* = 0.9).

FTIR (KBr): 3290, 2150, 1774 cm^{-1}.

^1H NMR: δ = 0.72 (d, 3 H, CH_3, ^3J = 4.3 Hz), 0.74 (d, 3 H, CH_3, ^3J = 4.3 Hz), 1.89–2.06 (m, 1 H, CH), 2.75 (s, 1 H), 3.81 (ddd, 1 H, CHN, ^3J = 8.5, 5.5, 4.3 Hz), 3.93 (dd, 1 H, CHO, ^3J = 5.5, ^2J = 9.2 Hz), 4.21 (dd, 1 H, CHO, ^3J = 8.5, ^2J = 9.2 Hz).

^{13}C NMR: δ = 15.0, 16.9, 28.9, 60.7, 61.3, 64.9, 72.2, 156.3.

MS (ESI/TOF): *m*/*z* (%) = 176 (M + 23).

HRMS (EI): *m*/*z* calcd for $C_8H_{11}NO_2$ $[M]^{+}\cdot$, 153.07898; found, 153.07853.

Metallated Enamines Derived from Oxazolidin-2-ones
Same procedure as above for compounds **2a–c**.

3-[1-(Tributylstannyl)vinyl]-1,3-oxazolidin-2-one (6α)
FTIR (NaCl): 1748 cm^{-1}.

H NMR: δ = 0.80–1.64 (m, 27 H, Bu), 3.73 (dd, 2 H, CH_2N, ^3J = 7.9, ^2J = 8.5 Hz), 4.40 (dd, 2 H, CH_2O, ^3J = 7.9, ^2J = 8.5 Hz), 4.51 [s, 1 H, $^3J_{Sn–H(cis)}$ = 40.9 Hz], 4.83 [s, 1 H, $^3J_{Sn–H(trans)}$ = 92.8, 96.4 Hz].

^{13}C NMR: δ = 12.1 ($^1J_{C–Sn}$ = 354.0, 368.7 Hz), 13.8, 25.7, 27.4 ($^3J_{C–Sn}$ = 61.0 Hz), 29.1 ($^2J_{C–Sn}$ = 19.5), 43.3, 62.1, 68.0, 104.4 ($^2J_{C–Sn}$ = 34.2 Hz), 147.1 ($^1J_{C–Sn}$ = 339.4, 356.5 Hz), 157.0.

MS (CI): *m*/*z* (%) = 404 (M + 1, 96), 421 (M + 18, 100), 346 (M – 57, 24).

HRMS (EI): *m*/*z* calcd for $C_{16}H_{30}NO_2Sn$ $[M – Me]^{+}\cdot$, 388.12985; found, 388.13114.

3-[(*Z*)-1-(Tributylstannyl)-2-(trimethylsilyl)vinyl]-1,3-oxazolidin-2-one [(*Z*)-7α]
FTIR (NaCl): 1745 cm^{-1}.

^1H NMR: δ = 0.14 (s, 9 H, Me_3Si), 0.75–1.61 (m, 27 H, Bu), 3.75 (t, 2 H, CH_2N, ^3J = 7.9 Hz), 4.36 (t, 2 H, CH_2O, ^3J = 7.9 Hz), 5.49 (s, 1 H, $^3J_{Sn–H}$ = 114.1, 119.0 Hz).

^{13}C NMR: δ = 0.9, 14.1 ($^1J_{C–Sn}$ = 344.2, 359.9 Hz), 27.4 ($^3J_{C–Sn}$ = 68.4 Hz), 29.1 ($^2J_{C–Sn}$ = 19.5 Hz), 44.1, 62.3, 122.7 ($^2J_{C–Sn}$ = 61.0 Hz), 156.5, 156.7.

HRMS (FAB): *m*/*z* calcd for $C_{16}H_{32}NO_2SiSn$ $[M – Bu]^{+}\cdot$, 418.12243; found, 418.1234.

(*Z*)-3-[1,2-Bis(trimethylstannyl)vinyl]-1,3-oxazolidin-2-one (8)
FTIR (NaCl): 1738 cm^{-1}.

^1H NMR: δ = 0.21 (s, 9 H, Me, $^2J_{Sn–H}$ = 52.5, 54.9 Hz), 0.23 (s, 9 H, Me, $^2J_{Sn-H}$ = 53.7, 56.2 Hz), 3.78 (dd, 2 H, CH_2N, ^3J = 7.3, ^2J = 8.5 Hz), 4.39 (t, 2 H, CH_2O, ^3J = 7.3, ^2J = 8.5 Hz), 5.65 (s, 1 H, $^3J_{Sn–H}$ = 40.3, $^2J_{Sn–H}$ = 134.3, 140.4 Hz)

^{13}C NMR: δ = –6.6 ($^1J_{C–Sn}$ = 341.8, 361.3 Hz), –4.3 ($^1J_{C–Sn}$ = 344.2, 358.9 Hz), 43.6, 62.4, 121.1 ($^1J_{C–Sn}$ = 478.5, 500.5, $^2J_{C–Sn}$ = 78.1 Hz), 155.9, 156.5

HRMS (FAB): *m*/*z* calcd for $C_{10}H_{20}NO_2{}^{118}Sn^{120}Sn$ $[M – Me]^{+}\cdot$, 423.95321; found, 423.954.

(*R*)-4-Phenyl-3-[1-(tributylstannyl)vinyl]-1,3-oxazolidin-2-one (9α)
$[\alpha]_D^{25}$ –18.8 (*c* = 1.2).

FTIR (NaCl): 1751 cm^{-1}.

^1H NMR: δ = 0.80–1.66 (m, 27 H, Bu), 4.09 (dd, 1 H, CHO, ^3J = 4.3, ^2J = 8.5 Hz), 4.46 [s, 1 H, $^3J_{Sn–H(cis)}$ = 42.7 Hz], 4.67 (t, 1 H, CHO, ^3J = 8.5 Hz), 4.71 [s, 1 H, $^3J_{Sn–H(trans)}$ = 95.8, 98.9], 5.16 (dd, 1 H, CHN, ^3J = 4.3, 8.5 Hz), 7.16–7.42 (m, 5 H, Ar).

^{13}C NMR: δ = 12.3 ($^1J_{C–Sn}$ = 354.0, 368.7 Hz), 13.9, 27.5 ($^3J_{C–Sn}$ = 61.3 Hz), 29.2 ($^2J_{C–Sn}$ = 19.5 Hz), 59.2, 70.5, 107.4 ($^2J_{C–Sn}$ = 29.3 Hz), 125.9, 128.6, 129.4, 139.1, 145.5 ($^1J_{C–Sn}$ = 341.8, 356.5 Hz), 157.4.

MS (CI): *m*/*z* (%) = 480 (M + 1, 100), 497 (M +1 85), 422 (M – 57, 14).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{28}NO_2Sn$ $[M – Bu]^{+}\cdot$, 422.1142; found, 422.11269.

(*R*)-4-Phenyl-3-[(*Z*)-1-(tributylstannyl)-2-(trimethylsilyl)vinyl]-1,3-oxazolidin-2-one (10α)
$[\alpha]_D^{25}$ 69.3 (*c* = 1.18).

FTIR (NaCl): 1744 cm^{-1}.

^1H NMR: δ = –0.04 (s, 9 H, Me_3Si), 0.66–1.63 (m, 27 H, Bu), 4.11 (dd, 1 H, CHO, ^3J = 7.9, ^2J = 8.5 Hz), 4.65 (t, 1 H, CHO, ^3J = 8.5 Hz), 5.28 (dd, 1 H, CHN, ^3J = 7.9, ^2J = 8.5 Hz), 5.46 (s, 1 H, $^3J_{Sn–H}$ = 118.4, 123.3 Hz), 7.16–7.40 (m, 5 H, Ar).

^{13}C NMR: δ = 0.4 ($^1J_{C–Si}$ = 53.7 Hz), 13.5 ($^1J_{C–Sn}$ = 341.8, 356.4 Hz), 13.7, 27.5 ($^3J_{C–Sn}$ = 68.4 Hz), 29.1 ($^2J_{C–Sn}$ = 17.1 Hz), 59.7, 70.2, 126.7, 128.3, 128.5 ($^2J_{C–Sn}$ = 63.5 Hz), 128.9, 137.2, 154.2 ($^1J_{C–Sn}$ = 385.7, 405.3 Hz), 156.8.

MS (CI): *m*/*z* (%) = 552 (M + 1, 100), 569 (M + 18, 8), 494 (M – 57, 60).

HRMS (FAB): *m*/*z* calcd for $C_{22}H_{36}NO_2SiSn$ $[M – Bu]^{+}\cdot$, 494.15373; found, 494.154.

(*R*)-4-Phenyl-3-[(*Z*)-bis(tributylstannyl)vinyl]-1,3-oxazolidin-2-one (11)
$[\alpha]_D^{25}$ 9.6 (*c* = 0.93).

FTIR (NaCl): 1747 cm^{-1}.

^1H NMR: δ = 0.62–1.66 (m, 54 H, Bu), 4.08 (dd, 1 H, CHO, ^3J = 6.7, ^2J = 8.5 Hz), 4.64 (dd, 1 H, CHO, ^3J = 8.5, ^2J = 9.1 Hz), 5.27 (dd, 1 H, CHN, ^3J = 6.7, 9.1 Hz), 5.54 (s, 1 H, $^3J_{Sn–H}$ = 30.5, $^3J_{Sn–H}$ = 125.7, 131.8 Hz), 7.14–7.42 (m, 5 H, Ar).

^{13}C NMR: δ =11.2 ($^1J_{C–Sn}$ = 332.0, 346.7 Hz), 13.2 ($^1J_{C–Sn}$ = 344.2, 358.9 Hz), 13.2, 13.8, 27.3 ($^3J_{C–Sn}$ = 53.7, 58.6 Hz), 27.7 ($^3J_{C–Sn}$ = 63.5, 68.4), 29.1 ($^2J_{C–Sn}$ = 19.5 Hz), 29.4 ($^2J_{C–Sn}$ = 19.5 Hz), 59.7, 70.4, 125.2 ($^1J_{C–Sn}$ = 405.3, 422.4, $^2J_{C–Sn}$ = 70.8 Hz), 126.5, 128.3, 129.1, 138.6, 153.6 ($^1J_{C–Sn}$ = 417.5, 437.0, $^2J_{C–Sn}$ = 80.6 Hz), 156.9.

MS (CI): *m*/*z* (%) = 769 ($M^{+}\cdot$).

HRMS (FAB): *m*/*z* calcd for $C_{31}H_{54}NO_2{}^{118}Sn^{120}Sn$ $[M – Bu]^{+}\cdot$, 710.21926; found, 710.2244.

(*S*)-4-Benzyl-3-[1-(tributylstannyl)vinyl]-1,3-oxazolidin-2-one (12α)

$[\alpha]_D^{25}$ 19.8 (*c* = 0.98).

FTIR (NaCl): 1746 cm^{-1}.

^1H NMR: δ = 0.81–1.70 (m, 27 H, Bu), 2.74 (dd, 1 H, CH_2, ^3J = 8.5, ^2J = 13.4 Hz), 3.26 (dd, 1 H, CH_2, ^3J = 2.4, ^2J = 13.4), 4.18 (m, 2 H, CH_2O), 4.38–4.48 (m, 1 H, CHN), 4.73 [s, 1 H, $^3J_{Sn-H(cis)}$ = 42.1], 5.18 [s, 1H, $^3J_{Sn-H(trans)}$ = 95.2, 98.9 Hz], 7.14–7.37 (m, 5 H, Ar).

^{13}C NMR: δ = 12.3 ($^1J_{C-Sn}$ = 351.7, 368.7 Hz), 13.9, 27.5 ($^3J_{C-Sn}$ = 61.0 Hz), 29.2 ($^2J_{C-Sn}$ = 17.1 Hz), 35.8, 55.3, 66.4, 105.3 ($^2J_{C-Sn}$ = 34.2 Hz), 127.3, 129.0, 129.4, 135.9, 145.9 ($^1J_{C-Sn}$ = 339.4, 354.0 Hz), 156.7.

HRMS (FAB): *m*/z calcd for $C_{20}H_{30}NO_2Sn$ $[M - Bu]^+\cdot$, 436.12985; found, 436.131.

(*S*)-4-Benzyl-3-[(*Z*)-1-(tributylstannyl)-2-(trimethylsilyl)vinyl]-1,3-oxazolidin-2-one [(*Z*)-13α]

$[\alpha]_D^{25}$ –97.4 (*c* = 2.1).

FTIR (NaCl): 1629cm^{-1}.

^1H NMR: δ = 0.20 (s, 9 H, Me_3Si), 0.80–1.65 (m, 27 H, Bu), 2.61 (dd, 1 H, CH_2, ^3J = 9.1, ^2J = 14.0 Hz), 3.29 (dd, 1 H, CH_2, ^3J = 3.1, ^2J = 14.0 Hz), 4.10 (dd, 1 H, CHO, ^3J = 6.1, ^2J = 8.5) Hz, 4.24 (t, 1 H, CHO, ^3J = 8.5, ^2J = 8.5 Hz), 4.51–4.65 (m, 1 H, CHN), 5.87 (s, 1 H, $^3J_{Sn-H}$ = 116.0, 120.9 Hz), 7.06–7.37 (m, 5 H, Ar).

^{13}C NMR: δ = 1.0 ($^1J_{C-Si}$ = 51.3 Hz), 13.8 ($^1J_{C-Sn}$ = 341.8, 358.9 Hz), 13.9, 27.7 ($^3J_{C-Sn}$ = 65.9 Hz), 29.3, 37.3, 55.3, 67.2, 127.2 ($^2J_{C-Sn}$ = 65.9 Hz), 127.3, 129.1, 129.3, 136.1, 156.0 ($^1J_{C-Sn}$ = 378.4, 395.5 Hz), 156.6.

MS (ESI/TOF): *m*/z (%) = 588 (M + 23, 100), 508 (M –57, 64).

HRMS (FAB): *m*/z calcd for $C_{23}H_{38}NO_2SiSn$ $[M - Bu]^+\cdot$, 508.16938; found, 508.1688.

(*S*)-4-Benzyl-3-[(*Z*)-bis(tributylstannyl)vinyl]-1,3-oxazolidin-2-one (14)

$[\alpha]_D^{25}$ –75.0 (*c* = 1.31).

FTIR (NaCl): 1744 cm^{-1}.

^1H NMR: δ = 0.82–1.72 (m, 54 H, Bu), 2.58 (dd, 1 H, CH_2, ^3J = 9.7, ^2J = 13.4 Hz), 3.32 (dd, 1 H, CH_2, ^3J = 3.1, ^2J = 13.4 Hz), 4.14 (dd, 1 H, CHO, ^3J = 4.9, ^2J = 8.5 Hz), 4.21 (t, 1 H, CHO, ^3J = 8.5 Hz), 4.52–4.66 (m, 1 H, CHN), 6.03 (s, 1 H, $^2J_{Sn-H}$ = 33.0, $^3J_{Sn-H}$ = 124.5, 130.0 Hz), 7.14–7.42 (m, 5 H, Ar).

^{13}C NMR: δ = 12.0 ($^1J_{C-Sn}$ = 334.7, 349.1 Hz), 13.3 ($^1J_{C-Sn}$ = 341.8, 361.3 Hz), 13.8, 13.9, 27.5 ($^3J_{C-Sn}$ = 58.6 Hz), 27.7 ($^3J_{C-Sn}$ = 65.9 Hz), 29.3, 29.4, 36.8, 55.2, 66.9, 123.7 ($^1J_{C-Sn}$ = 400.4, 417.5, $^2J_{C-Sn}$ = 73.2 Hz), 127.3, 129.1, 129.2, 136.3, 155.0 ($^1J_{C-Sn}$ = 417.5, 437.0, $^2J_{C-Sn}$ = 80.6 Hz), 156.3

HRMS (FAB): *m*/z calcd for $C_{32}H_{56}NO_2Sn_2$ $[M - Bu]^+\cdot$, 726.2355; found, 726.2351.

(*S*)-4-Isopropyl-3-[1-(tributylstannyl)vinyl]-1,3-oxazolidin-2-one (15α)

$[\alpha]_D^{25}$ –2.9 (*c* = 1.09).

FTIR (NaCl): 1743 cm^{-1}.

^1H NMR: δ = 0.74–1.62 (m, 33 H, Bu, CH_3), 2.40–2.56 (m, 1 H, CH), 4.20 (m, 3 H, CHN, CH_2O), 4.58 [s, 1 H, $^3J_{Sn-H(cis)}$ = 42.7 Hz], 4.95 [s, 1 H, $^3J_{Sn-H(trans)}$ = 96.4, 100.7 Hz).

^{13}C NMR:δ = 12.4 ($^1J_{C-Sn}$ = 351.6, 368.7 Hz), 13.9, 13.9, 25.3, 27.5 ($^3J_{C-Sn}$ = 61.0 Hz), 29.2 ($^2J_{C-Sn}$ = 19.5 Hz), 58.7, 62.8, 105.4 ($^2J_{C-Sn}$ = 34.2 Hz), 145.7 ($^1J_{C-Sn}$ = 346.7, 366.2 Hz), 157.1.

MS (ESI/TOF): *m*/z (%) = 446 (M + 1, 100), 388 (M – 57, 11).

HRMS (FAB): *m*/z calcd for $C_{16}H_{30}NO_2Sn$ $[M - Bu]^+\cdot$, 388.12985; found, 388.1306.

(*S*)-4-Isopropyl-3-[(*Z*)-1-(tributylstannyl)-2-(trimethylsilyl)vinyl]-1,3-oxazolidin-2-one [(*Z*)-16α]

$[\alpha]_D^{25}$ –124.6 (*c* = 1.21).

FTIR (NaCl): 1741 cm^{-1}.

^1H NMR: δ = 0.14 (s, 9 H, Me_3Si), 0.72–1.62 (m, 33 H, Bu, CH_3), 2.20–2.36 (m, 1 H, CH), 4.09 (ddd, 1 H, CHO, ^4J = 0.6, ^3J = 7.3, ^2J = 8.5 Hz), 4.24 (td, 1 H, CHO, ^4J = 0.6, ^3J = 8.5 Hz), 4.32–4.42 (m, 1 H, CHN), 5.69 (s, 1 H, $^3J_{Sn-H}$ = 117.8, 123.3 Hz).

^{13}C NMR: δ = 0.9 ($^1J_{C-Si}$ = 53.7 Hz), 13.7 ($^1J_{C-Sn}$ = 341.8, 356.5 Hz), 14.6, 18.2, 25.9, 27.7 ($^3J_{C-Sn}$ = 65.9 Hz), 29.2, 58.1, 63.1, 126.7 ($^2J_{C-Sn}$ = 107.4 Hz), 155.7 ($^1J_{C-Sn}$ = 385.7, 405.3 Hz), 157.0.

MS (ESI/TOF): *m*/z (%) = 540 (M + 23, 79), 460 (M – 57, 100).

HRMS (FAB): *m*/z calcd for $C_{19}H_{38}NO_2SiSn$ $[M - Bu]^+\cdot$, 460.16938; found, 460.17.

(*S*)-4-Isopropyl-3-[(*Z*)-bis(trimethylstannyl)vinyl]-1,3-oxazolidin-2-one (17)

$[\alpha]_D^{25}$ –63.0 (*c* = 1.24).

FTIR (NaCl): 1735cm^{-1}.

^1H NMR: δ = 0.20 (s, 9 H, $^2J_{Sn-H}$ = 52.5, 54.9 Hz), 0.21(s, 9 H, $^2J_{Sn-H}$ = 53.1, 55.5 Hz), 0.79 (d, 3 H, ^3J = 6.1 Hz), 0.87 (d, 3 H, ^3J = 6.7 Hz), 2.28–2.41 (m, 1 H), 4.08–4.30 (m, 2 H, CH_2O), 4.35–4.45 (m, 1 H, CHN), 5.86 (s, 1 H, $^3J_{Sn-H}$ = 43.3, $^2J_{Sn-H}$ = 137.3, 144.1 Hz).

^{13}C NMR: δ = –6.7 ($^1J_{C-Sn}$ = 341.8, 356.4), –4.3 ($^1J_{C-Sn}$ = 361.3, 376.0 Hz), 14.1, 17.9, 25.4, 57.3, 62.9, 124.3 ($^1J_{C-Sn}$ = 473.6, 495.6, $^2J_{C-Sn}$ = 80.6 Hz), 154.8, 156.7.

HRMS (FAB): *m*/z calcd for $C_{13}H_{26}NO_2Sn_2$ $[M - Me\cdot]^+$, 468.00075; found, 468.0007.

α-Stannyl Enamides Transmetallation/Trapping Experiments

A flame dried Schlenk tube is charged with the stannyl compound (0.3 mmol), placed under vacuum and then under nitrogen. Anhyd THF is added and the solution is cooled to –100 °C, and *n*-BuLi (2.4 equiv, 1.6 M/hexane, 0.72 mmol, 450 μL) is slowly added at –100 °C. The solution is stirred for 5 min and the electrophile (2.5 equiv, 0.75 mmol) is added (as a THF solution for ketones). Completion of the reaction is checked by TLC, H_2O (2 mL) is added and the cooling bath is removed and stirring is continued for 30 min. The resulting mixture is diluted with THF (50 mL), dried over Na_2SO_4, filtered and reduced in vacuo to a residue that was purified by flash chromatography over silica gel.

3-[1-(1-Hydroxyhexyl)vinyl]-1,3-oxazolidin-2-one (19)

FTIR (NaCl): 3434 (br), 1747, 1620 cm^{-1}.

^1H NMR: δ = 0.77–0.97 (m, 3 H), 1.18–1.88 (m, 8 H), 2.30 (br s, 1 H, OH), 3.50–3.65 (m, 2 H, CH_2O), 3.77–3.87 (m, 2 H, CH_2N), 4.04 (dd, 1 H, ^2J = 3.1, ^4J = 1.8 Hz), 4.23 (dd, 1 H, ^2J = 3.1, ^4J = 2.4 Hz), 4.95–5.05 (m, 1 H).

^{13}C NMR: δ = 13.9, 22.4, 23.5, 31.3, 35.3, 43.9, 59.3, 78.8, 80.5, 145.6, 157.4.

MS (ESI/TOF): *m*/z (%) = 214 (M + 1).

HRMS (EI): m/z calcd for $C_{11}H_{19}NO_3$ $[M]^+\cdot$, 213.13649; found, 213.13714.

3-[1-(1-Hydroxy-1,2-dimethylpropyl)vinyl]-1,3-oxazolidin-2-one (20)

FTIR (NaCl) : 3440 (br), 1766 cm^{-1}.

^1H NMR: δ = 0.90 (d, 3 H, ^3J = 6.7 Hz), 1.00 (d, 3 H, ^3J = 6.7 Hz), 1.48 (s, 3 H), 1.85 (hept, 1 H, ^3J = 6.7 Hz), 2.28 (br s, 1 H, OH) 3.51–3.70 (m, 2 H, CH_2N), 3.81 (dd, 2 H, CH_2O, ^3J = 5.5, ^2J = 11 Hz), 3.98 (d, 1 H, ^2J = 3.1 Hz), 4.20 (d, 1 H, ^2J = 3.1 Hz).

^{13}C NMR: δ = 16.0, 16.2, 24.8, 37.2, 43.8, 59.3, 80.1, 87.4, 128.3, 149.5.

MS (ESI/TOF) m/z (%): 200 (M + 1, 100), 222 (M + 23, 49).

HRMS (EI): *m*/*z* calcd for $C_{10}H_{17}NO_3$ $[M]^+\cdot$, 199.12084; found, 199.12073.

(*S*)-4-Benzyl-3-[1-(1-hydroxyhexyl)vinyl]-1,3-oxazolidin-2-one (21)

FTIR (NaCl): 3434 (br), 1760, 1621 cm^{-1}.

^1H NMR: δ = 0.86 (t, 3 H, ^3J = 6.7 Hz), 1.16–1.78 (m, 8 H), 3.10 (d, 3 H, CH_2, OH, ^3J = 7.3 Hz), 3.84–4.07 (m, 4 H, CH_2O, CHN, =CH), 4.12–4.20 (m, 1 H), 4.80–4.89 (m, 1 H), 7.16–7.34 (m, 5 H, Ar).

^{13}C NMR: δ = 13.9, 22.4, 23.4, 31.3, 33.5, 35.3, 57.5, 61.9, 78.7, 81.2, 126.7, 128.5, 129.1, 137.4, 145.5, 157.2.

MS (ESI/TOF): *m*/*z* (%) = 304 (M + 1, 100), 326 (M + 23, 11).

HRMS (EI): *m*/*z* calcd for $C_{18}H_{25}NO_3$ $[M]^+\cdot$, 303.18344; found, 303.18337.

(*S*)-4-Benzyl-3-[1-(1-hydroxy-1,2-dimethylpropyl)vinyl]-1,3-oxazolidin-2-one (22)

^1H NMR: δ = 0.84 (d, 3 H, ^3J = 6.7 Hz), 0.95 (d, 3 H, ^3J = 6.7 Hz), 1.22 (s, 3 H), 1.74 (hept, 1 H, ^3J = 6.7 Hz), 3.05–3.22 (m, 3 H, CH_2, OH), 3.79 (d, 1 H, ^2J = 3.1 Hz), 3.76–3.94 (m, 2 H, CH_2O), 3.97–4.08 (m, 1 H, CHN), 4.04 (d, 1 H, ^2J = 3.1 Hz).

^{13}C NMR: δ =16.0, 16.2, 24.9, 33.6, 37.1, 57.3, 62.5, 80.2, 87.5, 126.7, 128.5, 129.3, 137.5, 149.9, 156.6.

MS (ESI/TOF): *m*/*z* (%) = 290 (M + 1, 70), 312 (M + 23, 100).

FTIR (NaCl): 3503 (br), 1735 cm^{-1}.

HRMS (EI): m/z calcd for $C_{17}H_{23}NO_3$ $[M]^+\cdot$ 289.16779; found, 289.16829.

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