Iodine(III)-Mediated Cyclization of Unsaturated *O*-Alkyl Hydroxamates: Silyl-Assisted Access to α-Vinyl and α-(2-Silylvinyl) Lactams

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Abstract: The embodiment of lactam rings within a wealth of physiologically active natural products and pharmaceutical agents ensures that the development of synthetic methods, which facilitate the preparation of these saturated N-heterocycles, is of critical importance. Herein the development of a versatile method for the synthesis of 4 to 8-membered α-vinyl and α-(2-silylvinyl) lactams involving the iodine(III)-mediated oxidative cyclization of unsaturated *O*-alkyl hydroxamates, which encompass an allylsilane, is reported. Importantly, the outcome of this transformation can be effectively controlled through variation of the substitution pattern at the silicon center. While allyltrimethylsilanes undergo ring closure with desilylation to form α-vinyl lactams, the corresponding triisopropyl and triphenylsilanes cyclize without loss of the larger silyl group to form *E*-vinylsilanes with excellent stereoselectivity. From a mechanistic standpoint, it is proposed that this reaction proceeds via concerted alkene addition of a singlet nitrenium ion (or its equivalent) to form a bicyclic *N*-acyl-*N*-alkoxyaziridinium ion, which undergoes eliminative ring opening.

Key words: nitrenium ion, allylsilane, hypervalent iodine, *O*-alkyl hydroxamate, aziridinium

Allylsilanes are versatile nucleophiles, which undergo regiocontrolled addition and substitution with a broad range electrophiles.[1] While the role of electron-deficient carbon, oxygen, and sulfur species in this context has been extensively investigated, there are comparatively few examples of the reaction of nitrogen-based electrophiles with allylsilanes. Of the various transformations reported to date, including nitrene-mediated aziridination,[2] addition to aryldiazonium ions[3] and azo compounds,[4] the cycloaddition of azides,[5] and nitration with nitronium ion salts,[6,7] the reaction of allylsilanes with nitrenium ions (R_2N^+) is the least well studied. Indeed, only two examples of this process have previously been reported. Takeuchi has examined the reaction of arylnitrenium ions with cyclic allylic silanes in the presence of $AlCl_3$[8] while Abramovitch has employed allyltrimethylsilane as a nucleophilic trap for the photolytically generated 1,2,4-triazolyl cation.[9] The paucity of studies in this area, in common with the limited synthetic deployment of nitrenium ions in general, has historically arisen because of a lack of methods for the generation of these highly electron-deficient species under mild conditions.[10]

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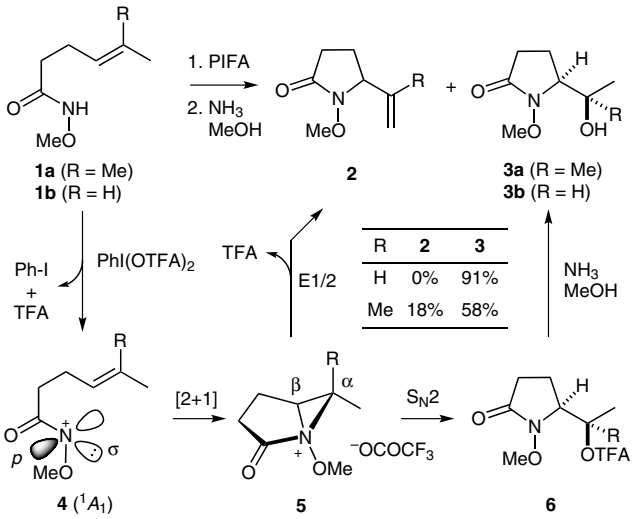
In this regard, we recently reported a versatile alkene oxamidation method for the preparation of α-hydroxyalkyl lactams **3**, which is believed to take place via the concerted intramolecular alkene addition of acylnitrenium ions **4** to form bicyclic aziridinium ions **5** (Scheme 1).[11] In most cases, concerted ion pair collapse of these highly reactive species occurs solely at the less encumbered α-position to yield α-trifluoroacetoxyalkyl lactams **6**. The nitrenium ion intermediates in this case appear to be singlet in nature and are generated under mild conditions, through the chemoselective N-oxidation of unsaturated *O*-alkyl hydroxamates **1** with phenyliodine(III) bis(trifluoroacetate) (PIFA).[12] In the current article, we report on the development of a versatile synthetic method for the preparation of 4–8-membered α-vinyl and α-(2-silylvinyl) lactams, which involves the oxidative cyclization of *O*-alkyl hydroxamates that encompass an allylsilane moiety rather than a simple alkene.

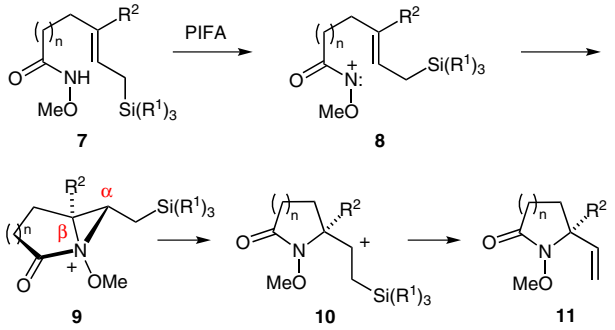


Scheme 1 Iodine(III)-mediated oxidative cyclization of unsaturated *O*-alkyl hydroxamates

Our interest in the reaction of nitrenium ions with allylsilanes arose during the development of the aforementioned oxamidation methodology and specifically with the observation that, in contrast to disubstituted olefin **1b**, trisubstituted alkene **1a**, underwent cyclization to form α-vinyl lactam **2** in addition to the expected oxamidation product **3a** (Scheme 1).[11a] From a mechanistic standpoint, the formation of compound **2** was rationalized in terms of the eliminative ring opening of the sterically encumbered

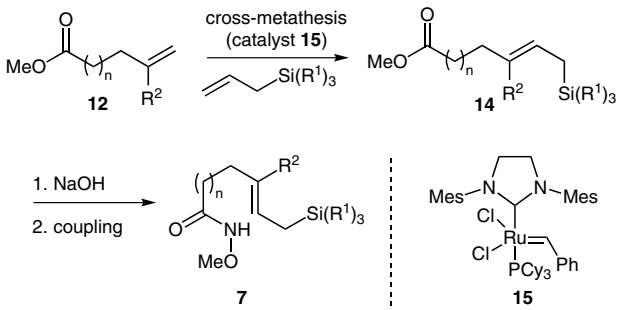
aziridinium ion **5** (R = Me).[13] That extended exposure of trifluoroacetate **6**, the first-formed product of substitutive ring opening, to trifluoroacetic acid did not change the product ratio **2**:**3a** added credence to our assumption that **2** arises directly from **5** rather than through the elimination of ester **6**.

In order to tap this unanticipated reaction manifold, we decided to explore the cyclization of allylsilane-based substrates **7** as a means to purposely promote eliminative ring opening and thus formation of α-vinyl lactams **11** (Scheme 2). In this case, it was anticipated that upon concerted alkene addition of nitrenium ion **8**,[14] the presence of a silylmethyl substituent in the resulting aziridinium ion **9** would not only promote elimination to β-silyl carbocation **10** through intercession of the β-effect,[1] but also disfavor substitutive ring opening at the neighboring α-position by virtue of its steric encumbrance. *A priori*, it was uncertain whether N-oxidation of the hydroxamate group in **7** could be achieved selectively since allylsilanes are known to undergo electrophilic substitution with iodine(III)-based reagents.[15,16]



Scheme 2 Nitrenium-alkene addition: silyl-assisted access to α-vinyl lactams

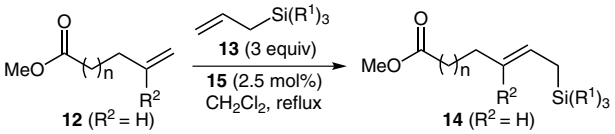
Our investigation commenced with the development of a general route to unsaturated *O*-alkyl hydroxamates **7**. As outlined in Scheme 3, our approach to these substrates centered on the installation of the allylsilane moiety through cross-metathesis between ω-unsaturated esters **12** (R^2 = H) and simple, commercially available allylsilanes **13**. The cross-metathesis of these nucleophilic alkenes is often efficient and has been successfully employed for the direct assembly of more complex allylsilanes in a number of cases.[17,18]



Scheme 3 General strategy for the preparation of unsaturated *O*-alkyl hydroxamate substrates **7**

As summarized in Table 1, allylsilane preparation via cross-metathesis was readily accomplished through the use of the Grubbs second-generation catalyst (Grubbs II, **15**),[19] using a three-fold excess of the appropriate allylsilane **13** in CH_2Cl_2 (0.5 M) at reflux. In all cases, but **14a** (Table 1, entry 1) and **14d** (entry 3), cross-metathesis proceeded with reasonable to high selectivity for the *E*-isomer. In cases where the *Z*-isomer was not detected by ^1H or ^{13}C NMR spectroscopy, a selectivity of greater than 25:1 is suggested. In other cases, chromatographic isomer separation was not possible and silane mixtures were necessarily carried forward. While the low diastereoselectivity observed during the formation of **14d** was unexpected, Gouverneur has previously noted that the *O*-benzyl analogue of β,γ-unsaturated ester **12a** undergoes cross-metathesis with only moderate selectivity (dr = 3:1).[17f]

Table 1 Preparation of Allylsilanes **14** via Cross-Metathesis[a]



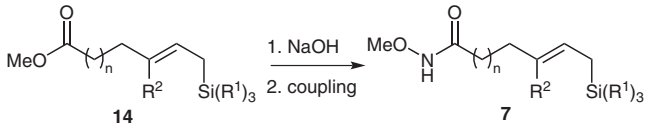
Entry	**12**	n	R	**14**	Yield (%)[b]	*E*/*Z* ratio[c]
1	**a**	0	Me	**a**	92	2:1
2	**b**	1	Me	**b**	90	>25:1
3	**d**[d]	2	Me	**d**	87	>25:1
4	**e**	3	Me	**e**	85	8:1
5	**f**	4	Me	**f**	80	10:1
6	**g**	1	*i*-Pr	**g**	75	2:1
7	**h**	2	*i*-Pr	**h**	68	6:1
8	**i**	3	*i*-Pr	**i**	57	6:1
9	**j**	1	Ph	**j**	83	>25:1
10	**k**	2	Ph	**k**	74	>25:1
11	**l**	3	Ph	**l**	37	>25:1

[a] Conditions: **12**, **13** (3 equiv), Grubbs-II (**15**; 2.5 mol%), CH_2Cl_2 (0.5 M), reflux.
[b] Isolated yields, after purification by flash chromatography.
[c] Isomer ratio determined by ^1H NMR spectroscopy.
[d] For the preparation of hydroxamate **7c**, see Table 2 and Scheme 4.

Introduction of the hydroxamate ester functionality necessary for the generation of the nitrenium ion intermediate was now accomplished by saponification of **14** and amide coupling. The latter step was accomplished by conversion of the carboxylic acids to the corresponding mixed anhydrides, using isobutyl chloroformate, and in situ coupling with methoxylamine hydrochloride in the presence of triethylamine (Table 2).

Trisubstituted *E*-allylsilane **7c** was not prepared through cross-metathesis, but rather from compound **16**, through

Table 2 Preparation of Unsaturated *O*-Alkyl Hydroxamates **7**[a]



Entry	**14**	n	R^1	R^2	**7**	Yield (%)[b]	*E*/*Z* ratio[c]
1	**a**	0	Me	H	**a**	74	2:1
2	**b**	1	Me	H	**b**	85	>25:1
3	**c**	2	Me	Me	**c**	89	>25:1[d]
4	**d**	2	Me	H	**d**	67	>25:1
5	**e**	3	Me	H	**e**	88	8:1
6	**f**	4	Me	H	**f**	63	10:1
7	**g**	1	*i*-Pr	H	**g**	67	2:1
8	**h**	2	*i*-Pr	H	**h**	36	6:1
9	**i**	3	*i*-Pr	H	**i**	61	6:1
10	**j**	1	Ph	H	**j**	53	>25:1
11	**k**	2	Ph	H	**k**	47	>25:1
12	**l**	3	Ph	H	**l**	48	>25:1

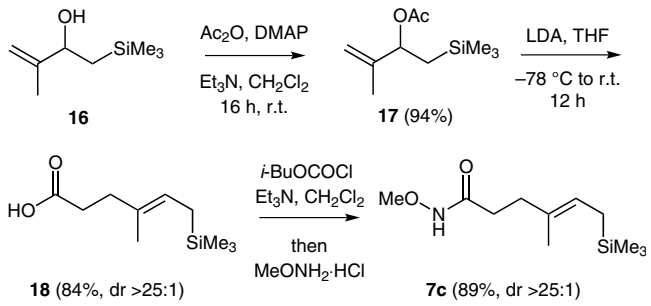
[a] Conditions: (1) NaOH (4 equiv), EtOH–H_2O (1:1), reflux, 2 h; (2) RCO_2H, *i*-BuOCOCl, Et_3N, CH_2Cl_2, –40 °C → r.t., 12 h, then $MeONH_2$·HCl (1.2 equiv), Et_3N, r.t., 12 h.

[b] Isolated yield over two steps, after purification by flash chromatography.

[c] Isomer ratio of determined by ^1H NMR spectroscopy.

[d] Compound **7c** was prepared via the route shown in Scheme 4.

the highly stereoselective Ireland–Claisen rearrangement of allylic acetate **17** following the method reported by Cane (Scheme 4).[20]

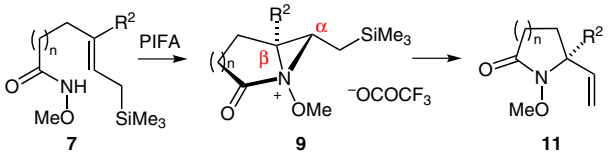


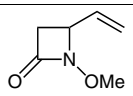
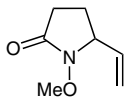
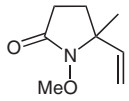
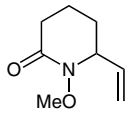
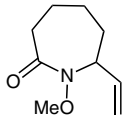
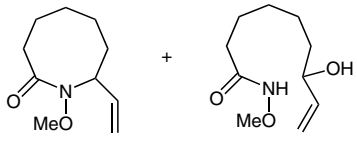
Scheme 4 Stereoselective synthesis of trisubstituted allylsilane **7c**

Having successfully assembled a group of substrates bearing various silyl and alkene substituents and also chain lengths, our goal was now to validate the feasibility of the nitrenium ion cyclization. While our alkene oxamidation methodology calls for the co-addition of trifluoroacetic acid as a means to improve cyclization efficiency,[11a] we opted to forgo this modification in light of its potential to cause substrate protodesilylation.[1] Accordingly, trimethylsilyl-substituted substrates **7a–f** were simply treated with a slight excess of phenyliodine(III) bis(trifluoroacetate) in CH_2Cl_2 at 0 °C (Table 3). In all cases, cyclization proceeded rapidly and was complete within 30 minutes, at which point the reactions were treated with a solution of anhydrous ammonia in methanol to destroy excess PIFA, neutralize the trifluoroacetic acid generated during this reaction, and solvolyze any ester addition products.

As is apparent from Table 3, this reaction is characterized by broad substrate scope and provides efficient access to 4–7- and even 8-membered lactams; only in the case of azocanone **11f** was a by-product formation noted. In this regard, secondary allylic alcohol **19** is thought to arise

Table 3 Scope of *O*-Alkyl Hydroxamate Cyclization: Trimethyl Allylsilanes[a,b]



Entry	Product	Yield (%)
1	 **11a**	67
2	 **11b**	72
3	 **11c**	72
4	 **11d**	91
5	 **11e**	87
6	 **11f** + **19**	**11f** (42%); **19** (24%)

[a] Conditions: **7**, PIFA (1.2 equiv), CH_2Cl_2 (0.15 M), 0 °C; then NH_3–MeOH, 20 min.

[b] Isolated yield of α-vinyl lactams, after purification by flash chromatography.

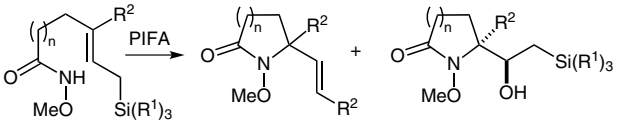
from **7f** through direct attack of PIFA at the allylsilane to form an allyl-λ^3-iodane. Nucleophilic displacement of iodobenzene with trifluoroacetate and hydrolysis, would then lead to the observed by-product.[21]

As indicated in Table 4, the cyclization of triisopropyl and triphenylsilane substrates **7g–l**, although more complex than that of their trimethylsilyl congeners, led to the welcome formation of *E*-vinylsilanes **20**. For example, while exposure of heptenamide **7h** (Table 4, entry 2) to PIFA lead to the formation of α-vinyl piperidinone **11d** and *anti*-oxamidation product **21h**, the major component of this reaction proved to be *E*-vinylsilane **20h**, which was generated in high yield and was readily separable from the minor products. Similar observations were noted during the formation of piperidinone **20k** (entry 5) and the azepanone systems **20i** and **20l** (entries 3 and 6), but not pyrrolidinones (entries 1 and 4). In the case of hexenamides **7g** and **7j**, cyclization exclusively generated *anti*-oxamidation addition product **21g** and α-vinyl lactam **11b**, respectively. Notably, the formation of **21g**, in common with the other addition products shown in Table 4, occured with complete stereocontrol. In light of our previous observations,[11] this process is assumed to proceed with overall *anti* stereochemistry.

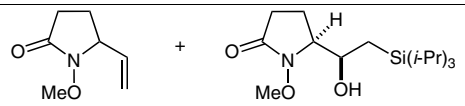
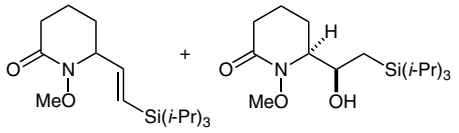
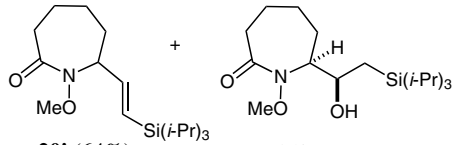
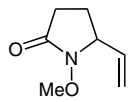
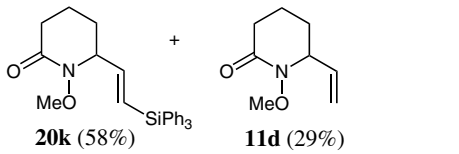
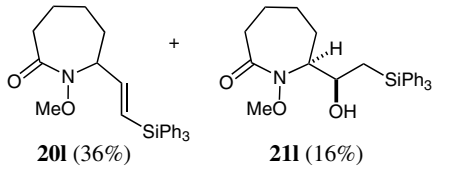
In order to account for the patterns of divergent, silyl-dependent reactivity highlighted in Tables 3 and 4, we have formulated the mechanistic rationale shown in Scheme 5. While we cannot discount the possibility that, in the case of allyltrimethylsilanes **7a–f**, product **11** forms through direct, concerted S_E'-reaction of the nitrenium ion intermediate **8** (pathway A), the stereospecific formation of *anti*-addition products **22** in the case of triisopropyl and triphenylsilanes suggests the intermediacy of aziridinium ion **9**. Upon formation, this strained bicyclic intermediate appears to have three possible fates: a) ring opening via concerted ion-pair collapse (pathway B); b) silyl-mediated ring opening with loss of the trialkylsilyl group (pathway C); and c) β-eliminative ring opening without loss of the silyl group and accompanying formation of *E*-vinylsilanes **20** (pathway D).

In the case of the trimethylsilyl-substituted substrates, attack of trifluoroacetate at the less sterically encumbered silicon center of **9**, or stabilized β-silyl carbocation **10**, and accompanying desilylation appears to be favored over ion pair collapse at the α-position, as initially anticipated. Nucleophilic attack at the more crowded silicon center of triisopropyl and triphenylsilyl-substituted **9** (or **10**),[22] on the other hand, is slower and as a result, β-elimination through proton loss to form ene-type products **20** predominates.[23] In contrast to simple alkenes,[11a] ion pair collapse while observed in these systems, is not the predominant pathway, perhaps as a result of the steric influence of the adjoining β-silyl group. The reason for the lack of vinylsilane formation during the cyclization of substrates **7g** and **7j** (Table 4, entries 1 and 4) remains unclear and await further investigation.

Table 4 Scope of *O*-Alkyl Hydroxamate Cyclization: Triisopropyl- and Triphenylallylsilanes[a]



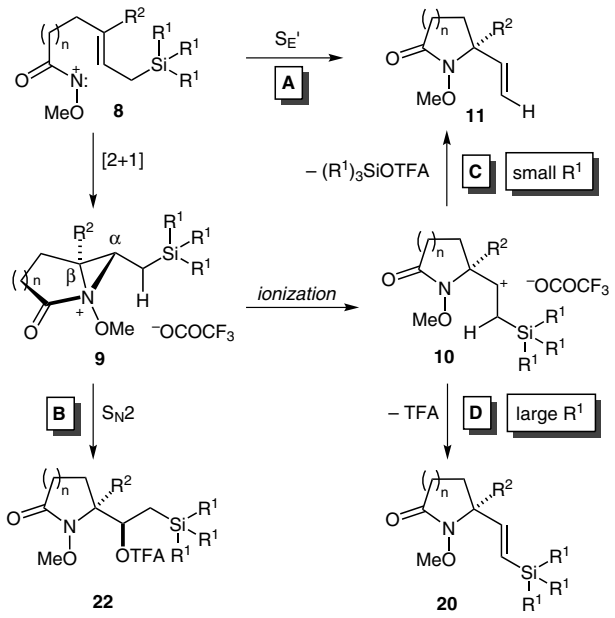
7 (R^1 = *i*-Pr, Ph; R^2 = H) **20** [R^2 = H, $Si(R^1)_3$] **11** (R^2 = H) **21** (dr >25:1)

Entry	7	Product(s) (Yield, %)[b]
1	**g**	 **11b** (15%) **21g** (61%)
2	**h**	 **20h** (74%) **21h** (12%) + **11d** (6%)
3	**i**	 **20i** (64%) **21i** (18%) + **11e** (4%)
4	**j**	 **11b** (54%)
5	**k**	 **20k** (58%) **11d** (29%)
6	**l**	 **20l** (36%) **21l** (16%) + **11e** (17%)

[a] Conditions: **7**, PIFA (1.2 equiv), CH_2Cl_2 (0.15 M), 0 °C; then NH_3–MeOH, 20 min.

[b] Isolated yields, after purification by flash chromatography.

In summary, we have successfully developed a versatile synthetic method for the preparation of 4- to 8-membered α-vinyl and α-(2-silylvinyl) lactams involving the chemoselective iodine(III)-mediated oxidative cyclization of unsaturated *O*-alkyl hydroxamates which encompass an allylsilane. Importantly, the outcome of this transformation can be effectively controlled through variation of the silyl substitution pattern. While allyltrimethylsilanes undergo ring closure with desilylation to form α-vinyl lac-



Scheme 5 Mechanistic rationale for divergent, silyl-dependent aziridinium ion ring opening

tams, the corresponding triisopropyl and triphenylsilanes cyclize without loss of the larger silyl group to form *E*-vinylsilanes with excellent stereoselectivity. The α-vinyl *N*-alkoxylactams, and corresponding NH lactams,[24] available through these divergent transformations are valuable building blocks for the preparation of complex natural products.[25] Application of our methodology in this context is in progress and will be reported in due course.

All nonaqueous reactions were carried out in oven- or flame-dried glassware under an atmosphere of dry nitrogen, unless otherwise noted. Except as otherwise indicated, all reactions were magnetically stirred and monitored by analytical TLC using Merck pre-coated silica gel plates with F_{254} indicator. Visualization was accomplished by UV light and/or $KMnO_4$ solution. Flash column chromatography was performed according to the method of Still[26] using silica gel 60 (mesh 230–400) supplied by E. Merck. Yields refer to chromatographically and spectrographically pure compounds, unless otherwise noted. CH_2Cl_2 and Et_3N were distilled from CaH_2 under an atmosphere of dry N_2. Sat. solutions of ammonia in MeOH (NH_3–MeOH) were prepared by bubbling anhyd gaseous NH_3 through cold (0 °C), anhyd MeOH for 20 min. Phenyliodine(III) bis(trifluoroacetate) [PIFA, $PhI(OTFA)_2$)] was prepared from $PhI(OAc)_2$ using the method reported by Loudon.[27] All other reagents and starting materials, unless otherwise noted, were purchased from commercial vendors and used without further purification. All melting points were determined in unsealed Pyrex capillaries with a Thomas Hoover Unimelt melting point apparatus and are uncorrected. IR spectra were recorded as thin films on NaCl plates using an ATI Mattson Genesis series FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 (400 MHz ^{1}H, 100 MHz ^{13}C) or a Bruker Avance 500 (500 MHz ^{1}H, 125 MHz ^{13}C) spectrometer. Chemical shift values (δ) are reported in ppm relative to residual $CHCl_3$ (δ = 7.27 for ^{1}H; δ = 77.23 for ^{13}C). High-resolution electrospray ionization (HRMS-ESI) mass spectra were obtained on a Micro Mass QTOF II instrument at the University of Illinois Research Resources Center.

Allylsilane Cross-Metathesis; General Procedure A

To a stirred solution of alkene (1 equiv) and allylsilane (3 equiv) in anhyd CH_2Cl_2 (0.5 M) under an atmosphere of N_2 at r.t. was added the Grubbs second-generation catalyst (Grubbs II) (2.5 mol%) in a single portion. The resulting solution was heated at reflux overnight, or until TLC (eluent: EtOAc–hexanes, 1:9) showed complete consumption of starting material, allowed to cool to r.t. and then filtered through a plug of Celite. The filter cake was washed with a mixture of EtOAc and hexanes (1:9, 20 mL), the combined filtrates concentrated under reduced pressure, and the resulting residue purified by flash chromatography over silica gel to provide the desired product (see Supporting Information for the individual preparation of the products).

Ester Saponification; General Procedure B

A solution of ester (1 equiv) and aq NaOH (1 M, 4 equiv) in a mixture of EtOH (0.2 M) and H_2O (0.2 M) was heated at reflux for 2 h, or until TLC (eluent: EtOAc–hexanes, 1:10) showed complete consumption of starting material. After cooling to r.t., the reaction mixture was acidified to pH 4–5 with aq HCl (1 M) and quickly extracted with EtOAc (5 ×). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting residue was purified by flash chromatography over silica gel to afford the desired product (see Supporting Information for the individual preparation of the products).

Amide Coupling; General Procedure C

To a stirred solution of carboxylic acid (1 equiv) in anhyd CH_2Cl_2 (0.12 M) under an atmosphere of N_2 at –40 °C (CO_2/MeCN) was added *i*-BuOCOCl (1.05 equiv) and Et_3N (1 equiv). After stirring for 10 min, the cold bath was removed and the reaction mixture stirred for 12 h at r.t., or until TLC (eluent: EtOAc–hexanes, 1:8) showed complete consumption of starting material. $MeONH_2$·HCl (1 equiv) and Et_3N (1 equiv) were then added and the mixture stirred for a further 12 h before being quenched with aq HCl (1 M). The biphasic mixture was extracted with EtOAc (3 ×) and the combined organic extracts were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting residue was purified by flash chromatography over silica gel to provide the desired product (see Supporting Information for the individual preparation of the products).

Oxidative Cyclization of *O*-Alkyl Hydroxamates; General Procedure D

To a stirred solution of unsaturated *O*-alkyl hydroxamate (1.0 equiv) in anhyd CH_2Cl_2 (0.1 M) at 0 °C was added solution of freshly prepared PIFA (1.2 equiv) in CH_2Cl_2 (0.1 M) via a cannula. After stirring for 30 min, or until TLC (eluent: EtOAc–hexanes, 1:1) showed complete consumption of starting material, a sat. solution of ammonia in anhyd MeOH (2 mL/mmol) was added, the reaction allowed to warm to r.t., and stirred for 15 min. The resulting mixture was concentrated under reduced pressure and purified by flash chromatography over silica gel to yield the observed products.

(±)-1-Methoxy-4-vinylazetidin-2-one (11a)

Following General Procedure D, reaction of **7a** (400 mg, 1.78 mmol) with PIFA (921 mg, 2.14 mmol) in CH_2Cl_2 (29 mL) followed by addition of sat. methanolic ammonia (11 mL) furnished a crude product, which was purified by flash chromatography over silica gel (EtOAc–hexanes, 1:1) to provide the title compound as a colorless oil (179 mg, 67%).

IR (film): 2939, 1776, 1461, 1429, 1313, 1193, 1043 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.93–5.84 (apt ddd, *J* = 18.8, 10.4, 8.4 Hz, 1 H), 5.50–5.45 (d, *J* = 17.9 Hz, 1 H), 5.35–5.32 (d, *J* = 10.3 Hz, 1 H), 4.33–4.29 (m, 1 H), 3.80 (s, 3 H), 2.96–2.91 (dd, *J* = 13.7, 7.9 Hz, 1 H), 2.51–2.48 (dd, *J* = 13.7, 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 135.4, 120.6, 64.3, 59.1, 39.2.

HRMS-EI: *m*/*z* calcd for $C_6H_9NO_2$ + Na $[M + Na]^+$: 150.1309; found: 150.1314.

(±)-1-Methoxy-5-vinylpyrrolidin-2-one (11b)
Following General Procedure D, reaction of **7b** (250 mg, 1.05 mmol) with PIFA (541 mg, 1.26 mmol) in CH_2Cl_2 (17.5 mL) followed by addition of sat. methanolic ammonia (6.6 mL) furnished a crude product, which was purified by flash chromatography over silica gel (EtOAc–hexanes, 1:1) to provide the title compound as a colorless oil (124 mg, 72%).

IR (film): 3413, 3081, 2981, 2939, 1720, 1425, 1247, 1058 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.79–5.73 (apt ddd, *J* = 17.0, 12.2, 5.2 Hz, 1 H), 5.35–5.34 (dd, *J* = 17.0, 1.0, 1.0 Hz, 1 H), 5.25–2.23 (d, *J* = 10.0 Hz, 1 H), 4.17–4.11 (apt ddd, *J* = 7.7, 7.2, 7.2 Hz, 1 H), 3.75 (s, 3 H), 2.39–2.17 (m, 3 H), 1.78–1.75 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.7, 136.6, 119.2, 63.4, 60.9, 27.1, 22.9.

HRMS-EI: *m*/*z* calcd for $C_{17}H_{11}NO_2$ + Na $[M + Na]^+$: 164.1575; found: 164.1573.

(±)-1-Methoxy-5-methyl-5-vinylpyrrolidin-2-one (11c)
Following General Procedure D, reaction of **7c** (75 mg, 0.43 mmol) with PIFA (222 mg, 0.52 mmol) in CH_2Cl_2 (7 mL) followed by addition of sat. methanolic ammonia (2.7 mL) furnished a crude product, which was purified by flash chromatography over silica gel (EtOAc–hexanes, 1:1) to provide the title compound as a colorless oil (60 mg, 78%).

IR (film): 3342, 2958, 2919, 1716, 1683, 1457, 1430, 1378, 1257, 1170 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 5.87–5.82 (dd, *J* = 17.4, 10.7 Hz, 1 H), 5.26–5.20 (d, *J* = 10.5 Hz, 1 H), 5.18–5.14 (d, *J* = 4.2 Hz, 1 H), 3.85 (s, 3 H), 2.37–2.28 (m, 2 H), 2.03–1.91 (m, 1 H), 1.89–1.84 (m, 1 H), 1.44 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.2, 140.1, 114.2, 64.8, 64.5, 30.4, 26.4, 22.7.

HRMS-EI: *m*/*z* calcd for $C_8H_{13}NO_2$ + Na $[M + Na]^+$: 178.1954; found: 178.1956.

(±)-1-Methoxy-6-vinylpiperidin-2-one (11d)
Following General Procedure D, reaction of **7d** (120 mg, 0.52 mmol) with PIFA (269 mg, 0.63 mmol) in CH_2Cl_2 (9 mL) followed by addition of sat. methanolic ammonia (3.3 mL) furnished a crude product, which was purified by flash chromatography over silica gel (EtOAc–hexanes, 1:1) to provide the title compound as a colorless oil (84 mg, 91%).

IR (film): 2937, 1668, 1444, 1398, 1332, 1285, 1141, 1070, 967 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 5.85–5.79 (apt ddd, *J* = 24.0, 10.3, 7.0 Hz, 1 H), 5.82–5.23 (m, 2 H), 4.25 (m, 1 H), 3.73 (s, 3 H), 2.46–2.43 (m, 2 H), 2.04–1.98 (m, 1 H), 1.86–1.79 (m, 2 H), 1.69–1.66 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.7, 163.7, 117.8,62.7, 62.1, 33.3, 30.4, 18.4.

HRMS-ESI: *m*/*z* calcd for $C_8H_{13}NO_2$ + Na $[M + Na]^+$: 178.1841; found: 178.1838.

(±)-1-Methoxy-7-vinylazepan-2-one (11e)
Following General Procedure D, reaction of **7e** (122 mg, 0.46 mmol) with PIFA (237 mg, 0.55 mmol) in CH_2Cl_2 (7.6 mL) followed by addition of sat. methanolic ammonia (2.9 mL) furnished a crude product, which was purified by flash chromatography over silica gel (EtOAc–hexanes, 1:1) to provide the title compound as a colorless oil (77 mg, 87%).

IR (film): 2930, 2860, 1727, 1667, 1447, 1285, 1047 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 5.93–5.88 (apt ddd, *J* = 17.2, 10.6, 5.8 Hz, 1 H), 5.31–5.26 (m, 2 H), 4.47–4.44 (m, 1 H), 3.77 (s, 3 H), 2.56–2.51 (m, 1 H), 5.47–2.42 (m, 1 H), 2.04–1.99 (m, 1 H), 1.90–1.85 (m, 1 H), 1.75–1.69 (m, 3 H), 1.62–1.57 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.2, 135.8, 116.9, 77.2, 64.3, 62.5, 35.9, 32.8, 25.1, 23.1.

HRMS-EI: *m*/*z* calcd for $C_{10}H_{17}NO_2$ + Na $[M + Na]^+$: 206.2372; found: 206.2380.

(±)-1-Methoxy-8-vinylazocan-2-one (11f) and (±)-7-Hydroxy-*N*-methoxynon-8-enamide (19)
Following General Procedure D, reaction of **7f** (150 mg, 0.54 mmol) with PIFA (276 mg, 0.64 mmol) in CH_2Cl_2 (9 mL) followed by addition of sat. methanolic ammonia (3.4 mL) furnished a crude product, which was purified by flash chromatography over silica gel (EtOAc–hexanes, 1:1) to provide the title compounds **11f** (47 mg, 42%) and **20** (29 mg, 24%) as colorless oils.

11f
IR (film): 2931, 2859, 1668, 1423, 1232, 1049 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.96–5.88 (app ddd, *J* = 17.2, 10.5, 4.7 Hz, 1 H), 5.31–5.25 (m, 2 H), 4.49–4.44 (m, 1 H), 3.77 (s, 3 H), 2.57–2.41 (m, 2 H), 2.04–1.91 (m, 1 H), 1.91–1.83 (m, 1 H), 1.76–1.68 (m, 4 H), 1.63–1.57 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.2, 135.8, 116.9, 64.3, 62.5, 32.8, 25.1, 23.1.

HRMS-EI: *m*/*z* calcd for $C_{10}H_{17}NO_2$ + Na $[M + Na]^+$: 206.2372; found: 206.2380.

19
IR (film): 3031, 2934, 2866, 1660, 1421 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.96–5.88 (app ddd, *J* = 17.2, 10.5, 4.7 Hz, 1 H), 5.31–5.25 (m, 2 H), 4.49–4.44 (m, 1 H), 3.77 (s, 3 H), 2.57–2.41 (m, 2 H), 2.04–1.91 (m, 1 H), 1.91–1.83 (m, 1 H), 1.76–1.68 (m, 4 H), 1.63–1.57 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.3, 135.4, 117.1, 69.4, 64.4, 62.5, 35.6, 29.9, 24.9, 22.4.

HRMS-EI: *m*/*z* calcd for $C_{10}H_{19}NO_3$ + Na $[M + Na]^+$: 224.2525; found: 224.2518.

(±)-1-Methoxy-5-vinylpyrrolidin-2-one (11b) and (*R)-1-Hydroxy-(*R**)-2-(triisopropylsilyl)ethyl-1-methoxypyrrolidin-2-one (21g)**
Following General Procedure D, reaction of **7g** (125 mg, 0.39 mmol) with PIFA (201 mg, 0.47 mmol) in CH_2Cl_2 (7 mL) followed by addition of sat. methanolic ammonia (2.4 mL) furnished a crude product, which was purified by flash chromatography over silica gel (EtOAc–hexanes, 1:1) to provide **11b** (9.6 mg, 15%) and **21g** (75.2 mg, 61%) as colorless oils.

21g
IR (film): 3424, 2939, 2865, 1695, 1463, 1272, 1060, 883 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.93 (m, 1 H), 3.82 (s, 3 H), 3.71–3.66 (m, 1 H), 2.71 (br s, 1 H), 2.39–2.22 (m, 1 H), 2.15–2.07 (m, 1 H), 1.95 (m, 1 H), 1.76–1.68 (m, 1 H), 1.04 (m, 21 H), 0.76 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 73.1, 66.3, 62.4, 61.9, 27.1, 19.0 (6 C), 12.8, 11.5 (3 C).

HRMS-EI: *m*/*z* calcd for $C_{16}H_{34}NO_3Si$ $[M + H]^+$: 316.2308; found: 316.2312.

(±)-1-Methoxy-6-vinylpiperidin-2-one (11d), (±)-6-[(*E*)-2-(Triisopropylsilyl)vinyl]-1-methoxypiperidin-2-one (20h), and (*R)-6-[(*R**)-1-Hydroxy-2-(triisopropylsilyl)ethyl]-1-methoxypiperidin-2-one (21h)**
Following General Procedure D, reaction of **7h** (110 mg, 0.35 mmol) with PIFA (181 mg, 0.42 mmol) in CH_2Cl_2 (6 mL) followed by addition of sat. methanolic ammonia (2.2 mL) furnished a crude product, which was purified by flash chromatography over silica gel

(EtOAc–hexanes, 1:1) to provide **11d** (4 mg, 6%), **20h** (81 mg, 74%), and **21h** (15 mg, 12%) as colorless oils.

20h
IR (film): 2939, 2856, 1690, 1463, 1272, 1062, 896 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 6.06–6.01 (dd, *J* = 18.8, 6.6 Hz, 1 H), 5.80–5.77 (dd, *J* = 18.8, 1.0 Hz, 1 H), 4.27–4.26 (m, 1 H), 3.75 (s, 3 H), 2.48–2.45 (app ddd, *J* = 6.4, 6.4, 2.4 Hz, 2 H), 2.05–2.00 (m, 1 H), 1.86–1.79 (m, 2 H), 1.72–1.65 (m, 1 H), 1.10–0.99 (m, 21 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.8, 146.1, 127.6, 65.4, 62.1, 33.4, 30.8, 19.2, 18.6 (6 C), 11.1 (3 C).

HRMS-EI: *m*/*z* calcd for $C_{17}H_{33}NO_2Si$ $[M + H]^+$: 313.2367; found: 313.2359.

21h
IR (film): 3249, 2939, 2856, 1742, 1569, 1463, 1272, 1062 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.82 (app ddd, *J* = 18.2, 3.8, 3.8 Hz, 1 H), 3.67 (s, 3 H), 3.66 (m, 1 H), 2.20–2.17 (m, 2 H), 1.64–1.39 (m, 4 H), 0.92 (m, 21 H), 0.82–0.75 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.4, 71.5, 70.2, 67.8, 29.1, 28.7 (3 C), 19.9, 19.1, 18.6 (6 C), 13.5.

HRMS-EI: *m*/*z* calcd for $C_{17}H_{35}NO_3Si$ + Na $[M + Na]^+$: 352.5402; found: 352.5399.

(±)-1-Methoxy-7-vinylazepan-2-one (11e), (±)-7-[(*E*)-2-(Triisopropylsilyl)vinyl]-1-methoxyazepan-2-one (20i), and (*R)-7-[(*R**)-1-Hydroxy-2-(triisopropylsilyl)ethyl]-1-methoxyazepan-2-one (21i)**
Following General Procedure D, reaction of **7i** (158 mg, 0.48 mmol) with PIFA (248 mg, 0.58 mmol) in CH_2Cl_2 (8 mL) followed by addition of sat. methanolic ammonia (3.0 mL) furnished a crude product, which was purified by flash chromatography over silica gel (EtOAc–hexanes, 1:1) to provide **11e** (6.5 mg, 4%), **20i** (115 mg, 64%), and **21i** (34 mg, 18%) as colorless oils.

20i
IR (film): 3457, 2939, 2863, 1737, 1668, 1461, 1234, 1197, 1047, 997, 892 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 6.09–6.06 (dd, *J* = 19.1, 3.8 Hz, 1 H), 5.82–5.78 (dd, *J* = 19.1, 3.8 Hz, 1 H), 4.29–4.25 (m, 1 H), 3.77 (s, 3 H), 2.55–2.51 (app ddd, *J* = 8.6, 6.0, 1.2 Hz, 1 H), 2.43–2.37 (app ddd, *J* = 14.5, 11.6, 1.9 Hz, 1 H), 2.11–2.07 (m, 1 H), 1.91–1.86 (app ddt, *J* = 12.0, 6.5, 3.5, 3.5 Hz, 1 H), 1.77–1.72 (m, 2 H), 1.68–1.65 (m, 1 H), 1.59–1.54 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.4, 144.8, 126.4, 66.4, 62.3, 35.9, 32.8, 25.2, 23.2, 19.1 (6 C), 11.1 (3 C).

HRMS-ESI: *m*/*z* calcd for $C_{18}H_{35}NO_2Si$ + Na $[M + Na]^+$: 348.2335; found: 348.2335.

21i
FTIR (film): 3407, 2939, 2863, 1644, 1461, 1045, 895 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 4.37–4.35 (app ddd, *J* = 10.0, 3.5, 3.5 Hz, 1 H), 3.87 (s, 3 H), 3.66–3.64 (app ddd, *J* = 9.0, 2.5, 2.5 Hz, 1 H), 2.58–2.52 (app ddd, *J* = 14.5, 11.6, 1.9 Hz, 1 H), 2.46–2.41 (app ddd, *J* = 14.5, 11.6, 1.9 Hz, 1 H), 2.00–1.93 (m, 1 H), 1.88–1.80 (m, 1 H), 1.75–1.60 (m, 2 H), 1.59–1.52 (m, 1 H), 1.13–1.04 (m, 21 H), 1.01–0.96 (dd, *J* = 14.5, 10.0 Hz, 1 H), 0.79–0.75 (dd, *J* = 15.0, 3.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.0, 70.8, 69.3, 63.6, 35.1, 28.9, 26.6, 25.2, 23.2, 19.0 (6 C), 11.4 (3 C).

HRMS-EI: *m*/*z* calcd for $C_{18}H_{38}NO_3Si$ $[M + H]^+$: 345.2630; found: 345.2621.

(±)-1-Methoxy-5-vinylpyrrolidin-2-one (11b)
Following General Procedure D, reaction of **7j** (256 mg, 0.65 mmol) with PIFA (312 mg, 0.73 mmol) in CH_2Cl_2 (5.1 mL) followed by addition of sat. methanolic ammonia (3.8 mL) furnished a crude product, which was purified by flash chromatography over silica gel (EtOAc–hexanes, 1:1) to provide the title compound as a colorless oil (36 mg, 54%). For analytical and spectral data, see above.

(±)-1-Methoxy-6-vinylpiperidin-2-one (11d) and (±)-(*E*)-1-Methoxy-6-[2-(triphenylsilyl)vinyl]piperidin-2-one (20k)
Following General Procedure D, reaction of **7k** (158 mg, 0.38 mmol) with PIFA (196 mg, 0.46 mmol) in CH_2Cl_2 (6.4 mL) followed by addition of sat. methanolic ammonia (2.4 mL) furnished a crude product, which was purified by flash chromatography over silica gel (EtOAc–hexanes, 1:15) to provide **11d** (27 mg, 29%) and **20k** (113 mg, 58%) as colorless oils.

20k
IR (film): 3403, 3066, 30.46, 2958, 2929, 2858, 1725, 1666, 1461, 1427, 1274, 1124 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.52–7.51 (m, 6 H), 7.39–7.27 (m, 9 H), 6.46–6.43 (dd, *J* = 7.0. 0.5, 0.5 Hz, 1 H), 6.10–6.06 (app ddd, *J* = 18.5, 0.5, 0.5 Hz, 1 H), 5.37 (app ddd, *J* = 17, 0.8, 0.8 Hz, 1 H), 3.72 (s, 3 H), 2.44–2.36 (m, 2 H), 2.34–2.27 (m, 2 H), 2.23–2.19 (m, 2 H), 1.83–1.761 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.3, 146.1, 136.1 (6 C), 135.3 (3 C), 129.9 (3 C), 128.4 (6 C), 127.6, 126.1, 65.4, 62.1, 33.4, 30.8.

HRMS-ESI: *m*/*z* calcd for $C_{26}H_{27}NO_2Si$ + Na $[M + Na]^+$: 437.1913; found: 437.1918.

(±)-1-Methoxy-7-vinylazepan-2-one (11e), (±)-(*E*)-1-Methoxy-7-[2-(triphenylsilyl)vinyl]azepan-2-one (20l), and (*R)-7-[(*R**)-1-Hydroxy-2-(triphenylsilyl)ethyl]-1-methoxyazepan-2-one (21l)**
Following General Procedure D, reaction of **7l** (129 mg, 0.31 mmol) with PIFA (160 mg, 0.37 mmol) in CH_2Cl_2 (6.0 mL) followed by addition of sat. methanolic ammonia (1.9 mL) furnished a crude product, which was purified by flash chromatography over silica gel (EtOAc–hexanes, 1:1) to provide **11e** (10 mg, 17%), **20l** (50 mg, 36%), and **21l** (23 mg, 16%) as colorless oils.

20l
IR (film): 3068, 2956, 2929, 2858, 1725, 1664, 1461, 1429, 1274, 1110 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.55–7.36 (m, 15 H), 6.48–6.44 (dd, *J* = 19.1, 3.8 Hz, 1 H), 6.16–6.12 (dd, *J* = 19.1, 3.8 Hz, 1 H), 4.56 (m, 1 H), 3.75 (s, 3 H), 2.55–2.51 (app ddd, *J* = 8.6, 6.0, 1.2 Hz, 1 H), 2.43–2.37 (app ddd, *J* = 14.5, 11.6, 1.9 Hz, 1 H), 2.11–2.07 (m, 1 H), 1.91–1.86 (app ddt, *J* = 18.0, 6.5, 3.5, 3.5 Hz, 1 H), 1.77–1.72 (m, 2 H), 1.68–1.65 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.5, 148.6, 136.1 (6 C), 135.3 (3 C), 129.9 (3 C), 128.4 (6 C), 126.4, 66.2, 62.4, 35.9, 32.6, 25.3, 23.1.

HRMS-ESI: *m*/*z* calcd for $C_{27}H_{29}NO_2Si$ + Na $[M + Na]^+$: 450.1865; found: 450.1868.

21l
IR (film): 3407, 2939, 2863, 1644, 1461, 1045 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.61–7.27 (m, 15 H), 4.15–4.10 (m, 1 H), 3.75 (s, 3 H), 3.65–3.58 (m, 1 H), 2.33–2.30 (m, 2 H), 1.82–1.75 (m, 4 H), 1.68–1.52 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.0, 146.1, 136.1 (6 C), 135.3 (3 C), 129.9 (3 C), 128.4 (6 C), 127.6, 69.3, 63.6, 35.1, 26.6, 25.2, 23.2.

HRMS-EI: *m*/*z* calcd for $C_{27}H_{31}NO_3Si$ + Na $[M + Na]^+$: 468.1971; found: 468.1969.

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