JOC Article

Solvent-Dependent Chemoselectivities in Additions of β-Carbonyl Imines to Allyltrimethylsilane with CTAN

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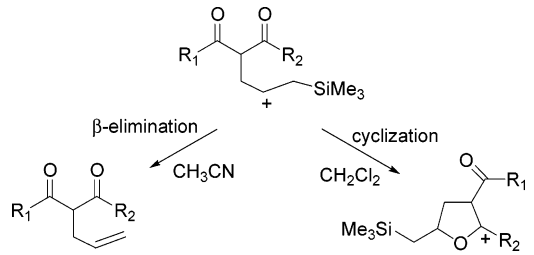
The oxidative coupling of β-carbonyl imines and allyltrimethylsilane with CTAN were investigated in CH_3CN and CH_2Cl_2. In CH_3CN allylation products were obtained predominantly, while in CH_2Cl_2, dihydropyrrole products were obtained exclusively. Solvent-assisted nucleophilic cleavage of the intermediate β-silyl cation is proposed to play a role in the solvent-dependent chemoselectivity.

Introduction

During the past two decades, there has been an increasing appreciation for the utility of Ce(IV) reagents for generating radicals and radical cations that can further react with other substrates to form C−C bonds.[1] Among these reactions, Ce(IV)-mediated oxidative additions of enolizable carbonyl compounds to activated olefins have received considerable attention.[2] Although ceric ammonium nitrate (CAN) is the most commonly utilized reagent for this purpose, its application is limited to polar organic solvents such as acetonitrile and methanol. The poor solubility of CAN can be avoided through the preparation of ceric tetra-*n*-butylammonium nitrate (CTAN), which contains a more lipophilic ammonium counterion.[3] We recently described the use of CTAN in the oxidative additions of 1,3-dicarbonyl to allyltrimethylsilane.[4] Interestingly, different chemoselectivities were observed in CH_3CN and CH_2Cl_2 leading to the formation of allylated and dihydrofuran products, respectively. It was proposed that oxidation of the 1,3-dicarbonyl substrate, subsequent addition to allyltrimethylsilane, and oxidation of the intermediate β-silyl radical produces a β-silyl cation. It was further postulated that the more polar CH_3CN provided a medium capable of affording a pathway to elimination whereas the less polar CH_2Cl_2 favored cyclization, which produced an oxo-stabilized cation (Scheme 1).

Enlightened by the previous study, we extended the work to the oxidative coupling of β-carbonyl imines. Allylation of β-carbonyl imines potentially provides a method for introducing functionality in the α position of a β-amino acid precursor, while addition followed by cyclization would provide a convenient route to dihydropyrroles. In the latter case, this methodology would offer an alternative and concise strategy for the synthesis of substituted dihydropyrroles.[5]

SCHEME 1



Results and Discussion

A series of β-carbonyl imines were synthesized in good to high yields by reacting an equimolar amount of the 1,3-dicarbonyl and corresponding amine in the presence of 4 Å molecular sieves and amberlyst H-15. All were found to be stable under normal column separations and purification with silica gel. The structures of the β-carbonyl imines are shown in Figure 1.

With the β-carbonyl imines in hand, we investigated the oxidative addition reactions of allyltrimethylsilane with CTAN in CH_3CN. The results are shown in Table 1. As expected, the reactions proceed through a β-scission pathway to afford allylation products. However, initial

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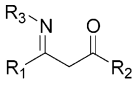
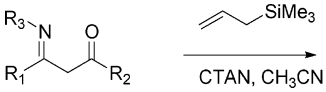
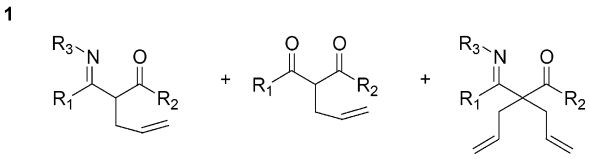


1a (R_1, R_2 = CH_3, R_3 = -CH_2Ph)
1b (R_1, R_2 = CH_3, R_3 = -$CH_2CH_2CH_3$)
1c (R_1, R_2 = CH_3, R_3 = -CH(Ph)(CO_2Me))
1d (R_1, R_2 = Ph, R_3 = -CH_2Ph)
1e (R_1 = CH_3, R_2 = -OCH_3, R_3 = -CH_2Ph)
1f (R_1 = CH_3, R_2 = -OCH_3, R_3 = -$CH_2CH_2CH_3$)
1g (R_1 = CH_3, R_2 = -OCH_3, R_3 = -CH(Ph)(CO_2Me))
1h (R_1 = CH_3, R_2 = -OCH_2CH_3, R_3 = -CH_2Ph)
1i (R_1 = CH_3, R_2 = -O-*t*-bu, R_3 = -CH_2Ph)
1j (R_1 + R_2 = -$CH_2CH_2CH_2$-, R_3 = -CH_2Ph)
1k (R_1 + R_2 = -$CH_2CH_2CH_2$-, R_3 = -$CH_2CH_2CH_3$)

FIGURE 1. Series of β-carbonyl imines utilized in these studies.

TABLE 1. Examples of CTAN-Mediated Oxidative Additions of β-Carbonyl Imines to Allyltrimethylsilane in CH_3CN





2 **3** **4**

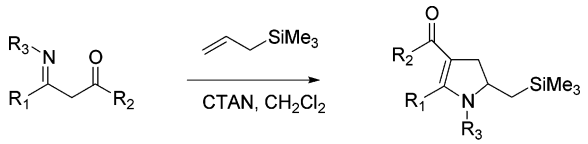
				yield (%)[b]		
entry	substrate	conditions[a]	product	**2**	**3**	**4**
1	**1a**	A	**3a**		62	
2	**1a**	B	**2a**, **3a**	52	15	
3	**1d**	B	**2d**	73		
4	**1e**	A	**2e**, **3e**	10	56	
5	**1e**	B	**2e**, **3e**	70	8	
6	**1f**	B	**2f**, **3f**	71	5	
7	**1g**	B	**2g**	44		
8	**1g**	C	**2g**, **4g**	56		12
9	**1h**	B	**2h**, **3h**	65	7	
10	**1i**	B	**2i**, **3i**	54	10	
11	**1j**	B	**2j**, **3j**	37	9	
12	**1k**	C	**2k**, **3k**, **4k**	46	11	16

[a] Conditions: (A) 2 equiv of CTAN/CH_3CN, 4 h, rt; (B) 2 equiv of CTAN/CH_3CN, 4 h, Et_3N, rt; (C) 4 equiv of CTAN/CH_3CN, 4 h, Et_3N, rt. [b] Isolated yield.

conditions (A in Table 1, entries 1 and 4) lead to hydrolysis upon workup, presumably through catalysis initiated by the Ce(III) product ion. To circumvent this, excess triethylamine (2 g) was added to the completed reaction and the precipitated Ce salts were filtered before aqueous workup. This protocol reduced hydrolysis of the imine and provided allylated β-carbonyl imines in good to moderate isolated yields. Substrates **1g** and **1j** were exceptions and the overall product yields (and conversion) were low in these two cases. The use of excess CTAN only slightly enhanced the yields and produced some of the diallylated products (entries 8 and 12).

With these initial studies complete, our attention turned next to the oxidative addition of the β-iminocarbonyls to allyltrimethylsilane in the less polar CH_2Cl_2. The reactions were carried out with 2 equiv of CTAN with addition of triethylamine before aqueous workup (condition B in Table 1). The results of these reactions are shown in Table 2.

TABLE 2. Cyclization Reactions in CH_2Cl_2



1 **5**

entry	substrate	product	yield (%)[a]
1	**1a**	**5a**	78
2	**1b**	**5b**	71
3	**1c**	**5c**	54
4	**1d**	**5d**	65
5	**1e**	**5e**	82
6	**1f**	**5f**	72
7	**1g**	**5g**	48
8	**1h**	**5h**	76
9	**1i**	**5i**	80
10	**1j**	**5j**	74

[a] Isolated yields. Reaction conditions: (D) 2 equiv of CTAN/CH_2Cl_2, 4 h, Et_3N, rt.

The reactions proceeded as expected and no allylation or hydrolyzed side products were observed in these reactions in contrast to analogous reactions of β-dicarbonyls.[4] The yields are good for those β-carbonyl imines obtained from benzyl and propylamine while yields from imines prepared from phenyl glycine methyl ester (**1c** and **1g**) were modest. This indicates that sterically encumbered imines inhibit the cyclization to some extent.

In previous work with diketones, most reactions with allyltrimethylsilane initiated by CTAN in CH_3CN provided predominantly allylated products with a small amount of cyclized dihydrofuran present as a side product. The opposite distribution was found in CH_2Cl_2. In the present studies with β-carbonyl imines the reactions are more selective with allylation occurring exclusively in CH_3CN and cyclized products formed exclusively in CH_2Cl_2.

Although selectivity in the present reactions is quite good, the role of solvent is unclear. The initial hypothesis was based on the supposition that solvent stabilization of an intermediate cation determines whether β-scission or cyclization occurs (described in Scheme 1). Another possible scenario involves solvent as a nucleophile in the displacement of the silyl group from the intermediate cation. Since the seminal work of Dinnocenzo describing the nucleophile-assisted cleavage of cation radicals,[6] it has been shown that nucleophilic solvents including alcohols and pyridines can accelerate the rate of cleavage of $-O-SiR_3^{\bullet+}$ and $-O-C^{\bullet+}$ cation radicals.[7,8] More recently, Eberlin and co-workers carried out studies that examined β-silyl cations formed upon the addition of *N*-acyliminium ions to allyltrimethylsilane in the gas phase.[9] These studies clearly showed that in the absence

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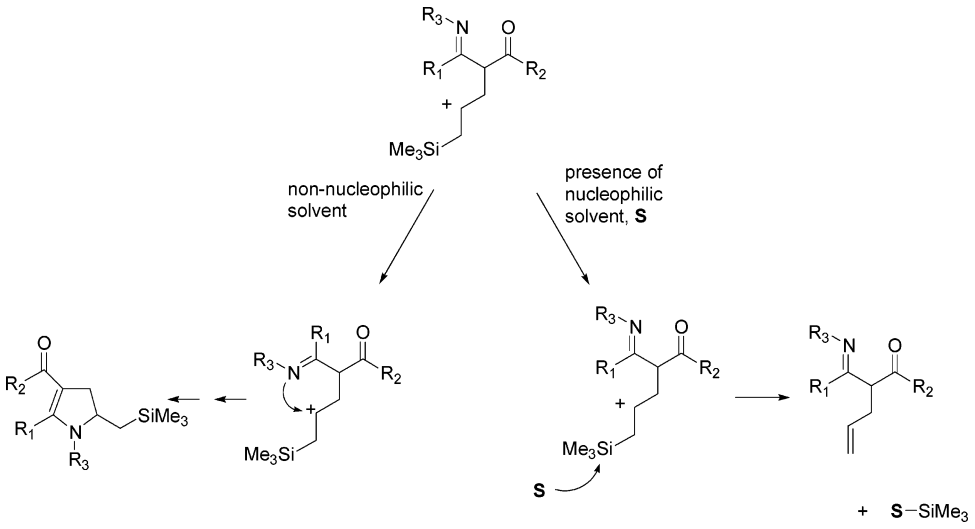
SCHEME 2



of nucleophiles, the intermediate β-silyl cations can reform reactants through fragmentation while the presence of a nucleophile led to β-scission, which produced allylated products.

The studies briefly described above support a mechanism where a nucleophile is necessary to effect cleavage of a β-silyl cation to an olefin. To determine if this mechanistic scenario is possible in the present system, reactions of **1j** and allyltrimethylsilane initiated by CTAN were carried out in CH_2Cl_2 containing 15% acetonitrile or methanol. In both cases, the addition of nucleophilic solvent resulted in the presence of **2j**, suggesting a role for nucleophilic solvent in the allylation reaction. In the reaction containing acetonitrile, the ratio **5j**:**2j** was 10:1, while the medium containing the more nucleophilic methanol produced a product ratio of 4:1. This supports a mechanism where the presence of a nucleophilic solvent acts to facilitate β-scission through the nucleophilic displacement of the silyl moiety of the β-silyl cation. In the absence of a nucleophilic solvent, the intermediate β-silyl cation is quenched by the presence of a proximal nucleophilic imine (Scheme 2).

Conclusions

The experimental observations reported herein show that solvent plays an important mechanistic role in determining the mechanism and outcome of Ce(IV)-mediated oxidative addition of allyltrimethylsilane to β-carbonyl imines. The combination of allyltrimethylsilane, CTAN, and a β-carbonyl imine produces good yields of highly substituted silylated pyrroles. The ease of conversion of the silyl moiety contained in the product into other functional groups potentially extends the versatility of this approach.[10] The generality of solvent-controlled chemoselectivity with use of lipophilic Ce(IV) oxidants in the synthesis of a variety of heterocycles is currently being explored. The results of these studies will be reported in due course.

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Experimental Section

Materials and General Methods. All oxidative additions were carried out under an inert atmosphere. Ceric tetrabutylammonium nitrate (CTAN) was prepared with ceric ammonium nitrate and tetrabutylammonium nitrate hydrogen sulfate and recrystalized in CH_2Cl_2.[3a] All substrates were purchased from Aldrich and used without further purification. CH_3CN and CH_2Cl_2 were distilled from CaO under nitrogen. NMR spectra were recorded on a Varian Unity Inova 500-MHz spectrometer. Mass spectra were performed on a Thermoquest 2000 series trace ion trap GC-MS.

Procedure for the Oxidative Addition Reactions Carried Out in CH_3CN. Condition A: CTAN (2 equiv) in 5 mL of CH_3CN solution was added dropwise to a stirred mixture of β-carbonyl imine compound and allyltrimethylsilane in 10 mL of CH_3CN. When TLC showed the starting material was fully consumed, the solvent was removed by rotary evaporation. Next, 50 mL of 1:1 hexane/EtOAc was added to precipitate Ce salts. After filtration, the filtrate was poured in water and extracted with 4 × 25 mL of ether. The extract was washed with brine and then dried with $MgSO_4$. The residue obtained after removal of solvent was chromatographed with a silica gel column with a mixture of hexane and EtOAc as eluent.

Condition B: CTAN (2 equiv) in 5 mL of CH_3CN solution was added dropwise to a stirred mixture of β-carbonyl imine compound and allyltrimethylsilane in 10 mL of CH_3CN. When TLC showed the starting material was fully consumed, the solvent was removed by rotary evaporation. Next, 50 mL of 1:1 hexane/EtOAc was added to the crude product to remove unreacted CTAN and filtered. Et_3N (2 mL) was added to the above solution and stirred for 30 min and then filtered. The filtrate was poured into water and extracted with 4 × 25 mL of ether. The extract was washed with brine and then dried with $MgSO_4$. The residue obtained after removal of solvent was chromatographed by silica gel column with a mixture of hexane and EtOAc as eluent.

Condition C: CTAN (4 equiv) in 10 mL of CH_3CN was added dropwise to a stirred mixture of β-carbonyl imine compound and allyltrimethylsilane in 10 mL of CH_3CN. The rest of the procedure is identical with that shown in condition 2A.

Procedure for the Oxidative Addition Reactions Carried Out in CH_2Cl_2. Condition D: CTAN (2 equiv) in 5 mL of CH_2Cl_2 was added to a stirred mixture of β-carbonyl imine compound and allyltrimethylsilane in 10 mL of CH_2Cl_2. After starting material was fully consumed, the solvent was removed by rotary evaporation and then 50 mL of 1:1 hexane/EtOAc was added to precipitate cerium salts. Next, 2 mL of Et_3N was

added to the above solution with stirring for 30 min. The solution was filtered and the filtrate was washed with water and brine. The organic extracts were dried with $MgSO_4$ and then concentrated. The residue was chromatographed with a silica gel column with a mixture of hexane and EtOAc as eluent.

Synthesis of 3-(1-Benzyliminoethyl)hex-5-en-2-one (2a). Procedure B was followed with use of 0.095 g of 4-benzyliminopentan-2-one (**1a**), 0.064 g of allyltrimethylsilane, and 1.12 g of CTAN. Crude NMR showed a mixture of **2a** and **3a**. Purification by flash chromatography (25 × 30 cm, EtOAc/hexane 1/5) provided 0.059 g of product **2a** (GC t_R = 11.43 min, TLC R_f 0.45, EtOAc/hexane 1/4) and 0.011 g of **3a** (spectroscopic data match the reported result[4]). ^{1}H NMR of **2a**[5b] (500 MHz, $CDCl_3$): δ 1.96 (s, 3H), 2.13 (s, 3H), 2.85−2.98 (m, 2H), 4.48 (s, 2H), 4.98−5.14 (m, 2H), 5.71−5.87 (m, 1H), 7.21−7.44 (m, 5H), 11.45 (br s, 1H).

Synthesis of 2-(Benzyliminophenylmethyl)-1-phenylpent-4-en-1-one (2d). Procedure B was followed with use of 0.162 g of 3-Benzylimino-1,3-diphenylpropan-1-one (**1d**), 0.064 g of allyltrimethylsilane, and 1.12 g of CTAN. Purification by flash chromatography (25 × 30 cm, EtOAc/hexane 1/3) provided 0.128 g of product **2d** (GC t_R = 25.62 min, TLC R_f 0.40, EtOAc/hexane 1/2). ^{1}H NMR (500 MHz, $CDCl_3$) of **2d**: δ 2.71−2.85 (m, 2H), 4.59 (s, 2H), 4.92−5.08 (m, 2H), 5.71−5.90 (m, 1H), 7.31−7.58 (m, 10H), 7.88−7.98 (m, 5H), 11.50 (s, 1H). ^{13}C NMR ($CDCl_3$) of **2d**: 196.32, 164.64, 137.28, 135.48, 135.29, 135.22, 130.48, 129.71, 128.68, 128.59, 128.51, 128.43, 128.02, 127.83, 127.78, 126.35, 115.90, 100.02, 46.23, 32.67. Mass M^+: 353.1 (M^+, 20), 276.1 (27), 262.1 (14), 248.1 (15), 171.1 (18), 105.1 (66), 91.1 (100), 77.1 (18).

Synthesis of 2-(1-Benzyliminoethyl)pent-4-enoic Acid Methyl Ester (2e). Procedure A was followed with use of 0.103 g of 3-benzyliminobutyric acid methyl ester (**1e**), 0.064 g of allyltrimethylsilane, and 1.12 g of CTAN. Purification by flash chromatography (25 × 30 cm, EtOAc/hexane 1/5) provided 0.086 g of product **2e** (GC t_R = 12.32 min, TLC R_f 0.40, EtOAc/hexane 1/4) and 0.013 g of **3e** as colorless liquids.[4] ^{1}H NMR (500 MHz, $CDCl_3$) of **2e**:[5b] 1.95 (s, 3H), 2.97−3.01 (d, J = 6.4 Hz, 2H), 3.73 (s, 3H), 4.42−4.44 (d, J = 6.4 Hz, 2H), 4.96−5.08 (m, 2H), 5.78−5.90 (m, 1H), 7.18−7.44 (m, 5H), 9.79 (br s, 1H).

Synthesis of 2-(1-Propyliminoethyl)pent-4-enoic Acid Methyl Ester (2f). Procedure B was followed with use of 0.078 g of 3-Propylimino-butyric acid methyl ester (**1f**), 0.064 g allyl trimethylsilane and 1.12 g of CTAN. Purification by flash chromatography (25 × 30 cm, EtOAc/hexane 1/5) provided 0.071 g of product **2f** (GC t_R = 11.01 min, TLC R_f 0.45, EtOAc/hexane 1/4) as a colorless liquid. ^{1}H NMR ($CDCl_3$) of **2f**: 0.94−1.02 (t, J = 7.0 Hz, 3H), 1.32−1.40 (m, 2H), 1.85 (s, 3H), 2.86−2.92 (d, J = 6.0 Hz, 2H), 3.14−3.26 (m, 2H), 3.71 (s, 3H), 4.93−5.08 (m, 2H), 5.75−5.87 (m, 1H), 8.95 (s, 1H). ^{13}C NMR ($CDCl_3$) of **2f**: 169.82, 163.77, 135.08, 116.35, 95.40, 58.16, 47.13, 33.38, 23.81, 14.25, 11.26. Mass M^+: 197.1 (M^+, 7), 182.1 (35), 168.1 (29), 154.1 (100), 127.1 (49), 91.1 (78), 81.1 (36).

Synthesis of 2-[1-(Methoxycarbonylphenylmethylimino)ethyl]pent-4-enoic Acid Methyl Ester (2g). Procedure B was followed with use of 0.132 g of 3-(methoxycarbonylphenylmethylimino)butyric acid methyl ester (**1g**), 0.064 g of allyl trimethylsilane, and 1.12 g of CTAN. Purification by flash chromatography(25 × 30 cm, EtOAc/hexane 1/4) provided 0.067 g of product **2g** (GC t_R = 15.98 min, R_f 0.40 EtOAc/hexane 1/3) as a light yellow liquid. ^{1}H NMR ($CDCl_3$) of **2g**: 1.82 (s, 3H), 2.78−2.92 (m, 2H), 3.69 (s, 3H), 3.72 (s, 3H), 4.95−5.13 (m, 2H), 5.26 (s, 1H), 5.66−5.82 (m, 1H), 7.34−7.55 (m, 5H). ^{13}C NMR ($CDCl_3$) of **2g**: 174.07, 171.76, 157.44, 135.55, 135.48, 128.36, 128.16, 127.74, 126.28, 126.23, 117.98, 90.33, 67.22, 55.98, 55.40, 37.84, 35.20, 27.50, 17.78. Mass M^+: 303.1 (6), 288.1 (22), 272.1 (36), 262.1 (30), 242.1 (95), 210.1 (70), 149.1 (67), 121.1 (100), 91.1 (56), 77.1 (31).

Synthesis of 2-Allyl-2-[1-(methoxycarbonylphenylmethylimino)ethyl]pent-4-enoic Acid Methyl Ester (4g). Procedure C was followed with use of 0.132 g of 3-(methoxycarbonylphenylmethylimino)butyric acid methyl ester (**1g**), 0.064 g of allyl trimethylsilane, and 2.24 g of CTAN. Purification by flash chromatography (25 × 30 cm, EtOAc/hexane 1/4) provided 0.086 g of product **2g** and 0.021 g of product **4g** (GC t_R = 17.32 min, TLC R_f 0.50, EtOAc/hexane 1/3) as a light yellow liquid. ^{1}H NMR ($CDCl_3$) of **4g**: 1.91 (s, 3H), 2.62−2.80 (m, 4H), 3.73 (s, 3H), 3.78 (s, 3H), 4.98−5.14 (m, 4H), 5.22 (s, 1H), 5.61−5.79 (m, 2H), 7.29−7.55 (m, 5H). ^{13}C NMR ($CDCl_3$) of **4g**: 173.97, 171.57, 169.92, 138.35, 138.35, 133.50, 132.13, 129.16, 128.37, 127.89, 127.77, 118.16, 118.08, 67.22, 60.29, 52.33, 51.94, 37.33, 36.02, 16.83. Mass M^+: 343.1 (1), 328.1 (15), 302.1 (18), 282.1 (13), 250.1 (23), 240.1 (35), 184.1 (14), 149.1 (36), 121.1 (100), 91.1 (45), 77.1 (53).

Synthesis of 2-(1-Benzyliminoethyl)pent-4-enoic Acid Ethyl Ester (2h). Procedure B was followed with use of 0.11 g of 3-benzyliminobutyric acid ethyl ester (**1h**), 0.064 g of allyl trimethylsilane, and 1.12 g of CTAN. Purification by flash chromatography (25 × 30 cm, EtOAc/hexane 1/4) provided 0.084 g of product **2h**[5b] (GC t_R = 12.47 min, TLC R_f 0.40, EtOAc/hexane 1/4) as a colorless liquid and 0.012 g of product **3h**.[4] ^{1}H NMR ($CDCl_3$) of **2h**: 1.21−1.28 (t, J = 7.0 Hz, 3H), 1.89 (s, 3H), 2.98−3.02 (d, J = 6.3 Hz, 2H), 4.10−4.16 (q, J = 7.0 Hz, 2H), 4.40−4.44 (d, J = 6.2 Hz, 2H), 5.02−5.12 (m, 2H), 5.72−5.84 (m, 1H), 7.11−7.43 (m, 5H), 9.33 (br s, 1H).

Synthesis of 2-(1-Benzyliminoethyl)pent-4-enoic Acid *tert*-Butyl Ester (2i). Procedure B was followed with use of 0.124 g of 3-benzyliminobutyric acid *tert*-butyl ester (**1i**), 0.064 g of allyl trimethylsilane, and 1.12 g of CTAN. Purification by flash chromatography (25 × 30 cm, EtOAc/hexane 1/4) provided 0.077 g of product **2i** (GC t_R = 14.30 min, TLC R_f 0.45 EtOAc/hexane 1/3) as a colorless liquid. ^{1}H NMR ($CDCl_3$) of **2i**: 1.46 (s, 9H), 1.87 (s, 3H), 2.60−2.77 (m, 2H), 4.59 (s, 2H), 5.02−5.16 (m, 2H), 5.77−5.89 (m, 1H), 7.17−7.45 (m, 5H), 8.85 (br s, 1H). ^{13}C NMR ($CDCl_3$) of **2i**: 172.85, 168.10, 133.83, 132.13, 129.16, 128.57, 128.25, 127.95, 126.36, 117.90, 95.88, 81.09, 54.29, 36.73, 27.95, 16.29. Mass M^+: 287.1 (M^+, 12), 272.1 (29), 258.1 (14), 247.1 (45), 146.1 (28), 129.1 (11), 101.1 (32), 91.1 (100), 57.1 (39).

Synthesis of 2-Allyl-3-propyliminocyclohexanone (2k). Procedure B was followed with use of 0.077 g of 3-benzyliminocyclohexanone (**1k**), 0.064 g of allyl trimethylsilane, and 1.12 g of CTAN. Purification by flash chromatography (25 × 30 cm, EtOAc/MeOH:20/1) provided 0.035 g of product **2k** (GC t_R = 11.49 min, TLC R_f 0.35 EtOAc/MeOH 10/1) as a light yellow solid. ^{1}H NMR ($CDCl_3$) of **2k**:[11] 1.02−1.08 (t, J = 7.0 Hz, 3H), 1.52−1.58 (m, 2H), 2.00−2.06 (t, J = 7.0 Hz, 2H), 2.32−2.48 (m, 4H), 2.94−2.98 (d, J = 6.2 Hz, 2H), 3.08−3.14 (m, 2H), 4.98−5.04 (m, 2H), 5.66−5.80 (m, 1H), 6.78 (s, 1H).

Synthesis of 2,2-Diallyl-3-propyliminocyclohexanone (4k). Procedure C was followed with use of 0.077 g of 3-benzyliminocyclohexanone (**1k**), 0.064 g of allyl trimethylsilane, and 2.24 g of CTAN. Purification by flash chromatography (25 × 30 cm, EtOAc/MeOH:20/1) provided 0.44 g of product **2k** and 0.018 g of product **4k** (GC t_R = 13.50 min, TLC R_f 0.50 EtOAc/MeOH 10/1) as a yellow liquid. ^{1}H NMR ($CDCl_3$) of **4k**: 0.92−0.95 (t, J = 7.1 Hz, 3H), 1.52−1.58 (h, 2H), 1.98−2.04 (t, J = 6.2 Hz, 2H), 2.48−2.73 (m, 8H), 3.11−3.16 (q, J = 7.1 Hz, 2H), 4.98−5.11 (m, 4H), 5.56−5.80 (m, 2H). ^{13}C NMR ($CDCl_3$) of **4k**: 210.19, 166.42, 139.01, 138.68, 117.27, 117.11, 61.37, 50.16, 40.56, 30.62, 30.30, 24.58, 20.26, 15.73, 11.40. Mass M^+: 233.1 (M^+, 3), 218.1 (24), 205.1 (33), 193.1 (100), 165.1 (18), 125.1 (16), 110.1 (20), 91.1 (24), 83.1 (12), 79.1 (35).

Synthesis of 1-(1-Benzyl-2-methyl-5-trimethylsilanylmethyl-4,5-dihydro-1*H*-pyrrol-3-yl)ethanone (5a). Procedure D was followed with use of 0.095 g of 4-benzyliminopentan-2-one (**1a**), 0.065 g of allyl trimethylsilane, and 1.12 g of CTAN. Product **5a** (0.117 g) (GC t_R = 16.28 min, TLC R_f 0.65, hexane/EtOAc 4/1) was obtained in a light red liquid and identified

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without further purification. ^{1}H NMR ($CDCl_3$) of **5a**: 0.098 (s, 9H), 1.00−1.08 (dd, J = 14.7 and 7.2 Hz, 1H), 1.18−1.26 (dd, J = 14.1 and 7.4 Hz,1H), 1.94 (s, 3H), 2.17 (s, 3H), 2.54−2.62 (m, 1H), 3.03−3.11 (m, 1H), 3.48−3.60 (m, 1H), 4.64 (s, 2H), 7.19−7.48 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) of **5a**: δ 195.41, 163.04, 138.04, 128.79, 128.34, 128.23, 127.39, 126.25, 100.88, 56.18, 46.89, 38.66, 27.78, 23.38, 14.87, −0.09. Mass M^+: 301.1 (M^+, 7), 286.1 (62), 270.2 (10), 258.1 (12), 228.1 (25), 214.1 (18), 152.1 (22), 137.1 (13), 110.1 (14), 91.1 (85), 73.1 (100).

Synthesis of 1-(2-Methyl-1-propyl-5-trimethylsilanylmethyl-4,5-dihydro-1*H*-pyrrol-3-yl)ethanone (5b). Procedure D was followed with use of 0.078 g of 4-propyliminopentan-2-one (**1b**), 0.065 g of allyl trimethylsilane, and 1.12 g of CTAN. Product **5b** (0.09 g) (GC t_R = 15.83 min, TLC R_f 0.7, hexane/EtOAc 4/1) was obtained in a light red liquid. ^{1}H NMR ($CDCl_3$) of **5b**: 0.09 (s, 9H), 0.91−0.98 (t, J = 7.0 Hz, 3H), 1.02−1.10 (dd, J = 14.2 and 7.1 Hz, 1H), 1.18−1.26 (dd, J = 14.0 and 7.4 Hz, 1H), 1.58−1.69 (q, J = 7.0 Hz, 2H), 1.98 (s, 3H), 2.10 (s, 3H), 2.46−2.56 (dd, J = 13.8 and 7.6, 1H), 2.94−3.04 (dd, J = 14.0 and 7.2, 1H), 3.24−3.32 (t, J = 7.0 Hz, 2H), 3.56−3.66 (m, 1H). ^{13}C NMR ($CDCl_3$) of **5b**: 196.52, 163.18, 108.23, 50.24, 46.22, 38.66, 27.10, 22.02, 13.50, 11.94, −0.89. Mass M^+: 253.1 (M^+, 4), 252.1 (18), 238.1 (85), 224.1 (32), 222.1 (12), 210.1 (25), 196.1 (12), 180.1 (14), 152.1 (21), 138.1 (14), 125.1 (12), 110.1 (17), 73.1 (100).

Synthesis of (4-Acetyl-5-methyl-2-trimethylsilanylmethyl-2,3-dihydropyrrol-1-yl)phenylacetic Acid Methyl Ester (5c). Procedure D was followed with use of 0.124 g of 1-methyl-3-oxobutylideneamino)phenylacetic acid methyl ester (**1c**), 0.065 g of allyl trimethylsilane, and 1.12 g of CTAN. Product **5c** (0.097 g) (GC t_R = 19.92 min, TLC R_f0.5, hexane/EtOAc 4:1) was obtained in a sticky pale yellow oil. ^{1}H NMR ($CDCl_3$) of **5c**: 0.057 (s, 9H), 0.98−1.06 (dd, J = 14.0 and 7.0 Hz, 1H), 1.16−1.24 (dd, J = 14.0 and 7.0 Hz, 1H), 2.02 (s, 3H), 2.13 (s, 3H), 2.49−2.57 (m, 1H), 2.98−3.06 (m, 1H), 3.52−3.63 (m, 1H), 3.77 (s, 3H), 5.37 (s, 1H), 7.26−7.47 (m, 5H). ^{13}C NMR ($CDCl_3$) of **5c**: 196.58, 171.53, 160.35, 135.30, 129.20, 129.06, 128.85, 128.64, 128.38, 128.26, 103.25, 69.27, 54.93, 48.72, 36.80, 27.55, 23.40, 13.54, −0.66. Mass M^+: 359.1 (M^+, 3), 344.1 (100), 316.1 (14), 300.1 (29), 286.1 (19), 272.1 (11), 258.1 (14), 228.1 (48), 210.1 (41), 186.1 (11), 167.1 (17), 149.1 (63), 137.1 (13), 96.1 (10), 87.1 (32), 73.1 (82).

Synthesis of Phenyl(2-phenyl-5-trimethylsilanylmethyl-4,5-dihydro-1*H*-pyrrol-3-yl)phenylmethanone (5d). Procedure D was followed with use of 0.157 g of 3-benzylimino-1,3-diphenylpropan-1-one (**1d**), 0.065 g of allyl trimethylsilane, and 1.12 g of CTAN. Product **5d** (0.138 g) (GC t_R = 28.97 min, TLC R_f 0.45, hexane/EtOAc 3/1) was obtained in a sticky pale yellow oil. ^{1}H NMR ($CDCl_3$) of **5d**: 0.09 (s, 9H), 1.00−1.08 (dd, J = 14.2 and 7.8 Hz, 1H), 1.16−1.24 (dd, J = 14.6 and 7.0 Hz, 1H), 2.40−2.48 (dd, J = 15.0 and 7.5 Hz 1H), 2.94−3.02 (dd, J = 14.2 and 7.8 Hz 1H), 3.58−3.70 (m, 1H), 4.70 (s, 2H), 7.10−7.16 (m, 5H), 7.28−7.42 (m, 8H), 7.54−7.62 (m, 2H). ^{13}C NMR ($CDCl_3$) of **5d**: 193.13, 161.46, 139.28, 135.65, 135.58, 134.62, 130.68, 129.58, 129.50, 128.88, 128.14, 127.54, 127.46, 126.22, 126.21, 110.10, 100.02, 57.86, 45.53, 37.54, 23.80, −0.91. Mass M^+: 425.1 (M^+, 24), 410.1 (35), 394.1 (12), 366.1 (22), 334.1 (32), 245.1 (26), 206.1 (17), 159.1 (22), 105.1 (55), 91.1 (100), 77.1 (24), 73.1 (35).

Synthesis of 1-Benzyl-2-methyl-5-trimethylsilanylmethyl-4,5-dihydro-1*H*-pyrrole-3-carboxylic Acid Methyl Ester (5e). Procedure D was followed with use of 0.103 g of 3-benzyliminobutyric acid methyl ester, 0.065 g of allyl trimethylsilane, and 1.12 g of CTAN. Product **5e** (0.130 g) (GC t_R = 16.78 min, TLC R_f 0.65, hexane/EtOAc 4/1) was obtained in a pale yellow oil. ^{1}H NMR ($CDCl_3$) of **5e**: 0.081 (s, 9H), 1.02−1.10 (dd, J = 14.0 and 7.1 Hz 1H), 1.20−1.28 (dd, J = 14.2 and 6.8 Hz, 1H), 2.05 (s, 3H), 2.44−2.52 (m, 1H), 2.96−3.04 (m, 1H), 3.48−3.54 (m, 1H), 3.72 (s, 3H), 4.64 (s, 2H), 7.29−7.53 (m, 5H). ^{13}C NMR ($CDCl_3$) of **5e**: 170.14, 166.85, 134.18, 129.38, 129.08, 128.15, 126.88, 126.36, 103.78, 59.52, 50.02, 43.69, 37.82, 25.46, 15.34, −0.95. Mass M^+: 317.1 (M^+, 0.5), 316.1 (21), 302.1 (73), 284.1 (26), 259.1 (12), 212.1 (36), 167.1 (42), 153.1 (32), 91.1 (100), 73.1 (65).

Synthesis of 2-Methyl-1-propyl-5-trimethylsilanylmethyl-4,5-dihydro-1*H*-pyrrole-3-carboxylic Acid Methyl Ester (5f). Procedure D was followed with use of 0.079 g of 3-propyliminobutyric acid methyl ester (**1e**), 0.065 g of allyl trimethylsilane, and 1.12 g of CTAN. Product **5f** (0.097 g) (GC t_R = 16.04 min, TLC R_f 0.65 hexane/EtOAc 4/1) was obtained in a pale yellow oil. ^{1}H NMR ($CDCl_3$) of **5f**: 0.07 (s, 9H), 0.90−0.98 (t, 3H), 1.02−1.10 (dd, J = 14.0 and 7.2 Hz, 1H), 1.18−1.26 (dd, J = 14.5 and 6.8 Hz, 1H), 1.54−1.66 (m, 2H), 2.07 (s, 3H), 2.46−2.58 (m, 1H), 2.96−3.08 (m, 1H), 3.14−3.22 (m, 2H), 3.47−3.55 (m, 1H), 3.76 (s, 3H). ^{13}C NMR ($CDCl_3$) of **5f**: 167.39, 160.42, 103.83, 57.92, 55.26, 49.31, 38.70, 23.42, 22.02, 14.05, 11.34, −0.65. Mass M^+: 269.1 (M^+, 25), 254.1 (60), 236.1 (23), 225.1 (41), 208.1 (40), 190.1 (14), 157.1 (23), 141.1 (16), 112.1 (35), 73.1 (100), 43.1 (36).

Synthesis of 1-(Methoxycarbonylphenylmethyl)-2-methyl-5-trimethylsilanylmethy l-4,5-dihydro-1*H*-pyrrole-3-carboxylic Acid Methyl Ester (5g). Procedure D was followed with use of 0.132 g of 3-(methoxycarbonylphenylmethylimino)butyric acid methyl ester (**1g**), 0.065 g of allyl trimethylsilane, and 1.12 g of CTAN. Product **5g** (0.091 g) (GC t_R = 20.78 min, TLC R_f 0.45 hexane/EtOAc 4/1) was obtained in a sticky light oil. ^{1}H NMR ($CDCl_3$) of **5g**: 0.082 (s, 9H), 1.02−1.12 (dd, J = 14.5 and 7.2 Hz, 1H), 1.20−1.30 (dd, J = 14.0 and 6.8 Hz 1H), 2.07 (s, 3H), 2.46−2.56 (m, 1H), 3.04−3.14 (m, 1H), 3.53−3.65 (m, 1H), 3.70 (s, 3H), 3.76 (s, 3H), 5.26 (s, 1H), 7.18−7.45 (m, 5H). ^{13}C NMR ($CDCl_3$) of **5g**: 171.67, 167.39, 163.15, 135.80, 130.88, 130.16, 128.67, 128.53, 127.26, 106.72, 64.97, 57.09, 47.75, 38.42, 36.82, 23.87, 14.09, −0.85. Mass M^+: 375.1 (M^+, 15), 360.1 (83), 332.1 (66), 314.1 (40), 286.1 (17), 240.1 (40), 228.1 (32), 203.1 (28), 155.1 (43), 112.1 (16), 91.1 (100), 73.1 (78).

Synthesis of 2-Phenyl-5-trimethylsilanylmethyl-4,5-dihydro-1*H*-pyrrole-3-carboxylic Acid Ethyl Ester (5h). Procedure D was followed with use of 0.125 g of 3-benzyliminobutyric acid ethyl ester (**1h**), 0.065 g of allyl trimethylsilane, and 1.12 g of CTAN. Product **5h** (0.126 g) (GC t_R = 16.91 min, TLC R_f 0.65 hexane/EtOAc 4/1)was obtained in a pale red oil. ^{1}H NMR ($CDCl_3$) of **5h**: 0.06 (s, 9H), 0.96−1.04 (dd, J = 14.0 and 7.0 Hz 1H), 1.14−1.22 (dd, J = 14.2 and 6.9 Hz, 1H), 1.30−1.36 (t, J = 7.0 Hz, 3H), 2.10 (s, 3H), 2.41−2.49 (dd, J = 14.2 and 7.0 Hz, 1H), 2.90−2.98 (dd, J = 14.2 and 7.1 Hz, 1H), 3.52−3.65 (m, 1H), 4.04−4.18 (q, J = 7.0 Hz, 2H), 4.59 (s, 2H), 7.12−7.46 (m, 5H). ^{13}C NMR ($CDCl_3$) of **5h**: 167.20, 162.48, 136.50, 128.85, 128.44, 127.75, 127.30, 126.26, 98.52, 61.88, 57.64, 45.96, 36.67, 25.68, 14.85, 13.14, −0.40. Mass M^+: 331.1 (M^+, 0.5), 316.1 (63), 288.1 (23), 278.1 (12), 243.1 (16), 228.1 (32), 163.1 (42), 157.1 (32), 91.1 (100), 73.1 (53).

Synthesis of 2-Phenyl-5-trimethylsilanylmethyl-4,5-dihydro-1*H*-pyrrole-3-carboxylic Acid *tert*-Butyl Ester (5i). Procedure D was followed with use of 0.123 g of 3-benzyliminobutyric acid *tert*-butyl ester (**1i**), 0.065 g of allyl trimethylsilane, and 1.12 g of CTAN. Product **5i** (0.144 g) (GC t_R = 17.86 min, TLC R_f 0.6 hexane/EtOAc 4/1) was obtained in a light red oil. ^{1}H NMR ($CDCl_3$) of **5i**: 0.06 (s, 9H), 0.98−1.06 (dd, J = 13.8 and 7.2 Hz, 1H), 1.16−1.24 (dd, J = 14.5 and 6.6 Hz, 1H), 1.46 (s, 9H), 2.10 (s, 3H), 2.41−2.49 (dd, J = 14.8 and 7.6 Hz,1H), 2.98−3.06 (dd, J = 14.6 and 7.6 Hz, 1H), 3.59−3.70 (m, 1H), 4.62 (s, 2H), 7.12−7.46 (m, 5H). ^{13}C NMR ($CDCl_3$) of **5i**: 169.72, 160.48, 137.65, 129.06, 128.61, 128.59, 127.14, 126.28, 101.98, 75.10, 56.70, 43.94, 38.60, 29.51, 23.87, 14.30, −0.77. Mass M^+: 359.1 (14), 344.1 (100), 316 (15), 312.1 (24), 282.1 (18), 219.1 (32), 154.1 (35), 101.1 (27), 91.1 (86), 73.1 (80).

Synthesis of 1-Benzyl-2-trimethylsilanylmethyl-1,2,3,5,6,7-hexahydroindol-4-one (5j). Procedure D was followed with use of 0.101 g of 3-benzyliminocyclohexanone (**1j**), 0.065 g of allyl trimethylsilane, and 1.12 g of CTAN. Product **5j** (0.119 g) (GC t_R = 18.49 min, TLC R_f 0.60 EtOAc/

MeOH 20/1) was obtained in a slick red oil. ^{1}H NMR ($CDCl_3$) of **5j**: 0.10 (s, 9H), 0.96−1.08 (dd, J = 14.2 and 7.4 Hz, 1H), 1.16−1.28 (dd, J = 14.4 and 7.0 Hz, 1H), 1.90−1.98 (m, 2H), 2.30−2.44 (m, 4H), 2.55−2.63 (m, 1H), 3.10−3.18 (m, 1H), 3.60−3.74 (m, 1H), 4.73 (s, 2H), 7.18−7.47 (m, 5H). ^{13}C NMR ($CDCl_3$) of **5j**: 195.17, 167.99, 136.30, 128.63, 128.42, 128.06, 127.18, 126.14, 109.40, 58.96, 46.75, 37.16, 36.64, 27.37, 23.42, 20.22, −0.91. Mass M^+: 313.1 (M^+, 16), 298.1 (100), 280.1 (51), 265.1 (14), 252.1 (22), 219.1 (17), 205.1 (20), 168.1 (27), 135.1 (23), 91.1 (90), 73.1 (65).

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Supporting Information Available: General methods, experimental protocols, and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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