A Two-Step Procedure for the Conversion of α,β-Unsaturated Aldehydes into γ-Azido-α,β-Unsaturated Nitriles[1]

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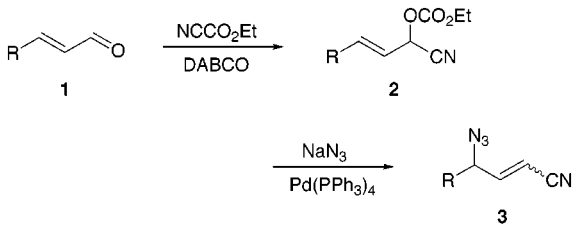
γ-Azido-α,β-unsaturated nitriles (**3**) are generally stable, richly functionalized compounds that may serve as useful precursors for the synthesis of a diverse array of biologically active molecules. Our interest in these compounds was further piqued by their obvious relationship to an intriguing class of unnatural γ-amino acids[2] first designed and explored by Hagihara et al.[3] This note reports an efficient, high-yield method for the preparation of the title compounds (**3**) from α,β-unsaturated aldehydes (**1**) via cyanohydrin carbonates (**2**). The two-step transformation is outlined in Scheme 1. The initial step features an expedient route to the intermediate allylic cyanohydrin carbonates (**2**) via concomitant cyanation−ethoxycarbonylation of aldehydes **1**. The desired γ-azido compounds **3** are then secured through a subsequent palladium(0)-catalyzed allylic azidation of **2**.

Scheme 1

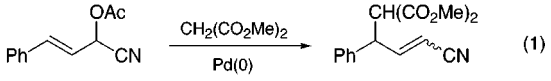


Results and Discussion

Cyanohydrin Carbonate Preparation. Cyanation−ethoxycarbonylation of α,β-unsaturated aldehydes **1a**−**e** occurs rapidly (15−120 min) and cleanly when they are reacted with ethyl cyanoformate (1.5 equiv) and catalytic DABCO (10 mol %) in THF at room temperature. Allylic cyanohydrin carbonates **2** are isolated in yields greater than 90% (Table 1). Ethyl cyanoformate serves a combined role as acylating agent and in situ source of cyanide ion, which reduces manipulation and exposure to additional toxic reagents. This procedure is a combination of conditions previously employed to prepare other acylated cyanohydrins.[4,5] Since we began our initial studies on this reaction, three other routes to cyanohydrin carbonates have appeared. There are some notable differences among the approaches; notwithstanding, only two examples involve α,β-unsaturated aldehydes. The procedure offered by Okimoto and Chiba[6] obtains cyanohydrin esters and carbonates via phase-transfer catalysis. Although yields are in the 80−90% domain, such a system may not be suitable for some water-sensitive substrates. In a process more similar to ours, Scholl et al.[7] and Shin et al.[8] prepared cyanohydrin carbonates from methyl cyanoformate and catalytic tributyltin cyanide. Organotin compounds may be invaluable as synthetic reagents, but they are also notorious for their volatility, acute toxicity, and problematic workups. A greater concern, however, is that this catalyst may be only marginally effective with α,β-unsaturated aldehydes. For example, *trans*-2-hexenal (**1b**) required 6 days of tin-catalyst exposure to reach a meaningful yield of methyl cyanohydrin carbonate, whereas the ethyl analogue (**2b**) can be conveniently prepared in just minutes with catalytic DABCO.

Finally, in the present method, no 1,4-addition product is observed. Michael addition has been previously identified as the major reaction pathway in the $Cp^*_2Sm(thf)_2$-catalyzed acetylcyanation of α,β-unsaturated carbonyl compounds.[9]

Palladium-Catalyzed Azidation. The earliest account of a palladium-catalyzed substitution reaction on an acylated α,β-unsaturated cyanohydrin was reported by Tsuji and co-workers in 1981.[10] An allylic cyanohydrin acetate was found to undergo regiospecific substitution with malonate ion via a 1,3-transposition reaction (eq 1).



(1)

Keinan and Roth later suggested the same substrate serve as a model to characterize nucleophilic reactivities in the presence of a palladium catalyst.[11] In a subsequent paper, Tsuji and co-workers reported the first example of an unsaturated cyanohydrin carbonate to undergo a palladium-catalyzed allylic substitution with a carbon nucleophile.[12] To our knowledge, the first and only instance of a palladium-catalyzed azidation of any acylated cyanohydrin derivative appeared in a 1989 article by Murahashi et al.[13] Here, the cyanohydrin acetate of crotonaldehyde was transformed into *trans*-γ-azidonitrile, **3a**. Interestingly, these researchers did not report the

(1) Presented in part by C.M.T. and H.Y.K. at the Southern California Conference on Undergraduate Research, November 23, 1996, Occidental College, Los Angeles; Abstracts Chem. IJ.3 and Chem. IJ.4, respectively.

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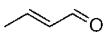
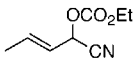
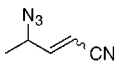
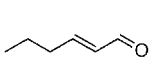
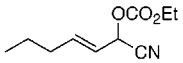
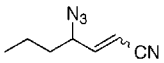
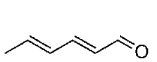
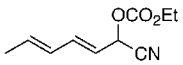
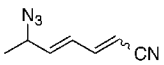
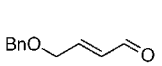
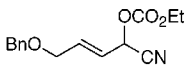
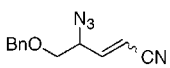
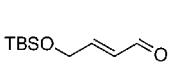
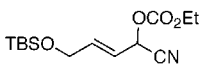
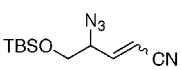
Table 1. Two-Step Conversion of α,β-Unsaturated Aldehydes into γ-Azido-α,β-Unsaturated Nitriles via a Pd(0)-Catalyzed Azidation of Allylic Cyanohydrin Carbonates[a]

entry	aldehyde	α–carbonate	yield, %[b]	γ-azide	yield, %[b]	*E*/*Z*[c]
1	 **1a**	 **2a**	96	 **3a**	87	2/1
2	 **1b**	 **2b**	97	 **3b**	85	3/2
3	 **1c**[d]	 **2c**	95	 **3c**	86[e]	1/1
4	 **1d**	 **2d**	93	 **3d**[f]	85	3/2
5	 **1e**	 **2e**	91	 **3e**	90	3/2

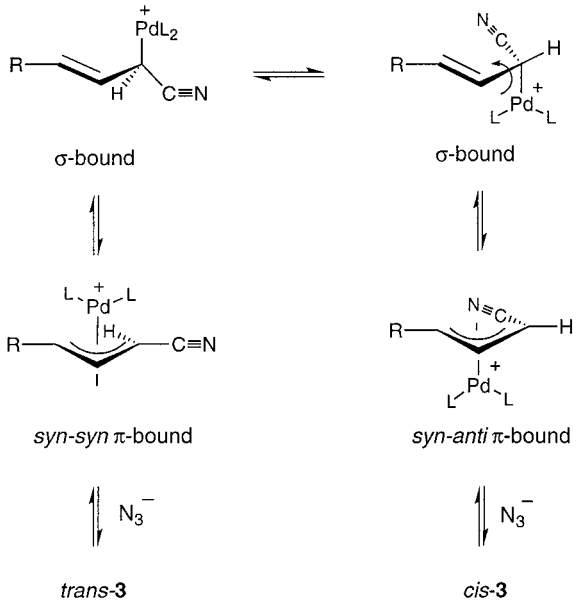
[a] For experimental conditions, see text. [b] Isolated yields. [c] Determined by ^{1}H NMR or GC analysis. [d] Contains ~5% of the (2*Z*,4*E*)-isomer. [e] No γ-azido product detected. [f] Decomposes slowly at −20 °C.

presence of any cis isomer, which is contrary to our own findings (vide infra).

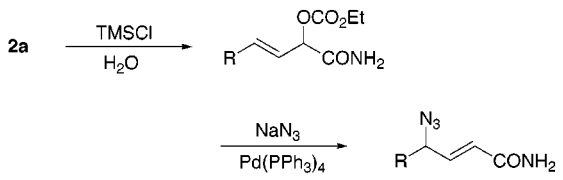
Table 1 illustrates that the palladium-catalyzed allylic substitution reaction with azide ion is an efficient route to γ-azido-α,β-unsaturated nitriles **3**. With the use of 1 mol % $Pd(PPh_3)_4$ and 2 equiv of NaN_3 in a THF/H_2O solution[14] at room temperature, the azidation reaction is complete in 30−95 min. The yields of **3a**−**e** range between 85% and 90%, and the reactions afford a stereochemical product mixture that is generally richer in the trans isomer as determined by GC and ^{1}H NMR. Structural assignments were resolved by ^{1}H NMR measurements of the vinylic coupling constants. Experimental evidence suggests that this isomeric ratio is equilibrium-controlled. This is based upon the observation that a THF/H_2O solution of pure *cis*-**3a** quickly reestablishes the equilibrium ratio of the *cis*- and *trans*-nitriles upon exposure to catalytic palladium(0). This result is consistent with a rapid π−σ−π interconversion pathway between the syn−syn and syn−anti π-allylpalladium complexes (Scheme 2).[15,16]

The relatively large proportion of the cis isomer in the product mixture was somewhat unexpected because π-allylpalladium complexes generally favor the more stable syn−syn isomer that eventually leads to (*E*)-olefinic products.[17] Evidently, stereocontrol in this instance may be attributable more to steric than to electronic effects. That is, the energy difference between the syn−syn and syn−anti π-bound intermediates may be lower than that normally observed because of the small steric congestion afforded by the sp-hybridized nitrile functionality. To test this hypothesis, the linear

Scheme 2



Scheme 3



cyano group of **2a** was converted[18] into the bulkier sp^2 carboxamide and then subjected to the usual azidation conditions (Scheme 3). The reaction afforded solely the trans isomer in good yield.

Significantly, the azidation reaction undergoes a clean 1,3-transposition with respect to the leaving group. This

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(16) An analogous π−σ−π interconversion has been suggested for palladium π-allyls derived from *E*- and *Z*-dienenitriles monoepoxides. David, H.; Dupuid, L.; Guillerez, M.-G.; Guibe, F. *Tetrahedron Lett.* **2000**, *41*, 3335−3338.

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(18) Basu, M. K.; Luo, F.-T. *Tetrahedron Lett.* **1998**, *39*, 3005−3006.

is apparently a manifestation of the energy-lowering effect of olefinic conjugative overlap with the π-orbitals in the cyano group. This stabilizing influence is likely responsible for suppression of the Winstein rearrangement[19] in allylic azides **3a**−**e** as well.

A few salient points have emerged from this study. Most conspicuous, perhaps, is the substitutive 1,5-transposition that dienyl carbonate **2c** readily undergoes (entry 3, Table 1). This substantially broadens the practical synthetic utility of the reaction. Entries 4 and 5 of Table 1 are evidence that popular hydroxy protecting groups are fully compatible with these reaction conditions. With only γ-azido products detected, the polar allylic oxygen atoms would appear to have no directing influence over the azide ion, contrary to what has been observed in some palladium-catalyzed allylic substitutions.

Conclusions

We have outlined the preparation of *cis*- and *trans*-γ-azido-α,β-unsaturated nitriles (**3**) from readily available α,β-unsaturated aldehydes (**1**). The overall yields for the two-step sequence, cyanocarboethoxylation and azidation, are excellent and range from 79% to 84%. We believe that this method provides an efficient entry way for the preparation of vinylogous amino acids, γ-amino acids, and other interesting peptidomimetic compounds. The palladium-catalyzed azidation of **2** occurs via a substitutive 1,3-transposition, except in the case of dienyl carbonate **2c** in which the analogous 1,5-mechanism is operative. Future work will focus on this latter substitutive rearrangement using other polyene cyanohydrin carbonates.

Experimental Section

General. Cyanation−ethoxycarbonylation reactions were conducted in flame-dried flasks under a blanket of nitrogen. All palladium(0)-catalyzed substitution reactions were run under inert atmosphere and protected from unnecessary exposure to light. Tetrahydrofuran was distilled from a midnight-blue solution of sodium benzophenone ketyl. Commercially available unsaturated aldehydes **1a**, **1b**, and **1c** were distilled prior to use. Benzyloxy aldehyde **1d** was prepared from the corresponding cis allylic alcohol[20,21] via oxidation with PCC in CH_2Cl_2. *tert*-Butyldimethylsilyloxy aldehyde **1e** could be secured by literature[22] precedent. All other reagents were used as received. NMR spectra were measured in $CDCl_3$ at either 200 or 400 MHz for proton and at 100 MHz for carbon. FTIR data were collected at a resolution of 4 cm^{-1}, and chromatographic purifications were performed by SiO_2 radial chromatography. Analytical TLC analyses were conducted on Baker Si 250 precoated glass plates (0.25 mm) and developed using ethanolic *p*-anisaldehyde reagent. New compounds were distilled bulb-to-bulb and submitted to the UCLA and UC Riverside Mass Spectrometry Facility for HRMS analysis.

CAUTION: Azido compounds may represent an explosion hazard when being concentrated under vacuum or stored neat. A safety shield and appropriate handling procedures are recommended.

Representative Example for the Cyanoethoxycarbonylation of α,β-Unsaturated Aldehydes. (*E*)-Crotonaldehyde Cyanohydrin Ethyl Carbonate (2a). To a dry flask charged with freshly distilled THF (1.9 mL) were added via syringe ethyl cyanoformate (0.42 mL, 4.3 mmol) and *trans*-crotonaldehyde (0.22 mL, 2.8 mmol). The stirred solution was cooled in an ice bath for 5 min prior to the addition of catalytic 1,4-diazabicyclo-[2.2.2]octane (DABCO; 31 mg, 10 mol %). The ice bath was removed, and the reaction was monitored by TLC analysis (1:1 hexanes/EtOAc). The reaction was quenched by dilution with 15 mL of ether. The single phase was first washed with saturated $NaHCO_3$ (2 × 4 mL) and brine (4 mL) and then subsequently dried over $MgSO_4$. Concentration under reduced pressure followed by radial chromatography (2 mm SiO_2 plate, 8:1 hexanes/EtOAc) and solvent removal afforded 454 mg (96%) of **2a** as a colorless oil: R_f 0.68 (SiO_2; 1:1 hexanes/EtOAc); ^{1}H NMR δ 6.19 (overlapping dq, J = 6.2, 13.4 Hz, 1H), 5.66−5.58 (m, 2H), 4.27 (q, J = 7.2 Hz, 2H), 1.72 (d, J = 6.7 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 153.6, 136.5, 121.2, 115.6, 65.6, 65.1, 17.9, 14.3; IR (neat) 2988, 1757, 1256, 1005 cm^{-1}.

(*E*)-2-Hexenal cyanohydrin ethyl carbonate (2b): R_f 0.64 (SiO_2; 1:1 hexanes/EtOAc); ^{1}H NMR δ 6.16 (dt, J = 6.8, 14.8 Hz, 1H), 5.65 (d, J = 6.7 Hz, 1H), 5.57 (ddt, J = 1.5, 6.7, 15.2 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.10 (q, J = 7.2 Hz, 2H), 1.44 (sextet, J = 7.3 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ 153.7, 141.3, 120.1, 115.6, 65.6, 65.2, 34.2, 21.7, 14.3, 13.7; IR (neat) 2965, 1760, 1260, 1006 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{15}NO_3$ (M^+), 197.1052; found, 197.1048.

(2*E*,4*E*)-Sorbaldehyde cyanohydrin ethyl carbonate (2c): R_f 0.64 (SiO_2; 1:1 hexanes/EtOAc); ^{1}H NMR δ 6.56 (dd, J = 10.1, 15.2 Hz, 1H), 5.95 (dq, J = 6.6, 15.2 Hz, 1H), 5.57 (dd, J = 6.9, 15.2 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 1.81 (d, J = 6.6 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 153.6, 138.9, 136.2, 129.2, 118.4, 115.4, 65.7, 65.1, 18.5, 14.3; IR (film) 2997, 1768, 1252, 998 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{13}NO_3$ (M^+), 195.0895; found, 195.0889.

(*E*)-5-Benzyloxy-2-pentenal cyanohydrin ethyl carbonate (2d): R_f 0.61 (SiO_2; 1:1 hexanes/EtOAc); ^{1}H NMR δ 7.38−7.27 (m, 5H), 6.27 (ddt, J = 1.2, 9.1, 15.5 Hz, 1H), 5.91 (ddt, J = 1.9, 6.3, 15.5 Hz, 1H), 5.75 (dd, J = 1.2, 5.0 Hz, 1H), 4.55 (s, 2H), 4.28 (dd, J = 1.2, 7.1 Hz, 2H), 4.10 (dt, J = 1.2, 4.5 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 153.6, 137.9, 136.4, 128.7, 128.0, 120.9, 115.2, 73.1, 68.7, 65.8, 64.5, 14.3; IR (film) 2986, 2868, 1757, 1254 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{18}NO_4$ (MH^+), 276.1236; found, 276.1236.

(*E*)-5-*t*-Butyldimethylsilyloxy-2-pentenal cyanohydrin ethyl carbonate (2e): R_f 0.40 (SiO_2; 5:1 hexanes/EtOAc); ^{1}H NMR δ 6.22 (ddt, J = 0.9, 3.4, 14.9 Hz, 1H), 5.83 (ddt, J = 2.1, 6.3, 14.9 Hz, 1H), 5.70 (dd, J = 1.0, 6.3 Hz, 1H), 4.30−4.16 (m, 4H), 1.30 (t, J = 7.1 Hz, 3H), 0.86 (s, 9H), 0.05 (s, 6H); ^{13}C NMR δ 153.6, 139.4, 118.8, 115.4, 65.7, 64.7, 62.1, 26.1, 18.5, 14.3, −5.2; IR (film) 2954, 1759, 1255, 1129, 839 cm^{-1}; HRMS (CI/NH_3) calcd for $C_{14}H_{29}N_2O_4Si$ (MNH_4^+), 317.1897; found, 317.1881.

Representative Example for the Pd-Catalyzed Azidation of Unsaturated Cyanohydrin Ethyl Carbonates. 4-Azido-2-pentenenitrile ((*E*,*Z*)-3a). To an ice-cold, stirred solution of cyanohydrin carbonate **2a** (200 mg, 1.2 mmol) and NaN_3 (156 mg, 2.4 mmol) in 6 mL of THF/H_2O (1:1, 0.2 M) was added catalytic $Pd(PPh_3)_4$ (14 mg, 1 mol %) in a single portion. The ice−water bath was removed, and the progress of the reaction was monitored by TLC (1:1 hexanes/EtOAc). The reaction was judged complete after 95 min and quenched by dilution with ether. The organic layer was removed, and the aqueous phase was extracted twice with additional aliquots of ether. The combined extracts were dried over $MgSO_4$ and then concentrated in vacuo via rotary evaporation. To ensure complete removal of Pd, the residue was passed through a short plug of SiO_2 layered with $MgSO_4$ ($MgSO_4/SiO_2$ = 1:4) with ether. The filtrate was evaporated to dryness, and the crude oil was purified via radial chromatography (1 mm SiO_2 plate; 1:1 hexanes/ethyl acetate) to afford 127 mg (87%) of (*E*,*Z*)-**3a** as a colorless oil. Separation of the *E*,*Z* diastereomers was realized by further chromatography using the solvent system 1:1 hexanes/CH_2Cl_2.

(*Z*)-3a: R_f 0.30 (SiO_2; 2:1 hexanes/CH_2Cl_2); ^{1}H NMR δ 6.37 (dd, J = 9.2, 10.9 Hz, 1H), 5.46 (d, J = 10.9 Hz, 1H), 4.58 (m, 1H), 1.43 (d, J = 7.0 Hz, 3H); ^{13}C NMR δ 151.9, 114.8, 101.4, 57.3, 19.7; IR (film) 2985, 2225, 2113, 1237 cm^{-1}.

(*E*)-3a: R_f 0.26 (SiO_2; 2:1 hexanes/CH_2Cl_2); ^{1}H NMR δ 6.59 (dd, J = 5.5, 16.8 Hz, 1H), 5.60 (dd, J = 16.8, 1.8 Hz, 1H), 4.19

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(m, 1H), 1.39 (d, J = 6.8 Hz, 3H); ^{13}C NMR δ 152.3, 116.6, 101.2, 57.6, 19.1; IR (film) 2984, 2229, 2111, 1252 cm^{-1}; HRMS (CI/NH_3) calcd for $C_5H_{10}N_5$ (MNH_4^+), 140.0936; found, 140.0943.

4-Azido-2-heptenenitrile ((*Z*)-3b): R_f 0.43 (SiO_2; 1:1 hexanes/CH_2Cl_2); ^{1}H NMR δ 6.32 (dd, J = 9.5, 10.9 Hz, 1H), 5.52 (d, J = 10.9 Hz, 1H), 4.43−4.36 (m, 1H), 1.70−1.30 (m, 4H), 0.96 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ 151.1, 113.8, 102.1, 61.9, 36.2, 19.0, 13.9; IR (film) 2973, 2886, 2228, 2109 cm^{-1}.

((*E*)-3b): R_f 0.38 (SiO_2; 1:1 hexanes/CH_2Cl_2); ^{1}H NMR δ 6.59 (dd, J = 6.0, 16.4 Hz, 1H), 5.61 (dd, J = 1.6, 16.4 Hz, 1H), 4.08−4.02 (m, 1H), 1.70−1.32 (m, 4H), 0.96 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ 151.6, 116.6, 101.7, 62.6, 35.9, 19.0, 13.8; IR (film) 2973, 2878, 2228, 2117 cm^{-1}; HRMS (EI) calcd for $C_7H_{11}N_4$ (M^+), 151.0984; found, 151.0984.

6-Azido-2,4-heptadienenitrile ((2*Z*,4*E*)-3c): R_f 0.18 (SiO_2; 4:1 hexanes/CH_2Cl_2); ^{1}H NMR δ 6.83 (t, J = 11.0 Hz, 1H), 6.71 (dd, J = 11.1, 15.0 Hz, 1H), 6.05 (dd, J = 7.0, 15.0 Hz, 1H), 5.29 (d, J = 11.0 Hz, 1H), 4.17 (quintet, J = 6.8 Hz, 1H), 1.36 (d, J = 6.7 Hz, 3H); ^{13}C NMR δ 148.0, 142.1, 127.5, 116.1, 99.0, 67.4, 58.6, 19.8; IR (film) 2981, 2215, 2207, 1646 cm^{-1}.

((2*E*,4*E*)-3c): R_f 0.12 (SiO_2; 4:1 hexanes/CH_2Cl_2); ^{1}H NMR δ 6.92 (dd, J = 11.1, 16.5 Hz, 1H), 6.26 (dd, J = 11.1, 15.7 Hz, 1H), 5.97 (dd, J = 6.2, 15.7 Hz, 1H), 5.36 (d, J = 16.5 Hz, 1H), 4.08 (quintet, J = 6.8 Hz, 1H), 1.11 (d, J = 7.0 Hz, 3H); ^{13}C NMR δ 149.1, 141.7, 128.7, 117.8, 100.5, 58.4, 19.8; IR (film) 2981, 2218, 2100, 1710 cm^{-1}; HRMS (CI/NH_3) calcd for $C_7H_{12}N_5$ (MNH_4^+), 166.1093; found, 166.0191.

4-Azido-5-benzyloxy-2-pentenenitrile ((*Z*)-3d): unstable oil; R_f 0.12 (SiO_2; 2:1 hexanes/CH_2Cl_2); ^{1}H NMR δ 7.39−7.29 (m, 5H), 6.44 (dd, J = 9.2, 11.2 Hz, 1H), 5.58 (dd, J = 1.2, 11.2 Hz, 1H), 4.65−4.50 (m, 3H), 3.57 (dd, J = 4.9, 10.1 Hz, 1H), 3.54 (dd, J = 4.6, 10.1 Hz, 1H); ^{13}C NMR δ 148.1, 137.4, 128.8, 128.3, 127.9, 114.7, 103.4, 73.8, 71.2, 60.9; IR (film) 2862, 2228, 2101, 1109 cm^{-1}.

((*E*)-3d): unstable oil; R_f 0.10 (SiO_2; 2:1 hexanes/CH_2Cl_2); ^{1}H NMR δ 7.40−7.26 (m, 5H), 6.87 (dd, J = 5.0, 16.2 Hz, 1H), 5.70 (dd, J = 1.9, 16.2 Hz, 1H), 4.58 (s, 2H), 4.28 (dddd, J = 1.9, 5.0, 6.9, 9.8 Hz, 1H), 3.64 (dd, J = 4.6, 9.8 Hz, 1H), 3.56 (dd, J = 6.9, 9.8 Hz, 1H); ^{13}C NMR δ 148.3, 137.2, 128.8, 128.3, 128.0, 116.5, 103.1, 73.9, 71.4, 61.6; IR (film) 2862, 2228, 2101, 1109 cm^{-1}.

4-Azido-5-*t*-butyldimethylsilyloxy-2-pentenenitrile ((*Z*)-3e): R_f 0.36 (SiO_2; 2:1 hexanes/CH_2Cl_2); ^{1}H NMR δ 6.33 (dd, J = 7.6, 11.2 Hz, 1H), 5.59 (d, J = 11.2 Hz, 1H), 4.46−4.40 (m, 1H), 3.82−3.70 (m, 2H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR δ 148.4, 114.9, 103.2, 65.3, 62.7, 25.9, 18.4, −5.4; IR (film) 2934, 2862, 2227, 2117 cm^{-1}.

((*E*)-3e): R_f 0.34 (SiO_2; 2:1 hexanes/CH_2Cl_2); ^{1}H NMR δ 6.58 (dd, J = 4.8, 16.0 Hz, 1H), 5.69 (dd, J = 1.8, 16.0 Hz, 1H), 4.16−4.10 (m, 1H), 3.79 (dd, J = 4.8, 10.4 Hz, 1H), 3.69 (dd, J = 7.2, 10.4 Hz, 1H), 0.92 (s, 9H), 0.10 (s, 6H); ^{13}C NMR δ 148.5, 116.6, 103.0, 65.5, 63.6, 25.9, 18.4, −5.4; IR (film) 2955, 2232, 2118, 1471 cm^{-1}; HRMS (CI/NH_3) calcd for $C_{11}H_{24}N_5OSi$ (MNH_4^+), 270.1750; found, 270.1739.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **2a**−**e** and **3a**−**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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