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$NbCl_3$-Catalyzed Intermolecular [2+2+2] Cycloaddition of Alkynes and α,ω-Dienes: Highly Chemo- and Regioselective Formation of 5-ω-Alkenyl-1,4-substituted-1,3-cyclohexadiene Derivatives

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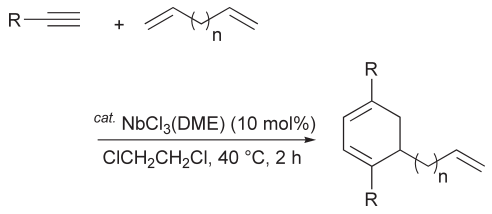

Intermolecular [2+2+2] cycloaddition of *tert*-butylacetylene with α,ω-dienes was successfully achieved by $NbCl_3$(DME) catalyst to afford 5-ω-alkenyl-1,4-disubstituted-1,3-cyclohexadienes in excellent yields with high chemo- and regioselectivity.

1,3-Cyclohexadienes are an important class of compounds and are widely employed in organic synthesis.[1] In addition, these compounds have been utilized as monomers for good transparency and heat resistance polymers.[2] Therefore, various methods for the preparation of substituted 1,3-cyclohexadienes have been investigated.[3] Recent methods to the access of these compounds include tandem diene−alkyne metathesis[4] and 1,6-electrocyclic reaction of 1,3,5-hexatrienes.[5] In contrast, transition metal-catalyzed [2+2+2] intermolecular cycloaddition by the reaction of two molecules of mono alkynes and one molecule of alkenes is one of the most simple and atom-economical methods for preparing 1,3-cyclohexadiene derivatives. However, this methodology mainly leads to the cyclotrimerization of alkynes[6,7] in preference to the desired cross-cyclotrimerization between alkynes and alkenes. Therefore, only a limited amount of work has been reported so far.[8,9] As a pioneering work for this synthetic protocol, Rothwell and co-workers reported the intermolecular cycloaddition of alkynes and alkenes leading to 1,3-cyclohexadienes by titanacyclopentadiene catalyst.[8] However, this method generally affords 1,3-cyclohexadienes in unsatisfactory yields and selectivities. In addition, this reaction pathway typically includes an isomerization step through 1,5-hydrogen shift of unstable low-valent titanium species such as the titananorbornene intermediate.[8] Alternatively, $NbCl_3$(DME) is a thermally stable low-valent early transition metal complex that shows high reactivity in several stoichiometric and catalytic reactions with alkynes.[10−13] As a preliminary attempt, we reported $NbCl_3$-(DME)-catalyzed intermolecular cycloaddition of alkynes and alkenes to substituted 1,3-cyclohexadienes.[14] However, this approach is still problematic with regard to access of the desired 1,3-cyclohexadienes in high yield and selectivity, which generally gives a cyclotrimerization byproduct of alkyne in substantial yields.[14] Therefore, the development of a novel and efficient methodology for chemo- and regioselective formation of 1,3-cyclohexadienes by [2+2+2] cycloaddition of alkenes and

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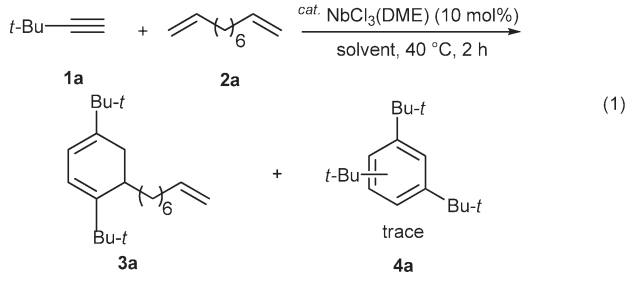
TABLE 1. $NbCl_3$-Catalyzed Reaction of *tert*-Butylacetylene (1a) with 1,9-Decadiene (2a)[a]

			yield[b]/%	
entry	catalyst	solvent	**3a**	**4a**
1	$NbCl_3$(DME)	$Cl(CH_2)_2Cl$	97 [81] (92)	trace
2[c]	$NbCl_3$(DME)	$Cl(CH_2)_2Cl$	65 (90)	7
3[d]	$NbCl_3$(DME)	$Cl(CH_2)_2Cl$	27 (94)	9
4	$NbCl_3$(DME)	$Cl(CH_2)_4Cl$	83 (91)	trace
5	$NbCl_3$(DME)	THF	9 (46)	26
6	$NbCl_3$(DME)	DME	nd[e]	n[e]
7	$NbCl_3$(DME)	toluene	nd[e]	nd[e]
8	$TaCl_3$(DME)	$Cl(CH_2)_2Cl$	nd[e]	nd[e]
9	$NbCl_5$	$Cl(CH_2)_2Cl$	nd[e,f]	nd[e,f]
10	Cp_2NbCl_2	$Cl(CH_2)_2Cl$	nd[e]	nd[e]
11	$VCl_3(THF)_3$	$Cl(CH_2)_2Cl$	nd[e]	nd[e]

[a] **1a** (2 mmol) was allowed to react with **2a** (4 mmol) in the presence of catalyst (0.2 mmol, 10 mol % based on **1a**) in solvent (1 mL) at 40 °C for 2 h. [b] Yields were determined by GC based on **1a** used. The number in square bracket shows isolated yield. The numbers in parentheses show the selectivity (%) of 1,4,5-substituted adduct. The regiochemistry of other isomers was not determined. [c] **1a** (2 mmol) and **2a** (2 mmol) were used. [d] **1a** (2 mmol) and **2a** (1 mmol) were used. [e] Not detected by GC. [f] The substrates **1a** and **2a** were converted thoroughly and an intractable mixture of unidentified oligomerization products was obtained.

alkynes remains an unsoluble problem and a challenging target. In this paper, we would like to report the excellent chemo- and regioselective [2+2+2] intermolecular cycloaddition reaction of 1-alkynes with α,ω-unconjugated dienes under the influence of $NbCl_3$(DME),[5a] affording 1,4,5-trisubstituted-1,3-cyclohexadiene derivatives in high to excellent yields (eq 1). The present reaction provides a novel protocol for the selective formation of ω-alkenyl-substituted-1,3-cyclohexadiene derivatives, which also enables the conversion to ω-acetyl-substituted 1,3-cyclohexadiene derivatives.



(1)

tert-Butylacetylene (**1a**) and 1,9-decadiene (**2a**) were chosen as model substrates and the reaction was carried out under various conditions (Table 1). For instance, a mixture of **1a** (2 mmol) and **2a** (4 mmol) in dichloroethane (1 mL) was allowed to react under the influence of a catalytic amount of $NbCl_3$(DME) (0.2 mmol, 10 mol %) at 40 °C for 4 h, giving 1,4-di-*tert*-butyl-5-(7-heptenyl)-1,3-cyclohexadiene (**3a**) in excellent yield (entry 1). In contrast to the previous paper,[14] the reaction proceeded highly chemo- and regioselectively to afford 1,4,5-trisubstituted-1,3-cyclohexadiene (**3a**) almost exclusively. In this reaction, only a negligible amount of tri-*tert*-butylbenzenes (**5a**) was detected by GC (entry 1). The regiostructure of the 1,4,5-substituted cycloaddition product (**3a**) was characterized by ^1H and ^{13}C NMR, which resonances were assigned by means of 2D HMQC and HMBC spectroscopies.

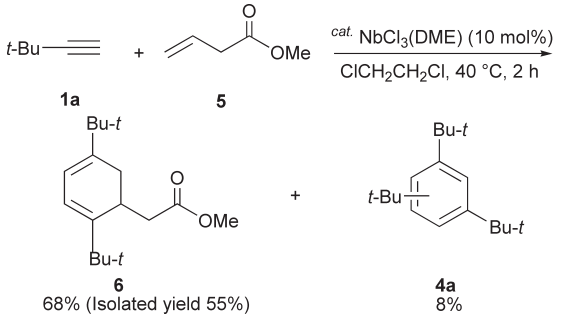
The yield of **3a** was influenced by the ratio of the substrate **1a** to **2a** and the best yield was obtained when the reaction of **1a** and **2a** was carried out with 1:2 molar ratio (entry 1). As the amount of **2a** was reduced, the yield of **3a** was lowered (entries 2 and 3). However, it is noteworthy that the reaction was exclusively subjected to react only the single alkene side of α,ω-dienes with the alkyne and **3a** was the sole cross-cycloaddition product.

The reaction was greatly affected by the solvent employed and halogenated solvents such as 1,2-dichloroethane and 1,4-dichlorobutane realized high selectivity of **3a** (entries 1 and 4). On the other hand, the use of other solvents such as THF, toluene, and DME resulted in a decrease in the yields of **3a** (entries 5−7).

As for the catalyst precursor of this reaction, a low-valent Nb(III) complex, $NbCl_3$(DME), is highly efficient. When the Ta(III) analogue, $TaCl_3$(DME), was used as a catalyst, even though **1a** was evidently converted during the reaction course, no desired 1,3-cyclohexadiene adduct was produced at all (entry 8). Other Nb(IV), Nb(V), and V(III) complexes such as $NbCl_5$, Cp_2NbCl_2, and $VCl_3(THF)_3$ were totally ineffective catalysts for the formation of cycloaddition products (entries 9−11).

Under the optimized condition as shown in Table 1, entry 1, reactions of various 1-alkynes (**1a**−**d**) with α,ω-dienes (**2b**−**e**) were examined (Table 2). The yields of the 1,3-cyclohexadiene adducts (**3**) were somewhat influenced by the alkyl chain length of the α,ω-dienes (**2**) and the reaction of **1a** with various α,ω-dienes (**2**) gave the corresponding 5-ω-alkenyl-1,4-di-*tert*-butyl-1,3-cyclohexadienes (**2b**−**e**) in good to excellent yields (56−97%) with high to excellent chemo- and regioselectivity (86→99%) (entries 1−5). In this reaction, the yield and selectivity of the reaction were greatly affected by the bulkiness and electronic nature of alkyne substituents. The best yield and selectivity for the formation of **3a** was achieved when the reaction was carried out with *tert*-butylacetylene (**1a**). On the other hand, the reaction of trimethylsilylacetylene (**1b**) with **2a** led to the mixture of the corresponding intermolecular cycloaddition products (**3f**) and the alkyne cyclotrimerization product (**4b**) (entry 6). Alkynes having less bulky substituents such as 1-hexyne (**1c**) and phenylacetylene (**1d**) resulted in alkyne tricyclomerization products (**4c**−**d**) as major adducts (entries 7 and 8).

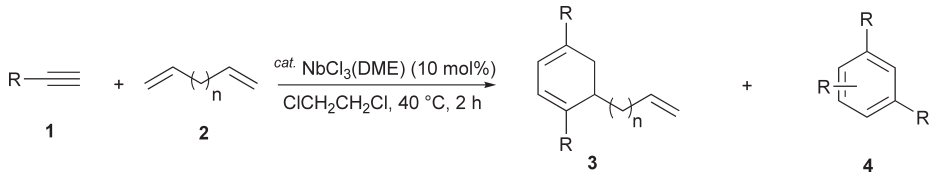
The reaction can be extended to the formation of ω-acetoxy-substituted 1,3-cyclohexadiene (eq 2). For instance, the reaction of **1a** (2 mmol) with methyl vinylacetate (**5**) (2 mmol) under optimized conditions afforded **6** in 68% yield as a single regioisomer (1,4,5-adduct) along with the formation of **4a** in 8% yield (eq 2).



(2)

For further exploitation of the synthetic application of the 5-ω-alkenyl-1,4-substituted-1,3-cyclohexadienes, the Pd(II)-catalyzed Wacker oxidation reaction of **3c** was carried

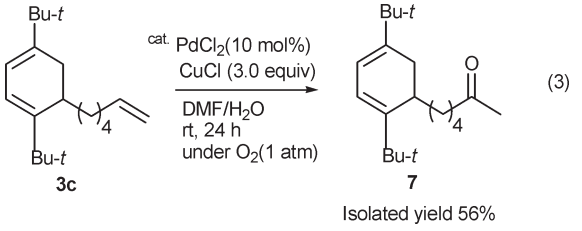
TABLE 2. $NbCl_3$-Catalyzed Reaction of Terminal Alkynes (1) with α,ω-Dienes (2)[a]



			yield/%[b]	
entry	alkyne (**1**) R	α,ω-diene (**2**)	**3**	**4**
1	*t*-Bu (**1a**)	1,9-decadiene (n = 6) (**2a**)	97 [81] (92) (**3a**)	trace
2	*t*-Bu (**1a**)	1,5-hexadiene (n = 2) (**2b**)	78 [63] (86) (**3b**)	6 (**4a**)
3	*t*-Bu (**1a**)	1,7-octadiene (n = 4) (**2c**)	84 [64] (91) (**3c**)	trace
4	*t*-Bu (**1a**)	1,11-dodecadiene (n = 8) (**2d**)	73 [64] (95) (**3d**)	trace
5	*t*-Bu (**1a**)	1,13-tetradecadiene (n = 10) (**2e**)	56 [36] (>99) (**3e**)	nd
6	Me_3Si (**1b**)	**2a**	[65] (>99) (**3f**)	18 (**4b**)
7	n-C_4H_9 (**1c**)	**2a**	nd	64 (**4c**)
8	Ph (**1d**)	**2a**	trace	48 (**4d**)

[a] **1** (2 mmol) was allowed to react with **2** (4 mmol) in the presence of $NbCl_3$(DME) (0.2 mmol, 10 mol % based on **1**) in 1,2-dichloroethane (1 mL) at 40 °C for 2 h. [b] Yields were determined by GC based on **1** used. The numbers in square brackets show isolated yields. The numbers in parentheses show the selectivity (%) of 1,4,5-substituted adducts. The regiochemistry of the other isomers was not determined.

out. The reaction of **3c** in the presence of $PdCl_2$ combined with CuCl under O_2 (1 atm)[15] led to the formation of **7**, as ω-acetyl-functionalized 1,3-cyclohexadienes in 56% isolated yield (eq 3). Since the substrates having oxo-functionality like ketones and aldehydes are not generally tolerated under the conditions in the low-valent early transition metal catalyst system,[10−12] this two-step synthesis provides an efficient protocol for the 1,3-cyclohexadienes having oxo-functionality in the molecule.



(3)

With regard to the reaction mechanism, the reaction would proceed in a similar manner to the previously reported pathway via the formation of a niobacyclopentadiene **A** by the reaction of two alkyne molecules, followed by the reaction with α,ω-dienes to form niobanorbornene species **B** as a key intermediate (Scheme 1).[14] In the present reaction, however, it was found that the ω-alkenyl moiety on the α,ω-dienes markedly affects the reactivity of the cycloaddition reaction as well as chemo- and regioselectivity. Although all attempts at isolation and spectral observation of the relevant niobium intermediates were unsuccessful, the ω-alkenyl group would coordinate to the niobium metal center as a directing group, which hampered the formation of undesired alkyne cyclotrimerization products (path A, Scheme 1). The directing group effect of the ω-alkenyl moiety presumably enhanced the reactivity of the alkenes, as well as improved selectivity of the resulting 1,3-cyclohexadiene products. However, the effect the chain length of the α,ω-dienes exerted on the regiochemistry of the reaction is not clearly explained at this moment. The detailed elucidation on the reaction mechanism based on the experimental evidence is currently in progress.

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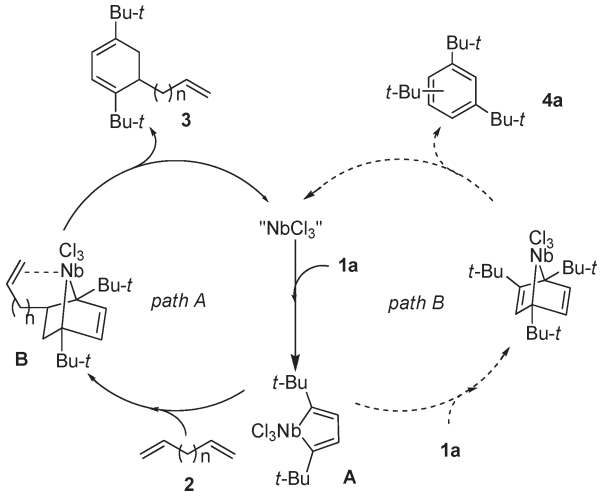
SCHEME 1. A Plausible Reaction Pathway



In conclusion, we have developed a new protocol to the highly chemo- and regioselective reaction for [2+2+2] cycloaddition of alkynes and alkenes leading to 5-ω-alkenyl-1,4-substituted-1,3-cyclohexadienes in high to excellent yields. Here, the ω-alkenyl group can be easily converted to the ω-acetyl group.

Further study on the scope and further synthetic application of this reaction will be performed in future work.

Experimental Section

A Typical Reaction Procedure for the Preparation of 3a (entry 1, Table 1). A mixture of *tert*-butylacetylene (**1a**) (164 mg, 2 mmol), 1,9-decadiene (**2a**) (552 mg, 4 mmol), $NbCl_3$(DME) (58 mg, 0.2 mmol), and 1,2-dichloroethane (1 mL) was stirred for 2 h at 40 °C under Ar. The yields of the products were estimated from the peak areas based on the internal standard technique using GC and **3a** was obtained in 97% yield. The product **3a** was isolated by silica gel column chromatography (*n*-hexane as eluent) in 81% yield (489 mg) as a colorless liquid.

3a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85−1.02 (m, 2H), 1.05 (s, 9H), 1.09 (s, 9H), 1.28−1.55 (m, 10H), 2.04 (m, 1H), 2.32,

(d, 2H), 4.92 (dt, J = 10.1, 1.7 Hz, 1H), 4.98 (dt, J = 15.4, 1.7 Hz, 1H), 5.69 (s, 2H) 5.74 (tt, J = 12.4, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5 (CH_2), 28.1 (CH_2), 28.2 (CH_2), 28.5 (CH_3), 28.7 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 29.6 (CH_3), 33.2 (CH), 33.8 (CH_2), 35.0 (C), 35.6 (C), 114.1 (CH_2), 115.4 (CH), 115.5 (CH), 139.2 (CH), 143.6 (C), 150.2 (C); IR (neat, cm^{-1}) 3069, 1830, 1768, 1648, 1597, 1361, 1103, 921; GC-MS (EI) m/z (rel intensity) 302 (9) [M^+], 190 (1), 175 (6), 119 (4), 79 (1), 57 (100); HRMS (EI) m/z calcd for $C_{22}H_{38}$ [M]$^+$ 302.2974, found 302.2979.

The Reaction of 1a with 5 (eq 2). A mixture of *tert*-butylacetylene (**1a**) (164 mg, 2 mmol), methyl vinylacetate (**5**) (200 mg, 2 mmol), $NbCl_3$(DME) (58 mg, 0.2 mmol), and 1,2-dichloroethane (1 mL) was stirred for 2 h at 40 °C under Ar. The yields of the products were estimated from the peak areas based on the internal standard technique using GC (68% (**6**) and 8% (**4a**)). The product **6** was isolated as pure form by silica gel column chromatography (*n*-hexane/ethyl acetate = 8/2 as eluent) in 55% yield (156 mg).

6: colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (s, 9H), 1.03 (s, 9H), 2.04 (m, 2H), 2.25−2.50 (m, 2H), 2.73 (m, 1H), 3.53 (s, 3H) 5.65(s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3 (CH), 29.2 (CH_2), 29.3 (CH_3), 29.5 (CH_3), 33.3 (CH_2), 34.9 (C), 35.6 (C), 51.3 (CH_3), 115.6 (CH), 117.0 (C), 143.8 (C), 147.3 (C), 173.6 (C); IR (neat, cm^{-1}) 2961, 2823, 1738, 1644, 1465, 1362, 1090 885; GC-MS (EI) m/z (rel intensity) 264 (2) [M]$^+$, 190 (16), 175 (100), 79 (1), 57 (55); HRMS (EI) m/z calcd for $C_{17}H_{28}O_2$ [M]$^+$ 264.2089, found 264.2089.

Preparation of 7 from 3c (eq 3). A mixture of **3c** (822 mg, 3 mmol), $PdCl_2$ (53 mg, 0.3 mmol), CuCl (297 mg, 3 mmol), and H_2O/DMF (0.3/2.7 mL) was stirred for 24 h at room temperature under O_2 (1 atm). The product **7** was isolated (by silica gel column chromatography with *n*-hexane/ethyl acetate = 8:2 as eluent) in 56% yield as pure form (483 mg).

7: colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 9H), 1.01 (s, 9H), 1.22−1.47 (m, 6H), 1.98 (m, 1H), 2.04 (s, 3H), 2.22 (m, 2H), 2.33 (t, J = 7.6 Hz, 2H), 5.62 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9 (CH_2), 27.0 (CH_2), 27.9 (CH_2), 28.1 (CH_2), 28.4 (CH_3), 29.5 (CH_3), 29.8 (CH_3), 33.0 (CH), 34.9 (C), 35.6 (C), 43.7 (CH_2), 115.5 (CH), 115.6 (CH), 143.5 (C), 149.9 (C), 209.3 (C); IR (neat, cm^{-1}) 3052, 1718, 1462, 1359, 1264, 834; GC-MS (EI) m/z (rel intensity) 290 (9) [M]$^+$, 191 (1), 177 (9), 99 (2), 79 (2), 57 (100); HRMS (EI) m/z calcd for $C_{20}H_{34}O$ [M]$^+$ 290.2610 found 290.2613

3b: colorless liquid; ^{1}H NMR (400 MHz; $CDCl_3$) δ 0.98 (s, 9H), 1.01 (s, 9H), 1.24−1.47 (m, 2H), 1.85−2.10 (m, 2H), 1.98−2.10 (m, 1H), 2.23 (d, J = 15.1 Hz, 2H), 4.85 (dt, J = 10.1, 1.8 Hz, 1H), 4.91 (dt, J = 15.1, 1.8 Hz, 1H), 5.63 (s, 2H), 5.71 (tt, J = 11.7, 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3 (CH_2), 28.0 (CH_2), 28.5 (CH_3), 29.6 (CH_3), 31.7 (CH_2), 32.4 (CH), 35.0 (C), 35.6 (C), 114.4 (CH_2), 115.7 (CH), 115.8 (CH), 138.8 (CH), 143.4 (C), 149.8 (C); IR (neat, cm^{-1}) 2963, 2869, 1641, 1479, 1392, 1367, 1264, 1021, 910; GC-MS (EI) m/z (rel intensity) 246 (12) [M]$^+$, 189 (3), 133 (4), 119 (8), 57 (100); HRMS (EI) m/z calcd for $C_{18}H_{30}$ [M]$^+$ 246.2348, found 246.2352.

3c: colorless liquid; ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.05 (s, 9H), 1.09 (s, 9H), 1.15−1.59 (m, 8H), 2.07 (m, 1H), 2.32 (d, ^3J = 14.9 Hz, 2H), 4.92 (dt, J = 10.2, 1.7 Hz, 1H), 4.98 (dt, J = 15.4, 1.7 Hz, 1H), 5.63 (s, 2H), 5.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0 (CH_2), 28.0 (CH_2), 28.2 (CH_2), 28.5 (CH_3), 29.1 (CH_2), 29.6 (CH_3), 33.2 (CH), 33.8 (CH_2), 35.0 (C), 35.6 (C), 114.2 (CH_2), 115.4 (CH), 115.5 (CH), 139.1 (CH), 143.5 (C), 150.1 (C); IR (neat, cm^{-1}) 2964, 2871, 1736, 1465, 1363, 1062, 885; GC-MS (EI) m/z (rel intensity) 274 (8) [M]$^+$, 175 (6), 83 (1), 79 (1), 57 (100); HRMS(EI) m/z calcd for $C_{20}H_{34}$ [M]$^+$ 274.2661, found 274.2653.

3d: colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 9H), 1.09 (s, 9H), 1.18−1.36 (m, 14H), 1.52 (m, 2H), 2.06 (m, 1H), 2.32 (d, J = 15.1, 2H), 4.93 (dt, J = 10.1, 1.4 Hz, 1H), 4.99 (dt, J = 15.6, 1.4 Hz, 1H), 5.69 (s, 2H), 5.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5 (CH_2), 28.1 (CH_2), 28.2 (CH_2), 28.4 (CH_3), 28.9 (CH_2), 29.1 (CH_2), 29.4 (CH_2), 29.5 (CH_3), 29.6 (CH_2), 29.7 (CH_2), 33.2 (CH_3), 33.8 (CH_2), 35.0 (C), 35.6 (C), 114.1 (CH_2), 115.3 (CH), 115.5 (CH), 139.2 (CH), 143.6 (C), 150.3 (C); IR (neat, cm^{-1}) 3056, 1818, 1769, 1642, 1363, 1062, 885; GC-MS (EI) m/z (rel intensity) 330 (8) [M]$^+$, 190 (1), 135 (1), 79 (1), 57 (100); HRMS(EI) m/z calcd for $C_{24}H_{42}$ [M]$^+$ 330.3289, found 330.3294.

3e: colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (s, 9H), 1.19−1.49 (m, 18H), 1.18−1.36 (d, J = 15.2, 2H), 1.32 (s, 9H), 1.94−2.03 (m, 3H), 4.85 (dt, J = 10.3, 1.4 Hz, 1H), 4.92 (dt, J = 15.6, 1.4 Hz, 1H), 5.61 (s, 1H), 5.62 (s, 1H), 5.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.6 (CH_2), 28.1 (CH_2), 28.2 (CH_2), 28.5 (CH_3), 28.9 (CH_2), 29.2 (CH_2), 29.5 (CH_2), 29.60 (CH_3), 29.63 (CH_2), 29.7 (CH_2), 29.8 (CH_2), 33.2 (CH), 33.8 (CH_2), 35.0 (C), 35.6 (C), 114.0 (CH_2), 115.3 (CH), 115.5 (CH), 139.2 (CH), 143.4 (C), 150.2 (C); GC-MS (EI) m/z (rel intensity) 358 (8) [M]$^+$, 190 (1), 175 (6), 91 (3), 57 (100); HRMS (EI) m/z calcd for $C_{26}H_{46}$ [M]$^+$ 358.3602, found 358.3617.

3f: colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 9H), 0.03 (s, 9H), 1.11−1.32 (m, 10H), 1.95−2.25 (m, 2H), 1.95−2.27 (d, J = 15.3 Hz, 2H), 2.07 (s, 1H), 4.89 (dt, J = 15.3 Hz, 1H), 5.73 (m, 2H), 6.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −2.7 (CH_3), −1.5 (CH_3), 27.3 (CH_2), 27.6 (CH_2), 28.7 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.4 (CH_2), 32.8 (CH), 33.6 (CH_2), 113.9 (CH_2), 130.8 (CH), 131.5 (CH), 138.2 (CH), 139.0 (C), 145.4 (C); IR (neat, cm^{-1}) 3075, 1640, 1602, 1440, 1247, 1169, 1071, 992; GC-MS (EI) m/z (rel intensity) 334 (3) [M]$^+$, 260 (1), 223 (2), 187 (1), 135 (47), 73 (100), 41 (3); HRMS (EI) m/z calcd for $C_{20}H_{38}Si_2$ [M]$^+$ 334.2512, found 334.2524

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Supporting Information Available: Copies of ^{1}H, ^{13}C, and 2D (HMQC and HMBC) NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.