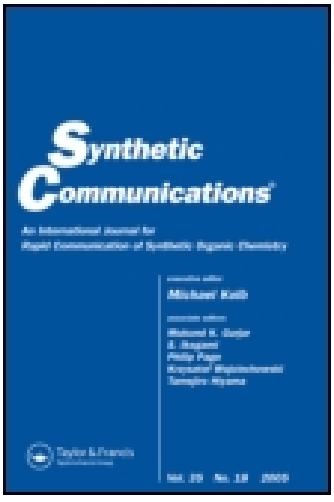

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A Simple, Concise, Stereocontrolled Synthesis of (8E,10Z)-Pentadecadien-1-ol Acetate

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A Simple, Concise, Stereocontrolled Synthesis of (*8E,10Z*)-Pentadecadien-1-ol Acetate

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Abstract: A simple, concise, and stereocontrolled synthesis of (*8E,10Z*)-pentadecadien-1-ol acetate involving a Cadiot–Chodkiewicz reaction as the key step is described

Keywords: Acetate, *Acrobasis vaccini*, Cadiot–Chodkiewicz reaction, diacetylene, pheromone

INTRODUCTION

The cranberry fruitworm, *Acrobasis vaccinni* Riley, is a member of the pyralidae family of the Lepidoptera.[1] It is the most important pest of cranberries and blueberries and is capable of considerably decimating these crops. Other host plants include huckleberries, dangleberries, beach plums, and apples. An effective agent for detecting, monitoring, and controlling this pest is needed.

McDonough et al.[2] reported that the composition of two compounds, (*8E,10Z*)-pentadecadien-1-ol acetate (**1**) and (*E*)-9-pentadecen-1-ol acetate (**2**), in a defined ratio range is a highly effective attractant for the male cranberry fruitworm. This composition provides a sensitive tool for the detection of this pest by attracting the male cranberry fruit worm moths to

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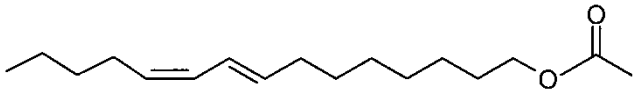
the field traps, thus helping the pest control. This composition also provides a means to detect, survey, monitor, and control the cranberry fruitworm.[2]



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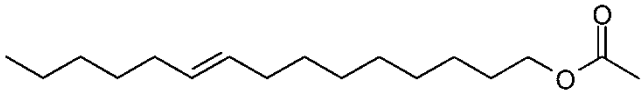

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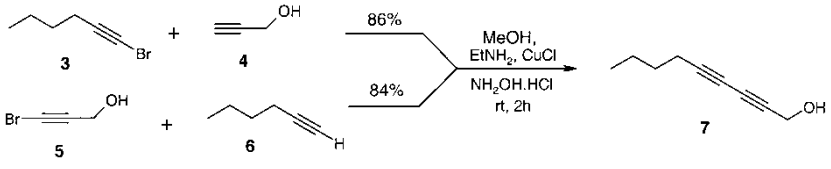
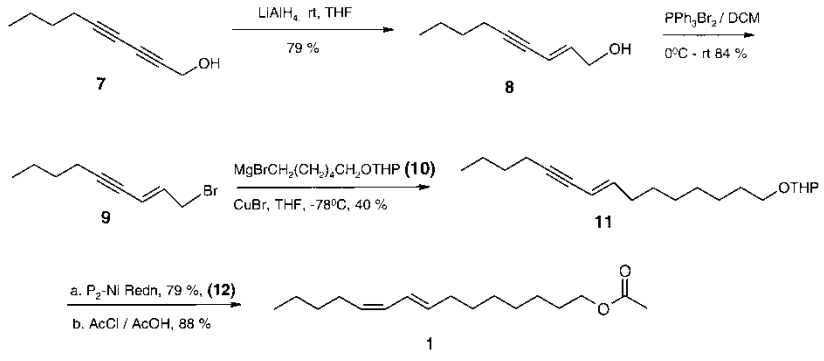
(*8E,10Z*)-Pentadecadien-1-ol acetate (**1**) is a major component of this composition. Lack of a good synthetic protocol to prepare compound (**1**) will limit its usage. Only two syntheses of **1** have been reported in the literature.[2,3] Both involve Wadsworth–Horner–Emmons and Wittig reactions respectively as the key steps to construct the olefin. However, these methods lack stereoselectivity and are lengthy.

RESULTS AND DISCUSSION

Herein, we wish to report a simple, concise, and highly selective synthetic strategy to prepare acetate **1** that utilizes the Cadiot–Chodkiewicz reaction[4] as the key step (Scheme 1). The Cadiot–Chodkiewicz reaction of 1-halogenoacetylenes with terminal acetylenes is a widely used protocol[4c] for the synthesis of asymmetrically disubstituted diacetylenes. This article delineates our synthetic strategy, which hinges on the Cadiot–Chodkiewicz reaction to assemble the required dialkynes, which then are preferentially converted to cis- and trans olefins. The Cadiot–Chodkiewicz coupling of 1-bromohexyne (**3**) with propargyl alcohol (**4**) is reported to furnish 2,4-nonadiyn-1-ol (**7**) in poor yield.[4f] We now report the synthesis of 2,4-nonadiyn-1-ol (**7**) in excellent yield, which is a marked improvement over the reported method. Thus, coupling 1-bromo-1-hexyne (**3**) with propargyl alcohol (**4**) or 3-bromoprop-2-yn-1-ol (**5**) and 1-hexyne (**6**) was



Scheme 1.



Scheme 2.

performed under modified Cadiot–Chodkiewicz conditions (Scheme 1). To achieve better yields, we changed the sequence of addition of reagents and varied molar quantities of reagents as well as the solvent. Under the optimized conditions, propargyl alcohol (**4**) was first treated with ethyl amine solution (70% w/w), then 1-bromo-1-hexyne (**3**) was added, and, lastly, CuCl. It was observed that freshly prepared CuCl, successively washed with glacial acetic acid, water, ethanol, and dry diethyl ether and then dried in vacuum was found to give the best results. Use of excess of ethyl-amine solution also was found to substantially increase the yield of coupling reaction. Thus as depicted in Scheme 1, we have significantly improved the yield in the coupling reaction.

The required (*8E*)-stereochemistry of the sex pheromone was obtained easily by selectively reducing one of the triple bonds with $LiAlH_4$[5] (Scheme 2). Trans geometry of the double bond was ascertained and confirmed by analysis of the ^1H NMR spectrum of (**8**).[6] Allyl alcohol (**8**) thus obtained was brominated with PPh_3Br_2[7] at 0°C to furnish (*2E*)-1-bromo-2-nonen-4-yne (**9**), which was then coupled with the Grignard reagent (**10**) catalyzed by Cu (I)[8] to get desired C_{15} skeleton (**11**).[9] The required (*10Z*) geometry was easily obtained by reducing the triple bond by P_2-Ni catalyst.[10] One-pot deprotection and protection with AcCl/AcOH led to the target molecule (**1**) in 88% yield (Scheme 2). Thus synthesis of (8E,10Z)-pentadecadien-1-ol acetate (**1**) was accomplished, starting from 1-bromo-1-hexyne (**3**) and propargyl alcohol (**4**), in 16% overall yield.

CONCLUSIONS

As compared to the methods reported in literature that involve Wittig reactions, lead to undesired isomers, and are lengthy, our protocol furnishes

the desired compound in a stereoseletive manner. Although the first step of our synthetic sequence is known, we have significantly improved the yield of 2,4-nonadiyn-1-ol (**7**). The chemistry utilized is operationally simple, effective, and efficient, and we believe that the sequence described here is a practical strategy for synthesis of (*8E, 10Z*)-pentadecadien-1-ol acetate (**1**).

EXPERIMENTAL

General Information

IR spectra were recorded on Matteson, UK, model, research series FT-IR. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 200 and MSL 300 spectrometers. The chemical shifts are reported in ppm (δ) using tetramethylsilane as internal standard. Mass spectra were recorded on a Finnigan MAT-1020-B-70 eV mass spectrometer. Propargyl alcohol and 1-hexyne were purchased from Aldrich Chemical Co. and used without further purification. 1-Bromo-1-hexyne (**3**) and 3-bromoprop-2-yn-1-ol (**5**) were prepared by the literature method.[11]

2,4-Nonadiyn-1-ol (7): To a stirred mixture of propargyl alcohol (**4**) (5.2 g, 92 mmol), ethyl amine (25 mL, aqueous solution, 70% w/w), and 1-bromo-1-hexyne (**3**) (13 g, 80 mmol) in MeOH (75 mL) in a round-bottomed flask, freshly prepared CuCl (170 mg, 1.7 mmol) was added. The reaction mixture turned yellowish green. At this point $NH_2OH.HCl$ ($\sim$1 g) was added, upon which the reaction mixture instantly turned yellow. The progress of the reaction was monitored by thin-layer chromatography. After completion, the reaction mixture was filtered through a short bed of celite. Methanol from the filtrate was removed on a rotary evaporator under reduced pressure. The residue was extracted with ethyl acetate (100 mL). The organic layer was washed with water (2 $\times$ 25 mL) and saturated brine solution (2 $\times$ 25 mL). The organic layer was dried over anhydrous sodium sulphate, filtered, and concentrated on a rotary evaporator to furnish crude diacetylene compound (**7**). Column chromatography on silica gel (60–120 mesh) (eluent: 10:90 ethyl acetate–petroleum ether) furnished 2,4-nonadiyn-1-ol (**7**) as a colorless liquid. Yield: 9.38 g (86%). 2,4-nonadiyn-1-ol (**7**) was also obtained by coupling 3-bromoprop-2-yn-1-ol (**4**) (6.80, 50 mmol) with 1-hexyne (**5**) (4.52 g, 55 mmol) under similar reaction conditions. Yield: 5.78 g (84%). IR ν_{max} ($CHCl_3$) cm^{-1}: 3540–3250 (broad band), 2933, 2867, 2254, 1458. ^{1}H NMR: ($CDCl_3$, 200 MHz) δ: 0.91 (t, 3H, $-CH_3$, J = 6 Hz), 1.35–1.62 (m, 4H), 2.08 (bs, –OH), 2.29 (t, 2H, $-C{\equiv}C-CH_2$, J = 6 Hz), 4.32 (s, 2H, $-CH_2OH$). ^{13}C NMR: ($CDCl_3$, 50 MHz) δ: 13.66 (q), 19.12 (t), 22.11 (t), 30.38 (t), 51.35 (t), 64.66 (s), 70.76 (s), 73.88 (s), 81.81 (s). Mass (m/z): 136 (M^+, 22), 121 (5), 117 (7), 107 (18), 91 (37), 77 (100), 65 (52).

(2*E*)- 2-Nonen-4-yn-1-ol (8): To $LiAlH_4$ (3.23 g, 85.2 mmol) covered with dry THF (10 mL), 2,4-nonadiyn-1-ol (**7**) (5.78 g, 42.6 mmol) in dry THF (25 mL) was added dropwise over 30 min. The reaction mixture was stirred at room temperature. The reaction was monitored by TLC. After completion (40 min), the reaction mixture was filtered through a short bed of celite. THF was removed on a rotary evaporator and the residue was extracted with diethyl ether. The organic layer was washed with 1N HCl (2×30 mL), water (2×30 mL water), brine (30 mL), dried over anhydrous sodium sulphate, filtered, and concentrated to give crude product. Column chromatography on silica gel (eluent: 8:92 ethyl acetate–petroleum ether) furnished (2*E*)- 2-nonen-4-yn-1-ol (**8**) as colorless oil. Yield: 4.62 g (79%). IR ν_{max}, ($CHCl_3$) cm^{-1}: 3540–3250 (broad band), 3010, 2954, 1626. ^1H NMR: ($CDCl_3$, 200 MHz) δ: 0.91 (t, 3H, $-CH_3$, J = 6 Hz), 1.35–1.62 (m, 4H), 2.01 (bs, –OH), 2.29 (t, 2H, $-C{\equiv}C-CH_2$, J = 6 Hz), 4.17 (d, 2H, $-C{=}C-CH_2-OH$, J = 8 Hz), 5.72 (ddt, 1H, $-C{\equiv}C-CH{=}CH-$, $J_1 = 16$ Hz, $J_2 = 4$ Hz, $J_3 = 2$ Hz), 6.15 (dt, 1H, $-CH{=}CH-CH_2$, $J_1 = 14$ Hz, $J_2 = 6$ Hz). ^{13}C NMR: ($CDCl_3$, 50 MHz) δ: 13.62 (q), 19.10 (t), 22.00 (t), 30.86 (t), 62.73 (t), 78.50 (s), 91.21 (s), 111.14 (d), 140.32 (d). Mass (m/z): 138 (M^+, 11), 123 (5), 109 (7), 95 (100), 81 (22), 67 (20). CHN analysis: $C_9H_{14}O$ calcd: C, 78.21%; H, 10.21%. Found: C, 77.92%; H, 10.46%.

(2*E*)-1-Bromo-2-nonen-4-yne (9): To an ice-cold stirred solution of PPh_3Br_2 (10.77 g, 24.7 mmol) in dry dichloromethane (35 mL), (*2E*)-2-nonen-4-yn-1-ol (**8**) (2.94 g, 21.3 mmol) in dry dichloromethane (15 mL) was added dropwise over 10 min. After stirring at the same temperature for 10 min, the reaction mixture was warmed to room temperature. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was diluted with ethyl acetate. The organic layer was washed with sodium thiosulphate (10% solution, 2×25 mL), water (3×30 mL), and brine (2×20 mL) and dried over anhydrous Na_2SO_4. The solvent, after filtration, was removed on a rotary evaporator to furnish crude allyl bromide. The crude product thus obtained was purified by column chromatography on silica gel (eluent: 4:96 ethyl acetate–petroleum ether) to get (*2E*)-1-bromo-2-nonen-4-yne (**9**) as a colorless liquid. Yield: 3.6 g (84%). IR ν_{max} ($CHCl_3$) cm^{-1}: 3020, 2954, 1626. ^1H NMR: ($CDCl_3$, 200 MHz) δ: 0.91 (t, 3H, $-CH_3$, J = 6 Hz), 1.35–1.61 (m, 4H), 2.29 (t, 2H, $C-C{\equiv}C-CH^2-$, J = 6 Hz), 3.97 (d, 2H, $-CH{=}CH-CH_2-Br$, J = 8 Hz), 5.72 (ddt, 1H, $-C{\equiv}C-CH{=}CH-$, $J_1 = 16$ Hz, $J_2 = 4$ Hz, $J_3 = 2$ Hz), 6.14 (dt, 1H, $-CH{=}CH-CH_2-$, $J_1 = 16$ Hz, $J_2 = 6$ Hz). ^{13}C NMR: ($CDCl_3$, 50 MHz) δ: 13.66 (q), 19.21 (t), 22.07 (t), 30.75 (t), 32.07 (t), 77.87 (s), 93.64 (s), 115.25 (d), 136.61 (d). Mass (m/z): 202 (M^+, 12), 200 ($M^+ - 2$, 12), 137 (14), 121 (70), 91 (65), 77 (100), 65 (22).

1-[(Tetrahydro-2H-pyran-2-yl)-oxy)-(*8E*)-pentadecadien-10-yne (11): Grignard reagent was prepared by refluxing Br-$(CH_2)_6$-OTHP (3.12 g,

11.85 mmol) prepared from 1,6-hexanediol with 47% HBr[12] followed by protection with 3,4-dihydro-2H-pyran [9] and Mg turnings (0.285 g, 11.85 mmol) in dry THF for 5 h with a catalytic amount of 1,2-dibromoethane under an inert atmosphere. The reaction mixture was cooled to room temperature and then gradually to -78°C. CuBr (41 mg, 0.27 mmol) was added followed by (*2E*)-1-bromo-2-nonen-4-yne (**9**) (0.518 g, 2.6 mmol) in THF (2 mL) dropwise over a 10-min period. The reaction mixture was stirred at -78°C for 2 h, slowly warmed to -40°C over a period of 30 min, and finally brought to room temperature and stirred for 2 h. The reaction was quenched with saturated NH_4Cl (1 mL) and extracted with ethyl acetate. The organic layer was washed with saturated NH_4Cl solution (2×1 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The title compound was purified by silver nitrate impregnated silica gel[13] (60–120 mesh) (eluent: 5:95 ethyl acetate–petroleum ether) to afford the title compound as a colorless liquid. Yield: 0.313 g (40%). IR: ν_{max} ($CHCl_3$) cm^{-1}: 3020, 2954, 1430, 1390, 1220. ^{1}H NMR: ($CDCl_3$, 200 MHz) δ: 0.91 (t, 3H, $-CH_3$, J = 6 Hz), 1.16–1.35 (m, 12H), 1.41–1.82 (m, 8H), 2.05 (q, 2H, J = 6 Hz), 2.28 (dt, 2H, $-C{\equiv}C-CH_2-$, $J_1 = 6$ Hz, $J_2 = 2$ Hz), 3.33–3.61 (m, 2H), 3.62–3.98 (m, 2H). 4.56 (t, 1H, J = 4 Hz), 5.44 (ddt, 1H, $-C{\equiv}C-CH = CH-$, $J_1 = 16$ Hz, $J_2 = 4$ Hz, $J_3 = 2$ Hz), 6.08 (dt, 1H, $-CH{=}CH-CH_2$-, $J_1 = 16$ Hz, $J_2 = 6$ Hz). **^{13}C NMR:** ($CDCl_3$, 50 MHz) δ: 13.66 (q), 19.21 (t), 19.83 (t), 22.15 (t), 25.79 (t), 26.37 (t), 29.02 (t), 29.20 (t), 29.46 (t), 29.94 (t), 31.01 (t), 31.19 (t), 33.06 (t), 62.39 (t), 67.69 (t), 79.45 (s), 88.68 (s), 98.93 (d), 110.29 (d), 143.08 (d). Mass (m/z): 306 (2), 288 (2), 263 (2), 191 (2), 171 (3), 135 (6), 119 (5), 85 (100), 67 (12), 56 (12). CHN analysis: $C_{20}H_{34}O_2$ calcd. C, 78.38%; H, 11.18%. Found: C, 78.62%; H, 11.32%.

1-[(Tetrahydro-2H-pyran-2-yl)-oxy]-(8*E*,10*Z*)-pentadecadiene (12): A two-necked round-bottomed flask (50 mL) was flushed with hydrogen. $Ni(OAc)_2 \cdot 4H_2O$ (204 mg) was dissolved in ethanol (8 mL), stirred at room temperature for 5 min, and again flushed with hydrogen. $NaBH_4$ (1M in ethanol, 0.5 mL) was added followed by ethylene diamine (3 drops). Immediately, the acetylenic compound (**11**) (300 mg) in ethanol (8 mL) was added and the resultant solution was stirred at room temperature. The progress of the reaction was monitored by TLC. After completion (30 min), the reaction mixture was filtered through short a bed of celite. Ethanol was removed and the residue was extracted with ethyl acetate. The organic layer was washed with water (10 mL) and then with brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuum. The diene thus obtained was purified by column chromatography silica gel (eluent: 2:98 ethyl acetate–pet. ether). Yield: 234 mg (79%). ^{1}H NMR: ($CDCl_3$, 200 MHz) δ: 0.91 (t, 3H, $-CH_3$, J = 6 Hz), 1.25–1.48 (m, 10H), 1.53–1.1.99 (m, 8H), 2.11–2.26 (m, 4H), 3.27–3.61 (m, 4H), 3.67–3.98 (m, 2H), 4.56 (t, 1H, J = 4 Hz), 5.29 (dt, 1H, $J_1 = 12$ Hz, $J_2 = 6$ Hz), 5.63

(dt, 1H, $J_1 = 15$ Hz, $J_2 = 6$ Hz), 5.93 (m, 1H), 6.23–6.39 (m, 1H). ^{13}C NMR: ($CDCl_3$, 50 MHz) δ: 13.66 (q), 19.37 (t), 22.00 (t), 25.23 (t), 25.90 (t), 27.09 (t), 28 86 (t), 29.05 (t), 29.44 (t), 30.48 (t), 31.61 (t), 32.56 (t), 61.95 (t), 67.32 (t), 98.48 (d), 125.31 (d), 128.30 (d), 129.67 (d), 132.22 (d). Mass (m/z): 308 (M^+, 4), 290 (5), 252 (4), 224 (4), 163 (4), 149 (6), 135 (8), 121 (8), 110 (12), 95 (10), 85 (100), 67 (15), 55 (8).

(8*E*,10*Z*)-Pentadecadien-1ol acetate (1): A mixture of diene (**12**) (225 mg, 0.72 mmol), acetyl chloride (87 mg, 1.08 mmol), and glacial acetic acid (1.5 mL) was stirred overnight at room temperature. The reaction mixture was poured on crushed ice and extracted with diethyl ether. The organic layer was washed with aqueous sodium bicarbonate (5%, 5 mL), water (5 mL), and brine (5 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuum. Column chromatography on silica gel (eluent 5:95 ethyl acetate–pet. ether) furnished the title compound. Yield: 180 mg (92%). IR ν_{max}: ($CHCl_3$) cm^{-1}: 3010, 2954, 1730, 1215,756. ^{1}H NMR: ($CDCl_3$, 200 MHz) δ: 0.91 (t, 3H, CH_3, J = 12 Hz, J = 6 Hz), 1.28–1.36 (m, 12 H), 1.63 (m, 2H), 2.03 (s, 3H), 2.03–2.16 (m, 4H), 4.05 (t, 2H, $-CH_2-O-COCH_3$, J = 6 Hz), 5.29 (dt, 1H, $J_1 = 12$ Hz, $J_2 = 6$ Hz), 5.63 (dt, 1H, $J_1 = 15$ Hz, $J_2 = 6$ Hz), 5.93 (m, 1H), 6.23–6.39 (m, 1H). ^{13}C NMR: ($CDCl_3$, 50 MHz) δ: 13.64 (q), 20.66 (q), 22.07 (t), 25.58 (t), 27.09 (t), 28.20 (t), 28.77 (t), 29.00 (t), 31.86 (t), 32.74 (t), 64.54 (t), 125.70 (d), 128.57 (d), 130.04 (d), 134.38 (d), 171.10 (s). Mass (m/z): 266 (M + , 22), 206 (12), 177 (5), 163 (7), 149 (13), 136 (25), 121 (50), 109 (69), 95 (100), 81 (60), 67 (40).

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REFERENCES

1. McDonough, L. M.; Averill, A. L.; Davis, H. G.; Smithhisler, C. L.; Murray, D. A. *J. Chem. Eco.* **1994**, *20* (12), 3269–3279.
2. McDonough, L. M.; Davis, H. G.; Smithhisler, C. L. US Patent 5,607,670, 1997.
3. Bestmann, H. J.; Joachim, S.; Otto, V. *Liebigs. Ann. Chem.* **1981**, 2117.
4. (a) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem. Int. Ed.* **2000**, *39* (15), 2633; (b) Ando, T.; Vu, M. H.; Yoshida, S.; Takahashi, N. *Agric. Biol. Chem.* **1982**, *46* (3), 717–722; (c) Rutledge, T. F. *Acetylenic Compounds*; Reinhold: New York, 1968; Chapter 6; (d) Cadiot, P.; Chodkiewicz, W. *Couplings of Acetylenes*; Viehe, H. G., Ed.; Marcel Dekker: New York, 1969;

(e) Brandsma, L. *Preparative Acetylene Chemistry*; Elsevier: Amsterdam, 1971; (f) Barbu, E.; Tsibouklis, J. *Tetrahedron Lett.* **1996**, *37* (28), 5023.
5. (a) Rossi, R.; Carpita, A. *Synthesis* **1977**, 561; (b) Solladie, G.; Berl, V. *Tetrahedron. Lett.* **1992**, *33* (24), 3477.
6. Aerssens, M. H. P. J.; van der Heiden, R.; Heus, M.; Brandsma, L. *Synth. Commun.* **1990**, *20* (22), 3421.
7. (a) Machinek, R.; Luttke, W. *Synthesis* **1975**, 255; (b) Sandri, J.; Viala, J. *Synth. Commun.* **1992**, *22* (20), 2945; (c) Buser, H. R.; Guerin, P. M.; Toth, M.; Szocs, G.; Schmid, A.; Francke, W.; Arn, H. *Tetrahedron Lett.* **1985**, *26*, 403; (d) Sonnet, P. E.; Oliver, J. E. *J. Org. Chem.* **1976**, *41* (20), 3279; (e) Anderson, A. G., Jr.; Freenor, F. *J. Org. Chem.* **1972**, *37* (4), 626.
8. (a) Mechelke, M. F.; Wiemer, D. F. *J. Org. Chem.* **1999**, *64*, 4821; (b) Yamamoto, A.; Fukumoto, T. *Agric. Biol. Chem.* **1989**, *53* (4), 1183; (c) Normant, J. F.; Commercon, A.; Gendreau, Y.; Bourgain, M.; Villieras, J. *Bull. Soc. Chim. Fr.* **1979**, 309; (d) Normant, J. F.; Commercon, A.; Bourgain, M.; Villieras, J. *Tetrahedron Lett.* **1975**, *44*, 3833; (e) Commercon, A.; Bourgain, M.; Delaumeny, M.; Normant, J. F.; Villieras, J. *Tetrahedron Lett.* **1975**, 3837; (f) Katzenellenbogen, J. A.; Corey, E. J. *J. Org. Chem.* **1972**, *37*, 1441; (g) Claesson, A.; Tamnefors, I.; Olsson, L.-I. *Tetrahedron Lett.* **1975**, 1509.
9. Bernady, K. F.; Floyd, M. B.; Poletto, J. F.; Weiss, M. J. *J. Org. Chem.* **1979**, *44* (9), 1438.
10. (a) Brown, C. A.; Ahuja, V. K. *J. Chem. Soc. Chem. Comm.* **1973**, 553; (b) Brown, H. C.; Brown, C. A. *J. Am. Chem. Soc.* **1963**, *53*, 1005; (c) Brown, C. A.; Brown, H. C. *J. Am. Chem. Soc.* **1963**, *53*, 1003.
11. Brandsma, L.; Verkruijsse, H. D. *Synthesis* **1990**, 984.
12. Kang, S.-K.; Kim, W.-S.; Moon, B.-H. *Synthesis* **1985**, 1161.
13. Williams, C. M.; Mander, L. N. *Tetrahedron* **2001**, *57* (3), 425 (and references cited therein).