Reaction of *N*-Aziridinylimines with Alkynylborane Reagents. A New Route to Allenes from Aldehydes and Ketones

Sunggak Kim,* Chang Mook Cho, and Joo-Yong Yoon

Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea

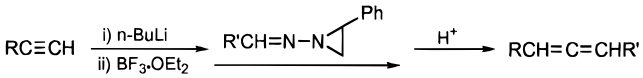
Received February 22, 1996

Nucleophilic addition of organometallic reagents to imines is synthetically useful[1] but somewhat difficult to achieve due to both the poor reactivity of imines as electrophilic acceptors and the tendency of easy enolization of imines by organometallic reagents such as Grignard reagents and organolithiums.[2] These problems have been solved by employing activated imine derivatives[3] and/or by the use of less basic reagents such as allylboranes,[4] allylstannanes,[5] organocopper reagents,[6] and organocerium reagents.[7]

Since Eschenmoser reported that *N*-aziridinylimines of α,*β*-epoxy ketones underwent thermal fragmentation,[8] *N*-aziridinylimines have been widely utilized as precursors of not only diazoalkanes[9] and carbenes[10] but also vinyl anions in Shapiro elimination.[11] In connection with our research interest in the synthetic utility of *N*-aziridinylimines, we reported the use of *N*-aziridinylimines in radical cyclizations[12] and in the generation of alkylidene carbenes.[13] We next have studied the feasibility of adding nucleophiles onto *N*-aziridinylimines and subsequent consecutive *β*-elimination to afford reductively alkylated anions as shown in Scheme 1. Initial studies were performed with alkynyllithium reagents. When (phenylethynyl)lithium was added to hydrocinnamaldehyde *N*-aziridinylimine (**2**), it failed to undergo addition onto the *N*-aziridinylimine and the starting material was recovered. Furthermore, alkynyl Grignard reagents, alkynylcuprates, and alkynylcerium reagents were also unsuccessful. We next turned our attention to the possibility of using alkynylborane reagents, known to be very effective for additions to aldimines by Akiba.[14] Alkynylborane reagents were prepared *in situ* from equimolar amounts of alkynyllithium reagent and boron trifluoride etherate. When an equimolar amount of (phenylethynyl)borane (**1a** or **1b**) was added to compound **2**, allene **5** was obtained in 55% yield. The use of 2 and 3 equiv of alkynylborane reagent gave better results, yielding allene **5** in 68% and 82% yield, respectively (Scheme 2). Thus, the remaining reactions were carried out with 3 equiv of alkynylborane reagents for each mole of *N*-aziridinylimines.

Table 1 summarizes the experimental results and illustrates the efficiency and scope of the present method. *N*-Aziridinylimines of aldehydes having α-hydrogens

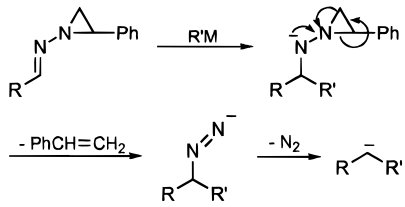
Table 1. Synthesis of Allenes from *N*-Aziridinylimines and Alkynylboranes[a]



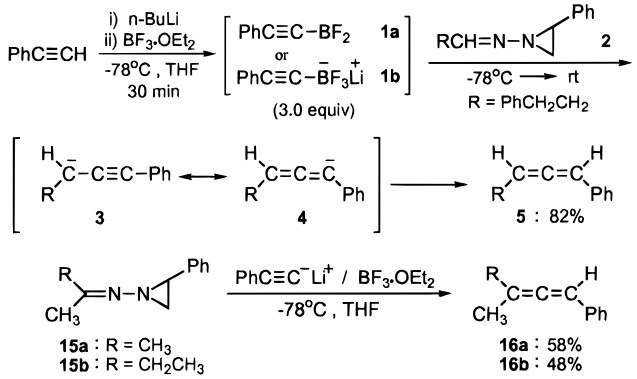
entry	R	R'	product		yield, %[b]
1	Ph	$PhCH_2CH_2$	$PhCH{=}C{=}CHCH_2CH_2Ph$	**5**	82
2	$CH_3(CH_2)_3$	$PhCH_2CH_2$	$CH_3(CH_2)_3CH{=}C{=}CHCH_2CH_2Ph$	**6**	78
3	$(CH_3)_3Si$	$PhCH_2CH_2$	$(CH_3)_3SiCH{=}C{=}CHCH_2CH_2Ph$	**7**	72
4	$(CH_3)_3Si$	$PhCH_2$	$(CH_3)_3SiCH{=}C{=}CHCH_2Ph$	**8**	62
5	$CH_3(CH_2)_3$	PhCH=CH	$CH_3(CH_2)_3CH{=}C{=}CHCH{=}CHPh$	**9**	83
6	Ph	CH_3CH=CH	$PhCH{=}C{=}CHCH{=}CHCH_3$	**10**	69
7	Ph	$(CH_3)_2CH$	$PhCH{=}C{=}CHCH(CH_3)_2$	**11**	52
8	$CH_3(CH_2)_3$		$CH_3(CH_2)_3CH{=}C{=}CH$	**12**	69
9	Ph	$(CH_3)_3C$	$PhCH{=}C{=}CHC(CH_3)_3$	**13**	17
10		$PhCH_2CH_2$		**14**	42

[a] All reactions were conducted according to the standard procedure. [b] The yield refers to the isolated yield by column chromatography.

Scheme 1



Scheme 2



(1) Volkmann, R. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 1, Chapter 1.12.

(2) (a) Stork, G.; Dowd, S. R. *J. Am. Chem. Soc.* **1963**, *85*, 2178. (b) Meyers, A. I.; Williams, D. R.; Druelinger, M. *J. Am. Chem. Soc.* **1976**, *98*, 3032. (c) Whitesell, J. K.; Whitesell, M. A. *J. Org. Chem.* **1977**, *42*, 377. (d) Alexakis, A.; Lensen, N.; Tranchier, J. P.; Mangeney, P. *J. Org. Chem.* **1992**, *57*, 4563.

(3) (a) Speckamp, W. N.; Hiemstra, H. *Tetrahedron* **1985**, *41*, 4367. (b) Davis, F. A.; Giangiordano, M. A.; Starner, W. E. *Tetrahedron Lett.* **1986**, *27*, 3957.

(4) (a) Yamamoto, Y.; Komatsu, T.; Maruyama, K. *J. Am. Chem. Soc.* **1984**, *106*, 5031. (b) Yamamoto, Y.; Nishii, S.; Maruyama, K.; Komatsu, T.; Ito, W. *J. Am. Chem. Soc.* **1986**, *108*, 7778.

(5) Keck, G. E.; Enholm, E. J. *J. Org. Chem.* **1985**, *50*, 146.

(6) (a) Bertz, S. H. *Tetrahedron Lett.* **1980**, *21*, 3151. (b) Wada, M.; Sakurai, Y.; Akiba, K. *Tetrahedron Lett.* **1984**, *25*, 1079.

(7) Denmark, S. E.; Weber, T.; Piotrowski, D. W. *J. Am. Chem. Soc.* **1987**, *109*, 2224.

(8) Felix, D.; Mueller, R. K.; Horn, U.; Joos, R.; Schreiber, J.; Eschenmoser, A. *Helv. Chim. Acta* **1972**, *55*, 1276.

(9) (a) Padwa, A.; Ku, H. *J. Org. Chem.* **1980**, *45*, 3756. (b) Schultz, A. G.; Dittami, J. P.; Eng, K. K. *Tetrahedron Lett.* **1984**, *25*, 1255. (c) Jones, G. B.; Moody, C. J.; Padwa, A.; Kassir, J. M. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1721.

(10) (a) Padwa, A.; Gareau, Y.; Xu, S. L. *Tetrahedron Lett.* **1991**, *32*, 983. (b) Padwa, A.; Austin, D. J.; Gareau, Y.; Kassir, J. M.; Xu, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2637. (c) Kim, S.; Cho, C. M. *Heterocycles* **1994**, *38*, 1971.

(11) Evans, D. A.; Nelson, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 774.

(12) (a) Kim, S.; Kee, I. S.; Lee, S. *J. Am. Chem. Soc.* **1991**, *113*, 9882. (b) Kim, S.; Kee, I. S. *Tetrahedron Lett.* **1993**, *34*, 4213.

(13) (a) Kim, S.; Cho, C. M. *Tetrahedron Lett.* **1994**, *35*, 8405. (b) Kim, S.; Cho, C. M. *Tetrahedron Lett.* **1995**, *36*, 4845.

(14) Wada, M.; Sakurai, Y.; Akiba, K. *Tetrahedron Lett.* **1984**, *25*, 1083.

S0022-3263(96)00370-2 CCC: $12.00

reacted readily and gave a good yield of allenes (Table 1, entries 1−4). The selective 1,2-addition of alkynylborane reagents to α,β-unsaturated *N*-aziridinylimines (Table 1, entries 5 and 6) was observed. It is of interest to note that the phenylthio group did not undergo elimination under the reaction conditions (Table 1, entry 8). The present method reaches a limit with *N*-aziridinylimine derived from sterically hindered trimethylacetaldehyde (Table 1, entry 9). When (phenylethynyl)borane was added to the *N*-aziridinylimine of trimethylacetaldehyde under the same conditions, the desired product was obtained in only 17% yield. Furthermore, we have examined the reaction of (phenylethynyl)borane with *N*-aziridinylimines of ketones (**15a** and **15b**), and the reaction afforded the desired allenes (**16a** and **16b**) in moderate yield (Scheme 2).

In summary, addition of alkynylborane reagents to *N*-aziridinylimines is a new, useful route to prepare various allenes from carbonyl compounds. Although various synthetic methods are available for allene synthesis,[15] the present method complements the existing synthetic methods.

Experimental Section

Typical Procedure for Synthesis of Allene 5. To a solution of phenylacetylene (61 mg, 0.6 mmol) in THF (2 mL) was slowly added *n*-butyllithium in *n*-hexane (2.5 M, 0.6 mmol) at −78 °C under nitrogen with stirring. After being stirred for 30 min, $BF_3{\cdot}OEt_2$ (74 μL, 0.6 mmol) was added to the solution, and the mixture was stirred for 10 min to prepare (phenylethynyl)borane. The *N*-aziridinylimine (51 mg, 0.2 mmol) of hydrocinnamaldehyde in THF (1.0 mL) was then added, and the reaction mixture was stirred for 20 min at −78 °C and for 2 h at room temperature. The resulting mixture was diluted with ether (20 mL) and treated with 10% aqueous NaOH solution. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate: *n*-hexane = 1:50) to afford 1,5-diphenyl-1,2-pentadiene (**5**) (36 mg) in 82% yield.

1,5-Diphenyl-1,2-pentadiene (5): ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.44−2.56 (m, 2H), 2.81−2.89 (m, 2H), 5.62 (q, 1H, *J* = 6.56 Hz), 6.13−6.19 (m, 1H), 7.16−7.37 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 30.5, 35.4, 94.3, 95.0, 125.9, 126.6, 126.7, 128.3, 128.5, 128.6, 134.8, 141.5, 205.3; IR (film) 1948 cm^{-1}; MS (EI/70 eV) *m/e* 220 $[M]^+$, 129 (100), 128, 115, 91; HRMS $[M]^+$ calcd for $C_{17}H_{16}$ 220.3140, found 220.3128. Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.34; H, 7.37.

1-Phenyl-3,4-nonadiene (6): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.81 (t, 3H, *J* = 7.00 Hz), 1.22−1.31 (m, 4H), 1.84−1.89 (m, 2H), 2.18−2.27 (m, 2H), 2.65 (t, 2H, *J* = 7.74 Hz), 4.99−5.06 (m, 2H), 7.09−7.21 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.8, 22.1, 28.5, 30.7, 31.3, 35.5, 90.2, 91.5, 125.7, 128.2, 128.5, 141.9, 204.0; IR (film) 1961 cm^{-1}; MS (EI/70 eV) *m/e* 200 $[M]^+$, 109 (100), 108, 95, 91. Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.01; H, 9.82.

1-(Trimethylsilyl)-5-phenyl-1,2-pentadiene (7): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.08 (s, 9H), 2.25−2.32 (m, 2H), 2.70 (t, 2H, *J* = 7.30 Hz), 4.80−4.94 (m, 2H), 7.17−7.27 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.0, 29.7, 36.0, 82.8, 83.0, 125.7, 128.2, 128.4, 141.9, 209.8; IR (film) 1938 cm^{-1} ; MS (EI/70 eV) *m/e* 216 $[M]^+$, 143, 125 (100), 124, 111, 91. Anal. Calcd for $C_{14}H_{20}Si$: C, 77.70; H, 9.32. Found: C, 77.29; H, 9.17.

1-(Trimethylsilyl)-4-phenyl-1,2-butadiene (8): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.06 (s, 9H), 3.30 (t, 2H, *J* = 5.46 Hz), 4.90−4.98 (m, 2H), 7.15−7.32 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.9, 34.6, 83.1 (2C), 126.0, 128.2, 128.4, 140.9, 210.1; IR (film) 1938 cm^{-1}. Anal. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97. Found: C, 76.94; H, 9.11.

1-Phenyl-1,3,4-nonatriene (9): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.93 (t, 3H, *J* = 7.04 Hz), 1.25−1.49 (m, 4H), 2.01−2.14 (m, 2H), 5.40 (q, 1H, *J* = 6.52 Hz), 5.91−6.05 (m, 1H), 6.48−6.65 (m, 2H), 7.19−7.41 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.8, 22.1, 28.4, 31.2, 92.6, 94.6, 113.7, 125.6, 126.1, 127.1, 127.7, 128.5, 129.7, 137.4, 208.2; IR (film) 1940 cm^{-1}. Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.27; H, 9.69.

1-Phenyl-1,2,4-hexatriene (10): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.78 (d, 3H, *J* = 6.00 Hz), 5.69−5.99 (m, 2H), 6.17−6.33 (m, 2H), 7.15−7.44 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.1, 95.7, 97.7, 125.5, 126.8, 126.9, 128.2, 128.8, 131.4, 208.2; IR (film) 1940 cm^{-1}. Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 91.97; H, 7.69.

5-Methyl-1-phenyl-1,2-pentadiene (11): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.08 (d, 3H, *J* = 6.80 Hz), 1.09 (d, 3H, *J* = 6.81 Hz), 2.38−2.48 (m, 1H), 5.58 (t, 1H, *J* = 6.14 Hz), 6.14−6.19 (m, 1H), 7.13−7.30 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.5, 22.6, 28.3, 95.6, 102.4, 126.4, 126.6, 128.5, 135.2, 203.6; IR (film) 1946 cm^{-1}. Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.01; H, 8.86.

1-Phenyl-2-(phenylthio)-3,4-nonadiene (12): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.80 (t, 3H, *J* = 6.82 Hz), 1.06−1.24 (m, 4H), 1.61−1.75 (m, 2H), 2.82−3.09 (m, 2H), 3.70−3.93 (m, 1H), 4.91−5.11 (m, 2H), 7.16−7.42 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.8, 22.0, 28.1, 30.9, 41.1, 50.1, 92.4, 93.0, 126.3, 126.9, 128.1, 128.4, 128.6, 129.2, 132.6, 134.7, 138.9, 204.3; IR (film) 1961 cm^{-1}. Anal. Calcd for $C_{21}H_{24}$: C, 81.76; H, 7.84. Found: C, 81.83; H, 7.90.

1-Phenyl-4,4-dimethyl-1,2-pentadiene[16] (13): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.11 (s, 9H), 5.55 (d, 1H, *J* = 6.4 Hz), 6.17 (d, 1H, *J* = 6.4 Hz), 7.23−7.28 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 28.8, 34.5, 89.6, 94.0, 125.6, 127.1, 128.5, 137.4, 205.2; IR (film) 1947 cm^{-1}.

1-(1,3-Dithianyl)-6-phenyl-2,3-hexadiene (14): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.71−1.91 (m, 1H), 2.04−2.15 (m, 1H), 2.28−2.43 (m, 4H), 2.73 (t, 2H, *J* = 7.54 Hz), 2.80−2.86 (m, 4H), 4.02 (t, 1H, *J* = 6.87 Hz), 5.12−5.20 (m, 2H), 7.15−7.30 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.8, 30.2, 30.3, 35.3, 35.4, 47.3, 87.3, 91.1, 125.8, 128.2, 128.5, 138.2, 204.9; IR (film) 1942 cm^{-1}. Anal. Calcd for $C_{16}H_{20}S_2$: C, 69.51; H, 7.29. Found: C, 69.19; H, 7.43.

Procedure for Synthesis of *N*-Aziridinylimine (15b). To a stirred methanol solution of 2-butanone (180 μL, 2.0 mmol) was added *N*-amino-2-phenylaziridine (2.2 mL, 2.2 mmol, 1.0 M solution in methanol) at 0 °C. After being stirred for 1 h at room temperature, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate:*n*-hexane = 1:5) to afford 316 mg (1.68 mmol, 84%) of **15b** as a 4.5:1 mixture of *E*- and *Z*-isomers.

Isopropylidene(2-phenylaziridin-1-yl)amine (15a): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.90 (s, 3H), 1.97 (s, 3H), 2.23 (d, 1H, *J* = 4.6 Hz), 2.35 (d, 1H, *J* = 7.5 Hz), 2.81 (dd, 1H, *J* = 4.5, 7.5 Hz), 7.19−7.35 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.6, 24.6, 40.3, 43.3, 125.9, 126.8, 128.0, 138.8, 166.6; IR (film) 1645, 1606, 1497, 1446, 1366, 699 cm^{-1}; MS (EI/70 eV) *m/e* 175 $[M]^+$, 104, 91, 78, 70 (100), 42, 41. Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.29; H, 8.21; N, 16.06.

(1-Methylpropylidene)(2-phenylaziridin-1-yl)amine (15b): *E*:*Z* = 4.5:1 (^{1}H NMR ratio); ^{1}H NMR (200 MHz, $CDCl_3$) *E* δ 1.06 (t, 3H, *J* = 7.4 Hz), 1.95 (s, 3H), 2.20 (q, 2H, *J* = 7.6 Hz), 2.25 (d, 1H, *J* = 4.5 Hz), 2.37 (d, 1H, *J* = 7.6 Hz), 2.80 (dd, 1H, *J* = 4.6, 7.5 Hz), 7.17−7.34 (m, 5H); *Z* δ 1.02 (t, 3H, *J* = 7.4 Hz), 1.89 (s, 3H), 2.25 (d, 1H, *J* = 4.5 Hz), 2.37 (d, 1H, *J* = 7.6 Hz), 2.51 (q, 2H, *J* = 7.6 Hz), 2.80 (dd, 1H, *J* = 4.6, 7.5 Hz), 7.17−7.34 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) *E*: δ 10.9, 17.0, 31.6, 40.6, 43.5, 126.0, 126.8, 128.1, 139.0, 170.6; *Z* δ 10.2, 22.1, 25.4, 40.6, 43.5, 126.0, 126.8, 128.1, 139.0, 170.6; IR (film) 1639, 1606,

(15) (a) Baldwin, J. E.; Adlington, R. M.; Crouch, N. P.; Hill, R. L.; Laffey, T. G. *Tetrahedron Lett.* **1995**, *36*, 7925. (b) Mikami, K.; Yoshida, A.; Matsumoto, S.; Feng, F.; Matsumoto, Y. *Tetrahedron Lett.* **1995**, *36*, 907. (c) Bailey, W. F.; Aspris, P. H. *J. Org. Chem.* **1995**, *60*, 754. (d) Reynolds, K. A.; Dopico, P. G.; Sundermann, M. J.; Hughes, K. A.; Finn, M. G. *J. Org. Chem.* **1993**, *58*, 1298. (e) Danheiser, R. L.; Choi, Y. M.; Menichincheri, M.; Stoner, E. J. *J. Org. Chem.* **1993**, *58*, 322. (f) Nantz, M. H.; Bender, D. M.; Janaki, S. *Synthesis* **1993**, 577. (g) Block, E.; Putman, D. *J. Am. Chem. Soc.* **1990**, *112*, 4072. (h) Reviews on the synthesis and reactions of allenes : Shuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; Wiley: New York, 1984. Pasto, D. J. *Tetrahedron* **1984**, *40*, 2805. Smadja, W. *Chem. Rev.* **1983**, *83*, 263.

(16) Caporusso, A. M.; Polizzi, C.; Lardicci, L. *J. Org. Chem.* **1987**, *52*, 3920.

1497, 1458, 1371, 698 cm^{-1} ; MS (EI/70 eV) *m/e* 189 $[M]^+$, 104, 91, 84 (100), 78, 56, 41. Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.30; H, 8.50; N, 15.06.

1-Phenyl-3-methyl-1,2-butadiene (16a): ^1H NMR (200 MHz, $CDCl_3$) δ 1.75 (s, 3H), 1.77 (s, 3H), 5.89−5.95 (m, 1H), 7.08−7.28 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.7, 21.0, 91.7, 96.1, 126.6, 128.5, 135.0, 208.0; IR (film) 1954 cm^{-1}. Anal. Calcd for $C_{11}H_{12}$: C, 91.62; H, 8.38. Found: C, 90.80; H, 8.16.

1-Phenyl-3-methyl-1,2-pentadiene[16] (16b): ^1H NMR (200 MHz, $CDCl_3$) δ 1.06 (t, 3H, J = 7.2 Hz), 1.80 (d, 3H, J = 3.0 Hz), 2.08 (dq, 2H, J = 7.2, 3.0 Hz), 6.05 (m, 1H), 7.17−7.25 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 19.3, 26.7, 92.3, 97.5, 125.7, 128.3, 128.5, 135.7, 207.6; IR (film) 1950 cm^{-1}.

Acknowledgment. We thank the Organic Chemistry Research Center and Korea Advanced Institute of Science and Technology for financial support of our research program.

Registry nos. provided by the author: 13, 109279-80-3; **16b**, 109182-91-4.

JO960370Z