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# Stereoselective Synthesis of (Z)- $\alpha$ , $\beta$ -Unsaturated Ketones via Hydromagnesiation of Alkynylsilanes

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#### ABSTRACT

Hydromagnesiation of alkynylsilanes **1** gives (Z)- $\alpha$ -silylvinyl Grignard reagents **2**, which are treated with alkyl iodides in the presence of CuI to give (Z)-1,2-disubstituted vinylsilanes **3** in high yields. Intermediates **3** can undergo the Friedel–Crafts acylation reactions with acyl chlorides to afford (Z)- $\alpha$ , $\beta$ -unsaturated ketones in good yields with high stereoselectivity.

 $\alpha$ , $\beta$ -Unsaturated ketones are important synthetic intermediates because of their versatile reactivities and many synthetic applications of them have been reported in the literature.<sup>[1]</sup> The great synthetic value of these  $\alpha$ , $\beta$ -unsaturated ketones derives from the fact that the positions  $\alpha$ ,  $\beta$ and  $\gamma$  to the carbonyl groups can be activated and functionalized by

1643

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1644

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Zhao and Cai

various means. A number of methods can be used for the stereoselective synthesis of (E)- $\alpha$ , $\beta$ -unsaturated ketones, such as the condensation reactions of dibutyl telluride with  $\alpha$ -halogenated ketones and aromatic aldehydes,<sup>[2]</sup> by the palladium catalyzed stepwise cross-coupling reactions of (E)-(2-bromoethenyl) diisopropoxyborane with  $\alpha$ -alkoxyalkenylzinc chlorides and organic halides,<sup>[3]</sup> by the conjugate addition of sulfonyl carbanions to nitroalkenes followed by ozonolysis and then the elimination of sulfinic acid,<sup>[4]</sup> by CeCl<sub>3</sub> mediated addition of Grignard reagents to  $\beta$ -enamino ketones,<sup>[5]</sup> and Nickel(0)-catalyzed hydroacylation of alkynes with aldehydes.<sup>[6]</sup> However, only a few methods for the synthesis of (Z)- $\alpha$ , $\beta$ -unsaturated ketones are available. The palladium catalyzed coupling reactions of alkenyl copper reagents with acid chlorides afforded (Z)- $\alpha$ , $\beta$ -unsaturated ketones.<sup>[7]</sup>

The phase transfer catalyzed hydroacylation of allenes with carbon monoxide, decacarbonyldimanganese and methyl iodide gave (Z)- $\alpha$ , $\beta$ -unsaturated ketones in a stereospecific process.<sup>[8]</sup>

Hydromagnesiation has emerged as a unique hydrometallation with some attractive features, such as the high regioselectivity and stereo-selectivity observed with alkynylsilanes.<sup>[9,10]</sup> We now wish to report that (Z)- $\alpha$ , $\beta$ -unsaturated ketones could be conveniently synthesized by hydromagnesiation of alkynylsilanes, followed by treatment with alkyl iodide and then the Friedel–Crafts acylation (Sch. 1).

Alkynylsilanes were easily prepared according to the literature procedure.<sup>[11]</sup> Hydromagnesiation of alkynylsilanes 1 at 25°C in ether for 6 h afforded (Z)- $\alpha$ -silylvinyl Grignard reagents 2, which were treated with methyl iodide at room temperature to give (Z)-1,2-disubstituted vinylsilanes 3 in high yields. The intermediates 2 was found to present low reactivity with alkyl halides other than methyl iodide, however, it was readily alkylated by alkyl iodides in the presence of 10 mol% CuI to



Scheme 1.

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Stereoselective Sy	vnthesis o	of $(Z)$ - $\alpha$ .	<b>B</b> -Unsaturated	Ketones
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1645

Entry	R	$R^1$	Catalyst	Product <sup>a</sup>	Yield <sup>b</sup> (%)
1	$n-C_4H_9$	CH <sub>3</sub>		3a	91
2	$n-C_4H_9$	$n-C_4H_9$	CuI	3b	86
3	$i-C_5H_{11}$	$CH_3$		3c	88
4	$i-C_5H_{11}$	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	CuI	3d	87
5	$n - C_6 H_{13}$	$CH_3$		3e	89
6	$n-C_{6}H_{13}$	n-C <sub>4</sub> H <sub>9</sub>	CuI	3f	85

*Table 1.* Synthesis of (Z)-1,2-disubstituted vinylsilanes 3.

<sup>a</sup>All compounds were characterized by <sup>1</sup>H NMR, IR and elemental analyses. <sup>b</sup>Isolated yield based on the alkynylsilane used.

afford (*Z*)-1,2-disubstituted vinylsilanes **3** in good yields. The typical results are summarized in Table 1. Investigation of the crude products **3** by <sup>1</sup>H NMR spectroscopy (300 MHz) showed isomeric purities of more than 96%. The olefinic proton signal of **3** characteristically splits into a triplet with coupling constant J = 7.0 Hz, which indicated that the hydromagnesiation of alkynylsilanes had taken place with strong preference for the addition of the magnesium atom at the carbon bearing the alkylsilyl group. Since the configuration of the intermediates **2** was known<sup>[9]</sup> and the coupling reaction of intermediates **2** with alkyl iodides occurs with retentive configuration, the configuration of products **3** can be defined.

Vinylsilanes are important synthetic intermediates because of the versatile reactivity of the silvl group and the carbon-carbon double bond.<sup>[12]</sup> (Z)-1,2-Disubstituted vinylsilanes 3 are also effective precursors for preparing (Z)- $\alpha$ , $\beta$ -unsaturated ketones. They can easily undergo the Friedel-Crafts acylation with acyl chlorides with retention of configuration providing a convenient route to (Z)- $\alpha$ , $\beta$ -unsaturated ketones. Thus, the Friedel–Crafts acylation of compounds 3 with acyl chlorides at 0°C in methylene chloride for 1 h afforded (Z)- $\alpha$ ,  $\beta$ -unsaturated ketones 4 in good yields with high stereoselectivity. Both aliphatic and aromatic acid chlorides could be used as the acylating agents. The experimental results are summarized in Table 2. While the geometries of products 4 were not rigorously established, a reasonable assumption is made that the Friedel-Crafts acylation reaction proceeds stereospecifically with complete retention of configuration.<sup>[13]</sup> The chemical shifts of the vinylic protons for 4a-l are in the range of 5.29-5.60 ppm, which is consistent with the (Z)-configuration of products  $4^{[14]}$ 

In summary, compared to other methods that have been reported,<sup>[7,8]</sup> the present method for the stereoselective synthesis of (Z)- $\alpha$ , $\beta$ -unsaturated ketones has the advantages of readily available starting



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#### 1646

#### Zhao and Cai

Entry	R	$R^1$	$R^2$	Product <sup>a</sup>	Yield <sup>b</sup> (%)
1	$n-C_4H_9$	CH <sub>3</sub>	CH <sub>3</sub>	<b>4</b> a	74
2	$n-C_4H_9$	CH <sub>3</sub>	Ph	<b>4</b> b	81
3	$n-C_4H_9$	$n-C_4H_9$	$CH_3$	4c	68
4	$n-C_4H_9$	$n-C_4H_9$	$4-ClC_6H_4$	<b>4</b> d	80
5	$i-C_5H_{11}$	CH <sub>3</sub>	CH <sub>3</sub>	<b>4</b> e	74
6	$i-C_5H_{11}$	$CH_3$	Ph	<b>4</b> f	76
7	$i-C_5H_{11}$	$n-C_4H_9$	CH <sub>3</sub>	<b>4</b> g	83
8	$i-C_5H_{11}$	$n-C_4H_9$	Ph	4 <b>h</b>	81
9	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	$CH_3$	<b>4i</b>	75
10	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	$CH_3$	$4-ClC_6H_4$	4j	69
11	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	$n-C_4H_9$	CH <sub>3</sub>	4k	71
12	$n - C_6 H_{13}$	$n-C_4H_9$	Ph	41	77

*Table 2.* Synthesis of (Z)- $\alpha$ , $\beta$ -unsaturated ketones 4.

<sup>a</sup>All compounds were characterized using <sup>1</sup>H NMR, IR, and elemental analyses. <sup>b</sup>Isolated yield based on the (Z)-1,2-disubstituted vinylsilane used.

materials, straightforward, simple procedures, mild reaction conditions, and high yields.

### **EXPERIMENTAL**

<sup>1</sup>H NMR spectra were recorded on an AZ-300 MHz spectrometer with TMS as an internal standard in CDCl<sub>3</sub> as solvent. IR spectra were obtained by use of neat capillary cells on a Shimadzu IR-435 instrument. Microanalyses were performed on Vario EL and Perkin-Elmer CHN 2400. All solvents were dried, deoxygenated and freshly distilled before use.

## General Procedure for the Synthesis of (*Z*)-1,2-Disubstituted Vinylsilanes 3a, 3c, and 3e

To a solution of isobutylmagnesium bromide (4.5 mmol) in diethyl ether (7 mL) was added  $Cp_2TiCl_2$  (50 mg, 0.2 mmol) at 0°C under Ar, and the mixture was stirred for 30 min at that temperature. To this solution was added alkynylsilane **1** (4.0 mmol), and the mixture was stirred for 6 h at 25°C. After removal of the ether under reduced pressure (2 h, r.t./2 torr), the residue was dissolved in THF (6 mL) and treated with methyl iodide (0.71 g, 5 mmol) at 0°C for 10 min and then at room

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#### Stereoselective Synthesis of (Z)- $\alpha$ , $\beta$ -Unsaturated Ketones

1647

temperature for 2h. The resulting mixture was treated with sat. aq. NH<sub>4</sub>Cl (25 mL) and extracted with Et<sub>2</sub>O ( $2 \times 30$  mL). The ethereal solution was washed with water ( $3 \times 30$  mL) and dried (MgSO<sub>4</sub>). Removal of solvent under reduced pressure gave an oil which was purified by column chromatography on silica gel using light petroleum as eluent.

**3a:**  $\delta_{\rm H}$  0.11 (s, 9H), 0.90 (t, 3H, J = 5.4 Hz), 1.08–1.60 (m, 4H), 1.74 (s, 3H), 1.85–2.40 (m, 2H), 5.84 (t, 1H, J = 7.0 Hz) ppm;  $\nu_{\rm max}$  2958, 2860, 1620, 1466, 1249, 838 cm<sup>-1</sup>; Anal. calcd. for C<sub>10</sub>H<sub>22</sub>Si: C, 70.59; H, 12.94. Found: C, 70.36; H, 12.79.

**3c:**  $\delta_{\rm H}$  0.11 (s, 9H), 0.87 (d, 6H, J = 6.4 Hz), 1.05–1.68 (m, 3H), 1.69 (s, 3H), 1.84–2.38 (m, 2H), 5.77 (t, 1H, J = 7.0 Hz) ppm;  $\nu_{\rm max}$  2955, 1618, 1467, 1384, 1366, 1248, 836 cm<sup>-1</sup>; Anal. calcd. for C<sub>11</sub>H<sub>24</sub>Si: C, 71.74; H, 13.04. Found: C, 71.50; H, 12.91.

**3e:**  $\delta_{\rm H}$  0.11 (s, 9H), 0.88 (t, 3H, J = 5.4 Hz), 1.10–1.65 (m, 8H), 1.73 (s, 3H), 1.84–2.41 (m, 2H), 5.81 (t, 1H, J = 7.0 Hz) ppm;  $\nu_{\rm max}$  2926, 2856, 1607, 1458, 1248, 837 cm<sup>-1</sup>; Anal. calcd. for C<sub>12</sub>H<sub>26</sub>Si: C, 72.73; H, 13.13. Found: C, 72.51; H, 13.02.

### General Procedure for the Synthesis of (Z)-1,2-Disubstituted Vinylsilanes 3b, 3d, and 3f

To a solution of isobutylmagnesium bromide (4.5 mmol) in diethyl ether (7 mL) was added Cp<sub>2</sub>TiCl<sub>2</sub> (50 mg, 0.2 mmol) at 0°C under Ar, and the mixture was stirred for 30 min at that temperature. To this solution was added alkynylsilane **1** (4.0 mmol), and the mixture was stirred for 6 h at 25°C. After removal of the ether under reduced pressure, the residue was dissolved in THF (7 mL), cooled to  $-10^{\circ}$ C, and treated with butyl iodide (0.828 g, 4.5 mmol) and CuI (76 mg, 0.4 mmol). The reaction mixture was brought to room temperature gradually and stirred for 2 h. After the usual workup (see above) the residue was chromatographed through a silica gel column using light petroleum as eluent.

**3b:**  $\delta_{\rm H}$  0.11 (s, 9H), 0.66–1.08 (m, 6H), 1.10–1.62 (m, 8H), 1.78–2.40 (m, 4H), 5.83 (t, 1H, J=7.0 Hz) ppm;  $\nu_{\rm max}$  2954, 2860, 1612, 1466, 1249, 848 cm<sup>-1</sup>; Anal. calcd. for C<sub>13</sub>H<sub>28</sub>Si: C, 73.58; H, 13.21. Found: C, 73.40; H, 13.13.

**3d:**  $\delta_{\rm H}$  0.12 (s, 9H), 0.78–1.05 (m, 9H), 1.08–1.64 (m, 7H), 1.74–2.38 (m, 4H), 5.83 (t, 1H, J=7.0 Hz) ppm;  $\nu_{\rm max}$  2955, 2871, 1612, 1466, 1384, 1366, 1248, 835 cm<sup>-1</sup>; Anal. calcd. for C<sub>14</sub>H<sub>30</sub>Si: C, 74.34; H, 13.27. Found: C, 74.19; H, 13.06.

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#### 1648

#### Zhao and Cai

**3f:**  $\delta_{\rm H}$  0.11 (s, 9H), 0.68–1.03 (m, 6H), 1.04–1.72 (m, 12H), 1.74–2.40 (m, 4H), 5.82 (t, 1H, J = 7.0 Hz) ppm;  $\nu_{\rm max}$  2958, 2857, 1612, 1466, 1249, 838 cm<sup>-1</sup>; Anal. calcd. for C<sub>15</sub>H<sub>32</sub>Si: C, 75.00; H, 13.33. Found: C, 75.11; H, 13.24.

### General Procedure for the Synthesis of (Z)- $\alpha$ , $\beta$ -Unsaturated Ketones 4a-l

To a stirred suspension of AlCl<sub>3</sub> (146 mg, 1.1 mmol) and (Z)-1,2disubstituted vinylsilane **3** (1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added a solution of the appropriate acyl chloride (1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) at 0°C and the mixture was stirred for1 h. The reaction mixture was treated with sat. aq. NaHCO<sub>3</sub> (10 mL) and extracted with Et<sub>2</sub>O (2 × 20 mL). The organic layer was washed with water (3 × 20 mL), dried (MgSO<sub>4</sub>) and concentrated in vacuo. The oily residue was purified by flash column chromatography on silica gel (EtOAc/light petroleum, 1:8) to give **4a–l** as oils.

**4a:**  $\delta_{\rm H}$  0.89 (t, 3H, J = 5.4 Hz), 1.08–1.80 (m, 4H), 1.90 (s, 3H), 2.04–2.50 (m, 5H), 5.55 (m, 1H) ppm;  $\nu_{\rm max}$  2958, 2870, 1690, 1641, 1467 cm<sup>-1</sup>; Anal. calcd. for C<sub>9</sub>H<sub>16</sub>O: C, 77.14; H, 11.43. Found: C, 76.89; H, 11.21.

**4b:**  $\delta_{\rm H}$  0.91 (t, 3H, J = 5.4 Hz), 1.05–1.75 (m, 4H), 1.91 (s, 3H), 2.05–2.41 (m, 2H), 5.50 (m, 1H), 7.18–7.63 (m, 3H), 7.65–7.97 (m, 2H) ppm;  $\nu_{\rm max}$  2957, 2872, 1665, 1598, 1448, 1337 cm<sup>-1</sup>; Anal. calcd. for C<sub>14</sub>H<sub>18</sub>O: C, 83.17; H, 8.91. Found: C, 83.26; H, 8.83.

**4c:**  $\delta_{\rm H}$  0.69–1.10 (m, 6H), 1.12–1.78 (m, 8H), 1.91–2.40 (m, 7H), 5.25 (m, 1H) ppm;  $\nu_{\rm max}$  2958, 2872, 1670, 1637, 1458 cm<sup>-1</sup>; Anal. calcd. for C<sub>12</sub>H<sub>22</sub>O: C, 79.12; H, 12.09. Found: C, 79.33; H, 12.14.

**4d:**  $\delta_{\rm H}$  0.67–1.11 (m, 6H), 1.12–1.83 (m, 8H), 1.98–2.41 (m, 4H), 5.42 (m, 1H), 7.39 (d, 2H, J = 9.0 Hz), 7.86 (d, 2H, J = 9.0 Hz) ppm;  $\nu_{\rm max}$  2957, 2865, 1666, 1595, 1490, 1445 cm<sup>-1</sup>; Anal. calcd. for C<sub>17</sub>H<sub>23</sub>OCI: C, 73.25; H, 8.26. Found: C, 73.40; H, 8.38.

**4e:**  $\delta_{\rm H}$  0.87 (d, 6H, J = 6.4 Hz), 1.09–1.78 (m, 3H), 1.92 (s, 3H), 2.01–2.41 (m, 5H), 5.50 (m, 1H) ppm;  $\nu_{\rm max}$  2960, 2871, 1690, 1640, 1467, 1384, 1366 cm<sup>-1</sup>; Anal. calcd. for C<sub>10</sub>H<sub>18</sub>O: C, 77.92; H, 11.69. Found: C, 77.65; H, 11.47.

**4f:**  $\delta_{\rm H}$  0.91 (d, 6H, J = 6.4 Hz), 1.08–1.81 (m, 3H), 1.91 (s, 3H), 2.04–2.42 (m, 2H), 5.45 (m, 1H), 7.16–7.61 (m, 3H), 7.65–7.98 (m, 2H) ppm;  $\nu_{\rm max}$  2955, 2870, 1664, 1598, 1448, 1384, 1366 cm<sup>-1</sup>; Anal. calcd. for C<sub>15</sub>H<sub>20</sub>O: C, 83.33; H, 9.26. Found: C, 83.05; H, 9.11.

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Stereoselective Synthesis of (Z)- $\alpha$ , $\beta$ -Unsaturated Ketones

1649

**4g:**  $\delta_{\rm H}$  0.70–1.10 (m, 9H), 1.11–1.80 (m, 7H), 1.95–2.41 (m, 7H), 5.29 (m, 1H) ppm;  $\nu_{\rm max}$  2957, 2871, 1670, 1637, 1466, 1384, 1366 cm<sup>-1</sup>; Anal. calcd. for C<sub>13</sub>H<sub>24</sub>O: C, 79.59; H, 12.24. Found: C, 79.35; H, 12.07.

**4h:**  $\delta_{\rm H}$  0.67–1.10 (m, 9H), 1.11–1.78 (m, 7H), 1.85–2.40 (m, 4H), 5.38 (m, 1H), 7.10–7.57 (m, 3H), 7.68–7.99 (m, 2H) ppm;  $\nu_{\rm max}$  2956, 2871, 1683, 1597, 1448, 1384, 1366 cm<sup>-1</sup>; Anal. calcd. for C<sub>18</sub>H<sub>26</sub>O: C, 83.72; H, 10.08. Found: C, 83.50; H, 9.85.

**4i:**  $\delta_{\rm H}$  0.90 (t, 3H, J = 5.4 Hz), 1.09–1.80 (m, 8H), 1.92 (s, 3H), 2.00–2.41 (m, 5H), 5.60 (m, 1H) ppm;  $\nu_{\rm max}$  2931, 2858, 1681, 1629, 1458 cm<sup>-1</sup>; Anal. calcd. for C<sub>11</sub>H<sub>20</sub>O: C, 78.57; H, 11.90. Found: C, 78.31; H, 11.71.

**4j:**  $\delta_{\rm H}$  0.90 (t, 3H, J = 5.4 Hz), 1.10–1.79 (m, 8H), 1.91 (s, 3H), 1.97–2.39 (m, 2H), 5.50 (m, 1H), 7.35 (d, 2H, J = 9.0 Hz), 7.84 (d, 2H, J = 9.0 Hz) ppm;  $\nu_{\rm max}$  2958, 2865, 1662, 1623, 1595, 1445 cm<sup>-1</sup>; Anal. calcd. for C<sub>16</sub>H<sub>21</sub>OCl: C, 72.59; H, 7.94. Found: C, 72.31; H, 7.69.

**4k:**  $\delta_{\rm H}$  0.69–1.10 (m, 6H), 1.12–1.81 (m, 12H), 1.95–2.41 (m, 7H), 5.35 (m, 1H) ppm;  $\nu_{\rm max}$  2958, 2872, 1683, 1632, 1466 cm<sup>-1</sup>; Anal. calcd. for C<sub>14</sub>H<sub>26</sub>O: C, 80.00; H, 12.38. Found: C, 79.75; H, 12.14.

**41:**  $\delta_{\rm H}$  0.68–1.10 (m, 6H), 1.11–1.79 (m, 12H), 1.90–2.41 (m, 4H), 5.37 (m, 1H), 7.10–7.49 (m, 3H), 7.60–8.05 (m, 2H) ppm;  $\nu_{\rm max}$  2957, 2859, 1683, 1622, 1598, 1448 cm<sup>-1</sup>; Anal. calcd. for C<sub>19</sub>H<sub>28</sub>O: C, 83.82; H, 10.29. Found: C, 83.58; H, 10.07.

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#### REFERENCES

- (a) House, H.O. *Modern Synthetic Reactions*, 2nd. Ed.; Benjamine, W.A., Ed.; New York, 1972; (b) Volkmann, R.A.; Andrews, G.G. J. Am. Chem. Soc. **1975**, *97*, 4777; (c) Stork, G.; Logusch, E.W. Tetrahedron Lett. **1979**, 3361; (d) House, H.O.; Umen, M.J. J. Org. Chem. **1973**, *38*, 3893; (e) Brown, H.C. Synthesis **1984**, 303.
- 2. Huang, X.; Xie, L.H.; Wu, H. J. Org. Chem. 1988, 53, 4862.
- 3. Ogima, M.; Hyuga, S.; Hara, S.; Suzuki, A. Chem. Lett. 1989, 1959.
- 4. Awen, B.Z.; Miyashita, M.; Shiratani, T.; Yoshikoshi, A.; Irie, H. Chem. Lett. **1992**, 767.

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#### 1650

#### Zhao and Cai

- 5. Bartoli, G.; Cimarelli, C.; Marcantoni, E.; Palmieri, G.; Petrini, M. J. Chem. Soc., Chem. Commun. **1994**, 715.
- 6. Tsuda, T.; Kiyoi, T.; Saegusa, T. J. Org. Chem. 1990, 55, 2554.
- 7. Jabri, N.; Alexakis, A.; Normant, J.F. Tetrahedron Lett. **1983**, 24, 5081.
- 8. Satyanarayana, N.; Alper, H. J. Chem. Soc., Chem. Commun. 1991, 8.
- 9. Sato, F.; Watanabe, H.; Tanaka, Y.; Yamaji, T.; Sato, M. Tetrahedron Lett. **1983**, *24*, 1041.
- 10. Sato, F. J. Organomet. Chem. 1985, 285, 53.
- 11. Eaborn, C.; Walton, D.R.M. J. Organomet. Chem. 1964, 2, 95.
- 12. Chan, T.H.; Fleming, I. Synthesis 1979, 761.
- 13. Fleming, I.; Pearce, A. J. Chem. Soc., Chem. Commun. 1975, 633.
- Chan, T.H.; Lau, P.W.K.; Mychajlowskij, W. Tetrahedron Lett. 1977, 3317.

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