

New synthesis of trimethylsilyl diphenylphosphinite

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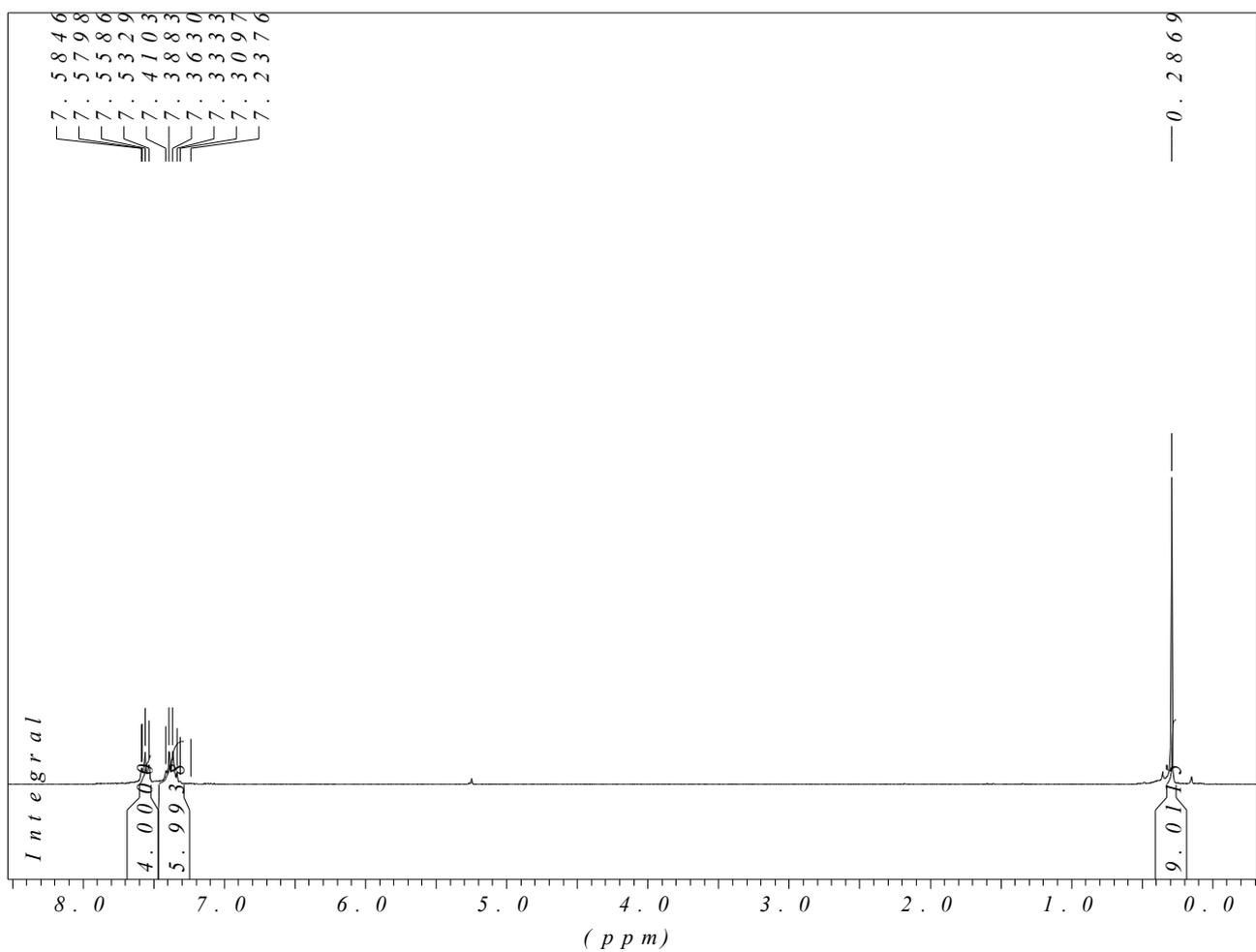
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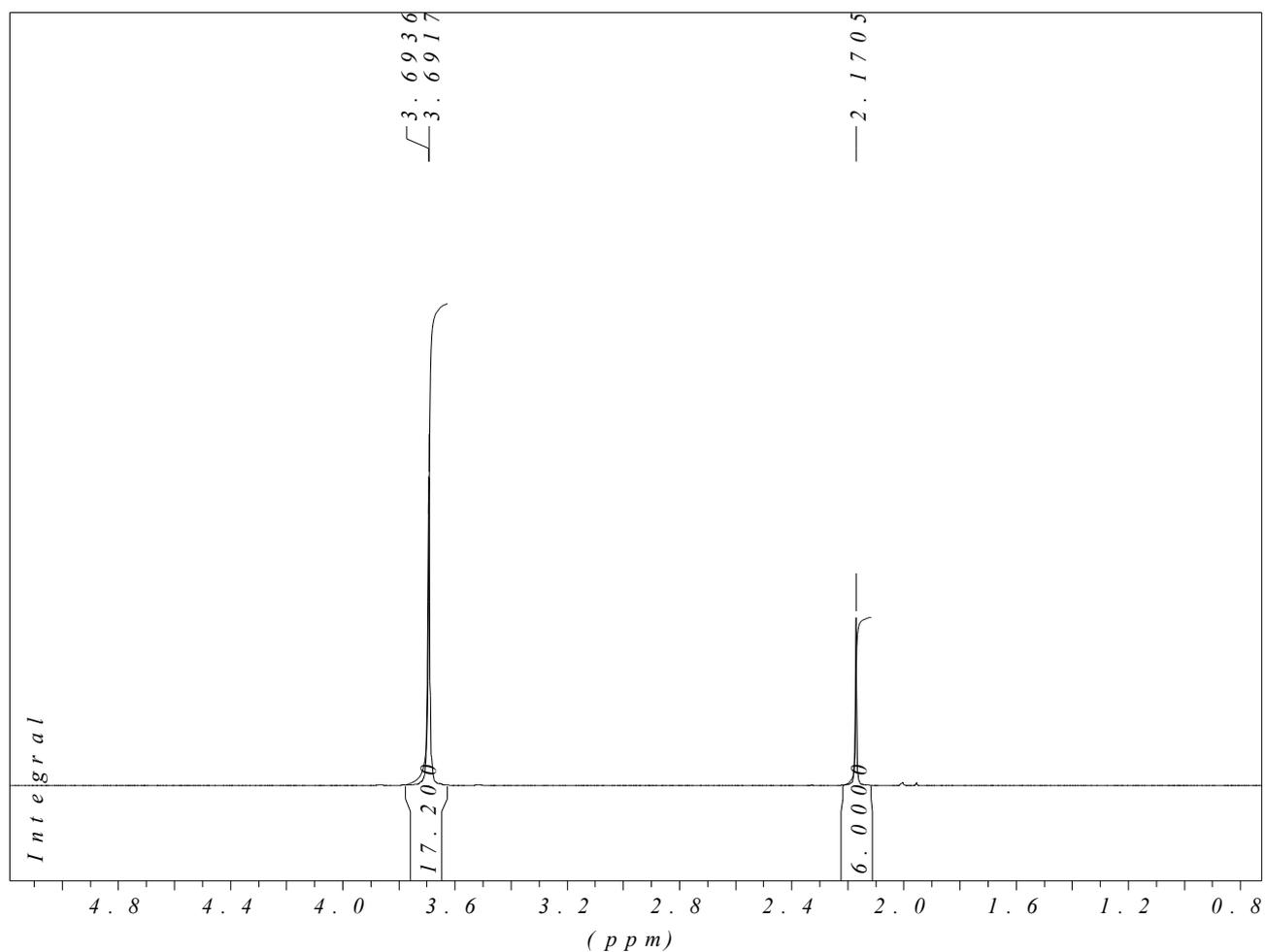
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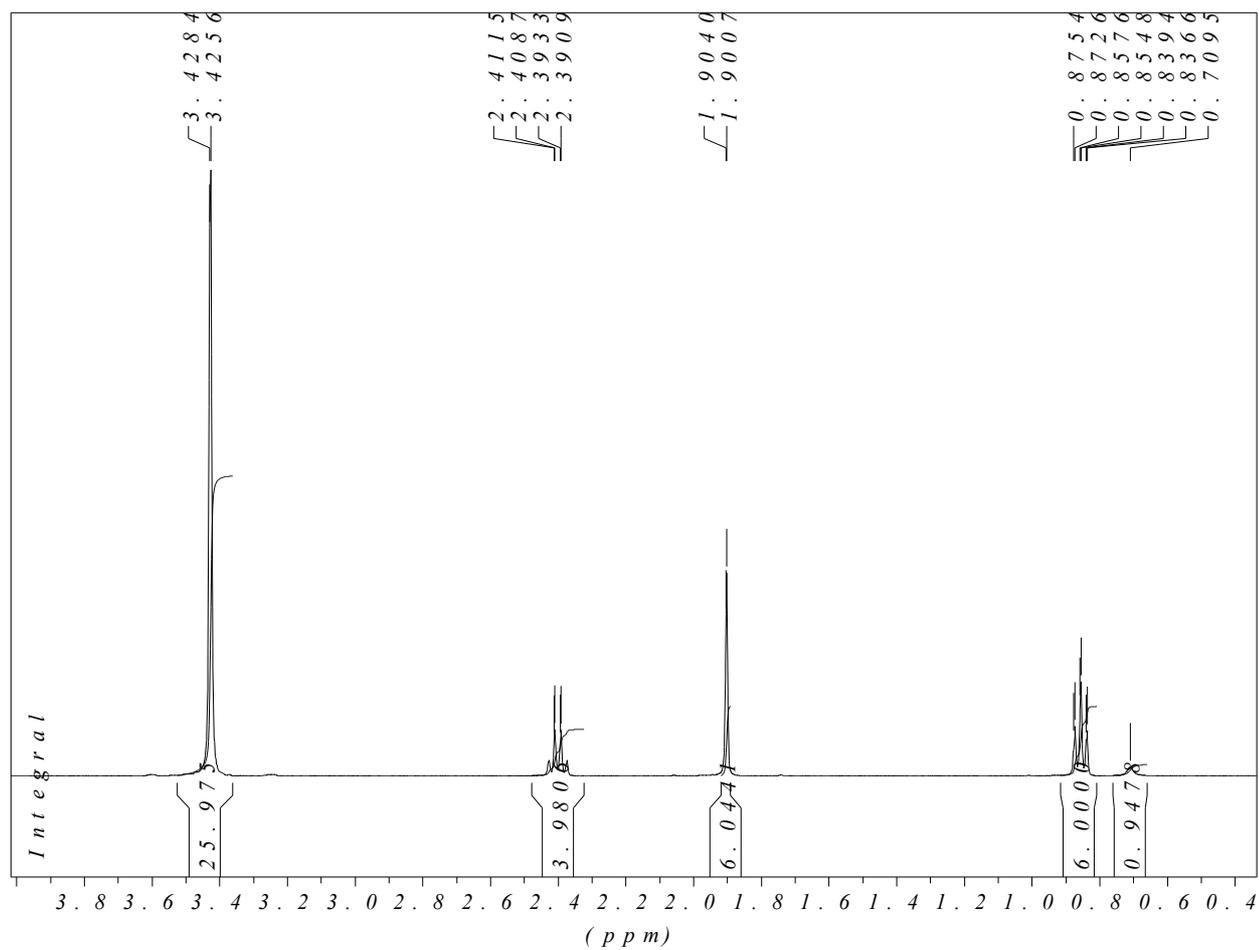


^1H NMR spectra of trimethylsilyl diphenylphosphinite (**1**), CDCl_3 , δ .

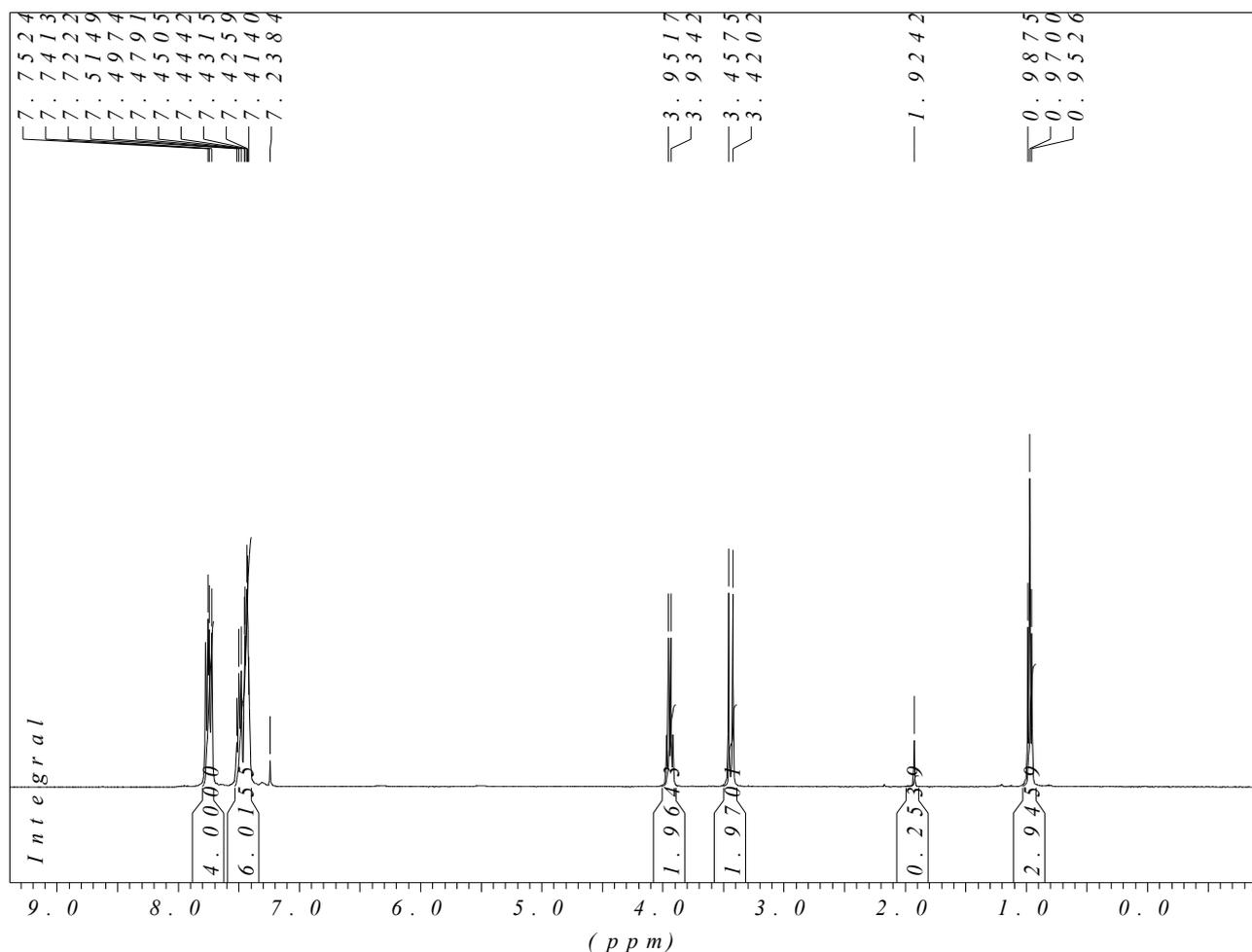


¹H NMR spectra of low-boiling fraction by synthesis of trimethylsilyl diphenylphosphinite (**1**) from hexamethyldisilazane (**3a**) and (2-hydroxyprop-2-yl)diphenylphosphine oxide (**2**) (CDCl₃, δ). (3,69 [s, 17H, 1,4-dioxane], 2,17 [s, 6H, 2 CH₃, acetone]).

¹H NMR spectra of low-boiling fraction in case compound **3b** is similar to spectra of low-boiling fraction in case compound **3a**.



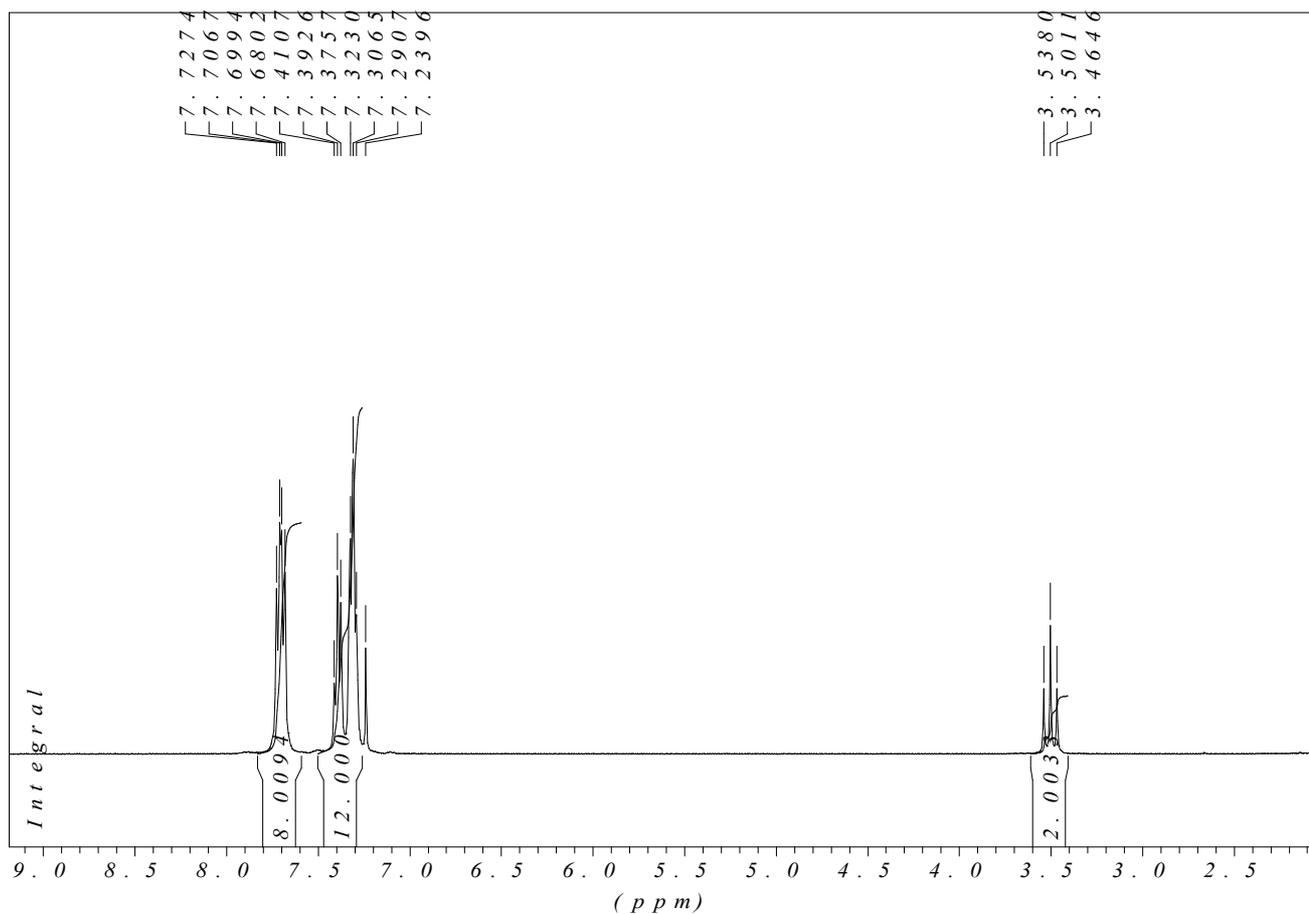
¹H NMR spectra of low-boiling fraction by synthesis of trimethylsilyl diphenylphosphinite (**1**) from diethyl(trimethylsilyl)amine (**3c**) and (2-hydroxyprop-2-yl)diphenylphosphine oxide (**2**) (CDCl₃, δ). (3,70 [s, 27 H, dioxane], 2,67 [q, ³J_{H,H} = 7.24, H, -CH₂-CH₃, HN(C₂H₅)₂], 2,17 [s, 6H, 2 CH₃, acetone], 1,12 [t, ³J_{H,H} = 7,24, 6H, -CH₂-CH₃, HN(C₂H₅)₂], 0.98 [br s, 1H, H-N, HN(C₂H₅)₂]).



¹H NMR spectra of ethyl (diphenylphosphoryl)acetate (**8**), (CDCl₃, δ).

Synthesis of ethyl (diphenylphosphoryl)acetate (**8**).

Ethyl bromoacetate (**6**) (1.23 g, 7.7 mmol) was added to 2 g (7.3 mmol) of trimethylsilyl diphenylphosphinite (**1**). Several minutes later, the reaction mixture warmed up and after cooling during 0.5 h became solid. Recrystallization from hexane-benzene gave 1.81 g (86%) of ethyl (diphenylphosphoryl)acetate (**8**). Mp 175-177 °C. ³¹P NMR {¹H}: 26,74. ¹H NMR: 7,77-7,52 [m, 4H, o-H, Ph], 7,50-7,42 [m, 6H, m,p-H, Ph], 3,94 [q, ³J_{H,H} = 5,26, 4H, O-CH₂-CH₃], 3,44 [d, ²J_{P,H} = 11,26, 2H, P-CH₂], 0,97 [t, ³J_{H,H} = 5,26, 3H, O-CH₂-CH₃]. Anal. calc. for C₁₆H₁₇O₃P: C 66.66, H 5.94, P 10.74; found: C 66.64, H 5.98, P 10.60.



^1H NMR spectra of bis(diphenylphosphoryl)methane (**9**), (CDCl_3 , δ).

Synthesis of bis(diphenylphosphoryl)methane (**9**).

(Chloromethyl)diphenylphosphine oxide (**7**) (1.92 g, 7.7 mmol) was added to 2 g (7.3 mmol) of trimethylsilyl diphenylphosphinite (**1**). The mixture was heated at 100 °C under reduced pressure 12 Torr for 1 h. Recrystallization from benzene-chloroform mixture afforded 2.52 g (83%) of bis(diphenylphosphoryl)methane (**9**), Mp 180-182 °C. ^{31}P NMR $\{^1\text{H}\}$: 24,64. ^1H NMR: 7,73-7,69 [m, 8H, o-H, Ph]; 7,41-7,29 [m, 12H, m,p-H, Ph]; 3,50 [t, $^2J_{\text{P,H}} = 11,08$, 2H, CH_2]. Anal. calc. for $\text{C}_{25}\text{H}_{22}\text{O}_2\text{P}_2$: C 72.11, H 5.33, P 14.88; found: C 72.27, H 5.19, P 14.9.