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REVISED MANUSCRIPT

SUPPORTING INFORMATION

A New Stereoselective Method for the Preparation of Allylic Alcohols

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Experimental Procedures

Unless otherwise noted, reagents were commercially available and were used without purification. Tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium/benzophenone ketyl. Dichloromethane was distilled from calcium hydride. All organolithium reagents were freshly titrated with 2,5-dimethoxybenzyl alcohol. Zinc chloride was dried at 150 °C at 0.1 mm overnight, then thoroughly ground by mortar and pestle in an inert atmosphere glovebox, and then dried again overnight at 150 °C at 0.1 mm. Ni(COD)₂ and anhydrous ZnCl₂ were stored and weighed in an inert atmosphere glovebox. All reactions were conducted in flame-dried glassware under a nitrogen or argon atmosphere.

General Procedure A for Alkylative Cyclization of Ynals. A 0.5 - 0.6 M solution of ZnCl₂ (2.5 - 3.0 equiv.) in THF was stirred at 0 °C, and the organolithium or Grignard reagent (3.7 - 4.5 equiv.) was added by syringe followed by stirring for 10 - 15 minutes at 0 °C. A 0.02 - 0.04 M THF solution of Ni(COD)₂ (0.05 - 0.20 equiv.) was added and the resultant mixture was immediately transferred by cannula to a 0.1 - 0.2 M solution of ynal (1.0 equiv.). After consumption of starting material by TLC analysis (typically 0.25 - 0.5 h at 0 °C), the reaction mixture was subjected to an extractive work-up (NH₄Cl/NH₄OH pH=8 buffer/Et₂O) followed by flash chromatography on SiO₂.

General Procedure B for Reductive Cyclization of Ynals. A 0.04 - 0.05 M solution of tributylphosphine (4 equiv. relative to Ni(COD)₂) in THF was added to Ni(COD)₂ (0.05 - 0.20 equiv.) at 25 °C followed by stirring for 3 - 5 minutes. The nickel solution was transferred to a 0.5 - 0.6 M solution of commercial Et₂Zn (2.5 - 3.5 equiv.) in THF at 0 °C, and the resultant mixture was immediately transferred by cannula to a 0.10 M 0 °C THF solution of ynal (1.0 equiv.). After consumption of starting material by TLC analysis (typically 0.25 - 2.0 h at 0 °C), the reaction mixture was subjected to an extractive work-up (NH₄Cl/NH₄OH pH=8 buffer/Et₂O) followed by flash chromatography on SiO₂.

General Procedure C for Three Component Couplings. A 1.0 M solution of ZnCl₂ (2.5 - 3.0 equiv.) in THF was stirred at 0 °C, and the organolithium or Grignard reagent (4.5 - 5.4 equiv.) was added by syringe followed by stirring for 10 - 15 minutes at 0 °C. A 0.05 M THF solution of Ni(COD)₂ (0.20 equiv.) and a solution containing the aldehyde (3.0 equiv.) and the alkyne (1.0 equiv., 0.3 - 0.4 M in THF relative to the alkyne) were added sequentially to the organozinc reagent. After consumption of starting material by TLC analysis (typically 0.25 - 0.5 h at 0 °C), the reaction mixture was subjected to an extractive work-up (NH₄Cl/NH₄OH pH=8 buffer/Et₂O) followed by flash chromatography on SiO₂. With the alkyne as the limiting reagent, the product derived from direct addition of the organozinc to the aldehyde was observed as a significant byproduct. In cases in which separation of this byproduct was problematic, slightly lower yields were obtained, with simpler purification, by employing the aldehyde as the limiting reagent.

(Z)-2-(Ethylidene)cyclopentyl benzoate (Table 1, entry 1). Following general procedure A, 5-hexynal (192 mg, 2.0 mmol), MeLi (6.4 mL, 9.0 mmol of a 1.4 M ether solution), ZnCl₂ (680 mg, 5.0 mmol), and Ni(COD)₂ (29 mg, 0.11 mmol) were employed, and the crude product was treated with benzoyl chloride (0.3 mL, 2.6 mmol) and pyridine (0.5 mL, 6.2 mmol) in CH₂Cl₂ (10 mL), to produce, after flash chromatography (19:1 hexanes: EtOAc), 300 mg (70 %) of product as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 8.03 (m, 2H), 7.54 (m, 1H), 7.43

(m, 2H), 5.92 (m, 1H), 5.64 (dq, $J = 2.0, 7.0$ Hz, 1H), 2.51 (m, 1H), 2.28 (m, 1H), 2.06 (m, 1H), 1.80 - 1.93 (m, 2H), 1.68 - 1.72 (m, 1H), 1.66 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz) δ 166.3, 141.1, 132.7, 130.7, 129.6, 128.3, 122.5, 74.2, 34.4, 32.1, 23.5, 14.8; IR (film) 1716 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$ 216.1150, found 216.1147 (M^+).

(Z)-2-(Benzylidene)cyclopentanol (Table 1, entry 2). Following general procedure A, 5-hexynal (96 mg, 1.00 mmol), PhMgBr (4.5 mL, 4.5 mmol of a 1.0 M THF solution), ZnCl_2 (360 mg, 2.6 mmol), and $\text{Ni}(\text{COD})_2$ (14 mg, 0.05 mmol) were employed to produce, after flash chromatography (4:1 hexanes: EtOAc), 126 mg (72%) of product as a colorless oil. Spectral data were identical to those previously reported. See ref. 16.

(Z)-2-(Pentylidene)cyclopentanol (Table 1, entry 3). Following general procedure A, 5-hexynal (100 mg, 1.04 mmol), *n*-BuLi (1.8 mL, 4.5 mmol of a 2.5 M hexane solution), ZnCl_2 (340 mg, 2.5 mmol), and $\text{Ni}(\text{COD})_2$ (14 mg, 0.05 mmol) were employed to produce, after flash chromatography (7:3 hexanes: Et₂O), 99 mg (62 %) of product as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 5.42 (dt, $J = 1.7, 7.4$ Hz, 1H), 4.66 (m, 1H), 2.40 (m, 1H), 2.15 (m, 3H), 1.73 - 1.82 (m, 3H), 1.61 (m, 1H), 1.33 (m, 5H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz) δ 145.0, 126.3, 71.1, 36.4, 32.2, 31.6, 29.0, 23.0, 22.4, 13.9; IR (film) 3352 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{10}\text{H}_{18}\text{O}$ 154.1358, found 154.1353 (M^+).

(Z)-2-(1-Phenylethylidene)cyclopentanol (Table 1, entry 4). Following general procedure A, 5-heptynal (114 mg, 1.04 mmol), PhMgBr (3.8 mL, 3.8 mmol of a 1.0 M THF solution), ZnCl_2 (340 mg, 2.5 mmol), and $\text{Ni}(\text{COD})_2$ (31 mg, 0.22 mmol) were employed to produce, after flash chromatography (4:1 hexanes: EtOAc), 126 mg (64%) of product as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.34 (m, 4H), 7.25 (m, 1H), 4.48 (m, 1H), 2.55 (dd, $J = 17.0, 7.0$ Hz, 1H), 2.33 (dt, $J = 17.0, 8.1$ Hz, 1H), 2.00 (m, 3H), 1.93 - 1.98 (m, 1H), 1.66 - 1.80 (m, 3H), 1.33 (m, 1H); ^{13}C NMR δ 143.4, 142.0, 132.4, 128.3, 127.6, 126.7, 72.8, 36.0, 29.7, 22.5, 21.8; IR (film) 3378 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{13}\text{H}_{16}\text{O}$ 188.1201, found 188.1202 (M^+).

(Z)-2-(1-Methylpentylidene)cyclopentanol (Table 1, entry 5). Following general procedure A, 5-heptynal (126 mg, 1.14 mmol), *n*-BuLi (1.5 mL, 3.8 mmol of a 2.5 M hexane solution), ZnCl₂ (340 mg, 2.5 mmol), and Ni(COD)₂ (55 mg, 0.20 mmol) were employed to produce, after flash chromatography (4:1 hexanes: EtOAc), 146 mg (76%) of product as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 4.65 (d, J = 4.5 Hz, 1H), 2.34 (dd, J = 16.8, 8.0 Hz, 1H), 2.21 (dt, J = 13.5, 7.5 Hz, 1H), 2.03-2.15 (m, 2H), 1.77 - 1.87 (m, 2H), 1.56-1.71 (m, 5H), 1.38 (m, 2H), 1.30 (m, 3H), 0.89 (t, J = 7.3 Hz, 3H); ¹³C NMR (125 MHz) δ 139.2, 132.5, 71.9, 36.5, 34.9, 30.8, 29.2, 23.0, 22.8, 18.7, 14.1; IR (film) 3322 cm⁻¹; HRMS (EI) *m/e* calcd for C₁₁H₂₀O 168.1514, found 168.1520 (M⁺). Anal. Calcd for C₁₁H₂₀O: C, 78.51; H, 11.98. Found: C, 78.52; H, 12.04.

(E)-2-(1-Phenylethylidene)cyclopentanol (Table 1, entry 6). Following general procedure A, 6-phenyl-5-hexynal (114 mg, 0.66 mmol), MeMgCl (0.75 mL, 2.25 mmol of a 3.0 M THF solution), ZnCl₂ (195 mg, 1.44 mmol), and Ni(COD)₂ (31 mg, 0.11 mmol) were employed to produce, after flash chromatography (3:1 hexanes: EtOAc), 90 mg (73%) of product as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.33 (m, 2H), 7.23 (m, 3H), 4.84 (m, 1H), 2.34-2.42 (m, 1H), 2.18 (m, 4H), 1.76-1.91 (m, 3H), 1.73 (m, 1H), 1.61 (m, 1H); ¹³C NMR δ 144.0, 141.9, 132.7, 128.0, 127.5, 126.5, 73.0, 36.5, 31.1, 23.7, 20.8; IR (film) 3352 cm⁻¹; HRMS (EI) *m/e* calcd for C₁₃H₁₆O 188.1201, found 188.1206 (M⁺).

(E)-2-(1-Phenylpropylidene)cyclopentanol (Table 1, entry 7). Following general procedure A, 6-phenyl-5-hexynal (114 mg, 0.66 mmol), EtMgCl (1.2 mL, 2.4 mmol of a 2.0 M THF solution), ZnCl₂ (195 mg, 1.44 mmol), and Ni(COD)₂ (32 mg, 0.11 mmol) were employed to produce, after flash chromatography (3:1 hexanes: EtOAc), 88 mg (67%) of product as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.32 (m, 2H), 7.23 (m, 1H), 7.17 (m, 2H), 4.85 (t, J = 3.7 Hz, 1H), 2.58 (q, J = 7.5 Hz, 2H), 2.27 (m, 1H), 2.06 (dt, J = 16.5, 8.5 Hz, 1H), 1.75 - 1.85 (m, 3H), 1.55 - 1.61 (m, 1H), 1.51 (m, 1H), 0.93 (t, J = 7.0, 3H); ¹³C NMR δ 142.5,

141.1, 139.7, 128.1, 128.0, 126.4, 72.4, 36.6, 30.7, 27.8, 23.4, 13.7; IR (film) 3313 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{14}\text{H}_{18}\text{O}$ 202.1358, found 202.1362 (M^+).

(Z)-1-Benzoyl-4-(ethylidene)pyrrolidin-3-ol (Table 1, entry 8) Following general procedure A, *N*-(benzoyl)-*N*-(prop-2-ynyl)-2-aminoethanal (50 mg, 0.25 mmol), methyllithium (0.72 mL, 1.0 mmol of a 1.4 mmol ether solution), zinc chloride (85 mg, 0.63 mmol), and $\text{Ni}(\text{COD})_2$ (7 mg, 0.03 mmol) were employed to produce, after chromatography (SiO_2 , 1:2 hexanes:EtOAc to pure EtOAc), 39 mg (0.17 mmol, 72 %) of product as a colorless oil that was homogeneous by TLC analysis. Two distinct rotamers were evident by 25 °C ^1H and ^{13}C NMR analysis. ^1H NMR (500 MHz, CDCl_3) δ 7.3-7.5 (m, 5H), 5.63 (m, 1H_{major}), 5.45 (m, 1H_{minor}), 4.88 (m, 1H_{minor}), 4.76 (m, 1H_{major}), 4.56 (d, $J = 16.0$ Hz, 1H_{major}), 4.28 (d, $J = 14.0$ Hz, 1H_{minor}), 4.06 (d, $J = 16.5$ Hz, 1H_{major}), 3.98 (d, $J = 13.5$ Hz, 1H_{major}), 3.87 (d, $J = 13.5$ Hz, 1H_{minor}), 3.70 (dd, $J = 14.0, 4.5$ Hz, 1H_{minor}), 3.60 (m, 1H_{both}), 2.99 (br s, 1H_{minor}), 2.80 (br s, 1H_{major}), 1.77 (m, 3H_{both}); ^{13}C NMR (125 MHz) δ 170.3, 170.1, 138.5, 137.7, 136.4, 136.1, 130.0, 128.3, 127.3, 127.0, 122.1, 121.8, 68.6, 67.2, 58.1, 55.0, 52.5, 49.2, 14.4, 14.2; IR (film) 1606, 1574 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ 217.1103, found 217.1100 (M^+).

2-(Methylidene)cyclopentyl benzoate (Table 2, entry 1). Following general procedure B, 5-hexynal (192 mg, 2.0 mmol), Et_2Zn (0.6 mL, 5.9 mmol), PBU_3 (0.4 mL, 1.6 mmol), and $\text{Ni}(\text{COD})_2$ (110 mg, 0.4 mmol) were employed, and the crude product was treated with benzoyl chloride (0.3 mL, 2.6 mmol) and pyridine (0.5 mL, 6.2 mmol) in CH_2Cl_2 (10 mL) to produce, after flash chromatography (19:1 hexanes: EtOAc), 300 mg (74 %) of product as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 8.05 (m, 2H), 7.54 (m, 1H), 7.43 (m, 2H), 5.70 (m, 1H), 5.25 (m, 1H), 5.13 (m, 1H), 2.53 (m, 1H), 2.37 (m, 1H), 2.14 (m, 1H), 1.83 - 1.96 (m, 2H), 1.76 (m, 1H); ^{13}C NMR (125 MHz) δ 166.4, 150.1, 132.8, 130.7, 129.6, 128.3, 110.6, 77.1, 33.1, 30.7, 22.6; IR (film) 1717 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2$ 202.0994, found 202.0994

(M⁺). The allylic alcohol was previously reported. Jitsukawa, K.; Kaneda, K.; Teranishi, S. *J. Org. Chem.* **1983**, *48*, 389.

(E)-2-(Ethylidene)cyclopentyl benzoate (Table 2, entry 2). Following general procedure B, 5-heptynal (220 mg, 2.0 mmol), Et₂Zn (0.6 mL, 5.9 mmol), PBU₃ (0.4 mL, 1.6 mmol), and Ni(COD)₂ (110 mg, 0.4 mmol) were employed, and the crude product was treated with benzoyl chloride (0.3 mL, 2.6 mmol) and pyridine (0.5 mL, 6.2 mmol) in CH₂Cl₂ (10 mL) to produce, after flash chromatography (19:1 hexanes: EtOAc), 289 mg (67%) of product as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 8.04 (m, 2H), 7.53 (m, 1H), 7.42 (m, 2H), 5.78 (m, 1H), 5.69 (m, 1H), 2.43 (m, 1H), 2.25 (m, 1H), 1.87-2.01 (m, 3H), 1.81 (m, 1H), 1.65 (dq, J = 6.8, 1.5 Hz, 3H); ¹³C NMR (125 MHz) δ 166.4, 141.6, 132.7, 130.9, 129.6, 128.2, 122.0, 78.2, 33.3, 27.0, 22.7, 14.9; IR (film) 1716 cm⁻¹; HRMS (EI) *m/e* calcd for C₁₄H₁₆O₂ 216.1150, found 216.1144 (M⁺). Anal. Calcd for C₁₄H₁₆O₂: C, 77.75; H, 7.46. Found: C, 77.68; H, 7.53. The allylic alcohol was previously reported. Khazanie, P. G.; Lee-Ruff, E. *Can. J. Chem.* **1973**, *51*, 3173.

(E)-2-(Benzylidene)cyclopentanol (Table 2, entry 3). Following general procedure B, 6-phenyl-5-hexynal (113 mg, 0.65 mmol), Et₂Zn (200 μL, 1.95 mmol), PBU₃ (110 μL, 0.44 mmol), and Ni(COD)₂ (30 mg, 0.11 mmol) were employed to produce, after flash chromatography (19:1 hexanes: EtOAc), 70 mg (62 %) of product as a colorless oil. Spectral data were identical to those previously reported. See ref. 16.

1-Benzoyl-4-(methylidene)pyrrolidin-3-ol (Table 2, entry 4) Following general procedure B, *N*-(benzoyl)-*N*-(prop-2-ynyl)-2-aminoethanal (48 mg, 0.24 mmol), diethylzinc (0.13 mL, 1.25 mmol), Ni(COD)₂ (14 mg, 0.05 mmol), and PBU₃ (51 mg, 0.25 mmol) were employed to produce, after chromatography (SiO₂, 1:2 to 1:4 hexanes:EtOAc), 38 mg (0.19 mmol, 79 %) of a 7:1 inseparable mixture of desired product and the corresponding ethyl-containing alkylative cyclization product as a colorless oil. Two distinct rotamers (2:1) were evident by 25 °C ¹H and ¹³C NMR analysis. ¹H NMR (500 MHz, CDCl₃) δ 7.3-7.5 (m, 5H), 5.26 (s, 1H_{major}), 5.23 (s,

1H_{minor}), 5.15 (s, 1H_{major}), 4.99 (s, 1H_{minor}), 4.62 (s, 1H_{minor}), 4.50 (s, 1H_{major}), 3.4-4.4 (m, 4H), (diagnostic signal for ethyl-substituted compound: δ 0.89 (m, 3H)); ^{13}C NMR (125 MHz) δ 170.6, 170.1, 147.1, 146.4, 135.9, 135.7, 130.2, 128.43, 128.35, 127.3, 127.0, 109.6, 109.4, 71.8, 70.9, 56.6, 53.6, 52.1, 49.0; IR (film) 1677, 1612, 1575 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2$ 203.0946, found 203.0944 (M^+); For the ethyl-substituted compound: HRMS (EI) m/e calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_2$ 231.1259, found 231.1258 (M^+).

(E)-1,3-Diphenyl-but-2-en-1-ol (Table 3, entry 1). Following general procedure C, benzaldehyde (106 μL , 1.0 mmol), phenylacetylene (132 μL , 1.2 mmol), MeLi (3.2 mL, 4.5 mmol of a 1.4 M ether solution), ZnCl_2 (340 mg, 2.5 mmol), and $\text{Ni}(\text{COD})_2$ (14 mg, 0.05 mmol) were employed to produce, after flash chromatography (4:1 hexanes: EtOAc), 134 mg (60 %) of product as a yellow oil. ^1H NMR (500 MHz, C_6D_6) δ 7.36 (m, 2H), 7.15 (m, 4H), 7.06 (m, 4H), 5.97 (dd, $J = 9.0, 1.0$ Hz, 1H), 5.39 (d, $J = 8.5$ Hz, 1H), 1.89 (m, 1H), 1.86 (d, $J = 1.0$ Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 144.3, 142.8, 136.2, 130.9, 128.4, 128.1, 127.1, 126.1, 125.9, 70.7, 15.9; IR (film) 3341 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{16}\text{H}_{16}\text{O}$ 224.1201, found 224.1195 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}$: C, 85.68; H, 7.19. Found: C, 85.69; H, 7.15. The alkene stereochemistry was assigned by observation of a 4.1 % NOE of the allylic methine proton (δ 5.39) upon irradiation of the vinyl methyl group (δ 1.86). Assignments were confirmed by H-C COSY NMR experiments. This compound was previously reported. Wasserman, H. H.; Aubrey, N. E. *J. Am. Chem. Soc.* **1955**, *77*, 590.

(E)-1-Phenyl-3-methylnon-2-en-1-ol (Table 3, entry 2). Following general procedure C, benzaldehyde (300 μL , 3.0 mmol), octyne (150 μL , 1.0 mmol), MeLi (3.8 mL, 5.3 mmol of a 1.4 M ether solution), ZnCl_2 (400 mg, 2.9 mmol), and $\text{Ni}(\text{COD})_2$ (54 mg, 0.20 mmol) were employed to produce, after flash chromatography (9:1 hexanes: EtOAc), 171 mg (74%) of product as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.34-7.40 (m, 4H), 7.27 (m, 1H), 5.48 (d, $J = 9.0$ Hz, 1H), 5.43 (dd, $J = 8.8, 1.3$ Hz, 1H), 2.07 (m, 1H), 2.04 (t, $J = 7.5$ Hz, 2H), 1.79 (d, $J = 1.0$ Hz, 3H), 1.44 (m, 2H), 1.29 (m, 6H), 0.90 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz) δ

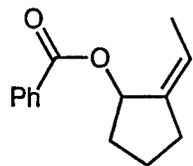
144.3, 139.1, 128.4, 127.2, 125.9, 70.6, 39.6, 31.7, 29.0, 27.6, 22.7, 16.7, 14.1; IR (film) 3354 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{16}\text{H}_{24}\text{O}$ 232.1827, found 232.1828 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{O}$: C, 82.70; H, 10.41. Found: C, 82.57; H, 10.43. The alkene stereochemistry was assigned by observation of a 4.6 % NOE of the allylic methine proton (δ 5.48) upon irradiation of the vinyl methyl group (δ 1.79). Assignments were confirmed by H-C COSY NMR experiments.

(E)-1-Phenyl-3-butylnon-2-en-1-ol (Table 3, entry 3). Following general procedure C, benzaldehyde (300 μL , 3.0 mmol), octyne (150 μL , 1.0 mmol), BuLi (1.8 mL, 4.5 mmol of a 2.5 M hexane solution), ZnCl_2 (340 mg, 2.5 mmol), and $\text{Ni}(\text{COD})_2$ (54 mg, 0.20 mmol) were employed to produce, after flash chromatography (9:1 hexanes: EtOAc), 195 mg (71%) of product as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.40 (m, 2H), 7.35 (m, 2H), 7.26 (m, 1H), 5.49 (d, $J = 9.0$, 1H), 5.40 (d, $J = 9.0$ Hz, 1H), 2.19 (m, 2H), 2.03 (t, $J = 7.5$ Hz, 2H), 1.8 (m, 1H), 1.27-1.44 (m, 12H), 0.93 (t, $J = 7.0$, 3H), 0.89 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (125 MHz) δ 144.3, 143.8, 128.4, 127.2, 127.0, 126.0, 70.3, 36.8, 31.7, 31.0, 30.5, 29.1, 27.9, 23.0, 22.6, 14.1, 14.0; IR (film) 3355 cm^{-1} HRMS (EI) m/e calcd for $\text{C}_{19}\text{H}_{30}\text{O}$ 274.2297, found 274.2293 (M^+). Anal. Calcd for $\text{C}_{19}\text{H}_{30}\text{O}$: C, 83.15; H, 11.02. Found: C, 83.07 ; H, 11.20. Sample contains less than 3 % of an impurity with distinct signals in the ^1H NMR proton spectrum at 6.7 and 6.2 ppm. This compound was previously reported. Boeckman, R. K. Jr.; O'Conner, K. J. *Tetrahedron Lett.* **1989**, 30, 3271.

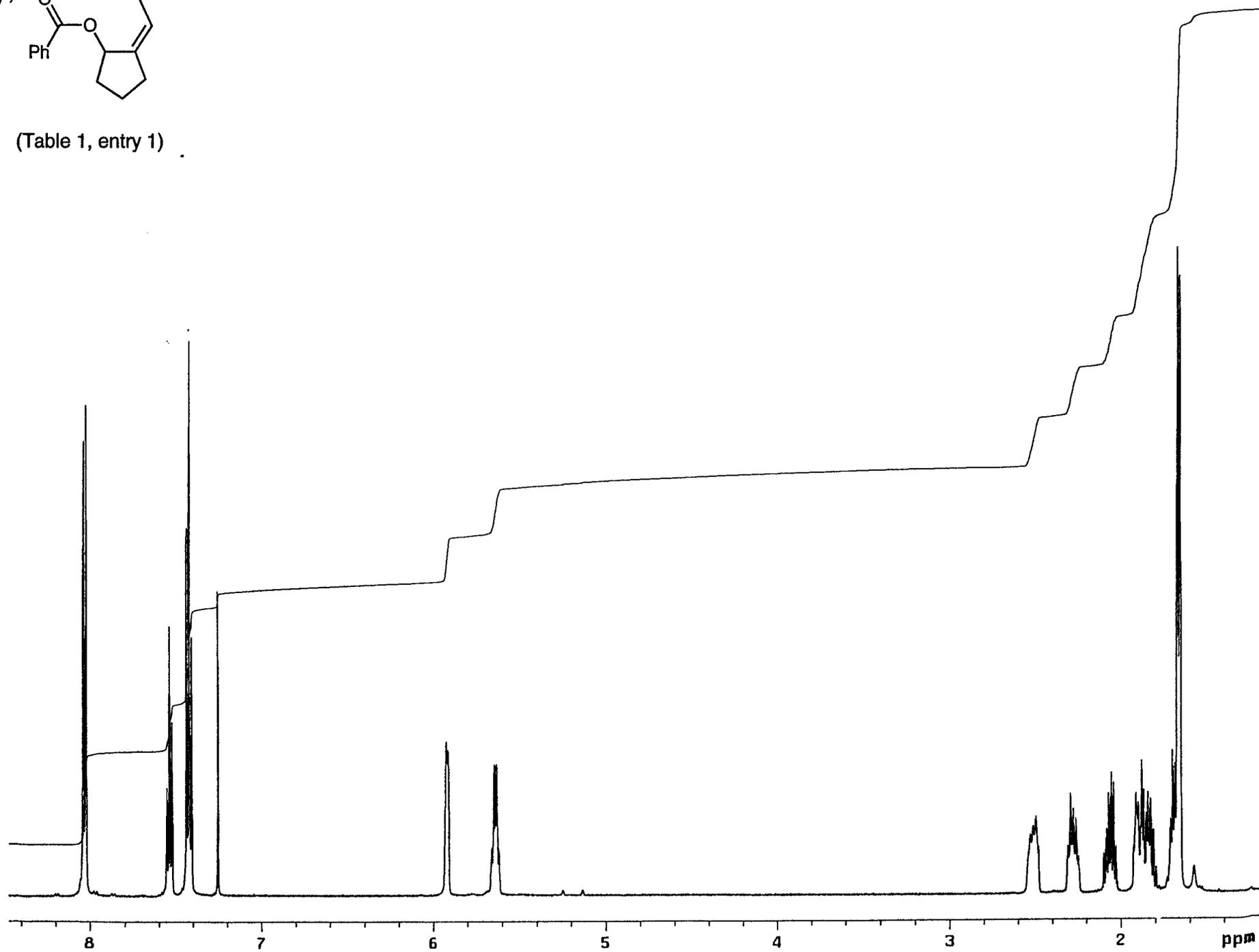
(E)-2-Methyl-5-phenyl-4-hexenyl-3-acetate (Table 3, entry 4). Following general procedure C, isobutyraldehyde (100 μL , 1.0 mmol), phenylacetylene (280 μL , 3.1 mmol), MeLi (3.2 mL, 4.5 mmol of a 1.4 M ether solution), ZnCl_2 (340 mg, 2.5 mmol), and $\text{Ni}(\text{COD})_2$ (54 mg, 0.20 mmol) were employed, and the crude mixture was treated with pyridine (0.24 mL, 3.0 mmol), acetic anhydride (95 μL , 1.0 mmol), and acetyl chloride (79 μL , 1.0 mmol) in CH_2Cl_2 (10 mL) to produce, after flash chromatography (95:5 hexanes: EtOAc), 60 mg (21%) of product as a yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.41 (m, 2H), 7.33 (m, 2H), 7.26 (m, 1H), 5.67 (dd,

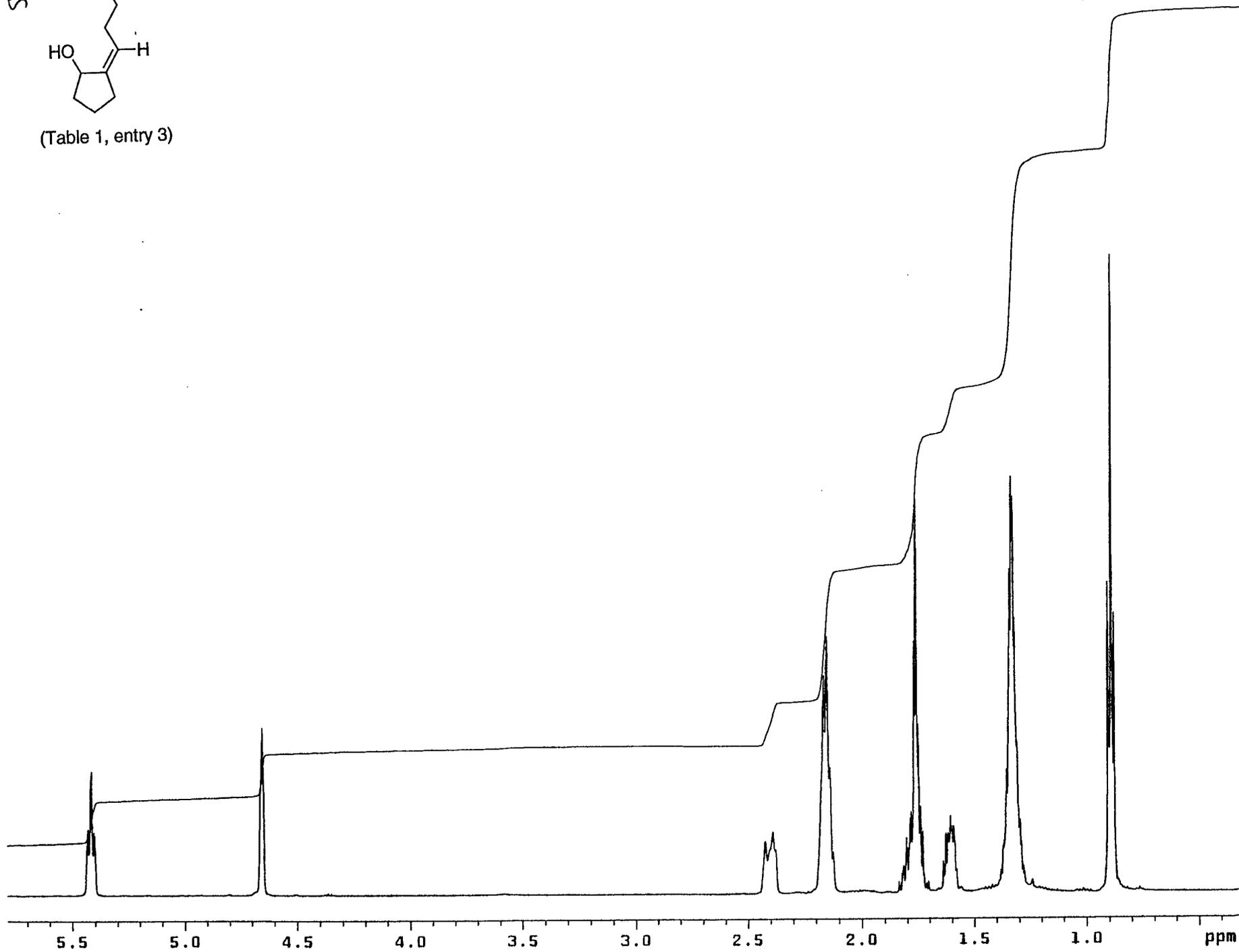
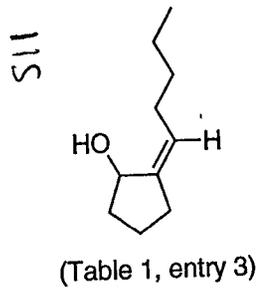
$J = 9.3, 1.3 \text{ Hz, 1H}$), 5.46 (dd, $J = 9.5, 7.0 \text{ Hz, 1H}$), 2.16 (d, $J = 1.5 \text{ Hz, 3H}$), 2.07 (s, 3H), 1.96 (octet, $J = 6.8 \text{ Hz, 1H}$), 0.98 (d, $J = 7.0 \text{ Hz, 3H}$), 0.95 (d, $J = 6.5 \text{ Hz, 3H}$); ^{13}C NMR (125 MHz) δ 170.5, 143.0, 139.5, 128.2, 127.3, 125.9, 125.0, 76.1, 32.8, 21.3, 18.4, 18.0, 16.8; IR (film) 1733 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$ 232.1463, found 232.1461(M^+).

S10

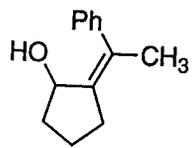


(Table 1, entry 1)

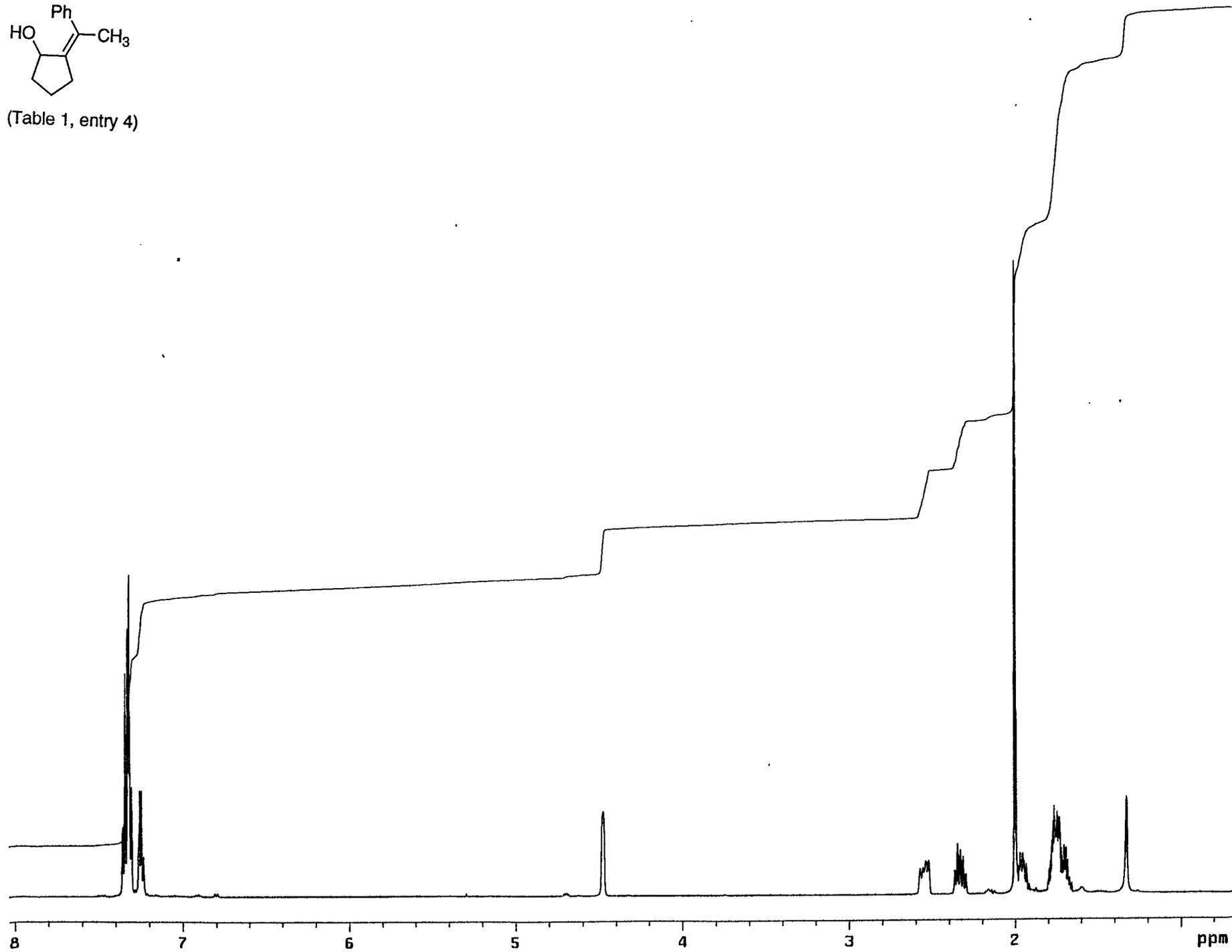




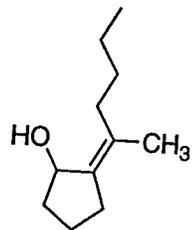
S12



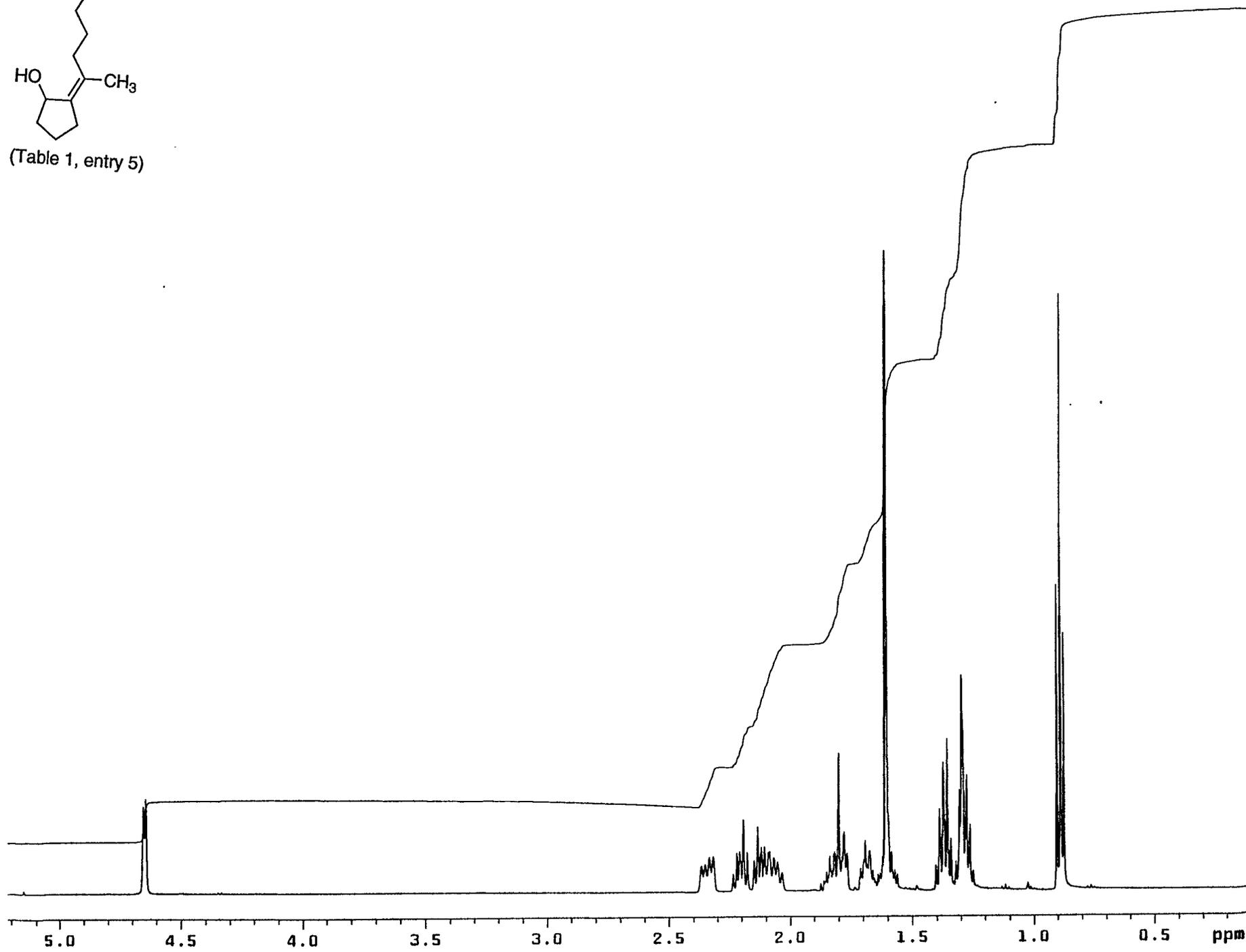
(Table 1, entry 4)



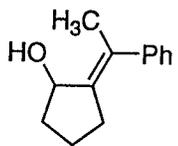
S13



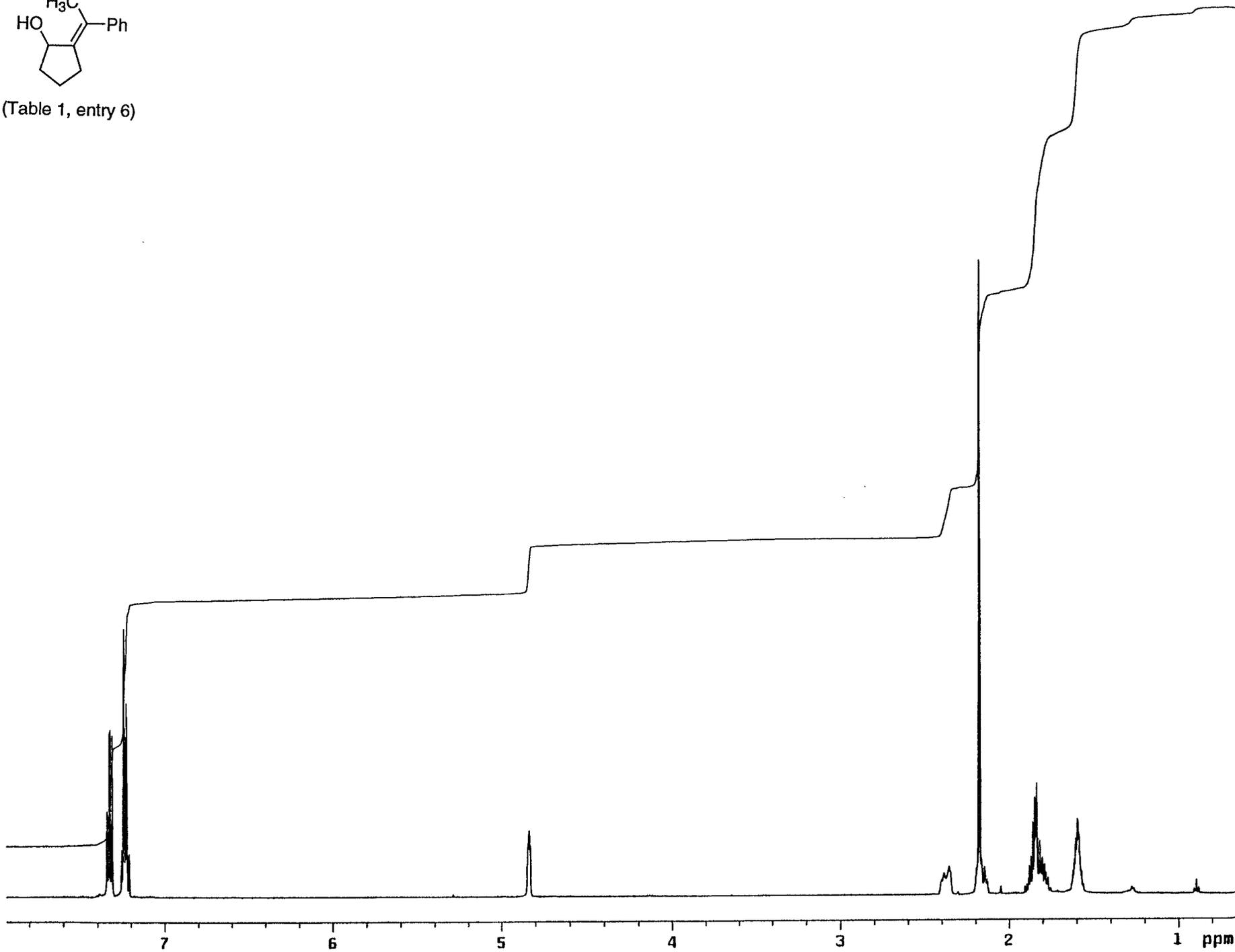
(Table 1, entry 5)



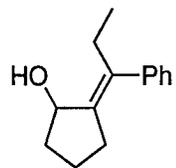
S14



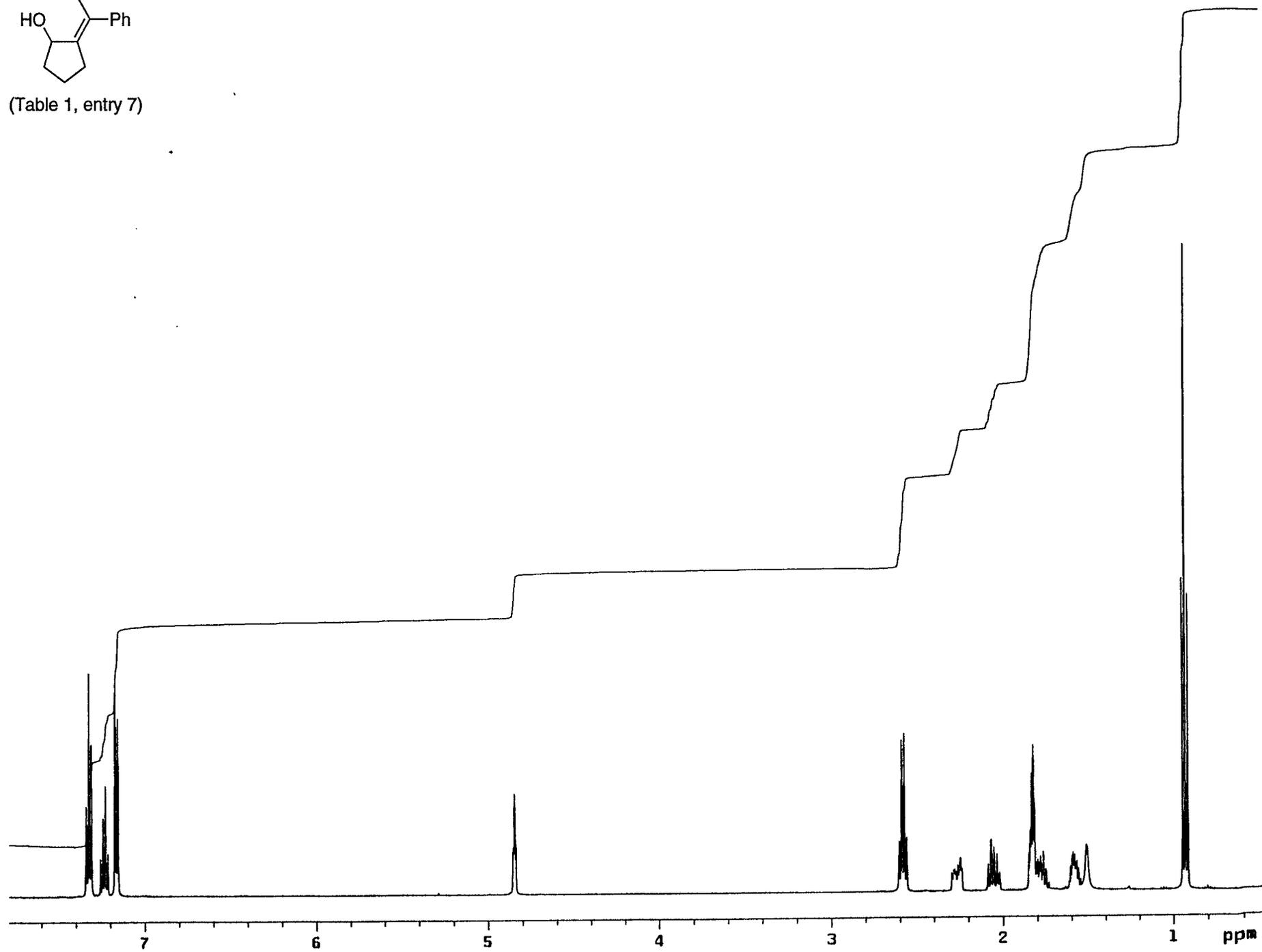
(Table 1, entry 6)



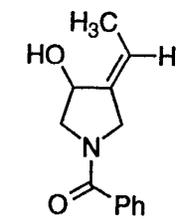
S15



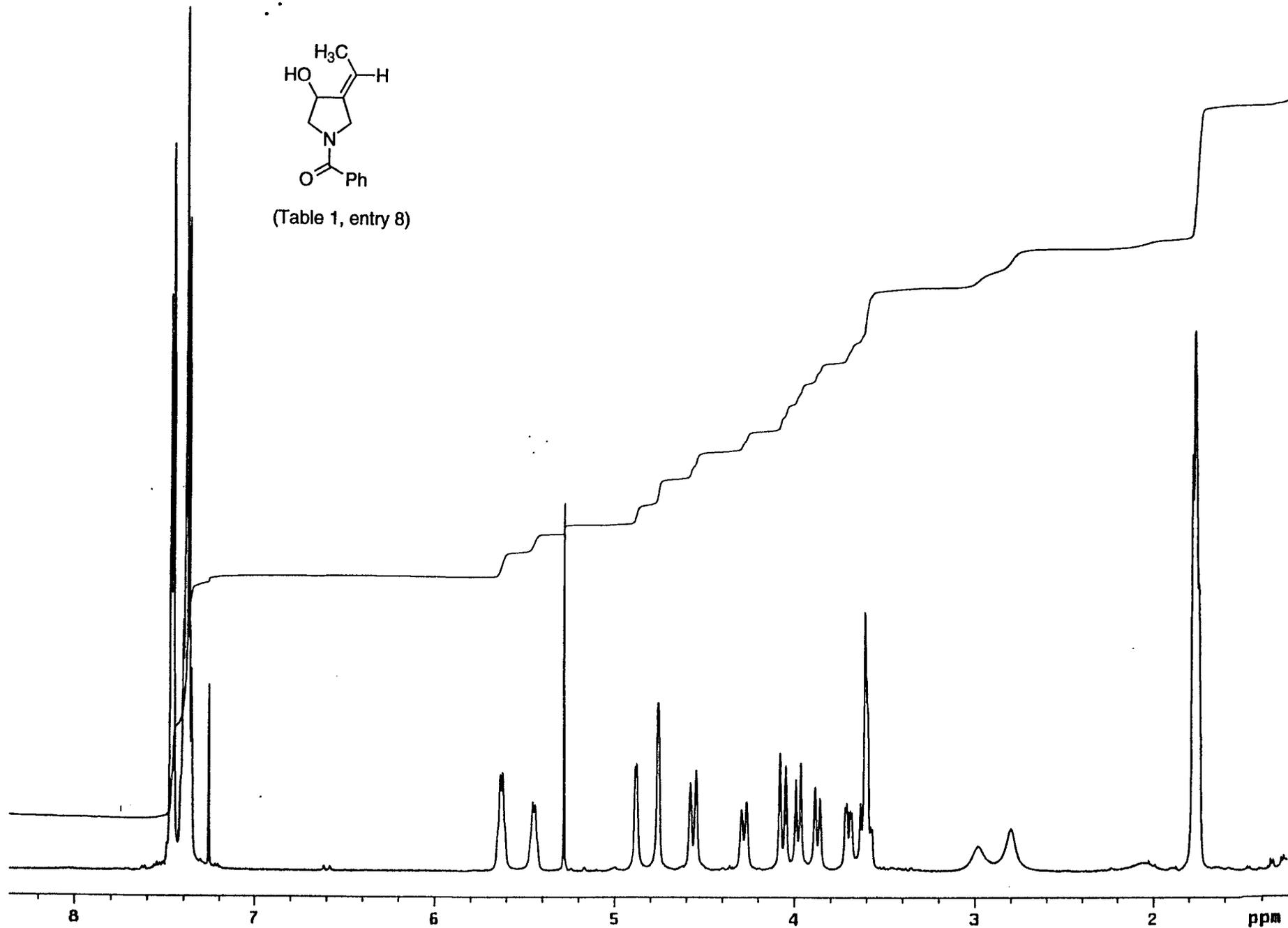
(Table 1, entry 7)



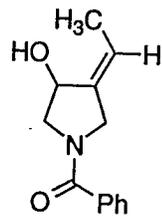
S16



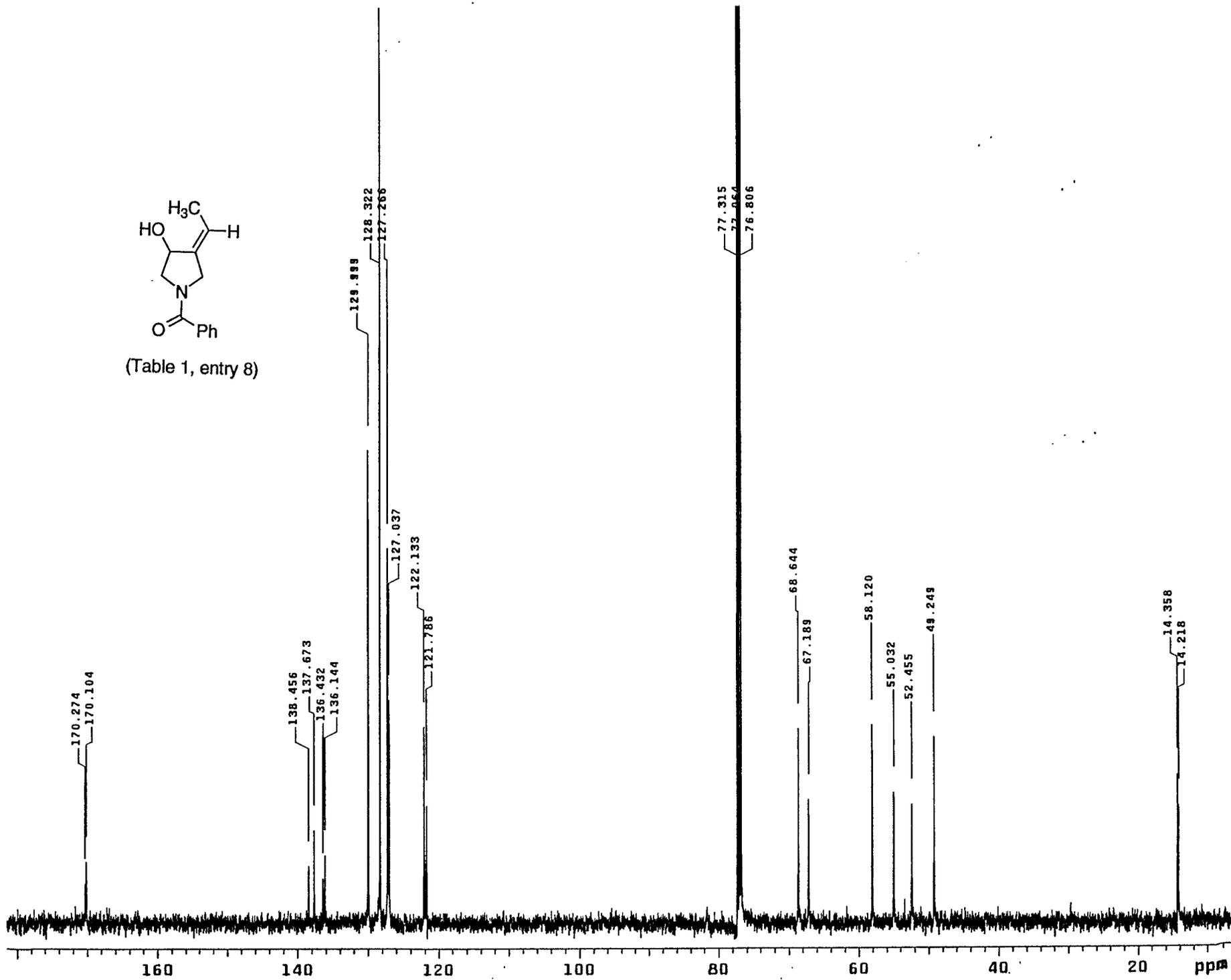
(Table 1, entry 8)



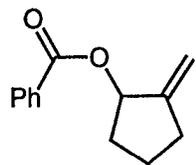
S17



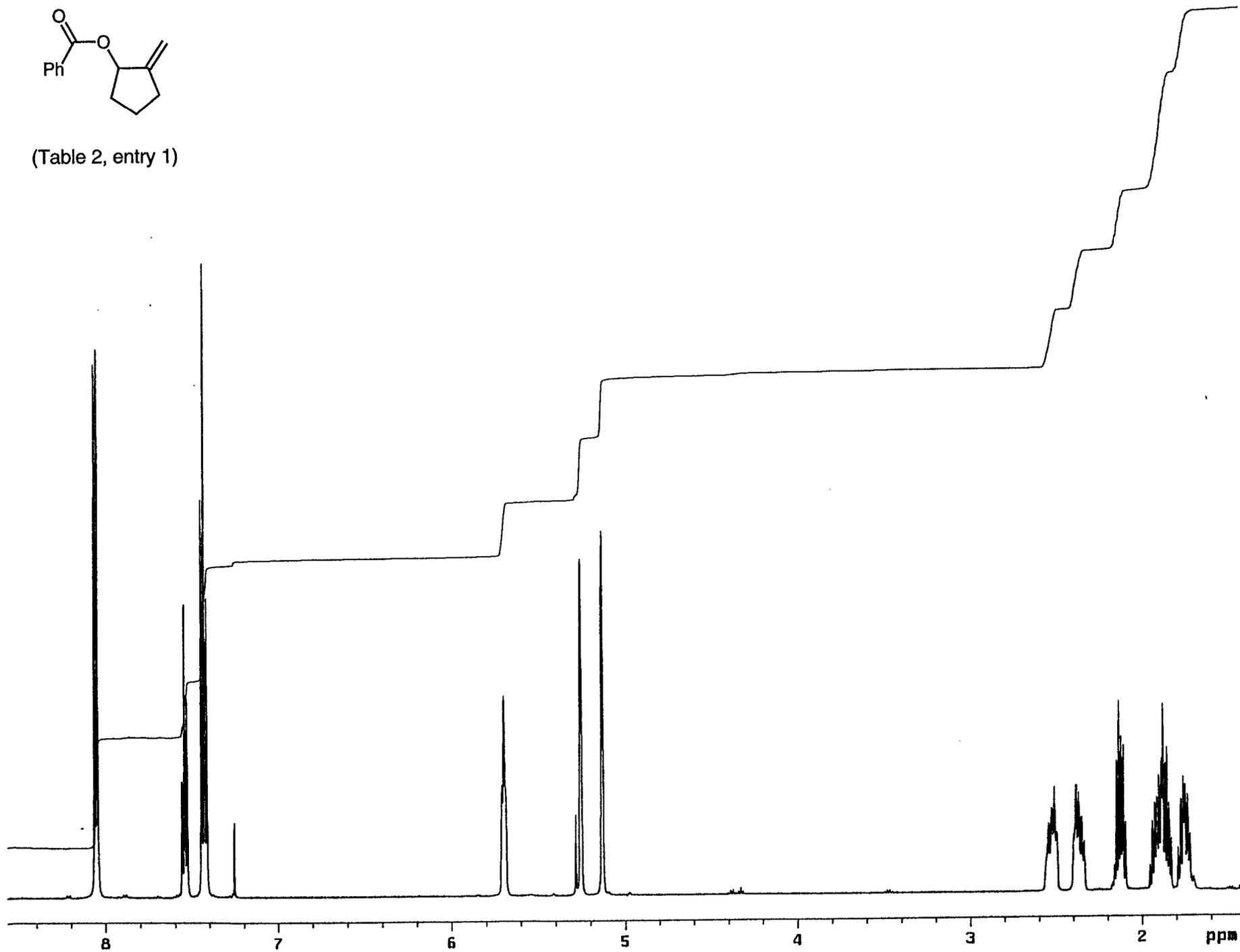
(Table 1, entry 8)

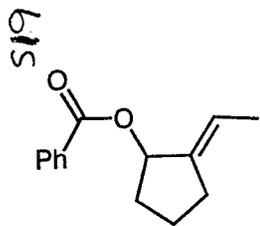


S18

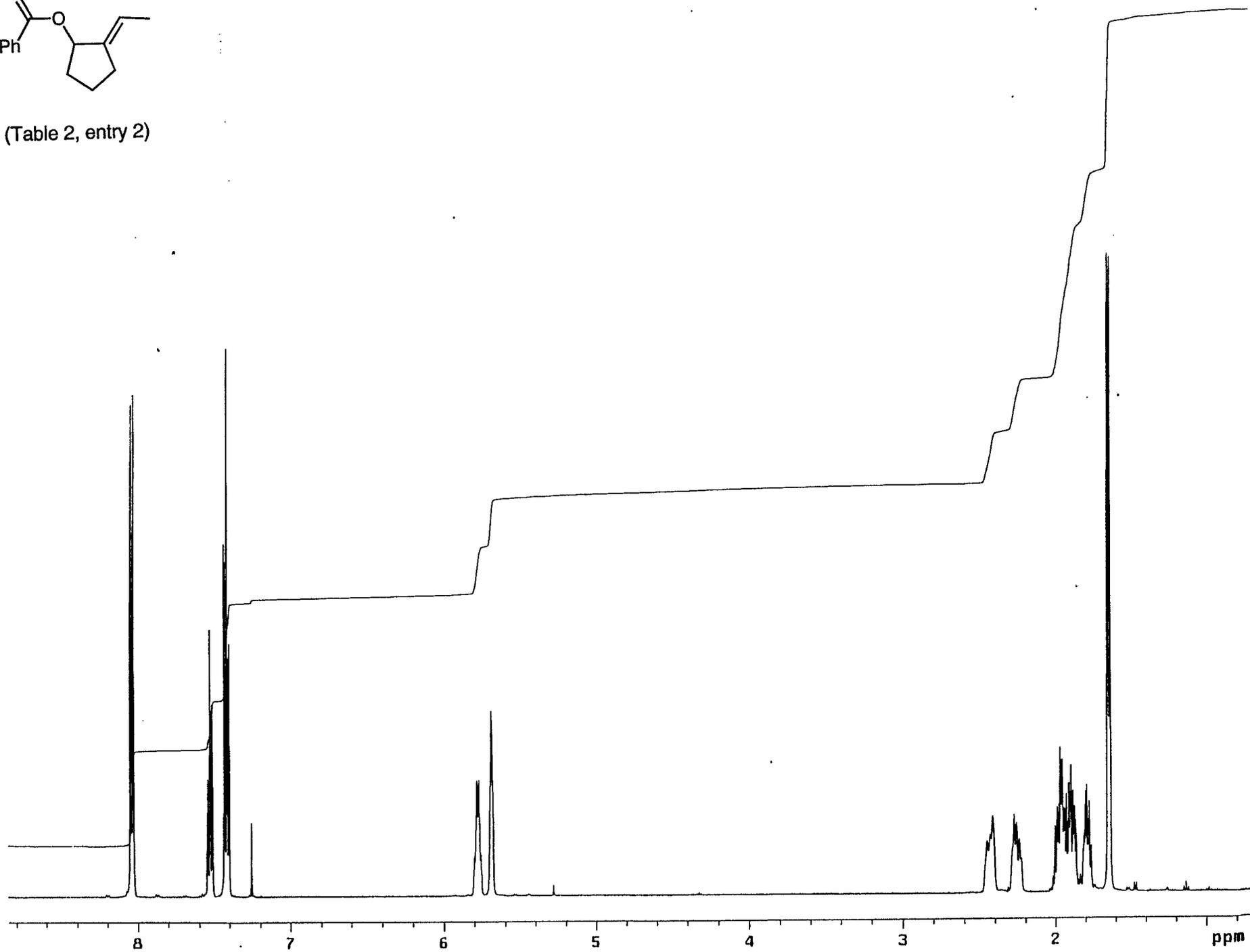


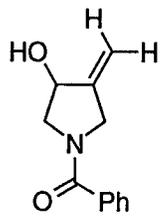
(Table 2, entry 1)



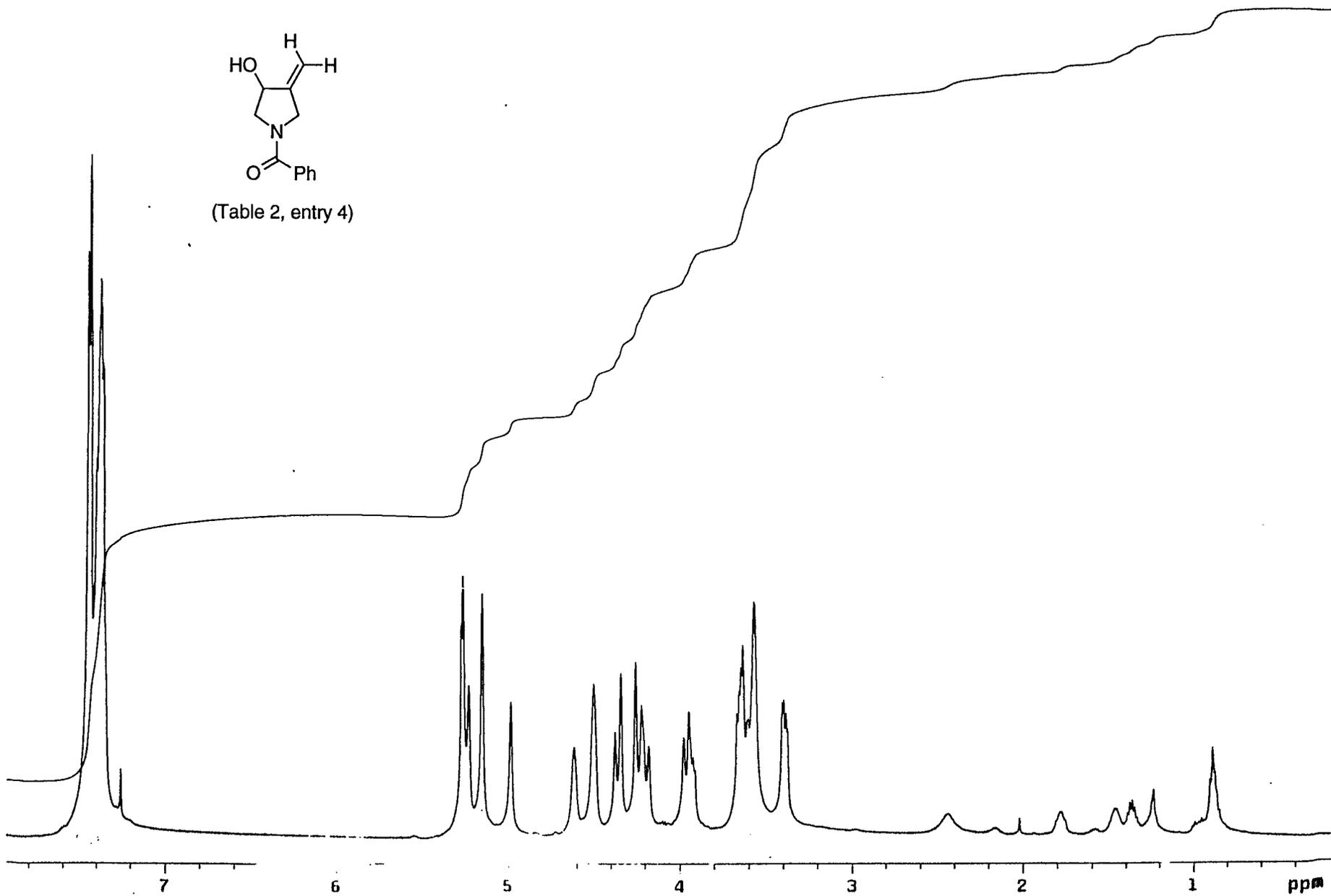


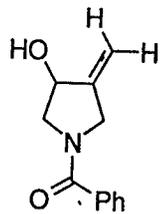
(Table 2, entry 2)



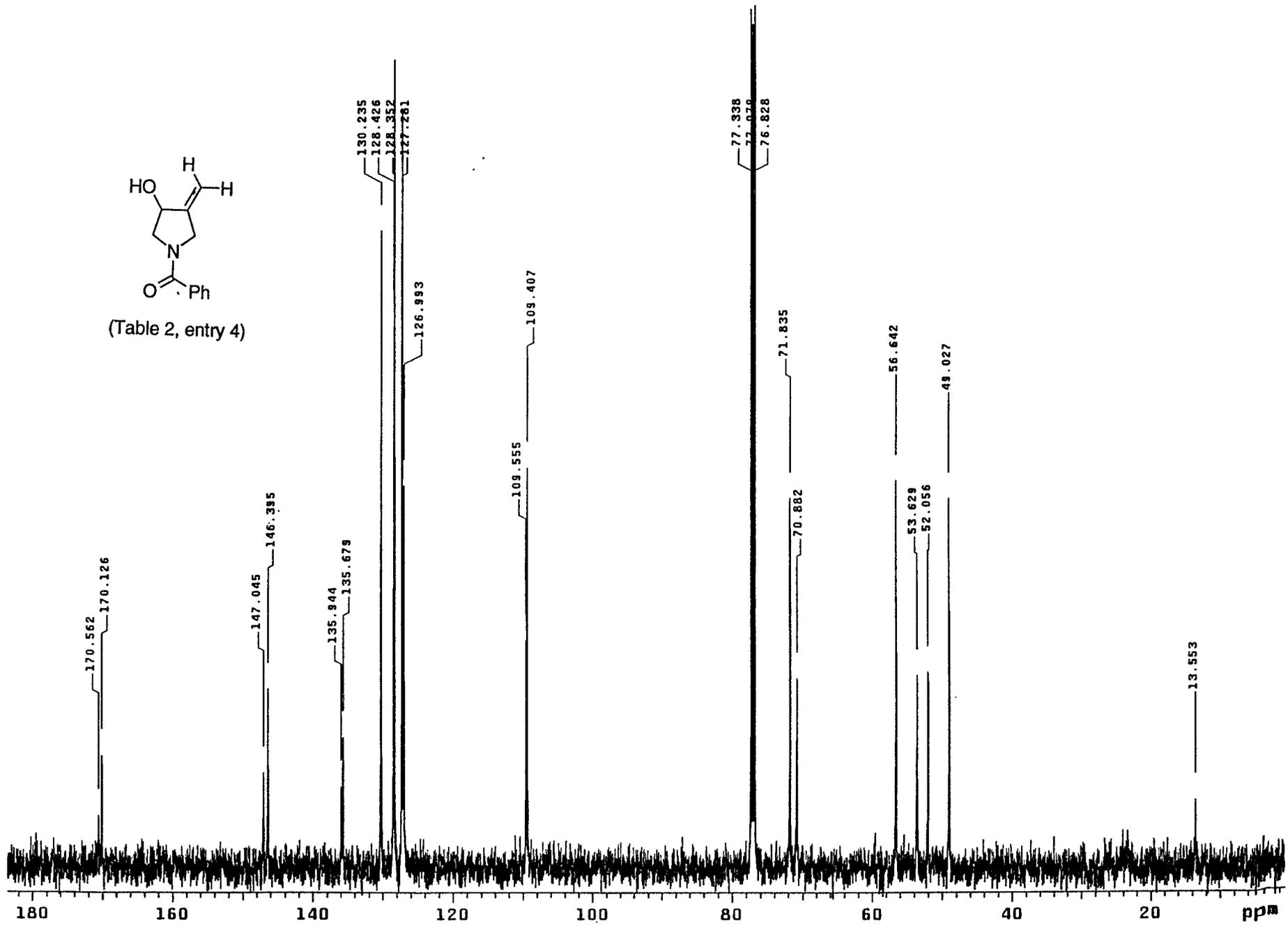


(Table 2, entry 4)

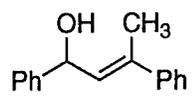




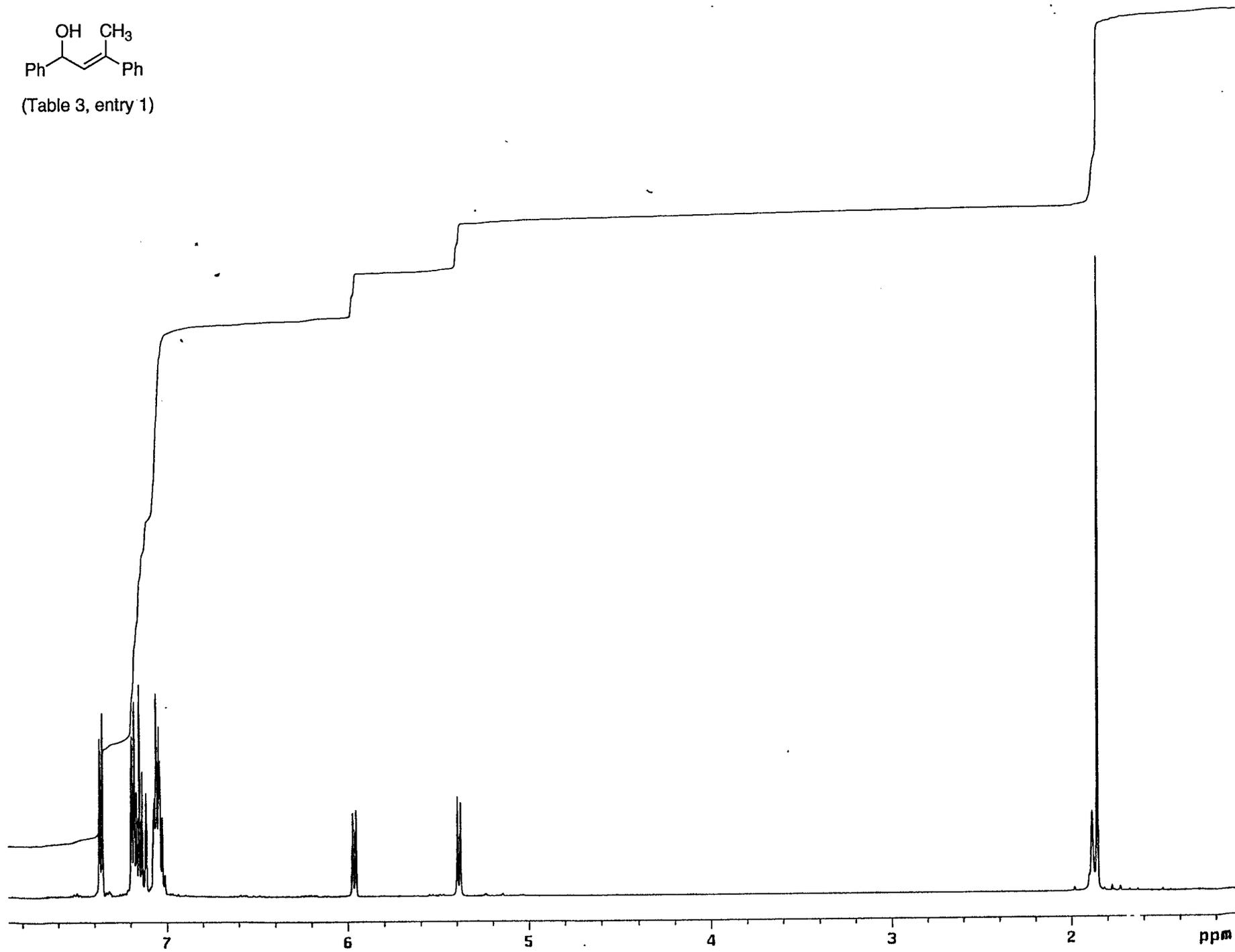
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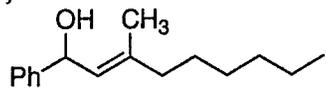
S22



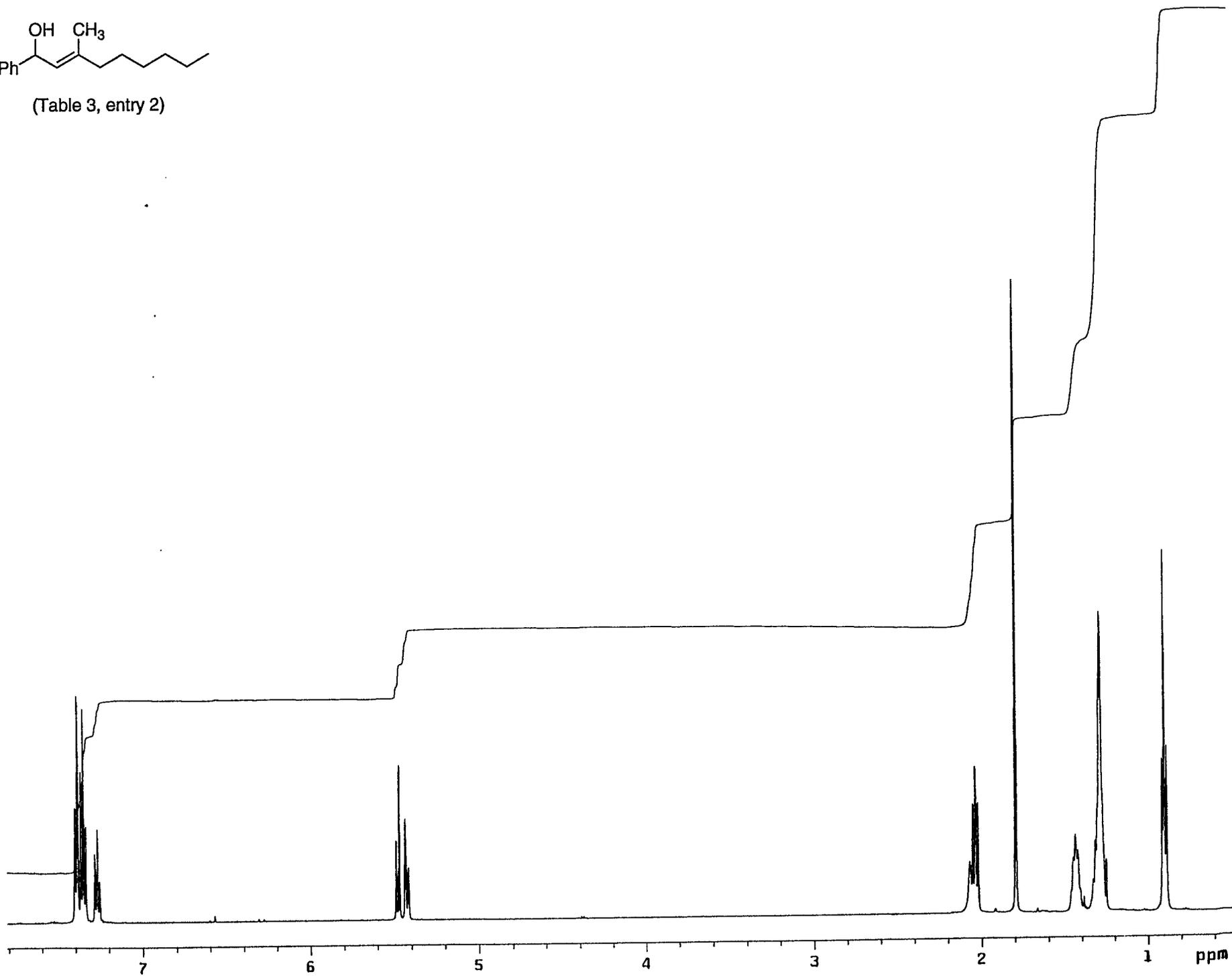
(Table 3, entry 1)



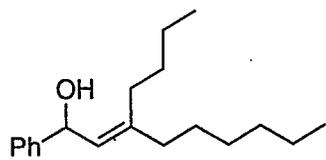
S23



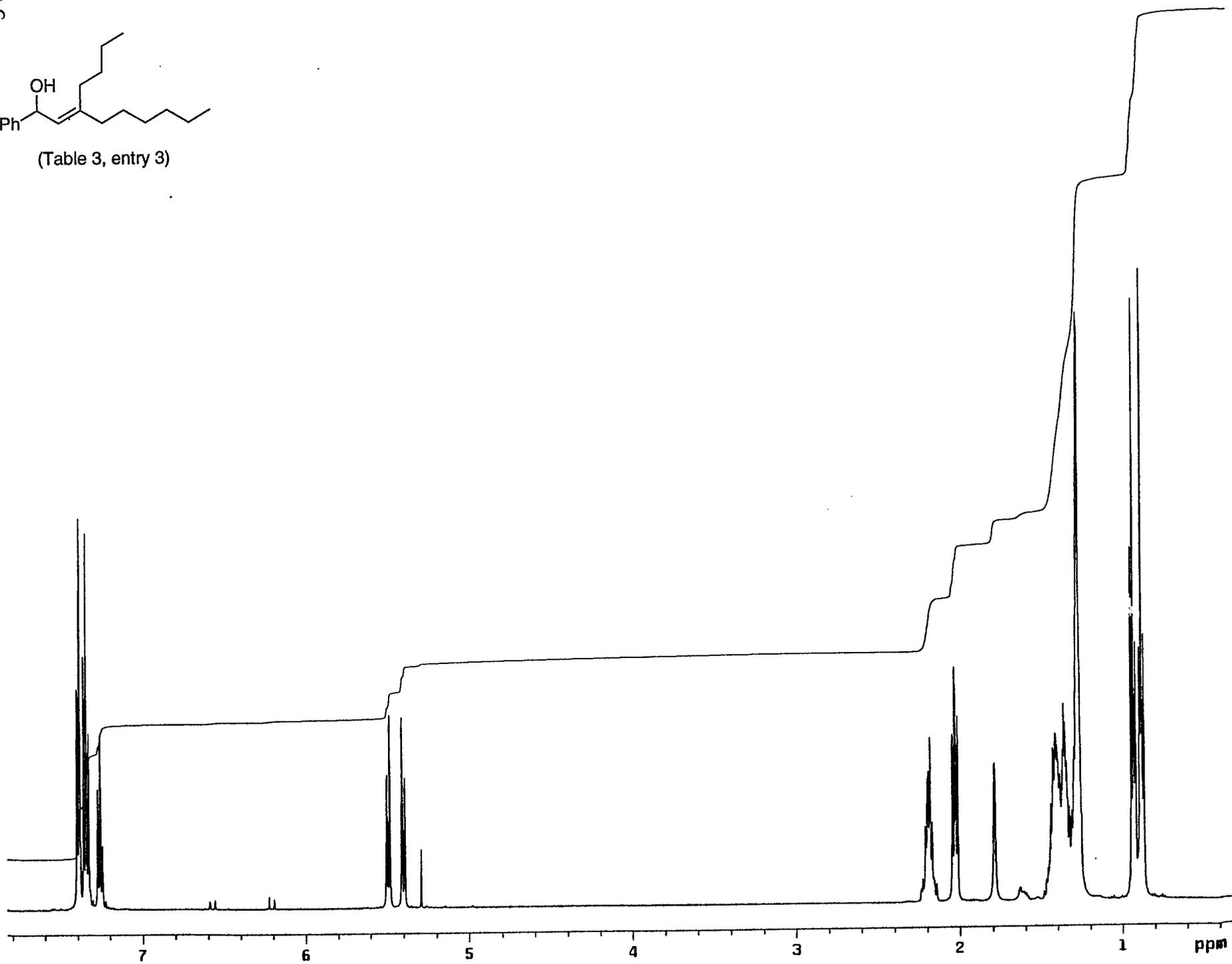
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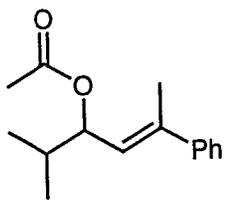
S24



(Table 3, entry 3)



S25



(Table 3, entry 4) .

