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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

J. Am. Chem. Soc., 1997, 119(38), 9065-9066, DOI: [10.1021/ja9719182](https://doi.org/10.1021/ja9719182)

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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 Et_2Zn (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 ($\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ pH=8 buffer/ Et_2O) followed by flash chromatography on SiO_2 .

General Procedure C for Three Component Couplings. A 1.0 M solution of ZnCl_2 (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 ($\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ pH=8 buffer/ Et_2O) followed by flash chromatography on SiO_2 . 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), ZnCl_2 (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 CH_2Cl_2 (10 mL), to produce, after flash chromatography (19:1 hexanes: EtOAc), 300 mg (70 %) of product as a colorless oil. ^1H NMR (500 MHz, CDCl_3) 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), $n\text{-BuLi}$ (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 $^\circ\text{C}$ ^1H and ^{13}C NMR analysis. ^1H NMR (500 MHz, CDCl_3) δ 7.3-7.5 (m, 5H), 5.63 (m, 1 H_{major}), 5.45 (m, 1 H_{minor}), 4.88 (m, 1 H_{minor}), 4.76 (m, 1 H_{major}), 4.56 (d, J = 16.0 Hz, 1 H_{major}), 4.28 (d, J = 14.0 Hz, 1 H_{minor}), 4.06 (d, J = 16.5 Hz, 1 H_{major}), 3.98 (d, J = 13.5 Hz, 1 H_{major}), 3.87 (d, J = 13.5 Hz, 1 H_{minor}), 3.70 (dd, J = 14.0, 4.5 Hz, 1 H_{minor}), 3.60 (m, 1 H_{both}), 2.99 (br s, 1 H_{minor}), 2.80 (br s, 1 H_{major}), 1.77 (m, 3 H_{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

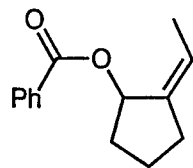
144.3, 139.1, 128.4, 127.2, 125.9, 70.6, 39.6, 31.7, 29.0, 27.6, 22.7, 16.7, 14.1; IR (film) 3354 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{16}\text{H}_{24}\text{O}$ 232.1827, found 232.1828 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{O}$: C, 82.70; H, 10.41. Found: C, 82.57; H, 10.43. 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.

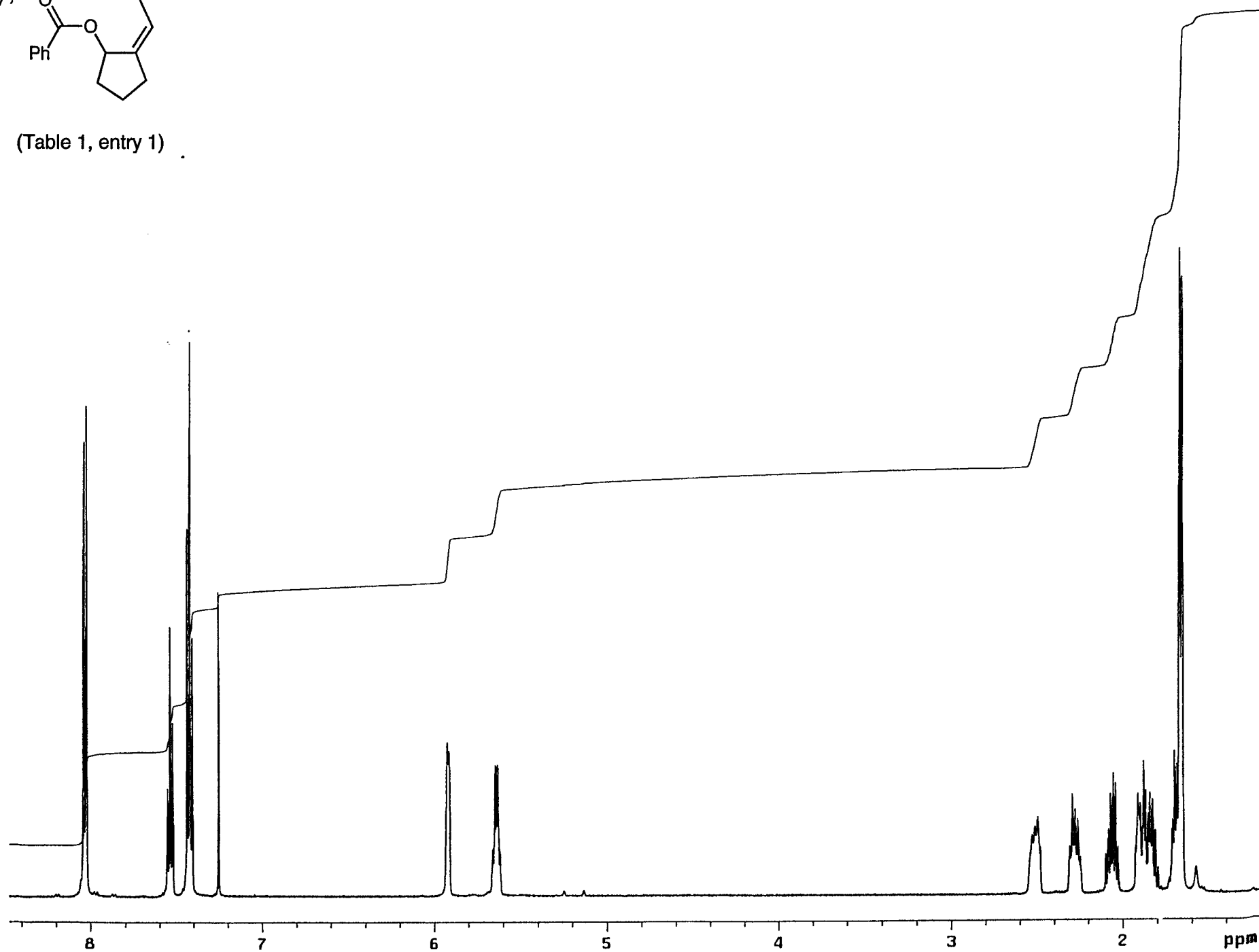
(E)-2-Methyl-5-phenyl-4-hexenyl-3-acetate (Table 3, entry 4). Following general procedure C, isobutyraldehyde (100 μL , 1.0 mmol), phenylacetylene (280 μL , 3.1 mmol), MeLi (3.2 mL, 4.5 mmol of a 1.4 M ether solution), ZnCl_2 (340 mg, 2.5 mmol), and $\text{Ni}(\text{COD})_2$ (54 mg, 0.20 mmol) were employed, 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,

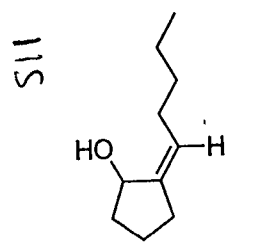
$J = 9.3, 1.3$ Hz, 1H), 5.46 (dd, $J = 9.5, 7.0$ Hz, 1H), 2.16 (d, $J = 1.5$ Hz, 3H), 2.07 (s, 3H), 1.96 (octet, $J = 6.8$ Hz, 1H), 0.98 (d, $J = 7.0$ Hz, 3H), 0.95 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (125 MHz) δ 170.5, 143.0, 139.5, 128.2, 127.3, 125.9, 125.0, 76.1, 32.8, 21.3, 18.4, 18.0, 16.8; IR (film) 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

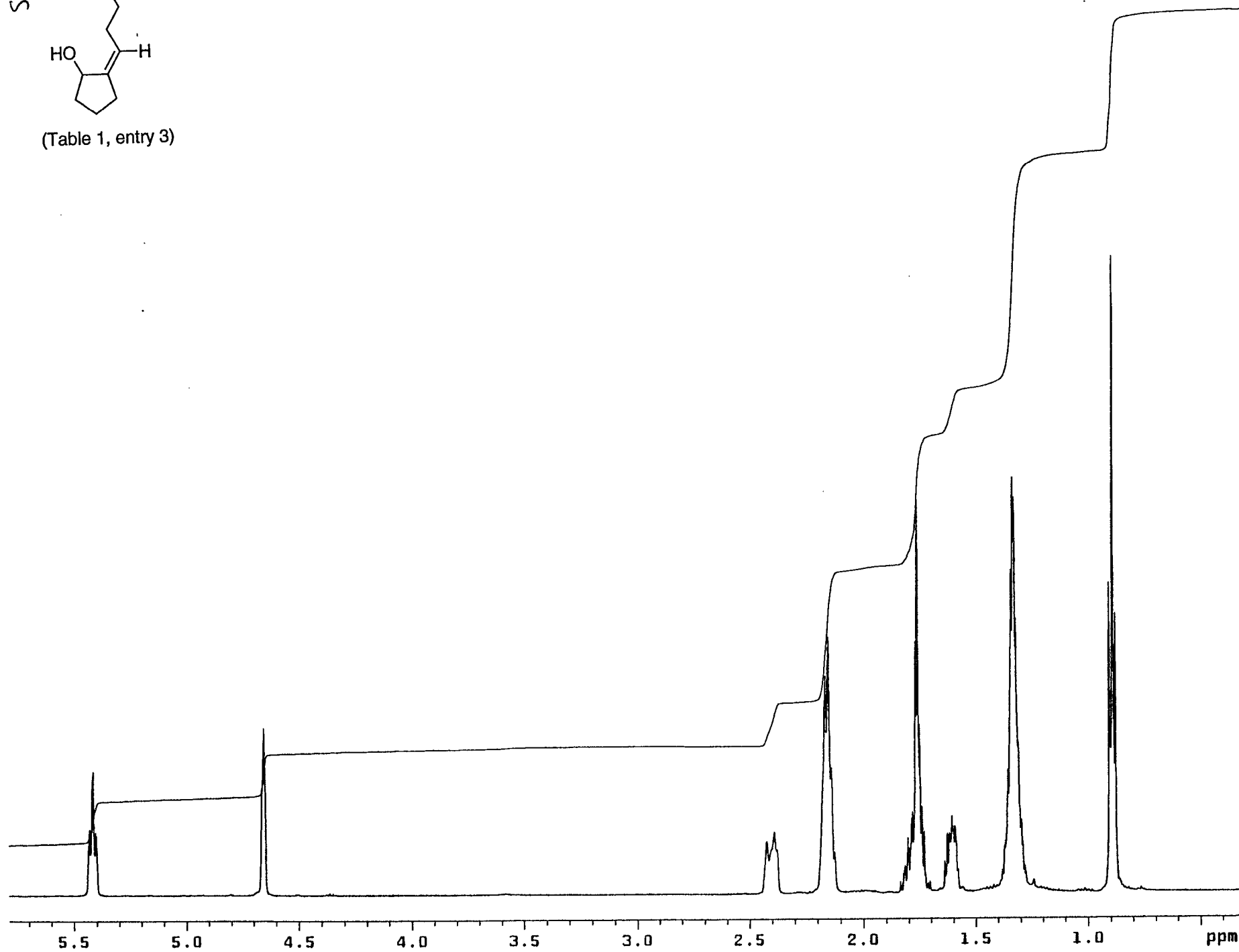


(Table 1, entry 1)

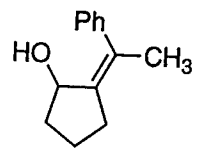




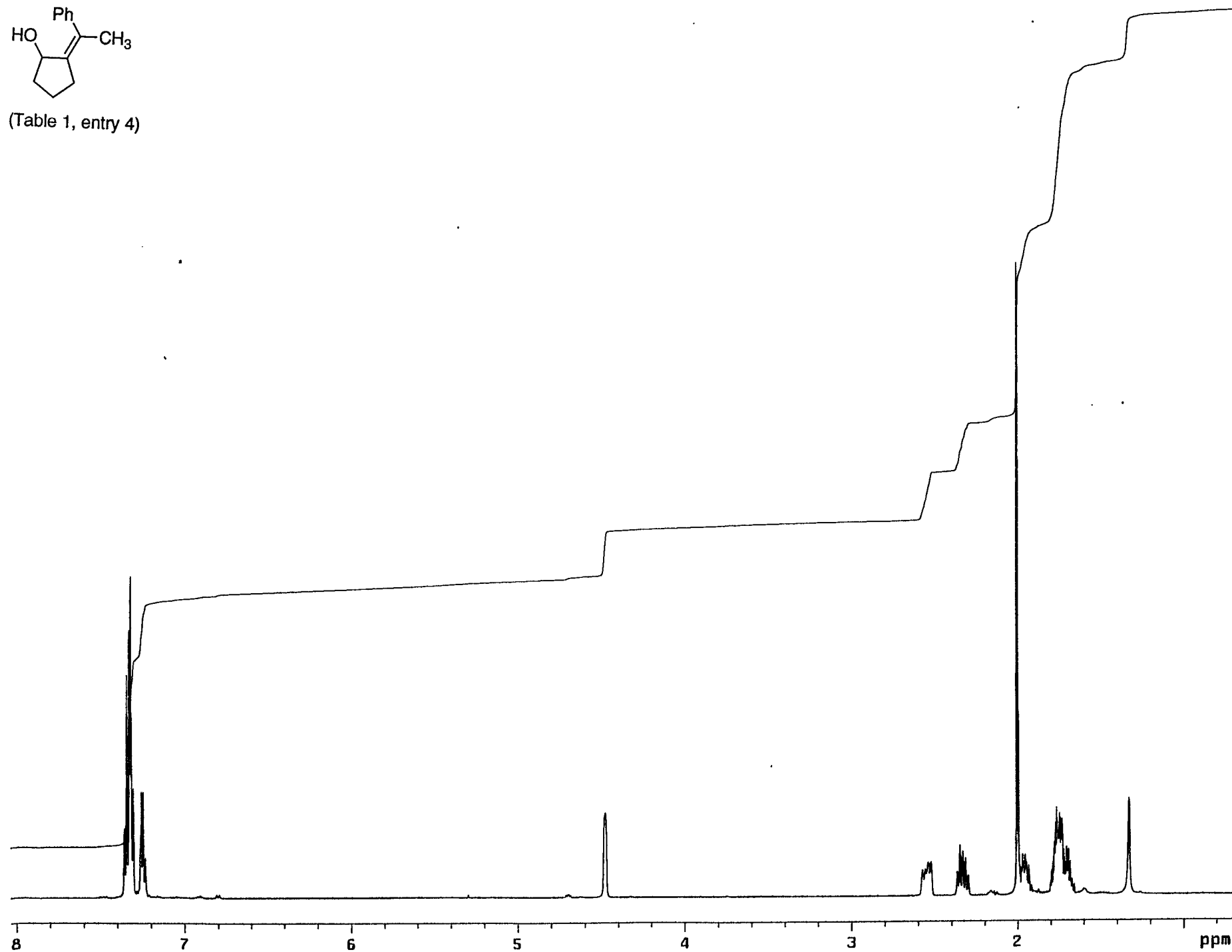
(Table 1, entry 3)



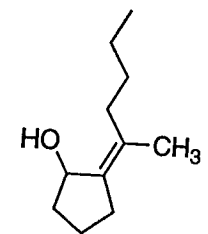
S12



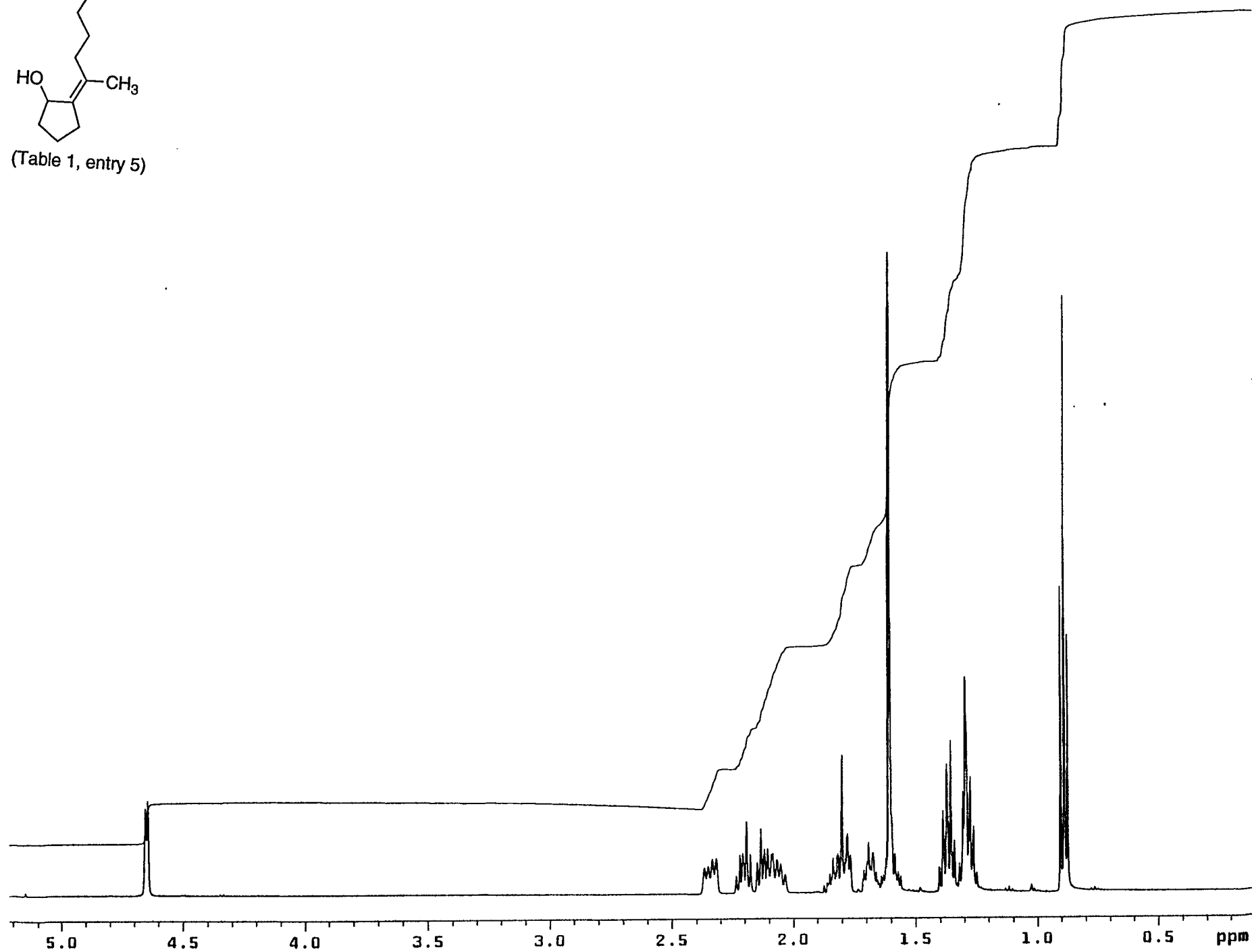
(Table 1, entry 4)



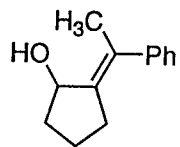
S13



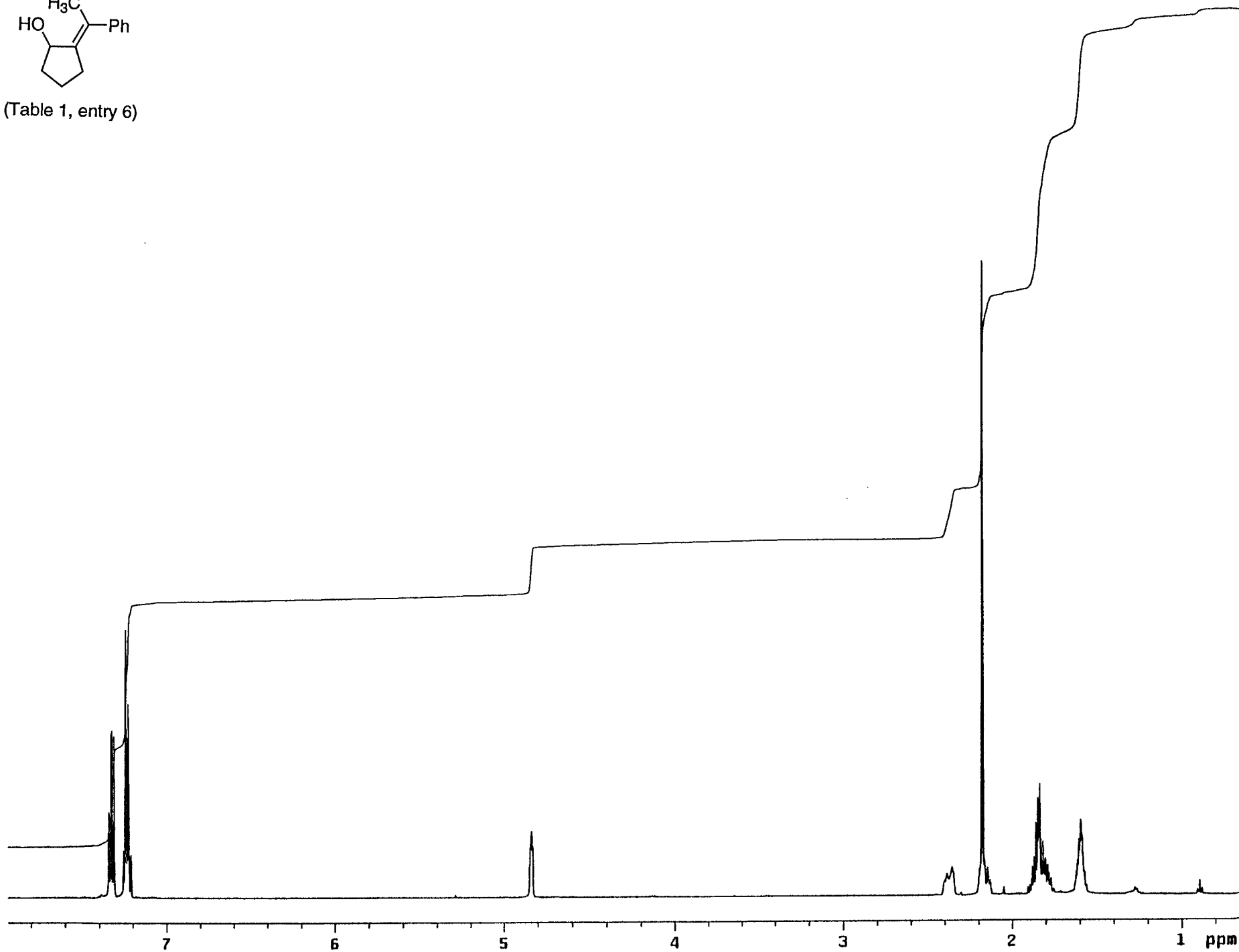
(Table 1, entry 5)



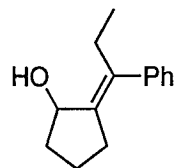
S14



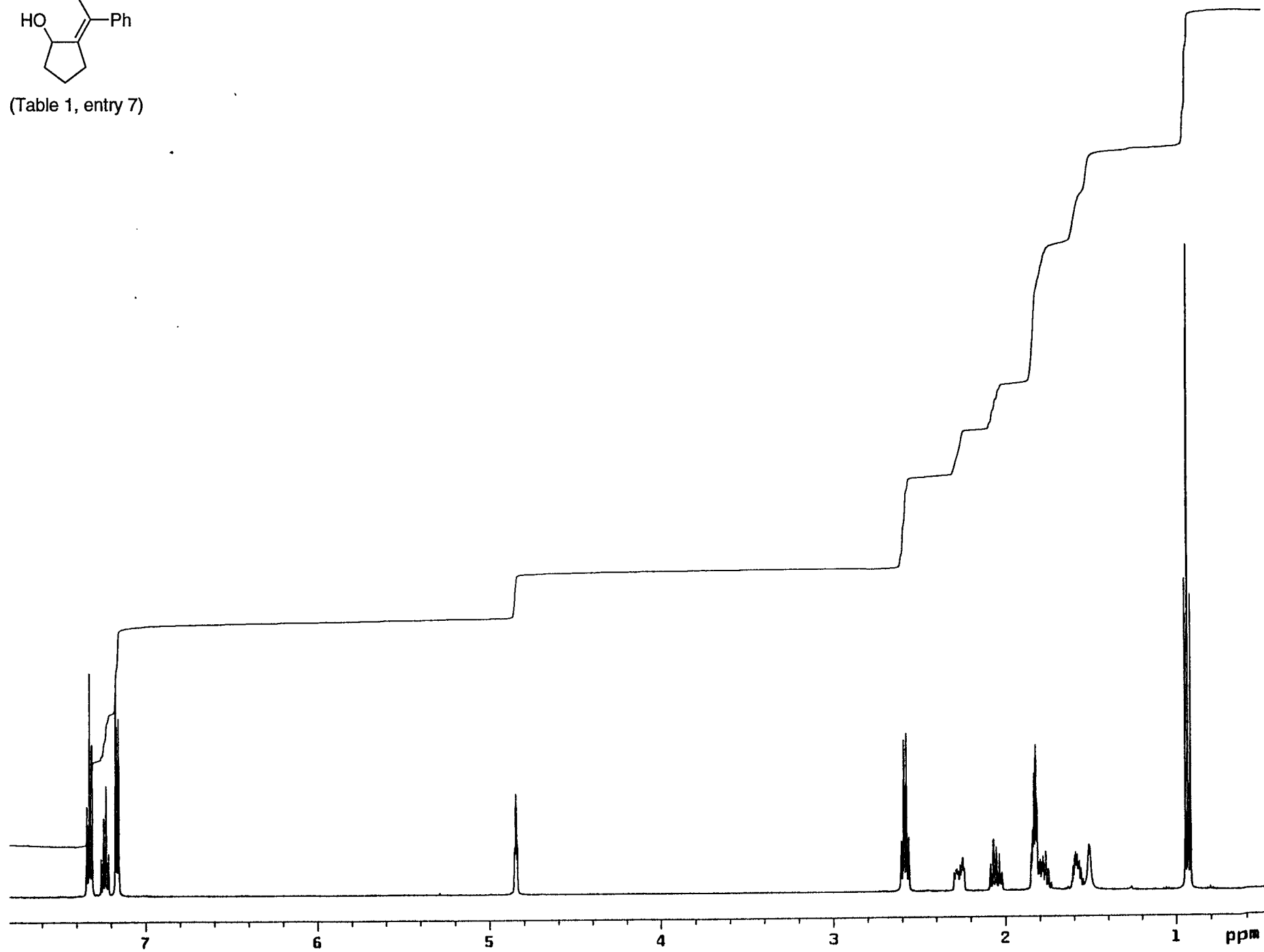
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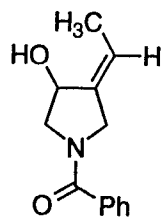
S15



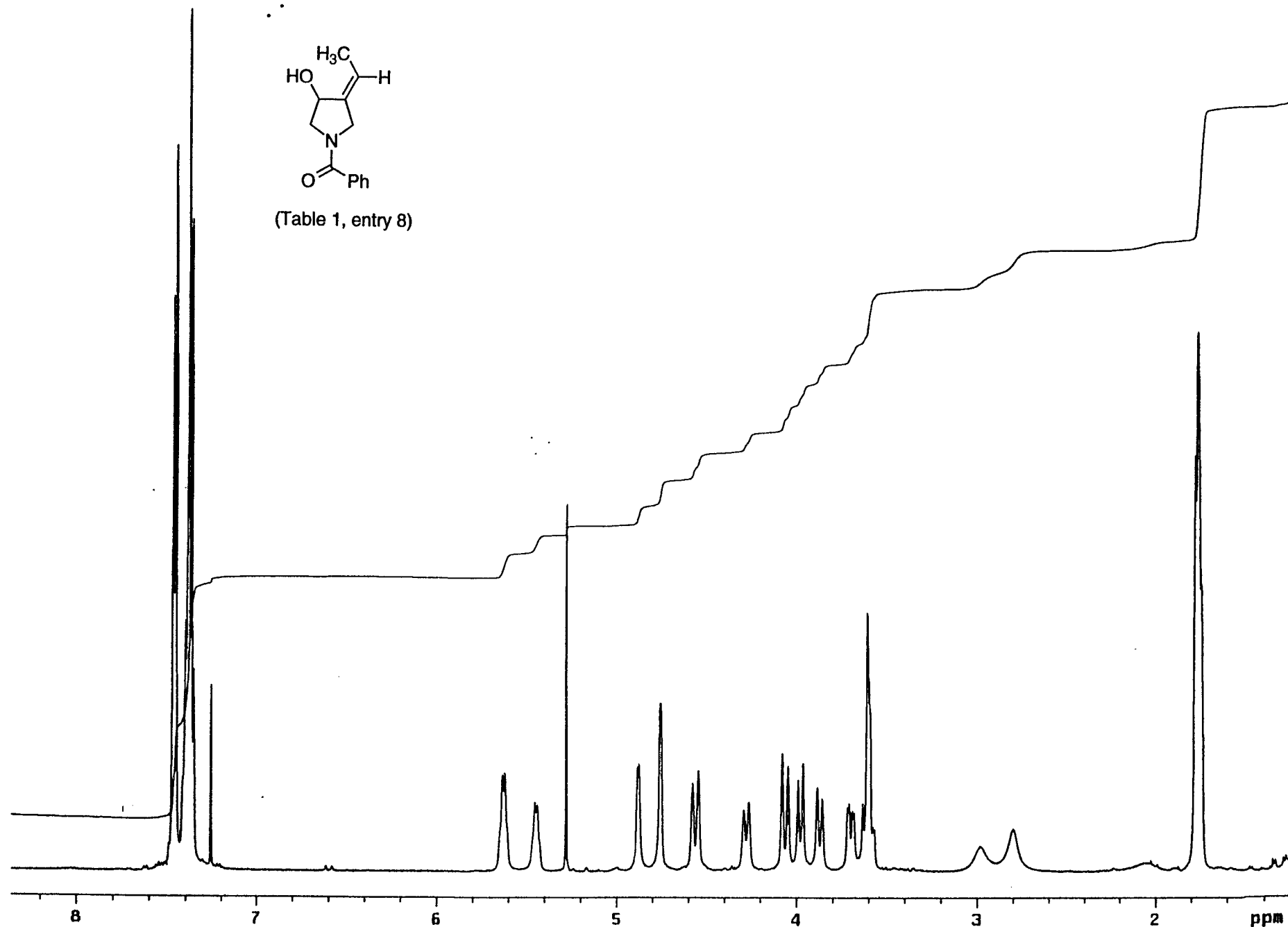
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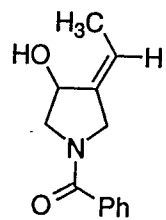
S16



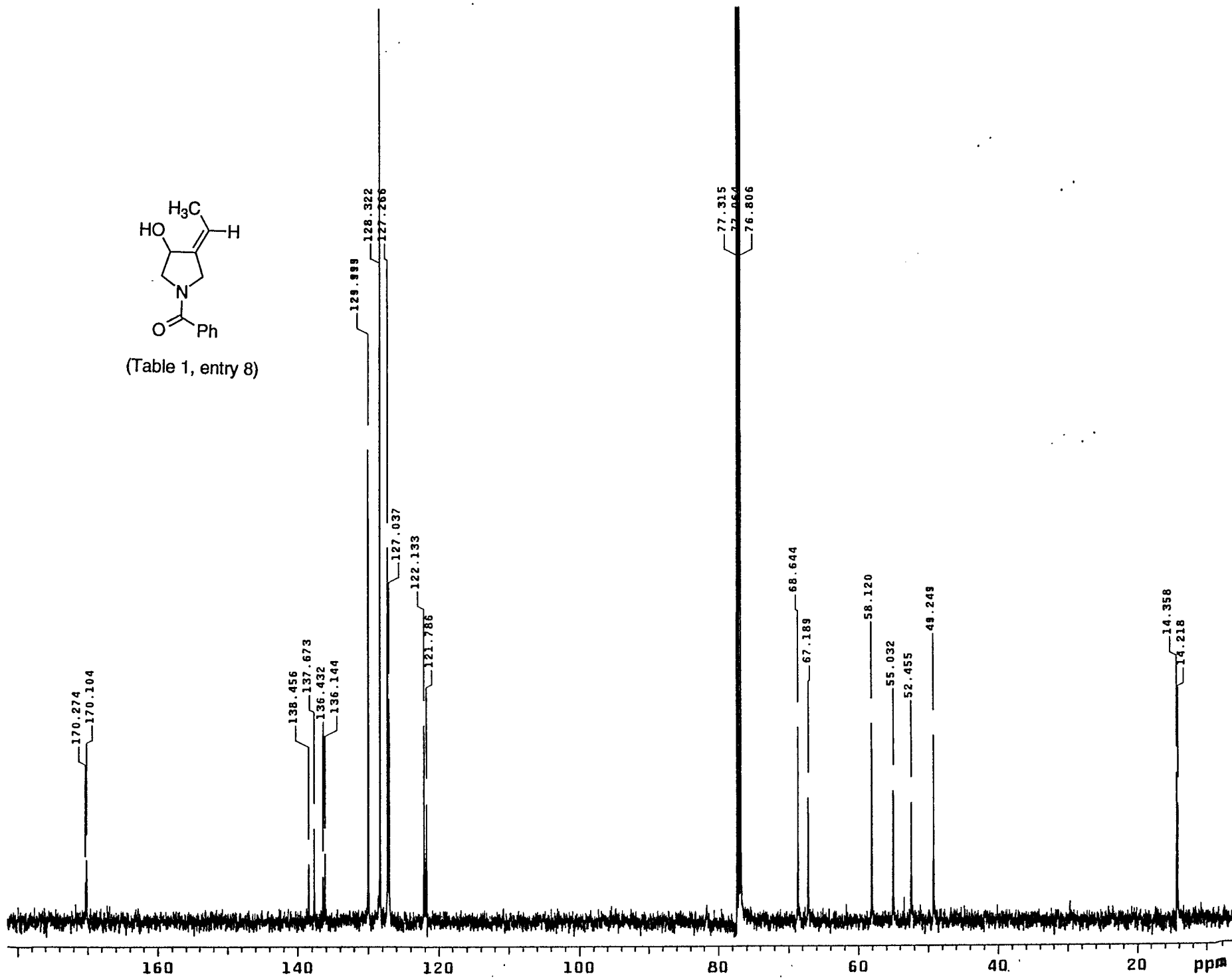
(Table 1, entry 8)



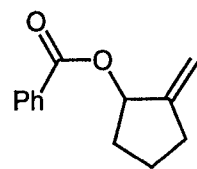
S17



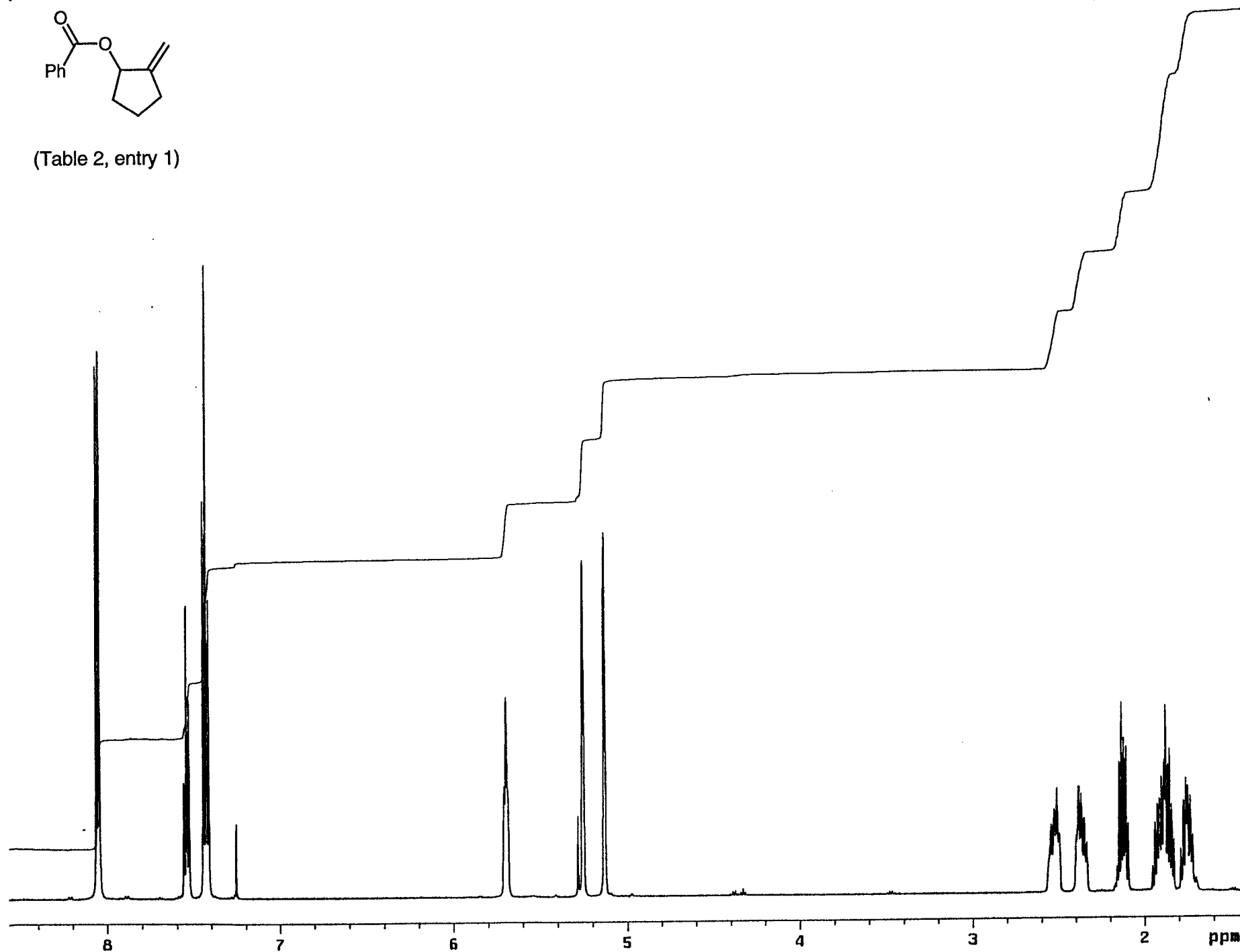
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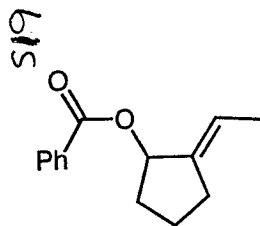


S18

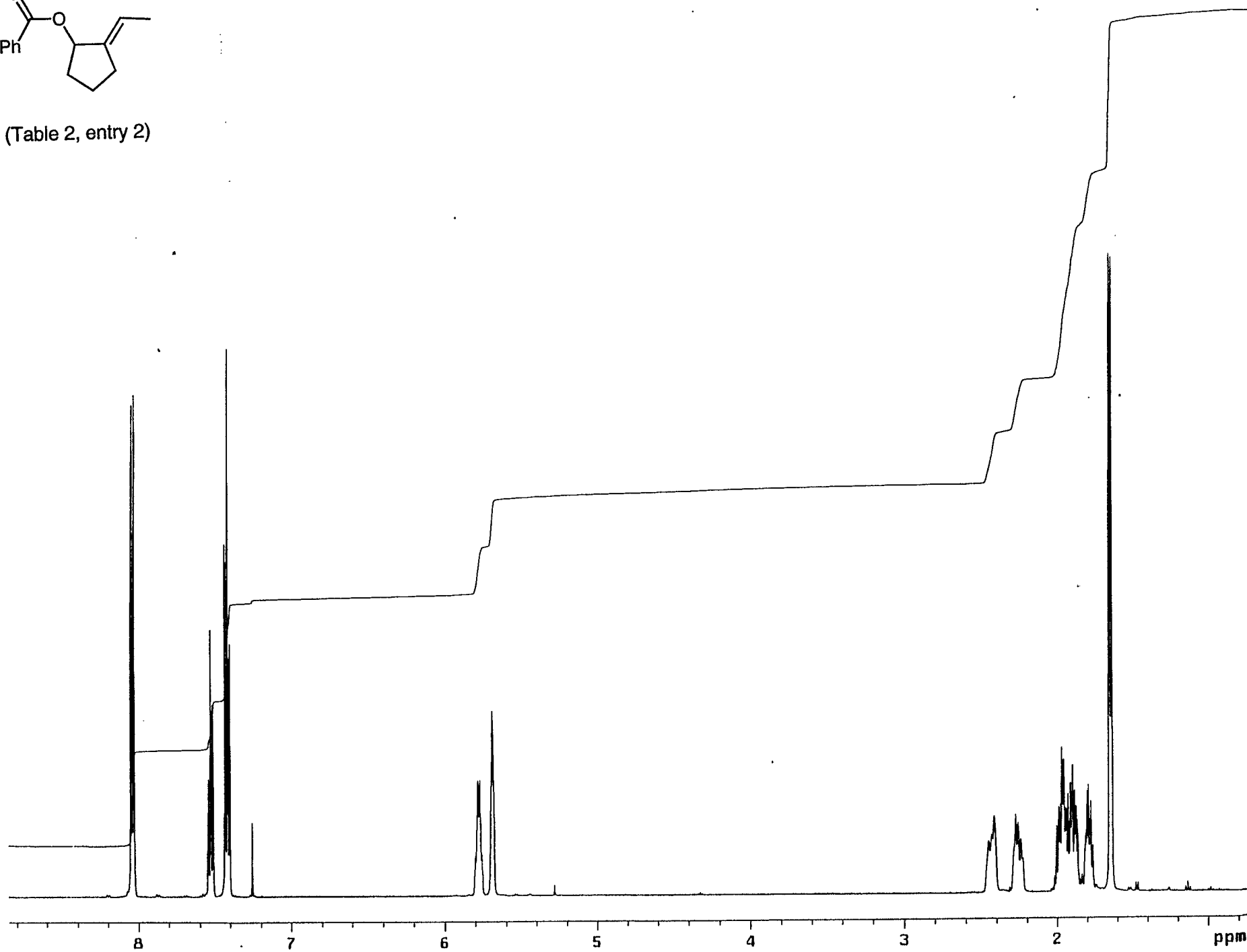


(Table 2, entry 1)

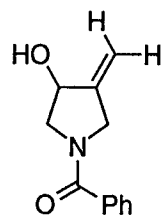




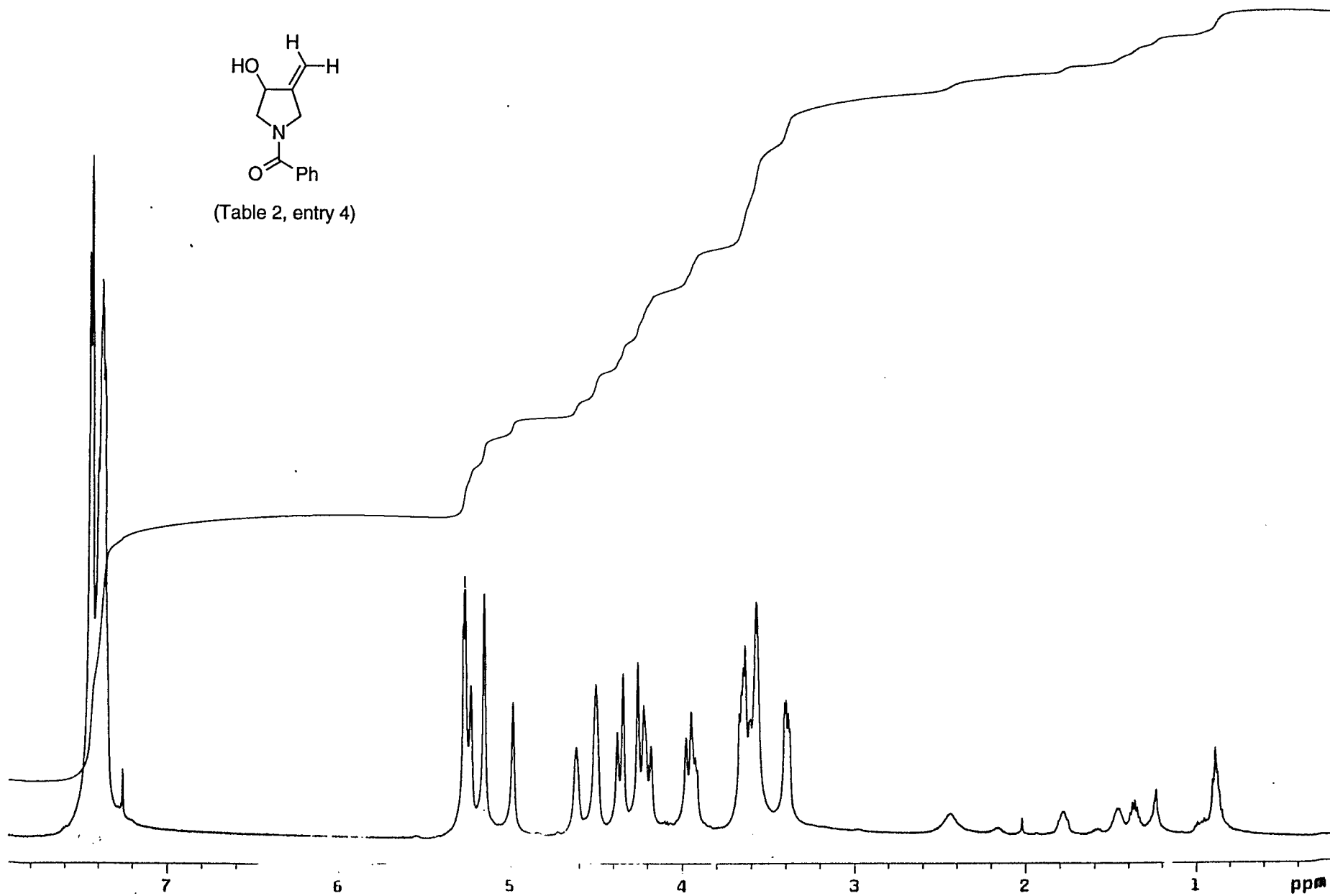
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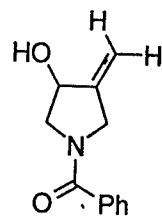
S20



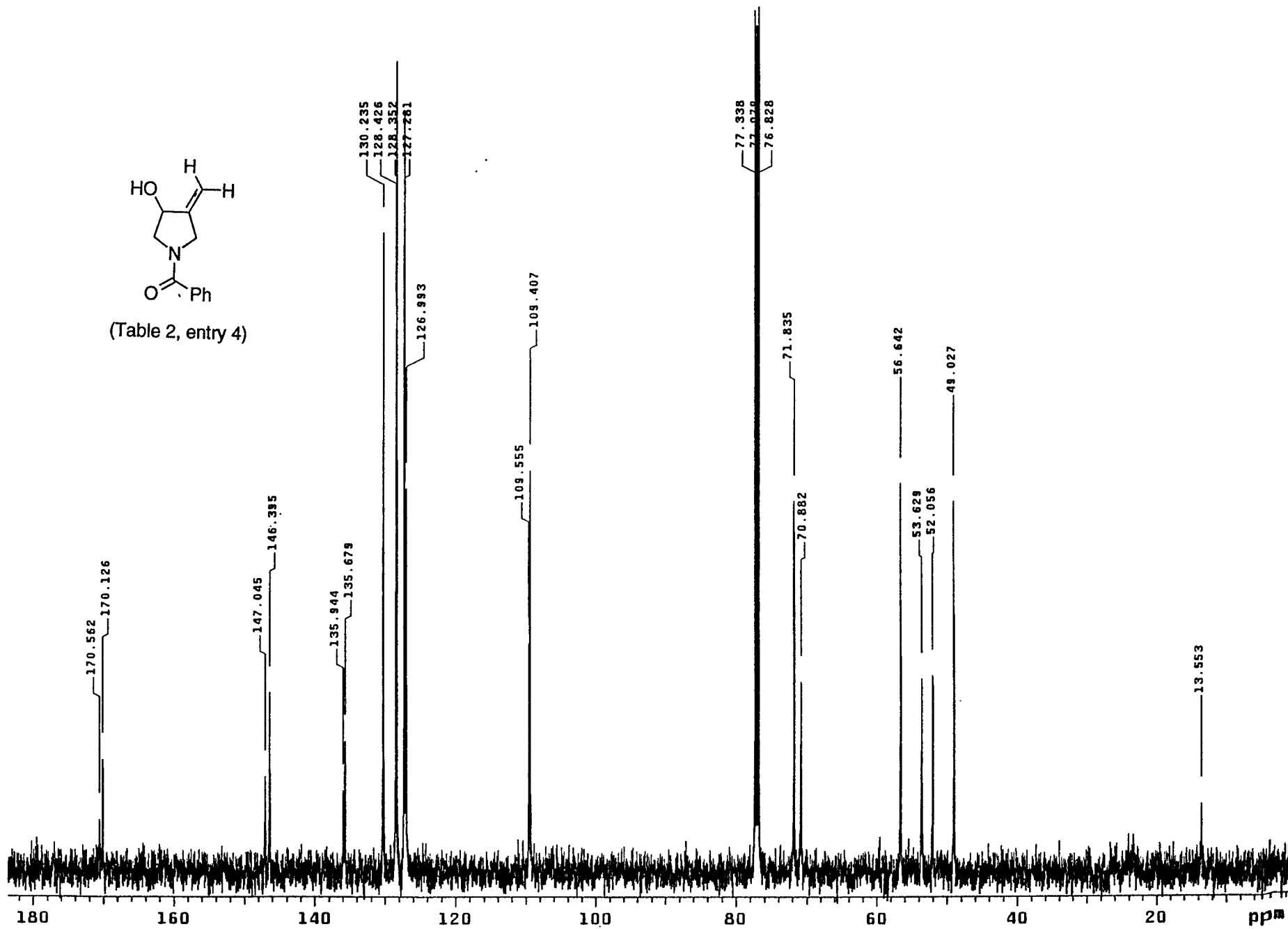
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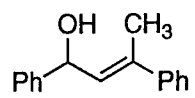
S21



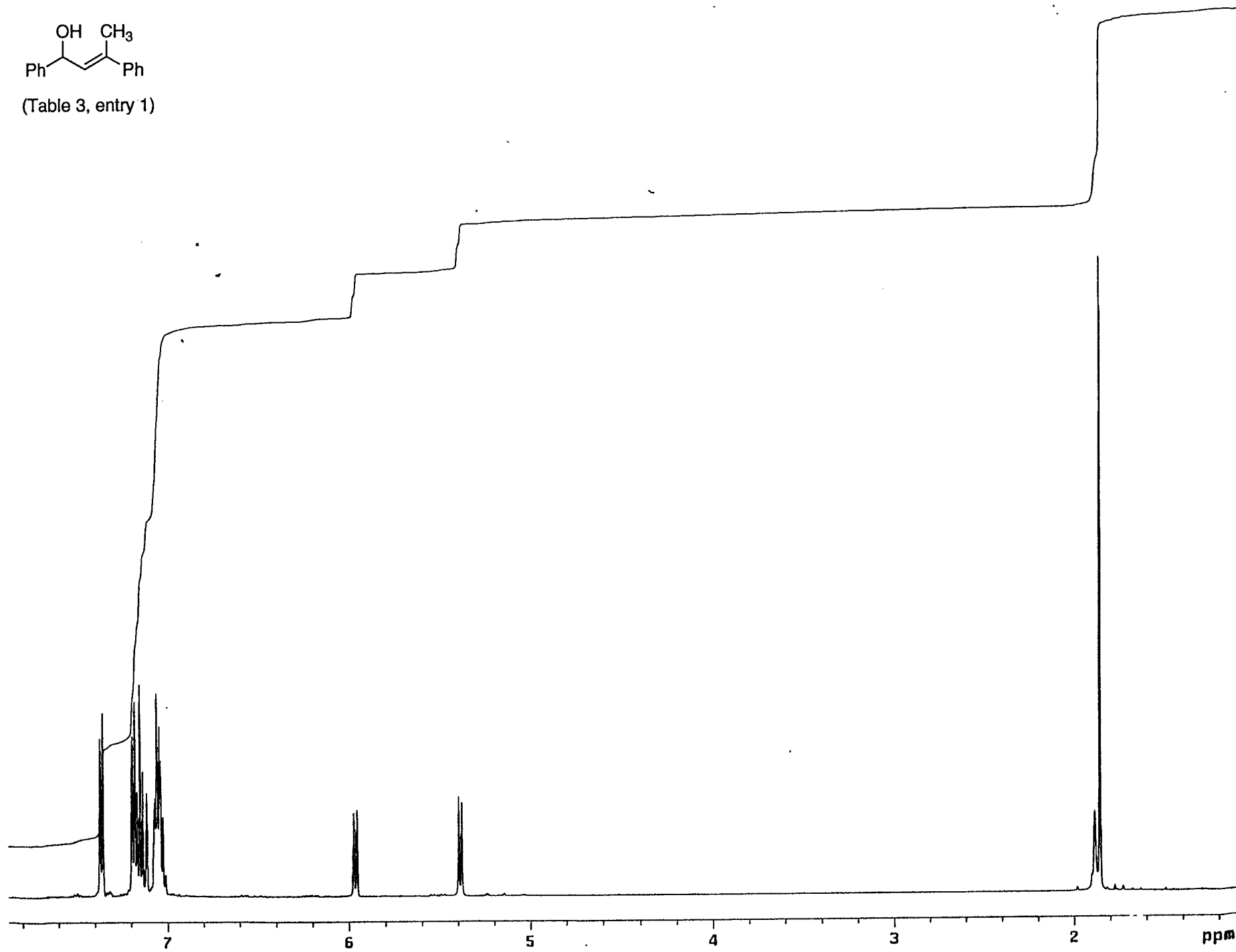
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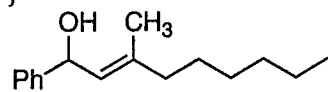
S22



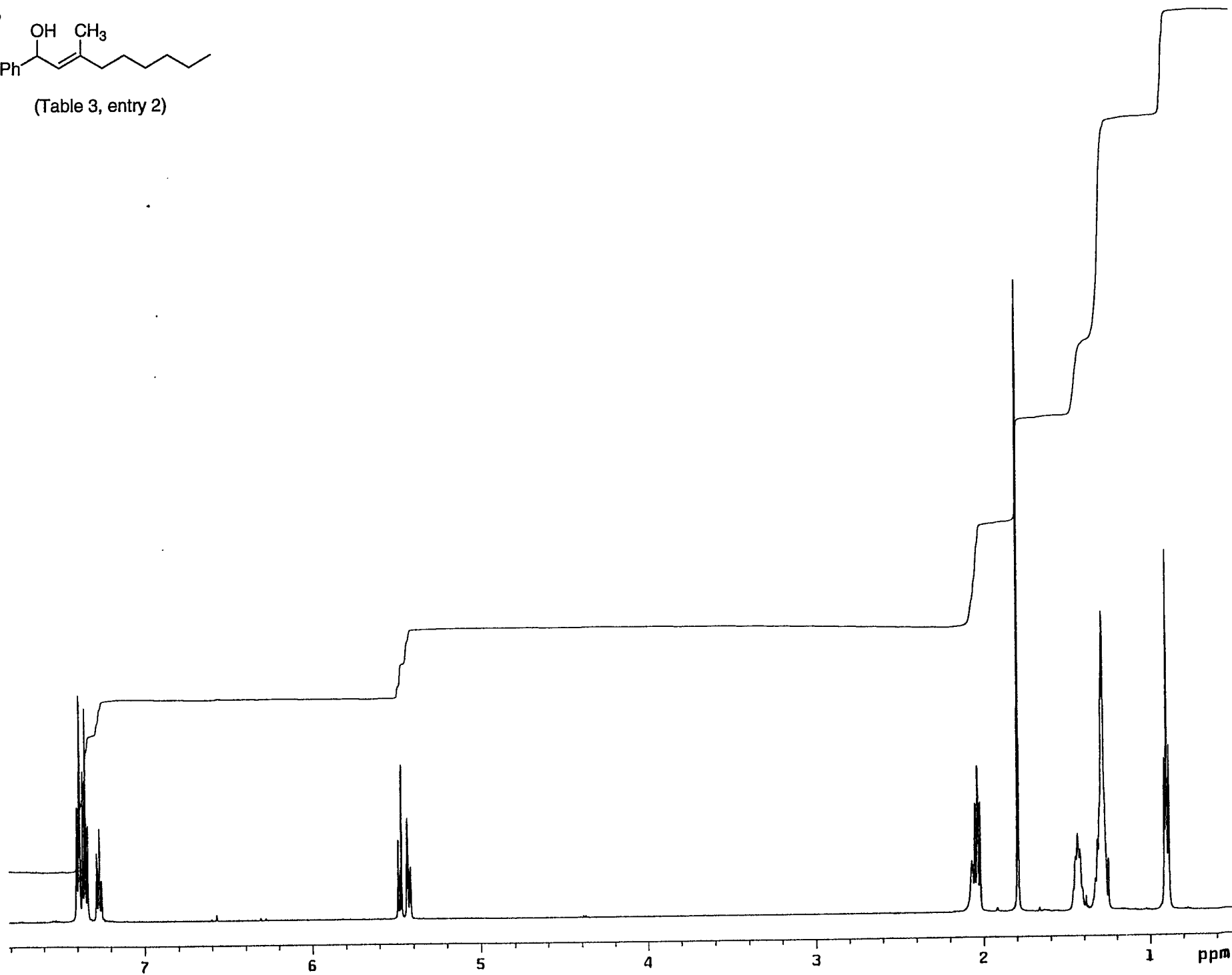
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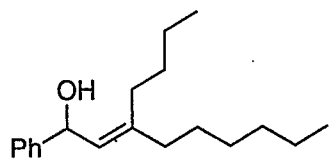
S23



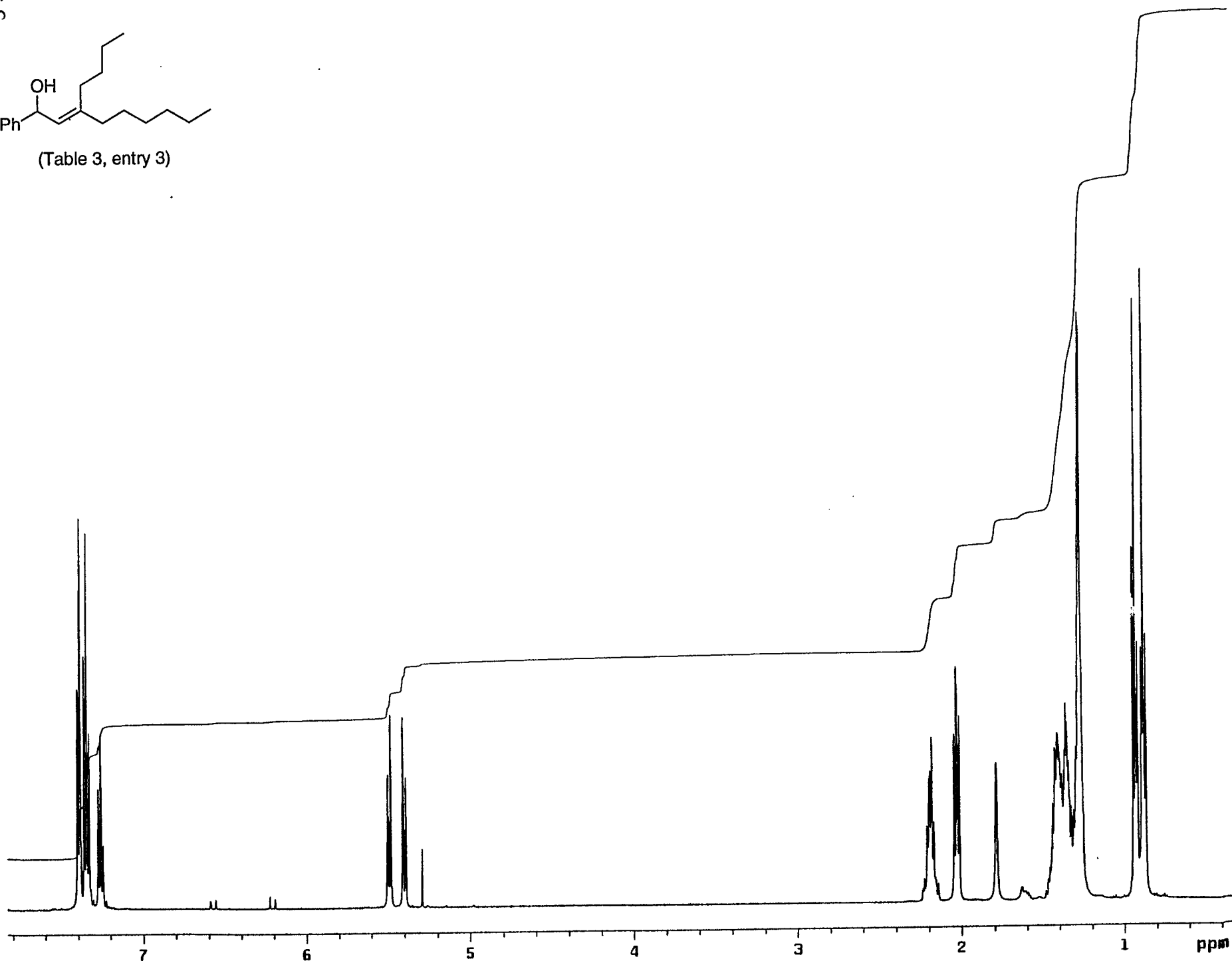
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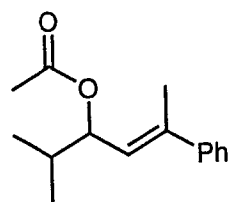
S24



(Table 3, entry 3)



S25



(Table 3, entry 4) .

