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Supporting Information

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Iridium- and Ruthenium-Catalyzed Sequential Reactions: Asymmetric α-Alkylative Reduction of Ketones with Alcohols

Gen Onodera,† Yoshiaki Nishibayashi,*, †† and Sakae Uemura†

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto, 615-8510, Japan

Institute of Engineering Innovation, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo, 113-8656, Japan

General Method. ^{1}H NMR (270 MHz) spectra were recorded using $CDCl_3$ as solvent. Optical rotations were measured on a JASCO DIP-1000. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use. Ruthenium complex (**1**) was prepared according to our previous procedure.[S1]

† Kyoto University

†† The University of Tokyo

Reaction of Ketone with Primary Alcohol in the Presence of $[IrCl(cod)]_2$ and 1. A typical experimental procedure for the reaction of acetophenone (**2a**) with 1-butanol (**3a**) catalyzed by $[IrCl(cod)]_2$ and $[RuCl_2(PPh_3)$(ip-FOXAP)] (**1**) is described below. In a 20 mL flask were placed KOH (5.8 mg, 0.10 mmol), $[IrCl(cod)]_2$ (13.1 mg, 0.020 mmol), and PPh_3 (21.4 mg, 0.082 mmol) under N_2. After the addition of **2a** (240.1 mg, 2.0 mmol) and **3a** (445.8 mg, 6.0 mmol), the reaction mixture was kept at 100 °C for 4 h. A solution of ^{i}PrOH containing ^{i}PrONa (0.080 mmol) and **1** (18.4 mg, 0.020 mmol) was added into the reaction mixture and then the reaction mixture was kept at room temperature for 2 h. For work-up, 1 *N* HCl aq. (0.5 mL) was added to the reaction mixture. The solvent was concentrated under reduced pressure, and then the residue was extracted with water (50 mL) and diethyl ether (50 mL x 3). The organic solution was dried over anhydrous $MgSO_4$. For isolation, the extract was concentrated under reduced pressure by an aspirator, and the residue was purified by silica gel column chromatography (10% EtOAc/*n*-hexane) to yield 267.7 mg (1.50 mmol, 75%, 94% ee) of (*R*)-1-phenyl-1-hexanol (**4aa**) as a white solid, which was identified by comparing its spectroscopic data with that in the literature.[S2] $[\alpha]^{28}_D$ +35.3 (c 1.04, $CHCl_3$). ^{1}H NMR δ 0.85-0.90 (m, 3H), 1.29-1.43 (m, 6H), 1.71-1.79 (m, 2H), 1.82 (d, 1H, *J* = 3.3 Hz), 4.64-4.70 (m, 1H), 7.24-7.36 (m, 5H). The ee value was determined by HPLC analysis with a Chiralcel OD column (eluent: *n*-hexane/2-propanol = 98/2, flow rate: 0.5 mL/min, column temperature: 30 °C, retention time: 34.72 min (*R*) and 46.60 min (*S*)). The absolute configuration was determined by comparison of the value of the optical rotation with that reported in literature ($[\alpha]^{24}_D$ –35.0 (c 0.88, $CHCl_3$), 92% ee (*S*)).[S3]

1-(4-Methylphenyl)-1-hexanol (4ba).[S4] Yield 72%. 98% ee. A white solid. The ee value was determined by HPLC analysis with a Chiralpak IA column (eluent: hexane/2-propanol = 98/2, flow rate: 0.5 mL/min, column temperature: 25 °C, retention time: 34.42 min and 38.22 min).

1-(3-Methylphenyl)-1-hexanol (4ca).[S5] Yield 77%. 96% ee. A colorless liquid. The ee value was determined by HPLC analysis with a Chiralcel OD column (eluent: hexane/2-propanol = 98/2, flow rate: 0.5 mL/min, column temperature: 30 °C, retention time: 27.22 min and 36.78 min).

1-(2-Methylphenyl)-1-hexanol (4da).[S6] Yield 52%. 97% ee. A colorless liquid. The ee value was determined by HPLC analysis with a Chiralpak AD column (eluent: hexane/2-propanol = 98/2, flow rate: 1.0 mL/min, column temperature: 30 °C, retention time: 15.70 min and 18.58 min).

(*R*)-1-(4-Methoxylphenyl)-1-hexanol (4ea).[S7] Yield 57%. 97% ee. A white solid. $[\alpha]^{28}_{D}$ +18.8 (c 1.02, CH_3OH). The ee value was determined by HPLC analysis with a Chiralcel OD column (eluent: hexane/2-propanol = 98/2, flow rate: 0.5 mL/min, column temperature: 30 °C, retention time: 51.04 min (*R*) and 57.72 min (*S*)). The absolute configuration was determined by comparison of the value of the optical rotation with that reported in literature ($[\alpha]^{23}_{D}$ +20.8 (c 1.0, CH_3OH), 96% ee (*R*)).[S7]

1-(4-Chlorophenyl)-1-hexanol (4fa).[S8] Yield 58%. 88% ee. A white solid. The ee value was determined by HPLC analysis with a Chiralpak AD column (eluent: hexane/2-propanol = 98/2, flow rate: 0.5 mL/min, column temperature: 30 °C, retention time: 36.32 min and 40.68 min).

1-(4-Fluorophenyl)-1-hexanol (4ga).[S9] Yield 15%. 95% ee. A white solid. The ee value was determined by HPLC analysis with a Chiralpak AD column (eluent: hexane/2-propanol = 97/3, flow rate: 0.5 mL/min, column temperature: 30 °C, retention time: 24.61 min and 27.26 min).

(*R*)-4-Methyl-1-phenyl-1-pentanol (4ab).[S2] Yield 51%. 96% ee. A white solid. $[\alpha]^{29}_{D}$ +36.5 (c 1.01, C_6H_6). The ee value was determined by HPLC analysis with a Chiralcel OD column (eluent: hexane/2-propanol = 98/2, flow rate: 0.5 mL/min, column temperature: 30 °C, retention time: 35.32 min (*R*) and 44.22 min (*S*)). The absolute configuration was determined by comparison of the value of the optical rotation with that reported in literature ($[\alpha]^{25}_{D}$ –33.23 (c 3.41, C_6H_6), 90% ee (*S*)).[S10]

(*R*)-1-Phenyl-1-heptanol (4ac).[S3] Yield 77%. 93% ee. A colorless liquid. $[\alpha]^{30}_{D}$ +32.0 (c 1.02, $CHCl_3$). The ee value was determined by HPLC analysis with a Chiralcel OD column (eluent: hexane/2-propanol = 98/2, flow rate: 0.5 mL/min, column temperature: 30 °C, retention time: 29.70 min (*R*) and 37.75 min (*S*)). The absolute configuration was determined by

comparison of the value of the optical rotation with that reported in literature ($[\alpha]^{24}_{D}$ –29.2 (c 0.89, $CHCl_3$), 92% ee (*S*)).[S3]

5-Methyl-1-phenyl-1-hexanol (4ad).[S2] Yield 79%. 96% ee. A white solid. The ee value was determined by HPLC analysis with a Chiralcel OD column (eluent: hexane/2-propanol = 98/2, flow rate: 0.5 mL/min, column temperature: 30 °C, retention time: 33.19 min and 43.43 min).

^{1}H NMR spectra of the produced alcohols are shown in the following pages (pages S5-S9).

References

[S1] a) Y. Nishibayashi, I. Takei, S. Uemura, M. Hidai, *Organometallics* **1998**, *17*, 3420; b) Y. Nishibayashi, I. Takei, S. Uemura, M. Hidai, M. *Organometallics* **1999**, *18*, 2291.

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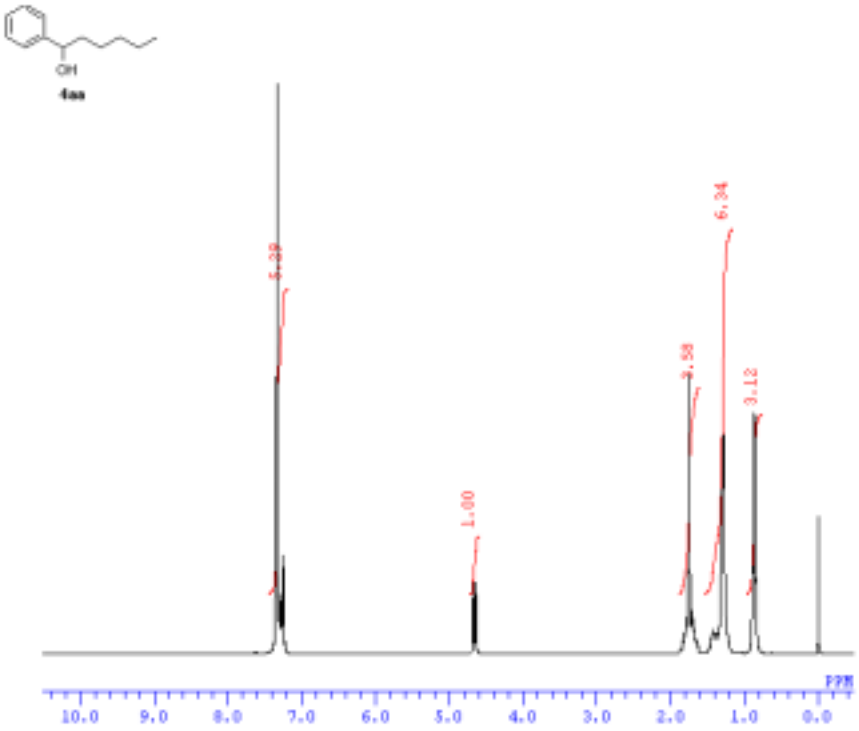


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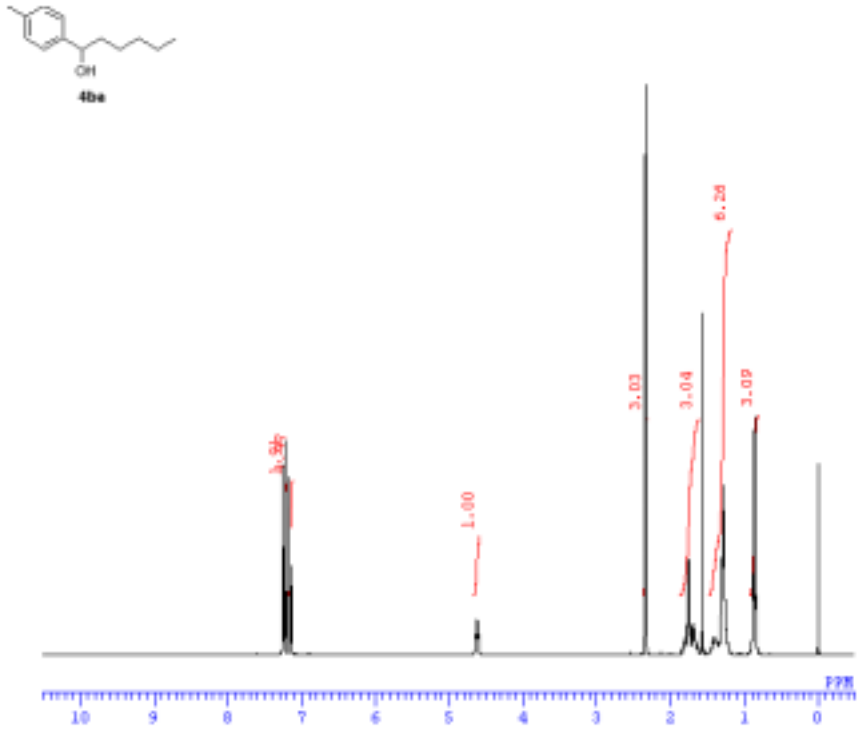


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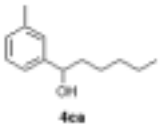

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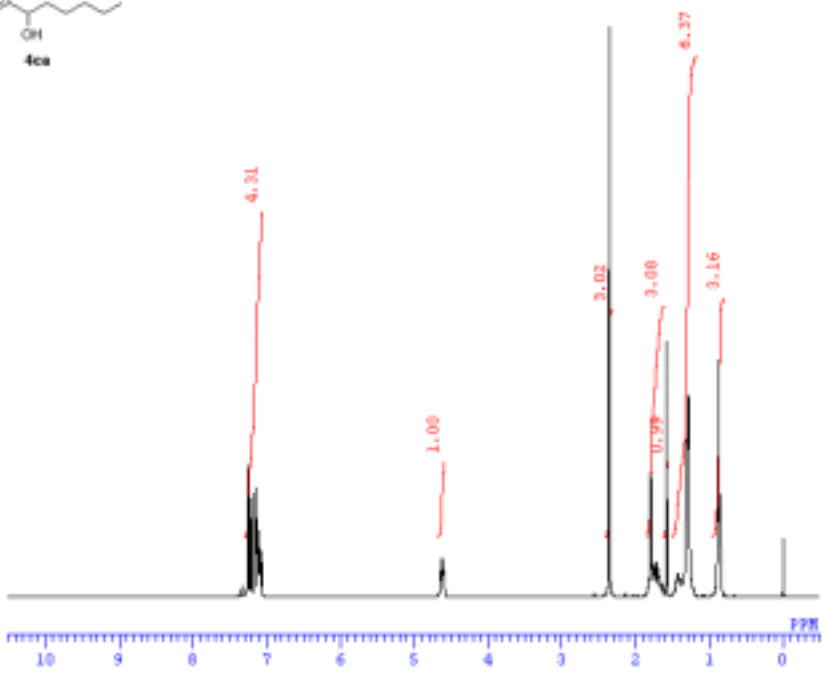


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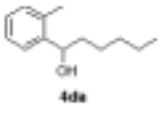

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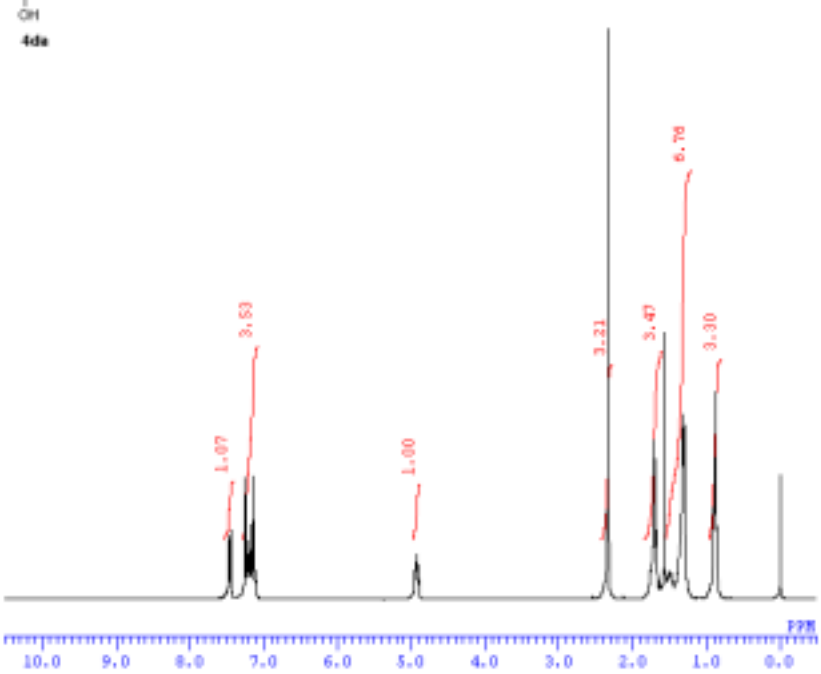


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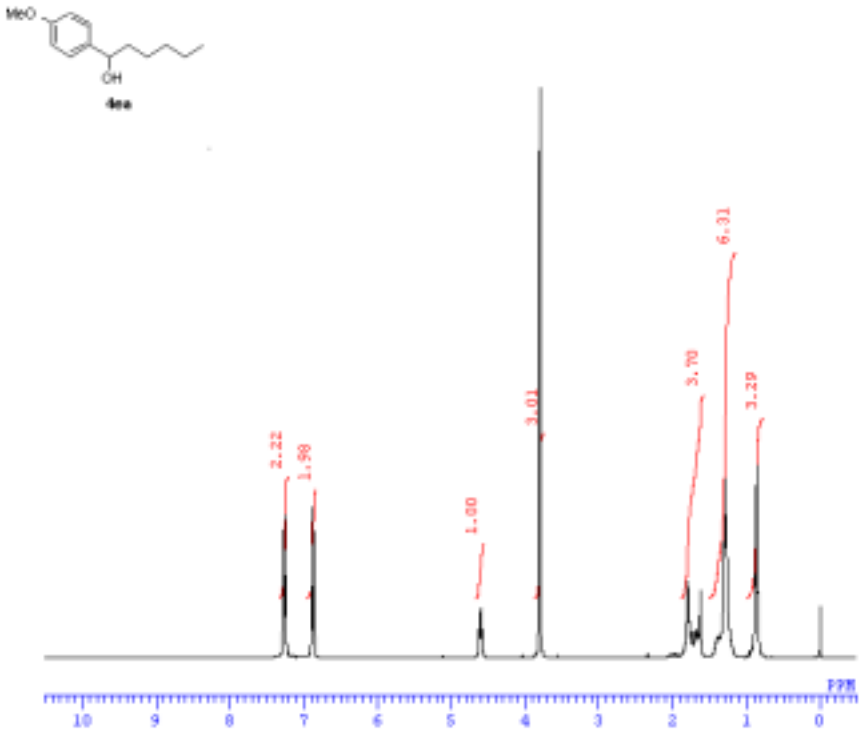


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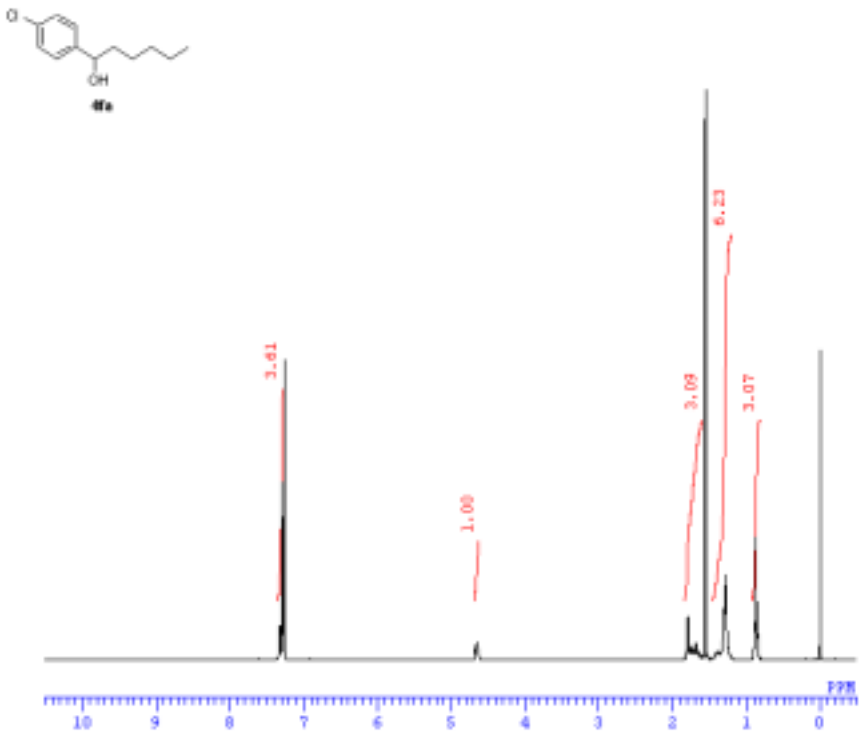


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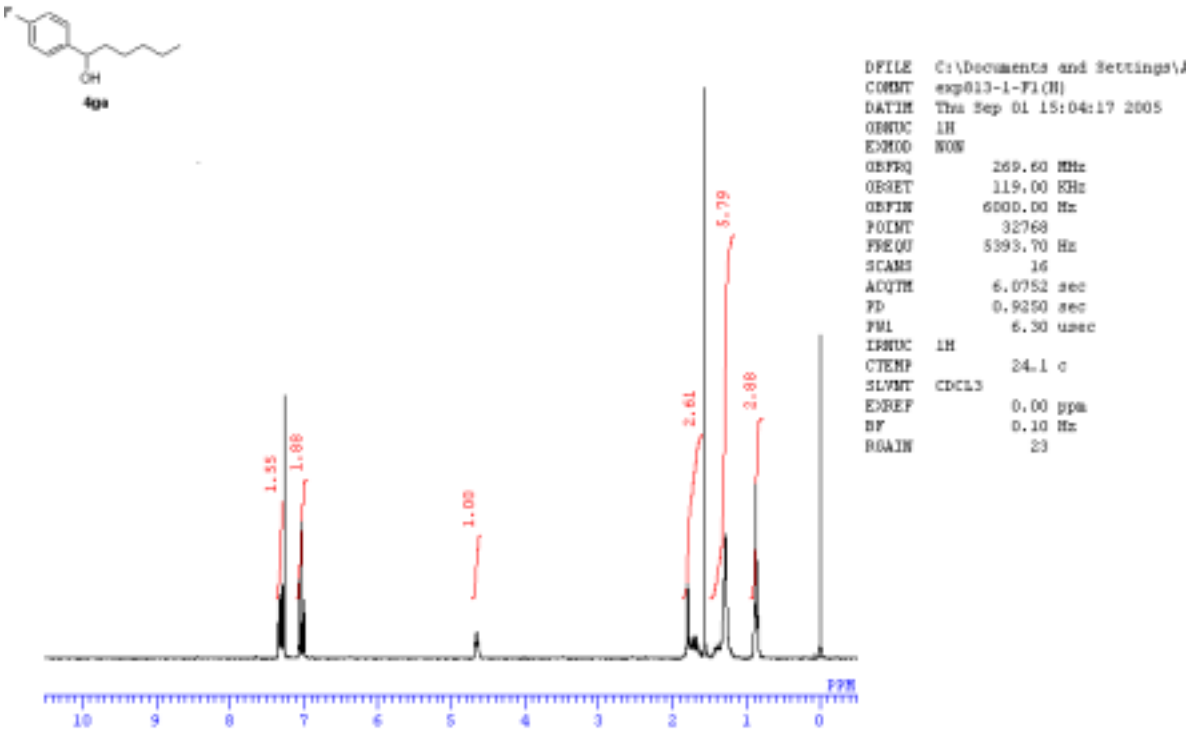
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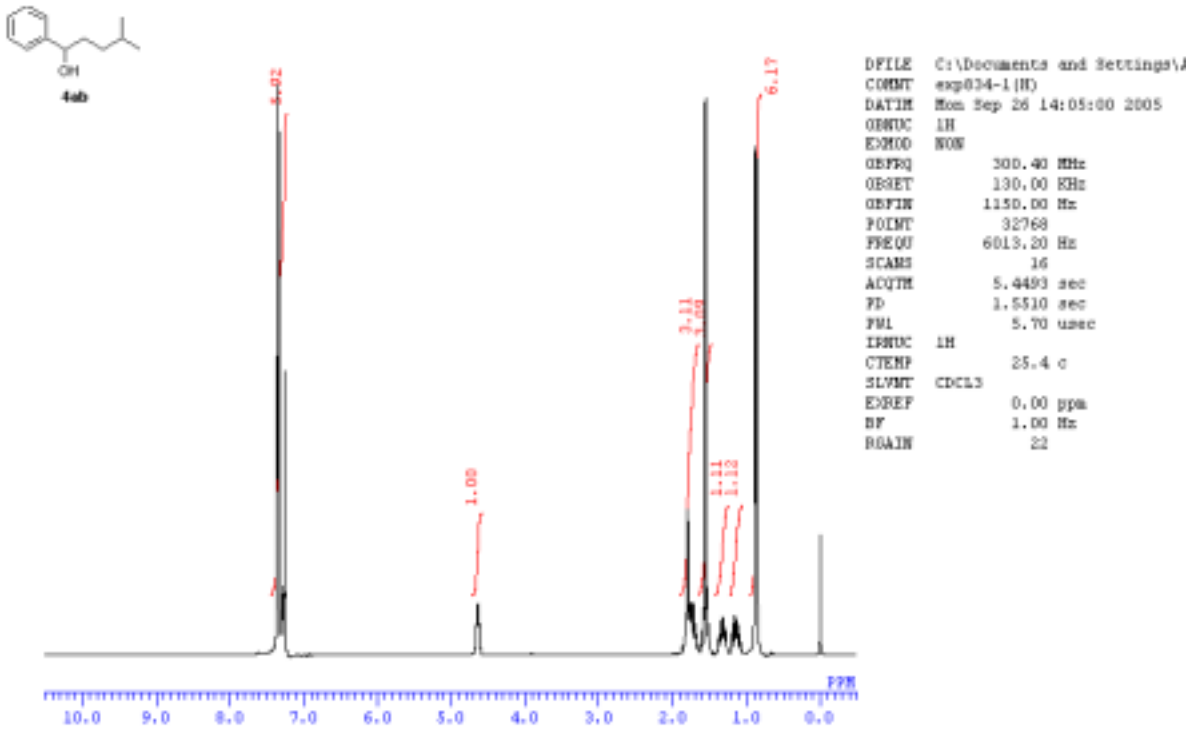
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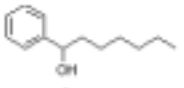

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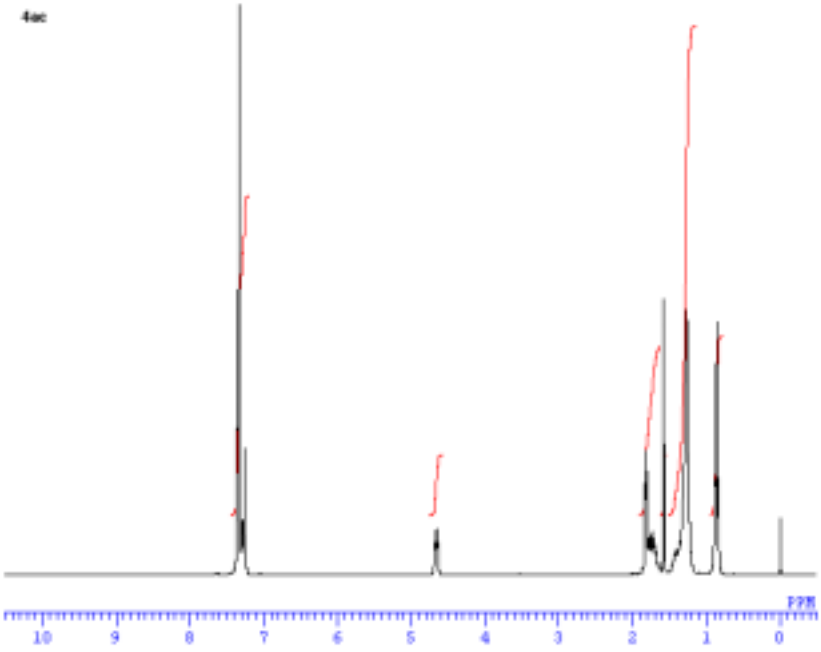


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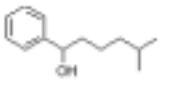

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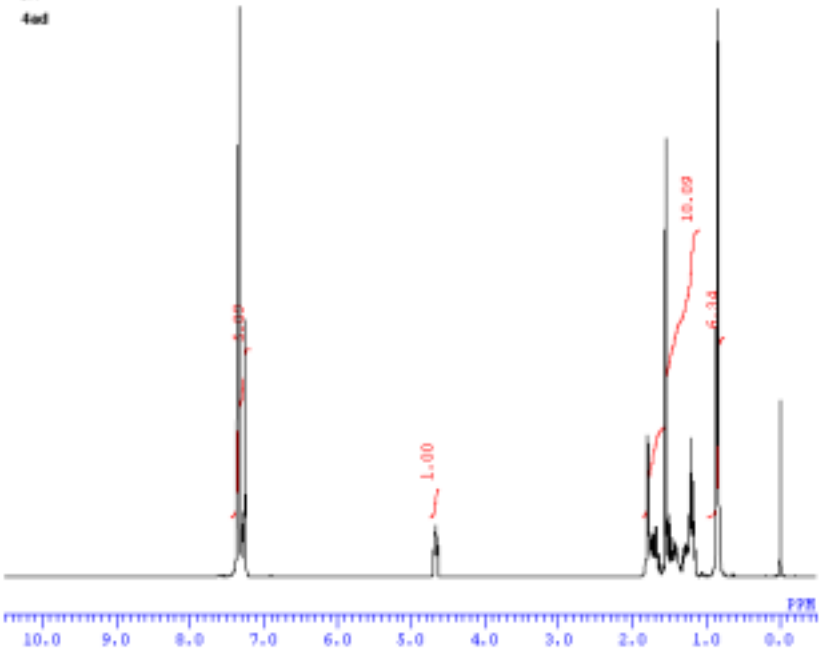


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