CHEMISTRY
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Supporting Information

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Ruthenium-Catalyzed Sequential Reactions: Deracemization of Secondary Benzylic Alcohols**

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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 (**2**) was prepared according to our previous procedure.[S1] Noyori ruthenium complexes **1** are purchased from Kanto Kagaku (Japan).

Dynamic kinetic resolution of racemic alcohols catalyzed by 1 and 2. A typical experimental procedure for the reaction of racemic 1-(4-bromophenyl)-1-ethanol (**3e**) catalyzed by {RuCl[(*S*,*S*)-tsdpen](mesitylene)} (**1b**) and [$RuCl_2(PPh_3)$(ip-FOXAP)] (**2**) is described below. In a 50 mL flask were placed KOH (1.1 mg, 0.02 mmol) and **1a** (6.2 mg, 0.010 mmol) under N_2. After the addition of racemic **3e** (201.1 mg, 1.00 mmol) in acetone (1.0 mL), the reaction mixture was kept at room temperature for 15 h. A solution of ^{i}PrOH (50 mL) containing ^{i}PrONa (0.020 mmol) and **2** (4.6 mg, 0.005 mmol) was added into the reaction mixture and then the mixture was kept at room temperature for 2 h. For work-up, 1 *N* HCl aq. (0.5 mL) was added to it. The solvent was concentrated under reduced pressure, and then the residue was added with water (50 mL) and then extracted with 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 PTLC (20% EtOAc/*n*-hexane) to yield 168.1 mg (0.84 mmol, 84% isolated yield, 92% ee) of (*R*)-1-(4-bromophenyl)-1-ethanol ((*R*)-**3e**) as a pale yellow oil, which was identified by comparing its spectroscopic data with those in literature.[S2] $[\alpha]^{24}_D$ +35.3 (c 0.90, $CHCl_3$). ^{1}H NMR δ 1.45 (t, 3H, *J* = 6 Hz), 1.90 (b, 1H), 4.85 (q, 1H, *J* = 6 Hz), 7.23 (d, 2H, *J* = 8 Hz), 7.45 (d, 2H, *J* = 8 Hz). The ee value was determined by HPLC analysis with a Chiralcel OD column (eluent: hexane/2-propanol = 95/5, flow rate: 0.5 mL/min, column temperature: 25 °C, retention time: 20.53 min (*S*) and 22.30 min (*R*)).

1-Phenyl-1-ethanol (3a).[S2] Yield 90%. 94% ee. A colorless oil. The ee value was determined by GLC analysis with a Chiraldex GTA column (50 m) (carrier gas: N_2 = 100 kPa, He = 100 kPa, column temperature: 80 °C, retention time: 35.64 min (*S*) and 36.35 min (*R*)).

1-(4-Methylphenyl)-1-ethanol (3b).[S3] Yield 92%. 92% ee. A colorless oil. 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: 25 °C, retention time: 43.19 min (*R*) and 45.54 min (*S*)).

1-(4-Fuluorophenyl)-1-ethanol (3c).[S2] Yield 90%. 90% ee. A colorless oil. The ee value was determined by HPLC analysis with a Chiralcel OJ-H column (eluent: hexane/2-propanol = 98/2, flow rate: 0.5 mL/min, column temperature: 25 °C, retention time:49.70 min (*R*) and 54.59 min (*S*)).

1-(4-Chlorophenyl)-1-ethanol (3d).[S2] Yield 99%. 89% ee. A colorless oil. The ee value was determined by HPLC analysis with a Chiralcel OD column (eluent: hexane/2-propanol = 97/3, flow rate: 0.5 mL/min, column temperature: 25 °C, retention time: 32.10 min (*S*) and 35.88 min (*R*)).

1-(4-Phenylphenyl)-1-ethanol (3f).[S4] Yield 99%. 93% ee. A white solid. The ee value was determined by HPLC analysis with a Chiralcel OD column (eluent: hexane/2-propanol = 95/5, flow rate: 0.5 mL/min, column temperature: 25 °C, retention time: 50.52 min (*S*) and 54.74 min (*R*)).

1-(3-Methylphenyl)-1-ethanol (3g).[S5] Yield 81%. 91% ee. A colorless oil. The ee value was determined by HPLC analysis with a Chiralcel OD column (eluent: hexane/2-propanol = 95/5, flow rate: 0.5 mL/min, column temperature: 25 °C, retention time: 20.22 min (*R*) and 26.00 min (*S*)).

1-(2-Methylphenyl)-1-ethanol (3h).[S5] Yield 93%. 2% ee. A colorless oil. The ee value was determined by HPLC analysis with a Chiralcel OJ-H column (eluent: hexane/2-propanol = 97/3, flow rate: 0.5 mL/min, column temperature: 25 °C, retention time: 31.39 min (*R*) and 33.35 min (*S*)).

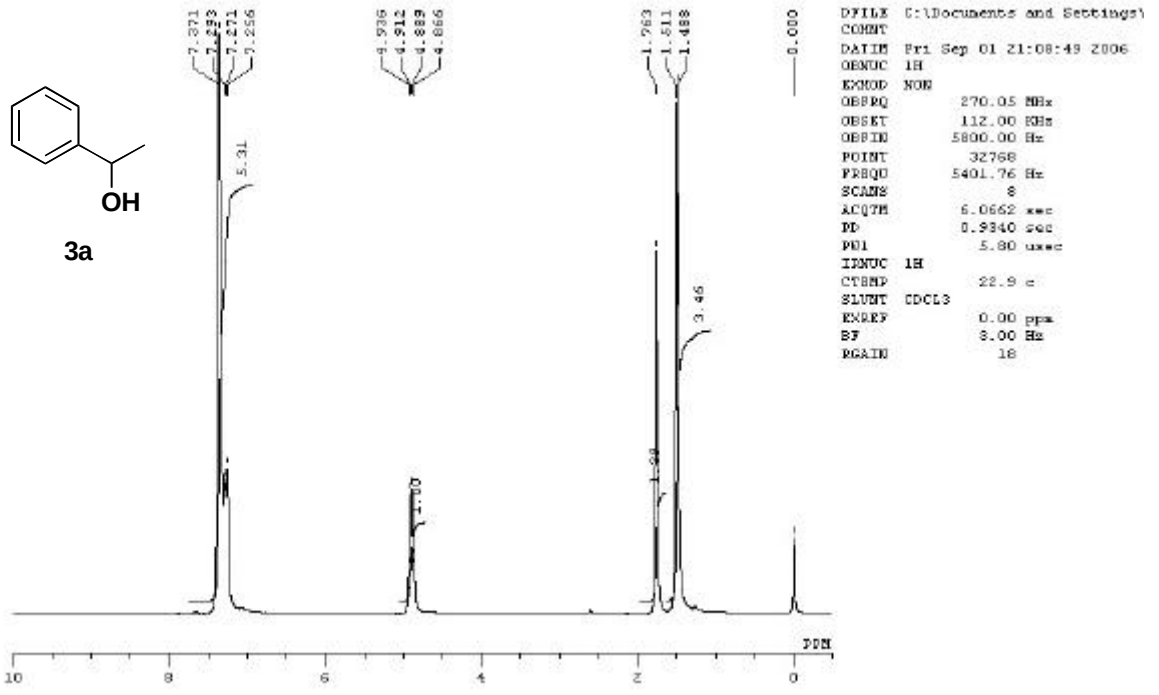
1-Phenyl-1-propanol (3i).[S3] Yield 88%. 95% ee. A colorless oil. The ee value was determined by HPLC analysis with a Chiralcel OD column (eluent: hexane/2-propanol = 97/3, flow rate: 0.5 mL/min, column temperature: 25 °C, retention time: 26.07 min (*R*) and 29.54 min (*S*)).

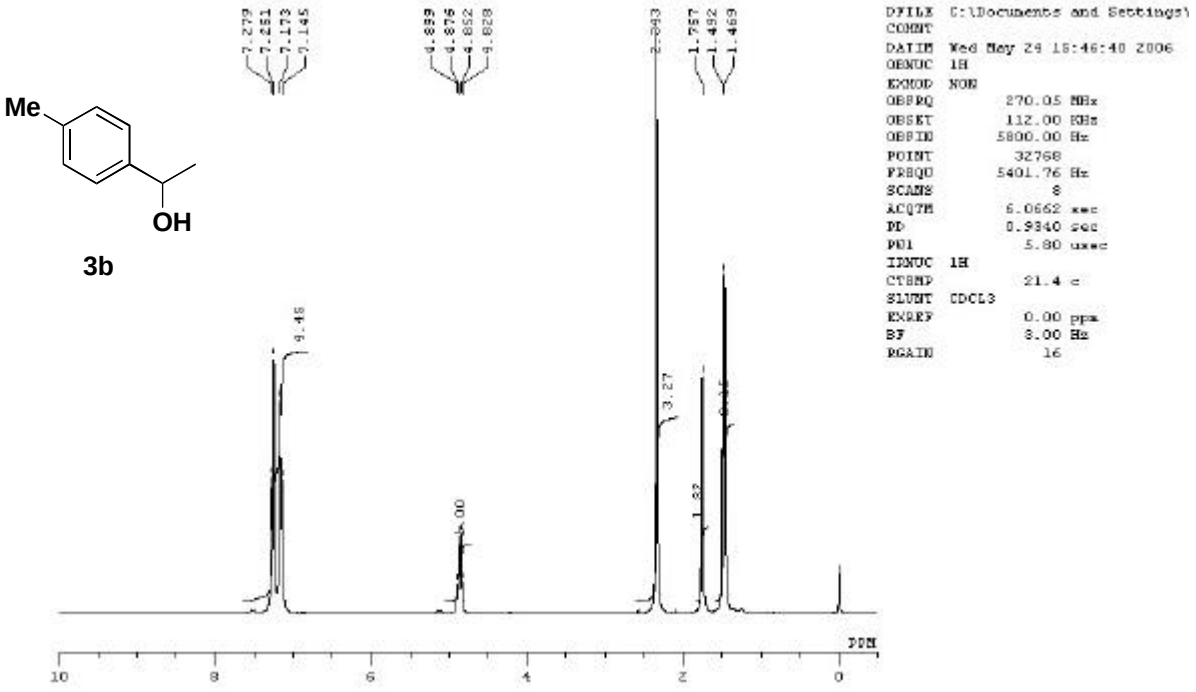
1-Phenyl-1-butanol (3j).[S3] Yield 85%. 90% ee. A colorless oil. The ee value was determined by HPLC analysis with a Chiralcel OD column (eluent: hexane/2-propanol = 97/3, flow rate: 0.5 mL/min, column temperature: 25 °C, retention time: 36.72 min (*R*) and 38.70 min (*S*)).

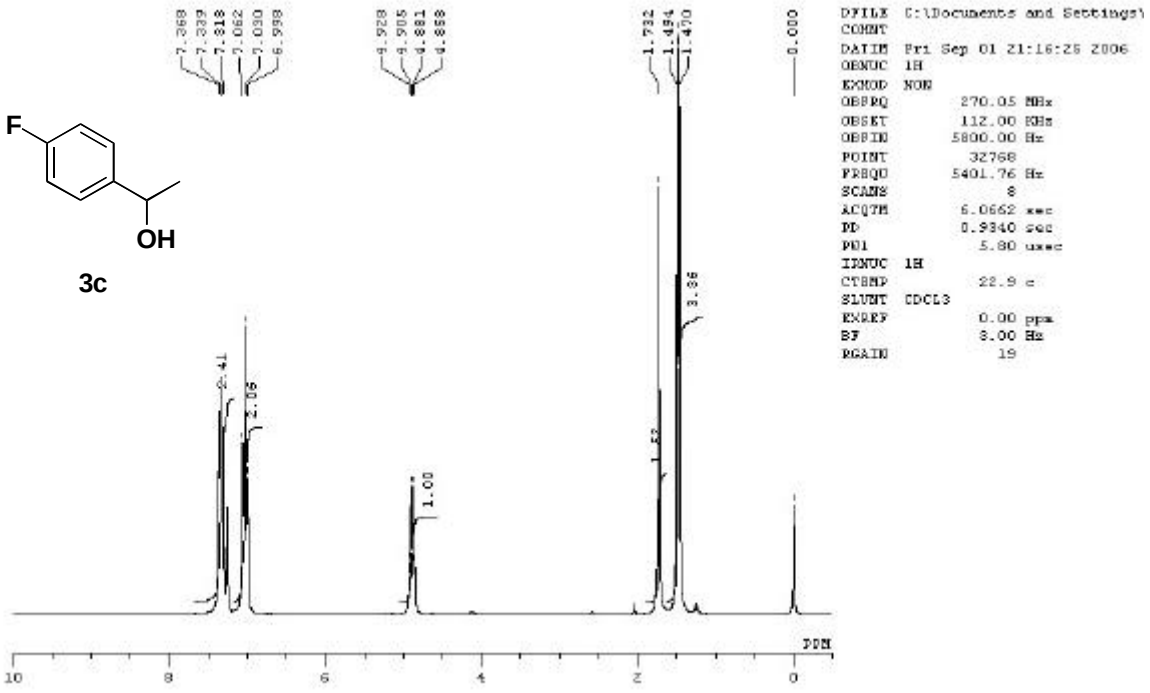
1-Phenyl-1-pentanol (3k).[S3] Yield 86%. 94% ee. A colorless oil. The ee value was determined by HPLC analysis with a Chiralcel OD column (eluent: hexane/2-propanol = 97/3, flow rate: 0.5 mL/min, column temperature: 25 °C, retention time: 33.88 (*R*) min and 36.98 min (*S*)).

1,4-Bis(1-hydroxyethyl)benzene (7).[S6] Yield 62% (*dl* : *meso* = 90 :10). >99% ee. A white solid. The ee value was determined by HPLC analysis with a Chiralcel OD column (eluent: hexane/2-propanol = 90/10, flow rate: 0.5 mL/min, column temperature: 25 °C, retention time:36.11 (*R*,*R*) min, 40.66 min (*S*,*S*), and 55.86 min (*meso*)).

^{1}H NMR spectra of the recovered alcohols (**3** and **7**) are shown in the following pages (pages S5-S10).



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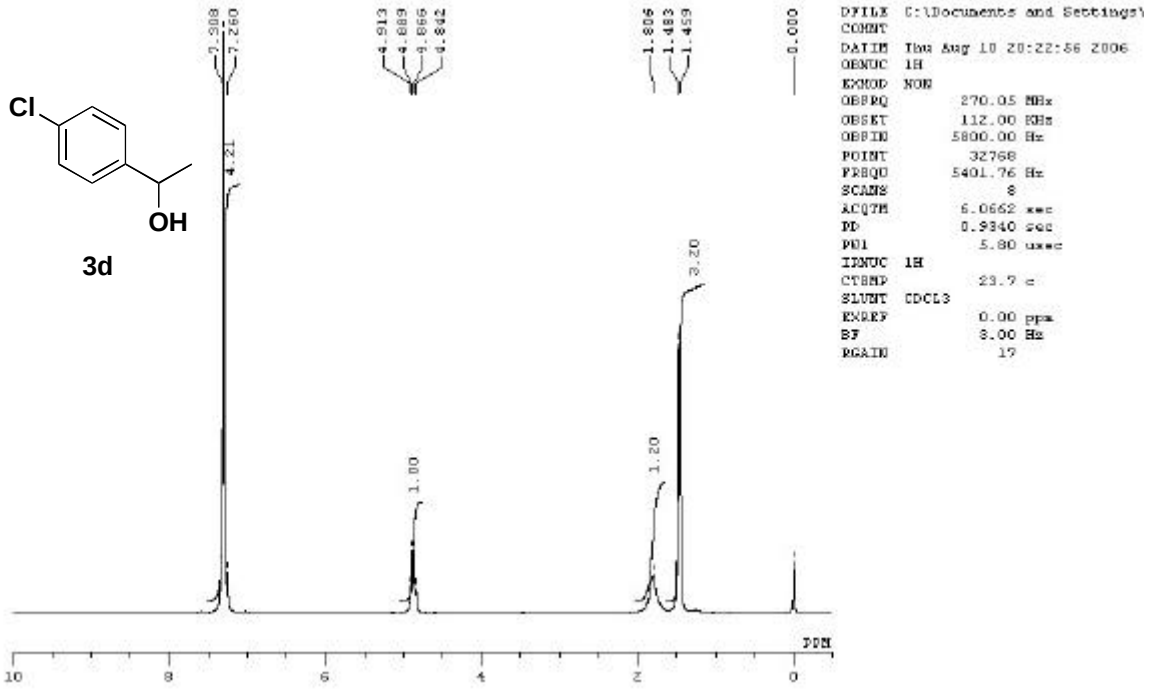
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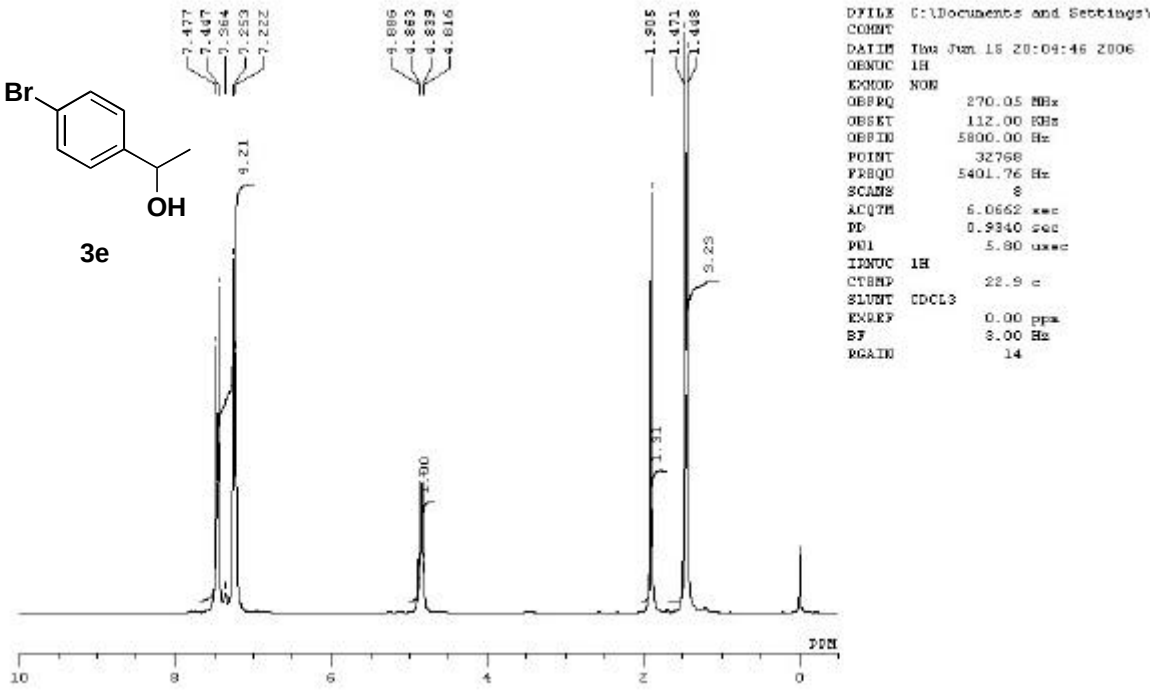
3d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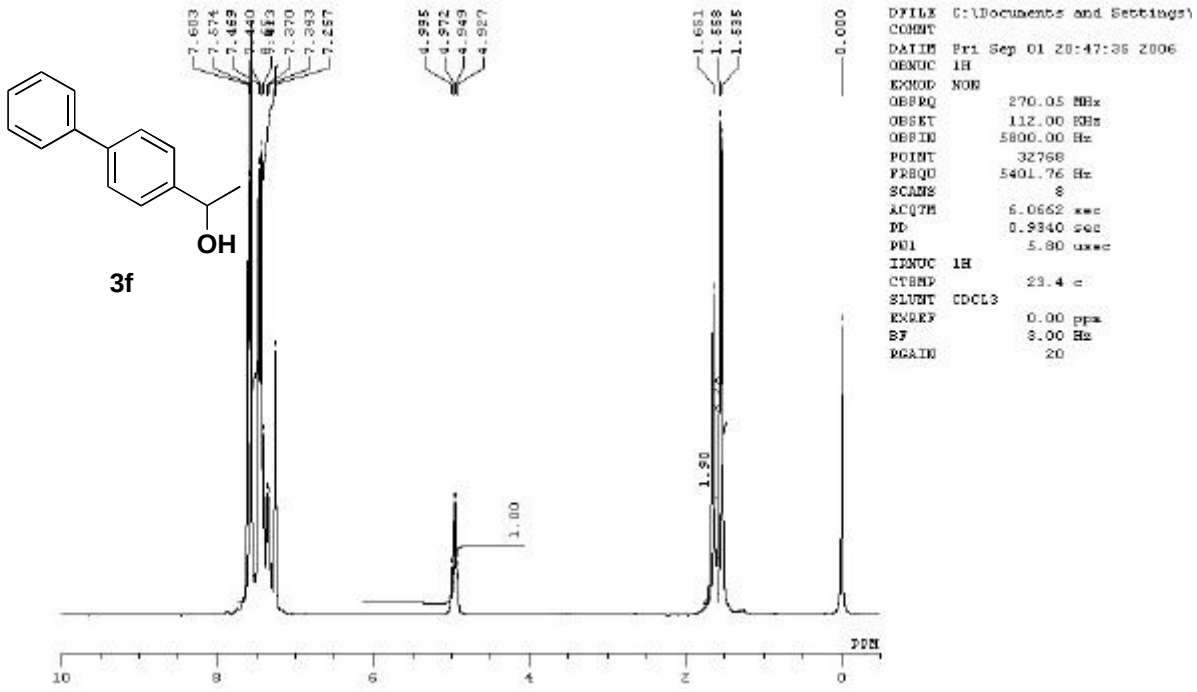
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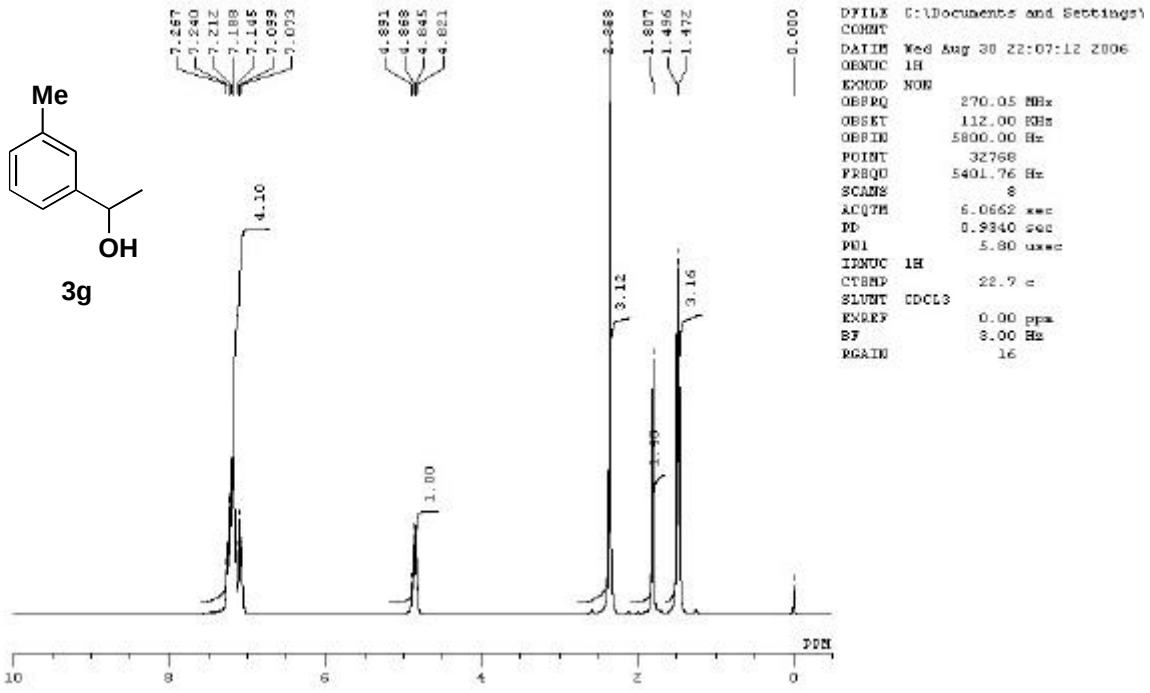
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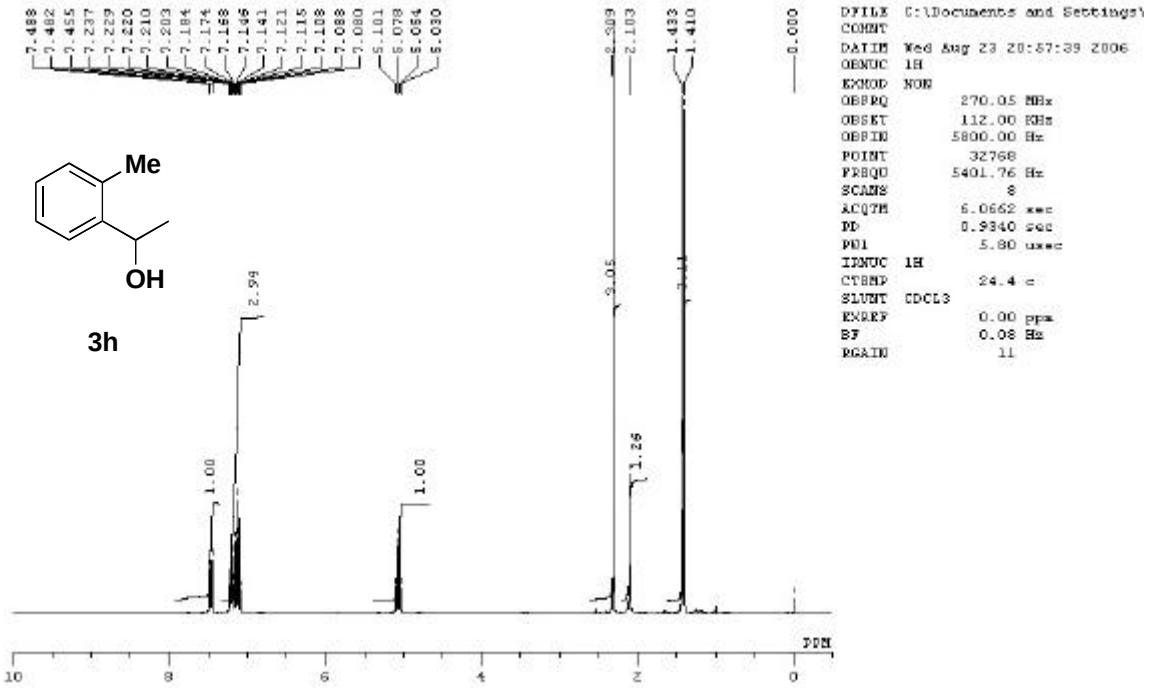
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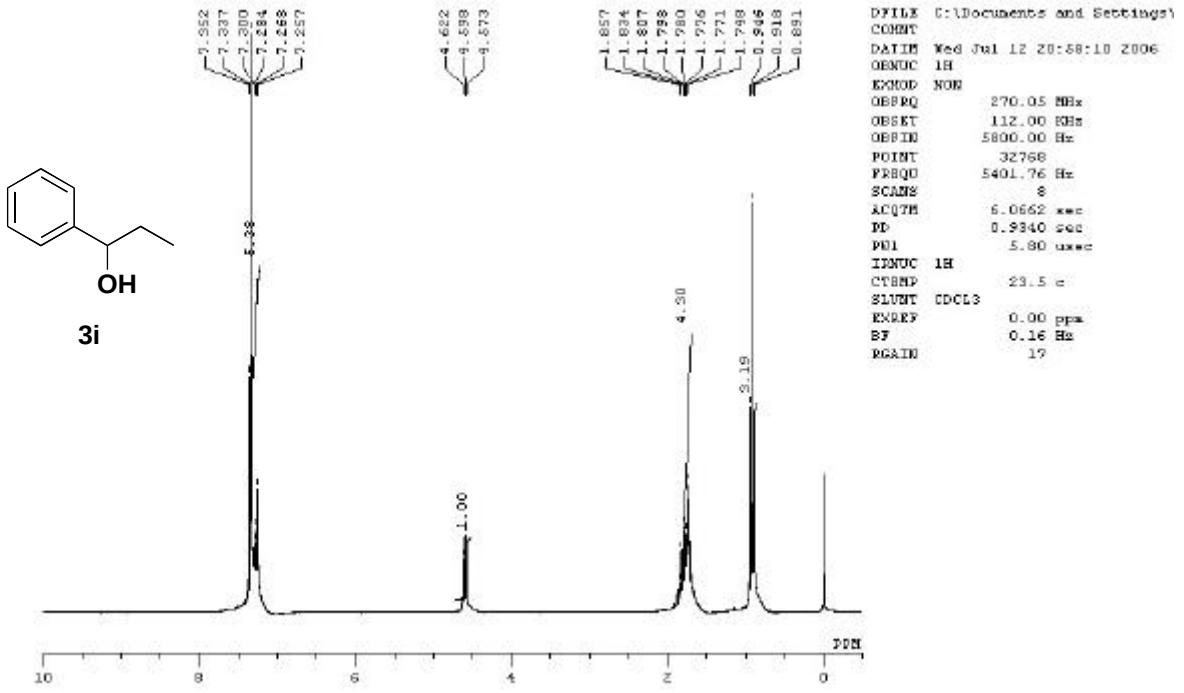
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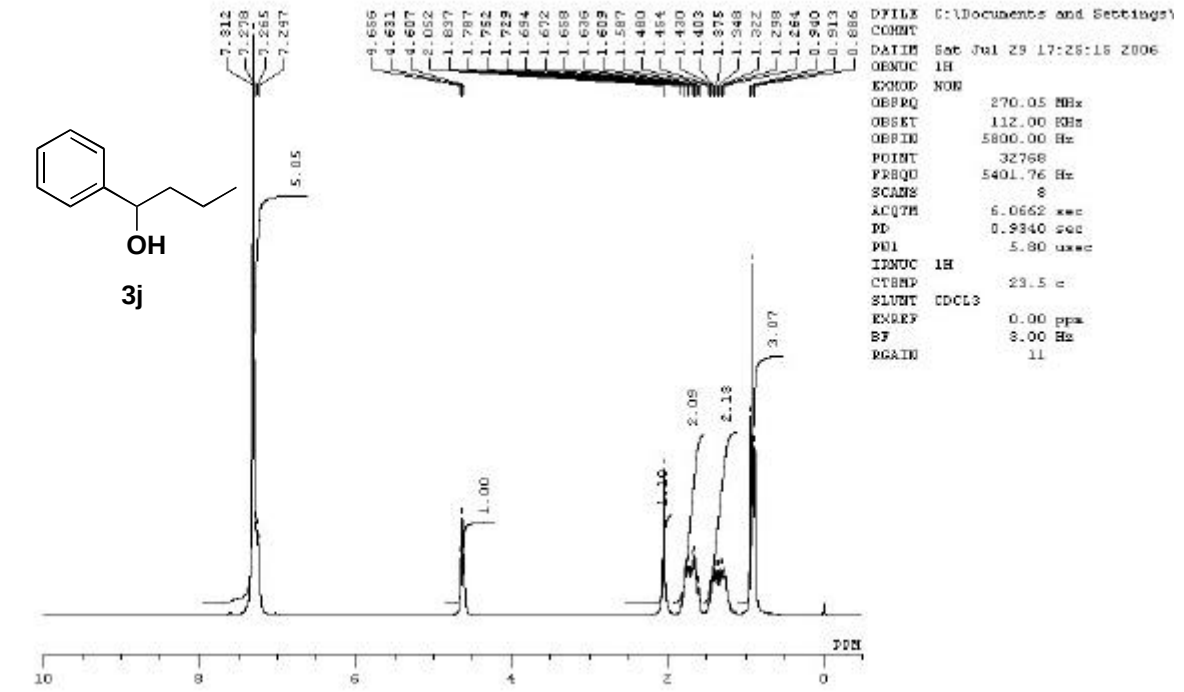
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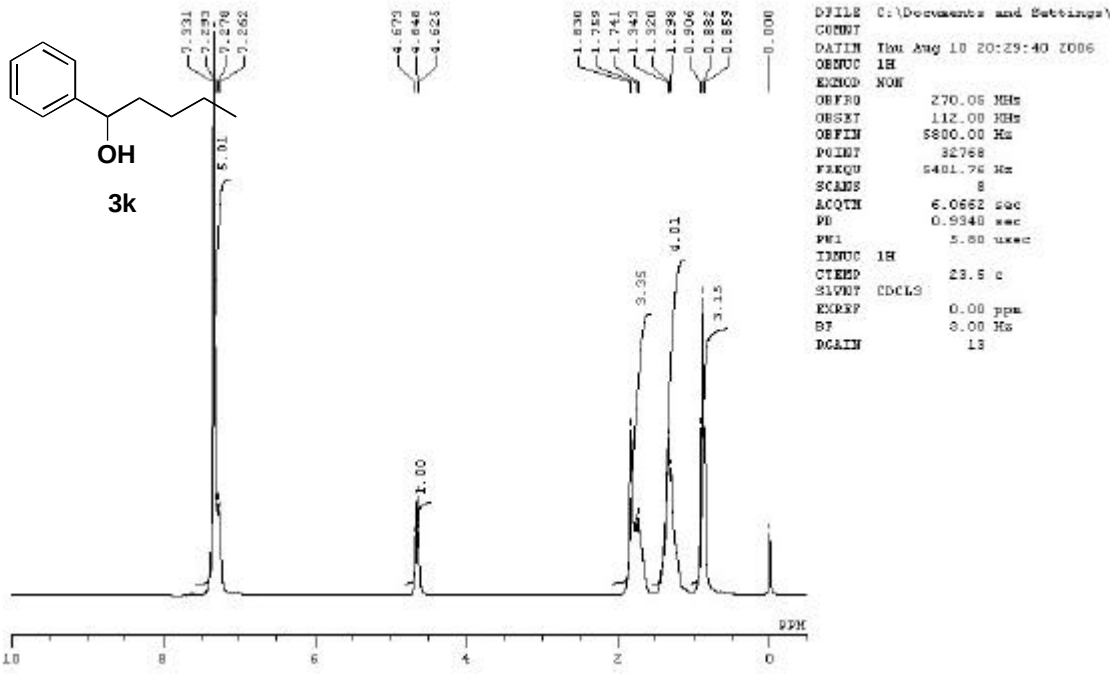
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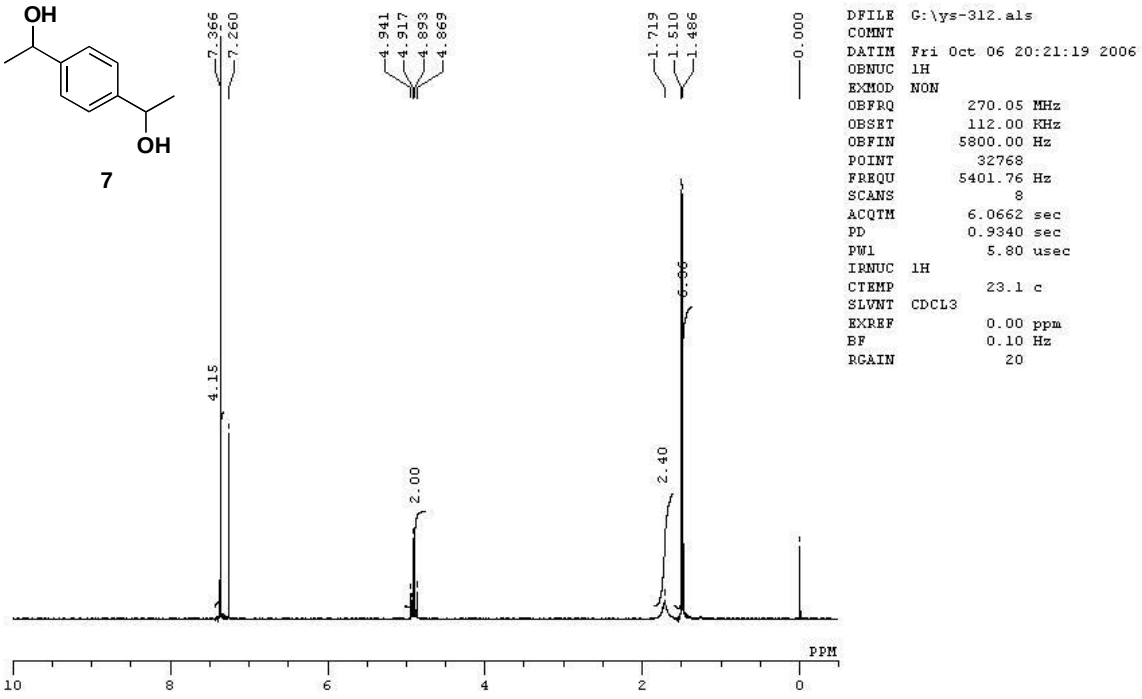
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[S1] a) Y. Nishibayashi, I. Takei, S. Uemura, M. Hidai, *Organometallics* **1998**, *17*, 3420; b) Y. Nishibayashi, I. Takei, S. Uemura, M. Hidai, M. *Organometallics* **1999**, *18*, 2291; c) G. Onodera, Y. Nishibayashi, S. Uemura, *Angew. Chem.* **2006**, *118*, 3903; *Angew. Chem. Int. Ed.* **2006**, *45*, 3819.

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