

Supplementary Materials: Ir-Catalyzed Reduction of Carbonyl Compounds Using Biogenetic Alcohols

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Materials and Methods

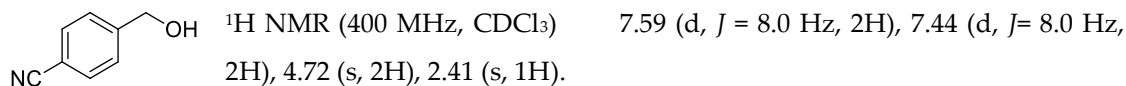
All reactions were carried out under argon atmosphere. 1,4-dioxane and D(+)-glucose was purchased from Wako Pure Chemical Industries. Ir complex was purchased from Furuya Metal Co., Ltd. Glucono- γ -lactone was purchased from Kishida chemical Co., which was used to LCMS analysis of the standard sample. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a JEOL JNM-LA400 spectrometer. Proton chemical shifts are relative to solvent peaks [chloroform: 7.27 (^1H), 77.00 (^{13}C)]. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light for visualization.

Catalytic reaction was performed as follows: aldehyde (0.25 mmol), sugar (0.25 mmol) and $[\text{IrCp}^*\text{Cl}_2]_2$ (5.0 mol%) were dissolved in H_2O (0.5 mL) and 1,4-dioxane (0.5 mL). The reaction mixture was stirred for 24 h at 85 °C. After cooling, the reaction mixture was diluted with H_2O and extracted with AcOEt. For GC analysis, a known amount of dodecane was added in the mixture, and product yield was determined by comparing the areas of GC spectra. For ^1H NMR analysis, the mixture was concentrated under reduce pressure and a crude ^1H -NMR spectra in CDCl_3 was obtained using a known amount of 1,1,2,2-tetrachloroethane as an internal standard. The yield was measured by integrating the H of benzylic position with respect to the 1,1,2,2-tetrachloroethane peak.

Product data

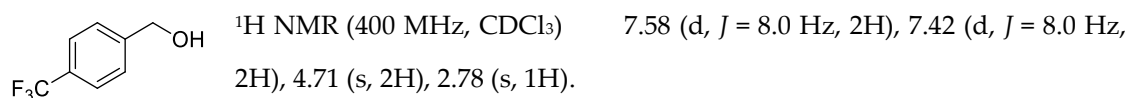
All the products shown in Table 1, 2 and 3 have already been reported in the literature. Their ^1H NMR data are as follows.

4-(hydroxymethyl)benzonitrile



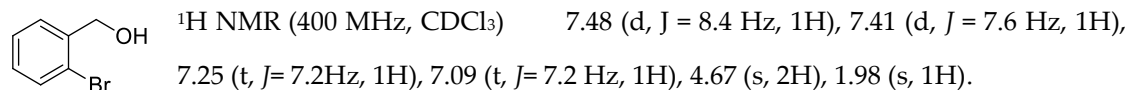
Ref. 1) M. Reza Naimi-Jamal, Javad Mokhtari Mohammad G. Dekamin, and Gerd Kaupp. *Eur. J. Org. Chem.* **2009**, 3567-3572.

(4-(trifluoromethyl)phenyl)methanol



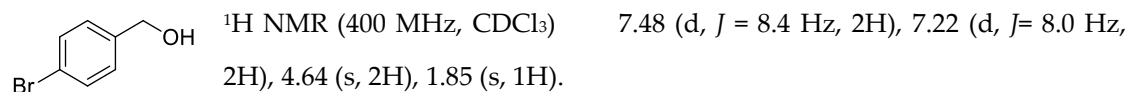
Ref. 2) S. Takebayashi and S. H. Bergens. *Organometallics*, **2009**, 28 (8), 2349-2351.

(2-bromophenyl)methanol



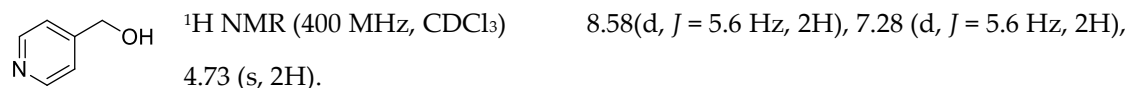
Ref.3) A. Clerici, N. Pastori, O. Porta. *Eur. J. Org. Chem*, **2002**, 3326-3335.

(4-bromophenyl)methanol



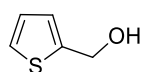
Ref. 4) M. Zhao, Z. Yu, S. Yan, Y. Li. *Tetrahedron Lett*, **2009**, 50 (32), 4624-4628.

pyridin-4-ylmethanol



Ref. 5) B. T. Cho, S. K. Kang, M. S. Kim, S. R. Ryu and D. K An. *Tetrahedron*, **2006**. 62, 8164-8168.

2-thiophenemethanol



$^1\text{H NMR}$ (400 MHz, CDCl_3) 7.25-7.21 (m, 1H), 6.98-6.93 (m, 2H), 4.79 (s, 2H), 1.79 (s, 1H).

Ref. 6) M. R. Nami-Jamal, J. Mokhtari, M.G. Dekamin and G. Kupp. *Eur. J. Org. Chem.* **2009**, 21, 3567-3572.

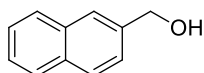
1-Nonanol



$^1\text{H NMR}$ (400 MHz, CDCl_3) 0.84 (m, 3H), 1.13-1.49 (m, 12H), 1.49-1.60 (m, 2H), 2.29 (t, $J = 7.6$ Hz, 1H), 3.60 (t, $J = 7.2$ Hz, 2 H).

Ref. 7) J. M. Brunel, *Tetrahedron*, **2007**, 63, 3899-3906.

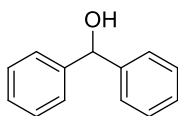
naphthalen-2-ylmethanol



$^1\text{H NMR}$ (400 MHz, CDCl_3) 7.83-7.79 (m, 4H), 7.48-7.43 (m, 3H), 4.84 (s, 2H), 1.62 (s, 1H).

Ref. 8) M. Kirihara, T. Noguchi, N. Okajima, S. Naito, Y. Ishizuka, A. Harano, H. Tsukiji, R. Takizawa. *Tetrahedron*, **2012**, 68 (5), 1515-1520.

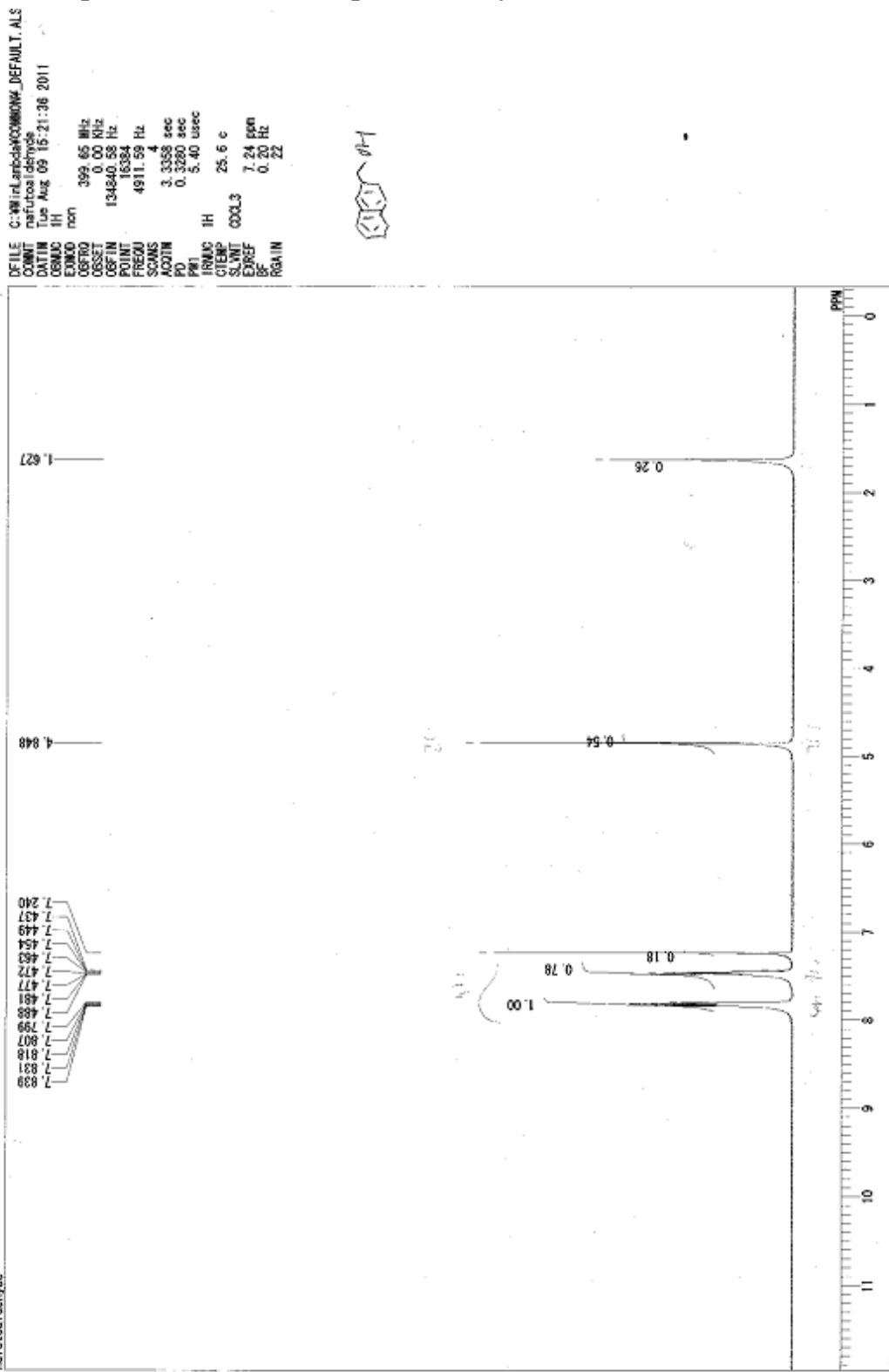
Benzhydrol



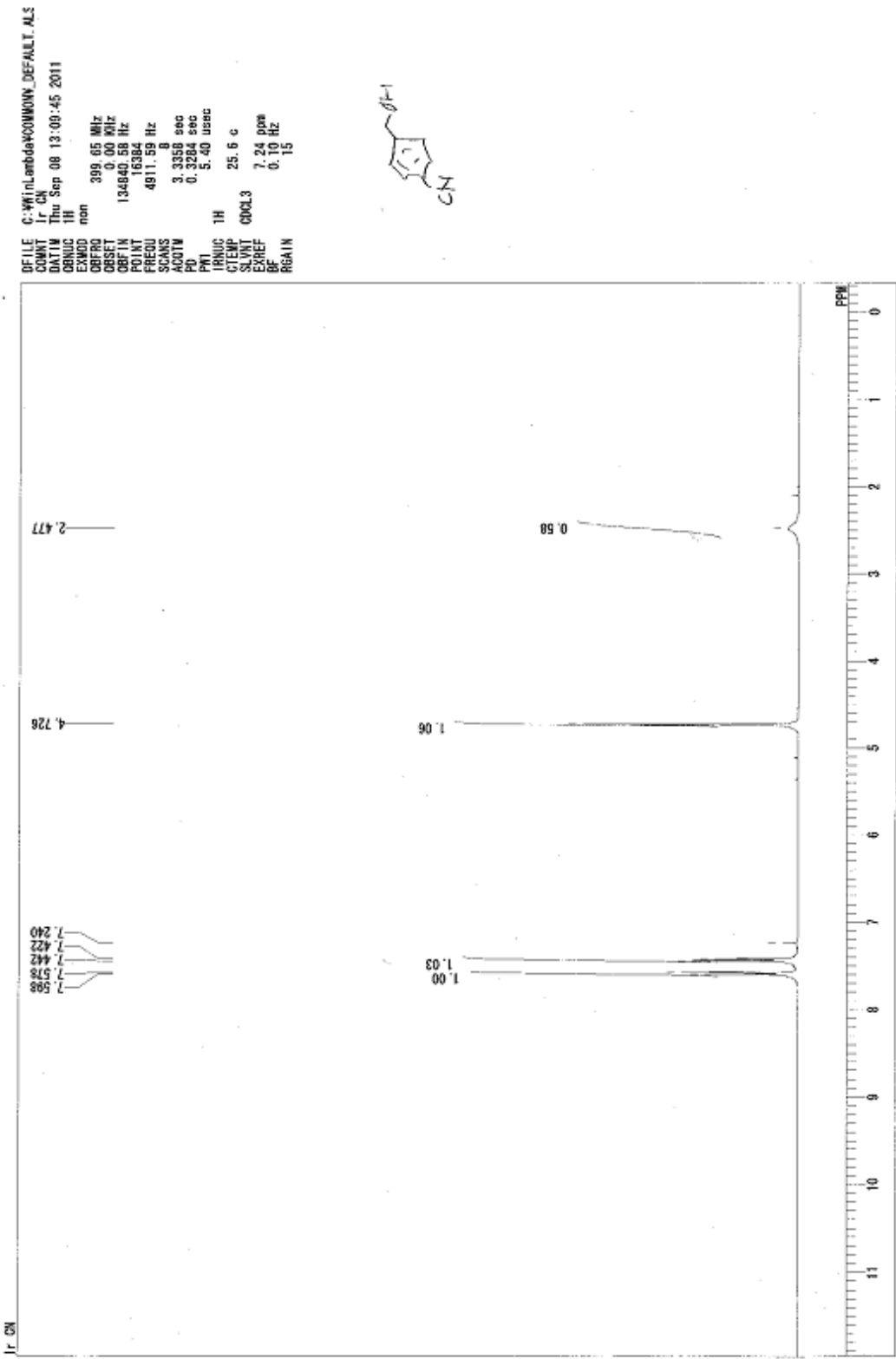
$^1\text{H NMR}$ (400 MHz, CDCl_3) 7.40-7.25 (m, 10H), 5.84 (s, 1H), 2.09 (s, 1H).

Ref. 9) F. E. Fernandez, M. C. Puerta and P. Valerga. *Organometallics*, **2011**, 30 (21), 5793-5802.

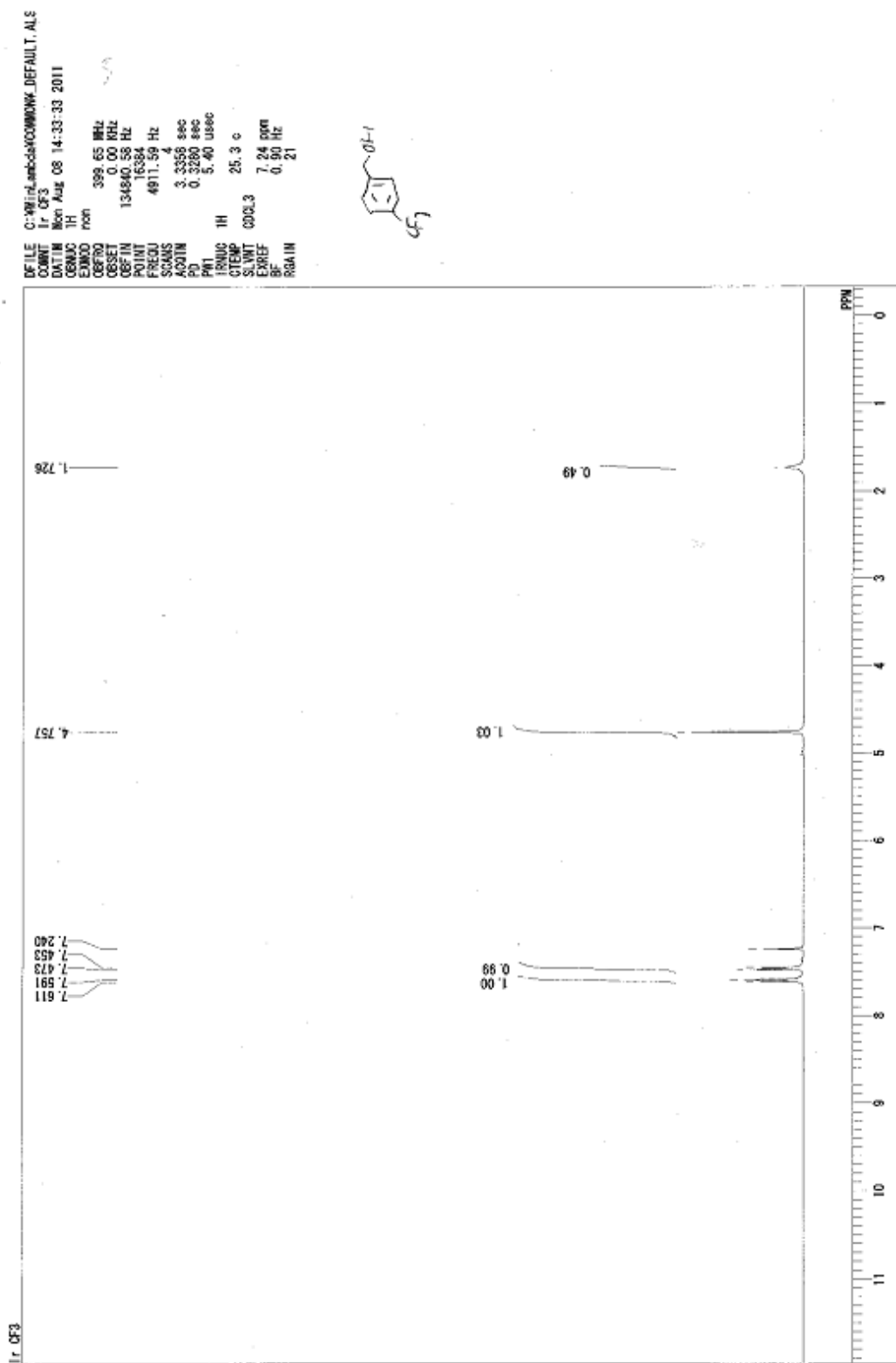
¹H NMR spectra ¹H NMR of Naphthalen-2-ylmethanol



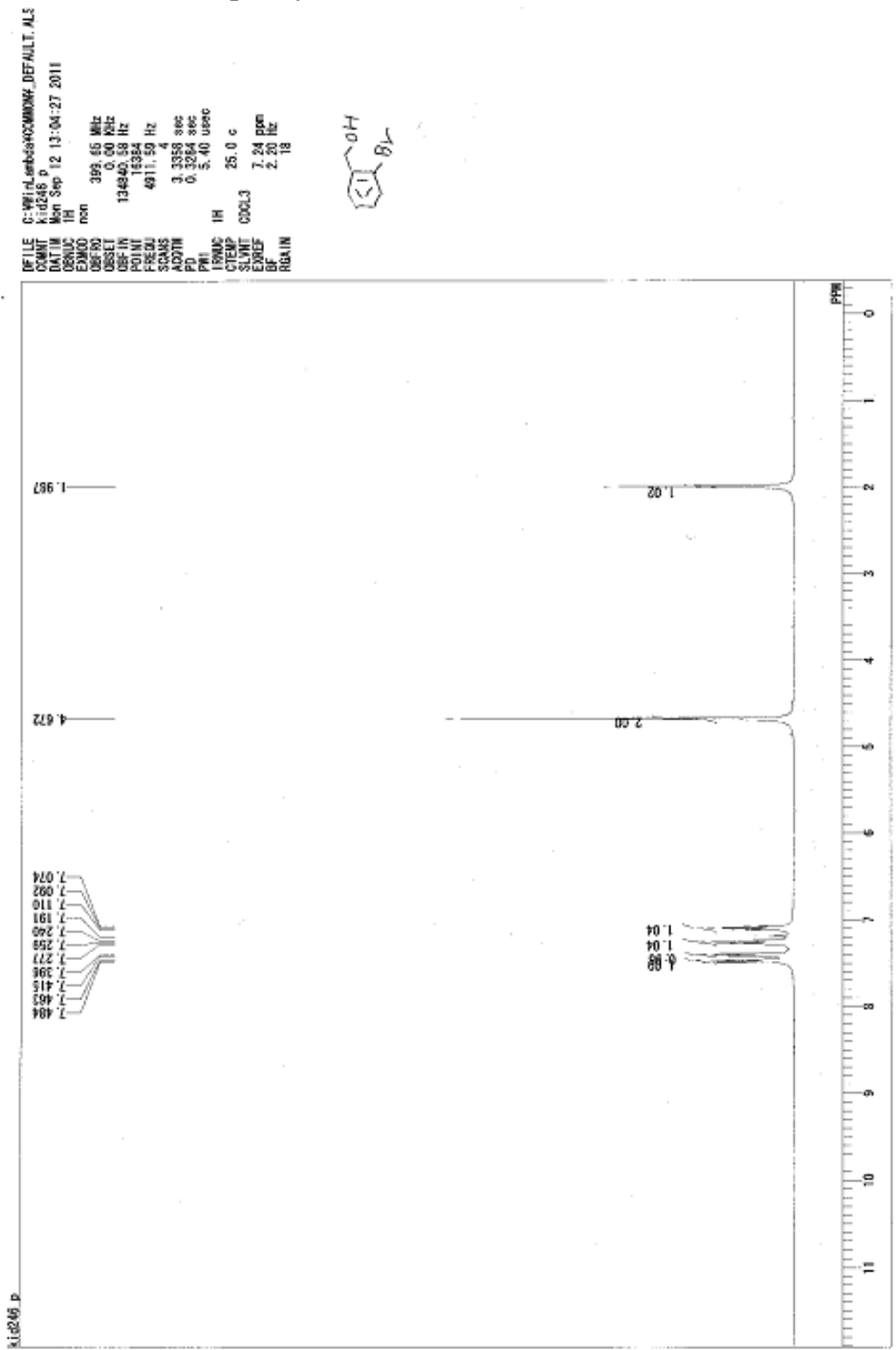
¹H NMR of 4-(hydroxymethyl)benzonitrile



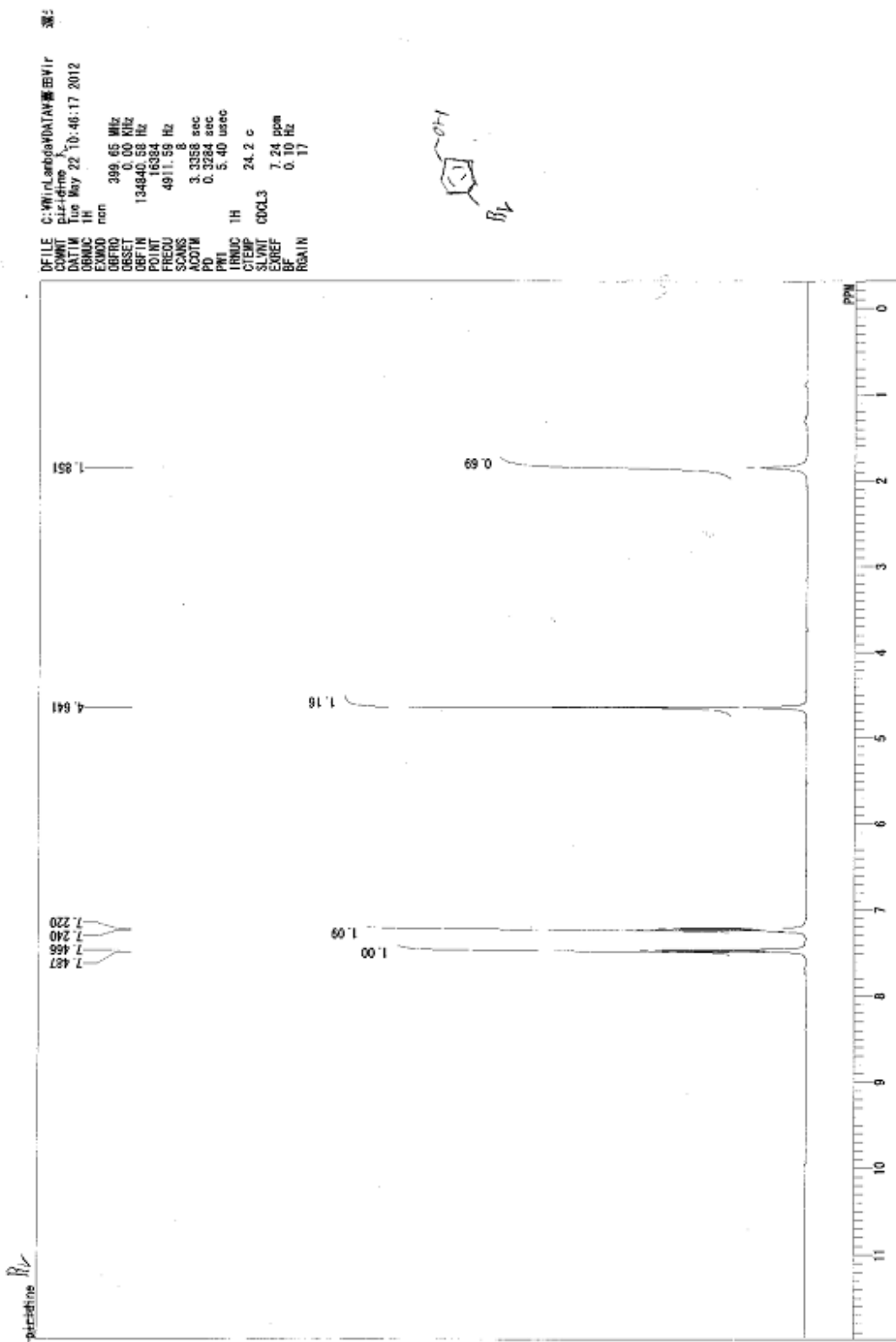
¹H NMR of (4-(trifluoromethyl)phenyl)methanol



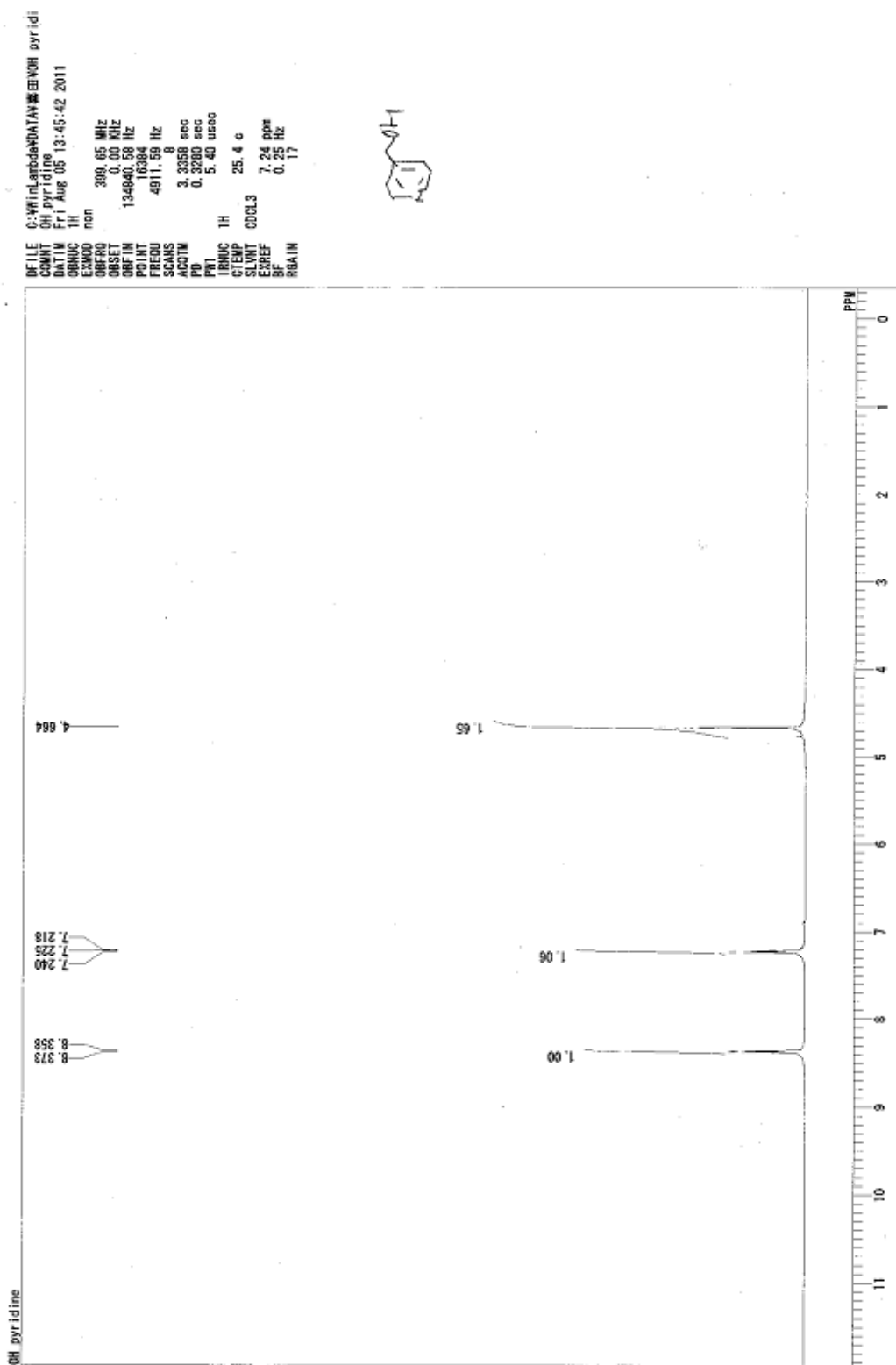
¹H NMR of (2-bromophenyl)methanol



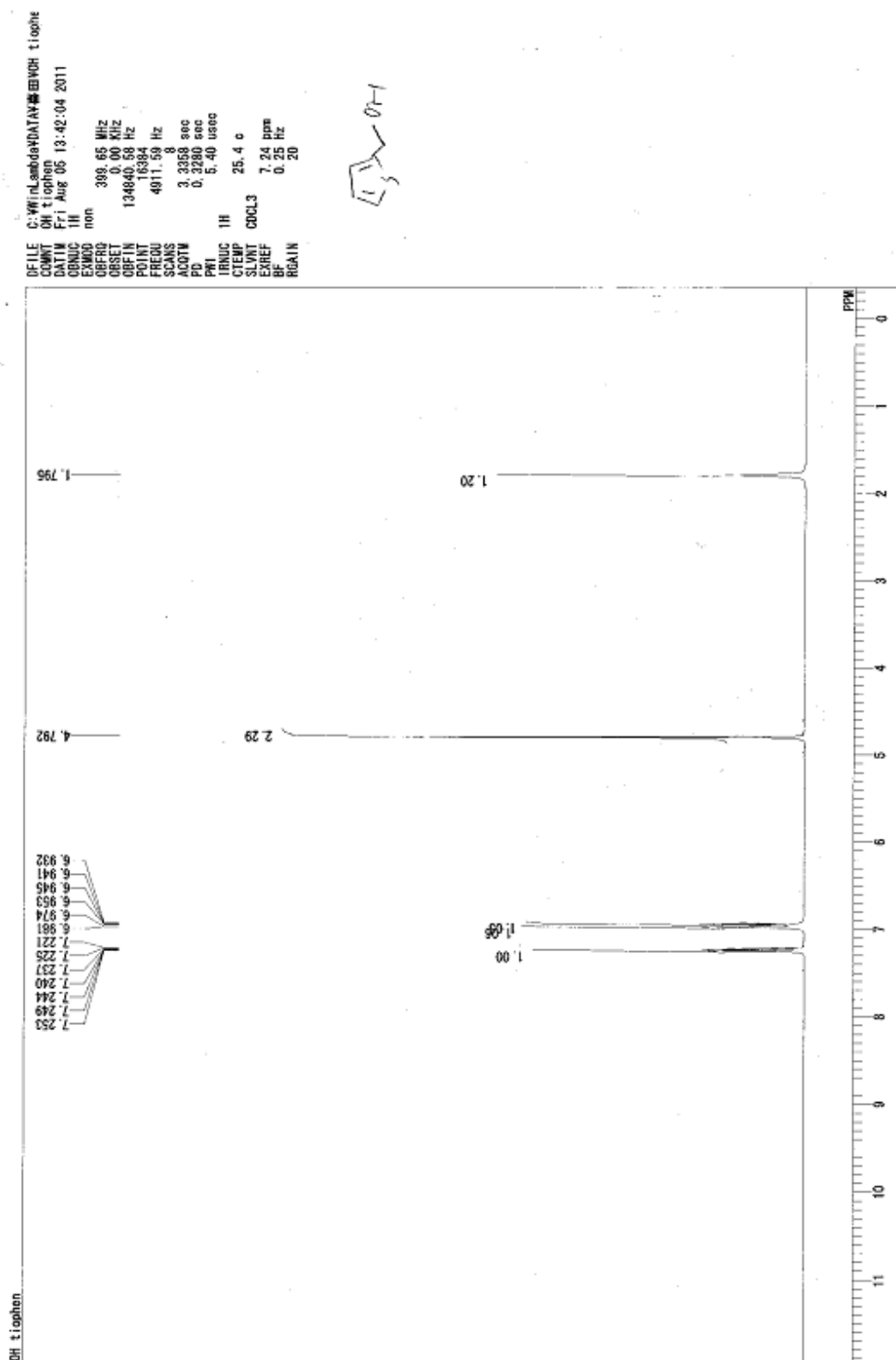
¹H NMR of (4-bromophenyl)methanol



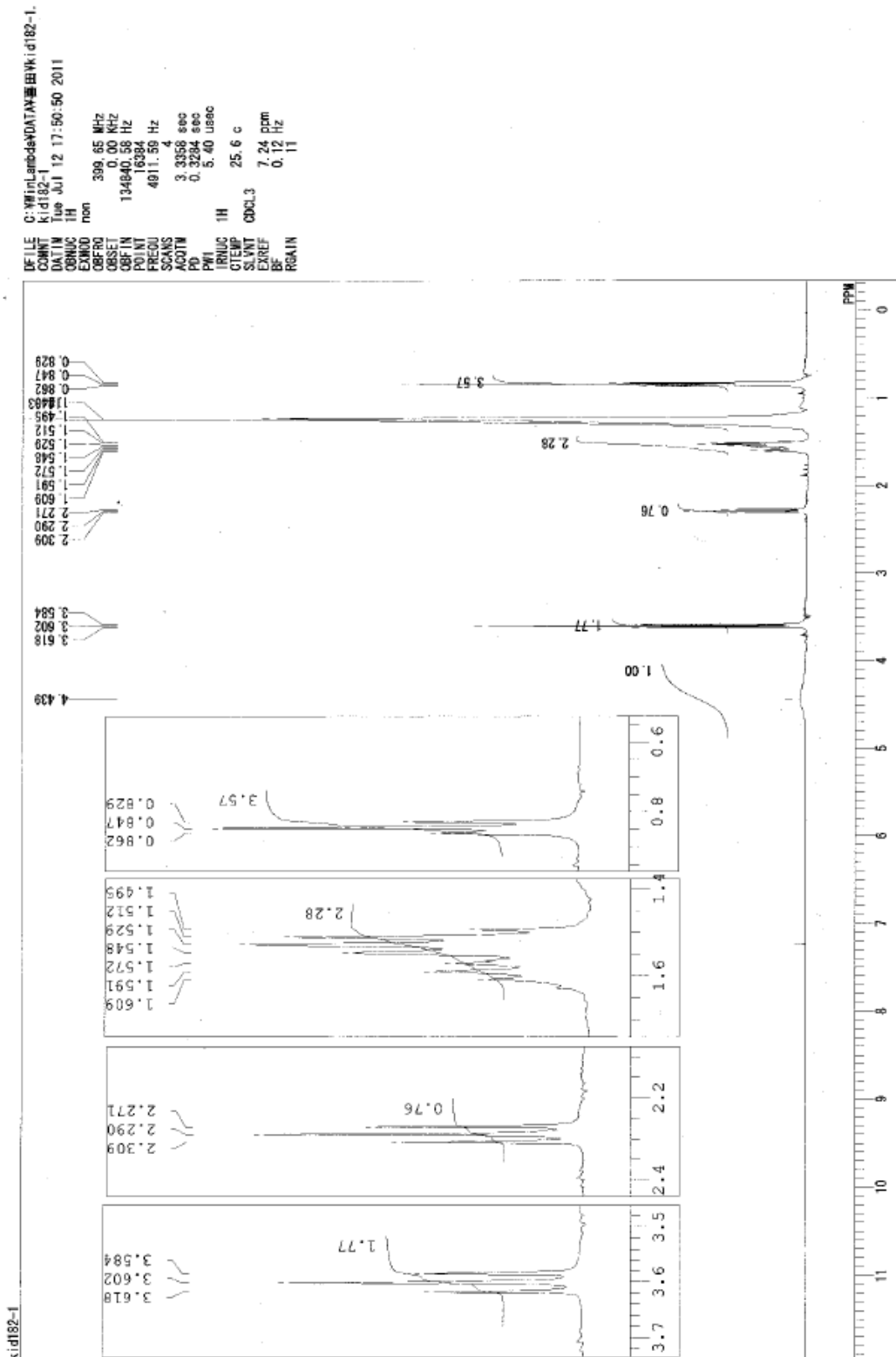
¹H NMR of pyridin-4-ylmethanol



¹H NMR of 2-thiophenemethanol



¹H NMR of 1-Nonanol



¹H NMR of Benzhydrol

