

Iridium-promoted conversion of terminal epoxides to primary alcohols under acidic conditions using hydrogen

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General considerations

(POCOP)IrCO,¹ indene oxide,² benzyloxirane,^{3,4} and 2-methyl-2-phenyloxirane⁴ were prepared as previously reported. All other chemicals and solvents were obtained from commercial vendors and used as received.

GC-MS data was collected using an Agilent 6890-5873 GC-MS equipped with an HP-5MS column (30 m x 0.25 mm x 0.25 μ m). GC-FID data was collected using an Agilent 7890A GC-FID equipped with an HP-5 column (30m x 0.32 mm x 0.25 μ m). NMR spectra were recorded on a Bruker AV500 spectrometer in CDCl₃ solvent.

Catalytic reactions were performed in a 10 mL high pressure reactor fitted with a PTFE liner and equipped with a pressure sensor and a programmable temperature controller. A new liner and stirbar were used for each reaction. A PTFE lid with a small hole for gas equilibration was placed on top of the liner. The well holding the thermocouple probe was covered with a heat-shrinkable PFA probe cover. These covers were purchased from Tef-Cap Industries Inc.

Typical hydrogenation procedure.

In air the reactor was charged with the epoxide substrate (1.4 mmol), dioxane (0.7 mL), (POCOP)IrCO (5.0 mg, 0.0081 mmol, 0.60 mol %), triflic acid (aq, 0.681 M, 0.010 mL, 0.50 mol %), and decane (25 μ L). The reactor was pressurized to 600 psi at room temperature. With magnetic stirring, the reactor was heated to 35 °C for 90 min then ramped to a temperature of 195 °C over 30 min. The reaction was held at 195 °C for 15 hours then allowed to cool to room temperature. The reactor was then vented. The reaction mixture was filtered through Celite ®. The reactor was thoroughly rinsed with THF (total volume, 5 mL). The rinses were filtered through Celite ® and combined with the reaction mixture. A sample of the filtrate (approximately 0.2 mL) was diluted using THF (final volume approximately 1.5 mL). The sample was then analyzed by GC-MS and GC-FID. Alcohol products were identified by comparison to authentic standards and quantified using calibration curves constructed using authentic samples. Isolated products were obtained after filtration through a plug of MgSO₄ and column chromatography on silica gel with hexanes and ethyl acetate (1:1 mixture) as the eluant.

1-Octanol. (87 mg, 48 %). Colorless oil. The ¹H NMR spectrum is consistent with previously reported data.^{5,6} ¹H NMR (CDCl₃, 500 MHz, 298 K) δ 3.65 (t, *J* = 6.7 Hz, 2H), 1.90 (br, 1H), 1.58 (m 2H), 1.31 (m, 10H), 0.90 (t, *J* = 6.9 Hz, 3H).

1-Dodecanol. (130 mg, 50 %). Colorless oil. The ¹H NMR spectrum is consistent with previously reported data.⁷ ¹H NMR (CDCl₃, 500 MHz, 298 K) δ 3.62 (t, *J* = 6.7 Hz, 2H), 2.05 (br, 1H), 1.56 (m 2H), 1.27 (m, 16H), 0.88 (t, *J* = 7.0 Hz, 3H).

3-Phenylpropanol. (71 mg, 38 %). Pale yellow oil. The ¹H NMR spectrum is consistent with previously reported data.^{5,8} ¹H NMR (CDCl₃, 500 MHz, 298 K) δ 7.33 (m, 2H), 7.25 (m, 3H), 3.71 (t, *J* = 6.5 Hz, 2H), (br, 1H), 2.75 (m, 2H), 1.94 (m, 2H).

2-Phenylethanol. (124 mg, 72 %). Colorless oil. The ¹H NMR spectrum is consistent with previously reported data.^{9,10} ¹H NMR (CDCl₃, 500 MHz, 298 K) δ 7.35 (m, 2H), 7.27 (m, 3H), 3.86 (t, *J* = 6.7 Hz, 2H), 2.89 (t, *J* = 6.7 Hz, 2H), 2.18 (br, 1H).

2-Phenylpropanol. (106 mg, 53 %). Pale yellow oil. The ¹H NMR spectrum is consistent with previously reported data.^{10,11} ¹H NMR (CDCl₃, 500 MHz, 298 K) δ 7.37 (m, 2H), 7.29 (m, 3H), 3.74 (d, *J* = 6.8 Hz, 2H), 2.98 (m, 1H), 2.56 (br, 1H), 1.31 (d, *J* = 7.0 Hz, 3H).

2-Indanol. (63 mg, 35 %). Off white solid. The ¹H NMR spectrum is consistent with previously reported data.^{10,12} ¹H NMR (CDCl₃, 500 MHz, 298 K) δ 7.28 (m, 2H), 7.20 (m, 2H), 4.71 (m, 1H), 3.24 (dd, *J* = 16.4, 5.9 Hz, 2H), 2.94 (dd, *J* = 16.3, 3.2 Hz, 2H), 2.04 (br, 1H).

Cyclopentylmethanol. (35 mg, 26 %). Pale yellow oil. The ¹H NMR spectrum is consistent with previously reported data.¹³⁻¹⁴ ¹H NMR (CDCl₃, 500 MHz, 298 K) δ 3.52 (d, 2H), 2.10 (m, 1H), 1.73 (m, 2H), 1.56 (m, 5H), 1.23 (m, 2H).

GC-FID data for Table 1

Table S1. GC-FID retention times and response factors for products from the reaction of epoxyoctane.

Compound	Retention time (min.)	Response factor (counts/M)
THF	2.87	n/a
dioxane	3.88	n/a
octane	6.07	3.07E6
octene isomers ^a	5.83-6.40	1.75E6
decane	9.12	2.98E6
octanal	9.18	1.99E6
1-octanol	9.84	2.37E6
1,2-octane diol	11.22	2.22E6
THF impurity	13.08	n/a
dioctyl ether	13.88	4.77E6

^a The response factor for 4-trans octene was used for all octene isomers.

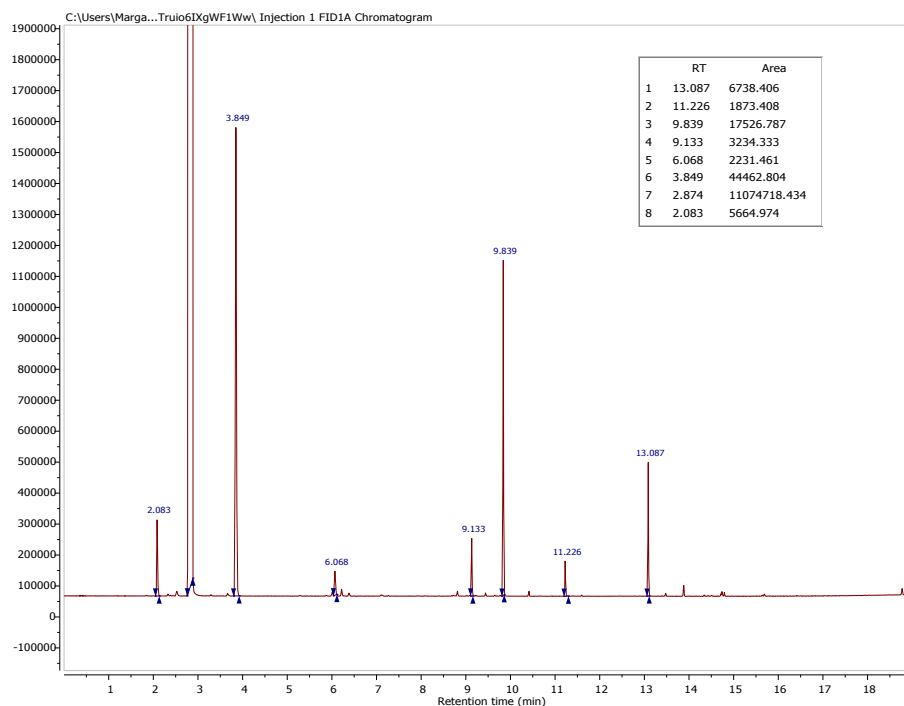


Figure 1. Chromatogram for Table 1 entry 1.

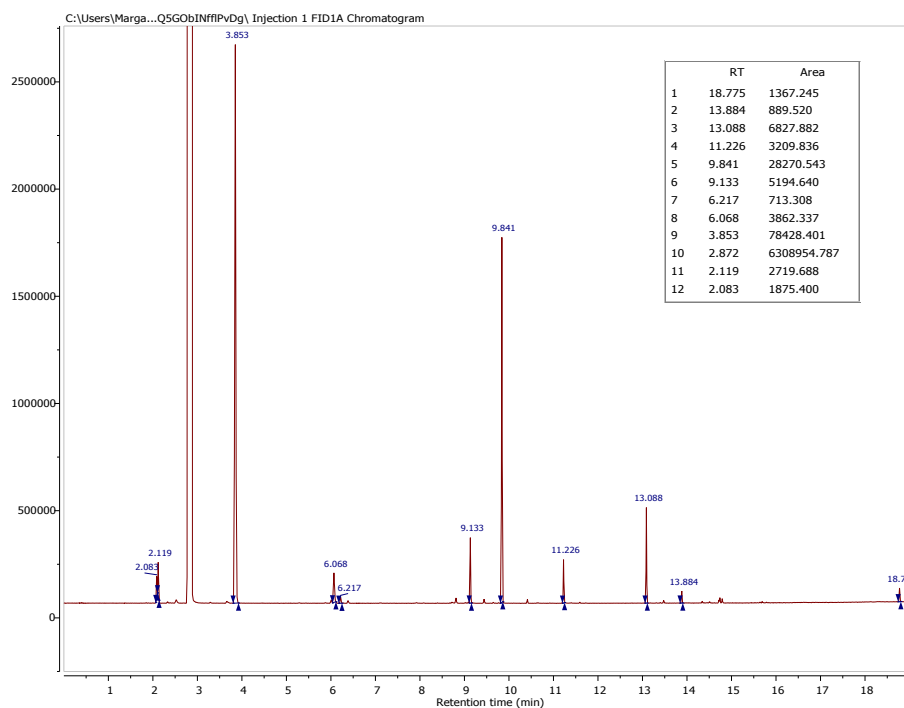


Figure 2. Chromatogram for Table 1 entry 2.

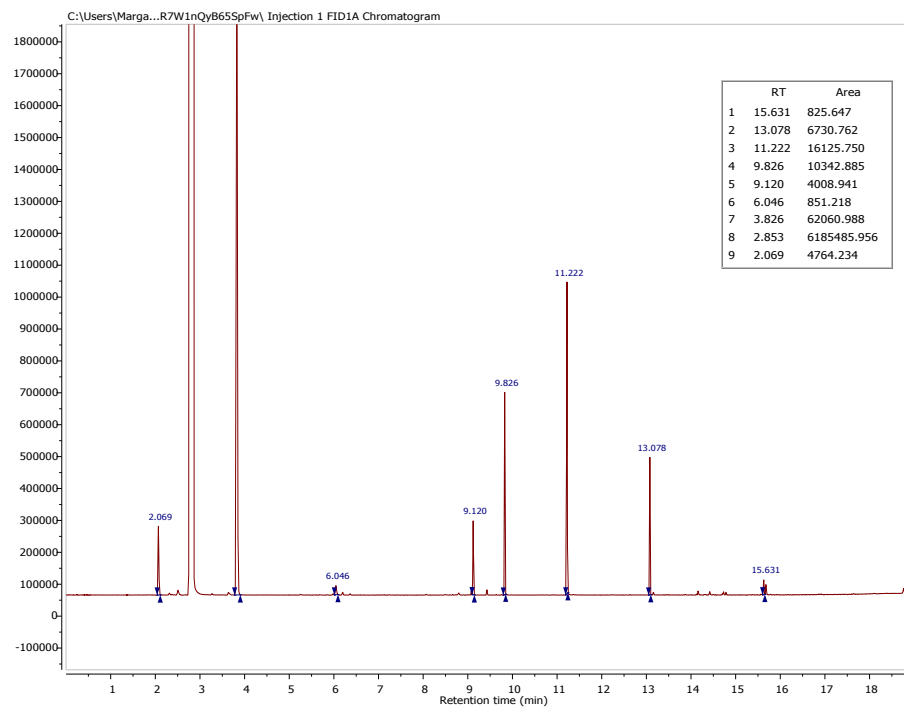


Figure 3. Chromatogram for Table 1 entry 3.

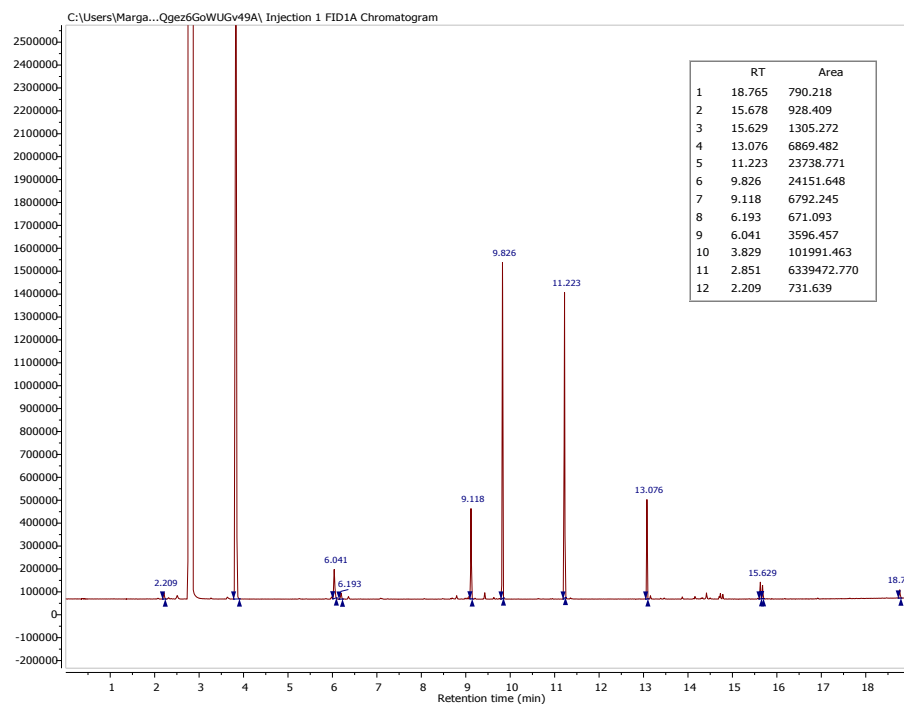


Figure 4. Chromatogram for Table 1 entry 4.

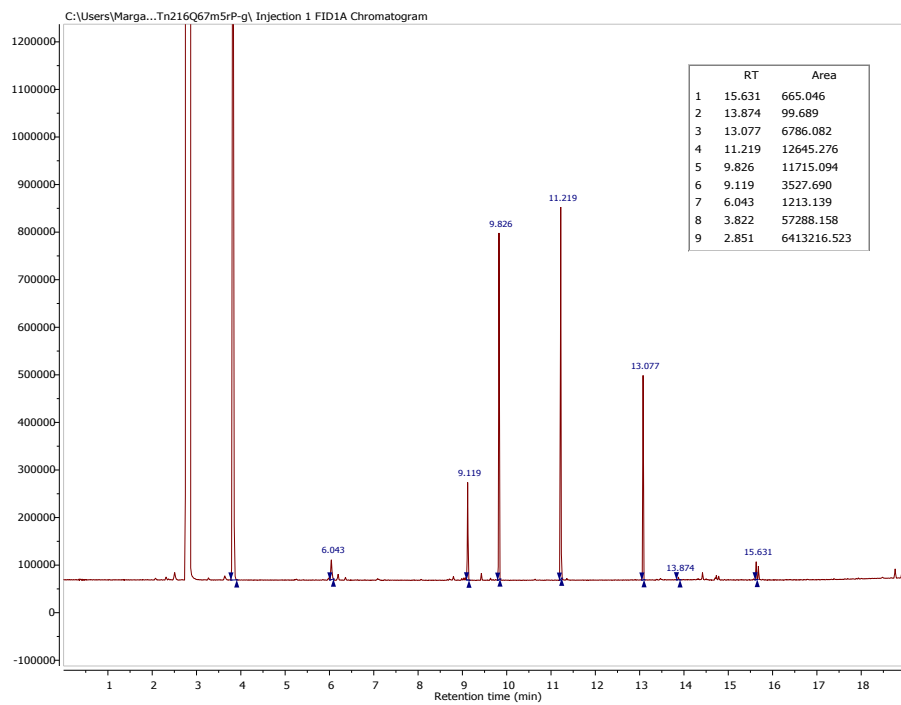


Figure 5. Chromatogram for Table 1 entry 5.

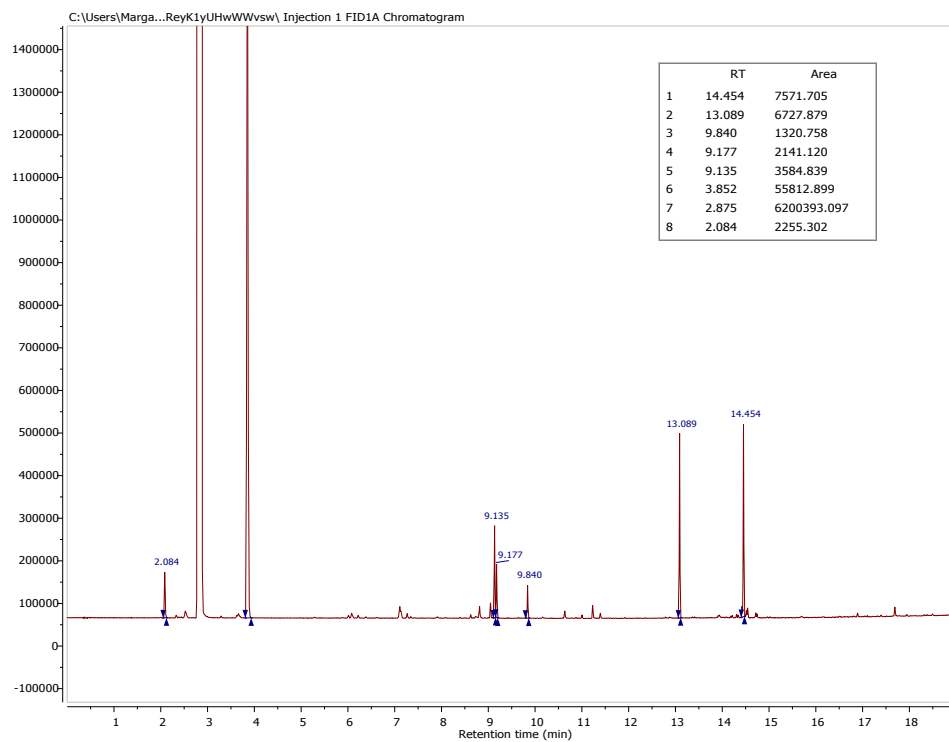


Figure 6. Chromatogram for Table 1 entry 6.

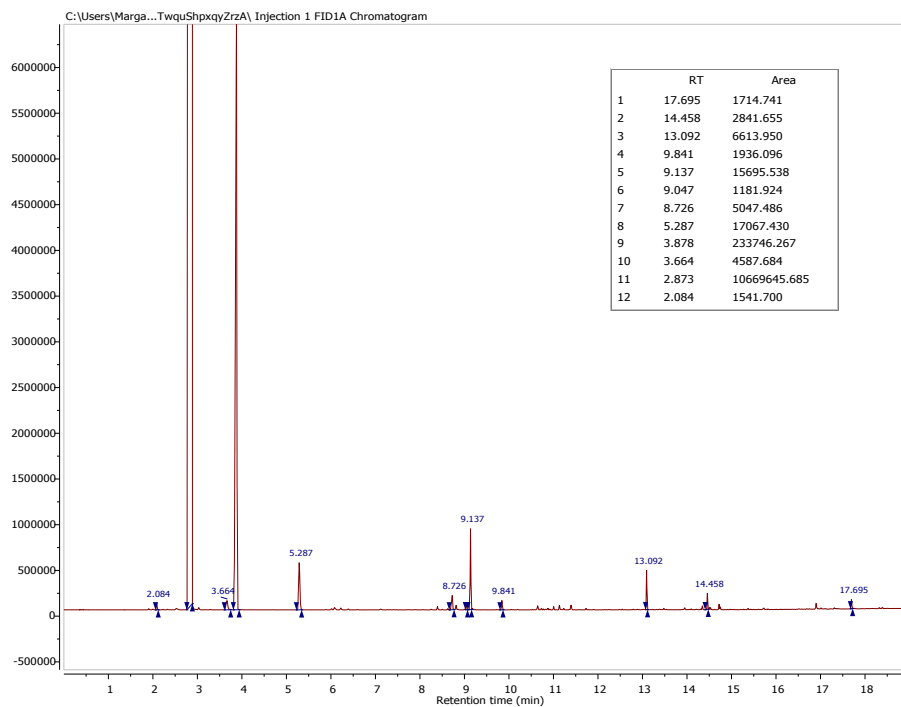


Figure 7. Chromatogram for Table 1 entry 7.

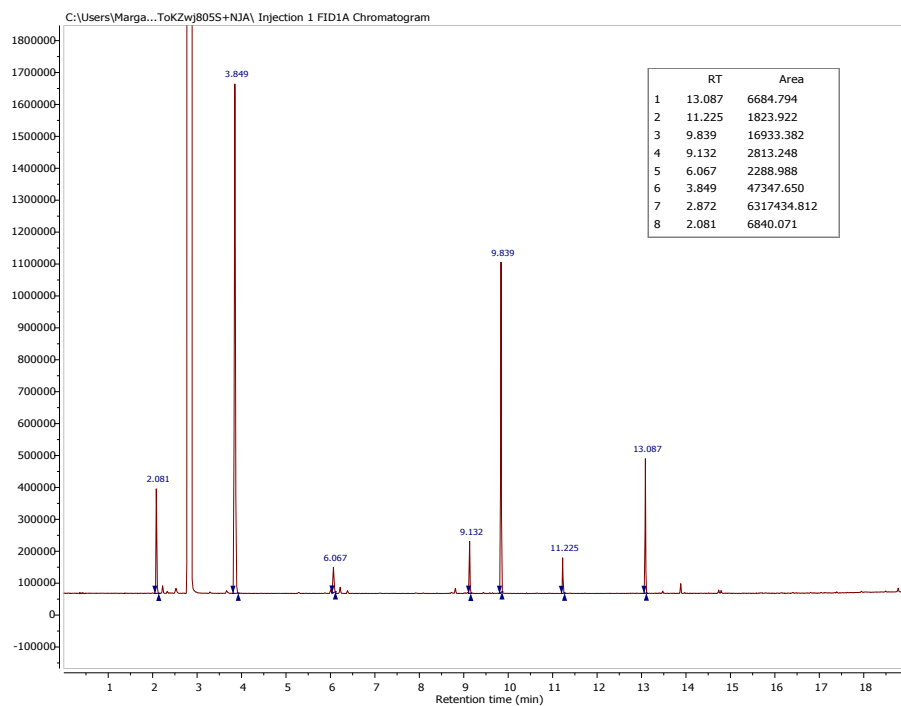


Figure 8. Chromatogram of a reaction starting with 1,2-octane diol rather than epoxyoctane.

¹H NMR spectra of isolated products

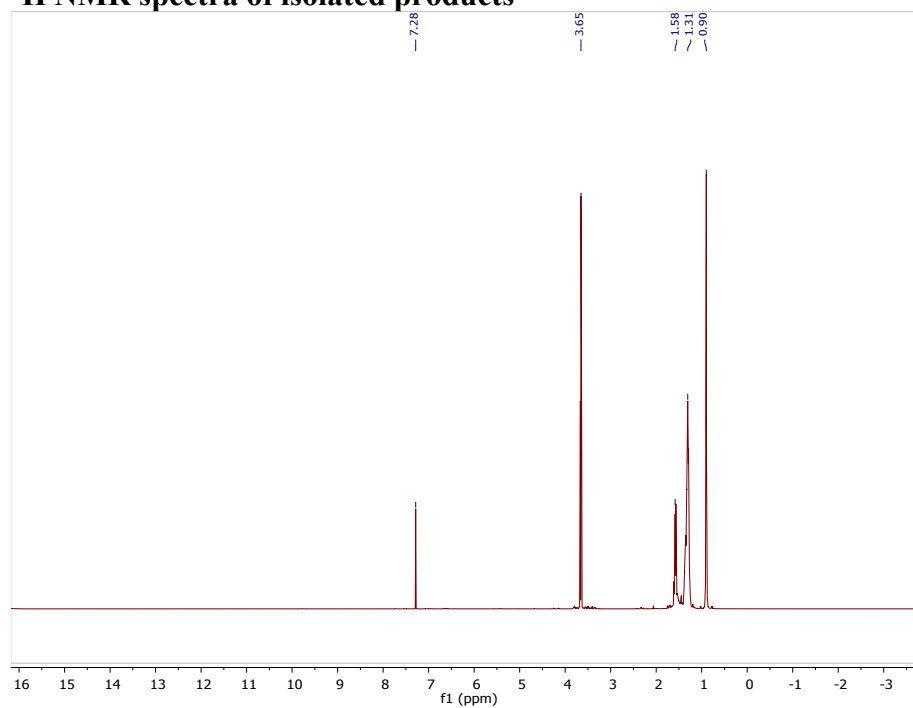


Figure 6. ¹H NMR spectrum of 1-octanol (Table 2, Entry 1)

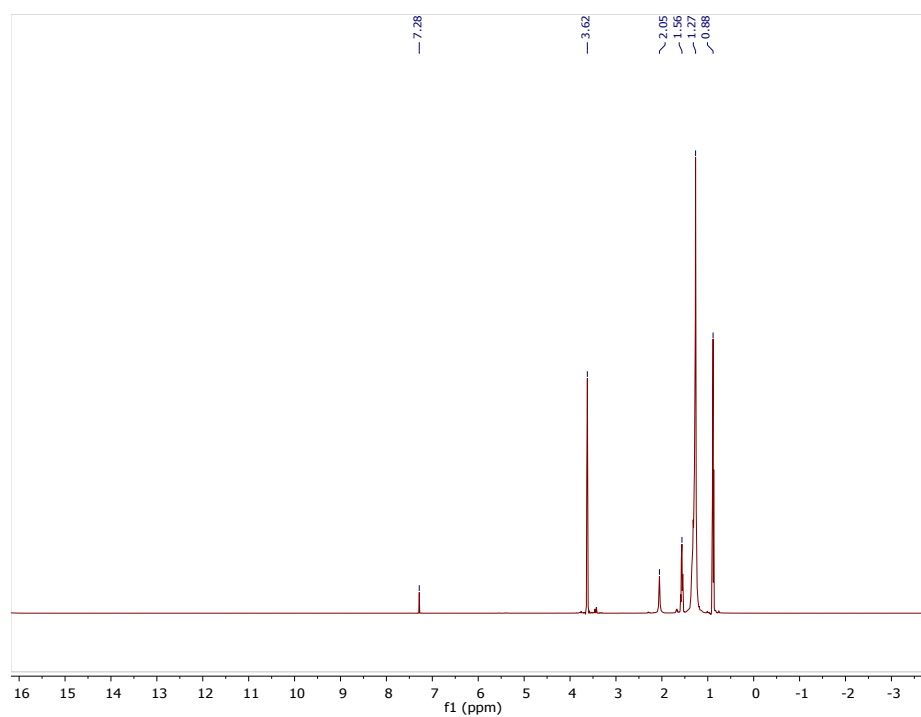


Figure 7. ¹H NMR spectrum of 1-dodecanol (Table 2, Entry 2)

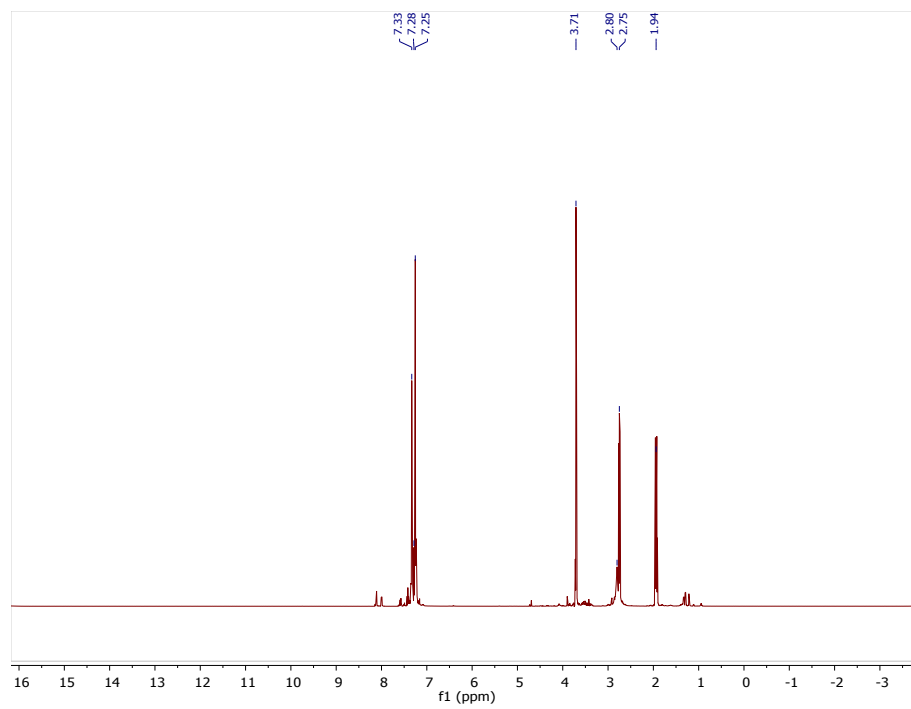


Figure 8. ¹H NMR spectrum of 3-phenylpropanol (Table 2, Entry 3)

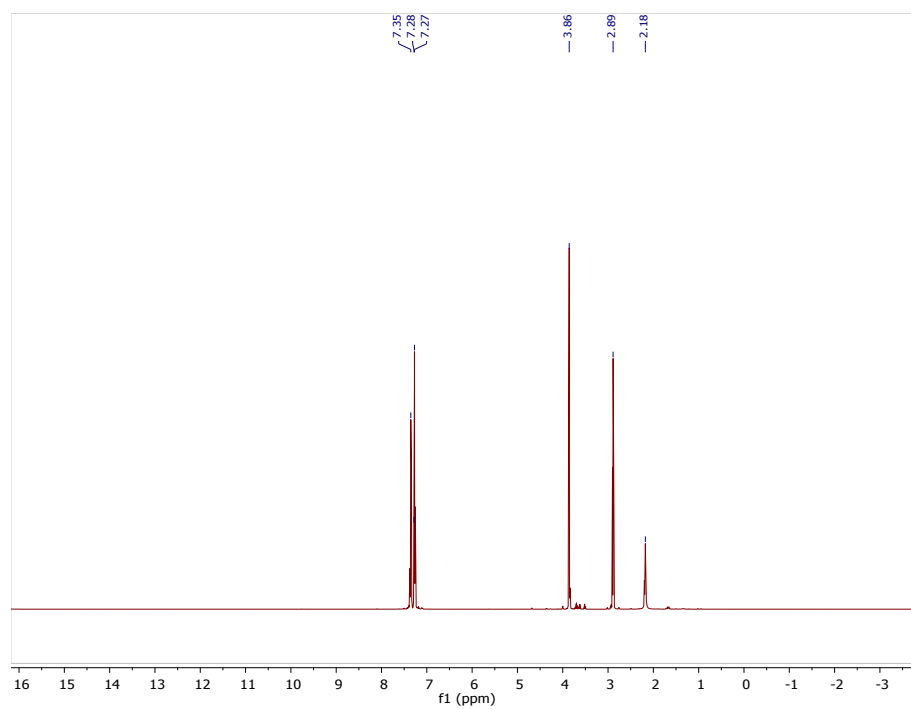


Figure 9. ¹H NMR spectrum of 2-phenylethanol (Table 2, Entry 4)

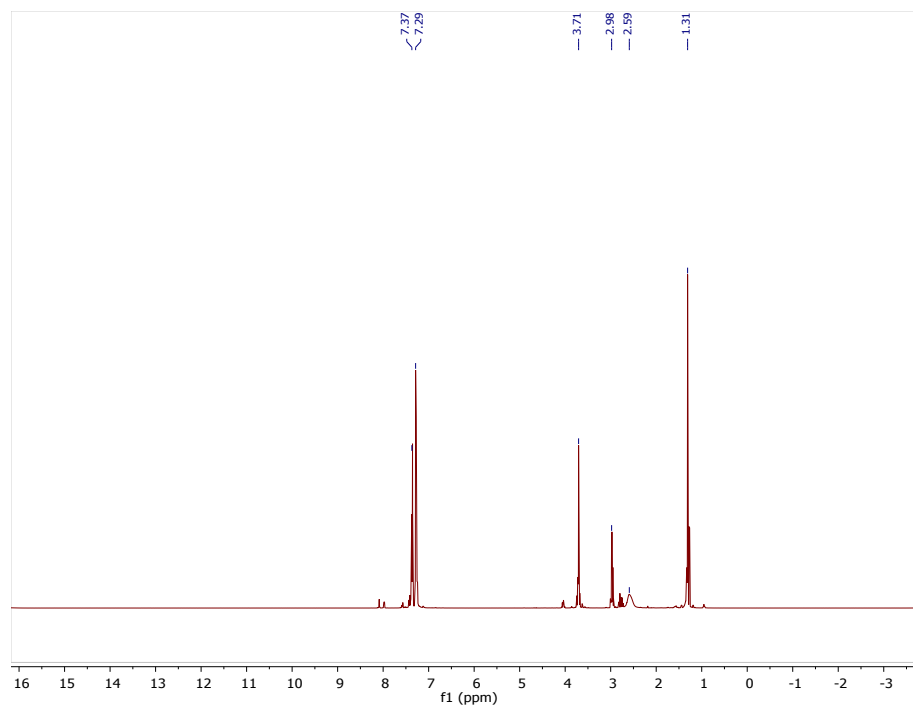


Figure 10. ¹H NMR spectrum of 2-phenylpropanol (Table 2, Entry 5)

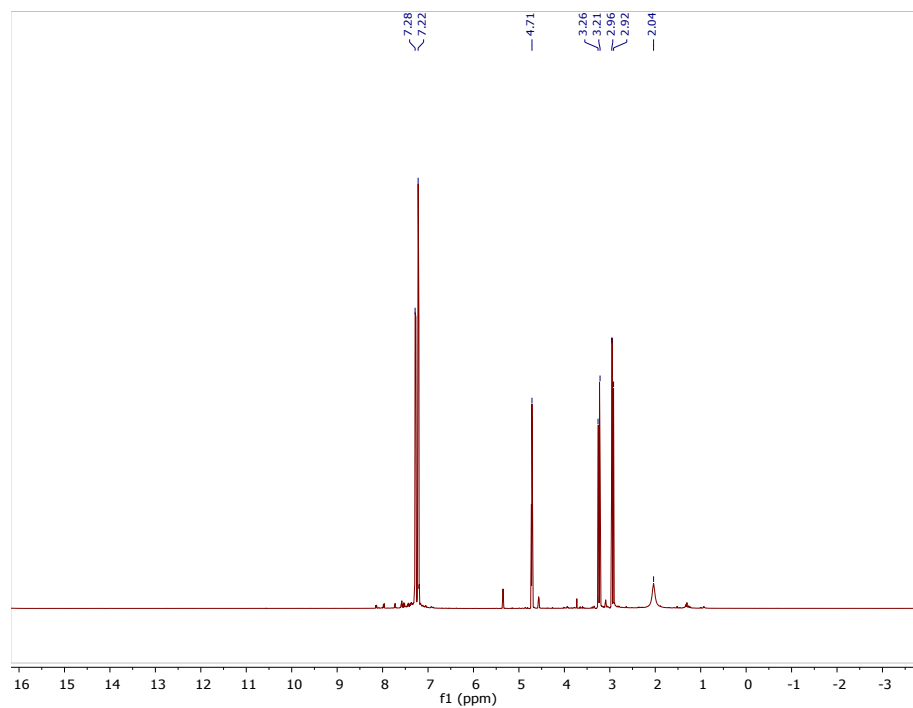


Figure 11. ¹H NMR spectrum of 2-indanol (Table 2, Entry 6)

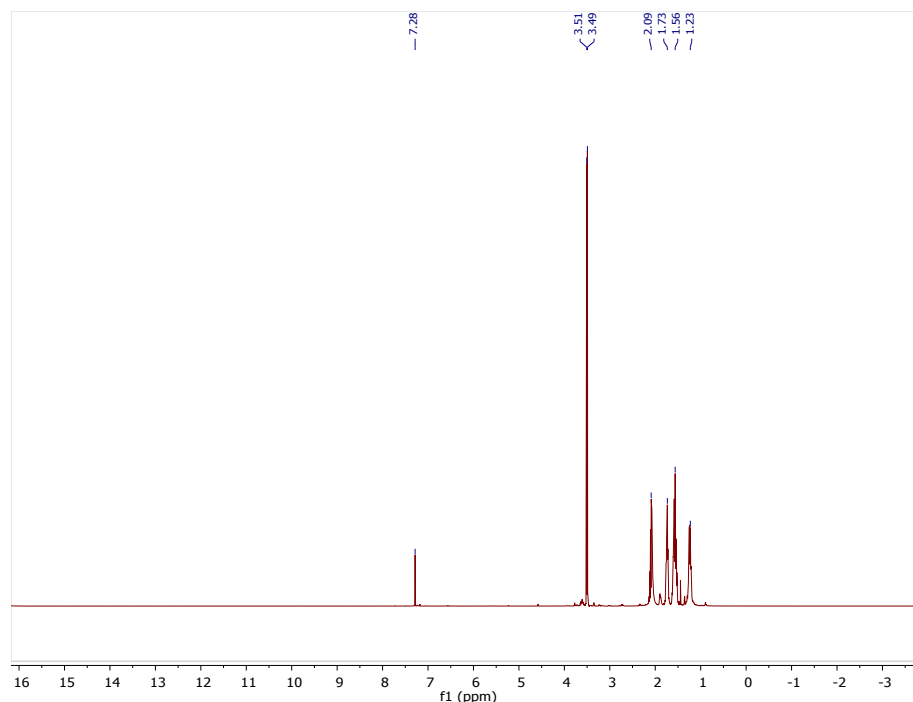


Figure 12. ^1H NMR spectrum of cyclopentanemethanol (Table 2, Entry 7)

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¹² *Spectral Database for Organic Compounds (SDBS); ^1H NMR spectrum*; SDBS No.: 6339; RN 4254-29-9; <http://riodb01.ibase.aist.go.jp/sdbs/> (accessed Sept. 6, 2018).

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