Supplementary Information for:

Cobalt-Catalyzed Transfer Hydrogenation of C=O and C=N Bonds

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Experimental Details

General Considerations. Unless specified otherwise, all reactions were carried out under a dry argon atmosphere using standard glove-box and Schlenk techniques. Deuterated solvents were purchased from Cambridge Isotope Laboratories and THF-d_8 was dried over Na metal. Anhydrous grade THF and isopropanol were obtained from Aldrich or Acros and stored over 4Å molecular sieves. ^{1}H NMR and ^{13}C NMR spectra were obtained at room temperature on a Bruker AV400 MHz spectrometer, with chemical shifts (δ) referenced to the residual solvent signal. GC-MS analysis was obtained using a Hewlett Packard 6890 GC system equipped with a Hewlett Packard 5973 mass selective detector. Isopropanol-d_1 and isopropanol-d_8 were purchased from Cambridge Isotope Laboratories. Cobalt complexes **1-6** were prepared according to previously published procedures.[1,2]

General procedure for the cobalt-catalyzed transfer hydrogenation. Under nitrogen, complex **1** (6.1 mg, 10 µmol) and H[BAr$^F{}_4$]·(Et$_2$O)$_2$ (10.1 mg, 10.0 µmol) were dissolved in THF/isopropanol (2 mL, v/v, 1:3) in a thick-walled glass vial or vessel equipped with a Teflon stopper and a stirbar. The substrate (a ketone, aldehyde, or imine, 0.5 mmol) was then added. The vessel was sealed and stirred at 25-80 °C (temperature depending on the substrate, as indicated in Table 1) for 24 h. The reaction was cooled to room temperature, the solvent was removed under vacuum, and the residue was purified by preparative TLC using *n*-hexane/ethyl acetate (3:1, v/v) as an eluent. Isolated products were characterized by ^{1}H NMR and GC-MS, with spectra matching those reported previously or authentic samples.

Transfer hydrogenation of acetophenone with added Hg. Under nitrogen, complex **1** (6.1 mg, 10 µmol) and H[BAr$^F{}_4$]·(Et$_2$O)$_2$ (10.1 mg, 10.0 µmol) were dissolved in THF/isopropanol (2 mL, v/v, 1:3) in a small glass vial. Acetophenone (60.0 mg, 0.50 mmol) and Hg metal (202 mg, 1.01 mmol) were then added and hexamethylbenzene (ca. 0.1 mmol) was also added as an internal standard. The resulting solution was stirred at 25 °C for 24 h, after which time the reaction mixture was exposed to air and diluted with dichloromethane. GC analysis revealed that 90% conversion of acetophenone to 1-phenylethanol had occurred.

Transfer hydrogenation of acetophenone with added trimethylphosphine. Complex **1** (6.1 mg, 10 µmol), H[BAr$^F{}_4$]·(Et$_2$O)$_2$ (10.1 mg, 10.0 µmol) and trimethylphosphine (20 µL of a 1.0 M solution in THF, 20 µmol) were dissolved in THF/isopropanol (2 mL, v/v, 1:3) in a small glass vial. Acetophenone (60 mg, 0.50 mmol) was then added and hexamethylbenzene (ca. 0.1 mmol) was also added as an internal standard. The reaction mixture was stirred at 25 °C for 24 h, after which time it was exposed to air and diluted with dichloromethane. GC analysis revealed that the yield of 1-phenylethanol was 77%.

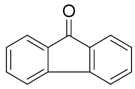
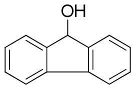
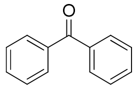
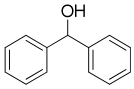
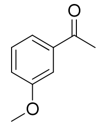
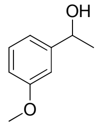
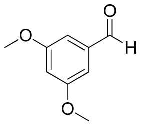
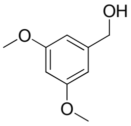
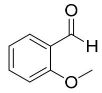
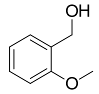
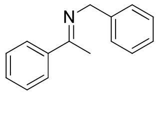
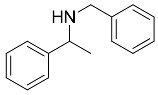
Transfer hydrogenation of acetophenone with added base (KO^{t}Bu). Complex **1** (6.1 mg, 10 µmol), H[BAr$^F{}_4$]·(Et$_2$O)$_2$ (10.1 mg, 10.0 µmol) and potassium *t*-butoxide (2.2 mg, 20 µmol) were dissolved in THF/isopropanol (2 mL, v/v, 1:3) in a small glass vial. Acetophenone (60 mg, 0.50 mmol) was then added and hexamethylbenzene (ca. 0.1 mmol) was also added as an internal standard. The resulting solution was stirred at 25 °C for 24 h, after which time it was exposed to air and diluted with dichloromethane. GC analysis revealed that the yield of 1-phenylethanol was 30%.

Transfer hydrogenation with isopropanol-d_1 (isopropanol-OD). In a glovebox, complex **1** (6.1 mg, 10 μmol) and H[BAr$^F{}_4$]·(Et$_2$O)$_2$ (10.1 mg, 10.0 μmol) were dissolved in THF (2.0 mL). Isopropanol-d_1 (0.5 mL) was then added, followed by acetophenone (60 mg, 0.50 mmol). The resulting solution was stirred at 25 °C for 24 h, the reaction mixture was exposed to air and the product was isolated by flash column chromatography as colorless oil (yield: 85%). Examination of the ^{1}H NMR spectrum revealed that the reaction product was 1-phenylethanol-d_1, where less than 2% of deuterium was incorporated into the benzylic C-H position of the product.

Transfer hydrogenation with isopropanol-d_8. In a glovebox, complex **1** (6.1 mg, 10 μmol) and H[BAr$^F{}_4$]·(Et$_2$O)$_2$ (10.1 mg, 10.0 μmol) were dissolved in THF (2.0 mL). Isopropanol-d_8 (0.5 mL) was then added, followed by acetophenone (60 mg, 0.50 mmol). The resulting solution was stirred at 25 °C for 24 h, the reaction mixture was exposed to air and the product was isolated by flash column chromatography as colorless oil (yield: 88%). Examination of the ^{1}H NMR spectrum revealed that the product was 1-phenylethanol-d_2, where deuterium was incorporated into both the benzylic C-H and O-H positions.

Monitoring transfer hydrogenation with isopropanol-d_8 by NMR. In a J-Young NMR tube, complex **1** (6.1 mg, 10 μmol) and H[BAr$^F{}_4$]·(Et$_2$O)$_2$ (10.1 mg, 10.0 μmol) were dissolved in THF-d_8 (0.3 mL). Isopropanol-d_8 (0.2 mL) was then added, followed by acetophenone (24 mg, 0.20 mmol). The resulting solution was allowed to stand at 25 °C and monitored periodically by ^{1}H NMR spectroscopy. Examination of the ^{1}H NMR spectra after 10 h and 20 h revealed no detectable diamagnetic cobalt species.

Table S1. Additional Examples of Cobalt-Catalyzed Transfer Hydrogenation.[a]

Entry	substrate	product	isolated yield (%)
1			96
2			98
3			95
4			99
5			96
6			9[b,c]

[a] Conditions: substrate (0.5 mmol) in isopropanol/THF (3:1 (v/v), 2 mL), 25 °C, 24 h. [b] Reaction run at 80 °C. [c] GC yield.

Spectroscopic data:

Spectroscopic data (NMR and GC-MS) for the alcohol and amine products matched those reported previously; examples are presented here.

^{1}H NMR and GC-MS data for selected isolated products:

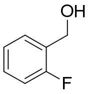
2-fluorobenzyl alcohol (92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (td, *J* = 7.3, 1.9 Hz, 1H), 7.31 – 7.19 (m, overlapping, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 9.2 Hz, 1H), 4.74 (s, 2H), 1.91 (s, 1H). GC-MS (m/z): 126 (calc. 126)

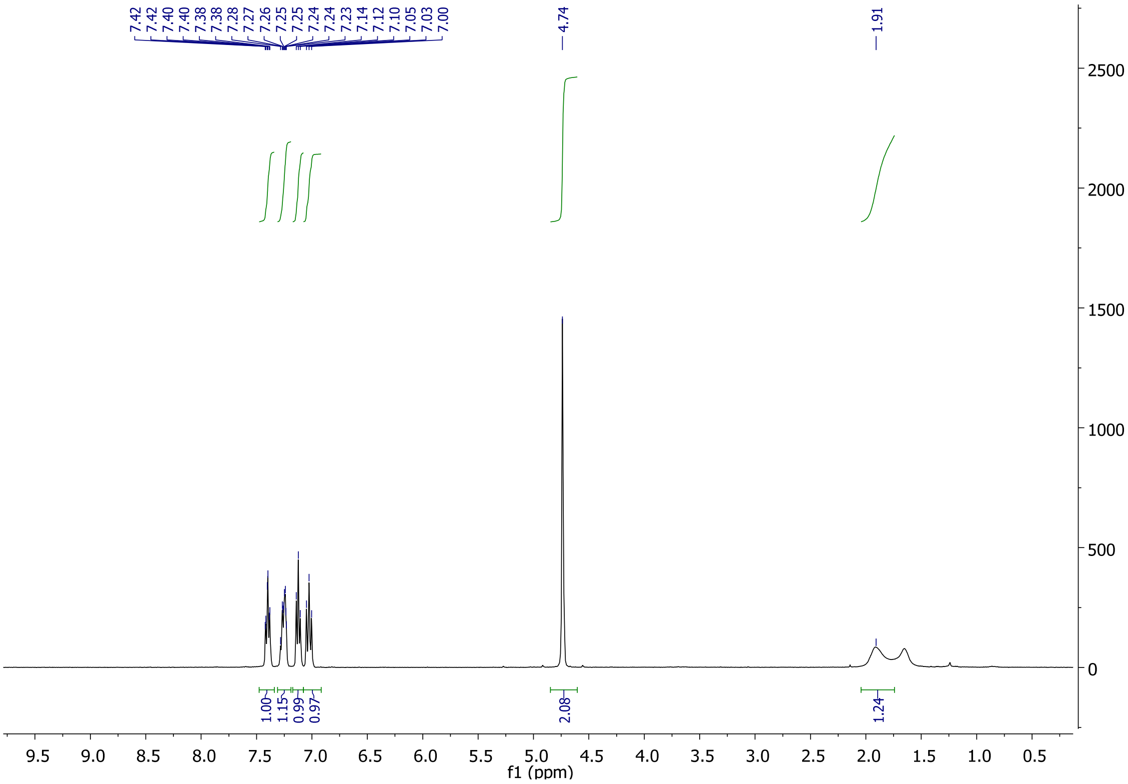
4-phenylbutan-2-ol (98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 7.18 (m, 3H), 3.82 (q, *J* = 6.2 Hz, 1H), 2.75 (m, 1H), 2.66 (m, 1H), 1.76 (m, 2H), 1.55 (s, 1H, H^{OH}), 1.22 (d, *J* = 6.1 Hz, 3H). GC-MS (m/z): 150 (calc. 150).

3-phenylpropanol (95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.20 – 7.10 (m, 3H), 3.56 – 3.28 (m, 2H), 2.64 – 2.40 (m, 2H), 1.81 – 1.51 (m, 2H). GC-MS (m/z): 136 (calc. 136)

2-Fluorobenzyl alcohol:

^{1}H NMR ($CDCl_3$):





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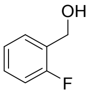
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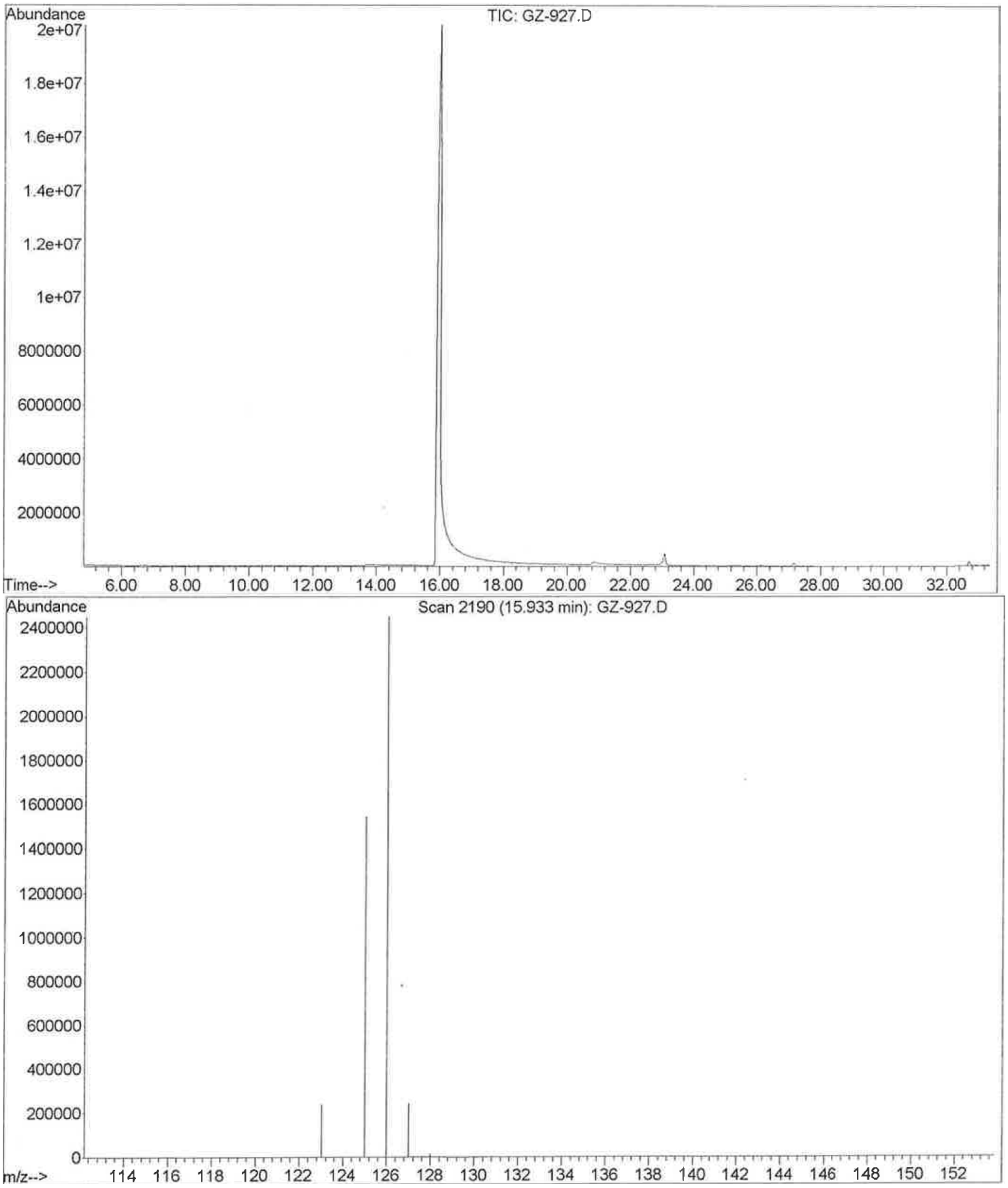
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200000
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m/z-->
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124
126
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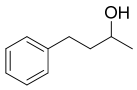
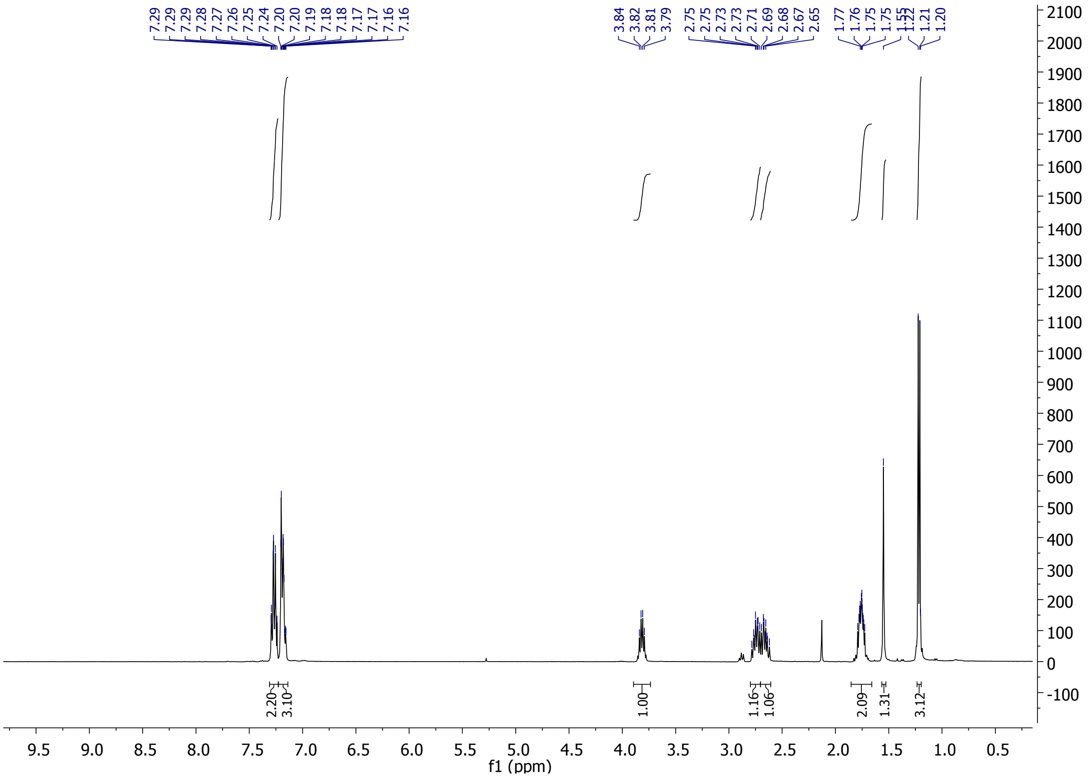
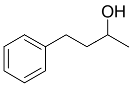
4-Phenylbutan-2-ol:

^{1}H NMR ($CDCl_3$):





GC-MS: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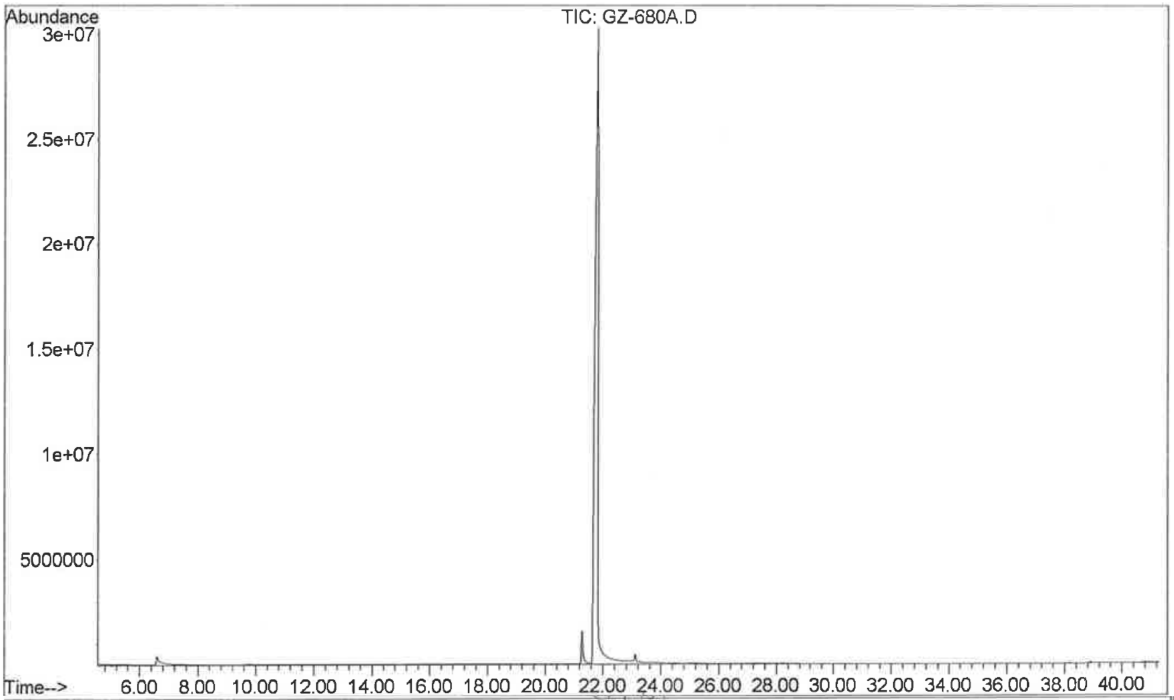
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1e+07
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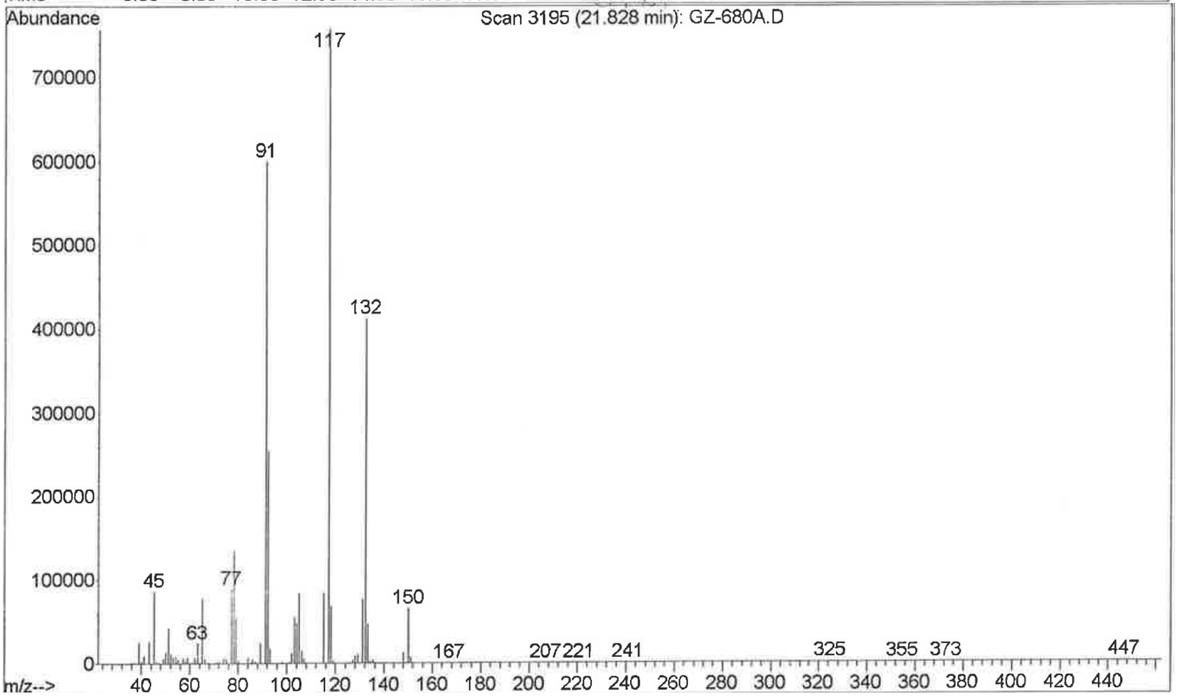
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45
77
63
167
207
221
241
325
355
373
447
m/z-->
40
60
80
100
120
140
160
180
200
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420
440

3-Phenylpropanol:

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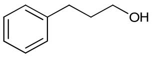

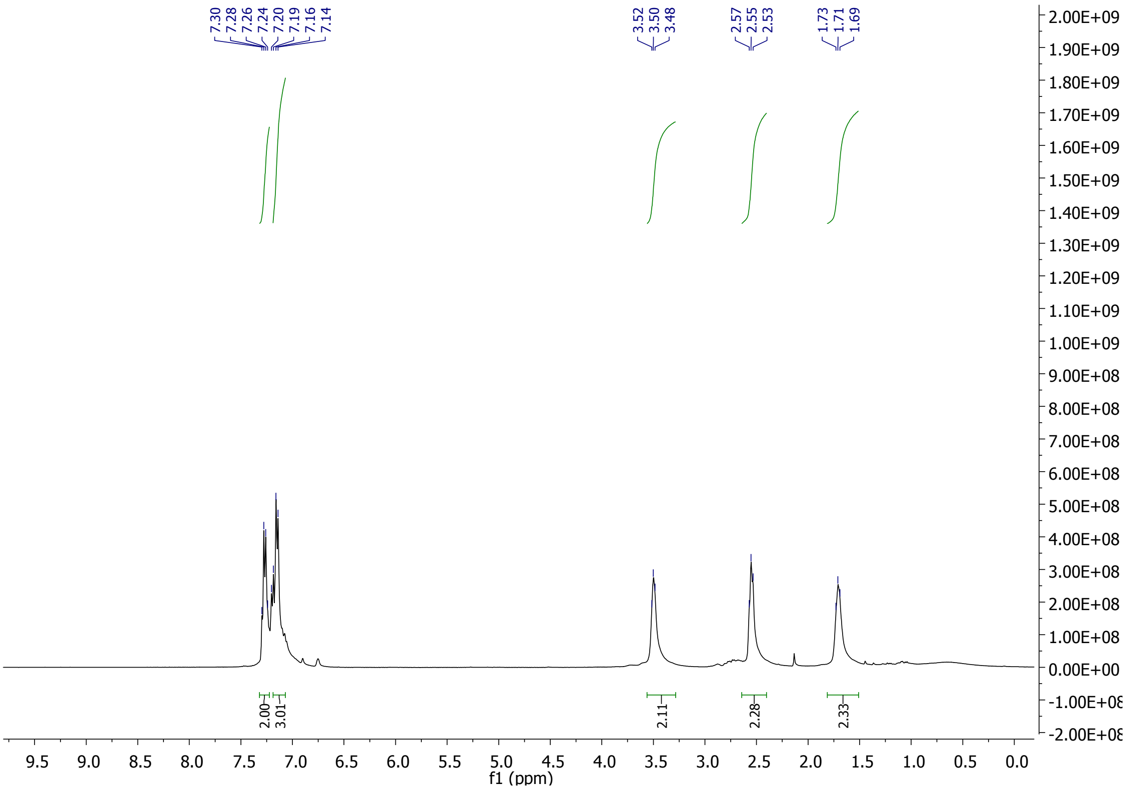

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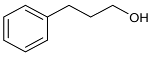
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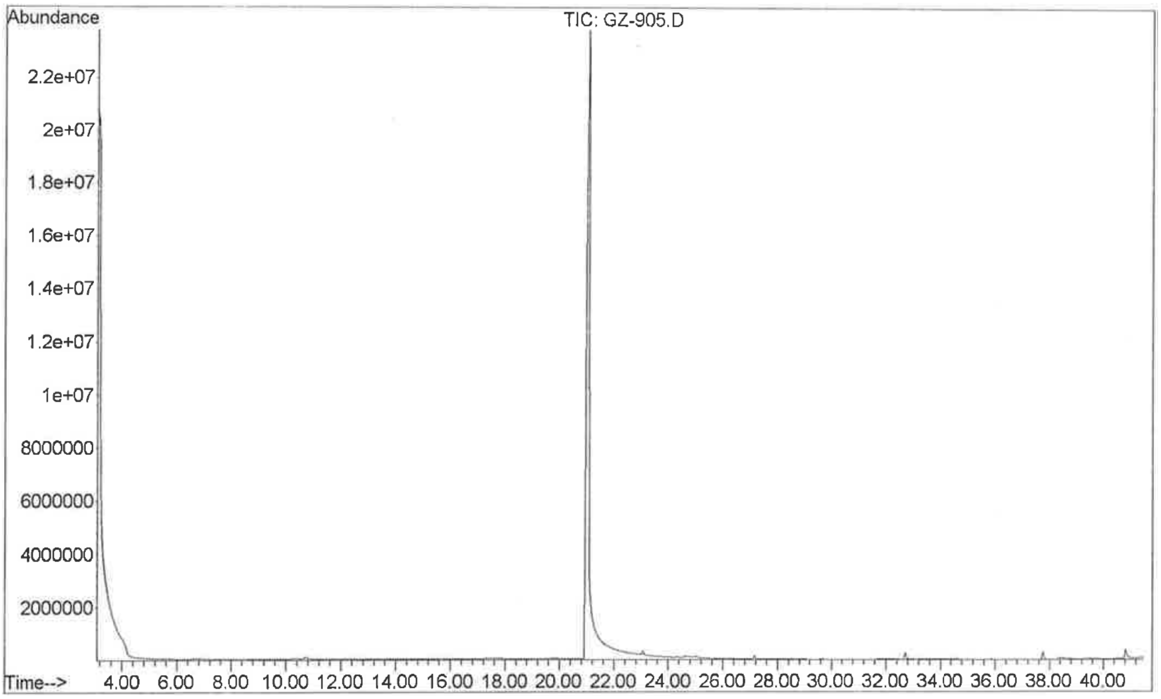
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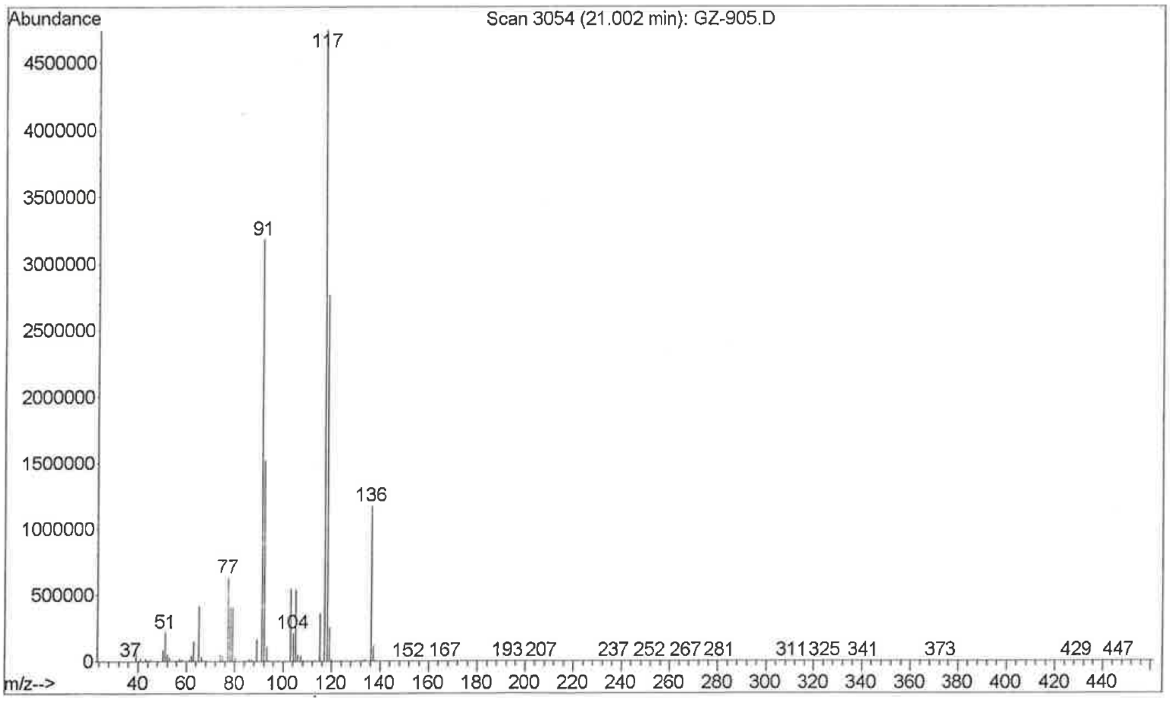
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51
104
37
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m/z-->
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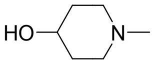

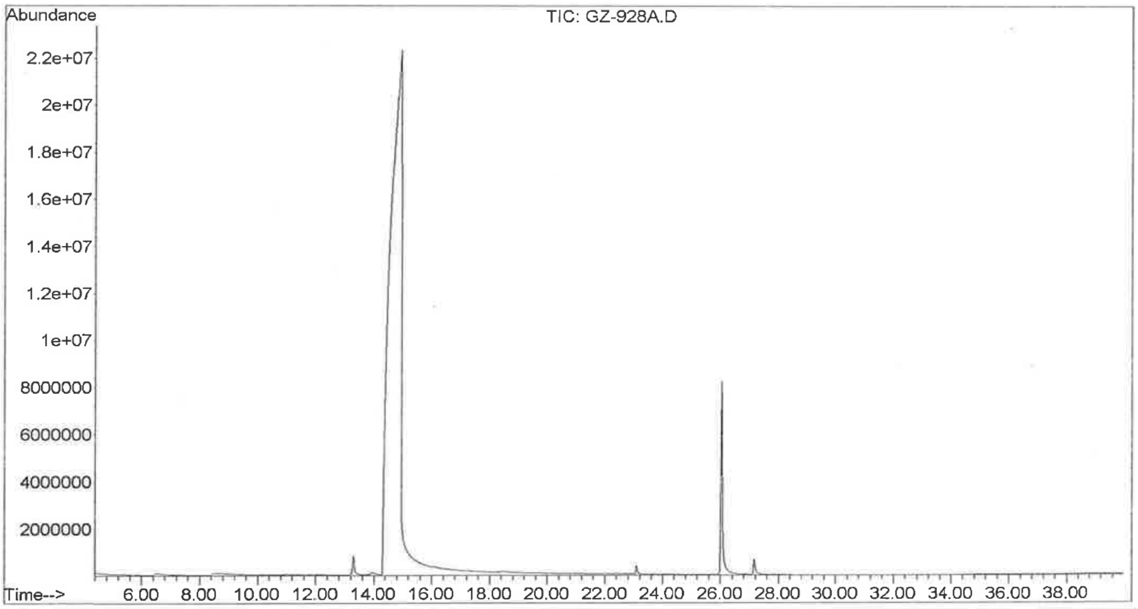

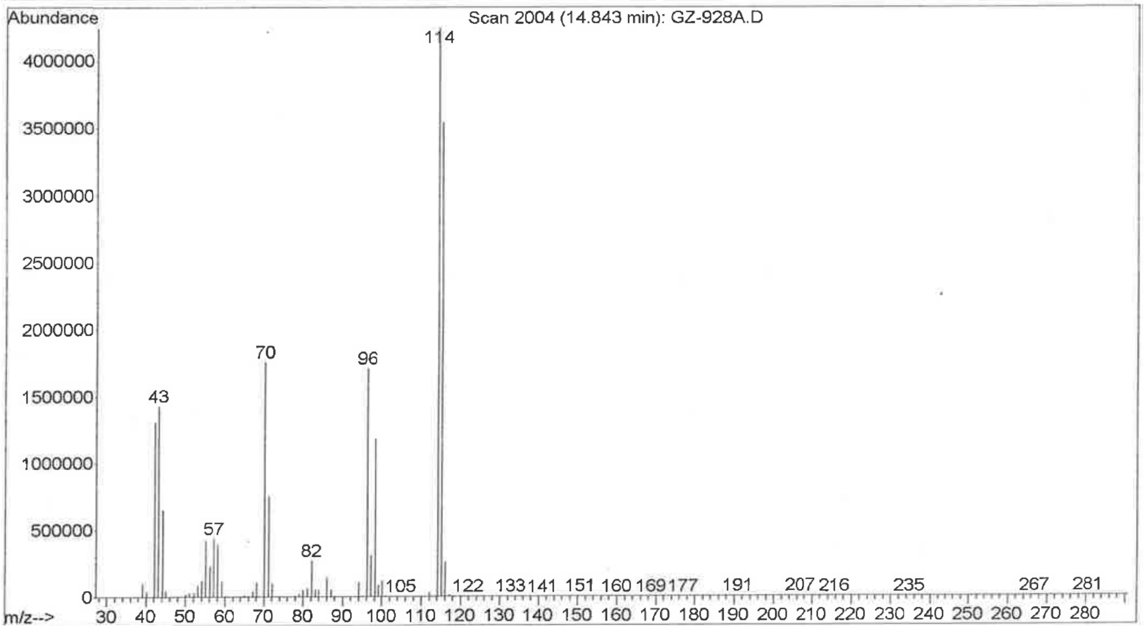

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[1] Zhang, G.; Scott, B. L.; Hanson, S. K. *Angew. Chem. Int. Ed.* **2012**, *51*, 12102-12106.

[2] Zhang, G.; Vasudevan, K. V.; Scott, B. L.; Hanson, S. K. *J. Am. Chem. Soc.* **2013**, *135*, 8668-8681.