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Electronic Supporting Information for

Alcohol Oxidation with H_2O_2 Catalyzed by a Cheap and Promptly Available Imine Based Iron Complex.

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Instruments and General Methods

Oxidation products were identified by comparison of their GC retention times and GC/MS with those of authentic compounds. GC analyses were carried out on a gas chromatograph equipped with a capillary methylsilicone column (30 m x 0.25 mm x 25 μm) Chrompack CP-Sil 5 CB. GC-MS analyses were performed with a mass detector (EI at 70eV) coupled with a gas chromatograph equipped with a melted silica capillary column (30 m x 0.2 mm x 25 μm) covered with a methylsilicone film (5% phenylsilicone, OV5). NMR spectra were recorded on either a BrukerDPX300 spectrometer and were internally referenced to the residual proton solvent signal. GC-MS analyses were performed with a mass detector (EI at 70eV) coupled with a gas chromatograph equipped with a melted silica capillary column (30 m x 0.2 mm x 25 μm) covered with a methylsilicone film (5% phenylsilicone, OV5).

Materials

Spectrometer All reagents and solvents were purchased at the highest commercial quality and were used without further purification unless otherwise stated. Iron (II) bis (trifluoromethanesulfonate) bis (acetonitrile) was prepared according to a literature procedure from Fe(II) chloride (Sigma Aldrich).[1] Solvents were purchased from Sigma Aldrich and used as received. Cyclohexanol, cyclopentanol, cycloheptanol, were filtered over a short pad of silica gel prior to use. 2-decanol, 4-methyl-2-pentanol, 2-methylcyclohexanol e 2,6-dimethylcyclohexanol were prepared by $NaBH_4$ reduction of the corresponding ketones according to a procedure reported in literature.[2] 4-nitrophenyl-1-ethanol, 4-cianophenyl-1-ethanol, 4-chlorophenyl-1-ethanol, 4-methylphenyl-1-ethanol and 4-methoxyphenyl-1-ethanol were synthesized from the corresponding 4-substituted acetophenones by $NaBH_4$ reduction following a published procedure.[3] Complex **4** was prepared according to a literature procedure.[4]

0.5 gram-scale oxidation

Cyclohexanol

20.63 mg of $Fe(OTf)_2 \cdot 2CH_3CN$ (47.32 μmol, 1 mol%), 95 μmol of 2-picolylaldehide (2 mol%), 95 μmol of 2-picolylamine (2 mol%) and 474 mg of cyclohexanol (500 μL, 4.73 mmol, 100 mol%) and CH_3CN (20 mL) were mixed in a round-bottom, 50 mL flask. H_2O_2 (1.3 mL, 11.8 mmol, 250 mol%) was added over 30 minutes by syringe pump under vigorous stirring at room temperature. The reaction was left stirring for additional 30 minutes, and the solvent is removed by rotatory evaporation. The residue is dissolved in CH_2Cl_2, dried over Na_2SO_4 and filtered over SiO_2. After rotatory evaporation of the solvent, pure cyclohexanone has been obtained (310 mg, 3.16 mmol, 67%).

Cycloheptanol

18.10 mg of $Fe(OTf)_2 \cdot 2CH_3CN$ (41.5 μmol, 1 mol%), 83 μmol of 2-picolylaldehide (2 mol%), 83 μmol of 2-picolylamine (2 mol%) and 474 mg of cycloheptanol (500 μL, 4.15 mmol, 100 mol%) and CH_3CN (20 mL) were mixed in a round-bottom, 50 mL flask. H_2O_2 (1.15 mL, 10.4 mmol, 250 mol%) was added over 30 minutes by syringe pump under vigorous stirring at room temperature. The reaction was left stirring for additional 30 minutes, and the solvent is removed by rotatory evaporation. The residue is dissolved in CH_2Cl_2, dried over Na_2SO_4 and filtered over SiO_2. After rotatory evaporation of the solvent, pure cycloheptanone has been obtained (230 mg, 2.05 mmol, 49%).

Competitive Oxidation Experiments

*Competitive Oxidations between cyclohexanol and benzene, cyclohexanol and toluene, cyclohexanol and 1-phenylethanol, cyclohexanol and 2-methylcylohexanol, cyclohexanol and 2,6-dimethylcylohexanol in the presence of complex **1**.*

The conditions were the same described in the general oxidation procedure (see Experimental), but 125 μmol of cyclohexanol and 125 μmol of benzene, toluene, 1-phenylethanol, 2-methylcylohexanol or 2,6-dimethylcylohexanol were added to the catalyst solution.

In the case of the reaction carried out in the presence of 10% phenol (25 μmol), the reaction conditions are those described in the general oxidation procedure (see Experimental).

*TPA-Fe (**4**) catalyzed oxidation of cyclohexanol and benzyl alcohol*

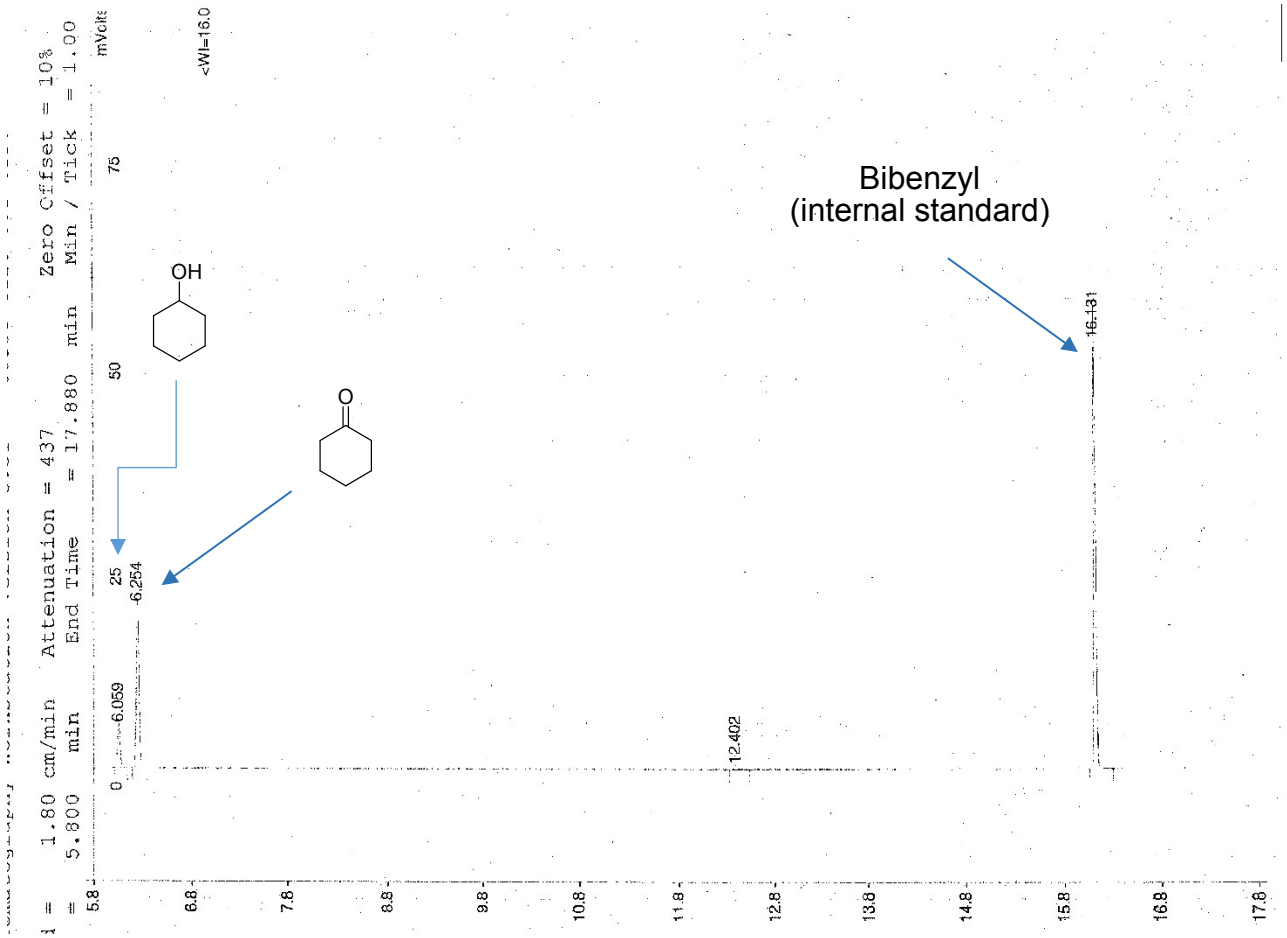
[(TPA)Fe(OTf)$_2$] (2.04 mg, 3.17 μmol), AcOH (158 μmol), cyclohexanol (158 μmol) and 1-phenylethanol (158 μmol) were dissolved in CH_3CN (700 μL). H_2O_2 (793 μmol from a 0.810 M solution in CH_3CN) was added over 30 minutes under vigorous stirring. After additional 60 minutes bibenzil (158 μmol) was added as an internal standard, the mixture was filtered over SiO_2 with AcOEt and injected into GC.

*Competitive Oxidations between cyclohexanol and 2-methylcylohexanol, cyclohexanol and 2,6-dimethylcylohexanol in the presence of complex **4**.*

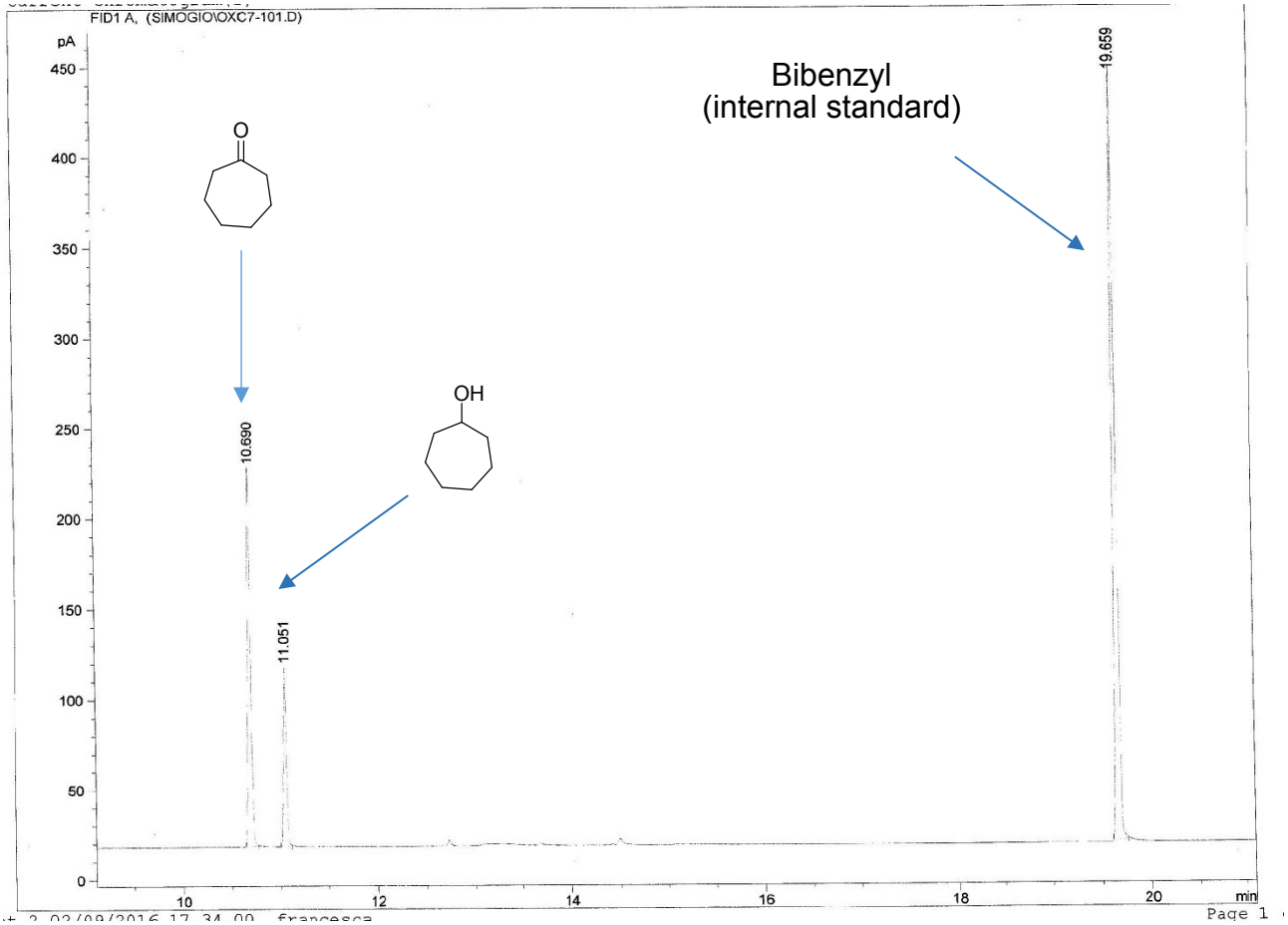
The conditions were the same described in the general oxidation procedure (see Experimental), but using complex **4** ([(TPA)Fe(OTf)$_2$]) instead of complex **1**, furthermore, 125 μmol of cyclohexanol and 125 μmol of 2-methylcylohexanol or 2,6-dimethylcylohexanol were added to the catalyst solution.

Selected examples of GC chromatograms

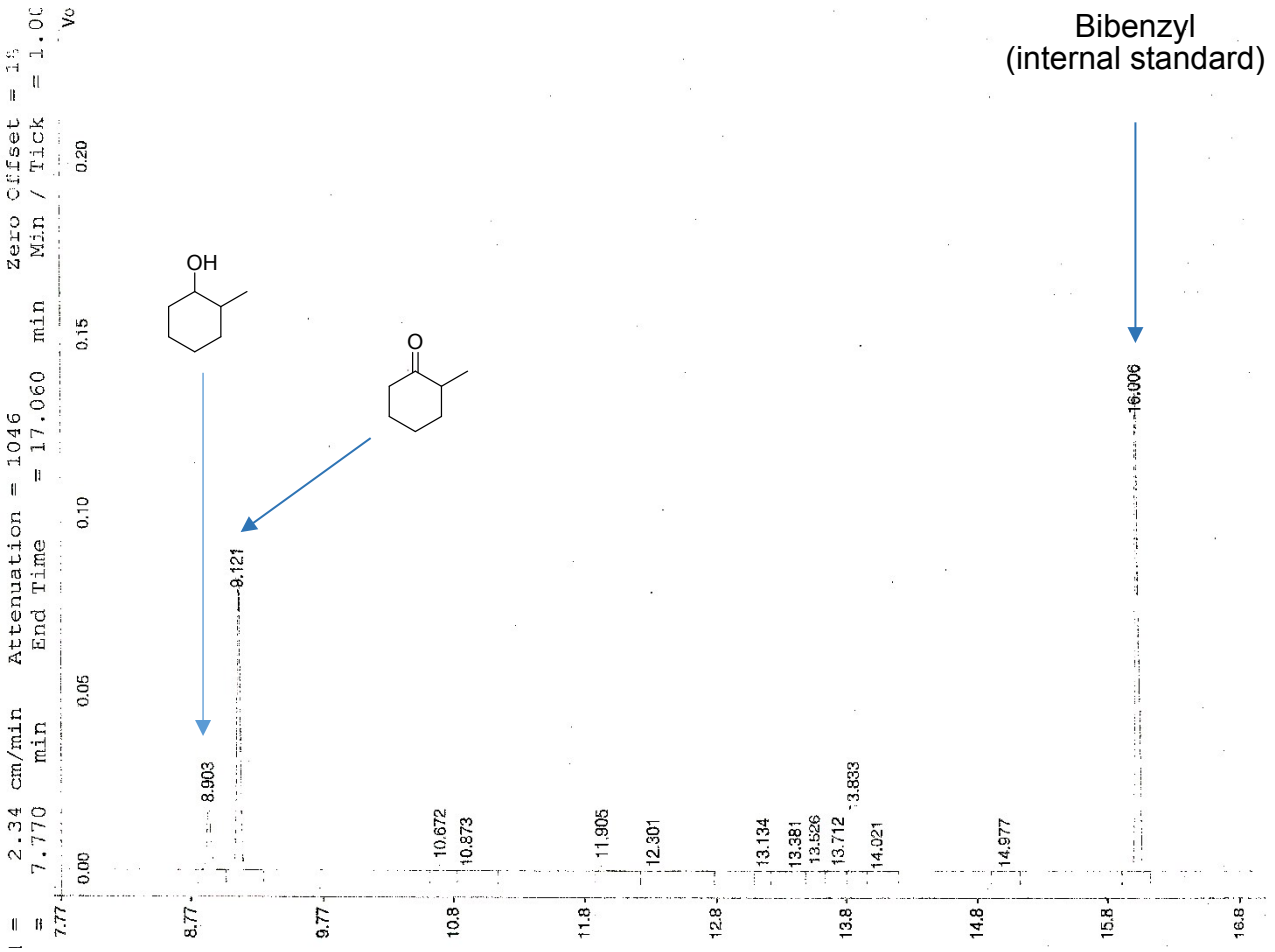
cyclohexanol oxidation



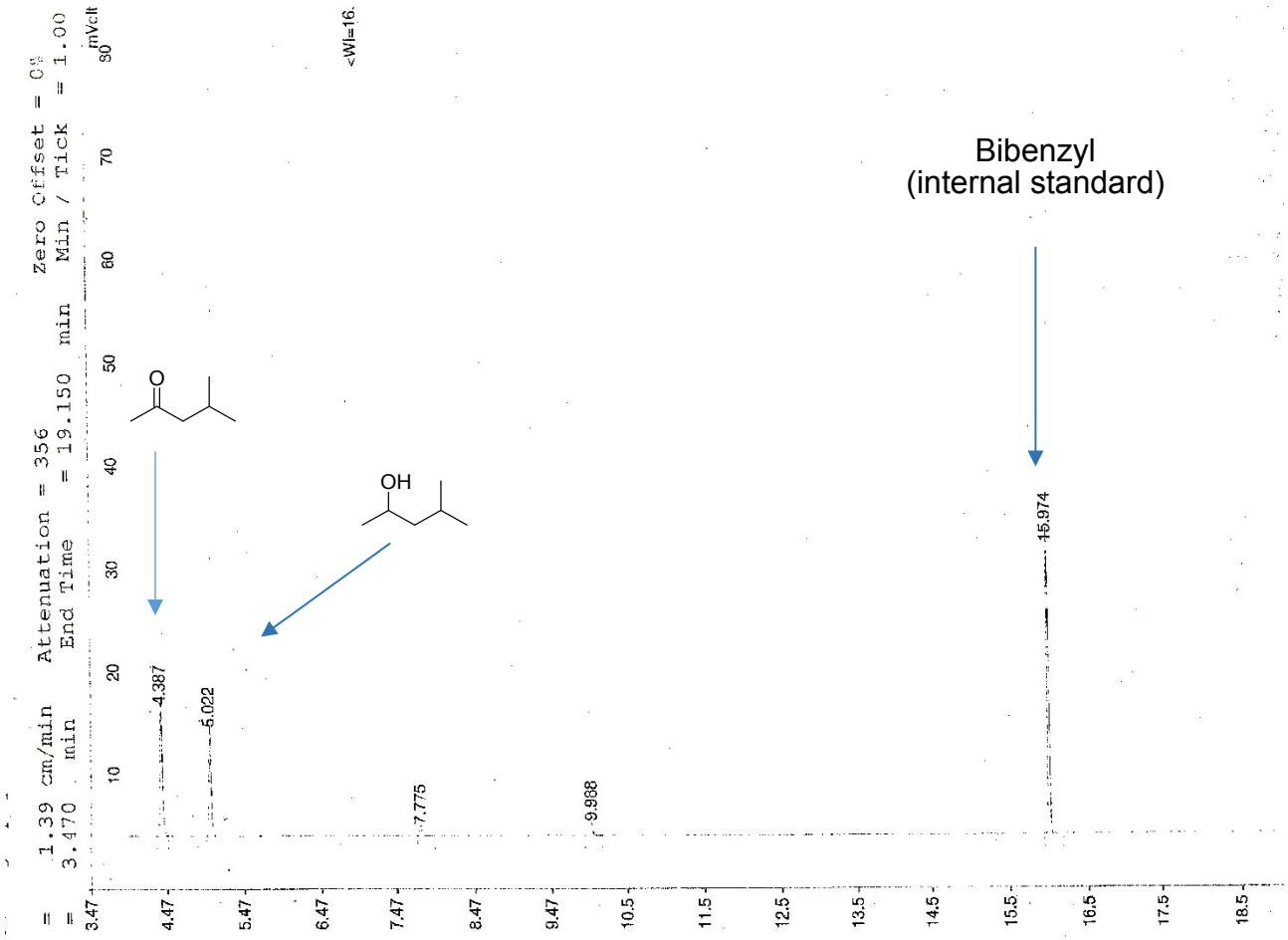
cycloheptanol oxidation



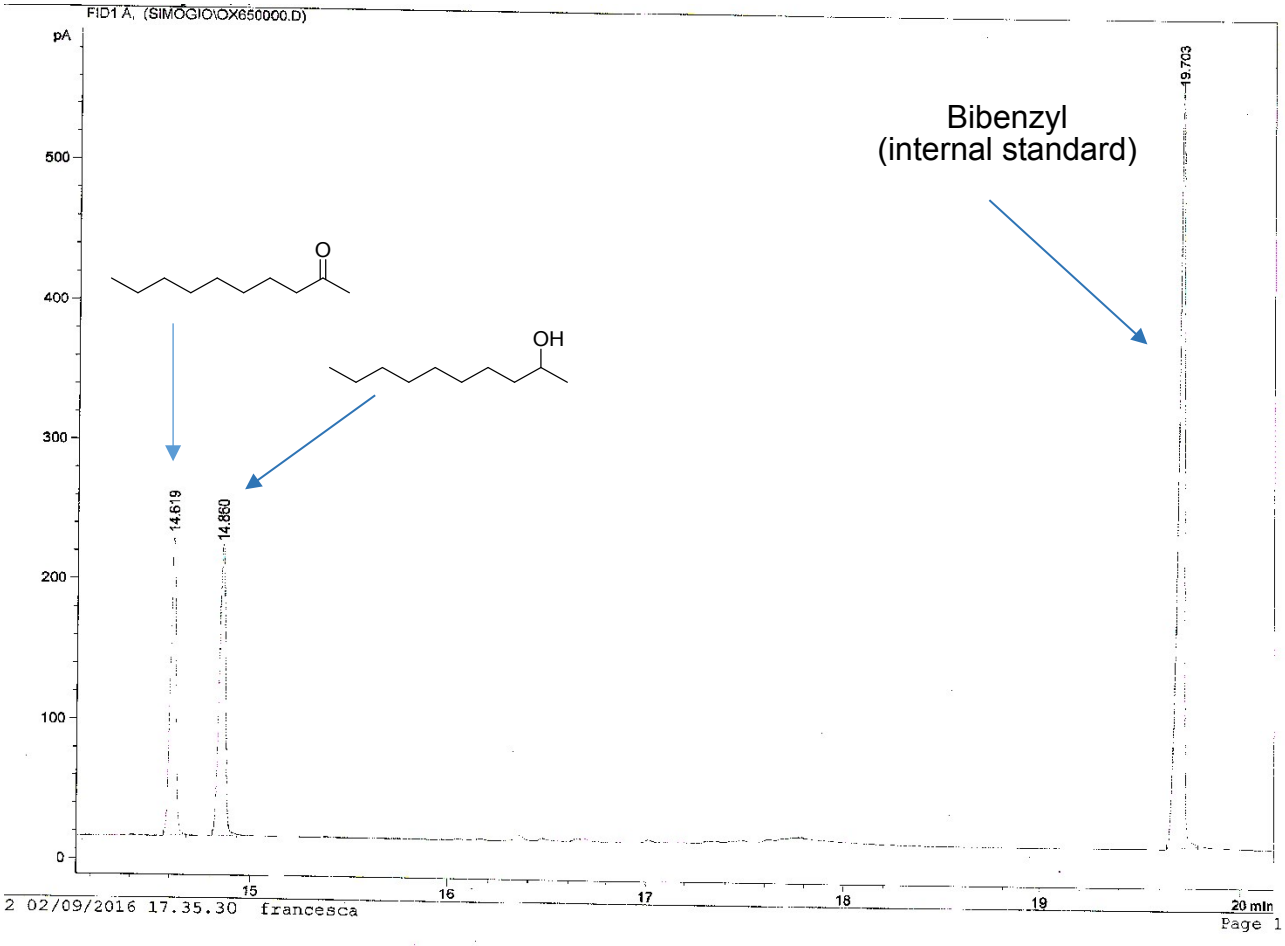
2-methylcyclohexanol oxidation



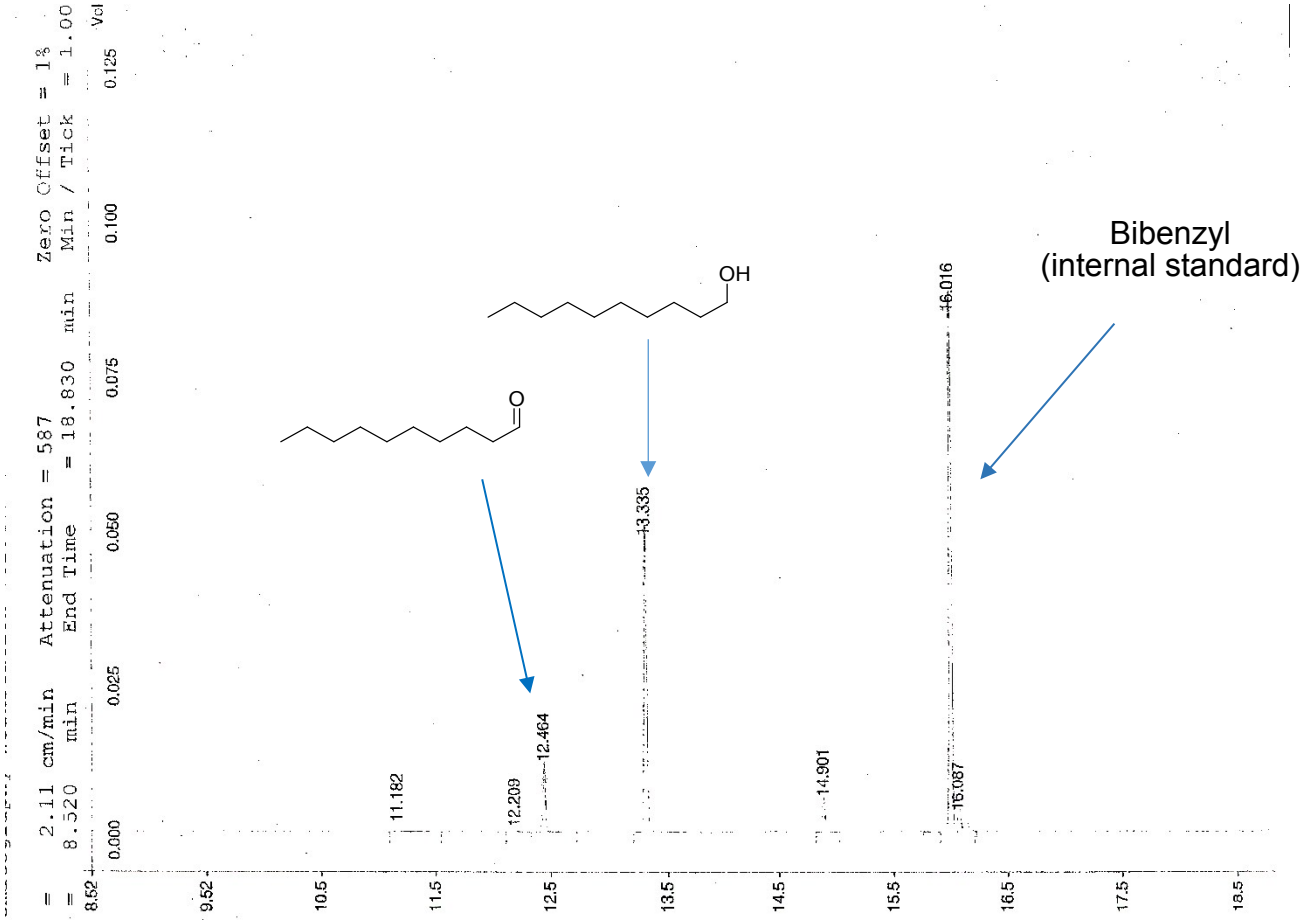
4-methyl-2-pentanol oxidation



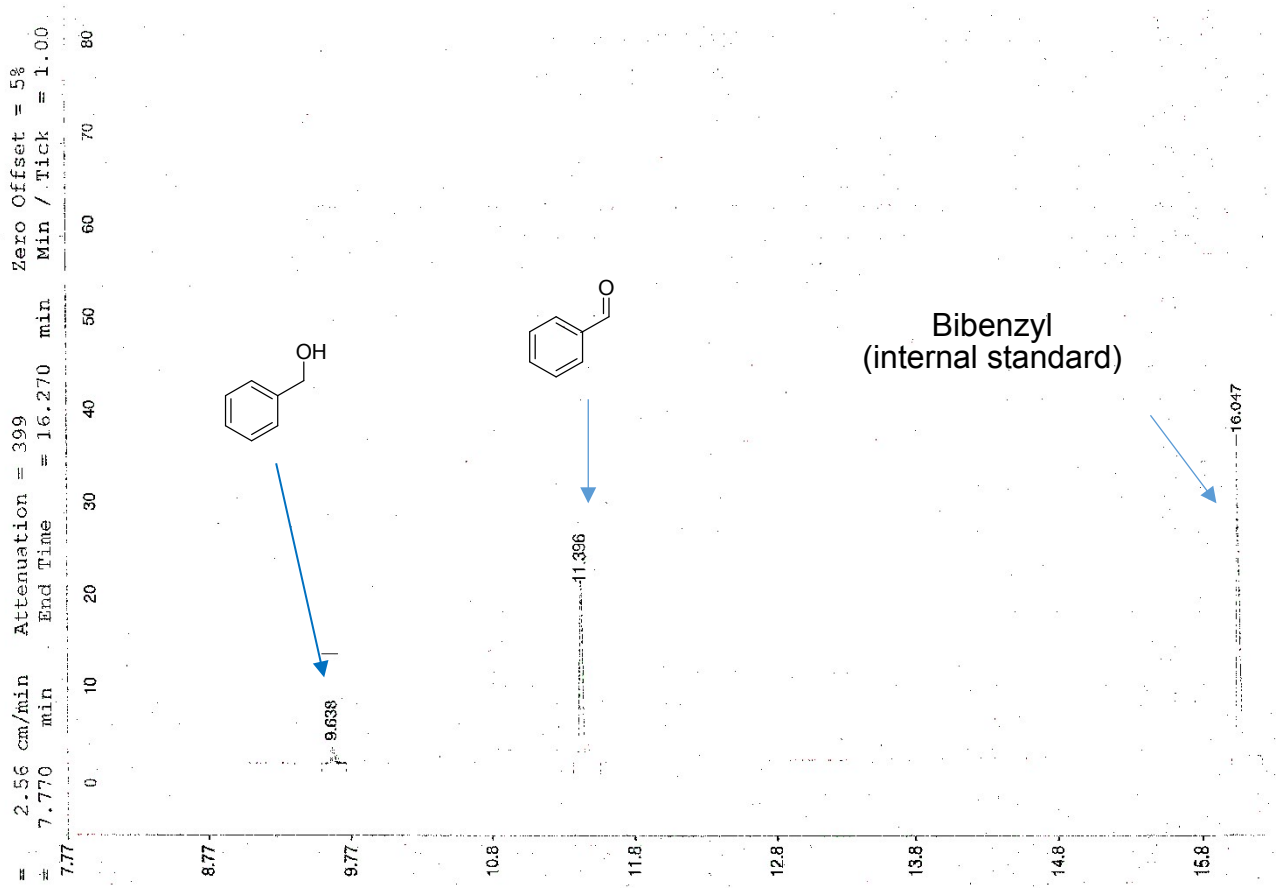
2-decanol oxidation



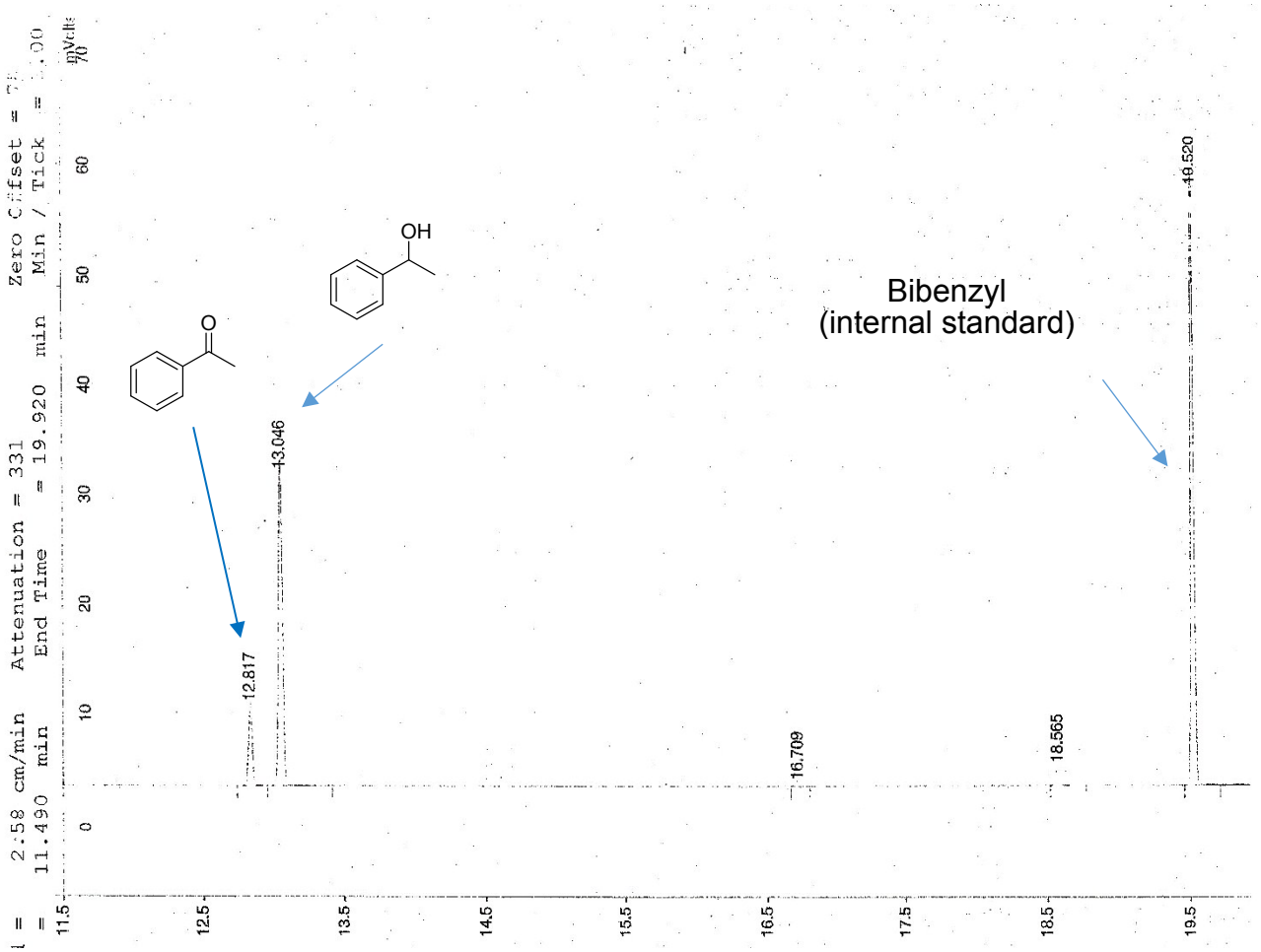
1-decanol oxidation



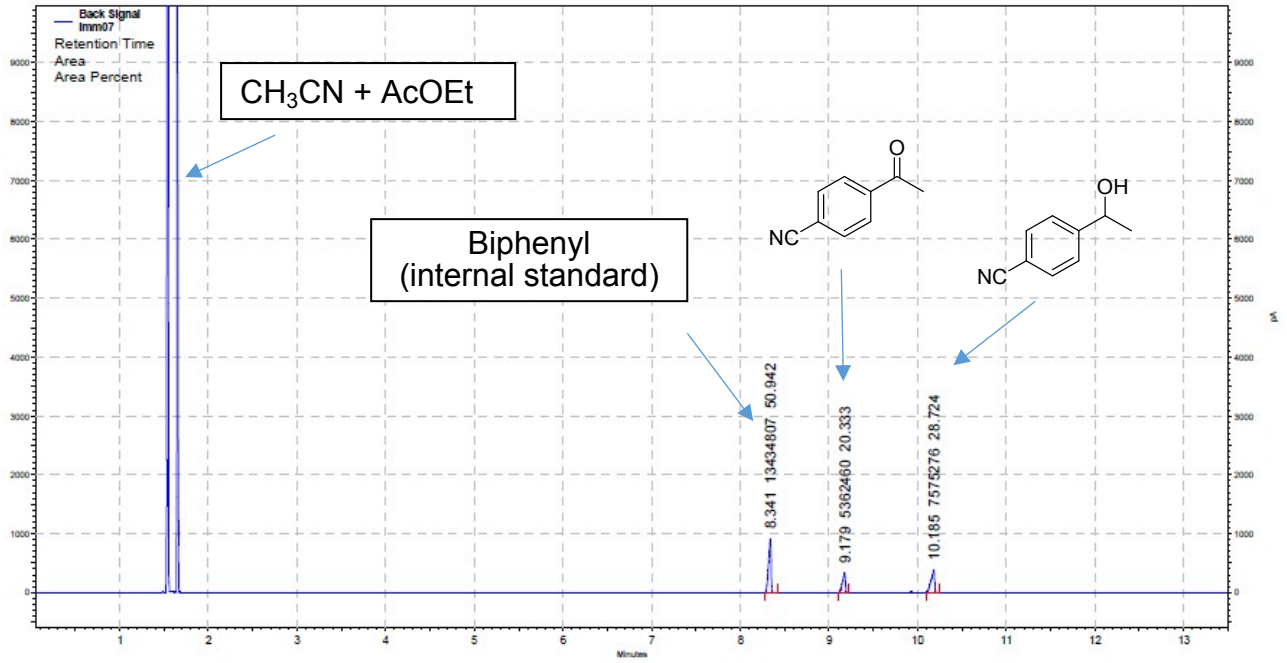
benzyl alcohol oxidation



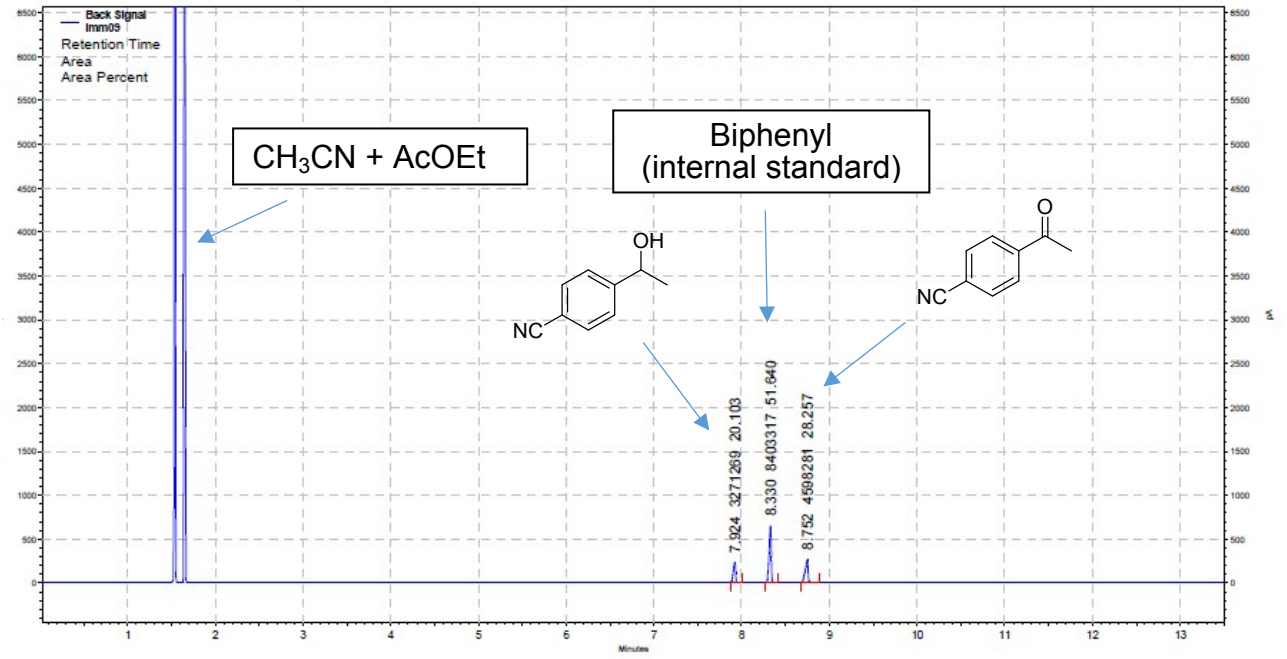
1-phenylethanol oxidation



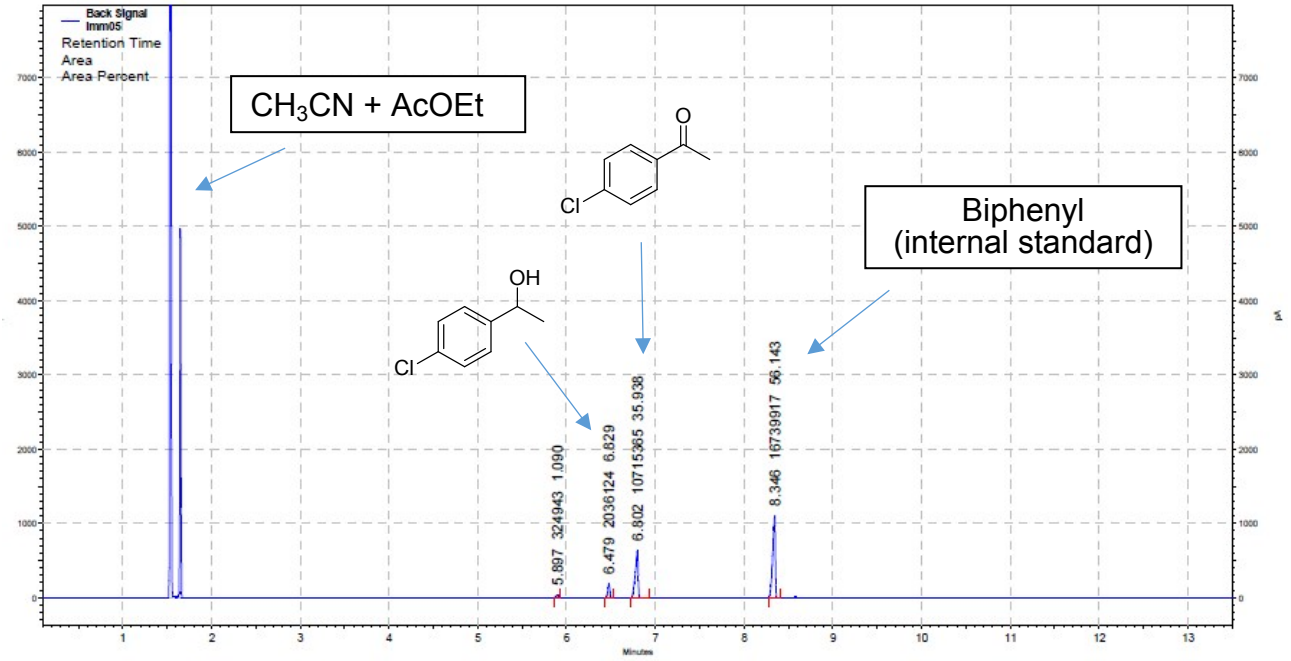
4-nitrophenyl-1-ethanol oxidation



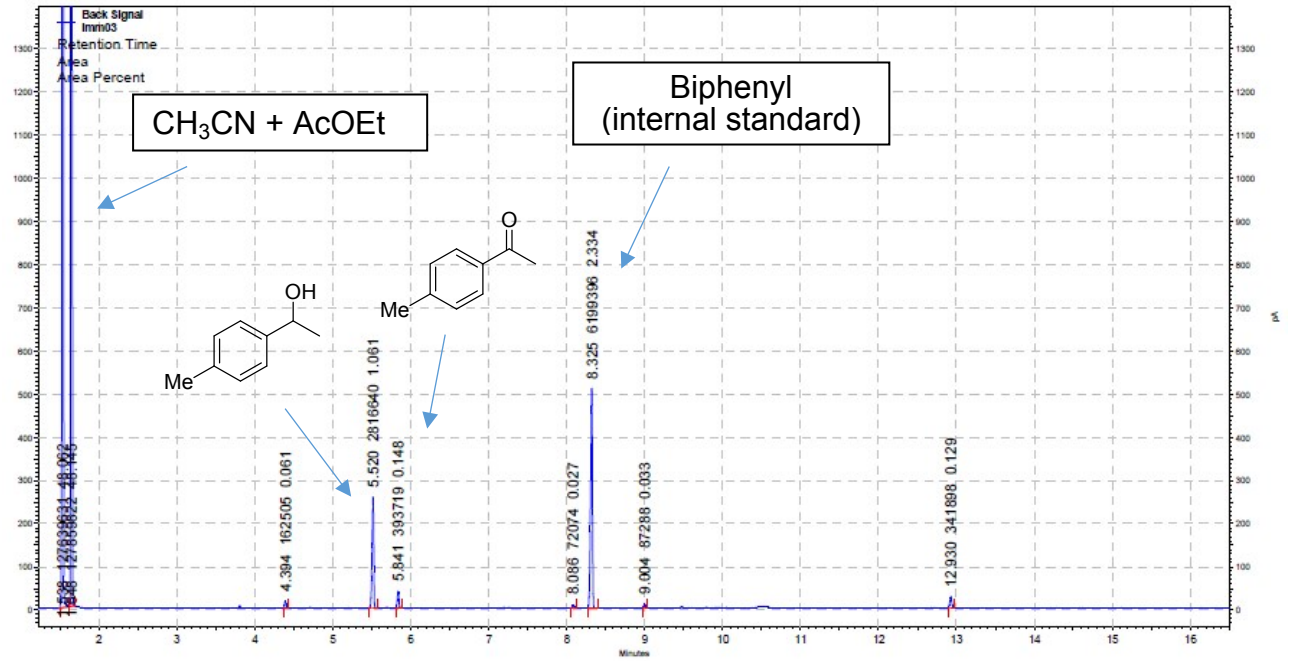
4-cianophenyl-1-ethanol oxidation



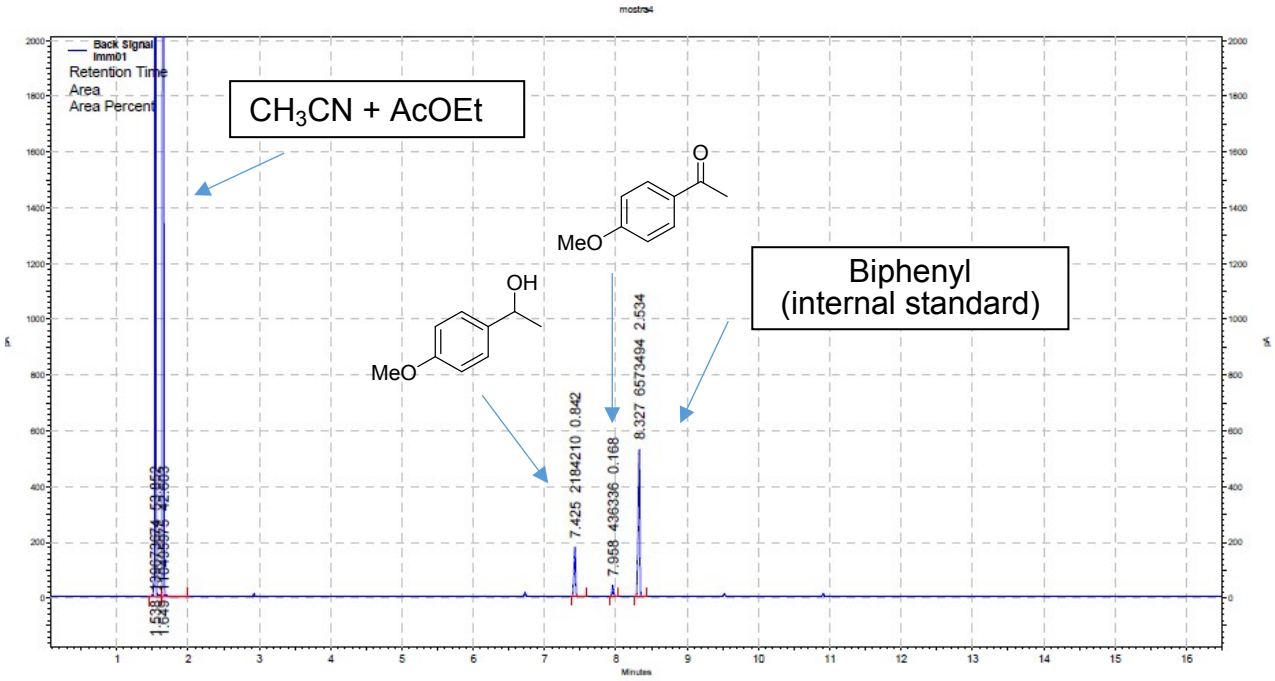
4-chlorophenyl-1-ethanol oxidation



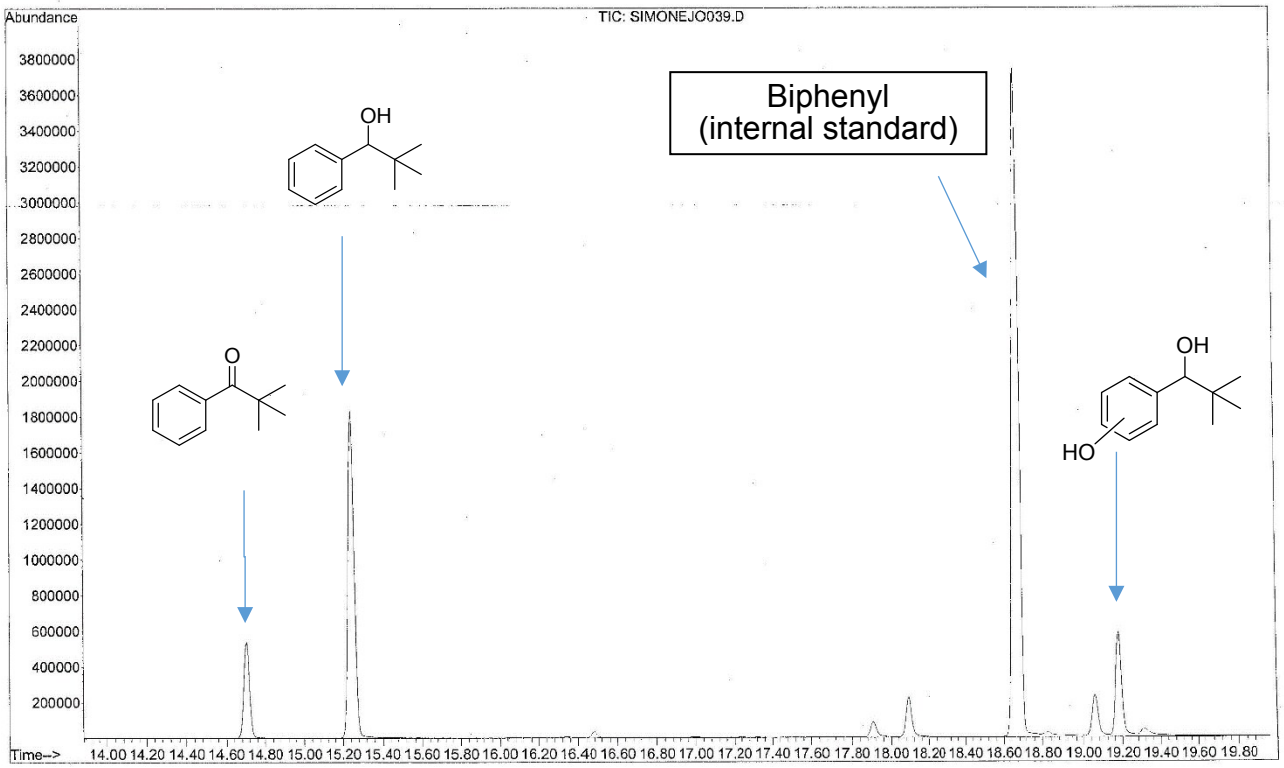
4-methylphenyl-1-ethanol oxidation



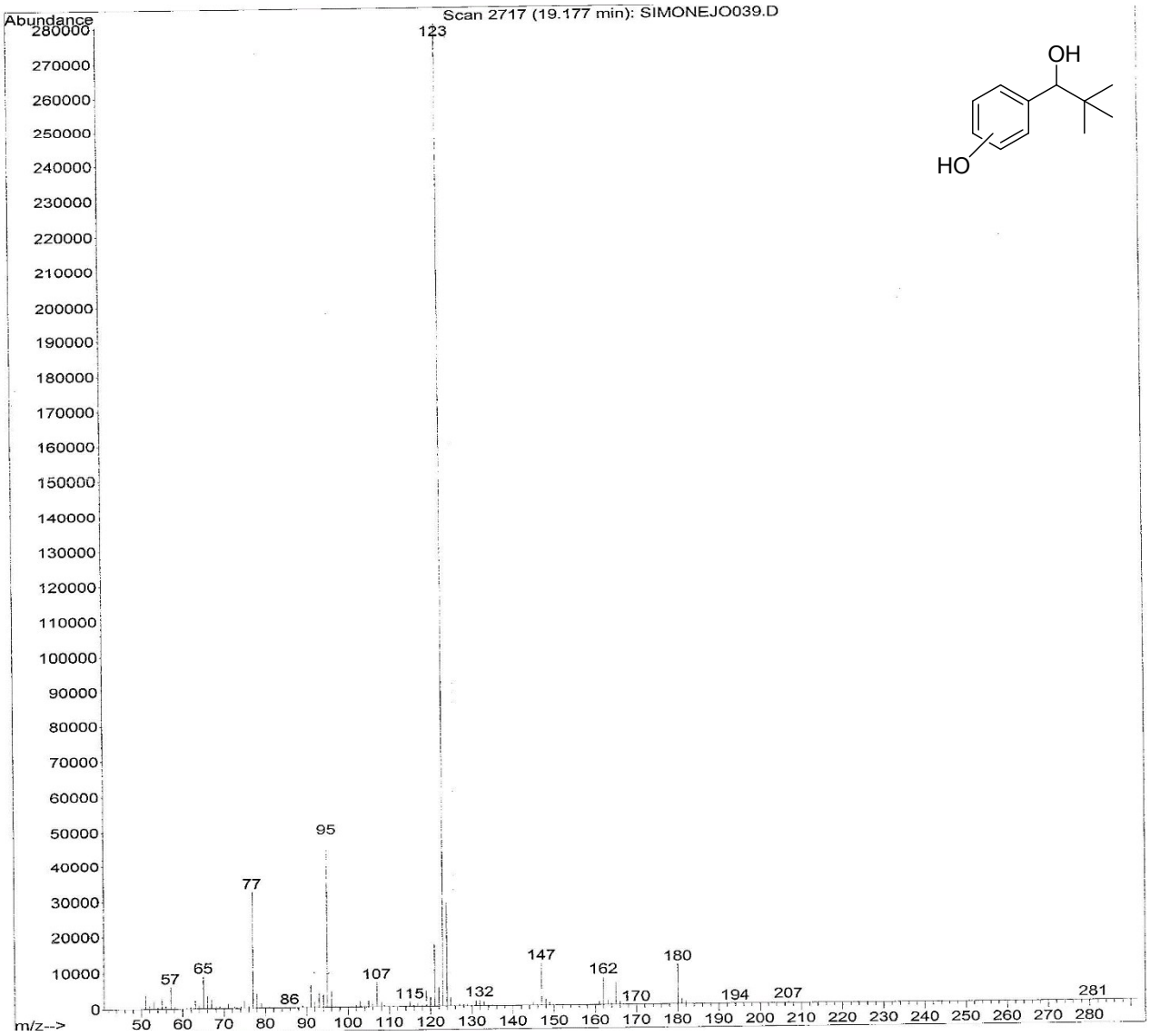
4-methoxyphenyl-1-ethanol oxidation



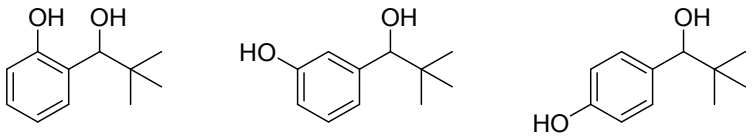
1-phenyl-2,2'-dimethylpropanol oxidation



Mass spectrum of the aromatic oxidation byproduct detected in 1-phenyl-2,2'-dimethylpropanol oxidation



This mass spectrum is in a very good agreement with those reported for compounds



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