Supporting Information

Synergistic catalysis relay within the TEMPO-functionalized periodic mesoporous organosilica with imidazolium framework in the aerobic oxidation of alcohols

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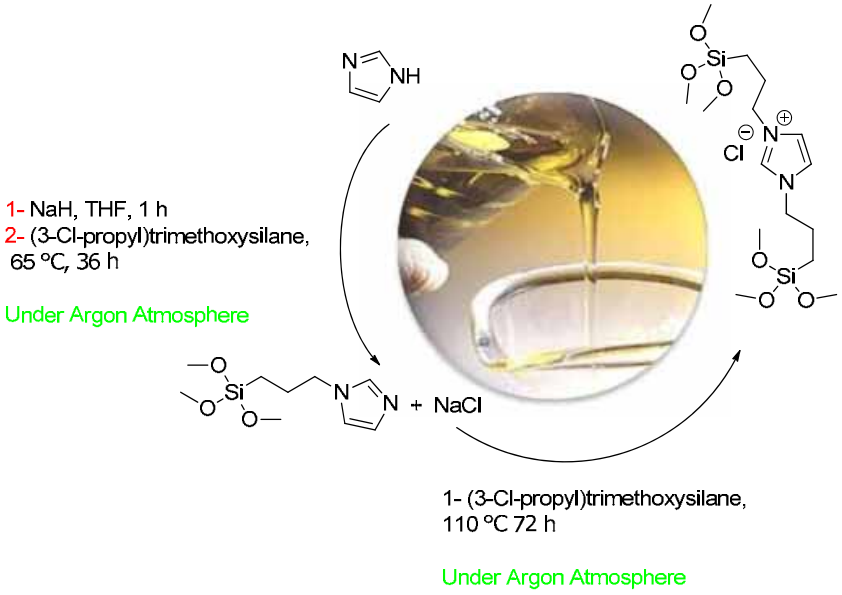
1-1- General procedure for synthesis of 1,3-bis(trimethoxysilylpropyl) imidazolium chloride ionic liquid :

The ionic liquid was prepared by few modifications of our last synthetic reports.[1] In a typical experiment, a suspension of sodium imidazolide in dry THF was prepared from the direct reaction of dried imidazole (29.4 mmol) and NaH 95% (32 mmol) at a two-neck flask containing dry THF (60 ml) under argon atmosphere. Then 3-chloropropyltrimethoxysilan (5.4 ml) were added to resulting suspension of sodium imidazolide and stirred at 65 °C for 36 h under argon atmosphere. After cooling the reaction mixture to room temperature, the solvent was removed under reduced pressure and 3-chloropropyltrimethoxysilan (5.4 ml) were added to the resulting oily products and the mixture was additionally stirred at 110 °C for 72 h (If the reaction mixture was very viscous small amount of toluene were added). (If the reaction mixture was very viscous small amount of toluene were added). Then, the reaction mixture were cooled down to room temperature and dry CH_2Cl_2 (60 ml) was added to remove the precipitated NaCl. In the next stage, CH_2Cl_2 phase was transferred to the well-dried/two-necks flask under inert atmosphere and the excess of CH_2Cl_2 removed under reduced pressure until the ionic liquid and unreacted starting materials obtained. Finally, ionic liquid was washed using dry toluene (5×50 ml) for remove of unreacted starting materials to give pure imidazolium ionic liquid.

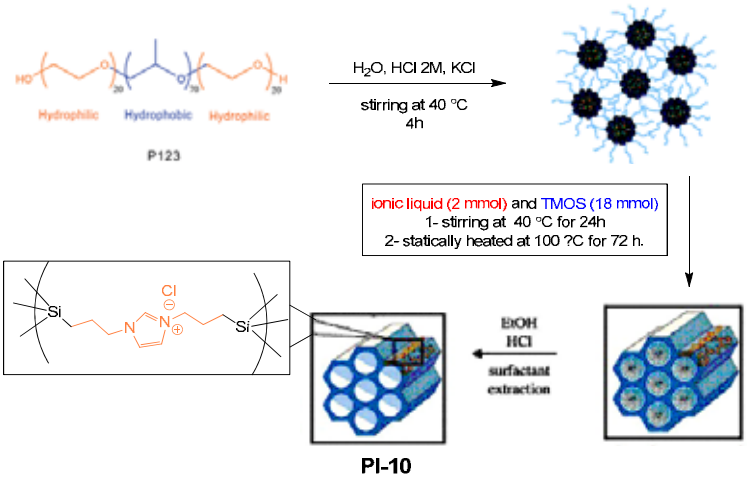


1-2- General procedure for synthesis of PMO-IL

PMO-IL was prepared according to our previously reported procedure.[1] In a typical synthesis, Pluronic P123 (1.67 g) and KCl (8.8 g) were added to a solution of distilled water (10.5 g) and HCl (2 M, 46.14 g) with stirring at 40 °C. After a clear homogeneous solution obtained, a pre-prepared homogeneous mixture of ionic liquid 1,3-bis(trimethoxysilylpropyl) imidazolium chloride (2 mmo l, 0.86 g) and tetramethoxysilane (18 mmol, 2.74 g), in super-dry methanol was rapidly added and stirred at the same temperature for 24 h. The temperature of resulting mixture was then raised to 100 °C and the content of flask was statically maintained at this temperature for 72 h. The obtained solid

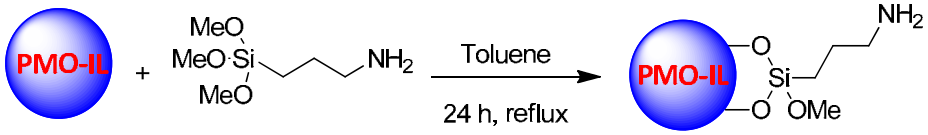
[1] B. Karimi, D. Elhamifar, J. H. Clark, and A. J. Hunt, *Chem. Eur. J.*, 2010, **16**, 8047 – 8053.

material containing surfactant was filtered, washed completely with deionized water, and dried at room temperature. The surfactant residue was then extracted from the materials through a Soxhlet apparatus by using ethanol (100 ml) and concentrate HCl (37%, 3 ml) for 24h.



1-3- General procedure for synthesis of PMO-IL-AMP

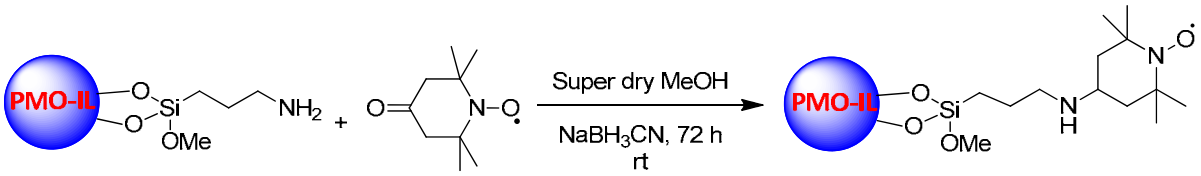
We used of grafting method for functionalized of PMO-IL with amine group.[2] Which is as follows: 3 g of synthesized PMO-IL was mixed and refluxed with 3-aminopropyltrimethoxysilane (1 mmol, 0.23 mL) in dry toluene for 18 h under argon atmosphere. The white solid materials were filtered and washed with toluene and ethanol in order to remove of ungrafted 3-aminopropyltrimethoxysilan. The material was then dried in oven at 105 ºC to give the PMO-IL-AMP at a loading of 0.35 mmol g^{-1} as determined by thermogravimetric analysis and confirmed by elemental analysis.



1-4- General procedure for synthesis of TEMPO@PMO-IL

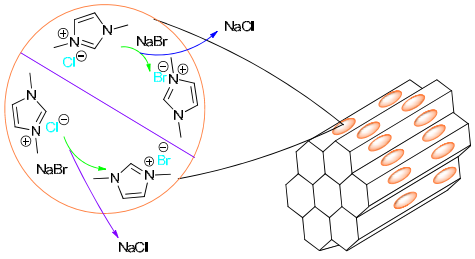
Reductive amination has been used for synthesis of TEMPO@PMO-IL.[2] To a mixture of PMO-IL-AMP (3 g) in super dry CH_3OH (50 mL), 4-Oxo-TEMPO (1.5 mmol, 0.281 g) was added. $NaBH_3CN$ (2 mmol, 0.125 g) was divided into three portions, the first part was added after 3 h, second part after 24 h and the third part after 48 h. The reaction mixture was stirred vigorously for 3 days at ambient temperature under argon atmosphere. The final product was separated by filtration and washed three times by water (20 ml), methanol (20 ml), and acetone (20 ml) and dried under vacuum at room temperature to give TEMPO@PMO-IL-Cl. The product stored in a refrigerator under inert atmosphere for the next uses.

[2] B. Karimi, A. Biglari, J. H. Clark, V. Budarin. *Angew. Chem.* **2007**, *119*, 7348–7351.



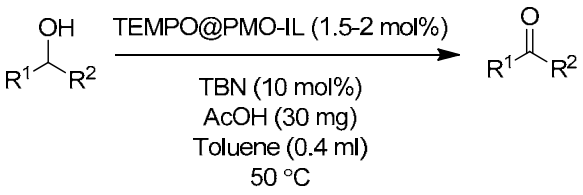
1-5-Typical procedure for ion exchange of chloride counter ion of ionic liquid by bromide anion

In a typical experiment, a suspension of TEMPO@PMO-IL-Cl (2 g) in in saturated aqueous solution of NaBr (25 ml) was stirred at ambient temperature for 24 h. The final product was separated by filtration and thoroughly washed with deionized water (6×50 ml) and acetone (25 ml), respectively, to remove the generated NaCl and the excess of NaBr the material and dried under vacuum to give TEMPO@PMO-IL-Br. The final product stored in a refrigerator under inert atmosphere.



1-6- A typical catalytic procedure for oxidation of alcohols using TEMPO@PMO-IL-Br

A mixture of alcohol (1 mmol), TBN (10 mol%), AcOH (30 mg) and catalyst (1.5-2 mol%) in toluene (0.5-1 mL) was prepared in a flask and charged with pure oxygen (balloon filled, O_2 1 atmosphere). The resulting mixture was stirred at 50 ºC for the time indicated in Table 2. The progress of the reaction was monitored by GC. After completion of the reaction, the solution was diluted with ethylacetate and the catalyst was separated by centrifuge. The resulting solution was then dried with sodium sulfate and the excess solvent was removed under reduced pressure to give the corresponding carbonyl compounds. The purity of the products was analyzed by GC or NMR without any chromatographic purification.



2- Characterizations of catalyst

The PMO-IL, PMO-IL-AMP and TEMPO@PMO-IL-Br were further characterized by IR, TEM, TGA, EPR, SAXC and surface pore analysis.

2-1- Instrument

The pore structures of the prepared materials were observed by transmission electron microscopy (Philips CM-200) and were verified further by the nitrogen sorption analysis. N_2 adsorption isotherms were measured at 77 K on Belsorp (BELMAX, Japan) analyzer using standard continuous procedures, and samples were first degassed at 353 K for 5 h. Specific surface area was determined from the linear part of the BET plot (P/P0 ≈ 0.05-0.15), the pore size distribution was calculated from the adsorption branch using Barrett–Joyner–Halenda (BJH) method, total pore volume was estimated based on the N_2 adsorbed at P/P0 ≈ 0.995. Thermogravimetric analysis was conducted from room temperature to 800 °C in an oxygen flow using a NETZSCH STA 409 PC/PG instrument. FT-IR spectra were recorded using a Bruker Vector 22 instrument after mixing the samples with KBr. Gas chromatography analyses were performed on Varian CP-3800 using a flame ionization detector (FID) using suitable internal standards. NMR spectra were recorded using a Brüker (^{1}H frequency: 400 MHz).

2-2- FT-IR spectroscopy

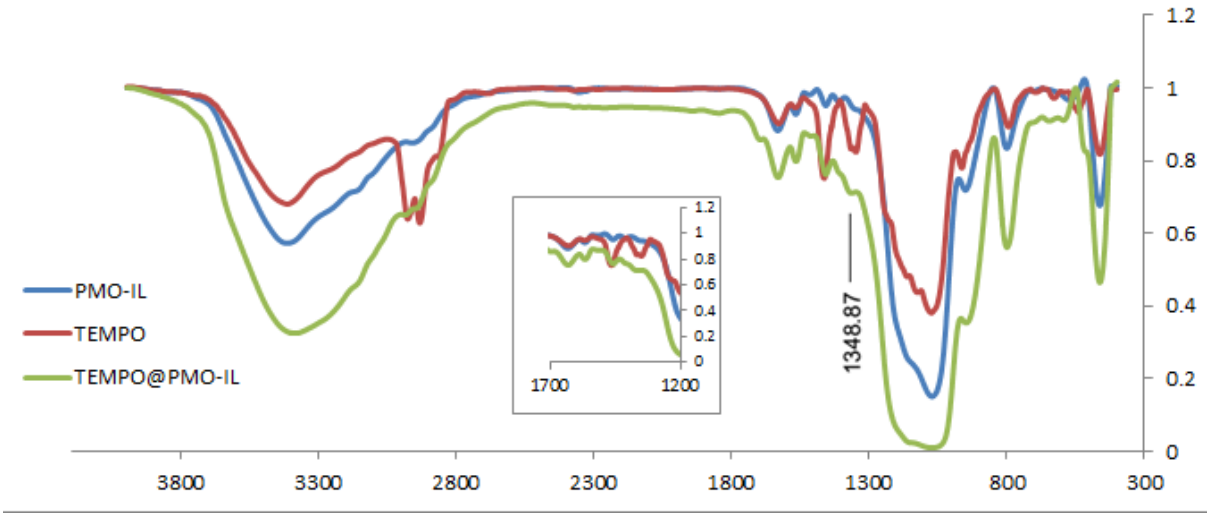


Fig. S1. FT-IR spectroscopy of PMO-IL, TEMPO and TEMPO@PMO-IL-Br

2-3- TEM image

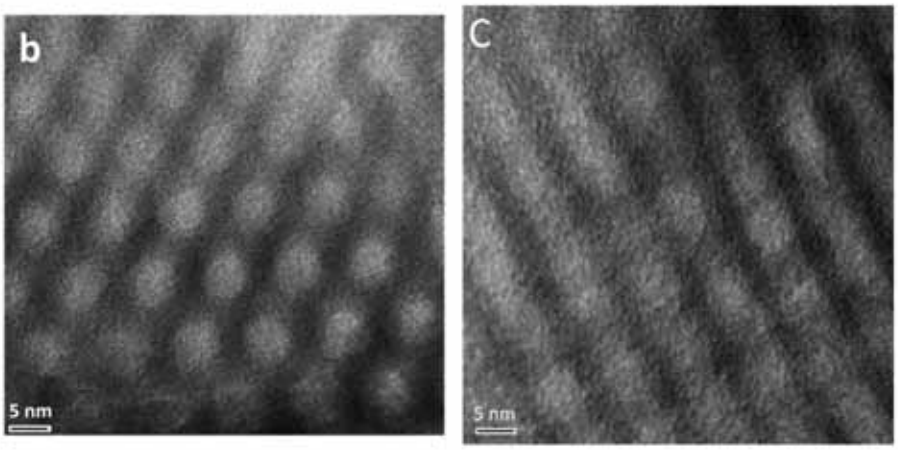


Fig. S2. TEM image of fresh TEMPO@PMO-IL-Br and after recycling from 8th (Scale bar: 5 nm)

2-4- TGA analysis of PMO-IL, PMO-IL-AMP and TEMPO@PMO-IL-Br

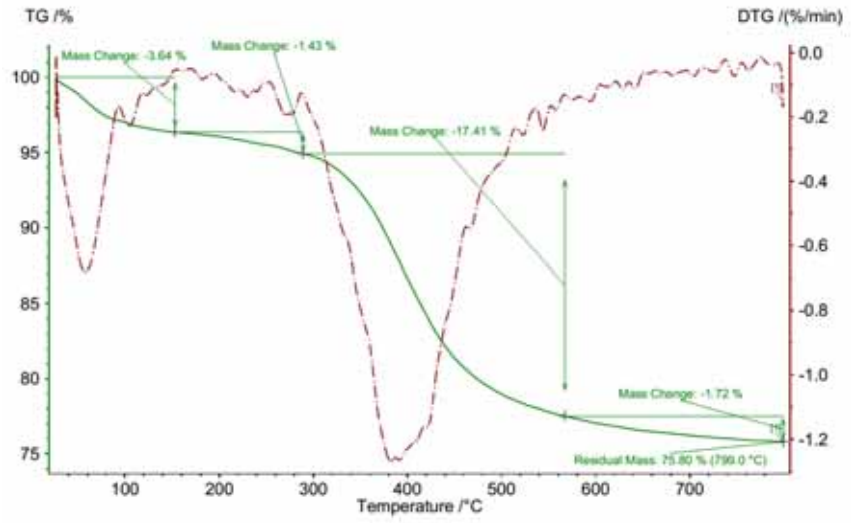


Fig. S3. TGA analysis of PMO-IL under O_2 flow

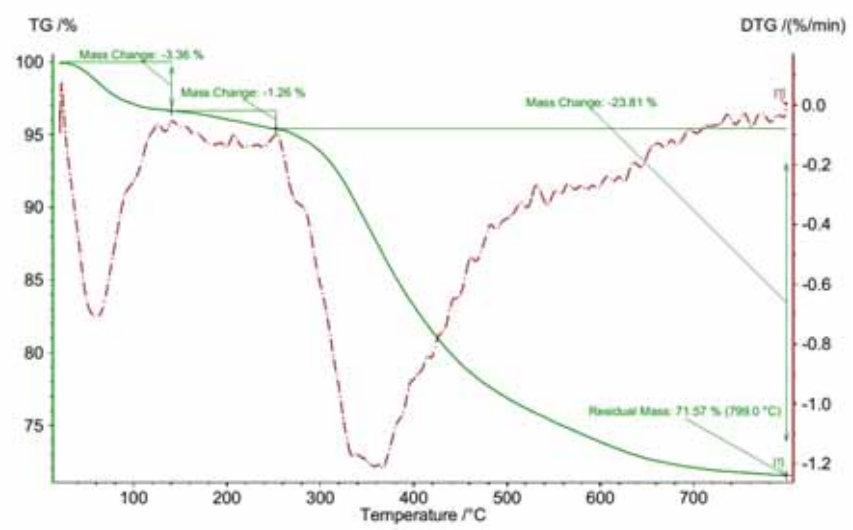


Fig. S4. TGA analysis of PMO-IL-AMP under O_2 flow

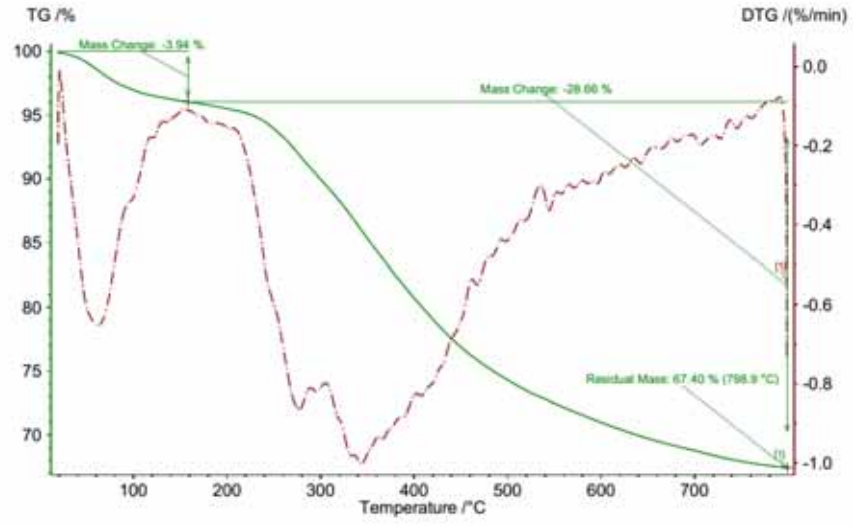


Fig. S5. TGA analysis of TEMPO@PMO-IL catalyst under O_2 flow

2-5- Small angle X-ray scattering (SAXC) of TEMPO@PMO-IL-Br

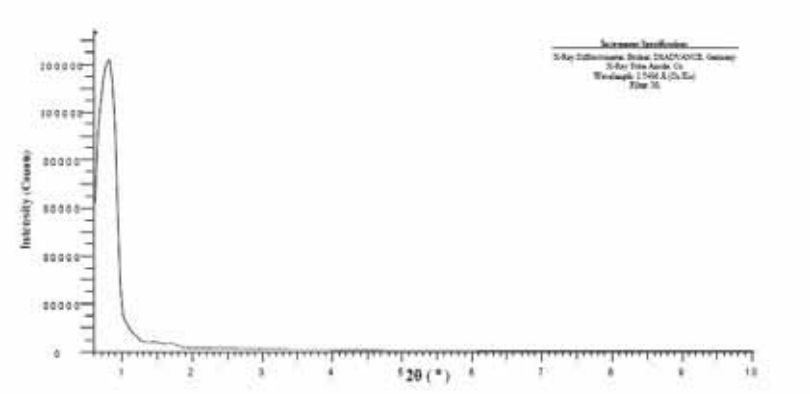


Fig. S6. Small angle X-ray scattering (SAXC) of TEMPO@PMO-IL-Br

2-6- Solid state EPR spectrum of TEMPO@PMO-IL-Br

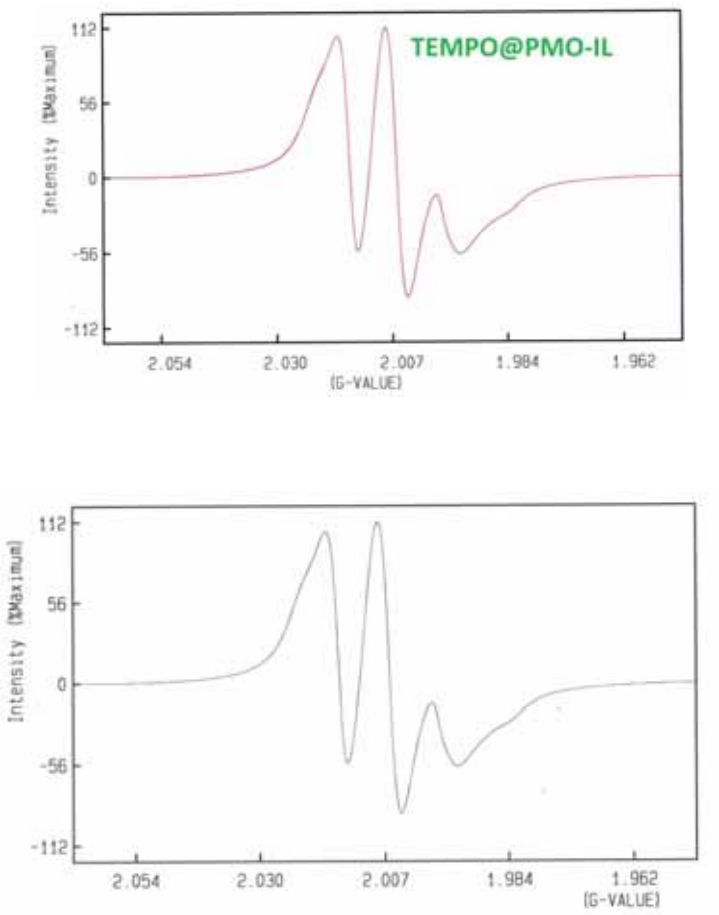


Fig. S7. Solid state EPR spectrum of TEMPO@PMO-IL-Br

2-7- Elemental Analysis (CHN analysis)

Table S1. Elementary analysis of the materials

	N%	C%	H%
PMO-IL	2.97	14.29	2.87
PMO-IL-AMP	4.36	14.76	2.92
TEMPO@PMO-IL	4.40	18.80	2.87

2-8- N_2 adsorption-desorption analyses of PMO-IL, PMO-IL-AMP, TEMPO@PMO-IL and recovered TEMPO@PMO-IL

N_2 adsorption analysis for all materials (PMO-IL, PMO-IL-AMP and TEMPO@PMO-IL) showed a typical type-IV isotherm pattern from P/P_0= 0.6-0.8 with a sharp hysteresis loop which is characteristic of highly ordered mesoporous materials and narrow pore size distribution with 2-dimensional hexagonal pore structure .

The nitrogen adsorption-desorption experiments showed the BET surface area of 578.8 m^2 g^{-1} for starting PMO-IL, 339.1 m^2 g^{-1} for PMO-IL-AMP and 351.5 m^2 g^{-1} for TEMPO@PMO-IL, Moreover, the total pore volume of 1.08 cm^3 g^{-1} for PMO-IL, 0.79 cm^3 g^{-1} for PMO-IL-AMP, 0.77 cm^3 g^{-1} for TEMPO@PMO-IL, and also BJH showed average pore diameters of 8.5 nm for PMO-IL, PMO-IL-AMP and TEMPO@PMO-IL.

The N_2 adsorption analysis of the recovered catalyst showed very similar isotherms to those of the fresh catalyst TEMPO@PMO-IL. The N_2 sorption diagram of the recovered catalyst TEMPO@PMO-IL interestingly showed a type-IV isotherm with relatively sharp hysteresis loop, which indicates that the high-ordered mesostructures have survived.

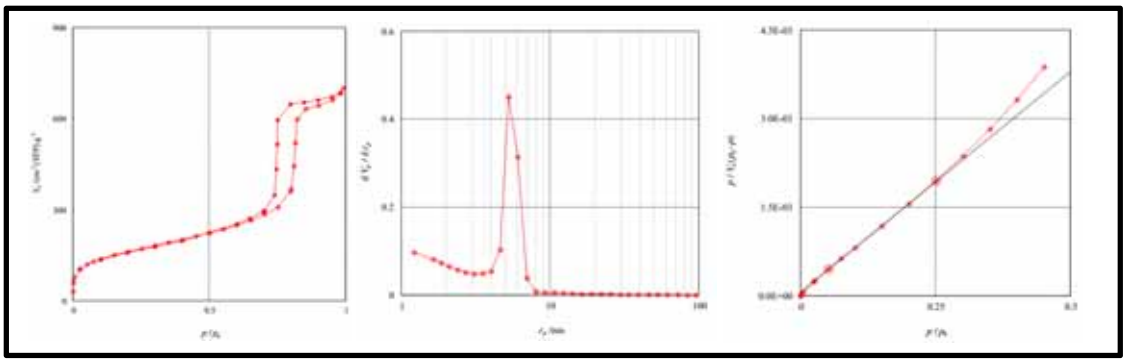


Fig S8. N_2 adsorption-desoprption isotherm, BJH average pore size diagram and BET plot of PMO-IL

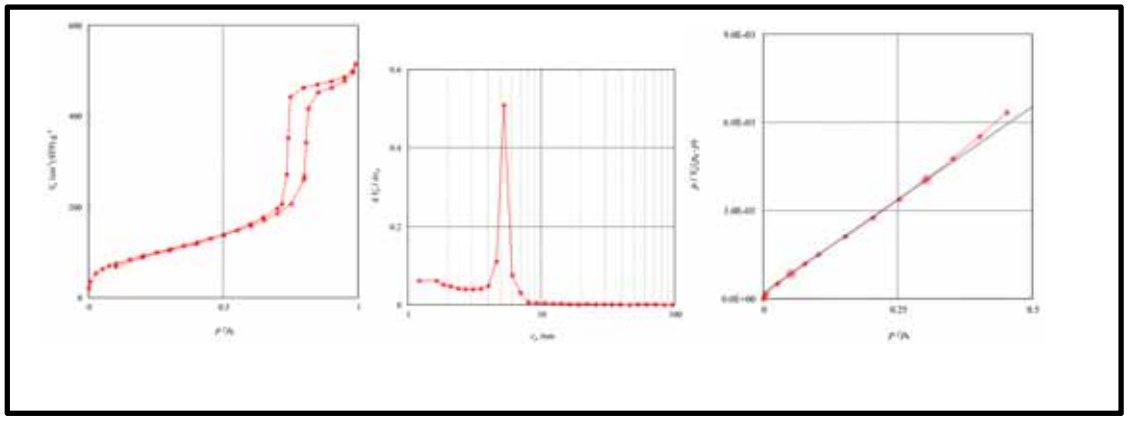


Fig S9. N_2 adsorption-desoprption isotherm, BJH average pore size diagram and BET plot of PMO-IL-AMP

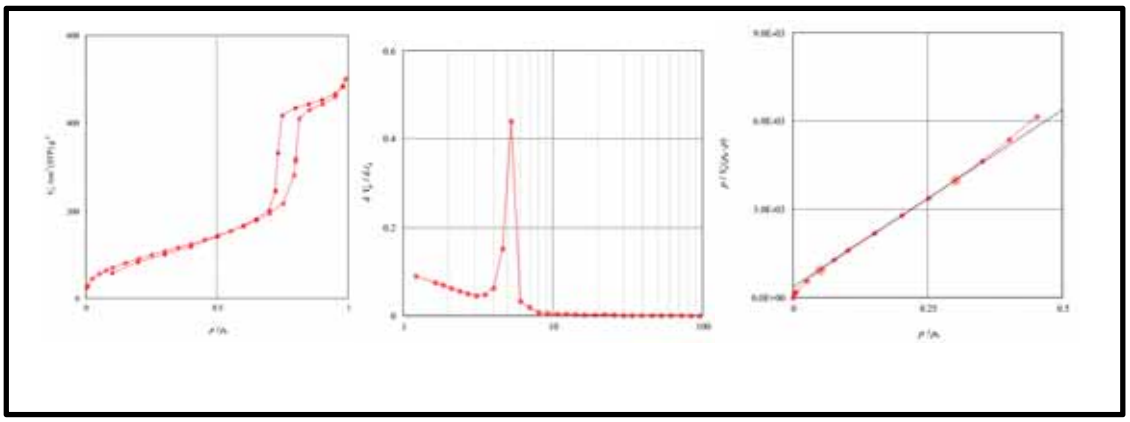


Fig S10. N_2 adsorption-desoprption isotherm, BJH average pore size diagram and BET plot of TEMPO@PMO-IL-Br

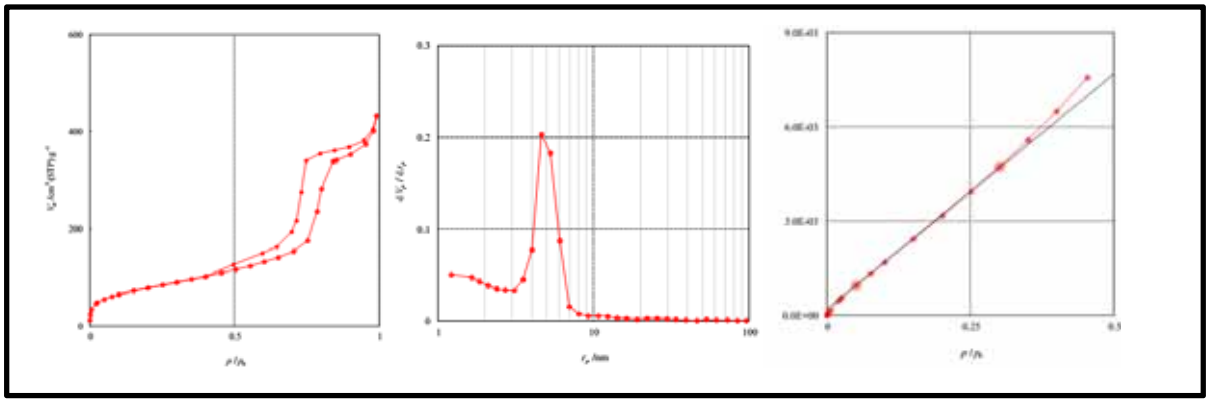
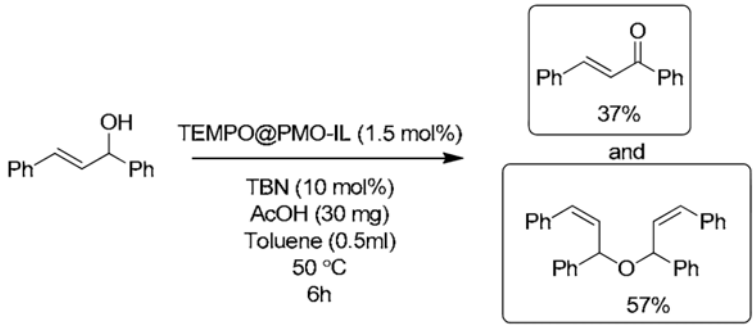


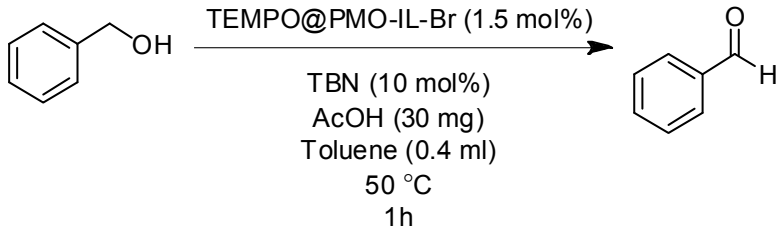
Fig S11. N_2 adsorption-desoprption isotherm, BJH average pore size diagram and BET plot of recycled TEMPO@PMO-IL-Br after the 8th oxidation of of benzyl alcohol

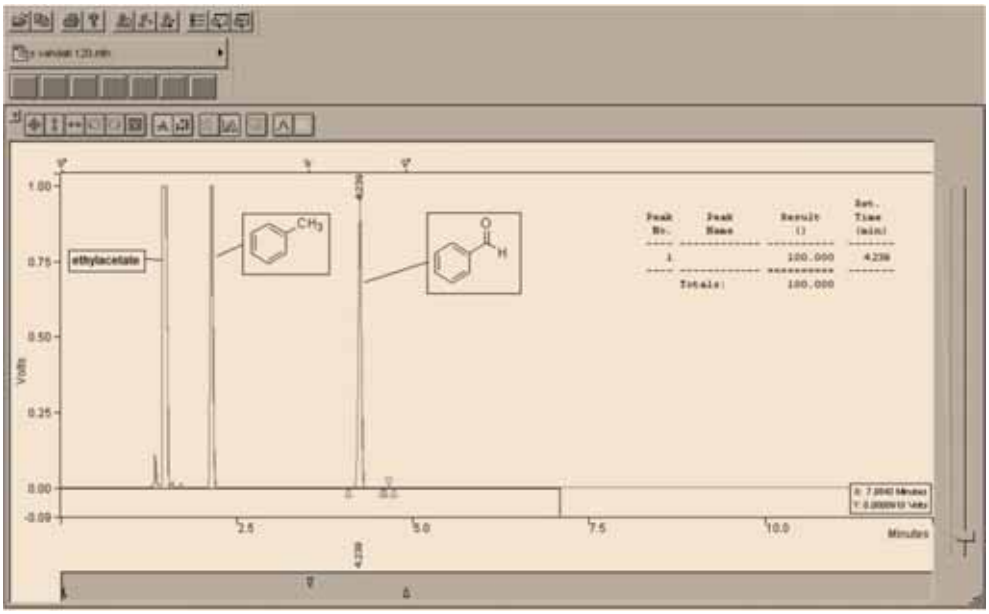


Scheme S1. Symmetrical ether formation in the aerobic oxidation of highly acid sensitive substrate (E)-1,3-diphenyl-2-propen-1-ol at the optimal condition

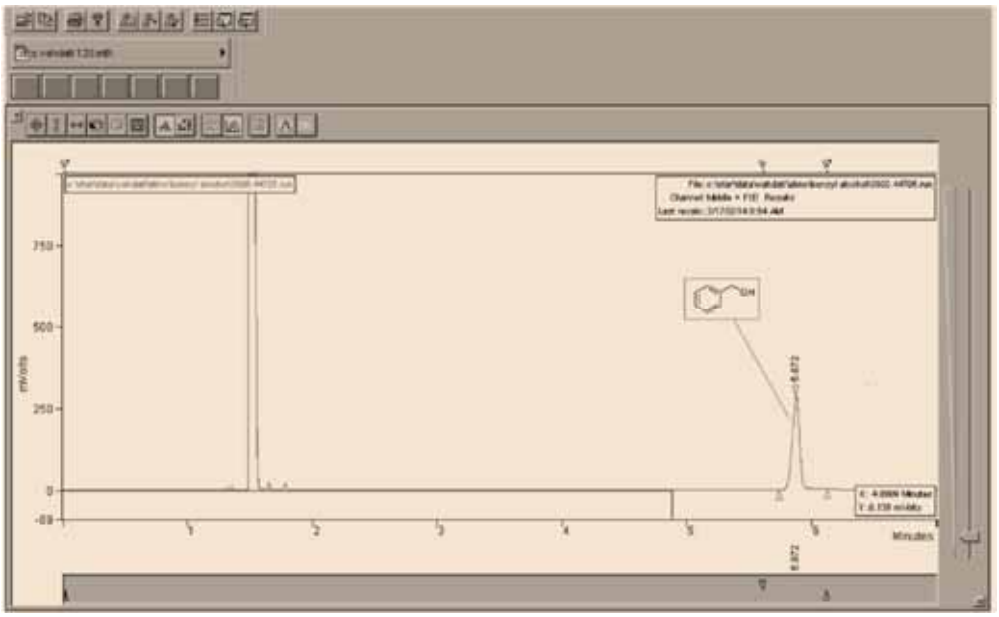
3- Some of the Gas chromatograms and NMR of oxidation of alcohols to ensure completion of reaction

Benzylalcohol

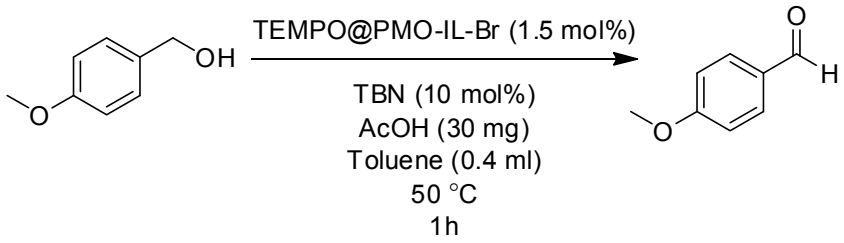


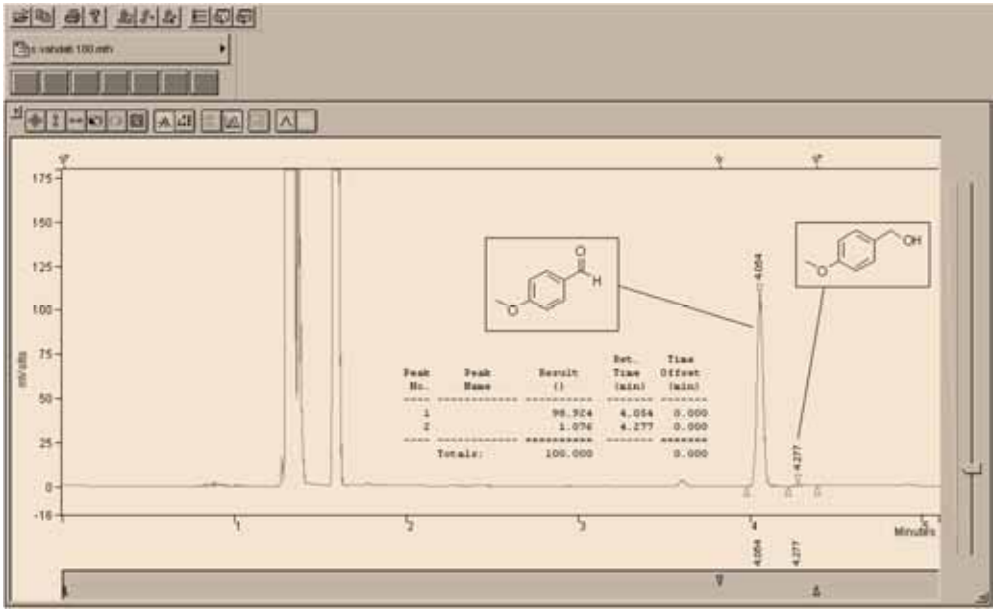


Blank of Benzylalcohol



4-methoxybenzylalcohol





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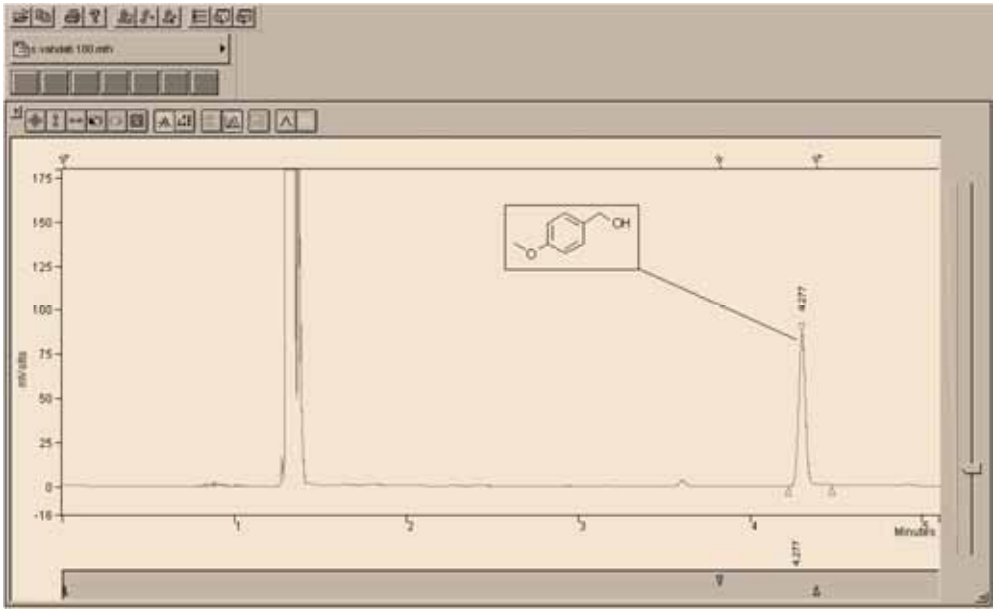
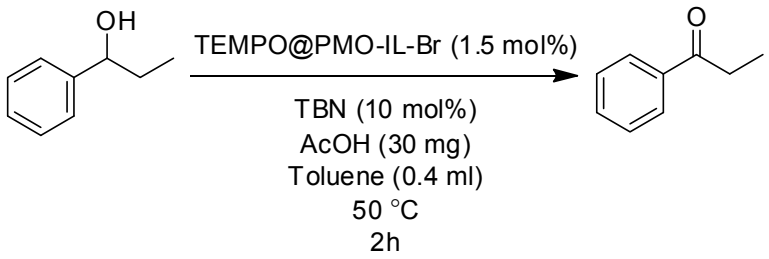
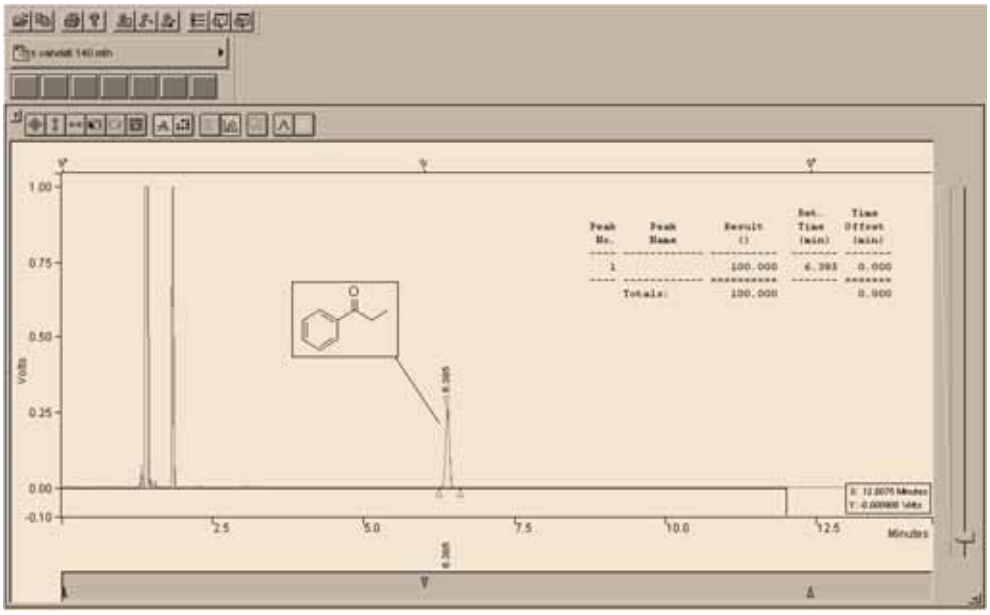


1-phenyl-1-propanol





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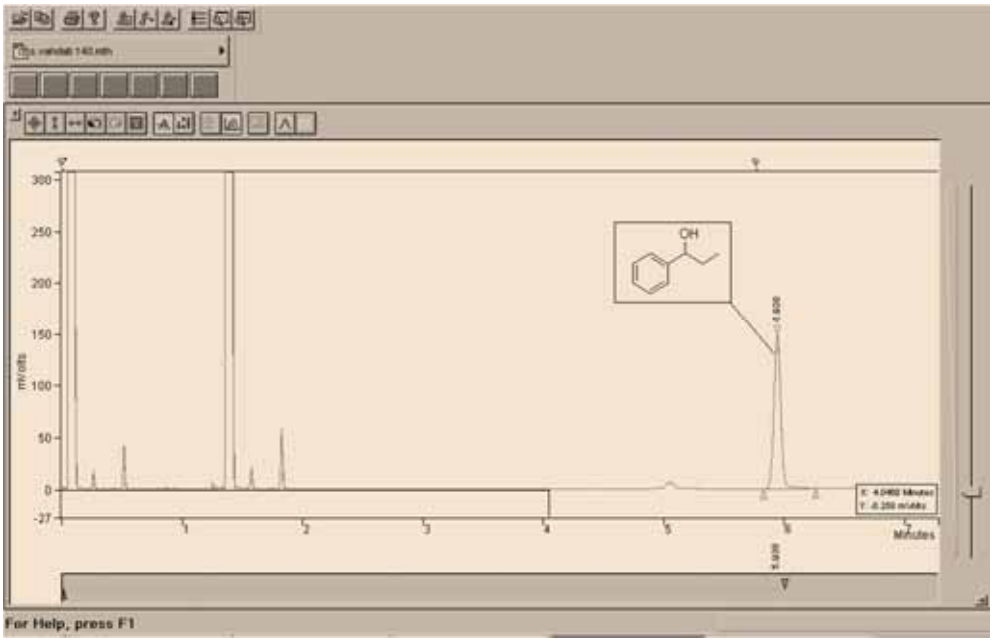
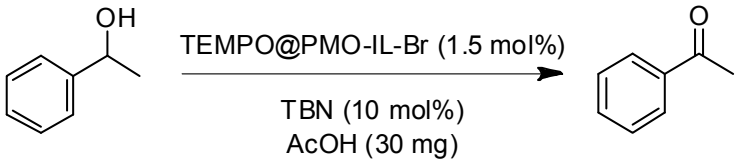
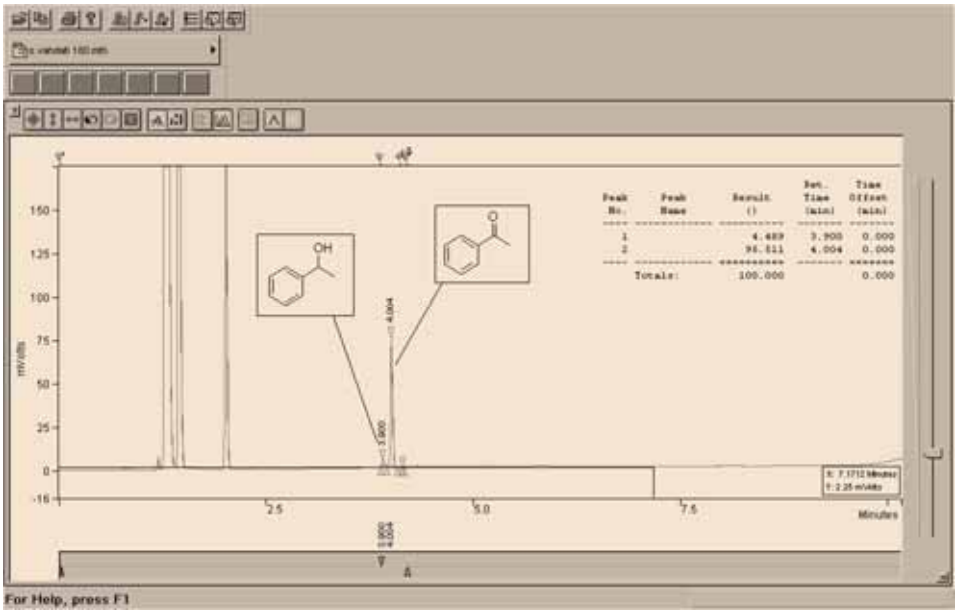


1-phenyl-1-ethanol



TBN (10 mol%)
AcOH (30 mg)
Toluene (0.4 ml)
50 °C
2h



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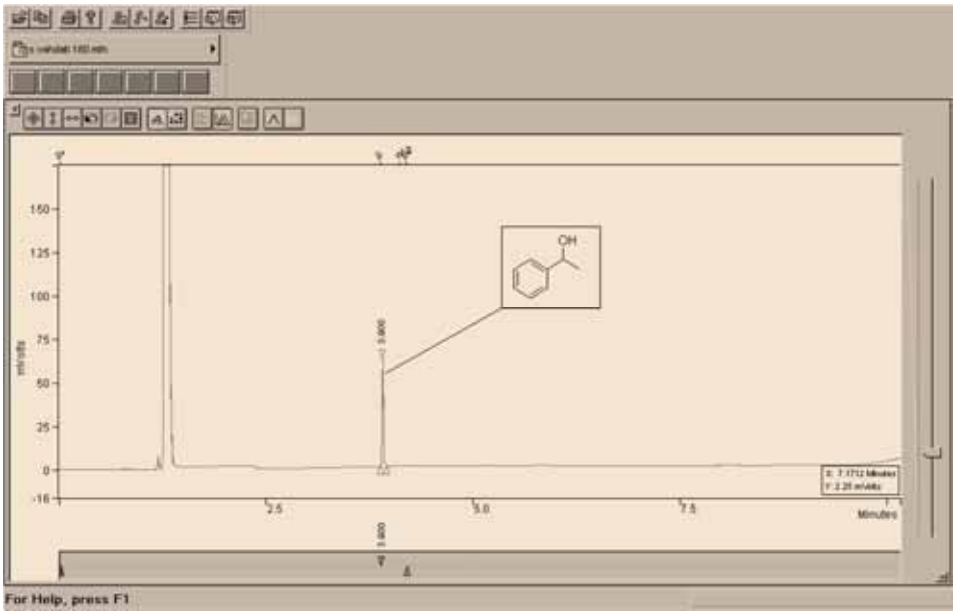
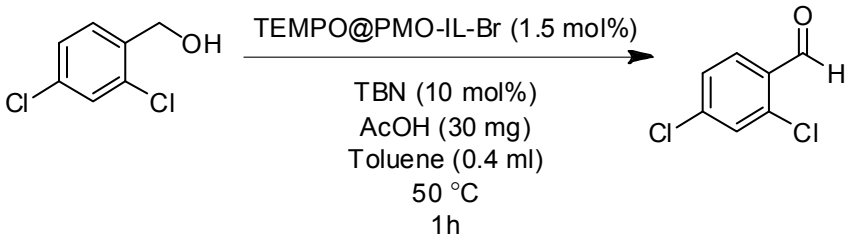
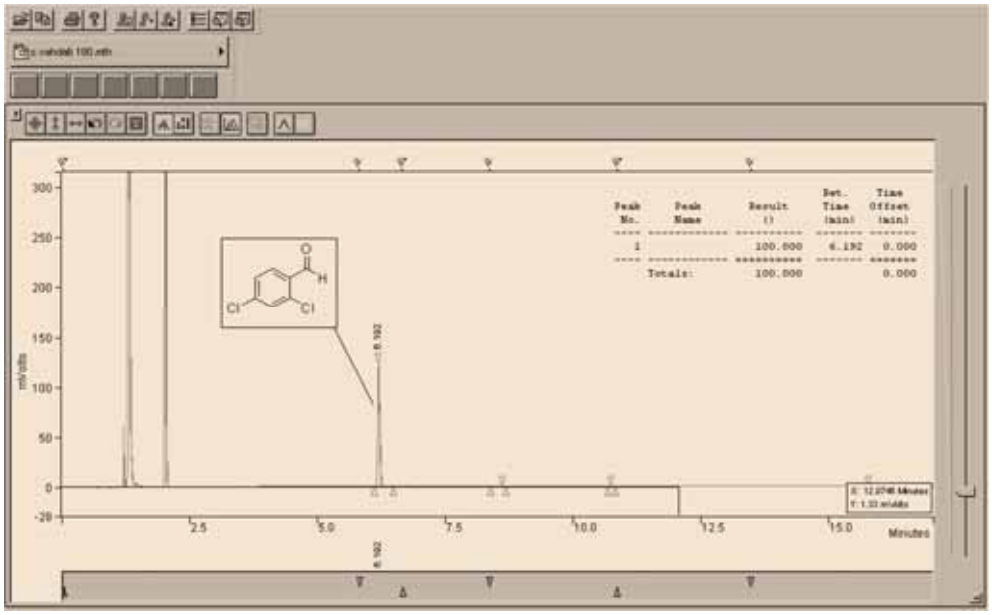


2,4-dichlorobenzylalcohol





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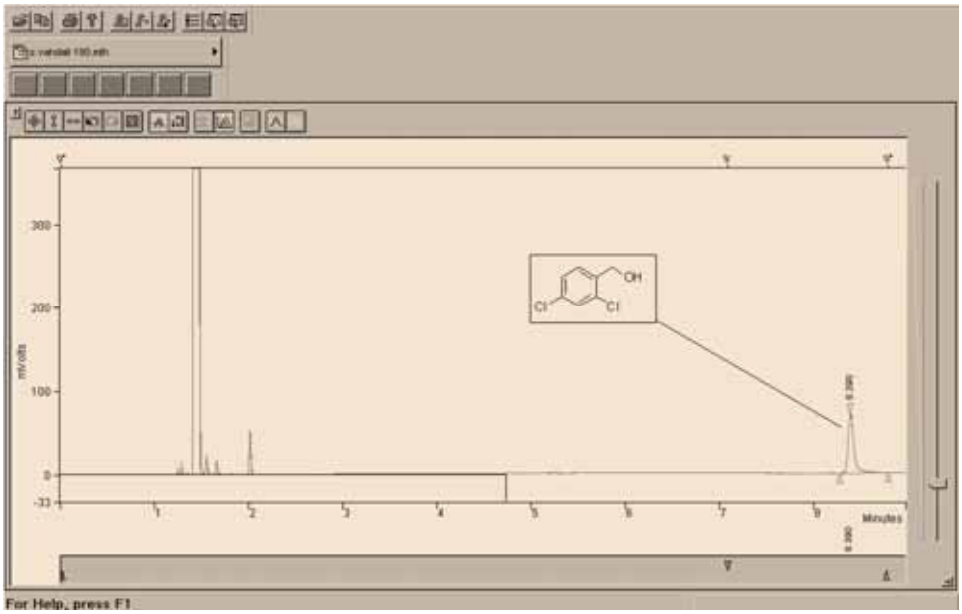
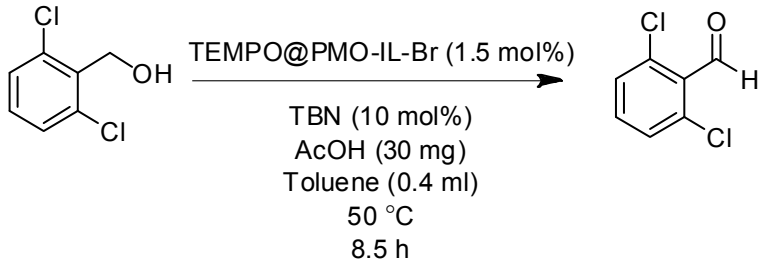
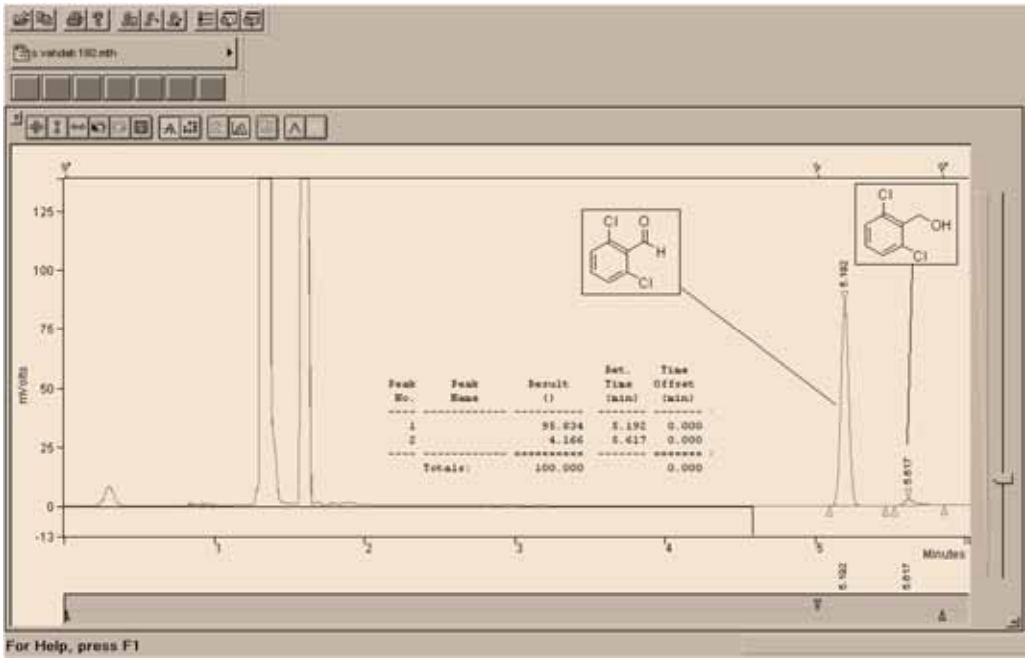


2,6-dichlorobenzylalcohol





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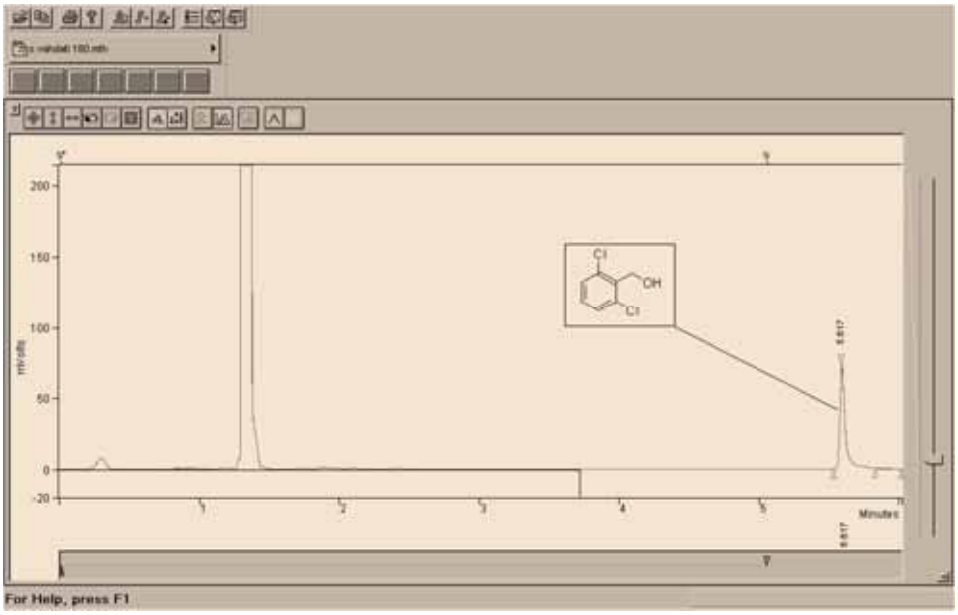
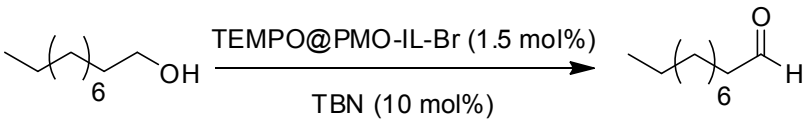
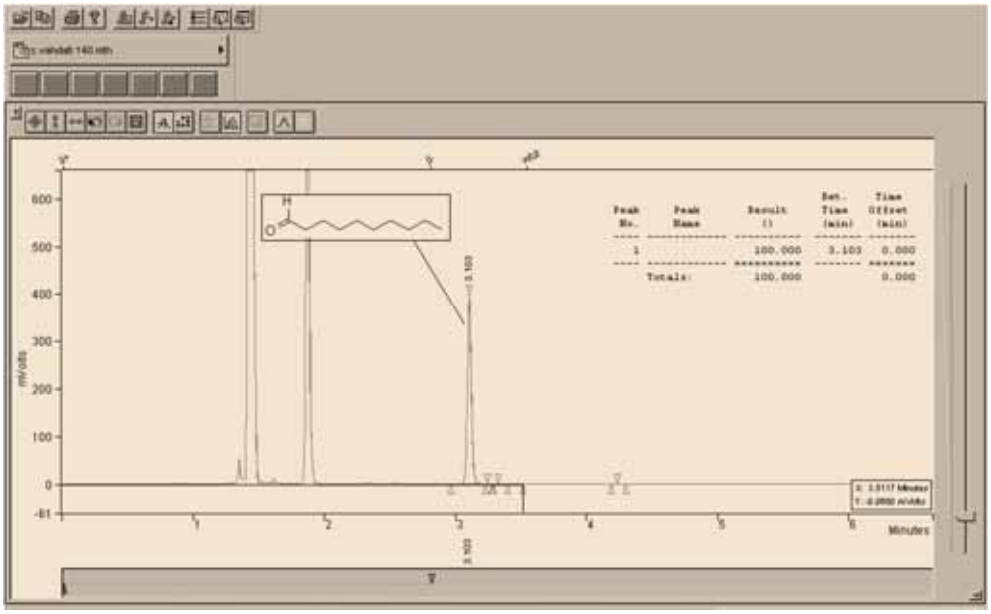


1-Decanol





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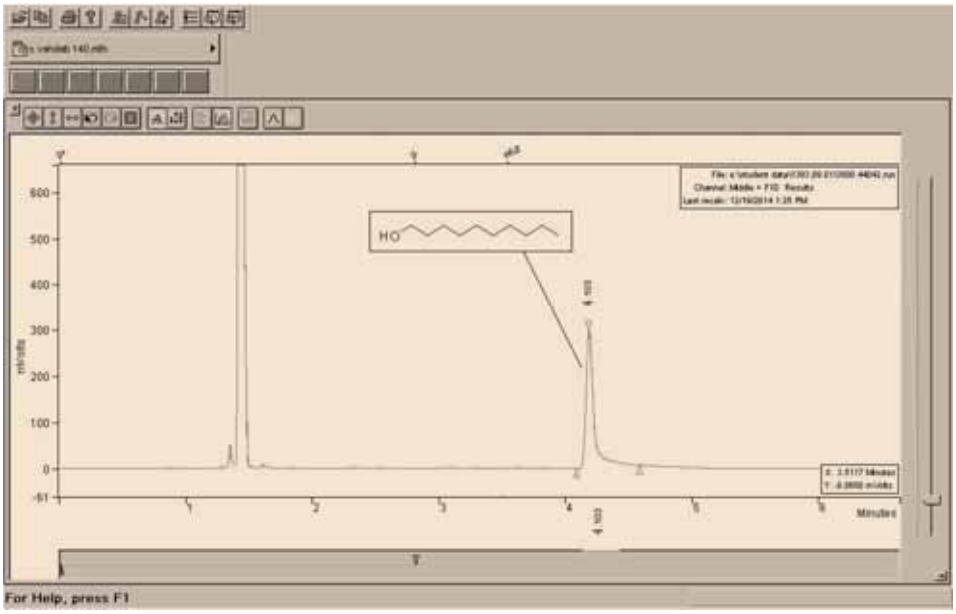
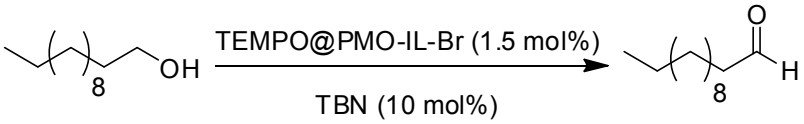
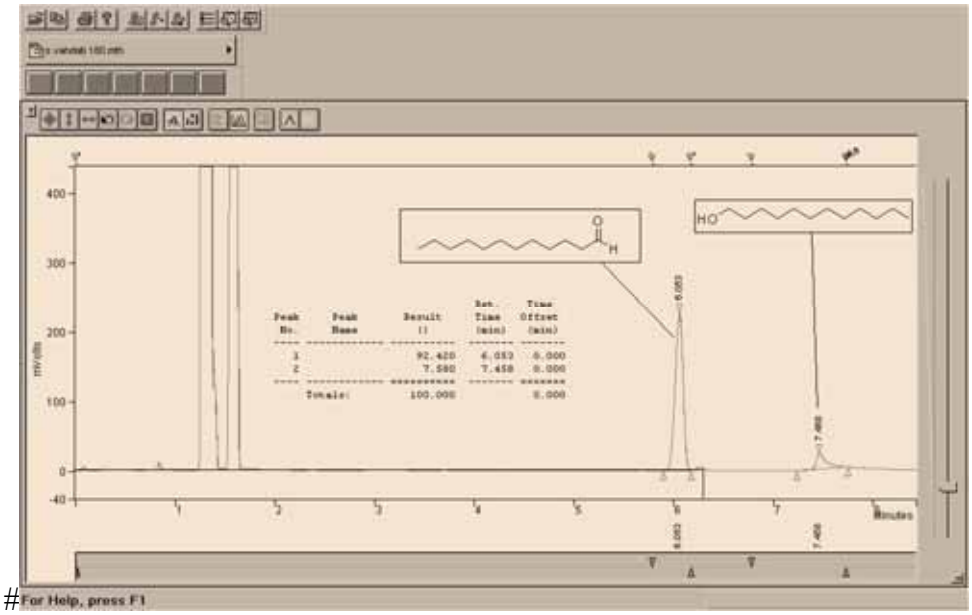


1-Dodecanol





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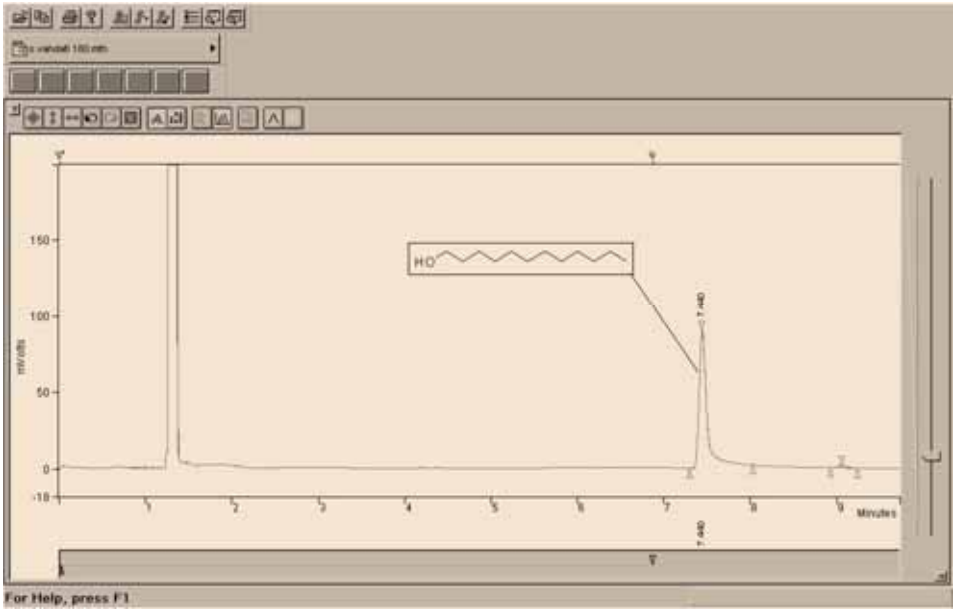
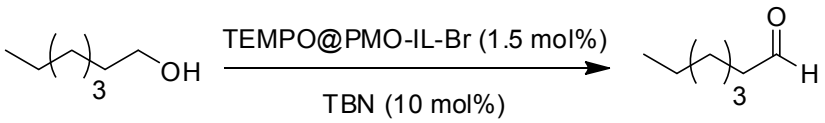
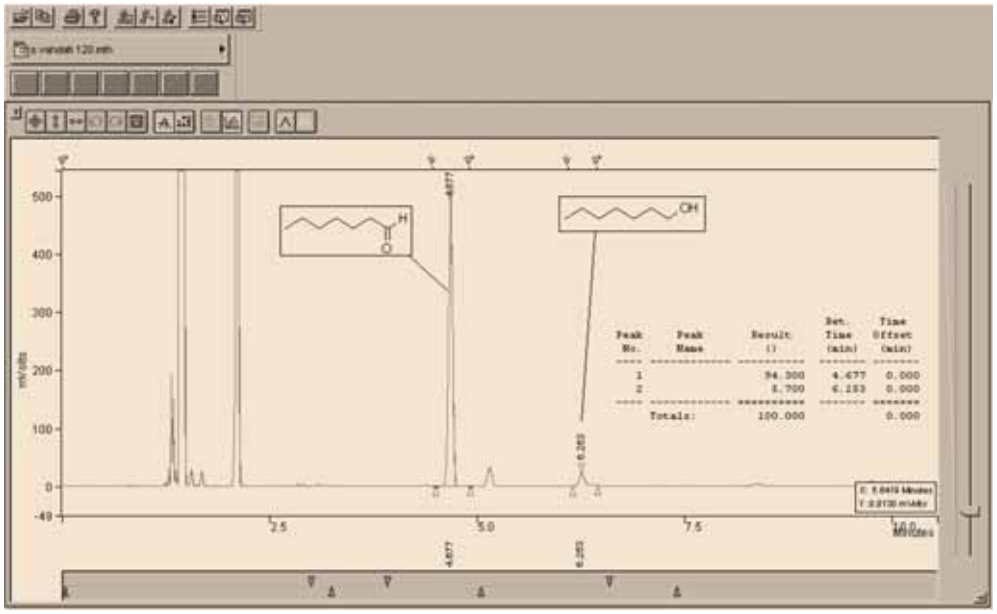


1-Heptanol





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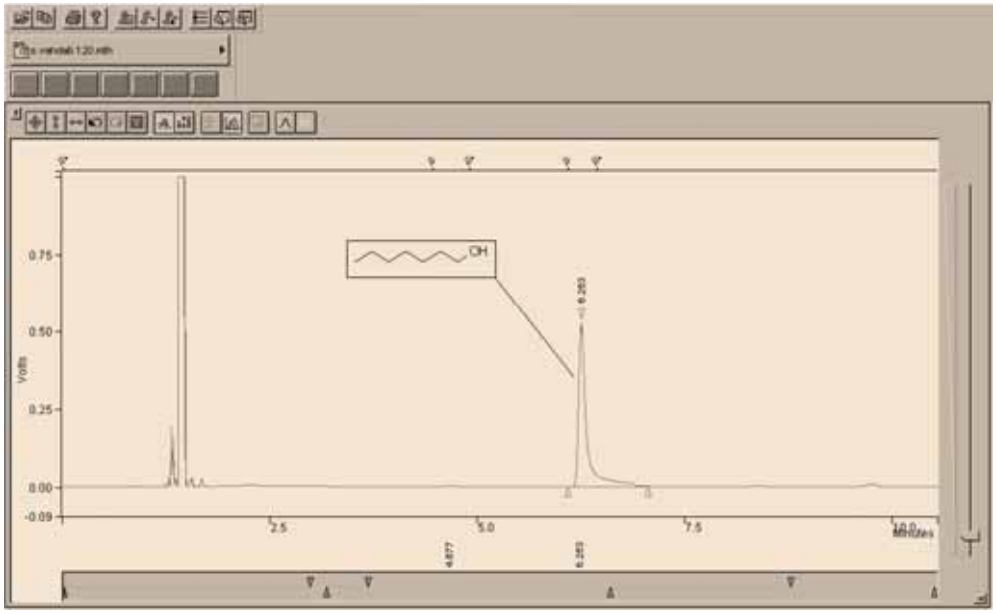
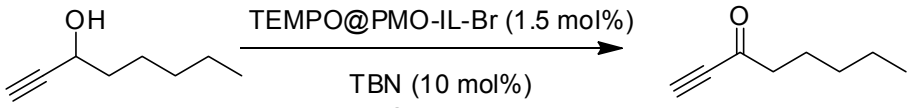
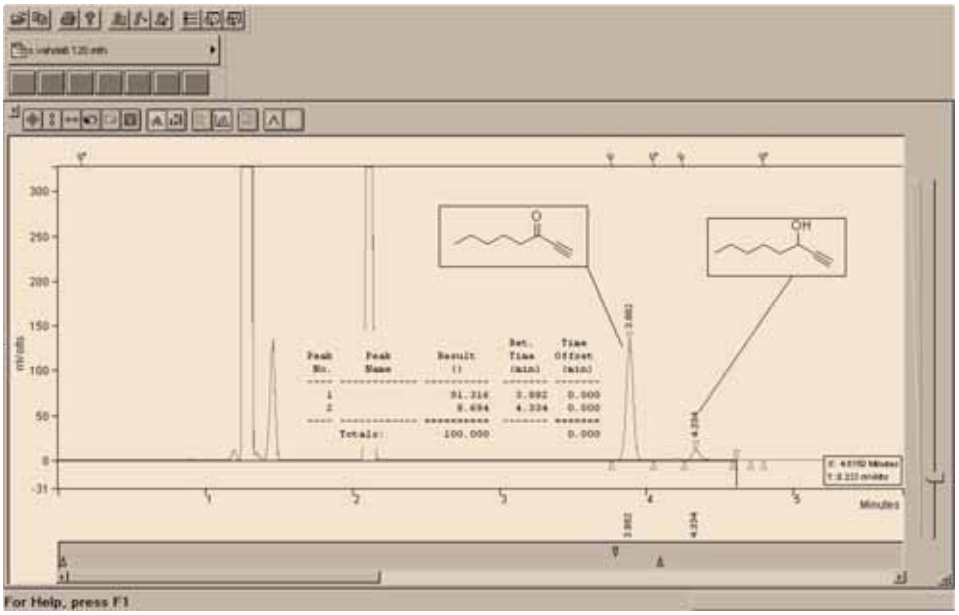


1-Octyn-3-ol





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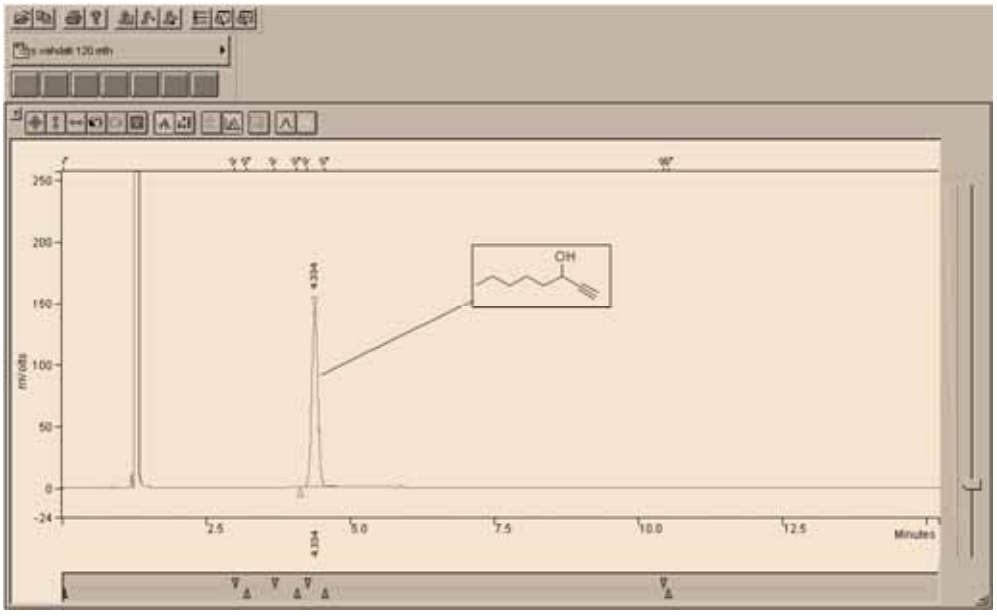
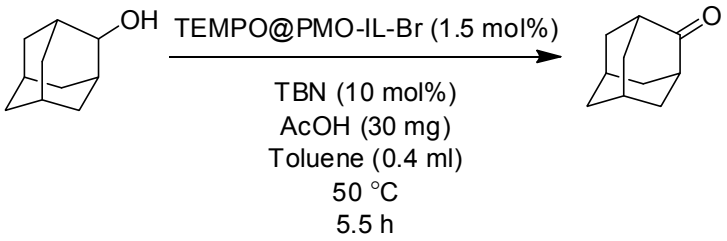
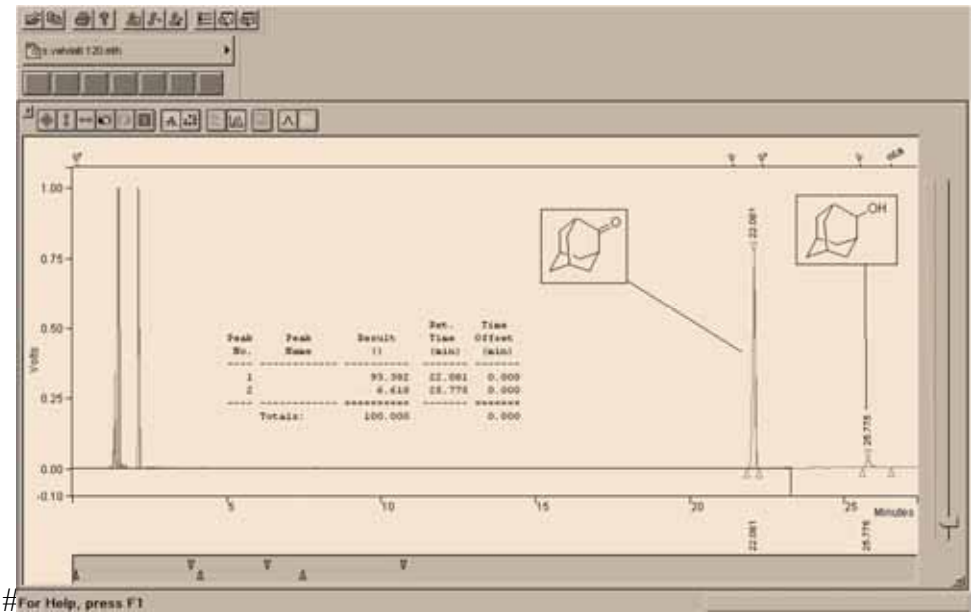


2-Adamantanol





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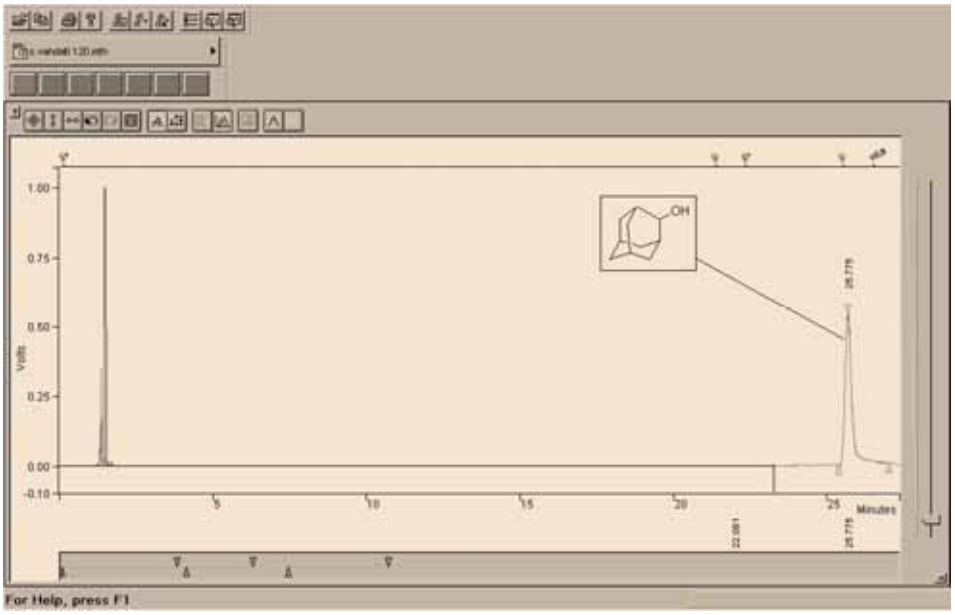
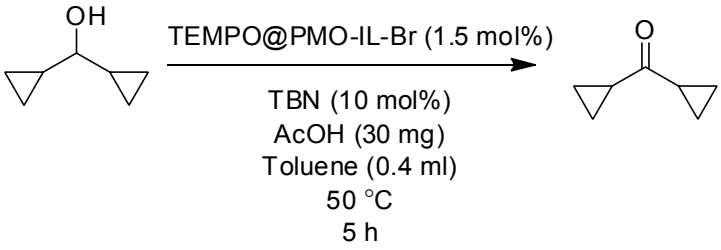
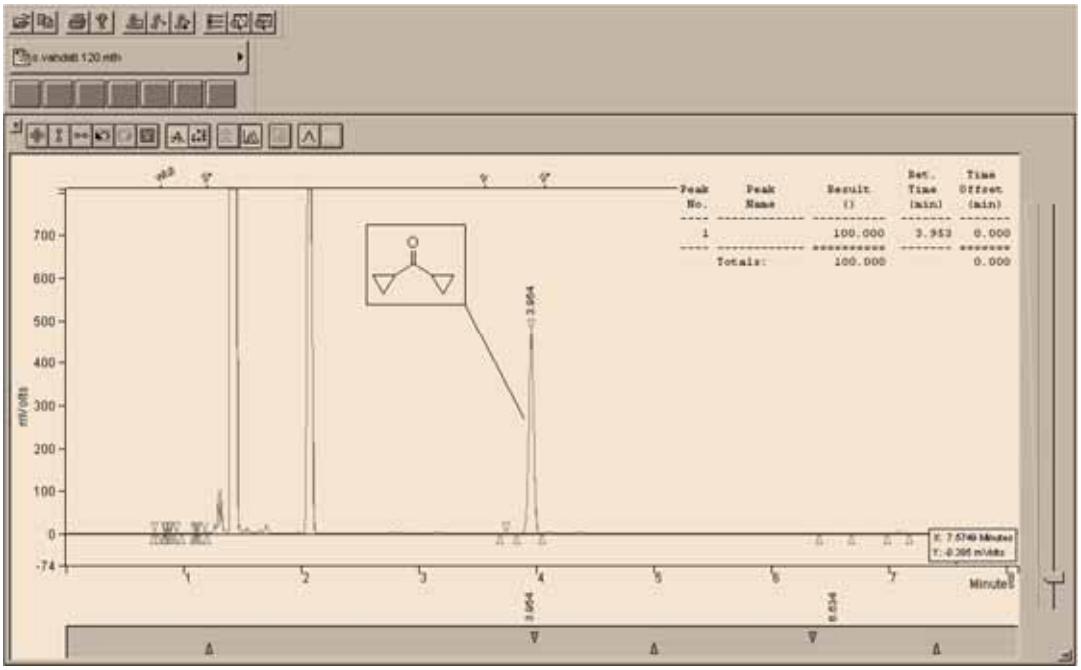


Dicyclopropylcarbinol





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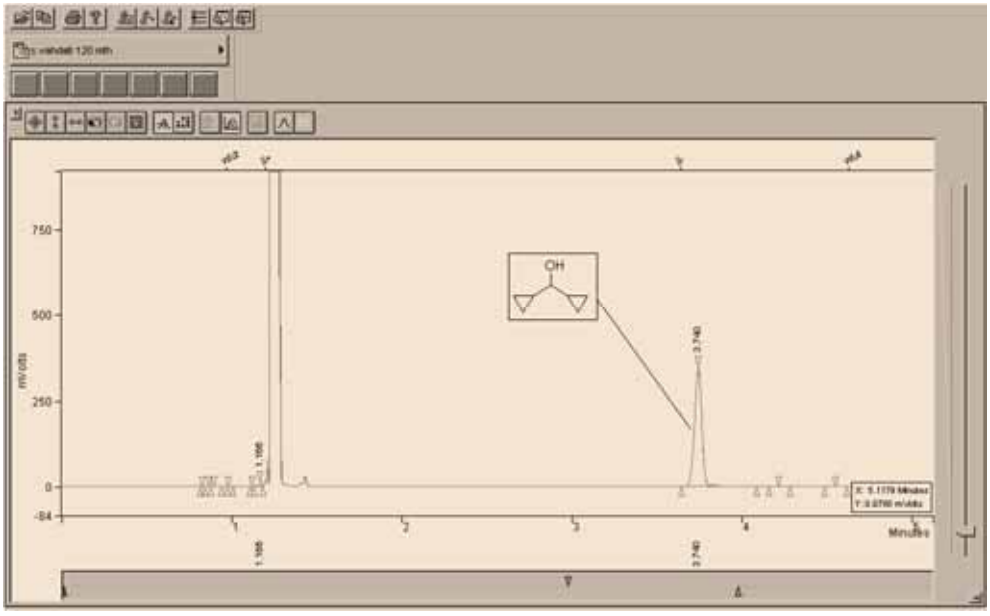
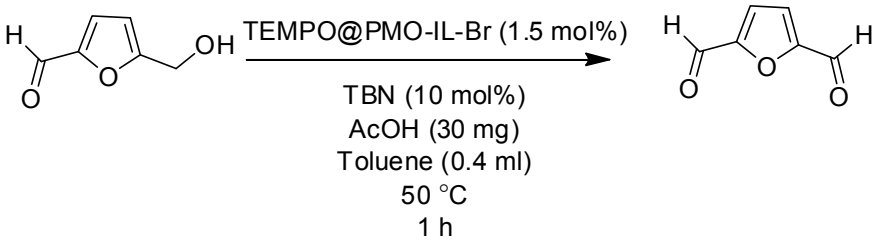
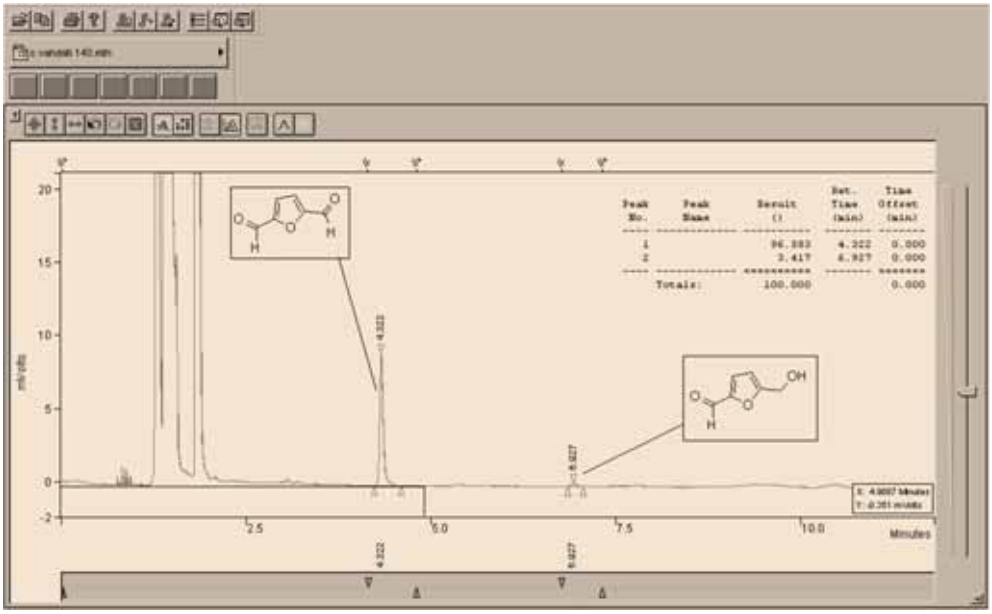


5-(hydroxymethyl)furan-2-carbaldehyde





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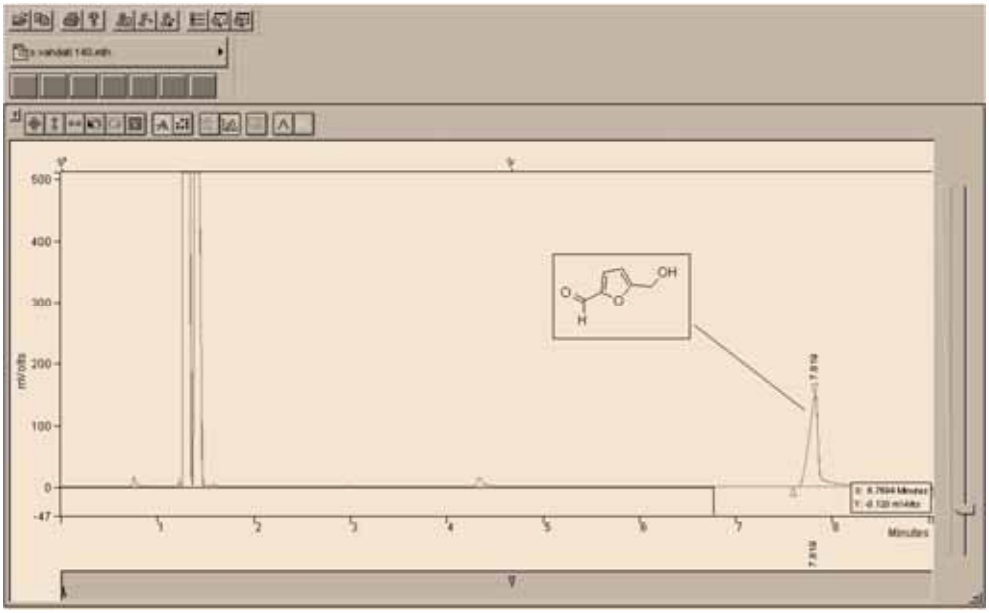
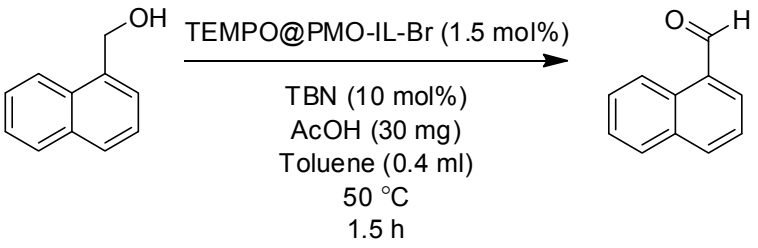
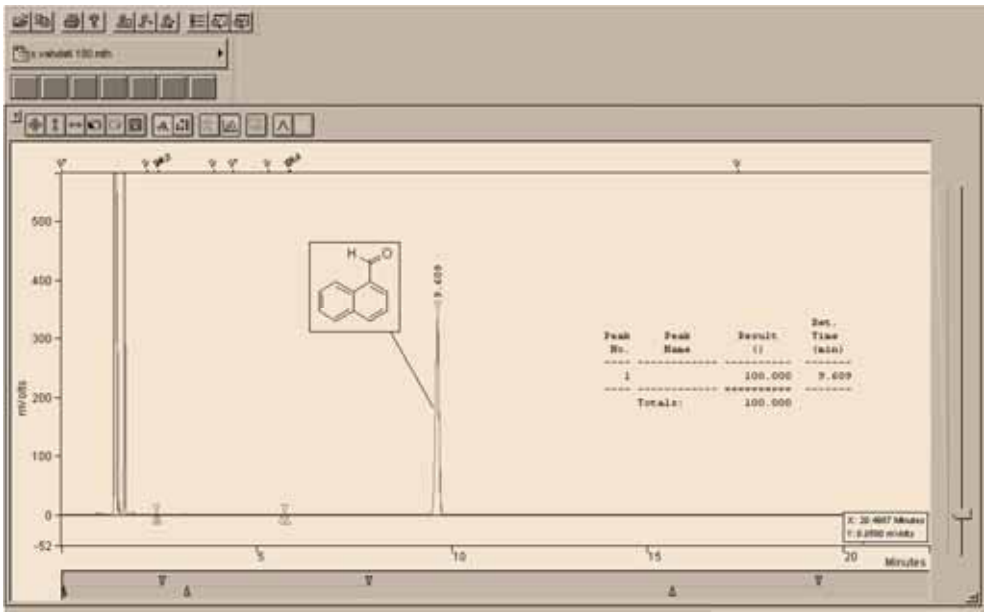


Naphthalenyl-1-methanol





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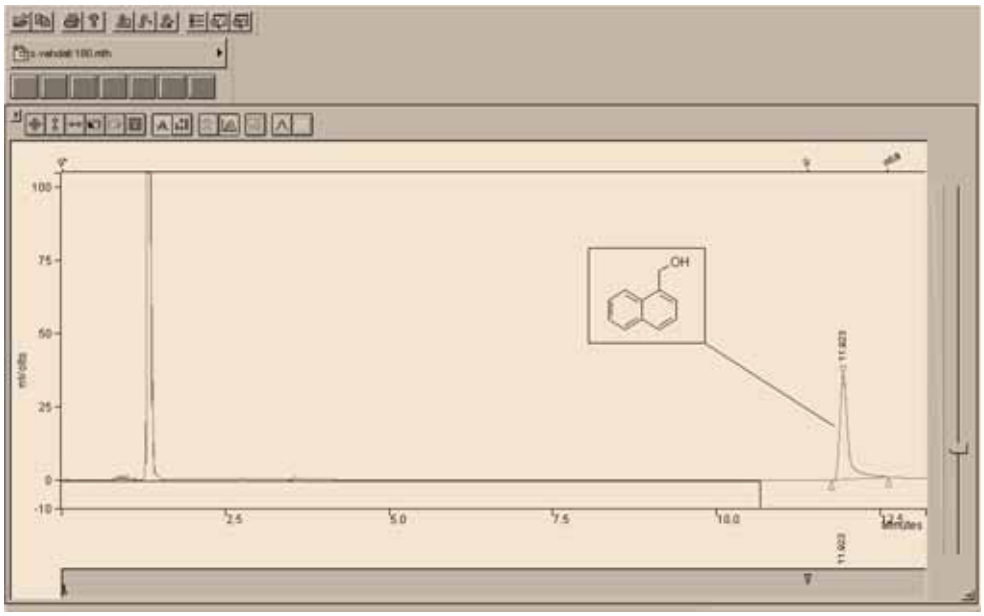
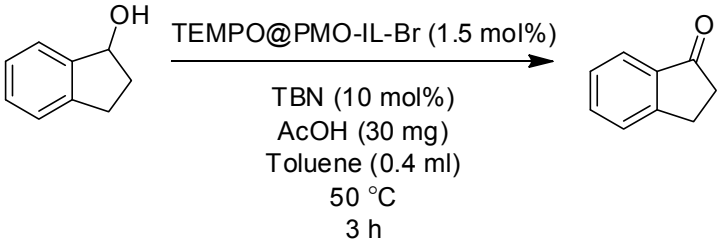
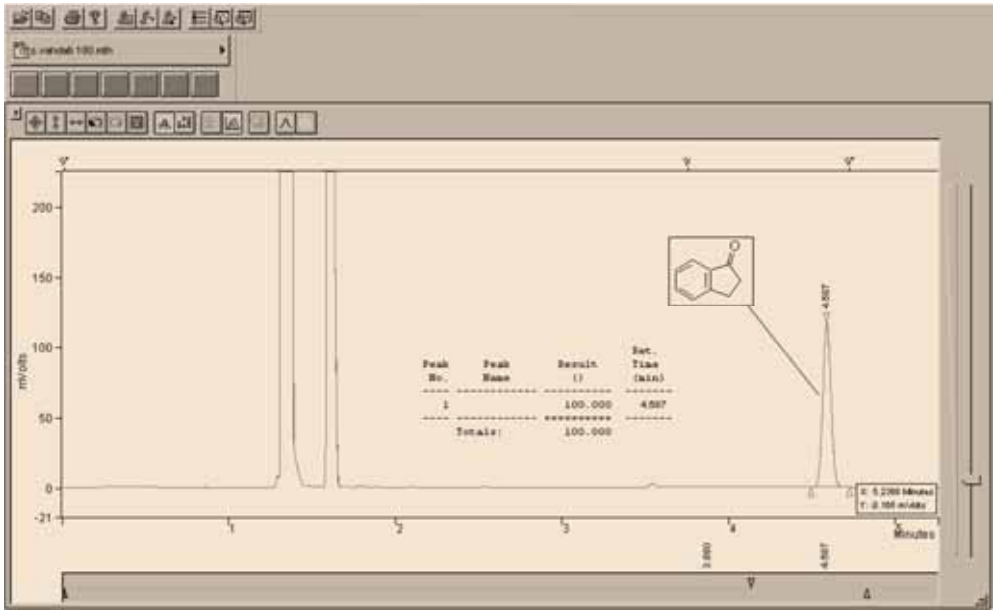


1-Indanol





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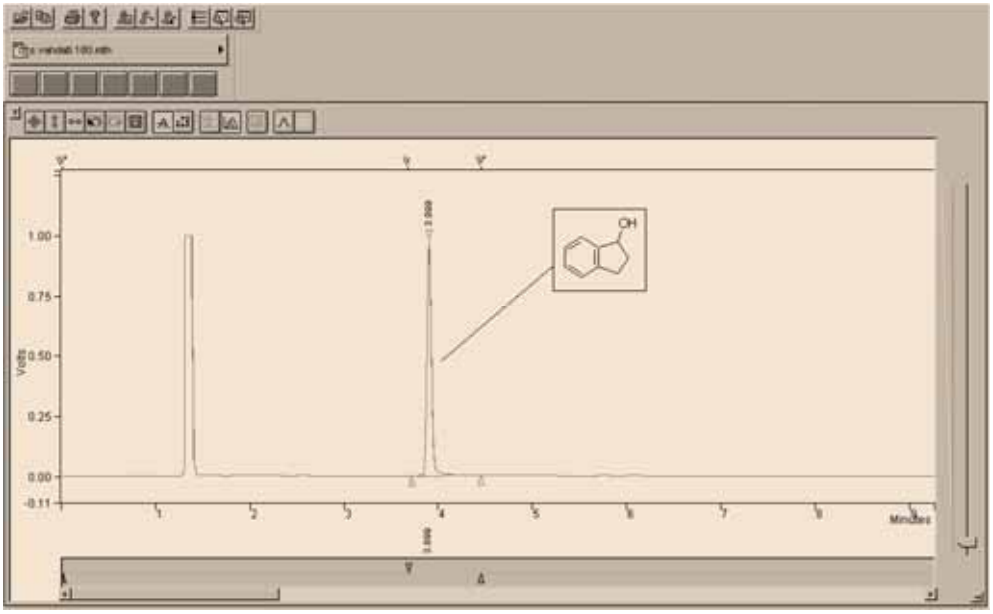
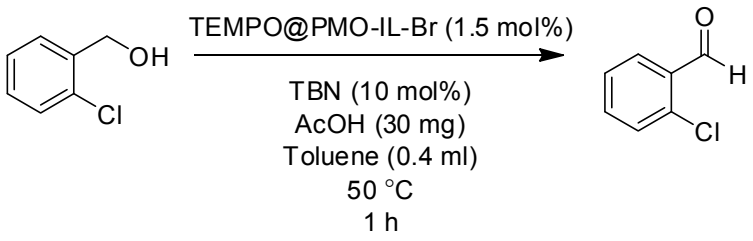
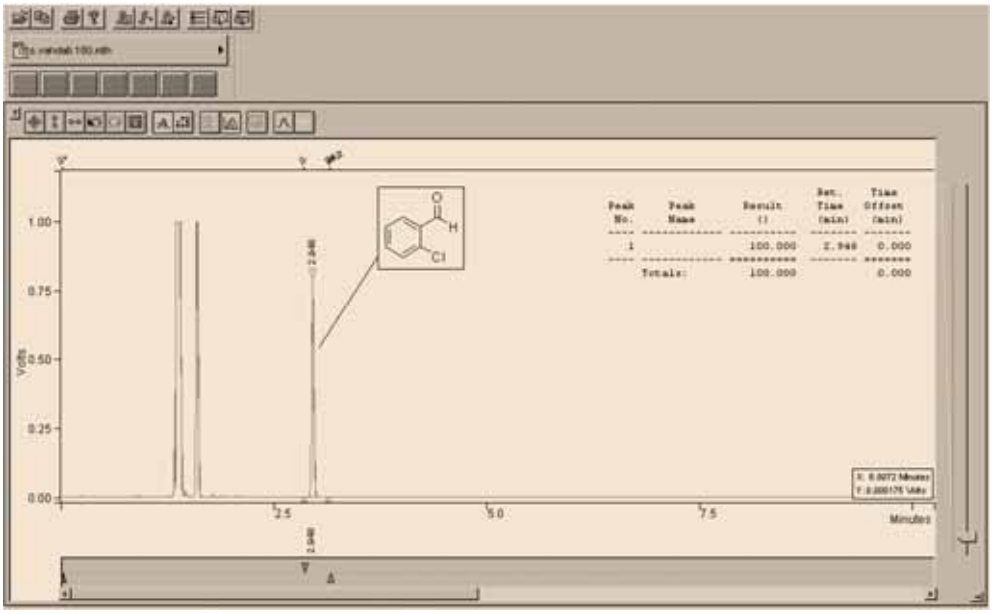


2-chlorobenzylalcohol





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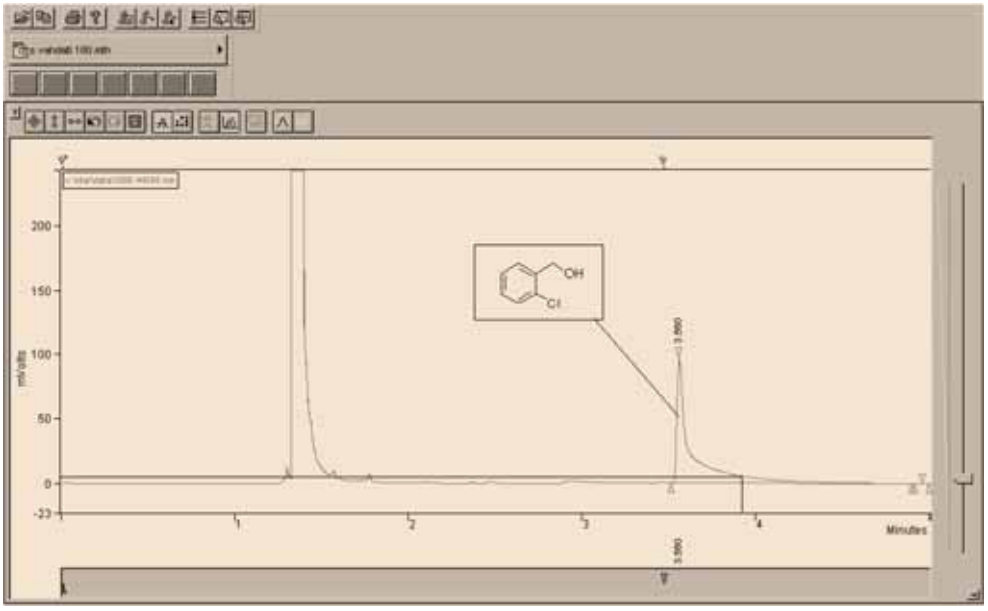
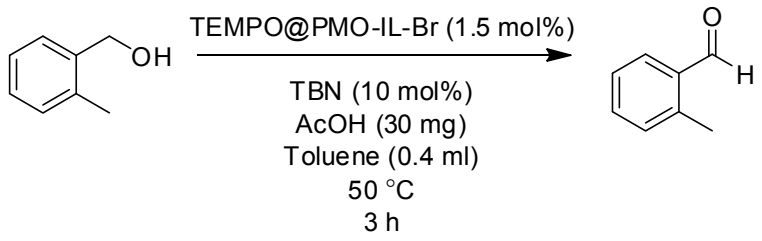
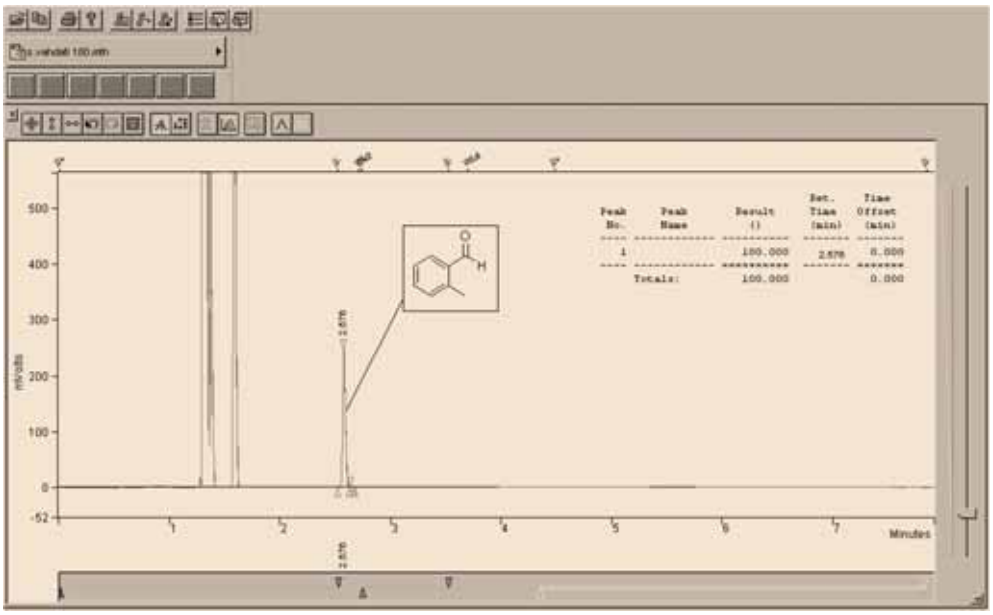


2-methylbenzylalcohol





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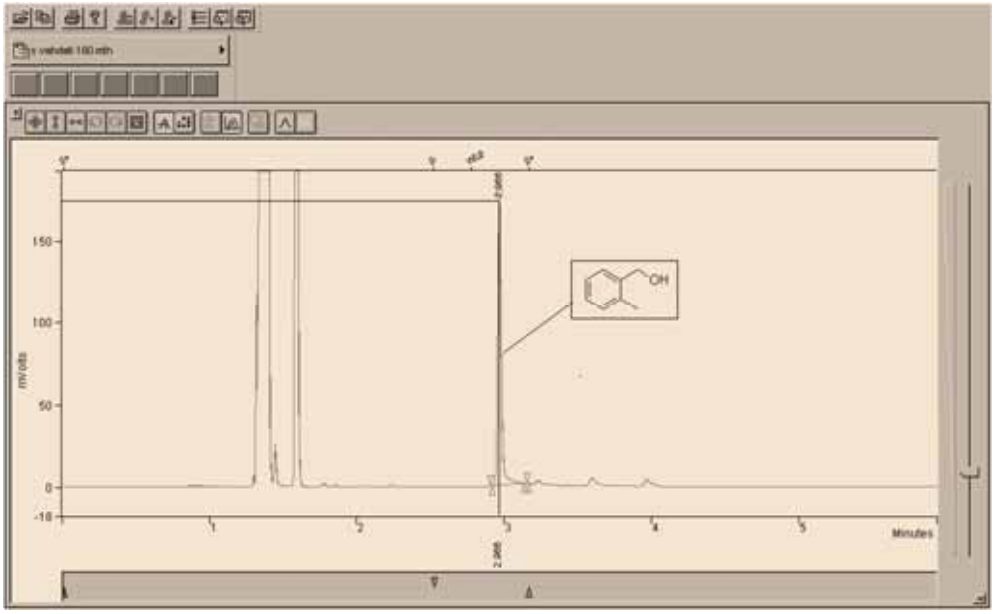
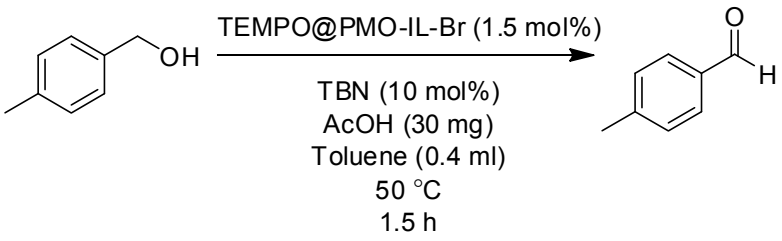
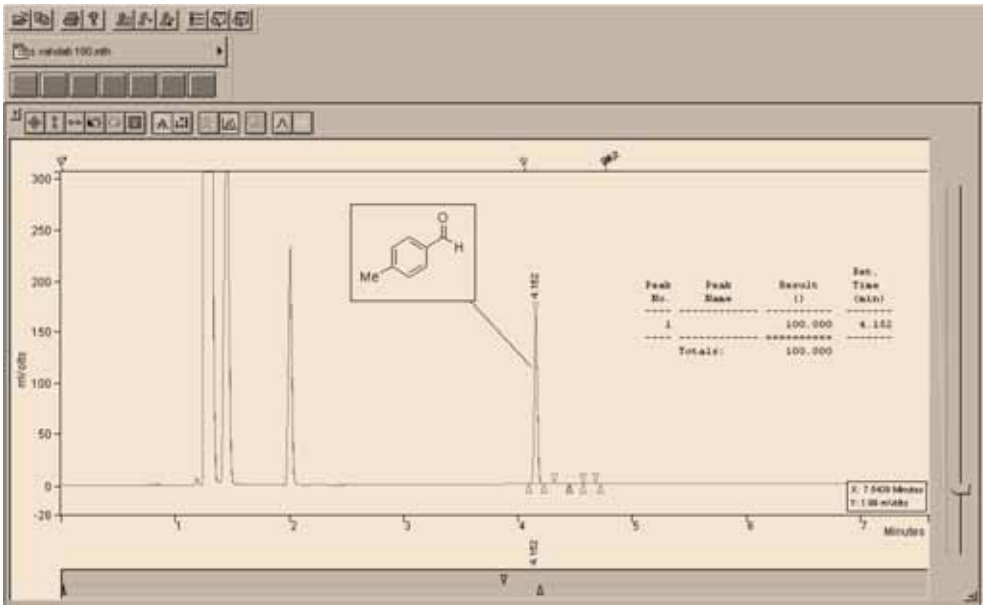
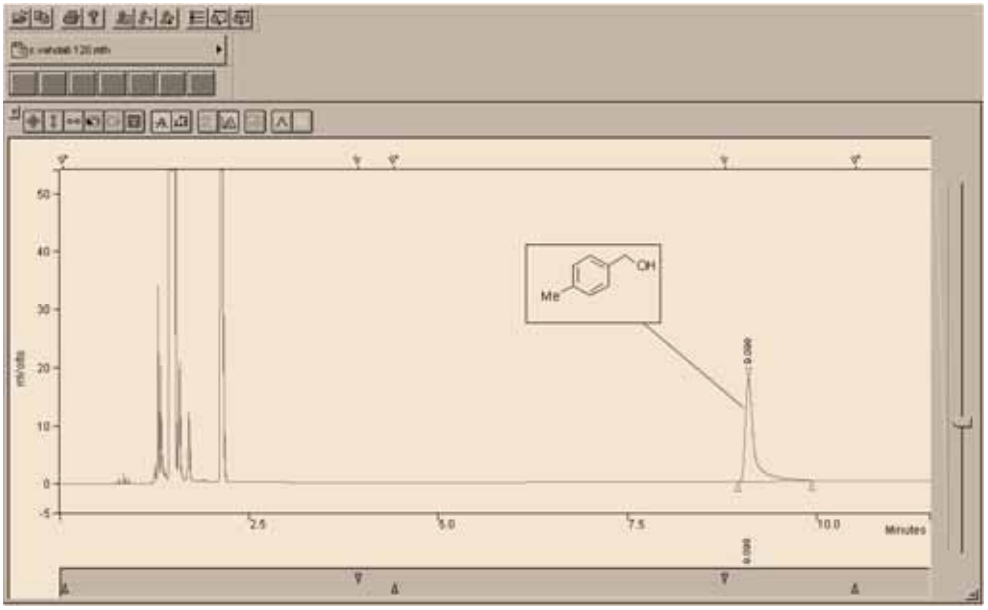


4-methylbenzylalcohol

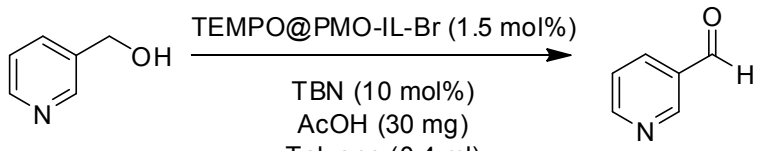


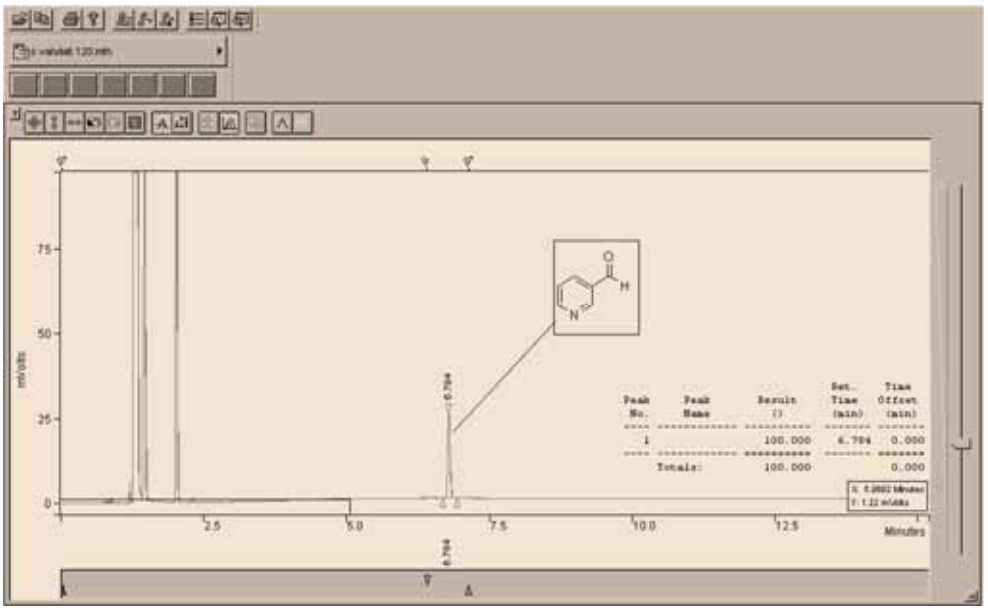


Blank of 4-methylbenzylalcohol

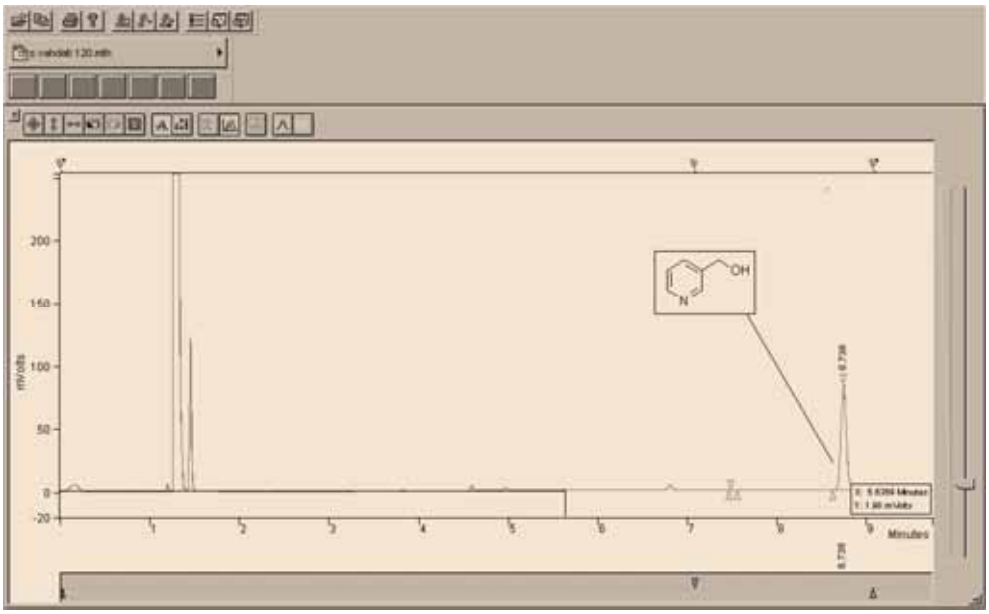


3-pyridylmethanol

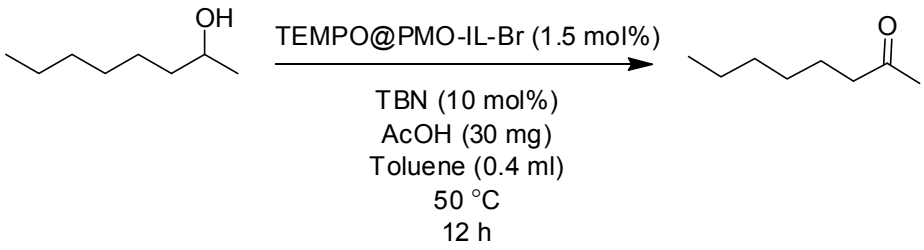


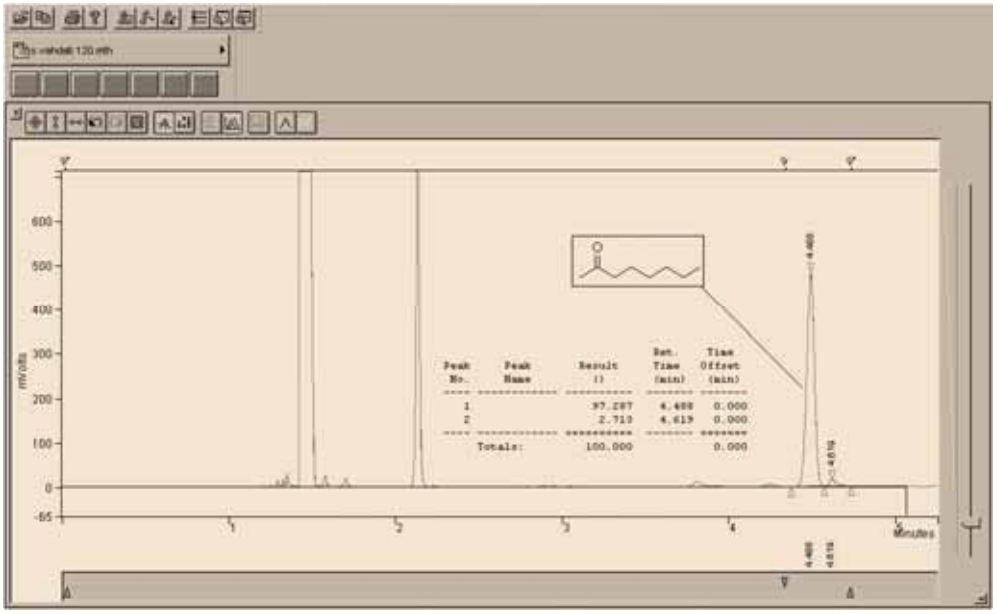


Blank of 3-pyridylmethanol



2-octanol





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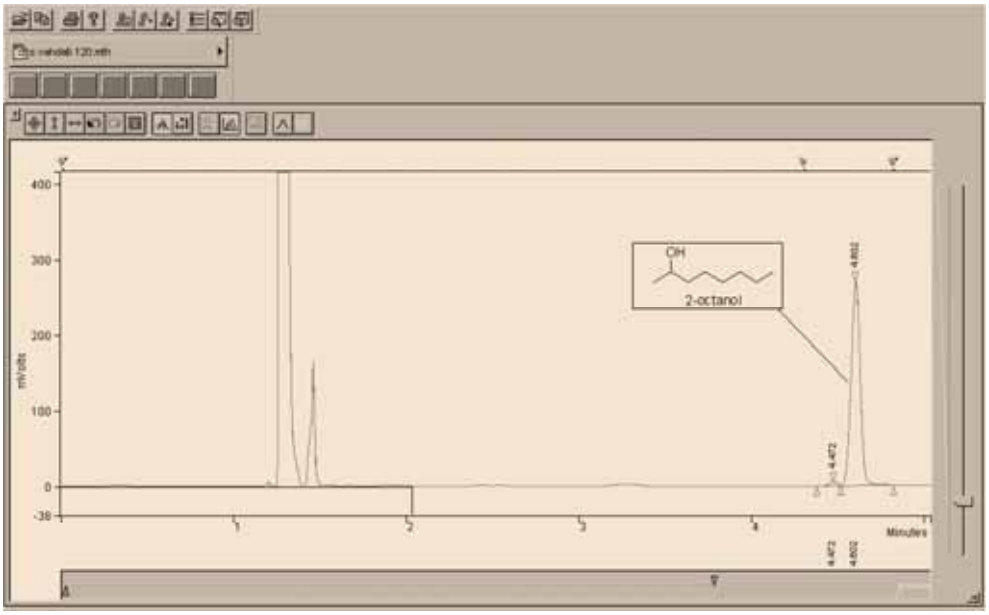
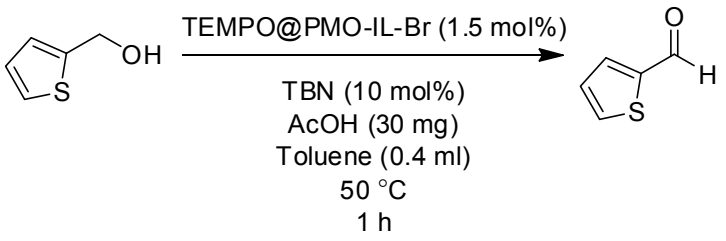
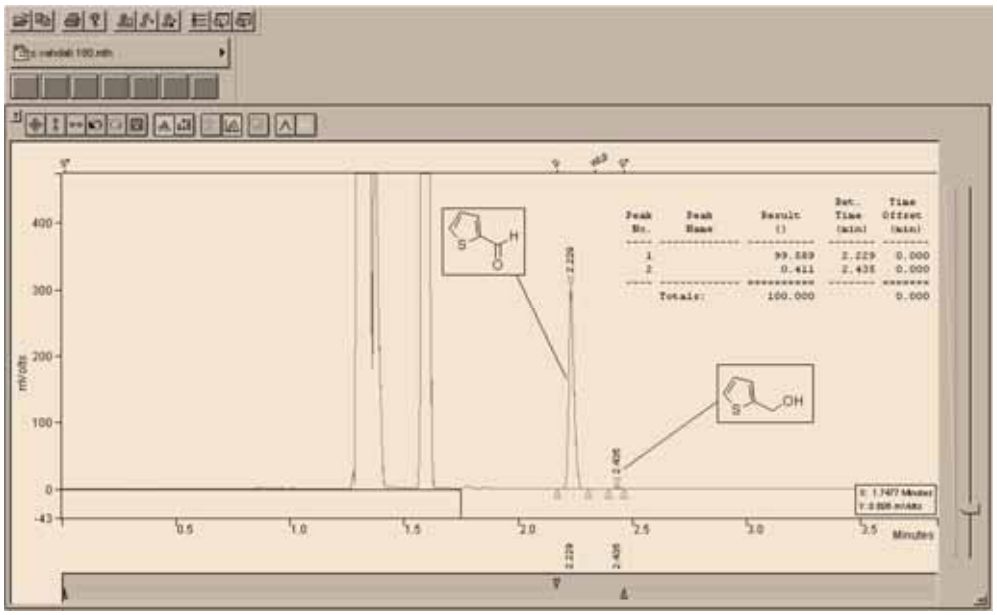


Thiophenyl-2-methanol





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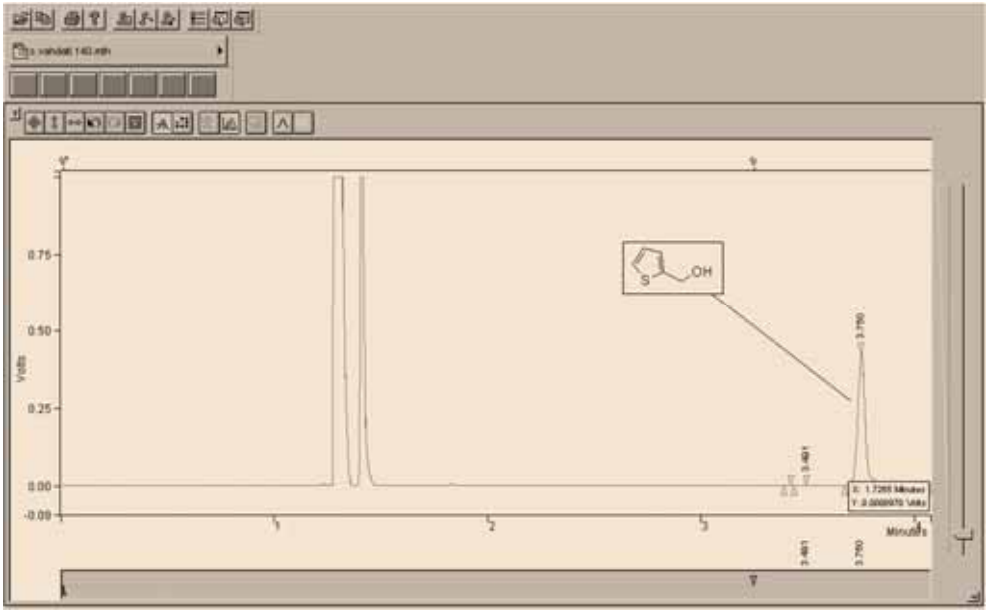
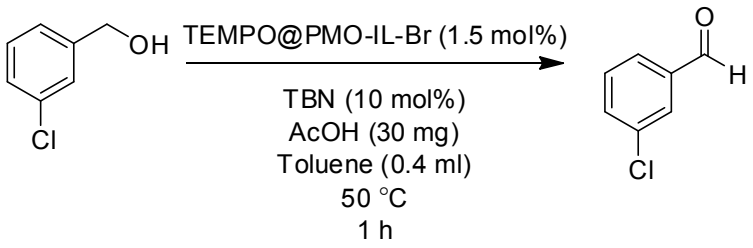
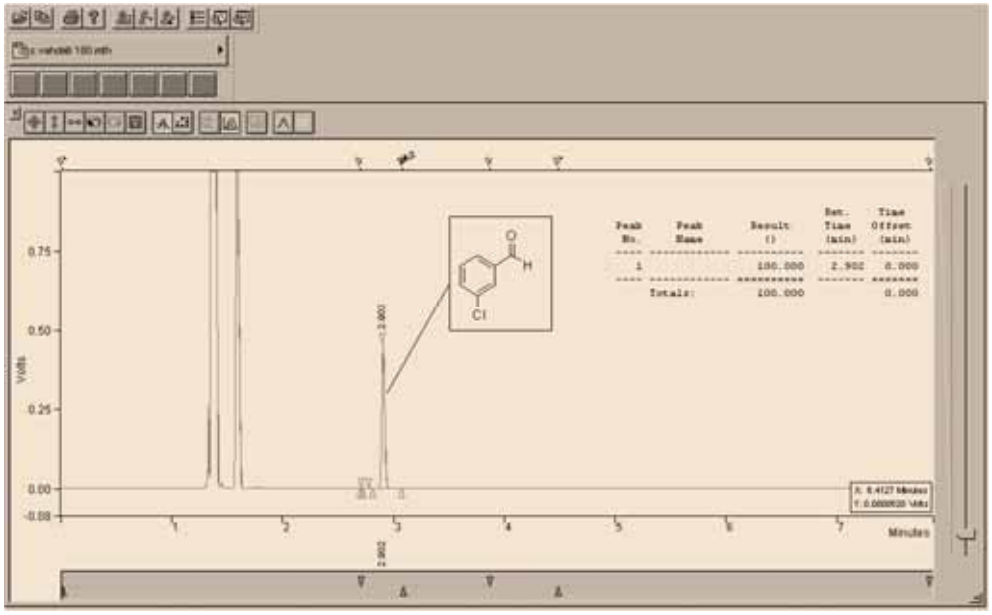
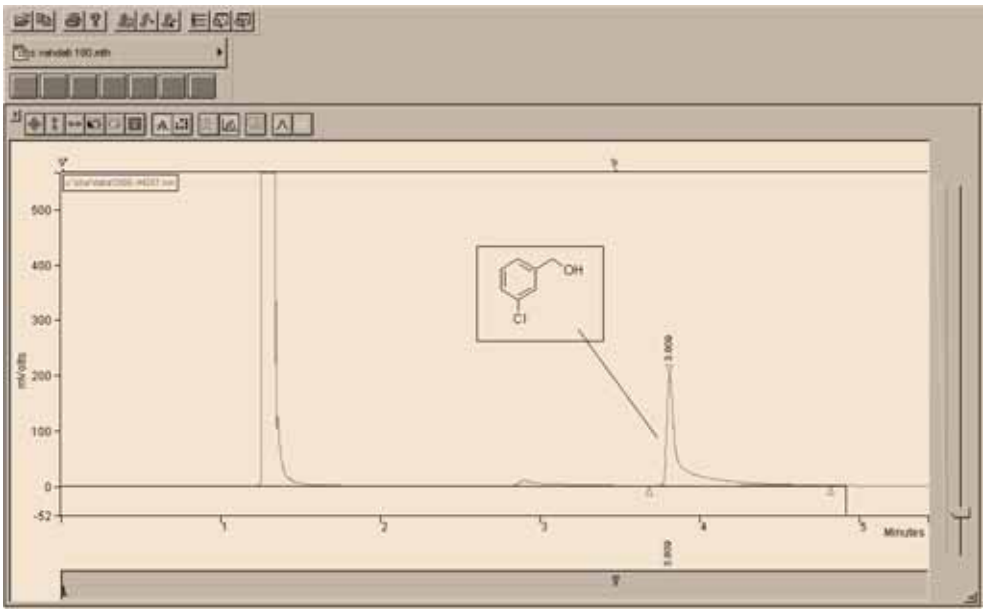


3-chlorobenzylalcohol

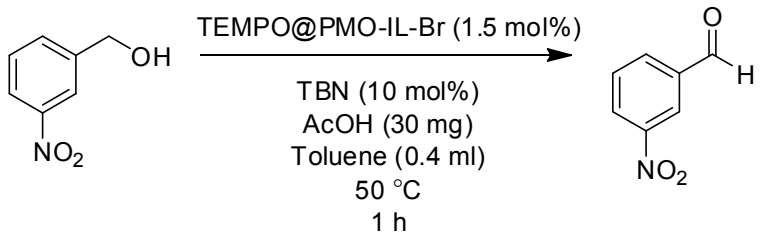


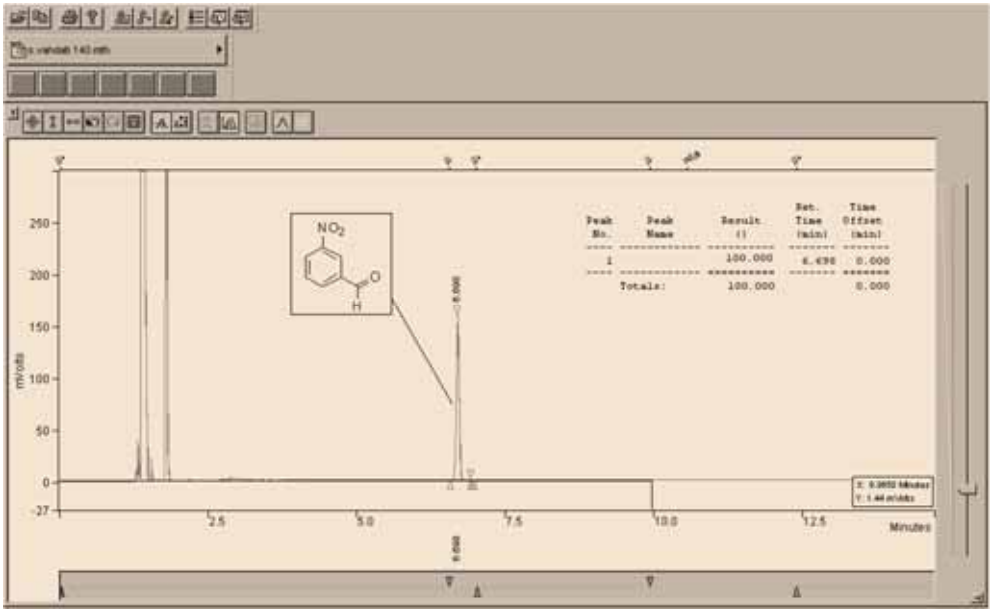


Blank of 3-chlorobenzylalcohol



3-Nitrobenzylalcohol





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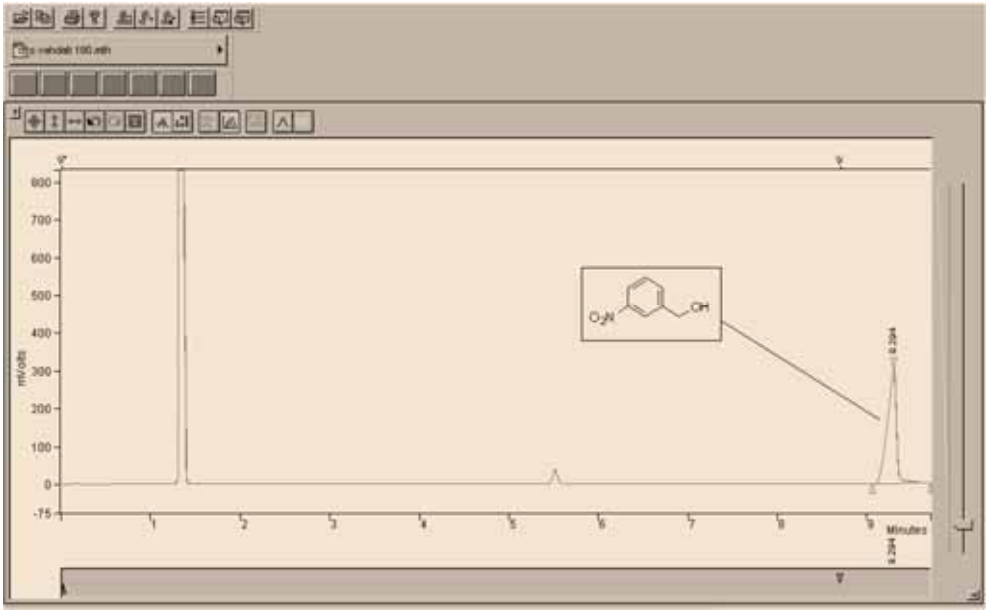
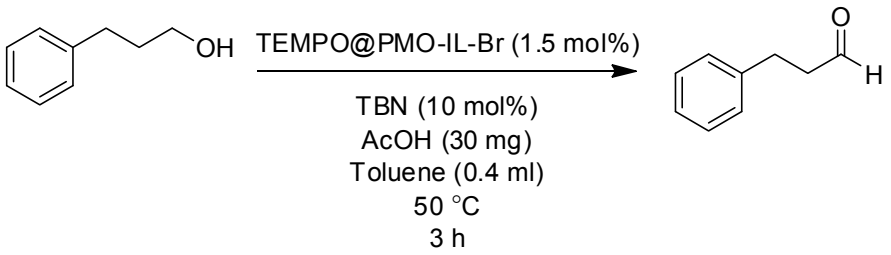
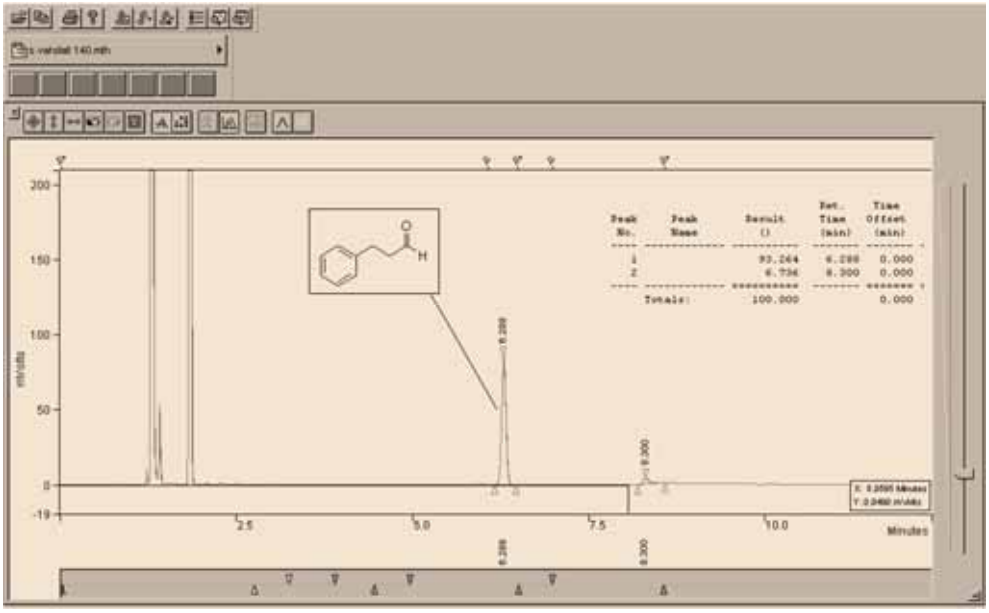


3-phenyl-1-propanol





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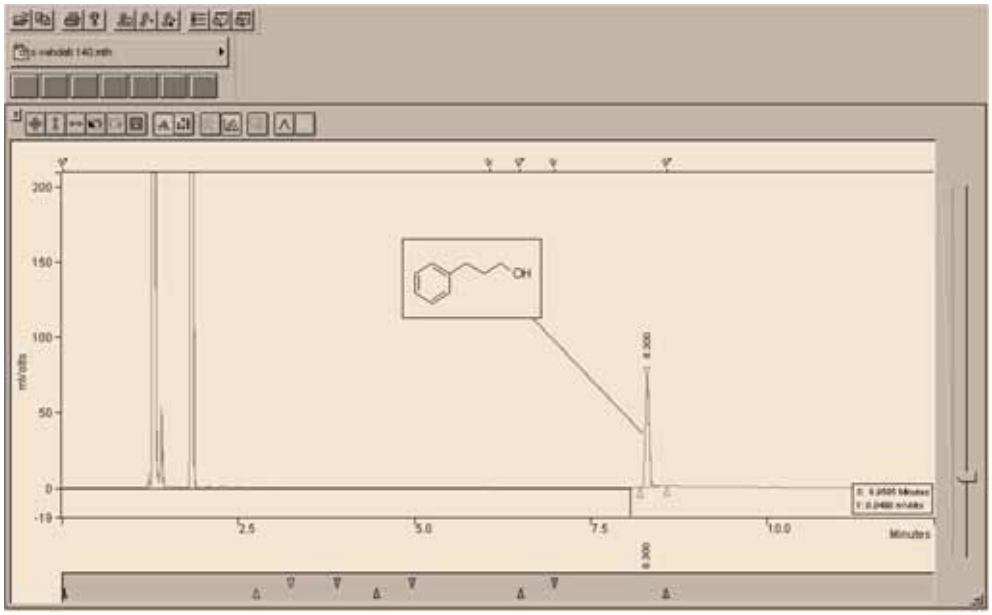
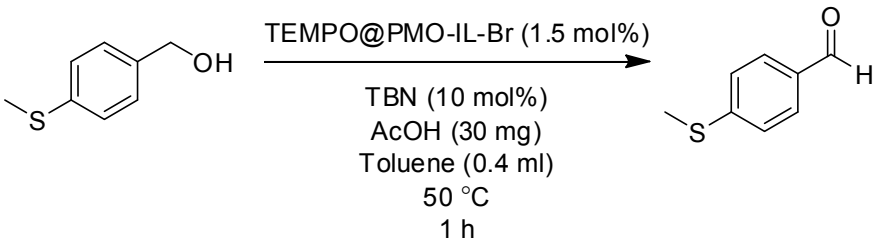
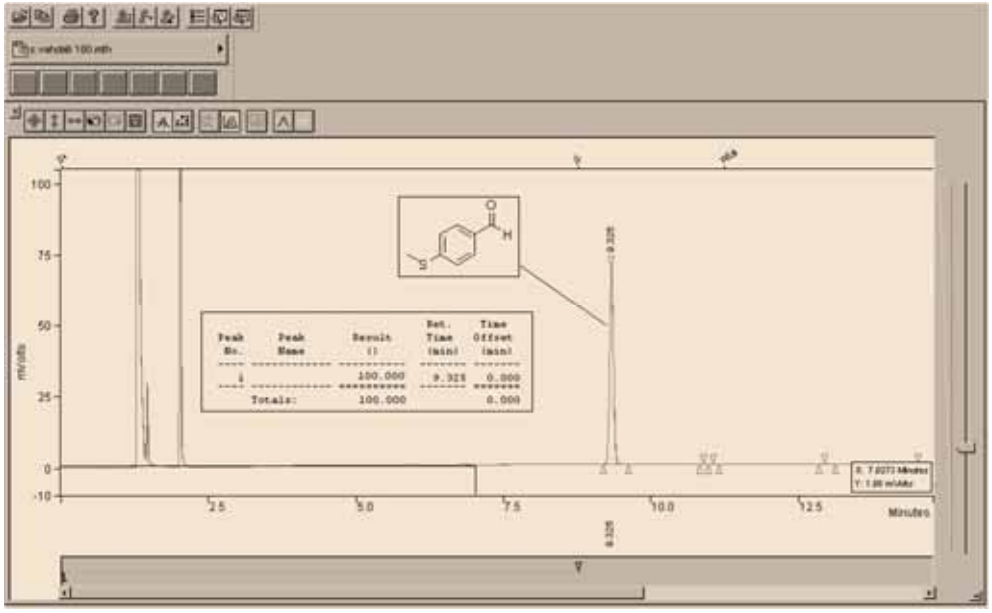


4-thiomethylbenzylalcohol





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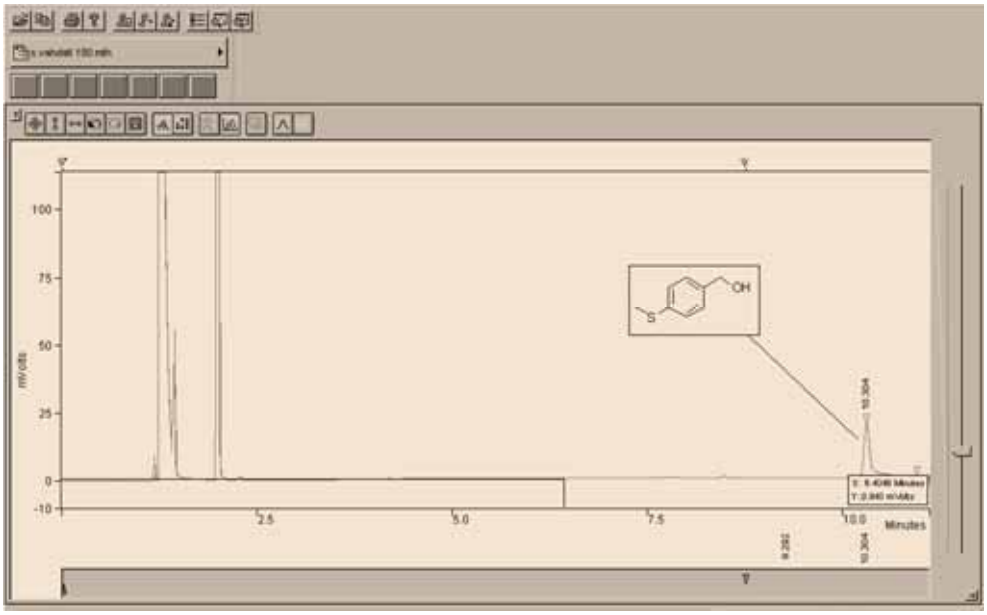
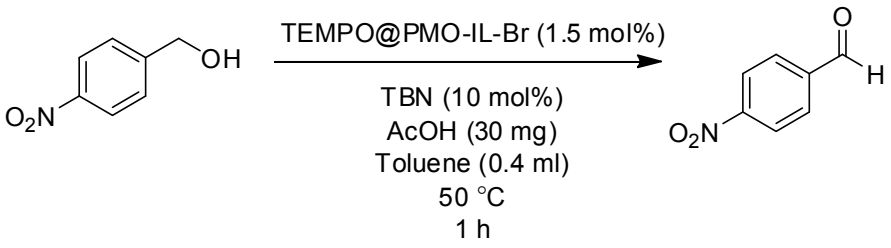
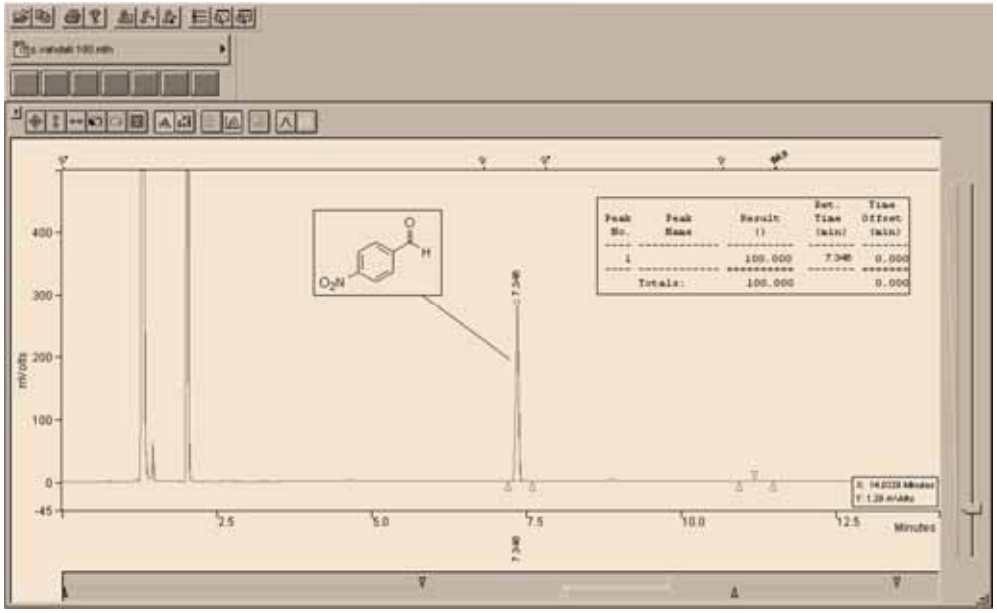
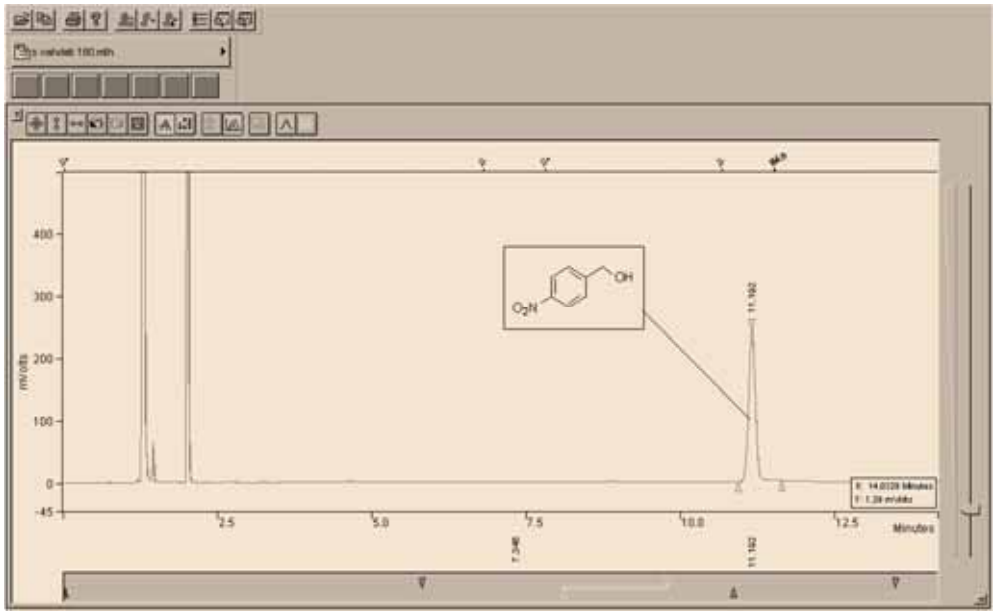


4-nitrobenzylalcohol

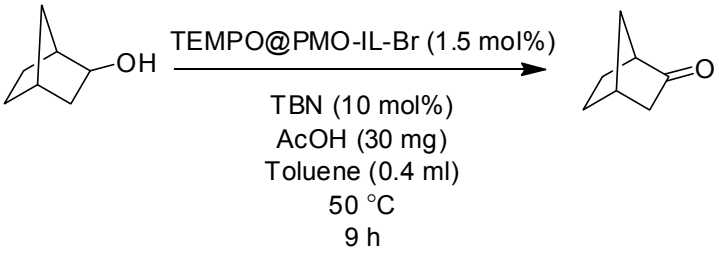


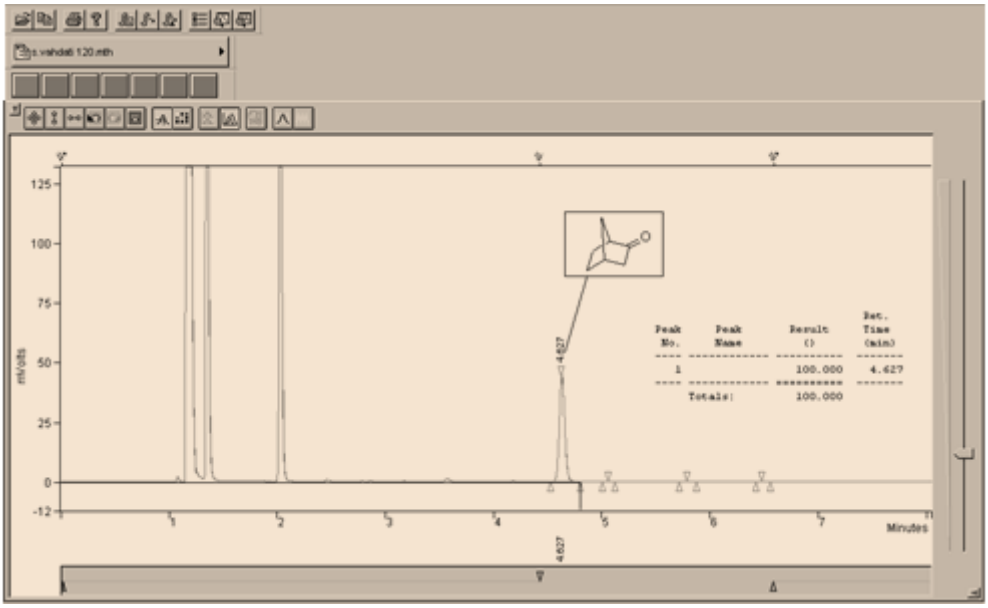


Blank of 4-nitrobenzylalcohol



2-Norbornano





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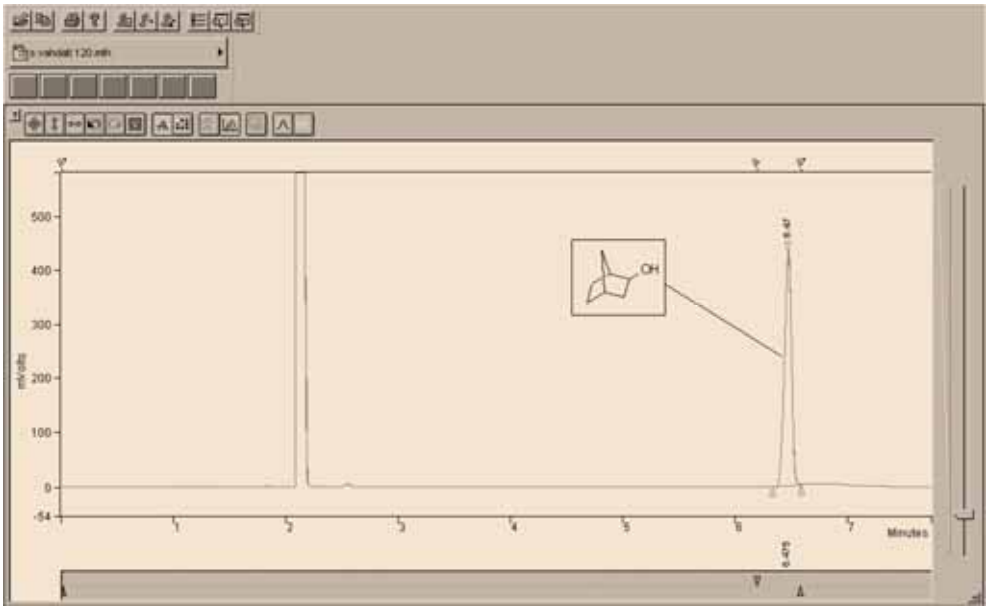
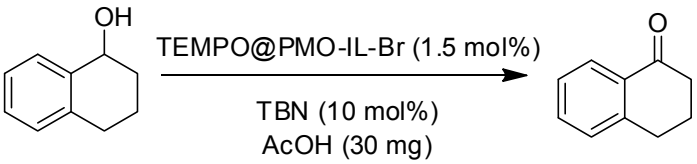
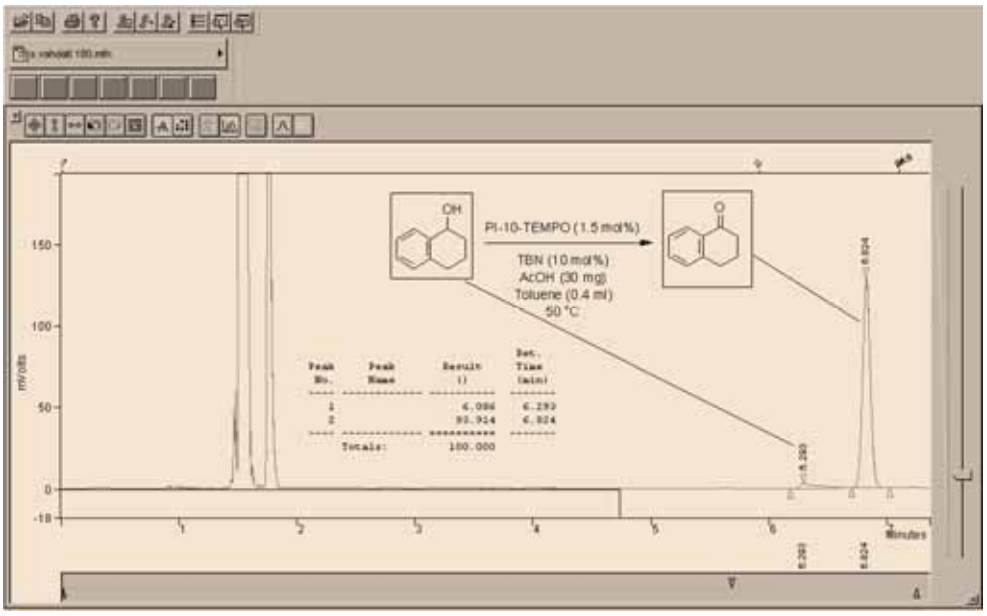
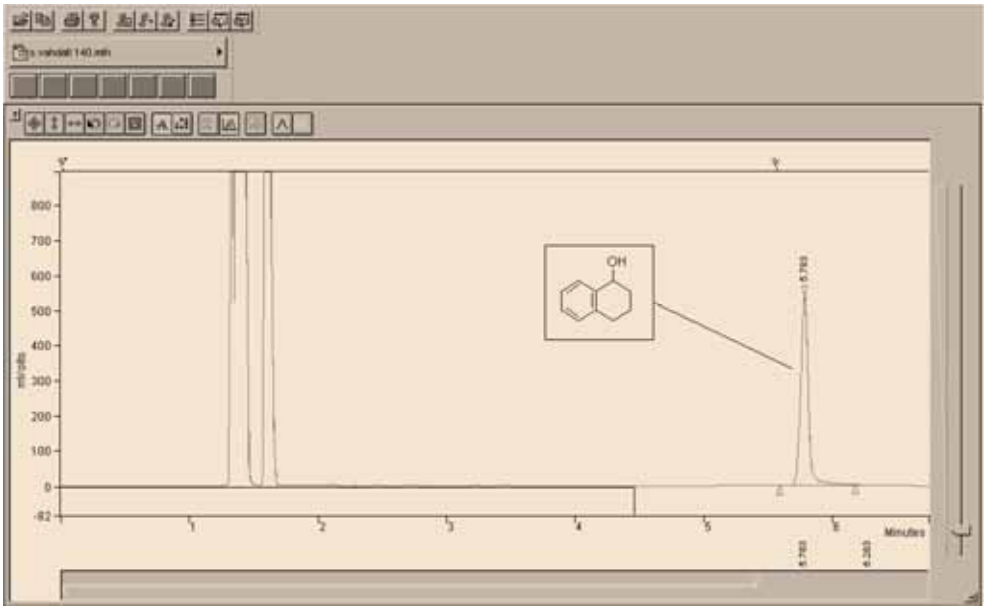


1-Tetralol

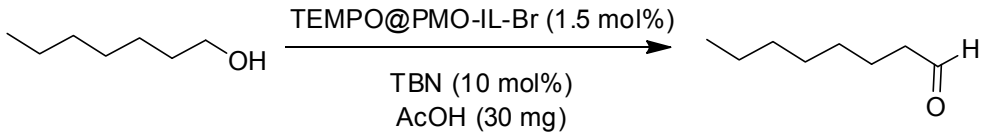


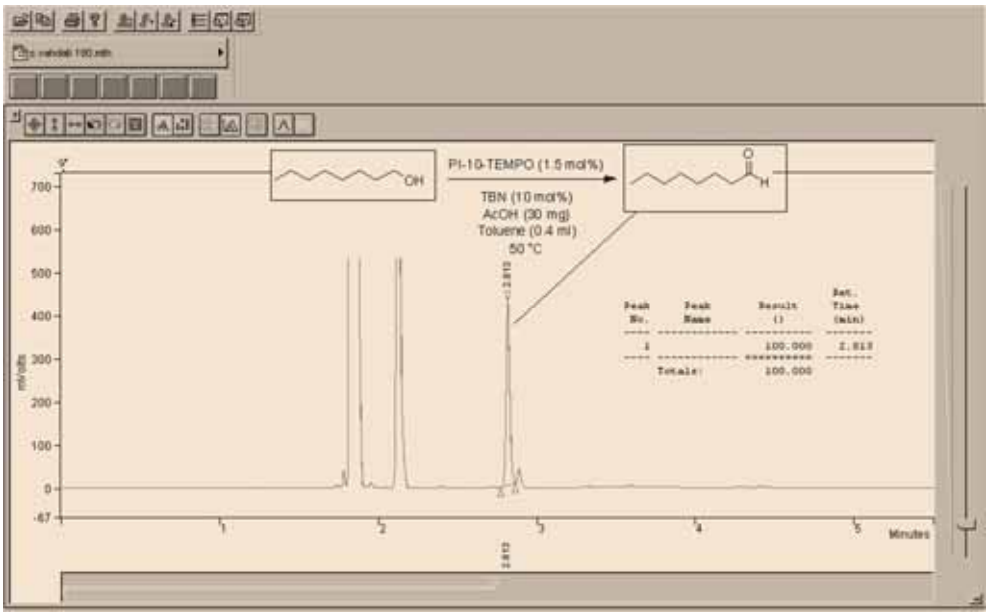


Blank of 1-Tetralol



1-Octanol





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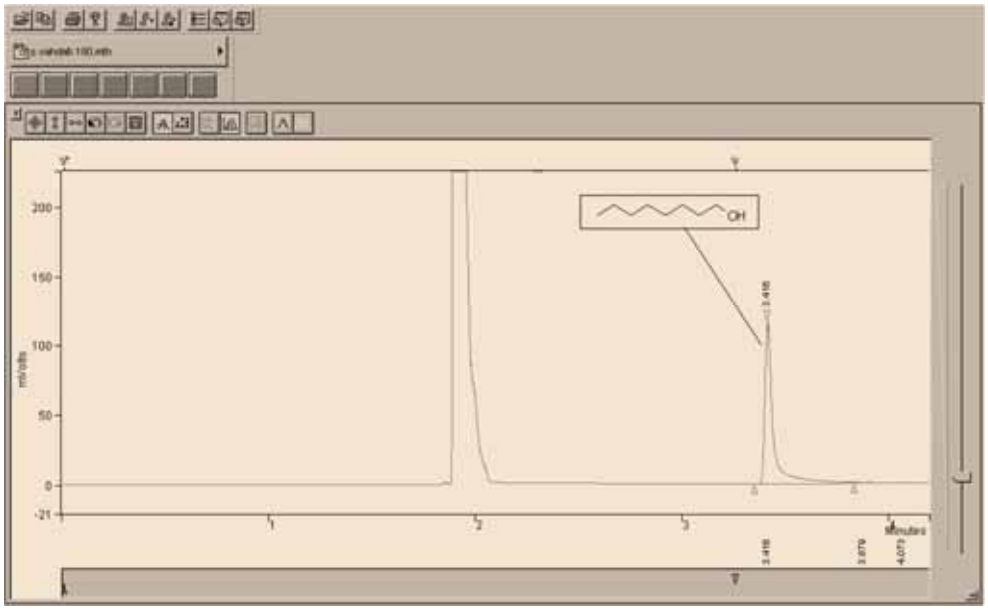
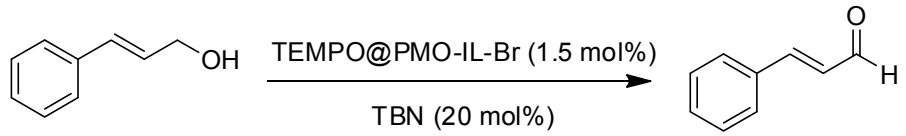
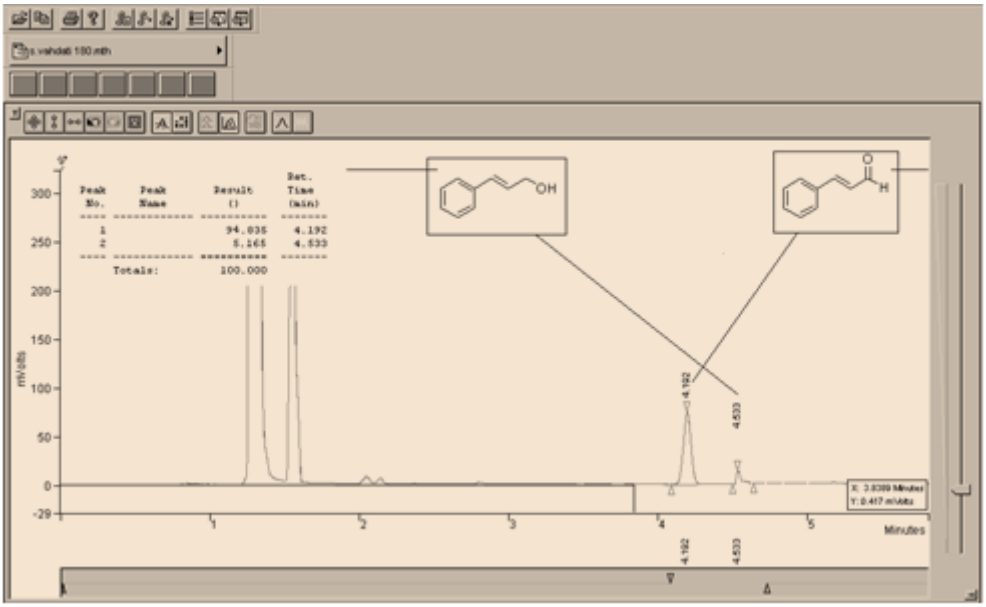
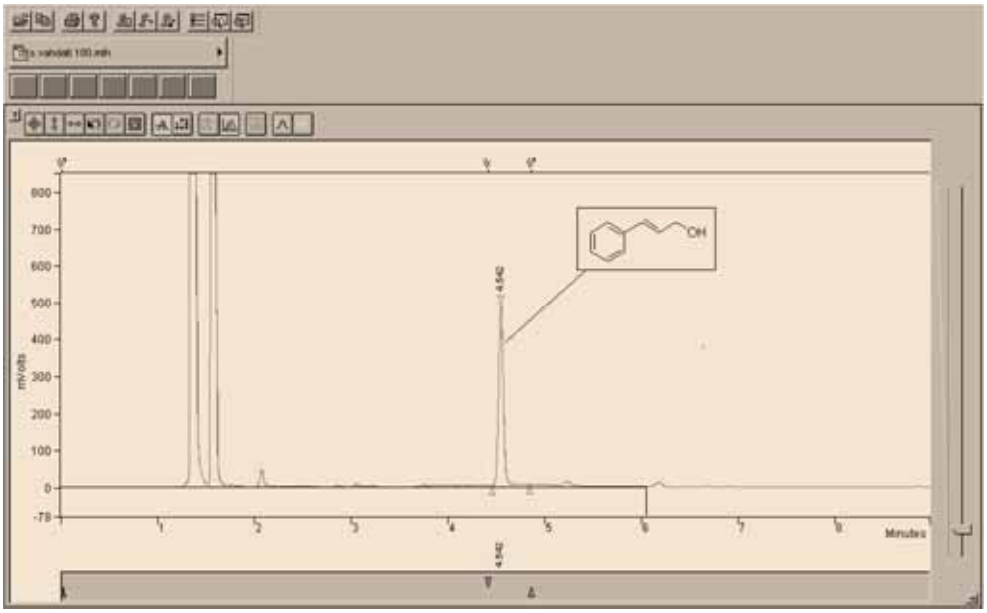


Cinnamylalcohol

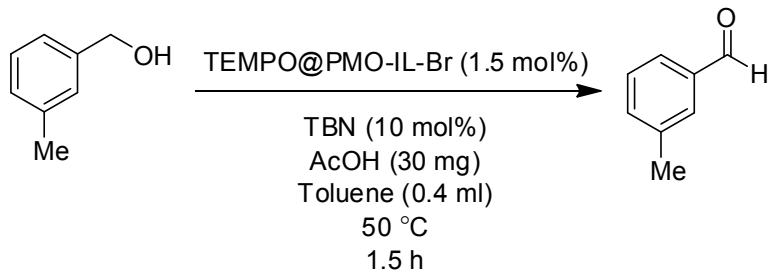


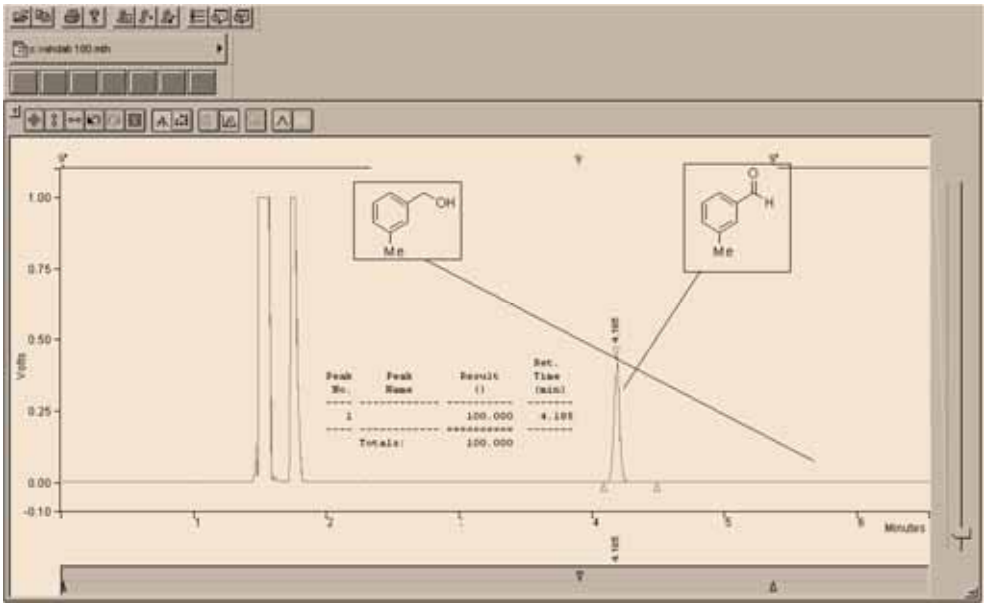


Blank of cinnamylalcohol

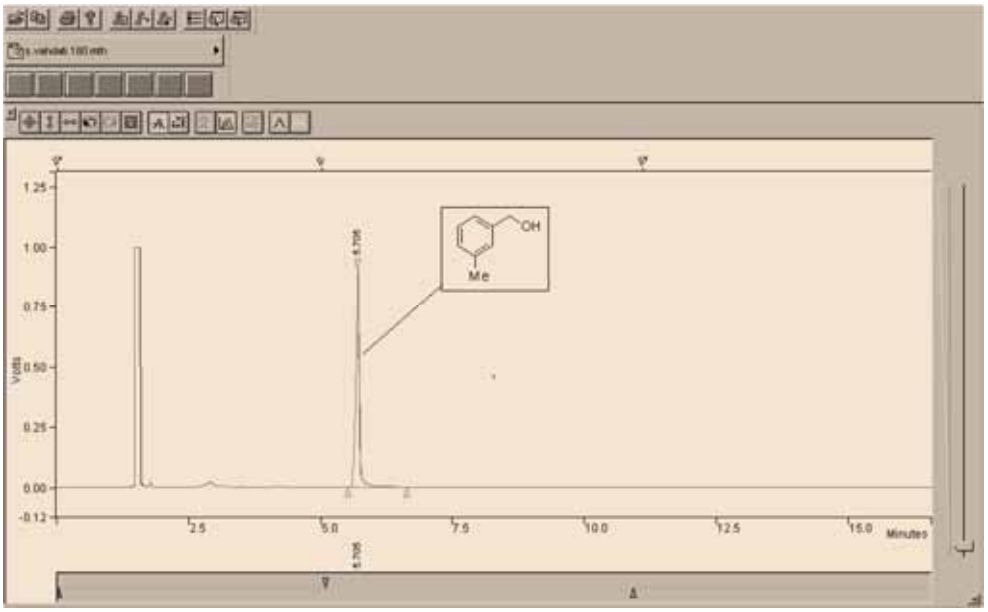


3-methylbenzylalcohol

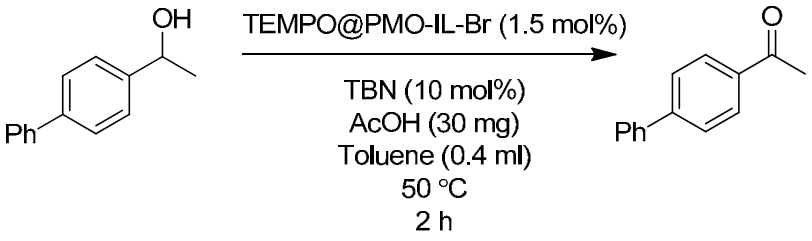


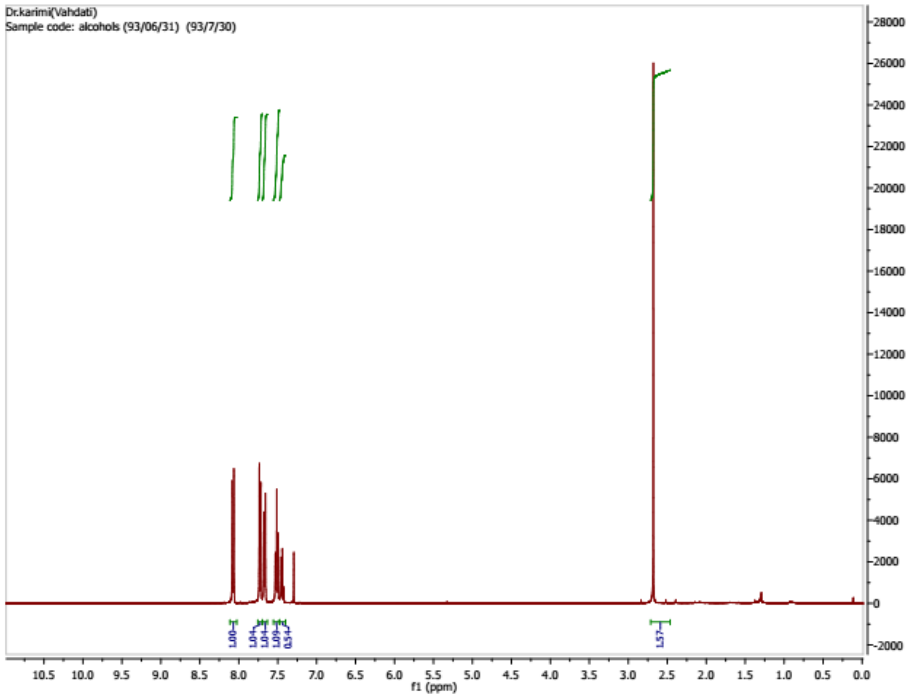


Blank of 3-methylbenzylalcohol



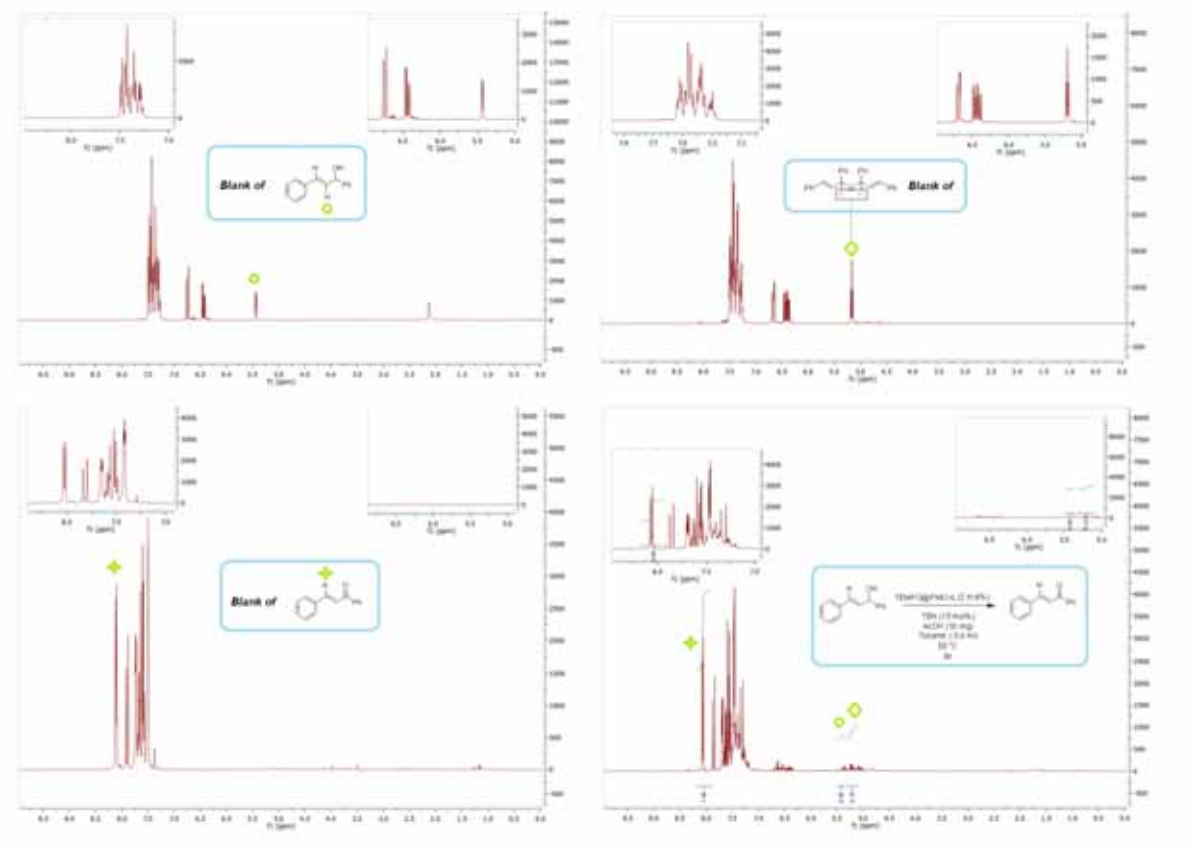
1-([1,1'-biphenyl]-4-yl)ethanol





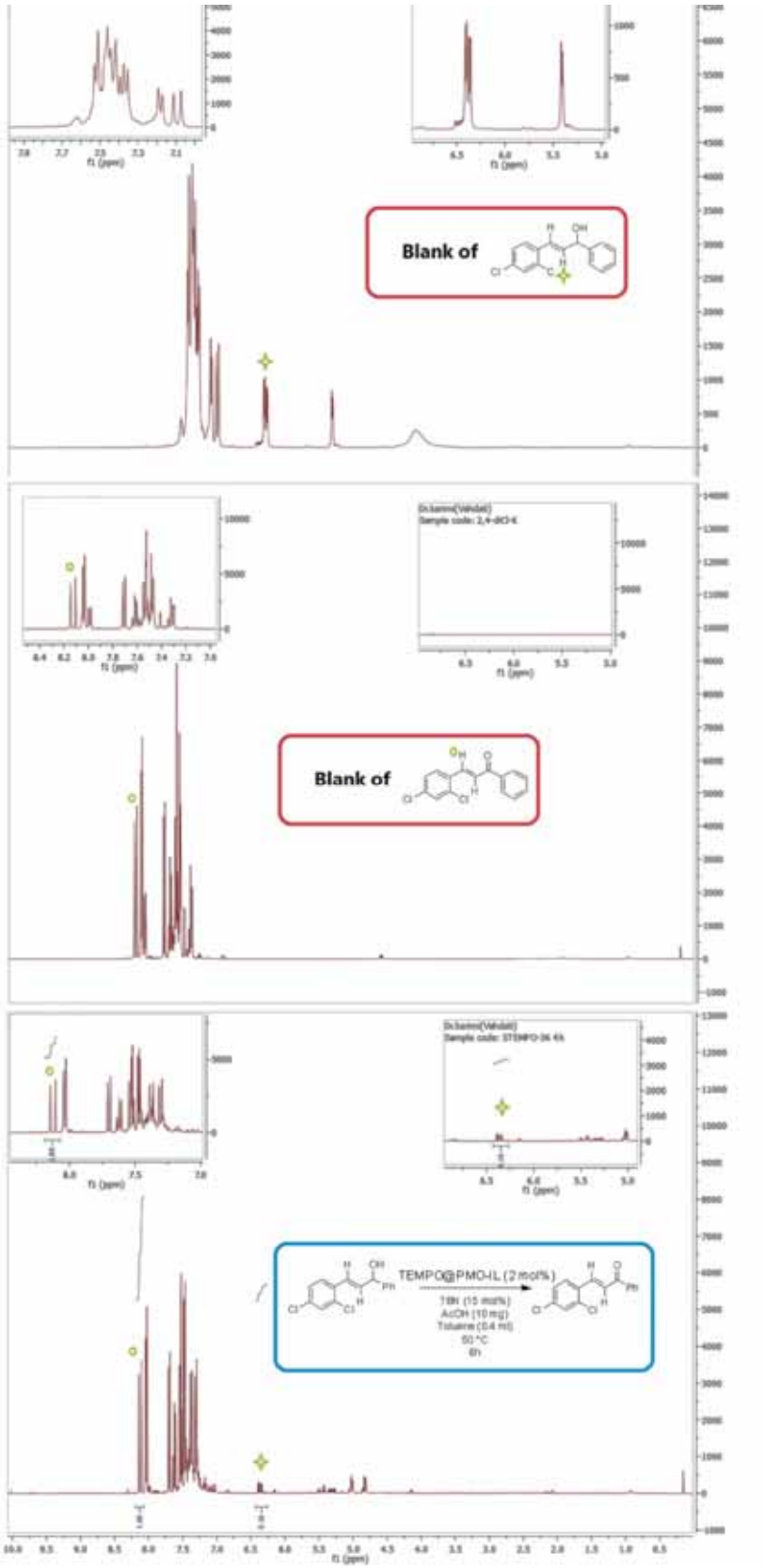
The [1]HNMR indicated oxidation of 1-([1,1'-biphenyl]-4-yl)ethanol was completed.

(E)-1,3-Diphenylprop-2-en-1-ol



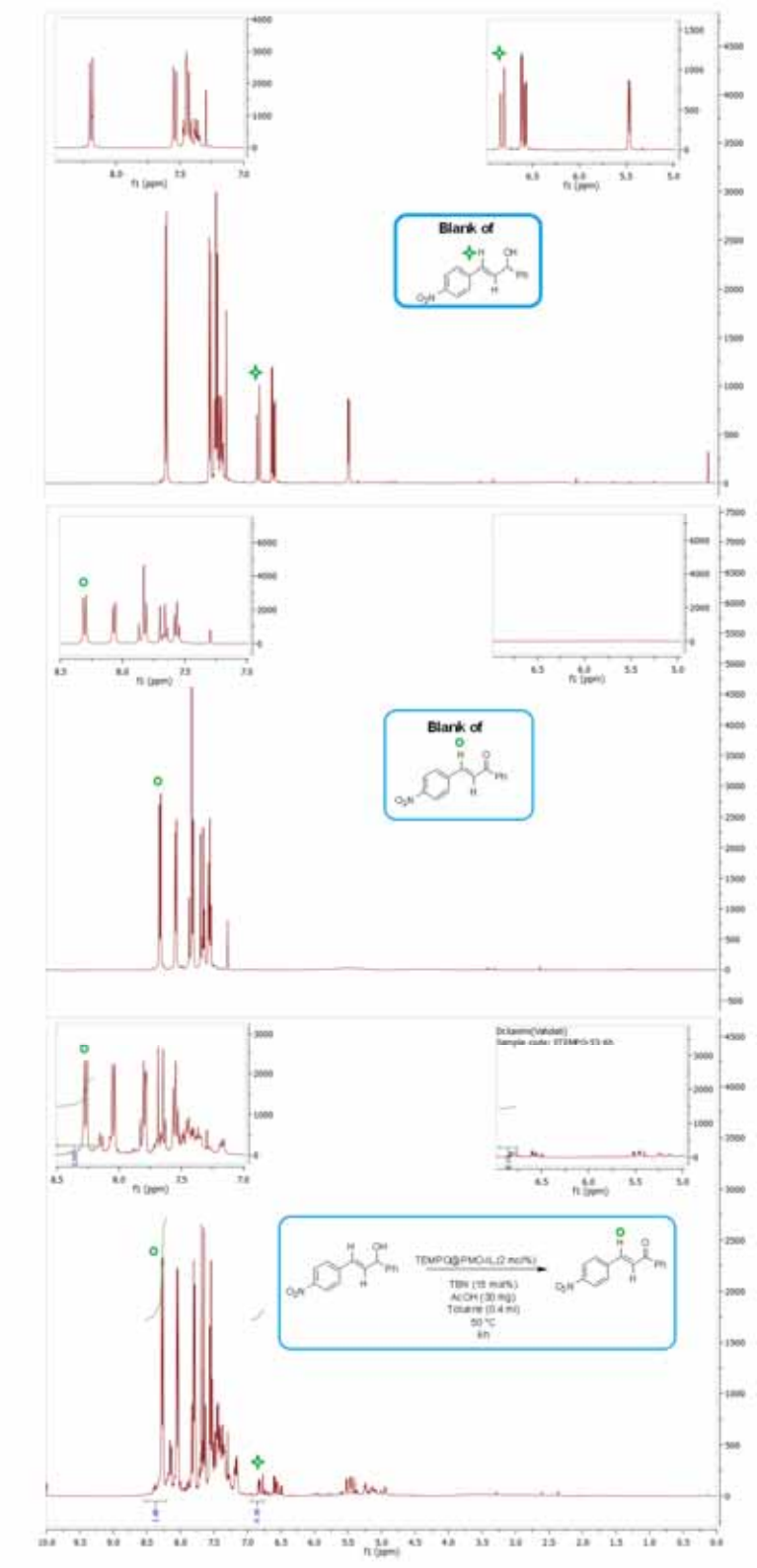
Yield = ($\int H_{ketone}$)/($\int H_{alcohol}+\int H_{ketone}+\int H_{ether}$)= (1)/(0.06+1+0.08)=87%

(E)-3-(2,4-dichlorophenyl)-1-phenylprop-2-en-1-ol



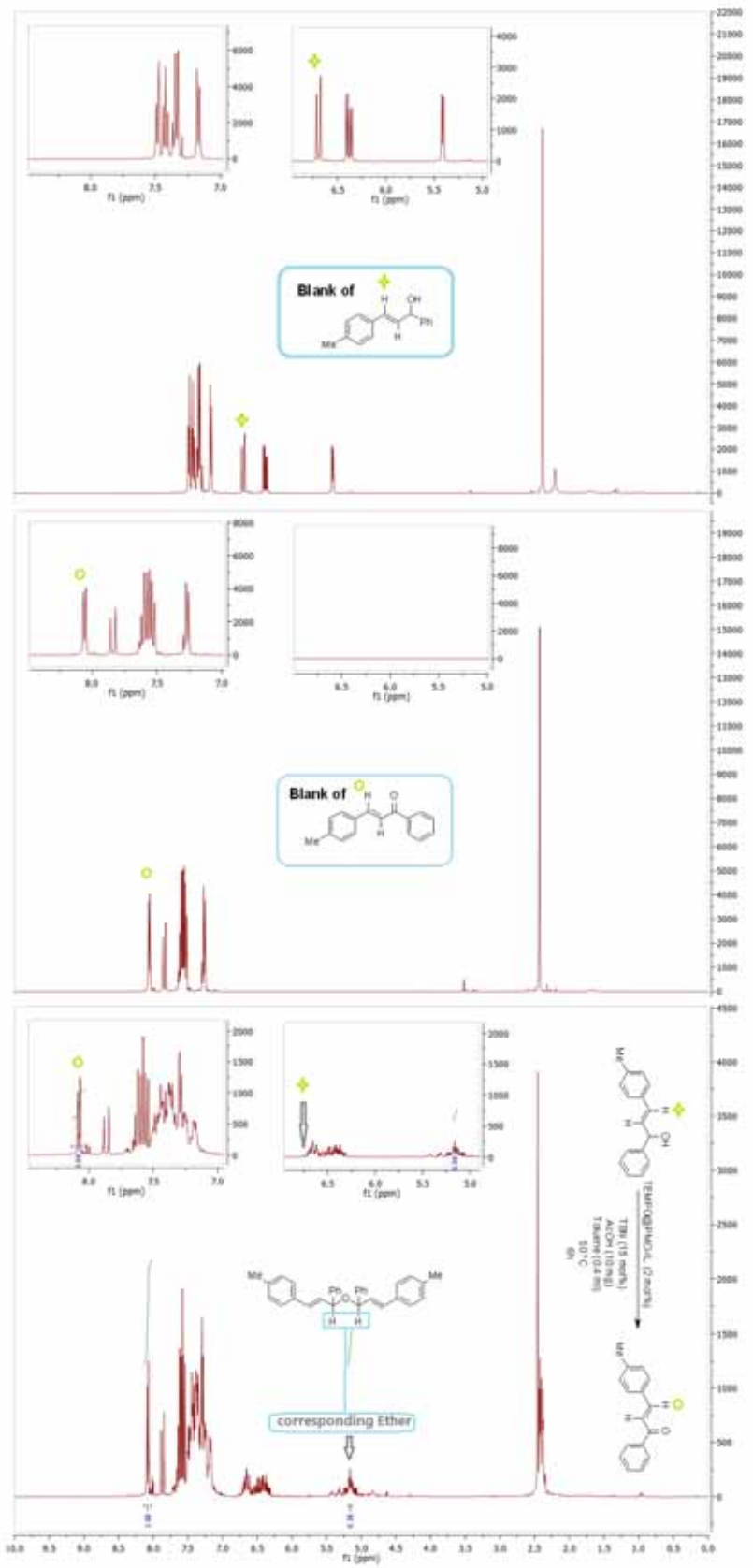
Yield = (∫H_{ketone})/(∫$H_{alcohol}$+∫H_{ketone}+∫H_{ether})=(1)/(1+.16+0)= 86%

(E)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-ol



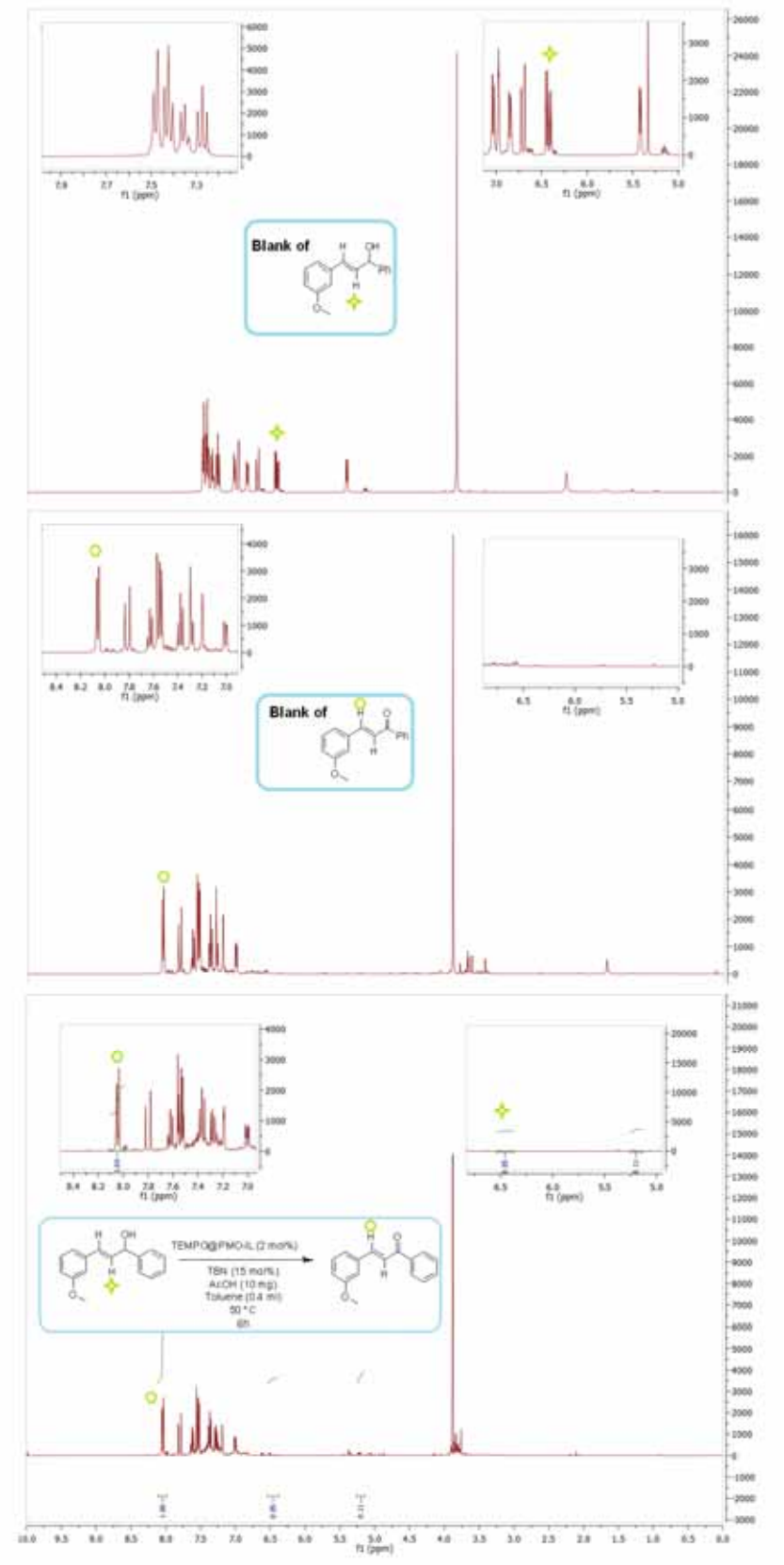
Yield = (∫H_{ketone})/(∫$H_{alcohol}$+∫H_{ketone}+∫H_{ether})=(1)/(1+0.1+0)= 90

(E)-3-(4-methylphenyl)-1-phenylprop-2-en-1-ol



Yield = (∫H_{ketone})/(∫$H_{alcohol}$+∫H_{ketone}+∫H_{ether})=(1)/(1+0+0.19)= 84%

(E)-3-(3-methoxyphenyl)-1-phenylprop-2-en-1-ol



Yield = (∫H_{ketone})/(∫$H_{alcohol}$+∫H_{ketone}+∫H_{ether})=(1)/(1+0.05+0.05)=90%