Polystyrene trimethyl ammonium chloride impregnated Rh(0) (Rh@PMe_3NCl) as a catalyst and methylating agent for esterification of alcohols through selective oxidation of methanol †

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Methods and materials

Reagents of high quality were purchased from Sigma Aldrich. Amberlite® IRA 900 (Chloride form) was purchased from Across Organics. Silica gel (60-120 mesh size) for column chromatography was procured from Sd Fine-chem Ltd. Commercial reagents and solvents were of analytical grade and were purified by standard procedures prior to use. Thin layer chromatography was performed using precoated silica gel plates 60 F254 (Merck) in UV light detector. GC-MS analysis was carried out on a Shimadzu (QP 2010) series GC-MS (Tokyo, Japan), equipped with a FID, AOC 5000 autosampler, DB-5MS capillary column (30 m × 0.25 mm i.e. with film thickness 0.25 μm). ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 300 spectrometer operating at 300 MHz (^{1}H) and 75 MHz (^{13}C)/ 600 MHz (^{1}H) and 150 MHz (^{13}C) respectively. Spectra were recorded at 25 °C in $CDCl_3$ [residual $CHCl_3$ (δ_H 7.26 ppm) or $CDCl_3$ (δ_C 77.00 ppm) and CD_3COCD_3 (δ_H 2.04 ppm) or CD_3COCD_3 (δ_C 28.9 and 206 ppm) as international standard] with TMS as internal standard. Chemical shifts were recorded in δ (ppm) relative to the TMS and $CDCl_3$ signal, coupling constants (J) are given in Hz and multiplicities of signals are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad singlet; qt, quartate. IR spectral data was recorded on IR Prestige-21 (CE) FTIR Shimadzu.

Preparation of Rh@PMe_3NCl catalyst

(a) Formation of catalytic quantity borohydride exchanged Amberlite resin

Amberlite® IRA 900 (Cl form) (Polystyrene trimethyl ammonium chloride resin, $[P(Me)_{3n}NCl_n]_m$) is a commercially available resin containing large number of repeating trimethyl ammonium chloride units , where the value of "n" and "m" is unknown. For simplification, $[P(Me)_{3n}NCl_n]_m$ has been represented as PMe_3NCl in the manuscript as well as in the supporting information.

The solution of 120 mg of $NaBH_4$ in 30 mL of water was added in 4 g of Amberlite® IRA 900 (Polystyrene trimethylammonium chloride, PMe_3NCl) (Across, BE) in 100 mL flask. The mixture was stirred for 4 h at room temperature. Then the borohydride exchanged resin was washed with water till pH became neutral and then with acetone to remove water from the solid surface. The borohydride exchanged resin beads were dried under reduced pressure.

(b) Procedure for preparation of Rh@PMe_3NCl

$RhCl_3.H_2O$ (10 mg) was added to a suspension of borohydride exchanged resin beads (PMe_3NCl) (1g) in a mixture of THF and DMF (1:1) (2 mL) and then the mixture was stirred at room-temperature to 80 ^oC for 1 h till the brown colour of solution was changed to blackish to colour less and simultaneously white solid beads were turned to blackish. After cooling, the beads were filtered through a cotton bed, washed with water and acetone, and dried under reduced pressure. The Rh@PMe_3NCl thus obtained could be useful in six catalytic reactions without significant loss of activity.

Charaterization data (HRTEM, single crystal analysis and Hg(0) test) for Rh@PMe_3NCl

(a) High resolution transmission electron micrograph (HRTEM) analysis of Rh@PMe_3NCl

The sample was applied on carbon coated copper grid (Electron Microscopy Science, CF 300-Cu, CARBON FILM, on 300 squre mesh copper grid) and analyzed for Transmission Electron Microscopy in Transmission 50 electron microscope JEOL 2100F.

(b) Single crystal image of Rh@PMe_3NCl by HRTEM

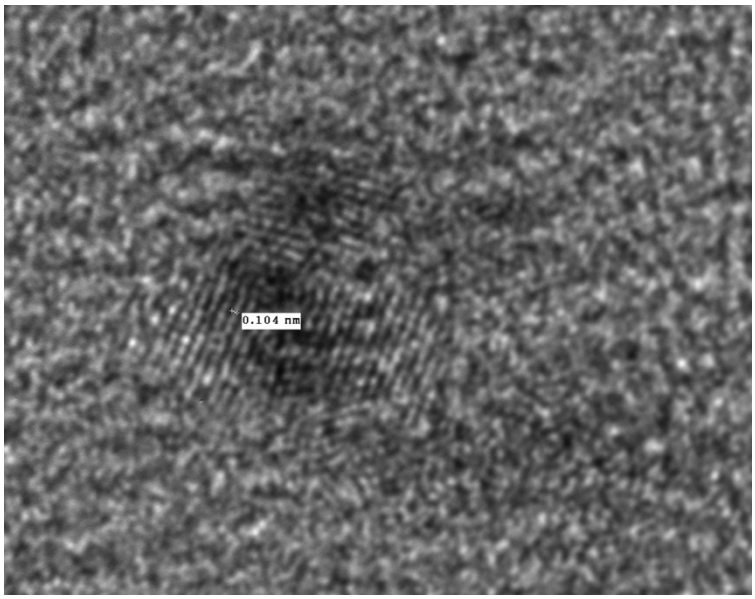


Fig. 1 HRTEM images confirmed the highly crystalline feature of rhodium nanoparticles with a crystalline spacing of 0.104 nm (manually calculated).

(c) Hg(0) poisoning test of Rh@PMe_3NCl for determining active Rh-species participating in the reaction

Hg(0) poisoning test was performed for the CDCM reactions of *p*-Me benzyl alcohol (**1a**) catalyzed by Rh-nanoparticles to identify the heterogeneity of present catalytic system. Hg(0) is well-known for its ability to poison metal(0) heterogeneous catalysts by either amalgam formation or being absorbed on

the surface to observe whether the rate of reaction gets affected or not by Hg(0).[1] Initially, Hg(0) (500 eqv.per Rh) was added to a mixture of Rh@PMe_3NCl (1eqv.), methanol (1.2 mL), Toluene (1.5 mL) and stirred at 100 ^oC for 2h. After that, *p*-Me benzyl alcohol, **1a** (50 eqv.) and NaO^tBu (150 eqv.) were added to this mixture and refluxed at 100 ^oC for 65 h. Our CDCM reaction was completely ceased by the addition of excess mercury indicating Rh(0) nanoparticles act as a heterogeneous catalyst and the presence of Rh(0) species in the system.

Recyclability test of Rh@PMe_3NCl

The recyclability experiment of Rh@PMe_3NCl was conducted on *p*-Me benzyl alcohol. After optimized conversion, the reaction mixture was filtered off through a cotton bed, washed several times with water and acetone properly, dried over rotary evaporator and the catalyst was recovered and reused for the same reaction. No significant loss of catalytic activity was observed up to six runs with negligible metal leaching.

ICP-AES study of the reaction mixture

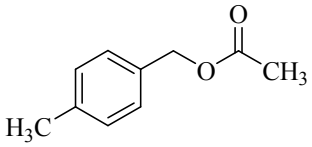
In the recyclability experiments, we have used 745 mg of Rh@PMe_3NCl (2 mol% Rh) for 200 mg of *p*-Me benzyl alcohol. 745 mg Rh@PMe_3NCl contains 3.37 mg rhodium metal as 10 mg $RhCl_3.H_2O$ was subjected to bind on 1 gm of borohydride exchanged polystyrene resin matrix. The reaction mixture was then digested with acidic solutions properly and analyzed for Inductively Coupled Plasma Spectrometry (ICP-AES). ICP-AES analysis carried out on ARCOS from M/S. Spectro, Germany. The results are shown below:

No. of cycles	Amount of Rh metal leached (ppm)	% age of Rh leached with respect to initial metal content
2nd cycle	0.031	0.04
4th cycle	0.075	0.11
6th cycle	0.336	0.49

ICP-AES analysis of the crude reaction mixture indicated that Rh-leaching into the products was very low.

Typical experimental procedure for oxidative "cross" esterifications using Rh@PMe_3NCl catalyst:

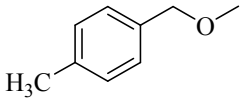
***p*-Me benzyl acetate (2a) (Table 1, entry 8)**



A mixture of *p*-Me benzyl alcohol (200mg, 1.63 mmol), NaO^{t}Bu (472 mg, 4.91 mmol), and Rh@PMe_3NCl (745 mg, 2 mol% Rh) were taken in an oven dried 50 mL round bottom flask. MeOH (1.2 mL) and toluene (1.5 mL) were added into the reaction mixture. The round bottom flask was then added with a condenser. The reaction was then heated at 100 ^{0}C for 65 h. After cooling to room temperature the reaction mixture was extracted with ethyl acetate (3x5 mL) and water (2mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by silica gel (mesh 60-120) chromatography-using (hexane: EtOAc = 98:2) as eluent to afford 171 mg (64%) of the title compound, *p*-Me benzyl acetate **2a**, as a colourless liquid. The same reaction was performed with CD_3OD to afford **2a** in 38% yield (main manuscript Scheme 3, (**b**)); ^{1}HNMR (600 MHz. $CDCl_3$) δ = 2.01 (s, 3H), 2.27 (s, 3H), 4.99 (s, 2H), 7.09 (d, 2H, *J* = 7.8 Hz), 7.17 (d, 2H, *J* = 7.8 Hz), ^{13}CNMR (150 MHz; $CDCl_3$) δ = 21.02, 21.16, 66.25, 128.42 (2C), 129.22 (2C), 132.90, 138.10, 170.93. IR (neat, cm^{-1}): 2955, 1738, 1518, 1225, 1182, 1020. GC-MS: m/z 164.

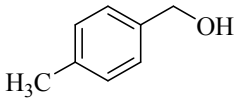
Synthesis and characterization data for the products of Scheme 2, Table 2 and 3, and of Scheme 4

1-(Methoxymethyl)-4-methylbenzene (2b) (Scheme 2, **(a))**



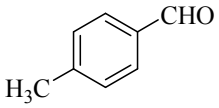
A mixture of *p*-Me benzyl alcohol (100mg, 0.818 mmol), NaO^{t}Bu (235 mg, 2.45 mmol), PMe_3NCl (500 mg) and 3mL of toluene were taken in an oven dried 50 mL round bottom flask and refluxed at 120 ^{0}C for 24h. The progress of reaction was monitored on TLC. After completion of reaction, the reaction was cooled, diluted with ethyl acetate and filtered through cotton bed. The combined organic layer was evaporated under reduced pressure and crude residue was purified by silica gel (mesh 60-120) column chromatography (hexane:EtOAc = 97:3) afforded **2b** as colorless liquid (45 mg, 40%).^{1}H NMR (600 MHz, $CDCl_3$) δ 2.17 (s, 3H), 3.37 (s, 3H), 4.42 (s, 2H), 7.17 (d, 2H, *J* = 9 Hz), 7.23 (d, 2H, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.12, 57.88, 74.55, 127.82 (2C), 129.04 (2C), 135.11, 137.31. GC-MS: m/z 136.

***p*-Me benzyl alcohol (1a) (**Scheme 2, **(c))**



A mixture of *p*-Me benzaldehyde (100mg, 0.83 mmol), NaO^{t}Bu (240 mg, 2.49 mmol), Rh@PMe_3NCl (379 mg, 2 mol% Rh), 1 mL of MeOH and 3mL of toluene were taken in an oven dried 50 mL round bottom flask and heated at 100 ^{0}C for 17h. The progress of reaction was monitored on TLC. After completion of reaction, the reaction was cooled, diluted with ethyl acetate and filtered through cotton bed. The combined organic layer was evaporated under reduced pressure and crude residue was purified by silica gel (mesh 60-120) column chromatography (hexane:EtOAc = 95:5) afforded **1a** as white solid (99 mg, 97%).^{1}H NMR (600 MHz, $CDCl_3$) δ 2.36 (s, 3H), 4.61 (s, 2H), 7.17 (d, 2H, *J* = 7.8 Hz), 7.24 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.06, 65.08, 127.05 (2C), 129.14 (2C), 137.25, 137.88.

***p*-Me benzaldehyde (1b) (**Scheme 2, **(d))**



A mixture of *p*-Me benzyl alcohol, **1a** (100mg, 0.818 mmol), NaO^{t}Bu (235 mg, 2.45 mmol), Rh@PMe_3NCl (372 mg, 2 mol% Rh) and 3mL of toluene were taken in an oven dried 50 mL round bottom flask and refluxed at 100 ^{0}C for 8h. The progress of reaction was monitored on TLC. After completion of reaction, the reaction was cooled, diluted with ethyl acetate and filtered through cotton bed. The combined organic layer was evaporated under reduced pressure and crude residue was purified by silica gel (mesh 60-120) column chromatography (hexane:EtOAc = 98:2) afforded **1b** as colorless liquid (85.5 mg, 87%).^{1}H NMR (600 MHz, $CDCl_3$) δ 2.43 (s, 3H), 7.32 (d, 2H, *J* = 7.8 Hz), 7.77 (d, 2H, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.88, 129.72 (2C), 129.86 (2C), 134.23, 145.56, 192.

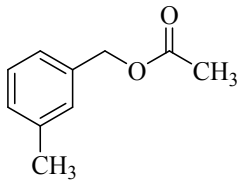
Formaldehyde (2c) (Scheme 2, **(e))**

A mixture of methanol (1.2 mL), NaO^{t}Bu (472 mg), Rh@PMe_3NCl (745 mg, 2 mol% Rh) and 1.5 mL of toluene were taken in an oven dried 50 mL round bottom flask and refluxed at 100 ^{0}C for 65h. The reaction mixture was then subjected to GC analysis. Formaldehyde **2c** was detected as shown in GC-spectra (given below).

***p*-Me benzyl acetate (2a) from acetaldehyde (**Scheme 2, **(f))**

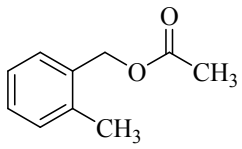
A mixture of *p*-Me benzyl alcohol (100mg, 0.818 mmol), acetaldehyde (108mg, 2.45 mmol), and 1.5 mL of toluene were taken in an oven dried 50 mL round bottom flask and stirred at 100 ^{0}C for 30 mins. A mixture of NaO^{t}Bu (235 mg, 2.45 mmol) and Rh@PMe_3NCl (372 mg, 2 mol% Rh) were then added to the reaction mixture and refluxed at 100 ^{o}C for 48 h. The progress of reaction was monitored on TLC. After completion of reaction, the reaction was cooled, diluted with ethyl acetate and filtered through cotton bed. The combined organic layer was evaporated under reduced pressure and crude residue was purified by silica gel (mesh 60-120) column chromatography (hexane:EtOAc = 98:2) afforded *p*-Me benzyl acetate as colorless liquid (94 mg, 70%). NMR, IR and GCMS-spectra are same as in **2a.**

***m*-Me benzyl acetate (2d) (Table 2, entry 1)**



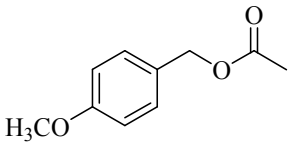
Prepared as described for *p*-Me benzyl alcohol, starting from **1d** (200 mg, 1.63 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2d** as colourless liquid (165 mg, 61%); ^{1}HNMR (300 MHz. $CDCl_3$) δ = 2.12 (s, 3H), 2.38 (s, 3H), 5.09 (s, 2H), 7.15-7.19 (m, 3H), 7.28 (s, 1H), ^{13}CNMR (75 MHz; $CDCl_3$) δ = 21.01, 21.32, 66.36, 125.32, 128.47, 129 (2C), 135.81, 138.27, 170.91. IR (neat, cm^{-1}): 2957, 1726, 1458, 1242, 1024. GC-MS: m/z 164.

***o*-Me benzyl acetate (2e) (Table 2, entry 2)**



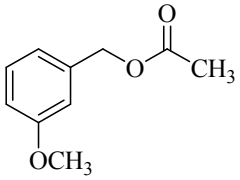
Prepared as described for *p*-Me benzyl alcohol, starting from **1e** (200 mg, 1.63 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2e** as colourless liquid (162 mg, 60%); ^{1}HNMR (300 MHz. $CDCl_3$) δ = 2.12 (s, 3H), 2.37 (s, 3H), 5.14 (s, 2H), 7.23-7.28 (m, 3H), 7.34 (d, 1H, *J* = 7.2 Hz), ^{13}CNMR (75 MHz; $CDCl_3$) δ = 18.85, 20.94, 64.70, 126.01, 128.53, 129.22, 130.35, 133.80, 136.96, 170.94. IR (neat, cm^{-1}): 2955, 1742, 1503, 1244, 1022. GC-MS: m/z 164.

***p*-MeO benzyl acetate (2f) (Table 2, entry 3)**



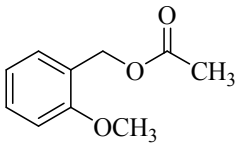
Prepared as described for *p*-Me benzyl alcohol, starting from **1f** (200 mg, 1.44 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2f** as colourless liquid (182 mg, 70%); ^{1}HNMR (600 MHz. $CDCl_3$) δ = 2.07 (s, 3H), 3.80 (s, 3H), 5.04 (s, 2H), 6.88 (d, 2H, *J* = 8.4 Hz), 7.29 (d, 2H, *J* = 8.4 Hz), ^{13}CNMR (150 MHz; $CDCl_3$) δ = 21.04, 55.27, 66.11, 113.95 (2C), 128.07, 130.10 (2C), 159.65, 170.96. IR (neat, cm^{-1}): 2955,1736, 1514, 1223, 1175, 1026. GC-MS: m/z 180.

***m*-MeO benzyl acetate (2g) (Table 2, entry 4)**



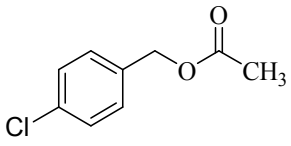
Prepared as described for *p*-Me benzyl alcohol, starting from **1g** (200 mg, 1.44 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2g** as colourless liquid (157 mg, 60%); ^{1}HNMR (600 MHz. $CDCl_3$) δ = 2.11 (s, 3H), 3.81 (s, 3H), 5.08 (s, 2H), 6.86 (d, 1H, *J* = 2.34 Hz), 6.89 (s, 1H), 6.93 (d, 1H, *J* = 7.5 Hz), 7.27 (t, 1H, *J* = 7.86 Hz), ^{13}CNMR (150 MHz; $CDCl_3$) δ = 20.93, 55.17, 66.10, 113.64, 113.68, 120.34, 129.57, 137.41, 159.71, 170.77. IR (neat, cm^{-1}): 2955, 1738, 1587, 1491, 1267, 1194, 1026. GC-MS: m/z 180.

***o*-MeO benzyl acetate (2h) (Table 2, entry 5)**



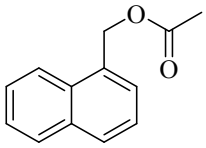
Prepared as described for *p*-Me benzyl alcohol, starting from **1h** (200 mg, 1.63 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2h** as colourless liquid (161 mg, 62%); ^{1}HNMR (600 MHz. $CDCl_3$) δ = 2.10 (s, 3H), 3.83 (s, 3H), 5.26 (s, 2H), 6.88 (d, 1H, *J* = 8.2 Hz), 6.95 (t, 1H, *J* = 7.44 Hz), 7.31 (q, 2H), ^{13}CNMR (150 MHz; $CDCl_3$) δ = 20.89, 55.24, 61.60, 110.31, 120.28, 124.08, 129.46, 129.61, 157.39, 170.85. IR (neat, cm^{-1}): 2941, 1732, 1495, 1223, 1177, 1024. GC-MS: m/z 180.

***p*-Cl benzyl acetate (2i) (Table 2, entry 6)**



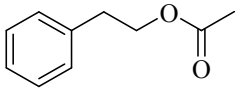
Prepared as described for *p*-Me benzyl alcohol, starting from **1i** (200 mg, 1.40 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2i** as colourless liquid (170 mg, 66%); ^{1}HNMR (600 MHz. $CDCl_3$) δ = 2.13 (s, 3H), 5.21 (s, 2H), 7.26 (d, 2H, *J* = 6 Hz), 7.39 (d, 2H, *J* = 5.4 Hz), ^{13}CNMR (150 MHz; $CDCl_3$) δ = 20.82, 63.85, 126.83, 129.46 (2C), 129.52 (2C), 133.64, 170.62. IR (neat, cm^{-1}): 2961, 1738, 1477, 1379, 1223, 1059, 1026. GC-MS: m/z 184.

(Naphthalen-5-yl)methyl acetate (2j) (Table 2, entry 7)



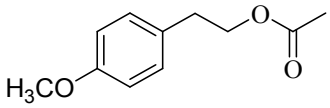
Prepared as described for *p*-Me benzyl alcohol, starting from **1j** (200 mg, 1.26 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2j** as colourless liquid (158 mg, 62%); ^{1}HNMR (300 MHz. $CDCl_3$) δ = 2.14 (s, 3H), 5.61 (s, 2H), 7.46-7.62 (m, 4H), 7.87-7.93 (m, 2H), 8.05 (d, 1H, *J* = 8.1 Hz), ^{13}CNMR (75 MHz; $CDCl_3$) δ = 20.92, 64.47, 123.45, 125.20, 125.87, 126.49, 127.41, 128.65, 129.22, 131.38, 131.54, 133.66, 170.85. IR (neat, cm^{-1}): 2957, 1732, 1512, 1364, 1219, 1020. GC-MS: m/z 200.

Phenethyl acetate (2k) (Table 3, entry 1)



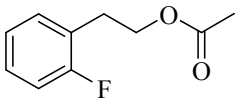
Prepared as described for *p*-Me benzyl alcohol, starting from **1k** (200 mg, 1.63 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2k** as colourless liquid (166 mg, 62%); ^{1}HNMR (600 MHz. $CDCl_3$) δ = 2.10 (s, 3H), 3.05 (t, 2H, *J* = 7.2Hz), 4.37 (t, 2H, *J* = 7.2 Hz), 7.36-7.45 (m, 5H), ^{13}CNMR (150 MHz; $CDCl_3$) δ = 19.92, 34.80, 64.51, 126.37, 128.38 (3C), 128.88, 138.26, 170.03. IR (neat, cm^{-1}): 2957, 1736, 1497, 1233, 1030. GC-MS: m/z 104 $[M-60]^{+}$.

***p*-MeO phenethyl acetate (2l) (Table 3, entry 2)**



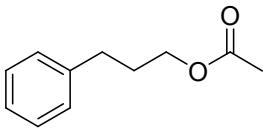
Prepared as described for *p*-Me benzyl alcohol, starting from **1l** (200 mg, 1.31 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2l** as colourless liquid (154 mg, 60%); ^{1}HNMR (300 MHz. $CDCl_3$) δ = 2.05 (s, 3H), 2.89 (t, 2H, *J* = 6.9 Hz), 3.81 (s, 3H), 4.25 (t, 2H, *J* = 7.2 Hz), 6.86 (d, 2H, *J* = 6.6 Hz), 7.15 (d, 2H, *J* = 8.4 Hz), ^{13}CNMR (150 MHz; CD_3COCD_3) δ = 19.92, 33.94, 54.56, 64.75, 113.79 (2C), 129.82 (2C),130.01, 158.50, 170.03. IR (neat, cm^{-1}): 2926, 1738, 1512, 1234, 1177, 1030. GC-MS: m/z 134 $[M-60]^+$.

2-F phenethyl acetate (2m) (Table 3, entry 3)



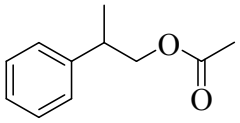
Prepared as described for *p*-Me benzyl alcohol, starting from **1m** (200 mg, 1.42 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2m** as colourless liquid (162 mg, 62%); ^{1}HNMR (600 MHz. $CDCl_3$) δ = 2.02 (s, 3H), 2.97 (t, 2H, *J* = 6.6 Hz), 4.28 (t, 2H, *J* = 7.2 Hz), 7.02-7.08 (m, 2H), 7.19-7.22 (m, 2H), ^{13}CNMR (150 MHz; $CDCl_3$) δ = 20.81, 28.46, 63.58, 115.35, 124.01, 124.77, 128.38, 131.10, 160.47, 162.10, 170.87. IR (neat, cm^{-1}): 2928, 1738, 1587, 1227, 1179, 1038. GC-MS: m/z 122 $[M-60]^+$.

3-phenylpropyl acetate (2n) (Table 3, entry 4)



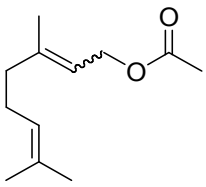
Prepared as described for *p*-Me benzyl alcohol, starting from **1n** (200 mg, 1.46 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 95:5) **2n** as colourless liquid (158 mg, 60%); ^{1}HNMR (300 MHz. $CDCl_3$) δ = 1.86-1.93 (m, 2H), 1.97 (s, 3H), 2.61 (t, 2H, *J* = 7.5 Hz), 4.01 (t, 2H, *J* = 6.3 Hz), 7.09-7.23 (m, 5H), ^{13}CNMR (75 MHz; $CDCl_3$) δ = 20.91, 30.14, 32.14, 63.81, 125.97, 128.35 (2C), 128.40 (2C), 141.17, 171.14. IR (neat, cm^{-1}): 2928, 1736, 1497, 1234, 1034. GC-MS: m/z 118 $[M-60]^+$.

2-phenylpropyl acetate (2o) (Table 3, entry 5)



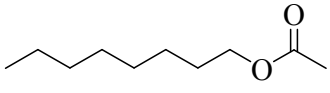
Prepared as described for *p*-Me benzyl alcohol, starting from **1o** (200 mg, 1.46 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2o** as colourless liquid (169 mg, 65%); ^{1}HNMR (600 MHz. $CDCl_3$) δ = 1.31 (d, 3H, *J* = 7.2 Hz), 2.02 (s, 3H), 3.10-3.11 (m, 1H), 4.13-4.22 (m, 2H), 7.23-7.25 (m, 5H), ^{13}CNMR (150 MHz; $CDCl_3$) δ = 17.99, 20.83, 69.30, 126.60, 127.19 (2C), 128.40 (2C), 143.09, 170.98. IR (neat, cm^{-1}): 2934, 1738, 1495, 1227, 1034. GC-MS: m/z 118 $[M-60]^+$.

3,7-dimethylocta-2,6-dienyl acetate (2p) (Table 3, entry 6)



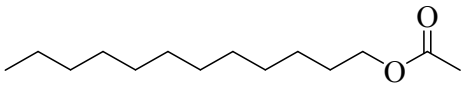
Prepared as described for *p*-Me benzyl alcohol, starting from **1p** (200 mg, 1.29 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2p** as colourless liquid (170 mg, 67%); ^{1}HNMR (300 MHz. $CDCl_3$) δ = 1.60-1.70 (m, 9H), 2.05-2.11 (m, 7H), 4.58 (d, 1H, *J* = 6.9 Hz), 5.08 (s, 1H), 5.34 (m, 1H), ^{13}CNMR (75 MHz; $CDCl_3$) δ = 16.38, 17.61, 20.98, 25.60, 26.23, 39.47, 61.34, 118.19, 123.68, 131.75, 142.19, 171.06. IR (neat, cm^{-1}): 2926, 1740, 1450, 1377, 1227. GC-MS: m/z 136 $[M-60]^+$.

Octyl acetate (2q) (Table 3, entry 7)



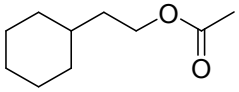
Prepared as described for *p*-Me benzyl alcohol, starting from **1q** (200 mg, 1.53 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2q** as colourless liquid (174 mg, 66%); ^{1}HNMR (600 MHz. $CDCl_3$) δ = 0.86-0.96 (m, 3H), 1.05-1.27 (m, 10 H), 1.57-1.61 (m, 2H), 2.03 (s, 3H), 4.03 (t, 2H, *J* = 6.6 Hz), ^{13}CNMR (150 MHz; $CDCl_3$) δ = 14.01, 20.93, 22.59, 25.88, 28.58, 29.18, 31.74, 64.60, 171.15. IR (neat, cm^{-1}): 2926, 1742, 1231, 1038. GC-MS: m/z 112 $[M-60]^+$.

Dodecyl acetate (2r) (Table 3, entry 8)



Prepared as described for *p*-Me benzyl alcohol, starting from **1r** (200 mg, 1.07 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2r** as colourless liquid (162 mg, 65%); ^{1}HNMR (600 MHz. $CDCl_3$) δ = 0.86 (t, 3H, *J* = 7.2 Hz), 1.24-1.28 (m, 17 H), 1.60 (m, 2H), 2.03 (s, 3H), 4.03 (t, 2H, *J* = 6.9 Hz), ^{13}CNMR (150 MHz; $CDCl_3$) δ = 14.02, 20.89, 22.63, 25.86, 28.55, 29.21, 29.30, 29.52, 29.58 (3C), 31.86, 64.57, 171.11. IR (neat, cm^{-1}): 2922, 1742, 1233, 1038. GC-MS: m/z 168 $[M-60]^+$.

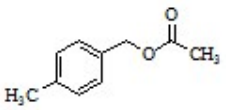
2-Cyclohexylethyl acetate (2s) (Scheme 4**)**

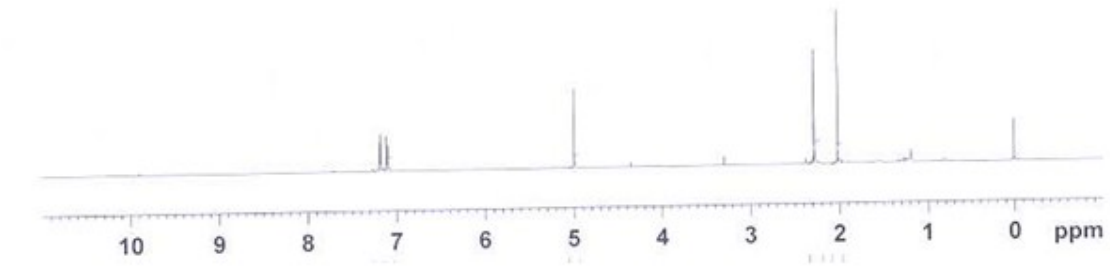


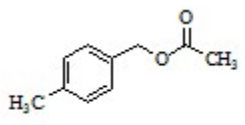
Prepared as described for *p*-Me benzyl alcohol, starting from **1s** (200 mg, 1.55 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2s** as colourless liquid (178 mg, 67%); ^{1}HNMR (600 MHz. $CDCl_3$) δ = 1.11-1.16 (m, 6H), 1.40-1.44 (m, 2H), 1.59-1.64 (m, 5H), 1.93 (s, 3H), 3.99 (t, 2H, *J* = 6.6 Hz), ^{13}CNMR (150 MHz; $CDCl_3$) δ = 20.70, 25.99 (2C), 26.28, 32.96 (2C), 34.36, 35.80, 62.45, 170.77. IR (neat, cm^{-1}): 2922, 2851, 1740, 1449, 1233. GC-MS: m/z 110 $[M-60]^+$.

^{1}H, ^{13}C NMR, and GC-MS Spectra for the products of Table 1, Scheme 2, Table 2 and 3, and of Scheme 4

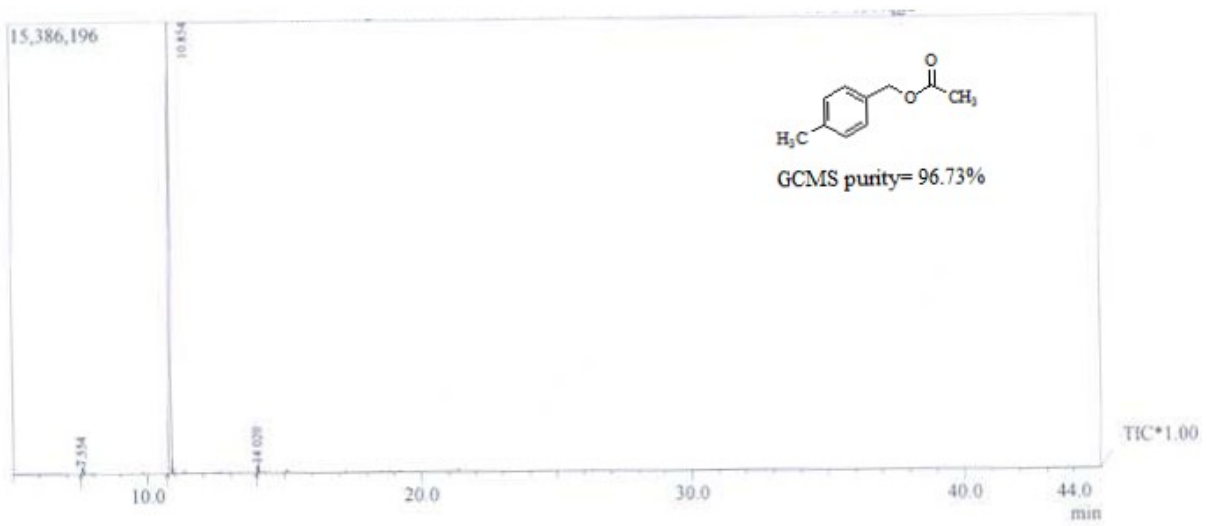
***p*-Me benzyl acetate (2a) (Table 1, entry 8)**

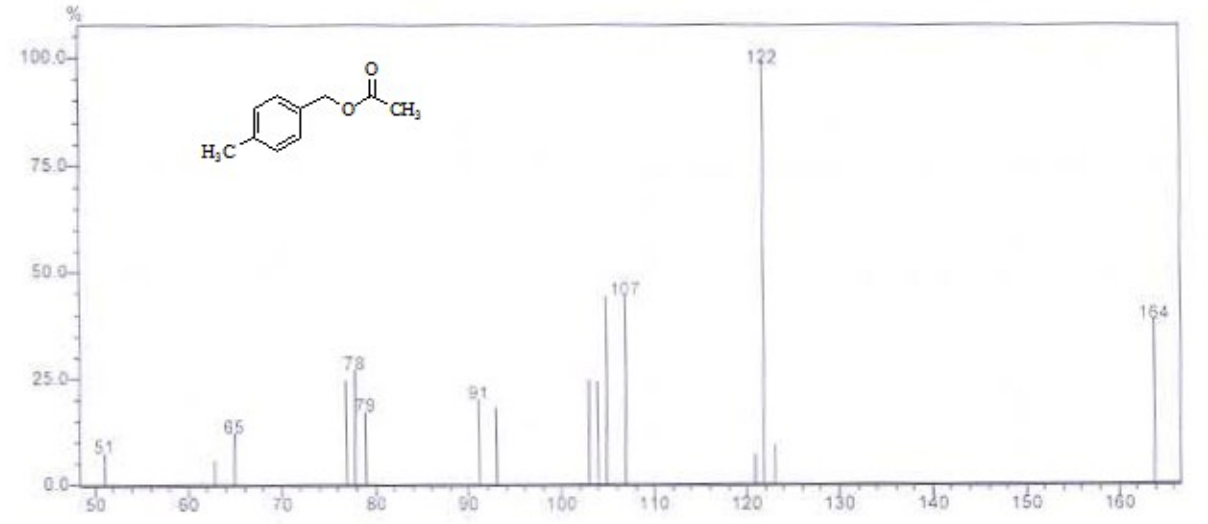

O
O
CH3
H3C


10
9
8
7
6
5
4
3
2
1
0
ppm

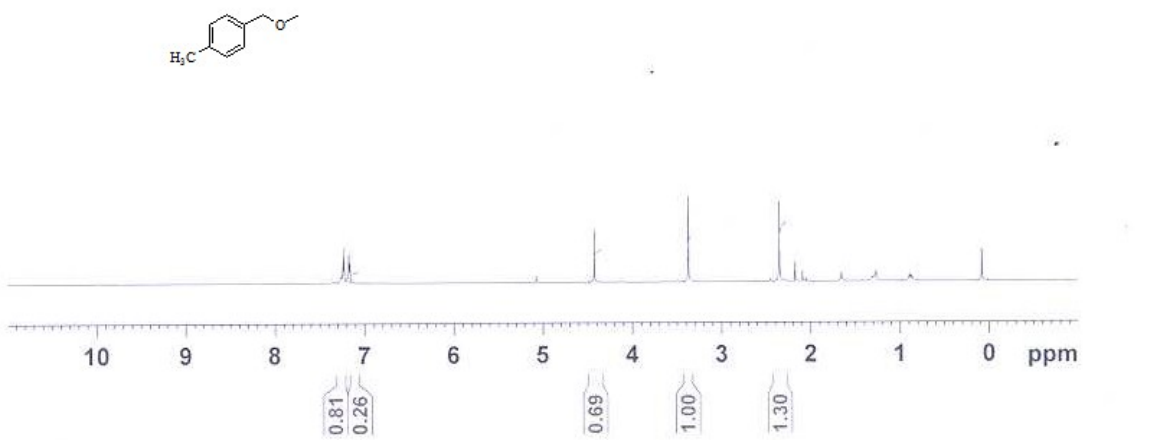

O
O
CH3
H3C

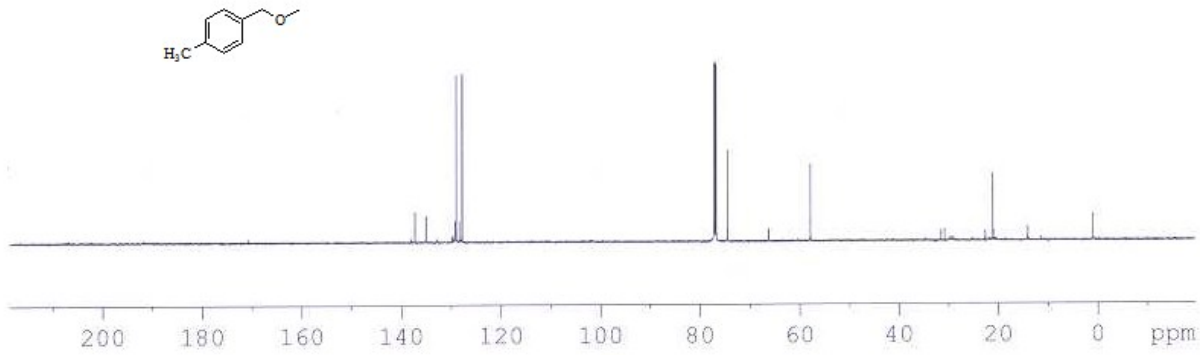
200
180
160
140
120
100
80
60
40
20
0
ppm

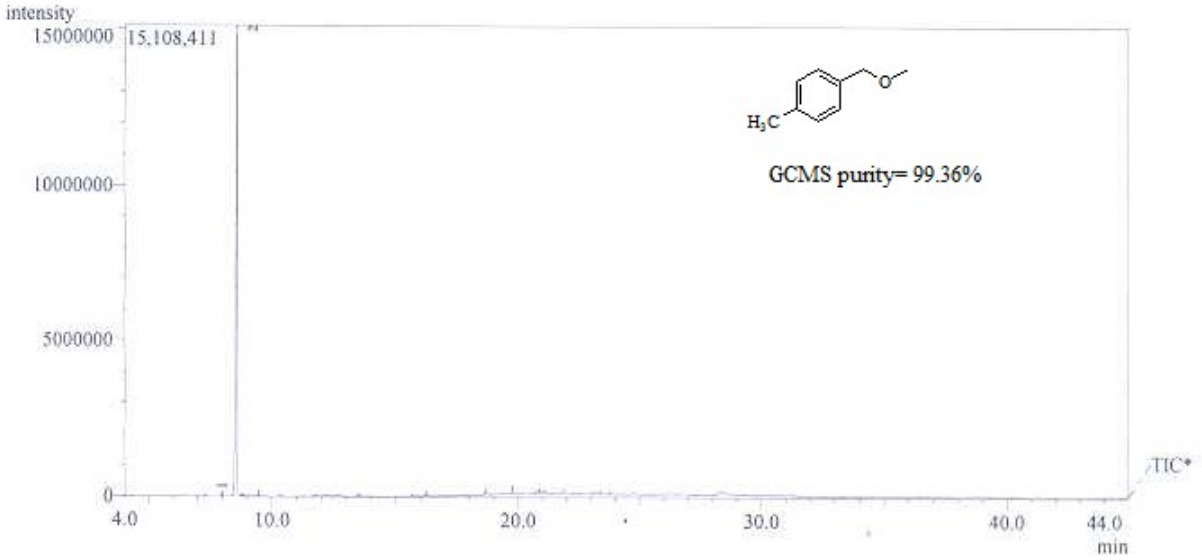


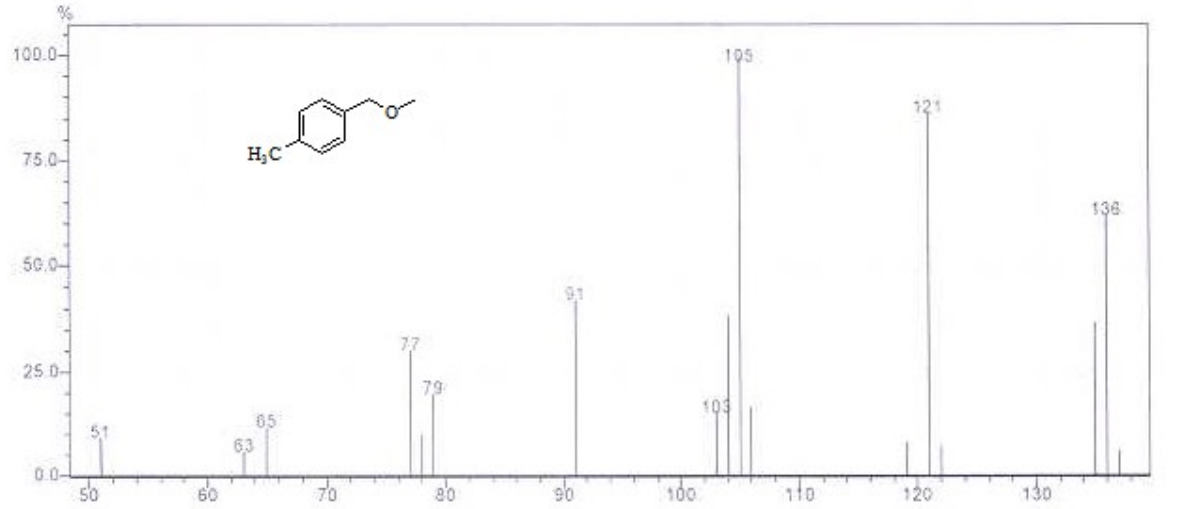


1-(methoxymethyl)-4-methylbenzene (2b) (Scheme 2, **(a))**

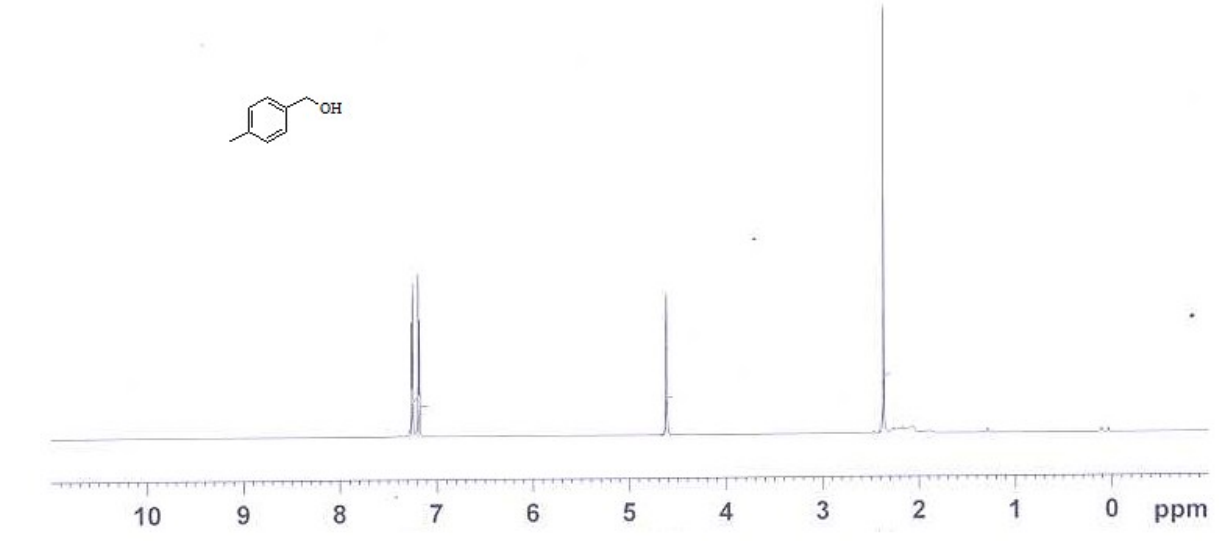

10
9
8
7
6
5
4
3
2
1
0
ppm
0.81
0.26
0.69
1.00
1.30

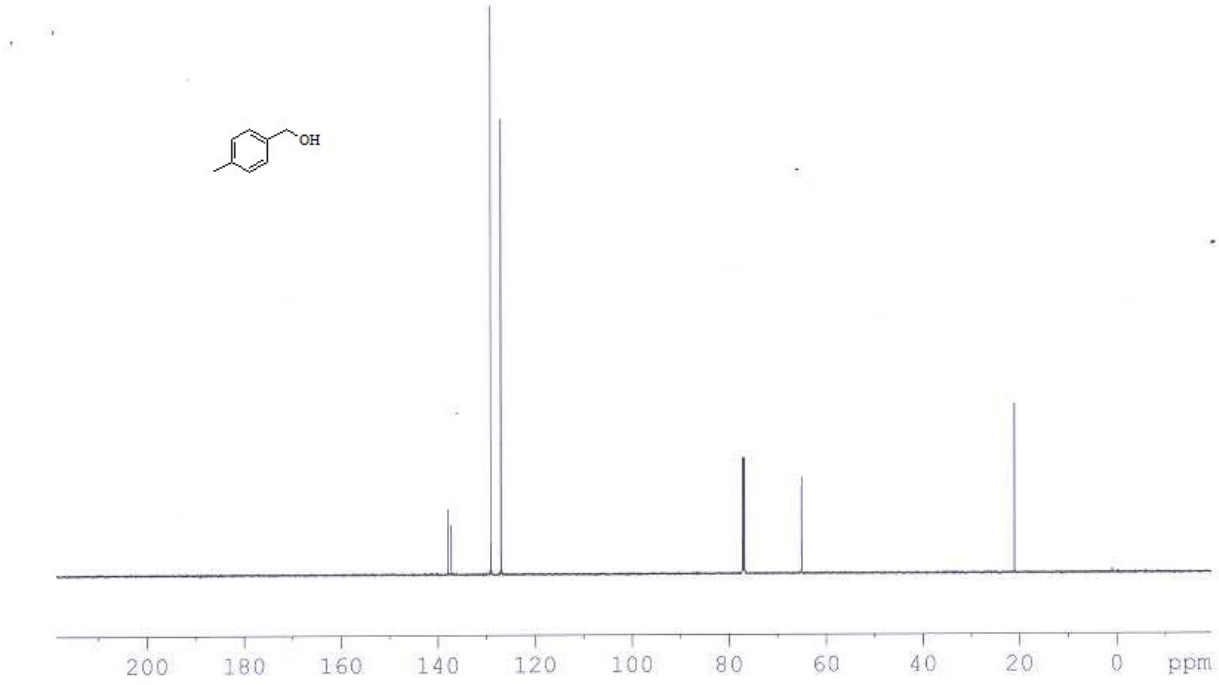

200
180
160
140
120
100
80
60
40
20
0
ppm



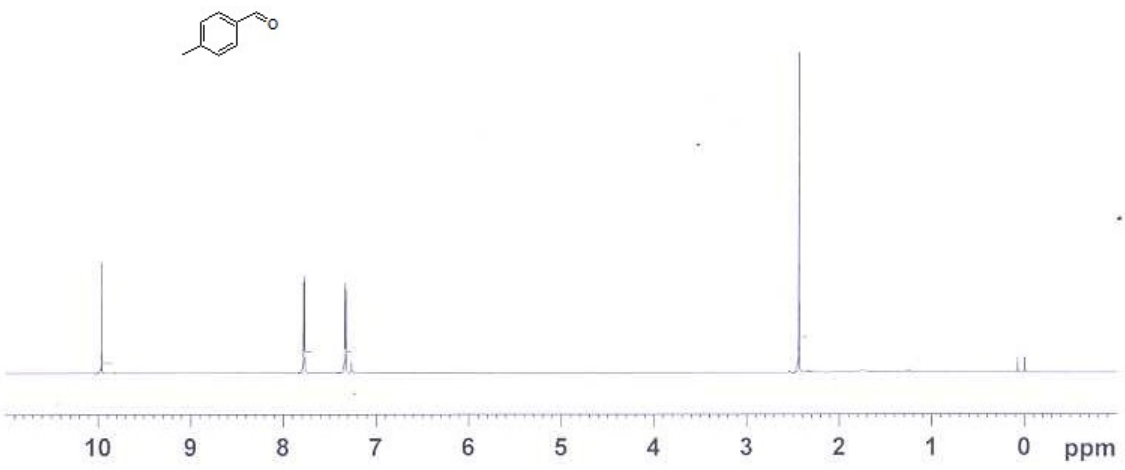


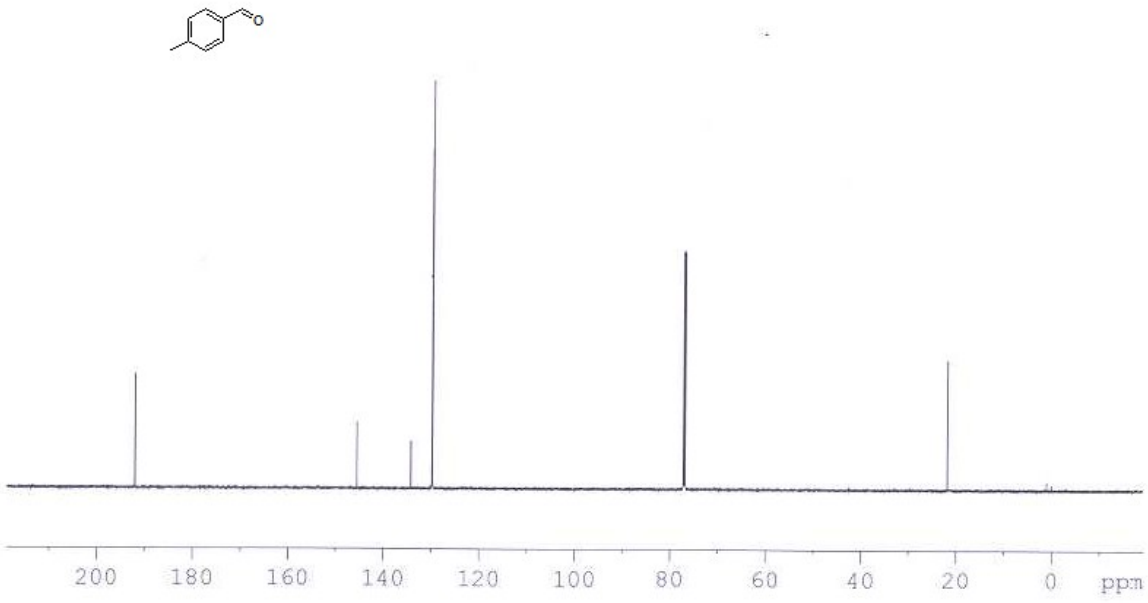
***p*-Me benzyl alcohol (1a) (**Scheme 2, **(c))**



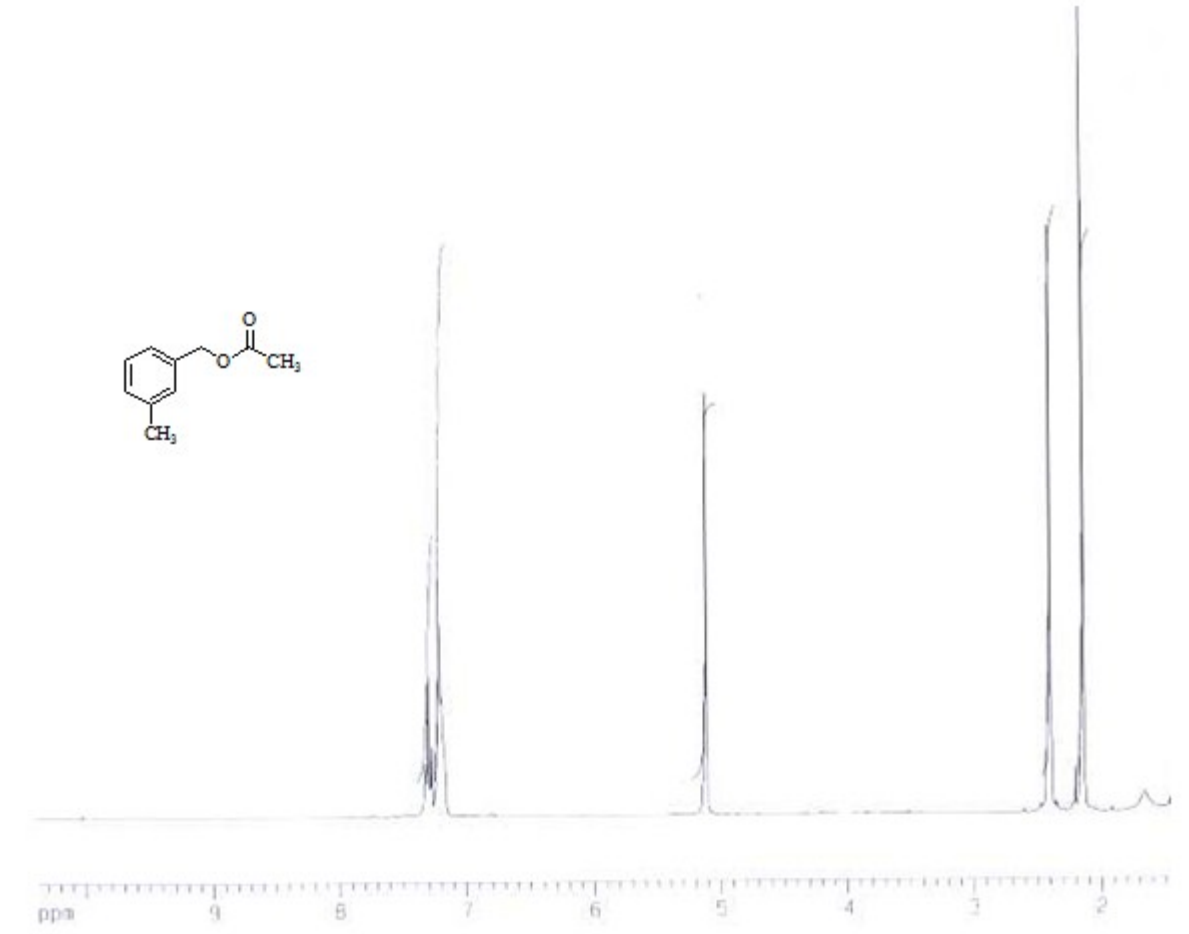


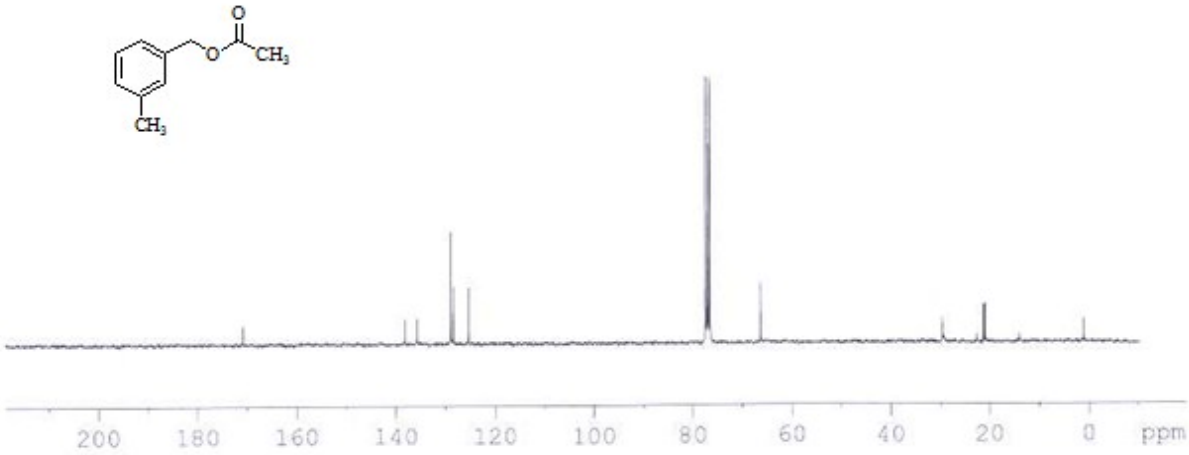
***p*-Me benzaldehyde (1b) (**Scheme 2, **(d))**

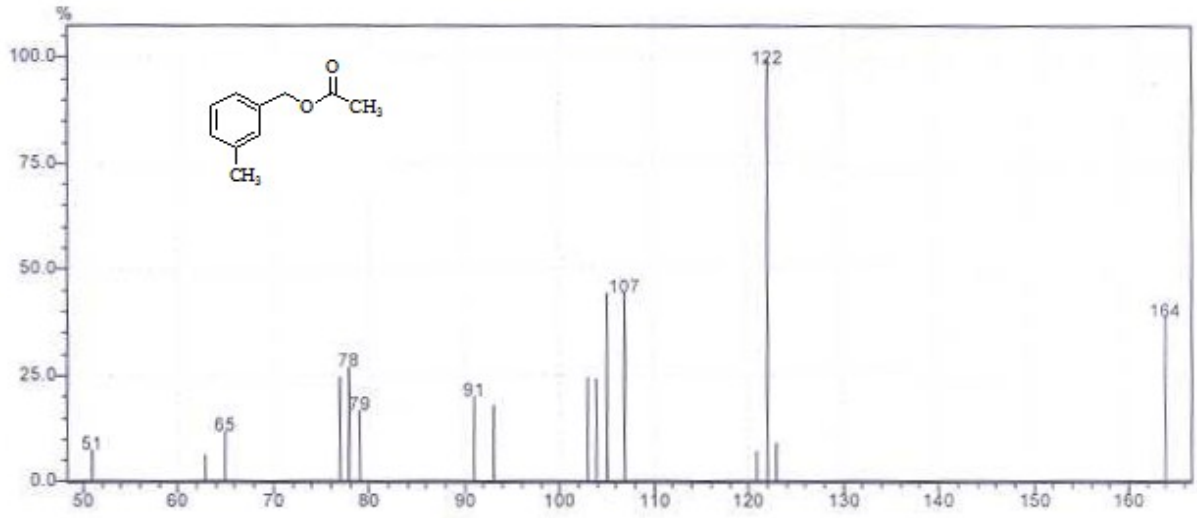




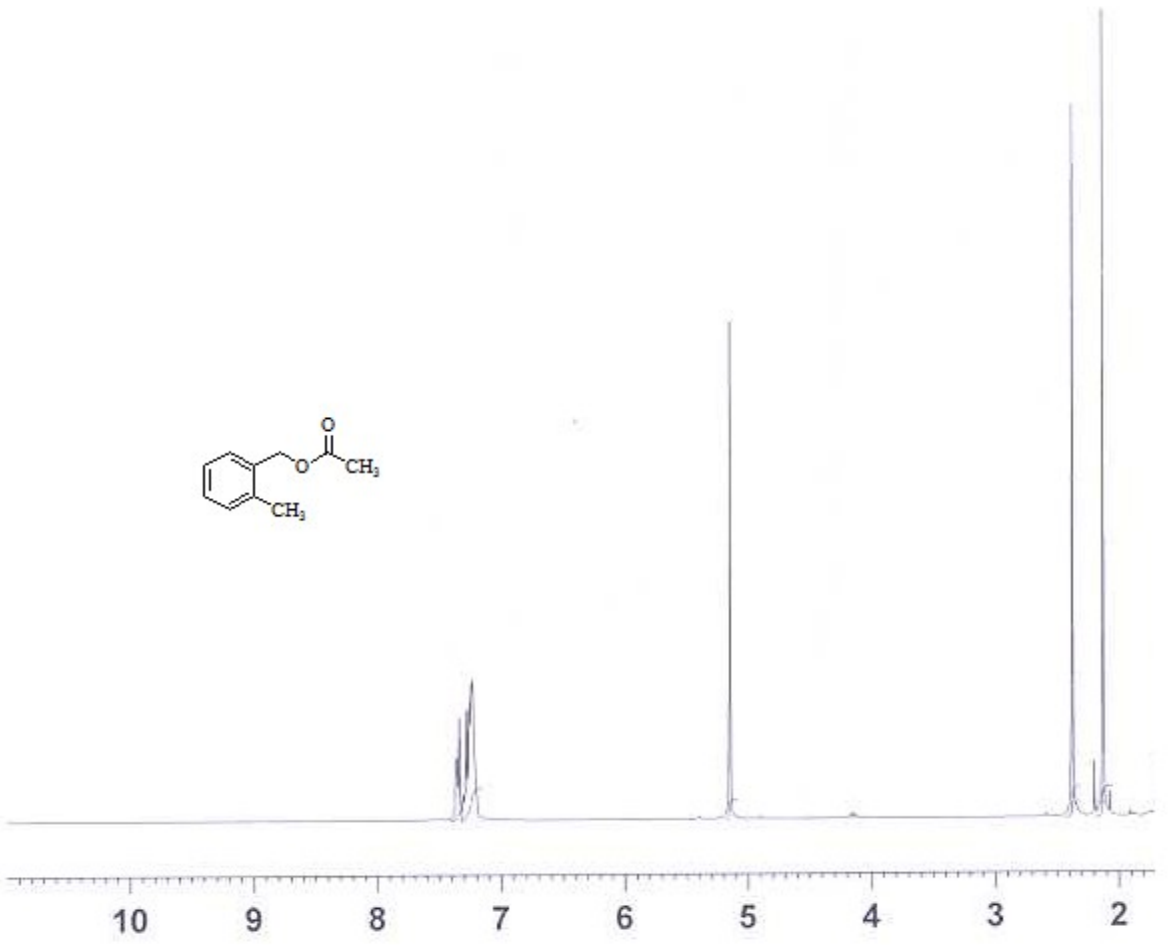
***m*-Me benzyl acetate (2d) (Table 2, entry 1)**

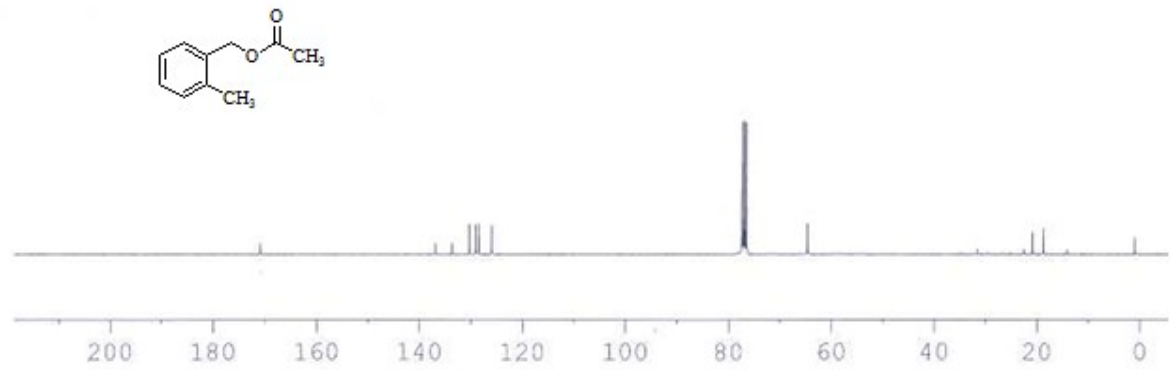

O
O
CH3
CH3
ppm
9
8
7
6
5
4
3
2

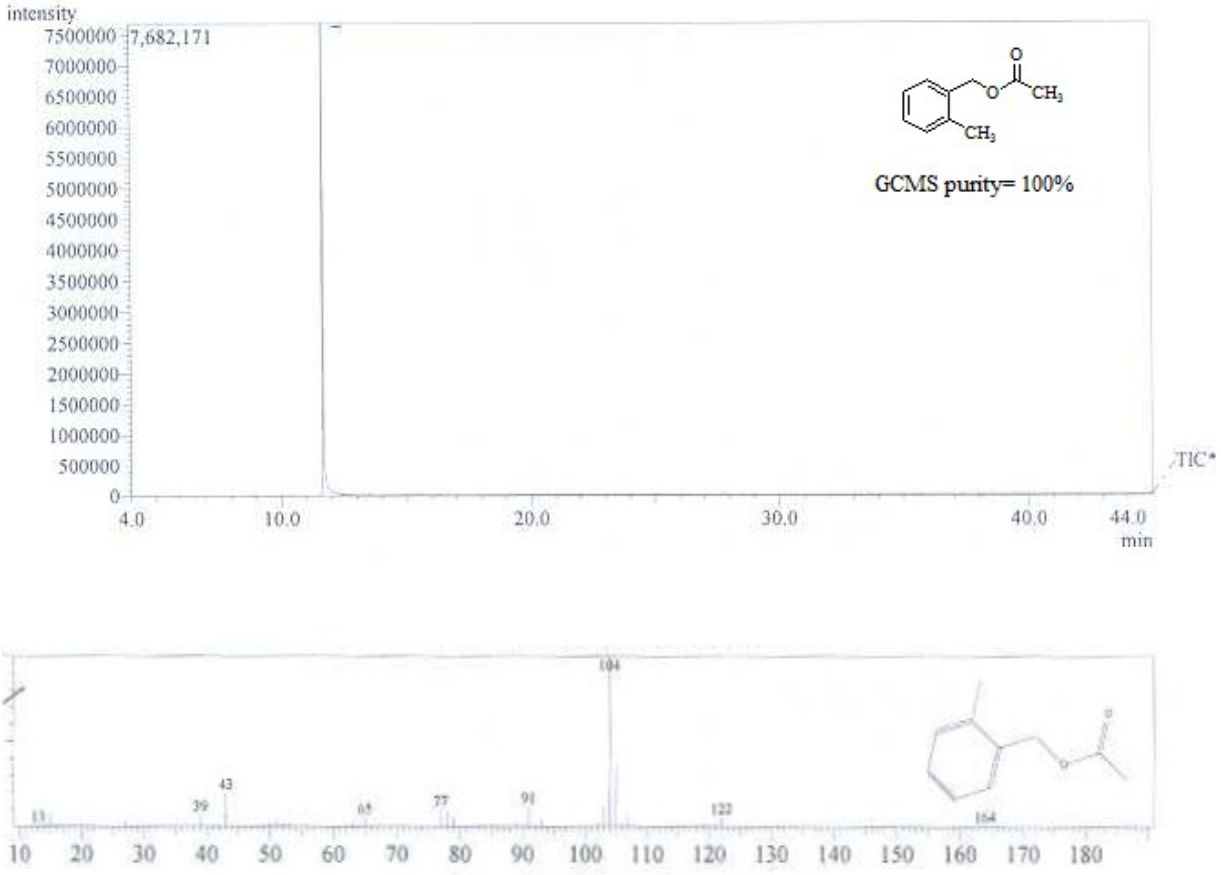

O
O
CH3
CH3
200
180
160
140
120
100
80
60
40
20
0
ppm



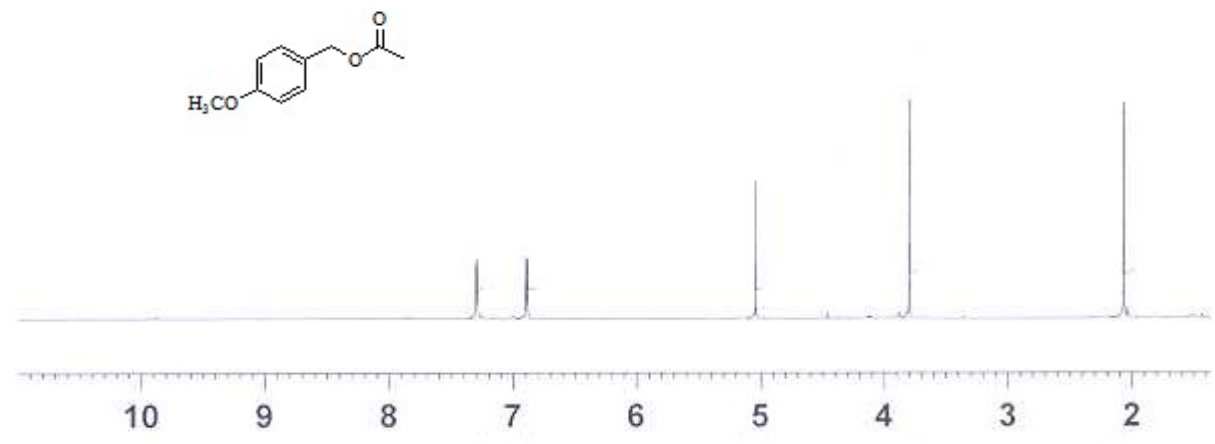
***o*-Me benzyl acetate (2e) (Table 2, entry 2)**

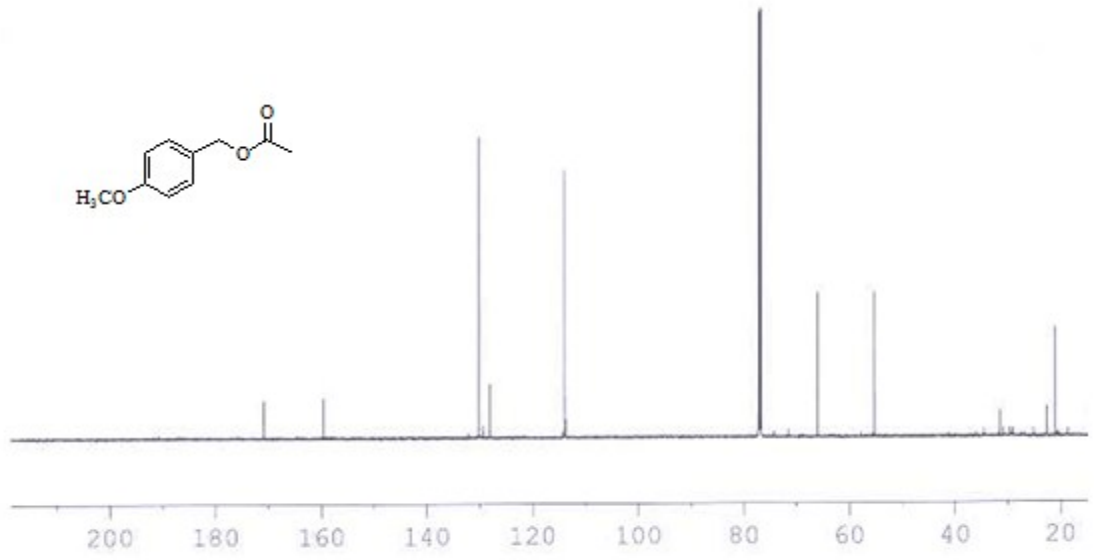

O
O
CH3
CH3
10
9
8
7
6
5
4
3
2

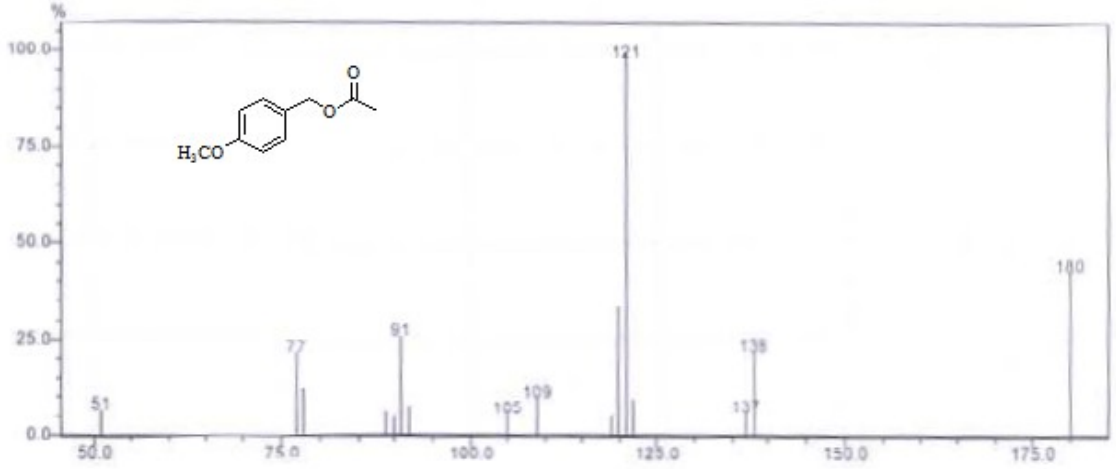

O
O
CH3
CH3
200
180
160
140
120
100
80
60
40
20
0



_p_-MeO benzyl acetate (2f) (Table 2, entry 3)




O
O
H3CO
200
180
160
140
120
100
80
60
40
20


%
100.0
75.0
50.0
25.0
0.0
O
O
H3CO
121
160
91
77
138
109
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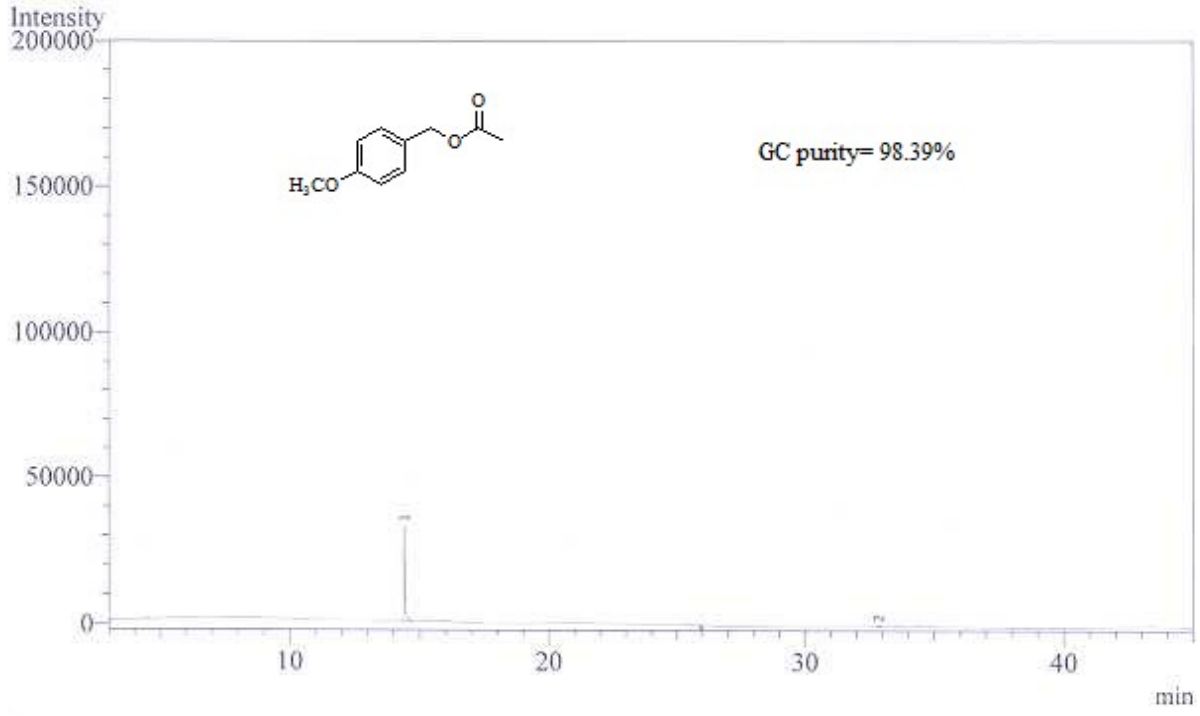
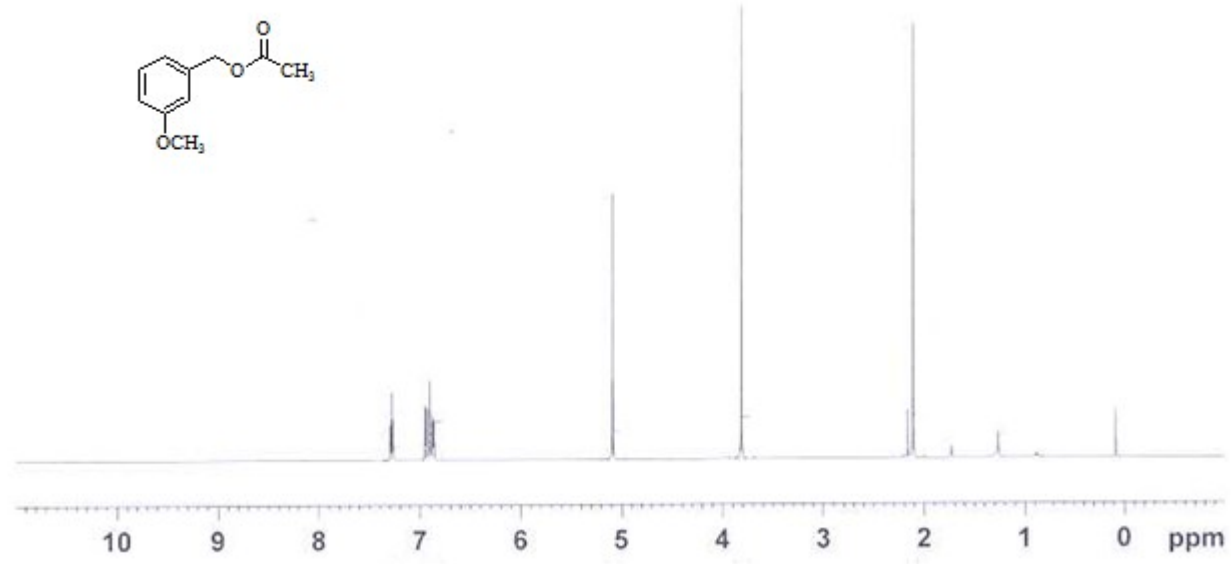
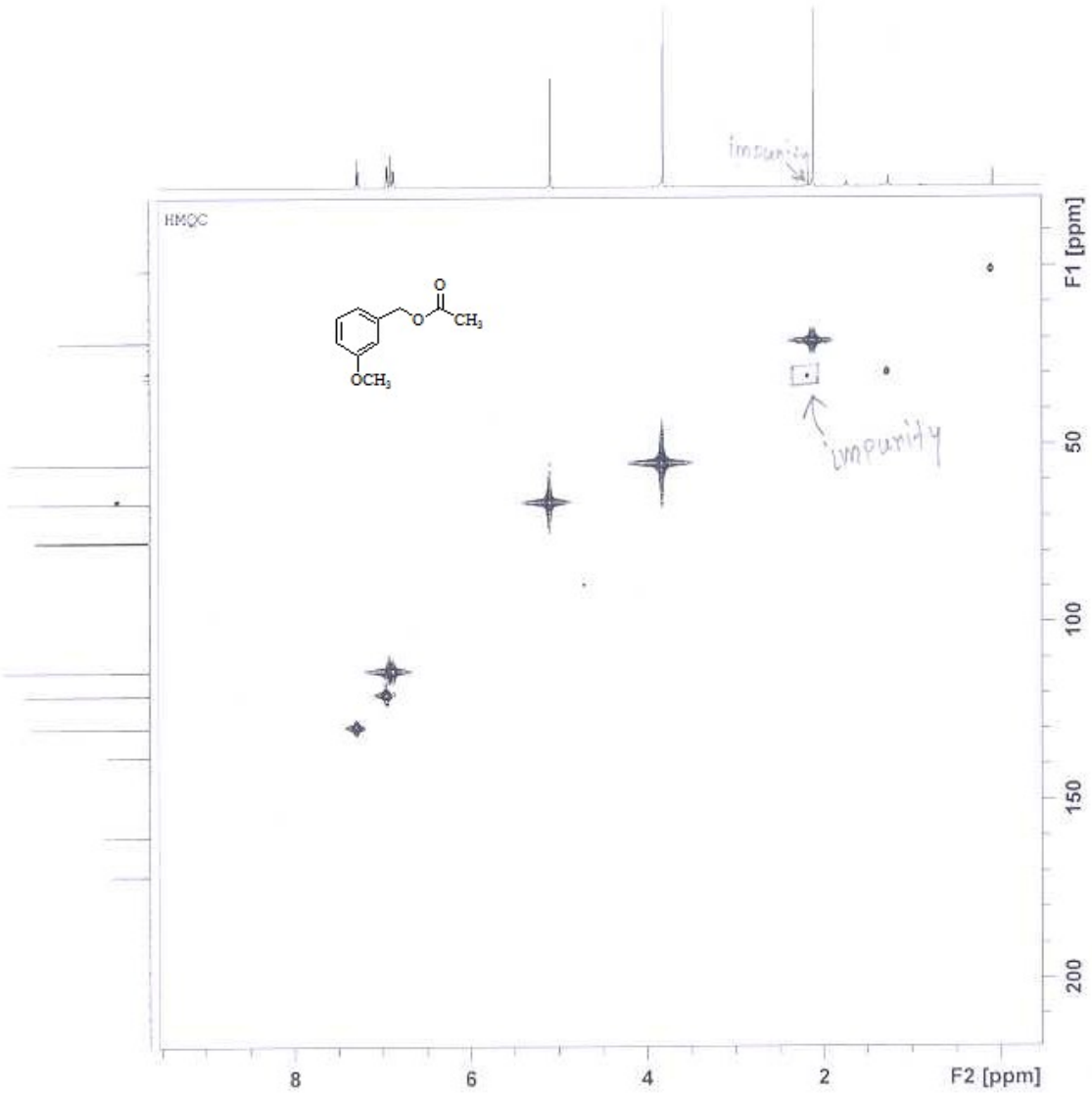
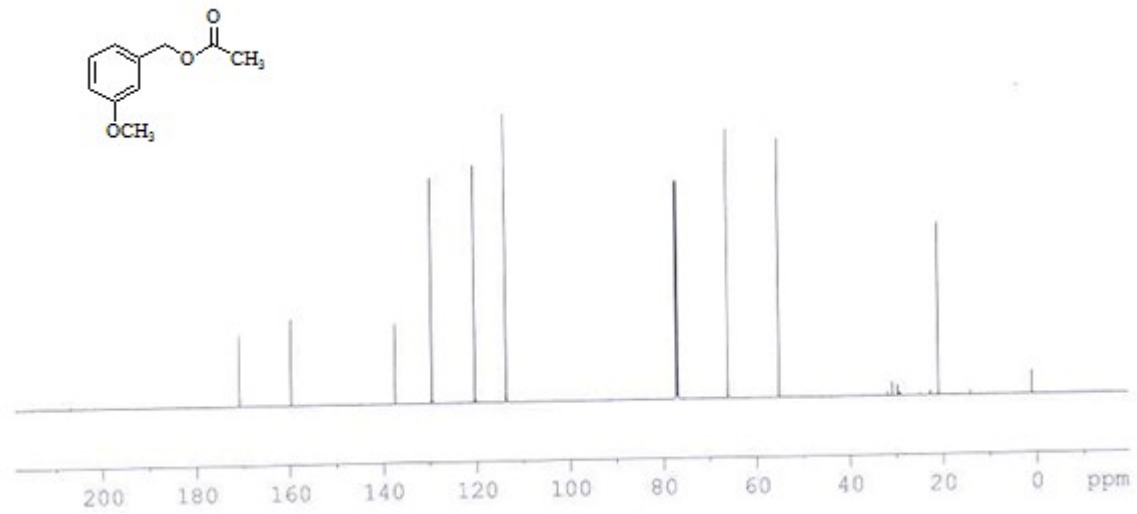
137
50.0
75.0
100.0
125.0
150.0
175.0

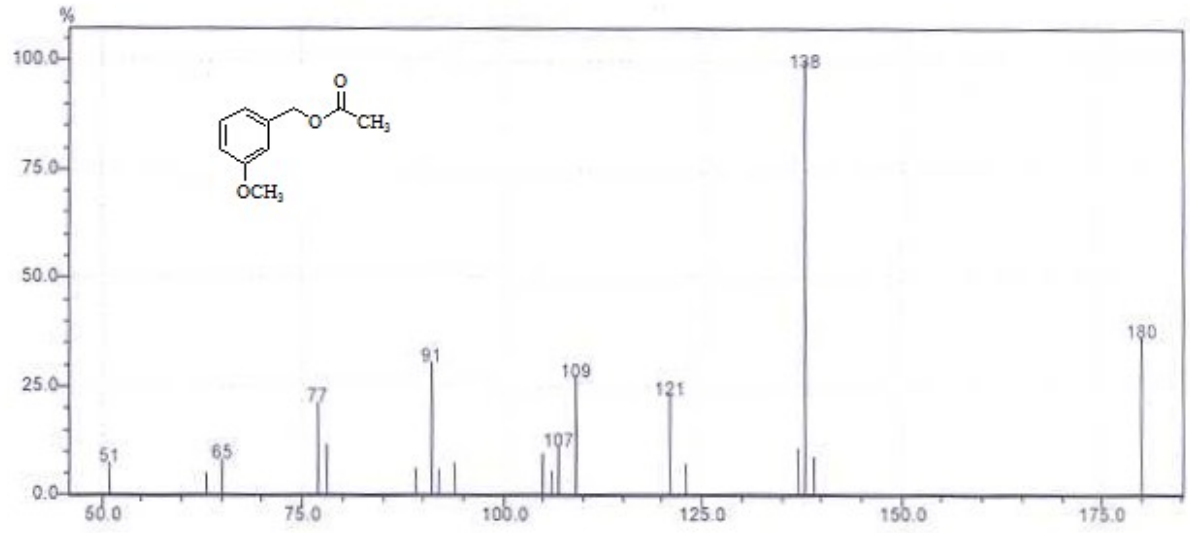


***m*-MeObenzyl acetate (2g) (Table 2, entry 4)**

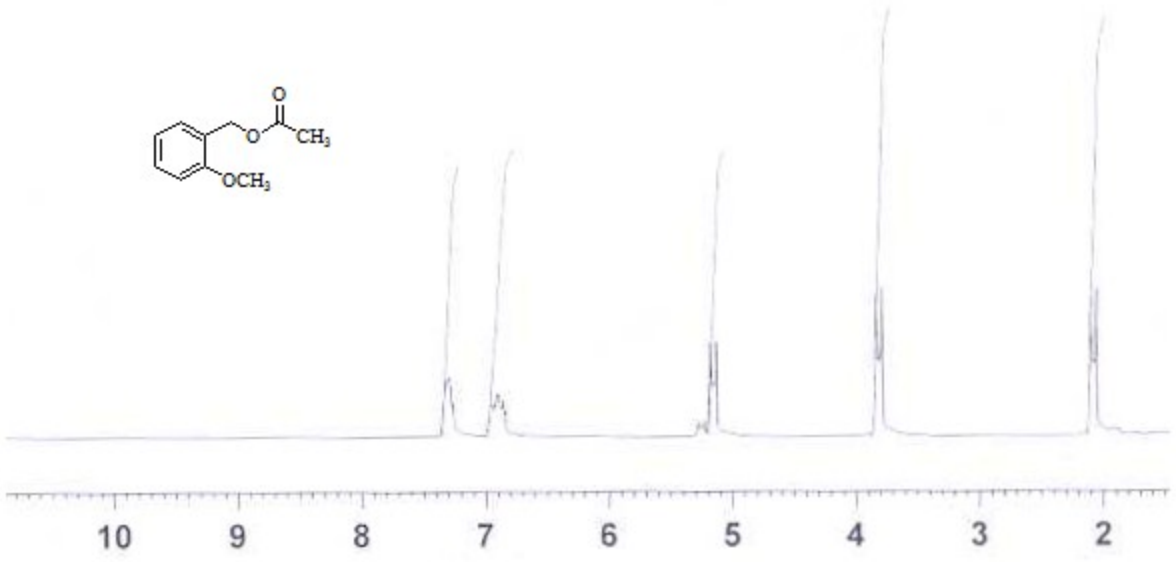


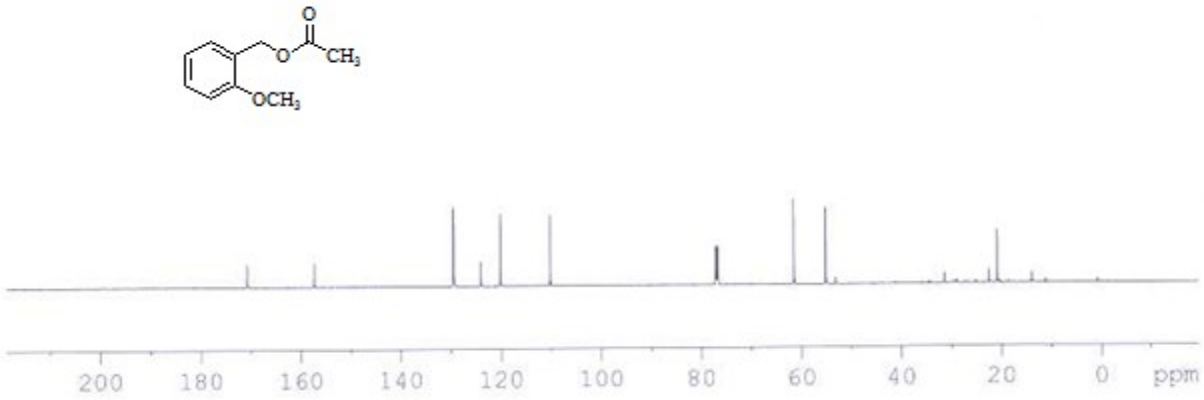

HMQC
impurity
impurity
F1 [ppm]
50
100
150
200
8
6
4
2
F2 [ppm]

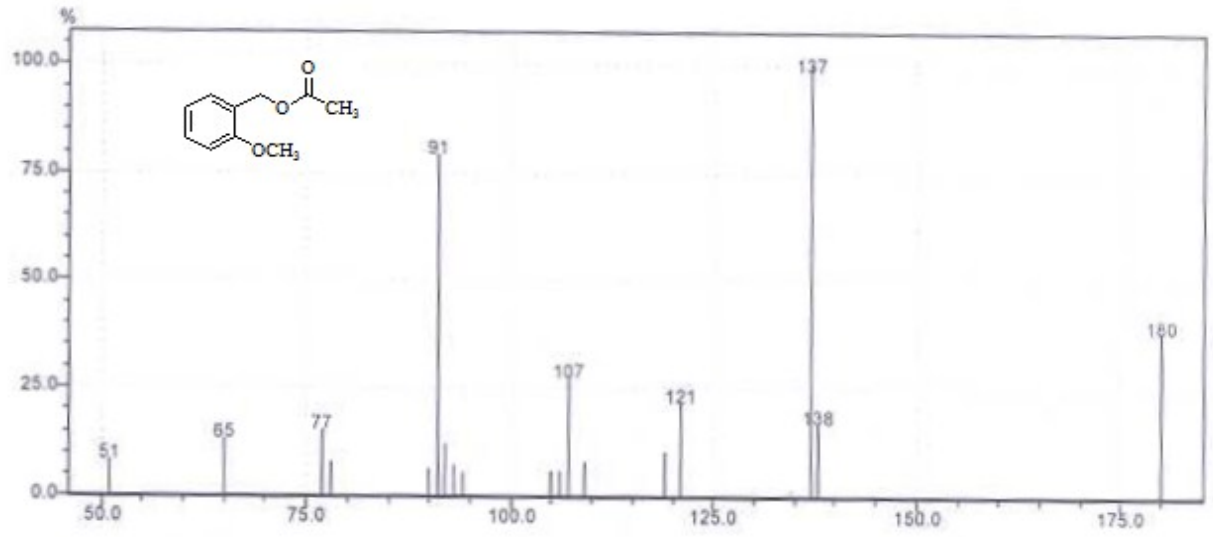


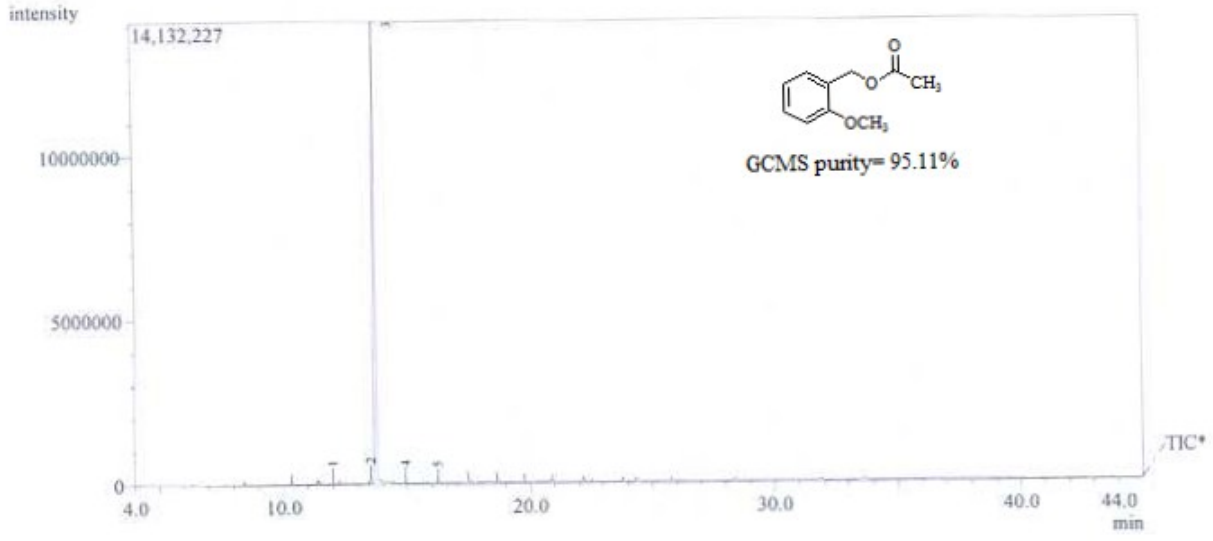


***o*-MeObenzyl acetate (2h) (Table 2, entry 5)**

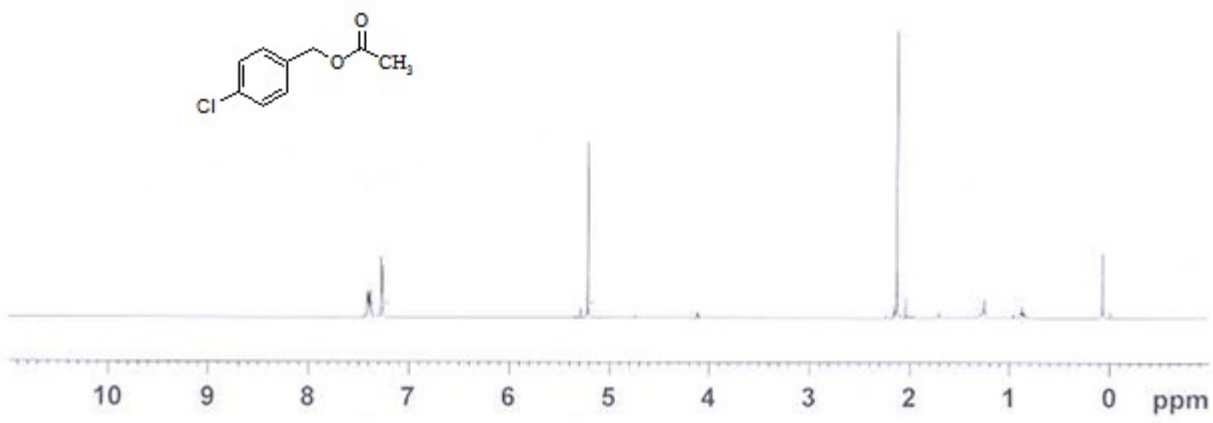

O
O
CH3
OCH3
10
9
8
7
6
5
4
3
2

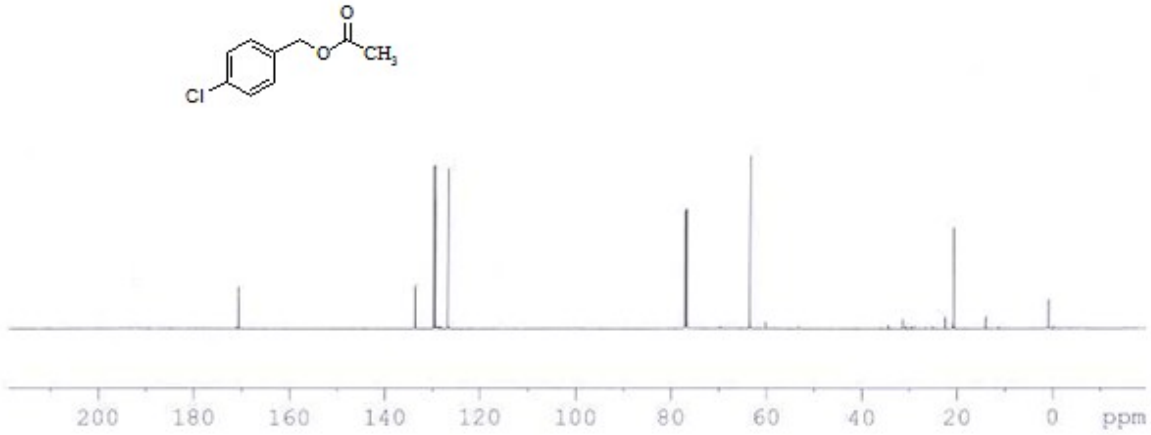

O
O
CH3
OCH3
200
180
160
140
120
100
80
60
40
20
0
ppm

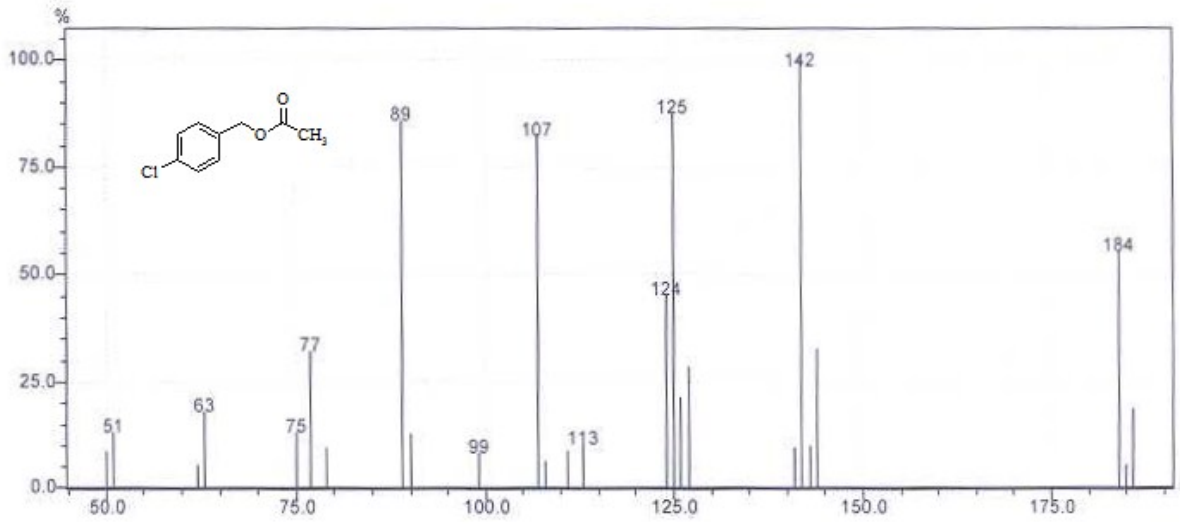




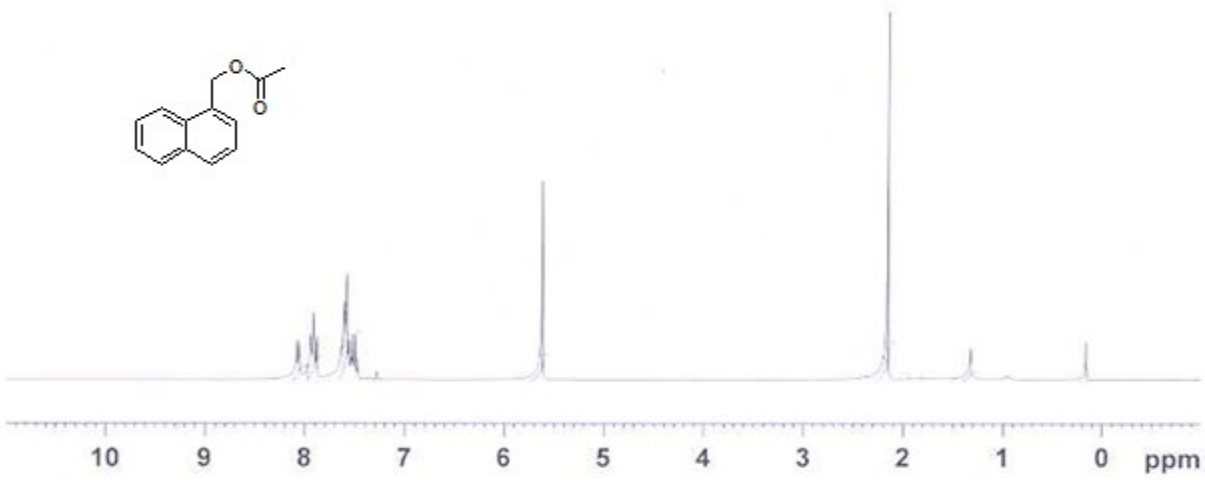
***p*-Cl benzyl acetate (2i) (Table 2, entry 6)**

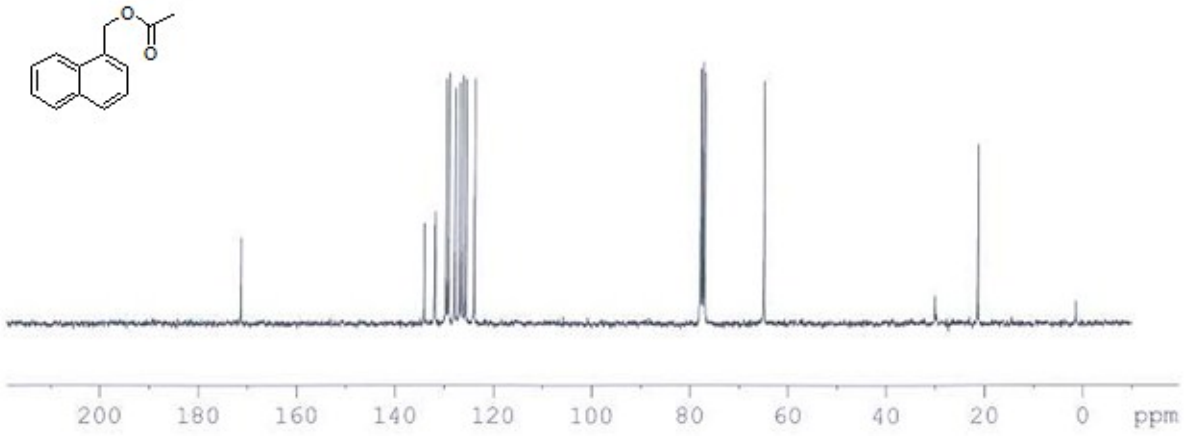


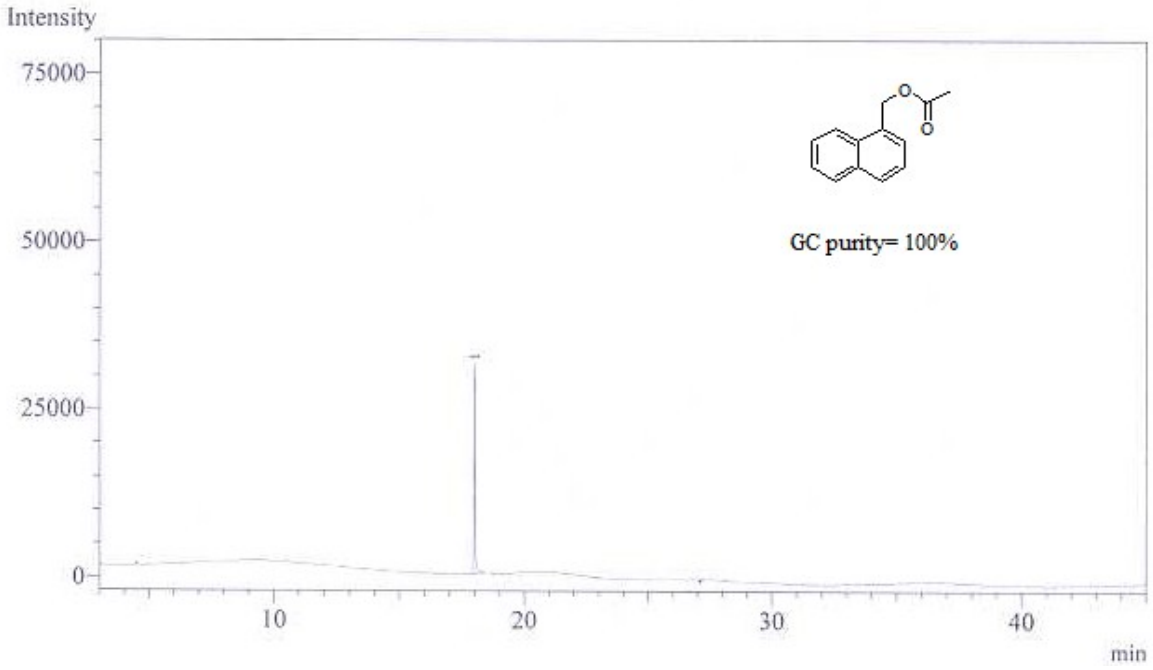


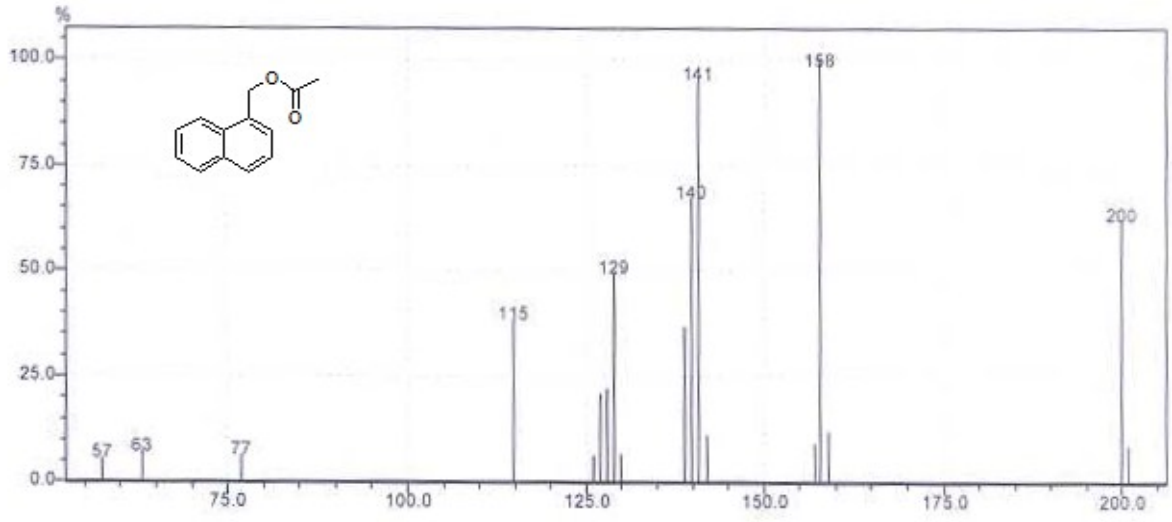


(naphthalen-5-yl)methyl acetate (2j) (Table 2, entry 7)

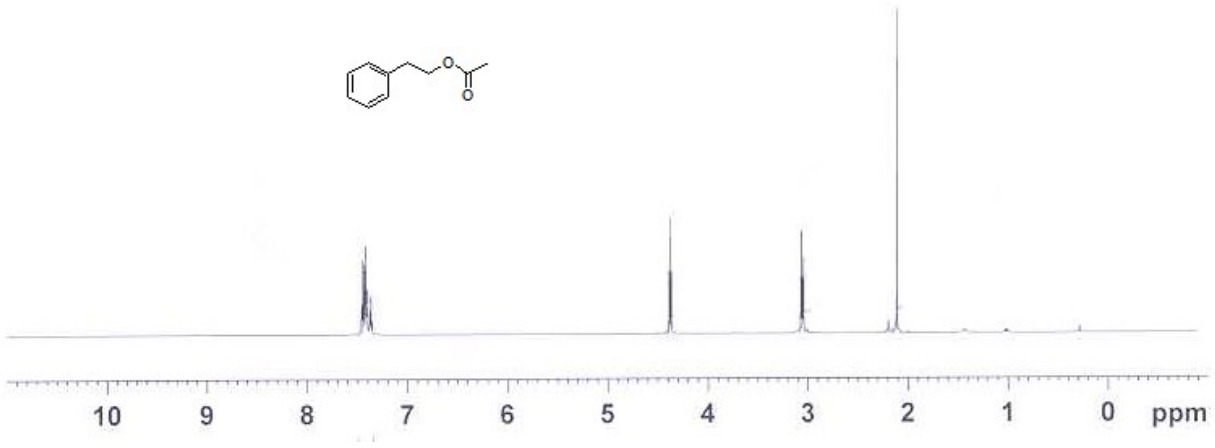

10
9
8
7
6
5
4
3
2
1
0
ppm

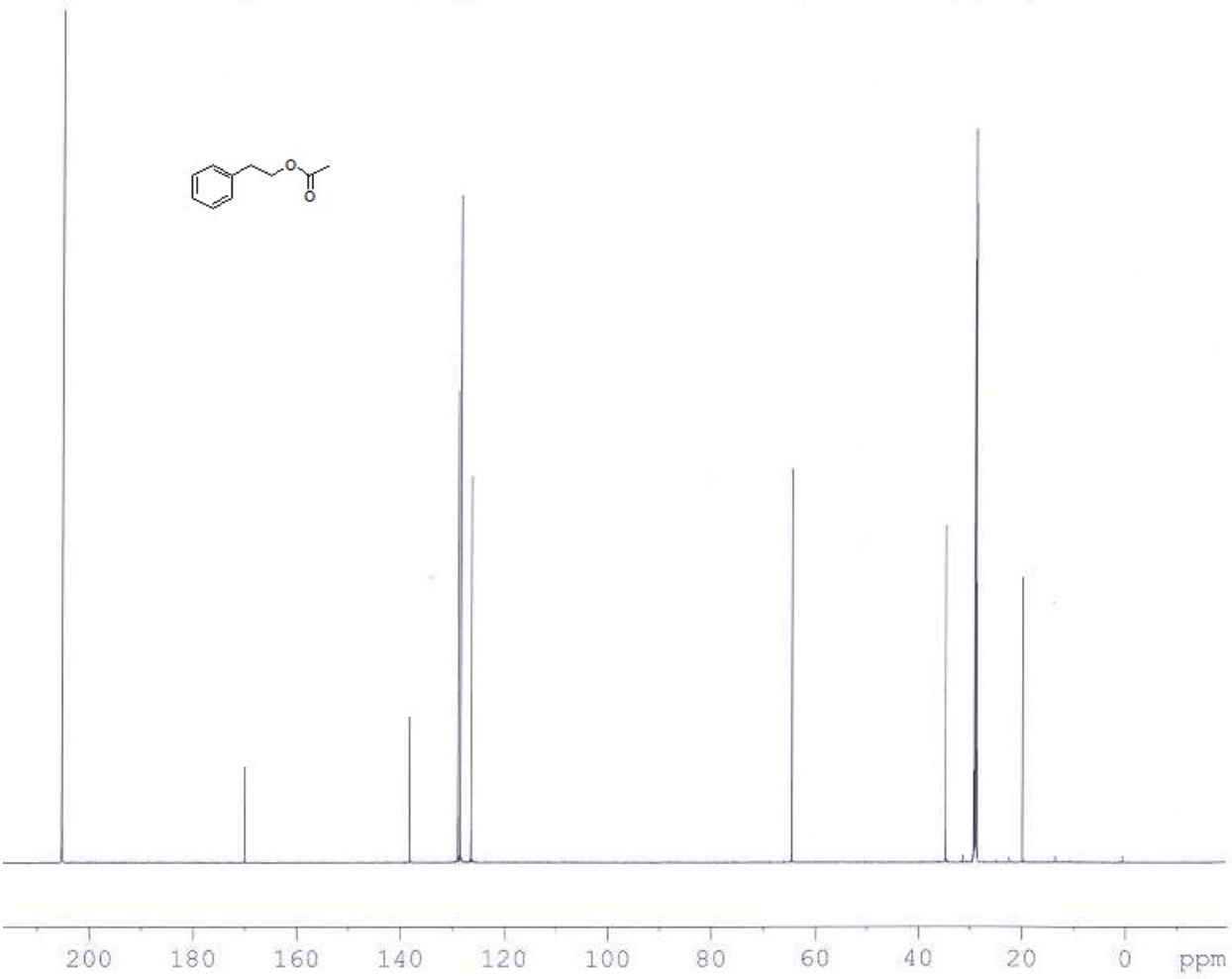

200
180
160
140
120
100
80
60
40
20
0
ppm

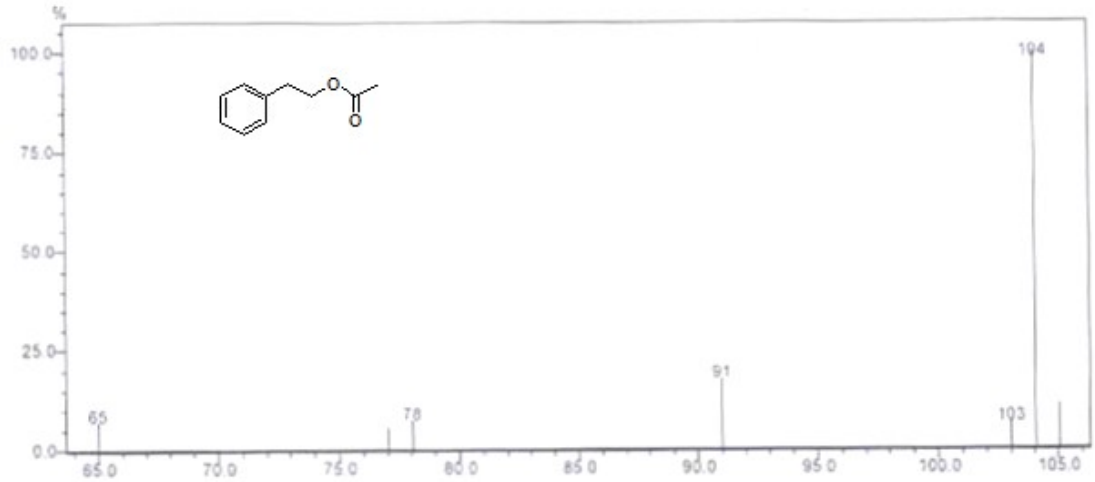




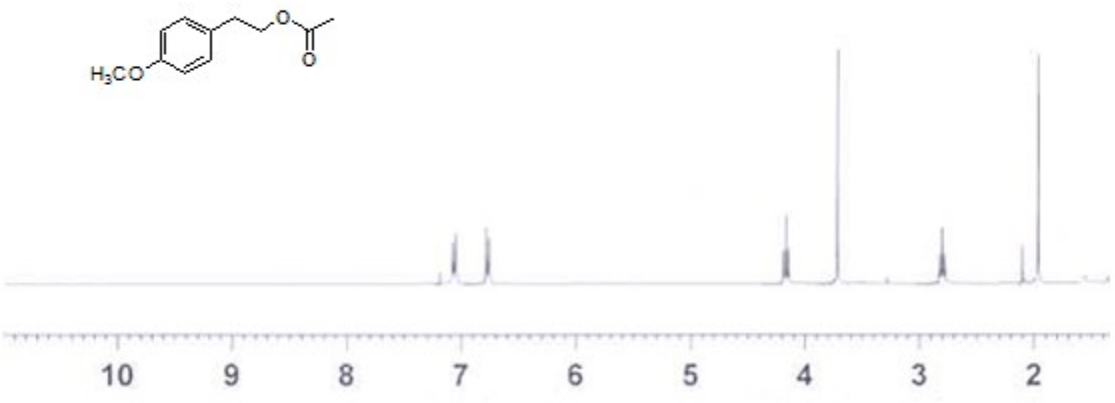
Phenethyl acetate (2k) (Table 3, entry 1)

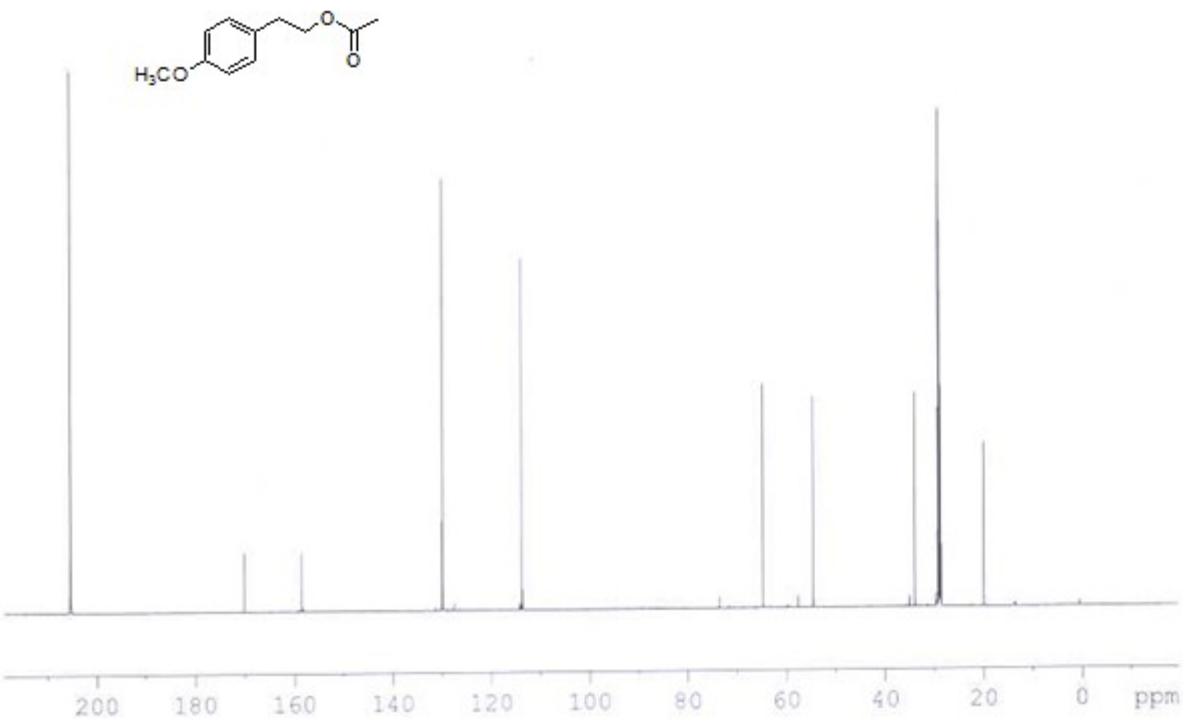

10
9
8
7
6
5
4
3
2
1
0
ppm

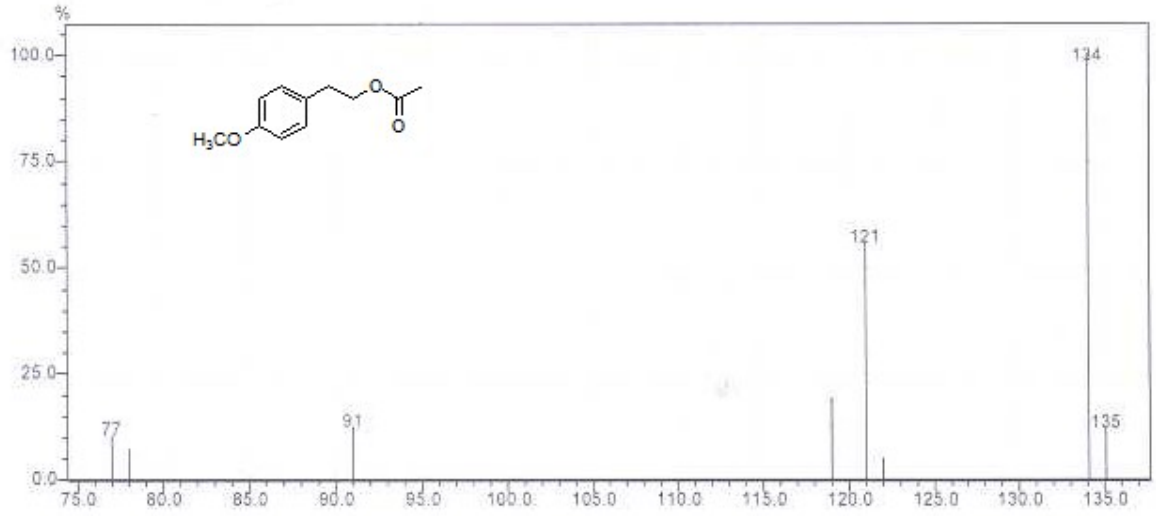

200
180
160
140
120
100
80
60
40
20
0
ppm



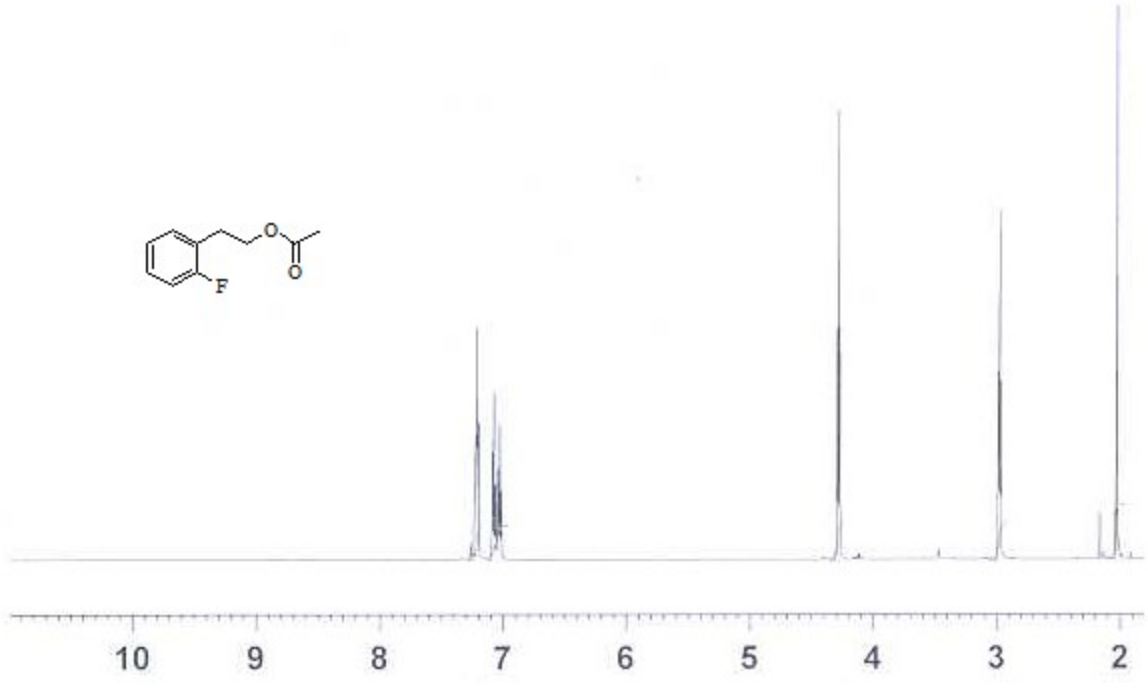
***p*-MeO phenethyl acetate (2l) (Table 3, entry 2)**

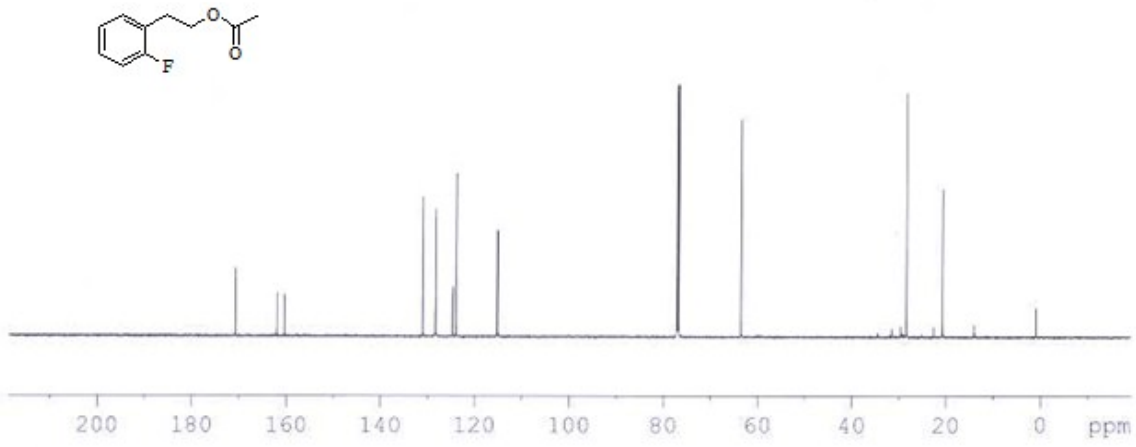


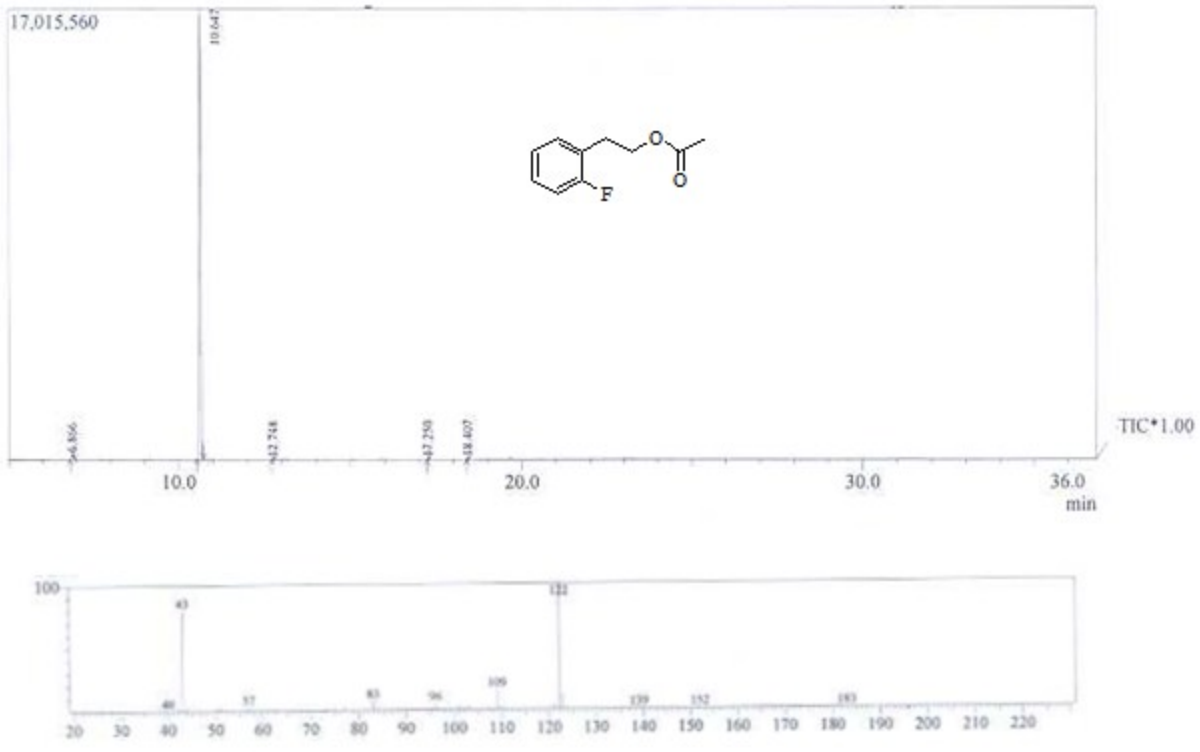




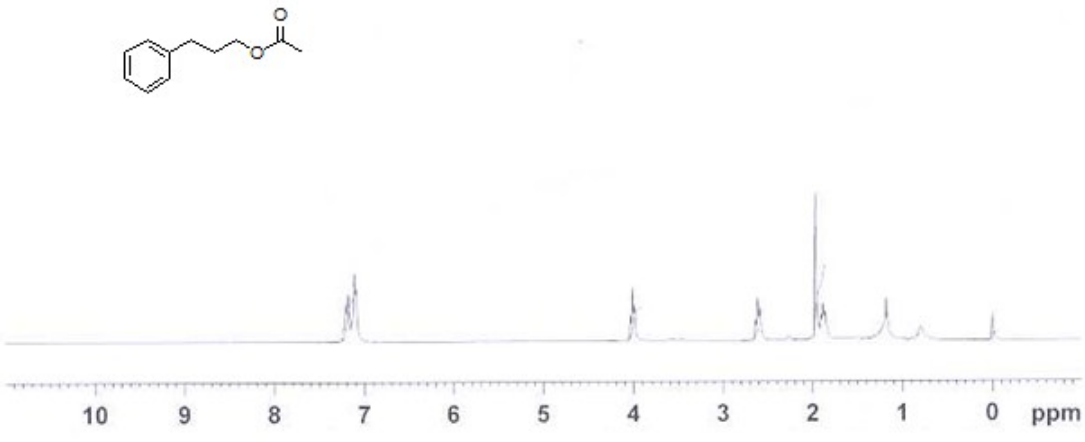
2-F phenethyl acetate (2m) (Table 3, entry 3)

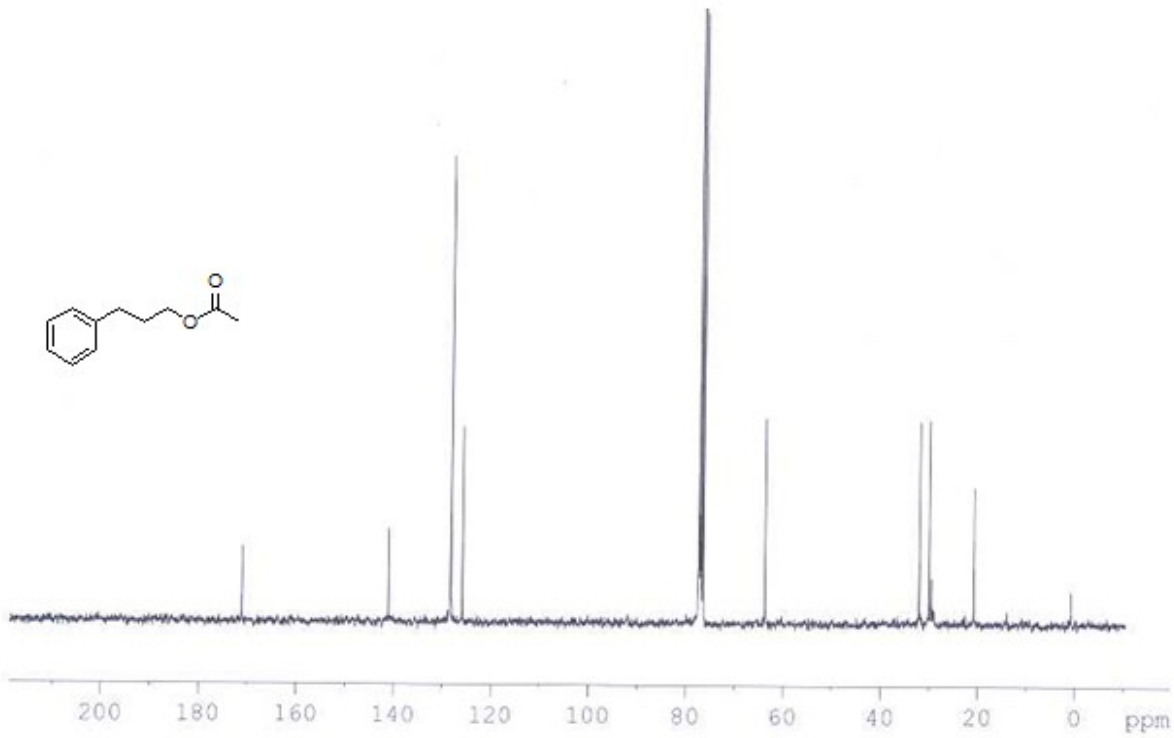

O
O
F
10
9
8
7
6
5
4
3
2

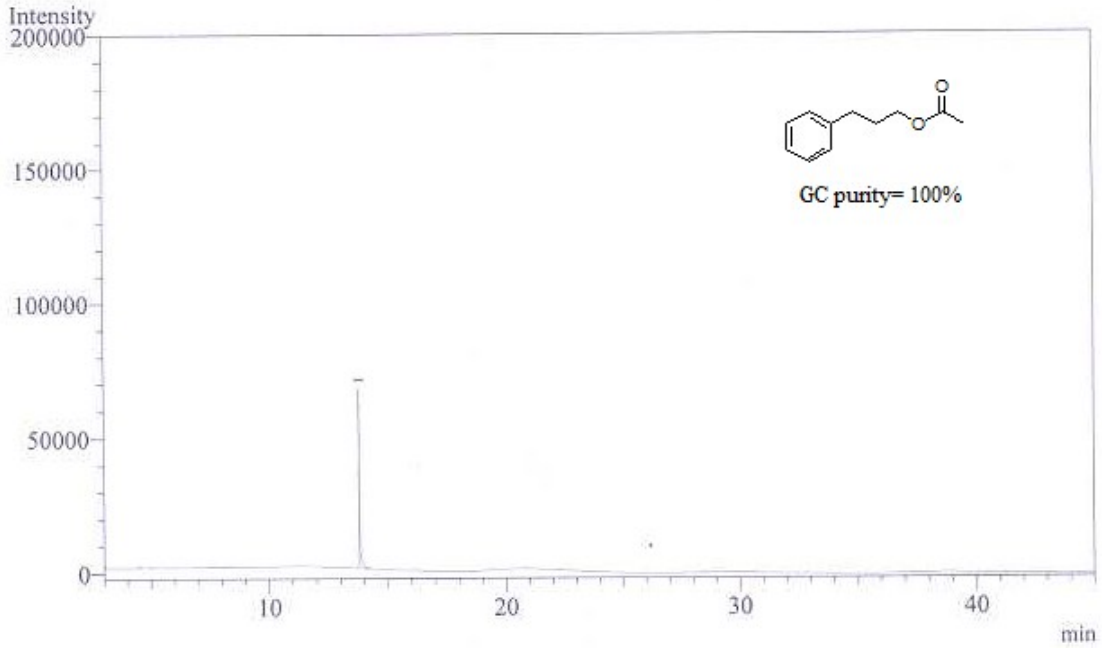

O
O
F
200
180
160
140
120
100
80
60
40
20
0
ppm

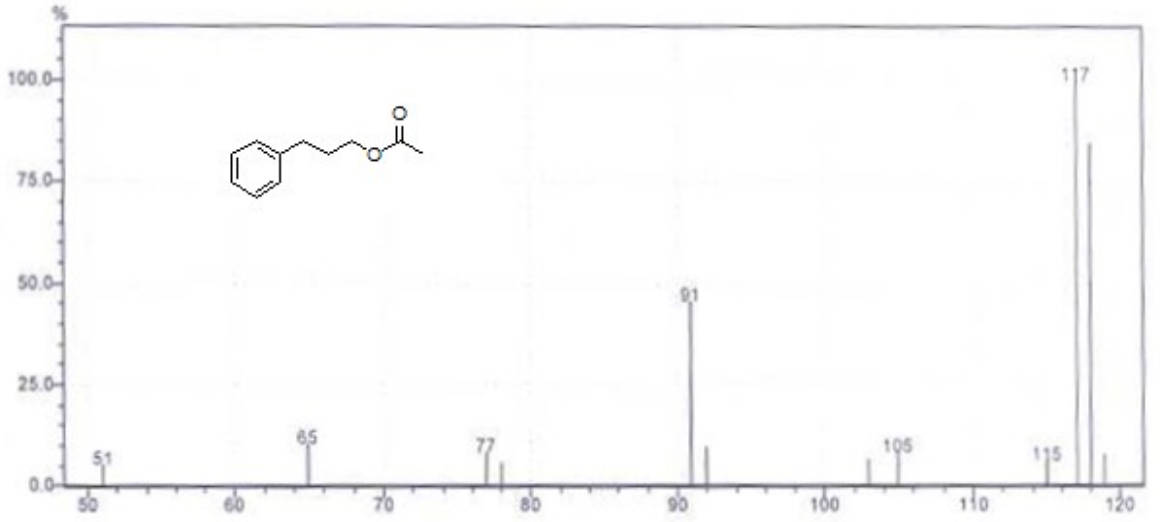


3-phenylpropyl acetate (2n) (Table 3, entry 4)

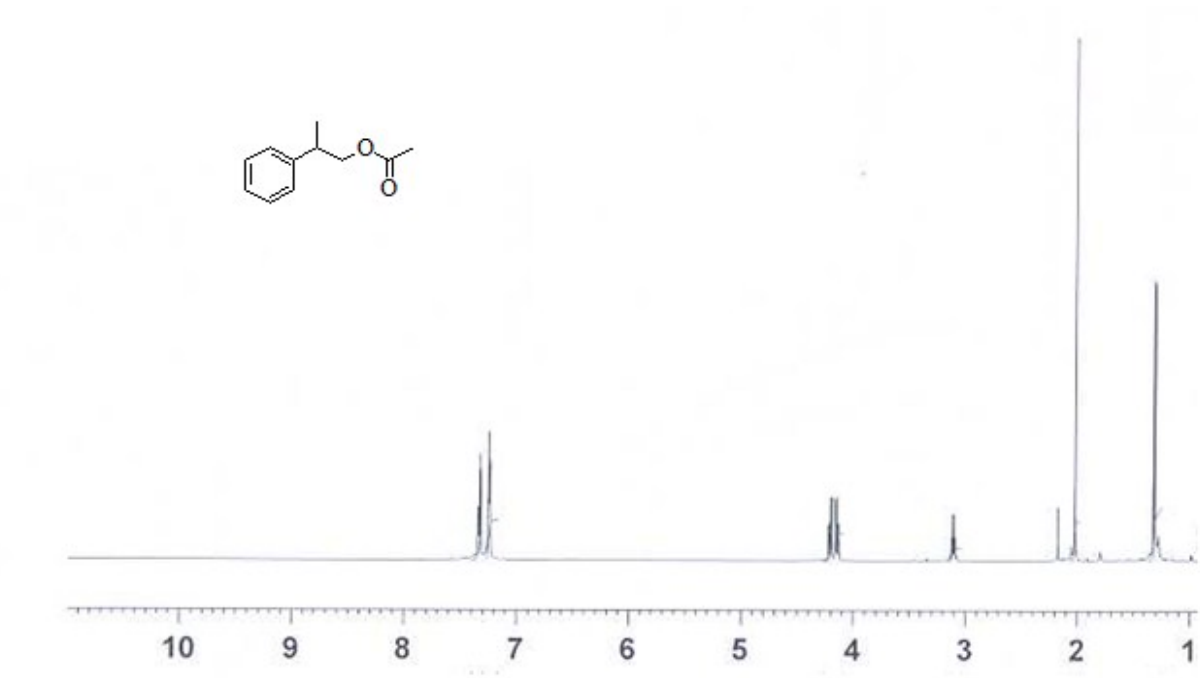


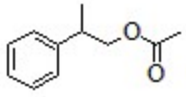

200
180
160
140
120
100
80
60
40
20
0
ppm

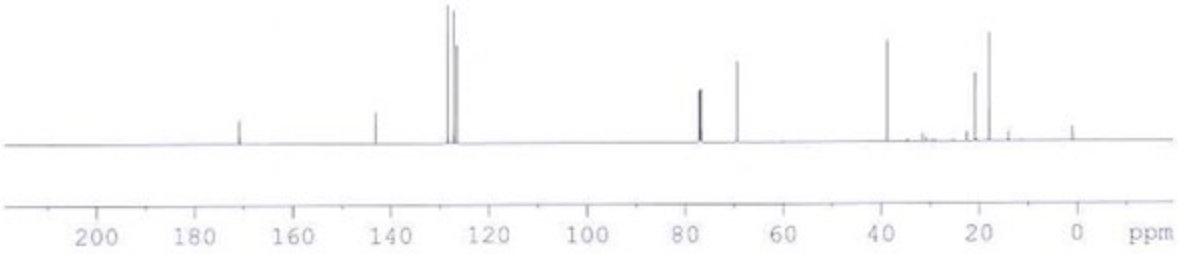

Intensity
200000
150000
100000
50000
0
10
20
30
40
min
GC purity= 100%

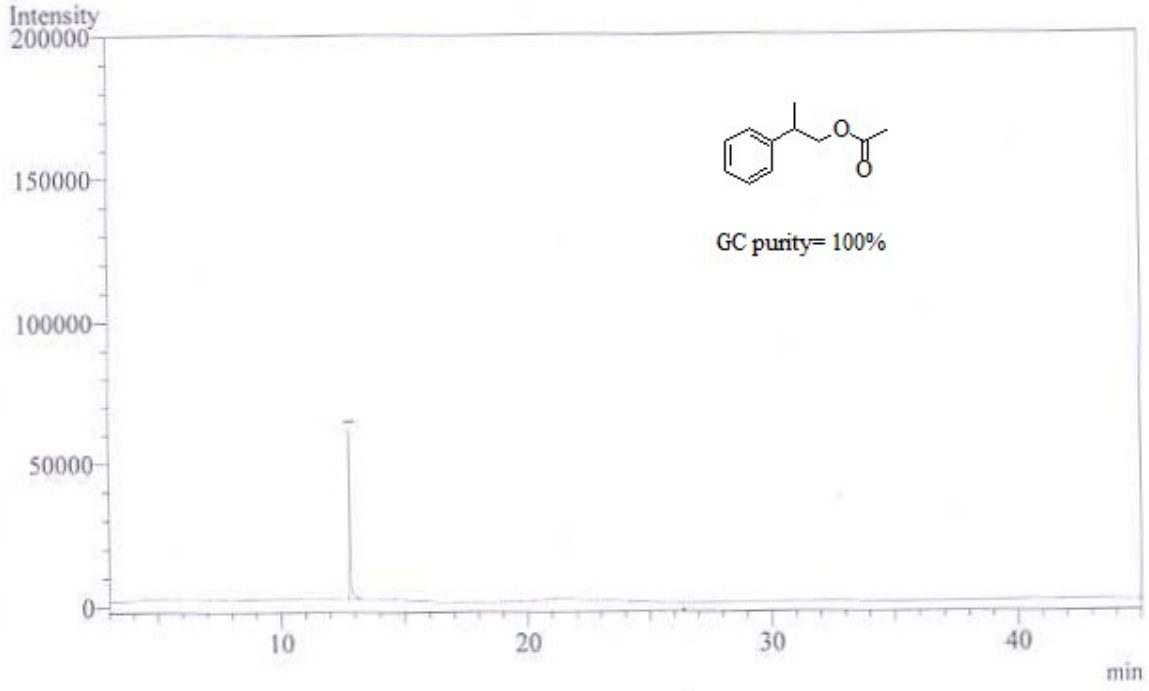


2-phenylpropyl acetate (2o) (Table 3, entry 5)

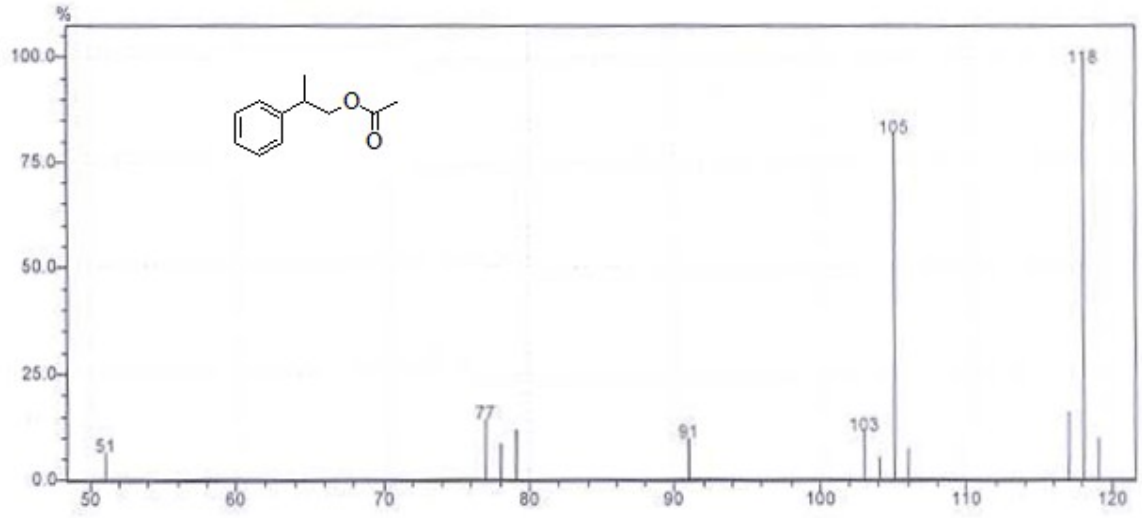




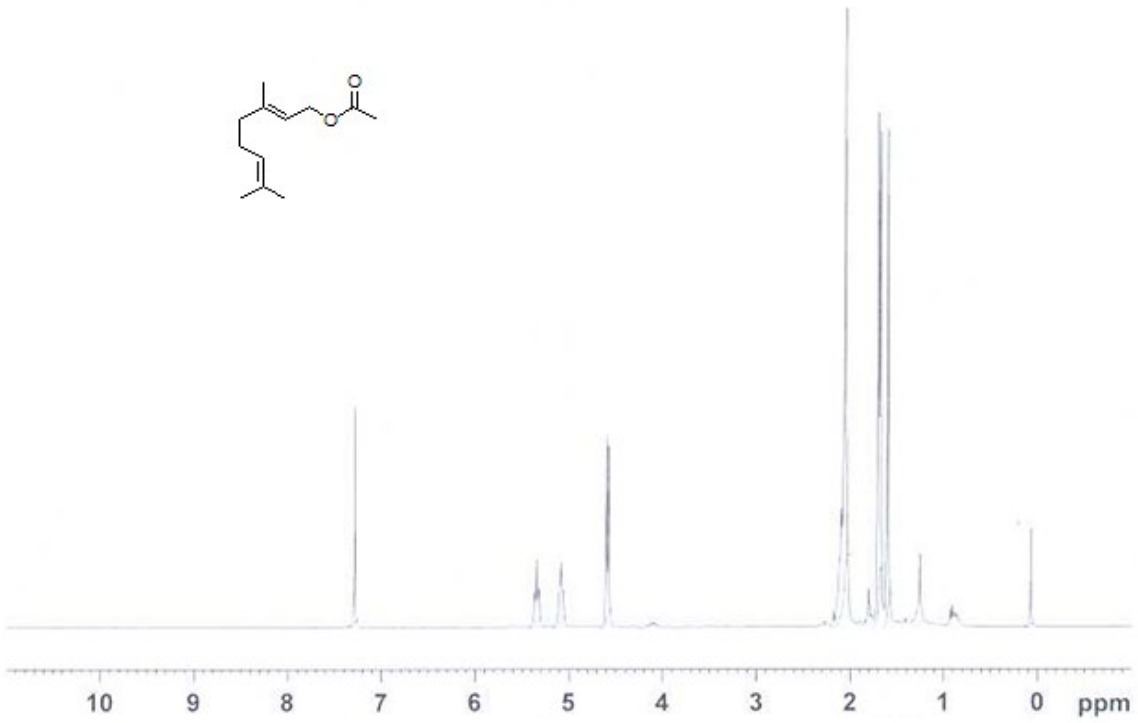


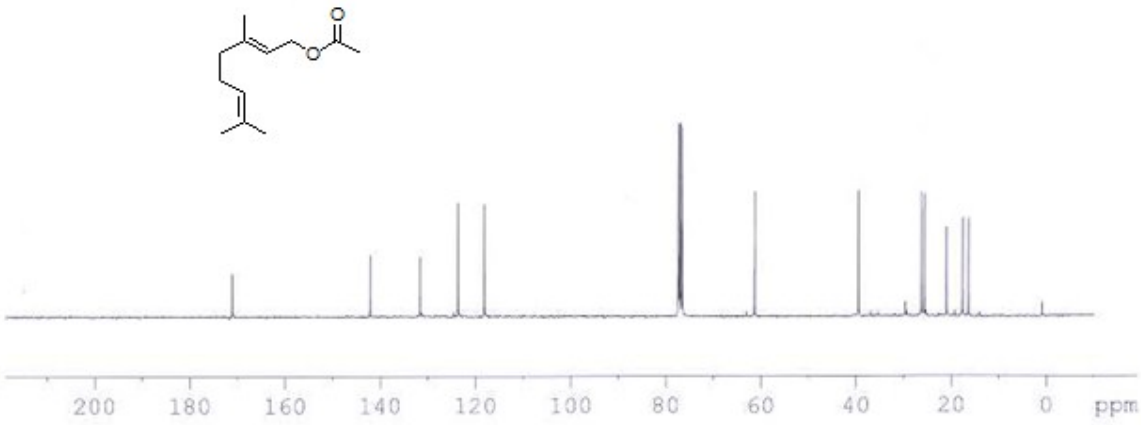


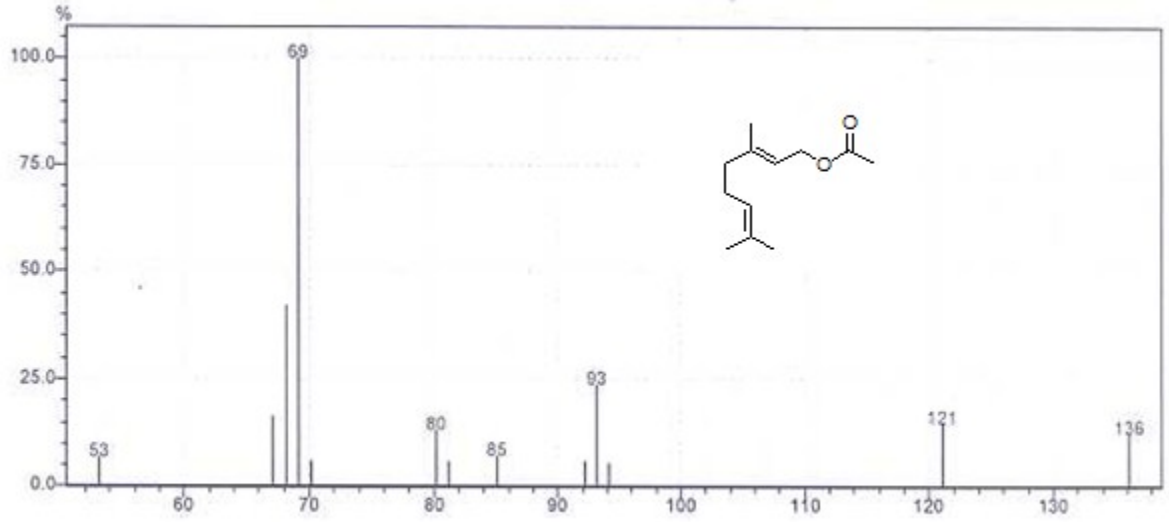
GC purity= 100%



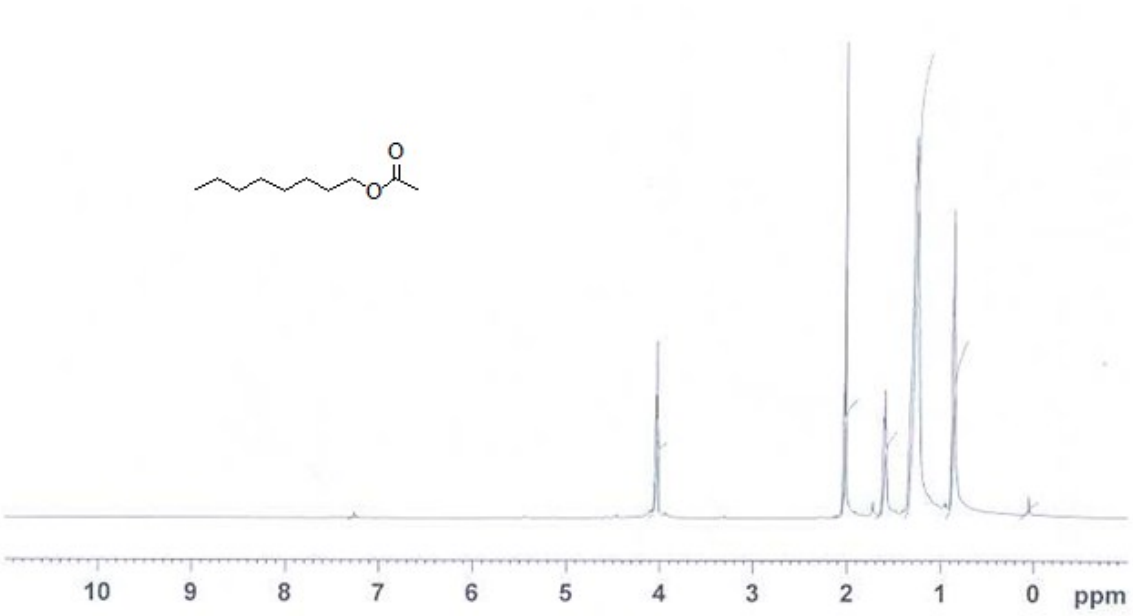
3,7-dimethylocta-2,6-dienyl acetate (2p) (Table 3, entry 6)

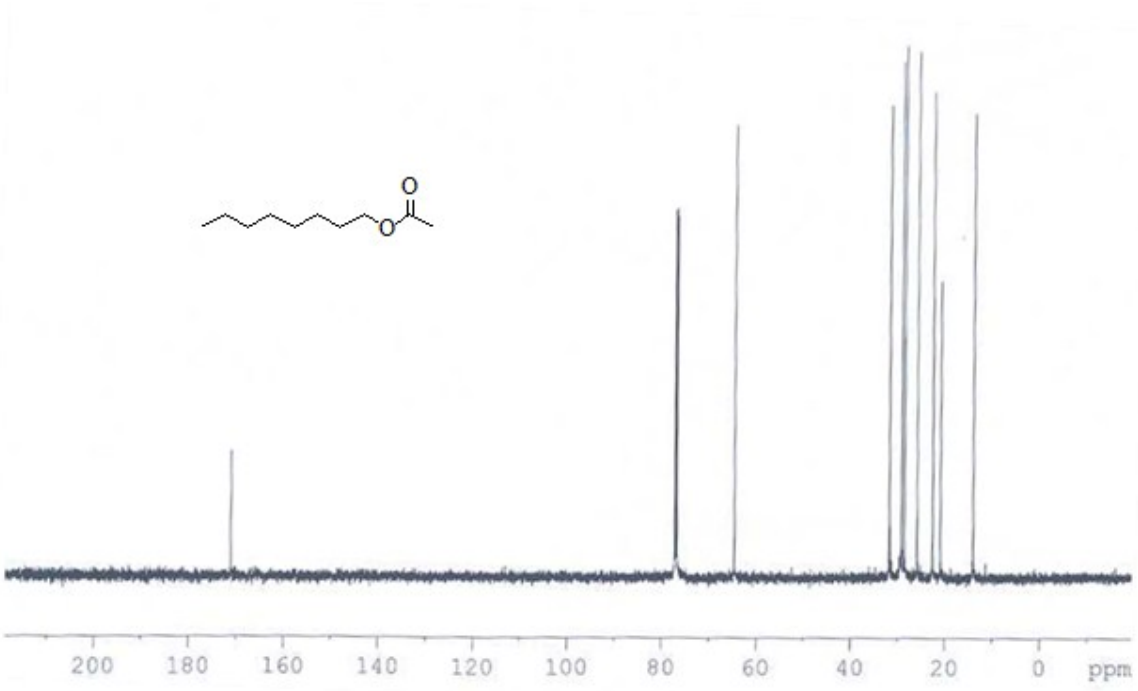


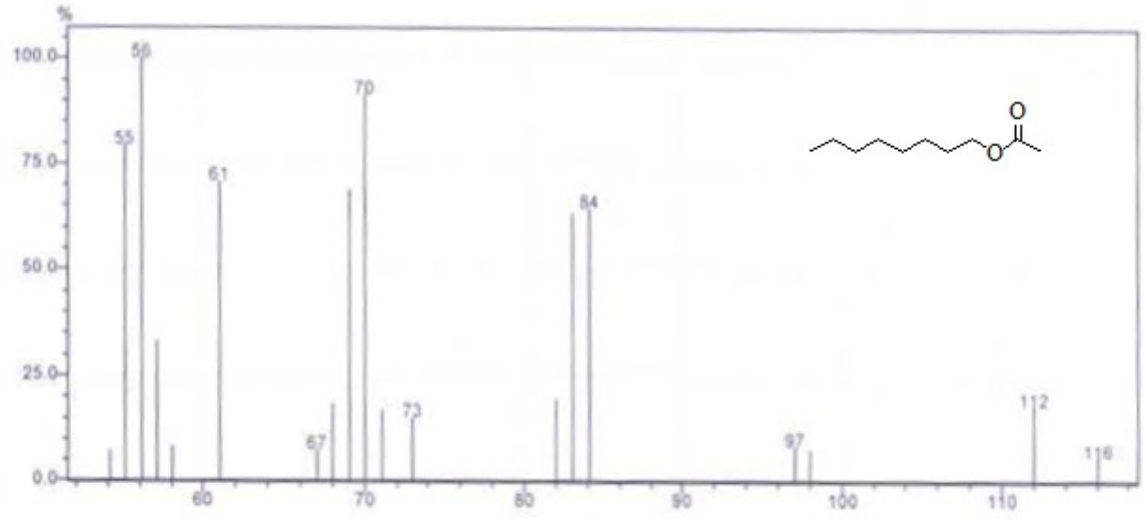




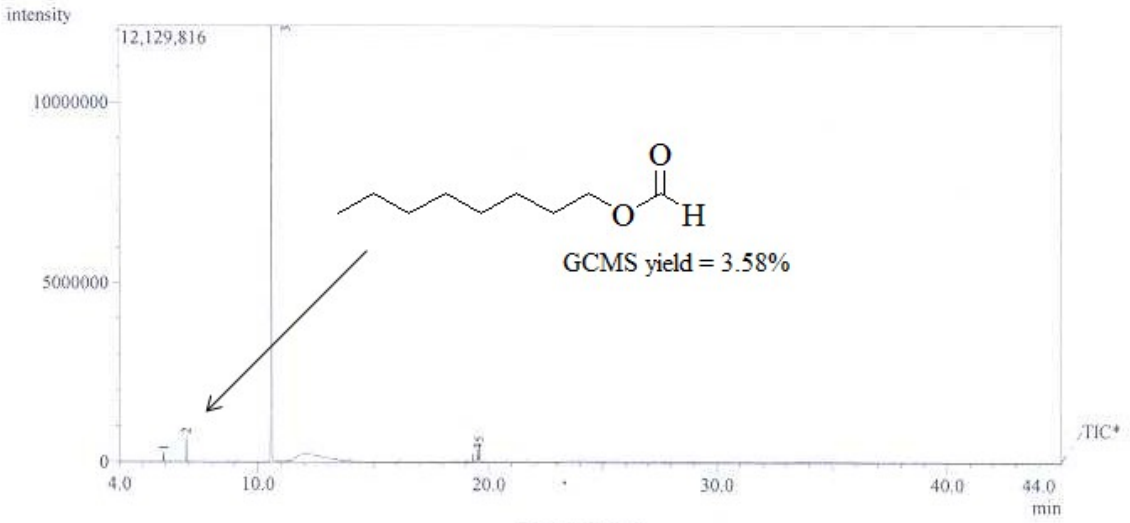
Octyl acetate (2q) (Table 3, entry 7)


O
O
10
9
8
7
6
5
4
3
2
1
0
ppm


O
O
200
180
160
140
120
100
80
60
40
20
0
ppm



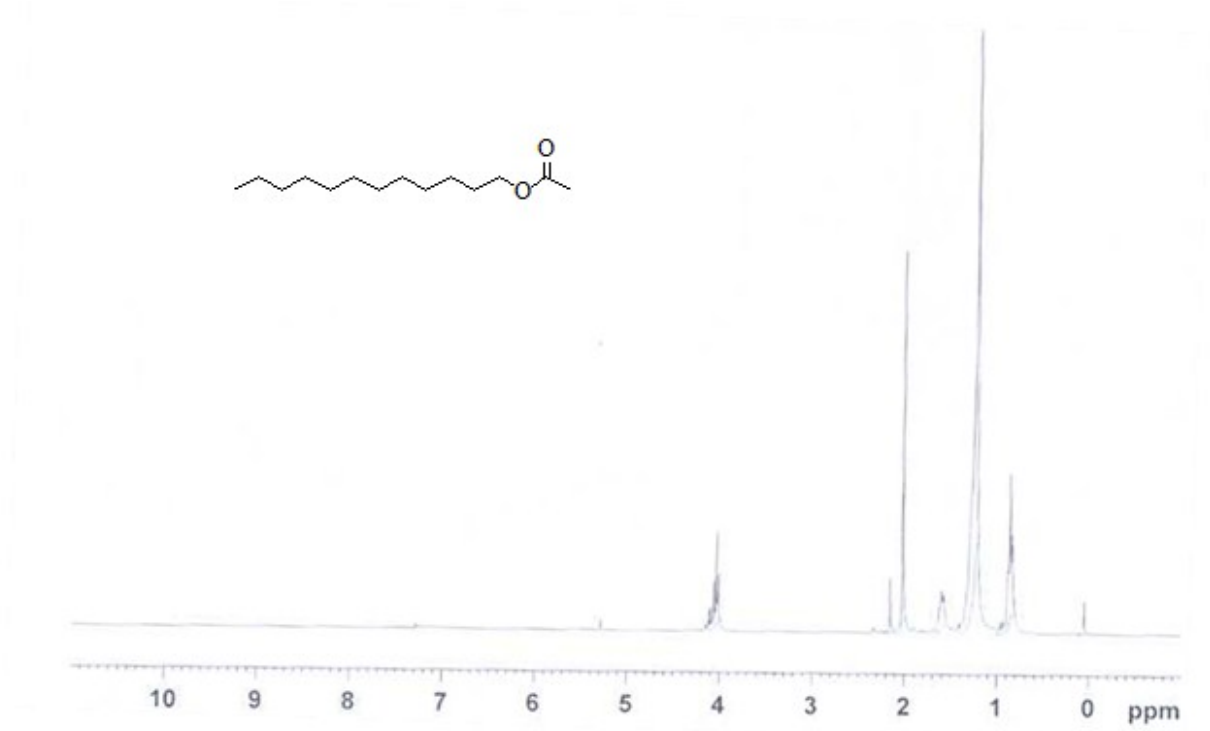
Octyl formate as by-product

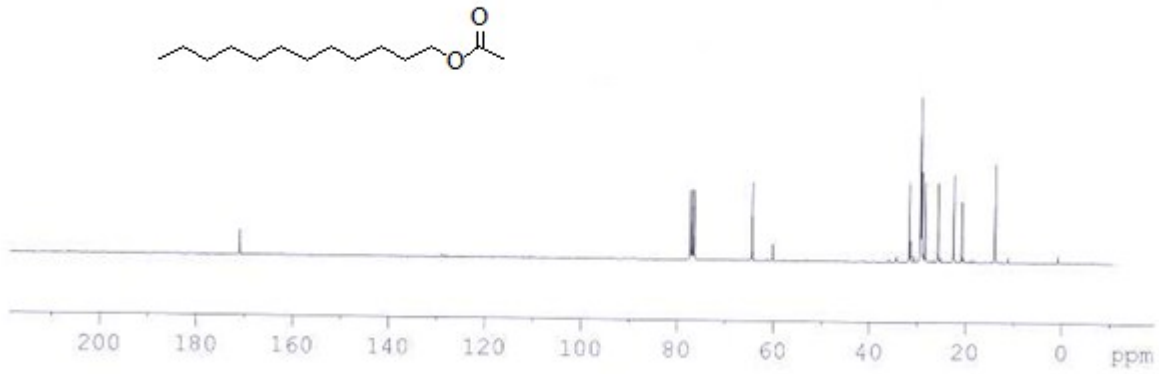


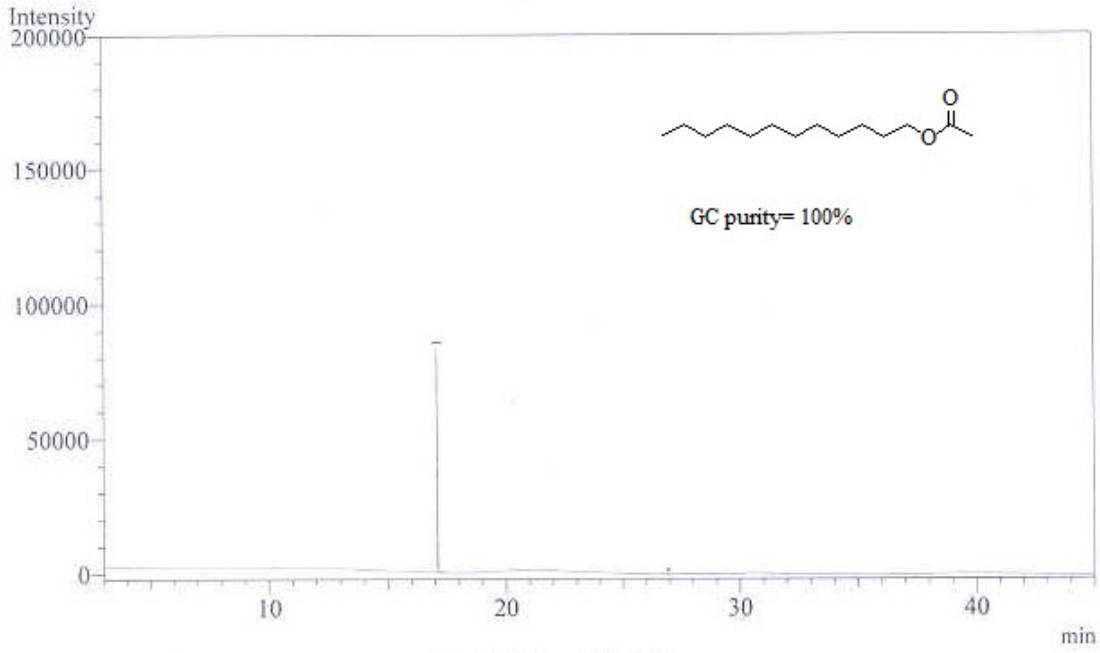
Peak Report TIC

Peak#	R.Time	Area	Height	Area%	Name
1	5.926	561592	268880	1.34	([(1Z)-1,3-DIPHENYL-1-PENTENYL]OXY)(TRIMETHYL)SILANE #
2	6.917	1499977	746503	3.58	OCTYL FORMATE
3	10.605	38444650	12069373	91.73	ACETIC ACID, OCTYL ESTER
4	19.530	480157	285092	1.15	NAPHTHALENE, DECAHYDRO-2-METHYL-
5	19.603	926357	499905	2.21	1-NONADECENE
		41912733	13869753	100.00	

Dodecyl acetate (2r) (Table 3, entry 8)



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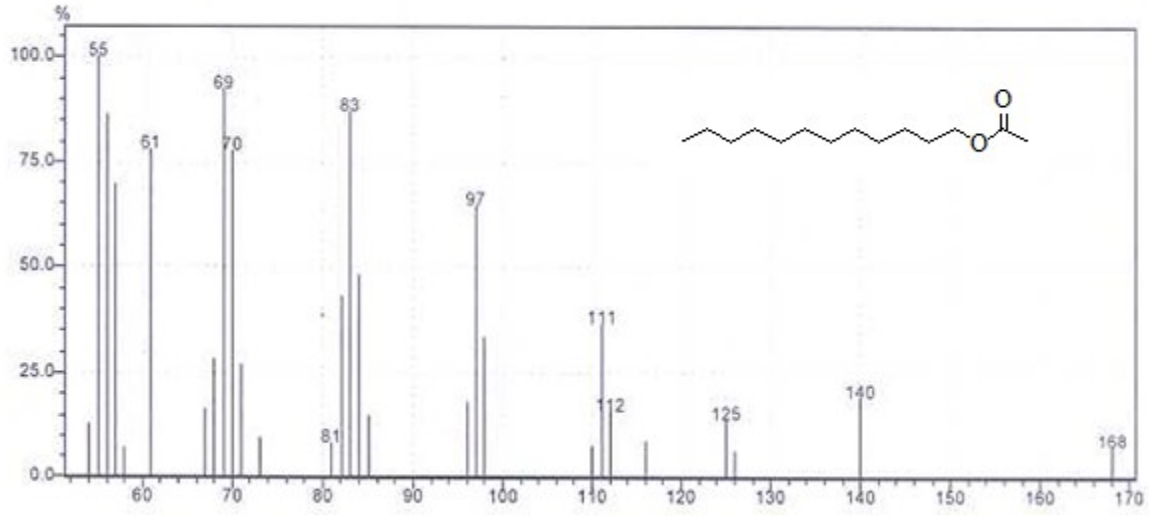
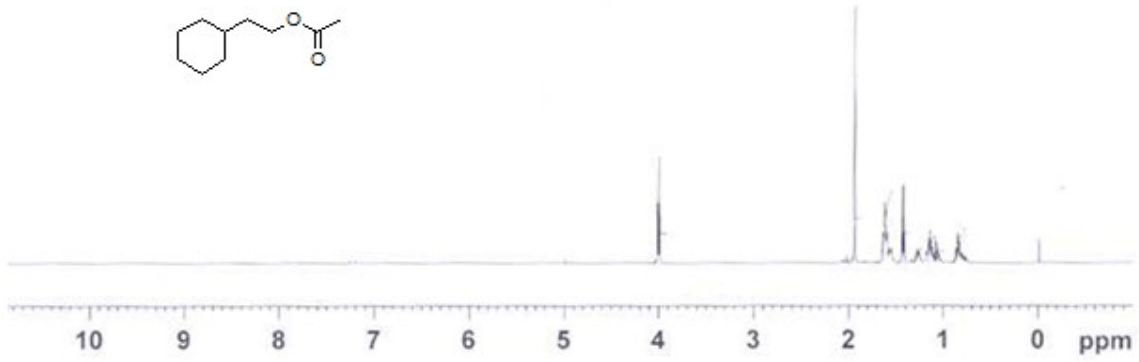
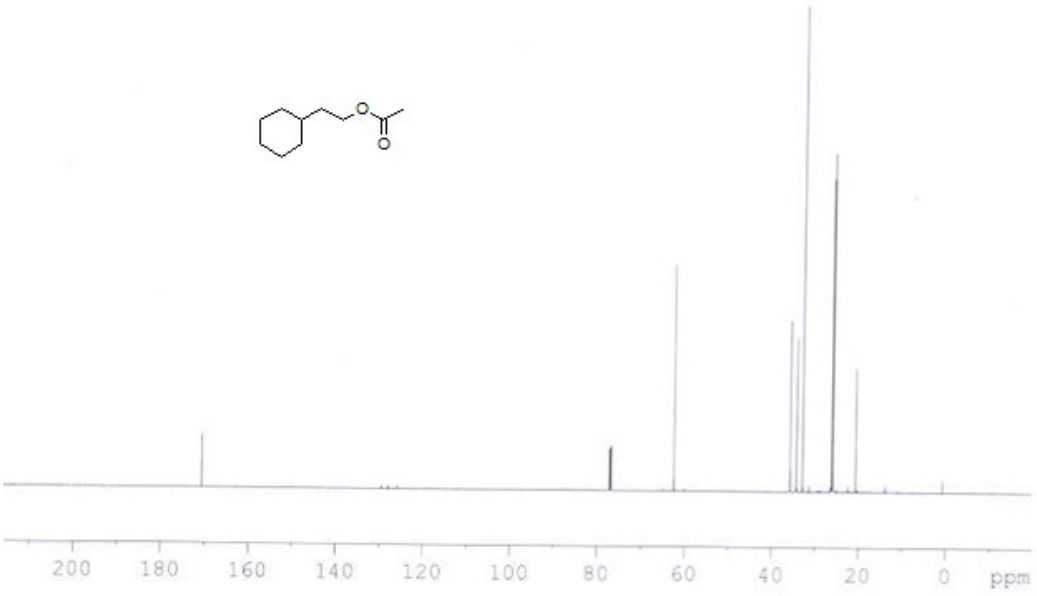
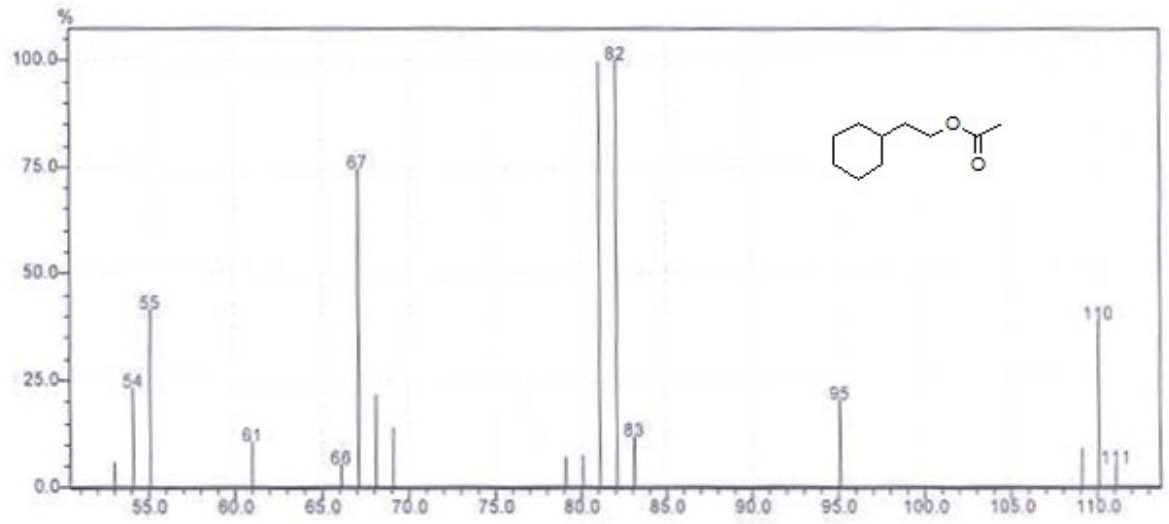
200000
150000
100000
50000
0
10
20
30
40
min
O
O
GC purity= 100%


%
100.0
75.0
50.0
25.0
0.0
55
69
61
70
83
97
111
112
81
125
140
168
60
70
80
90
100
110
120
130
140
150
160
170
O
O

Cyclohexyl Acetate (2s) (Scheme 4**)**



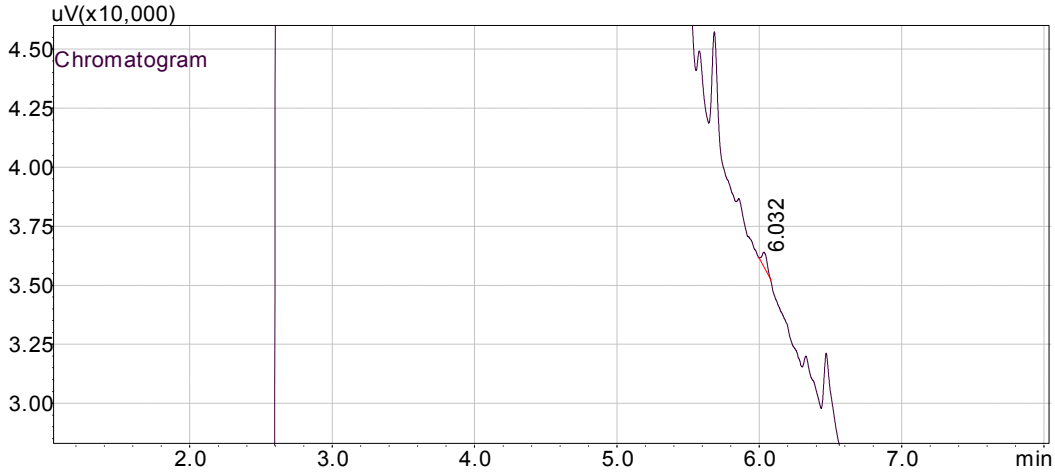


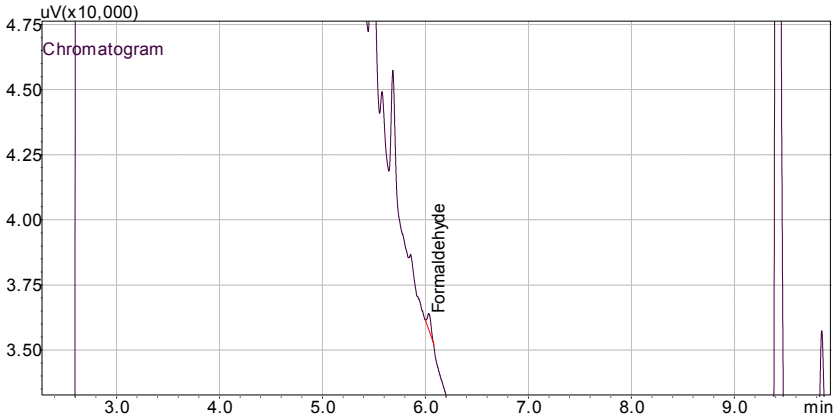


Detection of formaldehyde by Gas Chromatographic (GC) analysis

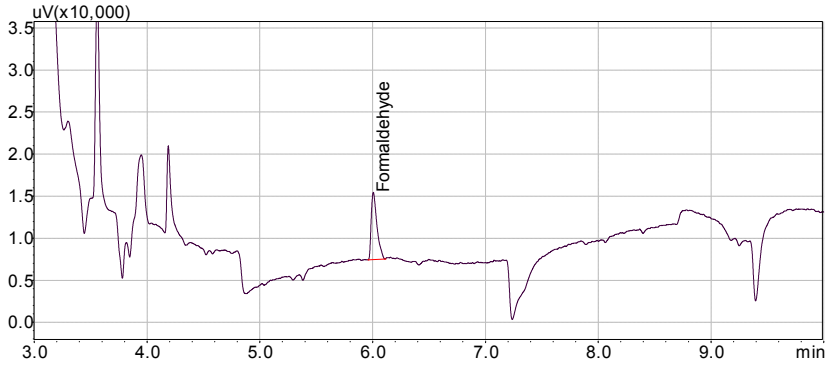
The presence of formaldehyde in reaction mixture was detected by Gas Chromatograph (SHIMADZU 2010) equipped with Ni^{63} electron capture detector (ECD). The chromatographic separation was performed using a RTX-5 column (30mX 0.25mm I.D. X 0.25µm) in split ratio of 50:1 with 1µL injection volume. The GC oven temperature was programmed as follows: initial temperature of 50 °C hold for 1 min, ramped at 5 °C per min to 100 °C hold for 3 min. The injector and detector temperatures were 180 °C and 280 °C, respectively.

GC chromatogram of formaldehyde generated in the reaction mixture





GC chromatogram of standard (formaldehyde)



References

1. T. Yasukawa, H. Miyamura, S. Kobayashi, *Chem. Soc. Rev.,* **43**, 1450 (2014).

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