Oxidative "reverse-esterification" of ethanol with benzyl/alkyl alcohols or aldehydes catalyzed by supported rhodium nanoparticles

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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. The XRD measurements were performed in 2-theta range 0-90^{o} on X'Pert Pro XRD, equipped with x'Celerator solid-state detector.

Preparation of supported rhodium (Rh@PS) catalyst

(a) Formation of catalytic quantity borohydride exchanged Amberlite resin

Amberlite® IRA 900 is an ion exchange resin consisting of large number of Polystyrene trimethylammonium chloride unit. 1 gm Amberlite® IRA 900 resin (Across, BE) and 30 mg of $NaBH_4$ were added into an 50 mL flask containg 10 mL aqueous solution. The mixture was then placed on magnetic stirrer and stirring continued for at least 4 hrs at room temperature. After optimal exchange of chloride ions by borohydride anions, the excess water solution was decanted and 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@PS

$RhCl_3.3H_2O$ (10 mg) was added to a suspension of borohydride exchanged resin beads (PR) (1g) in a mixture of THF and DMF (1:1) (2 mL) and then the mixture was stirred at room-temperature to 80 ^{o}C 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@PS thus obtained could be reused upto six cycles with consistent activity.

Charaterization data (HRTEM, Hg(0) test and Hot filtration experiment) for Rh@PS

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

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) Hg(0) poisoning test of Rh@PS for identifying the active Rh-species involved in the reaction

Mercury is a classical test to determine the heterogeneity of a catalyst of selective poisoning the metal(0) heterogeneous catalyst either by formation of amalgam or adsorption on metal surface.[1] Addition of mercury(0) (500 eqv. per Rh) to the reaction mixture containing *p*-OMe benzyl alcohol, **1a** (50 eqv.), KO^{t}Bu (200 eqv.) Rh@PS (1eqv.), ethanol (1.2 mL), 1,4-dioxane (1.2 mL) suppressed the oxidative esterification reaction completely indicating Rh(0) nanoparticles act as a true heterogeneous catalyst. This experiment also showed that Rh(0) species was only responsible for the described oxidative esterification reaction.

(c) Hot filtration test of Rh@PS

Hot filtration test was carried out with *p*-OMe benzyl alcohol (1 eqv.), ethanol (2 mL), KO^{t}Bu (4 eqv.), Rh@PS (2 mol% Rh) and 1,4-dioxane (1.2 mL) to imply the nature of the catalytic system for the esterification reaction. When this reaction mixture was refluxed at 125 ^{o}C for 20 h, the acetate ester **2a** was produced in 35% yield. After that, hot filtration was performed, no additional yield of product **2a** was observed upto 60 h exposure of the filtrate on heating at 125 ^{o}C. This result also implies that Rh(0) species, which is a real heterogeneous in nature, was participated during the course of the reaction.

Recyclability test of Rh@PS

The recyclability experiment of Rh@PS was done on *p*-OMe benzyl alcohol. After completion, the reaction mixture was filtered off through a cotton bed, washed with water and acetone properly, dried over rotary evaporator. Finally, the recovered dried catalyst was repeatedly used for the same reaction. The catalyst retained its activity upto six cycles of reaction with negligible metal leaching.

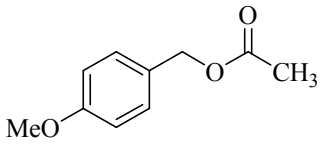
ICP-AES study of the reaction mixture

In the recyclability experiments, we have used 716 mg of Rh@PS (2 mol% Rh) for 200 mg of *p*-Me benzyl alcohol. 716 mg Rh@PS contains 2.79 mg rhodium metal when 10 mg $RhCl_3.3H_2O$ was allowed to bind on 1 gm of borohydride exchanged polystyrene resin matrix. After digesting the reaction mixture with acid solution, it was analyzed by 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	0.296	0.53
4th cycle	0.191	0.34
6th cycle	0.45	0.80

Typical experimental procedure for oxidative esterifications using Rh@PS catalyst:

***p*-OMe benzyl acetate (2a) (Table 1, entry 9)**

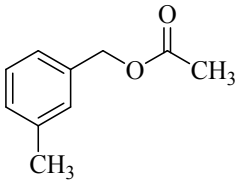


To an oven dried 50 mL round bottom flask equipped with a magnetic bar was charged *p*-MeO benzyl alcohol (200 mg, 1.44 mmol), KO^{t}Bu (649 mg, 5.79 mmol), and Rh@PS (716 mg, 2 mol% Rh. A combination of EtOH (2 mL) and 1,4-dioxane (1.2 mL) were added to the reaction mixture. After that, a condenser equipped with a rubber septum was tightly fitted to the round bottom flask. The reaction mixture was then refluxed under closed conditions at 120 ^{0}C for 55 h. Upon cooling, 2 mL H_2O was added to the reaction mixture and then was extracted with ethyl acetate (3x5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed *in vacuo*. The crude residue was purified by silica gel (mesh 60-120) chromatography-using (hexane: EtOAc = 98:2) as eluent to yield the title compound, *p*-OMe benzyl acetate **2a**, as a colourless liquid (195 mg, 75%). ^{1}H NMR (600 MHz; $CDCl_3$) δ (ppm) 2.09 (s, 3H), 3.82 (s, 3H), 5.06 (s, 2H), 6.90-6.92 (d, *J* = 8.4Hz, 2H), 7.31-7.33 (d, *J* =

8.4Hz, 2H). ^{13}C NMR (150 MHz; $CDCl_3$) δ (ppm) 21.01, 55.21, 66.07, 113.78 (2C), 128.00, 130.08 (2C), 159.58, 170.92. GC-MS (m/z): 180 [M]. IR (neat, cm^{-1}) : 2946, 1732, 1223 cm^{-1}.

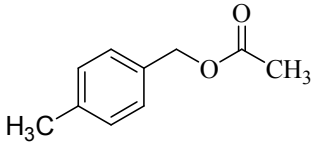
Synthesis and characterization data for the products of Table 2 and 3, and of Scheme 4

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



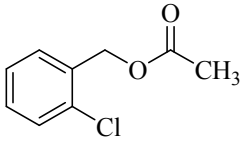
Prepared as described for *p*-Me benzyl alcohol, starting from **1b** (200 mg, 1.63 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2b** as colourless liquid (163 mg, 61%); ^{1}H NMR (300 MHz; $CDCl_3$) δ (ppm) 2.13 (s, 3H), 2.39 (s, 3H), 5.10 (s, 2H), 7.16-7.20 (m, 3H), 7.29-7.31 (m, 1H). ^{13}C NMR (75 MHz; $CDCl_3$) δ (ppm) 20.94, 21.29, 66.32, 125.29, 128.45, 128.96 (2C), 135.92, 138.23, 170.78. GC-MS (m/z): 164 [M]. IR (neat, cm^{-1}) : 2957, 1737, 1220.

p-Me benzyl acetate (2c) (Table 2, entry 2)



Prepared as described for *p*-Me benzyl alcohol, starting from **1c** (200 mg, 1.63 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2c** as colourless liquid (175 mg, 65%); ^{1}H NMR (600 MHz; $CDCl_3$) δ (ppm) 2.09 (s, 3H), 2.35 (s, 3H), 5.07 (s, 2H), 7.17-7.18 (d, J = 6.6 Hz, 2H), 7.25-7.26 (d, J = 6.6 Hz, 2H). ^{13}C NMR (150 MHz; $CDCl_3$) δ (ppm) 21.03, 21.17, 66.25, 128.42 (2C), 129.23 (2C), 132.90, 138.11, 170.94. GC-MS (m/z): 164 [M]. IR (neat, cm^{-1}) : 2927, 1737, 1224.

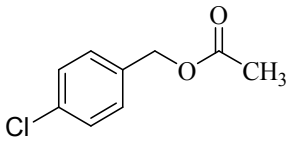
o-Cl benzyl acetate (2d) (Table 2, entry 3)



Prepared as described for *p*-OMe benzyl alcohol, starting from **1d** (200 mg, 1.40 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2d** as colourless liquid (148 mg, 57%); ^{1}H NMR (600 MHz; $CDCl_3$) δ (ppm) 2.14 (s, 3H), 5.22 (s, 2H), 7.26-

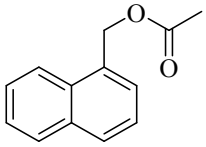
7.28 (m, 2H), 7.38-7.42 (m, 2H). ^{13}C NMR (150 MHz; $CDCl_3$) δ (ppm) 20.91, 63.66, 126.89, 129.53, 129.60, 129.87, 133.62, 133.72, 170.72. GC-MS (m/z): 184 [M]. IR (neat, cm^{-1}) : 2937, 1737, 1219.

***p*-Cl benzyl acetate (2e) (Table 2, entry 4)**



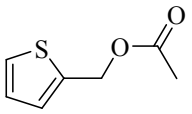
Prepared as described for *p*-OMe benzyl alcohol, starting from **1e** (200 mg, 1.40 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2e** as yellowish liquid (170 mg, 66%); ^{1}H NMR (600 MHz; $CDCl_3$) δ (ppm) 2.10 (s, 3H), 5.06 (s, 2H), 7.28-7.29 (d, *J* = 8.4 Hz, 2H), 7.32-7.33 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (150 MHz; $CDCl_3$) δ (ppm) 21.01, 65.49, 128.77 (2C), 129.69 (2C), 134.14, 134.43, 170.82. GC-MS (m/z): 184 [M]. IR (neat, cm^{-1}) : 2924, 1753, 1222.

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



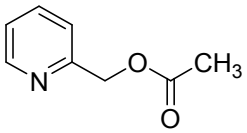
Prepared as described for *p*-OMe benzyl alcohol, starting from **1f** (200 mg, 1.26 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2f** as colourless liquid (176 mg, 70%); ^{1}H NMR (600 MHz; $CDCl_3$) δ (ppm) 2.12 (s, 3H), 5.58 (s, 2H), 7.45-7.48 (t, *J* = 7.8 Hz, 1H), 7.53-7.59 (m, 3H), 7.86-7.90 (dd, *J* = 7.8 Hz, 2H). 8.02-8.03 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (150 MHz; $CDCl_3$) δ (ppm) 21.06, 64.61, 123.57, 125.31, 125.99, 126.61, 127.54, 128.76, 129.34, 131.46, 131.65, 133.76, 171.01. GC-MS (m/z): 200 [M]. IR (neat, cm^{-1}) : 2931, 1732, 1220.

(thiophen-2-yl)methyl acetate (2g) (Table 2, entry 6)



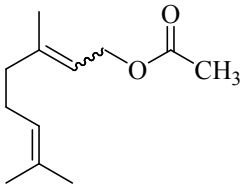
Prepared as described for *p*-OMe benzyl alcohol, starting from **1g** (200 mg, 1.75 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2g** as light yellowish liquid (138 mg, 50%); ^{1}H NMR (600 MHz; $CDCl_3$) δ (ppm) 2.08 (s, 3H), 5.25 (s, 2H), 6.98-6.99 (m 1H), 7.09 (d, *J* = 3.6 Hz, 1H), 7.31-7.32 (d, *J* = 5.4 Hz, 1H). ^{13}C NMR (150 MHz; $CDCl_3$) δ (ppm) 20.88, 60.40, 126.76, 126.78, 128.14, 137.86, 170.62. GC-MS (m/z): 156 [M]. IR (neat, cm^{-1}) : 2933, 1741, 1247.

(pyridin-2-yl)methyl acetate (2h) (Table 2, entry 7)



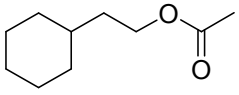
Prepared as described for *p*-OMe benzyl alcohol, starting from **1h** (200 mg, 1.83 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 95:5) **2h** as colourless liquid (148 mg, 53%); ^{1}H NMR (600 MHz; $CDCl_3$) δ (ppm) 2.14 (s, 3H), 5.20 (s, 2H), 7.20-7.22 (t, *J* = 6 Hz, 1H), 7.33-7.34 (d, *J* = 7.8 Hz, 1H), 7.67-7.68 (d, *J* = 7.8 Hz, 1H), 8.58 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (150 MHz; $CDCl_3$) δ (ppm) 20.92, 66.87, 121.86, 122.88, 136.76, 149.52, 155.75, 170.68. GC-MS (m/z): 108 $[M-43]^+$. IR (neat, cm^{-1}) : 2935, 1741, 1232.

3,7-dimethylocta-2,6-dienyl acetate (2i) (Table 2, entry 8)



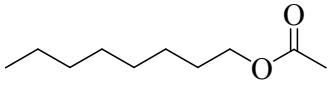
Prepared as described for *p*-OMe benzyl alcohol, starting from **1i** (200 mg, 1.29 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2i** as yellowish liquid (149 mg, 58%); ^{1}H NMR (300 MHz; Acetone-d_6) δ (ppm) 1.61 (s, 4H), 1.68 (s, 3H), 1.76 (s, 3H), 2.01 (s, 3H), 2.16 (s, 3H), 4.52-4.54 (m, 2H), 5.12-5.14 (m, 1H), 5.32-5.34 (m, 1H). ^{13}C NMR (75 MHz; Acetone-d_6) δ (ppm) 17.80, 20.93, 23.71, 25.96, 27.38, 32.76, 61.24, 120.70, 124.67, 132.43, 142.42, 170.79. GC-MS (m/z): 136 $[M-60]^+$. IR (neat, cm^{-1}) : 2957, 1737, 1236.

2-Cyclohexylethyl acetate (2j) (Table 2, entry 9)



Prepared as described for *p*-OMe benzyl alcohol, starting from **1j** (200 mg, 1.56 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2j** as colourless liquid (160 mg, 60%); ^{1}H NMR (600 MHz; $CDCl_3$) δ (ppm) 0.85-0.92 (m, 2H), 1.10-1.23 (m, 3H), 1.30-1.34 (m, 1H), 1.47-1.50 (q, *J* = 13.8 Hz, 2H), 1.60-1.69 (m, 5H), 2.01(s, 3H), 4.05-4.07 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz; $CDCl_3$) δ (ppm) 20.96, 26.21(2C), 26.40, 33.09 (2C), 34.46, 35.90, 62.69, 171.14. GC-MS (m/z): 110 $[M-60]^+$. IR (neat, cm^{-1}) : 2920, 1739, 1230.

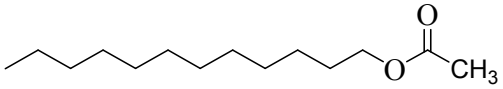
Octyl acetate (2k) (Table 2, entry 10)



Prepared as described for *p*-OMe benzyl alcohol, starting from **1k** (200 mg, 1.53 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2k** as

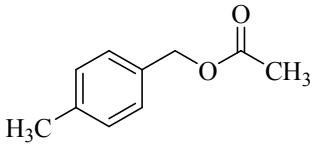
colourless liquid (160 mg, 60%); ^{1}H NMR (600 MHz; $CDCl_3$) δ (ppm) 0.86-0.88 (t, *J* = 7.2 Hz, 3H), 1.24-1.31 (m, 10H), 1.59-1.62 (t, *J* = 7.8 Hz, 2H), 2.03 (s, 3H), 4.03-4.05 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (150 MHz; $CDCl_3$) δ (ppm) 14.07, 21.01, 22.63, 25.91, 28.60, 29.18, 29.70, 31.78, 64.67, 171.24. GC-MS (m/z): 112 $[M-60]^+$. IR (neat, cm^{-1}) : 2925, 1736, 1222.

Dodecyl acetate (2l) (Table 2, entry 11)



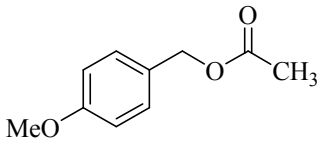
Prepared as described for *p*-OMe benzyl alcohol, starting from **1l** (200 mg, 1.07 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2l** as light yellowish liquid (140 mg, 57%); ^{1}H NMR (600 MHz; $CDCl_3$) δ (ppm) 0.84-0.87 (t, *J* = 7.2 Hz, 3H), 1.27-1.31 (m, 18H), 1.58-1.60 (t, *J* = 7.8 Hz, 2H), 2.02 (s, 3H), 4.01-4.04 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz; $CDCl_3$) δ (ppm) 14.03, 20.90, 22.64, 25.89, 28.60, 29.23, 29.31, 29.49, 29.54, 29.59, 29.60, 31.88, 64.60, 171.09. GC-MS (m/z): 168 $[M-60]^+$. IR (neat, cm^{-1}) : 2920, 1741, 1232.

***p*-Me benzyl acetate (2m) (Table 3, entry 1)**



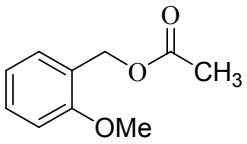
Prepared as described for *p*-OMe benzyl alcohol, starting from *p*-Me benzaldehyde **1m** (200 mg, 1.66 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2m** as colourless liquid (150 mg, 55%). NMR, GCMS and IR spectra of the title compound **2m** was same as that of **2c**.

***p*-OMe benzyl acetate (2n) (Table 3, entry 2)**



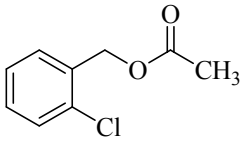
Prepared as described for *p*-OMe benzyl alcohol, starting from *p*-OMe benzaldehyde **1n** (200 mg, 1.47 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2n** as colourless liquid (134 mg, 51%). NMR, GCMS and IR spectra of the title compound **2n** was same as that of **2a**.

***o*-OMe benzyl acetate (2o) (Table 3, entry 3)**



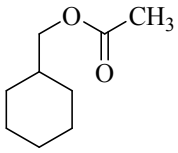
Prepared as described for *p*-OMe benzyl alcohol, starting from *o*-OMe benzaldehyde **1o** (200 mg, 1.47 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2o** as colourless liquid (132 mg, 50%); ^{1}H NMR (600 MHz; $CDCl_3$) δ (ppm) 2.01 (s, 3H), 3.75 (s, 3H), 5.08 (s, 2H), 6.79-6.81 (d, *J* = 6.6 Hz, 1H) 6.85-6.87 (t, *J* = 6.6 Hz, 1H), 7.20-7.24 (m, 2H). ^{13}C NMR (150 MHz; $CDCl_3$) δ (ppm) 21.03, 55.39, 61.73, 110.49, 120.40, 124.28, 129.58, 129.82, 157.52, 171.02. GC-MS (m/z): 180 [M]. IR (neat, cm^{-1}) : 2932, 1732, 1222.

_o_-Cl benzyl acetate (2p) (Table 3, entry 4)



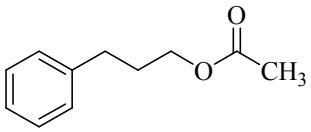
Prepared as described for *p*-OMe benzyl alcohol, starting from *o*-chloro benzaldehyde **1p** (200 mg, 1.42 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2p** as colourless liquid (151 mg, 57%). NMR, GCMS and IR spectra of the title compound **2p** was same as that of **2d**.

Cyclohexylmethyl acetate (2q) (Table 3, entry 5)



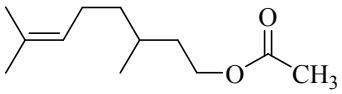
Prepared as described for *p*-OMe benzyl alcohol, starting from cyclohexane carbaldehyde **1q** (200 mg, 1.78 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2q** as yellowish liquid (183 mg, 66%); ^{1}H NMR (600 MHz; $CDCl_3$) δ (ppm) 0.93-1.01 (m, 3H), 1.19-1.32 (m, 4H), 1.64-1.73 (m, 4H), 2.04 (s, 3H), 3.86 (s, 2H). ^{13}C NMR (150 MHz; $CDCl_3$) δ (ppm) 20.93, 25.74 (2C), 26.36, 29.66 (2C), 37.05, 69.67, 171.27. GC-MS (m/z): 96 $[M-60]^{+}$. IR (neat, cm^{-1}) : 2968, 1745, 1257.

3-phenylpropyl acetate (2r) (Table 3, entry 6)



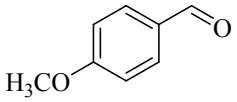
Prepared as described for *p*-OMe benzyl alcohol, starting from **1r** (200 mg, 1.49 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 95:5) **2r** as colourless liquid (107 mg, 40%). NMR, GCMS and IR spectra of the title compound **2t** has been matched with our previous study (see reference 13 in main manuscript).

3,7-dimethyloct-6-eny acetate (**2s**) (**Table 3, entry 7**)



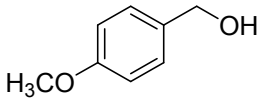
Prepared as described for *p*-OMe benzyl alcohol, starting from **1s** (200 mg, 1.29 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc = 98:2) **2s** as colourless liquid (116 mg, 45%); ^{1}H NMR (300 MHz; $CDCl_3$) δ (ppm) 0.90-0.94 (m, 3H), 1.27-1.35 (m, 4H), 1.60-1.62 (m, 4H), 1.68-1.70 (m, 4H), 2.06-2.09 (m, 4H), 4.07-4.14 (m, 1H), 4.53-4.57 (m, 1H), 5.10-5.11 (m, 1H). ^{13}C NMR (75 MHz; $CDCl_3$) δ (ppm) 17.63, 19.43, 21.00, 25.41, 26.35, 29.56, 35.49, 37.01, 63.05, 124.61, 131.32, 171.15. GC-MS (m/z): 138 [M-60]. IR (neat) : 2954, 1746, 1232 cm^{-1}.

***p*-OMe benzaldehyde (1t) (Scheme 4a)**



A mixture of *p*-OMe benzyl alcohol, **1a** (100mg, 0.7237mmol), KO^{t}Bu (244 mg, 2.17 mmol), Rh@PS (360 mg, 2 mol% Rh) and 2mL of 1,4-dioxane were taken in an oven dried 50 mL round bottom flask and refluxed at 120 ^{0}C for 5h. 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 **1t** as colorless liquid (87 mg, 88%).^{1}H NMR (600 MHz; $CDCl_3$) δ 3.86 (s, 3H), 6.97 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 2H), 9.85 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.48, 114.24 (2C), 129.87, 131.89 (2C), 164.54, 190.73.

***p*-OMe benzyl alcohol (1a) (Scheme 4b)**



A mixture of *p*-OMe benzaldehyde (100mg, 0.73 mmol), KO^{t}Bu (468 mg, 2.20 mmol), Rh@PS (365 mg, 2 mol% Rh), 2 mL of EtOH and 1.2 mL of 1,4-dioxane were taken in an oven dried 50 mL round bottom flask and heated at 120 ^{0}C for 15 h. The progress of reaction was monitored on TLC. After completion, the reaction was cooled, diluted with ethyl acetate and water and filtered through a 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 colourless liquid (80 mg, 79%).^{1}H NMR (600 MHz; $CDCl_3$) δ 3.80 (s, 3H), 4.59 (s, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.24, 64.90, 113.89 (2C), 128.58 (2C), 133.1, 159.13.

Acetaldehyde (2t) (Scheme 4c)

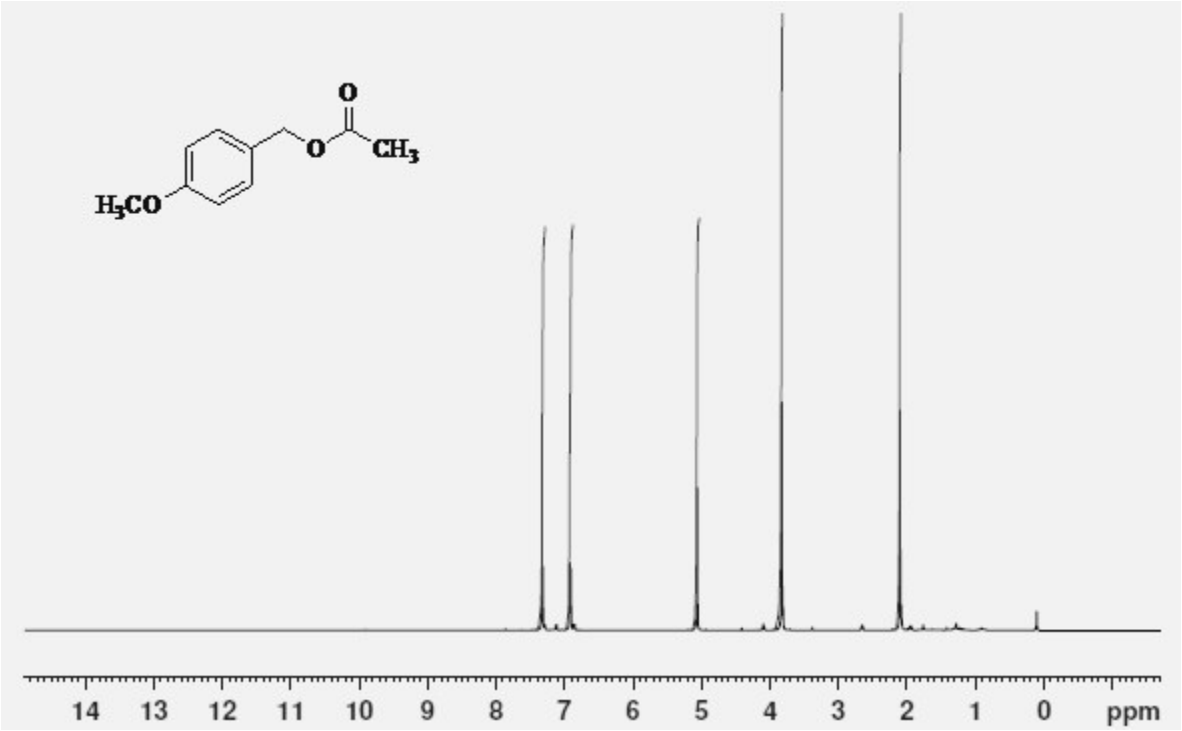
A mixture of ethanol (2 mL), KO^{t}Bu (649 mg), Rh@PS (716 mg, 2 mol% Rh) and 1.2 mL of 1,4-dioxane were taken in an oven dried 50 mL round bottom flask and refluxed at 120 ^{0}C for 55h. The reaction mixture was then analyzed by Infrared spectral study analysis. Formation of acetaldehyde **2t** was confirmed as compared with the standard as shown in IR-spectra (given below).

***p*-OMe benzyl acetate (2a) from acetaldehyde (Scheme 4d)**

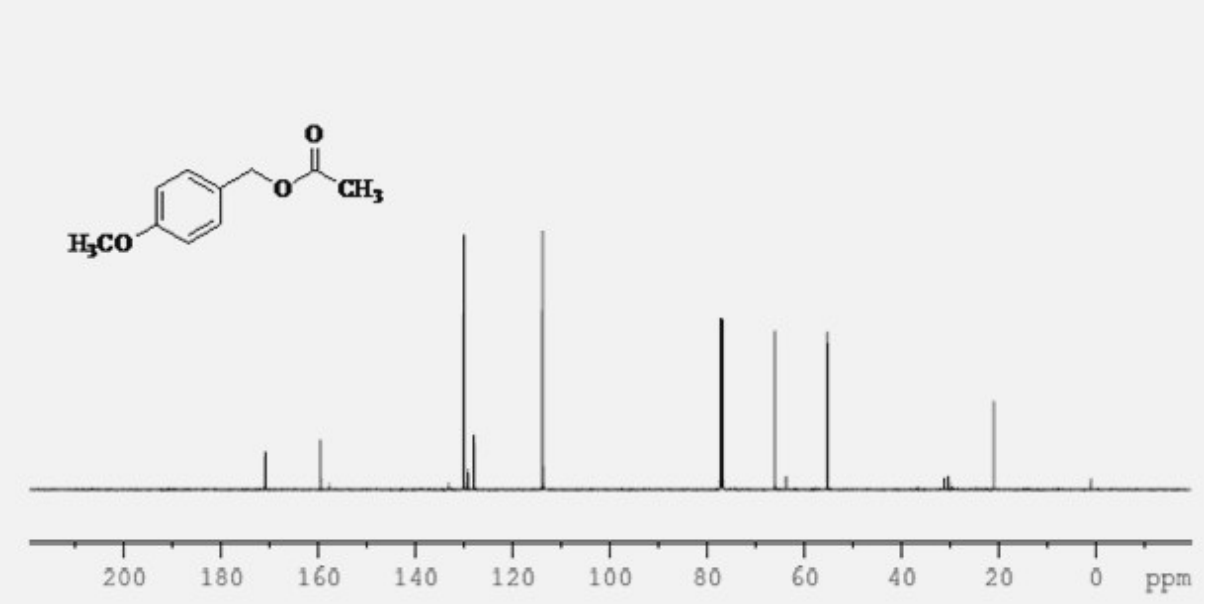
A mixture of *p*-OMe benzyl alcohol (100 mg, 0.723 mmol), acetaldehyde (187 mg, 4.34 mmol), and 2 mL of 1,4-dioxane were taken in an oven dried 50 mL round bottom flask and heated with continuous stirring at 120 ^{0}C for 2 h. A mixture of KO^{t}Bu (162 mg, 1.44 mmol) and Rh@PS (360 mg, 2 mol% Rh) were then added to the reaction mixture and refluxed at 120 ^{o}C for 42 h. The progress of reaction was monitored on TLC. After completion, 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*-OMe benzyl acetate as colorless liquid (85 mg, 65%). ^{1}H NMR (600 MHz; $CDCl_3$) δ (ppm) 2.08 (s, 3H), 3.81 (s, 3H), 5.04 (s, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (150 MHz; $CDCl_3$) δ (ppm) 21.05, 55.27, 66.11, 113.95 (2C), 128.07, 130.11 (2C), 159.65, 170.96. GC-MS (m/z): 180 [M]. IR-spectra was same as that of **2a**.

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

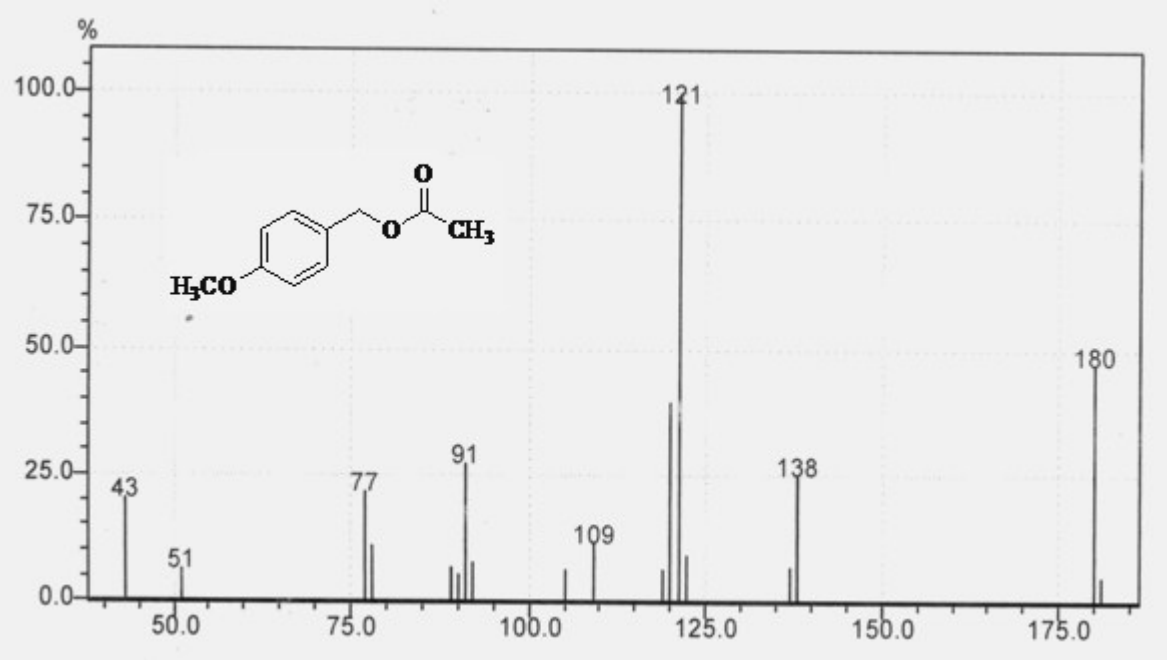
***p*-OMe benzyl acetate (2a) (Table 1, entry 9), ^{1}H NMR (600 MHz, $CDCl_3$)**



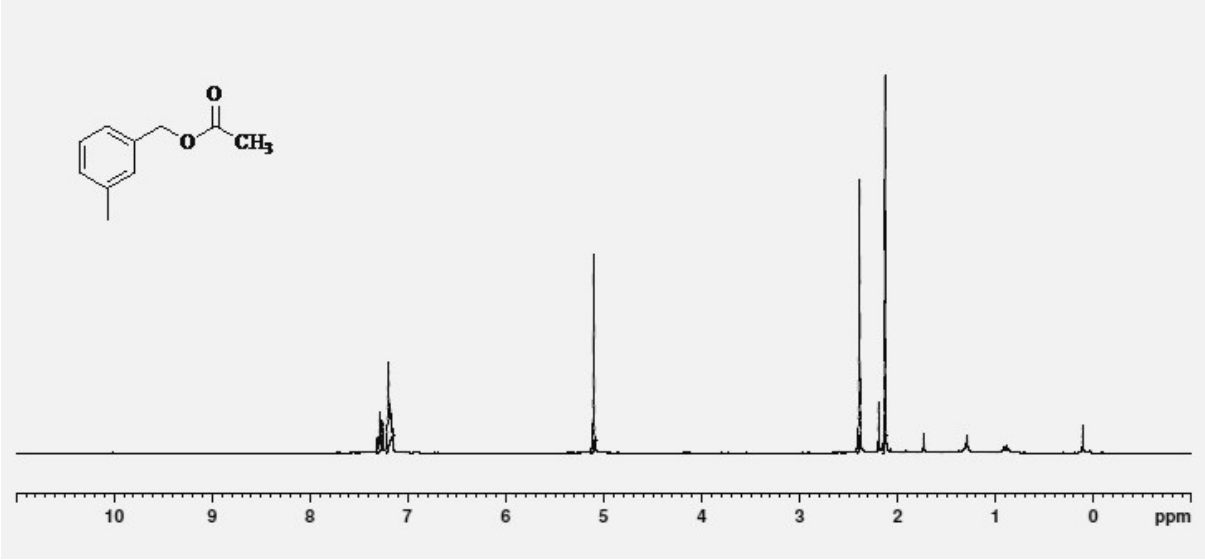
***p*-OMe benzyl acetate (2a) (Table 1, entry 9), ^{13}C NMR (150 MHz, $CDCl_3$)**



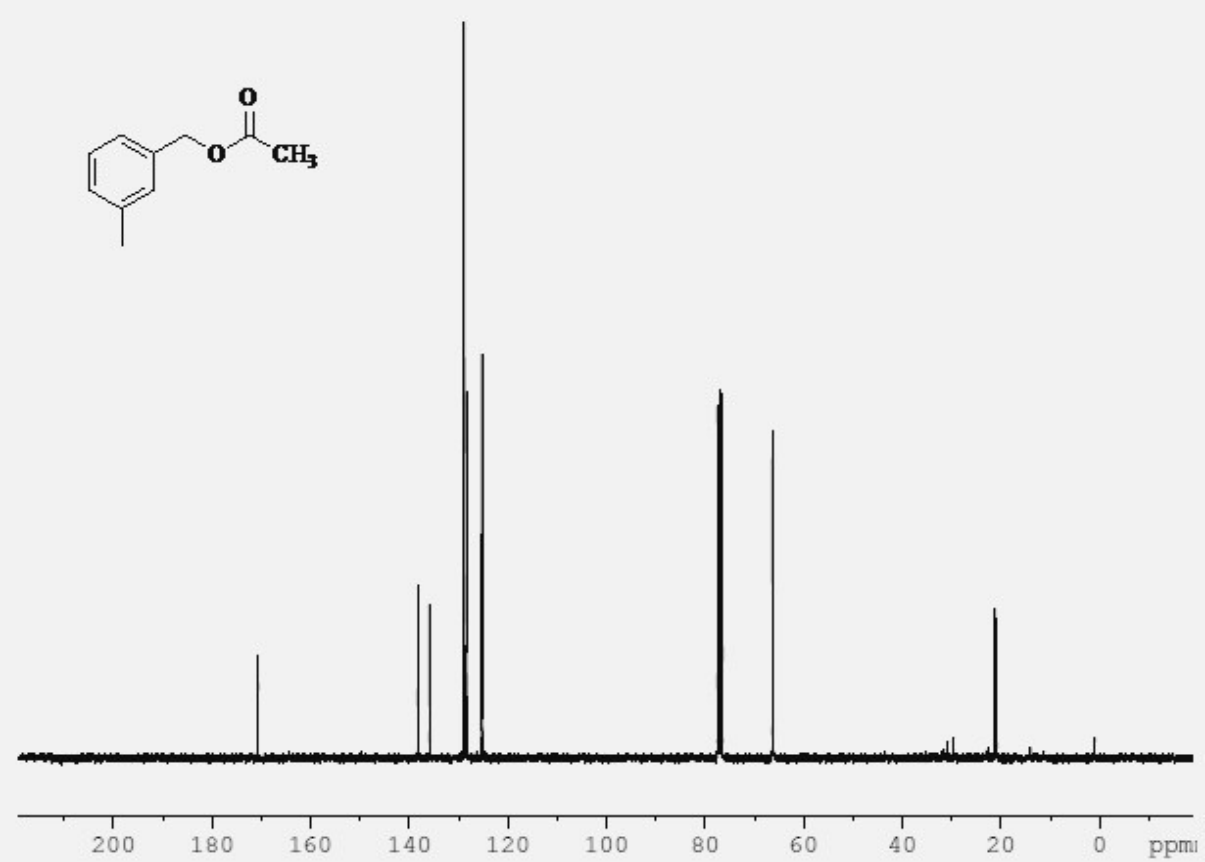
***p*-OMe benzyl acetate (2a) (Table 1, entry 9), GC-MS Spectra.**



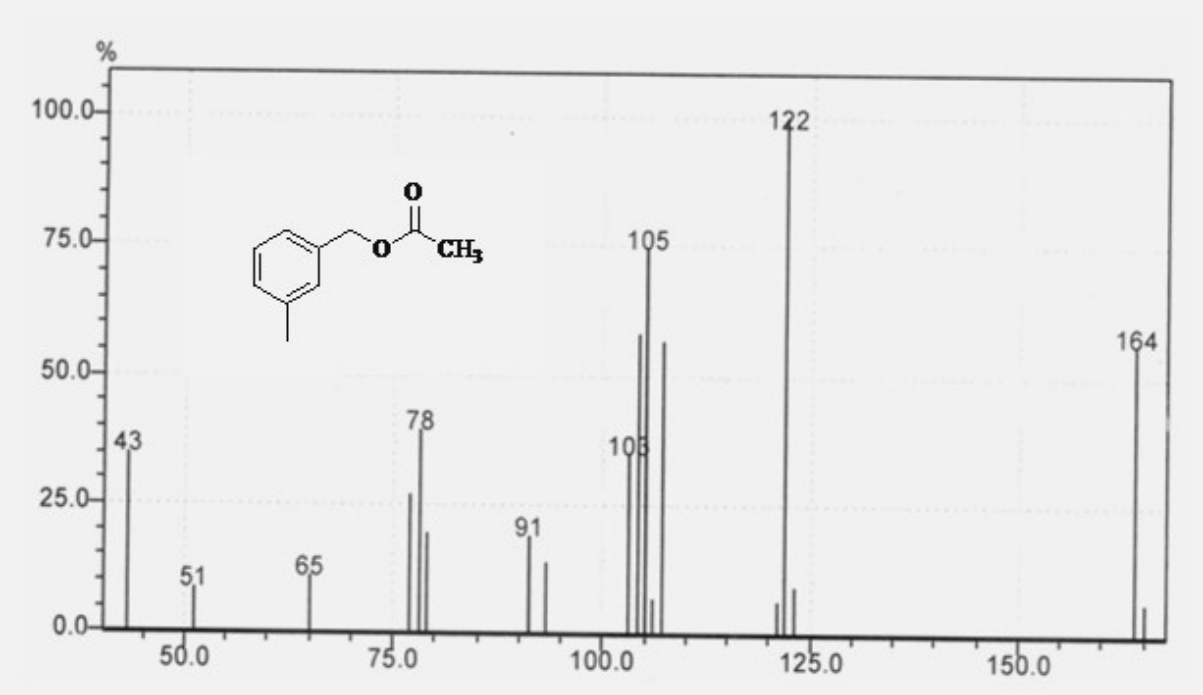
***m*-Me benzyl acetate (2b) (Table 2, entry 1), ^{1}H NMR (300 MHz, $CDCl_3$)**



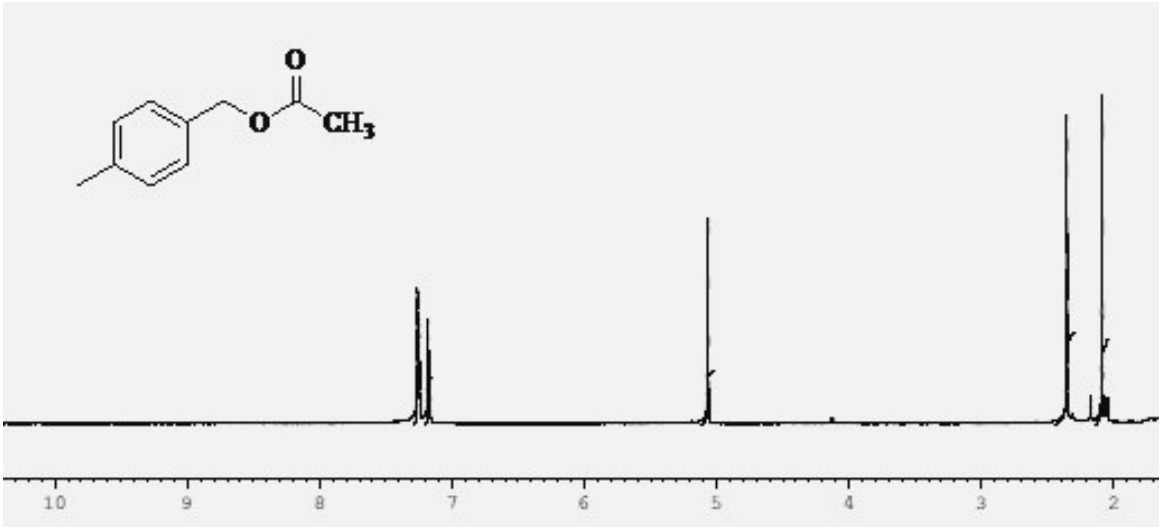
***m*-Me benzyl acetate (2b) (Table 2, entry 1), ^{13}C NMR (150 MHz, $CDCl_3$)**



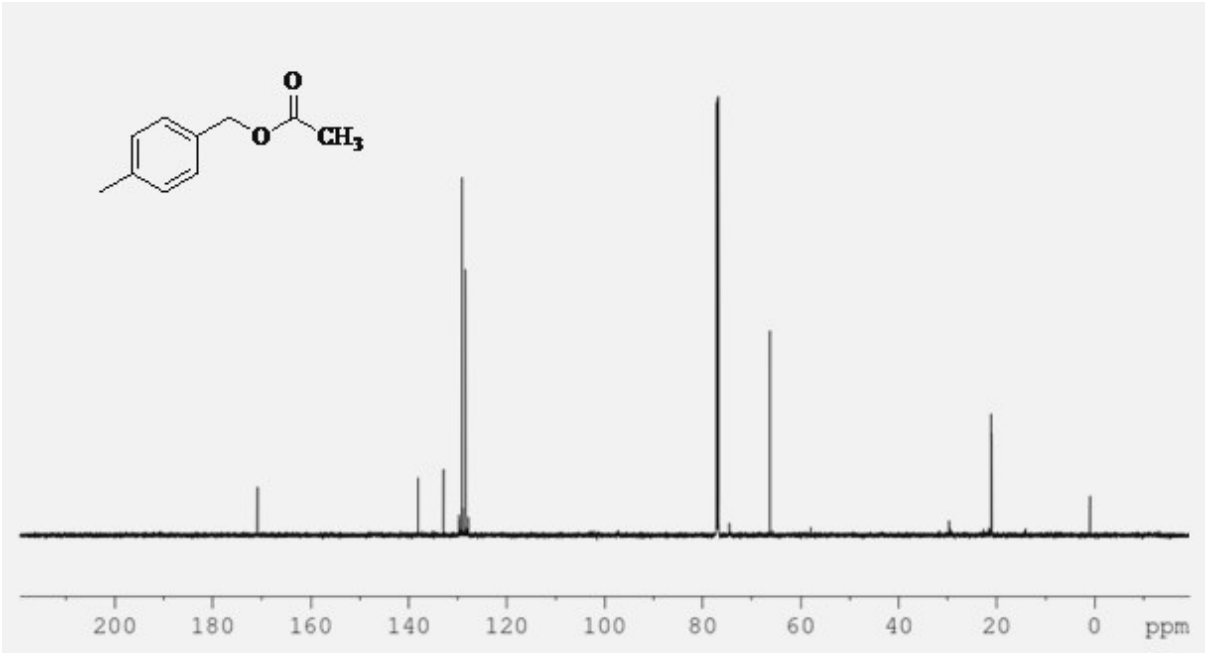
***m*-Me benzyl acetate (2b) (Table 2, entry 1), GC-MS Spectra**



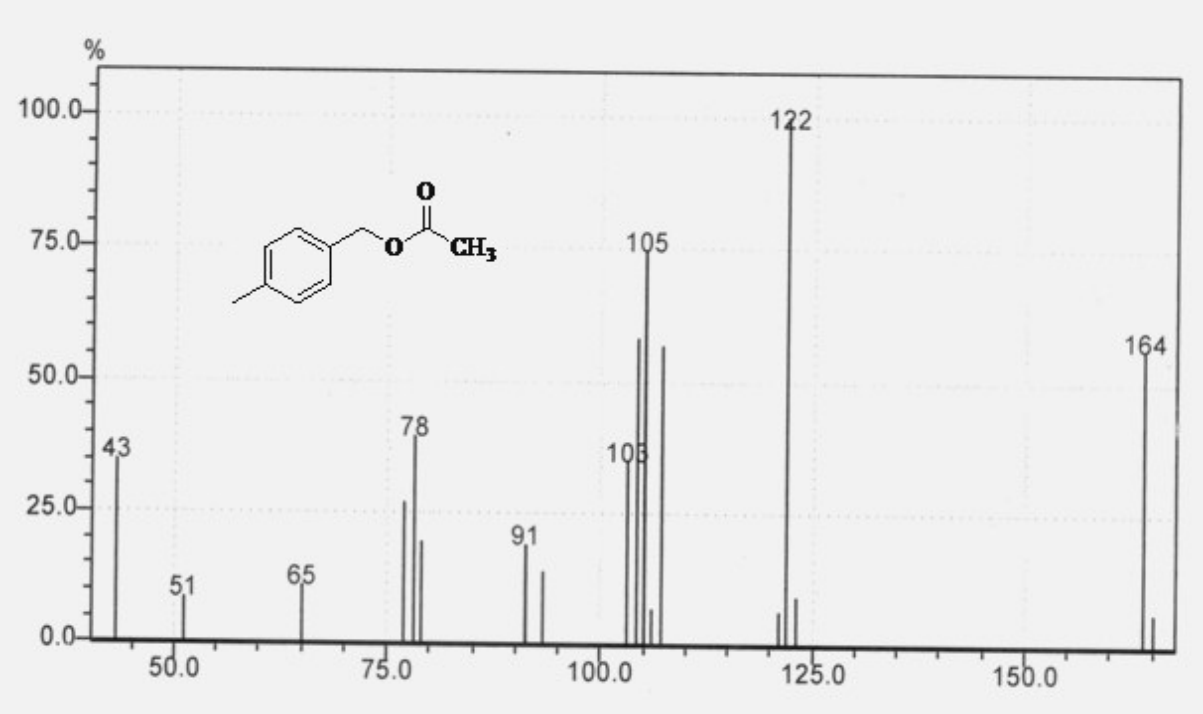
***p*-Me benzyl acetate (2c) (Table 2, entry 2), ^{1}H NMR (600 MHz, $CDCl_3$)**



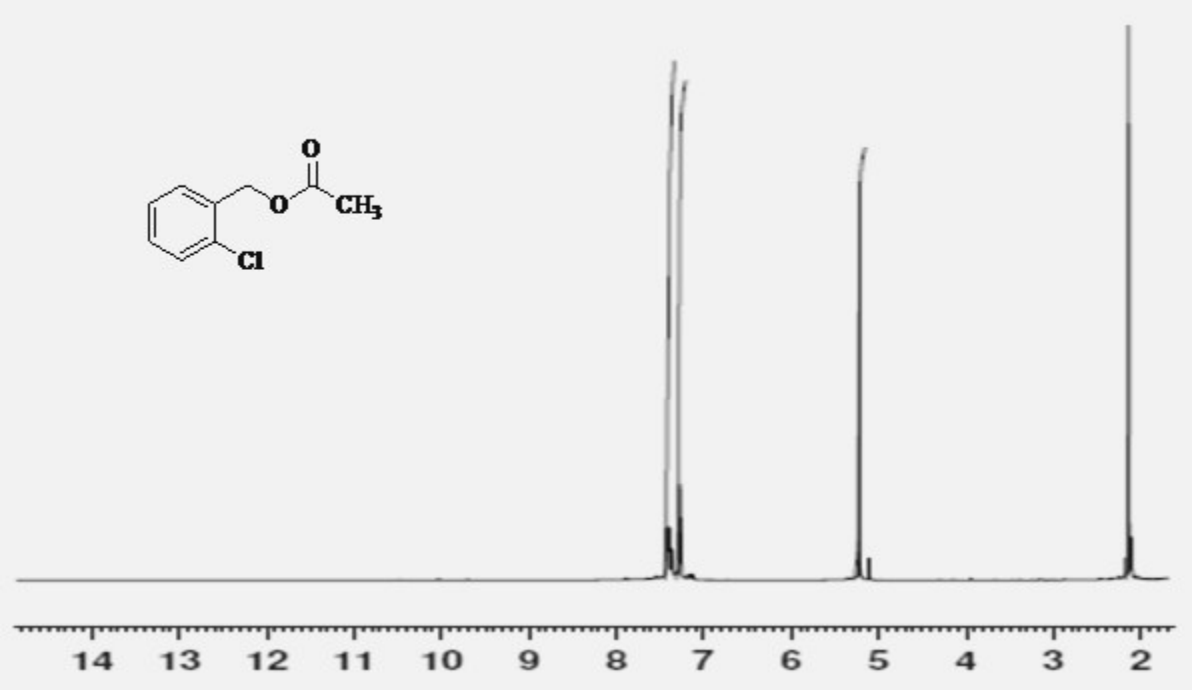
***p*-Me benzyl acetate (2c) (Table 2, entry 2), ^{13}C NMR (150 MHz, $CDCl_3$)**



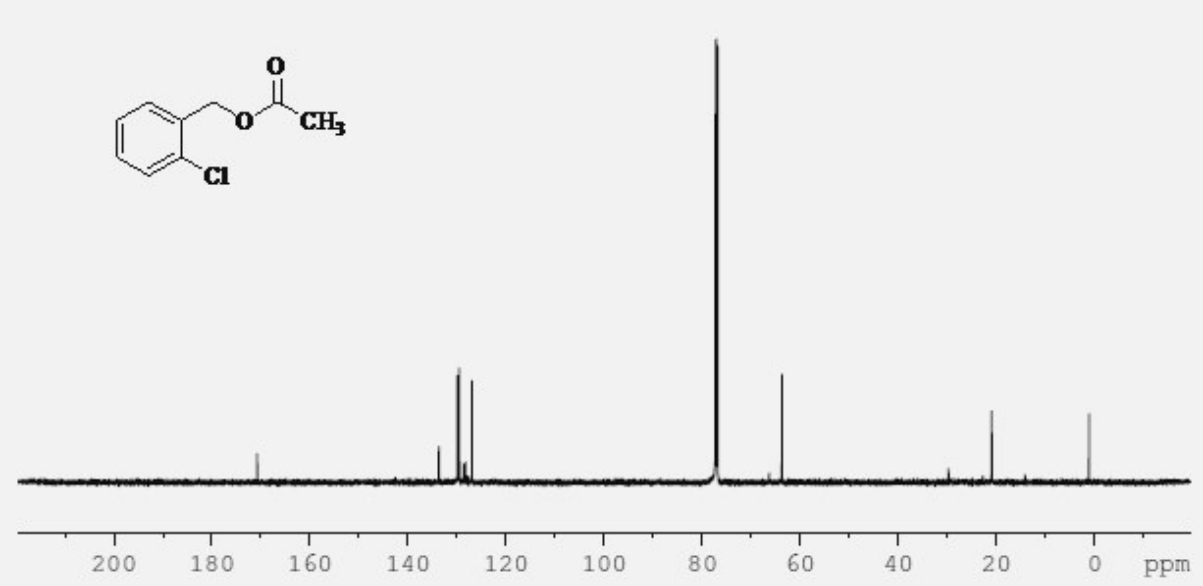
***p*-Me benzyl acetate (2c) (Table 2, entry 2), GC-MS Spectra**



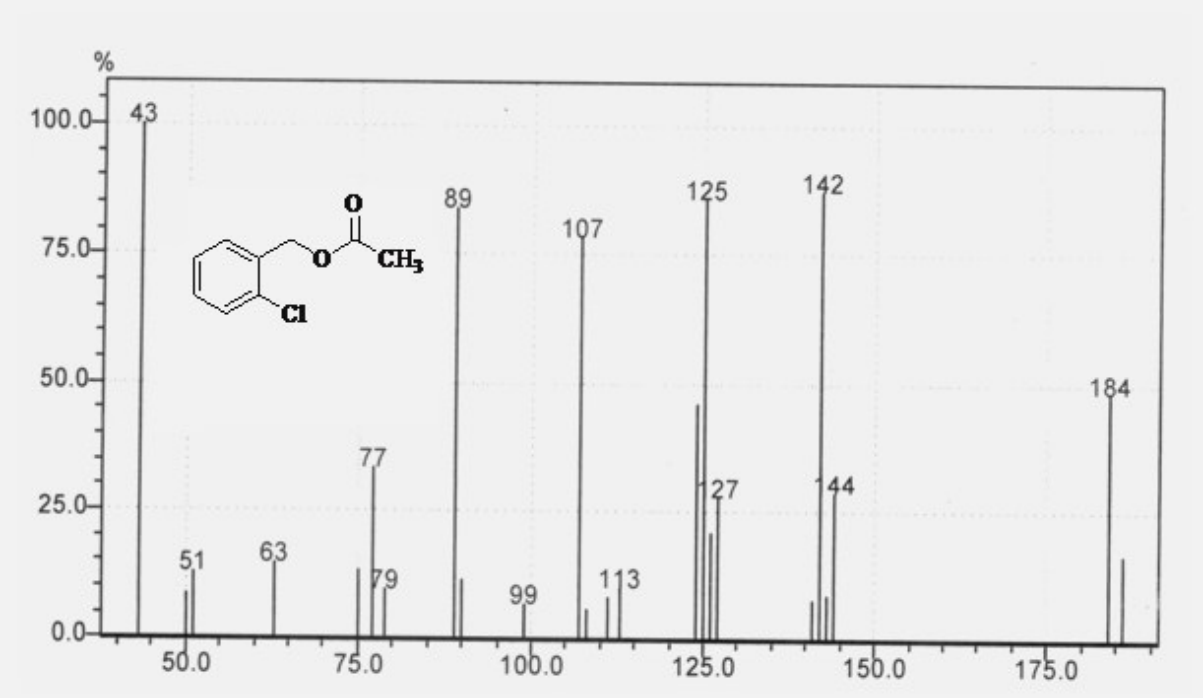
***o*-Cl benzyl acetate (2d) (Table 2, entry 3), ^{1}H NMR (600 MHz, $CDCl_3$)**



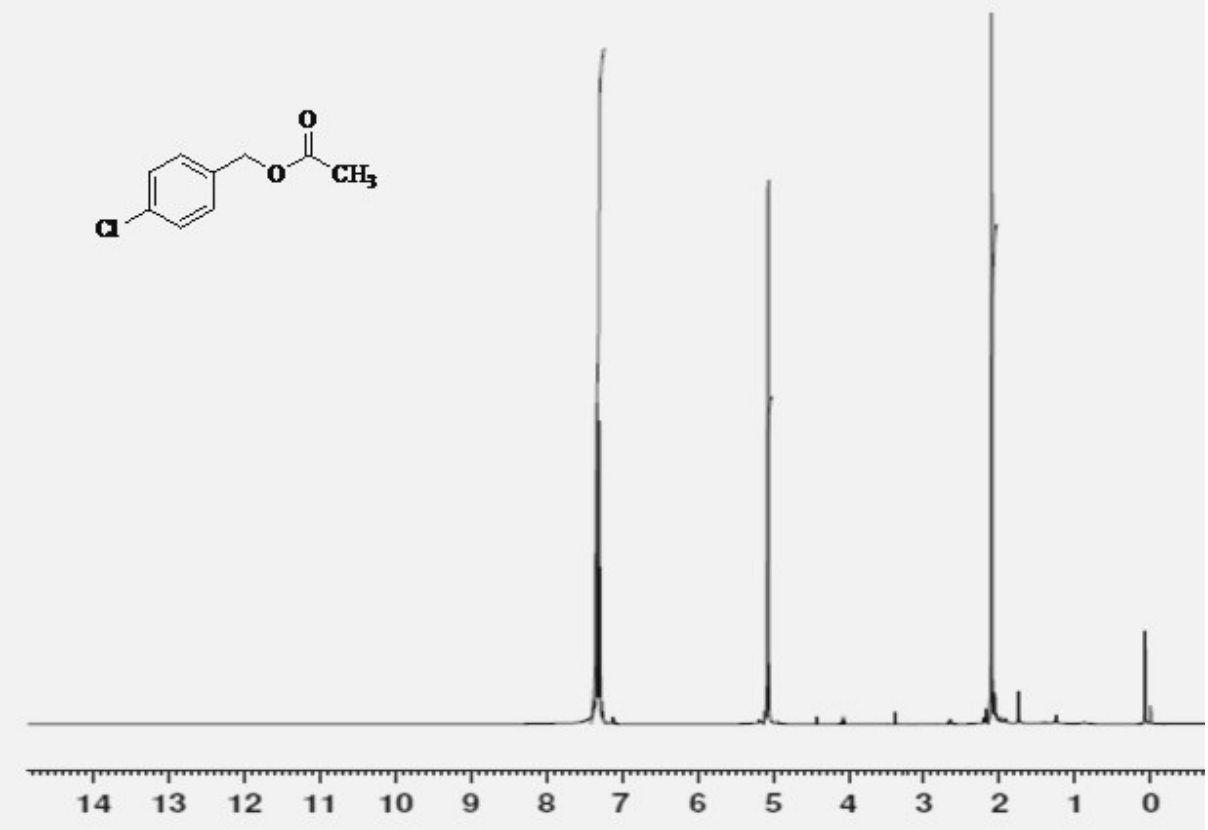
***o*-Cl benzyl acetate (2d) (Table 2, entry 3), ^{13}C NMR (150 MHz, $CDCl_3$)**



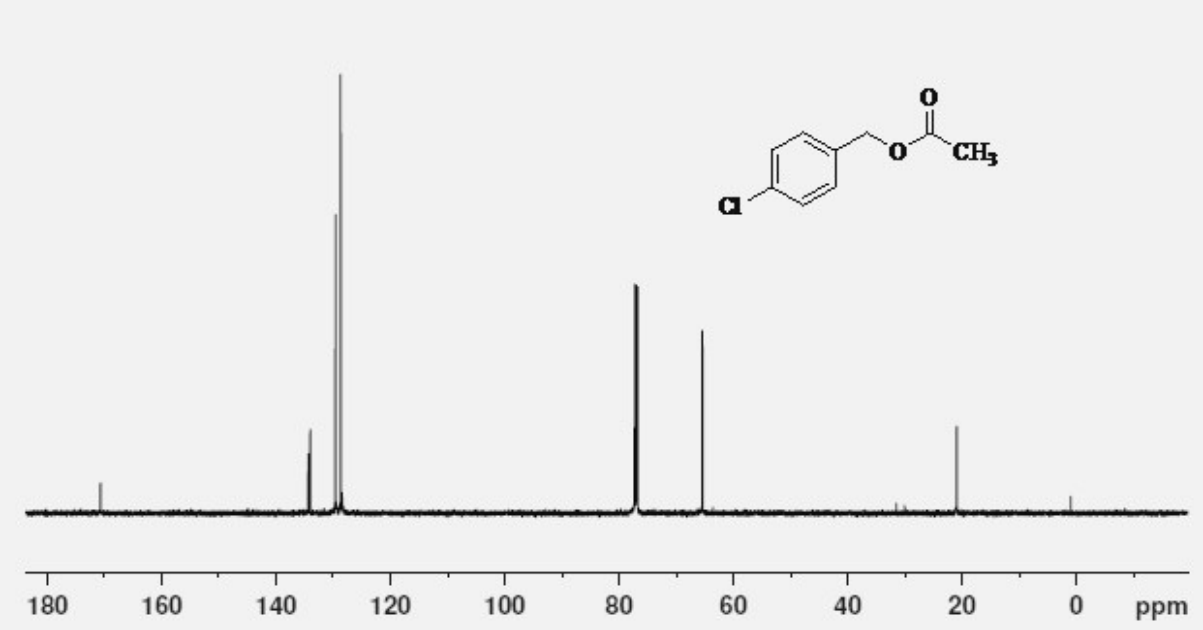
***o*-Cl benzyl acetate (2d) (Table 2, entry 3), GC-MS Spectra**



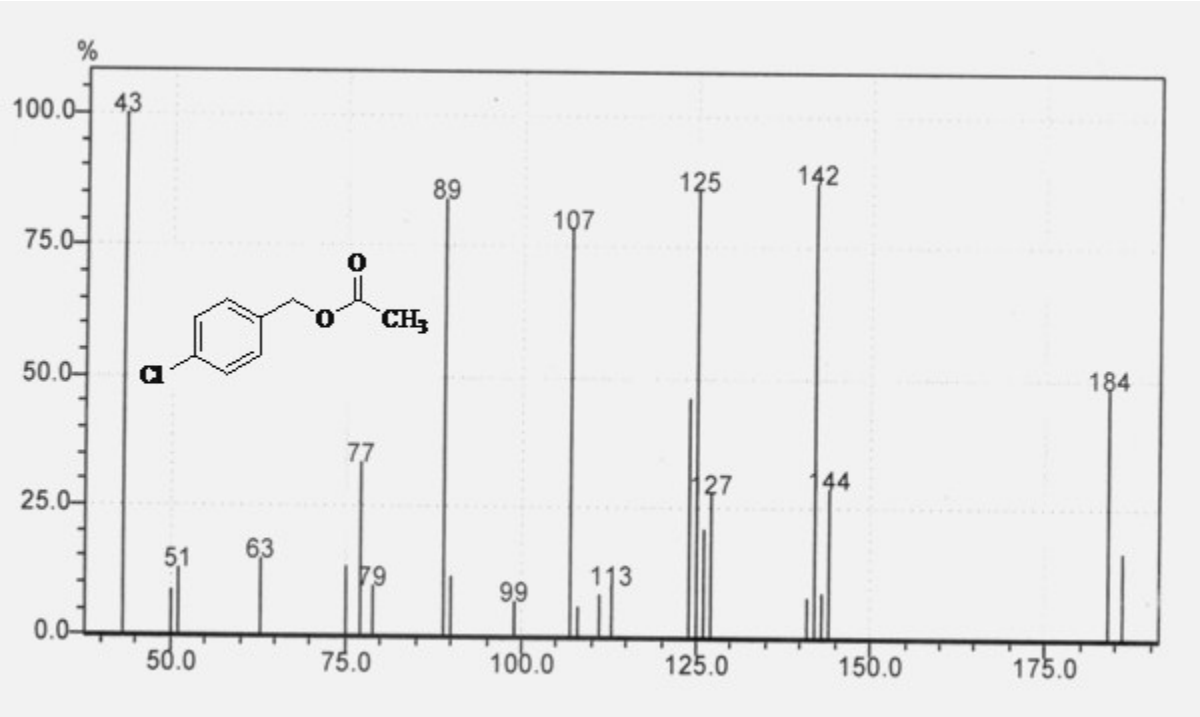
***p*-Cl benzyl acetate (2e) (Table 2, entry 4), ^{1}H NMR (600 MHz, $CDCl_3$)**



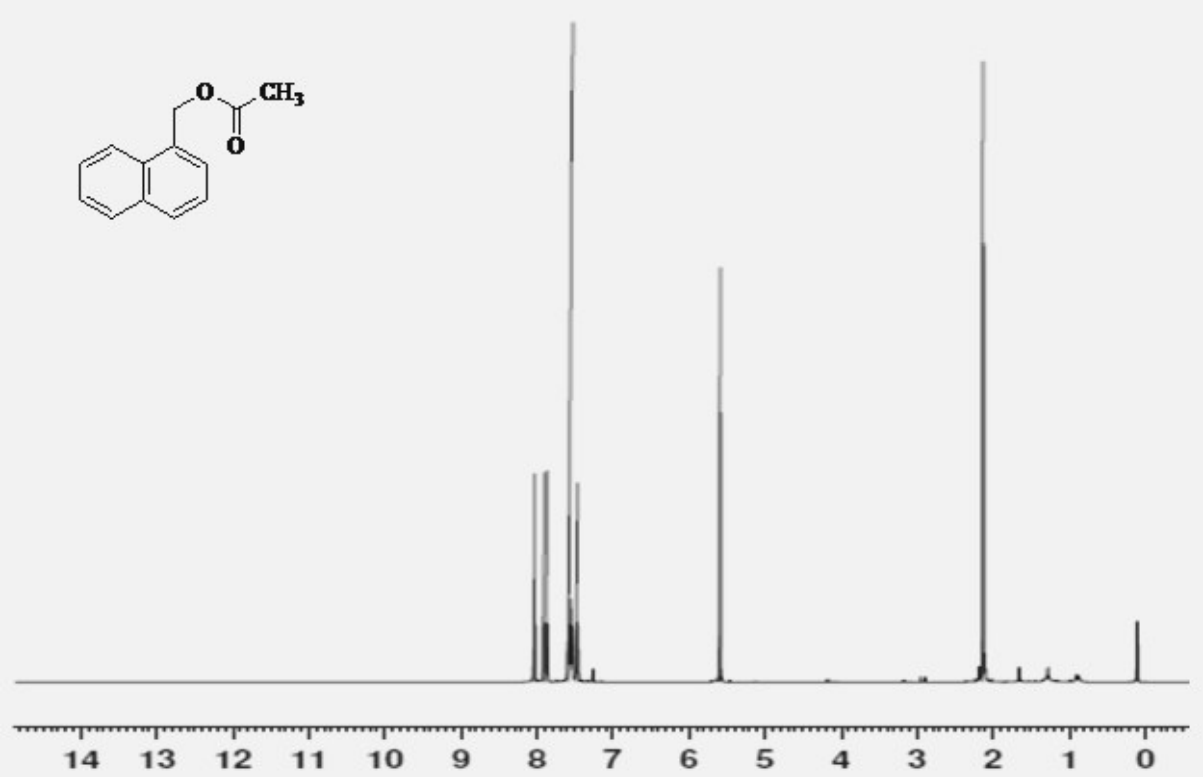
***p*-Cl benzyl acetate (2e) (Table 2, entry 4), ^{13}C NMR (150 MHz, $CDCl_3$)**



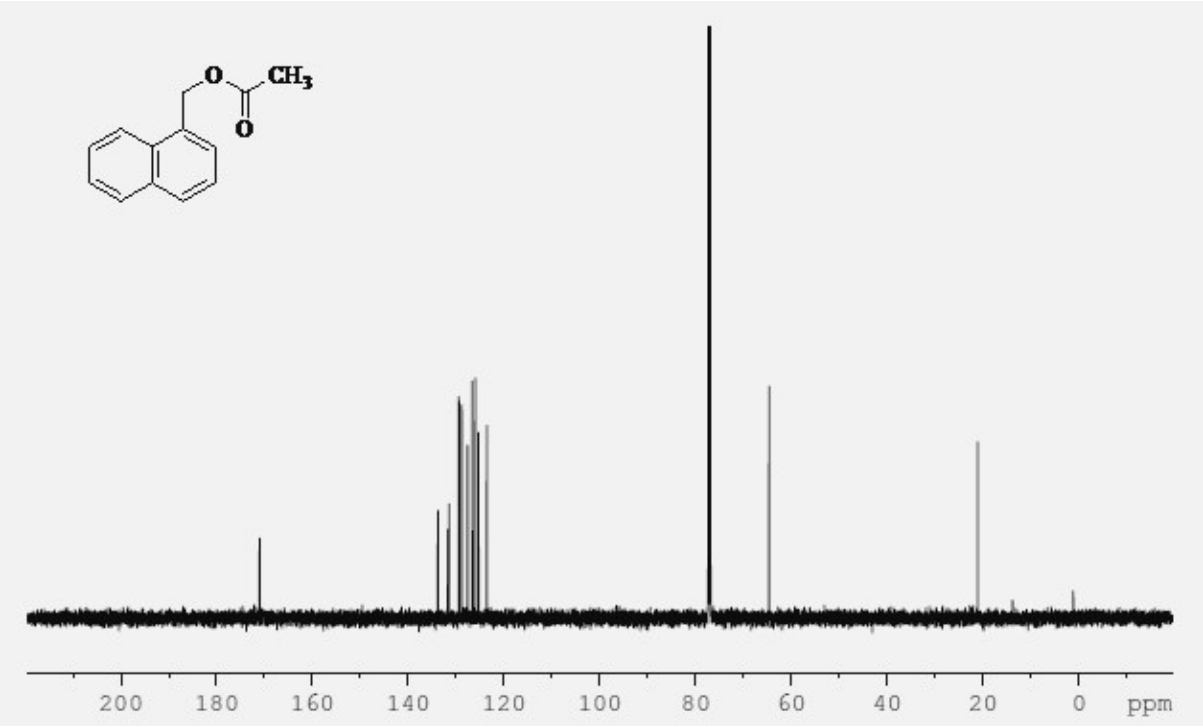
***p*-Cl benzyl acetate (2e) (Table 2, entry 4), GC-MS Spectra**



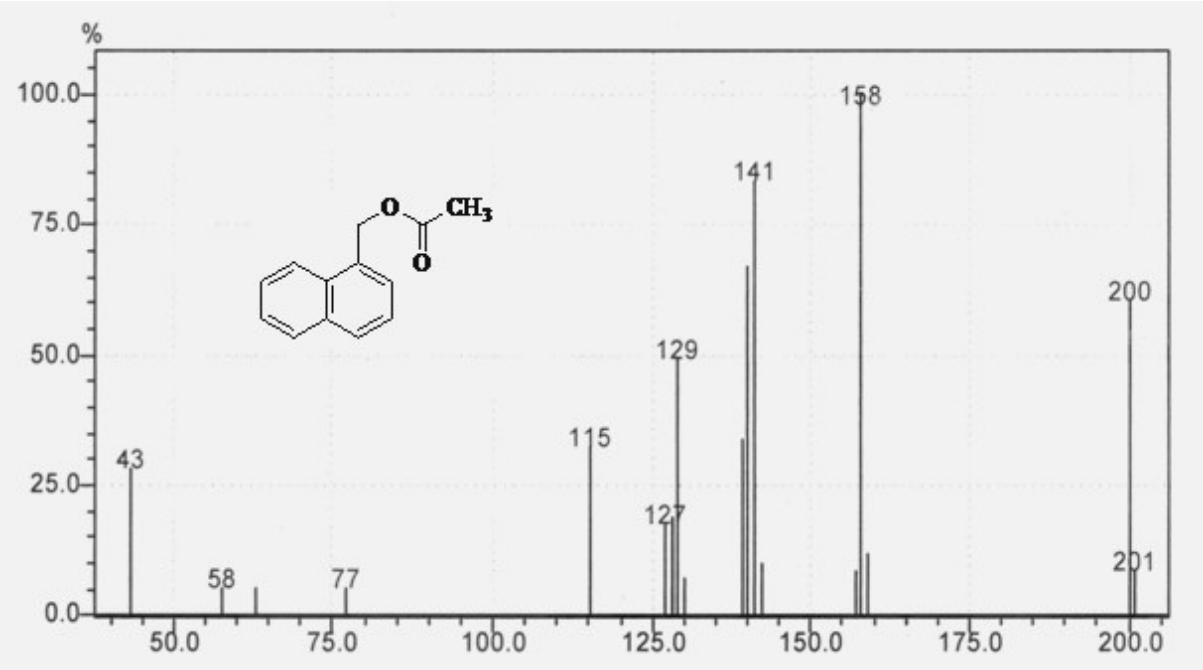
(naphthalen-5-yl)methyl acetate (2f) (Table 2, entry 5), ^{1}H NMR (600 MHz, $CDCl_3$)



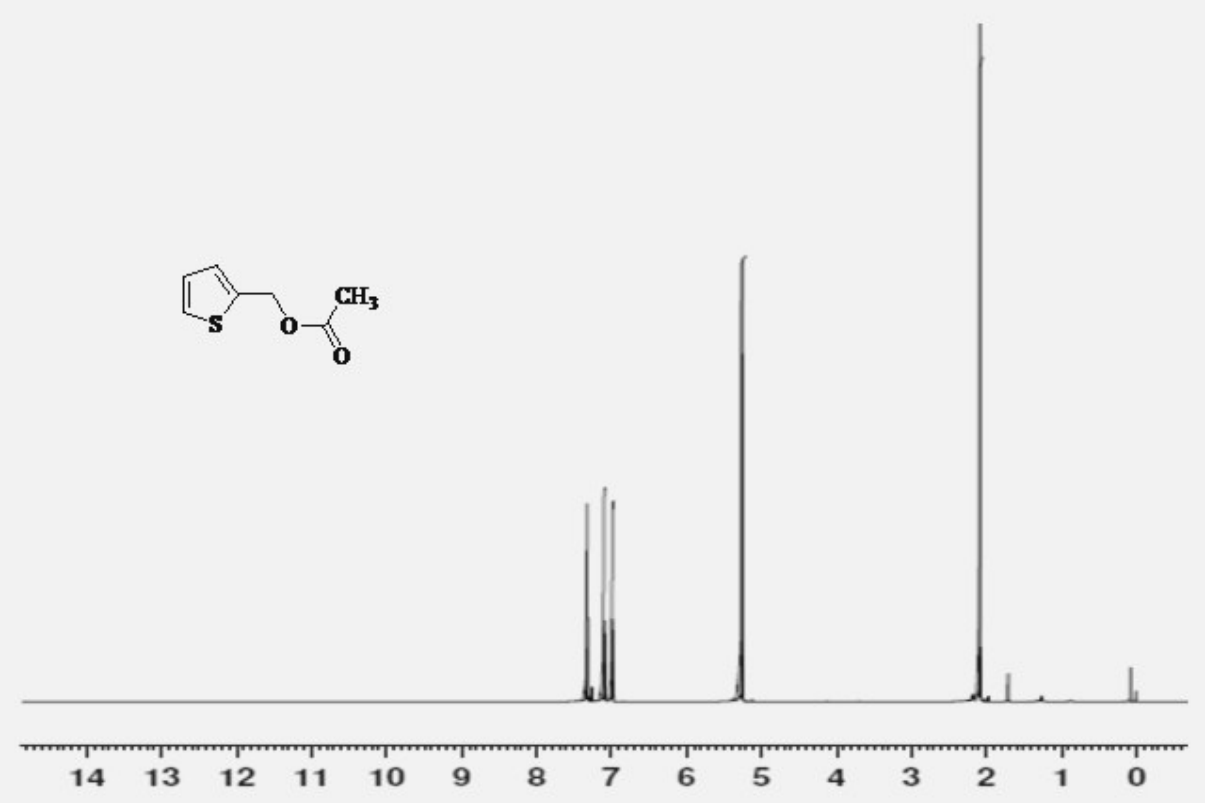
(naphthalen-5-yl)methyl acetate (2f) (Table 2, entry 5), ^{13}C NMR (150 MHz, $CDCl_3$)



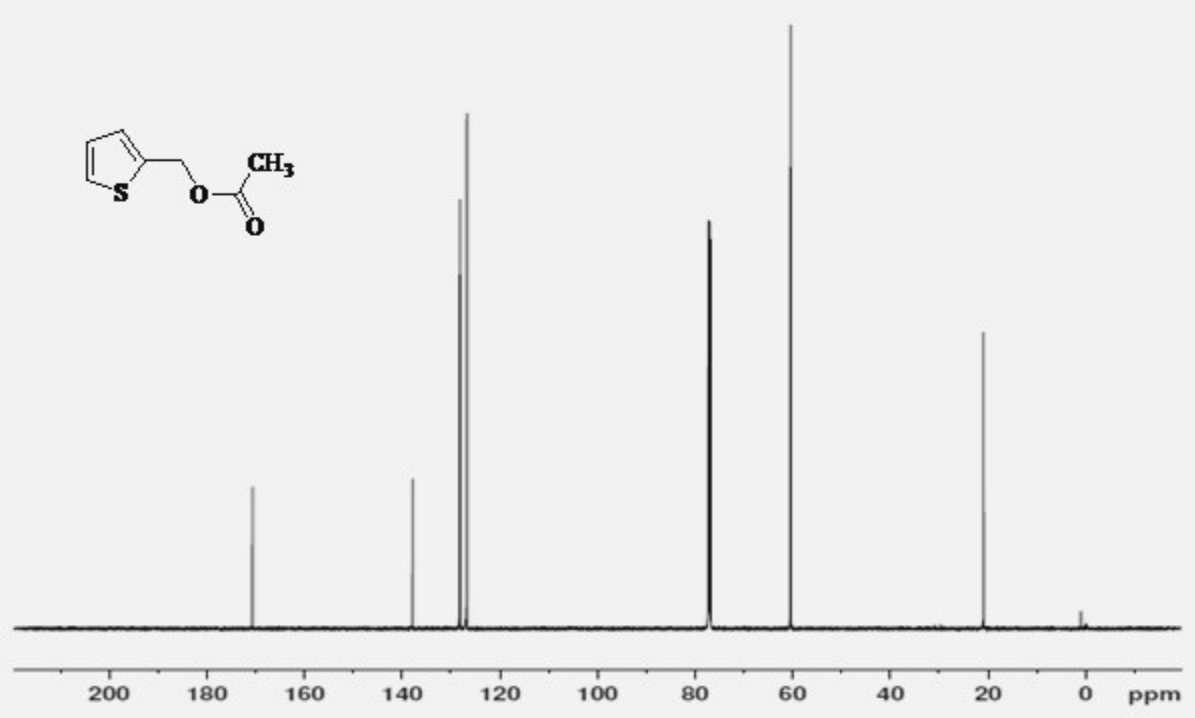
(naphthalen-5-yl)methyl acetate (2f) (Table 2, entry 5), GC-MS Spectra



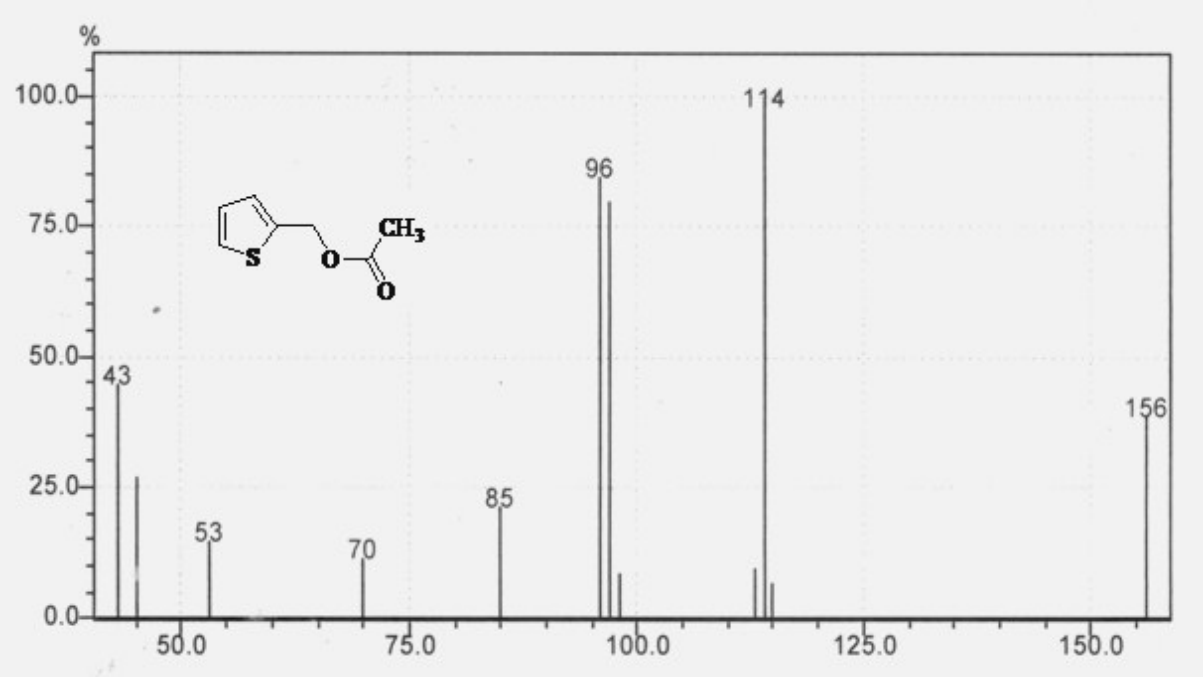
(thiophen-2-yl)methyl acetate (2g) (Table 2, entry 6), ^{1}H NMR (600 MHz, $CDCl_3$)



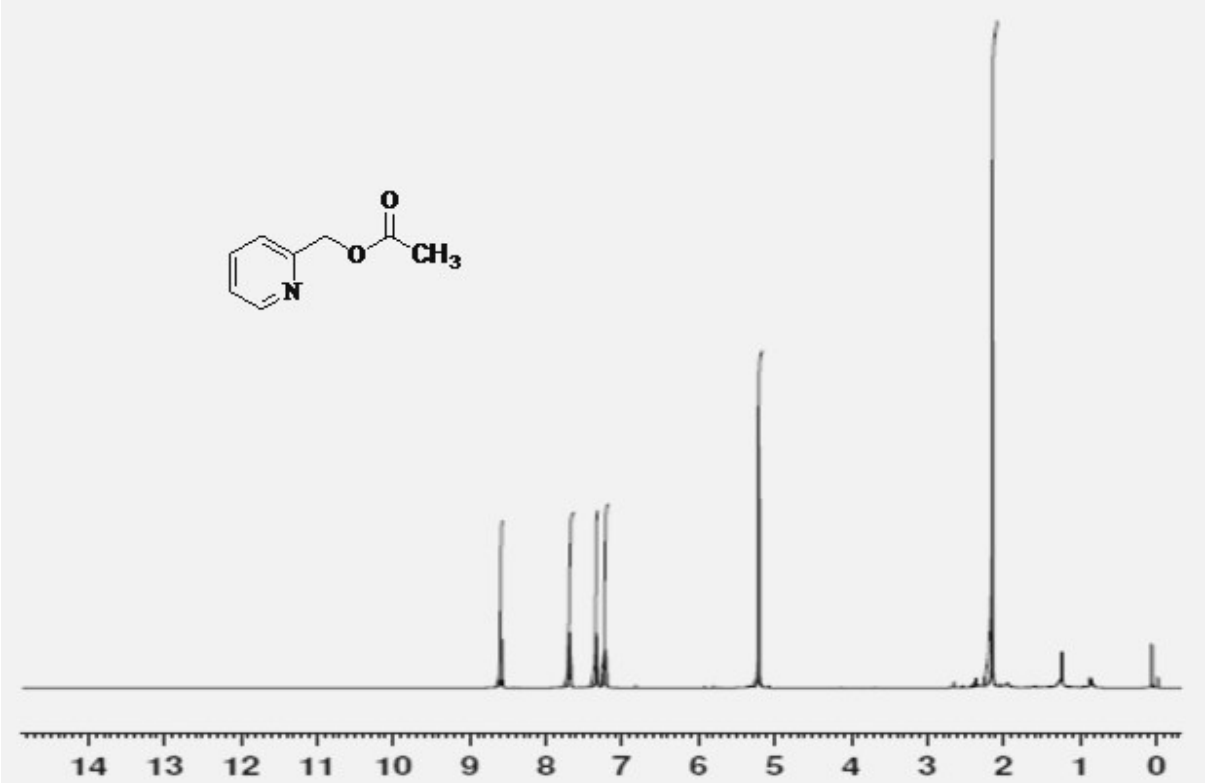
(thiophen-2-yl)methyl acetate (2g) (Table 2, entry 6), ^{13}C NMR (150 MHz, $CDCl_3$)



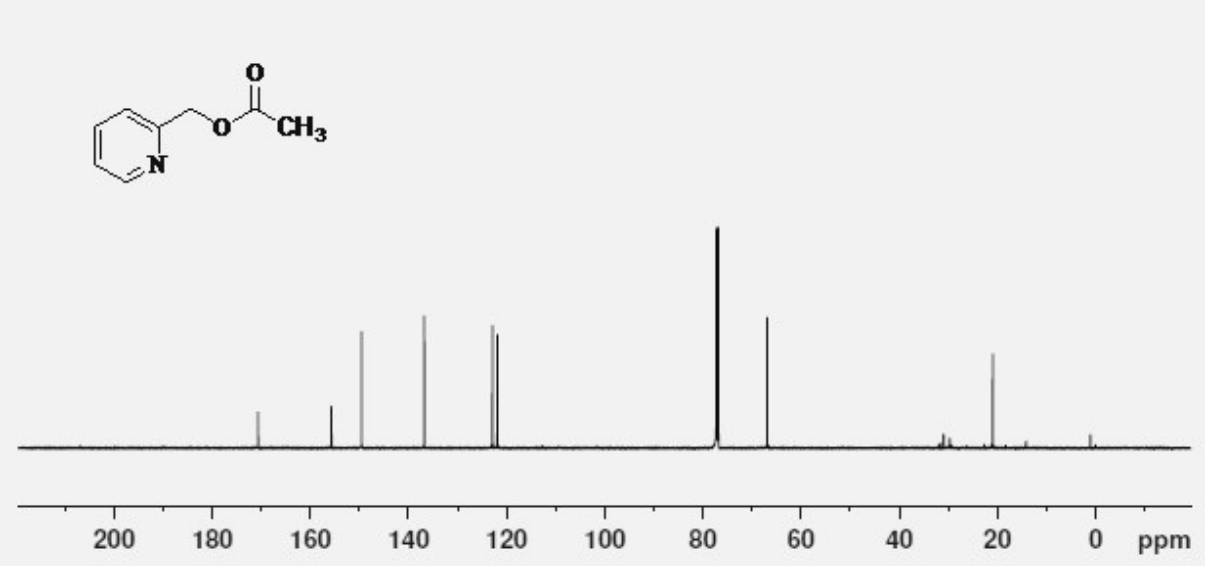
(thiophen-2-yl)methyl acetate (2g) (Table 2, entry 6), GC-MS Spectra



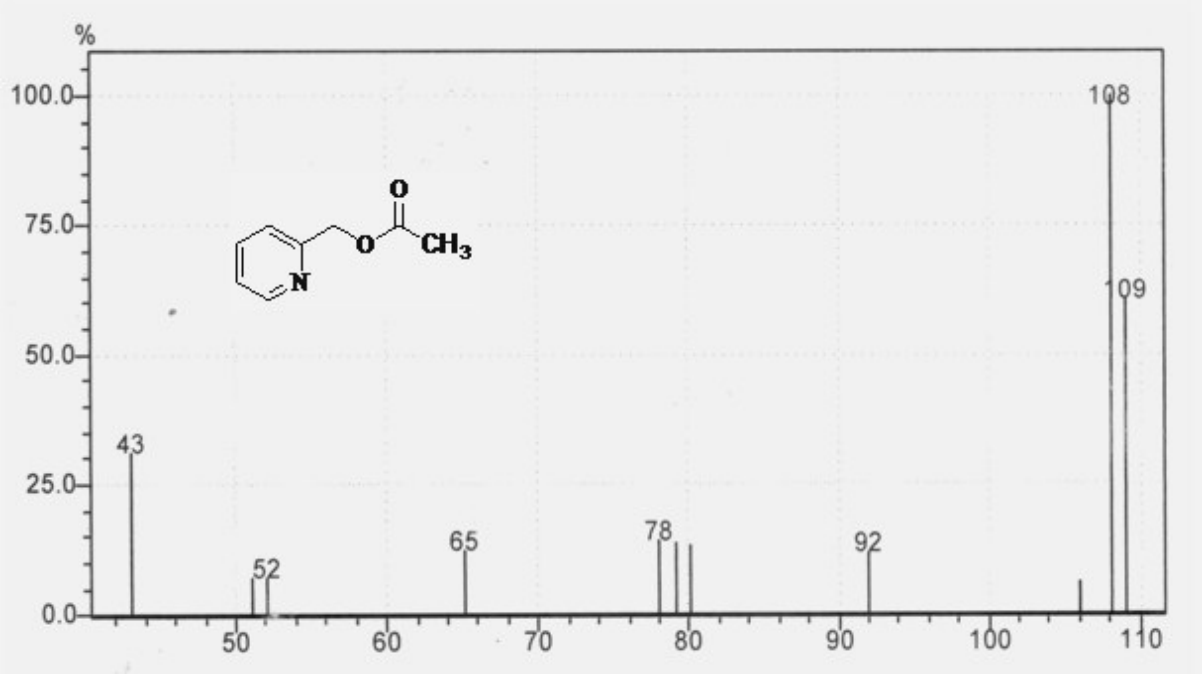
(pyridin-2-yl)methyl acetate (2h) (Table 2, entry 7), ^{1}H NMR (600 MHz, $CDCl_3$)



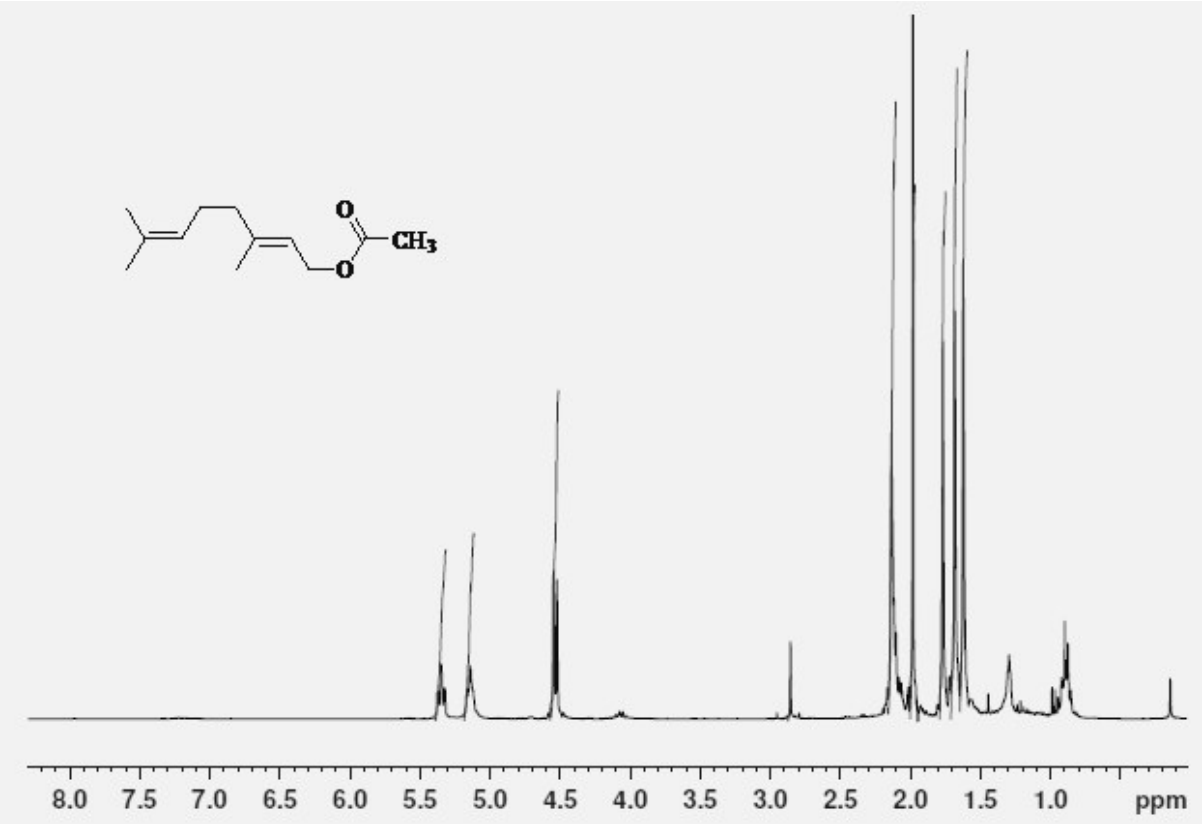
(pyridin-2-yl)methyl acetate (2h) (Table 2, entry 7), ^{13}C NMR (150 MHz, $CDCl_3$)



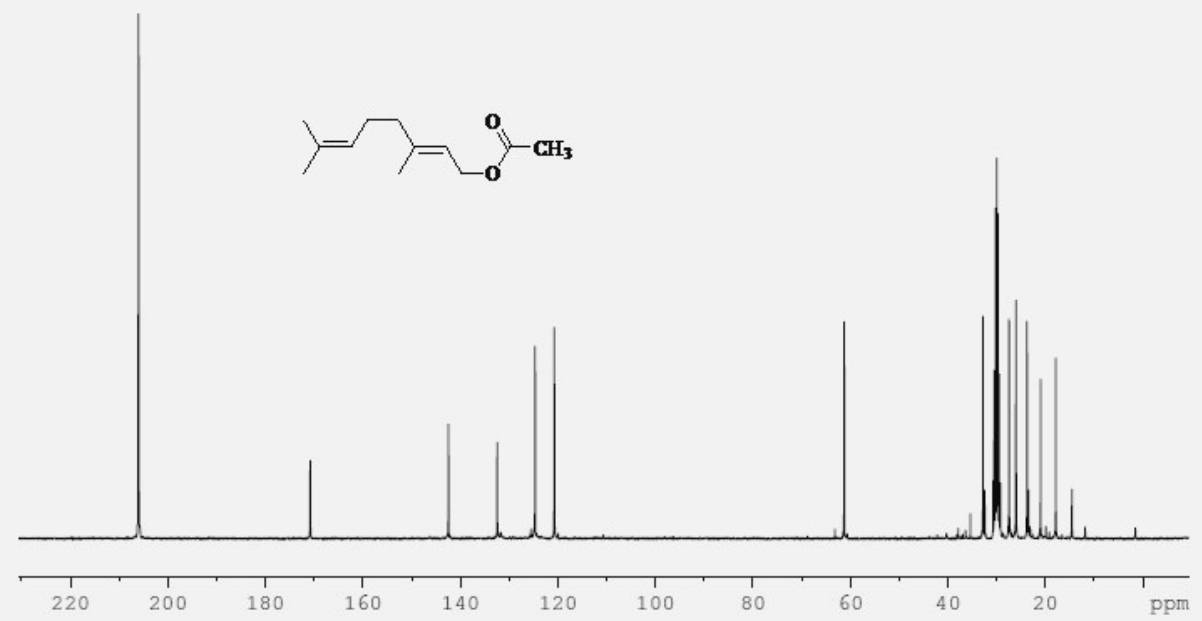
(pyridin-2-yl)methyl acetate (2h) (Table 2, entry 7), GC-MS Spectra



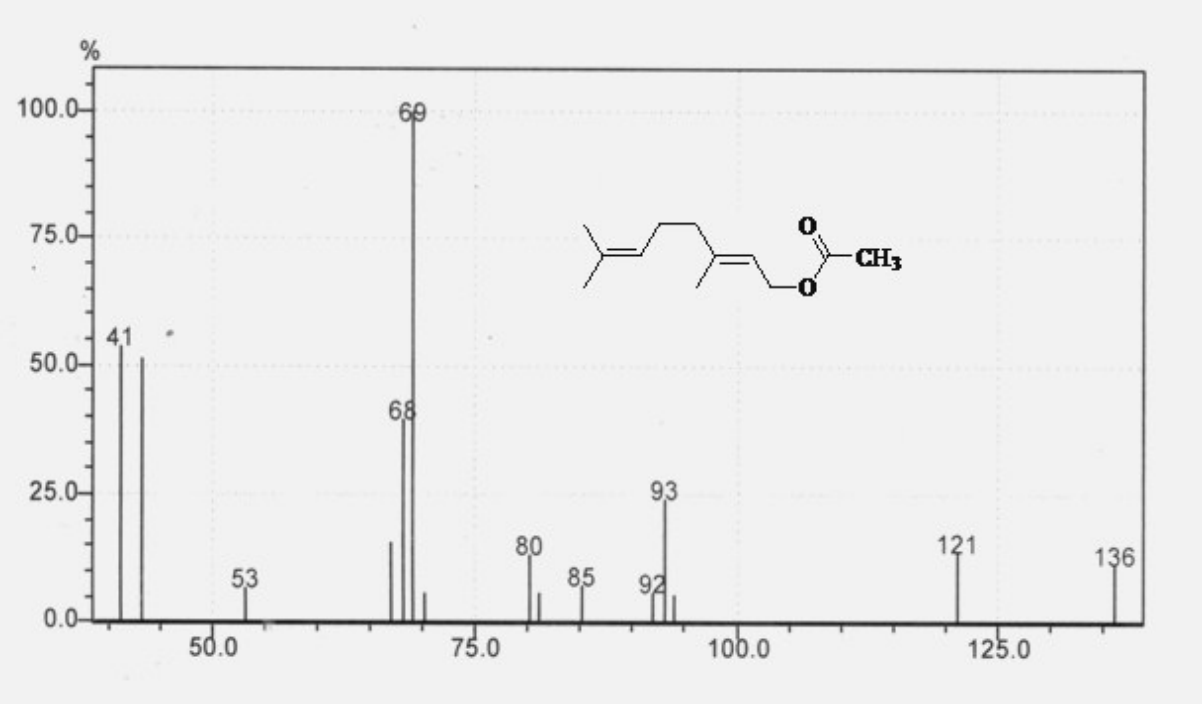
(E)-3,7-dimethylocta-2,6-dienyl acetate (2i) (Table 2, entry 8), ^{1}H NMR (300 MHz, acetone-D_6)



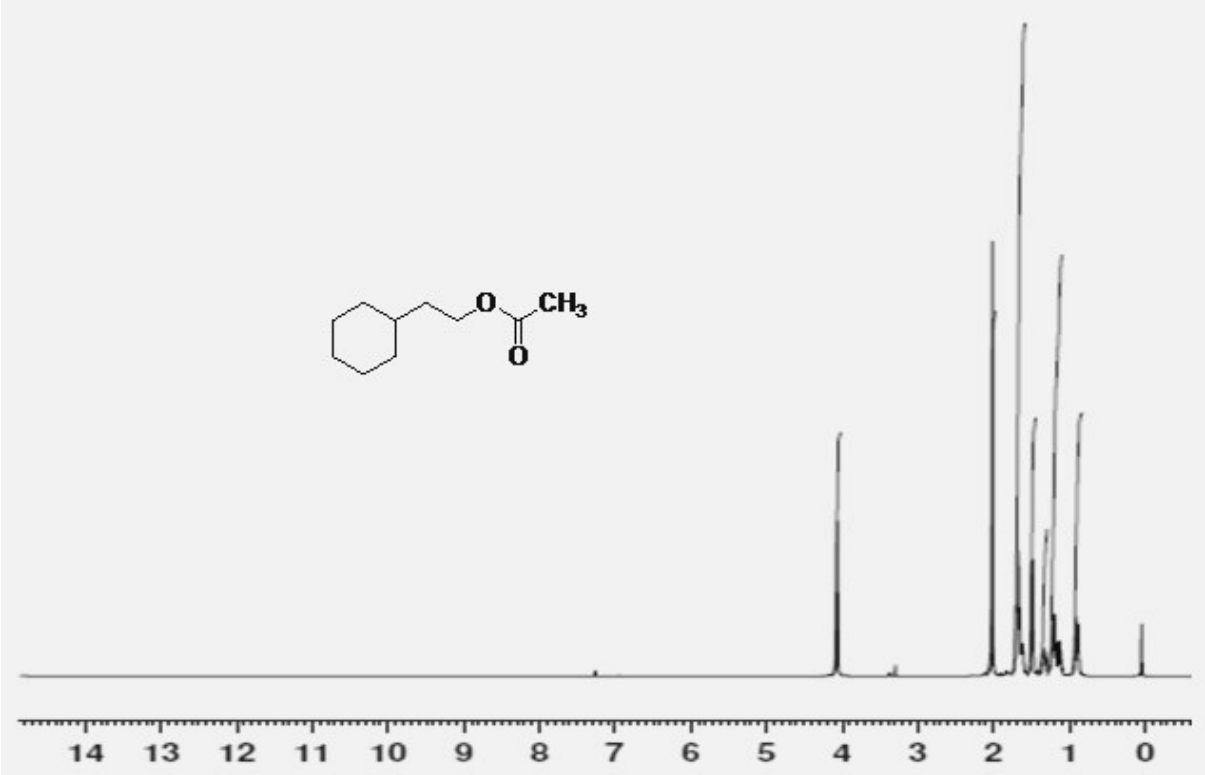
(E)-3,7-dimethylocta-2,6-dienyl acetate (2i) (Table 2, entry 8), ^{13}C NMR (75.5 MHz, acetone-D_6)



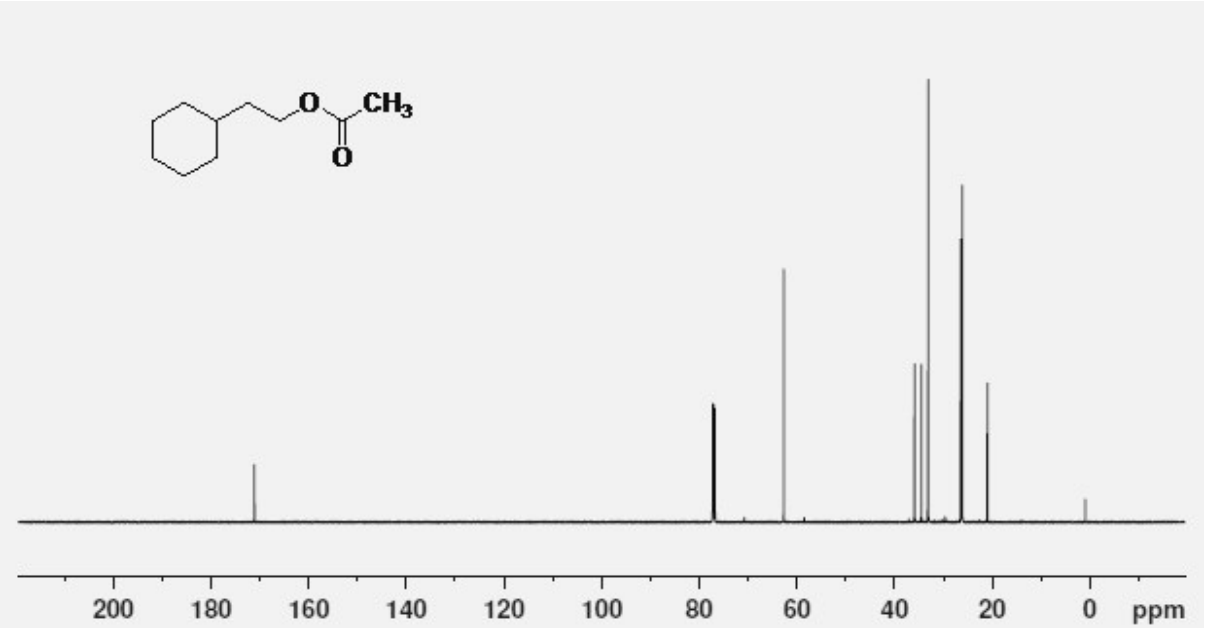
(E)-3,7-dimethylocta-2,6-dienyl acetate (2i) (Table 2, entry 8), GC-MS Spectra



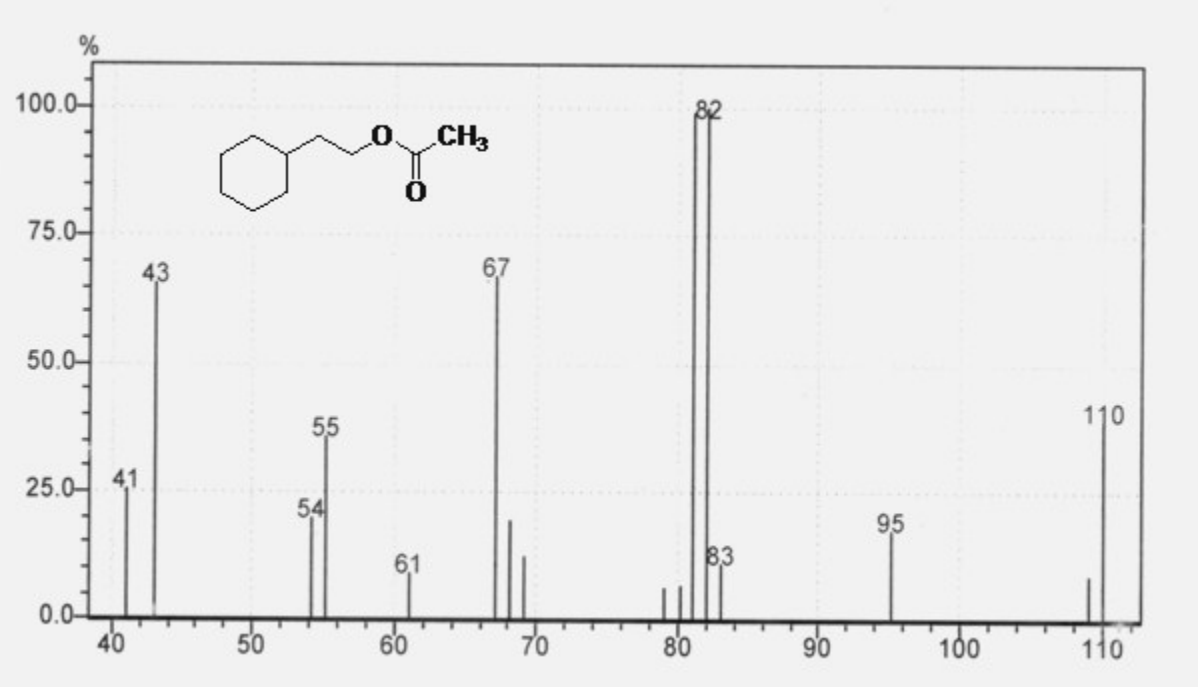
2-cyclohexylethyl acetate (2j) (Table 2, entry 9), ^{1}H NMR (600 MHz, $CDCl_3$)



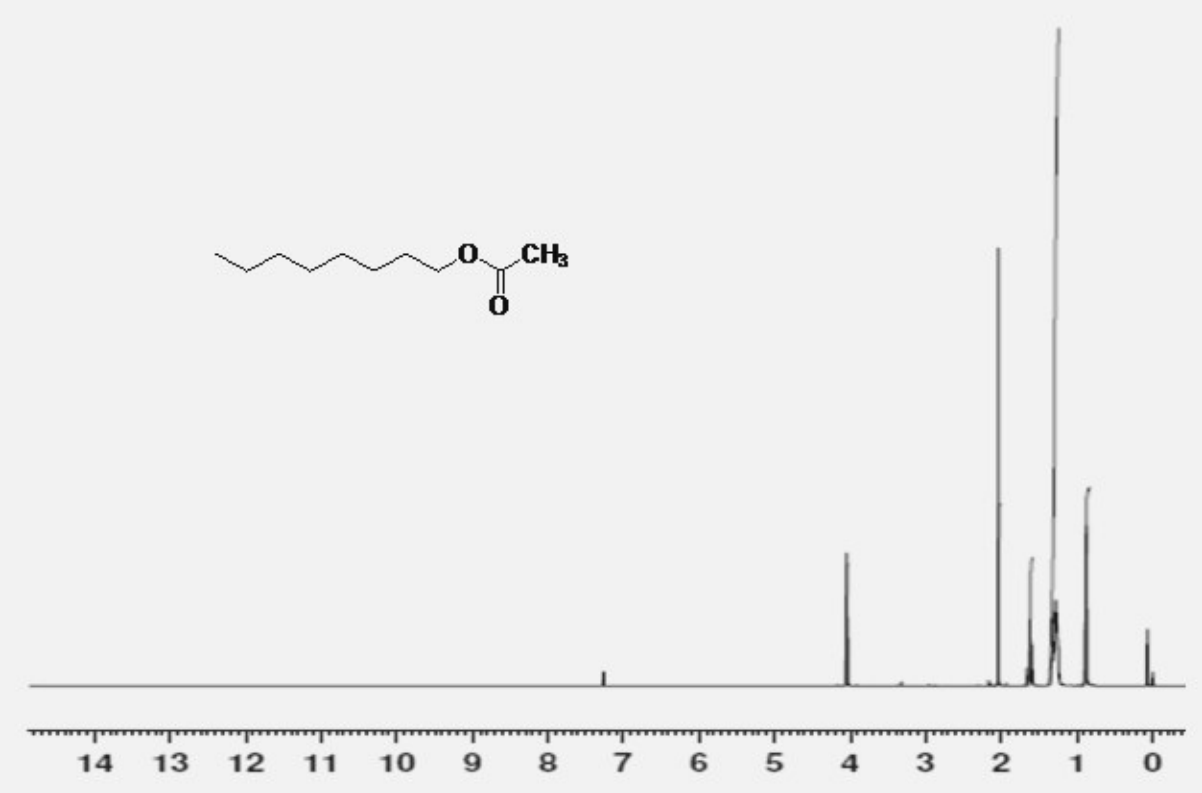
2-cyclohexylethyl acetate (2j) (Table 2, entry 9), ^{13}C NMR (150 MHz, $CDCl_3$)



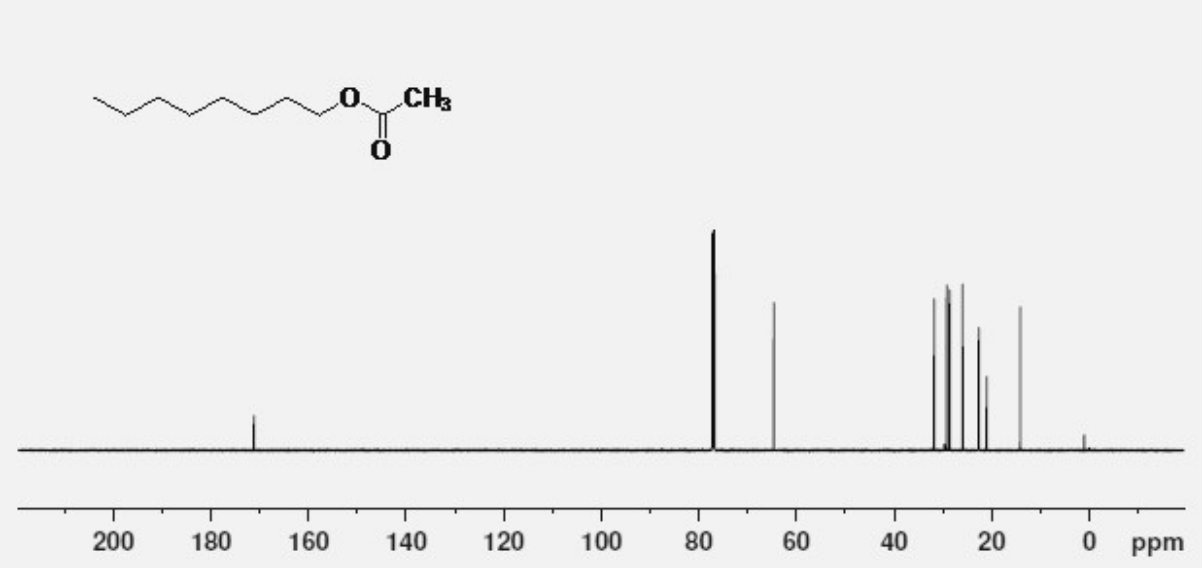
2-cyclohexylethyl acetate (2j) (Table 2, entry 9), GC-MS Spectra



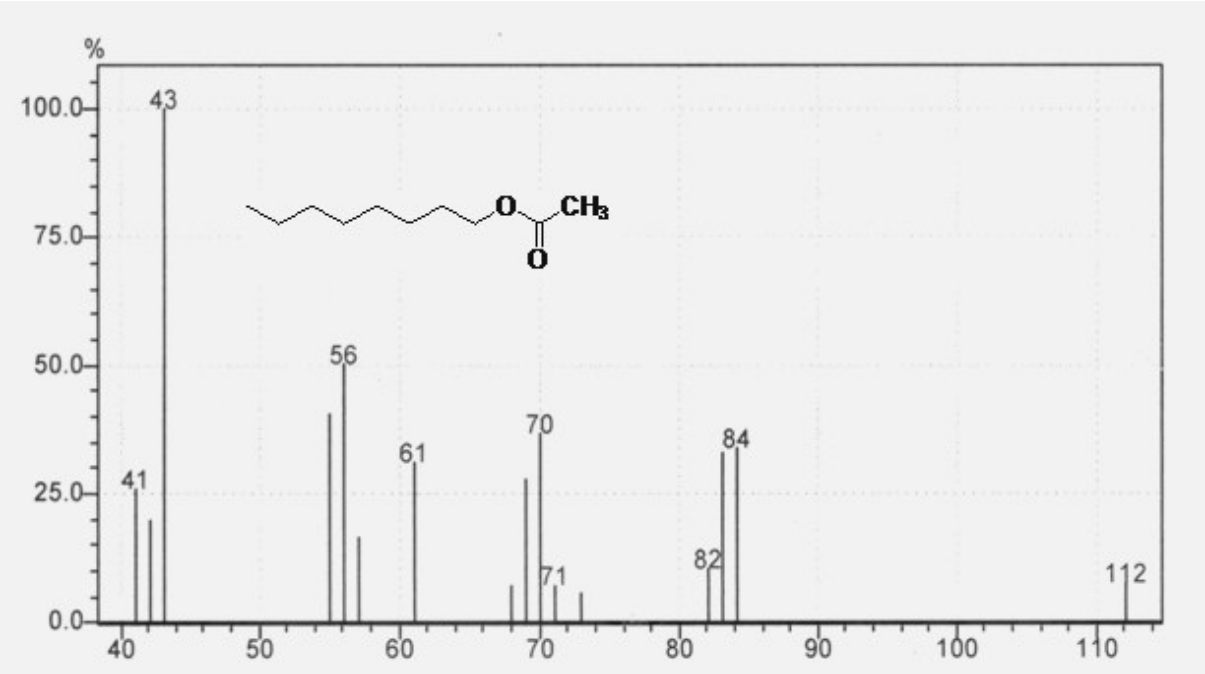
octyl acetate (2k) (Table 2, entry 10), ^{1}H NMR (600 MHz, $CDCl_3$)



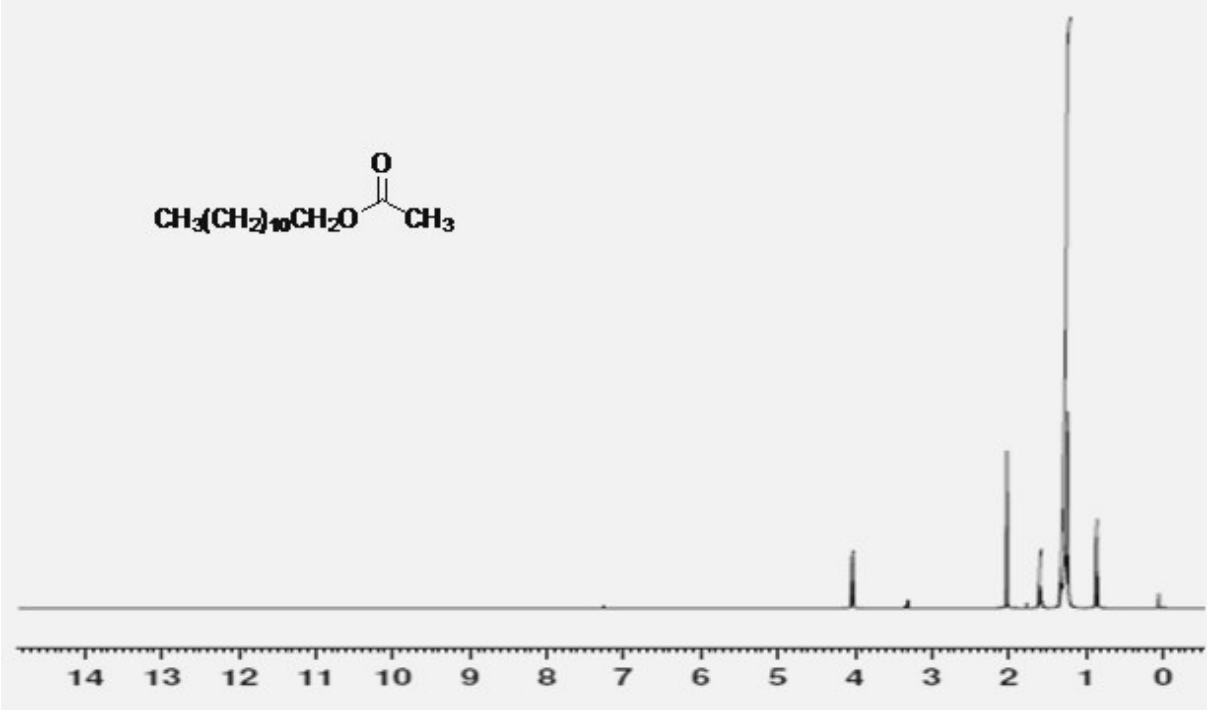
octyl acetate (2k) (Table 2, entry 10), ^{13}C NMR (150 MHz, $CDCl_3$)



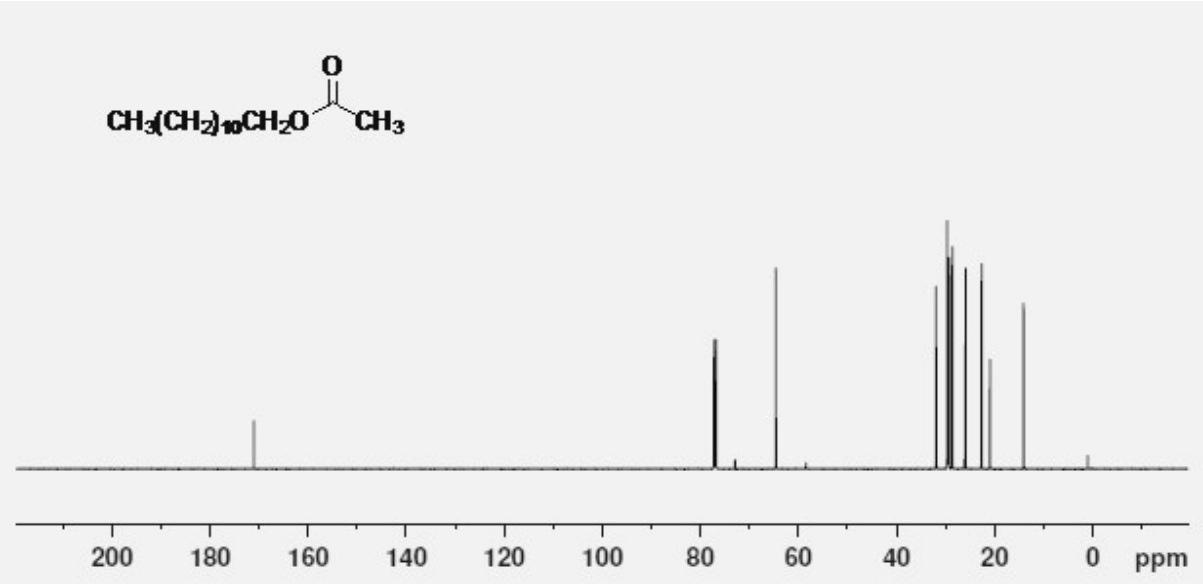
octyl acetate (2k) (Table 2, entry 10), GC-MS Spectra



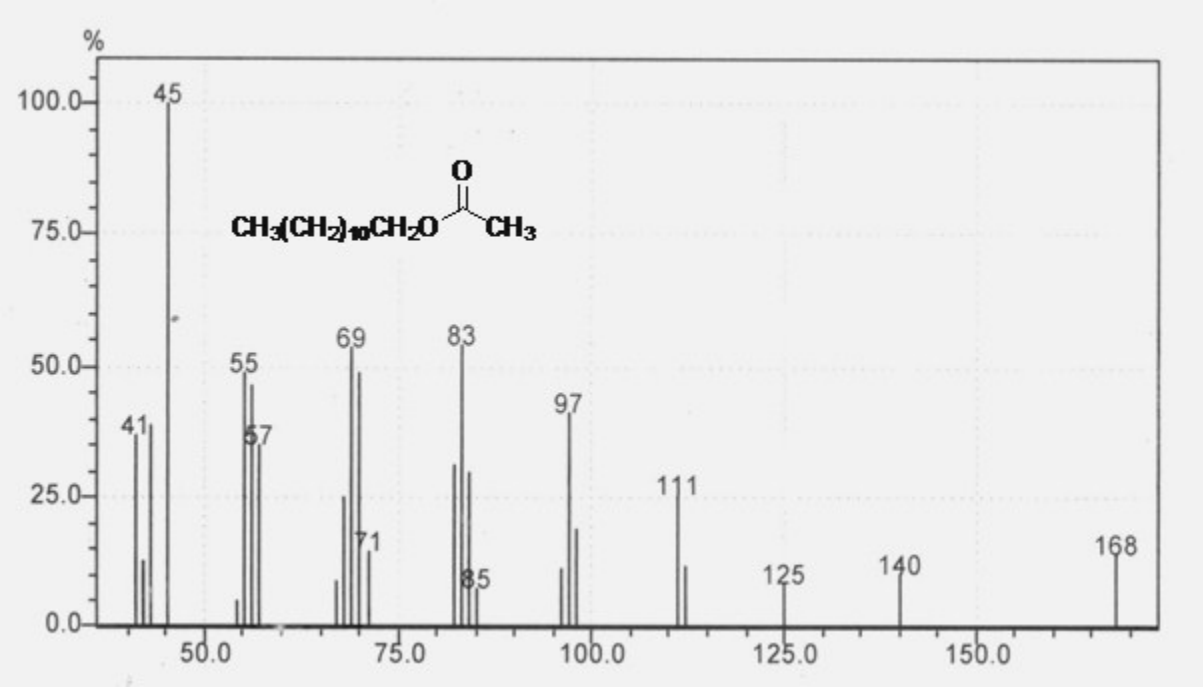
dodecyl acetate (2l) (Table 2, entry 11), ^{1}H NMR (600 MHz, $CDCl_3$)



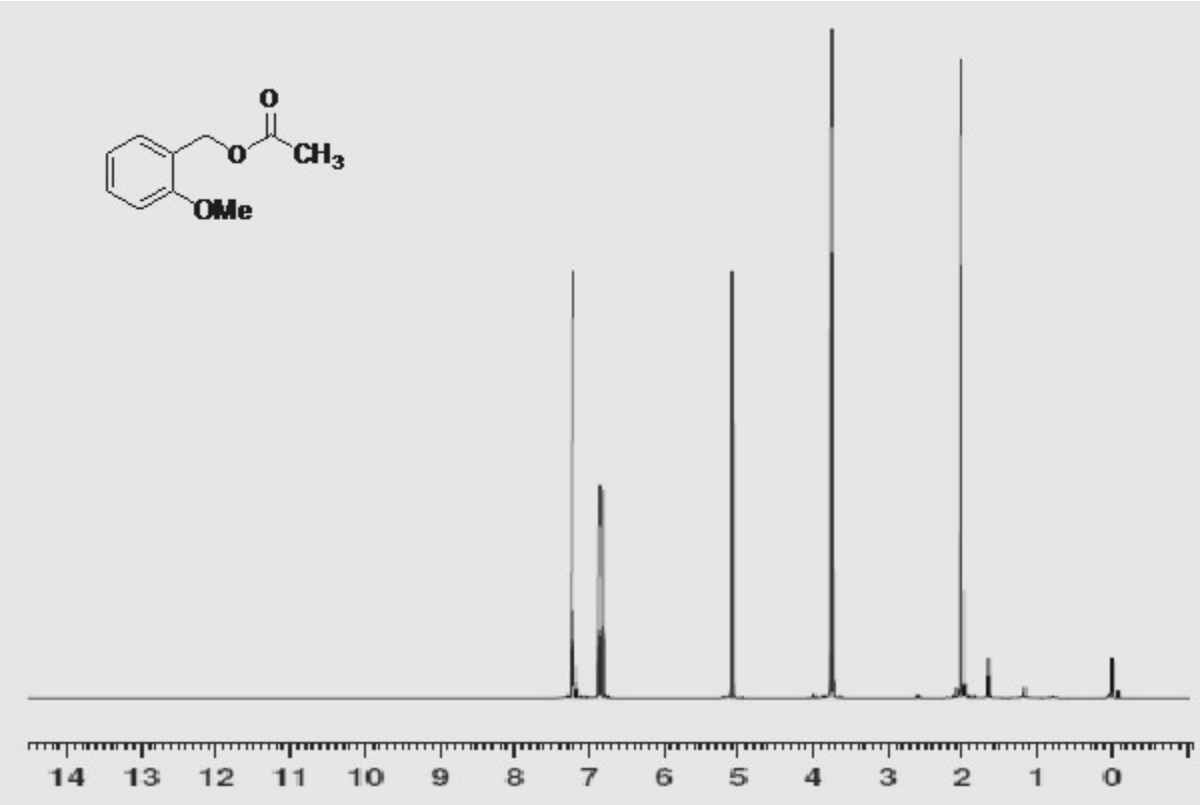
dodecyl acetate (2l) (Table 2, entry 11), ^{13}C NMR (150 MHz, $CDCl_3$)



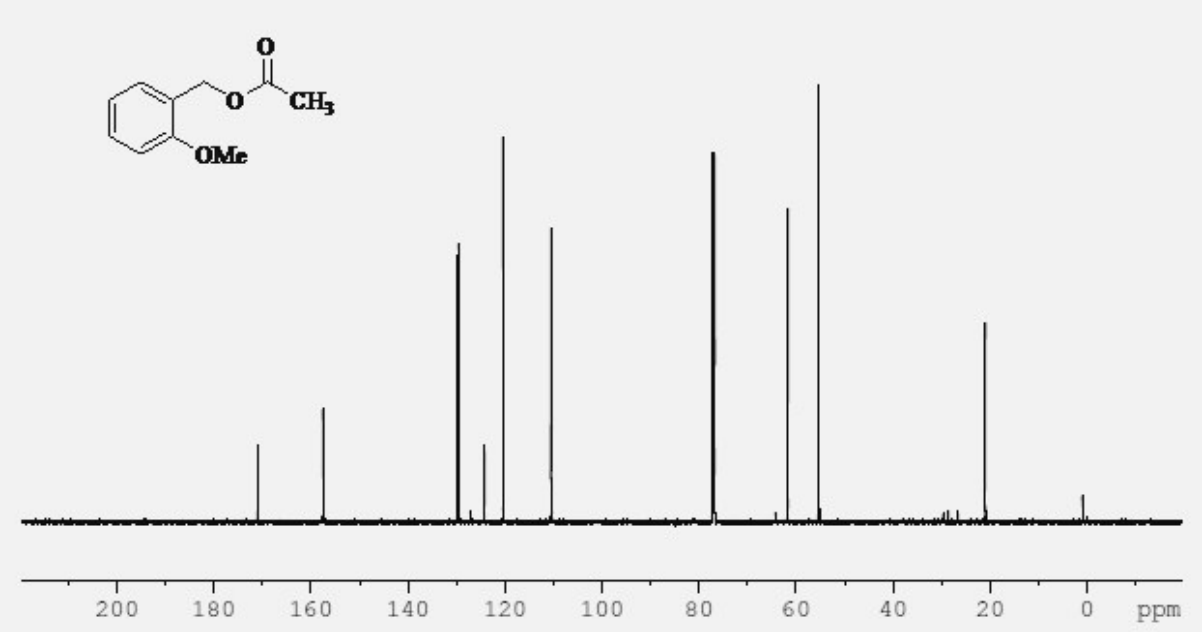
dodecyl acetate (2l) (Table 2, entry 11), GC-MS Spectra



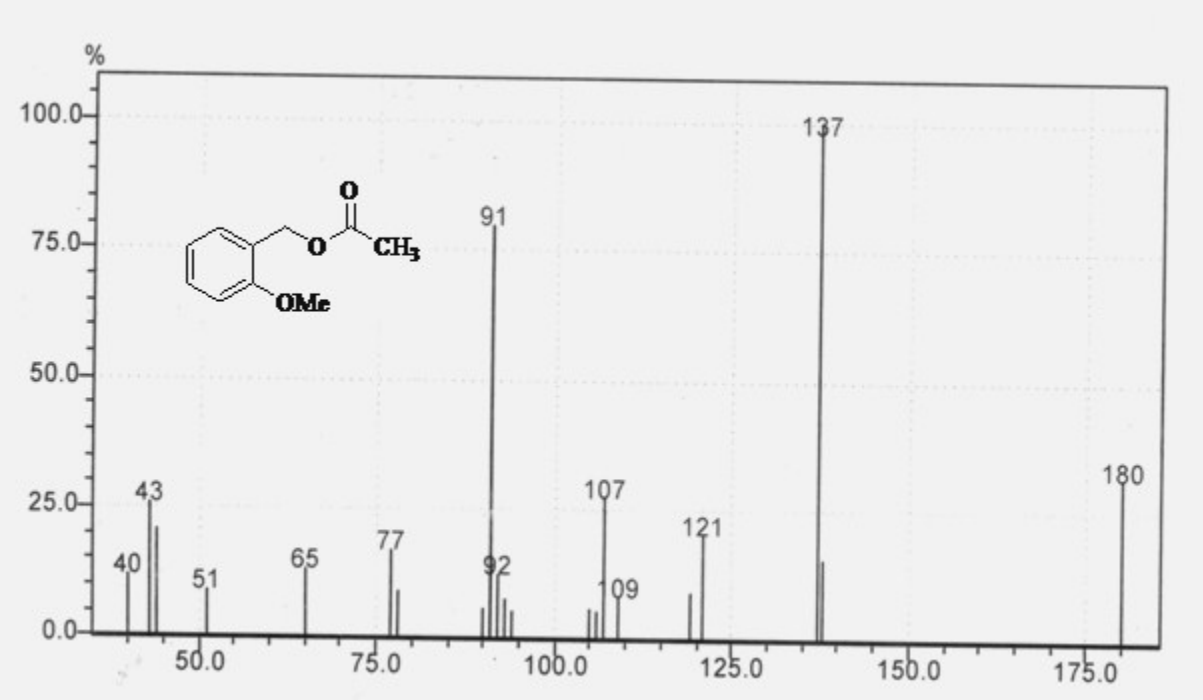
***o*-OMe benzyl acetate (2o) (Table 3, entry 2), ^{1}H NMR (600 MHz, $CDCl_3$)**



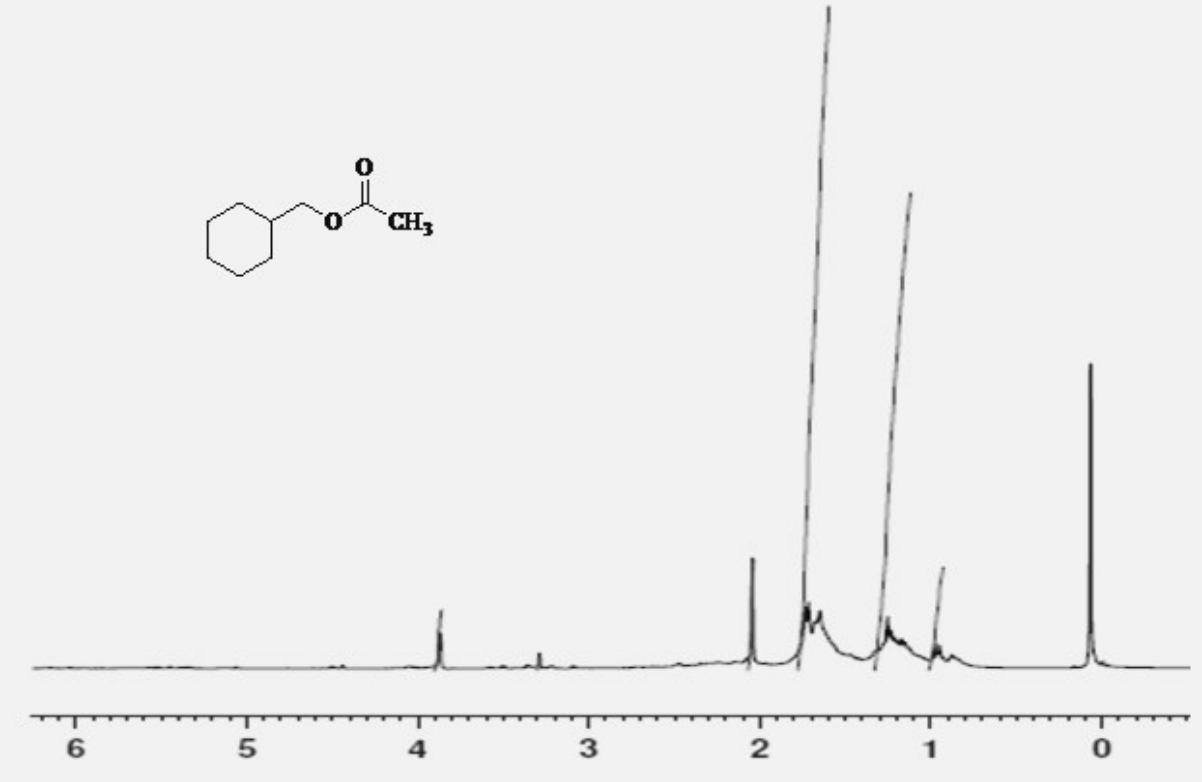
***o*-OMe benzyl acetate (2o) (Table 3, entry 2), ^{13}C NMR (150 MHz, $CDCl_3$)**



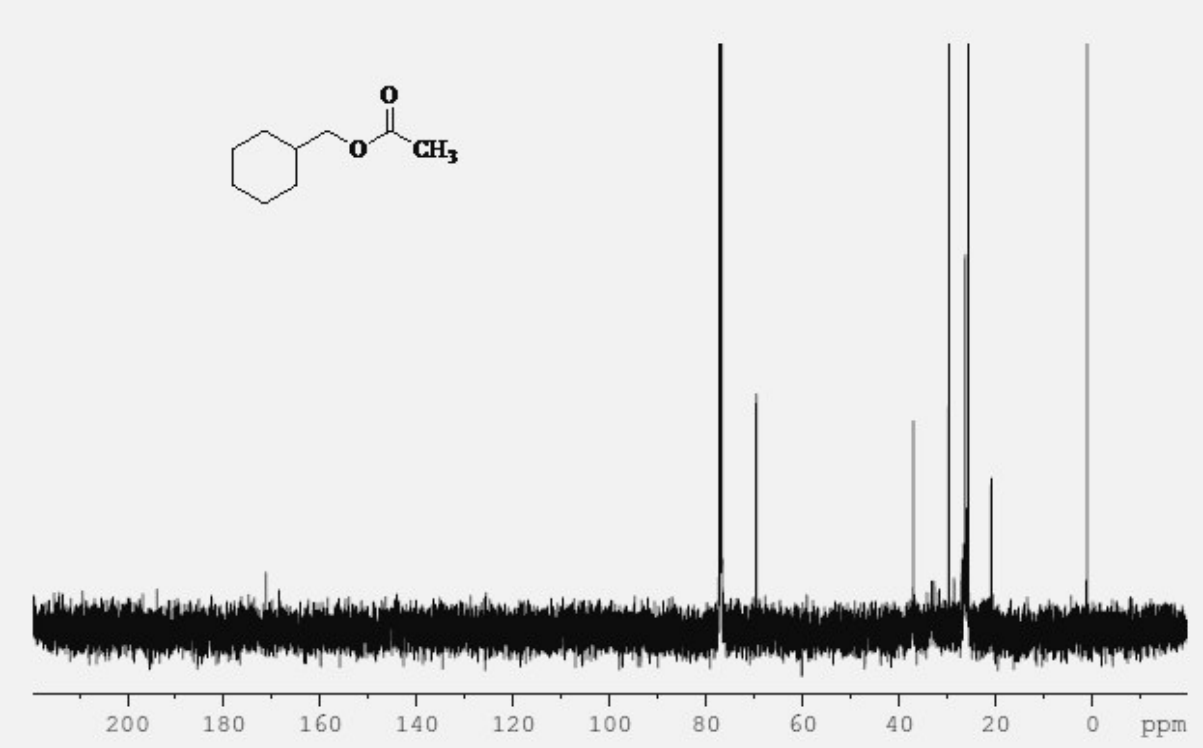
***o*-OMe benzyl acetate (2o) (Table 3, entry 2), GC-MS Spectra**



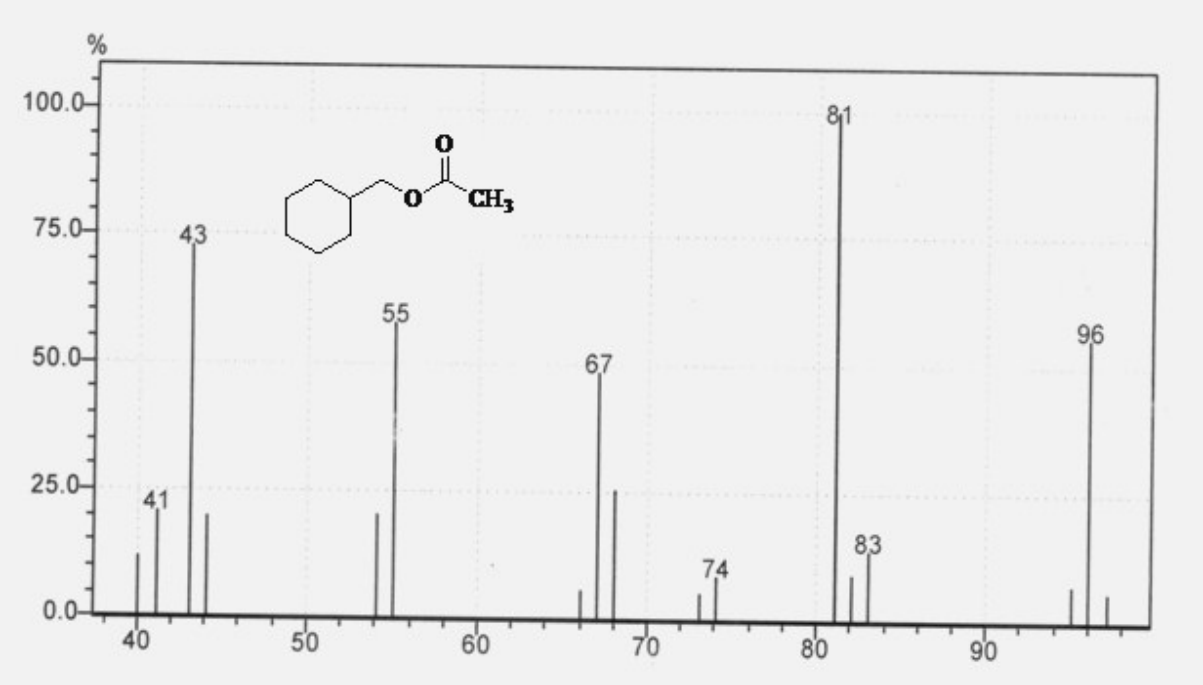
cyclohexylmethyl acetate (2q) (Table 3, entry 5), ^{1}H NMR (600 MHz, $CDCl_3$)



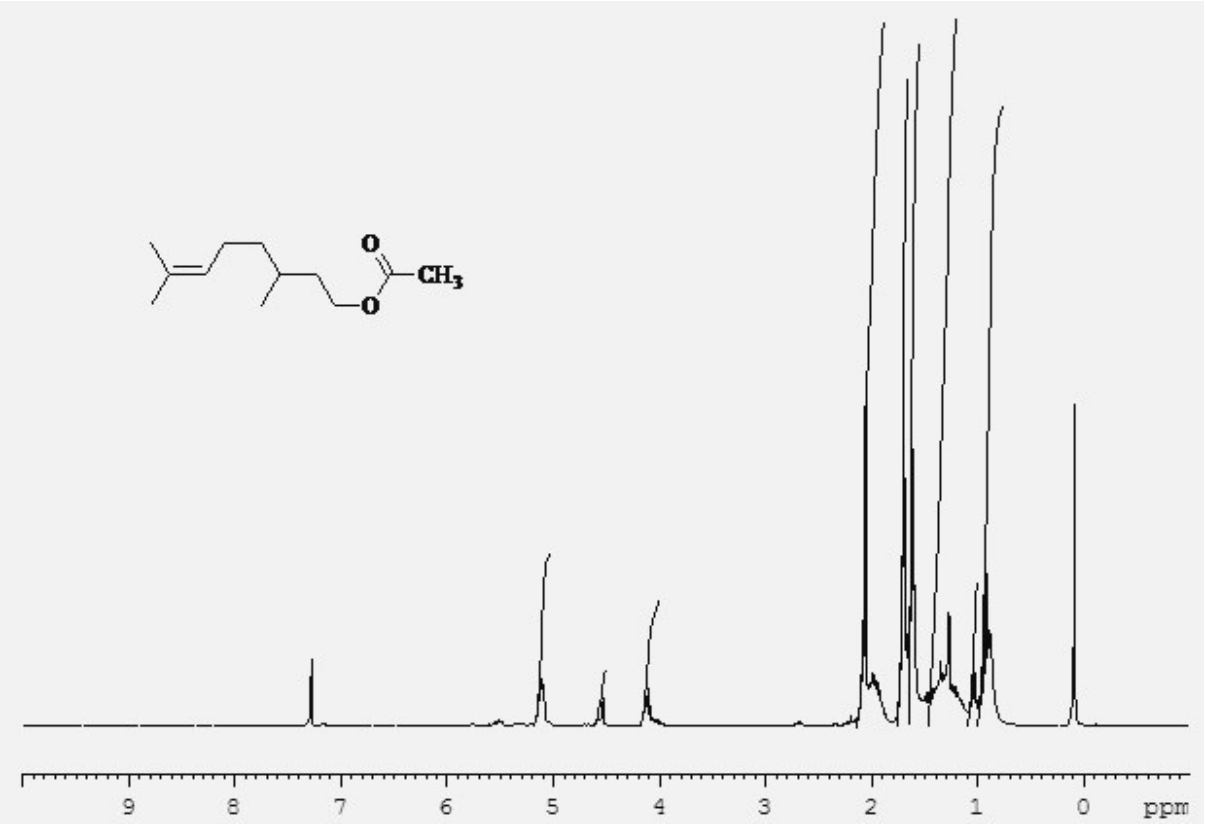
cyclohexylmethyl acetate (2q) (Table 3, entry 5), ^{13}C NMR (150 MHz, $CDCl_3$)



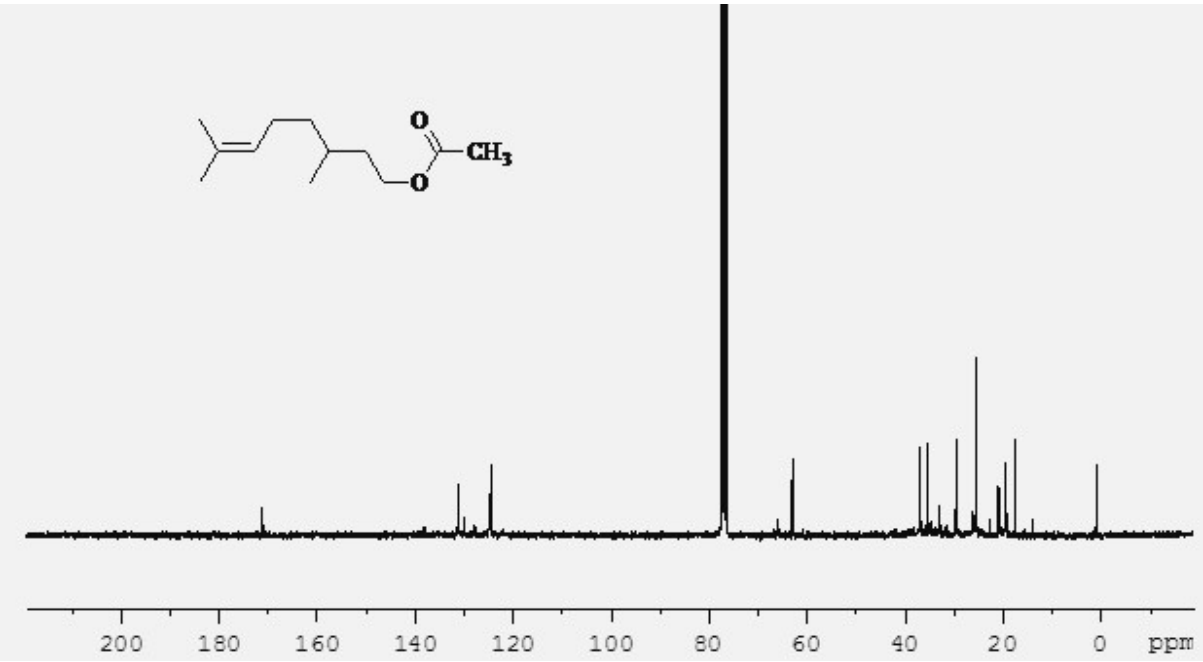
cyclohexylmethyl acetate (2q) (Table 3, entry 5), GC-MS Spectra



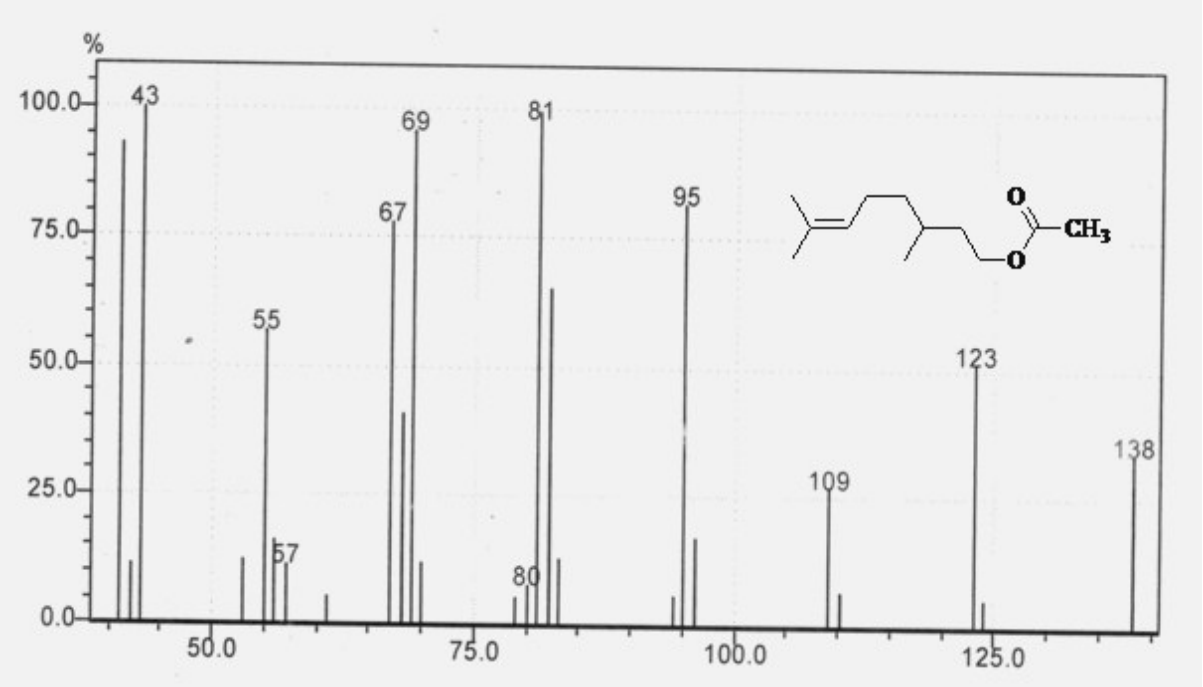
3,7-dimethyloct-6-enyl acetate (2s) (Table, entry), ^{1}H NMR (300 MHz, $CDCl_3$)



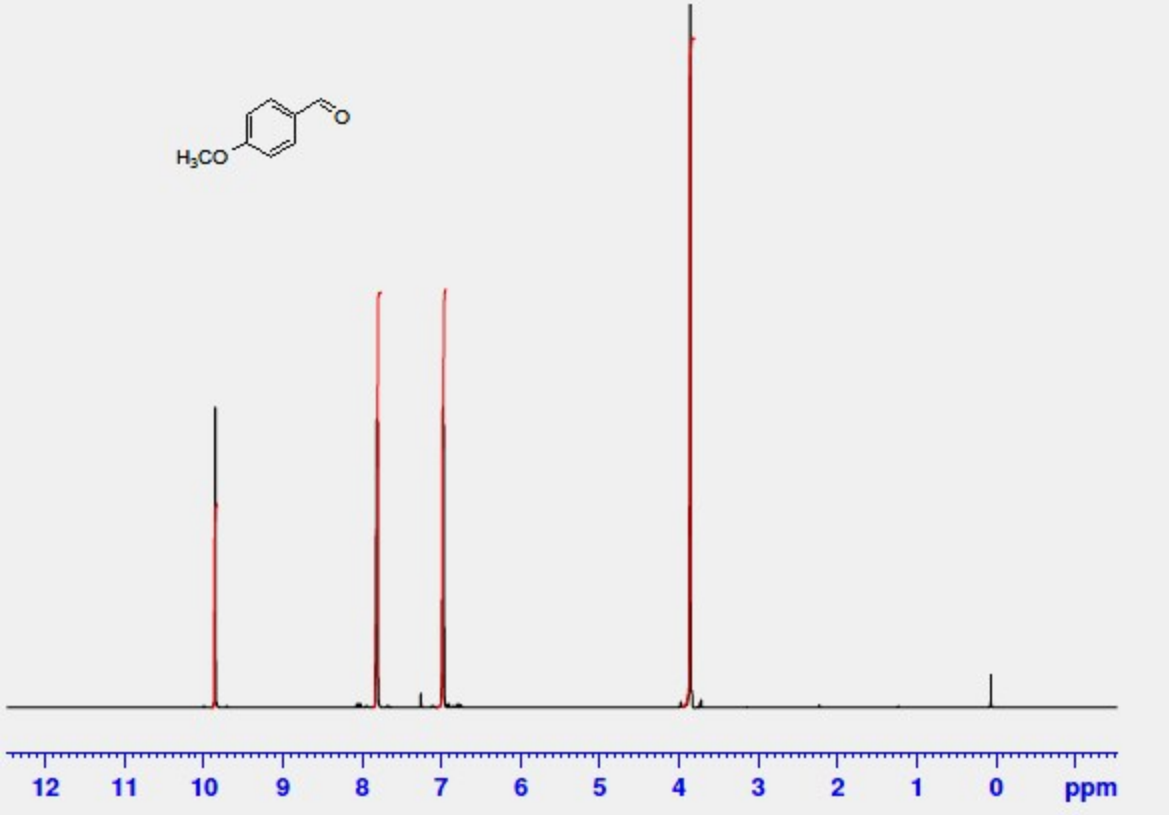
3,7-dimethyloct-6-enyl acetate (2s) (Table, entry), ^{13}C NMR (75 MHz, $CDCl_3$)



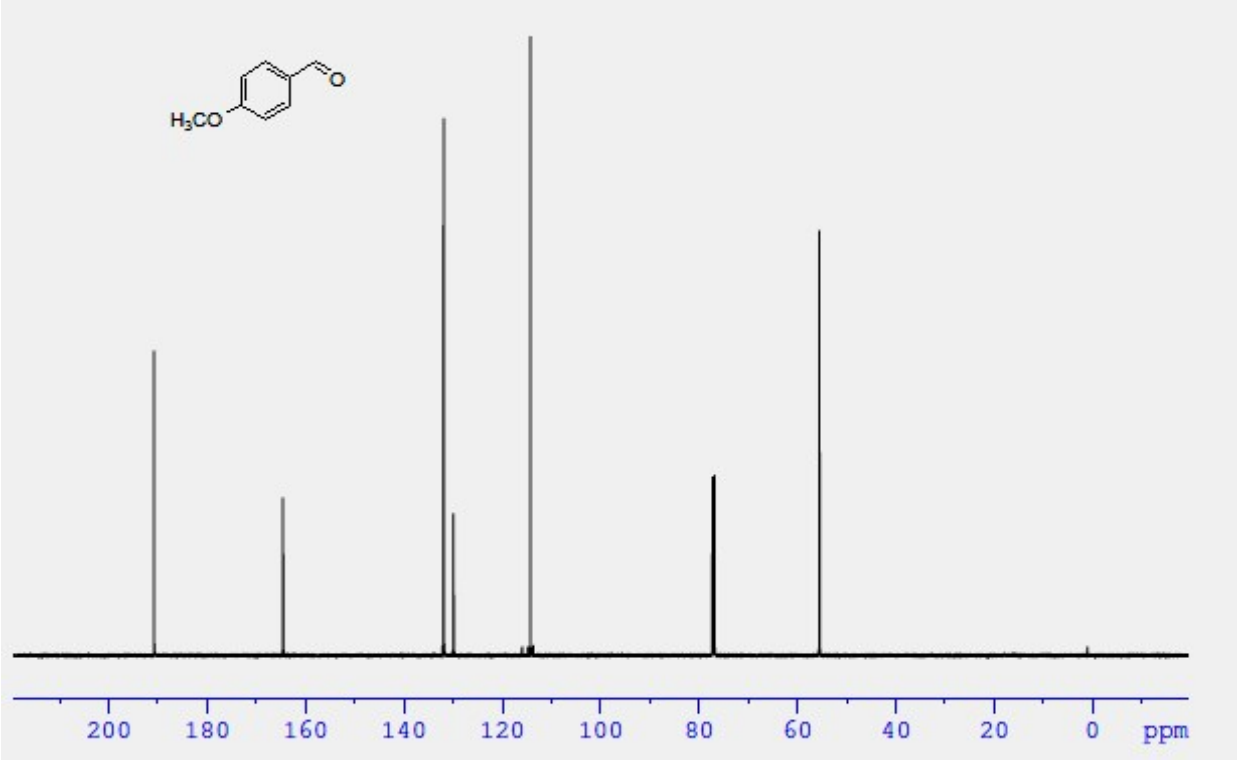
3,7-dimethyloct-6-enyl acetate (2s) (Table, entry), GCMS Spectra



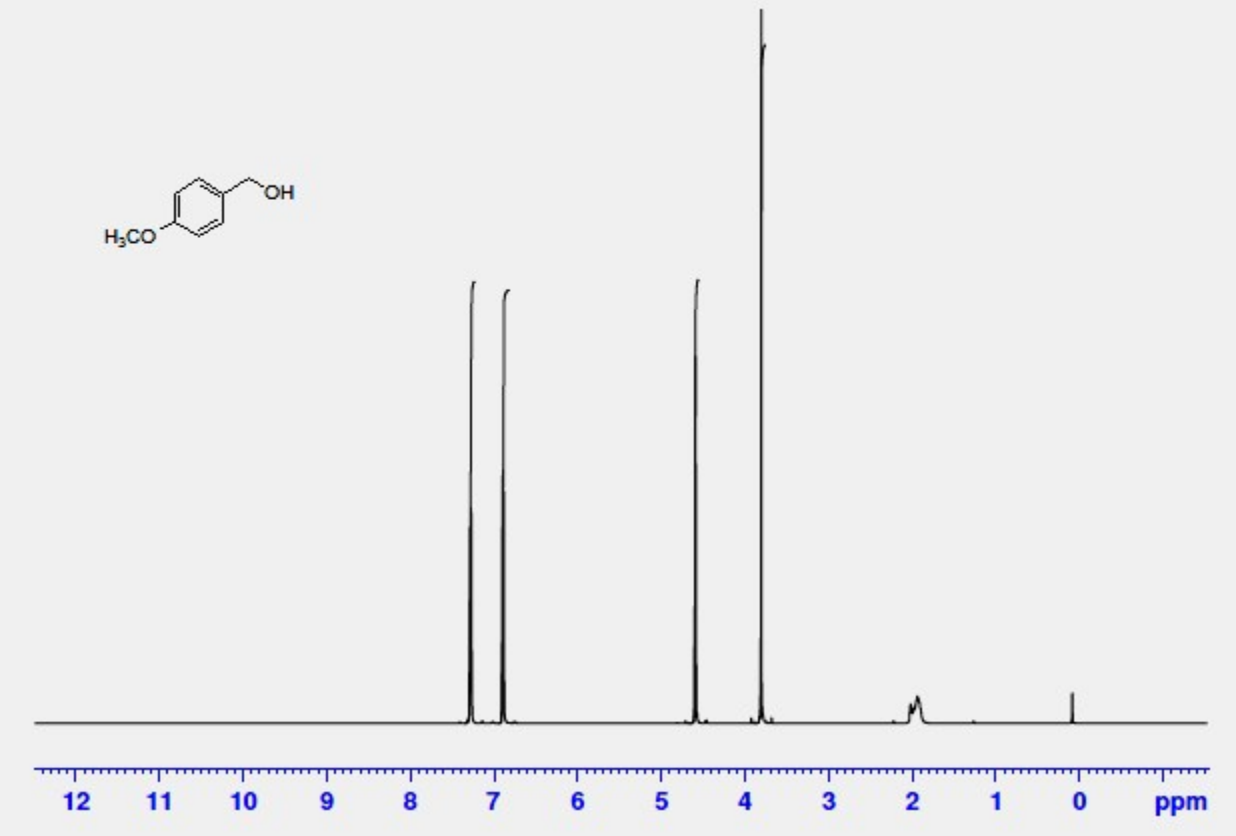
***p*-OMe benzaldehyde (1t) (Scheme 4a), ^{1}H NMR (600 MHz, $CDCl_3$)**



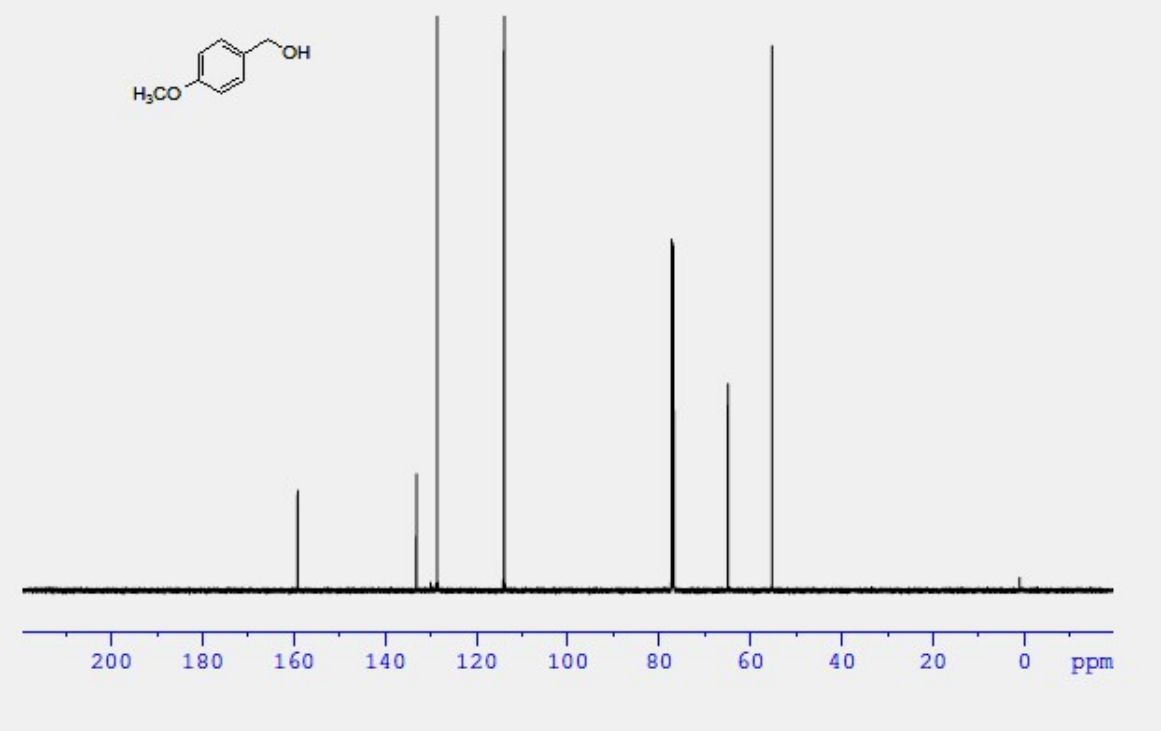
***p*-OMe benzaldehyde (1t) (Scheme 4a), ^{13}C NMR (150 MHz, $CDCl_3$)**



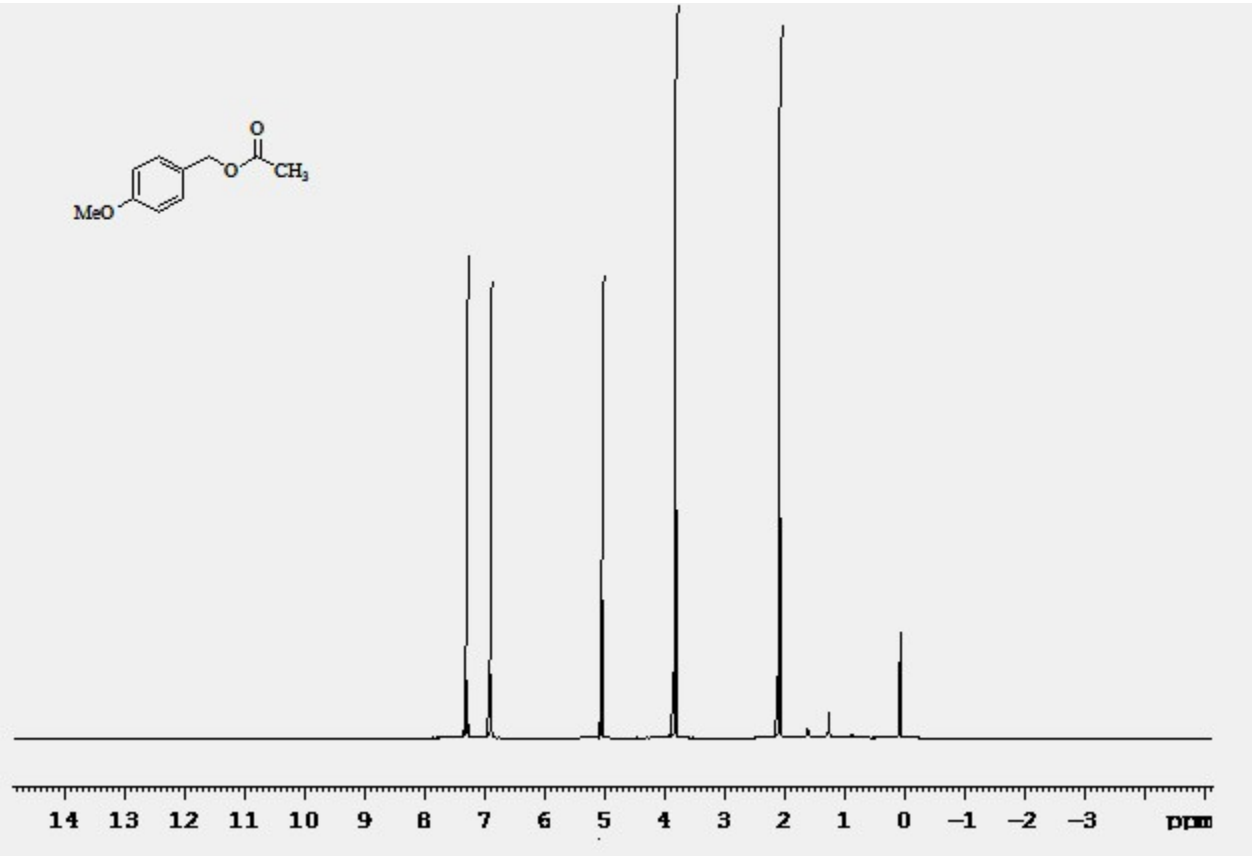
***p*-OMe benzyl alcohol (1a) (Scheme 4b), ^{1}H NMR (600 MHz, $CDCl_3$)**



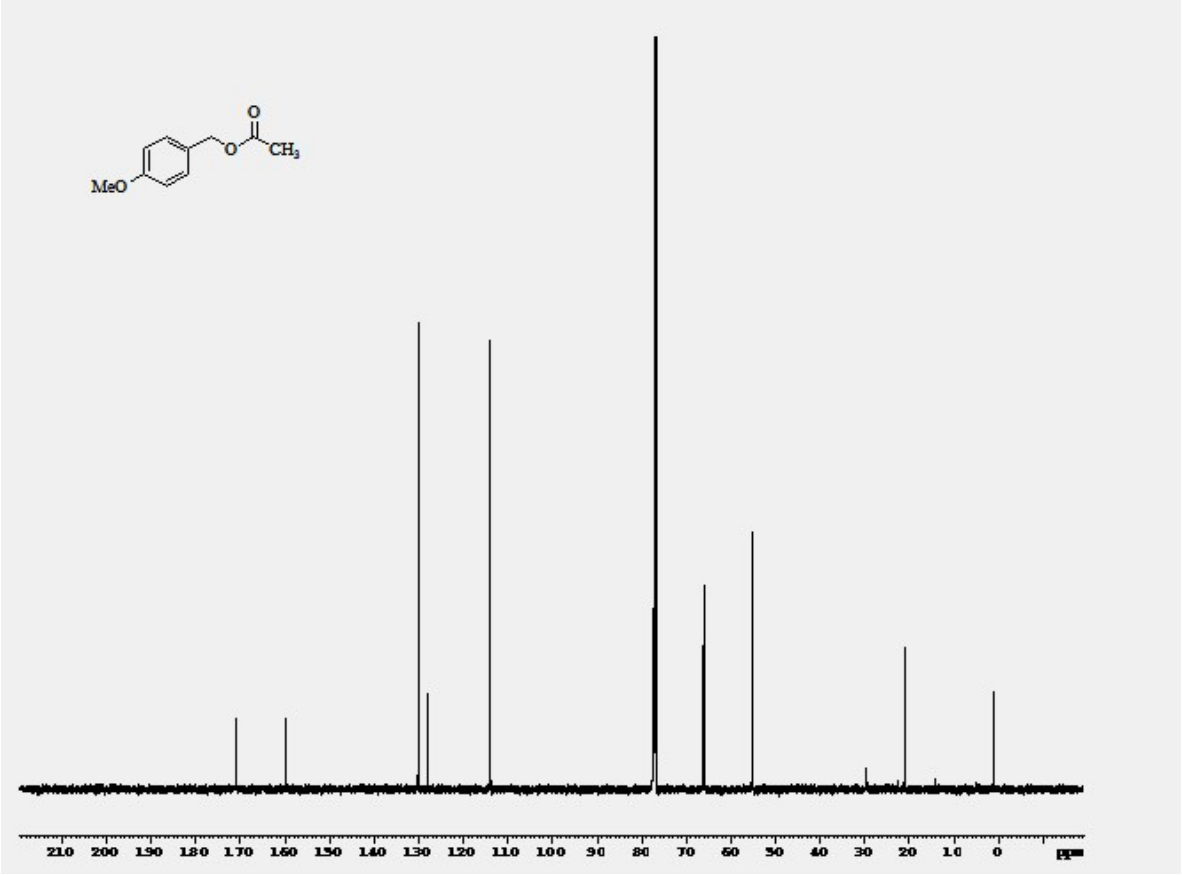
***p*-OMe benzyl alcohol (1a) (Scheme 4b), ^{13}C NMR (150 MHz, $CDCl_3$)**



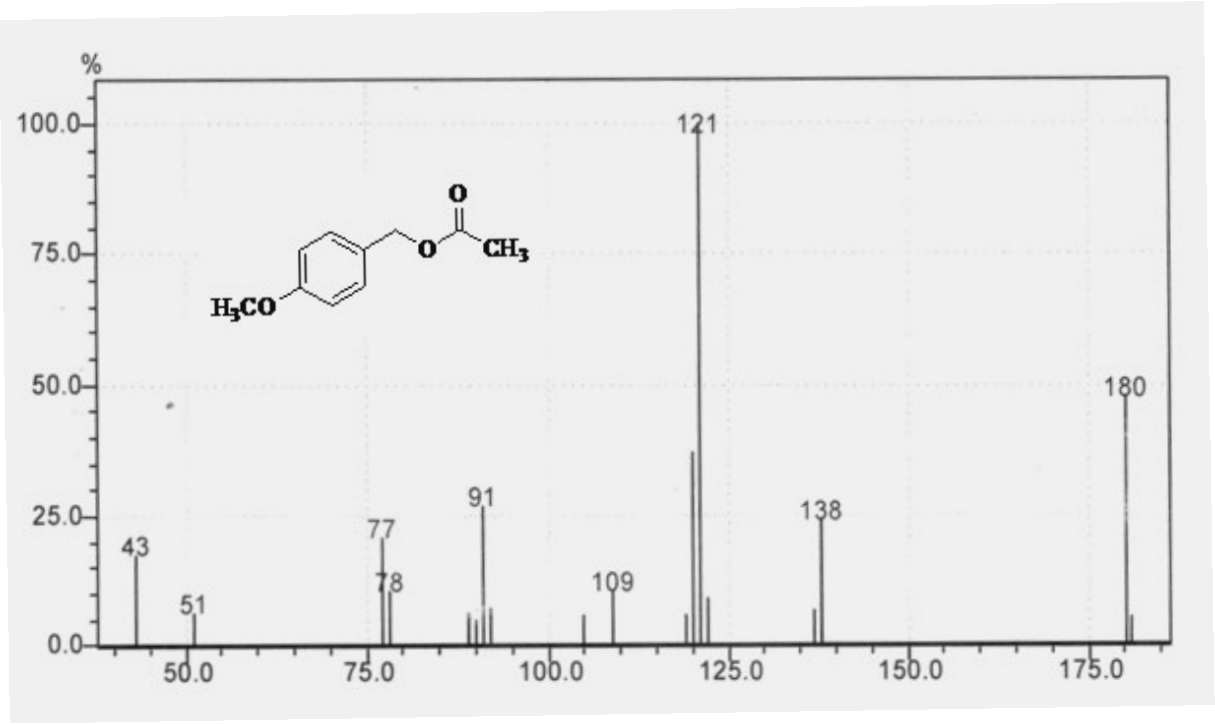
***p*-OMe benzyl acetate (2a) (Scheme 4d), ^{1}H NMR (600 MHz, $CDCl_3$)**



***p*-OMe benzyl acetate (2a) (Scheme 4d), ^{13}C NMR (150 MHz, $CDCl_3$)**



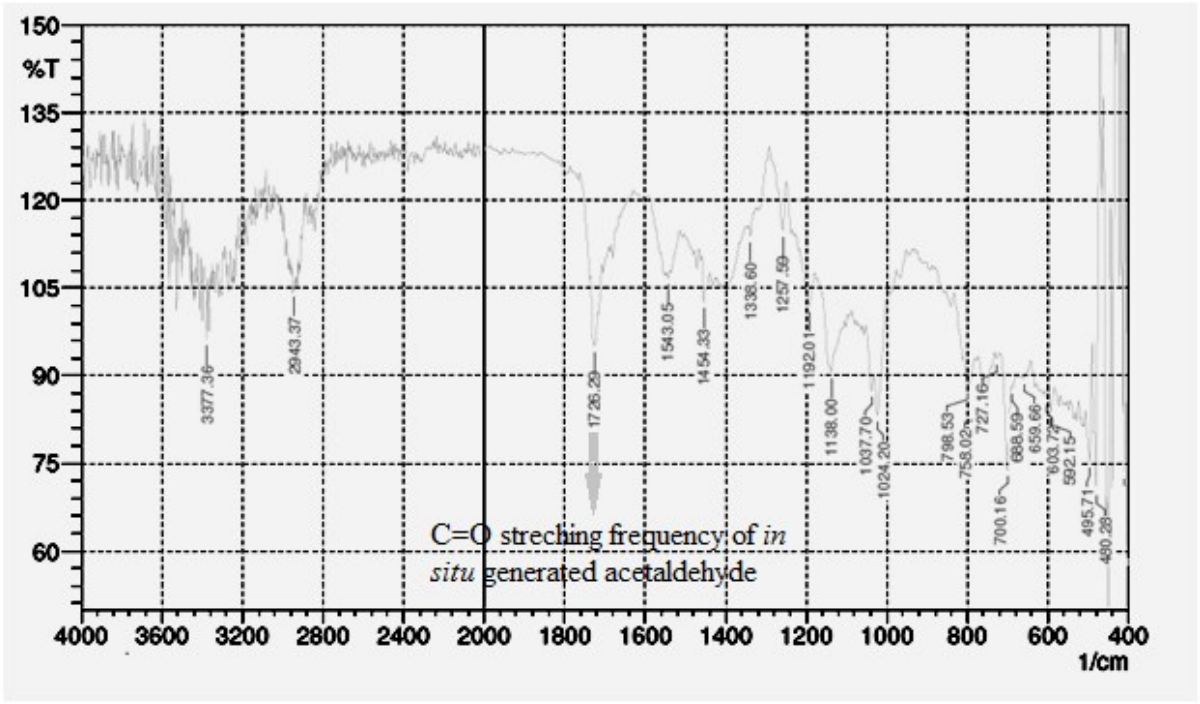
***p*-OMe benzyl acetate (2a) (Scheme 4d), GCMS spectra**



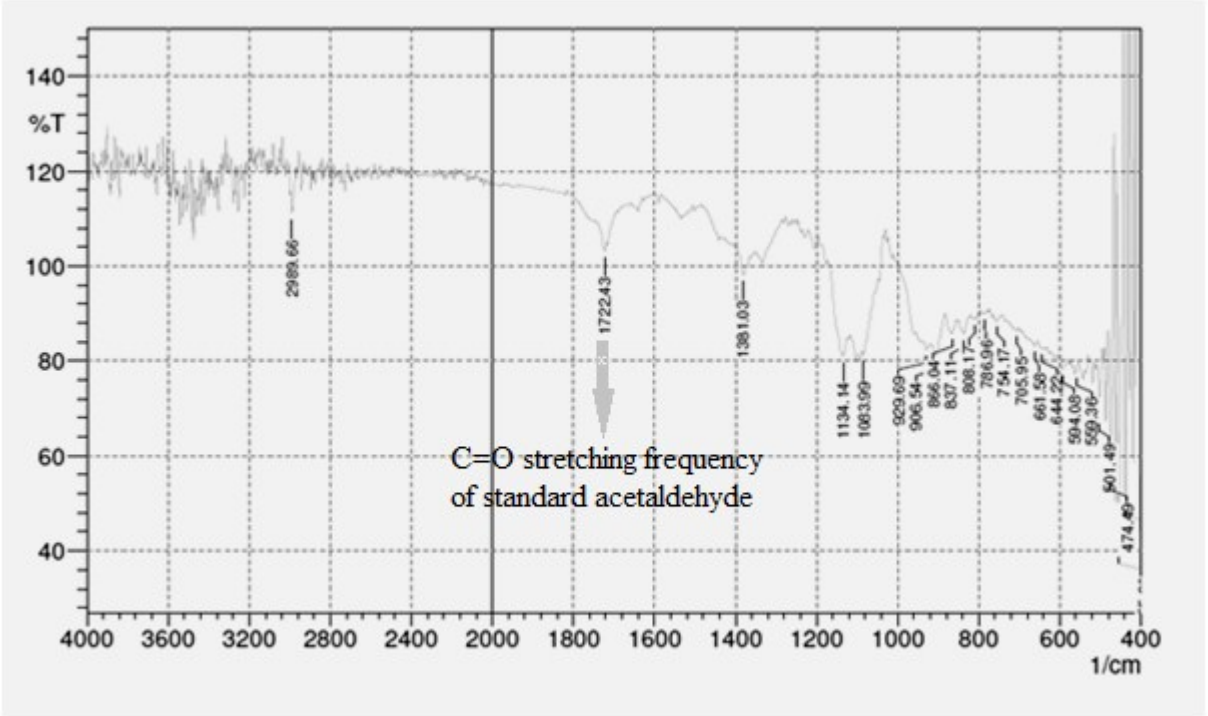
Detection of acetaldehyde (2t) by Fourier transformation Infrared spectroscopy (FTIR) analysis

The presence of acetaldehyde in reaction mixture was confirmed by Fast fourier infrared spectroscopy (FTIR) analysis. Generally, the carbonyl stretch C=O of saturated aliphatic aldehydes appears from 1740-1720 cm^{-1}. The C=O stretching frequency of standard acetaldehyde was found to be 1722.43 cm^{-1} while *in situ* formed acetaldehyde had the stretching frequency of 1726.29 cm^{-1}. This comparable stretching frequency values indicate that the oxidative esterification proceeds through the formation of acetaldehyde as intermediate.

FTIR spectra of acetaldehyde (2t) generated in the reaction mixture



FTIR spectra of standard acetaldehyde



References

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