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Supported Palladium Nanoparticles as Switchable Catalyst for Aldehyde Conjugate/s and Acetate Ester Synthesis from Alcohols

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1. General Information

Reagents of high quality were obtained from Sigma-Aldrich, Sd-Fine and Merck, and used without further purification. Amberlite® IRA 900 Cl^- resin used as polymer support (PS) (Chloride form) was purchased from Acros Organics. All reactions were monitored by TLC on Silica Gel $60F_{254}$ (Merck) using UV light detection. Column chromatographic separations have been carried out on silica gel 60-120 mesh and 60-200 mesh (Merck). The SEM analysis was performed on E1010 ion sputter Hitachi Japan. For the analysis, the nanoparticles were mounted on an aluminium stub using double sided tape. TEM image was taken using a carbon coated copper grid (Microscopy sciences) in a transmission electron microscope JEOL 2100F. ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance 600 and 300 spectrometer operating at 600 MHz, 300 MHz (^1H) and 150 MHz, 75 MHz (^{13}C) respectively. Chemical shifts were recorded in δ (ppm) relative to the TMS signal, coupling constants (*J*) are given in Hz and multiplicities of the signals are reported as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet. NMR spectras were recorded at 25 °C in $CDCl_3$ [residual $CHCl_3$ (δ_H 7.26 ppm) or $CDCl_3$ (δ_C 77.00 ppm). 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.d. with film thickness 0.25 μm).

Preparation of Pd@PS catalyst

The 1 g of Amberlite resin IRA 900 Cl^- form resin (Across, BE) (PS) was partially exchanged with borohydride ion (30 mg $NaBH_4$ in 10 mL of water) in a 25 mL round bottom flask for 4 h at room temperature. The resin (PS) was washed with water till the pH became neutral and then with acetone to remove water from the polymer surface. The partially borohydride exchanged resin beads were dried under reduced pressure. The dried borohydride exchanged resin beads were added into the warm (100 °C) solution of palladium acetate (10 mg) in DMF (3 mL). The mixture was stirred for 1 h or till the brown colored solution changed to colorless and simultaneously white solid beads turned black due to the impregnation of palladium nanoparticles on the surface giving Pd@PS catalyst. Pd@PS was filtered through a cotton bed, washed with water and acetone, and dried under reduced pressure.

Characterization of Pd@PS catalyst: An insight into the morphological and structural features of the synthesized Pd@PS catalyst was done by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and selected area electron diffraction (SAED) analysis. The SEM and SEM-EDS (energy dispersive spectra) (Fig. 1a-b) analysis of Pd@SS, showed the impregnation of palladium nanoparticles to the solid support. The low field TEM image (Fig 1c-d) further revealed the dispersion of maximum number of particles of average size in between 2-5 nm (Fig 1e) as calculated from (Fig 1d). The HRTEM image demonstrated the presence of Pd with interplanar distance of 0.22 and 0.19 nm that signifies the (111) and (200) planes of Pd in *fcc* arrangement (Fig. 1f). The FFT image of selected region also signifies the *fcc* arrangement of the palladium crystal. The SAED spectra of Pd@PS catalyst shows intense Debye Sherrer ring corresponding to (111) and (200) planes but diffused rings were observed corresponding to (220) and (311) planes.

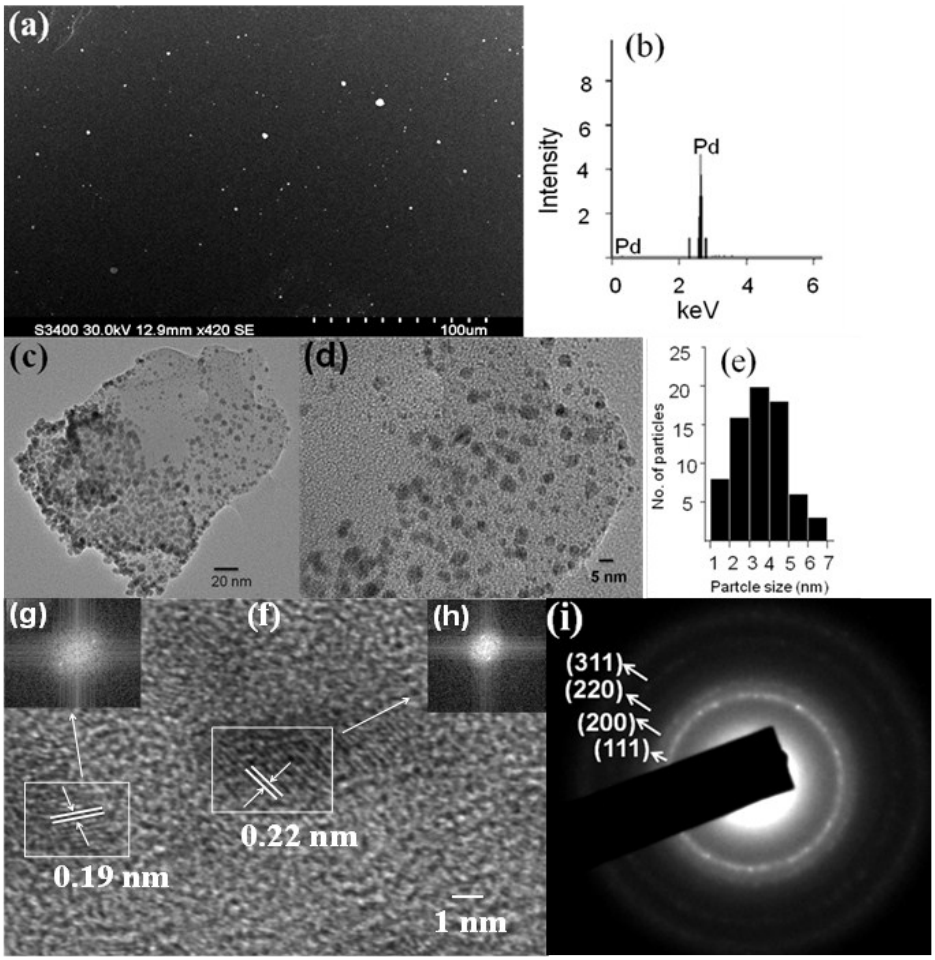
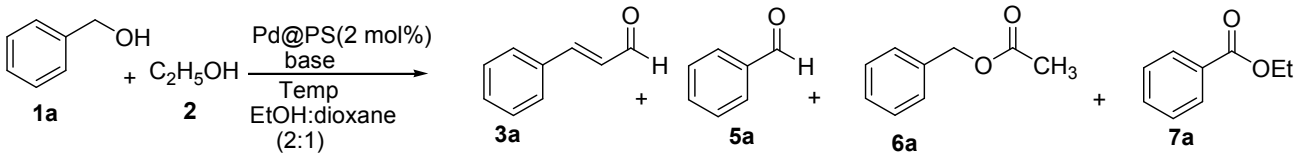


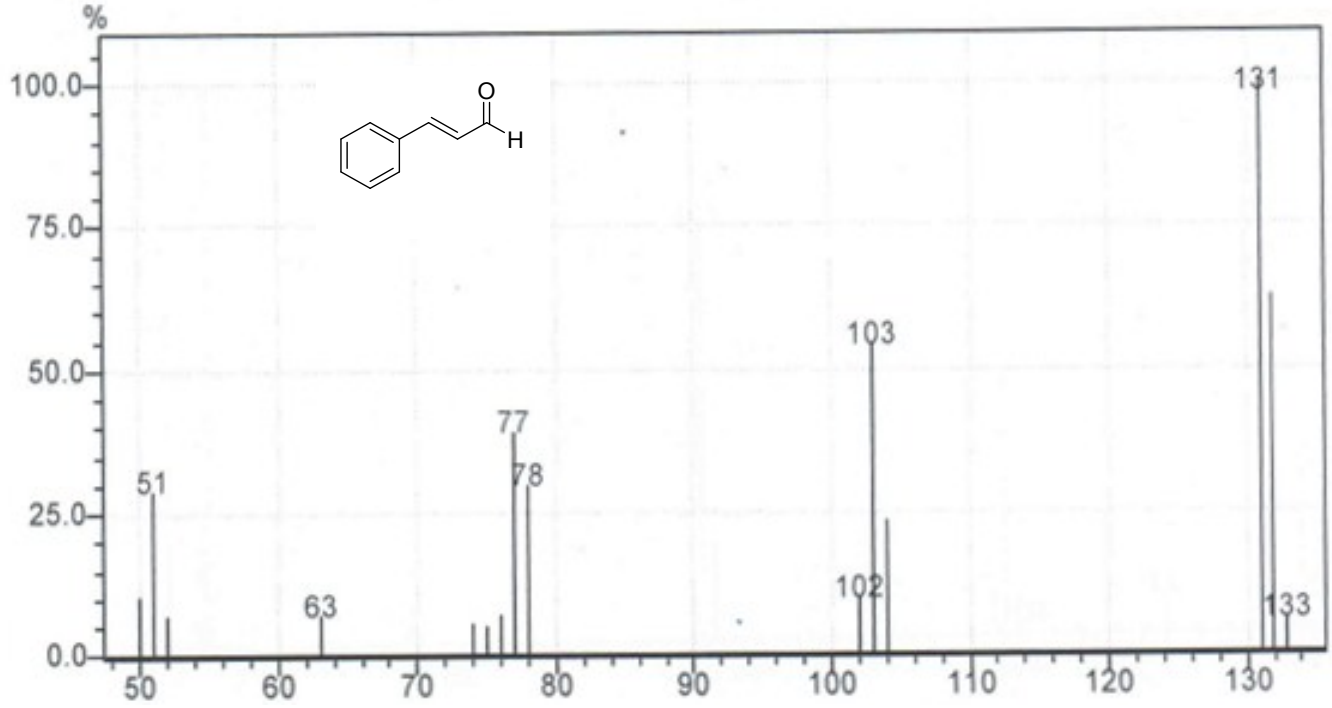
Fig. S1: SEM; **b**: SEM-EDS; **c**: low field-TEM image at 20 nm scale; **d**: at 5 nm scale; **e**: Particle size distribution histogram as calculated from **c**; **f**: HRTEM image showing lattice fringe spacing; **g:** FFT of selected region with fringe spacing 0.19 nm; **h**: FFT of selected region with fringe spacing 0.22 nm; **i**: SAED of Pd@PS

Table S1. Effect of temperature variation on the reaction under standard conditions (GCMS analysis)

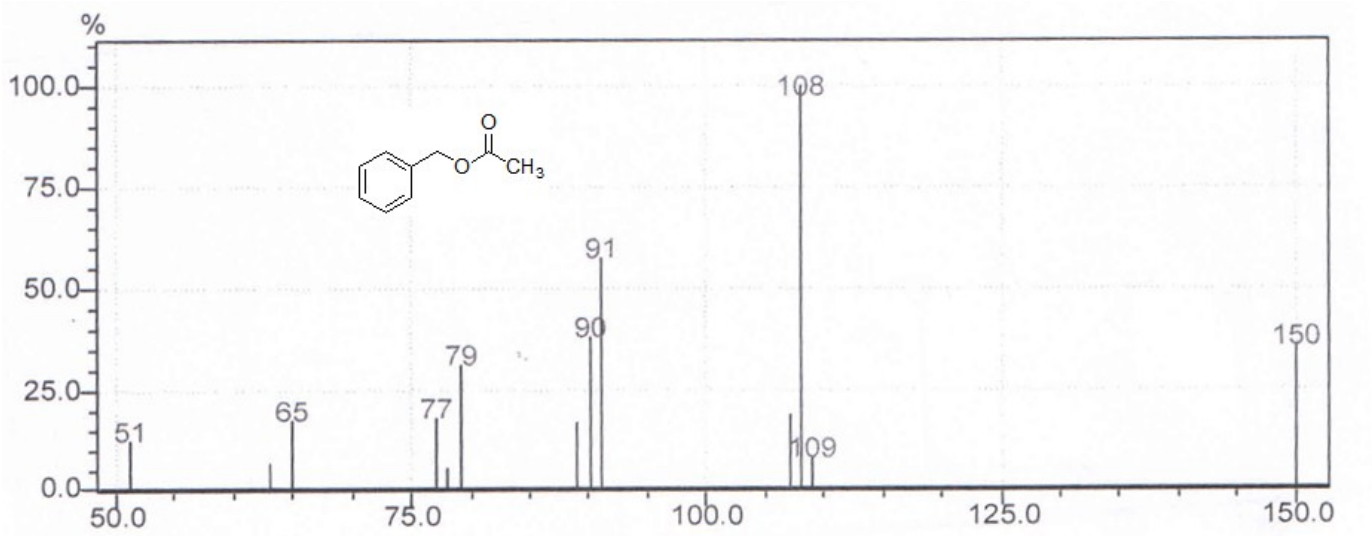


Entry	Base(equiv)	Temp(^oC)	Yield (%)			
			3a	**5a**	**6a**	**7a**
1	K_2CO_3 (4.0)	42	28	32	3	23
2	K_2CO_3 (4.0)	30	6	41	5	14

GC Mass spectra of **3a**



GC Mass spectra of **6a**



GC Mass spectra of **7a**

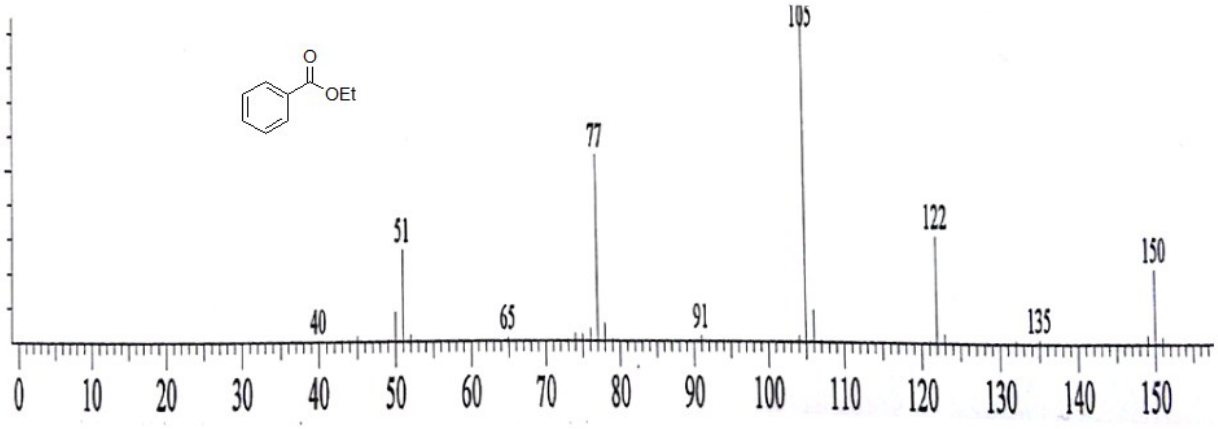
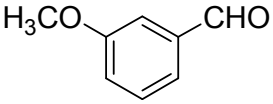
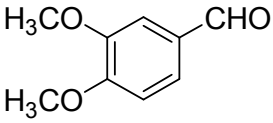
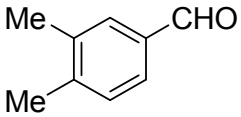
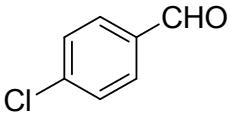
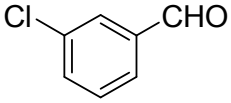
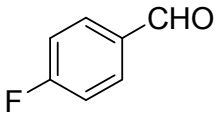
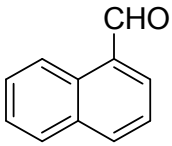
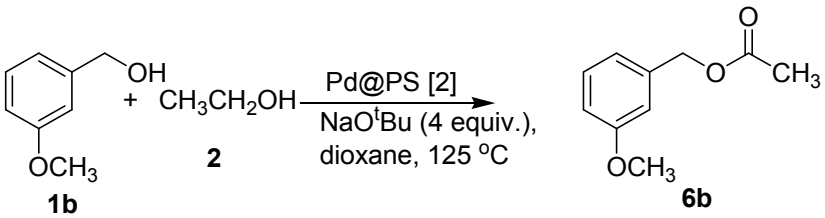


Table S2: Aldehydes obtained in the Table 2

 **5b**; 37[c]	 **5c;** 44[b]	 **5d;** 40[b]	 **5e;** 51[c]
 **5f;** 30[b]	 **5g;** 30[b]	 **5h;** 28[b]	

[b]Isolated yield. [c]GC-MS yield.

Table S3: Recyclability of Pd@PS for oxidative esterification reaction



No. of cycles	1st cycle	2nd cycle	3rd cycle	4th cycle	5th cycle
Yield **6b** (%)	62	61	61	58	51

ICP-AES study of reaction mixture was carried out using 3-methoxylbenzyl alcohol as substrate. The sample after complete digestion was subjected to ICP-AES analysis.

Table S4: Palladium leaching experiment by ICP-AES analysis

No. of cycle	1st cycle	3rd cycle	5th cycle
Leaching (ppm)	1.613	0.019	0.021

The characterization of Pd@PS catalyst by TEM studies after five cycles:

The TEM studies of Pd@PS catalyst after five cycles shows the presence of Pd nanoparticles on the surface. The Pd nanoparticles were found to be aggregated at few regions which may occur due to the present oxidative reaction conditons; this may lead to the lowering the yield of product in each cycle.

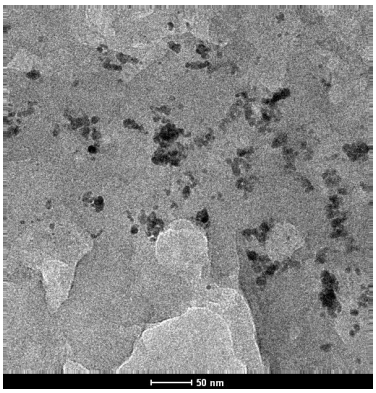


Fig. S2. TEM image of Pd@PS after five cycles.

Mercury Test

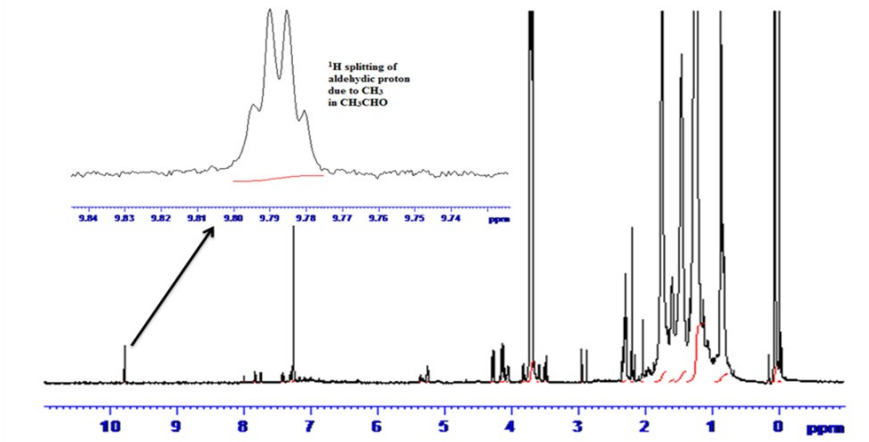
Mercury test was conducted by using 500 equiv. of Hg (metal) with respect to Pd (Pd@PS). Initially the catalyst was stirred with mercury metal for 5 minutes then the reactants 3-methoxy benzyl alcohol (**1b)** (1.45 mmol), NaO^{t}Bu (556 mg, 5.80 mmol.) ethanol (2.0 mL), 1,4-dioxane

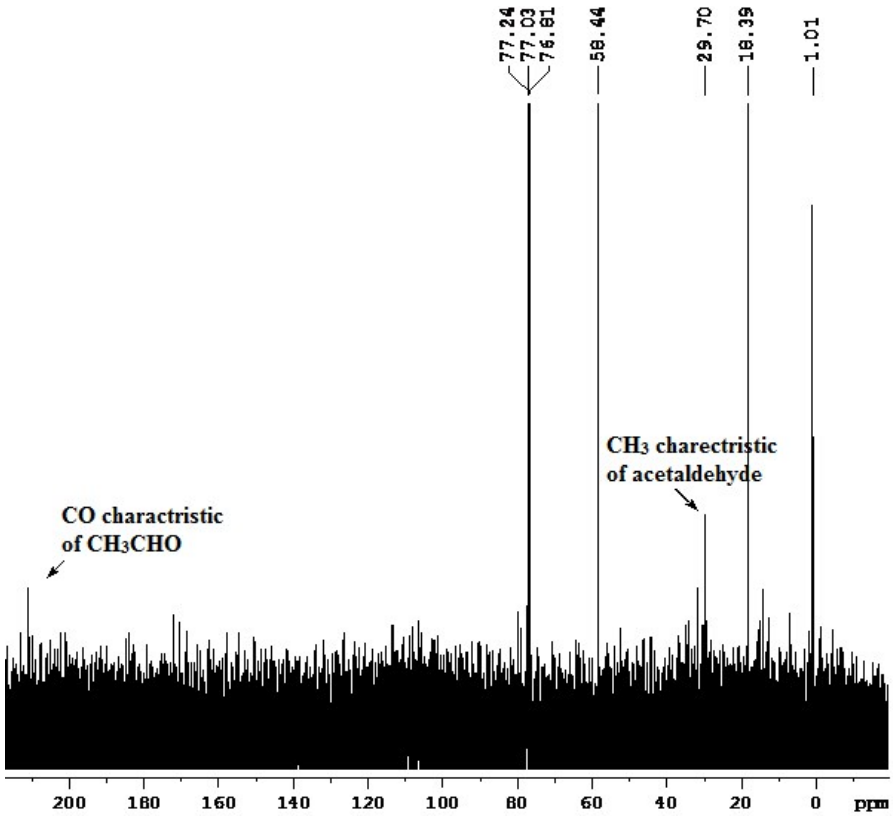
(1.5 mL) and the reaction was carried under standard condition. The experiment indicated that Pd(0) species as heterogeneous component participated in the oxidative esterification reaction.

In another study, Hg(0) poisoning experiment was carried out with our model substrate **1b** under optimized conditions. After 20 h of reaction time we have added Hg(0) to the reaction mixture and continued further up to 60 h. There was no further improvement in product formation which indicated that catalytic active species in the solution was Pd(0).

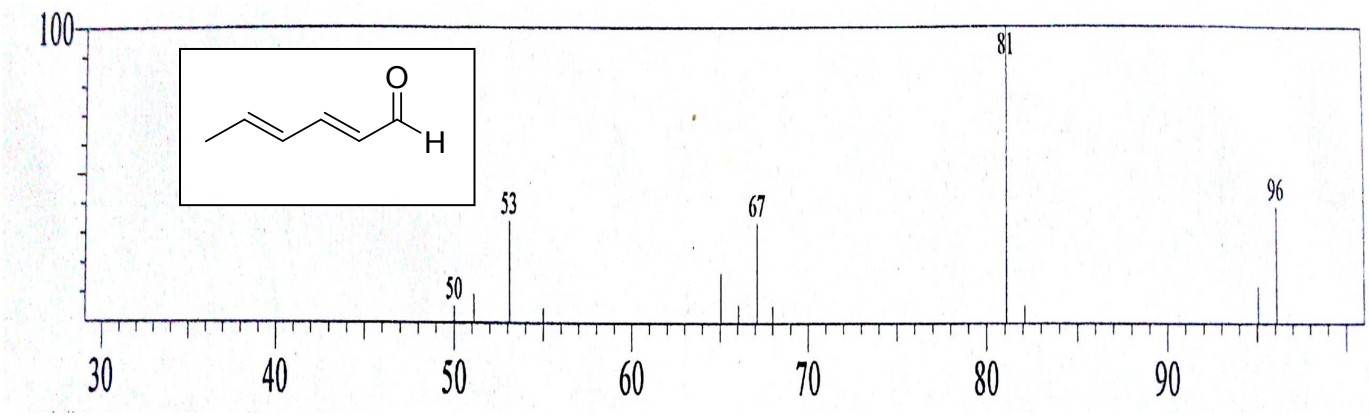
Identification of acetaldehyde: To a double necked round bottomed flask (RBF) was added ethanol (1 mL), Pd@PS catalyst (414 mg, 2 mol% Pd), K_2CO_3 (500 mg). The distillation system was setup using one neck of RBF and the oxygen gas was bubbled through the reaction mixture by balloon from the second neck. The reaction mixture was heated at temperature 60 ^{o}C for 24 h and the distillate was collected in the receiver kept in ice cooled water. The NMR studies of distillate revealed the presence of acetaldehyde in ethanol.

Crude NMR of acetaldehyde (8) in ethanol using $CDCl_3$ as solvent





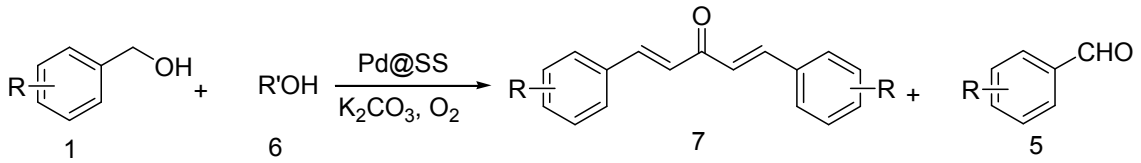
GC-MS spectra of 2,4-Hexadienal (self condensation product of acetaldehyde from ethanol oxidation)

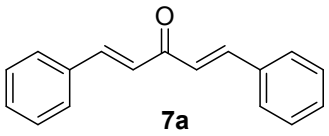
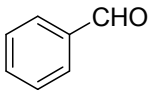
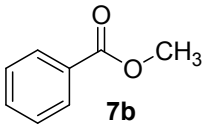
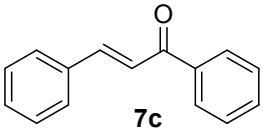
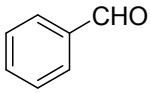


Reaction of benzyl alcohol with other aliphatic alcohols

The other aliphatic alcohols such as isopropanol, 2-phenylethanol and methanol were tested under the standard reaction conditions. The reaction of benzyl alcohol with isopropanol yielded dibenzylidene acetones **7a** as major product along with benzaldehyde as minor product. The same raction with methanol gave the corresponding methyl ester **7b** in 60% yield; while using 2-phenylethanol as the reactant afforded **7c** in 70% yield (Table S4).

Table S5: Optimization studies of benzyl alcohol with different alcohols for AC/s synthesis[a]

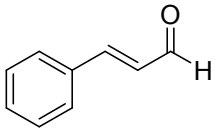


Entry	R	R'	Product	Yield [%]	Product	Yield [%]
1	H	$(CH_3)_2CH$	 **7a**	40	 **5a**	30
2[b]	H	CH_3	 **7b**	60	--	---
3	H	$PhCHCH_3$	 **7c**	70	 **5a**	traces

[a]Reaction conditions: 1a (0.92 mmol), 6 (18.5 equiv.), Pd@PS (2.0 mol%), solvent (1 mL), 24 h; isolated yields. [b]T = 55 ^{o}C due to high volatility of methanol.

Oxidative synthesis of aldehydes conjugates (AC/s) from benzyl alcohols and ethanol and characterization data:

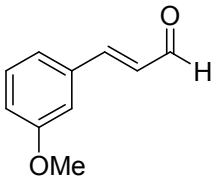
Cinnamaldehyde[1] (3a) (Table 1, entry 10)



Benzyl alcohol (100 mg, 0.92 mmol), ethanol (1.1 mL, 9.24 mmol), in presence of catalyst Pd@PS (414 mg, 2 mol % Pd), K_2CO_3 (4 equiv.) and 1,4-dioxane (1 mL) were taken in an oven dried reaction vial. The reaction was carried out for 24 h at 60 ^oC under bubbling oxygen supply through a balloon put over it. The reaction mixture after extraction with ethylacetate followed by silica gel column chromatography (60-120 mesh) with (Hexane:EtOAc = 98:2) afforded yellow liquid **3a** (61 mg, 50%); ^{1}HNMR (300 MHz, $CDCl_3$) δ 6.68-6.76 (dd, *J* = 7.7 Hz, 16.0 Hz, 1H), 7.41-7.45 (m, 4H), 7.50-7.57 (m, 2H), 9.70 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.4, 129.0, 131.2, 133.9, 152.8, 193.8. GC-MS: *m/z*= 133 $[M+1]^+$, 132 $[M]^+$, 131 $[M-1]^+$, 103 $[M-CHO]^+$, 78, 77.

(2*E*,4*E*)-5-phenylpenta-2,4-dienal (4a) detected as one of product in the reaction of benzyl alcohol and ethanol at 60 ^oC for 24 h. The ^{1}H NMR data of product from crude reaction mixture was compared with literature report.[2] GC-MS: *m/z*= 158 $[M]^+$, 129 $[M-CHO]^+$, 115, 102, 91, 78, 77.

(*E*)-3-(3-methoxyphenyl)acrylaldehyde (3b) (Table 2, entry 1)

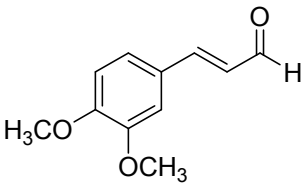


As described for the synthesis of **3a,** 3-methoxy benzyl alcohol (200 mg, 1.45 mmol) and ethanol (1688 µL, 28.96 mmol), in presence of Pd@PS (648 mg, 2 mol% Pd), K_2CO_3 (4 equiv.) and 1,4-dioxane (1 mL) for 48 h at 60 ^oC after silica gel column chromatography (Hexane:EtOAc = 98:2) afforded yellow liquid **3b** (94 mg, 40%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.66-6.74 (dd, *J* = 7.7 Hz, 15.9 Hz, 1H), 6.97-7.00 (m, 1H), 7.07-7.08 (m, 1H), 7.16 (d, *J* = 7.6, 1H), 7.32-7.37 (t, *J* = 7.9, 1H), 7.42-7.47 (m, 1H), 9.70 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 113.2, 117.1, 121.2, 128.8, 130.1, 135.3, 152.7, 160.0, 193.7. GC-MS: *m/z*= 162 $[M]^+$, 161 $[M-1]^+$, 147 $[M-CH_3]$, 131 $[M-OCH_3]^+$, 104, 91, 77.

(2*E*,4*E*)-5-(3-methoxyphenyl)penta-2,4-dienal (4b) (Table 2, entry 1) detected by GC-MS analysis as one of product in the reaction of 3-methoxyl benzyl alcohol and ethanol at 60 ^oC for

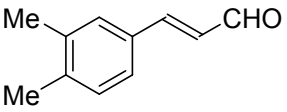
24 h. GC-MS: *m/z*= 188 $[M]^+$, 173 $[M-CH_3]$, 159 $[M-CHO]^+$, 144, 128, 117, 115, 102, 91, 81, 77.

(*E*)-3-(3,4-dimethoxyphenyl)acrylaldehyde (3c) (Table 2, entry 2)



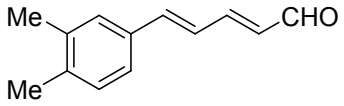
As described above for the synthesis of **3a** 3,4-dimethoxybenzyl alcohol (200 mg, 1.19 mmol) and ethanol (1376 µL, 23.60 mmol), in presence of Pd@PS (527 mg, 2 mol % Pd), K_2CO_3 (4 equiv.) and 1,4-dioxane (1 mL) for 48 h at 60 ^oC after silica gel column chromatography (Hexane:EtOAc = 98:2) afforded yellow liquid **3c** (87 mg, 38%); ^1H NMR (300 MHz, $CDCl_3$) δ 3.92, 3.93 (s, 6H), 6.57-6.65 (dd, *J* = 7.7 Hz, 15.8 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 7.07 (s, 1H), 7.14-7.17 (m, 1H), 7.41 (d, *J* = 15.8, 1H), 9.66 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.9, 56.0, 110.0, 111.2, 123.4, 126.7, 127.1, 149.4, 152.0, 152.7, 193.5. GC-MS: *m/z*= 192 $[M]^+$, 177 $[M-CH_3]^+$, 161 $[M-OCH_3]$, 149, 133, 121, 77.

3-(3,4-Dimethyl-phenyl)-propenal (3d) (Table 2, entry 3)



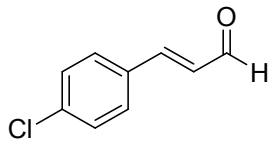
As described above for the synthesis of **3a** 3,4-dimethylbenzylalcohol (200 mg, 1.47 mmol) and ethanol (1856 uL, 29 mmol), in presence of Pd@PS (657 mg, 2 mol % Pd), K_2CO_3 (4 equiv.) and 1,4-dioxane (1 mL) for 48 h at 60 ^oC after silica gel column chromatography (Hexane:EtOAc = 98:2) afforded yellow liquid **3d** (47 mg, 20%); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.32 (s, 6H), 6.66-6.74 (dd, *J* = 7.8 Hz, 15.9 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.28- 7.36 (m, 2H), 7.45 (d, *J* = 15.9 Hz, 1H), 9.69 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz) δ 19.7, 19.9, 126.2, 127.5, 129.7, 130.3, 131.6, 137.4, 140.8, 153.3, 193.9. GC-MS: *m/z*= 160 $[M]^+$, 145 $[M-CH_3]^+$, 131 $[M+1-(CH_{3)2}]$, 115, 91, 77.

5-(3,4-Dimethyl-phenyl)-penta-2,4-dienal (4d) (Table 2, entry 3)



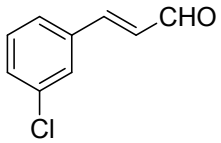
Produced as the other product in the reaction starting from 3,4-dimethylbenzylalcohol (200 mg, 1.47 mmol) and ethanol (1856 µL, 29 mmol), in presence of Pd@PS (657 mg, 2 mol% Pd), K_2CO_3 (4 equiv.) and 1,4-dioxane (1 mL) for 48 h at 60 ^oC purified by column chromatography (Hexane:EtOAc = 98:2) afforded yellow liquid **4d** (82 mg, 30%). ^1H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 6H), 6.23-6.31 (dd, *J* = 8.0 Hz, 15.1 Hz, 1H), 6.99 (d, *J* = 5.4 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.24-7.31 (m, 4H), 9.62 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz) δ 19.8, 125.1, 125.2, 128.7, 130.2, 130.9, 133.2, 137.2, 138.9, 142.8, 152.7, 193.7.

3-(4-chlorophenyl)acrylaldehyde[3] **(3e)** (Table 2, entry 4)



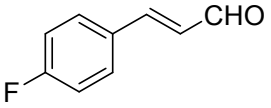
As described for synthesis of **3a,** 4-chloro benzyl alcohol (200 mg, 1.41 mmol) and ethanol (1688 µL, 28.0 mmol), in presence of Pd@PS (626 mg, 2 mol% Pd), K_2CO_3 (4 equiv.) and 1,4-dioxane (1 mL) for 48 h at 60 ^oC after silica gel column chromatography (Hexane:EtOAc = 98:2) afforded yellow solid **3e** (94 mg, 40%); ^1H NMR (300 MHz, $CDCl_3$) δ 6.64-6.72 (dd, *J* = 7.7 Hz, 16.0 Hz, 1H), 7.39-7.42 (m, 3H), 7.45-7.51 (m, 2H), 9.70 (d, *J* = 7.6, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.9, 129.4, 129.6, 132.5, 137.2, 151.0, 193.3.

3-(3-Chloro-phenyl)-propenal (3f) (Table 2, entry 5)



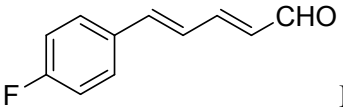
As described for synthesis of **3a,** 3-chloro benzyl alcohol (200 mg, 1.41 mmol) and ethanol (1688 µL, 28.0 mmol), in presence of Pd@PS (626 mg, 2 mol% Pd), K_2CO_3 (4 equiv.) and 1,4-dioxane (1 mL) for 24h at 60 ^oC after silica gel column chromatography (Hexane:EtOAc = 98:2) afforded yellow liquid **3f** (70 mg, 30%); ^1H NMR (600 MHz, $CDCl_3$) δ 6.69- 6.73 (dd, *J* = 7.56 Hz, 16.0 Hz, 1H), 7.38-7.46 (m, 4H), 7.55 (s, 1H), 9.71 (d, *J* = 7.5, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 126.5, 128.3, 129.7, 130.3, 131.1, 135.2, 135.8, 150.7, 193.3. GC-MS: *m/z*= 167 $[M+1]^+$, 166 $[M]^+$, 137 $[M+1-CHO]^+$, 131 [M-Cl], 112, 103, 77.

3-(4-Fluoro-phenyl)-propenal[4] (3g) (Table 2, entry 6)



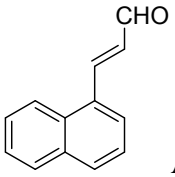
As described for the synthesis of **3a**, 4-fluorobenzylalcohol (200 mg, 1.59 mmol) and ethanol (1854 µL, 32 mmol), in presence of Pd@PS (707 mg, 2 mol% Pd), K_2CO_3 (4 equiv.) and 1,4-dioxane (1 mL) for 24 h at 60 ^oC after silica gel column chromatography (Hexane:EtOAc = 98:2) afforded yellow liquid **3g** (78 mg, 33%); ^1H NMR (600 MHz, $CDCl_3$) δ 6.63-6.37 (dd, *J* = 7.6 Hz, 16.2 Hz, 1H), 7.12-7.14 (t, *J*= 8.5 Hz, 2H), 7.44 (d, *J* = 16.0 Hz, 1H), 7.56-7.58 (m, 2H), 9.69 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (150 MHz) *δ* 116.3, 116.4, 128.4, 130.4, 130.5, 151.2, 163.6, 165.3, 193.3.

5-(4-Fluoro-phenyl)-penta-2,4-dienal (4g) (Table 2, entry 6)



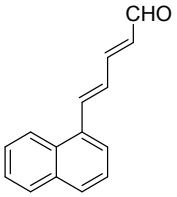
Detected in traces by reaction of 4-fluorobenzylalcohol (200 mg, 1.59 mmol) and ethanol (1854 µL, 32 mmol), in presence of Pd@PS (707 mg, 2 mol% Pd), K_2CO_3 (4 equiv.) and 1,4-dioxane (1 mL) for 24 h at 60 ^oC. GC-MS: *m/z*= 176 [M], 147 $[M\text{-}CHO]^+$, 133, 127, 75.

3-Naphthalen-1-yl-propenal[5] (3h) (Table 2, entry 7)



As described above for the synthesis of **3a**, 1-Napthalenemethanol (200 mg, 1.27 mmol) and ethanol (1483 µL, 25.4 mmol), in presence of Pd@PS (568 mg, 2 mol% Pd), K_2CO_3 (4 equiv.) and 1,4-dioxane (1 mL) for 48 h at 60° C after silica gel column chromatography (Hexane:EtOAc = 98:2) afforded yellow liquid **3h** (58 mg, 25%); ^1H NMR (600 MHz, $CDCl_3$) *δ* 6.82-6.86 (dd, *J* = 7.7 Hz, 15.6 Hz, 1H), 7.51-7.54 (m, 1H), 7.56-7.58 (m, 1H), 7.61-7.64 (m, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 8.18 (d, *J* = 8.4, 1H), 8.32 (d, *J* = 15.7 Hz, 1H), 9.85 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 122.7, 125.4, 125.7, 126.4, 127.2, 128.9, 130.8, 130.9, 131.1, 131.6, 133.7, 149.2, 193.6; GC-MS: *m/z*= 182 $[M]^+$, 181 $[M\text{-}1]^+$, 153 $[M\text{-}CHO]^+$, 128, 76.

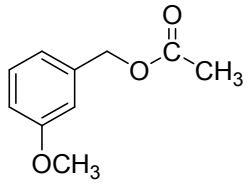
5-Naphthalen-1-yl-penta-2,4-dienal (4h) (Table 2, entry 7)



Produced as product in the reaction of 1-Napthalenemethanol (200 mg, 1.27 mmol) and ethanol (1483 µL, 25.4 mmol), in presence of Pd@PS (568 mg, 2 mol% Pd), K_2CO_3 (4 equiv.) and 1,4-dioxane (1 mL) for 48 h at 60°C after silica gel column chromatography (Hexane:EtOAc = 98:2) afforded yellow liquid **4h** (53 mg, 20%); ^{1}H NMR (600 MHz, $CDCl_3$) 6.31-6.34 (dd, *J* = 7.9 Hz, 15.6 Hz, 1H), 7.08-7.12 (m, 1H), 7.39-7.43 (m, 1H), 7.49-7.52 (m, 1H), 7.53-7.56 (m, 1H), 7.56-7.60 (m, 1H), 7.79 (d, *J* = 7.3 Hz, 1H), 7.83 (d, *J* = 15.2 Hz, 1H), 7.87-7.90 (m, 2H), 8.15 (d, *J* = 8.4 Hz, 1H), 9.67 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (150 MHz) δ 123.0, 124.5, 125.5, 126.2, 126.8, 128.7, 128.9, 130.0, 131.1, 131.8, 132.7, 133.7, 139.0, 152.0, 193.6. GC-MS: *m/z*= 208 $[M]^+$, 207 $[M-1]^+$, 179 $[M-CHO]^+$, 165, 152, 128, 89, 76.

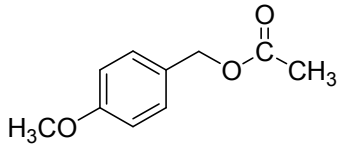
Oxidative esterification reaction of benzyl/alkyl alcohol with ethanol for acetate ester (AEs) synthesis and characterization data:

3-Methoxybenzylacetate[6] **(6b)** (Table 3, entry 5)



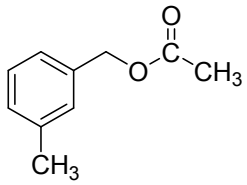
3-Methoxybenzyl alcohol **1b** (200 mg, 1.45 mmol), ethanol (2.0 mL) in presence of catalyst Pd@PS (648 mg, 2 mol% Pd), NaO^{t}Bu (4 equiv.) and 1,4-dioxane (1.2 mL) were taken in an oven dried RBF (50 mL). After that, a condenser equipped with a rubber septum was tightly fitted to the round bottom flask and the reaction was carried out for 60 h at 125 °C under reflux after extraction with ethyl acetate followed by silica gel column chromatography (60-120 mesh) (Hexane:EtOAc = 98:2) afforded colorless liquid **6b** (162 mg, 62%); ^{1}HNMR (600 MHz, $CDCl_3$) δ 2.26 (s, 3H), 3.97 (s, 3H), 5.23 (s, 2H), 7.01-7.03 (m, 1H), 7.09 (s, 1H), 7.09 (d, *J*= 7.56 Hz, 1H), 7.41-7.45 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.0, 55.2, 66.1, 113.6, 113.7, 120.4, 129.6, 137.4, 159.7, 170.8. GC-MS: *m/z*= 180 $[M]^+$, 138 $[M+1-COCH_3]$, 107 $[M+1-COCH_3-CH_3]^+$, 91, 79, 78.

4-Methoxybenzylacetate[6,7] **(6c)** (Table 4, entry 1)



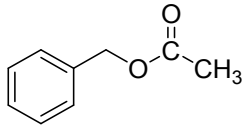
As described above for the synthesis of **6b**, 4-Methoxybenzyl alcohol **1i** (200 mg, 1.45 mmol), ethanol (2.0 mL) in presence of catalyst Pd@PS (648 mg, 2 mol% Pd), NaO^{t}Bu (4 equiv.) and 1,4-dioxane (1.5 mL) after extraction with ethyl acetate followed by silica gel column chromatography (60-120 mesh) (Hexane:EtOAc = 98:2) afforded colorless liquid **6c** (159 mg, 61%); ^{1}HNMR (600 MHz, $CDCl_3$) δ 2.06 (s, 3H), 3.78 (s, 3H), 5.03 (s, 2H), 6.88 (d, *J* = 8.64 Hz, 2H), 7.29 (d, *J* =8.58 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.8, 55.0, 65.9, 131.8, 128.0, 129.9, 159.5, 170.6. GC-MS: *m/z*= 180 $[M]^+$, 138 $[M+1-COCH_3]$, 107 $[M+1-COCH_3-CH_3]^+$, 91, 79, 78.

3-Methylbenzylacetate[6,7] **(6d)** (Table 4, entry 2)



As described above for the synthesis of **6b**, starting from 3-Methylbenzyl alcohol **1j** (200 mg, 1.64 mmol), ethanol (2.0 mL) in presence of catalyst Pd@PS (733 mg, 2 mol% Pd) after extraction with ethyl acetate followed by silica gel column chromatography (60-120 mesh) (Hexane:EtOAc = 98:2) afforded colorless liquid **6d** (156 mg, 58%); ^{1}HNMR (600 MHz, $CDCl_3$) δ 2.11 (s, 3H), 2.37 (s, 3H), 5.09 (s, 1H), 7.14-7.19 (m, 3H), 7.25-7.28 (t, *J* = 7.80 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.9, 21.2, 66.2, 125.2, 128.4, 128.9, 135.7, 138.1, 170.7. GC-MS: *m/z*= 164 $[M]^+$, 122 $[M+1-COCH_3]$, 107 $[M+1-COCH_3-CH_3]^+$, 91, 79, 78.

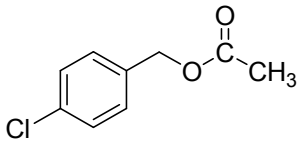
Benzyl acetate[8] **(6a)** (Table 4, entry 3)



As described for synthesis of **6b**, Benzyl alcohol (200 mg, 1.85 mmol), ethanol (2.0 mL) in presence of catalyst Pd@PS (826 mg, 2 mol% Pd), NaO^{t}Bu (4 equiv.) and 1,4-dioxane (1.5 mL) were taken in an oven dried RBF (50 mL). The reaction was carried out for

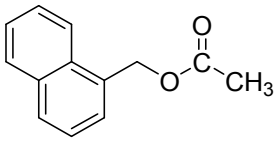
60 h at 125 ^{o}C under reflux. The reaction mixture after extraction with ethylacetate followed by silica gel column chromatography (60-120 mesh) (Hexane:EtOAc = 98:2) afforded colorless liquid **6a** (166 mg, 60%); ^{1}HNMR (600 MHz, $CDCl_3$) δ 2.11 (s, 3H), 5.12 (s, 2H), 7.33-7.38 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.9, 66.2, 128.2, 128.5, 135.9, 170.8. GC-MS: *m/z*= 150 $[M]^+$, 109, 108, 91, 90, 79, 77.

4-chlorobenzyl acetate[6,7] **(6e)** (Table 4, entry 4)



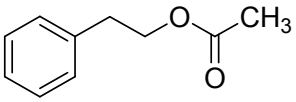
As described above for the synthesis of **6b**, 4-Chlorobenzyl alcohol **1e** (200 mg, 1.41 mmol), ethanol (2.0 mL) in presence of catalyst Pd@PS (630 mg, 2 mol% Pd), NaO^{t}Bu (4 equiv.) and 1,4-dioxane (1.5 mL) after extraction with ethyl acetate followed by silica gel column chromatography (60-120 mesh) (Hexane:EtOAc = 98:2) afforded colorless liquid **6e** (155 mg, 60%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.09 (s, 3H), 5.06 (s, 2H), 7.28-7.29 (m, 2H), 7.32-7.33 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.8, 55.0, 65.9, 131.8, 128.0, 129.9, 159.5, 170.6. GC-MS: *m/z*= 180 $[M]^+$, 138 $[M+1-COCH_3]$, 107 $[M+1-COCH_3-CH_3]^+$, 91, 79, 78.

(Naphthalen-4-yl)methyl acetate[6,7] **(6f)** (Table 4, entry 5)



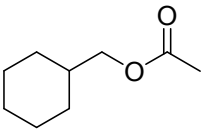
As described above for the synthesis of **6b**, Napthalene-1-methanol **1h** (200 mg, 1.27 mmol), ethanol (2.0 mL) in presence of catalyst Pd@PS (568 mg, 2 mol% Pd), NaO^{t}Bu (4 equiv.) and 1,4-dioxane (1.5 mL) after extraction with ethyl acetate followed by silica gel column chromatography (Hexane:EtOAc = 98:2) afforded yellow liquid **6f** (160 mg, 63%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.14 (s, 3H), 5.61 (s, 2H), 7.47-7.50 (m, 1H), 7.55-7.60 (m, 3H), 7.87-7.92 (m, 2H), 8.06 (d, *J* = 8.40 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.9, 64.4, 123.4, 125.2, 125.8, 126.5, 127.4, 128.6, 129.2, 131.3, 131.5, 133.6, 170.8. GC-MS: *m/z*= 200 $[M]^+$, 158 $[M+1-COCH_3]$, 141, 140, 129.

Phenylethylacetate[6] **(6g)** (Table 4, entry 6)



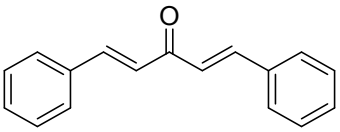
As described above for the synthesis of **6b**, 2-Phenylethanol **1k** (200 mg, 1.64 mmol), ethanol (2.0 mL) in presence of catalyst Pd@PS (733 mg, 2 mol% Pd), NaO^{t}Bu (4 equiv.) and 1,4-dioxane (1.5 mL) after extraction with ethyl acetate followed by silica gel column chromatography (60-120 mesh) (Hexane:EtOAc = 98:2) afforded colorless liquid **6g** (188 mg, 70%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.90 (s, 3H), 2.79-2.82 (t, *J* = 7.10 Hz, 2H), 4.14-4.17 (t, J= 7.14 Hz, 2H), 5.23 (s, 1H), 7.03-7.11 (m, 3H), 7.16-7.19 (t, J= 7.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.8, 34.9, 64.8, 126.4, 128.4, 128.7, 137.7, 170.8.

Cyclohexylmethyl acetate[7] (**6h)** (Table 4, entry 7)



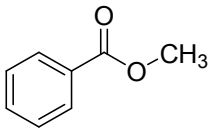
As described above for the synthesis of **6b**, 1-Cyclohexylmethanol **1l** (200 mg, 1.75 mmol), ethanol (2.0 mL) in presence of catalyst Pd@PS (782 mg, 2 mol% Pd), NaO^{t}Bu (4 equiv.) and 1,4-dioxane (1.5 mL) after extraction with ethyl acetate followed by silica gel column chromatography (60-120 mesh) in ethyl acetate: hexane (2:98) afforded colorless liquid **6h** (186 mg, 68%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.81-0.87 (m, 2H), 1.06-1.16 (m, 3H), 1.48-1.56 (m, 2H), 1.60-1.62 (m, 4H), 1.91 (s, 3H), 3.74-3.75 (d, J= 6.72 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.5, 25.4, 26.1, 29.4, 36.8, 69.3, 170.7.

1,5-diphenylpenta-1,4-dien-3-one (**7a**) (Table S4, entry 1)



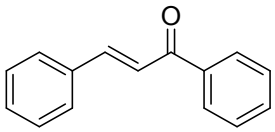
Benzyl alcohol (100mg, 0.926 mmol), and isopropanol (1.5 mL) as solvent , Pd@SS (0.02eq) , K_2CO_3 (511 mg, 3.704 mmol) under bubbling oxygen supply through balloon for 48 h at 80 ^{o}C after silica gel column chromatography in Ethyl acetate: Hexane (2:98) afforded **7a** yellow solid (43 mg, 40%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, *J* = 15.9, 2H), 7.43-7.45 (m, 6H), 7.64-7.66 (m, 4H), 7.70 (d, *J* = 15.9, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.5 (3C), 131.1 (2C), 131.7, 131.9, 153.4, 194.3. ESI-MS data: *m/z* calcd for $[M+H]^+$ $C_{17}H_{14}O$ 235.1045, obsd 235.1028.

Methyl benzoate (**7b**)[9] (Table S4, entry 2)



Benzyl alcohol (100 mg, 0.92 mmol), MeOH (1.5 mL) at 55 ^{o}C for 24 h under Pd@SS (0.02eq) , K_2CO_3 (508 mg, 3.68 mmol) under bubbling oxygen supply followed by column chromatography in silica gel using Etylacetate: Hexane (2:98) yielded **7b** as colorless liquid (81.6 mg, 60%). The NMR data was matched with the literatutre.

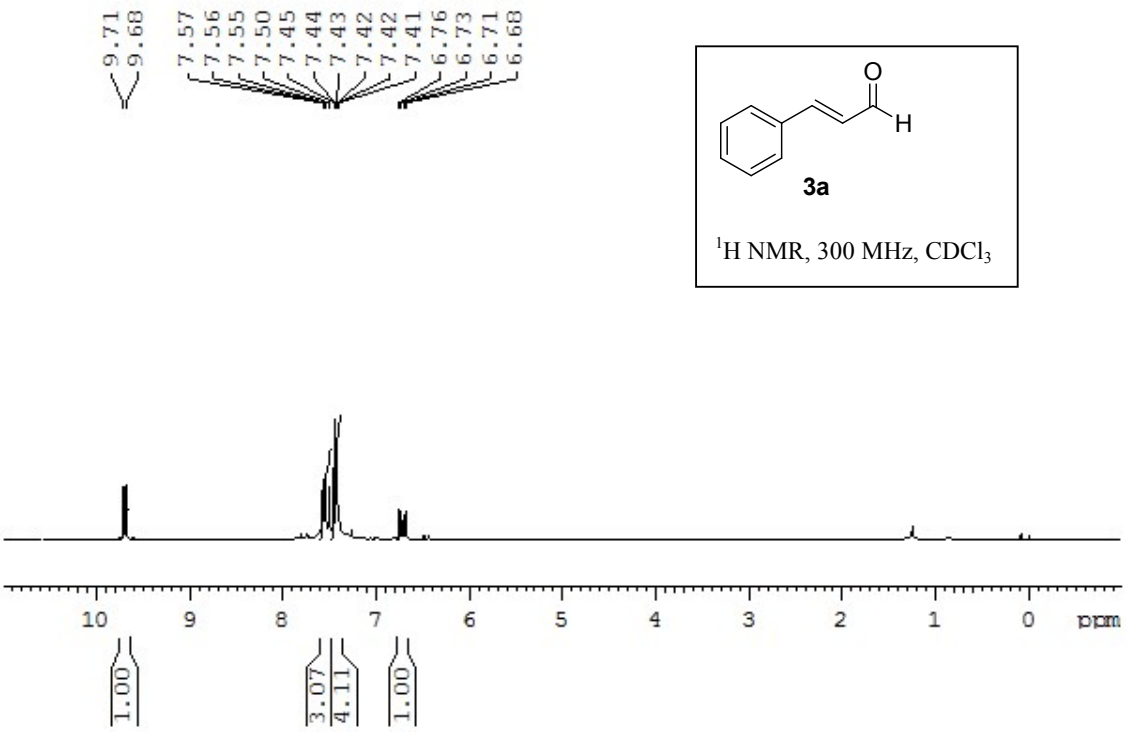
Chalcone (7c) (Table S4, entry 3)



Benzyl alcohol (100 mg, 0.92 mmol), 2-phenylethanol (112.24 mg, 0.92 mmol) at 80 ^{o}C for 24 h under Pd@SS (0.02eq) , K_2CO_3 (508 mg, 3.68 mmol) under bubbling oxygen supply using toluene as solvent followed by column chromatography in silica gel using Etylacetate: Hexane (2:98) yielded **7c** as colorless liquid (133 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-745 (m, 3H), 7.51-7.53 (m, 3H), 7.58-7.62 (m, 2H), 7.65-7.69 (m, 2H), 7.85 (d, *J* = 15.7, 1H), 8.04-8.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.5, 128.8, 128.9, 129.0, 129.4, 131.0, 133.2, 135.3, 138.6, 145.2, 190.9. ESI-MS data: *m/z* calcd for $[M+H]^+$ calcd. $C_{15}H_{12}O$ 209.0888 observed 209.0859.

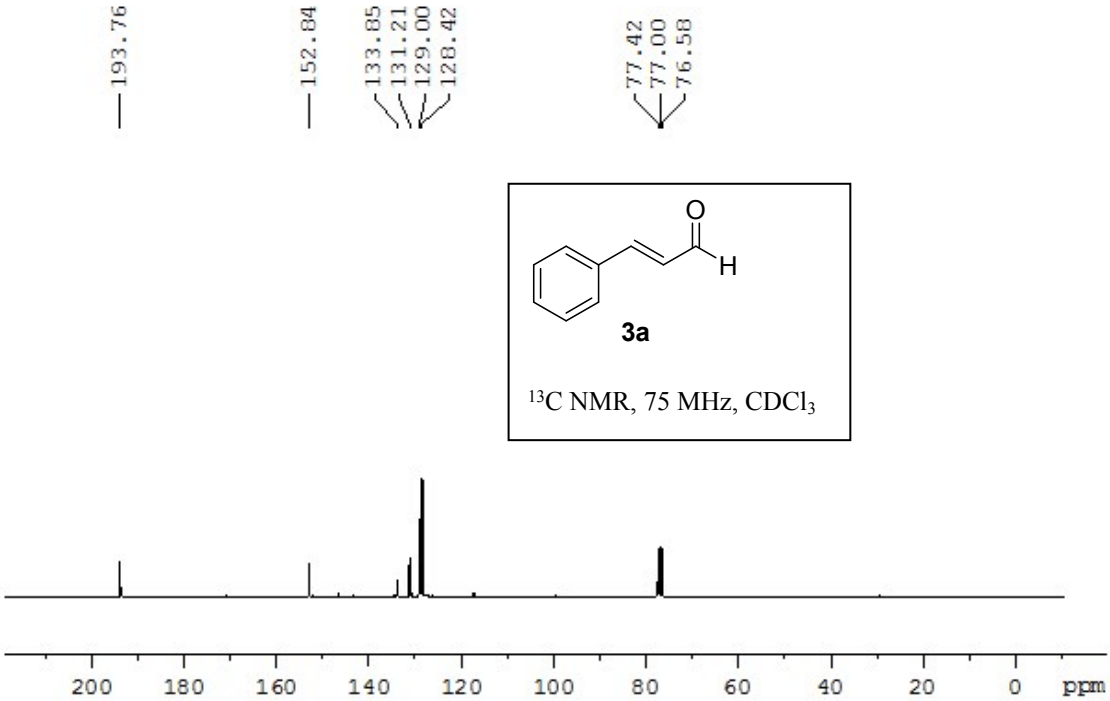
Spectral data (**^{1}H, ^{13}C and GC-MS spectra of compounds Table 1, Table 2, and Table 3**)

3a (Table 1, entry 10)



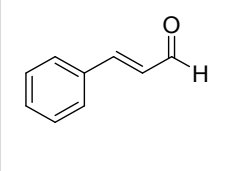
3a

^{1}H NMR, 300 MHz, $CDCl_3$

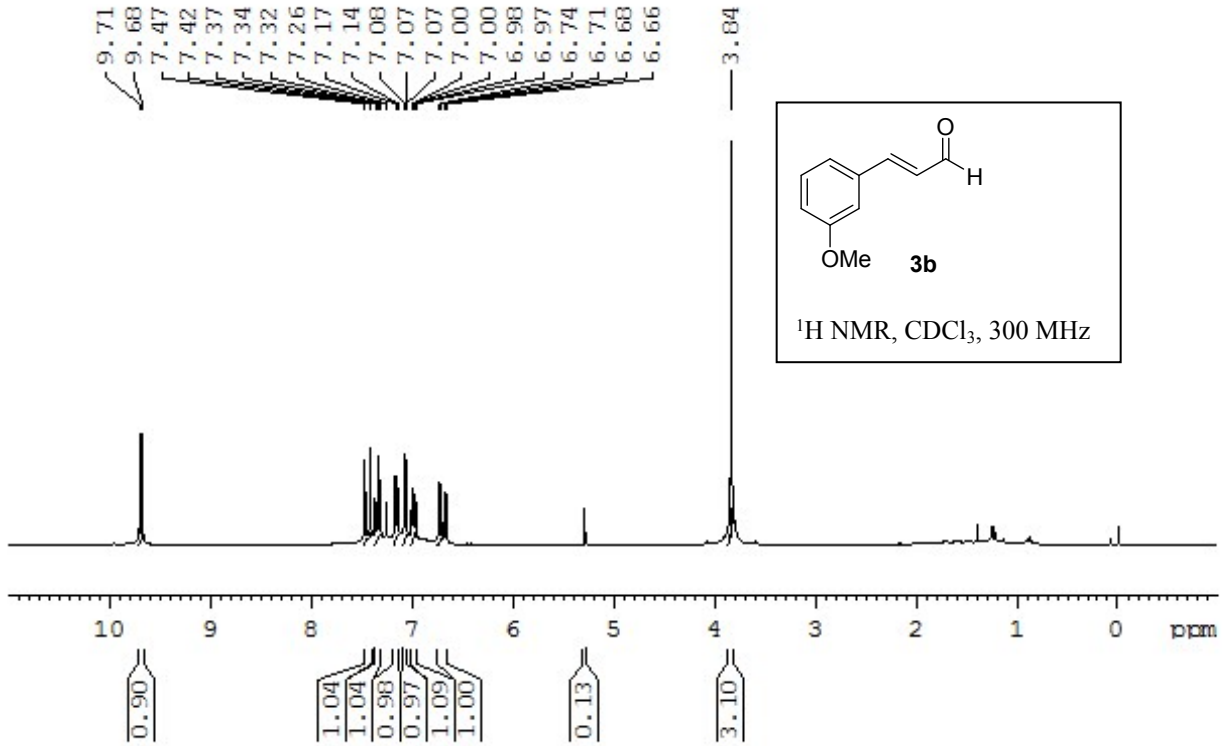


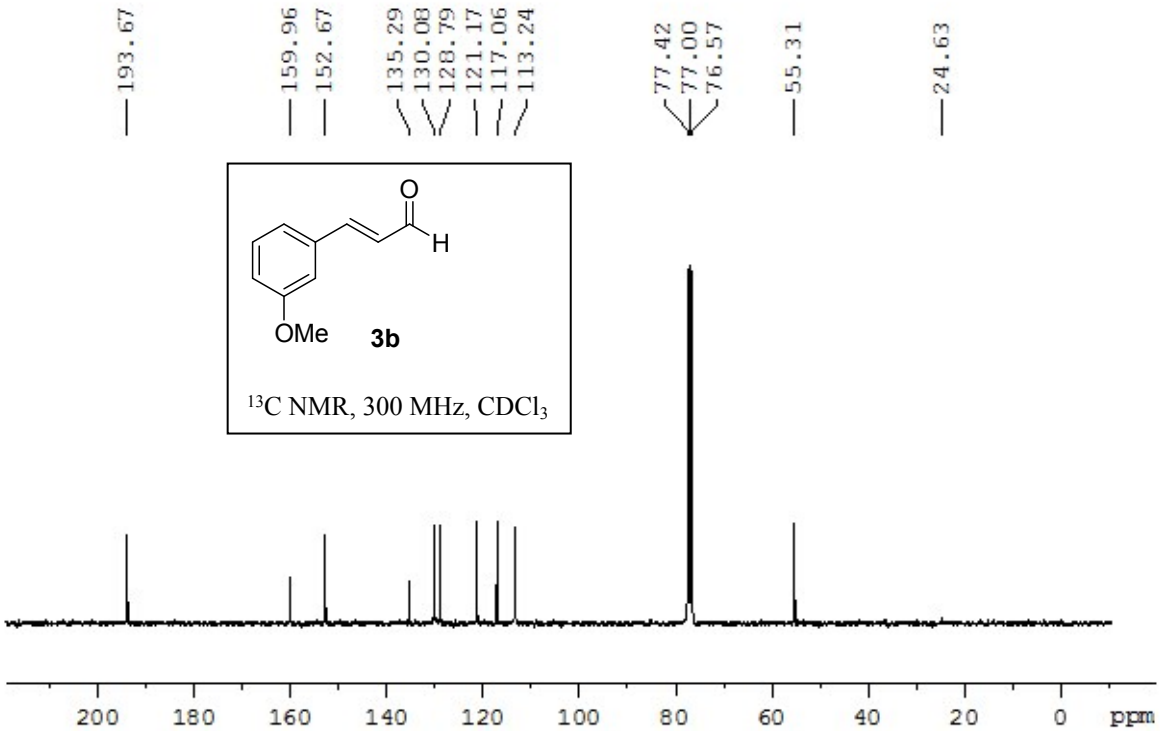
3a

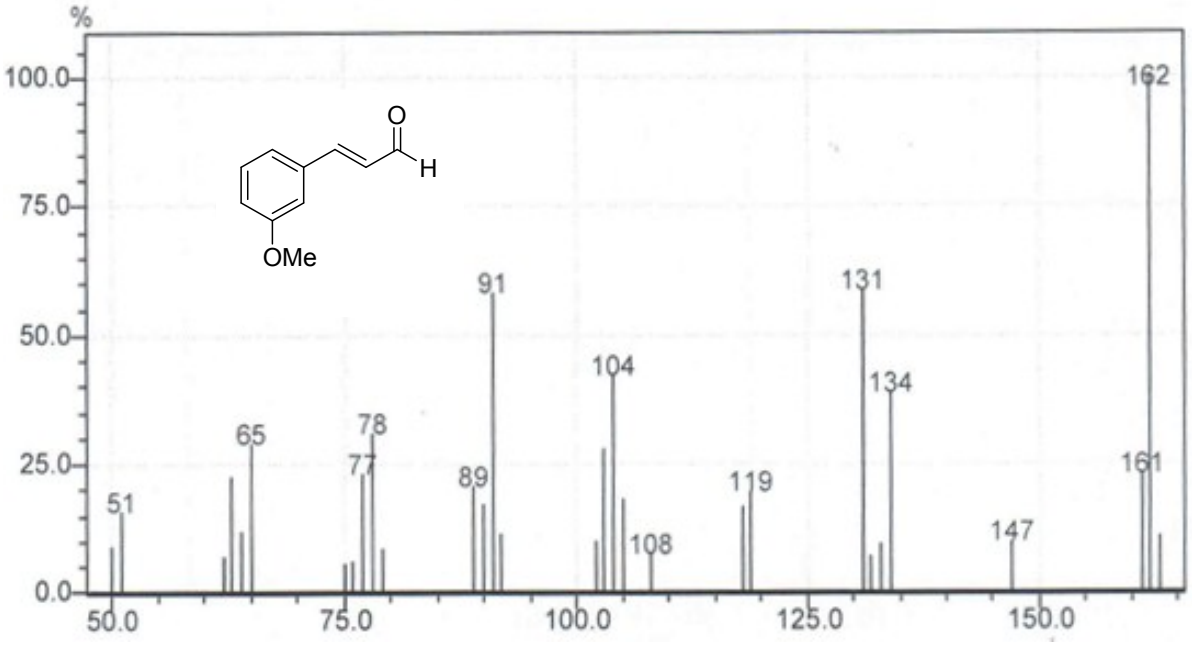
^{13}C NMR, 75 MHz, $CDCl_3$



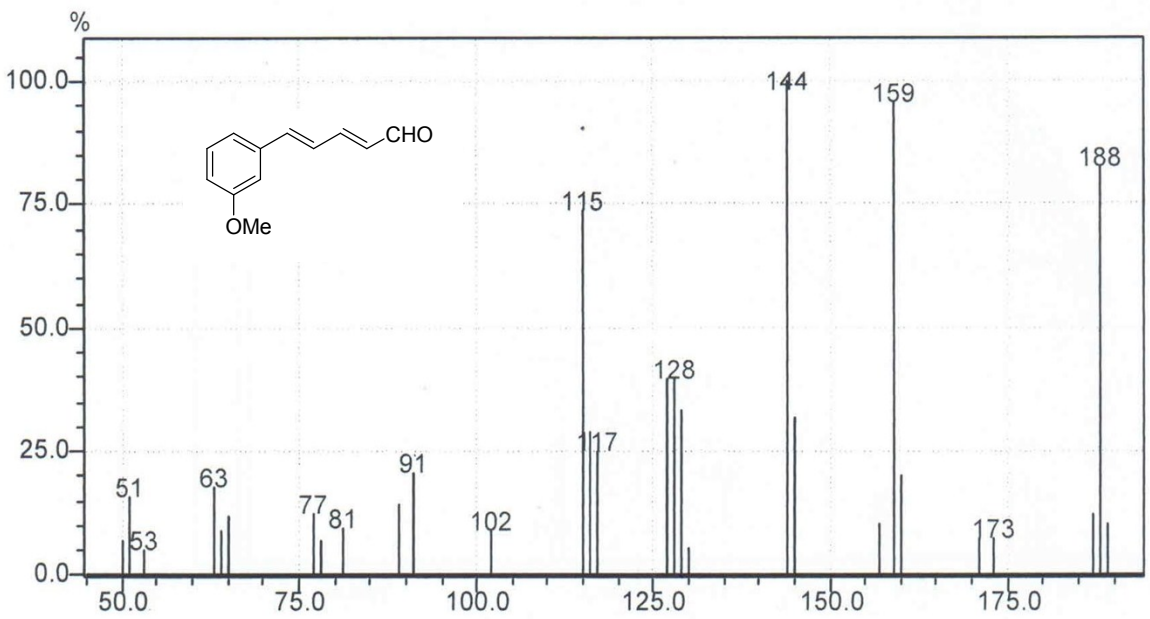
3b (Table 2, entry 1)



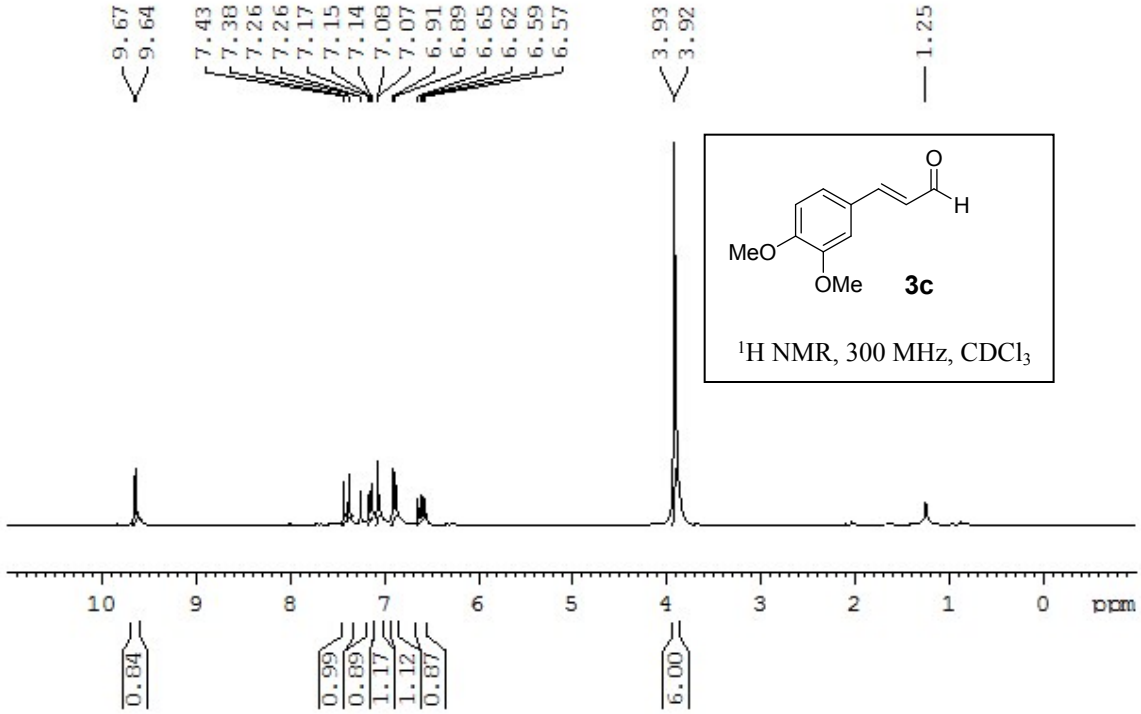


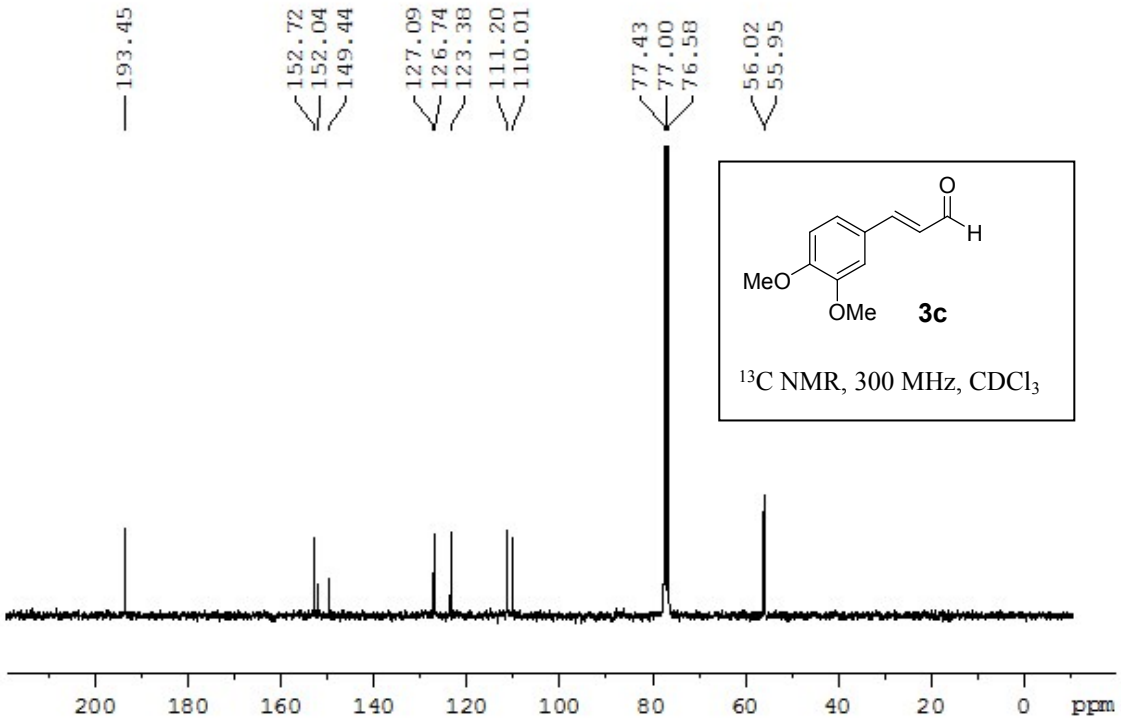


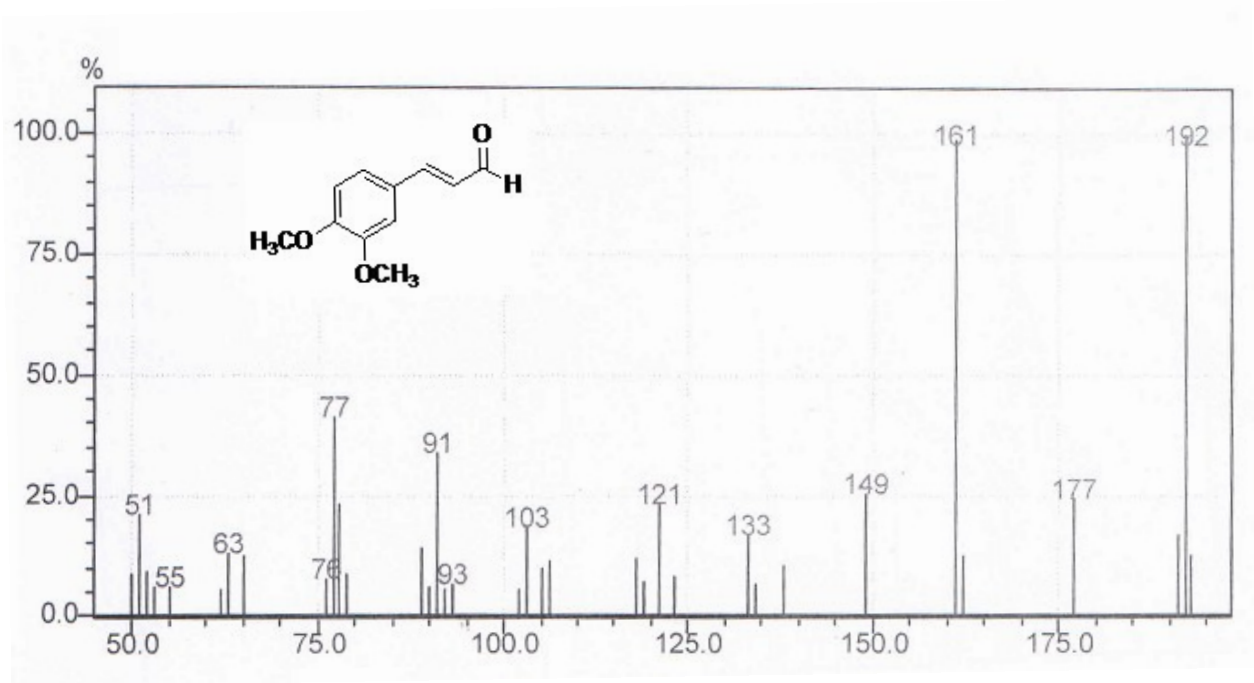
GCMS spectra of **4b** (Table 2, entry 1)



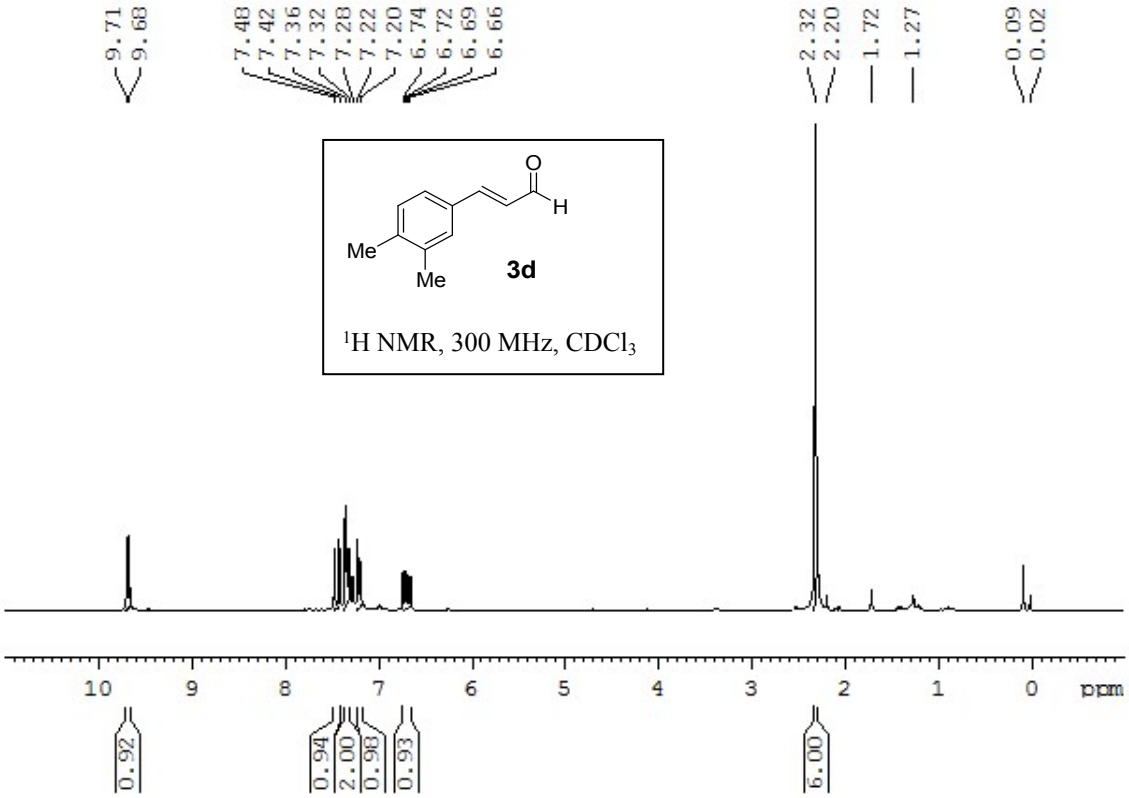
3c (Table 2, entry 2)

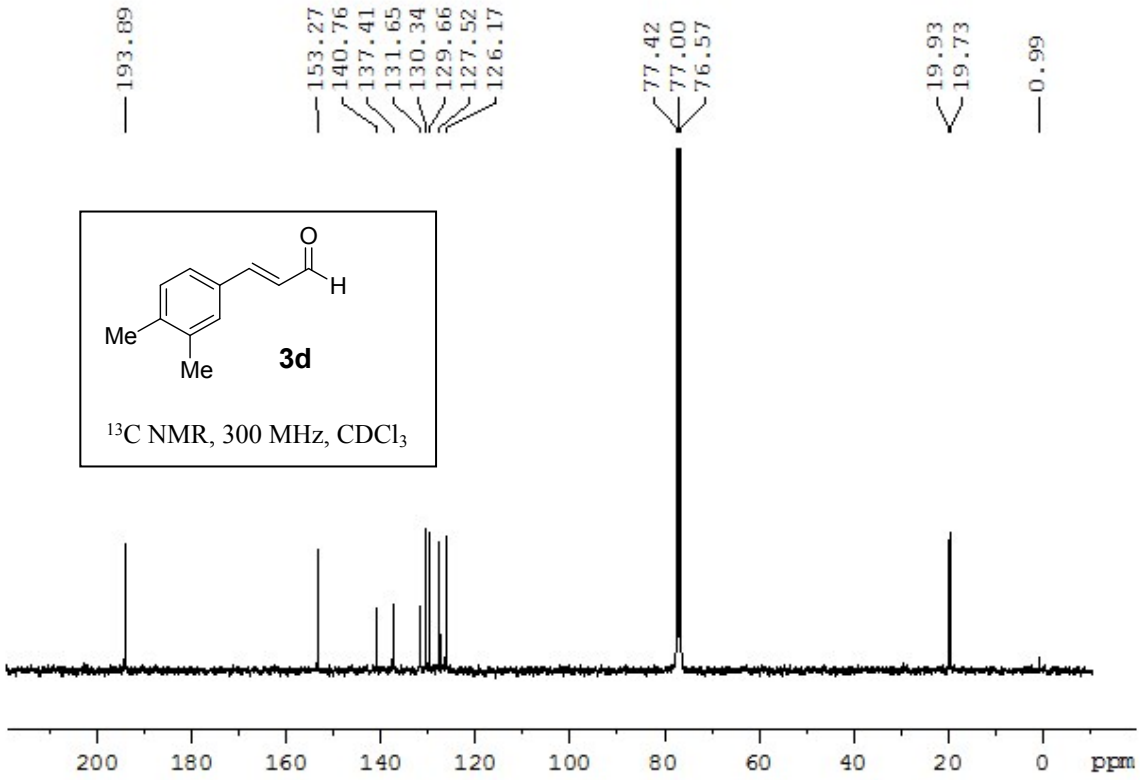


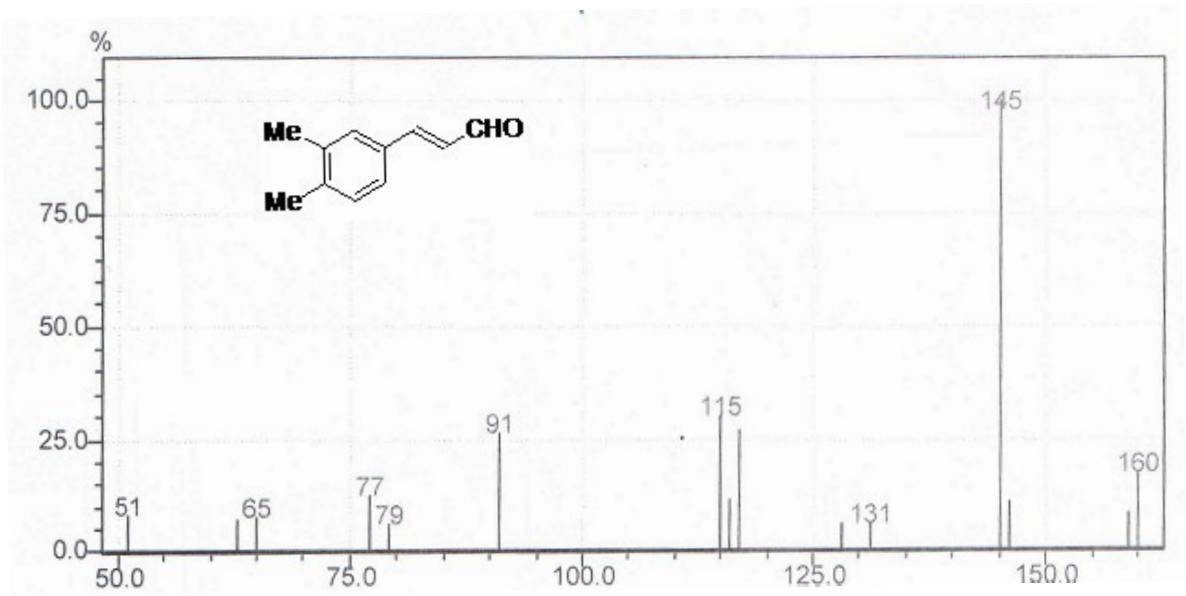




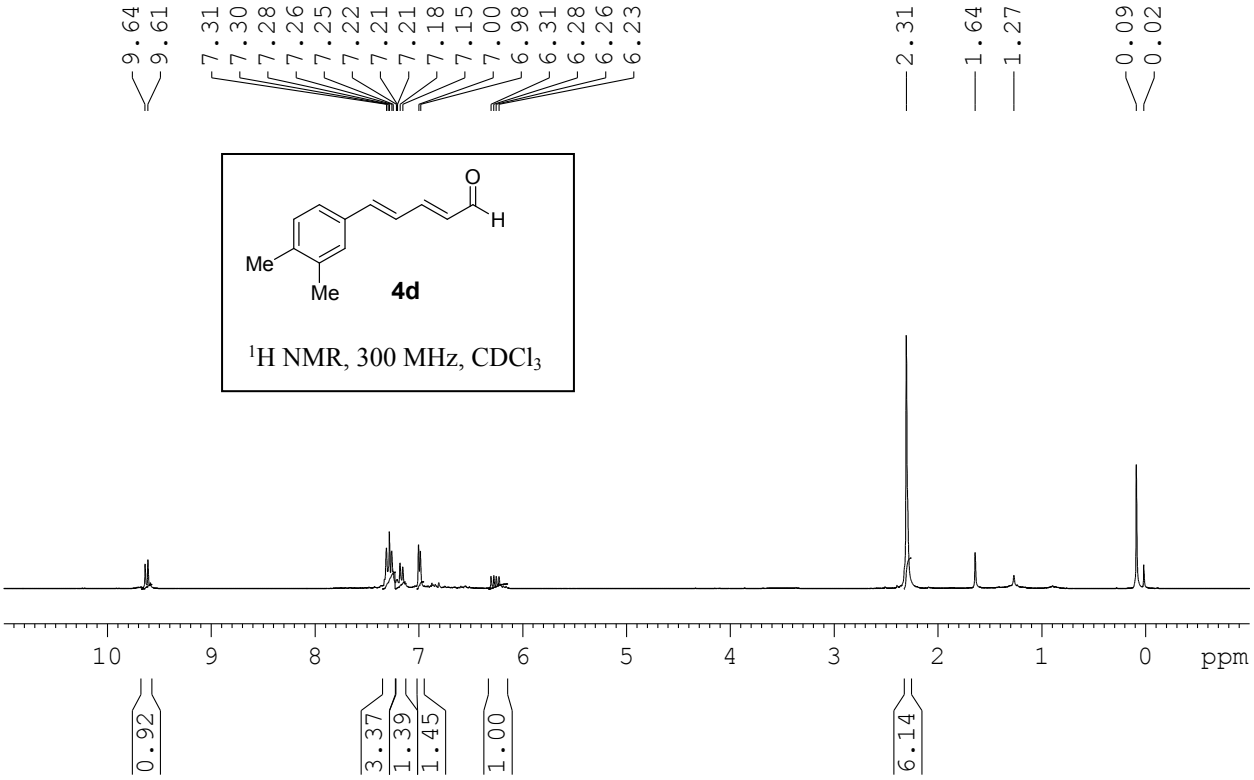
3d (Table 2, entry 3)

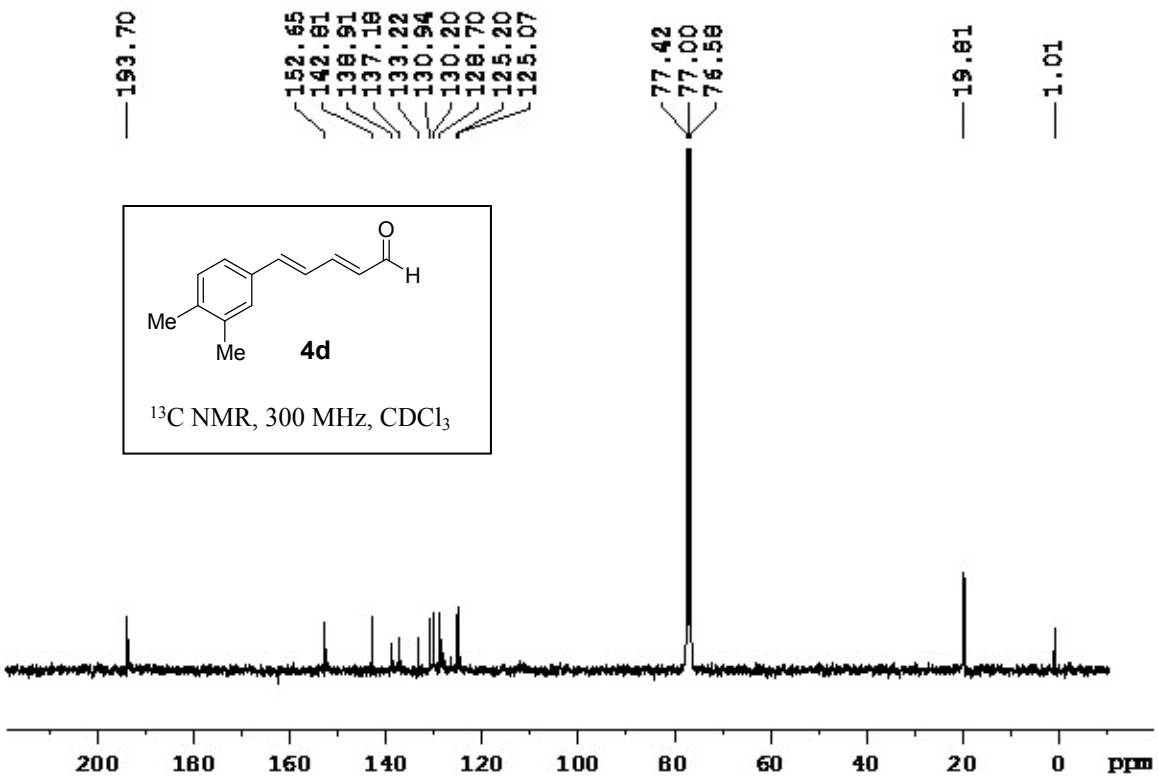

9.71
9.68
7.48
7.42
7.36
7.32
7.28
7.22
7.20
6.74
6.72
6.69
6.66
2.32
2.20
1.72
1.27
0.09
0.02
O
H
Me
Me
3d
^{1}H NMR, 300 MHz, $CDCl_3$
10
9
8
7
6
5
4
3
2
1
0
ppm
0.92
0.94
2.00
0.98
0.93
6.00


193.89
153.27
140.76
137.41
131.65
130.34
129.66
127.52
126.17
77.42
77.00
76.57
19.93
19.73
0.99
O
H
Me
Me
3d
^{13}C NMR, 300 MHz, $CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
ppm

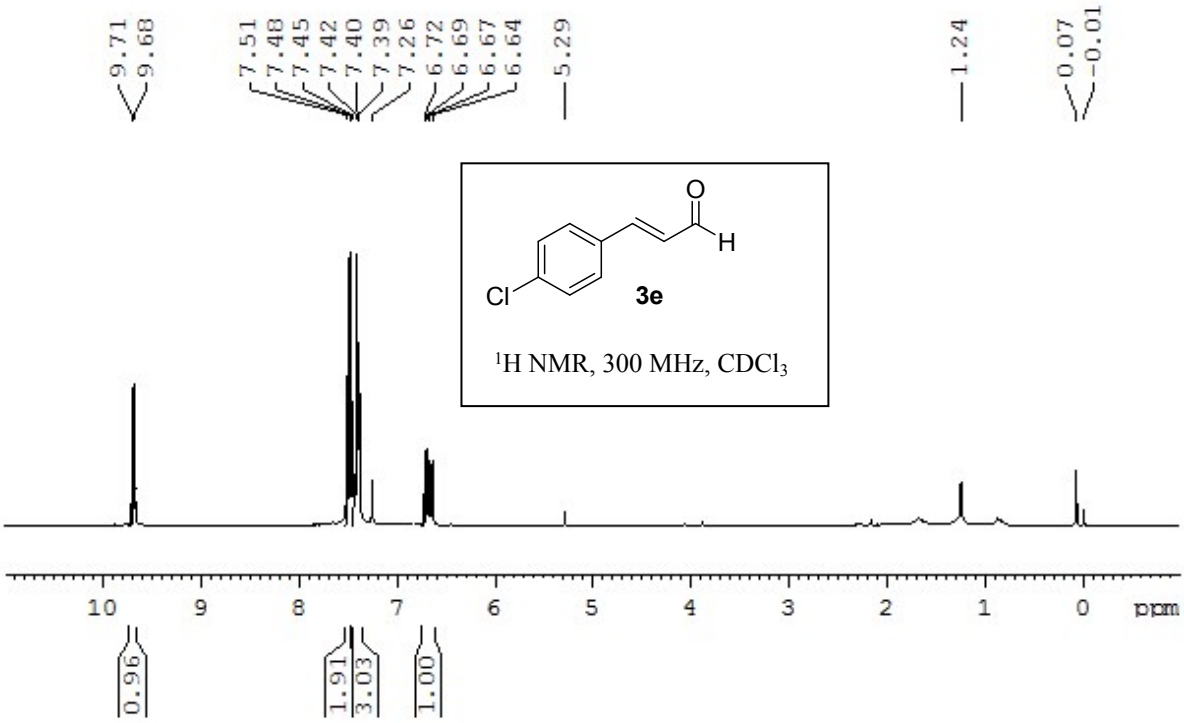

%
100.0
75.0
50.0
25.0
0.0
Me
Me
CHO
145
115
91
160
77
79
51
65
131
50.0
75.0
100.0
125.0
150.0

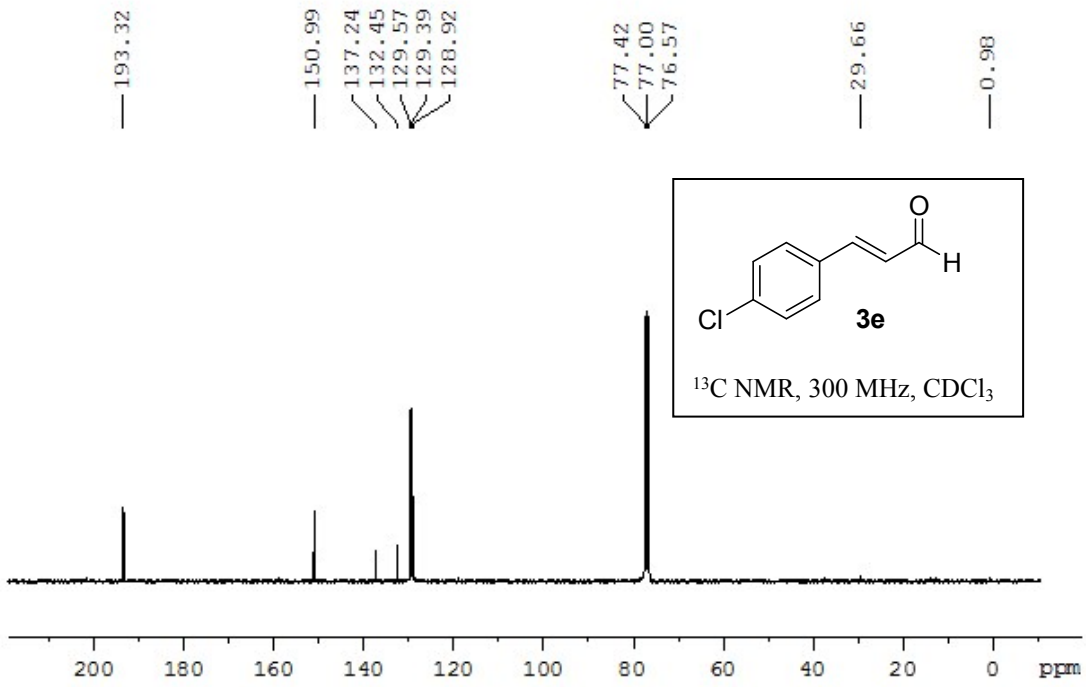
4d (Table 2, entry 3)



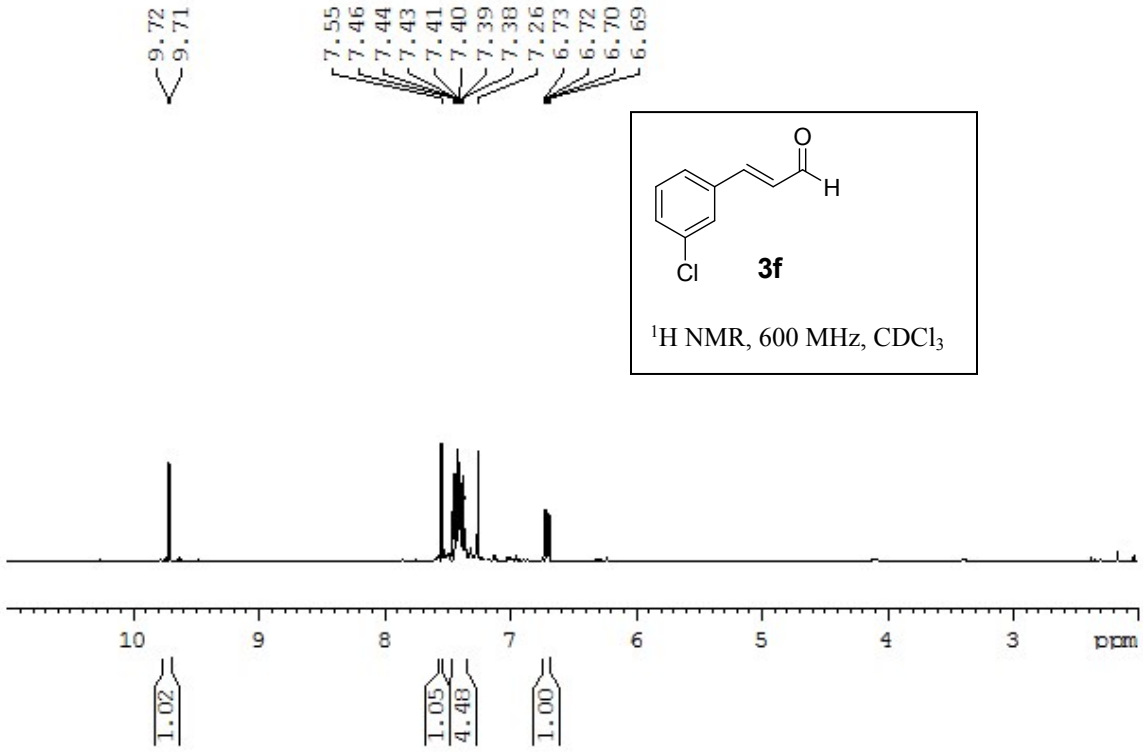


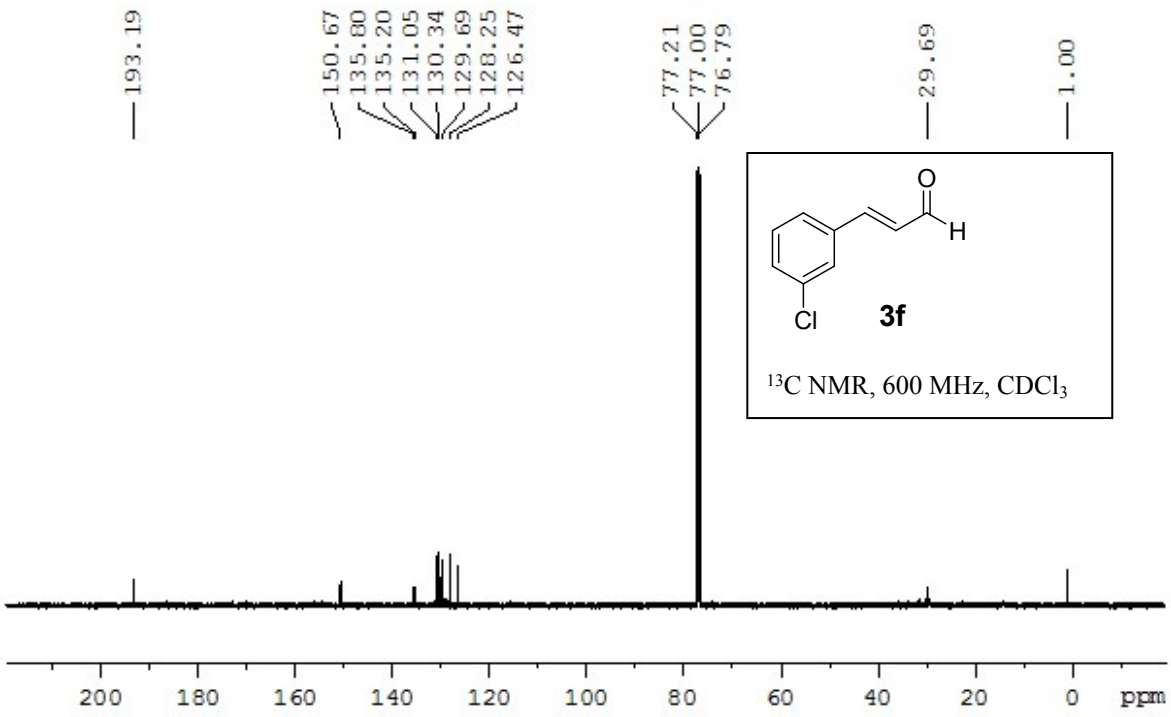
3e (Table 2, entry 4)

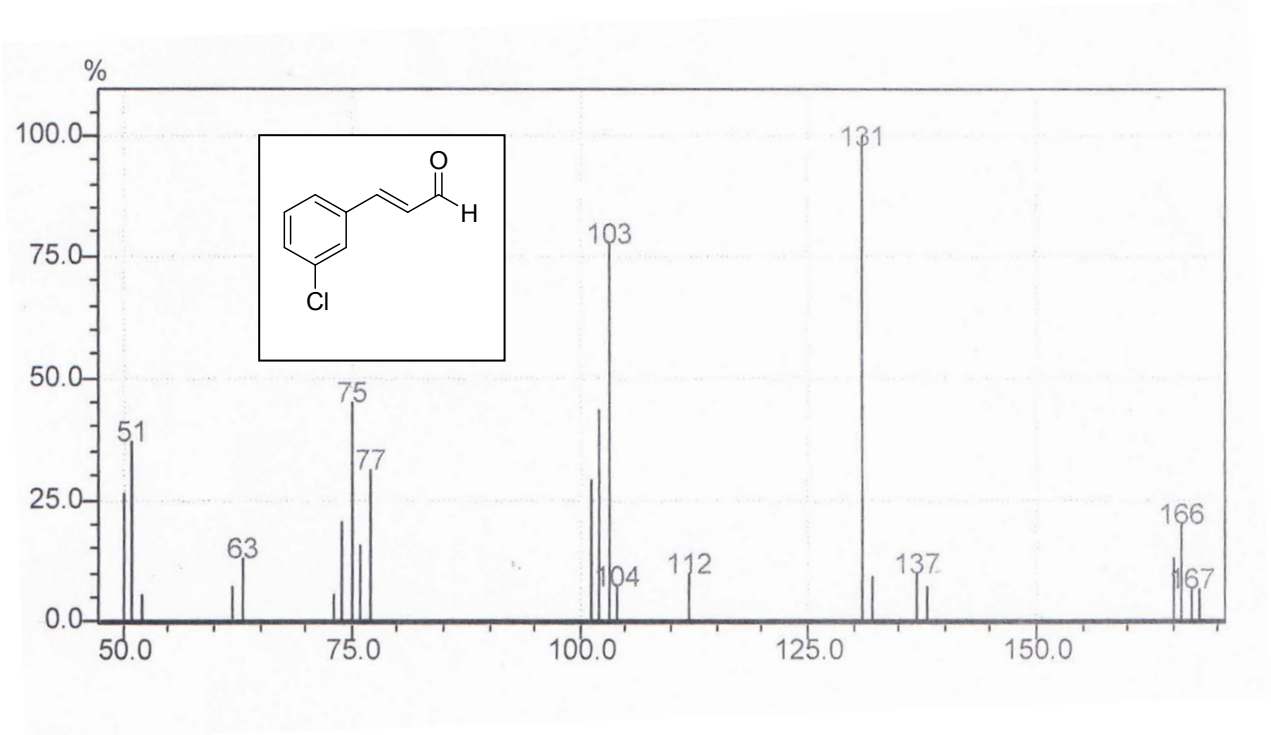




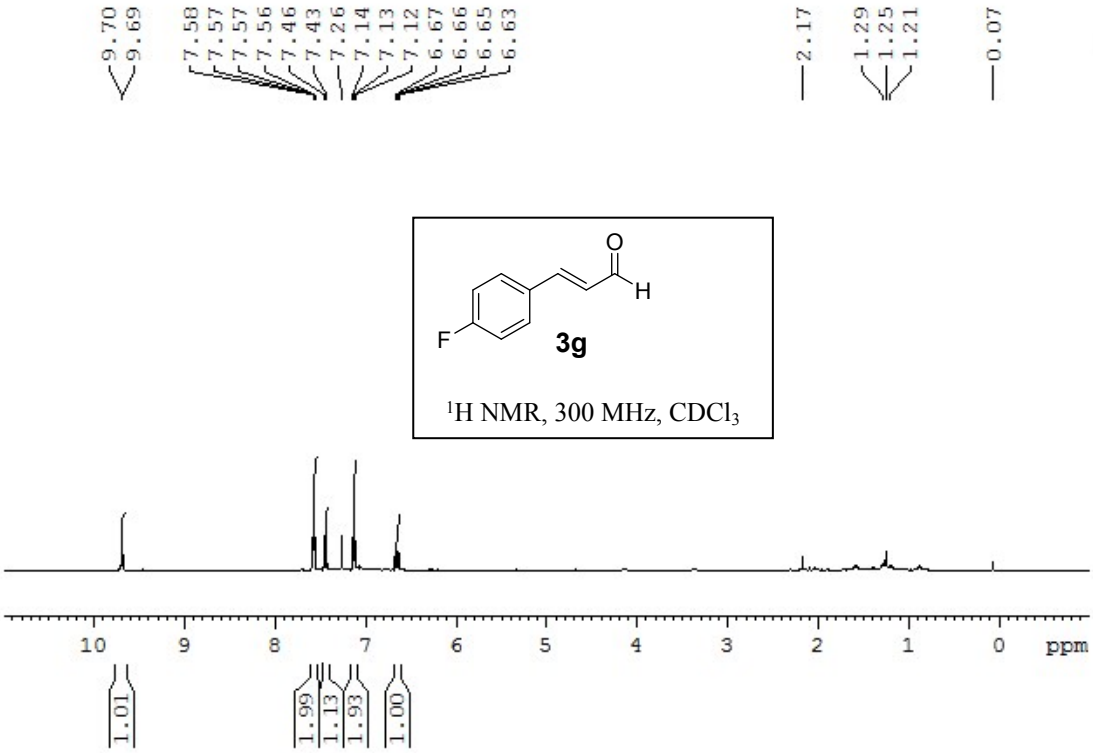
3f (Table 2, entry 5)

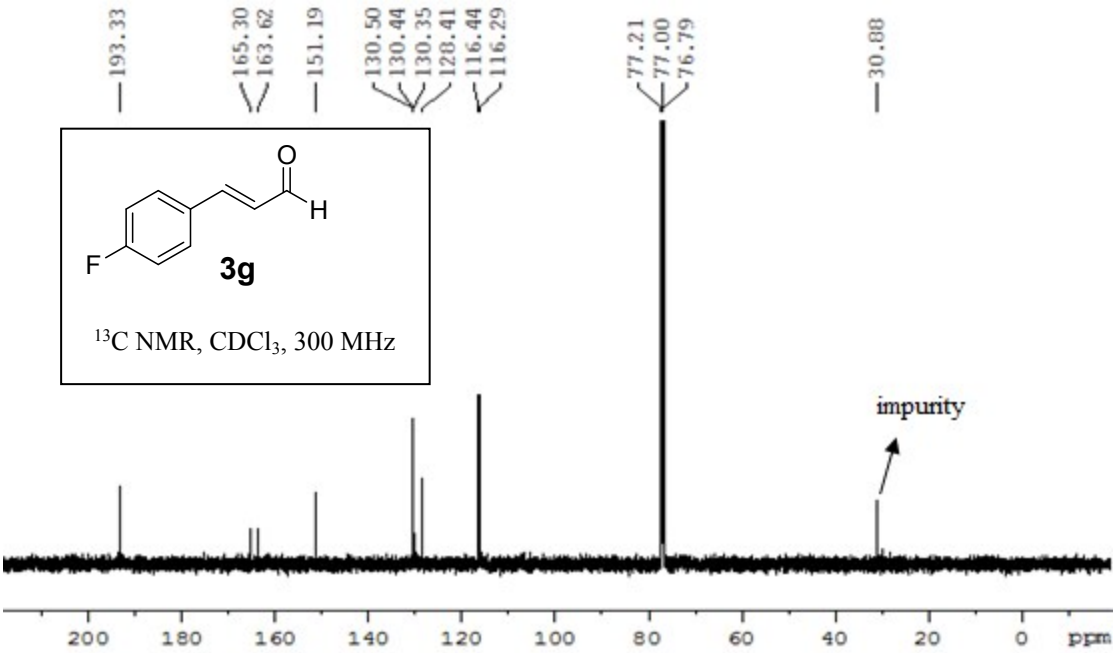



193.19
150.67
135.80
135.20
131.05
130.34
129.69
128.25
126.47
77.21
77.00
76.79
29.69
1.00
O
H
Cl
3f
^{13}C NMR, 600 MHz, $CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
ppm

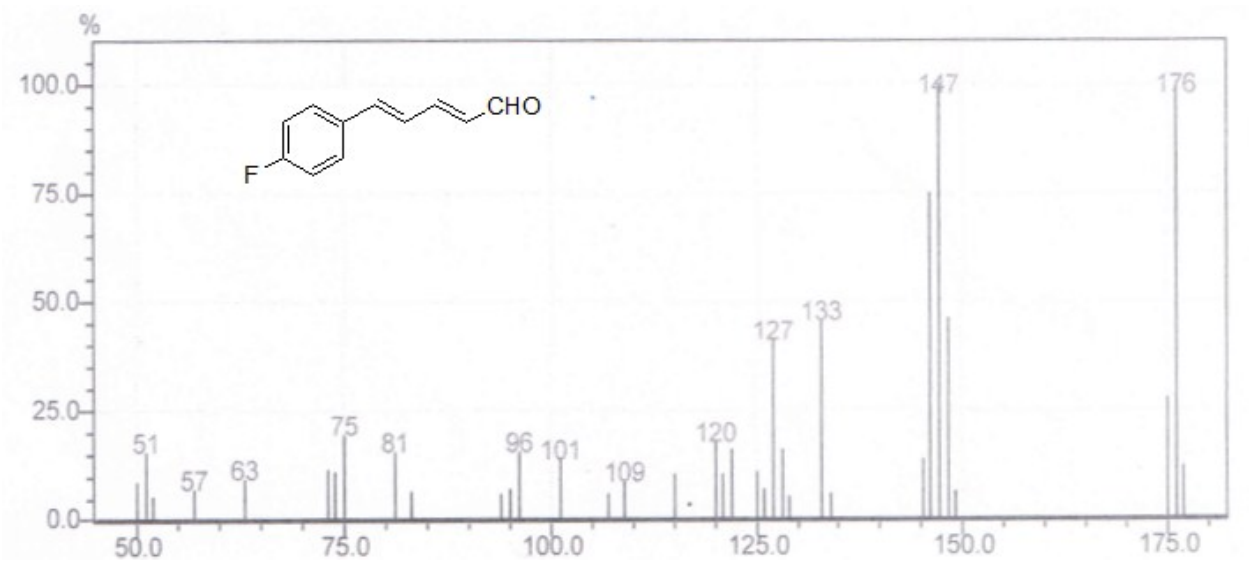


3g (Table 2, entry 6)

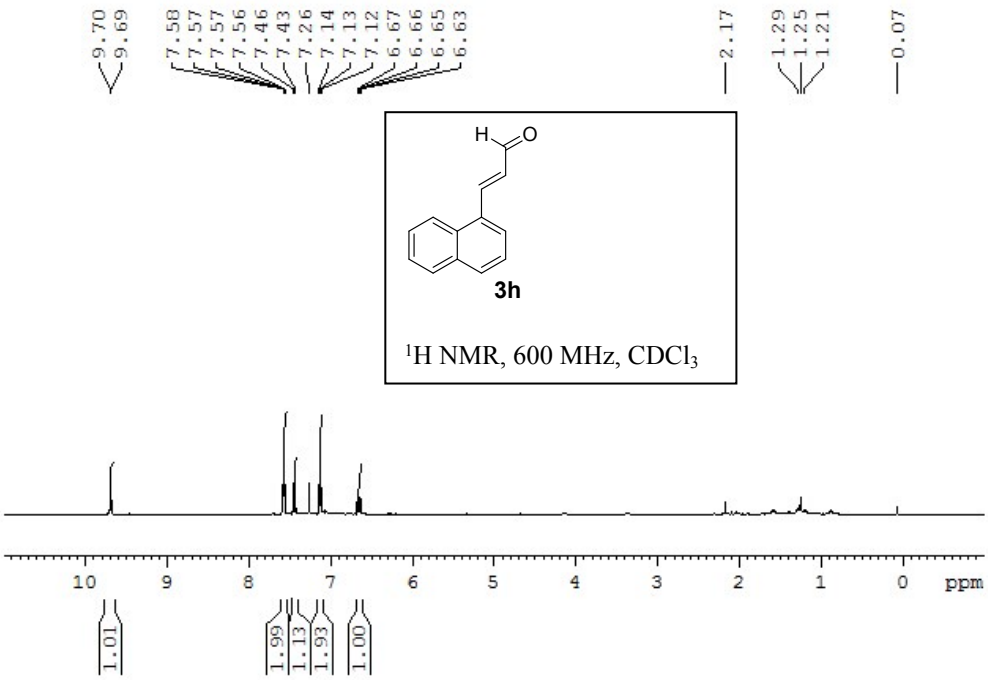


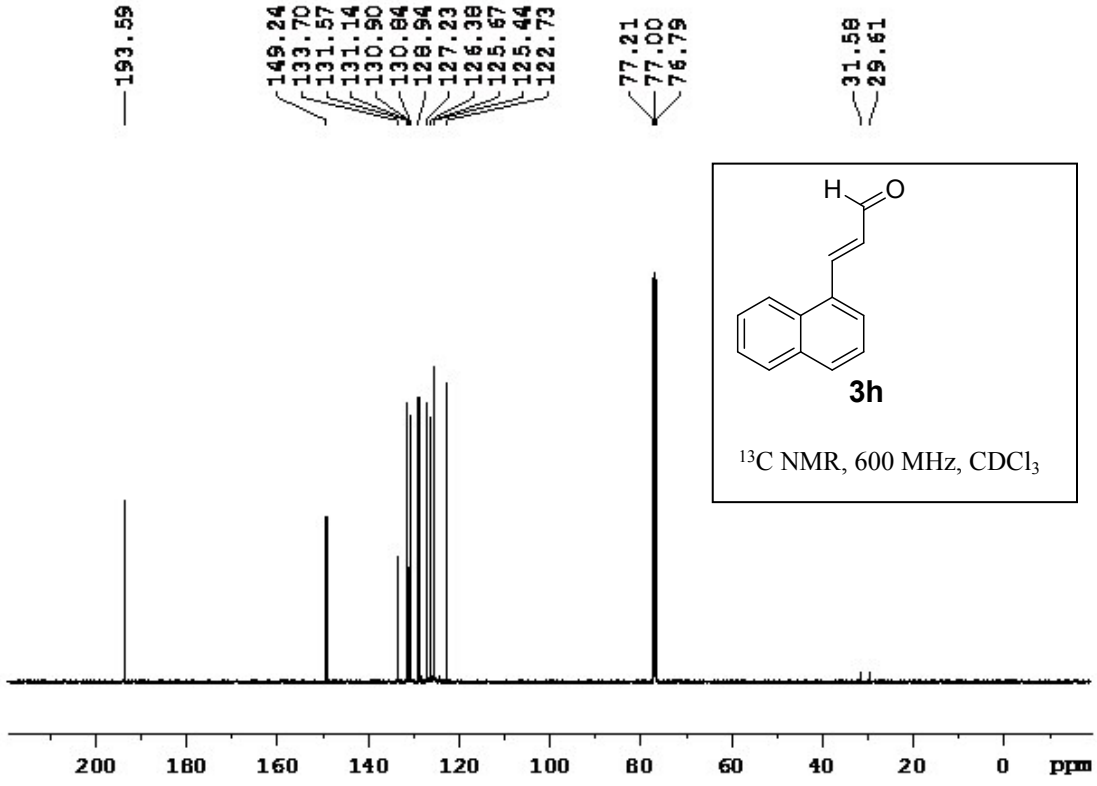


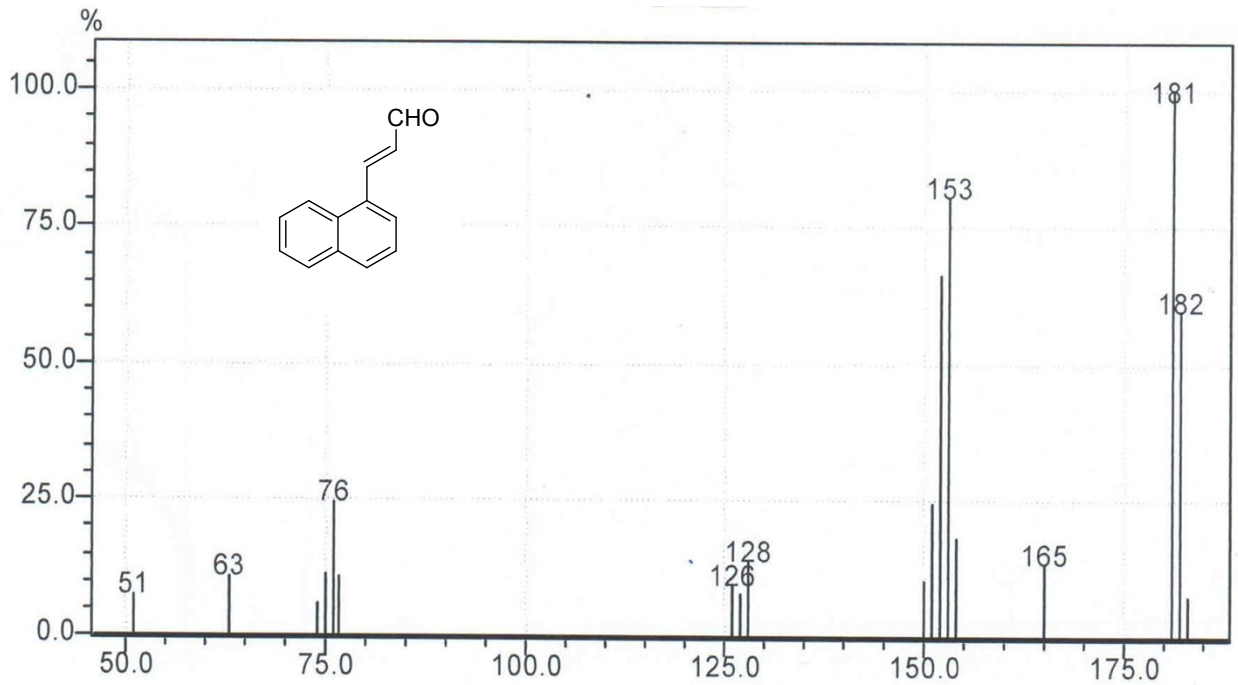
4g (Table 2, entry 6)



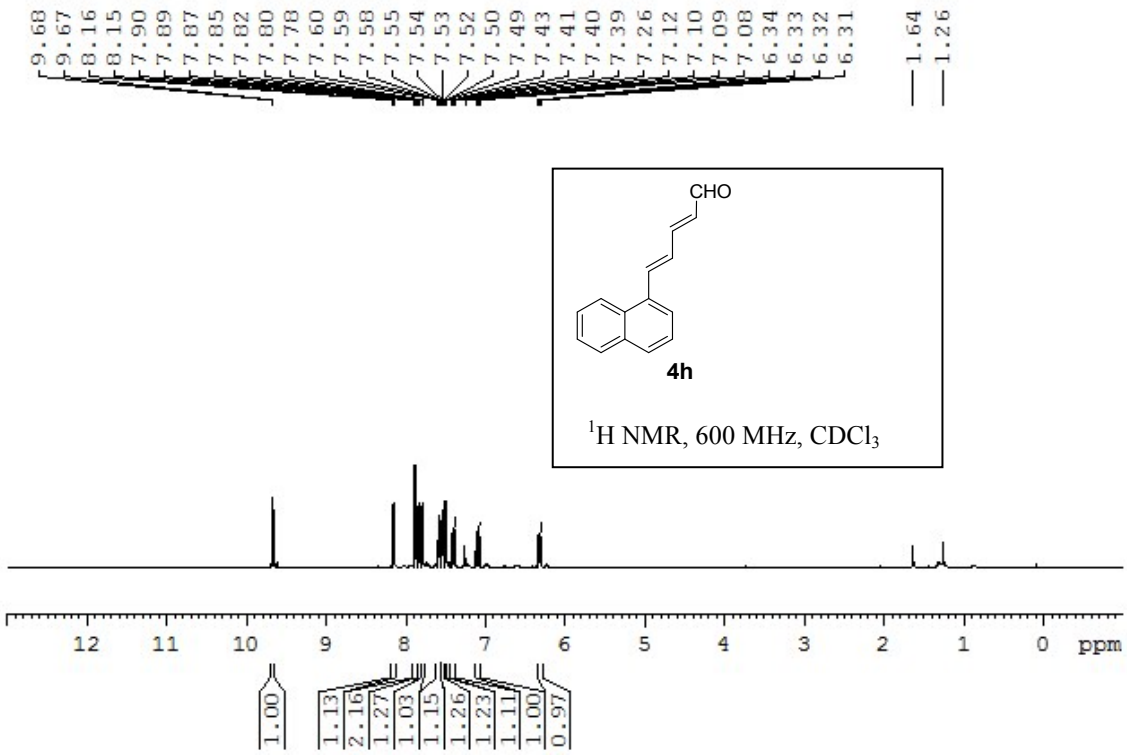
3h (Table 2, entry 7)

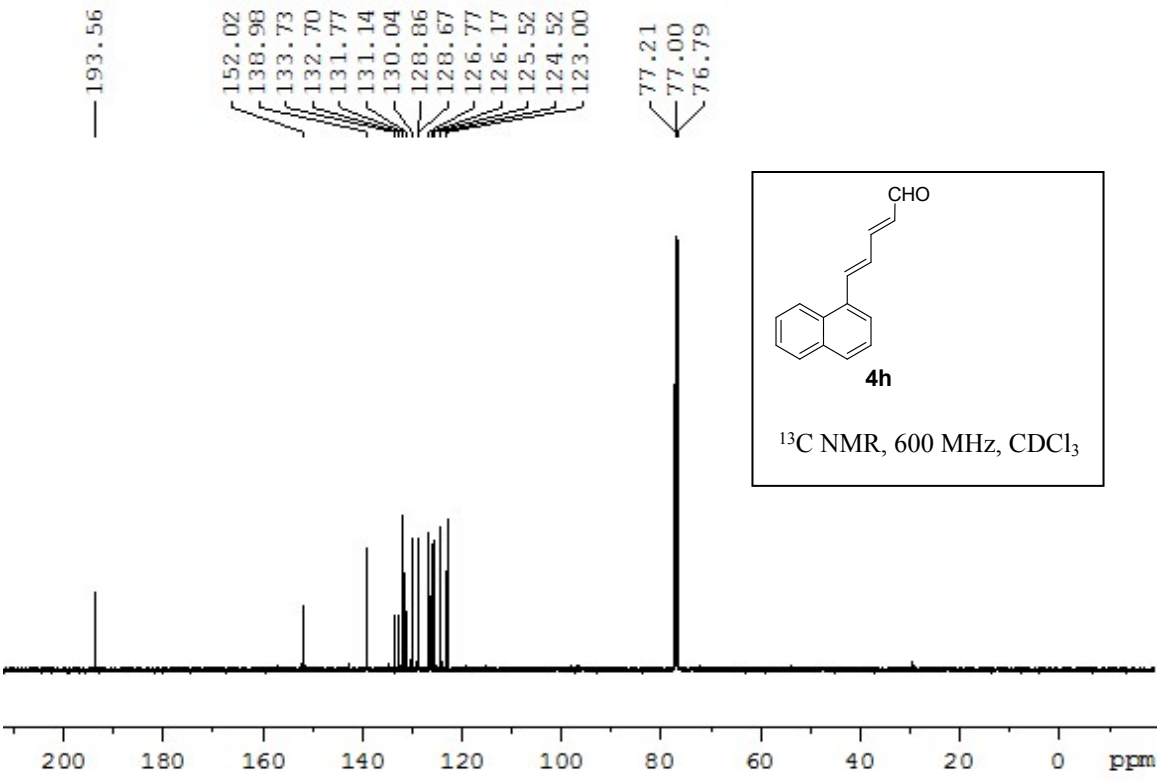

9.70
9.69
7.58
7.57
7.57
7.56
7.46
7.43
7.26
7.14
7.13
7.12
6.67
6.66
6.65
6.63
2.17
1.29
1.25
1.21
0.07
H
O
3h
^{1}H NMR, 600 MHz, $CDCl_3$
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.99
1.13
1.93
1.00

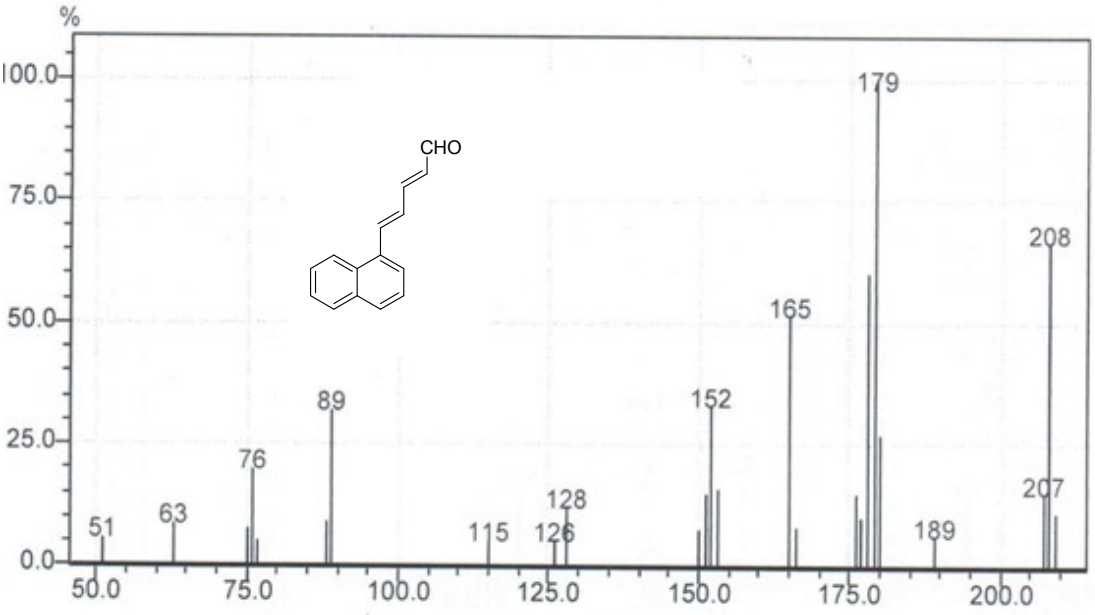

193.59
149.24
133.70
131.57
131.14
130.90
130.84
128.94
127.23
126.38
125.67
125.44
122.73
77.21
77.00
76.79
31.58
29.61
H
O
3h
^{13}C NMR, 600 MHz, $CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
ppm



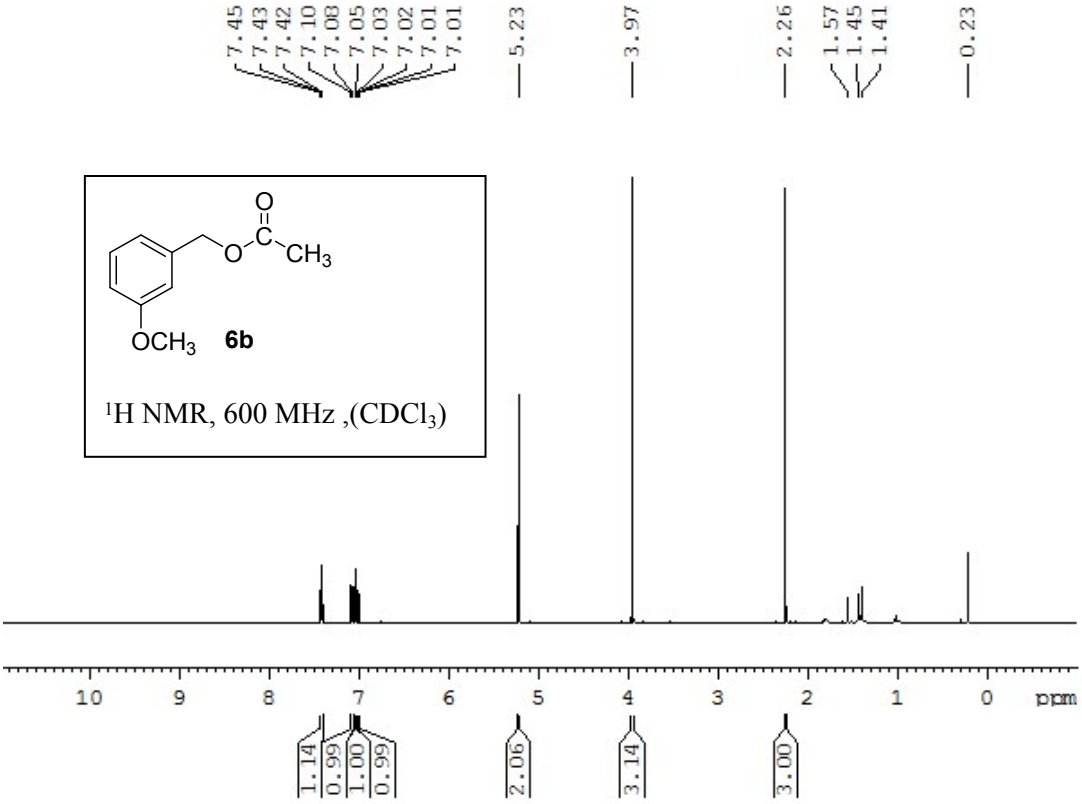
4h (Table 2, entry 7)

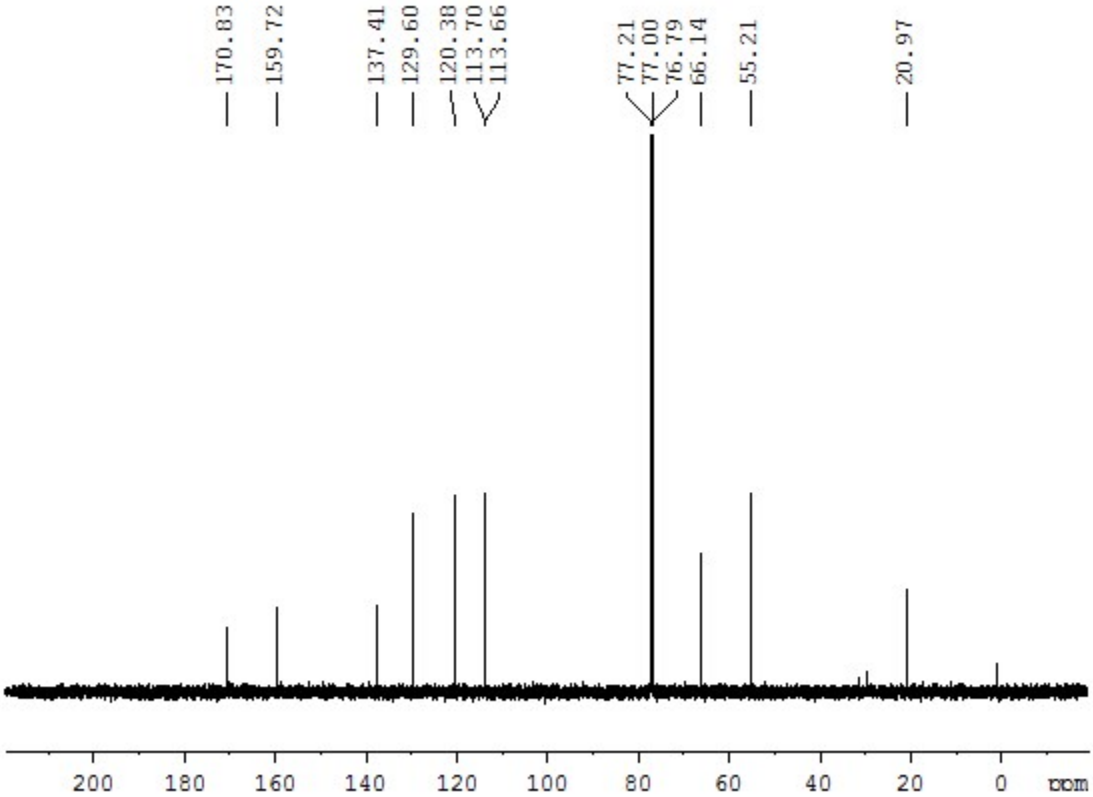


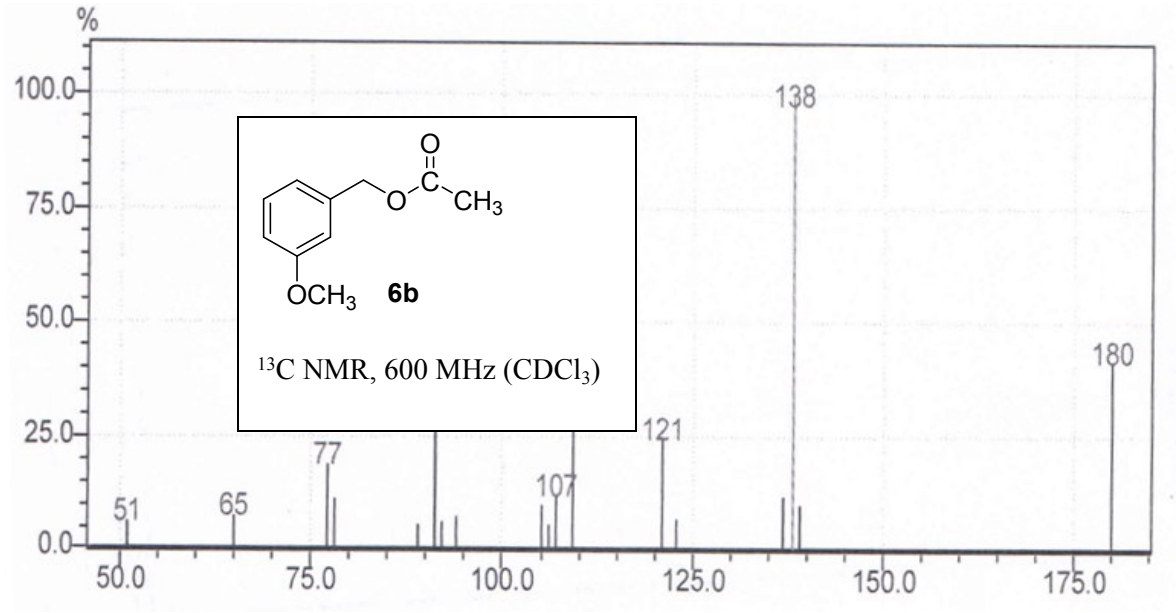

193.56
152.02
138.98
133.73
132.70
131.77
131.14
130.04
128.86
128.67
126.77
126.17
125.52
124.52
123.00
77.21
77.00
76.79
CHO
4h
^{13}C NMR, 600 MHz, $CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
ppm


%
100.0
75.0
50.0
25.0
0.0
CHO
179
208
165
152
89
76
63
51
128
126
115
207
189
50.0
75.0
100.0
125.0
150.0
175.0
200.0

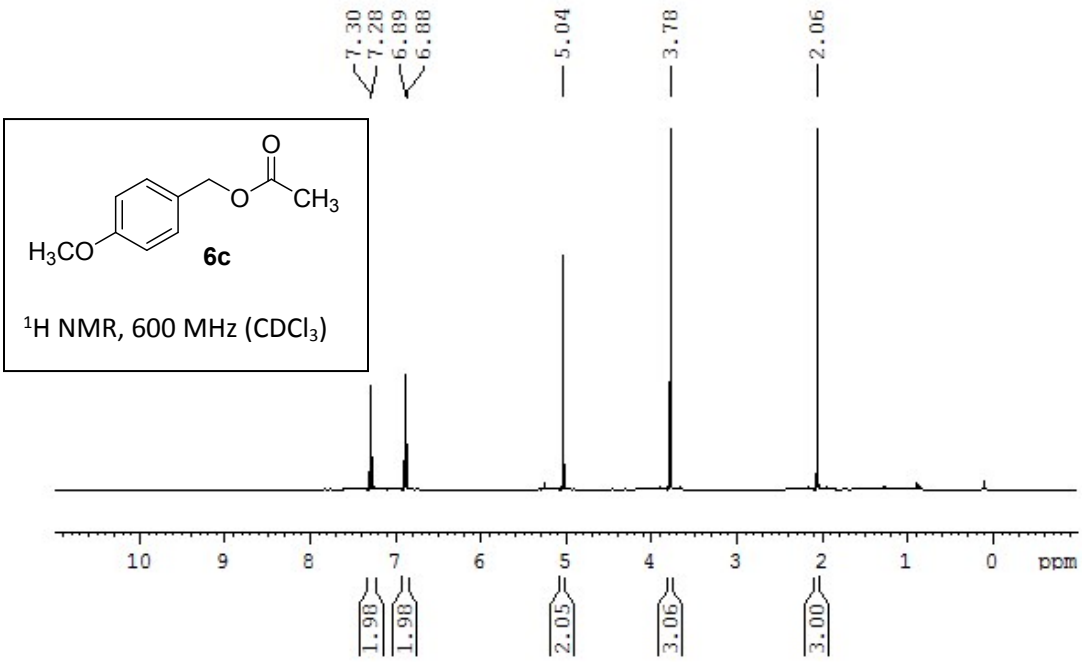
6b (Table 3, entry 1)

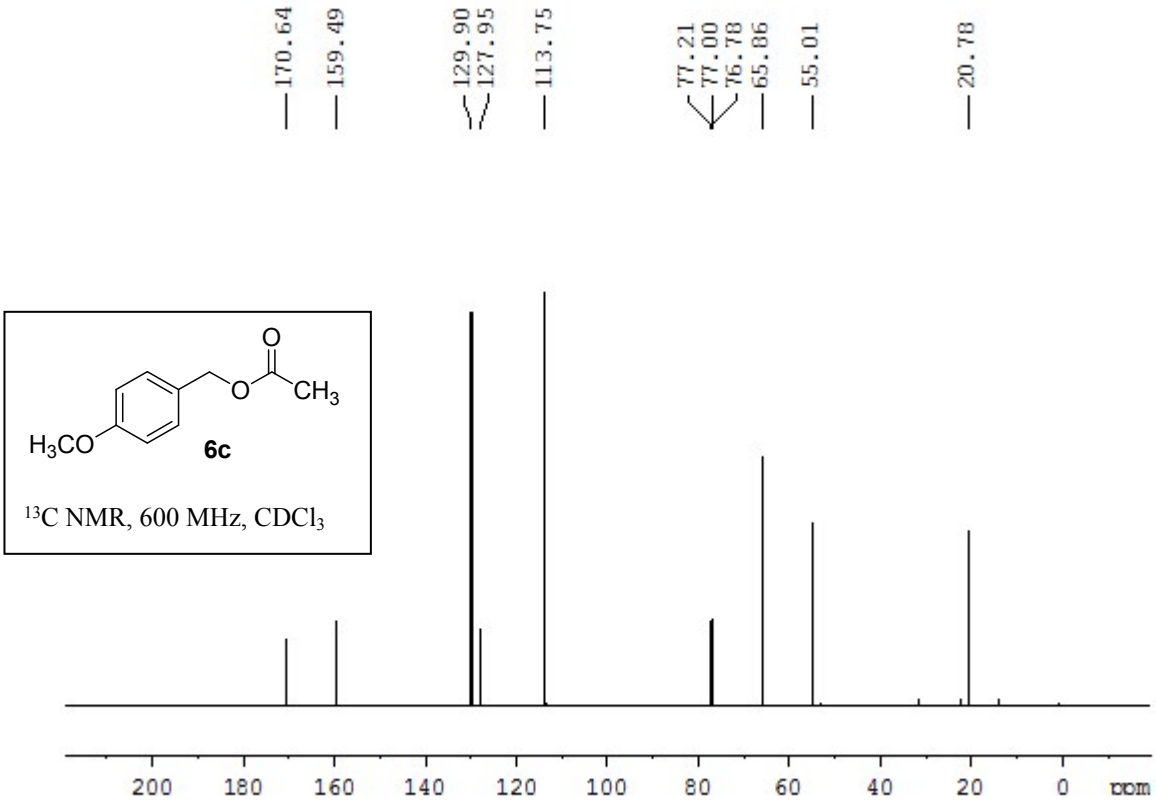


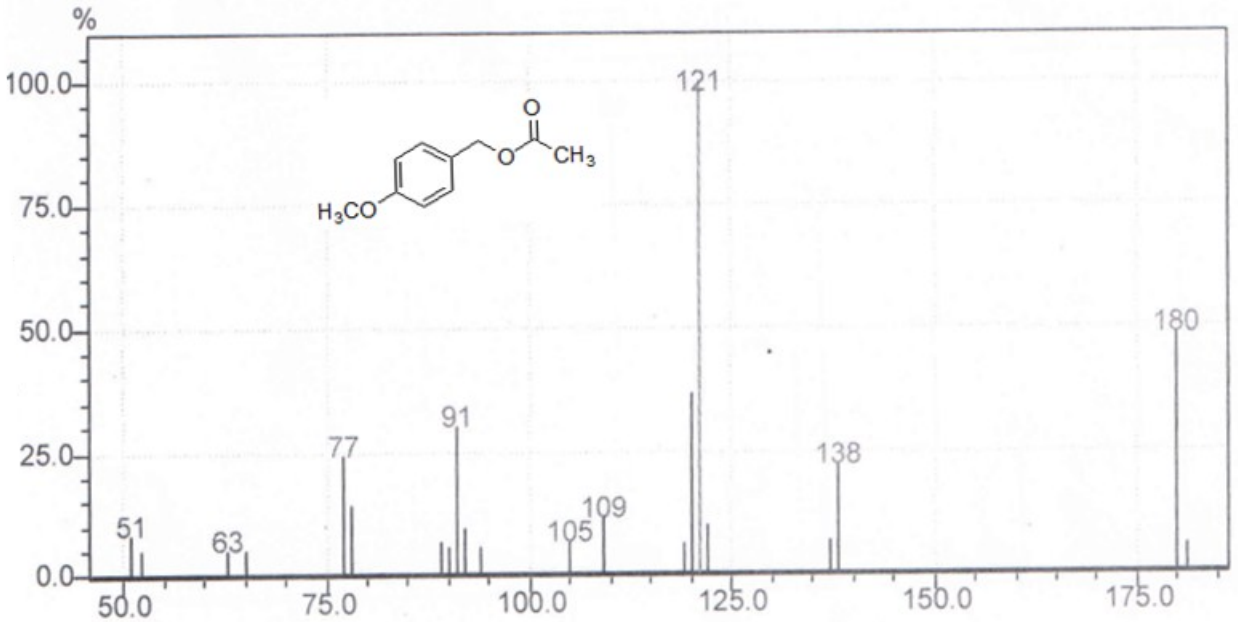




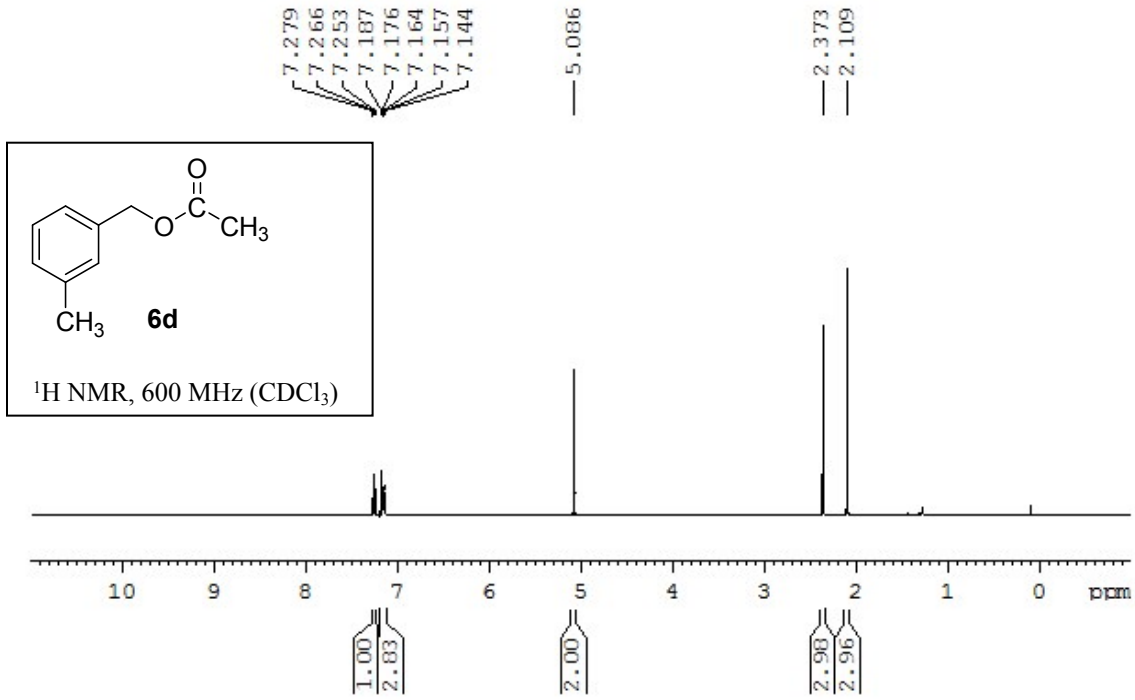
6c (Table 4, entry 1)

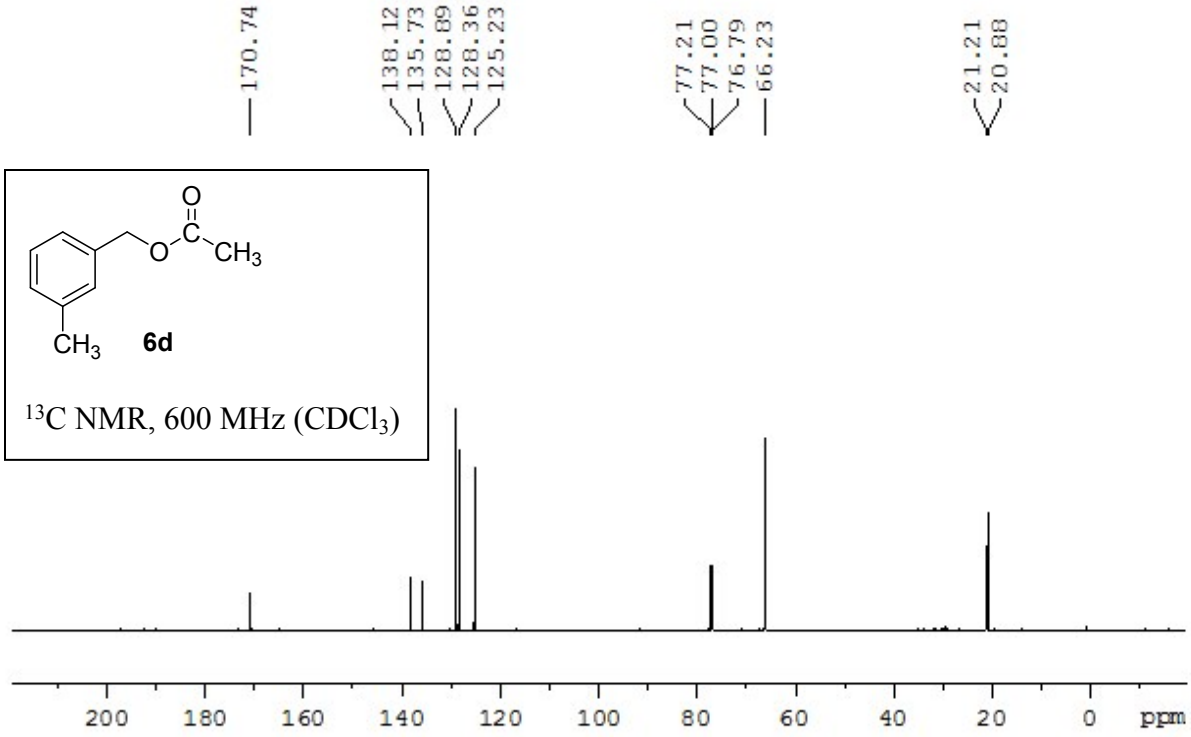

7.30
7.28
6.89
6.88
5.04
3.78
2.06
O
O
CH3
H3CO
6c
1H NMR, 600 MHz (CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.98
1.98
2.05
3.06
3.00

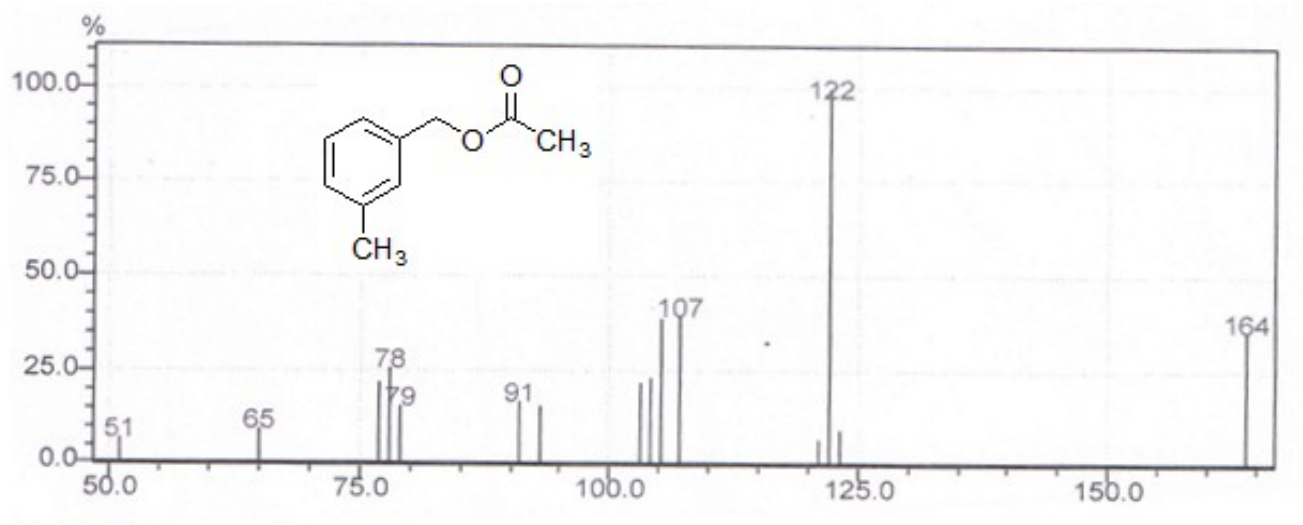

170.64
159.49
129.90
127.95
113.75
77.21
77.00
76.78
65.86
55.01
20.78
O
O
CH3
H3CO
6c
13C NMR, 600 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
0
ppm



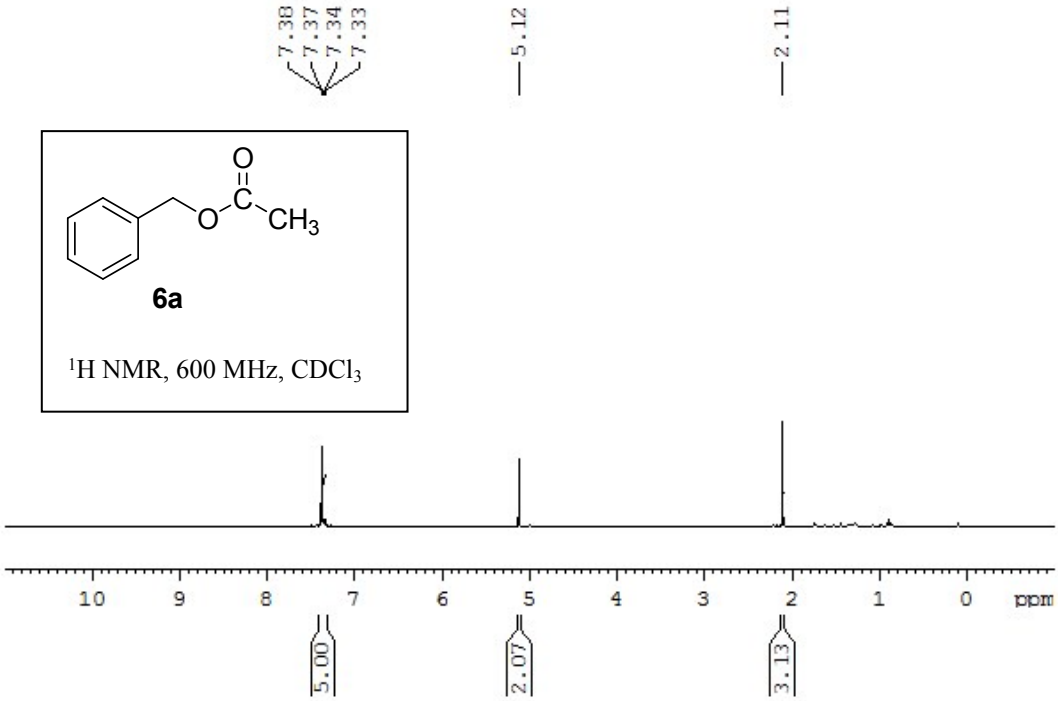
6d (Table 4, entry 2)

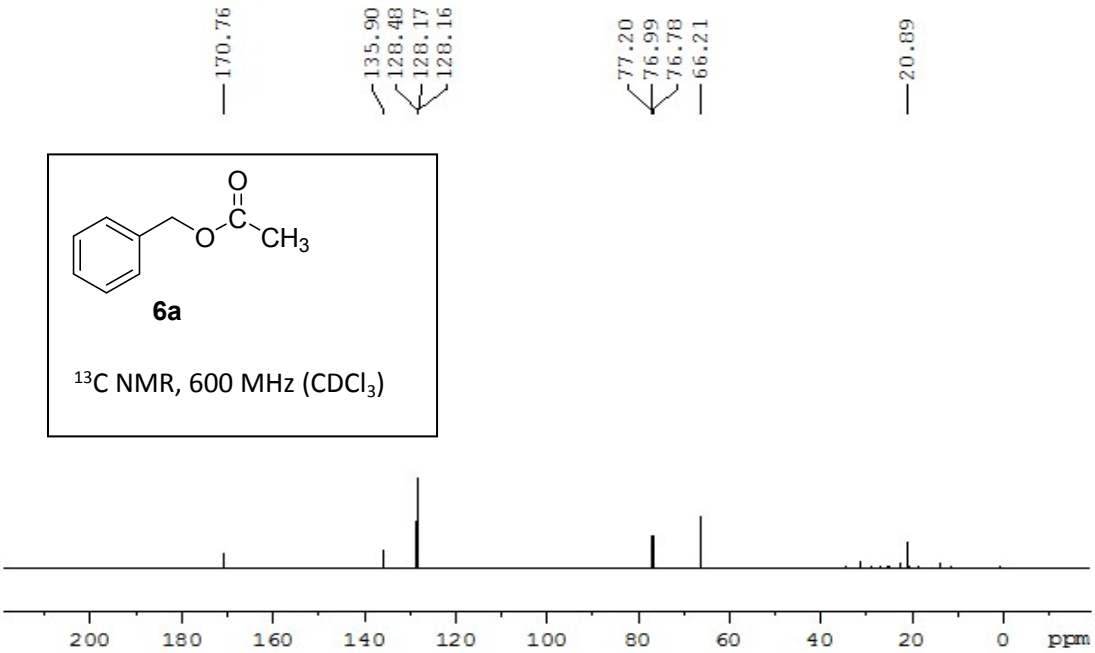




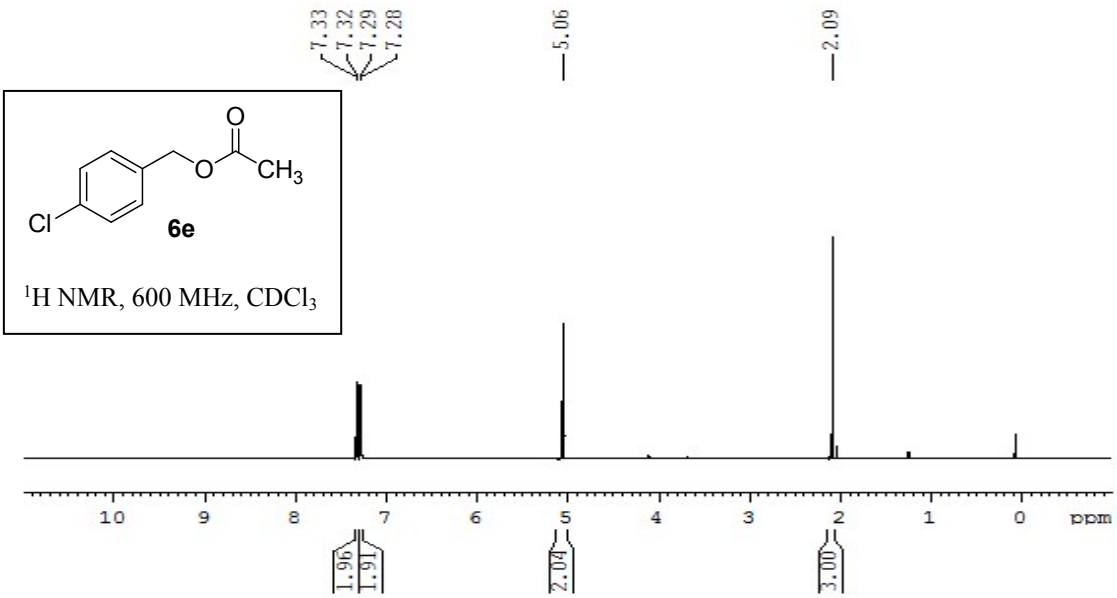


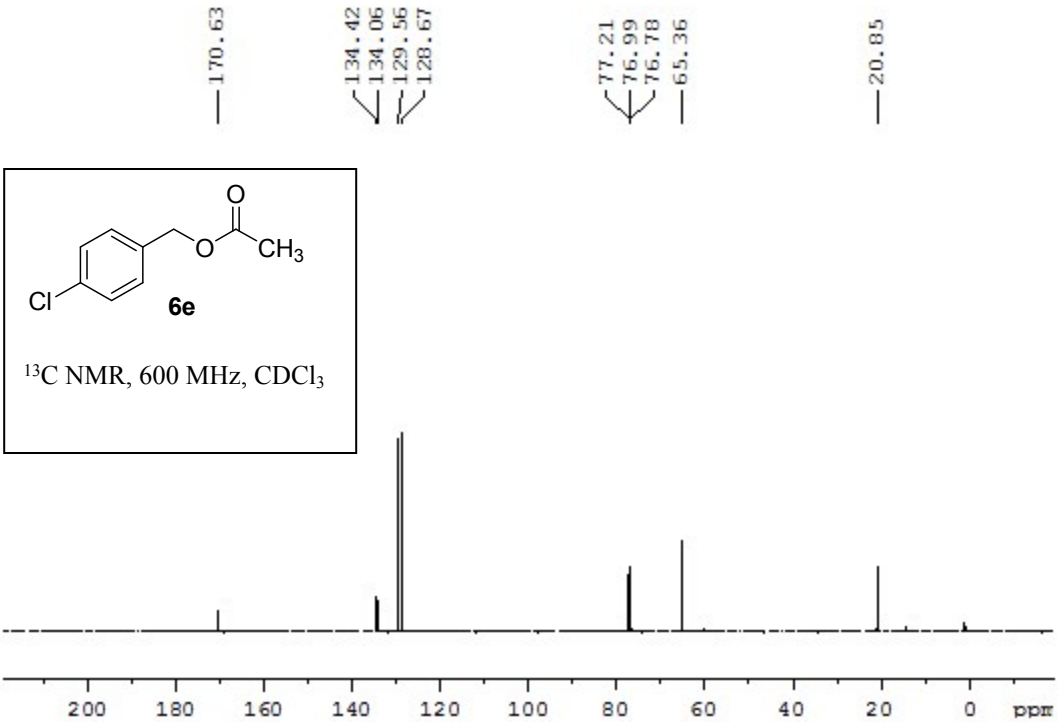
6a (Table 4, entry 3)

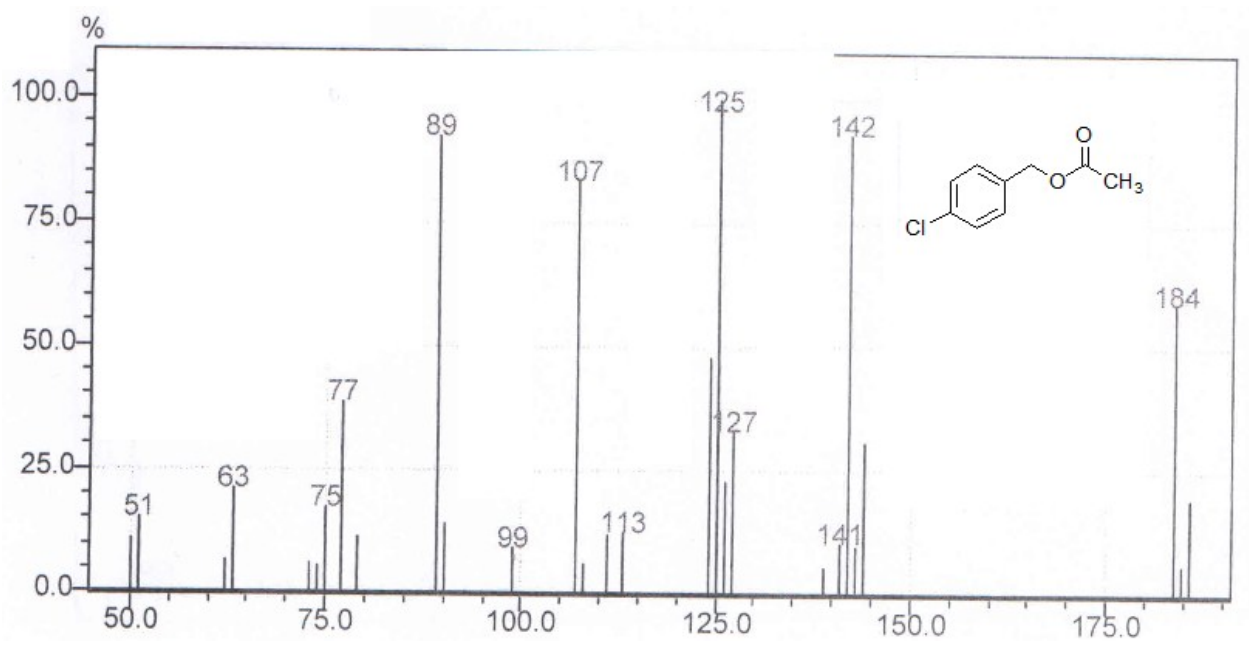




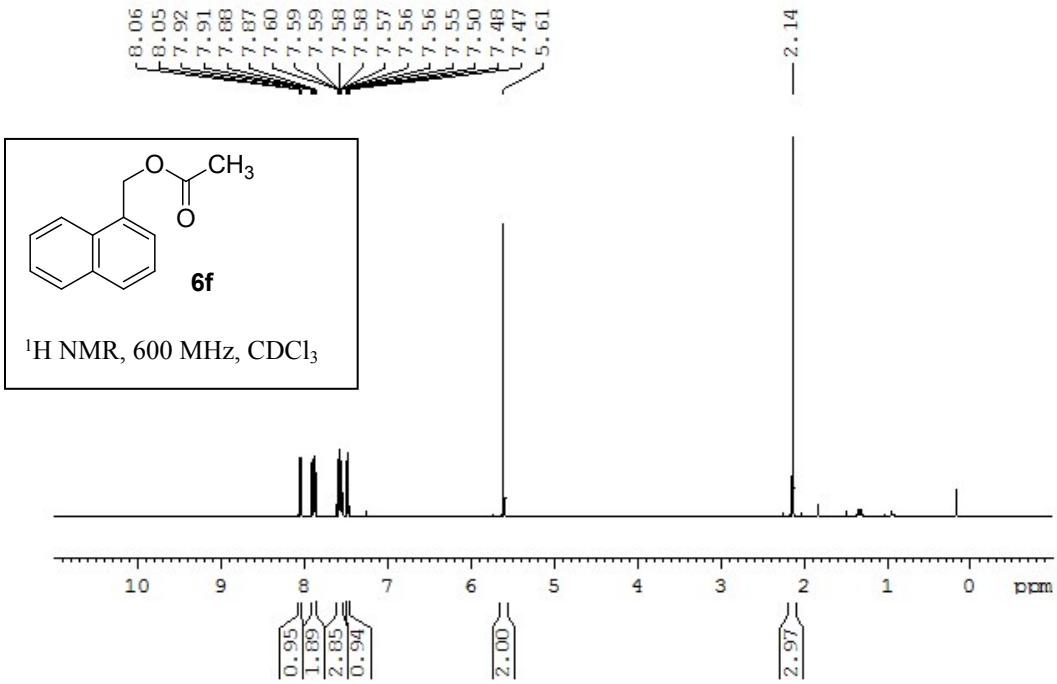
6e (Table 4, entry 4)

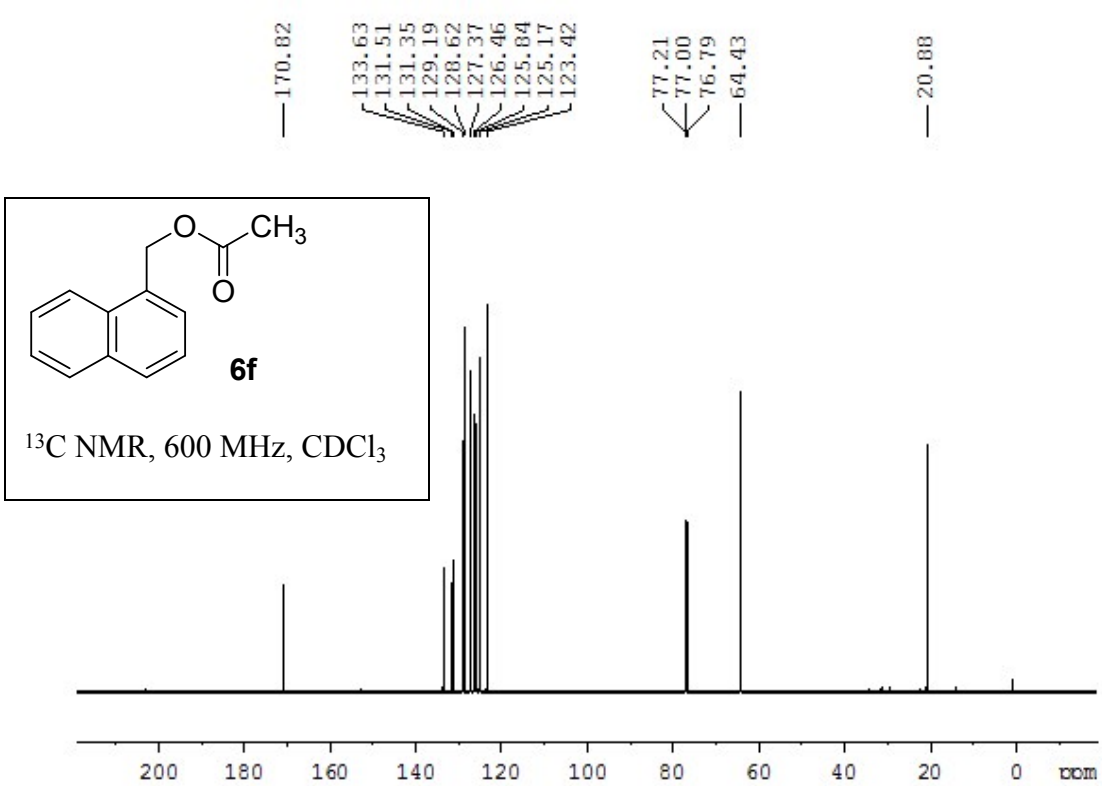

7.33
7.32
7.29
7.28
5.06
2.09
O
O
CH3
Cl
6e
1H NMR, 600 MHz, CDCl3
10
9
8
7
6
5
4
3
2
1
0
ppm
1.96
1.91
2.04
3.00

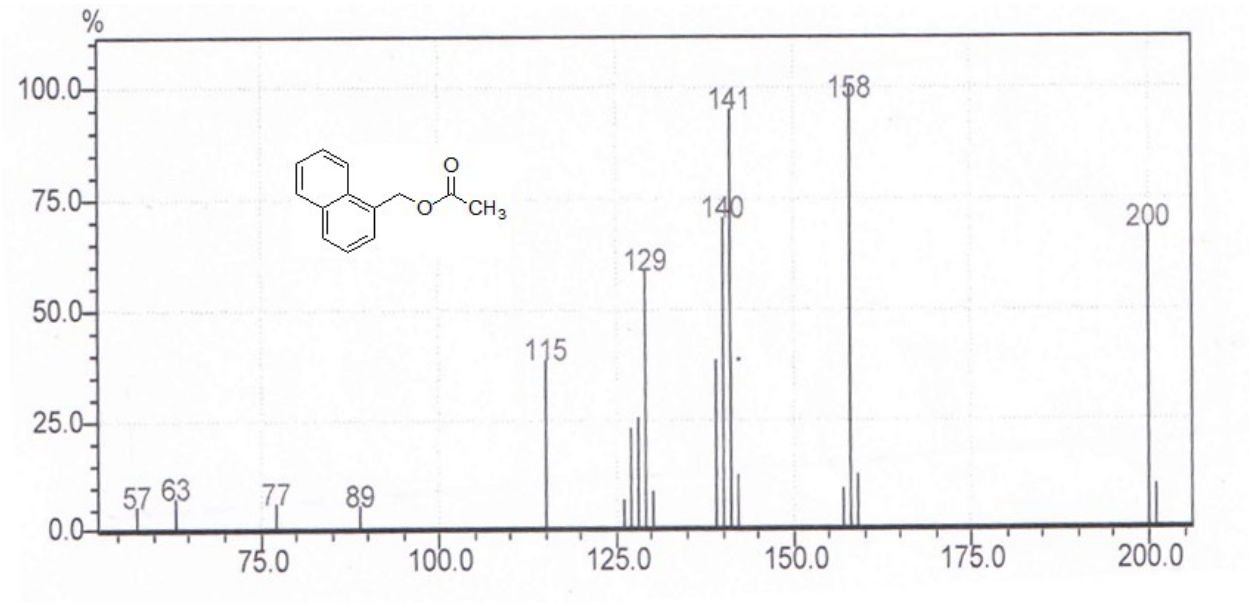

170.63
134.42
134.06
129.56
128.67
77.21
76.99
76.78
65.36
20.85
O
O
CH3
Cl
6e
13C NMR, 600 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
0
ppm



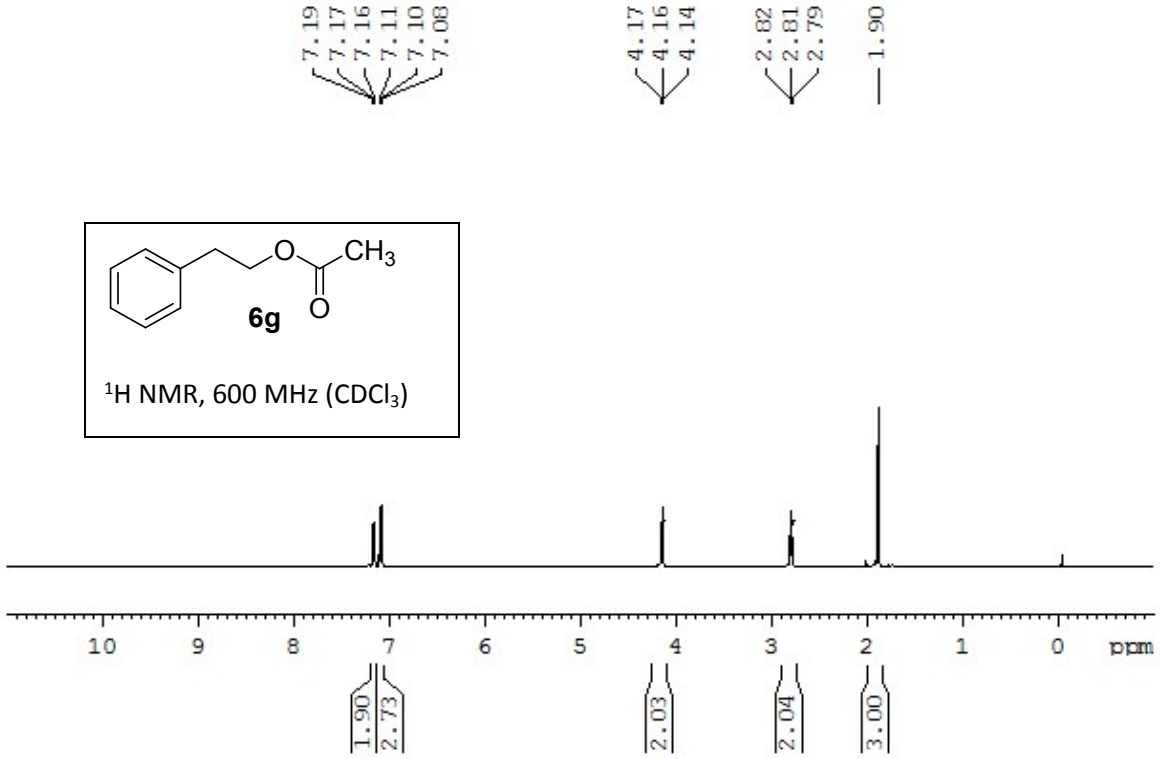
6f (Table 4, entry 5)

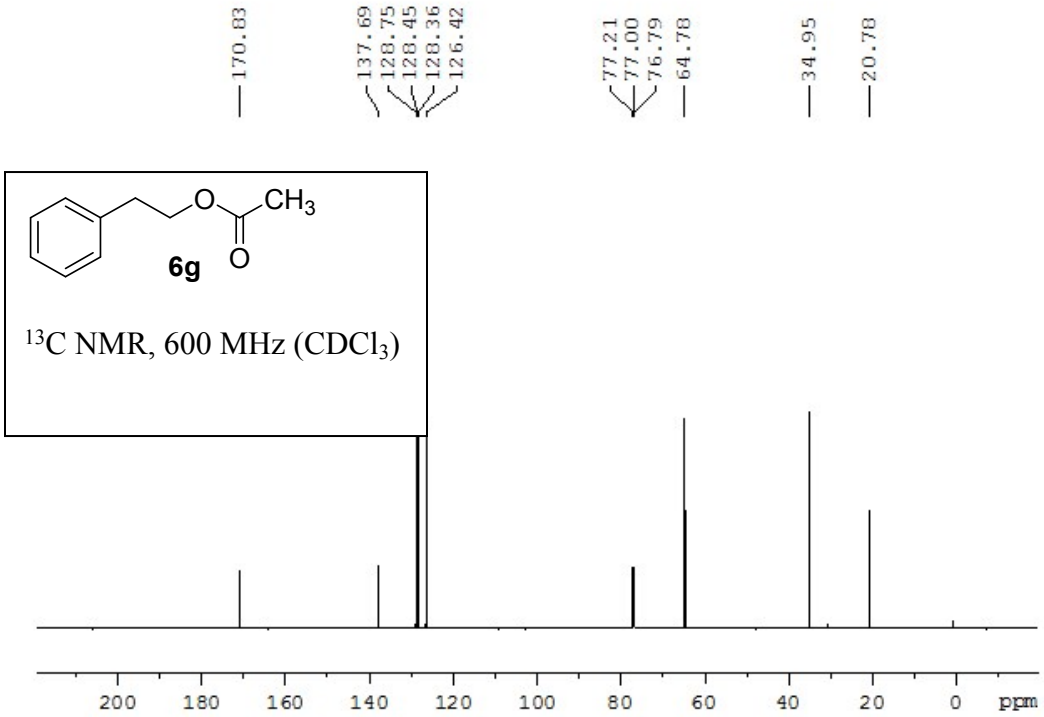




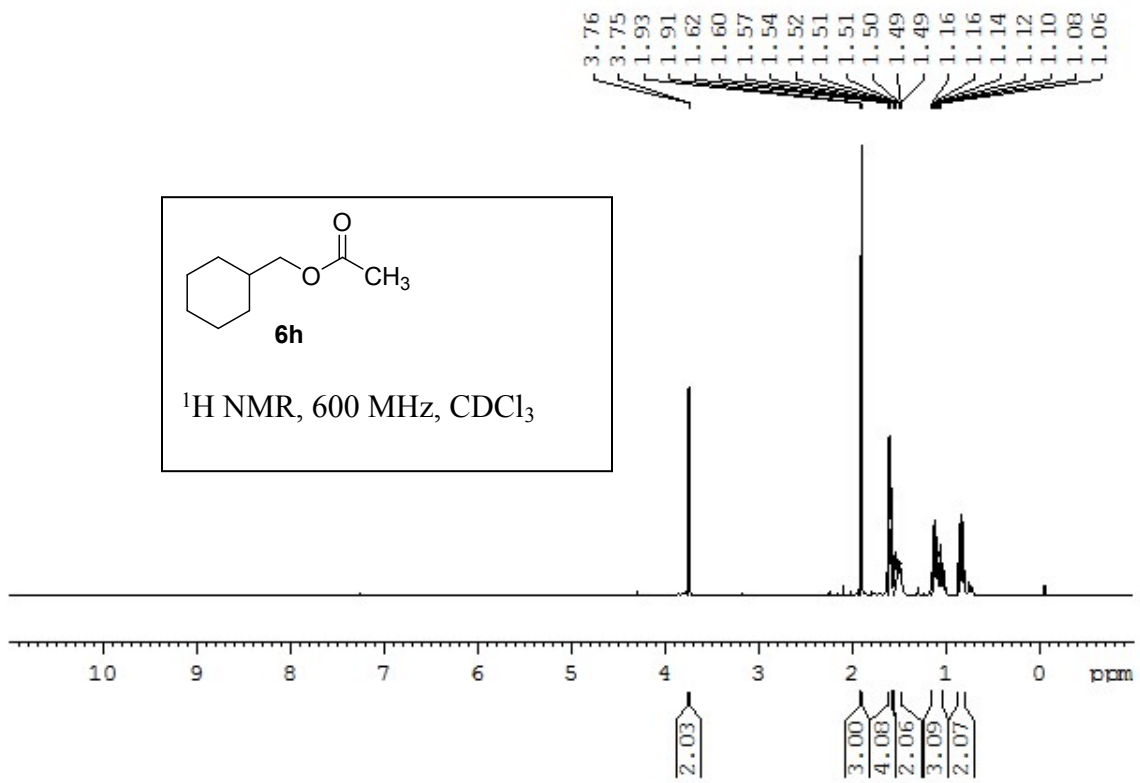


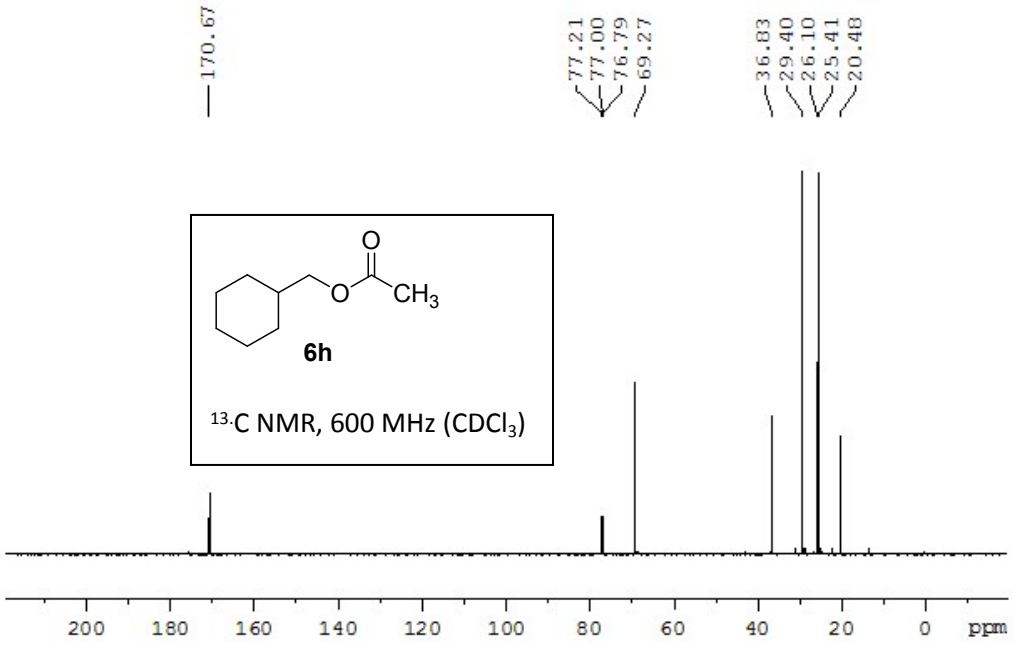
6g (Table 4, entry 6)



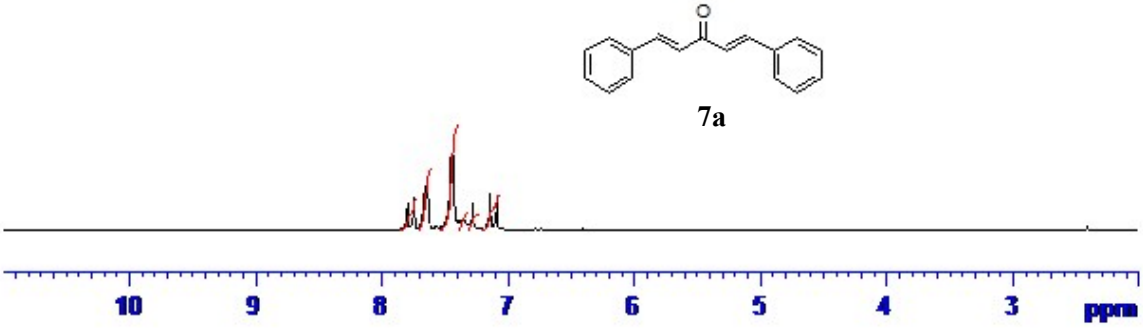


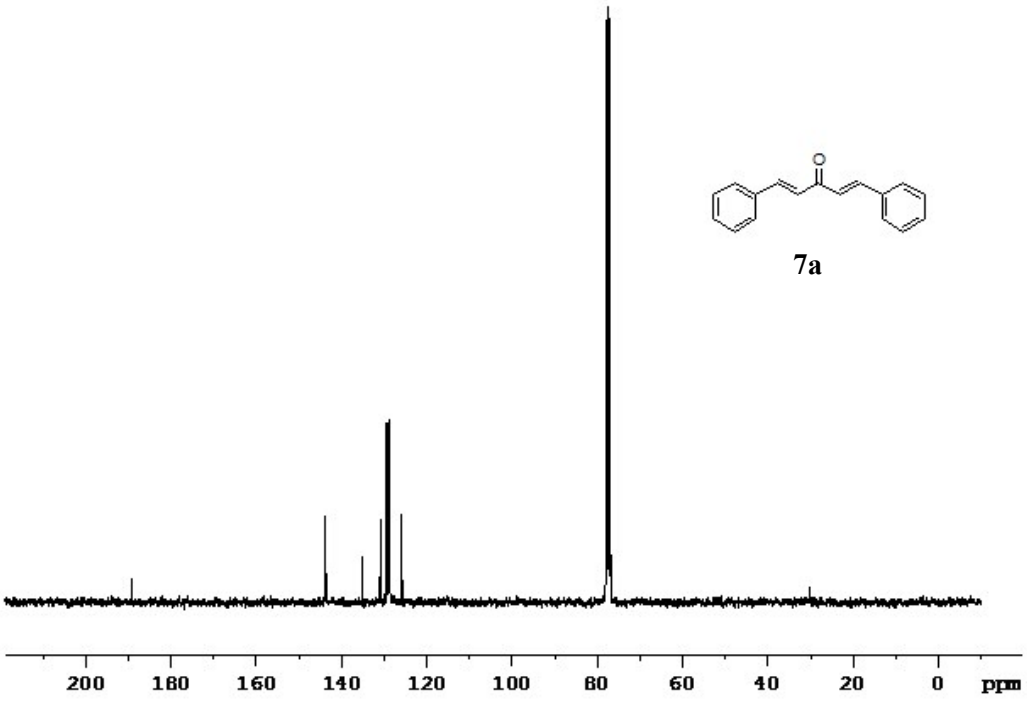
6h (Table 4, entry 7)

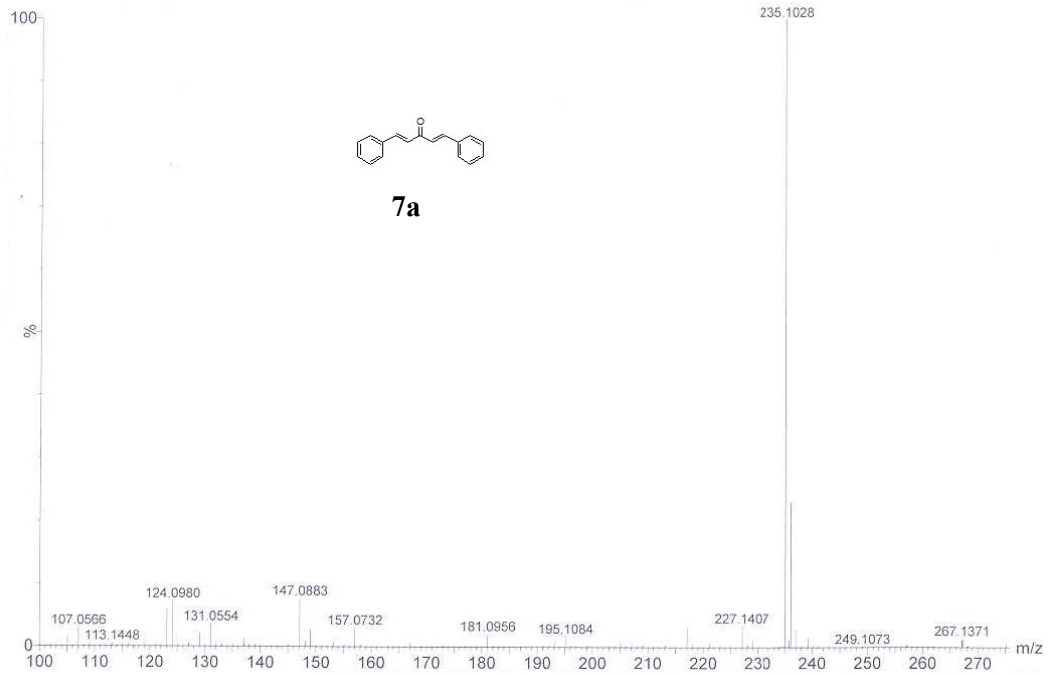




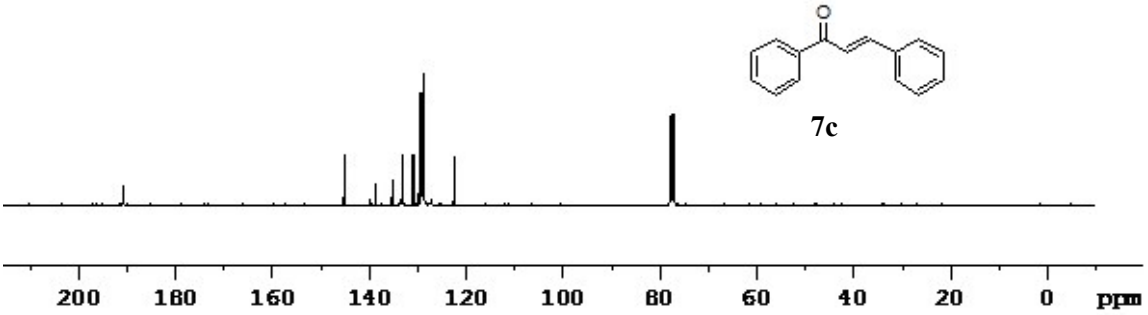
7a (Table S4, entry 1)

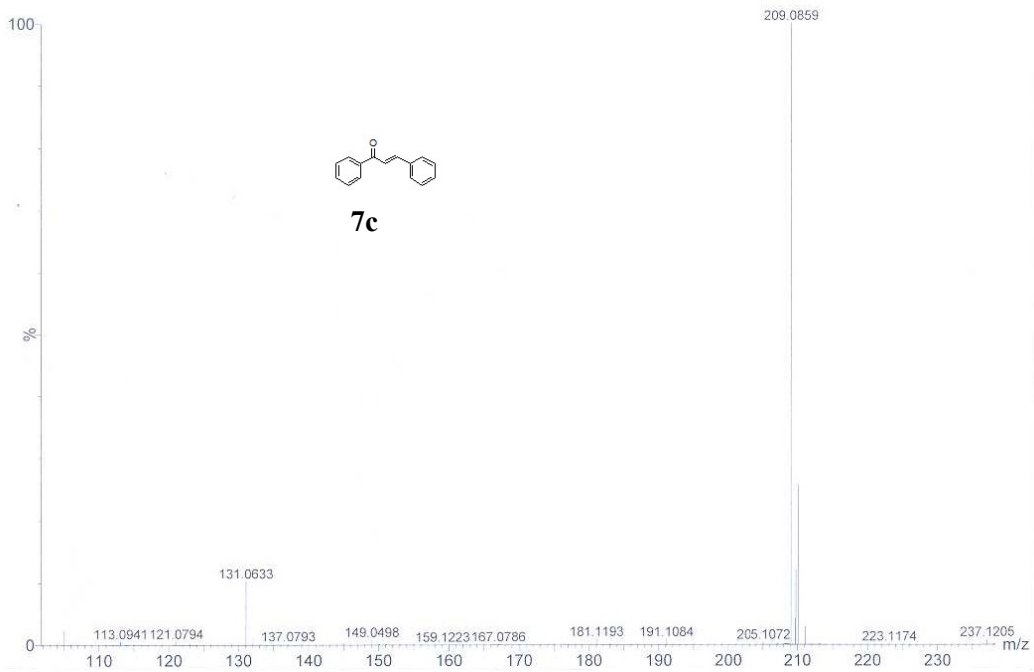

7a
10
9
8
7
6
5
4
3
ppm


7a
200
180
160
140
120
100
80
60
40
20
0
ppm



7c (Table S4, entry 3)





References

1. (a) M. Reid, D. J. Rowe, R. J. K. Taylor, *Chem. Comm*., **2003**, 2284–2285; b) T. S. Jianga, J.H. Li, *Chem. Commun*., **2009**, 7236–7238.
2. L. X. Shao, J. Li, B.Y. Wang, M. Shi, *Eur. J. Org. Chem.* **2010**, 6448–6453.
3. A. Nordqvist, C. Bjorkelid, M. Andaloussi, A. M. Jansson,S. L. Mowbray, A. Karlen, M. Larhed, *J. Org. Chem*. **2011**, *76*, 8986–8998.
4. G. Battistuzzi, S. Cacchi, G. Fabrizi, *Org. Lett*, **2003***,* 5, 777-780.
5. S. Noel, C. Luo, C. Pinel, L. Djakovitch, *Adv. Synth. Catal*. **2007**, *349*, 1128-1140.
6. N. R. Guha, D. Bhattacherjee, P. Das, *Catal. Sci. Technol*, **2015**, *5*, 2575.
7. N. R Guha, S. Sharma, D. Bhattacherjee, V. Thakur, R. Bharti, C. B. Reddy, P. Das, *Green Chem*., **2016**, *18*, 1206-1211.
8. Commercially available; Sigma Aldrich
9. S. Verma, R. B. N. Baig, C. Han, M. N. Nadagouda, R. S. Varma, *Green Chem*., **2016**, *18*, 251.