Supporting Information

Rhodium Fluorapatite Catalyst for the Synthesis of Trisubstituted Olefins Via Cross Coupling of Baylis-Hillman Adducts and Arylboronic Acids

M. Lakshmi Kantam,* K.B.Shiva kumar, B.Sreedhar

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad – 500 007, India

Fax: 91- 40-27160921; Tel: 91- 40-27193510; E-mail: mlakshmi@iict.res.in

General Remarks

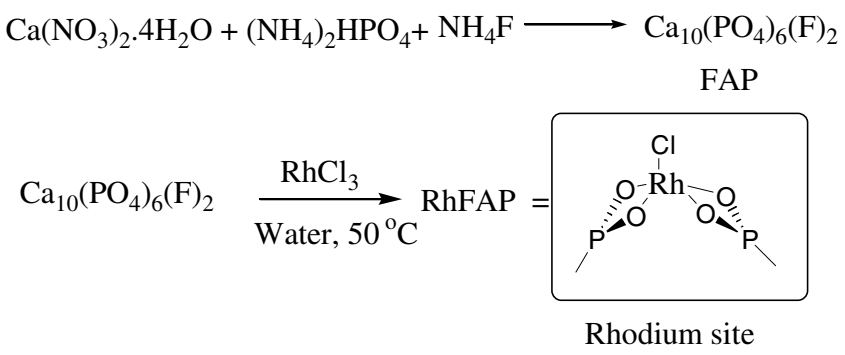
NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Coupling constants (J values) are reported in Hertz. Elemental analyses were carried out on a CHNS elemental analyzer. IR spectra were recorded on a FT-IR spectrometer. XPS spectra were recorded using the Mg Kα anode. X-ray powder diffraction (XRD) data were collected using Cu Kα radiation. MS experiments were performed on a low resolution magnetic sector mass spectrometer. All yields given refer to as isolated yields.

Preparation and Characterization Fluorapatite [FAP, $Ca_{10}(PO_4)_6(F)_2$] Catalysts :

FAP was obtained by co-precipitation method. A mixture of $(NH_4)_2HPO_4$ (7.92 g, 0.06 mol) and NH_4F (1 g, 0.027 mol) in 250 mL of water, maintained at a pH greater than 12 by addition of NH_4OH (15-20 mL), was introduced into 150 mL of a solution of $Ca(NO_3)_2 \cdot 4H_2O$ (23.6 g, 0.1 mol) under constant stirring. The suspension was refluxed for 4 h. The FAP crystallites were filtered, washed with water, dried overnight at 80 ºC and calcined in air at 500 ºC for 30 min. All the synthetic steps were carried out using doubly distilled water.

Rhodium Exchanged FAP (RhFAP) :

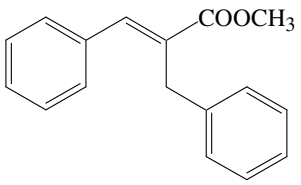
The FAP (1.0 g) was stirred with 25 mL of a 0.25 mmol aqueous $RhCl_3$ solution at 50 °C for 24 h. The obtained slurry was filtered, washed with deionized water, and dried overnight at 110 °C, yielding the RhFAP as a yellowish orange powder. The rhodium content was measured as 0.1 mmol g^{-1} using ICP-AES.



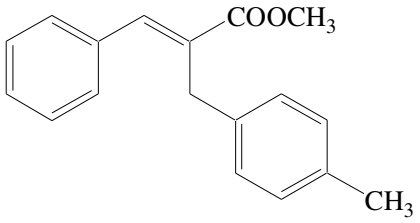
A typical procedure for synthesis of trisubstituted olefins :

In a typical experimental procedure, RhFAP (100 mg or Rh = 0.01 mmol) was added to a mixture of Baylis-Hillman adduct (1 mmol), arylboronic acid (1.2 mmol) and 1,5-cod (0.05 mmol) in methanol (4 mL) at 65 ^{o}C, and the mixture was stirred for 6 h. The progress of the reaction was monitored by TLC and on completion of the reaction, the reaction mixture was centrifuged and the centrifugate was concentrated under reduced pressure to give the crude product. The crude product was purified by column chromatography on silica gel to afford the corresponding trisubstituted olefins. The centrifuged catalyst was washed with methanol, dried and reused for next cycle.

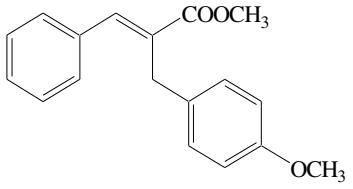
Characterization of the Products:



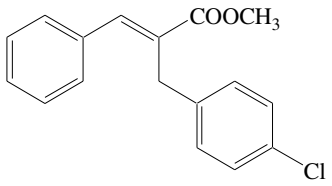
2-Benzyl-3-phenylacrylic acid methyl ester (Table 2, Entry 1): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 7.34-7.31 (m, 10H), 3.91(s, 2H), 3.74 (s, 3H), ^{13}C NMR (75 MHz, $CDCl_3$): δ =168.4, 140.9, 139.3, 135.2, 130.5, 129.1, 128.7,128.5, 128.4, 127.8, 126.0, 52.0, 33.1 MS: m/z = 252 (M^+). Anal. Calcd. For $C_{17}H_{16}O_2$: C, 80.93; H, 6.39; Found : C, 80.81; H, 6.34. A copy of the ^{1}H NMR spectra is provided



2-(4-Methylbenzyl)-3-phenylacrylic acid methyl ester (Table 2, Entry 2): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (s, 1H), 7.34-7.00 (m, 9H), 3.87(s, 2H), 3.73 (s, 3H), 2.31 (s, 3H), MS: m/z = 266 (M^+). Anal. Calcd. For $C_{18}H_{18}O_2$: C, 80.17; H, 6.81; Found : C, 80.05; H, 6.86. A copy of the ^{1}H NMR spectra is provided

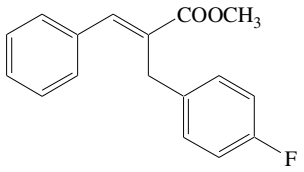


2-(4-Methoxybenzyl)-3-phenylacrylic acid methyl ester (Table 2, Entry 3): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (s, 1H), 7.33-7.24 (m, 5H), 7.03 (d, 2H, *J* = 8.3 Hz), 6.77 (d, 2H, *J* = 9.0 Hz), 3.84(s, 2H), 3.75 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 157.9, 140.5, 135.3, 131.2, 131.1, 129.1, 128.8, 128.6, 128.4, 113.9, 55.1, 32.2, 29.6. MS: m/z = 282 (M^+). Anal. Calcd. For $C_{18}H_{18}O_3$: C, 76.57; H, 6.43; Found : C, 76.41; H, 6.49. A copy of the ^{1}H NMR and ^{13}C NMR spectras are provided

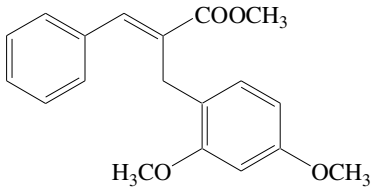


2-(4-Chlorobenzyl)-3-phenylacrylic acid methyl ester (Table 2, Entry 4): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 7.30 (m, 5H), 7.22 (d, 2H, *J* = 8.3 Hz), 7.01 (d, 2H *J* = 8.3 Hz), 3.87(s, 2H), 3.74 (s, 3H), MS: m/z = 286 (M^+). Anal. Calcd. For

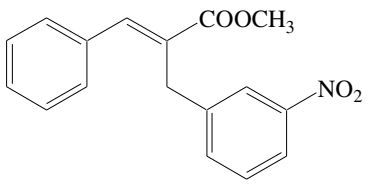
$C_{17}H_{15}ClO_2$: C, 71.20; H, 5.27; Found : C, 71.11; H, 5.22. A copy of the ^{1}H NMR spectra is provided



2-(4-Fluorobenzyl)-3-phenylacrylic acid methyl ester (Table 2, Entry 5): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (s, 1H), 7.33-6.90 (m, 9H), 3.87(s, 2H), 3.74 (s, 3H), MS: m/z = 270 (M^+). Anal. Calcd. For $C_{17}H_{15}FO_2$: C, 75.54; H, 5.59; Found : C, 75.67; H, 5.62. A copy of the ^{1}H NMR spectra is provided

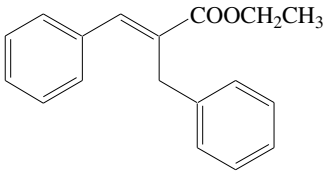


2-(2,4-Dimethoxybenzyl)-3-phenylacrylic acid methyl ester (Table 2, Entry 6): Colourless oil ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (s, 1H), 7.30-7.22 (m, 5H), 6.89 (d, 2H, *J* = 7.83 Hz), 6.40-6.30 (m, 2H), 3.77(s, 2H), 3.75 (s, 6H), 3.73 (s, 3H)
MS: m/z = 312 (M^+). Anal. Calcd. For $C_{19}H_{20}O_4$: C, 73.06; H, 6.45; Found : C, 72.90; H, 6.50. A copy of the ^{1}H NMR spectra is provided

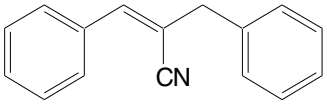


2-(3-nitrobenzyl)-3-phenylacrylic acid methyl ester (Table 2, Entry 7): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08-7.98 (m, 3H), 7.51-7.30 (m, 7H), 4.01 (s, 2H), 3.74 (s, 3H),

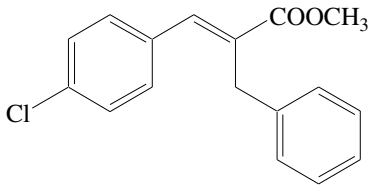
MS: m/z = 297 (M^+). Anal. Calcd. For $C_{17}H_{15}NO_4$: C, 68.68; H, 5.09; N, 4.71; Found : C, 68.56; H, 5.13; N, 4.66. A copy of the ^1H NMR spectra is provided



2-Benzyl-3-phenylacrylic acid ethyl ester (Table 2, Entry 8): ^1H NMR (300 MHz, $CDCl_3$): δ = 7.87 (s, 1H), 7.33-7.11 (m, 10H), 4.16 (q, 2H, *J* = 7.5 Hz), 3.91(s, 2H), 1.21 (s, 3H), MS: m/z = 266 (M^+). Anal. Calcd. For $C_{18}H_{18}O_2$: C, 81.17; H, 6.81; Found : C, 81.12; H, 6.75. A copy of the ^1H NMR spectra is provided

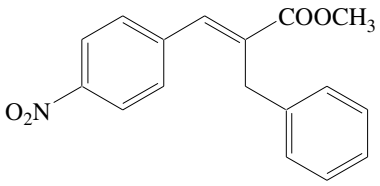


2-Benzyl-3-phenyl-acrylonitrile (Table 2, Entry 9) Colourless oil ^1H NMR (300 MHz, $CDCl_3$): δ = 7.69-7.22 (m, 10H), 6.89 (s, 1H), 3.65 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.0, 136.4, 133.5, 130.0, 128.8, 128.7, 128.6, 128.2 127.3, 118.6, 110.7, 42.12, 29.6. MS: m/z = 219 (M^+). Anal. Calcd. For $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39 Found : C, 87.60; H, 5.95; N, 6.35. A copy of the ^1H NMR and ^{13}C NMR spectras are provided

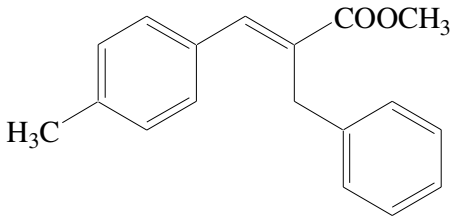


2-Benzyl-3-(4-chlorophenyl)-acrylic acid methyl ester (Table 2, entry 10) ^1H NMR (300 MHz, $CDCl_3$): δ = 7.82 (s, 1H), 7.30-7.10 (m, 9H), 3.89(s, 2H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4, 139.6, 139.0, 134.5, 133.7, 131.2, 130.5, 128.8 128.6, 127.8, 126.2, 52.2, 33.1. MS: m/z = 286 (M^+). Anal. Calcd. For $C_{17}H_{15}ClO_2$: C,

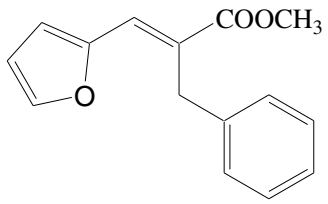
71.20; H, 5.27; Found : C, 71.09; H, 5.23. A copy of the ^{1}H NMR and ^{13}C NMR spectras are provided



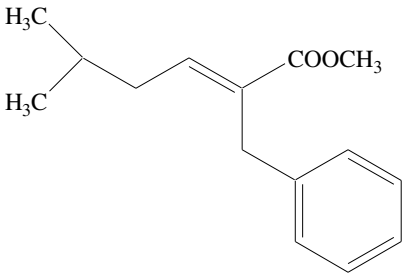
2-Benzyl-3-(4-nitrophenyl)-acrylic acid methyl ester (Table 2, entry 11) ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.19 (d, 2 H, *J* = 8.8 Hz), 7.88 (s, 1H), 7.46 (d, 2 H, *J* = 8.8 Hz), 7.30-7.09 (m, 5H), 3.89(s, 2H), 3.74 (s, 3H), MS: m/z = 297 (M^+). Anal. Calcd. For $C_{17}H_{15}NO_4$: C, 68.68; H, 5.09; N, 4.71 Found : C, 68.53; H, 5.11; N, 4.64. A copy of the ^{1}H NMR spectra is provided



2-Benzyl-3-(4-methylphenyl)-acrylic acid methyl ester (Table 2, Entry 12): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (s, 1H), 7.26-7.08 (m, 9H), 3.92(s, 2H), 3.72 (s, 3H), 2.33 (s, 3H), MS: m/z = 266 (M^+). Anal. Calcd. For $C_{18}H_{18}O_2$: C, 80.17; H, 6.81; Found : 80.14; H, 6.78. A copy of the ^{1}H NMR spectra is provided



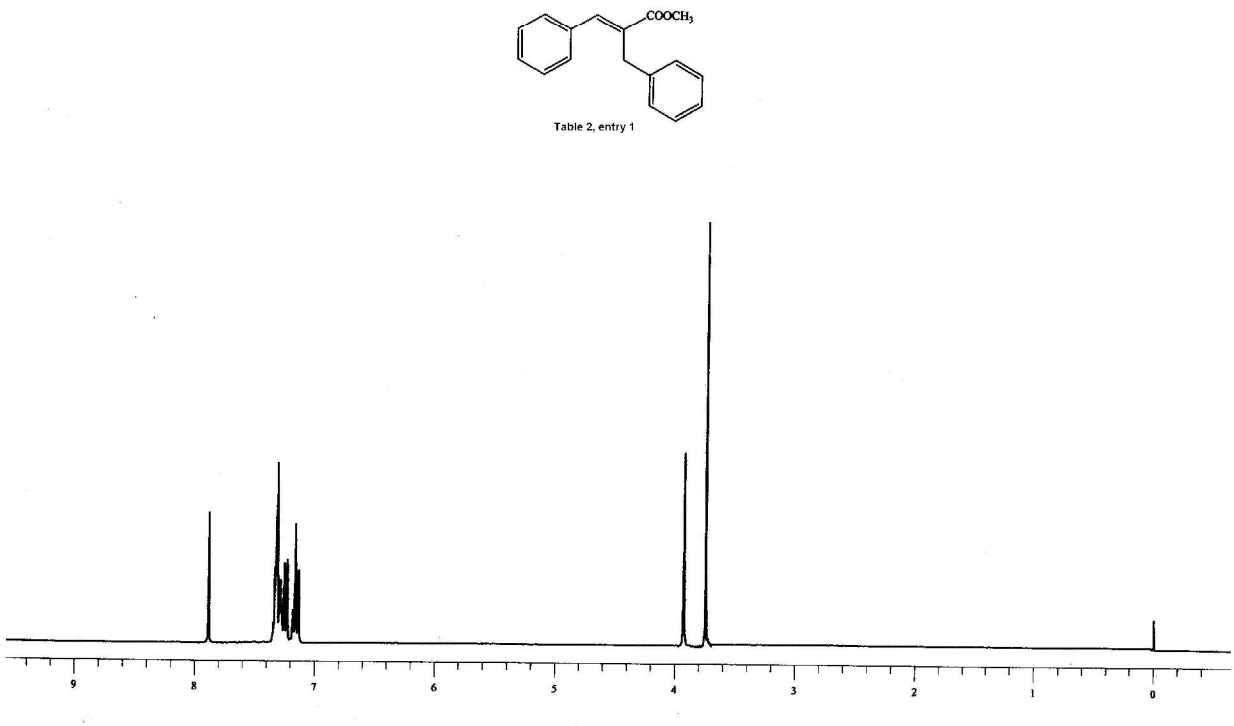
2-Benzyl-3-furan-2-yl-acrylic acid methyl ester (Table 2, Entry 13): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.47 (d, 1 H, *J* = 2.1 Hz), 7.20-7.10 (m, 5H), 6.57 (d, 1 H, *J* = 3.02 Hz), 6.42 (dd, 1 H, J_1 = 1.5 Hz, J_2 = 2.2 Hz), 4.1(s, 2H), 3.72(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.3, 151.2, 144.2, 139.3, 128.3, 128.2, 127.2, 126.6, 125.9, 115.6, 112.0, 52.0, 33.3. MS: m/z = 242 (M^+). Anal. Calcd. For $C_{15}H_{14}O_3$: C, 74.36; H, 5.82; Found : C, 74.37; H, 5.79. A copy of the ^{1}H NMR and ^{13}C NMR spectras are provided



2-Benzyl-5-methyl-hex-2-enoic acid methyl ester (Table 2, Entry 14): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22-7.10 (m, 5H), 6.91 (m, 1H, *J* = 7.55 Hz), 3.67 (s, 2H), 3.65 (s, 3H), 2.16 (t, 2H, *J* = 7.55 Hz), 1.76 (m, 1H), 0.93 (d, 6H, *J* = 6.79 Hz), MS: m/z = 232 (M^+). Anal. Calcd. For $C_{15}H_{20}O_2$: C, 77.55; H, 8.68; Found : C, 77.42; H, 8.57. A copy of the ^{1}H NMR spectra is provided

NMR spectra

^{1}H NMR



^{1}H NMR

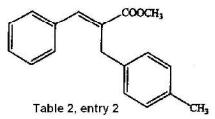
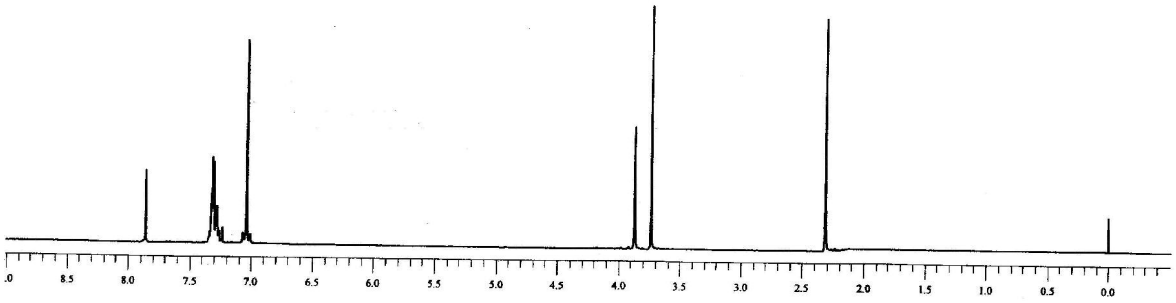
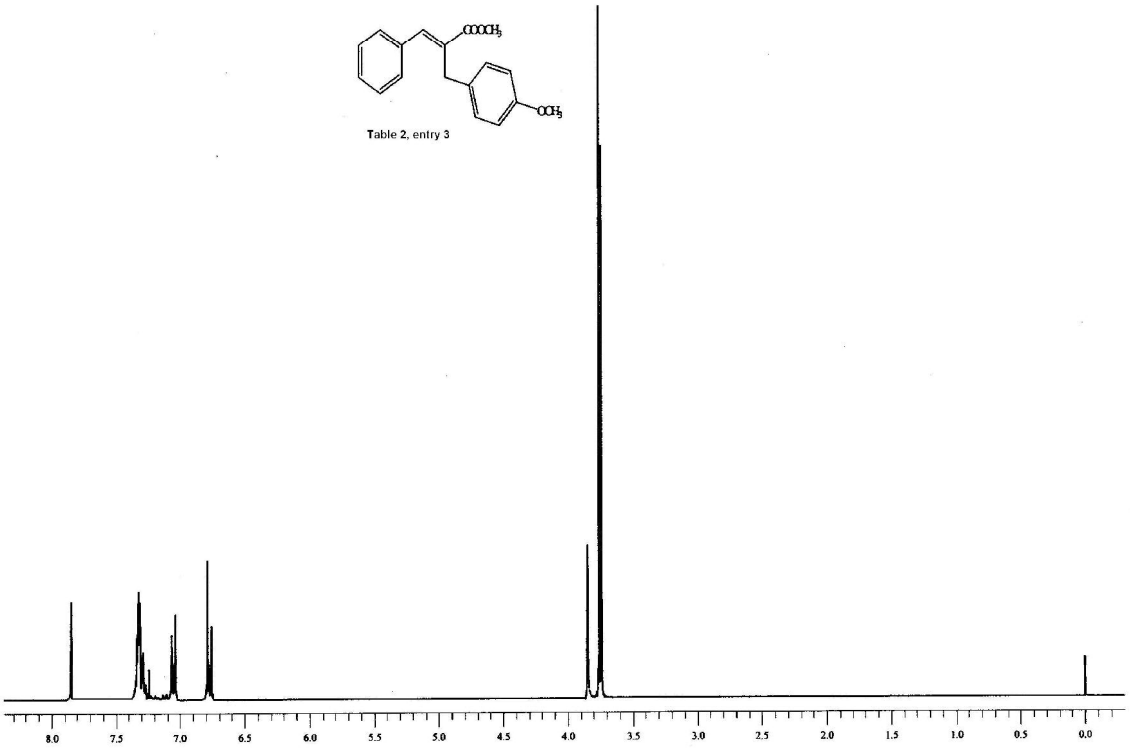


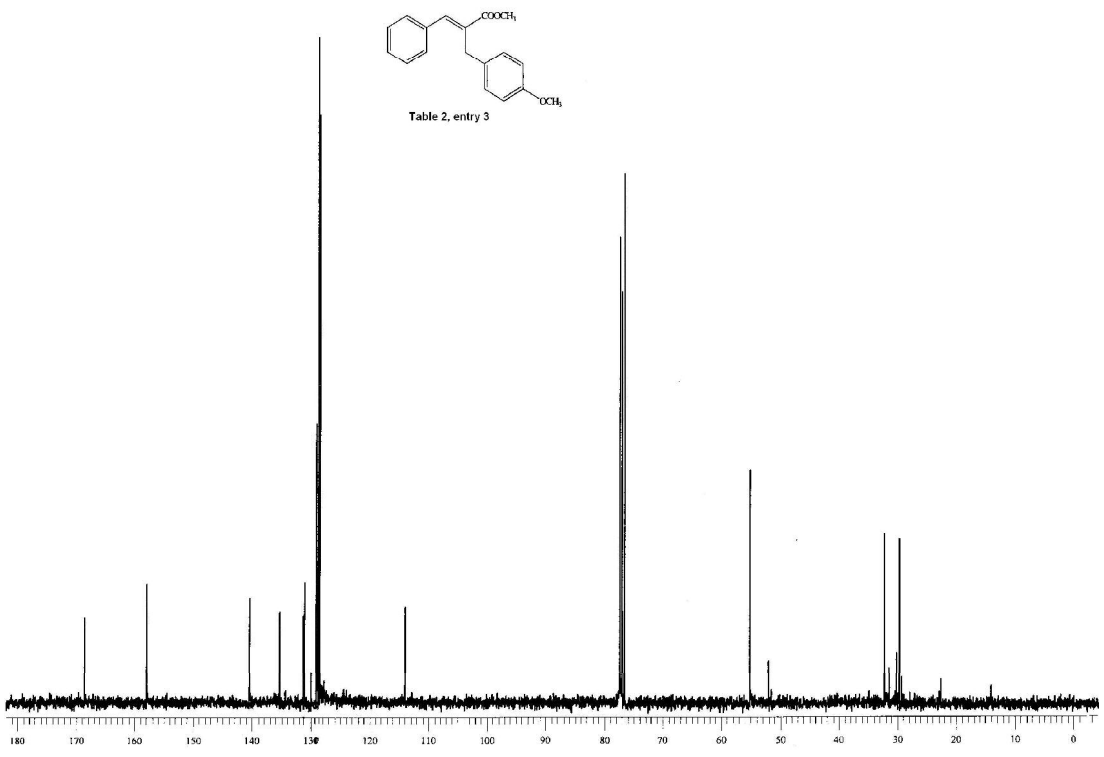
Table 2, entry 2



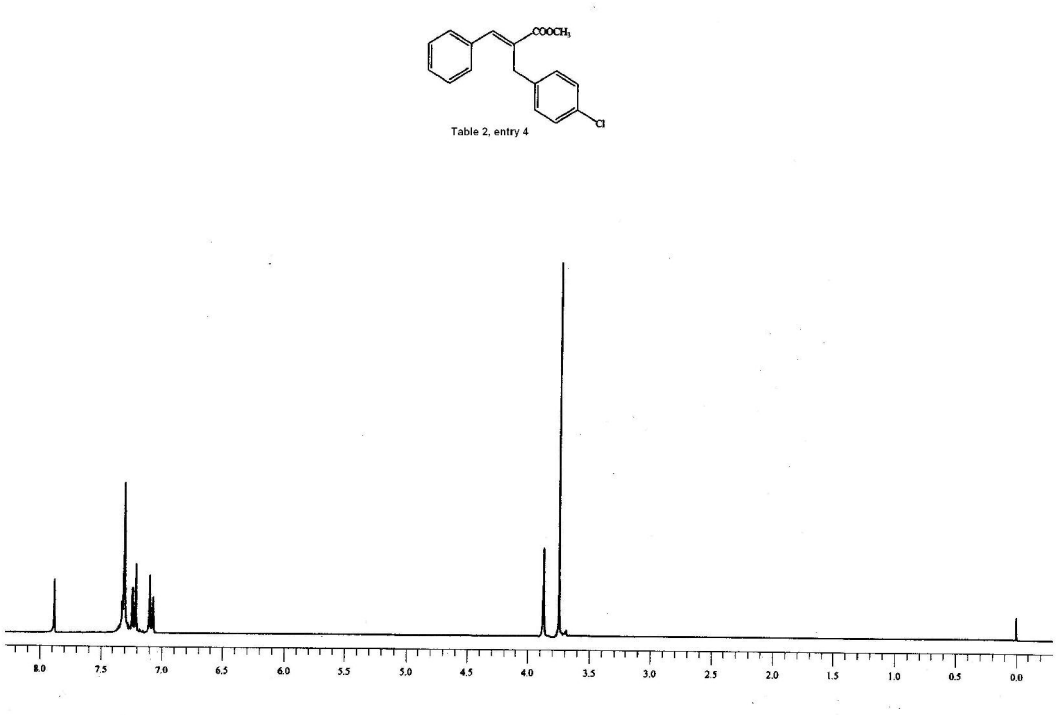
^{1}H NMR



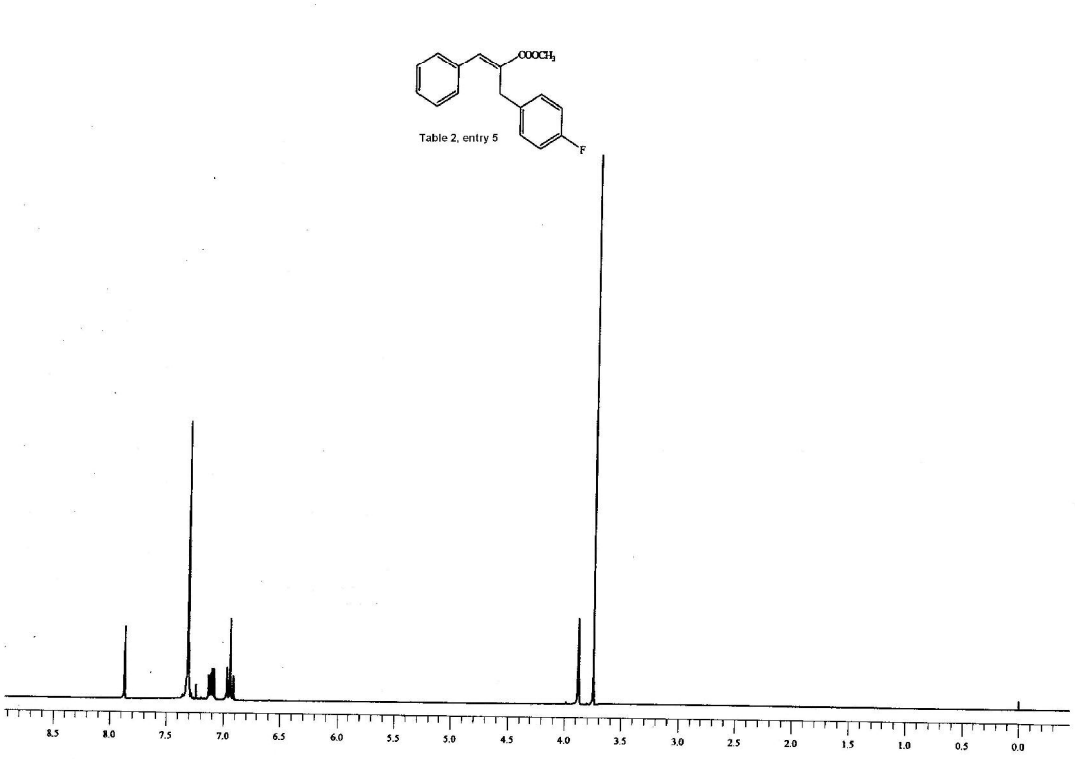
^{13}C NMR


COOCH3
OCH3
Table 2, entry 3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{1}H NMR


COOCH3
Cl
Table 2, entry 4
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

^{1}H NMR


COOCH3
F
Table 2, entry 5
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

^{1}H NMR

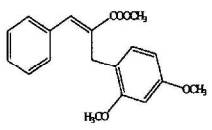
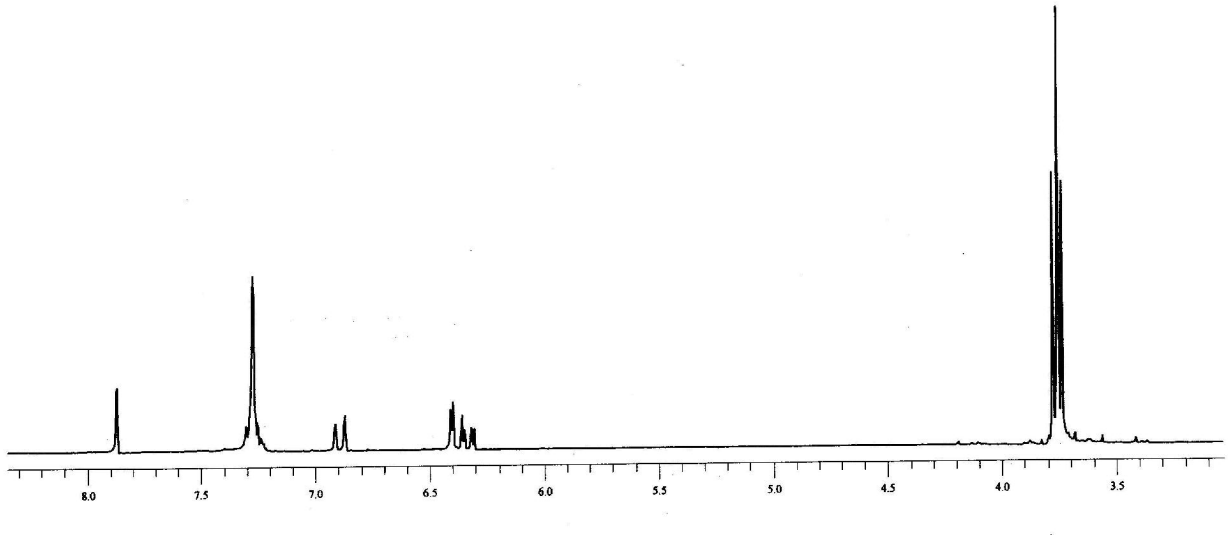


Table 2, entry 6



^{1}H NMR

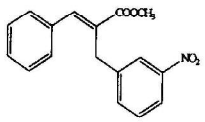
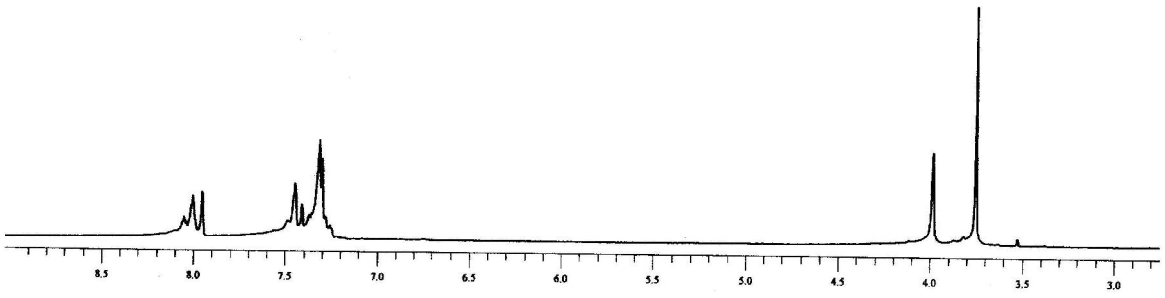


Table 2, entry 7



^{1}H NMR

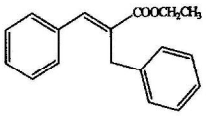
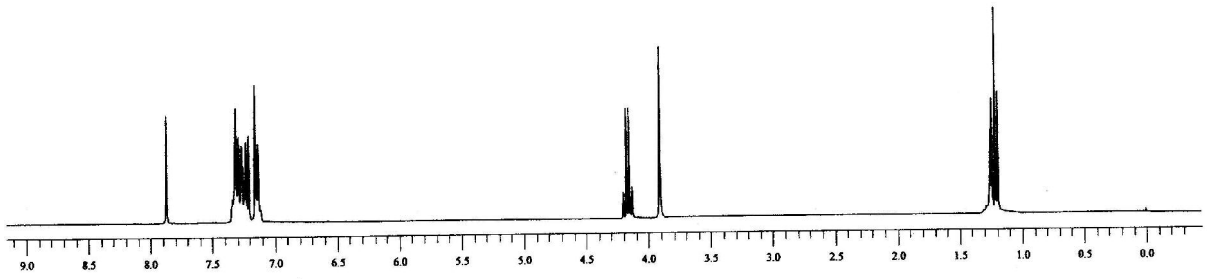


Table 2, entry 8



^{1}H NMR

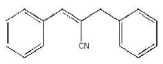
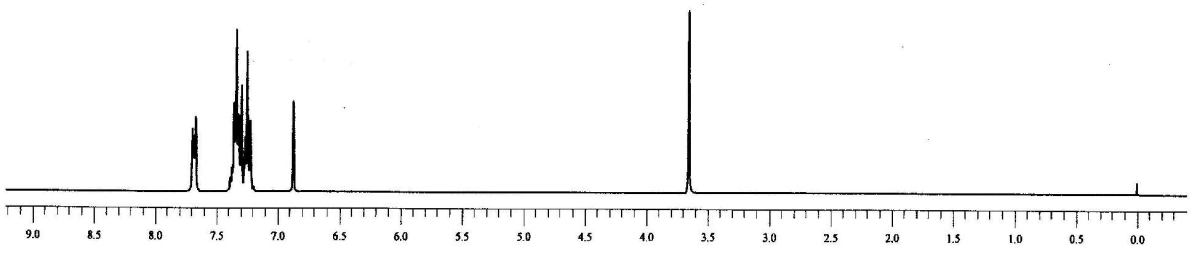
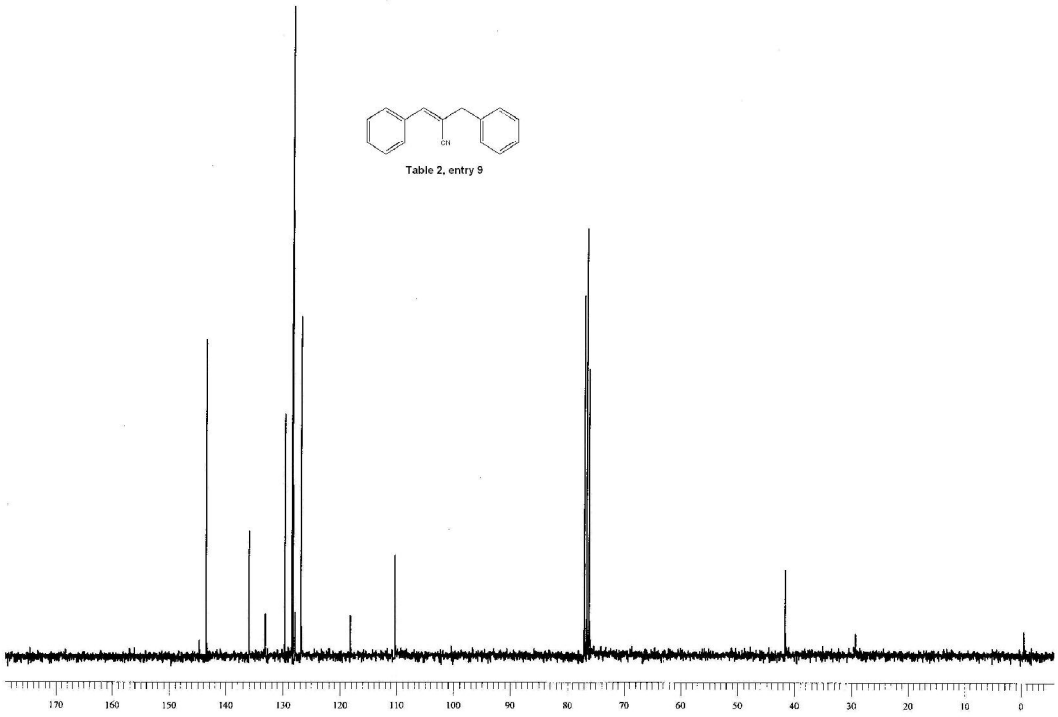


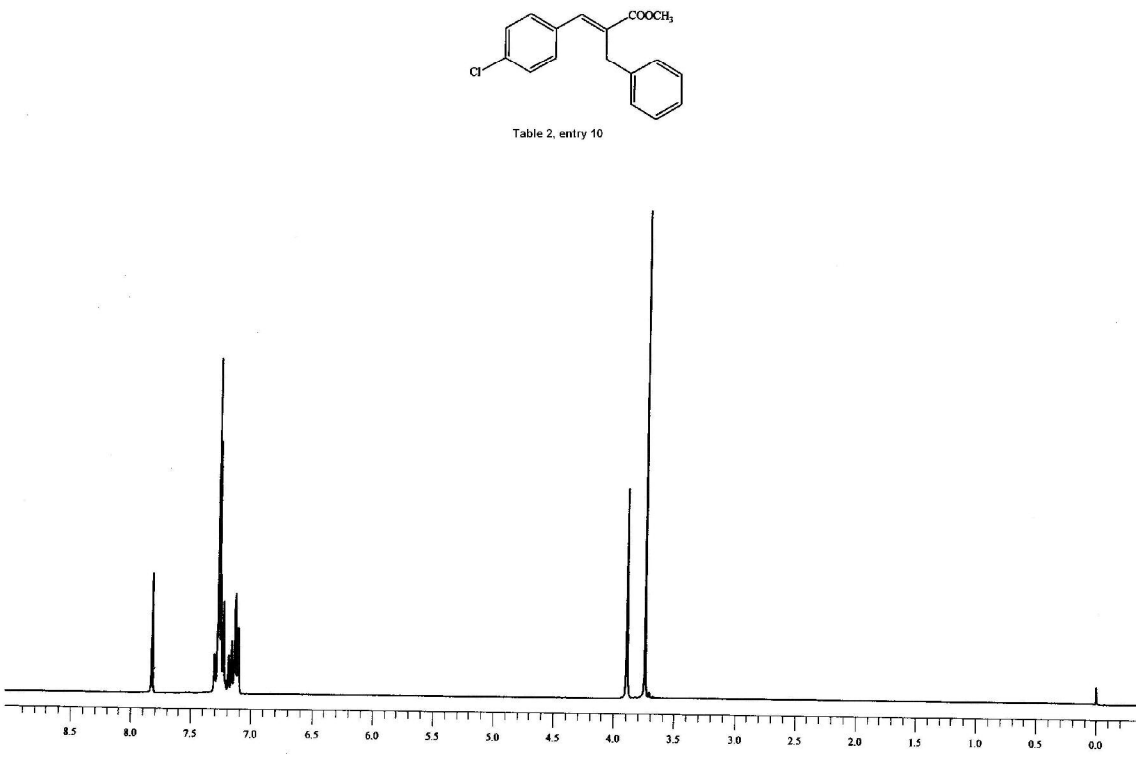
Table 2, entry 9



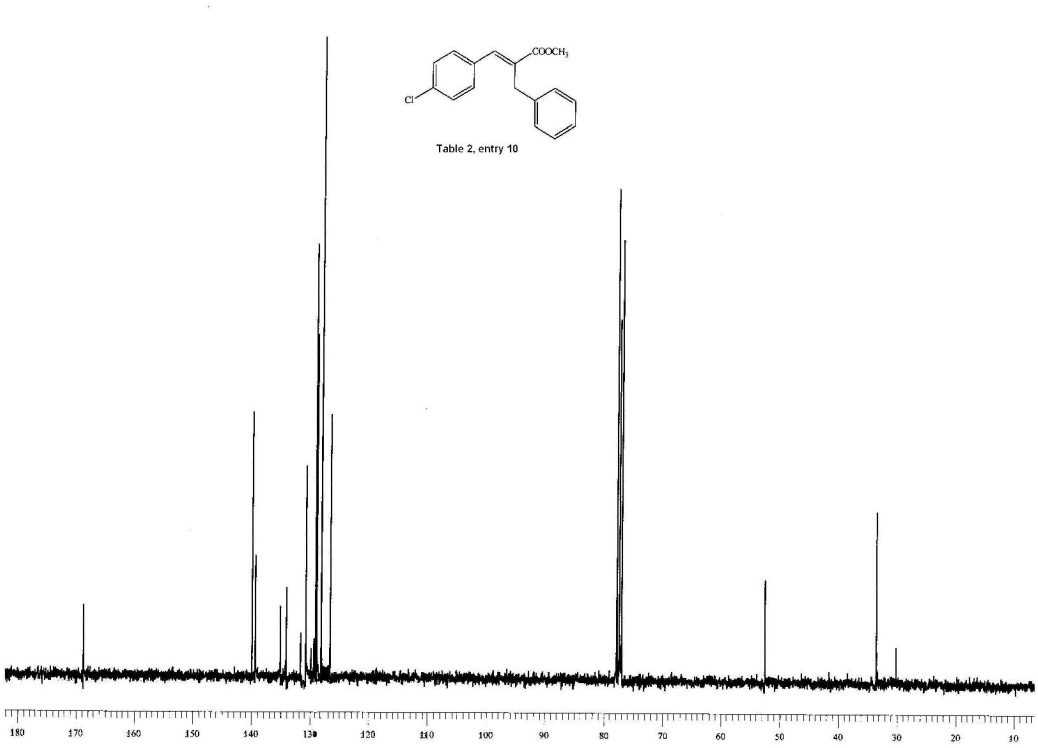
^{13}C NMR


OH
Table 2, entry 9
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

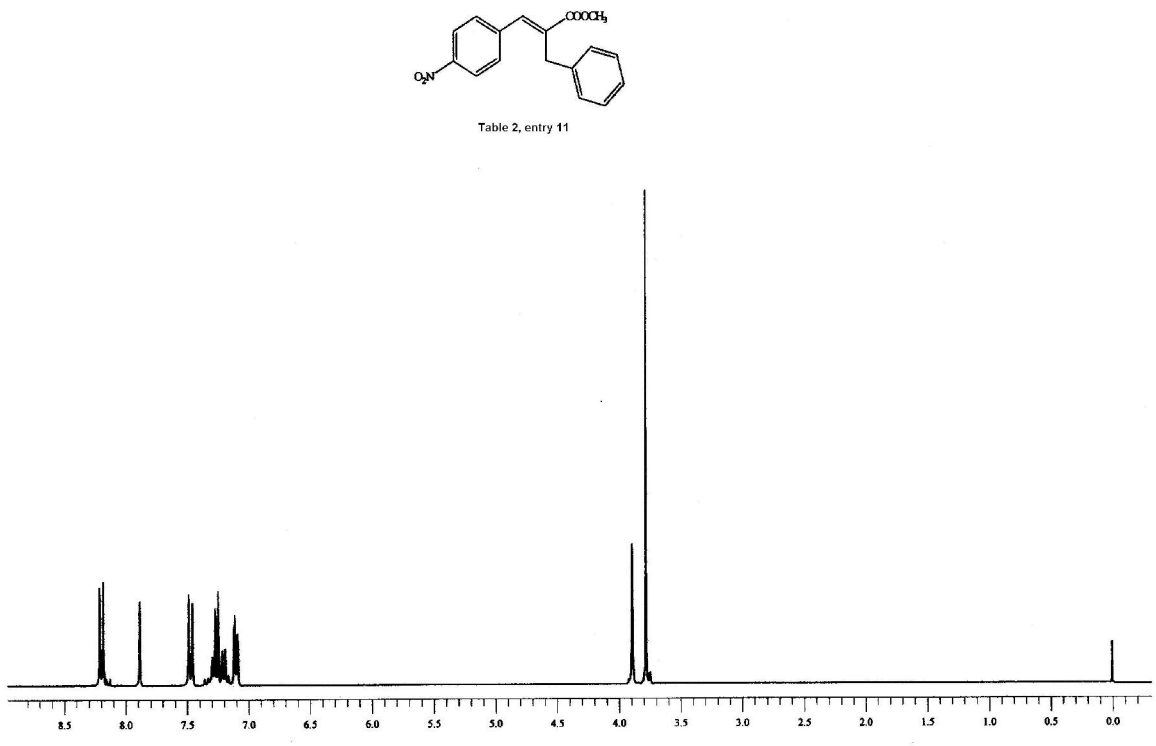
^{1}H NMR


COOCH3
Cl
Table 2, entry 10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

^{13}C NMR


COOCH3
Cl
Table 2, entry 10
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

^{1}H NMR


COOCH3
O2N
Table 2, entry 11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

^{1}H NMR

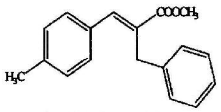
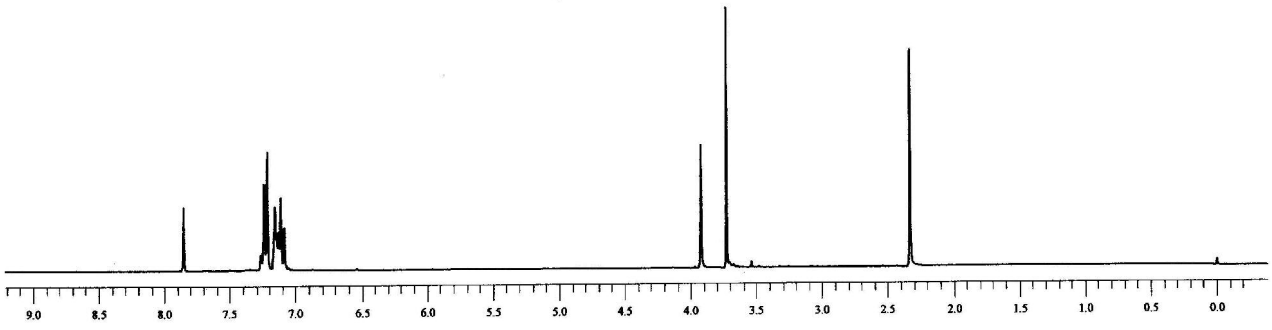
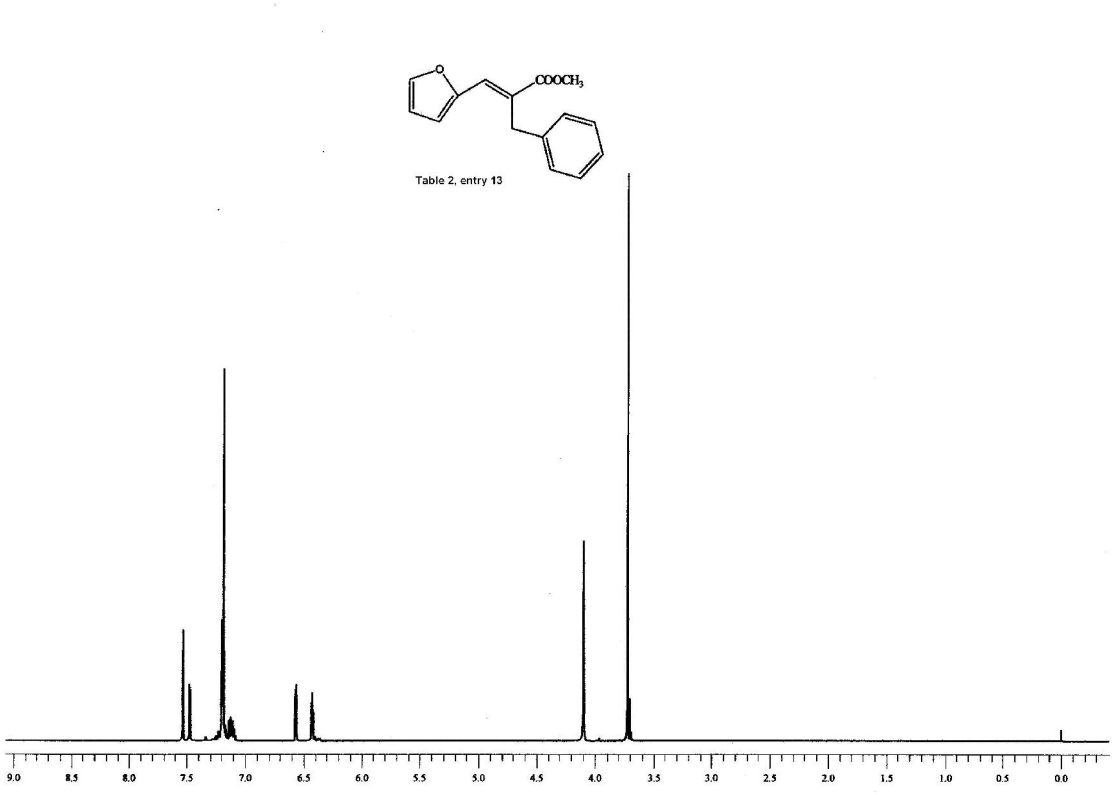


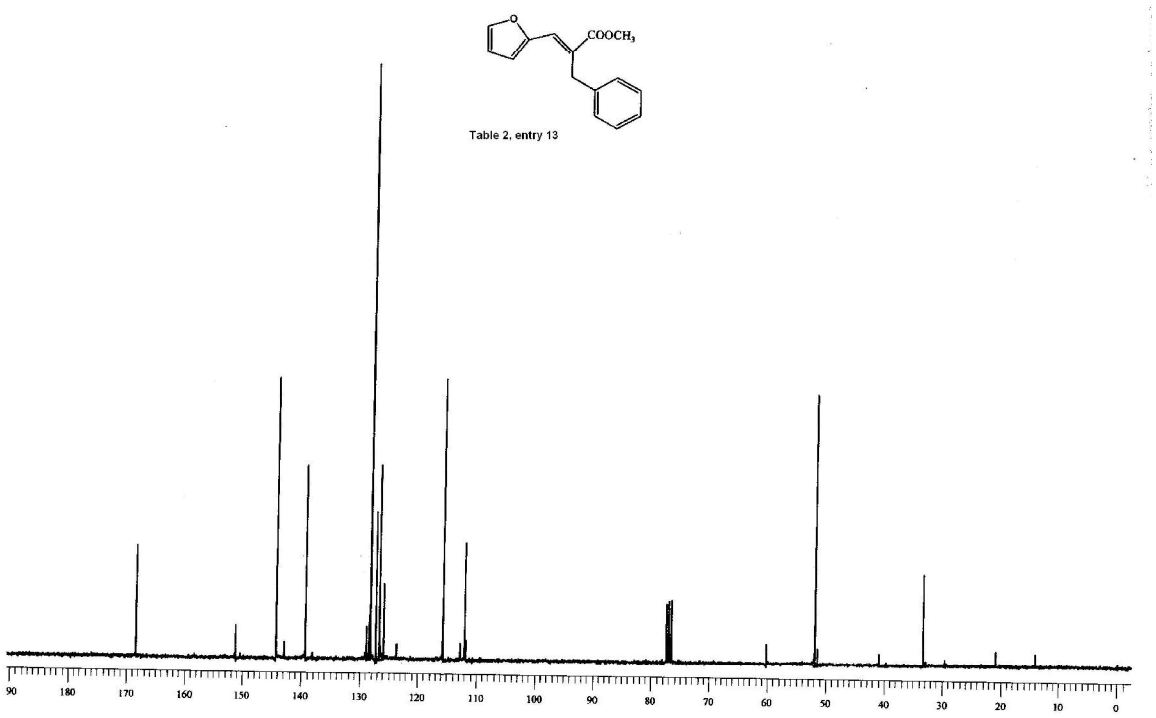
Table 2, entry 12



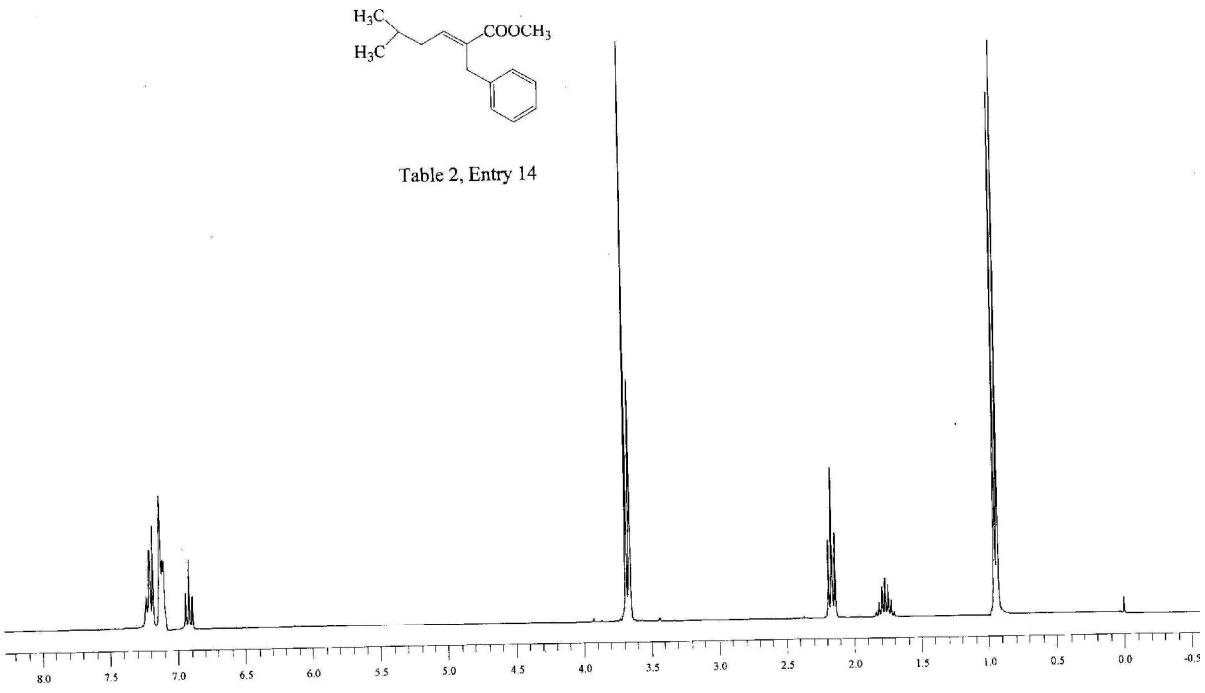
^{1}H NMR


COOCH3
Table 2, entry 13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

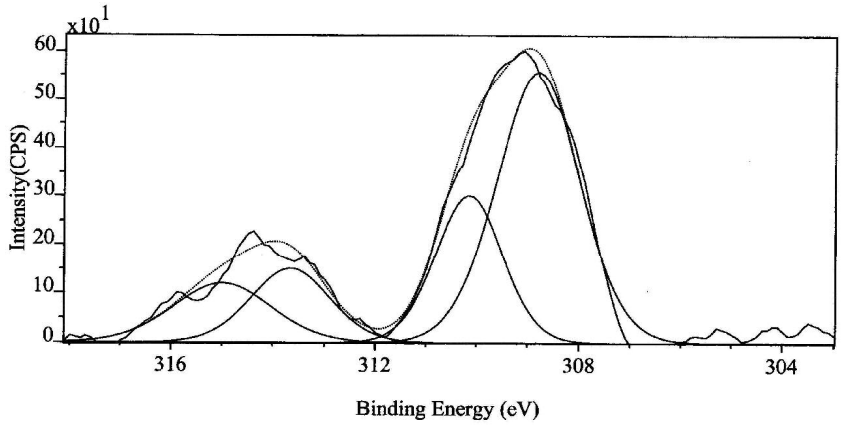
^{13}C NMR


COOCH3
Table 2, entry 13
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{1}H NMR

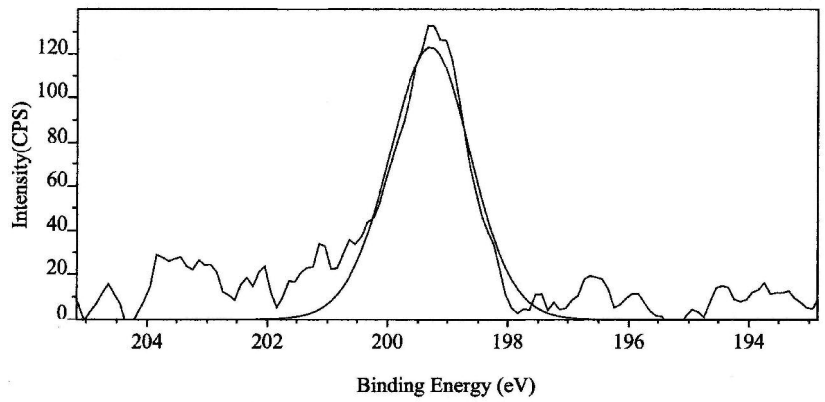

H3C
H3C
COOCH3
Table 2, Entry 14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

XPS of 'Rh' in RhFAP (Fresh catalyst)



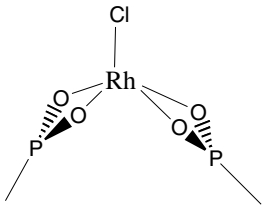
A high resolution narrow scan of 'Rh' showed peaks at 308.8 eV and 313.6 eV which are due to Rh $5d_{5/2}$ and Rh $5d_{3/2}$ respectively in +3 oxidation state

XPS of 'Cl' in RhFAP (Fresh catalyst)

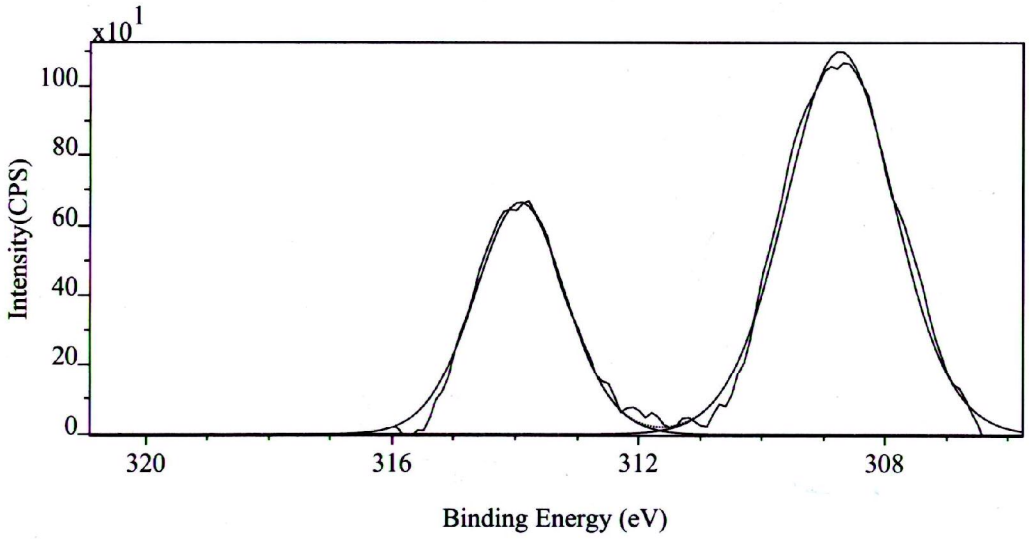


A high resolution narrow scan of 'Cl' showed peak at 199.3 eV (2p)

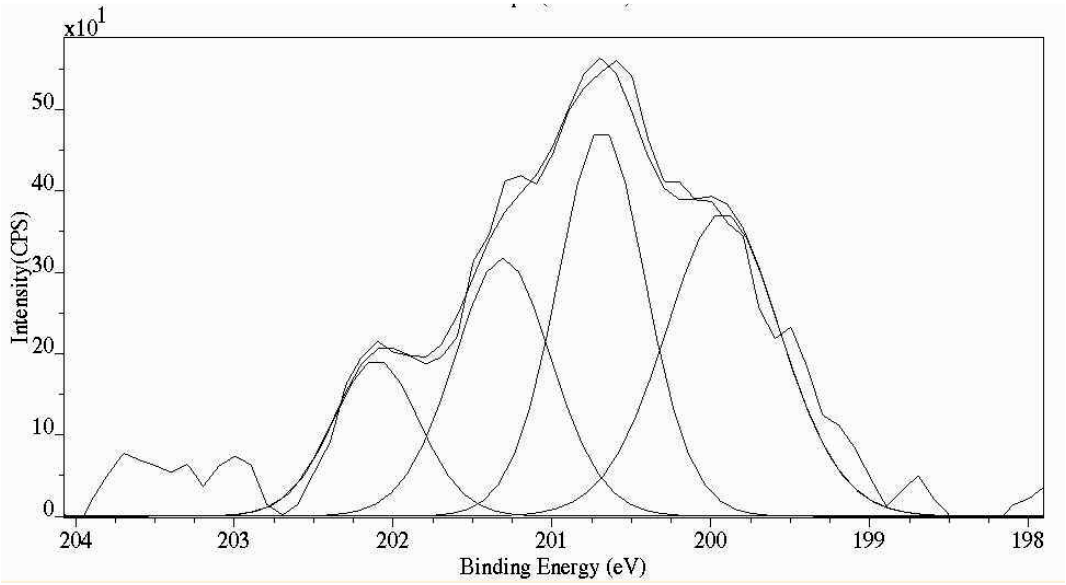
Proposed structure of RhFAP catalyst



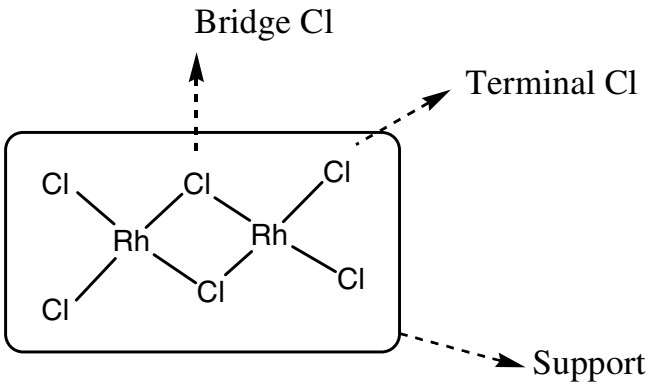
XPS of ‘ Rh’ in RhFAP -impregnated catalyst



$5d_{3/2}$ respectively in +3 oxidation state. The presence of chlorine was confirmed by XPS and EDAX analyses and the atomic ratio of Rh to Cl is 1:3. A high resolution narrow scan of ‘Cl’ showed peaks at 199.9 eV (Cl $2p_{3/2}$), 201.3 eV (Cl $2p_{1/2}$), 200.6 eV (Cl $2p_{3/2}$) and 202.0 eV (Cl $2p_{1/2}$),

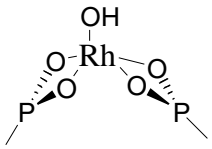


which shows that there are two types of chlorines present, the former two peaks refer to bridge chlorine and the later two peaks are attributed to terminal chlorines. Thus, XPS and EDAX analysis of 'Rh' and 'Cl" in RhFAP-impregnated catalyst shows that Rh exists as a dimer and is chemisorbed on to the surface of FAP.

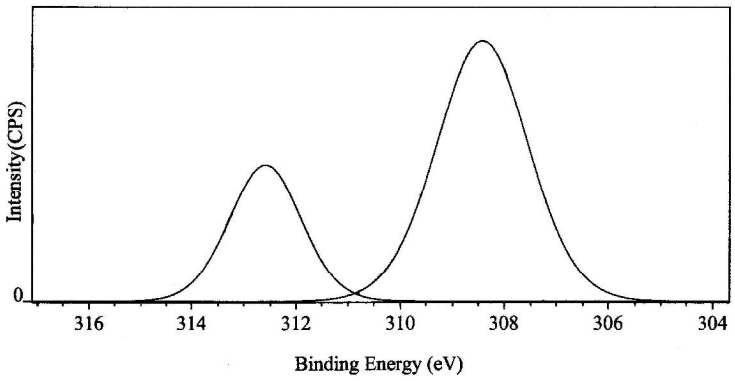


RhFAP-impregnated catalyst

Proposed structure of Used RhFAP catalyst



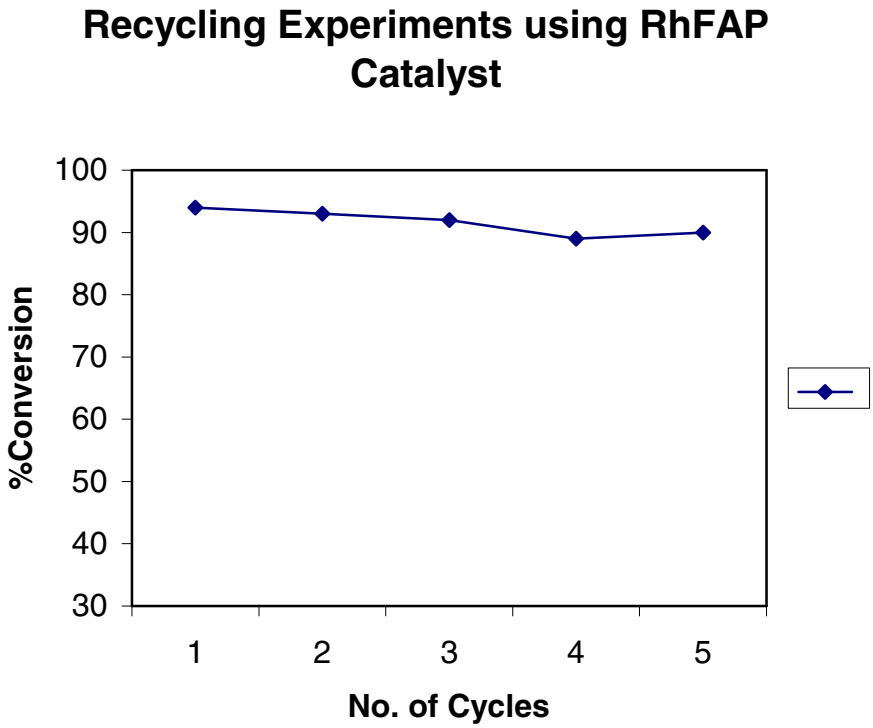
XPS of Used RhFAP catalyst



A cross coupling reaction of 3-hydroxy-2-methylene-3-phenylpropanoate with phenylboronic acid was carried out using fresh and reused catalyst under similar reaction conditions and the conversion was measured at one-hour intervals of time using G.C, which is tabulated below . There is not much difference in the conversion with the fresh and used catalyst.

Table 3. Kinetic study of a cross coupling reaction of 3-hydroxy-2-methylene-3-phenylpropanoate with phenylboronic acid using fresh and reused RhFAP catalyst (conversion of product is based on 3-hydroxy-2-methylene-3-phenylpropanoate)

Time (h)	% Conversion		
	Fresh RhFAP	1^{st} recycle	2^{nd} recycle
1	40.1	40.9	40.2
2	66.3	65.8	65.7
3	82.4	81.8	81.9
4	94.6	92.9	92.7
5	97.1	96.0	95.8
6	99.1	97.5	97.4


Recycling Experiments using RhFAP Catalyst
100
90
80
70
60
50
40
30
%Conversion
1
2
3
4
5
No. of Cycles