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Prussian blue as an efficient catalyst for Rate accelerations in the transesterification of *β*-Ketoesters

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Abstract:

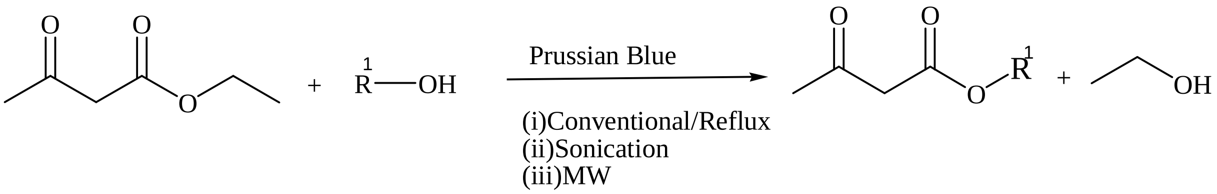
Prussian blue triggered transesterification of ethylacetoacetate with various alcohols underwent efficiently. The reaction is mild, eco-friendly and selective with good yields. The proposed reaction pathway depicts the formation of an intermediate by the interaction of *β*-ketoester with catalytic site of the Prussian blue, followed by nucleophilic attack of the alcohol at the electrophilic center followed by successive elimination of the proton to give the product. Observed longer reaction times under conventional conditions reduced amazingly under Sonication and Microwave irradiation followed enhanced yield of products.

Keywords: Prussian blue; efficient catalyst; transesterification; β-keto ester; sonication; microwave irradiation

Introduction

Transesterification is the process of exchanging the alkoxy group of an ester with the alkoxy group of an alcohol. These reactions are often catalyzed by the addition of an acid or base catalyst. The largest scale application of transesterification is in the synthesis of polyesters, in which diesters undergo transesterification with diols to form macromolecules [1]. This process has been used to recycle polyesters into individual monomers. Recent findings of Marchetti [2] et al show that triglycerides and sulfuric acid were suitable to perform the transesterification and direct esterification reaction to increase biodiesel production. Transesterification of ethyl acetoacetate with higher alcohols [3] has been reported using molecular sieves, in which they function as absorbents of alcohols. Over the years, quite a good amount of research has been and is being pursued at present all over the world on the transesterification reactions [4-20]. At times the attempts met with fruitful results, and sometimes the attempts demanded improvisations to meet the demands of the chemical industry and bio-diesel processing. The contribution of coordination complexes in the field of catalysis research has come a long way from the time of Werner and Jorgensen [21] and is still marching ahead. The current trends in the area of catalysis include the use of new types of catalysts that combine the practical advantages of both homogeneous as well as heterogeneous catalysts, achieving high yields and selectivity, and safe guard environmental safety. The β-ketoesters are versatile organic intermediates and have practical importance in preparative organic synthesis and can be used in lubricants as efficient friction modifiers [22] as potential antiviral drugs [23] and catalysts for various stereo selective reactions [24]. Prussian blue (PB) is a blue colored pigment and one of the most frequently used inorganic dyes. It is used in the preparation [25] of paints, printing inks, and laundry dye etc. It exists as water soluble ($KFe\{Fe(CN)_6\}xH_2O$) and water insoluble ($Fe_4\{Fe(CN)_6\}_3$ yH_2O) forms[26]. The micro-porous character of PB and its analogues find applications as adsorbent, as molecular sieves for separation [27] and catalytic processes [28]. It is used as an efficient tool for the removal of heavy metal ions in wine production [29]. Literature reports of PB indicated its electrochemical applications for battery building [30], electronic switching and as electro chromic devices [31]. Moreover, Prussian blue complex (PB) is can be easily prepared from economically cheap and laboratory desktop chemicals which are available even in undergraduate laboratories. Recently our group explored the utility of Werner type complexes as efficient catalyst for selective nitration of aromatic compounds [32, 33]. On the other hand we have also reported the Chemo selective transesterification [34] of β-Keto Esters using Manganese (II) salts as efficient Catalysts. Keeping in with these economically viable ongoing synthetic protocols, we want to present certain results on transesterification using PB as catalyst under conventional (stirring at room temp) and non-conventional methods such as Microwave irradiation [35] and Sonication [36].

Results and discussion



In order to optimize the conditions, control experiments were performed with a reaction mixture containing ethyl acetoacetate (5.0 mmol), phenol (5.0 mmol) and varied amounts of catalyst (P B) in the range of 0.2 to 3.0 mmol in toluene (20mL). Reaction mixture was stirred at 100-110 ^{0}C in a round bottom flask, which was provided with a distillation condenser to remove ethanol. Progress of the reaction was monitored by thin layer chromatography (TLC). Reactions afforded very good yield of product only when 1.0 mmol catalyst was used. Reaction was too sluggish below 1.0 mmol even after 24 hrs and under reflux conditions, and above 1.0 mmol reaction times and yield of the product did not differ much as shown in table -1.

In view of these observations, we have performed the under ultrasonic and microwave assisted (USA and MWA) conditions. A wide range of alcohols were used to explore PB catalysed transesterification of β-Keto Esters. Experimental results are summarized in **table-2**. Even though the reaction times are too long, very good yields of products are obtained. According to Pearson's HSAB theory [37], "Hard acids (HA) prefer to bind to hard bases (HB) and soft acids (SA) prefer to bind to soft bases (SB)". Fe (III) is a hard acid with sufficient number of vacant orbitals can easily form adducts with hard bases such as ethyl acetoacetate and hydroxy compounds. Ethyl acetoacetate being a harder base than hydroxy compound interaction between hard acid Fe (III) present in PB and hard base ethyl acetoacetate through two carbonyl oxygen atoms to form a cyclic intermediate is more likely. The cyclic intermediate thus formed then probably reacts with hydroxy compound and affords product with the elimination of ethyl alcohol and PB catalyst. Reaction sequence of the proposed mechanism is shown in **Scheme-2**. Further, it is interesting to note that the catalyst could be recycled without any problem.

In order to have an insight into the mechanistic aspects, IR and UV-Visible spectroscopic studies have been taken up. IR spectrum of ester (**Fig.1** in the absence of catalyst) depicted a strong band at 1735 cm^{-1} in addition to a small hump around 1640 cm^{-1} corresponding to carbonyl groups.

Since the transesterification reaction is studied in presence of alcohol, IR spectrum of ester was also scanned in presence of alcohol [isopropyl alcohol (IPA) as a specific case]. The IR spectrum of ester in presence of IPA (**fig.2)** furnished a broad band at 3705 cm^{-1}(corresponding to O-H stretching vibration), 1715and 1739 cm^{-1} (attributed to carbonyl groups). However, it is important to note that the band observed at 1640 cm^{-1} (in **fig.1**) shifted to 1715 cm^{-1}, which may probably indicate the formation of enolate intermediate. This observation is in accordance with literature reports [38]. In order to further strengthen the mechanism, UV-Visible spectroscopic studies of PB were taken up in presence and absence of ester and IPA mixture (f**ig-3**). The spectrum of PB (observed around 700nm) underwent a blue shift in presence of ester and IPA with a new band at 450 nm. This observation lends support for the formation of a cyclic intermediate due to the interaction of enolate species with PB. The intermediate thus formed further experiences the alkoxy (R^1-O) group attack at ester carbonyl before yielding final product as shown in **Scheme- 2.**

Comparison of the results obtained under three procedures made it possible to draw some general conclusions regarding the effect of sonication and MW irradiation on the transesterification. Data presented in table -2 clearly indicate that even though the yields of end products are by and large are similar with very good percentage, there is a remarkable change in the rates/ reaction times from conventional method to sonication and/or microwave irradiation. Reaction times reduced by almost ten times from conventional to Sonication conditions. This remarkable rate acceleration could be attributed to the “Cavitation phenomenon”, which is generated during ultra-sonication. A large amount of energy and pressure are released from the collapse of cavitation bubbles during sonication of the reaction [29-32], which may cause an increase in the fraction of activated molecules compared with normal reactions resulting in higher rates of the reaction. On the other hand MW irradiation generates volumetric nature of power dissipation in dielectric, which causes direct heating inside the sample [33-35]. This in situ mode of energy conversion leads to a fast heating rate with minimized thermal gradients. This leads to the reduction of the reaction times rapidly as observed in the present study from several hours (16-24 hrs) in conventional reaction to few minutes (45 min) in MWA reaction.

Conclusions

In conclusion, the authors demonstrated that Prussian blue, a typical Werner type complex, is an efficient catalyst for transesterification of β-ketoesters. This catalyst can be prepared in any undergraduate laboratory with inexpensive desktop chemicals. The reagent is operationally simple and environmentally safe and thus has an advantage over many literature reports. Ultrasonically assisted methodology reduced reaction times from 16-24 hrs (under reflux conditions) to about 2.5 hrs; while microwave assisted reactions could complete the transesterification within 8 to 10 minutes. These approaches are environmental friendly in terms of Energy saving and time saving requirements.

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Experimental

All the chemicals used in the present study were reagent grade, which were purchased procured from either from SD fine Chemicals (India), Ranbaxy (India) or Aldrich Chemicals. Prussian blue complex was prepared from the reaction of ferric chloride ($FeCl_3$) and potassium ferrocyanide (K_4 (Fe (CN)$_6$) according to standard procedures.

General Procedure for Transesterification under conventional method: Five (5.0 mmol) of alcohol (5.0 mmol) were added to five (5.0 mmol) of β - ketoester (5.0 mmol), and one (1.0 mmol) of Prussian blue catalyst in about twenty (20.0 mL) toluene in a round bottom (R.B) flask was stirred at 100-110 ^{0}C. The R. B. flask was provided with a distillation condenser to remove ethanol. Progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, contents of the R.B. flask was filtered and the filtrate concentrated to get crude product, which was purified by column chromatography on silica gel (ethyl acetate: petroleum ether) to afford the ester as a viscous colorless liquid in good yields. Products are characterized by spectroscopic data. Representative NMR spectroscopic data are presented in table -3.

General Procedure for Ultrasonically Assisted Transesterification: Methodology for **t**he ultrasonically assisted transesterification is almost similar to the one discussed in the foregoing section. Reaction mixture containing β - ketoesters (5.0 mmol), alcohol (5.0 mmol) and Prussian blue catalyst (1.0 mmol) and toluene (20.0 mL) was placed in a Sonicator bath at room temperature and progress of the reaction monitored by thin layer chromatography (TLC). After completion, the reaction mixture was filtered and concentrated the filtrate to get crude product. It was then purified by column chromatography on silica gel (ethyl acetate: petroleum ether) to get the ester as a viscous colorless liquid in good yields.

General Procedure for Microwave Assisted Transesterification: Microwave Assisted Transesterification was performed in the MW oven with a MW irradiation source consisting of magnetron tube operating at 2.45GHz.with power output that can be varied between 0 and 300 W. The flask containing mixture of β - ketoesters (5.0 mmol), alcohol (5.0 mmol) and Prussian blue catalyst (1.0 mmol) in toluene (20.0 mL) was placed in MW oven. The solutions were stirred by a magnetic stir bar to ensure high homogeneity. To prevent thermal gradients the reactions were carried out in 5.0 mL tubes and the progress of the reaction was monitored by thin layer.

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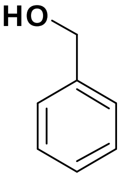
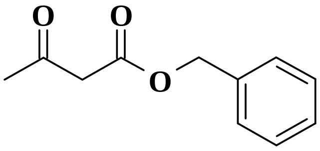
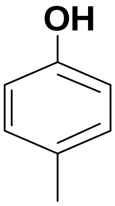
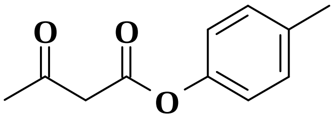
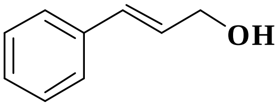
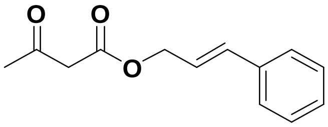
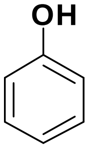
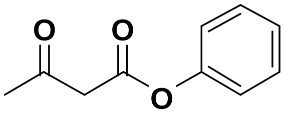
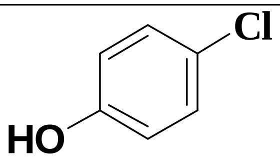
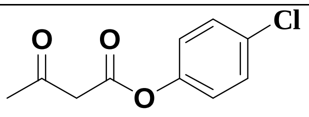
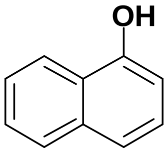
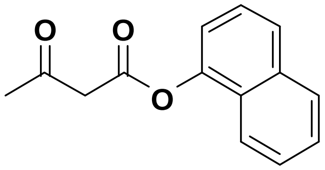
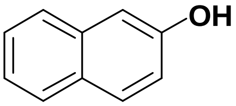
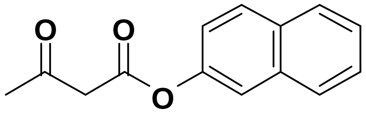
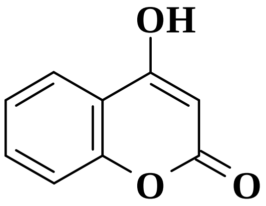
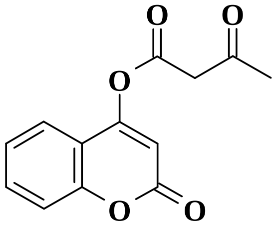
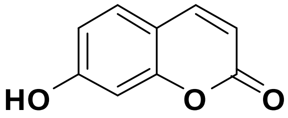
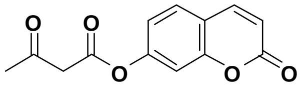
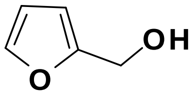
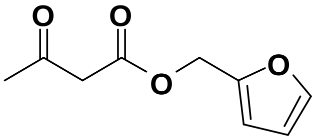
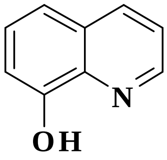
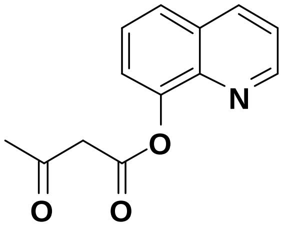
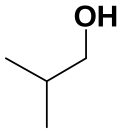
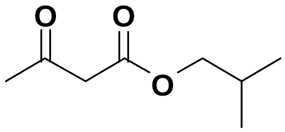
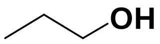
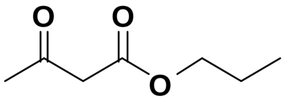
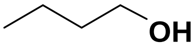
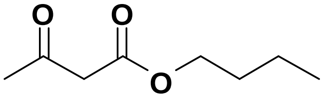
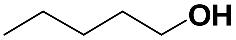
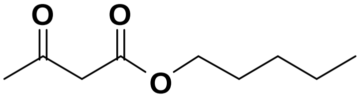
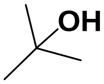
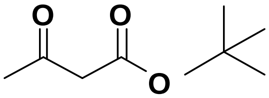
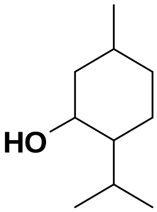
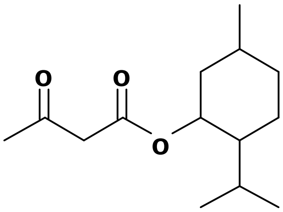
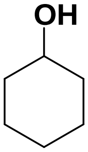
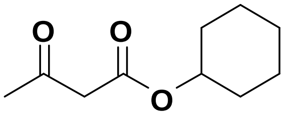
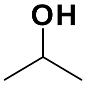
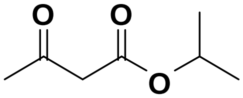
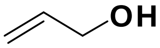
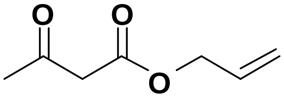
Table-1: Effect of [PB] on transesterification of Phenol

S.N.	**[PB] (mmol)**	**Time (hr)**	**Yield (%)**
1	0.10	28	60
2	0.25	26	64
3	0.50	26	65
4	0.75	25	65
5	1.00	24	68
6	2.00	24	67
7	5.00	23	68

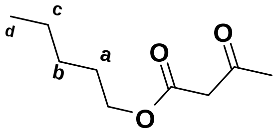
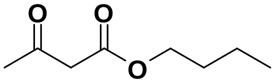
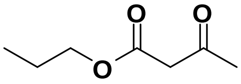
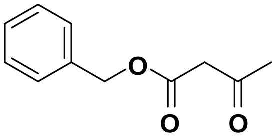
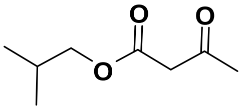
Table -2: Prussian blue catalyzed Transesterification of β-Ketoesters under conventional and Nonconventional conditions

Entry	Substrate	Product	Conventional		Sonication		Microwave	
			R.T (hr)	Yield (%)	R.T (hr)	Yield (%)	R.T (min)	Yield (%)
1.			19	75	2.15	74	08	84
2.			19	72	2.15	74	10	78
3.			20	75	2.15	75	10	80
4.			24	68	2.00	70	10	75
5.			22	68	2.15	70	10	75

6.			24	66	2.00	73	12	80
7.			24	68	2.15	74	11	75
8.			22	66	2.15	72	10	80
9			22	70	2.15	72	10	75
10			19	75	3.00	75	08	80
11			20	65	3.15	68	10	72
12			19	70	3.00	72	08	80
13			20	75	2.45	75	08	82

14			20	70	2.30	72	07	78
15			20	78	3.00	75	09	80
16			24	65	3.15	70	12	75
17			23	70	3.10	75	10	82
18			23	72	3.15	72	10	80
19			22	70	3.00	76	11	82
20			23	70	3.30	70	10	80

T able-3: NMR Spectroscopic Data for representative compounds

S. No	Compound name	NMR data
1	 **pentyl acetoacetate**	δ 4.18(t, 2H, -OCH_2), 3.42(s, 2H, >CH_2), 2.25(s, 3H, -$COCH_3$), 1.65(m, 2H, a-CH_2), 1.38(m, 2H, b-CH_2), 1.32(m, 2H, c-CH_2), 0.92(t, 3H, d-CH_3)
2	 **butyl 3-oxobutanoate**	δ 4.26(t, 2H, -OCH_2), 3.38(s, 2H, >CH_2), 2.25(s, 3H, -$COCH_3$), 1.72(m, 2H, CH_2), 1.56(m, 2H, -CH_2-), 0.92(t, 3H, CH_3)
3	 **Propyl acetoacetate**	δ 4.32(t, 2H, -OCH_2), 3.44(s, 2H, >CH_2), 2.26(s, 3H, -$COCH_3$), 1.72(m, 2H, CH_2), 0.96(t, 3H, CH_3)
4	 **Benzyl acetoacetate**	δ 7.42(m, 5H, Ar-H), 5.22(s, 2H, -OCH_2), 3.44(s, 2H, >CH_2), 2.22(s, 3H, -$COCH_3$)
5	 **Isobutyl acetoacetate**	δ 3.92(d, 2H, -OCH_2), 3.42(s, 2H, >CH_2), 2.20(s, 3H, -$COCH_3$), 1.96(m, 1H, >CH-), 0.92(d, 6H, -CH_3)

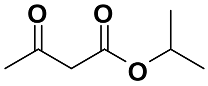
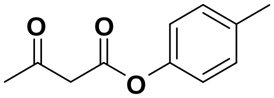
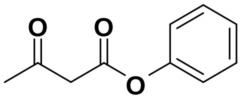
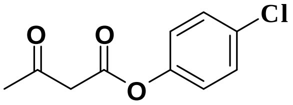
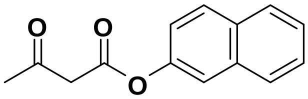
6	 **isopropyl 3-oxobutanoate**	δ 4.52(m, 1H, -O-CH), 3.46(s, 2H, >CH_2), 2.25(s, 3H, -$COCH_3$), 1.24(d, 6H, -CH_3)
7	 ***p*-tolyl 3-oxobutanoate**	δ 7.45(m, 4H, Ar-H), 3.46(s, 2H, >CH_2), 2.35(s, 3H, Ar-CH_3), 2.25(s, 3H, -$COCH_3$)
8	 **phenyl 3-oxobutanoate**	δ 7.52(m, 5H, Ar-H), 3.48(s, 2H, >CH_2), 2.28(s, 3H, -$COCH_3$)
9	 **4-chlorophenyl 3-oxobutanoate**	δ 7.55(m, 4H, Ar-H), 3.48(s, 2H, >CH_2), 2.26(s, 3H, -$COCH_3$)
10	 **Naphthalen-2-yl 3-oxobutanoate**	δ 7.42-8.14(m, 7H, Ar-H), 3.40(s, 2H, >CH_2), 2.22(s, 3H, -$COCH_3$)

Fig.1: Infrared Spectrum of Ethylacetoacetate (EAA)

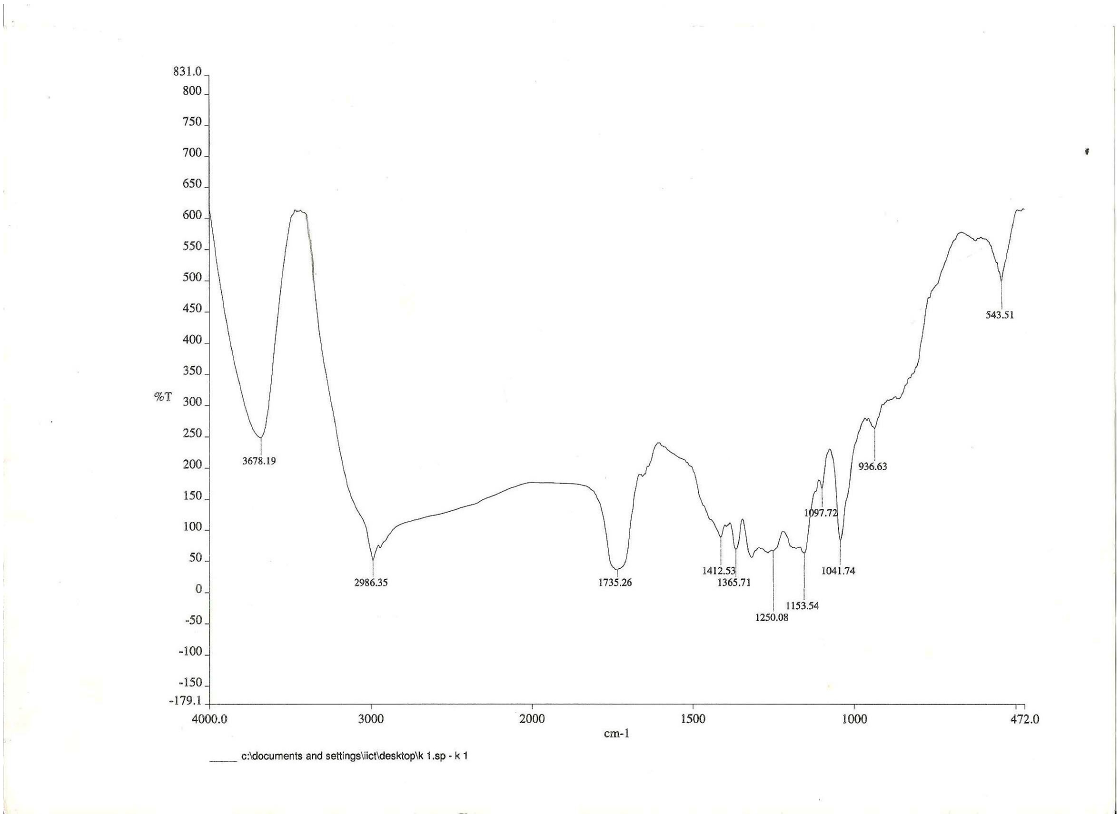


Fig.2: Infrared Spectrum of Ethylacetoacetate (EAA) + Isopropyl alcohol (IPA)

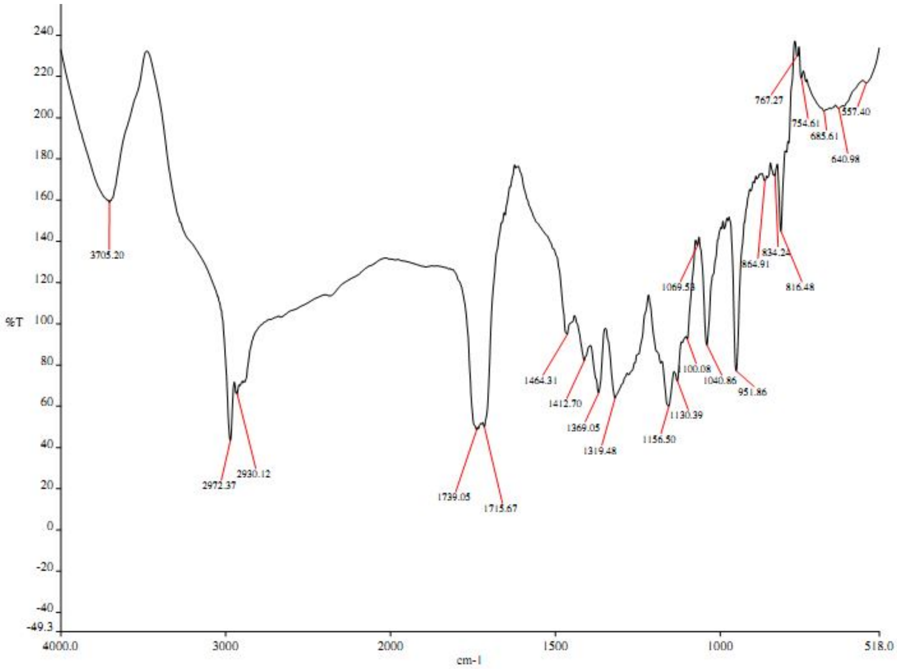
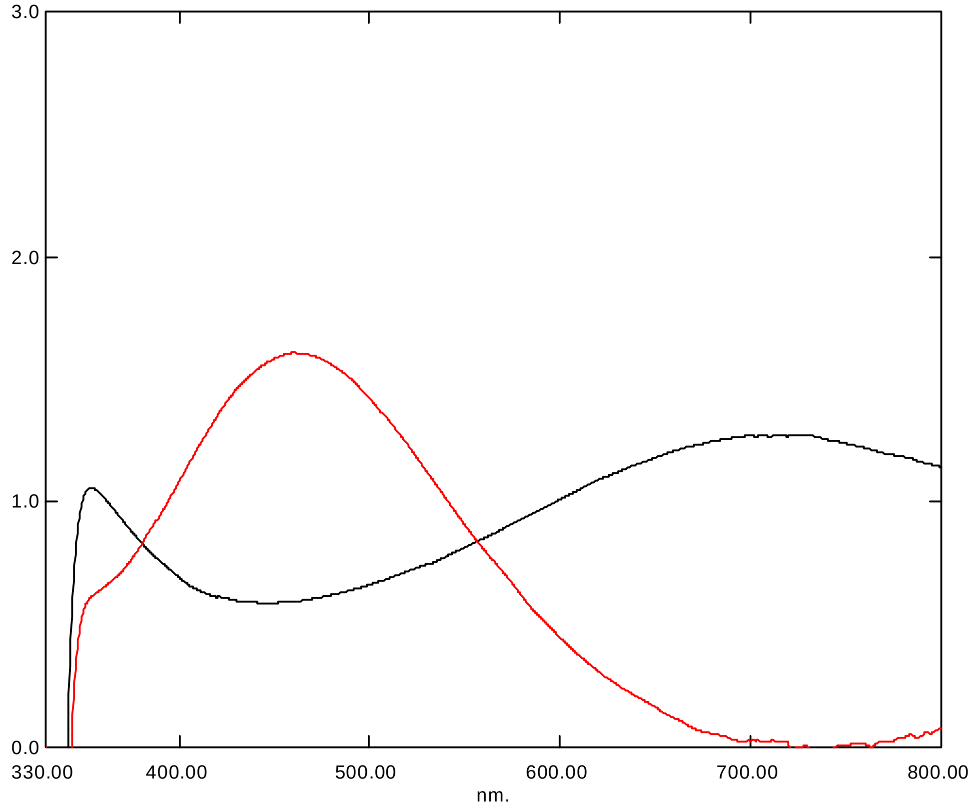
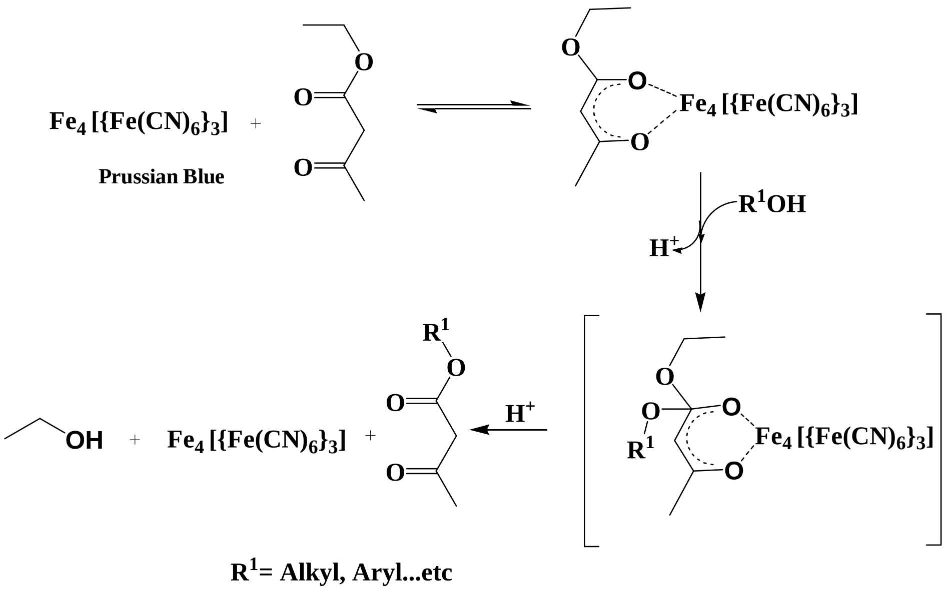


Fig.3: UV-Visible Spectrum of PB in presence and absence of (EAA+ IPA)





Scheme-2: Plausible mechanism of Prussian blue catalyzed Transesterification of *β*-Ketoesters