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RESEARCH LETTER

A green oxidation protocol for the conversion of secondary alcohols into ketones using heterogeneous nanocrystalline titanium (IV) oxide in polyethylene glycol

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The oxidation of secondary alcohols into corresponding ketones has been described using heterogeneous nanocrystalline TiO₂ as catalyst at a moderate temperature with quantitative yields. Use of H₂O₂ instead of O₂ (g) is the main feature of our methodology since maintenance of P_{O₂} (g) at elevated temperature is not easy. Besides, this catalyst could be recovered and reused for further reactions with consistent activity. Hence, our present protocol is economical and throughout clean consisting of green reagent, solvent, and catalyst.

Keywords: heterogeneous catalyst; oxidation; TiO₂-nanoparticles; green chemistry; recyclability

Introduction

The oxidation of alcohols to carbonyl compounds has great importance in synthetic organic chemistry due to their utility in variety of products, such as drugs, agro-chemicals, and fragrances (1,2). Alcohols have conventionally been oxidized by noncatalytic methods using stoichiometric amount of hazardous oxidants such as chromium and manganese compounds in the presence of strong mineral acids, which generate enormous amounts of poisonous metal salts as waste (3–5).

In view of increasing environmental concerns, many efforts have been made to develop the environmentally benign oxidation systems (6). In addition to this, various heterogeneously catalyzed protocols were reported, including the use of silver nanoparticles supported on hydrotalcites (7), metallic iron nanoparticles on MCM-41 (8), and highly expensive gold and palladium nanoparticles supported on metal oxides (9–12). However, most of the systems could be applicable for the oxidations of only activated substrates by using molecular O₂ (g) (13), or large quantities of additives such as bases and electron transfer mediators are required (14,15). Besides this, lethal V₂O₅ and ruthenium catalyst have also been used as catalysts in the toxic solvents such as toluene (16,17).

Some of the methods could be considered green but these methods are not throughout clean because sometimes these protocols utilize green catalyst but neither solvent nor reagent is green; sometimes green

solvents are used but catalysts and reagents are not under the periphery of greener reactions and vice versa. So there is a strong need to develop such a catalytic system which comprises all, that is, green catalyst, solvent, and reagent.

Industry favors catalytic processes induced by heterogeneous catalysts over homogeneous processes in view of the ease of handling, simple work-up, and recyclability. Titanium dioxide is a green heterogeneous prominent material for various kinds of industrial applications, for example, in the selective reduction of NO_x in stationary sources, organic synthesis, photovoltaic devices, and sensors (18–22). Despite this, researchers are not able to explore catalytic activity of sole nanocrystalline titanium (IV) oxide for oxidation reactions.

We chose polyethylene glycol (PEG) as solvent because PEG and its derivatives are commonly known to be inexpensive, thermally stable, environmentally benign media for chemical reactions and moreover having an almost negligible vapor pressure (23–25).

In continuation of our progressive program toward the development of green and sustainable synthetic methods (26–28) for organic synthesis and the role of transition metal catalysts in such syntheses (29,30), we would like to report a novel and efficient method for the oxidation of secondary alcohols to ketones using green catalytic system which involves TiO₂-np as heterogeneous catalyst, H₂O₂ as reagent, and PEG as green solvent.

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Results and discussion

To validate our hypothesis, we initially examined the oxidation of diphenylcarbinol in absence of nanocrystalline TiO₂. Reaction was performed in PEG-400 using equivalent amount of diphenylcarbinol and aqueous H₂O₂. This reaction mixture was continuously stirred at 70–75°C in oil bath for 6 hours (Scheme 1).

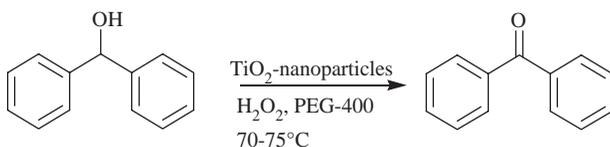
Under these reaction conditions diphenylcarbinol was converted into benzophenone with only 27% yield. Then the conversion was further improved by introducing 10 mol% of nanocrystalline TiO₂ and surprisingly yield reached up to 92%. Furthermore, the reaction temperature had a great influence on this transformation. The reaction gave only 40% conversion at 40–50°C and in case of diphenylcarbinol, traces of product were obtained.

Different nanoparticles were used to catalyze the same oxidation reaction. But nano TiO₂ was found to be the most effective among all the catalysts used (Table 1).

The increased catalytic activity of nano-TiO₂ over the commercially available bulk TiO₂ and other nano oxides may be attributed to the higher surface area for nano-TiO₂. This is thought to be due to morphological differences; whereas larger crystallites have only a small percentage of reactive sites on the surface, smaller crystallites will possess a much higher surface concentration of such sites (shown in powder XRD pattern in Figure 1) crystal corners, edges or ion vacancies (31).

Next, we investigated the effect of different solvents. Solvents having low boiling point did not give good results because reaction was performed at 70–75°C. Due to environment point of view, we chose PEG as a solvent then we have screened our reaction with PEG having different molecular weights. We found that the conversion was gradually decreased with increase in the molecular weight of the PEG from 400 to 800, being presumably ascribed to the increasing mass limitation of dispersion of TiO₂ nano powder in the liquid phase which decreased the activity of the catalyst (Table 2).

Different oxidizing agents were used to oxidize the diphenylcarbinol under similar reaction conditions. Hydrogen peroxide was found to be an excellent



Scheme 1. Model reaction for oxidation using TiO₂ nanoparticles.

Table 1. Oxidation of alcohols using different nanocrystalline metal oxides.^a

Entry	Nanoparticles	Time (h)	Yield (%) ^b
1	CuO	8	38
2	ZnO	8	40
3	MgO	8	50
4	TiO ₂	6	92

^aReaction conditions: diphenylcarbinol (1 mmol), hydrogen peroxide (1 mmol) and 10 mol% nanocrystals nm; PEG-400; temperature 70–75°C.

^bIsolated yields.

oxidizing agent. The reason is that active oxygen availability in case of hydrogen peroxide is higher in comparison to other oxidants (15).

It was important to optimize the concentration of H₂O₂ to get maximum yield of product. For this, the same amount of alcohol was treated with different concentrations of hydrogen peroxide as depicted in Figure 2. We found that equivalent amount of hydrogen peroxide gave maximum yield of product without giving other side products. Notably, reaction could not be performed without aqueous H₂O₂ as the oxidant.

To test the generality and scope of nano TiO₂ catalyzed reaction, an array of structurally divergent alcohols were tested. As shown in Table 4, both aliphatic and aromatic secondary alcohols can be easily oxidized into the corresponding carbonyl compounds in fair to high yield. In general, substrate having electron donating group showed higher activity than those having electron withdrawing groups. Moreover, groups such as –OCH₃, –Cl, and –CH₃ were ineffective during course of reaction.

The literature suggested that superoxide species O₂[–] over metal oxide and zeolitic system usually act as active species in radical reactions (32,33). This highly active species may react with alcohol and form its free

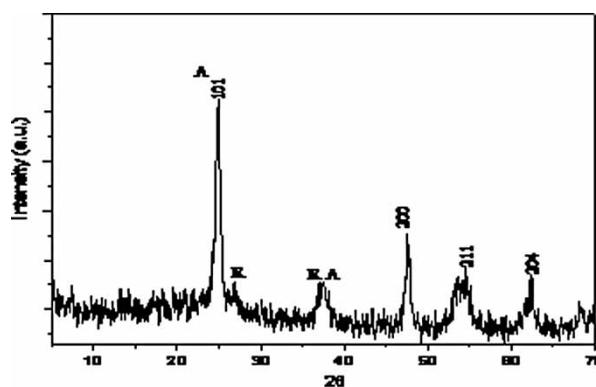


Figure 1. Powder XRD pattern of nanocrystalline titanium (IV) oxide.

Table 2. Screening of solvent for oxidation reaction.

Entry	Solvent	Yield (%) ^b
1	CH ₂ Cl ₂	40
2	THF	37
3	MeOH	42
4	PEG-400	92
5	PEG-600	85
6	PEG-800	80

^aReaction conditions: diphenylcarbinol (1 mmol), hydrogen peroxide (1 mmol) and 10 mol% nano TiO₂ (50 ± 2) nm; solvent; temperature 70–75°C.

^bIsolated yields.

radical which could be easily converted into product as shown in Scheme 2.

The formation of products was confirmed by disappearance of peak between 3200 and 3500 cm⁻¹ due to H–O bond of unsaturated alcohols and appearance of characteristic stretching bands of –C=O– at 1650–1730 cm⁻¹ for ketones in the IR spectra. In the ¹H NMR spectra disappearance of broad band of “alcoholic” proton confirmed the formation of products.

For practical applications of heterogeneous systems, the lifetime of the catalyst and its level of reusability are very important factors. To clarify this issue, we established a set of experiments for the oxidation of diphenylcarbinol using the recycled nano-TiO₂ catalyst. After completion of the first reaction to afford the corresponding ketones, the catalyst was recovered by dissolving the product in chloroform followed by filtration.

TiO₂ remained as residue which was then washed with ethyl acetate and finally dried at 100°C for 5 hours. A new reaction was performed with obtained nano TiO₂ and fresh reactant and H₂O₂, under similar reaction conditions. The TiO₂-nanoparticles could be reused at least four times with change in slight activity, as shown in Figure 3.

It was further confirmed by Transmission electron microscopy (TEM) technique. Both fresh and recovered catalysts were observed under TEM to understand the shape and size of the particles. Figure 4a shows the fresh nano-particles having size range 20–

Table 3. Oxygen availability in various oxidants.

Oxidants	% Active O	By-product
H ₂ O ₂	47	H ₂ O
t-BuOOH	18	t-BuOH
CH ₃ COOOH	22	CH ₃ COOH
NaOCl	22	NaCl
KIO ₄	8	KIO ₃

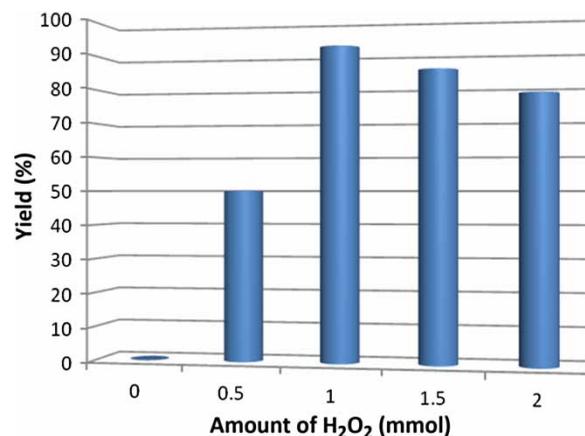


Figure 2. Optimization of concentration of H₂O₂. Reaction conditions: diphenylcarbinol (1 mmol), hydrogen peroxide (1 mmol) and 10 mol% nano TiO₂ (50 ± 2) nm; PEG-400; temperature 70–75°C. Isolated yields.

50 nm, with well-defined shapes. Figure 4b shows the TEM image of the used catalyst after four recycles. Interestingly, it was observed that the shape and size of the particles remain unchanged even after recycling.

This supports that the morphology of the catalyst remains the same even after recycling. Besides this, powder diffraction (XRD) patterns of the fresh and used nano TiO₂ do not differ in the range of 2θ = 0°–70°. This also confirms the fact that the structure and morphology of the catalyst remain the same during the course of the reaction.

Experimental

General

The materials procured from Sigma-Aldrich and Merck were used without further purification. Melting points are determined on Buchi 530 (Buchi laborfehnik AG, CH-9230, Falawil). Mass spectra were recorded in a TOF-mass spectrometer model no. KC455. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker spectrosSpin 400 and 100 MHz, respectively. All NMR samples were run in CDCl₃, and chemical shifts are expressed as ppm relative to internal Me₄Si.

Procedure for oxidation of alcohols

A measure of 10 mol% of nanocrystalline titanium (IV) oxide was added to the reaction mixture of diphenylcarbinol (1 mmol) and 30% aqueous H₂O₂ (1 mmol) in PEG-400 (3 ml). This reaction mixture was continuously stirred at 70–75°C in the oil bath for 6 hours. The progress of reaction was continuously monitored by Thin layer chromatography (TLC).

Table 4. Nanocrystalline titanium (IV) oxide catalyzed oxidation of alcohol into ketones.^a

Entry	Alcohols	Products	Time (h)	Yield (%) ^b
1	Diphenylcarbinol	Benzophenone	6	92
2	1,2,3,4-Tetrahydro-1-naphthol	3,4-Dihydro-2H-naphthalen-1-one	7	87
3	2-Methylbenzhydrol	2-Methylbenzophenone	8	90
4	9-Hydroxyfluoren	Fluoren-9-one	7	92
5	4,4'-Dimethoxybenzhydrol	4,4'-Dimethoxybenzophenone	8	94
6	α -Methyl-2-naphthalene-methanol	1-Naphthalen-2-yl-ethanone	6	90
7	4-Chlorobenzhydrol	4-Chlorobenzophenone	8	88
8	2-Phenylethanaol	Acetophenone	10	85
9	Cyclohexanol	Cyclohexanone	11	82
10	Cyclopentanol	Cyclopentanone	11	80

^aReaction conditions: Alcohol (1 mmol), hydrogen peroxide (1 mmol) and 10 mol% nano TiO₂ (50 ± 2) nm; PEG-400; temperature 70–75°C.

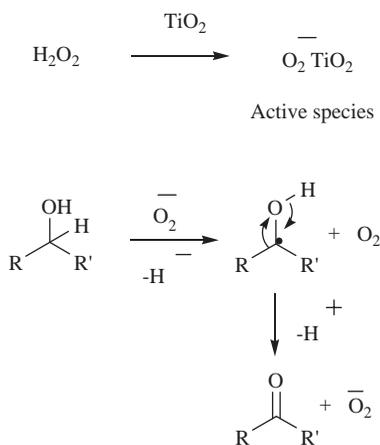
^bIsolated yields.

After accomplishment of the reaction, excess of water was added and the reaction mixture was further stirred at room temperature for 2 hours. In case of solid product (Benzophenone), reaction mixture was filtered to get the solid product. This solid product was dissolved in ethyl acetate followed by centrifuge to recover the TiO₂-nanoparticles. But in case of liquid, products were extracted with diethyl ether and dried over anhydrous sodium sulphate. Solvent was recovered in vacuo. Subsequently, the crude products were purified by column chromatography using 80:20 (hexane:chloroform) as an eluent.

Spectral data of some compounds

Benzophenone (Table 4, entry 1)

(White solid) IR_{v_{max}}(KBr) 1664 cm⁻¹ (CO). ¹H NMR (400 MHz, TMS, CDCl₃): δ 7.44–7.51 (m, 4H), 7.62–7.75 (2H, m), 7.80. (4H, m). ¹³C NMR (100 MHz, TMS, CDCl₃): δ 129.90, 132.30, 137.54, 197.21. *m/z* (GC-MS, HR-MS): 182.07 (M⁺).



Scheme 2. Proposed reaction mechanism for the oxidation.

Fluoren-9-one (Table 4, entry 4)

(White solid) IR_{v_{max}}(KBr) 1721 cm⁻¹ (CO). ¹H NMR (400 MHz, TMS, CDCl₃): δ 7.16–7.20 (2H, m), 7.36–7.42 (m, 4H), 7.56 (2H, J = 8 Hz, d). ¹³C NMR (100 MHz, TMS, CDCl₃): δ 120.25, 124.28, 129.00, 134.10, 134.63, 144.39, 193.87. *m/z* (GC-MS, HR-MS): 179.92 (M⁺).

1-Naphthalen-2-yl-ethanone (Table 4, entry 6)

(Brownish solid) IR_{v_{max}}(KBr) 1675 cm⁻¹ (CO). ¹H NMR (400 MHz, TMS, CDCl₃): δ 2.62 (3H, s), 7.42–7.54 (2H, 2m), 7.76–7.82 (2H, m), 7.87 (1H, J = 8 Hz, d), 7.92–7.96 (1H, J_{ab} = 8 Hz, J_{ac} = 4 Hz, dd), 8.37 (1H, s). ¹³C NMR (100 MHz, TMS, CDCl₃): δ 26.67, 123.82, 126.74, 127.77, 128.37, 130.16, 132.44, 134.40, 135.54, 198.04. *m/z* (GC-MS, HR-MS): 168.96 (M⁺).

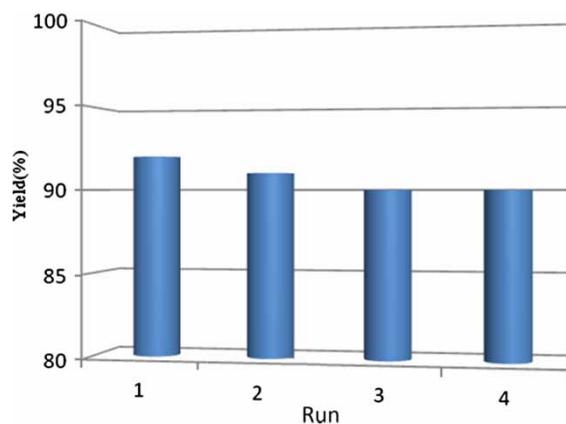


Figure 3. Recycling studies of nano-TiO₂ oxidation reaction. ^aReaction conditions: diphenylcarbinol (1 mmol), hydrogen peroxide (1 mmol) and 10 mol% nano TiO₂ (50 ± 2) nm; PEG-400; temperature 70–75°C. Isolated yields.

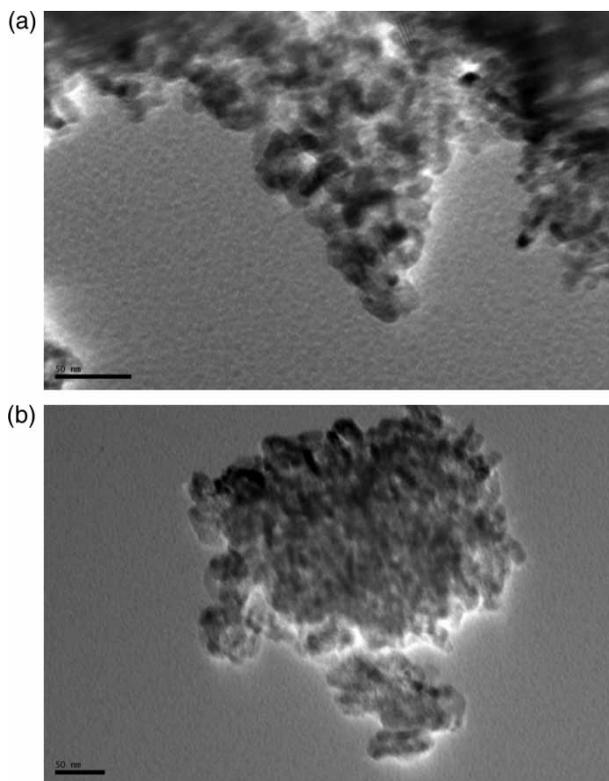


Figure 4. (a) TEM image of fresh nanoparticles. (b) TEM image of recycled nanoparticles.

Conclusion

We have developed an economical and facile method for the oxidation of secondary alcohols into corresponding ketones. Simple work-up, mild reaction conditions, and only water as a side product make this present protocol eco-friendly. In addition to this recyclability of nano TiO₂, use of nontoxic solvent makes this protocol imperative in the field of organic synthesis.

Acknowledgements

Saurav Bhardwaj and Arti Jain thank CSIR and UGC, respectively, New Delhi, for their fellowships.

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Supporting Information

A green oxidation protocol for the conversion of secondary alcohols into ketones using heterogeneous nanocrystalline titanium (IV) oxide in PEG.

Contents:

- 1: General experimental details.
- 2: Experimental characterization data for all compounds.
- 3: Copies of product ¹H NMR, IR and ¹³C NMR. (1, 4, 5, 6)

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Chemistry, University of Delhi, Delhi-110007, India

General

The materials procured from Sigma-Aldrich and Merck, were used without further purification. Melting points are determined on Buchi 530 (Buchi laborfehnik AG, CH-9230, Falawil). Mass spectra were recorded in a TOF-mass spectrometer model no. KC455. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker spectrospin 400 and 100 MHz respectively. All NMR samples were run in CDCl₃ and chemical shifts are expressed as ppm relative to internal Me₄Si.

Experimental

10 mol% nanocrystalline titanium (IV) oxide were added to the reaction mixture of diphenylcarbinol (1mmol) and H₂O₂ (1mmol) in PEG-400 (3 ml). This reaction mixture was continuously stirred at 70–75 °C in the oil bath for 6 hrs. The progress of reaction was continuously monitored by T.L.C. After completion of the reaction, excess of water was added and the reaction mixture was further stirred at room temperature for 2 hrs. In case of solid product, reaction mixture was filtered to get the solid product. This solid product was dissolved in ethyl acetate followed by centrifuge to recover the nano TiO₂. But in case of liquid, product was extracted with diethyl ether and dried over sodium sulphate. Solvent was recovered in vacuum. Subsequently the crude products were purified by column chromatography using 80:20 (hexane:chloroform) as an eluent.

1. Benzophenone (White solid) IR_{v_{max}}(KBr) 1664 cm⁻¹ (CO). ¹H NMR (400 MHz, TMS, CDCl₃): δ 7.44–7.51 (m, 4H), 7.62–7.75 (2H, m), 7.80. (4H, m).

¹³C NMR (100 MHz, TMS, CDCl₃): δ 129.90, 132.30, 137.54, 197.21. m/z (GC-MS, HR-MS): 182.07 (M⁺).

2. 3,4-Dihydro-2H-naphthalen-1-one (Yellowish liquids) IR_{v_{max}}(KBr) 1681 cm⁻¹ (CO). ¹H NMR (400 MHz, TMS, CDCl₃): δ 2.56 (t, J = 12 Hz, 2H), 2.68–2.80 (m, 2H), 2.91 (t, J = 12 Hz, 2H), 7.23–7.43 (m, 3H), 8.00 (1H, J = 6 Hz, d). ¹³C NMR (100 MHz, TMS, CDCl₃): δ 23.01, 29.13, 38.83, 126.30, 127.67, 128.11, 132.27, 133.66, 144.07, 198.35. m/z (GC-MS, HRMS): 145.85 (M⁺).

3. 2-Methylbenzophenone (White solid) IR_{v_{max}}(KBr) 1665 cm⁻¹ (CO). ¹H NMR (400 MHz, TMS, CDCl₃): δ 2.23 (s, 3H), 7.15–7.78 (m, 9H), ¹³C NMR (100 MHz, TMS, CDCl₃): δ 14.20, 28.19, 127.11, 130.11, 138.41, 139.50, 187.10. m/z (GC-MS, HRMS): 196.01 (M⁺).

4. Fluoren-9-one (White solid) IR_{v_{max}}(KBr) 1721 cm⁻¹ (CO). ¹H NMR (400 MHz, TMS, CDCl₃): δ 7.16–7.20 (2H, m), 7.36–7.42 (m, 4H), 7.56 (2H, J = 8Hz, d). ¹³C NMR (100 MHz, TMS, CDCl₃): δ 120.25, 124.28, 129.00, 134.10, 134.63, 144.39, 193.87. m/z (GC-MS, HR-MS): 179.92 (M⁺).

5. 4,4'-Dimethoxybenzophenone (White solid) IR_{v_{max}}(KBr) 1638 cm⁻¹ (CO). ¹H NMR (400 MHz, TMS, CDCl₃): δ 3.72 (6H, s), 6.76 (2H, J = 8 Hz, d), 7.85 (2H, J = 8 Hz, d) ¹³C NMR (100 MHz, TMS, CDCl₃): δ 55.56–55.67 (1C, J = 32, q) 112.97, 130.91, 132.38, 162.99, 194.64. m/z (GC-MS, HR-MS): 242.04 (M⁺).

6. 1-Naphthalen-2-yl-ethanone (brownish solid) IR_{v_{max}}(KBr)1675 cm⁻¹ (CO). ¹H NMR (400 MHz, TMS, CDCl₃): δ 2.62 (3H, s), 7.42–7.54 (2H, 2m), 7.76–7.82 (2H, m), 7.87 (1H, J = 8 Hz, d), 7.92–7.96 (1H, J_{ab}=8 Hz, J_{ac}=4 Hz, dd), 8.37 (1H, s). ¹³C NMR (100 MHz, TMS, CDCl₃): δ 26.67, 123.82, 126.74, 127.77, 128.37, 130.16, 132.44, 134.40, 135.54, 198.04. m/z (GC-MS, HR-MS): 168.96 (M⁺).

7. 4-Chlorobenzophenone (White solid) IR_{v_{max}}(KBr)IR 1657 cm⁻¹¹¹H NMR (400 MHz, TMS, CDCl₃): δ 7.45–7.52 (m, 4H), 7.58–7.63 (m, 1H), 7.75–7.79 (m, 4H), ¹³C NMR (100 MHz, TMS, CDCl₃): δ 128.41, 128.70, 130.0, 131.54, 132.77, 135.91, 137.23, 138.92, 195.54,. m/z (GC-MS, HR-MS): 215.76 (M⁺).

8. Acetophenone (Colorlessliquid) IR_{v_{max}}(KBr) 1678 cm⁻¹ (CO). ¹H NMR (400 MHz, TMS, CDCl₃): δ 2.55 (3H, s), 7.32–7.68 (3H, m), 7.94 (2H, J = 8 Hz, d), ¹³C NMR (100 MHz, TMS, CDCl₃): δ 26.47, 128.26, 128.56, 133.00, 136.95, 197.90. m/z (GC-MS, HR-MS): 121.06 (M⁺).

9. Cyclohexanone (Colorless liquid) IR_{v_{max}}(KBr) 1710 cm⁻¹ (CO). ¹H NMR (400 MHz, TMS, CDCl₃): δ 1.50–2.10 (6H, m), 2.35 (4H, J = 11.86 Hz, t). ¹³C

NMR (100 MHz, TMS, CDCl_3): δ 25.24, 27.10, 42.02, 211.55. m/z (GC-MS, HRMS): 97.56 (M^+).

10. Cyclopentanone (Colorless liquid) IR_{vmax} (KBr) 1745 cm^{-1} (CO). ^1H NMR (400 MHz, TMS, CDCl_3): δ 1.88 (4H, t), 2.33 (4H, t). ^{13}C NMR (400 MHz, TMS, CDCl_3): δ 23.30, 38.28, 220.14. m/z (GC-MS, HR-MS): 82.89 (M^+).

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