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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

Mazaahir Kidwai\*, Saurav Bhardwaj and Arti Jain

Department of Chemistry, Green Research Laboratory, University of Delhi, Delhi 110007, India

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The oxidation of secondary alcohols into corresponding ketones has been described using heterogeneous nanocrystalline TiO<sub>2</sub> as catalyst at a moderate temperature with quantitative yields. Use of H<sub>2</sub>O<sub>2</sub> instead of O<sub>2</sub> (g) is the main feature of our methodology since maintenance of P<sub>O<sub>2</sub></sub> (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; TiO<sub>2</sub>-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 O<sub>2</sub> (g) (13), or large quantities of additives such as bases and electron transfer mediators are required (14,15). Besides this, lethal V<sub>2</sub>O<sub>5</sub> 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<sub>x</sub> 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 TiO<sub>2</sub>-np as heterogeneous catalyst, H<sub>2</sub>O<sub>2</sub> as reagent, and PEG as green solvent.

\*Corresponding author. Email: kidwai.chemistry@gmail.com

## Results and discussion

To validate our hypothesis, we initially examined the oxidation of diphenylcarbinol in absence of nanocrystalline TiO<sub>2</sub>. Reaction was performed in PEG-400 using equivalent amount of diphenylcarbinol and aqueous H<sub>2</sub>O<sub>2</sub>. This reaction mixture was continuously stirred at 70–75°C in oil bath for 6 hours (Scheme 1).

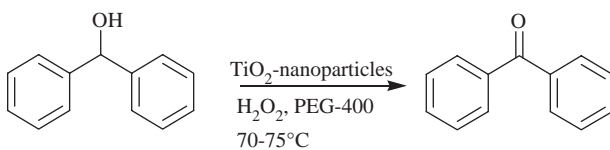
Under these reaction conditions diphenylcarbinol was converted into benzophenone with only 27% yield. Then the conversion was further improved by introducing 10 mol% of nanocrystalline TiO<sub>2</sub> and surprisingly yield reached up to 92%. Furthermore, the reaction temperature had a great influence 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 TiO<sub>2</sub> was found to be the most effective among all the catalysts used (Table 1).

The increased catalytic activity of nano-TiO<sub>2</sub> over the commercially available bulk TiO<sub>2</sub> and other nano oxides may be attributed to the higher surface area for nano-TiO<sub>2</sub>. 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> nanoparticles.

Table 1. Oxidation of alcohols using different nanocrystalline metal oxides.<sup>a</sup>

Entry	Nanoparticles	Time (h)	Yield (%) <sup>b</sup>
1	CuO	8	38
2	ZnO	8	40
3	MgO	8	50
4	TiO <sub>2</sub>	6	92

<sup>a</sup>Reaction conditions: diphenylcarbinol (1 mmol), hydrogen peroxide (1 mmol) and 10 mol% nanocrystals nm; PEG-400; temperature 70–75°C.

<sup>b</sup>Isolated 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 H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> as the oxidant.

To test the generality and scope of nano TiO<sub>2</sub> 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 –OCH<sub>3</sub>, –Cl, and –CH<sub>3</sub> were ineffective during course of reaction.

The literature suggested that superoxide species O<sub>2</sub><sup>•−</sup> 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

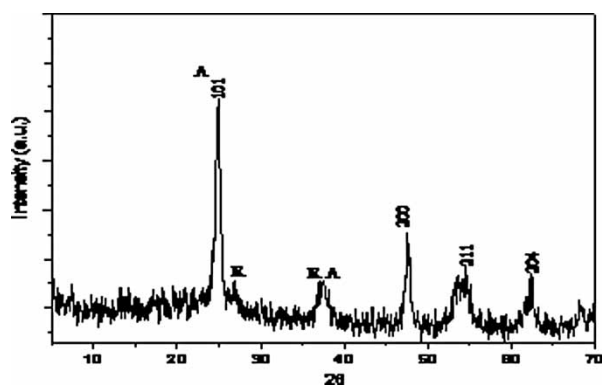


Figure 1. Powder XRD pattern of nanocrystalline titanium (IV) oxide.

Table 2. Screening of solvent for oxidation reaction.

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

<sup>a</sup>Reaction conditions: diphenylcarbinol (1 mmol), hydrogen peroxide (1 mmol) and 10 mol% nano TiO<sub>2</sub> (50 ± 2) nm; solvent; temperature 70–75°C.

<sup>b</sup>Isolated 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<sup>-1</sup> due to H–O bond of unsaturated alcohols and appearance of characteristic stretching bands of –C=O– at 1650–1730 cm<sup>-1</sup> for ketones in the IR spectra. In the <sup>1</sup>H 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-TiO<sub>2</sub> 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.

TiO<sub>2</sub> 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 TiO<sub>2</sub> and fresh reactant and H<sub>2</sub>O<sub>2</sub>, under similar reaction conditions. The TiO<sub>2</sub>-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 <sub>2</sub> O <sub>2</sub>	47	H <sub>2</sub> O
t-BuOOH	18	t-BuOH
CH <sub>3</sub> COOOH	22	CH <sub>3</sub> COOH
NaOCl	22	NaCl
KIO <sub>4</sub>	8	KIO <sub>3</sub>

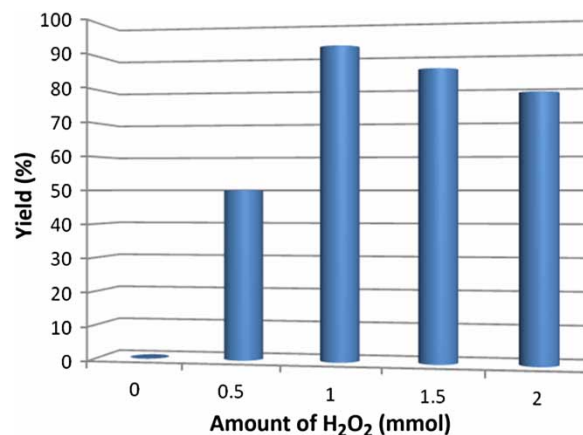


Figure 2. Optimization of concentration of H<sub>2</sub>O<sub>2</sub>. Reaction conditions: diphenylcarbinol (1 mmol), hydrogen peroxide (1 mmol) and 10 mol% nano TiO<sub>2</sub> (50 ± 2) nm; PEG-400; temperature 70–75°C. Isolated yields.

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 TiO<sub>2</sub> 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. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker spectrosSpin 400 and 100 MHz, respectively. All NMR samples were run in CDCl<sub>3</sub>, and chemical shifts are expressed as ppm relative to internal Me<sub>4</sub>Si.

### 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 H<sub>2</sub>O<sub>2</sub> (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.<sup>a</sup>

Entry	Alcohols	Products	Time (h)	Yield (%) <sup>b</sup>
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	$\alpha$ -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

<sup>a</sup>Reaction conditions: Alcohol (1 mmol), hydrogen peroxide (1 mmol) and 10 mol% nano TiO<sub>2</sub> (50 ± 2) nm; PEG-400; temperature 70–75°C.

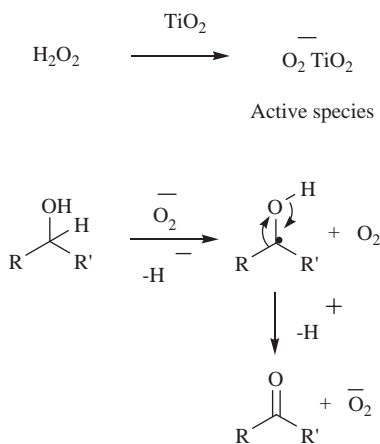
<sup>b</sup>Isolated yields.

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 TiO<sub>2</sub>-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<sub>v<sub>max</sub></sub>(KBr) 1664 cm<sup>-1</sup> (CO). <sup>1</sup>H NMR (400 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  7.44–7.51 (m, 4H), 7.62–7.75 (2H, m), 7.80. (4H, m). <sup>13</sup>C NMR (100 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  129.90, 132.30, 137.54, 197.21. *m/z* (GC-MS, HR-MS): 182.07 (M<sup>+</sup>).



Scheme 2. Proposed reaction mechanism for the oxidation.

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

(White solid) IR<sub>v<sub>max</sub></sub>(KBr) 1721 cm<sup>-1</sup> (CO). <sup>1</sup>H NMR (400 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  7.16–7.20 (2H, m), 7.36–7.42 (m, 4H), 7.56 (2H, J = 8 Hz, d). <sup>13</sup>C NMR (100 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  120.25, 124.28, 129.00, 134.10, 134.63, 144.39, 193.87. *m/z* (GC-MS, HR-MS): 179.92 (M<sup>+</sup>).

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

(Brownish solid) IR<sub>v<sub>max</sub></sub>(KBr) 1675 cm<sup>-1</sup> (CO). <sup>1</sup>H NMR (400 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  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<sub>ab</sub> = 8 Hz, J<sub>ac</sub> = 4 Hz, dd), 8.37 (1H, s). <sup>13</sup>C NMR (100 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup>).

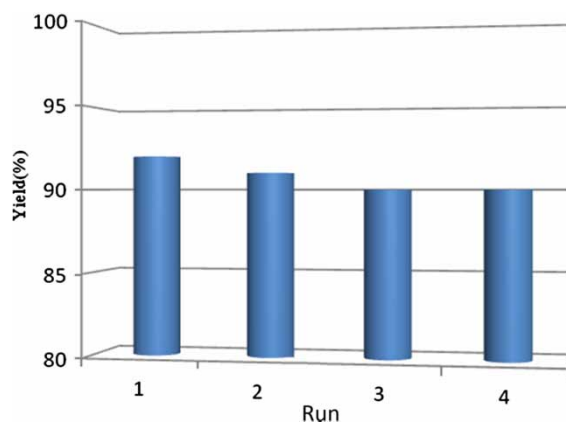


Figure 3. Recycling studies of nano-TiO<sub>2</sub> oxidation reaction. <sup>a</sup>Reaction conditions: diphenylcarbinol (1 mmol), hydrogen peroxide (1 mmol) and 10 mol% nano TiO<sub>2</sub> (50 ± 2) nm; PEG-400; temperature 70–75°C. Isolated yields.

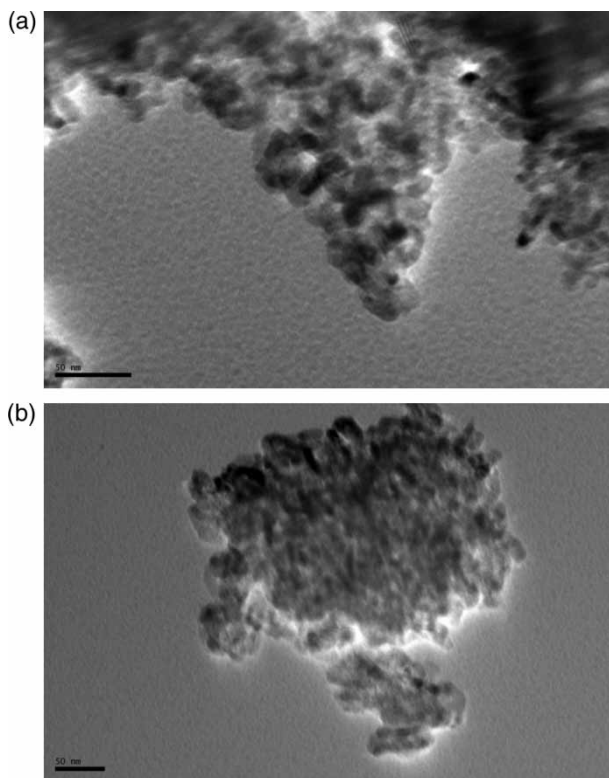


Figure 4. (a) TEM image of fresh nanoparticles. (b) TEM image of recycled nanoparticles.

### 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 TiO<sub>2</sub>, use of nontoxic solvent makes this protocol imperative in the field of organic synthesis.

### Acknowledgements

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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 <sup>1</sup>H NMR, IR and <sup>13</sup>C NMR. (1, 4, 5, 6)

Mazaahir Kidwai\* and Saurav Bhardwaj and Arti jain  
Green Chemistry Research Laboratory, Department of  
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. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker spectrosin 400 and 100 MHz respectively. All NMR samples were run in CDCl<sub>3</sub> and chemical shifts are expressed as ppm relative to internal Me<sub>4</sub>Si.

### Experimental

10 mol% nanocrystalline titanium (IV) oxide were added to the reaction mixture of diphenylcarbinol (1mmol) and H<sub>2</sub>O<sub>2</sub> (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 TiO<sub>2</sub>. 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<sub>v<sub>max</sub></sub>(KBr) 1664 cm<sup>-1</sup> (CO). <sup>1</sup>H NMR (400 MHz, TMS, CDCl<sub>3</sub>): δ 7.44–7.51 (m, 4H), 7.62–7.75 (2H, m), 7.80. (4H, m).

<sup>13</sup>C NMR (100 MHz, TMS, CDCl<sub>3</sub>): δ 129.90, 132.30, 137.54, 197.21. m/z (GC-MS, HR-MS): 182.07 (M<sup>+</sup>).

**2. 3,4-Dihydro-2H-naphthalen-1-one** (Yellowish liquids) IR<sub>v<sub>max</sub></sub>(KBr) 1681 cm<sup>-1</sup> (CO). <sup>1</sup>H NMR (400 MHz, TMS, CDCl<sub>3</sub>): 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). <sup>13</sup>C NMR (100 MHz, TMS, CDCl<sub>3</sub>): 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<sup>+</sup>).

**3. 2-Methylbenzophenone** (White solid) IR<sub>v<sub>max</sub></sub>(KBr) 1665 cm<sup>-1</sup> (CO). <sup>1</sup>H NMR (400 MHz, TMS, CDCl<sub>3</sub>): δ 2.23 (s, 3H), 7.15–7.78 (m, 9H), <sup>13</sup>C NMR (100 MHz, TMS, CDCl<sub>3</sub>): δ 14.20, 28.19, 127.11, 130.11, 138.41, 139.50, 187.10. m/z (GC-MS, HRMS): 196.01 (M<sup>+</sup>).

**4. Fluoren-9-one** (White solid) IR<sub>v<sub>max</sub></sub>(KBr) 1721 cm<sup>-1</sup> (CO). <sup>1</sup>H NMR (400 MHz, TMS, CDCl<sub>3</sub>): δ 7.16–7.20 (2H, m), 7.36–7.42 (m, 4H), 7.56 (2H, J = 8Hz, d). <sup>13</sup>C NMR (100 MHz, TMS, CDCl<sub>3</sub>): δ 120.25, 124.28, 129.00, 134.10, 134.63, 144.39, 193.87. m/z (GC-MS, HR-MS): 179.92 (M<sup>+</sup>).

**5. 4,4'-Dimethoxybenzophenone** (White solid) IR<sub>v<sub>max</sub></sub>(KBr) 1638 cm<sup>-1</sup> (CO). <sup>1</sup>H NMR (400 MHz, TMS, CDCl<sub>3</sub>): δ 3.72 (6H, s), 6.76 (2H, J = 8 Hz, d), 7.85 (2H, J = 8 Hz, d) <sup>13</sup>C NMR (100 MHz, TMS, CDCl<sub>3</sub>): 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<sup>+</sup>).

**6. 1-Naphthalen-2-yl-ethanone** (brownish solid) IR<sub>v<sub>max</sub></sub>(KBr)1675 cm<sup>-1</sup> (CO). <sup>1</sup>H NMR (400 MHz, TMS, CDCl<sub>3</sub>): 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<sub>ab</sub> = 8 Hz, J<sub>ac</sub> = 4 Hz, dd), 8.37 (1H, s). <sup>13</sup>C NMR (100 MHz, TMS, CDCl<sub>3</sub>): 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<sup>+</sup>).

**7. 4-Chlorobenzophenone** (White solid) IR<sub>v<sub>max</sub></sub>(KBr)IR 1657 cm<sup>-1</sup><sup>11</sup>H NMR (400 MHz, TMS, CDCl<sub>3</sub>): δ 7.45–7.52 (m, 4H), 7.58–7.63 (m, 1H), 7.75–7.79 (m, 4H), <sup>13</sup>C NMR (100 MHz, TMS, CDCl<sub>3</sub>): 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<sup>+</sup>).

**8. Acetophenone** (Colorlessliquid) IR<sub>v<sub>max</sub></sub>(KBr) 1678 cm<sup>-1</sup> (CO). <sup>1</sup>H NMR (400 MHz, TMS, CDCl<sub>3</sub>): δ 2.55 (3H, s), 7.32–7.68 (3H, m), 7.94 (2H, J = 8 Hz, d), <sup>13</sup>C NMR (100 MHz, TMS, CDCl<sub>3</sub>): δ 26.47, 128.26, 128.56, 133.00, 136.95, 197.90. m/z (GC-MS, HR-MS): 121.06 (M<sup>+</sup>).

**9. Cyclohexanone** (Colorless liquid) IR<sub>v<sub>max</sub></sub>(KBr) 1710 cm<sup>-1</sup> (CO). <sup>1</sup>H NMR (400 MHz, TMS, CDCl<sub>3</sub>): δ 1.50–2.10 (6H, m), 2.35 (4H, J = 11.86 Hz, t). <sup>13</sup>C



NMR (100 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  25.24, 27.10, 42.02, 211.55.  $m/z$  (GC-MS, HRMS): 97.56 ( $\text{M}^+$ ).

**10. Cyclopentanone** (Colorless liquid)  $\text{IR}_{\text{vmax}}$  (KBr)  $1745 \text{ cm}^{-1}$  (CO).  $^1\text{H}$  NMR (400 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  1.88 (4H, t), 2.33 (4H, t).  $^{13}\text{C}$  NMR (400 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  23.30, 38.28, 220.14.  $m/z$  (GC-MS, HR-MS): 82.89 ( $\text{M}^+$ ).

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