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ARTICLE TYPE

Dual catalysis with magnetic chitosan: direct synthesis of cyclic carbonates from olefins with carbon dioxide using isobutyraldehyde as sacrificial reductant

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Chitosan coated magnetic nanoparticles were synthesized and used as support for the immobilization of cobalt(II) acetylacetonate complex [Co(acac)₂] and quaternary ¹⁰ triphenylphosphonium iodide [P⁺Ph₃Br⁻] targeting -NH₂ and -OH moieties located on the surface of chitosan. The synthesized material was used as catalyst for one pot direct synthesis of cyclic carbonates from olefins via oxidative carboxylation approach with carbon dioxide using ¹⁵ isobutyraldehyde as sacrificial reductant and molecular oxygen as oxidant. After the reaction, the catalyst was recovered by external magnet and reused for several runs without significant loss in catalytic activity and no leaching was observed during this course.

- ²⁰ Bio-based and biodegradable polymers have received considerable interest in recent decades mainly due to the limited availability of fossil fuel and growing environmental concerns. Apart from their wide spread applications in biomedical domain;¹ they also have been widely used as catalyst carriers in chemical
- ²⁵ reactions.² Among the various known biopolymers, chitosan (CS) owing to its low cost, non toxicity, biocompatibility, and multifunctional properties has found extensive applications in various areas including as catalyst support for chemical transformations.³ It comprises a great quantity of hydroxyl and ³⁰ amine groups, which can be used for the further functionalization
- as well as immobilization of metal complexes through covalent attachment. This kind of chitosan-metal complexes has been successfully used as heterogeneous catalysts in plethora of reactions including hydrogenation, oxidation, adsorption and relumerization ⁴ Apart from this chamical instability lower
- ³⁵ polymerization.⁴ Apart from this, chemical instability, lower surface area, dissolution of chitosan and lower disperse ability are some major issues associated with the use of chitosan.⁵ Recently, employing magnetic Fe₃O₄ nanoparticles to construct a recyclable heterogeneous catalyst has led to a particular interest due to the
- ⁴⁰ facile and efficient recovery of the catalyst from the reaction mixture with an external magnetic field.⁶ Encapsulation of magnetic nanoparticles with chitosan not only combine the low cost and biodegradability brought by the natural polymeric support with a high surface area and facile magnetic separation
- ⁴⁵ but also contributes to the amelioration of chemical stability and disperses ability.⁷

Chemical activation and conversion of carbon dioxide to high

value products is one of the most challenging areas in current decades both from economical and environmental points of view.

- ⁵⁰ One of the most successful examples in the area of CO₂ utilization is the production of five membered cyclic carbonates.⁸ Cyclic carbonates due to their higher boiling points, low toxicity, high solubility, and biodegradability have an important market as aprotic polar solvents and precursors for biomedical applications
- ⁵⁵ as well as for engineering plastics.⁹ Various catalysts including quaternary ammonium and phosphonium salts, alkali metal salts, Lewis acids, transition metal complexes, ionic liquids and organocatalyst have been reported for the coupling reaction of epoxide and carbon dioxide to yield cyclic carbonate.¹⁰ However,
- ⁶⁰ such a cycloaddition generally requires the initial synthesis of an epoxide, which involves toxic or costly reagents and requires a tedious workup procedure for separation. The direct synthesis of cyclic carbonates from corresponding olefins and CO₂, so-called "oxidative carboxylation" constitutes an environ-economic ⁶⁵ approach due to the low cost and easy accessibility of olefins as well as avoidance of initial synthesis and separation of epoxides. The hitherto known methods for oxidative carboxylation of olefins with O₂/CO₂ using metal catalysts are associated with the drawbacks of poor product yields, use of expensive metals such ⁷⁰ as ruthenium and harsh reaction conditions for example high temperature and higher CO₂ pressure.¹¹

In the present paper, we describe an efficient heterogeneous magnetically separable chitosan modified with Co(II) acetylacetonate and triphenylphosphonium bromide as catalyst 75 for the direct one pot synthesis of cyclic carbonates via oxidative carboxylation of olefins with carbon dioxide using molecular oxygen as oxidant and isobutyraldehyde as sacrificial reducing agent (Scheme 1).



Scheme 1 oxidative carboxylation of olefin

Result and Discussion

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Synthesis and characterization of catalyst

The synthetic strategy adopted for the immobilization of cobalt(II) acetylacetonate complex $[Co(acac)_2]$ and guaternary s triphenylphosphonium bromide $[P^+Ph_3Br^-]$ to magnetic chitosan is shown in Scheme 2. Initially chitosan coated magnetic particles were prepared via co-precipitation method by mixing FeCl₃.6H₂O, FeCl₂.4H₂O and required amount of chitosan followed by the addition of aqueous ammonia for 30 min in a 10 Teflon coated reactor. After completion of the reaction, the particles were recovered by external magnet and washed with deionized water for several times.¹² As synthesized magnetic chitosan i.e. MCS was subsequently used as support for the immobilization of Co(acac)₂ to give Co(acac)₂@MCS by using -15 NH₂ groups presented on chitosan. Finally the synthesized Co(acac)2@MCS treated with 3-bromowas propyltrimethoxysilane (BPTMS) followed by the reaction with triphenylphosphine to give magnetic chitosan immobilized cobalt acetylacetonate and quaternary phosphonium bromide denoted as 20 Co(acac)2-QPB@MCS catalyst (Scheme 2).



- The cobalt loading in the synthesized catalyst was found to be 25 0.31 mmol cobalt/g (1.8 wt% Co) as determined by ICP-AES analysis. The amount of phosphorus in the synthesized catalyst was found to be 0.16 mmol/g as determined by ICP. The possible reason for the poor loading of phosphorus may be due to lesser degree of substitution of hydroxyl groups of chitosan with 3-
- ³⁰ bromopropyl trimethoxysilane followed by subsequent reaction with triphenylphosphine.

The morphological features of the synthesized MCS and Co(acac)₂-QPB@MCS were determined by transmission electron microscopy (TEM) (Fig. 1). As shown in Fig 1, the MCS

- ³⁵ exhibited spherical (Fig. 1b) whereas Co(acac)₂-QPB@MCS revealed spheroidal morphology (Fig. 1c). The average size of the Co(acac)₂-QPB@MCS nano-composite spheres was found to be in the range of 50-100 nm. The appearance of black spot indicated the uniformly ingrained iron nanoparticles in the matrix
- ⁴⁰ of chitosan. The lattice fringes for Fe_3O_4 phase with an interplanar d-spacing of 0.235 nm, corresponding to the (311) plane can be clearly seen in the HRTEM image of an individual particle of MCS (Fig. 1d).¹³



45 Fig. 1 HRTEM image of a) Fe₃O₄ nano particles; b) MCS; c) Co(acac)₂-QPB@MCS; d) MCS

Furthermore, XPS analyses was carried out to demonstrate the successful anchoring of Co(acac)₂ and P⁺Ph₃Br⁻ onto MCS. An apparent indication of anchoring of Co(acac)₂ and P⁺Ph₃Br⁻ onto 50 MCS can be deduced by the appearance of C, N, O, Si, Br, P, Fe and Co elements in the wide scan XPS spectra of Co(acac)2-QPB@MCS (Fig 2a). The high-resolution XPS spectrum of Fe 2p for MCS showed two peaks at 711.1 and 724.6 eV corresponding to $Fe2p_{3/2}$ and $Fe2p_{1/2}$ in magnetic Fe_3O_4 55 nanoparticles respectively (Fig 2b).¹⁴ However, the intensity of Fe2p peak is nearly invisible due to the matrix of chitosan. The split bands in high resolution XPS spectrum of Co2p for Co(acac)₂@MCS at 780.1 and 795.8 eV were observed due to the $Co2p_{3/2}$ and $Co2p_{1/2}$ of homogeneous $Co(acac)_2$ complex. 60 However, the shifting of these bands in the immobilized catalyst suggested the successful grafting of Co(acac)₂ onto chitosan support via covalent attachment (Fig. 2c).¹⁵





The FTIR spectra of MCS, Co(acac)₂@MCS and Co(acac)₂-QPB@MCS are given in supporting information (Fig. S1). FTIR spectrum of MCS displayed characteristic peaks at 3400-3500 cm⁻¹ (N-H, O-H), 2800-3000 (C-H), 1620 (N-H), 1050 cm⁻¹ (C-⁵ O-C) and 595 cm⁻¹ (Fe-O). After the Schiff condensation of cobalt complex, and anchoring of P⁺Ph₃Br⁻ moiety, the significant changes in the FTIR spectra of chitosan were observed. There are new bands at 1724, 1450 and 780 cm⁻¹ are corresponding to the C=O, C=C (aromatic) and C-H (aromatic) stretching.

¹⁰ XRD pattern of as synthesized materials and chitosan is shown in Fig. 3. XRD pattern of chitosan shows two characteristics peak at $2\theta = 11.2$ and 21.8 while in case of Co(acac)₂-QPB@MCS, two new peaks of lower intensity are appeared due to the ingrained nanoparticles of Fe₃O₄ in chitosan matrix at $2\theta = 35.3$ ¹⁵ and 38.1 corresponding to the (311) and (222) planes respectively.¹⁶ Peaks at $2\theta = 11.2$ and 21.8, have also become sharper than native chitosan, it might be because of the phase transformation of synthesized material from amorphous to crystalline nature by the precipitation reaction of iron and ²⁰ chitosan. It is to be noted that owing to the low concentration of Co loaded on MCS, we could not see the signature of Co.



Fig. 3 a) XRD spectra; b) TGA spectra

The thermal stability of the chitosan and Co(acac)₂-QPB@MCS ²⁵ was determined by TGA analysis as shown in Fig. 3. The thermo gram of Co(acac)₂-QPB@MCS catalyst exhibits a first stage mass loss of 3-5 % below 150 °C due to the loss of the occluded solvents both on the surface and in the pores of the particles. The second stage continuous mass loss starts around 220 °C due to the ³⁰ decomposition of organic moieties presented on the surface of the

³⁰ decomposition of organic moleties presented on the surface of the catalyst and chitosan itself. The variation in thermal events of chitosan and Co(acac)₂-QPB@MCS proved the formation of the new material.

Catalytic Activity

³⁵ The synthesized catalyst was first tested for the synthesis of styrene carbonate from O₂/CO₂ and styrene using acetonitrile as

solvent at 100 °C (Scheme 3).



Scheme 3 Oxidative carboxylation of styrene

In an effort to find the best catalytic system, various catalysts (2 mol %) such as MCS, Co(acac)₂@MCS, QPB@MCS, and Co(acac)₂-QPB@MCS were screened. The results of these experiments are summarized in Table 1. To our delight, ⁴⁵ Co(acac)₂-QPB@MCS catalyst showed high efficiency for this reaction under described conditions. The reaction was found to be very slow in the absence of any catalyst or using MCS and QPB@MCS as catalyst (Table 1, entry 1, 2, 3 and 4). The use of physical mixture of Co(acac)₂@MCS and QPB@MCS (1:1) as

⁵⁰ catalyst provided lower yield of the product (Table 1, entry 6). These results suggested that the covalent grafting of $Co(acac)_2$ and P⁺Ph₃Br⁻ moieties to MCS had a significant effect on catalytic activity (Table 1, entry 5).

In order to confirm the formation of epoxide during the 55 reaction and to establish the mechanism, we performed the reaction of styrene in the absence of carbon dioxide under otherwise identical experimental conditions. The progress of the reaction was monitored by GC, which confirmed the formation of styrene epoxide as the major product along with about 17 % of 60 benzaldehyde as the by-product (Table 1, entry 7). Based on these studies and in analogy to the existing report we proposed a plausible mechanistic pathway for the reaction.¹⁷ The reaction might involve the formation of isopropylacyl radical from isobutyraldehyde via an electron transfer to the cobalt (II) 65 complex which subsequently added with oxygen to give oxometal-complex radical and then peroxide-metal-complex radical. These reactive peroxo-metal intermediates reacted with olefin to give styrene oxide and benzaldehyde. The styrene oxide further reacted with carbon dioxide to give corresponding cyclic 70 carbonate.

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Table I Catalytic activity of various catalysts									
S.N.	Catalyst	Styrene Conversion (%)	CC Selectivity (%)	SO Selectivity (%)	Banzaldehyde Selectivity (%)	CC Yield (%)	TOF (h ⁻¹)		
1.	-	-	-	-	-	-	-		
2.	1	15.5	-	7.4	8.1	-	-		
3.	2	92.3	-	52.7	39.6	-	-		
4.	3	5.4	1.7	1.1	2.6	0.1	0.01		
5.	4	95.2	73.1	1.4	20.7	69.6	9.25		
6.	2 + 3	87	62.4	8.9	15.7	54.3	7.10		
7 ^b	4*	93.1	-	76.2	16.9	-	-		

^{*a*} Reaction conditions: styrene (20 mmol, 2.28 mL), catalyst (0.5 g), acetonitrile (10 mL), isobutyraldehyde (25 mmol, 2.28 mL) at 100 °C, 5 bar pressure of O₂ and 30 bar pressure of CO₂ for 10 h. TOF : Turn Over Frequency (h⁻¹), CC: Cyclic Carbonate, SO: Styrene Oxide; ^bIn the absence of carbon dioxide

The effect of other parameters, such as CO₂/O₂ pressure, reaction 5 temperature and reaction time was also investigated (Fig. 4). At ambient temperature (25 °C) the reaction rate was found to be slow and depended on the O2/CO2 pressure applied. The yield of the product was found to be increased with increasing O₂ and CO₂ pressure. It was found that efficient and selective conversion ¹⁰ of styrene could be achieved at 100 $^{\circ}$ C, 5 bar pressure of O₂ and 30 bar pressure of CO₂ (Fig. 4). Further increase in temperature and reaction pressure did not affect the catalytic activity to any significant extent. Similarly, the reaction was found to increase with reaction time at 100 °C, 5 bar pressure of CO₂ and 30 bar 15 pressure of CO₂ and showed the highest yield in 10 h. Further increase in reaction time did not improve the results to any significant extent. When other solvents such as dichloromethane, DMF and toluene were used in place of acetonitrile the yield of product was found to be decreased significantly (Fig. 4).



Fig. 4 a) effect of O_2 pressure on the yield; b) effect of temperature and pressure on the yield; c) effect of solvent on the yield; d) recyclability of catalyst

- ²⁵ Furthermore, the reusability of the catalyst was examined for subsequent four runs under described experimental conditions (Fig. 4). The yield of styrene carbonate was found to be almost same in all cases, indicating that the catalyst is highly stable and can be recycled for several runs with consistent catalytic activity. These recycled for several runs with consistent catalytic activity.
- ³⁰ These results clearly indicated the merits of the developed heterogeneous catalyst.

Once the optimal conditions for this reaction were established, we looked at examining the utility of this methodology. Thus, the scope of the reaction was tested with respect to other substituted ³⁵ olefins and the results of these experiments are summarized in Table 2. All the substrates either containing electron donating or

- withdrawing groups were found to be nearly equally reactive and afforded moderate to good product yields (Table 2). All the experiments were carried out in a stainless steel (15 ml) autoclave 40 equipped with a stirrer. After completion of the reaction, the
- ⁴⁰ equipped with a stiffer. After completion of the reaction, the reaction mixture was cooled to room temperature and the heterogeneous catalyst was easily recovered by applying external magnate. The obtained organic layer was concentrated under reduced pressure to give crude product. The crude product was ⁴⁵ further purified using column chromatography to give the desired product.

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4.^a

-				1	1
Entry	Epoxide	Product	Conv. (%) ^b	CC Selec. (%) ^b	CC Yield (%) ^c
1			95.2	69.6	67
2			96.1	72.4	70
3			96.3	78.2	76
4	\bigcirc		96.0	80.1	78
5		∘⊸	98.1	87.3	85
6			96.6	79.6	76
7	CI		97.4	82.5	80
8	n-Bu —	n-Bu	98.1	88.3	85

^aReaction conditions: substrate (20 mmol), acetonitrile (10 ml), catalyst (0.5 g, 0.155 mmol), isobutyraldehyde (2.28 mL, 25 mmol) at 100 °C, 5 5 bar pressure of O2 and 30 bar pressure of CO2 for 10 h; ^bdetermined by GC-MS using n-butanol as internal standard; ; 'Isolated yields

Conclusions

We have demonstrated for the first time the use of magnetically separable heterogenized homogeneous catalyst prepared by ¹⁰ anchoring of Co(acac)₂ and $P^+Ph_3Br^-$ on to magnetic chitosan via covalent attachment for oxidative carboxylation of olefins using O_2/CO_2 to give cyclic carbonates. The present method offers a number of advantages such as use of molecular oxygen as oxidant, facile recovery of the catalyst by external magnet, higher 15 catalytic activity and higher product yield. The developed methodology represents the utilization of carbon dioxide in a sustainable manner which can further be used for large scale synthesis of carbonates directly from easily available olefins.

Experimental

20 Materials

High purity carbon dioxide (99.99%) and oxygen compressed cylinders were purchased from Sigma-Gases, India. Chitosan, triphenylphosphine and 3-bromopropyltrimethoxysilane were procured from Sigma Aldrich. FeCl₃.6H₂O, FeCl₂.4H₂O and 25 Co(acac)₂ were purchased from Merck India. Acetonitrile,

ethanol and toluene were indented from Alfa Aesar India. All other substrates were purchased form sigma Aldrich used as received and no further purification was done.

Techniques Used

30 FTIR Spectra was recorded on Perkin-Elmer FT-IR X-1760 IR spectrophotometer using potassium bromide. TEM analysis is done using FEI-Tecnai G2 Twin TEM operating at an acceleration voltage of 200 kV. For TEM a very dilute aqueous dispersion of catalyst was deposited on carbon coated copper 35 grid. Thermo gravimetric analyses (TGA) of samples were carried out using a thermal analyzer TA-SDT Q-600. Analysis was carried out in the temperature range of 40 to 600 °C under nitrogen flow with heating rate 10 °C/min. For determining Co content of catalyst, ICP-AES analysis was carried out by 40 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, DRE, PS-3000UV, Leeman Labs Inc, USA). XRD pattern of this sample was obtained with a Bruker AXS D8 Advanced SWAX Diffrectometer using CuKa (1=0.15406 nm radiation). X-ray photoelectron spectroscopy (XPS, JPS-45 9010TRX, JEOL Ltd.) measurements were carried out using thin films of developed catalyst deposited on carbon tape. All XPS measurements were executed using a MgK α line as the X-ray source. The ¹H NMR spectra were recorded on a Bruker Avance 500 Spectrometer in CDCl₃ as a standard and the chemical shifts 50 are expressed in parts per million (ppm) relative to

Detailed experimental procedure for the preparation of Co(acac)2-QPB@MCS

tetramethylsilane (TMS) as the internal standard.

Modified magnetic chitosan particles (MCS) were obtained by ss co-precipitation method as following the literature procedure.¹² Co-precipitation reaction was carried out by mixing 1.0%(w/v) chitosan in the mixture of FeCl₃.6H₂O (0.32M) and FeCl₂.4H₂O (0.2M) at 50 °C followed by addition of liquid ammonia. Cobalt acetylacetonate Co(acac)₂ was immobilized on the magnetic 60 chitosan via Schiff condensation utilizing -NH2 moiety. 2.0 g of modified magnetic chitosan was treated with 0.5 g of Co(acac)₂ in 25 ml of toluene under refluxing condition for 24 h. The Co(acac)₂ functionalized magnetic chitosan Co(acac)₂@MCS was then first reacted with 3-bromopropyl trimethoxysilane (2 mL) 65 and further with triphenylphosphine (1.0 g) in toluene for immobilizing QPBr utilizing -OH moieties under refluxing condition for 24 h to get Co(acac)₂-QPB@MCS. The solid material thus obtained was separated by external magnate and thoroughly washed with ethanol and dried under vacuum.

Typical experimental procedure for synthesis of styrene carbonate

Styrene (20 mmol, 2.28 mL), catalyst Co(acac)₂-QPB@MCS (0.5g, 0.155 mmol) and isobutyraldehyde (2.28 mL, 25 mmol) 75 were charged in to the 15 ml high pressure stainless steel reactor using acetonitrile (10 mL) as a solvent[†]. The reactor was sealed and purged with oxygen to replace all others gases. Reactor was then initially charged with O_2 up to 5 bar pressure. The reaction mixture was stirred for 6 h at 100 °C. After this, the reactor was 80 further pressurized with CO₂ up to 35 bar and the reaction mixture was further stirred for next 4 h at 100 °C. After this the reactor was placed into ice water and unreacted O₂/CO₂ gases were released slowly by passing through a cold trap containing ethanol. After depressurization, the reaction mixture was 85 transferred in a beaker and the catalyst was separated by applying external magnate. The obtained organic layer was concentrated

Table 2: oxidative carboxylation of various olefins catalyzed by catalyst

under reduced pressure to give crude product. Further purification of the product is done using column chromatography.

[†]Caution! During the experiments, the high pressures of O_2 together with organic substrates (olefin, isobutyraldehyde and s solvent) and oxidation catalyst may give a potentially explosive mixture

Styrene Carbonate.¹⁸ ¹H NMR: δ 4.38-4.43 (1 H, m), 4.85-4.89 (1 H, t, *J*=8.3 Hz), 5.68-5.72 (1 H, t, *J*=8.1 Hz), 7.39-7.49 (5 H, m); ¹³C NMR: δ 70.1, 78.1, 126.1, 129.1, 129.7, 136.2, 155.1

 10 4-methyl styrene Carbonate. $^{19}\,^{1}$ H NMR: δ 2.29-2.35 (3 H, t), 4.35-4.41 (1 H, m), 4.82-4.88 (1 H, t), 5.65-5.70 (1 H, t), 7.36-7.45 (4 H, m); 13 C NMR: δ 20.2, 70.0, 77.9, 126.3, 130.2, 130.7, 136.1, 155.2

Benzyl Carbonate.¹⁸ δ 2.45-2.50 (1 H, m), 2.91-2.96 (1 H, m), ¹⁵ 4.48-4.53 (1 H, m), 4.63-4.68 (1 H, m), 5.02-5.09 (1 H, m), 7.07-7.11 (2 H, m), 7.17-7.22 (3 H, m); ¹³C NMR: 41.1, 70.0, 79.8, 128, 129.2, 130.3, 138.1, 155.7.

Cyclohexene Carbonate.¹⁸ ¹H NMR: δ 1.4-1.63 (4 H, m), 1.79-1.91 (4 H, m), 4.62-4.81 (2 H, m); ¹³C NMR: δ 18.9, 26.8, 75.6, ²⁰ 155.5

Propylene Carbonate.¹⁸ ¹H NMR: δ 3.8-4.0 (3 H, d), 4.4-4.47 (1 H, m), 4.62-4.66 (1 H, m), 5.1-5.3 (1 H, m); ¹³C NMR: δ 43.5, 66.9, 74.2, 154.4

Cyclohexyl Ethylene Carbonate (Fig. S2 & S3). ¹H NMR: δ 25 1.18 (2H, m), 1.21-1.32 (1H, m), 1.32-1.46 (2 H, m), 1.65-1.76 (4 H, m), 1.89 (2 H, m), 4.36 (1 H, m), 4.51 (1 H, m), 4.73 (1 H, m); ¹³C NMR: δ 25.99, 27.26, 27.74, 38.38, 66.04, 83.61, 155.19.

Chloropropylene Carbonate.¹⁸ ¹H NMR: δ 3.74-3.87 (2 H, m), 4.38-4.43 (1 H, m), 4.60-4.64 (1 H, m), 5.0-5.1 (1 H, m); ¹³C ³⁰ NMR: δ 43.9, 67.1, 74.7, 154.9

1-Butylene Carbonate.¹⁸ ¹H NMR: δ 0.93 (3 H, t), 1.51 (1 H, m), 1.90-2.02 (1 H, m), 4.45-4.57 (2 H, m), 4.71 (1 H, t); ¹³C NMR: δ 8.65, 25.81, 70.05, 81.34, 155.39.

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Notes and references

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Dual catalysis with magnetic chitosan: direct synthesis of cyclic carbonates from olefins with carbon dioxide using isobutyraldehyde as sacrificial reductant

Subodh Kumar, Nikita Singhal, Raj K. Singh, Piyush Gupta, Raghuvir Singh and Suman L. Jain MCS H₃CO H₃ CH₃ H₃CO СНа BrPh O₂/CO₂ ⊖ Ph₃Br)-сно H_3 r, CH--OCH₃ Н₃С СН3 осн. MCS 10