Supporting Information

Silica-based Magnetic Manganese Nanocatalyst – Applications in the Oxidation of Organic Halides and Alcohols

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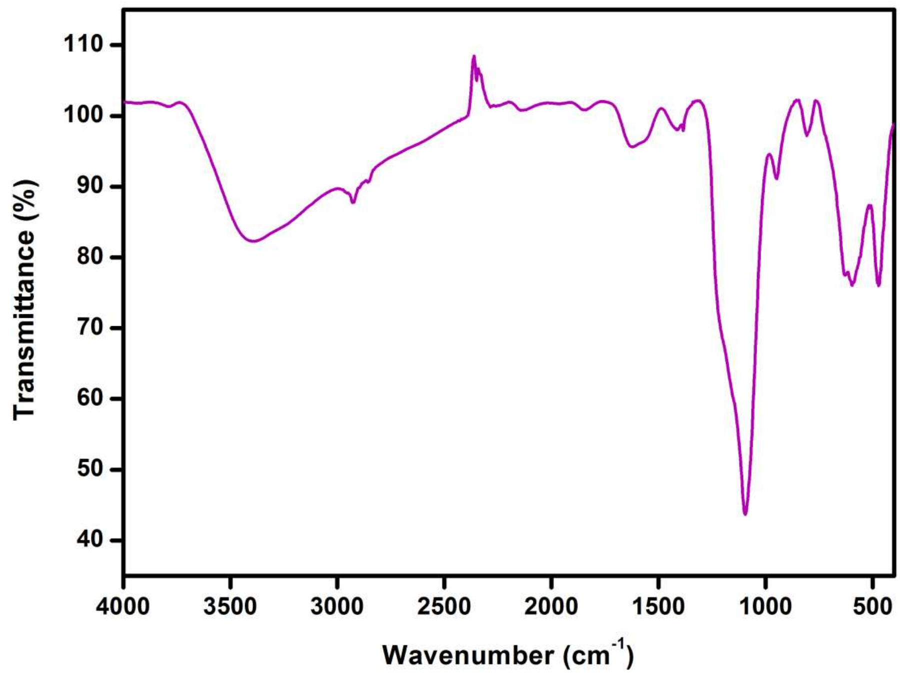


Figure S1a. FT-IR spectra of Mn-Ac@ASMNP

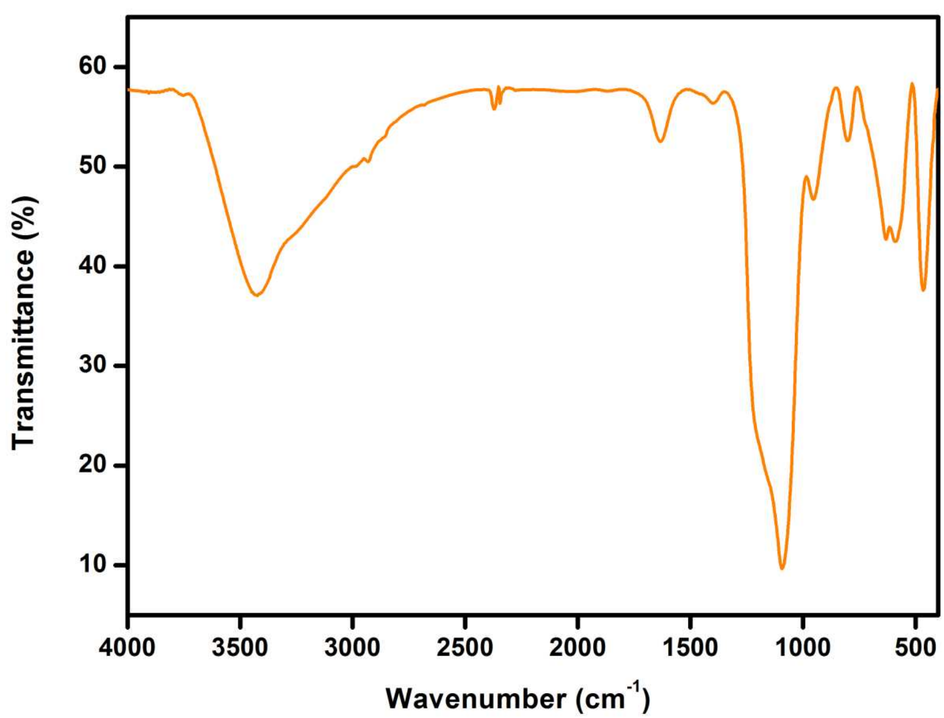


Figure S1b. FT-IR spectra of ASMNP

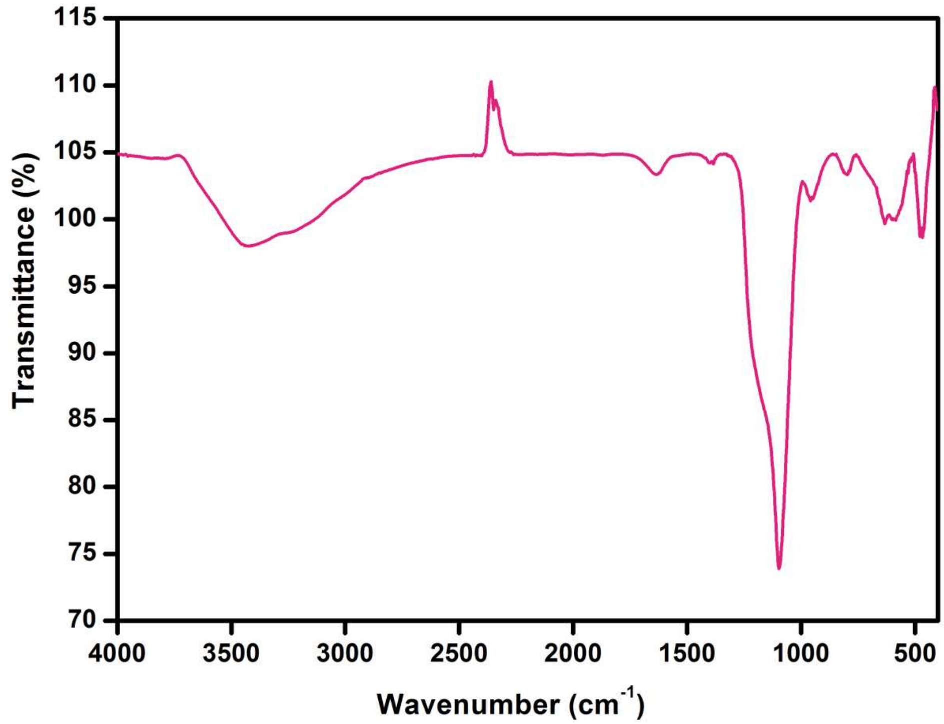


Figure S1c. FT-IR spectra of SMNP

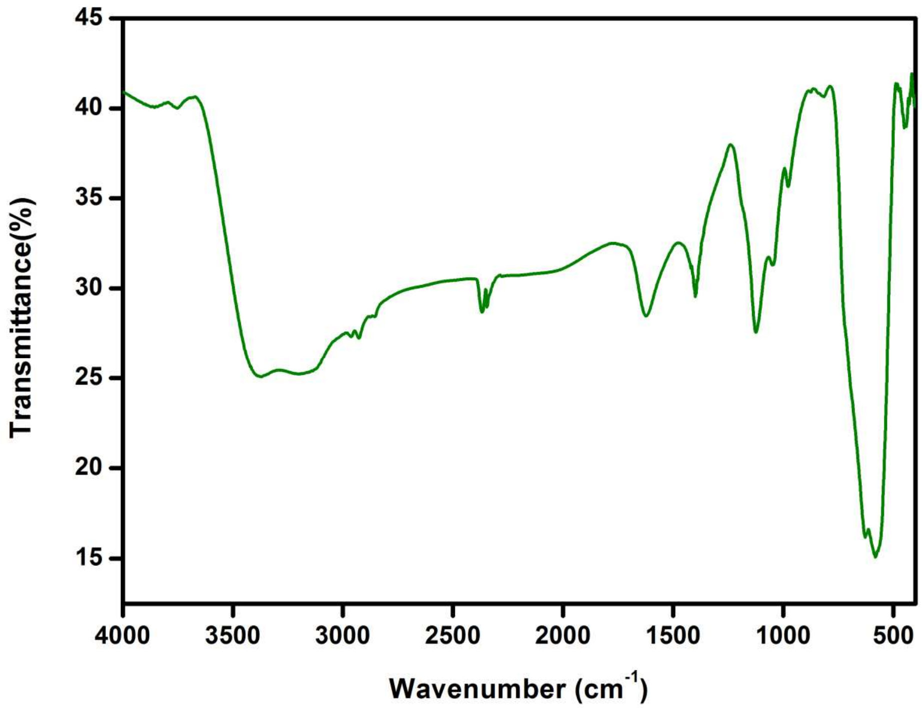


Figure S1d. FT-IR spectra of MNP

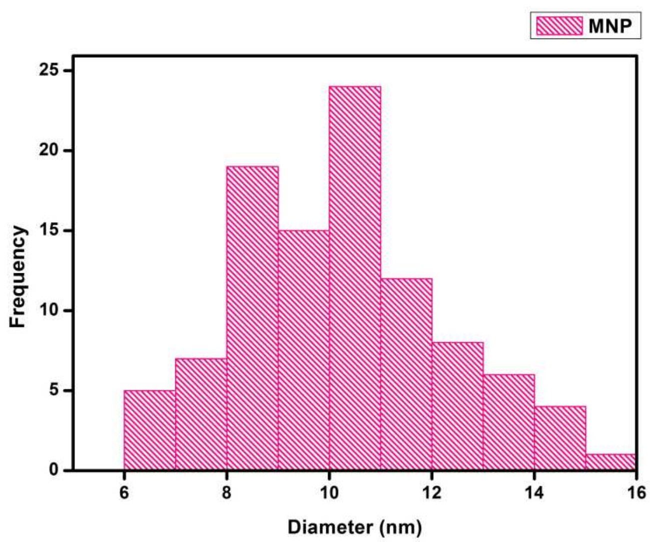


Figure S2. Size distribution histogram for MNPs

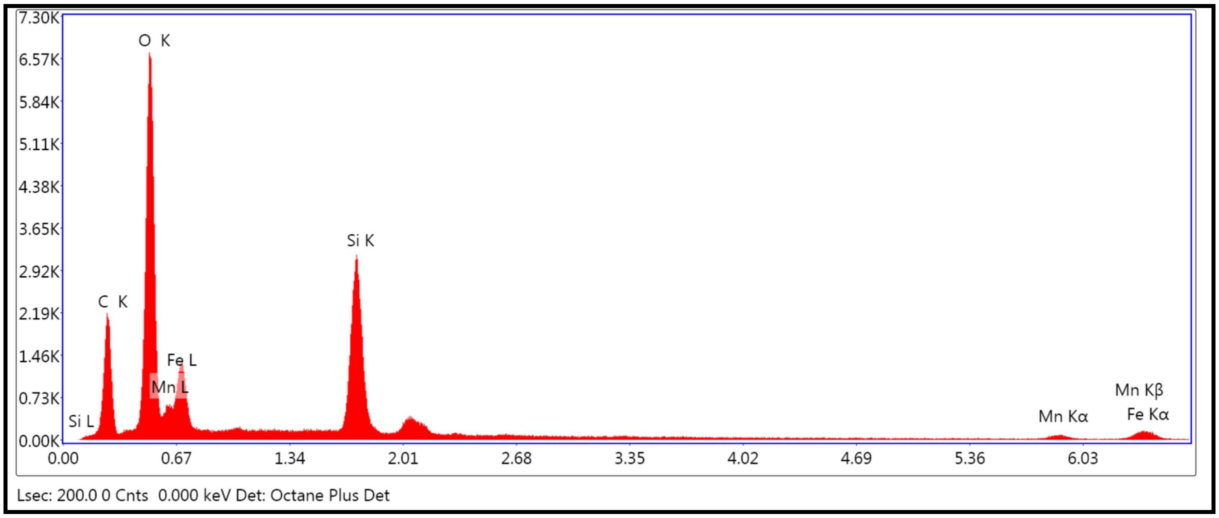
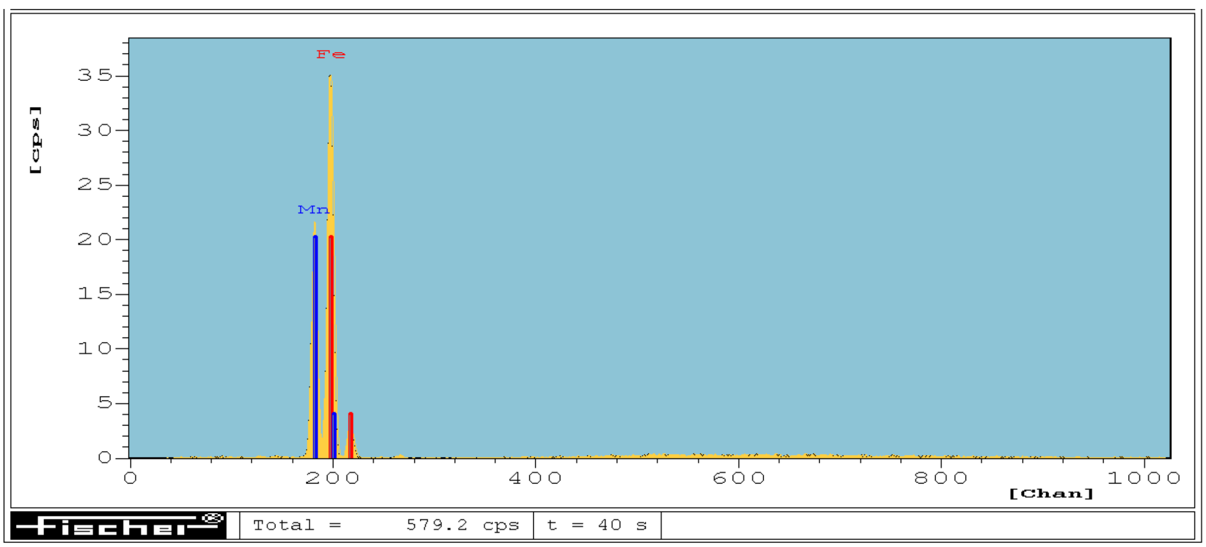


Figure S3. EDS pattern of Mn-Ac@ASMNPs



Meas. para. (foreground spectrum):
High voltage = 50 kV (875) Prim. Filter = Al1000
Collimator 4 = 2.00 Dm. Anode current 138 uA
Meas. distance = 0.04 mm

List of spectra:
Foreground: Measured spectrum

Figure S4. ED-XRF Spectrum of Mn-Ac@ASMNP

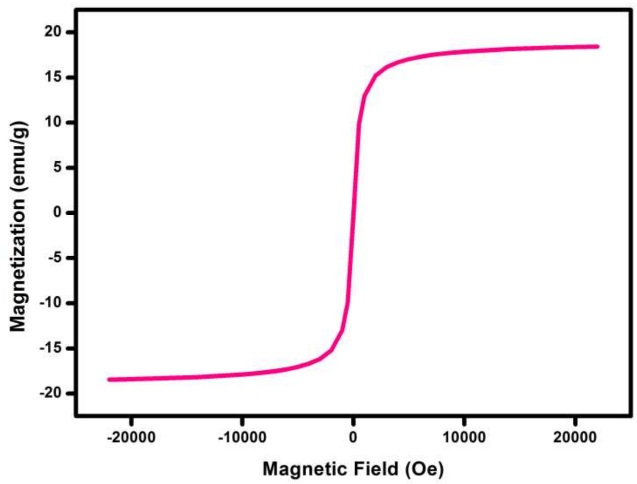


Figure S5. Magnetization curve obtained by VSM at room temperature for re-used Mn-Ac@ASMNPs

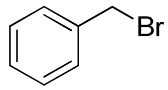
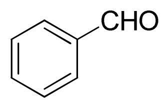
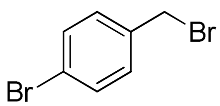
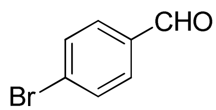
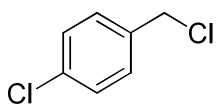
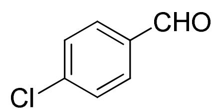
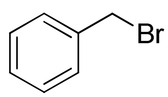
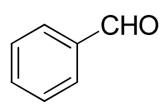
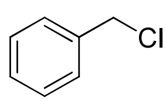
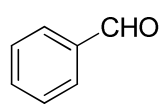
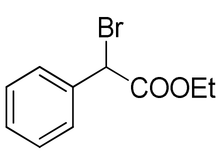
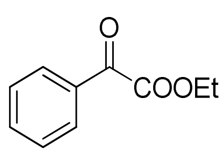
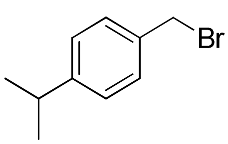
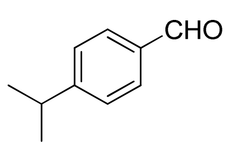
Table S1. Screening of manganese catalyst for the oxidation of organic halides.[a]

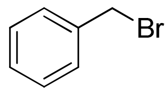
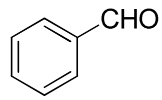
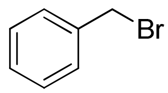
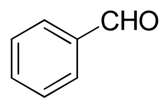
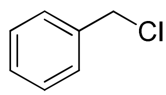
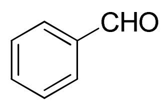
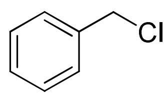
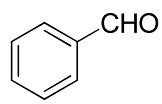
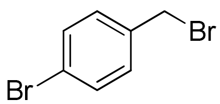
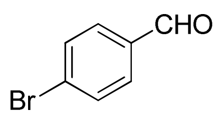
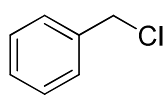
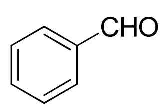
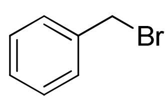
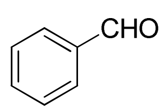
Entry	Catalyst	Oxidant	Yield (%)[b]
1.	No	H_2O_2	41
2.	$Mn(acac)_3$ (20mg)	H_2O_2	80[c]
3.	*Mn-Ac@ASMNP* (10 mg)	H_2O_2	59[d]
4.	*Mn-Ac@ASMNP* (15 mg)	H_2O_2	76[e]
5.	*Mn-Ac@ASMNP* (20 mg)	H_2O_2	95[f]
6.	*Mn-Ac@ASMNP* (25 mg)	H_2O_2	94[g]
7.[*]	*Mn-Ac@ASMNP* (20 mg)	-	-

[a]Reaction conditions: Benzyl bromide (1 mmol), H_2O_2 (1 mL), Ethanol (6 mL), reflux, 1.5 h
[b]Yield was determined by GC-MS; Amount of *Mn-Ac@ASMNP*: [c]20 mg, [d]10 mg, [e]15 mg, [f]20 mg, [g]25 mg.
[*]Reaction performed without hydrogen peroxide.

Furthermore, a comparison of the catalyst with earlier reported heterogeneous catalysts for oxidation of organic halides is depicted in Table S2; present organic-inorganic hybrid nanocatalyst (Mn-Ac@ASMNP) offers considerable advantages in terms of cost, yield, short reaction time and non-toxic characteristics in addition to inherent advantages of a heterogeneous catalytic system.

Table S2. Comparison of Mn-Ac@ASMNP with literature precedents using both homogeneous and heterogeneous catalysts for the oxidation of organic halides to carbonyl compounds.

No	Benzyl halide	Carbonyl Compound	Catalyst	Reaction conditions	Yield (%)	Ref.
1			Mg-Al Hydrotalcites	DMSO, HT 40% w/w of benzylic halide, 140 ^oC, 6h	82	1
2			Mag-Mo	H_2O_2, Ethanol, reflux, 4h	95	2
3			Co(salen)-POM	H_2O_2, CH_3CN, 25 ^oC, 2h	95	3
4			N-methylmorpholine N-oxide	[emim]Cl, KI, MW, 100 ^oC, 2 min	95	4
5			H_5IO_6	$[C_{12}mim][FeCl_4]$, 30 ^oC, 2 h	94	5
6*			$Ru(bpy)_3Cl_2$	4-methyoxypyridine, Li_2CO_3, DMA, air, 25 ^oC, Sunlight, 9 h	78	6
7*			TEMPO/KNO_2,	O_2, H_2O, KBr, reflux, 4 h	92	7

8*			$NaIO_4$-DMF	150 °C, 40 min	80	8
9*			KNO_3/CTAB	KOH, reflux, 3 h	91	9
10			H_5IO_6/V_2O_5	[bmpy]PF_6, 50 °C, 3 h	92	10
11*			TMA/H_2O_2	H_2O, reflux, 30 min	82	11
12			Modified Crosslinked polyacrylamide anchored Schiff base-cobalt complex	H_2O_2, H_2O, 75 °C, 4 h	90	12
13			V_2O_5	H_2O_2, H_2O, reflux, 6h	70	13
14			*Mn-Ac@ASMNP*	H_2O_2, ethanol, reflux, 1.5h	95	Present work

* Homogeneous catalyst

NMR Characterization data of compounds

Table 1, entry 1: Benzaldehyde

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.84-7.24 (m, 5H), 9.99 (s, 1H).

Table 1, entry 3: 4-methylbenzaldehyde

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 2.35 (s, 3H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 9.87(s, 1H).

Table 1, entry 5: 4-methoxybenzaldehyde

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 3.86 (s, 3H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 9.85 (s, 1H).

Table 1, entry 7: 4-chlorobenzaldehyde

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.51 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 9.96 (s, 1H).

Table 1, entry 8: 4-nitrobenzaldehyde

^{1} H NMR (400 MHz, $CDCl_3$): *δ* 8.05 (d, *J* = 8.4 Hz, 2H), 8.37 (d, *J* = 8.4 Hz, 2H), 10.14 (s, 1H).

Table 1, entry 12: 4-chloroacetophenone

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 2.57 (s, 3H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H).

Table 1, entry 13: 4-methoxyacetophenone

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 2.54 (s, 3H), 3.89 (s, 3H), 6.92 (d, *J* = 6.12 Hz, 2H), 7.92 (d, *J* = 6.12 Hz, 2H).

Table 1, entry 14: Cyclohexanone

^{1} H NMR (400 MHz, $CDCl_3$): *δ* 1.672 (t, *J*= 6.8 Hz, 2H), 1.803-1.790 (m, 4H), 2.275 (t, *J* = 6.8 Hz, 4H).

Table 1, entry 17: Acetophenone

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 2.582 (s, 3H), 7.448 (t, *J*=6.08Hz, 2H), 7.536 (d, *J*= 7.64 Hz, 1H), 7.939 (d, *J*=6.8Hz, 2H).

Table 1, entry 19: Benzophenone

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.58-7.44 (m, 6H), 7.76 (d, *J* = 7.6, 4H).

NMR Spectra of selected compounds

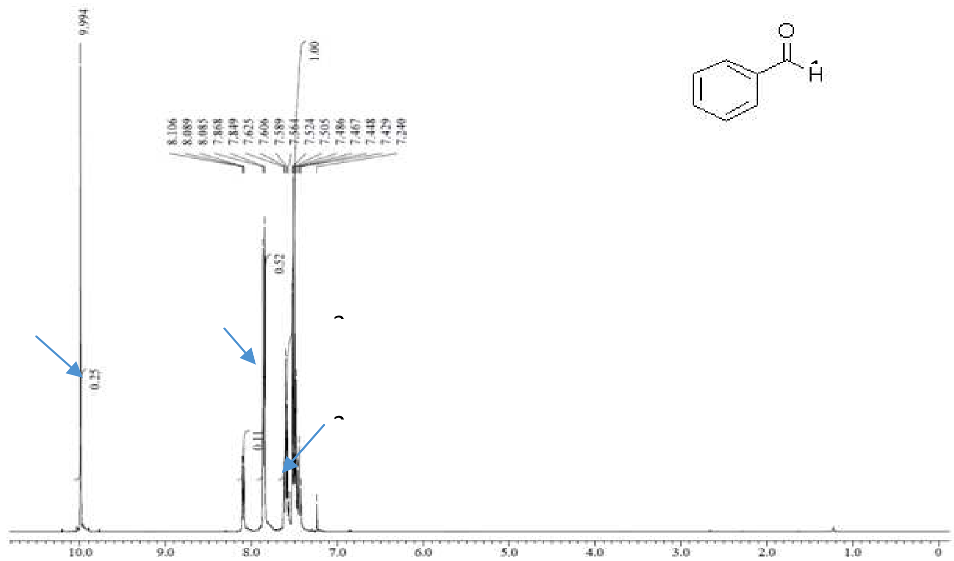


Figure S6a: ^{1}H NMR spectrum of products, entries 1 and 2, Table 1.

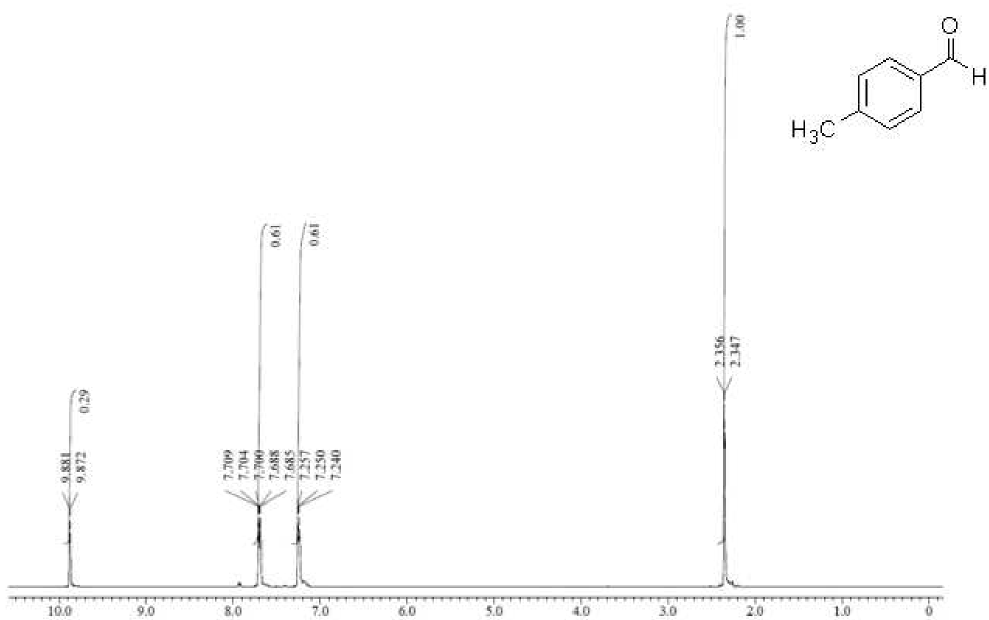


Figure S6b : ^{1}H NMR of product of entry 3, Table 1.

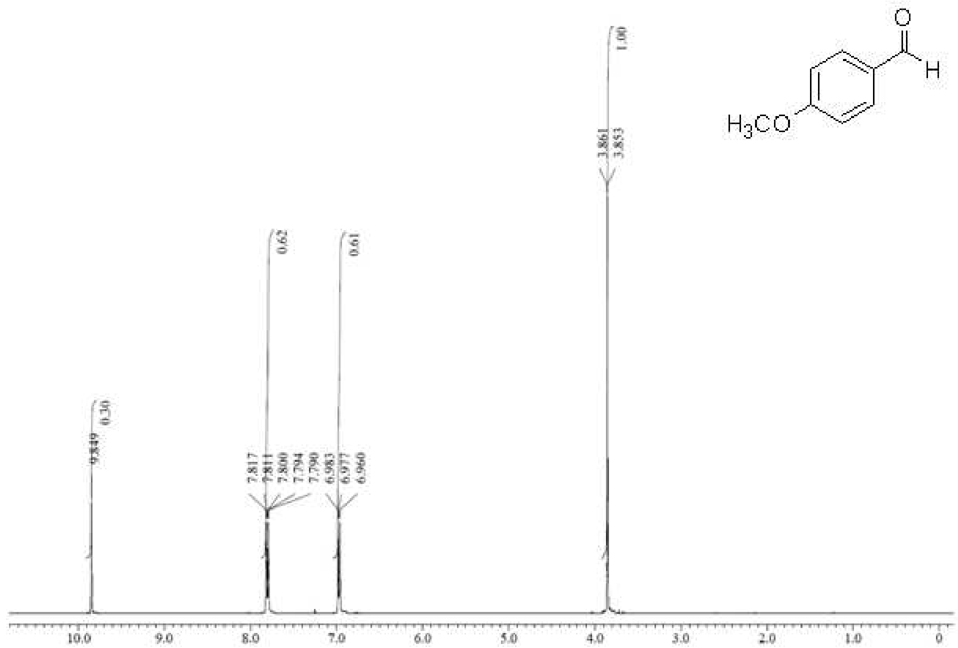


Figure S6c: ^{1}H NMR of product of entry 5, Table 1.

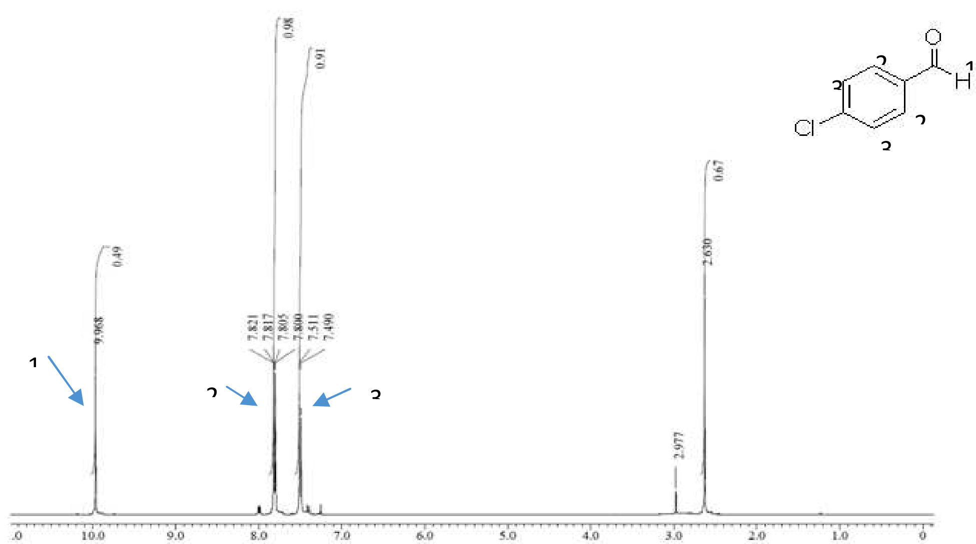


Figure S6d: ^{1}H NMR of products of entries 4 and 7 Table 1.

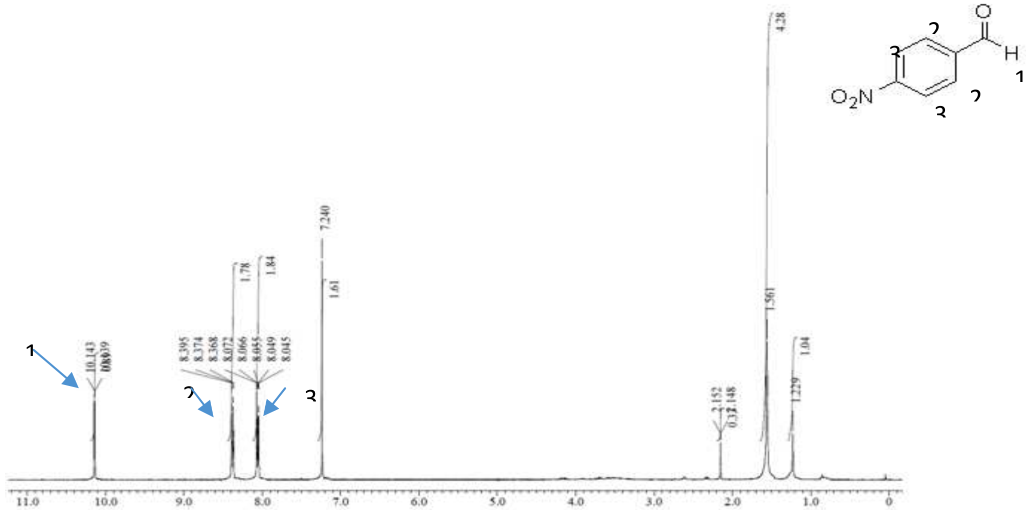


Figure S6e: [1]H NMR of products of entries 8 and 9, Table 1.

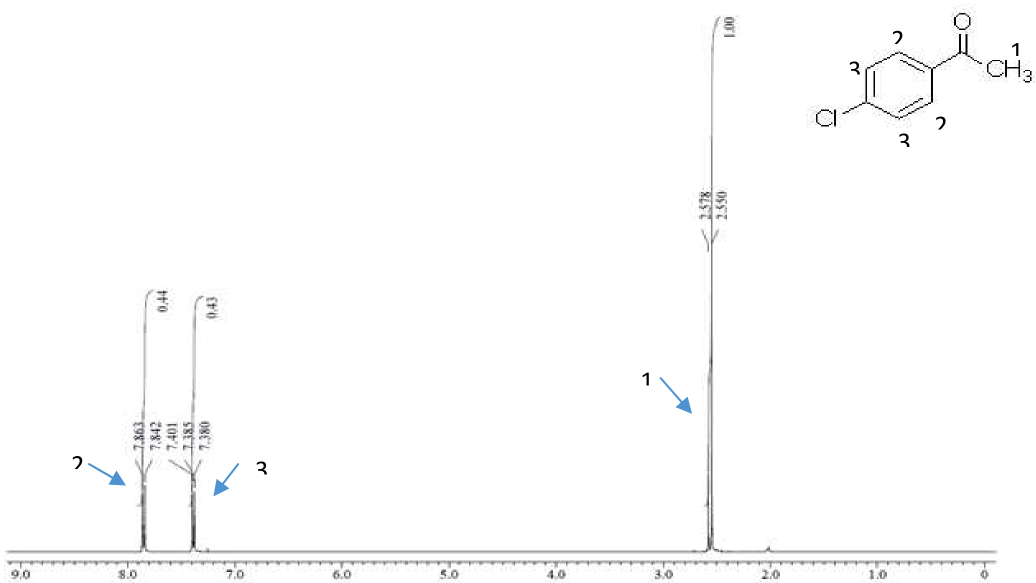


Figure S6: f [1]H NMR of product of entry 12, Table 1.

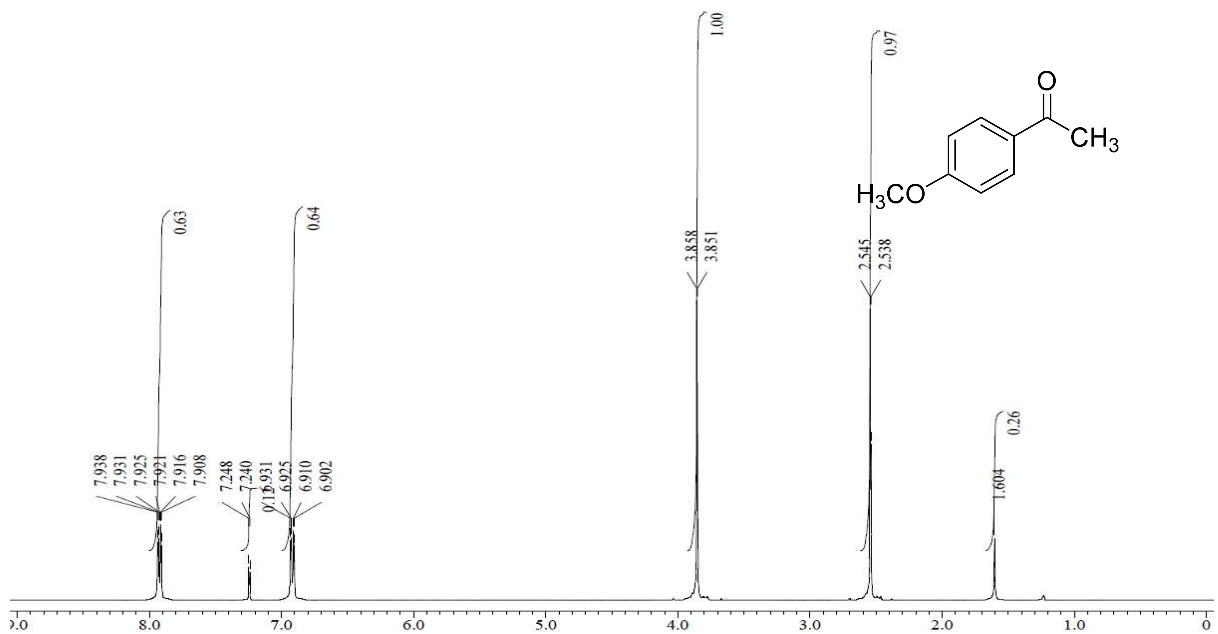


Figure S6g: ^{1}H NMR of product of entry 13, Table 1.

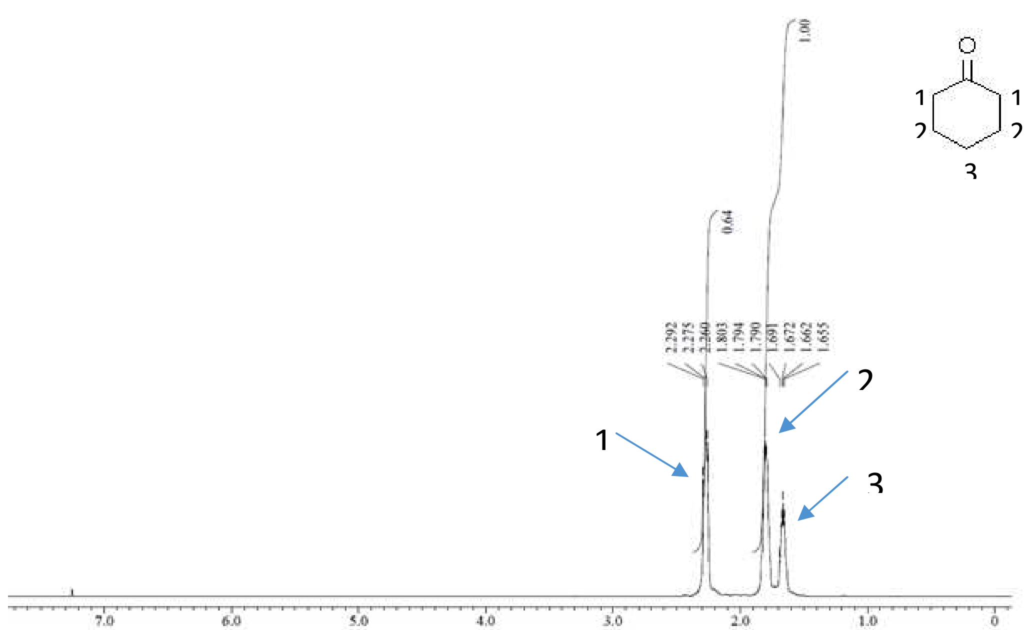


Figure S6h: ^{1}H NMR of product of entry 14, Table 1.

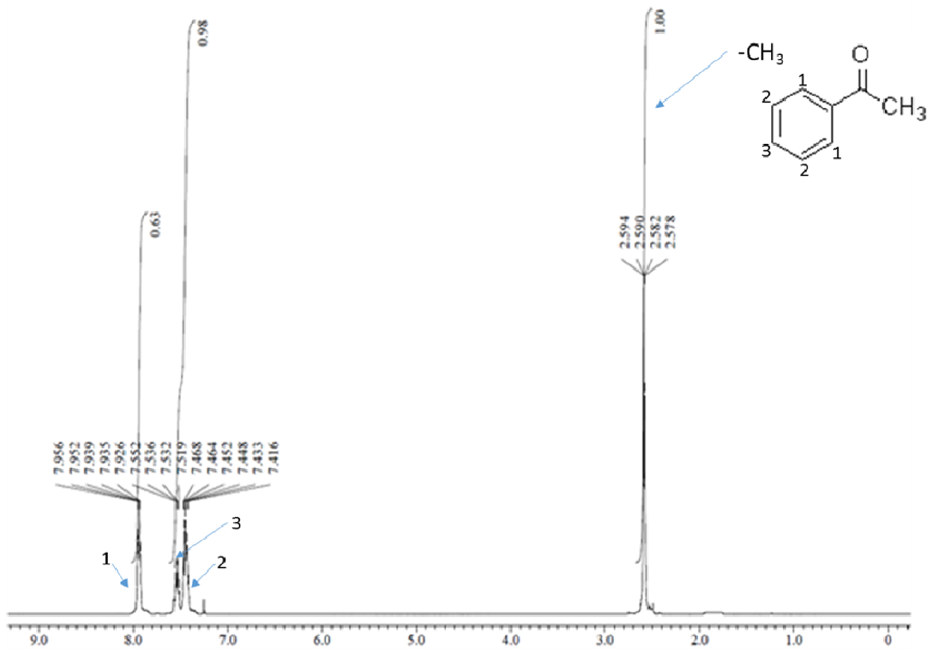


Figure S6i: ^{1}H NMR of product of entry 17, Table 1.

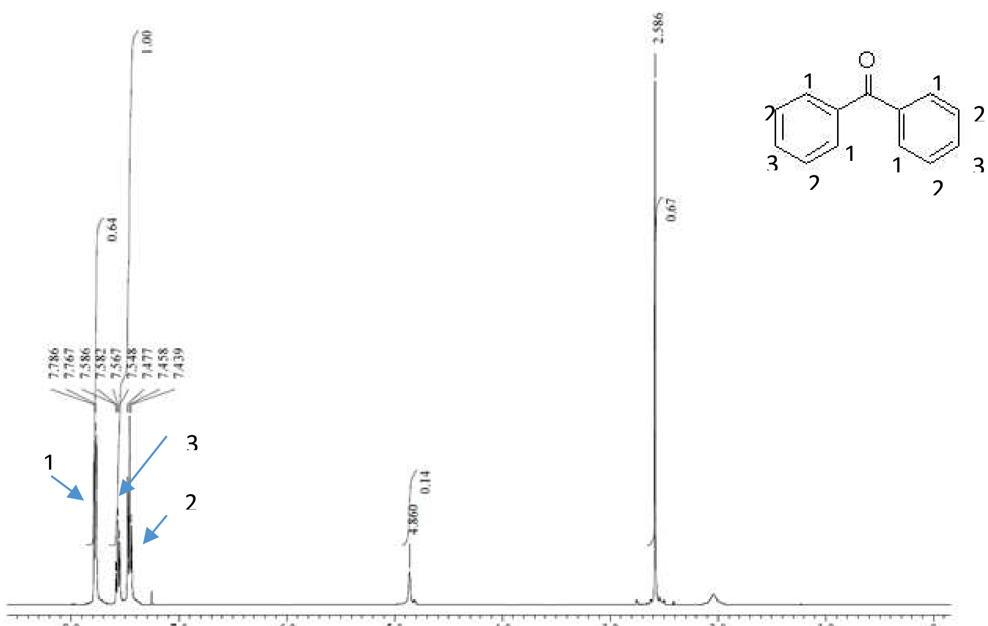


Figure S6j: ^{1}H NMR of product of entry 19, Table 1.

References -

1. Kshirsagar, S. W.; Patil, N. R.; Samant, S. D. Mg–Al hydrotalcites as the first heterogeneous basic catalysts for the Kornblum oxidation of benzyl halides to benzaldehydes using DMSO. *Tetrahedron Lett.* **2008,** *49*, 1160-1162.
2. Bayat, A.; Shakourian-Fard, M.; Ramezanpour, S.; Mahmoodi Hashemi, M. A green procedure for direct oxidation of organic halides to aldehydes and ketones catalyzed by a molybdate-based catalyst. *New J. Chem.* **2015,** *39*, 3845-3851.
3. Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Mohammadpoor-Baltork, I.; Rasouli, N. Investigation of catalytic activity of cobalt–Schiff base complex covalently linked to the polyoxometalate in the alkene and benzyl halide oxidation with hydrogen peroxide. *Catal. Commun.* **2008,** *9*, 219-223.
4. Khumraksa, B.; Phakhodee, W.; Pattarawarapan, M. Rapid oxidation of organic halides with N-methylmorpholine N-oxide in an ionic liquid under microwave irradiation. *Tetrahedron Lett.***2013,** *54*), 1983-1986.
5. Hu, Y. L.; Liu, Q. F.; Lu, T. T.; Lu, M. Highly efficient oxidation of organic halides to aldehydes and ketones with H5IO6 in ionic liquid [C12mim][$FeCl_4$]. *Catal. Commun.* **2010,** *11*, 923-927.
6. Su, Y.; Zhang, L.; Jiao, N. Utilization of natural sunlight and air in the aerobic oxidation of benzyl halides. *Org.Lett.* **2011,** *13*, 2168-2171.
7. Liu, Q.; Lu, M.; Yang, F.; Wei, W.; Sun, F.; Yang, Z.; Huang, S. Aerobic Oxidation of Benzylic Halides to Carbonyl Compounds with Molecular Oxygen Catalyzed by TEMPO/KNO_2 in Aqueous Media. *Synth.Commun.* **2010,** *40*, 1106-1114.
8. Das, S.; Panigrahi, A. K.; Maikap, G. C. $NaIO_4$–DMF: a novel reagent for the oxidation of organic halides to carbonyl compounds. *Tetrahedron Lett.* **2003,** *44*, 1375-1377.
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