

Supporting Information

**Heterogeneous Sodium-Manganese Oxide Catalyzed Aerobic  
Oxidative Cleavage of 1,2-Diols**

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## **Author Contributions**

V.E. Conceptualization: Lead; Data curation: Equal; Investigation: Lead; Methodology: Lead; Supervision: Lead; Writing—original draft: Lead; Writing—review & editing: Equal

C.L. Data curation: Equal; Investigation: Equal; Methodology: Equal; Writing—original draft: Supporting; Writing—review & editing: Equal

P.C. Methodology: Supporting; Writing—original draft: Supporting; Writing—review & editing: Supporting

P.A. Conceptualization: Supporting; Funding acquisition: Lead; Project administration: Supporting; Supervision: Supporting; Writing—original draft: Supporting; Writing—review & editing: Supporting.

## General methods

All common reagents and solvents were obtained from Sigma-Aldrich, Alfa Aesar and Acros Organics and were used without any further purification. Non-commercially available 1,2-diols were prepared by reduction of corresponding commercial diketones according to a known procedure.<sup>[1]</sup> NMR spectra were obtained on an Agilent DD2 400 MHz NMR spectrometer. Chemical shifts are expressed in parts per million (ppm,  $\delta$ ), with tetramethylsilane (TMS) as reference. All coupling constants ( $J$ ) are absolute values and are expressed in Hertz (Hz). The following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, etc. GC were recorded on a Shimadzu GC-2010 Plus, equipped with an Agilent J&W GC column, DB-5, 60 m x 0.25 mm x 0.25  $\mu$ m, using He as carrier gas, with a flame ionization detector (FID). All analyses were performed including dodecane as internal standard. FTIR spectra were recorded on a FTIR/Raman Thermo Nicolet 6700 spectrometer, in ATR mode. ICP-AES measurements were performed using the Perkin Elmer Optima 3000. Samples of 10 mg were digested and dissolved in 2% HNO<sub>3</sub> acid, and were quantified against external standards. SEM and EDX analyses were performed using the Hitachi SU-70 field emission microscope. Samples were pre-dried in vacuum overnight, and were examined with a 10kV beam power under ultra-high vacuum without surface treatment. For EDX analyses, 5 random quadrants were selected per sample for composition analyses. XRPD measurements were performed on a Rigaku SmartLab X-ray Diffractometer equipped with a Cu line-focus sealed tube and a NaI SC70 scintillation detector. Measurements were made with a 40 kV, 44 mA beam, with an incident slit of 2/3 deg and a length limiting slit of 5.00 mm, in the range 2 $\theta$  from 10° to 90° locked couple scan type, a step size of 0.05° and a scan speed of 10.33 deg/min. TGA was performed with a TA Instruments Q50, under a flow of N<sub>2</sub>, on 5 mg of material. XPS analysis was performed using a ThermoScientific ESCALAB 250 instrument. Spectra were collected using a monochromatic Al X-ray source. A low energy electron flood and top-side contact were used for charge neutralization. Survey spectra were collected using a pass energy of 150 eV. Multiplex composition scans were acquired with 20 eV pass energy. Products were characterized by NMR spectroscopy and by GC, by comparison of their retention times with those of pure standards.

## Preparation of Na-Mn LMO catalyst

In a typical synthesis, 178 mg (0.9 mmol) of manganese(II) chloride tetrahydrate (MnCl<sub>2</sub>·4H<sub>2</sub>O) were dissolved in 9 mL of deionized water, in a 100 mL flask. Under magnetic stirring (400 rpm), 0.279 mL (2.7 mmol) of a 30% aqueous solution of hydrogen peroxide were added in one portion. The colorless resulting solution (solution A) was stirred for 5 min at room temperature. Then, a solution of 1536 mg (38.4 mmol) of sodium hydroxide (NaOH) in 2 mL of deionized water (solution B) was added to solution A, in one portion. A black suspension formed immediately. The sides of the flask were rinsed with 10 mL of deionized water, then the suspension was stirred (800 rpm) at room temperature for 90 min. The suspension was filtered (Whatman® glass microfiber filters, 4.25 cm diameter, reference 1820042) then rinsed with 3 portions of 100 mL deionized water, then one portion of 50 mL ethanol. The resulting black solid should not be fully left to dry before the end of all rinses, to preserve its activity. The solid was then collected and dried in air, in an oven at 105 °C for 18 h.

## Representative procedure of 1,2-diol aerobic oxidative cleavage

In a typical reaction, a mixture of *meso*-hydrobenzoin (42.9 mg, 0.2 mmol), Na-Mn LMO (1 mol%) and 1-butanol (1 mL) was added in a 7 mL flask, equipped with a O<sub>2</sub> balloon. The reaction mixture was heated to 100 °C under magnetic stirring (400 rpm) for 1 h. After reaction, the mixture was cooled to room temperature and the catalyst separated by filtration. The reaction analysis was performed by GC, using dodecane as internal standard. Most reactions were performed in duplicate. For product isolation, the same

procedure was followed in the same proportions, on 1 mmol of *meso*-hydrobenzoin. The product was isolated after filtration then concentration under reduced pressure, in presence of cyclohexane or dichloromethane to remove traces of 1-butanol.

### Reaction procedure for domino reactions

#### Ethyl 3-phenyl-2-propenoate (**5**)

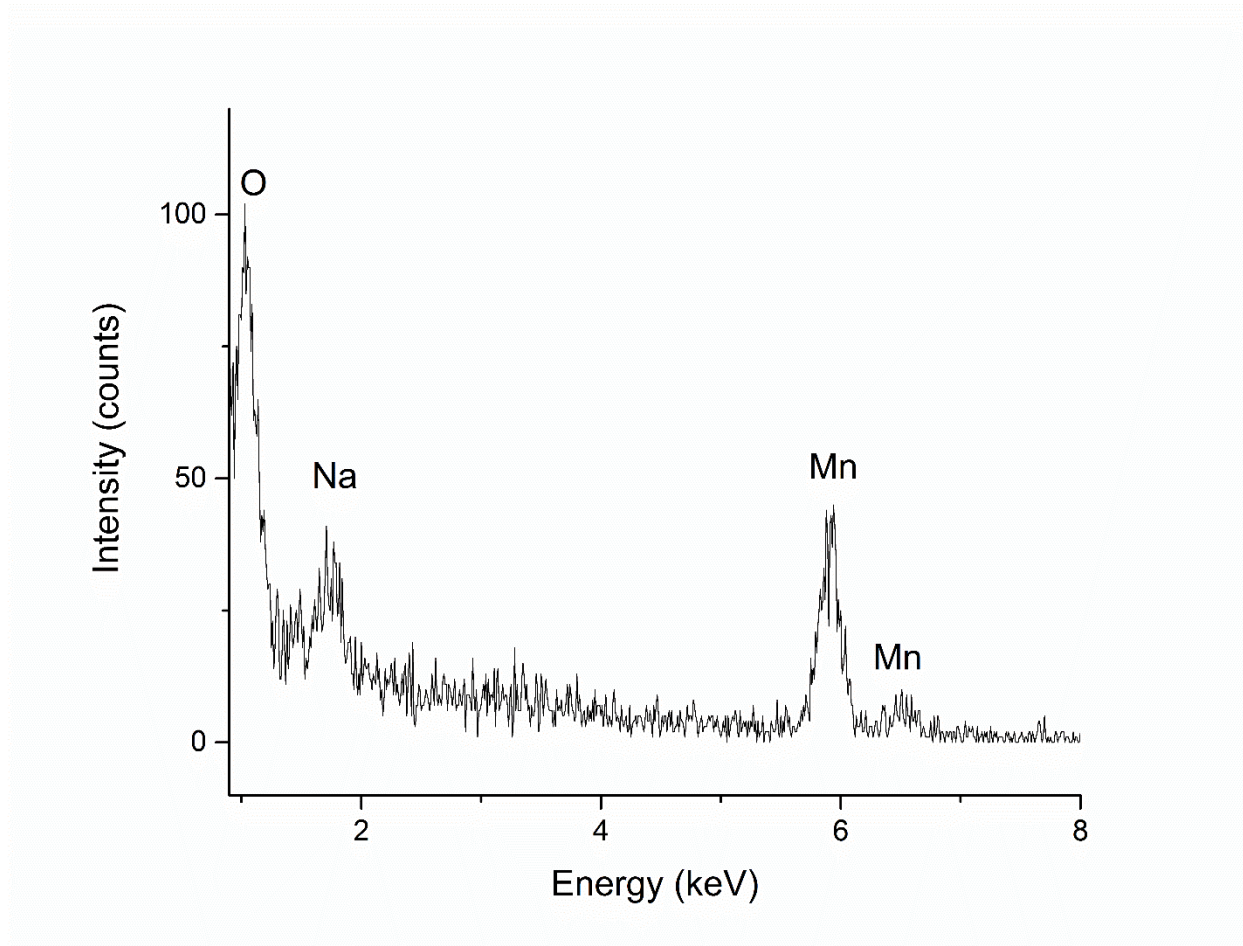
A mixture of *meso*-hydrobenzoin (42.9 mg, 0.2 mmol), (carbethoxymethylene)triphenylphosphorane (209 mg, 0.6 mmol), Na-Mn LMO (10 mol%) and 1-butanol (1 mL) was added in a 7 mL flask, equipped with a O<sub>2</sub> balloon. The reaction mixture was heated to 100 °C under magnetic stirring (400 rpm). The progress of the reaction was followed by GC, using dodecane as internal standard. After 1 h, the mixture was cooled to room temperature and the catalyst separated by filtration. Yield and *Z/E* ratios were determined by <sup>1</sup>H NMR.

#### (2*E*)-1,3-diphenyl-2-propen-1-one (**6**)

A mixture of *meso*-hydrobenzoin (42.9 mg, 0.2 mmol), acetophenone (52.9 mg, 0.44 mmol), sodium hydroxide (10 mol%), Na-Mn LMO (10 mol%) and 1-butanol (1 mL) was added in a 7 mL flask, equipped with a O<sub>2</sub> balloon. The reaction mixture was heated to 100 °C under magnetic stirring (400 rpm). The progress of the reaction was followed by GC, using dodecane as internal standard. After 1 h, the mixture was cooled to room temperature and the catalyst separated by filtration. The mixture was neutralized by HCl<sub>aq</sub> 1M, extracted with diethyl ether, and then concentrated under reduced pressure. Yield and *Z/E* ratios were determined by <sup>1</sup>H NMR.

#### [*N(E)*]-*N*-(phenylmethylene)cyclohexanamine (**8**)

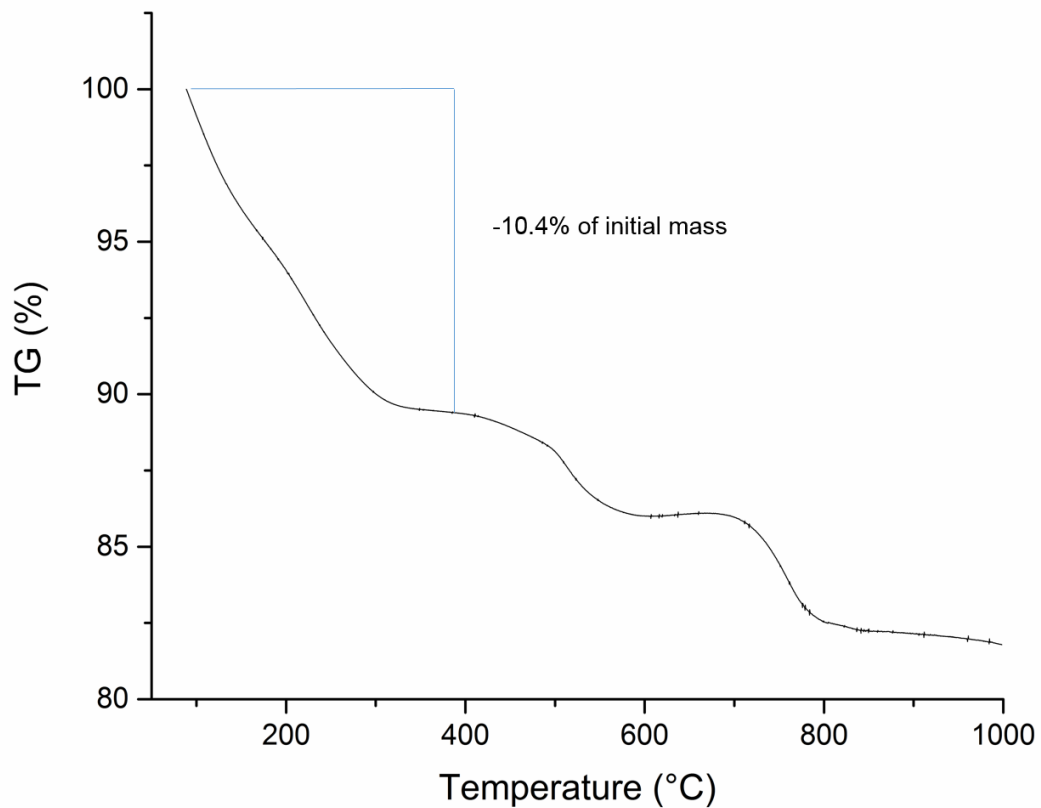
A mixture of *meso*-hydrobenzoin (42.9 mg, 0.2 mmol), cyclohexylamine (43.6 mg, 0.44 mmol), Na-Mn LMO (10 mol%) and 1-butanol (1 mL) was added in a 7 mL flask, equipped with a O<sub>2</sub> balloon. The reaction mixture was heated to 100 °C under magnetic stirring (400 rpm). The progress of the reaction was followed by GC, using dodecane as internal standard. After 1 h, the mixture was cooled to room temperature and the catalyst separated by filtration. Yield and *Z/E* ratios were determined by <sup>1</sup>H NMR.



**Figure S1.** EDX spectrum of Na-Mn LMO.

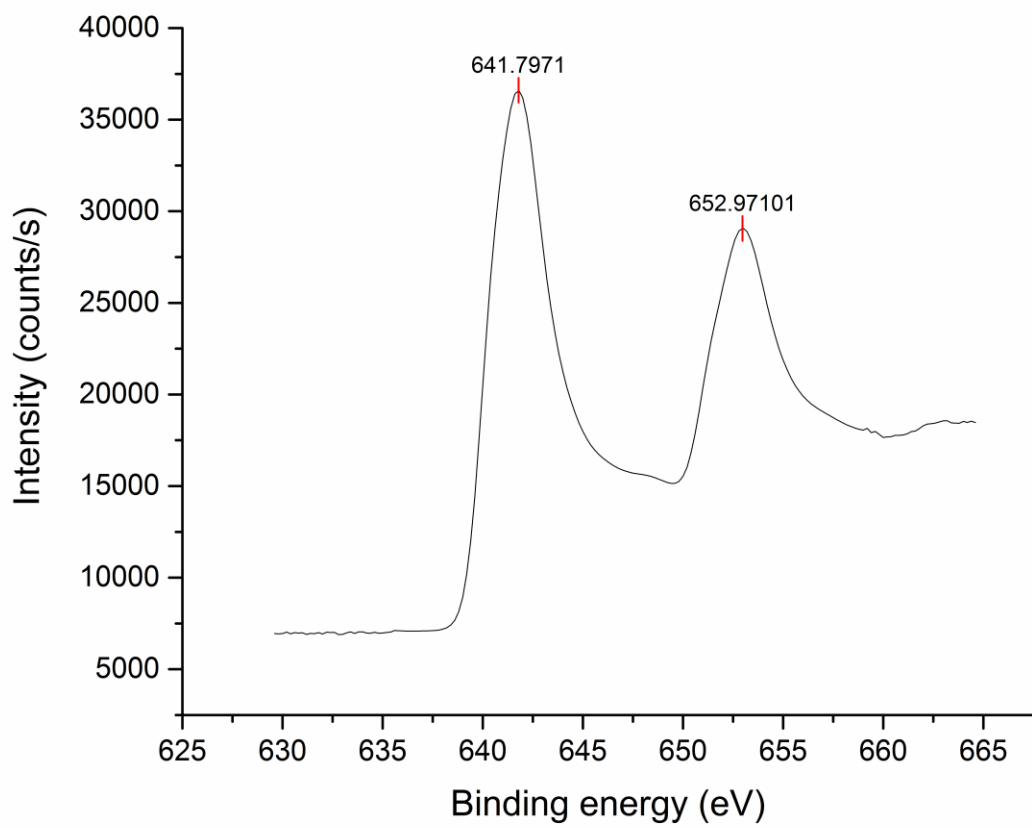
**Table S1.** ICP-AES analysis of Na-Mn LMO.

Detected elements	wt%	sd (wt%)
Mn	52.76	0.65
Na	6.05	0.16

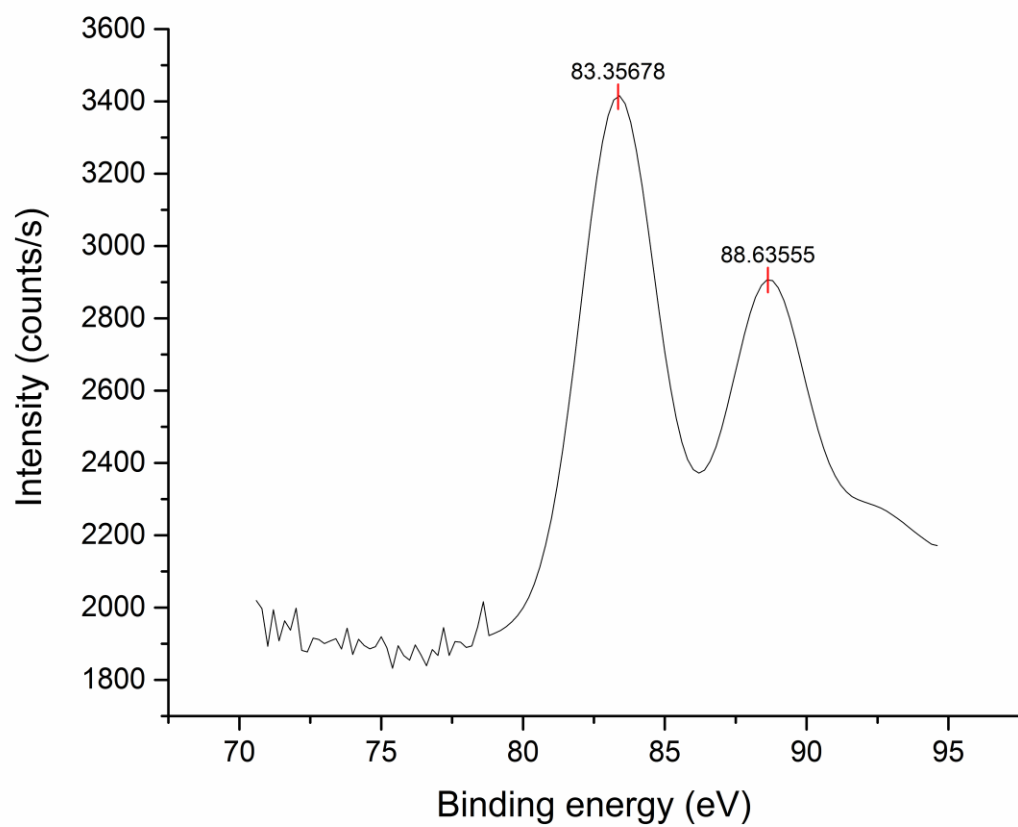


**Figure S2.** Thermogravimetric analysis of Na-Mn LMO showing the loss of H<sub>2</sub>O corresponding to 10.4% of initial mass. Following plateaux observed beyond 400 °C correspond to the loss of oxygen and to the successive formation of Mn<sub>2</sub>O<sub>3</sub> then Mn<sub>3</sub>O<sub>4</sub>.

According to ICP-AES and TG analyses, Na-Mn LMO can be formulated as Na<sub>0.274</sub>MnO<sub>2</sub>·0.6 H<sub>2</sub>O (Calculated: Na, 6.05; Mn, 52.80, O, 39.98. Found: Na, 6.05; Mn, 52.76; O, 40.02)



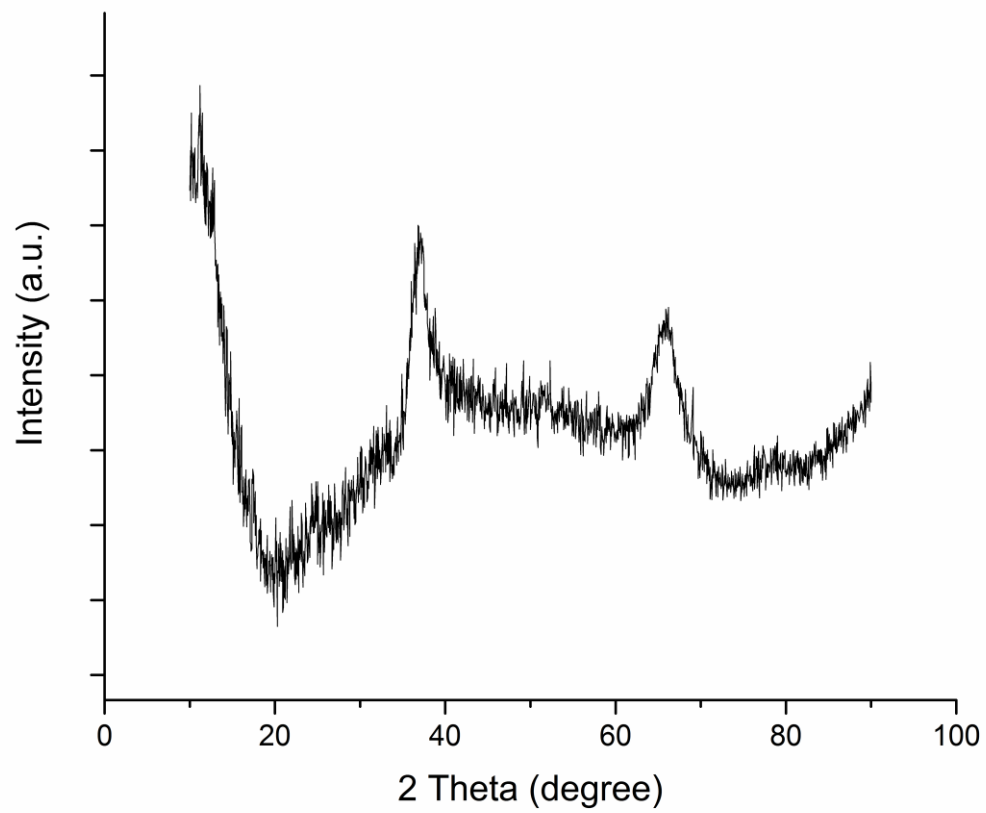
**Figure S3.** XPS spectrum of Na-Mn LMO for Mn 2p.



**Figure S4.** XPS spectrum of Na-Mn LMO for Mn 3s.

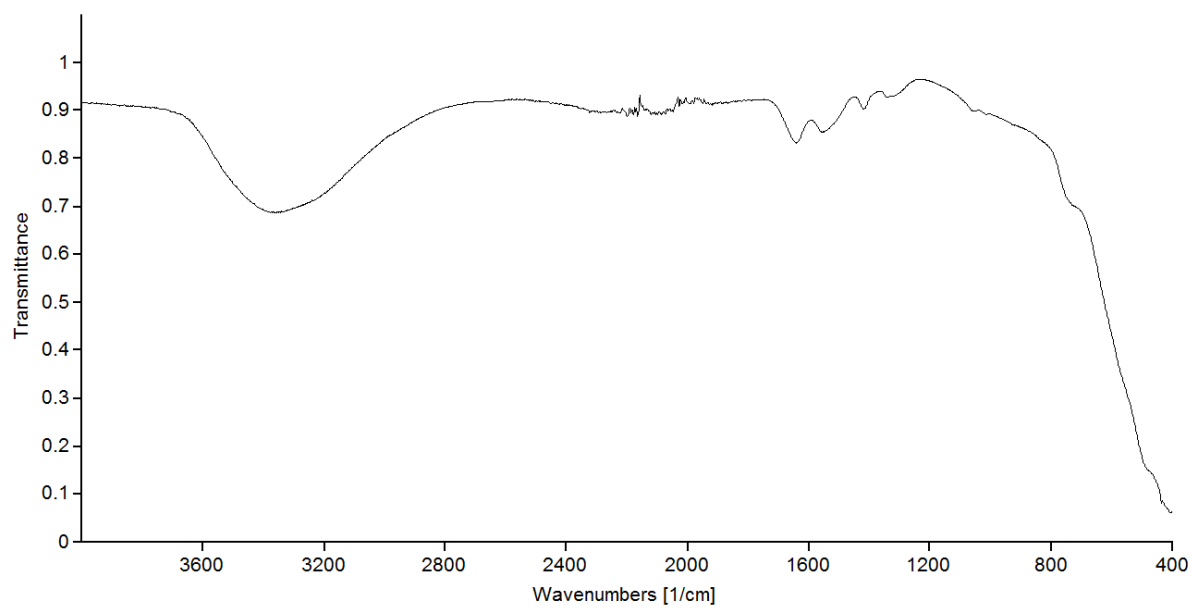
Observed energy values are characteristic of a mixed valence for Mn, intermediate between +3 and +4.<sup>[2]</sup>





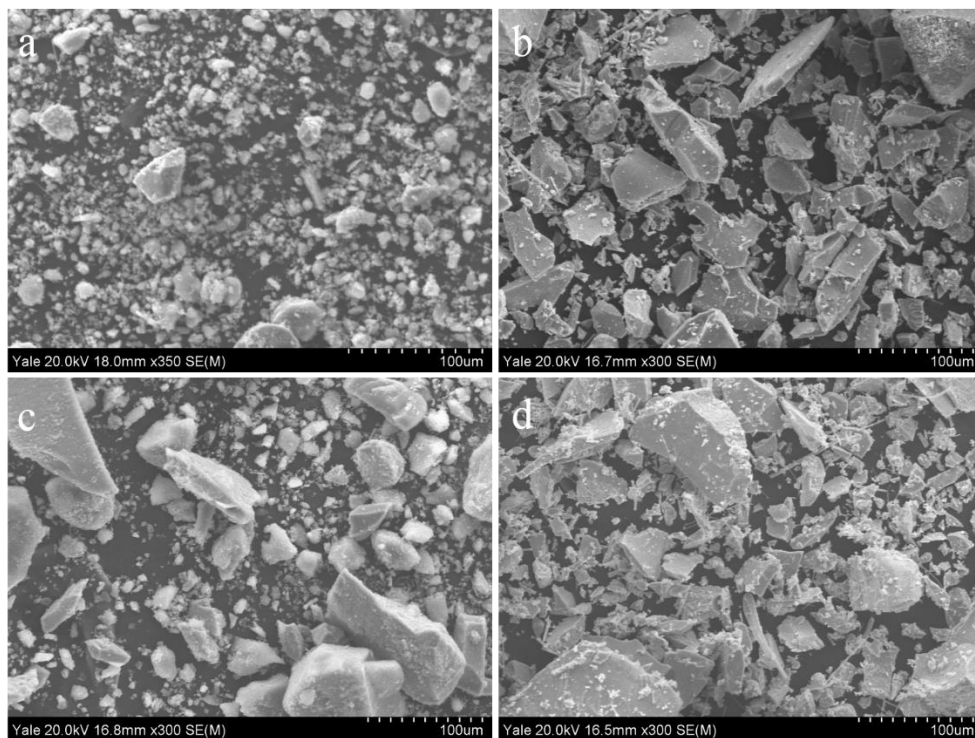
**Figure S5.** XRPD spectrum of Na-Mn LMO.

The diffraction pattern can be indexed to birnessite phase (reference PDF Card No.: 00-043-1456).



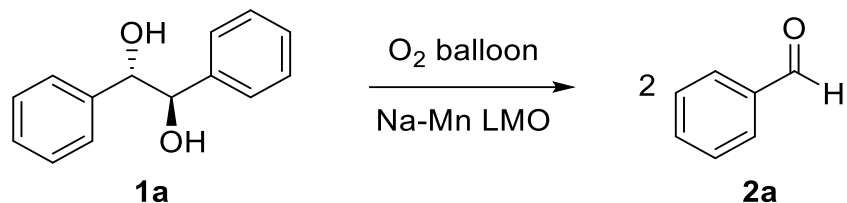
**Figure S6.** FTIR spectrum of Na-Mn LMO.

The FTIR spectrum displays a strong absorption at 400 cm<sup>-1</sup>, characteristic of layered Mn oxides.



**Figure S7.** SEM images of catalysts prepared in different basic conditions: a) with NaOH, 1.8 mol.L<sup>-1</sup>, b) with NaOH, 2.2 mol.L<sup>-1</sup>, c) with NaOH, 2.54 mol.L<sup>-1</sup>, d) with CsOH, 1.8 mol.L<sup>-1</sup>.

**Table S2.** Optimization of *meso*-hydrobenzoin oxidative cleavage catalyzed by Na-Mn LMO.<sup>[a]</sup>



Entry	Catalyst (Mn mol%)	Solvent	T [°C]	t [h]	Conversion [%] <sup>[b]</sup>	Selectivity [%] <sup>[b,c]</sup>
1	10	acetonitrile	25	24	22	>99
2	10	acetonitrile	78	3	29	>99
3	10	ethyl acetate	78	3	19	>99
4	10	toluene	78	3	42	>99
5	10	2-butanone	78	3	7	>99
6	10	water	78	3	10	>99
7	10	acetic acid	78	3	36	>99
8	10	ethanol	78	3	98	>99
9	10	1-butanol	100	1	100	>99
10	1	1-butanol	100	1	99	>99

[a] Reaction conditions: *meso*-hydrobenzoin (42.9 mg, 0.2 mmol), Na-Mn LMO (1-10 mol% Mn), 1 mL of solvent, O<sub>2</sub> balloon. [b] Conversion and selectivity were determined by GC using dodecane as internal standard. Remaining mass balance is recovered starting materials. [c] Ratio of benzaldehyde yield to conversion as a percentage.

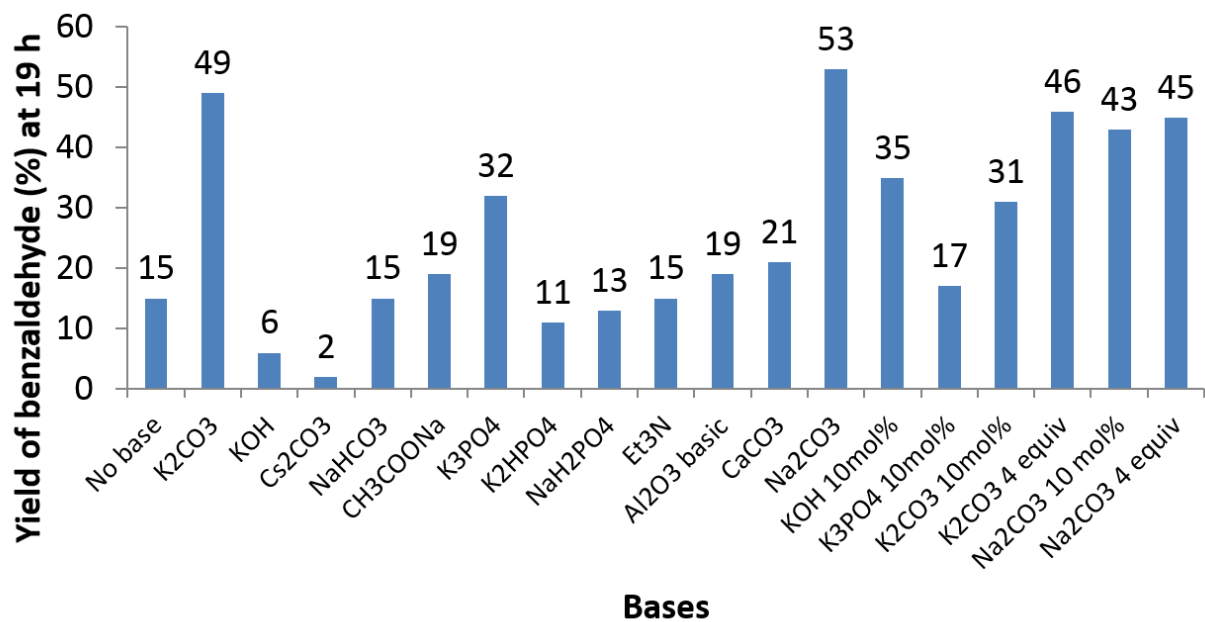
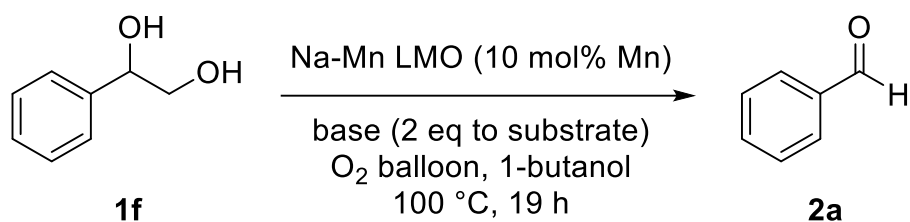
#### Average TOF for the oxidative cleavage of *meso*-hydrobenzoin

Reaction conditions: *meso*-hydrobenzoin (429 mg, 2 mmol), Na-Mn LMO (0.1 mol% Mn), 1-butanol (10 mL), 100 °C, O<sub>2</sub> balloon, yield after 1 h was 18 %. The Na-Mn LMO catalyst displayed a turnover number (TON) of 180 (moles of *meso*-hydrobenzoin converted per mole of catalyst), corresponding to a turnover frequency (TOF) of 180 h<sup>-1</sup> in the initial 60 minutes.

**Table S3.** Influence of basicity on catalyst morphology and activity in oxidative cleavage of *meso*-hydrobenzoin **1a**<sup>[a]</sup>

Base used for catalyst preparation	Concentration of the base (mol.L <sup>-1</sup> )	Yield of <b>2a</b> (%) <sup>[b]</sup>	Average particle size (μm) <sup>[c]</sup>	sd (μm) <sup>[c]</sup>
NaOH	0.17	84	6.7	2.1
NaOH	0.85	93	5.3	1.5
NaOH	1.80	99	4.9	1.3
NaOH	2.20	14	32.5	7.7
NaOH	2.54	18	33.3	9.6
CsOH	1.80	15	40.0	8.0
TMA·OH	1.80	47	24.4	7.9

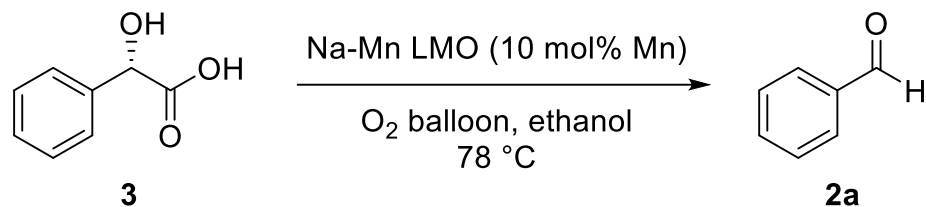
[a] Reaction conditions: *meso*-hydrobenzoin (42.9 mg, 0.2 mmol), catalyst (1 mol% Mn), 1-butanol (1 mL), O<sub>2</sub> balloon, 100 °C, 1 h. [b] Determined by GC using dodecane as internal standard. Remaining mass balance is recovered starting materials. [c] Determined by SEM measurements.



**Figure S8.** Comparison of bases efficiency on oxidative cleavage of 1-phenyl-1,2-ethanediol **1f**.

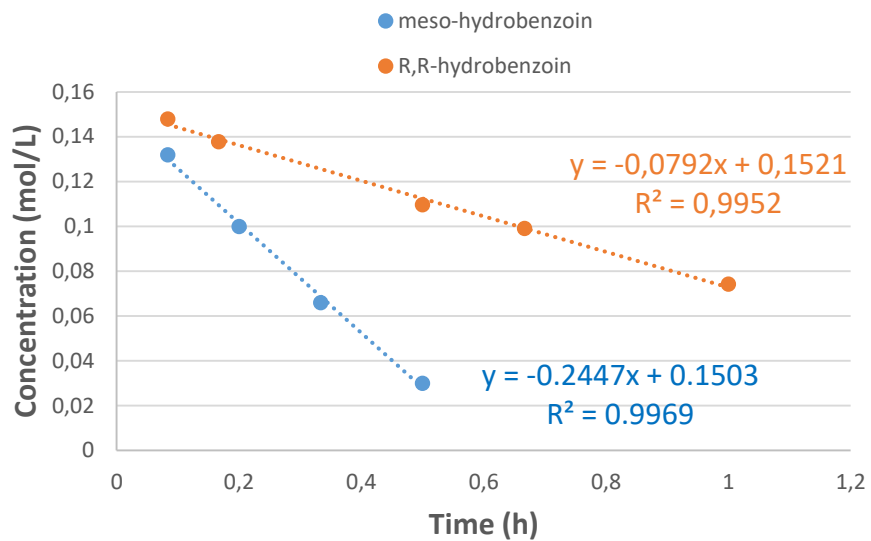
Reaction conditions: 1-phenyl-1,2-ethanediol (0.2 mmol), Na-Mn LMO (10 mol% Mn), 1-butanol (1 mL), base (0.4 mmol, unless otherwise specified), O<sub>2</sub> balloon, 19 h. Yield determined by GC using dodecane as internal standard.

**Table S4.** Oxidative cleavage of (S)-mandelic acid.<sup>[a]</sup>



Entry	Base	<i>t</i> [h]	Conversion [%] <sup>[b]</sup>	Selectivity [%] <sup>[b,c]</sup>
1	-	27	80	>99
2	Na <sub>2</sub> CO <sub>3</sub> <sup>[d]</sup>	7	83	>99

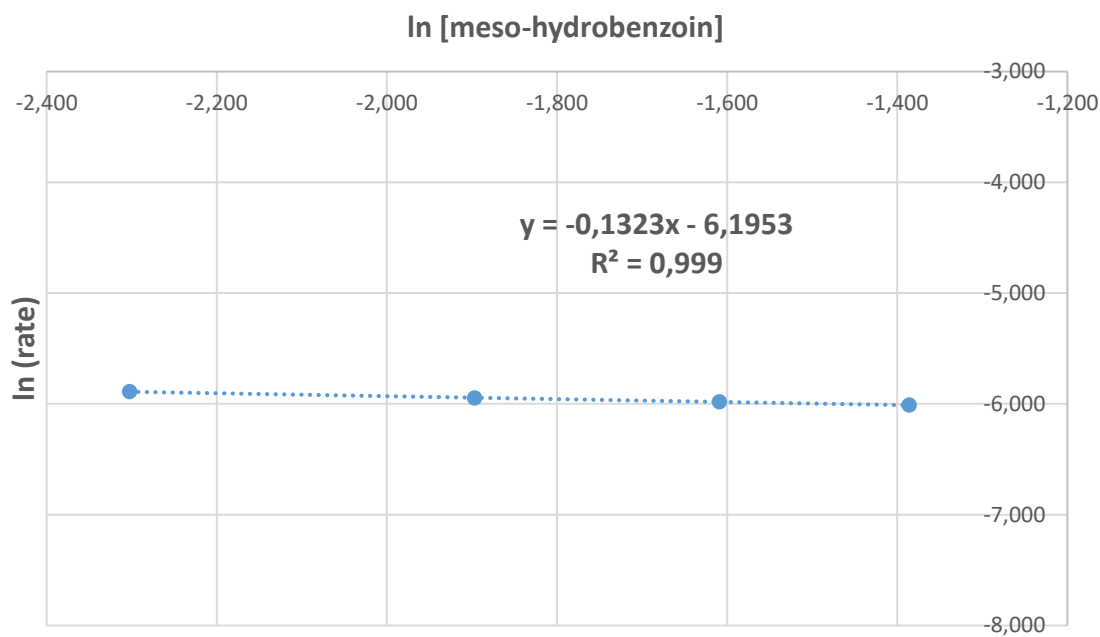
[a] Reaction conditions: (S)-mandelic acid (0.2 mmol), Na-Mn LMO (10 mol% Mn), ethanol (1 mL), O<sub>2</sub> balloon, 78 °C. [b] Conversion and selectivity were determined by GC using dodecane as internal standard. [c] Ratio of benzaldehyde yield to conversion as a percentage. Remaining mass balance is recovered starting materials. [d] 2 equivalents toward substrate.



**Figure S9.** Kinetic comparison of the oxidative cleavage of *meso*- and (*R,R*)- hydrobenzoin by Na-Mn LMO.

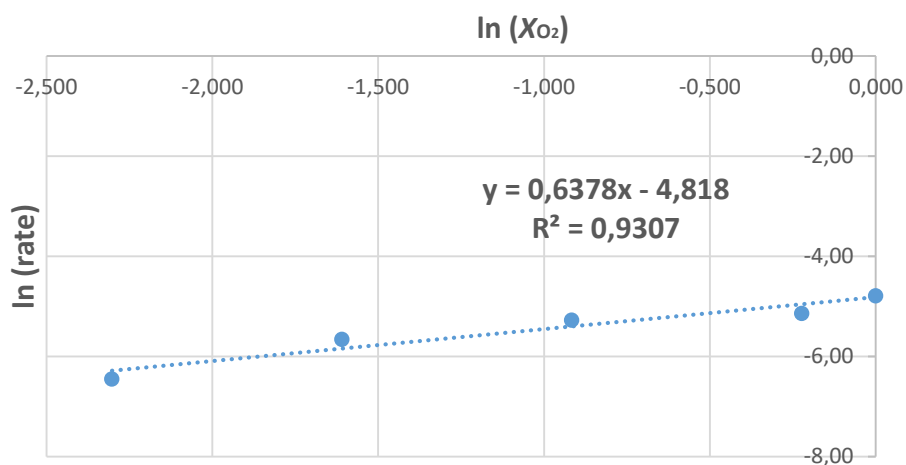
Reaction conditions: substrate (0.2 mmol), Na-Mn LMO (1 mol% Mn), 1-butanol (1 mL), O<sub>2</sub> balloon, 100 °C.





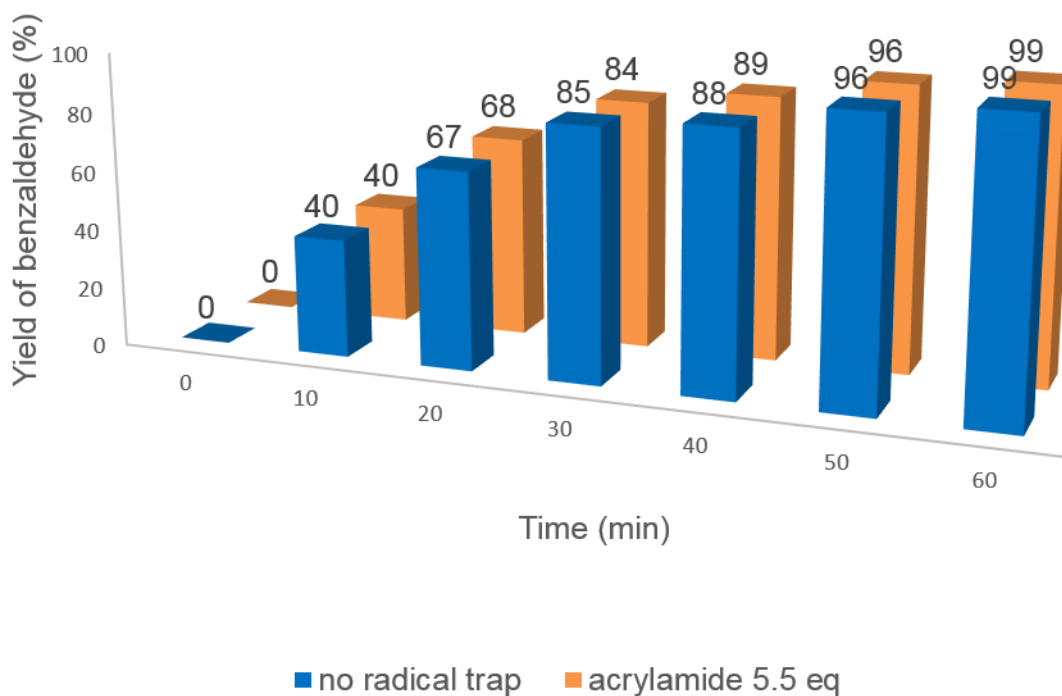
**Figure S10.** In-In plot of the rate of *meso*-hydrobenzoin cleavage vs concentration of *meso*-hydrobenzoin.

Reaction conditions: Na-Mn LMO (20 mg), 1-butanol (10 mL), O<sub>2</sub> balloon, 100 °C, stirring at 850 rpm. The range of *meso*-hydrobenzoin concentration is from 0.100 to 0.250 mol.L<sup>-1</sup>.



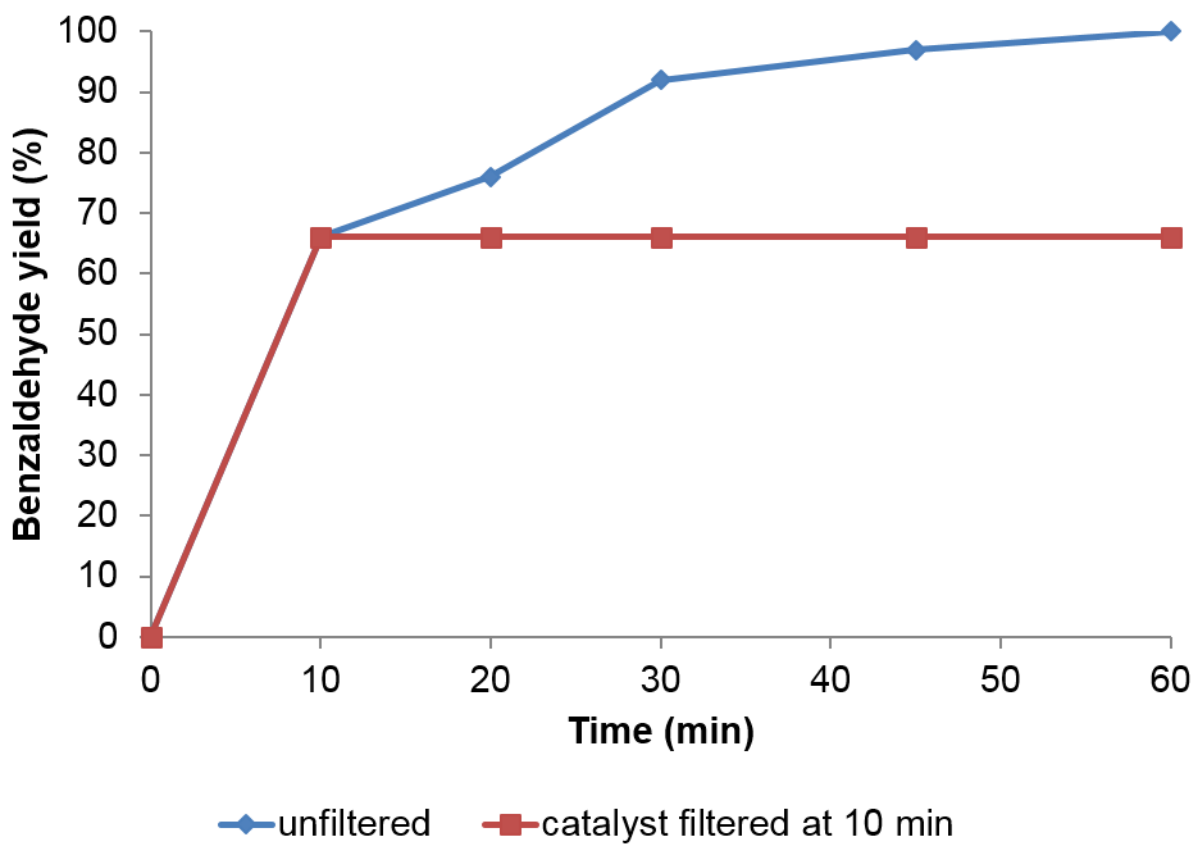
**Figure S11.** In-In plot of the rate of *meso*-hydrobenzoin cleavage vs  $X_{O_2}$  (mole fraction of  $O_2$  in the influx gas).

Reaction conditions: *meso*-hydrobenzoin (2 mmol), Na-Mn LMO (1 mol% Mn), 1-butanol (10 mL), gas flow was kept at  $2 \text{ L}\cdot\text{min}^{-1}$  using  $N_2$  as a make-up gas ( $P = 1 \text{ atm}$ ),  $80 \text{ }^\circ\text{C}$ . The range of  $X_{O_2}$  in the influx gas is from 0.1 to 1.0.



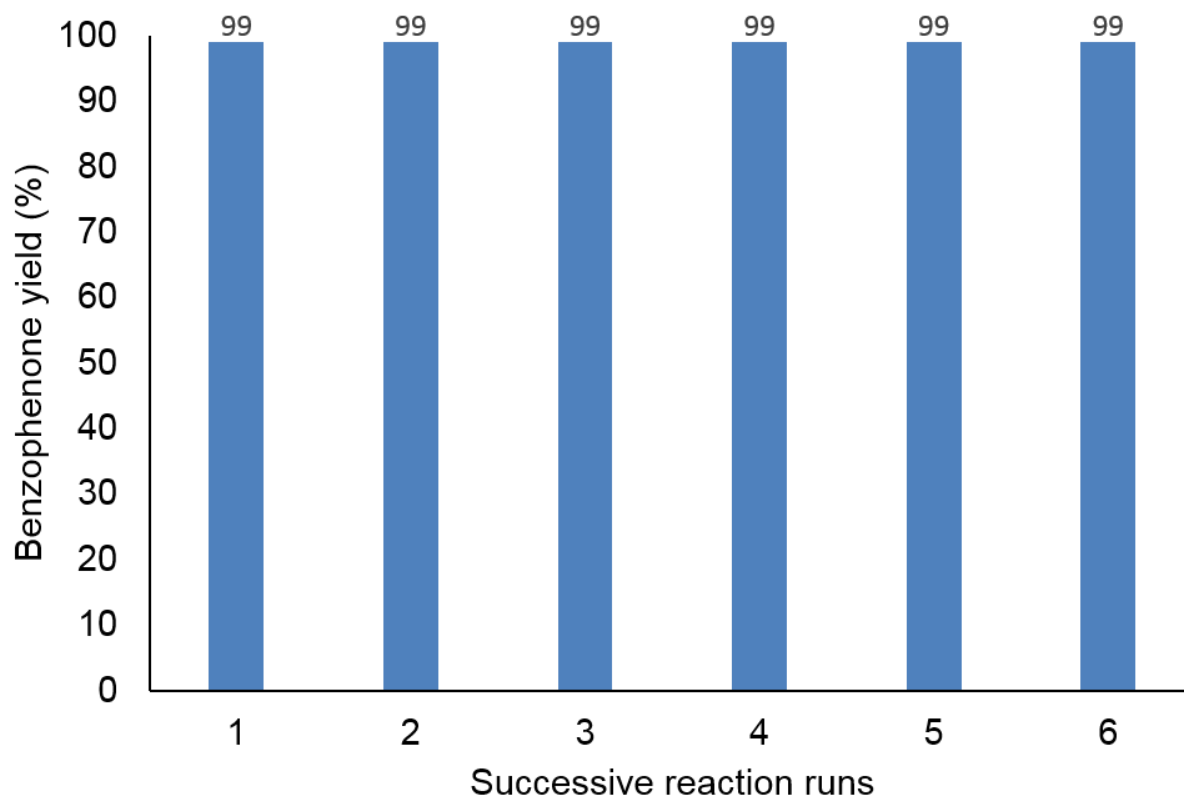
**Figure S12.** Oxidative cleavage of *meso*-hydrobenzoin by Na-Mn LMO, in presence and in absence of acrylamide, as radical trap.

Reaction conditions: *meso*-hydrobenzoin (0.2 mmol), Na-Mn LMO (1 mol% Mn), 1-butanol (1 mL), O<sub>2</sub> balloon, 100 °C. Reaction in presence of acrylamide was performed with 5.5 eq of acrylamide (1.1 mmol).



**Figure S13.** Effect of catalyst removal on the oxidative cleavage of *meso*-hydrobenzoin.

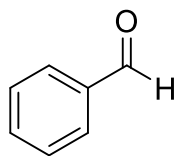
Reaction conditions: *meso*-hydrobenzoin (42.9 mg, 0.2 mmol), Na-Mn LMO (1 mol% Mn), 1-butanol (1 mL), O<sub>2</sub> balloon, 100 °C, 1 h. After 10 min, Na-Mn LMO was removed by filtration then the reaction was continued with the filtrate. Yield of benzaldehyde was determined by GC using dodecane as internal standard.



**Figure S14.** Recycling experiments of Na-Mn LMO catalyst.

Reaction conditions: benzopinacol (73.3 mg, 0.2 mmol), Na-Mn LMO (1 mol% Mn), 1-butanol (1 mL), O<sub>2</sub> balloon, 100 °C, 1 h. After reaction, the catalyst was recovered by centrifugation, rinsed with 2 x 4 mL of ethanol, and then dried in oven under air at 105 °C for 2 h. Yield of benzophenone was determined by GC using dodecane as internal standard.

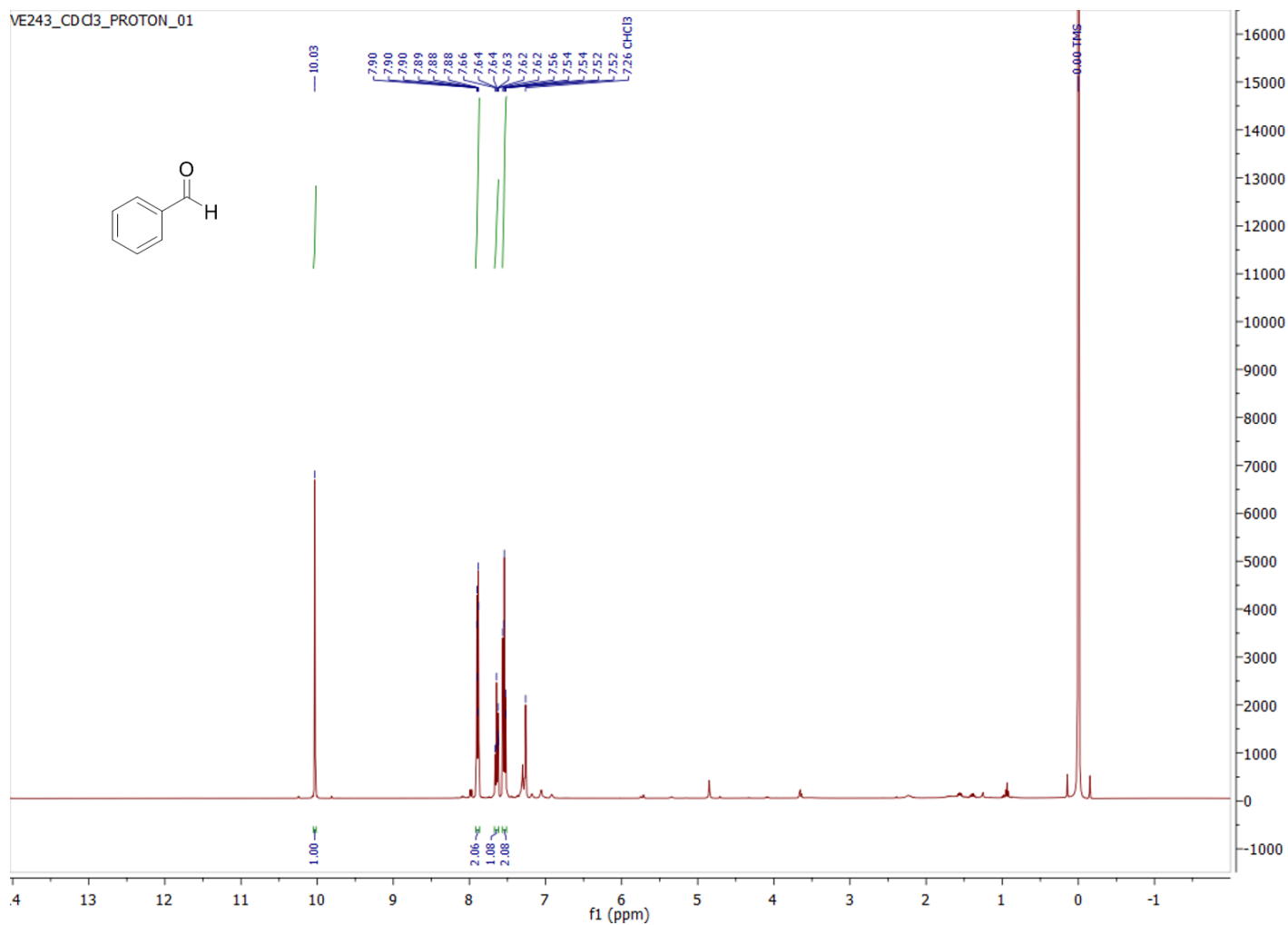
## NMR data for characteristic compounds

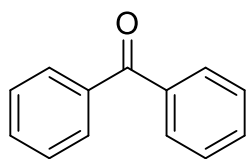
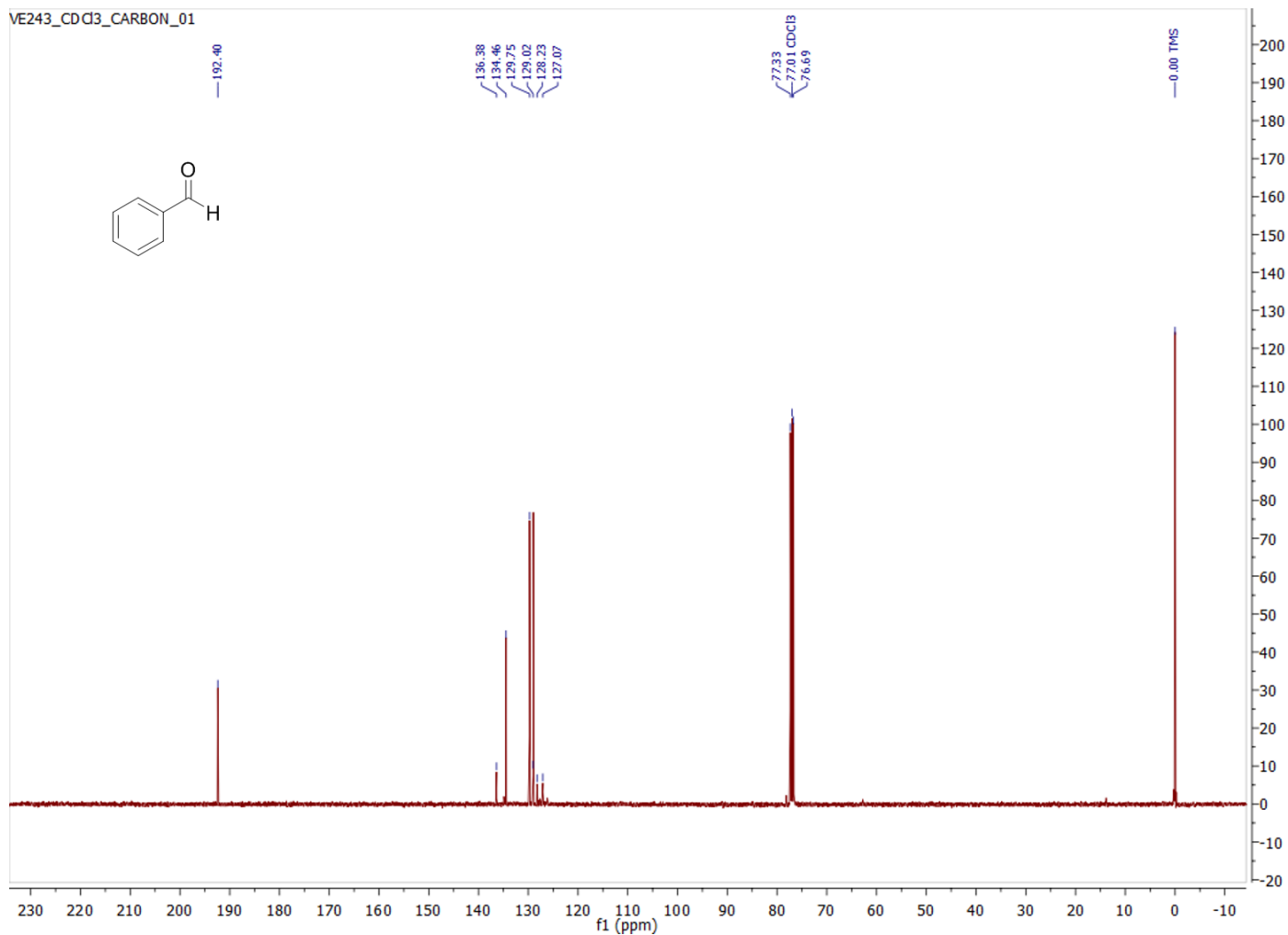


**2a**

### Benzaldehyde **2a**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  10.03 (s, 1H), 7.92 – 7.86 (m, 2H), 7.67 – 7.62 (m, 1H), 7.54 (dd,  $J = 8.1, 6.8$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  192.40, 136.38, 134.46, 129.75, 129.02, 128.23, 127.07.

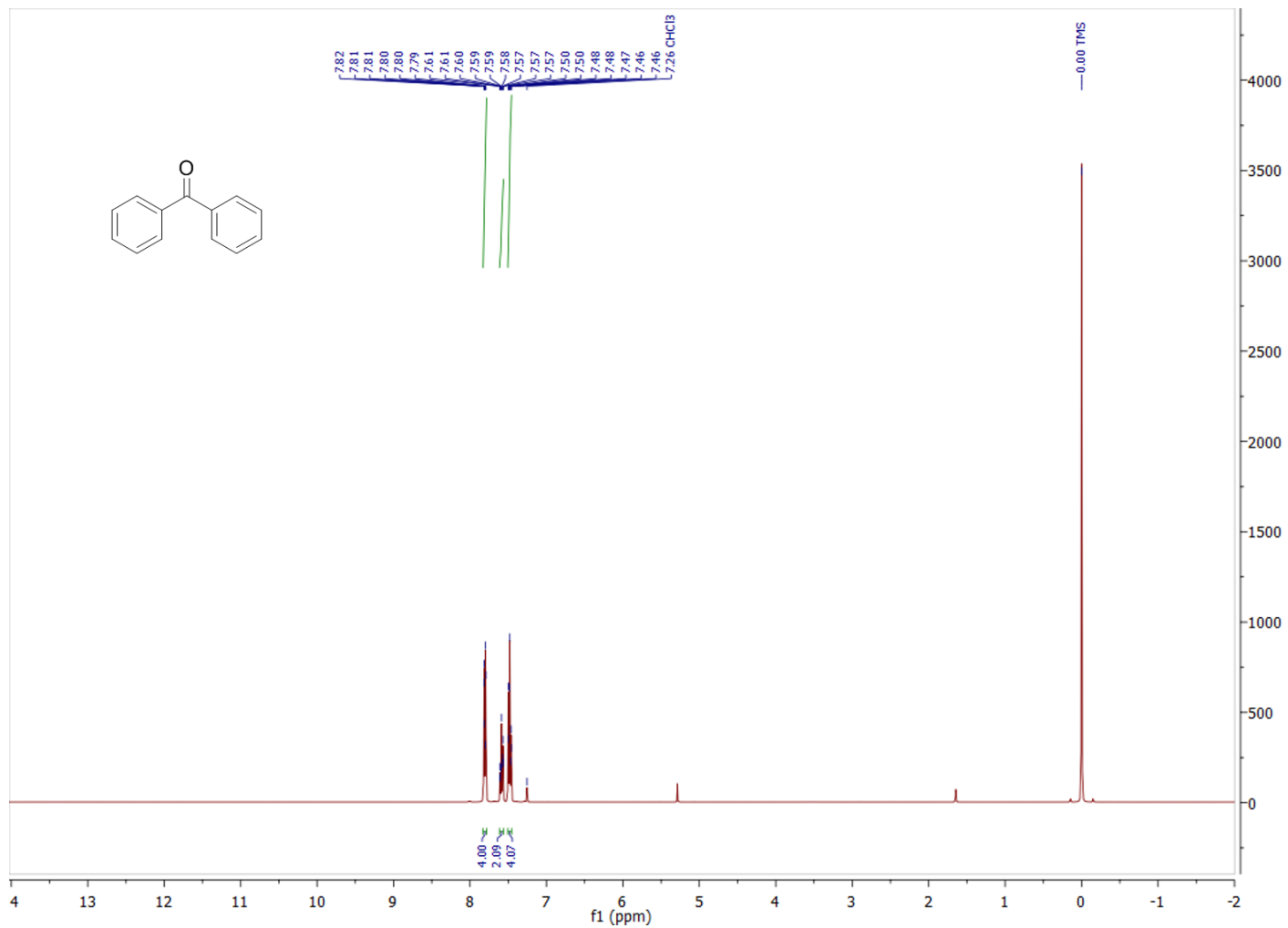




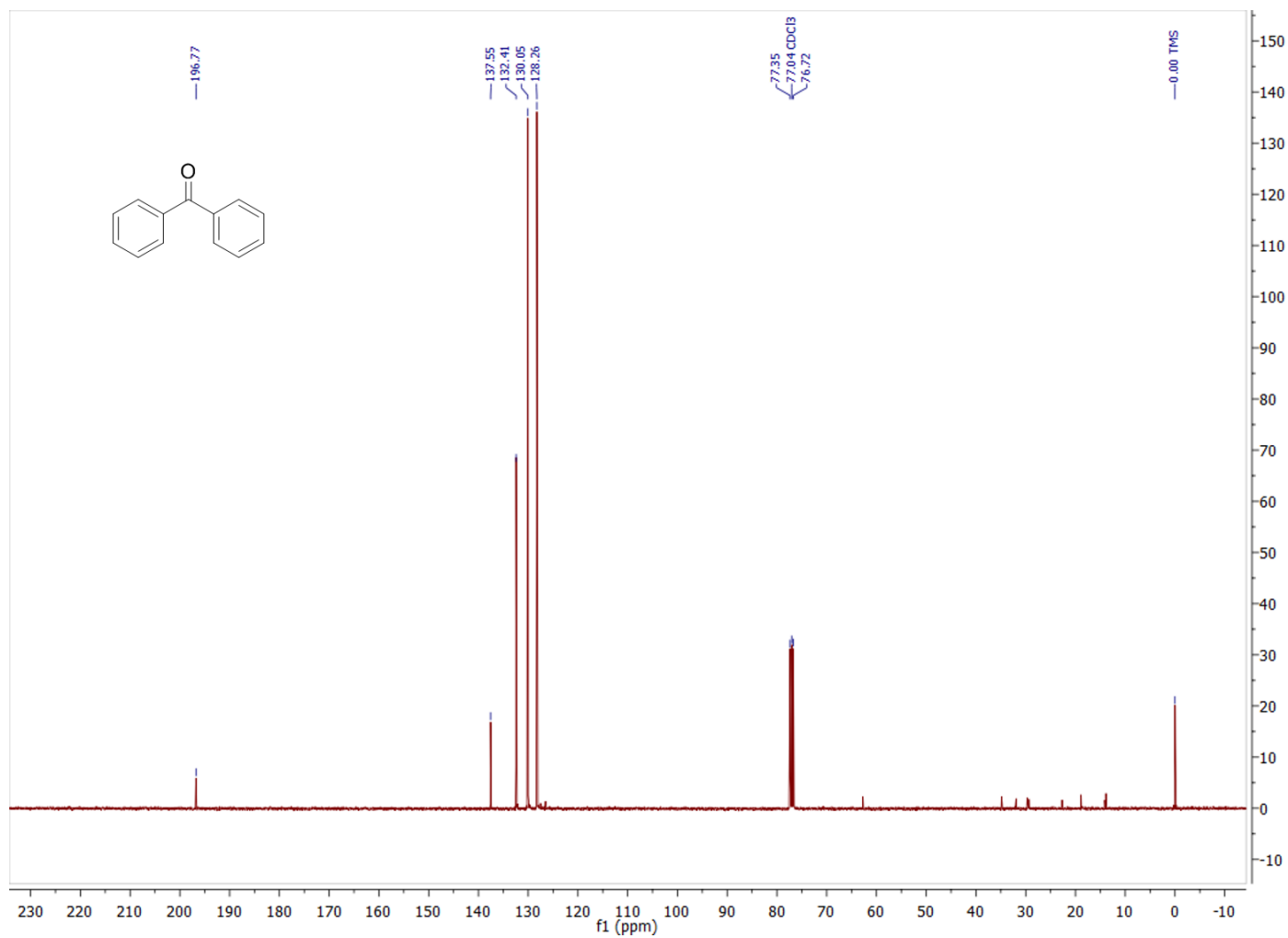
**2b**

Benzophenone **2b**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.83 – 7.78 (m, 4H), 7.61 – 7.56 (m, 2H), 7.51 – 7.46 (m, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  196.77, 137.55, 132.41, 130.05, 128.26.







- [1] K. S. Anju, S. Ramakrishnan, A. P. Thomas, E. Suresh, A. Srinivasan, *Org. Lett.* **2008**, *10*, 5545.  
[2] J. L. Junta, M. F. Hochella, *Geochim. Cosmochim. Acta* **1994**, *58*, 4985.