Supporting Information

Design and Synthesis of Highly Efficient Heterogeneous MnCo$_2$O$_4$ Oxide Catalyzed Alcohol Oxidation: DFT Insight into Synergistic Effect between Oxygen Deficiencies and Bimetal Species

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1. General Information

Urea (AR grade), manganese (II) acetate tetrahydrate (MCT, AR grade), cobalt (II) nitrate hexahydrate (CNH, 99%) and Ethylene Glycol (EG, 99%) were purchased from Adamas Reagent, Ltd. (USA). Benzyl alcohol (ACS grade, >99%), MnO$_2$ (>99%), MnO and CoO were purchased from were obtained from Sinopharm Chem Reagent Co., Ltd. (China). Other commercially available reagents were purchased from Acros, Sigma-Aldrich and Alfa Aesar Chemical Company.

2. Synthesis of FeCo$_2$O$_4$

A homogeneous mixture was prepared by vigorously stirring cobalt (II) nitrate hexahydrate (20.0 mmol), iron nitrate (III) nonahydrate (20.0 mmol) and ethylene glycol (80.0 mL) at room temperature for 20 min, then urea (80 mmol) was added into the mixture under vigorously stirring to form FeCo$_2$O$_4$ precursors. The precursors were stirred for 30 min at room temperature and transferred into stainless steel autoclave for another 5 h at 150 ºC. After filtration, an orange-yellow powder was dried at 80 ºC for 10 h. Then the final black catalysts of ~2 g were obtained by calcination under air atmosphere at 350 ºC.

3. Synthesis of MoCo$_2$O$_4$

A homogeneous mixture was prepared by vigorously stirring cobalt (II) nitrate hexahydrate (20.0 mmol), sodium molybdate tetrahydrate (20.0 mmol) and ethylene glycol (80.0 mL) at room temperature for 20 min, then urea (80 mmol) was added into the mixture under vigorously stirring to form MoCo$_2$O$_4$ precursors. The precursors were stirred for 30 min at room temperature and transferred into stainless steel autoclave for another 5 h at 150 ºC. After filtration, the powder was dried at 80 ºC for 10 h. Then the final black catalysts of ~2 g were obtained by calcination under air atmosphere at 350 ºC.

4. Synthesis of CuCo$_2$O$_4$

A homogeneous mixture was prepared by vigorously stirring cobalt (II) nitrate hexahydrate (20.0 mmol), copper (II) nitrate hydrate (20.0 mmol) and ethylene glycol (80.0 mL) at room temperature for 20 min, then urea (80 mmol) was added into the mixture under vigorously stirring to form MoCo$_2$O$_4$ precursors. The precursors were stirred for 30 min at room temperature and transferred into stainless steel autoclave for another 5 h at 150 ºC. After filtration, the powder was dried at 80 ºC for 10 h. Then the final black catalysts of ~2 g were obtained by calcination under air atmosphere at 350 ºC.

## 5. Computational Details

All simulations were carried out by means of the CP2K program package.[1].Unrestricted Kohn- Sham DFT was used as the electronic structure method in the framework of the Gaussian and plane waves method [2, 3]. PBE functional [4] with Grimme D3 correction [5] was used to describe the system. Since the generalized gradient functional fails to reproduce the correlated elements, we adopted the "+U" Hubbard correction[6] for the 3d electrons. It's known that quantitatively the results depend on the choice of U value. In this work, according to the reported data for 3d transition metal oxides[7, 8, 9], a U value of 3.3 eV was used, which provided a satisfying over- all description of the electronic structure and surface reactivity[8]. The Goedecker-Teter-Hutter (GTH) pseudopotentials[10, 11], DZVP-MOLOPT-GTH basis sets[2] were utilized to describe the molecules. A plane-wave energy cut-off of 500 Ry was employed.

A cubic conventional unit cell containing 32 oxygen and 24 cobalt atoms, as shown in the **Figure S1** for Co$_3$O$_4$, was used to model the bulk Co$_3$O$_4$. The calculated lattice constant was 8.012 Å. For comparison, we also modeled MnCo$_2$O$_4$ with 1/3 of cobalt atoms substituted, as shown in **Figure S1**.
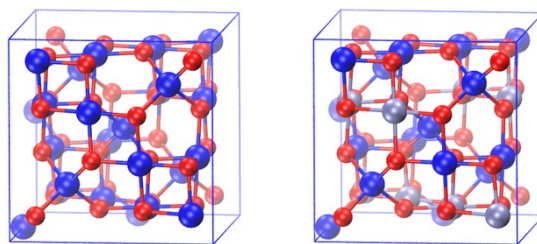
Figure S1. Bulk structure of Co_3O_4 (left) and $MnCo_2O_4$ (right). The blue spheres are Co atoms; ice blues spheres are Mn atoms and red spheres are oxygen atoms.
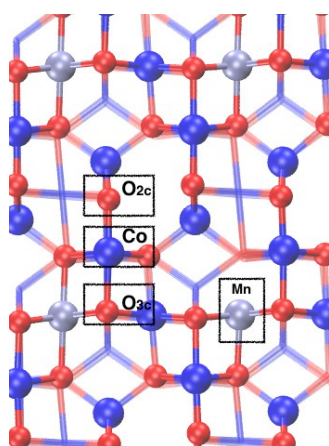
Figure S2. Top view of $MnCo_2O_4$ (-110) surface. The exposed Co^{3+} ions, two-coordinated oxygen, and three-coordinated oxygen atoms are labeled as Co, O2c and O3c, respectively. The oxygen atoms adjacent to Mn^{3+}/Co^{3+} are labeled as O_{Mn} and O_{Co}, Colour code: white is hydrogen, grey is carbon, red is oxygen, blue is cobalt, ice blue is manganese and transparent purple is an oxygen vacancy.

The surface we used to calculate the reaction profile was (-110) surface, the corresponding vertical plane (2 2 0) had been determined from our TEM results (**Figure 2**). The $MnCo_2O_4$ (-110) surface is drawn in **Figure S2**.

The formation energy of single vacancies within bulk or on surface was obtained with respect to the energy of oxygen in the gas phase following the equation:

$$E_{vac}^{O_2} = E_{bulk/sur}^{vac} - \frac{1}{2}E_{O_2}(g) - E_{bulk/sur}$$

where $E_{bulk/sur}^{vac}$ is the energy of the bulk or surface with the oxygen vacancy, and E_{O_2} is the energy of oxygen molecule in the gas phase.

To avoid the self-interaction of oxygen vacancy between images, the formation energy of oxygen vacancies was calculated within a supercell of (2x2x2).
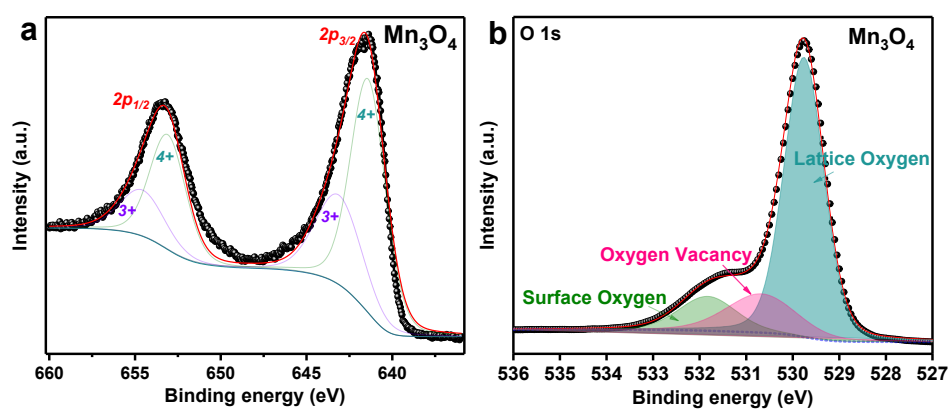
References

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6. **Materials charactizations**

Table S1. Structural parameters of Co_3O_4, Mn_3O_4, and CMO-n catalysts.

Sample	S_{BET} (m²/g)	S_{EXT} (m²/g)	V_{meso} (cm³/g)	D(4V/A) (nm)
Co_3O_4	5.3	-	0.03	450
Mn_3O_4	10.2		0.13	30.8
$MnCo_2O_4$	60.4	56.4	0.26	15.5
T-$MnCo_2O_4$	66.5	55.8	0.27	15.7

Figure S3. Mn 2p (a) and O 1s (b) XPS spectra of Mn_3O_4 sample.
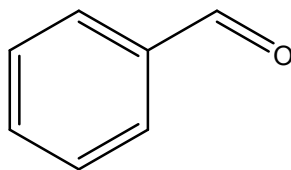
4. NMR data

(1) 4-methylbenzaldehyde
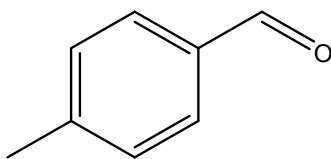
White Oil ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.88 (s, 1H), 7.70 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 191.97 (s), 145.54 (s), 134.20 (s), 129.77 (d, J = 12.0 Hz), 21.83 (s).
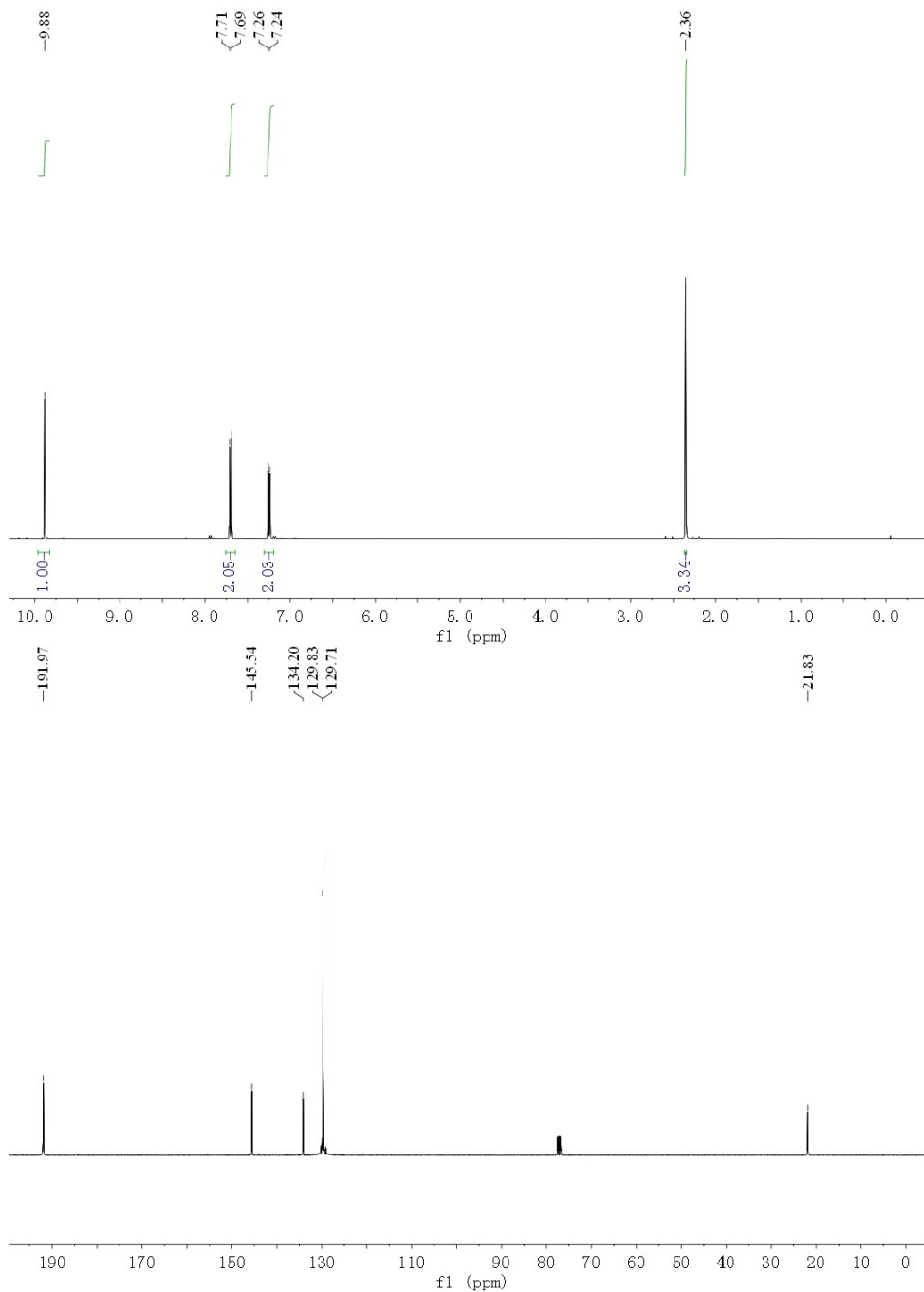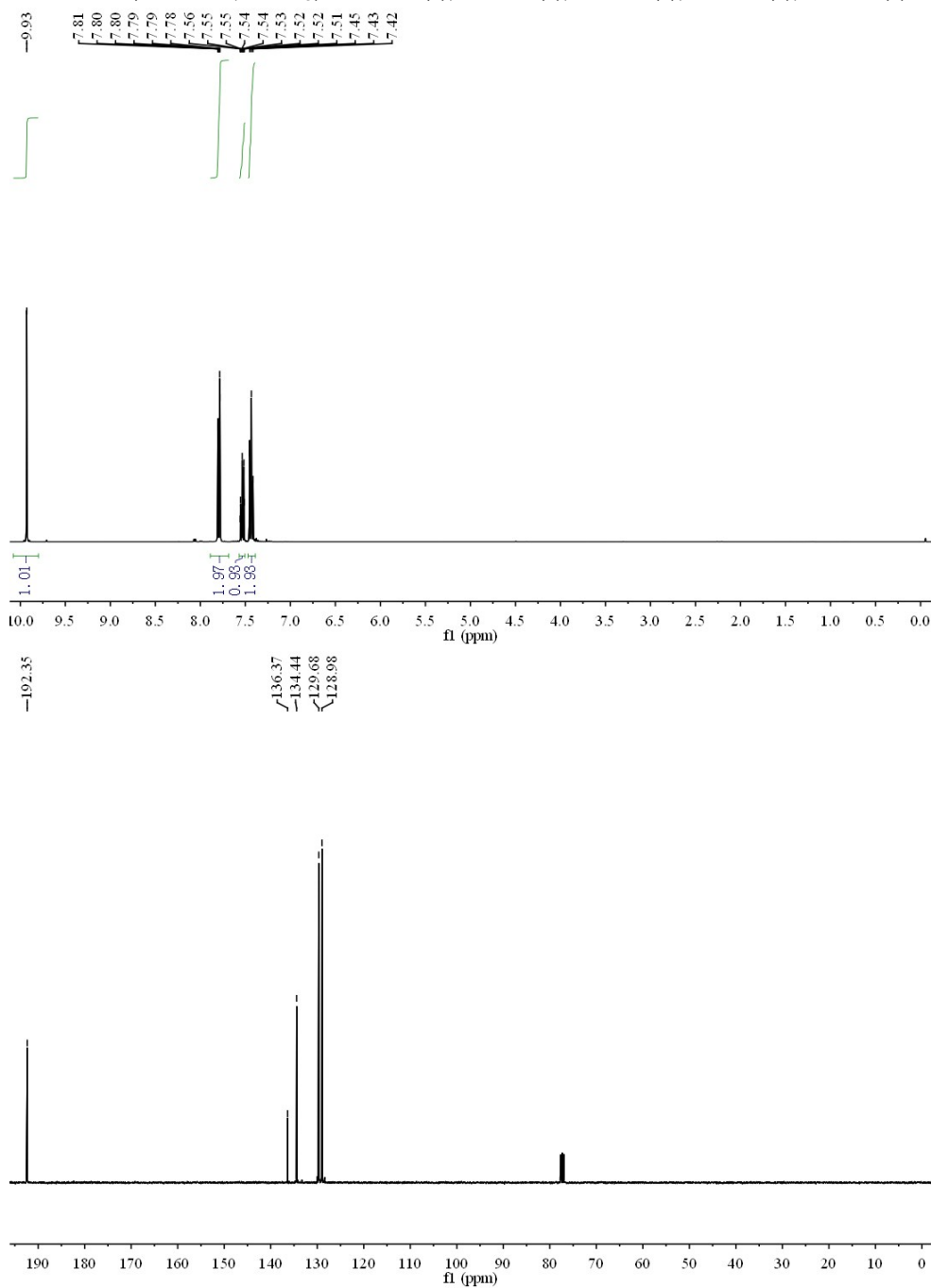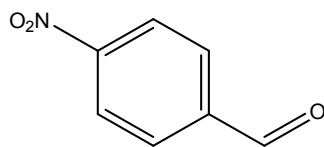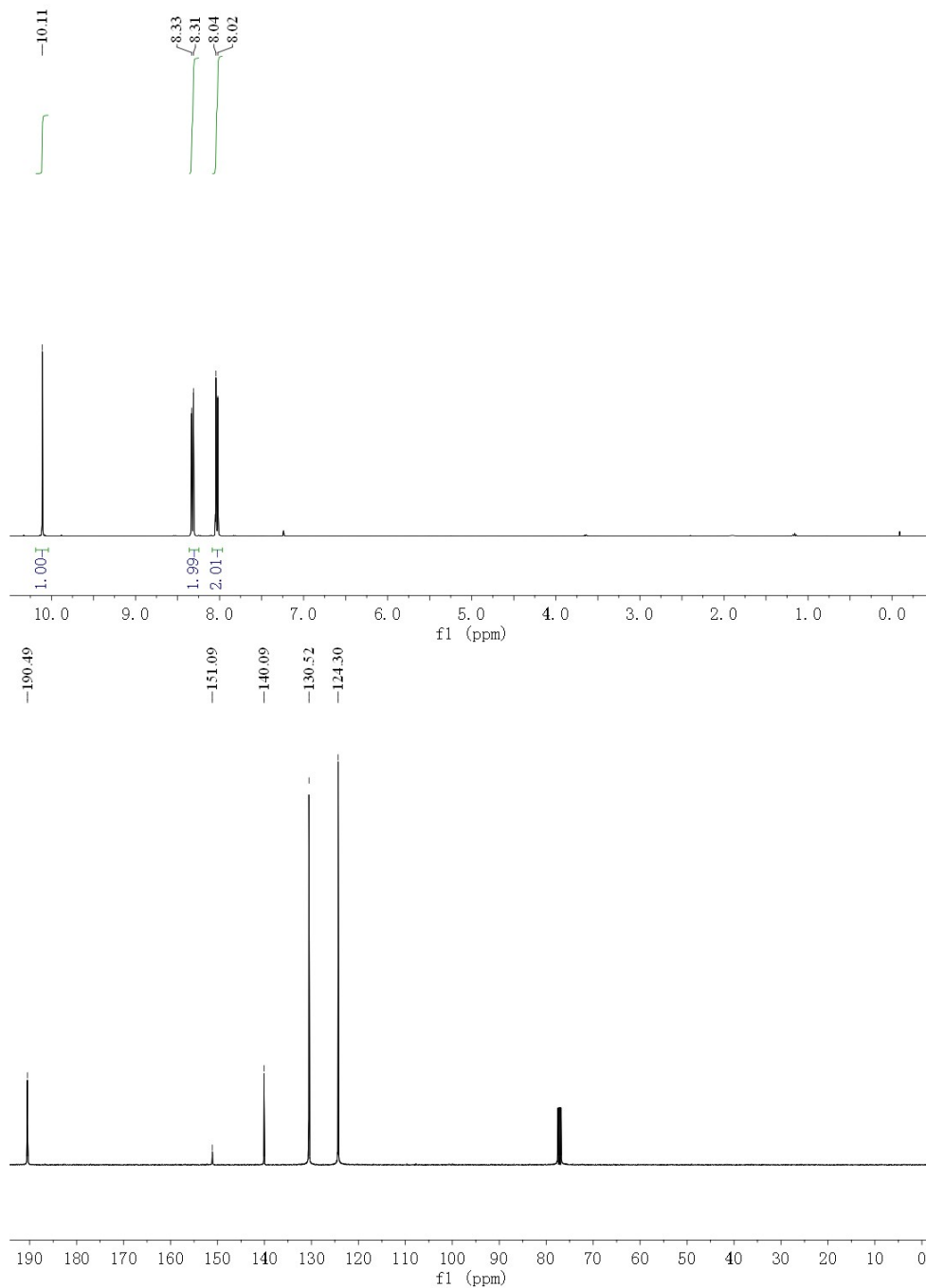
(2) benzaldehyde

White Oil ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.93 (s, 1H), 7.89 – 7.68 (m, 2H), 7.57 – 7.50 (m, 1H), 7.43 (t, J = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 192.35 (s), 136.37 (s), 134.44 (s), 129.68 (s), 128.98 (s).
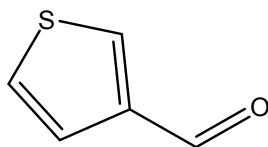
(3) 4-nitrobenzaldehyde

Yellow Oil ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.11 (s, 1H), 8.32 (d, *J* = 8.6 Hz, 2H), 8.03 (d, *J* = 8.9 Hz, 2H).
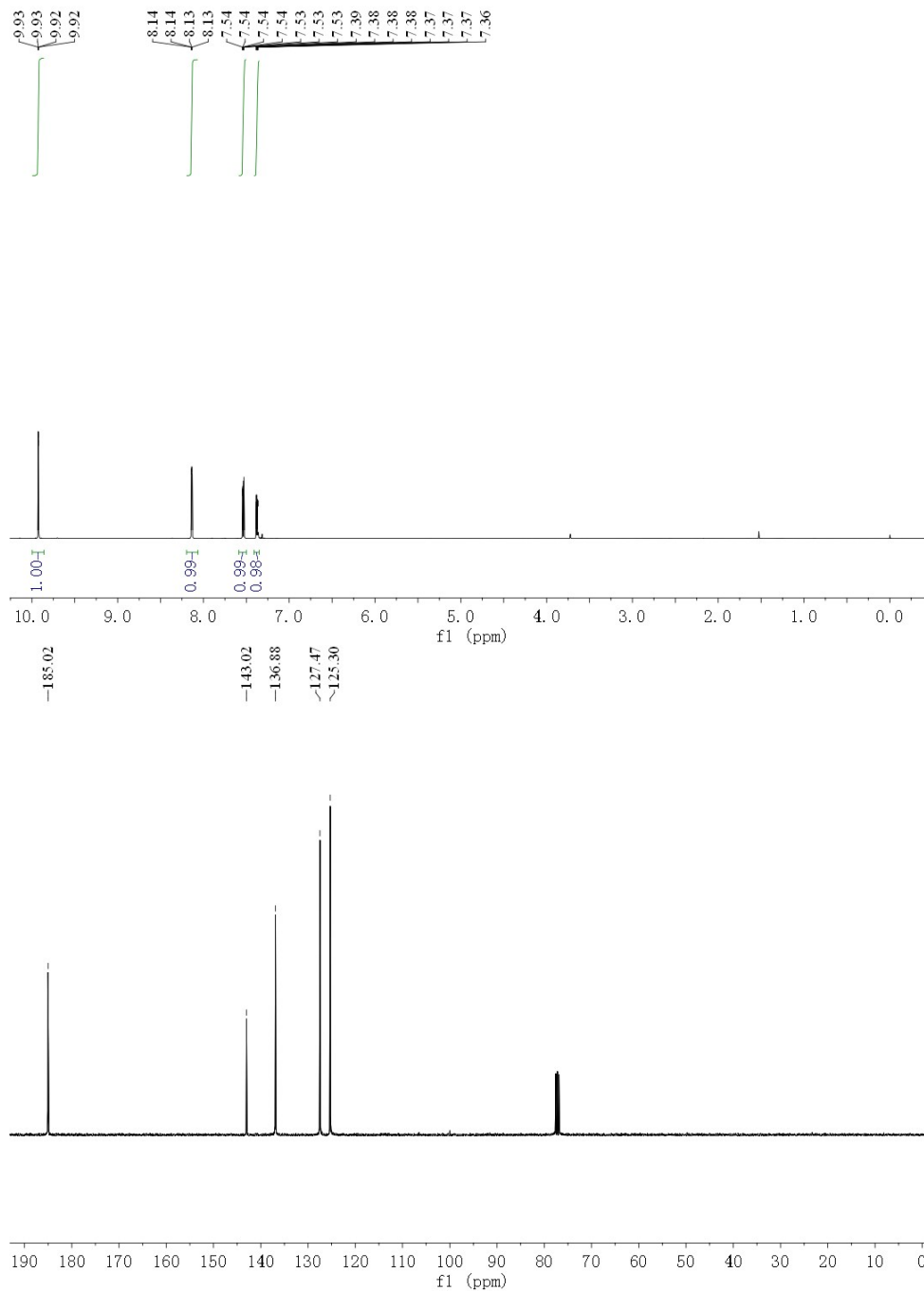[3]C NMR (101 MHz, CDCl$_3$) δ 190.49 (s), 151.09 (s), 140.09 (s), 130.52 (s), 124.30 (s).
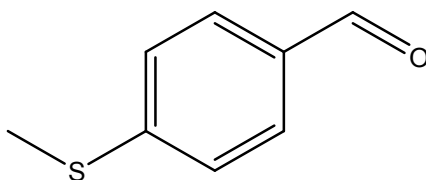
(4) thiophene-3-carbaldehyde

Yellow Oil ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.99 – 9.86 (m, 1H), 8.14 (dd, J = 2.9, 1.2 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.37 (ddd, J = 5.1, 2.9, 0.9 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 185.02 (s), 143.02 (s), 136.88 (s), 127.47 (s), 125.30 (s).

(5) 4-(methylthio)benzaldehyde

Yellow Oil ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.90 (s, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 2.51 (s, 3H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 191.28 (s), 147.95 (s), 132.88 (s), 129.99 (s), 125.13 (s), 14.65 (s).