

A novel Mn@MOF-303 as catalyst for the highly efficient *S*- formylation of benzyl thiols with CO₂

Supporting Information

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General Information

Unless otherwise stated, all manipulations were performed under a dry nitrogen or carbon dioxide atmosphere using Schlenk-line techniques. Chemicals used were commercially purchased and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer in CDCl_3 with tetramethylsilane (TMS) as the internal standard. Power X-ray diffraction (PXRD) was tested on an Ultima IV X-ray diffractometer using $\text{Cu K}\alpha$ radiation in the 2θ range of $3\text{-}50^\circ$ ($\lambda = 0.154178$ nm). Morphologies of samples were characterized by scanning electron microscope (SEM, ZEISS, MERLIN Compact).

Synthesis and Characterization of Mn@MOF-303

Preparation of MOF-303¹

3,5-pyrazoledicarboxylic acid monohydrate (7.50 g, 43.1 mmol) and NaOH (2.60 g, 65 mmol) were dissolved in deionized water (750 mL). The resulting mixture was sonicated for 10 min and heated in a pre-heated oven at 100°C for 30 min until the solution was clear. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (10.4 g, 43.1 mmol) was then added to the solution. Any precipitate was dissolved by vigorous shaking. The hot reaction mixture was placed in a pre-heated oven at 100°C and left for 15 hours. The white powder formed were collected and washed with water three times per day for two days. The white solid was subsequently washed with methanol for two days, three times per day and dried in air. The product was then activated under dynamic vacuum for 6 hours at room temperature until the pressure was below 100 mbar. After that, the MOF sample was heated at 100°C for 6 hours and then at 150°C for another 6 hours to yield activated MOF-303 crystals (3.6 g).

Preparation of Mn@MOF-303

The suspension of MOF-303 (198 mg, 1.0 mmol) with $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (245 mg, 1.0 mmol) in CH_3CN (15 mL) was stirred at 70°C for 48 hours, giving yellow powder at the bottom of the vial. The metalated Mn@MOF-303 was washed with 10 mL of fresh CH_3CN for 3 times. The resulting Mn@MOF-303 was activated under dynamic vacuum at room temperature for 4 hours, and then at 120°C for 12 hours.

Characterization of Mn@MOF-303

The FT-IR of MOF-303 and Mn@MOF-303 were performed (Fig S4). By comparing the FT-IR spectrum of MOF-303 and Mn@MOF-303, we found that the peaks around 1000 cm^{-1} and 1500

cm⁻¹ are different. This suggested the formation of new bonds (Mn–N coordination bond) by introduction of Mn(OAc)₂ into MOF-303. However, we could not find any relevant literature to determine which is the characteristic peak of the Mn–N bond.

The 77 K nitrogen sorption experiments were conducted by a Micromeritics ASAP 2460 instrument. The sample-loaded tubes soaked in the liquid nitrogen bath during the experiments to maintain a constant temperature environment of 77 K (Figure S1, S5 and S7).

Partial Experimental Content of *S*-Formylation

General Procedure of the *S*-Formylation Products

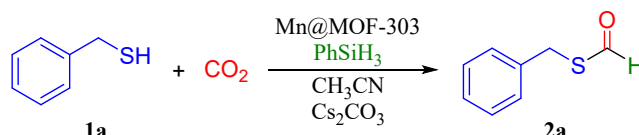
Benzyl thiols (**1**, 1.0 mmol), Cs₂CO₃ (0.02 mmol), PhSiH₃ (1.5 mmol) and Mn@MOF-303 (20 mg) were introduced in a sealed 10 mL Schlenk tube, 2 mL CH₃CN was then added. The reaction was placed at atmospheric pressure of CO₂ (1 atm) and stirred for 12 h at 25°C. When the reaction finished, saturated salt solution (10 mL) was then added and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄, and the organic solvent was evaporated on a rotatory evaporator. The crude was purified by flash chromatography on silica gel (PE/EtOAc) to give the corresponding products **2**.

Optimization of Solvents and Bases for *S*-Formylation

The reaction of benzyl thiol (**1a**, 1.0 mmol) and CO₂ (1 atm) was chosen as a model reaction with Mn@MOF-303 (10 mg) in the presence of PhSiH₃ (1.5 mmol) and Cs₂CO₃ (0.02 mmol) at 25 °C for 12 h in acetonitrile. Initially, the reaction was carried out in the absence of catalyst, giving the desired product **2a** in 39%, whereas no desired product was observed in the absence of Cs₂CO₃ (Table S1, entries 1 and 2). This result showed that Cs₂CO₃ was essential to polarize **1a** and increase its nucleophilic capability on CO₂. In comparison, Mn(OAc)₂, MOF-303 and Mn@MOF-303 were used as catalysts to give the desired product **2a** in 50% yield, 48% yield and 85% yield, respectively (Table S1, entries 3-5). The result revealed that both Mn(OAc)₂ and MOF-303 could promote the conversion of the reaction. And the yield of **2a** could reach 85% in the presence of Mn@MOF-303 with Mn element and MOF-303. Maybe the Mn element could activate the substrate (PhSiH₃ or **1a**) and MOF-303 could adsorb CO₂ to participate in the formylation. Solvent and base were important factors in the catalysis. Subsequently, different solvents (THF,

CH₂Cl₂ and CH₃OH) and bases (LiO^tBu, NaOH and Et₃N) were investigated (Table S1, entries 6-11). It was confirmed that CH₃CN and Cs₂CO₃ is the optimal solvent and base respectively. Thus, the reaction of benzyl thiol (**1a**, 1.0 mmol) and CO₂ (1 atm) with Mn@MOF-303 (10 mg) in the presence of PhSiH₃ (1.5 mmol) and Cs₂CO₃ (0.02 mmol) at 25 °C for 12 h in acetonitrile was chosen as a model reaction for further optimizing.

Table S1 Optimization of Reaction Conditions ^a



Entry	Catalyst	Base	Solvent	Yield(%) ^b
1	—	Cs ₂ CO ₃	CH ₃ CN	39
2	Mn@MOF-303	—	CH ₃ CN	Trace
3	Mn(OAc) ₂	Cs ₂ CO ₃	CH ₃ CN	50
4	MOF-303	Cs ₂ CO ₃	CH ₃ CN	48
5	Mn@MOF-303	Cs ₂ CO ₃	CH ₃ CN	85
6	Mn@MOF-303	Cs ₂ CO ₃	THF	63
7	Mn@MOF-303	Cs ₂ CO ₃	CH ₂ Cl ₂	31
8	Mn@MOF-303	Cs ₂ CO ₃	CH ₃ OH	20
9	Mn@MOF-303	LiO ^t Bu	CH ₃ CN	49
10	Mn@MOF-303	NaOH	CH ₃ CN	11
11	Mn@MOF-303	Et ₃ N	CH ₃ CN	trace

^a Reaction conditions: **1a** (1.0 mmol), CO₂ (1 atm), PhSiH₃ (1.5 mmol), Cs₂CO₃ (0.02 mmol), catalyst (20 mg), CH₃CN (2 mL) at 25 °C. ^b Isolated yield.

Control Experiment of Mn@MOF-303 with Phenylsilane

PhSiH₃ (3 mmol) and Mn@MOF-303 (40 mg) were introduced in a sealed 10 mL Schlenk tube, 3 mL CH₃CN was then added. The reaction was stirred for 12 h at 25°C. When the reaction finished, the “reacted” catalyst was filtered and washed with CH₃CN (3 × 5 mL). The white solid was dried under vacuum at room temperature for 1 hour. The FT-IR of the “reacted” catalyst was investigated (shown in Fig. S3). It was found that no clear characteristic peaks appeared in the spectrum compared with the spectrum of Mn@MOF-303. It is possible that the bonds in intermediate **I** are particularly weak or the intermediate **I** is too reactive to be stable.

DFT Calculations

DFT calculations were then performed to optimize the geometry and calculate the Gibbs free

energy of the reaction on the Gaussian 16 program² with the B3LYP functional³. The geometry optimization and transit state search were performed using the def2-svp basis set for all atoms. Single point energies were calculated at the B3LYP/def2tzvp level on optimized geometries.⁴

Related Figures of Experiment

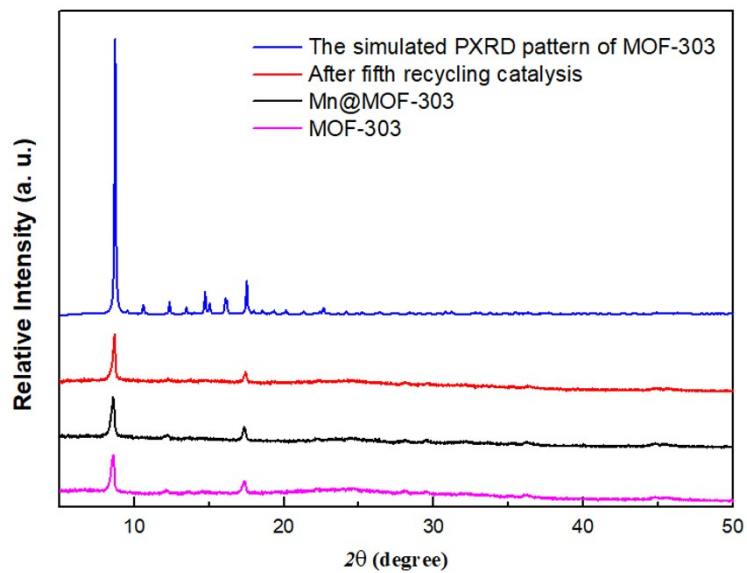


Fig. S1 PXRD patterns of Mn@MOF-303 and MOF-303.

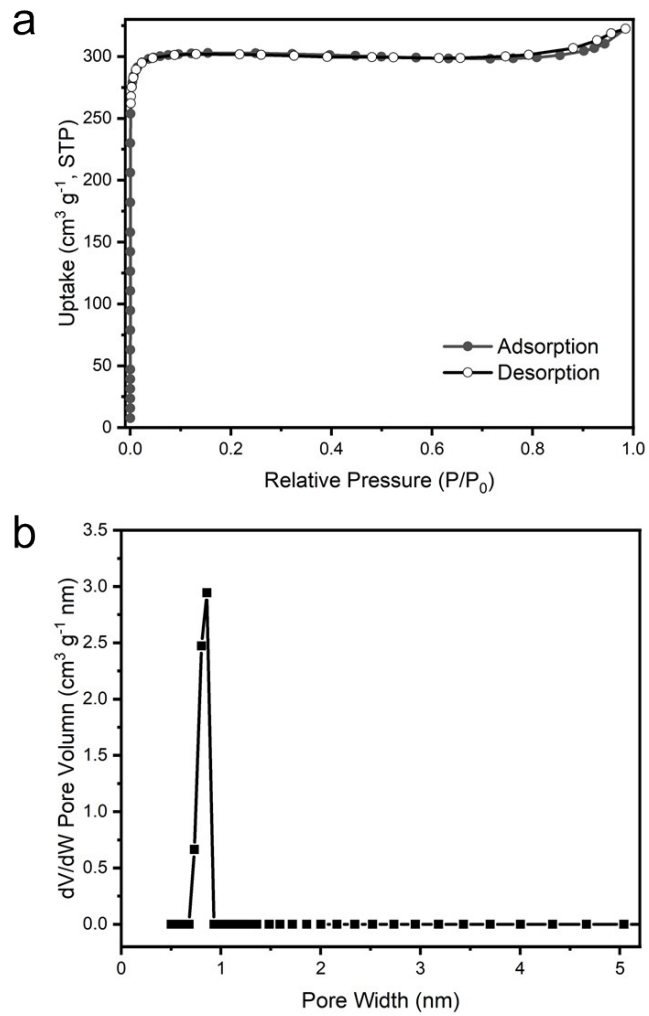


Fig. S2 The N₂ sorption isotherms of MOF-303 (a) and the pore width distribution (b) calculated by DFT method.

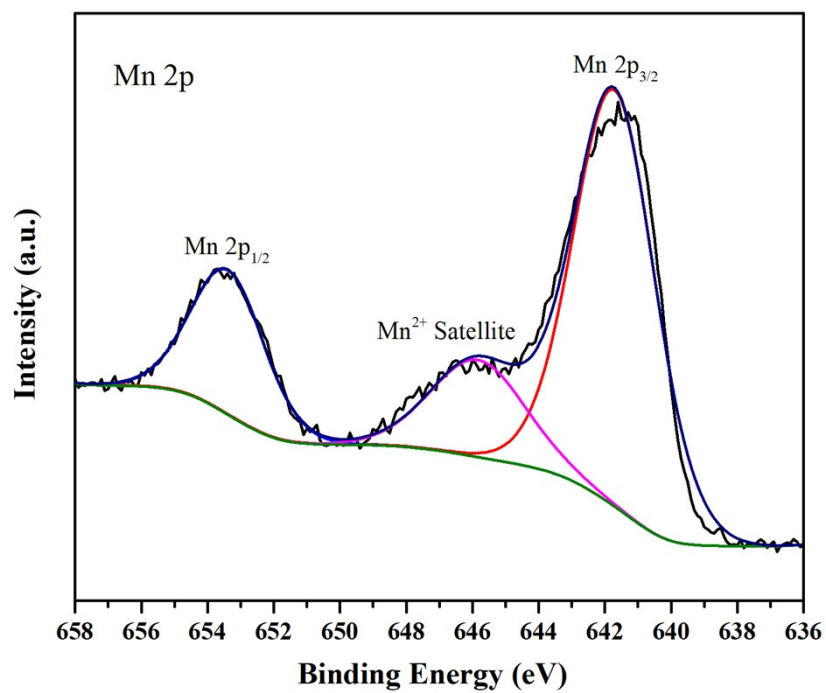


Fig. S3 The Mn XPS spectrum of Mn@MOF-303.

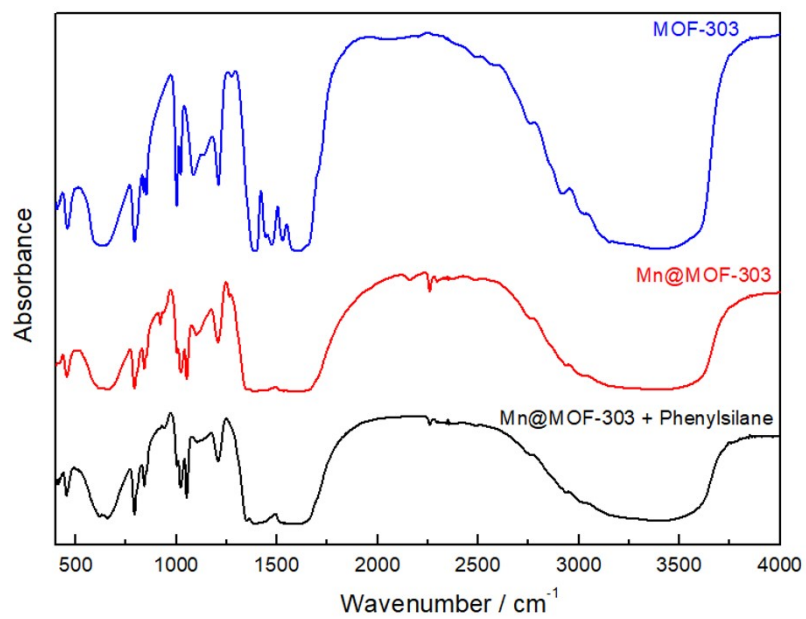


Fig. S4 The FT-IR spectrum of MOF-303, Mn@MOF-303 and “reacted” Mn@MOF-303.

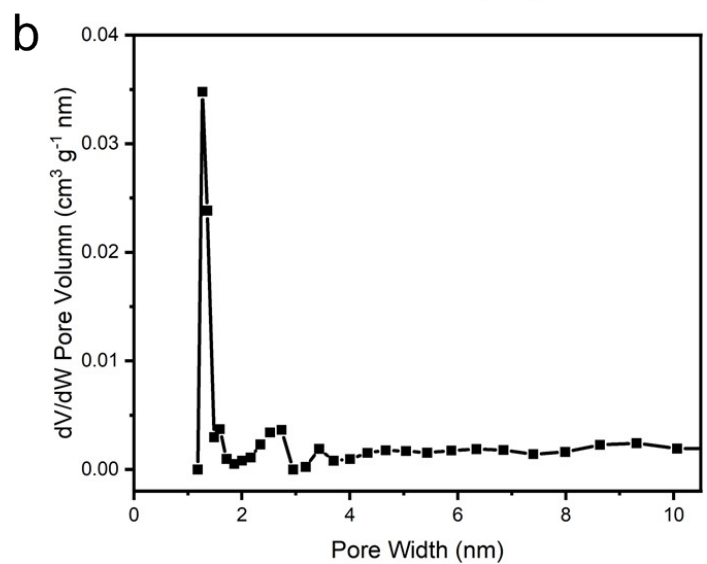
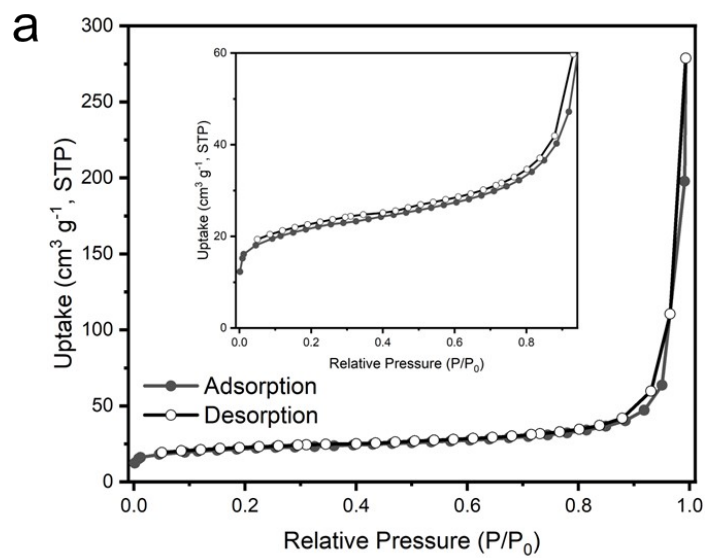


Fig. S5 The N_2 sorption isotherms of Mn@MOF-303 (a) and the pore width distribution (b) calculated by DFT method.

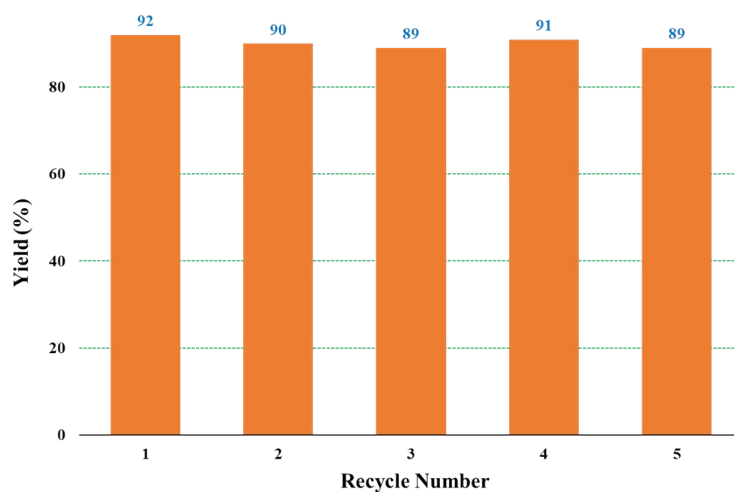


Fig. S6 Recycling experiments on the S-formylation of benzyl thiol (**1a**) and CO_2 .

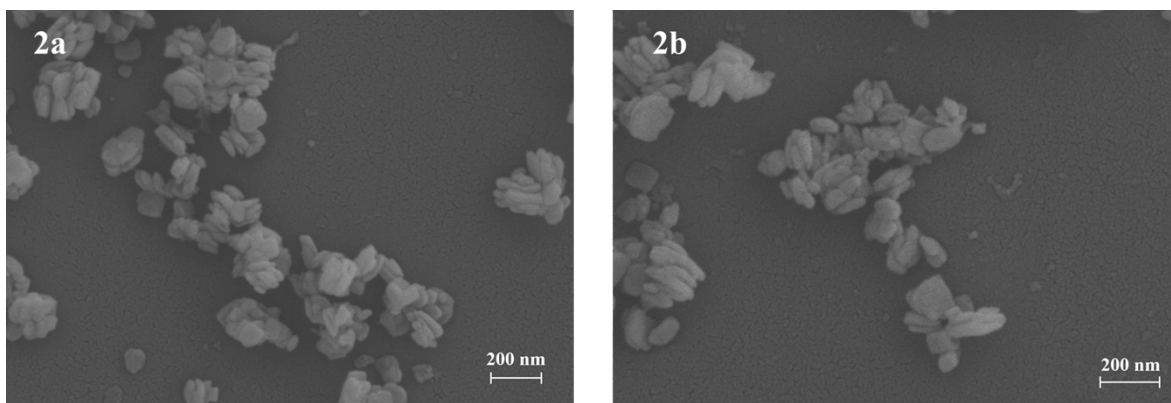


Fig. S7 SEM images of the uncirculated Mn@MOF-303 (**2a**) and recycled Mn@MOF-303 (**2b**).

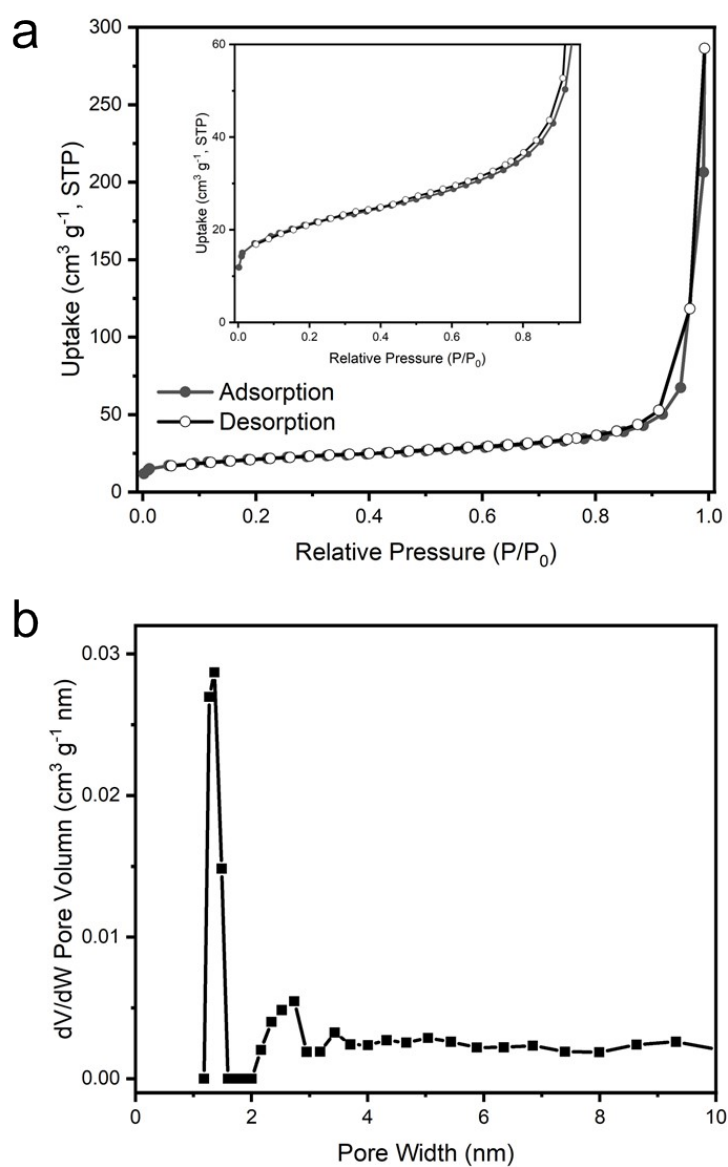


Fig. S8 The N_2 sorption isotherms of recycled Mn@MOF-303 (a) and the pore width distribution (b) calculated by DFT method.

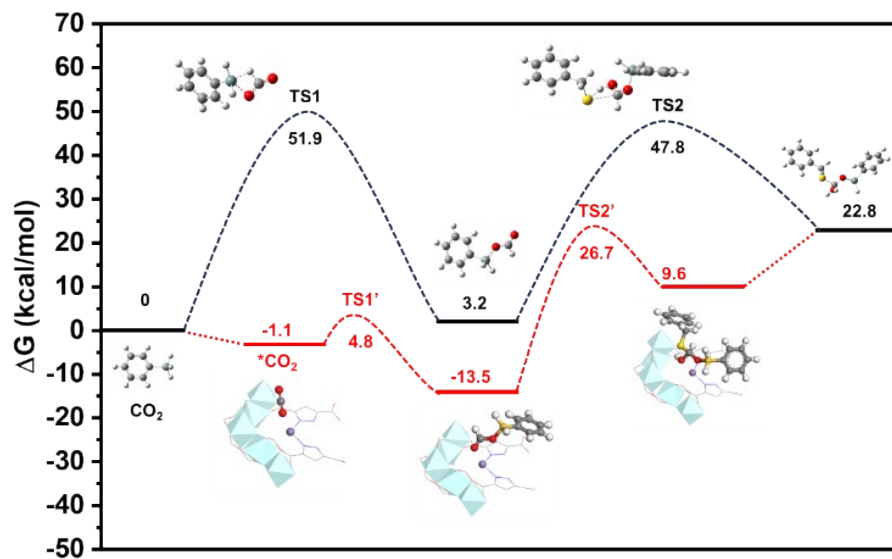


Fig. S9 Gibbs free energy diagram of CO₂ hydrosilylation and PhCH₂SH nucleophilic addition. (a) The energy data (in red) is the energy of each intermediate state with Mn@MOF-303 as the catalyst. (b) The energy data (in blue) is the calculated Gibbs free energy of CO₂ intermediate without MOF-303.

NMR Data of the Products (2)

S-benzyl methanethioate (2a)⁵

¹H NMR (500 MHz, CDCl₃) δ 10.16 (s, 1H), 7.33-7.24 (m, 5H), 4.22 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 186.72 (s), 136.77 (s), 128.81 (d, *J* = 14.4 Hz), 127.53 (s), 30.78 (s).

S-(4-methylbenzyl) methanethioate (2b)⁵

¹H NMR (500 MHz, CDCl₃) δ 10.07 (s, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 4.11 (s, 2H), 2.24 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 136.27 (s), 132.65 (s), 128.40 (s), 127.74 (s), 29.52 (s), 20.07 (s).

S-(4-(tert-butyl)benzyl) methanethioate (2c)⁵

¹H NMR (500 MHz, CDCl₃) δ 10.05 (s, 1H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 4.10 (s, 2H), 1.21 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 186.94 (s), 150.56 (s), 133.67 (s), 128.61 (s), 125.73 (s), 34.57 (s), 31.36 (s), 30.46 (s).

S-(4-methoxybenzyl) methanethioate (2d)⁵

¹H NMR (500 MHz, CDCl₃) δ 10.17 (s, 1H), 7.25 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.20 (s, 2H), 3.81 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 186.97 (s), 159.02 (s), 130.06 (s), 128.76 (s), 114.17 (s), 55.28 (s), 30.36 (s).

S-(4-chlorobenzyl) methanethioate (2e)⁵

¹H NMR (500 MHz, CDCl₃) δ 10.18 (d, *J* = 5.8 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.27-7.22 (m, 2H), 4.19 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 186.37 (s), 135.47 (s), 133.40 (s), 130.24 (s), 128.89 (s), 30.05 (s).

S-(2-methylbenzyl) methanethioate (2f)⁵

¹H NMR (500 MHz, CDCl₃) δ 10.20 (s, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.22-7.09 (m, 3H), 4.24 (s, 2H), 2.39 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 186.87 (s), 138.52 (s), 136.71 (s), 129.63 (s), 128.71 (s), 128.36 (s), 125.96 (s), 30.76 (s), 21.39 (s).

S-(2-chlorobenzyl) methanethioate (2g)⁵

¹H NMR (500 MHz, CDCl₃) δ 10.18 (s, 1H), 7.47 (dd, *J* = 5.6, 3.7 Hz, 1H), 7.40 (dd, *J* = 5.5, 3.8 Hz, 1H), 7.24 (dd, *J* = 5.8, 3.5 Hz, 2H), 4.36 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 186.57 (s), 134.67 (s), 134.15 (s), 131.20 (s), 129.64 (s), 129.08 (s), 127.12 (s), 28.70 (s).

S-(3-methylbenzyl) methanethioate (2h)⁵

¹H NMR (500 MHz, CDCl₃) δ 10.17 (s, 1H), 7.36 (s, 1H), 7.26-7.23 (m, 3H), 4.30 (s, 2H), 2.41 (s,

3H). ^{13}C NMR (126 MHz, CDCl_3) δ 186.87 (s), 138.52 (s), 136.71 (s), 129.63 (s), 128.71 (s), 128.36 (s), 125.96 (s), 30.76 (s), 21.39 (s).

S-(2,4,6-trimethoxybenzyl) methanethioate (2i) ⁵

^1H NMR (500 MHz, CDCl_3) δ 10.33 (s, 1H), 6.13 (s, 2H), 4.32 (s, 2H), 3.84 (s, 6H), 3.83 (s, 3H).

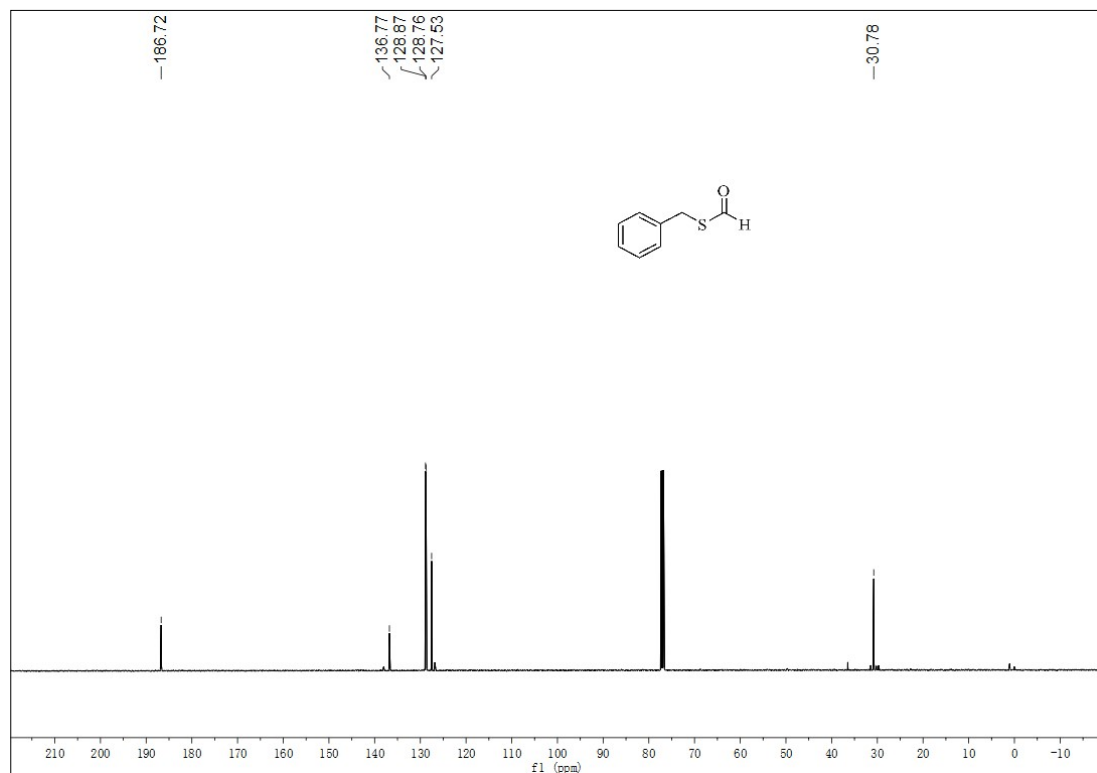
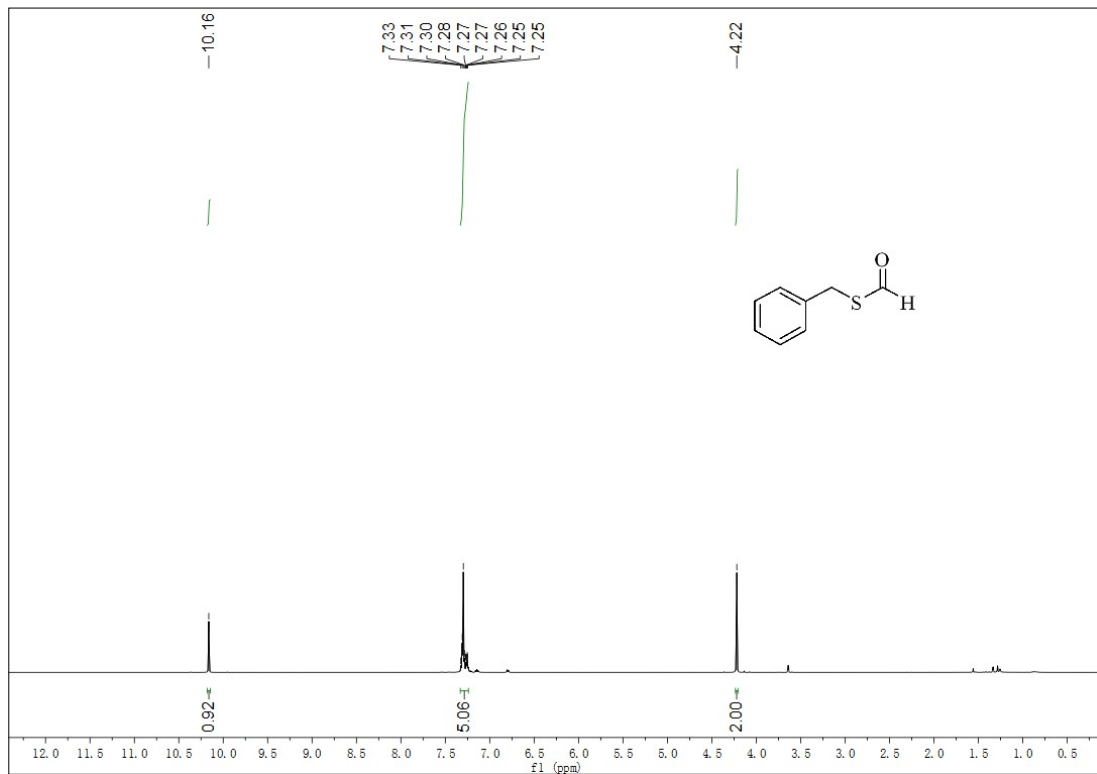
^{13}C NMR (126 MHz, CDCl_3) δ 190.60 (s), 161.04 (s), 159.00 (s), 105.00 (s), 90.52 (s), 55.79 (s), 55.37 (s), 20.44 (s).

References

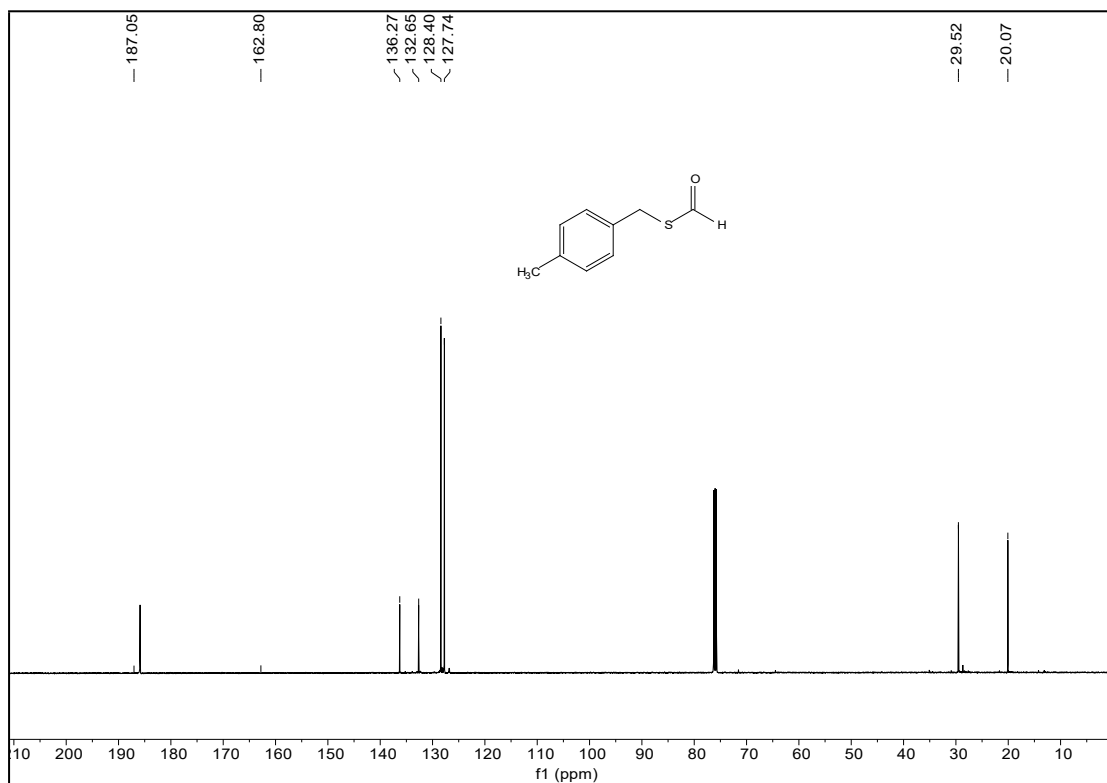
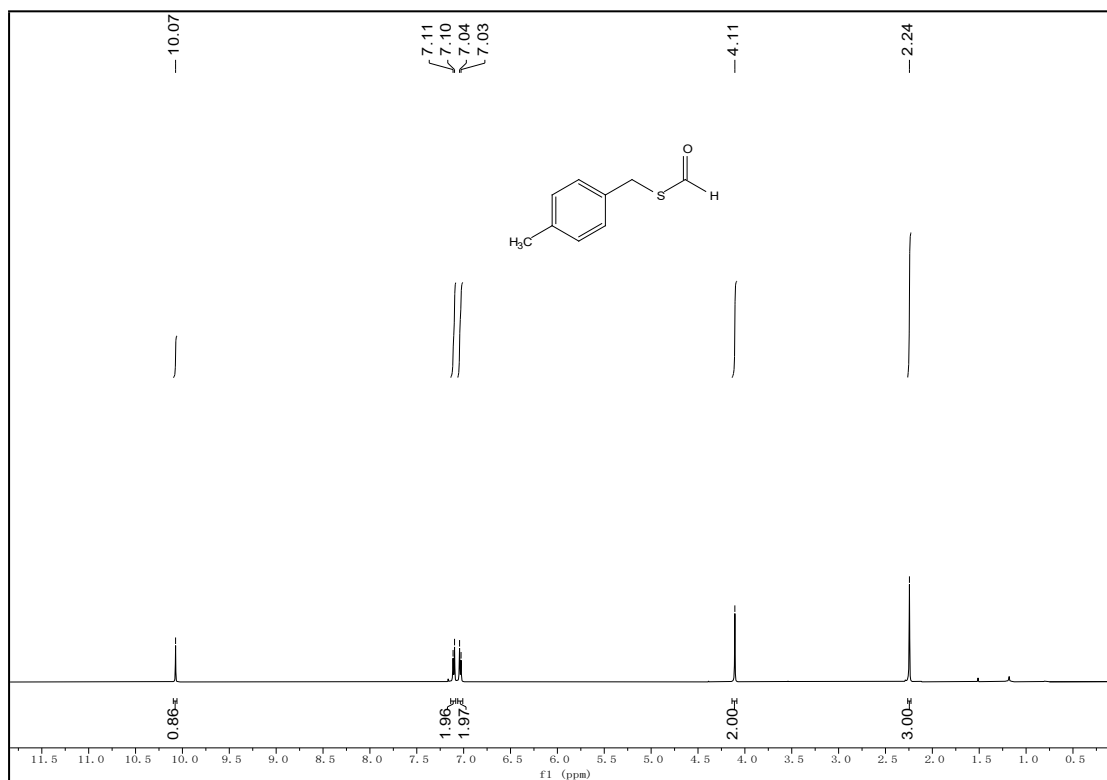
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NMR spectra

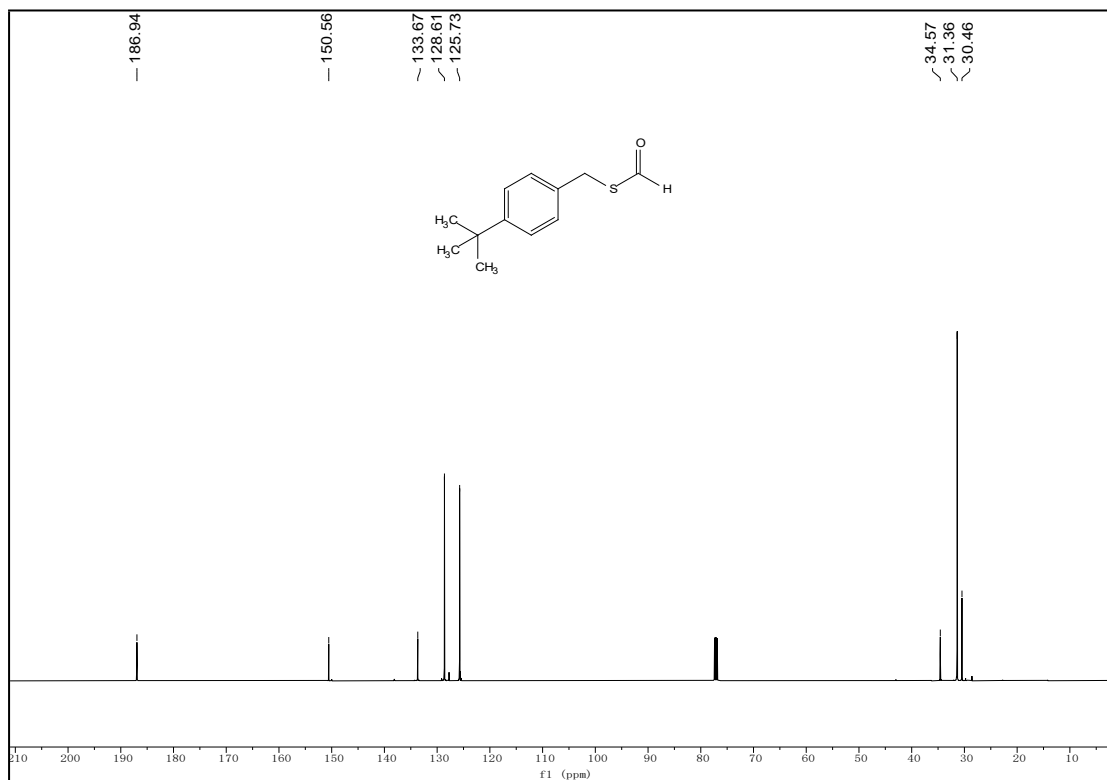
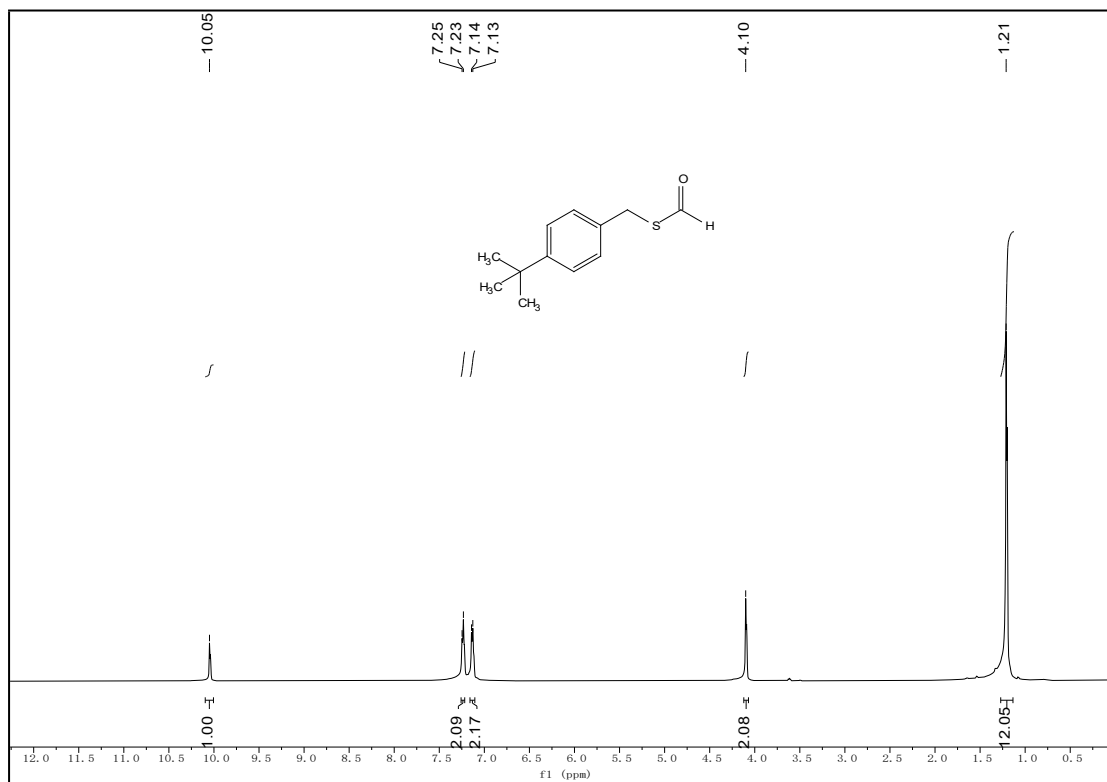
S-benzyl methanethioate (2a)



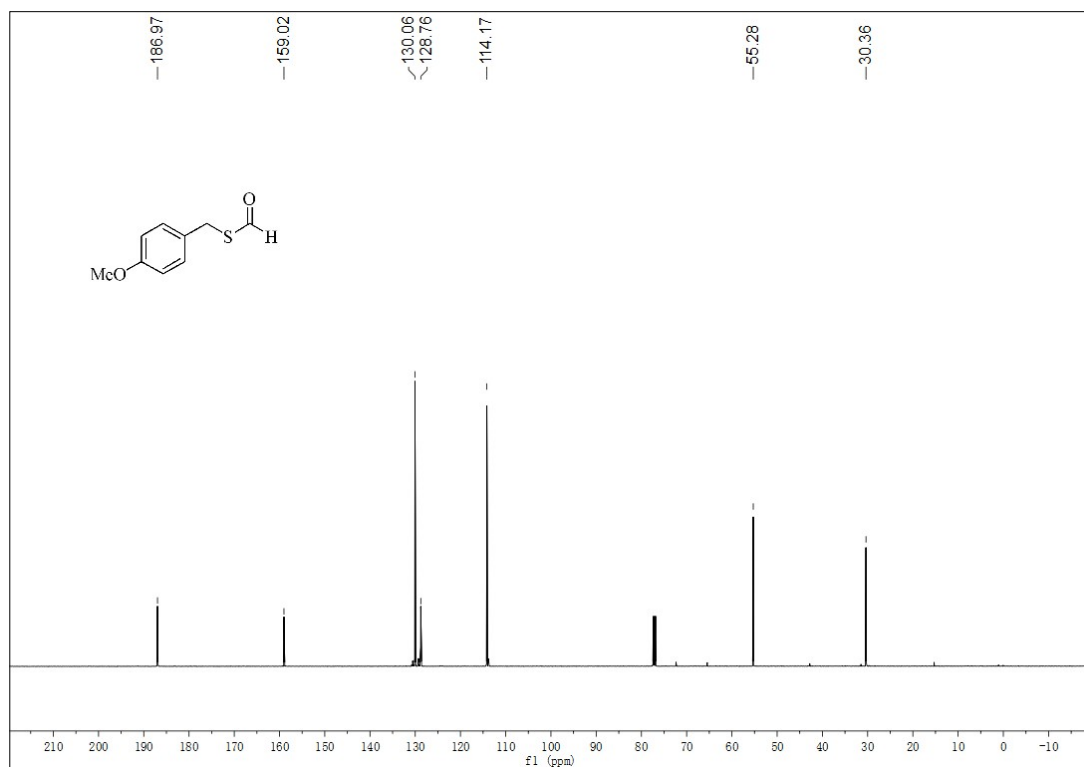
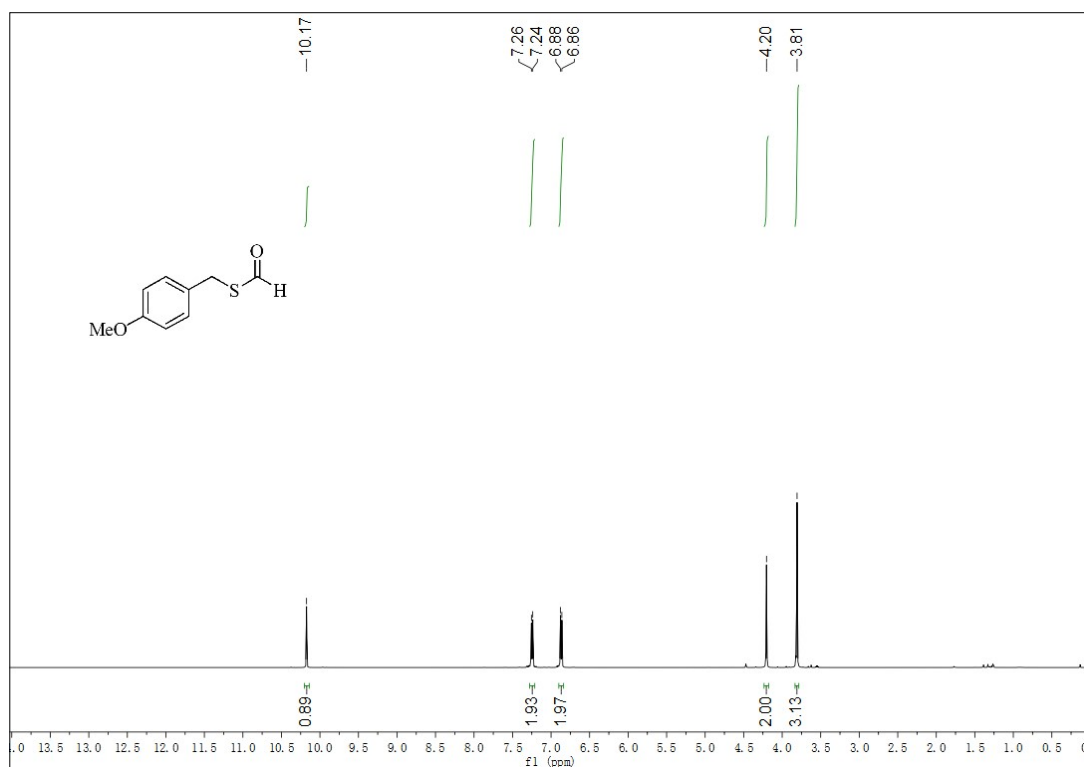
S-(4-methylbenzyl) methanethioate (2b)



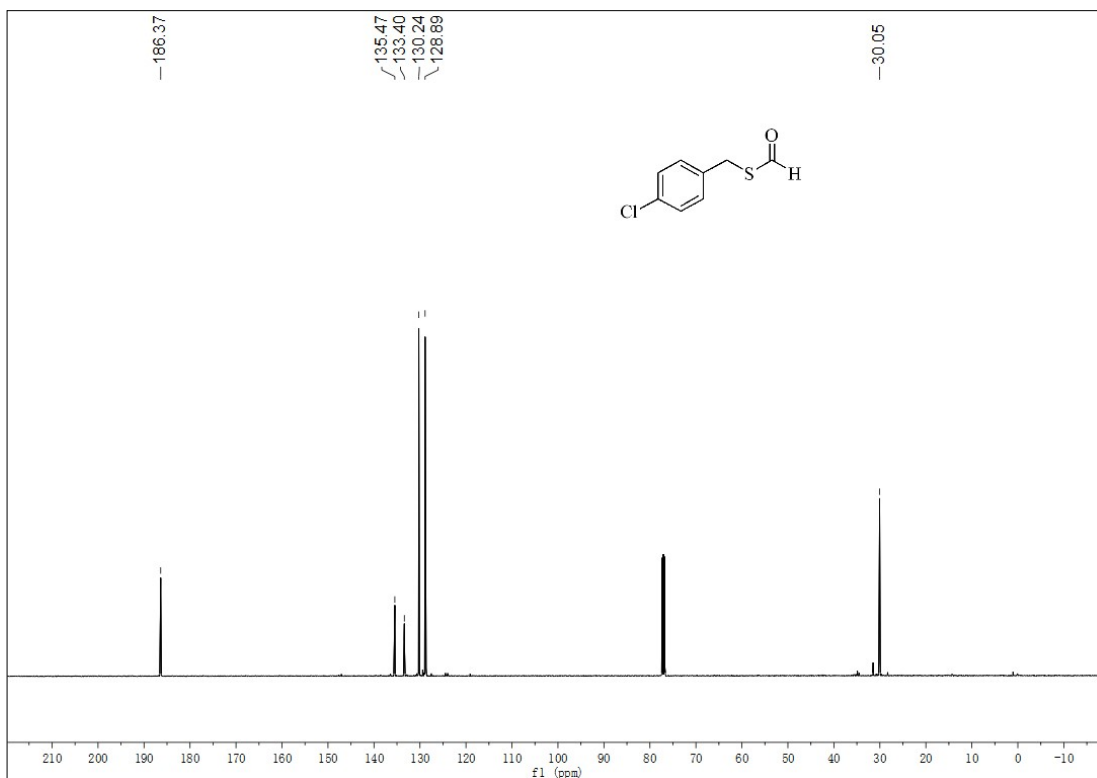
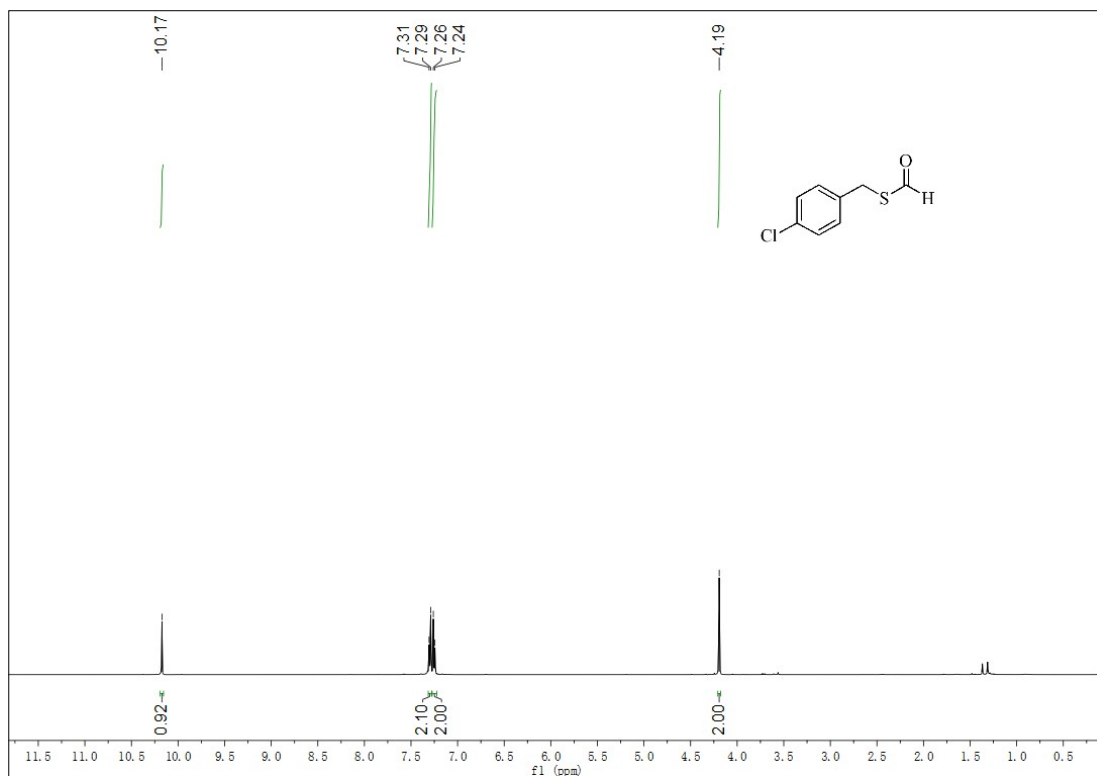
S-(4-(tert-butyl)benzyl) methanethioate (2c)



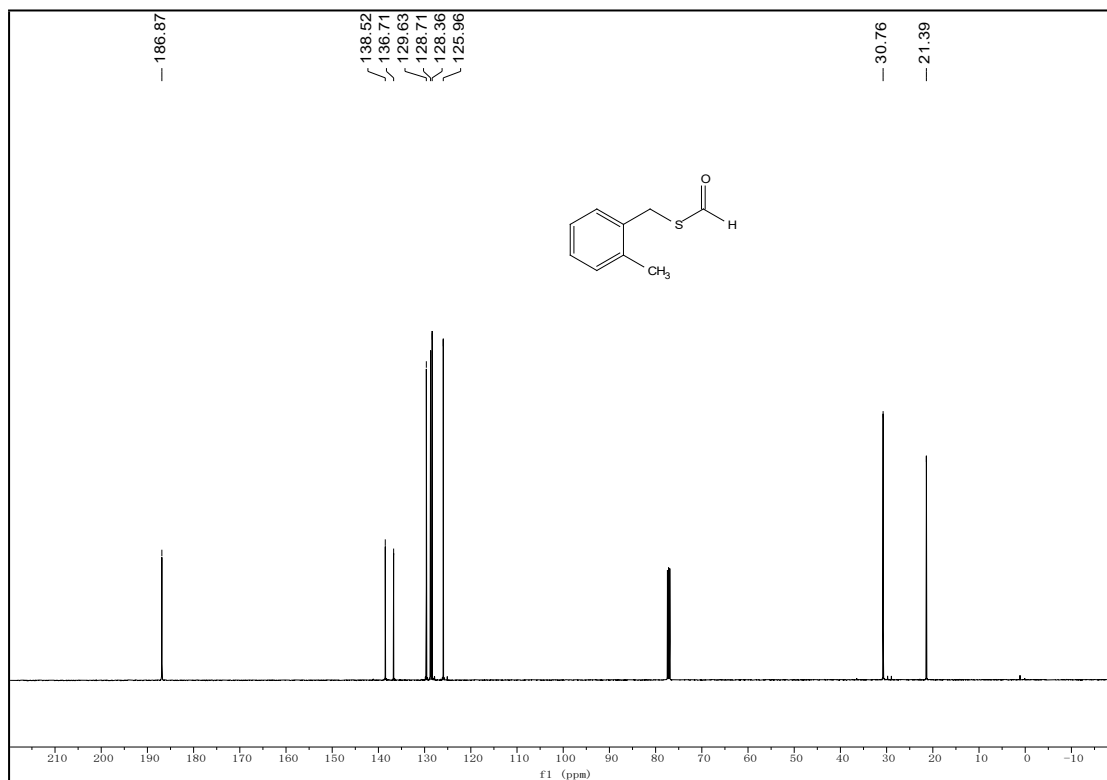
S-(4-methoxybenzyl) methanethioate (2d)



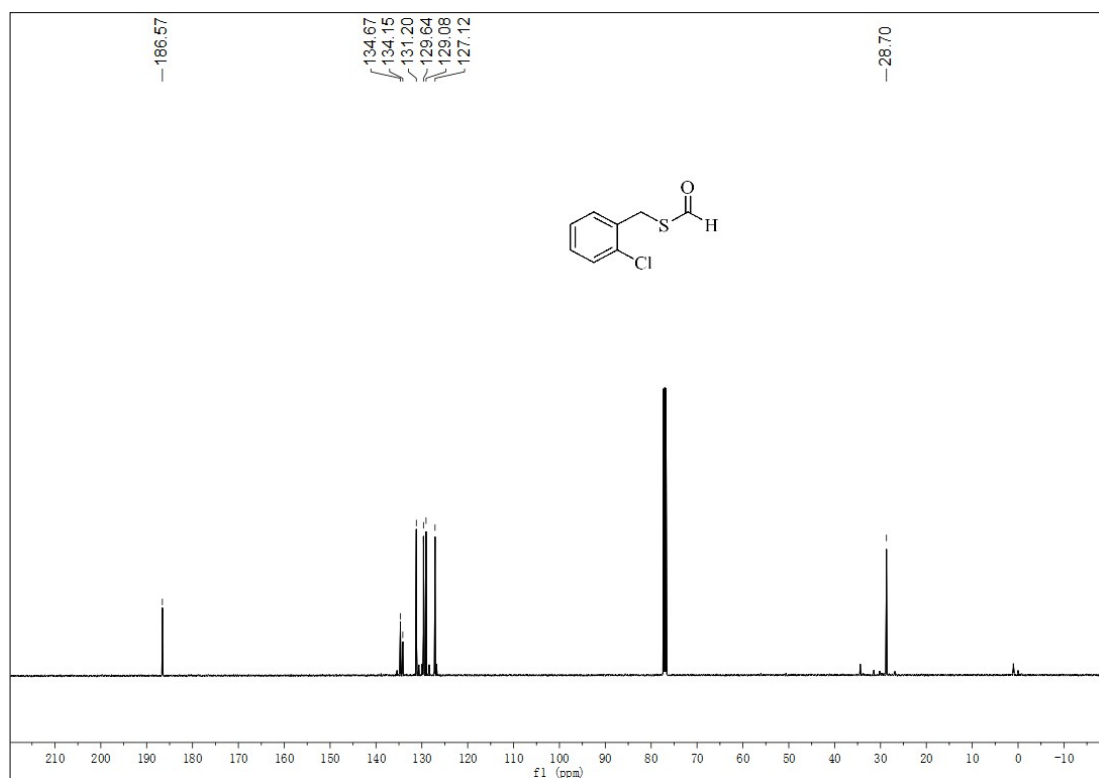
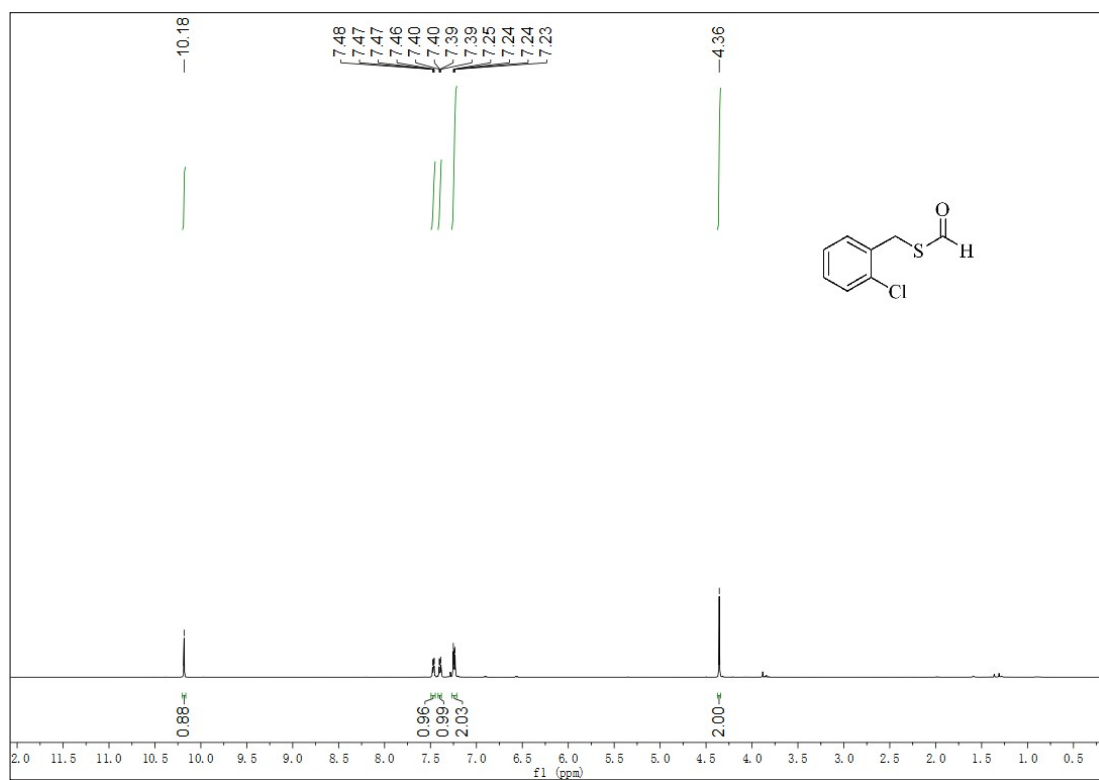
S-(4-chlorobenzyl) methanethioate (2e)



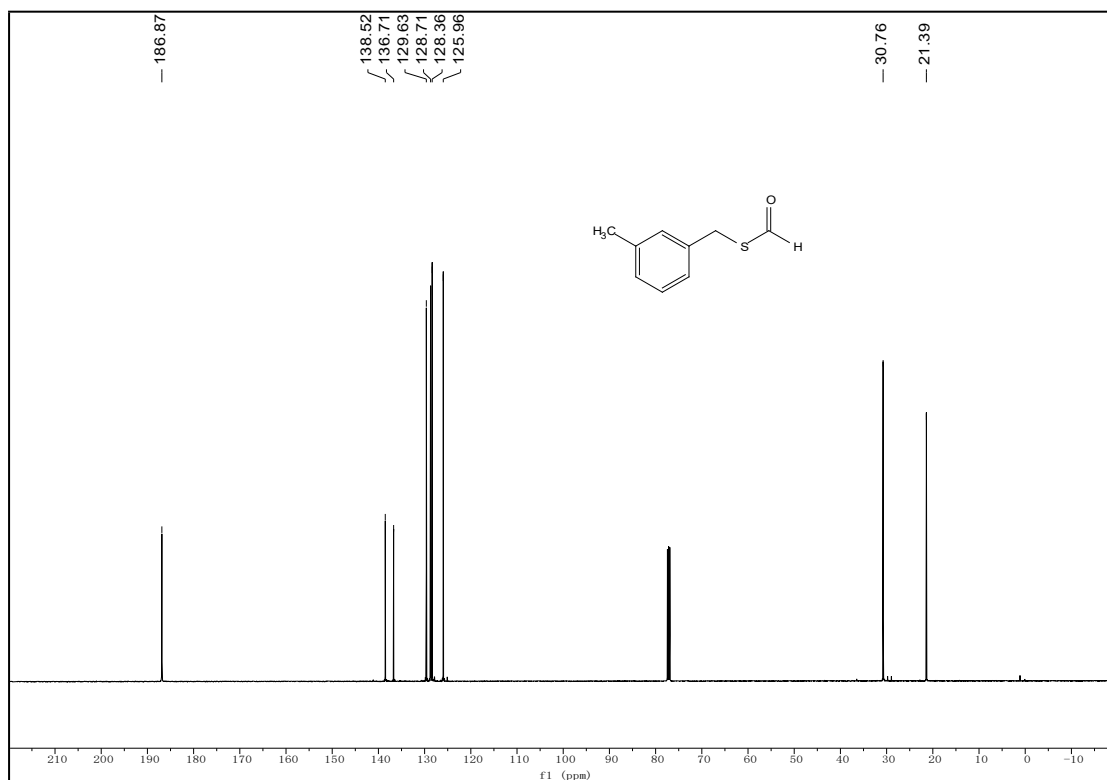
S-(2-methylbenzyl) methanethioate (2f)



S-(2-chlorobenzyl) methanethioate (2g)



S-(3-methylbenzyl) methanethioate (2h)



S-(2,4,6-trimethoxybenzyl) methanethioate (2i)

