Electronic Supplementary Information

New porous Co(II)-metal organic framework for high sorption selectivity and affinity for CO_2, and efficient catalytic oxidation of benzyl alcohols to benzaldehydes †

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Contents

I Tables

Table S1. Selected bonds lengths [Å] and angles [º] for **I**.

Complex **I**			
Co(1)-O(1)#1	2.024(2)	O(3)-Co(2)-N(1)#8	85.71(10)
Co(1)-O(1)	2.024(2)	O(4)-Co(2)-O(5)	84.49(9)
Co(1)-O(4)#2	2.155(2)	O(7)#7-Co(2)-O(2)#6	98.86(10)
Co(1)-O(4)#3	2.155(2)	O(7)#7-Co(2)-O(4)	94.38(10)
Co(1)-O(8)#4	2.063(2)	O(7)#7-Co(2)-O(5)	83.33(10)
Co(1)-O(8)#5	2.063(2)	O(7)#7-Co(2)-N(1)#8	88.21(10)
Co(2)-O(2)#6	2.141(2)	N(1)#8-Co(2)-O(2)#6	92.40(10)
Co(2)-O(3)	2.072(2)	N(1)#8-Co(2)-O(4)	171.31(9)
Co(2)-O(4)	2.160(2)	N(1)#8-Co(2)-O(5)	87.58(10)
Co(2)-O(5)	2.162(2)	C(22)-N(2)-C(23)	112.6(13)
Co(2)-O(7)#7	2.089(2)	C(22)-N(2)-C(24)	126.5(14)
Co(2)-N(1)#8	2.100(3)	C(24)-N(2)-C(23)	116.6(12)
N(2)-C(22)	1.354(15)	O(10)-C(22)-N(2)	111.6(15)
N(2)-C(23)	1.504(17)	O(10)-C(22)-H(22)	124.2
N(2)-C(24)	1.359(14)	N(2)-C(22)-H(22)	124.2
C(22)-H(22)	0.9500	N(2)-C(23)-H(23A)	109.5
C(23)-H(23A)	0.9800	N(2)-C(23)-H(23B)	109.5
C(23)-H(23B)	0.9800	N(2)-C(23)-H(23C)	109.5
C(23)-H(23C)	0.9800	H(24A)-C(24)-H(24B)	109.5
C(24)-H(24A)	0.9800	H(24A)-C(24)-H(24C)	109.5
C(24)-H(24B)	0.9800	H(24B)-C(24)-H(24C)	109.5
C(24)-H(24C)	0.9800	H(3A)-N(3)-H(3B)	107.8
N(3)-H(3A)	0.9100	C(25)-N(3)-H(3A)	109.1
N(3)-H(3B)	0.9100	C(25)-N(3)-H(3B)	109.1
N(3)-C(25)	1.364(10)	C(25)-N(3)-C(26)	112.6(9)
N(3)-C(26)	1.623(13)	C(26)-N(3)-H(3A)	109.1
C(25)-H(25A)	0.9800	C(26)-N(3)-H(3B)	109.1
C(25)-H(25B)	0.9800	H(23A)-C(23)-H(23B)	109.5
C(25)-H(25C)	0.9800	H(23A)-C(23)-H(23C)	109.5
C(26)-H(26A)	0.9800	H(23B)-C(23)-H(23C)	109.5
C(26)-H(26B)	0.9800	N(2)-C(22)-H(22)	124.2
C(26)-H(26C)	0.9800	N(2)-C(23)-H(23A)	109.5
O(1)#1-Co(1)-O(1)	180.0	N(2)-C(23)-H(23B)	109.5
O(1)-Co(1)-O(4)#2	84.89(10)	N(2)-C(23)-H(23C)	109.5
O(1)-Co(1)-O(4)#3	95.11(10)	H(23A)-C(23)-H(23B)	109.5
O(1)#1-Co(1)-O(4)#2	95.11(10)	H(23A)-C(23)-H(23C)	109.5

O(1)#1-Co(1)-O(4)#3	84.89(10)	H(23B)-C(23)-H(23C)	109.5
O(1)#1-Co(1)-O(8)#5	89.54(10)	N(2)-C(24)-H(24A)	109.5
O(1)#1-Co(1)-O(8)#4	90.46(10)	N(2)-C(24)-H(24B)	109.5
O(1)-Co(1)-O(8)#4	89.54(10)	N(2)-C(24)-H(24C)	109.5
O(1)-Co(1)-O(8)#5	90.46(10)	N(3)-C(25)-H(25A)	109.5
O(4)#2-Co(1)-O(4)#3	180.0	N(3)-C(25)-H(25B)	109.5
O(8)#4-Co(1)-O(4)#3	85.91(9)	N(3)-C(25)-H(25C)	109.5
O(8)#5-Co(1)-O(4)#2	85.91(9)	H(25A)-C(25)-H(25B)	109.5
O(8)#4-Co(1)-O(4)#2	94.09(9)	H(25A)-C(25)-H(25C)	109.5
O(8)#5-Co(1)-O(4)#3	94.09(9)	H(25B)-C(25)-H(25C)	109.5
O(8)#5-Co(1)-O(8)#4	180.00(12)	N(3)-C(26)-H(26A)	109.5
O(2)#6-Co(2)-O(4)	95.39(9)	N(3)-C(26)-H(26B)	109.5
O(2)#6-Co(2)-O(5)	177.81(10)	N(3)-C(26)-H(26C)	109.5
O(3)-Co(2)-O(2)#6	86.90(10)	H(26A)-C(26)-H(26B)	109.5
O(3)-Co(2)-O(4)	90.86(9)	H(26A)-C(26)-H(26C)	109.5
O(3)-Co(2)-O(5)	90.92(10)	H(26B)-C(26)-H(26C)	109.5
O(3)-Co(2)-O(7)#7	171.80(9)		

Symmetry Codes: #1-x+1, -y+2, -z+2; #2: -x+3/2, y+1/2, -z+3/2; #3: x-1/2, -y+3/2, z+1/2; #4: x, y, z+1; #5: -x+1, -y+2, -z+1; #6: -x+3/2, y-1/2, -z+3/2; #7: -x+3/2, y-1/2, -z+1/2; #8: -x+1, -y+1, -z+1.

Table S2. Hydrogen bonds for **1**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4A)...O(6)	0.815(19)	1.84(2)	2.621(3)	160(4)
O(4)-H(4B)...O(9)	0.826(19)	1.96(2)	2.747(4)	160(4)
C(22)-H(22)...O(9)	0.95	2.32	3.145(16)	144.3
C(24)-H(24A)...O(2)#2	0.98	2.53	3.314(14)	136.9
N(3)-H(3A)...O(6)	0.91	1.85	2.714(6)	158.5
N(3)-H(3B)...O(10)	0.91	1.70	2.578(14)	162.6

Symmetry Codes: -x+3/2, y+1/2,-z+3/2

Table S3. Comparison of selectivity for CO_2 over CH_4 at 298 K for **I'** and reported complexes.

Complexes	Selectivity	References
MIL-53(Al)	2.3	1
MOF-205-OBn	2.7	2
ZJNU-63	3.5	3
JLU-Liu18	4.5	4
MFM-130a	7.1	5
JLU-Liu46	9.8	6
$(Me_2NH_2)_2[Co_3(L)_2(H_2O)_2]$•2DMF	**12.8**	**This work**
[Ni(btzip)(H_2btzip)]·2DMF·2H_2O	13.9	7
{[PbZn($L)_2$]·DMA·H_2O}$_n$	16.2	8

Table S4. Comparison of selectivity for CO_2 over CH_4 at 273 K for **I'** and reported complexes.

Complexes	Selectivity	References
ZJNU-63	4.2	3
ZIF-95	4.3	9
ZIF-100	5.9	9
HKUST-1	7.1	10
MFM-130a	9.4	5
Cu_2(pbpta)	12	11
ZJU-16	38	12
$\{[PbZn(L)_2]\cdot DMA\cdot H_2O\}_n$	41.3	9
$(Me_2NH_2)_2[Co_3(L)_2(H_2O)_2]$•2DMF	**112**	**This work**

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Table S5. Optimization of the oxidation reactions[a]

Entry	Solvent	Cat (mol %)	Additive(mol %)	Time (h)	[b]Yield (%)
1	toluene	**I'**(3 mol %)	proline (40%)	3h	21
2	2-propanol	**I'**(3 mol %)	proline (40%)	3h	NR
3	H_2O	**I'**(3 mol %)	proline (40%)	3h	<5
4	Acetic acid	**I'**(3 mol %)	proline (40%)	3h	<5
5	DMSO	**I'**(3 mol %)	proline (40%)	3h	37
6	CH_3CN	**I'**(3 mol %)	proline (40%)	3h	95
7	THF	**I'**(3 mol %)	proline (40%)	3h	NR
8	CH_2Cl_2	**I'**(3 mol %)	proline (40%)	3h	Trace
9	DMF	**I'**(3 mol %)	proline (40%)	3h	47
10[c]	CH_3CN	**I'**(3 mol %)	-	3h	41[c]
11	CH_3CN	**I'**(3 mol %)	proline (5%)	3h	52
12	CH_3CN	**I'**(3 mol %)	proline (15%)	3h	68
13	CH_3CN	**I'**(3 mol %)	proline (30%)	3h	80
14	CH_3CN	**I'**(3 mol %)	proline (30%)	3h	89
15	CH_3CN	-	proline (40%)	3h	NR
16	CH_3CN	**I'**(1 mol %)	proline (40%)	3h	83
17	CH_3CN	**I'**(2 mol %)	proline (40%)	3h	89
18	CH_3CN	**I'**(5 mol %)	proline (40%)	3h	95
19	CH_3CN	$Co(NO_3)_2$(3mol %)	proline (40%)	3h	Trace
20	CH_3CN	$Co(OAc)_2$(3mol %)	proline (40%)	3h	Trace

[a]Reaction conditions: **1a** (0.2 mmol), **I'**(3 mol %), solvent (2 mL), proline (x mol %), for 3 h.
[b]Isolated yield; [c]The by-product is benzoic acid, yield 13%, conversion 54%; no reaction (NR).

II Figures

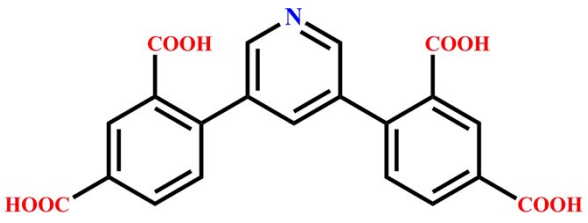


Fig. S1 The chemical structure of the v-shaped 3,5-di(2,4-dicarboxylphenyl)pyridine organic ligand H_4L.

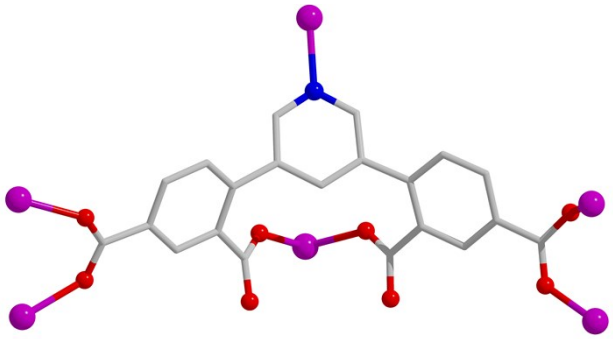


Fig. S2 The coordination model of carboxylic groups of the ligand in **I**: $\eta^2\mu_2\chi^2$ and $\eta^1\mu_1\chi^1$ (η-number of coordination bonds donated from the O atom of carboxylic groups from ligand; μ-number of metal centers bond the O atom of carboxylic groups from ligand; χ-number of coordination bonds).

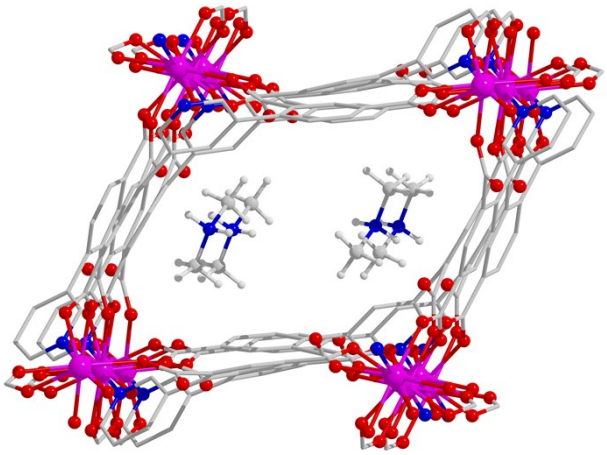
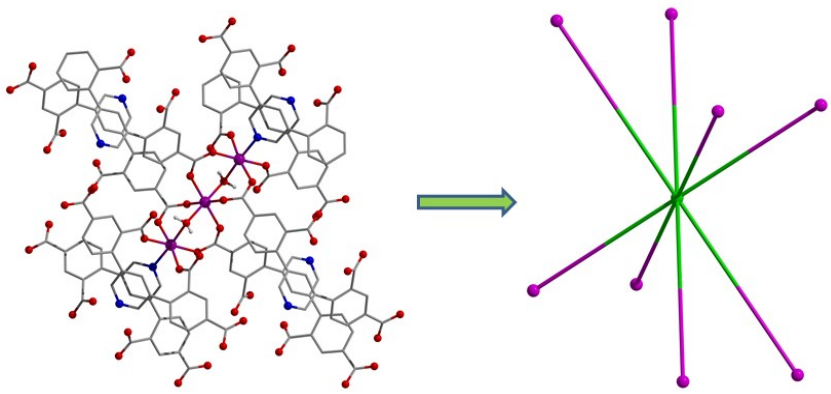
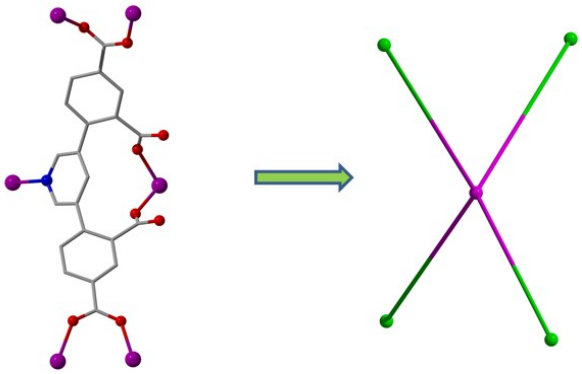


Fig.S3 The 1D porous network contains dimethyl ammonium ions [$Me_2NH_2^+$] of **I**.



(a)



(b)

Fig. S4 Topology analysis for **I**: (a) simplified for the trinuclear SBUs $[Co_3(COO)_4(H_2O)_2N_2]$ as 8-connected nodes; (b) simplified for the organic ligand L^{4-} as 4-connected nodes.

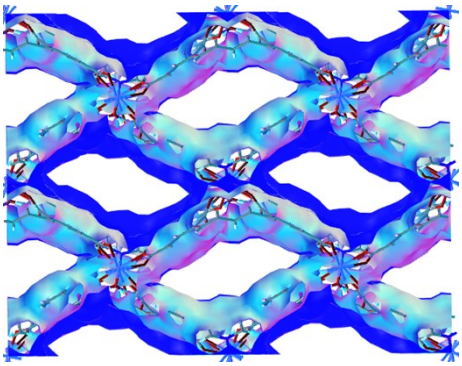


Fig. S5 Pore structure of **I** from Materials Studio 6.0.

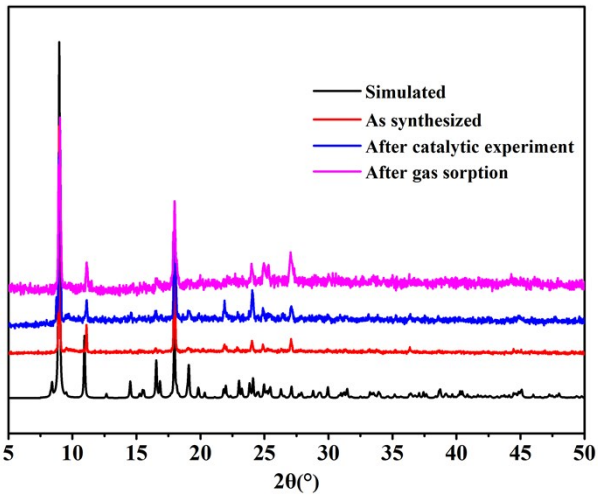


Fig. S6 PXRD patterns of **I** (simulated from crystal data; as synthesized; after catalytic and gas sorption experiments).

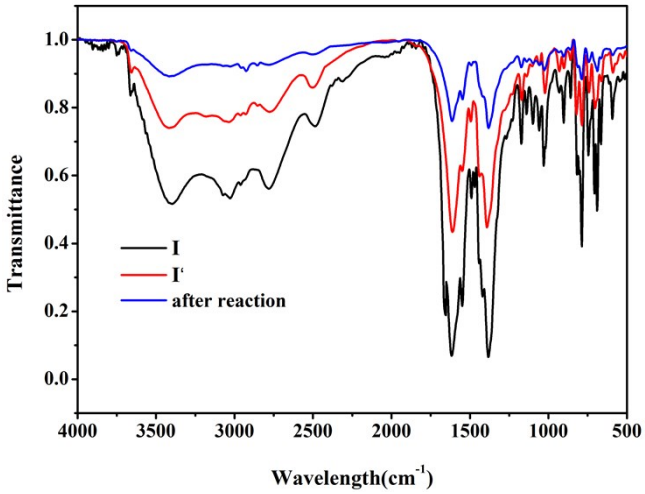


Fig. S7 The FT-IR spectra of complexes **I**, **I'** and the sample after catalytic reaction. The characteristic C=O vibration at 1663 cm^{-1} of DMF in **I** is absent in **I'**, indicating the complete removal of DMF.

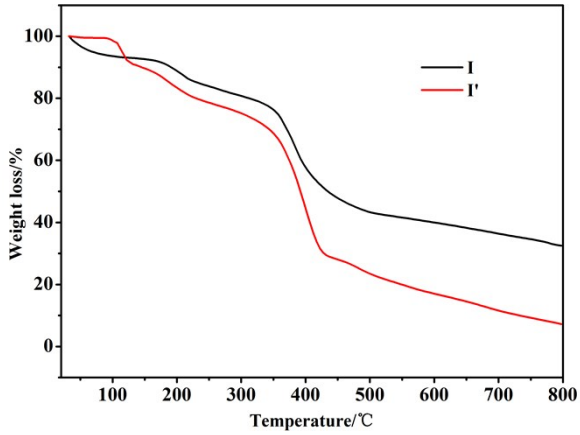


Fig. S8 TGA curves of the as-synthesized **I** and desolvated samples **I'**.

Gas adsorption test

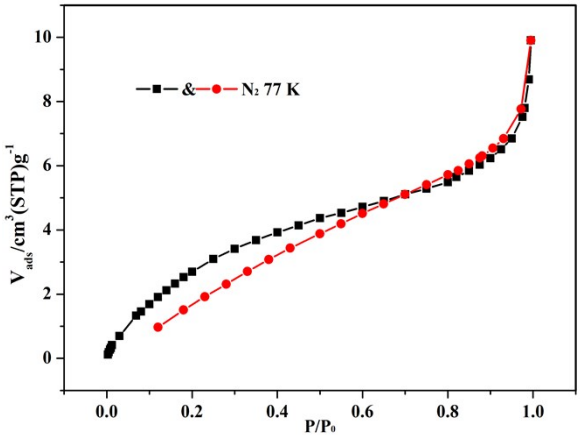


Fig. S9 N_2 adsorption isotherm for **I'** at 77 K.

IAST adsorption selectivity calculation:

The experimental isotherm data for pure CO_2 and CH_4 (measured at 273 and 298 K) were fitted using a Langmuir-Freundlich (L-F) model:

$$q = \frac{a * b * p^c}{1 + b * p^c}$$

Where q and p are adsorbed amounts and pressures of component i, respectively. The adsorption selectivities for binary mixtures of CO_2/CH_4 at 273 and 298 K, defined by

$$S_{ads} = (q_1 / q_2) / (p_1 / p_2)$$

Where qi is the amount of i adsorbed and pi is the partial pressure of i in the mixture.

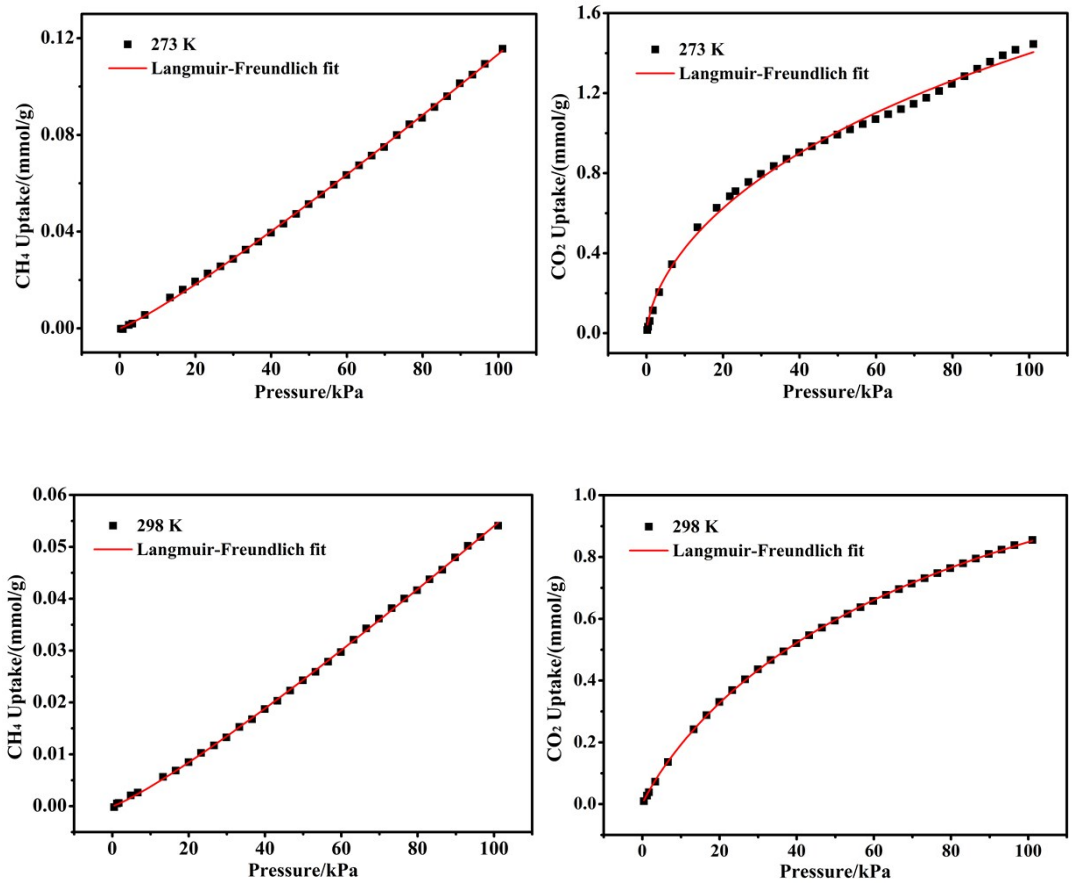


Fig. S10 CH_4 adsorption isotherms of **I'** at 273 K with fitting by L-F model: a = 8.2443, b = 7.189×10^{-5}, c = 1.14407, Chi^2 = 4.18×10^{-7}, R^2 = 0.99969; CO_2 adsorption isotherms of **I'** at 273 K with fitting by L-F model: a = 5.01081, b = 0.02217, c = 0.62107, Chi^2 = 8.01×10^{-4}, R^2 = 0.99559; CH_4 adsorption isotherms of **I'** at 298 K with fitting by L-F model: a =2.93833, b = 8.84887×10^{-5}, c = 1.16282, Chi^2 = 7.89072×10^{-8}, R^2 = 0.99973; CO_2 adsorption isotherms of **I'** at 298 K with fitting by L-F model: a = 1.64397, b = 0.01654, c = 0.90479, Chi^2 = 6.5063×10^{-6}, R^2 = 0.99991.

Calculation of sorption heat for CO_2 uptake using Virial 2 model

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} aiN^i + \sum_{i=0}^{n} biN^i \quad Q_{st} = -R \sum_{i=0}^{m} aiN^i$$

The above equation was applied to fit the combined CO_2 isotherm data for **I'** at 273 and 298 K, where P is the pressure, N is the adsorbed amount, T is the temperature, ai and bi are virial coefficients, and m and n are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and R is the universal gas constant.

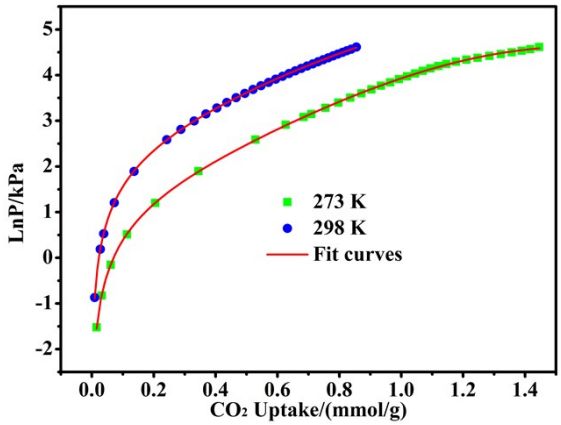
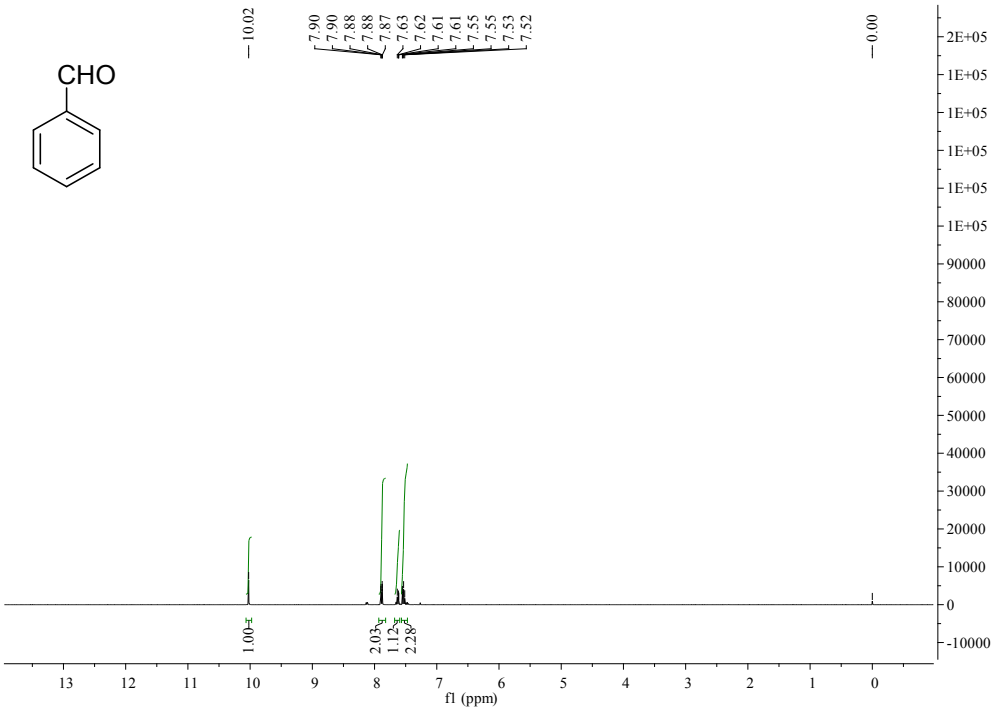
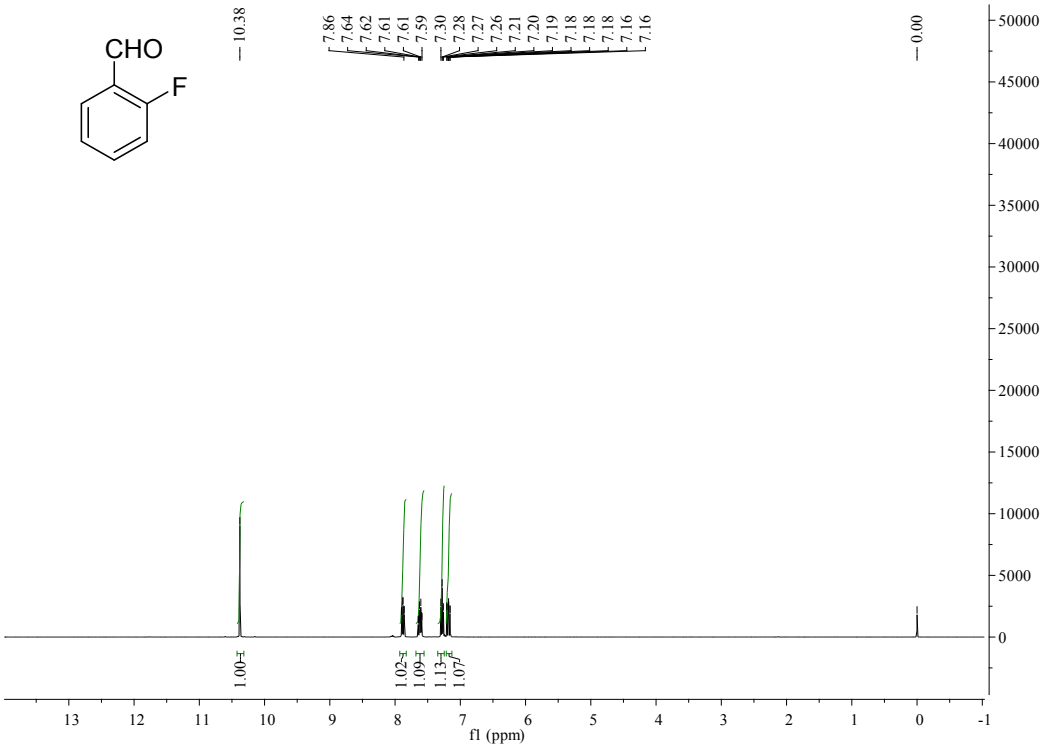


Fig. S11 CO_2 adsorption isotherms for **I'** fitted by Virial model. Fitging results: a0 = -3791.44891; a1 = -295.74484; a2 = 886.17577; a3 = 278.32264; a4 = -345.5531; a5 = 81.96688; b0 = 16.49525; b1 = 1.83753; b2 = -2.73299; Chi^2 = 1.26359×10^{-4}; R^2 = 0.99994.

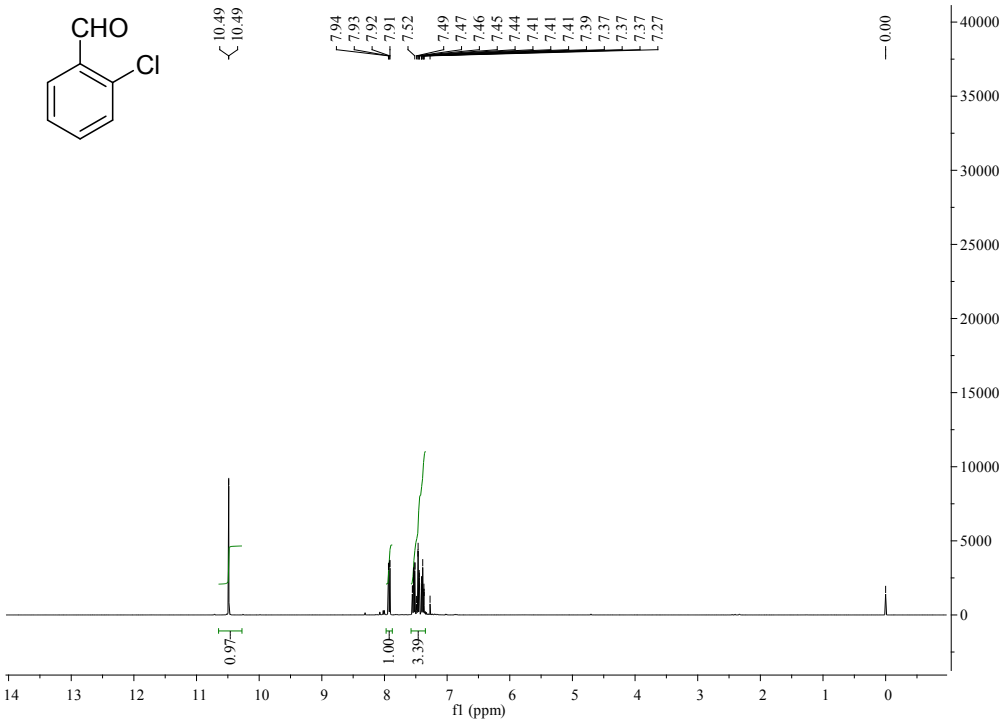
^{1}H NMR spectra of compound **2a**



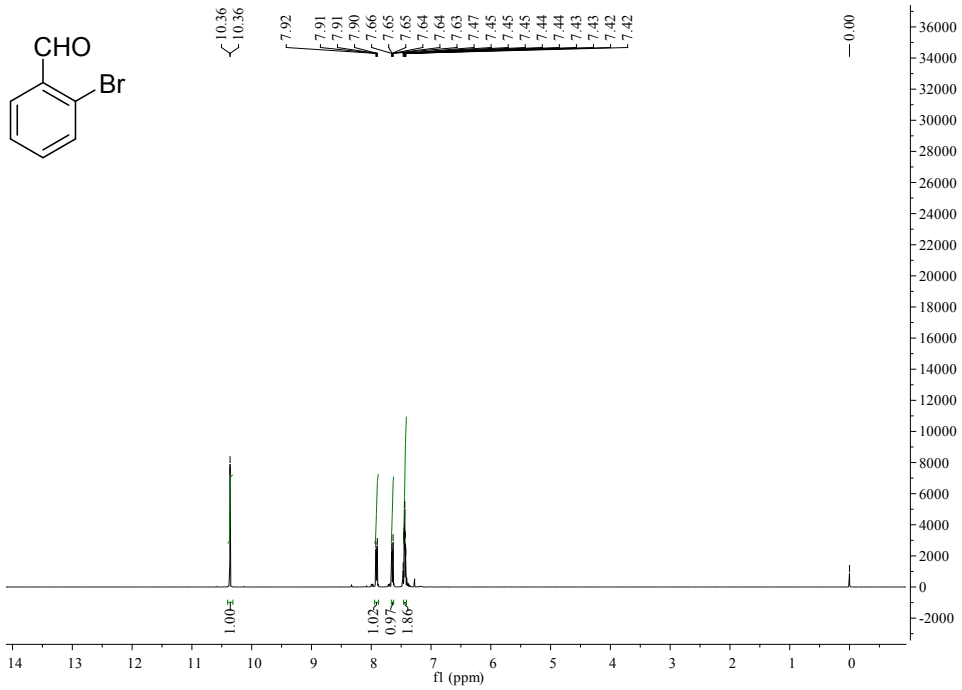
^{1}H NMR spectra of compound **2b**



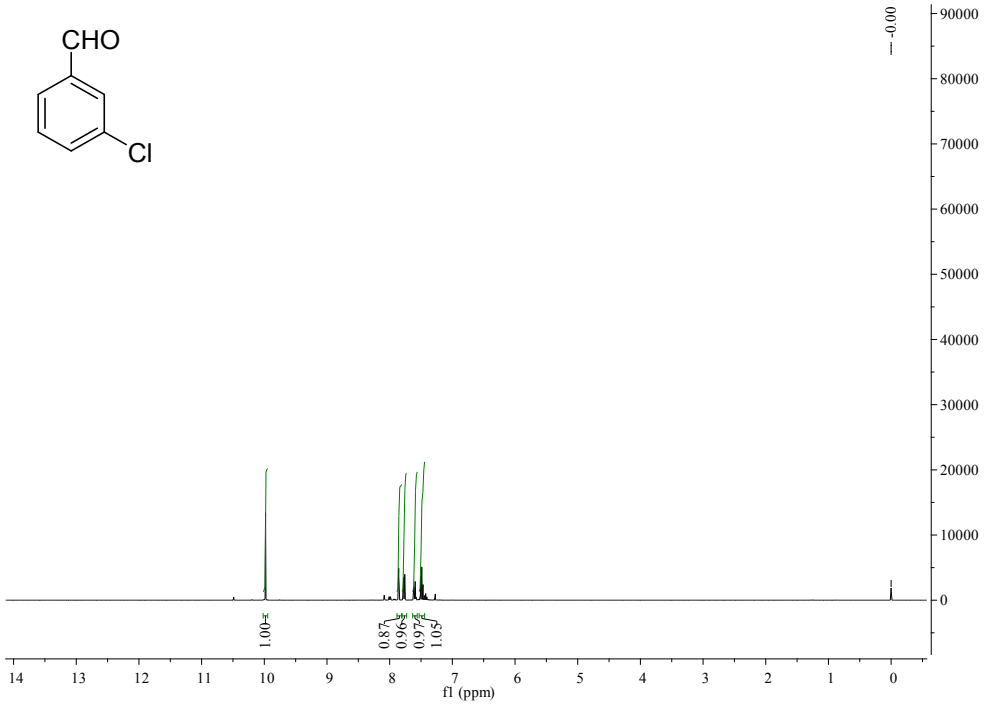
^{1}H NMR spectra of compound **2c**



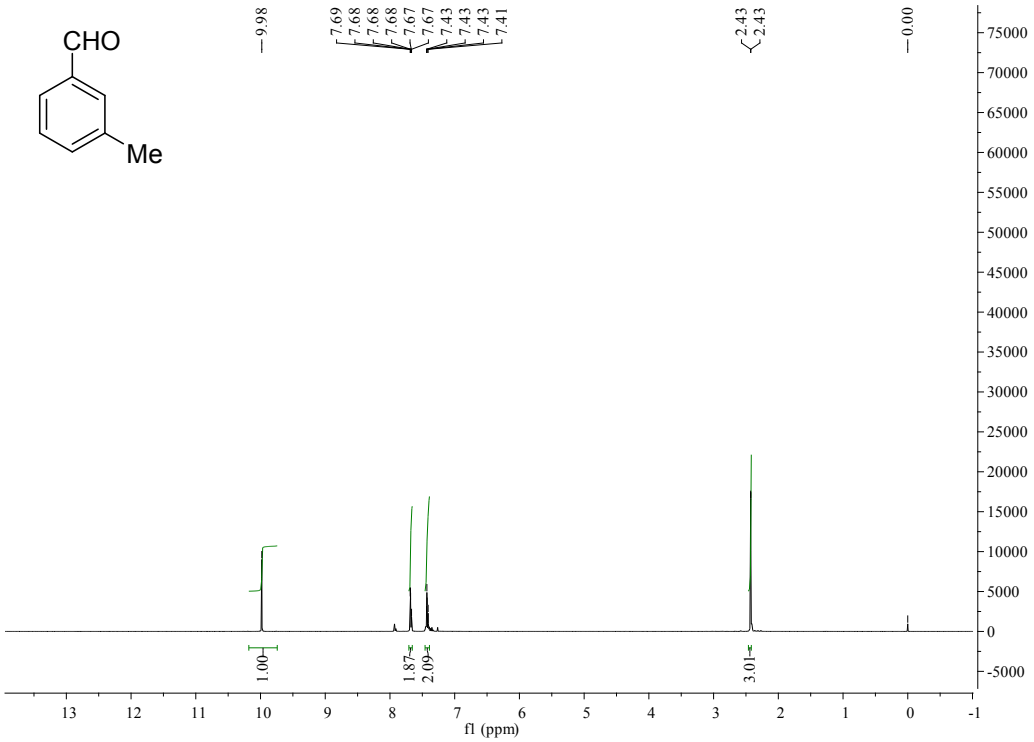
^{1}H NMR spectra of compound **2d**



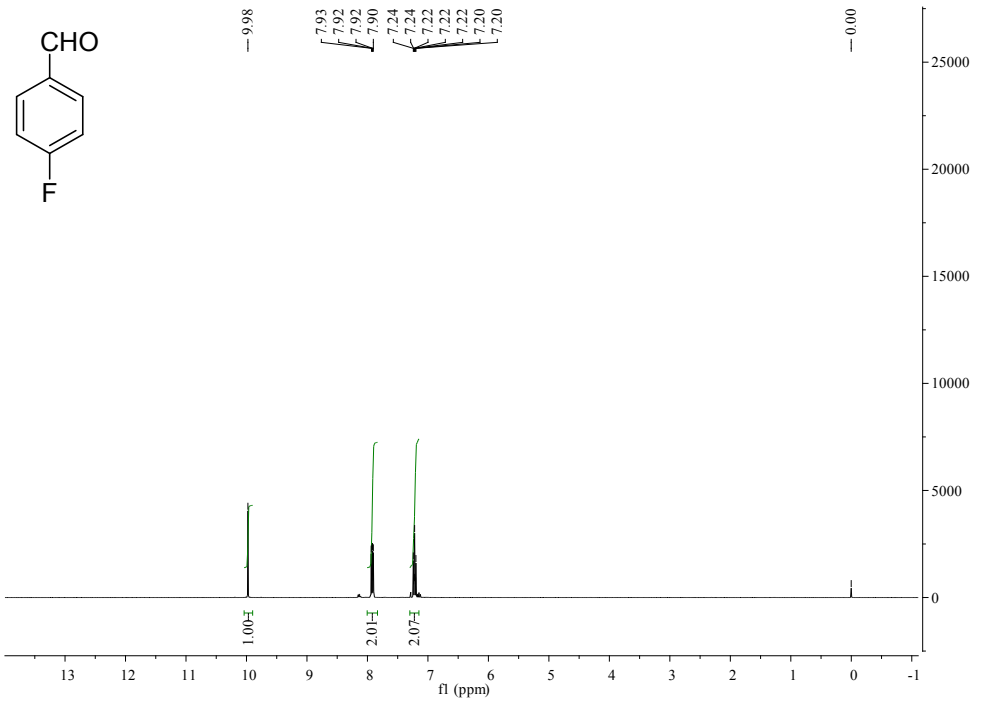
^{1}H NMR spectra of compound **2e**



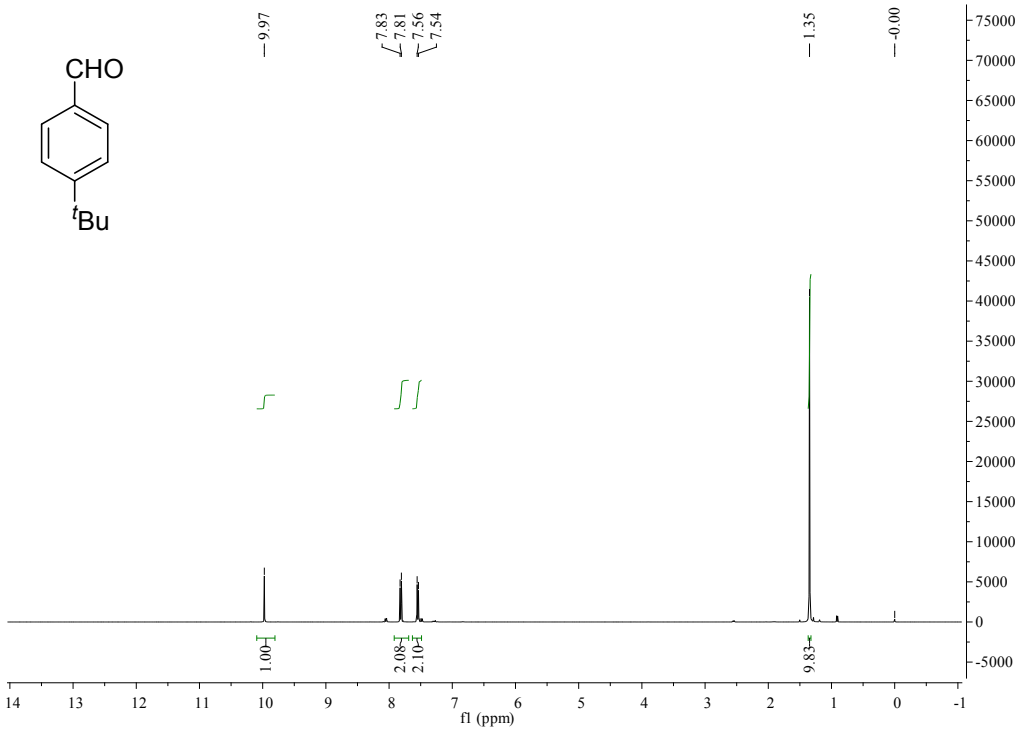
^{1}H NMR spectra of compound **2f**



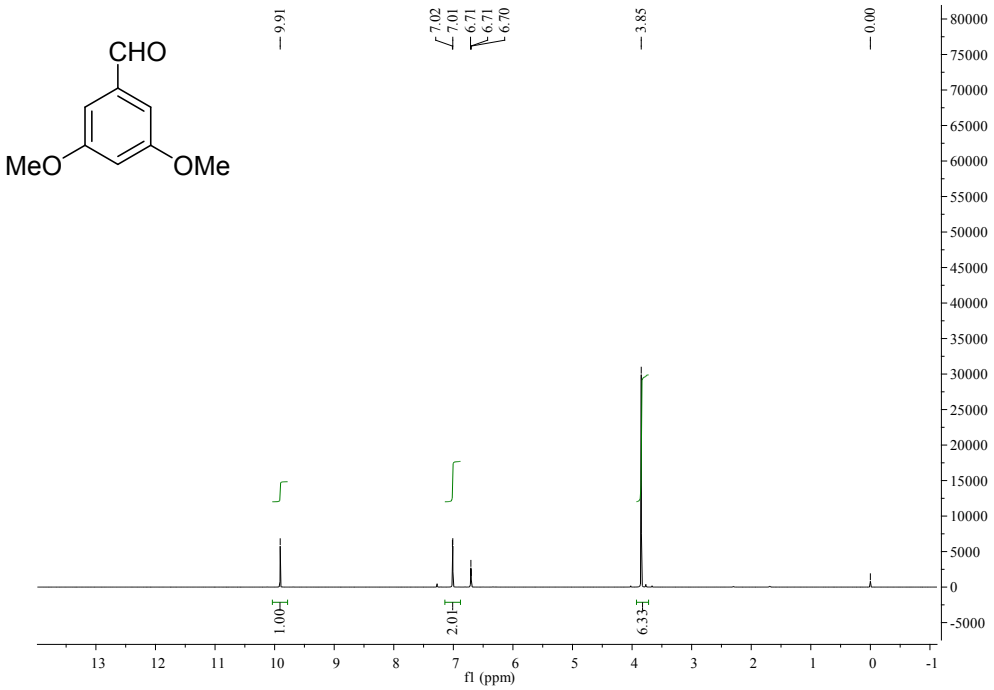
^{1}H NMR spectra of compound **2g**



^{1}H NMR spectra of compound **2h**



^{1}H NMR spectra of compound **2i**



^{1}H NMR spectra of compound **2j**

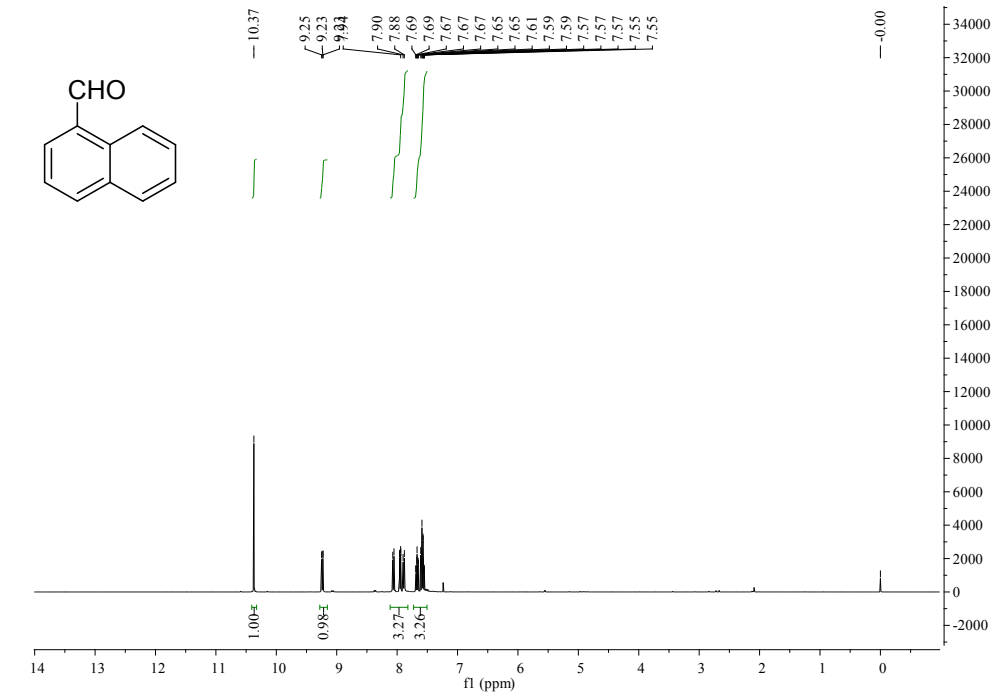


Fig. S12 ^{1}H NMR spectra for the catalytic oxidation of benzyl alcohols into benzaldehydes (^{1}H NMR).