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PII: S0040-4020(15)30082-X

DOI: 10.1016/j.tet.2015.09.054

Reference: TET 27151

To appear in: *Tetrahedron*

Received Date: 27 July 2015

Revised Date: 20 September 2015

Accepted Date: 22 September 2015

Please cite this article as: Zhao H, Chen Q, Wei L, Jiang Y, Cai M, A highly efficient heterogeneous aerobic alcohol oxidation catalyzed by immobilization of bipyridine copper(I) complex in MCM-41, *Tetrahedron* (2015), doi: 10.1016/j.tet.2015.09.054.

A highly efficient heterogeneous aerobic alcohol oxidation catalyzed by immobilization of bipyridine copper(I) complex in MCM-41

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ABSTRACT

A heterogeneous copper(I)-catalyzed aerobic oxidation of primary benzylic and allylic alcohols to aldehydes was achieved under air in EtOH at 50 ºC in the presence of 5 mol% of MCM-41-immobilized bipyridine copper(I) complex [MCM-41-bpy-CuI] and 5 mol% of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) using aqueous ammonia as base, yielding a variety of aromatic and α,β-unsaturated aldehydes in good to excellent yields. This heterogeneous copper catalyst can be easily recovered by a simple filtration of reaction solution and reused for at least 10 consecutive trials without any decreases in activity. The use of recyclable heterogeneous copper catalyst and green reagents, such as air as oxidant and ethanol as solvent, made the system attractive for environmentally sustainable processes.

Keywords: Aerobic alcohol oxidation; Supported copper complex; Bipyridine ligand; MCM-41; Heterogeneous catalysis

1. Introduction

The oxidation of alcohols into aldehydes or ketones is a ubiquitous transformation in synthetic organic chemistry[1] and enormous efforts have been devoted to the development of aerobic oxidation methods.[2] The development of copper-catalyzed oxidation systems with economically and environmentally benign oxidants such as

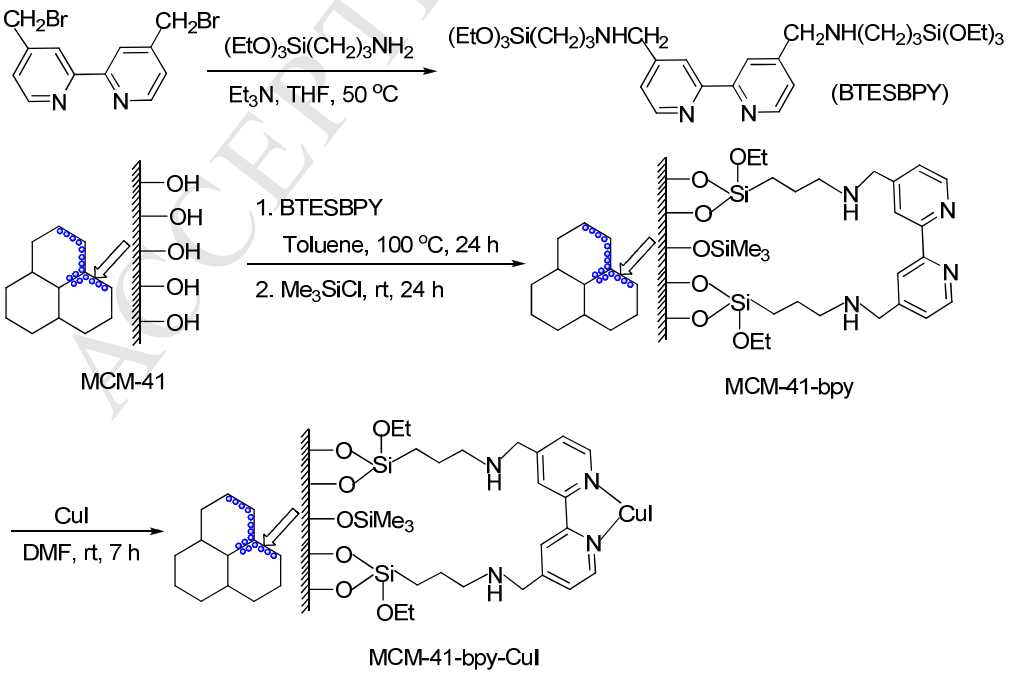
oxygen or air is of particular interest because copper is an inexpensive, abundant metal and the reduction product is water.[3] Since Semmelhack first reported the CuCl/TEMPO-catalyzed aerobic oxidation of alcohols to aldehydes or ketones,[4] the copper-catalyzed aerobic alcohol oxidations have received much attention.[5] Marko *et al.* reported a CuCl/1,10-Phen/$DBADH_2$ catalytic system for aerobic oxidation of primary and secondary alcohols into aldehydes and ketones using K_2CO_3 as a base in toluene.[6] Sheldon *et al.* described a $CuBr_2$/bpy/TEMPO catalytic system with $KOBu^t$ as a base in an acetonitrile/water (2:1) solvent mixture.[7] Koskinen *et al.* reported a $Cu(OTf)_2$/bpy/TEMPO catalytic system using NMI (*N*-methylimidazole) and/or DBU as a base in MeCN.[8] More recently, Stahl *et al.* have developed a highly efficient CuOTf/bpy/TEMPO/NMI catalytic system in which the use of Cu(I) source improved the performance of the catalyst and substrate scope.[9] Although these copper-catalyzed aerobic alcohol oxidations are highly efficient, the problem with homogeneous catalysis is the difficulty to separate the catalyst from the reaction mixture and the impossibility to reuse it in consecutive reactions. It is well known that homogeneous catalysis might result in heavy metal contamination of the isolated product, which is a particularly significant drawback for its application in the pharmaceutical industry. In contrast, heterogeneous catalysts can be easily separated from the reaction mixture by a simple filtration of the reaction solution and reused in successive reactions provided that the active sites have not become deactivated. Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the development of green chemical processes.[10,11] From the standpoint of environmentally benign organic

synthesis, the development of immobilized copper catalysts is challenging and important. In an ideal system, they can be recovered by simple filtration and re-used infinitely, and the contamination of products by copper is prevented. In spite of considerable effort dedicated to heterogeneous copper-catalyzed carbon-carbon and carbon-heteroatom bond formation reactions over the last several years,[12] to the best of our knowledge, the aerobic alcohol oxidation catalyzed by heterogeneous copper complexes has not been reported until now.

The discovery of mesoporous material MCM-41 has given an enormous stimulus to research in heterogeneous catalysis and provided a new possible candidate for a solid support for immobilizing homogeneous catalysts.[13] MCM-41 has a regular pore diameter of *ca.*5 nm and a specific surface area > 700 $m^2 g^{-1}$ and rich silanol groups in the inner walls.[14] To date, functionalized MCM-41-immobilized palladium or rhodium complexes have been prepared and successfully used in organic reactions.[15] Very recently, we have reported the first preparation of 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized copper(I) complexes [MCM-41-2N-CuI(CuCl)] and found that they are highly efficient and recyclable heterogeneous catalysts for the homo- and heterocoupling of terminal alkynes[12d] and C–N or C–S bond formation reactions.[12h,16] In continuing our efforts to develop greener synthetic pathways for organic transformations, our new approach, described in this paper, was to design and synthesize a novel MCM-41-immobilized bipyridine copper(I) complex [MCM-41-bpy-CuI], which was used as an effective copper catalyst for the aerobic alcohol oxidation under mild conditions.

2. Results and discussion

A novel MCM-41-immobilized bipyridine copper(I) complex [MCM-41-bpy-CuI] was synthesized starting from 3-aminopropyltriethoxysilane, 4,4'-bis(bromomethyl)-2,2'-bipyridine,[17] mesoporous material MCM-41, and CuI according to Scheme 1. Firstly, the reaction of 3-aminopropyltriethoxysilane with 4,4'-bis(bromomethyl)-2,2'-bipyridine in THF at 50 °C in the presence of triethylamine for 6 h gave 4,4'-bis[3-(triethoxysilyl)propylaminomethyl]-2,2'-bipyridine (BTESBPY), which reacted with MCM-41 in toluene at 100 °C for 24 h, followed by the silylation with Me_3SiCl in toluene at room temperature for 24 h to generate bipyridine-functionalized MCM-41 [MCM-41-bpy]. Then MCM-41-bpy reacted with CuI in DMF at room temperature for 7 h to afford the MCM-41-immobilized bipyridine copper(I) complex [MCM-41-bpy-CuI] as a pale blue powder.



Scheme 1.

X-ray powder diffraction (XRD) patterns of the parent MCM-41 and the modified material MCM-41-bpy-CuI are displayed in Fig. 1. The small angle X-ray powder diffraction (XRD) analysis of the MCM-41-bpy-CuI indicated that, in addition to an intense diffraction peak (100), two higher order diffraction peaks (110) and (200) were also detected and became weak and diffuse, which could be due to contrast matching between the silicate framework and organic moieties which are located inside the channels of MCM-41, therefore the chemical bonding procedure did not diminish the structural ordering of the parent MCM-41.

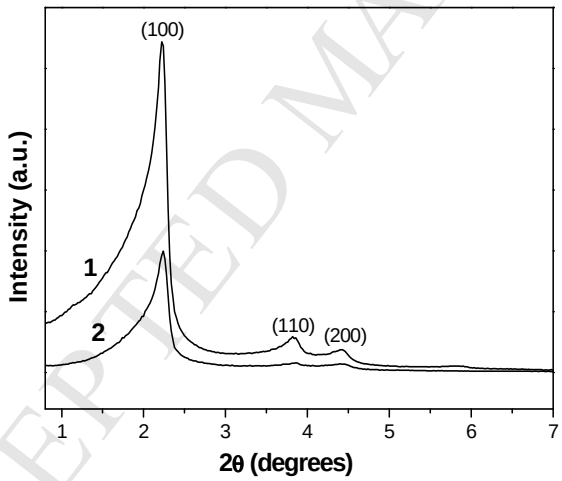


Fig. 1 XRD patterns of the parent MCM-41 (1) and MCM-41-bpy-CuI (2).

The N_2 adsorption-desorption isotherms and pore size distributions for MCM-41 and MCM-41-bpy-CuI are presented in Fig. 2 and Fig. 3, respectively. The isotherm of parent MCM-41 in Fig. 2 is of type IV as defined by IUPAC, characteristic of mesoporous materials according to the classification. Compared to parent MCM-41, the modified material MCM-41-bpy-CuI also gave reversible type IV N_2 sorption

isotherm, but exhibited a decreased uptake of N_2 owing to the incorporation of the bpy ligand and the further silylation with Me_3SiCl and coordination with CuI. As shown in Fig. 3, the pore volume and size of MCM-41-bpy-CuI reduced apparently compared to parent MCM-41, also indicating the organic moieties were introduced into the inner channels, but the pore still remained a narrow distribution. The parent MCM-41 had surface area of 902 m^2 g^{-1} and diameter of 2.7 nm, however, MCM-41-bpy-CuI had surface area of 658 m^2 g^{-1} and diameter of 2.2 nm. These results indicated that the bipyridine copper(I) complex has been successfully grafted onto MCM-41.

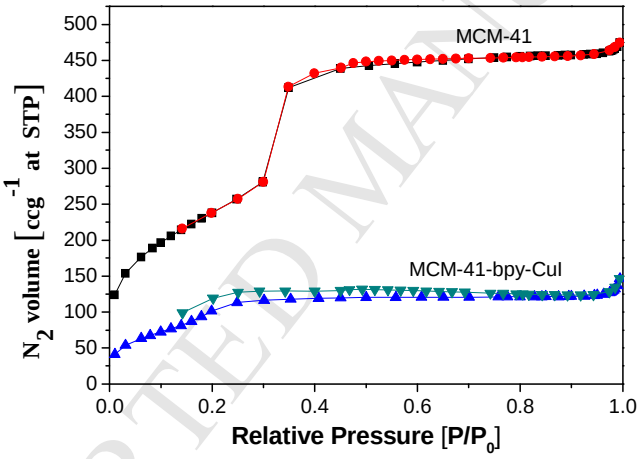


Fig. 2 N_2 adsorption/desorption isotherms of MCM-41 and MCM-41-bpy-CuI

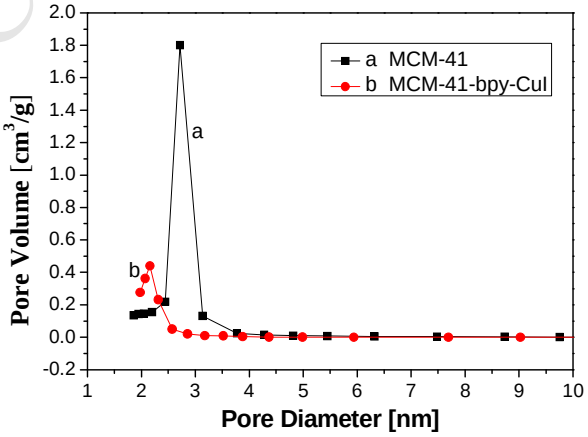
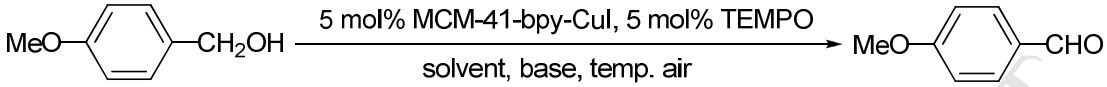


Fig. 3 Pore size distributions of MCM-41 and MCM-41-bpy-CuI

Initially, 4-methoxyphenylmethanol was selected as the model substrate to optimize the oxidation conditions, and the results are presented in Table 1. An 85% yield of the product was obtained when the oxidation reaction was performed at 30 ºC in EtOH with aqueous ammonia as a base (Table 1, entry 1). Notably, neither carboxylic acid nor ester as byproduct was detected. Among the solvents examined [EtOH, MeCN, MeCN/H_2O, DMSO, DMF, and toluene], both EtOH and MeCN gave good yields, while other solvents were substantially less effective (Table 1, entries 2-6). We then turned our attention to investigate the effect of base on the oxidation reaction. When NMI or ^{t}BuOK was used as a base, good yield was also obtained, but aqueous ammonia was the best choice due to its low cost (Table 1, entries 1, 7 and 8). Other bases such as K_2CO_3, Na_2CO_3 and K_3PO_4 were inferior to aqueous ammonia (Table 1, entries 9-11). The reaction was very slow in the absence of a base and a low yield was observed (Table 1, entry 12). When reaction temperature was raised to 50 °C, the reaction rate was increased obviously and an excellent yield was achieved (Table 1, entry 13). Finally, the amount of supported copper catalyst was also screened, and 5.0 mol% loading of copper was found to be optimal (Table 1, entry 13), a lower yield was observed and a longer reaction time was required when the amount of the catalyst was decreased (Table 1, entry 15). Increasing the amount of copper catalyst could shorten the reaction time, but did not increase the yield of 4-methoxybenzaldyhyde (Table 1, entry 16). Thus, the optimized reaction conditions for this oxidation reaction involved the use of the MCM-41-bpy-CuI (5 mol%), aqueous ammonia (1.0 equiv), in

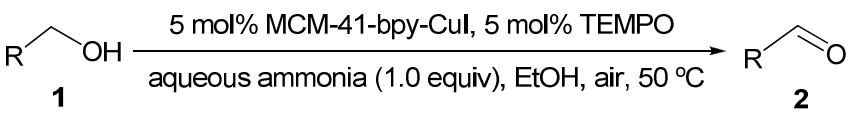
EtOH at 50 °C under air for 24 h (Table 1, entry 13).

Table 1 The optimization of heterogeneous copper-catalyzed alcohol oxidation[a]



Entry	Solvent	Base	Temp. (°C)	Time (h)	Yield (%)[b]
1	EtOH	$NH_3 \cdot H_2O$	30	48	85
2	MeCN	$NH_3 \cdot H_2O$	30	48	81
3	MeCN/H_2O (2/1)	$NH_3 \cdot H_2O$	30	48	68
4	DMSO	$NH_3 \cdot H_2O$	30	48	54
5	DMF	$NH_3 \cdot H_2O$	30	48	46
6	Toluene	$NH_3 \cdot H_2O$	30	48	34
7	EtOH	NMI	30	48	84
8	EtOH	^{t}BuOK	30	48	79
9	EtOH	K_2CO_3	30	48	57
10	EtOH	Na_2CO_3	30	48	55
11	EtOH	K_3PO_4	30	48	50
12	EtOH	None	30	72	37
13	EtOH	$NH_3 \cdot H_2O$	50	24	97
14	EtOH	$NH_3 \cdot H_2O$	80	24	92
15[c]	EtOH	$NH_3 \cdot H_2O$	50	48	72
16[d]	EtOH	$NH_3 \cdot H_2O$	50	15	95

[a] All reactions were performed using 4-methoxyphenylmethanol (0.5 mmol), TEMPO (0.025 mmol), base (0.5 mmol) and MCM-41-bpy-CuI (0.025 mmol) in solvent (1.0 mL) under air. [b] Isolated yield. [c] 2 mol% copper catalyst was used. [d] 10 mol% copper catalyst was used.



Scheme 2.

To examine the scope for this heterogeneous copper-catalyzed aerobic alcohol oxidation reaction, we have investigated the reactions using a variety of primary benzylic and allylic alcohols as the substrates under the optimized ambient conditions (Scheme 2) and the results are summarized in Table 2. To our delight, most tested substrates could be selectively transformed into the corresponding aldehydes in good to excellent yields and over oxidation products such as acids or esters were not detected by GC-MS during the reaction. A number of functional groups were tolerated. The reactions were particularly efficient for electron-rich and -neutral benzylic alcohols. For example, benzylic alcohols with electron-donating substituents such as methyl, methoxy, and dimethylamino groups on the benzene ring underwent the oxidation reaction very smoothly to afford the corresponding substituted benzaldehydes **2b-g** in excellent yields (Table 2, entries 2-7). Satisfactory results were also obtained for most electron-deficient benzylic alcohols except for strongly electron-deficient 4-nitrobenzyl alcohol and 3-nitrobenzyl alcohol which gave moderate yields of desired products **2l** and **2m** on a prolonged reaction time (Table 2, entries 8-13). In addition, benzylic alcohols carrying an *ortho* substituent were found to readily participate in the reaction. For instance, the reactions of 2-methylbenzyl alcohol, 2-methoxybenzyl alcohol, 2-aminobenzyl alcohol, and 2-halobenzyl alcohols provided good to excellent yields of the corresponding *ortho*-substituted benzaldehydes **2n-s** under the optimized reaction conditions (Table 2, entries 14-19). It is noteworthy to mention that the oxidation protocol also allowed the smooth transformation of 1-naphthyl-

methanol and heterocyclic alcohols into the corresponding 1-naphthaldehyde (**2t**) and heteroaromatic aldehydes **2u**-**w** in good to excellent yields (Table 2, entries 20-23). The oxidation reaction of the aryl-substituted primary allylic alcohol, (*E*)-cinnamyl alcohol, could also proceed effectively under the standard conditions to give the desired (*E*)-cinnamaldehyde (**2x**) in good yield (Table 2, entry 24), however, the alkyl-substituted primary allylic alcohols such as geraniol did not work (Table 2, entry 25). In addition, the aerobic oxidation of secondary alcohols like 1-phenylethanol into acetophenone was inhibited, which might be ascribed to the steric effect of the methyl group in the α-position (Table 2, entry 26). We attempted to carry out the oxidation of aliphatic alcohols such as 1-octanol, unfortunately, no desired 1-octanal (**2a'**) was detected under the optimized reaction conditions (Table 2, entry 27). We also performed the reaction on a gram-scale. 4-Methylbenzyl alcohol (1.221 g, 10 mmol) was stirred at 50 ºC for 26 h in the presence of MCM-41-bpy-CuI (0.8 g, 0.5 mmol), TEMPO (80 mg, 0.5 mmol), aqueous ammonia (10 mmol, 25-28%, w/w) in EtOH (20 mL) under air to afford 1.128 g of the desired product (**2b**) in 94% yield (Table 2, entry 28).

Table 2 Heterogeneous copper-catalyzed aerobic oxidation of primary alcohols to aldehydes[a]

Entry	R	Time (h)	Product	Yield (%)[b]
1	Ph	22	PhCHO (**2a**)	91
2	4-MeC_6H_4	23	4-MeC_6H_4CHO (**2b**)	96
3	4-$MeOC_6H_4$	24	4-$MeOC_6H_4$CHO (**2c**)	97
4	3,4-$Me_2C_6H_3$	18	3,4-$Me_2C_6H_3$CHO (**2d**)	96

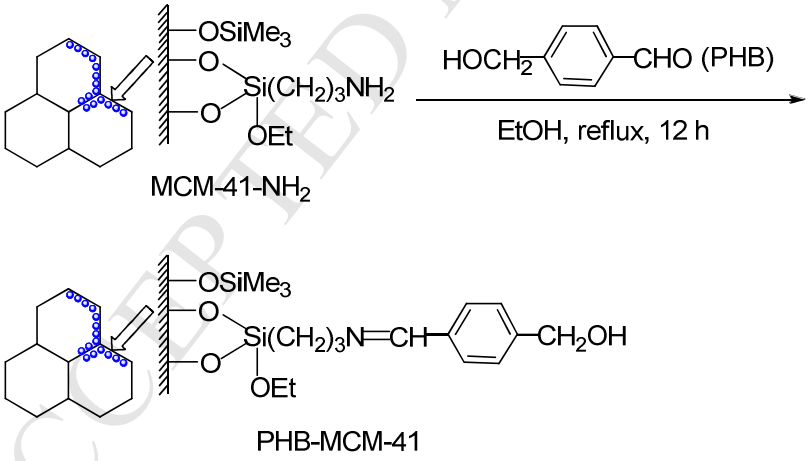
5	3,4-$(MeO)_2C_6H_3$	24	3,4-$(MeO)_2C_6H_3CHO$ (**2e**)	98
6	3,4-$CH_2O_2C_6H_3$	30	3,4-$CH_2O_2C_6H_3CHO$ (**2f**)	94
7	4-$Me_2NC_6H_4$	24	4-$Me_2NC_6H_4CHO$ (**2g**)	92
8	4-ClC_6H_4	26	4-ClC_6H_4CHO (**2h**)	92
9	4-BrC_6H_4	24	4-BrC_6H_4CHO (**2i**)	94
10	4-FC_6H_4	24	4-FC_6H_4CHO (**2j**)	93
11	4-$AcNHC_6H_4$	24	4-$AcNHC_6H_4CHO$ (**2k**)	91
12	4-$O_2NC_6H_4$	48	4-$O_2NC_6H_4CHO$ (**2l**)	58
13	3-$O_2NC_6H_4$	48	3-$O_2NC_6H_4CHO$ (**2m**)	55
14	2-MeC_6H_4	24	2-MeC_6H_4CHO (**2n**)	94
15	2-$MeOC_6H_4$	24	2-$MeOC_6H_4CHO$ (**2o**)	93
16	2-ClC_6H_4	24	2-ClC_6H_4CHO (**2p**)	91
17	2-BrC_6H_4	24	2-BrC_6H_4CHO (**2q**)	90
18	2-$H_2NC_6H_4$	48	2-$H_2NC_6H_4CHO$ (**2r**)	79
19	2,4-$Cl_2C_6H_3$	24	2,4-$Cl_2C_6H_3CHO$ (**2s**)	91
20	1-naphthyl	36	1-naphthaldehyde (**2t**)	83
21	2-thienyl	22	2-thiophenaldehyde (**2u**)	98
22	2-furyl	36	2-furaldehyde (**2v**)	65
23	3-pyridyl	36	3-pyridinaldehyde (**2w**)	78
24	(*E*)-PhCH=CH	48	(*E*)-PhCH=CHCHO (**2x**)	83
25	geraniol	48	geranial (**2y**)	0
26	1-phenylethanol	48	acetophenone (**2z**)	0
27	1-octanol	48	1-octanal (**2a'**)	0
28[c]	4-MeC_6H_4	26	4-MeC_6H_4CHO (**2b**)	94

[a] All reactions were performed using 0.5 mmol of alcohol, 0.5 mmol of aqueous ammonia (25-28%, w/w), 5 mol% of TEMPO and 5 mol% of MCM-41-bpy-CuI in EtOH (1.0 mL) at 50 °C under air. [b] Isolated yield. [c] Reaction run on 10 mmol scale.

To verify whether the observed catalysis was due to the heterogeneous catalyst MCM-41-bpy-CuI or to a leached copper species in solution, we performed the hot

filtration test[18] and three-phase test.[19] We focused on the aerobic oxidation reaction of benzyl alcohol. We filtered off the MCM-41-bpy-CuI complex after 10 h of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (50 °C) in order to avoid possible recoordination or precipitation of soluble copper upon cooling. We found that, after this hot filtration, no further reaction was observed and no copper could be detected in the hot filtered solution by ICP-AES analysis. These results suggest that the Cu is not being leached out from the solid surface of the catalyst during the oxidation reaction. To perform three-phase test, we have chosen benzylic alcohol, *p*-(hydroxymethyl)benzaldehyde (PHB) that is anchored on the surface of the 3-aminopropyl-functionalized MCM-41 [MCM-41-NH_2][20] to give PHB-MCM-41 as shown in Scheme 3. A solution of *p*-tolyl-methanol (0.5 mmol), aqueous ammonia (0.5 mmol, 25-28%, w/w), TEMPO (0.025 mmol) in EtOH (2 mL) was stirred in the presence of MCM-41-bpy-CuI (0.025 mmol) and PHB-MCM-41 (0.5 g) at 50 ºC under air for 24 h. The reaction mixture was cooled to room temperature, then filtered and washed with EtOH. The collected filtrate was purified and analyzed by GC and ^{1}H NMR, which showed about 96% of *p*-tolylmethanol converted to 4-methylbenzaldehyde as expected for the aerobic oxidation reaction of benzylic alcohols. The residue obtained from the filtration was then hydrolyzed by 2 N aqueous HCl under refluxing condition. It was neutralized and extracted with ethyl acetate and finally analyzed by GC and ^{1}H NMR. The only compound obtained in this process was *p*-(hydroxymethyl)benzaldehyde (PHB). The expected product of *p*-(hydroxymethyl)benzaldehyde in the oxidation reaction is

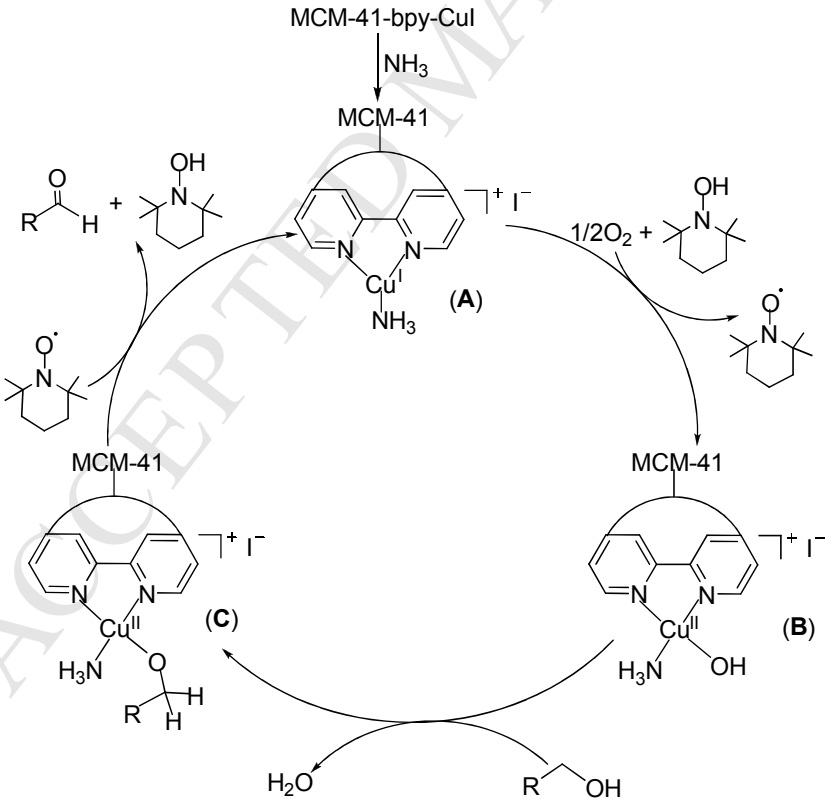
terephthalaldehyde and it was not detected from the liquid phase test. However, it was found that the oxidation of *p*-(hydroxymethyl)benzaldehyde (PHB) could proceed smoothly under the optimized reaction conditions to give terephthalaldehyde in 89% yield after 30 h. So it is clearly evident that the *p*-(hydroxymethyl)benzaldehyde remains unreacted inside the mesopores of PHB-MCM-41. Hence, the *p*-(hydroxyl-methyl)benzaldehyde has not participated in the oxidation reaction, while anchored on the functionalized MCM-41. If there will be any leaching of copper species from MCM-41-bpy-CuI, the anchored *p*-(hydroxylmethyl)benzaldehyde would have also participated in the above oxidation reaction. However, this is not the case for our present catalyst.



Scheme 3.

Recently, Stahl *et al.* have reported the detailed mechanistic studies of copper-catalyzed aerobic oxidation reaction of alcohols, this heterogeneous copper-catalyzed aerobic oxidation of primary benzylic and allylic alcohols may proceed through a

mechanism analogous to that proposed for the Cu(I)/bpy/TEMPO catalytic system (Scheme 4).[21] First, NH_3 coordinates to a copper(I) species of MCM-41-bpy-CuI to provide an MCM-41-immobilized bipyridine copper(I) salt (**A**), which was oxidized by O_2 in the presence of TEMPOH to give an MCM-41-immobilized bipyridine Cu^{II}–OH intermediate (**B**). The latter undergoes a ligand exchange reaction with alcohol leading to an MCM-41-immobilized bipyridine Cu^{II}–alkoxide intermediate (**C**). Then the newly generated intermediate (**C**) could be oxidized by TEMPO through a hydrogen abstraction mechanism, to afford the corresponding aldehyde and regenerate the MCM-41-immobilized bipyridine copper(I) salt (**A**).



Scheme 4.

For any heterogeneous catalytic system, it is very important to know its ease of

separation and possible reuse. We next investigated the recyclability of the MCM-41-bpy-CuI by using the aerobic oxidation reaction of 4-methoxyphenylmethanol (0.5 mmol) in the presence of MCM-41-bpy-CuI (0.025 mmol) and TEMPO (0.025 mmol) in EtOH (1.0 mL) with aqueous ammonia (0.5 mmol) as base at 50 ºC under air for 24 h. Each time, after completion of the reaction, the catalyst was separated by simple filtration and washed with ethanol and diethyl ether. After being air-dried, it can be reused directly without further purification. As shown in Fig. 4, the recovered copper catalyst was used in the next run, and almost consistent activity was observed for 10 consecutive cycles. In addition, copper leaching in the immobilized catalyst was also determined. The copper content of the catalyst was found by ICP analysis to be 0.62 mmol/g after ten consecutive runs, only 1.6% of copper had been lost from the MCM-41 support. The high stability and excellent reusability of this heterogeneous copper catalyst should result from the chelating action of bidentate bipyridine ligand on copper and the mesoporous structure of the MCM-41 support. The result is important from industrial and environmental points of view. The high catalytic activity and excellent reusability of the MCM-41-bpy-CuI make it a highly attracttive heterogeneous copper catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

3. Conclusions

In summary, we have developed a novel, practical and environmentally friendly catalyst system for the aerobic oxidation reaction of primary benzylic and allylic

alcohols by using an MCM-41-immobilized bipyridine copper(I) complex [MCM-41-bpy-CuI] as catalyst. This catalytic system encompassed a broad substrate scope, oxidizing a range of primary benzyl alcohols and (*E*)-cinnamyl alcohol to the corresponding aldehydes in good to excellent yields under mild conditions using air as the ultimate oxidant. The use of recyclable heterogeneous copper catalyst and green reagents, such as air as oxidant and ethanol as solvent, made the system attractive for environmentally sustainable processes.

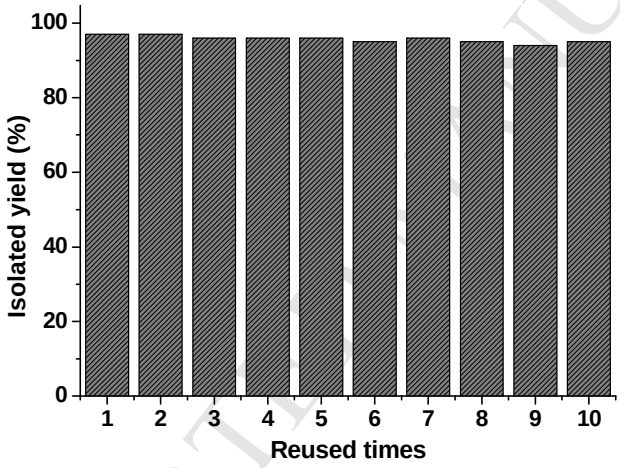


Fig. 4 Recycle of the MCM-41-bpy-CuI catalyst

4. Experimental

4.1. Physical measurements and materials

All chemicals were obtained from commercial suppliers and used as received, unless otherwise noted. 4,4'-Bis(bromomethyl)-2,2'-bipyridine[17] and mesoporous material MCM-41[22] were prepared according to literature procedures. All solvents were distilled and dried before use. All oxidation products were characterized by

comparison of their spectra and physical data with authentic samples. IR spectra were determined on a Perkin-Elmer 683 instrument. ^{1}H NMR spectra (400 MHz) were recorded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra (100 MHz) were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ as solvent. Copper content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation). Nitrogen adsorption/desorption isotherms were obtained using a Bel Japan Inc. Belsorp-HP at 77 K. Prior to gas adsorption measurements materials were degassed for 6 h at 423 K. X-ray powder diffraction patterns were obtained on Damx-rA (Riguka).

4.2. Preparation of 4,4'-bis[3-(triethoxysilyl)propylaminomethyl]-2,2'-bipyridine (BTESBPY)

Et_3N (1.52 g, 15 mmol) and 3-aminopropyltriethoxysilane (3.32 g, 15 mmol) were added to a solution of 4,4'-bis(bromomethyl)-2,2'-bipyridine (0.513 g, 1.5 mmol) in THF (10 mL), and the mixture was stirred at 50 °C under Ar for 6 h. After cooling the solution to room temperature, hexane (30 mL) was added and the mixture was filtered through a short $MgSO_4$ column to remove the ammonium salt. The clear solution was then concentrated and dried under vacuum at 100 °C for 24 h to produce the title compound as a pale yellow viscous oil in 92% yield. ^{1}H NMR (400 MHz, C_6D_6): δ = 8.78 (s, 2H), 8.57 (d, J = 4.2 Hz, 2H), 7.08 (d, J = 4.2 Hz, 2H), 3.76 (q, J = 7.0 Hz, 12H), 3.51 (s, 4H), 2.42 (t, J = 7.0 Hz, 4H), 1.68-1.62 (m, 4H), 1.14 (t, J = 7.0 Hz, 18H), 0.74-0.68 (m, 4H). ^{13}C NMR (100 MHz, C_6D_6): δ = 156.8, 151.3, 149.3, 123.2,

120.7, 58.5, 53.1, 52.4, 23.9, 18.6, 8.4. Anal. Calcd. for $C_{30}H_{54}N_4O_6Si_2$: C, 57.86; H, 8.74; N, 8.99. Found: C, 57.63; H, 8.52; N, 8.78.

4.3. Preparation of MCM-41-bpy

A solution of BTESBPY (2.368 g, 3.8 mmol) in dry chloroform (18 mL) was added to a suspension of 1.881 g of the MCM-41 in dry toluene (180 mL). The mixture was stirred for 24 h at 100 °C. Then the solid was filtered and washed by $CHCl_3$ (2 × 20 mL), and dried in vacuum at 160 °C for 5 h. The dried white solid was then soaked in a solution of Me_3SiCl (3.1 g) in dry toluene (100 mL) at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3 × 20 mL) and diethyl ether (3 × 20 mL), and dried in vacuum at 120 °C for 5 h to obtain 2.963 g of hybrid material MCM-41-bpy. The nitrogen content was found to be 2.91 mmol g^{-1} by elemental analysis.

4.4. Preparation of MCM-41-bpy-CuI complex

In a small Schlenk tube, 1.00 g of the above-functionalized MCM-41 (MCM-41 -bpy) was mixed with CuI (0.15 g, 0.78 mmol) in dry DMF (10 mL). The mixture was stirred at room temperature for 7 h under an argon atmosphere. The solid product was filtered by suction, washed with DMF and acetone and dried at 40 °C/26.7 Pa under Ar for 5 h to give 1.069 g of a pale blue copper complex (MCM-41-bpy-CuI). The nitrogen and copper contents were found to be 2.67 mmol g^{-1} and 0.63 mmol g^{-1}, respectively.

4.5. General procedure for the aerobic alcohol oxidation

Under an air atmosphere, a Schlenk tube was charged with MCM-41-bpy-CuI (40 mg, 0.025 mmol), alcohol (0.5 mmol), TEMPO (4 mg, 0.025 mmol), aqueous ammonia (0.5 mmol, 25-28%, w/w) and EtOH (1.0 mL). The mixture was stirred at 50 °C for 18-48 h. After completion of the reaction, the reaction mixture was cooled to room temperature, diluted with ethyl acetate (10 mL), and filtered. The MCM-41-bpy-CuI complex was washed with EtOH (2 × 5 mL), and Et_2O (5 mL) and reused in the next run. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum/ethyl acetate = 15:1 to 10:1) to provide the desired product.

*4.5.1. Benzaldehyde (**2a**).*[5h] Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.98 (s, 1H), 7.84 (d, J = 7.2 Hz, 2H), 7.61-7.57 (m, 1H), 7.49 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.4, 136.5, 134.5, 129.8, 129.1. IR (film, cm^{-1}): 1708, 1596, 1203, 736.

*4.5.2. 4-Methylbenzaldehyde (**2b**).*[4] Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 7.6 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.8, 145.4, 134.3, 129.8, 129.7, 21.8. IR (film, cm^{-1}): 2926, 1702, 1605, 1168, 808.

*4.5.3. 4-Methoxybenzaldehyde (**2c**).*[5h] Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.89 (s, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8, 164.6, 132.0, 129.9, 114.3, 55.6. IR (film, cm^{-1}): 1682, 1595, 1256, 1157, 1022, 830.

*4.5.4. 3,4-Dimethylbenzaldehyde (**2d**).*[23] Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.94 (s, 1H), 7.65 (s, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 2.34 (s, 6H). ^{13}C

NMR (100 MHz, $CDCl_3$): δ = 192.1, 137.5, 134.7, 133.5, 130.6, 130.2, 127.7, 20.1, 19.5. IR (film, cm^{-1}): 1691, 1607, 1242, 908, 731.

*4.5.5. 3,4-Dimethoxybenzaldehyde (**2e**).*[23] Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.86 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 1.2 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 154.6, 149.7, 130.2, 126.6, 110.5, 109.3, 56.1, 56.0. IR (film, cm^{-1}): 1682, 1590, 1513, 1268, 1137, 728.

*4.5.6. 3,4-Methylenedioxybenzaldehyde (**2f**).* White solid, m.p. 36–37 °C (ref.[24] m.p. 35–36 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.82 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.34 (s, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.08 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.1, 153.1, 148.7, 132.0, 128.5, 108.3, 107.0, 102.1. IR (KBr, cm^{-1}): 1686, 1604, 1490, 1447, 1254, 1037.

*4.5.7. 4-(Dimethylamino)benzaldehyde (**2g**).* White solid, m.p. 72–73 °C (ref.[25] m.p. 73–75 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.75 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 3.09 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.3, 154.3, 132.0, 125.1, 111.0, 40.1. IR (KBr, cm^{-1}): 2904, 2795, 1659, 1589, 1231, 810.

*4.5.8. 4-Chlorobenzaldehyde (**2h**).* White solid, m.p. 44–45 °C (ref.[5h] m.p. 46–47 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.99 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8, 141.0, 134.8, 130.9, 129.5. IR (KBr, cm^{-1}): 1706, 1592, 1285, 909, 734.

*4.5.9. 4-Bromobenzaldehyde (**2i**).* White solid, m.p. 57–58 °C (ref.[5h] m.p. 56–57 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.98 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* =

8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 135.1, 132.5, 131.0, 129.8. IR (KBr, cm^{-1}): 1686, 1586, 1572, 1203, 808.

*4.5.10. 4-Fluorobenzaldehyde (**2j**).*[23] Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.97 (s, 1H), 7.94-7.89 (m 2H), 7.22 (t, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.3, 166.6 (d, $^1J_{C\text{-}F}$ = 255.1 Hz), 133.2, 132.2 (d, $^3J_{C\text{-}F}$ = 9.6 Hz), 116.4 (d, $^2J_{C\text{-}F}$ = 22.2 Hz). IR (KBr, cm^{-1}): 1701, 1598, 1506, 1231, 908, 731.

*4.5.11. 4-Acetamidobenzaldehyde (**2k**).* White solid, m.p. 157–158 °C (ref.[26] m.p. 156–157 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.93 (s, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.79 (s, 1H), 7.72 (d, J = 8.0 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.9, 169.6, 145.3, 131.6, 131.3, 119.0, 24.7. IR (KBr, cm^{-1}): 3264, 1690, 1674, 1597, 1533, 831.

*4.5.12. 4-Nitrobenzaldehyde (**2l**).* Yellow solid, m.p. 104–105 °C (ref.[5h] m.p. 105–106 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.17 (s, 1H), 8.41 (d, J = 7.6 Hz, 2H), 8.09 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.1, 151.2, 140.1, 130.4, 124.3. IR (KBr, cm^{-1}): 1709, 1604, 1531, 1345, 905.

*4.5.13. 3-Nitrobenzaldehyde (**2m**).* Yellow solid, m.p. 57–58 °C (ref.[24] m.p. 58–59 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.14 (s, 1H), 8.72 (s, 1H), 8.50 (d, J = 7.6 Hz, 1H), 8.25 (d, J = 7.6 Hz, 1H), 7.79 (t, J = 8.0 Hz, 1H),. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 189.6, 148.9, 137.5, 134.6, 130.4, 128.5, 124.4. IR (KBr, cm^{-1}): 1705, 1616, 1535, 1353, 908, 730.

*4.5.14. 2-Methylbenzaldehyde (**2n**).*[24] Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.28 (s, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.50-7.26 (m, 3H), 2.68 (s, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 192.6, 140.6, 134.3, 133.5, 132.0, 131.7, 126.3, 19.4. IR (film, cm^{-1}): 1695, 1601, 908, 731.

*4.5.15. 2-Methoxybenzaldehyde (**2o**).*[23] Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 10.47 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.04-6.97 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.7, 161.9, 135.9, 128.6, 125.1, 120.7, 111.7, 55.7. IR (film, cm^{-1}): 1689, 1602, 1248, 909, 728.

*4.5.16. 2-Chlorobenzaldehyde (**2p**).*[23] Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 10.50 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.56-7.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.6, 137.9, 135.0, 132.6, 130.6, 129.4, 127.2. IR (film, cm^{-1}): 1698, 1592, 1267, 909, 732.

*4.5.17. 2-Bromobenzaldehyde (**2q**).*[23] Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 10.38 (s, 1H), 7.94-7.91 (m, 1H), 7.67-7.44 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7, 140.6, 135.2, 133.9, 129.9, 127.9, 127.0. IR (film, cm^{-1}): 1696, 1587, 1265, 1199, 907.

*4.5.18. 2-Aminobenzaldehyde (**2r**).*[23] Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.90 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.13 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1, 150.0, 135.8, 135.2, 118.9, 116.4, 116.2. IR (film, cm^{-1}): 3324, 1719, 1663, 1480, 747.

*4.5.19. 2,4-Dichlorobenzaldehyde (**2s**).* White solid, m.p. 69–70 °C (ref.[23] m.p. 71–73 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 10.42 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.49 (s, 1H), 7.38 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.5, 141.1, 138.5, 130.9, 130.5, 130.3, 128.0. IR (KBr, cm^{-1}): 1678, 1574, 1557, 1373, 822.

*4.5.20. 1-Naphthaldehyde (**2t**).*[23] Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 10.41 (s, 1H),

9.26 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.72-7.58 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3, 136.3, 135.2, 133.8, 131.6, 130.6, 129.0, 128.4, 126.9, 124.9, 124.8. IR (film, cm^{-1}): 1689, 1573, 1217, 1170, 909.

*4.5.21. 2-Thiophenaldehyde (**2u**).*[5d] Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.95 (s, 1H), 7.79-7.76 (m, 2H), 7.24-7.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.8, 144.2, 136.0, 134.9, 128.2. IR (film, cm^{-1}): 1661, 1516, 1418, 1213, 908, 725.

*4.5.22. 2-Furaldehyde (**2v**).*[23] Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.68 (s, 1H), 7.71 (s, 1H), 7.27 (s, 1H), 6.62 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9, 152.9, 148.1, 121.2, 112.6. IR (film, cm^{-1}): 1669, 1568, 1463, 1392, 1017, 747.

*4.5.23. 3-Pyridinaldehyde (**2w**).*[5d] Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.13 (s, 1H), 9.09 (s, 1H), 8.86 (d, *J* = 4.4 Hz, 1H), 8.19 (d, *J* = 7.6 Hz, 1H), 7.52-7.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 154.6, 152.0, 135.7, 131.5, 124.0. IR (film, cm^{-1}): 1707, 1589, 1246, 907, 727.

*4.5.24. (E)-Cinnamaldehyde (**2x**).*[23] Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.71 (d, *J* = 7.6 Hz, 1H), 7.58-7.56 (m, 2H), 7.48 (d, *J* = 16.0 Hz, 1H), 7.45-7.42 (m, 3H), 6.72 (dd, *J* = 7.6, 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.8, 152.8, 134.0, 131.3, 129.1, 128.6, 128.5. IR (film, cm^{-1}): 1670, 1624, 1449, 1119, 970, 745.

Acknowledgements

We thank the National Natural Science Foundation of China (No. 21272044) and Scientific Research Fund of Education Department of Jiangxi Province (KJLD13022)

for financial support.

References

1. Tojo, G.; Fernandez, M. In *Oxidation of Alcohols to Aldehydes and Ketones*; Tojo, G. Ed.; Springer: New York, **2010**.
2. (a) Arends, I. W. C. E.; Sheldon, R. A. In *Modern Oxidation Methods*; Backvall, J.-E. Ed.; Wiley-VCH Verlag Gmb & Co.: Weinheim, Germany, **2004**; pp 83–118; (b) Sheldon, R. A.; Arends, I. W. C. E.; ten Brink, G.-J.; Dijksman, A. *Acc. Chem. Res.* **2002**, *35*, 774-781; (c) Mallat, T.; Baiker, A. *Chem. Rev.* **2004**, *104*, 3037-3058; (d) Stahl, S. S. *Angew. Chem. Int. Ed.* **2004**, *43*, 3400-3420; (e) Sigman, M. S.; Jensen, D. R. *Acc. Chem. Res.* **2006**, *39*, 221-229; (f) Matsumoto, T.; Ueno, M.; Wang, N.; Kobayashi, S. *Chem. Asian J.* **2008**, *3*, 196-214; (g) Parmmeggiani, C.; Cardona, F. *Green Chem.* **2012**, *14*, 547-564.
3. (a) Tang, B. X.; Song, R. J.; Wu, C. Y.; Liu, Y.; Zhou, M. B.; Wei, W. T.; Deng, G. B.; Yin, D. L.; Li, J. H. *J. Am. Chem. Soc.* **2010**, *132*, 8900-8901; (b) Wang, Y. F.; Chen, H.; Zhu, X.; Chiba, S. *J. Am. Chem. Soc.* **2012**, *134*, 11980-11981; (c) Liu, Q.; Wu, P.; Yang, Y. H.; Zeng, Z. Q.; Liu, J.; Yi, H.; Lei, A. W. *Angew. Chem. Int. Ed.* **2012**, *51*, 4666-4670.
4. Semmelhack, M. F.; Schmid, C. R.; Cortes, D. A.; Chou, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 3374-3376.
5. (a) Ansari, I. A.; Gree, R. *Org. Lett.* **2002**, *4*, 1507-1510; (b) Contel, M.; Izuel, C.; Laguna, M.; Villuendas, P. R.; Alonso, P. J.; Fish, R. H. *Chem. Eur. J.* **2003**, *9*, 4168-4176; (c) Jiang, N.; Ragauskas, A. *Org. Lett.* **2005**, *7*, 3689-3692; (d) Jiang, N.; Ragauskas, A. *J. Org. Chem.* **2006**, *71*, 7087-7090; (e) Ragagnin, G.; Betzemeier, B.; Quici, S.; Knochel, P. *Tetrahedron* **2002**, *58*, 3985-3991; (f) Mannam, S.; Alamsetti, S. K.; Sekar, G. *Adv. Synth. Catal.* **2007**, *349*, 2253-2258; (g) Figiel, P. J.; Sibaouih, A.; Ahmad, J. U.; Nieger, M.; Raisanen, M. T.; Leskela, M.; Repo, T. *Adv. Synth. Catal.* **2009**, ***351***, 2625-2632; (h) Mase, N.; Mizumori, T.; Tatemoto, Y. *Chem. Commun.* **2011**, *47*, 2086-2088.
6. Marko, I. E.; Giles, P. R.; Tsukazaki, M.; Brown, S. M.; Urch, C. J. *Science*

1996, *274*, 2044-2046.

7. Gamez, P.; Arends, I. W. C. E.; Reedijk, J.; Sheldon, R. A. *Chem. Commun.* **2003**, 2414-2415.
8. Kumpullainen, E. T. T.; Koskinen, A. M. P. *Chem. Eur. J.* **2009**, *15*, 10901-10911.
9. (a) Hoover, J. M.; Stahl, S. S. *J. Am. Chem. Soc.* **2011**, *133*, 16901-16910; (b) Hoover, J. M.; Stahl, S. S. *Org. Synth.* **2013**, *90*, 240-250; (c) Hoover, J. M.; Ryland, B. L.; Stahl, S. S. *J. Am. Chem. Soc.* **2013**, *135*, 2357-2358.
10. Poliakoff, M.; Fitzpatrick, J. M.; Farren, T. R.; Anastas, P. T. *Science* **2002**, *297*, 807-810.
11. Nasir Baig, R. B.; Varma, R. S. *Chem. Commun.* **2013**, *49*, 752-754.
12. (a) Nasir Baig, R. B.; Varma, R. S. *Chem. Commun.* **2012**, *48*, 2582-2584; (b) Benyahya, S.; Monnier, F.; Wong Chi Man, M.; Bied, C.; Ouazzani, F.; Taillefer, M. *Green Chem.* **2009**, *11*, 1121-1123; (c) Chtchigrovsky, M.; Primo, A.; Gonzalez, P.; Molvinger, K.; Robitzer, M.; Quignard, F.; Taran, F. *Angew. Chem. Int. Ed.* **2009**, *48*, 5916-5919; (d) Xiao, R.; Yao, R.; Cai, M. *Eur. J. Org. Chem.* **2012**, 4178-4184; (e) Nasir Baig, R. B.; Varma, R. S. *Green Chem.* **2013**, *15*, 1839-1843; (f) Likhar, P. R.; Roy, S.; Roy, M.; Kantam, M. L.; Lal De, R. *J. Mol. Catal. A: Chem.* **2007**, *271*, 57-62; (g) Benyahya, S.; Monnier, F.; Taillefer, M.; Wong Chi Man, M.; Bied, C.; Ouazzani, F. *Adv. Synth. Catal.* **2008**, *350*, 2205-2208; (h) Xiao, R.; Zhao, H.; Cai, M. *Tetrahedron* **2013**, *69*, 5444-5450; (i) Yang, J.; Li, P.; Wang, L. *Tetrahedron* **2011**, *67*, 5543-5549.
13. (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710-714; (b) Jia, M.; Seifert, A.; Thiel, W. R. *Chem. Mater.* **2003**, *15*, 2174-2180; (c) Taguchi, A.; Schuth, F. *Micropor. Mesopor. Mater.* **2005**, *77*, 1-45; (d) Martin-Aranda, R. M.; Cejka, J. *Top. Catal.* **2010**, *53*, 141-153.
14. Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834-10843.

15. (a) Mehnert, P. C.; Weaver, D. W.; Ying, J. Y. *J. Am. Chem. Soc.* **1998**, *120*, 12289-12296; (b) Mukhopadhyay, K.; Sarkar, B. R.; Chaudhari, R. V. *J. Am. Chem. Soc.* **2002**, *124*, 9692-9693; (c) Baleizao, C.; Corma, A.; Garcia, H.; Leyva, A. *J. Org. Chem.* **2004**, *69*, 439-446; (d) Cai, M.; Zheng, G.; Ding, G. *Green Chem.* **2009**, *11*, 1687-1693; (e) Shyu, S.-G.; Cheng, S.-W.; Tzou, D.-L. *Chem. Commun.* **1999**, 2337-2338.

16. (a) Zhao, H.; He, W.; Yao, R.; Cai, M. *Adv. Synth. Catal.* **2014**, *356*, 3092-3098; (b) Cai, M.; Yao, R.; Chen, L.; Zhao, H. *J. Mol. Catal. A: Chem.* **2014**, *395*, 349-354; (c) Cai, M.; Xiao, R.; Yan, T.; Zhao, H. *J. Organomet. Chem.* **2014**, *749*, 55-60.

17. Will, G.; Boschloo, G.; Rao, S. N.; Fitzmaurice, D. *J. Phys. Chem. B* **1999**, *103*, 8067-8079.

18. Lempers, H. E. B.; Sheldon, R. A. *J. Catal.* **1998**, *175*, 62-69.

19. Das, D. D.; Sayari, A. *J. Catal.* **2007**, *246*, 60-65.

20. Hao, W.; Sha, J.; Sheng, S.; Cai, M. *J. Mol. Catal. A: Chem.* **2009**, *298*, 94-98.

21. (a) Hoover, J. M.; Ryland, B. L.; Stahl, S. S. *ACS Catal.* **2013**, *3*, 2599-2605; (b) Ryland, B. L.; McCann, S. D.; Brunold, T. C.; Stahl, S. S. *J. Am. Chem. Soc.* **2014**, *136*, 12166-12173.

22. Lim, M. H.; Stein, A. *Chem. Mater.* **1999**, *11*, 3285-3295.

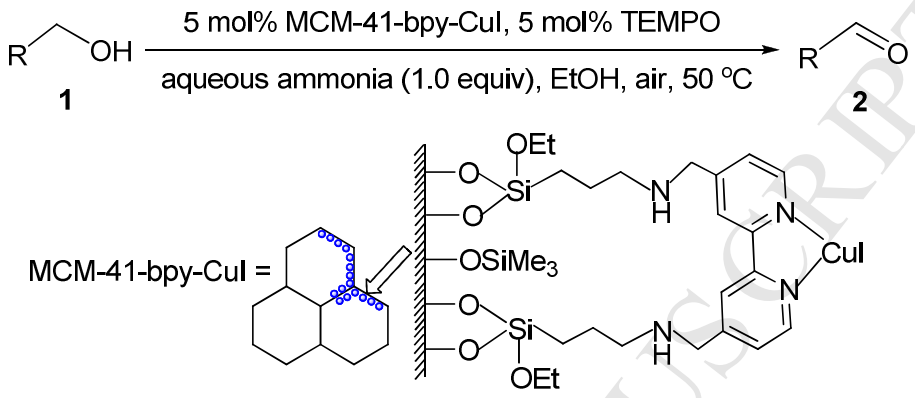
23. Zhang, G.; Han, X.; Luan, Y.; Wang, Y.; Wen, X.; Xu, L.; Ding, C.; Gao, J. *RSC Adv.* **2013**, *3*, 19255-19258.

24. Lipshutz, B. H.; Hageman, M.; Fennewald, J. C.; Linstadt, R.; Slack, E.; Voigtritter, K. *Chem. Commun.* **2014**, *50*, 11378-11381.

25. Rueping, M.; Vila, C.; Szadkowska, A.; Koenigs, R. M.; Fronert, J. *ASC Catal.* **2012**, *2*, 2810-2815.

26. Gooβen, L. J.; Khan, B. A.; Fett, T.; Treu, M. *Adv. Synth. Catal.* **2010**, *352*, 2166-2170.

Graphical Abstract



Supporting Information for:

A highly efficient heterogeneous aerobic alcohol oxidation catalyzed by immobilization of bipyridine copper(I) complex in MCM-41

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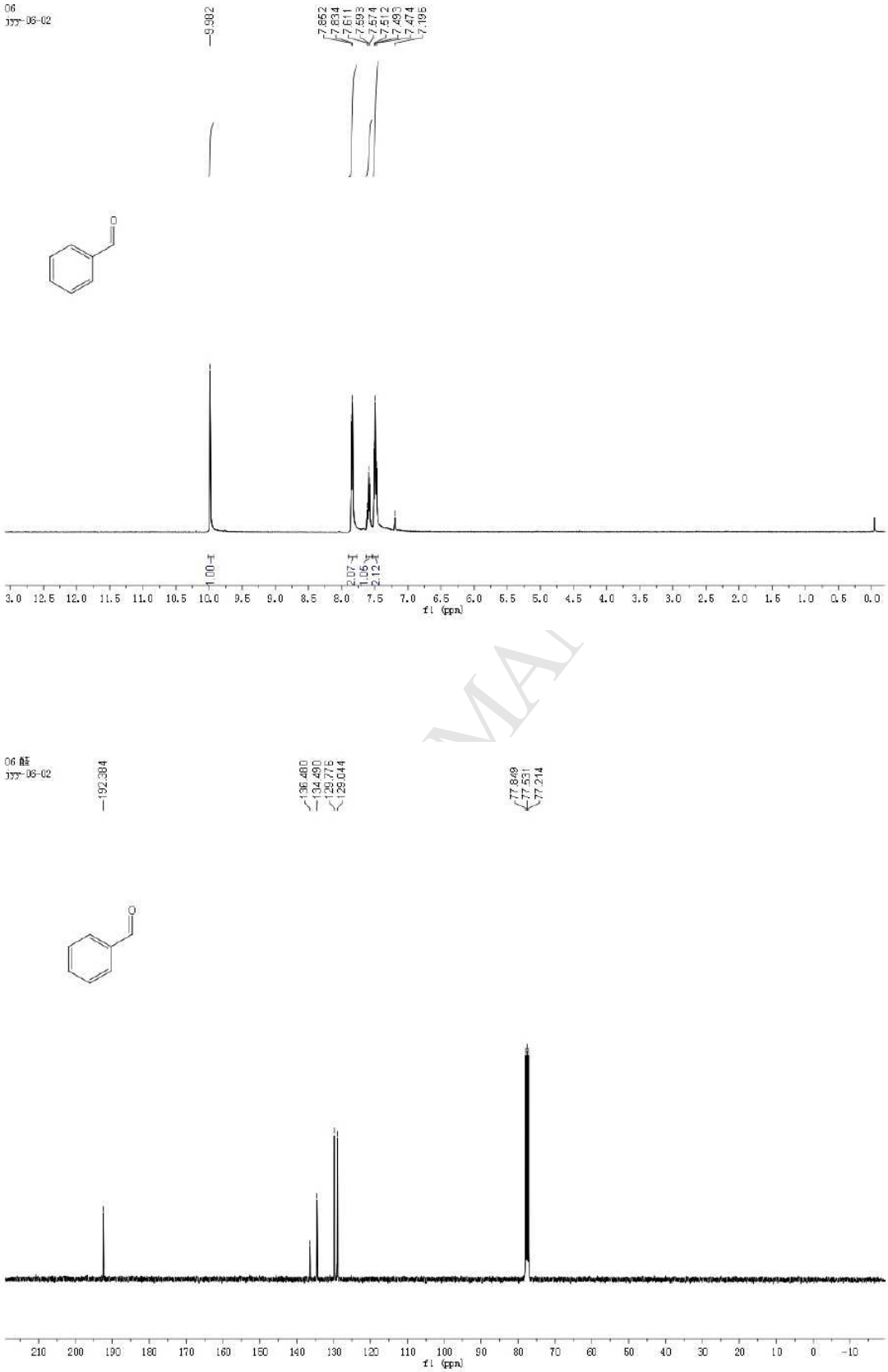
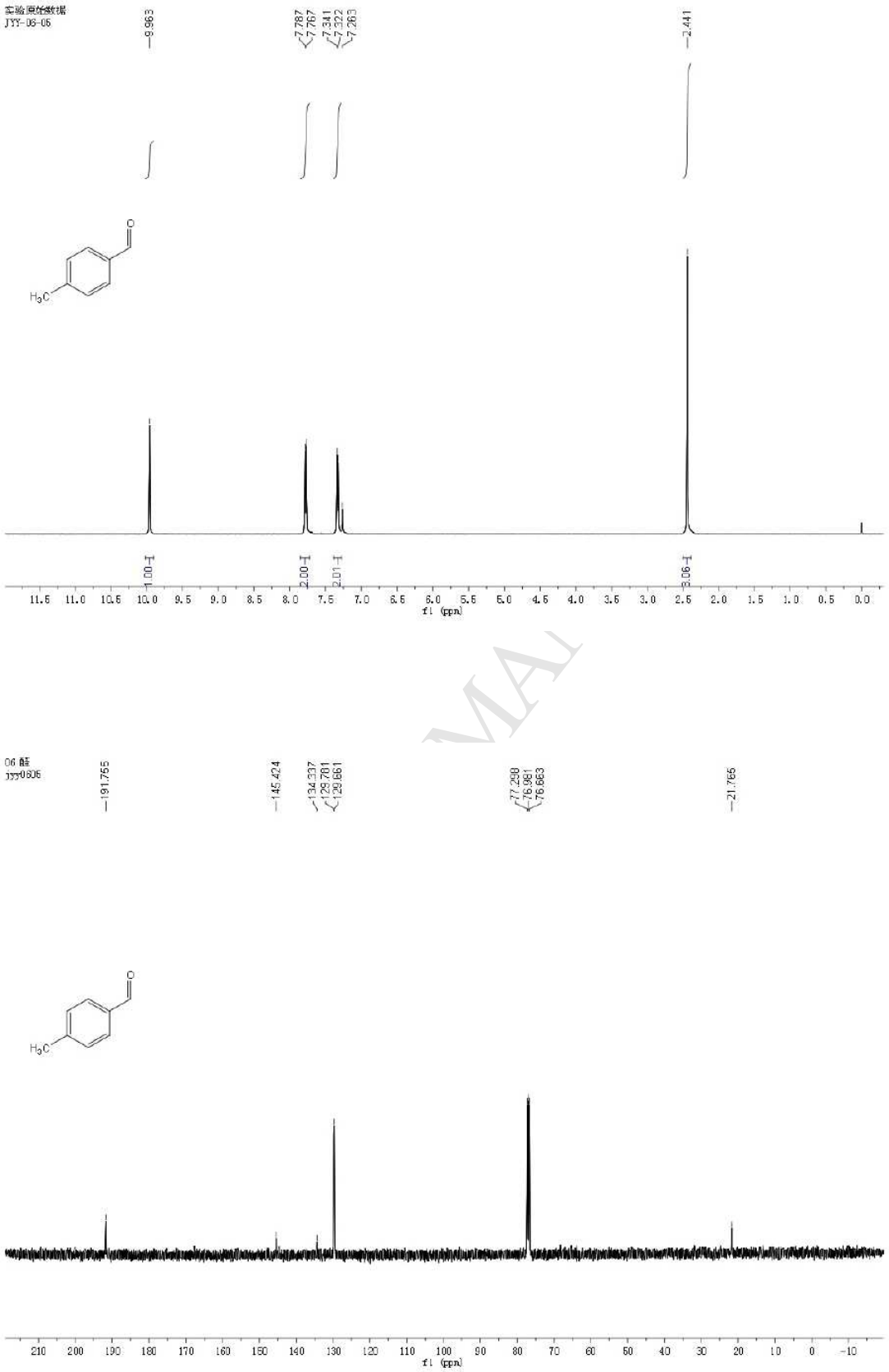
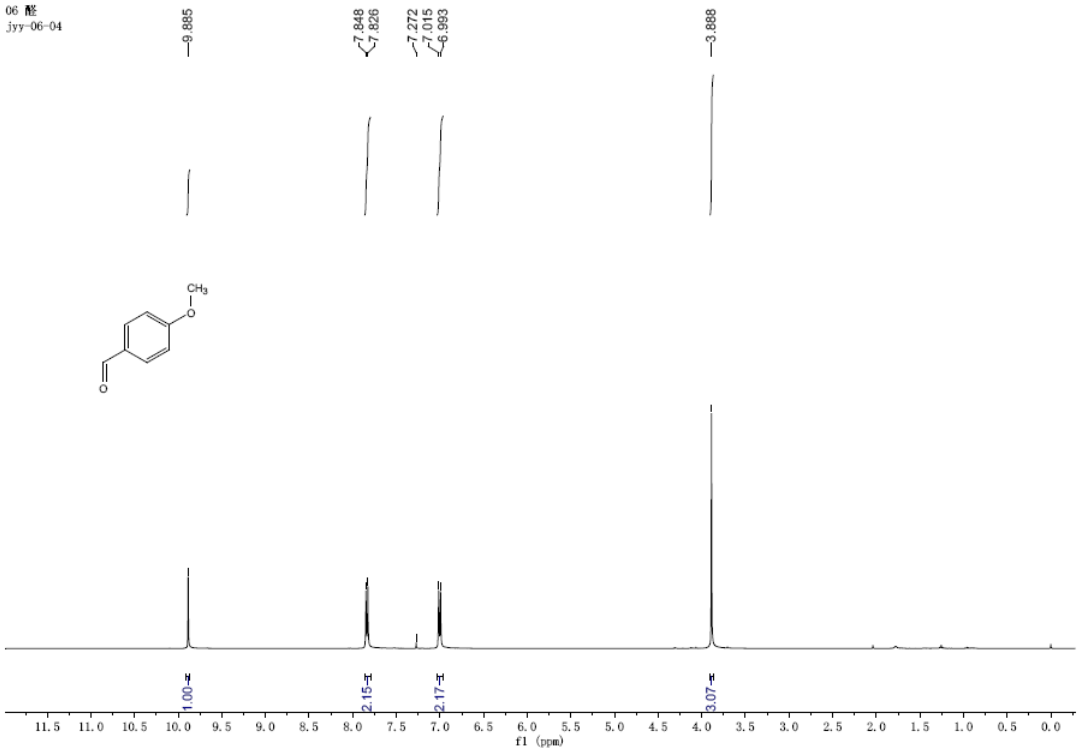
^{1}H NMR and ^{13}C NMR spectra of compounds **2a-2x.**

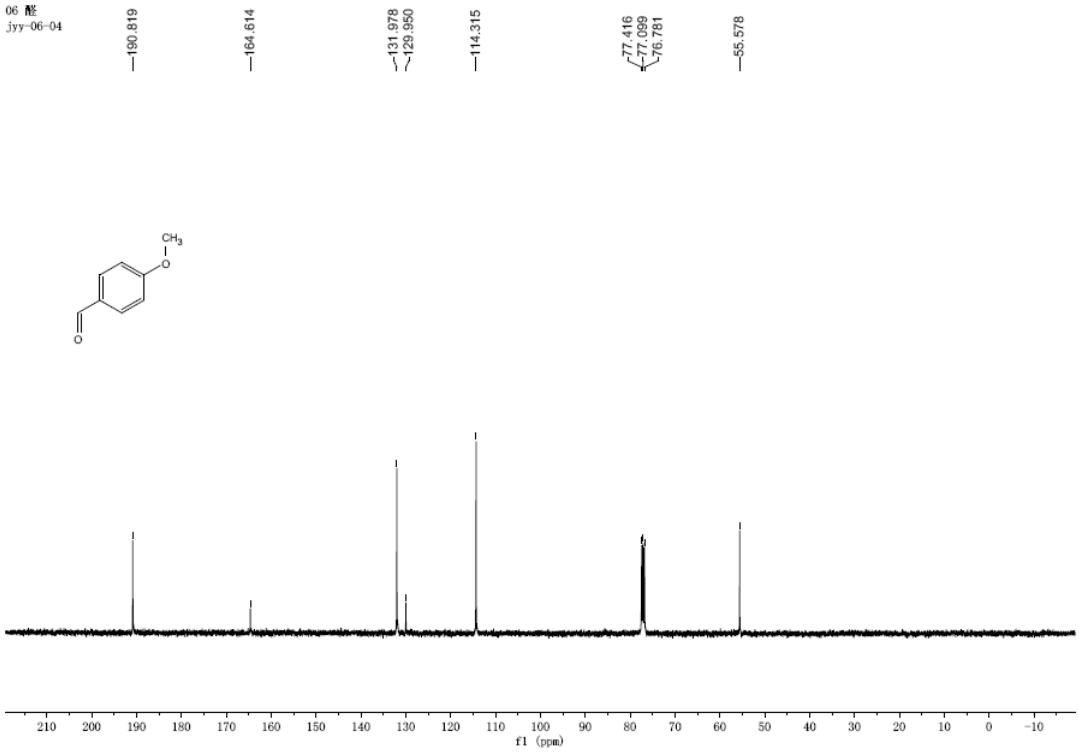


^{1}H NMR and ^{13}C NMR of compound **2a**

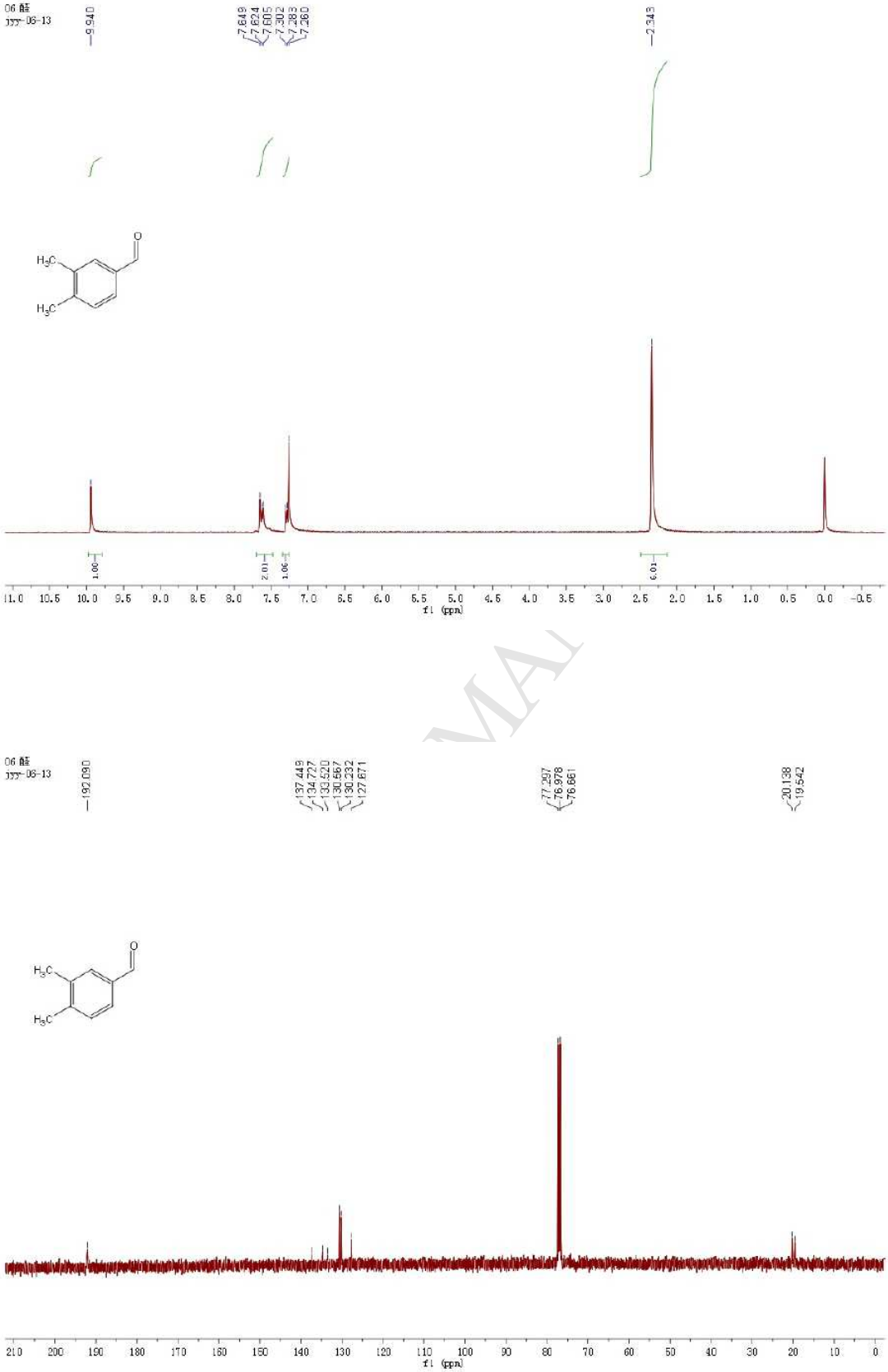


^{1}H NMR and ^{13}C NMR of compound **2b**





^{1}H NMR and ^{13}C NMR of compound **2c**



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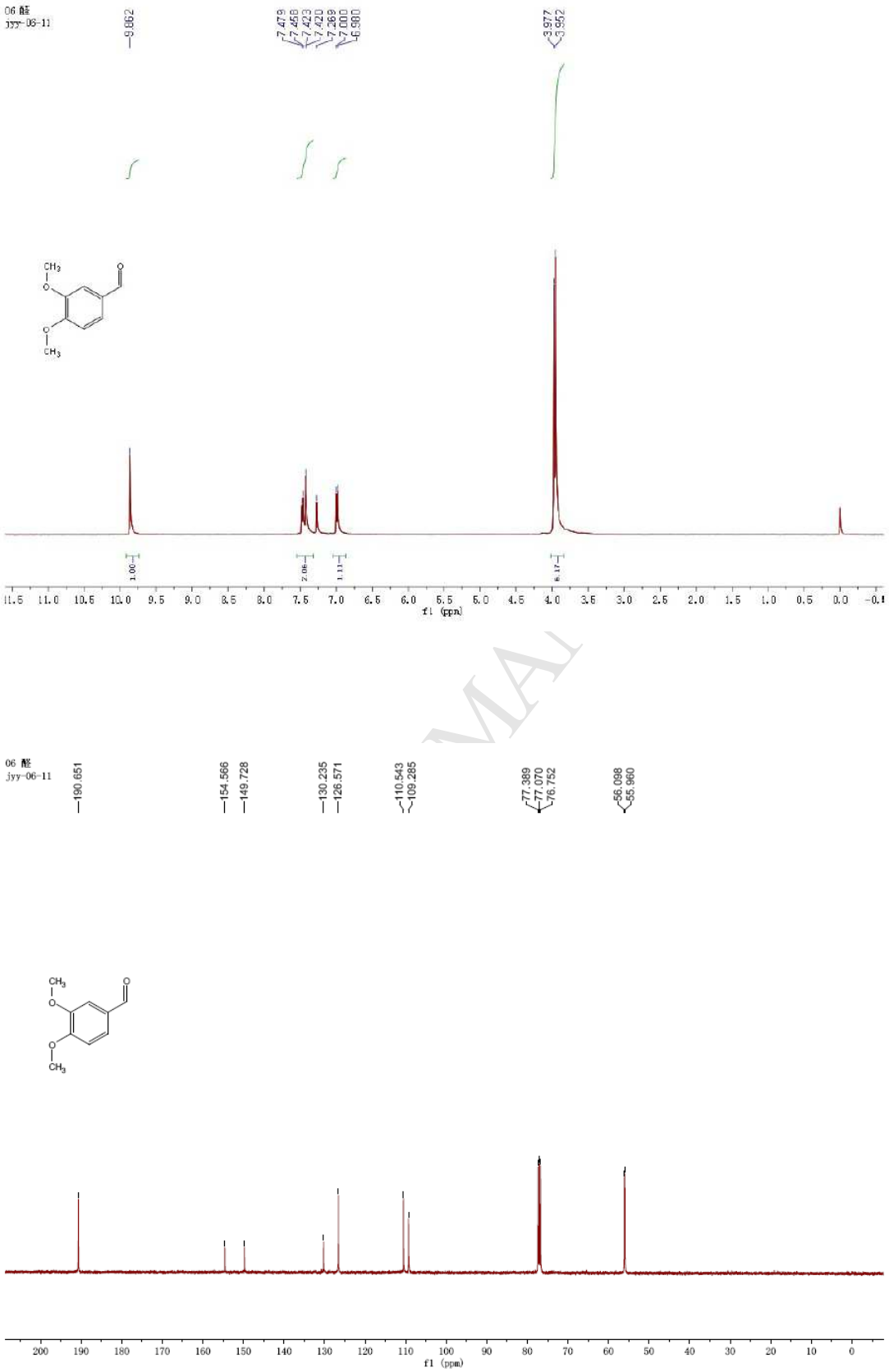
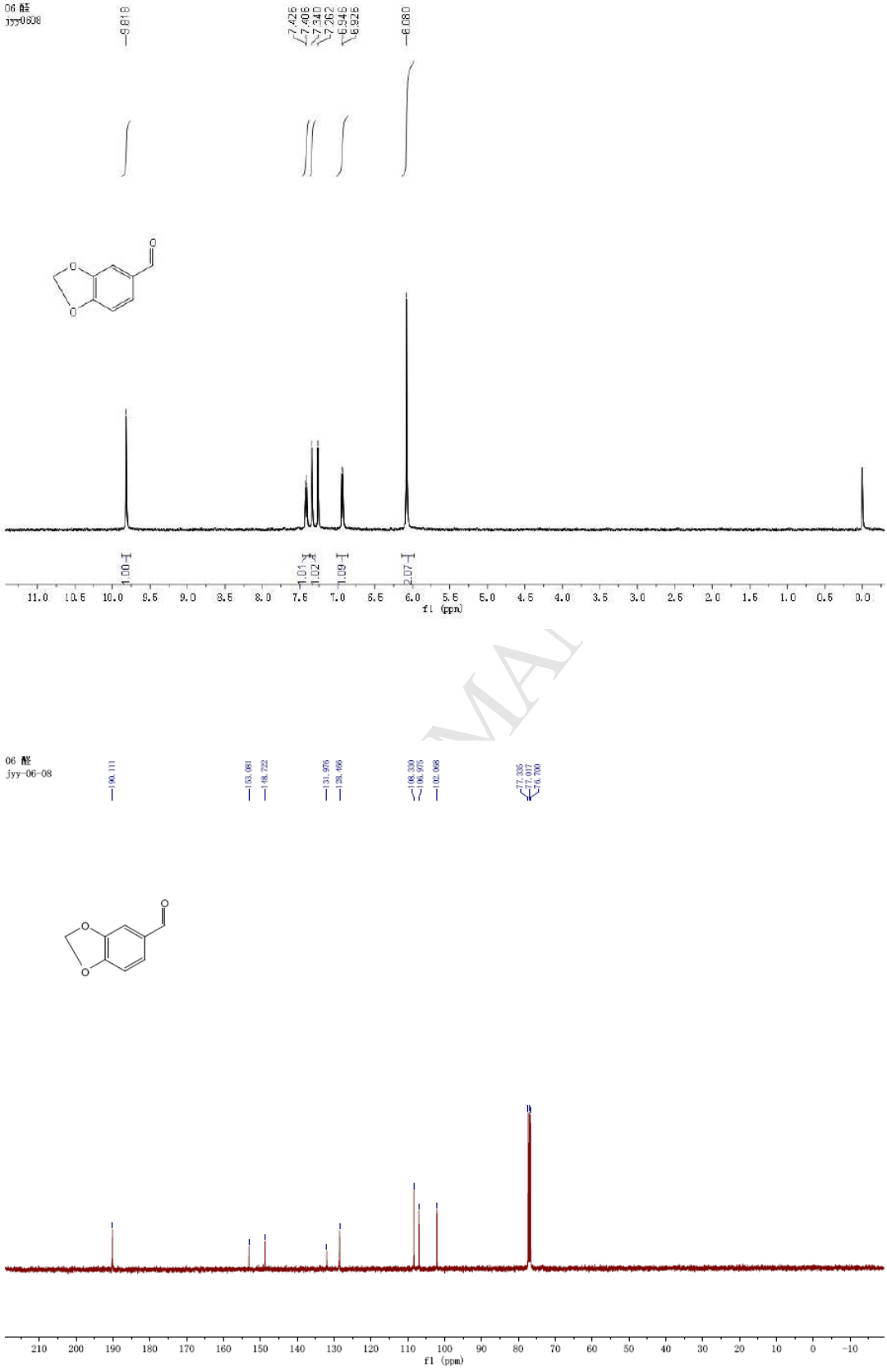
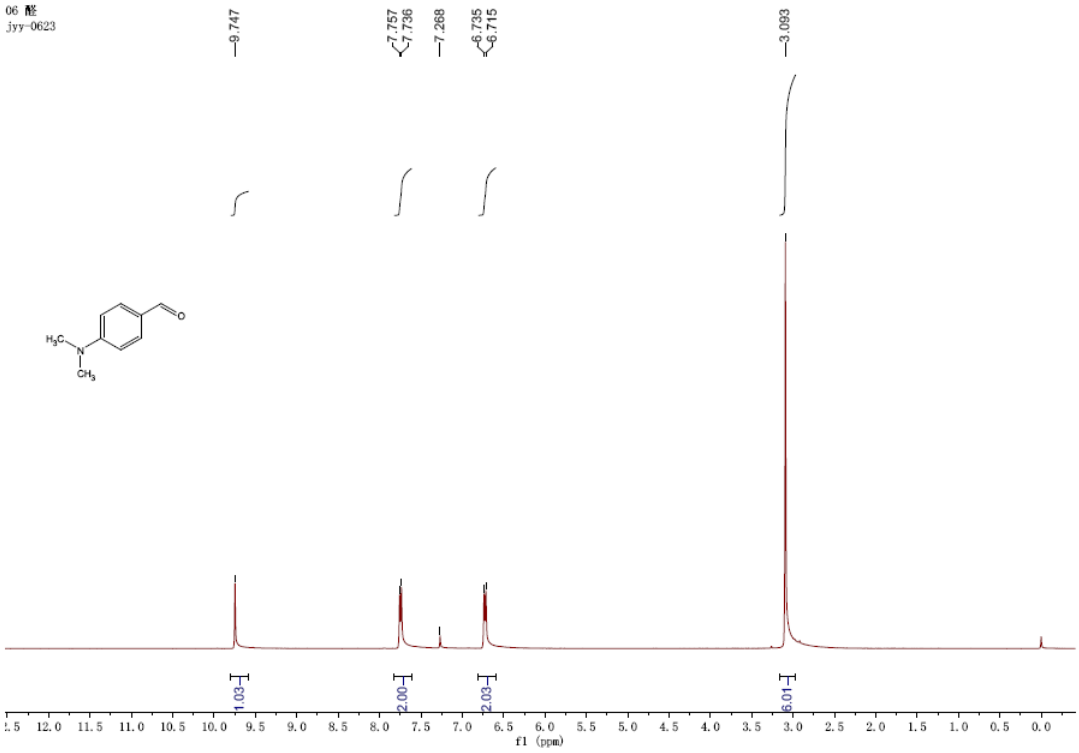
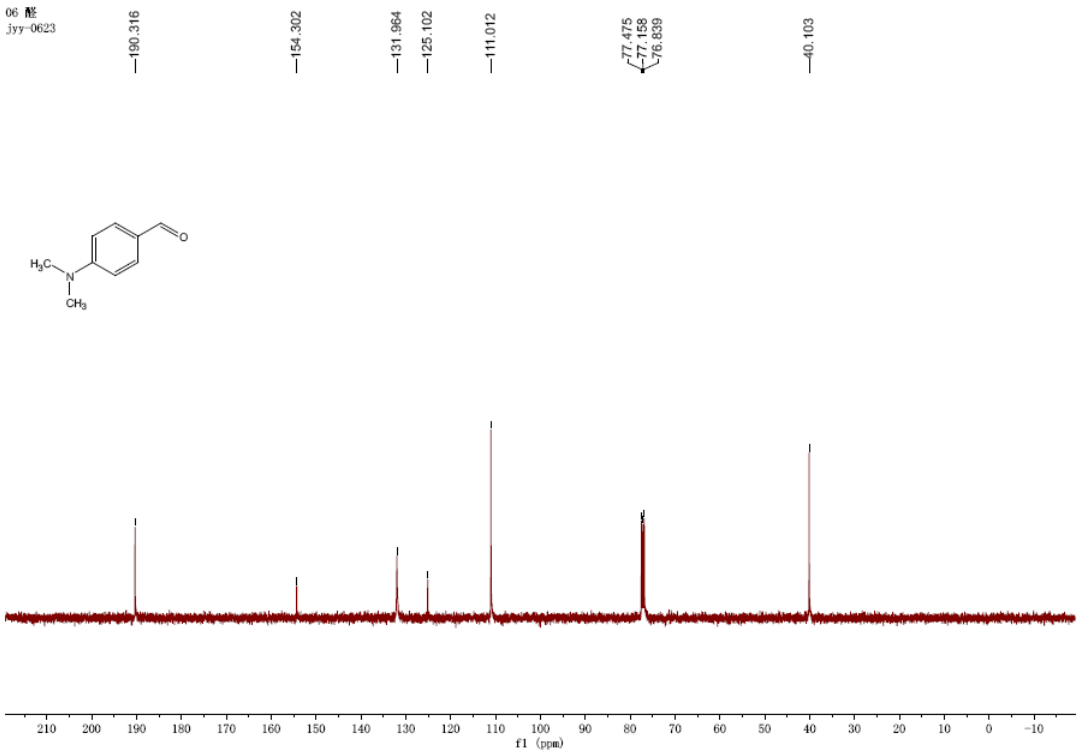


^{1}H NMR and ^{13}C NMR of compound **2e**

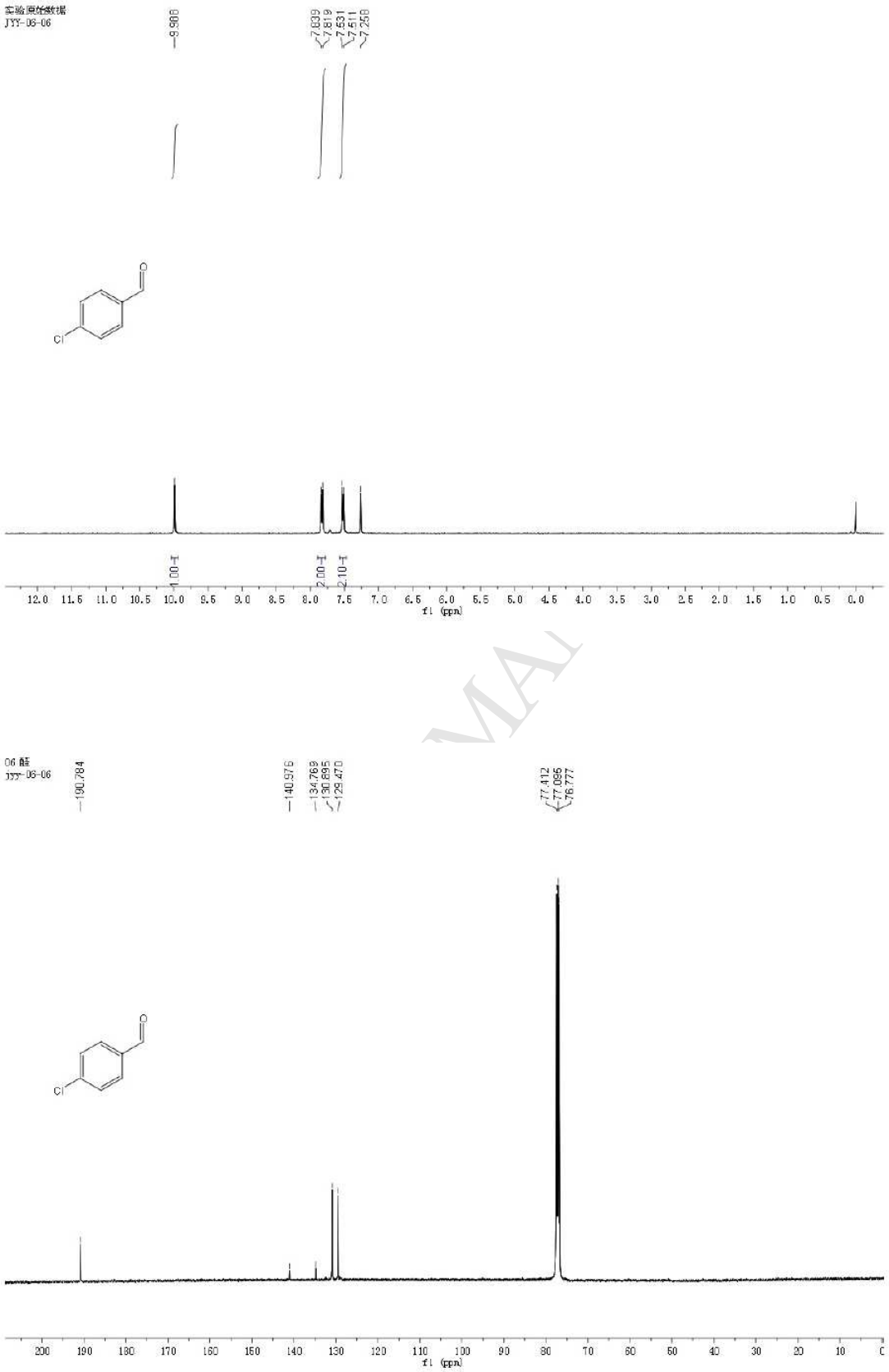


^{1}H NMR and ^{13}C NMR of compound **2f**

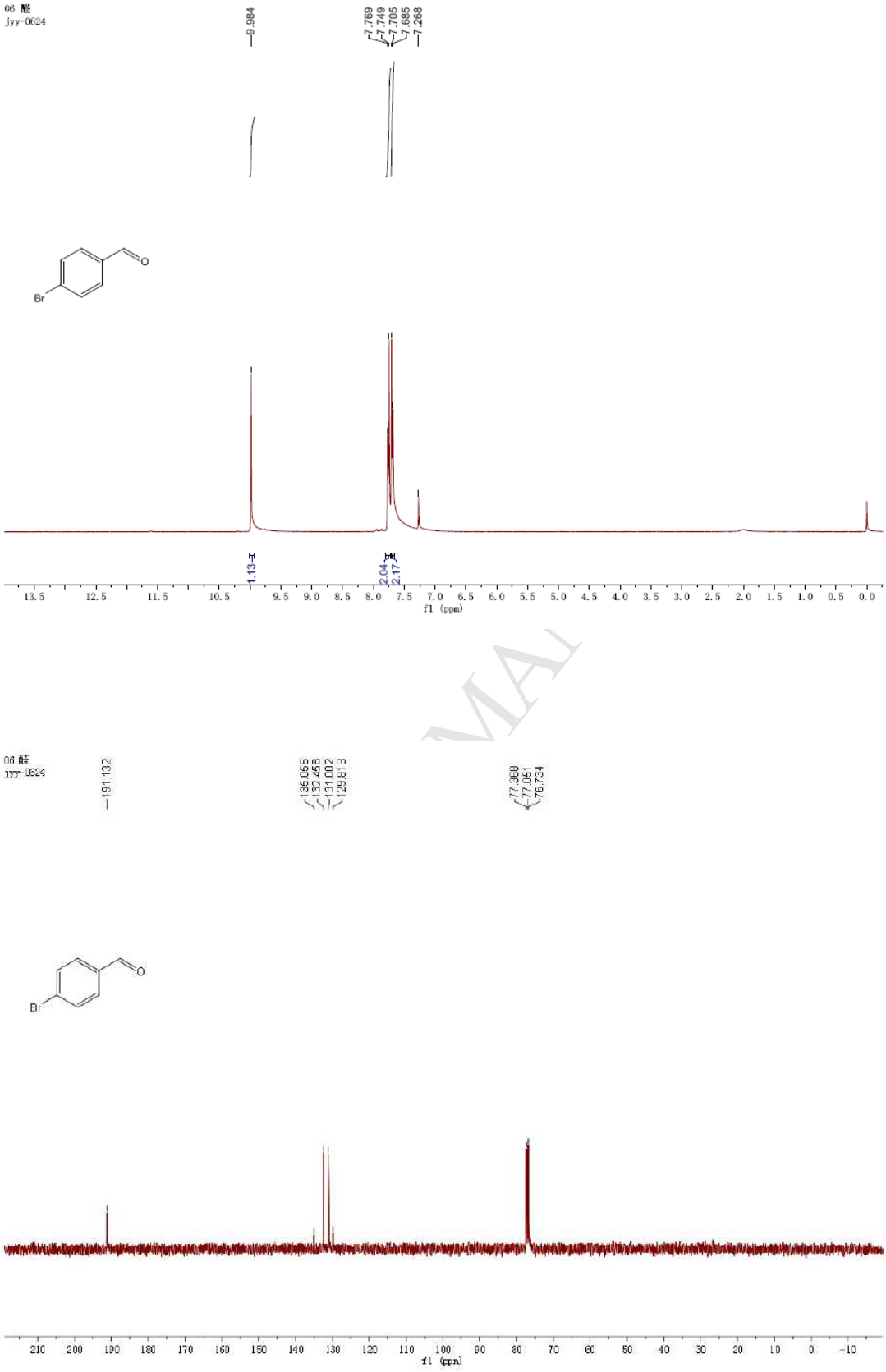




^{1}H NMR and ^{13}C NMR of compound **2g**



^{1}H NMR and ^{13}C NMR of compound **2h**



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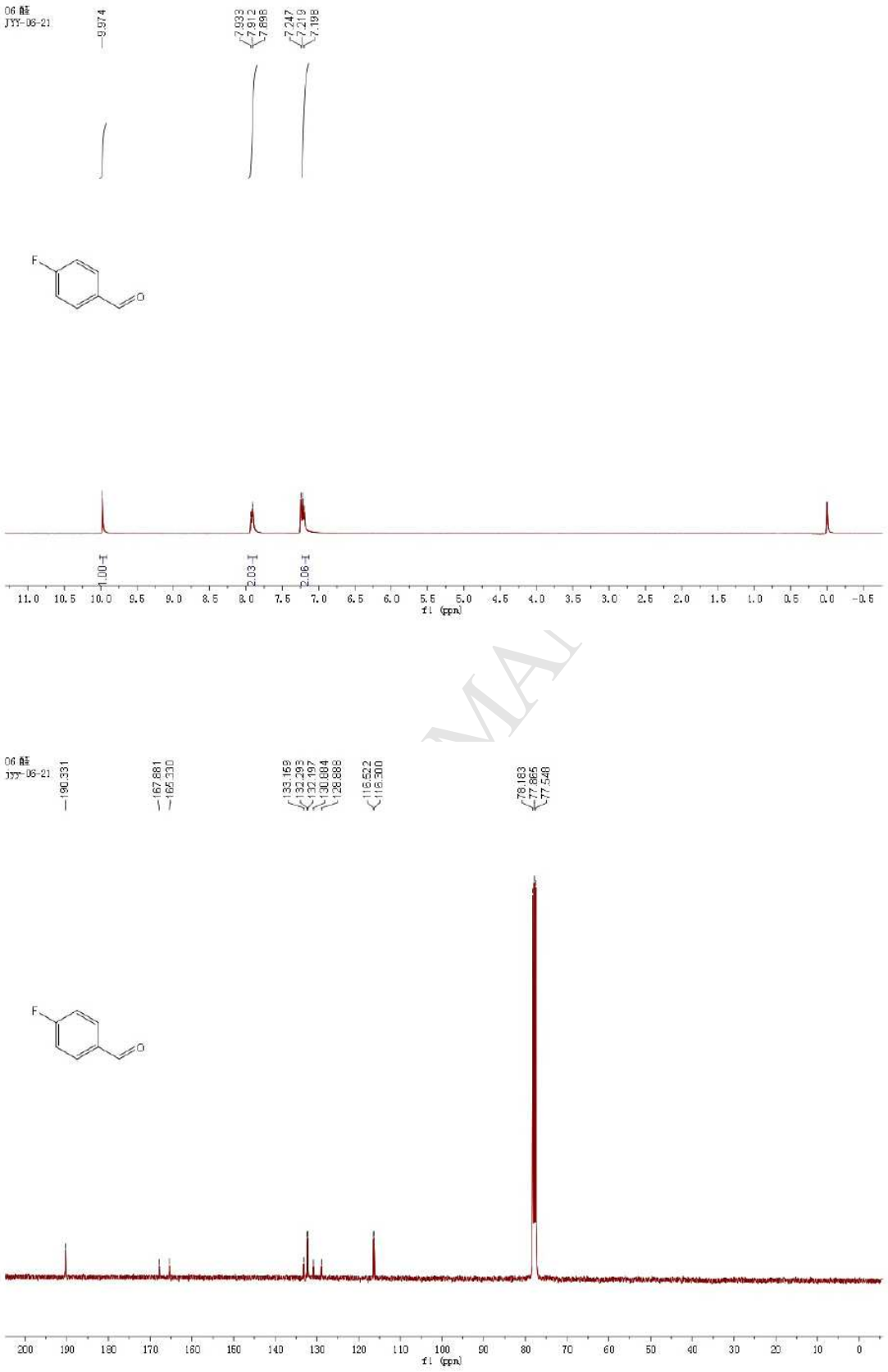
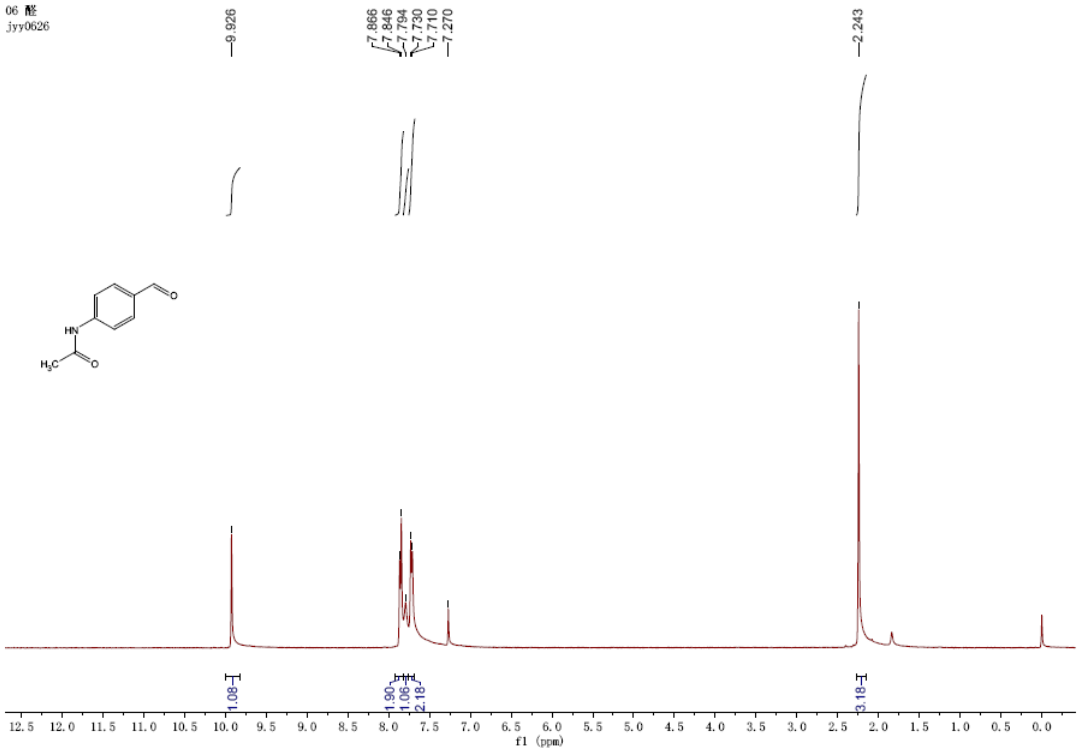
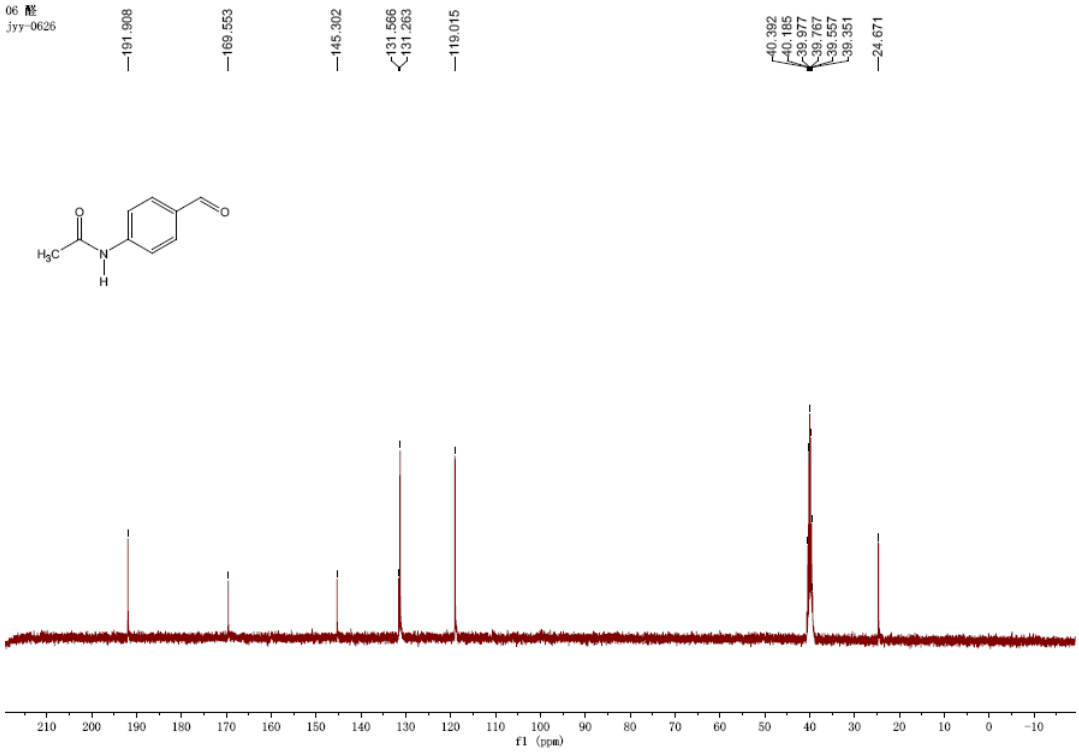
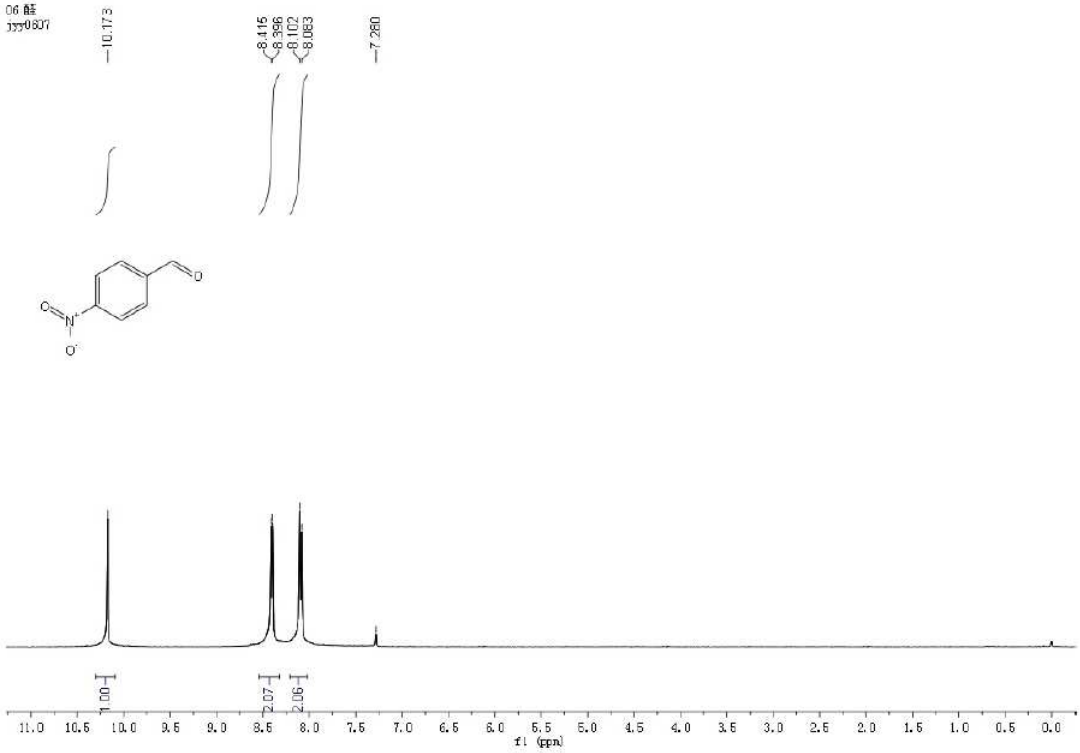


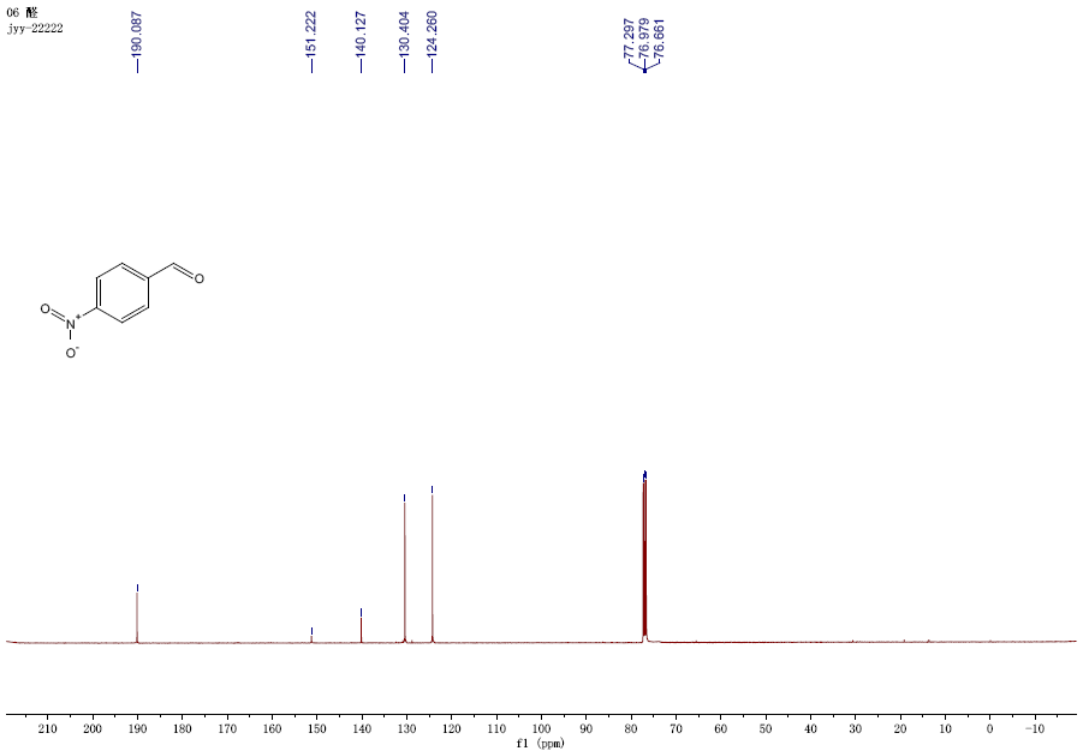
^{1}H NMR and ^{13}C NMR of compound **2j**



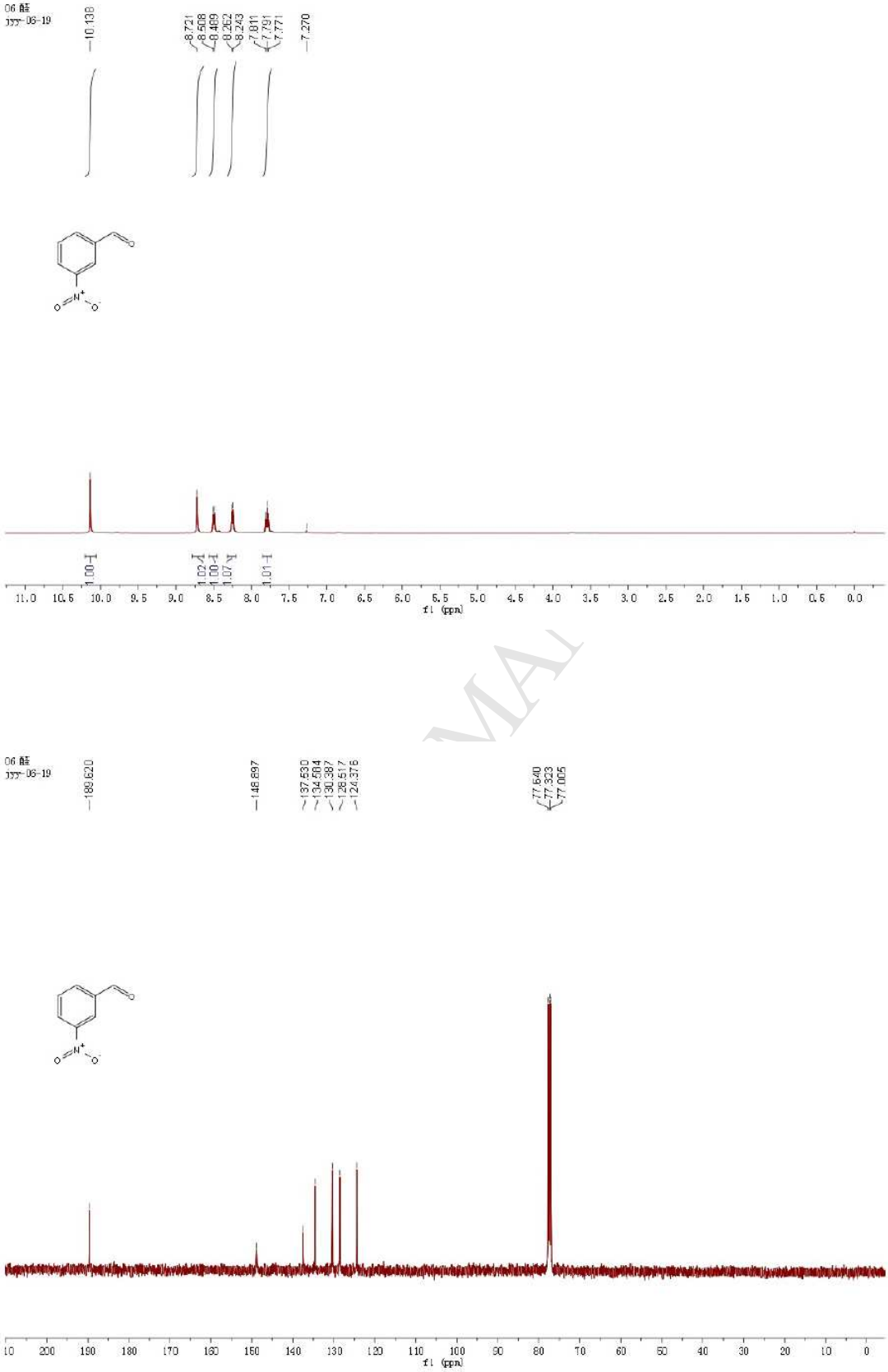


^{1}H NMR and ^{13}C NMR of compound **2k**

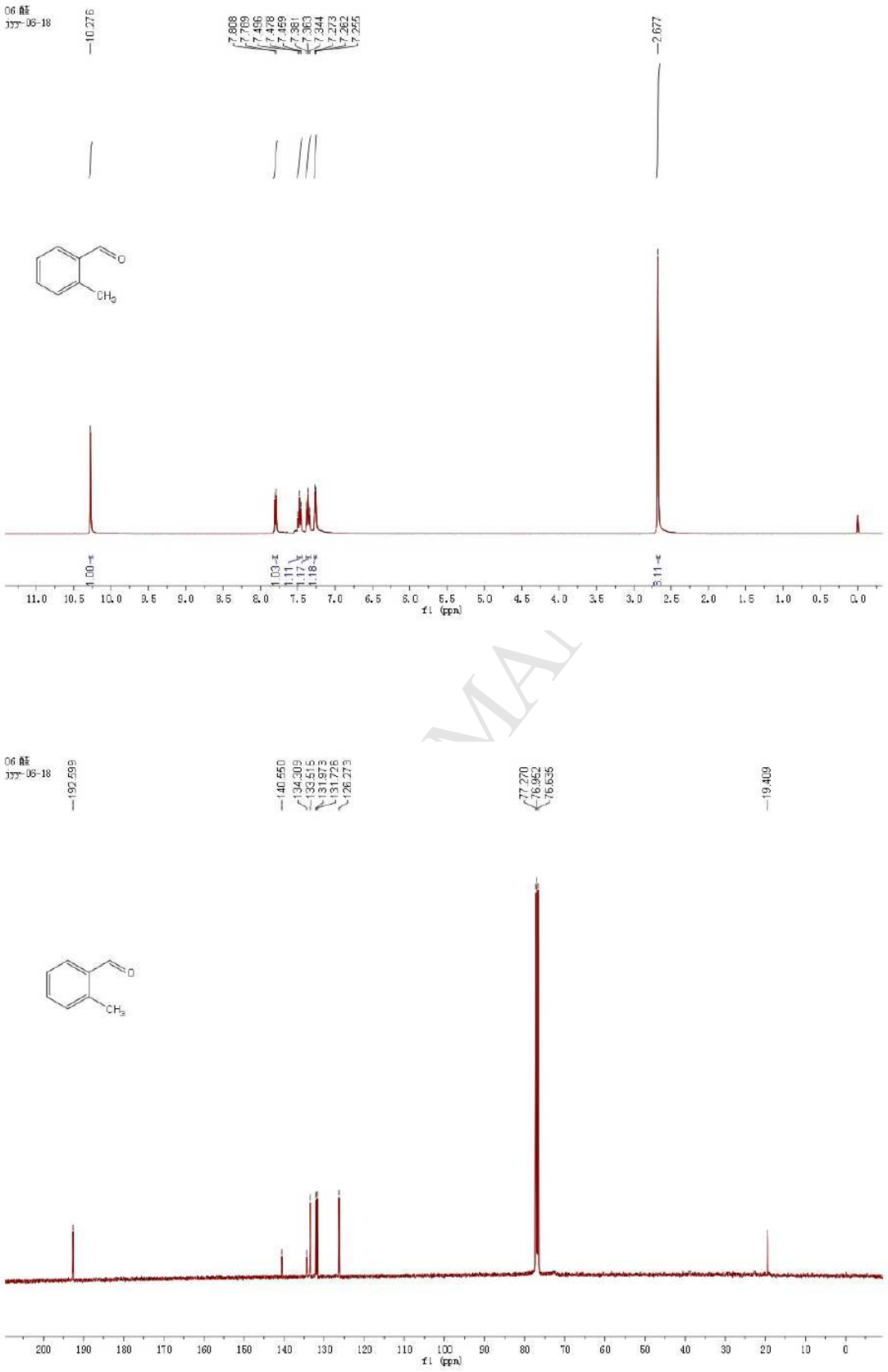




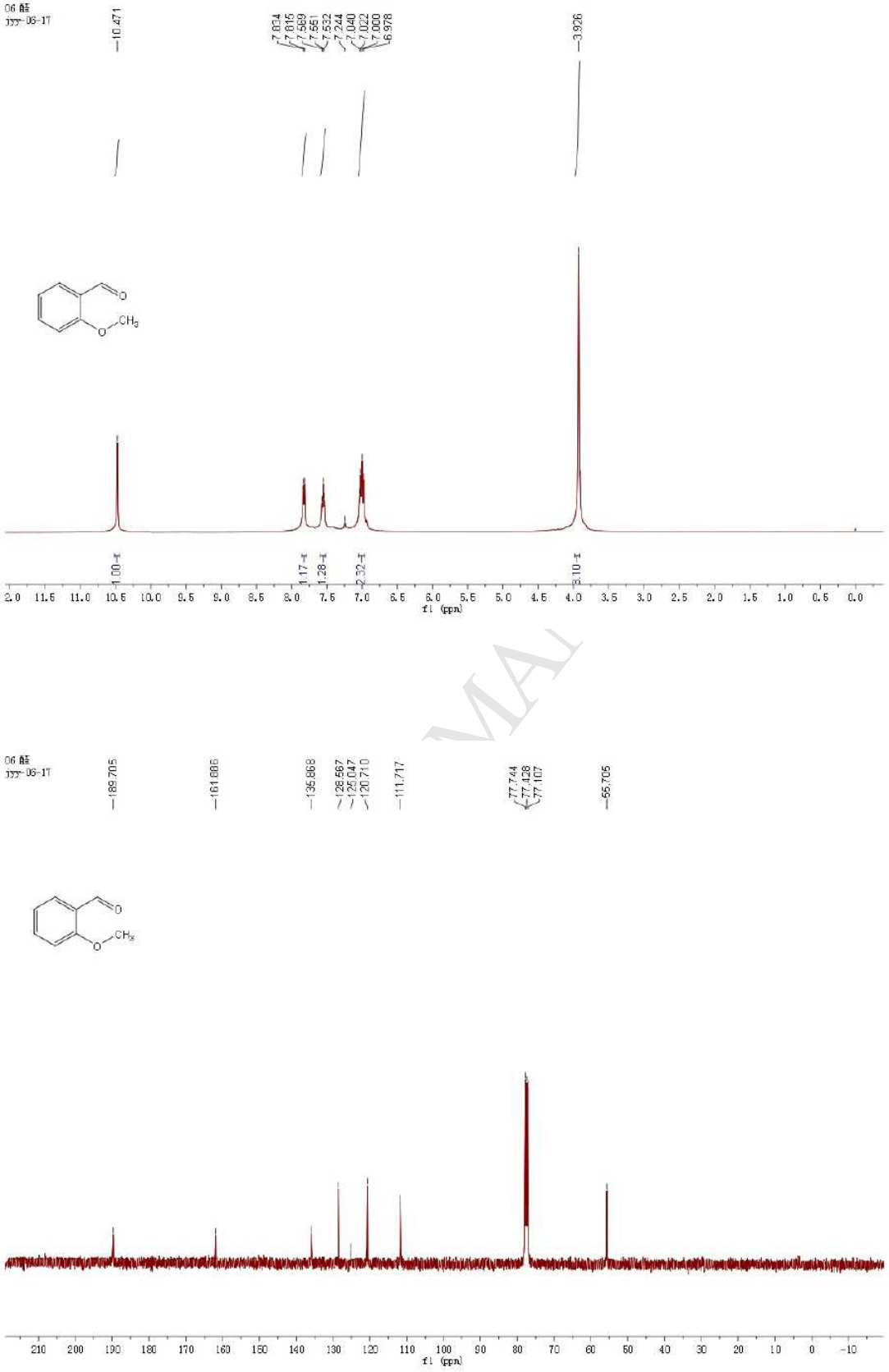
^{1}H NMR and ^{13}C NMR of compound **2l**



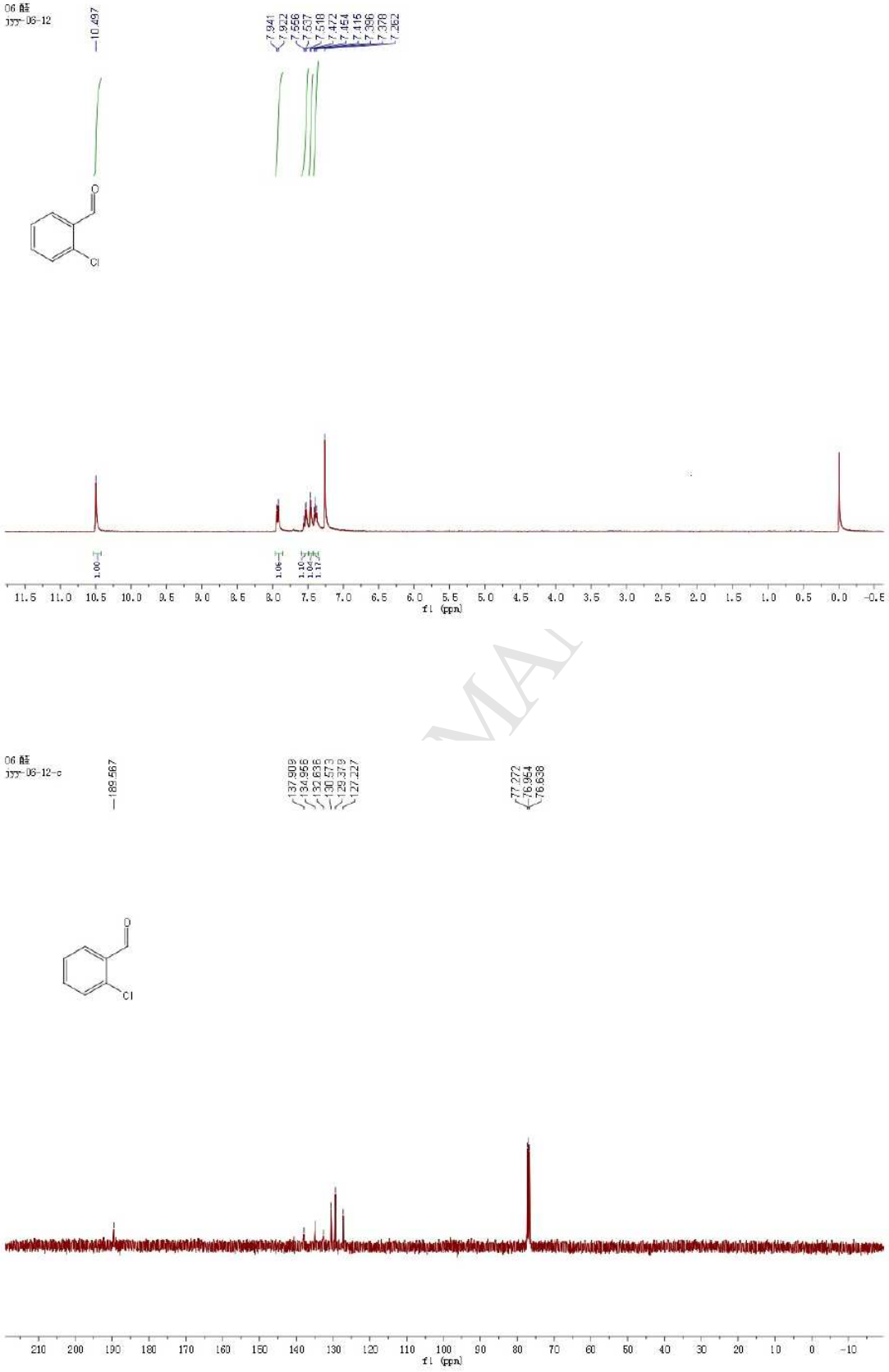
^{1}H NMR and ^{13}C NMR of compound **2m**



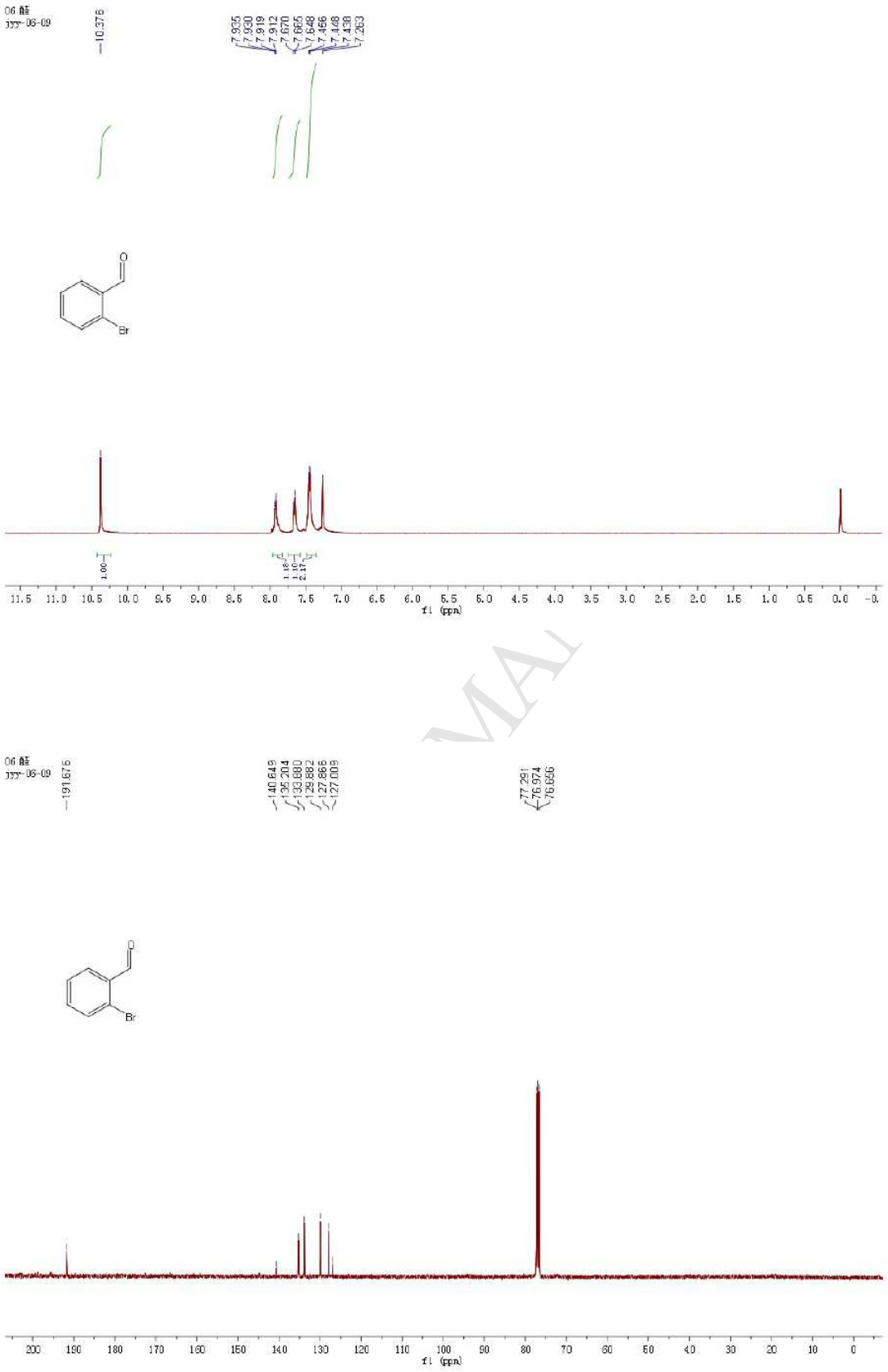
^{1}H NMR and ^{13}C NMR of compound **2n**



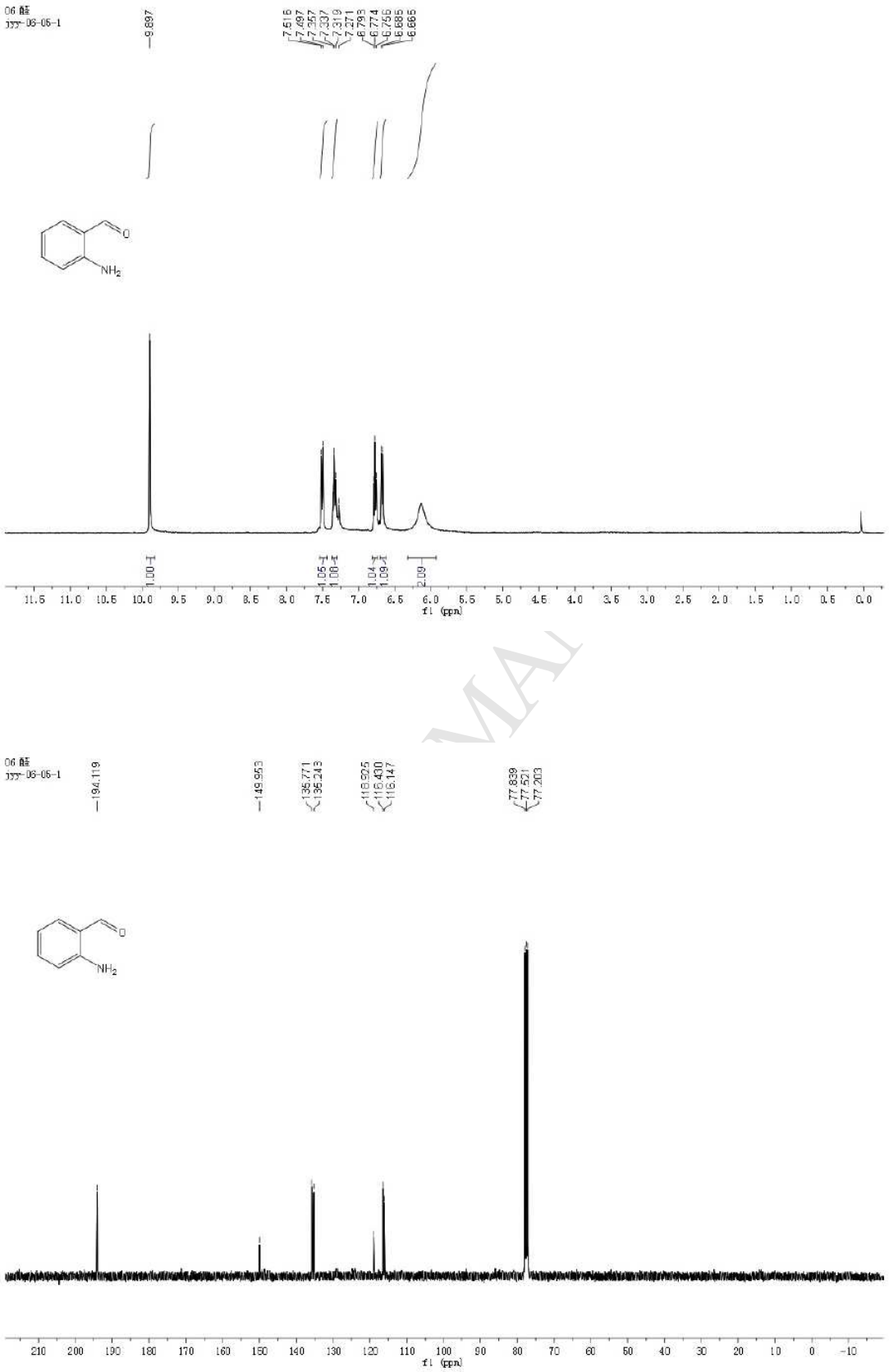
^{1}H NMR and ^{13}C NMR of compound **2o**



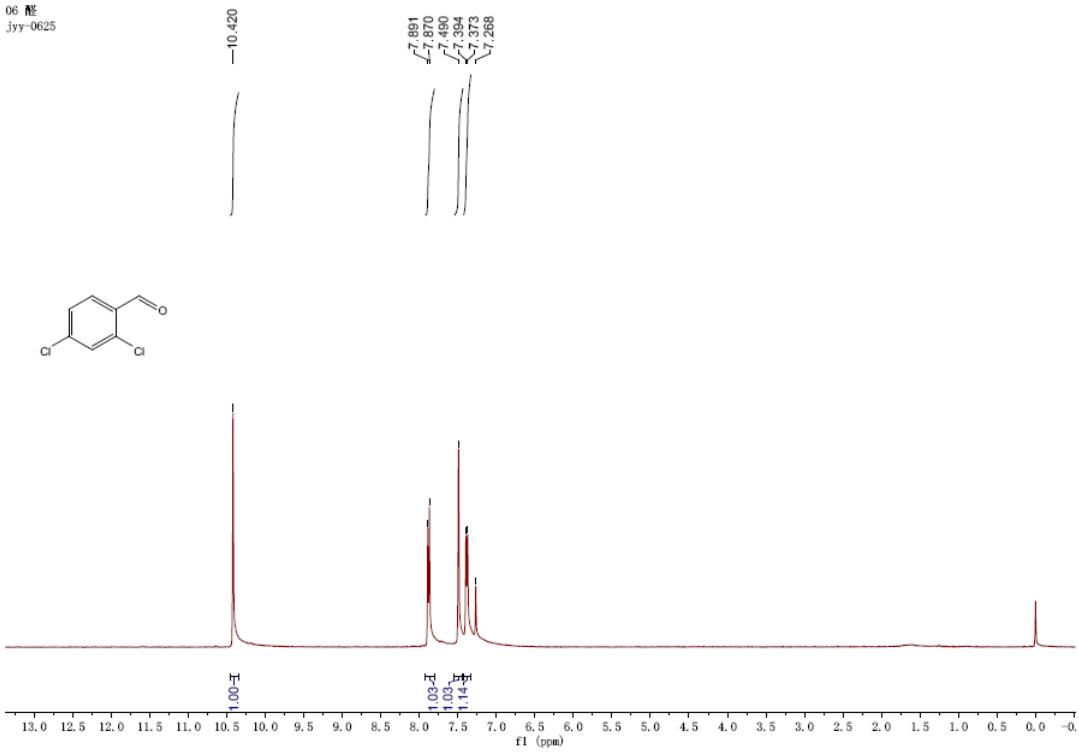
^{1}H NMR and ^{13}C NMR of compound **2p**

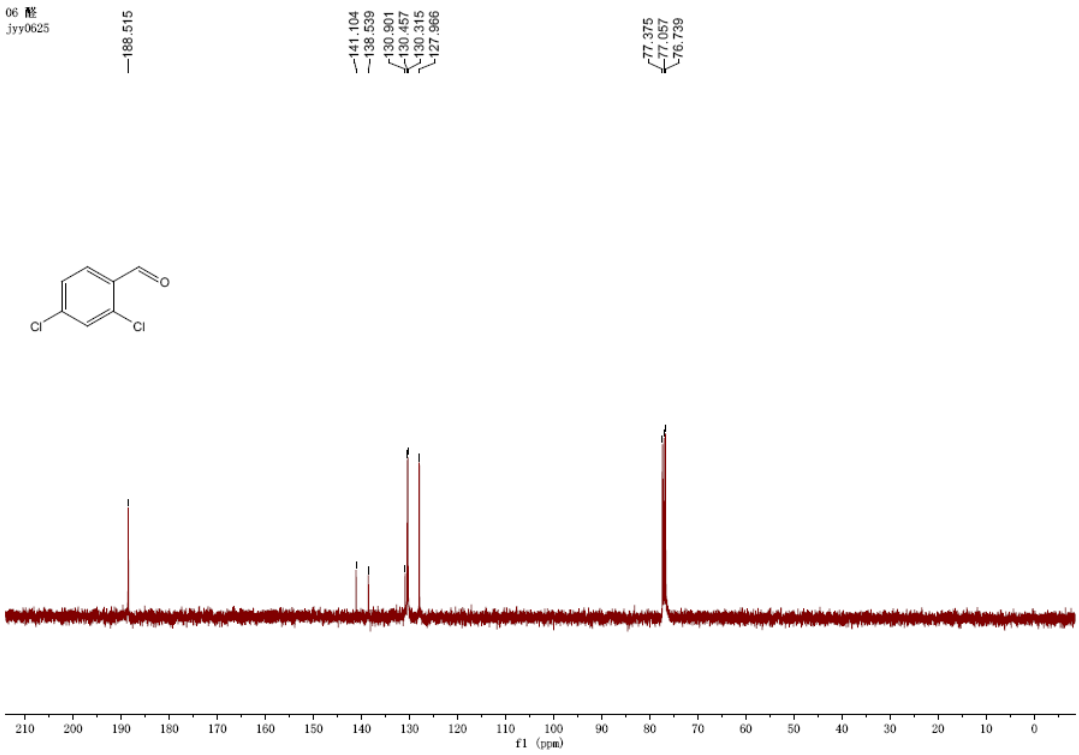


^{1}H NMR and ^{13}C NMR of compound **2q**

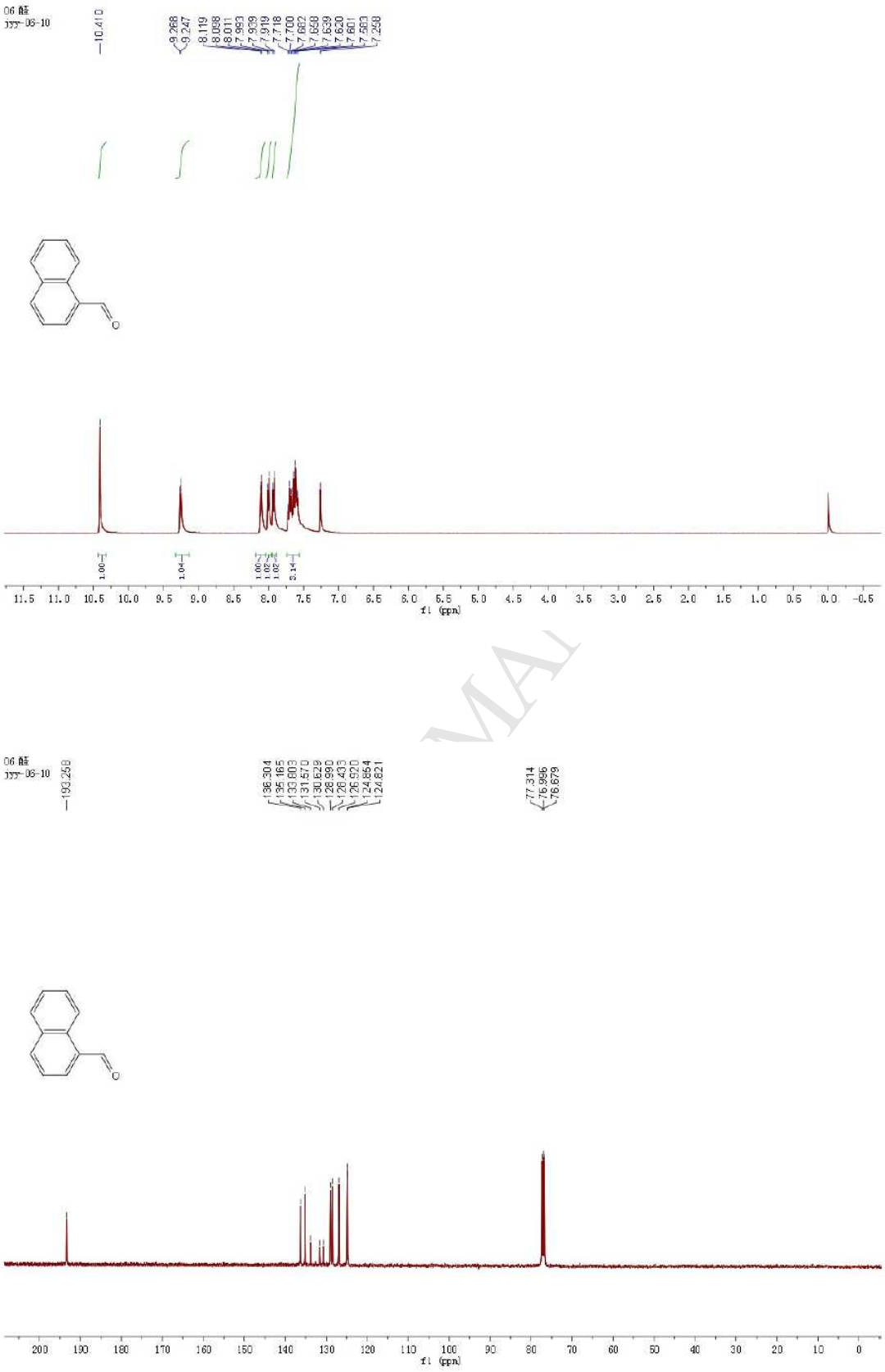


^{1}H NMR and ^{13}C NMR of compound **2r**

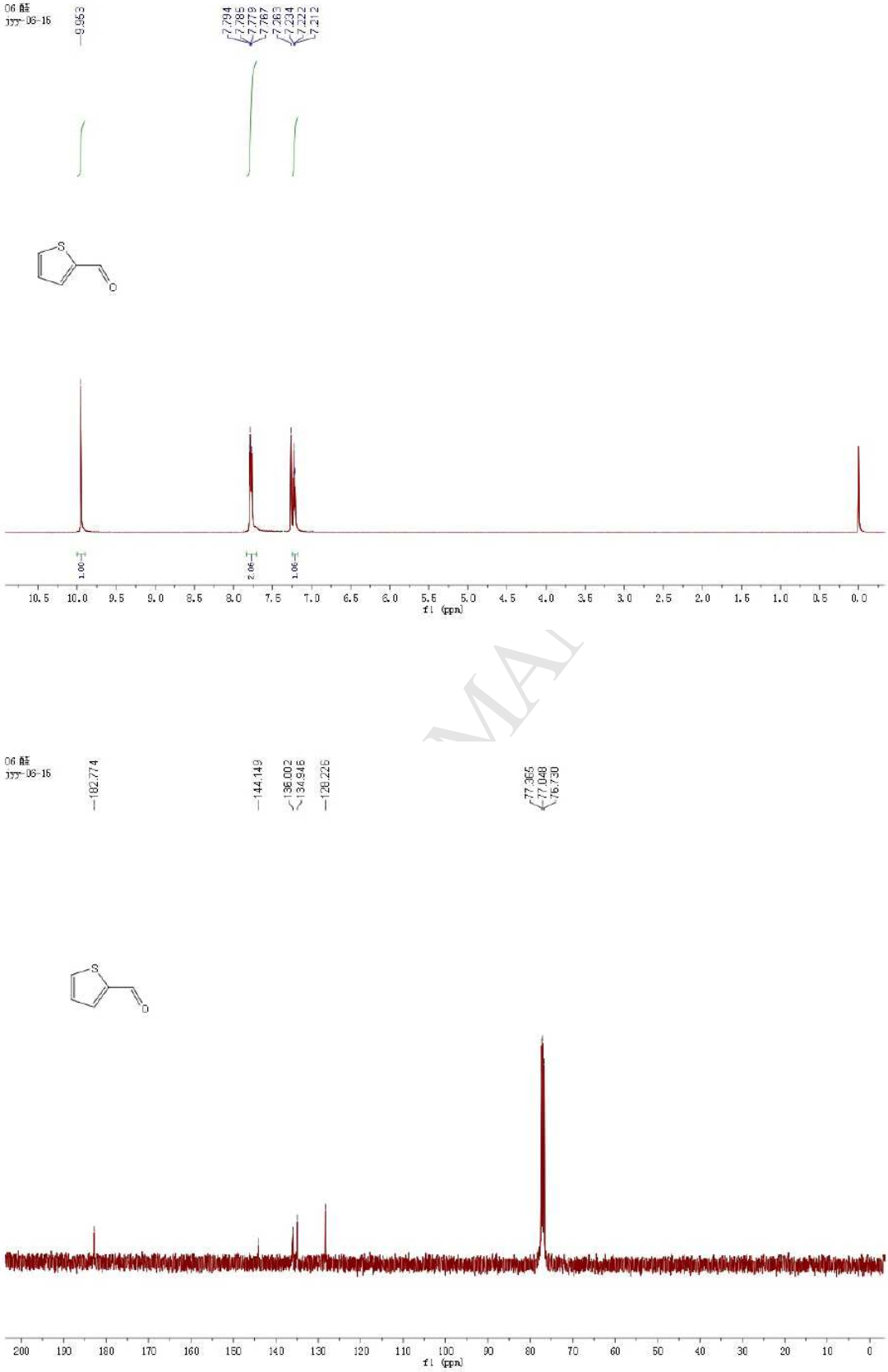




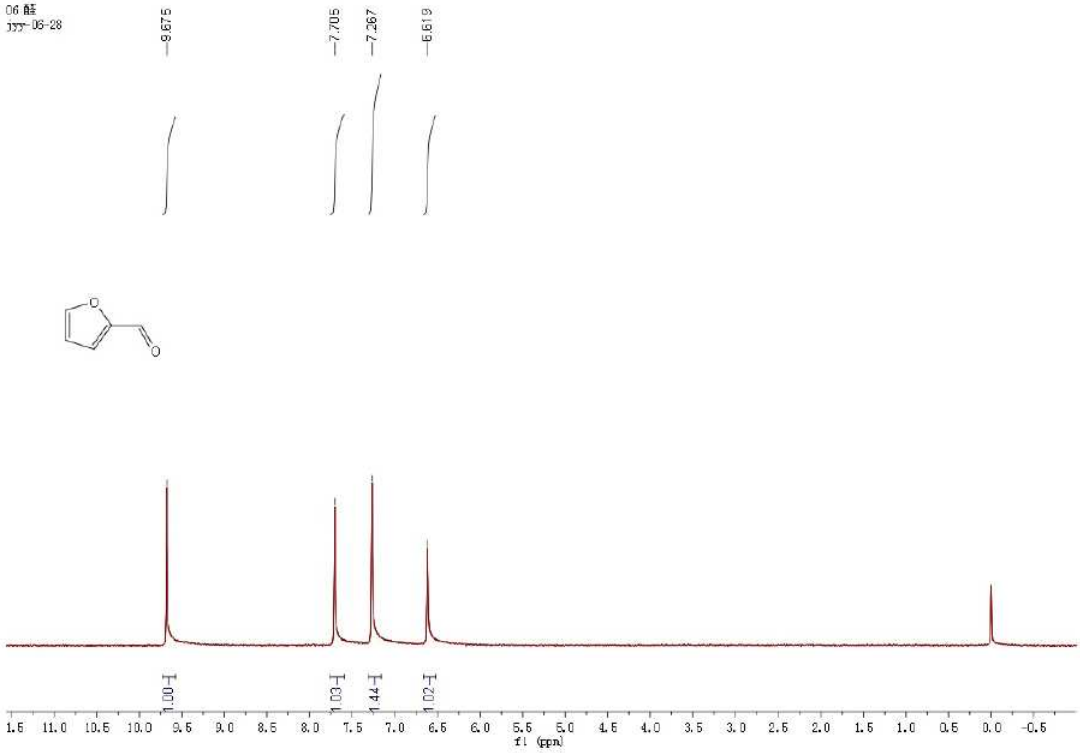
^{1}H NMR and ^{13}C NMR of compound **2s**

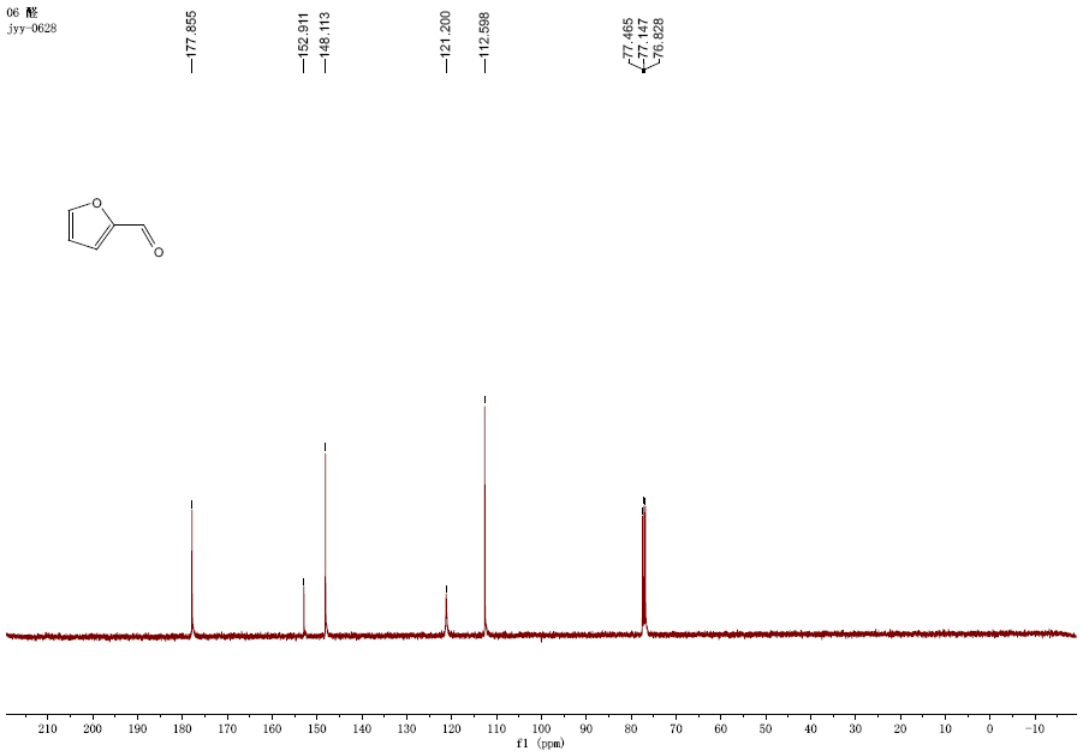


^{1}H NMR and ^{13}C NMR of compound **2t**

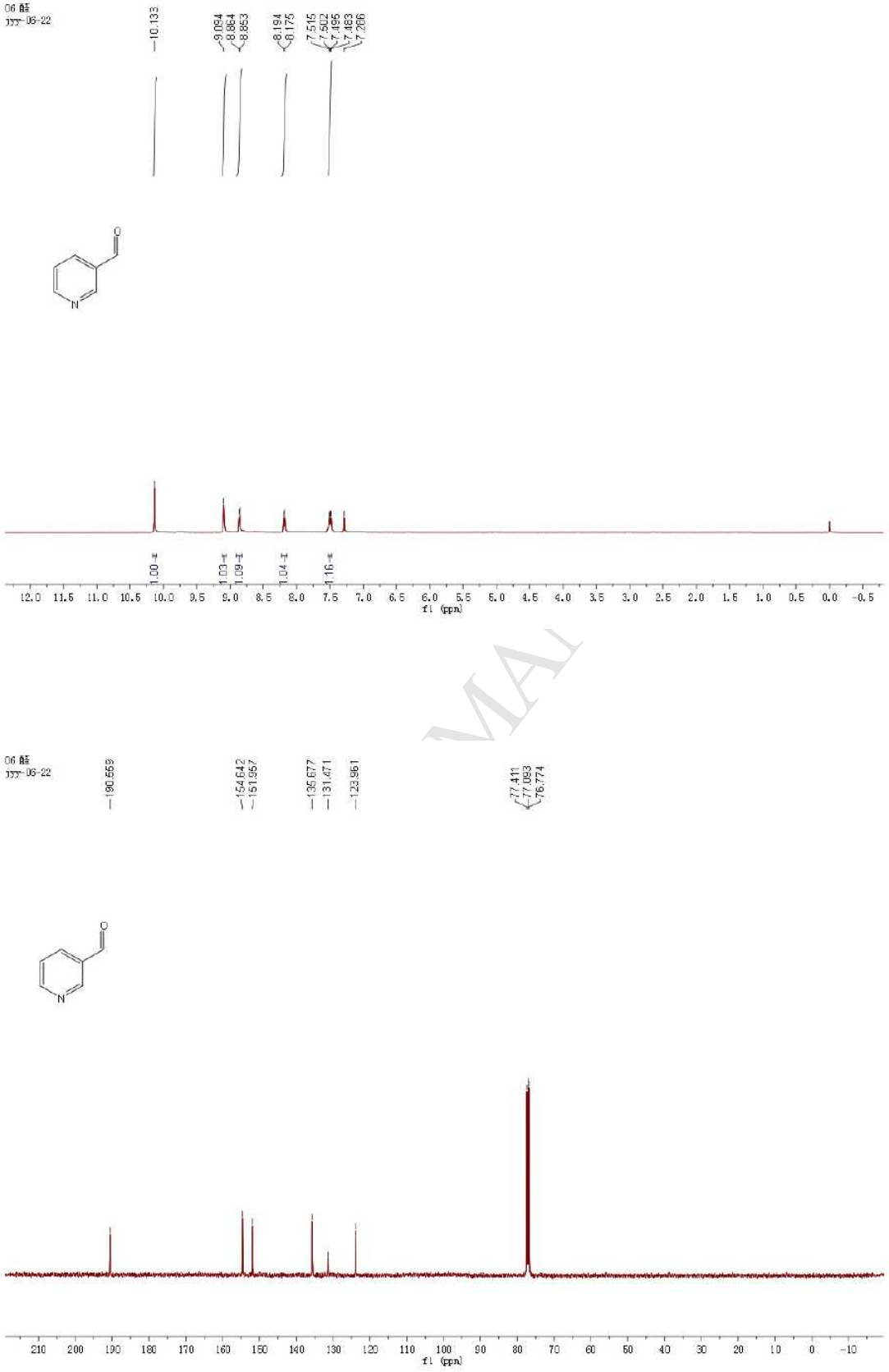


^{1}H NMR and ^{13}C NMR of compound **2u**

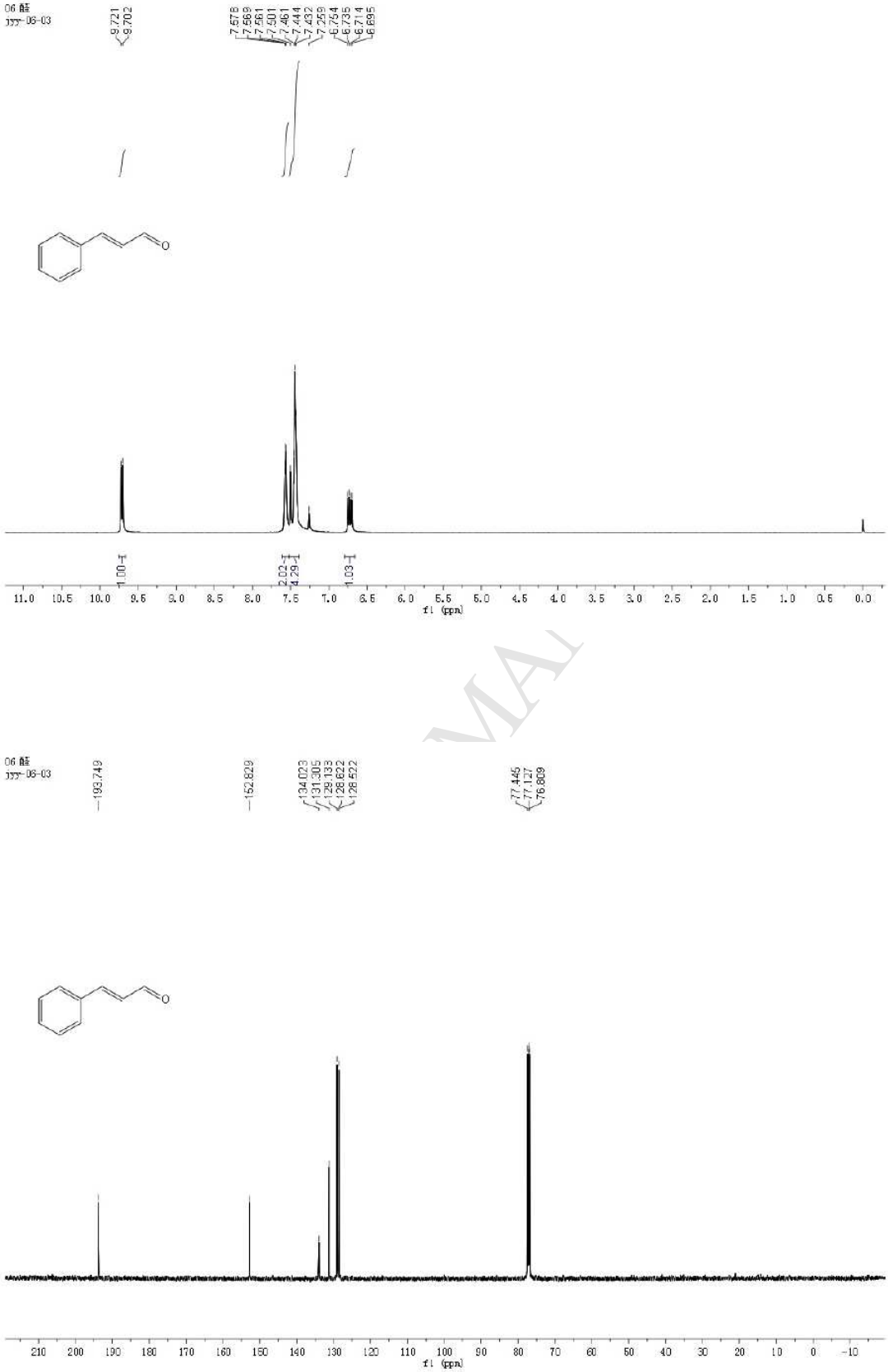




^{1}H NMR and ^{13}C NMR of compound **2v**



^{1}H NMR and ^{13}C NMR of compound **2w**



^{1}H NMR and ^{13}C NMR of compound **2x**