# *Electronic Supplementary Information*

## Highly Practical and Efficient Preparation of Aldehydes and Ketones from Aerobic Oxidation of Alcohols with an Inorganic-ligand Supported Iodine Catalyst

Mengqi Zhang,[a,§] Yongyan Zhai,[a,§] Shi Ru,[a,§] Dejin Zang,[b] Sheng Han,[*a] Han Yu, [*a,b] and Yongge Wei[*b,c]

[a]School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, P.R. China.

[b]Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China.

[c]State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Beijing 100191, P.R. China.

[§]Contributed equally to this work.

E-mail: scihanyu@163.com, yonggewei@mail.tsinghua.edu.cn Hansheng654321@sina.com

## Content

## I. Supporting general information

All reagents were purchased from Sigma-Aldrich and Adamas-beta and all the chemicals were of analytical grade and used as received. Thermo Fisher Scientific production of Nicolet iN10 recorded the FT-IR spectra. UV-vis spectrophotometer (Beijing Purkinje General Instrument production of TU-1900) recorded the UV spectra. And X-Ray Diffractometer (Japan Science Corporation production of D/max 2200PC ) recorded the crystal structure of $(NH_4)_5[IMo_6O_{24}]$. In addition,GC mass spectra were recorded on Shimadzu GCMS-QP2010 with RTX-5MS column (0.25 mm× 30 m). $^1$H and $^{13}$C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker AVANCE III 500 MHz (500 MHz for proton, 125MHz for carbon) spectrometer and Bruker AVANCE III 400MHz (400MHz for proton, 100MHz for carbon) with tetra-methylsilane as the internal reference using $CDCl_3$ or DMSO-$d_6$ as solvent in all cases, and chemical shifts were reported in parts per million (ppm, δ). Moreover, column chromatography was performed using 200-300 mesh silica gel.

## II. Support graphic information

### i. Preparation of inorganic-ligand supported iodine-catalyst

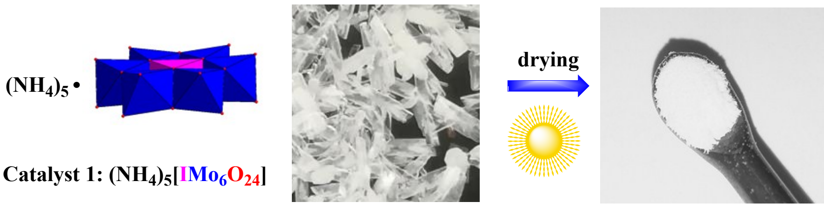



**Fig. S1 Structure and appearance of $(NH_4)_5[IMo_6O_{24}]$**

The hybrid Anderson-type polyoxometalate, $(NH_4)_5[IMo_6O_{24}]$ was synthesized according to procedures described elsewhere with minor modification[1]. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (3.70g 13.8mmol) was dissolved in water (30 mL) and then heated to 95 $^o$C. $H_5IO_6$ (0.68 g 3.0mmol) was dissolved in water (9mL), which was slowly added to the solution with stirring. The mixture was stirred for 1h after complete addition. The solution color was colorless, and the filter residue was removed by hot filtration. The filtrate was washed with ethanol to give a white suspension. After two days, a solid is obtained and collected by filtration. The cake was washed with ethanol and the alcohol-washed product was dried in a vacuum oven to give a white powdery solid. The ammonium salt $(NH_4)_5[IMo_6O_{24}]$ was recrystallized twice from hot water. The solution was filtered while hot and allowed to evaporate. After a period of time, colorless and transparent crystals (2.8 g) were collected, some of which were suitable for structural analysis [2].

## ii. Raman spectra of catalyst 1

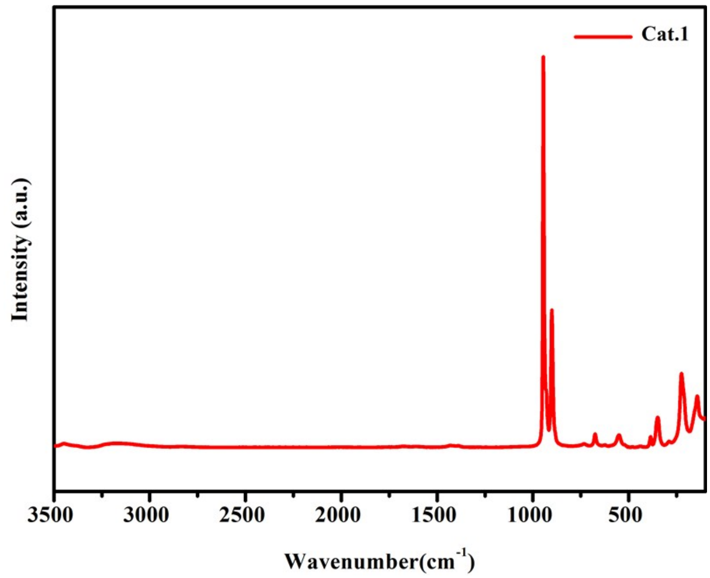



**Fig. S2 Raman spectra of catalyst 1**

## iii. FT-IR spectra of catalysts 1

FT-IR spectra analysis was further carried out to verify the structure of $(NH_4)_5[IMo_6O_{24}]$ in the synthetic process. As shown in Fig. S3. there are two broad bands at 3470 $cm^{-1}$ and 3157 $cm^{-1}$ derived from the stretching vibration of -OH, suggesting the presence of a lattice and coordinated water. Those at 942 $cm^{-1}$ and 902 $cm^{-1}$ could be assigned to the terminal Mo=O bond. The characteristic peaks which appear at 692 and 625 $cm^{-1}$ were ascribed to surrounding heteropoly cations of the bridged Mo-O-Mo. In addition, the peak at 474 $cm^{-1}$ was designated to the vibration of the Mo-O-I ,which demonstrates the successful synthesis of the $(NH_4)_5[IMo_6O_{24}]$ catalyst. The IR and Raman activities are shown in Fig S3. and Fig. S2. Experimentally, bands were observed in the IR and Raman spectra in this region which can be readily assigned on the basis of their position and intensity.

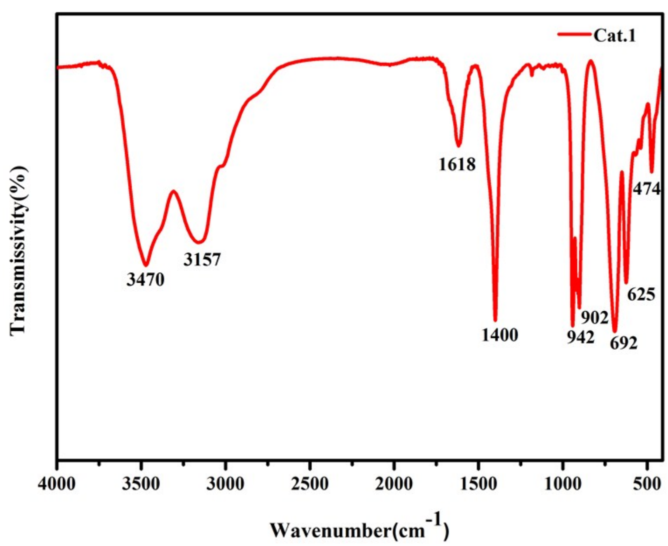



**Fig. S3 FT-IR spectra of catalysts 1**

### iv. XRD spectra of catalyst 1

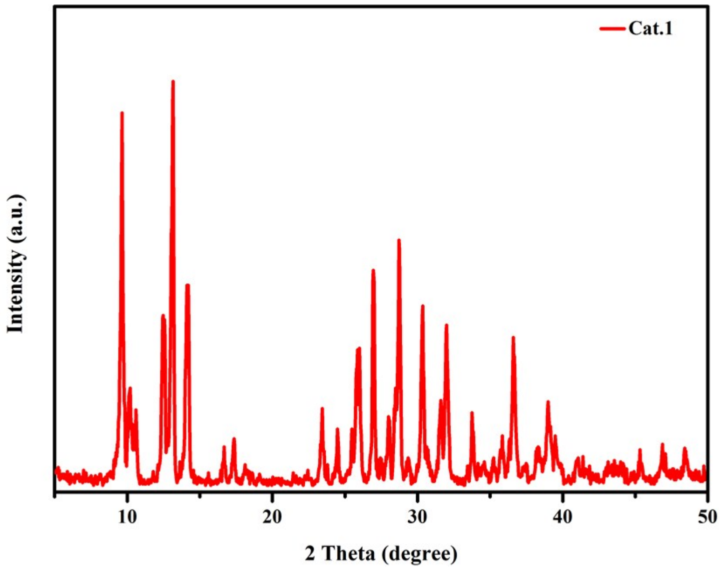



**Fig. S4 XRD spectra of catalyst 1**

### v. UV-vis spectra of catalyst 1

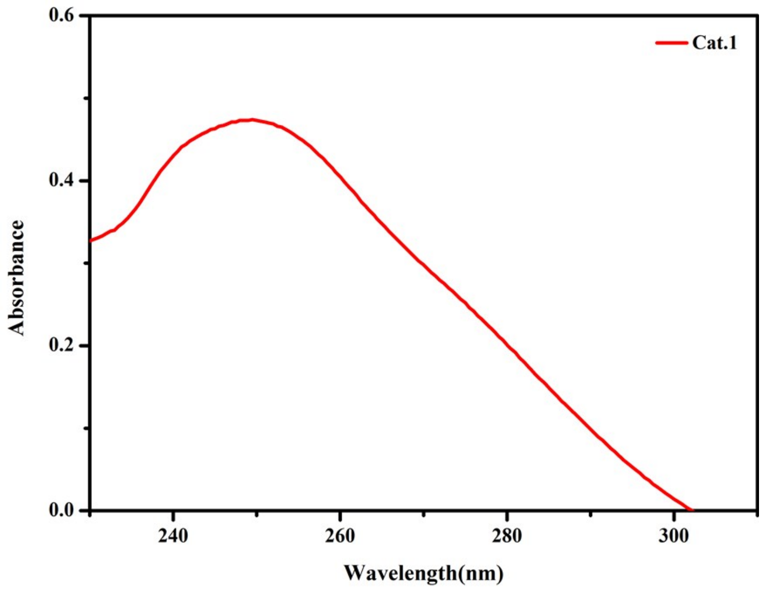



**Fig. S5 UV-vis spectra of catalyst 1**

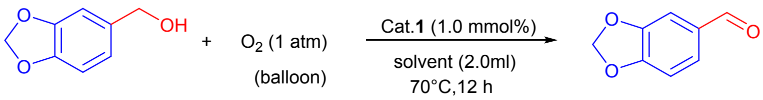
## III. General procedure for catalytic oxidation of alcohols

Alcohol (1.0 mmol), NaCl (10% mmol), catalyst 1 (1 mmol%) and aqueous acetonitrile (2.0 mL) were added to a tube. Then the mixture was stirred at 70 °C for 5-24 hours. During this period, oxygen gas balloons were used as the sole oxidant. The reaction progress was monitored by TLC and GC-MS. Yield was determined by GC-MS analysis. After completion of the reaction, small amounts of ethyl acetate and pure water were added into the reaction mixture. The organic phase was extracted with ethyl acetate and dried over anhydrous sodium sulfate. The crude product was obtained by evaporating the solvent and purified through flash column chromatography on silica gel using (PE/EA=10:1) to afford the desired product. The solid catalyst was isolated by filtration and used for the next runs.

## IV. Supporting chart information

### i. Optimization of reaction solvent

**Table S1. The effect of solvent[a,b,c]**




| Entry | Solvent | Sel. (%)[b] | Yield (%)[c] |
|---|---|---|---|
| 1 | $H_2O$ | 88 | 79 |
| 2 | $CH_3CN$ | 86 | 75 |
| 3 | DCM | 86 | 62 |
| 4 | Dioxane | 80 | 43 |
| 5 | DMF | 81 | 50 |
| 6 | DMSO | 84 | 56 |
| 7 | $H_2O/CH_3CN$ | 96 | 91 |
| 8 | $H_2O$/DCM | 84 | 75 |
| 9 | $H_2O$/Dioxane | 88 | 73 |
| 10 | $H_2O$/DMF | 83 | 78 |
| 11 | $H_2O$/DMSO | 89 | 80 |

[a] Reaction conditions: Cat. **1** (1.0 mmol %), piperitol (2.0 mmol), $O_2$ (1 atm), and solvent (2 mL) at 70°C, Volume ratio: v/v=1/1, unless otherwise noted. [b,c] Selectivity and yields were calculated by GC and confirmed by GC-MS.

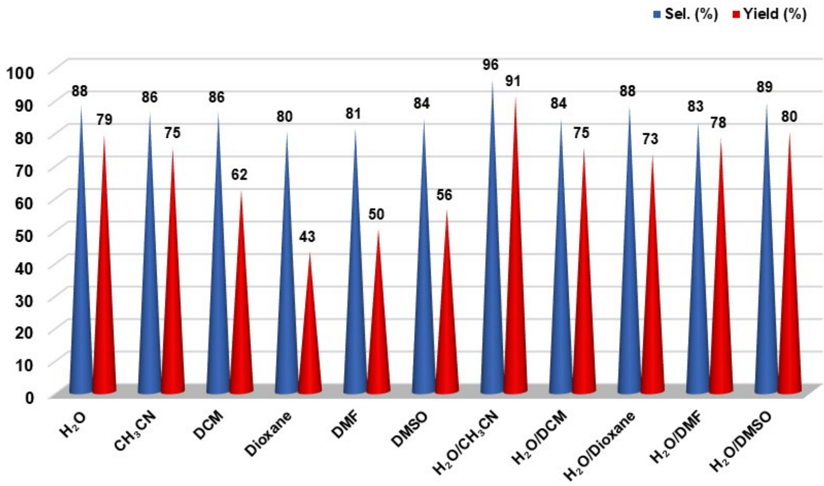
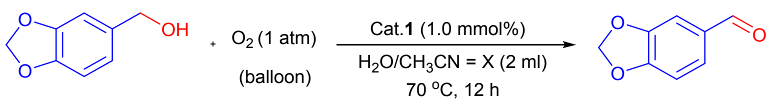



**Fig. S6 The effect of solvent**

## Table S2. The effect of water [a,b,c]




| Entry | $H_2O/CH_3CN$ (v : v) | Sel. (%)[b] | Yield (%)[c] |
|---|---|---|---|
| 1 | 0.5:1 | 88 | 82 |
| 2 | 1:1 | 96 | 91 |
| 3 | 2:1 | 90 | 83 |
| 4 | 3:1 | 88 | 82 |
| 5 | 4:1 | 93 | 87 |
| 6 | 5:1 | 85 | 80 |

[a] Reaction conditions: Cat. **1**(1.0 mmol %), piperitol (2.0 mmol), $O_2$ (1 atm), and solvent (2 mL) at 70 °C, unless otherwise noted. [b,c] Selectivity and yields were calculated by GC and confirmed by GC-MS.

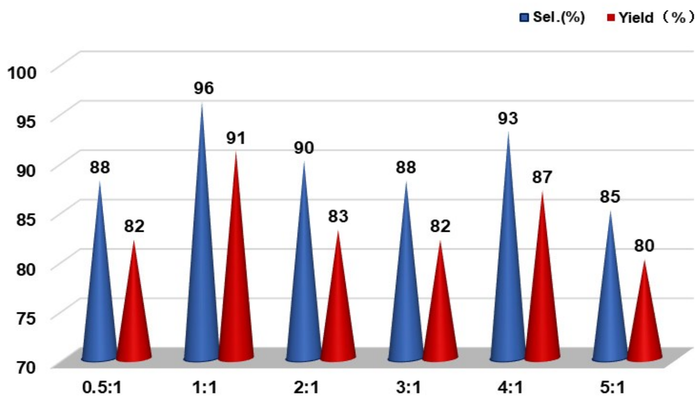
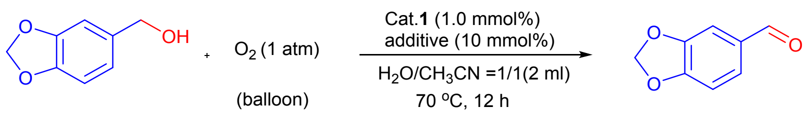



**Fig. S7 The effect of water**

## ii. Optimization of additive

**Table S3. Optimization of reaction conditions with the oxidation of piperonyl alcohol as a model substrate [a,b,c]**




| Entry | Cat. (mmol%) | Additive (10 mmol%) | Sel.(%)[b] | Yield (%)[c] |
|---|---|---|---|---|
| 1 | 1 | $K_3PO_4$ | 93 | 90 |
| 2 | 1 | $K_2CO_3$ | 89 | 85 |
| 3 | 1 | NaClO | 83 | 72 |
| 4 | 1 | $Na_2CO_3$ | 85 | 71 |
| 5 | 1 | $NaHCO_3$ | <5 | <1 |
| 6 | 1 | $Na_2SO_4$ | 84 | 70 |
| 7 | 1 | $NaNO_2$ | 71 | 56 |
| 8 | 1 | NaBr | 77 | 63 |
| 9 | 1 | NaCl | 99 | 95 |
| 10 | 1 | $NH_4Cl$ | 94 | 91 |
| 11 | 1 | $CH_3ONa$ | 89 | 84 |
| 12 | 1 | $Et_3N$ | 94 | 92 |
| 13 | 0.1 | NaCl | 90 | 86 |
| 14 | 0.5 | NaCl | 94 | 91 |
| 15[d] | 1 | NaCl | 82 | 80 |
| 16[e] | 1 | NaCl | 91 | 88 |
| 17[f] | 1 | NaCl | 85 | 72 |

[a]Reaction conditions: Cat. **1** (1.0 mmol%), piperitol (2.0 mmol), $O_2$ (1 atm),additive (10 mmol%) and $H_2O/CH_3CN$=1/1 (2 mL) at 70 °C. Unless otherwise noted. [b]Selectivity were determined by GC and confirmed by GC-MS. [c]Yields were calculated from $^1H$ NMR spectra. [d]at 25 °C. [e]at 80 °C. [f]Reactions were carried out under atmospheric air.

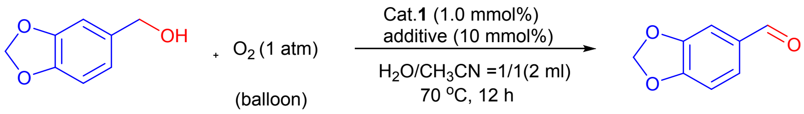
**Table S4. Optimization of reaction conditions with the oxidation of lauryl alcohol as a model substrate [a,b,c,d]**

$$\underset{\text{(lauryl alcohol)}}{n\text{-}C_{12}H_{25}OH} + \underset{\text{(balloon)}}{O_2\ (1\ \text{atm})} \xrightarrow[\substack{H_2O/CH_3CN = 1/1\ (2\ \text{ml}) \\ 70\ ^oC,\ 12\ h}]{\substack{\text{Cat.}\mathbf{1}\ (1.0\ \text{mmol\%}) \\ \text{additive (10 mmol\%)}}} \underset{\text{(lauraldehyde)}}{n\text{-}C_{11}H_{23}CHO} + \underset{\text{(lauric acid)}}{n\text{-}C_{11}H_{23}CO_2H}$$

| Entry | Additive (10 mol%) | Sel. (%) [b] | Yield of lauraldehyde (%) [c] | Yield of lauric acid (%) [d] |
|---|---|---|---|---|
| 1 | $Na_2CO_3$ | 50 | 20 | 70 |
| 2 | $Na_2SO_4$ | 46 | 17 | 68 |
| 3 | NaAc | 97 | 92 | - |
| 4 | $NaClO_4$ | 18 | 5 | 81 |
| 5 | $NaHSO_4$ | 65 | 32 | 60 |
| 6 | NaF | 66 | 34 | 51 |
| 7 | NaCl | 19 | 5 | 93 |
| 8 | NaBr | 53 | 22 | 75 |
| 9 | NaI | 44 | 16 | 82 |
| 10 | $K_2SO_3$ | 41 | 14 | 73 |
| 11 | $MgSO_3$ | 35 | 11 | 63 |
| 12 | $CaSO_3$ | 17 | 5 | 9 |
| 13[e] | NaAc | 67 | 35 | - |
| 14[f] | NaAc | 88 | 80 | 5 |
| 15[g] | NaAc | 90 | 86 | 7 |
| 16[h] | NaAc | 94 | 90 | - |

[a] Reaction conditions: Cat. **1** (1.0 mmol%), lauryl alcohol (2.0 mmol), $O_2$ (1 atm), additive (10 mmol%) and $H_2O/CH_3CN$=1/1 (2 mL) at 70$^o$C. Unless otherwise noted. [b] Selectivity of lauraldehyde were determined by GC and confirmed by GC-MS. [c,d] Yields were calculated from $^1$H NMR spectra.[e] At 25 $^o$C. [f] At 45 $^o$C. [g] At 80 $^o$C. [h] Reactions were carried out under atmospheric air, 24 h.

**Table S5 .The effect of different cation [a,b,c]**




| Entry | Cat. (mol%) | Additive (10 mmol%) | Sel.(%)[b] | Yield (%)[c] |
|---|---|---|---|---|
| 1 | 1 | NaCl | 99 | 95 |
| 2 | 1 | KCl | 80 | 65 |
| 3 | 1 | RbCl | 83 | 67 |
| 4 | 1 | CsCl | 88 | 70 |
| 5 | 1 | $NH_4Cl$ | 94 | 90 |
| 6 | 1 | $CaCl_2$ | 76 | 59 |
| 7 | 1 | $MgCl_2$ | 82 | 66 |
| 8 | 1 | $ZnCl_2$ | 58 | 37 |
| 9 | 1 | LiCl | 63 | 41 |

[a] Reaction conditions: Cat. **1** (1.0 mol%), piperitol (2.0 mmol), $O_2$ (1 atm),additive (10 mmol%) and $H_2O/CH_3CN$=1/1 (2 mL) at 70°C. Unless otherwise noted. [b] Selectivity were determined by GC and confirmed by GC-MS. [c] Yields were calculated from $^1H$ NMR spectra.

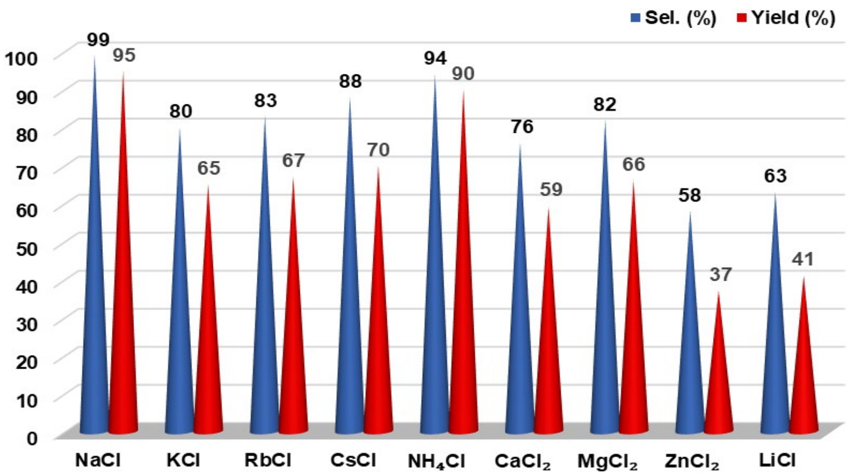
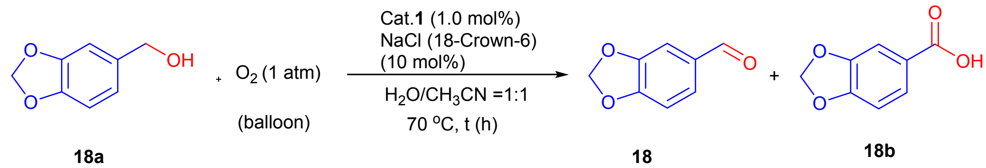



**Fig. S8 The effect of different cation**

**Table S6. Monitoring the reaction of piperitol with NaCl and 18-Crown-6 [a,b,c,d]**




| Time (h) | Content of 18a (%)[b] | Content of 18 (%) [c] | Content of 18b (%)[d] |
|---|---|---|---|
| 1 | 97 | <1 | - |
| 2 | 70 | 28 | - |
| 3 | 58 | 40 | - |
| 4 | 45 | 53 | - |
| 5 | 31 | 64 | - |
| 6 | 26 | 71 | - |
| 7 | 19 | 77 | - |
| 8 | 14 | 80 | - |
| 9 | 13 | 82 | - |
| 10 | 10 | 85 | - |
| 11 | 7 | 89 | - |
| 12 | <5 | 91 | - |

[a]Reaction conditions: Cat. **1** (1.0 mol%), piperitol (5.0 mmol), $O_2$ (1 atm),additive (10 mmol%) and $H_2O/CH_3CN$=1/1 (10 mL) at 70°C. Unless otherwise noted. [b,c,d] Content were determined by GC and confirmed by GC-MS.

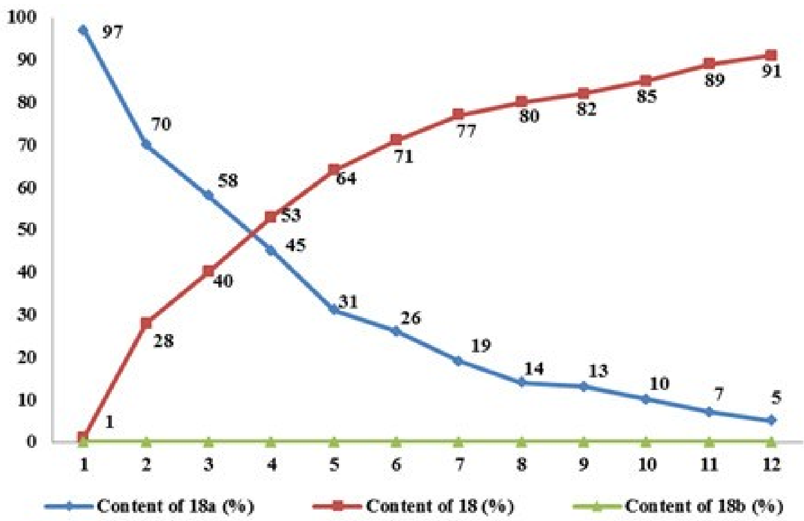
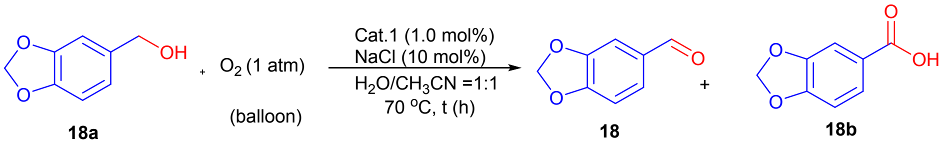



**Fig. S9 Monitoring the reaction of piperitol with NaCl and 18-Crown-6**

**Table S7. Monitoring the reaction of piperitol with NaCl [a,b,c,d]**




| Time (h) | Content of 18a (%)[b] | Content of 18 (%) [c] | Content of 18b (%)[d] |
|---|---|---|---|
| 1 | 87 | 12 | - |
| 2 | 66 | 30 | - |
| 3 | 54 | 44 | - |
| 4 | 40 | 57 | - |
| 5 | 27 | 70 | - |
| 6 | 23 | 75 | - |
| 7 | 18 | 80 | - |
| 8 | 15 | 83 | - |
| 9 | 12 | 87 | - |
| 10 | 9 | 90 | - |
| 11 | 7 | 92 | - |
| 12 | <5 | 97 | - |

[a]Reaction conditions: Cat. **1** (1.0 mol%), piperitol (5.0 mmol), $O_2$ (1 atm),additive (10 mmol%) and $H_2O/CH_3CN$=1/1 (10 mL) at 70°C. Unless otherwise noted. [b]、[c]、[d]Content were determined by GC and confirmed by GC-MS.

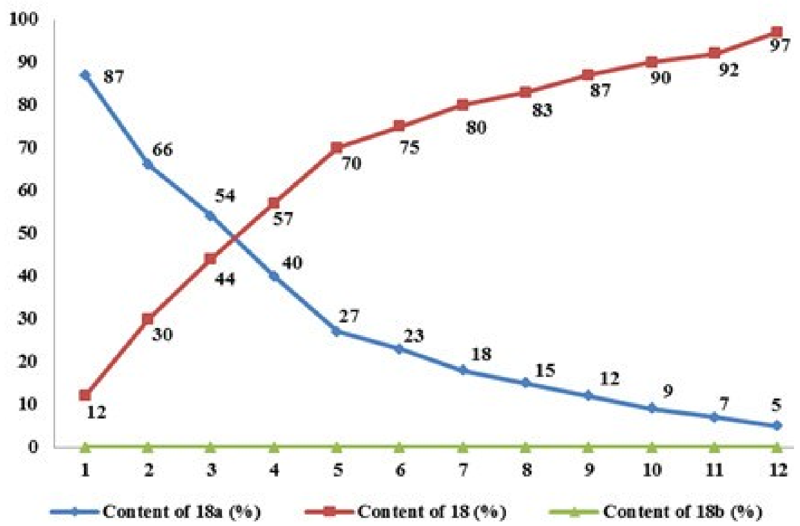
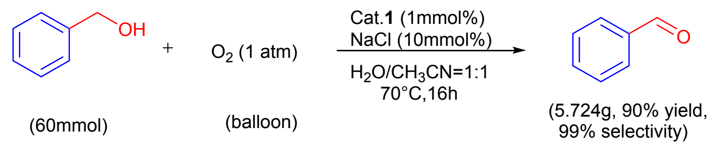



**Fig. S10 Monitoring the reaction of piperitol with NaCl**

## iii. Gram-scale oxidation of benzyl alcohol and recycling ability of Cat.1

**Table S8. Gram-scale oxidation of benzyl alcohol and recycling effect of Cat.1** **a**,b




| **Recovery times** | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| Yield(%)[b] | 90 | 88 | 83 | 77 | 70 | 66 |

[a] The reaction was carried out on a 60 mmol scale of benzaldehyde, Cat. **1** (1.0 mol%), $O_2$ (1 atm), additive (10 mmol%) and $H_2O/CH_3CN$=1/1(120 ml) at 70°C. The reaction mixtures were calculated by GC and confirmed by GC-MS. [b]Yields were calculated from GC-Ms.

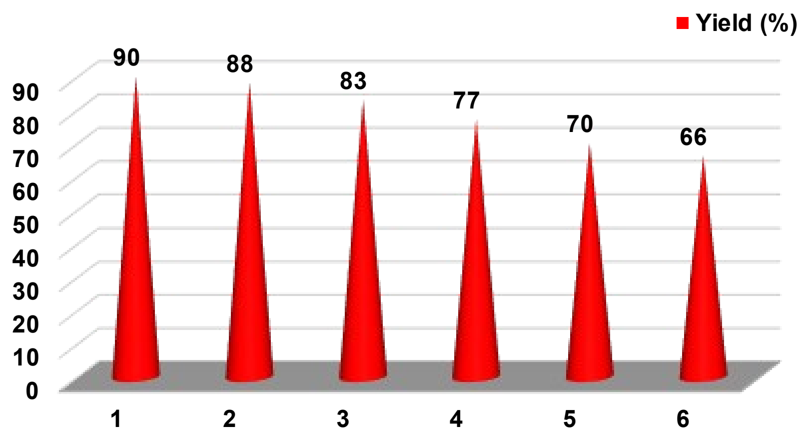



**Fig. S11 Recycling experiments for the Cat. 1**

## IV. Recycling experiments of catalyst for the oxidative reaction

The iodine catalyst precipitated after the oxidative reaction experiments and was recovered for reuse. The recovered catalyst was characterized by FT-IR (Figure. S12.). The infrared image contains a red line of fresh catalyst and a blue line for the catalyst recycled five times.

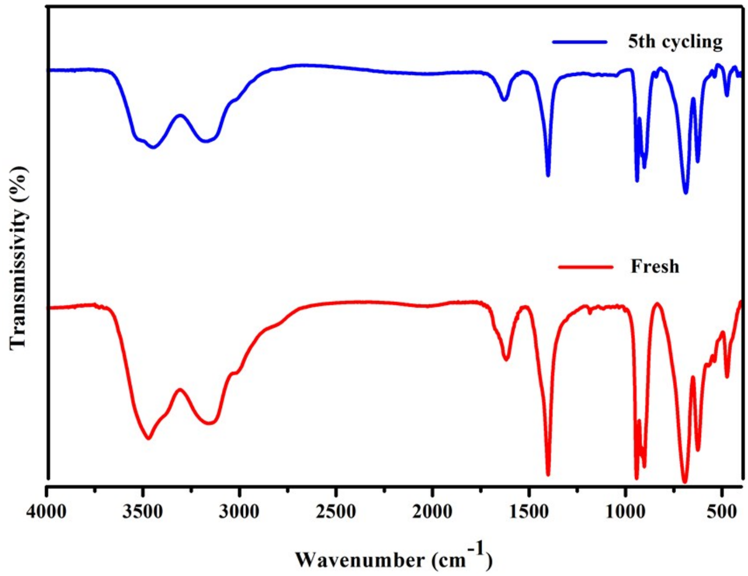



**Fig. S12 FT-IR spectra of the Cat. 1 before and after reaction**

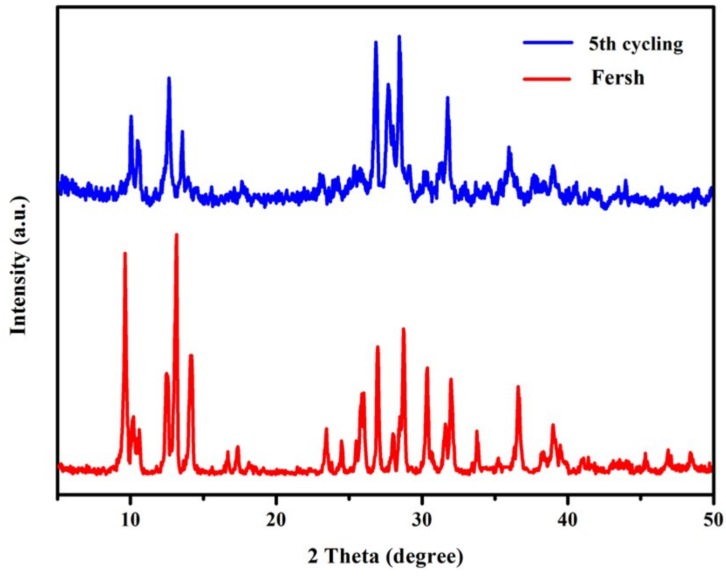



**Fig. S13 XRD spectra of the Cat. 1 before and after reaction**

## V. Cyclic voltammograms

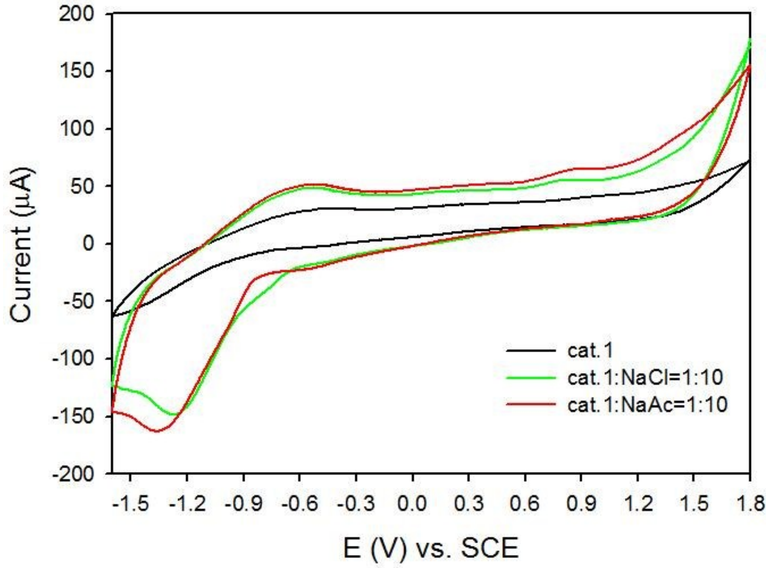



**Fig. S14 Cyclic voltammograms of catalyst 1, catalyst 1/NaCl(1:10) and catalyst 1/NaAc(1:10).** The cyclic voltammograms image contains a black line of (A) cyclic voltammograms of catalyst 1, a green line of (B) cyclic voltammograms of catalyst 1/NaCl (1:10) and a red line of (C) cyclic voltammograms of catalyst 1/NaAc (1:10).

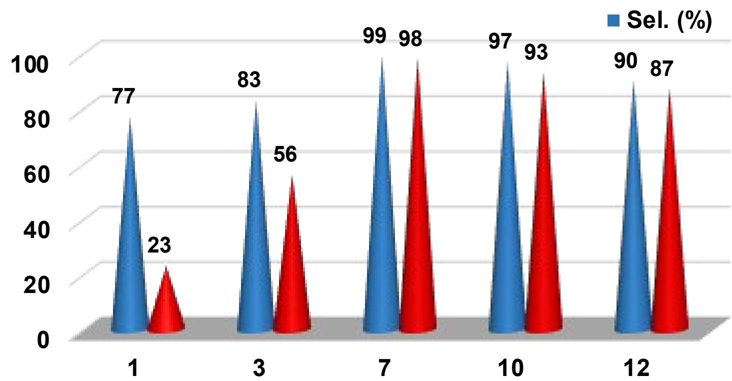



**Fig. S15** Screening of pH on the catalytic oxidation of piperitol. Reaction conditions: Cat. 1 (1.0 mol%), piperitol (1.0 mmol), $O_2$ (1 atm), NaCl (10 mol%) and MeCN/$H_2O$=1/1 (2 mL) at 70°C. Unless otherwise noted. Selectivity were determined by GC and confirmed by GC-MS. Yields were calculated from $^1$H NMR spectra.

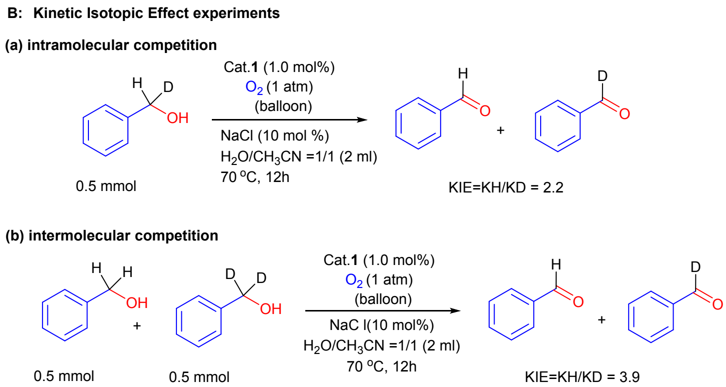
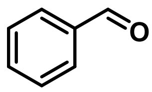



**Fig. S16** Experimental studies providing insight into the mechanism of the iodine-catalyzed oxidation of alcohols.

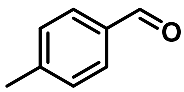
## VI. References

1 (a) A. M. Fedosseev, M. S. Grigoriev, N. A. Budantseva, I. B. Shirokova, E. Antic-Fidancev and J.-C. Krupa. *J. Lumin.,* 2000, **87**, 1065-1068; (b) D. Honda, S. Ikegami, T. Inoue, T. Ozeki and A. Yagasaki. *Inorg. Chem.,* 2007, **46**, 1464-1470.
2 (a) Adam J. Bridgeman. *Chem. Eur. J.* 2006, **12**, 2094-2102. (b) H. L, P. Li, Y. Liu, L. Hao, W. Ren, W. Zhu, C. Deng, F. Yang. *Chem. Eng. J.,* 2017, **313**, 1004-1009. (c) A. M. Khenkin, R. Neumann. *Adv. Synth. Catal.,* 2003, **34**, 1017-1021.

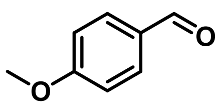
## VII. NMR data of products



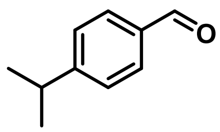

**Benzaldehyde (2):** Colorless liquid.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.06 (dd, J = 8.2, 1.3 Hz, 2H), 7.81 (ddd, J = 7.4, 4.1, 1.3 Hz, 1H), 7.71 (dd, J = 10.7, 4.5 Hz, 2H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.44 (s), 136.41 (s), 134.49 (s), 129.76 (s), 129.01 (s).



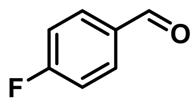

**p-Tolualdehyde (3):**Pale yellow liquid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.93 (d, J = 2.9 Hz, 1H), 7.76 – 7.73 (m, 2H), 7.30 (d, J = 7.5 Hz, 2H), 2.40 (d, J = 2.7 Hz, 3H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.95 (s), 145.52 (s), 134.21 (s), 129.75 (d, J = 14.9 Hz), 21.81 (s).



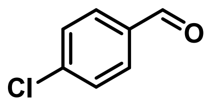
**4-Methoxybenzaldehyde (4):** Yellow liquid.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.81 (d, J = 2.5 Hz, 1H), 7.80 – 7.74 (m, 2H), 6.96 – 6.91 (m, 2H), 3.81 (dd, J = 4.3, 3.0 Hz, 3H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 190.86 (s), 164.63 (s), 132.01 (s), 129.94 (s), 114.33 (s), 55.60 (s).



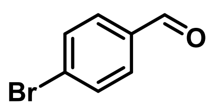
**4-Isopropylbenzaldehyde (5):** Yellow liquid.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.75 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 1.21 (d, J = 7.1 Hz, 6H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 190.86 (s), 164.63 (s), 132.01 (s), 129.94 (s), 114.33 (s), 55.60 (s).



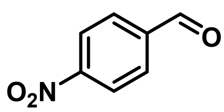
**4-Fluorobenzaldehyde (6):** Pale yellow liquid.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.91 (dd, J = 8.5, 5.5 Hz, 2H), 7.21 (t, J = 8.5 Hz, 2H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 190.50 (s), 166.52 (d, J = 256.7 Hz), 132.98 (s), 132.23 (d, J = 9.7 Hz), 116.34 (d, J = 22.3 Hz).



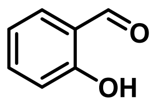
**4-Chlorobenzaldehyde (7):** Colorless flaky crystal.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.85 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 190.90 (s), 140.99 (s), 134.76 – 134.71 (m), 130.93 (s), 129.48 (s).



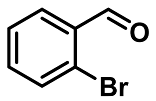
**4-Bromobenzaldehyde (8):** Yellow solid.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.14 (s), 135.06 (s), 132.45 (s), 131.00 (s), 129.80 (s).



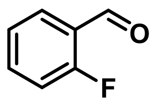
**4-Nitrobenzaldehyde (9):** Pale yellow solid.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 10.33 (s, 1H), 8.55 (d, J = 8.6 Hz, 2H), 8.25 (d, J = 8.6 Hz, 2H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 190.39 (s), 151.11 (s), 140.07 (s), 130.52 (s), 124.32 (s).



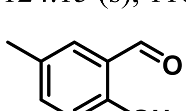

**2-Hydroxybenzaldehyde (10):** Colorless clarifying oily liquid.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 11.04 (s, 1H), 9.90 (s, 1H), 7.58 – 7.52 (m, 2H), 7.05 – 6.99 (m, 2H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.63 (s), 161.63 (s), 137.01 (s), 133.75 (s), 120.27 (d, J = 103.1 Hz), 117.61 (s).



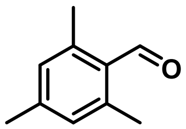

**2-Bromobenzaldehyde (11):** White solid.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 10.39 (s, 1H), 7.94 (dd, J = 7.1, 2.1 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.50 – 7.44 (m, 2H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.97 (s), 135.39 (s), 133.93 (s), 129.89 (s), 127.95 (s), 100.01 (s).



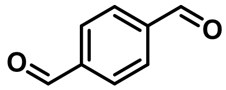

**2-Fluorobenzaldehyde (12):** Yellow liquid.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 10.55 (s, 1H), 8.05 (dd, J = 10.4, 4.2 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.45 (dd, J = 9.6, 5.5 Hz, 1H), 7.38 – 7.33 (m, 1H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 187.26 (d, J = 8.3 Hz), 164.73 (d, J = 258.7 Hz), 136.39 (d, J = 8.9 Hz), 128.72 (s), 124.67 (d, J = 3.7 Hz), 124.15 (s), 116.54 (d, J = 20.5 Hz).



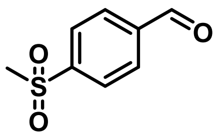

**5-Methylsalicylaldehyde (13):** Pale yellow crystal.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 10.85 (s, 1H), 9.87 (s, 1H), 7.36 (d, J = 6.3 Hz, 2H), 6.91 (d, J = 9.1 Hz, 1H), 2.35 (s, 3H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.59 (s), 159.56 (s), 138.06 (s), 133.41 (s), 129.16 (s), 120.37 (s), 117.40 (s), 20.23 (s).



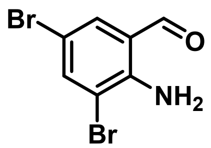
**2,4,6-Trimethylbenzaldehyde (14):** Yellow liquid.$^1$H NMR (500 MHz, $CDCl_3$) δ 10.57 (s, 1H), 6.91 (s, 2H), 2.59 (s, 6H), 2.33 (s, 3H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.97 (s), 143.83 (s), 141.48 (s), 130.53 (s), 130.01 – 128.52 (m), 21.45 (s), 20.47 (s).



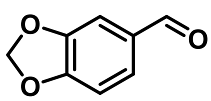
**Terephthalaldehyde (15):** White crystals.$^1$H NMR (500 MHz, $CDCl_3$) δ 10.30 (s, 2H), 8.22 (s, 4H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.55 (s), 140.00 (s), 130.15 (s).



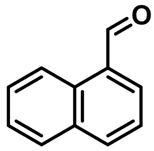
**4-Methanesulfonyl-benzaldehyde (16):** Pale yellow solid.$^1$H NMR (400 MHz, DMSO) δ 9.94 (d, J = 5.3 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.40 – 7.35 (m, 2H), 2.37 (d, J = 5.2 Hz, 3H).$^{13}$C NMR (100 MHz, DMSO) δ 193.16 (s), 145.86 (s), 134.67 (s), 130.29 (d, J = 11.5 Hz), 22.00 (s).



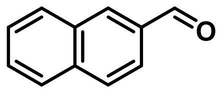
**2-Amino-3,5-dibromobenzaldehyde (17):** Pale yellow solid.$^1$H NMR (500 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.74 (d, J = 2.1 Hz, 1H), 7.60 (d, J = 2.1 Hz, 1H), 6.72 (s, 2H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.95 (s), 145.92 (s), 139.85 (s), 137.09 (s), 110.77 (s), 106.69 (s).



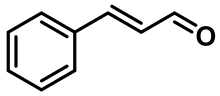
**Heliotropin (18): White solid**.$^1$H NMR (500 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.39 – 7.36 (m, 1H), 7.28 (s, 1H), 6.89 (d, J = 7.9 Hz, 1H), 6.04 (s, 2H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 190.25 (s), 153.10 (s), 148.69 (s), 131.85 (s), 128.61 (s), 108.32 (s), 108.01 (s), 106.83 (s), 102.13 (s).



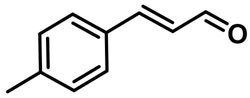
**1-Naphthaldehyde (19)**: Pale yellow solid. $^1$H NMR (500 MHz, $CDCl_3$) δ 10.41 (s, 1H), 9.28 (d, J = 8.6 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.99 (d, J = 7.0 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.65 – 7.59 (m, 2H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 193.57 (s), 136.69 (s), 135.31 (s), 133.75 (s), 131.42 (s), 130.55 (s), 129.09 (s), 128.51 (s), 126.99 (s), 124.90 (s).



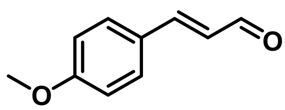
**2-Naphthaldehyde (20):** White crystals. $^1$H NMR (501 MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.37 (s, 1H), 8.05 – 7.92 (m, 4H), 7.65 (dt, J = 14.7, 7.1 Hz, 2H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 192.26 (s), 136.49 (s), 134.54 (s), 132.68 (s), 129.55 (s), 129.13 (s), 128.10 (s), 127.11 (s), 122.81 (s).



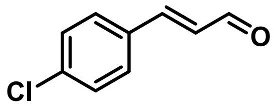
**Cinnamaldehyde (21):** Pale yellow oily liquid.$^1$H NMR (500 MHz, $CDCl_3$) δ 9.71 (d, J = 7.7 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.50 – 7.42 (m, 4H), 6.72 (dd, J = 16.0, 7.7 Hz, 1H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 193.72 (s), 152.80 (s), 134.03 (s), 131.30 (s), 129.13 (s), 128.59 (s), 128.53 (s).



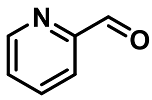
**4-Methylcinnamaldehyde(22):** yellow liquid.$^1$H NMR (500 MHz, $CDCl_3$) δ 9.66 (dd, J = 7.7, 0.5 Hz, 1H), 7.47 – 7.45 (m, 2H), 7.42 (s, 1H), 7.23 (d, J = 7.8 Hz, 2H), 6.68 (dd, J = 15.9, 7.7 Hz, 1H), 2.39 (s, 3H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 193.87 (s), 153.07 (s), 142.00 (s), 131.33 (s), 129.86 (s), 128.57 (s), 127.65 (s), 21.57 (s).



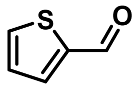
**4-Mmethoxycinnamaldehyde (23):** Light yellow solid.$^1$H NMR (500 MHz, $CDCl_3$) δ 9.81 (d, J = 2.5 Hz, 1H), 7.80 – 7.73 (m, 2H), 6.97 – 6.90 (m, 2H), 3.81 (dd, J = 4.3, 3.0 Hz, 3H).[13]C NMR (125 MHz, $CDCl_3$) δ 190.86 (s), 164.63 (s), 132.01 (s), 129.94 (s), 114.33 (s), 55.60 (s).



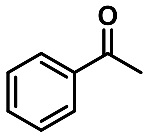
**4-Chlorocinnamaldehyde (24):** Light yellow solid.[1]H NMR (500 MHz, DMSO) δ 9.68 (d, J = 7.7 Hz, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 16.0 Hz, 1H), 7.55 (d, J = 8.4 Hz, 2H), 6.90 (dd, J = 15.9, 7.7 Hz, 1H).[13]C NMR (125 MHz, DMSO) δ 194.88 (s), 153.81 (s), 141.91 (s), 131.87 (s), 130.18 (s), 129.27 (s), 128.12 (s).



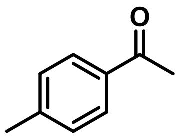
**2-Pyridinecarboxaldehyde (25):** yellow liquid.[1]H NMR (500 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.83 (d, J = 4.5 Hz, 1H), 8.00 (d, J = 7.7 Hz, 1H), 7.91 (t, J = 7.6 Hz, 1H), 7.58 – 7.54 (m, 1H).[13]C NMR (125 MHz, $CDCl_3$) δ 193.47 (s), 152.84 (s), 150.24 (s), 137.10 (s), 127.89 (s), 121.74 (s).



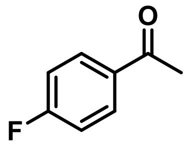
**2-Thiophenecarboxaldehyde (26):** Pale yellow oily liquid.[1]H NMR (500 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.73 (dd, J = 12.0, 4.1 Hz, 2H), 7.18 – 7.15 (m, 1H).[13]C NMR (125 MHz, $CDCl_3$) δ 183.10 (s), 143.95 (s), 136.58 (s), 135.21 (s), 128.44 (s).



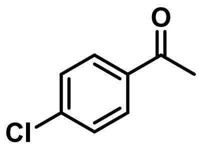
**Acetophenone (38):** Colorless transparent liquid.[1]H NMR (400 MHz, DMSO) δ 7.95 (d, J = 7.2 Hz, 2H), 7.65 – 7.59 (m, 1H), 7.53 – 7.48 (m, 2H), 2.57 (d, J = 0.8 Hz, 3H).[13]C NMR (100 MHz, DMSO) δ 198.49 (s), 137.46 (s), 133.81 (s), 129.31 (s), 128.81 – 128.78 (m), 27.32 (s).



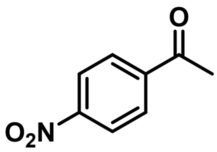
**4-Methylacetophenone (39):** Colorless oil liquid.$^1$H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 7.7 Hz, 2H), 2.60 (s, 3H), 2.43 (s, 3H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 197.93 (s), 143.91 (s), 134.71 (s), 129.26 (s), 128.46 (s), 26.56 (s), 21.66 (s).



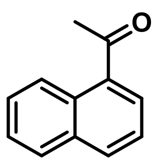

**4-Fluoroacetophenone (40):** Colorless clear liquid.$^1$H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.10 (t, J = 8.7 Hz, 2H), 2.56 (s, 3H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.56 (s), 166.79 (s), 133.56 (s), 130.97 (d, J = 9.4 Hz), 115.77 (s), 115.59 (s), 26.58 (s).



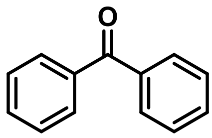

**4-Chloroacetophenone (41):** White liquid.$^1$H NMR (500 MHz, DMSO) δ 7.96 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 2.58 (s, 3H).$^{13}$C NMR (125 MHz, DMSO) δ 197.36 (s), 138.58 (s), 135.93 (s), 130.52 (s), 129.22 (s), 27.15 (s).



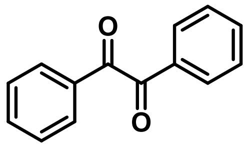

**4-Nitroacetophenone (42):** Pale yellow solid.$^1$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 8.6 Hz, 2H), 8.13 (d, J = 8.6 Hz, 2H), 2.70 (s, 3H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.31 – 196.26 (m), 150.42 – 150.37 (m), 141.40 (s), 129.32 (s), 123.88 (s), 26.99 (s).



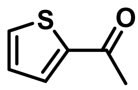

**1-Acetylnaphthalene (43):** Pale yellow liquid.$^1$H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 8.7 Hz, 1H), 7.91 (ddd, J = 21.4, 19.0, 8.2 Hz, 3H), 7.55 (dddd, J = 28.0, 15.4, 7.4, 4.4 Hz, 3H), 2.73 (s, 3H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ 201.79 (s), 135.36 (s), 134.00 (s), 133.06 (s), 130.18 (s), 128.78 (s), 128.46 (s), 128.08 (s), 126.46 (s), 126.06 (s), 124.38 (s), 29.96 (s).



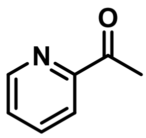
**Benzophenone (44):** colorless solid.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 7.3 Hz, 4H), 7.62 (t, J = 7.4 Hz, 2H), 7.51 (t, J = 7.6 Hz, 4H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 176.41 – 176.35 (m), 137.60 (s), 132.47 (s), 130.11 (s), 128.31 (s).



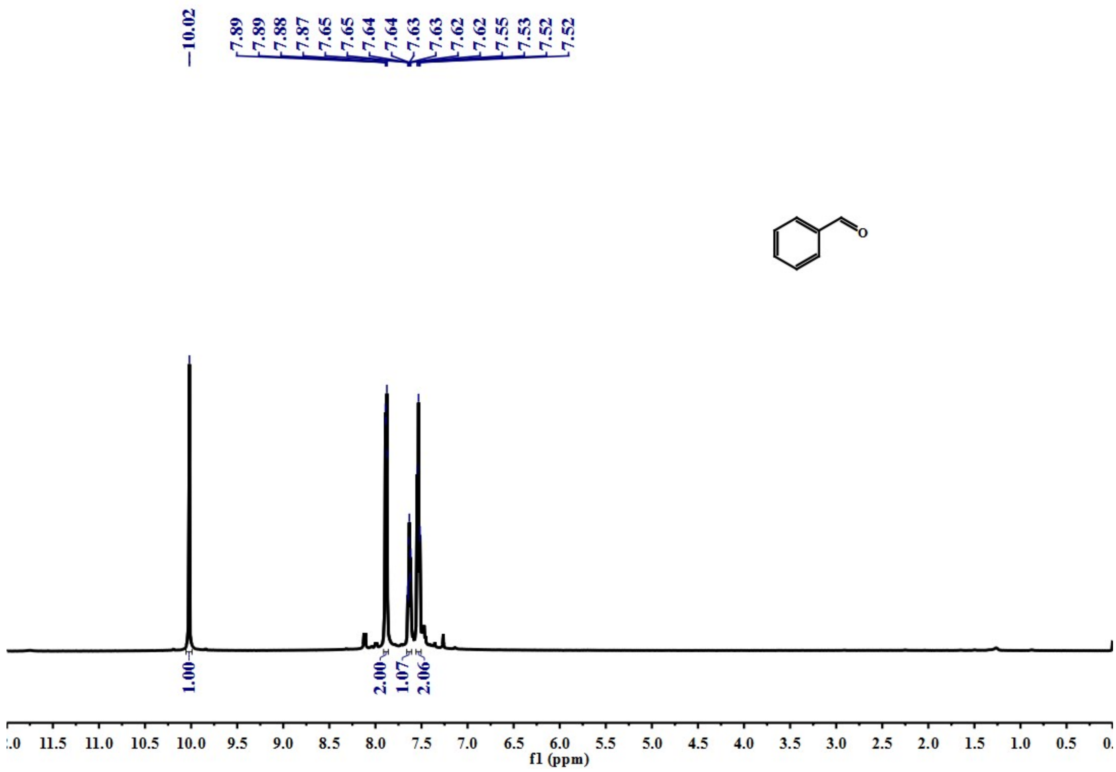
**Benzil (45):** Yellow solid.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 4H), 7.68 (t, J = 7.4 Hz, 2H), 7.54 (t, J = 7.8 Hz, 4H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 194.57 (s), 134.89 (s), 133.04 (s), 129.92 (s), 129.04 (s).



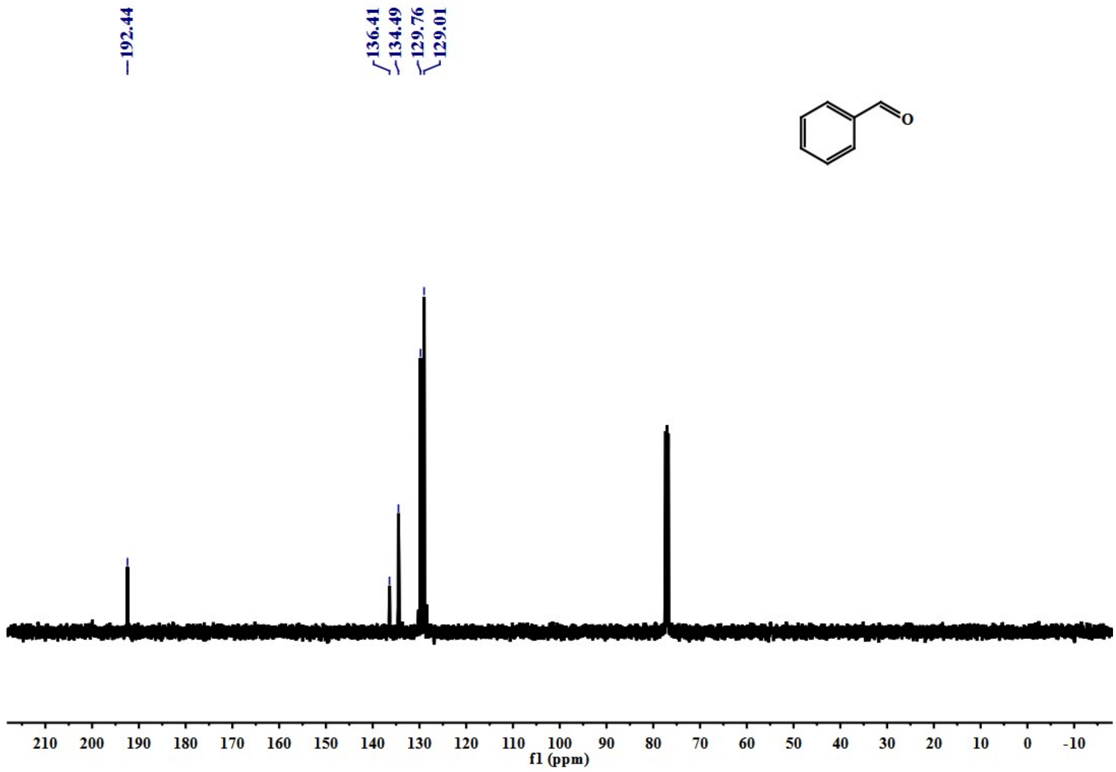
**2-Acetylthiophene (46):** Pale yellow liquid.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, J = 3.5, 1.1 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.14 – 7.09 (m, 1H), 2.57 – 2.52 (m, 3H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 190.57 (s), 144.43 (s), 133.80 (s), 132.63 (s), 128.19 (s), 26.73 (s).



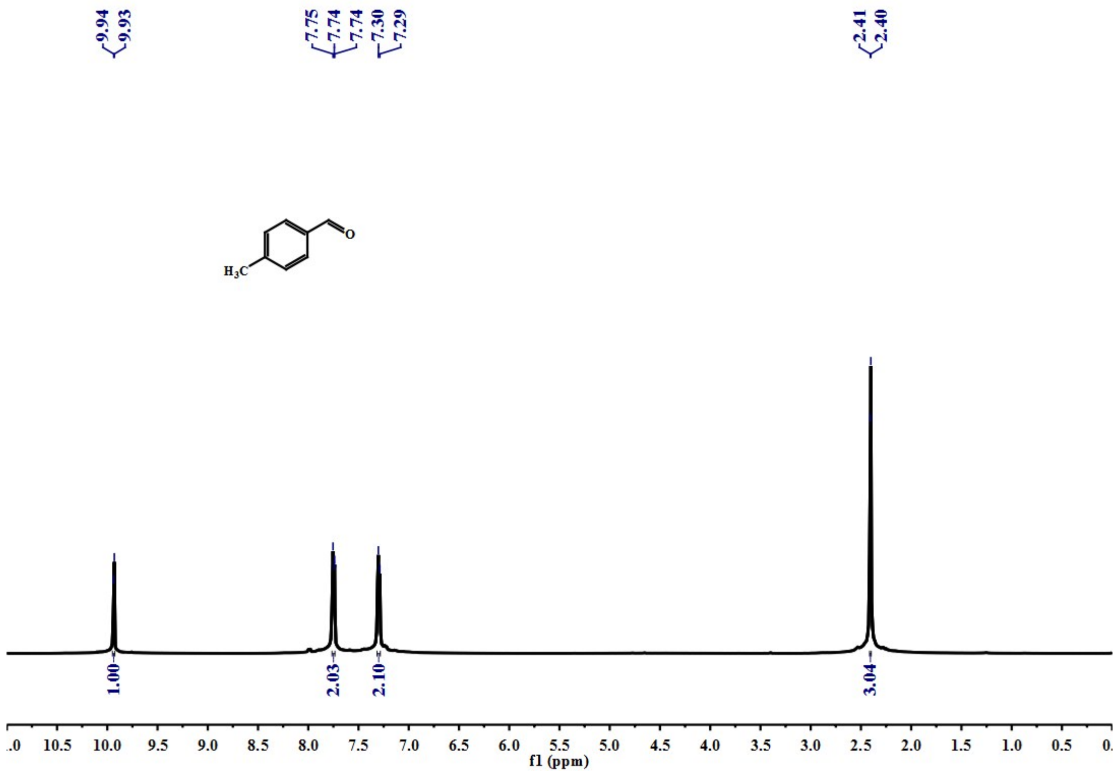
**2-Acetylpyridine (47):** Pale yellow solid.$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, J = 3.9, 0.7 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.70 (td, J = 7.8, 1.6 Hz, 1H), 7.34 (ddd, J = 7.4, 4.8, 1.1 Hz, 1H), 2.58 (s, 3H).$^{13}$C NMR (125 MHz, $CDCl_3$) δ 200.16 (s), 153.57 (s), 149.00 (s), 136.86 (s), 127.12 (s), 121.66 (s), 25.82 (s).



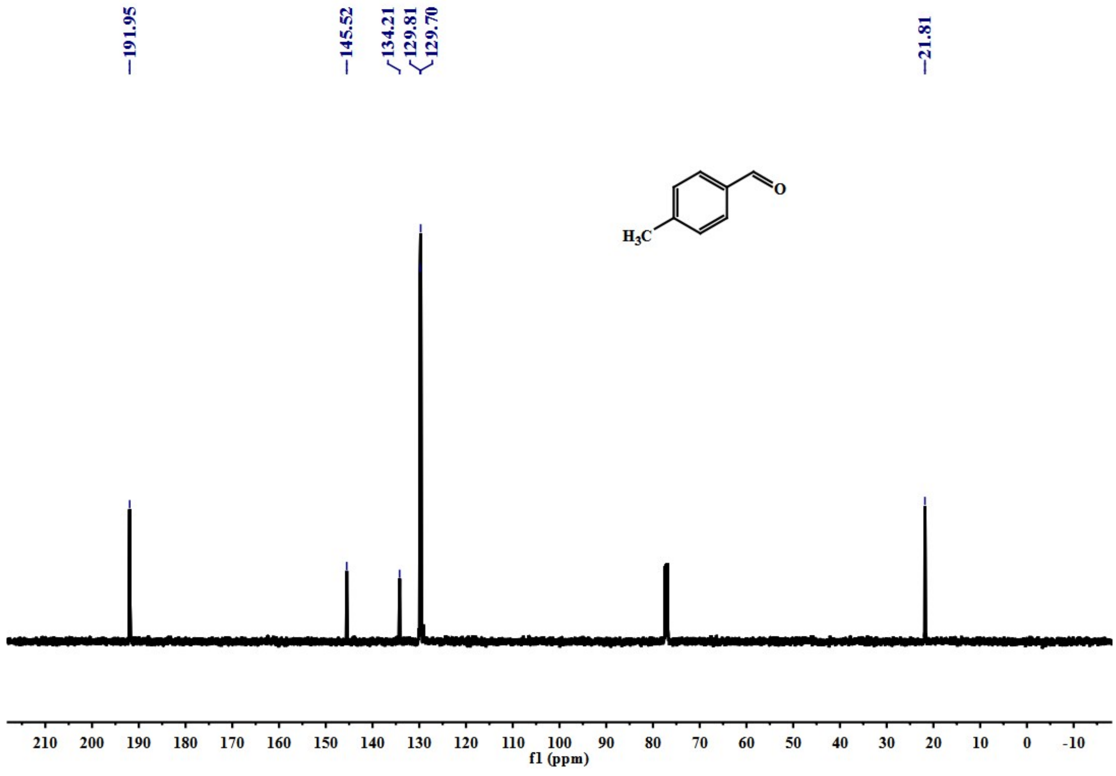

$^{1}H$ NMR spectra of **2**(500 MHz, $CDCl_3$)



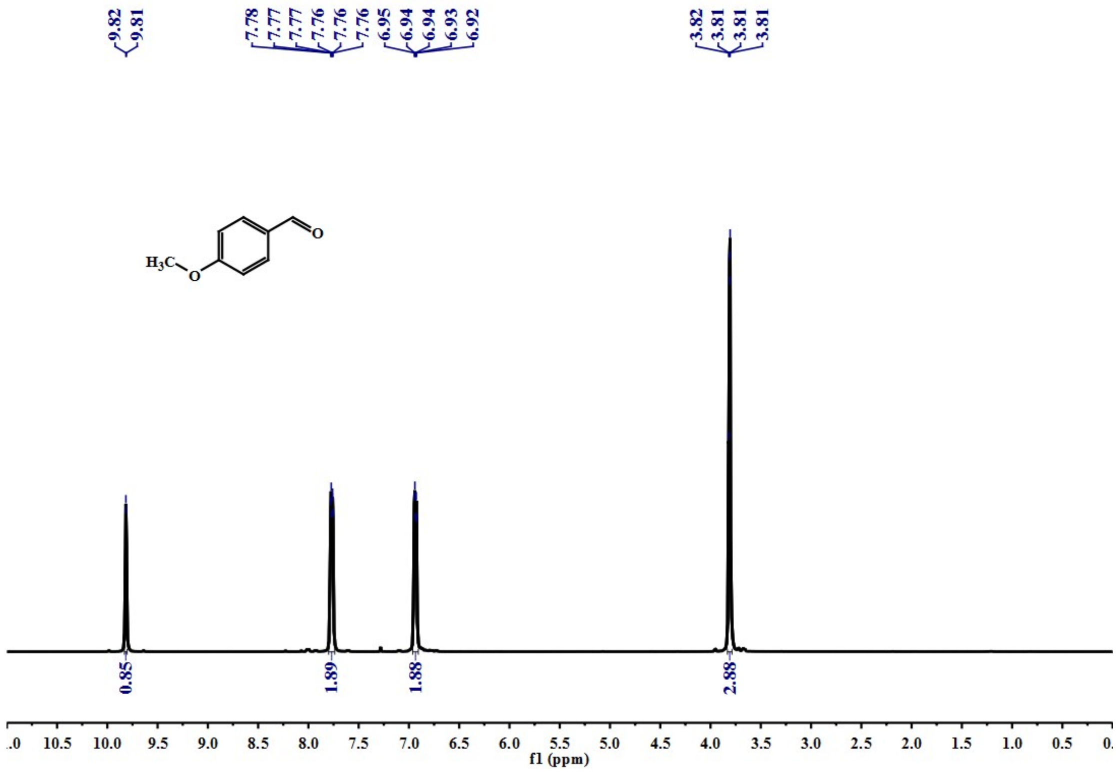

$^{13}C$ NMR spectra of **2**(125 MHz, CDCl3)



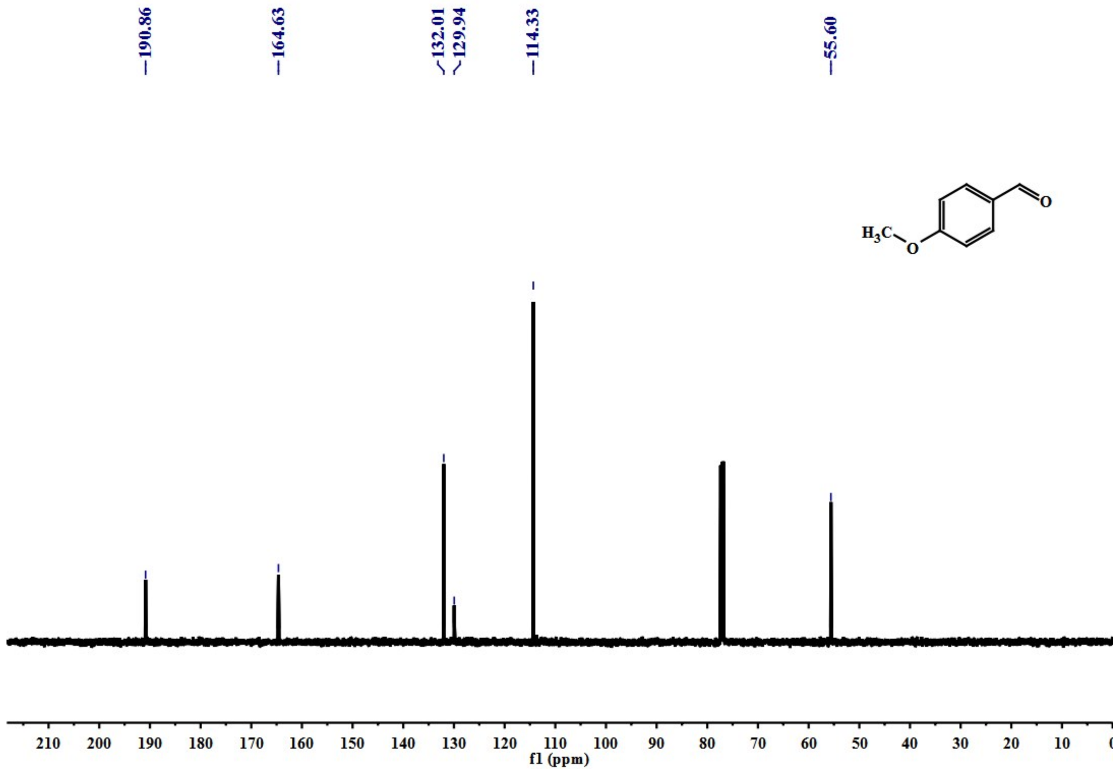

$^{1}H$ NMR spectra of **3**(500 MHz, $CDCl_3$)



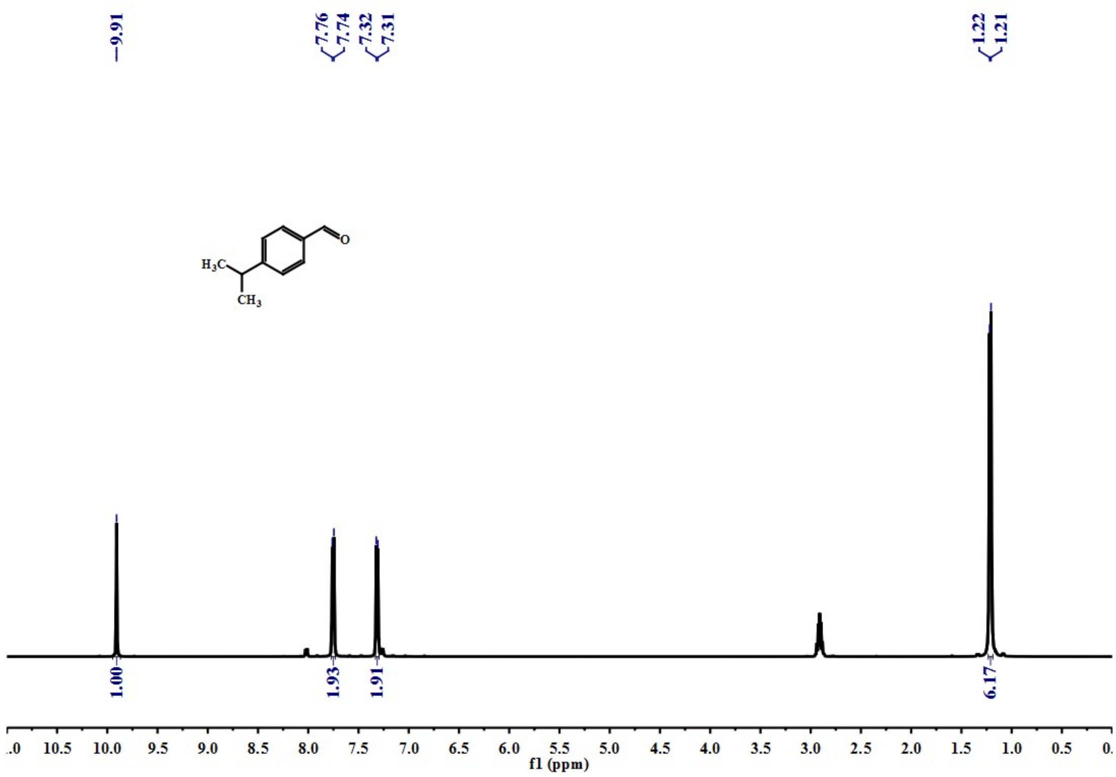

$^{13}C$ NMR spectra of **3**(125 MHz, CDCl3)



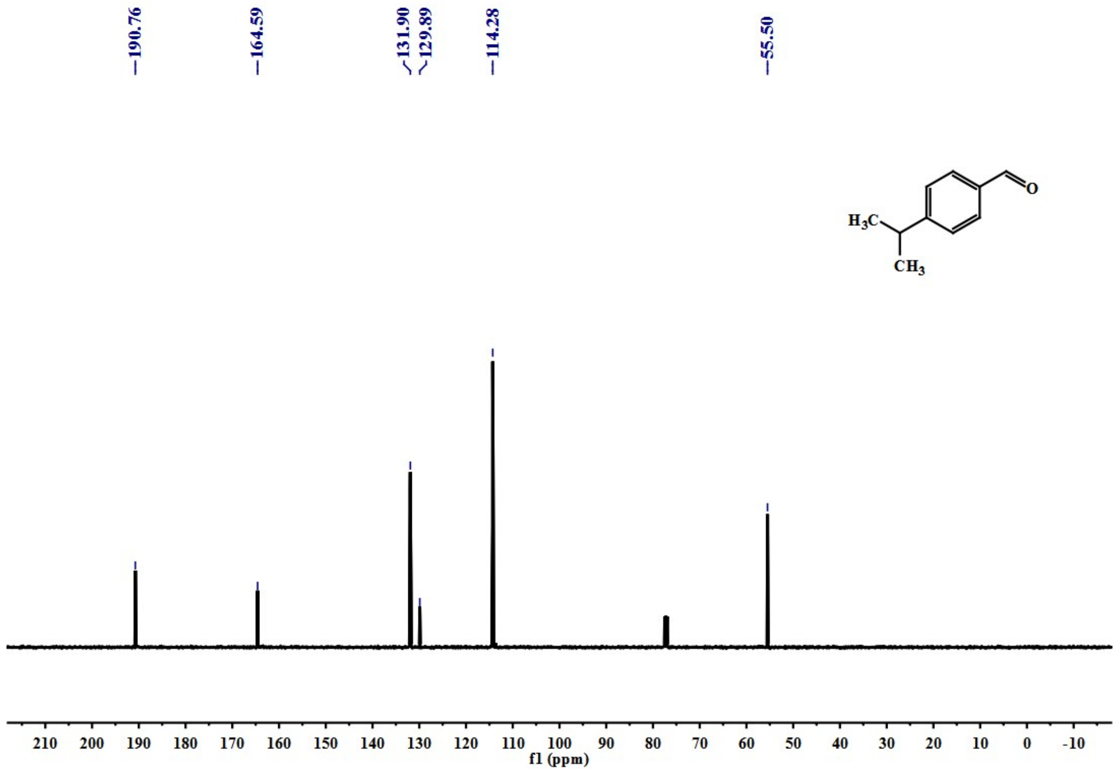

$^{1}$H NMR spectra of **4**(500 MHz, $CDCl_3$)



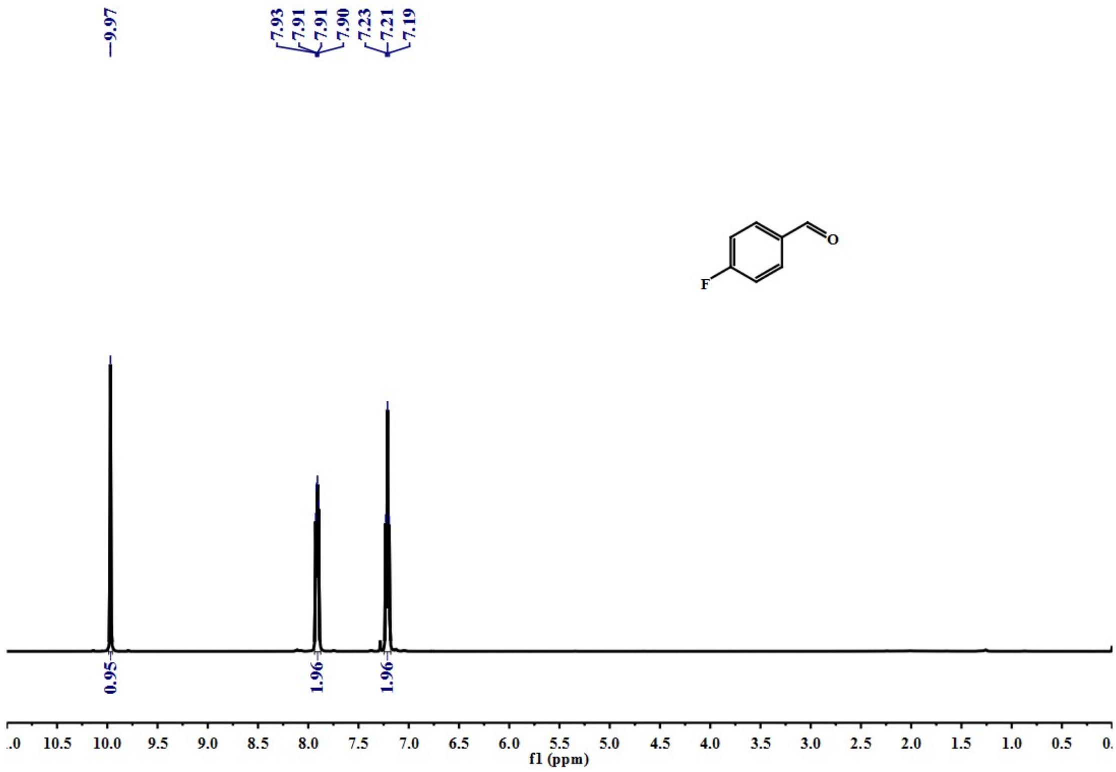

$^{13}$C NMR spectra of **4**(125 MHz, $CDCl_3$)



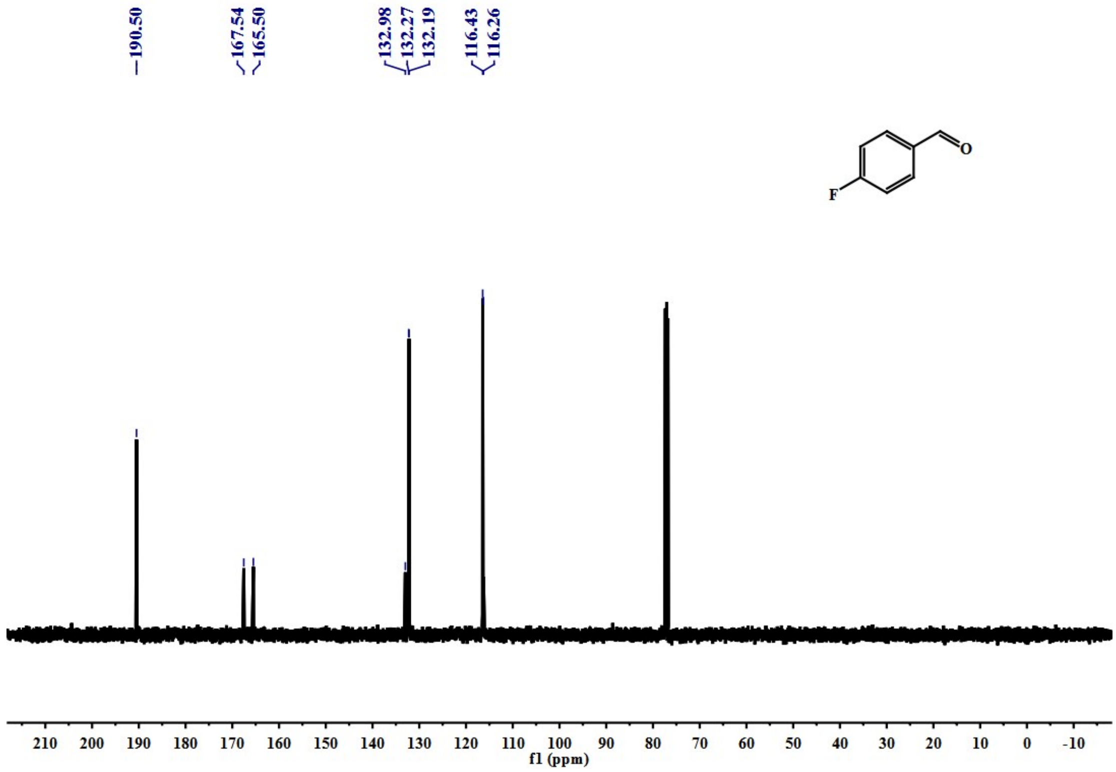

$^{1}H$ NMR spectra of **5**(500 MHz, $CDCl_3$)



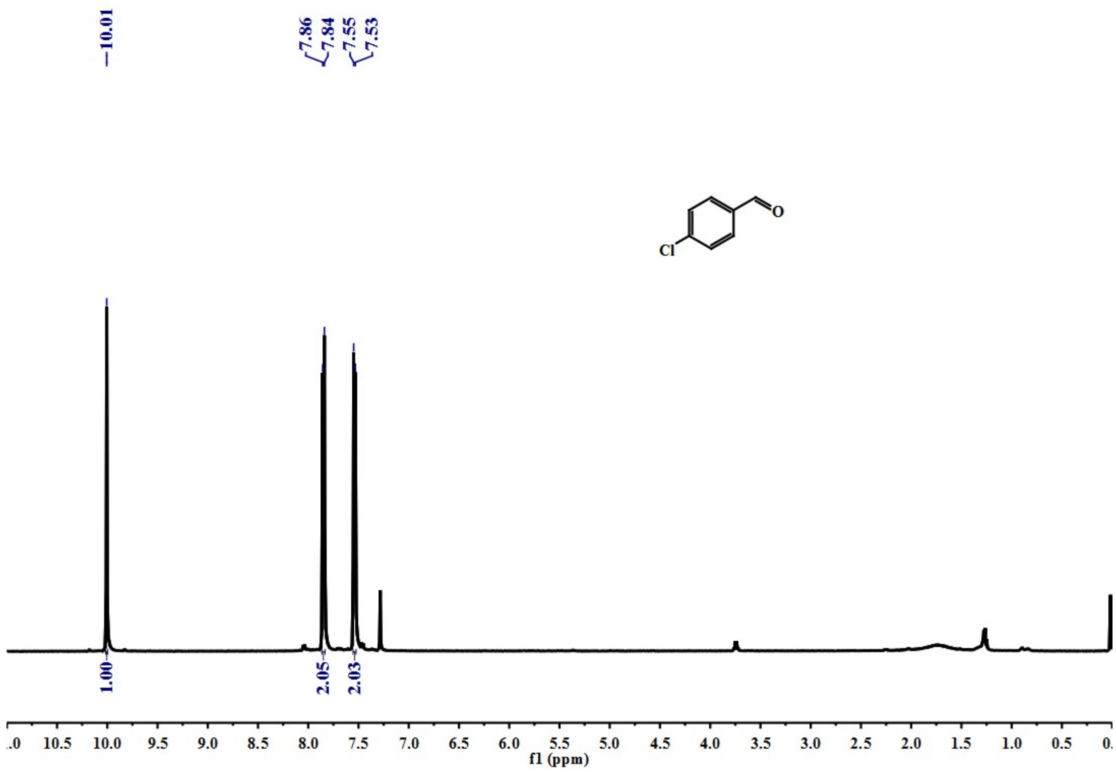

$^{13}C$ NMR spectra of **5**(125 MHz, $CDCl_3$)



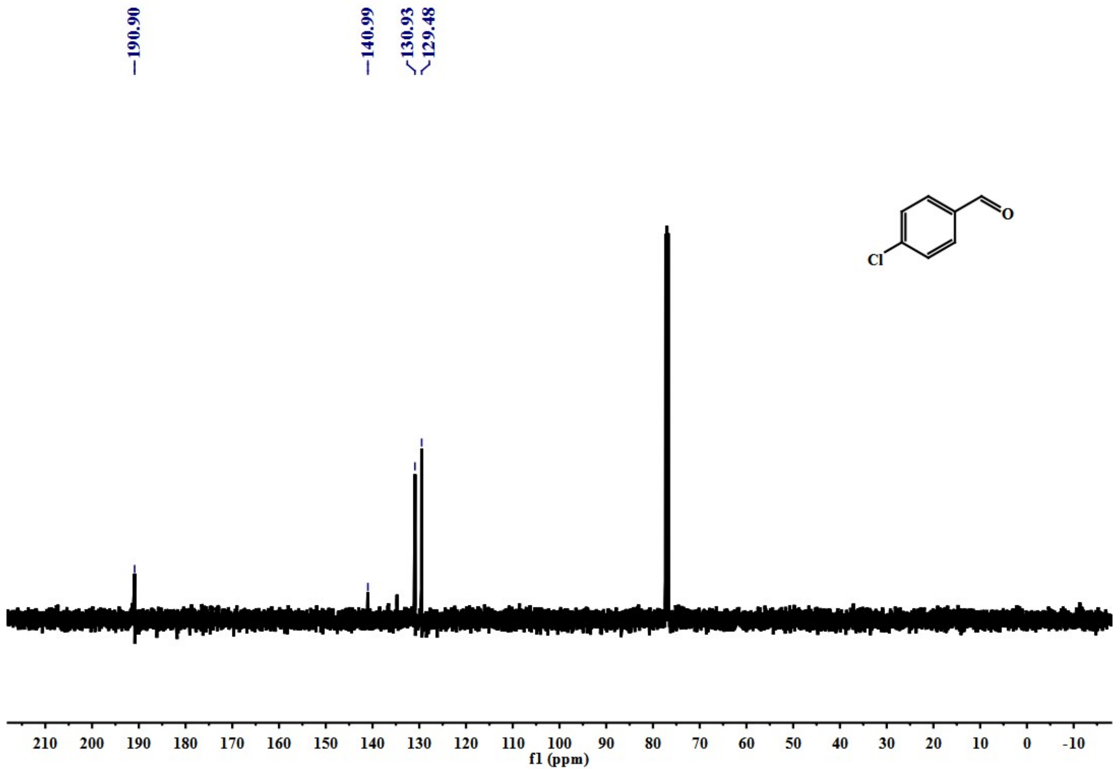

$^{1}H$ NMR spectra of **6**(500 MHz, $CDCl_3$)



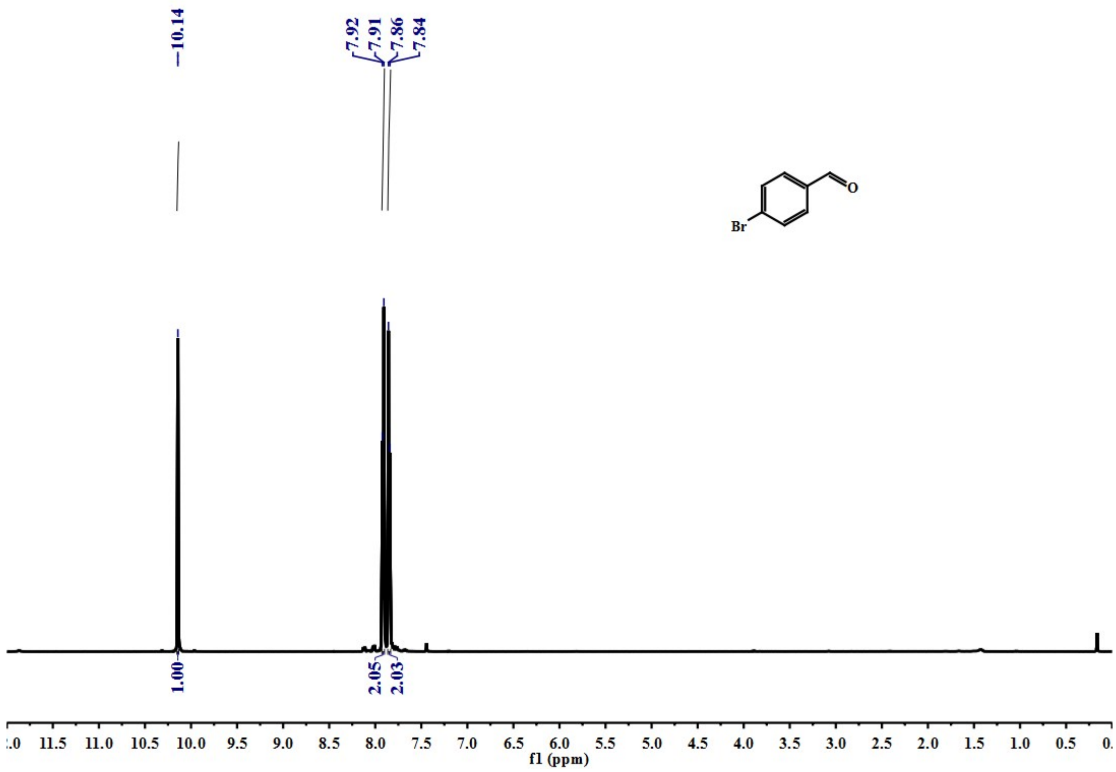

$^{13}C$ NMR spectra of **6**(125 MHz, $CDCl_3$)



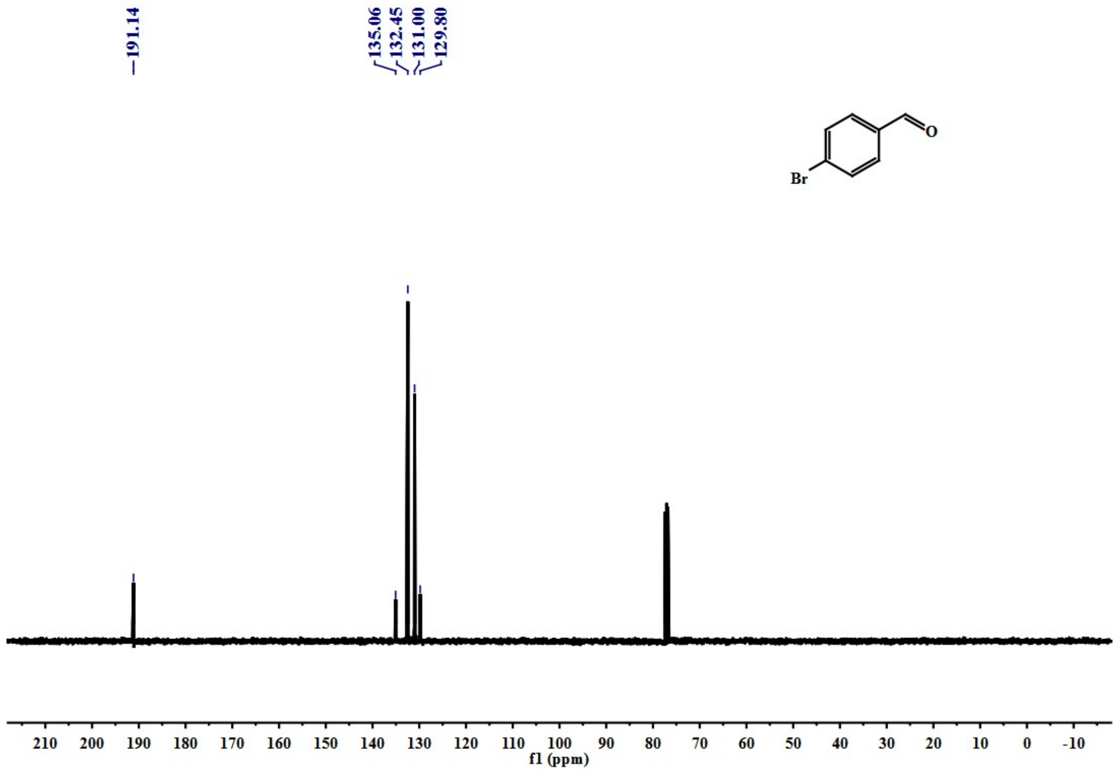

$^{1}$H NMR spectra of **7**(500 MHz, $CDCl_3$)



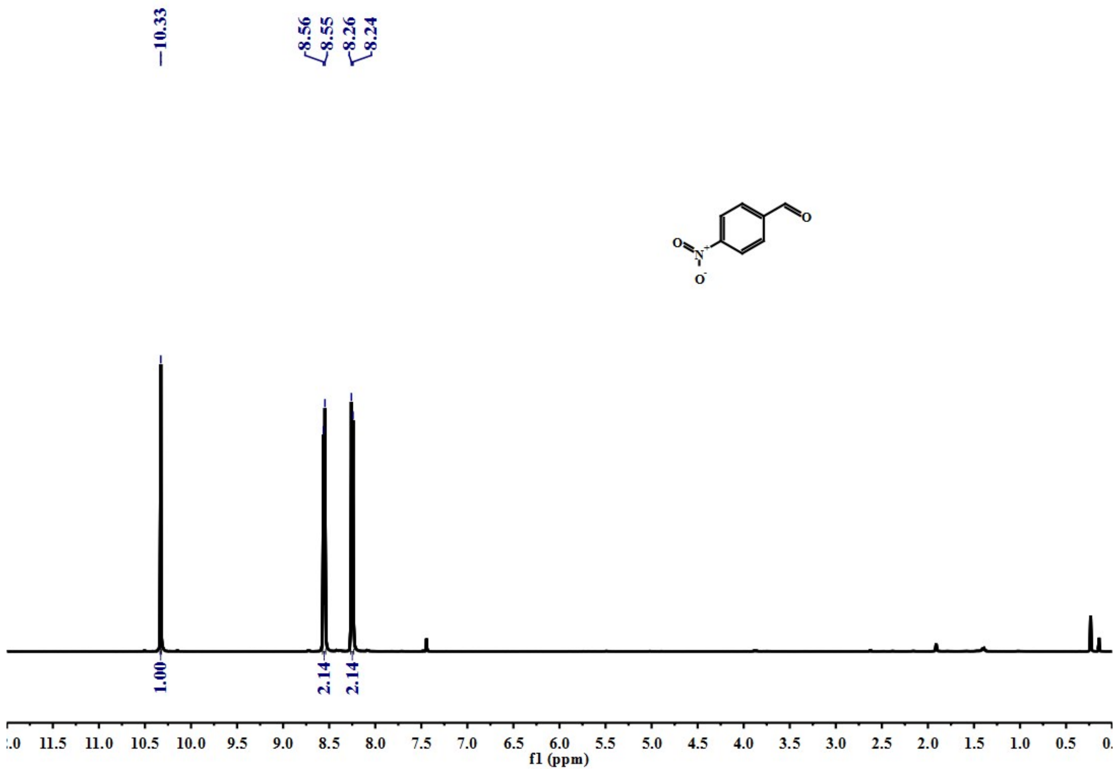

$^{13}$C NMR spectra of **7** (125 MHz, $CDCl_3$)



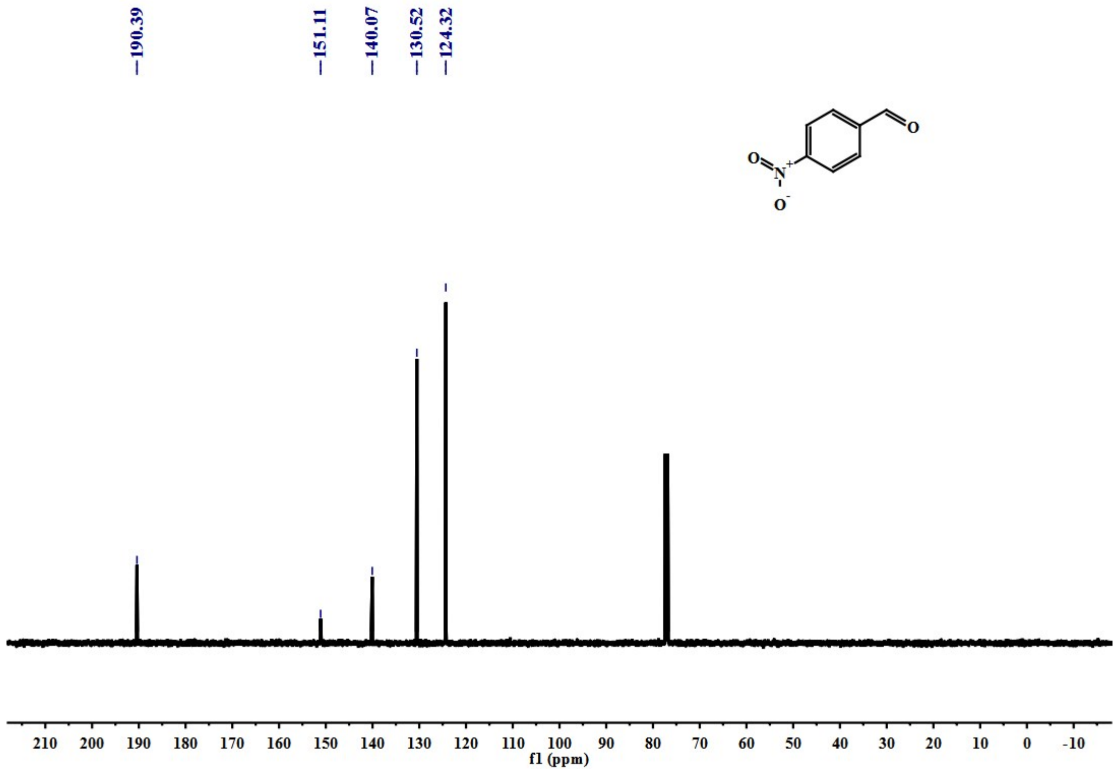

[1]H NMR spectra of **8**(500 MHz, $CDCl_3$)



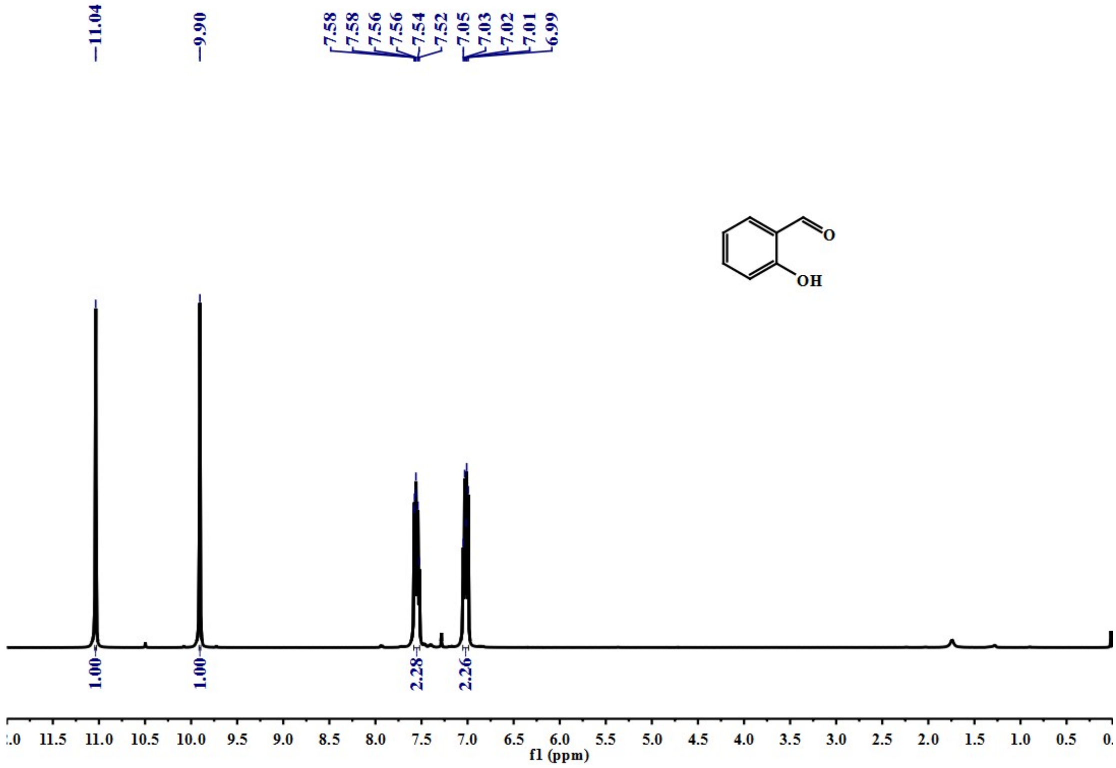

[13]C NMR spectra of **8**(125 MHz, $CDCl_3$)



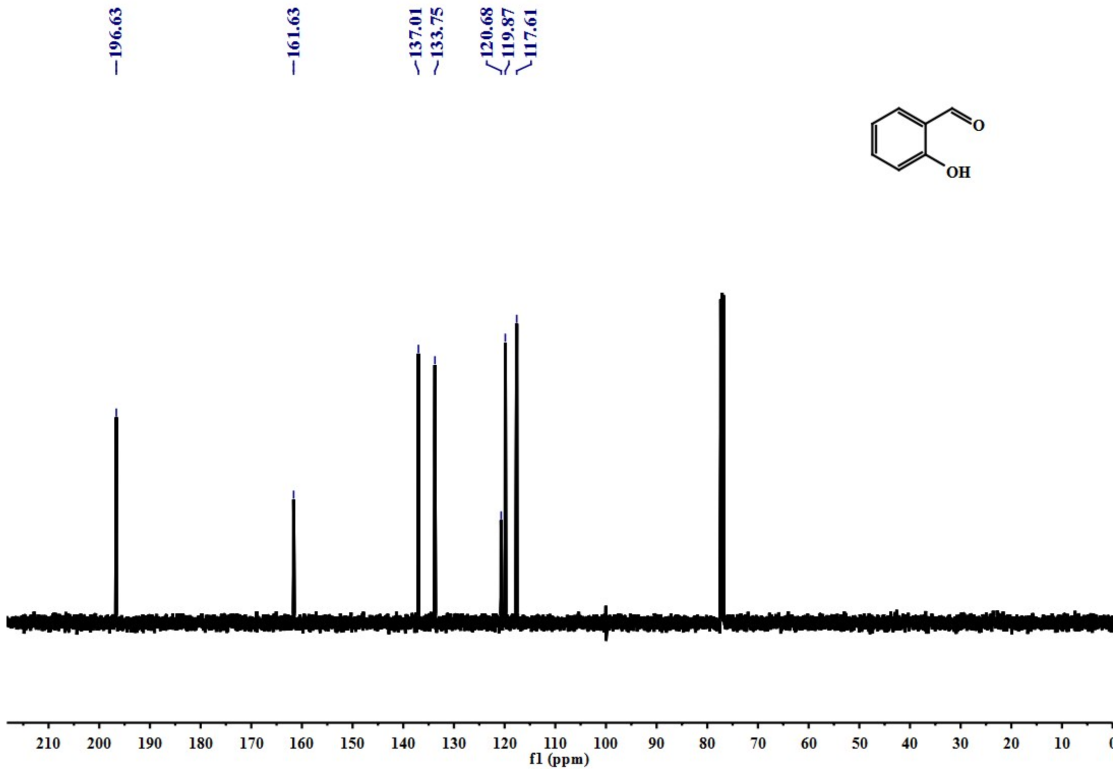

$^{1}$H NMR spectra of **9**(500 MHz, $CDCl_3$)



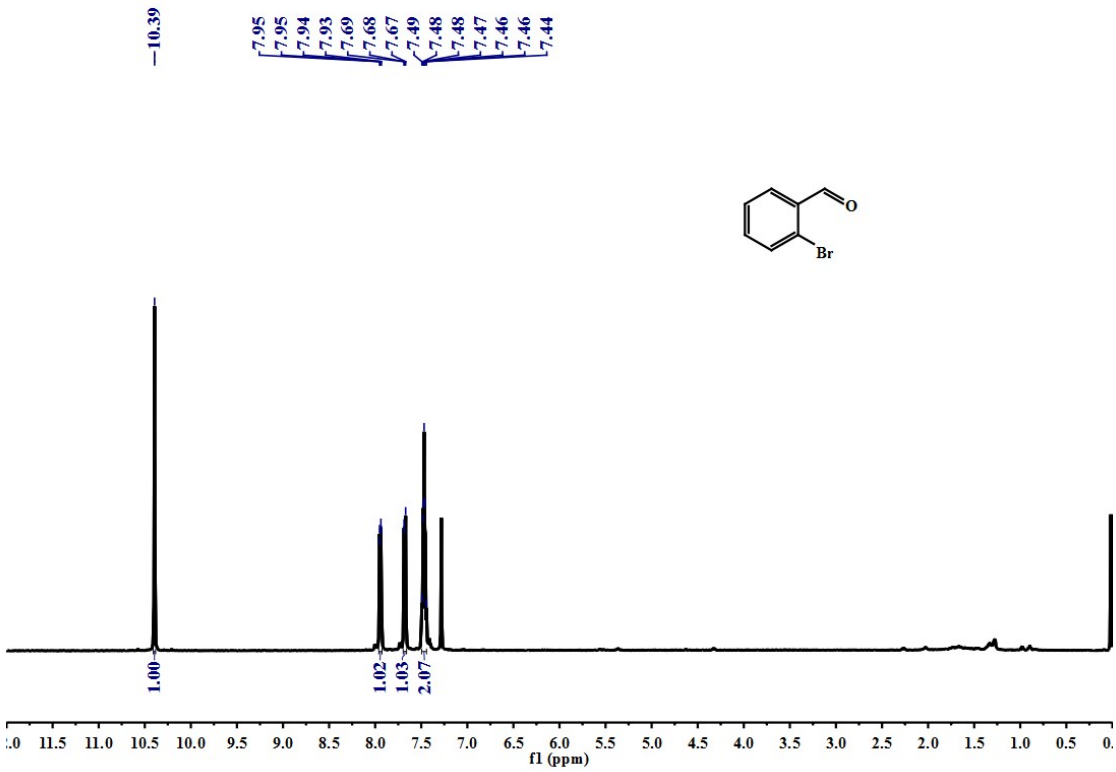

$^{13}$C NMR spectra of **9**(125 MHz, $CDCl_3$)



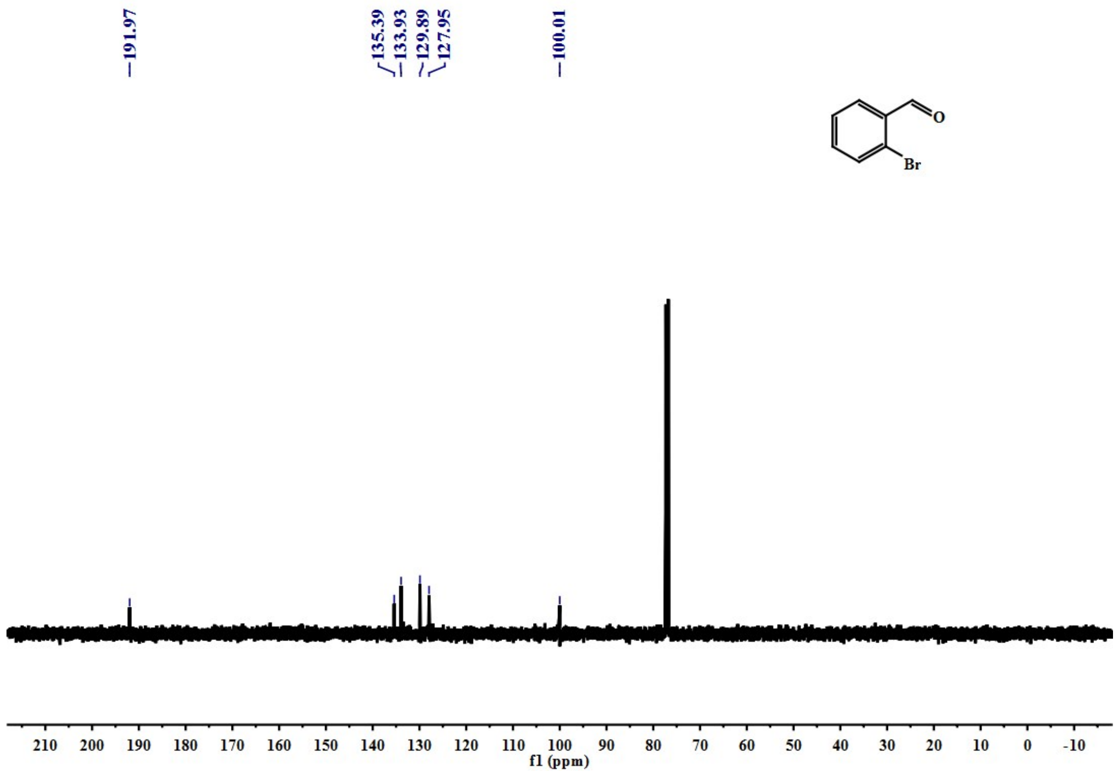

$^{1}H$ NMR spectra of **10**(500 MHz, $CDCl_3$)



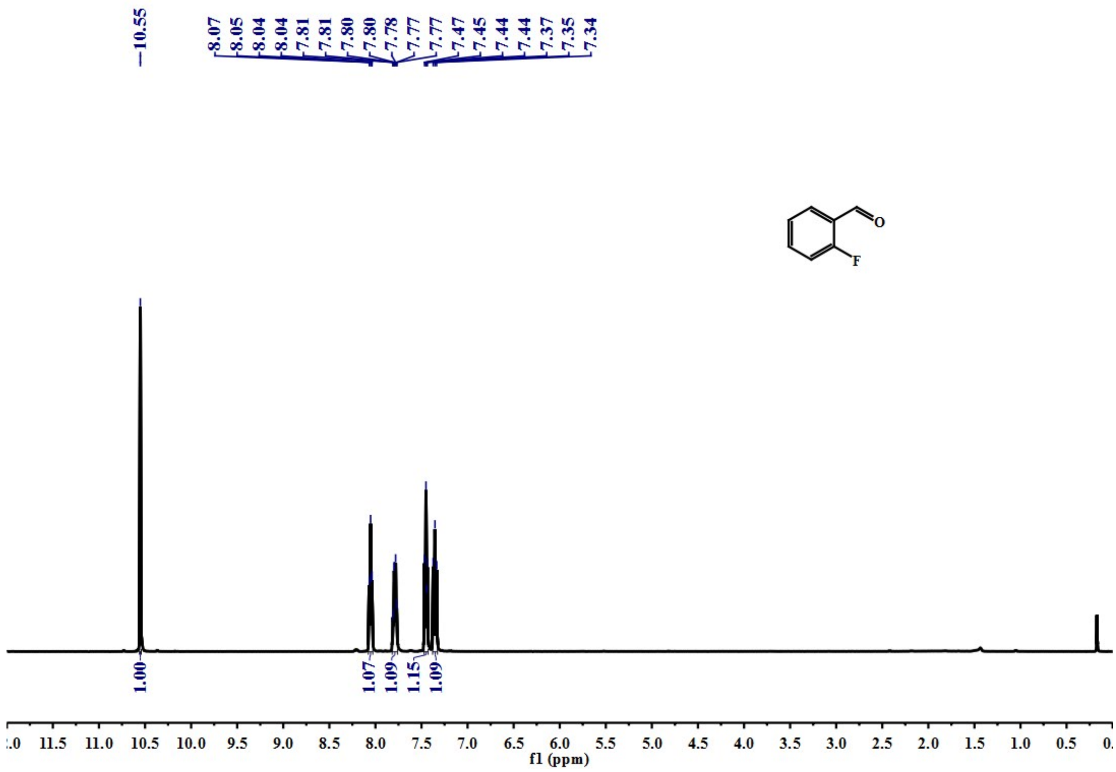

$^{13}C$ NMR spectra of **10**(125 MHz, $CDCl_3$)



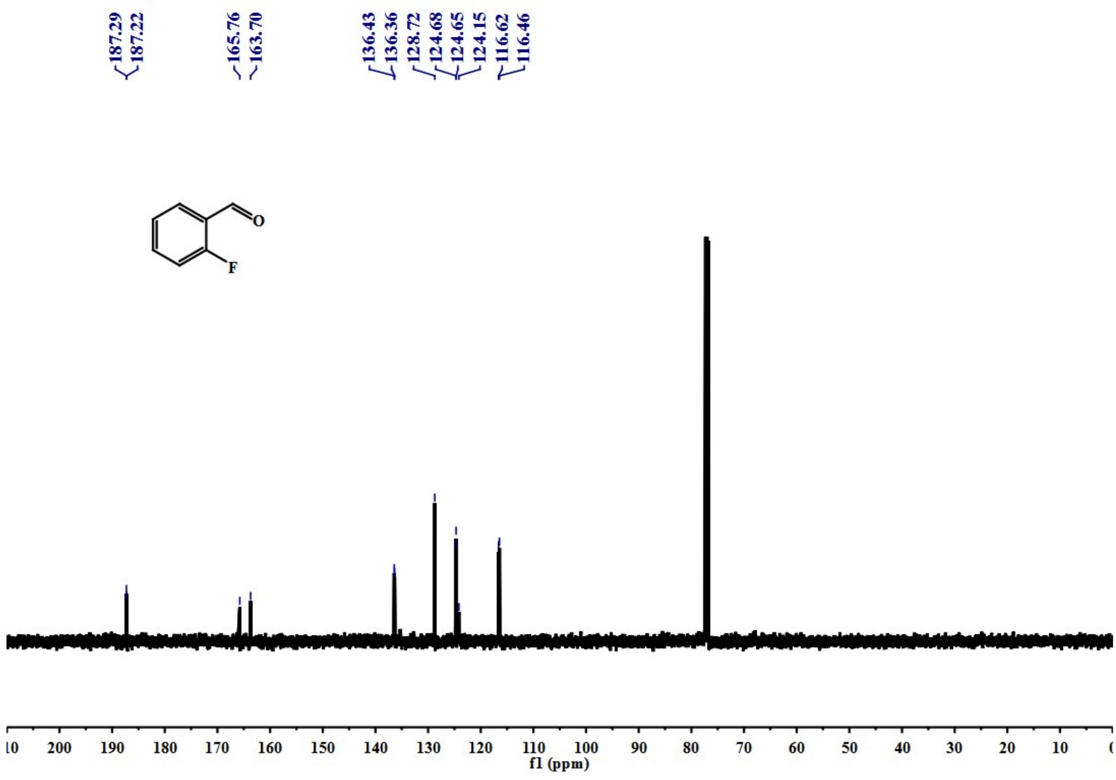

[1]H NMR spectra of **11**(500 MHz, $CDCl_3$)



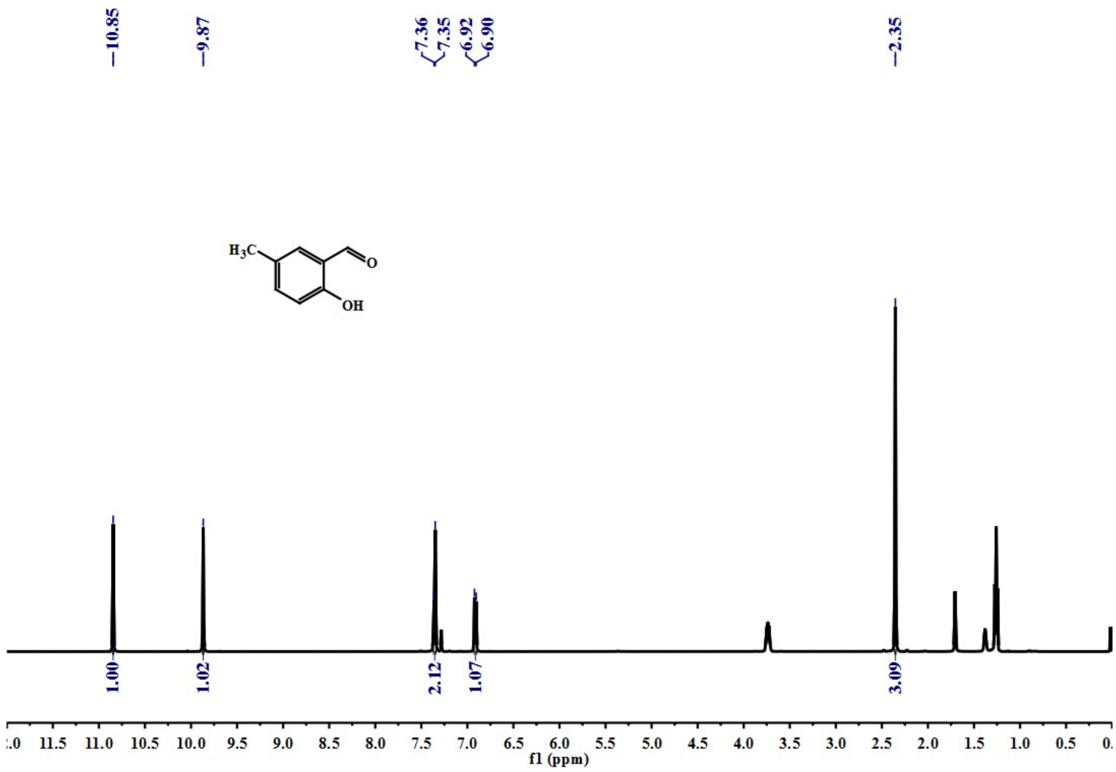

[13]C NMR spectra of **11**(125 MHz, $CDCl_3$)



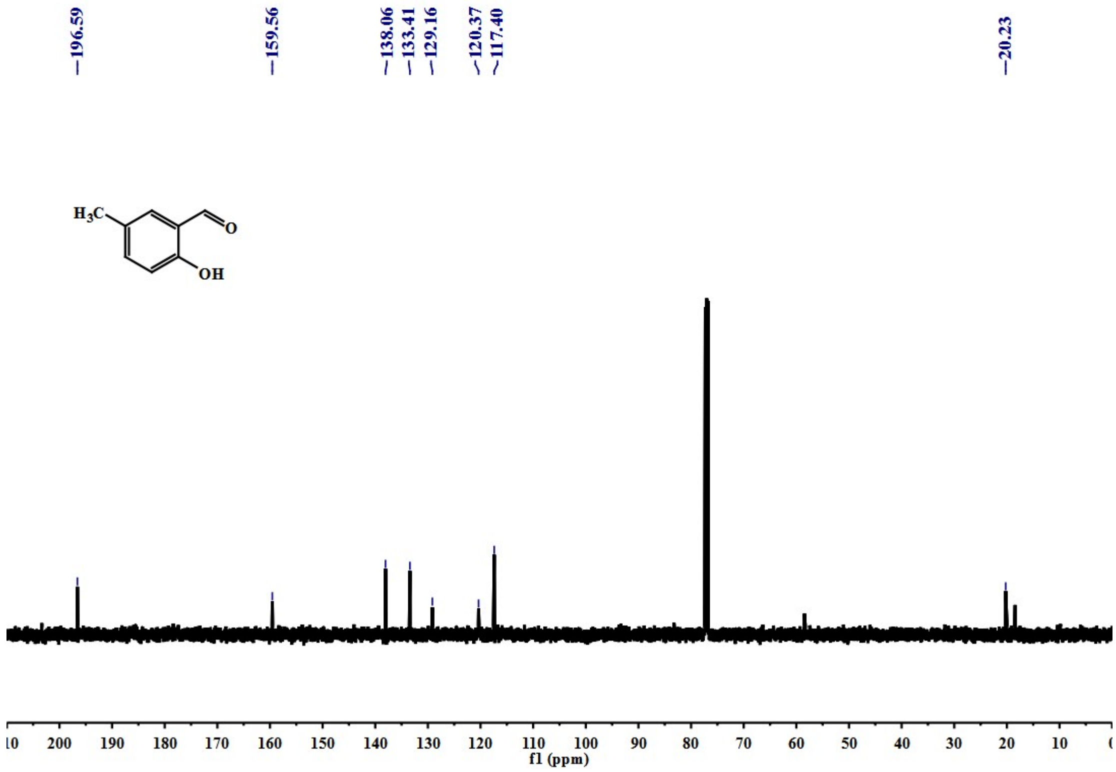

$^{1}$H NMR spectra of **12**(500 MHz, $CDCl_3$)



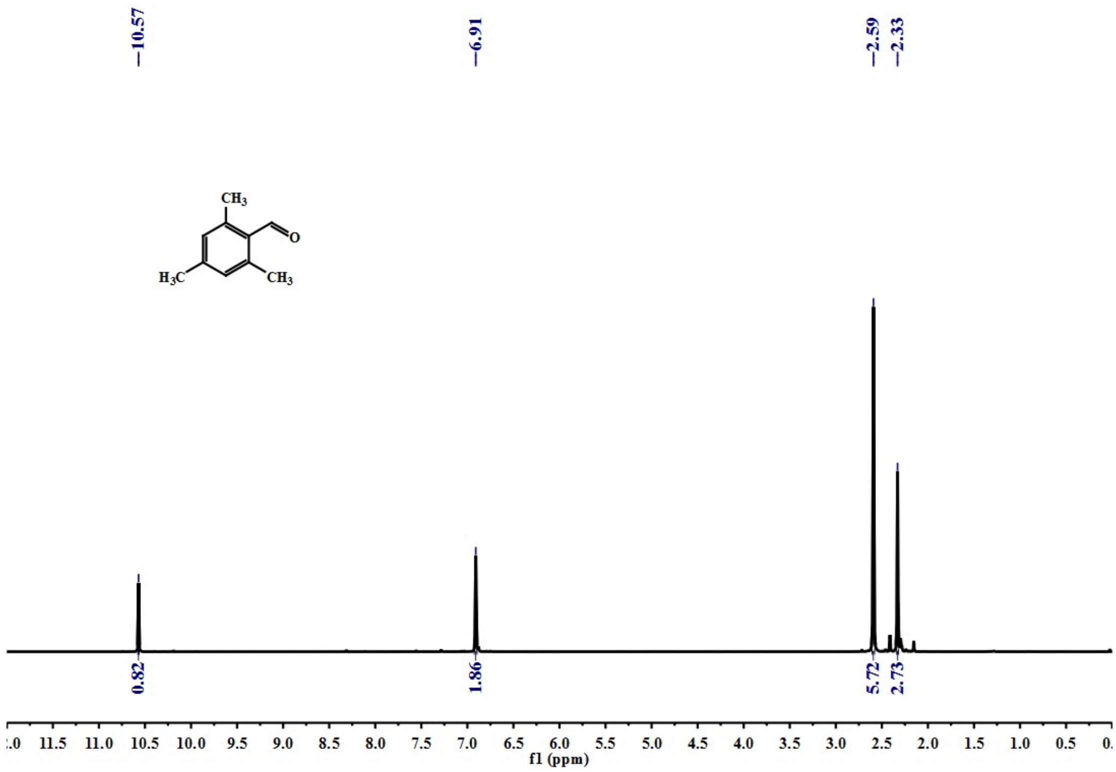

$^{13}$C NMR spectra of **12**(125 MHz, $CDCl_3$)



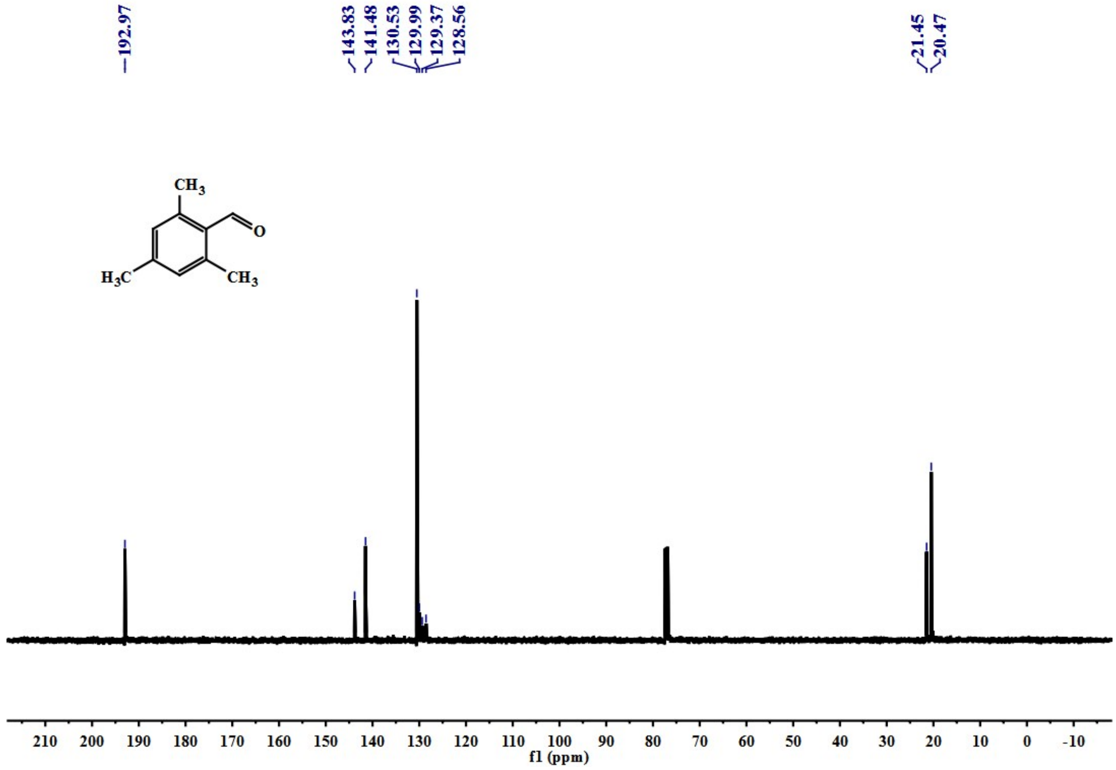

$^{1}H$ NMR spectra of **13**(500 MHz, $CDCl_3$)



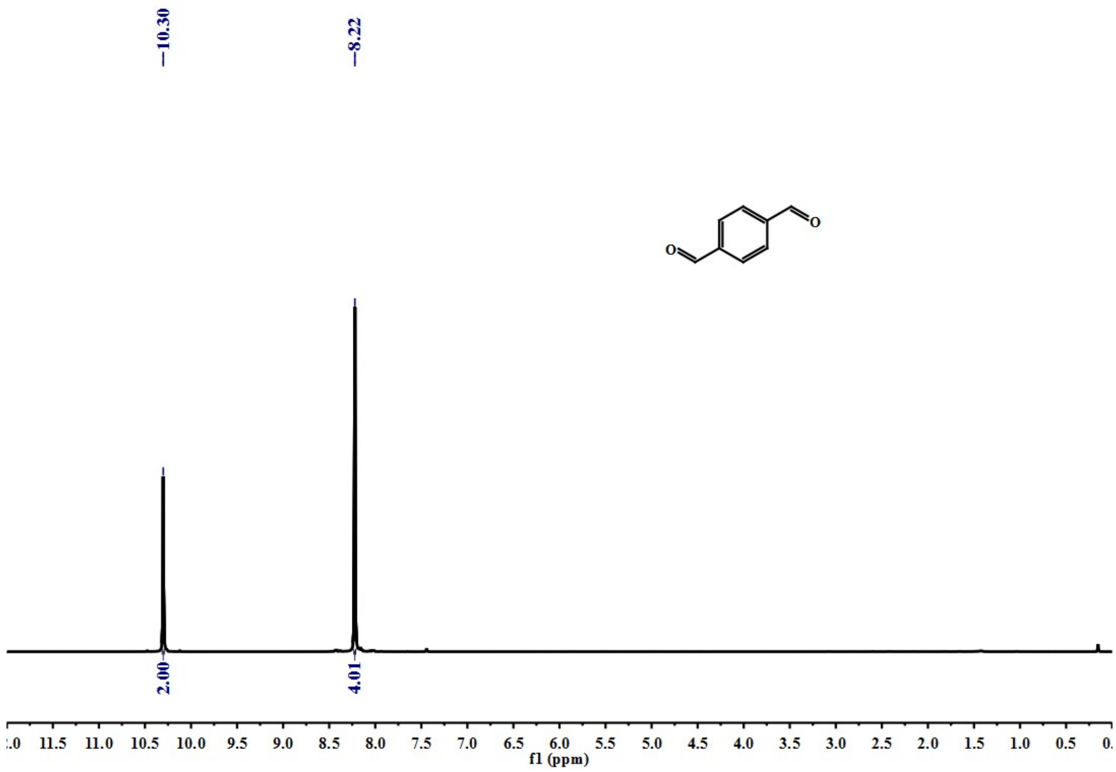

$^{13}C$ NMR spectra of **13**(125 MHz, $CDCl_3$)



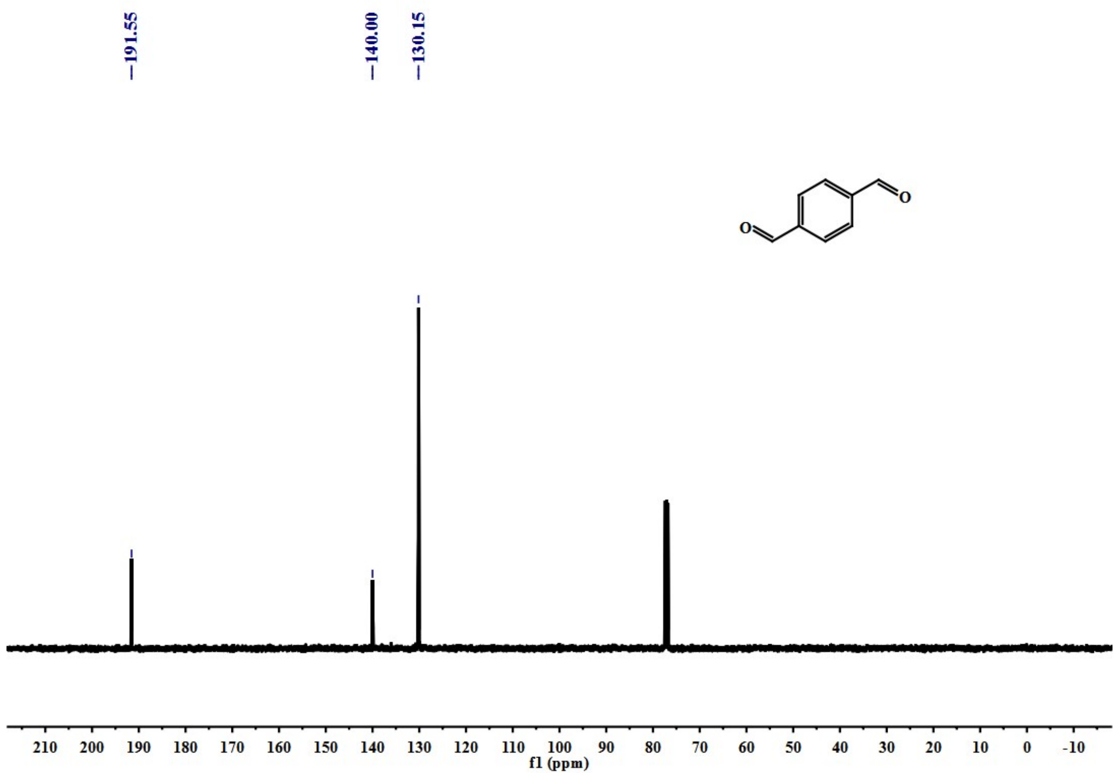

$^{1}$H NMR spectra of **14**(500 MHz, $CDCl_3$)



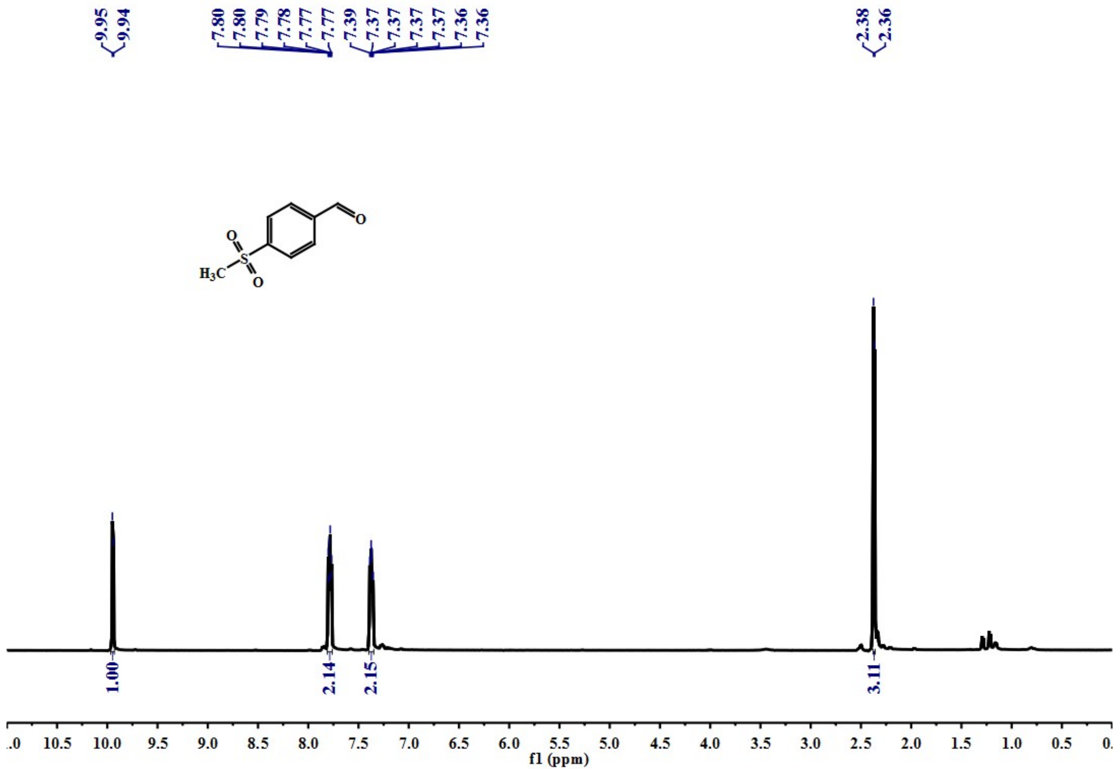

$^{13}$C NMR spectra of **14**(125 MHz, $CDCl_3$)



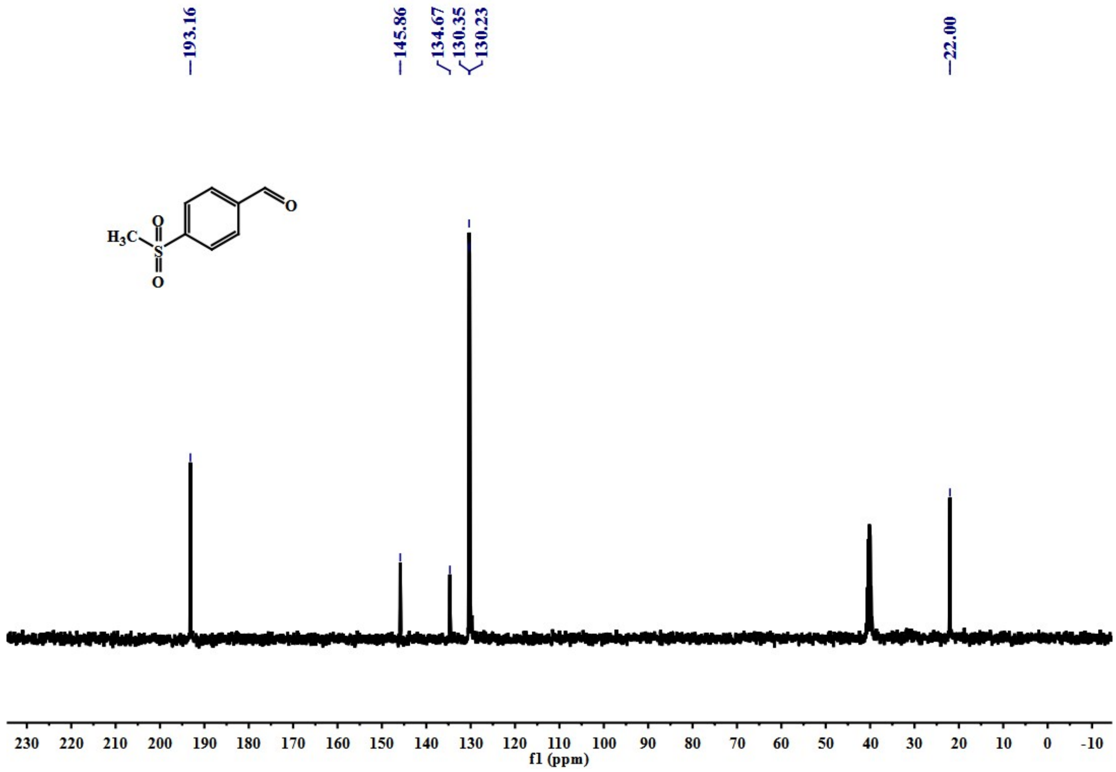

$^{1}H$ NMR spectra of **15**(500 MHz, $CDCl_3$)



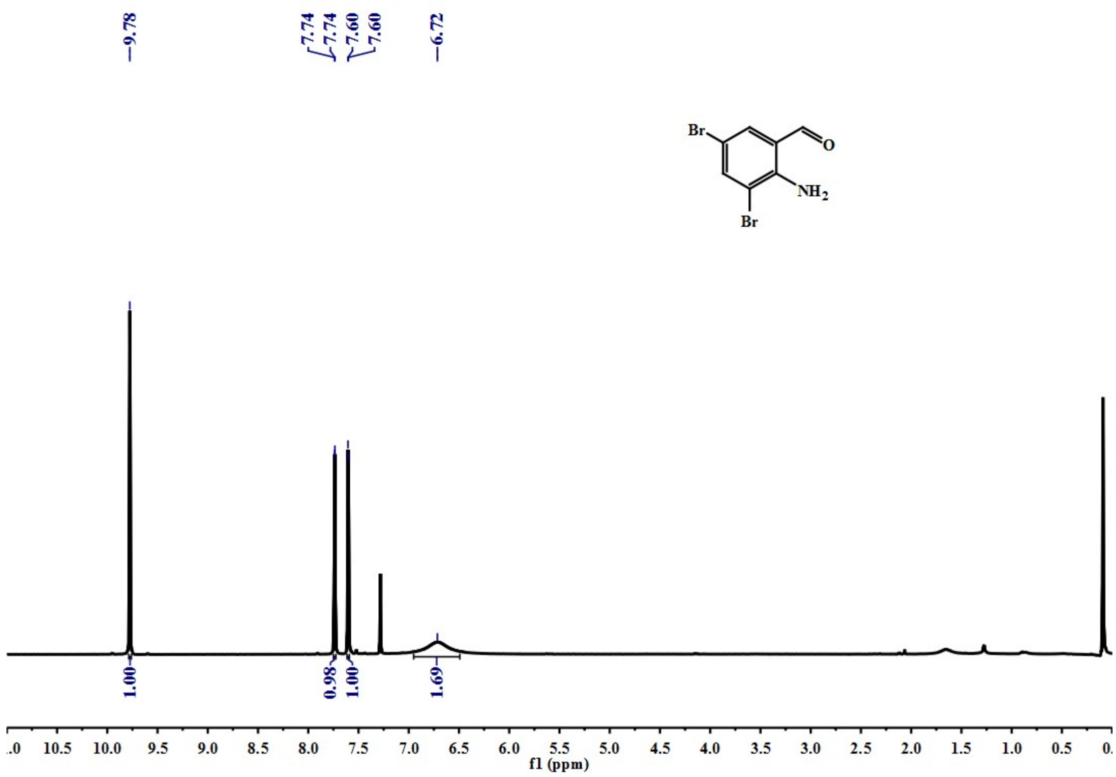

$^{13}C$ NMR spectra of **15**(125 MHz, $CDCl_3$)



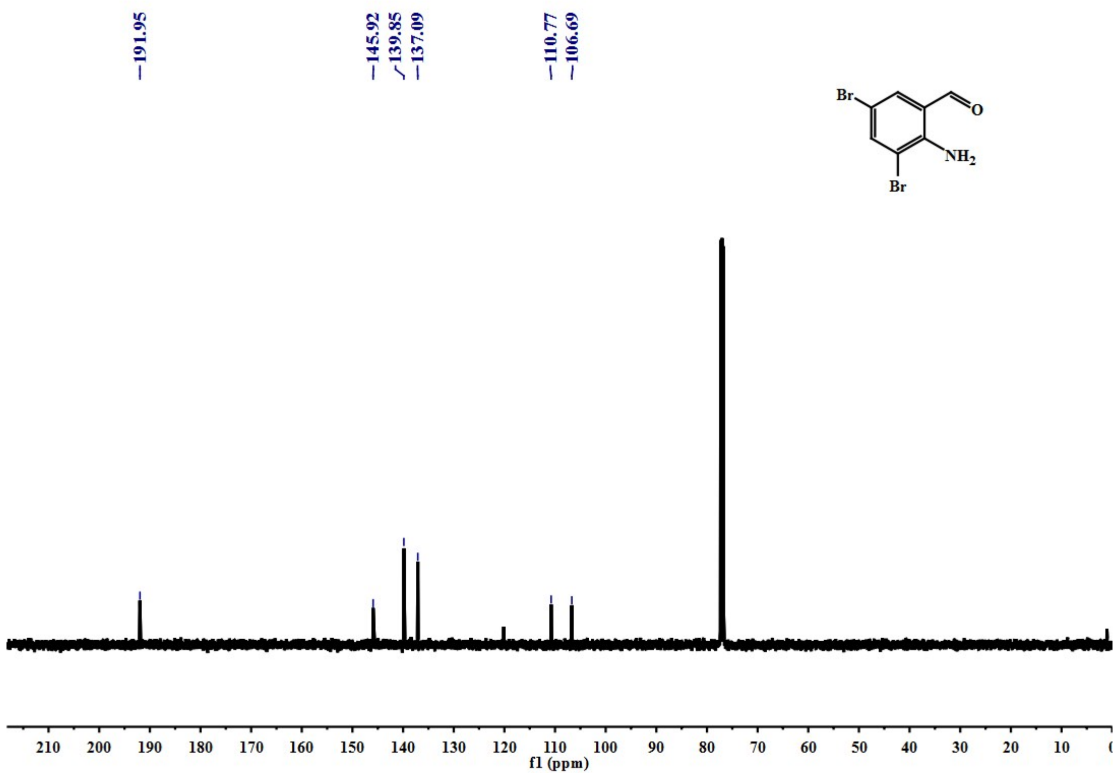

$^1$H NMR spectra of **16**(400 MHz, DMSO)



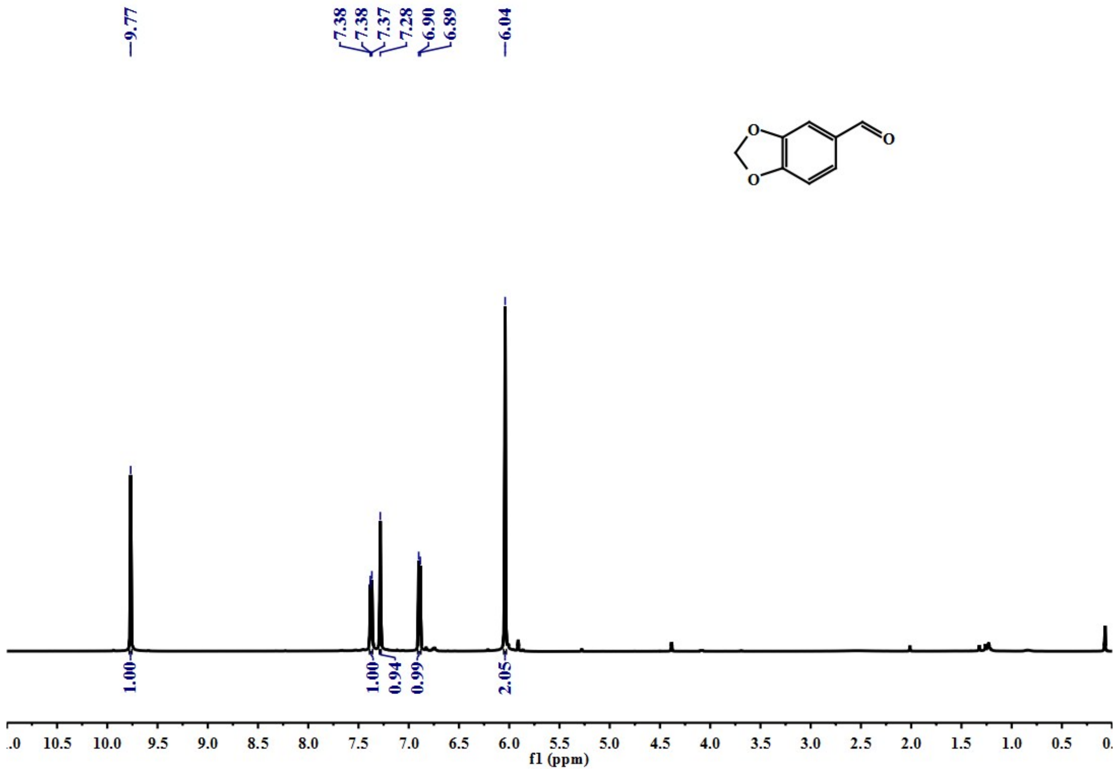

$^{13}$C NMR spectra of **16**(100 MHz, DMSO)



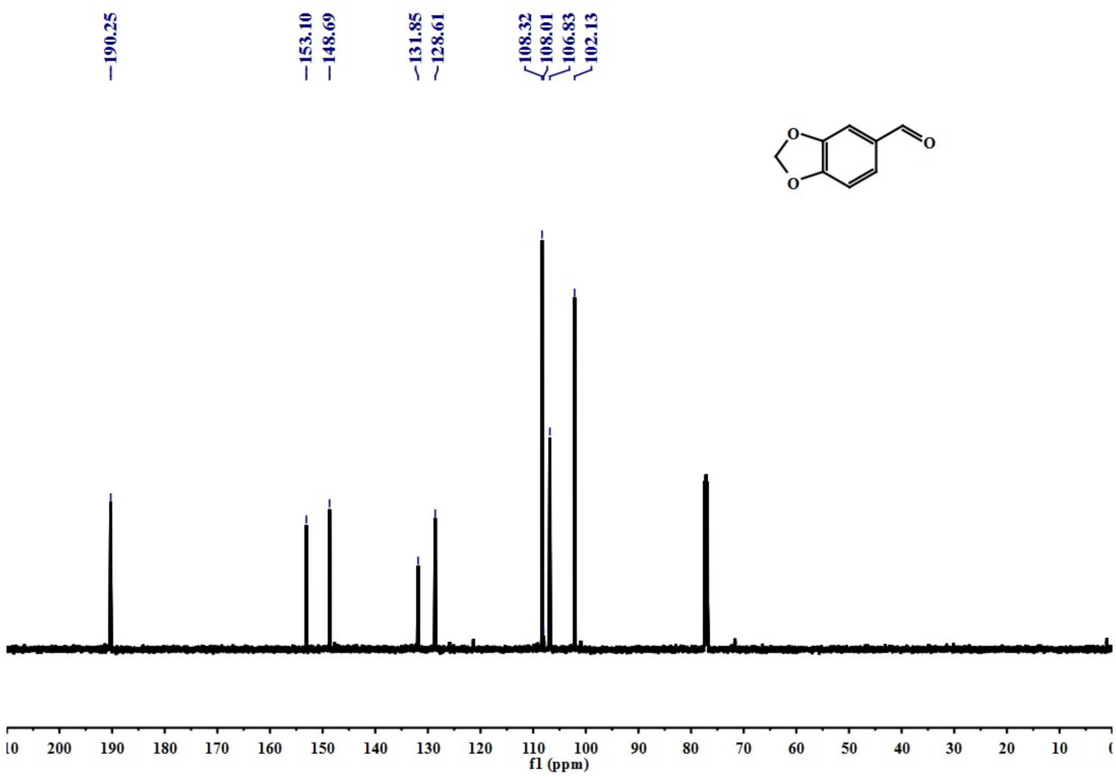

$^{1}H$ NMR spectra of **17**(500 MHz, $CDCl_3$)



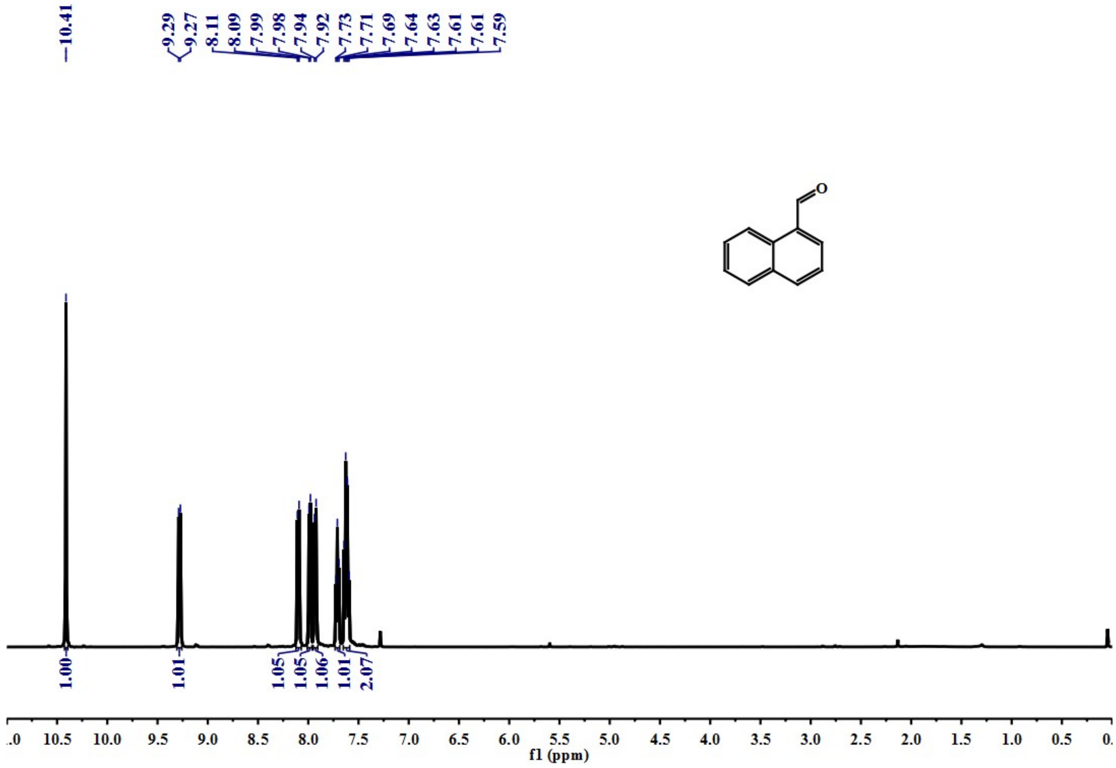

$^{13}C$ NMR spectra of **17**(125 MHz, $CDCl_3$)



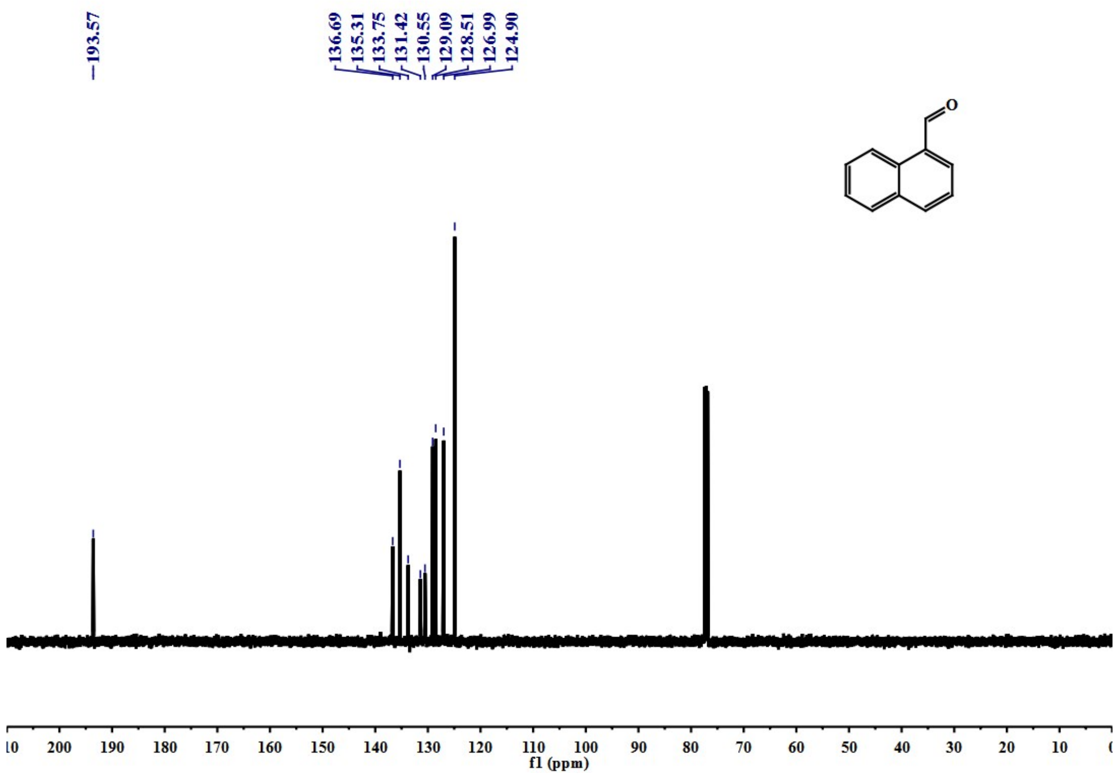

$^{1}$H NMR spectra of **18**(500 MHz, $CDCl_3$)



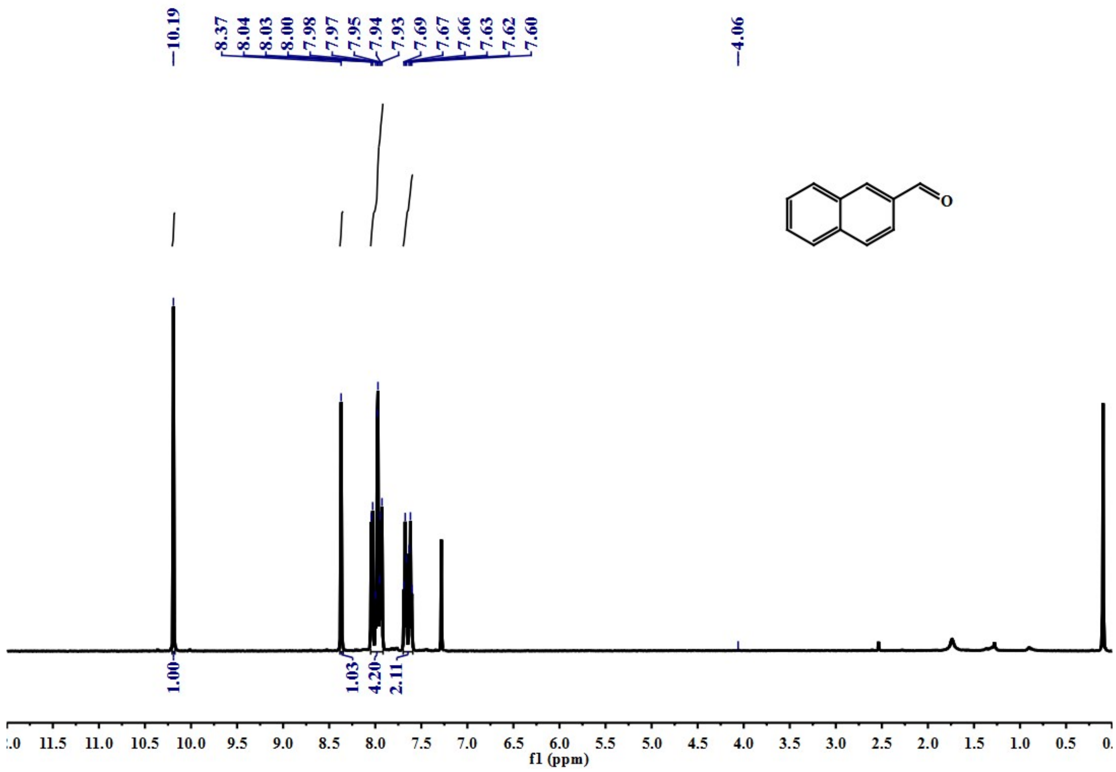

$^{13}$C NMR spectra of **18**(125 MHz, $CDCl_3$)



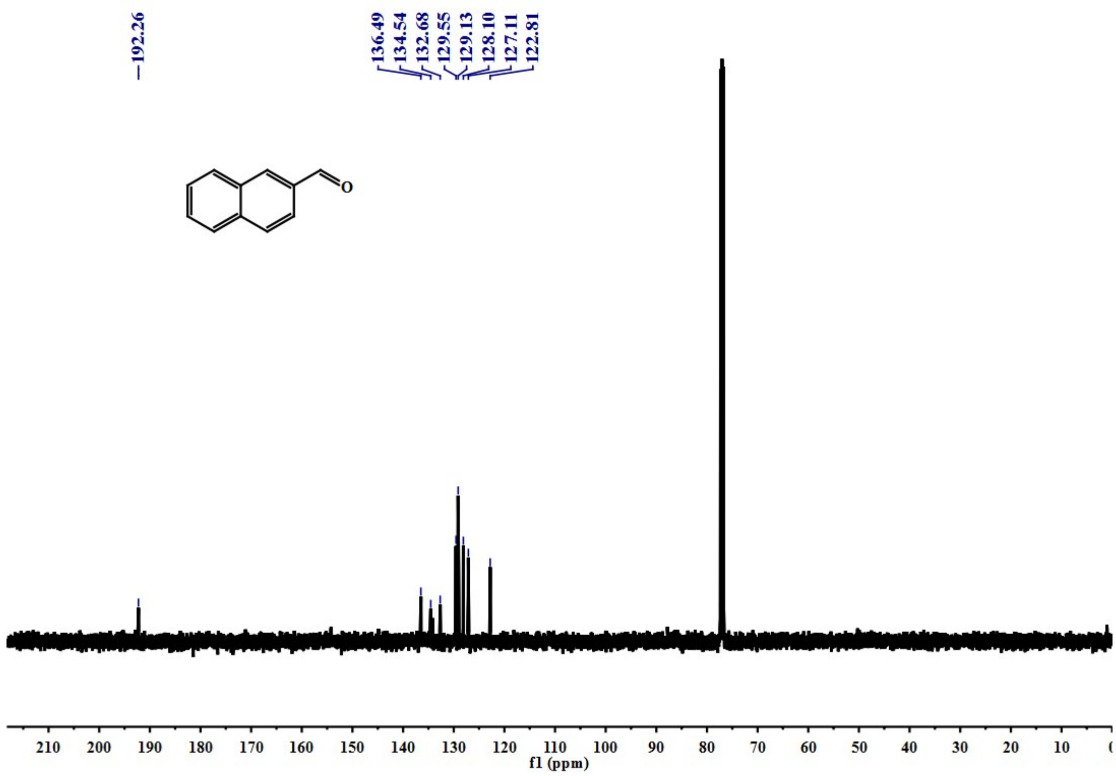

$^{1}H$ NMR spectra of **19**(500 MHz, $CDCl_3$)



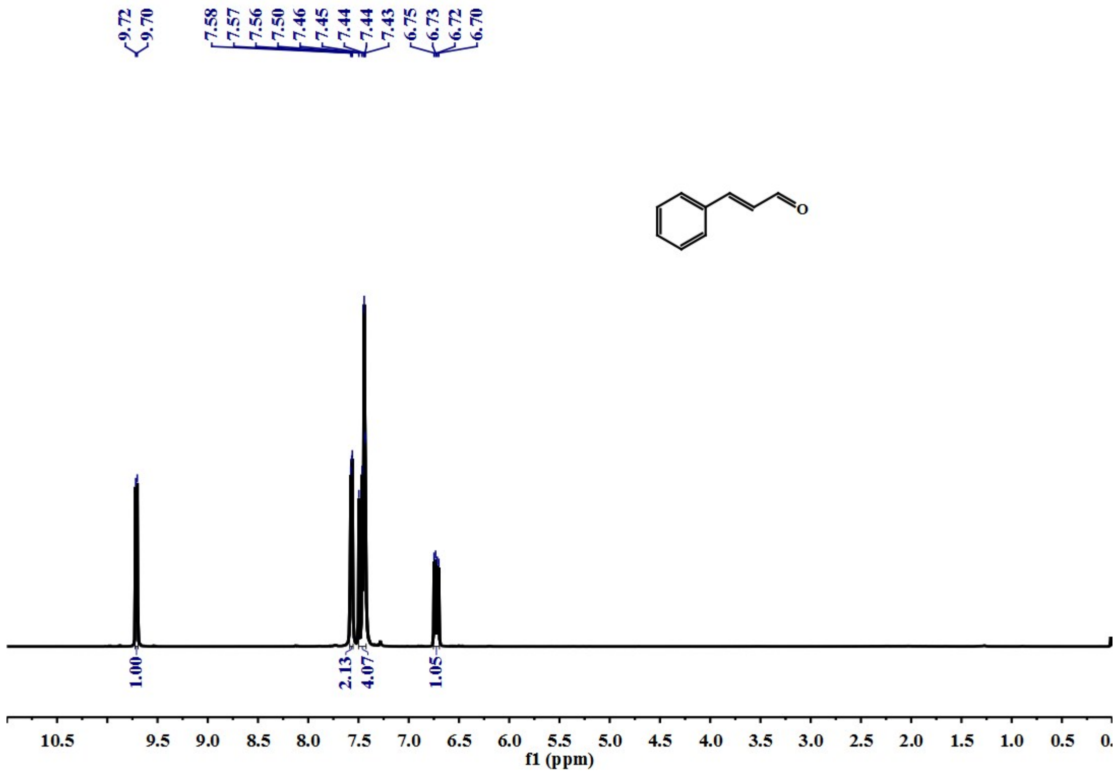

$^{13}C$ NMR spectra of **19**(125 MHz, $CDCl_3$)



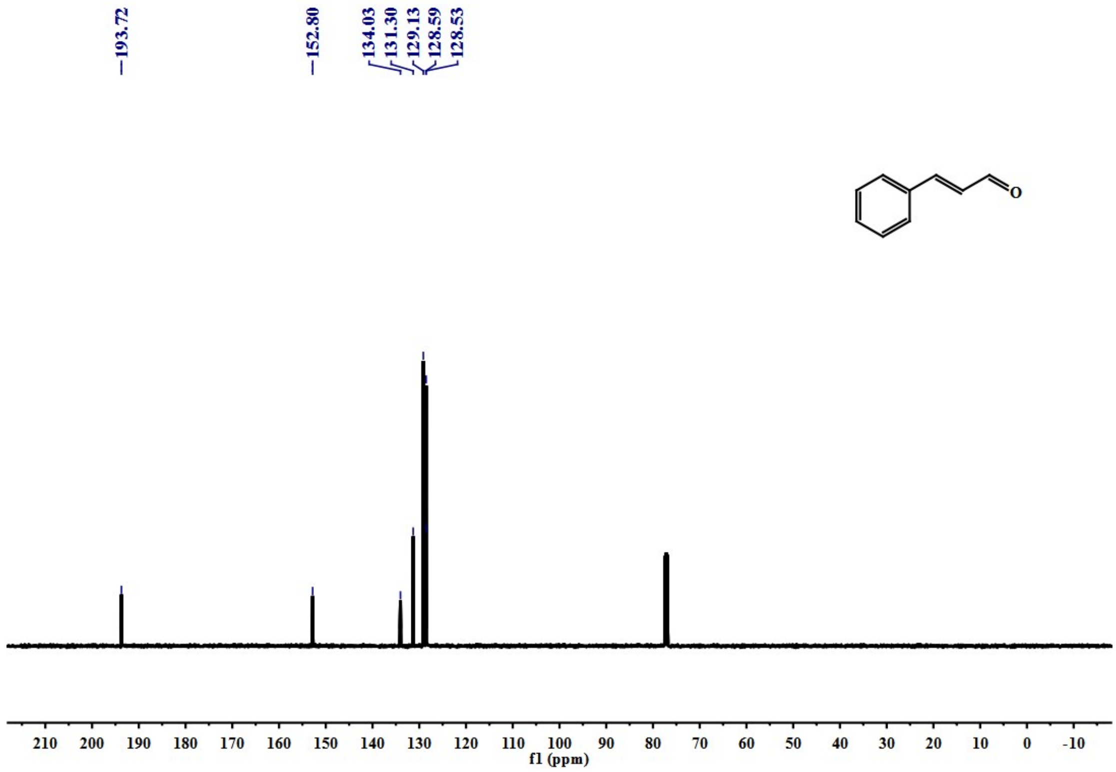

$^{1}H$ NMR spectra of **20**(500 MHz, $CDCl_3$)



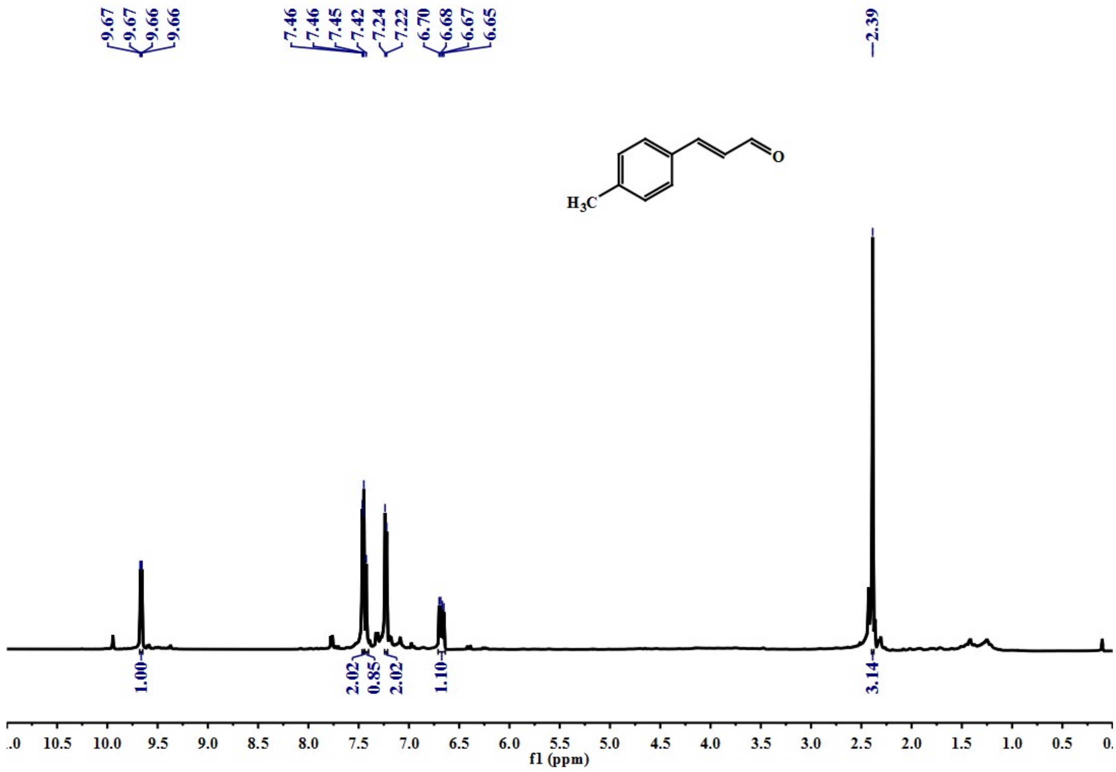

$^{13}C$ NMR spectra of **20**(125 MHz, $CDCl_3$)



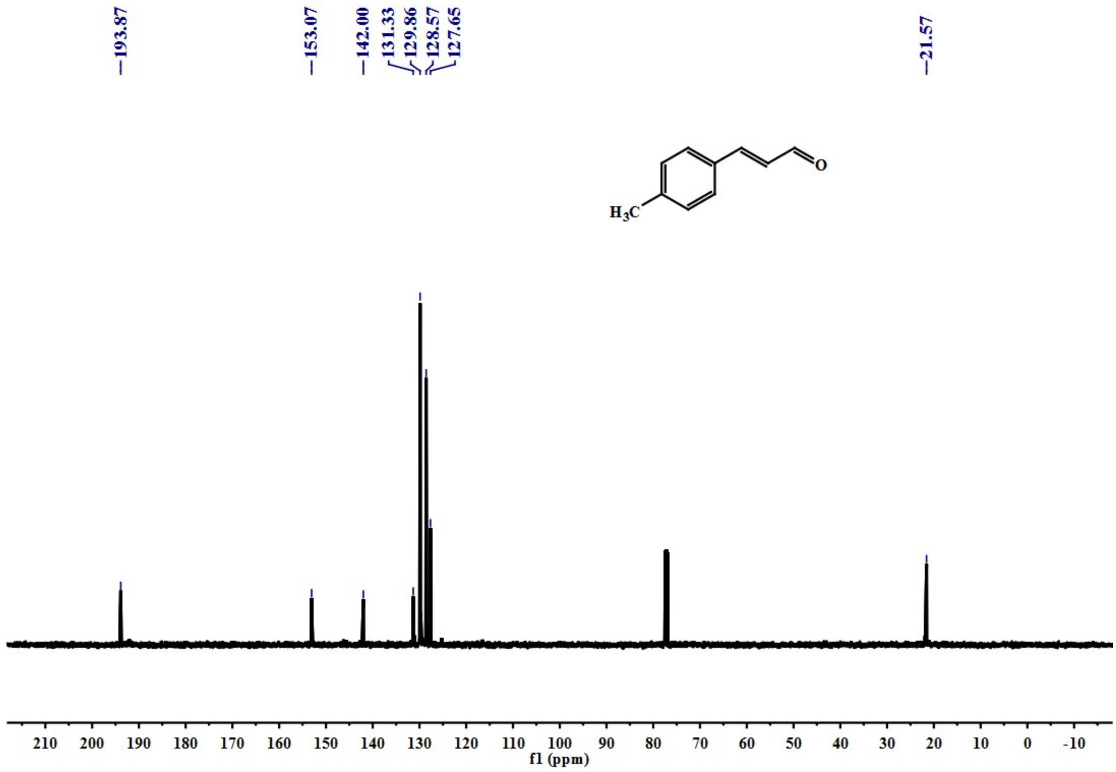

$^{1}$H NMR spectra of **21**(500 MHz, $CDCl_3$)



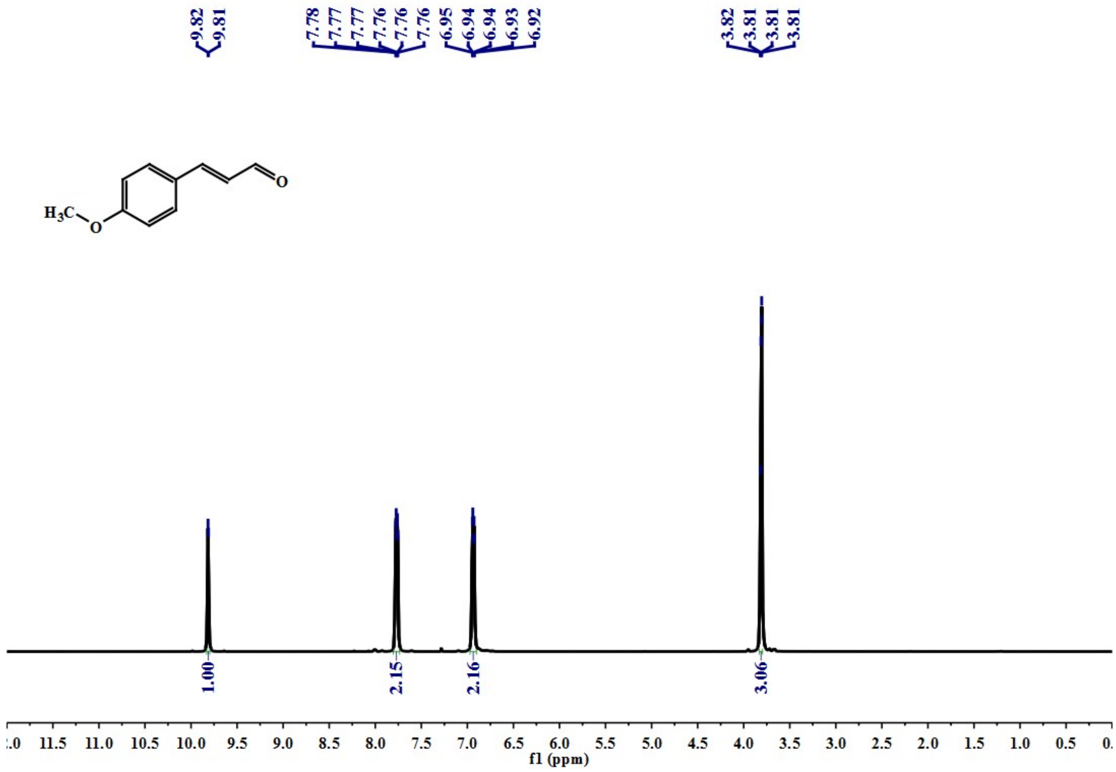

$^{13}$C NMR spectra of **21**(125 MHz, $CDCl_3$)



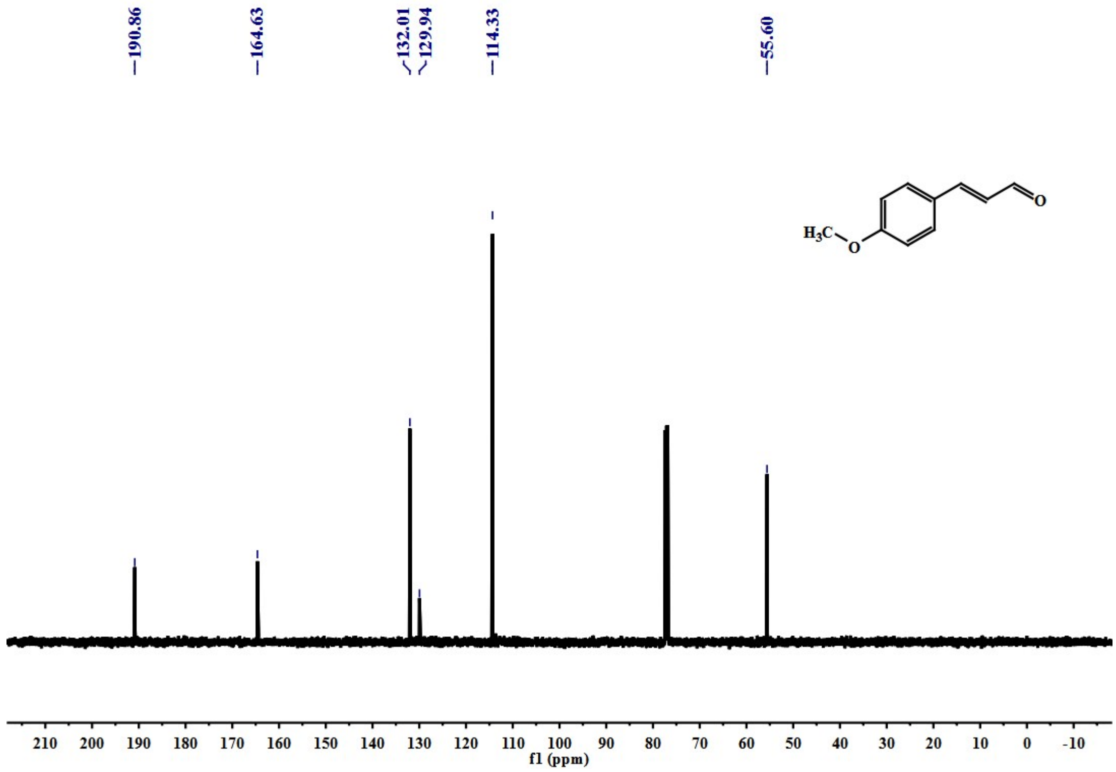

[1]H NMR spectra of **22**(500 MHz, $CDCl_3$)



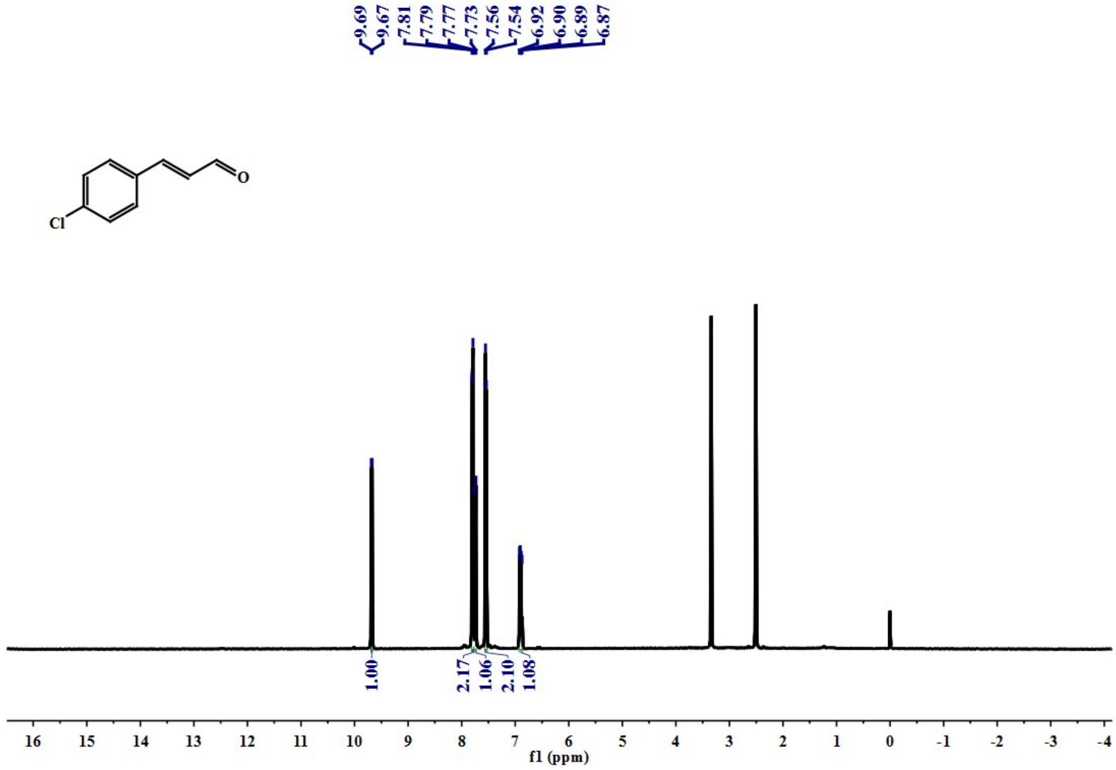

[13]C NMR spectra of **22**(125 MHz, $CDCl_3$)



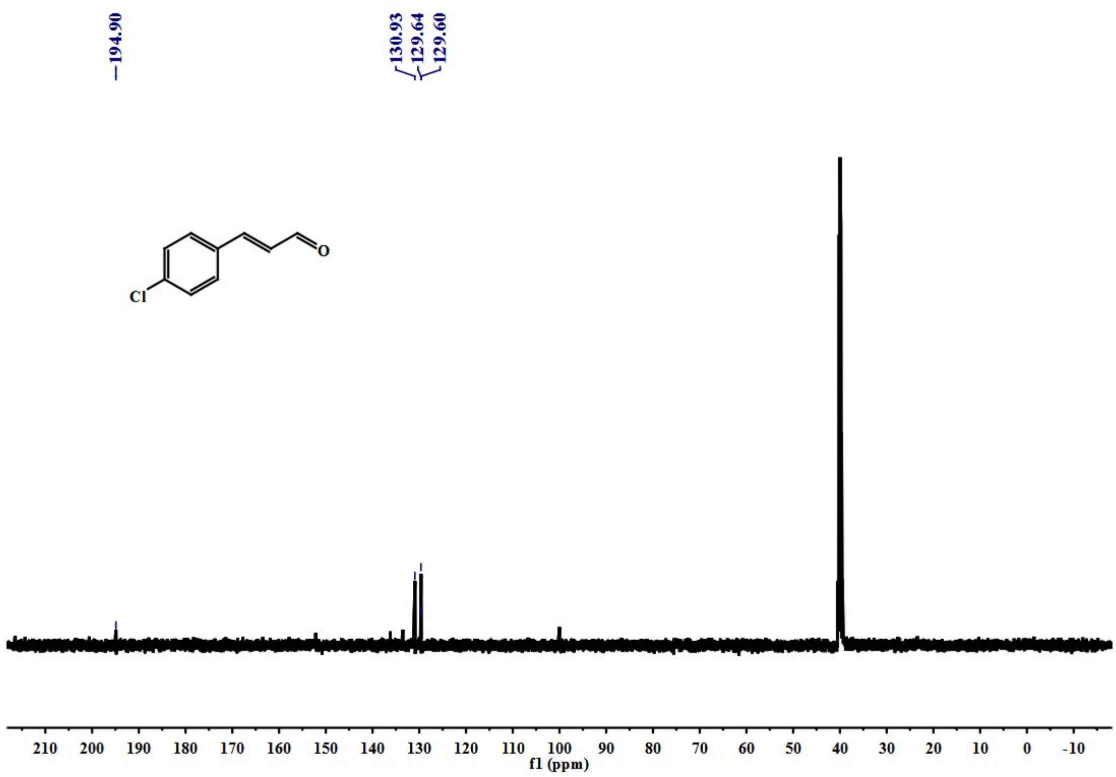

[1]H NMR spectra of **23**(500 MHz, $CDCl_3$)



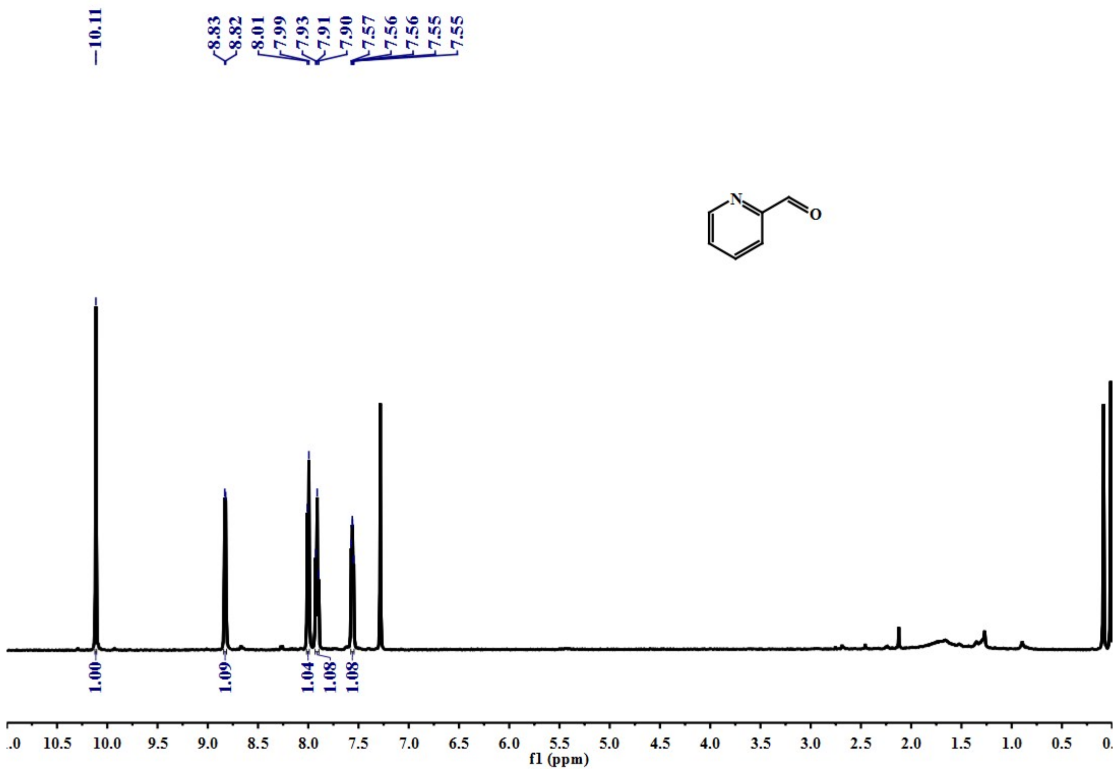

[13]C NMR spectra of **23**(125 MHz, $CDCl_3$)



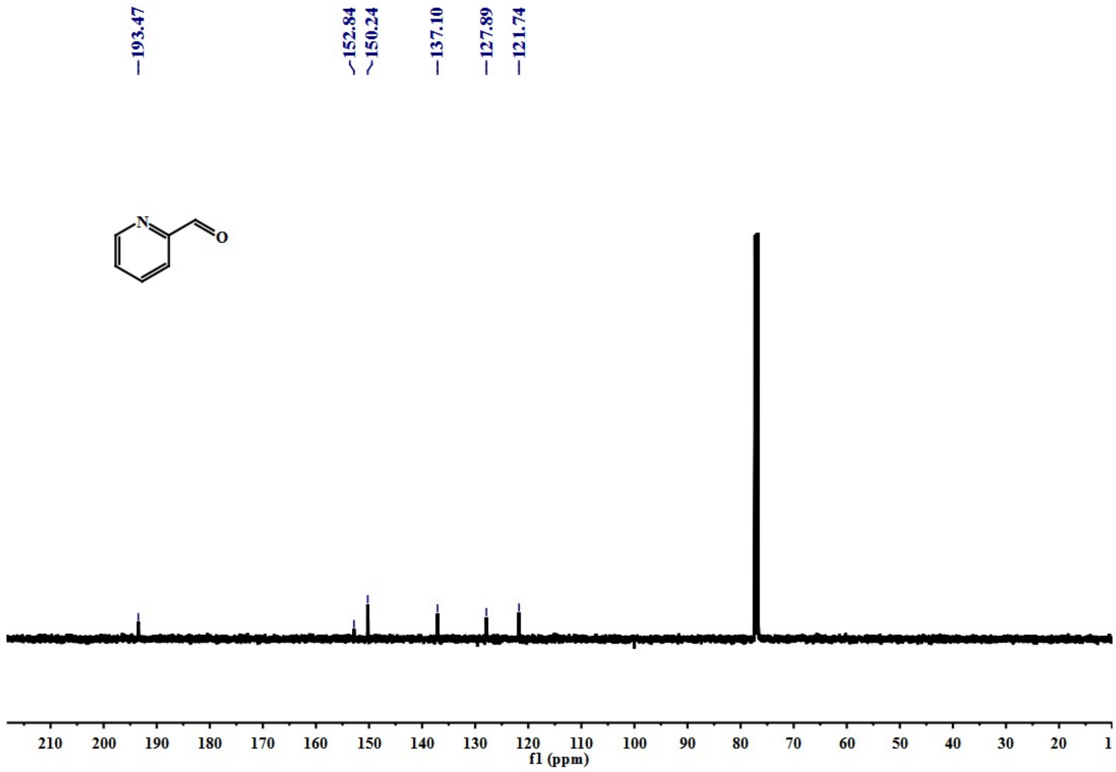

$^{1}$H NMR spectra of **24**(500 MHz,DMSO)



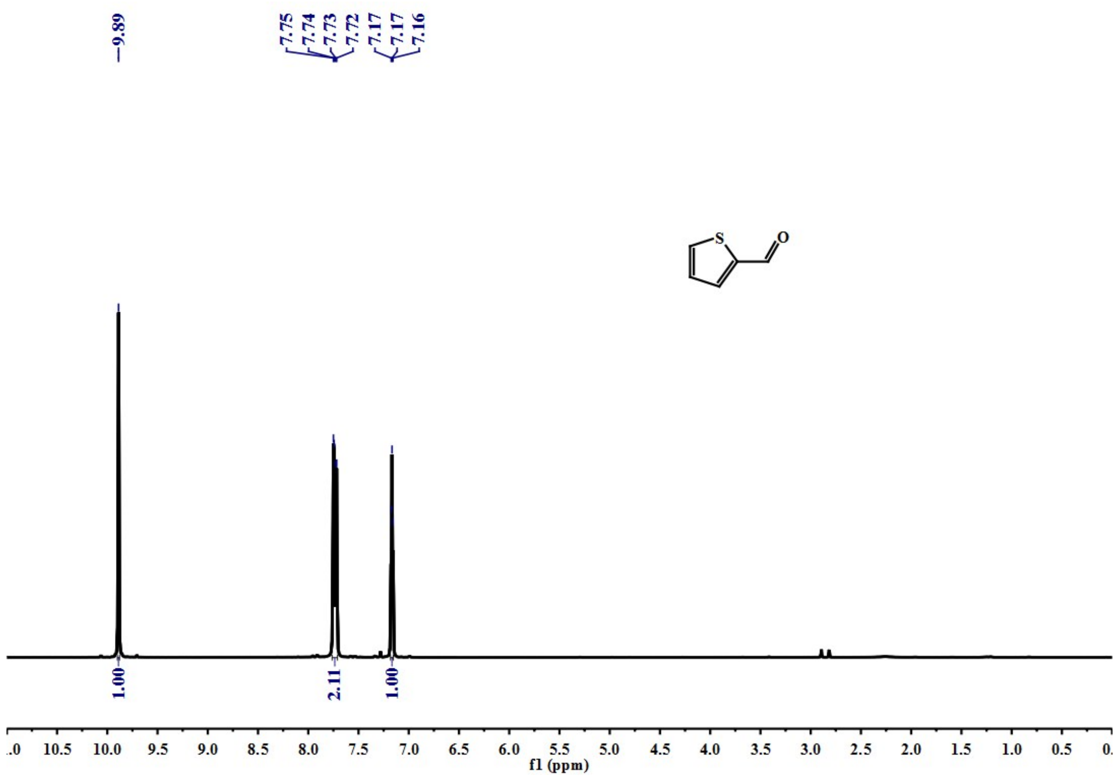

$^{13}$C NMR spectra of **24**(125 MHz, DMSO)



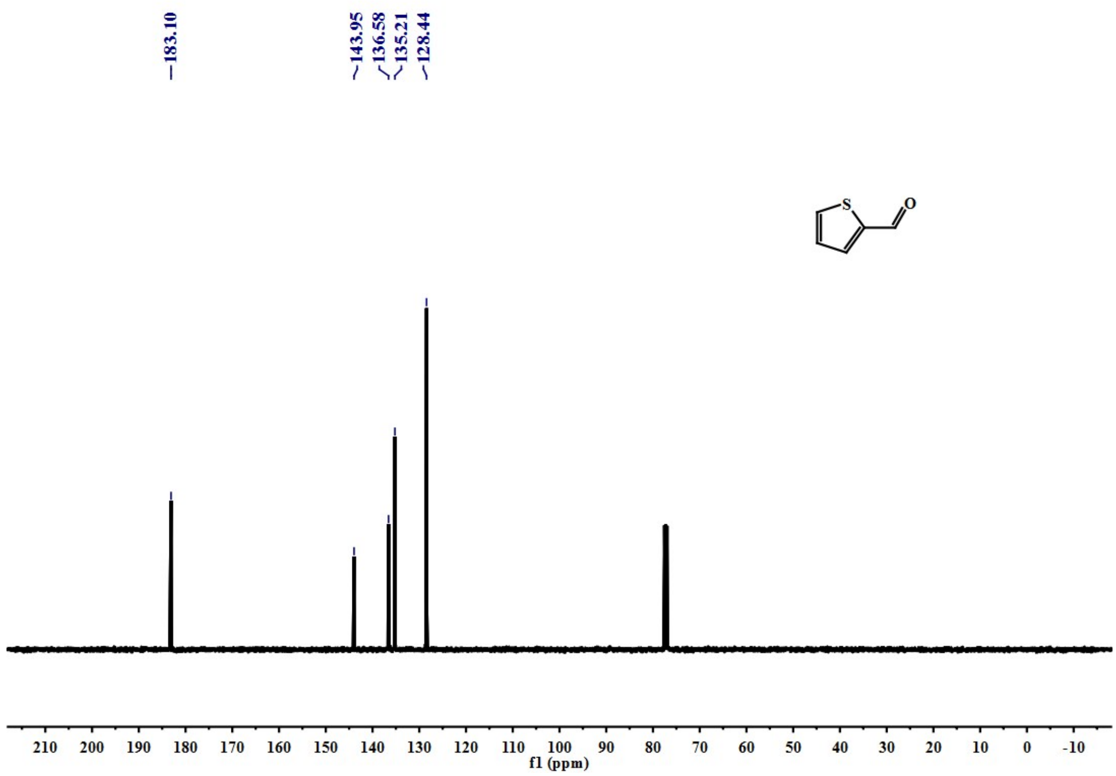

$^{1}H$ NMR spectra of **25**(500 MHz, $CDCl_3$)



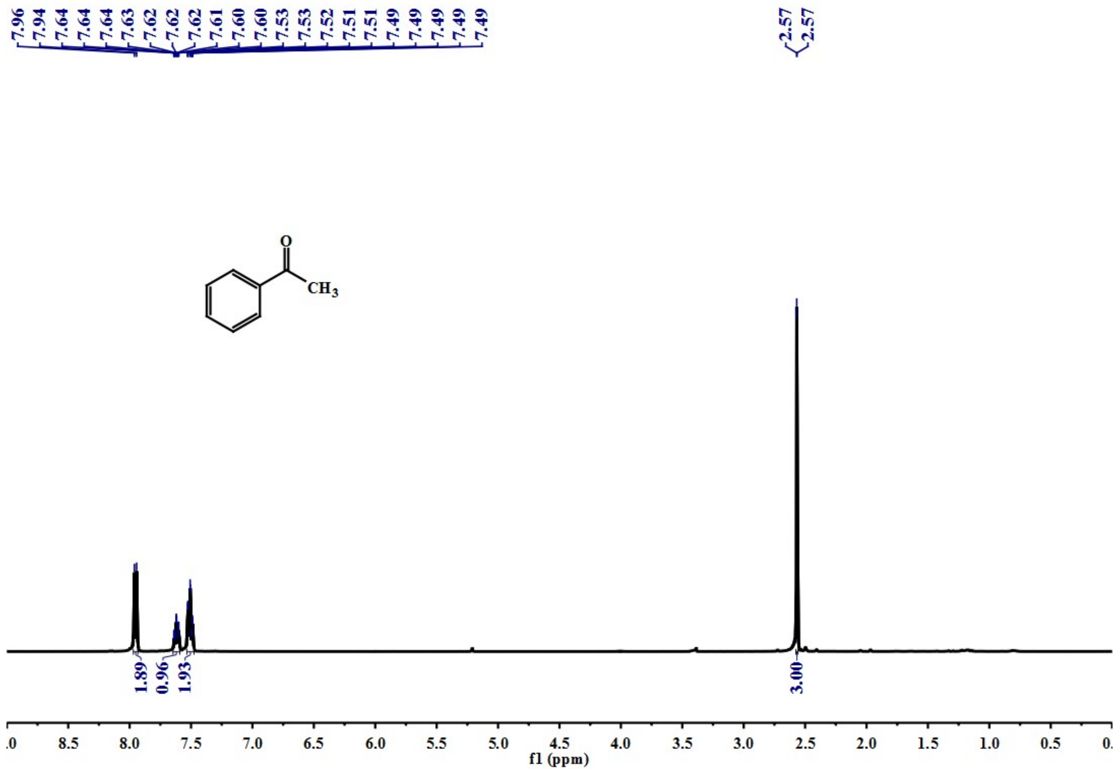

$^{13}C$ NMR spectra of **25**(125 MHz, $CDCl_3$)



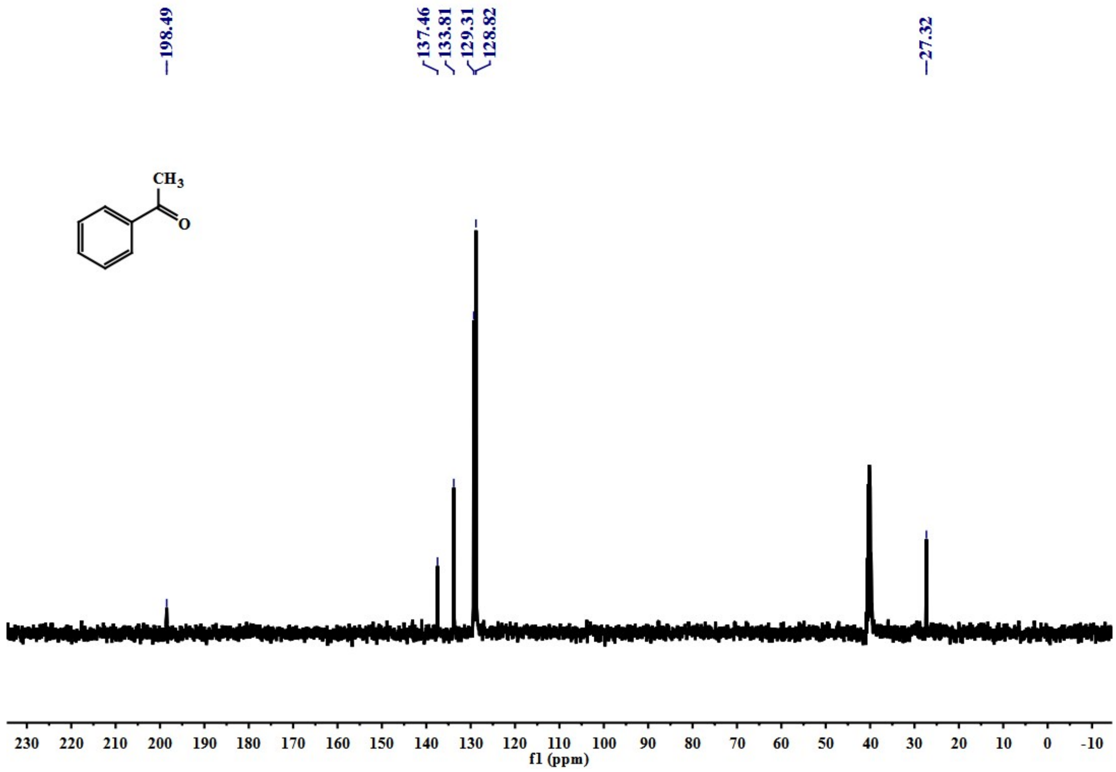

$^{1}$H NMR spectra of **26**(500 MHz, $CDCl_3$)



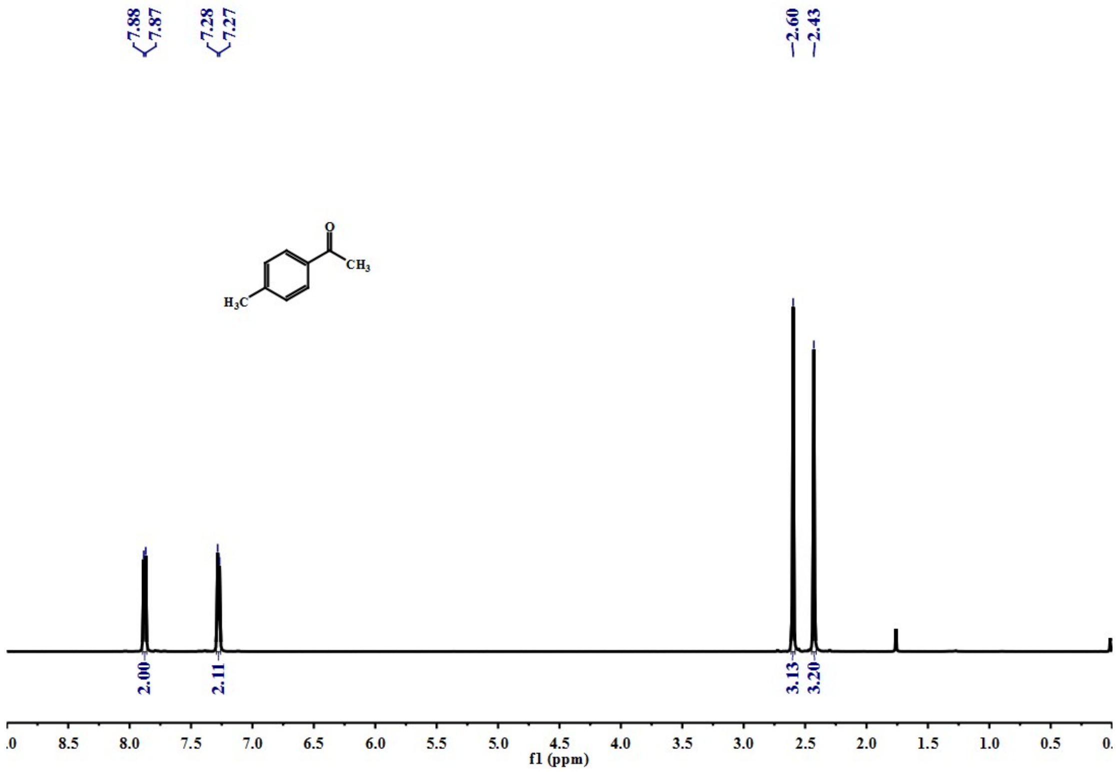

$^{13}$C NMR spectra of **26**(125 MHz, $CDCl_3$)



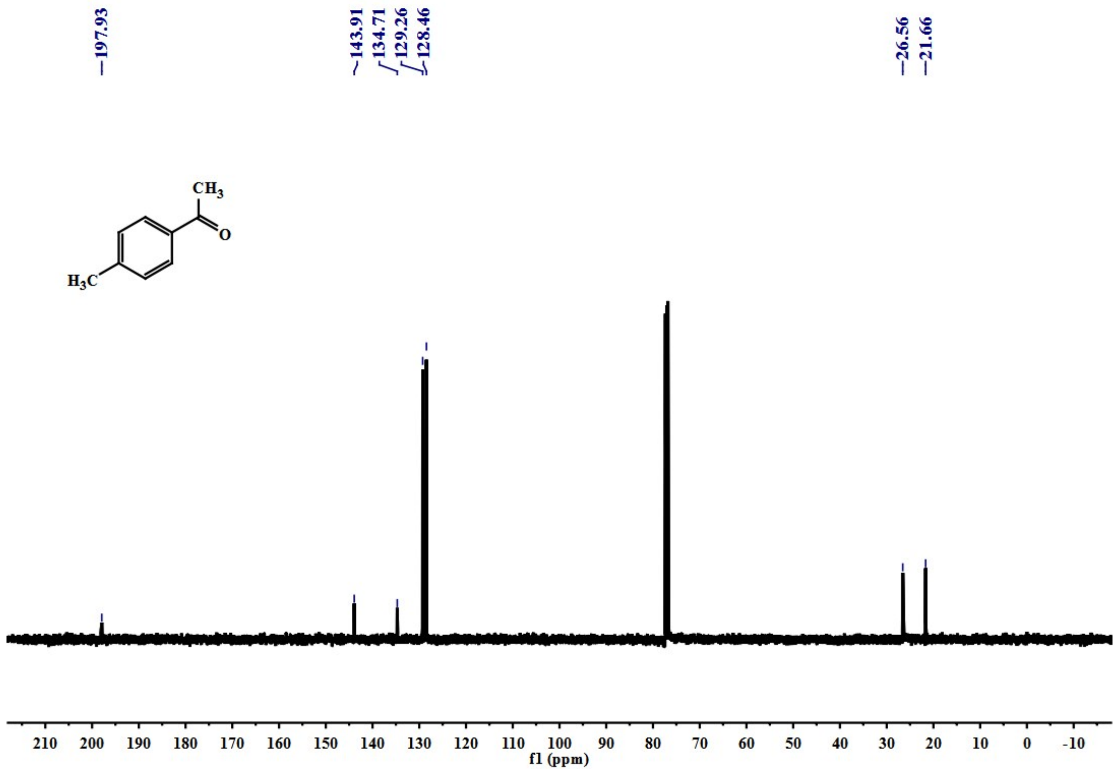

$^1$H NMR spectra of **38**(400 MHz, DMSO)



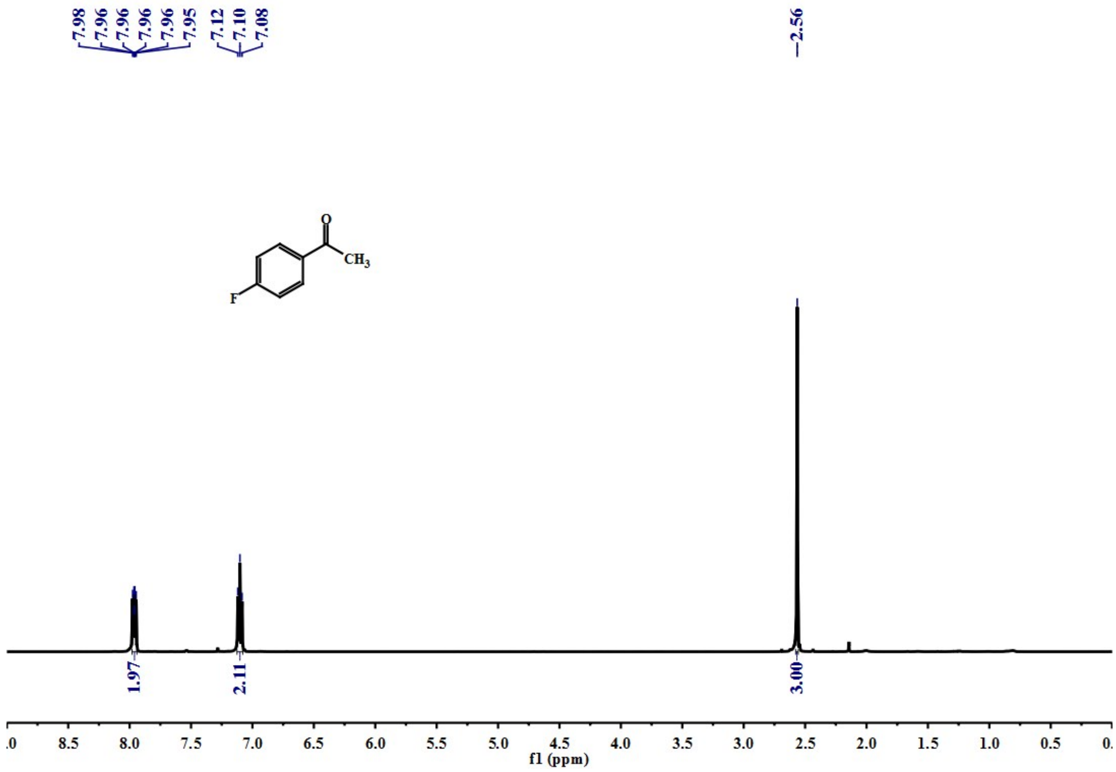

$^{13}$C NMR spectra of **38**(100 MHz, DMSO)



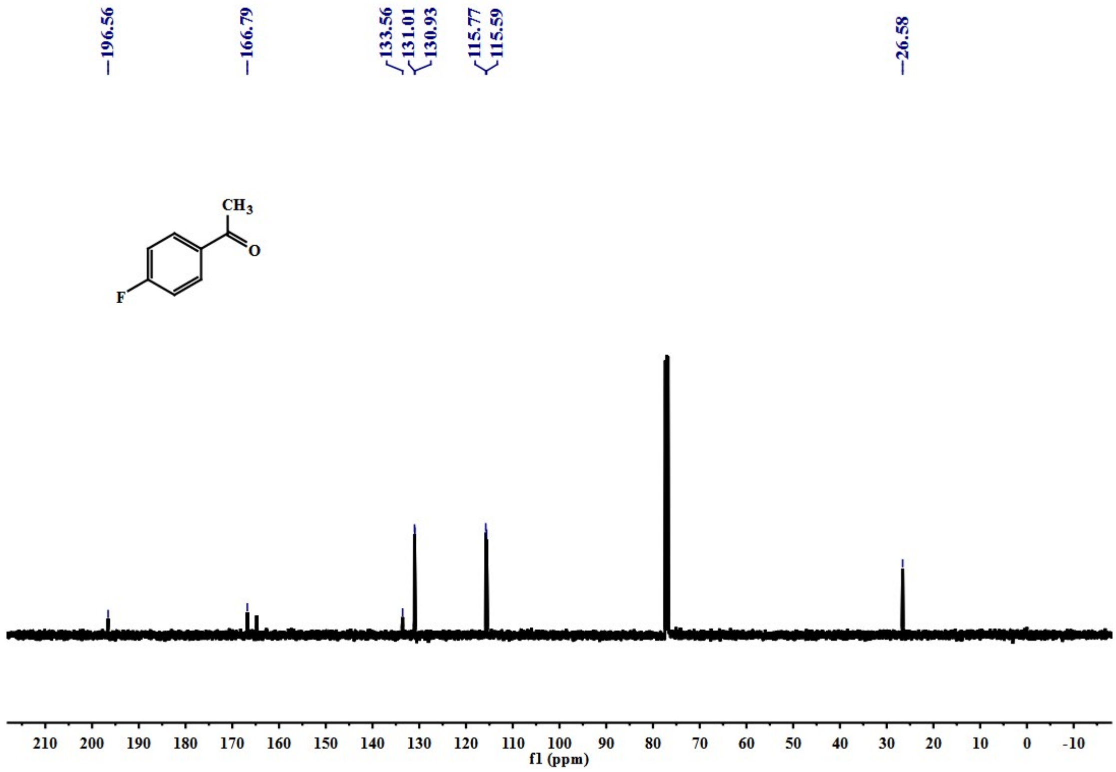

$^1$H NMR spectra of **39**(500 MHz, $CDCl_3$)



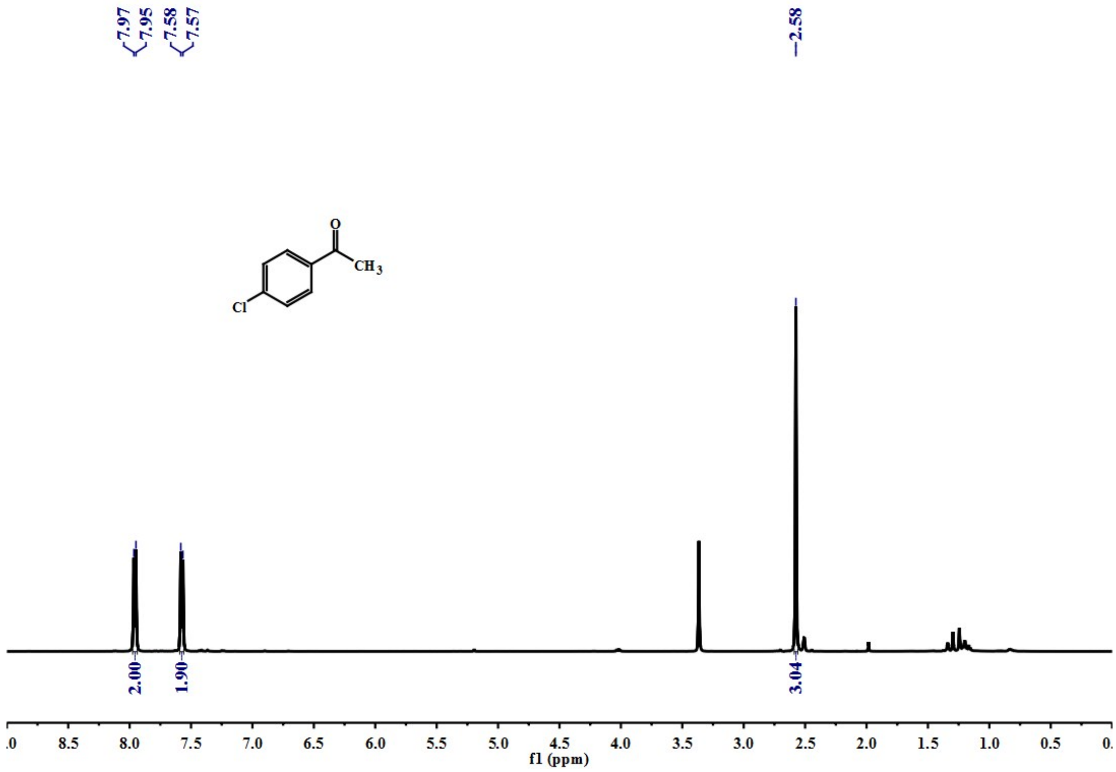

$^{13}$C NMR spectra of **39**(125 MHz, $CDCl_3$)



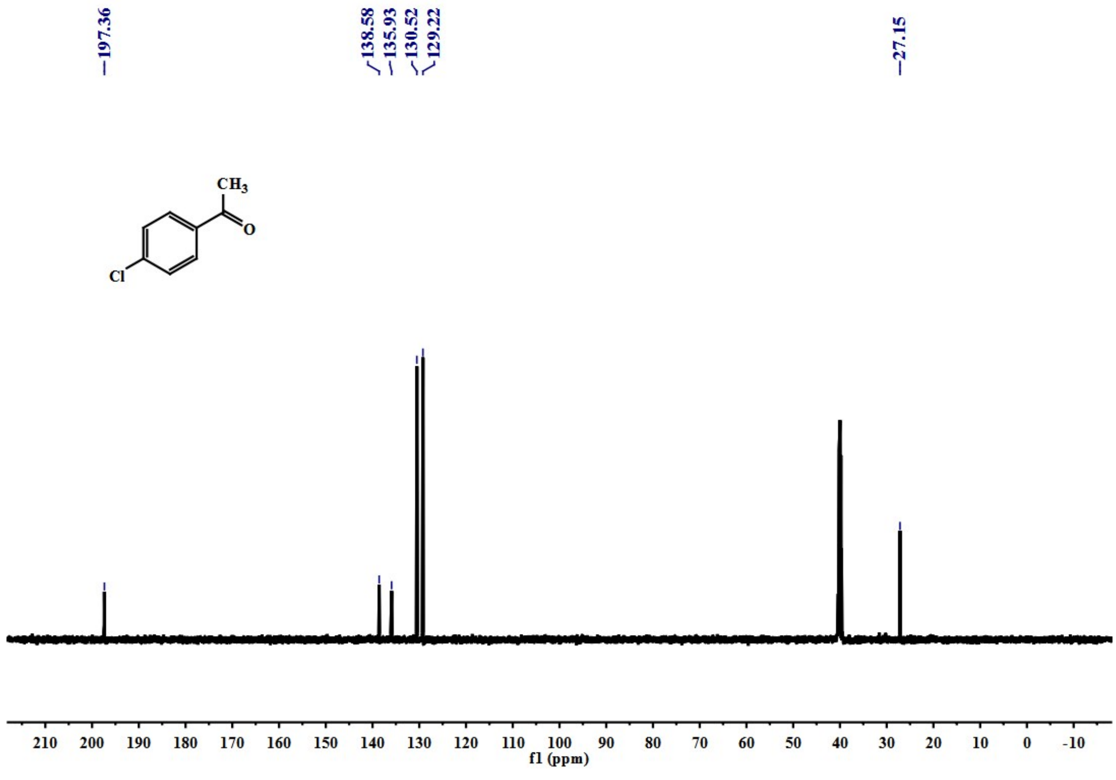
$^{1}H$ NMR spectra of **40**(500 MHz, $CDCl_3$)



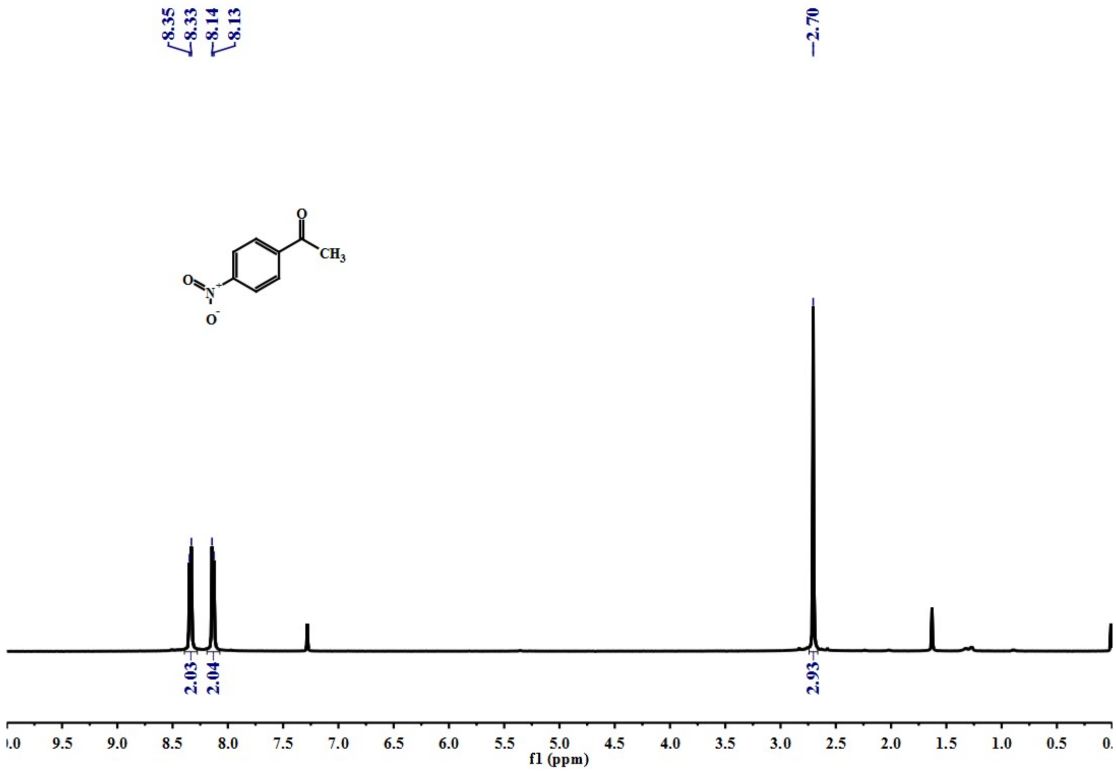
$^{13}C$ NMR spectra of **40**(125 MHz, $CDCl_3$)



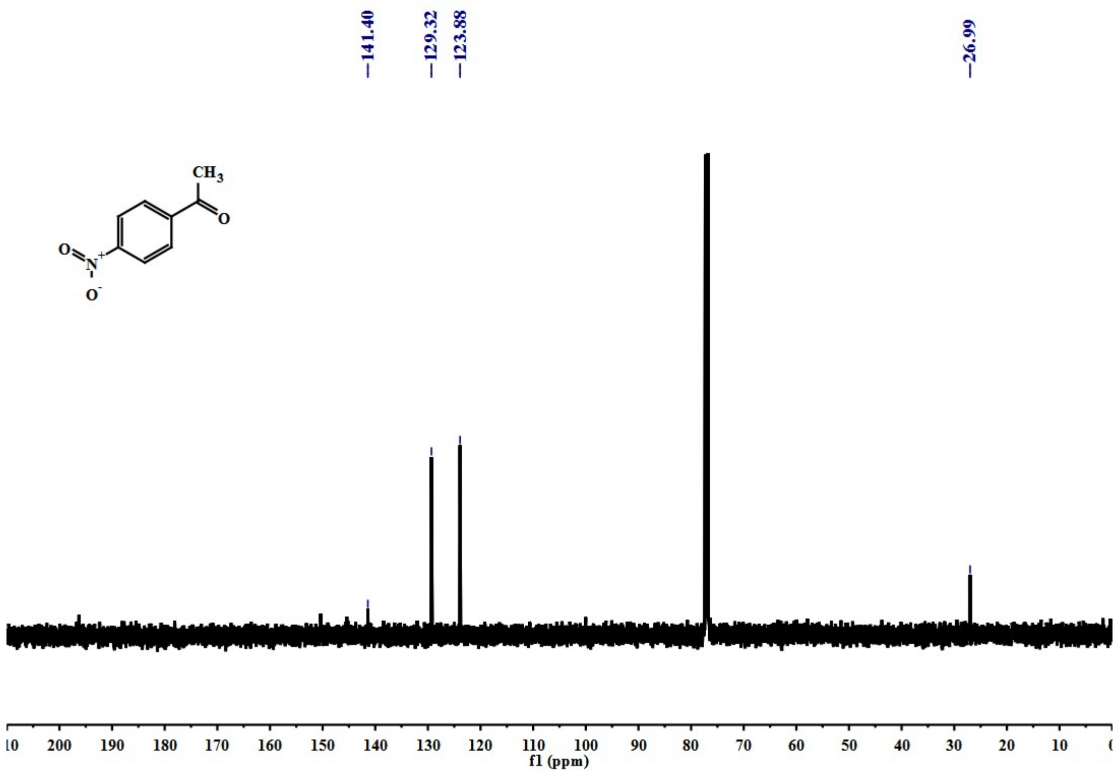

$^{1}H$ NMR spectra of **41**(500 MHz,DMSO)



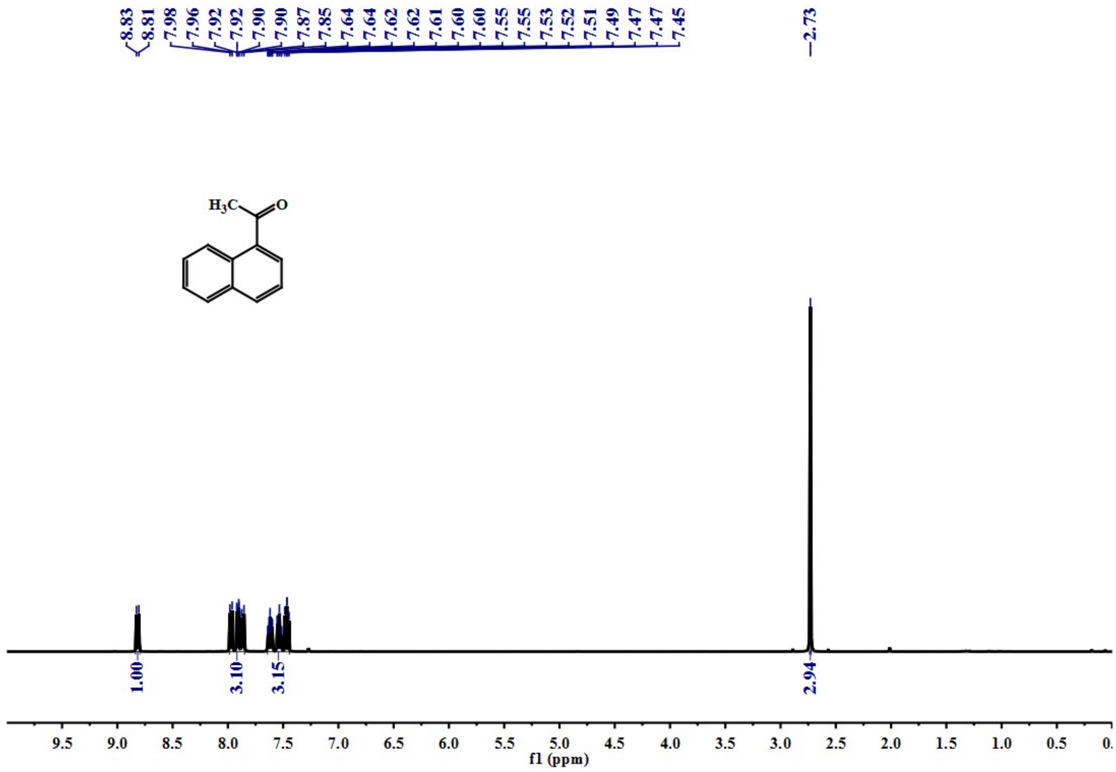

$^{13}C$ NMR spectra of **41**(125 MHz,DMSO)



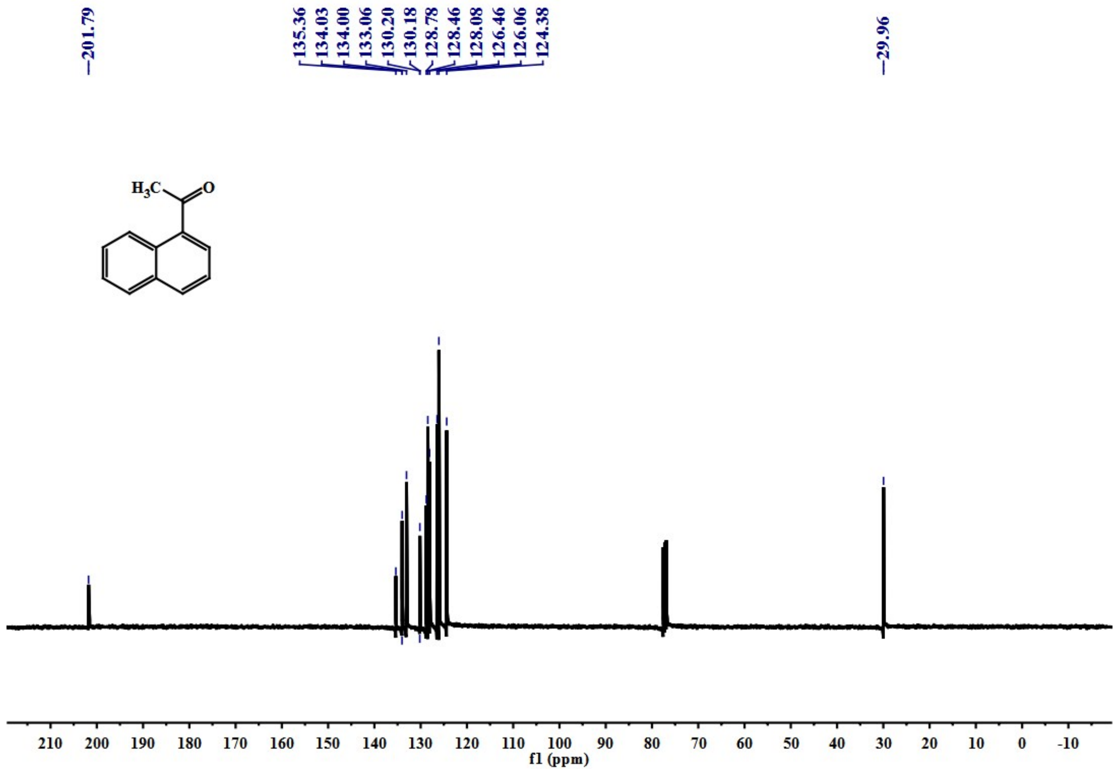

$^{1}$H NMR spectra of **42**(500 MHz, $CDCl_3$)



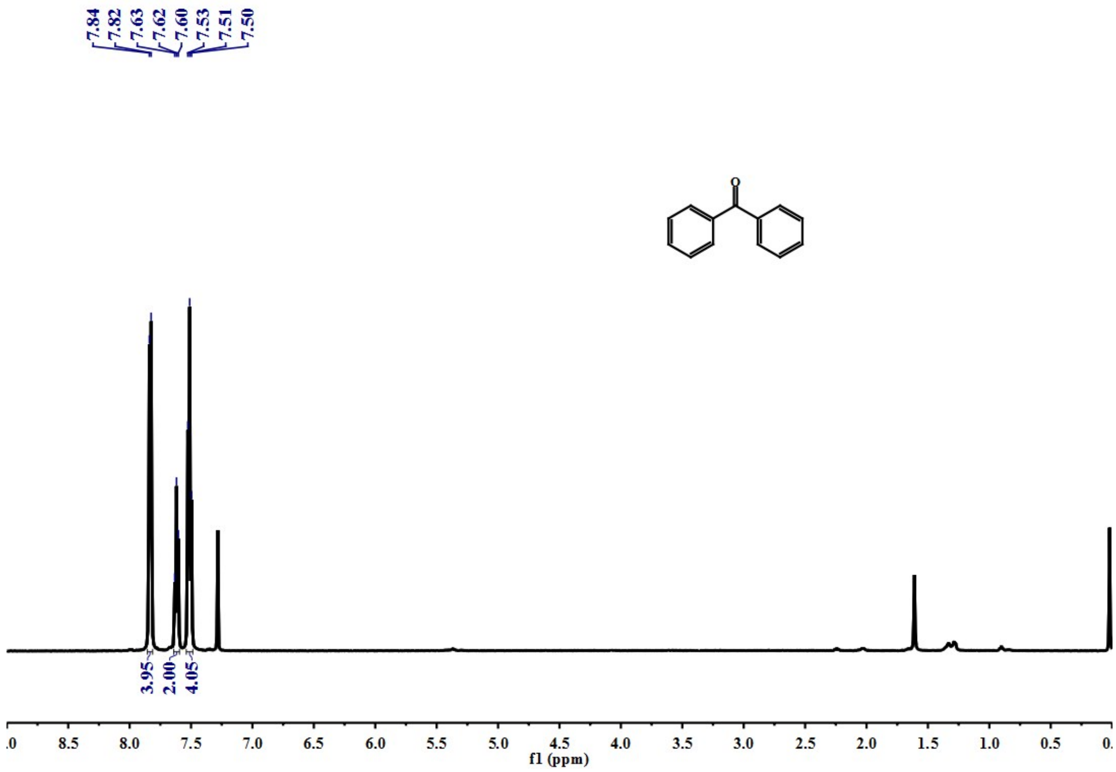

$^{13}$C NMR spectra of **42**(125 MHz, $CDCl_3$)



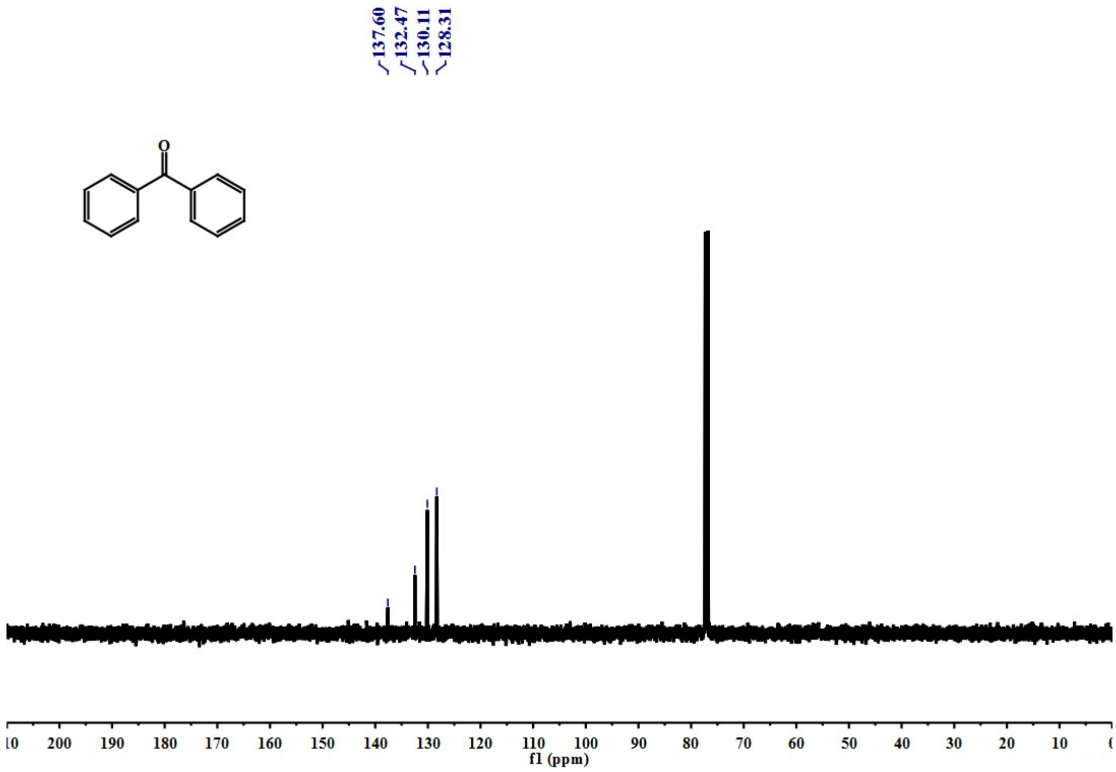

[1]H NMR spectra of **43**(400 MHz, $CDCl_3$)



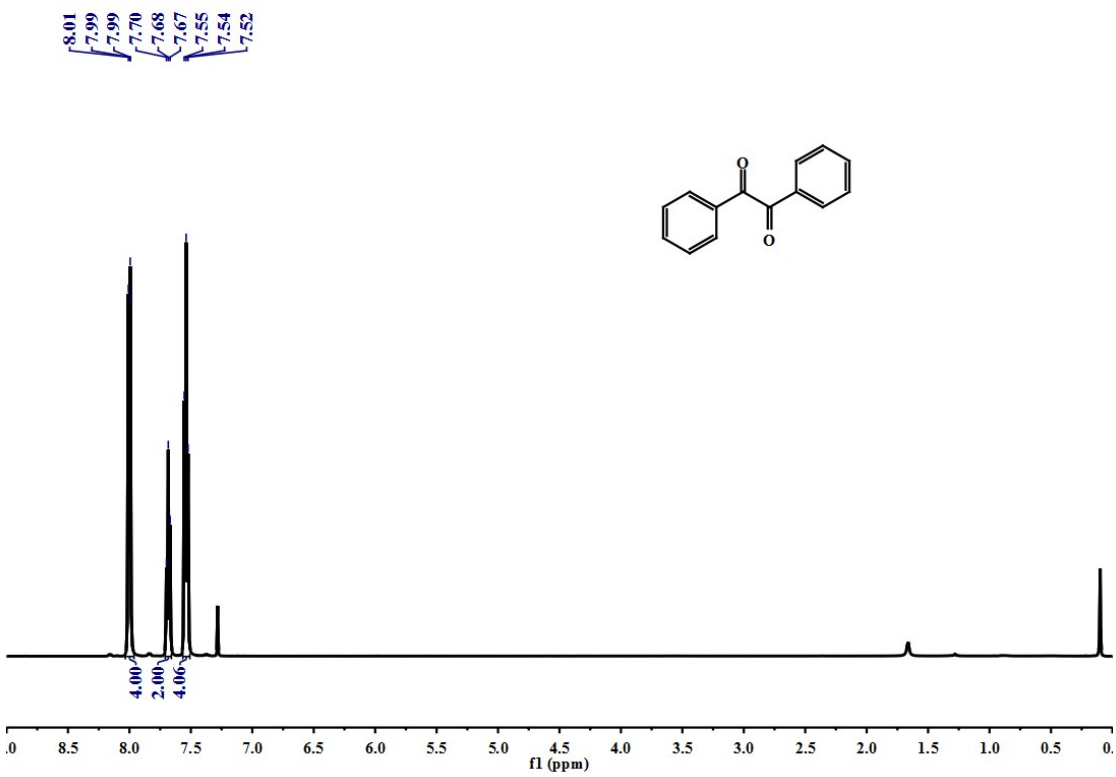

[13]C NMR spectra of **43**(100 MHz, $CDCl_3$)



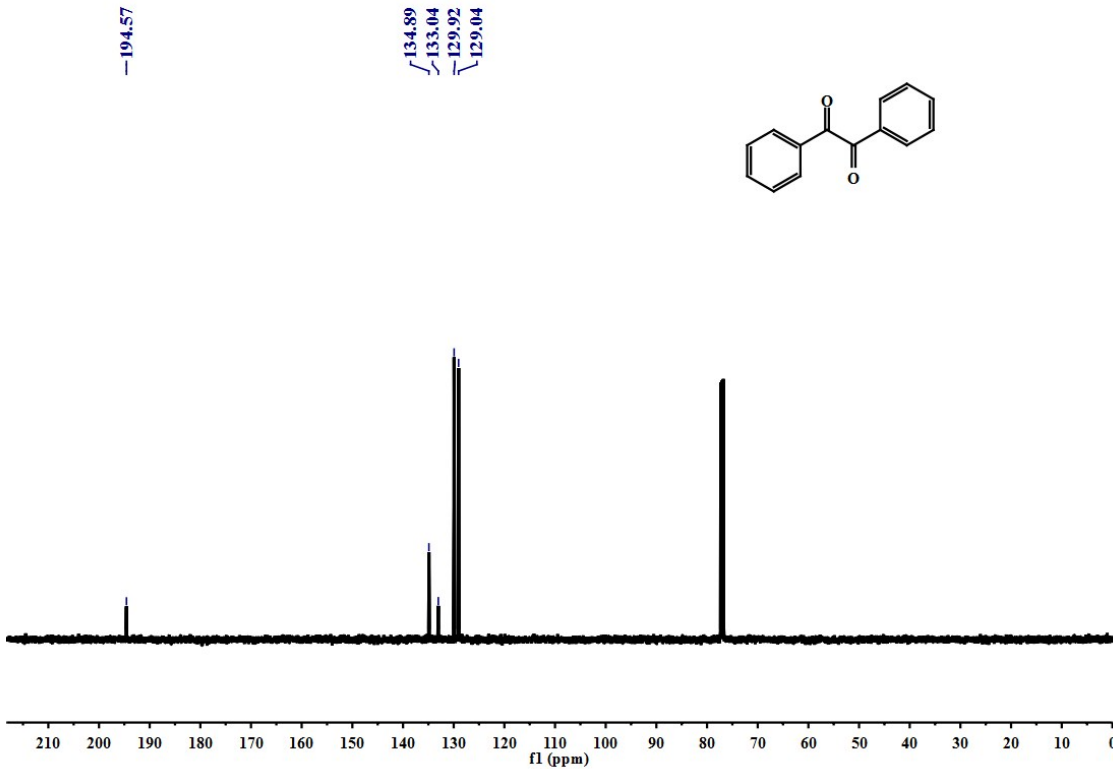

$^{1}$H NMR spectra of **44**(500 MHz, $CDCl_3$)



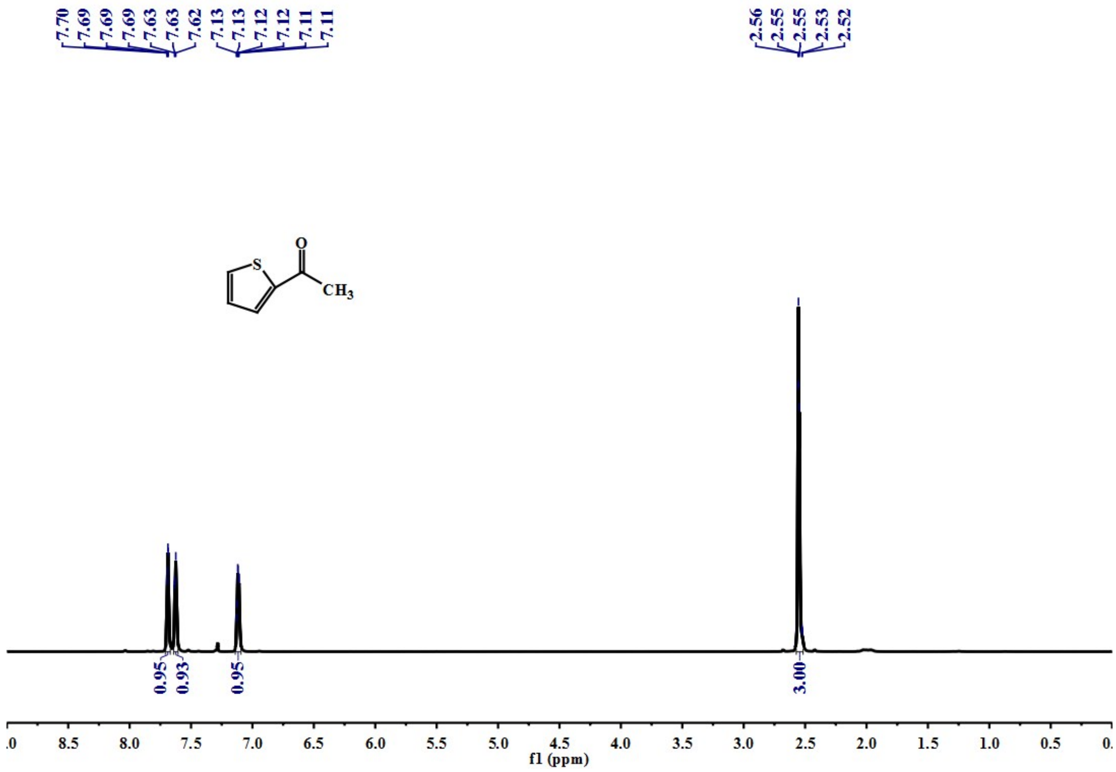

$^{13}$C NMR spectra of **44**(125 MHz, $CDCl_3$)



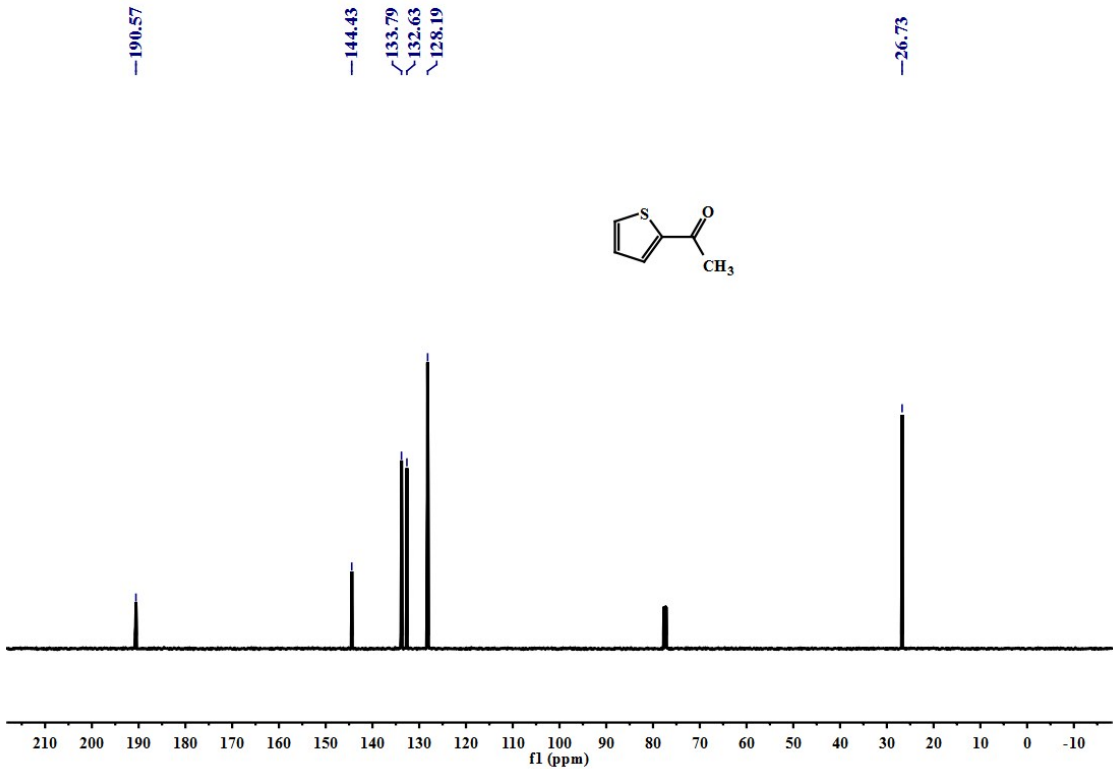

$^{1}$H NMR spectra of **45**(500 MHz, $CDCl_3$)



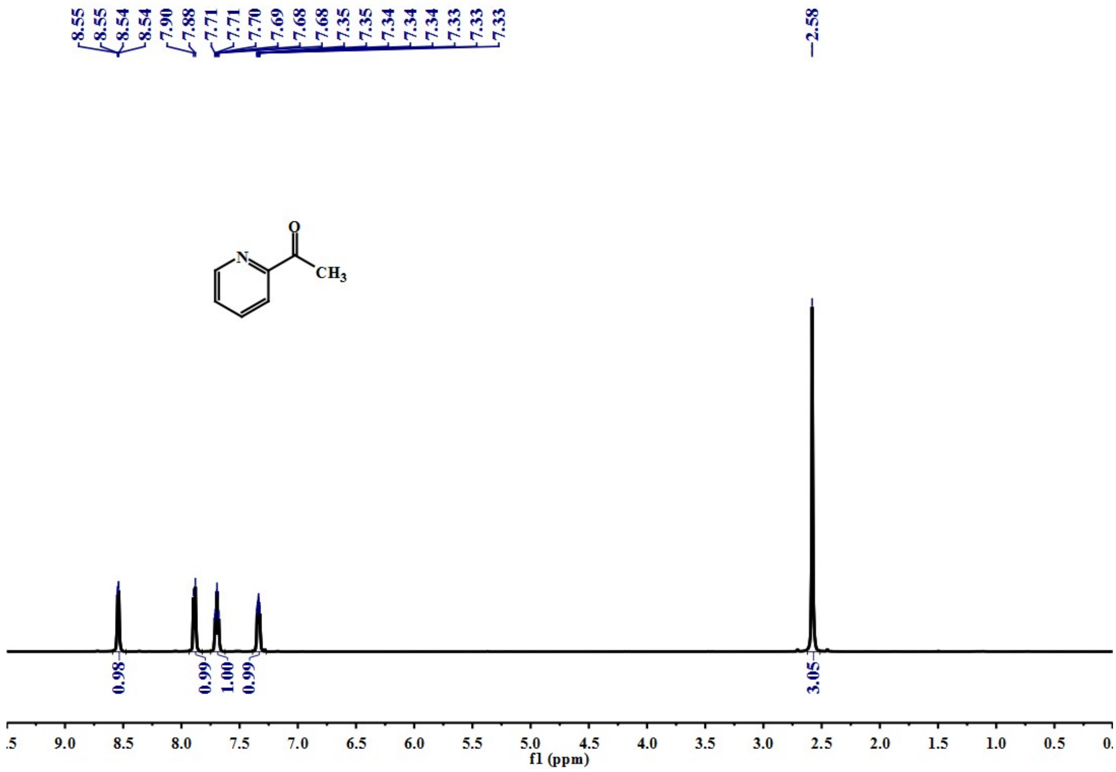

$^{13}$C NMR spectra of **45**(125 MHz, $CDCl_3$)



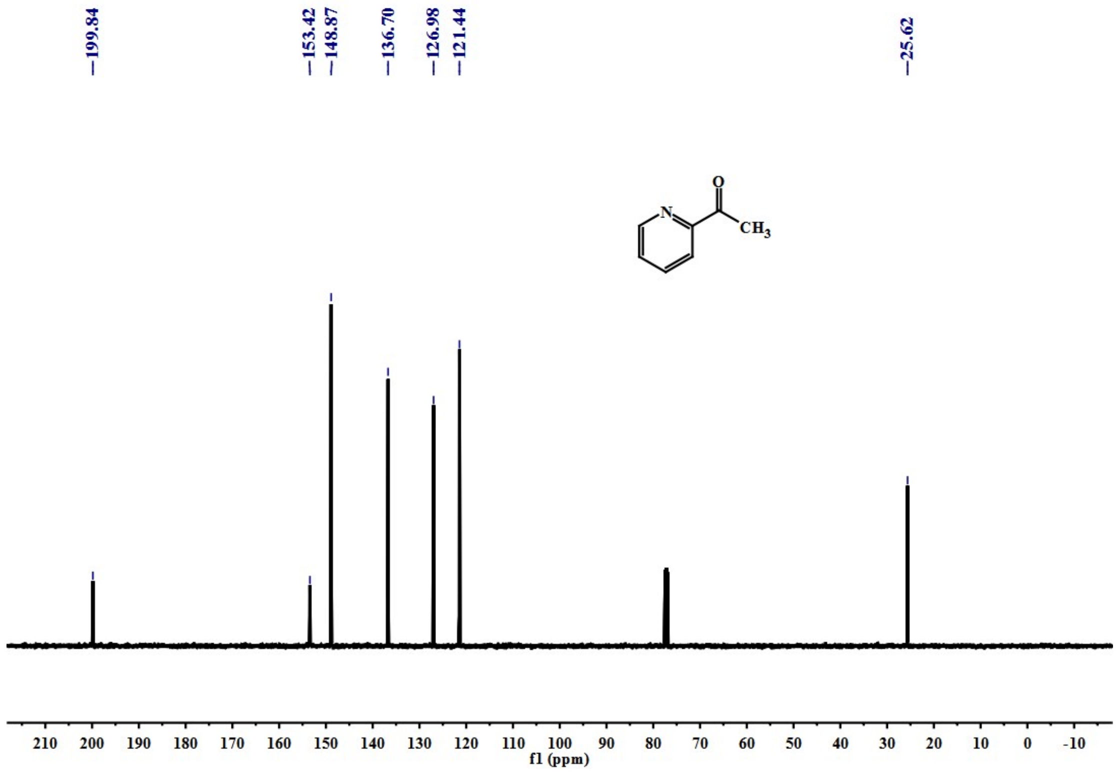
$^1$H NMR spectra of **46**(500 MHz, $CDCl_3$)



$^{13}$C NMR spectra of **46**(125 MHz, $CDCl_3$)




$^{1}$H NMR spectra of **47**(500 MHz, $CDCl_3$)




$^{13}$C NMR spectra of **47**(125 MHz, $CDCl_3$)