**Electronic Supplementary Information for**

# Selective oxidative cleavage of terminal olefins into aldehydes catalyzed by copper(II) complex

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## Supporting Information

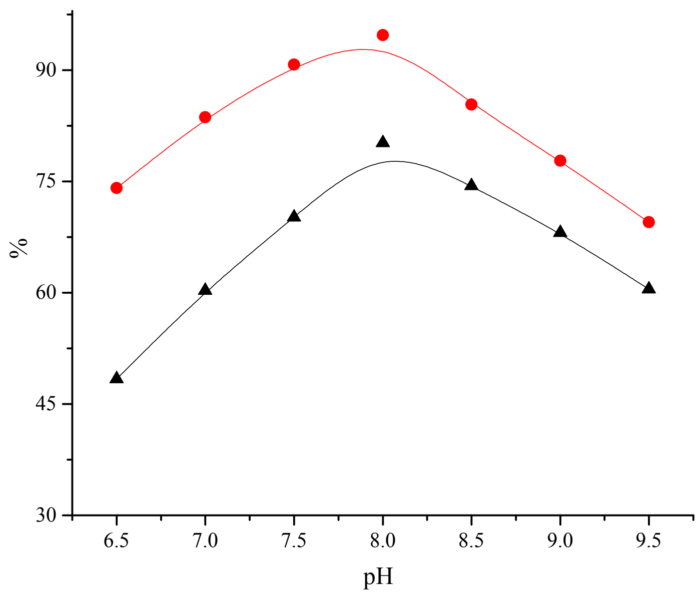


**Fig. S1** The yield and selectivity of benzaldehyde as a function of solution pH for the catalytic oxidation of styrene. $[styrene]_0$ = 0.05 mol·L$^{-1}$, $[H_2O_2]_0$ = 0.25 mol·L$^{-1}$, [LCu] = 2×10$^{-4}$ mol·L$^{-1}$, pH8.0, 30 ℃. ▲ yield, ● selectivity

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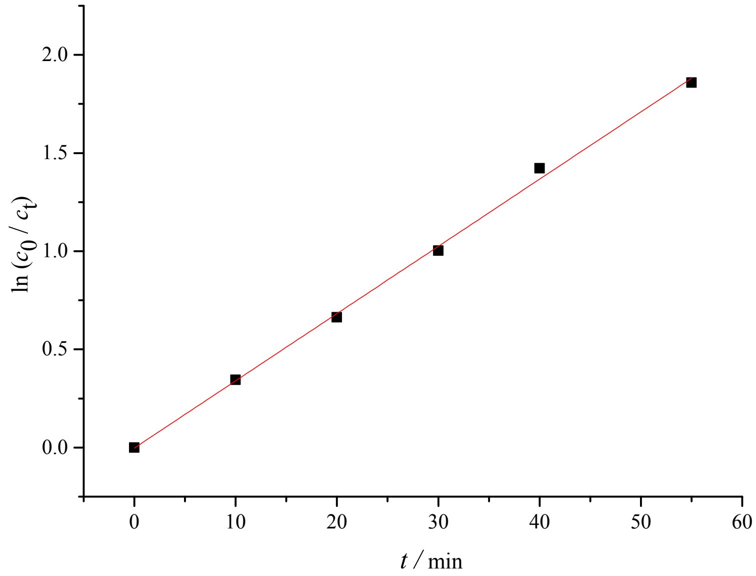



**Fig. S2** Plots of ln($c_0$/$c_t$) *vs.* reaction time $t$ for the oxidation of styrene. [styrene]$_0$ = 0.01 mol·L$^{-1}$, [$H_2O_2$]$_0$ = 0.2 mol·L$^{-1}$, [LCu] = 4×10$^{-5}$ mol·L$^{-1}$, pH8.0, 30 ℃.

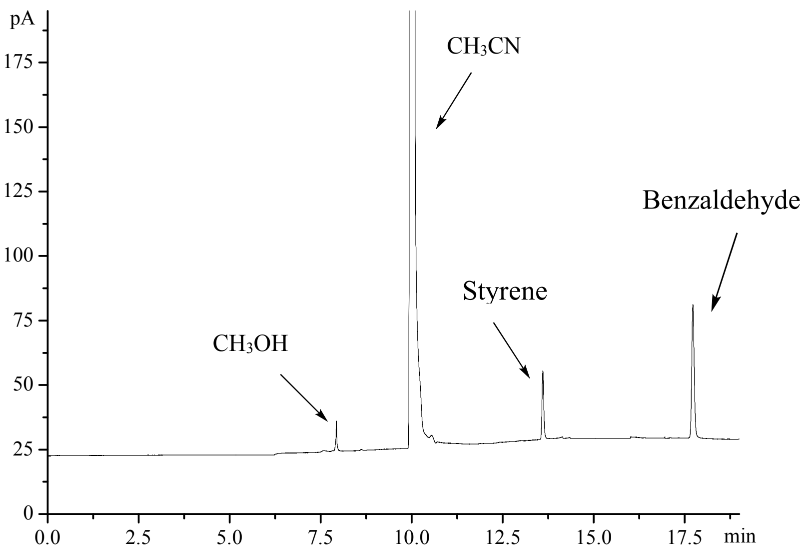



**Fig. S3** GC profile of styrene oxidation reaction in acetonitrile after 1 h. [styrene]$_0$ = 0.05 mol·L$^{-1}$, [$H_2O_2$]$_0$ = 0.25 mol·L$^{-1}$, [LCu] = 2×10$^{-4}$ mol·L$^{-1}$, pH8.0, 30 ℃.

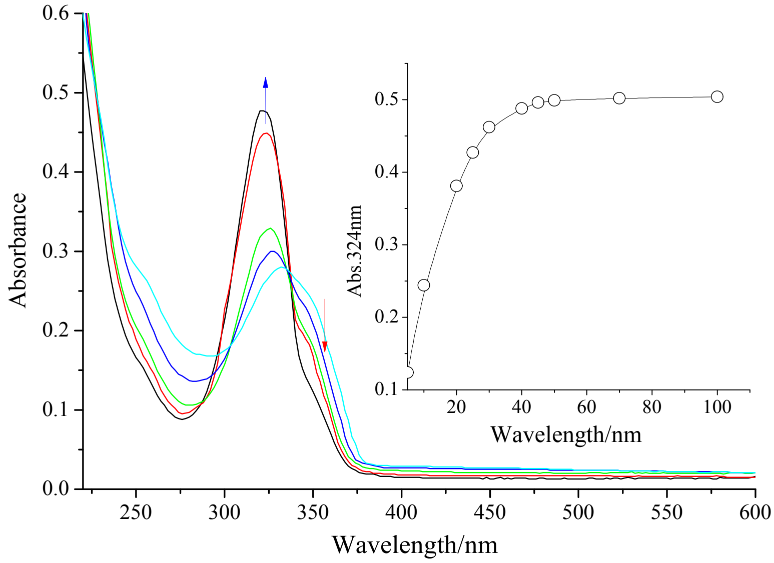



**Fig. S4** The UV-Vis spectral changes showing the reactive species vs time *t* at pH8.0 and 30 ℃. Insert: time course of absorbance change of the active species at 324 nm.

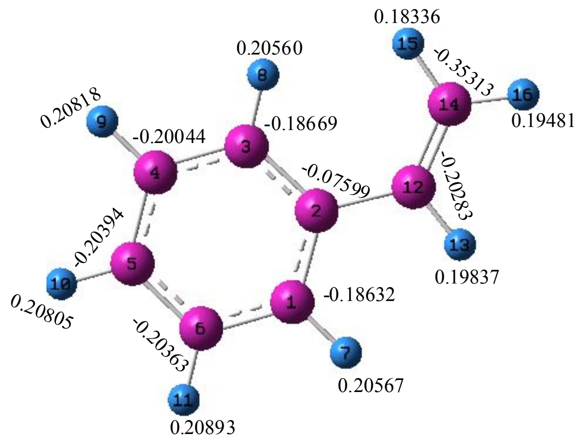



**Fig. S5** NBO charge distributions of styrene were carried out at the mpwb95/6-311G(d, p) pop=nbo level. (carbon atoms are illustrated in red, hydrogen atom in blue).

## Methods

### Typical Method for isolation of aldehydes 2a, 2b, 2c, 2d, 2e, 2g, 2i, 2k and 2l

The typical oxidative cleavage reaction solution in Table 3 containing 0.5 mol·L$^{-1}$ olefin, 2×10$^{-3}$ mol·L$^{-1}$ copper(II) complex and 2.5 mol·L$^{-1}$ $H_2O_2$. After the resulting mixture was stirred at 30 ℃ for 1 h, the mixture was then extracted with dichloromethane, and the combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered and the solvent removed under vacuum. The crude product was purified via a standard silica gel chromatography using hexanes/ethyl acetate (=10/1-1/1, v/v) as eluent to give the desired aldehyde product. To ensure the general synthetic utility of our catalytic system, isolated products were characterized by NMR (in $CDCl_3$ with TMS as an internal standard) and ESI-MS. All the reactions were performed at least three times to establish the reproducibility and reliability.

**NMR data for aldehyde 2a, 2b, 2c, 2d, 2e, 2g, 2i, 2k and 2l matched that reported in literatures.**[S1-S3]

Benzaldehyde[S1], **2a**, yield: 73.2%. $^1$H NMR (400MHz, $CDCl_3$) δ 7.53-7.56 (m, 2H), 7.62-7.67 (m, 1H), 7.88-7.91 (m, 2H), 10.03 (s, 1H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 192.43, 136.37, 134.48, 129.74, 129.00. ESI-MS: m/z 107.05 (Calcd. for [$M^+$+1]: 107.04).

4-methyl-benzaldehyde[S1], **2b**, yield: 72.2%. $^1$H NMR (400MHz, $CDCl_3$) δ 2.43 (s, 3H), 7.32 (d, J=8.0 Hz, 2H), 7.77 (d, J=8.0 Hz, 2H), 9.96 (s, 1H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 191.98, 145.54, 134.17, 129.83, 129.70, 21.86; ESI-MS: m/z 121.07 (Calcd. for [$M^+$+1]: 121.06).

4-methoxy-benzaldehyde[S1], **2c**, yield: 70.3%. $^1$H NMR (400MHz, $CDCl_3$) δ 3.88 (s, 1H), 7.00 (d, J=8.0 Hz, 2H), 7.84 (d, J=8.0 Hz, 2H), 9.88 (s, 1H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 190.87. 164.61, 132.00, 129.92, 114.32, 55.60; ESI-MS: m/z 137.05 (Calcd. for [$M^+$+1]: 137.05).

3,4-Dimethoxybenzaldehyde[S1], **2d**, yield: 73.0%. $^1$H NMR (400MHz, $CDCl_3$) δ 3.96 (s, 3H), 3.99 (s, 3H), 7.00 (d, J=8.0 Hz, 1H), 7.43 (d, J=1.6 Hz, 1H), 7.47-7.50 (dd, J=8.0 2.0 Hz, 1H), 9.87 (s, 1H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 190.96, 154.46, 149.59, 130.11, 126.96, 110.35, 108.83, 56.21, 56.03; ESI-MS: m/z 167.07 (Calcd. for [$M^+$+1]: 166.06).

4-hydroxy-3-methoxybenzaldehyde [S1], **2e**, yield: 70.1%. $^1$H NMR (400MHz, $CDCl_3$) δ 3.99 (s, 1H), 6.31 (s, 1H), 7.06 (d, J=8.0 Hz, 1H), 7.44-7.46 (m, 2H), 9.85 (s, 1H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 190.94, 151.69, 147.15, 129.87, 127.58, 114.34, 108.80, 56.13; ESI-MS: m/z 153.04 (Calcd. for [$M^{+}$+1]: 153.02).

4-Bromobenzaldehyde[S1], **2g**, yield: 68.8%. $^{1}$H NMR (400MHz, $CDCl_3$) δ 7.71 (d, J=8.0 Hz, 2H), 7.77 (d, H=8.0 Hz, 2H), 10.00 (s, 1H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 191.12, 135.04, 132.45, 130.99, 129.81; ESI-MS: m/z 184.90 (Calcd. for [$M^{+}$+1]: 184.96 ).

4-Nitrobenzaldehyde[S1], **2i**, yield: 61.9%. $^{1}$H NMR (400MHz, $CDCl_3$) δ 8.09-8.12 (m, 2H), 8.42 (d, J=8.0 Hz, 2H), 10.18 (s, 1H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 190.35, 151.13, 140.04, 130.62, 124.34; ESI-MS: m/z 152.01 (Calcd. for [$M^{+}$+1]: 152.03).

Phenylacetaldehyde[S2], **2k**, yield: 51.1%. $^{1}$H NMR (400MHz, $CDCl_3$) δ 3.72 (d, J=2.4 Hz, 2H), 7.25-7.43 (m, 5H), 9.78 (t, J=2.4 Hz, 1H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 199.56, 131.86, 129.66, 129.03, 127.45, 50.60; ESI-MS: m/z 143.07 (Calcd. for [$M^{+}$+Na]: 143.06).

Heptaldehyde [S3], **2l**, yield: 56.5%. $^{1}$H NMR (400MHz, $CDCl_3$) δ 0.85-0.89 (m, 3H), 1.29 (s, 6H), 1.58-1.65 (m, 2H), 2.39-2.43 (td, J=7.2 2.0 Hz, 2H), 9.75 (t, J=1.6 Hz, 1H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 202.90, 43.87, 31.51, 28.80, 22.42, 22.00, 13.95; ESI-MS: m/z 115.10 (Calcd. for [$M^{+}$+1]: 115.10).

## Notes and References


S1 N. Jiang and A. J. Ragauskas, *Org. Lett.,* 2005, **7**, 3689.

S2 A. D. Chowdhury, R. Ray and G. K. Lahiri, *Chem. Commun.,* 2012, **48**, 5497.

S3 V. Kogan, M. M. Quintal and R. Neumann, *Org. Lett.*, 2005, **7**, 5039.


## NMR spectra

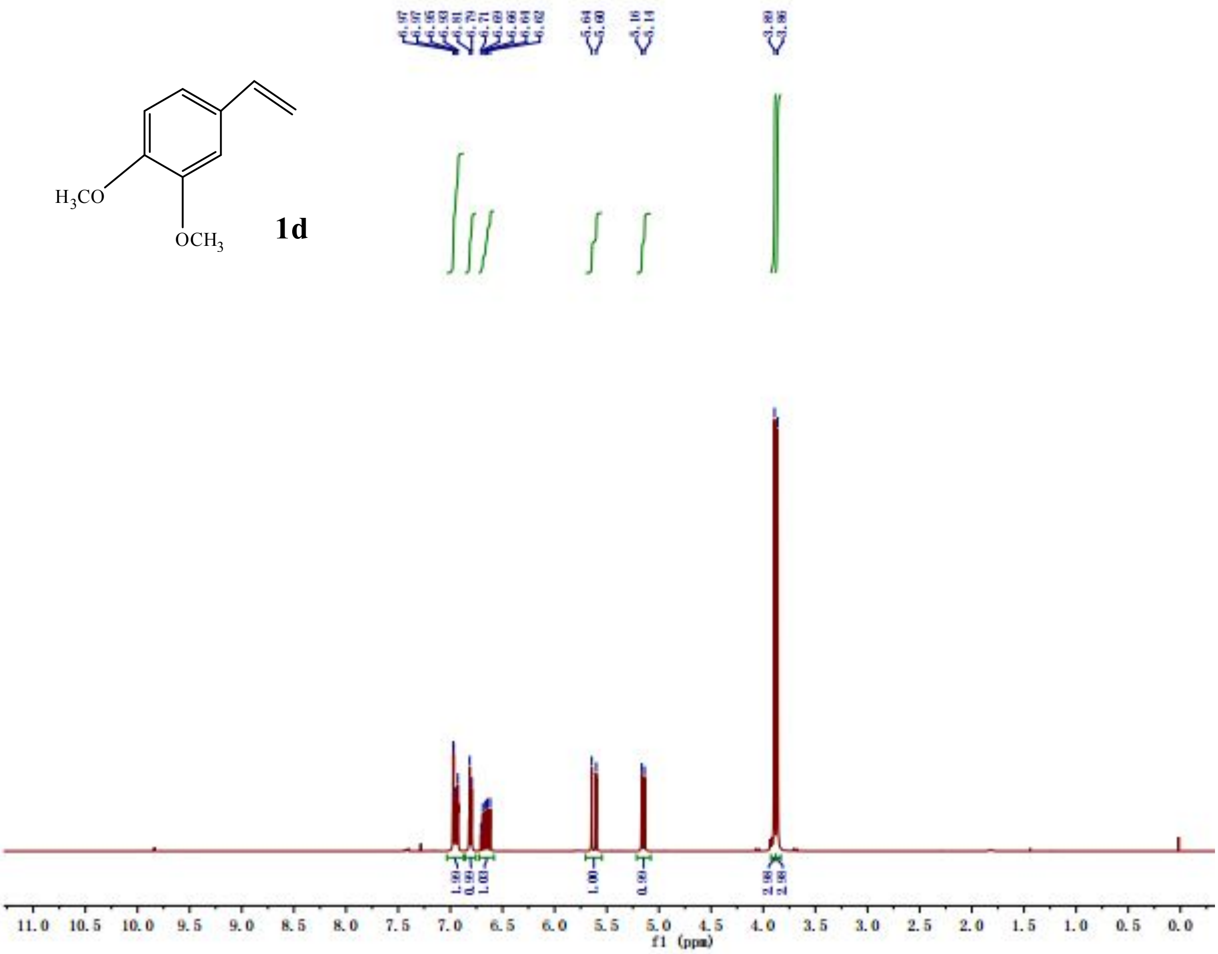


**Fig. S6** The [1]HNMR spectrum of the 1,2-dimethoxy-4-vinylbenzene (**1d**).

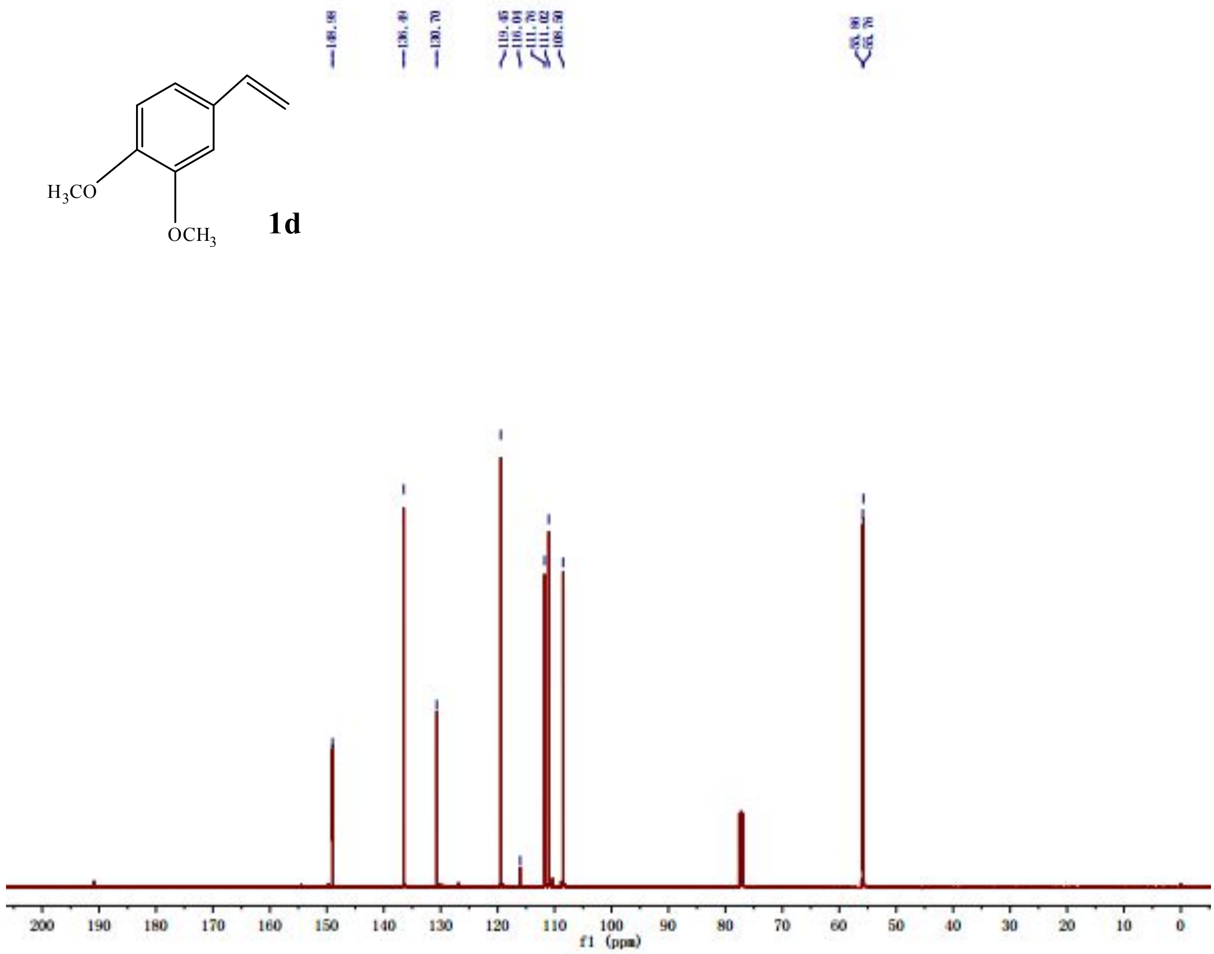



**Fig. S7** The $^{13}$CNMR spectrum of the 1,2-dimethoxy-4-vinylbenzene (**1d**).

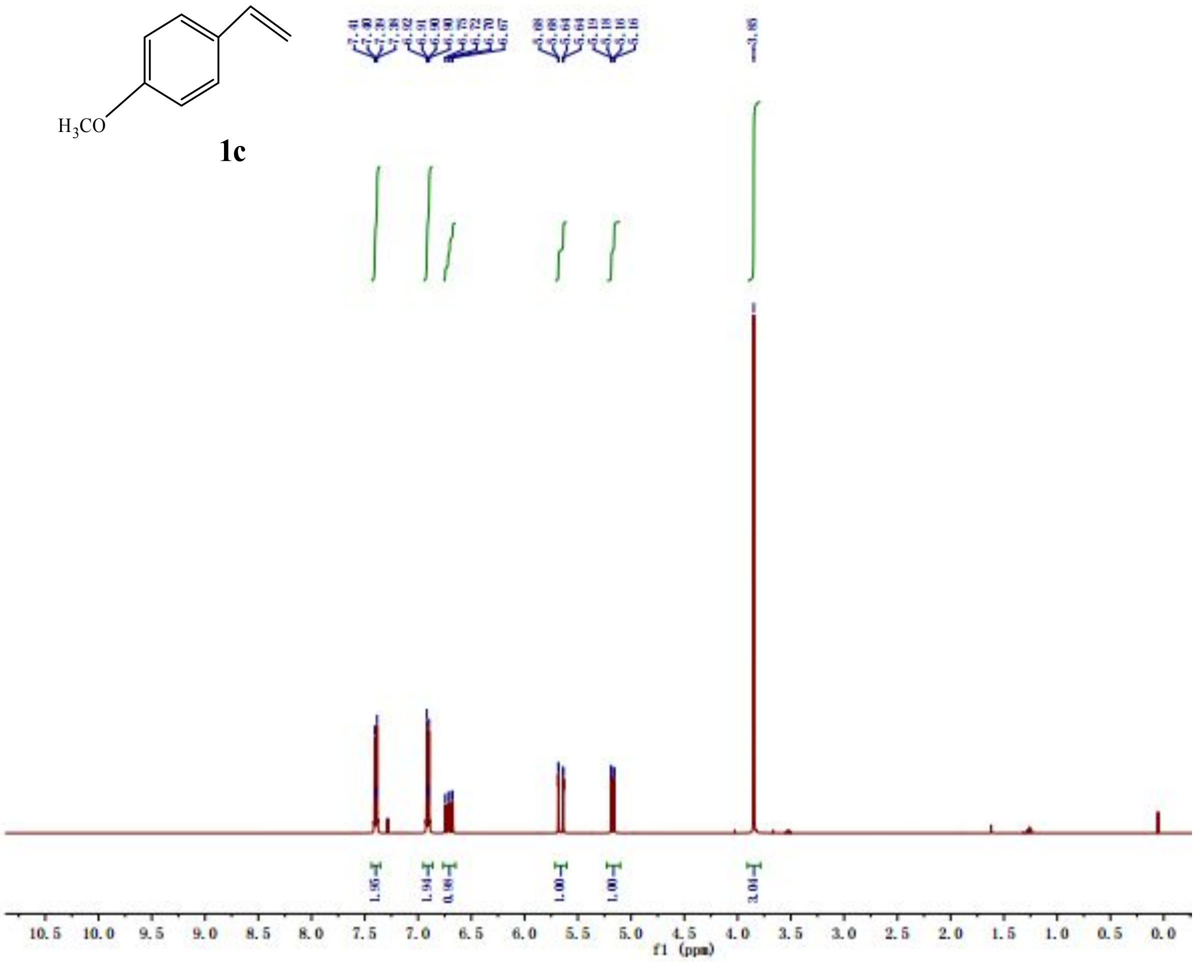


**Fig. S8** The $^{1}$HNMR spectrum of the 1-methoxy-4-vinylbenzene (**1c**).

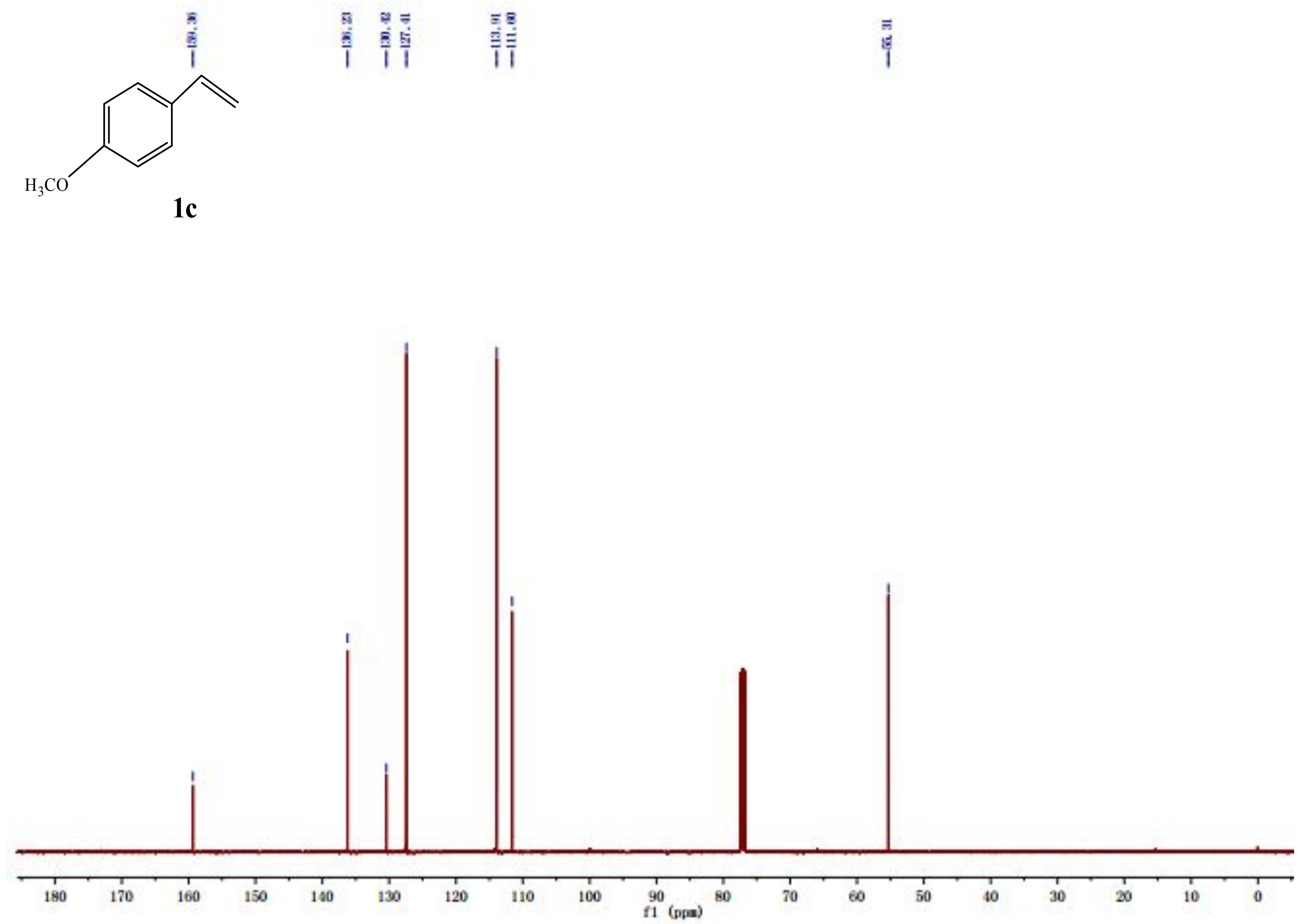
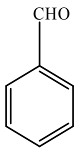



**Fig. S9** The $^{13}$CNMR spectrum of the 1-methoxy-4-vinylbenzene (**1c**).



2a

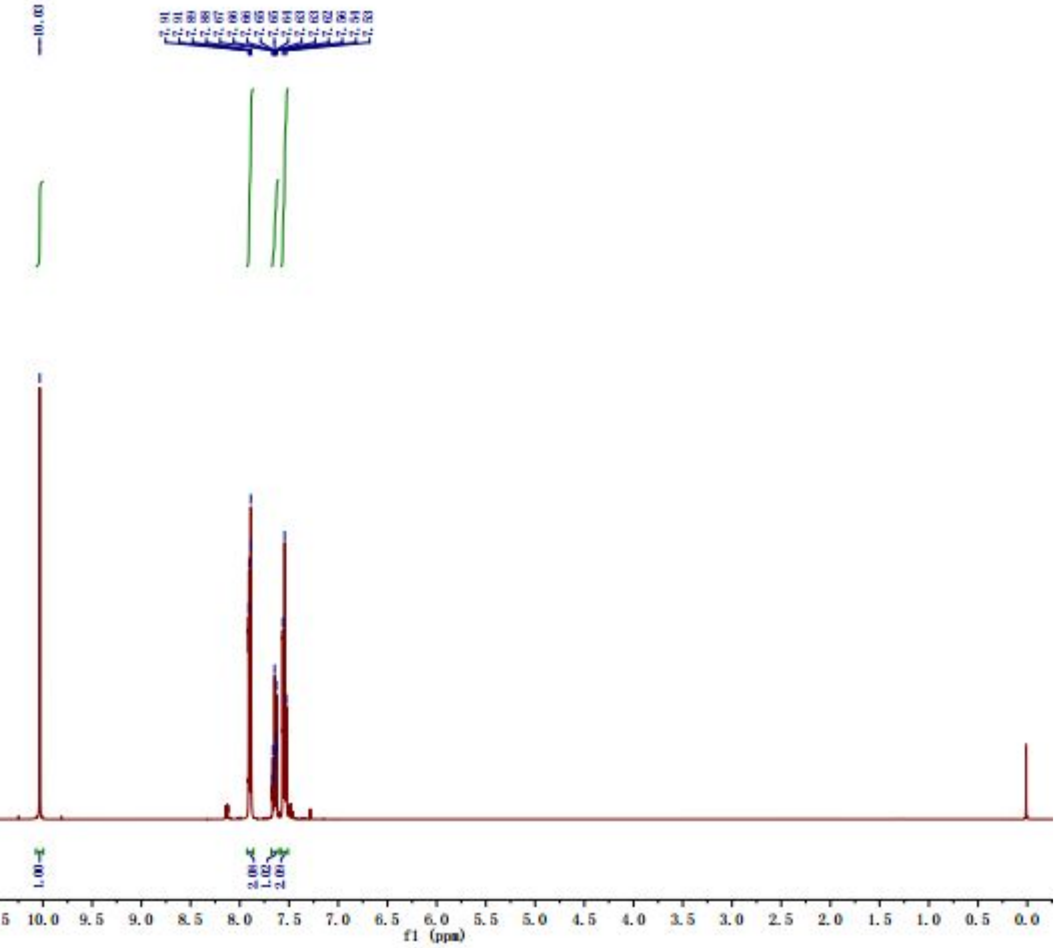


**Fig. S10** The $^{1}$HNMR spectrum of the Benzaldehyde (**2a**).

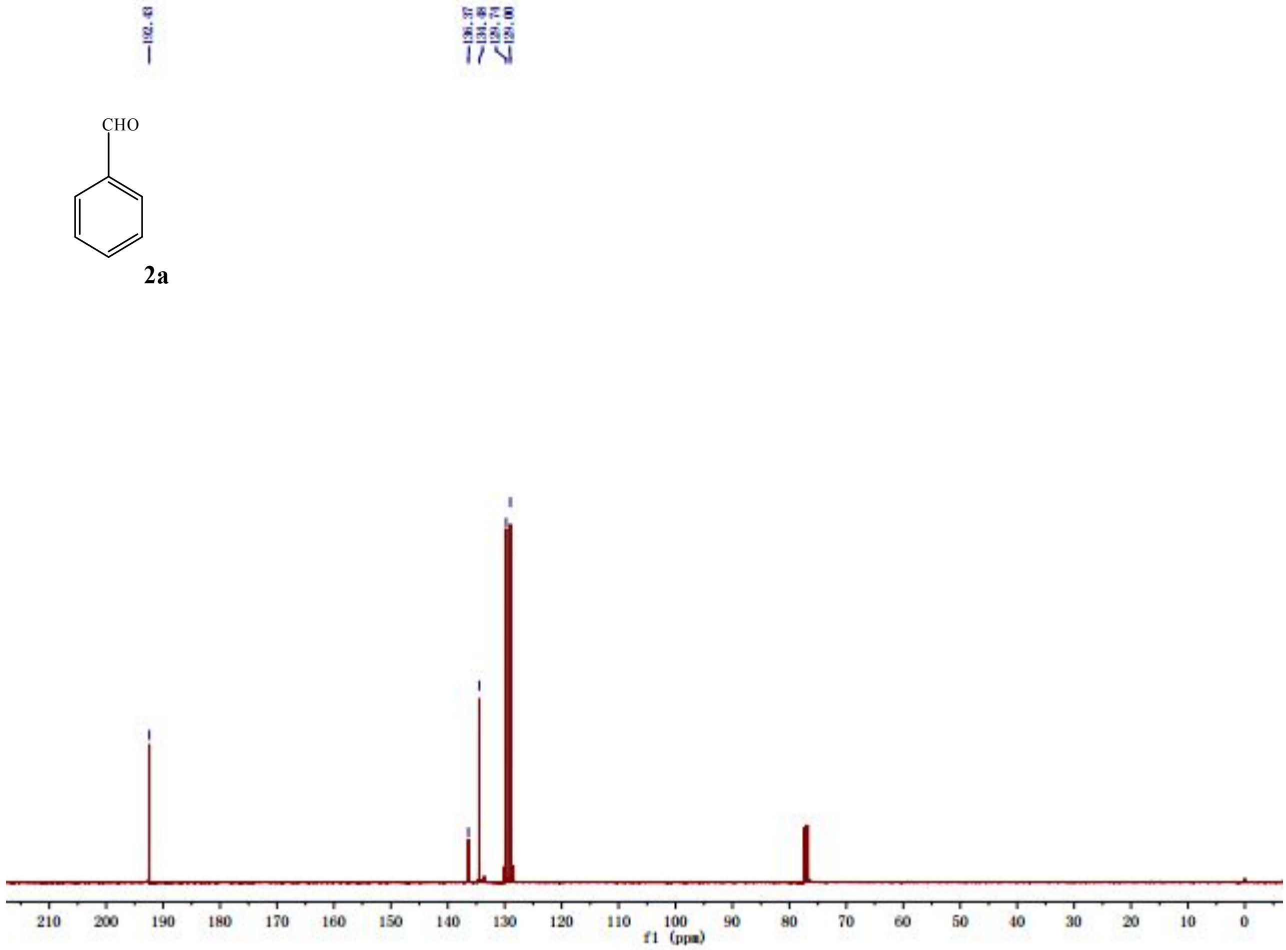



**Fig. S11** The $^{13}$CNMR spectrum of the Benzaldehyde (**2a**).

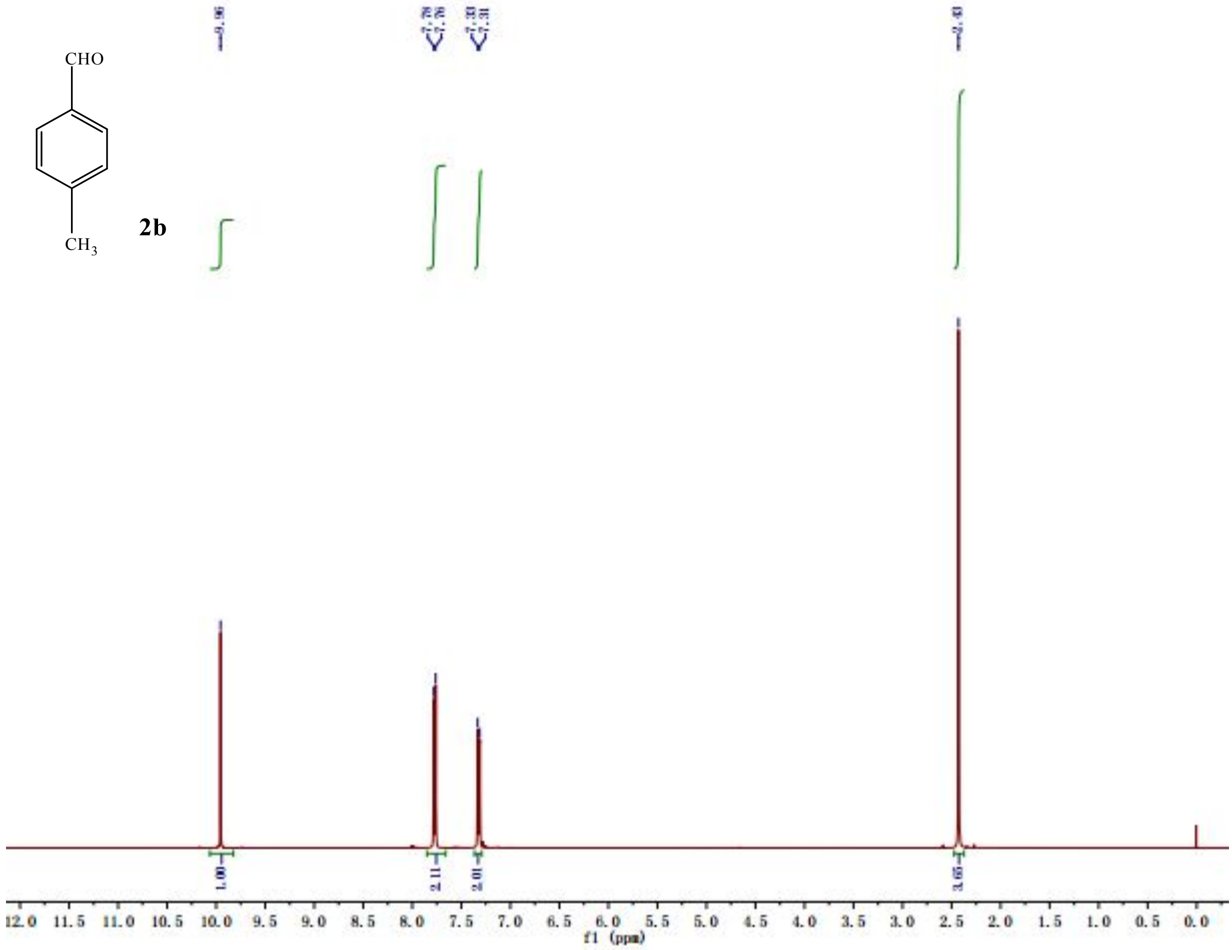


**Fig. S12** The [13]HNMR spectrum of the 4-methyl-benzaldehyde (**2b**).

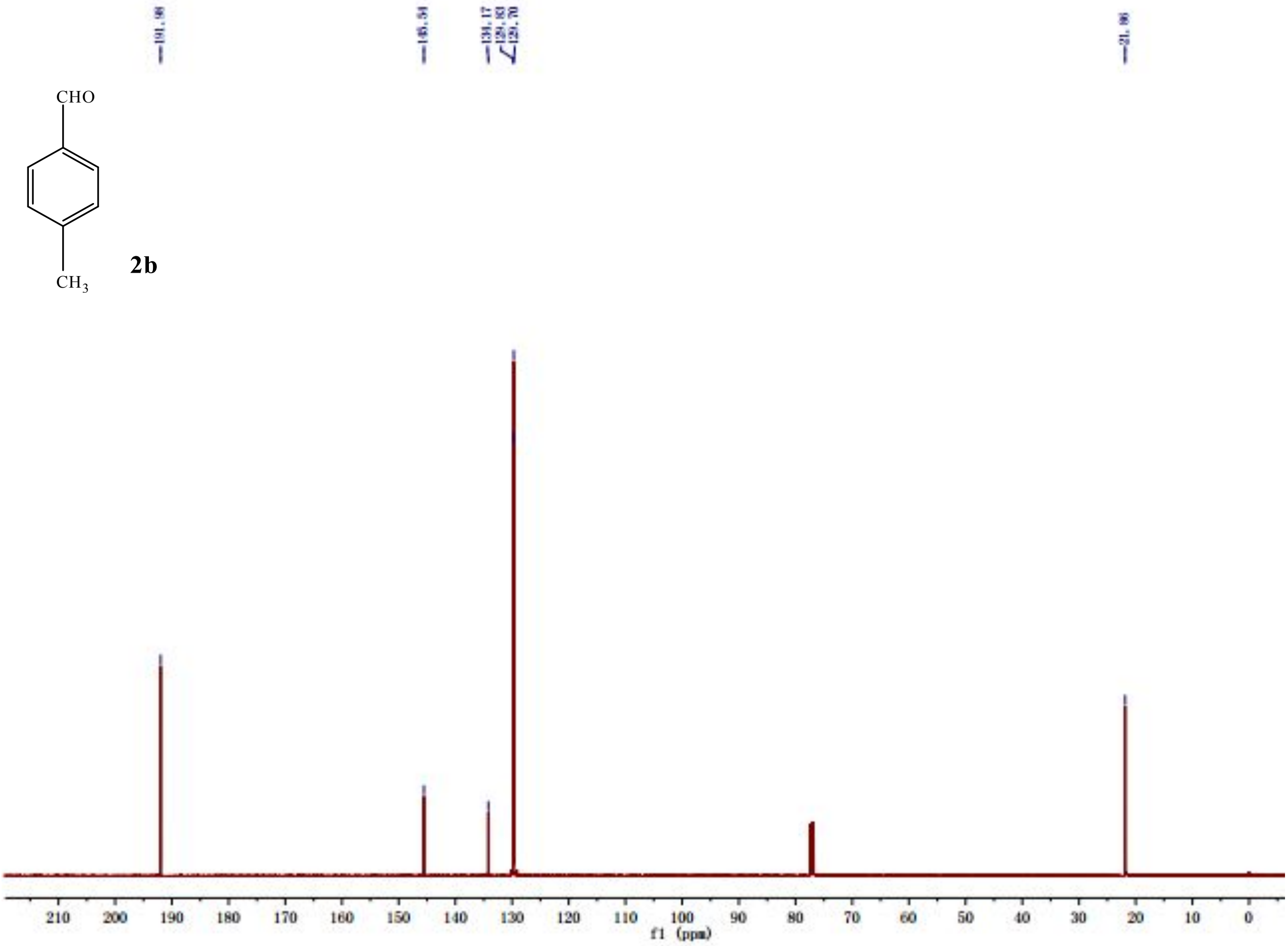
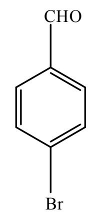



**Fig. S13** The [13]CNMR spectrum of the 4-methyl-benzaldehyde (**2b**).



2g

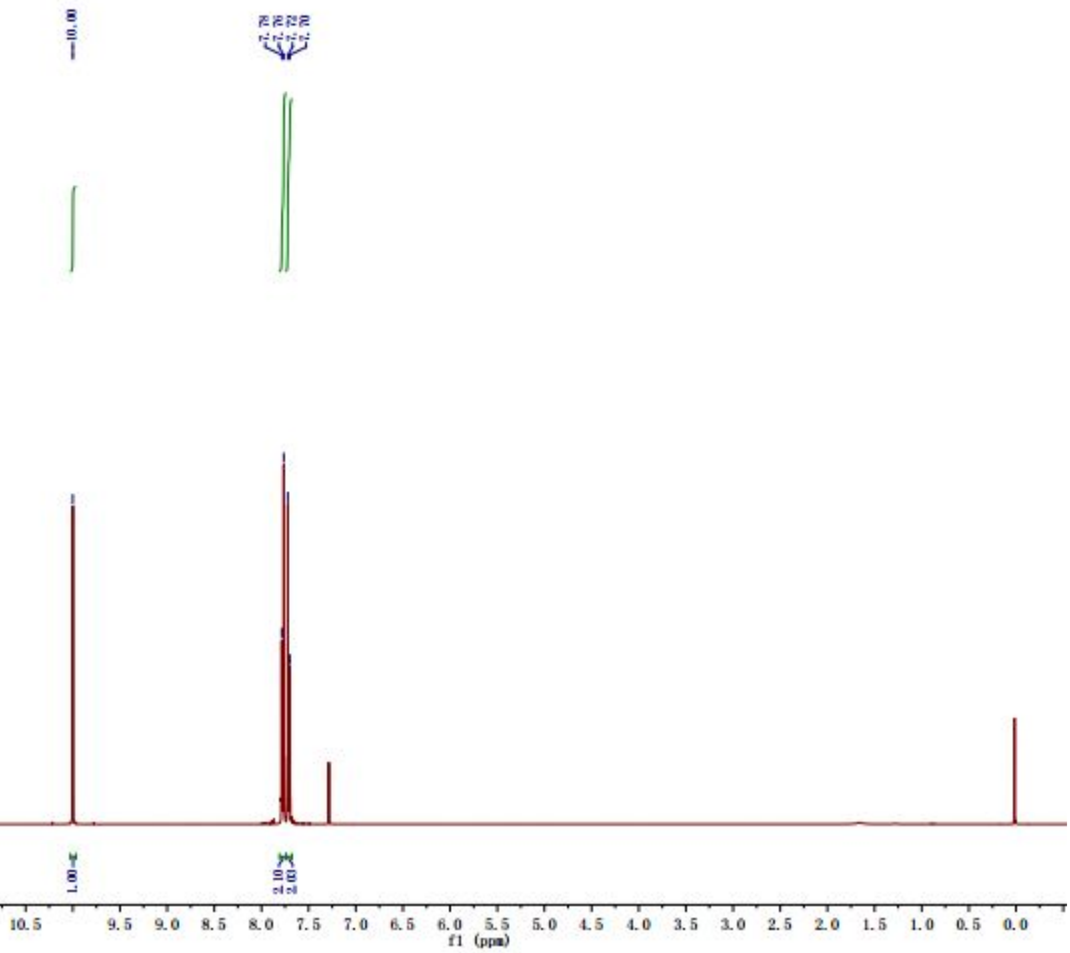



**Fig. S14** The [13]HNMR spectrum of the 4-Bromobenzaldehyde (**2g**).

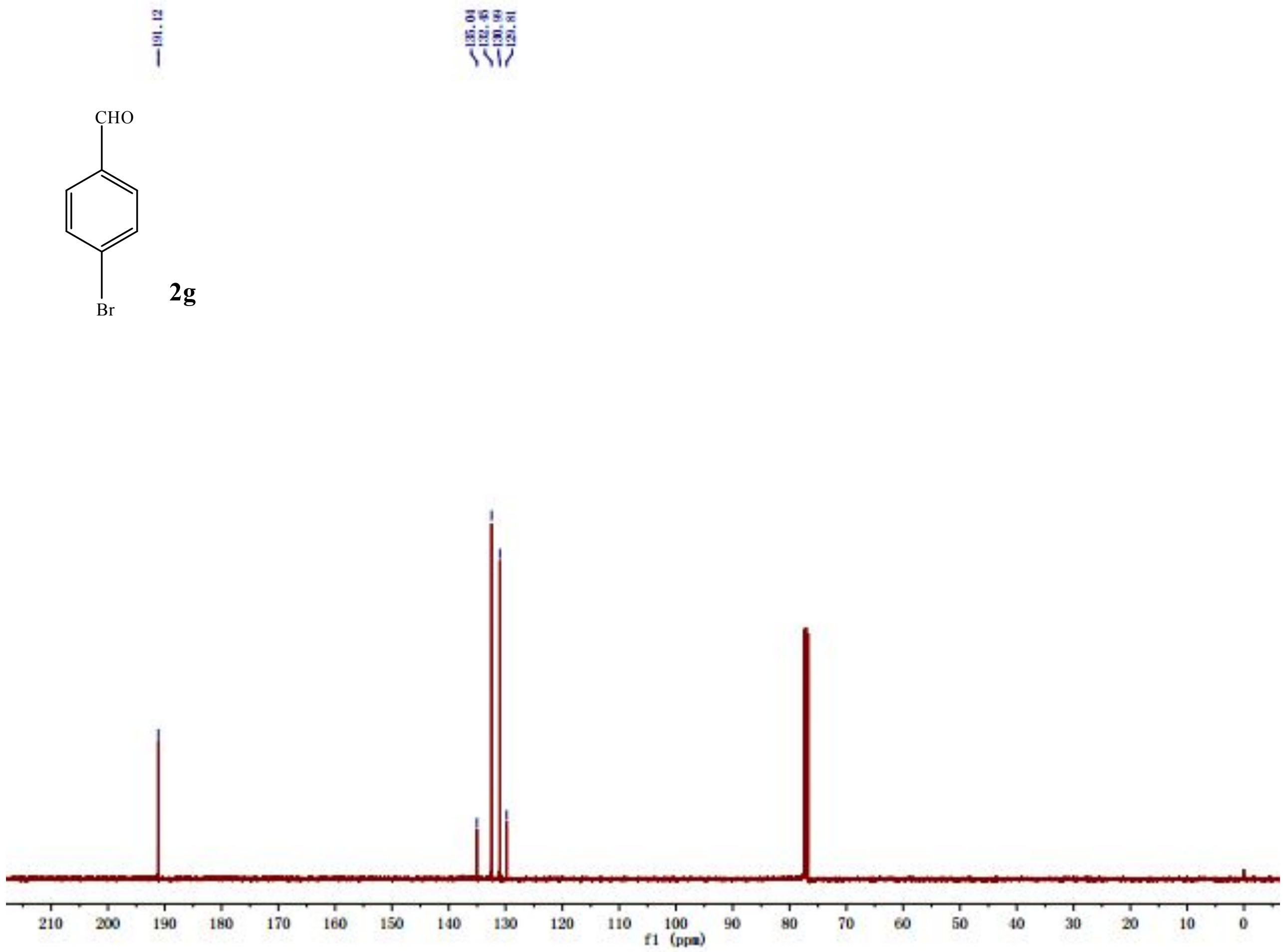



**Fig. S15** The $^{13}$CNMR spectrum of the 4-Bromobenzaldehyde (**2g**).

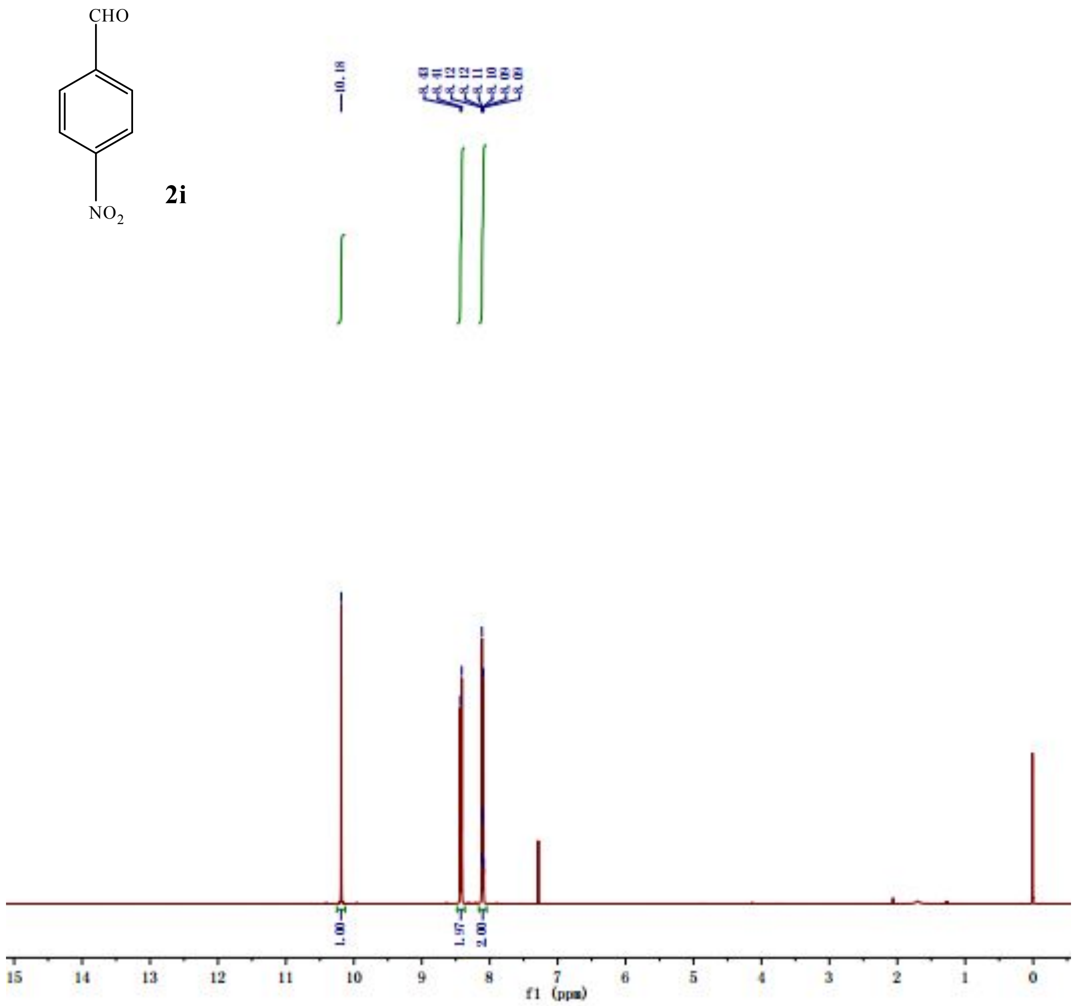



**Fig. S16** The [13]HNMR spectrum of the 4-Nitrobenzaldehyde (**2i**).

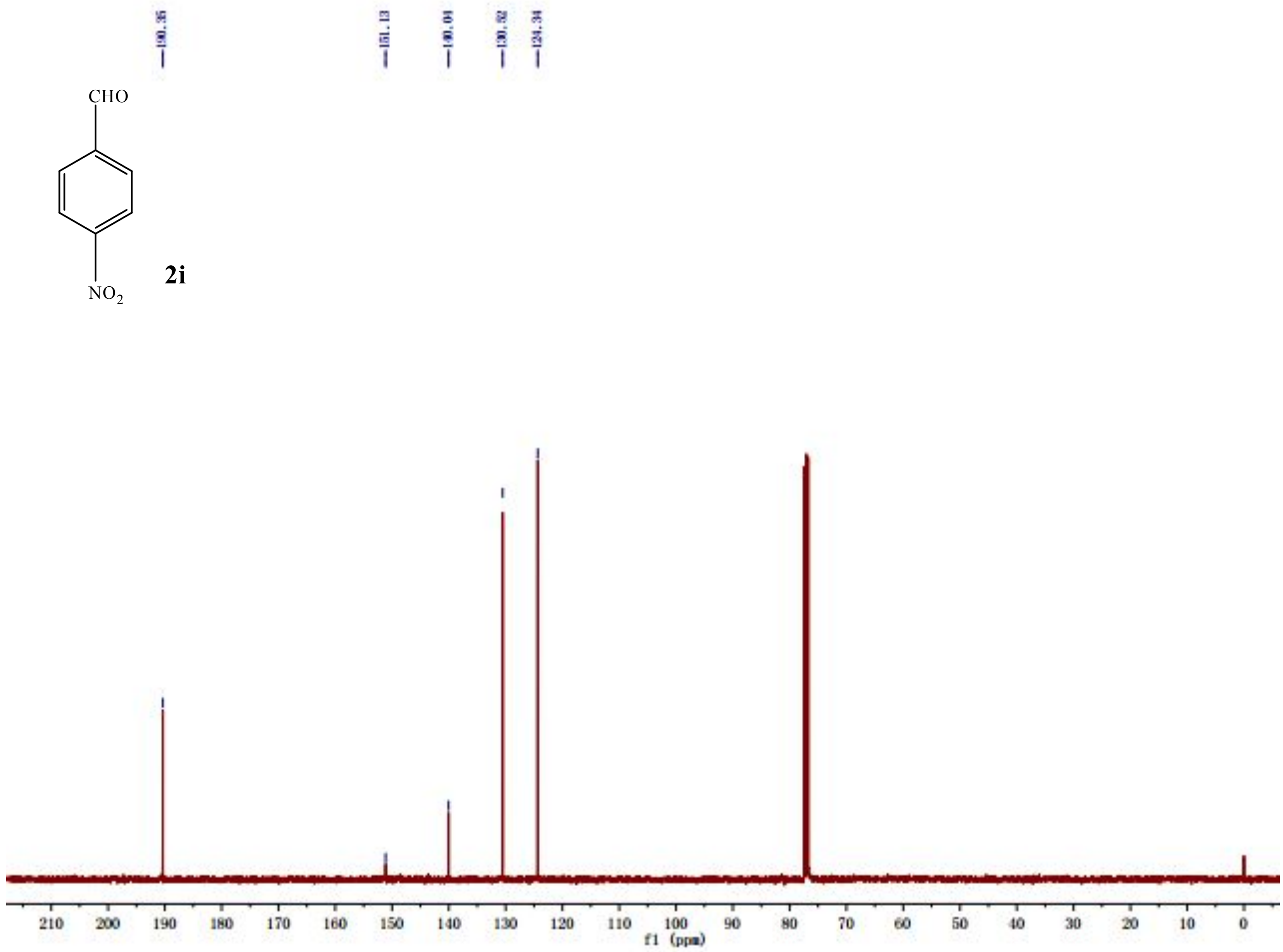



**Fig. S17** The [13]CNMR spectrum of the 4-Nitrobenzaldehyde (**2i**).

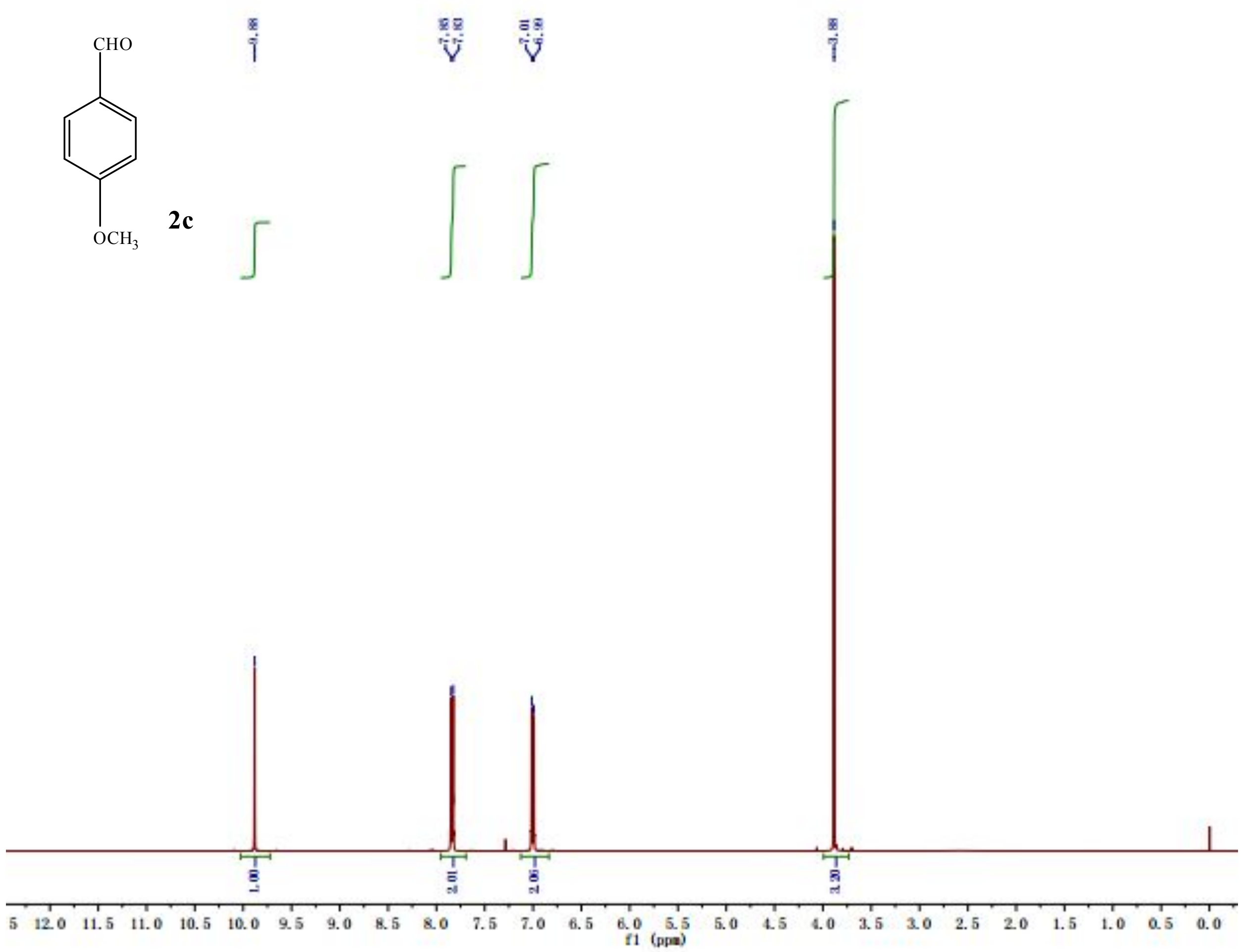



**Fig. S18** The [13]HNMR spectrum of the 4-methoxy-benzaldehyde (**2c**).

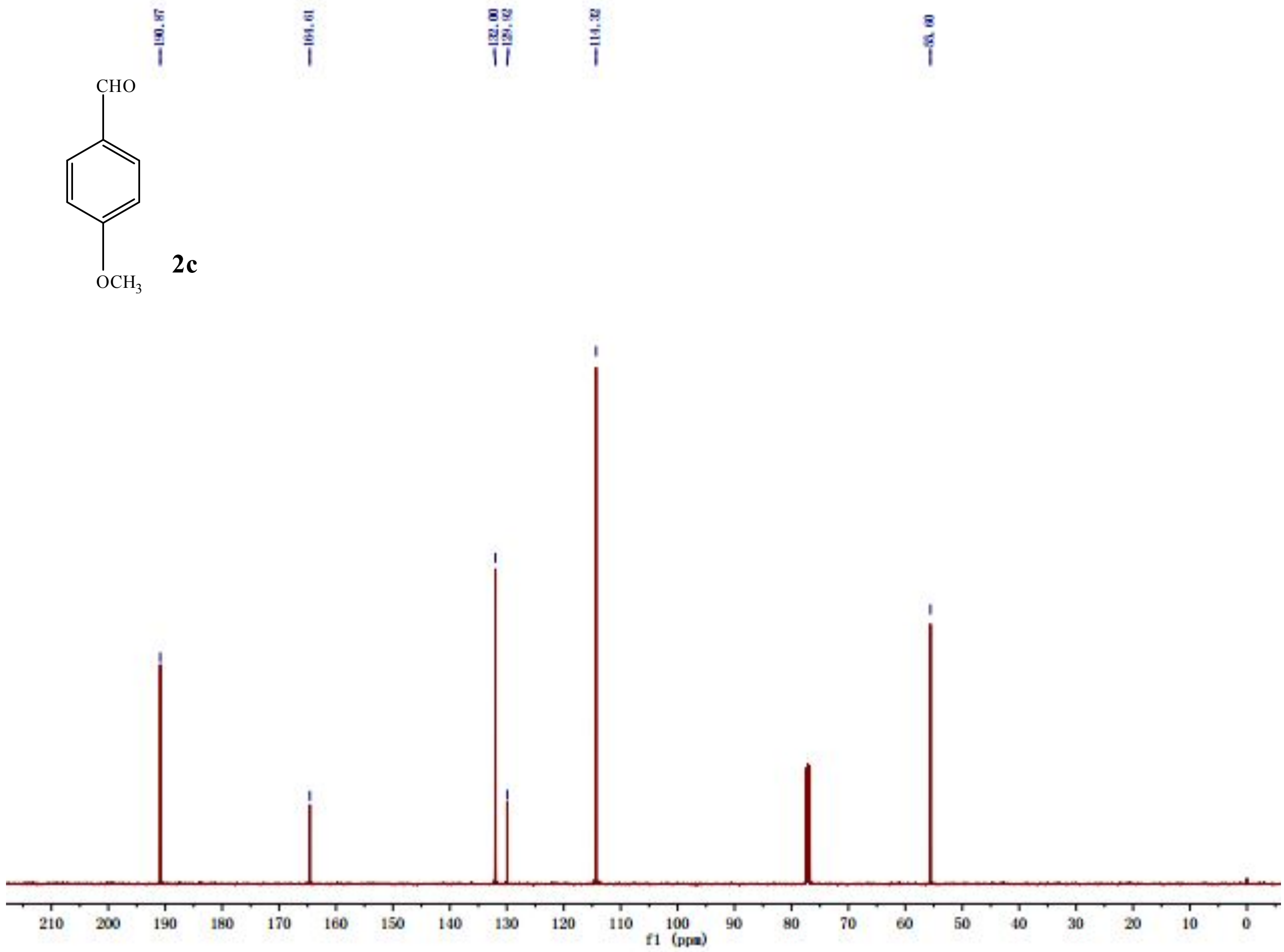



**Fig. S19** The $^{13}$CNMR spectrum of the 4-methoxy-benzaldehyde (**2c**).

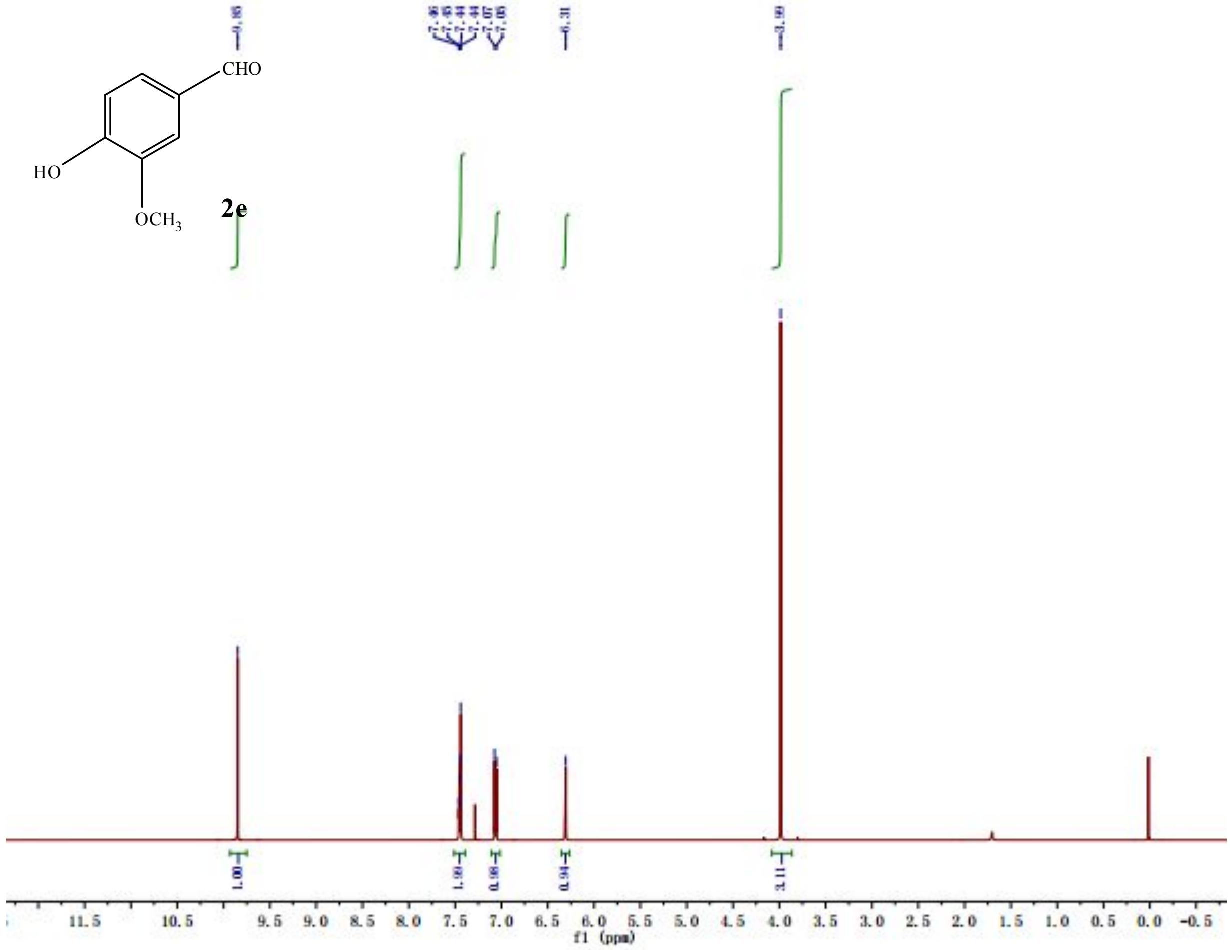
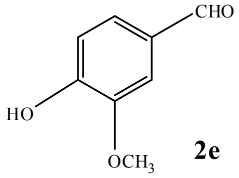


**Fig. S20** The [13]HNMR spectrum of the 4-hydroxy-3-methoxybenzaldehyde (**2e**).




2e

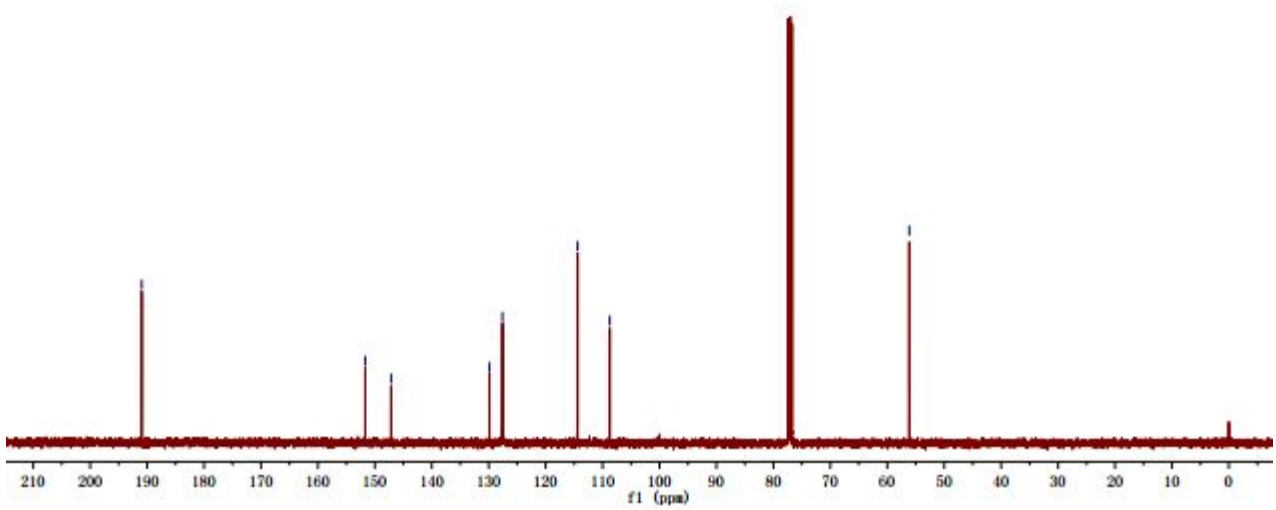



**Fig. S21** The $^{13}$CNMR spectrum of the 4-hydroxy-3-methoxybenzaldehyde (**2e**).

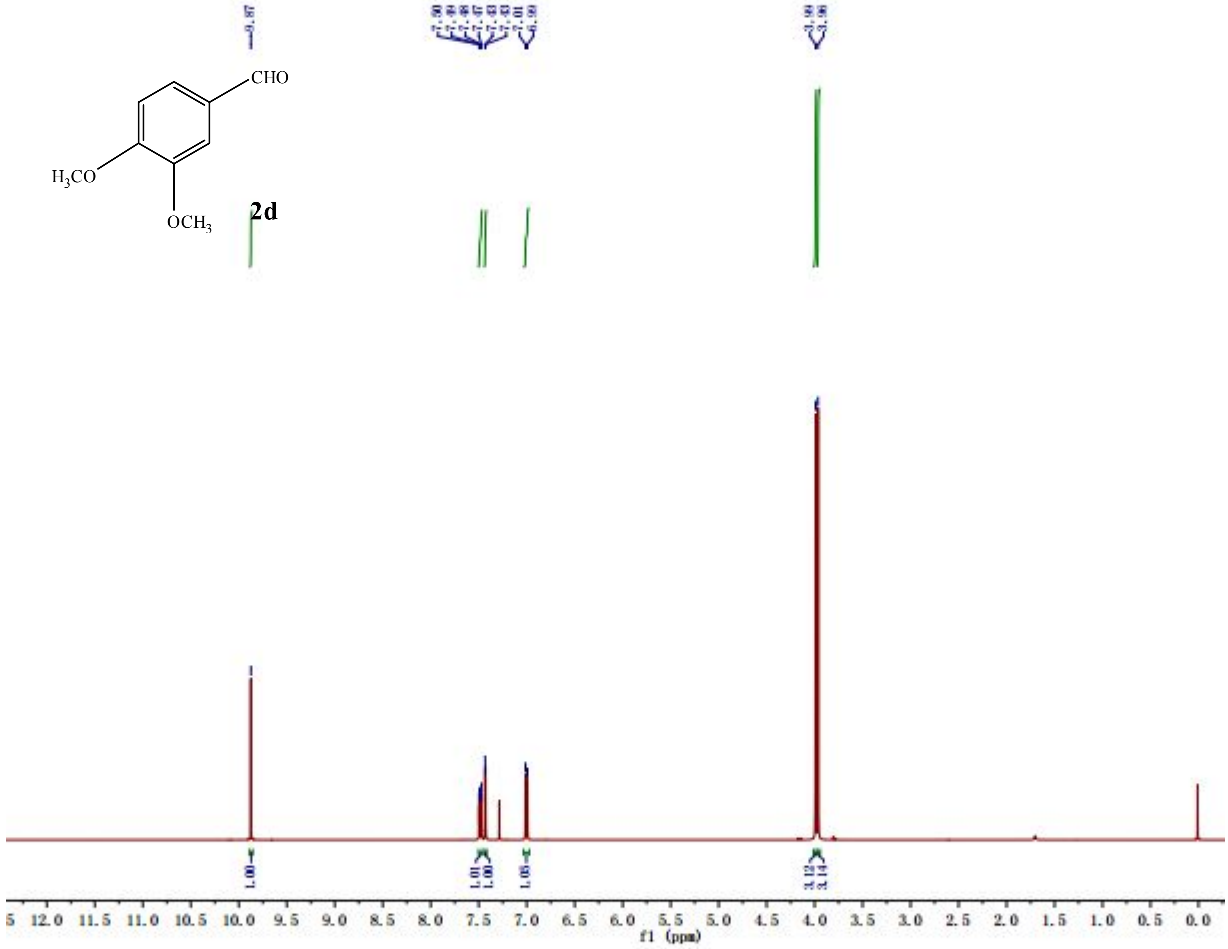


**Fig. S22** The 13HNMR spectrum of the 3,4-Dimethoxybenzaldehyde (**2d**).

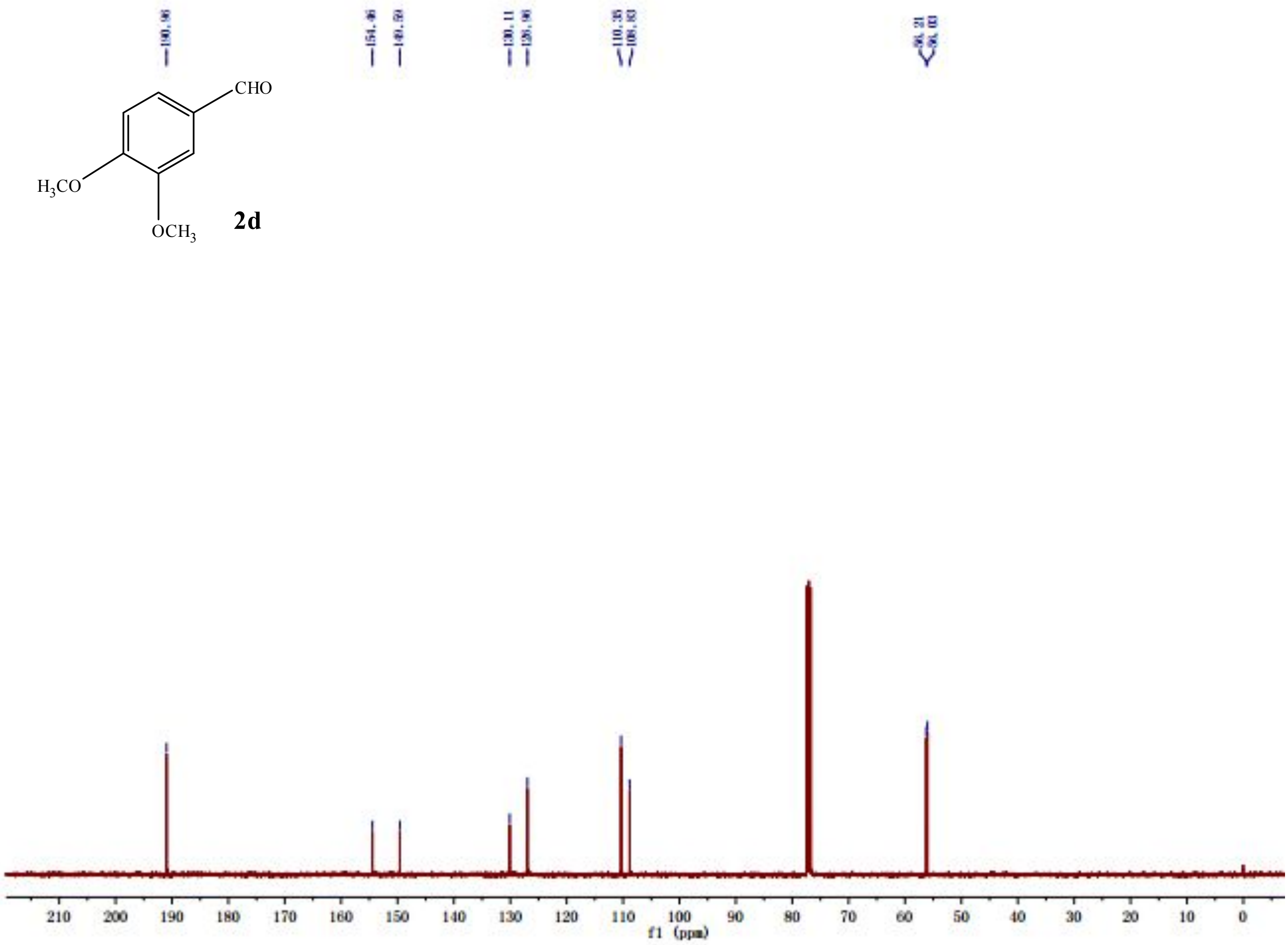
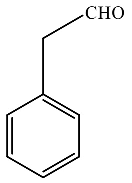



**Fig. S23** The [13]CNMR spectrum of the 3,4-Dimethoxybenzaldehyde (**2d**).




**2k**

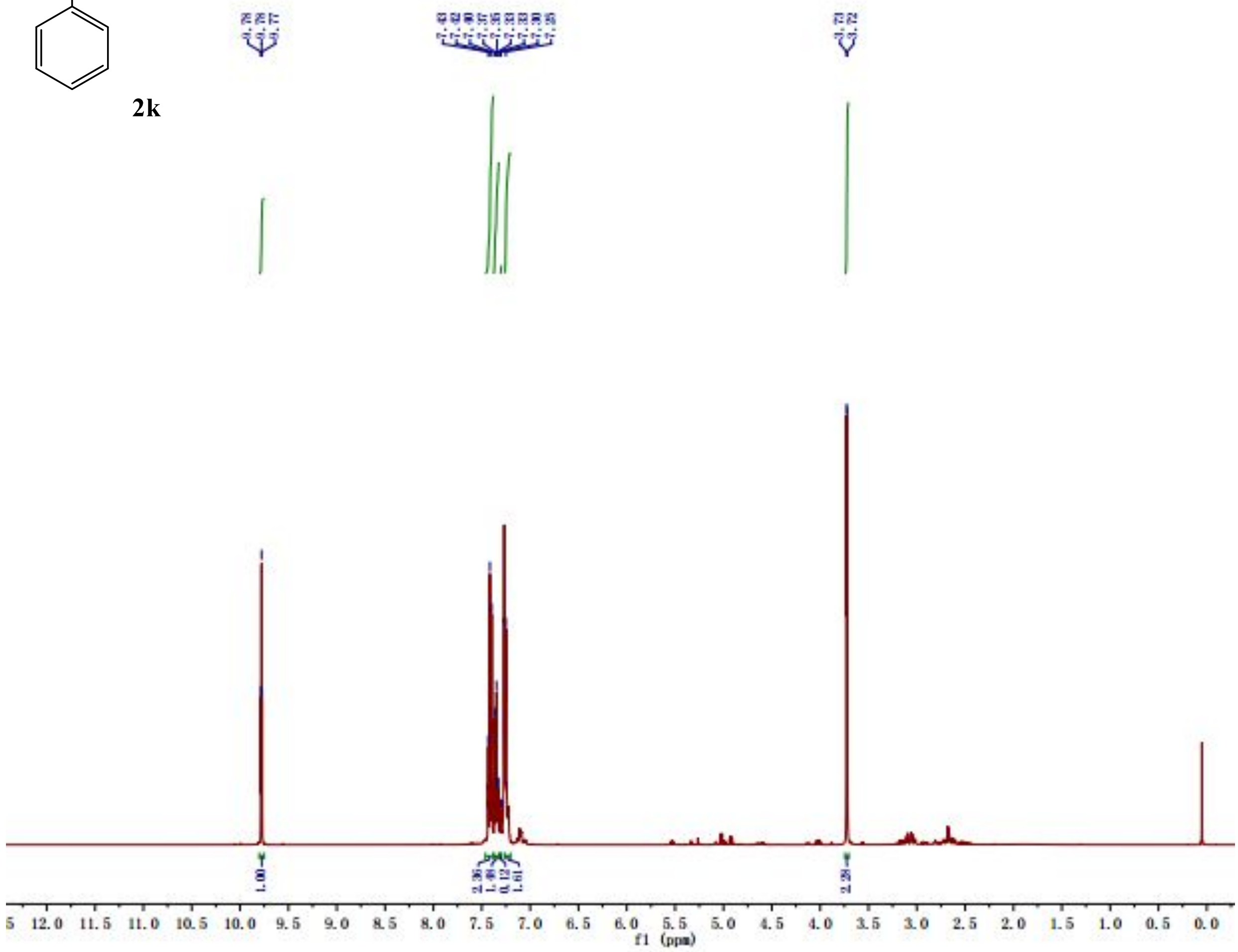
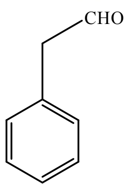


**Fig. S24** The [13]HNMR spectrum of the Phenylacetaldehyde (**2k**).



2k

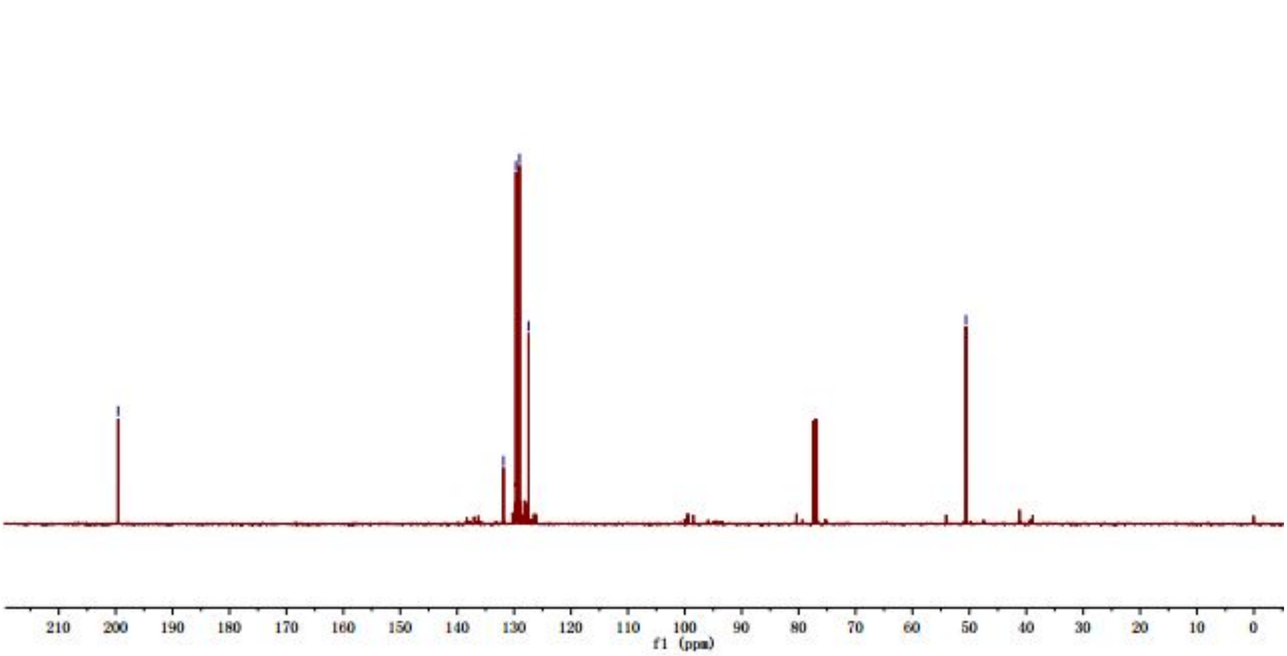



**Fig. S25** The $^{13}$CNMR spectrum of the Phenylacetaldehyde (**2k**).

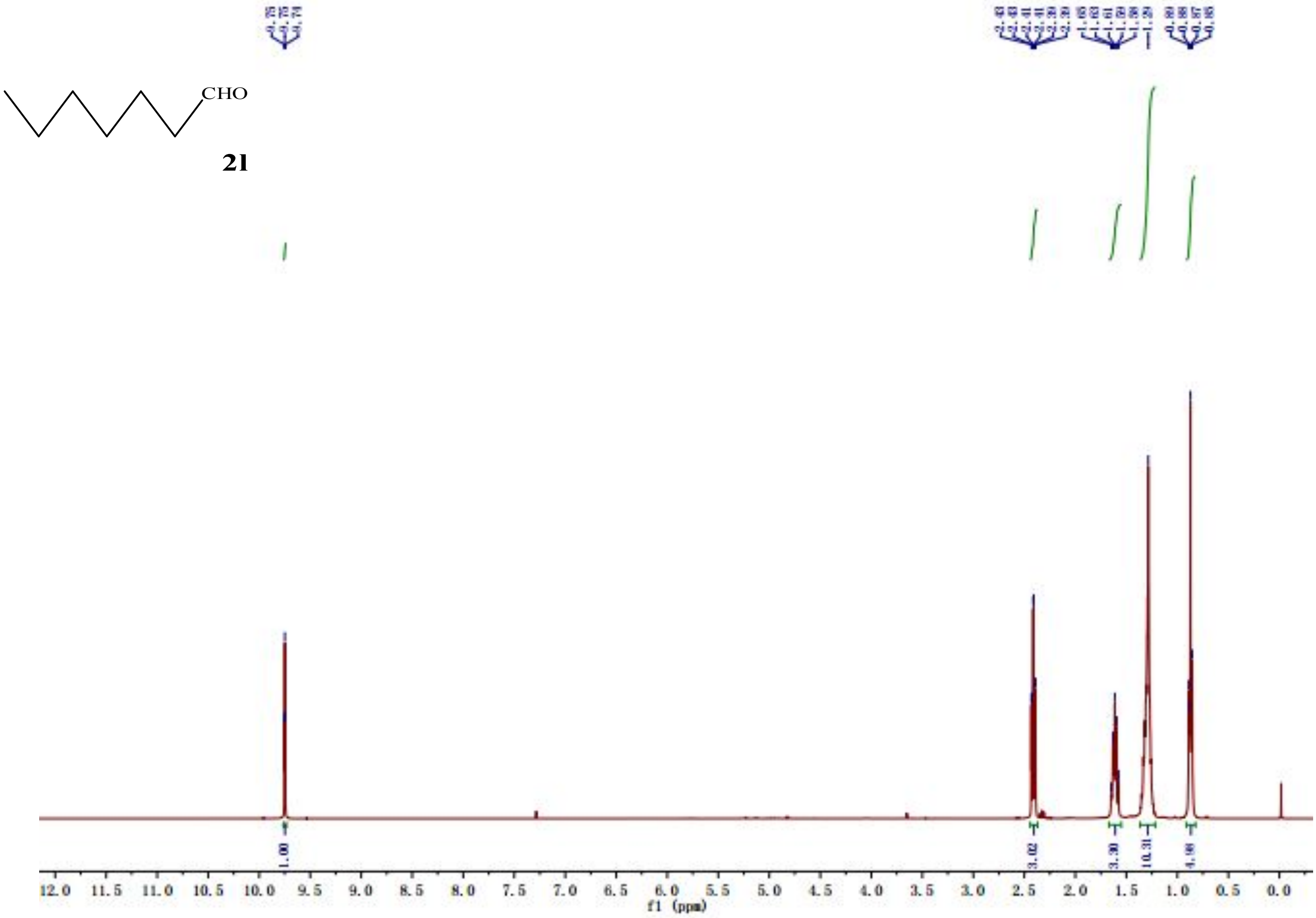


**Fig. S26** The [13]HNMR spectrum of the Heptaldehyde (**2l**).

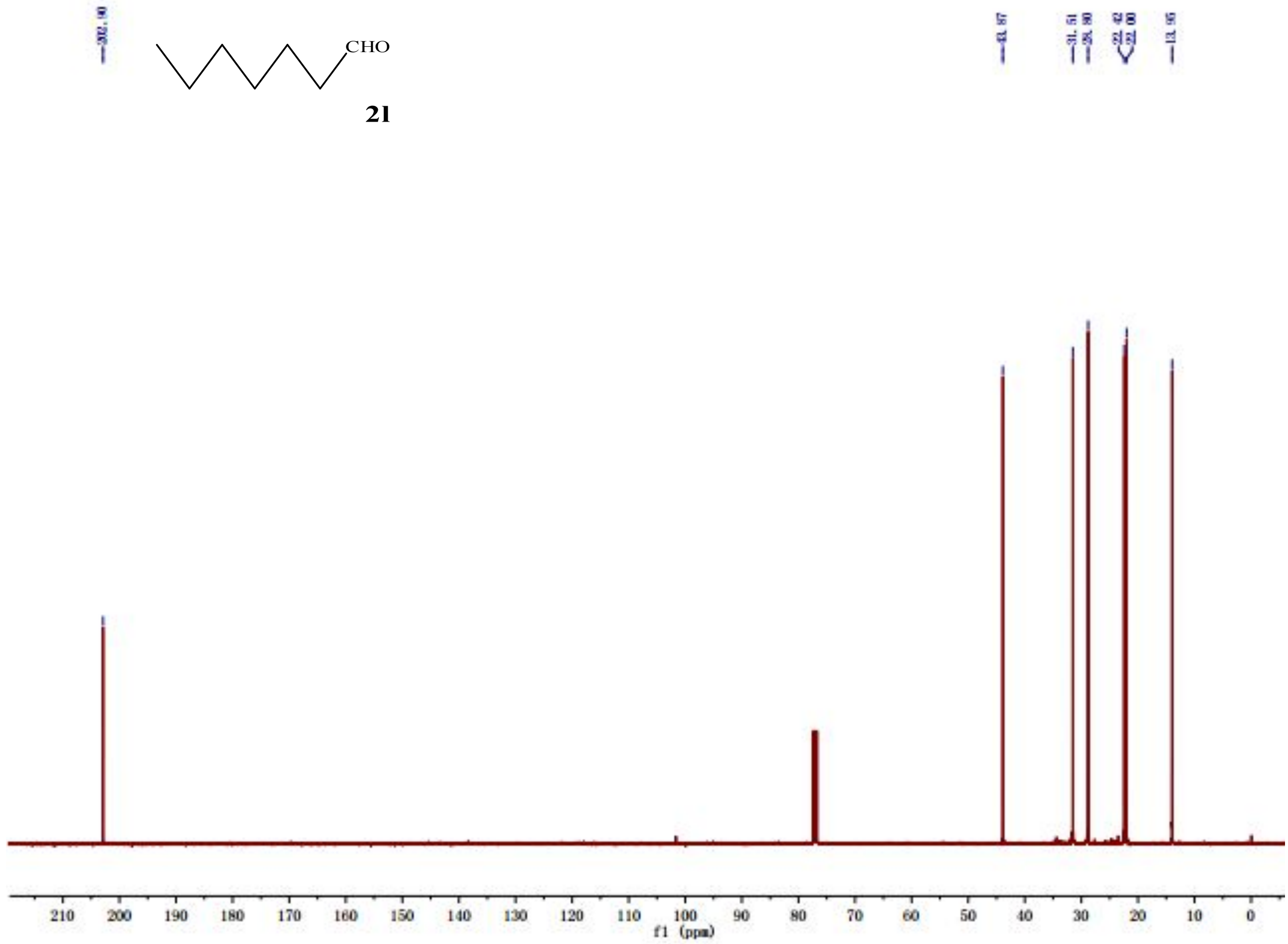



**Fig. S27** The $^{13}$CNMR spectrum of the Heptaldehyde (**2l**).