Supporting Information

Ball-Milled Co-N-C Nanocomposite for Benzylic C-H Bond Oxidation: a Facile, Practical and Recyclable Catalyst under Neat Conditions and Atmospheric Pressure Oxygen

Shoujie Nie,[a,#] Jun Wang,[a,#] Xiang Huang,[a] Xiyu Niu,[a] Li Zhu[b] and Xiaoquan Yao[a,*]

[a] *Department of Applied Chemistry, College of Material Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, PR China*

[b] *Department of Chemistry, School of Pharmacy, Nanjing Medical University, Nanjing 211166, PR China*

Fax: +86-25-52112626; Phone: +86-25-52112906;

Table of contents

# These authors contributed equally to this work

* E-mail: yaoxq@nuaa.edu.cn

1. Materials and characterization methods

$Co(NO_3)_2 \cdot 6H_2O$ and melamine were purchased from Sinopharm Chemical Reagent Co. Ltd., and other chemicals were purchased from Aladdin Chemical Reagent Co. Ltd. All of the chemicals were in analytical grade and used as received without further purification. The morphology of the samples and energy dispersive spectromete (EDS) mapping were examined by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, Philips Tecnai 12). The crystal structures of the synthesized materials were analyzed by X-ray diffraction (XRD, Bruker D8, Cu K^{a}) within a 2θ range of 5-90^{o} and the scanning rate was 5^{o}/min. Nitrogen adsorption-desorption isotherms and pore size distribution were characterized with a Micrometrics ASAP2020 analyzer at 77 K. X-ray photoelectron spectroscopy (XPS) measurements were carried out on Kratos AXIS Ultra spectrometer with a source gun of Al K^{a} and spot size of 400 μm. FT-IR spectrum was measured on a Thermo Scientific Nicolet iN10 MX FT-IR Microscope. The scanning scope is 500~4000 cm^{-1}.The catalytic activity was determined by gas chromatography (GC, Beijing Beifen-Ruili Analytic Instrument (Group) Co., Ltd. SP-3420A) with a SE-54 capillary column and a FID detector. The structure of each product were verified by a Bruker 400 MHz nuclear magnetic resonance spectrometer with deuterated chloroform as solvent and TMS as the internal reference.

2. Preparation and characterization of catalyst

2.1 Catalyst preparation

Preparation of Co-N-C-8:

$Co(NO_3)_2 \cdot 6H_2O$ (1.83 g) and melamine (3.00 g) were added into a 100 mL zirconia grinding jar equipped with zirconia milling beads. The powder mixture was subjected to continuous mechanochemical reaction in a planetary ball mill with a rotational speed of 580 rpm at room temperature for 6h. After milling, a grey-green solid was obtained, which was then ground into powder. Noted as Co-N-C-8.

Preparation of g-C_3N_4-Co-8: Melamine was used as raw material to prepare g-C_3N_4 by direct calcination at 550 ^oC according to a reported method,[s1] and g-C_3N_4 was obtained as a yellow solid. The g-C_3N_4-Co-8 was then prepared by a facile impregnation-roasting method: A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.42 g) and g-C_3N_4 (1.00 g) were added into 50 mL ethanol, and the suspension was stirred at 60 ^oC for 8 h to remove the solvent; the residue was then dried at 60 ^oC under reduced pressure for another 12 h. After that, a yellow solid was obtained, and was then ground into powder. Note it as g-C_3N_4-Co-8.

Preparation of Co-N-C-550-8:

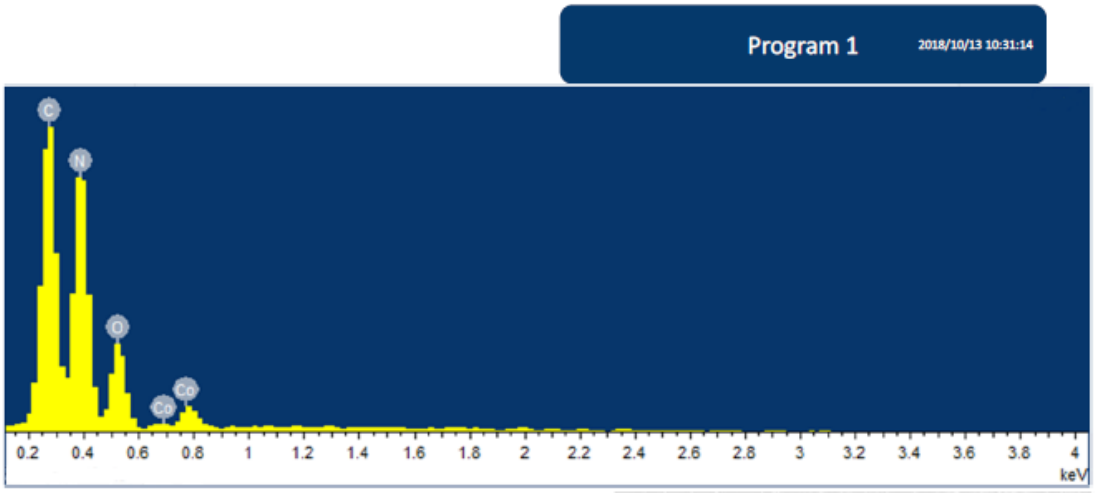
In a typical procedure, the sample, Co-N-C-8, prepared by ball-milling method from $Co(NO_3)_2 \cdot 6H_2O$ and melamine, was heated to 550 °C for 4 h at a rate of 2 °C/min under N_2 atmosphere to obtain the final Co-N-C-550-8 composite.

2.2 Activation of catalyst

Co-N-C-8 (3.00 g) was put into a 100 mL flask which equipped with a thermometer and O_2 gas inlet. The powder stirred at 60 ^oC with continuous O_2 gas flow (*ca.* 2 mL/min) for 5 h. After heating, a deep brown powder was obtained.

2.3 Characterization of the Co-N-C nanocomposite

Scheme S1. EDS spectrum and report for Co-N-C-8 nanocomposite



Spectrogram Processing :

There are no overlooked peaks.

Processing Options :

All elements have been analyzed. (normalized)

Repeat Number = 4

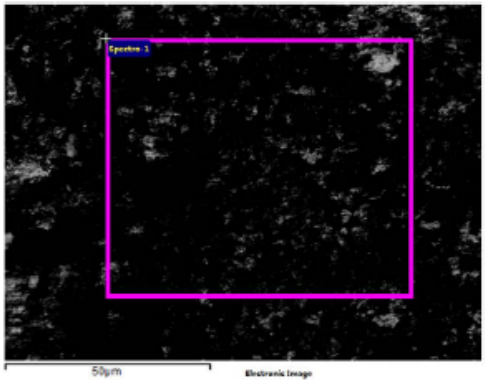
Standard Sample :

C CaCO3 1-Jun-1999 12:00 AM

N Not defined 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

Co Co 1-Jun-1999 12:00 AM



Elements	Weight Percent	Atom Percent
C K	35.86	45.03
N K	35.23	37.93
O K	14.03	13.23
Co L	14.88	3.81
Total	100.00	

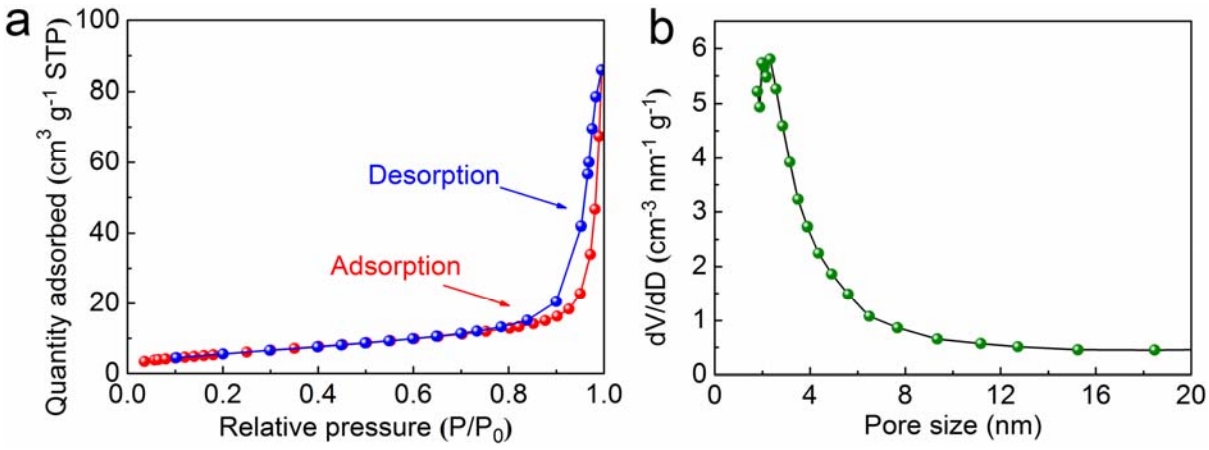


Figure S1. N_2 adsorption–desorption isotherms and the corresponding pore-size distribution curves of Co-N-C-8

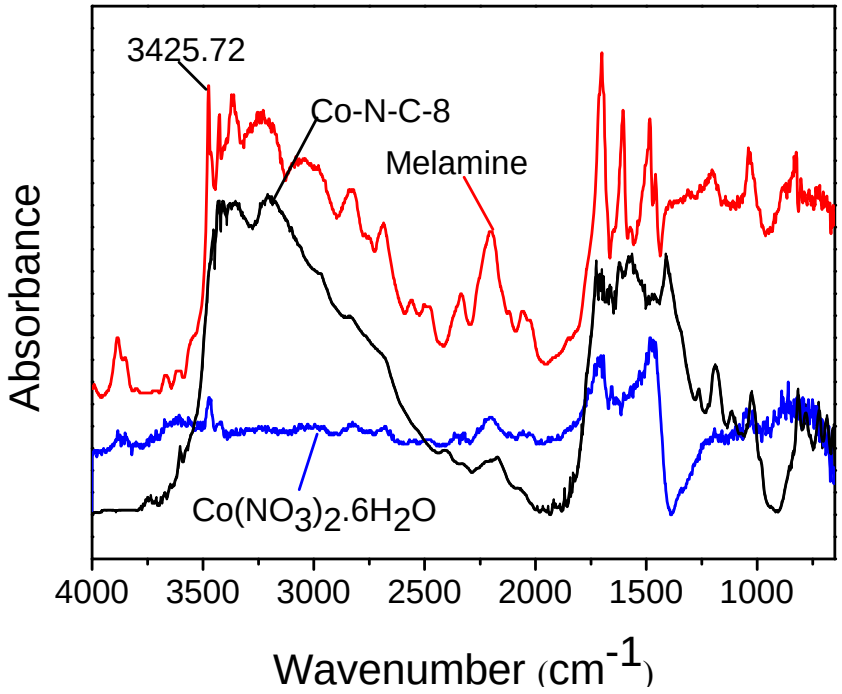


Figure S2. FT-IR spectrum of Co-N-C-8 and raw materials

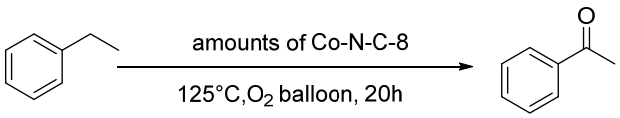
3. Experimental section

3.1 Co-N-C catalyzed ethylbenzene oxidation

The catalytic oxidation of ethylbenzene were carried out in a 35 mL Schlenk tube. Initially, 32.3 mg of Co-N-C-8 catalyst were added into the tube. After filled with pure oxygen, ethylbenzene (1.0 mL, 8.2 mmol) was injected into the tube. Conveniently, cold finger was equipped and an oxygen balloon was connected on the branch pipe to provide oxidant. The reaction mixture was stirred under 125 ^{o}C for 20 h. After the reaction, ether (5 mL) was added to dilute the reaction mixture, and the solid catalyst was recovered by filtration. The filtrate was then analyzed directly by gas chromatography.

3.2 Condition optimization for the selective oxidation of ethylbenzene (1a)

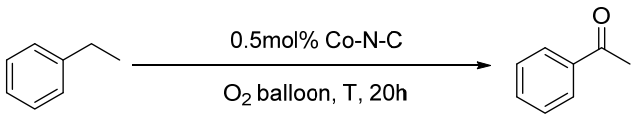
Table S1. Screening catalyst loading for the selective oxidation of ethylbenzene[a]



Entry	Catalyst Content	Conversion [b]	Selectivity [b]
1	0.3 mol%	90%	94%
2	0.5 mol%	93%	96%
3	1 mol%	86%	89%

[a] Reaction conditions: catalyst (Co-N-C-n) (0.3-1) mol%, ethylbenzene 8.2 mmol, O_2 balloon 125℃, 20 h.[b] Conversion and Selectivity were determined by GC.

Table S2. Screening temperature for the selective oxidation of ethylbenzene[a]

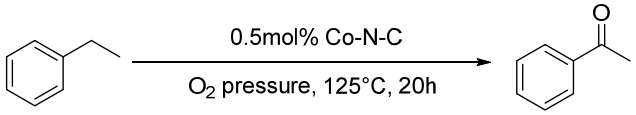


Entry	Temperature/^{o}C	Conversion [b]	Selectivity [b]
1	105	68%	98%
2	110	71%	97%
3	115	74%	94%
4	120	83%	95%
5	125	93%	96%
6	130	84%	88%

[a] Reaction conditions: catalyst (Co-N-C-n) 0.5 mol%, ethylbenzene 8.2 mmol, O_2 balloon, 20 h.[b] Conversion and

Selectivity were determined by GC.

Table S3. Screening pressure of oxygen for the selective oxidation of ethylbenzene[a]



Entry	Pressure of oxygen	Conversion [b]	Selectivity [b]
1	1 atm	93%	96%
2	21 atm	81%	80%
3	42 atm	91%	73%

[a] Reaction conditions: catalyst (Co-N-C-n) 0.5 mol%, ethylbenzene 8.2 mmol,125℃,20 h.[b] Conversion and Selectivity were determined by GC.

Table S4. Screening the ratio of melamine to cobalt.

Entry	Catalyat ratio ($m_{melamine}$: m_{Co})	Conv. (%)	Sel.(%)	Yield (%)[b]
1	4:1	92	90	83
2	5:1	93	93	86
3	6:1	84	92	77
4	7:1	86	94	81
5	**8:1**	**93**	**96**	**89**
6	9:1	72	96	69
7	10:1	66	95	63
8	11:1	58	98	57
9	12:1	72	96	69
10	13:1	59	96	57

[a] Reaction conditions: catalyst (Co-N-C-n) 0.5mol%, ethylbenzene 8.2 mmol, O_2 balloon 125℃, 20 h. [b] Yields were determined by GC.

3.3 Kinetic study for the catalytic oxidative of ethylbenzene

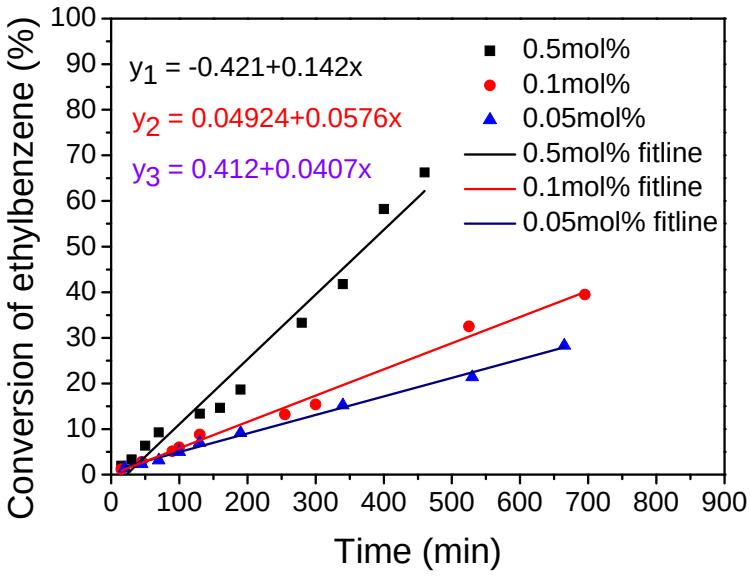


Figure S3. Kinetic study for the catalytic oxidative of ethylbenzene.

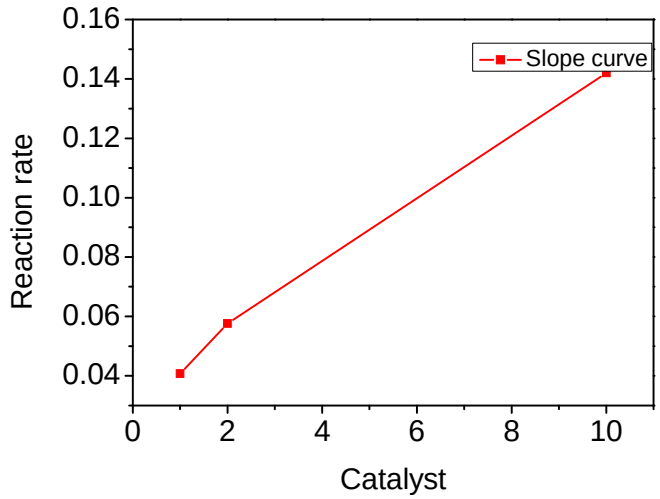
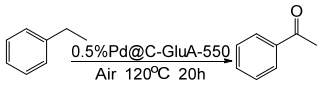
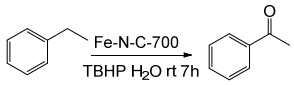
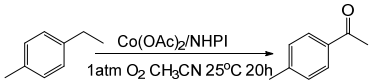
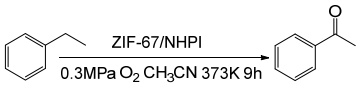
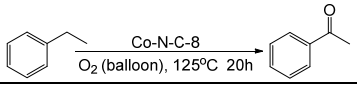


Figure S4 Kinetic curve for catalyst loading and reaction rate (with 0.05 mol% of catalyst as unit 1)

Table S5 TOF data for some literatures and our current work

Entry	Reaction	Con.(%)	Sel.(%)	TOF(h^{-1})	Ref.
1		14.2	94	245	S10
2		99	99	25	S11
3		87	47	4	S12
4		71	84	132	S13
5		95	98	9	This work (based on Co)

3.4 The recyclability of the Co-N-C catalyst

Following the procedure described in 3.1, the solid catalyst was recovered by filtration, and washed by ether (5 mL x 3). The collected catalyst was dried under vacuum at 80 ^{o}C overnight, and reused for next reaction.

Table S6. Recycling of the Co-N-C-8 catalyst

Entry	Run	Conv.（%）	Sel.（%）	Yield(%)[b]
1	1	93	96	89
2	2	89	96	85
3	3	91	93	85
4	4	90	92	83
5	5	89	93	83

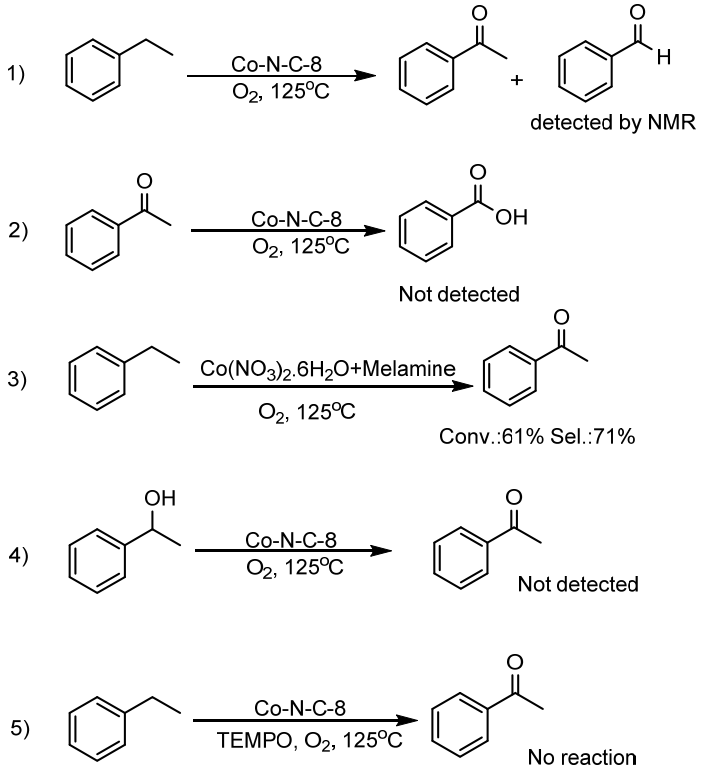
[a] Reaction conditions: catalyst (Co-N-C-8, 0.5 mol%) , ethylbenzene 8.2 mmol, O_2 balloon, 125℃, 20 h.

[b] Yields were determined by GC.

4. Mechanism investigation

4.1 Controlled experiments for mechanism investigation.

Scheme S2. Controlled experiments



4.2 GC-MS analysis for reaction mixture

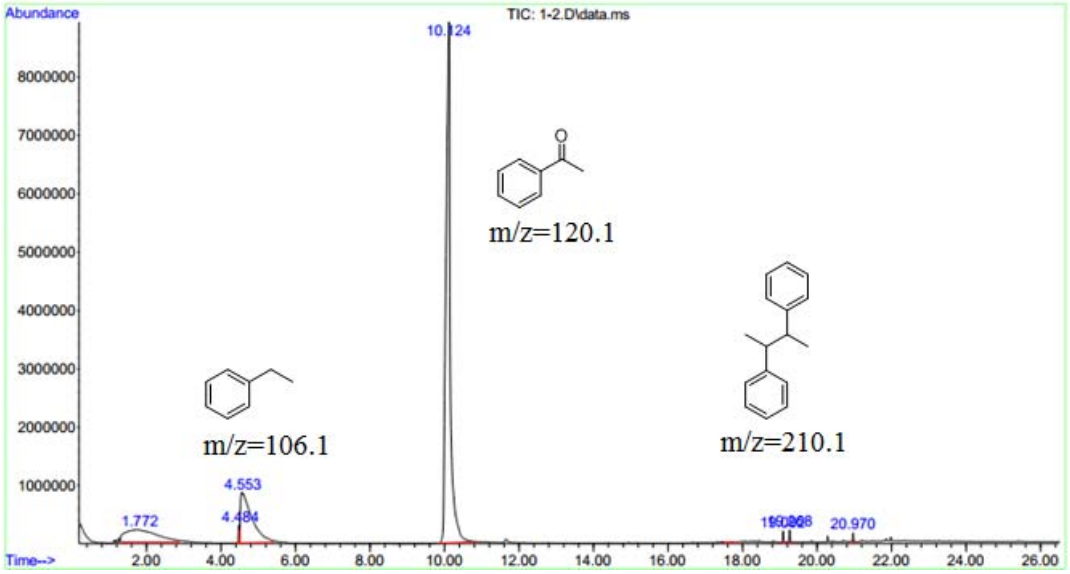
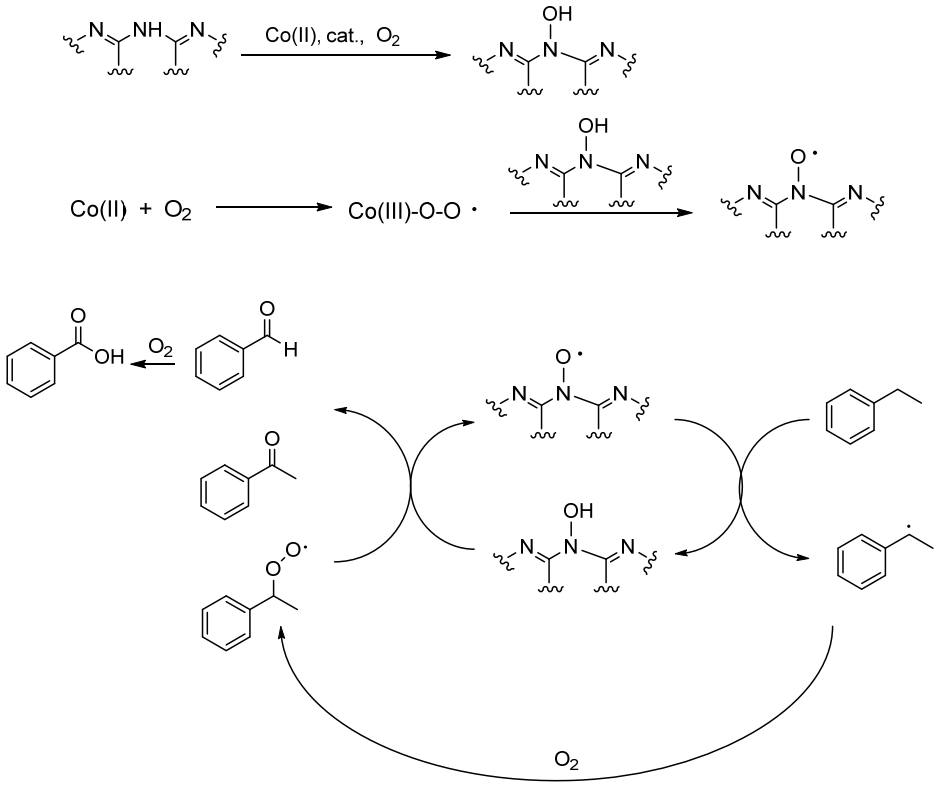


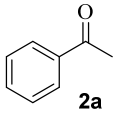
Figure S5. GC-MS analysis result.

4.3 Proposed mechanism based on Ishii-type-like catalytic system

Scheme S3. The plausible mechanism for the catalytic oxidation of ethylbenzene



Characterization for compounds

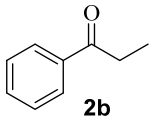


2a

Acetophenone (2a)[s2]

Colorless liquid, 93% yield, purified by flash chromatography, PE:EA=15:1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.41(t, *J* = 7.2 Hz, 2H), 2.55 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.13, 137.11, 132.10, 128.57, 128.30, 26.58.

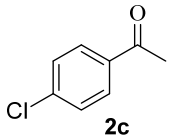


2b

Propiophenone (2b)[s2]

Colorless liquid, 83% yield, purified by flash chromatography, PE:EA=15:1;

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.86 (d, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 2.90 (q, *J* = 7.2 Hz, 2H), 1.13 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 199.73, 135.91, 131.81, 127.51, 126.93, 30.72, 7.20.



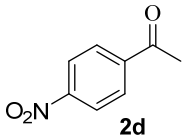
2c

4-chloroacetophenone (2c)[s3]

Colorless liquid, 71% yield, purified by flash chromatography, PE:EA=15:1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 2.63 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.84, 139.54, 135.44, 129.75, 128.90, 26.56



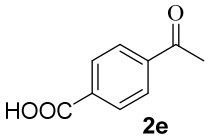
2d

4-nitroacetophenone (2d)[s3]

Yellow solid, 53% yield**,** purified by flash chromatography, PE:EA=15:1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H), 2.67 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.34, 150.41, 141.41, 129.34, 123.89,

27.01.

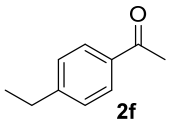


2e

4-acetylbenzoic acid (2e)[s4]

White solid,48% yield, purified by flash chromatography, PE:EA=1:1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 2.69 (q, J = 7.6 Hz, 2H), 2.56 (s, 3H), 1.25 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.56, 143.01, 135.82, 130.38, 128.72, 127.66, 127.28 , 126.50 , 120.50.

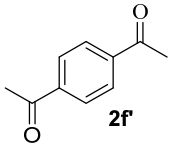


2f

4-ethylacetophenone (2f)[s5]

Colorless liquid, 63% yield**,** purified by flash chromatography, PE:EA=15:1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 2.69 (q, J = 7.6 Hz, 2H), 2.56 (s, 3H), 1.25 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.56, 143.01, 135.82, 130.38, 128.72, 127.66, 127.28, 126.50, 120.50.

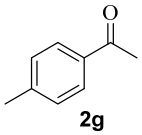


2f'

1,4-diacetylbenzene (2f')[s6]

White solid, 22% yield**,** purified by flash chromatography, PE:EA=15:1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.1 (s, 4H), 2.65(s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.50, 140.20, 128.51, 26.91; **^{13}C NMR** (101 MHz, CDCl3) δ 197.82, 150.04, 134.94, 128.56, 128.07 , 28.94 , 26.51, 15.20.



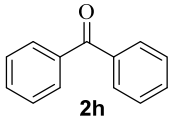
2g

4-methylacetophenone (2g)[s3]

Colorless liquid, 75% yield**,** purified by flash chromatography, PE:EA=15:1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.48 (s, 3H), 7.16 (d, J = 8 Hz, 2H), 7.76

(d, J = 8 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 21.6 26.5 128.5 129.3 134.8 143.9 197.9

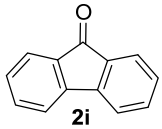


2h

Benzophenone (2h)[s2]

White solid, 84% yield**,** purified by flash chromatography, PE:EA=15:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.6 Hz, 4H), 7.59 (t, J = 7.6 Hz, 2H), 7.48 (t, J = 7.6 Hz, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.72, 137.59, 132.40, 120.04, 128.27.

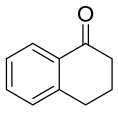


2i

9-fluorenone (2i)[s2]

Yellow solid, 81% yield, purified by flash chromatography, PE:EA=15:1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.2 Hz, 2H), 7.45–7.51 (m,4H), 7.28 (dt, J = 1.2, 7.2 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.95, 144.46, 134.72, 134.18, 129.11, 124.34, 120.34.

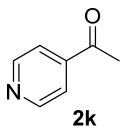


2j

α-tetralone (2j)[s2]

Colorless liquid, 72% yield, purified by flash chromatography, PE:EA=15:1;

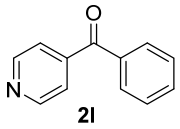
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 0.8 Hz, 7.6 Hz, 1H), 7.46 (td, J = 1.6 Hz, 7.6 Hz, 1H), 7.24–7.32 (m, 2H); 2.97 (t, J = 6 Hz, 2H), 2.65 (t, J = 6.4 Hz, 2H), 2.10–2.17 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.38, 144.52, 133.42, 132.64, 128.61, 127.16, 126.64, 39.19, 29.72, 23.31.



2k

4-acetylpyridine (2k)[s7]

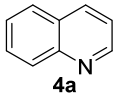
Colorless liquid, 63% yield, purified by flash chromatography, PE:EA:TEA=15:1:1; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (d, J = 4.0 Hz, 2H), 7.70 (dd, J = 4.0, 8.0Hz, 2H), 2.61 (s, 3H); **^{13}C NMR** (101 MHz, CDCl3) δ 197.3, 150.9, 142.6, 121.2, 26.6.



2l

4-benzoylpyridine (2l)[s7]

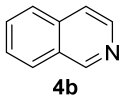
Light yellow solid, 84% yield, purified by flash chromatography, PE:EA:TEA=15:1:1; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (d, J = 4.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.65 (t, J = 8.0Hz, 1H), 7.59 (d, J = 4.0 Hz, 2H), 7.52 (t, J = 8.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.1, 150.3, 144.3, 135.8, 133.6, 130.1, 128.7, 122.9.



4a

quinoline (4a)[s8]

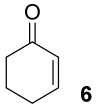
Colorless liquid, 84% yield, purified by flash chromatography, PE:EA:TEA=30:1:1; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (dd, J = 4.2, 1.6 Hz, 1H), 8.12 (d, J = 8.5 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.68 (t, J = 8.4Hz, 1H), 7.54 – 7.44 (t, J = 7.2Hz 1H), 7.32 (t, J = 4, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ150.39, 148.29, 136.00, 129.45, 129.43, 128.27, 127.79, 126.51, 121.05 .



4b

isoquinoline (4b)[s9]

Colorless liquid, 83% yield, purified by flash chromatography, PE:EA:TEA=30:1:1; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.53 (d, J = 5.8 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.71 – 7.56 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.56, 143.01, 135.82, 130.38, 128.72, 127.66, 127.28, 126.50, 120.50.



6

2-Cyclohexen-1-one (6)[s2]

Colorless liquid, 63% yield, purified by flash chromatography, PE:EA= 40:1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (dt, J = 10.0, 4.1 Hz, 1H), 6.03 (dt, J = 10.1, 1.8 Hz, 1H), 2.44 (dd, J = 8.7, 4.8 Hz, 1H), 2.40–2.30 (m, 1H), 2.17–1.85 (m, 1H); **^{13}C NMR** (101 MHz, CDCl3) δ 199.77, 150.68, 129.95, 77.33, 77.07, 76.75, 38.13, 25.69, 22.75.

References:

S1. Yan, S. C.; Li, Z. S.; Zou, Z. G. Photodegradation Performance of g-C_3N_4 Fabricated by Directly Heating Melamine. *Langmuir* **2009**, *25*, 10397-10401.

S2. Ishii, Y.; Nakayama, K.; Takeno, M.; Sakaguchi, S.; Iwahama, T.; Nishiyama, Y. A Novel Catalysis of N-Hydroxyphthalimide in the Oxidation of Organic Substrates by Molecular-Oxygen. *J. Org. Chem.* **1995**, *60*, 3934-3935.

S3. Hu, Y. K.; Chen, L.; Li, B. D. NHPI/tert-butyl Nitrite: A Highly Efficient Metal-Free Catalytic System for Aerobic Oxidation of Alcohols to Carbonyl Compounds Using Molecular Oxygen as the Terminal Oxidant. *Catal. Commun.* **2016**, *83*, 82-87.

S4. Cacchi, S.; Cotet, C. L.; Fabrizi, G.; Forte, G.; Goggiamani, A.; Martin, L.; Martinez, S.; Molins, E.; Moreno-Manas, M.; Petrucci, F.; Roig, A.; Vallribera, A. Efficient Hydroxycarbonylation of Aryl Iodides Using Recoverable and Reusable Carbon Aerogels Doped with Palladium Nanoparticles as Catalyst. *Tetrahedron* **2007**, *63*, 2519-2523.

S5. Liu, S.; Jiang, P.; Song, G. L.; Liu, R.; Zhu, H. J. Synthesis and Optical Properties of a Series of Thermally Stable Diphenylanthrazolines. *Dyes Pigments* **2009**, *81*, 218-223.

S6. Lee, S. W.; Lee, K.; Seomoon, D.; Kim, S.; Kim, H.; Kim, H.; Shim, E.; Lee, M.; Lee, S.; Kim, M.; Lee, P. H. Highly Efficient Pd-Catalyzed Carbonylative Cross-Coupling Reactions with Tetraorganoindates. *J. Org. Chem.* **2004**, *69*, 4852-4855.

S7. Liu, J. M.; Zhang, X.; Yi, H.; Liu, C.; Liu, R.; Zhang, H.; Zhuo, K. L.; Lei, A. W. Chloroacetate-Promoted Selective Oxidation of Heterobenzylic Methylenes under Copper Catalysis. *Angew. Chem. Int. Ed.* **2015**, *54*, 1261-1265.

S8. Jung, D.; Kim, M. H.; Kim, J. Cu-Catalyzed Aerobic Oxidation of Di-tert-butyl Hydrazodicarboxylate to Di-tert-butyl Azodicarboxylate and Its Application on Dehydrogenation of 1,2,3,4-Tetrahydroquinolines under Mild Conditions. *Org. Lett.* **2016**,

18, 6300-6303.

S9. Abraham, R. J.; Reid, M. H-1 Chemical Shifts in NMR. Part 18. Ring Currents and π-electron effects in hetero-aromatics. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1081-1091.

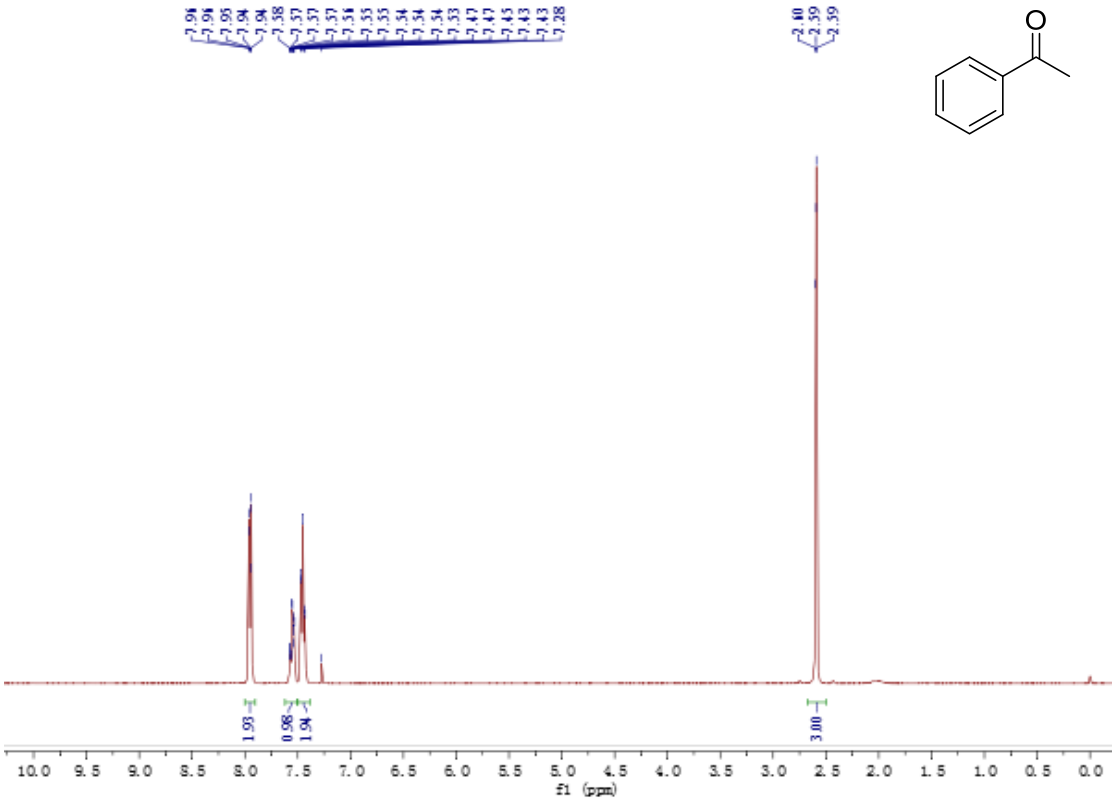
S10. Zhang, P.; Gong, Y.; Li, H.; Chen, Z.; Wang, Y. Solvent-Free Aerobic Oxidation of Hydrocarbons and Alcohols with Pd@N-Doped Carbon from Glucose. *Nat. Commun*. **2013**, *4*, 1593.

S11. Liu, W.; Zhang, L.; Liu, X.; Liu, X.; Yang, X.; Miao, S.; Wang, W.; Wang, A.; Zhang, T. Discriminating Catalytically Active FeN_x Species of Atomically Dispersed Fe-N-C Catalyst for Selective Oxidation of the C-H Bond. *J. Am. Chem. Soc.* **2017**, *139*, 10790–10798.

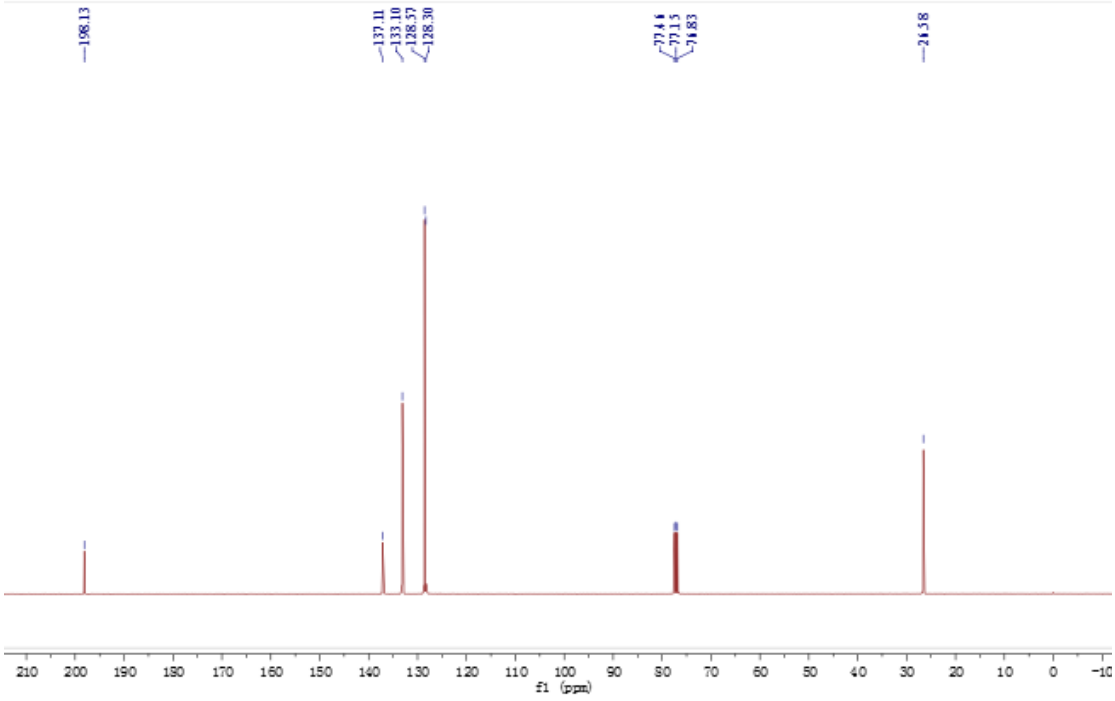
S12. Yoshino, Y.; Hayashi, Y.; Iwahama, T.; Sakaguchi, S.; Ishii, Y. Catalytic Oxidation of Alkylbenzenes with Molecular Oxygen under Normal Pressure and Temperature by N-Hydroxyphthalimide Combined with $Co(OAc)_2$. *J. Org. Chem.* **1997,** *62*, 6810-6813.

S13. Li, H. Y.; Ma, H.; Wang, X. H.; Gao, J.; Chen, C.; Shi, S.; Qu, M. J.; Feng, N.; Xu, J. Efficient Oxidation of Ethylbenzene Catalyzed by Cobalt Zeolitic Imidazolate Framework ZIF-67 and NHPI. *J. Energy Chem.* **2014,** *23*, 742-746.

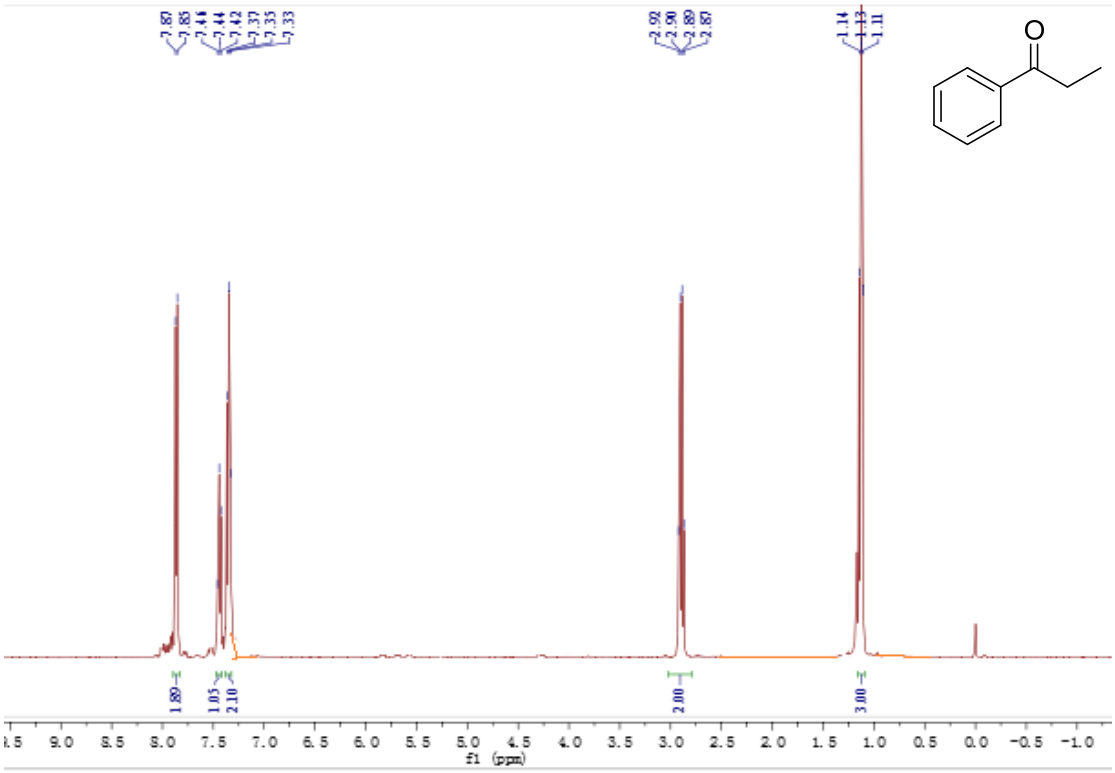
2a Acetophenone ^{1}H NMR (400 MHz, CDCl3)



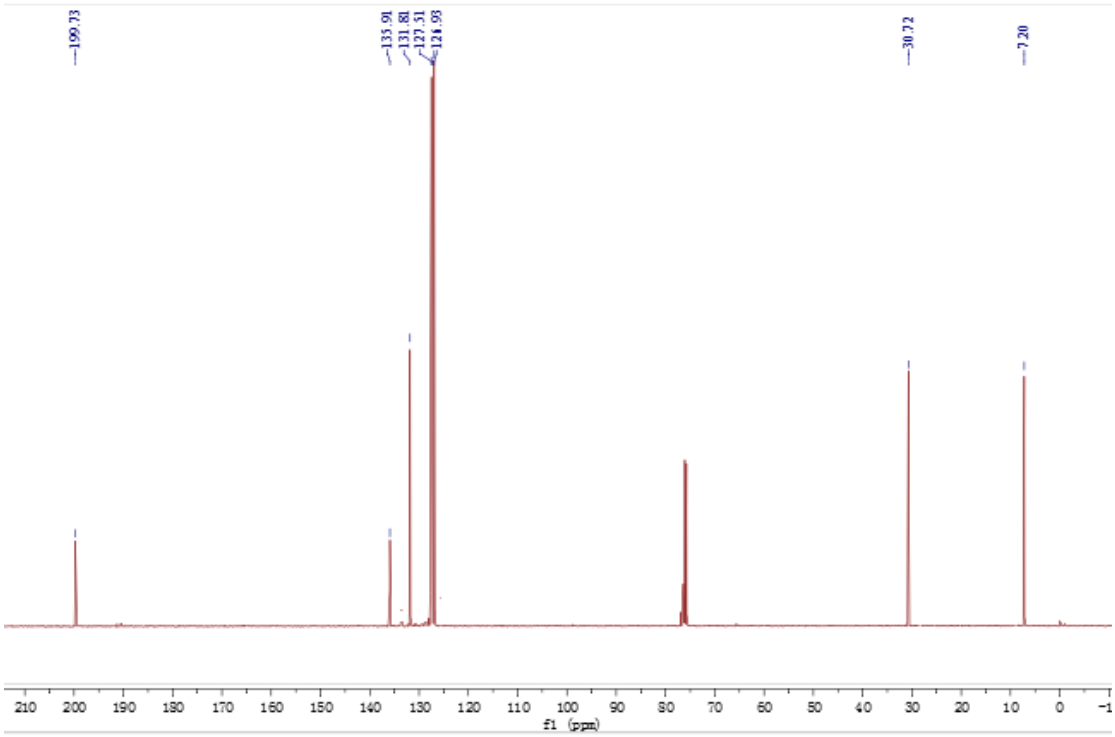
2a Acetophenone ^{13}C NMR (101MHz, CDCl3)



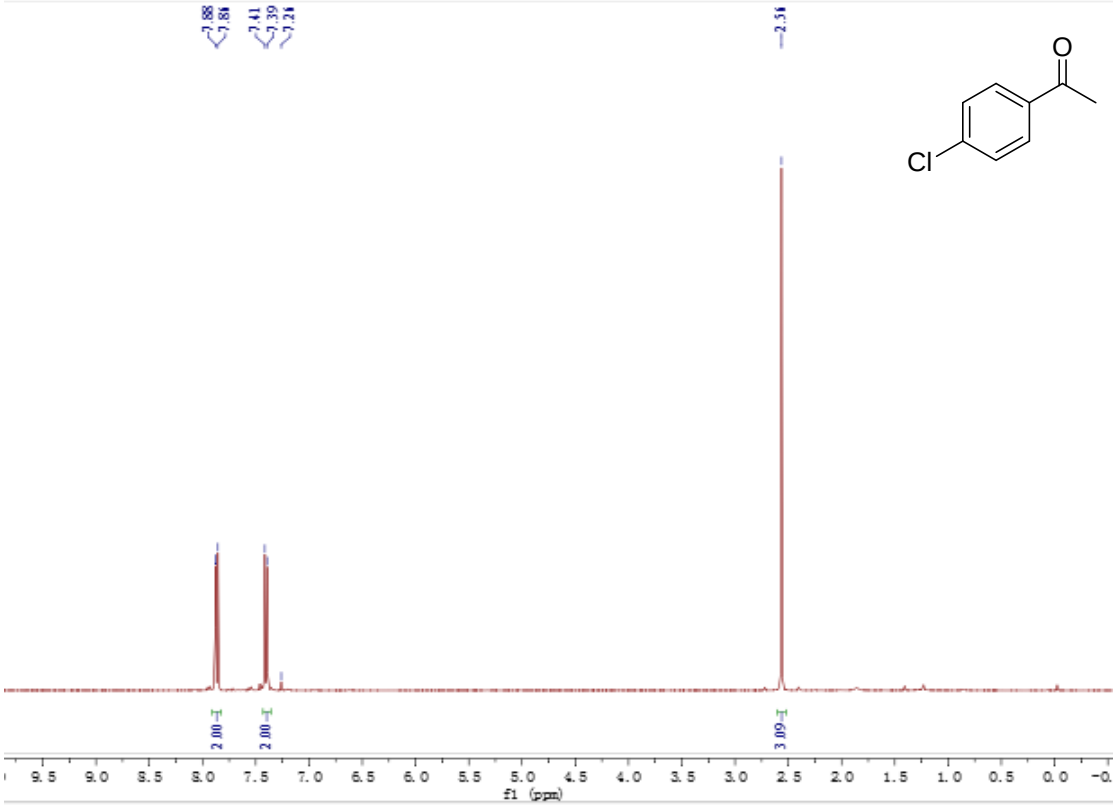
2b Propiophenone ^{1}H NMR (400 MHz, $CDCl_3$)



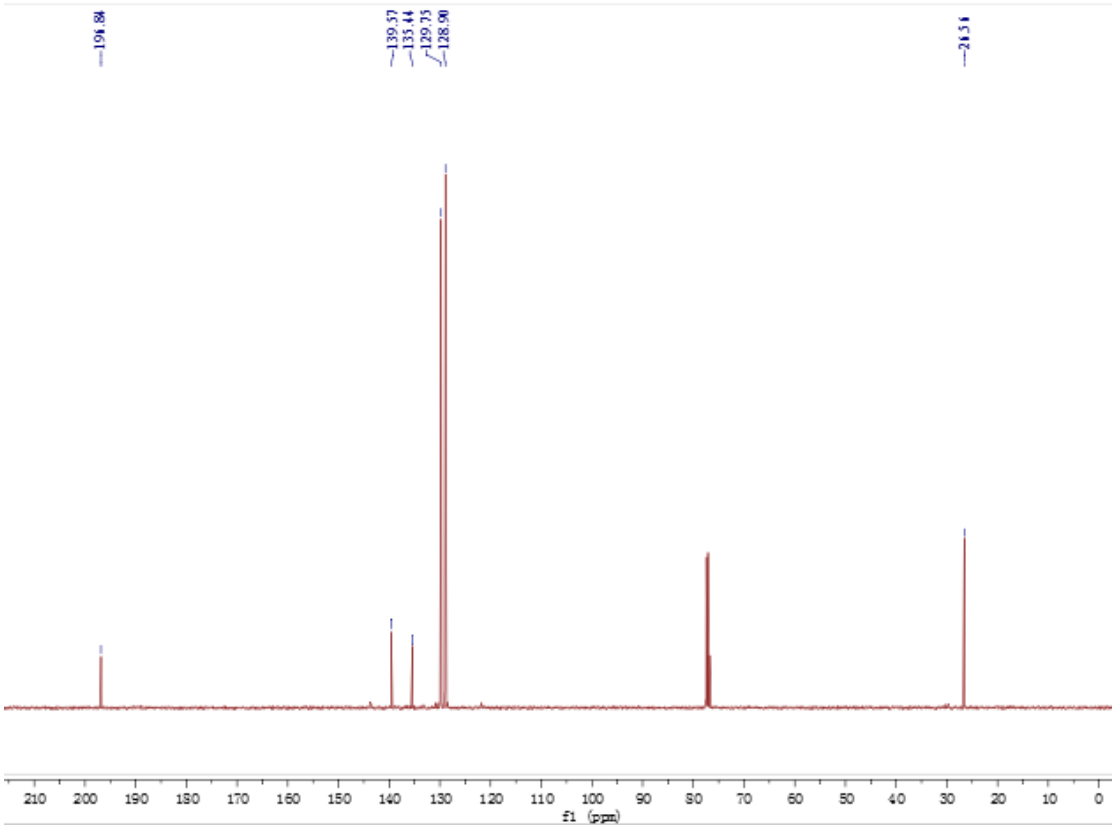
2b Propiophenone ^{13}C NMR (101 MHz, $CDCl_3$)



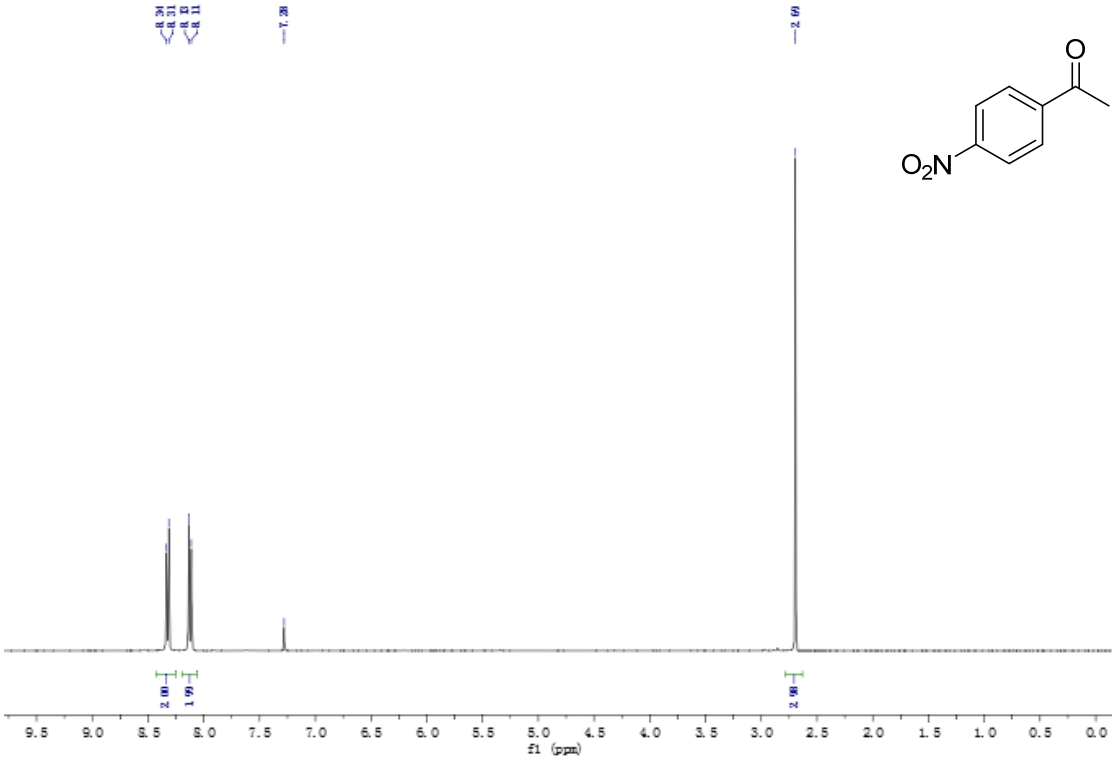
2c 4-chloroacetophenone ^{1}H NMR (400MHz, CDCl3)



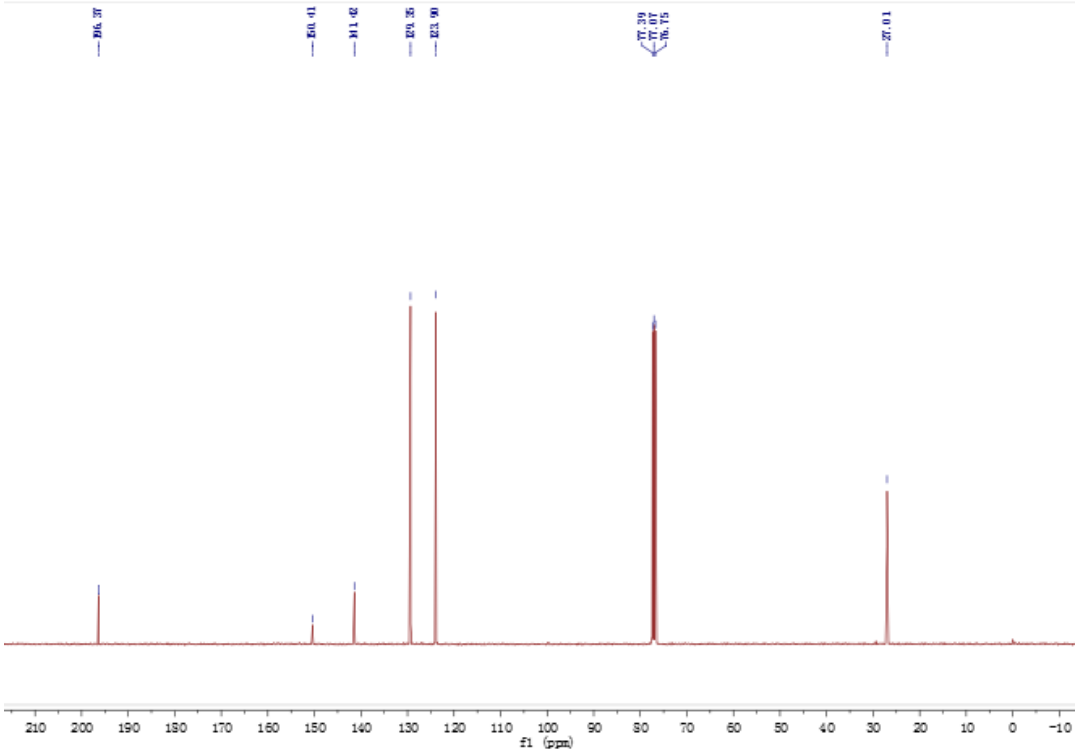
2c 4-chloroacetophenone ^{13}C NMR (101MHz, CDCl3)



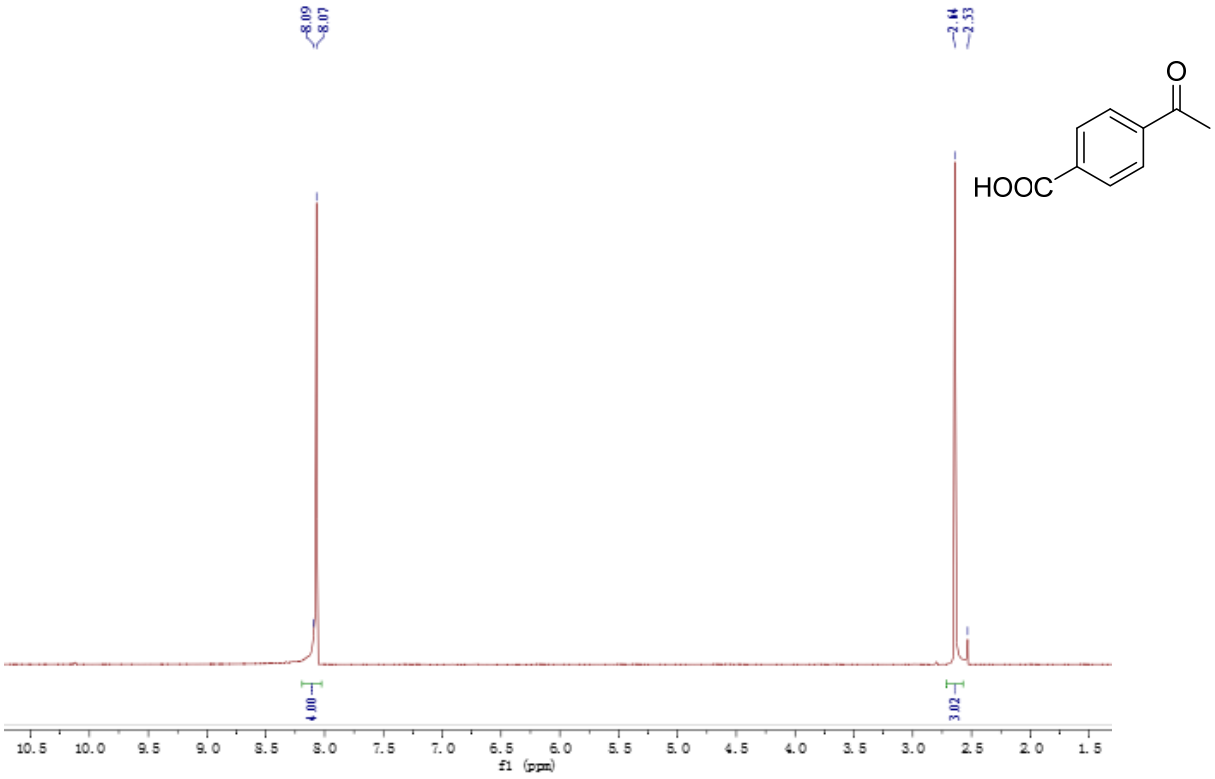
2d 4-nitroacetophenone ^{1}H NMR (400 MHz, $CDCl_3$)



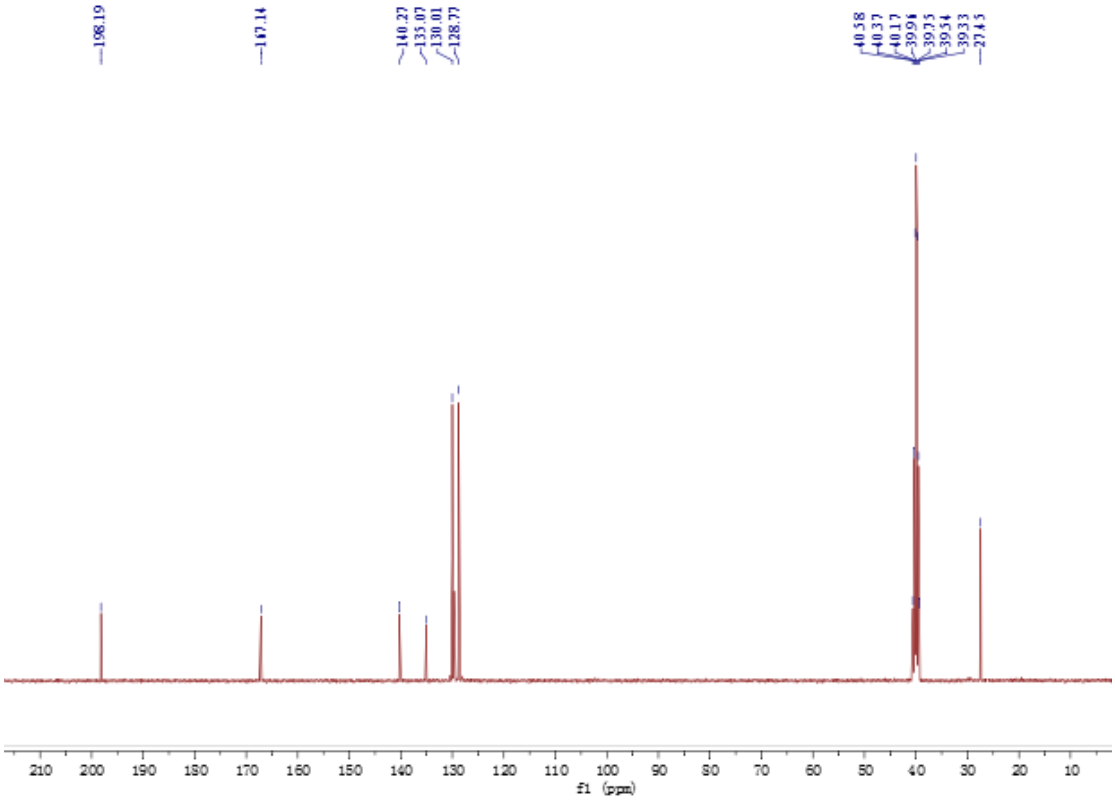
2d 4-nitroacetophenone ^{13}C NMR (101 MHz, $CDCl_3$)



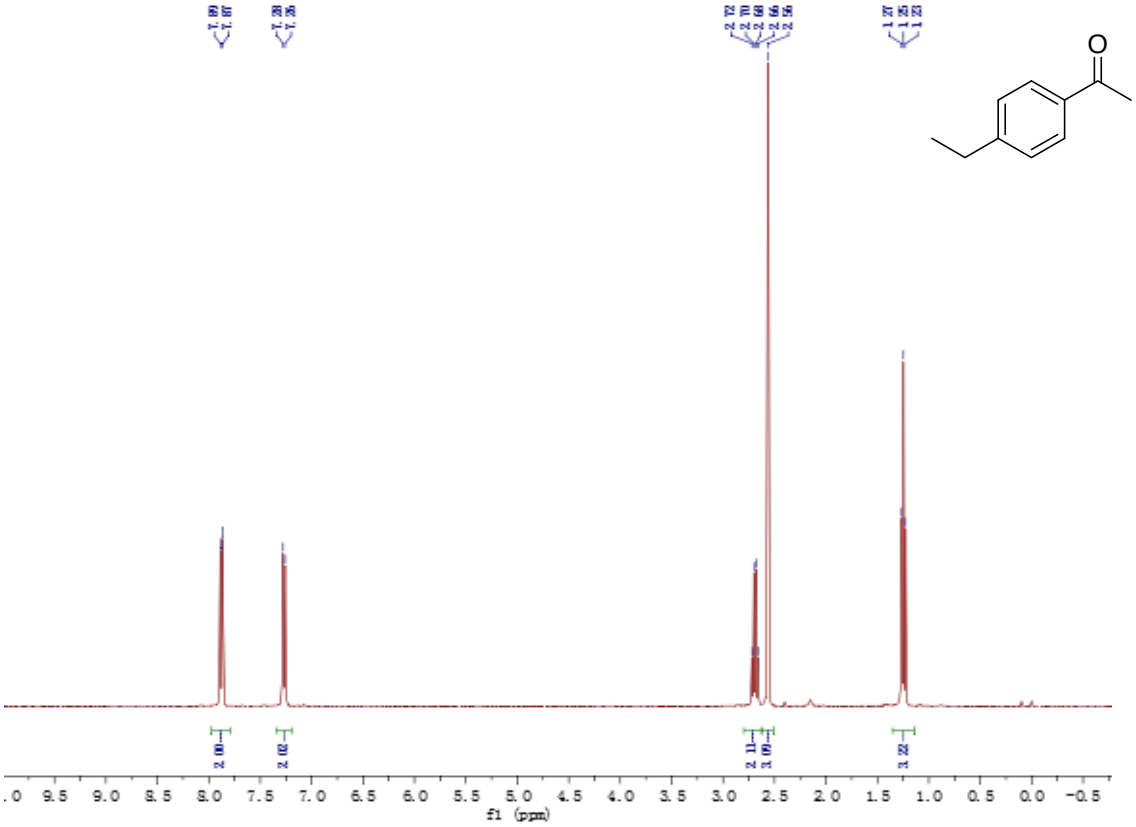
2e 4-acetylbenzoic acid ^{1}H NMR (400 MHz, $CDCl_3$)



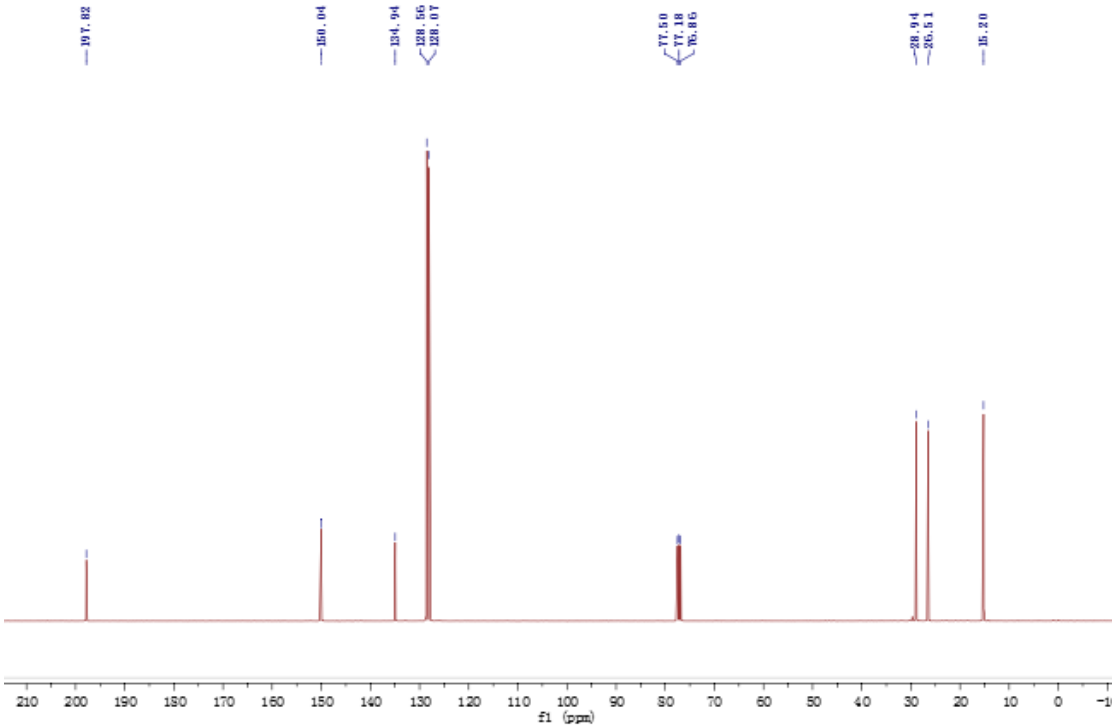
2e 4-acetylbenzoic acid ^{13}C NMR (101 MHz, $CDCl_3$)



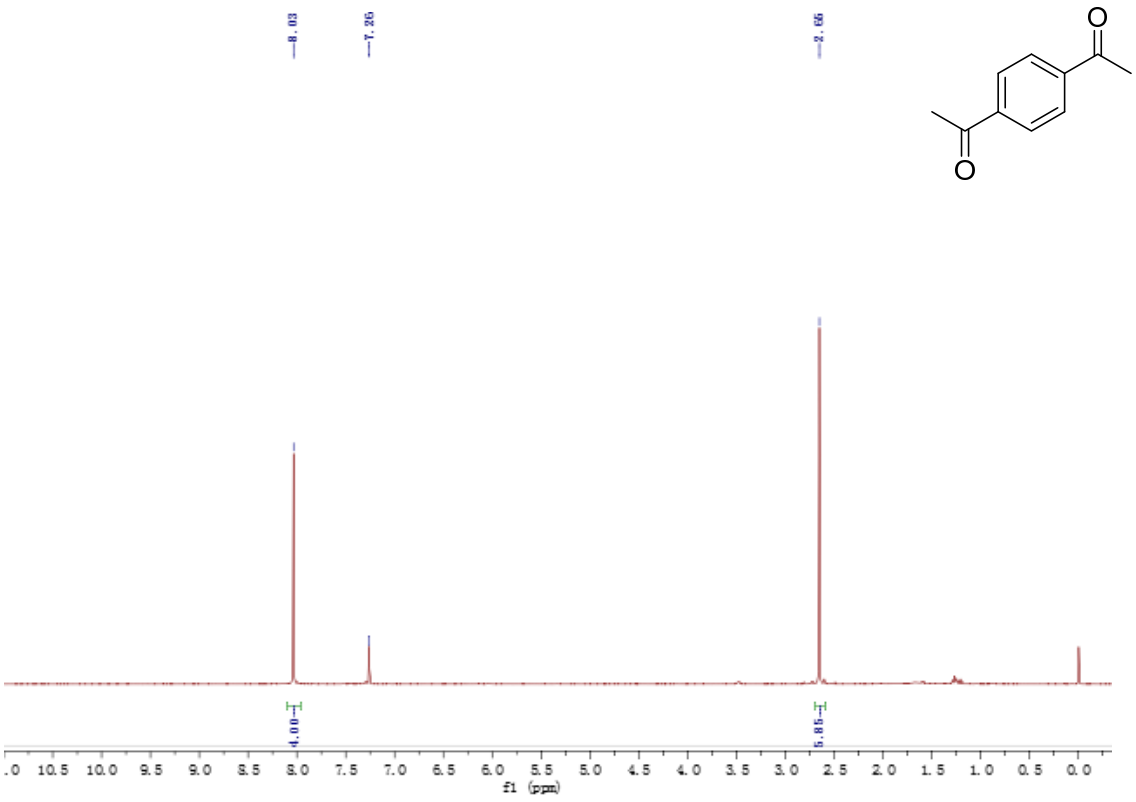
2f 4-ethylacetophenone ^{1}H NMR (400 MHz, $CDCl_3$)



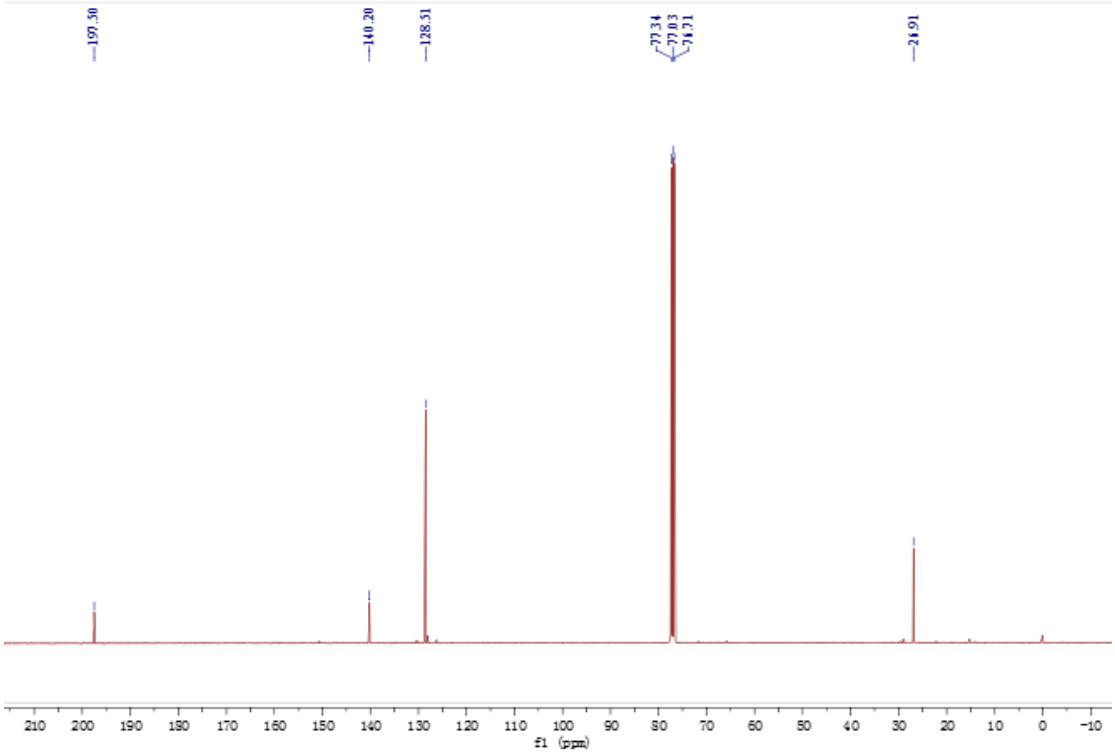
2f 4-ethylacetophenone ^{13}C NMR (101 MHz, $CDCl_3$)



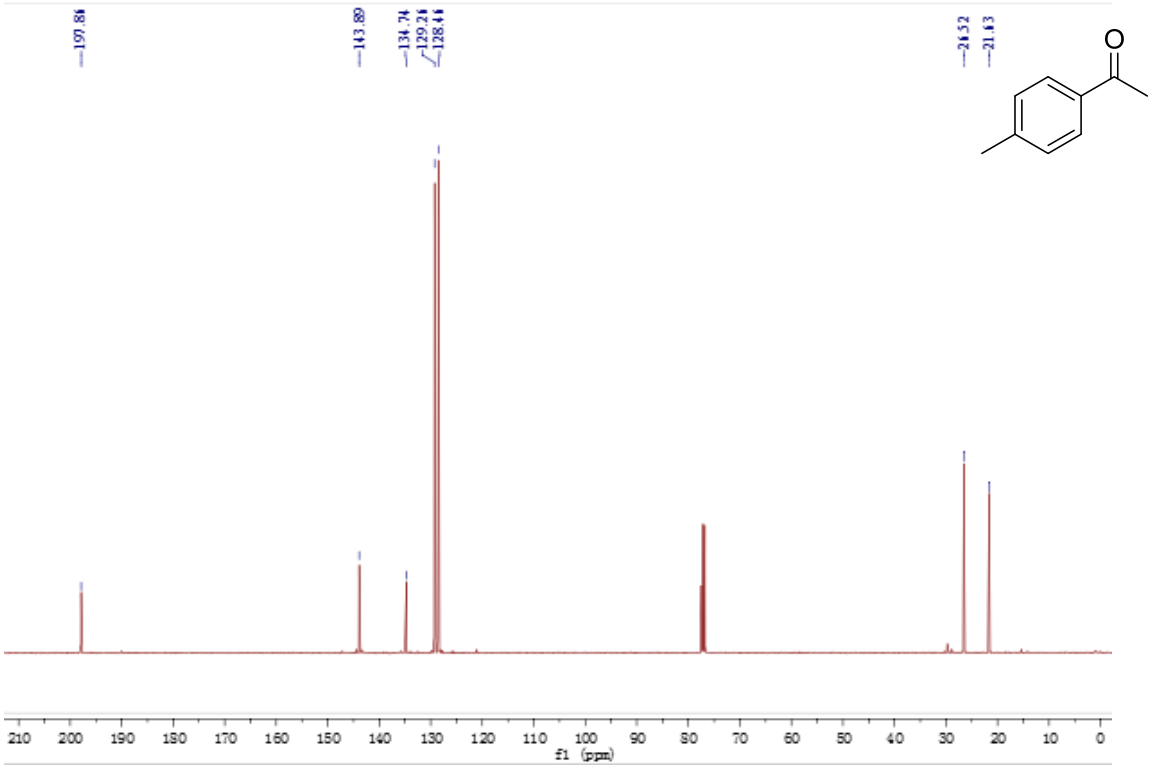
2g 1,4-diacetylbenzene ^{1}H NMR (400 MHz, $CDCl_3$)



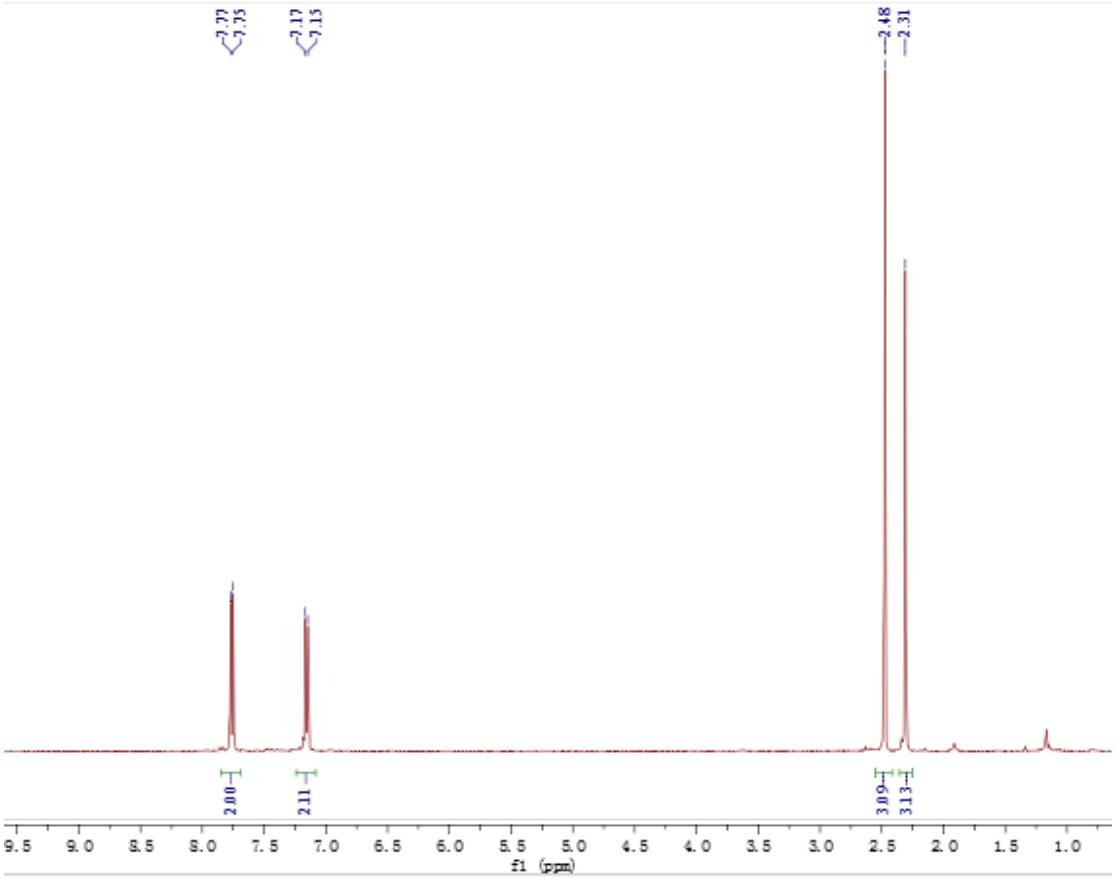
2g 1,4-diacetylbenzene ^{13}C NMR (101MHz, $CDCl_3$)



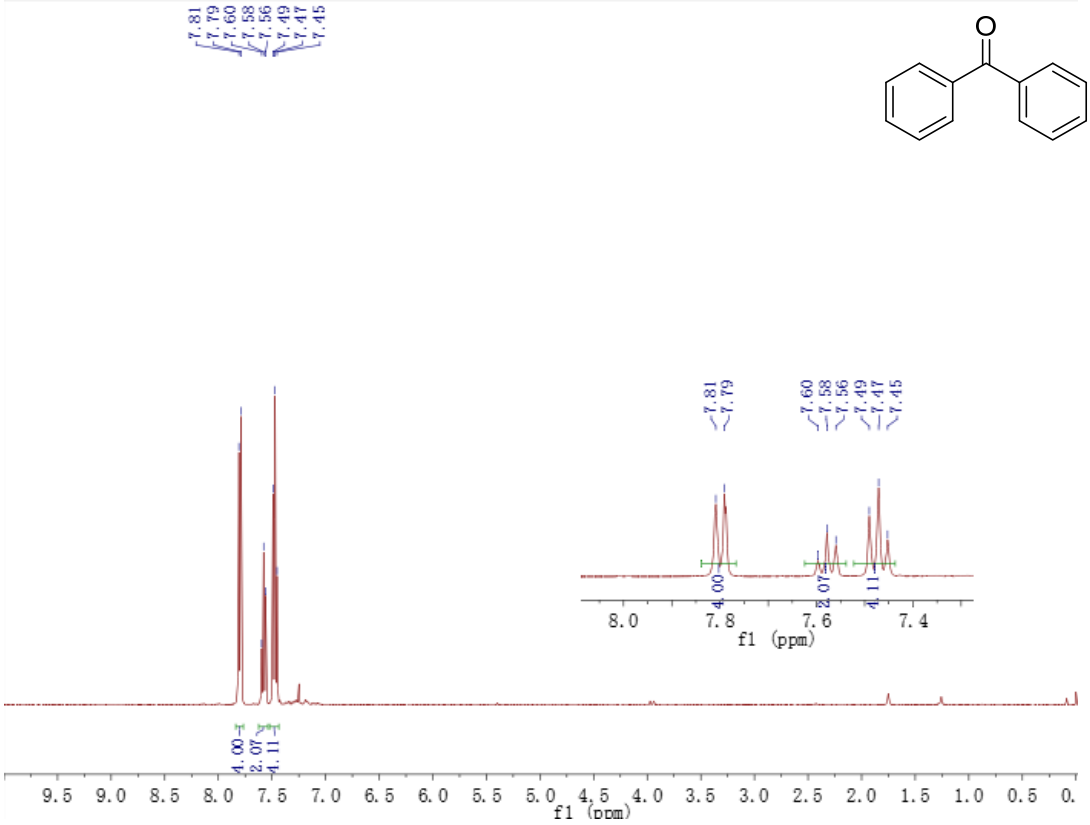
2h 4-methylacetophenone ^{1}H NMR (400 MHz, $CDCl_3$)



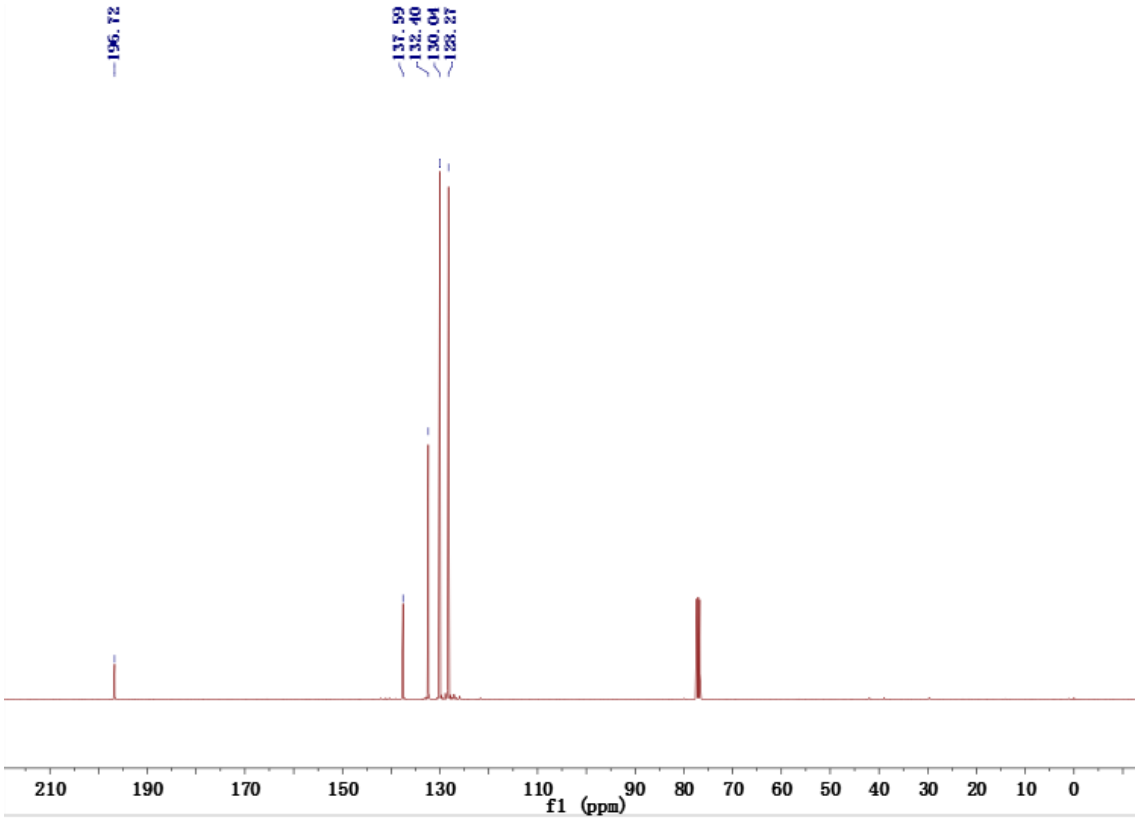
2h 4-methylacetophenone ^{13}C NMR (101 MHz, $CDCl_3$)



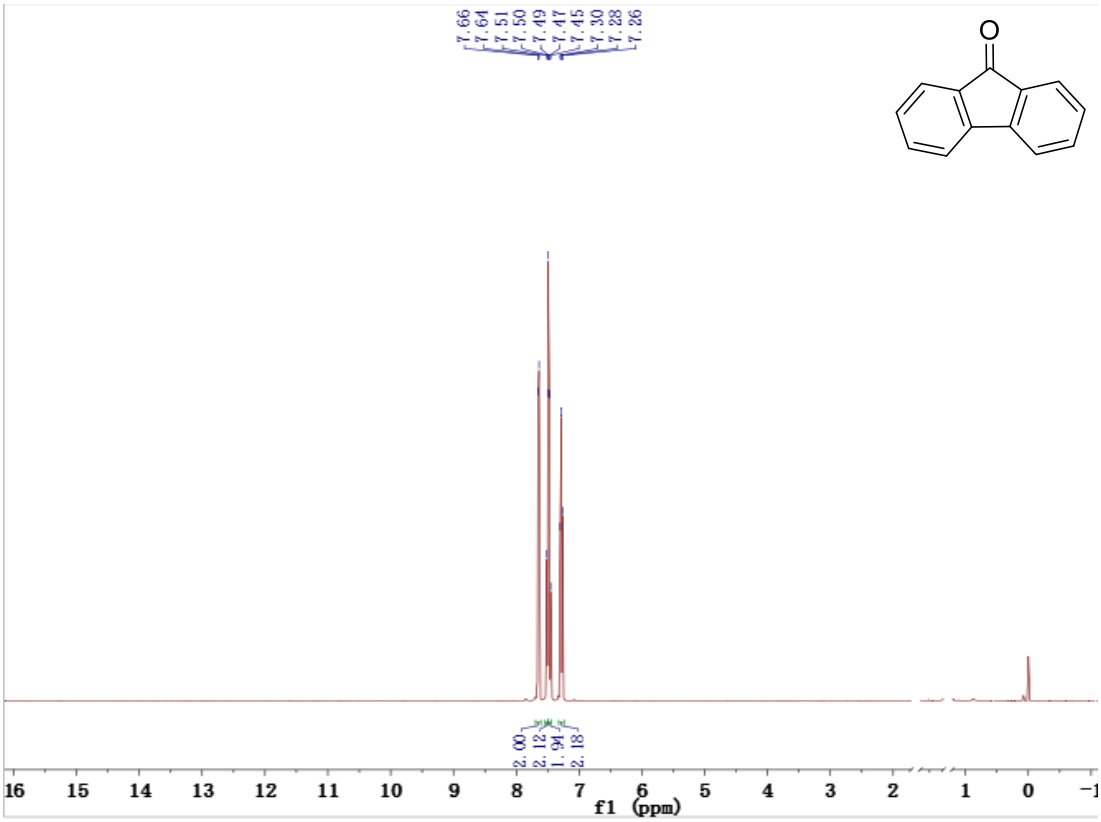
2i Benzophenone ^{1}H NMR (400 MHz, $CDCl_3$)



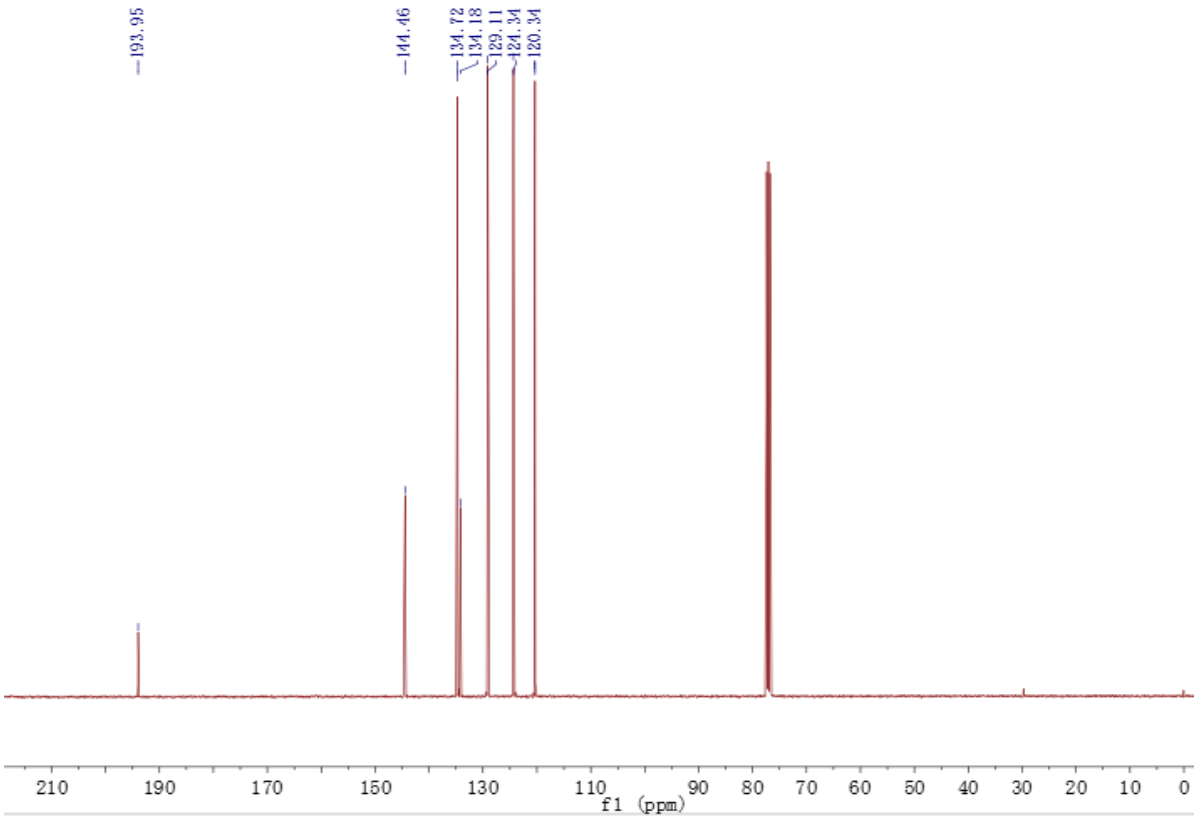
2i Benzophenone ^{13}C NMR (101MHz, $CDCl_3$)



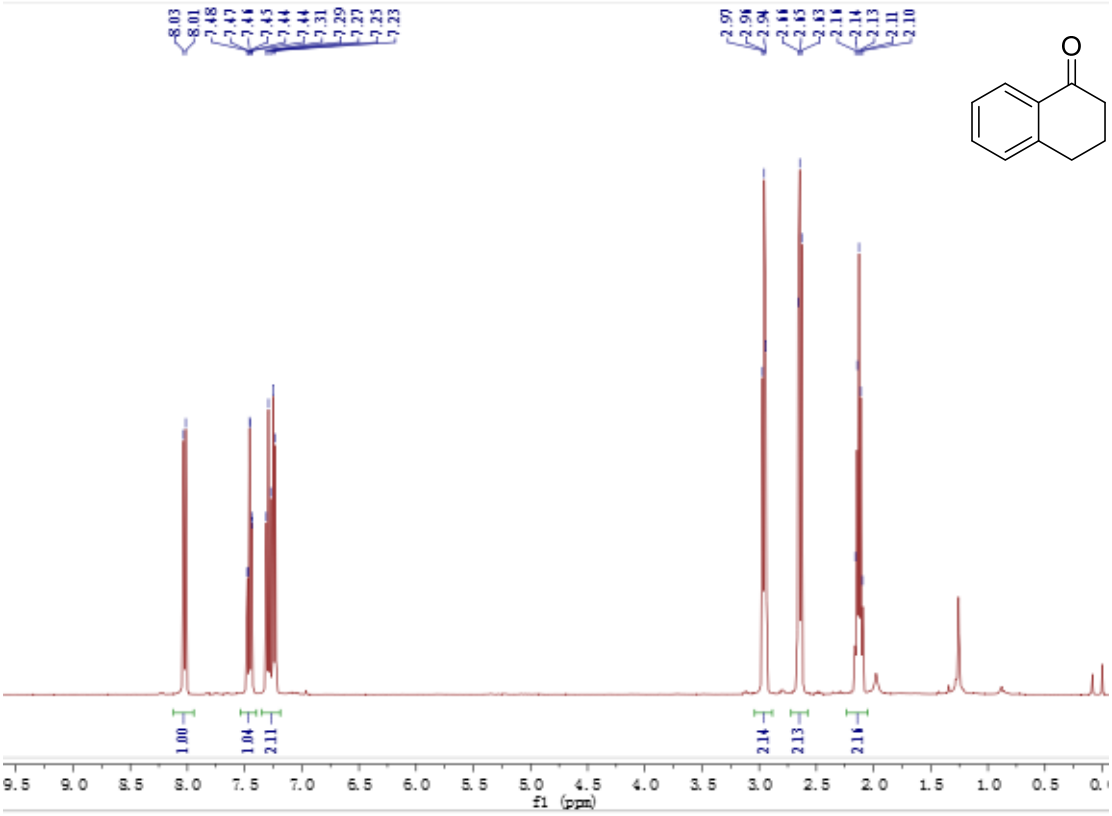
2j 9-fluorenone ^{1}H NMR(400 MHz, $CDCl_3$)

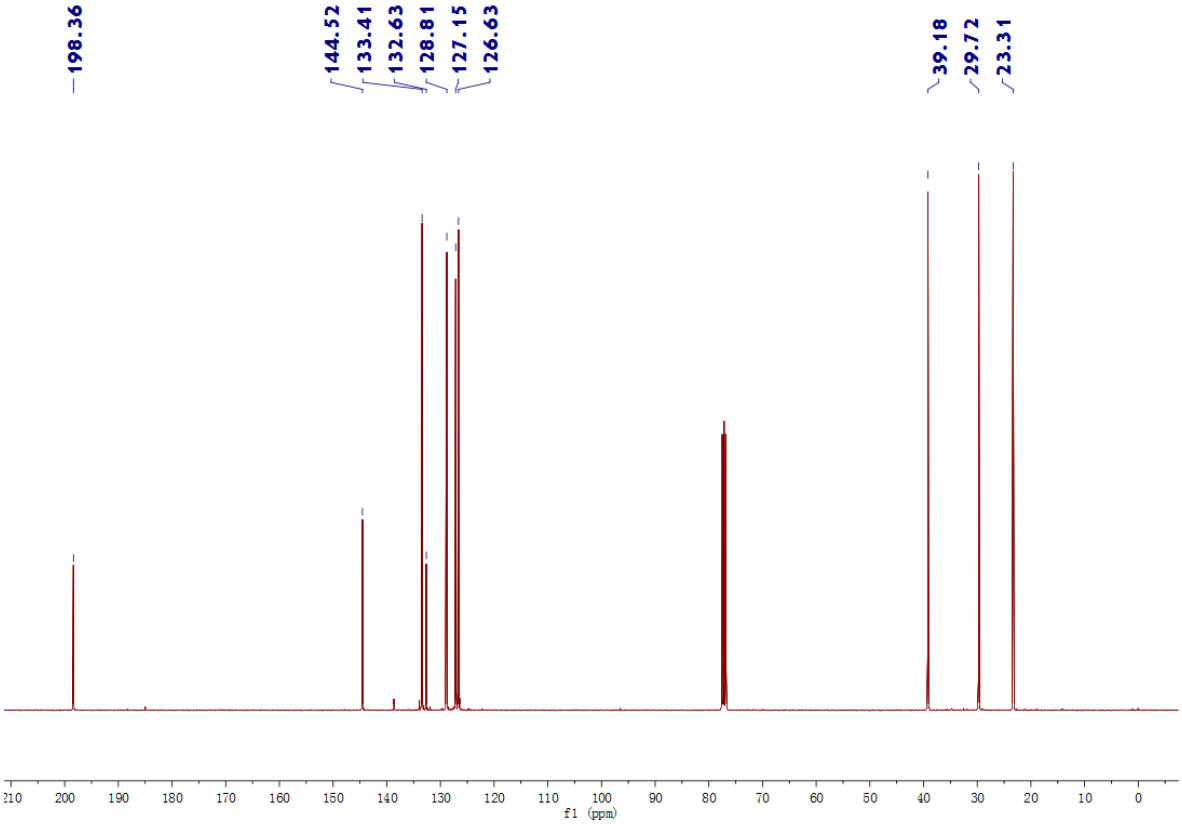


2j 9-fluorenone ^{13}C NMR(101 MHz, $CDCl_3$)

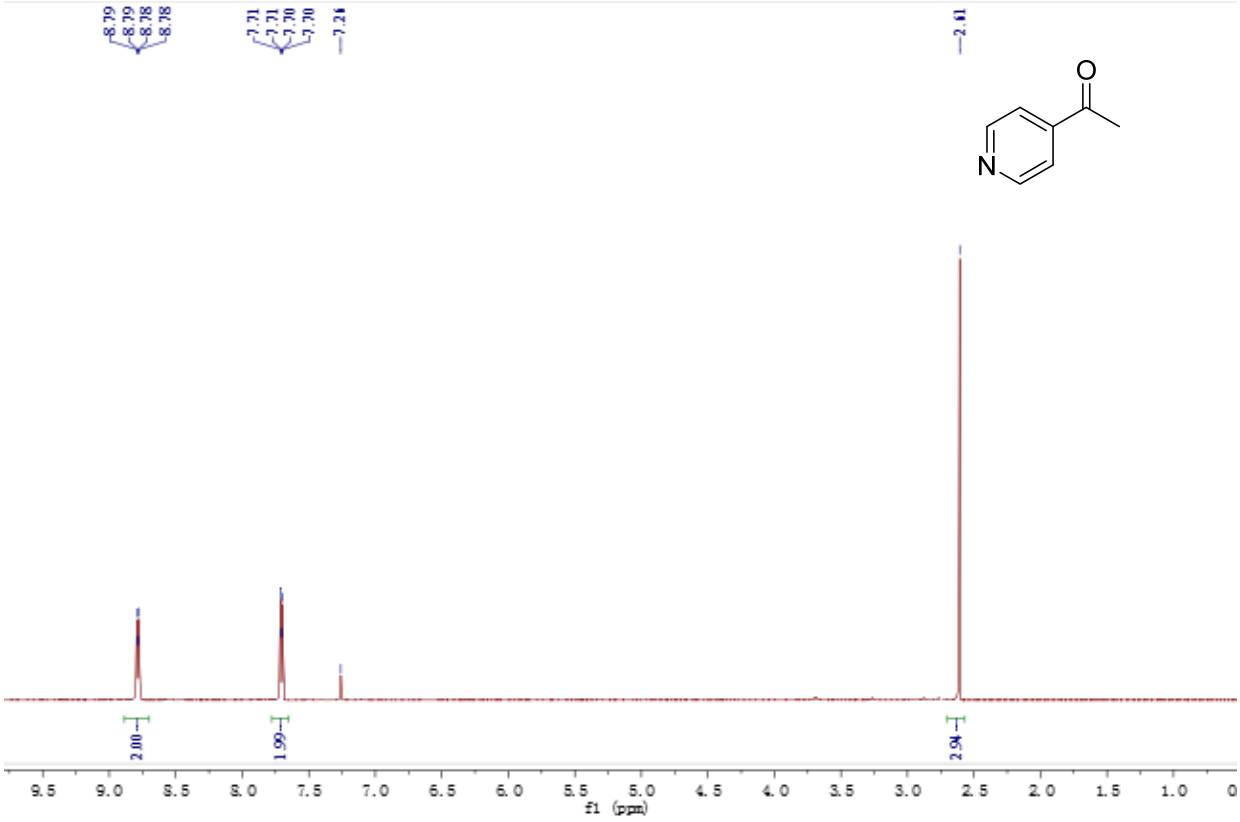


2k α-Tetralone ^{1}H NMR (400 MHz, $CDCl_3$)

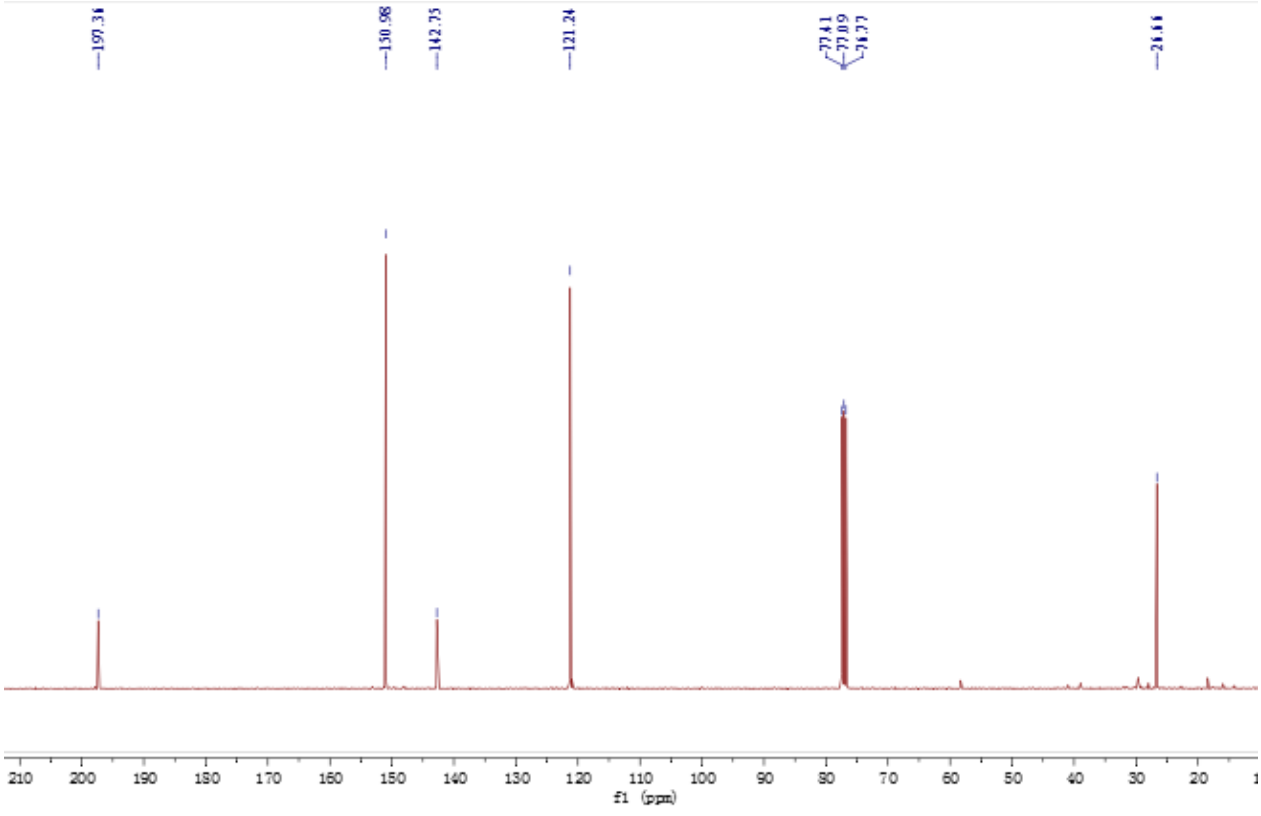




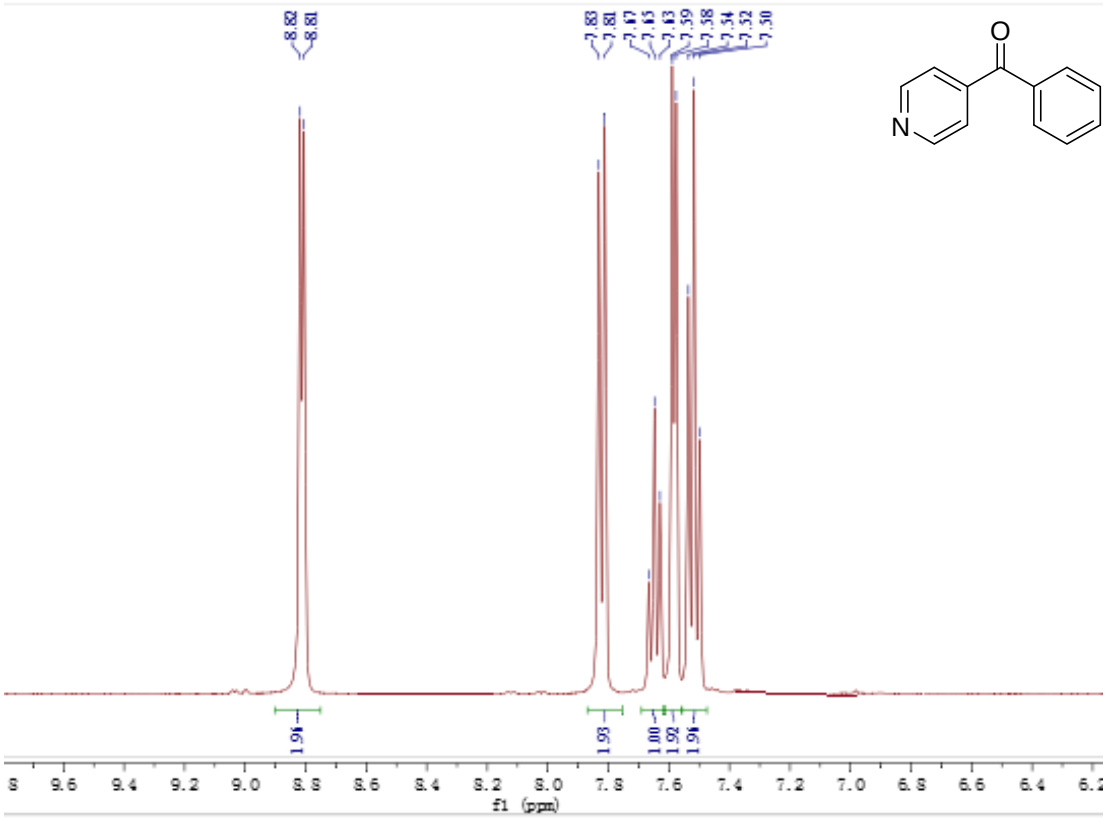
2l 4-acetylpyridine ^{1}H NMR (400 MHz, $CDCl_3$)



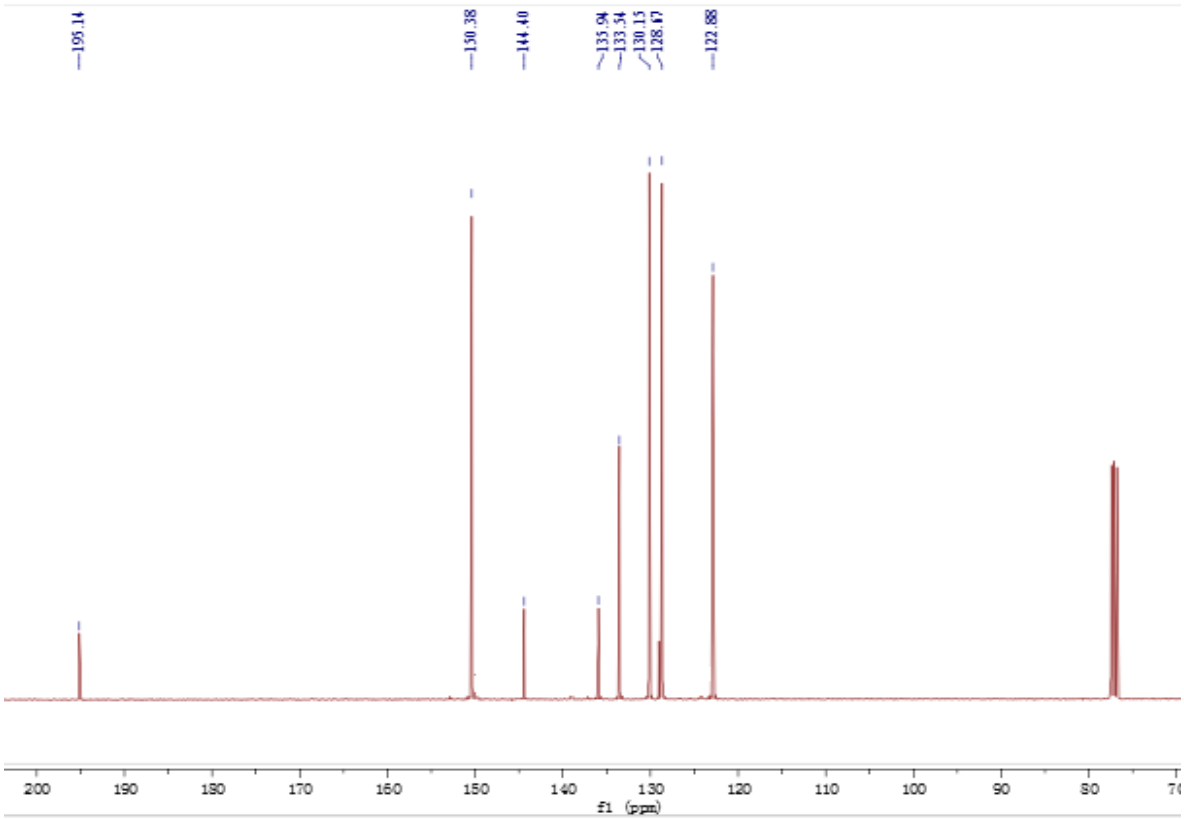
2l 4-acetylpyridine ^{13}C NMR (101 MHz, $CDCl_3$)



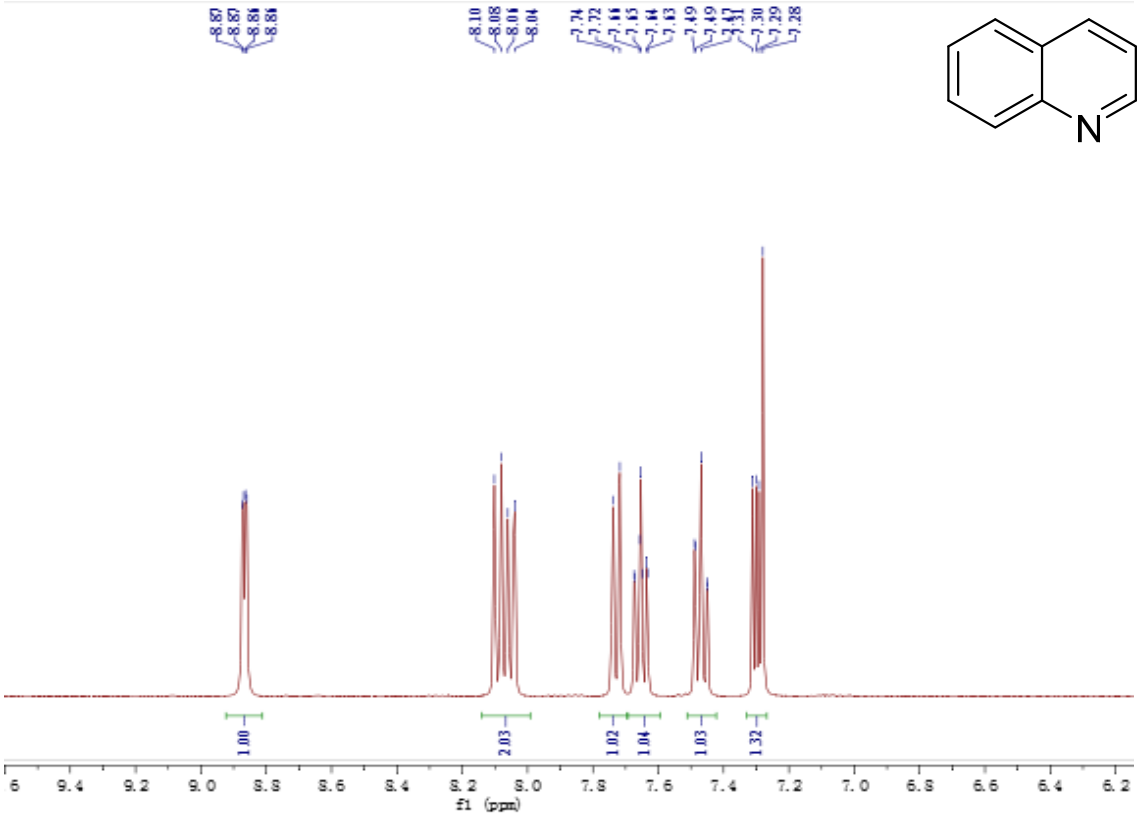
2m 4-benzoylpyridine ^{1}H NMR (400 MHz, $CDCl_3$)



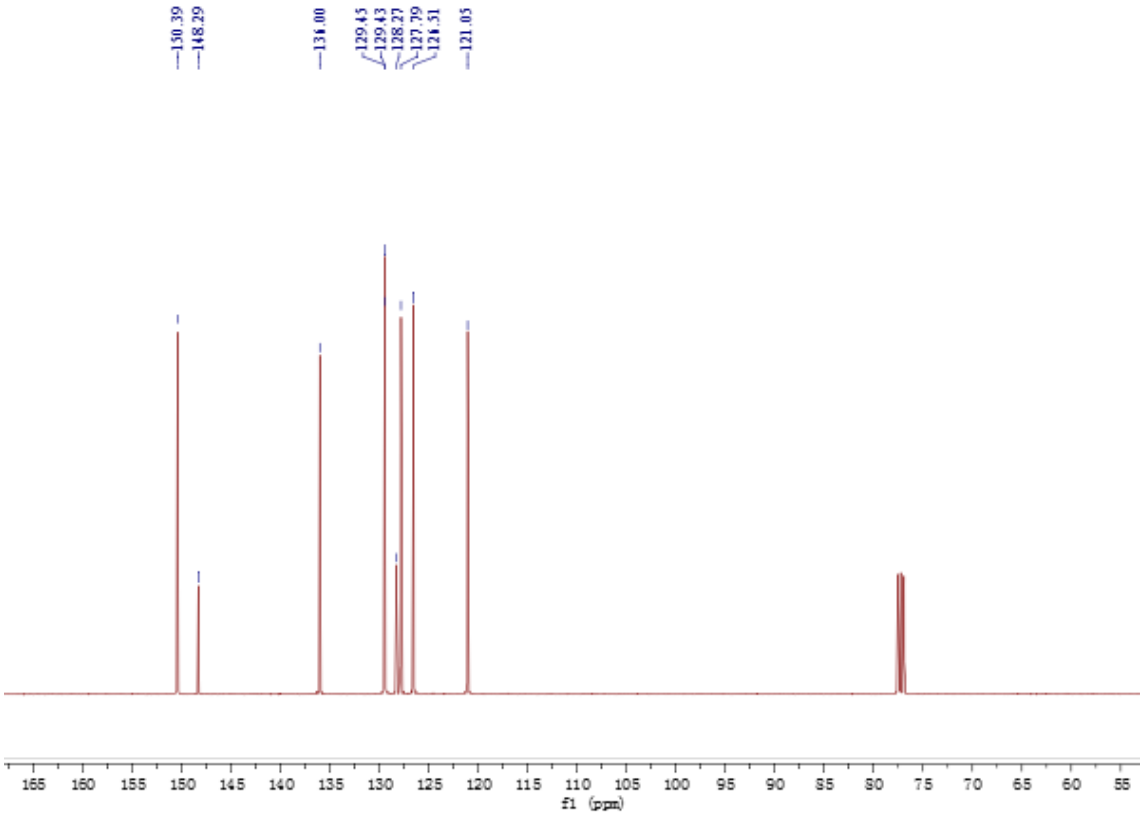
2m 4-benzoylpyridine ^{13}H NMR (101 MHz, $CDCl_3$)



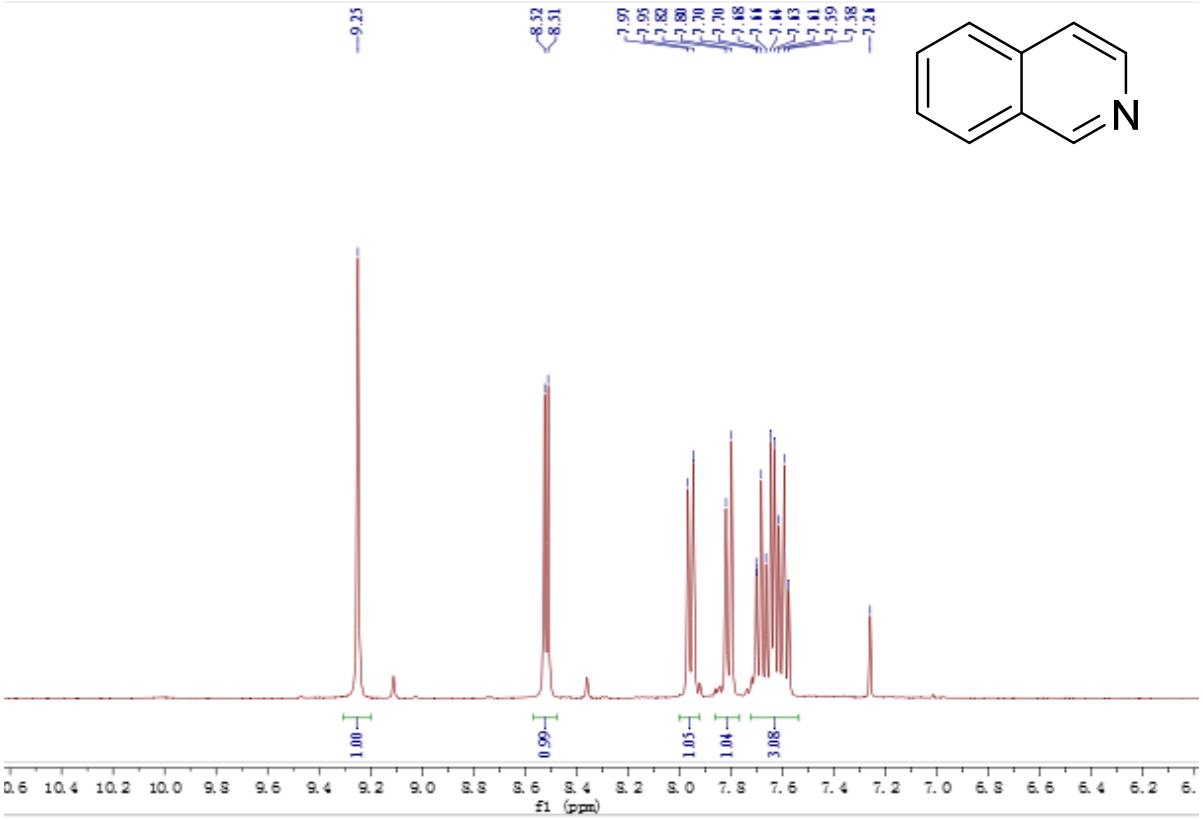
3c quinoline ^{1}H NMR (400 MHz, $CDCl_3$)



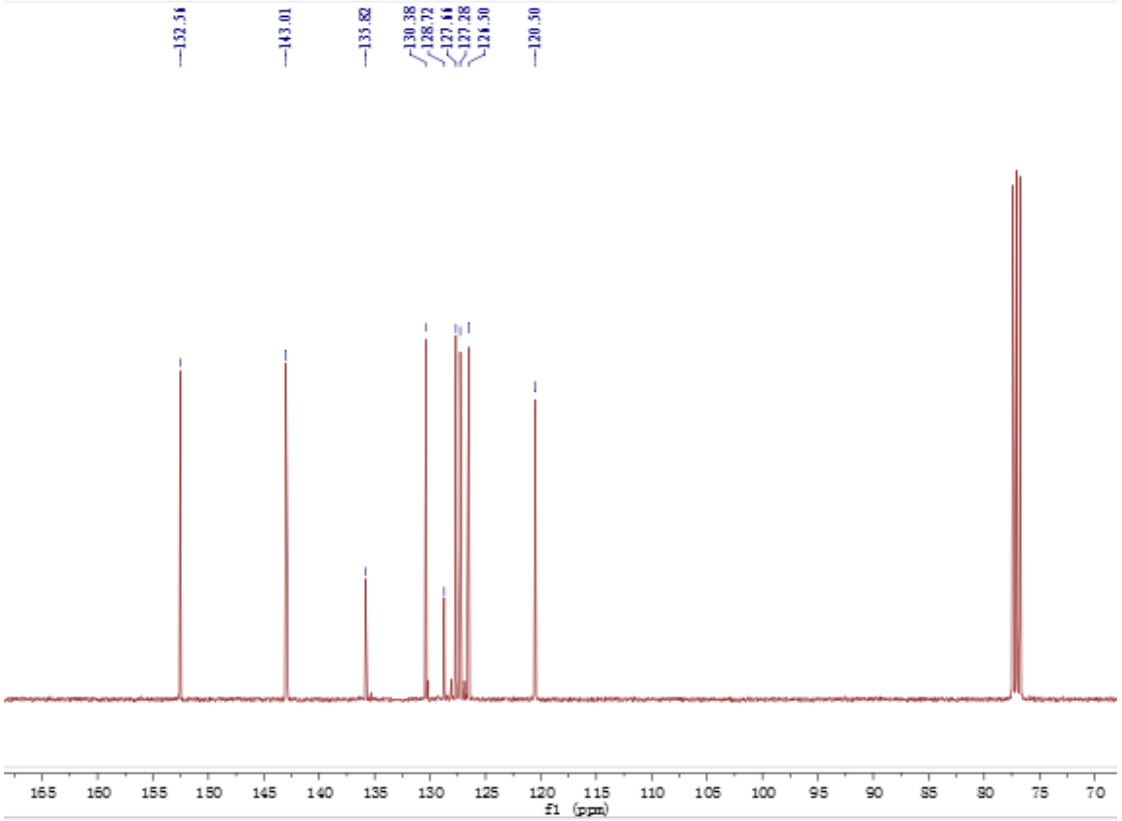
3c quinoline ^{13}C NMR (101 MHz, $CDCl_3$)



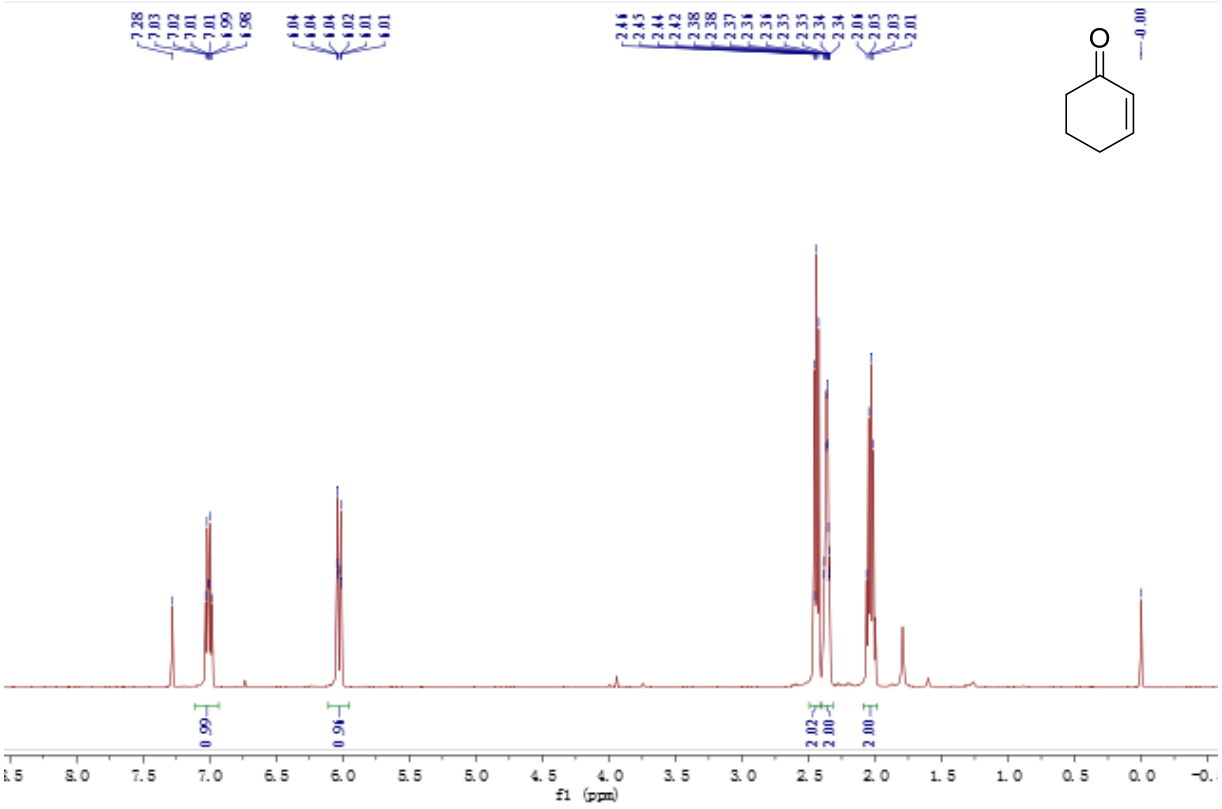
3d isoquinoline ^{1}H NMR (400 MHz, $CDCl_3$)



3d isoquinoline ^{13}C NMR (101 MHz, $CDCl_3$)



4b 2-Cyclohexen-1-one ^{1}H NMR (400 MHz, $CDCl_3$)



4b 2-Cyclohexen-1-one ^{13}C NMR (101 MHz, $CDCl_3$)