Support information for

Selective Hydrogenation of Nitroaromatics to *N*-arylhydroxylamines in a Micro-Packed Bed Reactor with Passivated Catalyst

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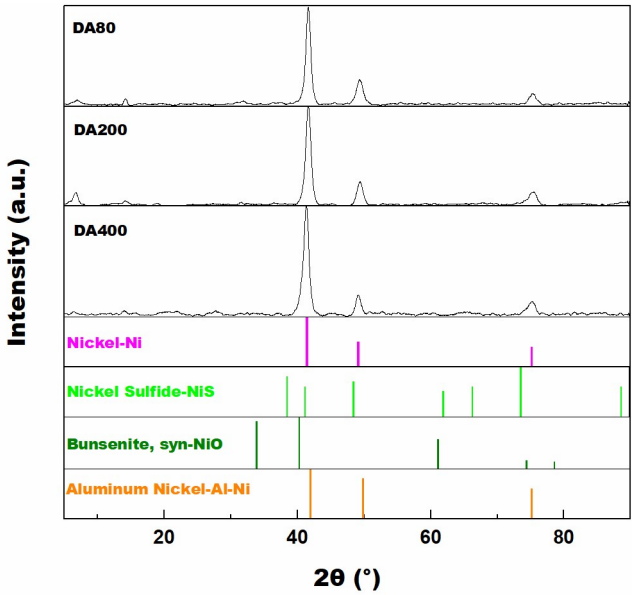
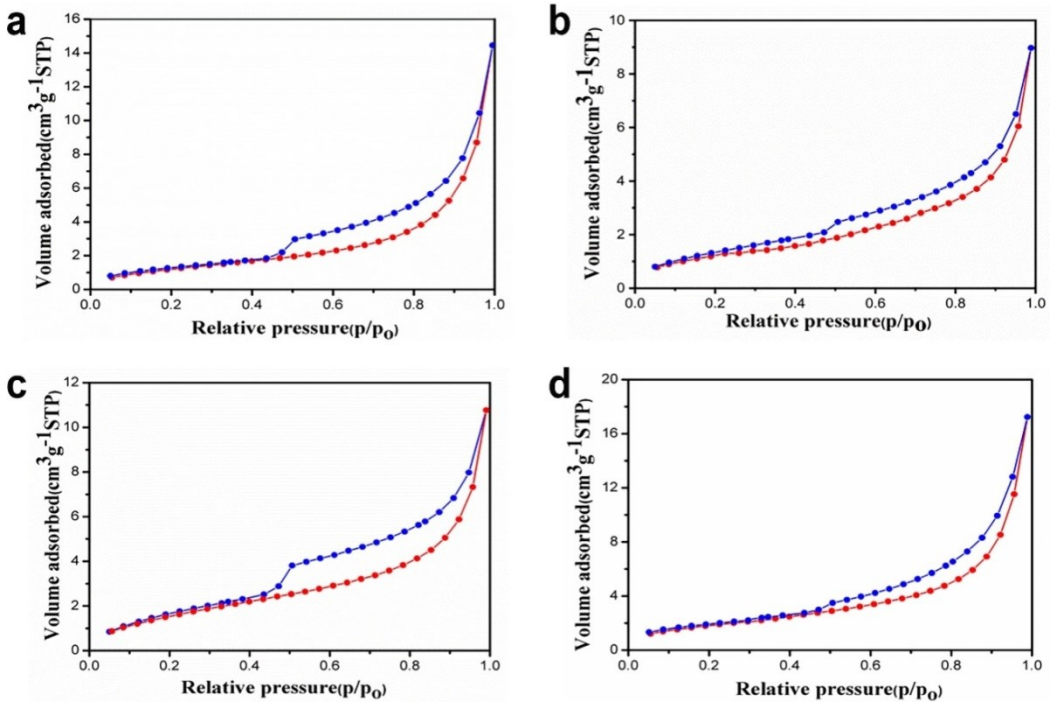
a) Powder X-ray diffraction data for passivated catalysts

Figure S1. XRD patterns for passivated catalysts



b) BET data for passivated catalysts

Figure S2. BET patterns of passivated catalysts (a is DA80; b is DA200; c is DA400; d is DA400r)



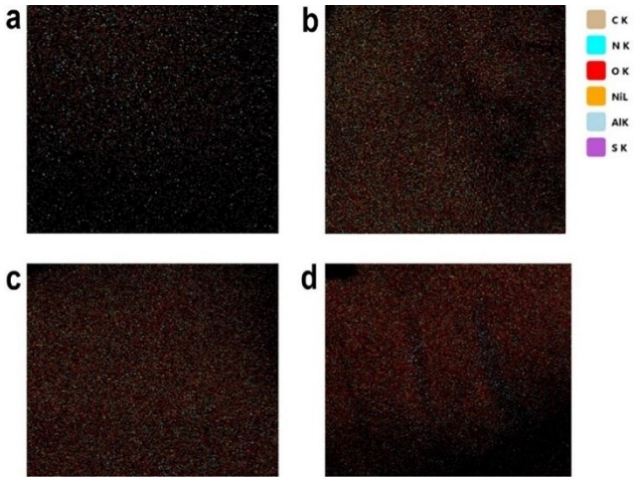
c) Elementary analysis data for passivated catalysts

Table S1. Elementary analysis

NO	catalyst	Weight	N [%]	C [%]	H [%]	S [%]	N area	C area	H area	S area
1		2.9430	0.46	5.31	1.571	2.779	317	2049	551	897
2	DA80	3.2090	0.43	5.07	1.495	2.726	332	2228	664	961
3		2.8460	0.48	5.44	1.581	2.792	323	2008	470	871
4		3.2830	0.29	4,74	1.656	2.406	216	2030	1085	866
5	DA200	3.4270	0.37	4.60	1.605	2.409	285	2082	1128	906
6		3.8450	0.26	4.37	1.576	2.383	226	2387	1500	1008
7		2.2930	0.15	5.62	2.021	2.154	75	1257	558	532
8	DA400	2.1750	0.21	5.87	2.058	2.169	104	1223	455	507
9		2.2230	0.15	5.73	2.023	2.082	75	1212	468	497
10		2.3790	0.57	5.78	2.035	2.538	324	1506	694	656
11	DA400r	3.8680	0.53	4.19	1.776	2.230	582	2219	2045	948
12		3.5300	0.53	4.48	1.872	2.309	511	2096	1869	894

d) EDS data for passivated catalysts

Figure S3. EDS spectra of different catalysts: DA80(a), DA200(b), DA400(c), DA400r(d)



2. Pre-optimization in batch reactor

Before the continuous-flow optimization, a pilot optimization was conducted in autoclave (Table S2). Firstly, different solvent was examined under this standard condition, showing the THF as the optimal choice for this transformation. Although the previous reports indicated the product selectivity may related with the solvent's dielectric constant, our results didn't show the similar tendency. This may be due to the higher rate of dehalogenation or hydrogenation of other functional groups.

The temperature examination showed the transformation performed better at -7 °C. The higher temperature resulted in catalyst activation, whose selectivity dropped dramatically. The results indicate the selectivity reducing with increasing the reaction temperature.

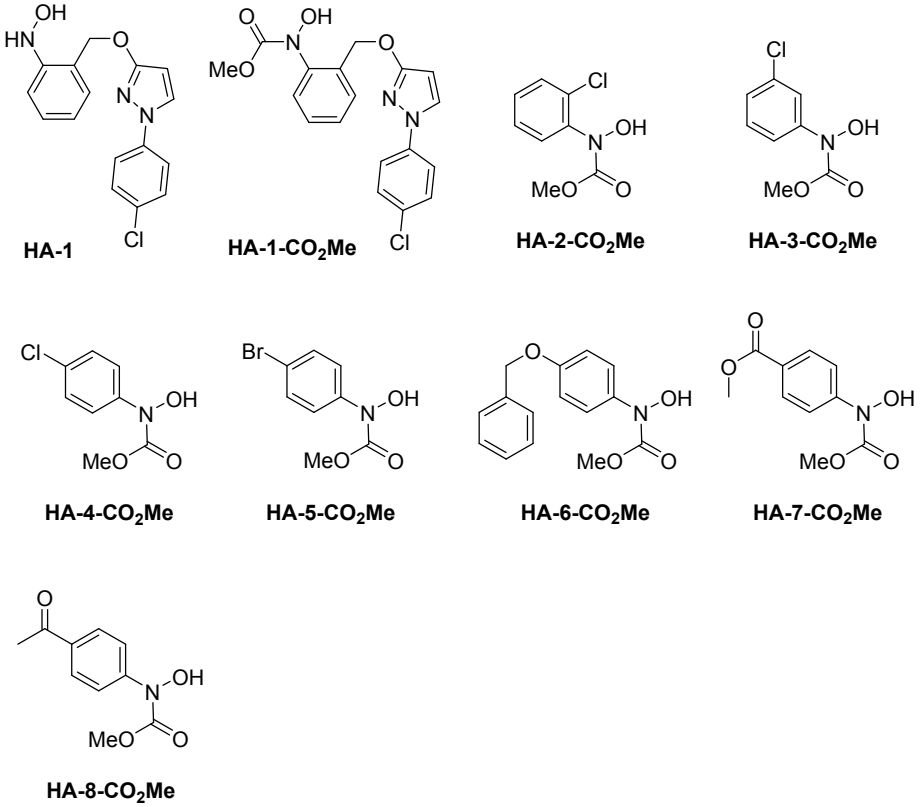
The amount of catalyst loading also have some influence on the outcomes, where higher loading provided a much higher conversion but poor selectivity, which may due to the more catalytic opportunity in the system.

Finally, the reaction time was examined. As expected, during the reaction process, the hydroxylamine, as the intermediate, changed with reaction developing. And the optimal reaction time was found to be 32 hrs, rendering the conversion over 99% with a selectivity of 97%.

Table S2. Pre-optimization in autoclave

entry	cat. Loading(%)	Solvent	temp. °C	time hrs	%Yield %HA-1	%Yield %AM-1	%Select.	%Conv.
1	**5**	**THF**	**-8**	**29**	**78.1%**	**8.9%**	**89.8%**	**87.0%**
2	5	DCM	-8	29	44.1%	55.9%	44.1%	100.0%
3	5	EtOAc	-8	29	56.1%	41.8%	57.3%	97.9%
4	5	EtOH:THF(1:9)	-8	29	9.8%	90.2%	9.8%	100.0%
5	5	1,4-dioxiane	-8	29	0.0%	100.0%	0.0%	100.0%
6	5	THF	-10	27	12.5%	2.4%	83.9%	14.9%
7	**5**	**THF**	**-7**	**27**	**80.5%**	**2.7%**	**96.8%**	**83.1%**
8	5	THF	-5	27	79.8%	20.2%	79.8%	100.0%
9	5	THF	0	27	65.3%	33.5%	66.1%	98.7%
10	3	THF	**-7**	26	28.4%	0.4%	98.7%	28.8%
11	5	THF	**-7**	26	73.5%	4.8%	93.9%	78.3%
12	**7**	**THF**	**-7**	**26**	**82.5%**	**12.9%**	**86.5%**	**95.4%**
13	10	THF	**-7**	26	66.3%	30.9%	68.2%	97.2%
14	5	THF	**-7**	15	30.4%	1.1%	96.5%	31.6%
15	5	THF	**-7**	24	54.6%	5.3%	91.1%	59.9%
16	**5**	**THF**	**-7**	**32**	**96.8%**	**3.0%**	**97.0%**	**99.7%**
17	5	THF	**-7**	48	23.2%	76.8%	23.2%	100.0%
18	5	THF	**-7**	52	0.0%	100.0%	0.0%	100.0%

3. Product data and Copies of Spectra



Scheme S1. Substrates scope of nitroaromatics.

N-(2-(((1-(4-chlorophenyl)-1H-pyrazol-3-yl)oxy)methyl)phenyl)hydroxylamine. (**HA-1**). Light yellow solid, mp:98-103 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.51-8.37 (m, 2H), 8.19 (s, 1H), 7.86-7.76 (m, 2H), 7.60-7.50 (m, 2H), 7.37-7.16 (m, 3H), 6.90-6.78 (m, 1H), 6.12 (d, J = 2.7 Hz, 1H), 5.23 (s, 2H); HR-MS[ESI]: $C_{16}H_{14}ClN_3O_2$ for $[M+Na]^+$, calculated 338.0673, found 338.0668.

Methyl(2-(((1-(4-chlorophenyl)-1H-pyrazol-3-yl)oxy)methyl)phenyl)(hydroxy)carbamate. (**HA-1-CO$_2$Me**). White solid (99.5% yield), mp: 130-132 °C(ref.[1] mp: 131-132 °C) ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.42 (s, 1H), 8.41 (d, J = 2.7 Hz, 1H), 7.83-7.76 (m, 2H), 7.60 (dd, J = 6.7, 2.9 Hz, 1H), 7.56-7.51 (m, 2H), 7.40 (dd, J = 5.1, 3.4 Hz, 3H), 6.11 (d, J = 2.6 Hz, 1H), 5.30 (s, 2H), 3.70 (s, 3H). HR-MS [ESI]: $C_{18}H_{16}ClN_3O_4$ for $[M+Na]^+$, calculated 396.0727, found 396.0730.

Methyl (2-chlorophenyl)(hydroxy) carbamate (**HA-2-CO$_2$Me**). Yellow solid (83.5% yield), mp:103-105 °C; FT-IR (ν_{max}/cm^{-1}) 771, 1053, 1133, 1445, 1715, 3320; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.79 (s, 1H), 7.57-7.44 (m, 2H), 7.41-7.28 (m, 2H), 3.81 (s, 3H);^{13}C NMR (126 MHz, CDCl3) δ 157.18, 138.51, 132.58, 130.14, 129.98, 129.57, 127.62, 53.94; HR-MS(ESI) for $[C_8H_8ClNO_3+Na]^+$, calculated 224.0091, found 224.0092.

Methyl (3-chlorophenyl)(hydroxy)carbamate(**HA-3-CO$_2$Me**). Yellow solid, (79.2% yield), mp:78-81 °C; FT-IR (ν_{max}/cm^{-1}) 726, 781, 869, 1053, 1592, 1682, 3196.^{1}H NMR (400 MHz, DMSO-d6) δ 10.58 (s, 1H), 7.62 (t, J = 2.1 Hz, 1H), 7.57 - 7.50 (m, 1H), 7.41 (t, J = 8.2 Hz, 1H), 7.24 - 7.17 (m, 1H), 3.79 (s, 3H).^{13}C NMR (126 MHz, DMSO) δ 154.93, 143.97, 133.30, 130.58, 124.13, 119.38, 118.28, 53.54. HR-MS[ESI]: $C_8H_8ClNO_3$ for $[M+Na]^+$, calculated 224.0091, found 224.0082.

***Methyl(4-chlorophenyl)(hydroxy)carbamate* (HA-4-CO_2Me).** Light yellow solid, (87.47% yield), mp:63-65 °C (lit.[2] mp:64-65 °C); FT-IR (ν_{max}/cm^{-1}) 831, 1046, 1490, 1668, 3251; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.52 (s, 1H), 7.61-7.54 (m, 2H), 7.48-7.41 (m, 2H), 3.78 (s, 3H); HR-MS[ESI]: $C_8H_8ClNO_3$ for $[M+Na]^+$, calculated 224.0091, found 224.0085.

***Methyl(4-bromophenyl)(hydroxy)carbamate* (HA-5-CO_2Me).** Light yellow solid, (88.36% yield), mp:90-92 °C(lit.[2], mp:90-92 °C); FT-IR (ν_{max}/cm^{-1}) 832, 1004, 1446, 1682, 3445; ^{1}H NMR (400 MHz, DMSO-d6) δ 10.52 (s, 1H), 7.60-7.54 (m, 2H), 7.54-7.48 (m, 2H), 3.77 (s, 3H); HR-MS[ESI]: $C_8H_8BrNO_3$ for $[M+Na]^+$, calculated 267.9586, found 267.9572.

***Methyl(4-(benzyloxy)phenyl)(hydroxy)carbamate* (HA-6-CO_2Me).** Red solid, (81.90% yield), mp: 87-90 °C; FT-IR (ν_{max}/cm^{-1}) 699, 748, 838, 1120,1243, 1703, 3224; ^{1}H NMR (400 MHz, DMSO-d6) δ 9.44 (s, 1H), 7.47-7.34 (m, 7H), 7.01-6.93 (m, 2H), 5.07 (s, 2H), 3.66 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ156.21, 155.57, 137.48, 136.08, 128.89, 128.28, 128.11, 123.97, 115.05, 69.85, 53.13; HR-MS[ESI]: $C_{15}H_{15}NO_4$ for $[M+H]^+$, calculated 274.1961, found 274.1948.

***Methyl4-(hydroxy(methoxycarbonyl)amino)benzoate* (HA-7-CO_2Me).** Yellow solid, (34.71% yield), mp:100-103 °C; FT-IR (ν_{max}/cm^{-1}) 853, 1385, 1726, 1737, 3225; ^{1}H NMR (400 MHz, DMSO-d6) δ 10.65 (s, 1H), 8.02-7.94 (m, 2H), 7.79-7.69 (m, 2H), 3.86 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ 166.19, 154.74, 146.53, 130.28, 124.77, 118.57, 53.62, 52.37; HR-MS[ESI]: $C_{10}H_{11}NO_5$ for $[M+Na]^+$, calculated 248.0535, found 248.0498.

***Methyl(4-acetylphenyl)(hydroxy)carbamate* (HA-8-CO_2Me).** Yellow solid, (89.46% yield), mp:141-144 °C; FT-IR (ν_{max}/cm^{-1}) 849, 1599, 1660, 1715, 3175; ^{1}H NMR (400 MHz, DMSO-d6) δ 10.64 (s, 1H), 7.98 (d, J = 8.9 Hz, 2H), 7.72 (d, J = 8.9 Hz, 2H), 3.81 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ 197.00, 154.75, 146.40, 132.42, 129.44, 118.48, 53.63, 26.94; HR-MS[ESI]: $C_{10}H_{11}NO_4$ for $[M+Na]^+$, calculated 232.0566, found 232.0555.

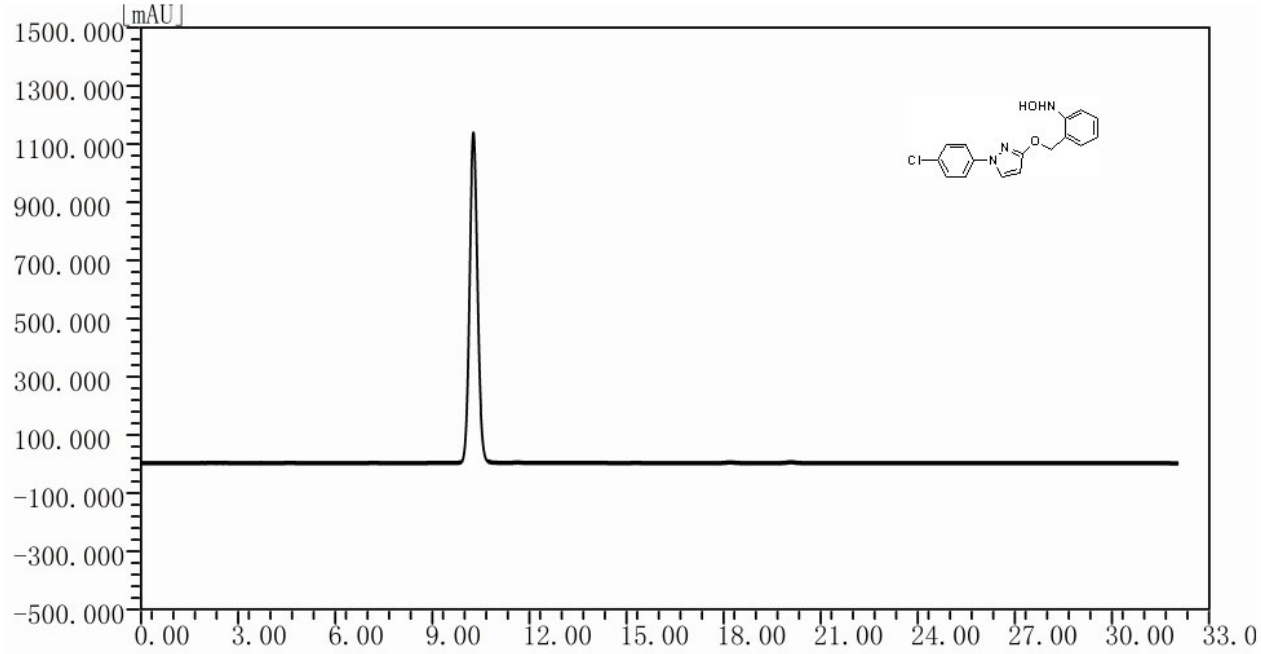


Figure S4 HPLC spectra for the outcoming reaction (The only signal from **HA-1**)

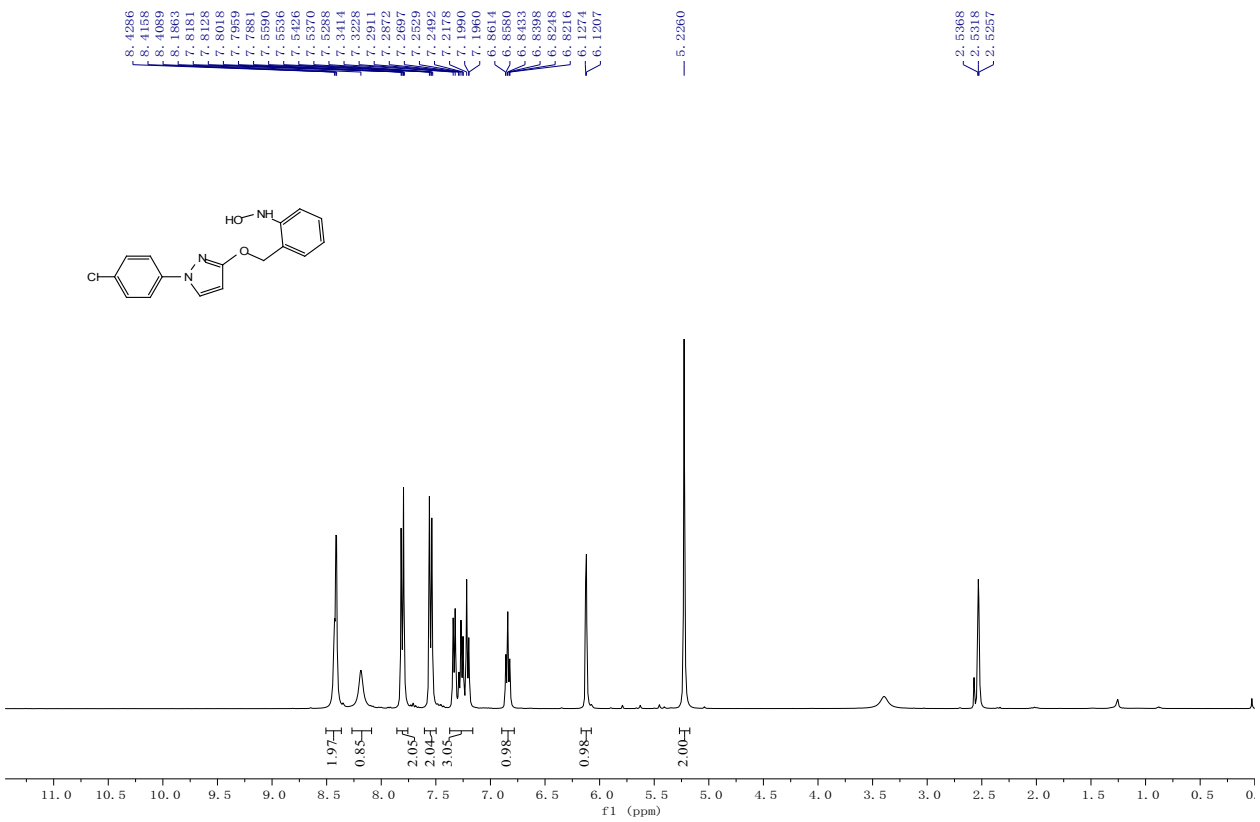


Figure S5 ^{1}H-NMR spectra for HA-1

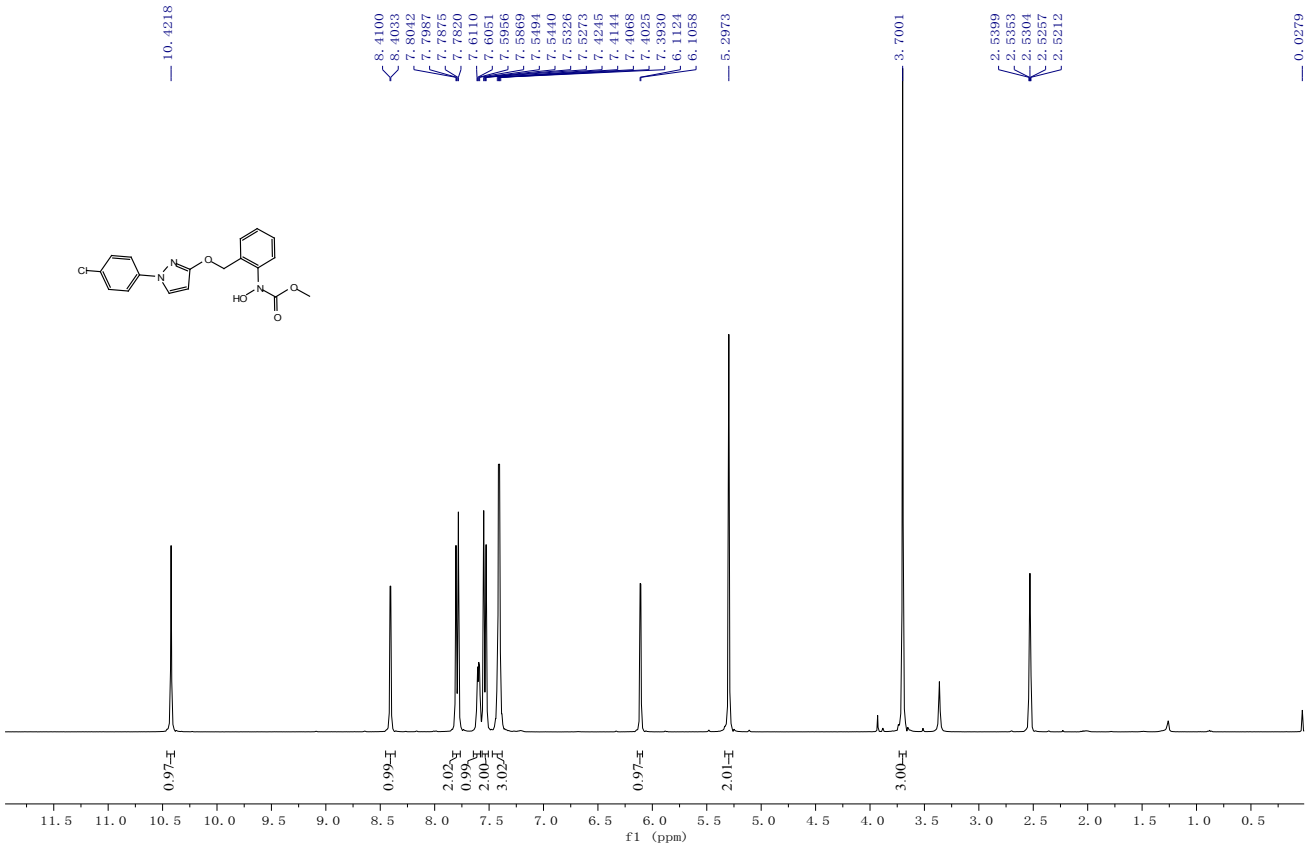


Figure S6 ^{1}H-NMR spectra for HA-1-CO_2Me

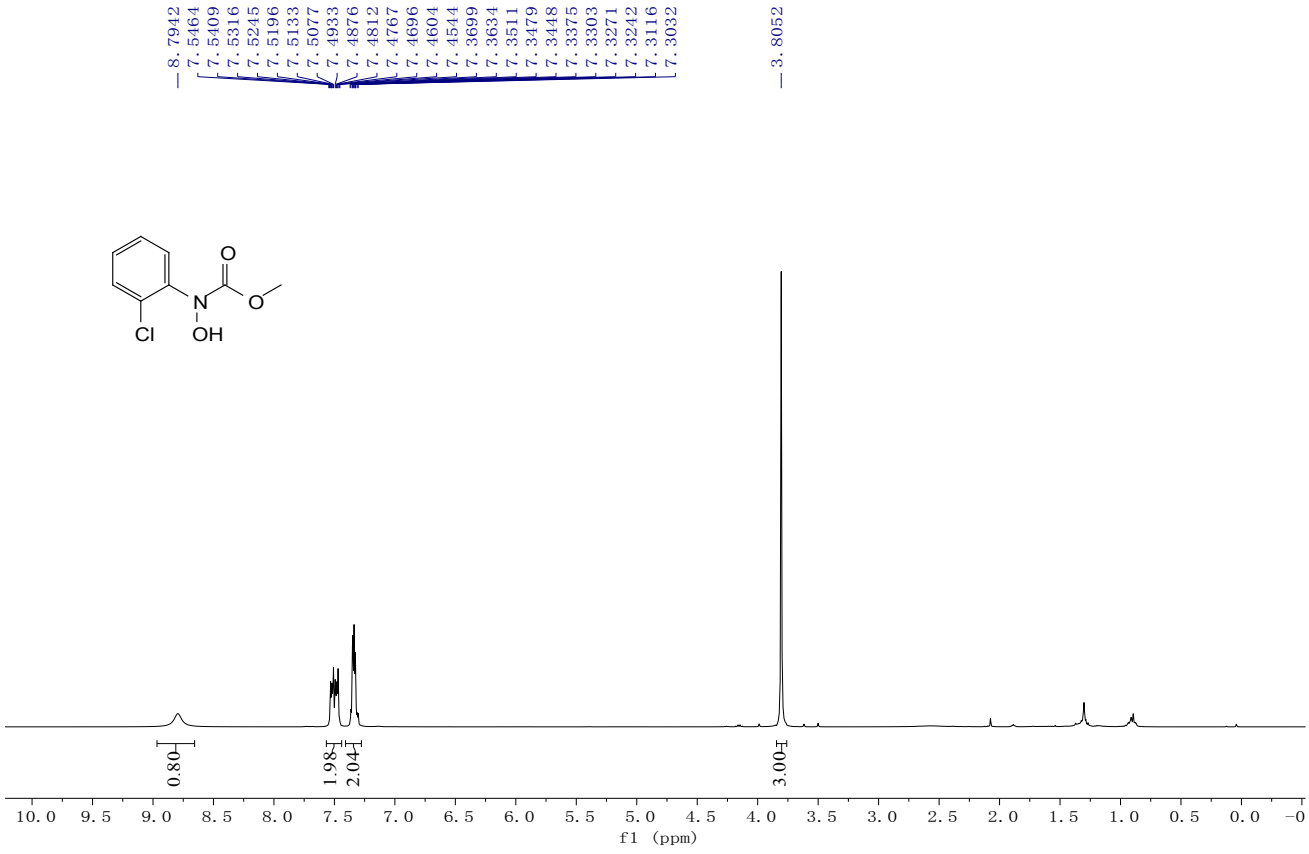


Figure S7 ^{1}H-NMR spectra for HA-2-CO_2Me

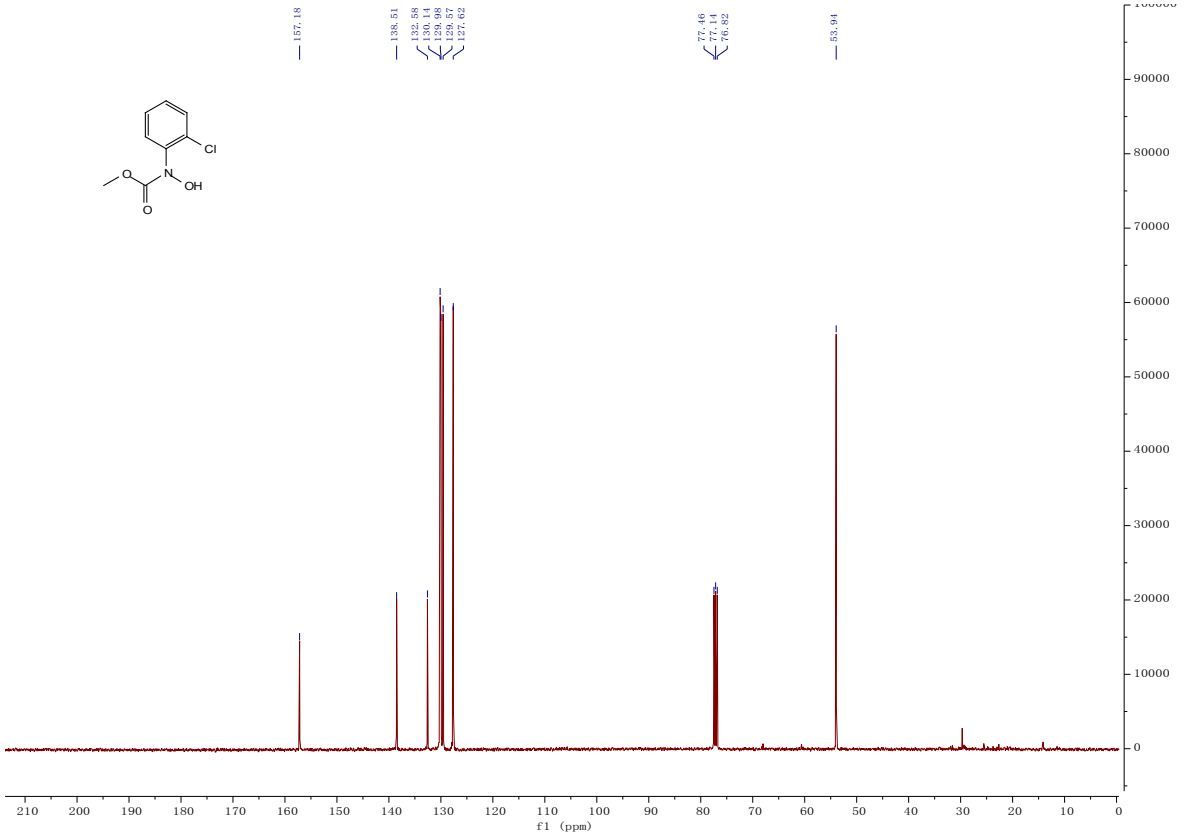


Figure S8 ^{13}C-NMR spectra for HA-2-CO_2Me

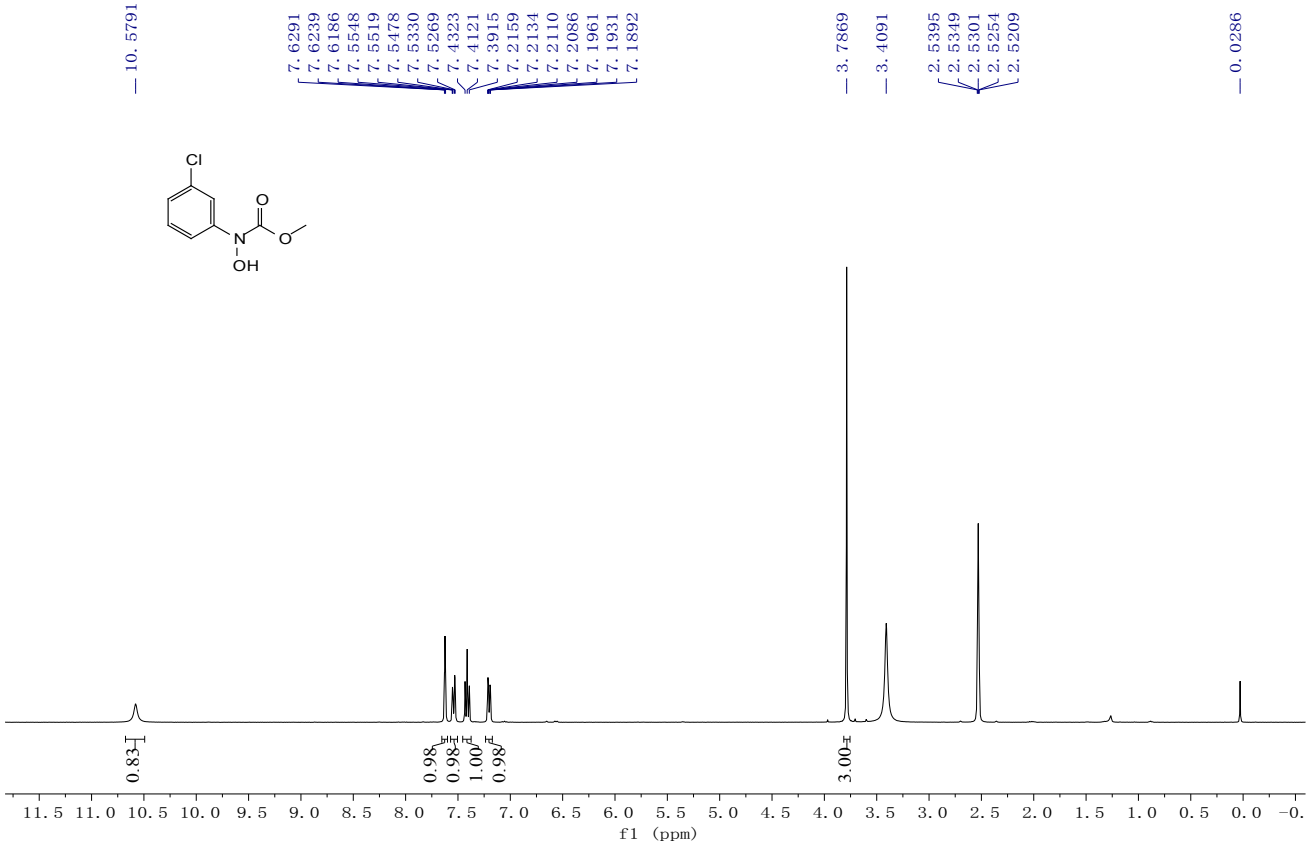


Figure S9 ^{1}H-NMR spectra for HA-3-CO_2Me

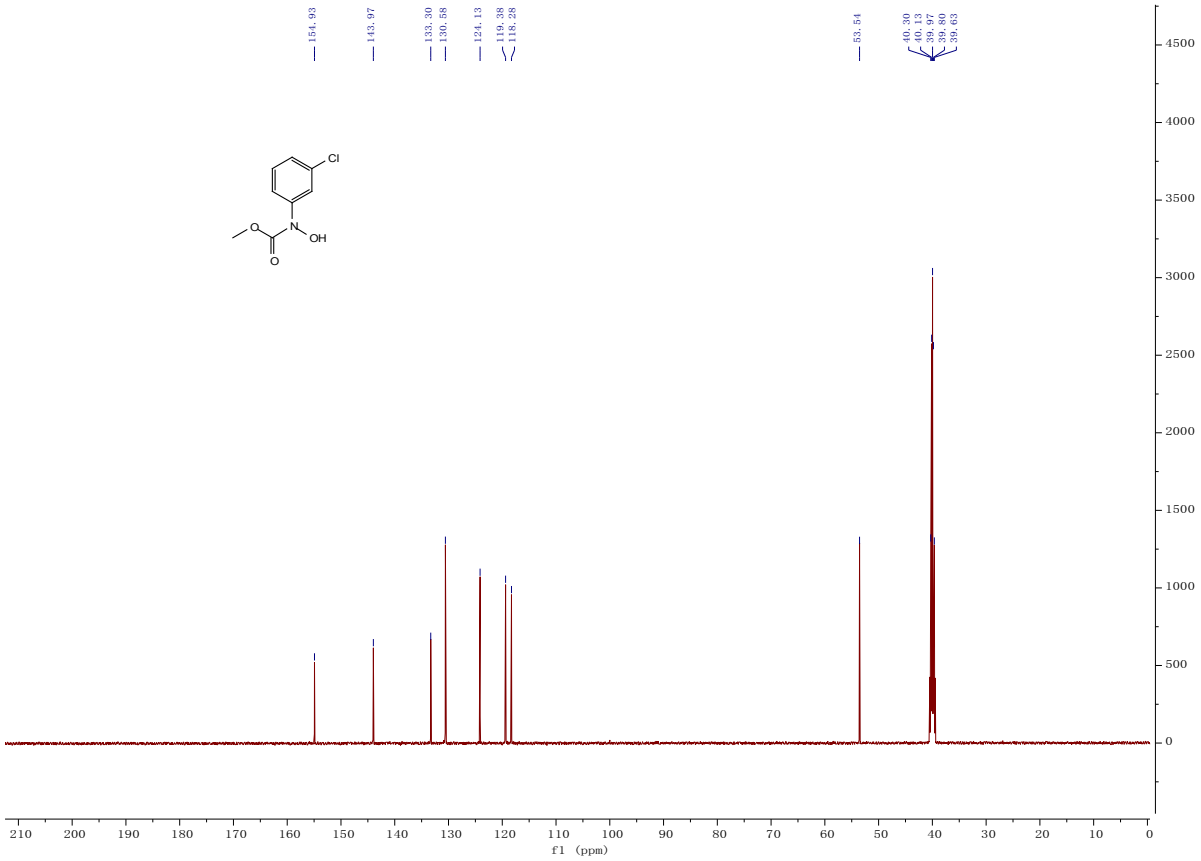


Figure S10 ^{13}C-NMR spectra for HA-3-CO_2Me

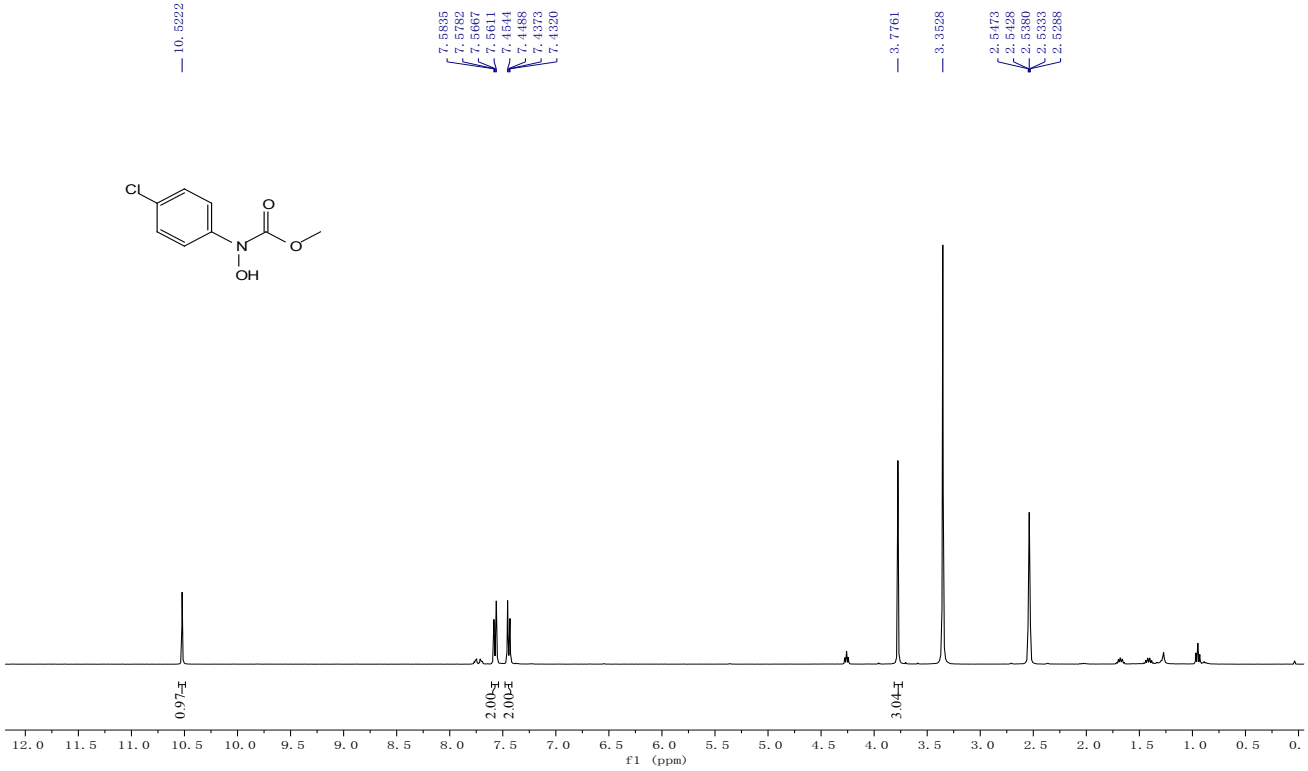


Figure S11 ^{1}H-NMR spectra for HA-4-CO_2Me

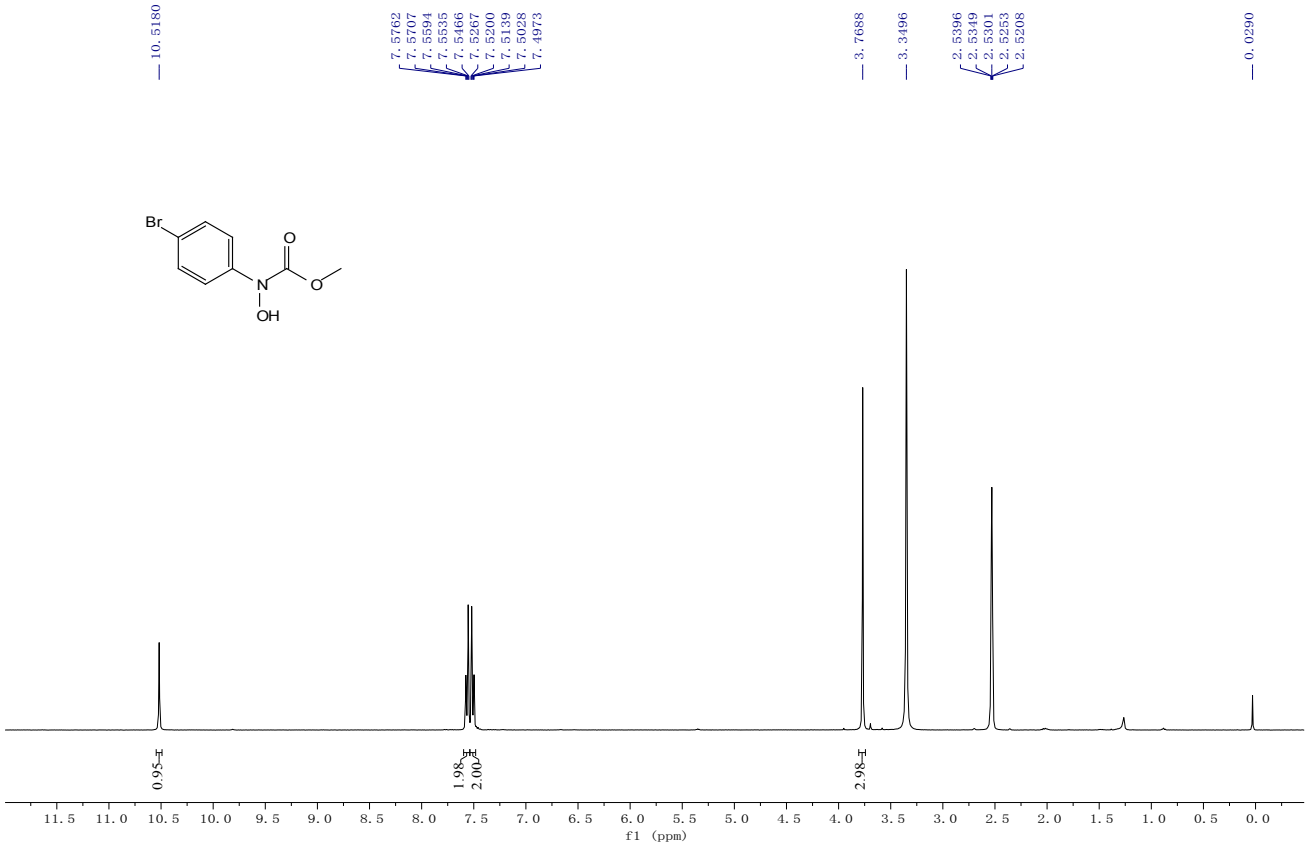


Figure S12 ^{1}H-NMR spectra for HA-5-CO_2Me

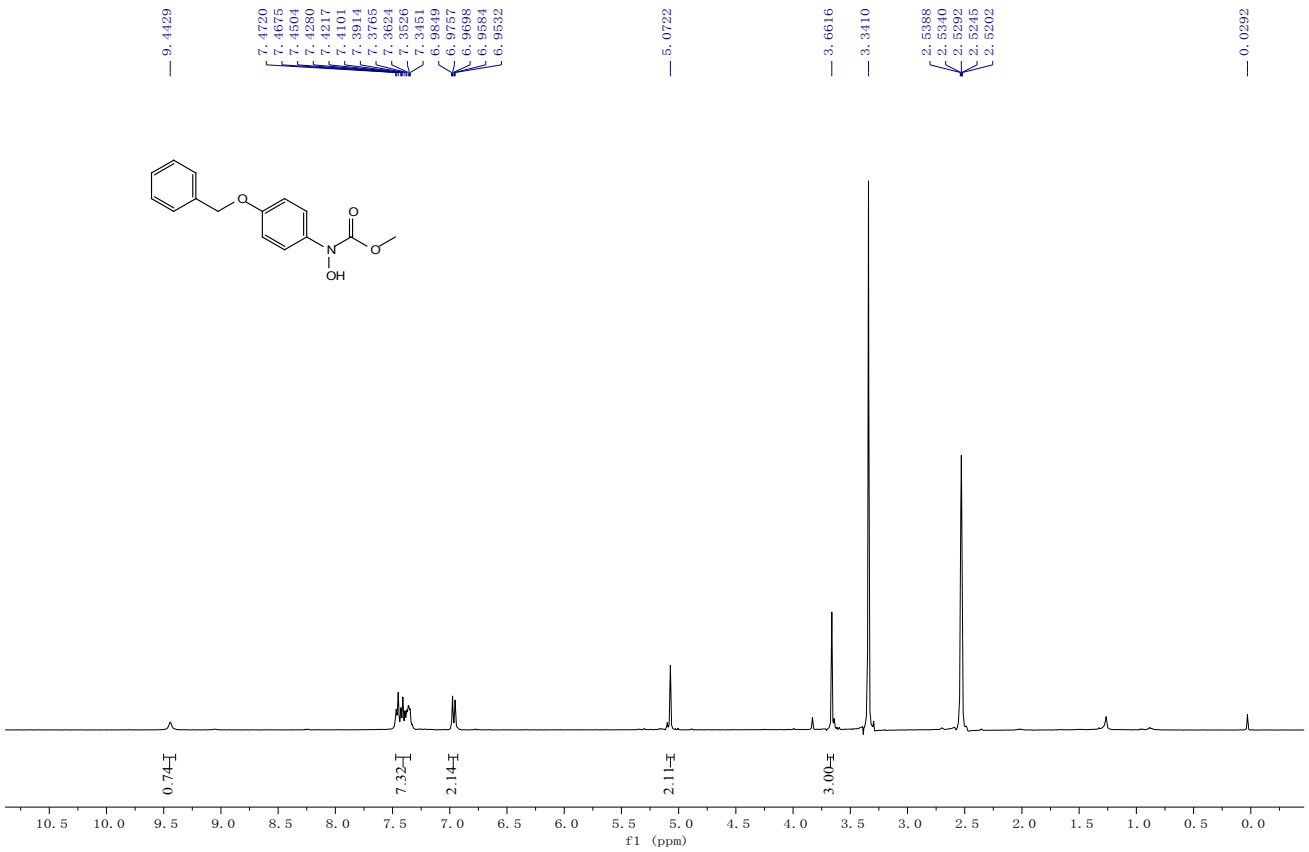


Figure S13 ^{1}H-NMR spectra for HA-6-CO_2Me

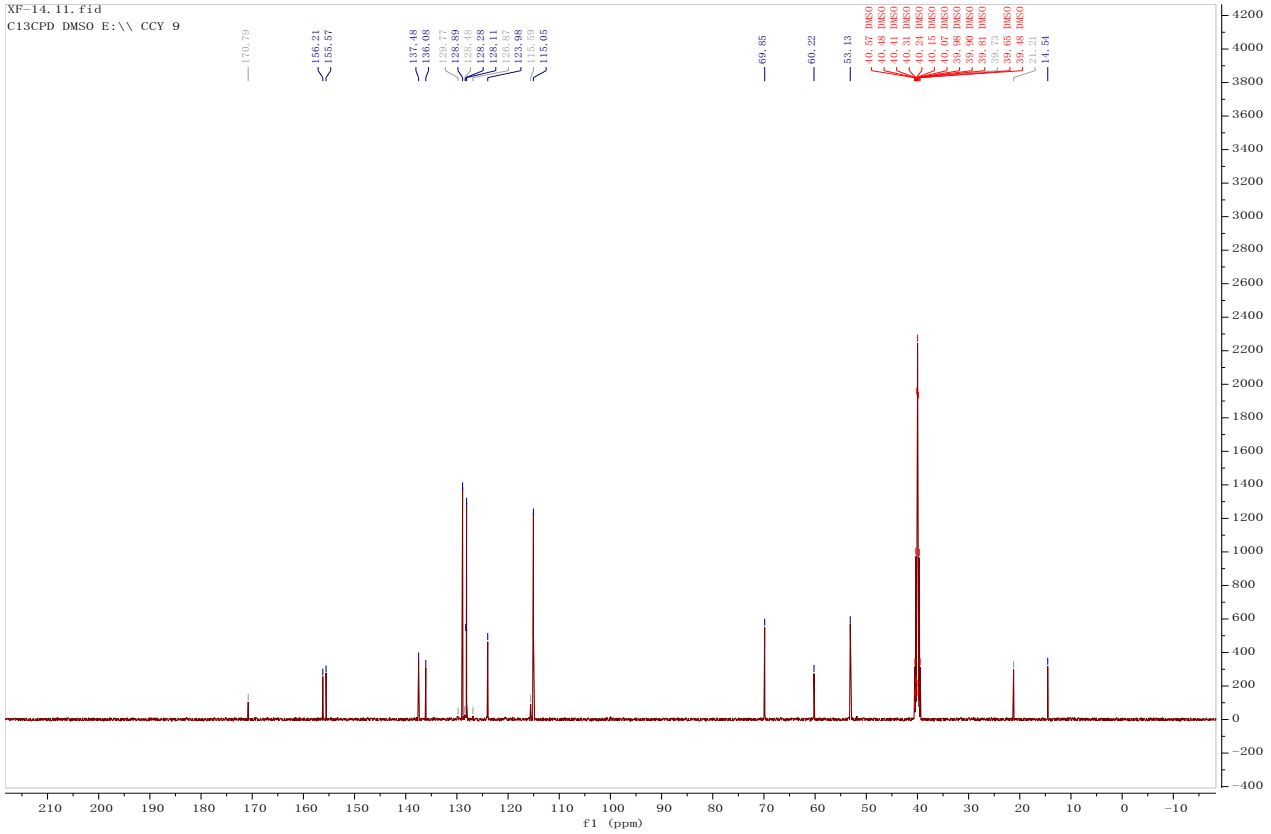


Figure S14 ^{13}C-NMR spectra for HA-6-CO_2Me

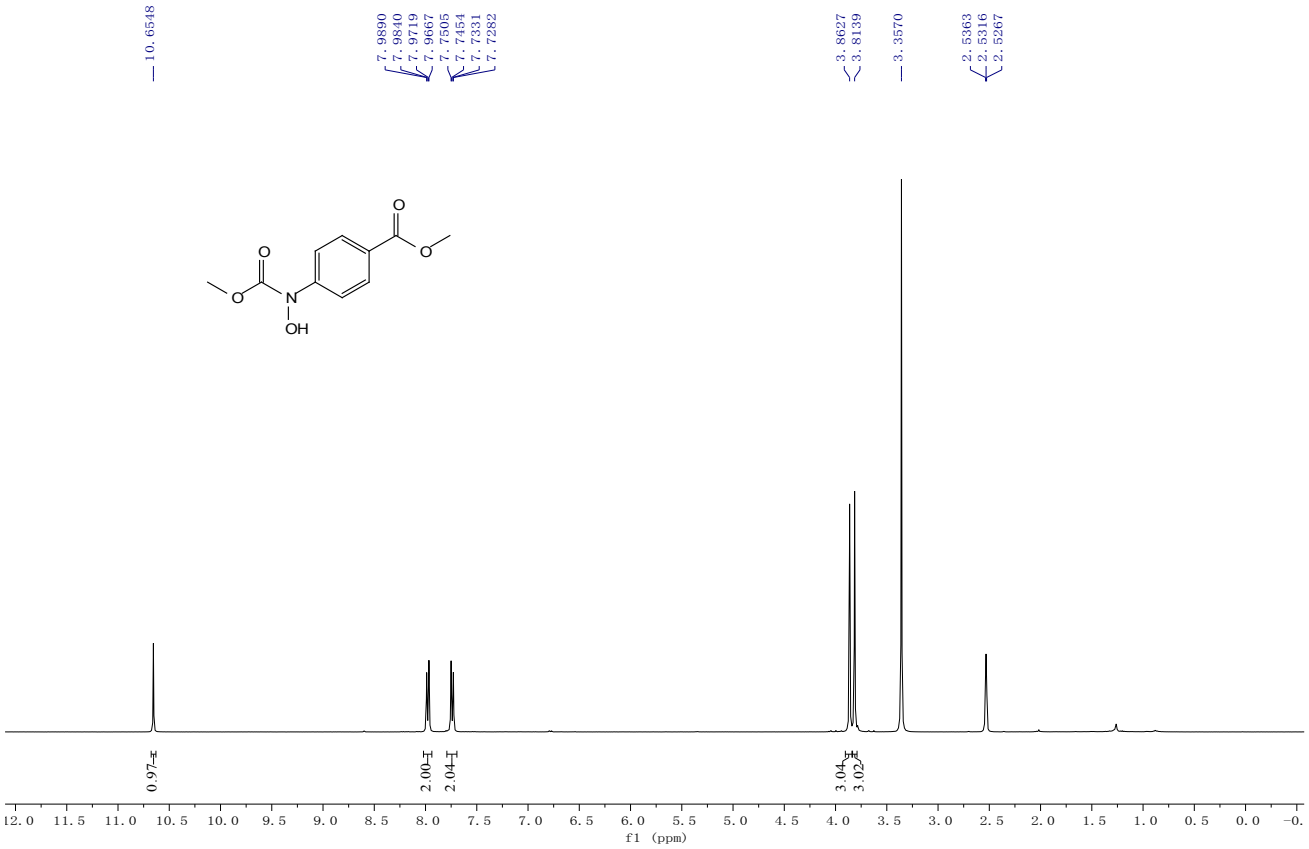


Figure S15 ^{1}H-NMR spectra for HA-7-CO_2Me

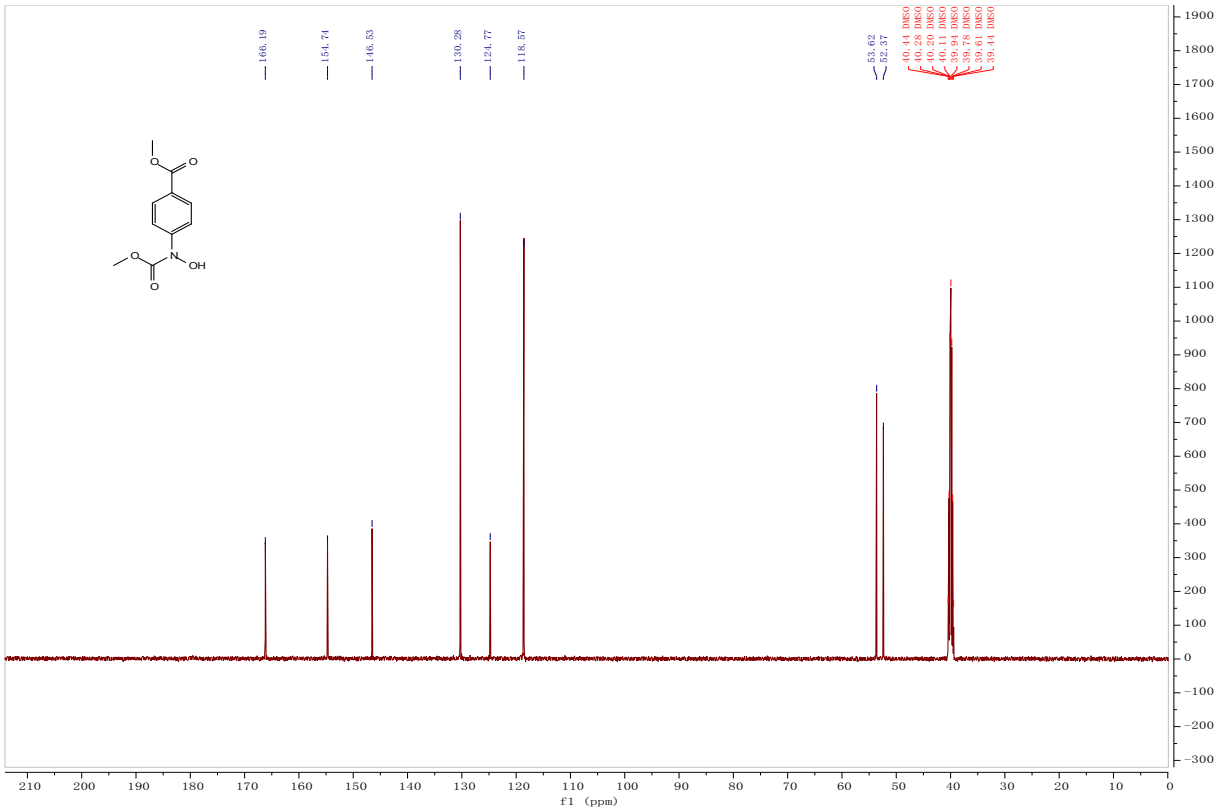


Figure S16 ^{13}C-NMR spectra for HA-7-CO_2Me

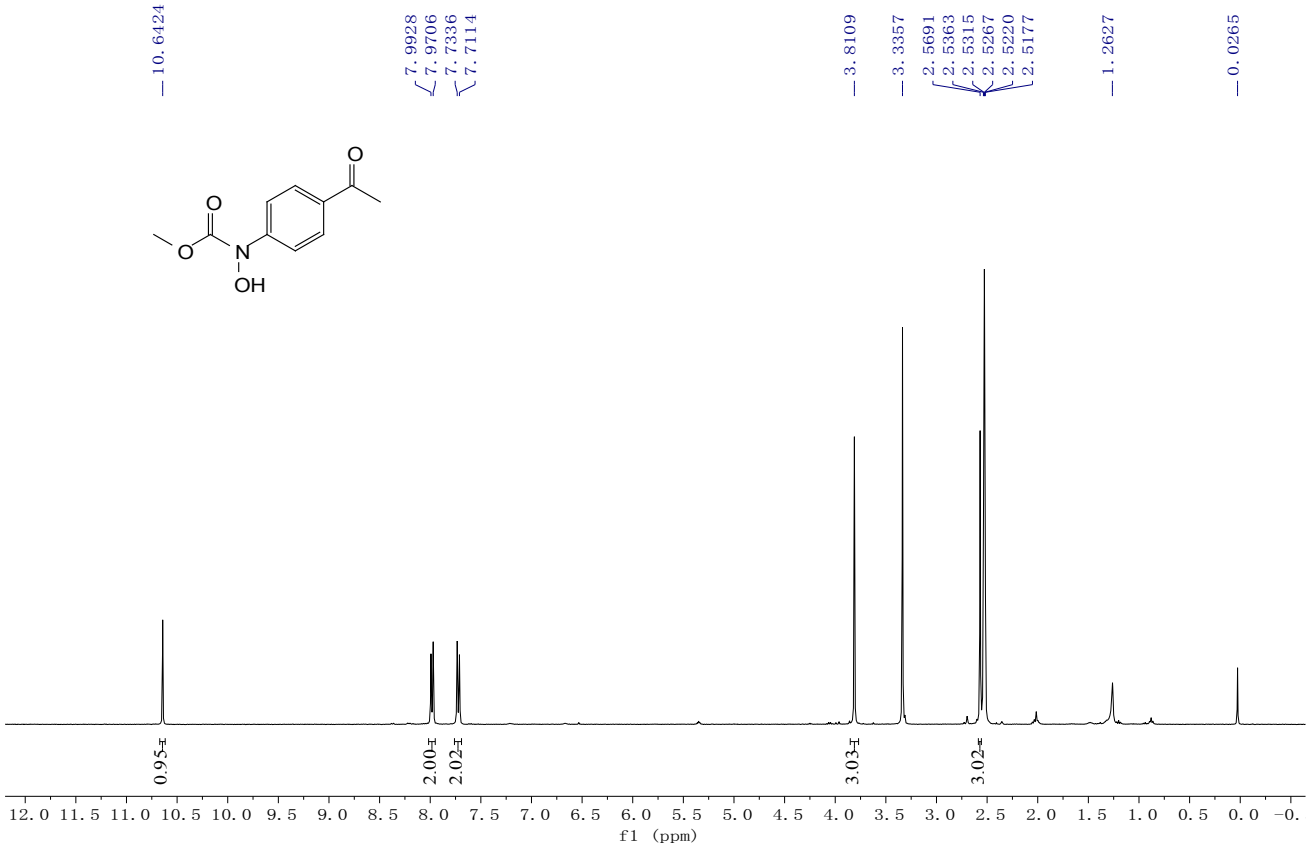


Figure S17 ^{1}H-NMR spectra for HA-8-CO_2Me

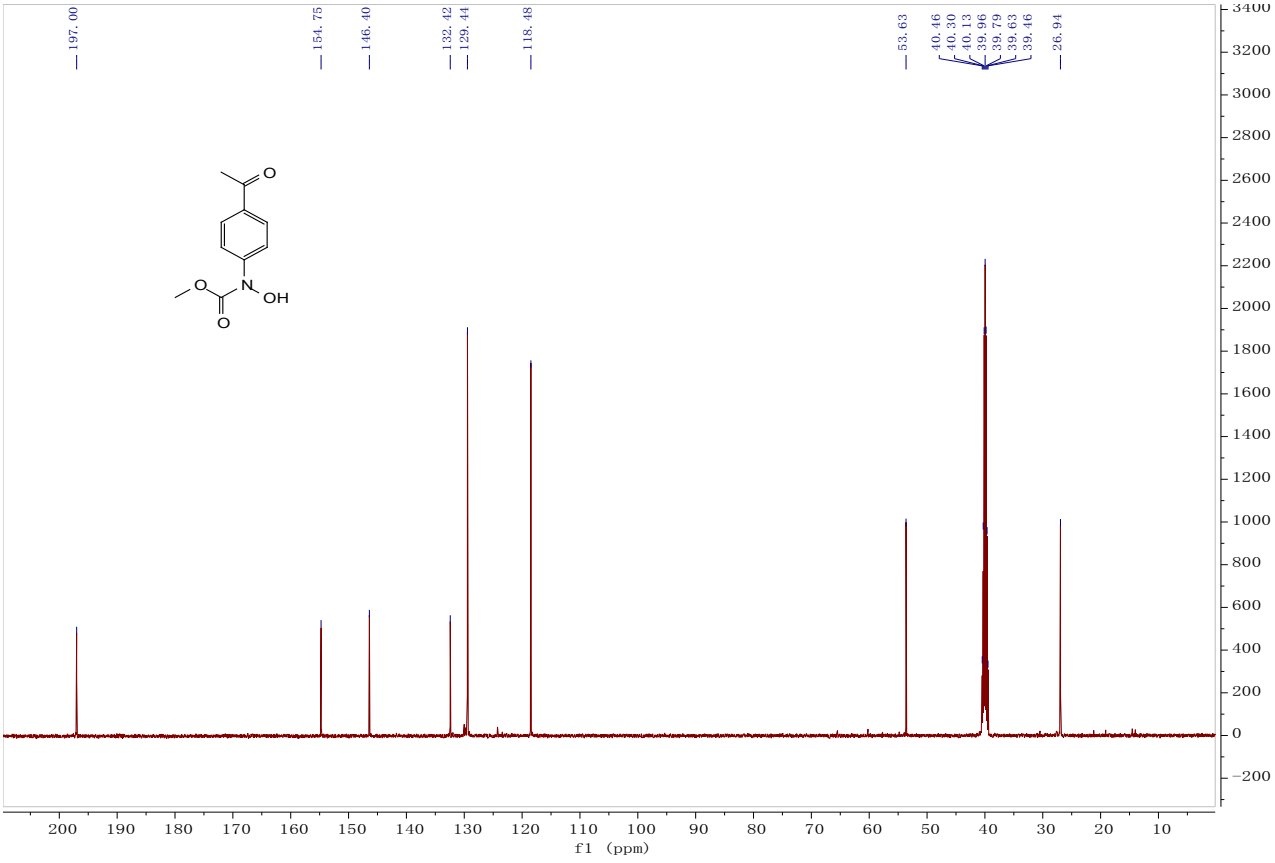


Figure S18 ^{13}C-NMR spectra for HA-8-CO_2Me

Reference：

1. H. J. Ma, Q. L. Cao, Y. F. Ma, J. P. Ni. *Agrochemicals*, 2013, 52(6): 408-410.
2. A. Porzelle, M. D. Woodrow, N. C. O. Tomkinson. *Org. Lett.,* 2010, 12(7): 1492-1495.