Electronic Supplementary Material (ESI) for RSC Advances.
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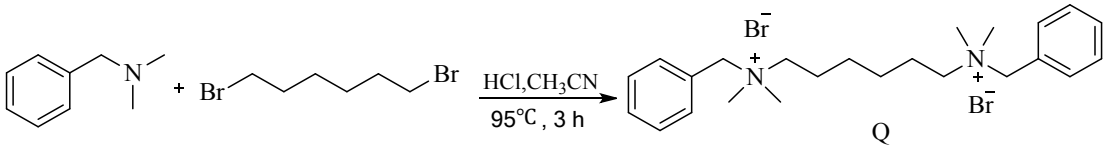

Q

Scheme 1. Preparation route of Q

Mass Spectrum SmartFormula Report

Analysis Info

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Method	DEFAULT.m	Operator	BDAL@CN
Sample Name	20160731-2ymy	Instrument / Ser#	micrOTOF-Q II 10429
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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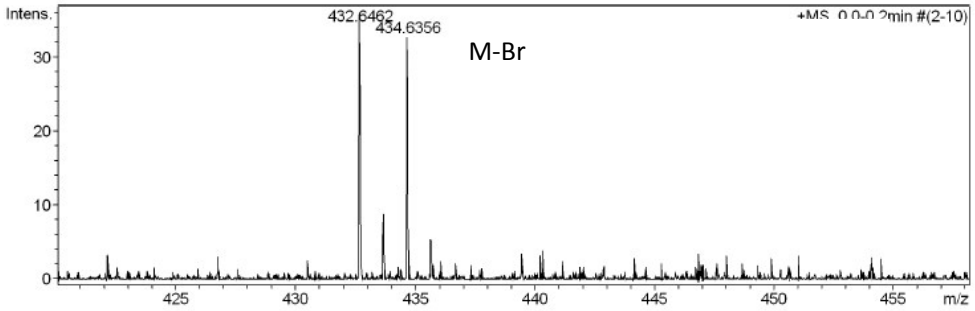
Scan End	3000 m/z	Set Collision Cell RF	650.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	FWHM
1	432.6462	8263	70.0	36	0.0524
2	434.6356	8817	63.9	33	0.0493

Bruker Compass DataAnalysis 4.0 printed: 7/31/2016 12:02:54 PM Page 1 of 1

Figure 1. Mass spectrum of Q.

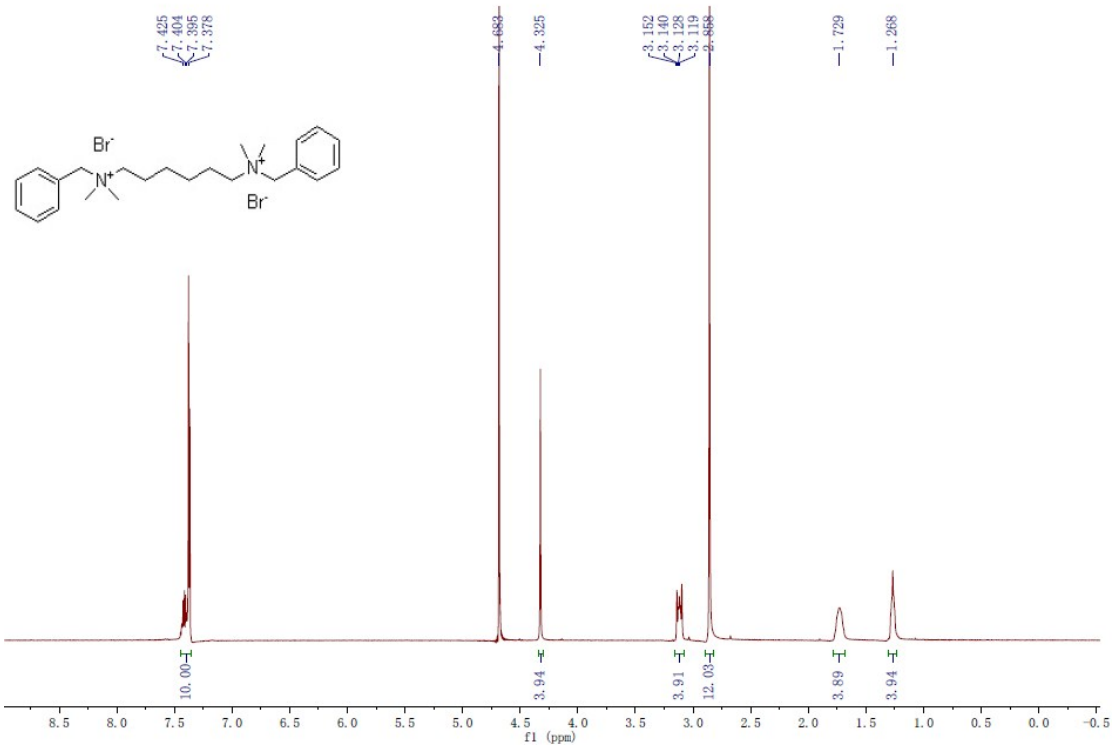


Figure 2. ^{1}H NMR Spectrum of Q.

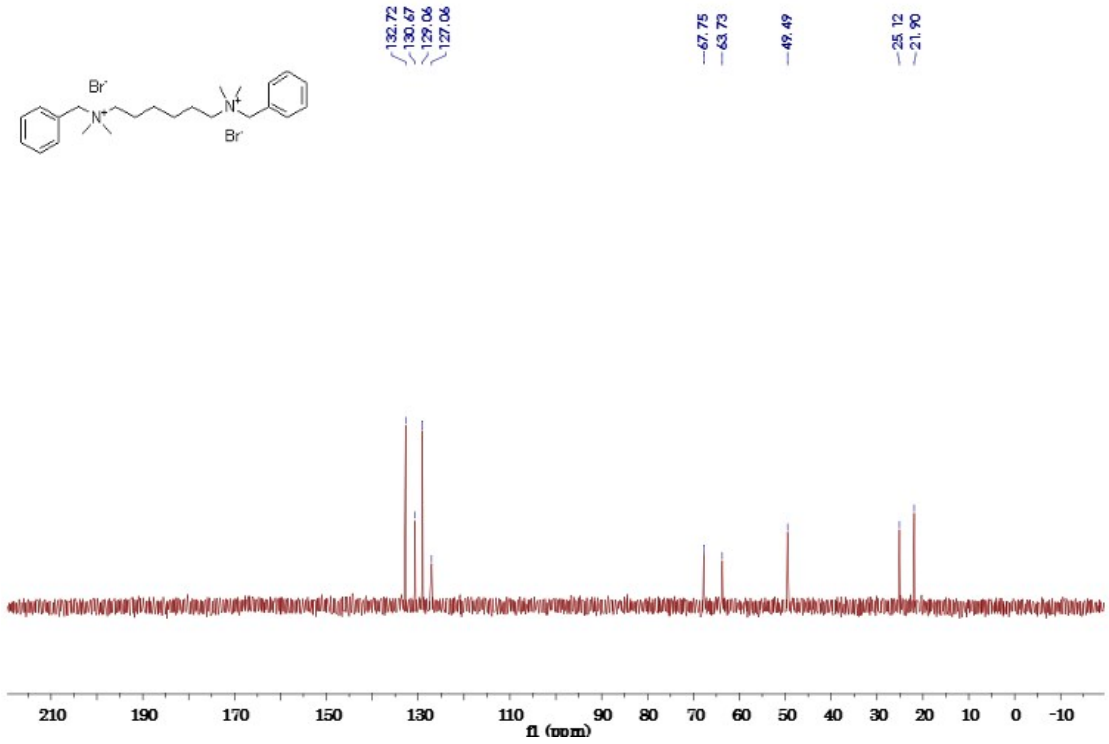


Figure 3. ^{13}C NMR Spectrum of Q.

Preparation of Q-MMT

Q-MMT and Cu-Q-MMT materials were prepared by a method similar to our previous reported method [7] (Seen in supporting information). Montmorillonite (0.25 g) was dispersed in deionized H_2O (60 mL) and stirred at 70 ºC for 1 h to form a suspension. Aqueous solution of Q (20 mL, 22 mmol/L) was slowly added to the suspension within 2 h. Then the mixture was sonicated at 70 ºC for 1 h before equilibrated 1(2 h at room temperature. The system was filtered and the filter cake was washed with deionized water until no Br^- was detected by $AgNO_3$ solution. The solid was dried in vacuum at 70 ºC for 12 h and grounded into powder which is labelled as Q-MMT.

Preparation of Cu-Q-MMT

Ethanol (5 mL) and deionized water (10 mL) was added to the mixture of $CuCl_2$ (14.31 mg) and Q-MMT (0.2 g). The suspension was stirred at 50 ºC for 12 h before cooled down to room temperature. Aqueous solution of $NaBH_4$ (5 mL, n ($NaBH_4$): n (Cu) = 10: 1) was slowly added to the suspension within 2 h. The reaction mixture was filtered and the filter cake was washed with deionized water until no Cl^- was detected by $AgNO_3$ solution. The solid was dried in vacuum at 60 ºC for 12 h and grounded into powder to obtain Cu-Q-MMT.

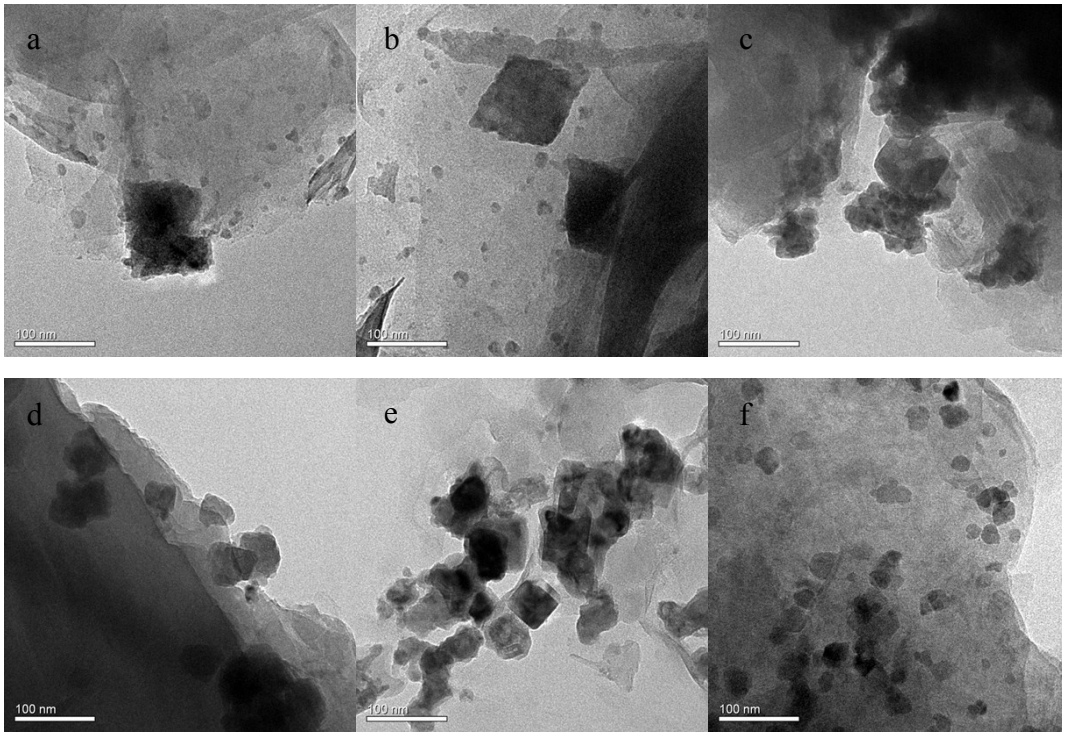


Figure 4. TEM micrographs of the different copper loadings of catalysts and recycled Cu-Q-MMT, Cu loading of catalysts a, b, c, d and e are 0.4 mmol,1 mmol, 2 mmol, 3 mmol, 4 mmol per gram, respectively, in preparation and f is the recycled Cu-Q-MMT.

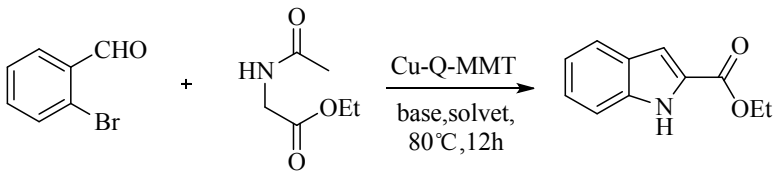


Table 1. Effect of base and solvent.

Entry	Solvent	Volume(mL)	Base	Equiv base	Yield (%)[a]
1	DMSO	2	Cs_2CO_3	2	74.4，85.2[b]
2	DMSO	1.5	Cs_2CO_3	2	83.5[b]
3	DMSO	2.5	Cs_2CO_3	2	83.8[b]
4	DMSO	3	Cs_2CO_3	2	81.2[b]
5	DMSO	2	Cs_2CO_3	1	40.5
6	DMSO	2	Cs_2CO_3	3	73.8
7	DMSO	2	K_2CO_3	2	44.2
8	DMSO	2	NaOAc	2	3.1
9	DMSO	2	K_2HPO_4	2	1
10	DMSO	2	pyridine	2	1
11	DMSO	2	NaOH	2	50
12	DMSO	2	KOH	2	34.6
13	DMSO	2	TMG	2	14.4
14	DMSO	2	$KHCO_3$	2	12.1
15	DMSO	2	K_3PO_4	2	50
16	DMF	2	Cs_2CO_3	2	56.5
17	NMP	2	Cs_2CO_3	2	50
18	Toluene	2	Cs_2CO_3	2	32.5
19	Dioxane	2	Cs_2CO_3	2	33.3
20	3- pentanone	2	Cs_2CO_3	2	67.6
21	Cyclohexanone	2	Cs_2CO_3	2	trace
22	2-Me-THF	2	Cs_2CO_3	2	55
23	Ethanol	2	Cs_2CO_3	2	1
24	Acetonitrile	2	Cs_2CO_3	2	21.6

[a] the amount of Cu-Q-MMT is 15 mg; [b]the amount of Cu-Q-MMT is 52.5 mg

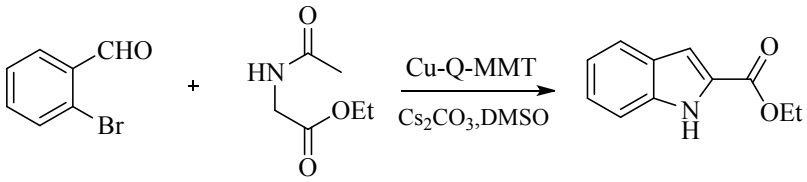


Table 2. Effect of reaction temperature and the amount of catalyst.

Entry	Catalyst/mg	T/°C	Time(h)	Yield
1	15	80	8	71
2	15	80	12	74.4
3	15	80	16	74.1
4	15	80	20	76.2
5	15	80	24	75.3
6	15	70	12	2.4
7	15	90	12	73.9
8	15	100	12	75.2
9	30	80	12	79.9
10	45	80	12	83.3
11	52.5	80	12	85.2
12	60	80	12	83.2

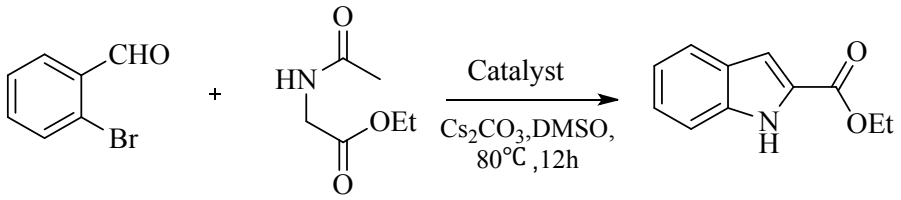
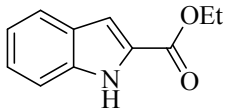


Table 3. Effect of different Cu loading of the catalyst

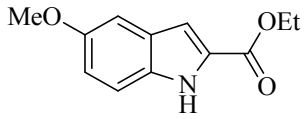
Entry	Catalyst of different Cu loading[a]	Time/h	yield
1	1-Cu-Q-MMT	12	50.5
2	2.5-Cu-Q-MMT	12	63.4
3	5-Cu-Q-MMT	12	63.7
4	Cu-Q-MMT	12	74.4
5	10-Cu-Q-MMT	12	62.1

[a]In the preparation of catalyst, the Cu loading of 1-Cu-Q-MMT, 2.5-Cu-Q-MMT, 5-Cu-Q-MMT, Cu-Q-MMT and 10-Cu-Q-MMT are 0.4 mmol,1 mmol, 2 mmol, 3 mmol and 4 mmol per gram, respectively.

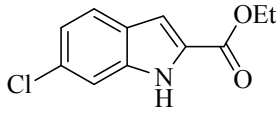
Characterization data



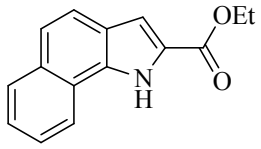
ethyl 1H-indole-2-carboxylate (white solid)
HRMS-ESI: calculated for $[M+Na]^+$ = 212.0688, found 212.0664
^{1}H NMR (400 MHz, DMSO) δ 11.87 (s, 1H), 7.66 (d, 1H), 7.45 (d, 1H), 7.26 (t, 1H), 7.15 (s, 1H), 7.08 (t, 1H), 4.34 (q, 2H), 1.34 (t, 3H).
^{13}C NMR (126 MHz, DMSO) δ 161.79, 137.83, 127.82, 127.19, 125.08, 122.52, 120.63, 113.04, 108.13, 60.89, 14.78.



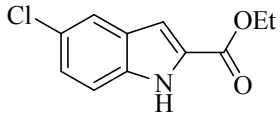
ethyl 5-methoxy-1H-indole-2-carboxylate (white solid)
HRMS-ESI: calculated for $[M+Na]^+$ = 242.0793, found 242.0788
^{1}H NMR (400 MHz, DMSO) δ 7.82 (d, 1H), 7.58 (d, 1H), 7.46 (d, 1H), 6.96 (m, 3.0 Hz, 1H), 6.77 (d, 1H), 4.20 (q, 2H), 3.80 (s, 3H), 1.26 (t, 4H).
^{13}C NMR (126 MHz, DMSO) δ 161.72, 154.41, 133.18, 127.99, 127.50, 116.69, 113.93, 107.72, 102.43, 60.78, 55.69, 14.80.



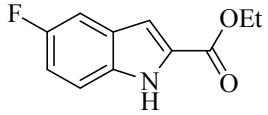
ethyl 6-chloro-1H-indole-2-carboxylate (white solid)
HRMS-ESI: calculated for $[M+Na]^+$ = 246.0298, found 246.0287
^{1}H NMR (400 MHz, DMSO) δ 12.01 (s, 1H), 7.67 (d, 1H), 7.44 (s, 1H), 7.16 (d, 1H), 7.09 (m, 1.7 Hz, 1H), 4.33 (q, 2H), 1.32 (t, 3H).
^{13}C NMR (126 MHz, DMSO) δ 161.50, 138.03, 129.70, 128.85, 125.97, 124.18, 121.25, 112.40, 108.28, 61.11, 14.75.



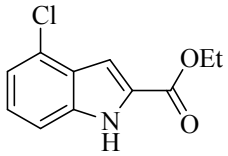
ethyl 1H-benzo[g]indole-2-carboxylate (yellow solid)
HRMS-ESI: calculated for $[M+Na]^+$ = 262.0844, found 262.0825
^{1}H NMR (400 MHz, DMSO) δ 12.74 (s, 1H), 8.75 (d, 1H), 7.92 (d, 1H), 7.68 (d, 1H), 7.53 (m, 6.4 Hz, 4H), 7.28 (d, 1H), 4.36 (q, 2H), 1.36 (t, 3H).
^{13}C NMR (126 MHz, DMSO) δ 161.67, 133.60, 131.85, 128.87, 126.49, 126.31, 125.84, 123.57, 122.66, 122.62, 121.93, 121.65, 110.11, 60.78, 14.87.



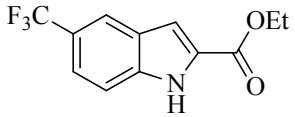
ethyl 5-chloro-1H-indole-2-carboxylate (white solid)
HRMS-ESI: calculated for $[M+Na]^+$ = 246.0298, found 246.0275
^{1}H NMR (400 MHz, DMSO) δ 12.08 (s, 1H), 7.72 (d, 1H), 7.45 (d, 1H), 7.25 (m, 1H), 7.11 (d, 1H), 4.33 (q, 2H), 1.33 (t, 3H).
^{13}C NMR (126 MHz, DMSO) δ 161.48, 136.19, 129.28, 128.18, 125.23, 125.13, 121.56, 114.72, 107.65, 61.14, 14.73.



ethyl 5-fluoro-1H-indole-2-carboxylate (white solid)
HRMS-ESI: calculated for $[M+Na]^+$ = 230.0593, found 230.0598
^{1}H NMR (400 MHz, DMSO) δ 11.99 (s, 1H), 7.48 – 7.37 (m, 2H), 7.12 (s, 2H), 4.33 (q, 2H), 1.33 (t, 3H).
^{13}C NMR (126 MHz, DMSO) δ 161.52, 158.63, 156.78, 134.57, 129.47, 127.26, 127.18, 114.42, 114.34, 114.14, 113.93, 108.07, 108.03, 106.61, 106.42, 61.05, 14.74.

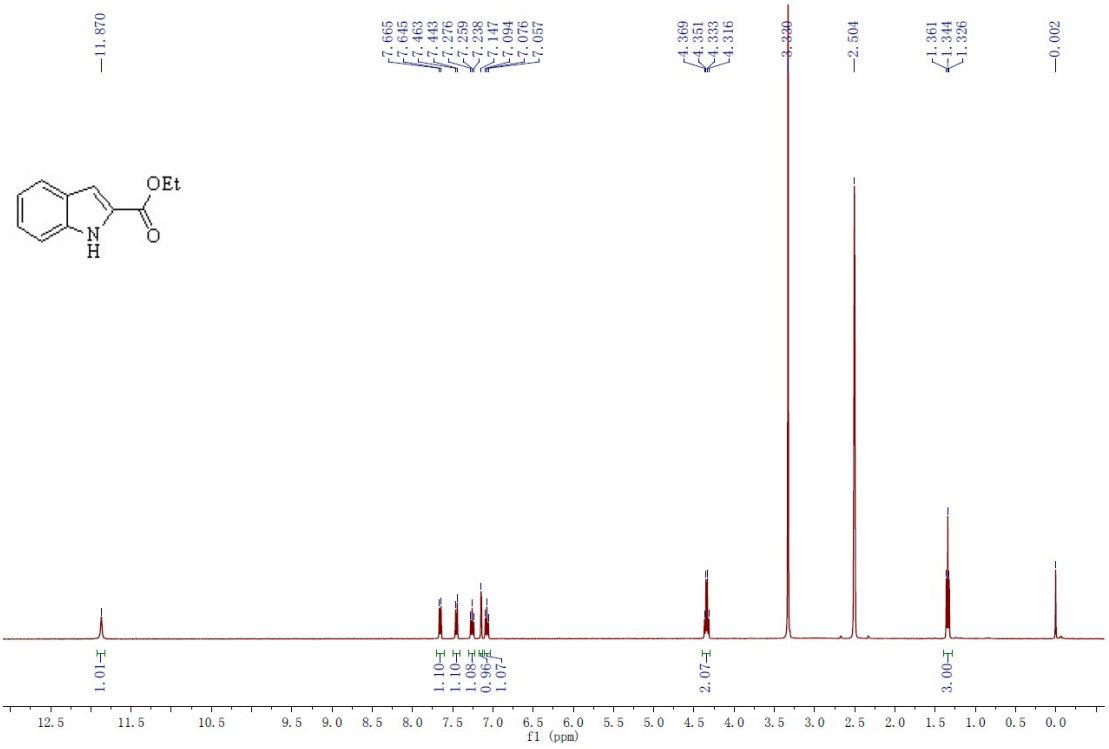


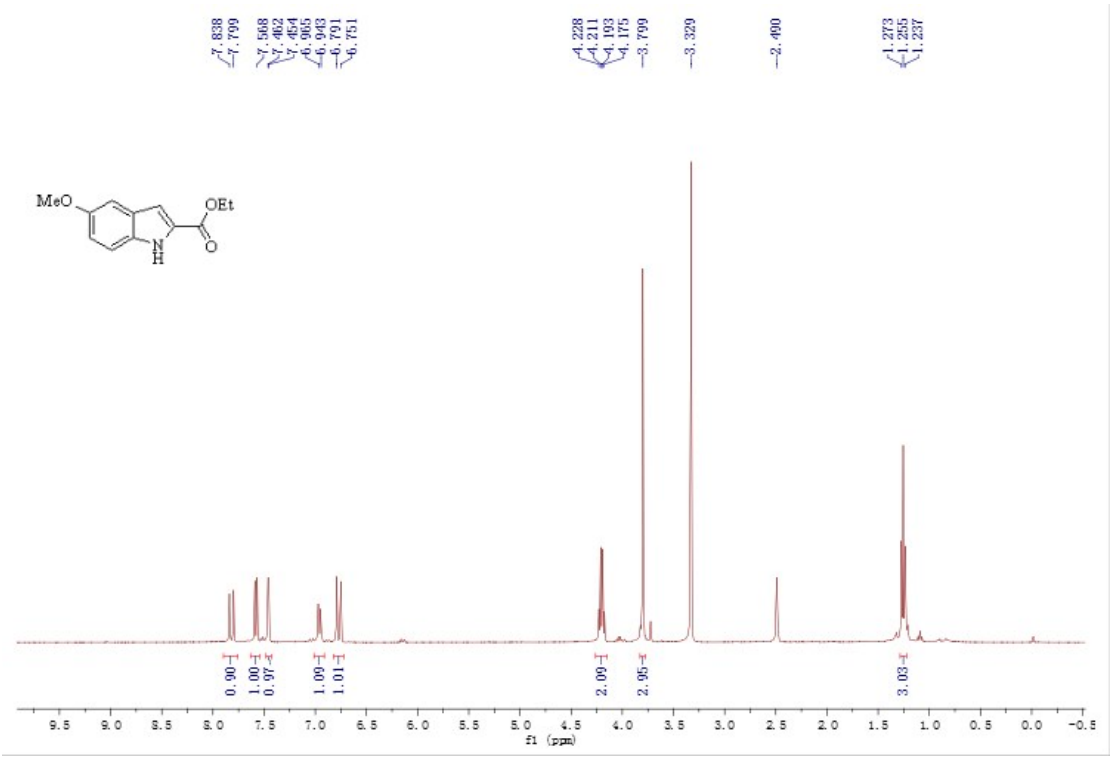
ethyl 4-chloro-1H-indole-2-carboxylate (white solid)
HRMS-ESI: calculated for $[M+Na]^+$ = 246.0298, found 246.0307
^{1}H NMR (400 MHz, DMSO) δ 12.29 (s, 1H), 7.44 (d, 1H), 7.31 – 7.23 (m, 1H), 7.18 (d, 1H), 7.11 (d, 1H), 4.37 (q, 2H), 1.36 (t, 3H).
^{13}C NMR (101 MHz, DMSO) δ 161.32, 138.40, 128.73, 126.31, 125.87, 125.85, 120.23, 112.29, 105.64, 61.24, 14.69.



ethyl 5-(trifluoromethyl)-1H-indole-2-carboxylate (white solid)
HRMS-ESI: calculated for $[M+Na]^+$ = 280.0561, found 280.0563
^{1}H NMR (400 MHz, DMSO) δ 12.34 (s, 1H), 8.15 (s, 1H), 7.64 (d, 1H), 7.55 (d, 1H), 7.32 (s, 1H), 4.38 (q, 2H), 1.36 (t, 3H).
^{13}C NMR (101 MHz, DMSO) δ 161.39, 139.03, 129.94, 127.03, 126.42, 124.34, 121.62, 121.31, 121.13, 121.10, 120.59, 120.55, 114.03, 109.10, 61.28, 14.70.

^{1}H NMR of products

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4.175
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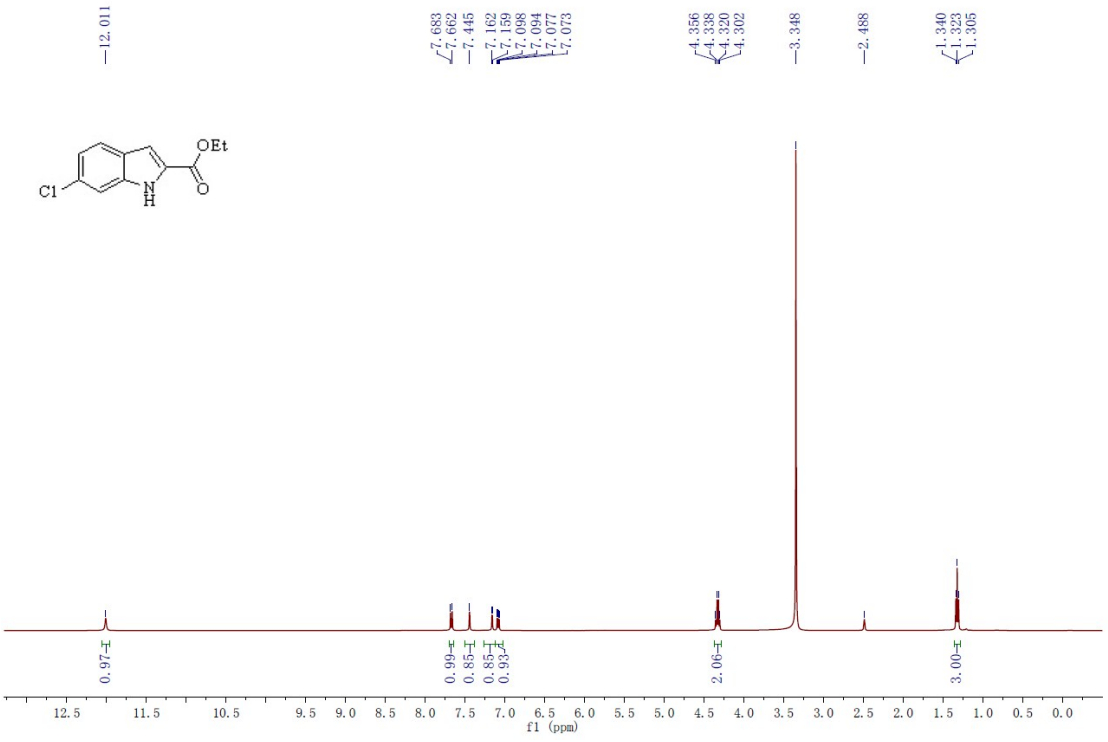
f1 (ppm)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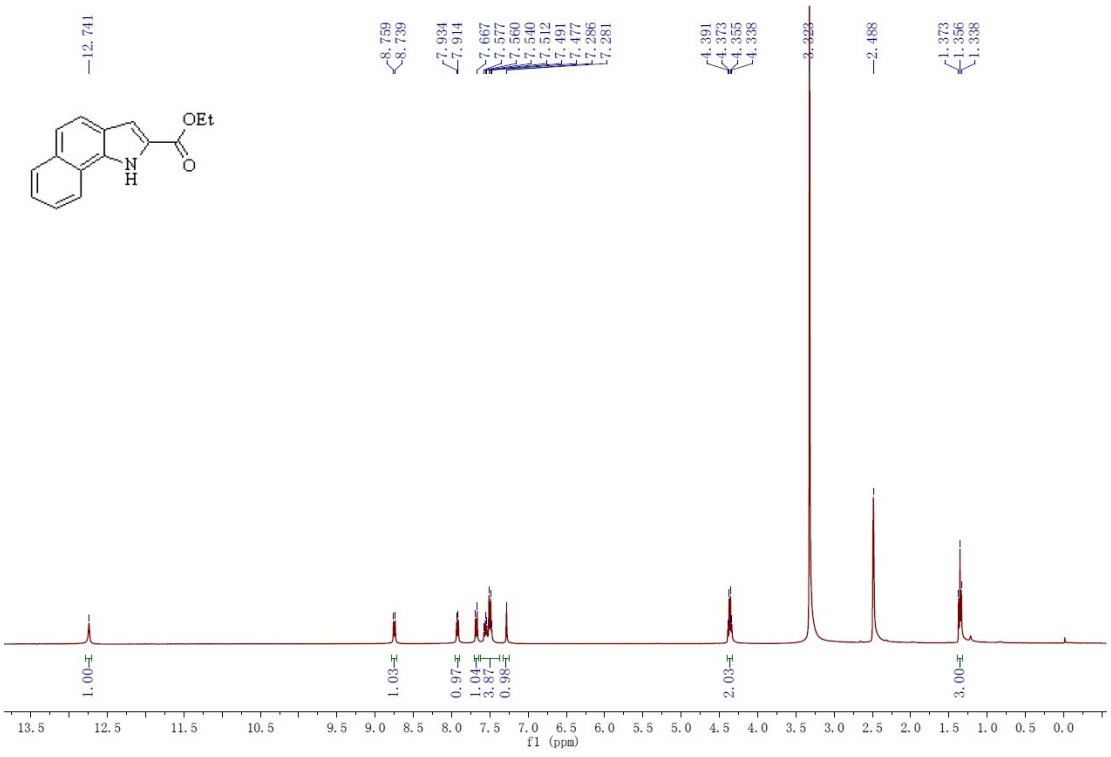
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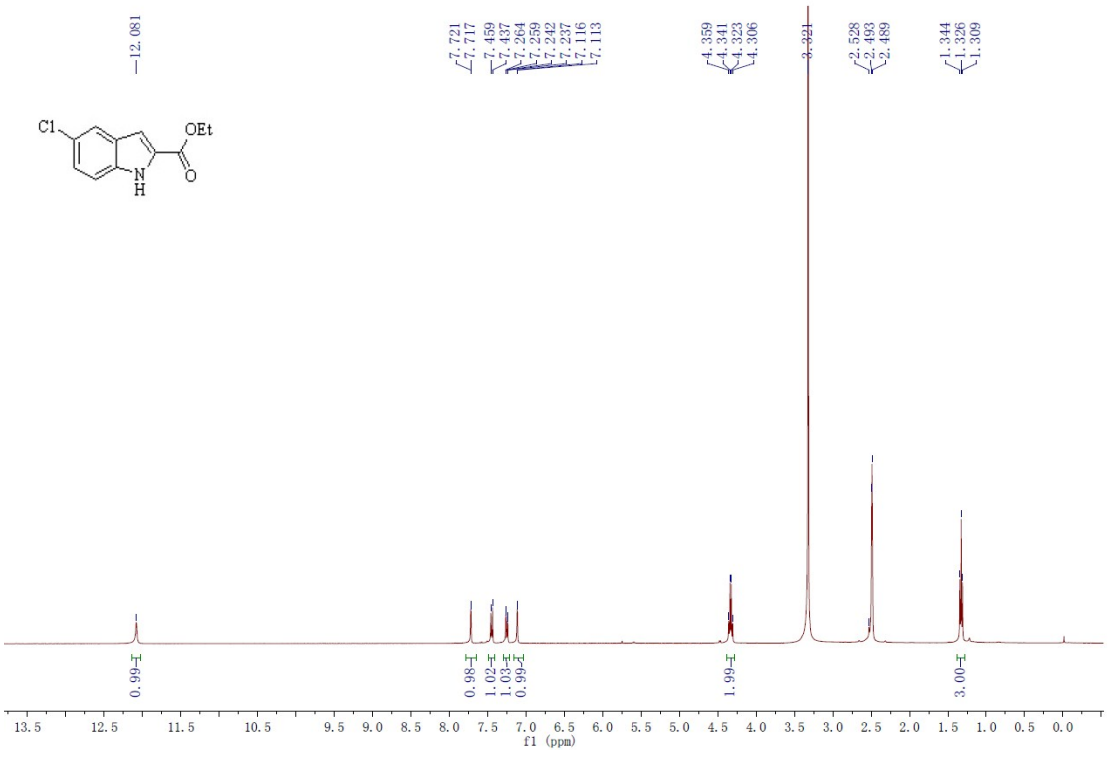
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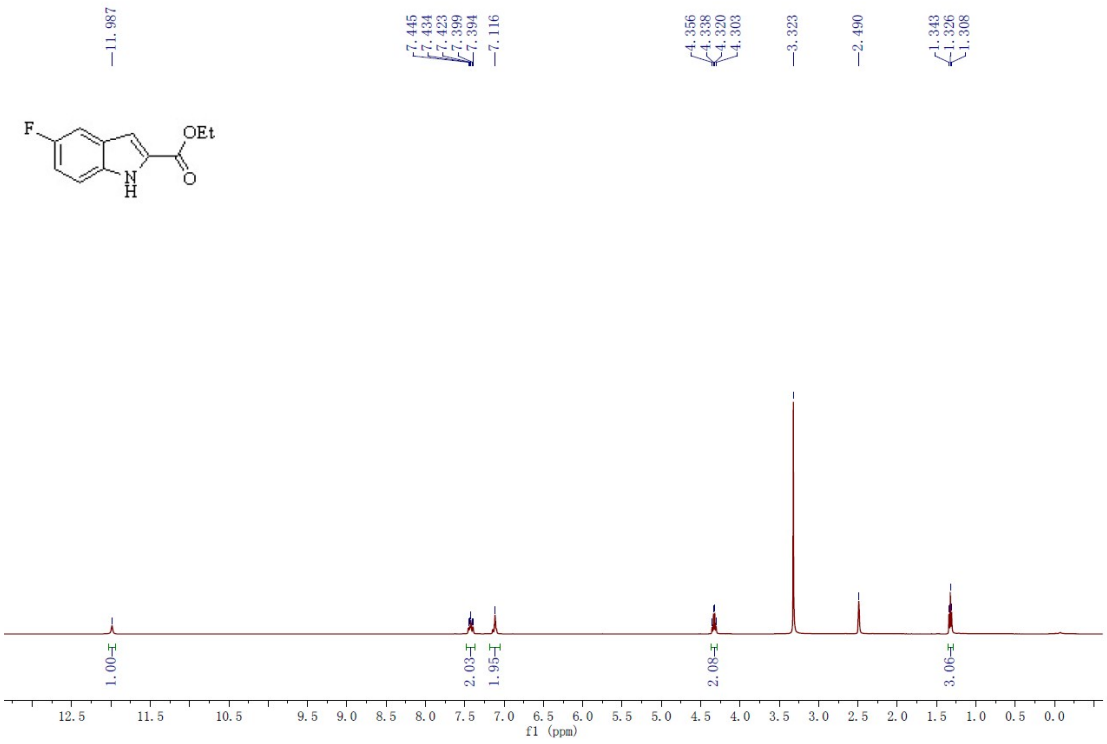
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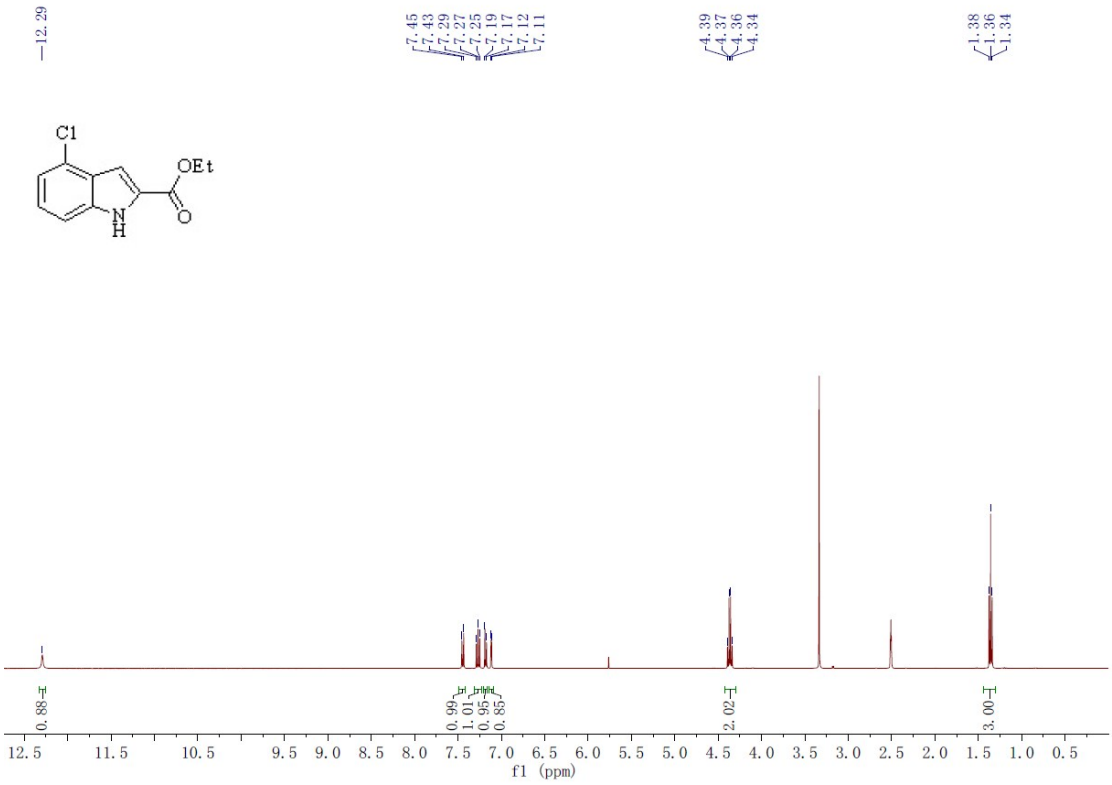
f1 (ppm)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1.34
Cl
OEt
O
N
H
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1.01
0.95
0.85
2.02
3.00
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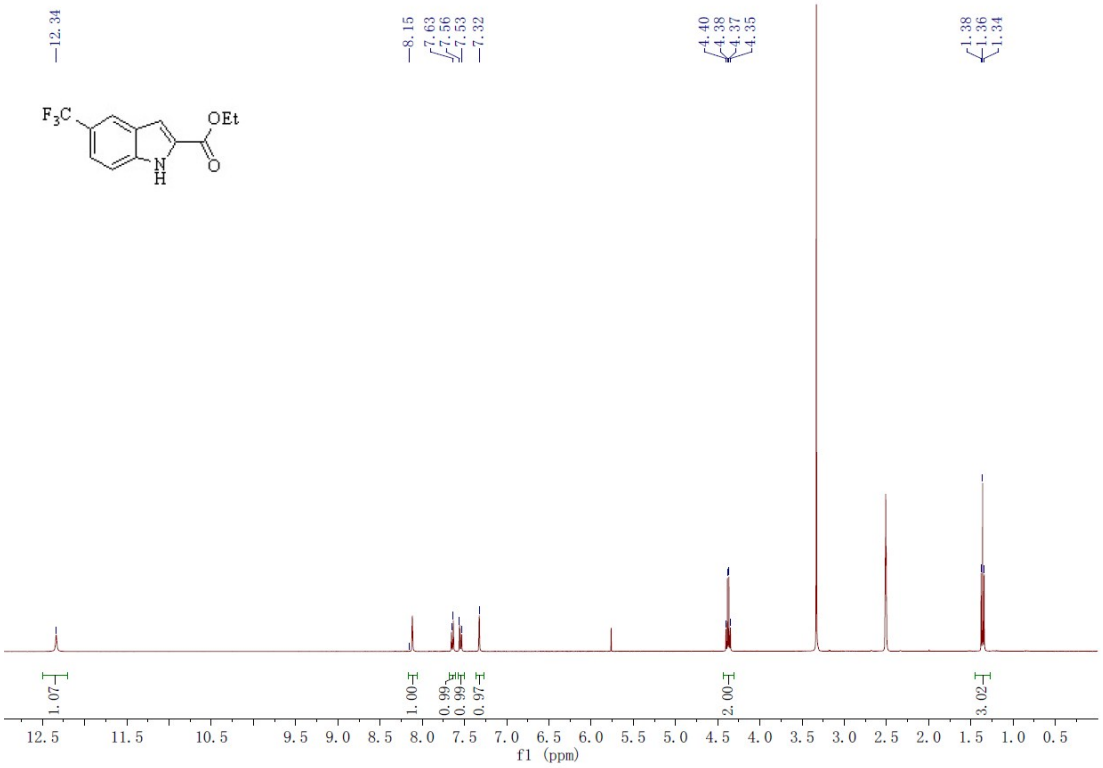
f1 (ppm)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H
O
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1.00
0.99
0.99
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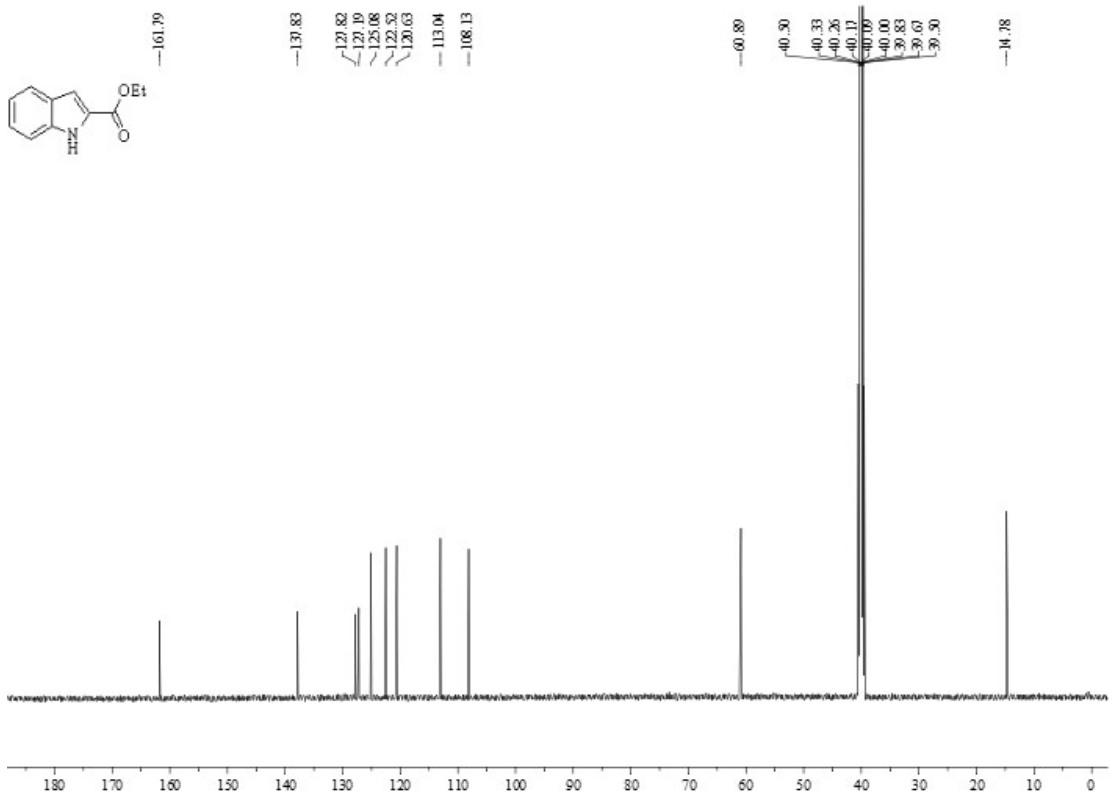
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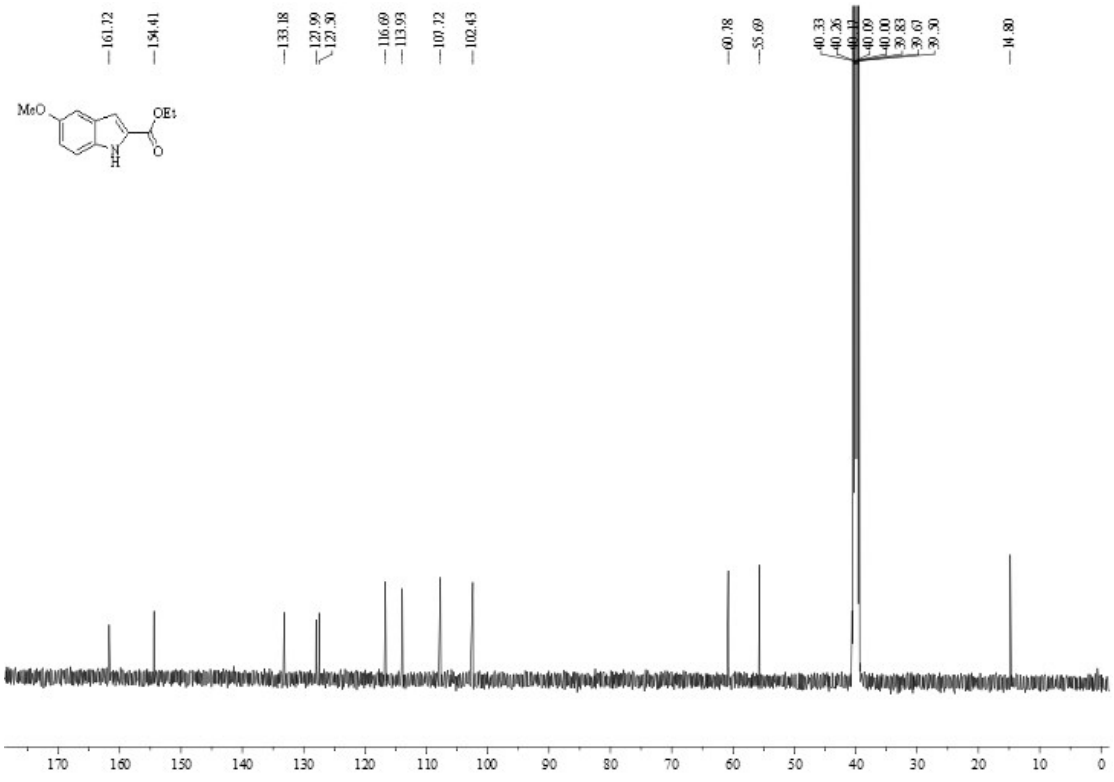
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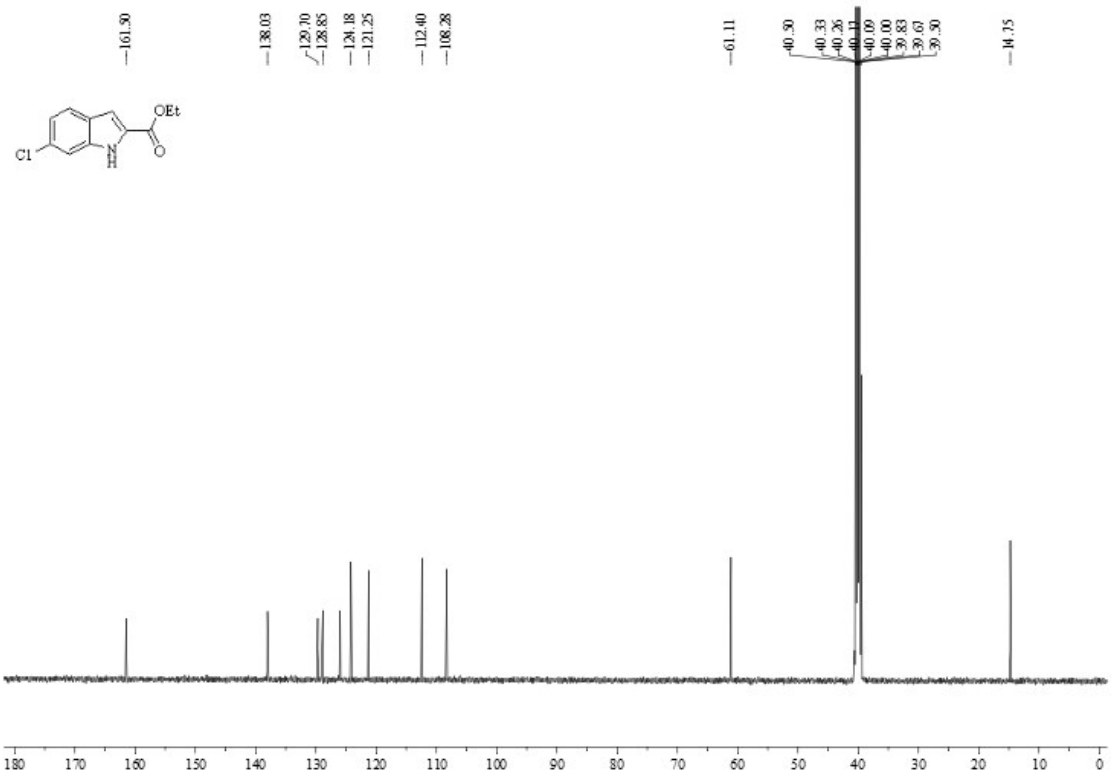
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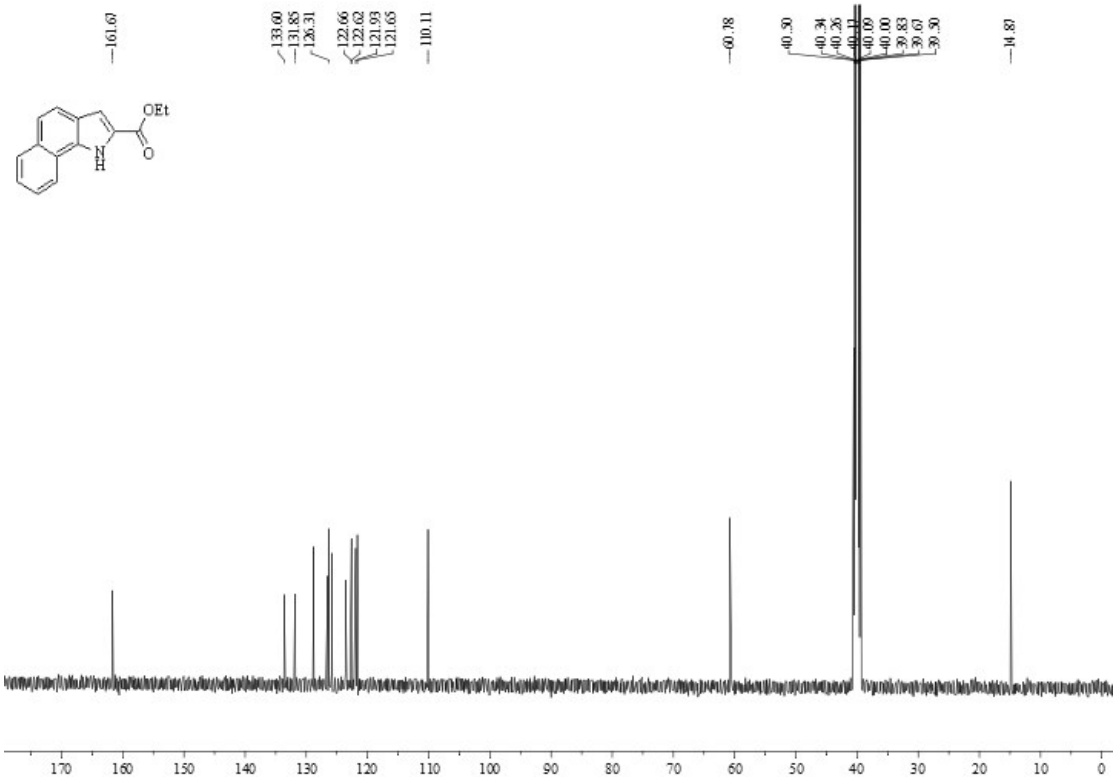
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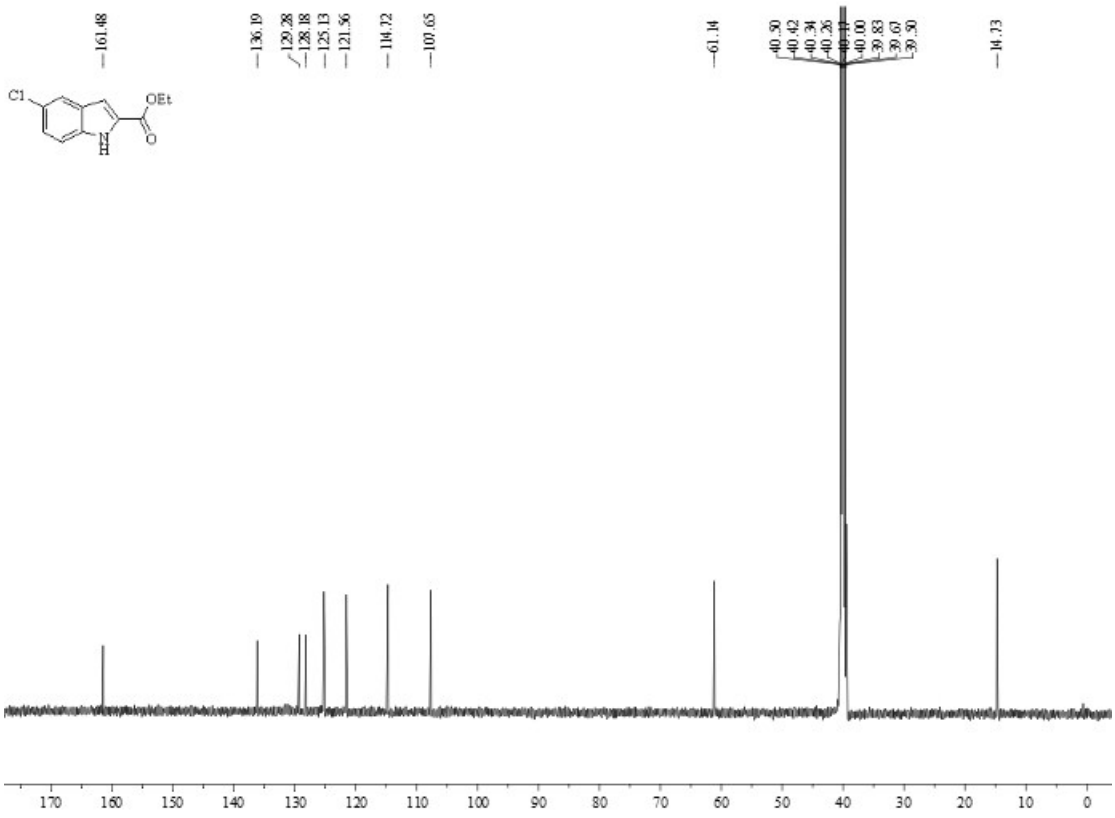
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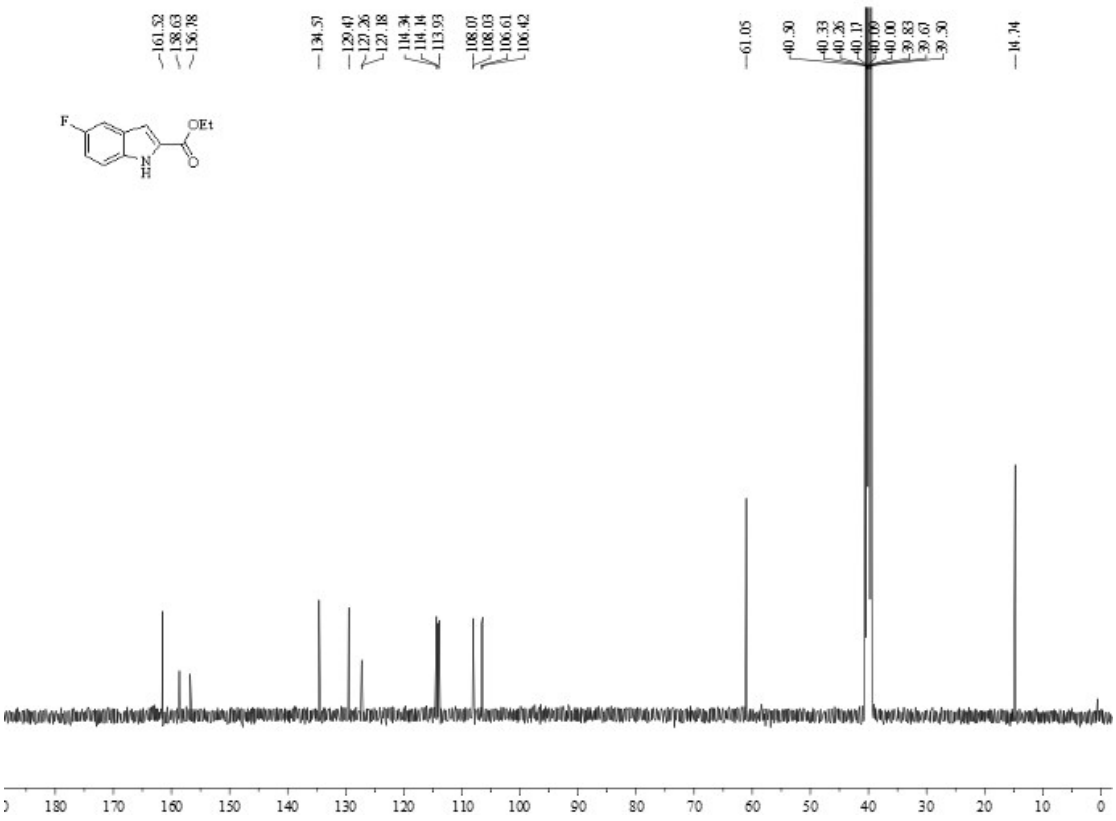
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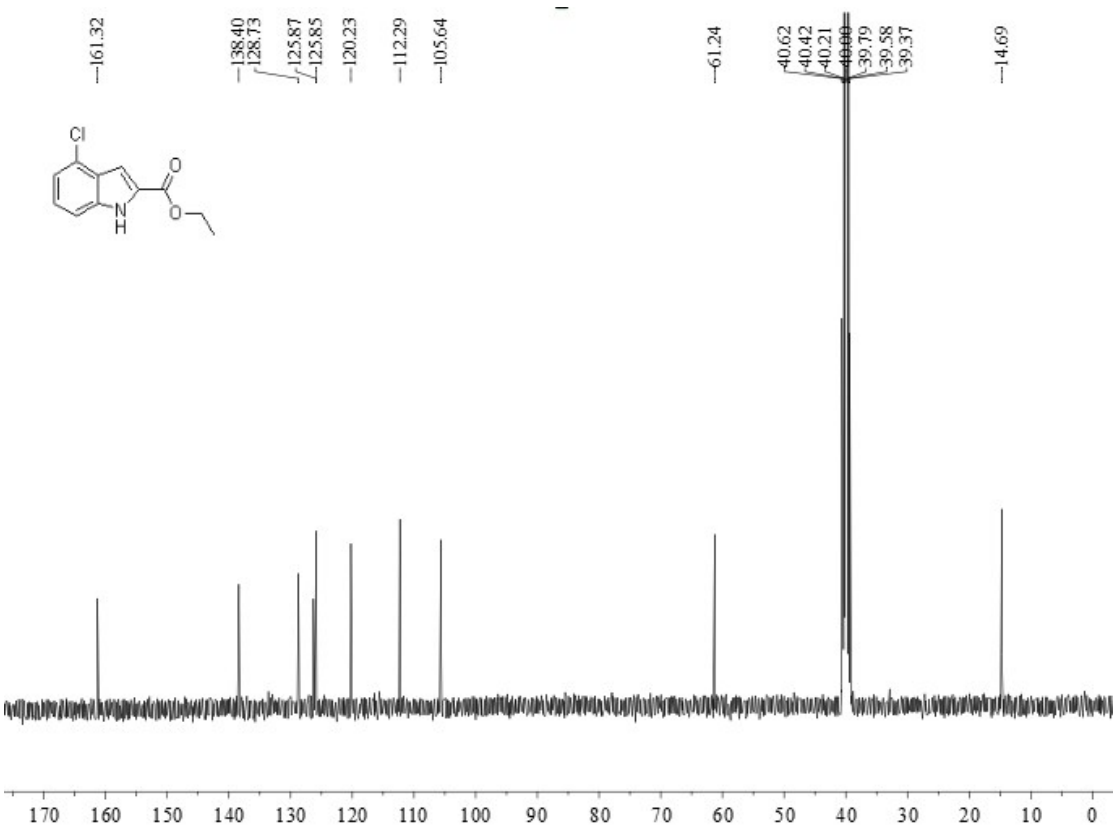
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