Supporting Information

Visible light-induced $FeCl_3$-catalyzed chlorination of C–H bonds with $MgCl_2$

Jing Huang [a,b], Yidong Liu [b], Xia Tian[b], Shao-Fei Ni*[c], Shen Li [b], Zhan-Hui Zhang*[a], Dong Li [c], Shouxin Liu*[b]

[a]College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, P. R. China.
E-mail: zhanhui@hebtu.edu.cn

[b] State Key Laboratory of Molecular chemistry for Drug,Hebei Collaborative Innovation Center of New Drug Creation, Hebei University of Science &Technology, Shijiazhuang 050018, P. R. China.

E-mail: chsxliu@hotmail.com

[c] Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province Shantou University, Shantou, Guangdong, 515063 P. R. China.

E-mail: sfni@stu.edu.cn

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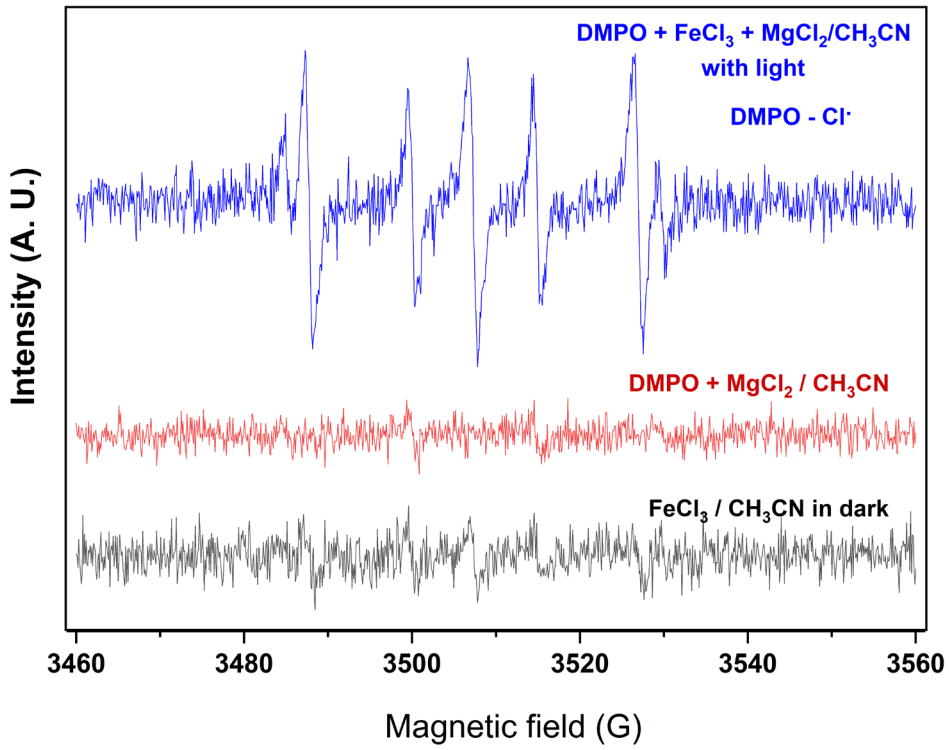
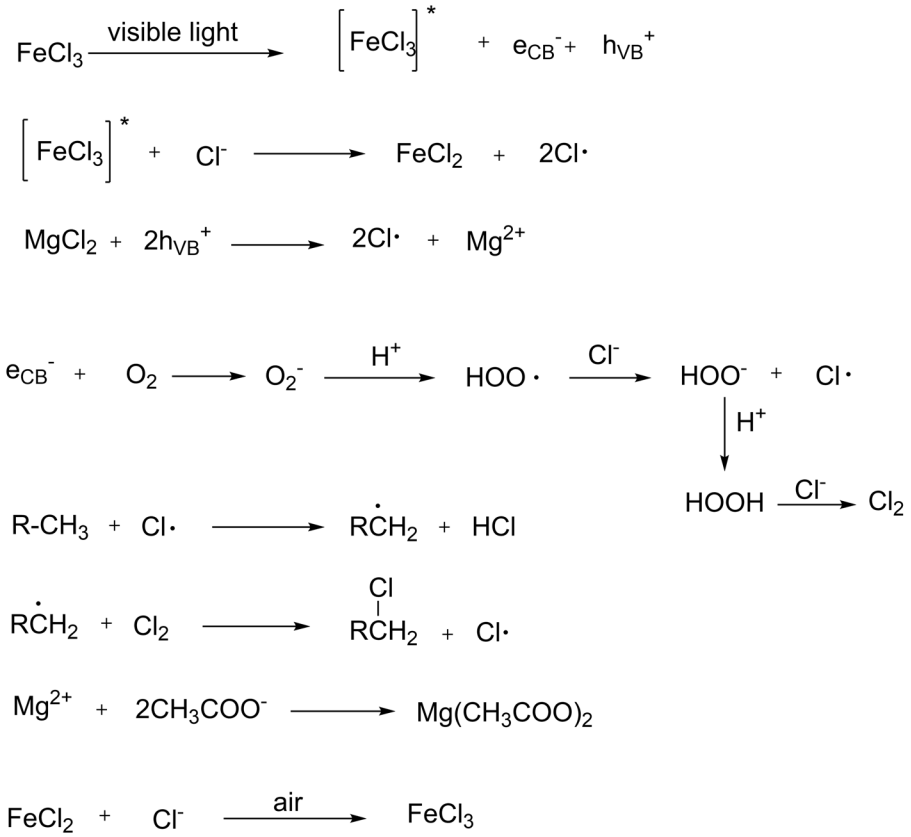
Section 1. Radical trapping experiments



[Electron paramagnetic resonance (EPR) spectra were recordedon a Bruker A300 spectrophotometer. EPR spectrawere obtained on solutionsamples (100 mM), using 1−20mW microwavepower and 100kHz field modulation with theamplitude set to 1G. The g-values for each EPR spectrum were extracted from simulations performed using Easy Spin (v5.2.23).]

Figure S1. ESR spectra of DMPO capturing generated chlorine radical

Section 2. Further details of the proposed mechanism



Scheme S1 Chlorination reaction mechanism

Section 3. DFT studies experiments

Computational details:

All calculations were performed using Gaussian 16, Revision A.03 package.[1] All of the reactants, intermediates, transition states, products were optimized by the DFT with the ωB97X-D functional.[2] For geometry optimizations and frequency calculations, BS-I basis set system was employed. In BS-I, we employed 6-31G(d) basis sets for all atom. All the stationary structures were characterized with no imaginary frequency and the transition state structures (TSs) were characterized with a single imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were performed on the TSs. The solvent effect of acetonitrile was evaluated through the SMD method,[3] in which a better basis system BS-II was used. In BS-II, we employed def2tzvp basis sets for all atom. All reported energies are free energies at a concentration of 1 M.

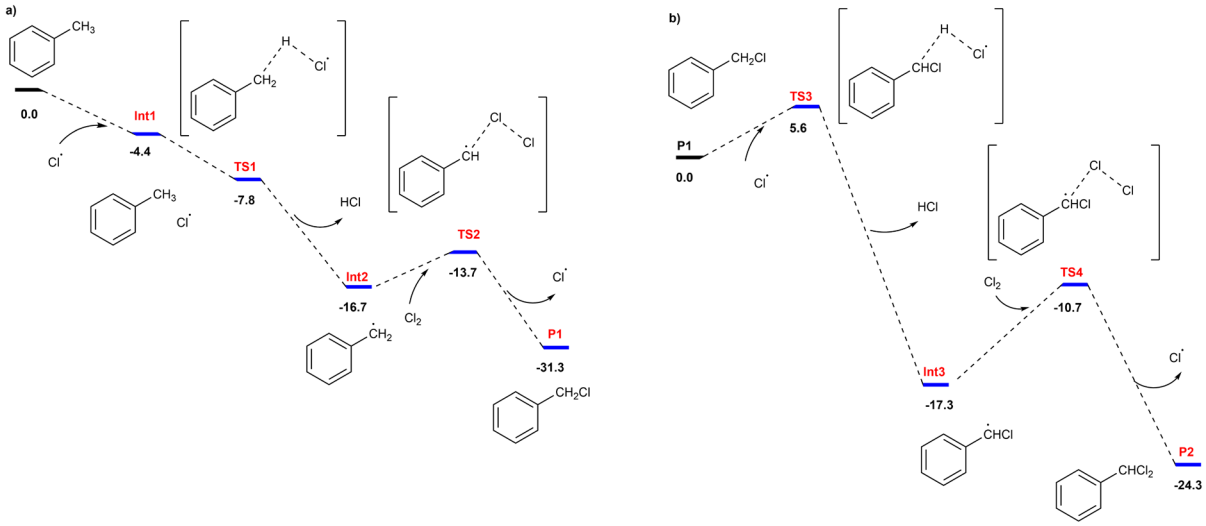


Figure S2. DFT calculations on the chlorination of toluene reaction

Cartesian coordinates of the optimized structures:

Int1

E = -731.586799 a.u.

0 2

C	-3.33784600	-1.41834900	1.06193400
C	-2.48271700	-0.72453300	0.21641000
C	-2.62472600	0.65437500	0.04826200
C	-3.61814000	1.33613700	0.75284400
C	-4.47182500	0.64341300	1.60143500
C	-4.33267800	-0.73306800	1.75582000
H	-3.22451300	-2.49116400	1.18941900
H	-1.69523300	-1.25358700	-0.31880900
H	-3.71458200	2.41177800	0.64051400
H	-5.24650700	1.17956000	2.14428500
H	-5.00019800	-1.27412200	2.41951200
C	-1.66831200	1.40642700	-0.81543800
H	-1.25860000	0.79848600	-1.64037700
H	-2.10093200	2.32639600	-1.24037600
Cl	0.68998460	2.27312728	0.83792692
H	-0.81576484	1.70772164	-0.18903168

TS1

E = -731.586482 a.u.

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C	-3.33404600	-1.41834900	1.06193400
C	-2.47891700	-0.72833300	0.21641000
C	-2.61332600	0.66197500	0.04066200
C	-3.61814000	1.33993700	0.75664400

C	-4.47182500	0.64721300	1.60143500
C	-4.33267800	-0.73306800	1.75582000
H	-3.22451300	-2.49116400	1.18561900
H	-1.69523300	-1.25738700	-0.31880900
H	-3.71838200	2.41557800	0.64051400
H	-5.24650700	1.17956000	2.14428500
H	-5.00019800	-1.27412200	2.41951200
C	-1.69871200	1.39122700	-0.82303800
H	-1.17500000	0.80988600	-1.58337700
H	-2.03253200	2.36819600	-1.17577600
Cl	0.55371200	2.22101100	0.74636900
H	-0.69463700	1.74906600	-0.07988400

Int2

E = -270.811959 a.u.

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C	-3.02388584	-1.22748275	1.30395430
C	-2.12391529	-0.36951162	0.67117473
C	-2.52258761	0.91771202	0.31153962
C	-3.82214377	1.34707371	0.58360373
C	-4.72198725	0.48908944	1.21580760
C	-4.32273678	-0.79815585	1.57637452
H	-2.70923276	-2.24215501	1.58781424
H	-1.09976476	-0.70801949	0.45723569
H	-4.13627270	2.36202716	0.29989819
H	-5.74626212	0.82717860	1.43035579
H	-5.03223678	-1.47430259	2.07493681
C	-1.52899795	1.86513725	-0.38614587
H	-1.61011280	1.74894167	-1.44672070
H	-1.75391604	2.87679324	-0.11994292

TS2

E = -1191.123726 a.u.

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C	0.01245500	0.32461400	0.29914000
C	-0.01576500	-0.23537000	1.56376400
C	1.18842900	-0.51962000	2.26697600
C	2.41554800	-0.20570200	1.61821300
C	2.43021500	0.35404900	0.35337100
C	1.23220800	0.62361100	-0.31593700
H	-0.91963100	0.53501700	-0.21705600
H	-0.96601800	-0.46295100	2.03947100
H	3.34882700	-0.41031100	2.13606000
H	3.37902500	0.58732200	-0.12084100

H	1.24907500	1.06501100	-1.30751600
C	1.16631800	-1.08081100	3.55844700
H	0.22856400	-1.31323800	4.05213800
H	2.08642300	-1.29043000	4.09378400
Cl	1.02045700	4.26325300	4.34883800
Cl	1.07809300	2.39800200	3.58228600

P1

E = -1191.167568 a.u.

0 2

C	-2.09702315	-0.07912676	0.00086200
C	-0.70186315	-0.07912676	0.00086200
C	-0.00432515	1.12862424	0.00086200
C	-0.70197915	2.33713324	-0.00033700
C	-2.09680415	2.33705524	-0.00081600
C	-2.79440515	1.12884924	0.00018000
H	-2.64678215	-1.03144376	0.00131200
H	-0.15235515	-1.03163976	0.00217700
H	-0.15177915	3.28927624	-0.00039600
H	-2.64692615	3.28933624	-0.00176900
H	-3.89400915	1.12903224	0.00000000
C	1.53567459	1.12873627	0.00174986
H	1.89292155	1.14115381	-1.00677402
H	1.89198081	1.99615182	0.51705186
Cl	2.12197863	-0.31833783	0.81404544
Cl	2.91222360	-2.39721996	2.32693036

TS3

E = -1191.158292 a.u.

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C	0.32105900	0.77210900	0.00896200
C	0.52212900	0.86295600	1.38221100
C	1.49520800	0.08047500	2.00603400
C	2.26844000	-0.79127100	1.23716900
C	2.06939100	-0.88185900	-0.13660800
C	1.09491800	-0.10040500	-0.75242400
H	-0.44152700	1.38132800	-0.46643400
H	-0.07996800	1.54659500	1.97572800
H	3.03110700	-1.39921400	1.71721100
H	2.67339000	-1.56501200	-0.72598000
H	0.93706100	-0.17298200	-1.82427900
C	1.71661500	0.17695200	3.48530900
H	2.08078500	-0.75915200	3.91057700
Cl	2.92371200	1.44506700	3.93023800

H	0.79226700	0.45859200	4.01197900
Cl	-1.50552800	0.09913700	4.44363500

Int3

E = -730.393263 a.u.

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C	-0.00012500	0.19050100	0.16580900
C	0.04614900	-0.03192000	1.53162500
C	1.28616100	-0.18305900	2.18751400
C	2.47457500	-0.08831000	1.43854700
C	2.41723500	0.13495600	0.07244300
C	1.18454900	0.27401300	-0.56783300
H	-0.95834400	0.30217000	-0.33100800
H	-0.87284800	-0.08350800	2.10848000
H	3.43310100	-0.18983200	1.93585300
H	3.33679600	0.20480200	-0.49956300
H	1.14729400	0.45098900	-1.63819400
C	1.27067500	-0.39009700	3.61106700
H	0.34249300	-0.67673900	4.09306600
Cl	2.65599000	-0.99081600	4.43680900

TS4

E = -1650.702169 a.u.

0 2

C	-0.00012500	0.19050100	0.16580900
C	0.04614900	-0.03192000	1.53162500
C	1.28616100	-0.18305900	2.18751400
C	2.47457500	-0.08831000	1.43854700
C	2.41723500	0.13495600	0.07244300
C	1.18454900	0.27401300	-0.56783300
H	-0.95834400	0.30217000	-0.33100800
H	-0.87284800	-0.08350800	2.10848000
H	3.43310100	-0.18983200	1.93585300
H	3.33679600	0.20480200	-0.49956300
H	1.14729400	0.45098900	-1.63819400
C	1.27067500	-0.39009700	3.61106700
H	0.34249300	-0.67673900	4.09306600
Cl	0.73804200	3.77369200	5.34406800
Cl	1.00919900	1.81047500	4.39120800
Cl	2.65599000	-0.99081600	4.43680900

P2

E = -1650.735062 a.u.

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C	-0.00012500	0.16800100	0.17480900
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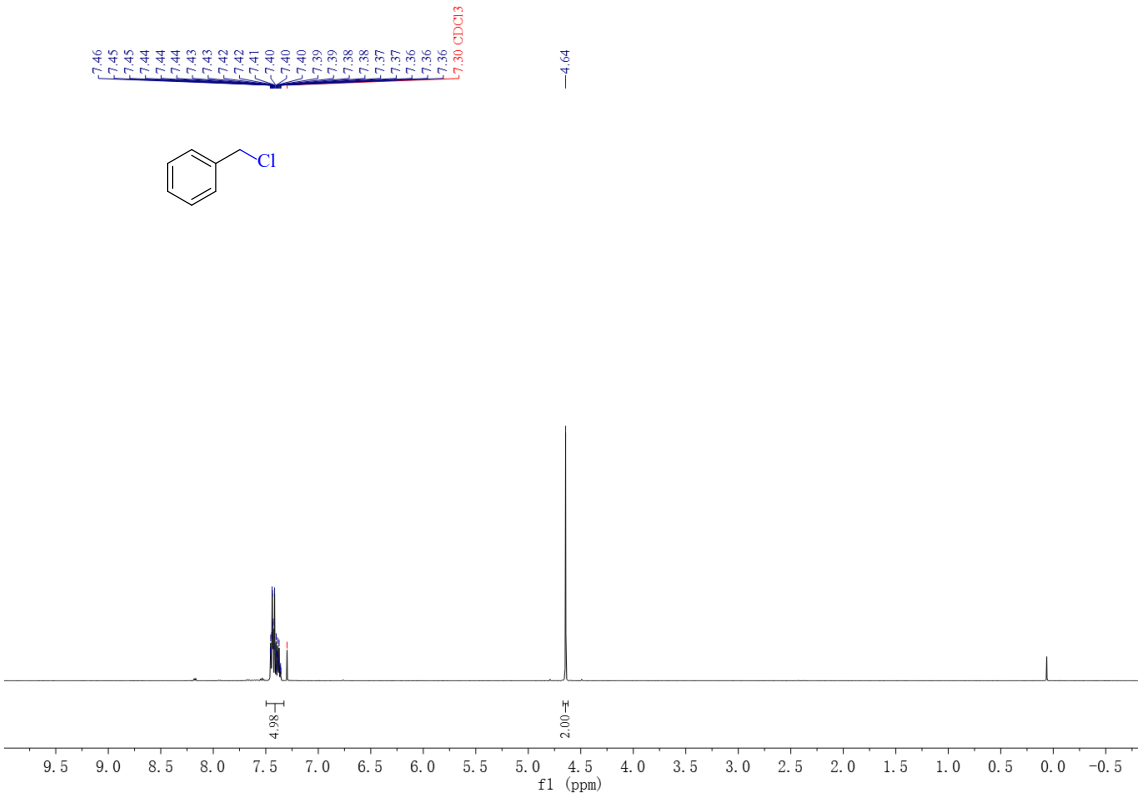
C	2.47007500	-0.05681000	1.46104700
C	2.41723500	0.12145600	0.08594300
C	1.18454900	0.25151300	-0.55433300
H	-0.95834400	0.26617000	-0.32650800
H	-0.87284800	-0.02500800	2.13098000
H	3.42410100	-0.12683200	1.96735300
H	3.33679600	0.17780200	-0.48606300
H	1.14729400	0.41498900	-1.62469400
C	1.26617500	-0.12459700	3.70106700
H	0.34699300	-0.59123900	4.09756600
Cl	0.72004200	3.87719200	5.40706800
Cl	1.05869900	1.56297500	4.26520800
Cl	2.62899000	-0.96381600	4.43230900

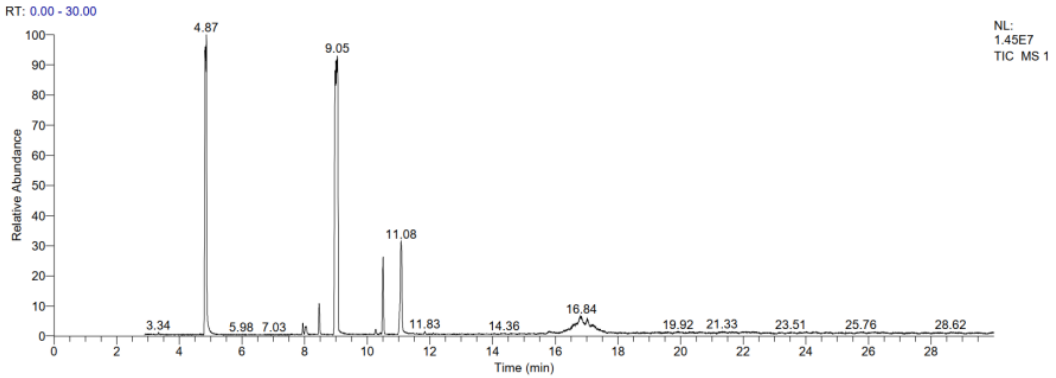
Section 4. NMR and GS-MS spectra

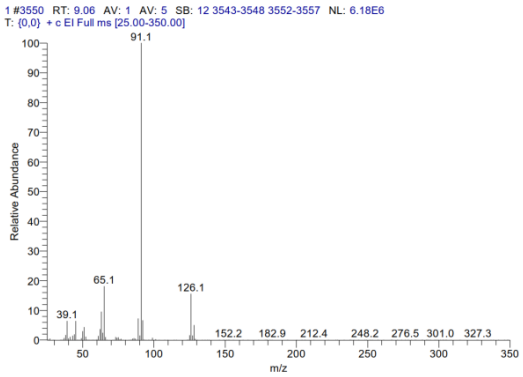
Chlorination of toluene

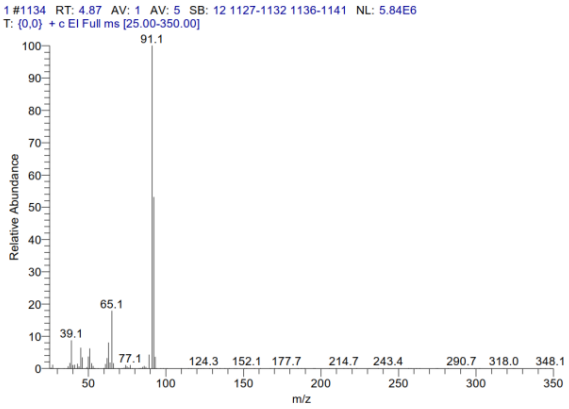
^{1}HNMR of (chloromethyl)benzene (2a)



GS-MS of Chlorination of toluene reaction solution

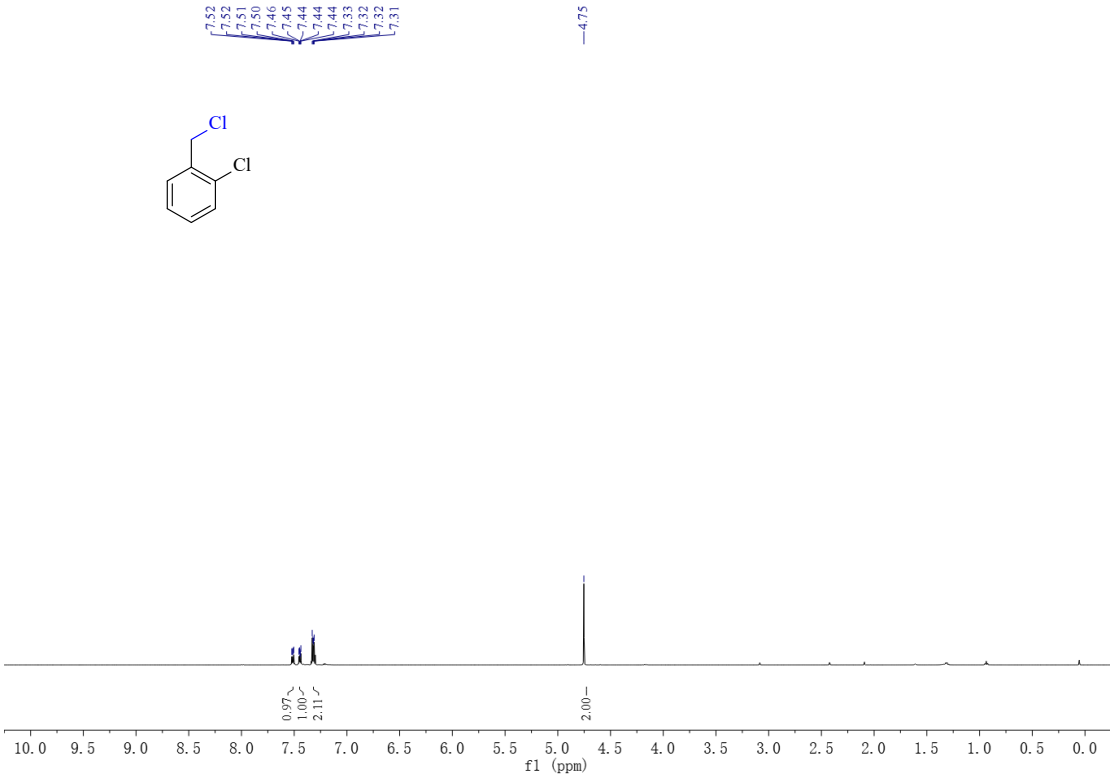




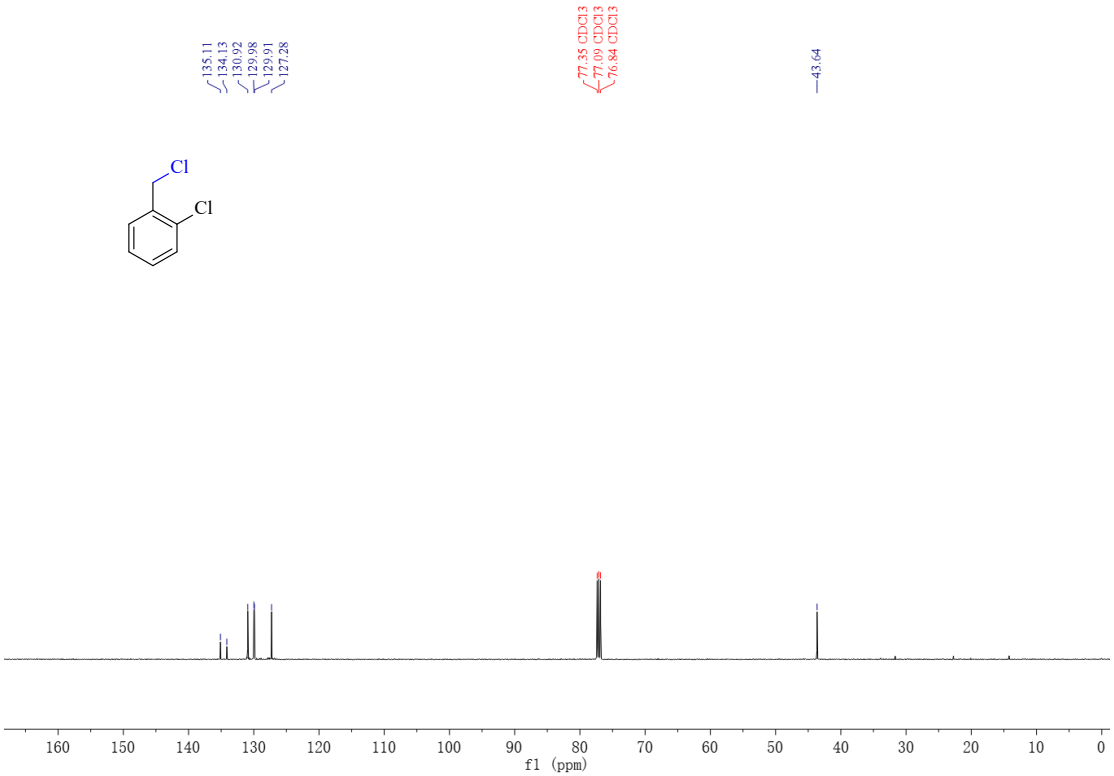


Chlorination of o-Cl-toluene

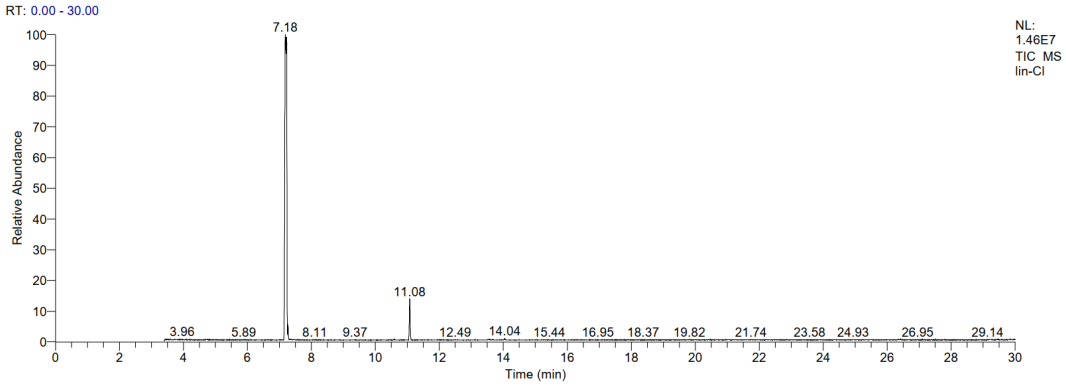
^{1}HNMR of 2-Chlorobenzyl chloride (2b)

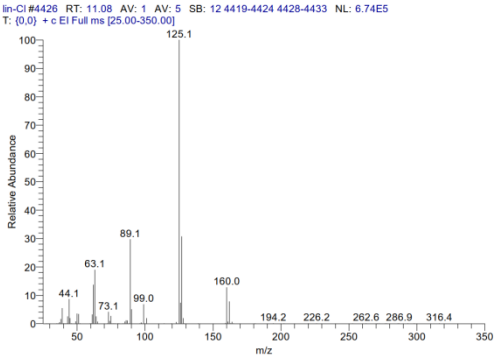


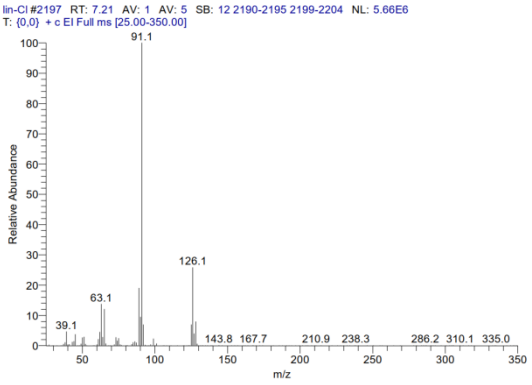
^{13}CNMR of 2-Chlorobenzyl chloride (2b)



GS-MS of Chlorination of o-Cl-toluene reaction solution

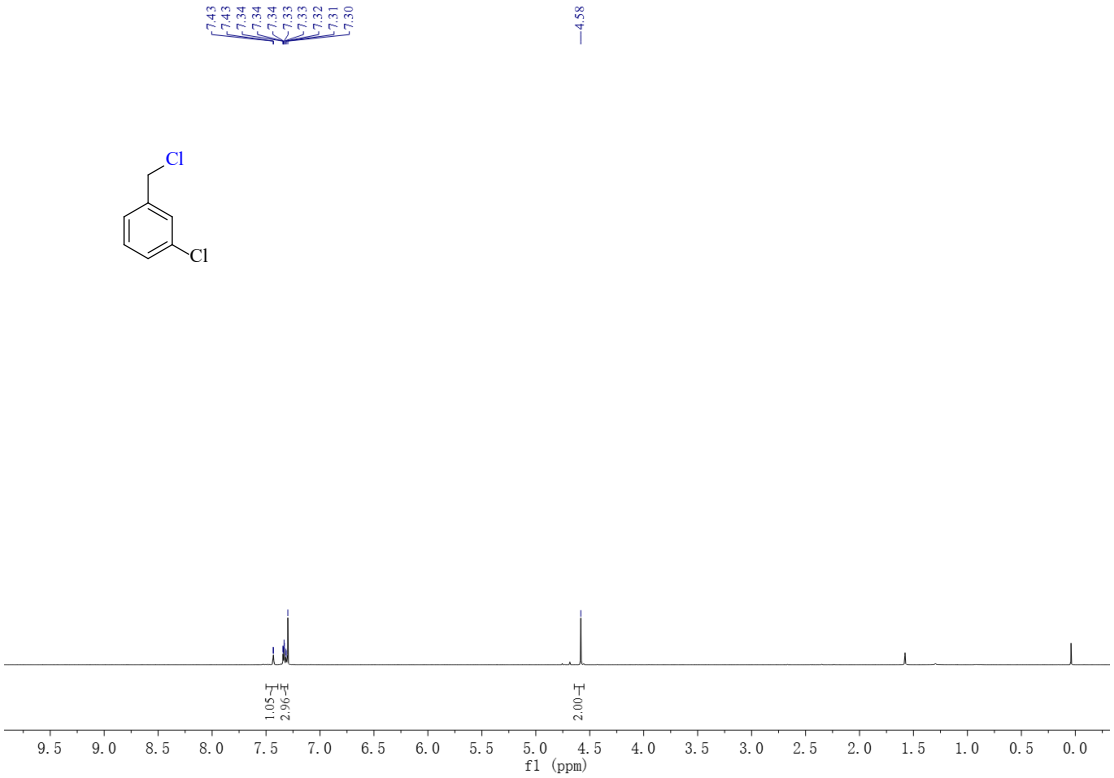




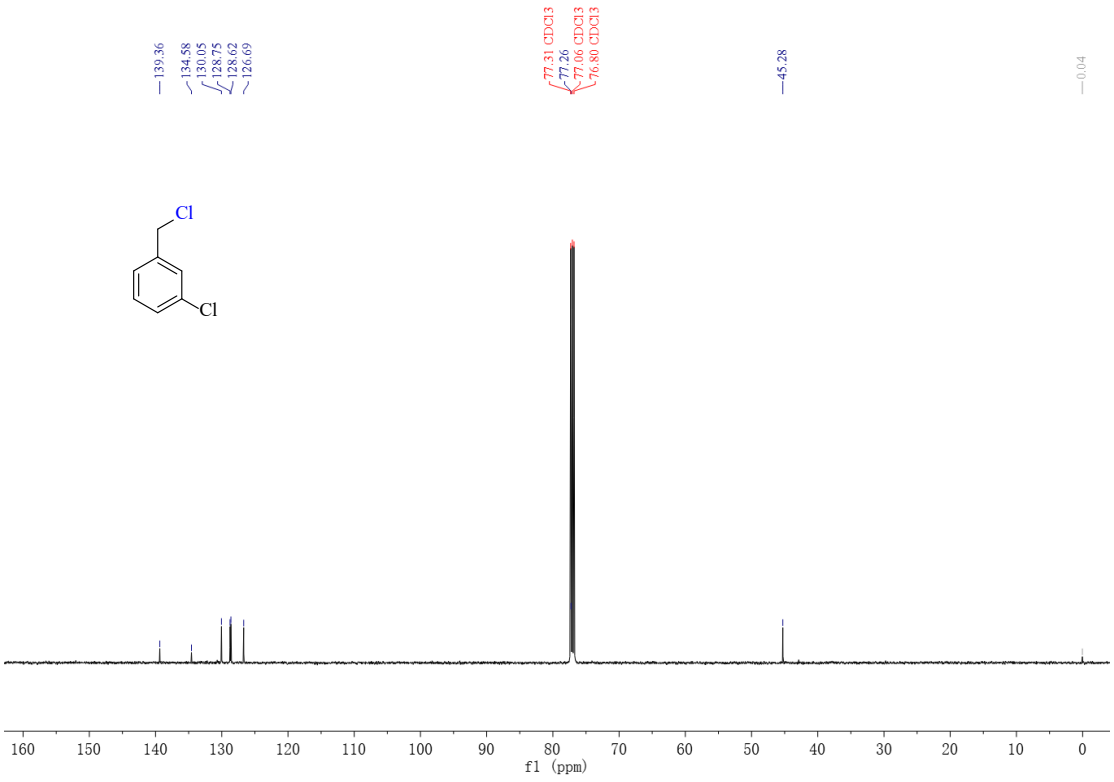


Chlorination of m-Cl-toluene

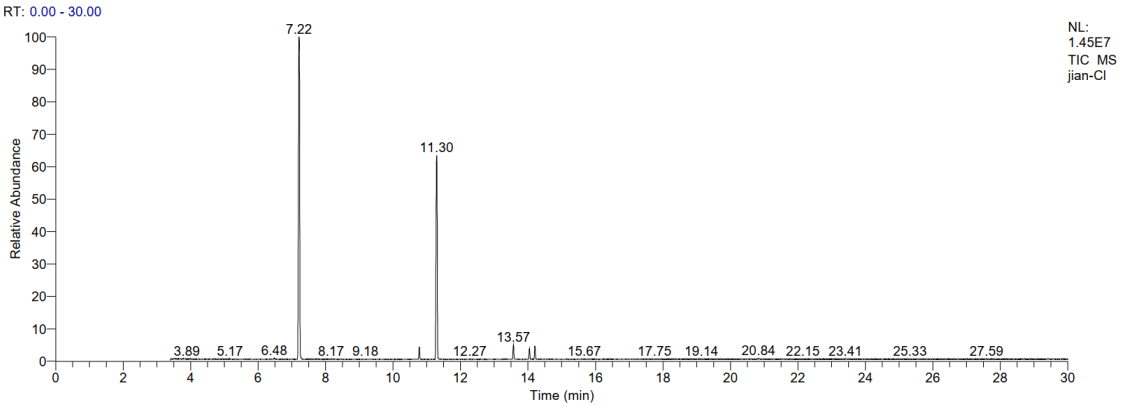
[1]HNMR of 3-Chlorobenzyl chloride (2c)

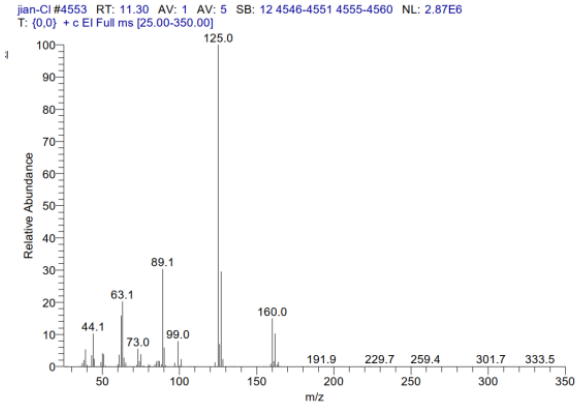


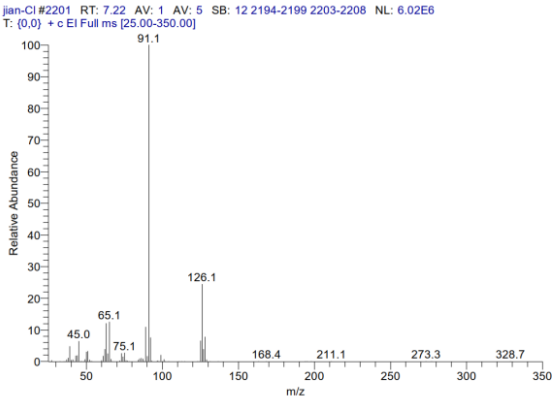
[13]CNMR of 3-Chlorobenzyl chloride (2c)



GS-MS of Chlorination of *m*-Cl-toluene reaction solution

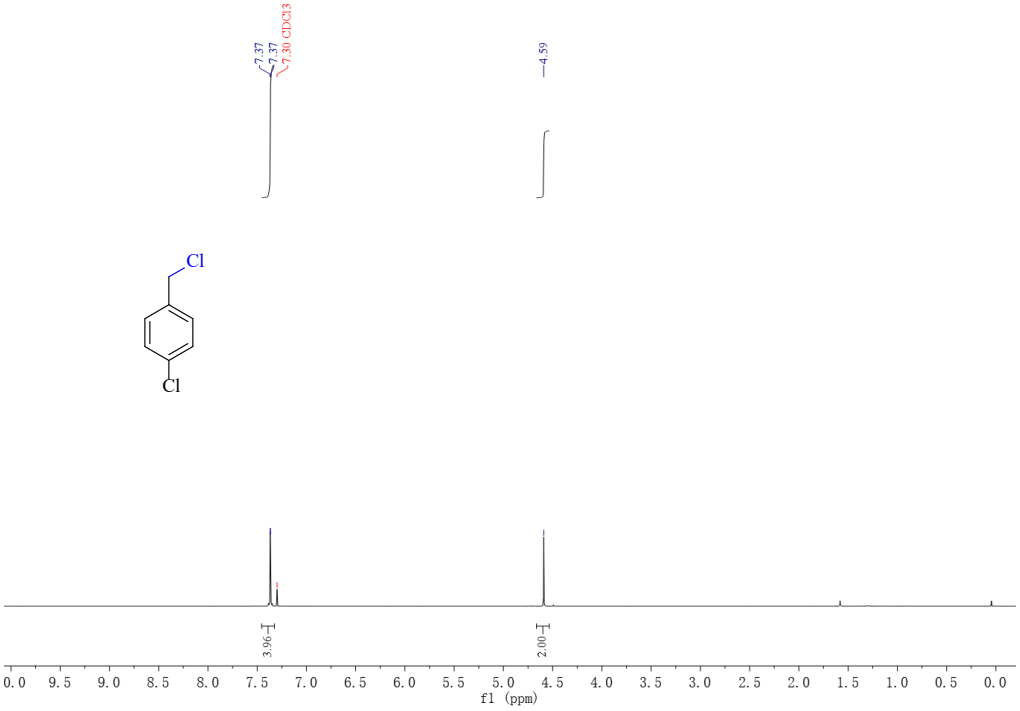




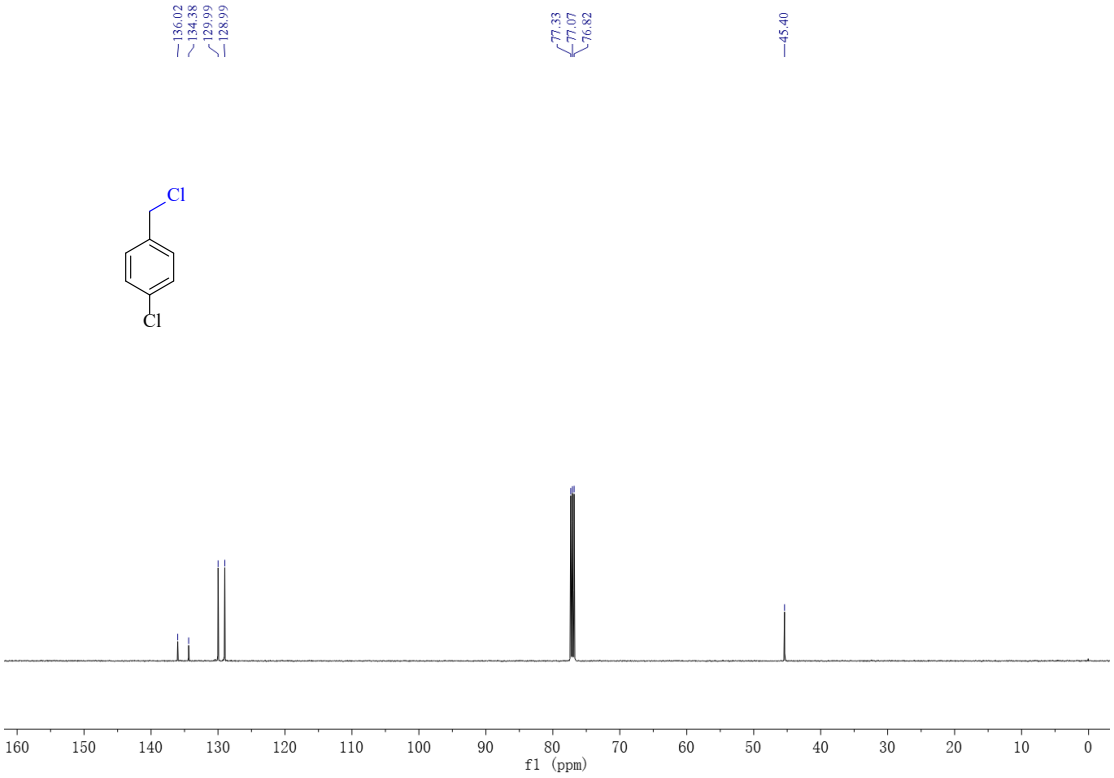


Chlorination of p-Cl-toluene

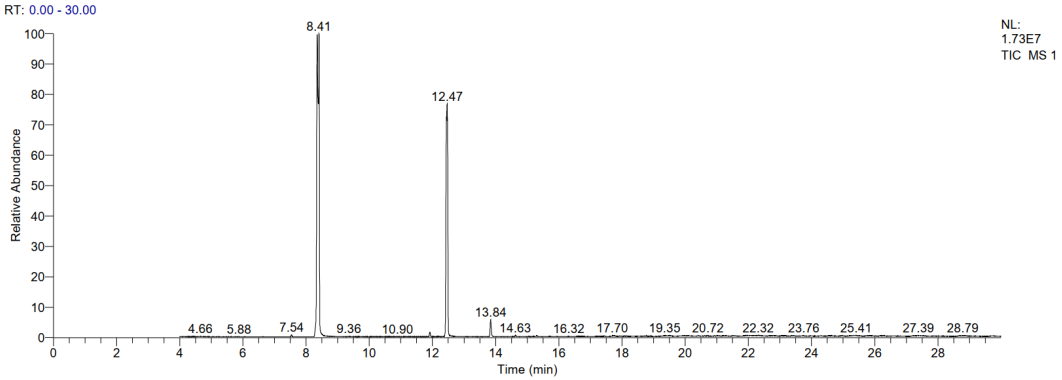
^{1}HNMR of 4-Chlorobenzyl chloride (2d)

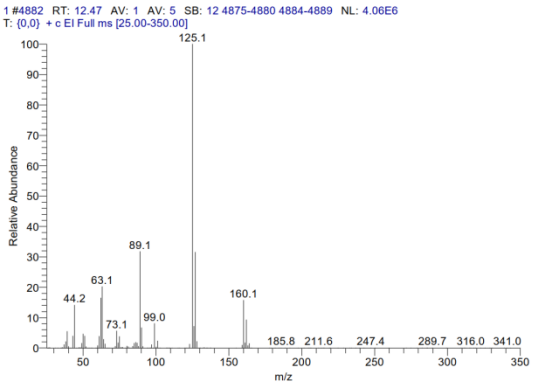


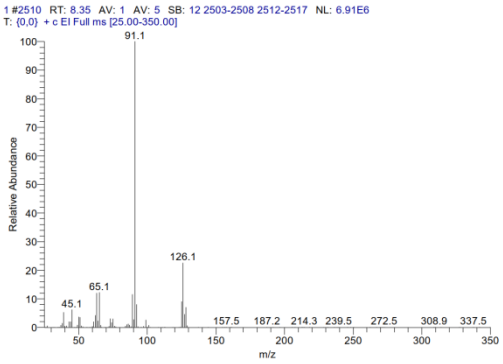
^{13}CNMR of 4-Chlorobenzyl chloride (2d)



GS-MS of Chlorination of *p*-Cl-toluene reaction solution

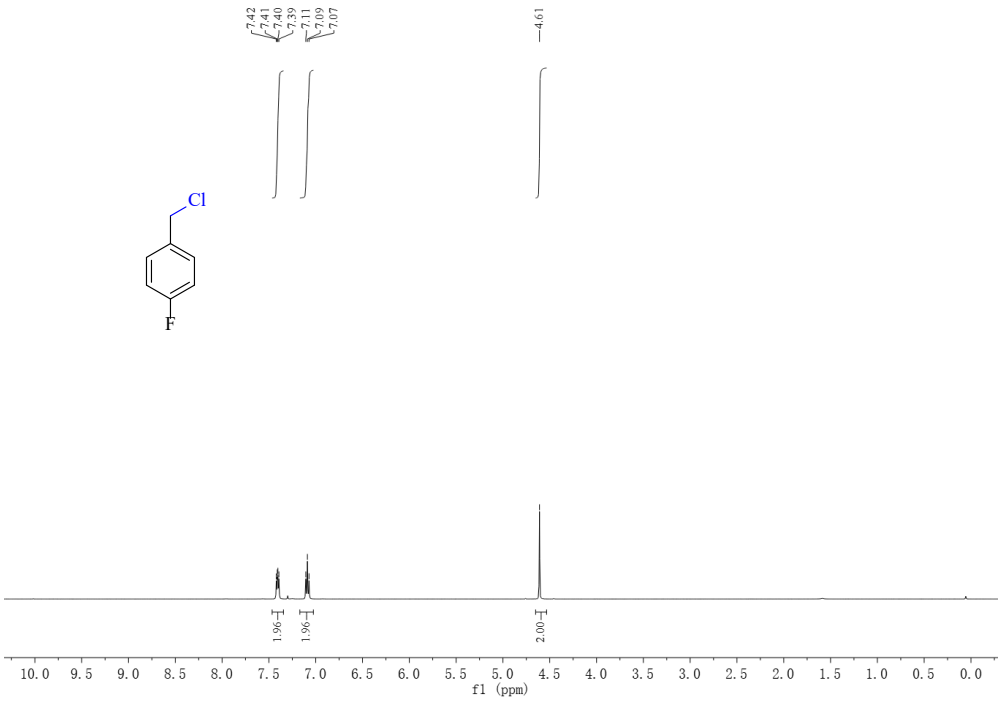




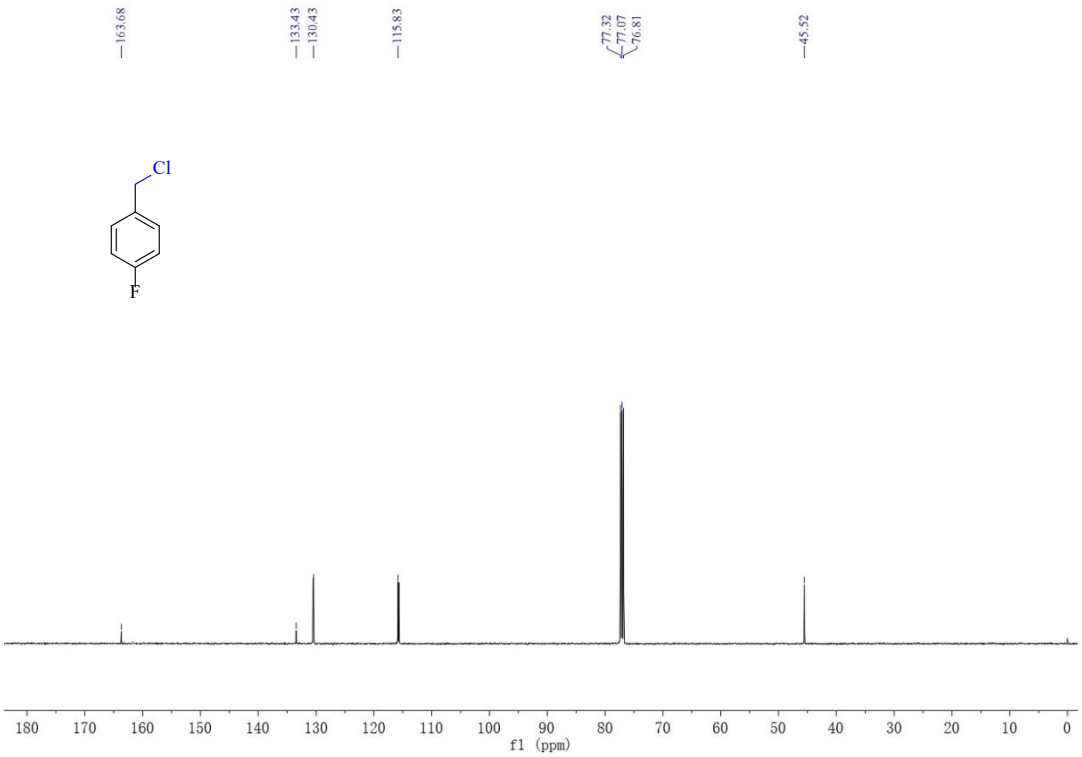


Chlorination of 4-F-toluene

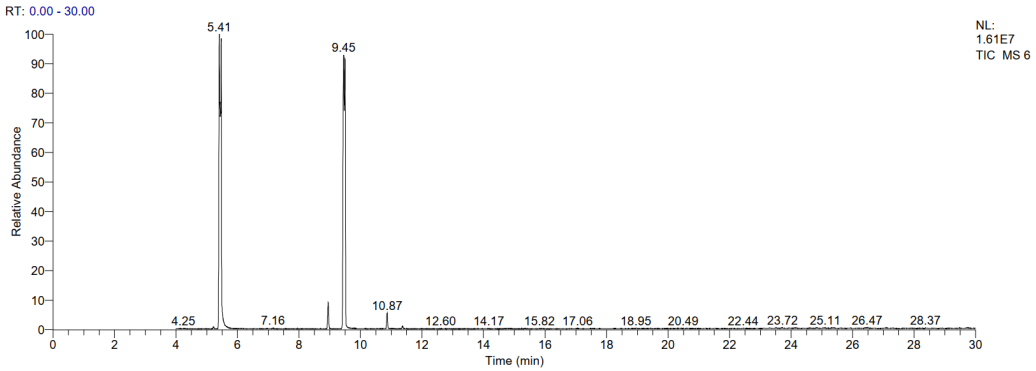
[1]HNMR of 4-Fluorobenzyl chloride (2e)

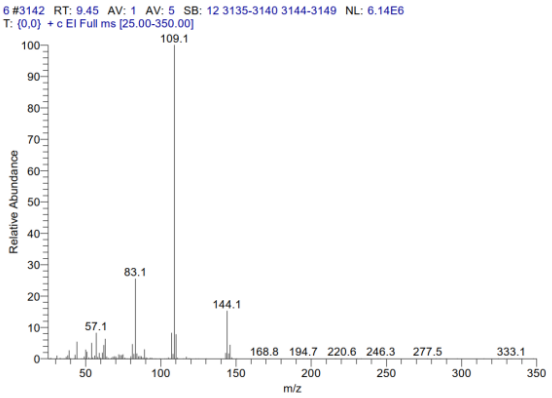


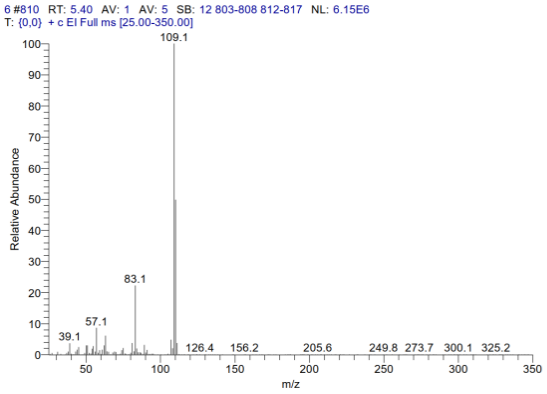
[13]CNMR of 4-Fluorobenzyl chloride (2e)



GS-MS of Chlorination of 4-F-toluene reaction solution

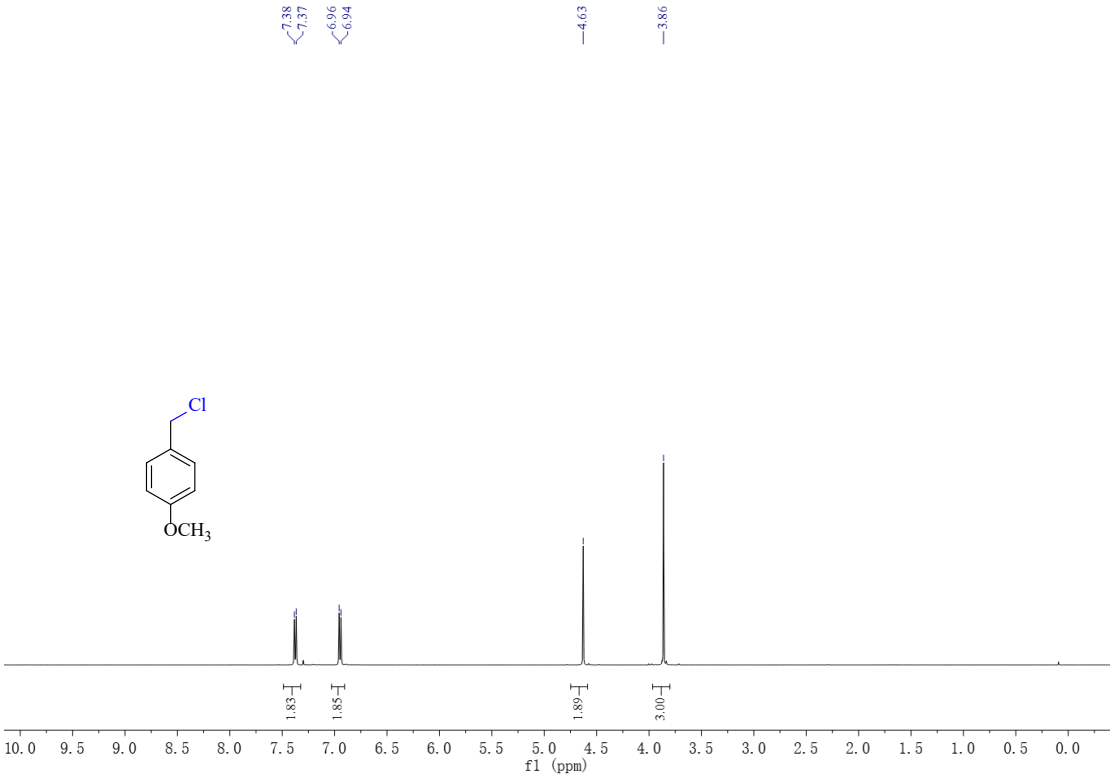




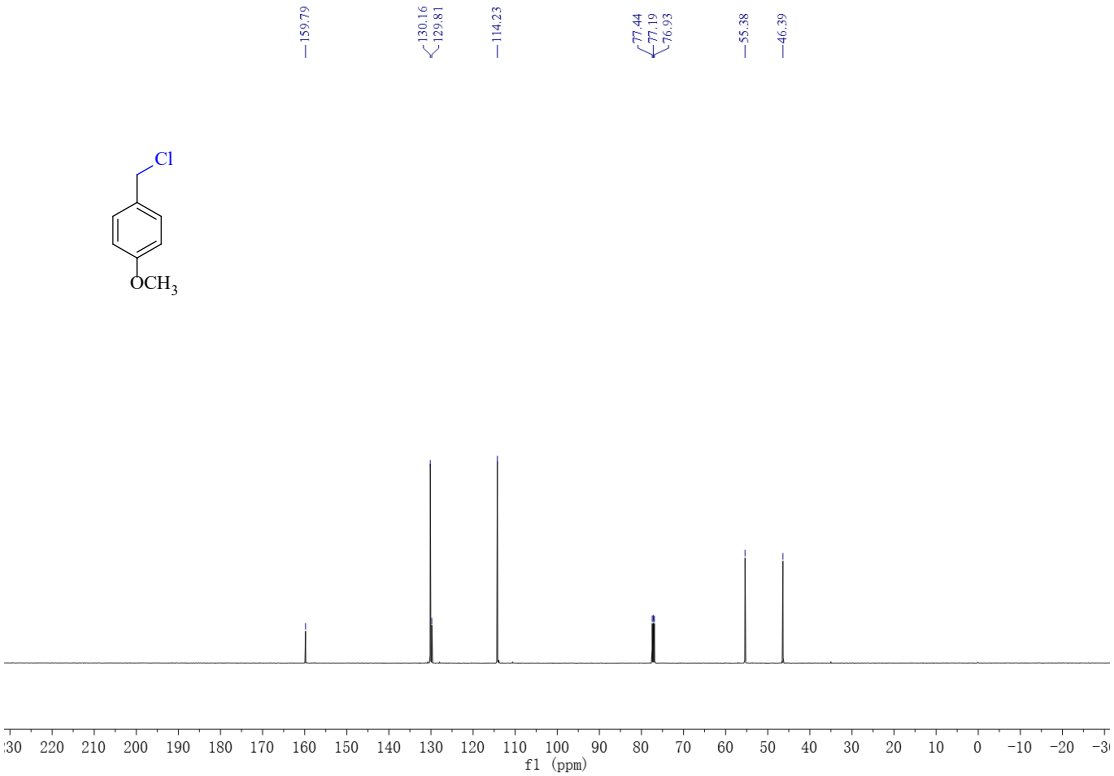


Chlorination of 4-OMe-toluene

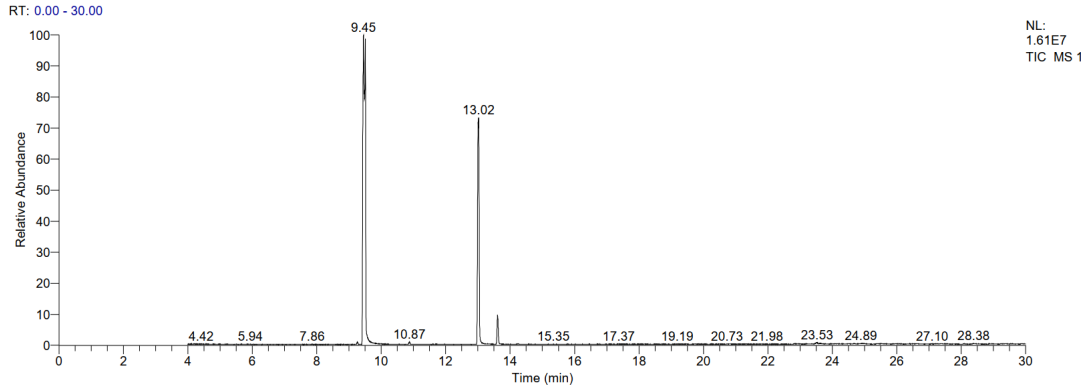
[1]HNMR of 4-Methoxybenzyl chloride (2f)

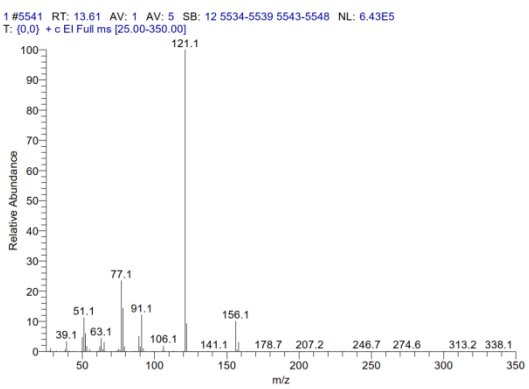


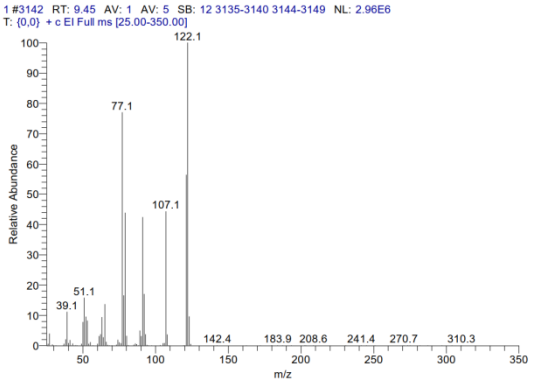
[13]CNMR of 4-Methoxybenzyl chloride (2f)



GS-MS of Chlorination of 4-OMe-toluene reaction solution

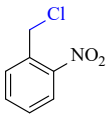


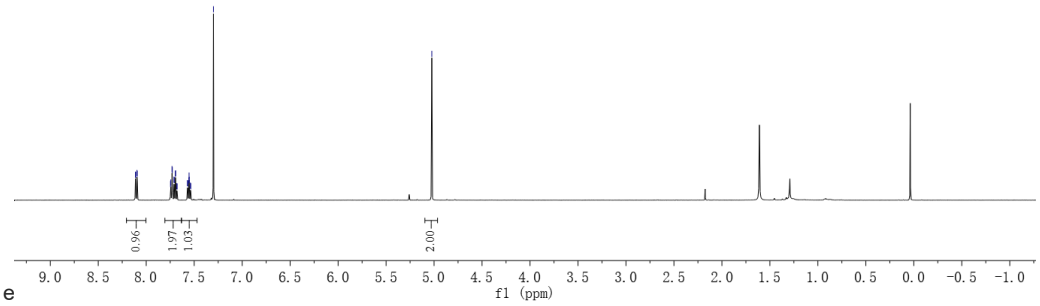




Chlorination of o-NO_2-toluene

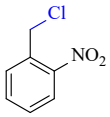
[1]HNMR of 2-Nitrobenzyl chloride (2g)

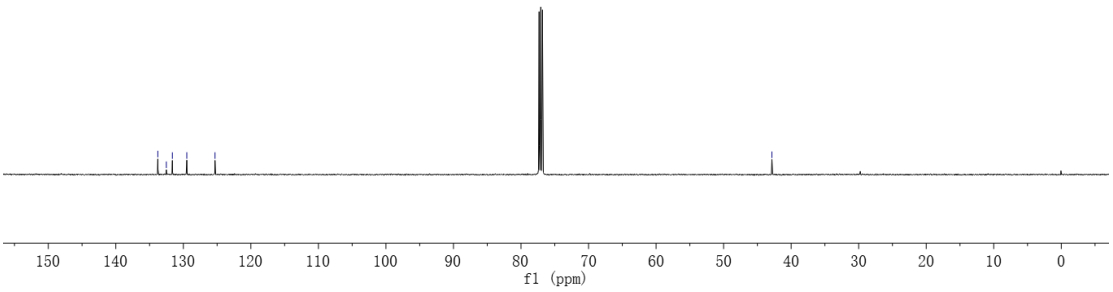




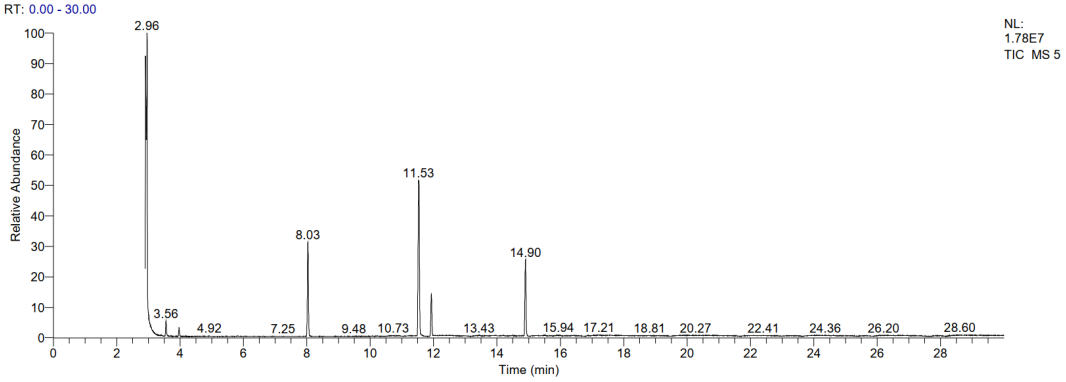
e

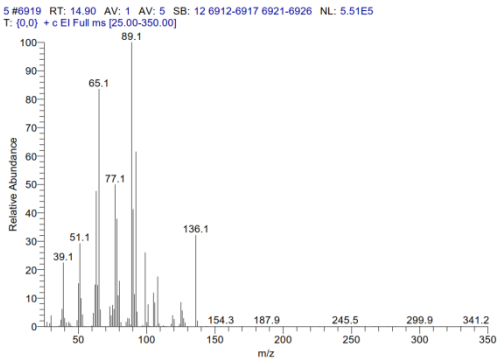
[13]CNMR of 2-Nitrobenzyl chloride (2g)

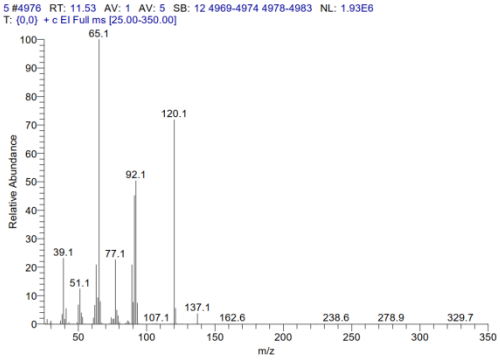




GS-MS of Chlorination of *o*-NO_2-toluene reaction solution

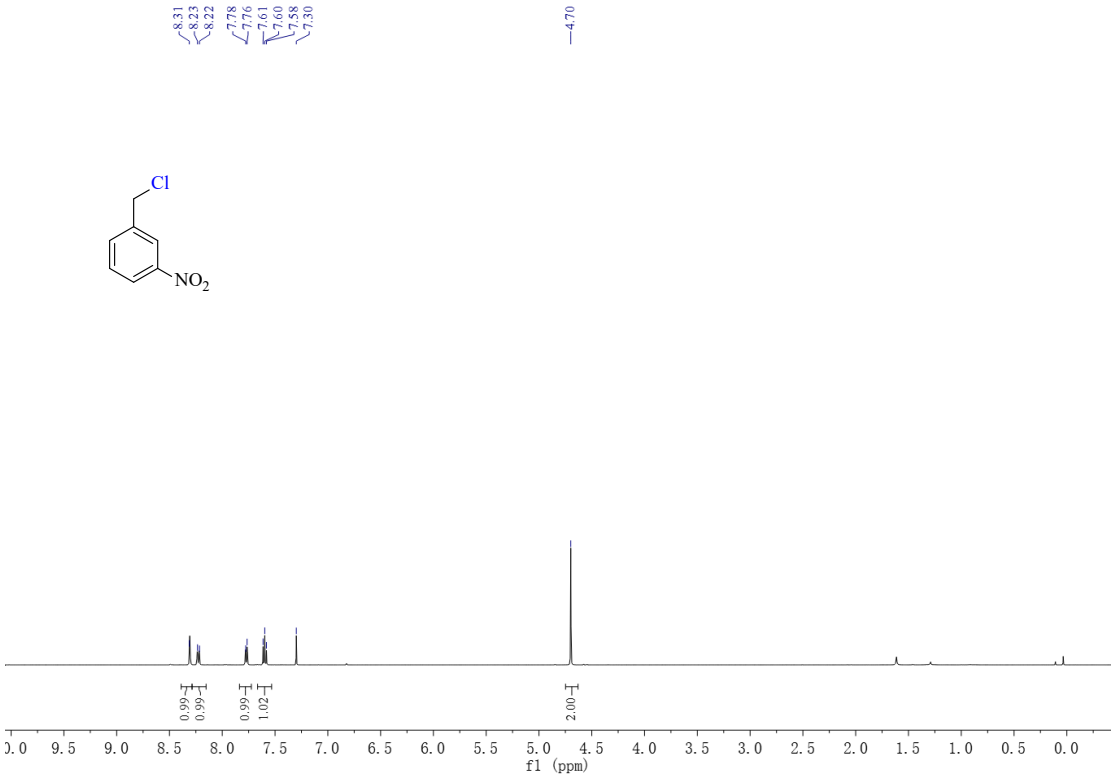




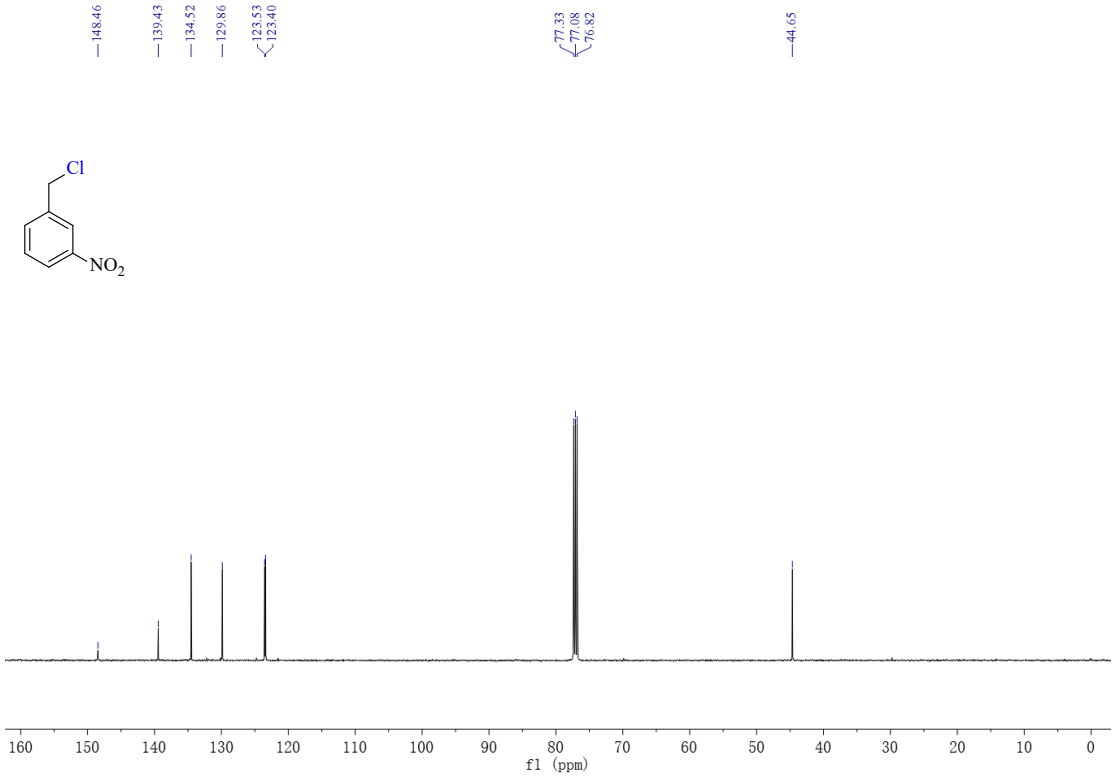


Chlorination of m-NO_2-toluene

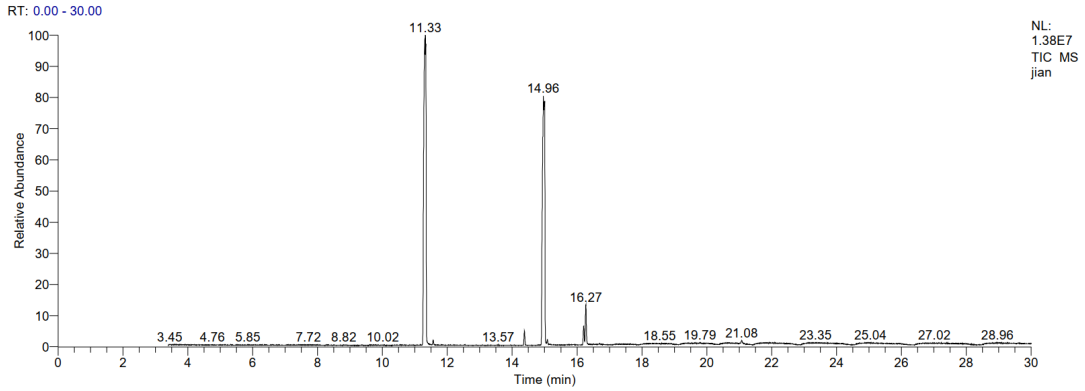
^{1}HNMR of 3-Nitrobenzyl chloride (2h)

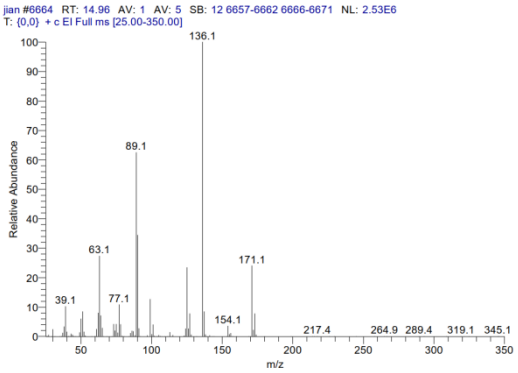


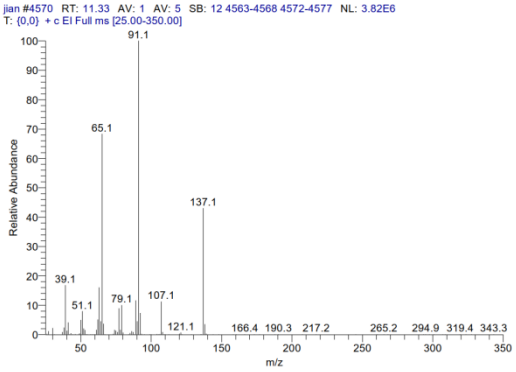
^{13}CNMR of 3-Nitrobenzyl chloride (2h)



GS-MS of Chlorination of *m*-NO_2-toluene reaction solution

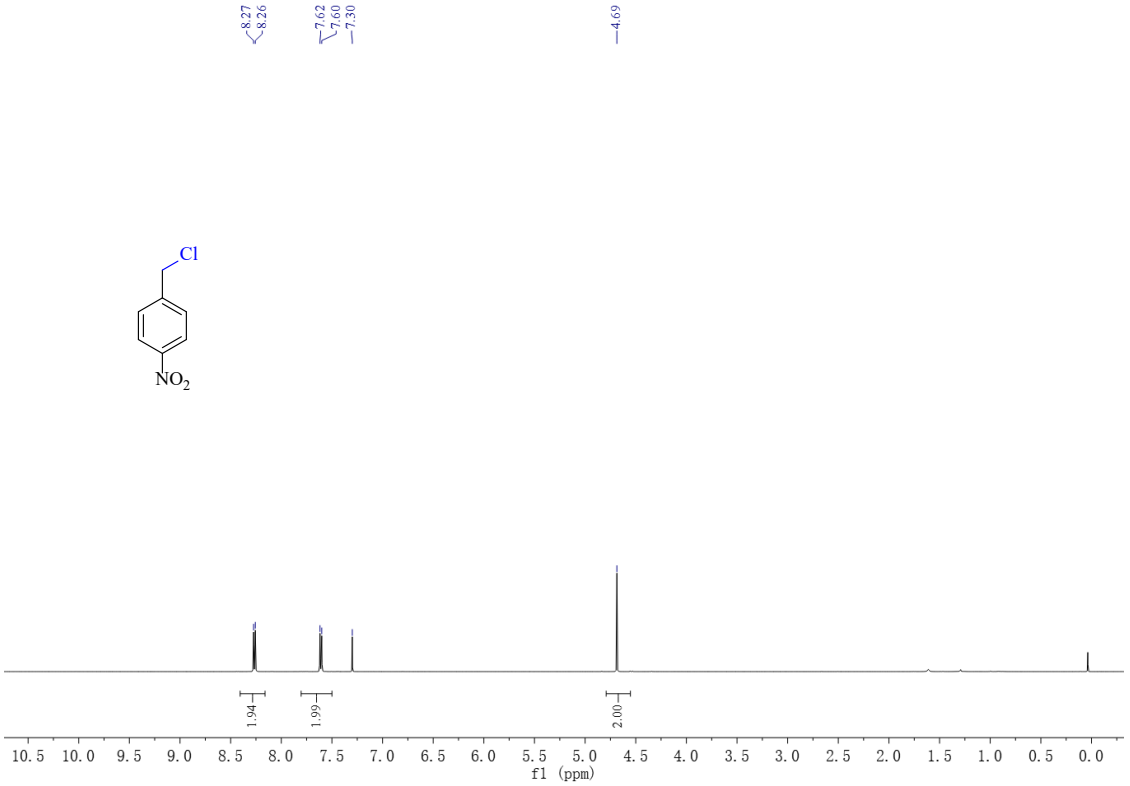




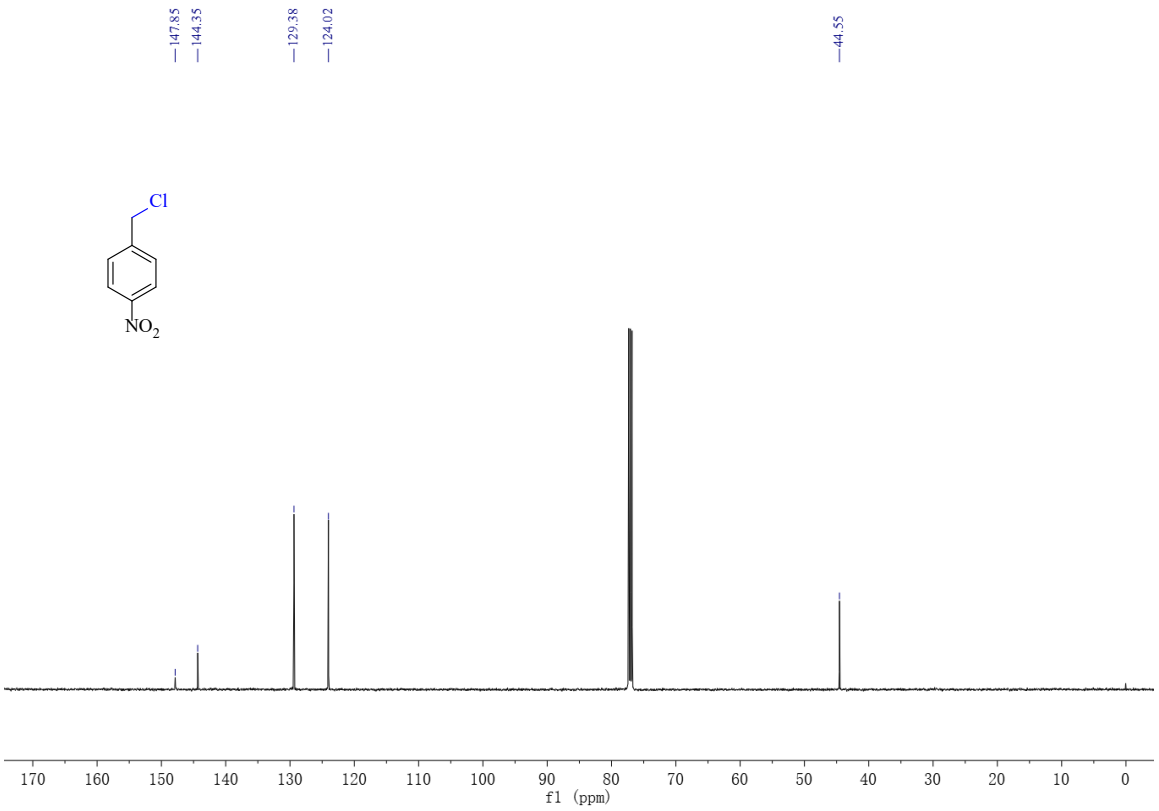


Chlorination of p-NO_2-toluene

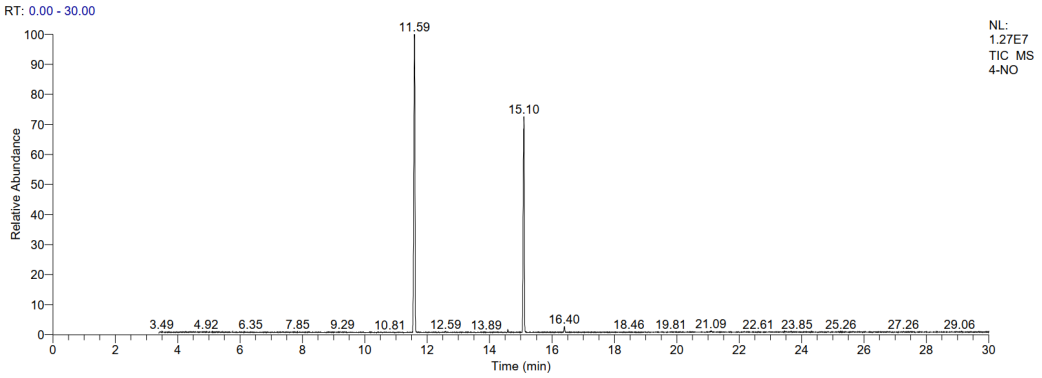
^{1}HNMR of 3-Nitrobenzyl chloride (2i)

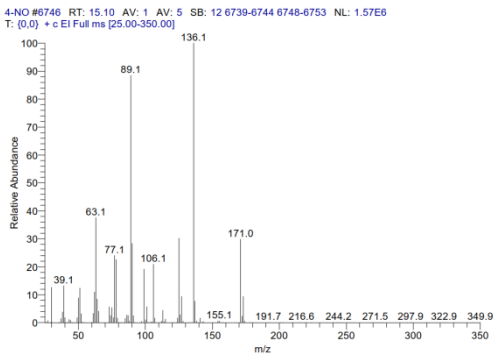


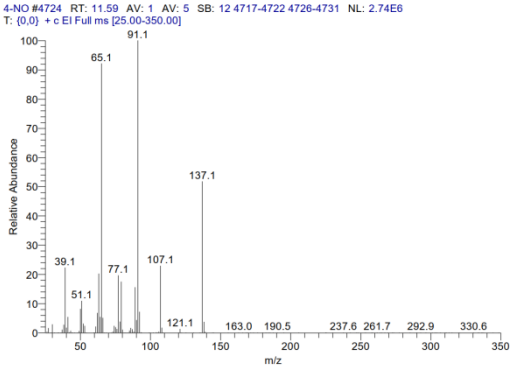
^{13}CNMR of 3-Nitrobenzyl chloride (2i)



GS-MS of Chlorination of *p*-NO_2-toluene reaction solution

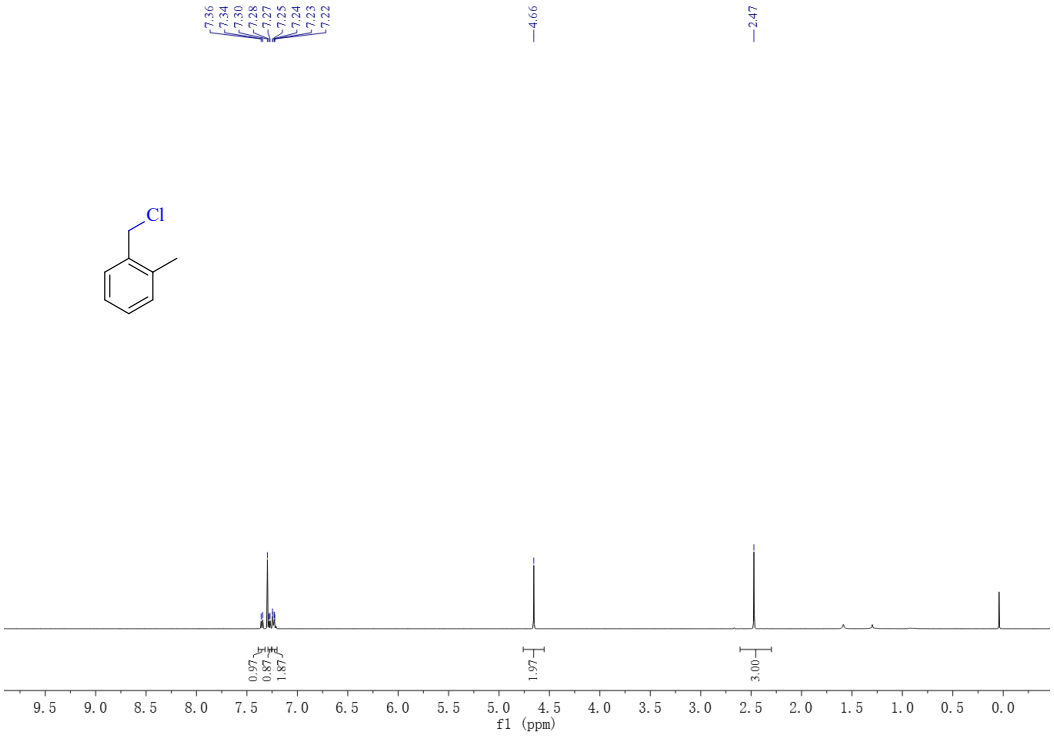




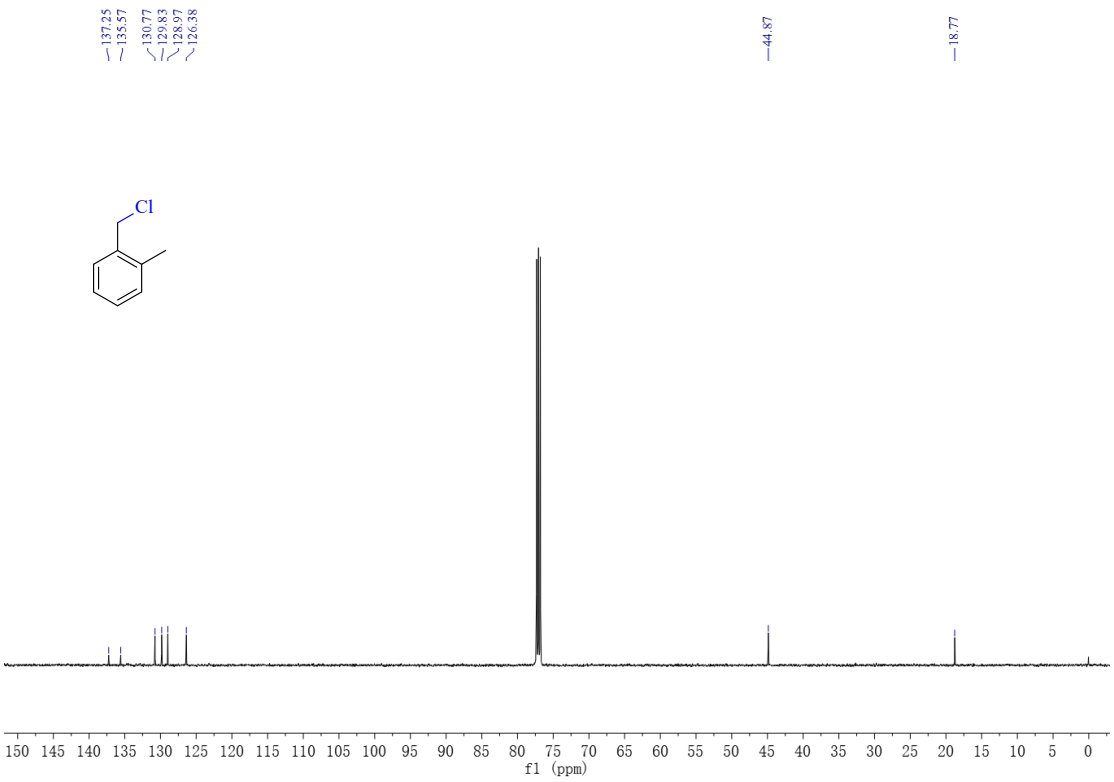


Chlorination of o-Xylene

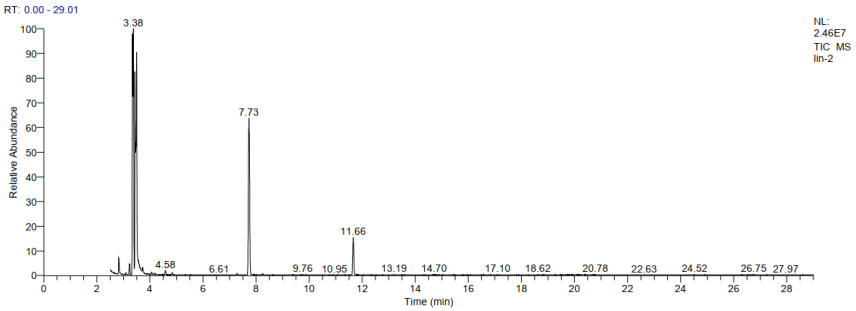
^{1}H NMR of 2-Methylbenzyl chloride(2j)

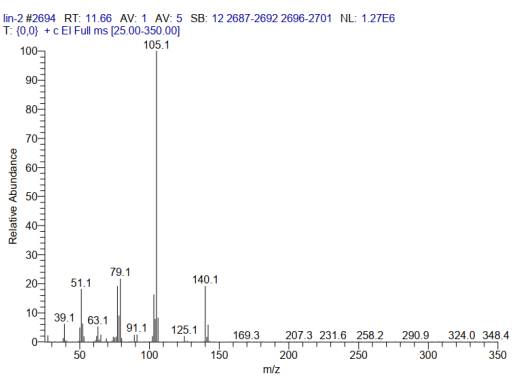


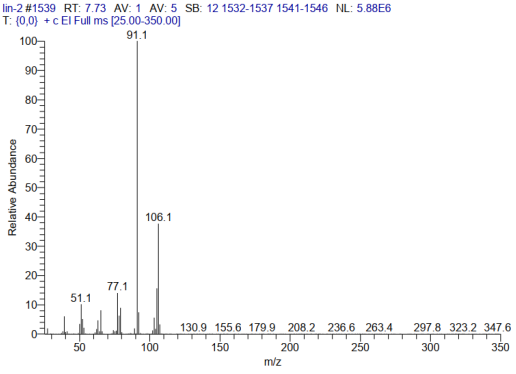
^{13}CNMR of ^{1}H NMR of 2-Methylbenzyl chloride(2j)



GS-MS of Chlorination of *o*-Xylene reaction solution

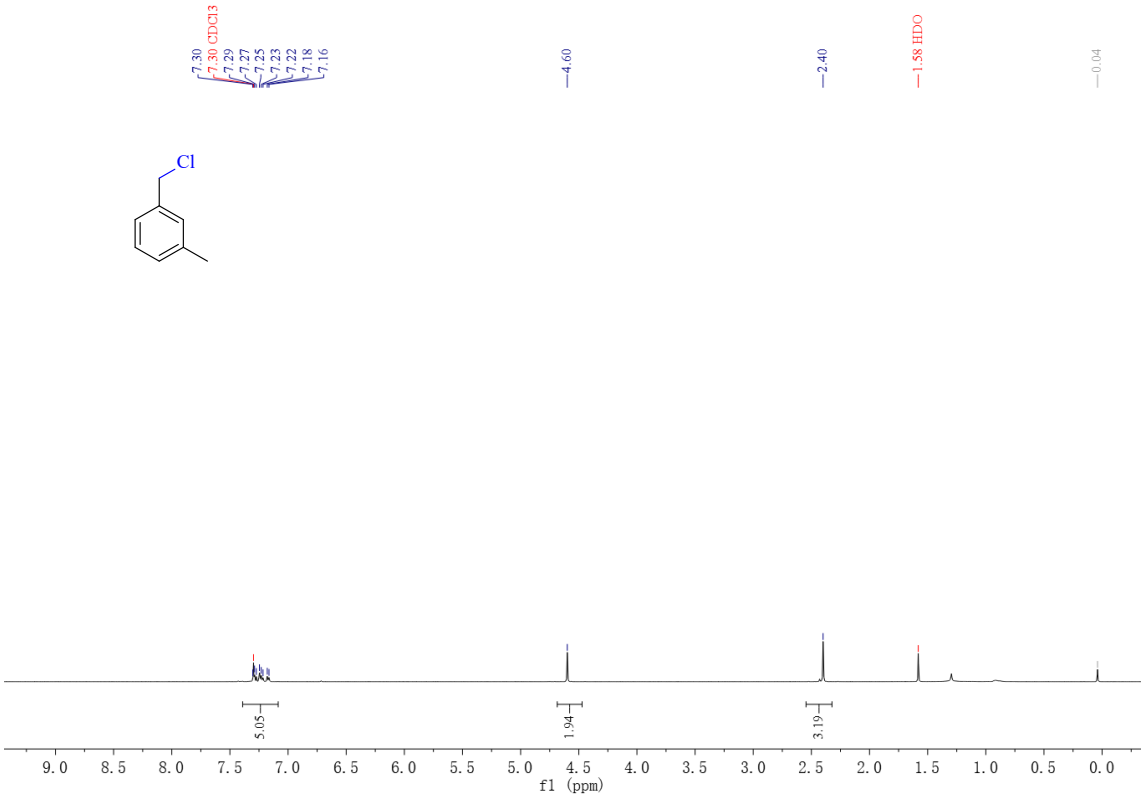




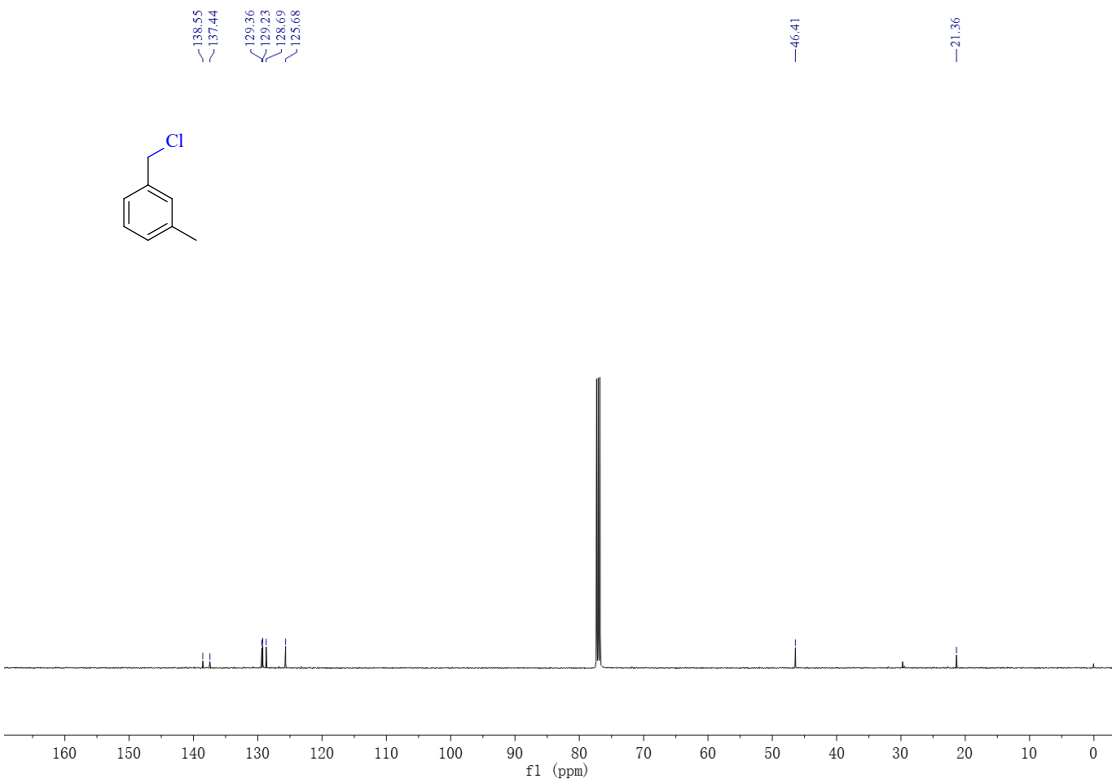


Chlorination of m-Xylene

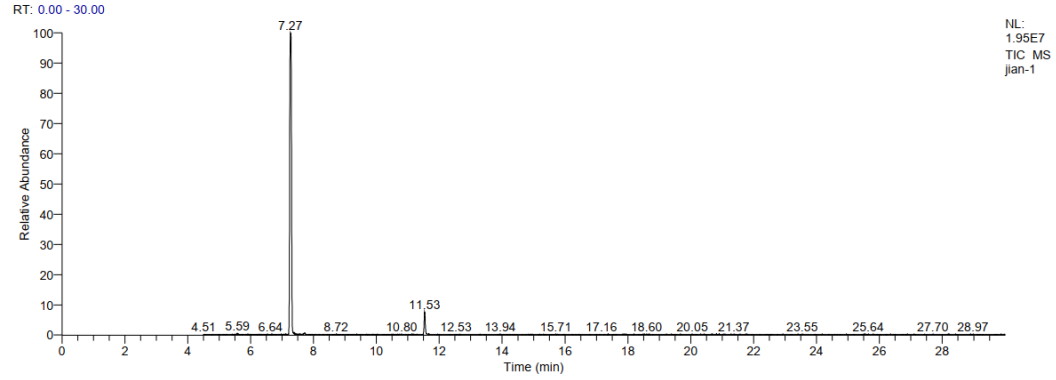
^{1}H NMR of 3-Methylbenzyl chloride (2k)

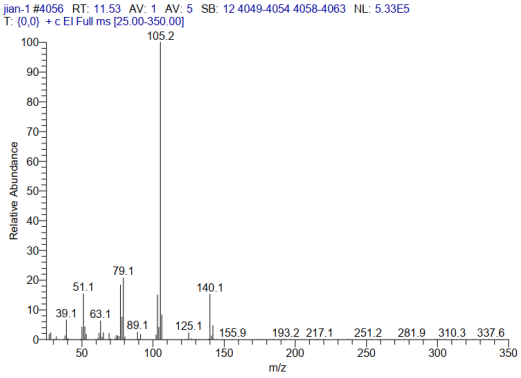


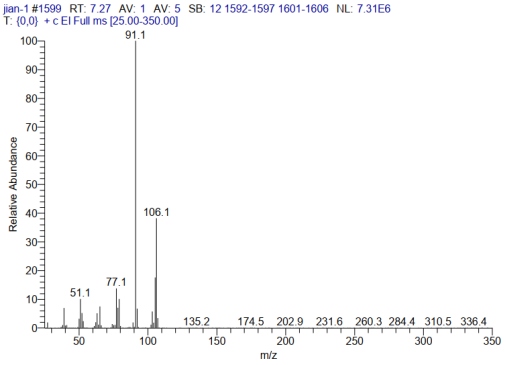
^{13}CNMR of 3-Methylbenzyl chloride (2k)



GS-MS of Chlorination of *m*-Xylene reaction solution

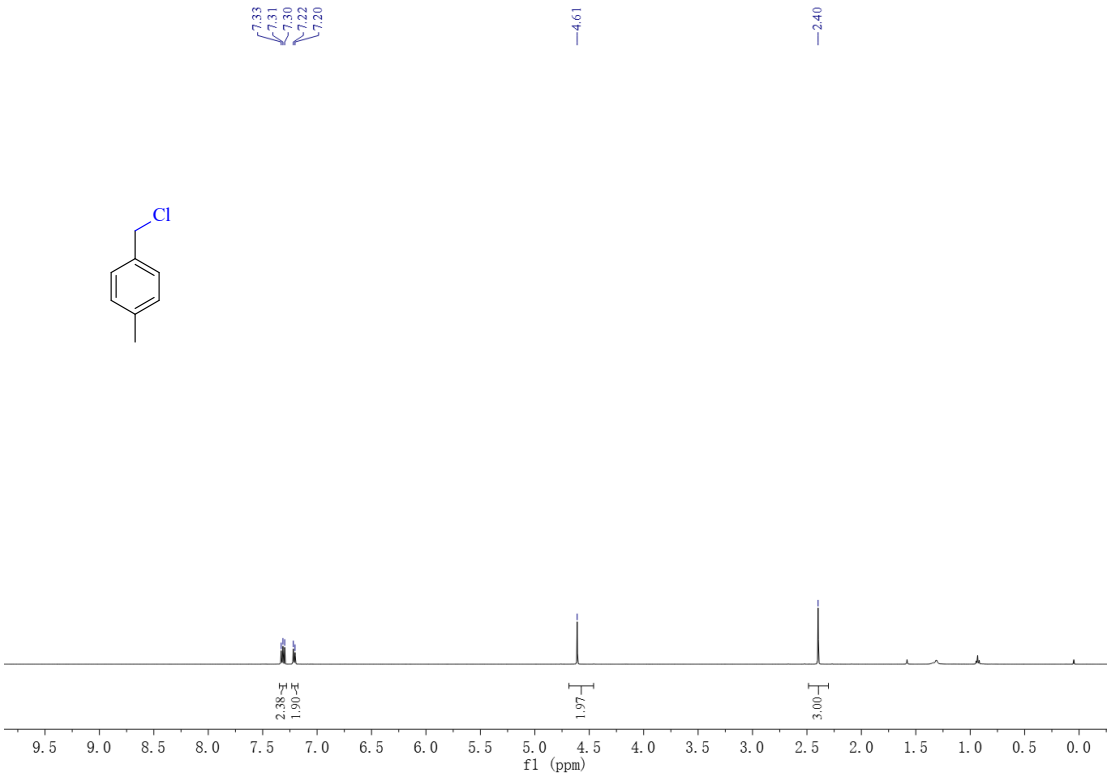




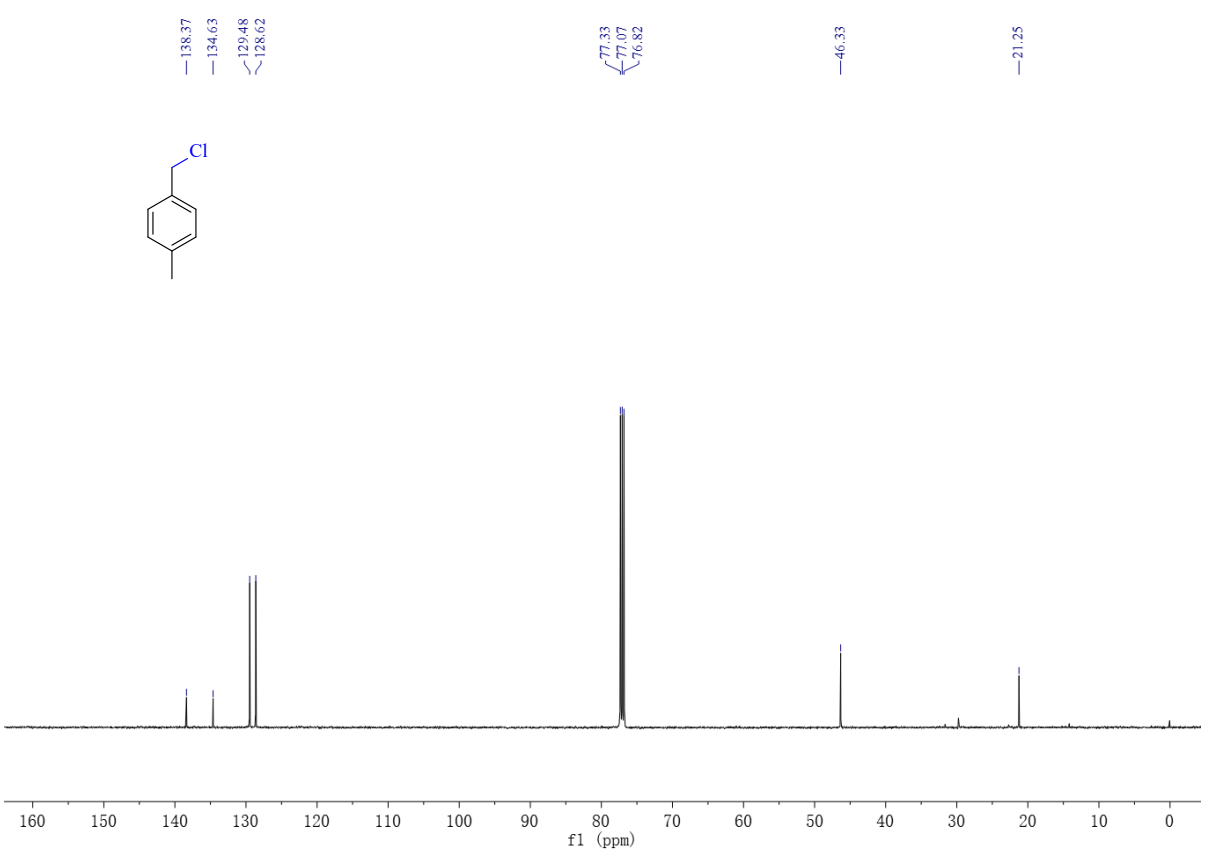


Chlorination of p-Xylene

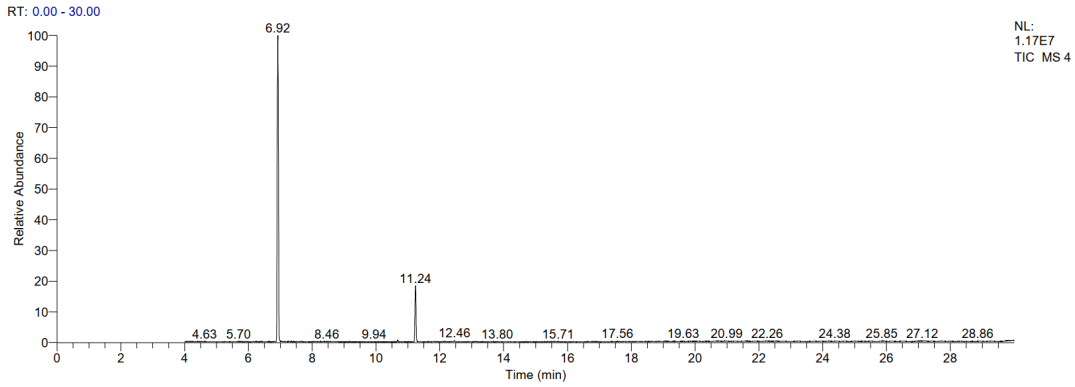
^{1}H NMR of 4-Methylbenzyl chloride (2l)

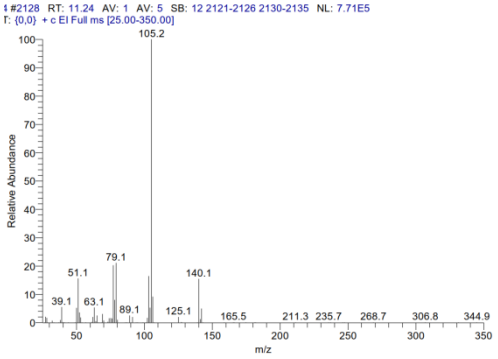


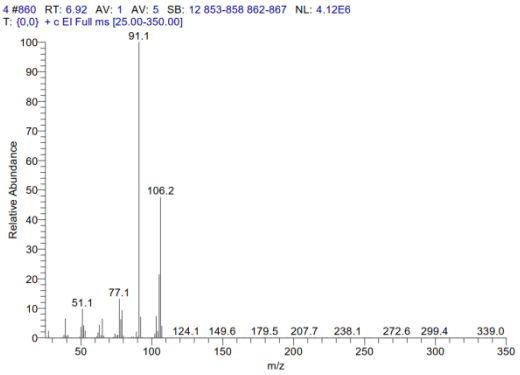
^{13}CNMR of 4-Methylbenzyl chloride(2l)



GS-MS of Chlorination of *p*-Xylene reaction solution

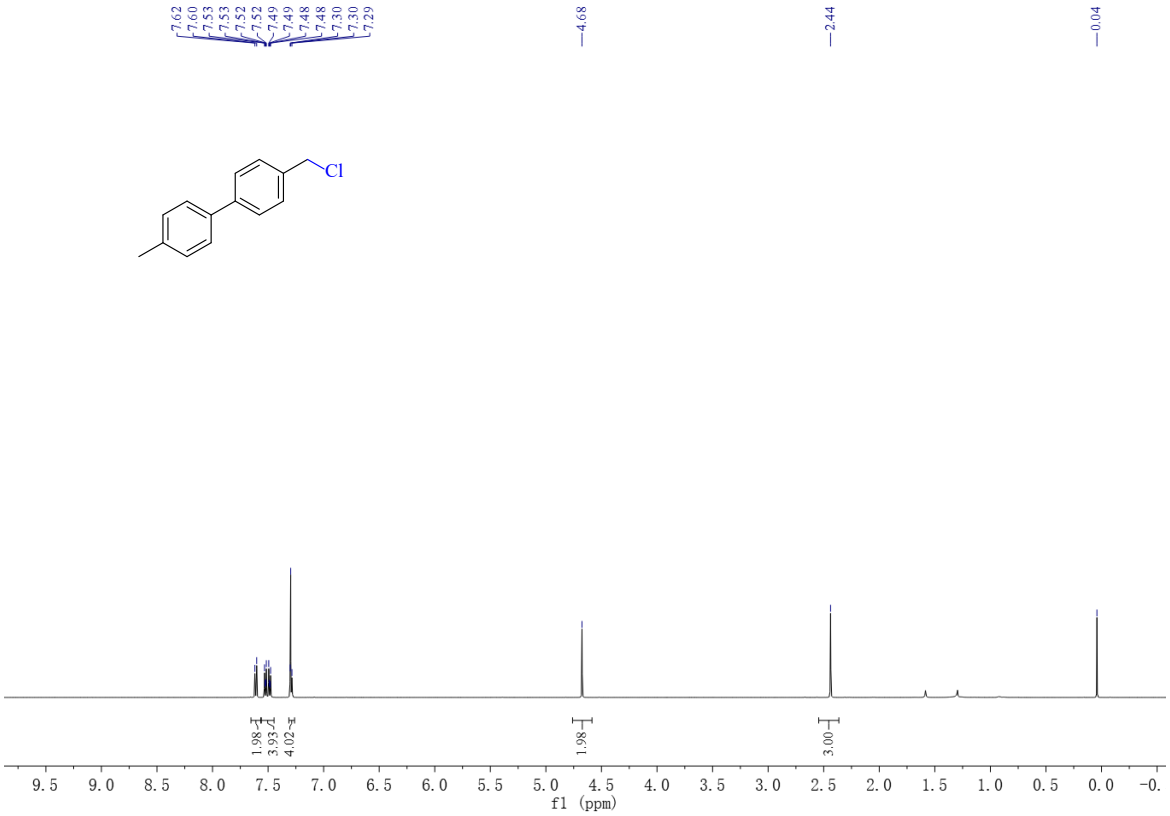




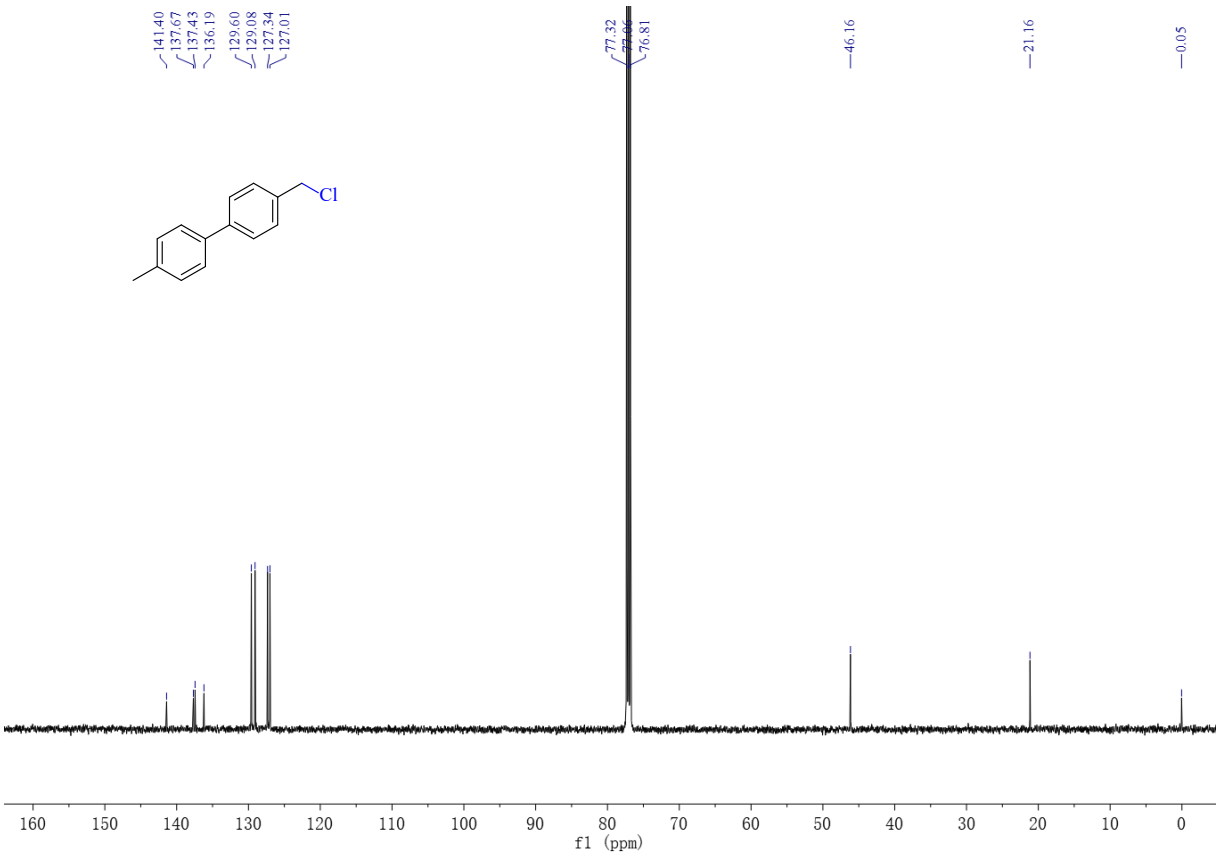


Chlorination of 4,4'-dimethyl-1,1'-biphenyl

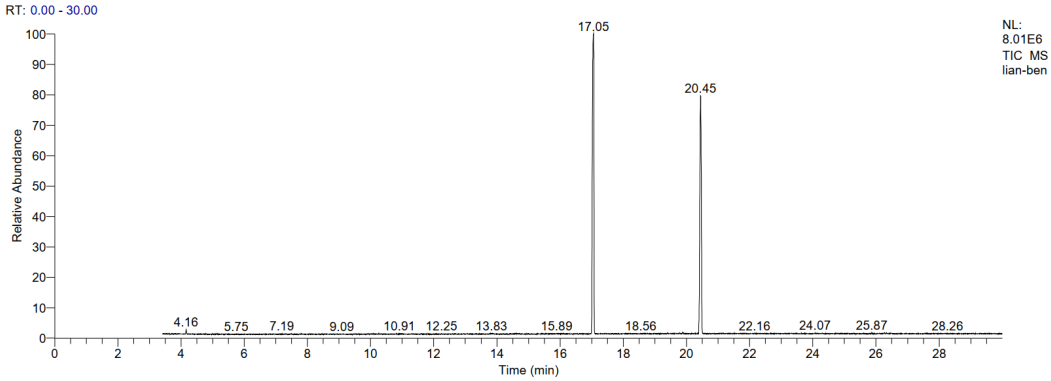
^{1}H NMR of 4-Chloromethyl-4'-methylbiphenyl (2m)

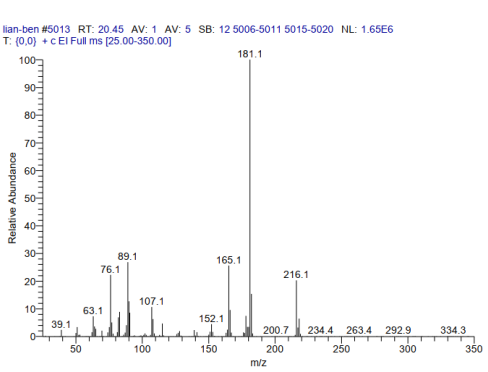


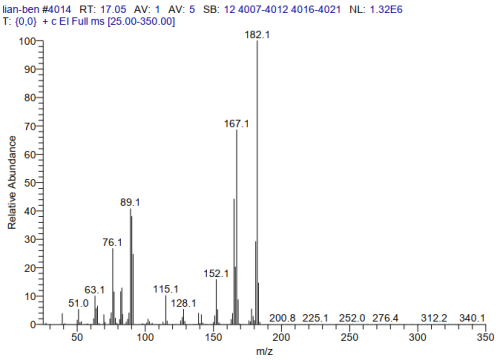
^{13}CNMR of 4-Chloromethyl-4'-methylbiphenyl (2m)



GS-MS of Chlorination of 4,4'-dimethyl-1,1'-biphenyl reaction solution

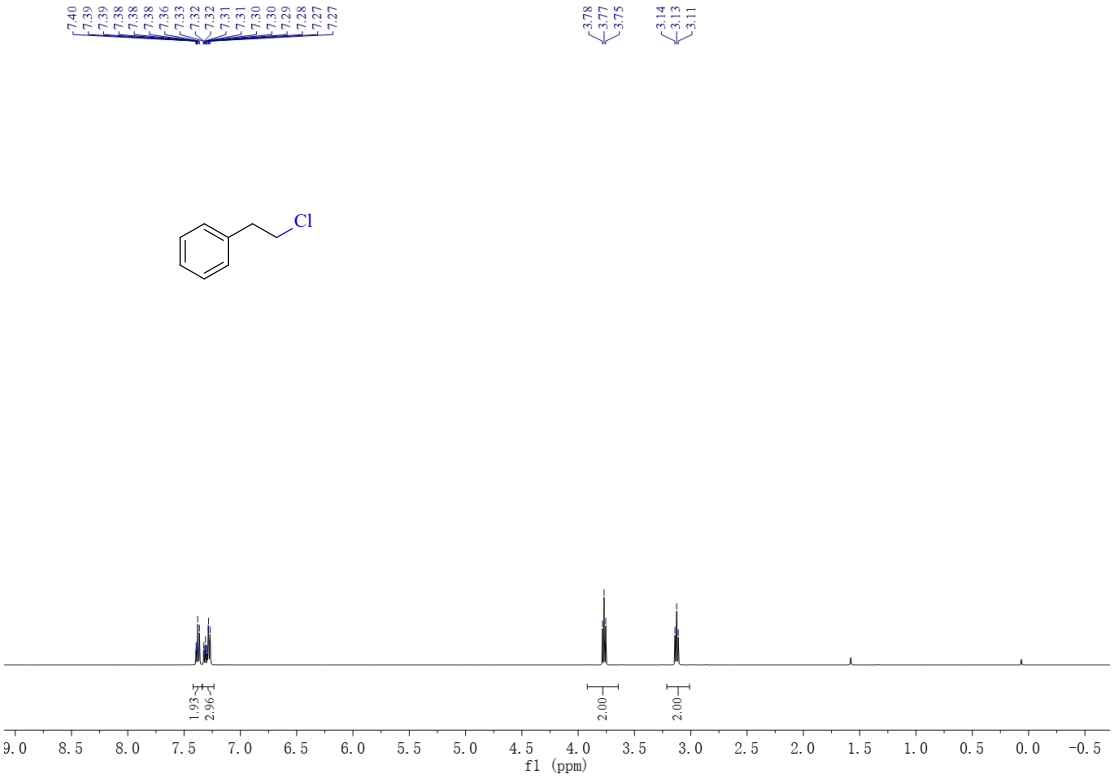




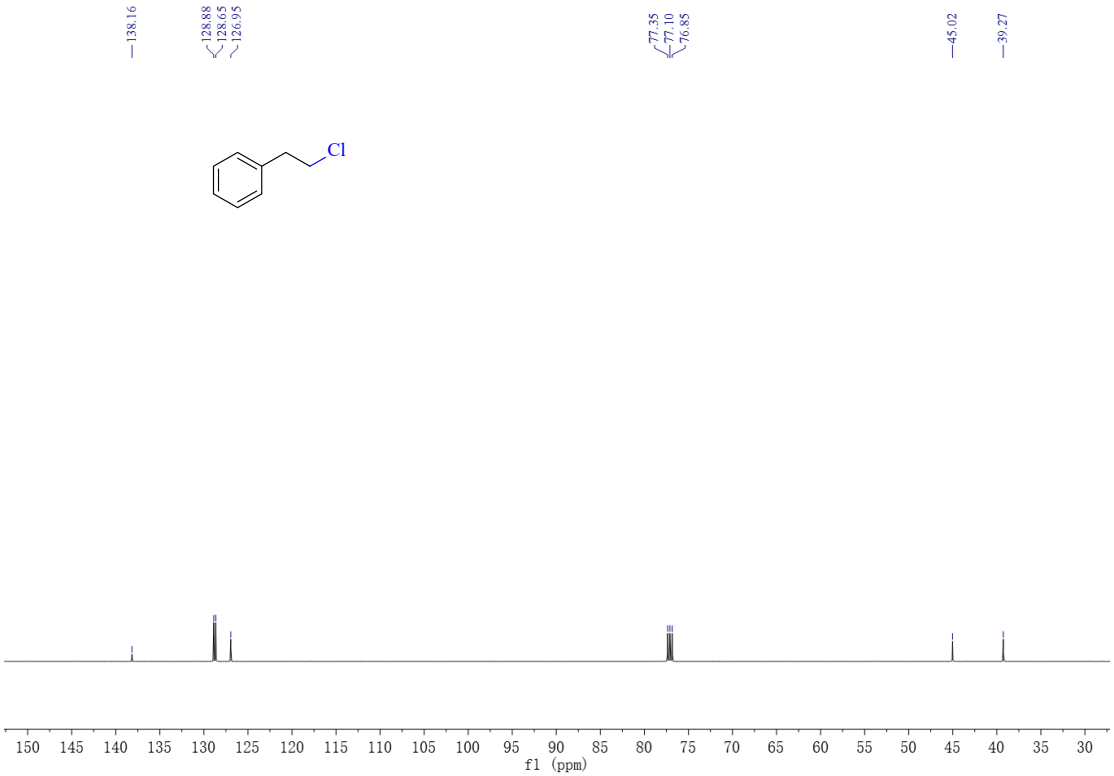


Chlorination of ethylbenzene

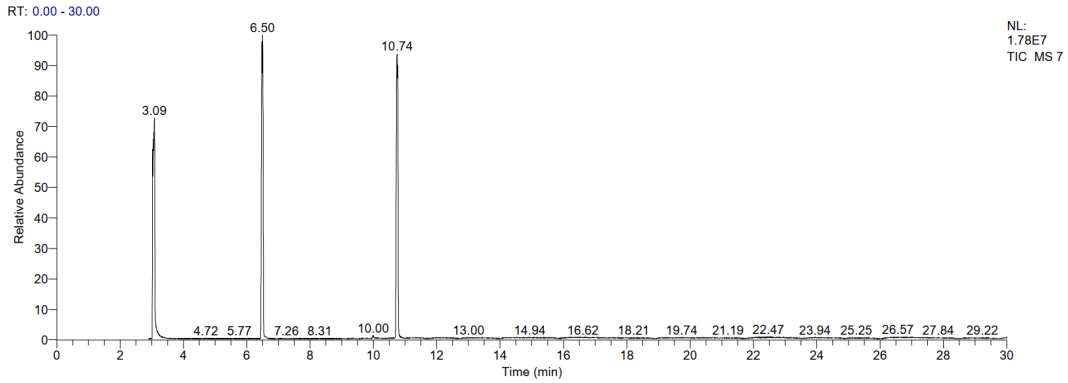
[1]HNMR of (2-chloroethyl)benzene (2n)

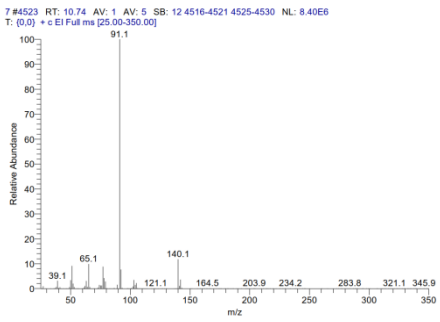


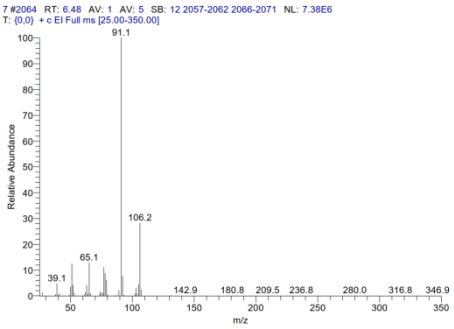
[13]CNMR of (2-chloroethyl)benzene (2n)



GS-MS of Chlorination of ethylbenzene reaction solution

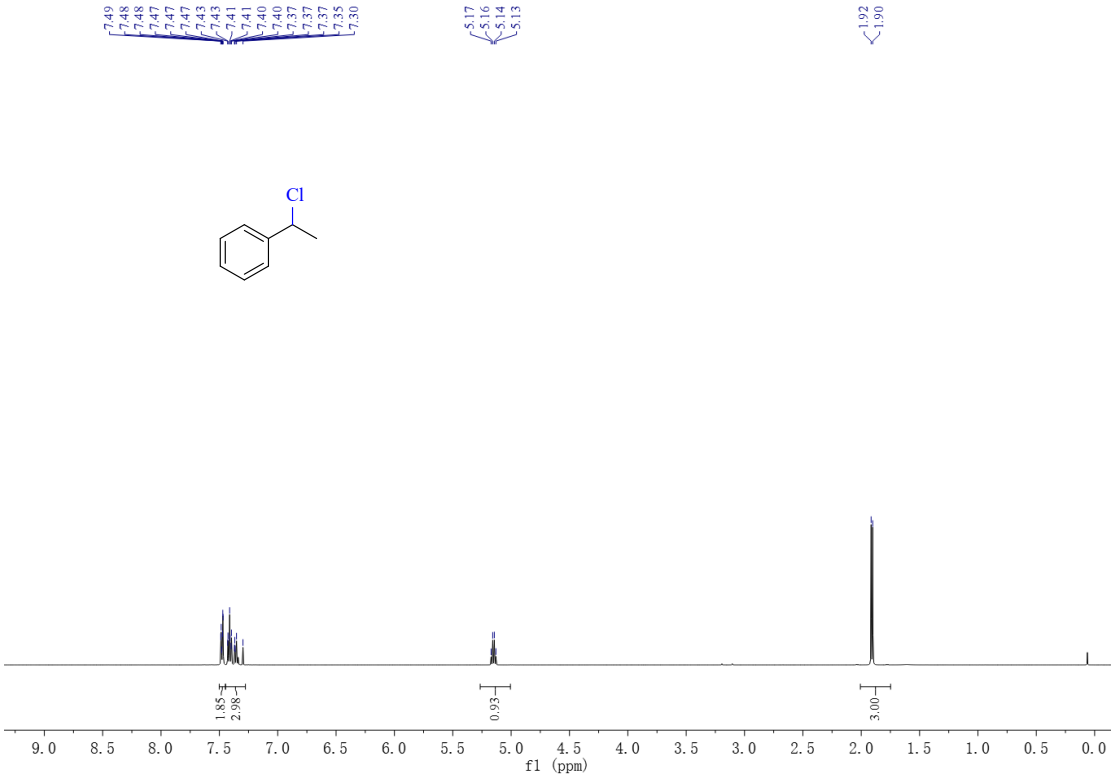




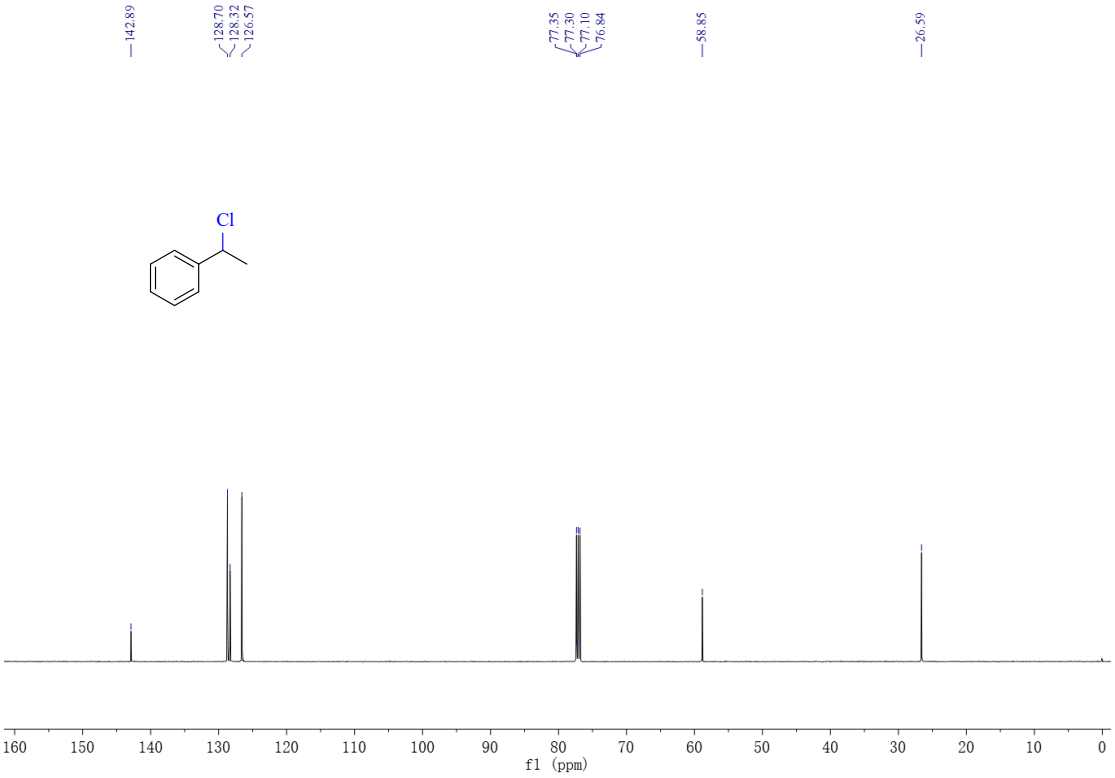


Chlorination of ethylbenzene

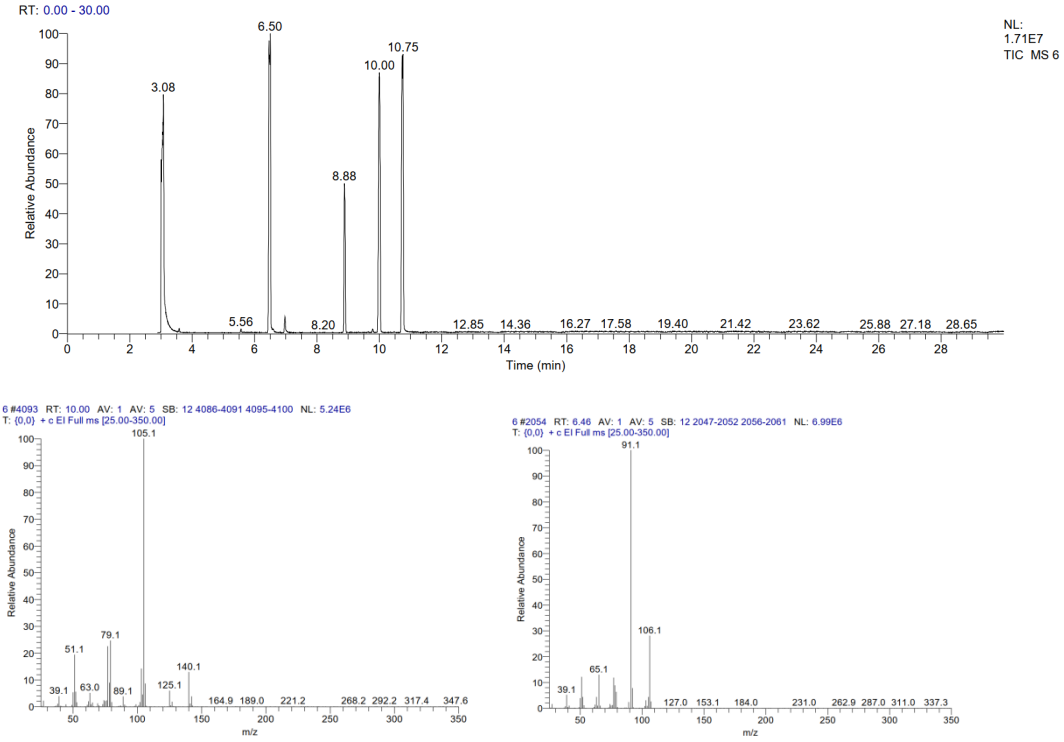
^{1}HNMR of (1-chloroethyl)benzene (2o)



^{13}CNMR of (1-chloroethyl)benzene (2o)

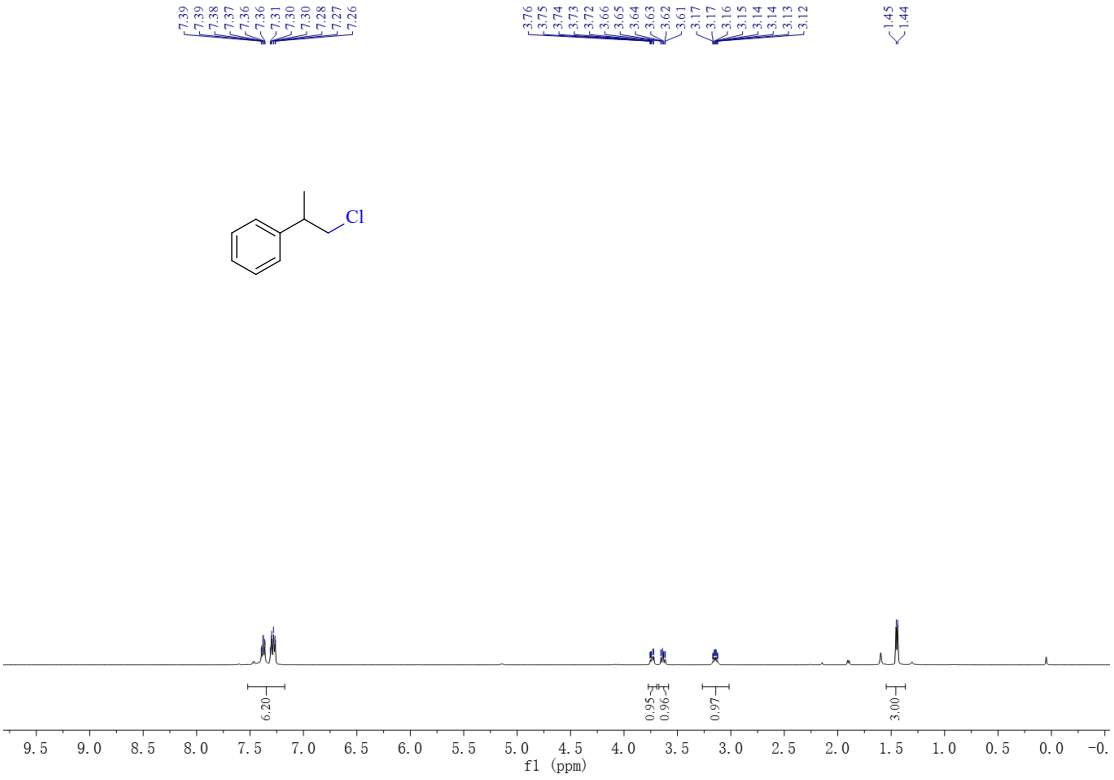


GS-MS of Chlorination of reaction solution

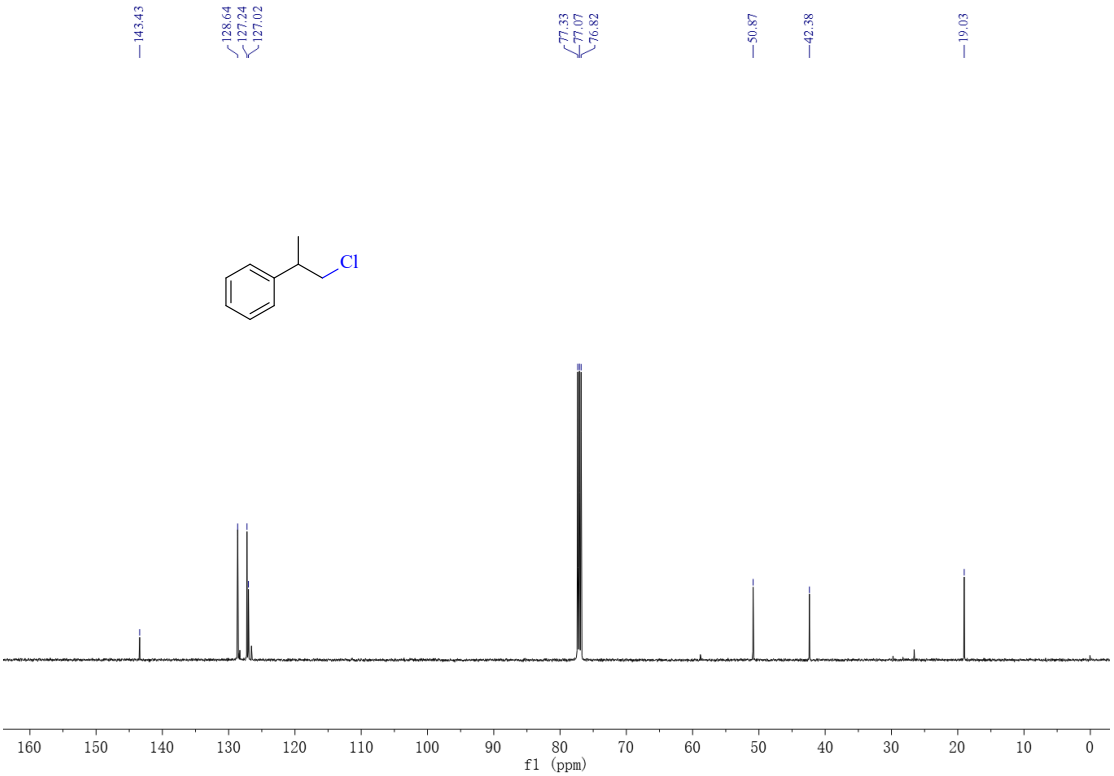


Chlorination of isopropylbenzene

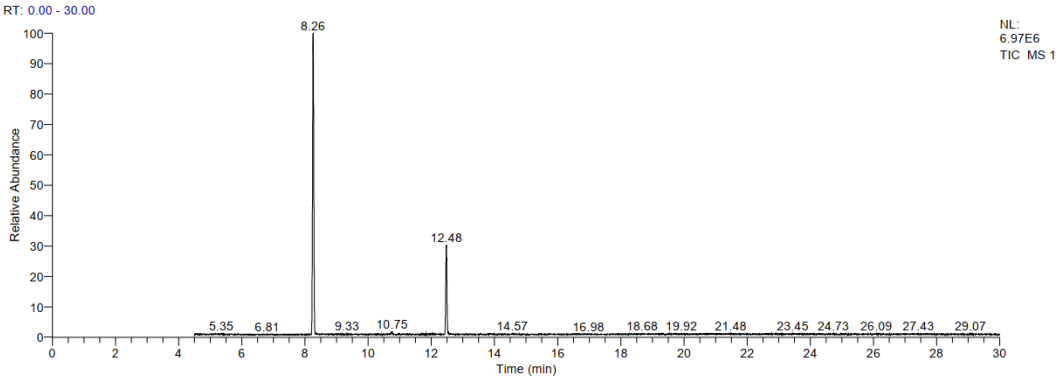
^{1}HNMR of (2-chloro-1-methylethyl)benzene (2p)

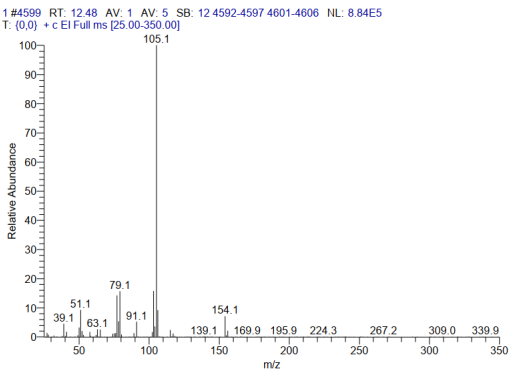


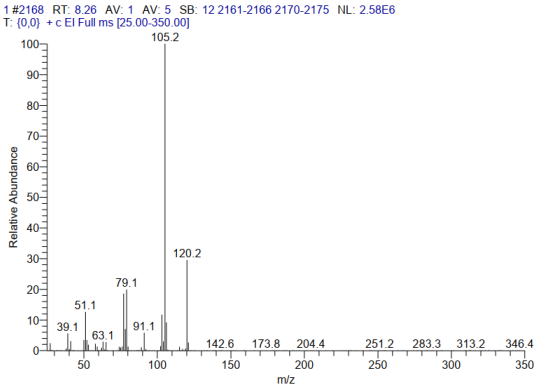
^{13}CNMR of (2-chloro-1-methylethyl)benzene (2p)



GS-MS of Chlorination of isopropylbenzene reaction solution

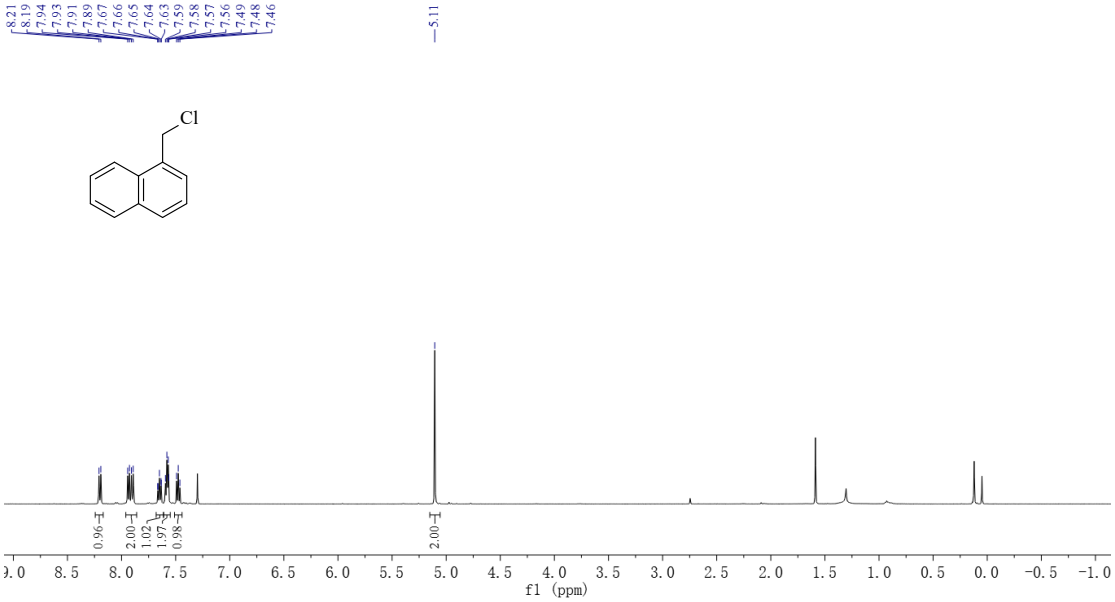




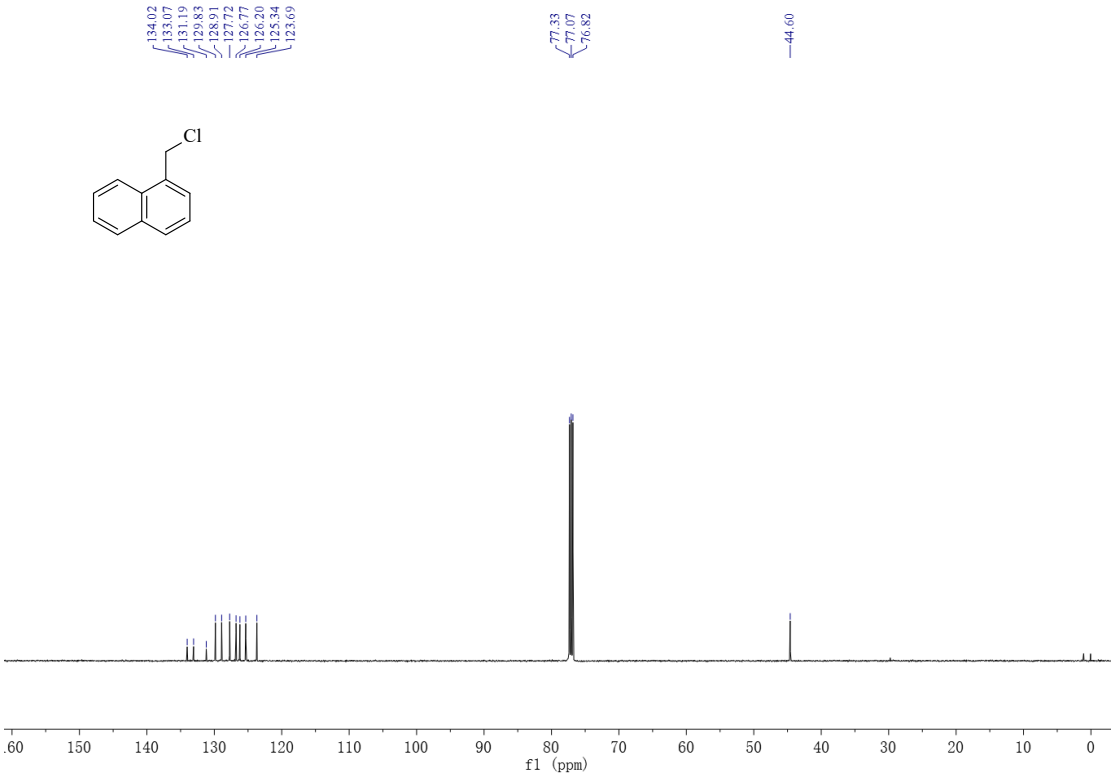


Chlorination of 1-methylnaphthalene

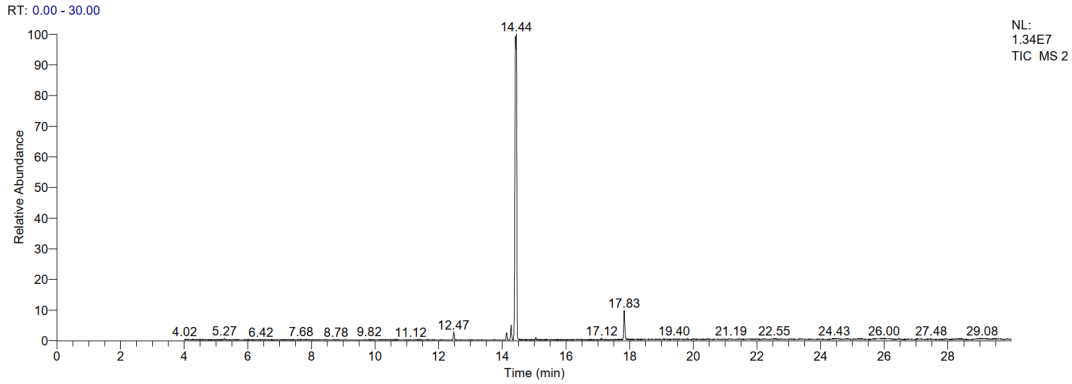
[1]HNMR of 1-(chloromethyl)naphthalene (2r)

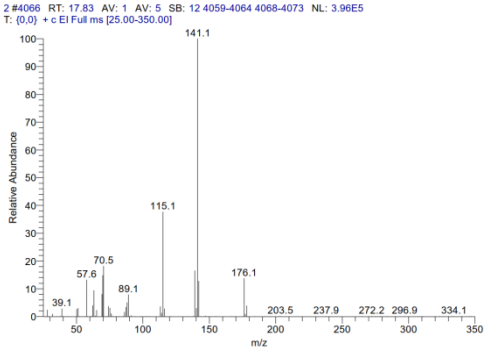


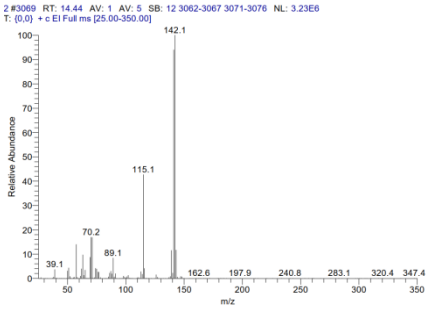
[13]CNMR of 1-(chloromethyl)naphthalene (2r)



GS-MS of Chlorination of 1-methylnaphthalene reaction solution

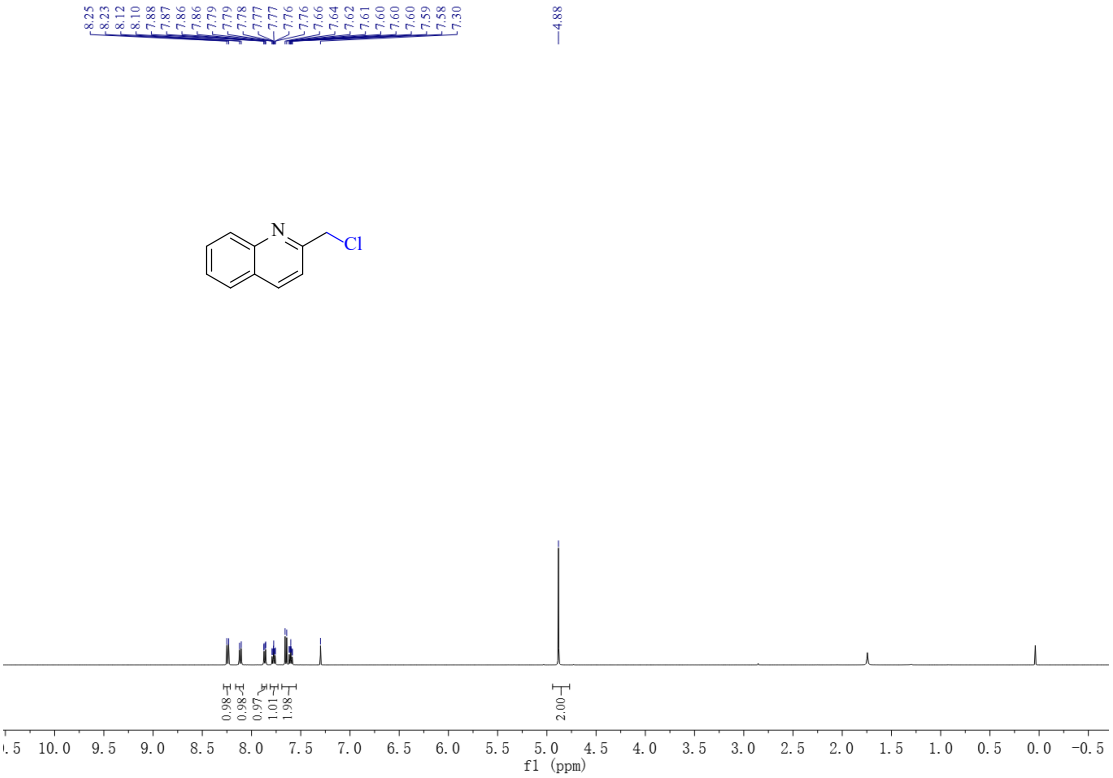




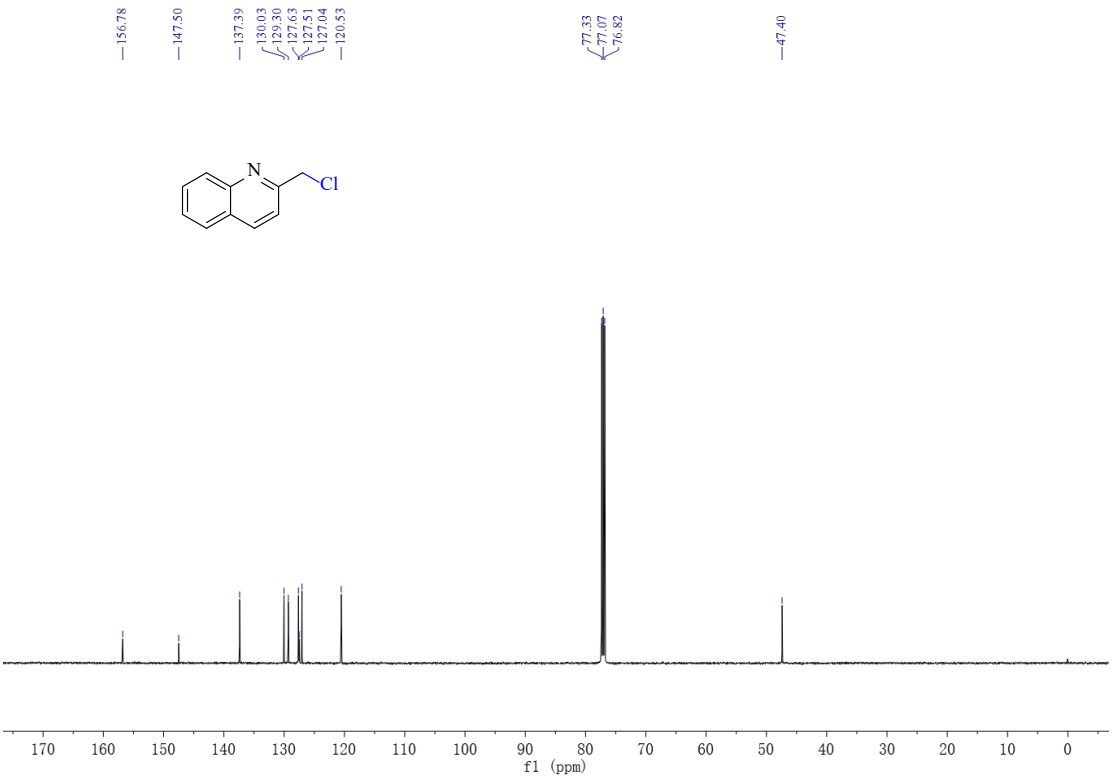


Chlorination of 2-methylquinoline

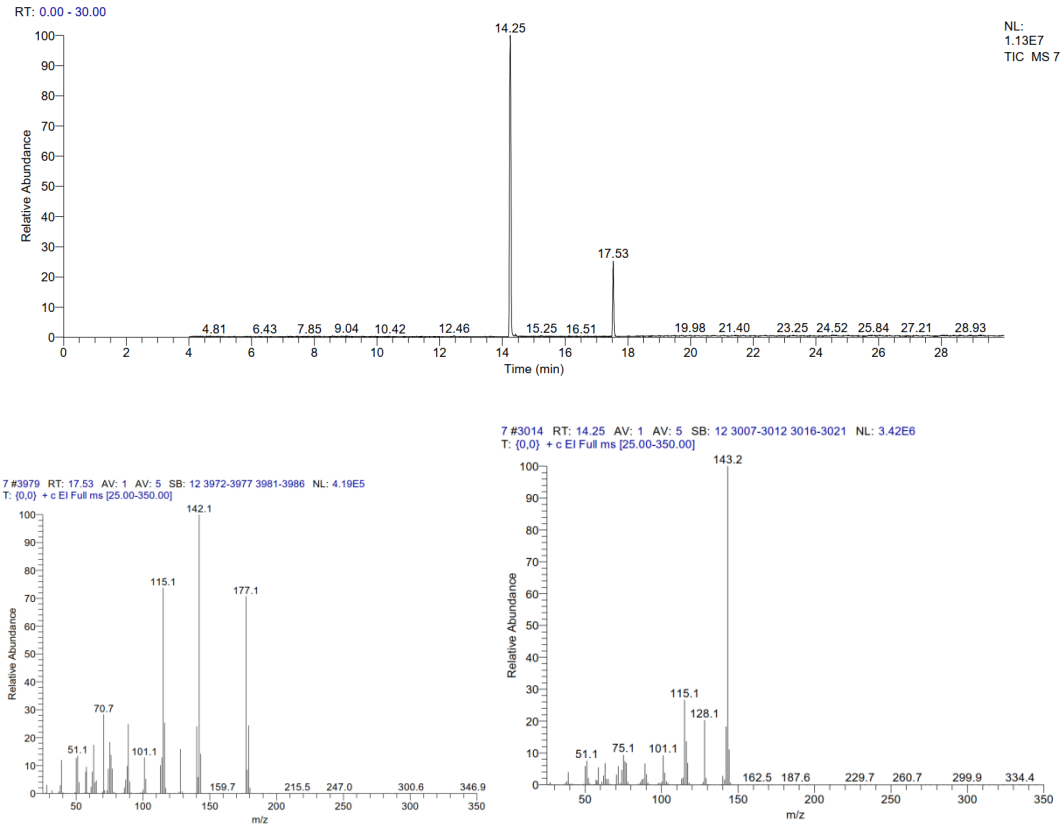
^{1}HNMR of 2-(chloromethyl) quinoline (2s)



^{13}CNMR of 2-(chloromethyl) quinoline (2s)

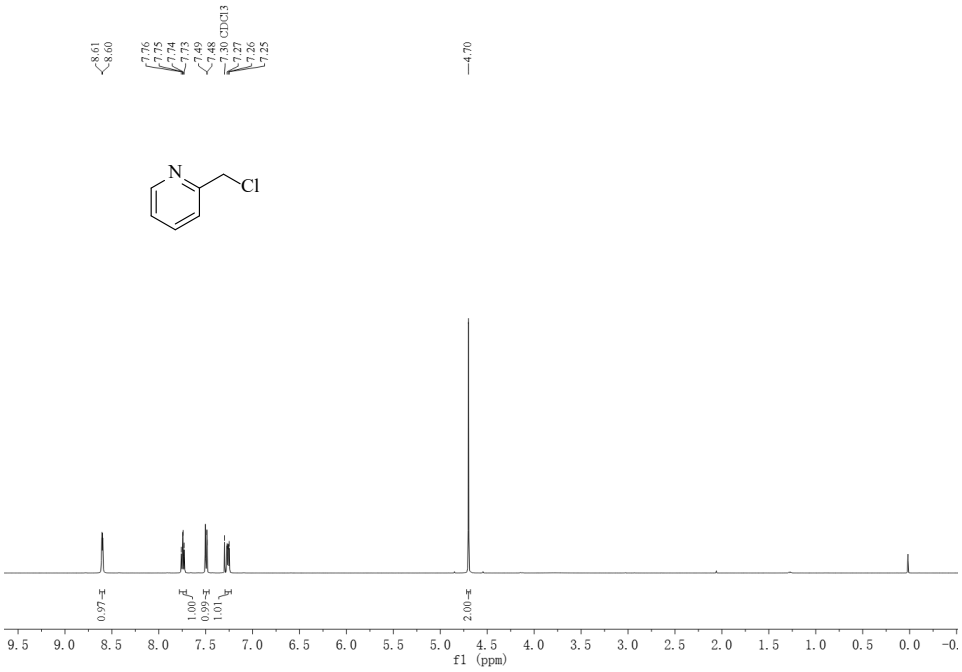


GS-MS of chlorination of 2-methylquinoline reaction solution

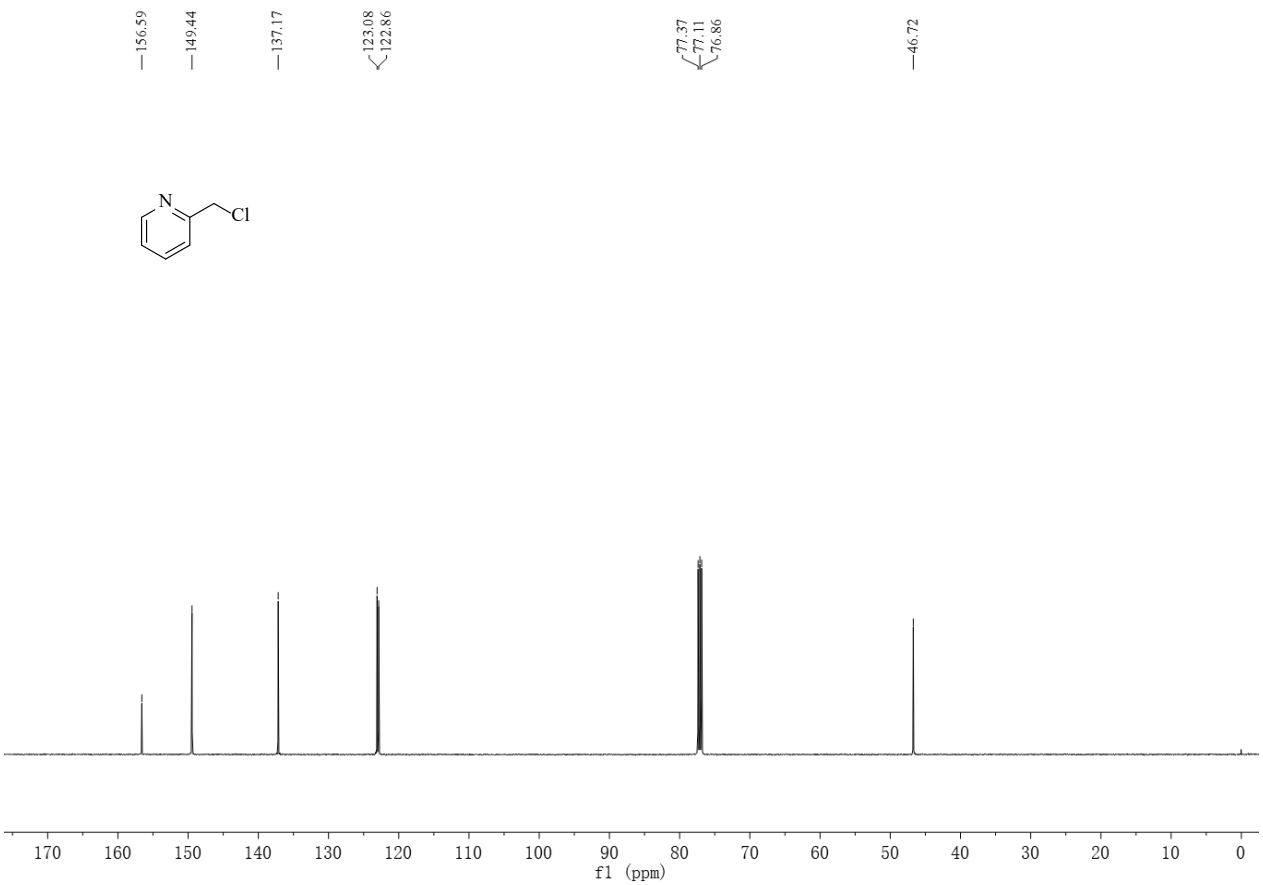


Chlorination of 2-methylpyridine

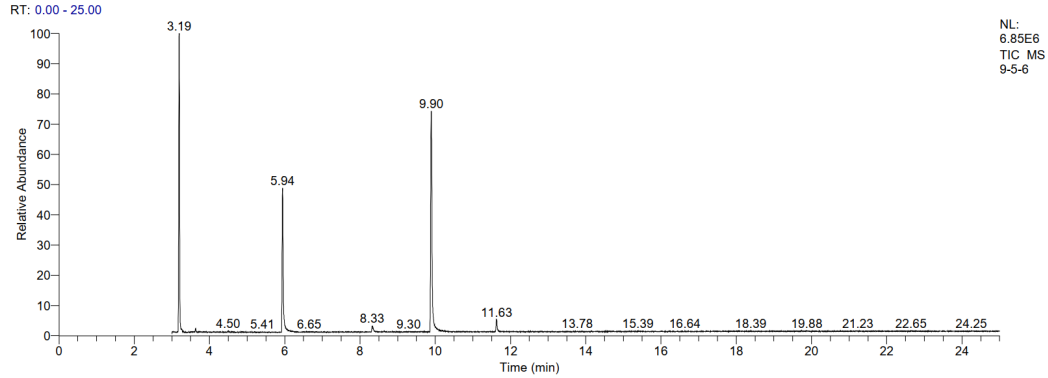
[1]HNMR of 2-(chloromethyl) pyridine (2t)

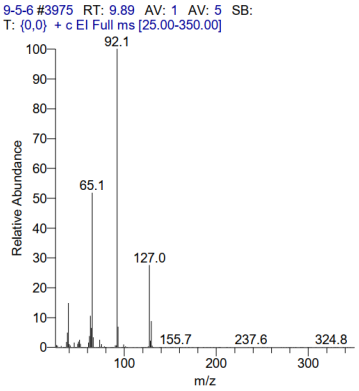


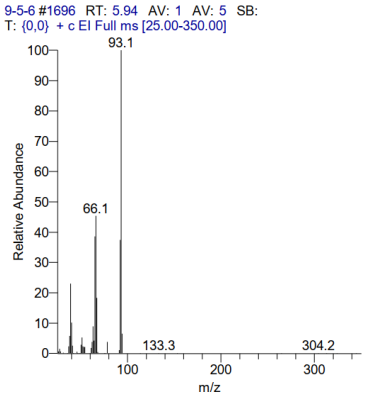
[13]CNMR of 2-(chloromethyl) pyridine (2t)



GS-MS of chlorination of 2-methylpyridine reaction solution

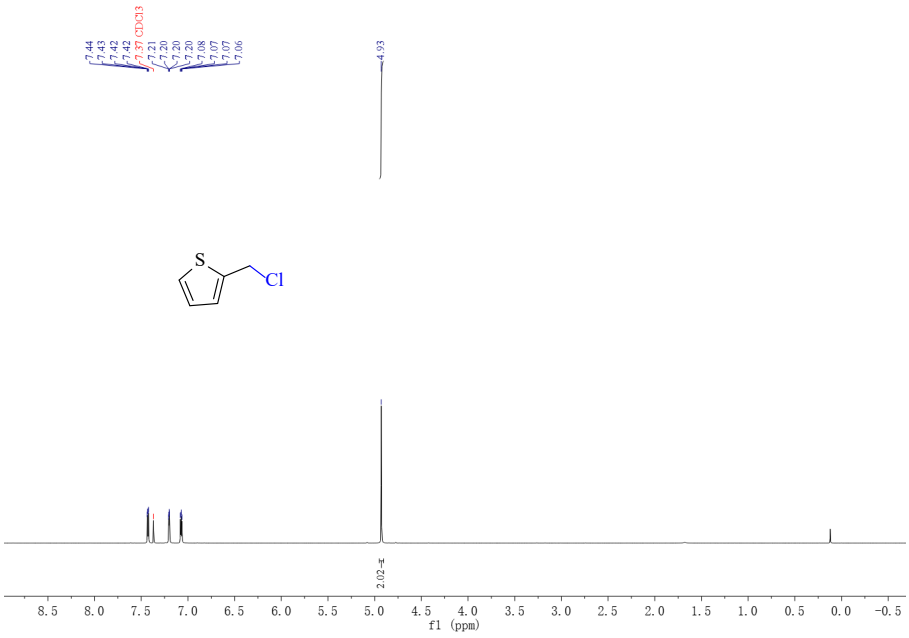




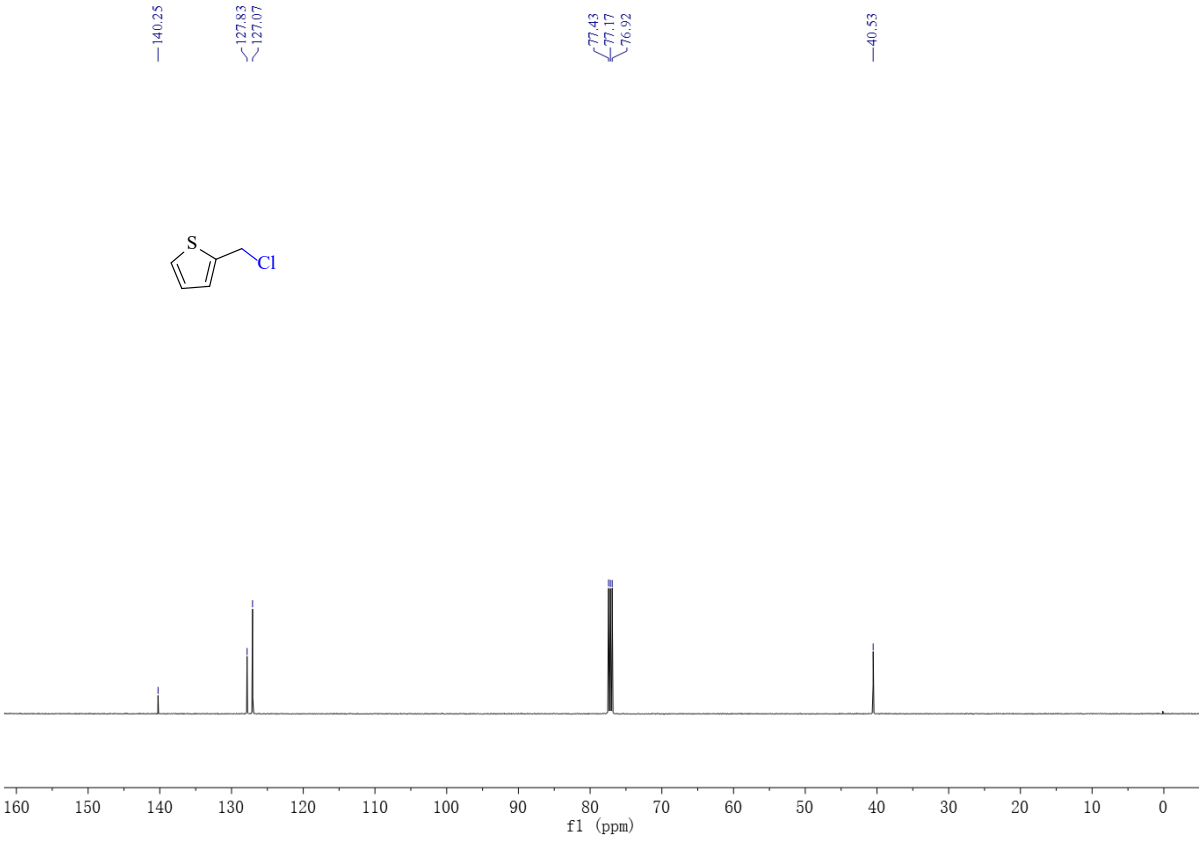


Chlorination of 2-Methylthiophene

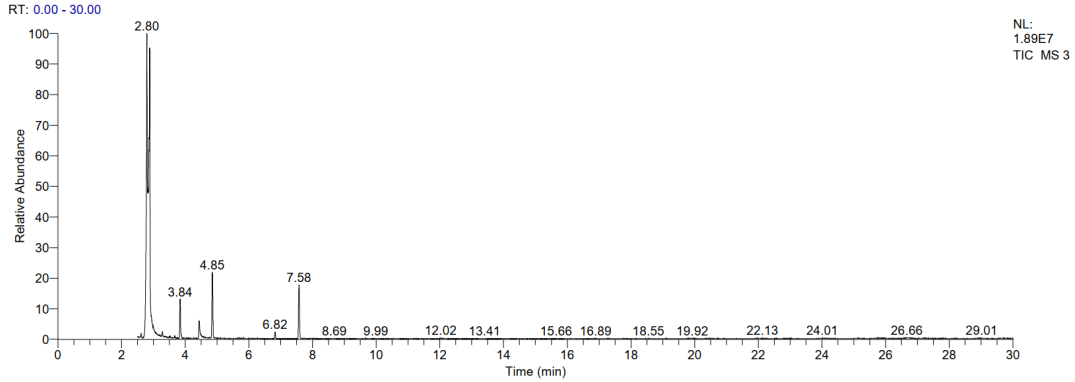
[1]HNMR of 2-(chloromethyl) thiophene (2u)

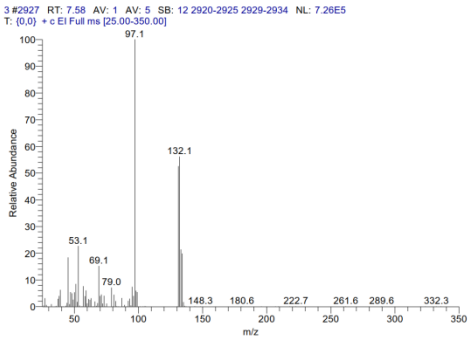


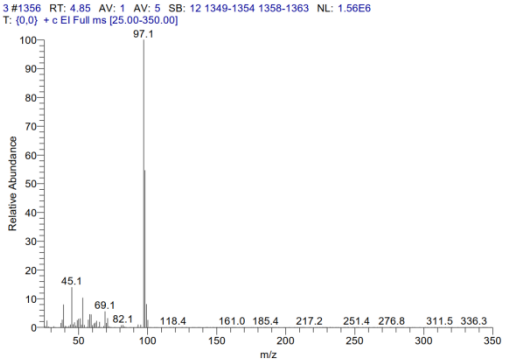
[13]CNMR of 2-(chloromethyl) thiophene (2u)



GS-MS of chlorination of 2-Methylthiophene reaction solution

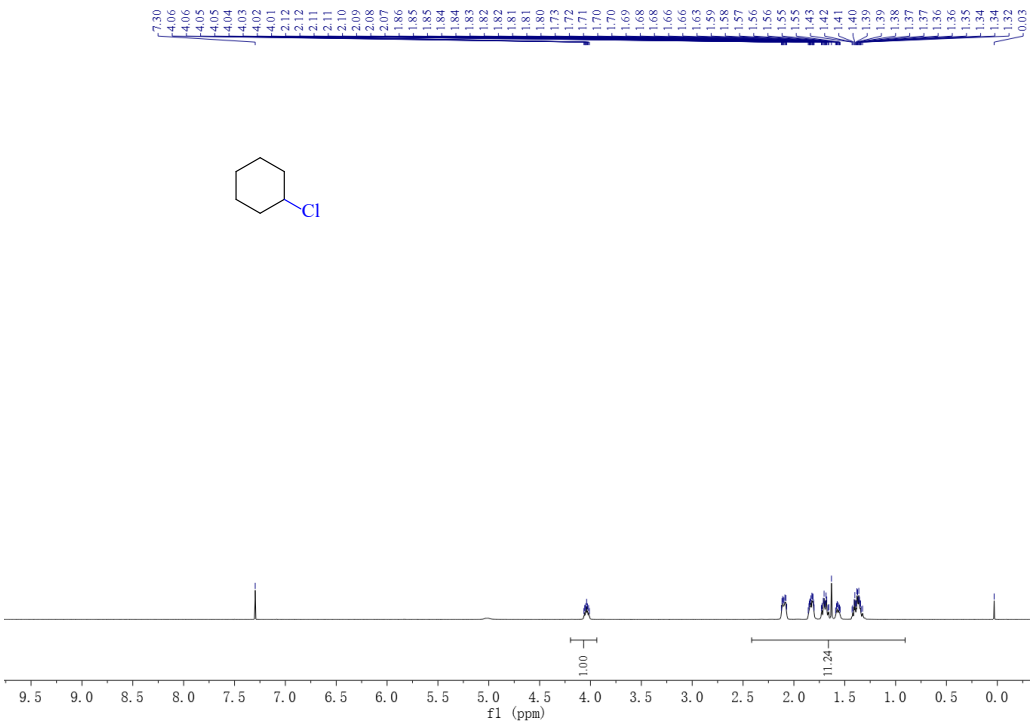




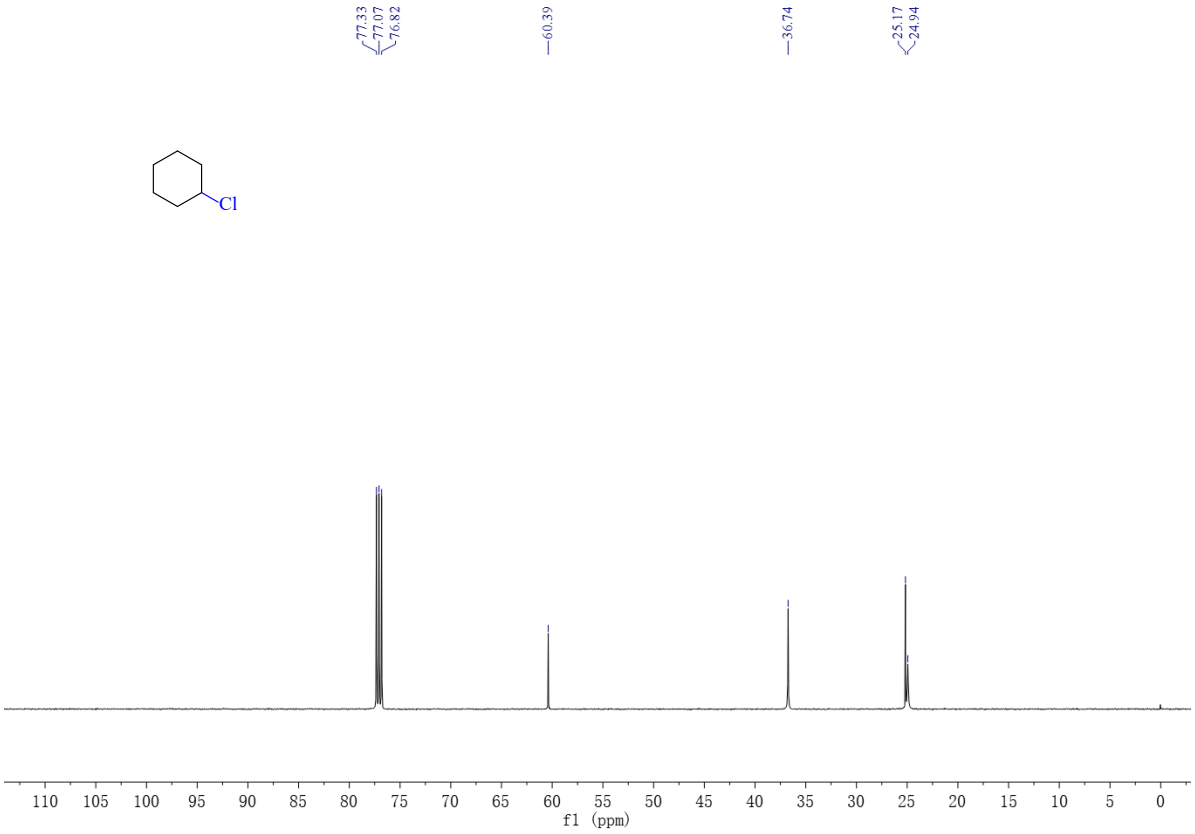


Chlorination of cyclohexan

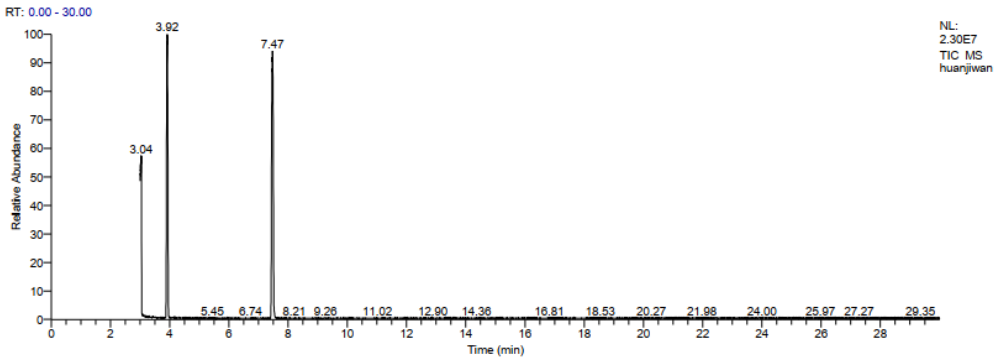
^{1}HNMR of Chlorocyclohexane (2w)

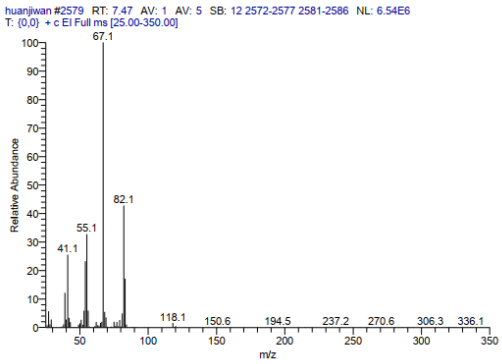


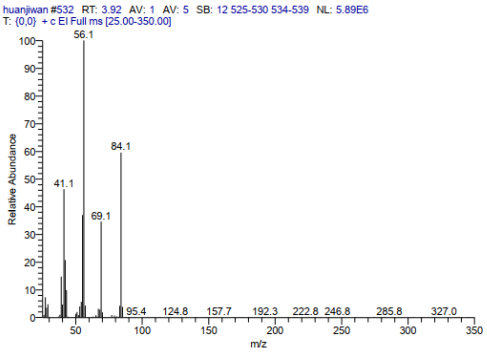
^{13}CNMR of Chlorocyclohexane (2w)



GS-MS of chlorination of cyclohexan reaction solution

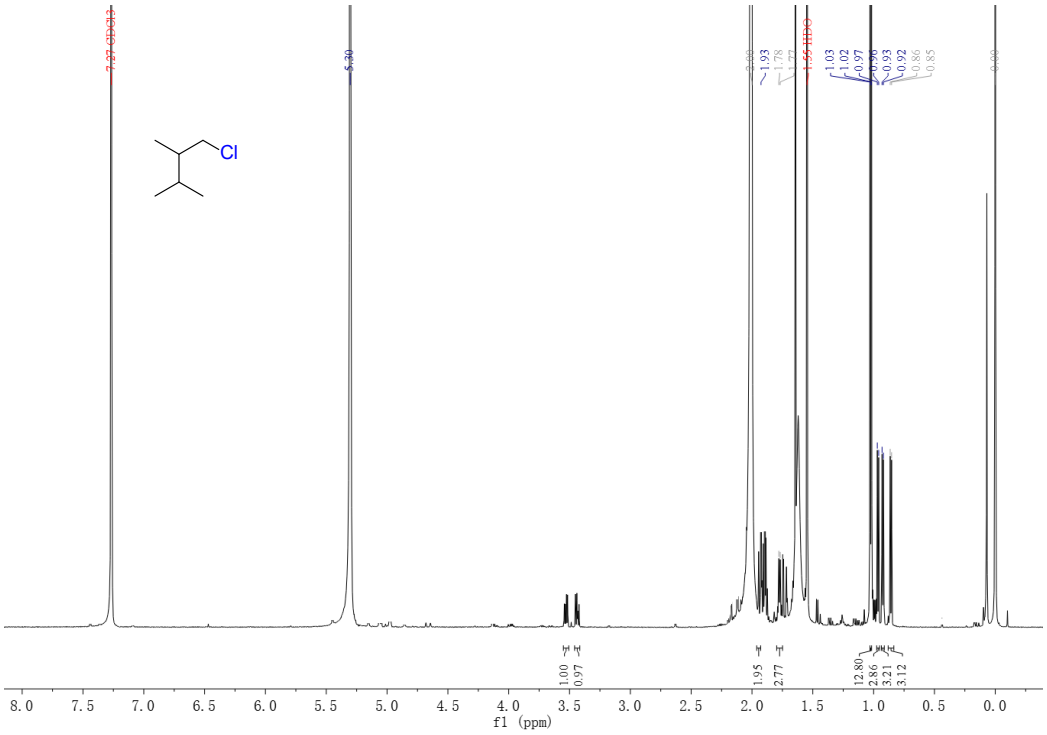




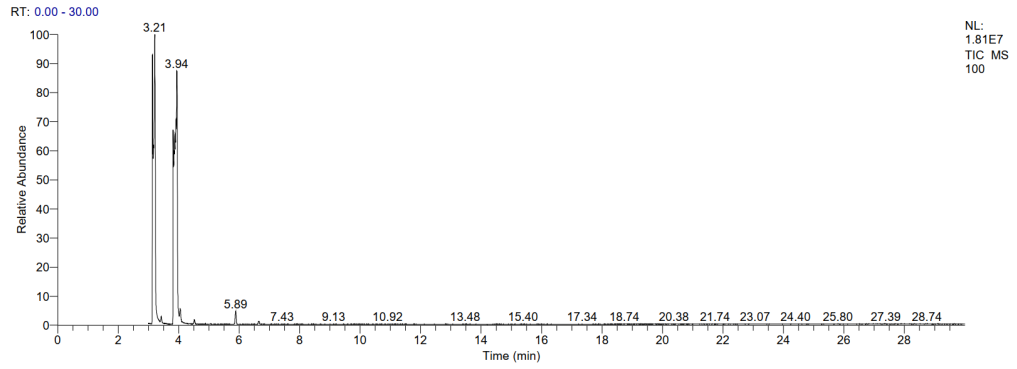


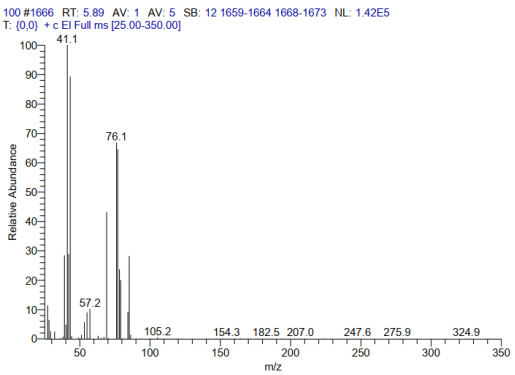
Chlorination of 2,3-dimethylbutane

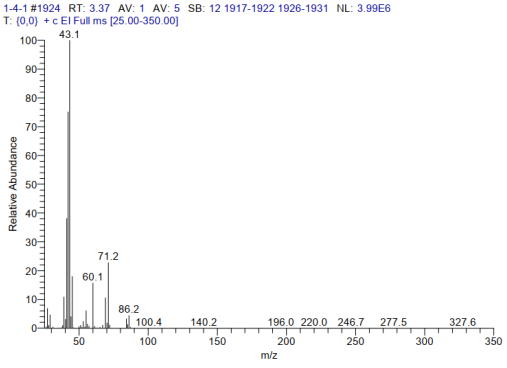
[1]HNMR of 1-chloro-2,3-dimethylbutane（2x）



GS-MS of chlorination of 2,3-dimethylbutane reaction solution

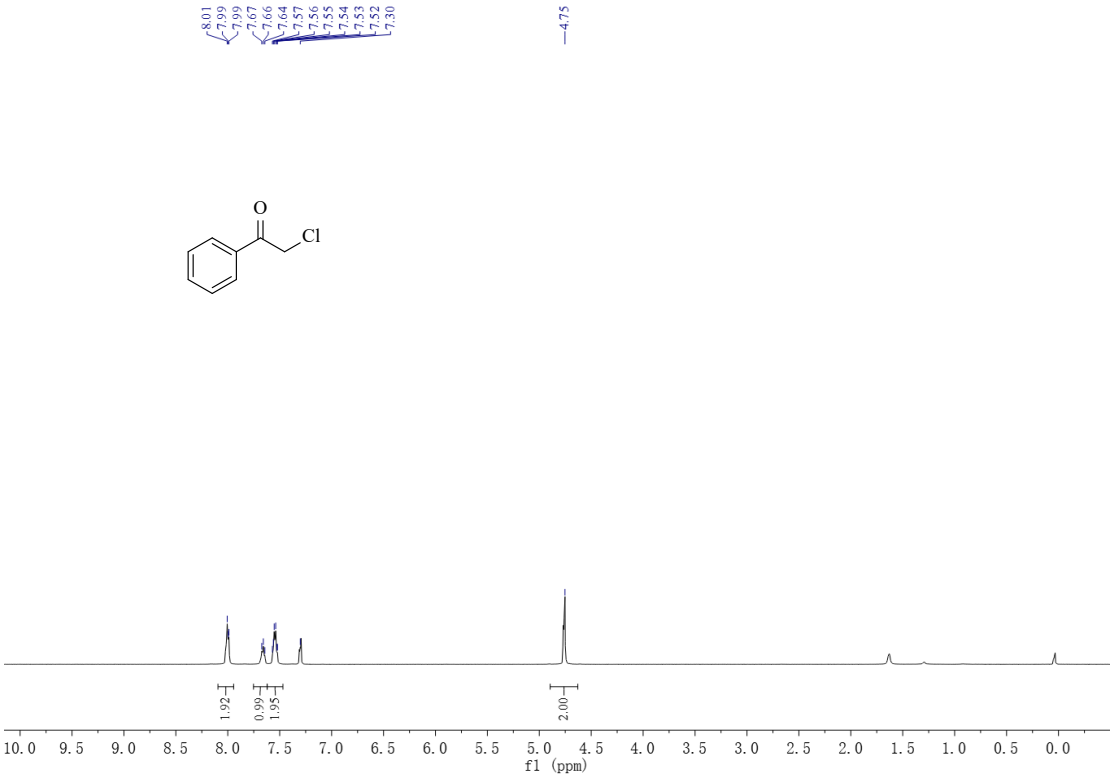




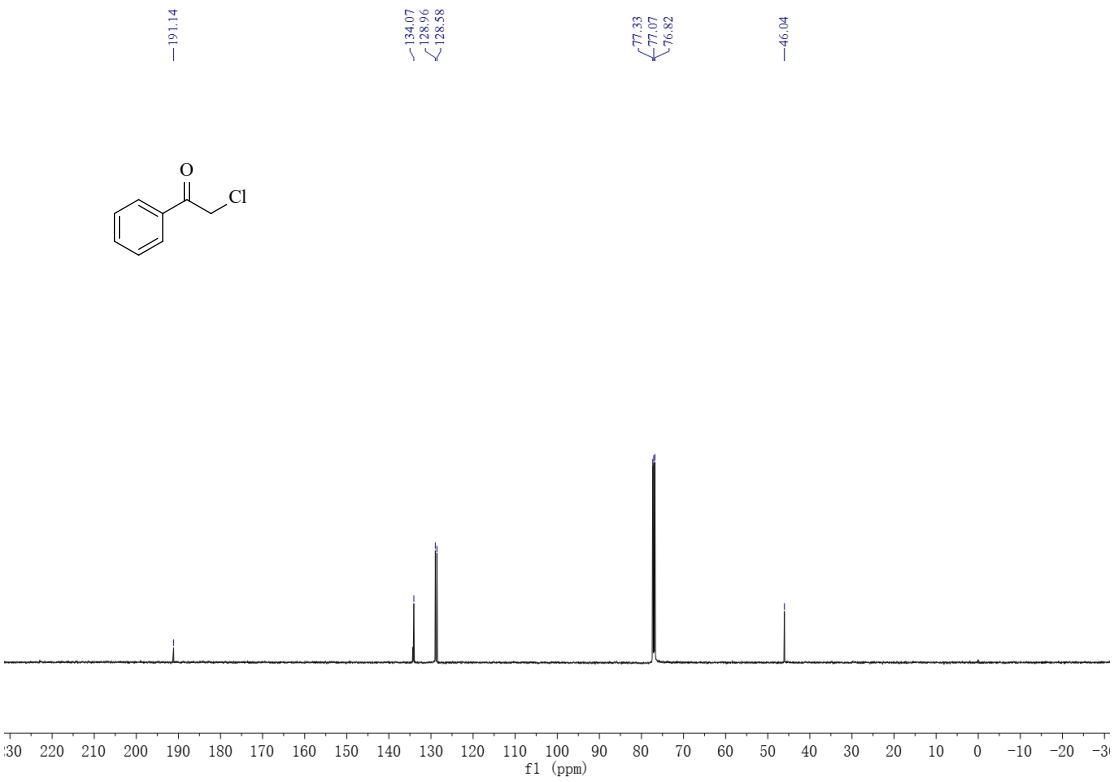


Chlorination of acetophenone

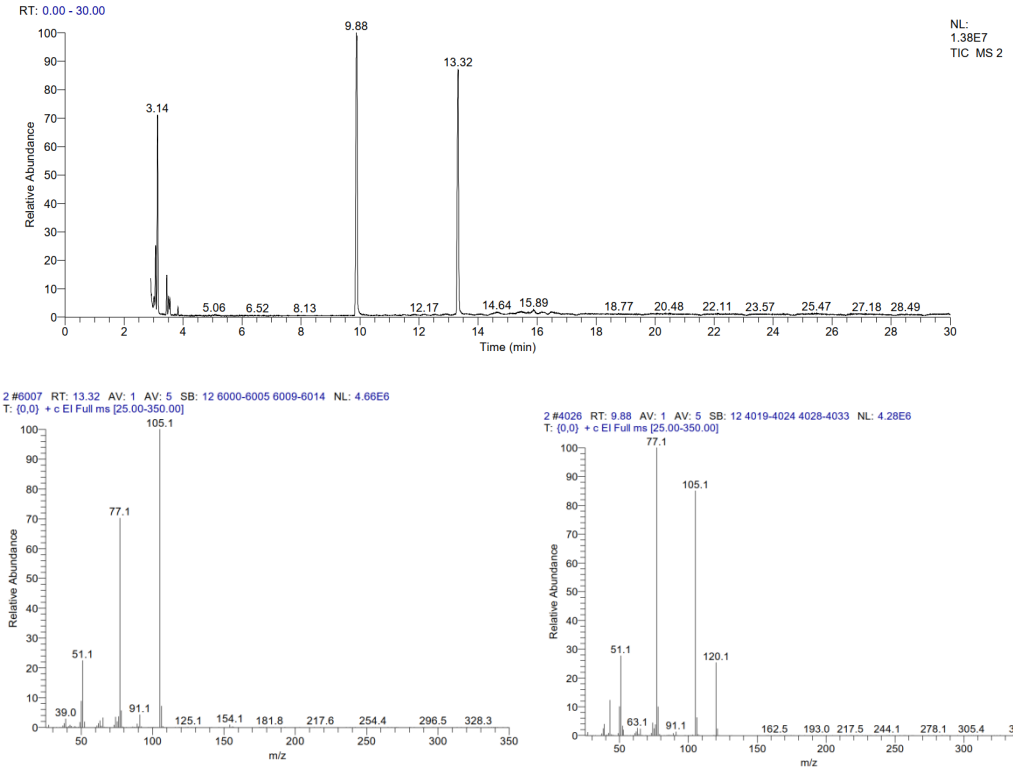
[1]HNMR of 2-Chloroacetophenone (4a)



[13]CNMR of 2-Chloroacetophenone (4a)

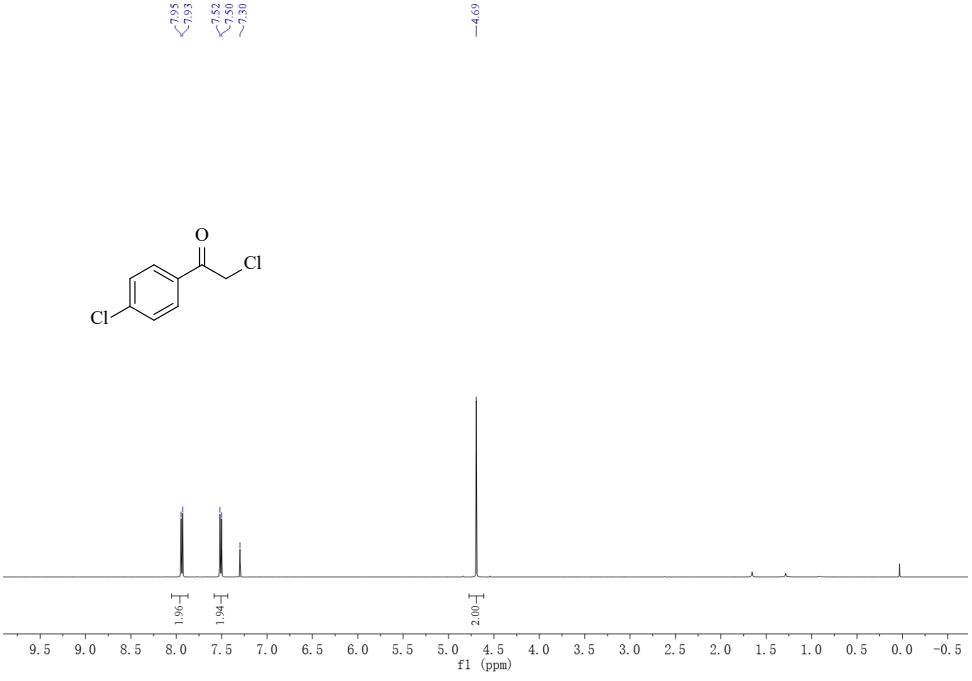


GS-MS of chlorination of acetophenone reaction solution

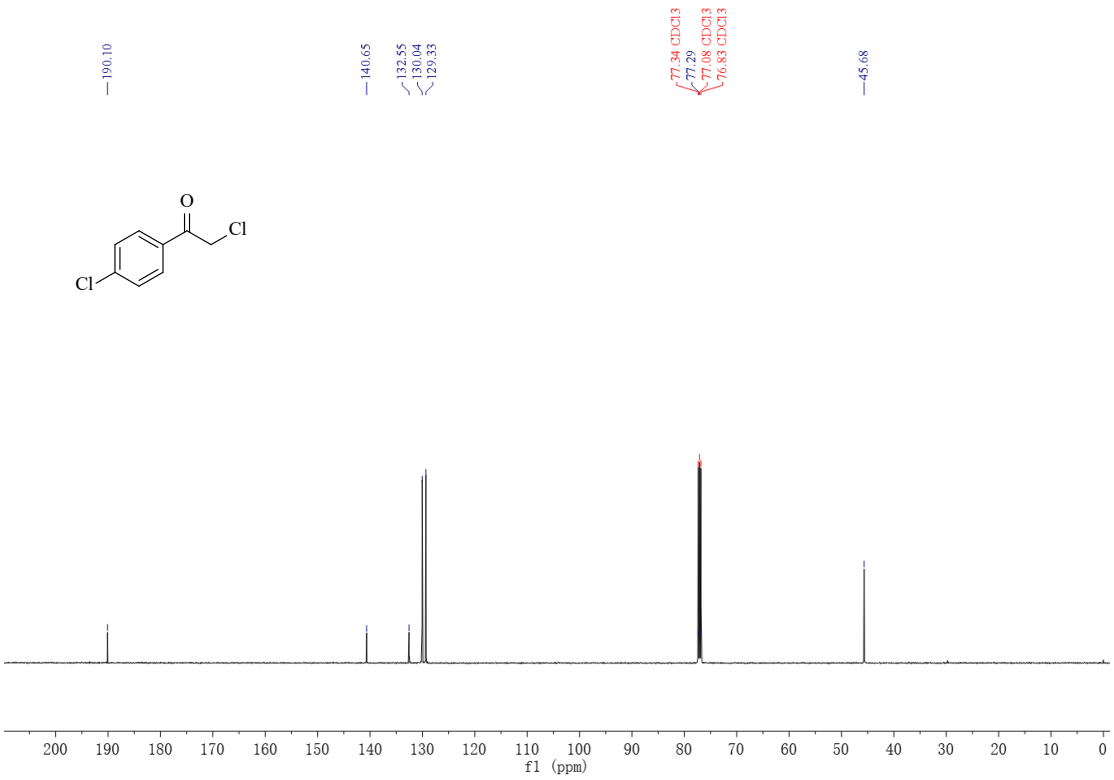


Chlorination of 4-Cl-acetophene

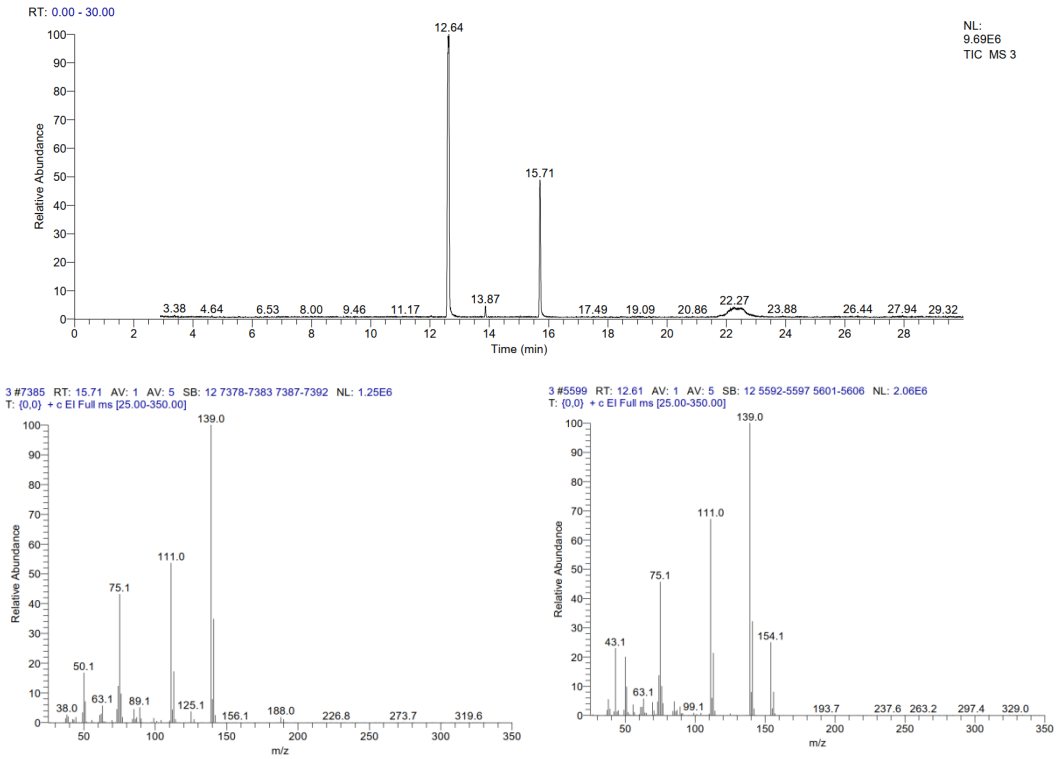
^{1}HNMR of 2,4′-Dichloroacetophenone (4b)



^{13}CNMR of 2,4′-Dichloroacetophenone (4b)

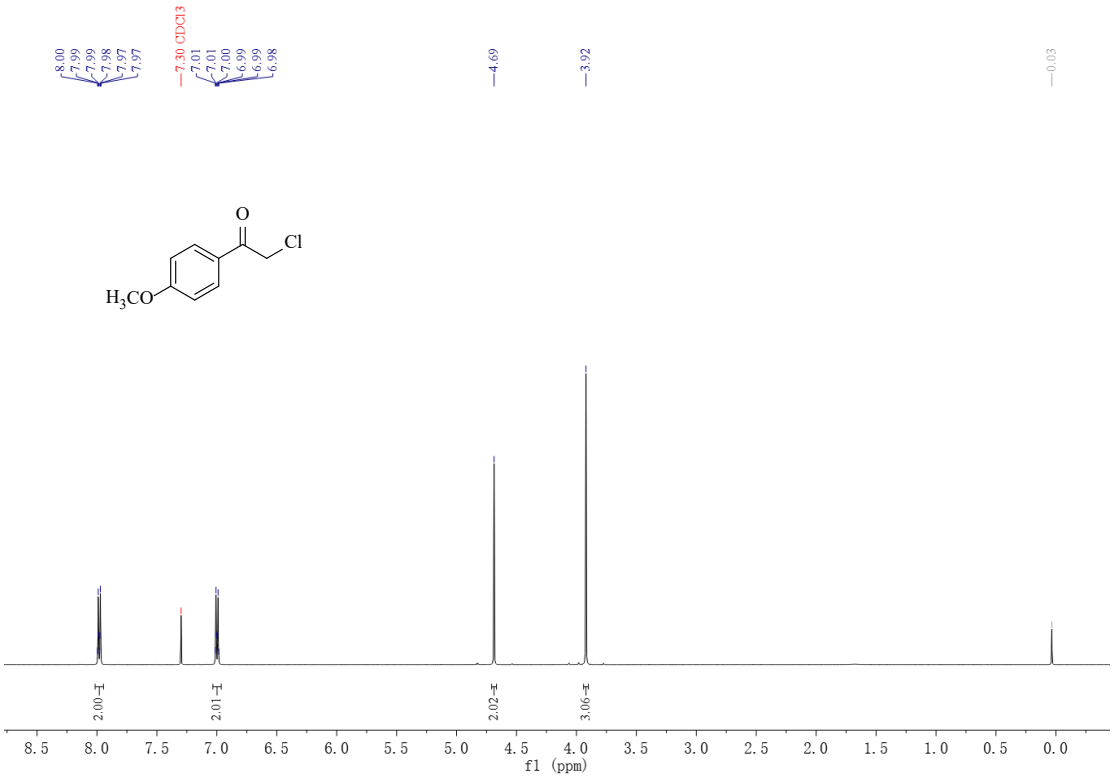


GS-MS of chlorination of 4-Cl-acetophene reaction solution

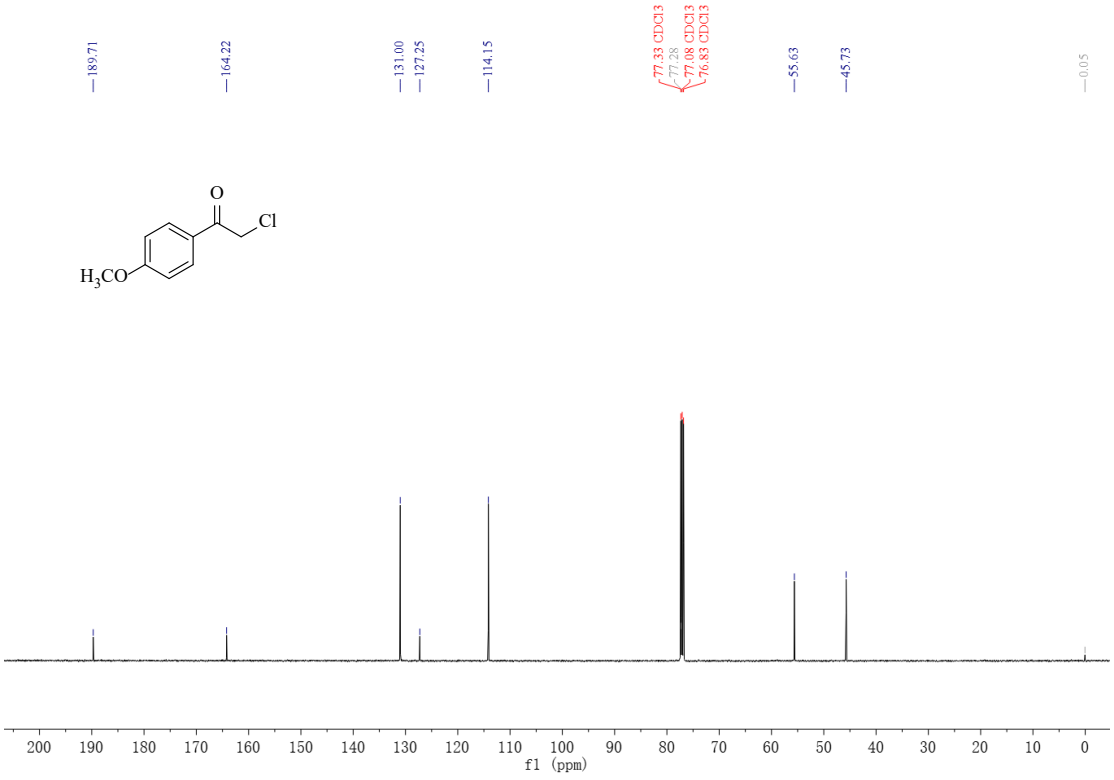


Chlorination of 4-OMe-acetophene

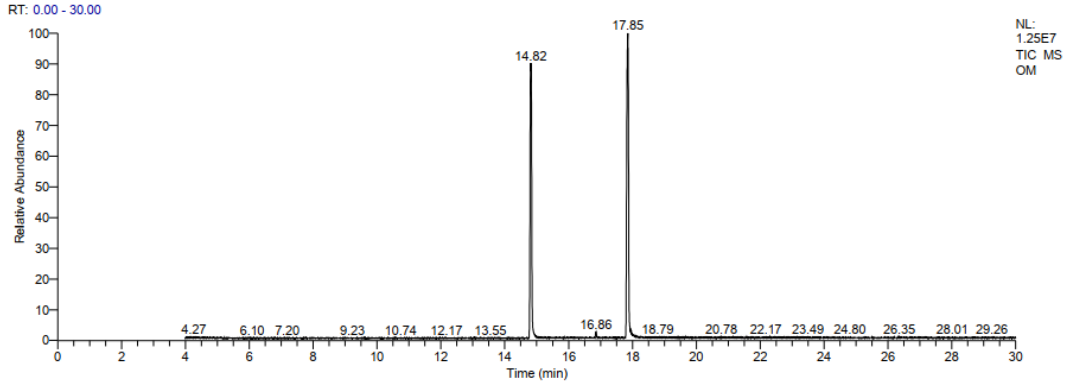
[1]HNMR of 2-Chloro-1-(4-methoxyphenyl)ethanone (4c)

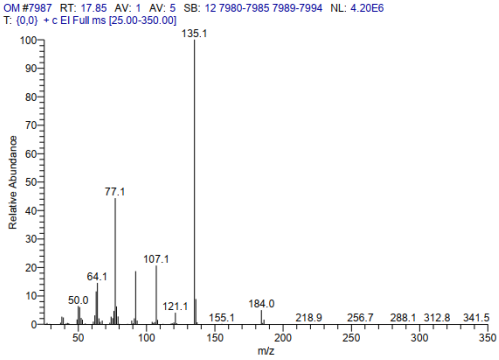


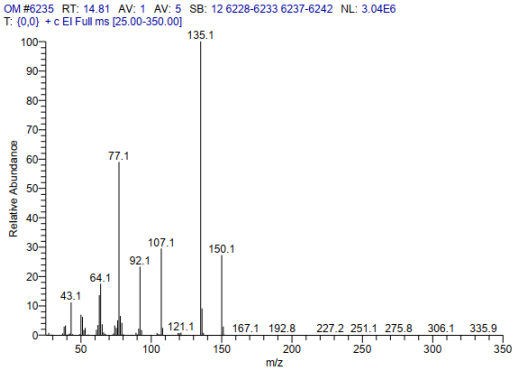
[13]CNMR of 2-Chloro-1-(4-methoxyphenyl)ethanone (4c)



GS-MS of chlorination of 4-OMe-acetophene reaction solution

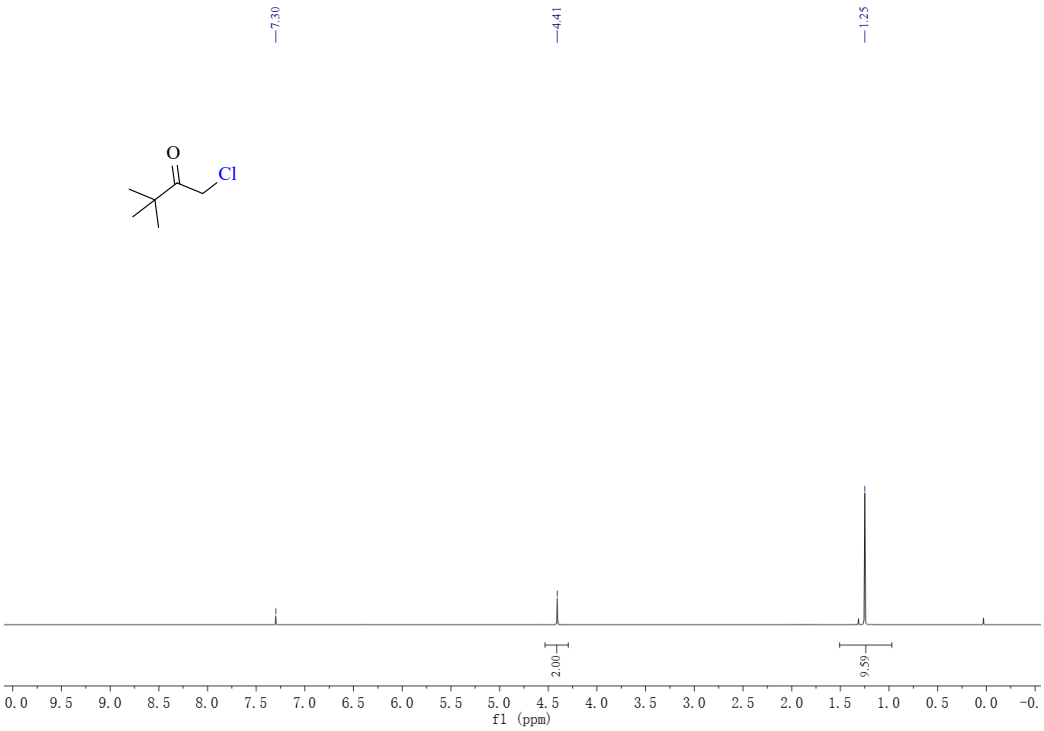




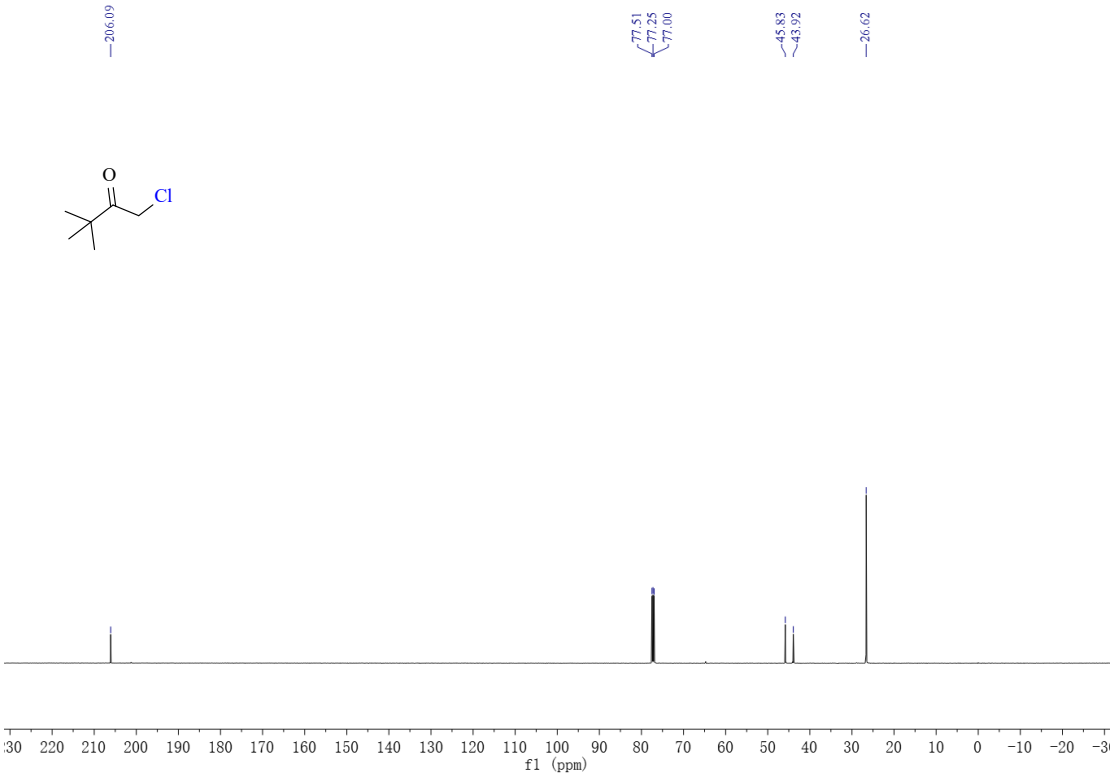


Chlorination of 3,3-dimethyl-2-butanone

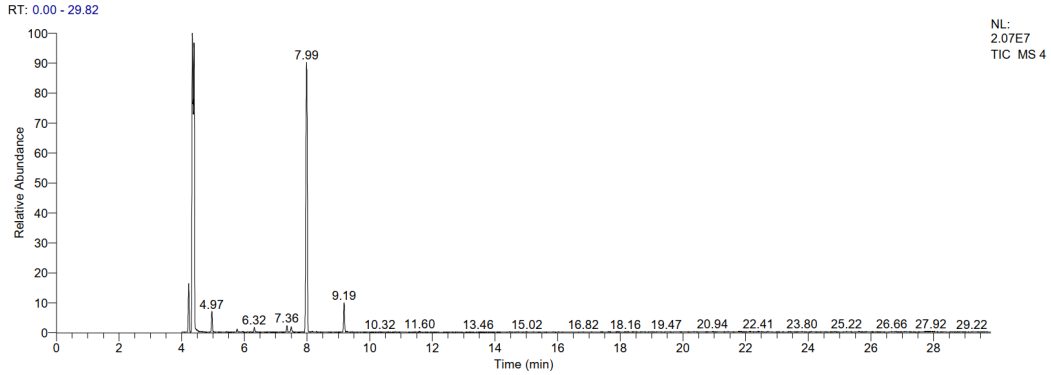
[1]HNMR of 1-Cl-3,3-dimethyl-2-butanone (4d)

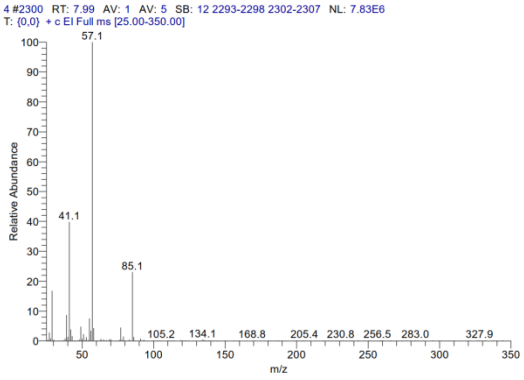


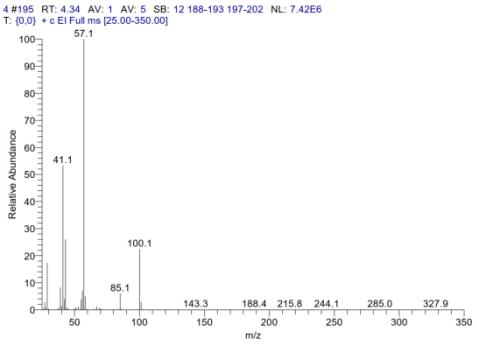
[13]CNMR of 1-Cl-3,3-dimethyl-2-butanone (4d)



GS-MS of chlorination of 3,3-dimethyl-2-butanone reaction solution

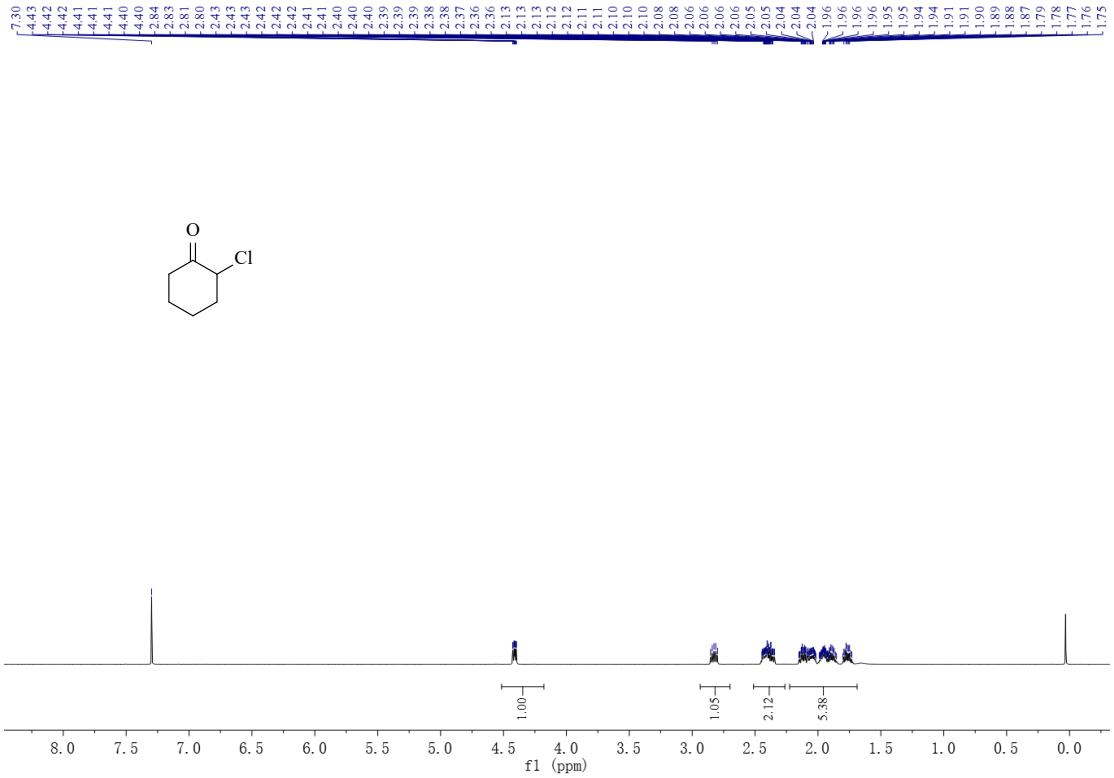




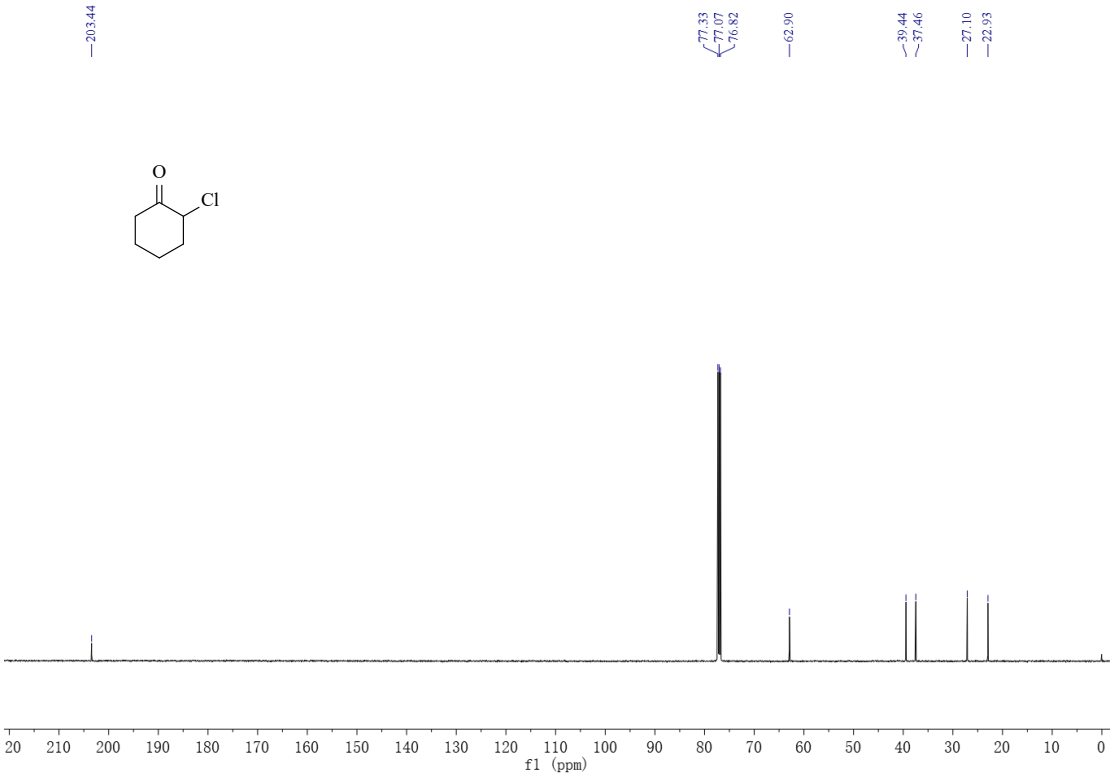


Chlorination of cyclohexanone

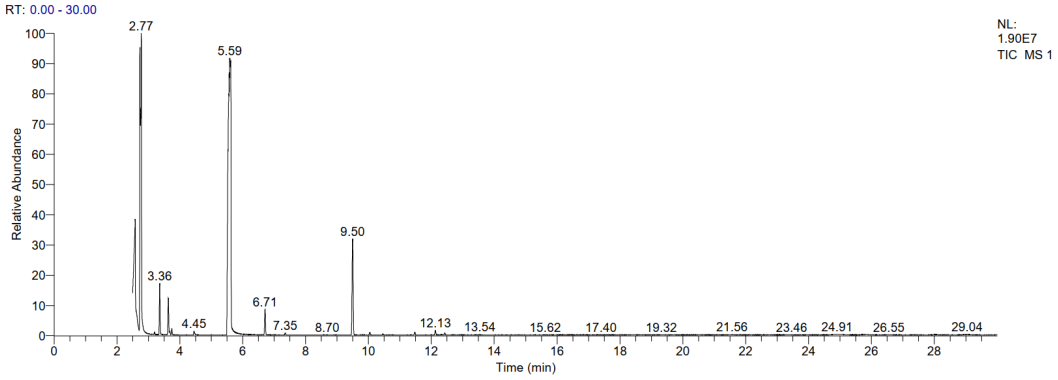
^{1}HNMR of 2-Cl-cyclohexanone (4e)

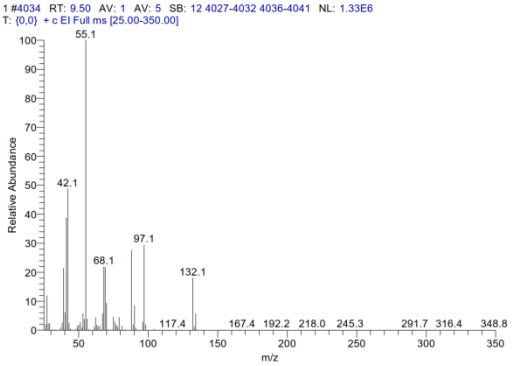


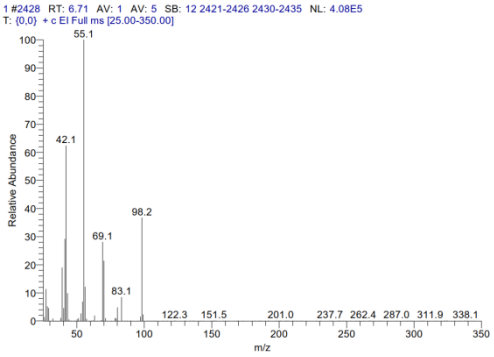
^{13}CNMR of 2-Cl-cyclohexanone (4e)



GS-MS of chlorination of cyclohexanone reaction solution







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