

## Supporting Information

# Highly selective halogenation of unactivated C(sp<sup>3</sup>)-H with NaX under co-catalysis of visible light and Ag@AgX

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## Experimental

### General experimental

The morphology of the Ag/AgBr or Ag/AgCl composite was characterized using a scanning electron microscope (SEM; Hitachi S4800 SEM) with an accelerating voltage of 30.0 kV. The crystallinity was determined by X-ray diffraction (XRD) using a diffractometer with Cu-K $\alpha$  radiation (Shimadzu Lab-X XRD-6000). The accelerating voltage and applied current were 40 kV and 30 mA. The composition was verified by energy dispersive X-ray analysis (EDX, equipped with SEM JSM-6360LV). The light absorption properties were measured using UV-vis diffuse reflectance spectrophotometer (DRS, JASCO, UV-550) with a wavelength range of 200–900 nm. A 300W xenon lamp ( $\lambda > 290\text{nm}$ , PLS-SXE300CUV, perfectlight Instruments Co. Ltd., Beijing) was used as light source, and the average light intensity was  $78.5\text{mw/cm}^{-2}$  (UV-A radiation meter). GC were recorded on SHIMADZU 2014C. GC-MS data were measured with Thermo Scientific ISQ QD.  $^1\text{H}$ NMR were recorded on a Bruker Avance II 500 spectrometer in  $\text{CDCl}_3$  unless stated otherwise, using tetramethylsilane as an internal reference, operated at 500.13 for 1H, and J values are given in Hz.

### Preparation and of nano Ag/AgBr and Ag/AgCl

The Ag/AgBr or Ag/AgCl composite was prepared by a one-step chemical bath method at low temperature. In a typical case, 0.51g  $\text{AgNO}_3$  and 0.625g polyvinyl pyrrolidone (PVP, K30) were dissolved in 50 mL of 1.4 M nitric acid solution under magnetic stirring at room temperature. Then 50 mL of 0.06M NaBr or KCl aqueous solution was added to the mixture by dropwise for 30 min. The reaction system was stirred for another 30 min and then heated in water bath at 80°C for 3 h. The precipitate was collected by centrifugation. The solid was dispersed to the solution of 50 mL deionized water and 0.10g  $\text{AgNO}_3$ . The suspension solution was irradiated with UV irradiation for 20 min in the presence of sodium formate (1m L 0.02 M). The resulting product was collected and washed thoroughly with deionized water and absolute ethanol, and then dried at 70 °C in air for 12 h.

### Nano Ag/AgBr characterization

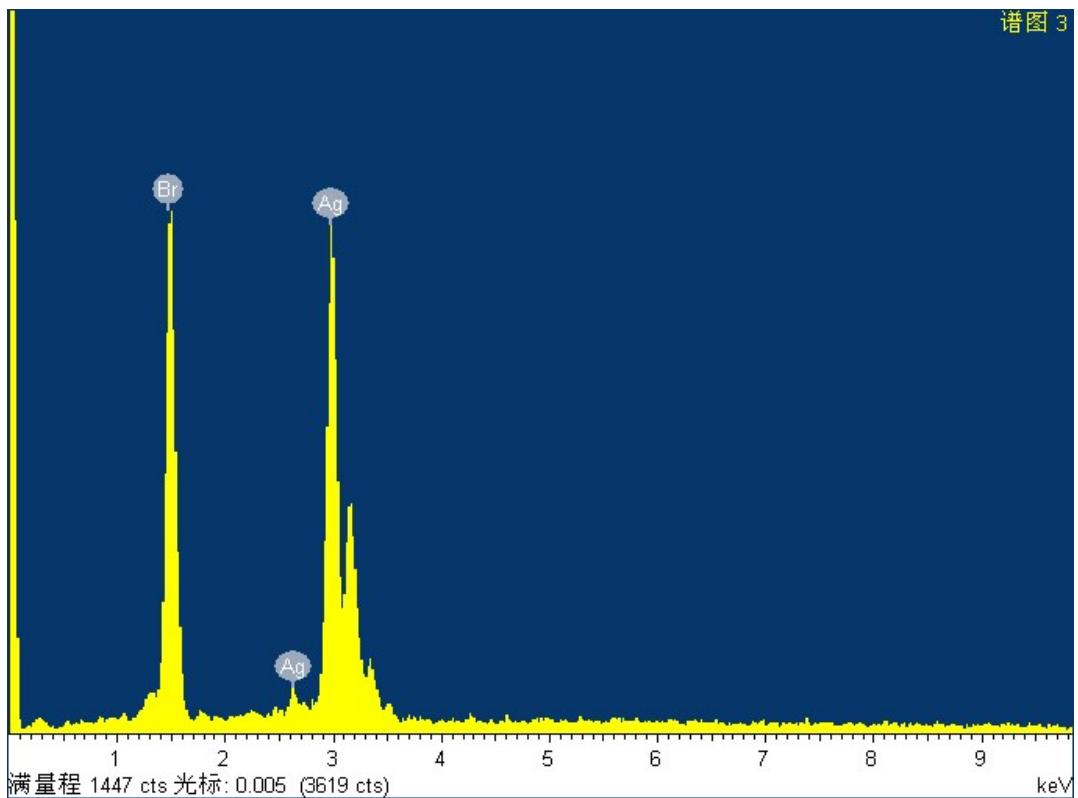
Ag /AgBr, EDX, nano Ag 4.5% mol sample:

Br      KBr    1-Jun-1999 12:00 AM

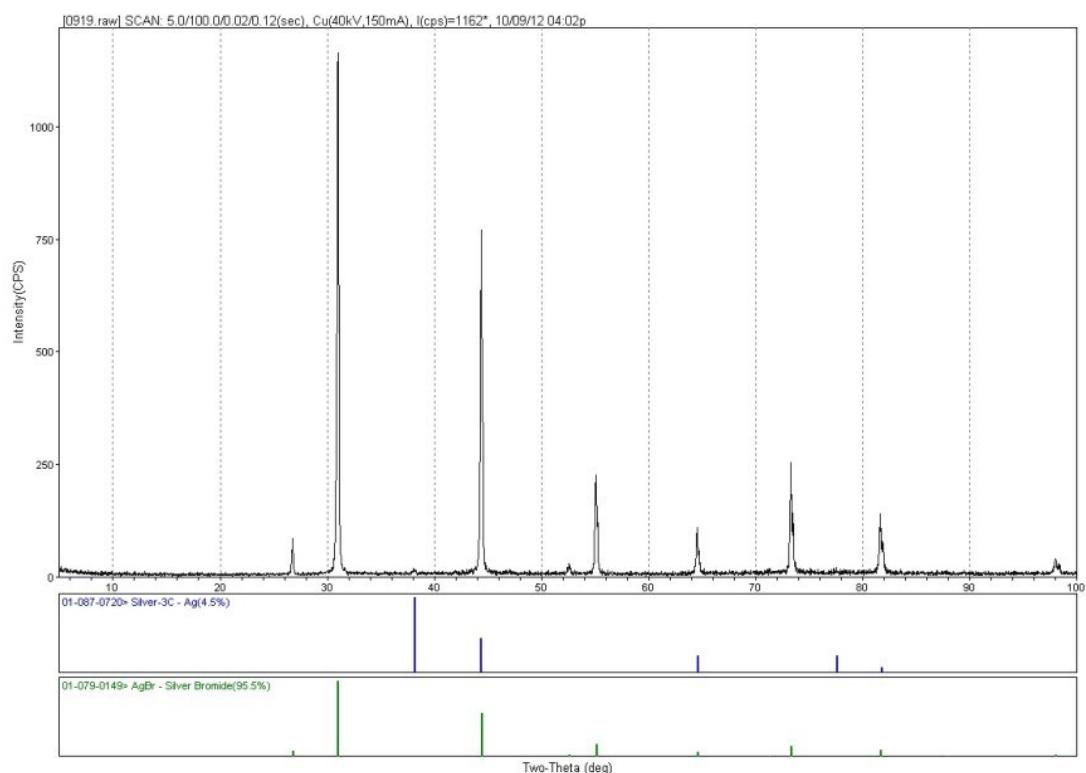
Ag      Ag    1-Jun-1999 12:00 AM

Elem.	Weight	Atom
	%	%
Br L	40.43	47.81
Ag L	59.57	52.19
Total	100.00	

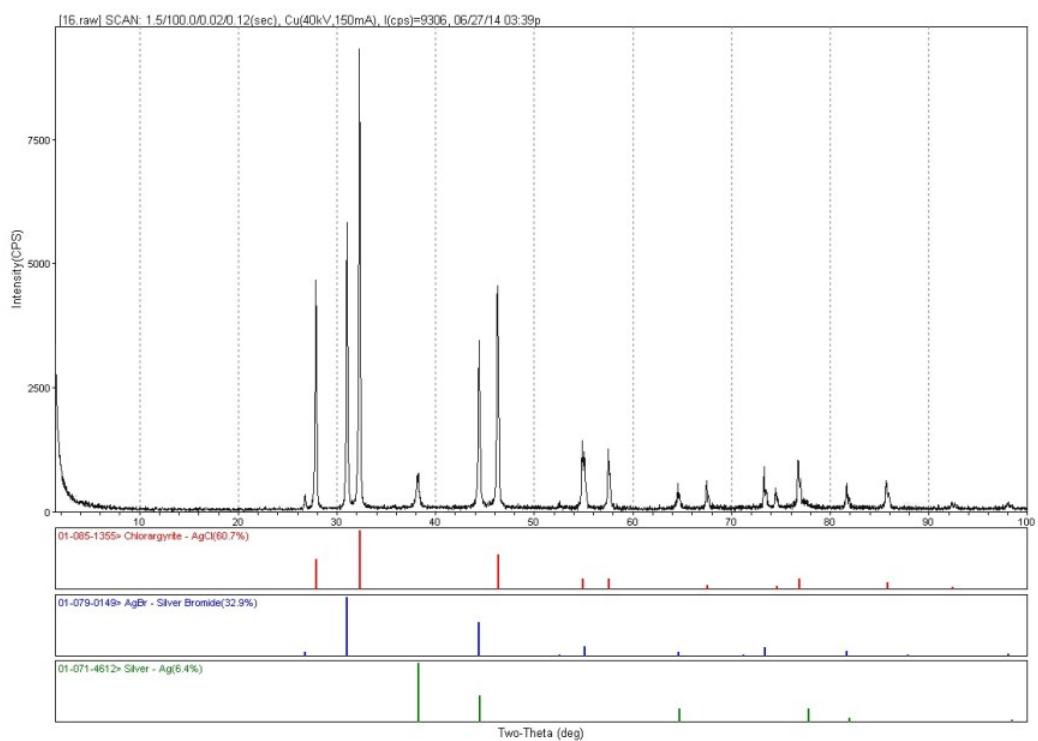
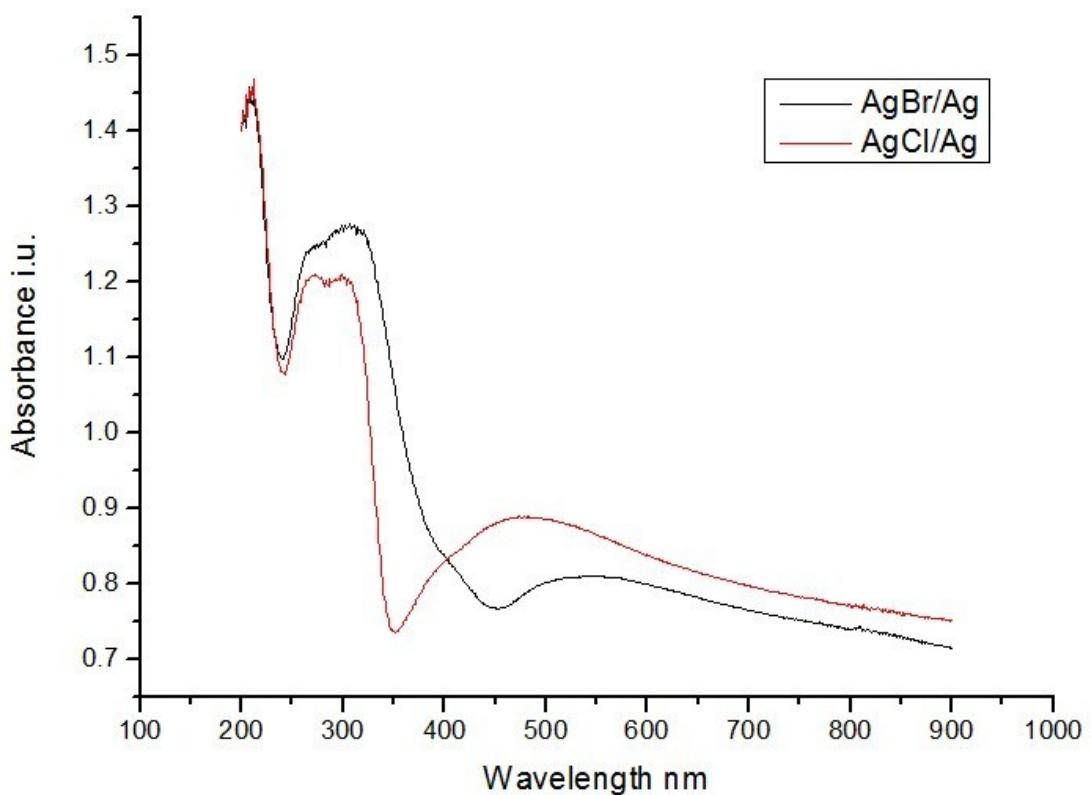
谱图 3



Ag /AgBr, XRD, nano Ag 4.5 %mol

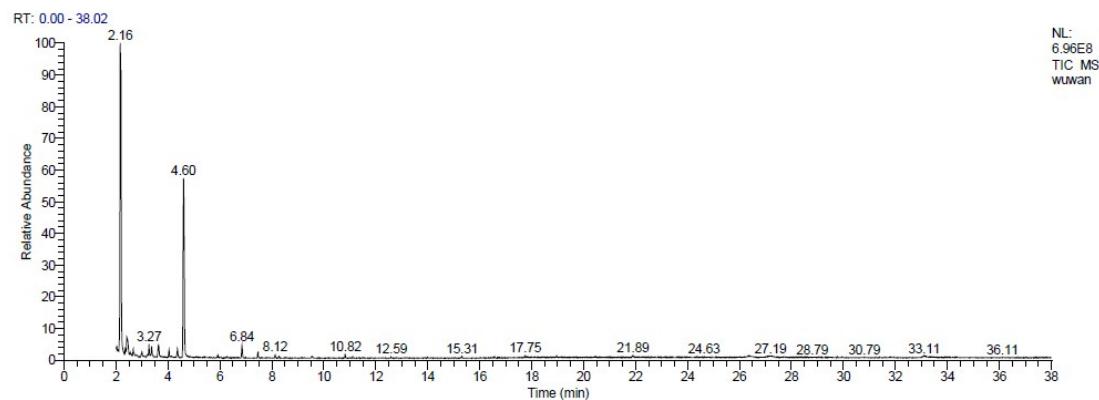


Ag/AgBr and Ag/AgCl, UV-Vis diffuse reflectance spectra



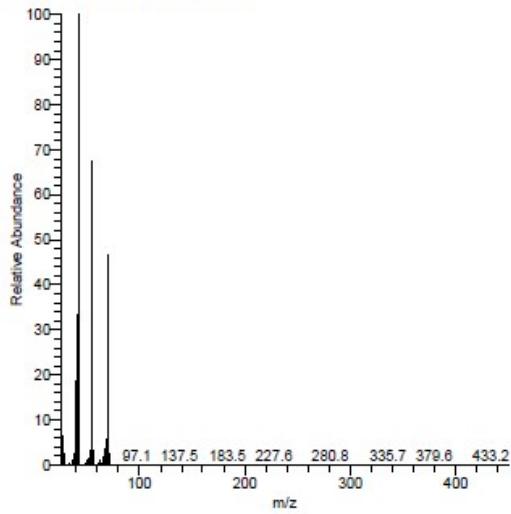
X-ray diffraction of catalyst Ag@AgCl after the reaction

**The photocatalytic halogenation of alicyclic hydrocarbon  
The reaction solution of cyclopentane chlorination**

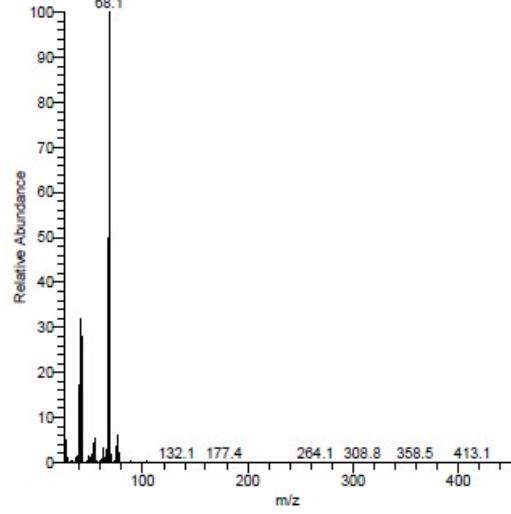


GC of the cyclopentane chlorination reaction mixture

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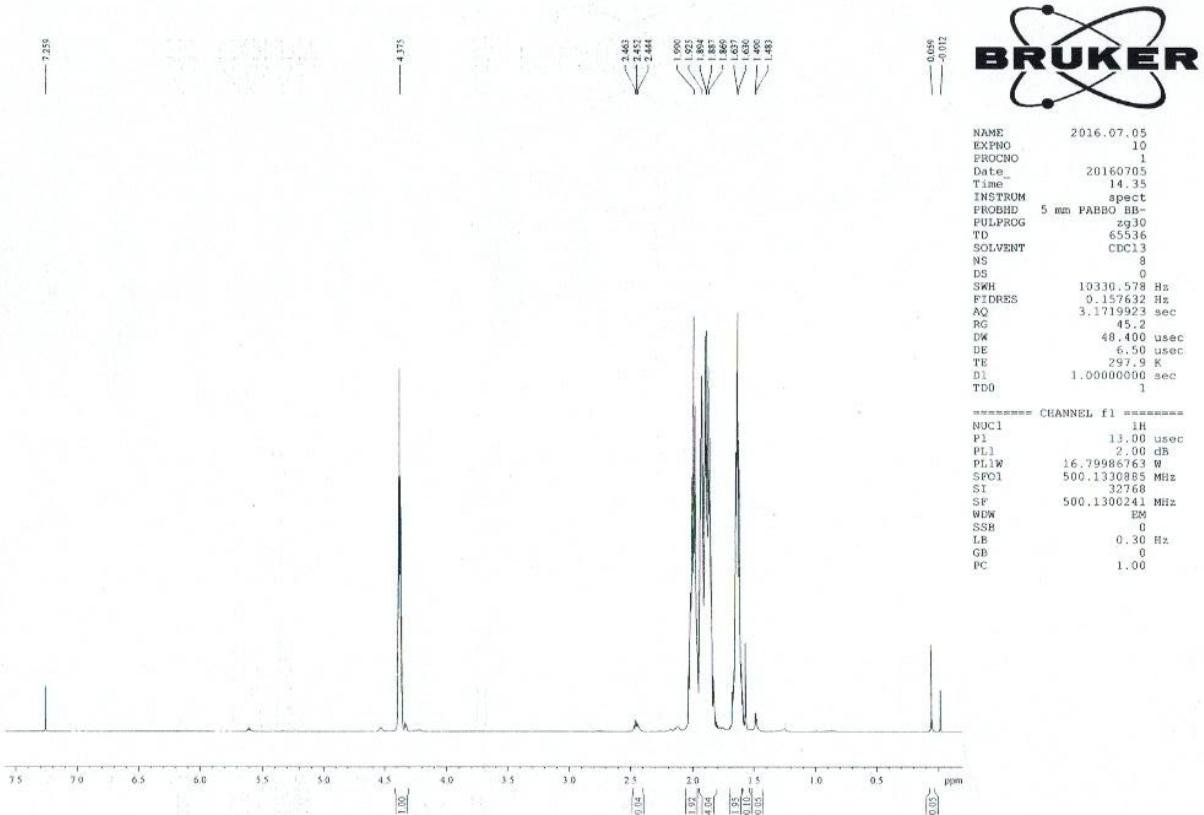


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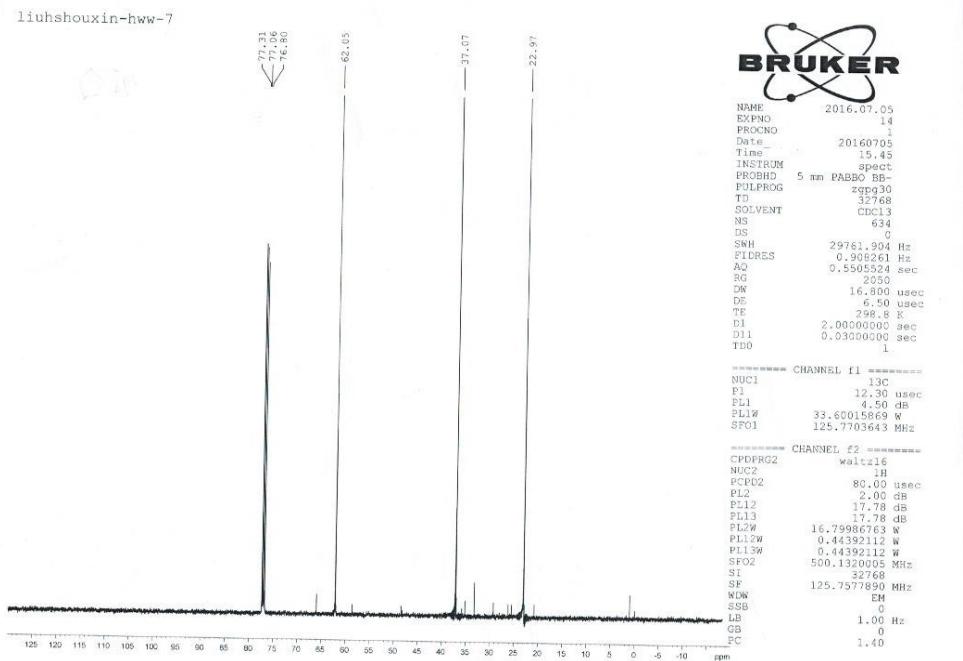


GC-MS of the cyclopentane chlorination reaction solution

liuhshouxin-hww-7

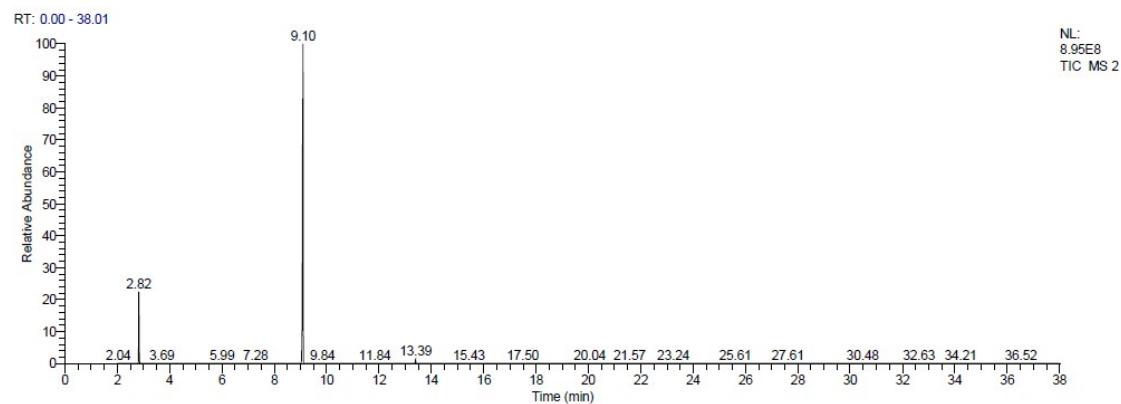


liuhshouxin-hww-7

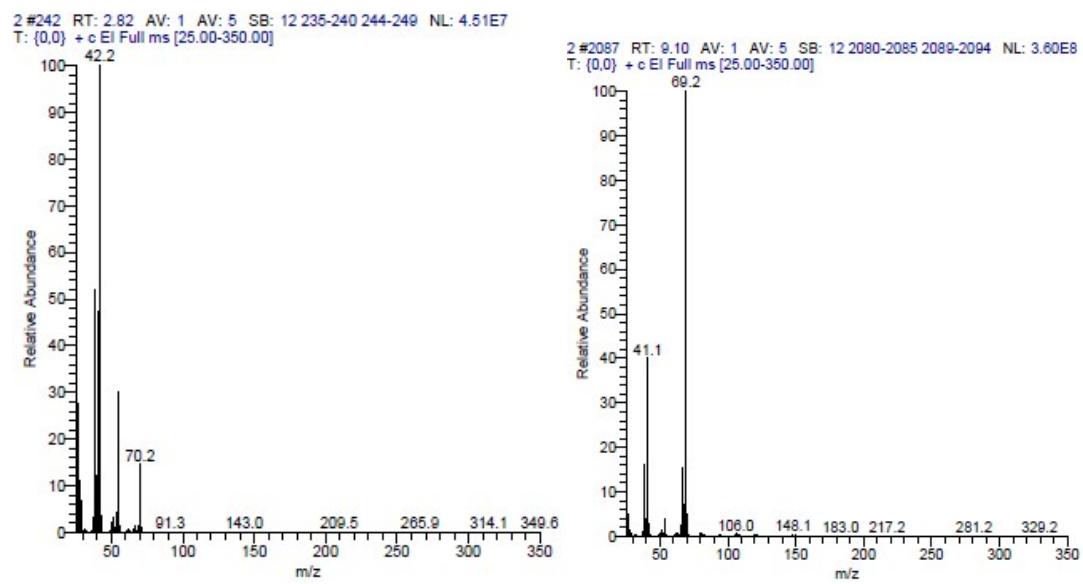


## NMR of the cyclopentane chlorination reaction mixture

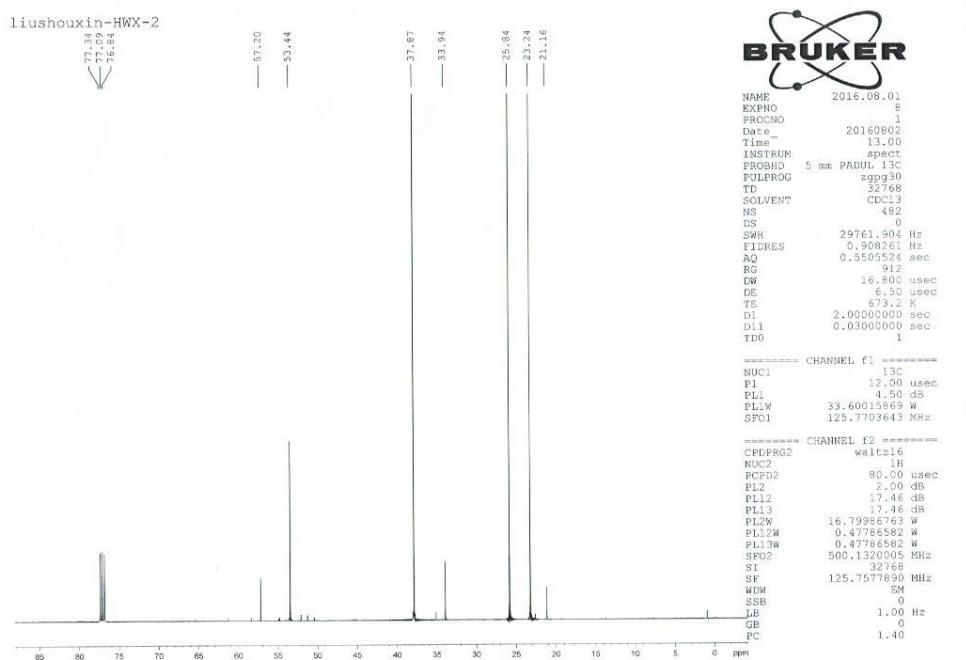
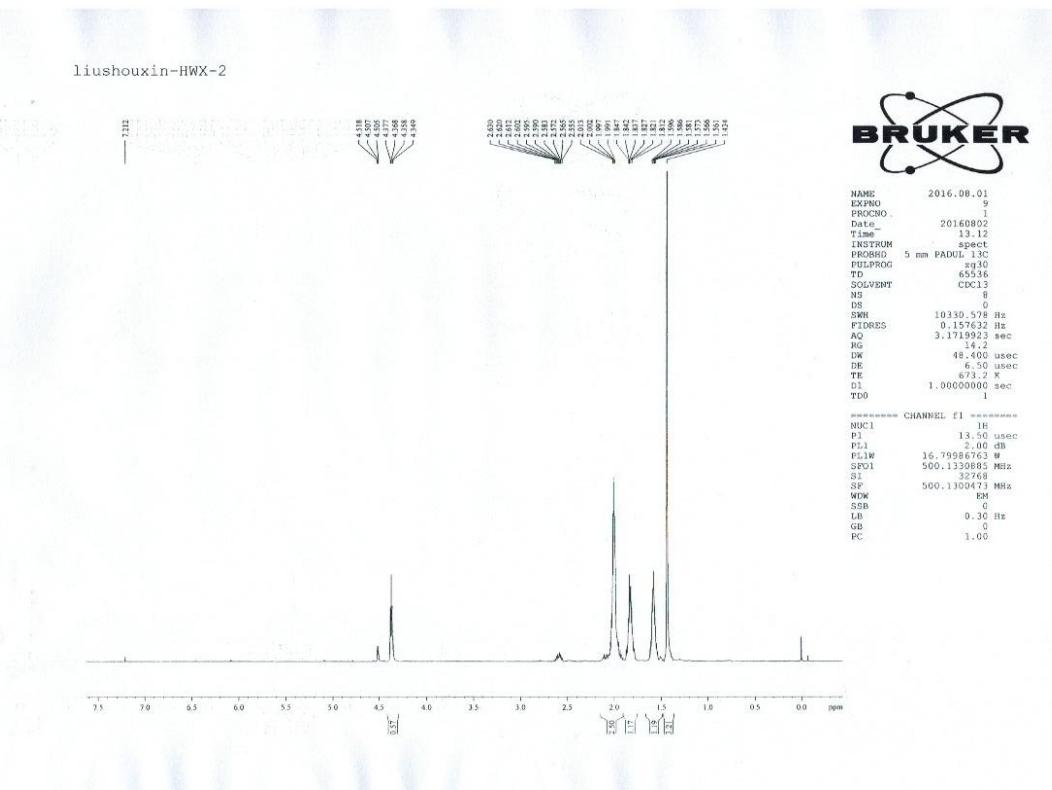
## The reaction solution of cyclopentane bromination



GC of the cyclopentane bromination reaction mixture

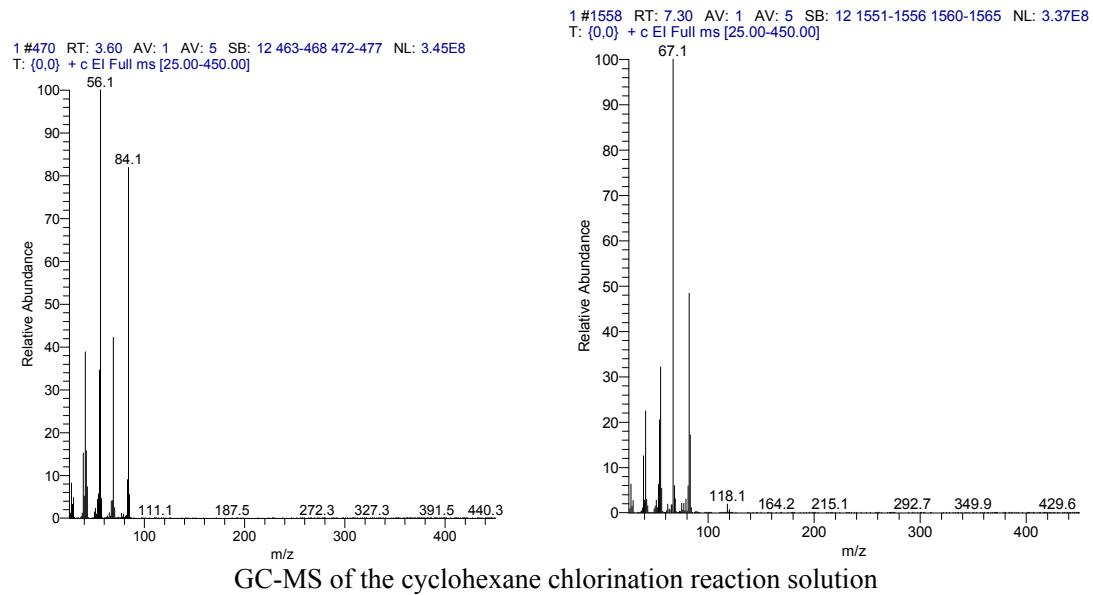
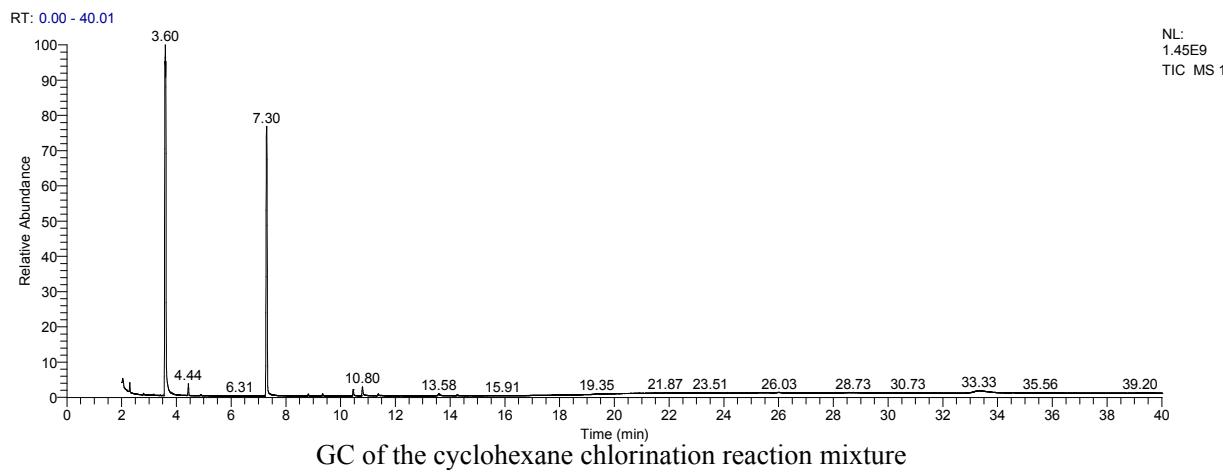


GC-MS of the cyclopentane bromination reaction solution

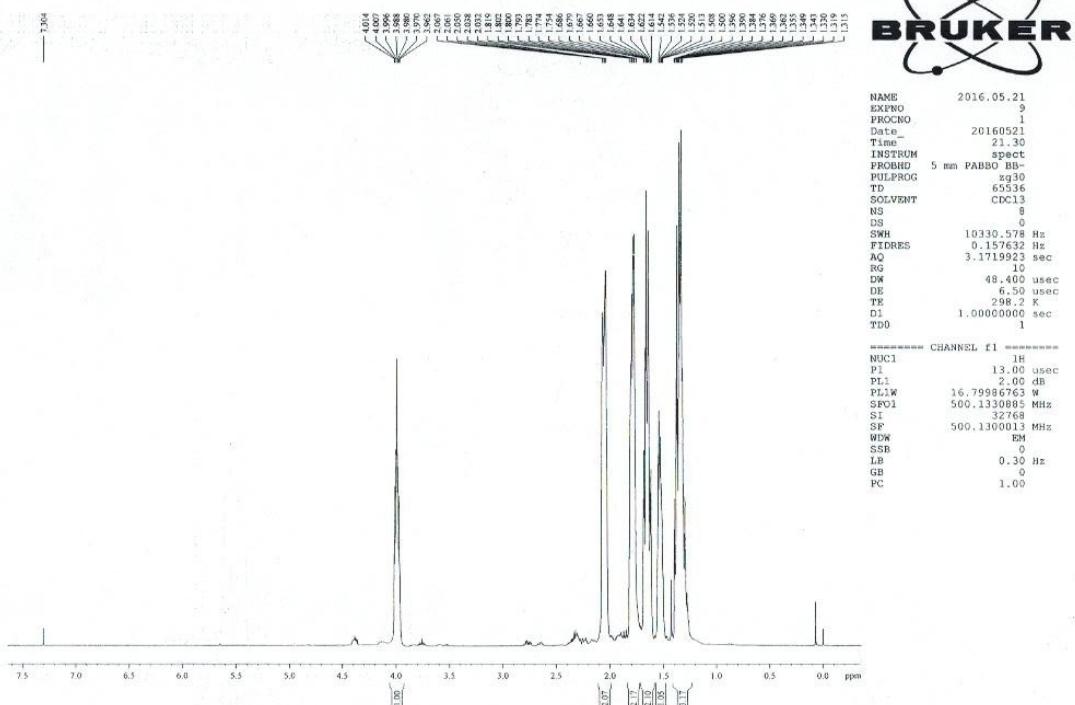


NMR of the cyclopentane bromination reaction mixture from Ag/AgCl catalysis

## The reaction solution of cyclohexane chlorination



liushouxin-hjw-3



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PROCNO 1  
Date 20160521  
Time 21.30  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 8  
DS 0  
SWR 10330.523 Hz  
FIDRES 0.157632 Hz  
AQ 3.1719923 sec  
RG 10  
DW 48.400 usec  
DE 6.50 usec  
TE 298.0 K  
D1 0.0000000 sec  
TDD 1

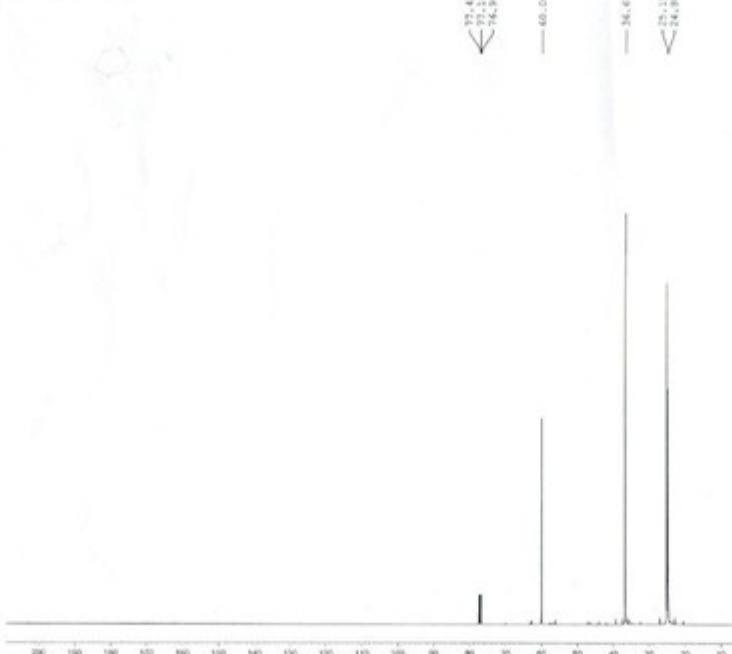
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PL1 2.00 dB  
PL2W 16.79986763 W  
SF01 500.1330805 MHz  
SI 32768  
SF 500.1390013 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

NAME 2016.05.21  
EXPNO 12  
PROCNO 1  
Date 20160521  
Time 21.42  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpp30  
TD 32768  
SOLVENT CDCl3  
NS 8192  
DS 0  
SWR 29741.904 Hz  
FIDRES 0.098261 Hz  
AQ 0.3505524 sec  
RG 2056  
DW 16.800 usec  
DE 6.50 usec  
TE 298.0 K  
D1 2.0000000 sec  
D11 0.0300000 sec  
TDD 1

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PL1 1.50 dB  
PL2W 33.60015869 W  
SF01 125.7773643 MHz

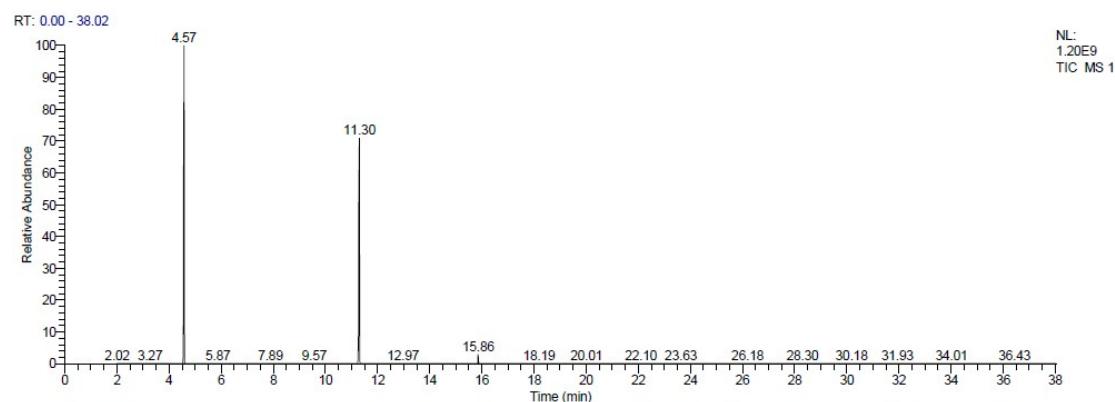
===== CHANNEL E2 =====  
CP90PG2 w1t16  
NUC2 1H  
NUC3 1H  
SF02 80.000000 Hz  
PL1 2.50 dB  
PL2 17.78 dB  
PL3 17.78 dB  
PL4W 16.79986763 W  
PL2W 0.44392112 W  
PL3W 0.44392112 W  
SF02 300.1320265 MHz  
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WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

liushouxin-hjw-3

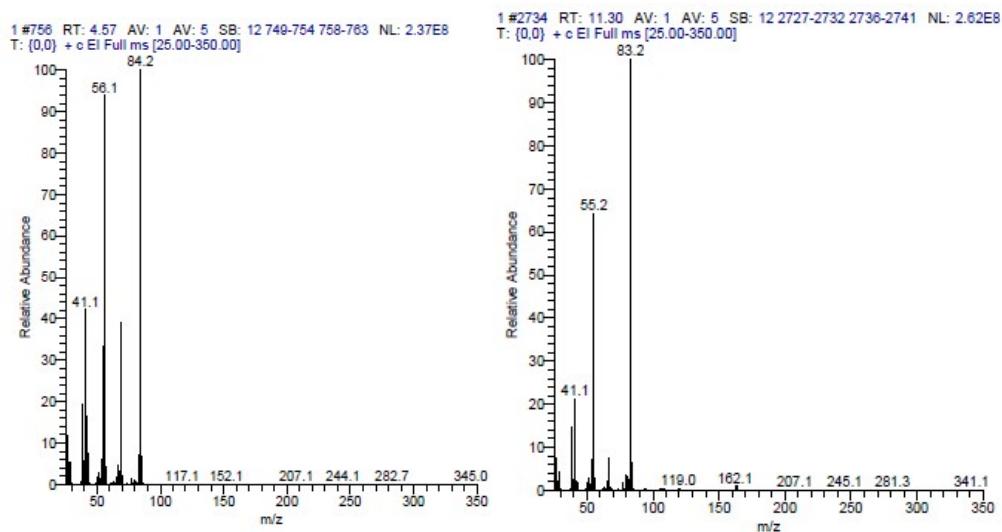


NMR of the cyclohexane chlorination reaction mixture

## The reaction solution of cyclohexane bromination

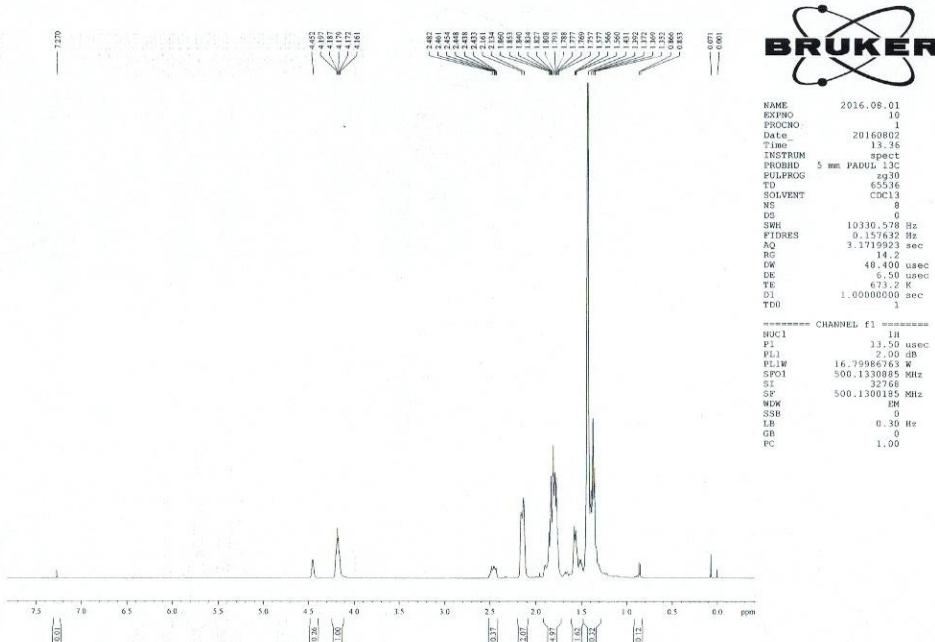


GC of the cyclohexane bromination reaction mixture

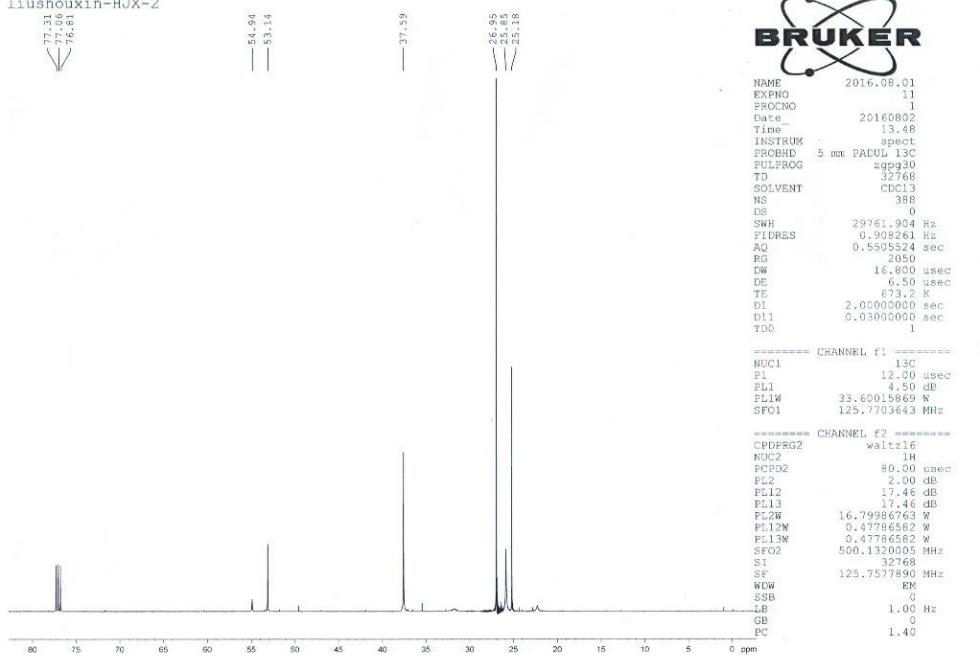


GC-MS of the cyclohexane bromination reaction solution

liushouxin-HJX-2

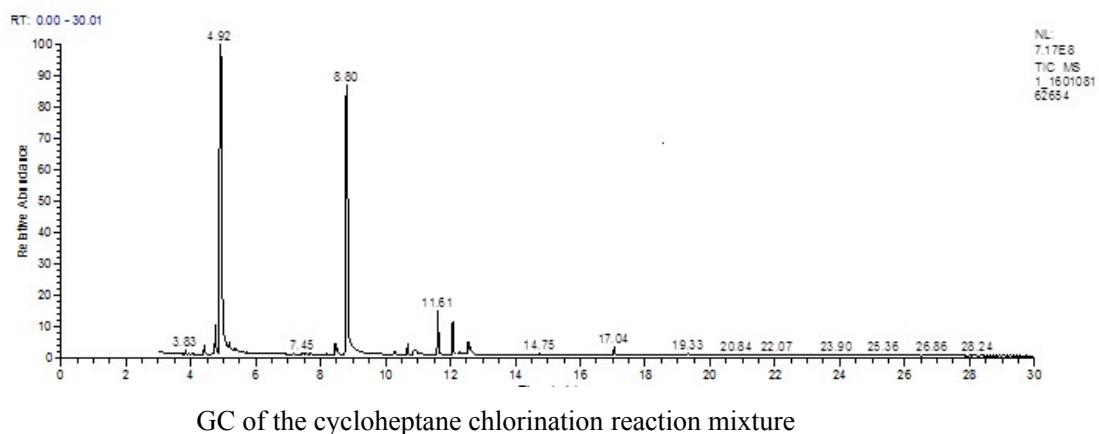


liushouxin-HJX-2

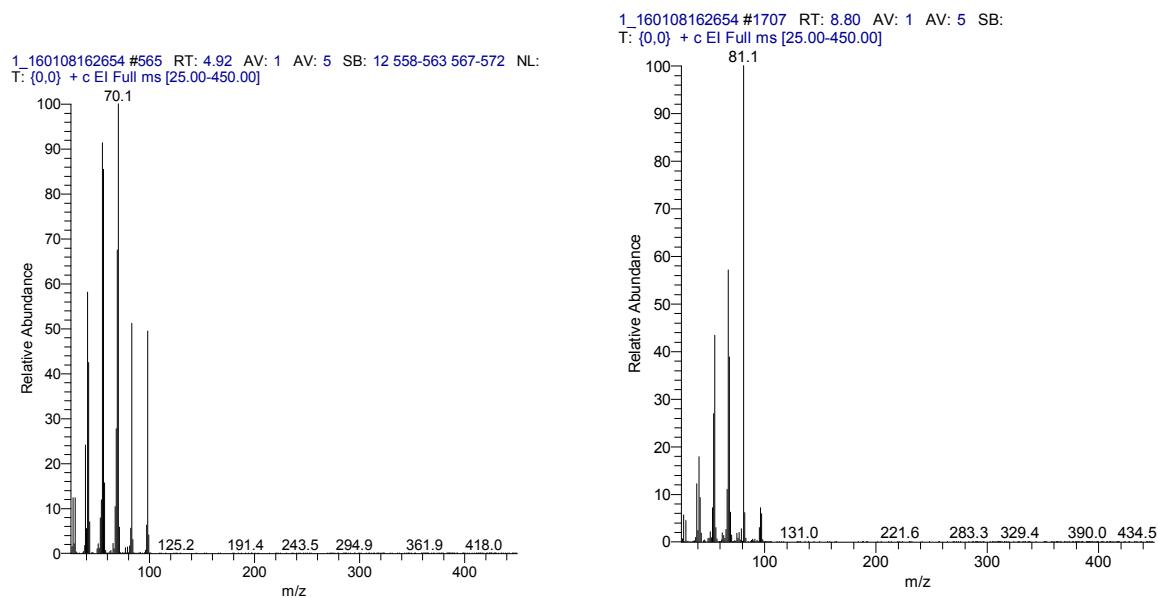


NMR of the cyclohexane bromination reaction mixture from Ag/AgCl catalysis

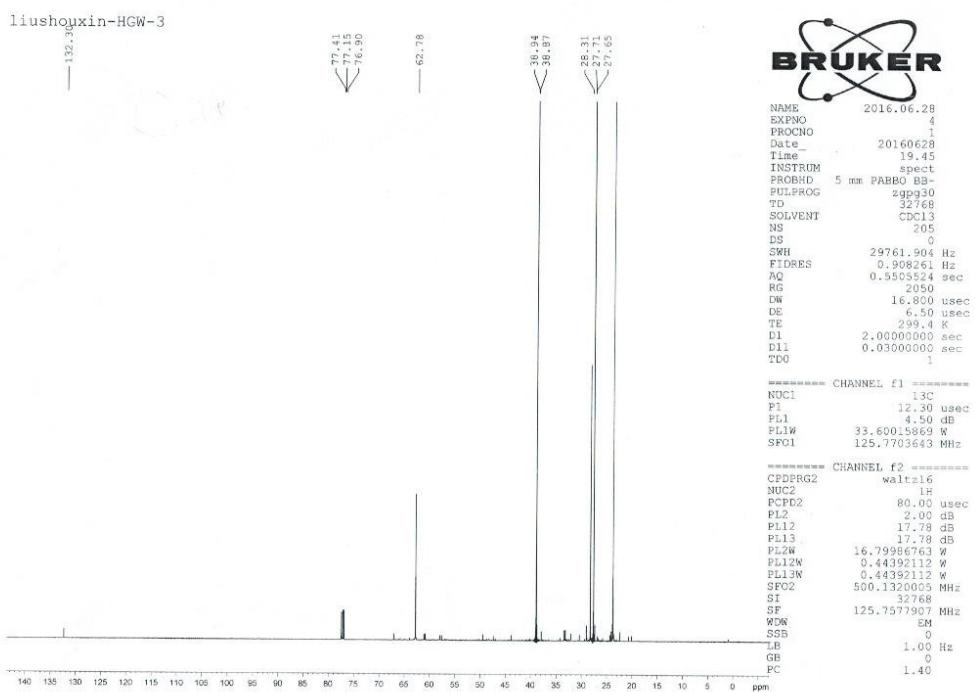
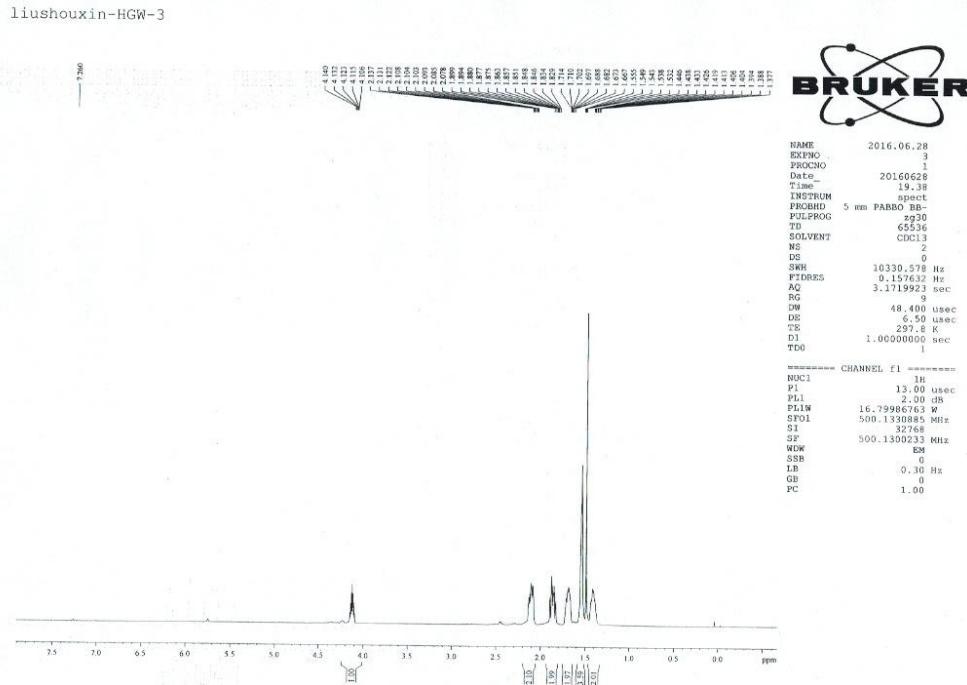
## The reaction solution of cycloheptane chlorination



GC of the cycloheptane chlorination reaction mixture

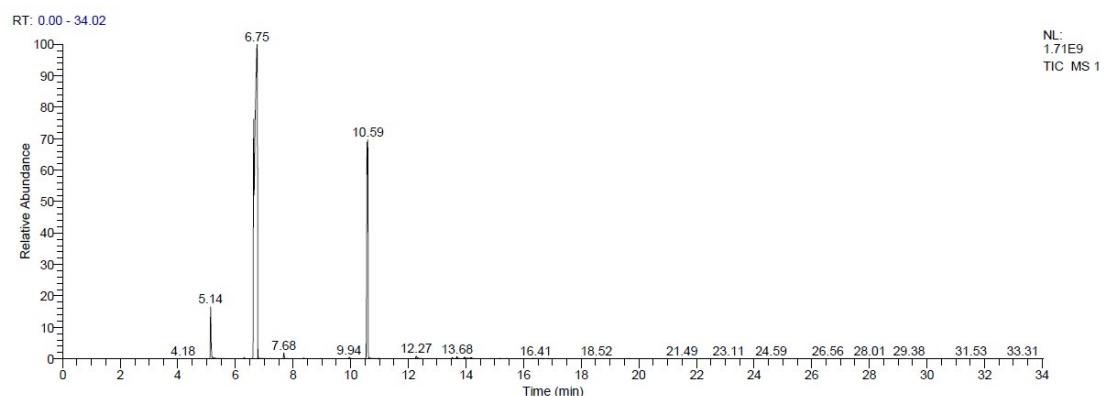


GC-MS of the cycloheptane chlorination reaction solution

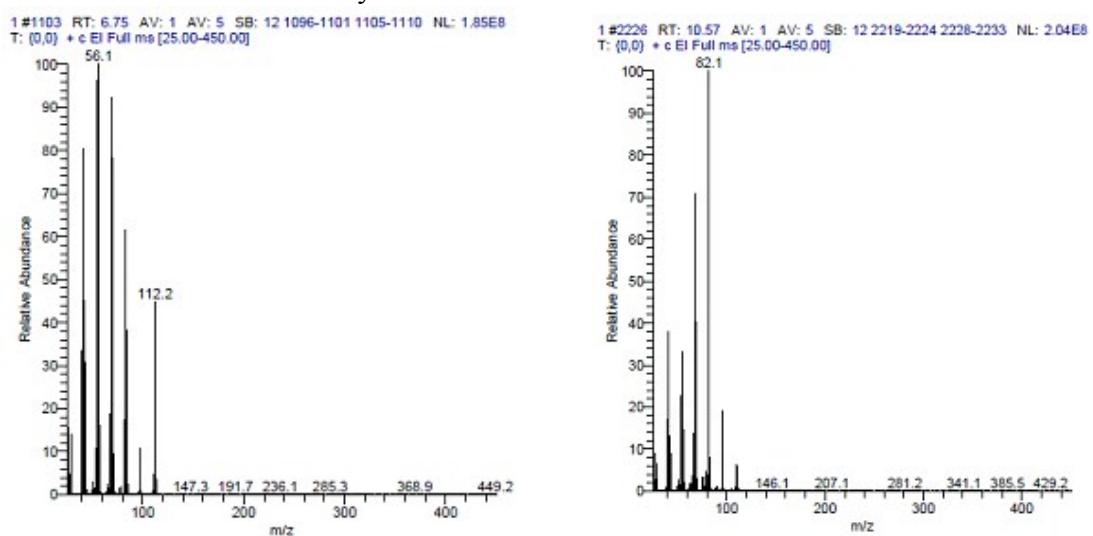


## NMR of the cycloheptane chlorination reaction solution

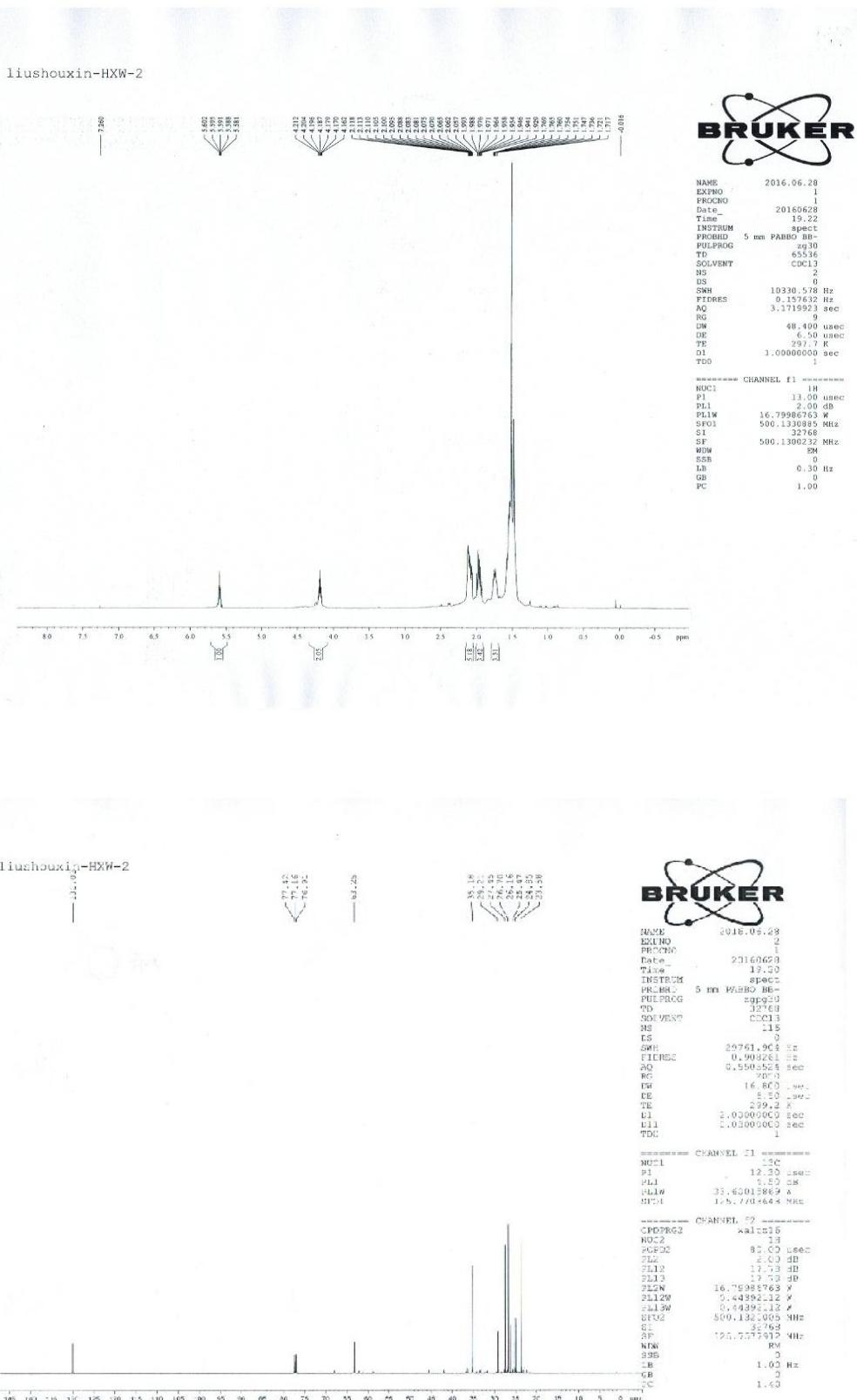
## The reaction solution of cyclooctane chlorination



GC of the cyclooctane chlorination reaction mixture

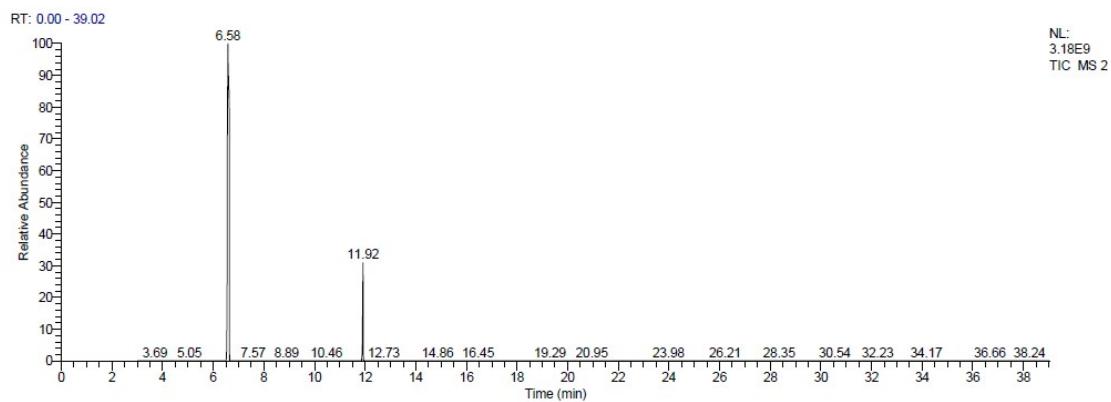


GC-MS of the cyclooctane chlorination reaction mixture

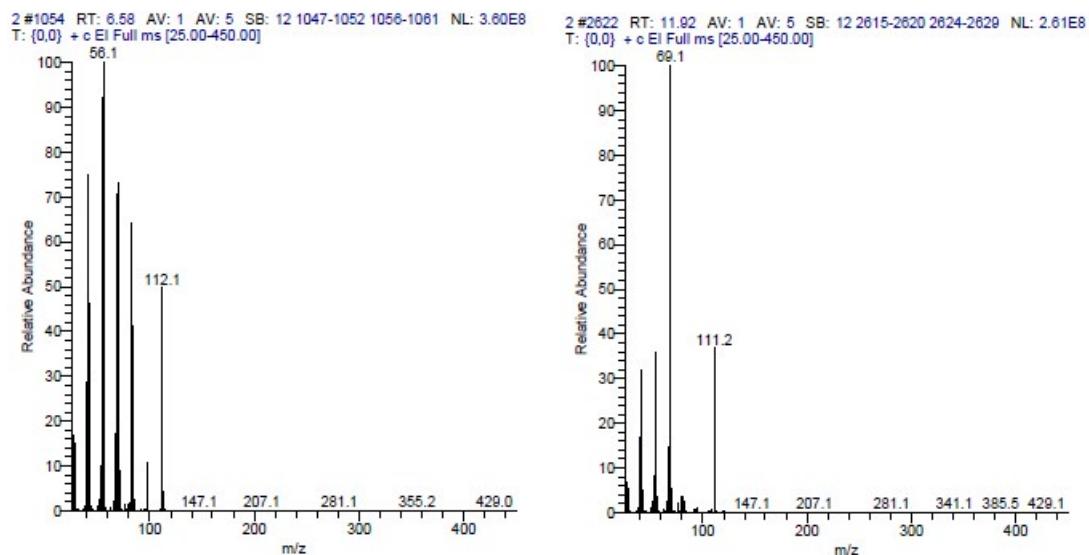


#### NMR of the cyclooctane chlorination reaction mixture

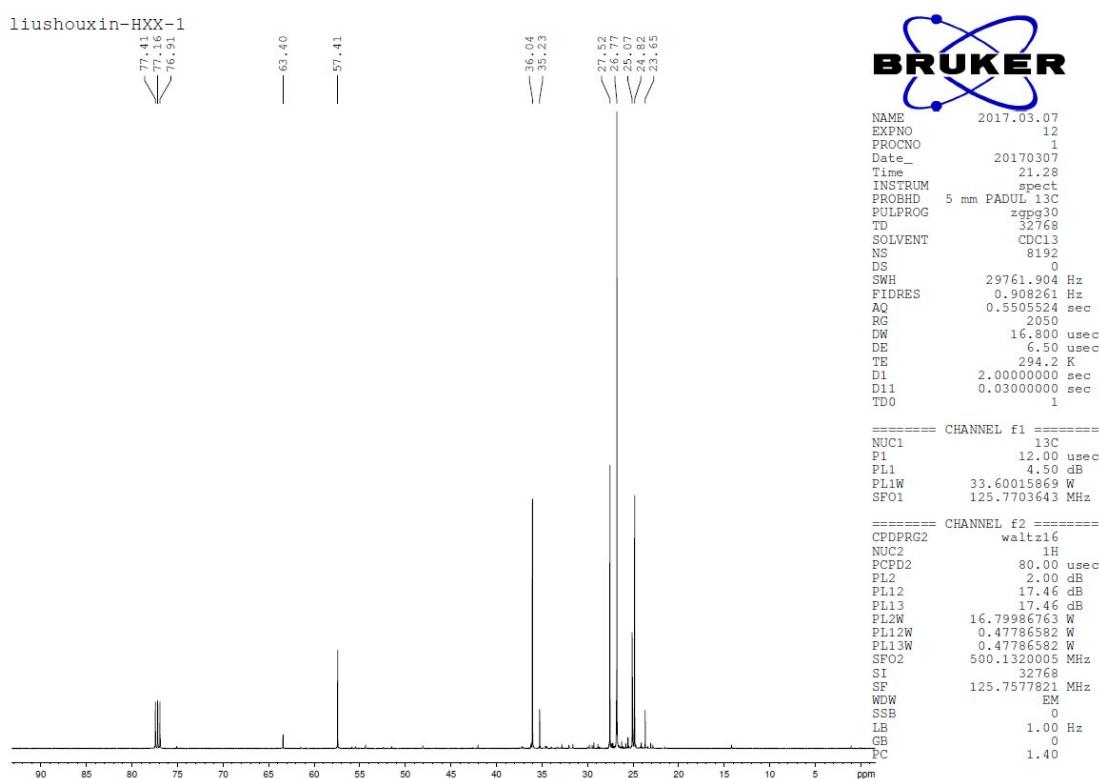
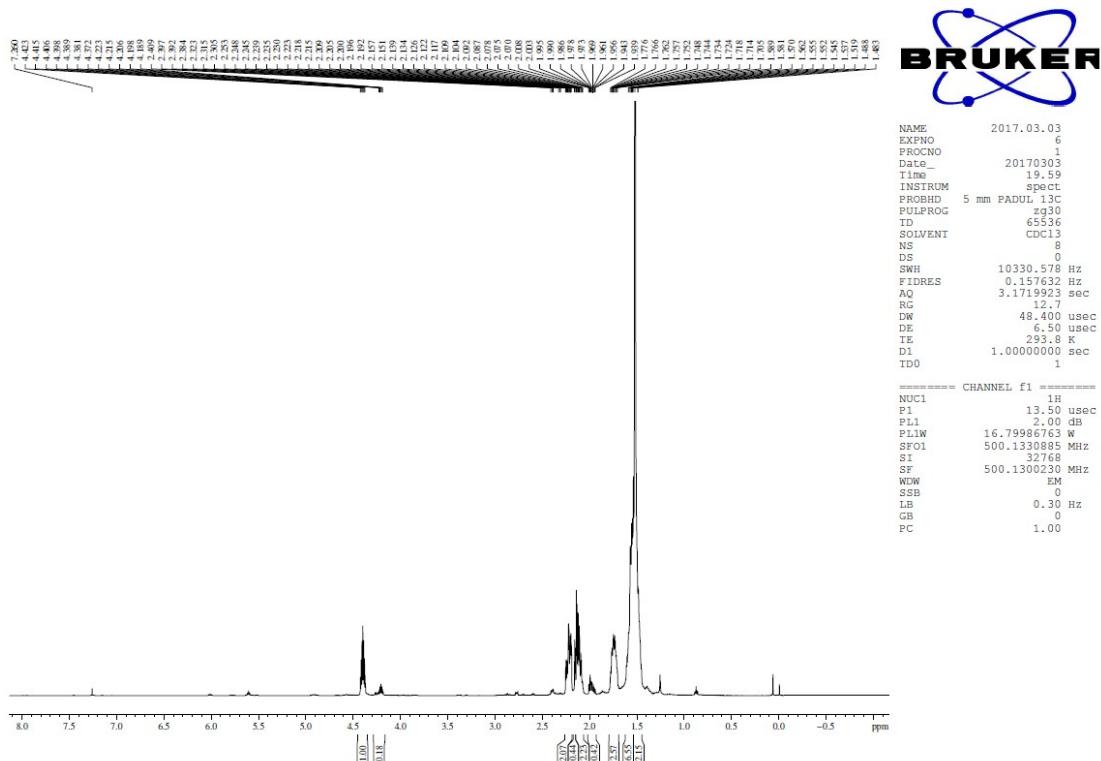
## The reaction solution of cyclooctane bromination



GC of the cyclooctane bromination reaction mixture

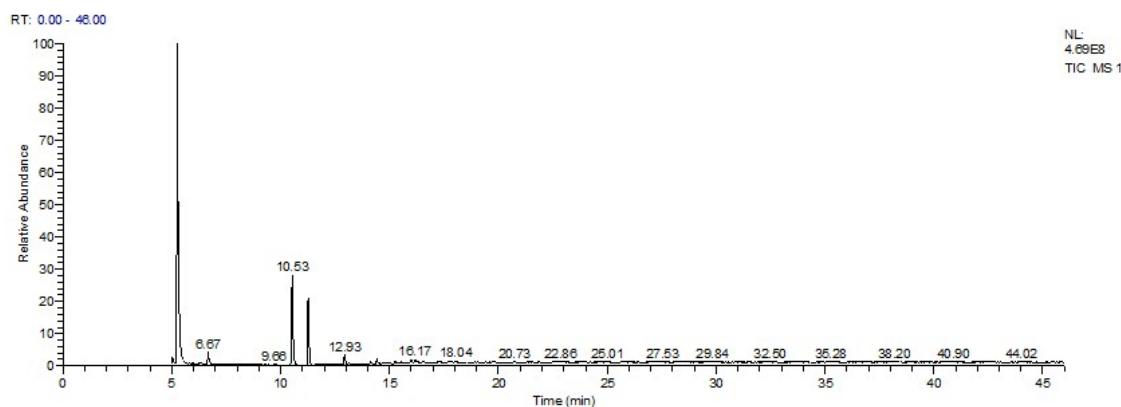


GC-MS of the cyclooctane bromination reaction mixture

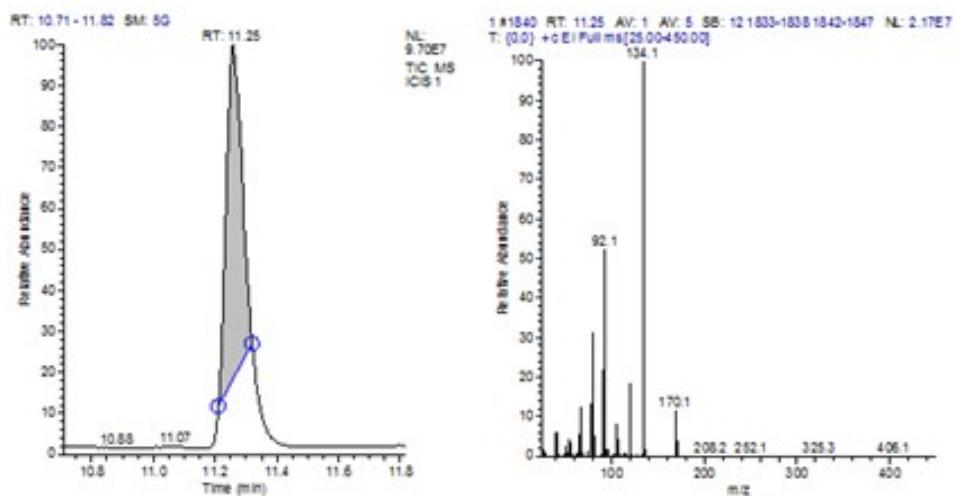
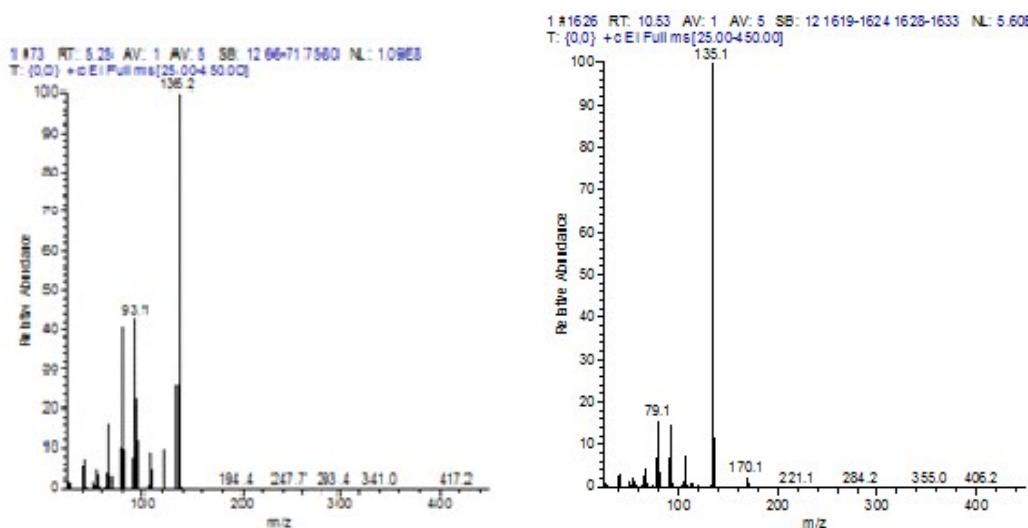


## NMR of the cyclooctane bromination reaction mixture

## The halogenation of adamantine

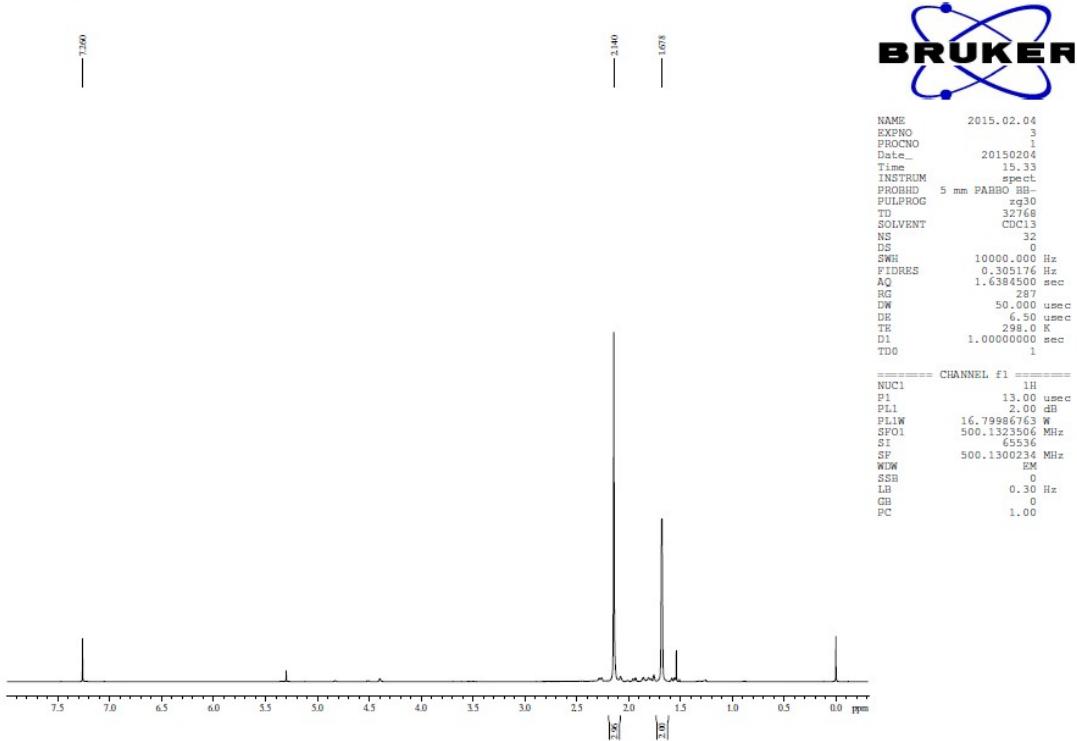


## GC of the adamantine chlorination reaction mixture

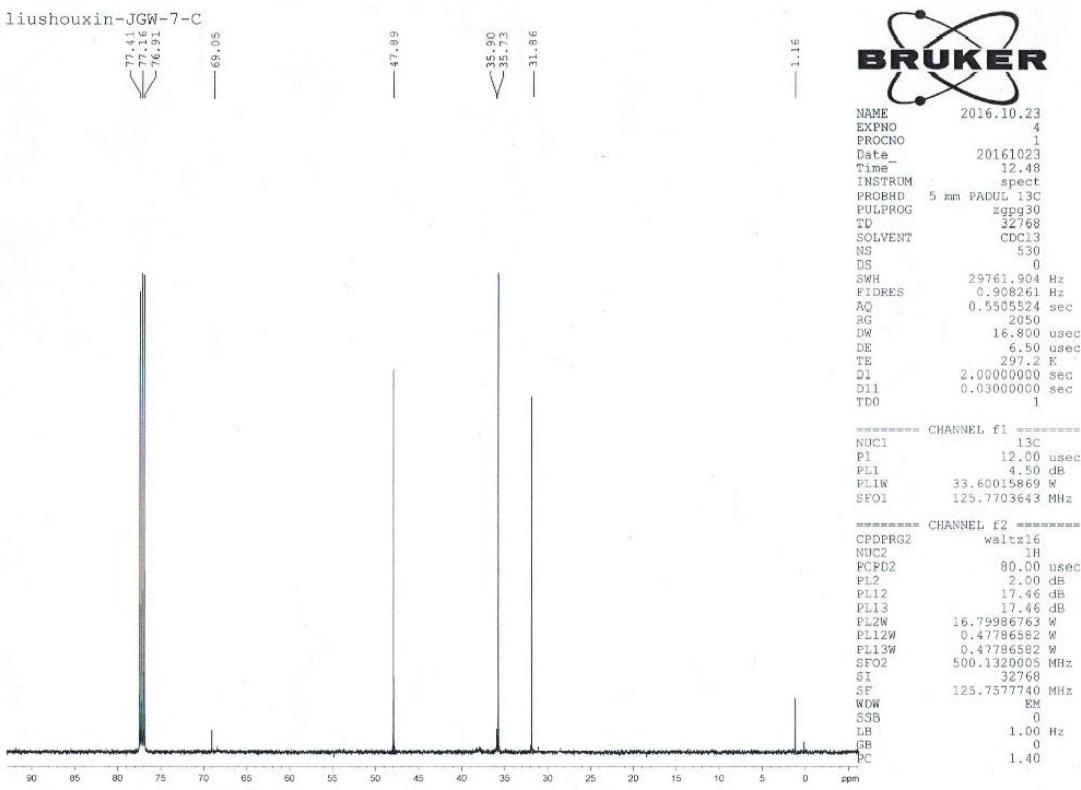


GC-MS of the adamantine chlorination reaction mixture

TZQ-12-CDC13

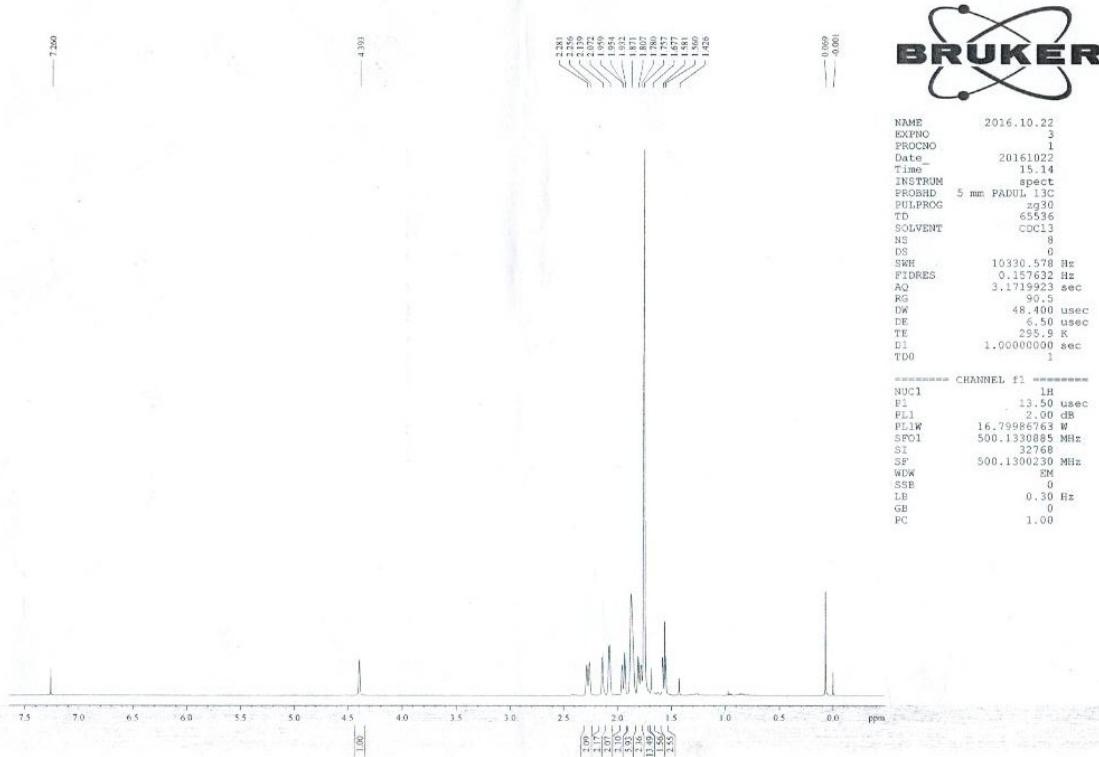


liushouxin-JGW-7-C

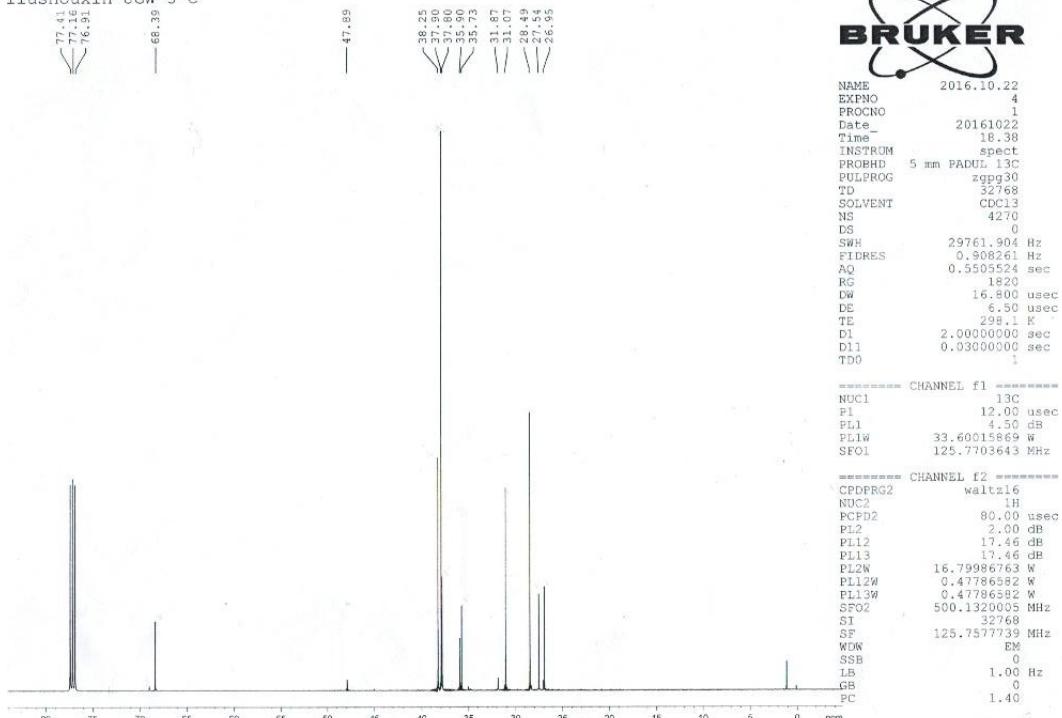


NMR of the adamantine chlorination reaction mixture (1-Cl-adamantine)

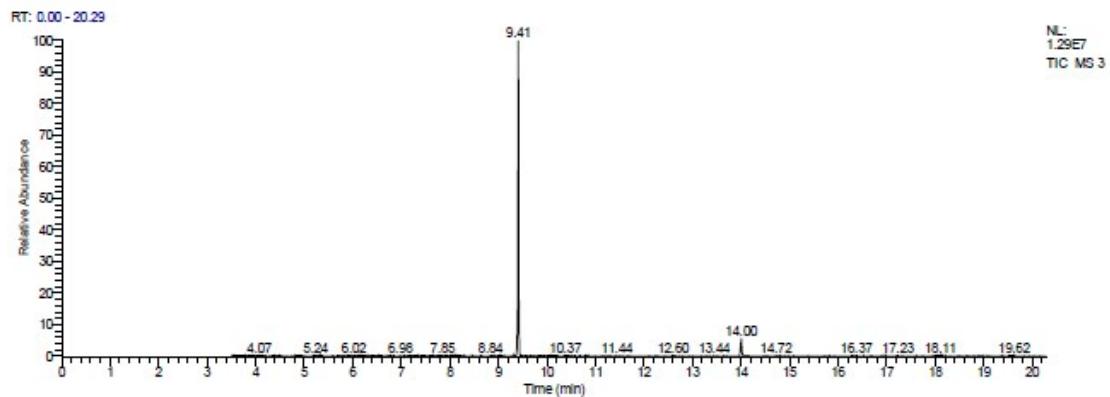
liushouxin-JGW-5



liushouxin-JGW-5-C

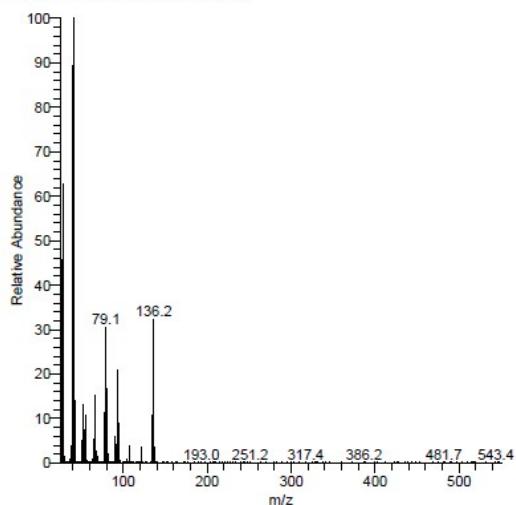


NMR of the adamantine chlorination reaction mixture (adamantine and 2-Cl-adamantine)

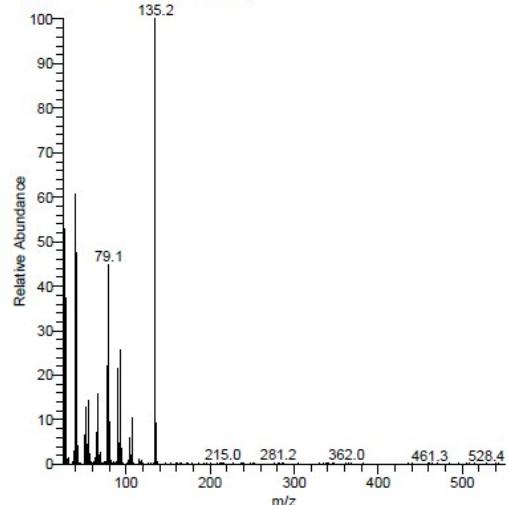


GC of the adamantine bromination reaction mixture

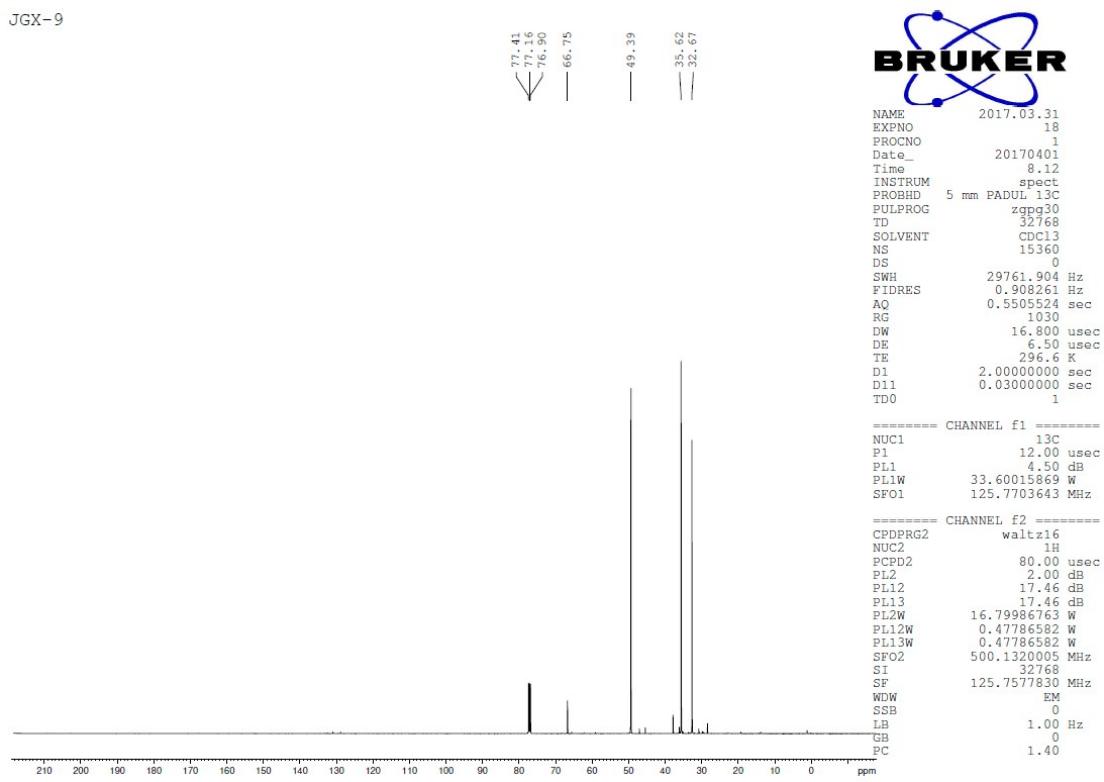
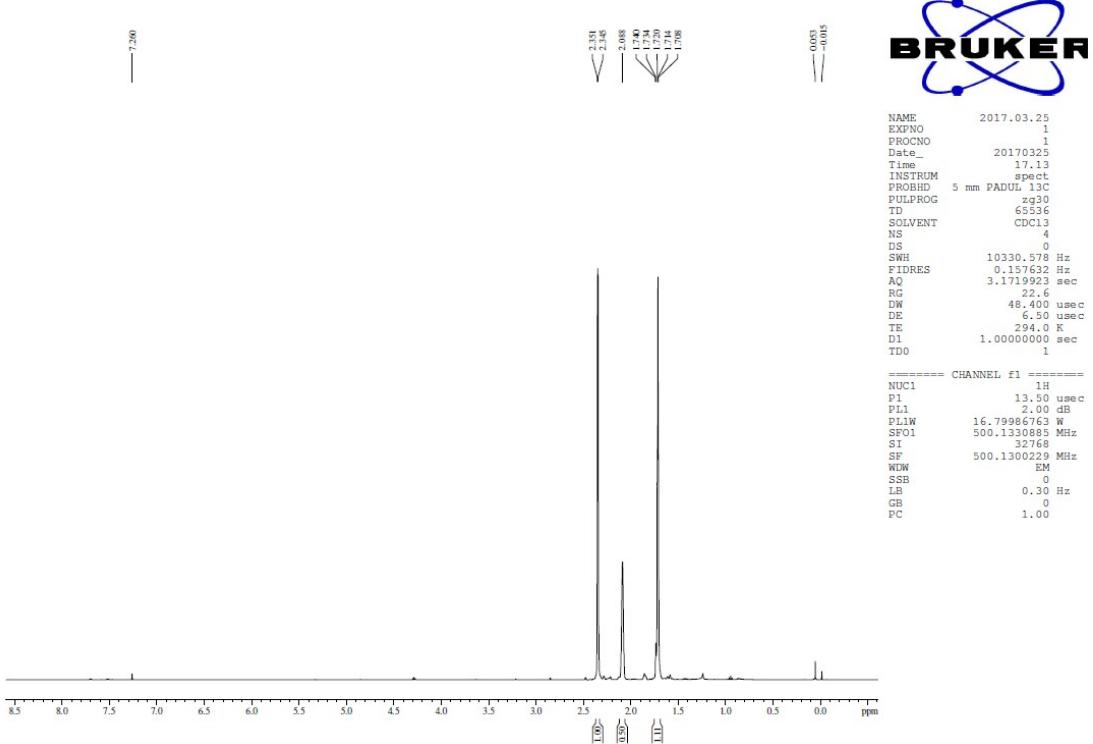
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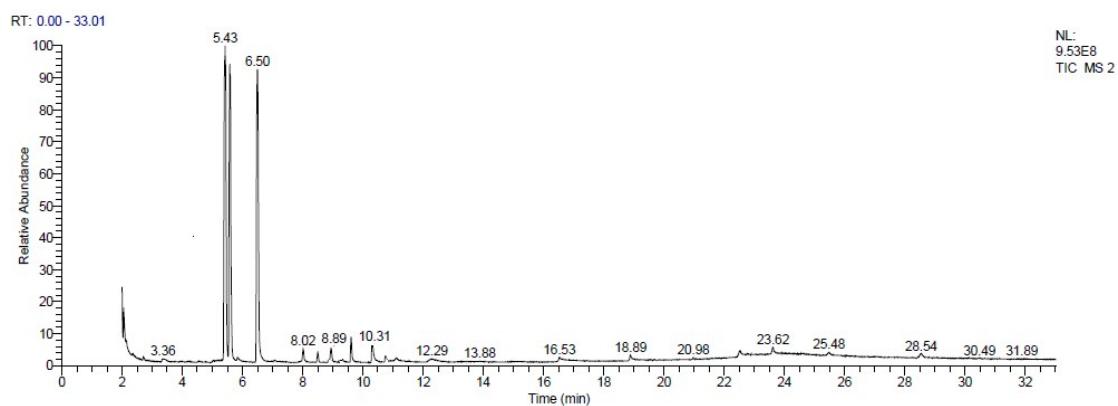
GC-MS of the adamantine bromination reaction mixture



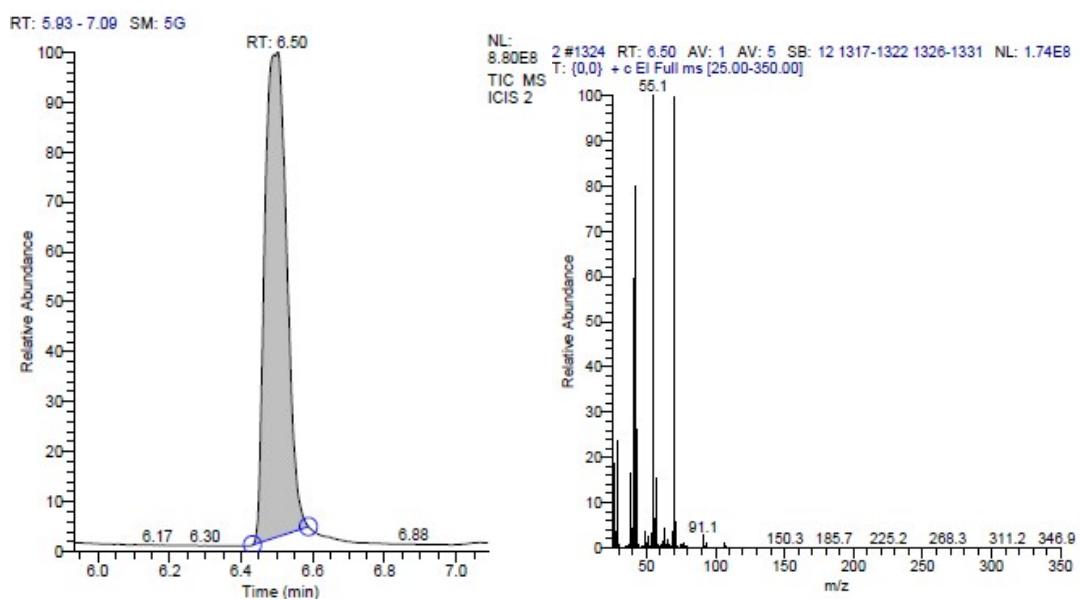
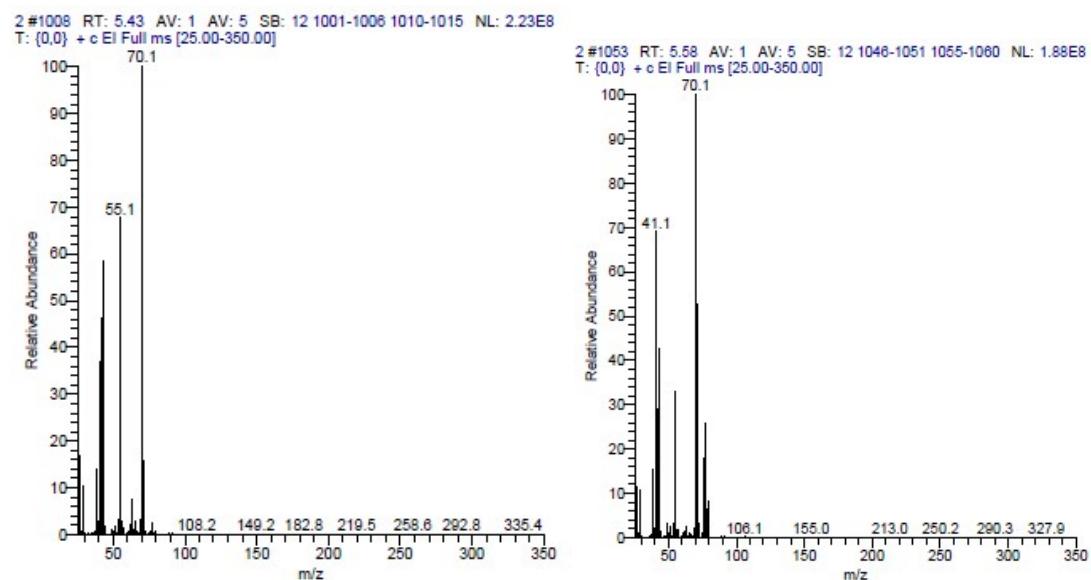
NMR of the adamantine bromination reaction mixture

## The chlorinations of chain alkanes

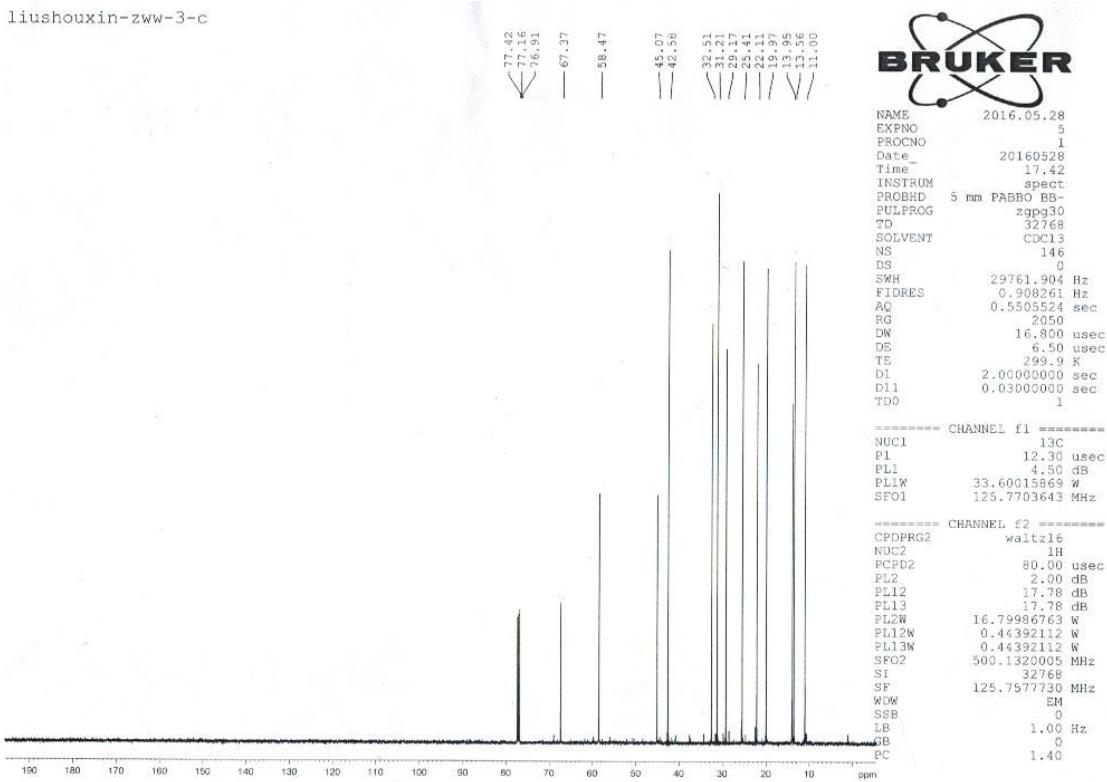
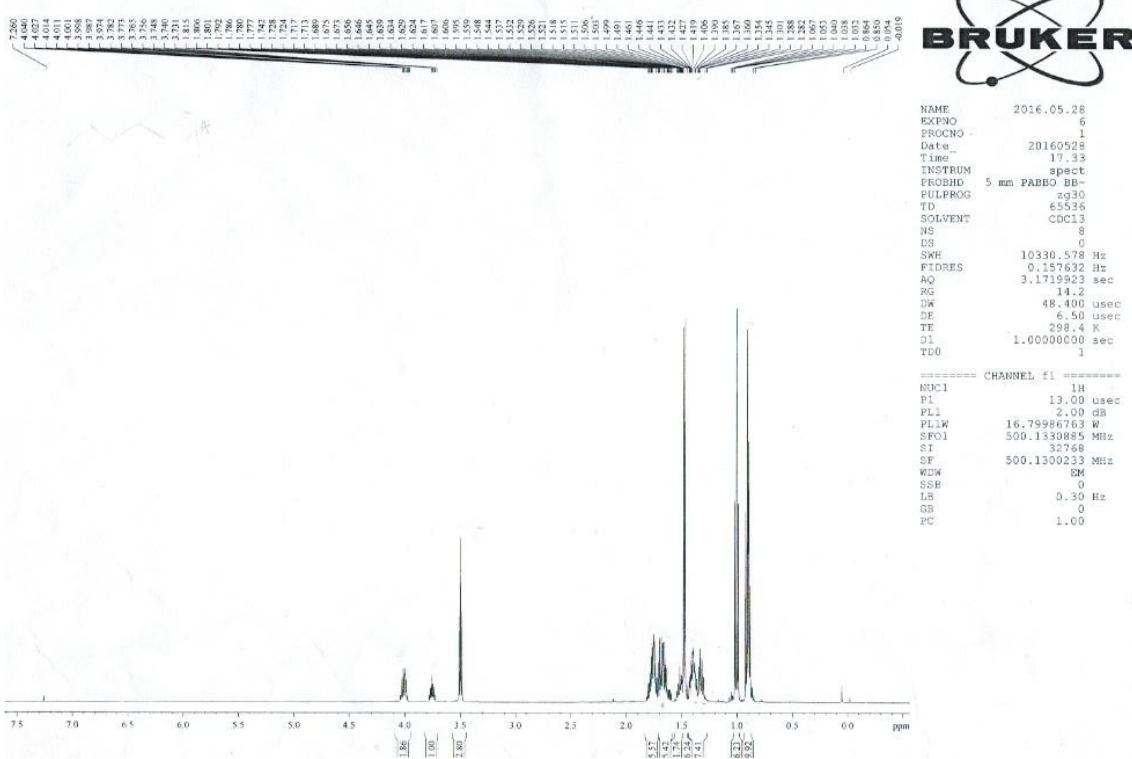
### Chlorination of *n*-pentane



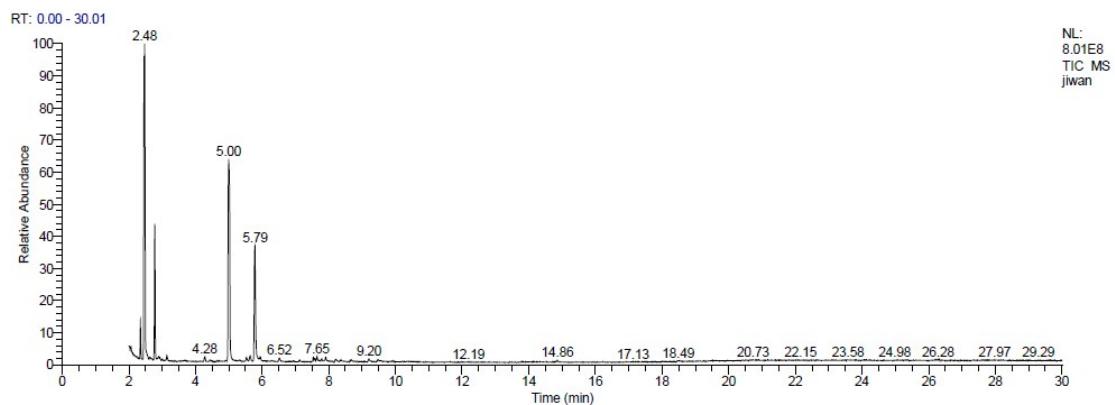
GC of the chlorination reaction mixture of *n*-pentane



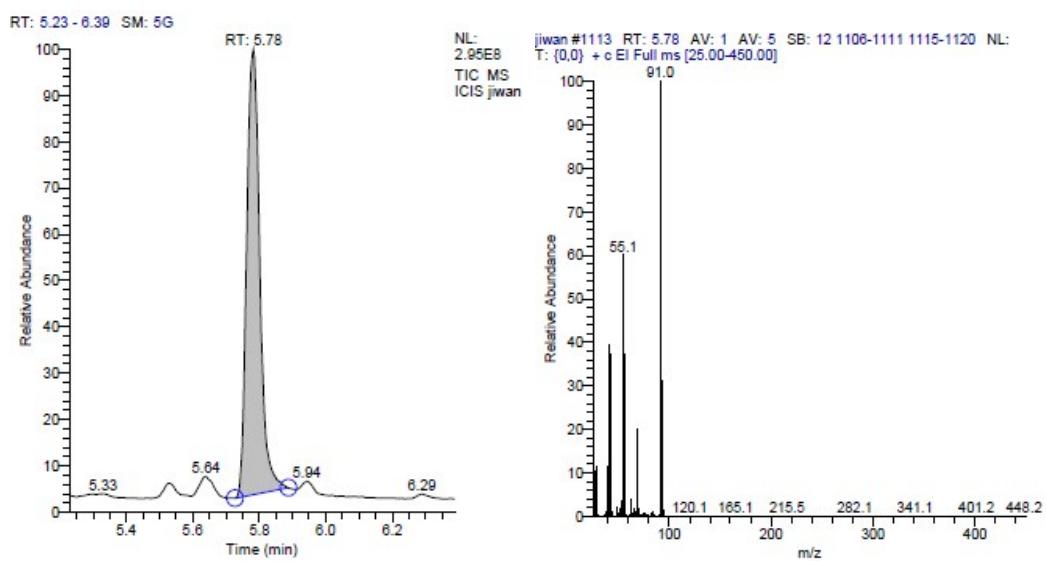
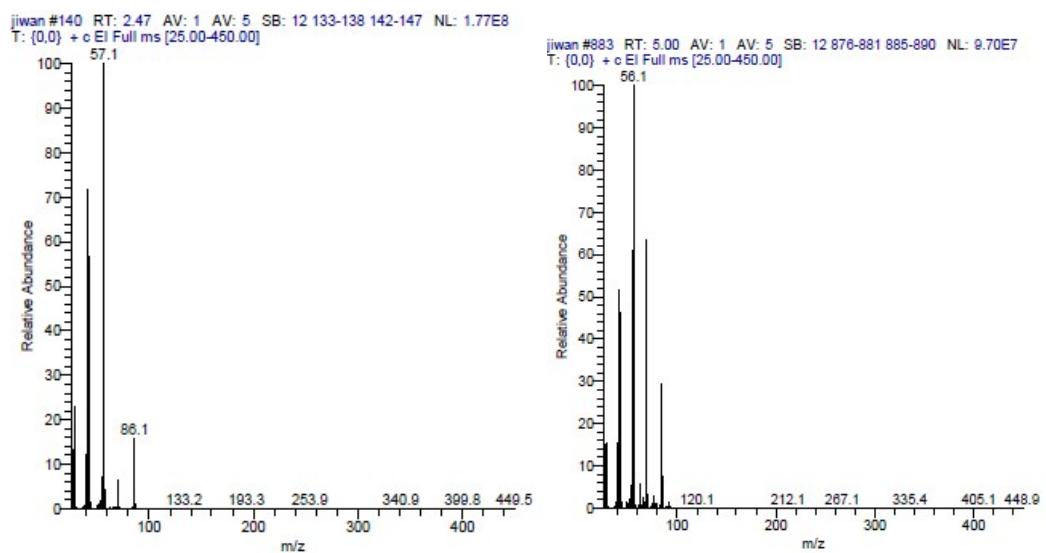
GC-MS of the chlorination reaction mixture of *n*-pentane



## Chlorination of *n*-hexane

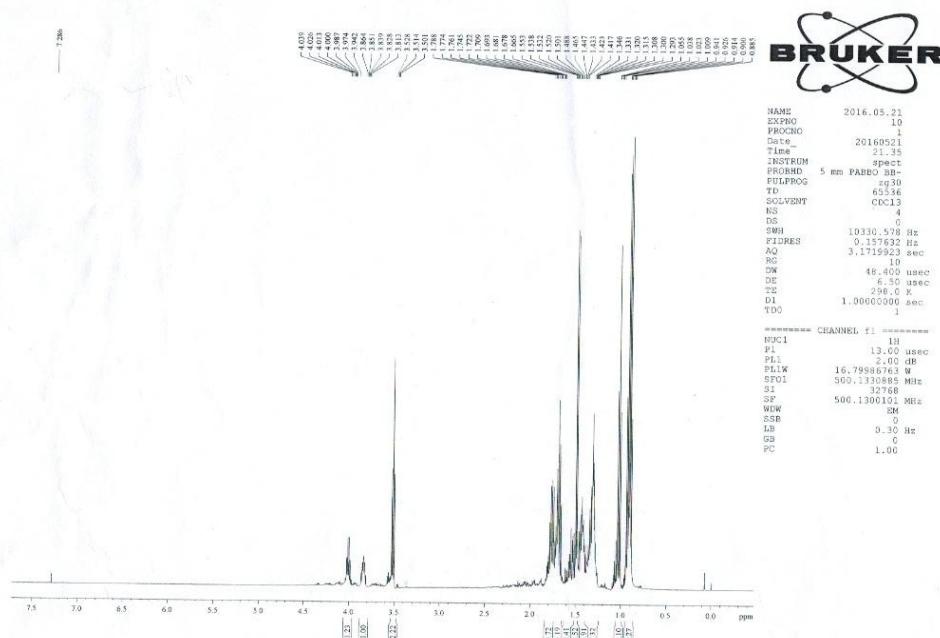


GC of the chlorination reaction mixture of *n*-hexane

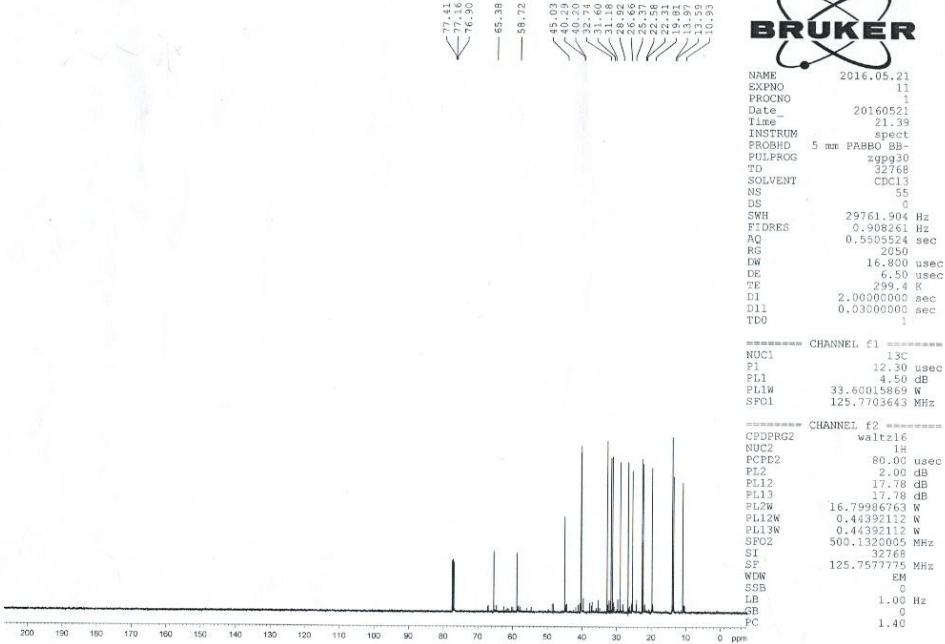


GC-MS of the chlorination reaction mixture of *n*-hexane

liushouxin-zjw-4

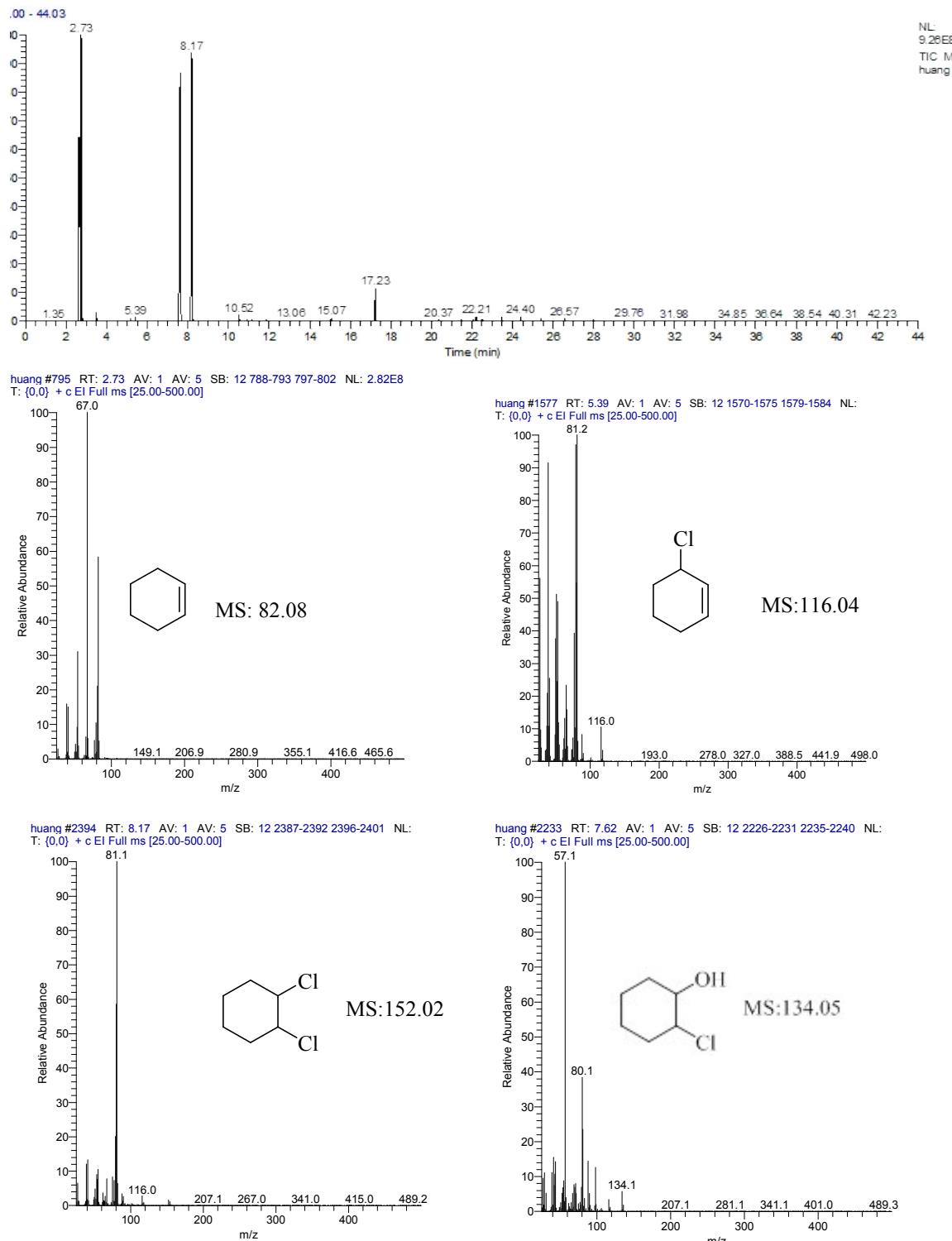


liushouxin-zjw-4



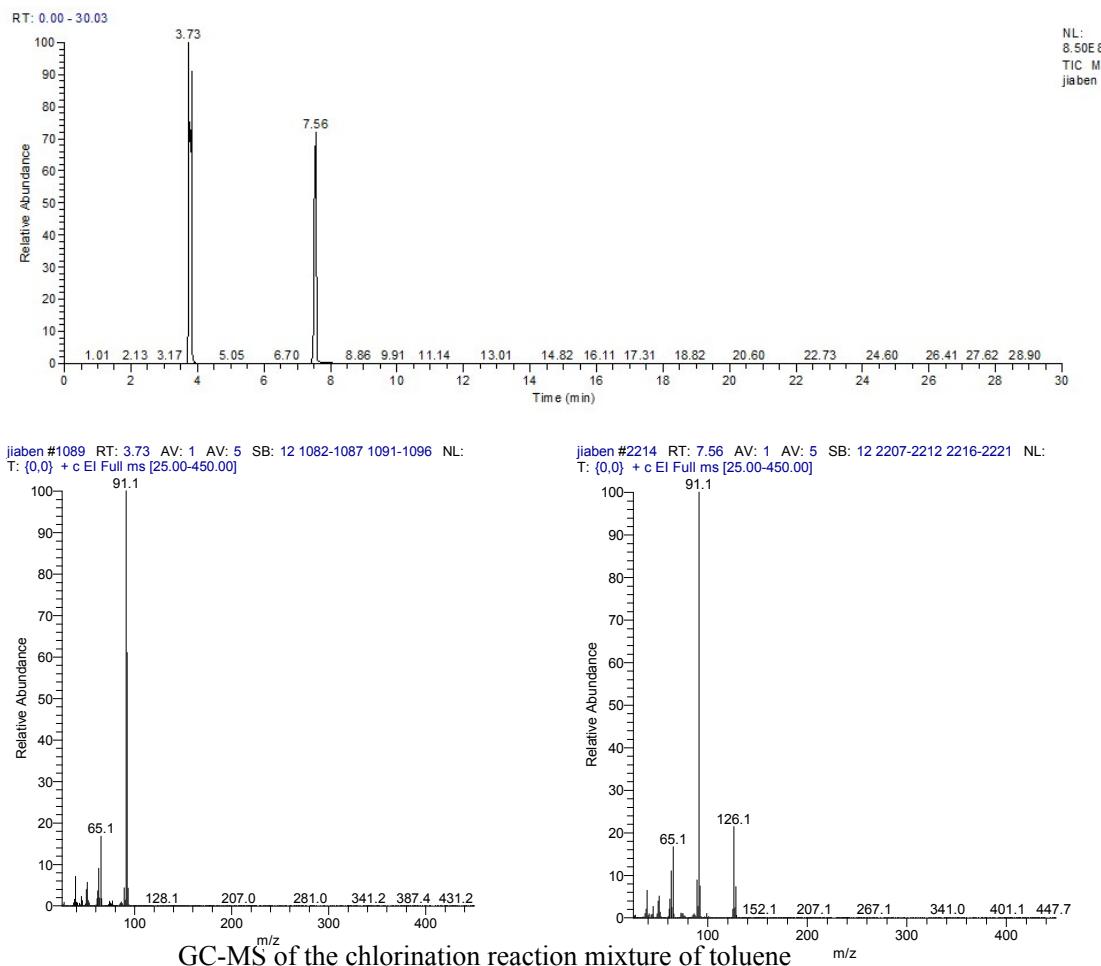
NMR of the chlorination reaction mixture of *n*-hexane

## The chlorination products of cyclohexene

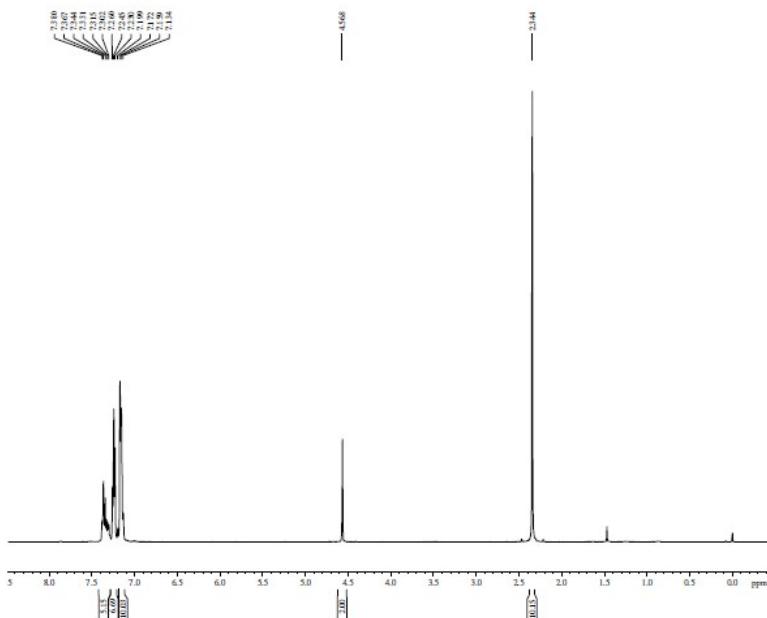


GC-MS of the chlorination reaction mixture of cyclohexene

## The halogenation of $\alpha$ -H at alkylbenzene Chlorination of toluene by Ag/AgCl catalyzation



liushouxin---benzyl chloride---zqlhb

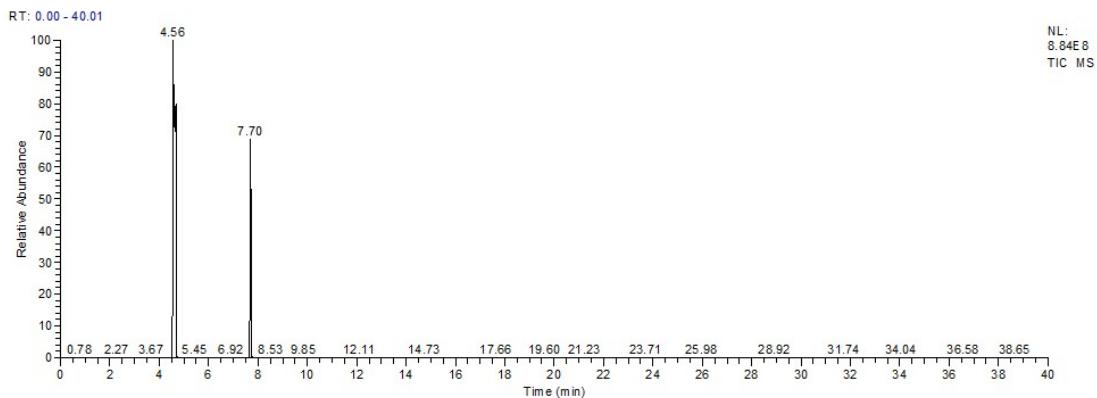


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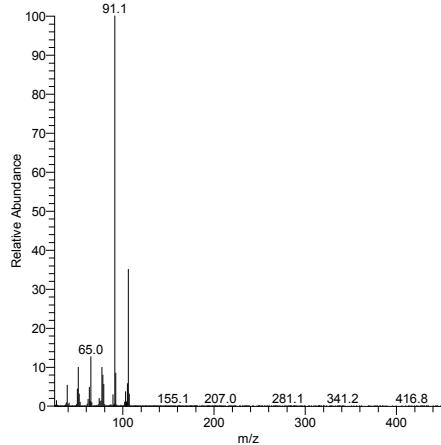
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PROCNO        1
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Time_         14.27
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TD           32768
SOLVENT       CDCl3
NS            1
DS            2
SWH          10330.578 Hz
FIDRES       0.315264 Hz
AQ            1.586000 sec
RG            90.5
DW           48,400 usec
DE            6.50 usec
TE            297.5 K
D1           1.0000000 sec
TD0           1
===== CHANNEL f1 =====
NUC1          1H
P1            13.00 usec
PL1           2.00 dB
PL1W        16.799999 MHz
SP1W        500.1300442 MHz
SI            32768
SF           500.1300442 MHz
WDW          EM
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LB            0.30 Hz
GB           0
PC           1.00

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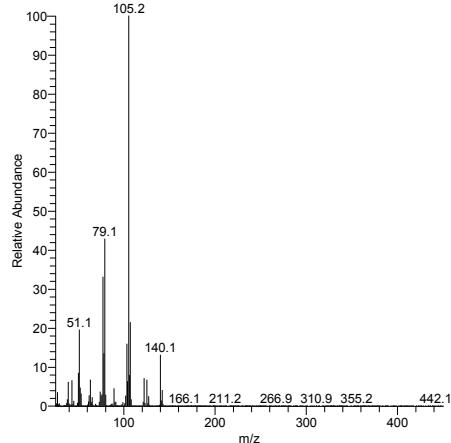
<sup>1</sup>H NMR of the the chlorination reaction mixture of toluene



1 #1331 RT: 4.56 AV: 1 AV: 5 SB: 12 1324-1329 1333-1338 NL: 3.07E8  
T: {0.0} + c El Full ms [25.00-450.00]

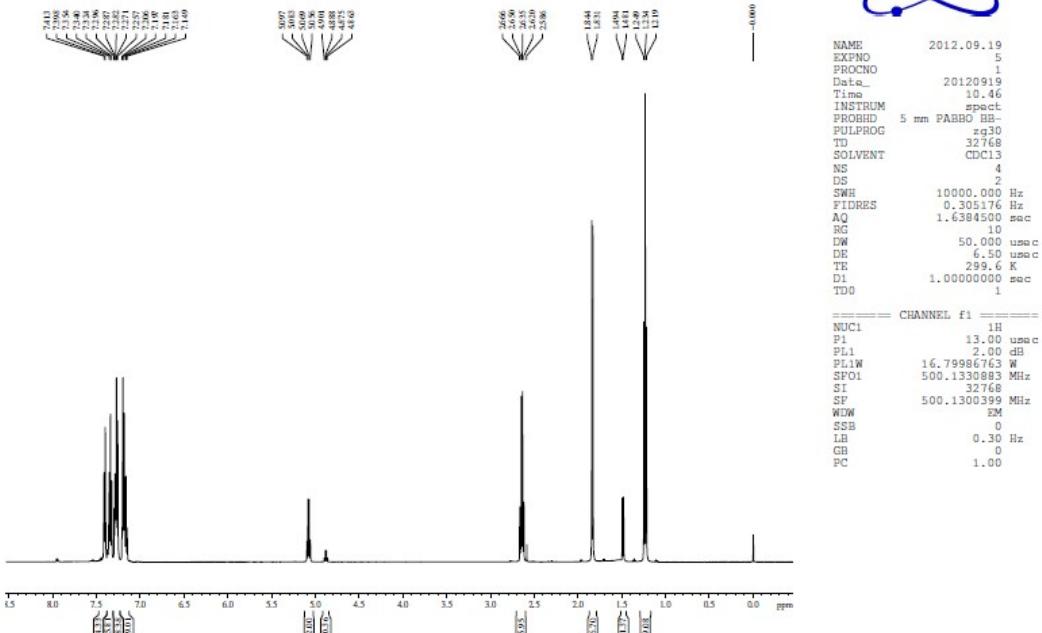


1 #2256 RT: 7.70 AV: 1 AV: 5 SB: 12 2249-2254 2258-2263 NL: 1.52E8  
T: {0.0} + c El Full ms [25.00-450.00]



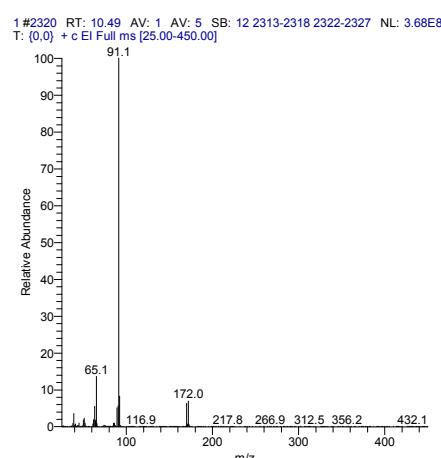
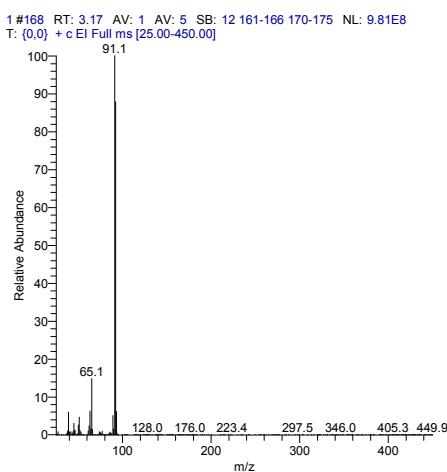
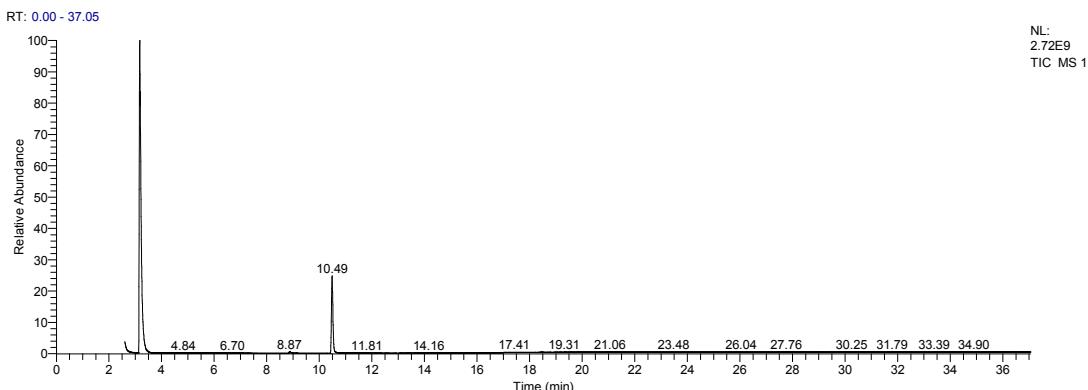
GC-MS of the chlorination reaction mixture of ethylbenzene

liushouxin-zqyb

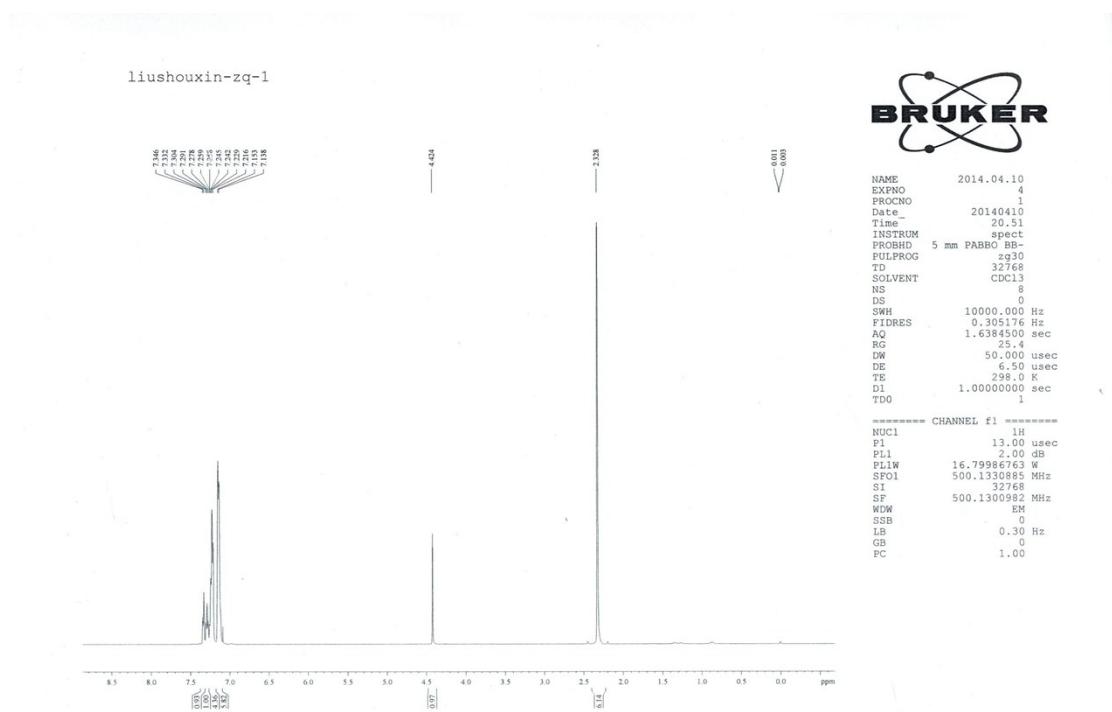


<sup>1</sup>H NMR of the chlorination reaction mixture of ethylbenzene

### Bromination of toluene by the Ag/AgBr catalyzation

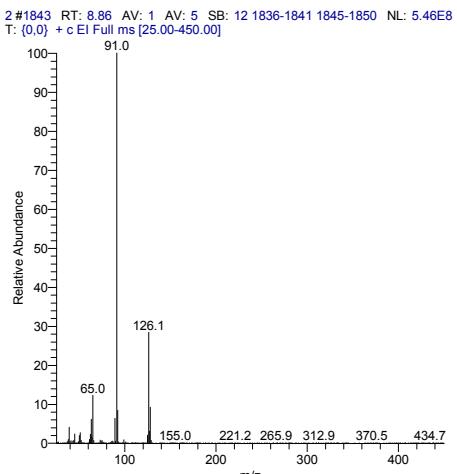
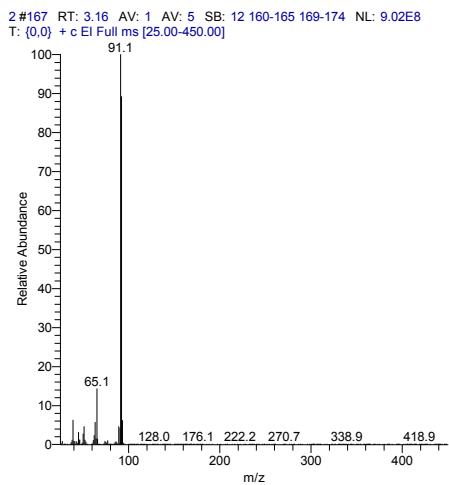
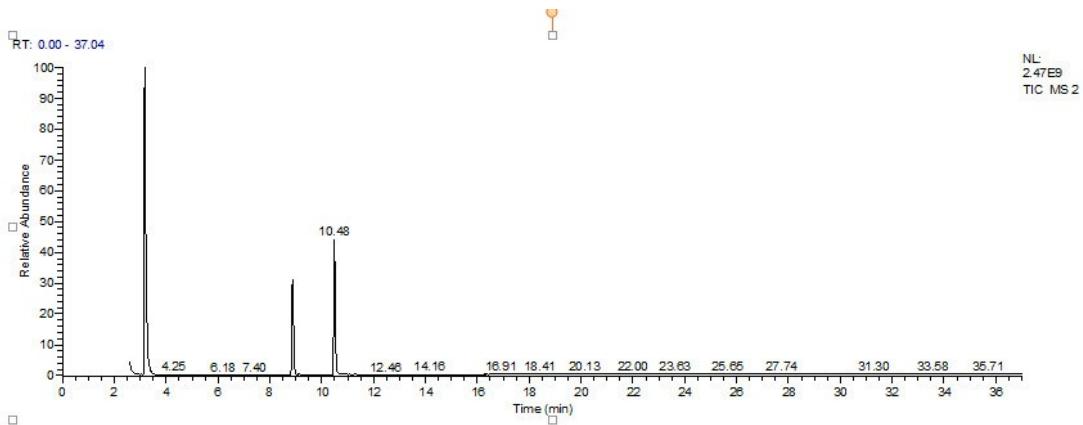


GC-MS of the bromination reaction mixture of toluene

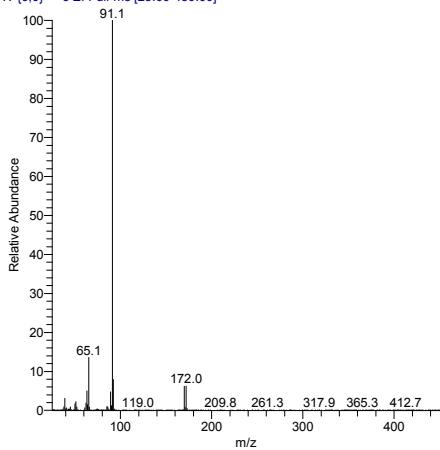


### NMR of the bromination reaction mixture of toluene

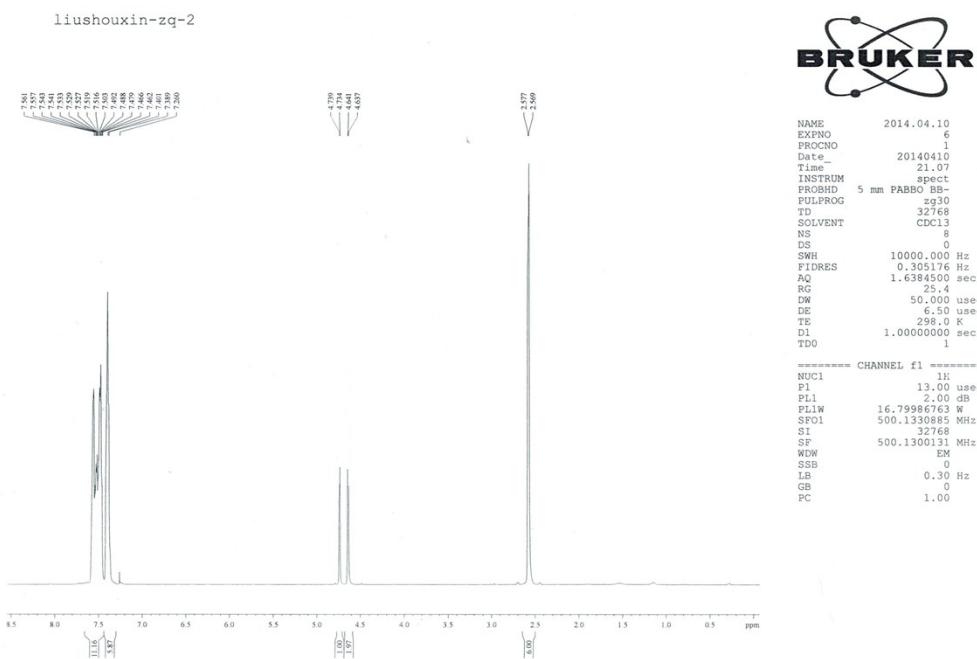
### Bromination of toluene by Ag/AgCl catalyzation



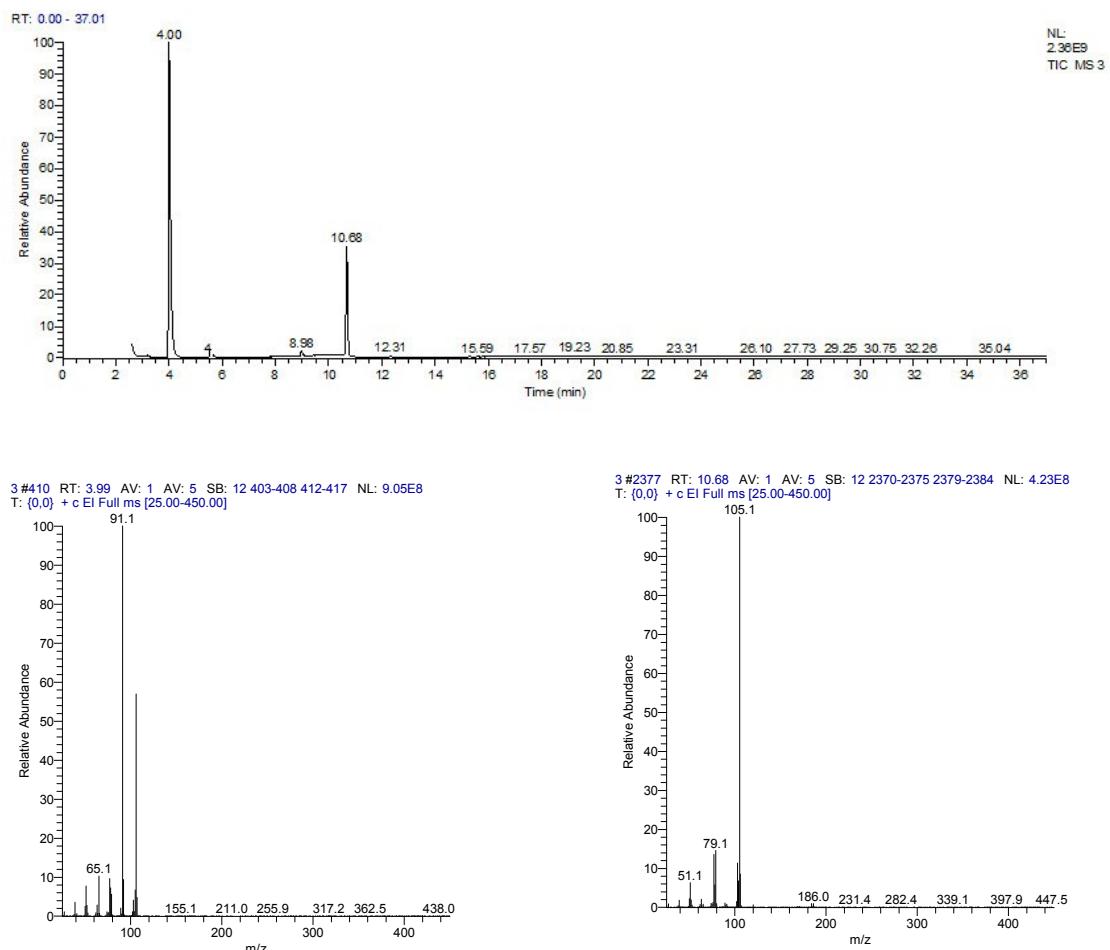
2 #2319 RT: 10.48 AV: 1 AV: 5 SB: 12 2312-2317 2321-2326 NL: 6.23E8  
T: (0,0) + c El Full ms [25.00-450.00]



GC-MS of the bromination reaction mixture of toluene

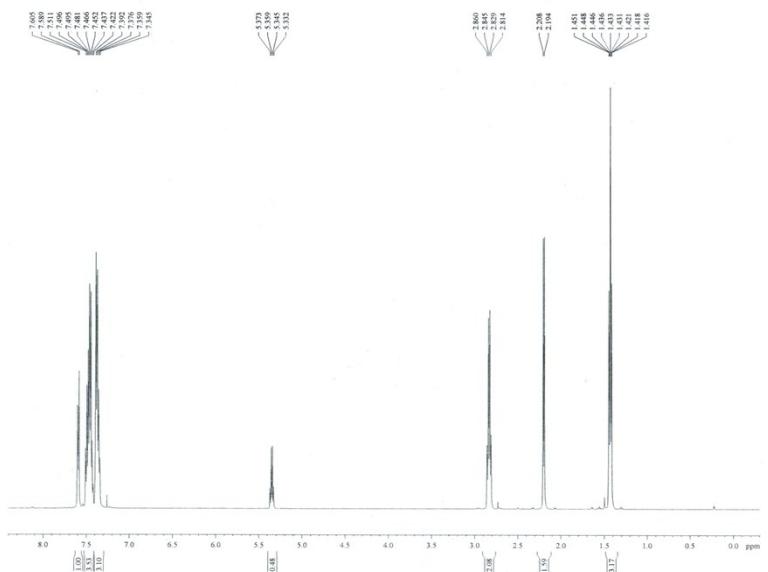


## Bromination of ethylbenzene by Ag/AgBr catalyzation



GC-MS of the bromination reaction mixture of ethylbenzene

liushouxin-zq-3

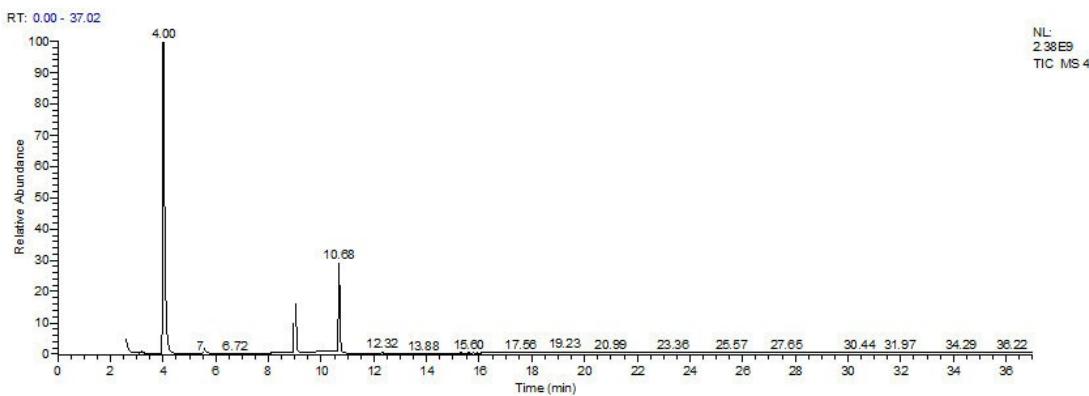


NAME: 2014.04.10  
 EXPNO: 8  
 PROCNO: 1  
 Date.: 20140410  
 Time: 21.22  
 INSTRUM: Bruker  
 PROBHD: 5 mm PABBO BB-  
 PULPROG: zg30  
 TD: 32768  
 SOLVENT: CDCl3  
 NS: 8  
 DS: 0  
 SWH: 10000.000 Hz  
 FIDRES: 0.0305176 Hz  
 AQ: 1.6300 sec  
 RG: 25.4  
 DW: 50.000 usec  
 DE: 6.50 usec  
 TB: 298.0 K  
 D1: 1.0000000 sec  
 TDO: 0

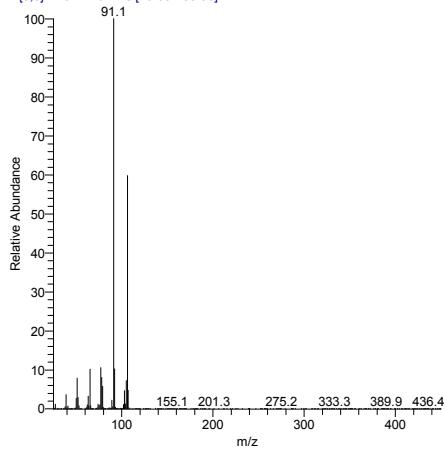
===== CHANNEL f1 =====  
 NUC1: 1H  
 PI: 13.00 usec  
 P1L: 2.00 dB  
 PL1W: 16.79986763 μs  
 SF01: 500.13300135 MHz  
 SI: 32768  
 SF: 500.13300131 MHz  
 WDW: EM  
 SSB: 0  
 LB: 0.30 Hz  
 GB: 0  
 PC: 1.00

NMR of the bromination reaction mixture of ethylbenzene

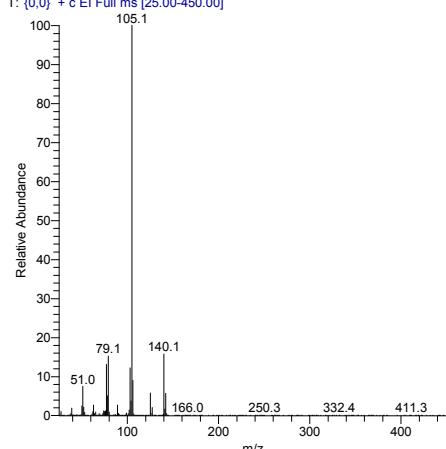
## Bromination of ethylbenzene by Ag/AgCl catalyzation



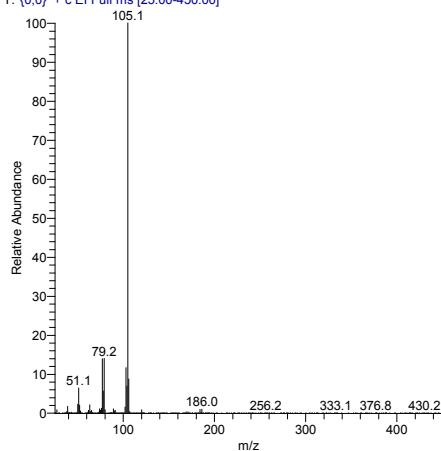
4 #413 RT: 4.00 AV: 1 AV: 5 SB: 12 406-411 415-420 NL: 8.86E8  
T: {0.0} + c El Full ms [25.00-450.00]



4 #1876 RT: 8.98 AV: 1 AV: 5 SB: 12 1869-1874 1878-1883 NL: 5.45E8  
T: {0.0} + c El Full ms [25.00-450.00]



4 #2376 RT: 10.68 AV: 1 AV: 5 SB: 12.2369-2374 2378-2383 NL: 3.38E8  
T: (0,0) + c El Full ms [25.00-450.00]



### GC-MS of the bromination reaxction mixture of ethylbenzene

liushouxin-zq-4



```

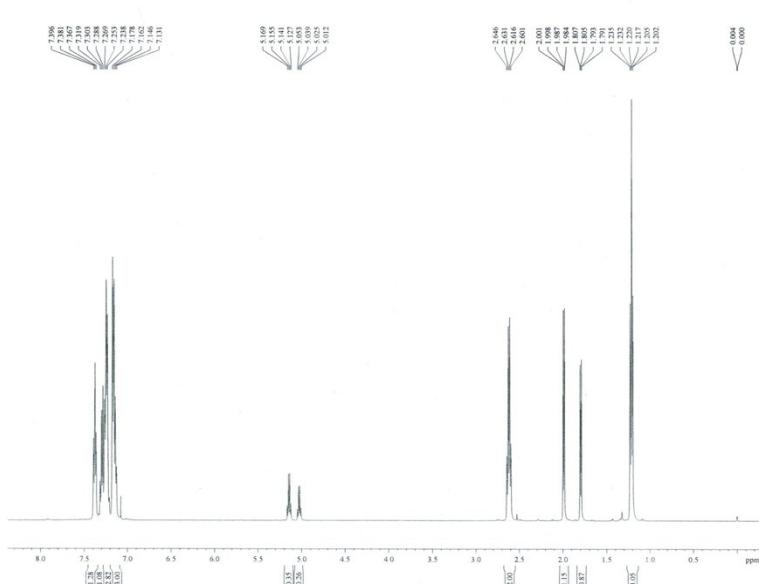
NAME      2014.04.10_05
PRCNO      1
Date      20140410
Time      20.59
INSTRUM   spect
PROD      5 mm PABBO BRU
PULPROG  zg30
TD        32768
SOLVENT   CDCl3
NS        8
DS        0
SWH      10000.000 Hz
FIDRES   0.305176 Hz
AQ        1.6384500 sec
RG        25.00
DW        5.00 usec
DE        6.50 usec
TE        298.0 K
D1        1.0000000 sec
TDO      1

```

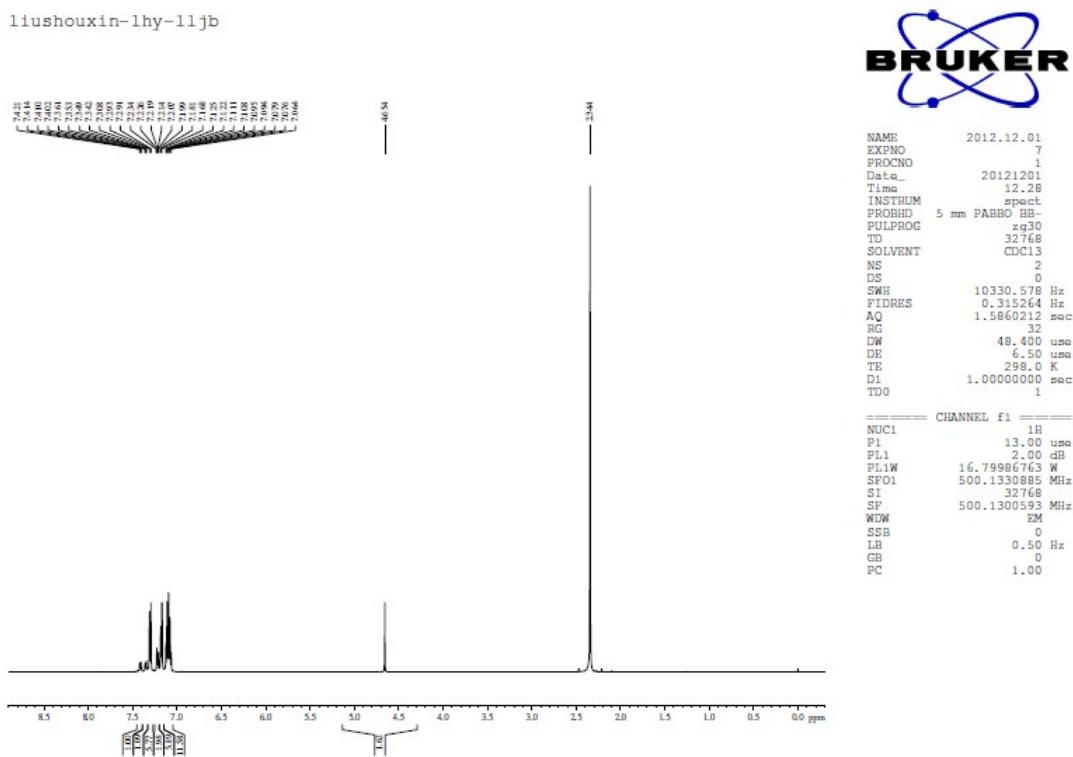
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===== CHANNEL f1 =====
NUC1      1H
P1        13.00 usec
PL1       0.00 dB
PL1W     16.79986763 M
SF01      500.1330885 MHz
SI        32768
SF      500.1301034 MHz
WDW      EM
SSB      0
LB        0.30 Hz
GB      0
FC        1.00

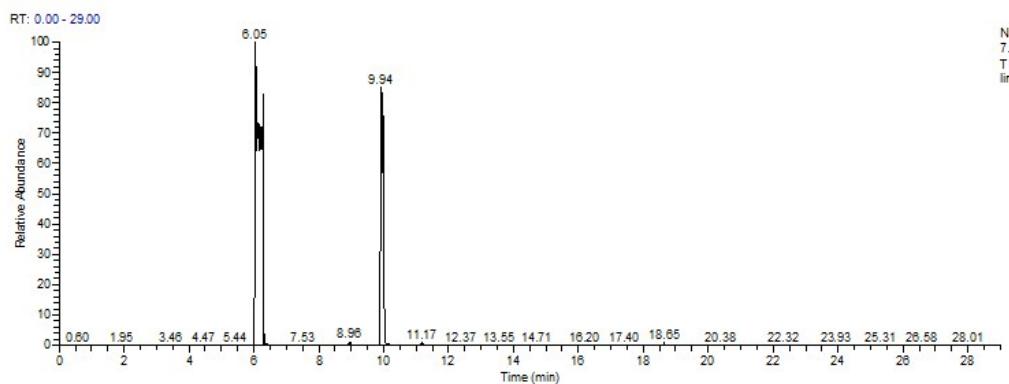
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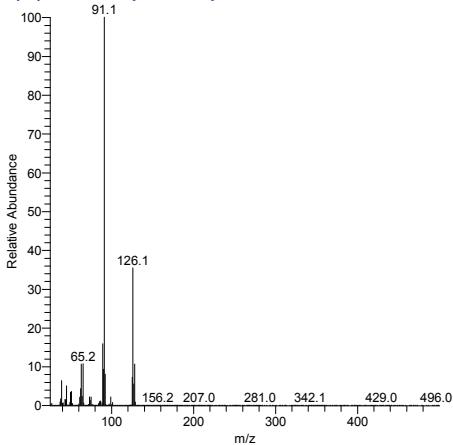
### NMR of the bromination reaction mixture of ethylbenzene



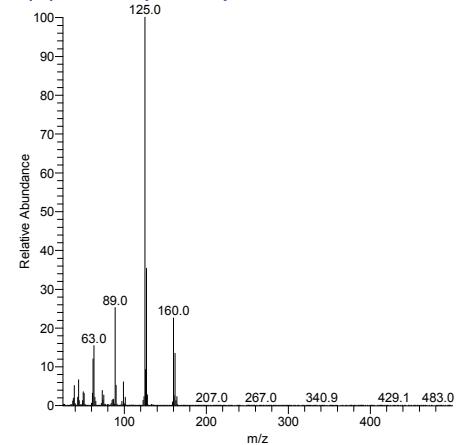
<sup>1</sup>H NMR of the chlorination reaction mixture of 2-chlorotoluene



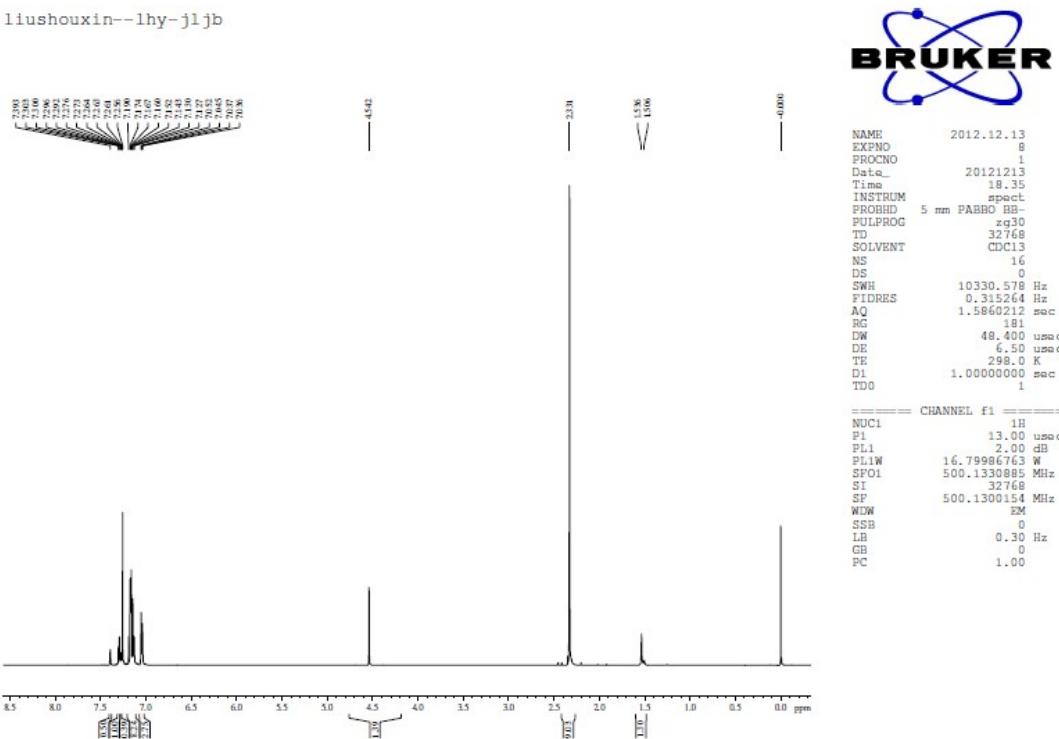
linlvjiaben #1770 RT: 6.05 AV: 1 AV: 5 SB: 12 1763-1768 1772-1777 NL:  
T: {0,0} + c El Full ms [25.00-500.00]



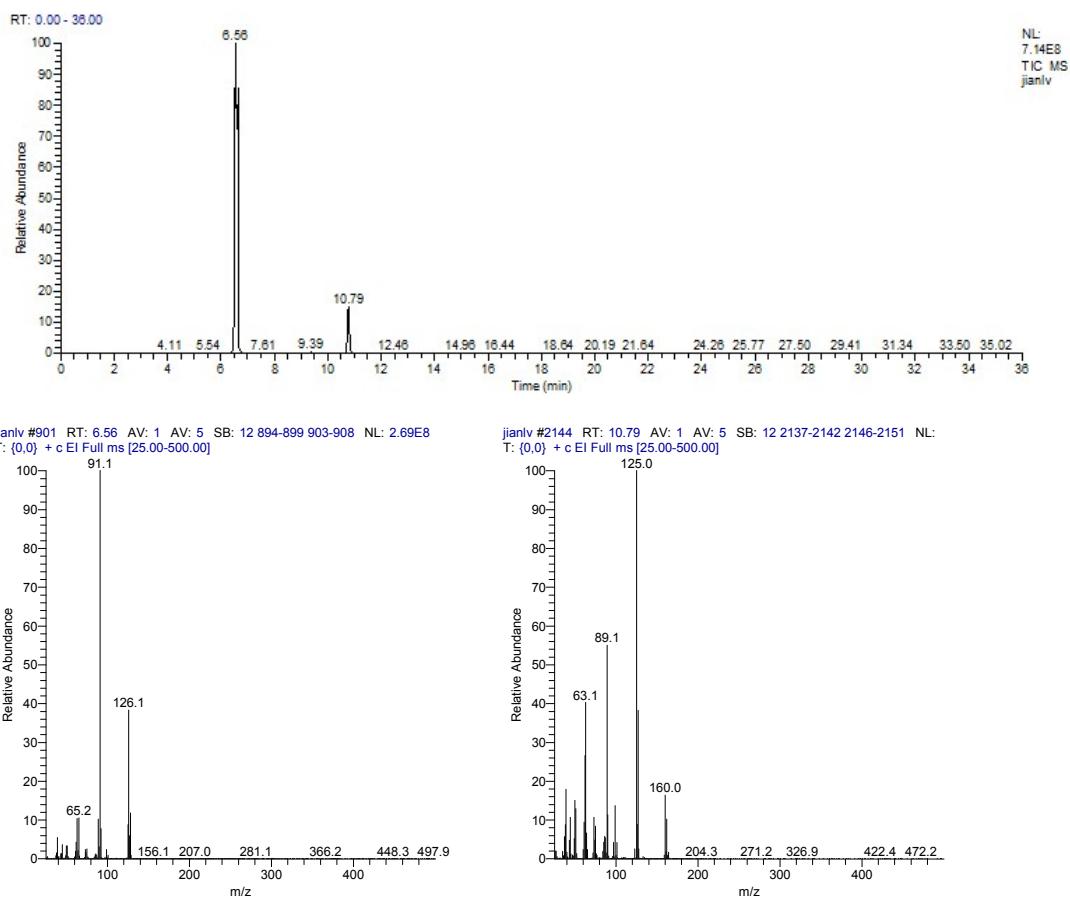
linvjiaben #2913 RT: 9.94 AV: 1 AV: 5 SB: 12 2906-2911 2915-2920 NL:  
T: {0,0} + c EI Full ms [25.00-500.00]



## GC-MS of the chlorination reaction mixture of 2-chlorotoluene

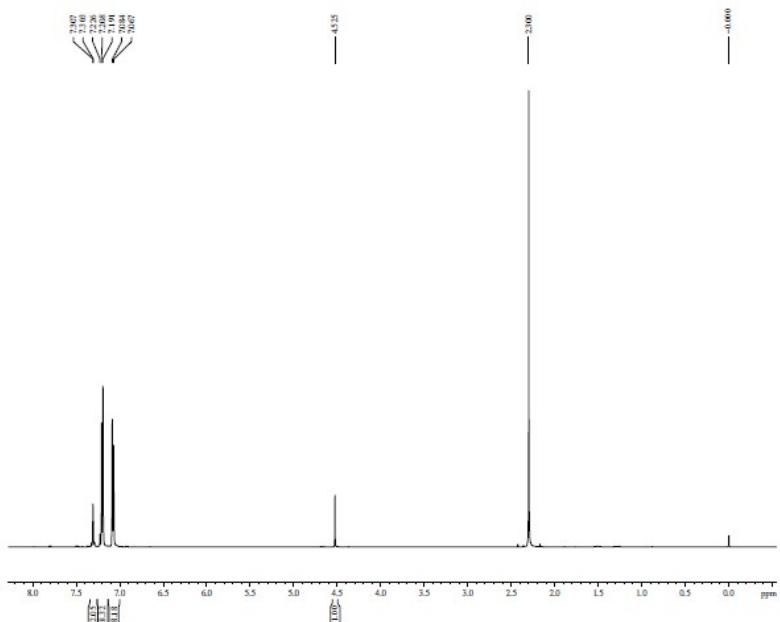


<sup>1</sup>H NMR of the chlorination reaction mixture of 3-chlorotoluene



## GC-MS of the chlorination reaction mixture of 3-chlorotoluene

liushouxin-lhy-dljb



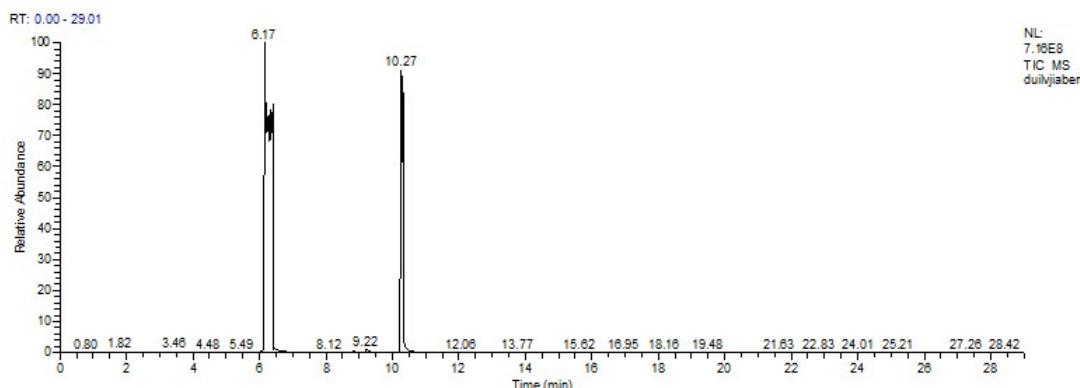
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PROCNO    8
PROCNO    1
Date_    20121201
Time   12.39
INSTRUM spect
PROBODM  5 mm PABBO
PULPROG zg30
TD      32768
SOLVENT   CDCl3
NS       4
DS        0
SWH     10330.578 Hz
FIDRES   0.3152612 Hz
AQ      1.5860212 sec
RG      80.6
DW      48.400 usec
DE       6.50 usec
TE      298.0 K
D1      1.0000000 sec
TD0      1

===== CHANNEL f1 =====
NUC1           1H
P1      13.00 usec
PL1      1.00 dB
P1,W     16.799967644 MHz
SF01    500.1330885 MHz
SI      32768
SF      500.1300303 MHz
WDW          EM
SSB          0
LB      0.50 Hz
GB      0
PC      1.00

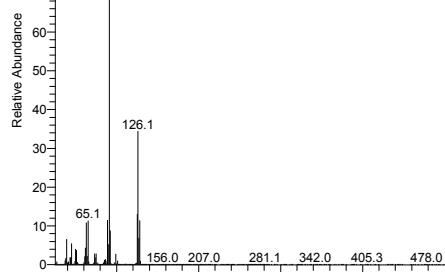
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<sup>1</sup>H NMR of the chlorination reaction mixture of 4-chlorotoluene

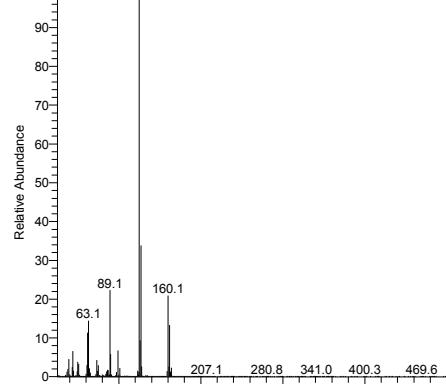


RT: 0.00 - 29.01  
T: (0.0) + c El Full ms [25.00-500.00]

dulvjaben #1805 RT: 6.17 AV: 1 AV: 5 SB: 12 1798-1803 1807-1812 NL:  
T: (0.0) + c El Full ms [25.00-500.00]

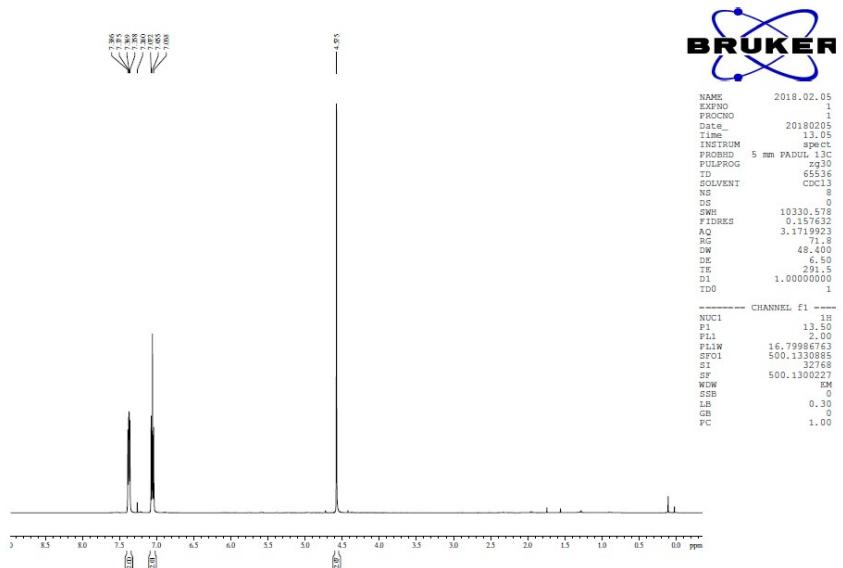


dulvjaben #3013 RT: 10.28 AV: 1 AV: 5 SB: 12 3006-3011 3015-3020  
T: (0.0) + c El Full ms [25.00-500.00]

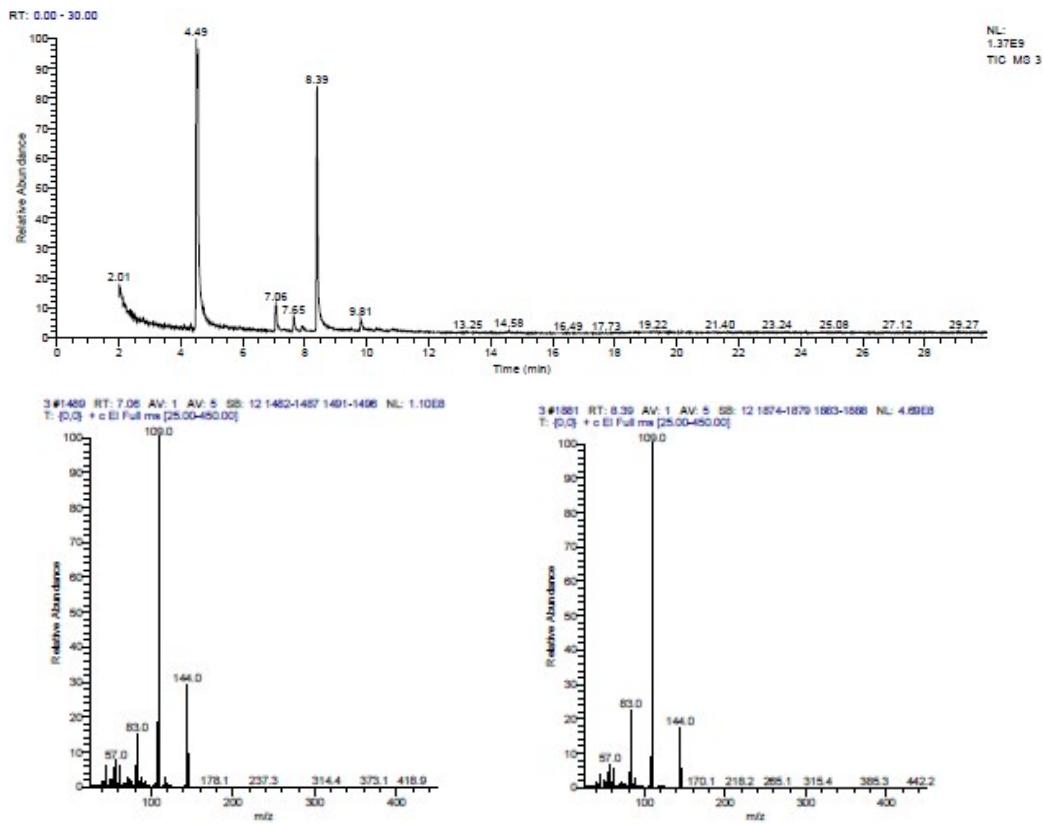


GC-MS of the chlorination reaction mixture of 4-chlorotoluene

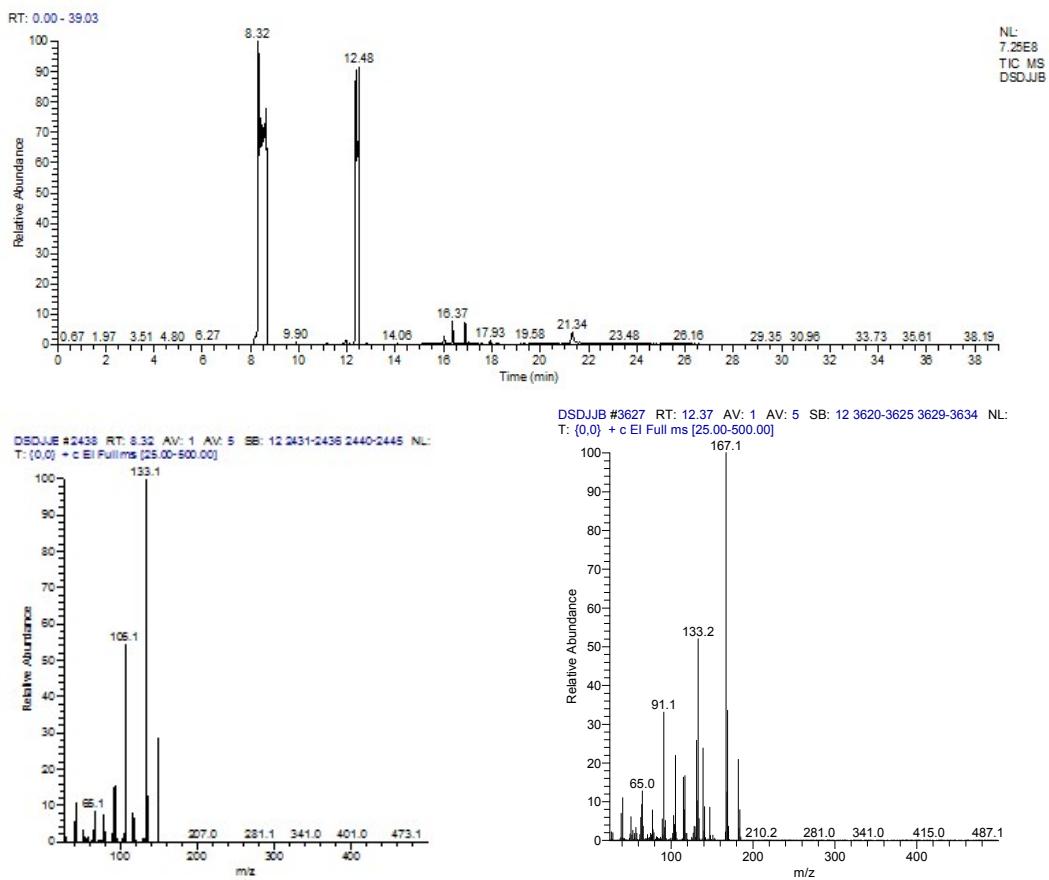
liushouxin-TZQ-4



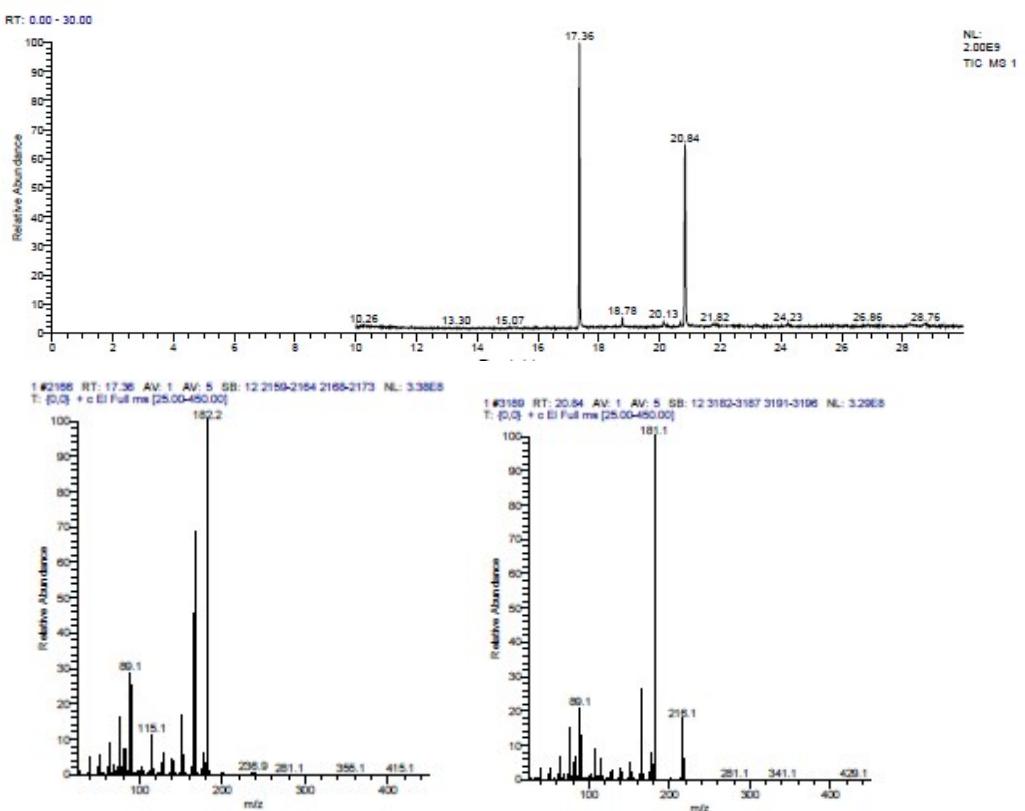
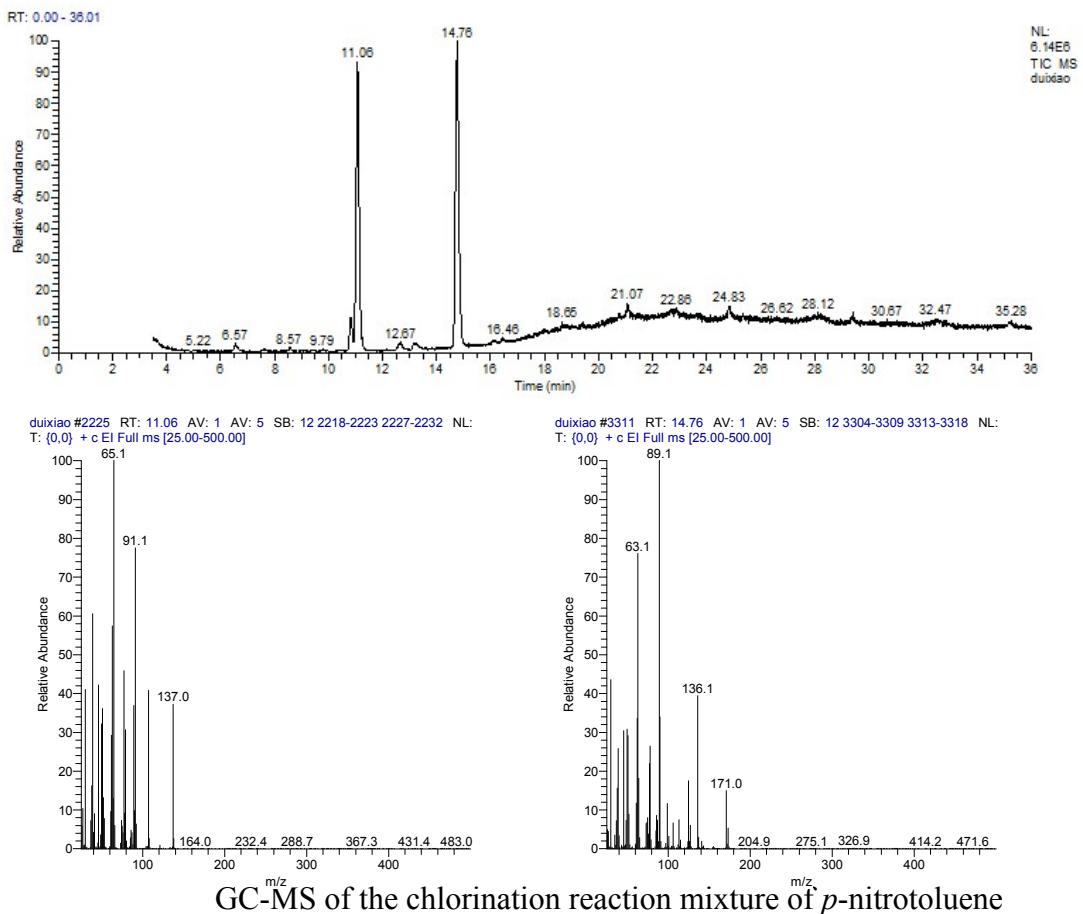
### <sup>1</sup>H NMR of the chlorination reaction mixture of 4-fluorotoluene



### GC-MS of the chlorination reaction mixture of 4-fluorotoluene



GC-MS of the chlorination reaction mixture of 4-*t*-butyltoluene



GC-MS of the chlorination reaction mixture of 4,4'-dimethylbiphenyl