Supporting Information

Highly selective halogenation of unactivated C(sp^3)-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-Kα 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 (λ>290nm, PLS-SXE300CUV, perfectlight Instruments Co. Ltd., Beijing) was used as light source, and the average light intensity was 78.5mw/cm^{-2} (UV-A radiation meter). GC were recorded on SHIMADZU 2014C . GC-MS data were measured with Thermo Scientific ISQ QD. ^{1}HNMR were recorded on a Bruker Avance II 500 spectrometer in CDCl3 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 $AgNO_3$ 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 $AgNO_3$. 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.

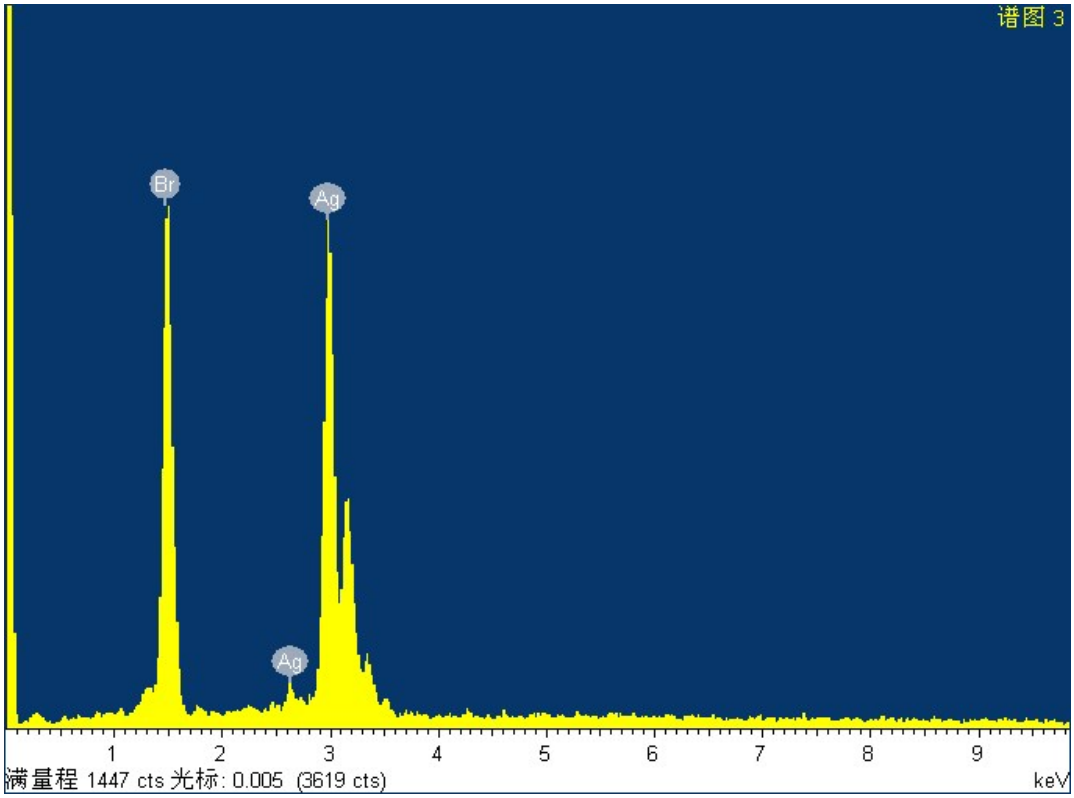
Nano Ag/AgBr characterization

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

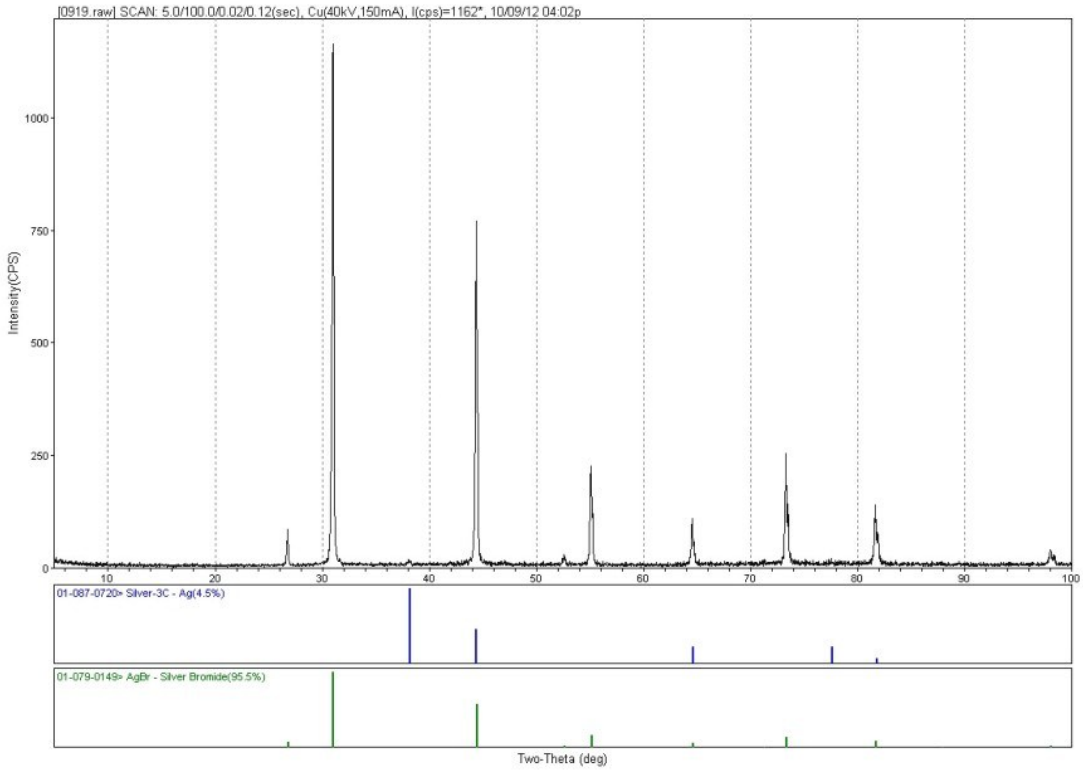
Br KBr 1-Jun-1999 12:00 AM

Ag Ag 1-Jun-1999 12:00 AM

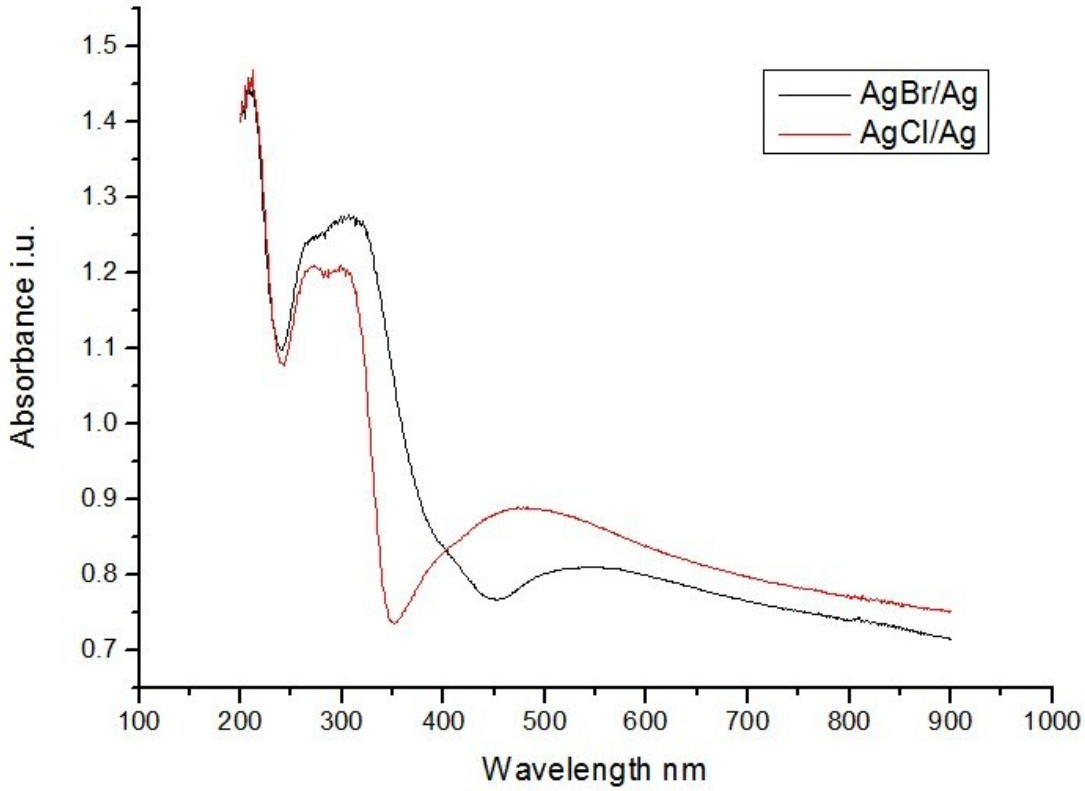
Elem.	Weight %	Atom %
Br L	40.43	47.81
Ag L	59.57	52.19
Total	100.00	

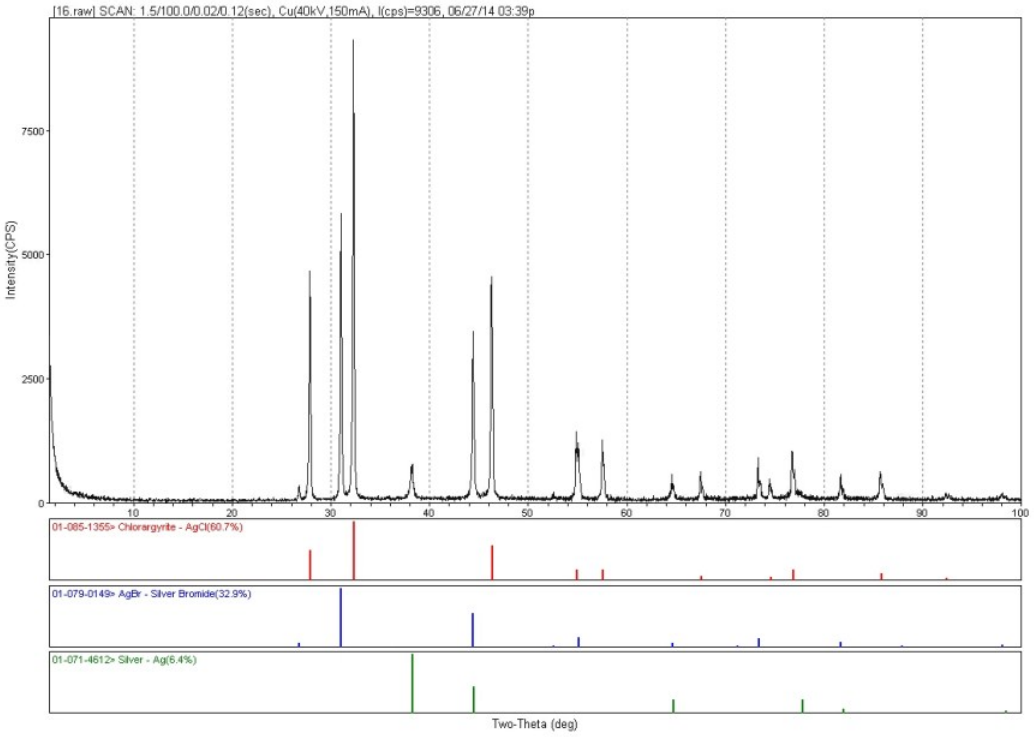


Ag /AgBr, XRD, nano Ag 4.5 %mol



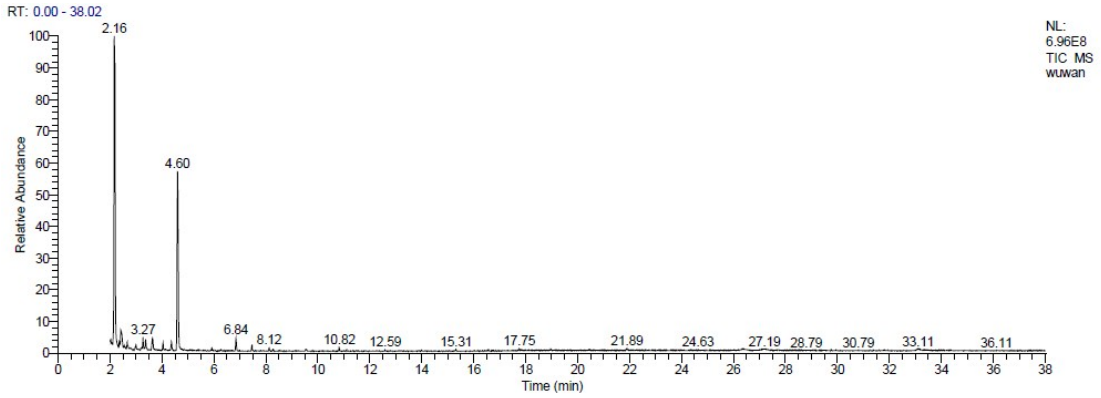
Ag/AgBr and Ag/AgCl, UV-Vis diffuse reflectance spectra



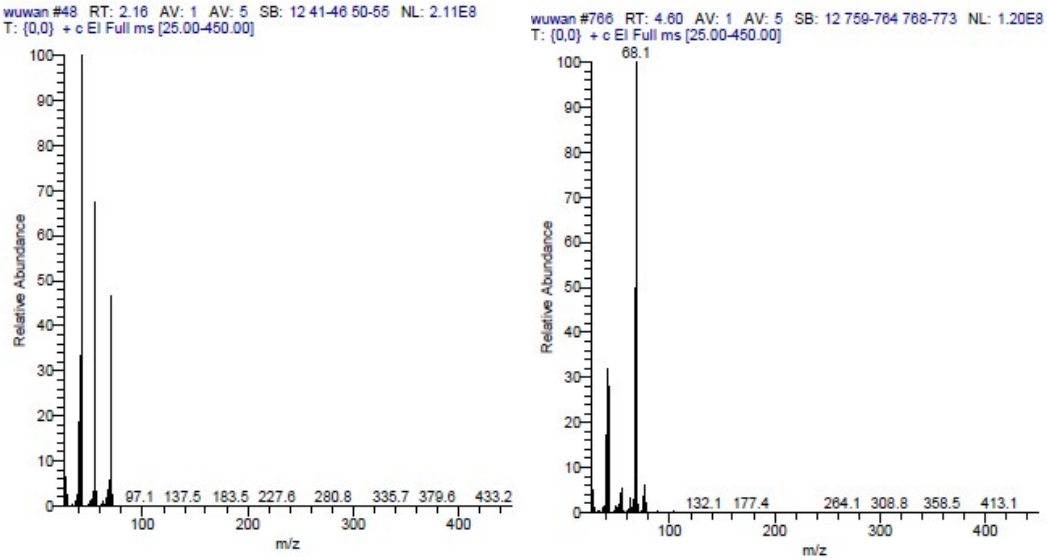


X-ray diffraction of catalyst Ag@AgCl after the reaction

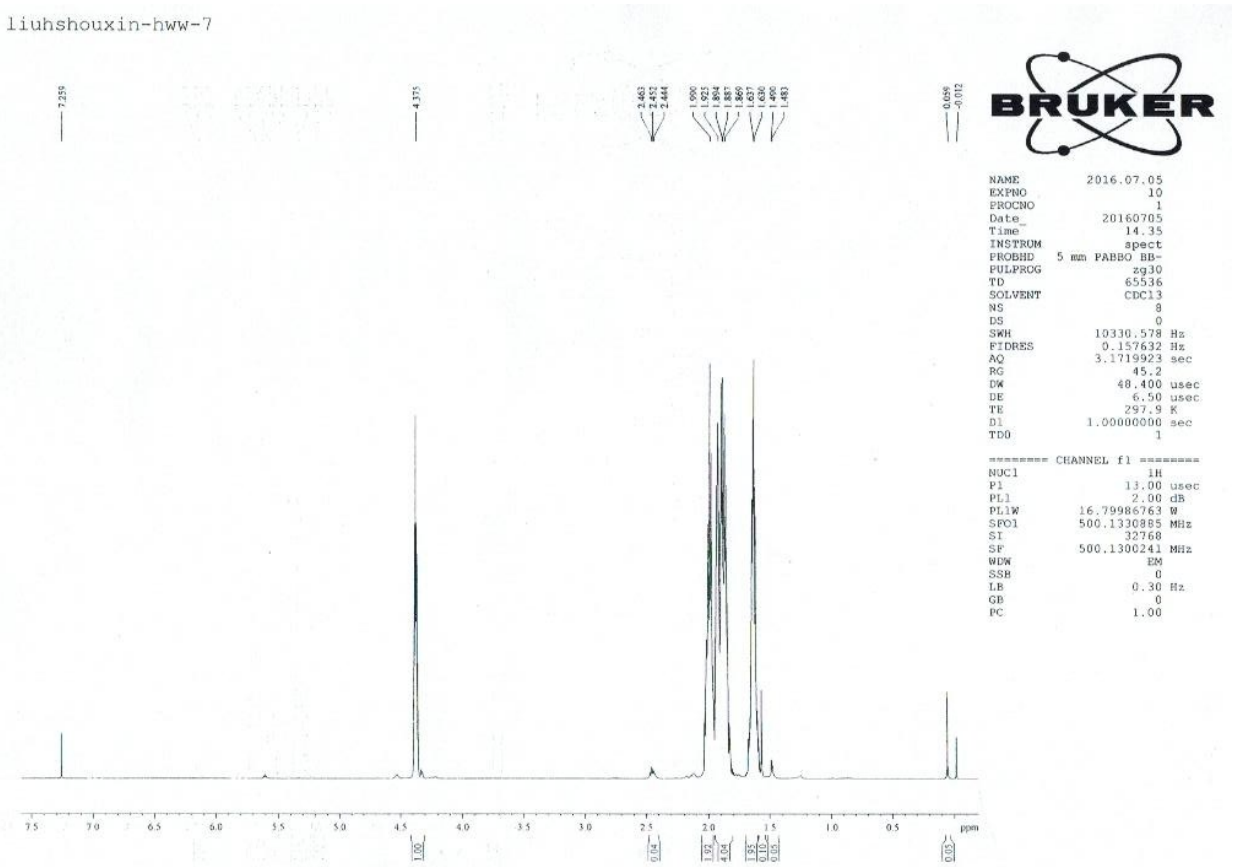
The photocatalytic halogenation of alicyclic hydrocarbon
The reaction solution of cyclopentane chlorination

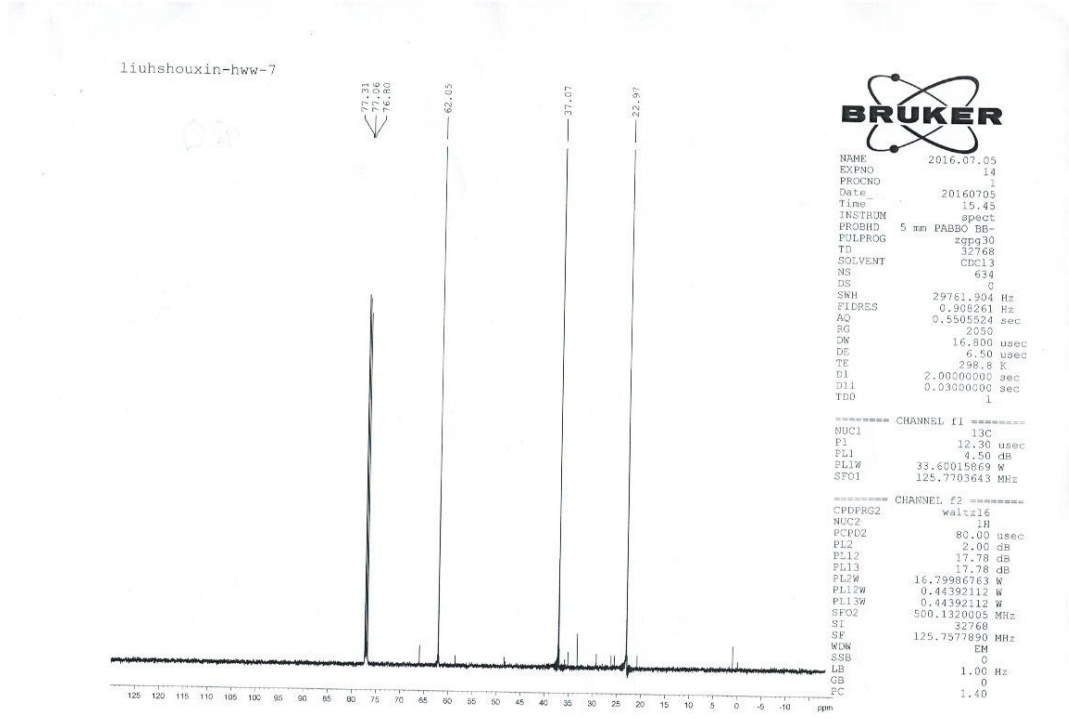


GC of the cyclopentane chlorination reaction mixture



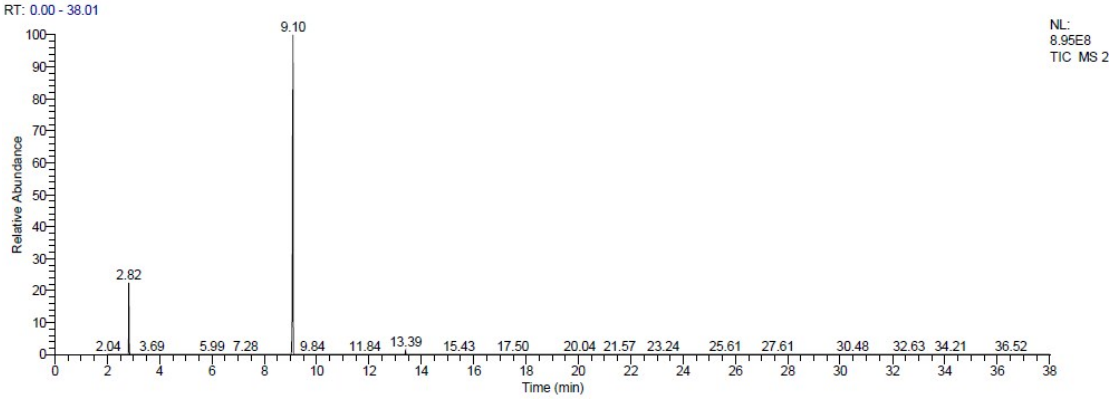
GC-MS of the cyclopentane chlorination reaction solution





NMR of the cyclopentane chlorination reaction mixture

The reaction solution of cyclopentane bromination



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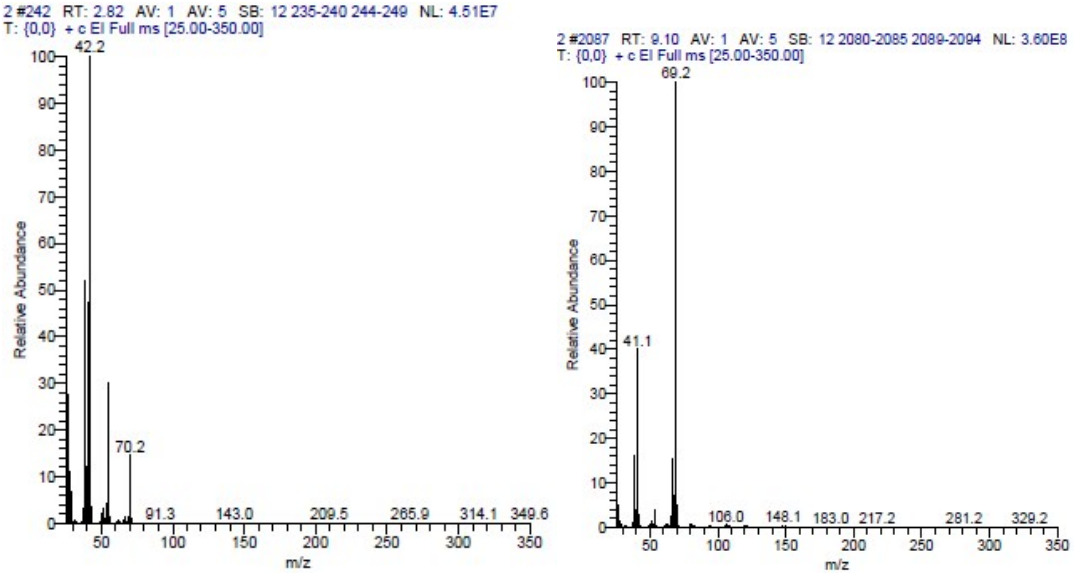

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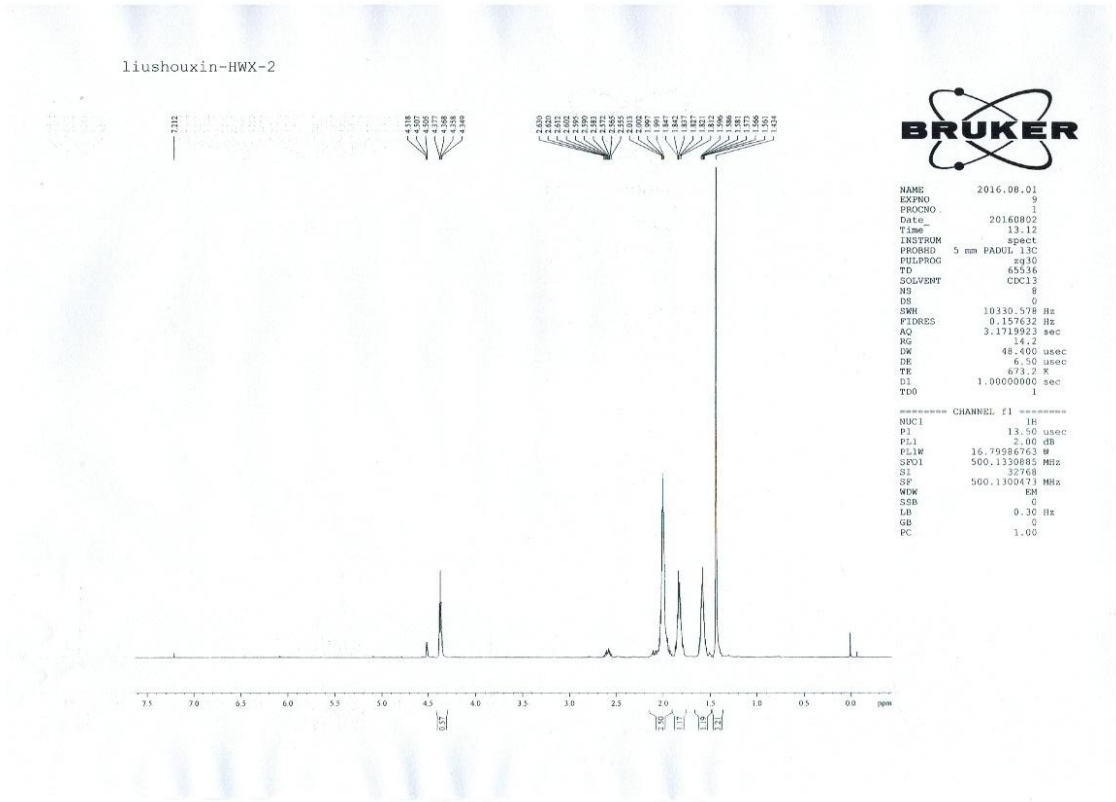
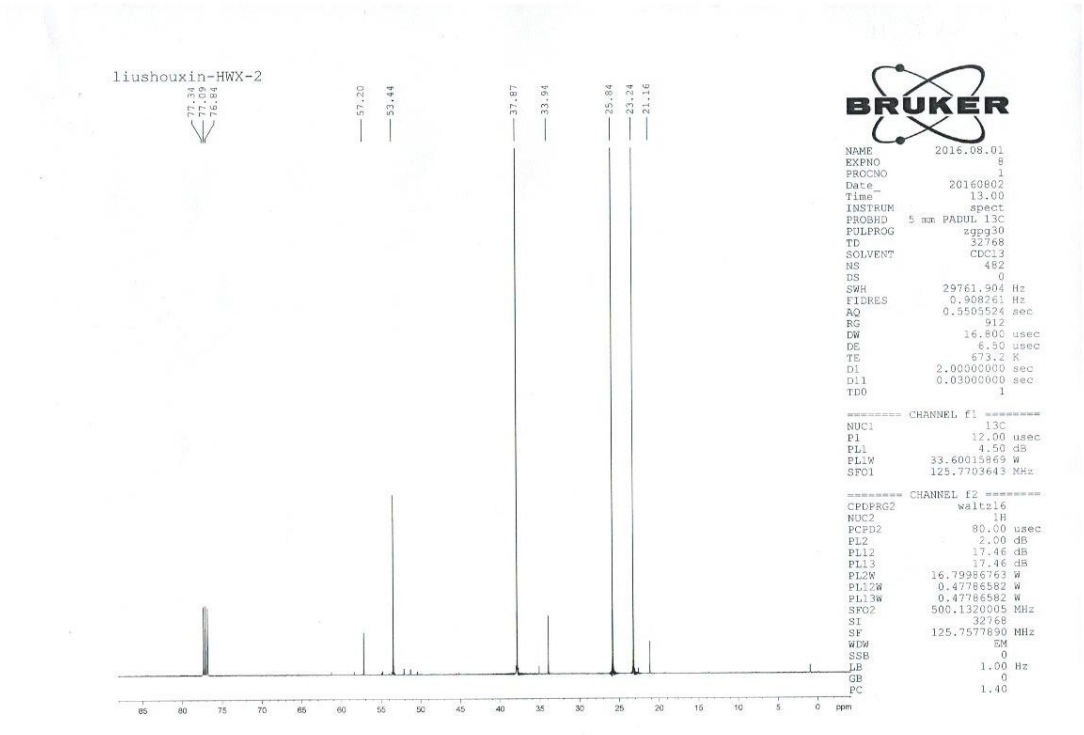
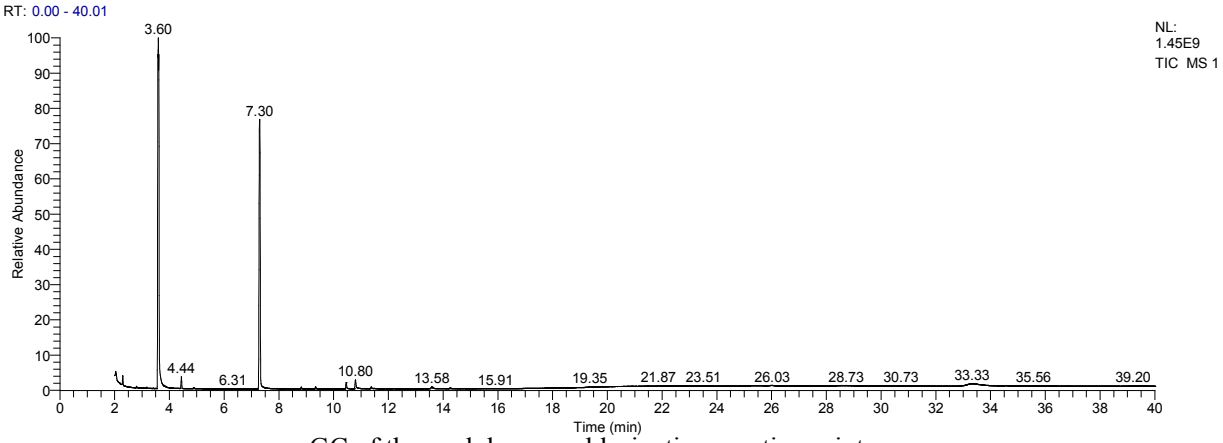




NMR of the cyclopentane bromination reaction mixture from Ag/AgCl catalysis

The reaction solution of cyclohexane chlorination



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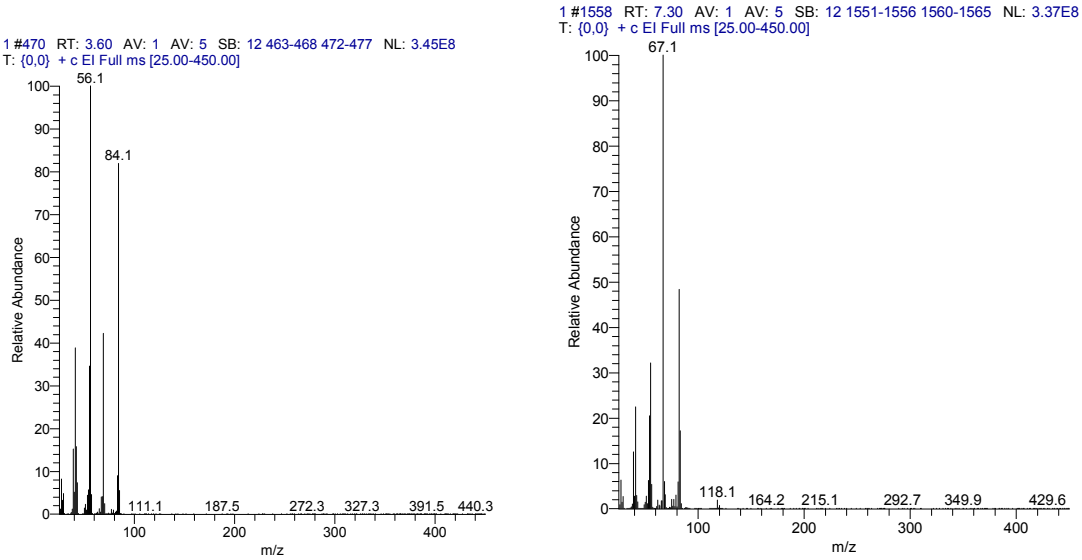

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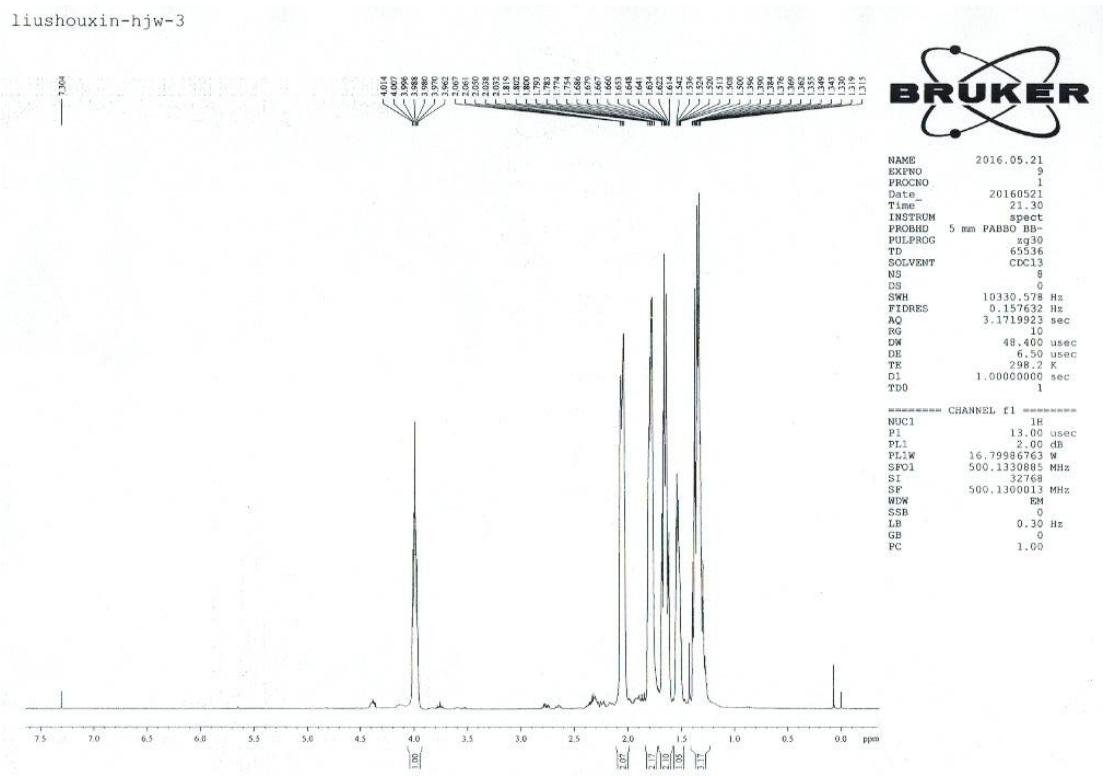
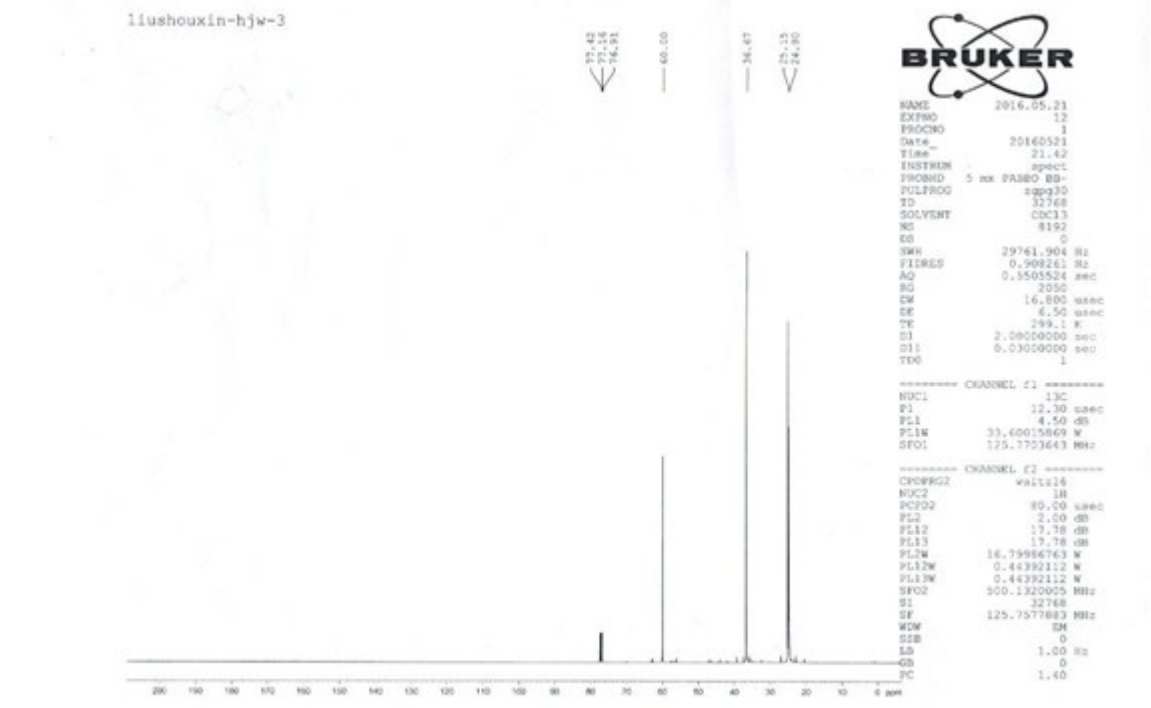
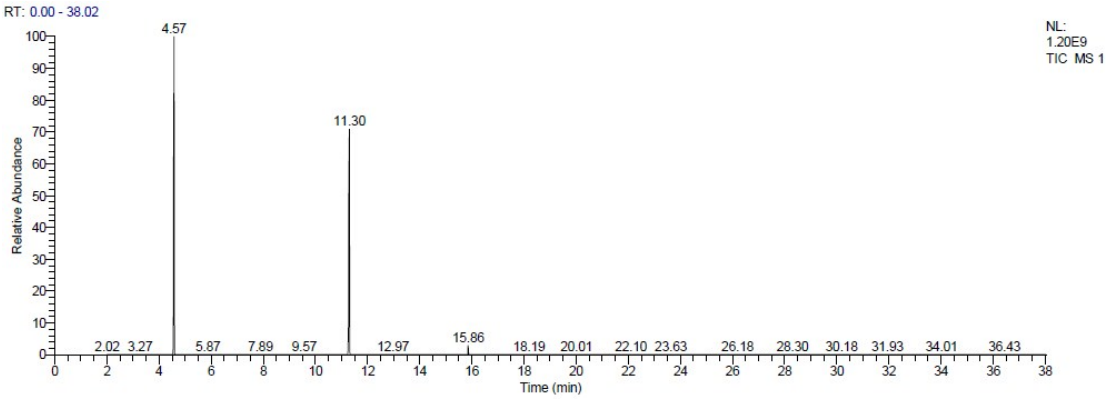




NMR of the cyclohexane chlorination reaction mixture

The reaction solution of cyclohexane bromination



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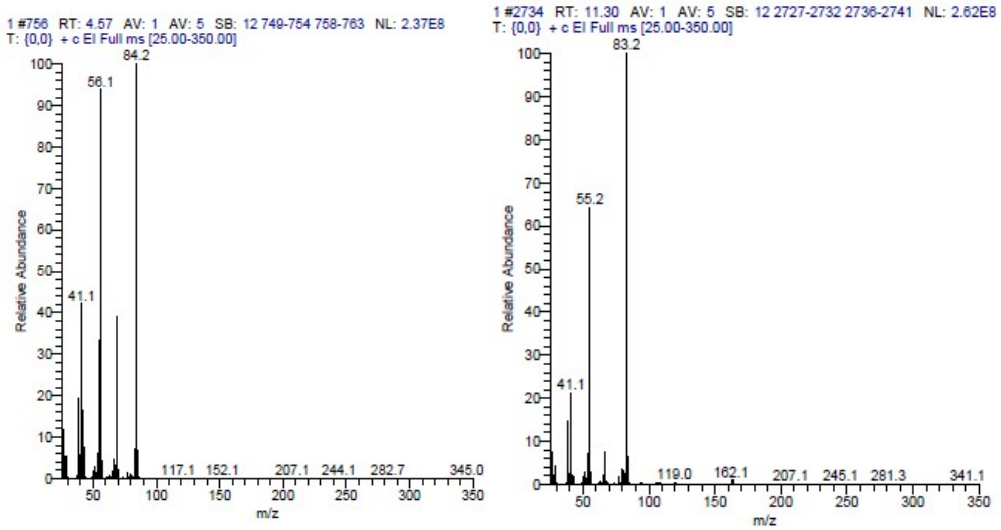
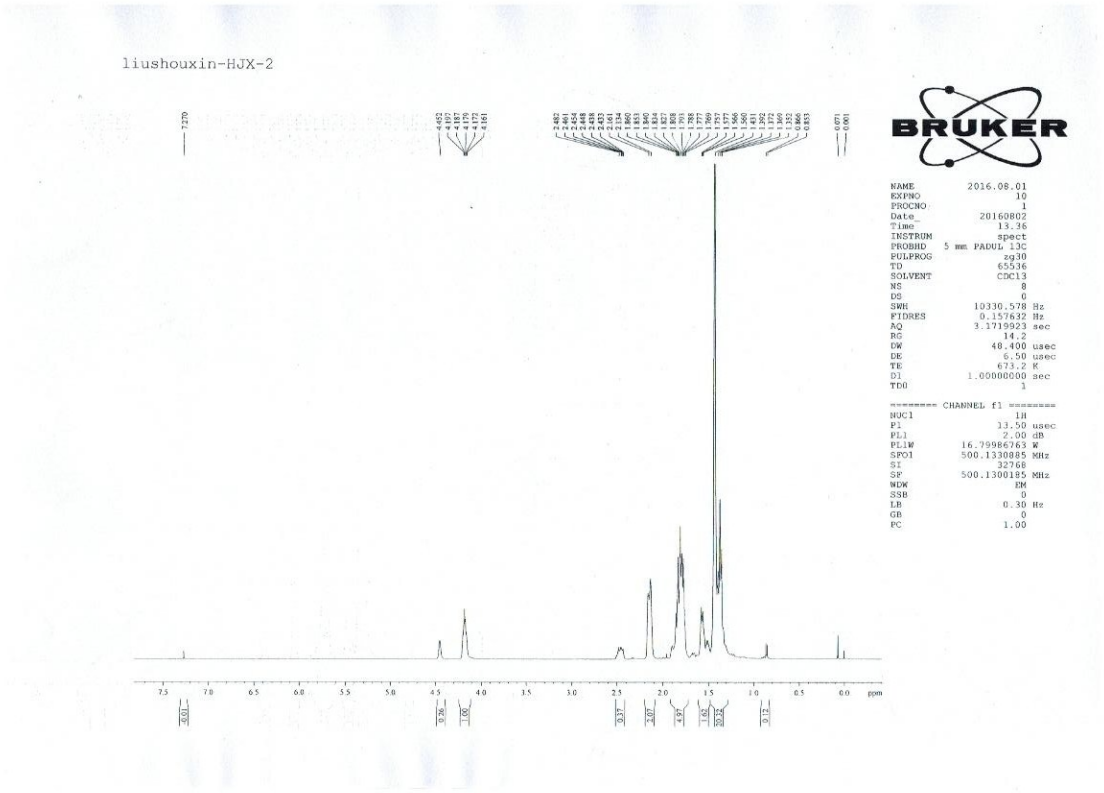
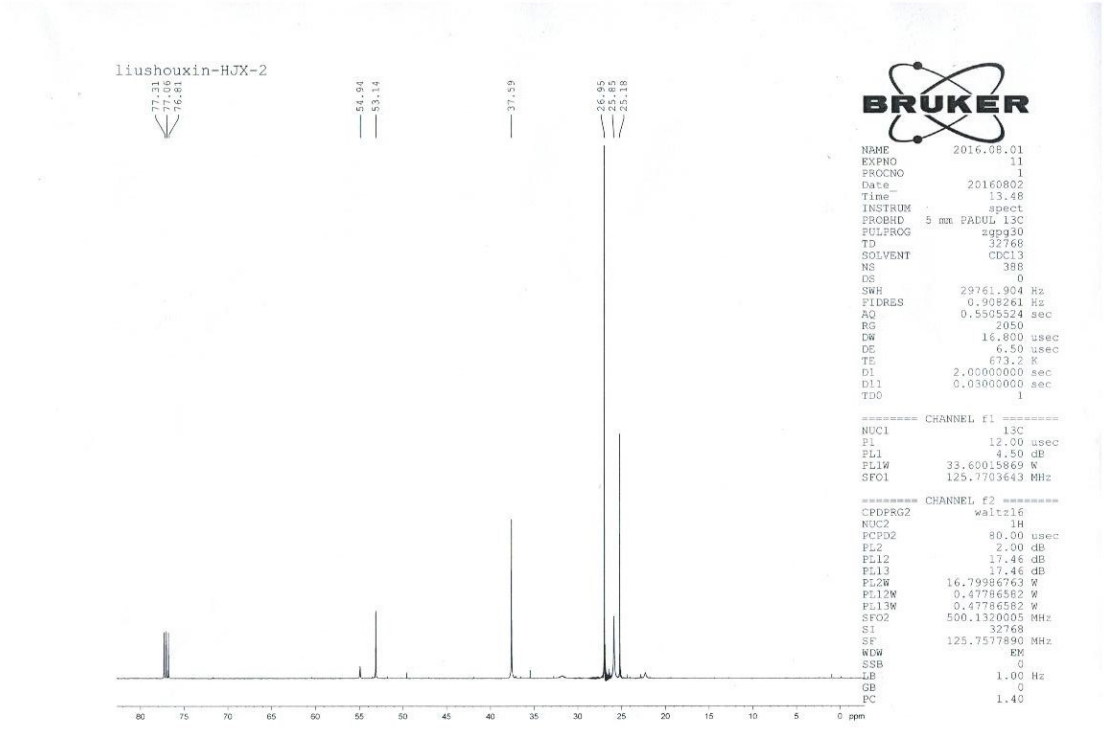


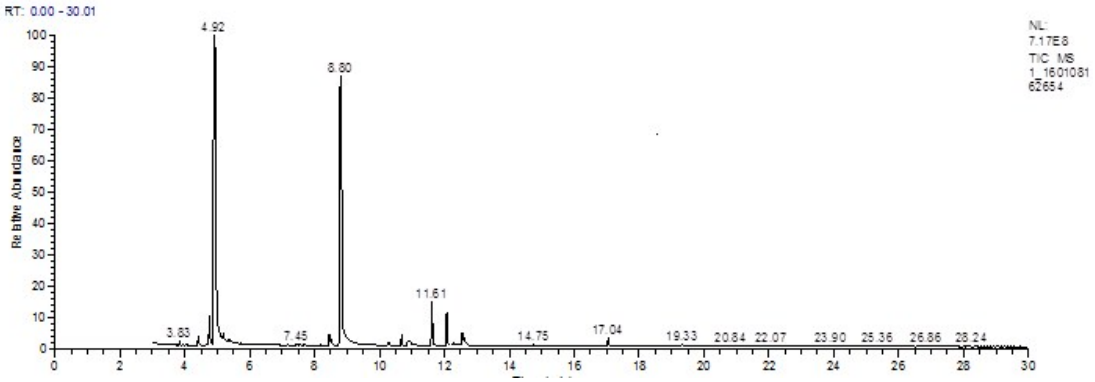
GC-MS of the cyclohexane bromination reaction solution



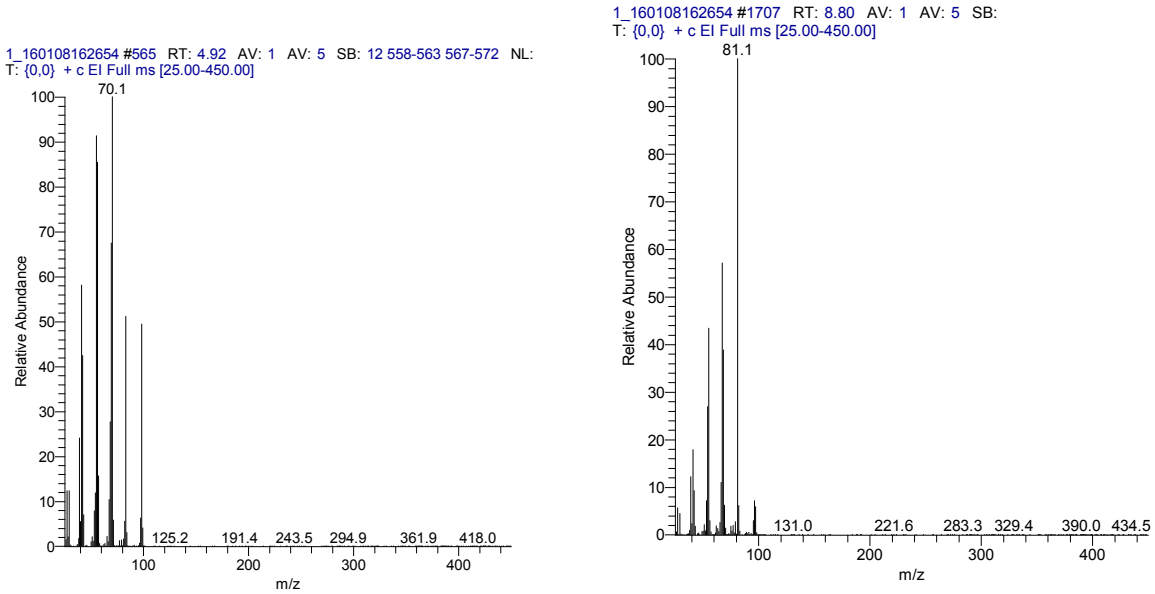


NMR of the cyclohexane bromination reaction mixture from Ag/AgCl catalysis

The reaction solution of cycloheptane chlorination



GC of the cycloheptane chlorination reaction mixture



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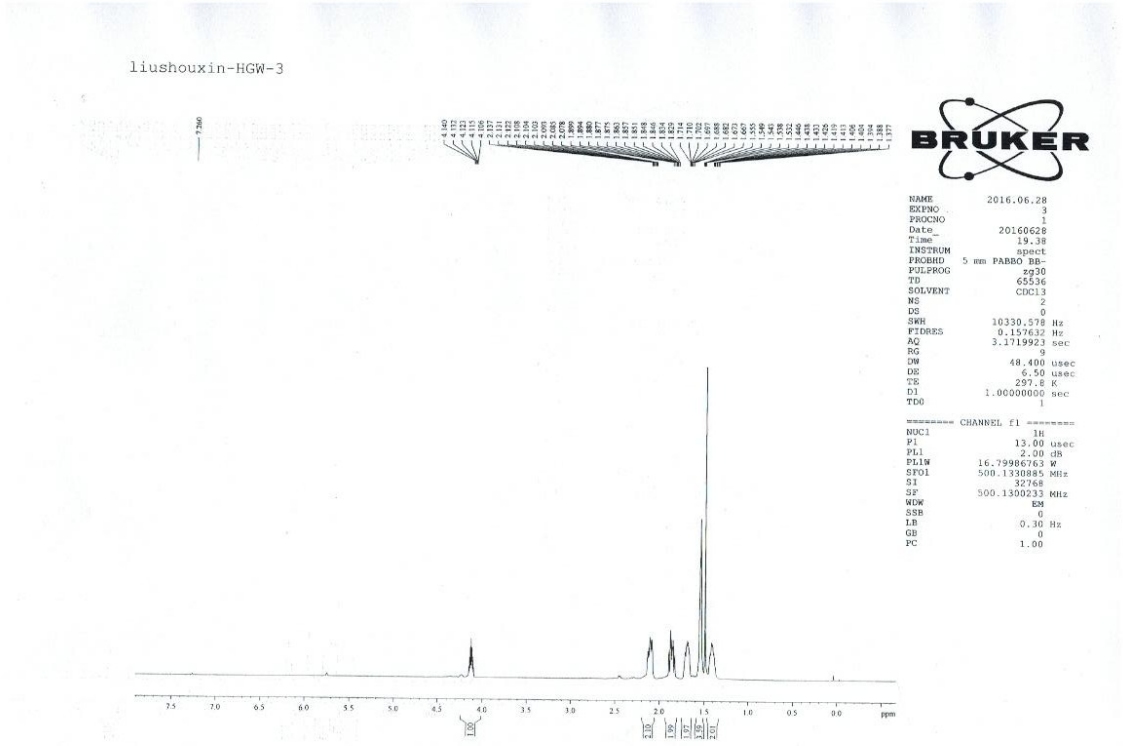
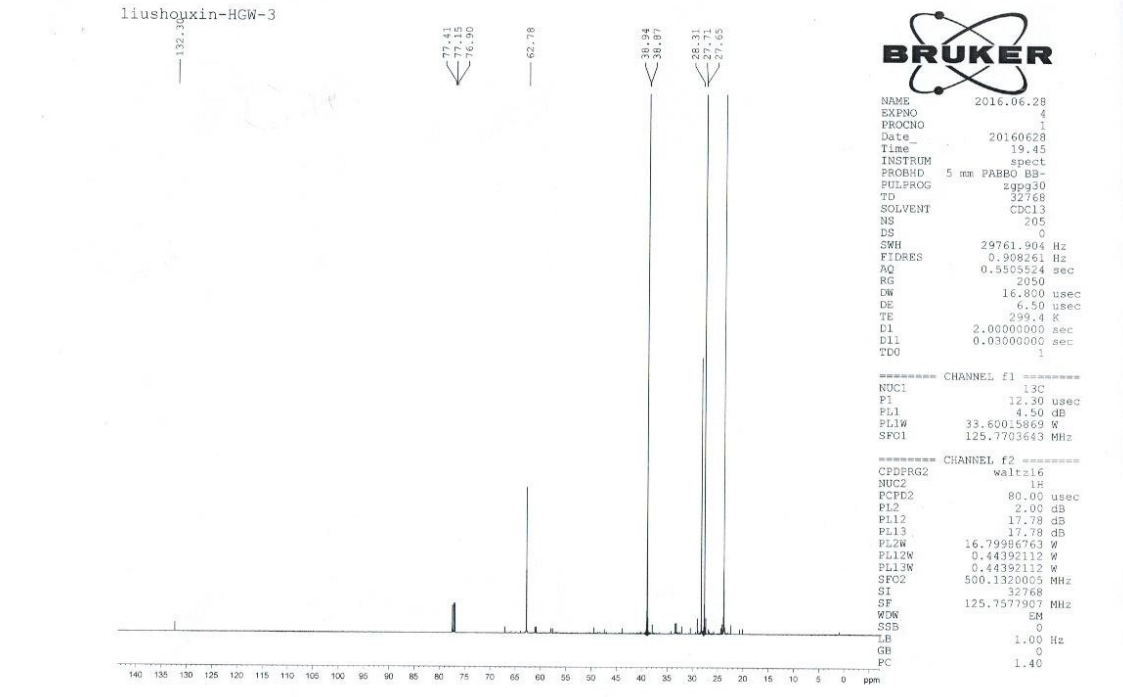
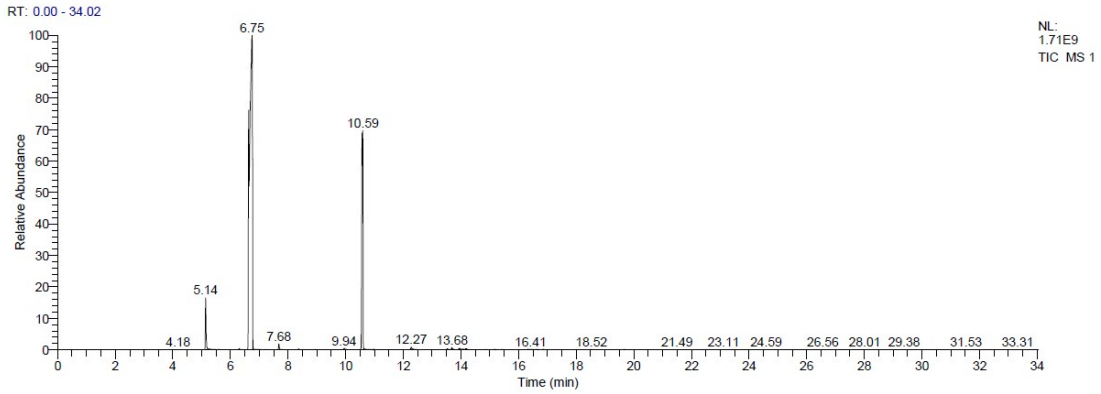


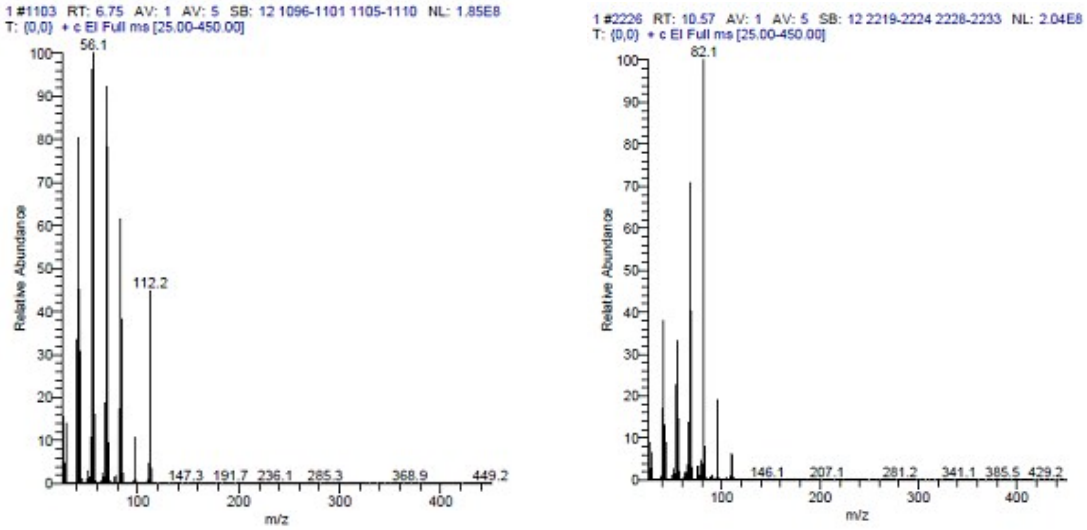


NMR of the cycloheptane chlorination reaction solution

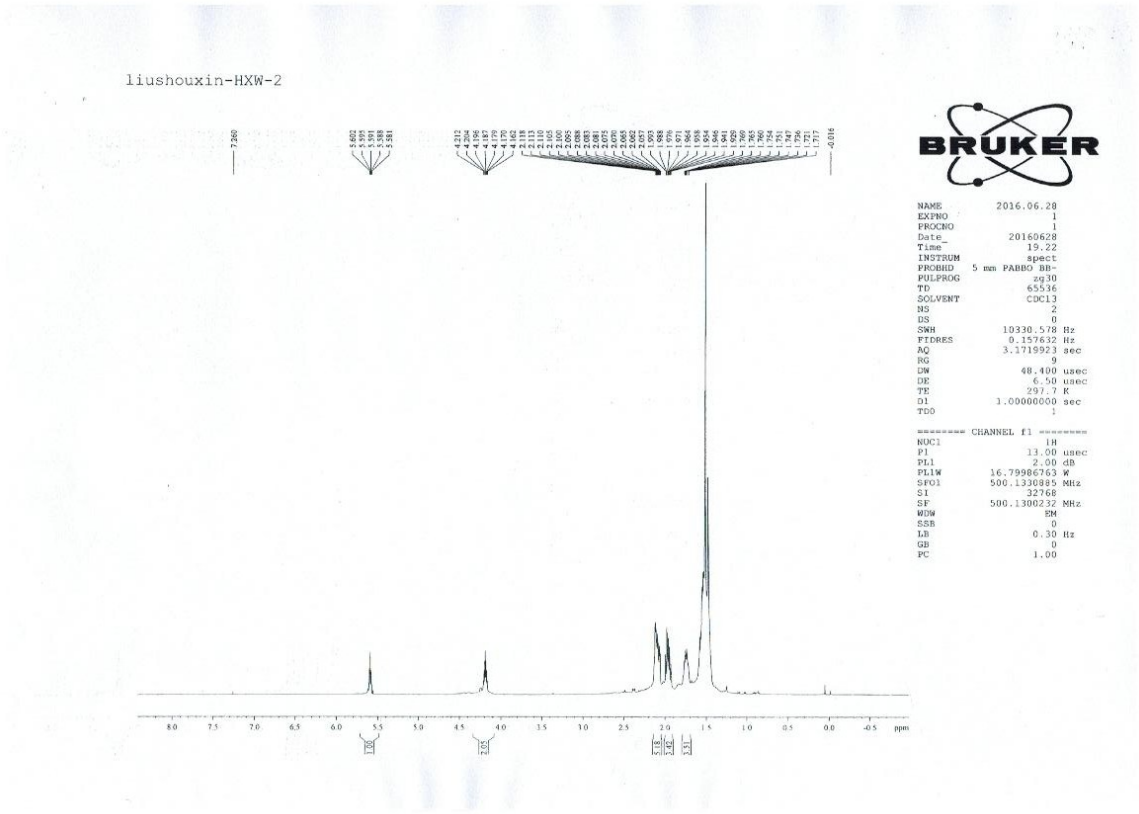
The reaction solution of cyclooctane chlorination

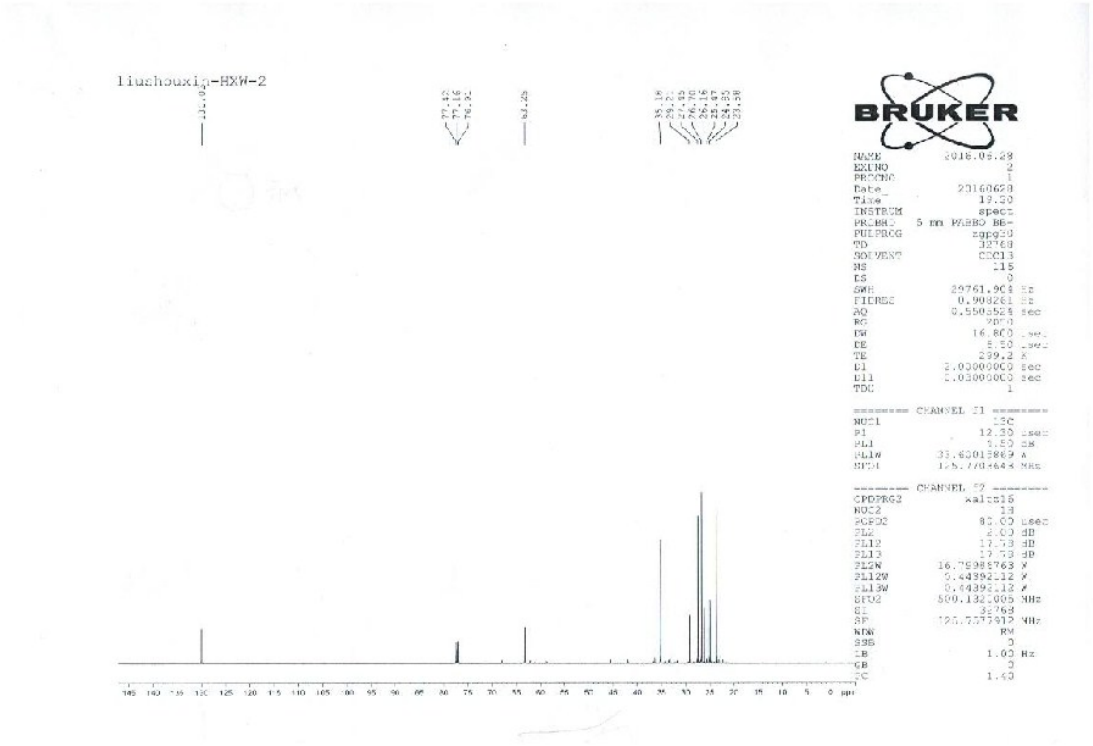


GC of the cyclooctane chlorination reaction mixture



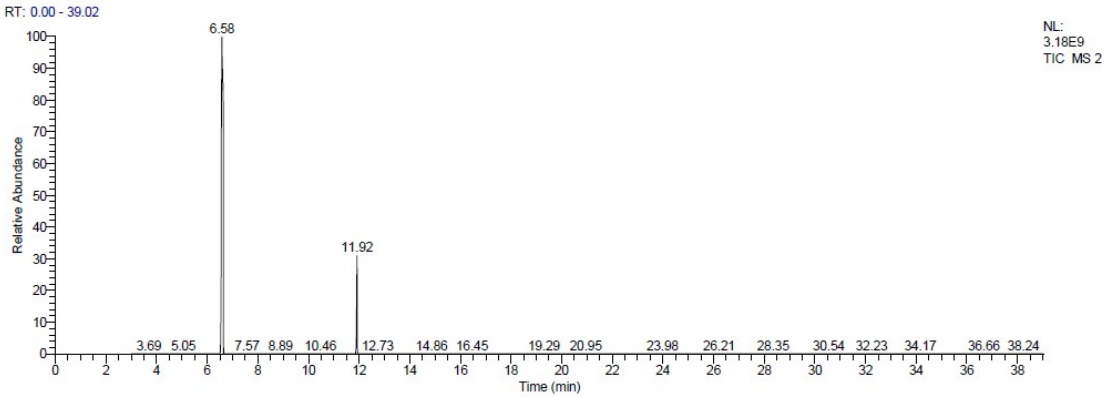
GC-MS of the cyclooctane chlorination reaction mixture





NMR of the cyclooctane chlorination reaction mixture

The reaction solution of cyclooctane bromination



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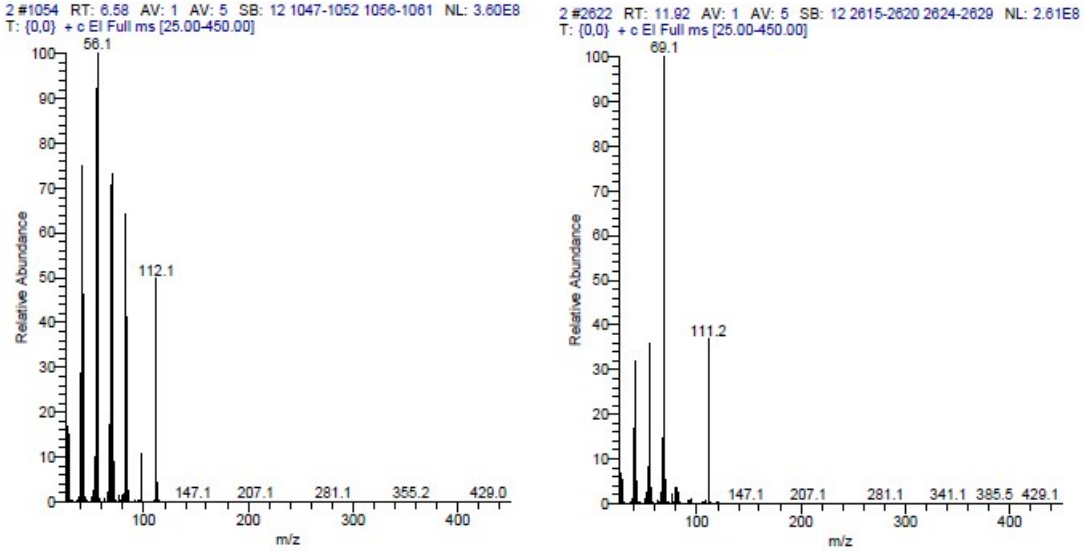
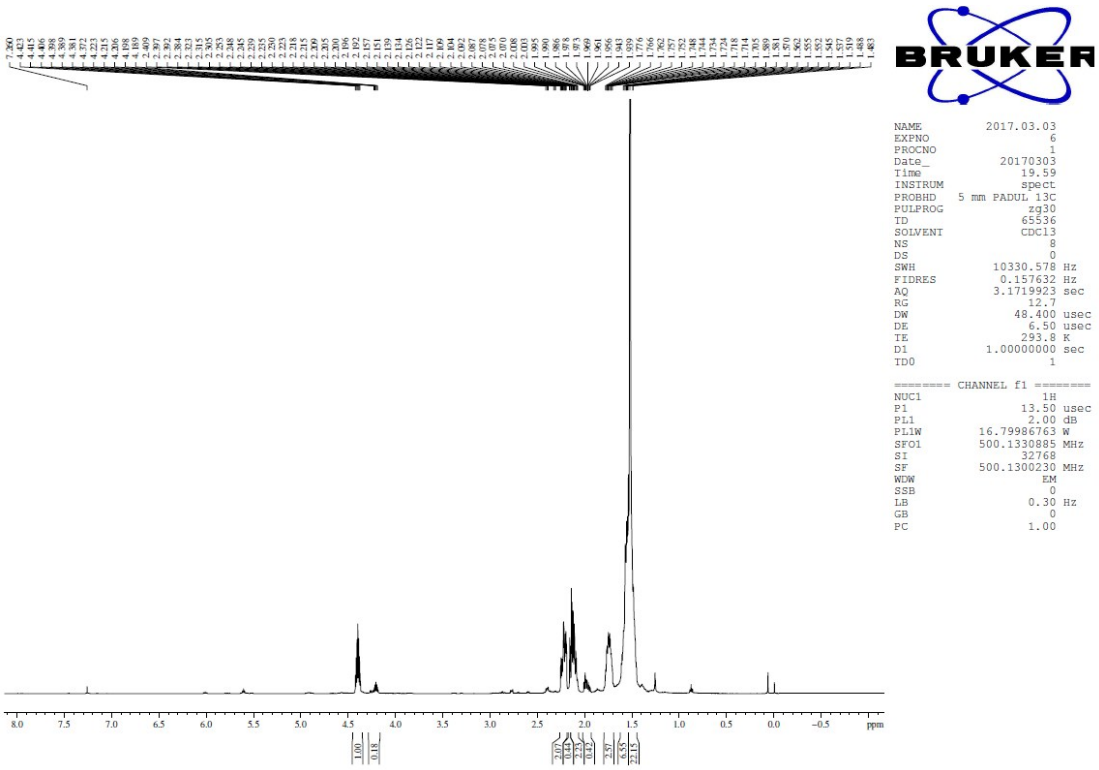


GC-MS of the cyclooctane bromination reaction mixture



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PROCNO	1
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TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	12.7
DW	48.400 usec
DE	6.50 usec
TE	293.8 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	13.50 usec
PL1	2.00 dB
PL1W	16.79986763 W
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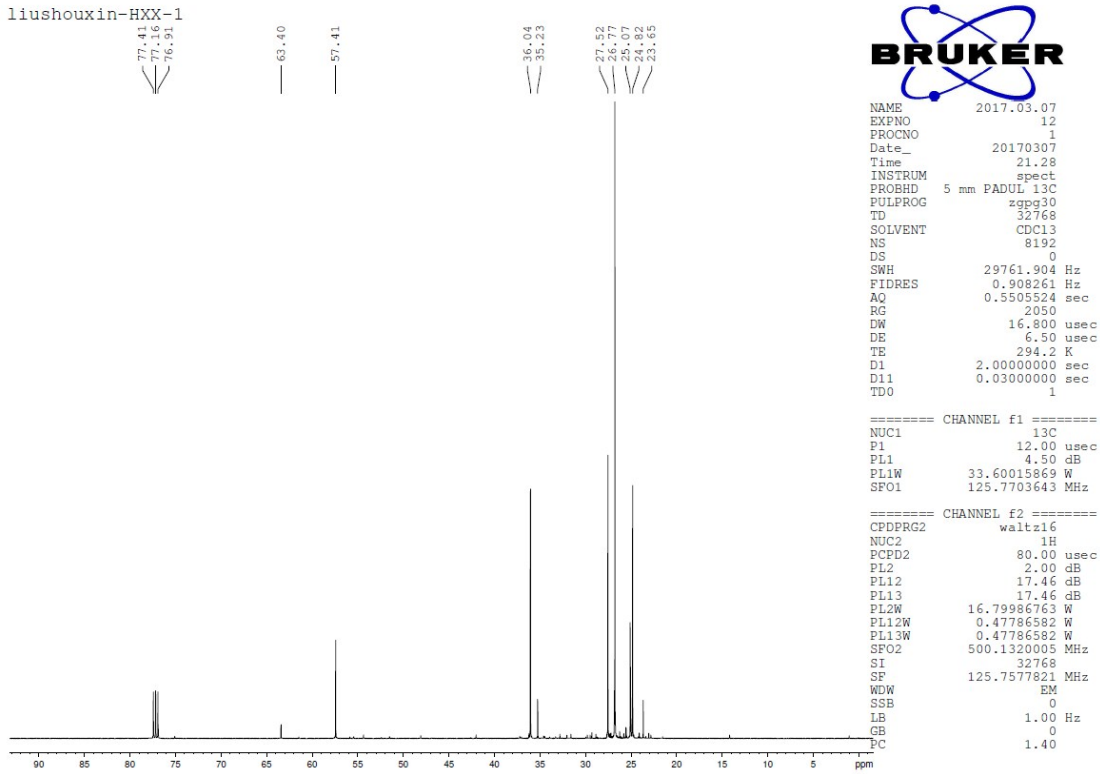
SI	32768
SF	500.1300230 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



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SOLVENT	CDCl3
NS	8192
DS	0
SWH	29761.904 Hz
FIDRES	0.908261 Hz
AQ	0.5505524 sec
RG	2050
DW	16.800 usec
DE	6.50 usec
TE	294.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
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NUC1	13C
P1	12.00 usec
PL1	4.50 dB
PL1W	33.60015869 W
SFO1	125.7703643 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	2.00 dB
PL12	17.46 dB
PL13	17.46 dB
PL2W	16.79986763 W
PL12W	0.47786582 W
PL13W	0.47786582 W
SFO2	500.1320005 MHz
SI	32768
SF	125.7577821 MHz
WDW	EM
SSB	0
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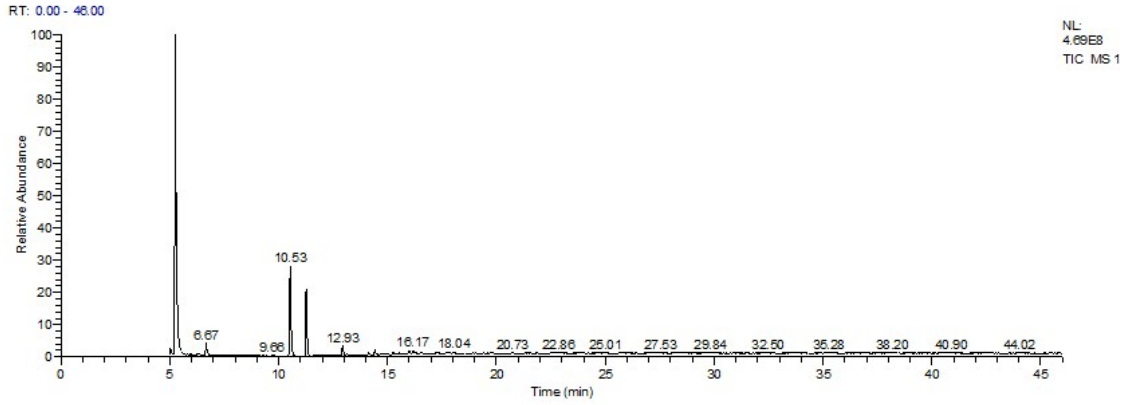
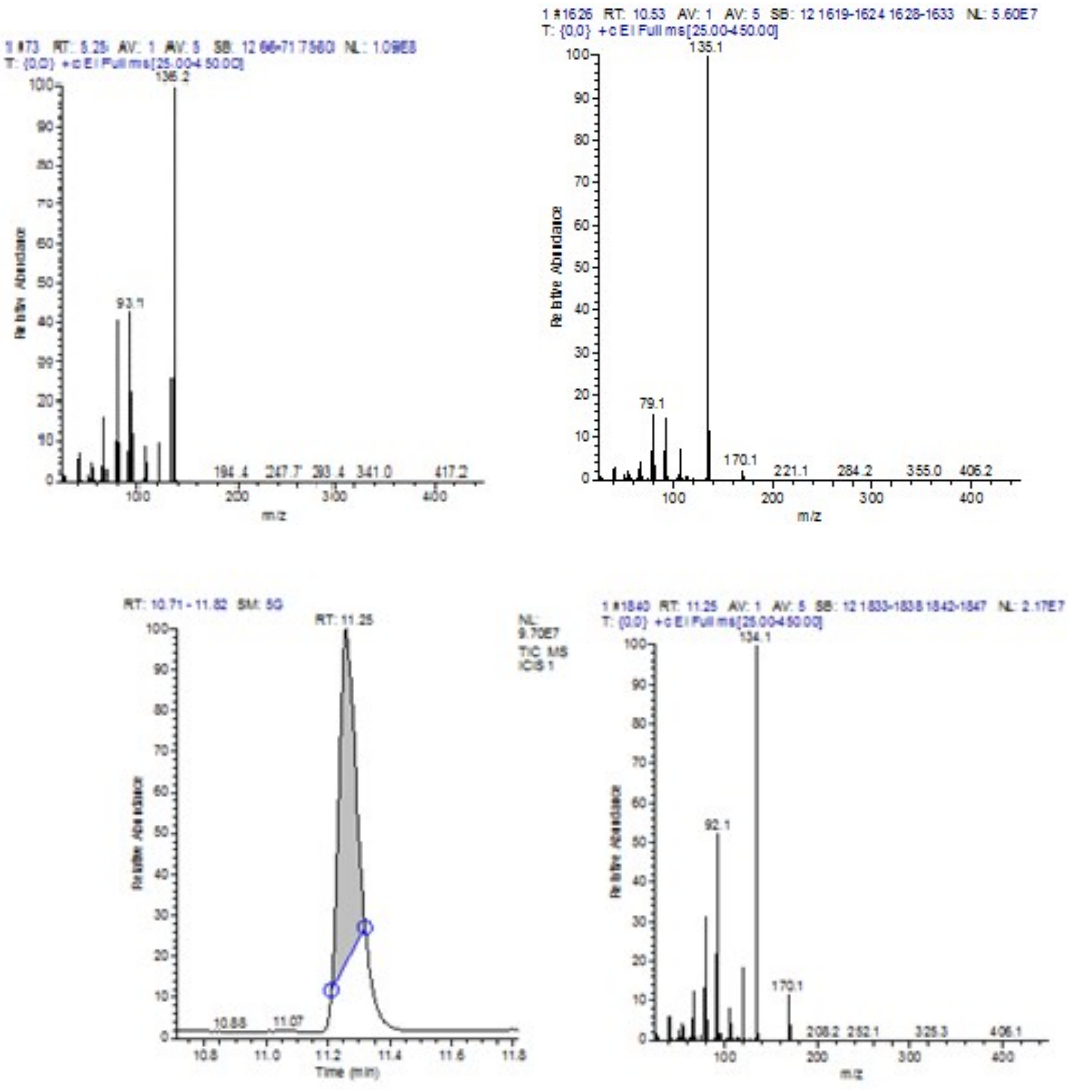
PC	1.40

NMR of the cyclooctane bromination reaction mixture

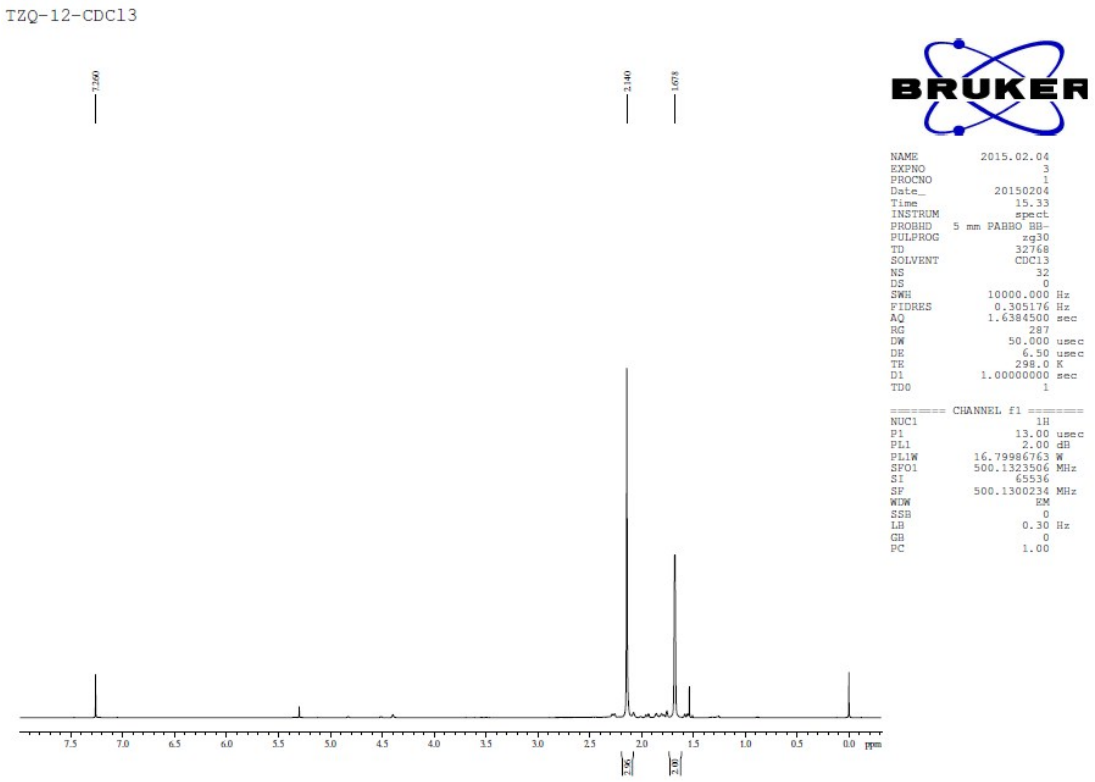
The halogenation of adamantine

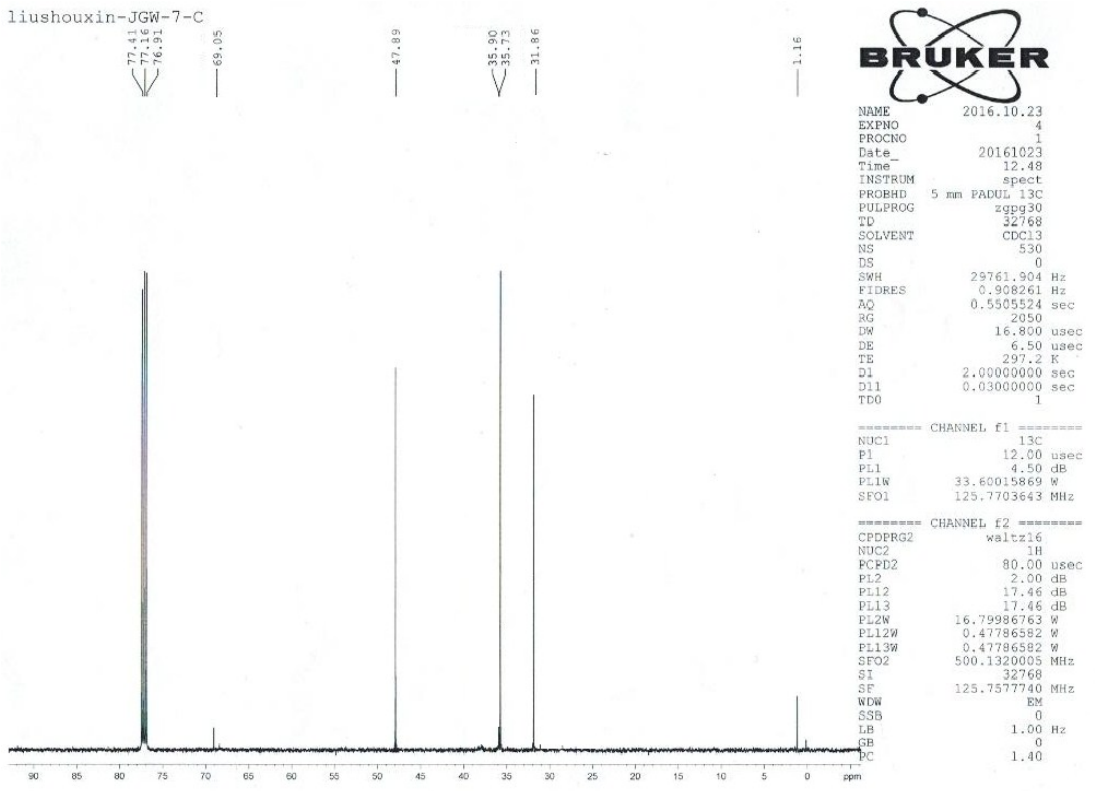


GC of the adamantine chlorination reaction mixture

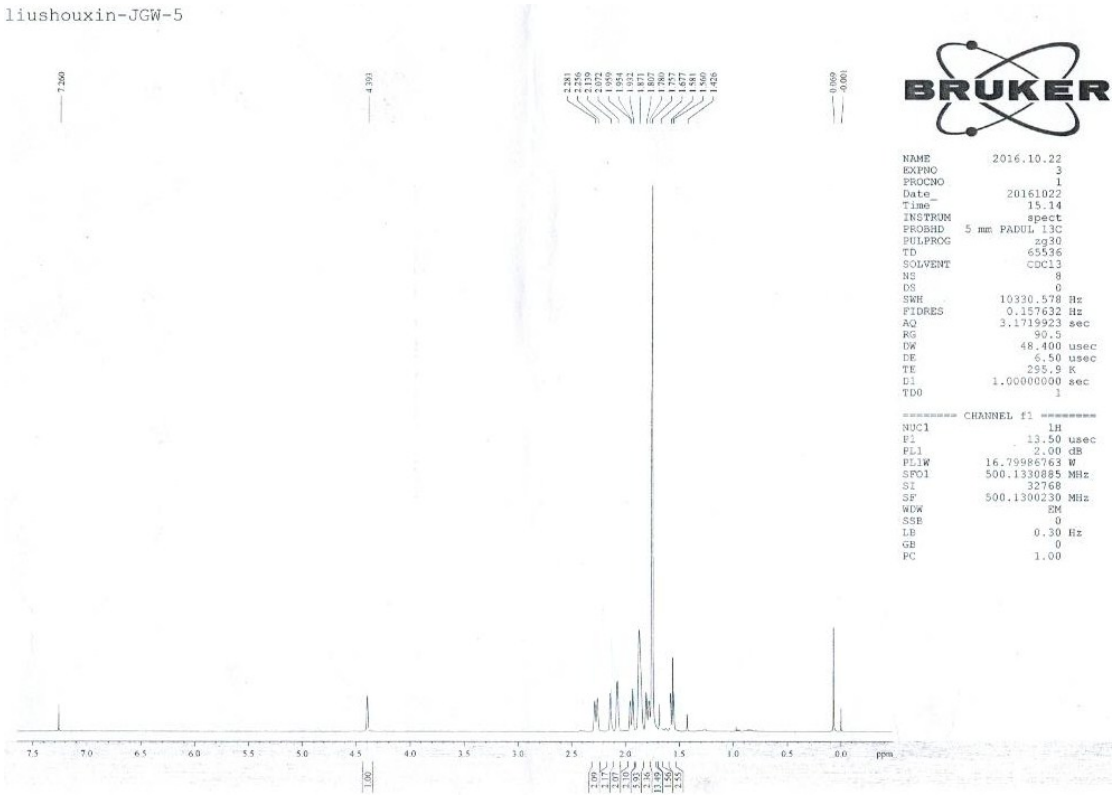


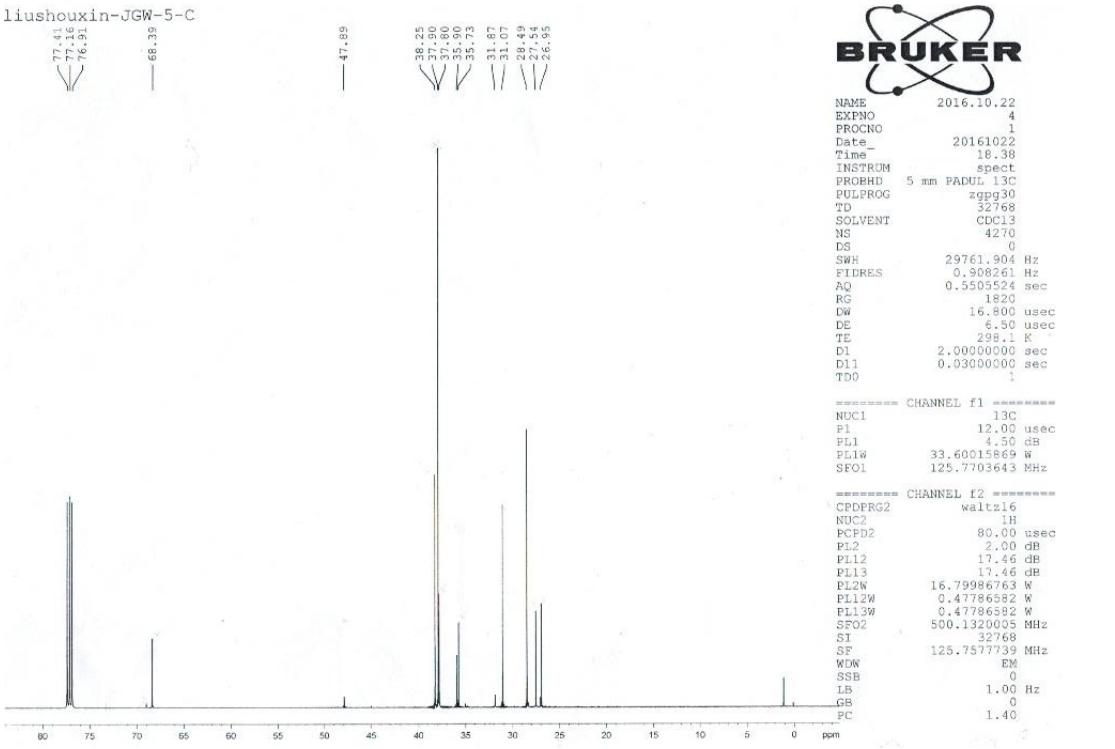
GC-MS of the adamantine chlorination reaction mixture



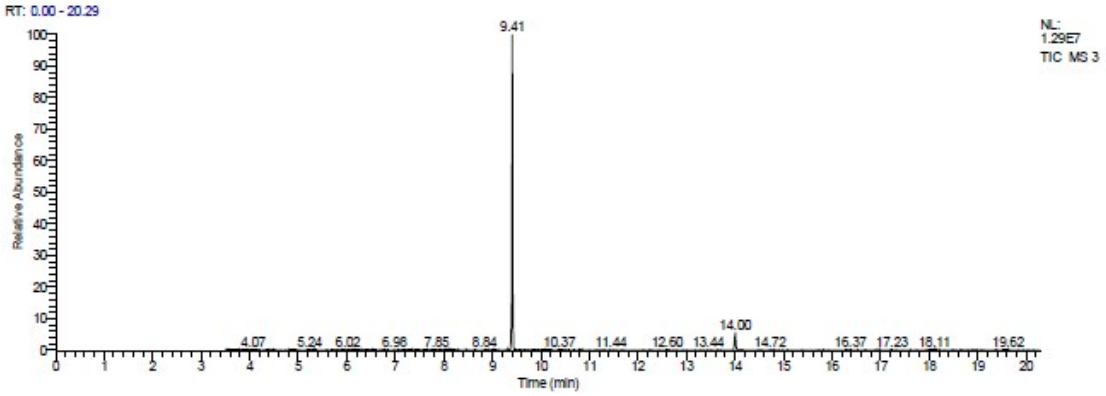


NMR of the adamantine chlorination reaction mixture (1-Cl-adamantine)

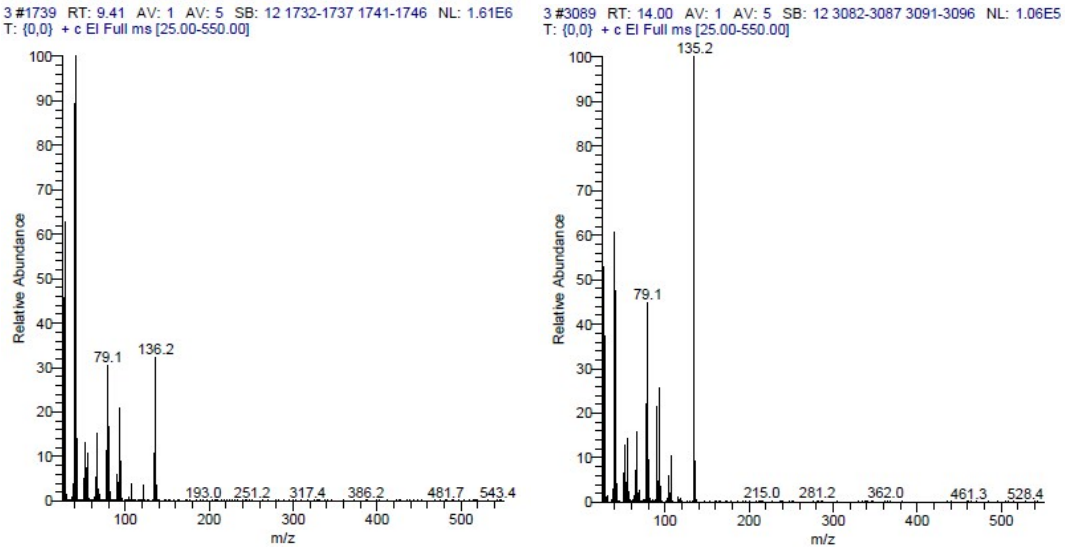




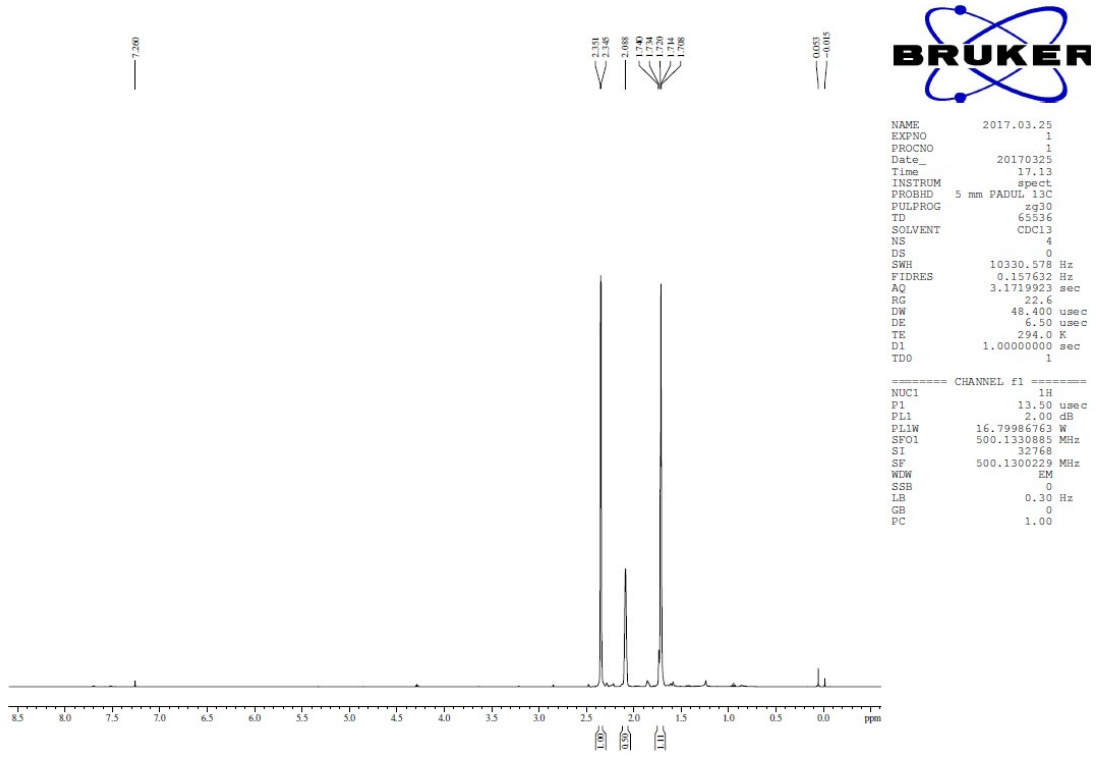
NMR of the adamantine chlorination reaction mixture (adamantine and 2-Cl-adamantine)

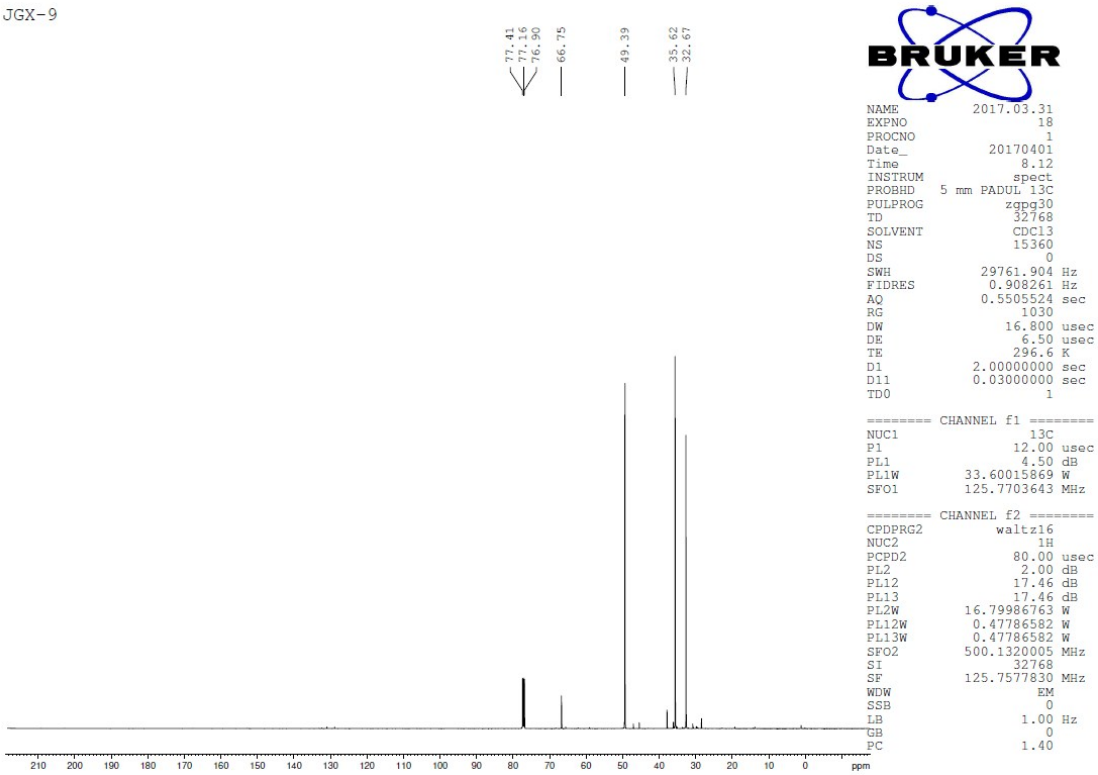


GC of the adamantine bromination reaction mixture



GC-MS of the adamantine bromination reaction mixture

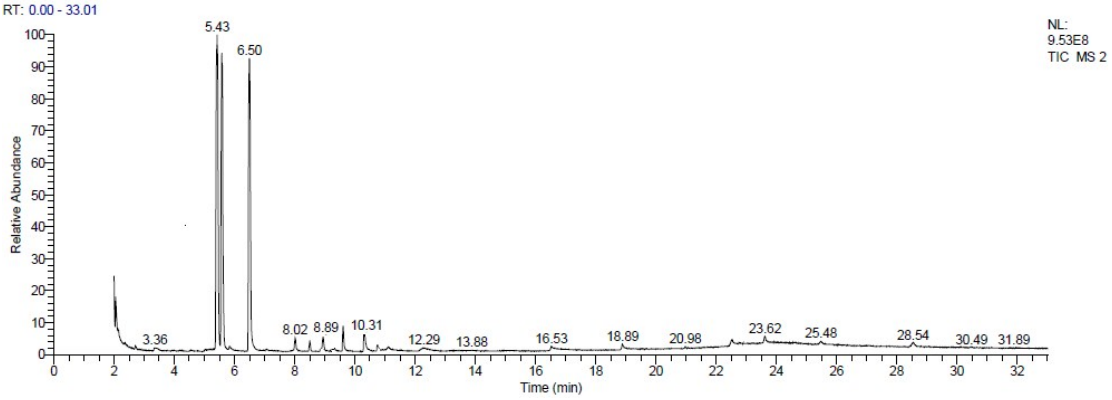




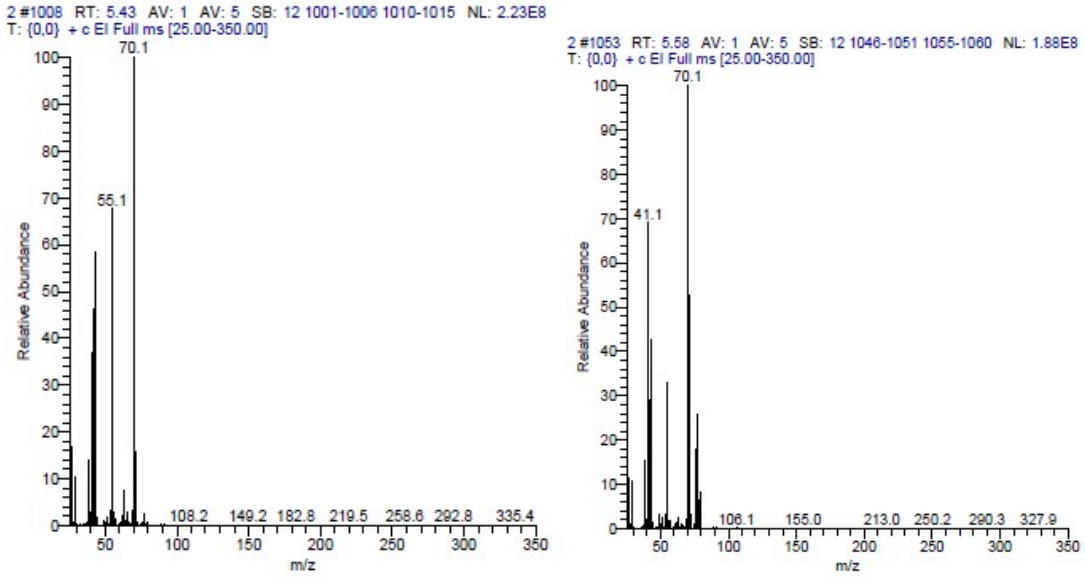
NMR of the adamantine bromination reaction mixture

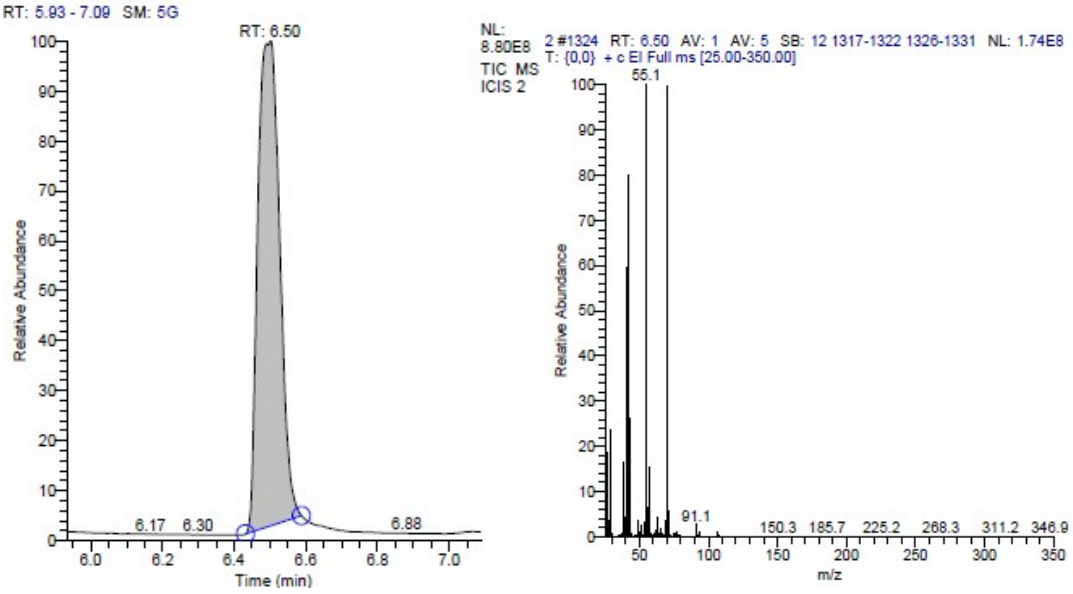
The chlorinations of chain alkanes

Chlorination of *n*-pentane

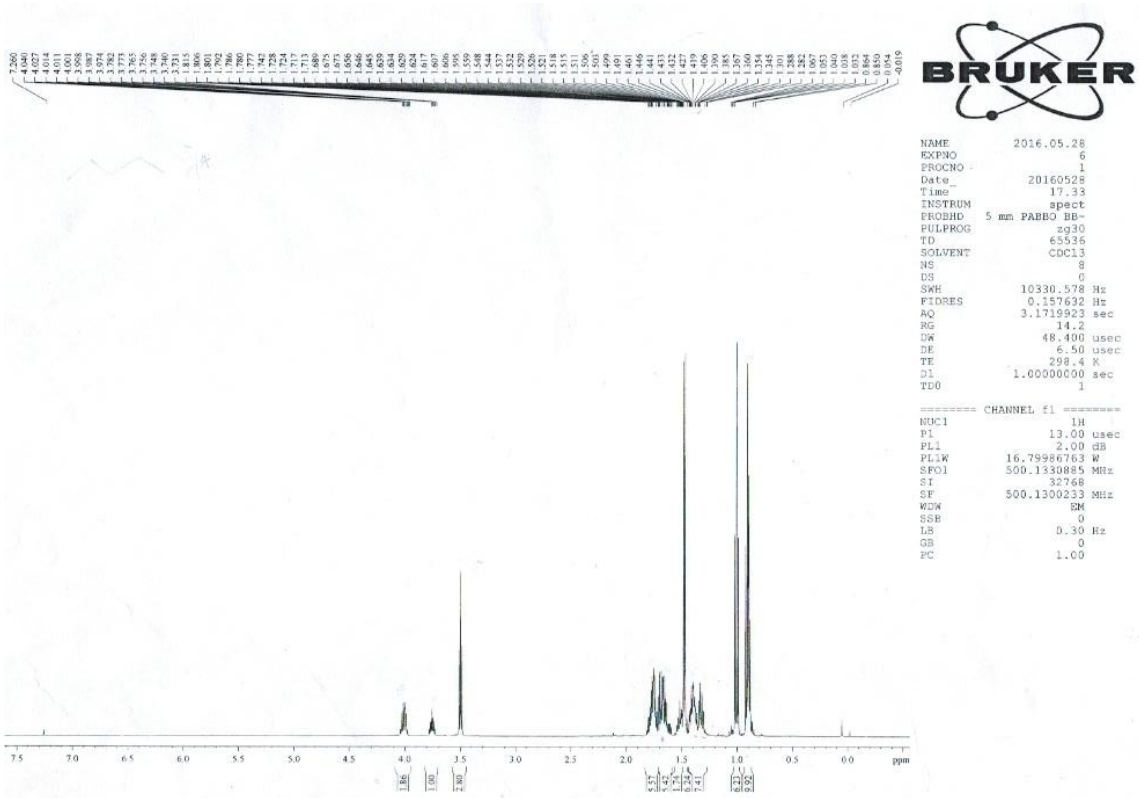


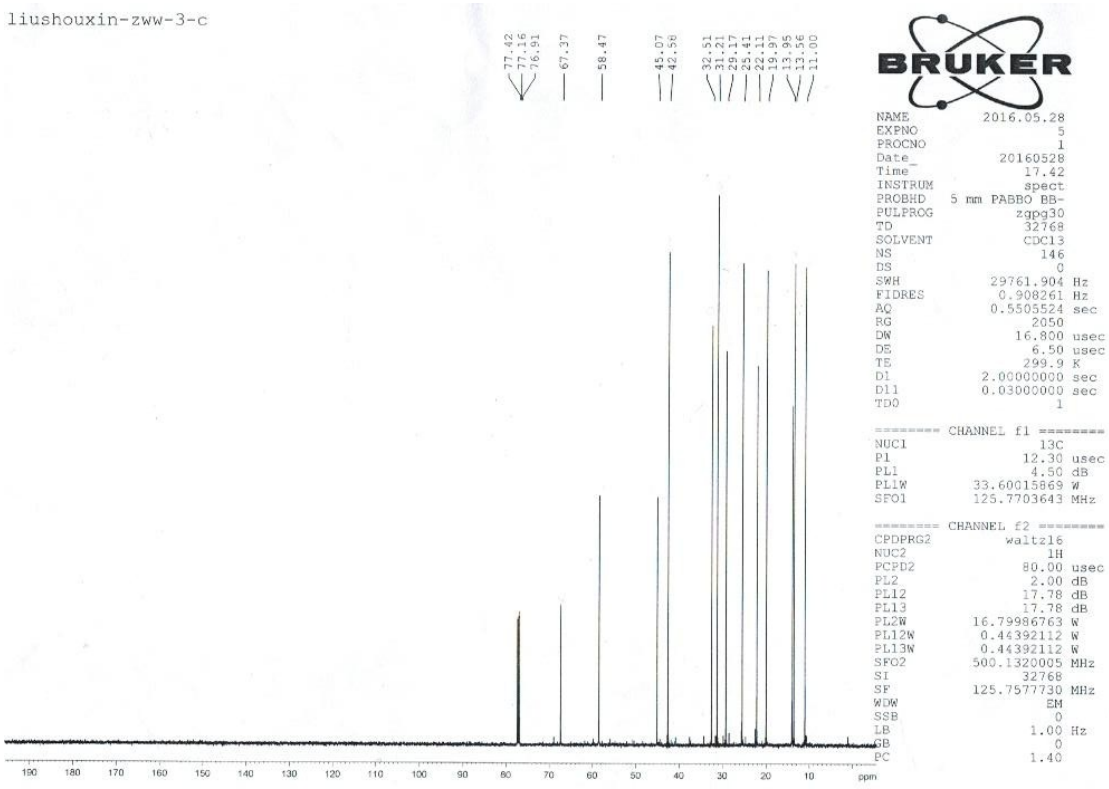
GC of the chlorination reaction mixture of *n*-pentane





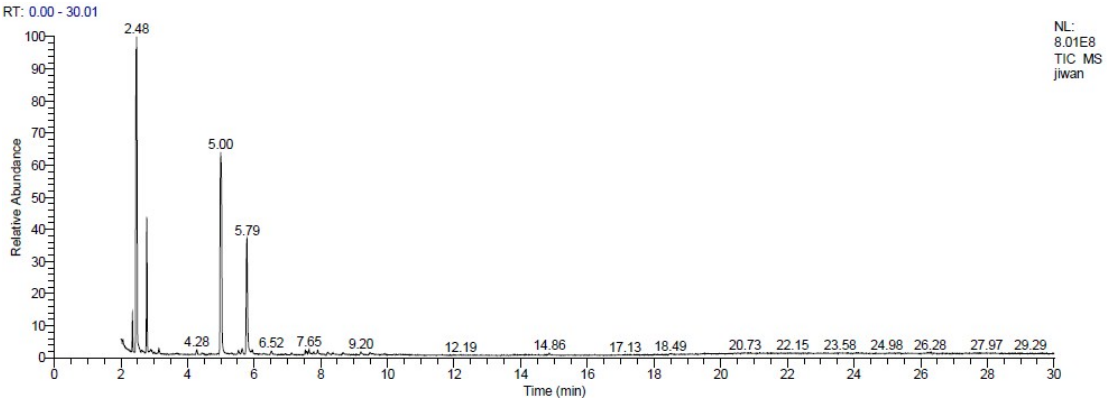
GC-MS of the chlorination reaction mixture of *n*-pentane



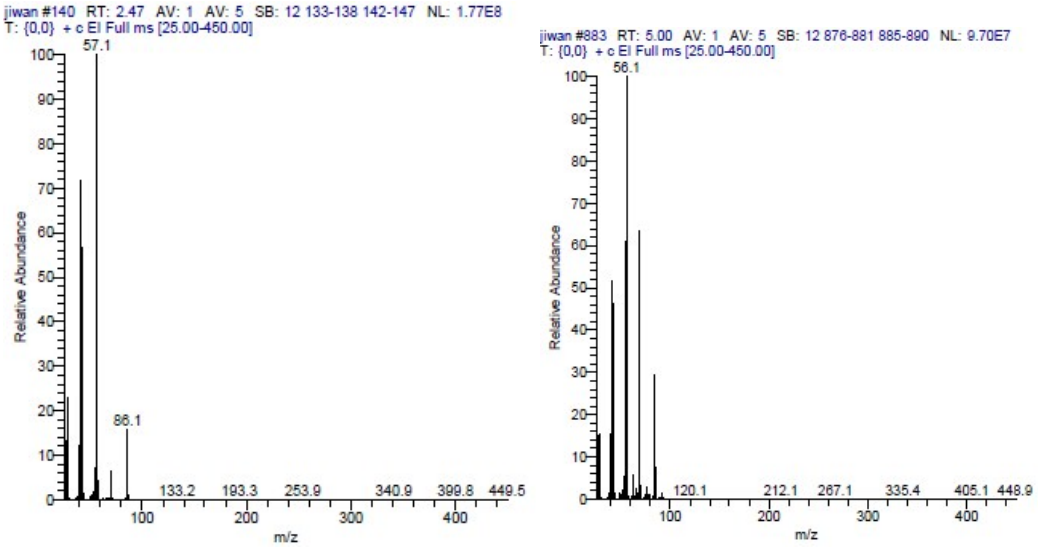


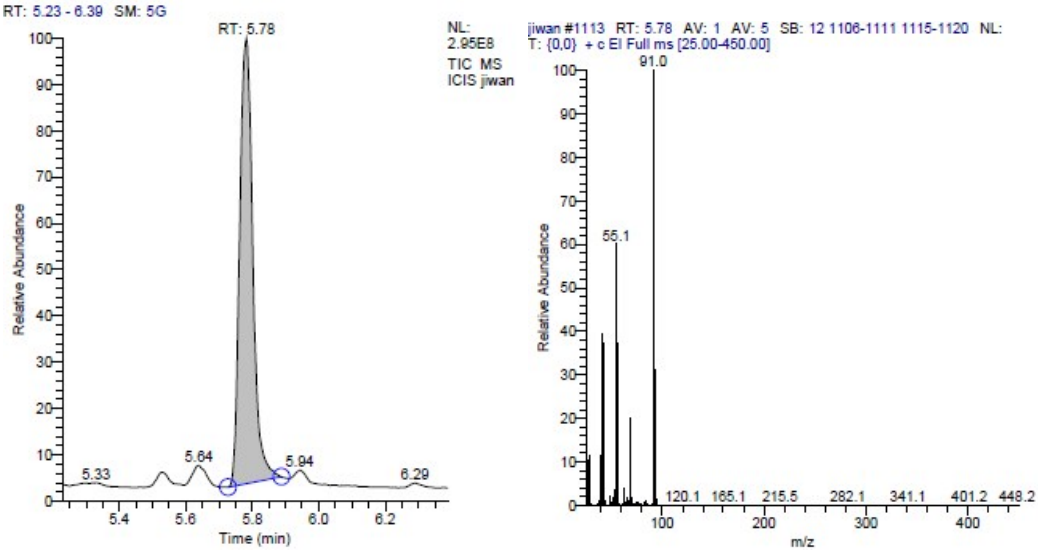
NMR of the chlorination reaction mixture of *n*-pentane

Chlorination of *n*-hexane

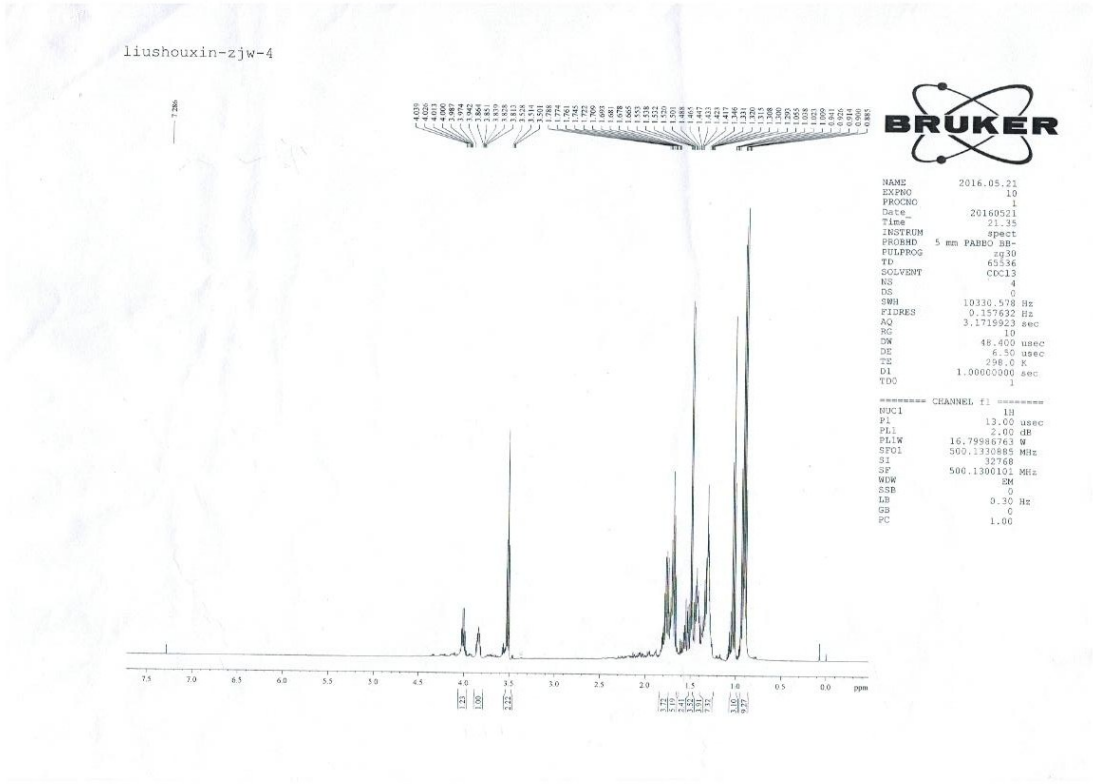


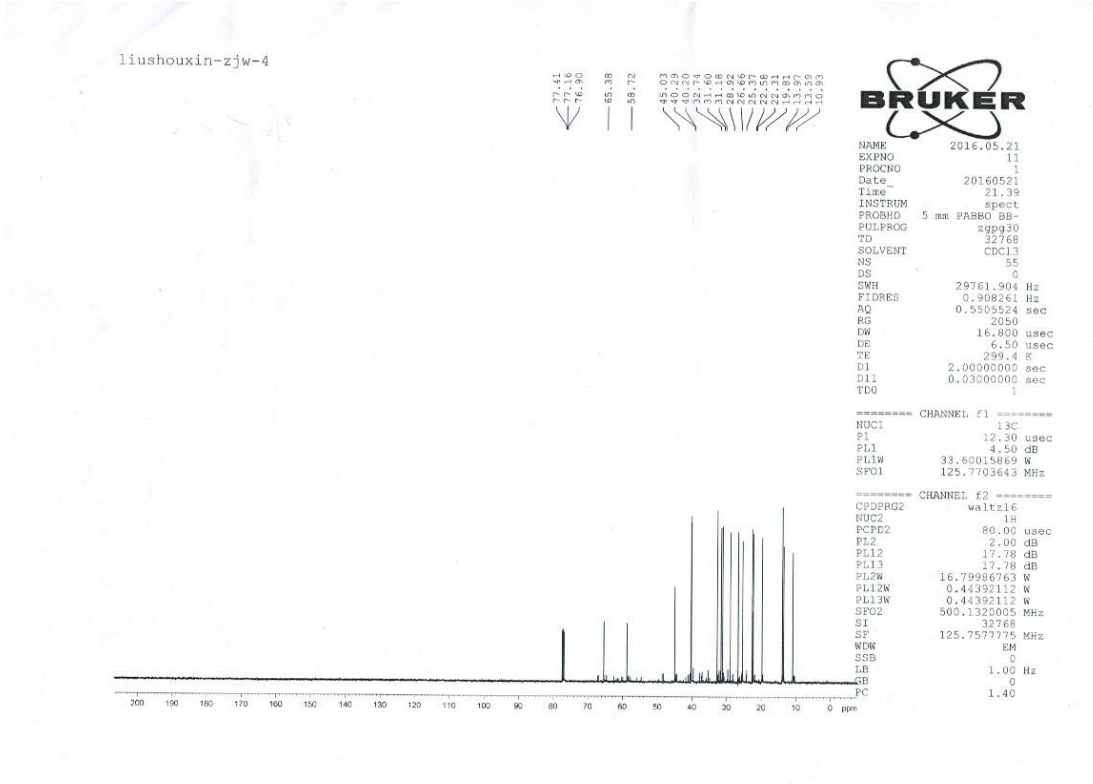
GC of the chlorination reaction mixture of *n*-hexane





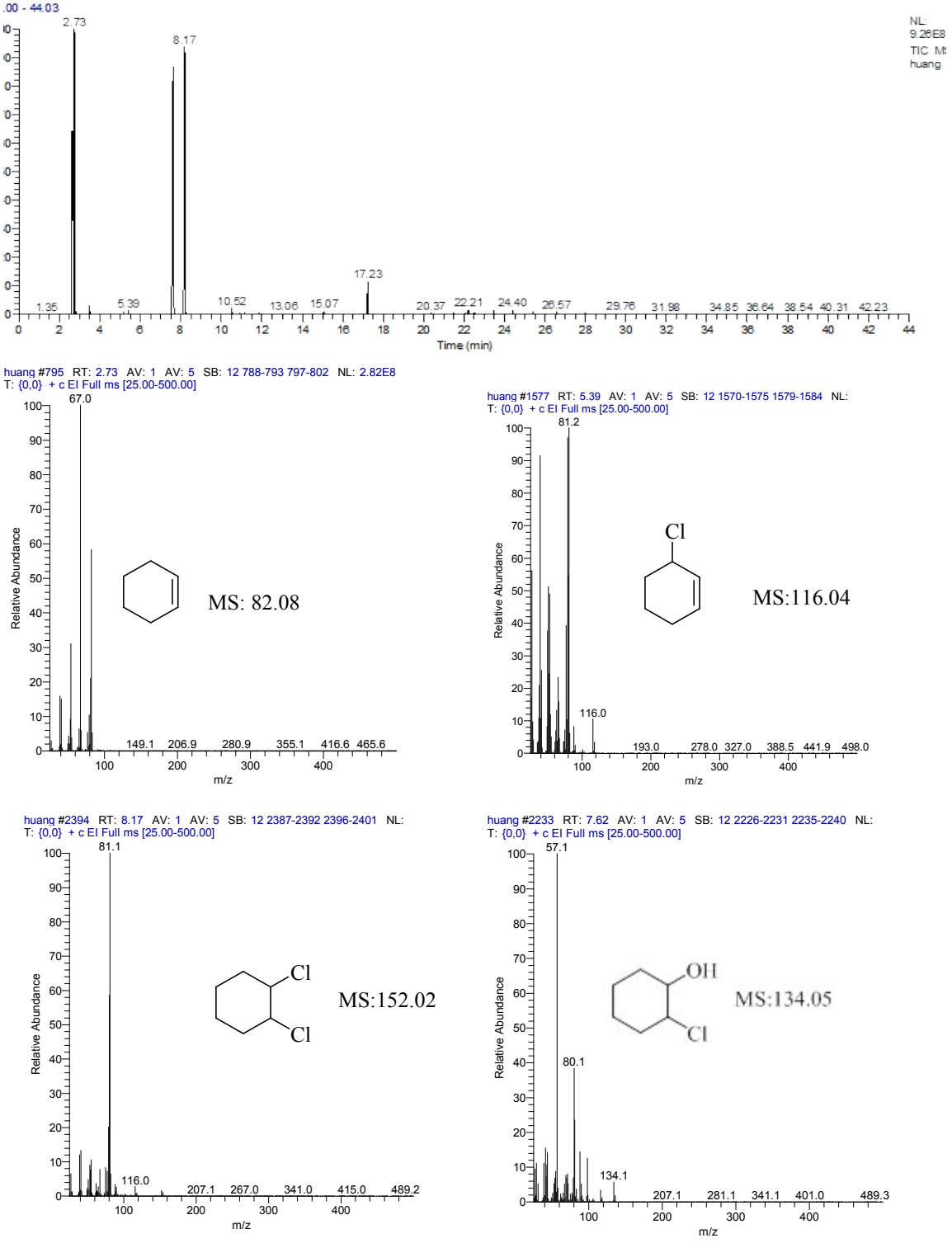
GC-MS of the chlorination reaction mixture of *n*-hexane





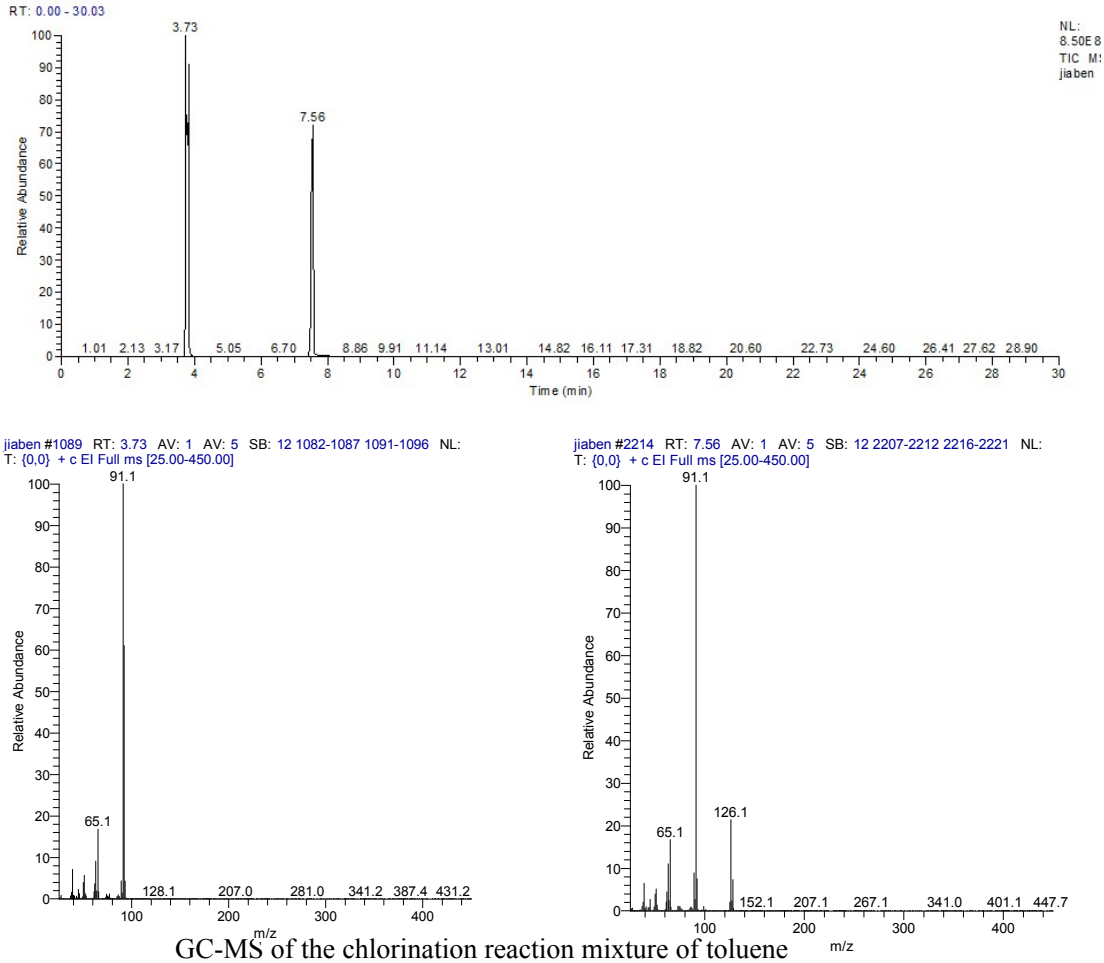
NMR of the chlorination reaction mixture of *n*-hexane

The chlorination products of cyclohexene

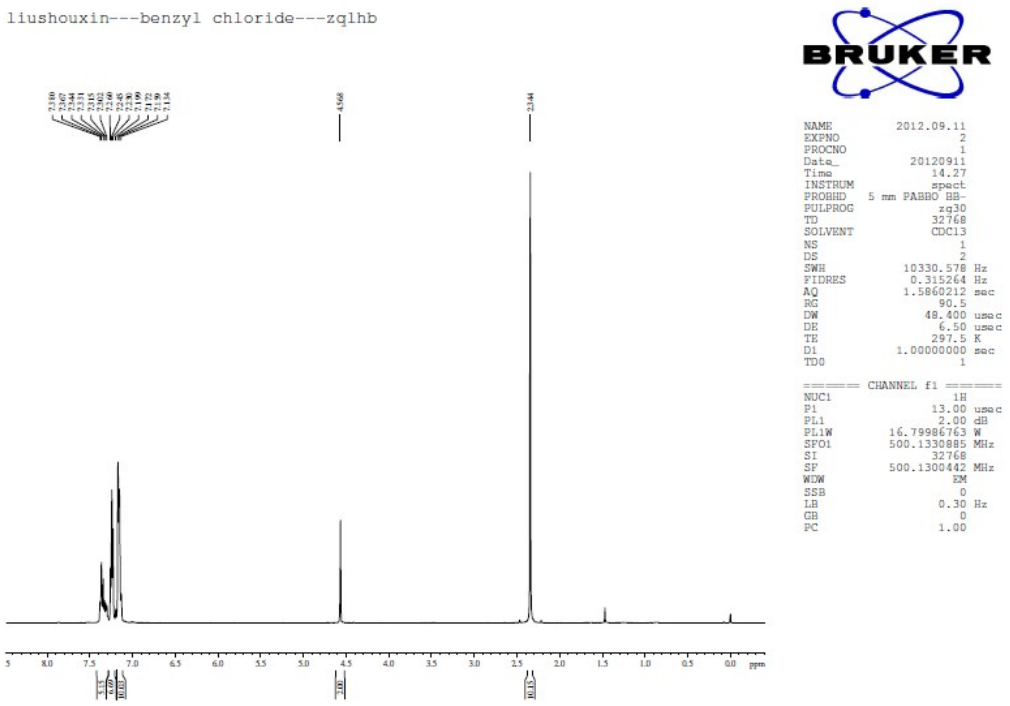


GC-MS of the chlorination reaction mixture of cyclohexene

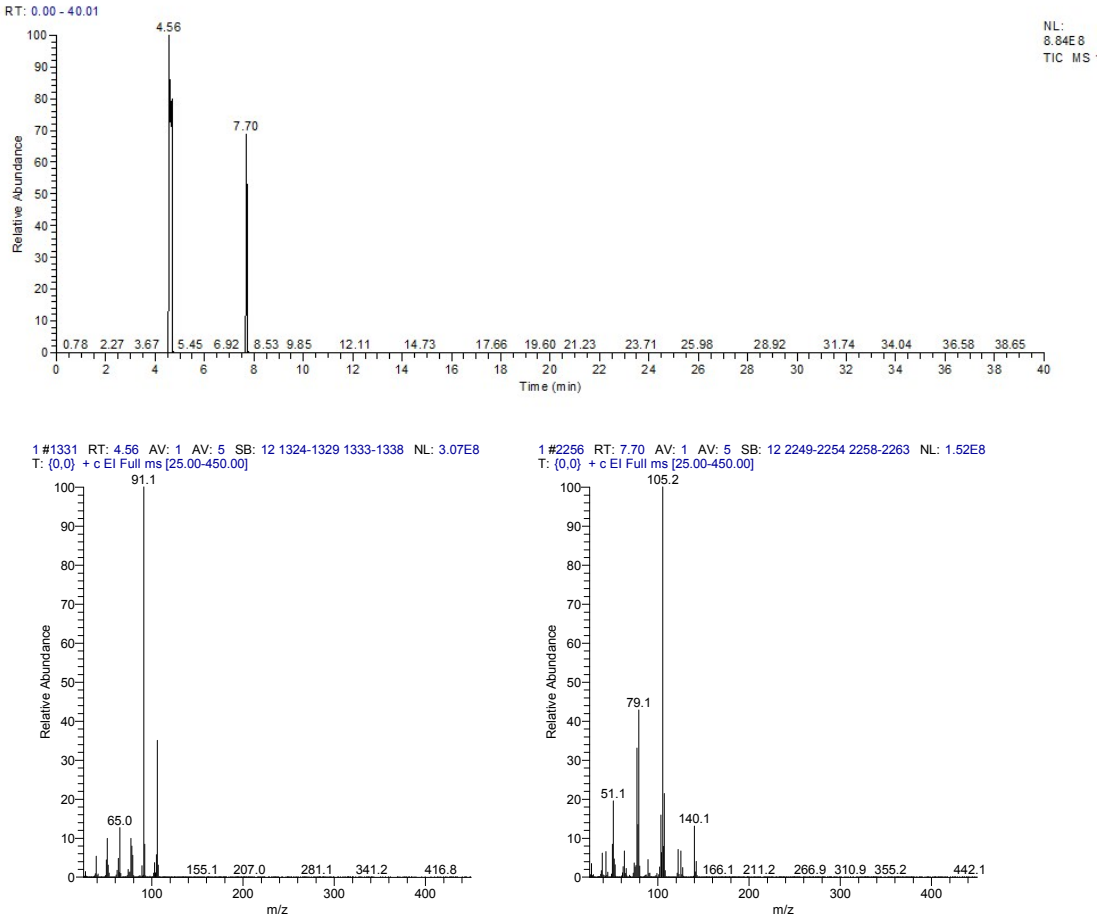
The holagenation of α-H at alkylbenzene
Chlorination of toluene by Ag/AgCl catalyzation



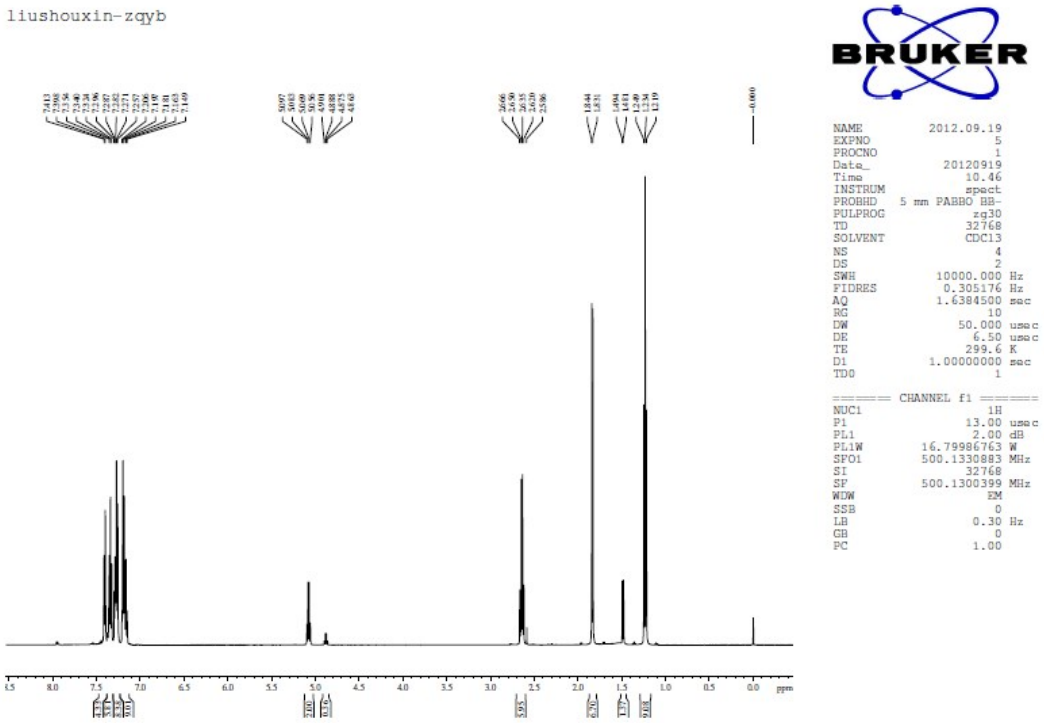
GC-MS of the chlorination reaction mixture of toluene



^{1}H NMR of the the chlorination reaction mixture of toluene

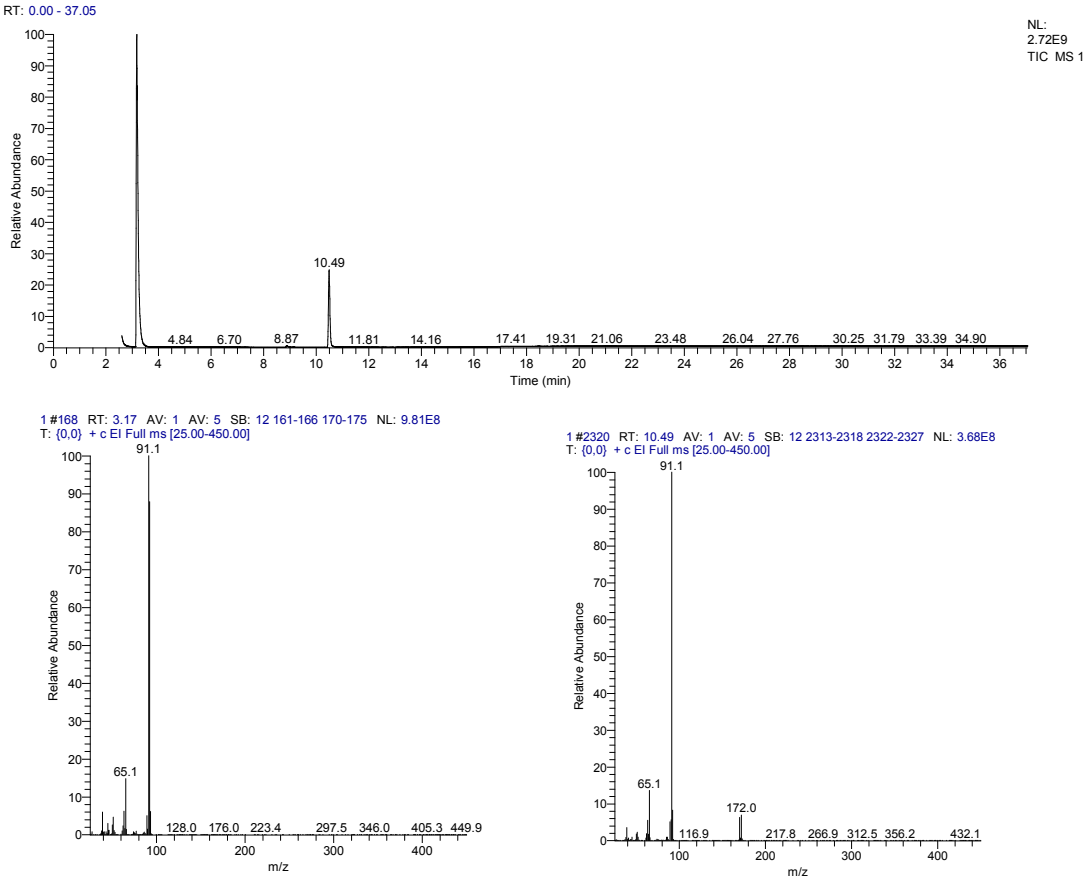


GC-MS of the chlorination reaction mixture of ethylbenzene

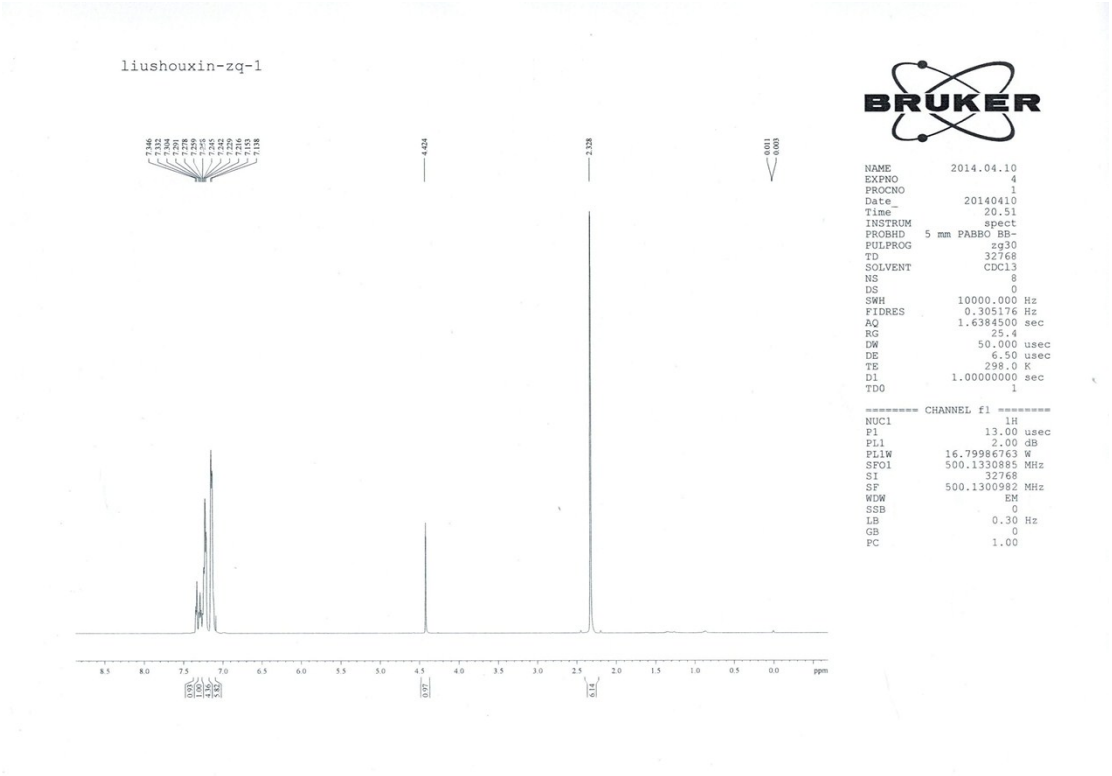


^{1}H NMR of the chlorination reaction mixture of ethylbenzene

Bromination of toluene by the Ag/AgBr catalyzation

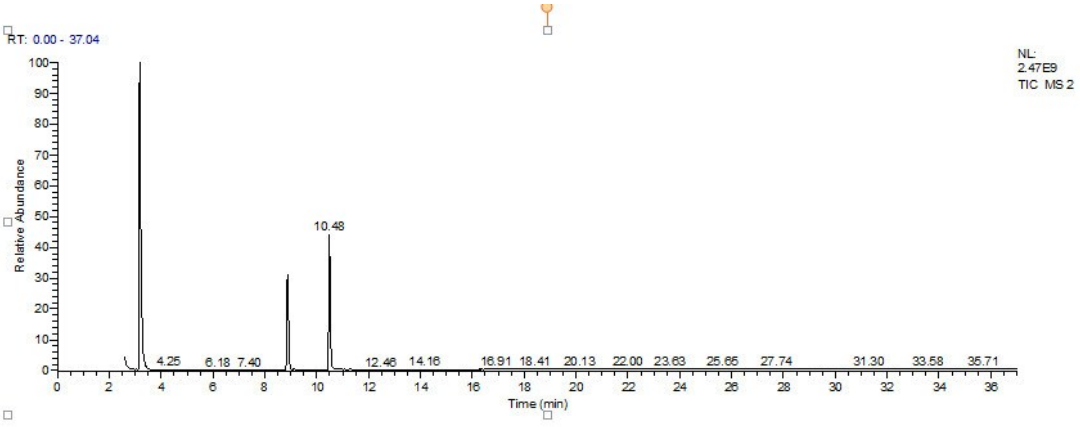


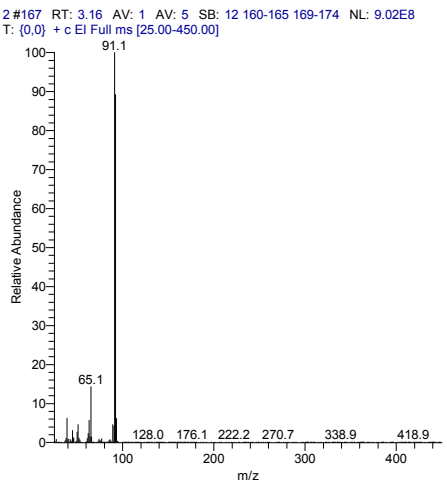
GC-MS of the bromination reaction mixture of toluene

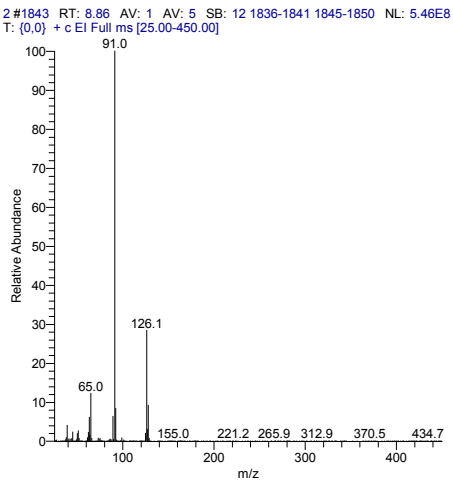


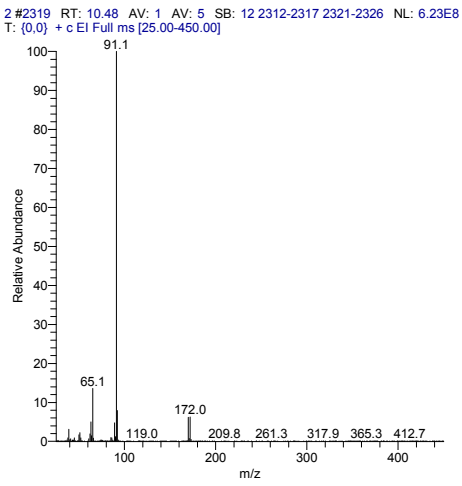
NMR of the bromination reaction mixture of toluene

Bromination of toluene by Ag/AgCl catalyzation

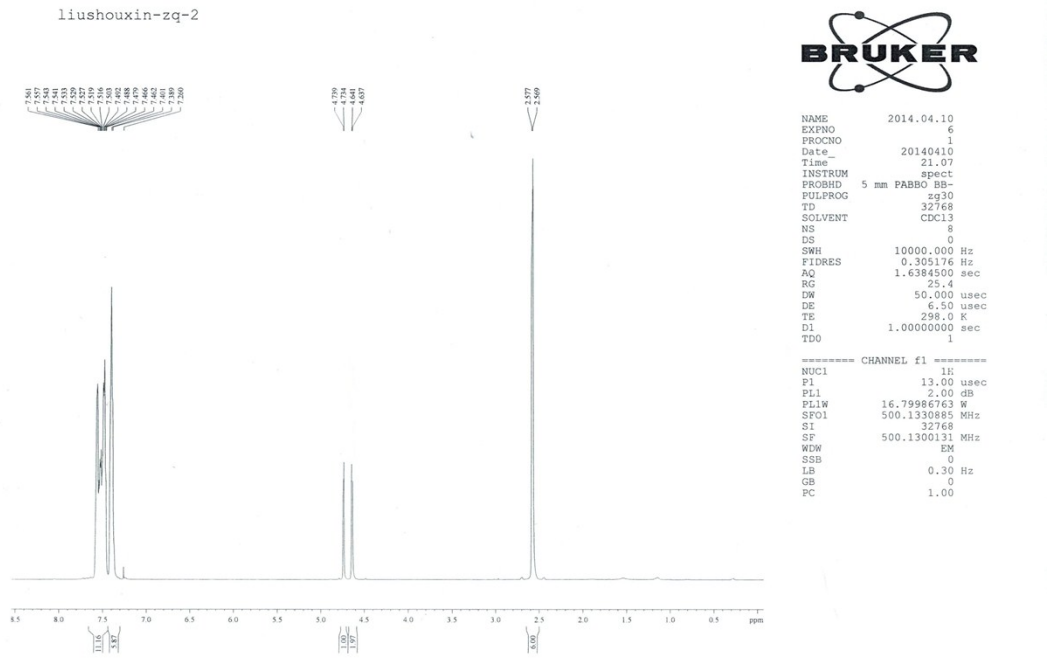






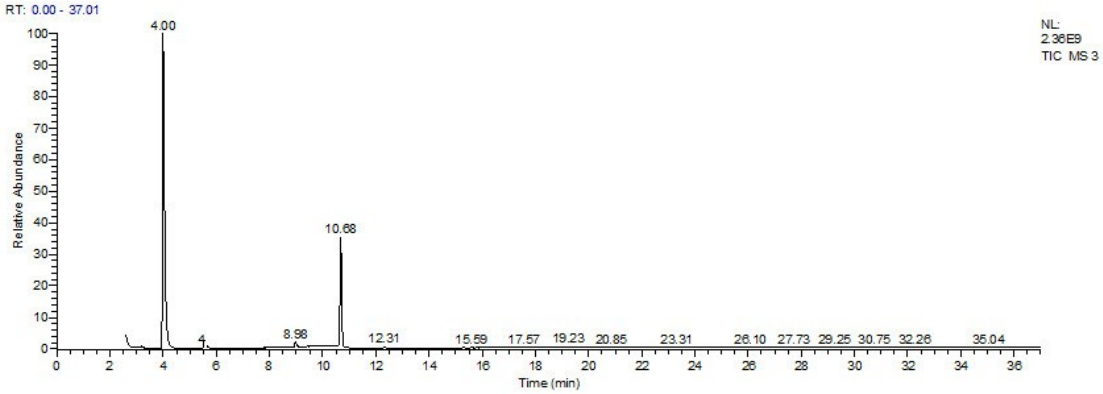


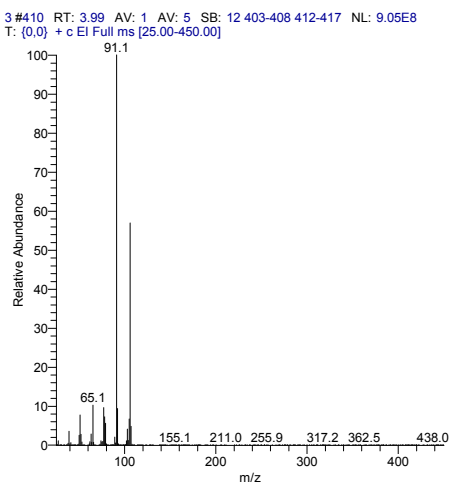
GC-MS of the bromination reaction mixture of toluene

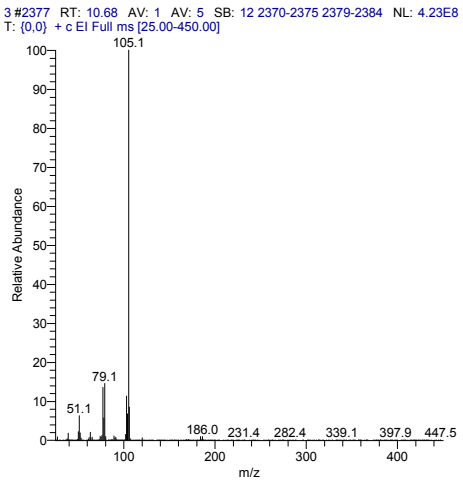


NMR of the bromination reaction mixture of toluene

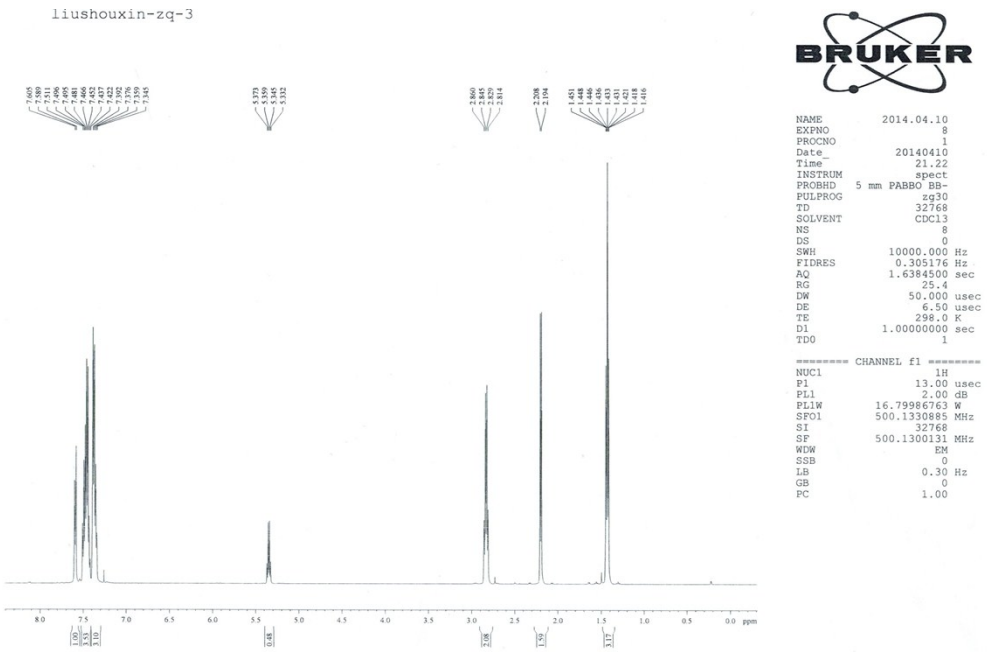
Bromination of ethylbenzene by Ag/AgBr catalyzation





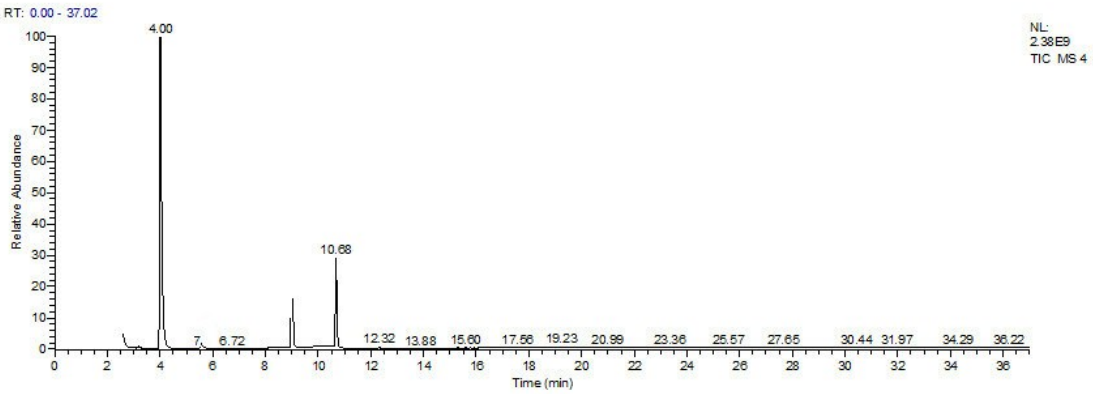


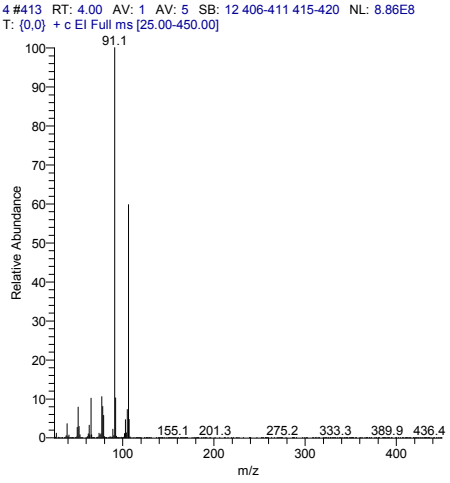
GC-MS of the bromination reaction mixture of ethylbenzene

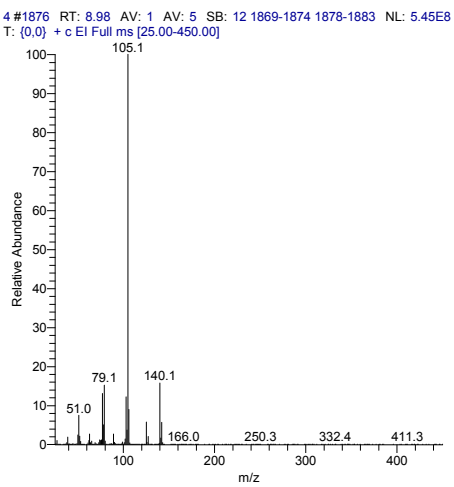


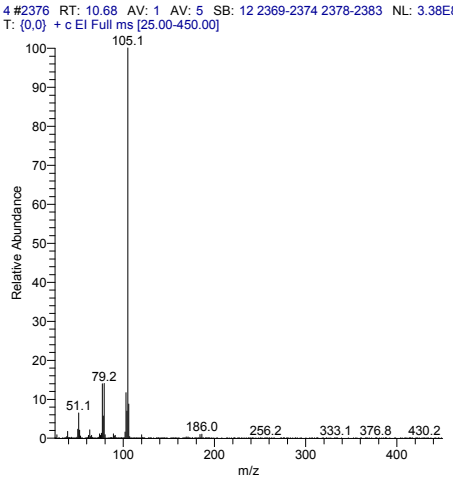
NMR of the bromination reactionmixture of ethylbenzene

Bromination of ethylbenzene by Ag/AgCl catalyzation

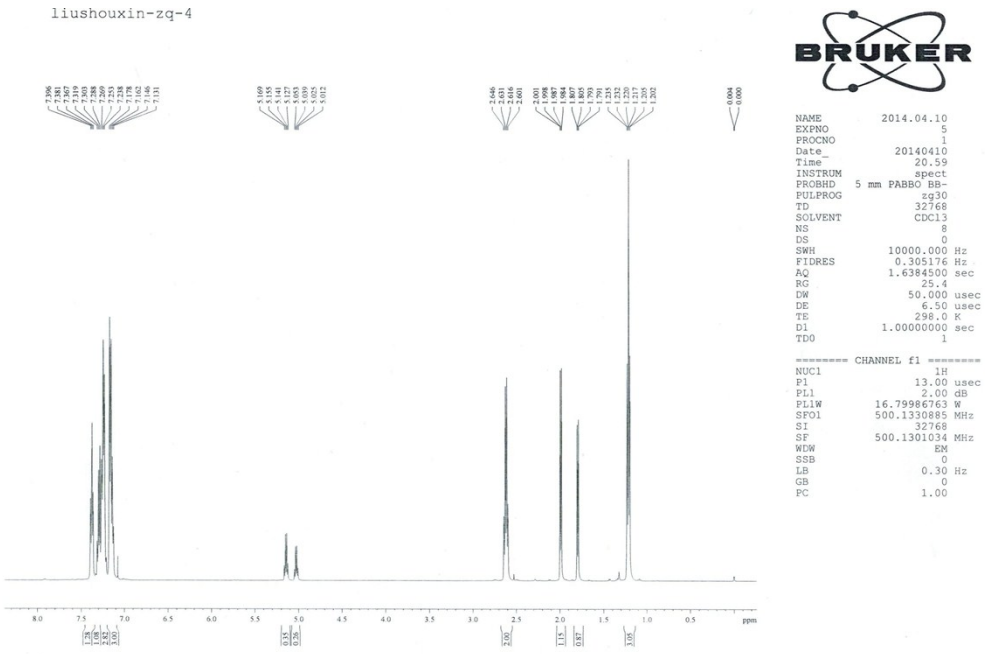




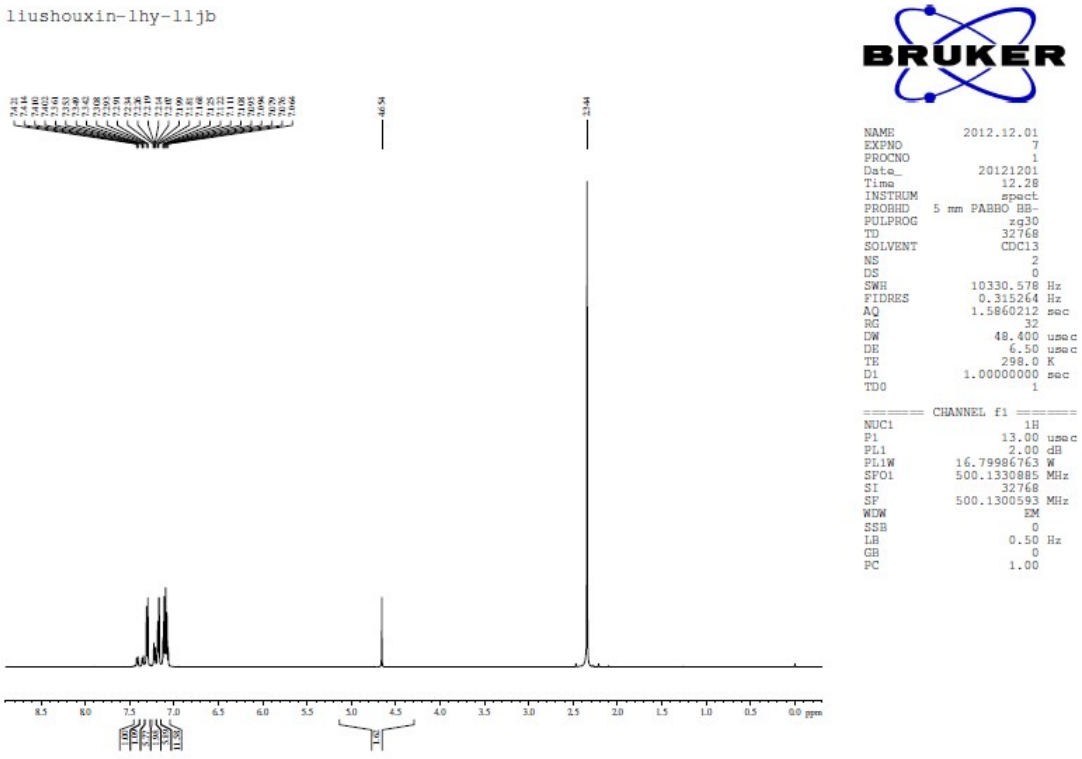




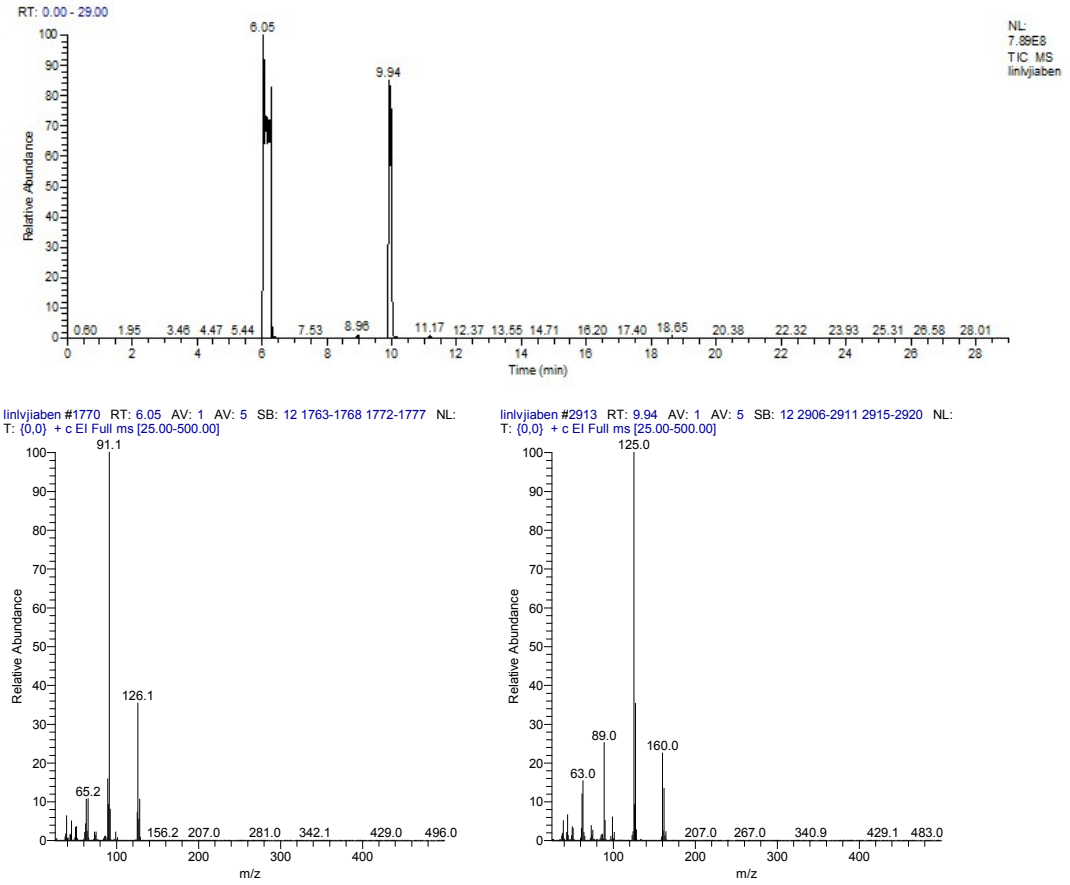
GC-MS of the bromination reaxction mixture of ethylbenzene



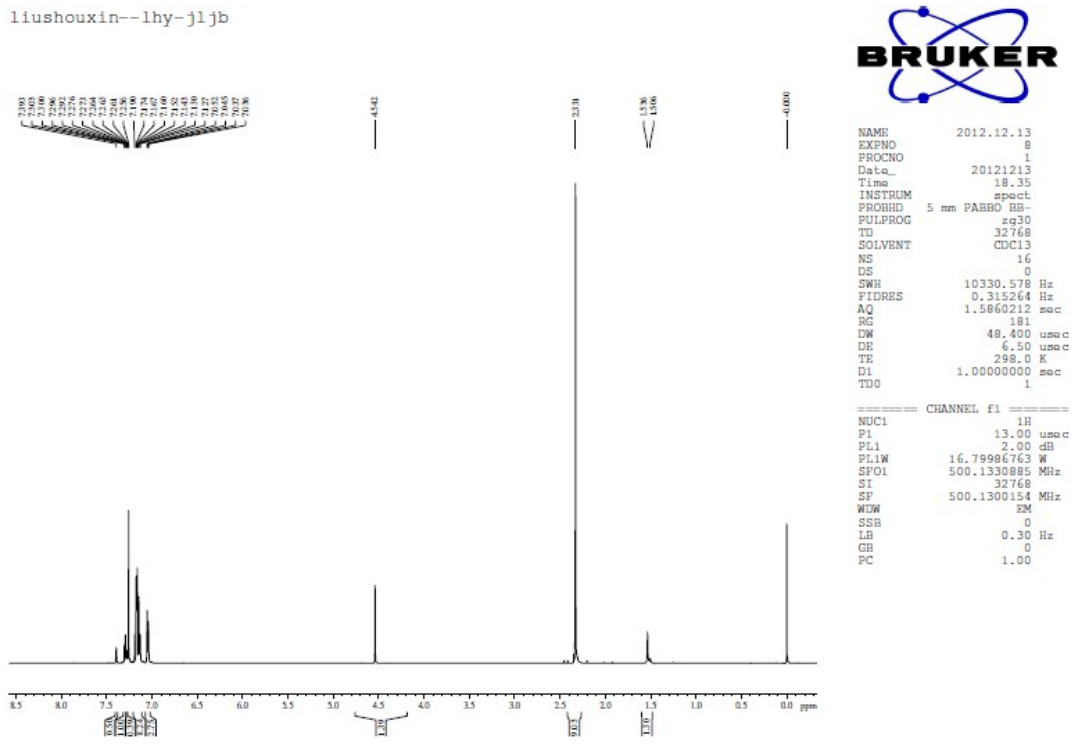
NMR of the bromination reaction mixture of ethylbenzene



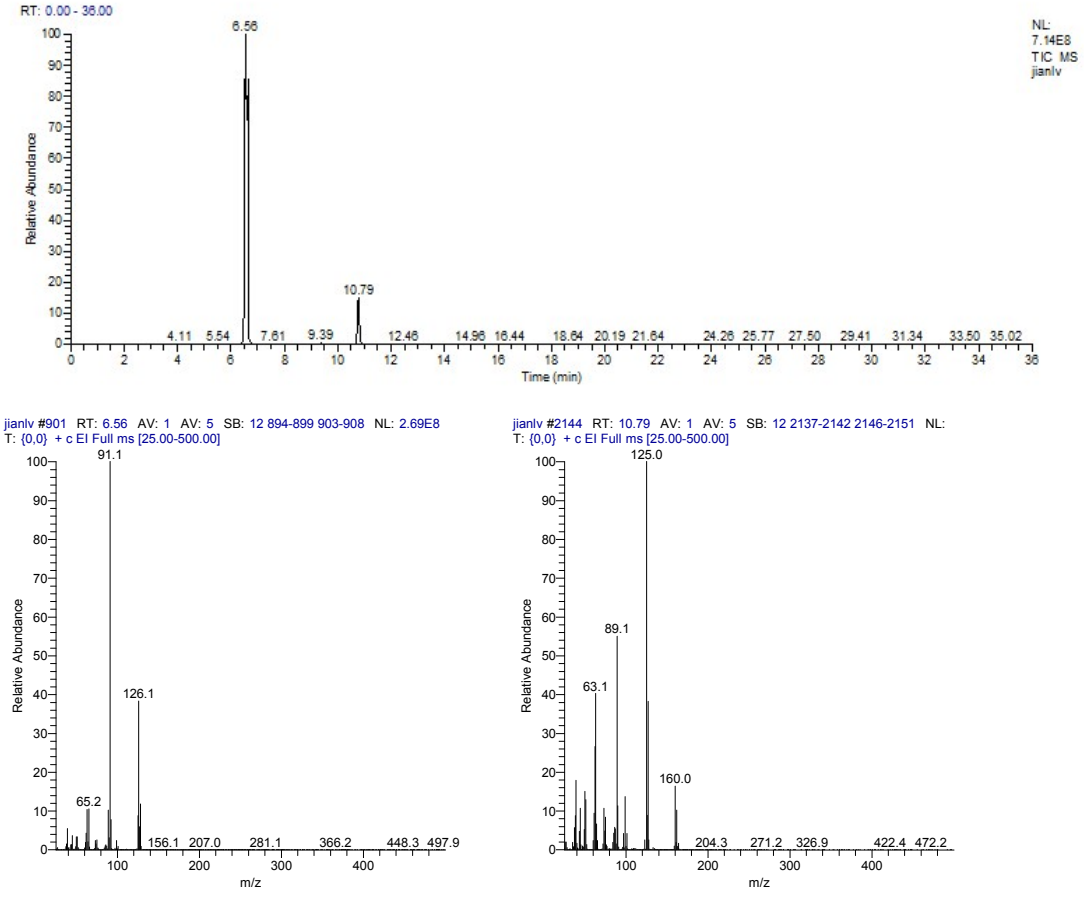
^{1}H NMR of the chlorination reaction mixture of 2-chlorotoluene



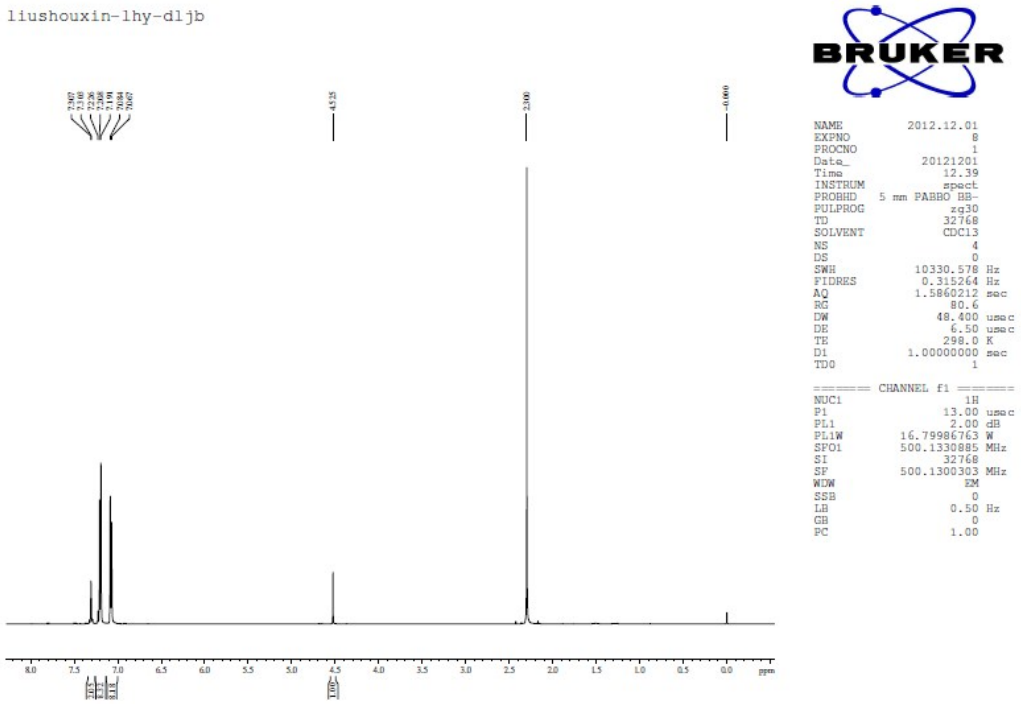
GC-MS of the chlorination reaction mixture of 2-chlorotoluene



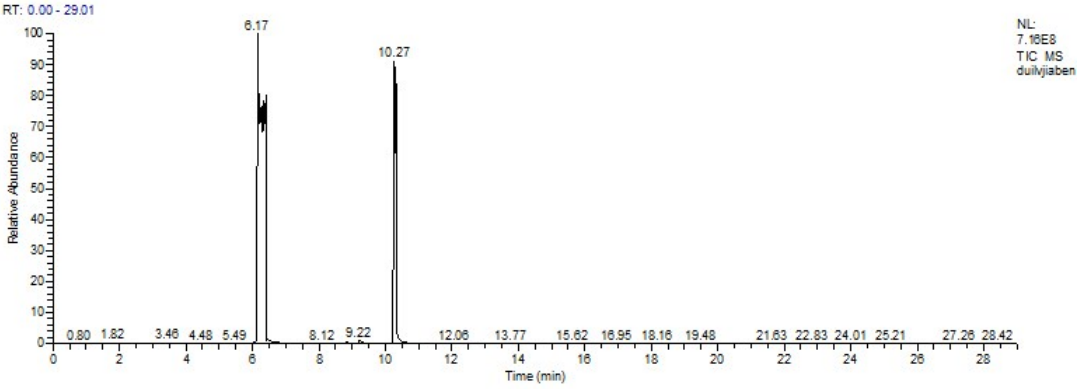
^{1}H NMR of the chlorination reaction mixture of 3-chlorotoluene

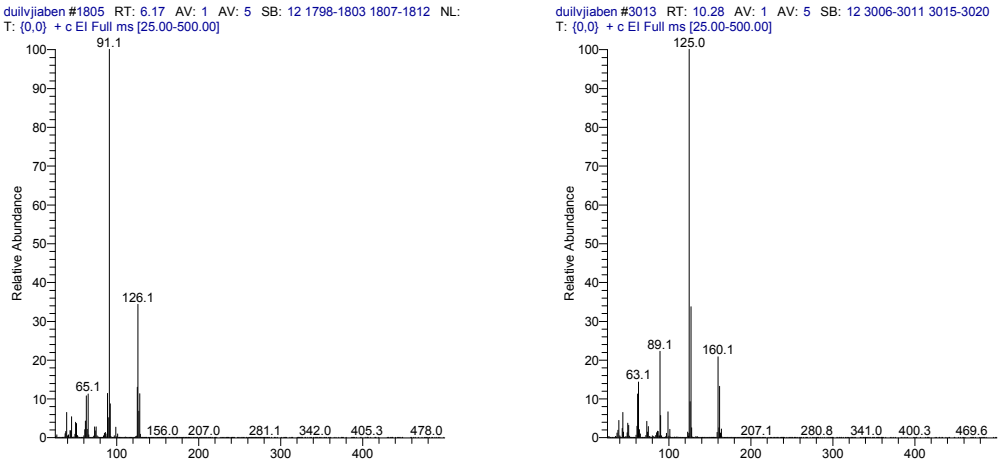


GC-MS of the chlorination reaction mixture of 3-chlorotoluene

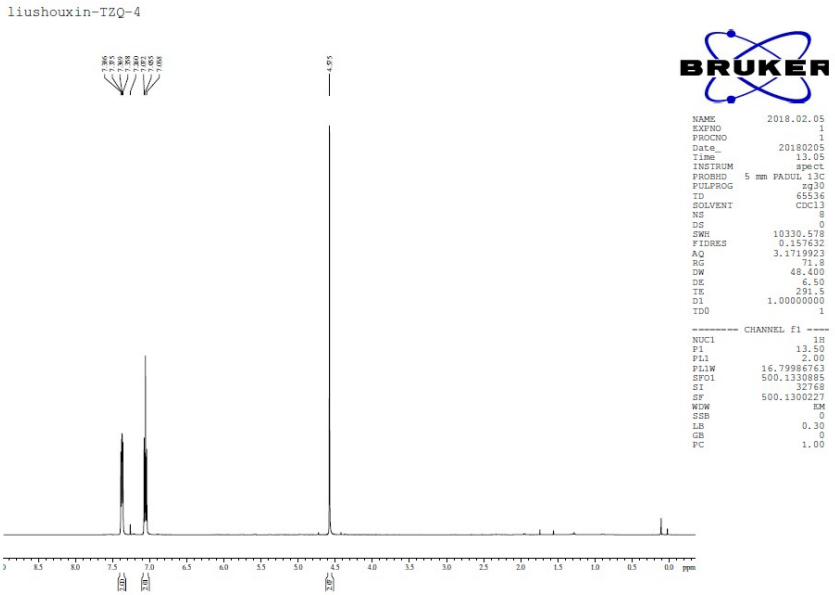


^{1}H NMR of the chlorination reaction mixture of 4-chlorotoluene

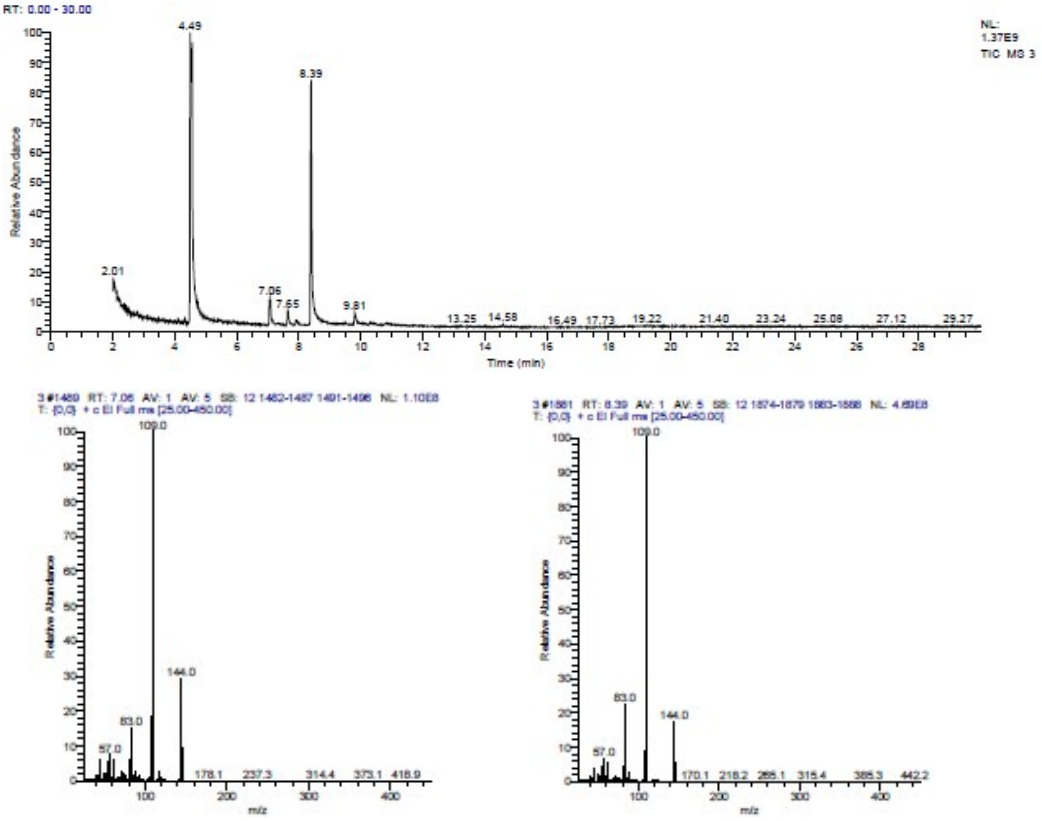




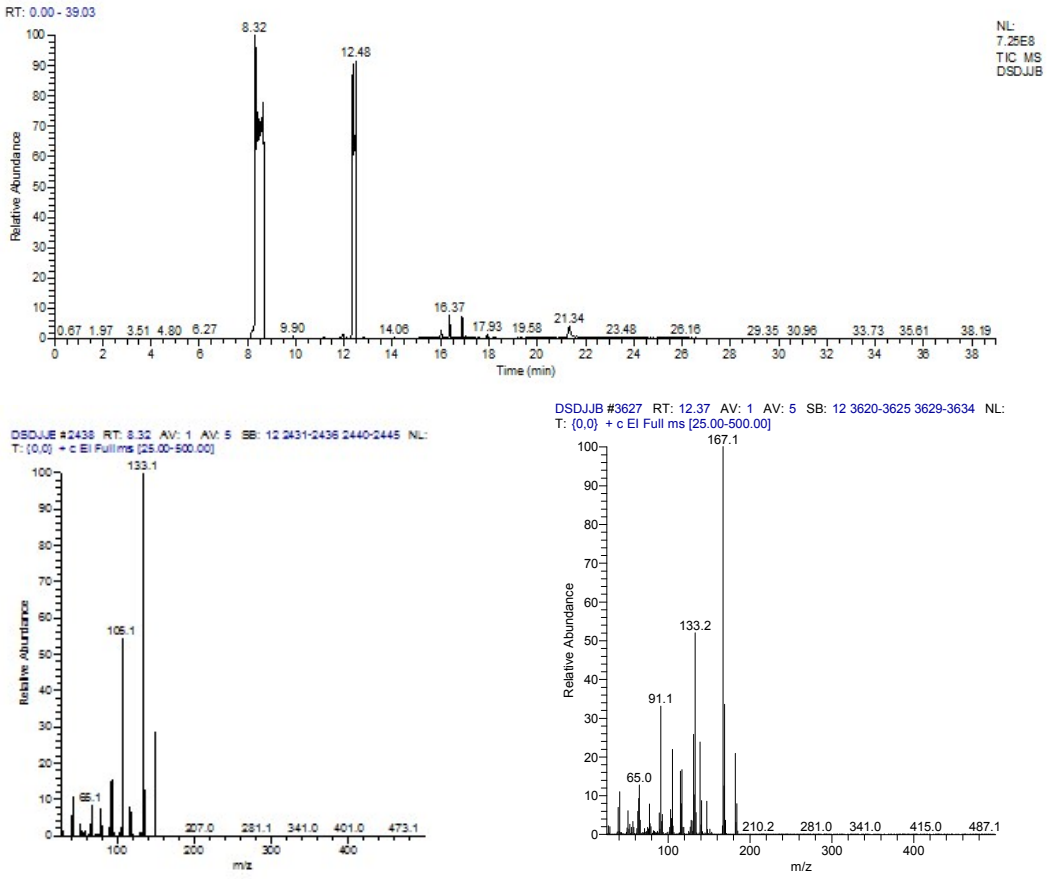
GC-MS of the chlorination reaction mixture of 4-chlorotoluene



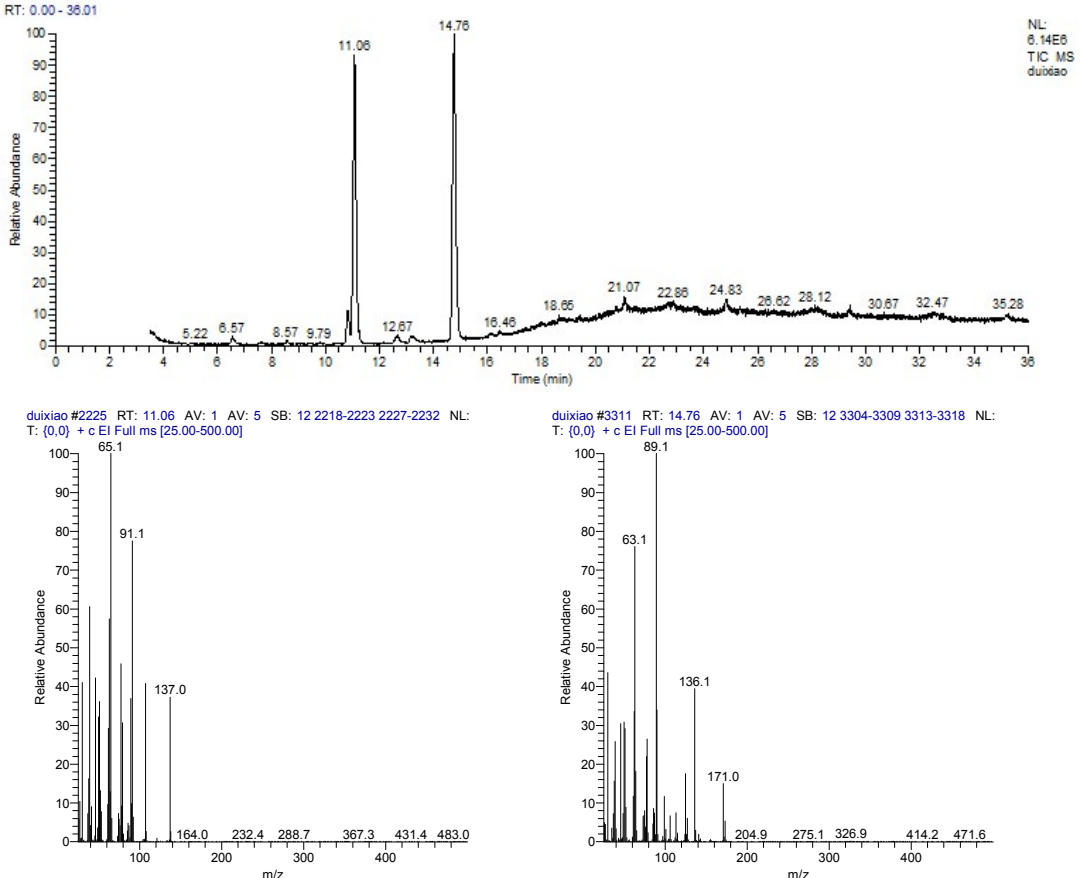
^{1}H NMR of the chlorination reaction mixture of 4-fluorotoluene



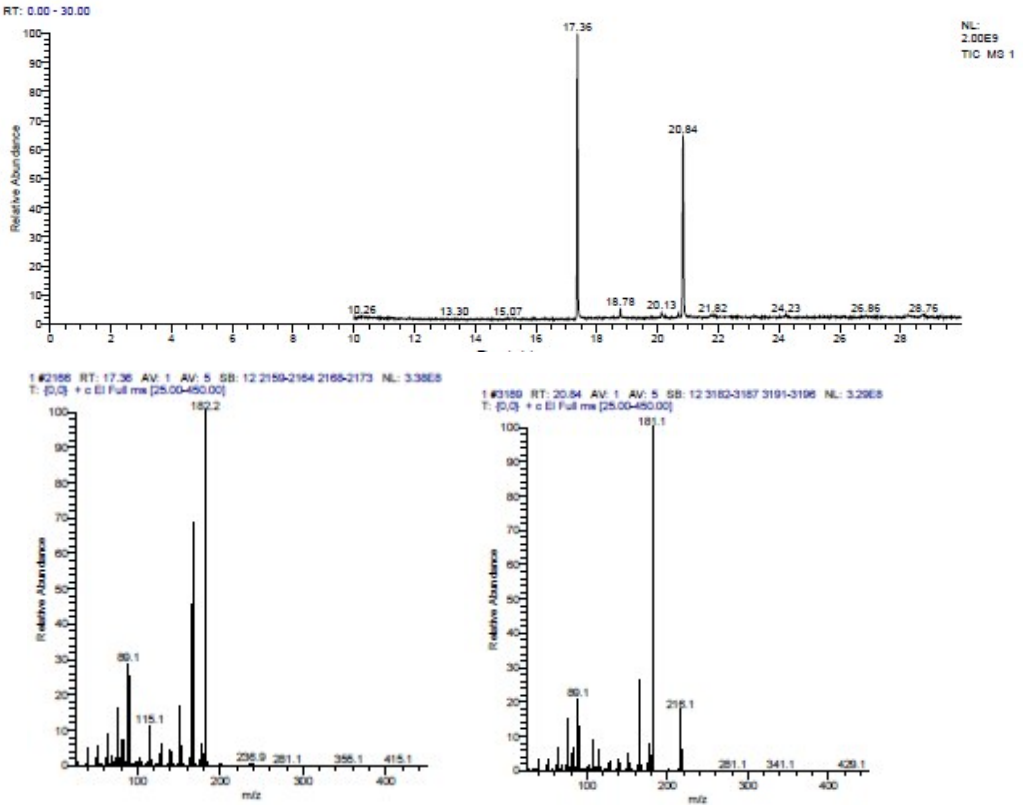
GC-MS of the chlorination reactionmixture of 4-fluorotoluene



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



GC-MS of the chlorination reaction mixture of *p*-nitrotoluene



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