

Supporting Information

Cu@CuCl-visible light co-catalysed chlorination of C(sp³)-H bonds with MCl_n solution and photocatalytic serial reactor-based synthesis of benzyl chloride

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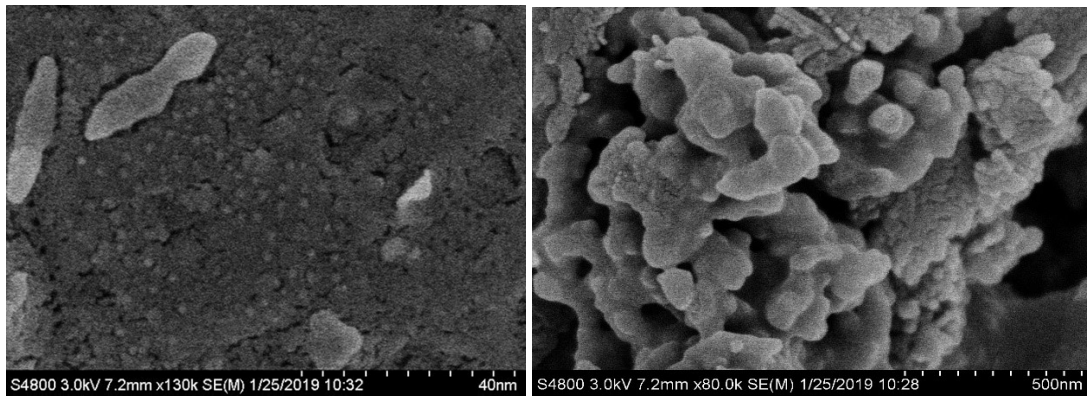
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The XRD of the catalyst separated from the reactor in the catalytic reaction state.



SEM of Cu/CuCl

CuCl exists in particles of 50-100 nanometers in diameter, and Cu particles with a diameter of 5 nm are evenly distributed on the surface of cuprous chloride particles.

The equipment system of triple serial reactor-based chlorination of toluene

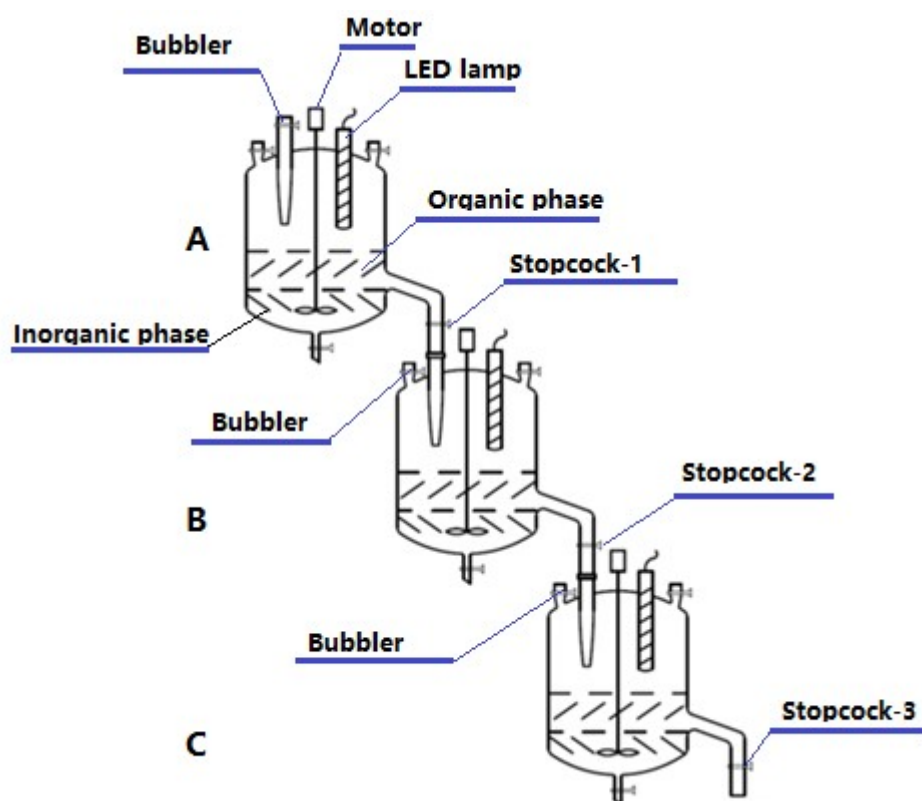
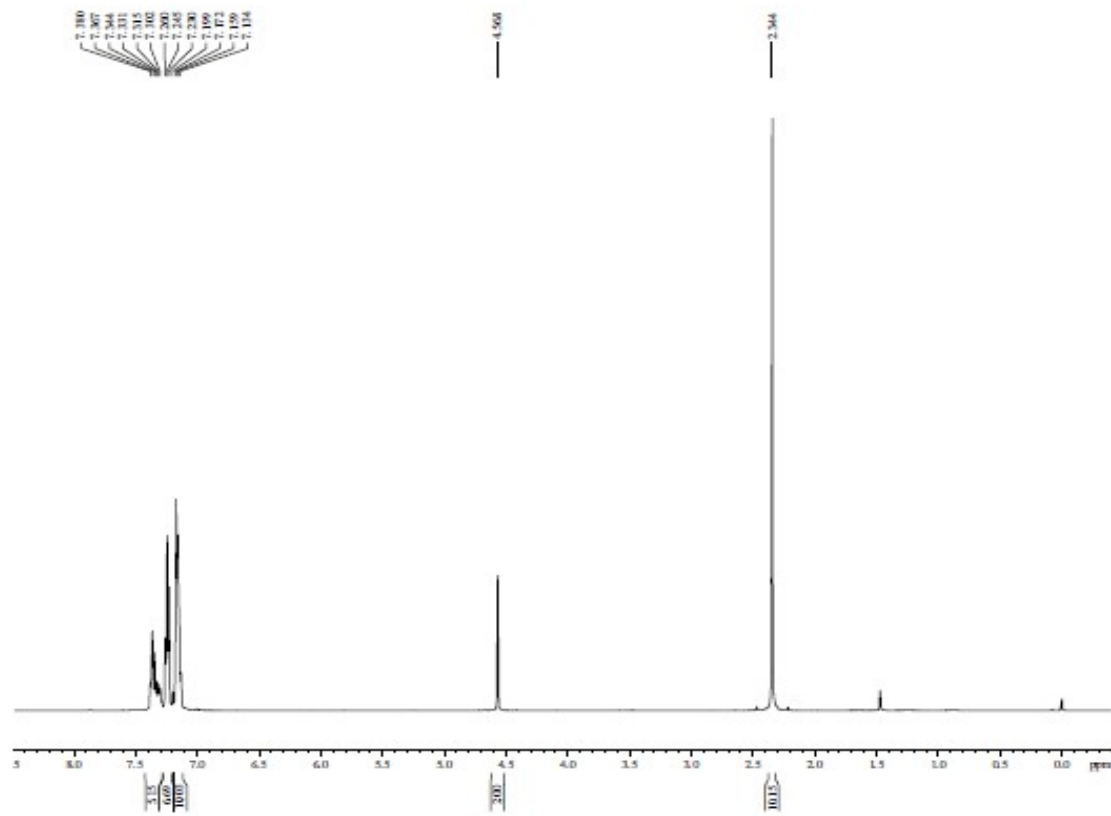
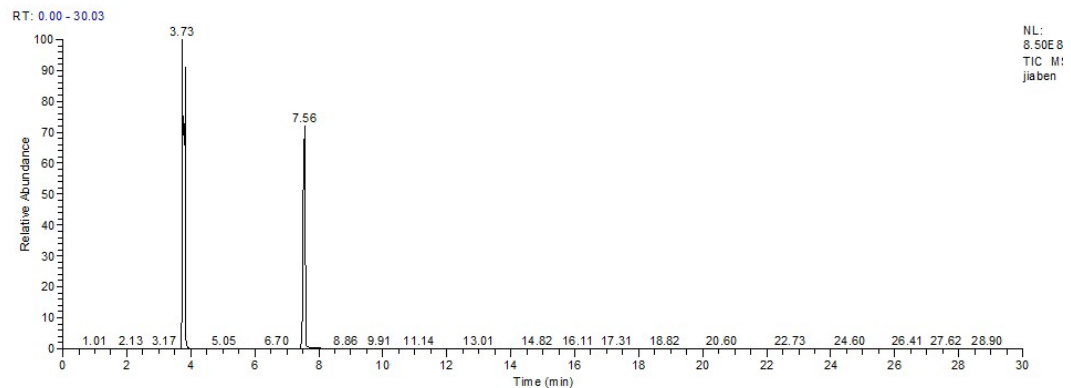


Diagram of the triple serial reactor-based photocatalytic reactor system for chlorination of toluene

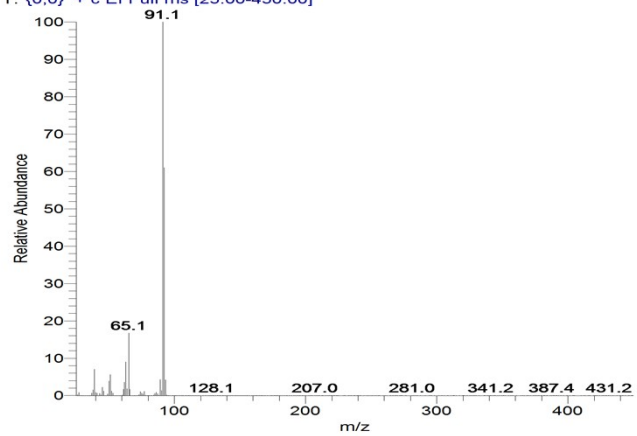
The equipment system of triple serial reactor-based chlorination of toluene shown in figure. The system includes three photocatalytic reactor A, B, C, which installed with mechanical stirrer, LED lamp and bubblers. The mixture of bittern 120 mL, 12 mL HOAc, 0.2 g nano-Cu@CuCl (about 10 mol% loading level with nano-Cu), and 0.42 g tetrabutylammonium chloride (TBAC) was charged in each of the three photoreactors. Then toluene (0.5 mol) was added to A reactor and react for 2 h with stirring at room temperature under visible light (LED lamp) irradiation. After stewing 10 mins, and open stopcock-1, the organic phase was transformed to B reactor and was continually treated for 2h in the same conditions. The organic phase in B reactor was transformed to C reactor through opening stopcock-2, and repeated over process. After the reaction ended, the organic mixture in C reactor was separated through opening stopcock-3, dried over anhydrous MgSO_4 and filtered to collect the solution, which was fractionated to give 57g (90%) benzyl chloride.



¹H NMR of chlorination mixture of toluene

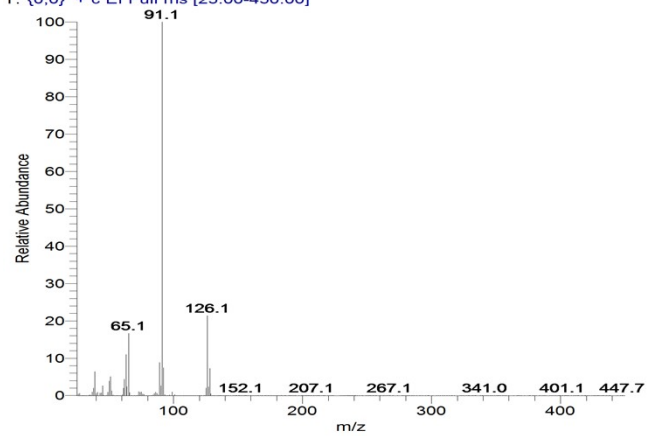


jjaben #1089 RT: 3.73 AV: 1 AV: 5 SB: 12 1082-1087 1091-1096 NL:
T: {0,0} + c EI Full ms [25.00-450.00]



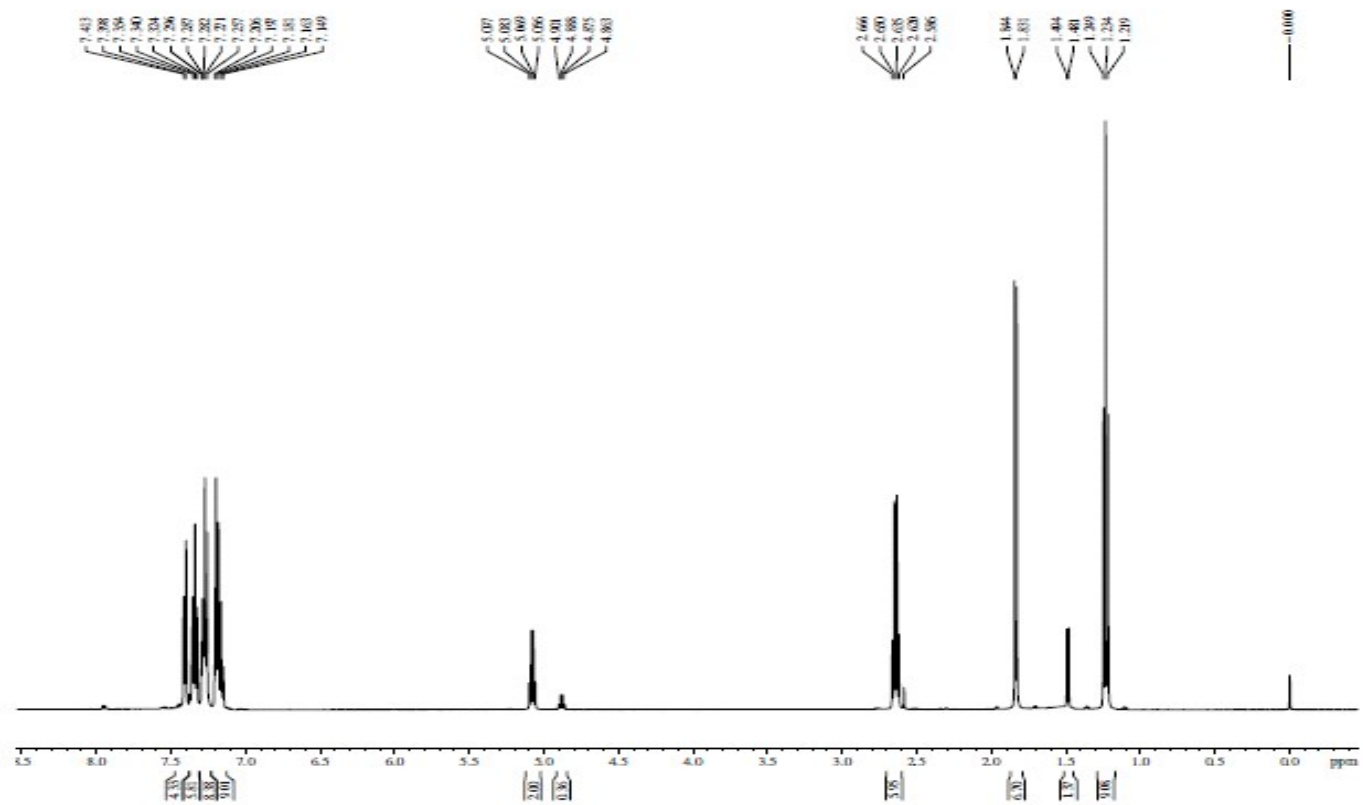
Substrate

jjaben #2214 RT: 7.56 AV: 1 AV: 5 SB: 12 2207-2212 2216-2221 NL:
T: {0,0} + c EI Full ms [25.00-450.00]



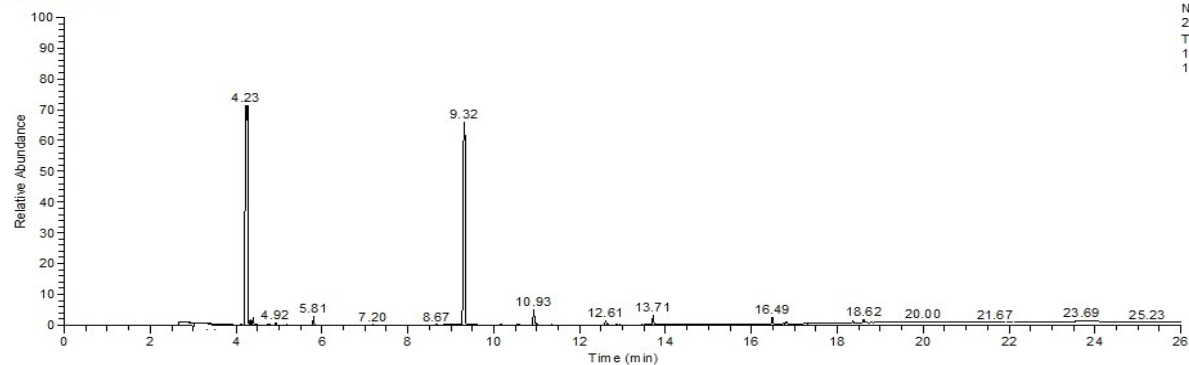
Product

GS-MS of chlorination mixture of toluene



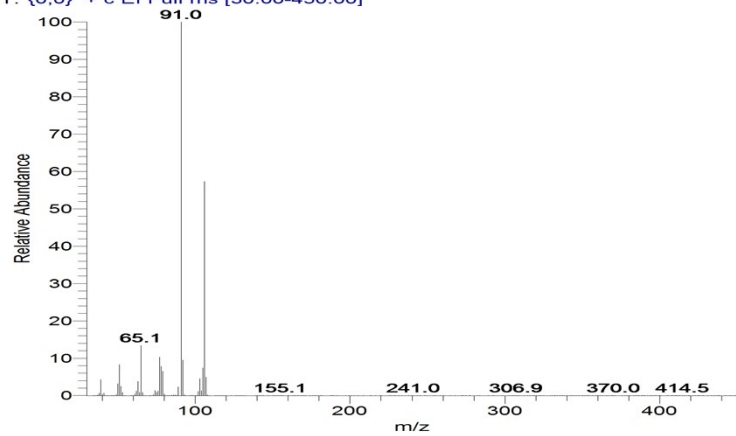
¹H NMR of chlorination mixture of ethylbenzene

RT: 0.00 - 26.03



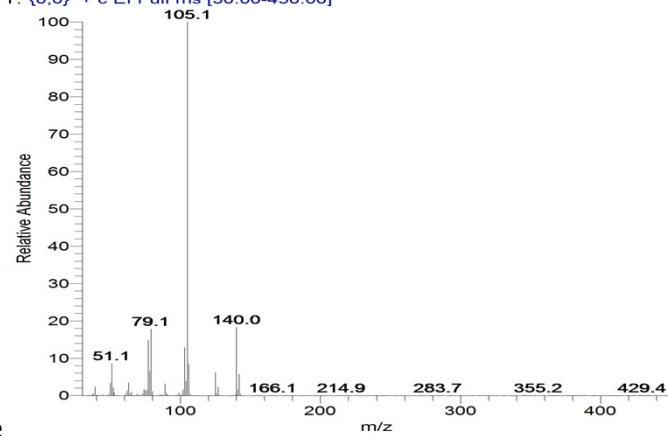
NL:
2.95E9
TIC_MS
1#_130129
153914

1#_130129153914 #755 RT: 4.27 AV: 1 AV: 5 SB: 12 748-753 757-762
T: {0,0} + c EI Full ms [30.00-450.00]



Substrate

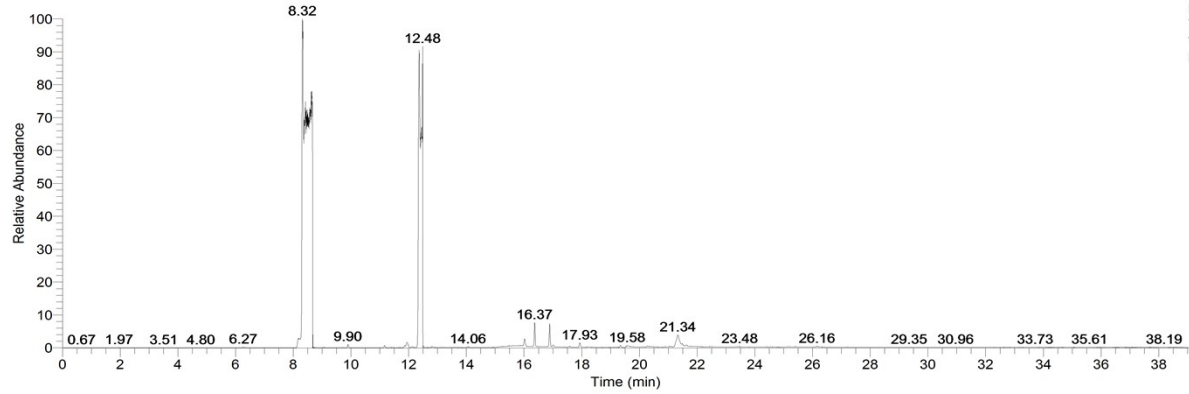
1#_130129153914 #2241 RT: 9.32 AV: 1 AV: 5 SB:
T: {0,0} + c EI Full ms [30.00-450.00]



Product

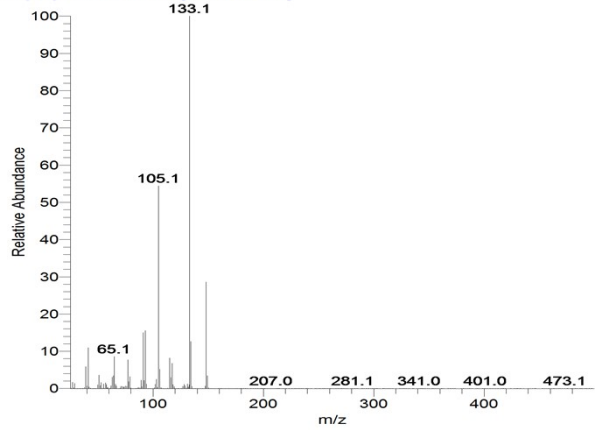
GS-MS of chlorination mixture of ethylbenzene

RT: 0.00 - 39.03



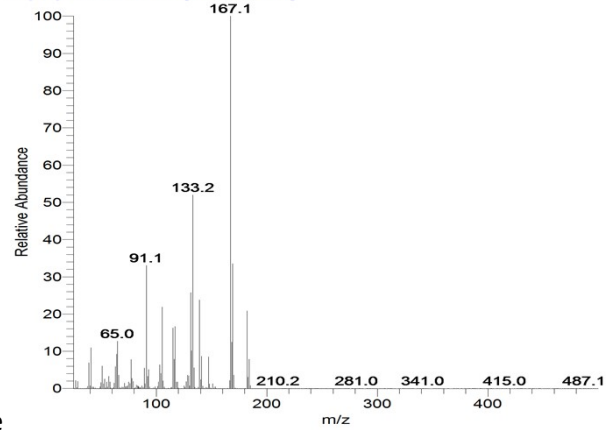
NL:
7.25E8
TIC MS
DSDJJB

DSDJJB #2438 RT: 8.32 AV: 1 AV: 5 SB: 12 2431-2436 2440-2445 NL:
T: (0,0) + c EI Full ms [25.00-500.00]



Substrate

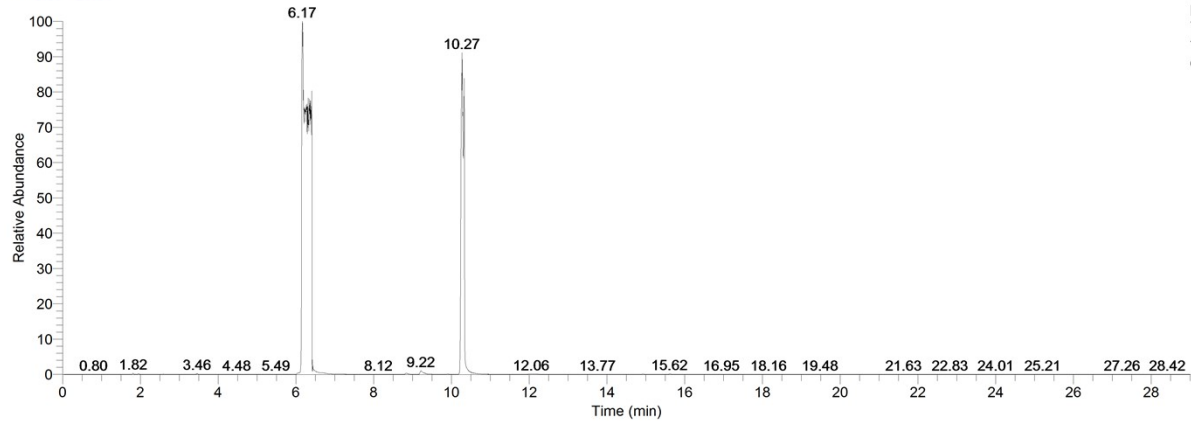
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T: (0,0) + c EI Full ms [25.00-500.00]



Product

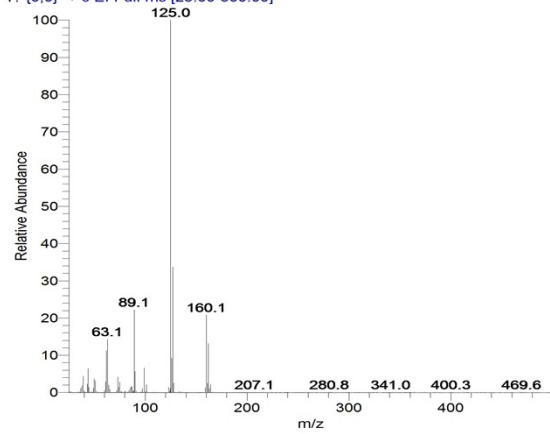
GS-MS of chlorination mixture of 4-*t*-Bu-toluene

RT: 0.00 - 29.01



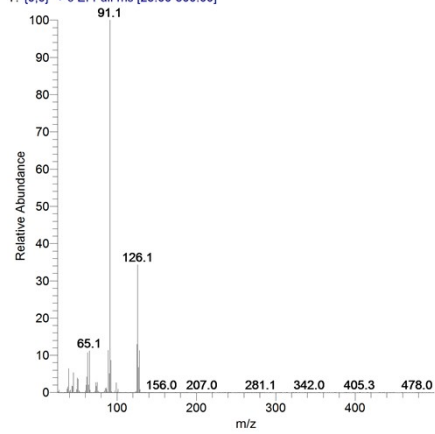
NL:
7.16E8
TIC MS
duilvjaben

duilvjaben #3013 RT: 10.28 AV: 1 AV: 5 SB: 12 3006-3011 3015-3020
T: {0,0} + c EI Full ms [25.00-500.00]



Substrate

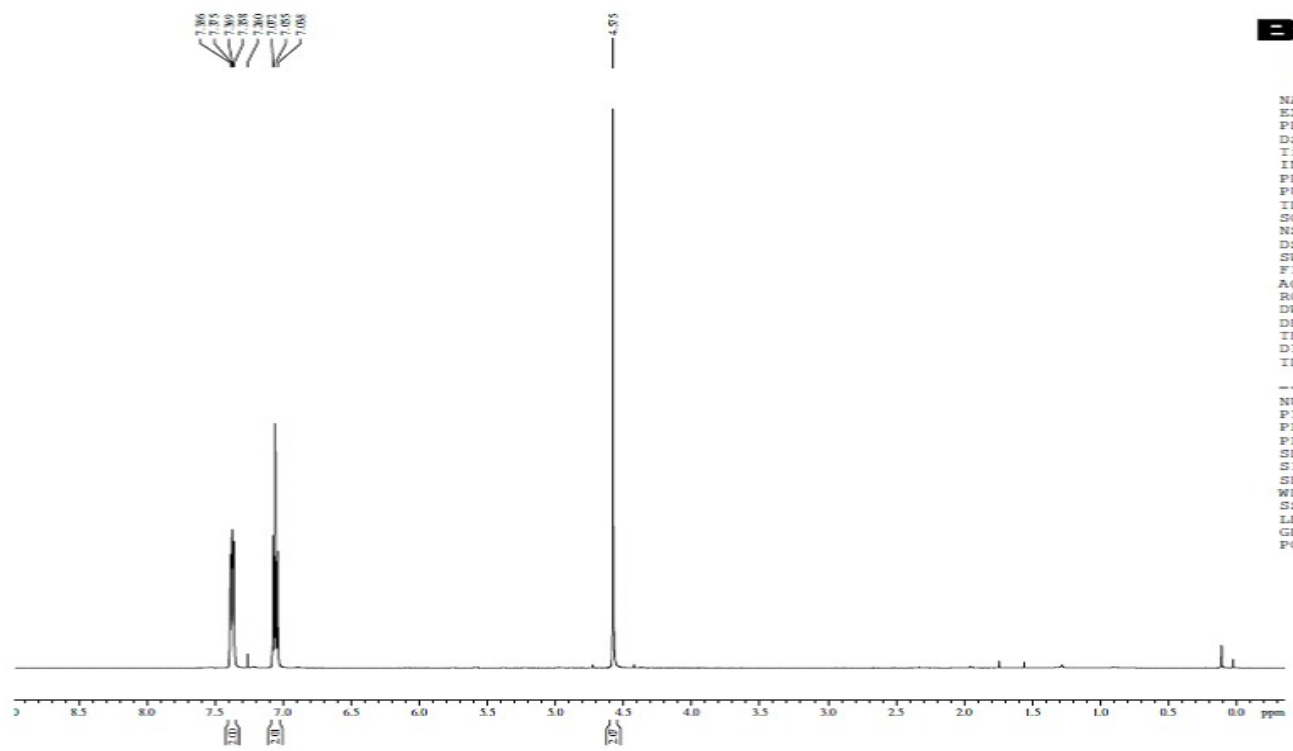
duilvjaben #1805 RT: 6.17 AV: 1 AV: 5 SB: 12 1798-1803 1807-1812 NL:
T: {0,0} + c EI Full ms [25.00-500.00]



Product

GS-MS of chlorination mixture of 4-Cl-toluene

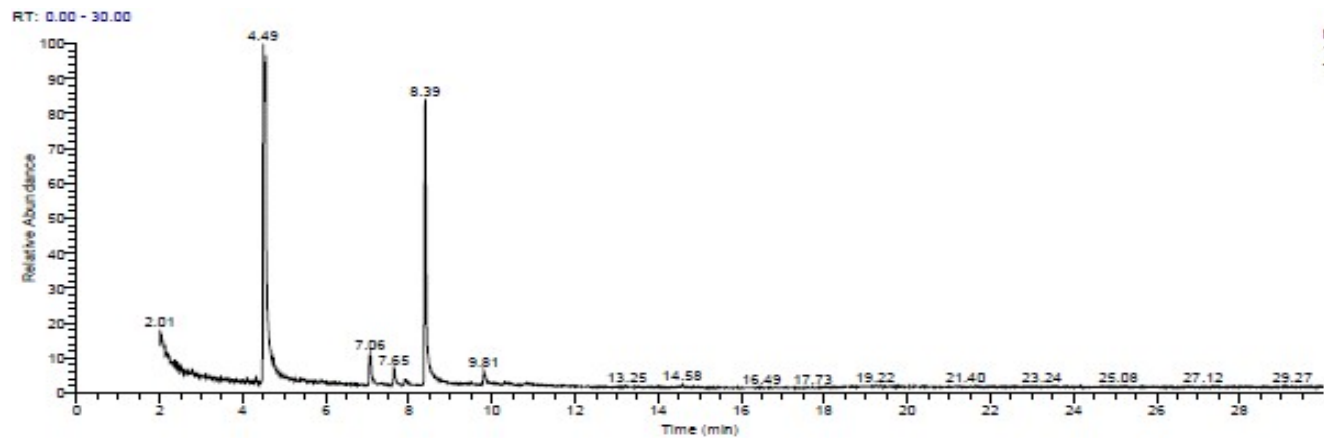
liushouxin-TZQ-4



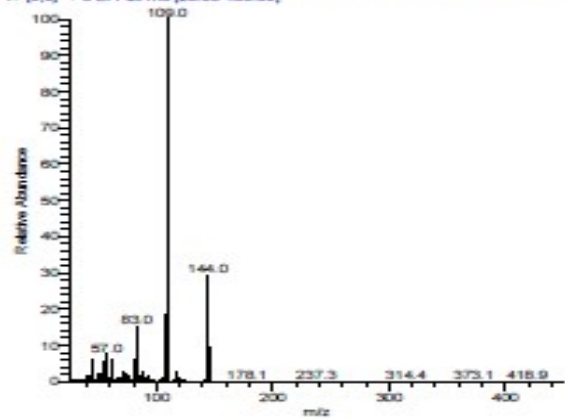
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PROCNO        1
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Time          13.05
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PULPROG       zg30
ID            65536
SOLVENT       CDCl3
NS            8
DS            0
SWH           10330.578
FIDRES        0.157632
AQ            3.1719923
RG            71.8
DW            48.400
DE            6.50
TE            291.5
D1            1.00000000
ID0           1
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----- CHANNEL f1 -----
NUC1          1H
P1            13.50
PL1           2.00
PL1W          16.79986763
SFO1          500.1330885
SI            32768
SF            500.1300227
WDW           EM
SSB           0
LB            0.30
GB            0
PC            1.00
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¹H NMR of chlorination mixture of 4-fluorotoluene

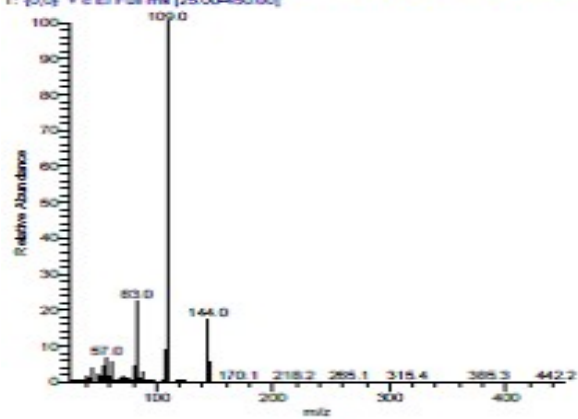


3 #1489 RT: 7.06 AV: 1 AV: 5 SS: 12 1482-1487 1491-1496 NL: 1.10E8
T: [D,C] + e EI Full ms [25.00-450.00]



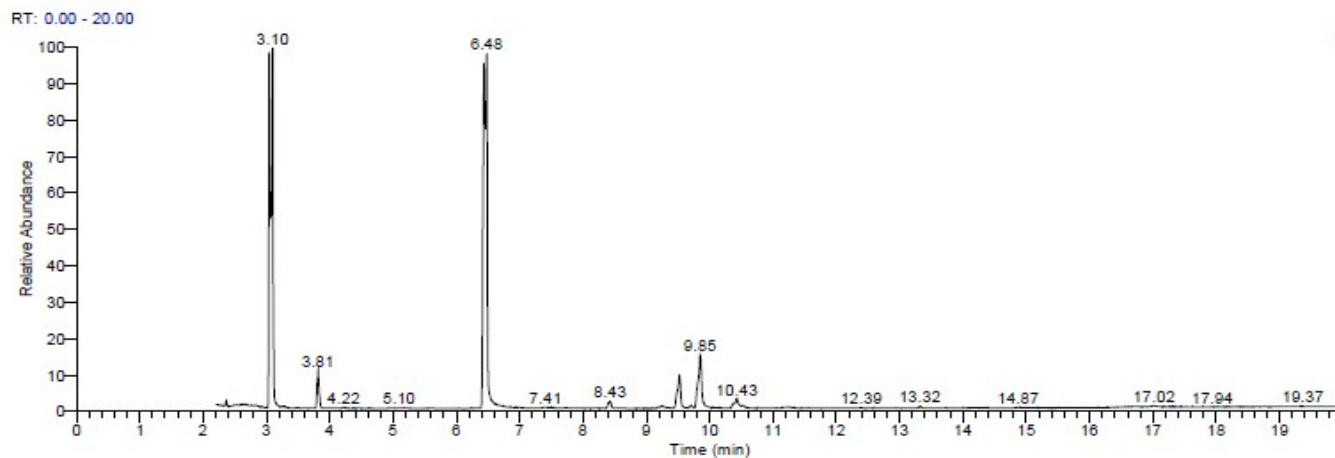
Substrate

3 #1581 RT: 8.39 AV: 1 AV: 5 SS: 12 1574-1579 1583-1588 NL: 4.69E8
T: [D,C] + e EI Full ms [25.00-450.00]

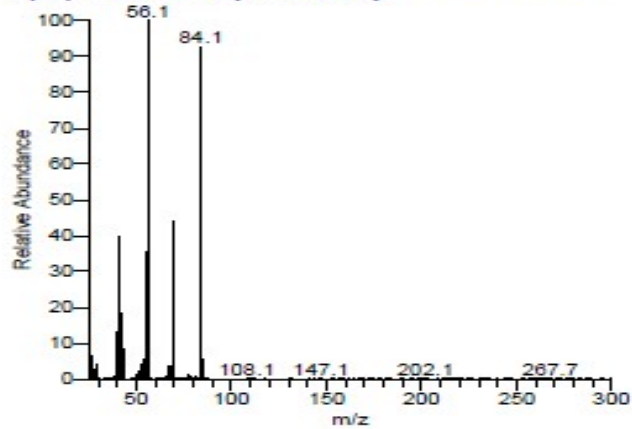


Product

GC-MS of chlorination mixture of 4-fluorotoluene

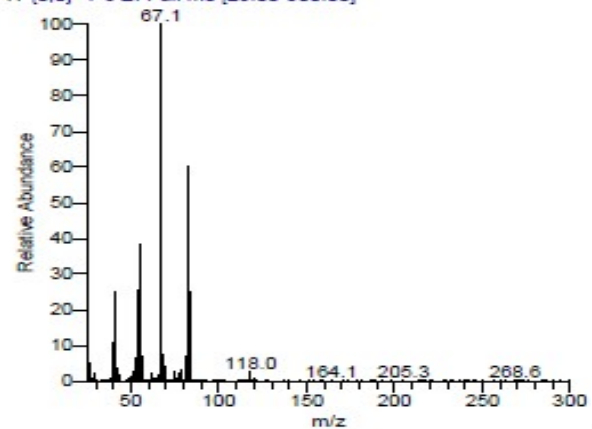


2 #265 RT: 3.10 AV: 1 AV: 5 SB: 12 258-263 267-272 NL:
T: (0,0) + c EI Full ms [25.00-300.00]



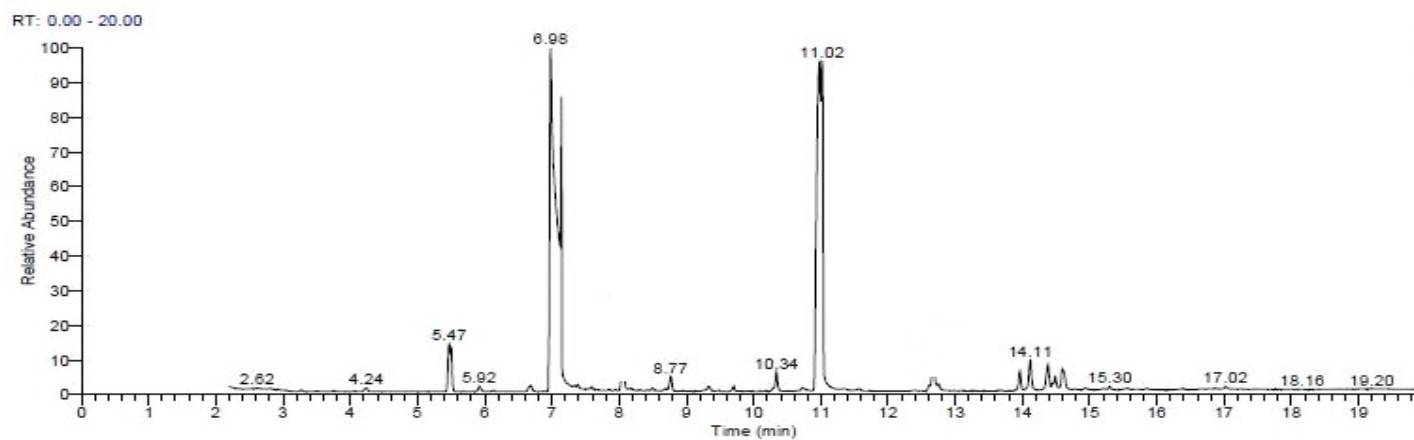
Substrate

2 #1246 RT: 6.44 AV: 1 AV: 5 SB:
T: (0,0) + c EI Full ms [25.00-300.00]

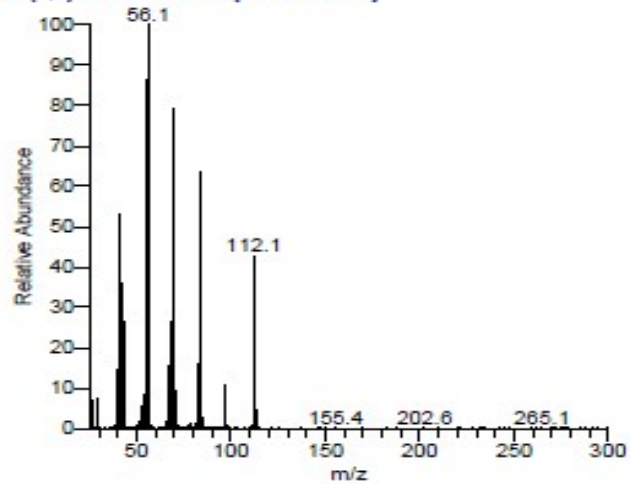


Product

GS-MS of chlorination mixture of cyclohexane

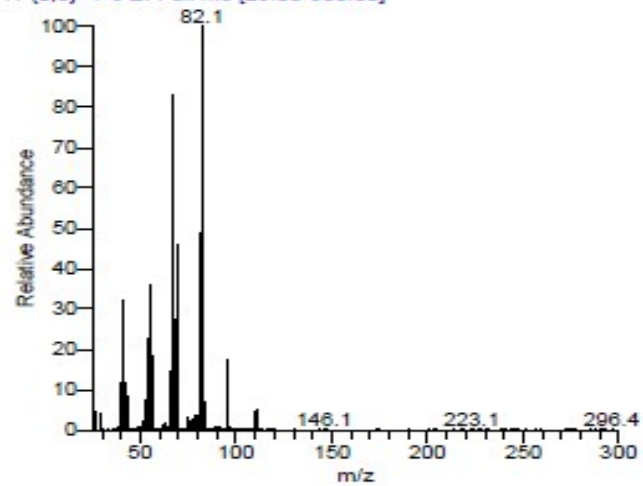


2 #1406 RT: 6.98 AV: 1 AV: 5 SB:
T: (0,0) + c EI Full ms [25.00-300.00]



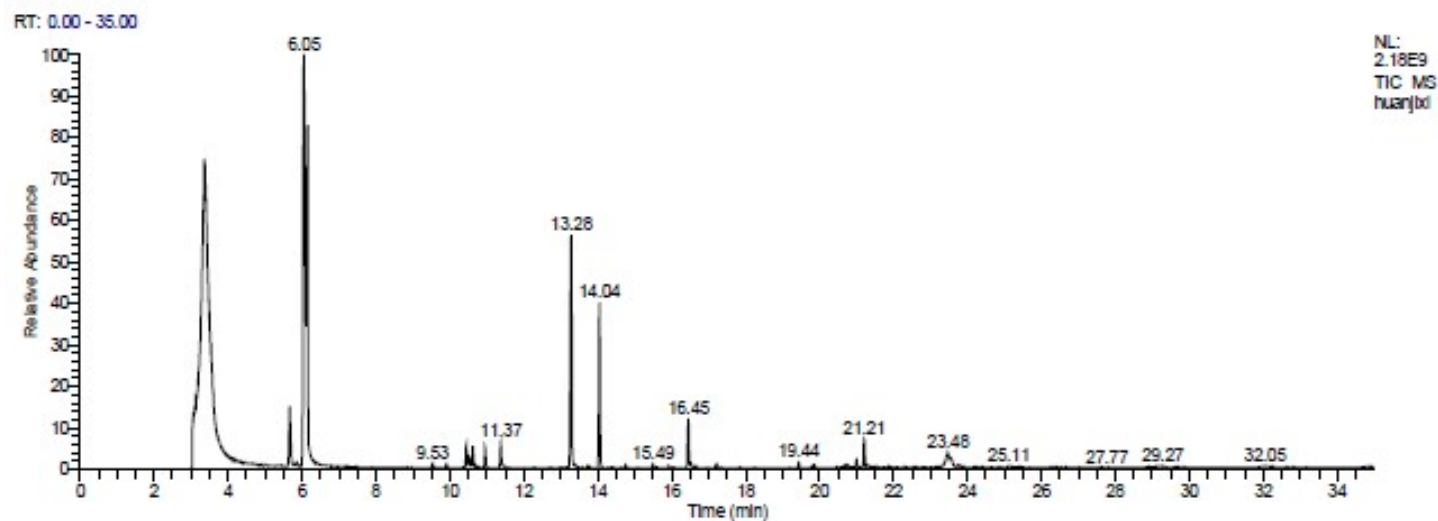
Substrate

2 #2595 RT: 11.02 AV: 1 AV: 5 SB:
T: (0,0) + c EI Full ms [25.00-300.00]

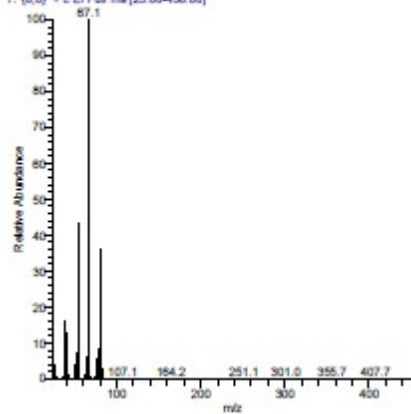


Product

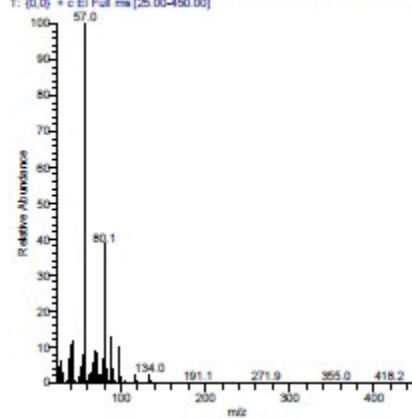
GS-MS of chlorination mixture of cyclooctane



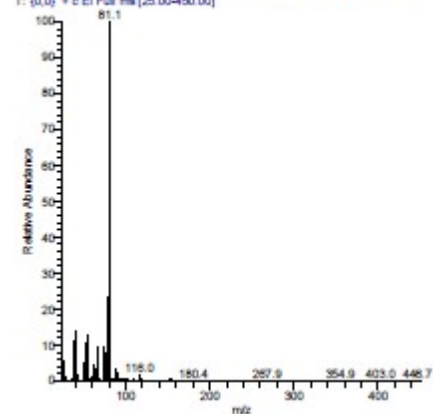
huanj(b) #898 RT: 6.05 AV: 1 AV: 5 SB: 12 891-898 900-905 NL: 7.38E8
T: (0.0) + c EI Full ms [25.00-450.00]



huanj(b) #8024 RT: 13.28 AV: 1 AV: 5 SB: 12 3017-3022 3026-3031 NL:
T: (0.0) + c EI Full ms [25.00-450.00]

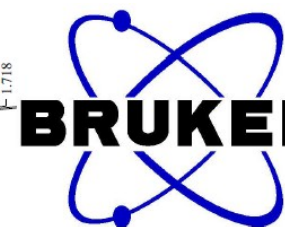
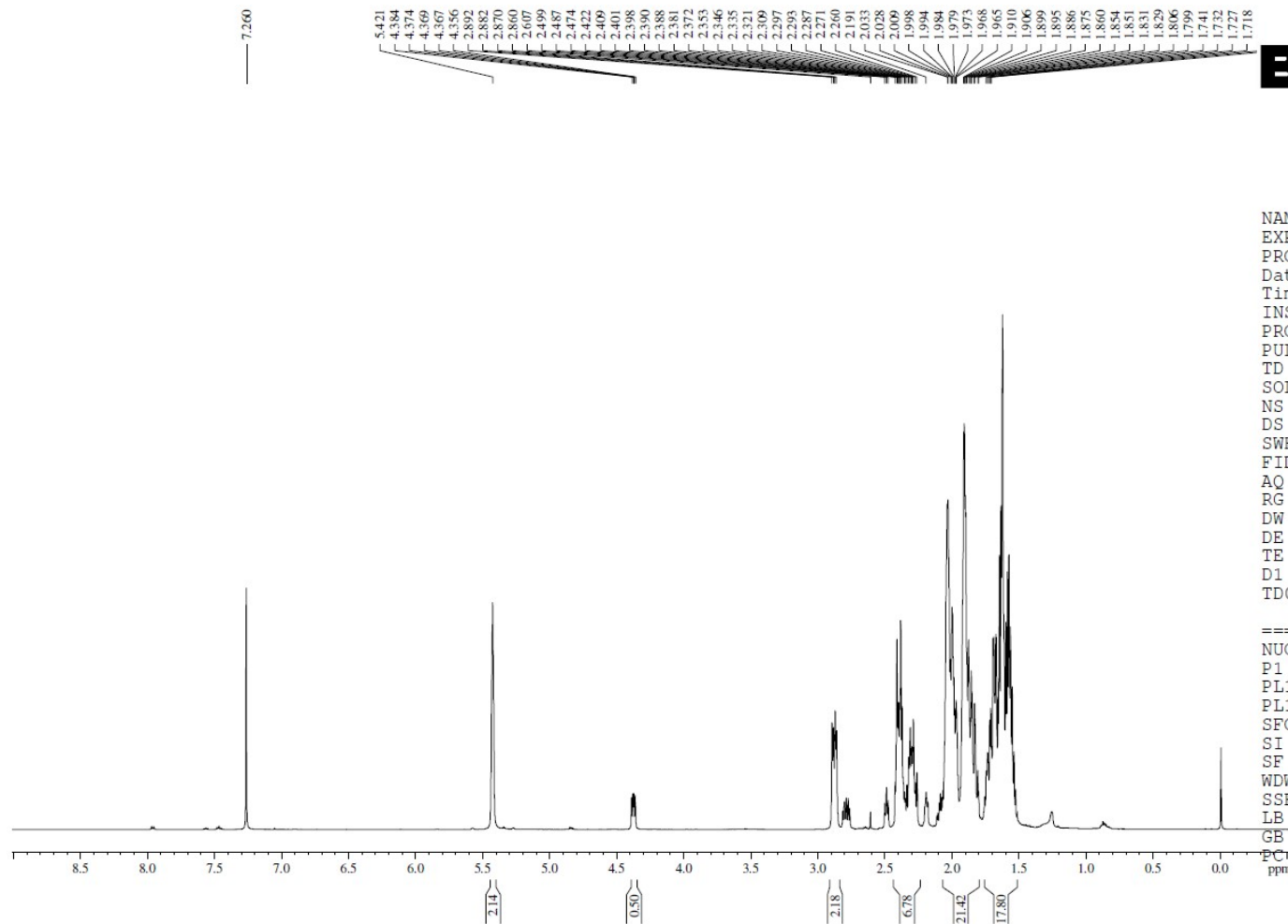


huanj(b) #3348 RT: 14.04 AV: 1 AV: 5 SB: 12 3041-3048 3250-3295 NL:
T: (0.0) + c EI Full ms [25.00-450.00]



GS-MS of chlorination mixture (substate, 2-Cl-hexanole and 1,2-di-Cl-hexane) of cyclohexene

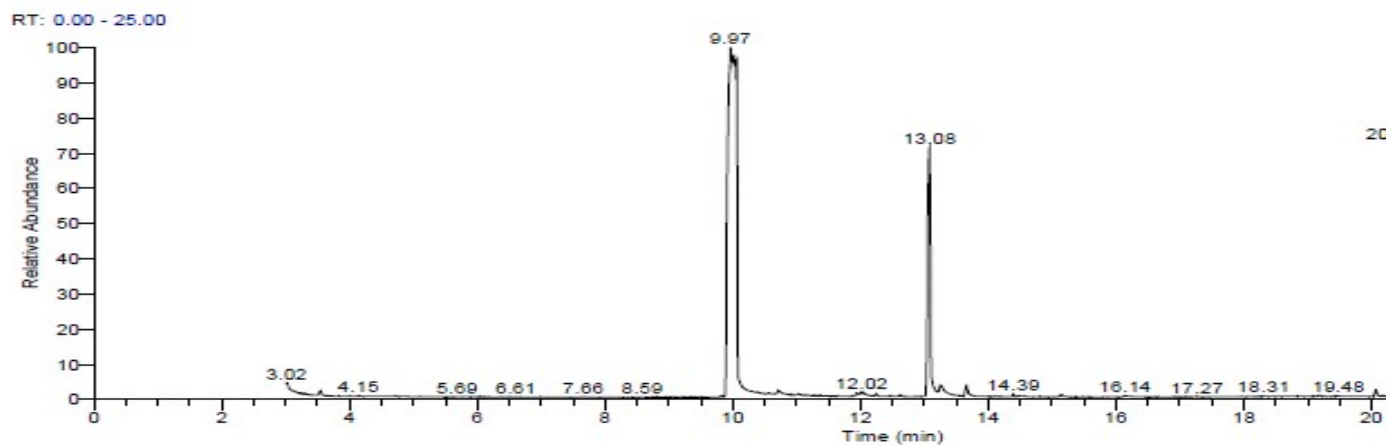
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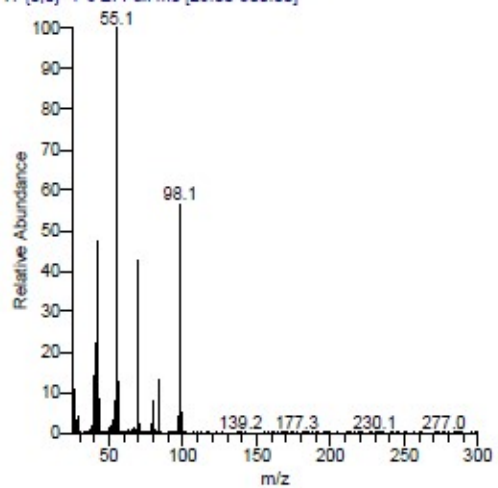
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PROCNO        1
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PULPROG       zg30
TD            65536
SOLVENT       CDC13
NS            64
DS            0
SWH           10000.000
FIDRES        0.152588
AQ            3.2768500
RG            128
DW            50.000
DE            6.50
TE            298.0
D1            1.00000000
TD0           1
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```
===== CHANNEL f1 =====
NUC1           1H
P1             13.50
PL1            2.00
PL1W          16.79986763
SFO1          500.1325007
SI             32768
SF            500.1300229
WDW            EM
SSB            0
LB             1.00
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¹H NMR of chlorination mixture of cyclohexanone

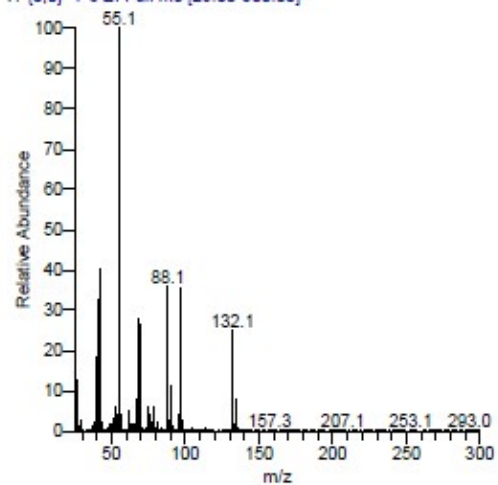


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Substrate

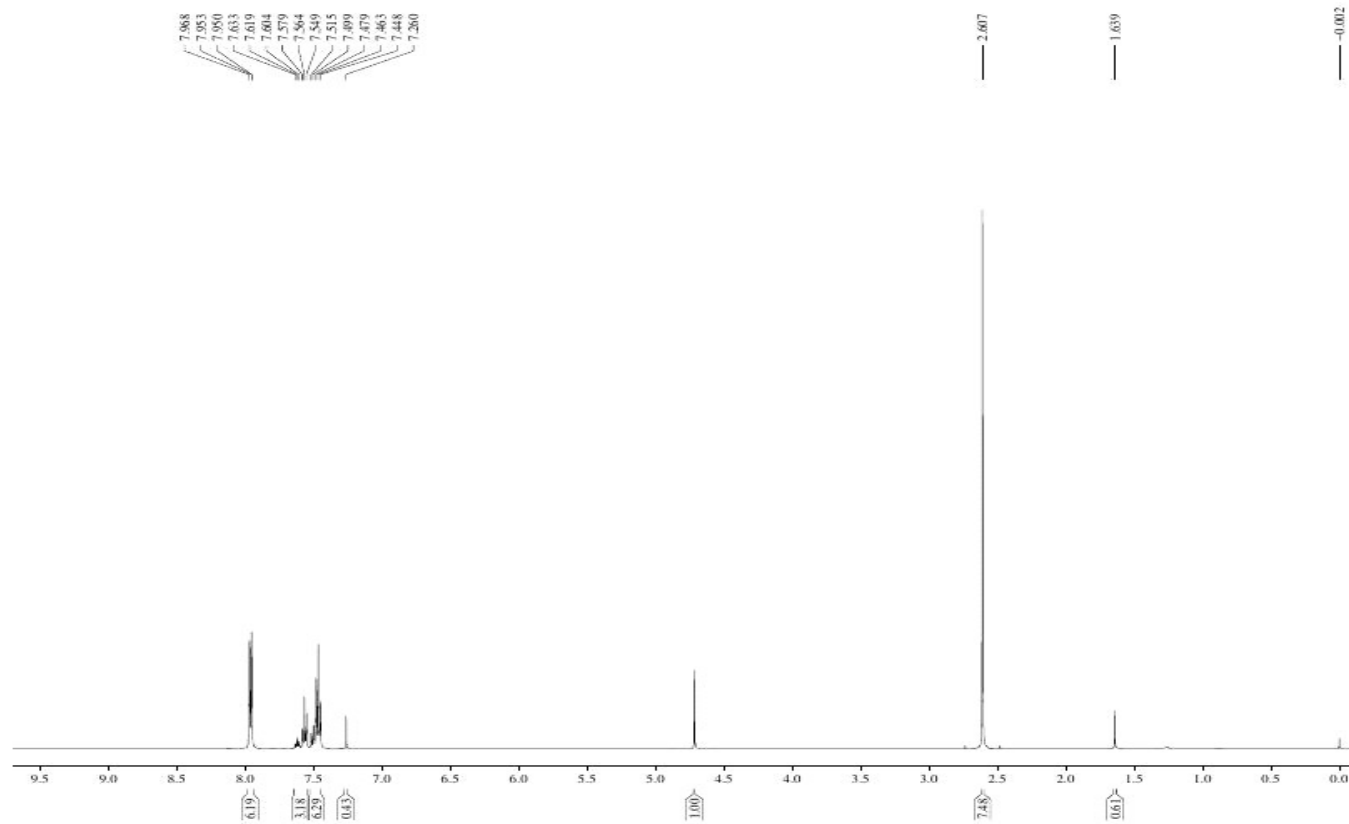
3 #2064 RT: 13.08 AV: 1 AV: 5 SB:
T: (0,0) + c EI Full ms [25.00-300.00]



Product

GS-MS of chlorination mixture of cyclohexanone

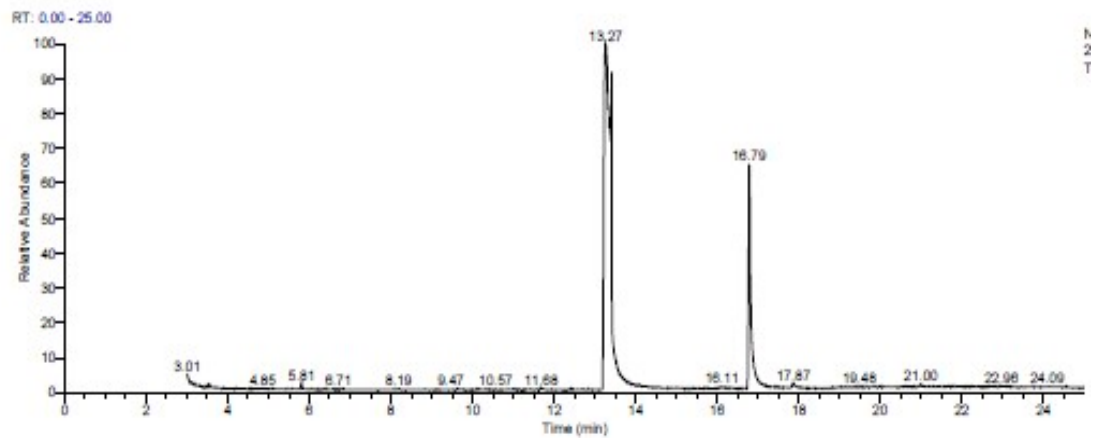
lsx-1-5



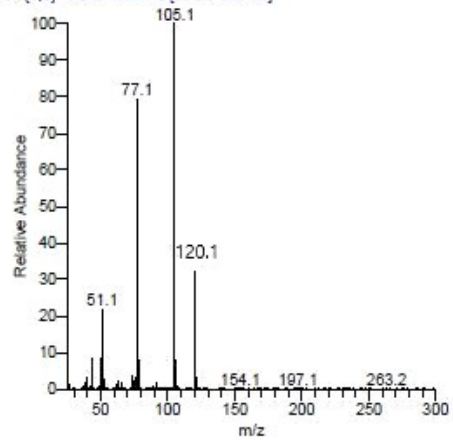
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PULPROG       zg30
TD            65536
SOLVENT       CDC13
NS            32
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SWH           10000.000
FIDRES        0.152588
AQ            3.2768500
RG            203
DW            50.000
DE            6.50
TE            298.0
D1            1.00000000
TD0           1

===== CHANNEL f1 =====
NUC1          1H
P1            13.50
PL1           2.00
PL1W         16.79986763
SFO1         500.1325007
SI            32768
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WDW           EM
SSB           0
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ppm
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¹H NMR of chlorination mixture of acetophenone

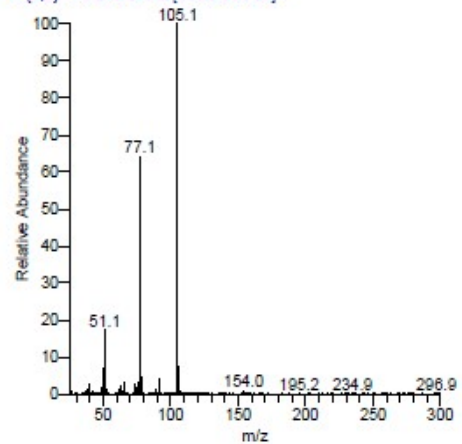


2 #3012 RT: 13.24 AV: 1 AV: 5 SB:
T: (0.0) + c EI Full ms [25.00-300.00]



Substrate

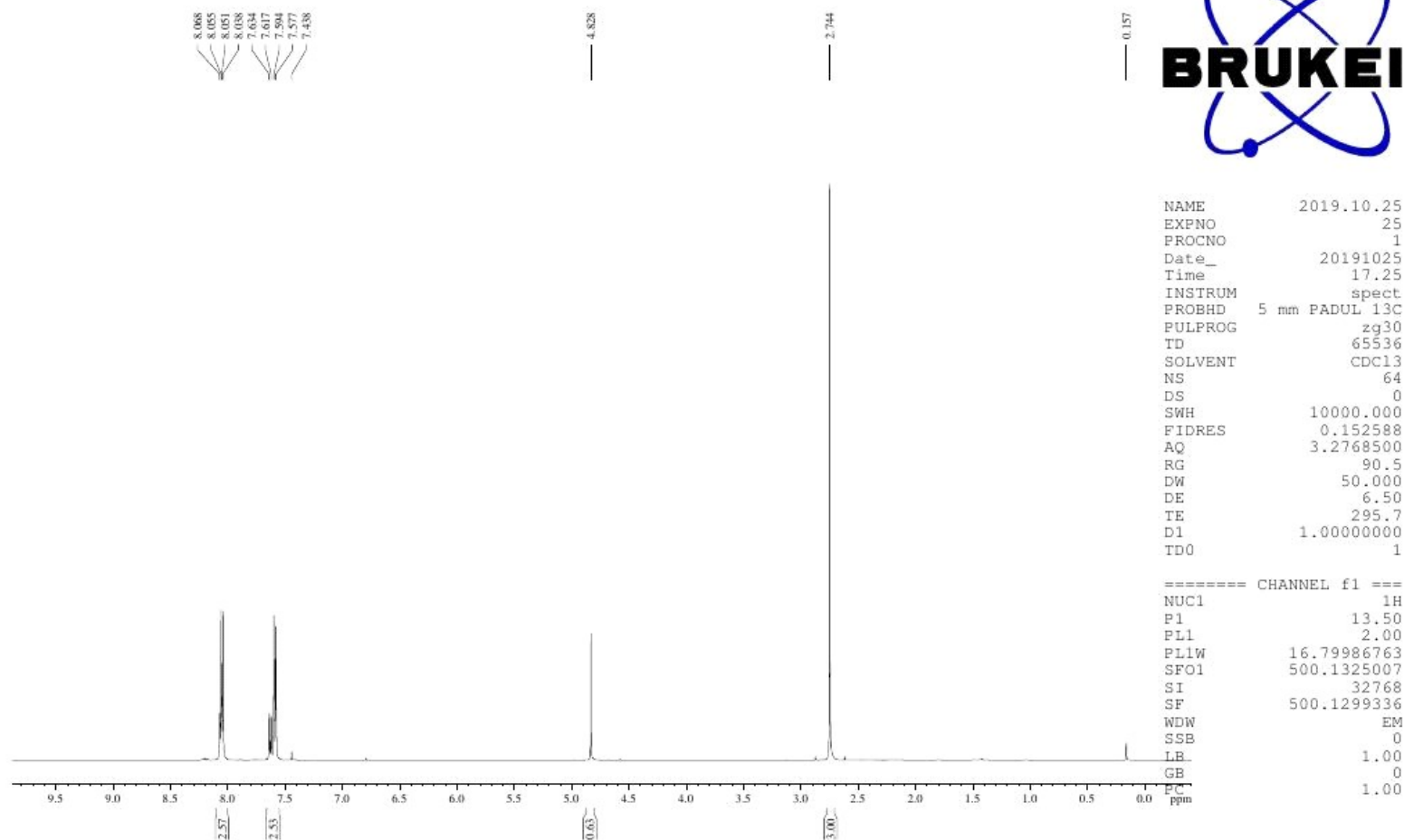
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T: (0.0) + c EI Full ms [25.00-300.00]



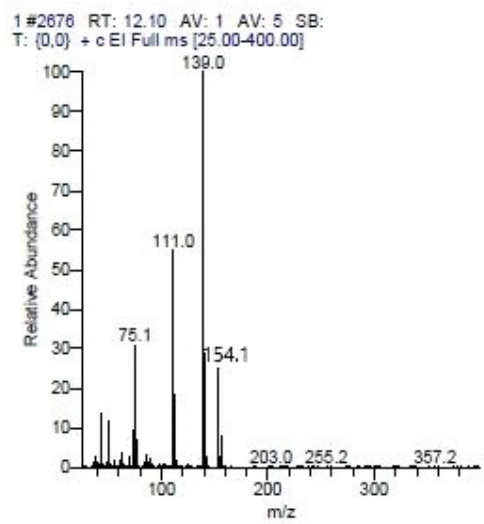
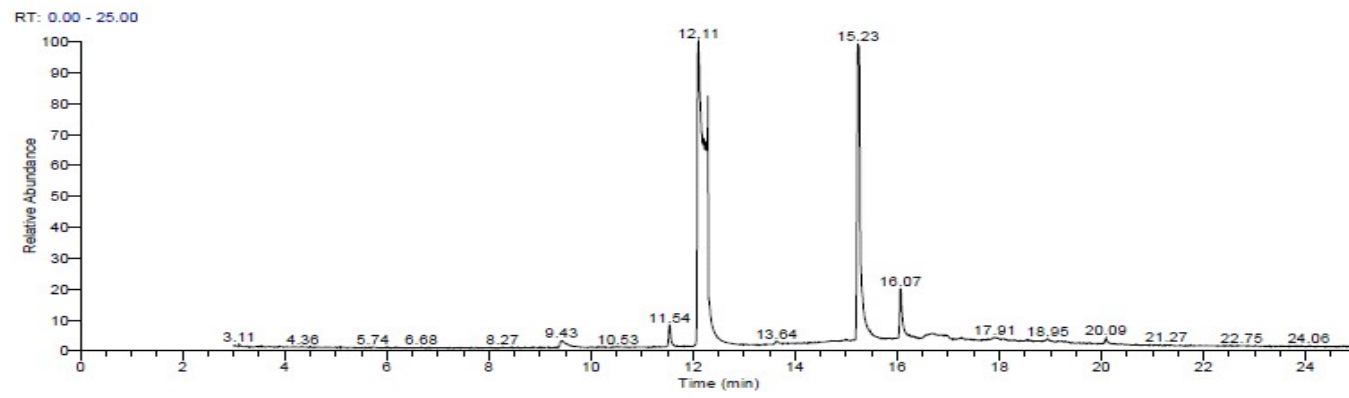
Product

GS-MS of chlorination mixture of acetophenone

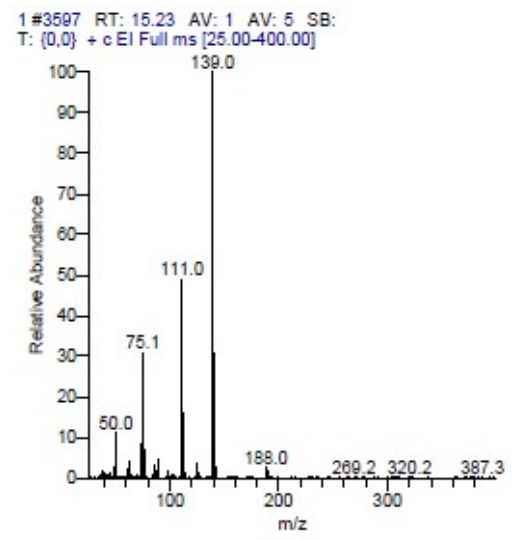
liushouxin-lbyt-2



¹H NMR of chlorination mixture of 4-Cl-acetophene

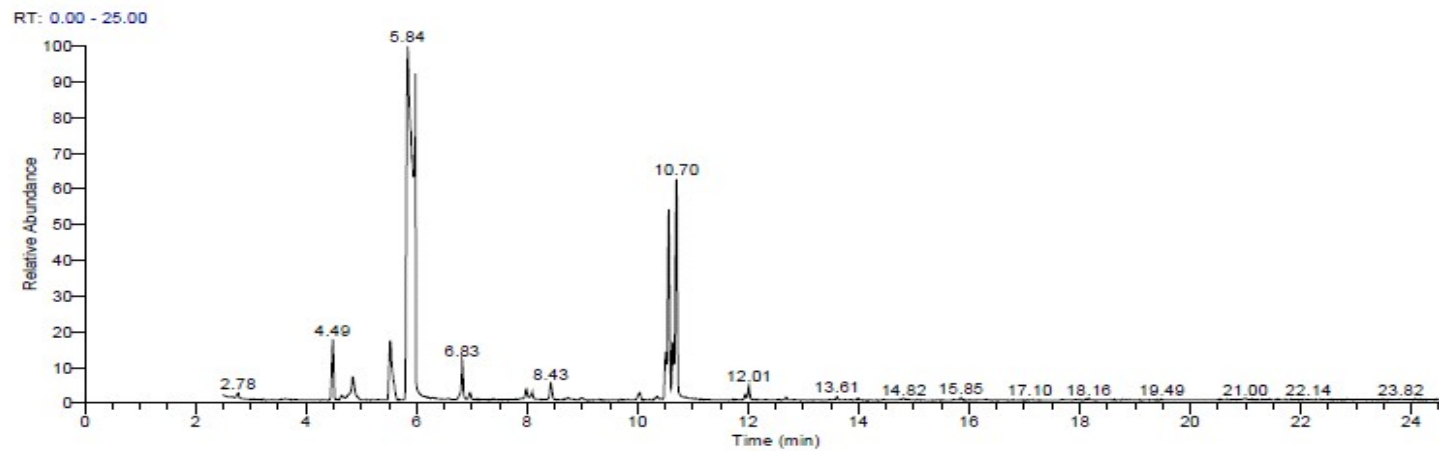


Substrate

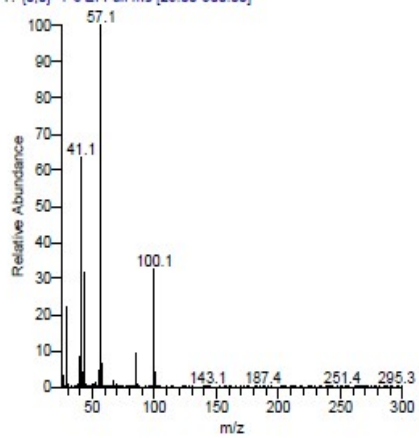


Product

GS-MS of chlorination mixture of 4-Cl-acetophene

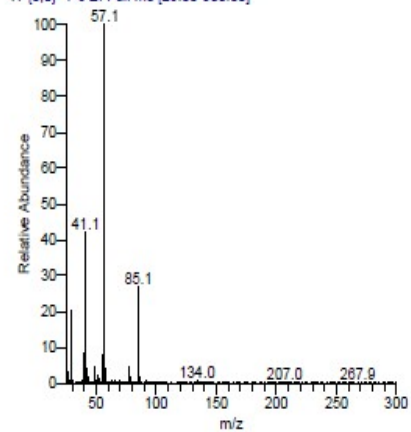


2#983 RT: 5.84 AV: 1 AV: 5 SB: 12 976-981 985-990 NL:
T: (0,0) + c EI Full ms [25.00-300.00]



Substrate

2#2413 RT: 10.70 AV: 1 AV: 5 SB:
T: (0,0) + c EI Full ms [25.00-300.00]



Product

GS-MS of chlorination mixture of 3,3-dimethyl-2-butanone