Supporting Information

Chlorotrimethylsilane (TMSCl): An Efficient Silicon-based Lewis Acid Mediator in Allylic Alkylation Using Diethylzinc Reagent

Wen-Hui Deng, Fei Ye, Xing-Feng Bai, Li Li*, Tao Song, Yun-Long Wei, Li-Wen Xu*

Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 310012, P. R. China. Fax: 86 2886 5135; Tel: 86 2886 5135; E-mail: liwenxu@hznu.edu.cn and *licpxulw@yahoo.com*

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

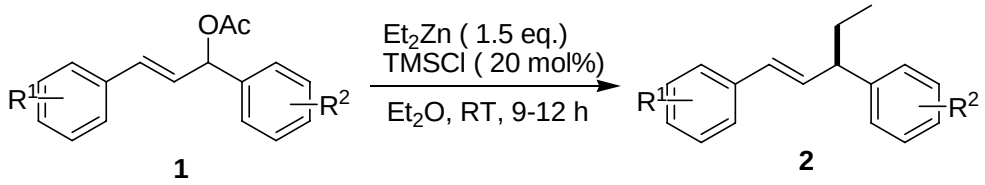
DOI: 10.1039/b000000x

Table of Contents

S-1. General information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by thin layer chromatography using silica gel. All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under positive pressure of argon. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. ^{1}H NMR was recorded at 400 MHz or 500 MHz: chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm). ^{13}C NMR was recorded at 125 MHz: chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.20 ppm). The ESI - MS analysis of the samples was operated on an LCQ advantage mass spectrometer (ThermoFisher Company, USA), equipped with an ESI ion source in the positive ionization mode, with data acquisition using the Xcalibur software (Version 1.4). Toluene was dried and distilled over CaH_2. THF were distilled from sodium benzophenone ketyl.

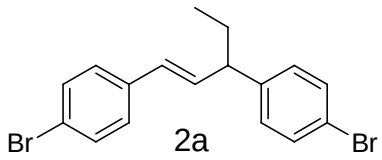
S-2. General procedures for TMSCl-catalyzed allylic alkylation



1 **2**

Substrate **1a** (1 mmol) was added to dried Schlenk tube and dissolved in dry Et_2O (1.0 mL) under N_2 atmosphere. TMSCl (25 ul, 0.2 mmol) was then added dropwise to the above solution. The solution was cooled to 0 ^{o}C. Diethylzinc (1.5 mmol, 1.5 mL of 1 M toluene solution) was added dropwise to the above solution. The mixture was stirred at room temperature for 9-12 h before quenched with aqueous saturated HCl. The layers were separated and the aqueous layer was extracted with ethyl acetate (5 mL × 2). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica

gel to give the addition product **2a,** yield = 96%, A colorless liquid.



2a

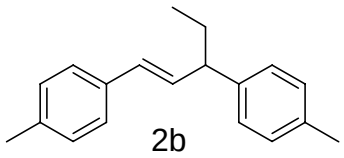
yield = 96%, A colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 16.4, 8.4 Hz, 4H), 7.16 (d, J = 7.2 Hz , 2H), 7.07 (d, 7.2 Hz, 2H), 6.21-6.31 (m, 2H), 3.24 (q, J = 6.8 Hz , 1H), 1.707-1.833 (m, 2H), 0.875 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 136.4, 134.5, 131.7, 131.7, 129.6, 128.8, 127.8, 121.0, 120.1, 50.4, 28.7, 12.3.

IR (cm^{-1}, neat) 2961, 2927, 2872, 1486, 1460, 1401, 1378, 1179, 1100, 1072, 1008, 965, 820, 716, 668, 631, 613.

GC-MS: calcd for $C_{17}H_{16}Br_2$ [M]: 300.0; Found: 300.0.


2b

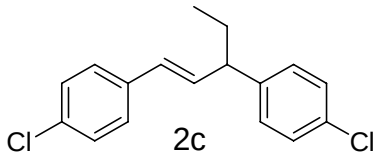
yield = 94%, A colorless liquid .

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8 Hz , 2 H), 7.05-7.15 (m, 6H), 6.22-6.37 (m, 2H), 3.24 (q, J = 7.2 Hz , 1H), 2.30 (d, J = 6.4 Hz, 6H), 1.75-1.82 (m, 2H), 0.89 (t, J = 7.4Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 136.9, 135.8, 135.3, 133.7, 129.5, 127.9, 126.4, 50.9, 29.2, 21.4, 21.3, 12.6.

IR (cm^{-1}, neat) 3021, 2960, 2922, 2871, 1512, 1453, 1377, 1108, 1038, 1020, 964, 813, 799, 723

GC-MS: calcd for $C_{19}H_{22}$ [M]: 250.1 ; Found: 250.1.



2c

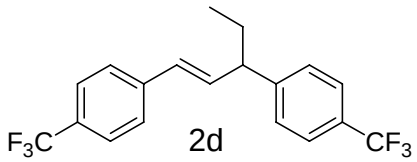
yield = 95.50%, A colorless liquid .

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 7.6 Hz , 2 H), 7.22(s, 4H), 7.13(d, J = 7.6 Hz, 2H), 6.21-6.32 (m, 2H), 3.25 (q, J = 14.8, 7.6 Hz, 1H), 1.71-1.84 (m, 2H), 0.88 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 136.1, 134.5, 132.9, 132.1, 129.2, 128.8, 127.6, 50.4, 28.8, 12.4.

IR (cm^{-1}, neat) 2962, 2928, 2873, 1489, 1461, 1405, 1378, 1178, 1089, 1013, 965, 825, 719, 692, 661, 644, 630.

GC-MS: calcd for $C_{17}H_{16}Cl_2$ [M]: 290.0 ; Found:290.0.



2d

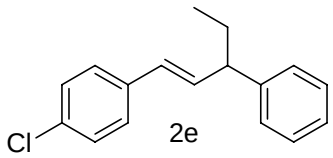
yield =55.7%, A colorless liquid .

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8 Hz , 2 H), 7.53 (d, J = 8 Hz, 2 H), 7.35 (d, J = 8 Hz, 2 H), 6.37-6.45 (m, 2H), 3.41 (q, J = 7 Hz, 1H), 1.58 (s, 1H), 0.922 (t, J = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 134.8, 128.0, 127.4, 127.3, 127.0, 125.3, 124.5, 124.5, 49.8, 28.7, 27.5, 11.1.

IR (cm^{-1}, neat) 2926, 2855, 1617, 1458, 1417, 1323, 1259, 1164,1121, 1067,1017, 968, 838, 699.

GC-MS: calcd for $C_{19}H_{16}F_2$ [M]:358.1 ; Found: 358.1.



2e

yield =98.6%, A colorless liquid .

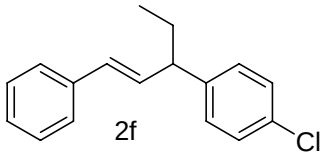
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32 - 7.12 (m, 9 H), 6.38 - 6.22 (m, 2H);3.30 - 3.22 (m, 1H), 1.84 -1.71 (m, 2H), 0.91 - 0.86 (m, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 143.1, 135.2, 133.7, 129.3, 128.7, 128.5, 127.9,

127.5, 126.5, 126.4, 51.1, 50.4, 28.9, 12.5, 12.4.

IR (cm^{-1}, neat) 3026, 2961, 2927, 2872, 1599, 1490, 1451, 1404, 1378, 1090, 1029, 1013, 964, 824, 747, 695.

GC-MS calcd for $C_{17}H_{17}Cl$ [M]: 256.1; Found: 256.1.



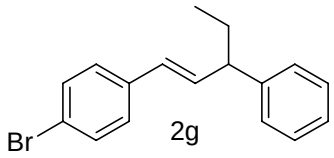
yield =97.0%, A colorless liquid .

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.21 (m, 9 H), 6.45-6.30 (m, 2H);3.37-3.31 (m, 1H), 1.92-1.81 (m, 2H), 0.98-0.94 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 135.0, 133.6, 129.1, 128.6, 128.6, 128.6, 127.7, 127.4, 126.3, 126.2, 51.0, 50.3, 28.8, 12.3, 12.2.

IR (cm^{-1}, neat) 3026, 2961, 2928, 2872, 1599, 1491, 1452, 1405, 1378, 1091, 1029, 1013, 964, 824, 747, 696.

GC-MS: calcd for $C_{17}H_{17}Cl$ [M]: 256.1; Found: 256.1.



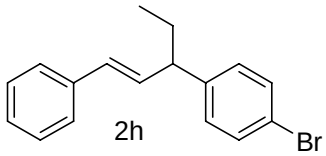
yield =94.3%, A colorless liquid .

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.4 Hz, 1H) , 7.36 (d, J = 8.4 Hz, 1 H), 7.32-7.15(m, 6 H), 7.08(d, J = 8.4 Hz, 1 H), 6.38-6.22 (m, 2H); 3.30-3.22 (m, 1H), 1.84-1.73 (m, 2H), 0.91-0.86 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 133.6, 131.7, 130.0, 129.6, 128.7, 128.7, 128.5, 127.8, 127.4, 126.5, 126.3, 51.1, 50.5, 28.8, 12.5, 12.4.

IR (cm^{-1}, neat) 3025, 2961, 2927, 2872, 1487, 1451, 1400, 1378, 1072, 1029, 1009, 964, 821, 746, 695.

GC-MS: calcd for $C_{17}H_{17}Br$ [M]: 300.1; Found: 300.1.



2h

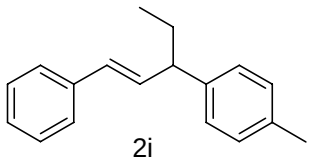
yield =91.0%, A colorless liquid .

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 1H) , 7.36 (d, J = 8.4 Hz, 1 H), 7.33-7.15(m, 7 H), 6.38-6.22 (m, 2H), 3.30-3.22 (m, 1H), 1.84-1.71 (m, 2H), 0.91-0.86 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 143.6, 137.5, 136.7, 135.2, 133.6, 131.6, 130.0, 129.6, 128.6, 128.4, 127.8, 127.3, 126.4, 126.3, 120.8, 120.0, 51.1, 50.4, 28.8, 28.8, 12.4, 12.3.

IR (cm^{-1},neat) 3025, 2961, 2927, 2872, 1590, 1487, 1451, 1400, 1378, 1179, 1072, 1029, 1009, 964, 821, 746, 695.

GC-MS: calcd for $C_{17}H_{17}Br$ [M]: 300.1; Found: 300.1.



2i

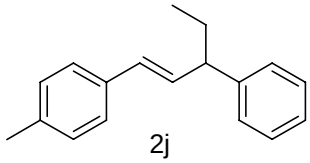
yield = 98.4%, A colorless liquid .

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.2 Hz, 1 H) , 7.27 (d, J =7.6 Hz, 1 H), 7.24-7.11 (m, 6 H), 7.06 (d, J = 8.0 Hz, 1 H), 6.34-6.23 (m, 2H);3.30-3.23(m, 1H), 2.29(d, J = 7.2 Hz, 3 H), 1.82-1.78 (m, 2H), 0.90 (t , J = 7.4 Hz, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ=144.9, 141.6, 137.9, 136.8, 135.8, 134.6, 133.4, 129.3, 128.6, 127.9, 127.8, 127.1, 126.3, 51.2, 50.7, 29.0, 21.3, 21.2, 12.5.

IR (cm^{-1}, neat) 3024, 2960, 2924, 2872, 1513, 1493, 1451, 1377, 1029, 963, 813, 796, 747, 696.

GC-MS: calcd for $C_{18}H_{20}$ [M]: 236.2; Found: 236.2.



2j

yield =95.0%, A colorless liquid.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.32-7.03 (m, 9 H), 6.37-6.23 (m, 2 H), 3.27-3.23(m, 1 H) , 2.29-2.27 (dd, J = 10.5, 3 Hz, 3H), 1.81-1.78 (m, 2H), 0.91-0.87 (m, 3H).

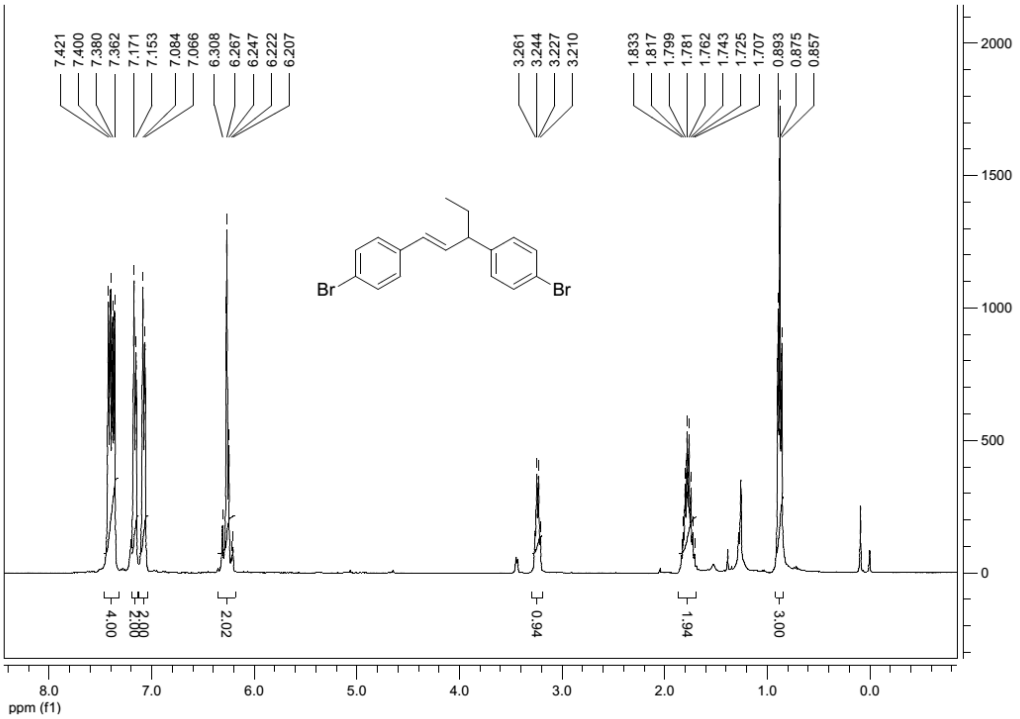
^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 141.7, 134.7, 133.4, 129.6, 129.5, 128.4, 128.7, 127.9, 127.8, 127.2, 126.4, 126.3, 51.2, 50.8, 29.1, 29.0, 21.2, 12.6.

IR (cm^{-1}, neat) 3024, 2960, 2924, 2872, 1513, 1493, 1450, 1029, 963, 813, 795, 747, 694.

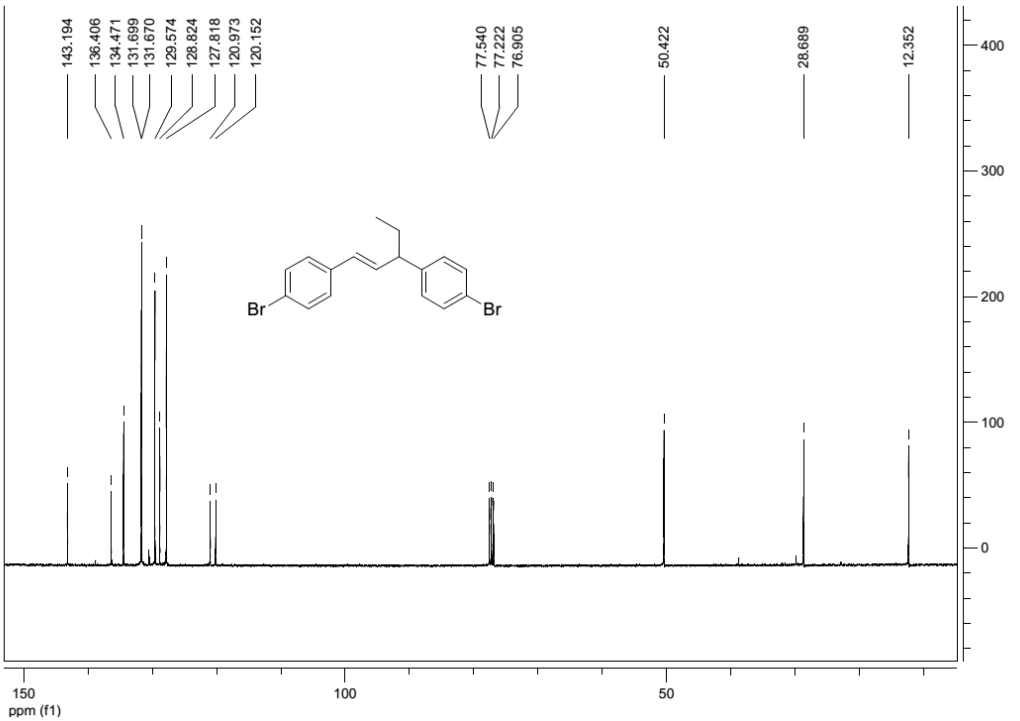
GC-MS: calcd for $C_{18}H_{20}$ [M]: 236.2; Found: 236.2.

S-3 NMR Charts of Products 2

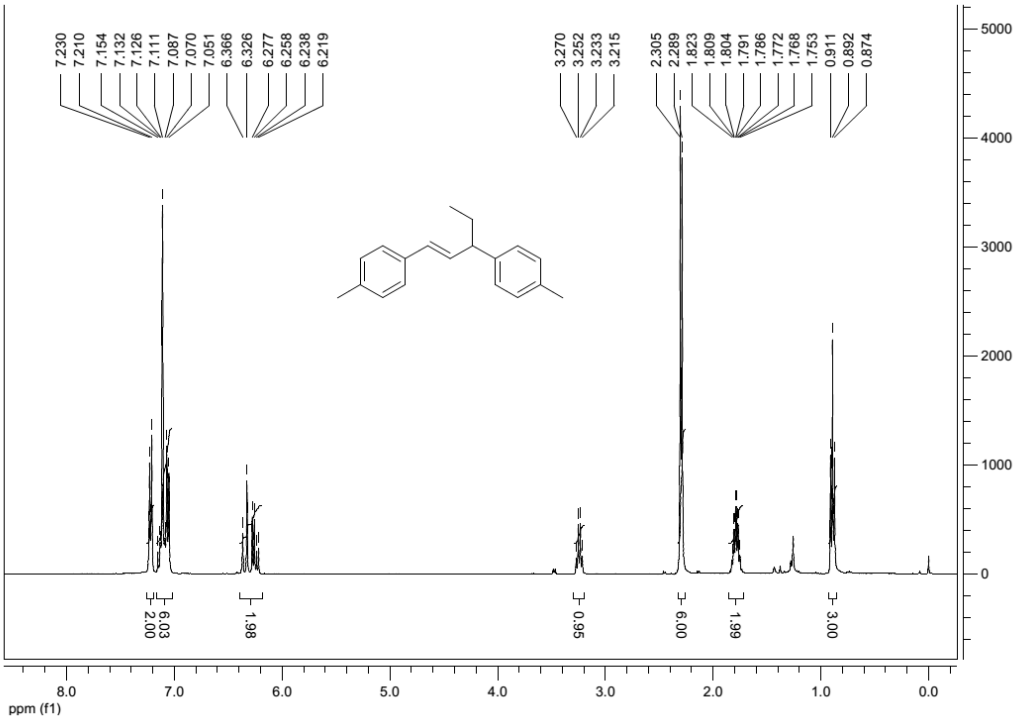
^{1}H NMR of **2a**



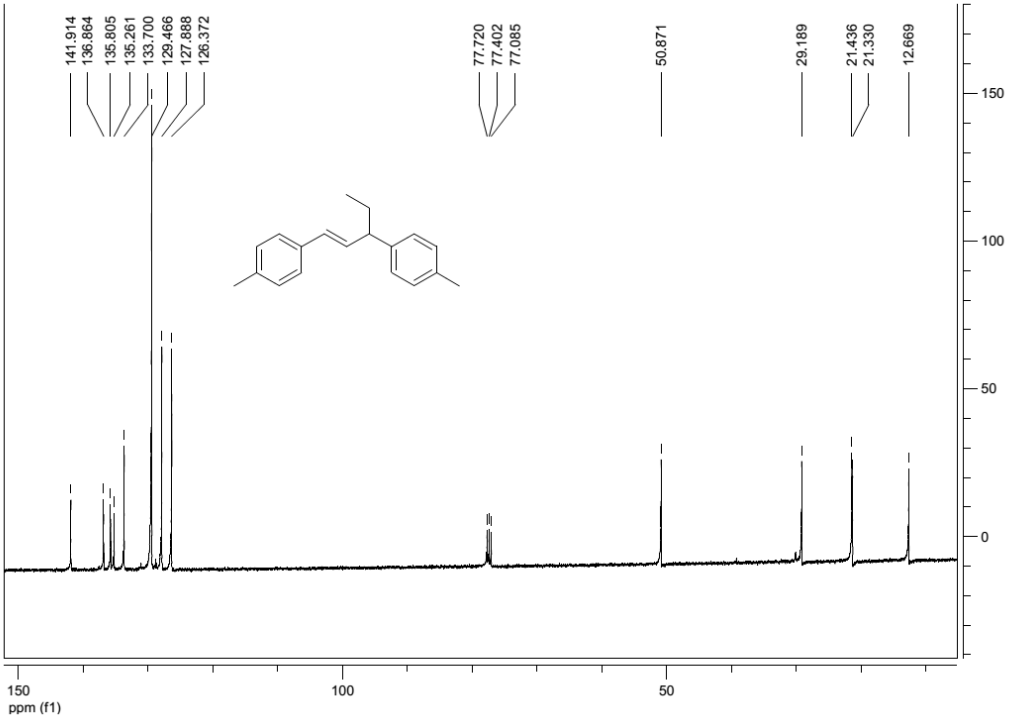
^{13}C NMR of **2a**



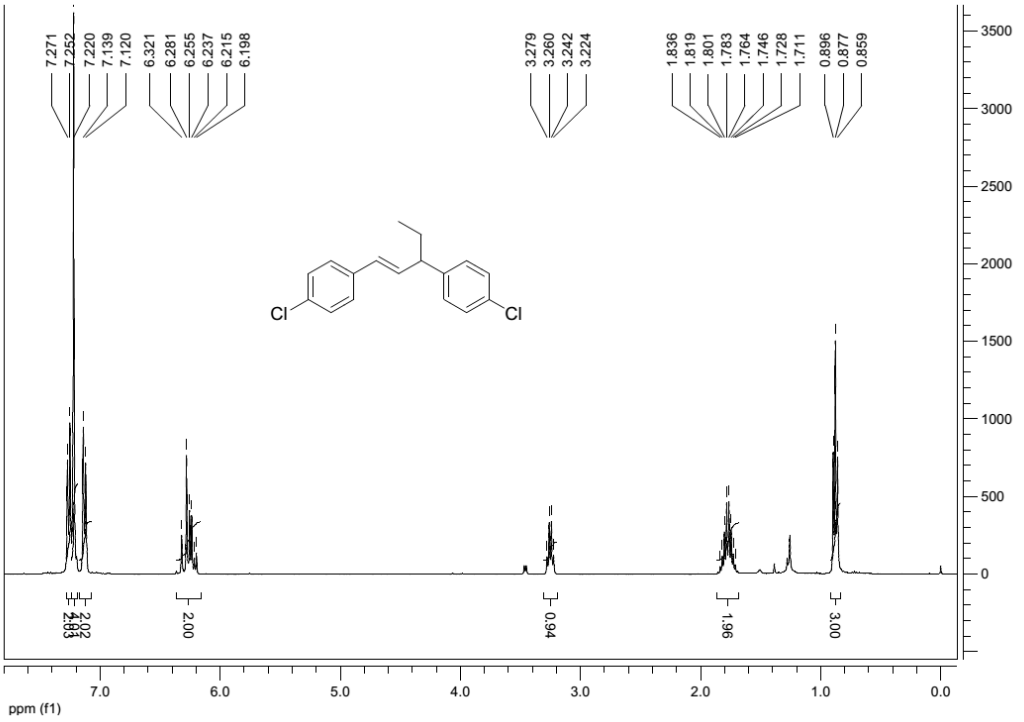
^{1}H NMR of **2b**



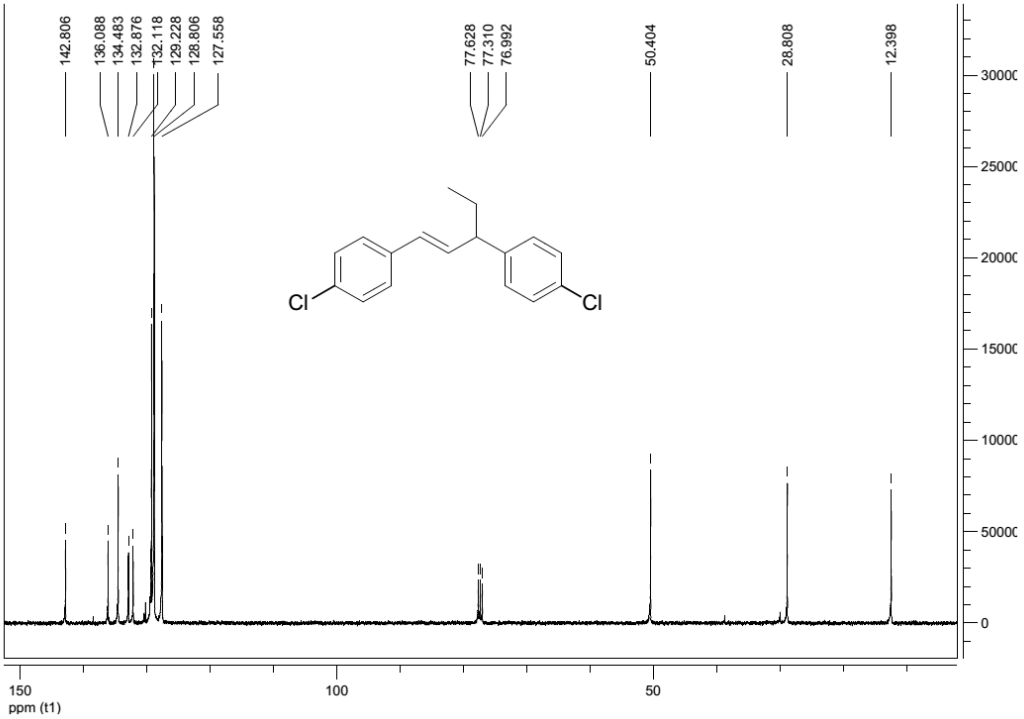
^{13}C NMR of **2b**



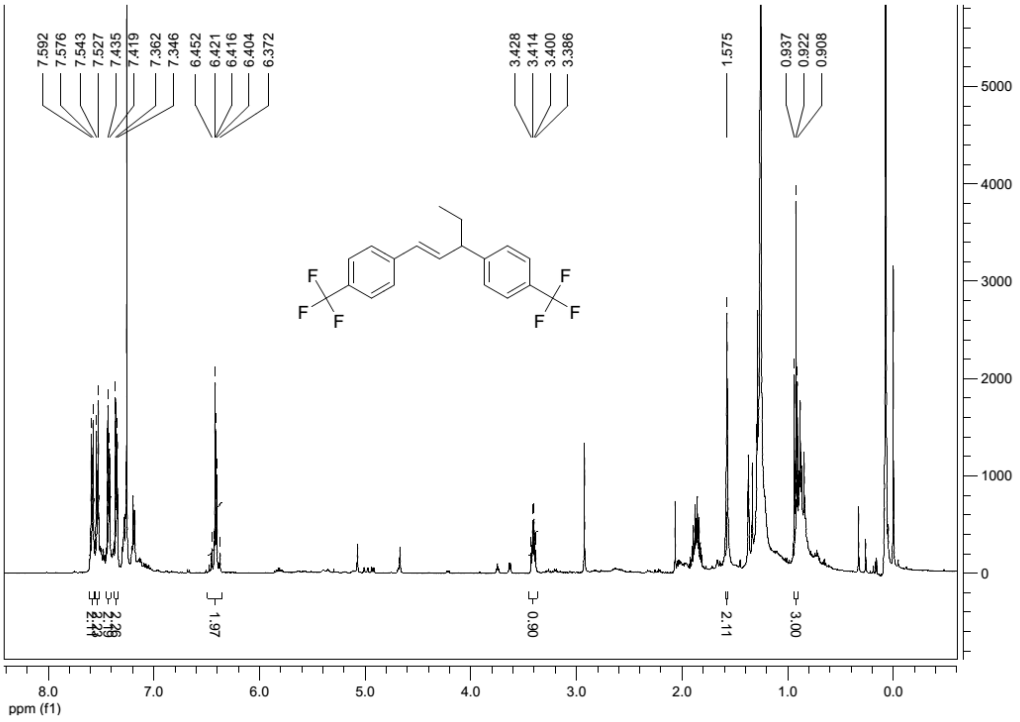
^{1}H NMR of **2c**



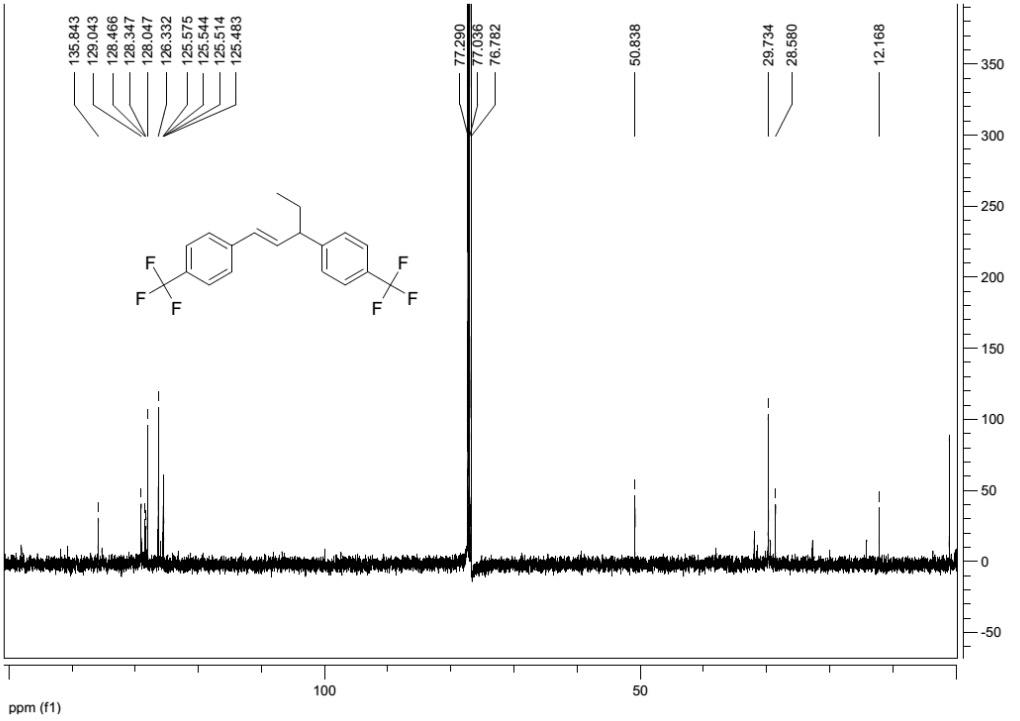
^{13}C NMR of **2c**



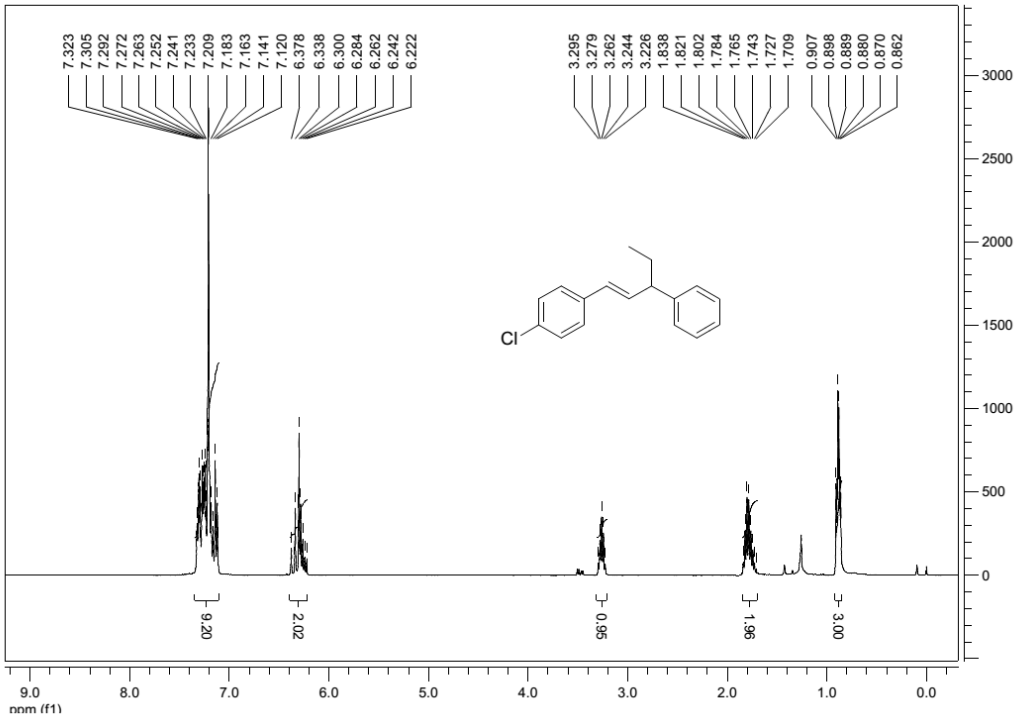
^{1}H NMR of **2d**



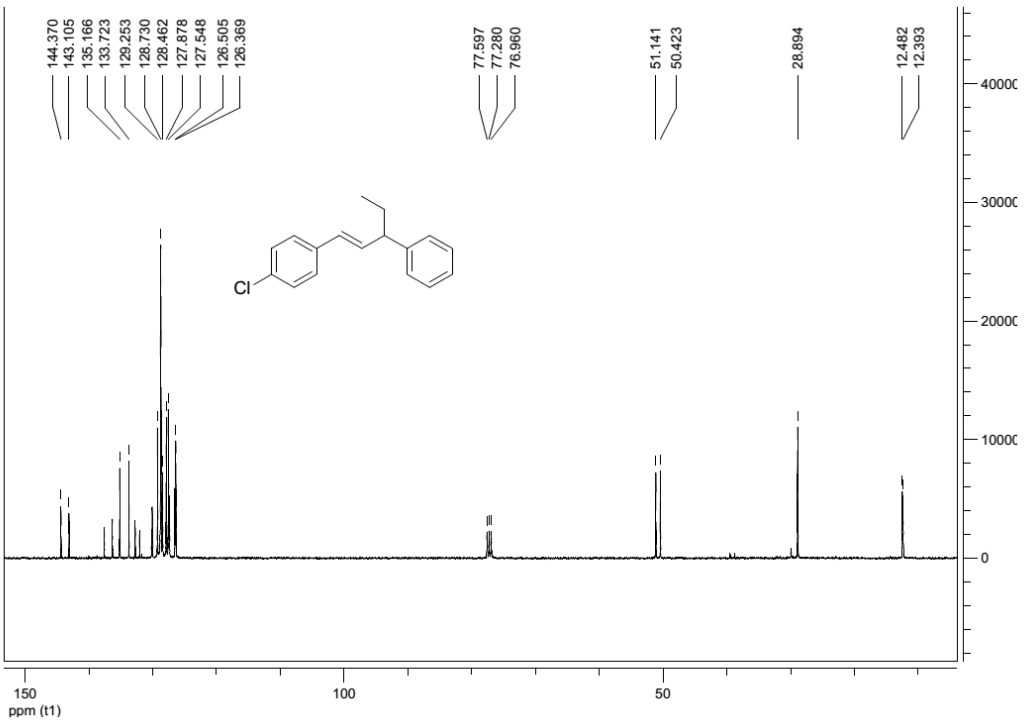
^{13}C NMR of **2d**



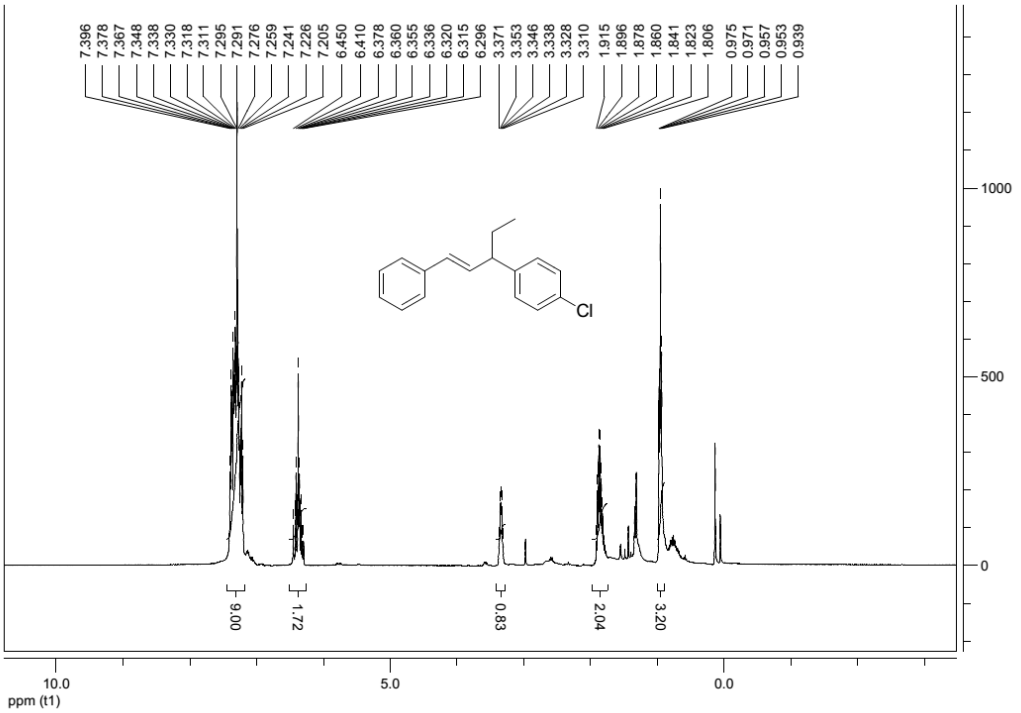
^{1}H NMR of 2e



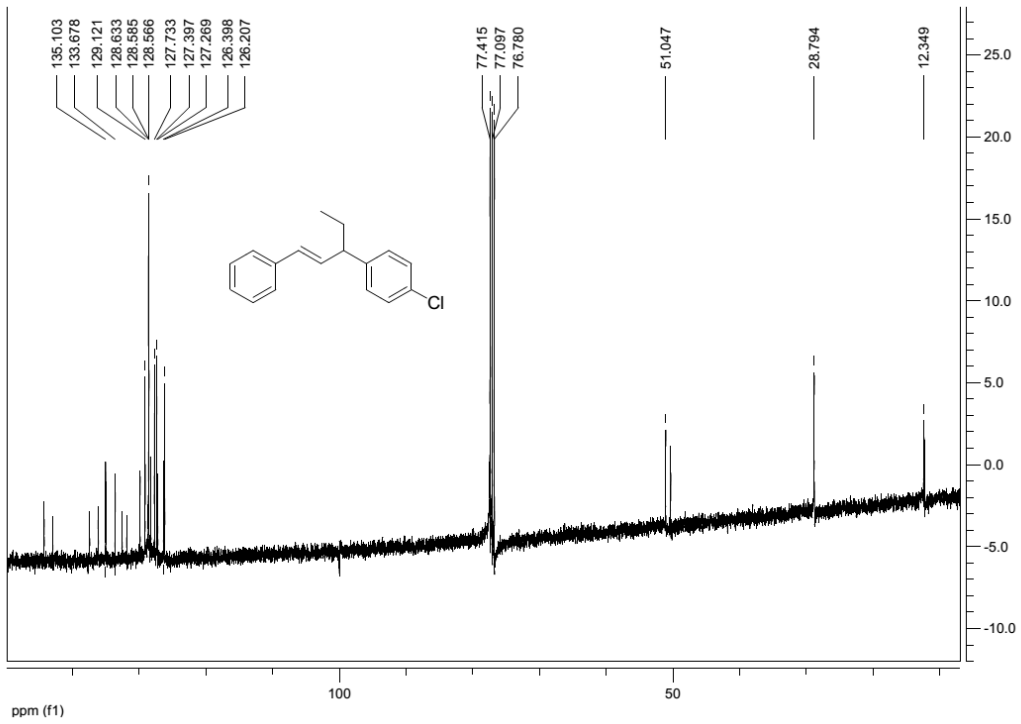
^{13}C NMR of **2e**



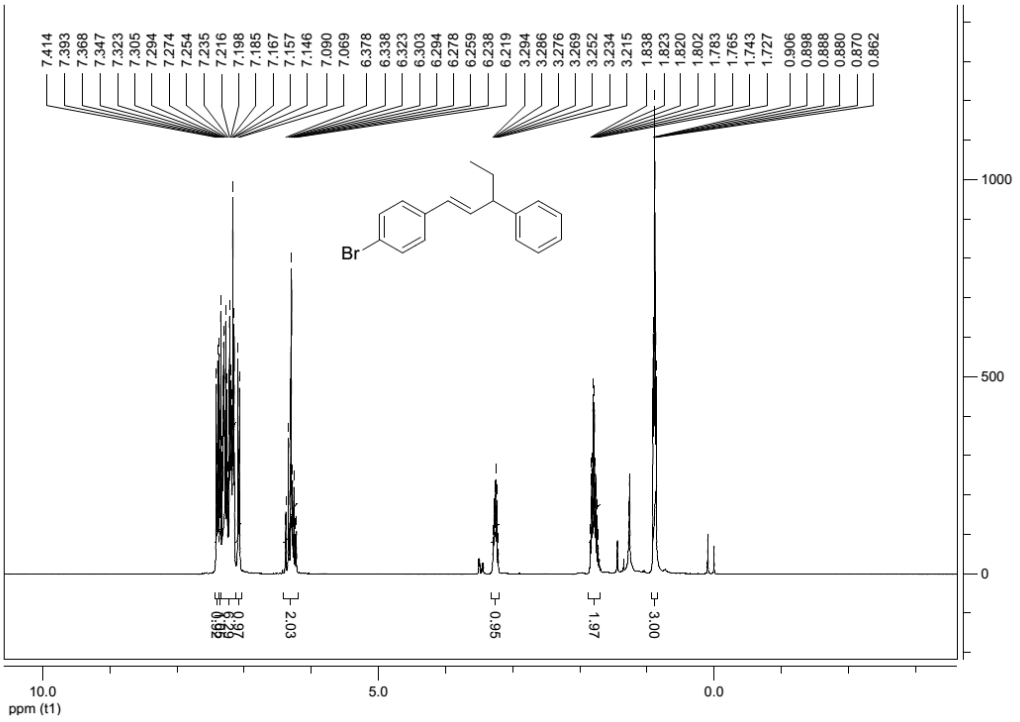
^{1}H NMR of **2f**



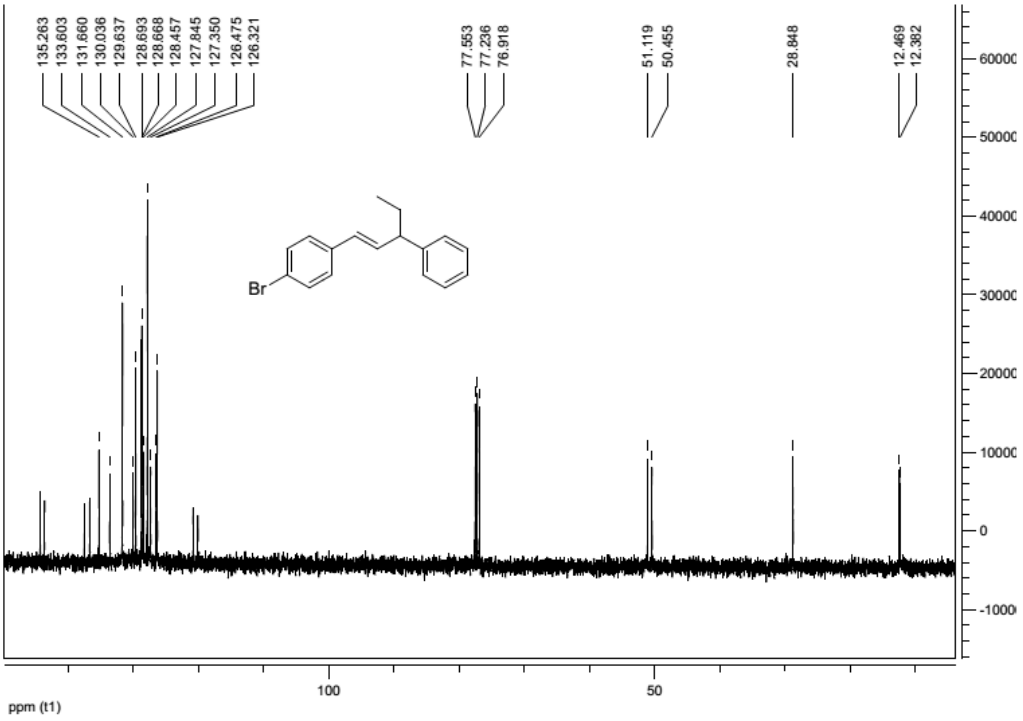
^{13}C NMR of **2f**



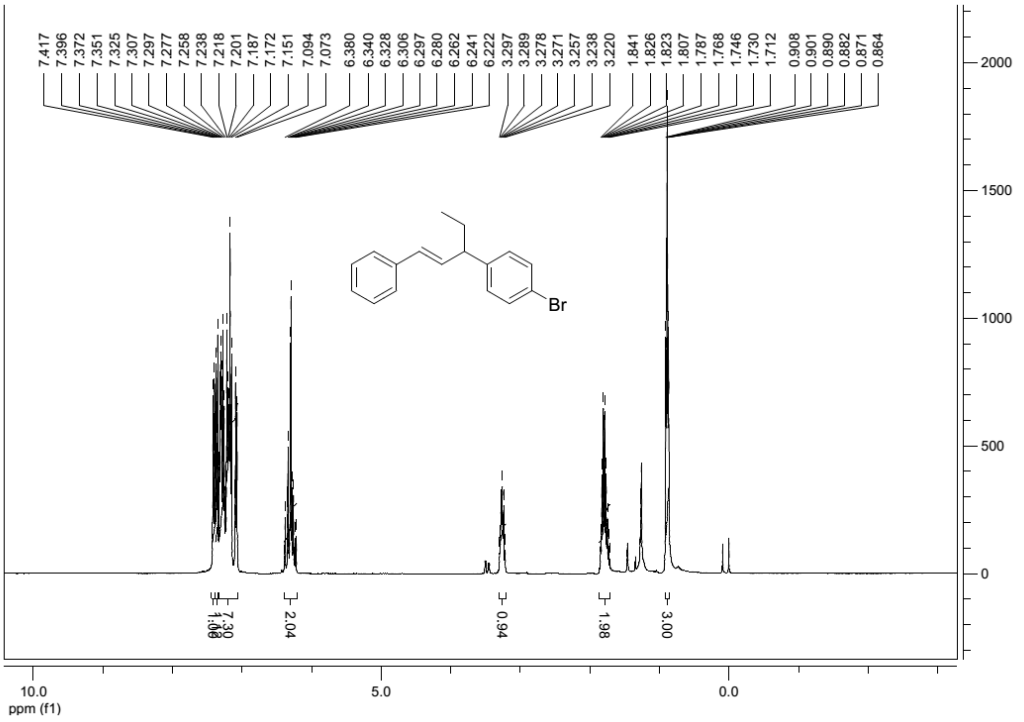
^{1}H NMR of **2g**



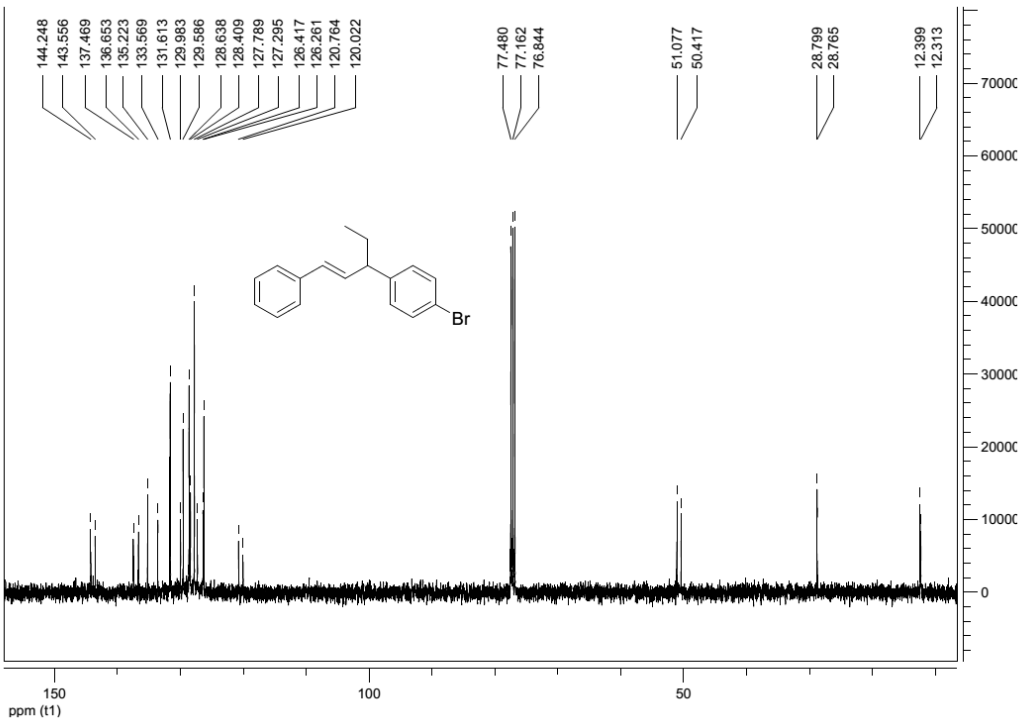
^{13}C NMR of **2g**



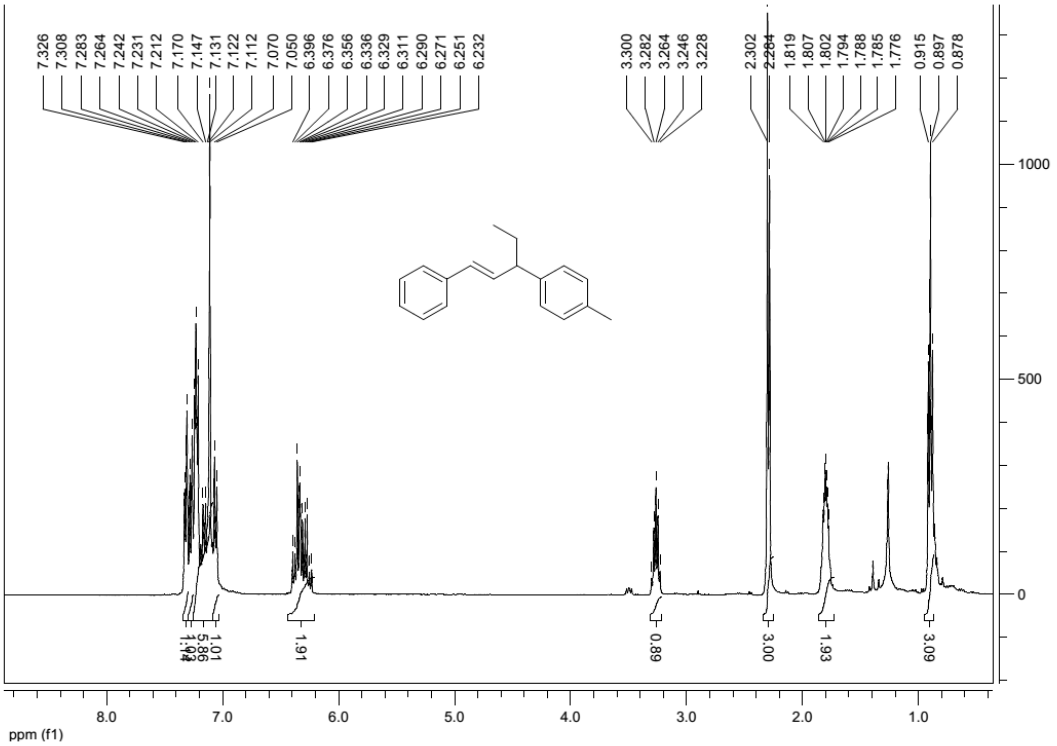
^{1}H NMR of **2h**



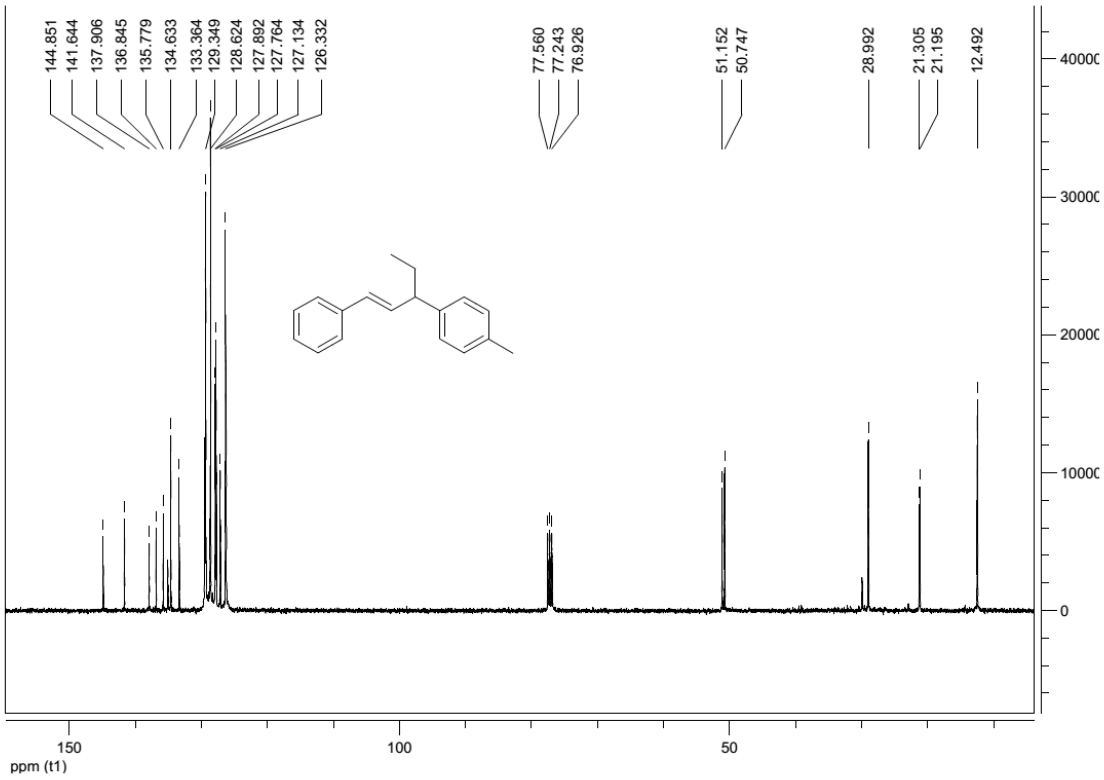
^{13}C NMR of **2h**



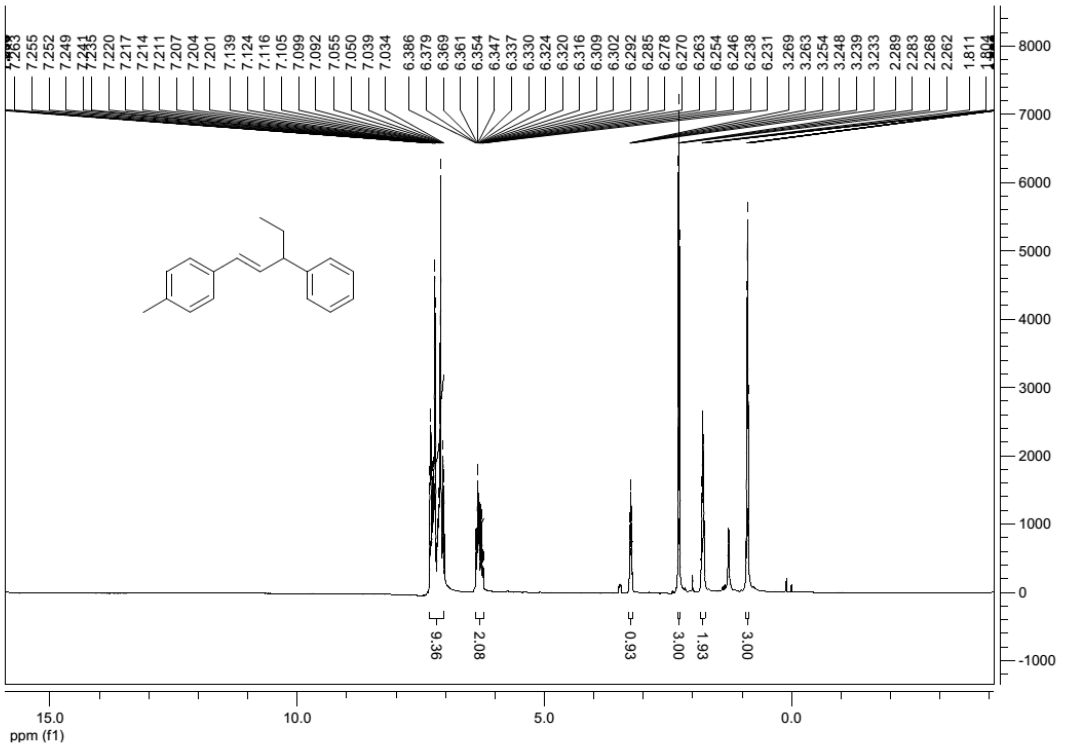
^{1}H NMR of **2i**



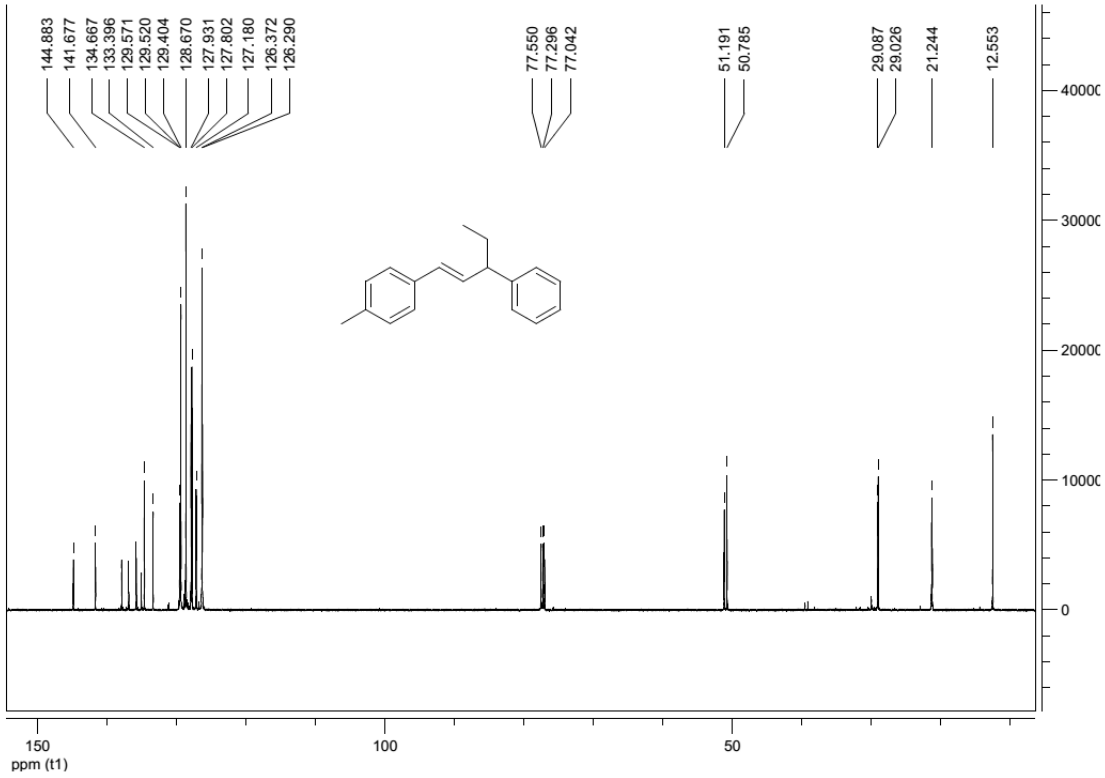
^{13}C NMR of **2i**



^{1}H NMR of **2j**

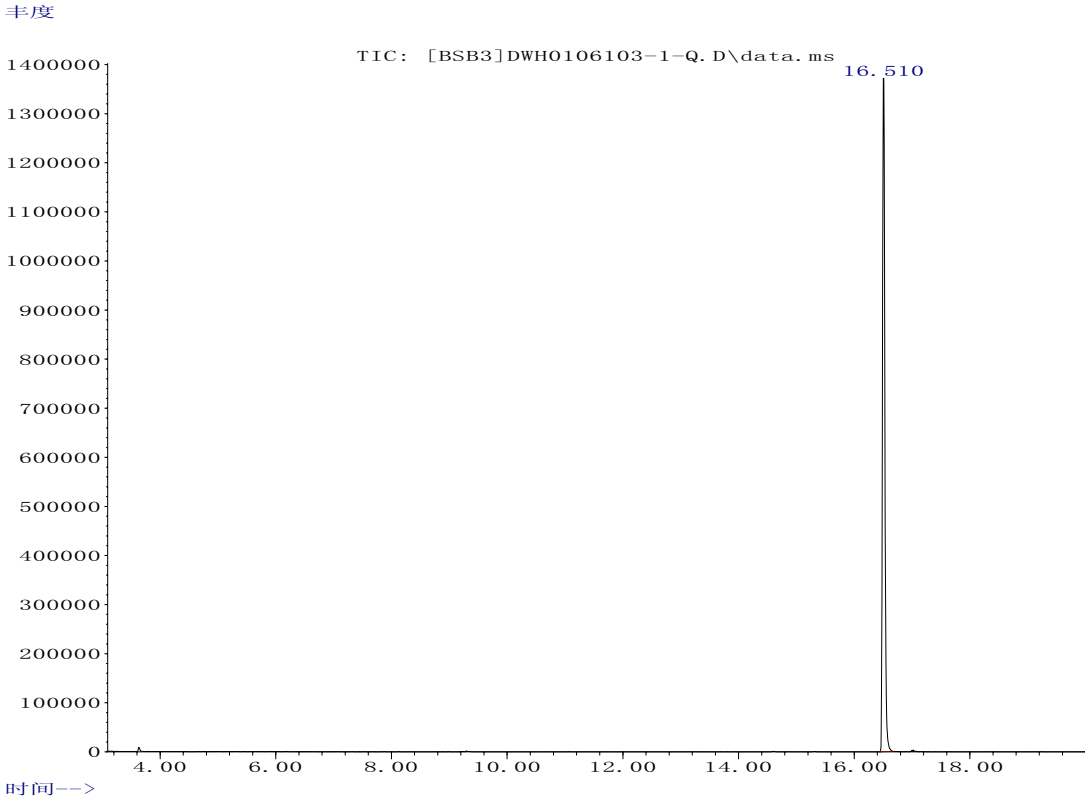

7.283
7.255
7.252
7.249
7.241
7.235
7.220
7.217
7.214
7.211
7.207
7.204
7.201
7.139
7.124
7.116
7.105
7.099
7.092
7.055
7.050
7.039
7.034
6.386
6.379
6.369
6.361
6.354
6.347
6.337
6.330
6.324
6.320
6.316
6.309
6.302
6.292
6.285
6.278
6.270
6.263
6.254
6.246
6.238
6.231
3.269
3.263
3.254
3.248
3.239
3.233
2.289
2.283
2.268
2.262
1.811
1.804
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
6.39
2.08
0.93
3.00
1.93
3.00
15.0
10.0
5.0
0.0
ppm (f1)

^{13}C NMR of **2j**

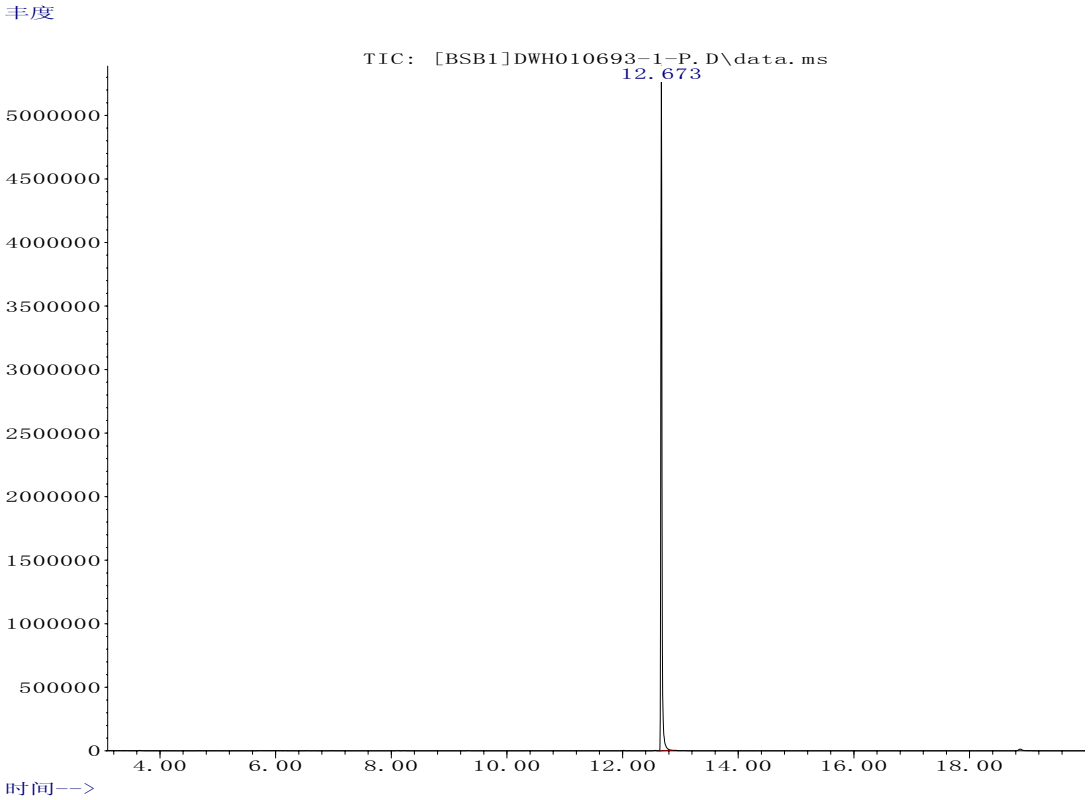

144.883
141.677
134.667
133.396
129.571
129.520
129.404
128.670
127.931
127.802
127.180
126.372
126.290
77.550
77.296
77.042
51.191
50.785
29.087
29.026
21.244
12.553
40000
30000
20000
10000
0
150
100
50
ppm (t1)

S-4 GC-MS analysis of Products 2

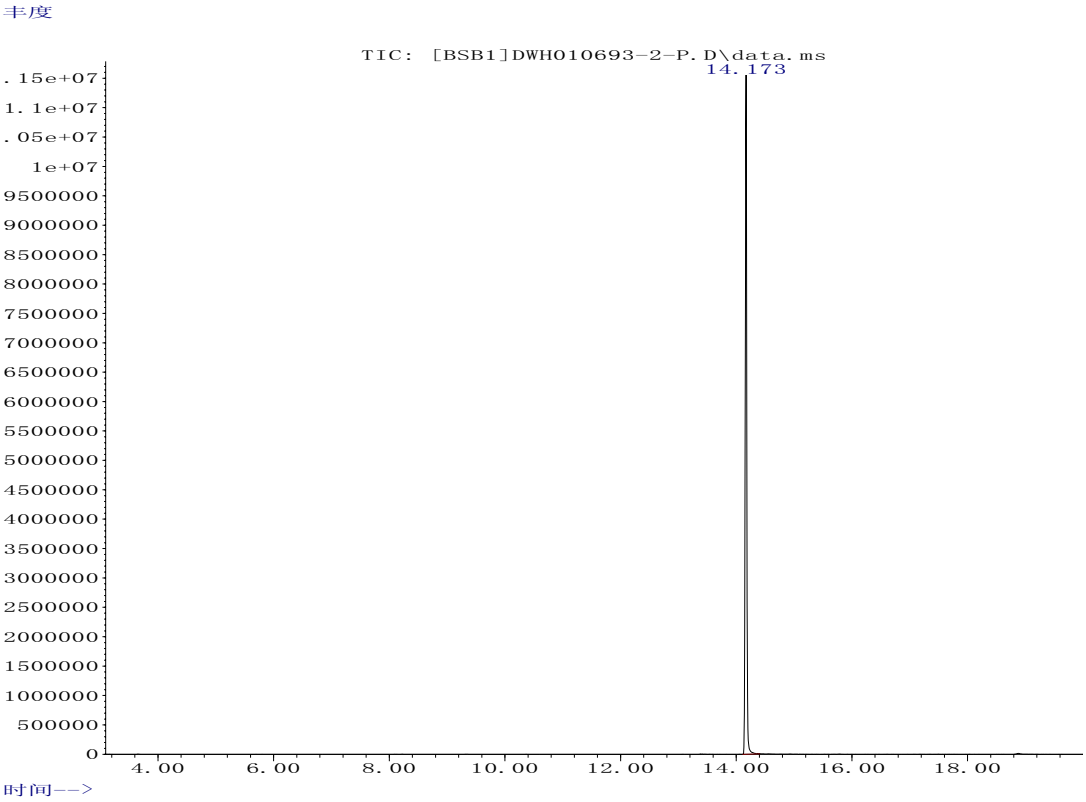
2a



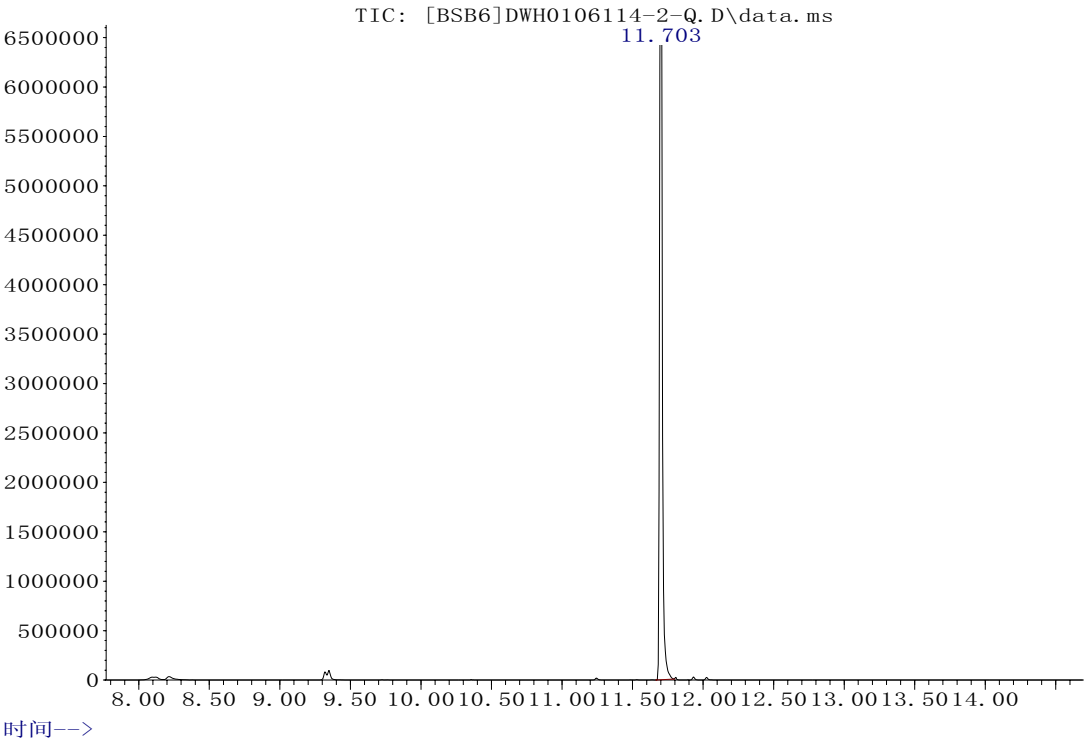
2b


丰度
TIC: [BSB1]DWH010693-1-P.D\data.ms
12.673
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
时间-->
丰度
扫描 1533 (12.676 分): DWH010693-1-P.D\data.ms
221.1
129.0
250.1
105.0
191.0
77.0
165.0
51.0
281.1
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
60
80
100
120
140
160
180
200
220
240
260
280
m/z-->

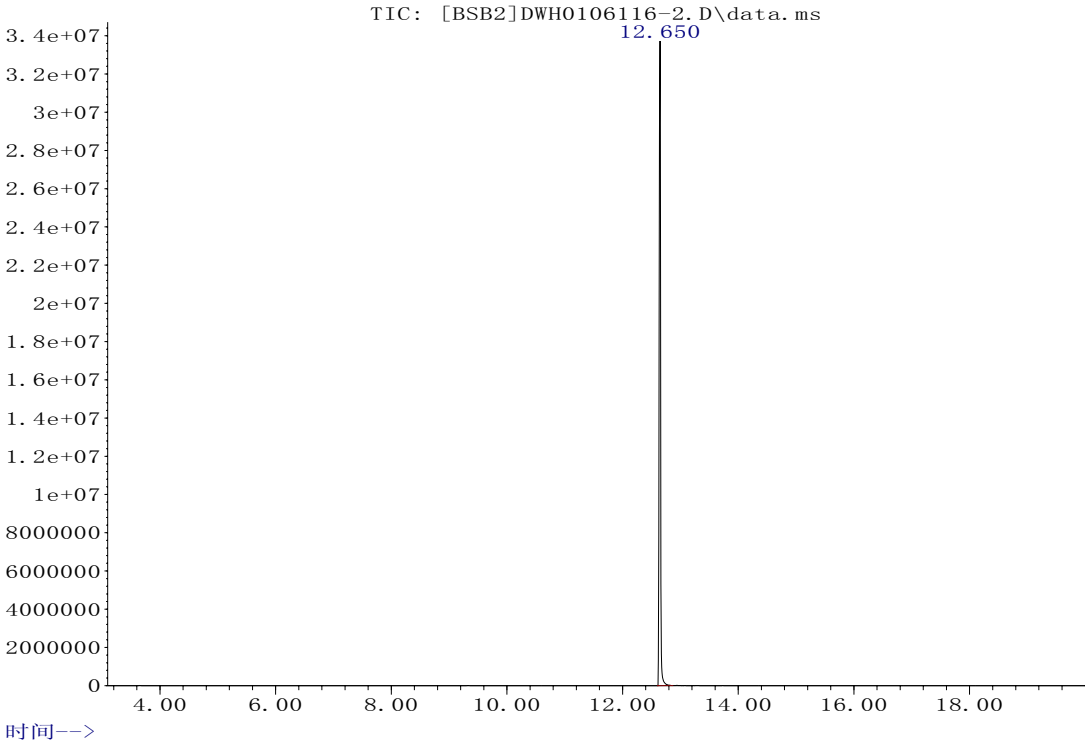
2c


丰度
TIC: [BSB1]DWH010693-2-P.D\data.ms
14.173
.15e+07
1.1e+07
.05e+07
1e+07
9500000
9000000
8500000
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
时间-->
丰度
扫描 1647 (13.389 分): DWH010693-2-P.D\data.ms
227.0
115.0
192.1
262.0
149.0
94.6
75.0
51.0
132.2
166.0
209.0
280.9
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
60
80
100
120
140
160
180
200
220
240
260
280
m/z-->

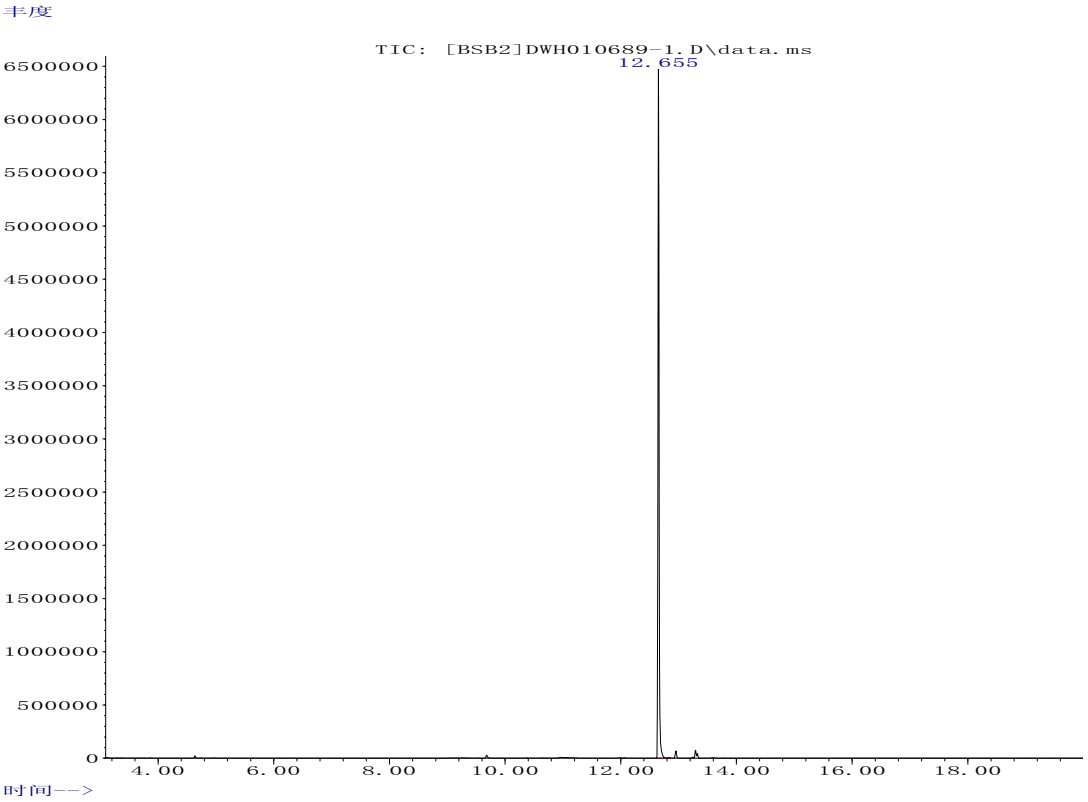
2d


丰度
TIC: [BSB6]DWH0106114-2-Q.D\data.ms
11.703
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
8.00 8.50 9.00 9.50 10.00 10.50 11.00 11.50 12.00 12.50 13.00 13.50 14.00
时间-->
丰度
扫描 1377 (11.701 分): DWH0106114-2-Q.D\data.ms
261.1
330.1
159.0
109.1
77.1
192.1
233.0
295.1
371.1
429.1
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420
m/z-->

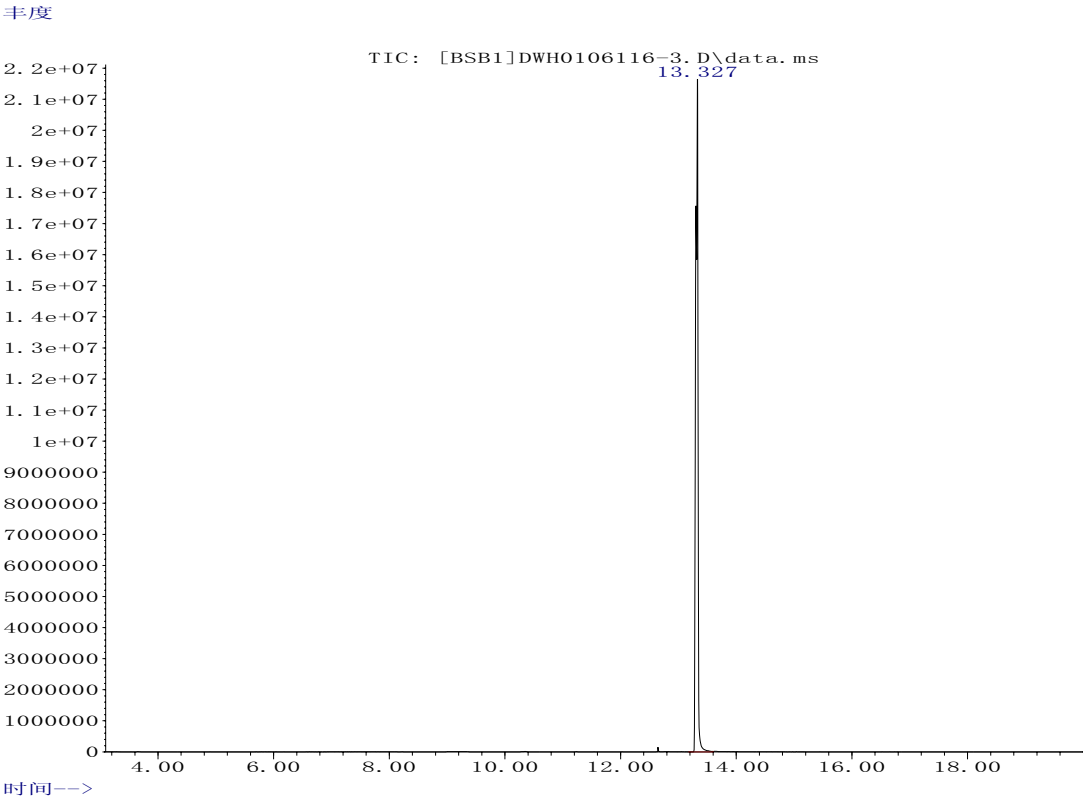
2e


丰度
TIC: [BSB2]DWH0106116-2.D\data.ms
12.650
3.4e+07
3.2e+07
3e+07
2.8e+07
2.6e+07
2.4e+07
2.2e+07
2e+07
1.8e+07
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
0
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
时间-->
丰度
扫描 1527 (12.639 分): DWH0106116-2.D\data.ms
227.1
115.1
192.1
149.0
256.1
91.1
65.1
132.1
166.1
210.0
281.0
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
60
80
100
120
140
160
180
200
220
240
260
280
m/z-->

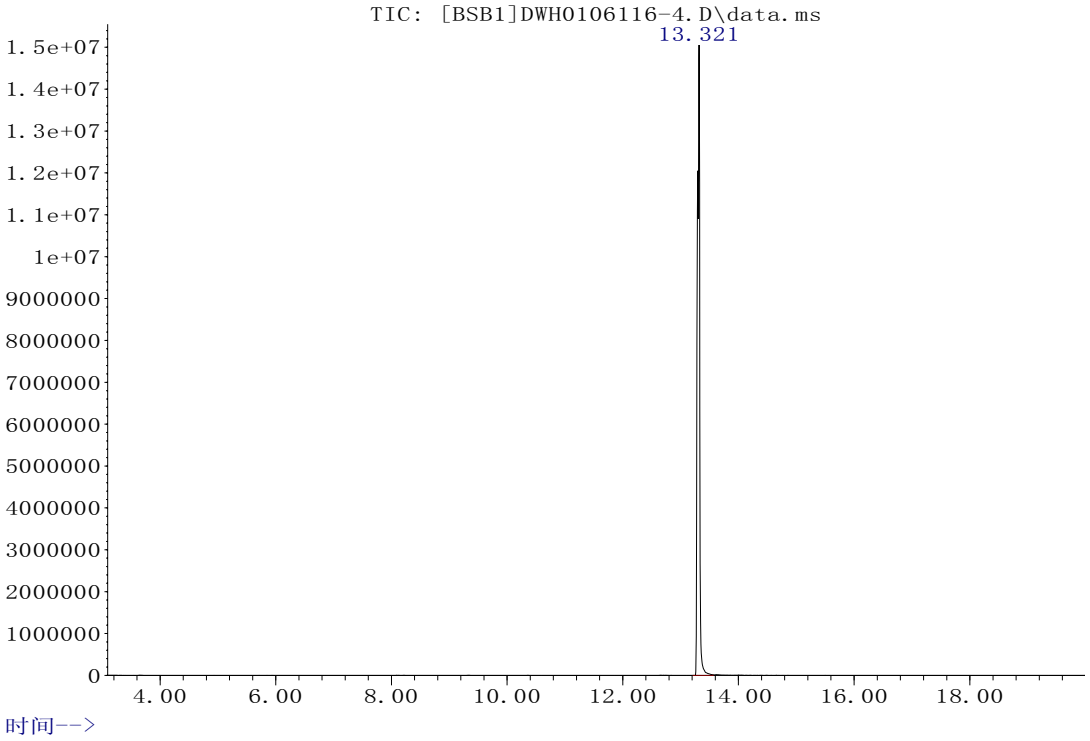
2f

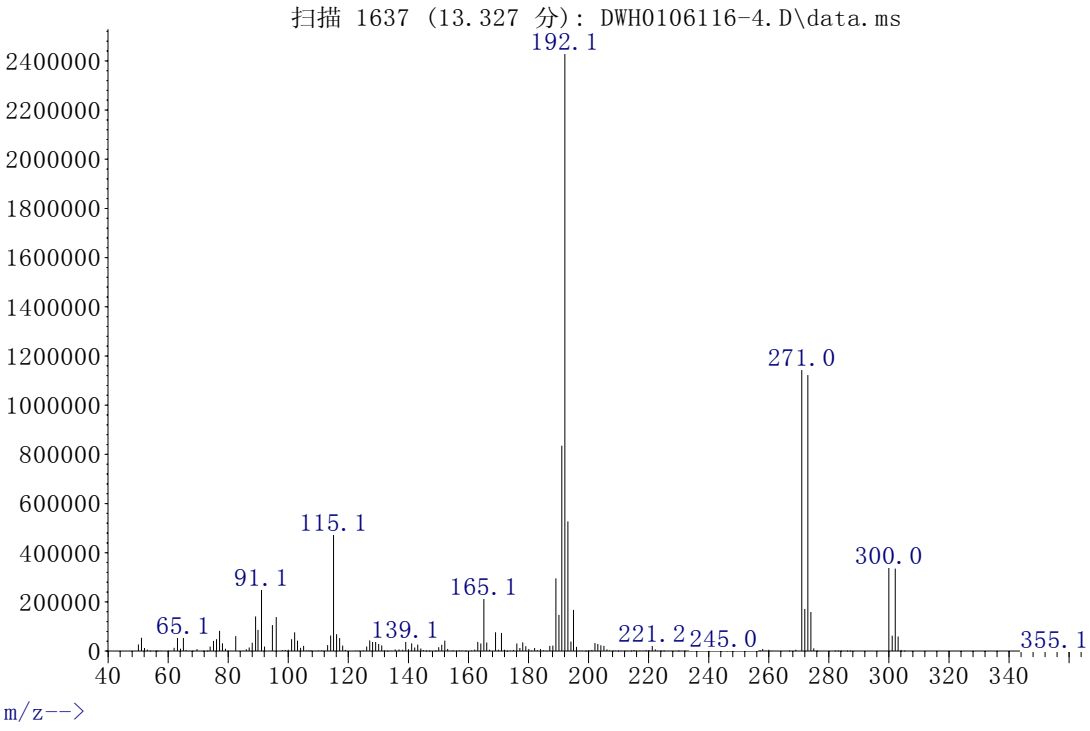

丰度
TIC: [BSB2]DWH010689-1.D\data.ms
12.655
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
时间-->
丰度
扫描 1529 (12.651 分): DWH010689-1.D\data.ms
227.0
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
115.0
192.1
149.0
91.0
256.1
65.0
280.9
355.0
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
m/z-->

2g

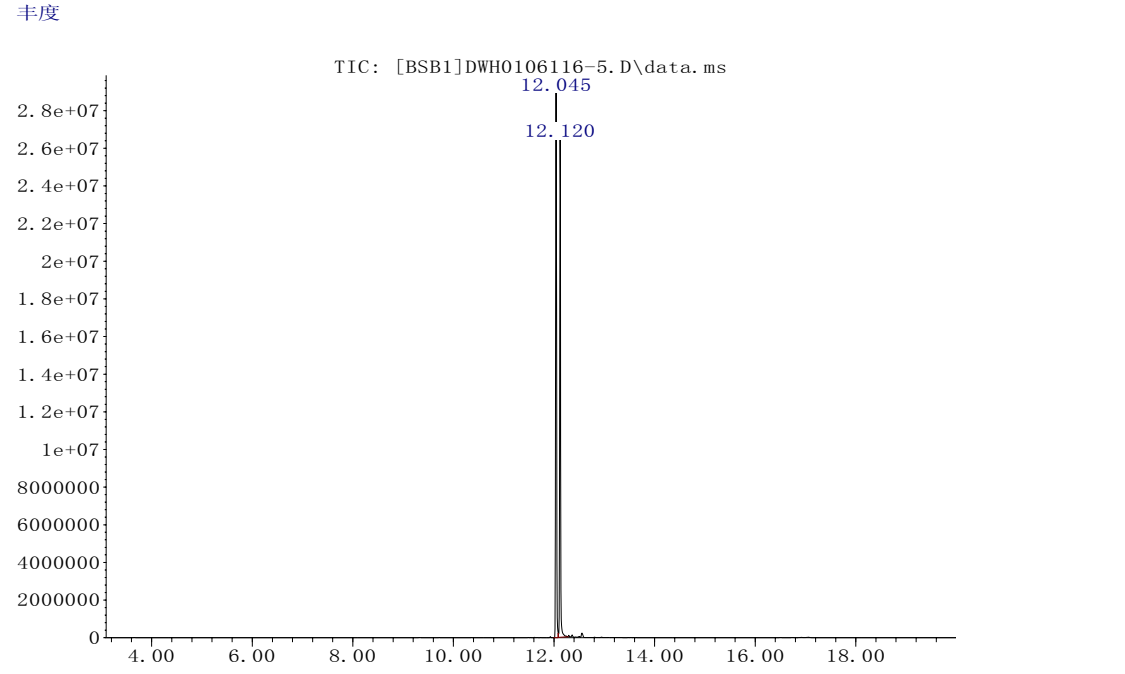

丰度
TIC: [BSB1]DWHO106116-3.D\data.ms
13.327
2.2e+07
2.1e+07
2e+07
1.9e+07
1.8e+07
1.7e+07
1.6e+07
1.5e+07
1.4e+07
1.3e+07
1.2e+07
1.1e+07
1e+07
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
时间-->
丰度
扫描 1635 (13.314 分): DWHO106116-3.D\data.ms
192.1
271.0
115.1
91.1
165.1
300.1
65.1
139.1
221.1
243.0
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
60
80
100
120
140
160
180
200
220
240
260
280
300
m/z-->

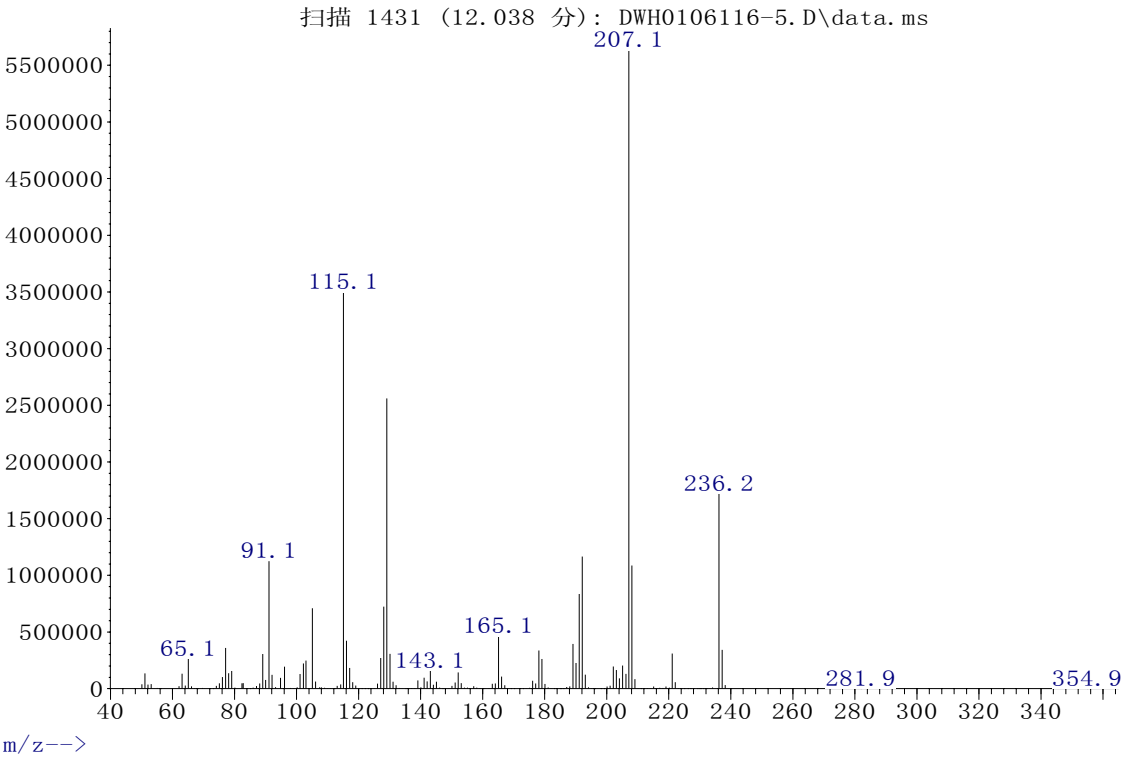
2h

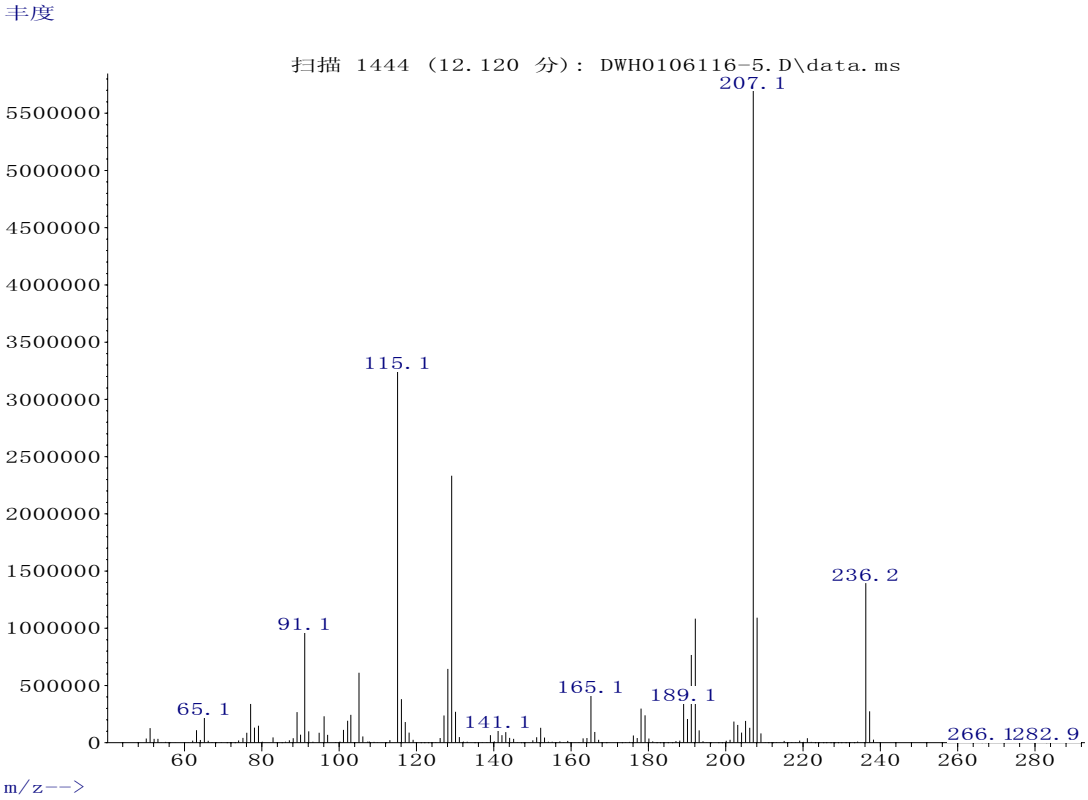

丰度
TIC: [BSB1]DWH0106116-4.D\data.ms
13.321
1.5e+07
1.4e+07
1.3e+07
1.2e+07
1.1e+07
1e+07
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
时间-->


丰度
扫描 1637 (13.327 分): DWH0106116-4.D\data.ms
192.1
271.0
115.1
300.0
91.1
165.1
65.1
139.1
221.2
245.0
355.1
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
m/z-->

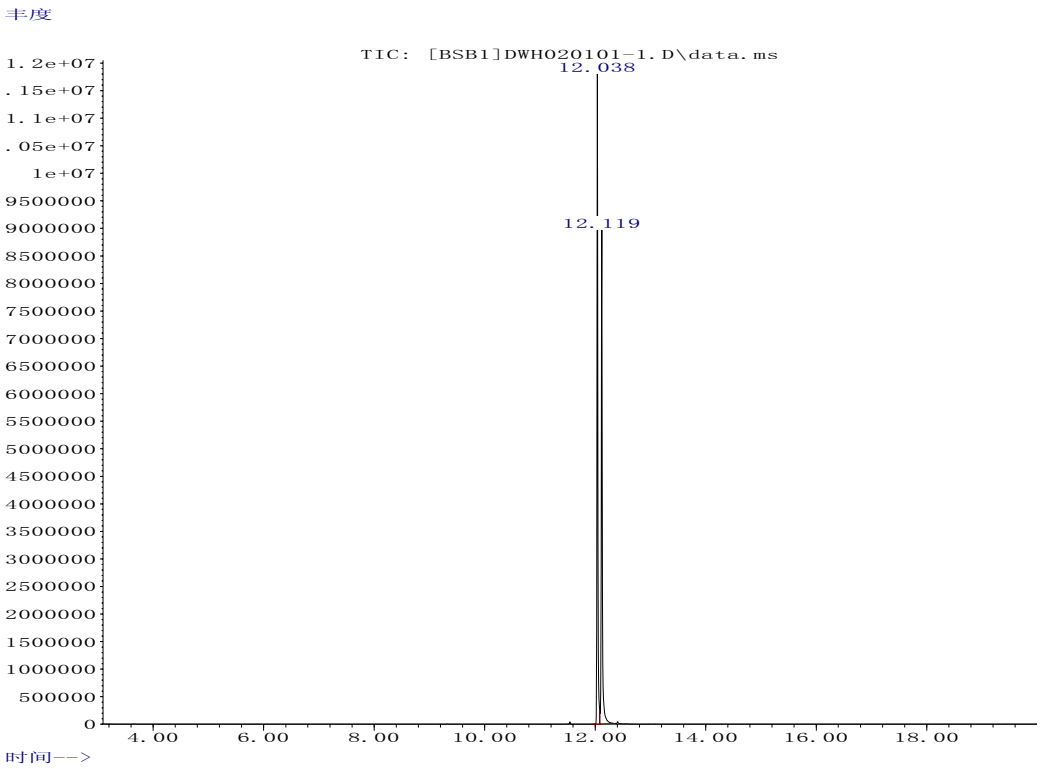
2i

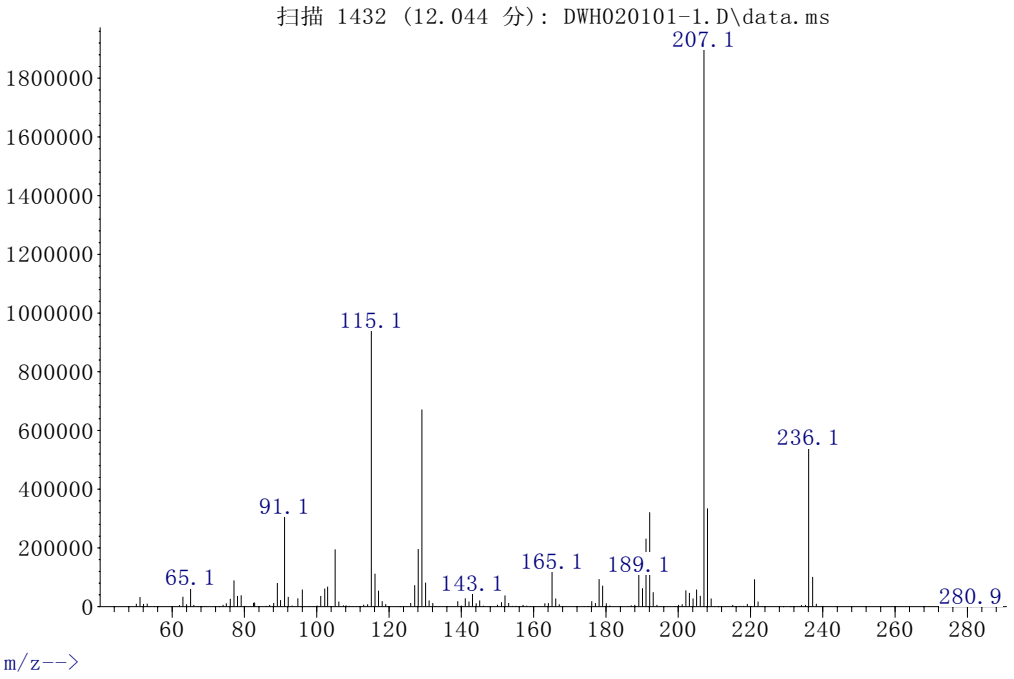

丰度
TIC: [BSB1]DWH0106116-5.D\data.ms
12.045
12.120
2.8e+07
2.6e+07
2.4e+07
2.2e+07
2e+07
1.8e+07
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
0
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
时间-->


丰度
扫描 1431 (12.038 分): DWH0106116-5.D\data.ms
207.1
115.1
236.2
91.1
165.1
65.1
143.1
281.9
354.9
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
m/z-->


丰度
扫描 1444 (12.120 分): DWHO106116-5.D\data.ms
207.1
115.1
236.2
91.1
65.1
165.1
189.1
141.1
266.1
282.9
m/z-->
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
60
80
100
120
140
160
180
200
220
240
260
280

2j


丰度
TIC: [BSB1]DWHO20101-1.D\data.ms
12.038
12.119
时间-->
1.2e+07
1.15e+07
1.1e+07
1.05e+07
1e+07
9500000
9000000
8500000
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00


丰度
扫描 1432 (12.044 分): DWH020101-1.D\data.ms
207.1
115.1
236.1
91.1
65.1
143.1
165.1
189.1
280.9
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
60
80
100
120
140
160
180
200
220
240
260
280
m/z-->