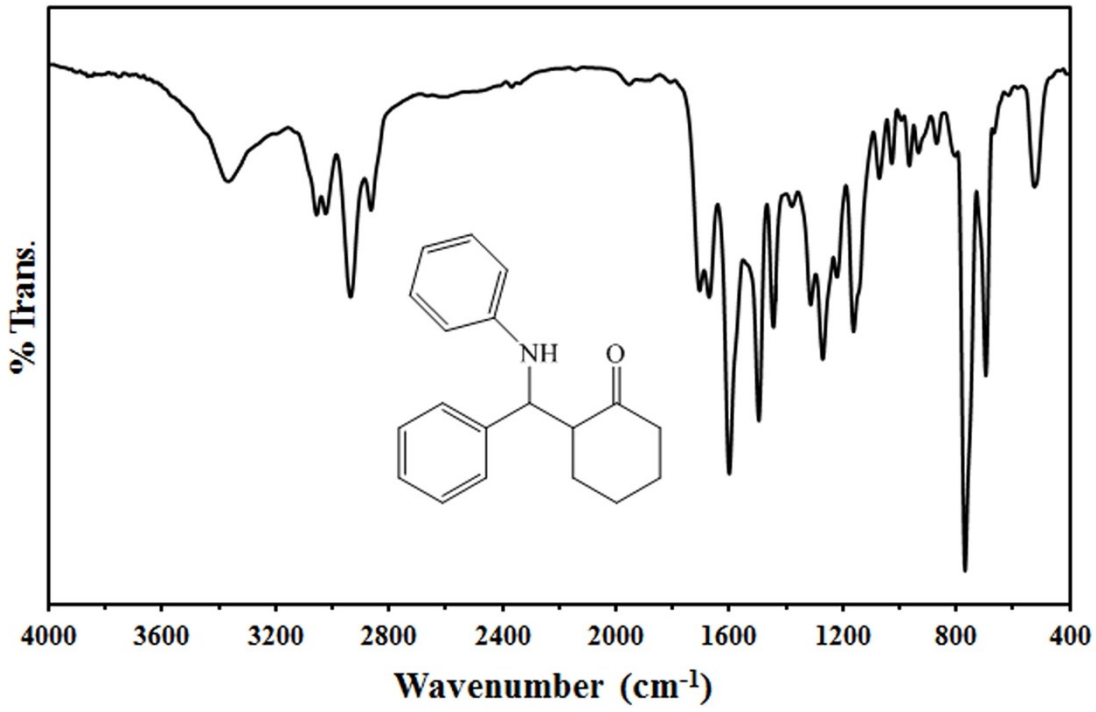
Supporting Information for

$H_3PW_{12}O_{40}$ supported on Functionalized Polyoxometalates Organic–Inorganic Hybrids Nanoparticles as efficient catalysts for three-component Mannich-type reactions in water

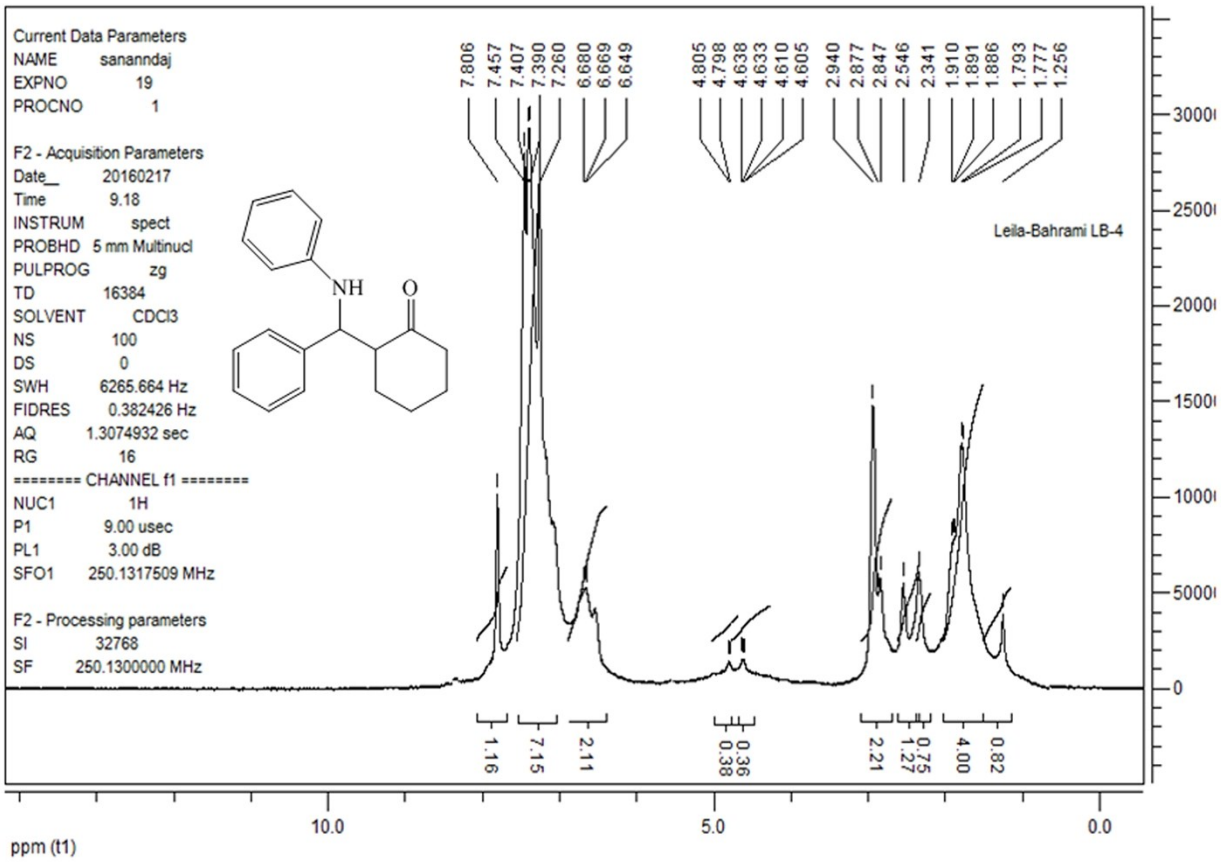
Roushan Khoshnavazi[a*], Leila Bahrami,[a] Forugh Havasi,[a] Elham Naseri[a]

[a]*Department of chemistry, University of Kurdistan P.O. Box 66135-416, Sanandaj, Iran*

FT-IR, ^{1}H NMR, ^{13}C NMR and Mass spectra of new organic products



*Corresponding Author: *E-mail address* :
r.khoshnavazi@uok.ac.ir, khoshnavazi@yahoo.com,
(R. Khoshnavazi)
Fax/Tel: +98 871 6624133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PL1 3.00 dB
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F2 - Processing parameters
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O
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6.669
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4.638
4.633
4.610
4.605
2.940
2.877
2.847
2.546
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1.910
1.891
1.886
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1.777
1.256
Leila-Bahrami LB-4
1.16
7.15
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2.21
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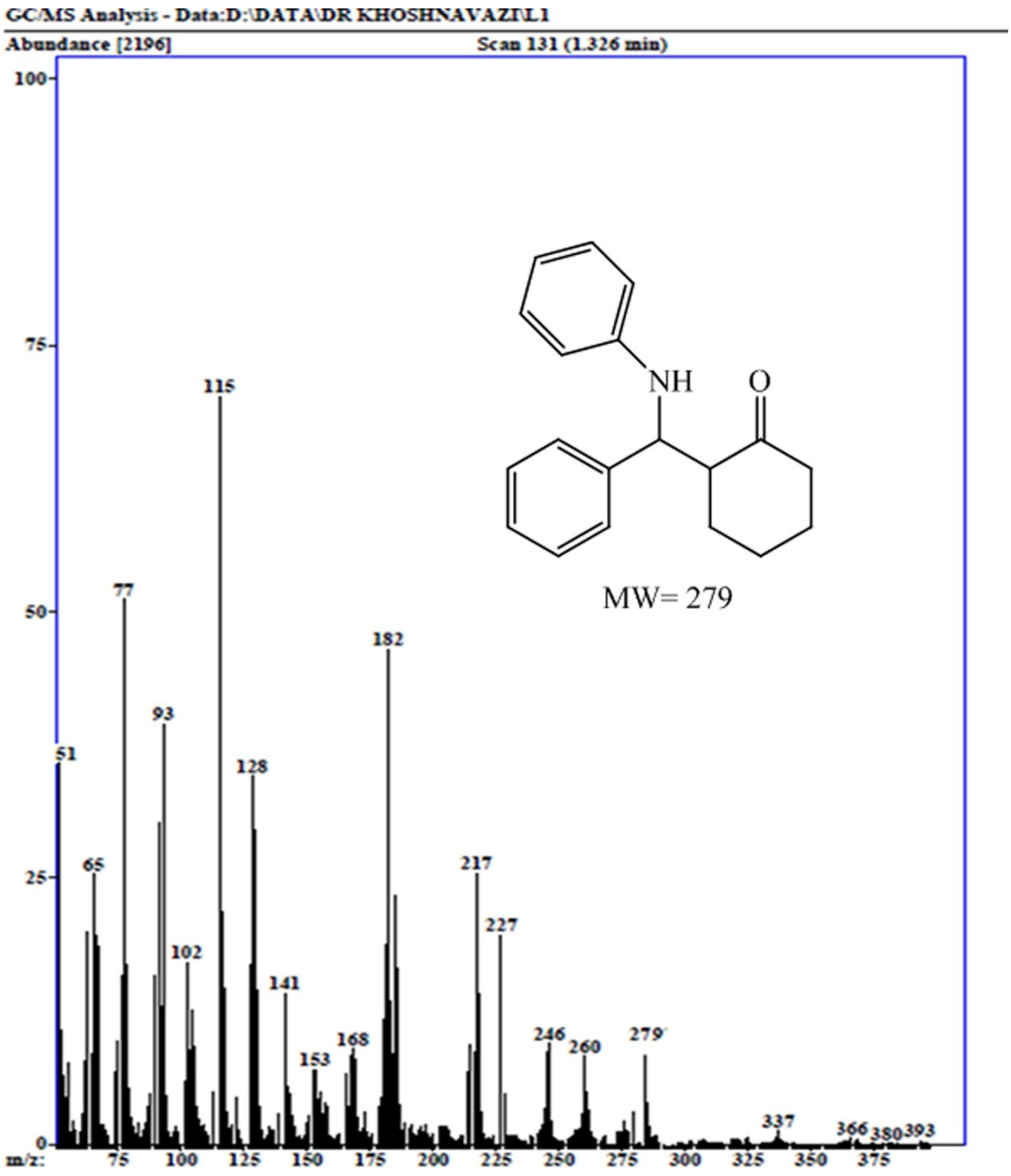
ppm (t1)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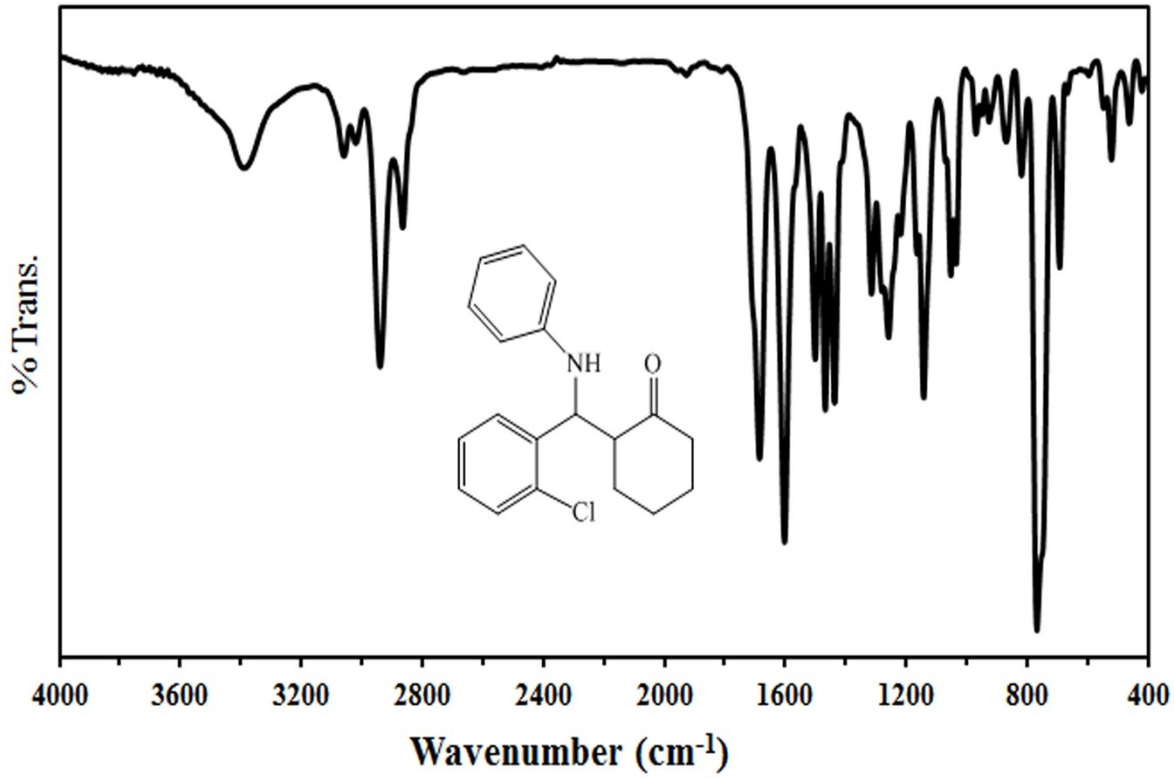
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O
Cl
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2400
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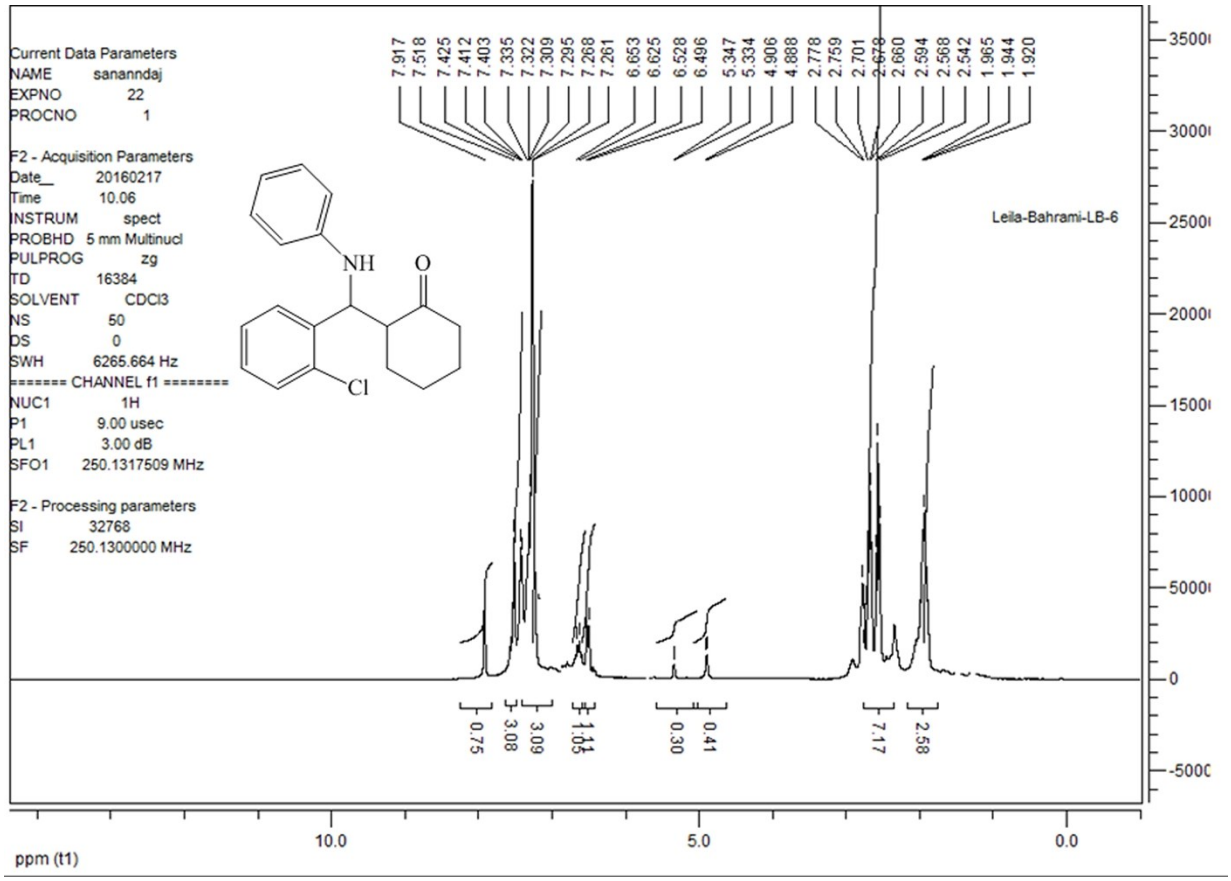
1600
1200
800
400
Wavenumber (cm-1)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SFO1 250.1317509 MHz
F2 - Processing parameters
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NH
O
Cl
Leila-Bahrami-LB-6
7.917
7.518
7.425
7.412
7.403
7.335
7.322
7.309
7.295
7.268
7.261
6.653
6.625
6.528
6.496
5.347
5.334
4.906
4.888
2.778
2.759
2.701
2.678
2.660
2.594
2.568
2.542
1.965
1.944
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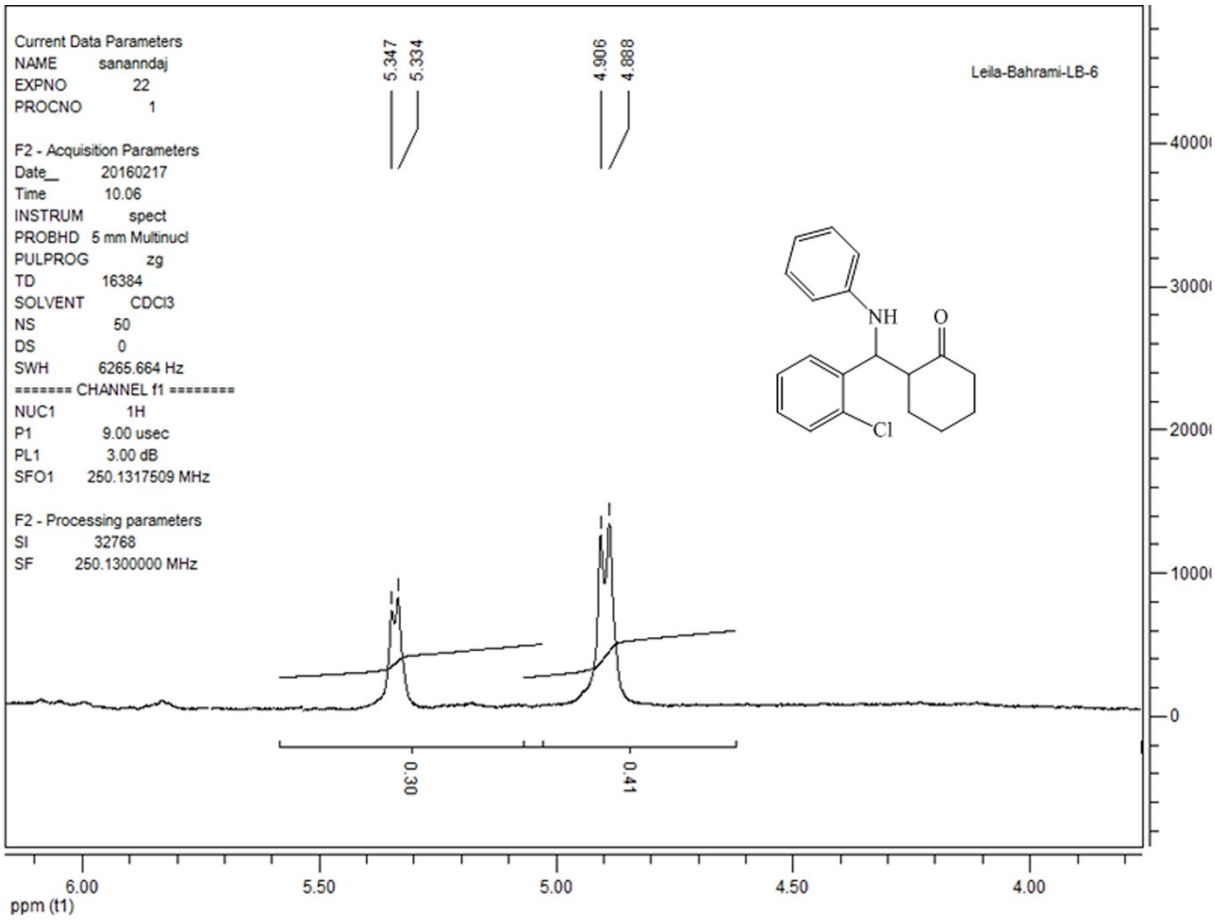
3.09
0.30
0.41
7.17
2.58
10.0
5.0
0.0
ppm (t1)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PULPROG zg
TD 16384
SOLVENT CDCl3
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DS 0
SWH 6265.664 Hz
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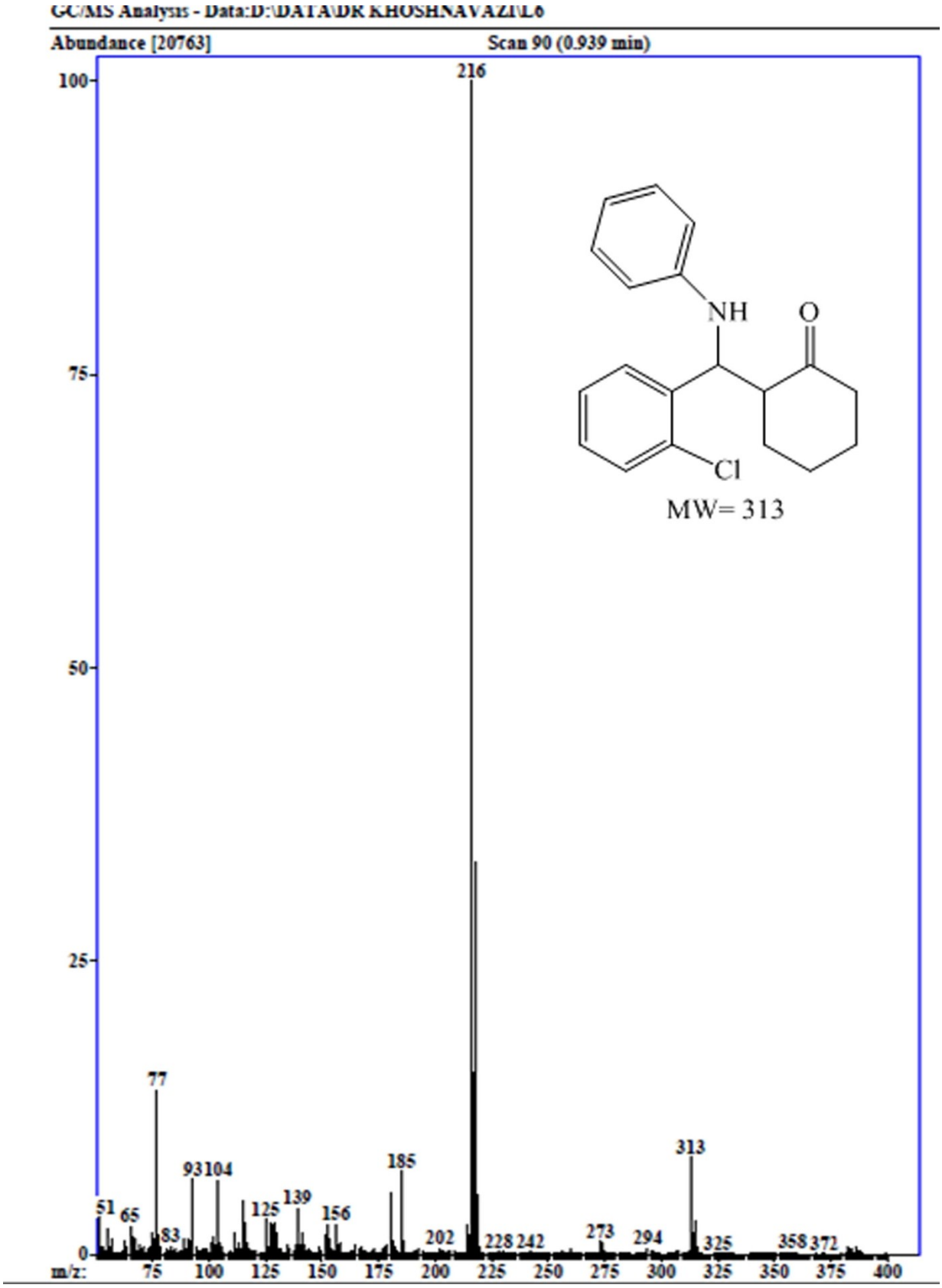
P1 9.00 usec
PL1 3.00 dB
SFO1 250.1317509 MHz
F2 - Processing parameters
SI 32768
SF 250.1300000 MHz
5.347
5.334
4.906
4.888
Leila-Bahrami-LB-6
NH
O
Cl
0.30
0.41
6.00
5.50
5.00
4.50
4.00
ppm (t1)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25
0
m/z:
75
100
125
150
175
200
225
250
275
300
325
350
375
400
216
77
51
65
83
93
104
125
139
156
185
202
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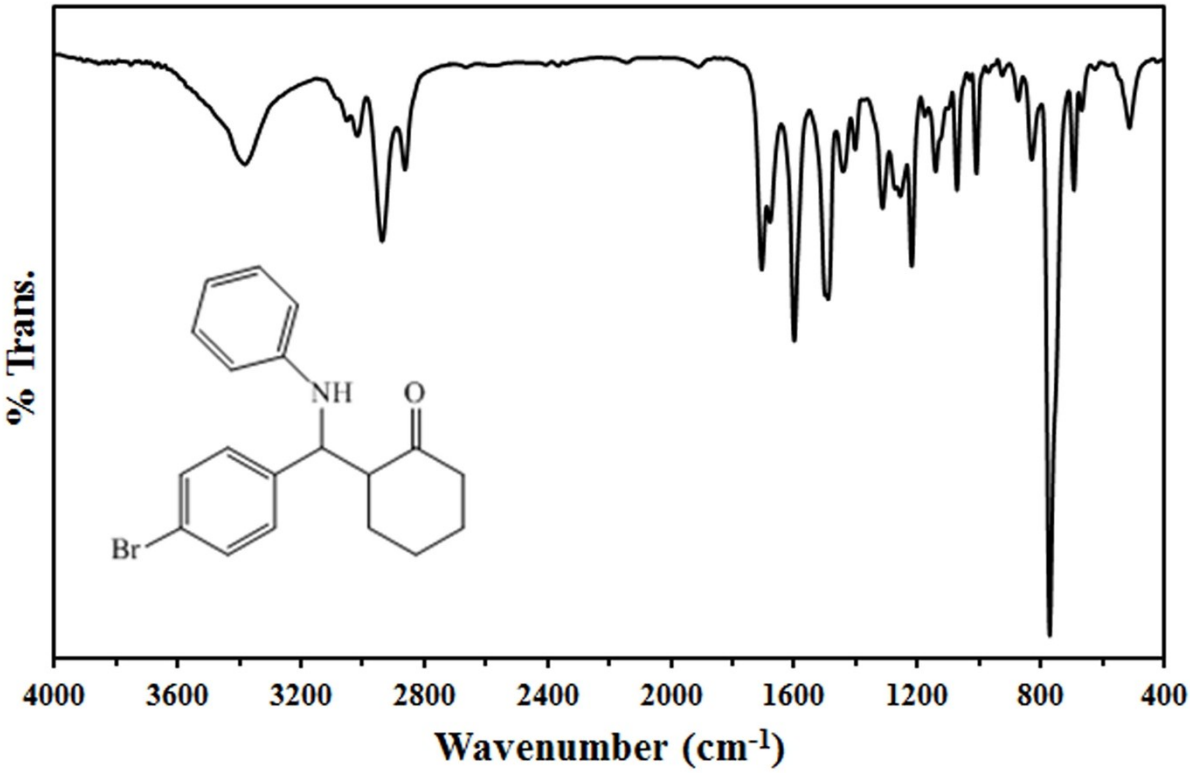
313
325
358
372
NH
O
Cl
MW= 313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O
Br
4000
3600
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2800
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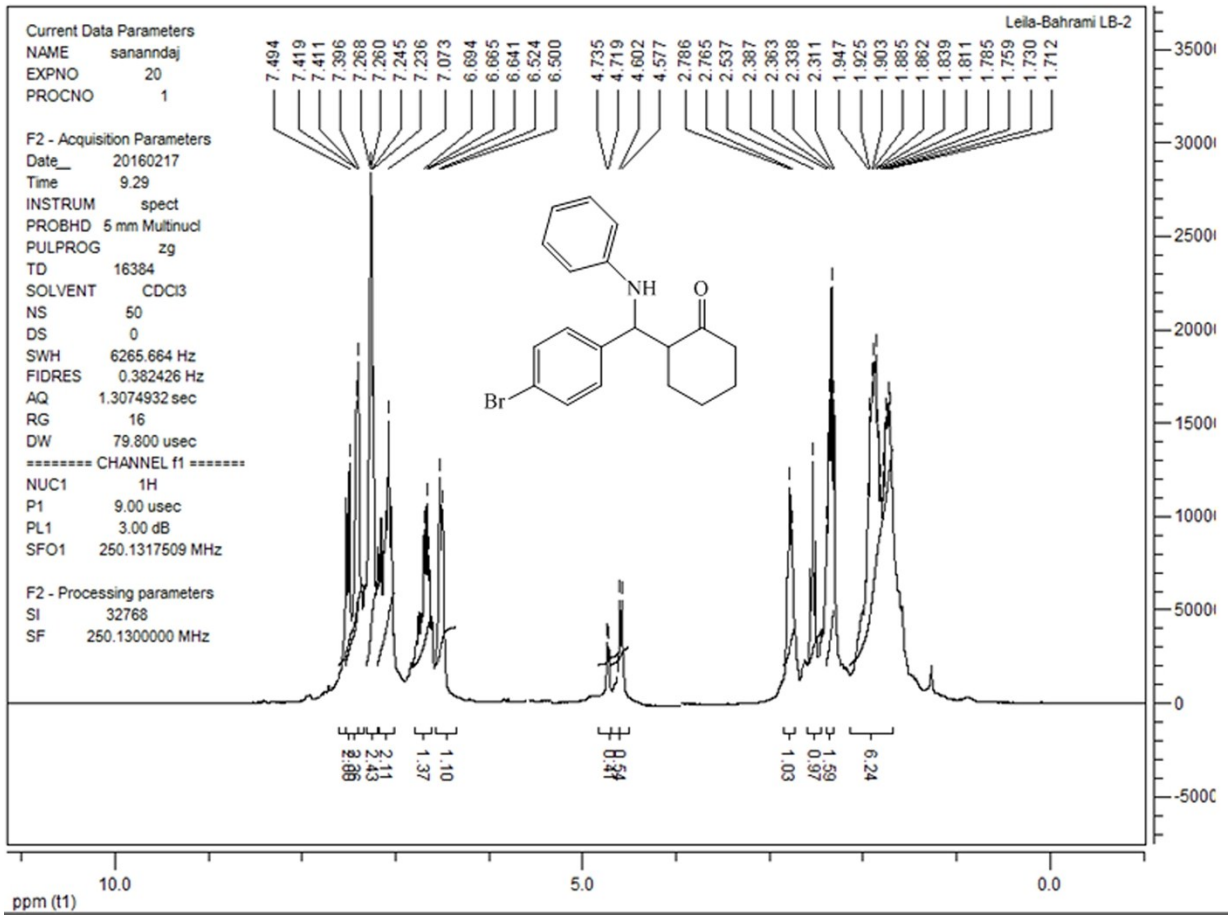
2000
1600
1200
800
400
Wavenumber (cm-1)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Time 9.29
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PULPROG zg
TD 16384
SOLVENT CDCl3
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DS 0
SWH 6265.664 Hz
FIDRES 0.382426 Hz
AQ 1.3074932 sec
RG 16
DW 79.800 usec
======== CHANNEL f1 =======
NUC1 1H
P1 9.00 usec
PL1 3.00 dB
SFO1 250.1317509 MHz
F2 - Processing parameters
SI 32768
SF 250.1300000 MHz
7.494
7.419
7.411
7.396
7.268
7.260
7.245
7.236
7.073
6.694
6.665
6.641
6.524
6.500
4.735
4.719
4.602
4.577
2.786
2.765
2.537
2.387
2.363
2.338
2.311
1.947
1.925
1.903
1.885
1.862
1.839
1.811
1.785
1.759
1.730
1.712
NH
O
Br
2.86
2.11
2.43
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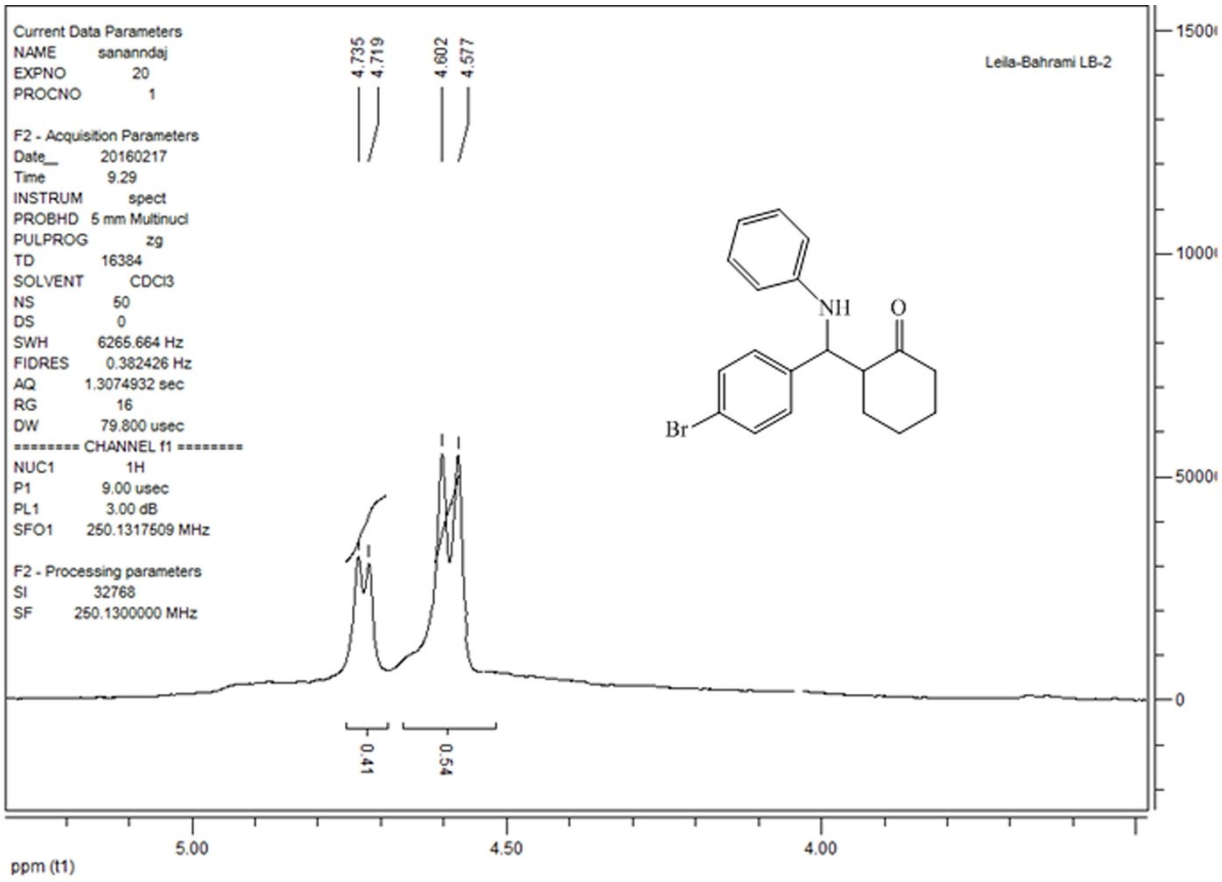
ppm (t1)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SOLVENT CDCl3
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SWH 6265.664 Hz
FIDRES 0.382426 Hz
AQ 1.3074932 sec
RG 16
DW 79.800 usec
======== CHANNEL f1 ========
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P1 9.00 usec
PL1 3.00 dB
SFO1 250.1317509 MHz
F2 - Processing parameters
SI 32768
SF 250.1300000 MHz
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4.719
4.602
4.577
Leila-Bahrami LB-2
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O
Br
0.41
0.54
5.00
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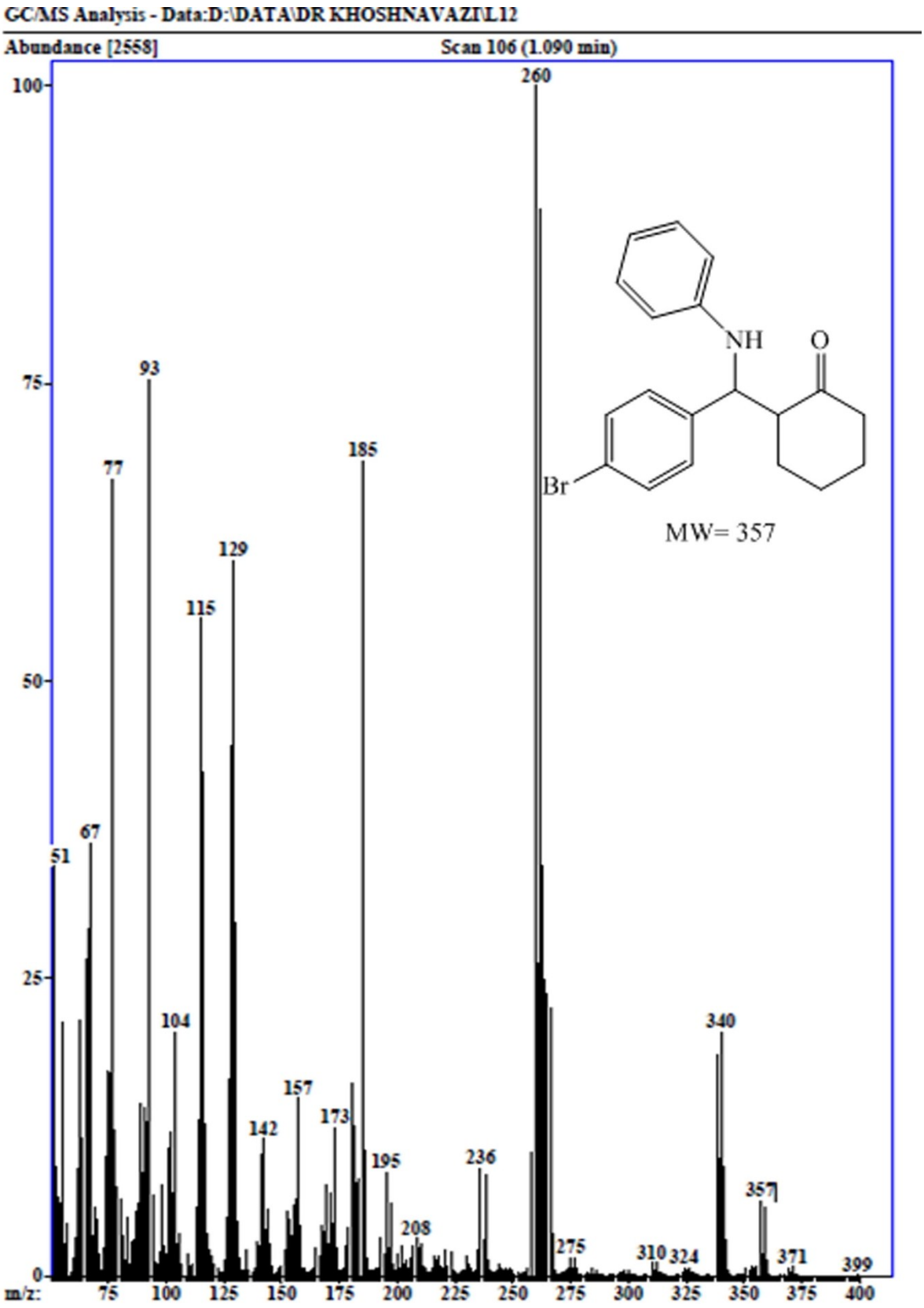
4.00
ppm (t1)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150
175
200
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250
275
300
325
350
375
400
260
93
77
185
129
115
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Br
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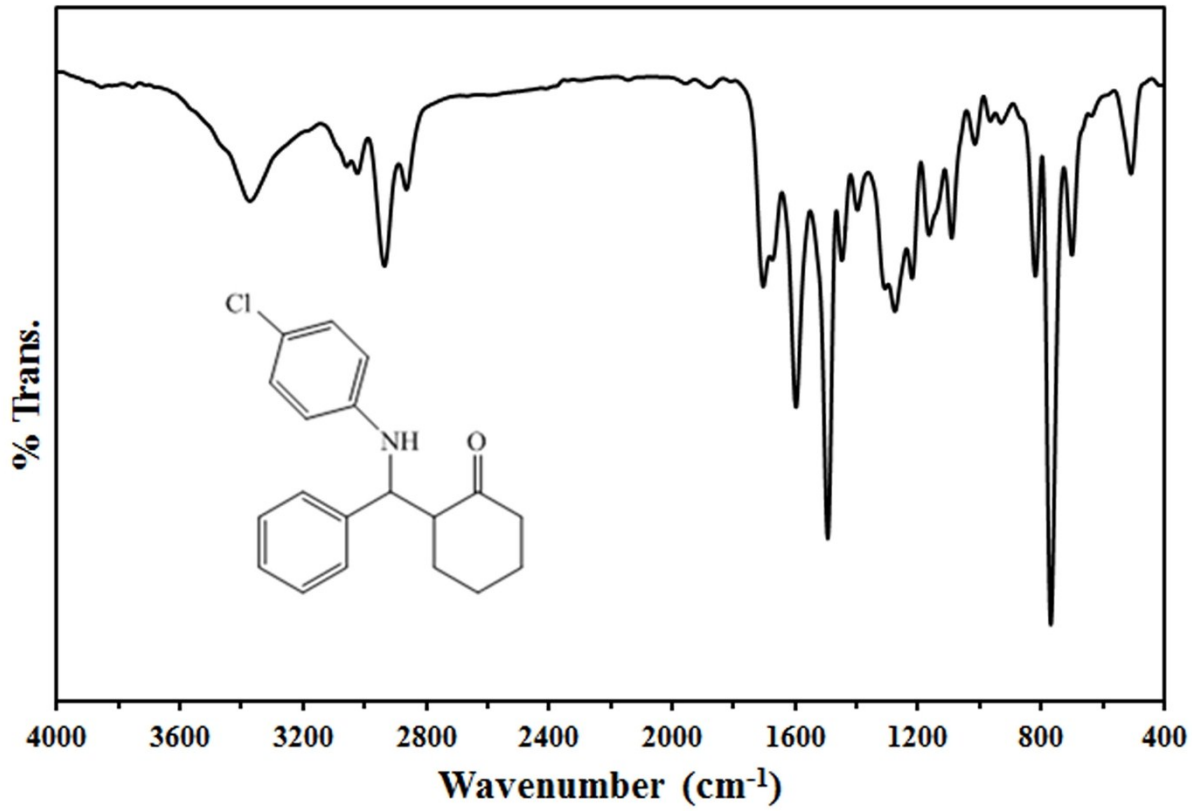
% Trans.
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800
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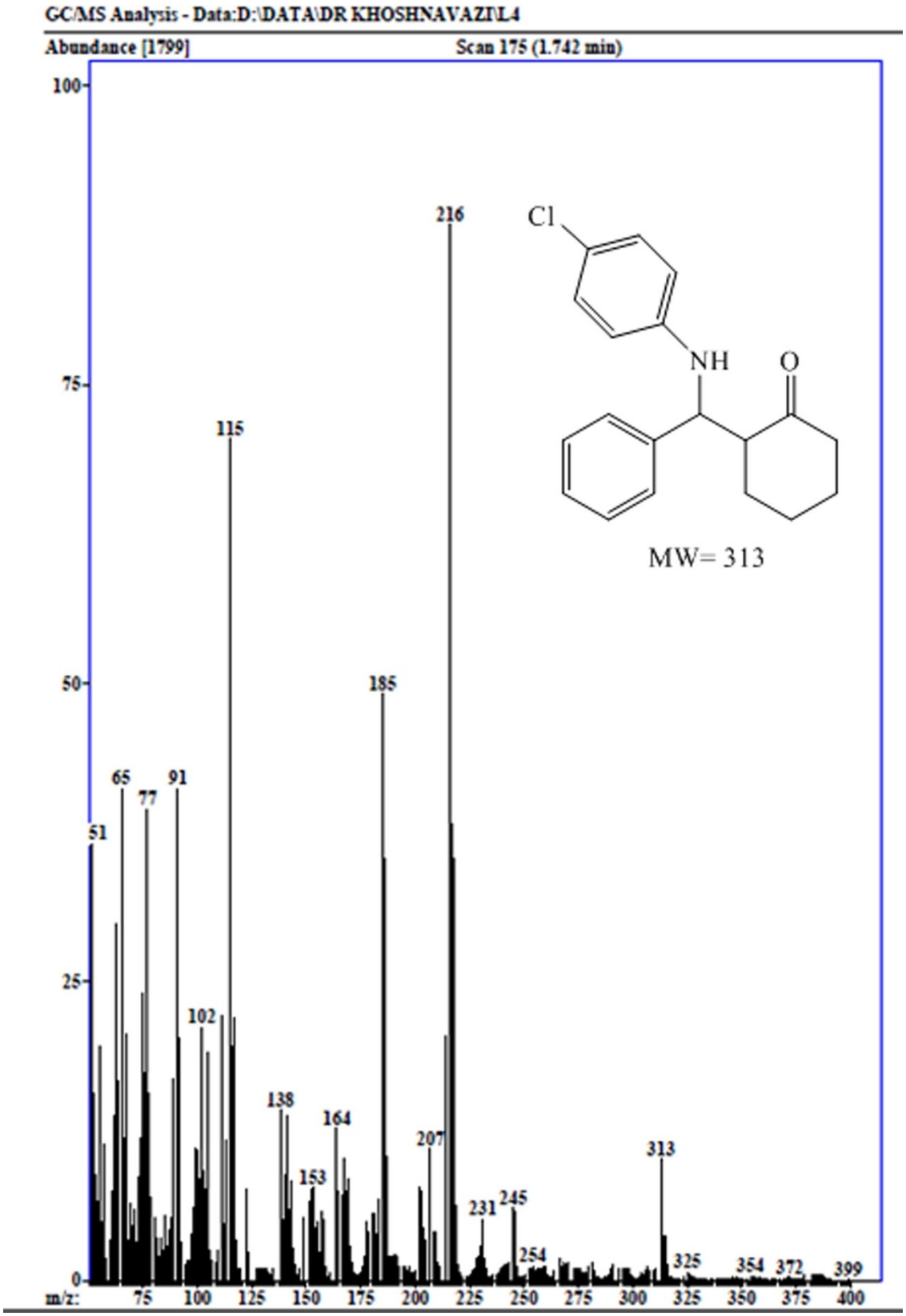
Wavenumber (cm-1)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m/z:
75 100 125 150 175 200 225 250 275 300 325 350 375 400
216
115
185
65
91
77
51
102
138
164
153
207
313
231
245
254
325
354
372
399
Cl
NH
O
MW= 313

Detailed XRD analysis

XRD patterns of starting materials of β-$SiW_9O_{34}^{10-}$ (Fig. Sa) and PDA are crystalline in the solid state, while X-ray powder diffractions show that HybPOM is typical amorphous state, implying that the hybrid materials have less-ordered structures (Fig. Sb). However, it can see XRD of HybPOM contain XRD pattern of both β-$SiW_9O_{34}^{10-}$ and PPD. X-ray diffraction (XRD) measurements were also performed to obtain crystalline structural information for the GO, GO-Fe_3O_4, GO@Fe_3O_4@HybPOM. The broad diffraction peak around 18.72° corresponds to C (002) reflection of GO (Fig. S inset). For the GO-Fe_3O_4 the intense diffraction peaks indexed to (220), (311), (400), (422), (511), (440), and (533) planes appearing at 2θ = 30.52°, 35.85°, 43.58°, 53.96°, 57.43°, 63.16° and 74.65° respectively, and the peak positions and relative intensities match well with the standard XRD data for the cubic phase Fe_3O_4 with a face-centered cubic (fcc) structure (JCPDS No. 19−629) (Fig. Sc).[31] Disappearance of the reflection plane at (002) and merging of the planes of Fe_3O_4 show the good interfacial interaction between the planes. The XRD of GO@Fe_3O_4@HybPOM show corresponding peaks of the GO-Fe_3O_4 and the amorphous XRD pattern of HybPOM as background, respectively (Fig. Sd).

R. Khoshnavazi, L. Bahrami and F. Havasi, *RSC Adv*., 2016, **6**, 100962.

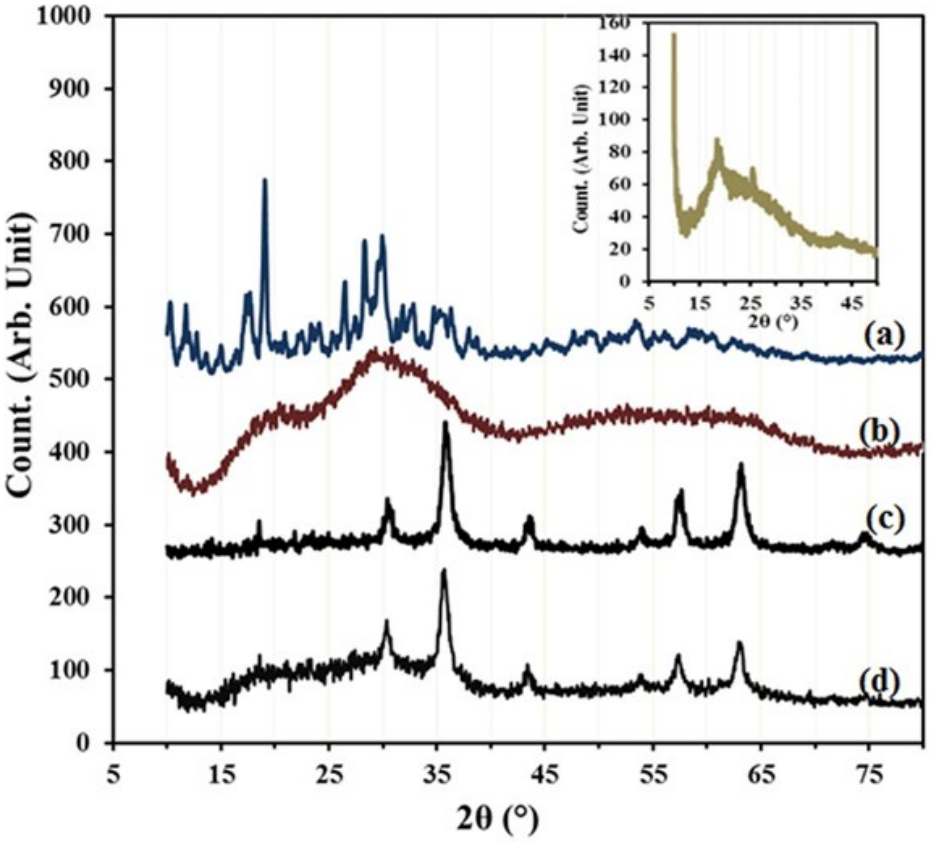

Fig. S XRD spectra of (a) $Na_9H[\beta\text{-}XW_9O_{34}]\cdot nH_2O$, (b) HybPOM, (c) GO@$Fe_3O_4$ (d) GO@Fe_3O_4@HybPOM and GO(inset).

R. Khoshnavazi, L. Bahrami and F. Havasi, *RSC Adv*., 2016, **6**, 100962.