Synthesis of Green [60]Fullerene Derivative through Cage-Opening Reactions

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Content

Compound **1** was prepared according to the same procedure as in Zhang, Q. Y.; Jia, Z. S.; Liu, S. M.; Zhang, G.; Xiao, Z.; Yang, D. Z.; Gan, L. B.; Wang, Z. M.; Li, Y. L. *Org. Lett.*, **2009**, *11*, 2772.

Electrochemical measurements

A conventional three-electrode system is used, with a platinum ultra-microelectrode (Pt UME, diameter: 25 um) as the working electrode, a platinum wire and a Ag wire as the counter and quasi-reference electrodes, respectively. Ferrocene served as an internal standard. Before being used, the Pt UME was polished using alumina powder with 0.05 um, and then sonicated in ethanol and water for 3 minutes, respectively. DPV measurements were carried out in toluene solution containing 0.05 mol/L THA-Tf_2N as supporting electrolyte (Scan rate: 20 mVs^{-1}). All the solutions were purged with argon for at least 25 minutes to remove oxygen prior to experiments. All experiments were carried out at room temperature (22 ± 2 ^{o}C).

Proposed mechanism for the conversion of compound 2 to 3

The mechanism probably starts from protonation of the imino nitrogen next to the lactone carbonyl group to form intermediate **A**. The regio-selectivity is due to favourable intramolecular H-bond formation. It is well known that iodine does not form strong bond to fullerene. Iodofullerene derivatives are quite rare.[1] Thus I and OH groups in **B** were readily eliminated through **C** to form **D**. The final step from **D** to **3** is a facile intramolecular Friedel-Crafts process, which is facilitated by the flexible amino group instead of the rigid imino group in the precursor and by formation of a six-membered ring. Lewis acid mediated Friedel-Crafts hydroarylation of C_{60} has been reported to form isomerically pure multiadducts selectively.[2]

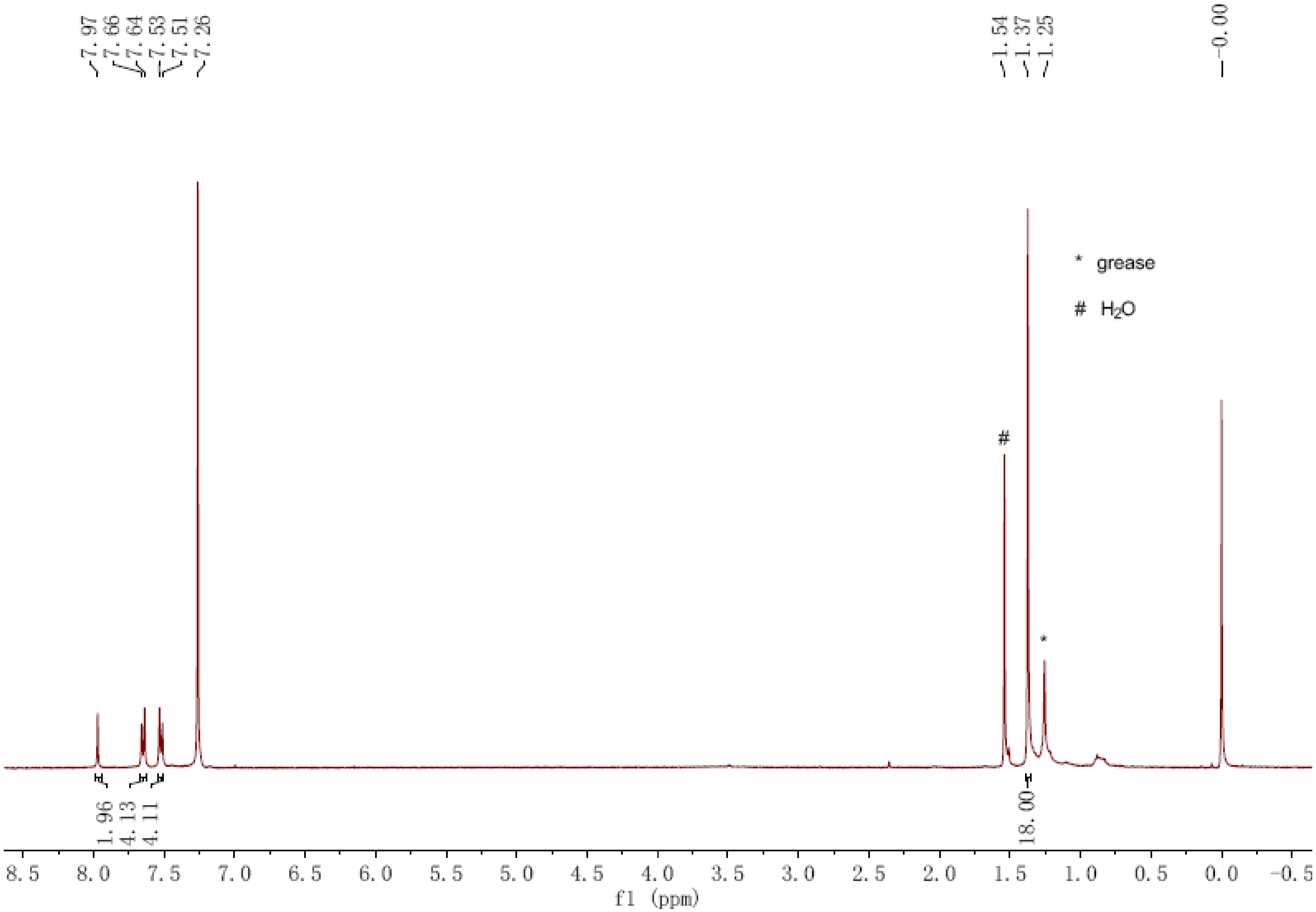
Alternatively, the conversion may undergo an iodide mediated reductive aromatization process to eliminate the two OH groups in **2**, followed by a proton catalyzed cyclizing isomerization process. As above, the regio-selectivity is due to favourable intramolecular H-bond formation. (we thank one of the reviewers for proposing this mechanism).

[1] For a rare example see: S. H. Huang, X. B. Yang, X. Zhang, X. Q. Hu, L. B. Gan, S. W. Zhang, *Synlett* 2006, **8**, 1266.

[2] A. Iwashita, Y. Matsuo, E. Nakamura, *Angew. Chem. Int. Ed.* 2007, **46**, 3513.

Or

Scheme Possible mechanisms for HI induced reactions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7.64
7.53
7.51
7.26
1.54
1.37
1.25
-0.00
* grease
# H_2O
#
*
1.96
4.13
4.11
18.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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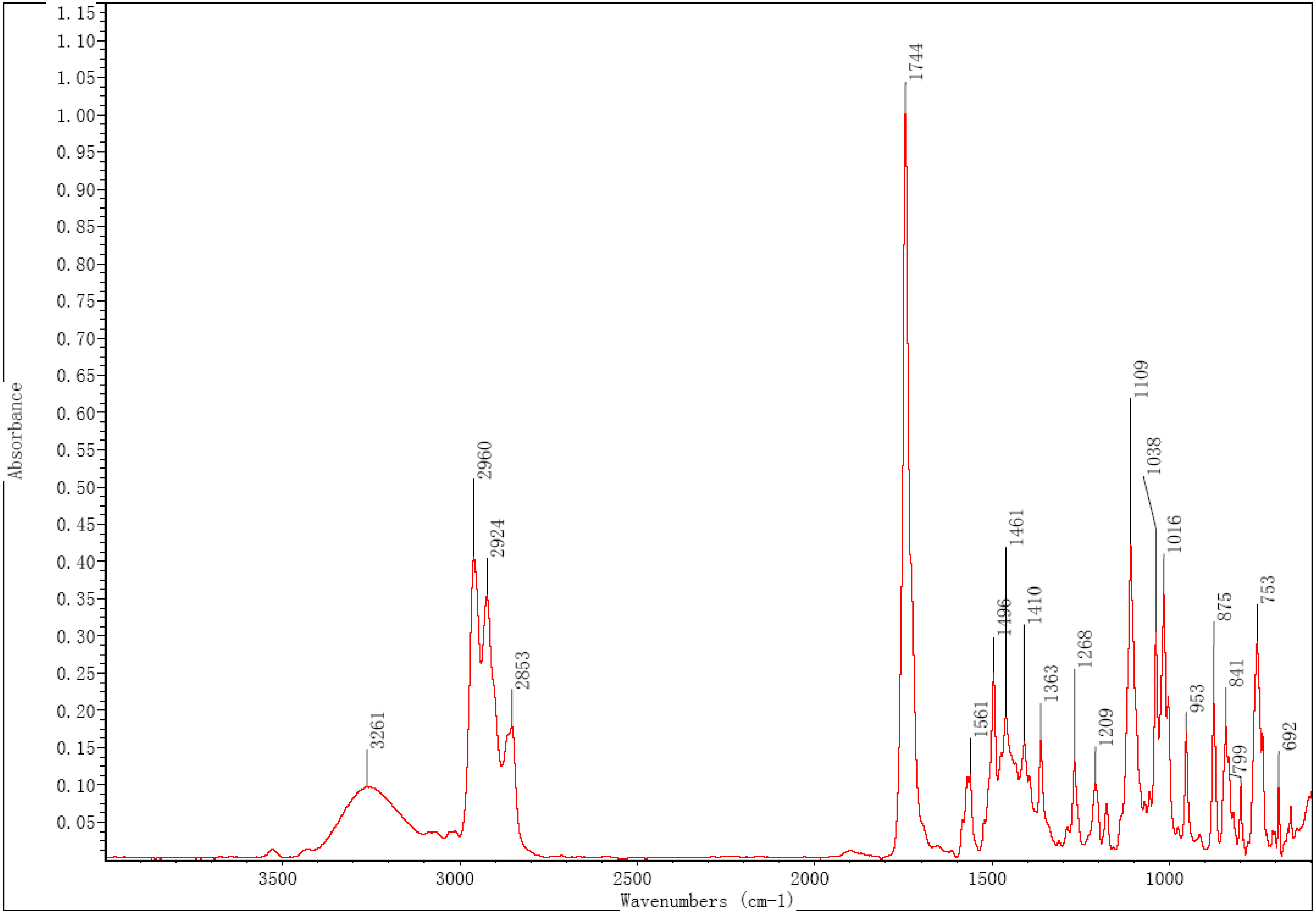
0.5
0.0
-0.5
f1 (ppm)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1.05
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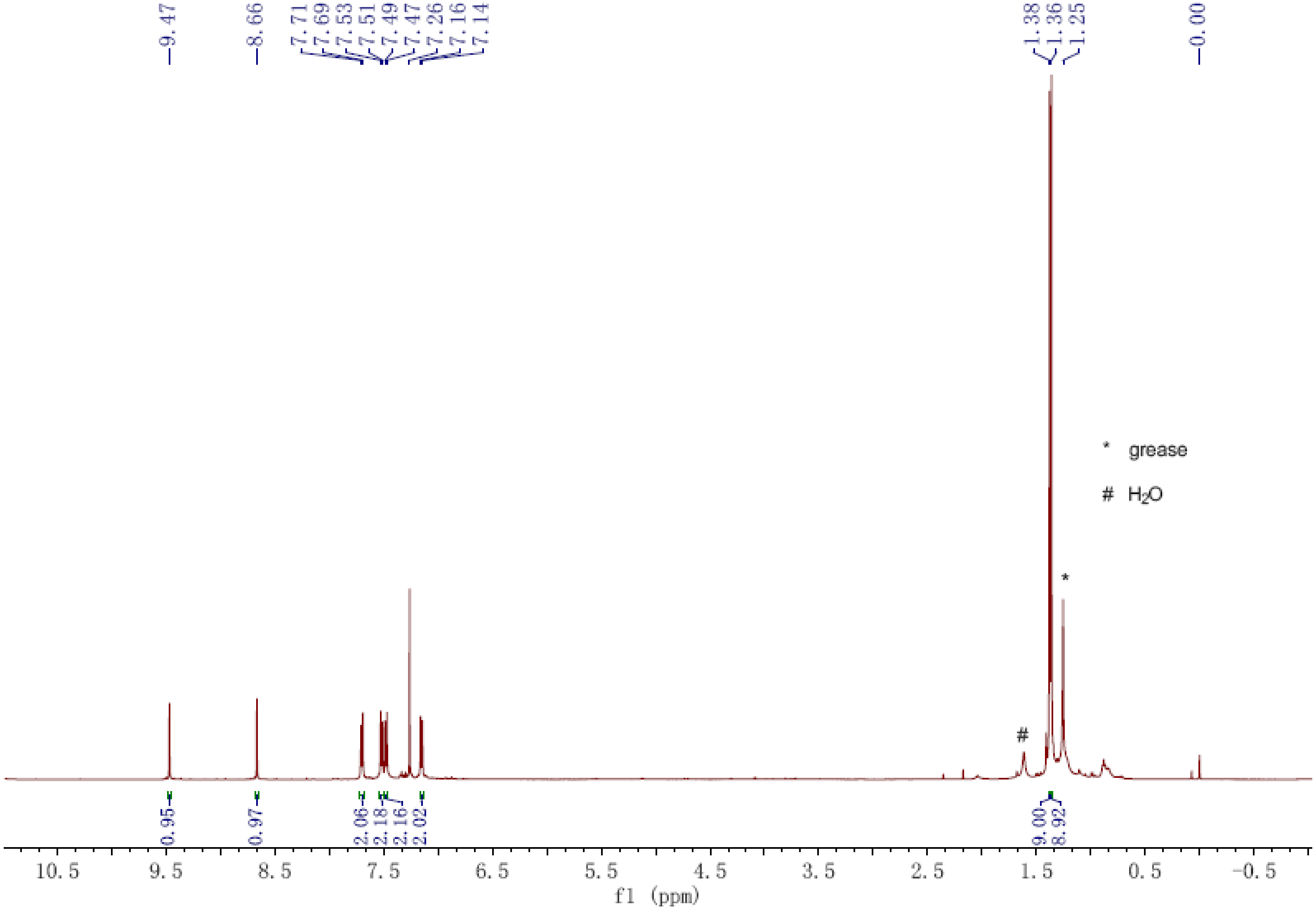
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
3261
2960
2924
2853
1744
1561
1496
1461
1410
1363
1268
1209
1109
1038
1016
953
875
841
799
753
692
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)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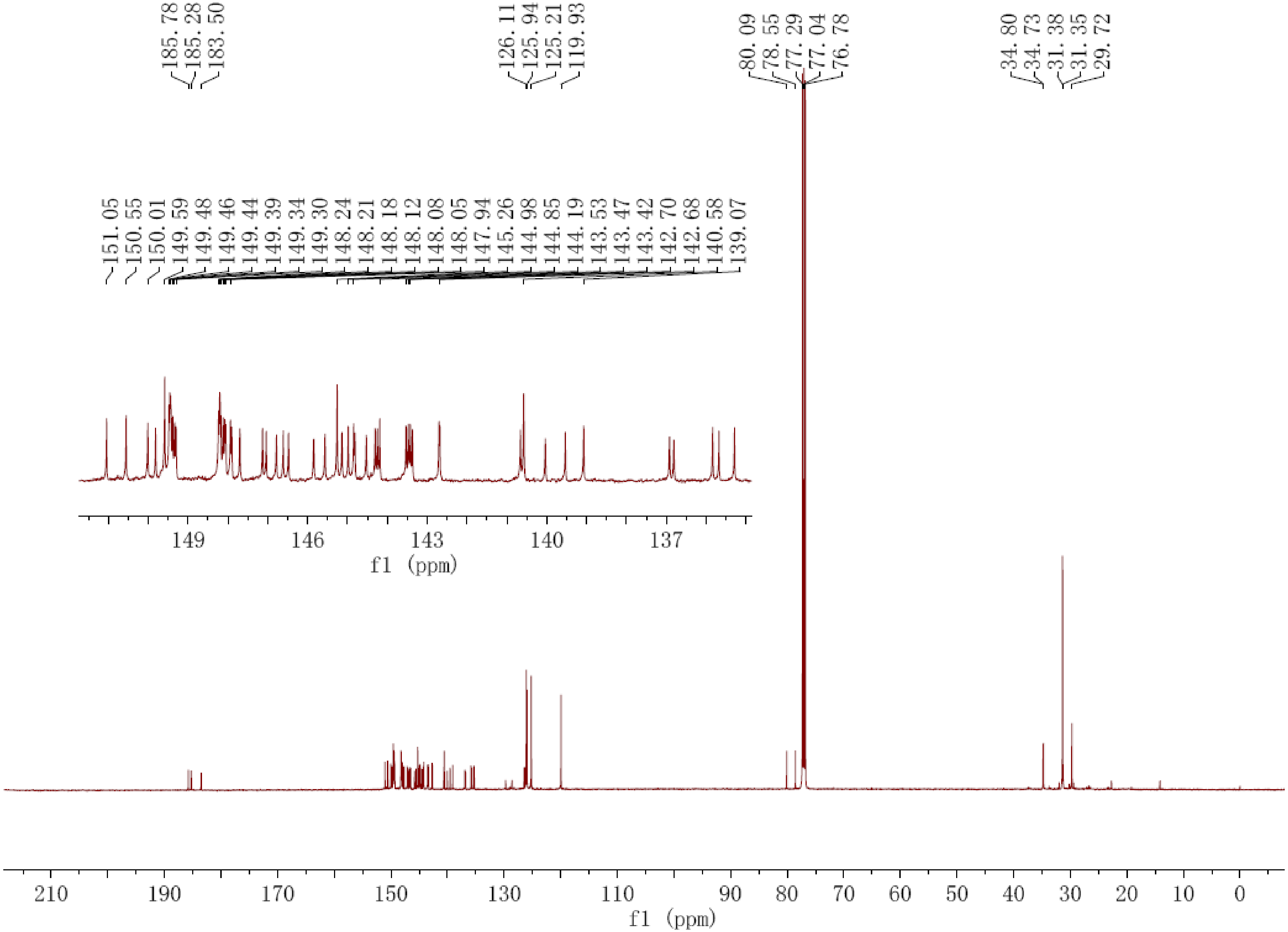
7.71
7.69
7.53
7.51
7.49
7.47
7.26
7.16
7.14
1.38
1.36
1.25
0.00
* grease
# H2O
*
#
0.95
0.97
2.06
2.18
2.16
2.02
9.00
8.92
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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185.28
183.50
126.11
125.94
125.21
119.93
80.09
78.55
77.29
77.04
76.78
34.80
34.73
31.38
31.35
29.72
151.05
150.55
150.01
149.59
149.48
149.46
149.44
149.39
149.34
149.30
148.24
148.21
148.18
148.12
148.08
148.05
147.94
145.26
144.98
144.85
144.19
143.53
143.47
143.42
142.70
142.68
140.58
139.07
149
146
143
140
137
f1 (ppm)
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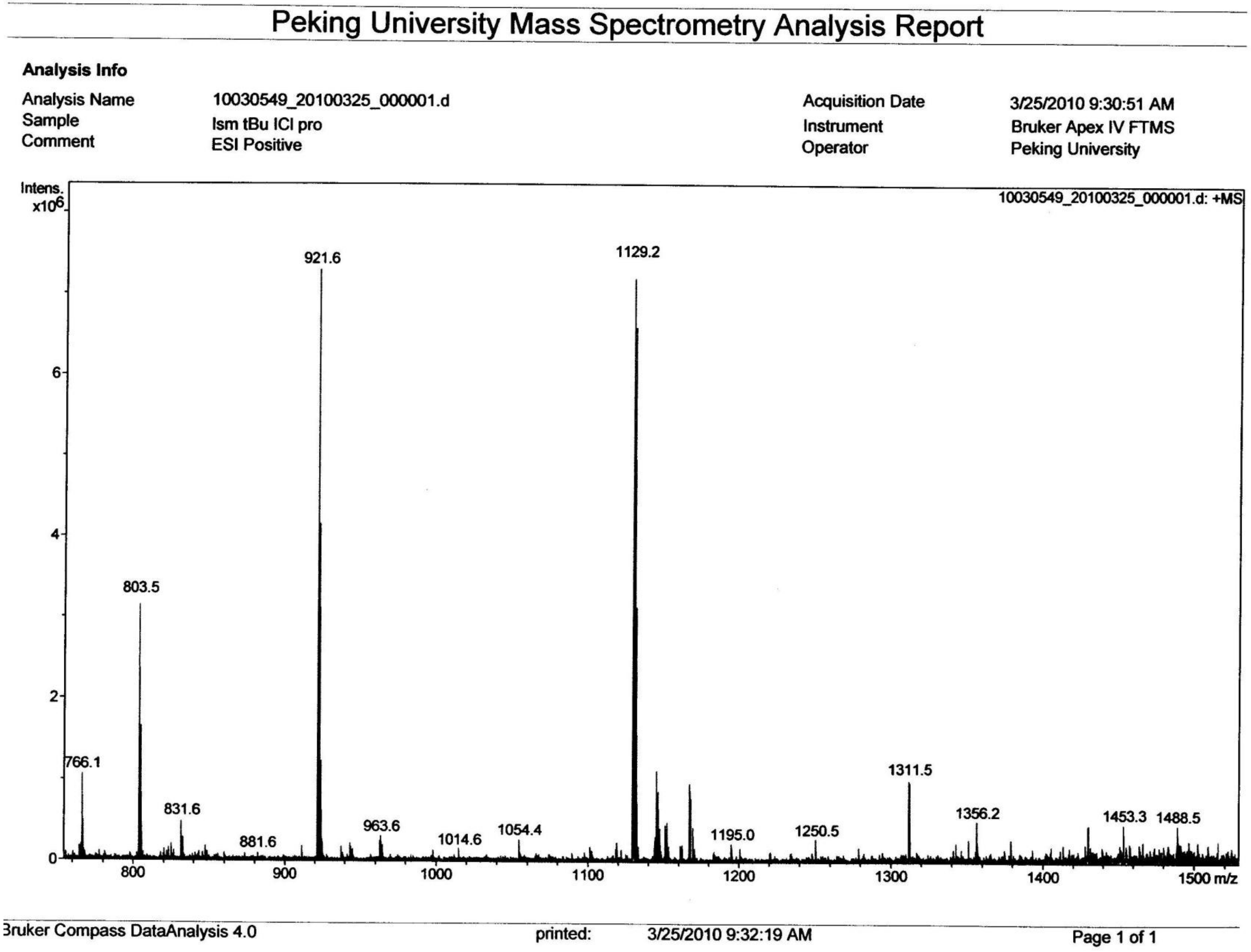
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



Peking University Mass Spectrometry Analysis Report

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Sample	Ism tBu ICl pro	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University

Bruker Compass DataAnalysis 4.0 printed: 3/25/2010 9:32:19 AM Page 1 of 1

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

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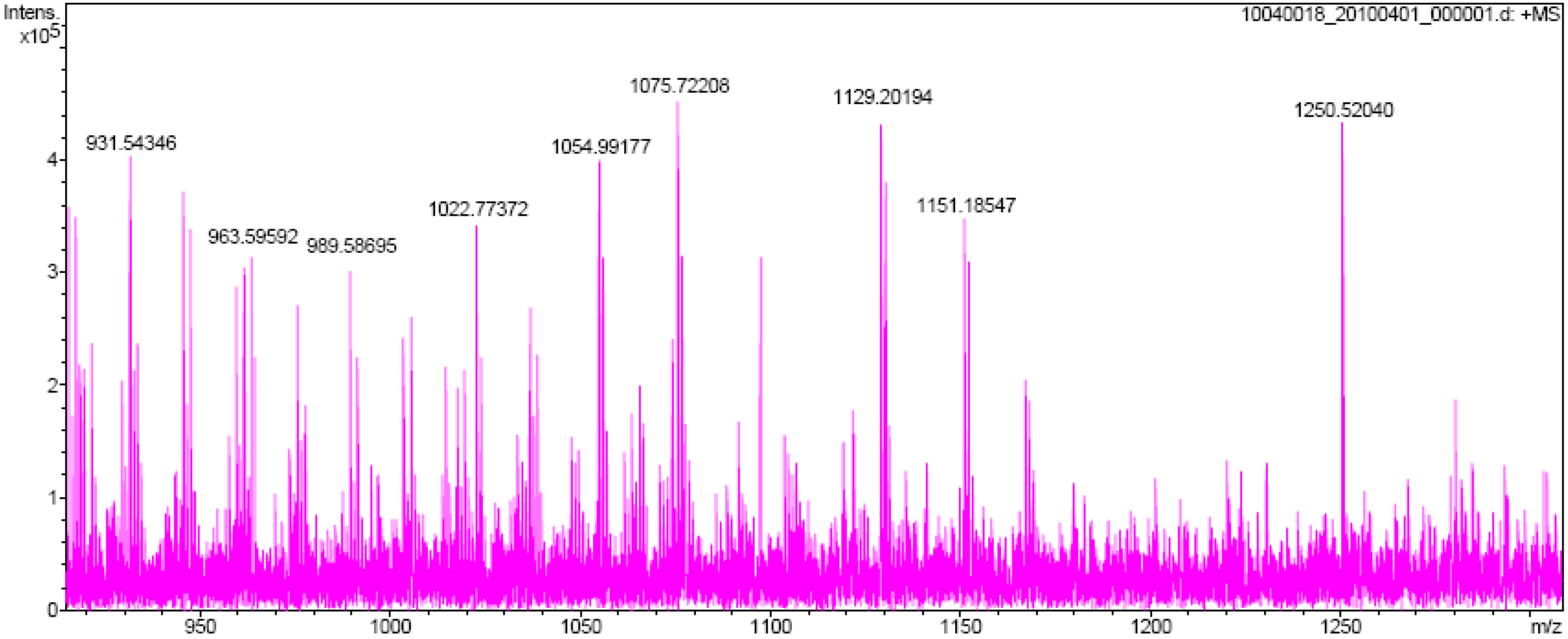
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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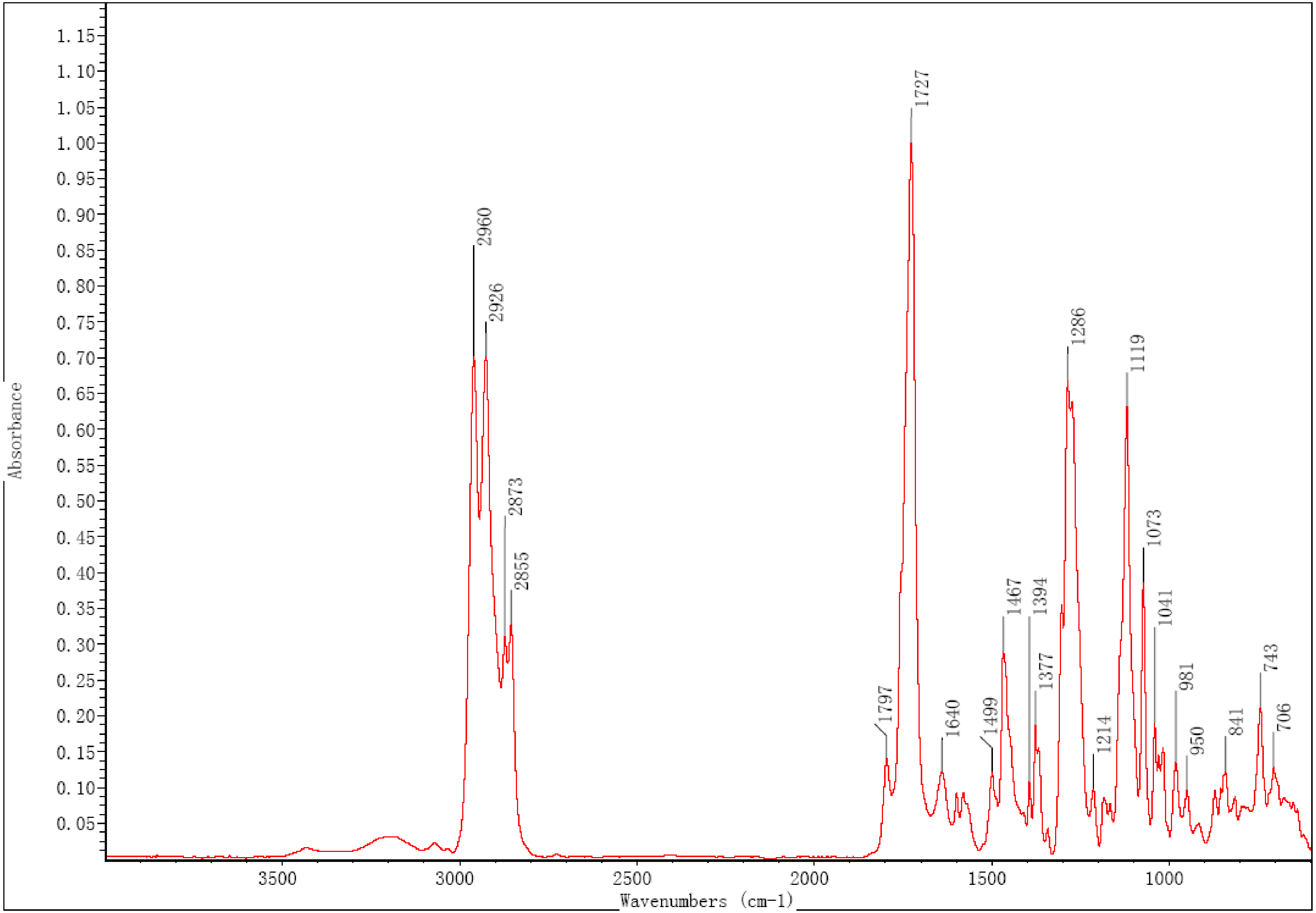
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1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)
2960
2926
2873
2855
1797
1727
1640
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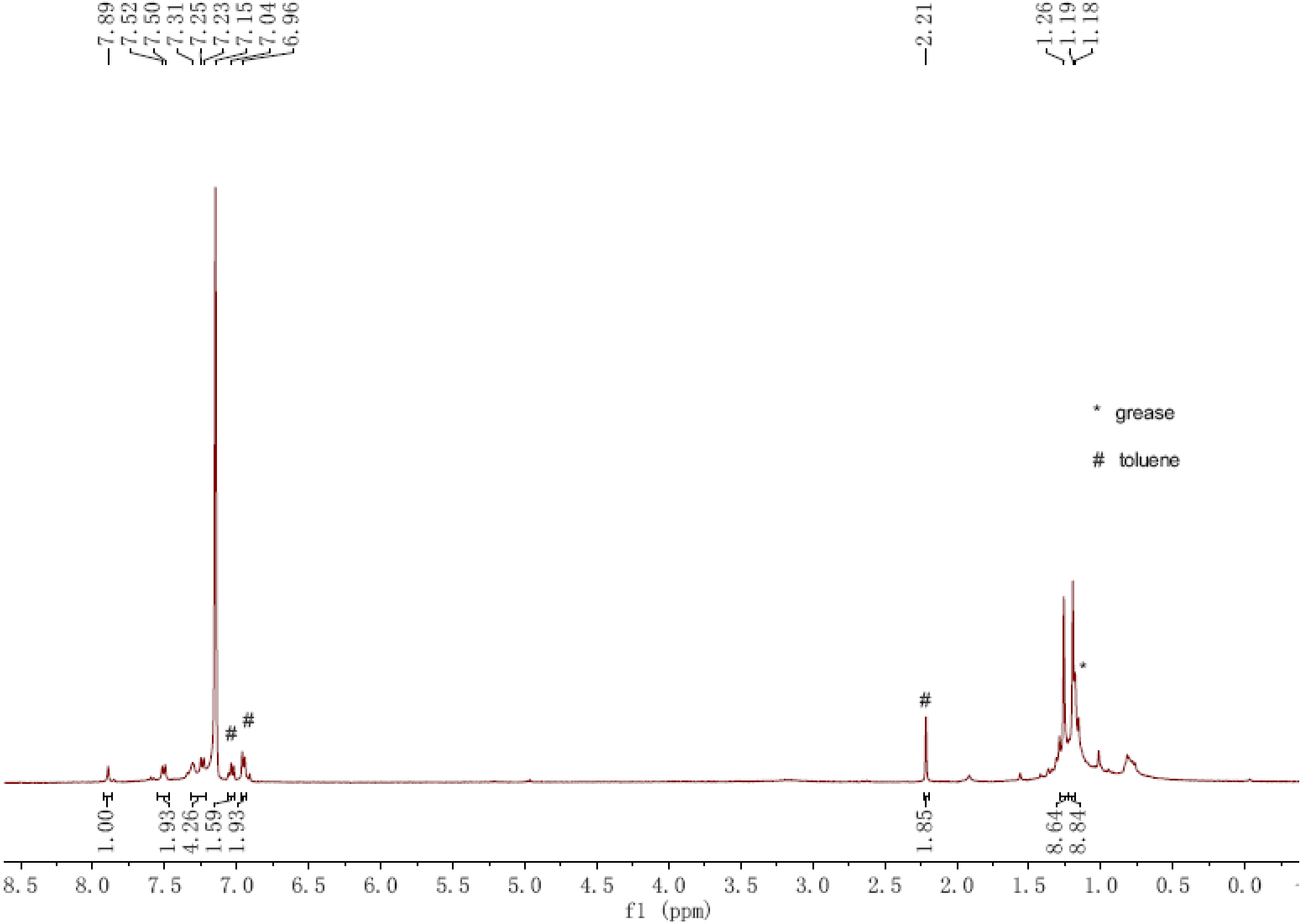
1467
1394
1377
1286
1214
1119
1073
1041
981
950
841
743
706


7.89
7.52
7.50
7.31
7.25
7.23
7.15
7.04
6.96
2.21
1.26
1.19
1.18
* grease
# toluene
#
#
#
*
1.00
1.93
4.26
1.59
1.93
1.85
8.64
8.84
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

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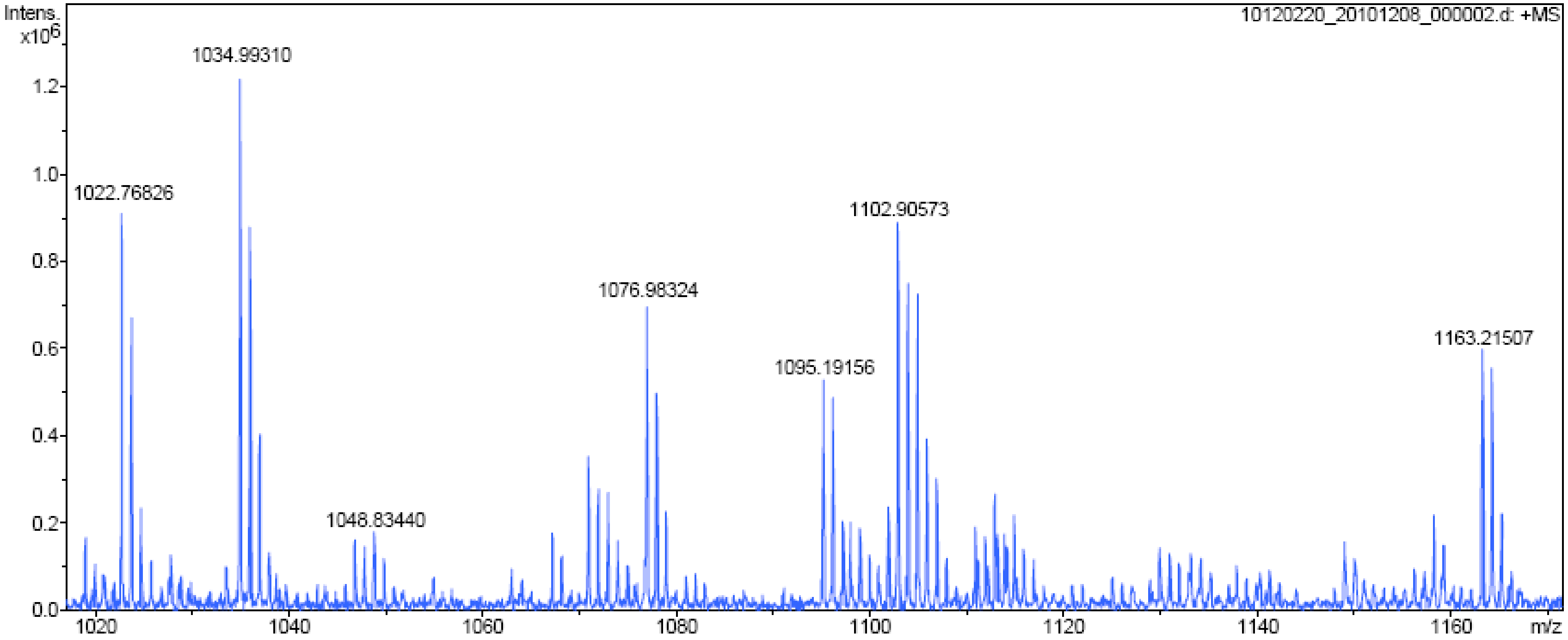
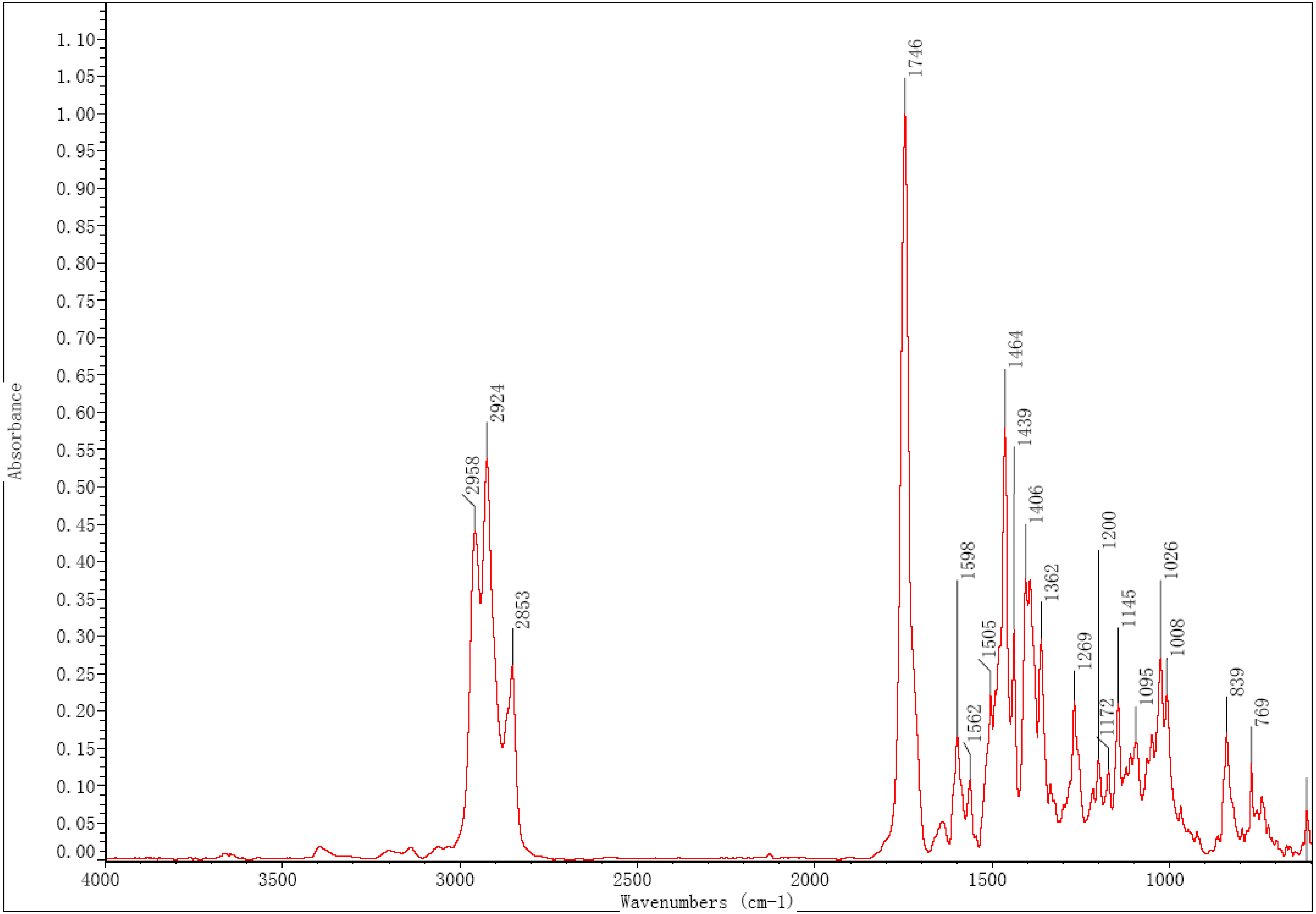
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1095.19156	1	C 80 H 27 N 2 O 5	100.00	1095.19145	-0.1	-0.1	53.8	68.5	even	ok


Absorbance
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)
2958
2924
2853
1746
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1026
1008
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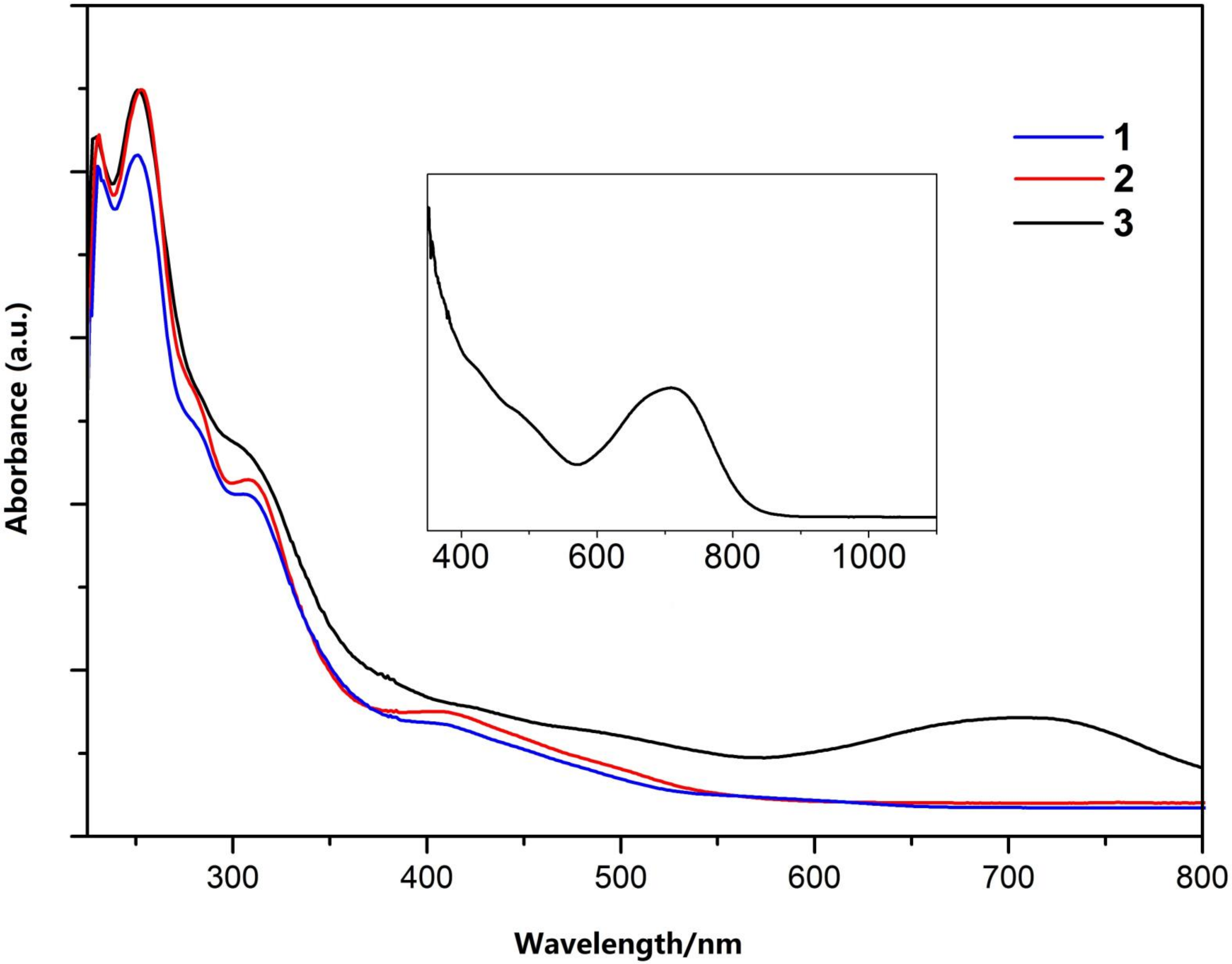
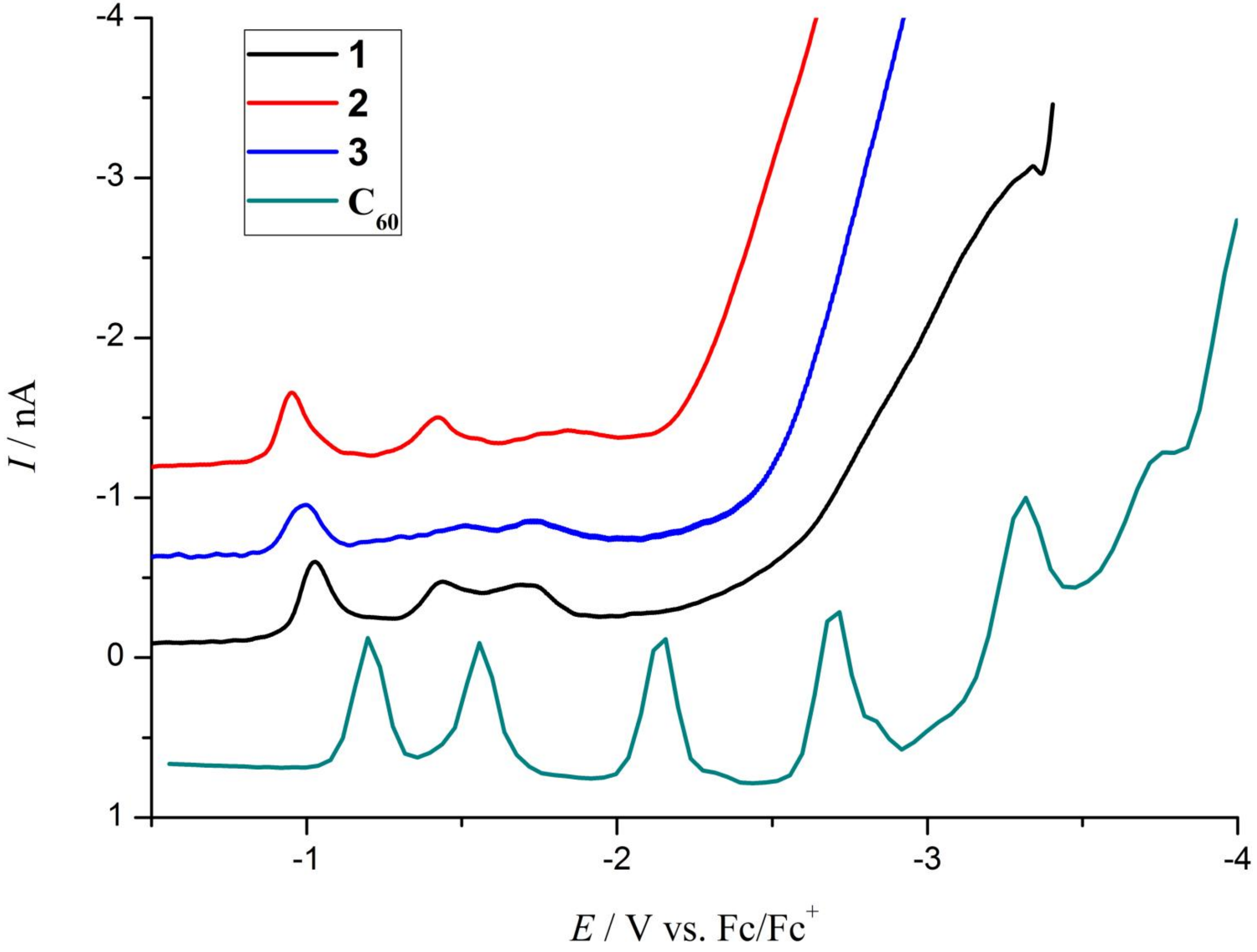
769



UV-Vis spectra in CH_2Cl_2 at r.t.

UV-Vis spectra in CH_2Cl_2 at r.t.

Compound	**Concentration mol/L**	**Wavelength nm**	ε_m
1	6.0×10^{-6}	250	2.2×10^{5}
		304	1.0×10^{5}
2	5.9×10^{-6}	252	2.0×10^{5}
		307	9.2×10^{4}
3	0.47×10^{-3}	709	7.3×10^{3}
	4.7×10^{-6}	251	1.6×10^{5}
		303	7.6×10^{4}
		709	1.5×10^{4}
	4.7×10^{-7}	249	2.5×10^{5}
		307	1.1×10^{5}
		709	2.4×10^{4}



Conditions for DPV measurements: toluene solution containing 0.05 mol/L tetrahexylammonium bis (trifluoromethylsulfonyl) imide (THA-Tf_2N) as supporting electrolyte, ferrocene (Fc) as an internal standard, platinum microelectrode (diameter 25 μm) as the working electrode, a platinum wire and a Ag wire as the counter and quasi-reference electrodes, respectively. Scan rate: 20 mVs^{-1}