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Supporting Information

Formyl azido substituted nitro hexaazaisowurtzitane – synthesis, characterization and energetic properties

Kai Dong,Yuan Wang, Xu-Bin Gong, Jing Zhang, Cheng-Hui Sun*[a], and Si-Ping Pang*[a,b]

School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China

State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology Beijing 100081, P.R. China

Detailed computational information

1. Optimized structure of compound 6

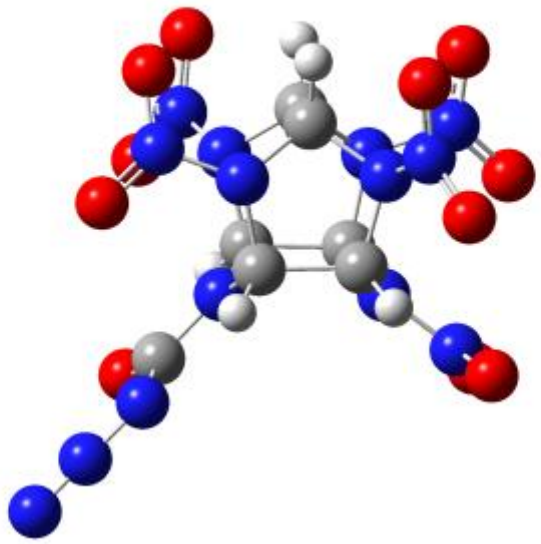


Table S1. Cartesian coordinates of the optimized structure of **6**

	X	Y	Z
O	2.45796300	-2.03220700	2.45686000
N	2.35116100	-0.82657200	2.31958900
O	2.83306200	0.04998400	3.01305900
N	1.63261700	-0.38580300	1.14765500
C	0.98416700	0.91433600	1.27141700
C	0.62548500	-1.33838200	0.61725500
N	-0.35096500	0.49345700	0.49345700
H	1.47414500	1.52885800	2.01935600
C	0.97511100	1.63657300	-0.15022400
N	0.73634500	-1.46135100	-0.81044100
C	-0.78230800	-0.68885300	0.95056600
H	0.77128800	-2.31265100	1.07569100
N	-1.28275000	1.45581300	2.09292200
N	-0.39671100	1.73985800	-0.62379500
N	1.55555900	0.81202900	-1.21639500
H	1.44859700	2.61117700	-0.09686600
C	0.61070500	-0.25129700	-1.59269700
N	-1.48935000	-0.36775700	-0.27228200
H	-1.40485700	-1.33628000	1.56128900
O	-0.83368300	2.57031100	2.33035300
O	-2.44068200	1.07458200	2.19234400

N	-0.69155100	2.90870000	-1.41424600
C	-0.76770100	0.43850800	-1.22692600
N	2.92915300	0.56619300	-1.20972900
H	0.69948400	-0.50929000	-2.64444600
C	-2.80364600	-0.71955000	-0.56090200
O	-0.03264100	3.90254100	-1.16670900
O	-1.61615700	2.80139200	-2.19951200
H	-1.40487600	0.60432500	-2.09270500
O	3.60247700	1.32661700	-0.52553700
O	3.31554100	-0.35353400	-1.91572000
O	-3.37437100	-0.38317600	-1.57669300
N	-3.34583100	-1.54500400	0.45537600
N	-4.54078200	-1.85737400	0.26686700
N	-5.61406400	-2.20530000	0.20726500
N	1.32567100	-2.62033900	-1.37704600
O	1.61256300	-3.51172100	-0.59430700
O	1.43040900	-2.62978900	-2.59041700

2. Optimized structure of compound 7

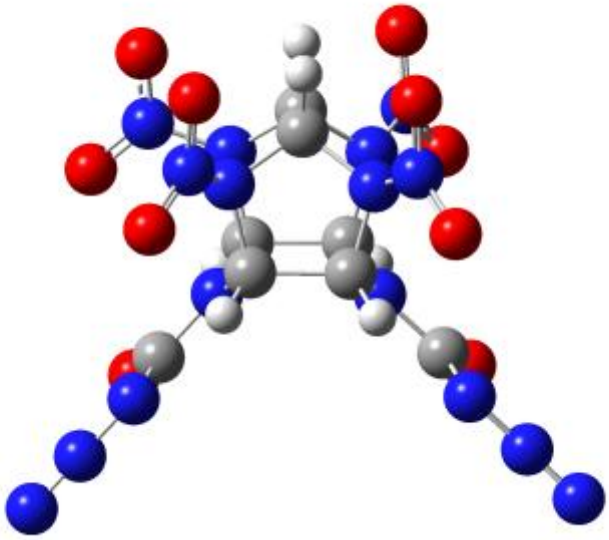


Table S2. Cartesian coordinates of the optimized structure of 7

	X	Y	Z
O	2.67101100	-2.72069500	-0.78383800
O	3.16333300	-0.85341600	-1.83712700
O	2.10302300	2.29370500	-2.13613600
N	1.03946500	-1.35736100	-1.41979100
N	2.39578500	-1.65737200	-1.32923800
C	1.87442800	2.01660600	-0.97849000

N	1.09934500	0.93441000	-0.58386000
N	2.32059500	2.75587600	0.14993600
C	0.59110800	0.03300600	-1.59689200
C	0.76184400	0.59332800	0.77731000
N	3.03889200	3.73534300	-0.13975600
C	-0.97247800	-0.14369300	-1.44075500
H	0.88271100	0.42162200	-2.56990700
N	1.28464900	-0.74287400	1.12464500
C	-0.81372600	0.44319000	0.92757100
H	1.17591800	1.33208900	1.45775600
N	3.6985390	4.64250300	-0.27833900
C	0.08251300	-2.08668700	-0.58319600
N	-1.16647300	-1.58166400	-1.13370700
N	-1.45059200	0.67476500	-0.34994200
H	-1.52609400	0.11448700	-2.34022100
N	2.07191200	-0.85162400	2.31118100
C	0.19148500	-1.70372700	0.96225200
N	-0.99568900	-0.95136300	1.36476000
H	-1.22660700	1.11536900	1.67432100
H	0.16914000	-3.15922800	-0.72245800
N	-1.75742000	-2.37948700	-2.16441200
C	-2.56959400	1.46970200	-0.55641100
O	2.15783500	-1.96518000	2.79906100
O	2.62997500	0.17036200	2.67948900
H	0.33738600	-2.58250700	1.58278300
N	-1.51430500	-1.18309800	2.66456800
O	-1.53849300	-3.57904700	-2.10881400
O	-2.47919000	-1.79207800	-2.95212200
O	-3.12834300	1.57783300	-1.62738700
N	-2.93032700	2.15413800	0.63454800
O	-1.31660700	-2.29288300	3.13370500
O	-2.16319700	-0.27159000	3.15760500
N	-3.93855100	2.88136100	0.51432500
N	-4.83592800	3.56812400	0.52849900

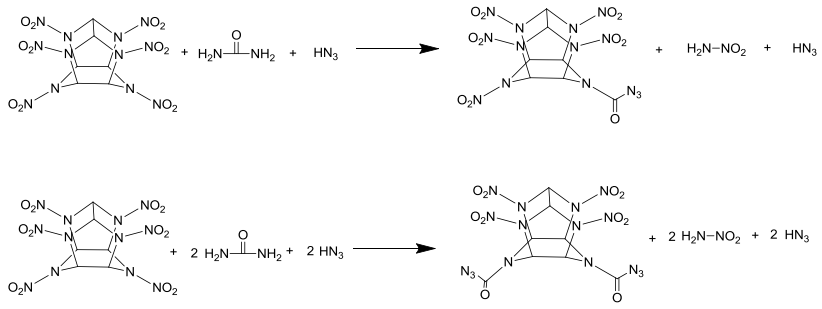
3. Detonation performances

Heat of formation

Isodesmic reaction, in which numbers of electron pairs and chemical bond types are conserved, has been employed very successfully to give heats of formation more accurate than semi-empirical calculation.

For the folowing isodesmic reactions, heat of formation (ΔH298K) can be calculated according to the following equation:

$\Delta H_{298K} = \sum \Delta H_{f,P} - \sum \Delta H_{f,R}$



Where $\Delta H_{f,R}$ and $\Delta H_{f,P}$ are the heat of formation for reactants and products at 298.15K, respectively. Meanwhile, ΔH_{298K} can be also obtained from the following expression:

$\Delta H_{298K} = \Delta E_{298K} - \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta(nRT)$

Where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies of the products and the reactants; ΔH_T is thermal correction from 0K to 298.15K. Consequently, the heat of formation can be worked out by using ΔH_{298K} and heat of formation of other reactants and products. The data in needed can be obtained from literatures and handbooks.

Table S3. Calculated total energy (E_0), zero-point energy (ZPE) and thermal correction (H_T)

	E_0/a.u.	ZPE/(kJ/mol)	H_T/(kJ/mol)
6	-1863.64812571	610.8698	68.06083
7	-1936.10841755	639.2042	73.61901
2	-2014.69841499	788.4612	81.12532
3	-2093.32821805	936.7468	88.66575

Detonation performances of the related compounds were calculated using Kamlet-Jacbos (K-J) equations as follows.

$$D=1.01（NM^{1/2}Q^{1/2}）^{1/2}(1+1.3\rho)$$

$$P=1.558\rho^2NM^{1/2}Q^{1/2}$$

where D represents detonation velocity ($km•s^{-1}$), P is detonation pressure (GPa); N, moles of detonation gases per gram of explosive; M, average molecular weight of these gases; Q, chemical energy of detonation ($kJ•g^{-1}$); ρ, density of explosive ($g•cm^{-3}$).

Table S4 shows the methods for calculating parameters of the explosive in CaHbOcNd form. All the nitrogen atoms are converted into N_2, the oxygen atoms are considered to form H_2O first and then CO_2 with carbon atoms. The remaining carbon atoms will exist in solid state. If there is any oxygen atom left, they will form O_2.

Table S4. Methods for parameters calculation in K-J equations

	C≥2a+b/2	2a+b/2>c≥b/2	b/2>c
N	(b+2c+2d)/4M[a]	(b+2c+2d)/4M’	(b+d)/2M’
M	4 M’/(b+2c+2d)	(56d+88c-8b)/(b+2c+2d)	(2b+28d+32c)/(b+d)
$Q*10^{-3}$	(28.9b+94.05a+0.239ΔH °f)/M’[b]	[28.9b+94.05(c/2−b/4)+0.239ΔH °f]/M’	(57.8c+0.23ΔH °f)/M’

[a] M’ is molecular weight of explosive. [b] $\Delta H°_f$ is heat of formation of explosive

Sensitivity

The impact sensitivity was tested on a type 12 tooling according to “up” and “down” method. A 5.0kg weight was dropped from a set height onto a 30mg sample placed on 150 grit garnet sandpaper. Each subsequent test was made at the next lower height if explosion occurred and at the next higher height if no explosion happened. 50 drops were made from different heights, and an explosion or non-explosion was recorded to determine the results. It is worth noting that in the early stage of testing the impact sensitivity, the experimental result (Compound **6** and **7**, both above 20J) just as presented in the lastest “New Trends in Research of Energetic Materials” (NTREM) conference in Czech, was much higher than the current values (Compound **6**, 6J; Compound **7**, 11J), which could be attributed to the malfunction of the sensitivity testing machine before.

Spectrometric Data

Compound 9

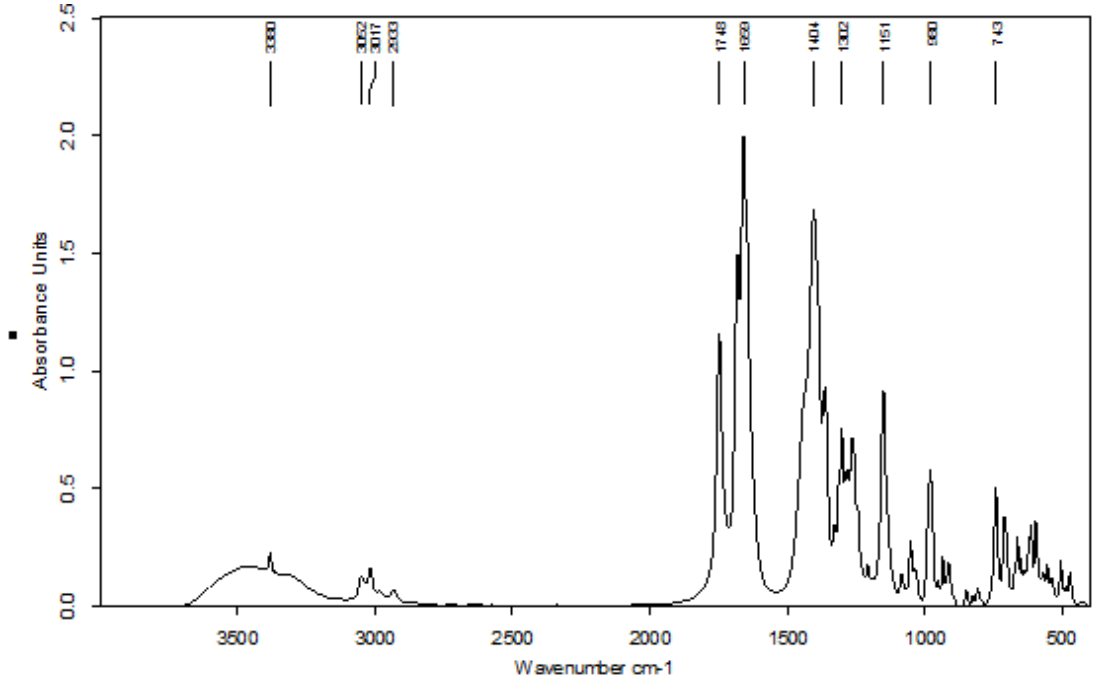


Figure S1. IR spectrum

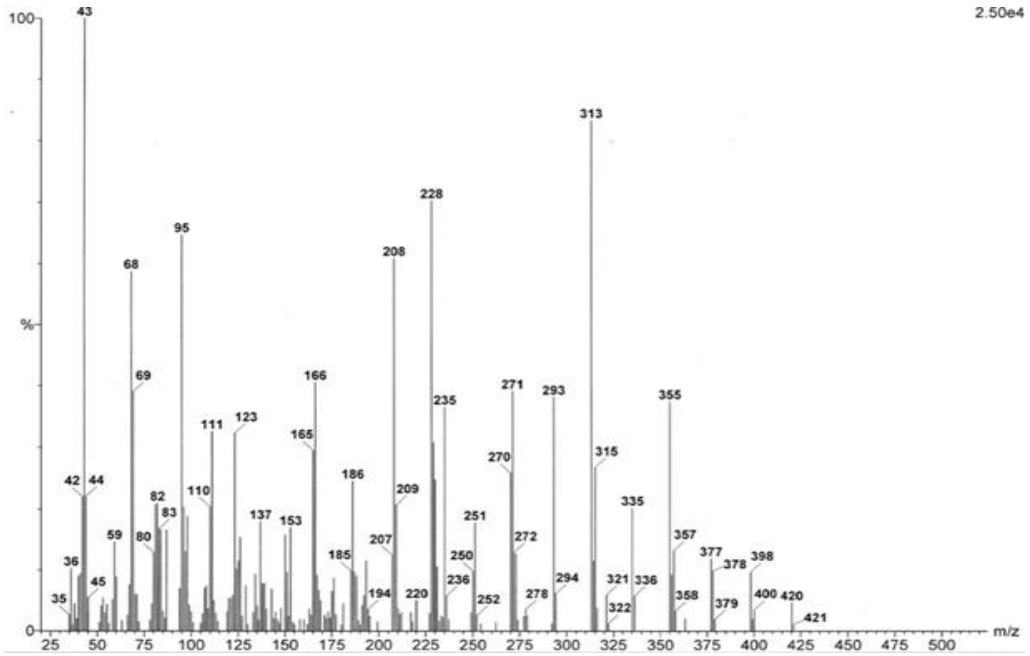


Figure S2. EI-MS spectrum

Compound 10

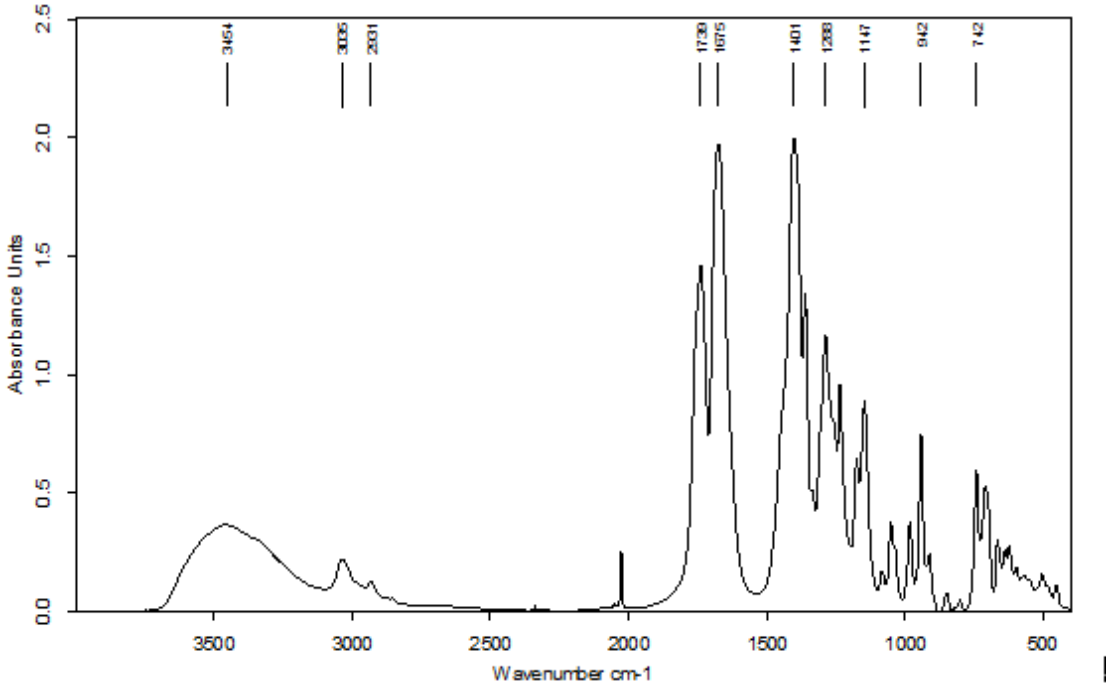


Figure S3. IR spectrum

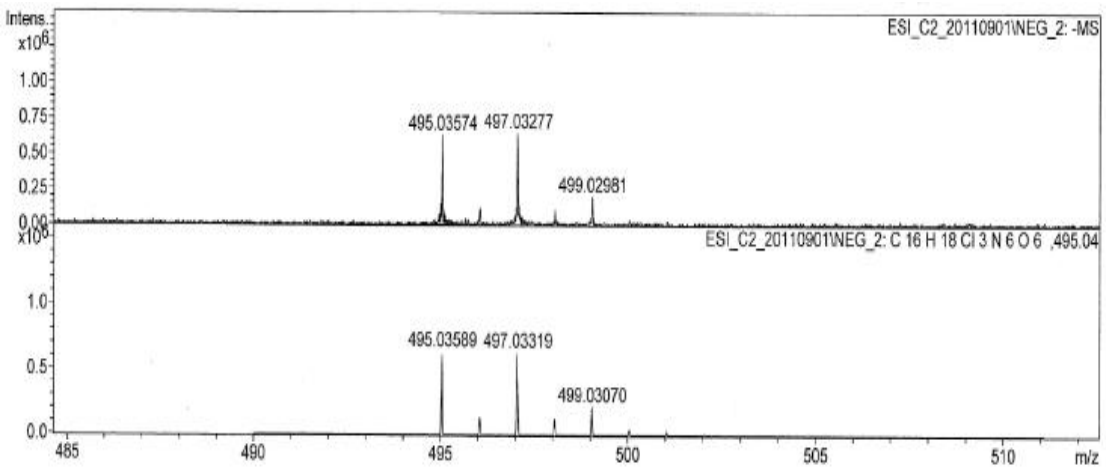


Figure S4. ESI-MS spectrum

Compound 6

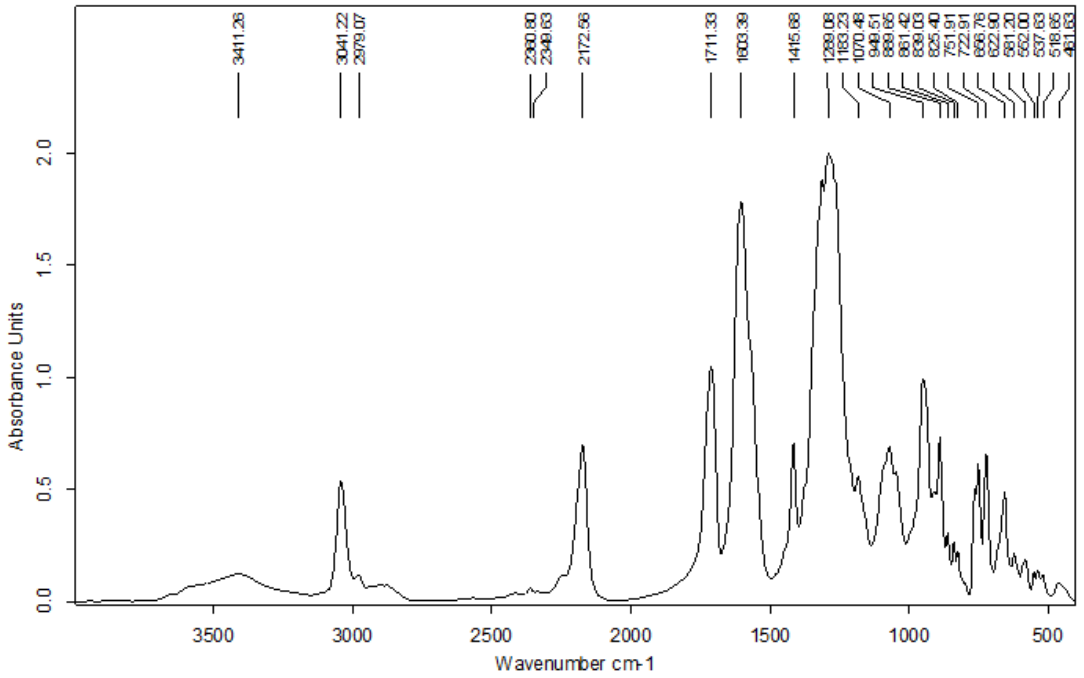


Figure S5. IR spectrum

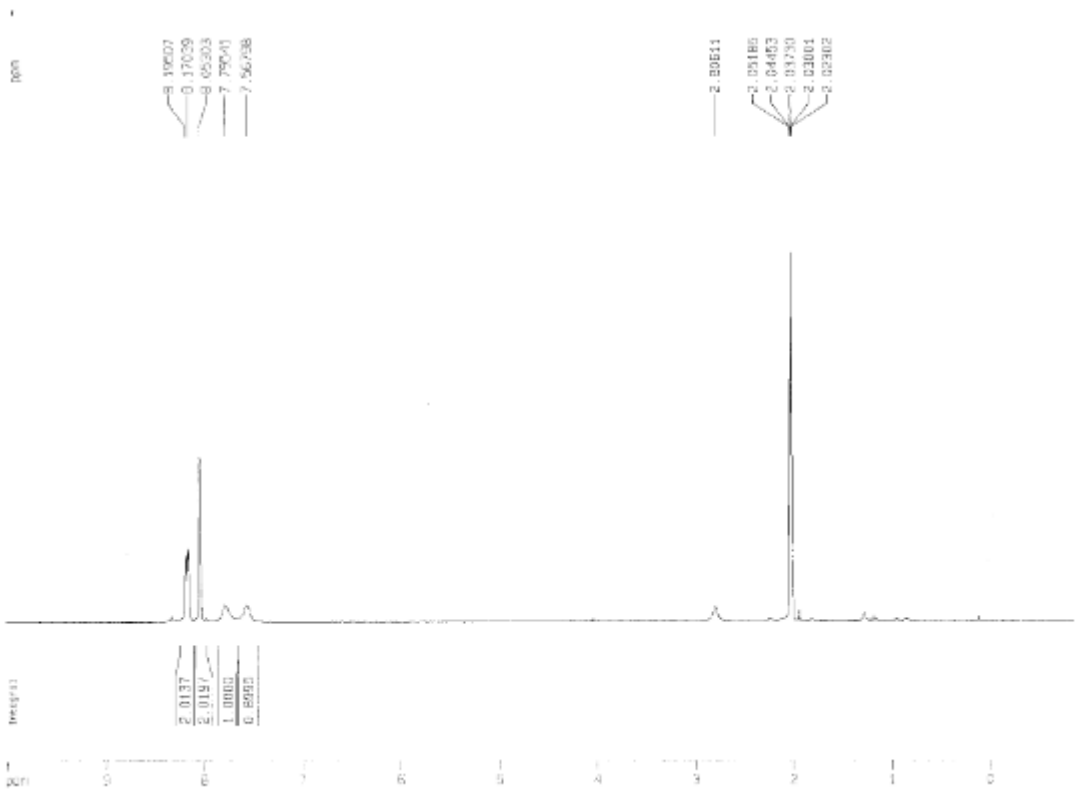


Figure S6. ^{1}H NMR spectrum

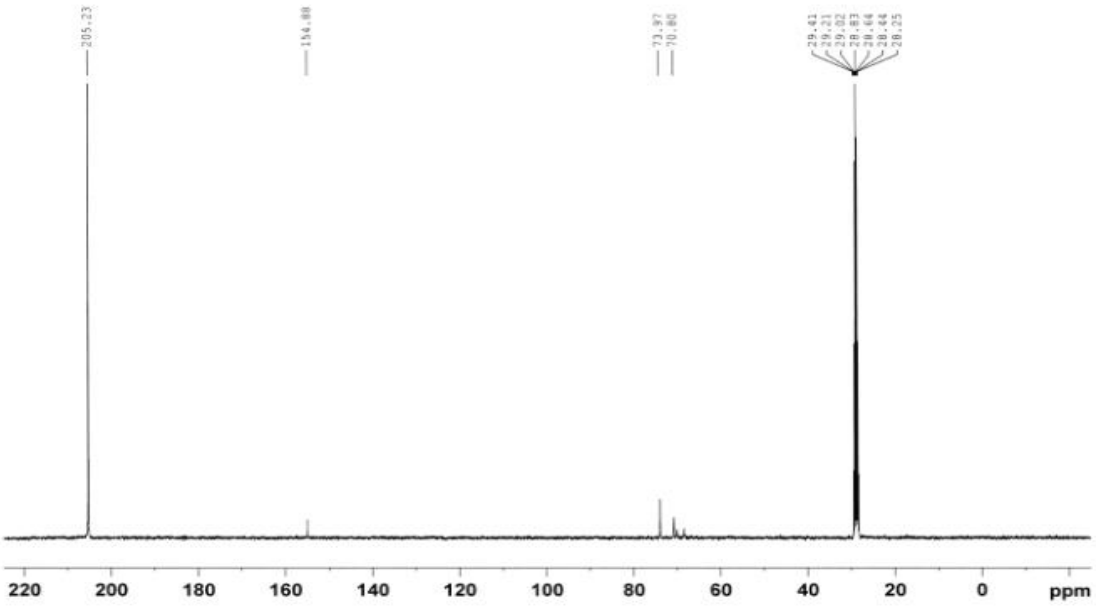


Figure S7. ^{13}C NMR spectrum

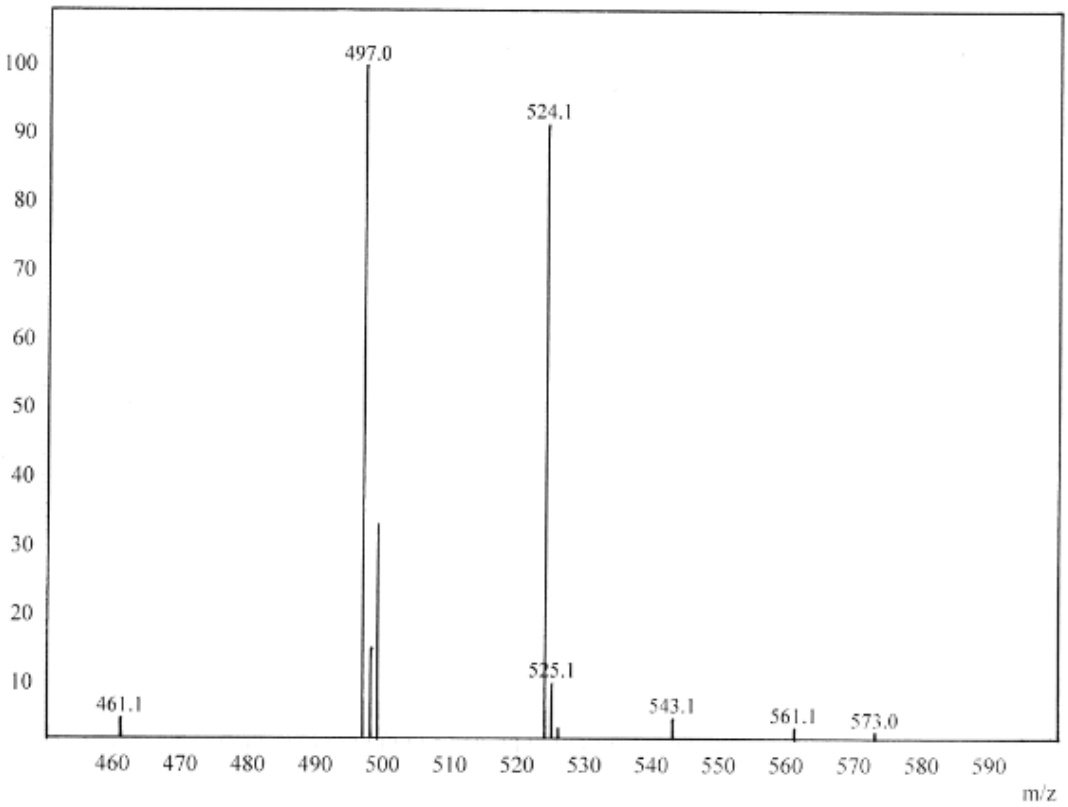


Figure S8. ESI-MS spectrum

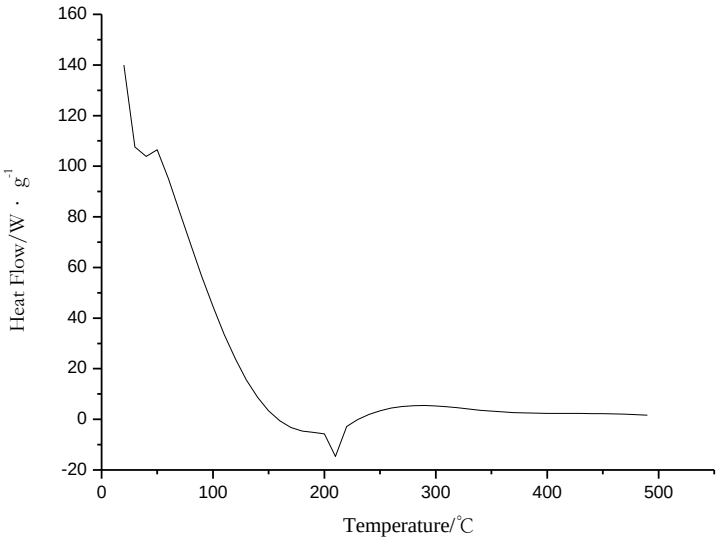


Figure S9. DSC curve

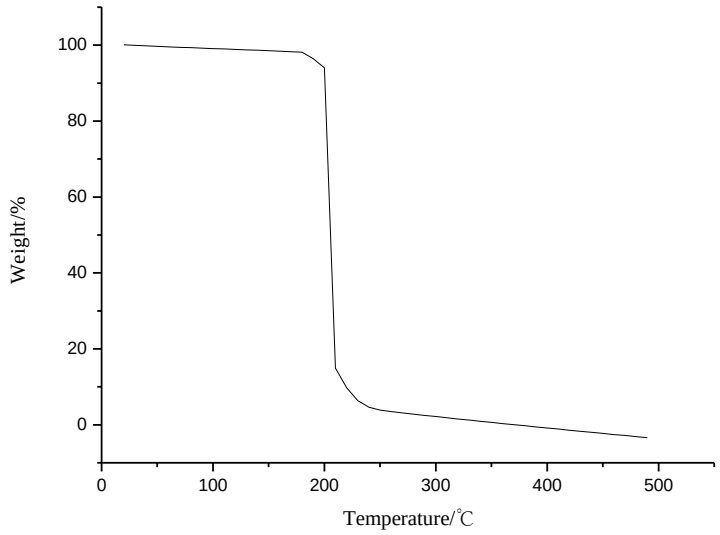


Figure S10. TGA curve

Compound 7

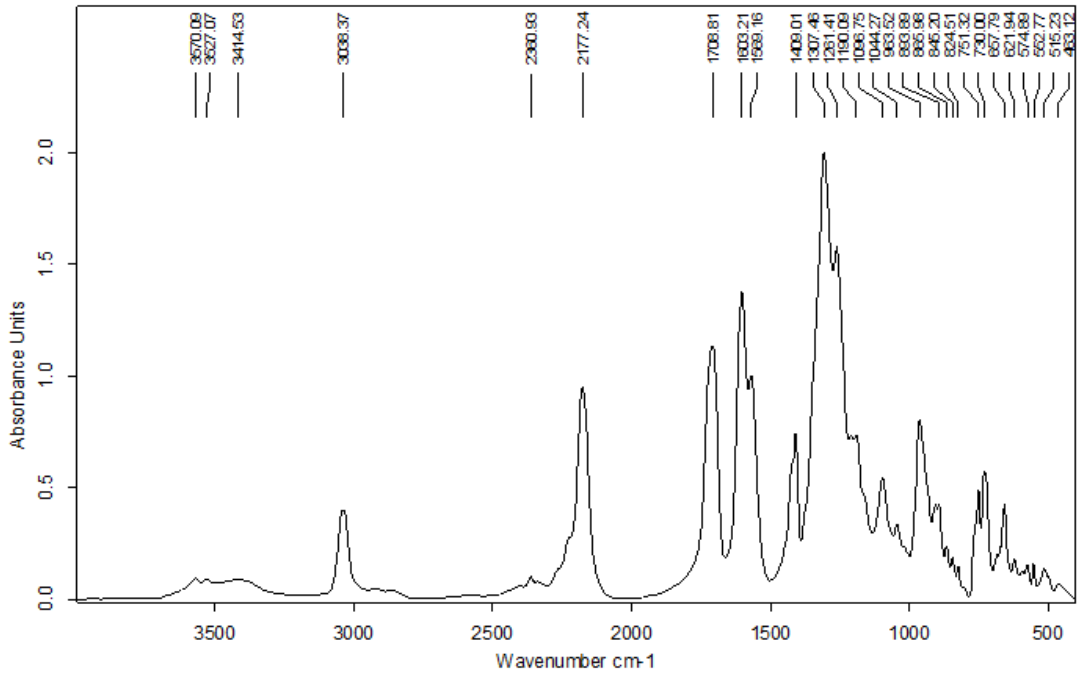


Figure S11. IR spectrum

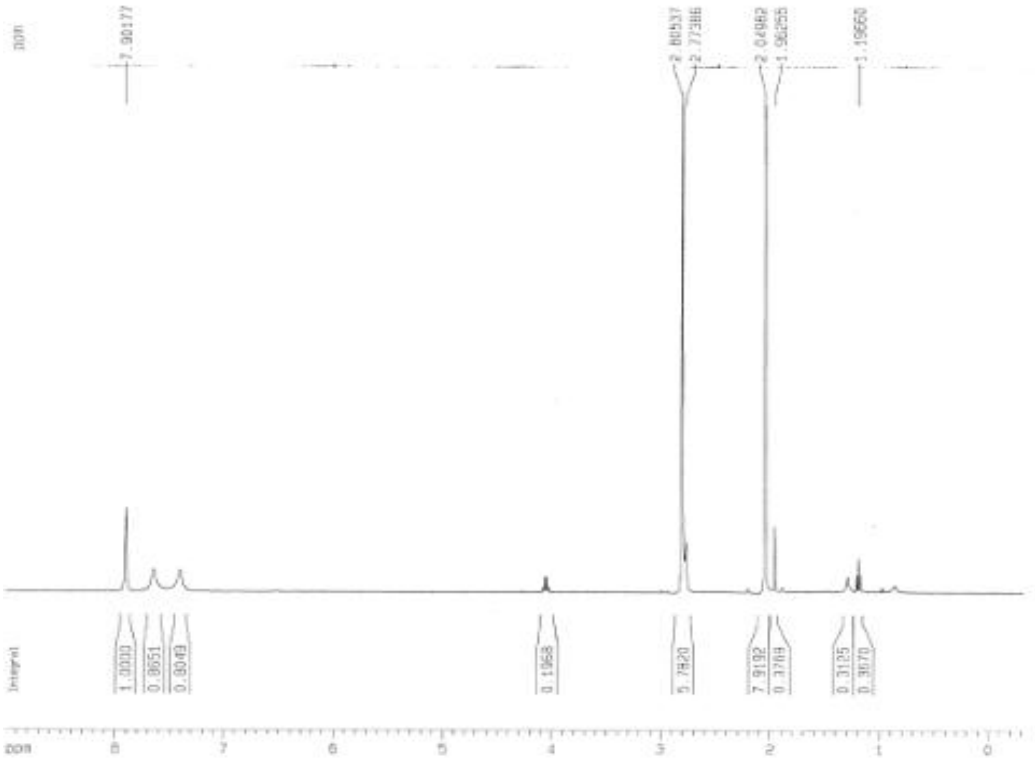


Figure S12. ^{1}H NMR spectrum

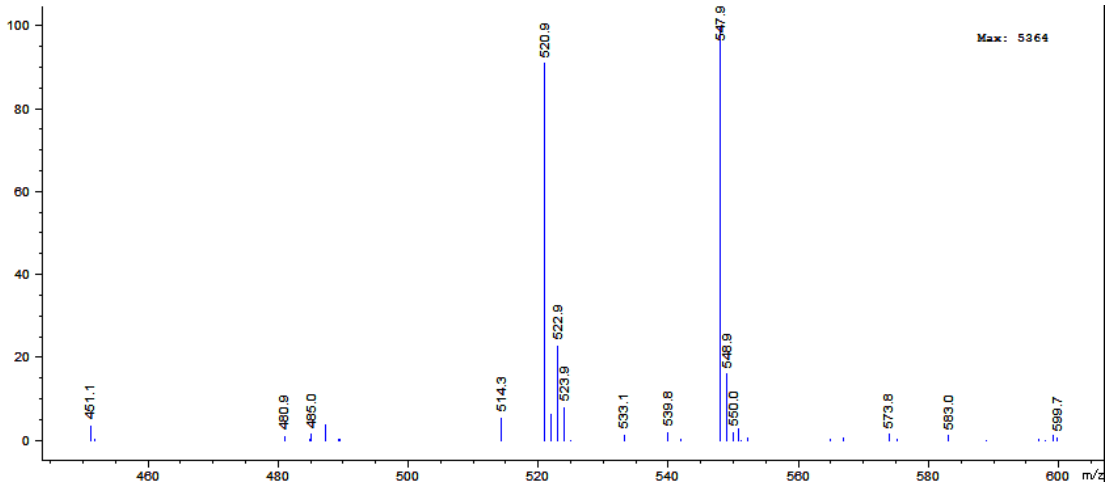


Figure S13. ESI-MS spectrum

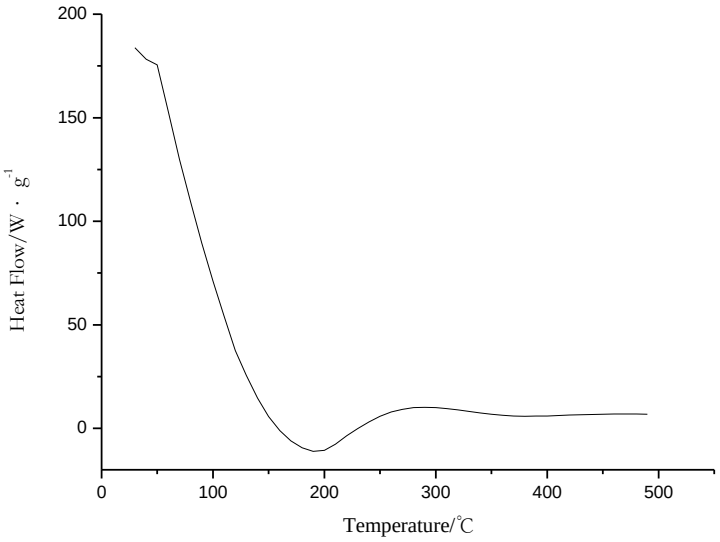


Figure S14. DSC curve

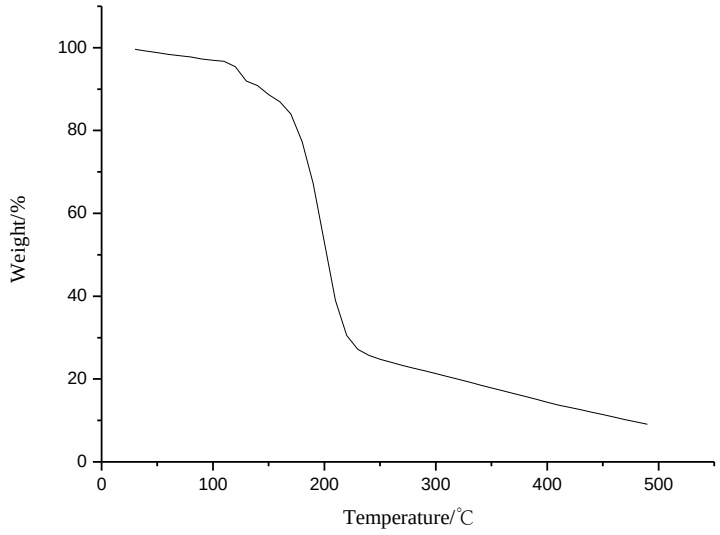


Figure S15. TGA curve

Compound 13

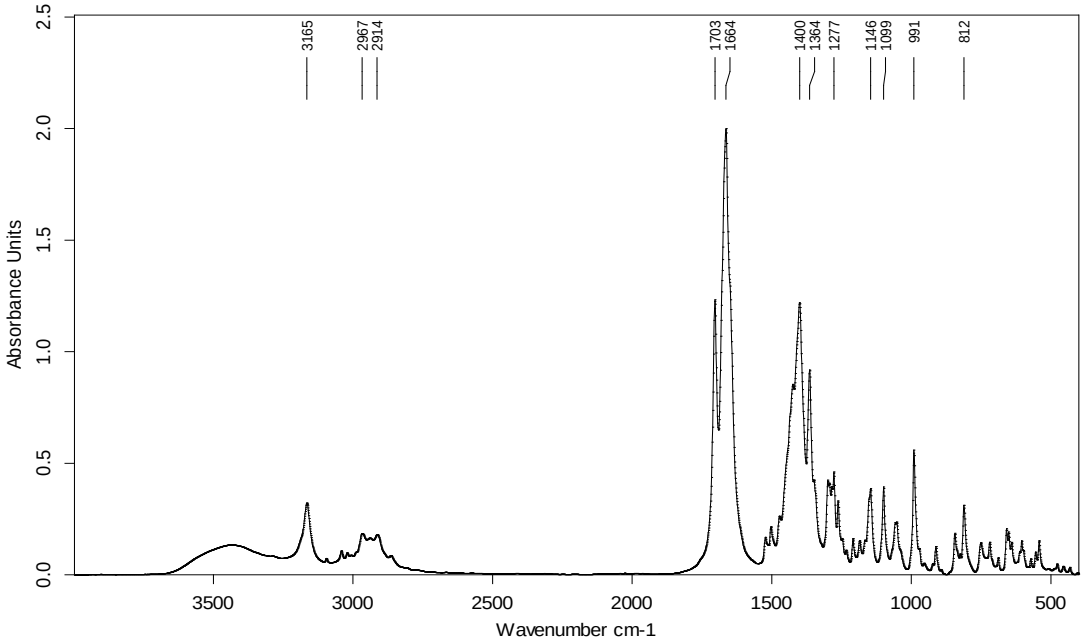


Figure S16. IR spectrum

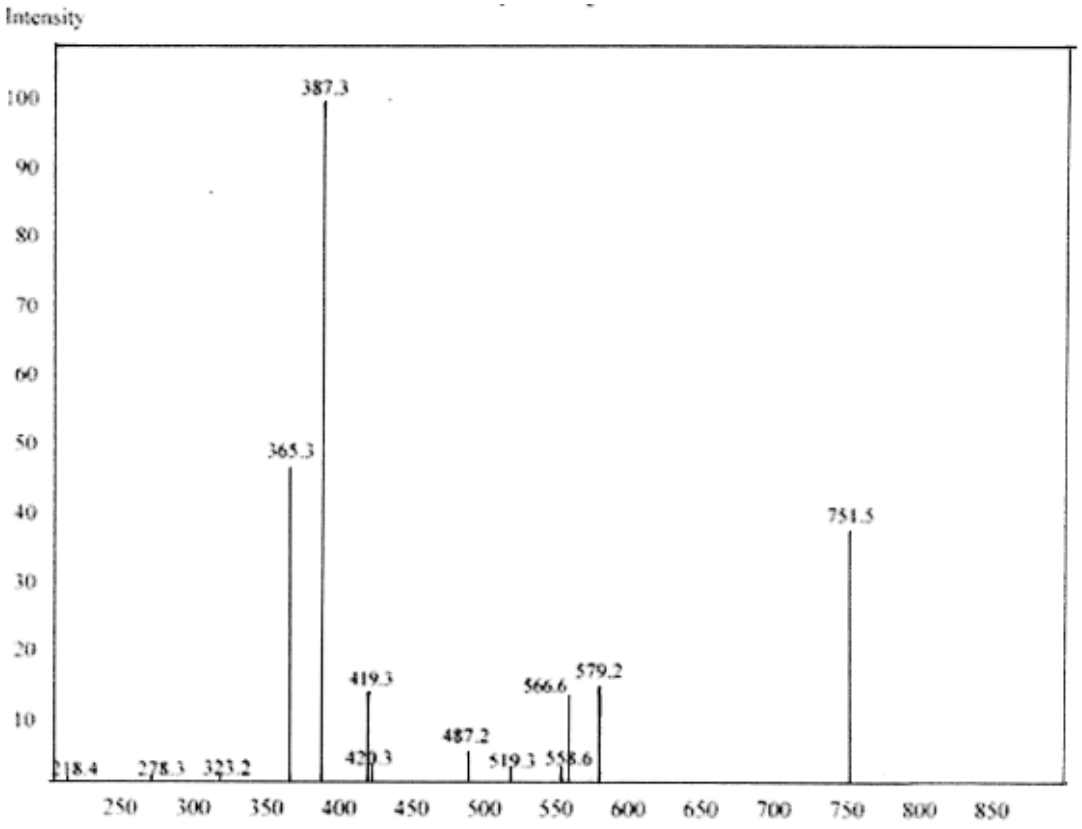


Figure S17. ESI-MS spectrum