Supplementary Material

Synthesis and DFT studies of novel aminoimidazodipyridines using 2-(3*H*-imidazo[4,5-*b*]pyrid-2-yl)acetonitrile as an efficient key precursor

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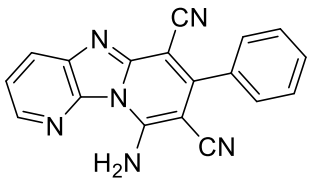
^{1}H and ^{13}C NMR spectra



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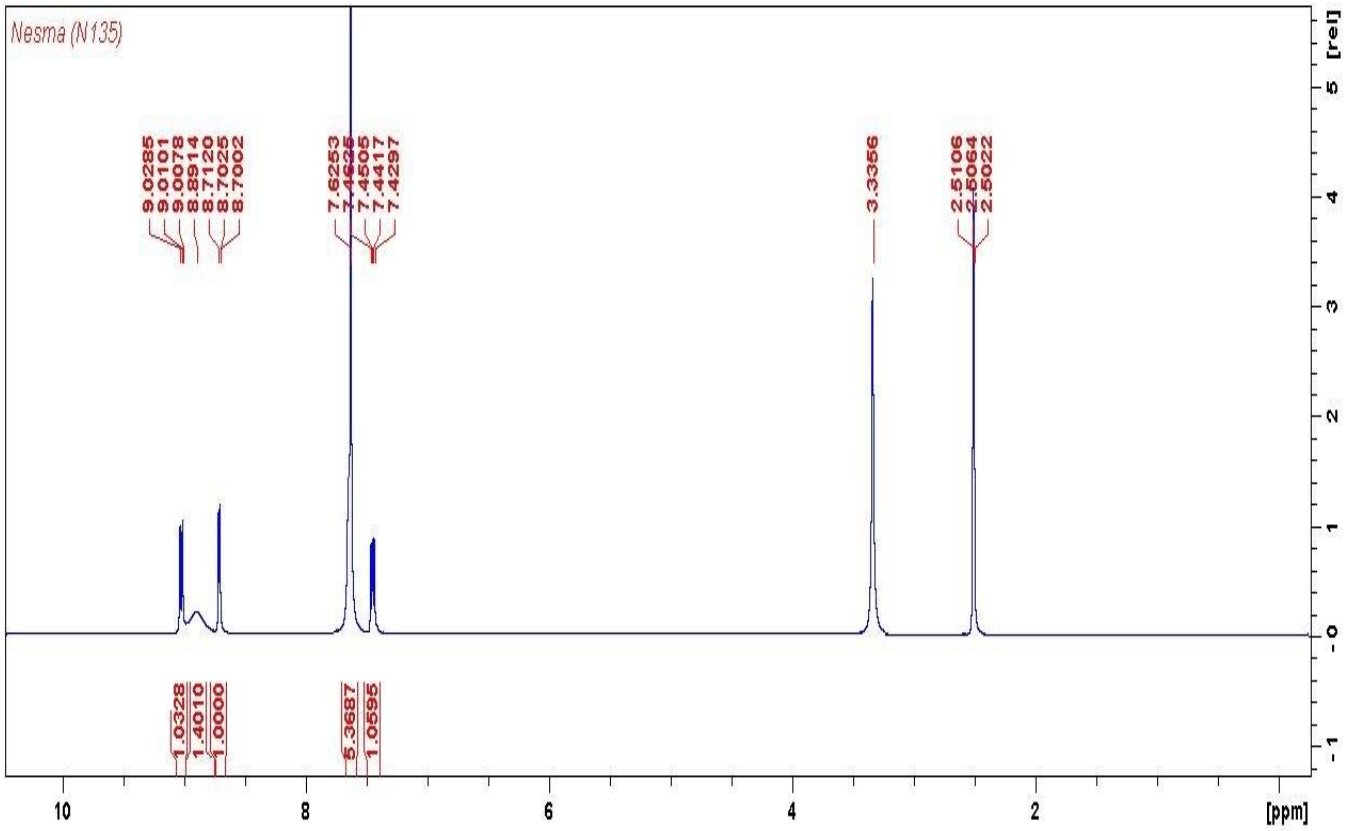

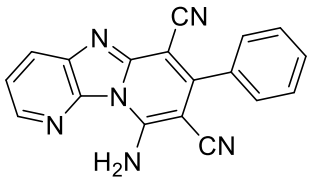
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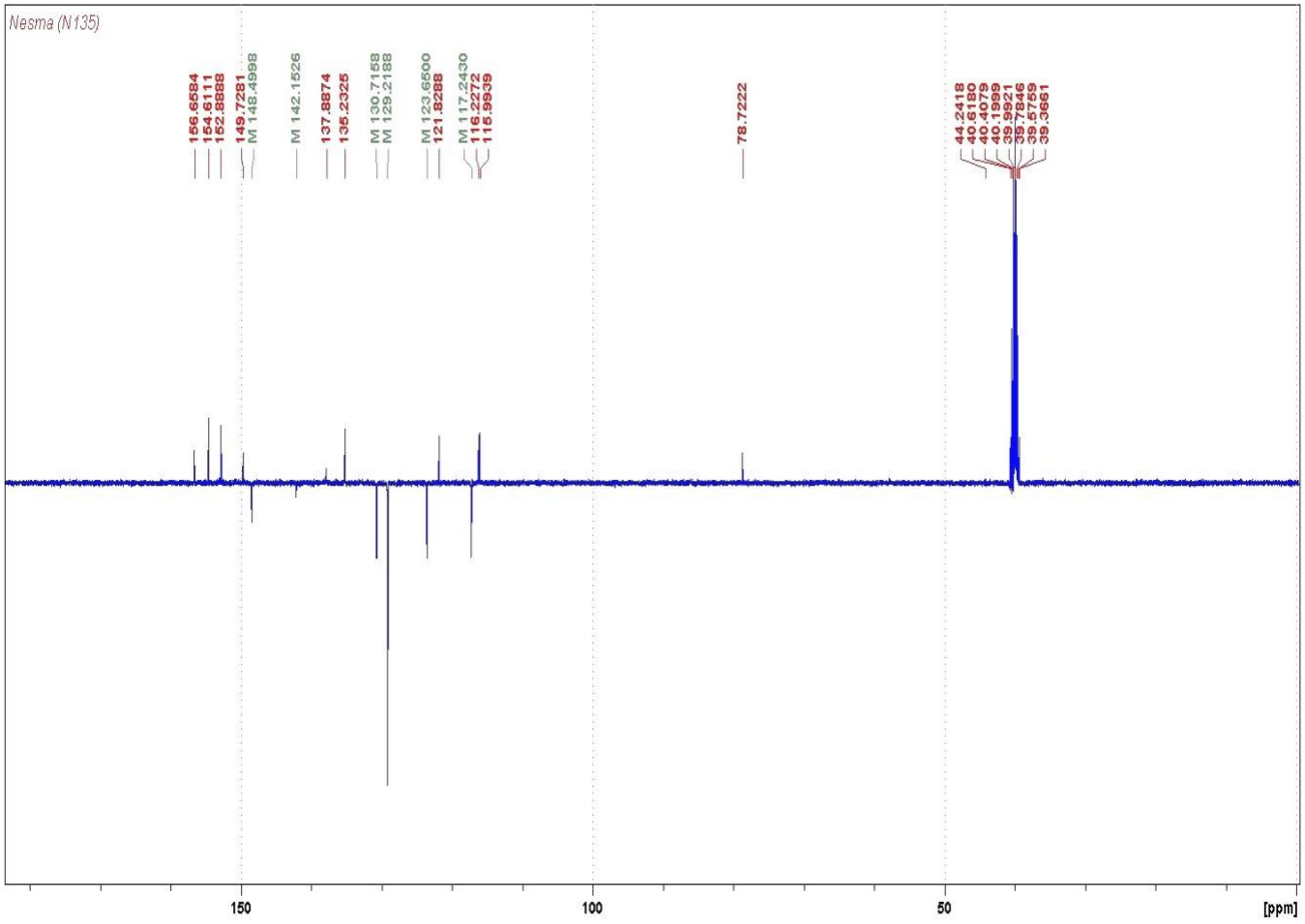
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M 129.2188
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M 117.2430
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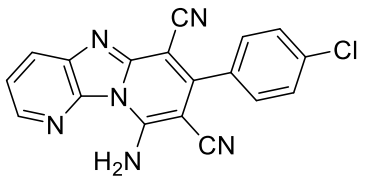
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Cl
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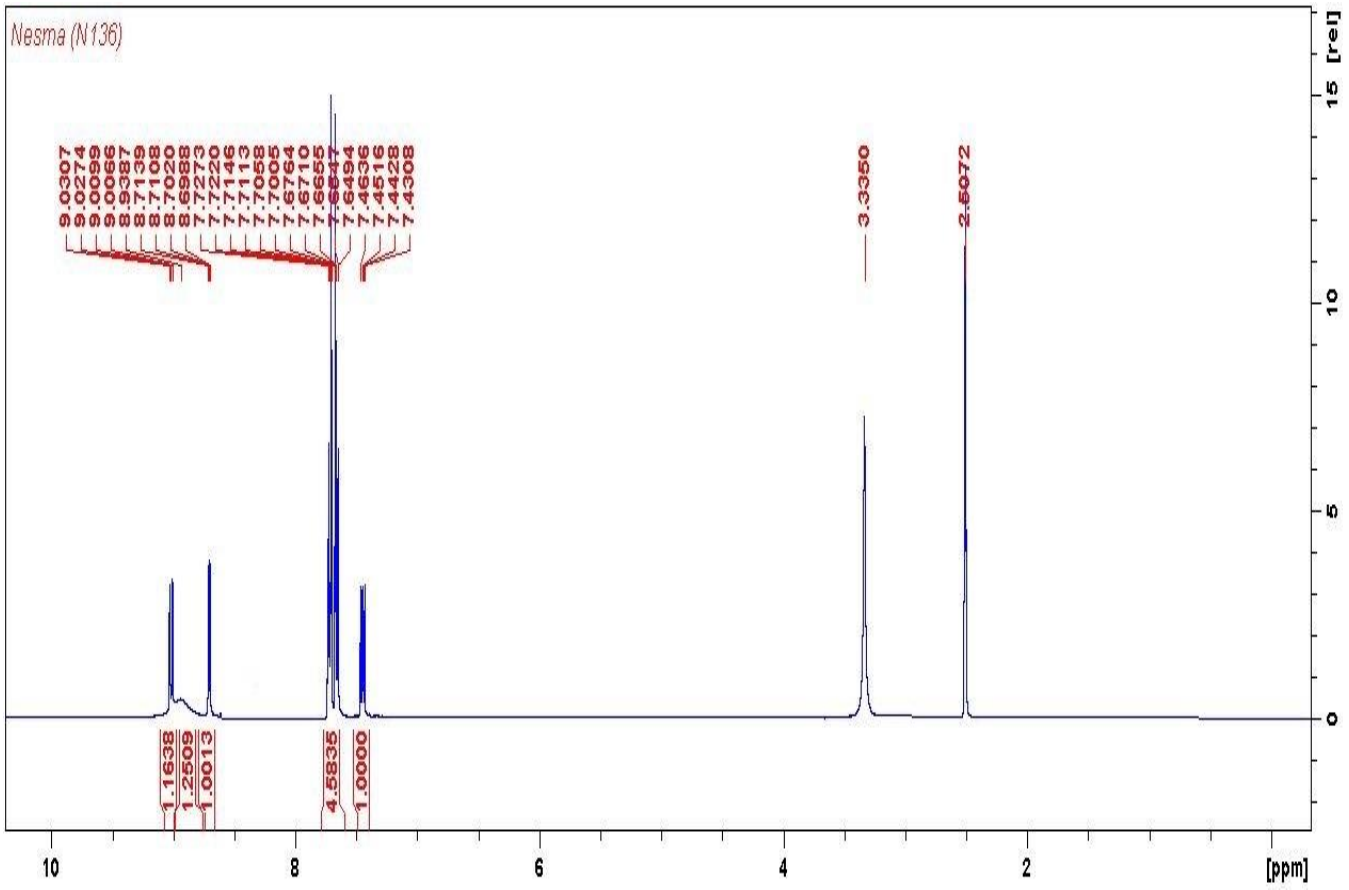
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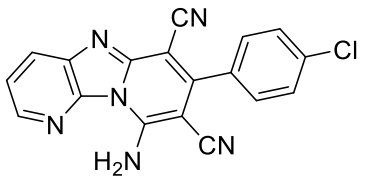
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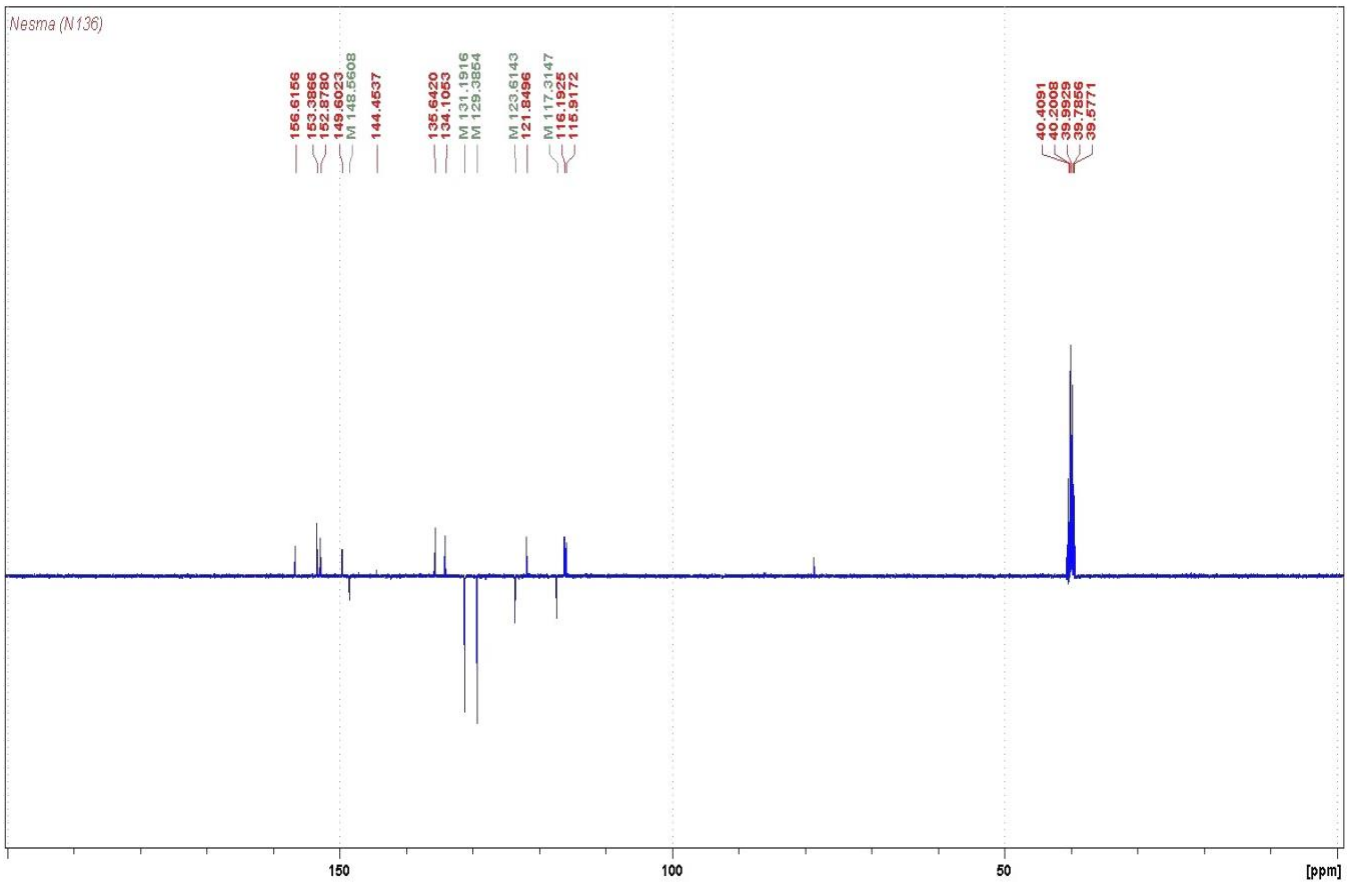
H_2N

12b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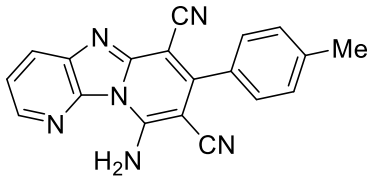
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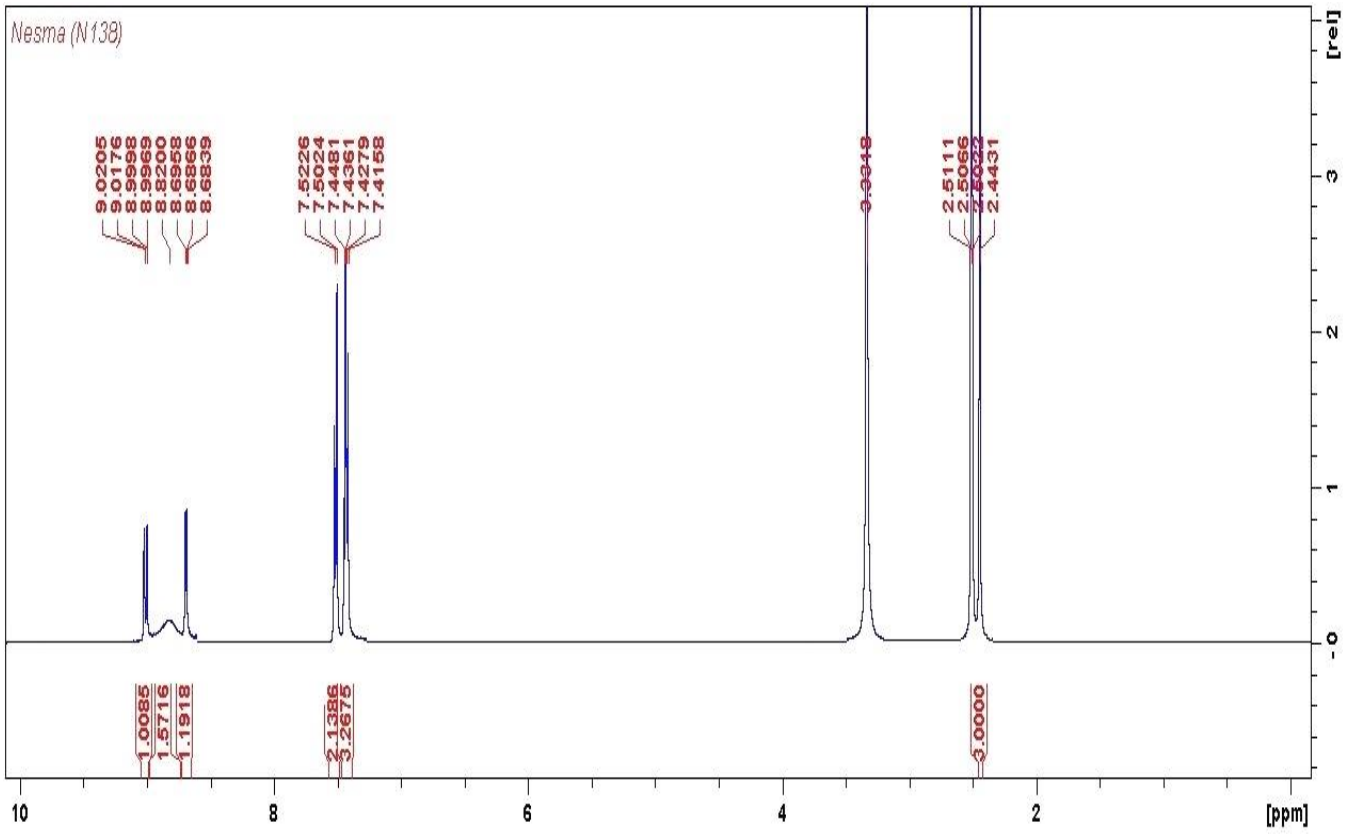
H_2N

12c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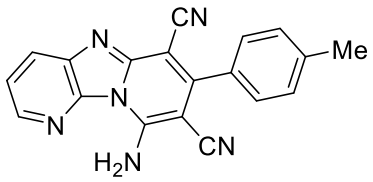
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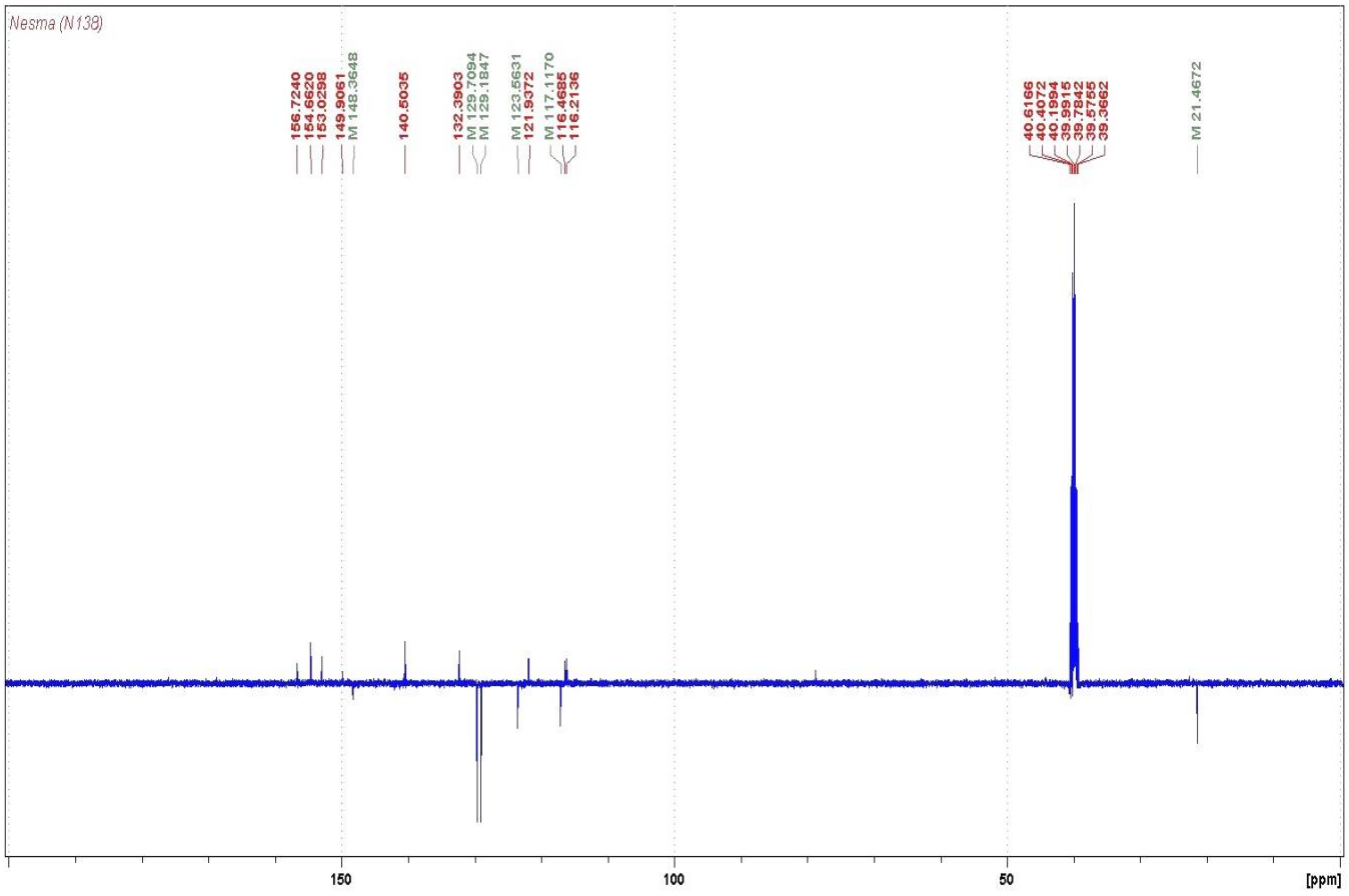
12c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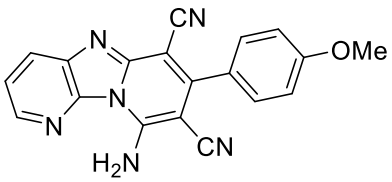
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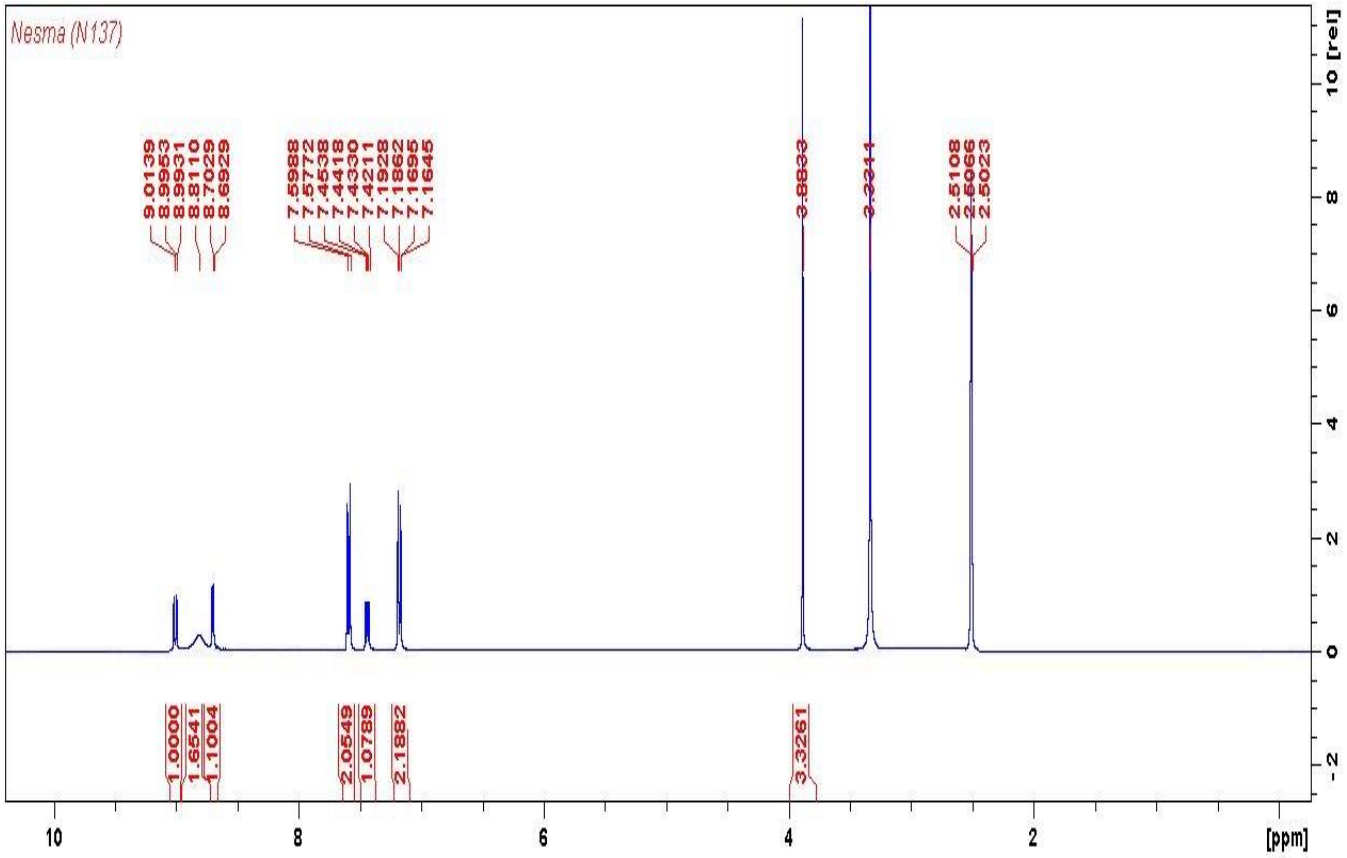
N
N
H2N
CN

12d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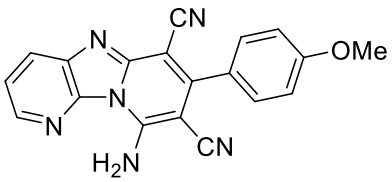
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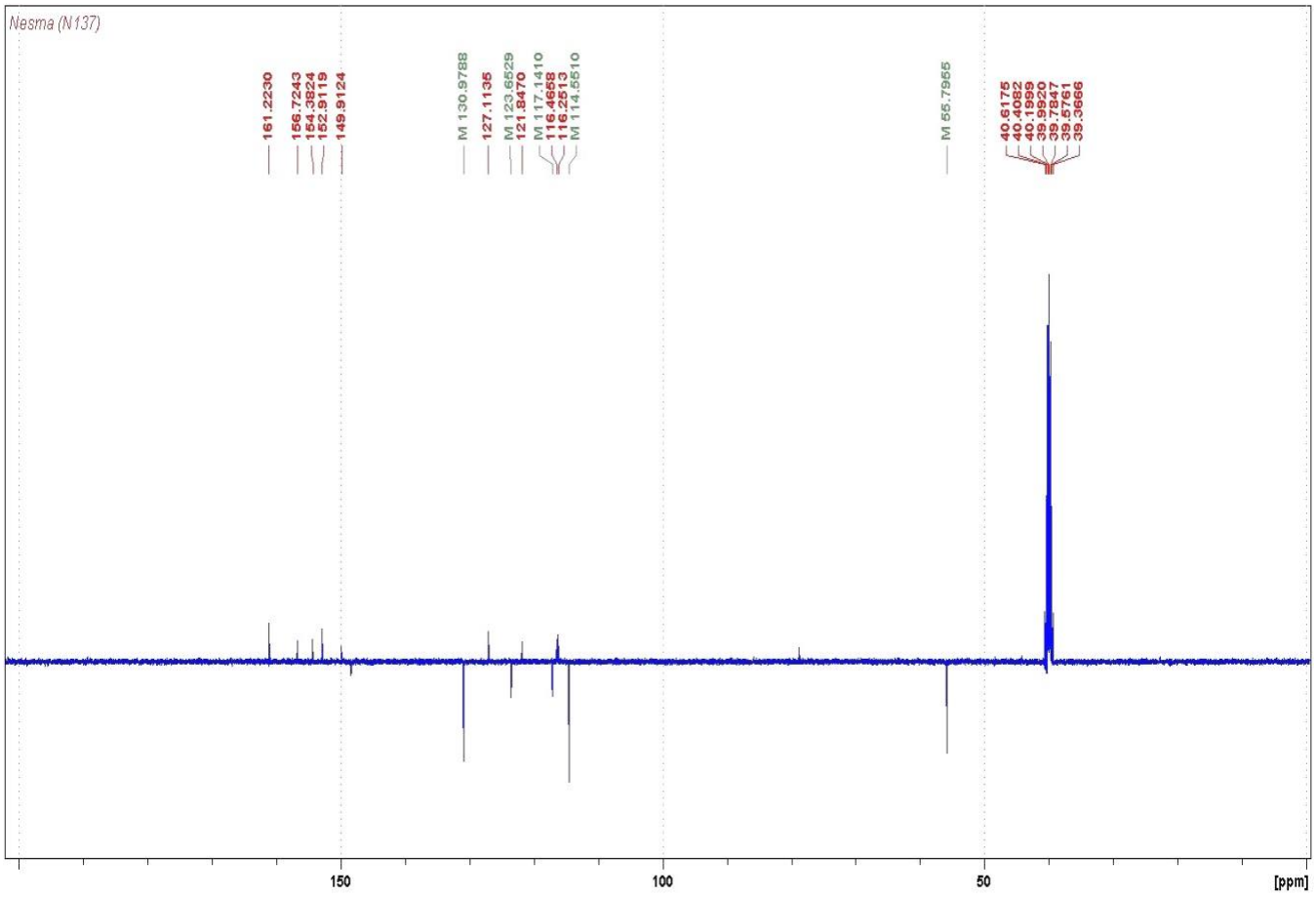
OMe
N
N
CN
H_2N

12d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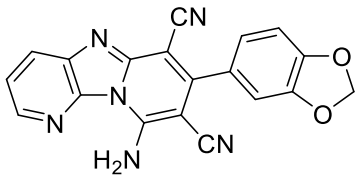
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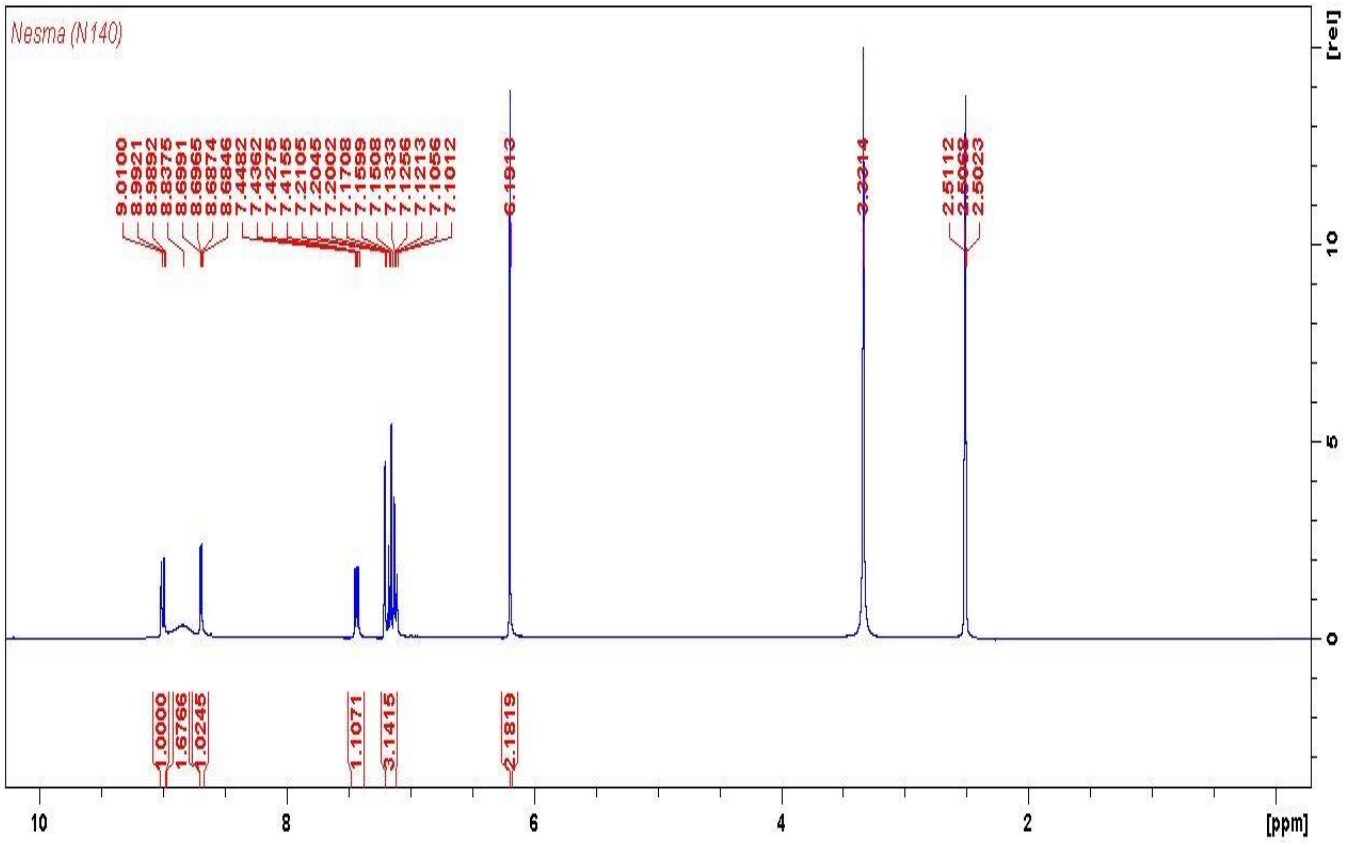
12e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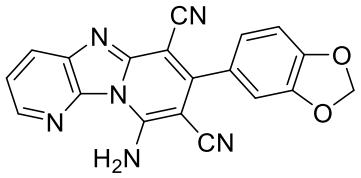
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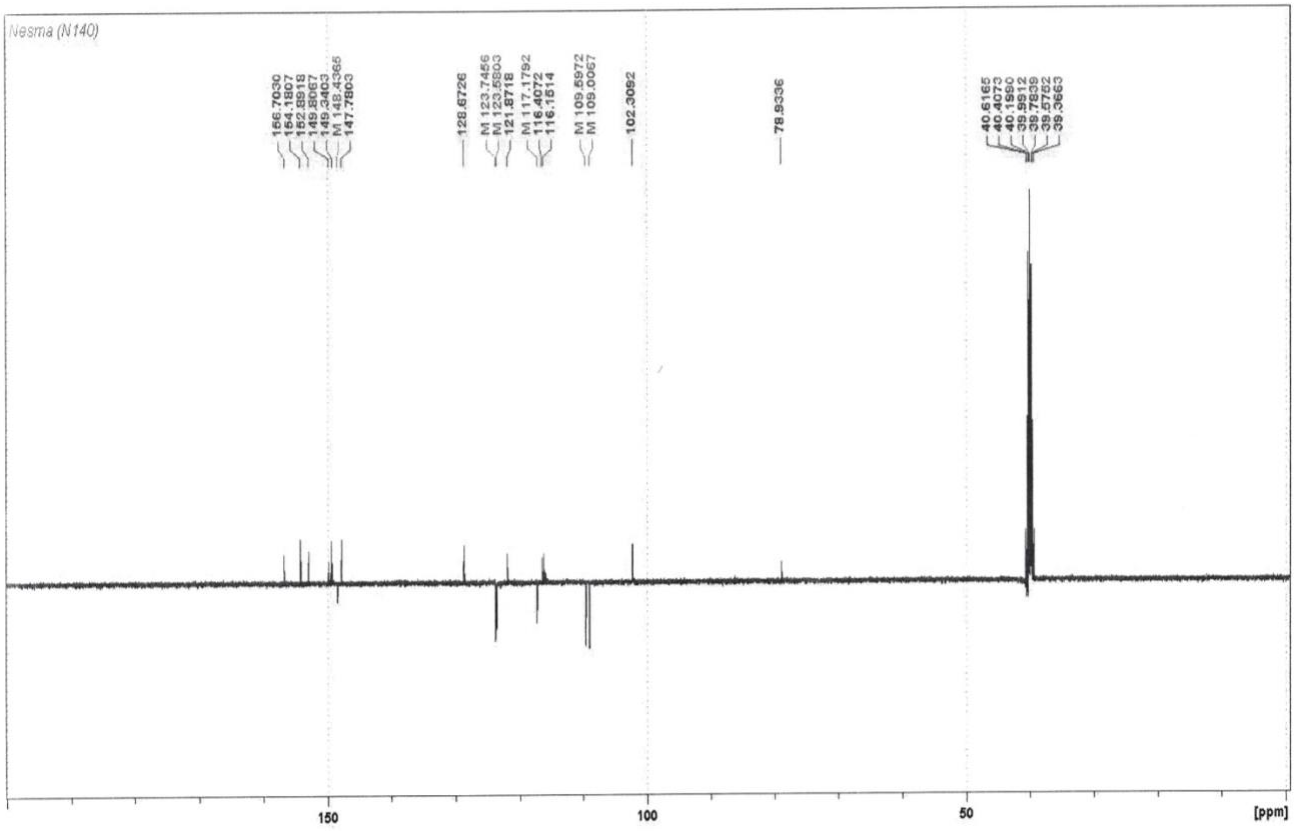
N
CN
H_2N

12e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M 123.7456
M 123.5803
121.8718
M 117.1792
116.4072
116.1514
M 109.5972
M 109.0067
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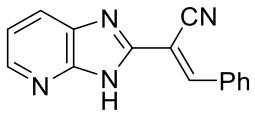
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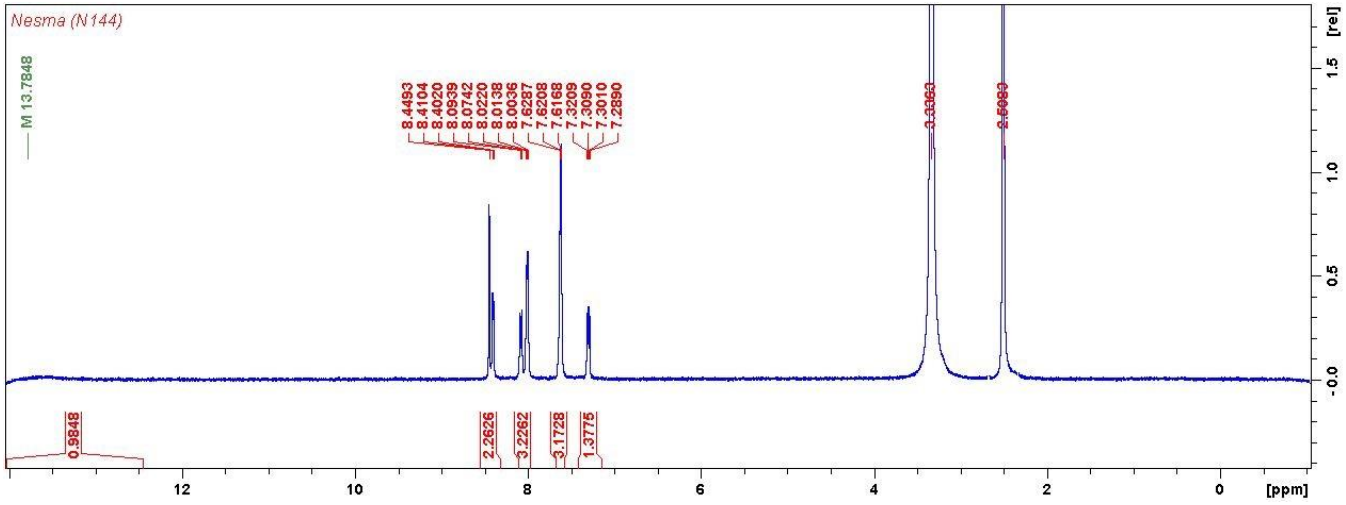
H
N
Ph

20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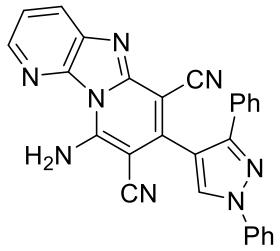
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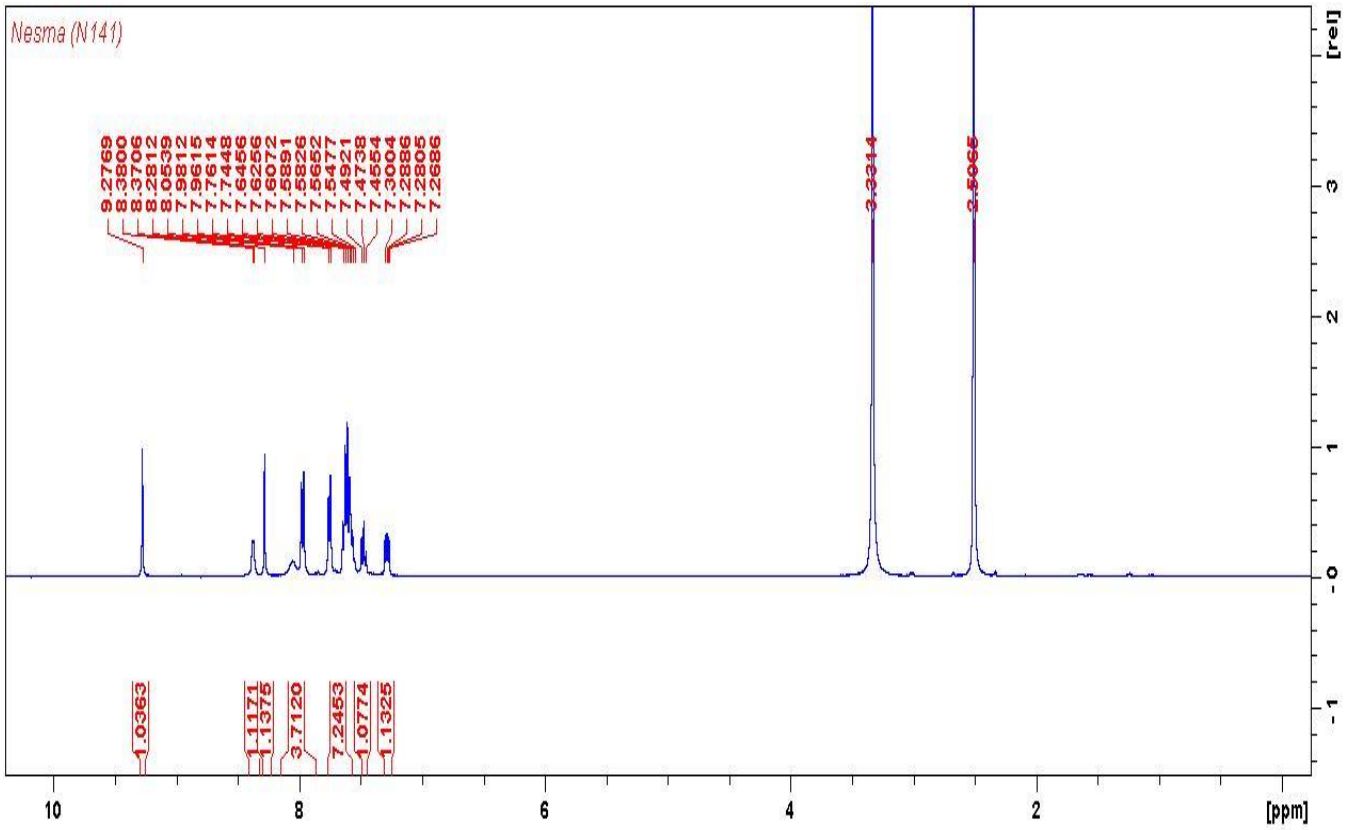
22a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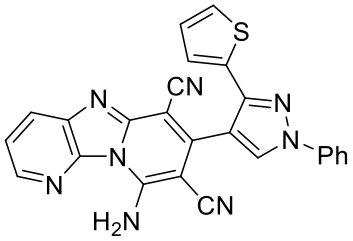
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Ph
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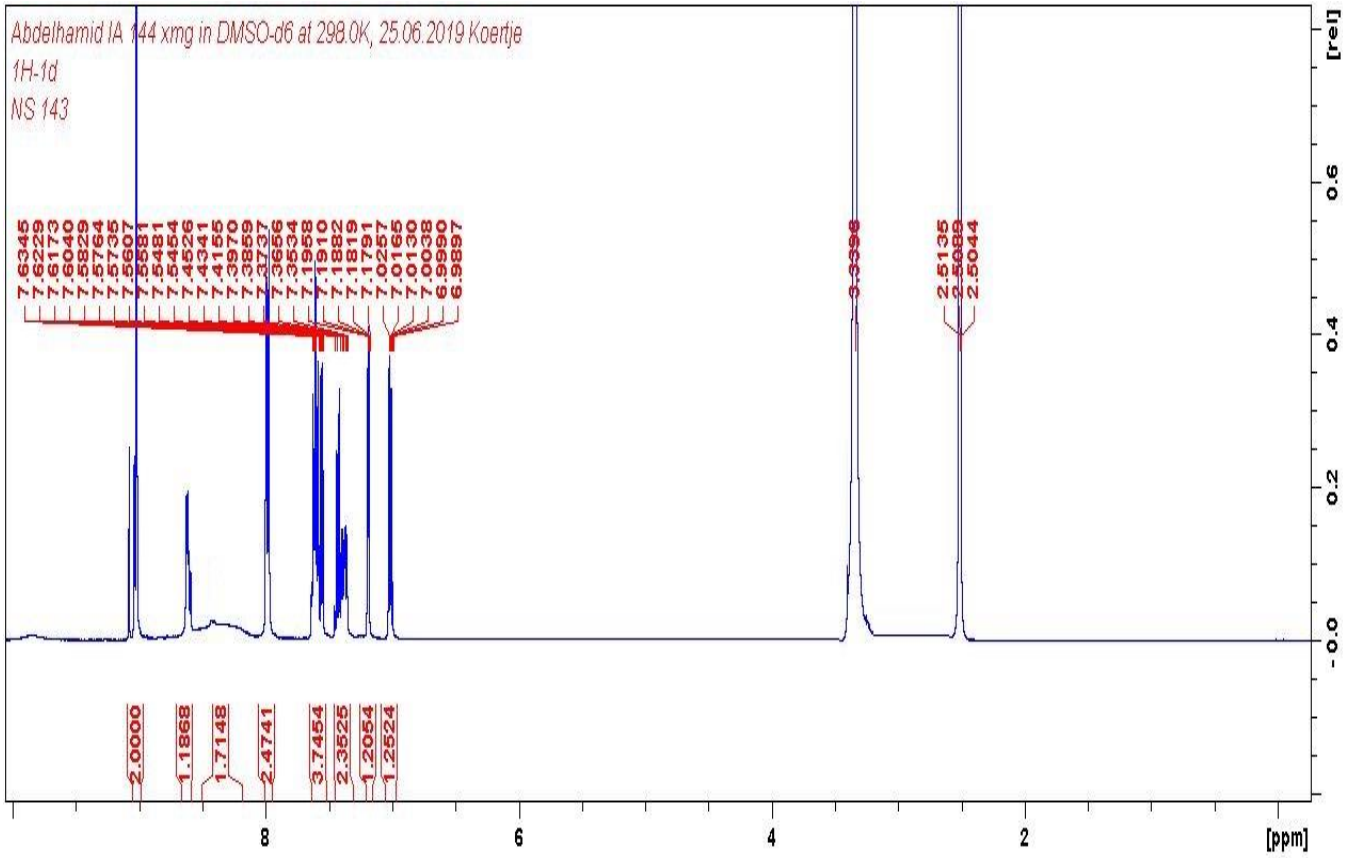
H2N
CN

22b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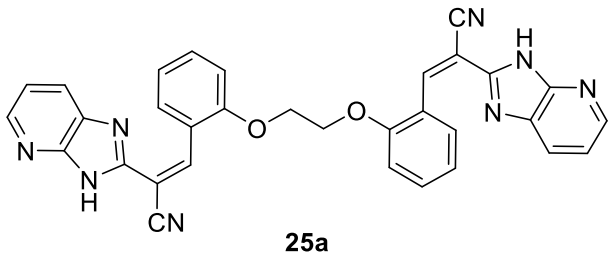

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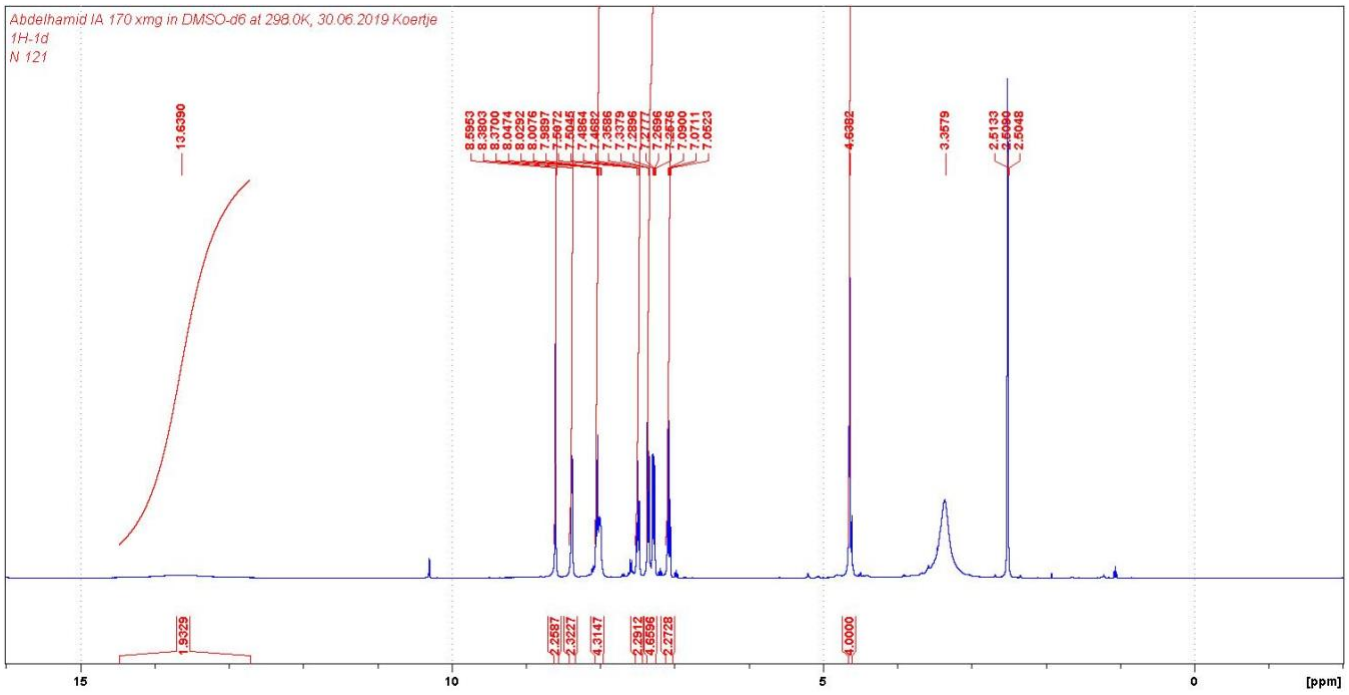
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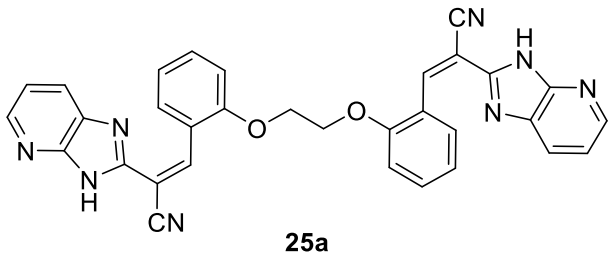

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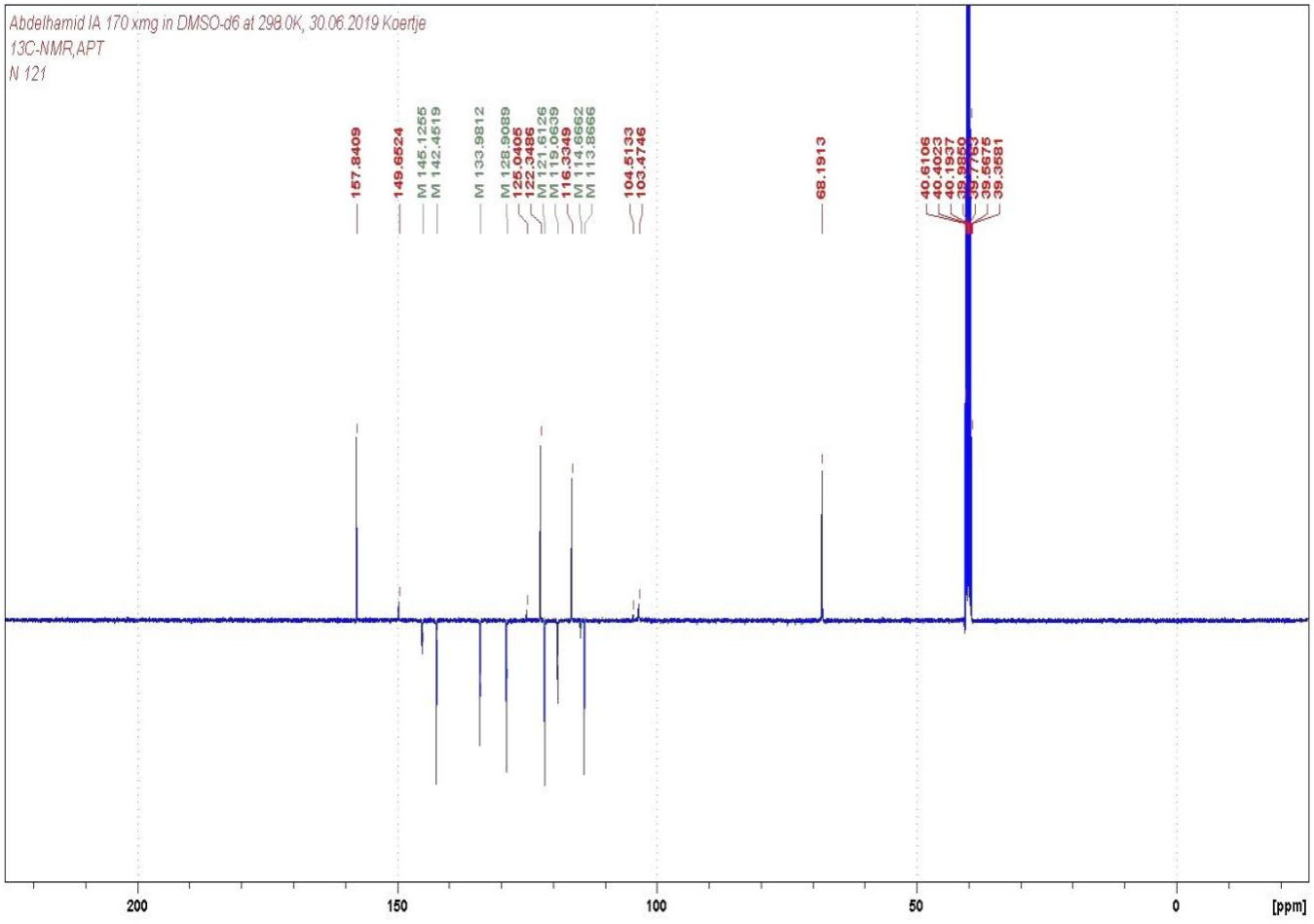
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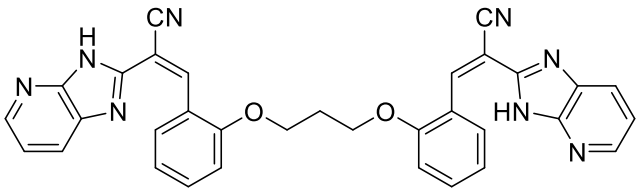

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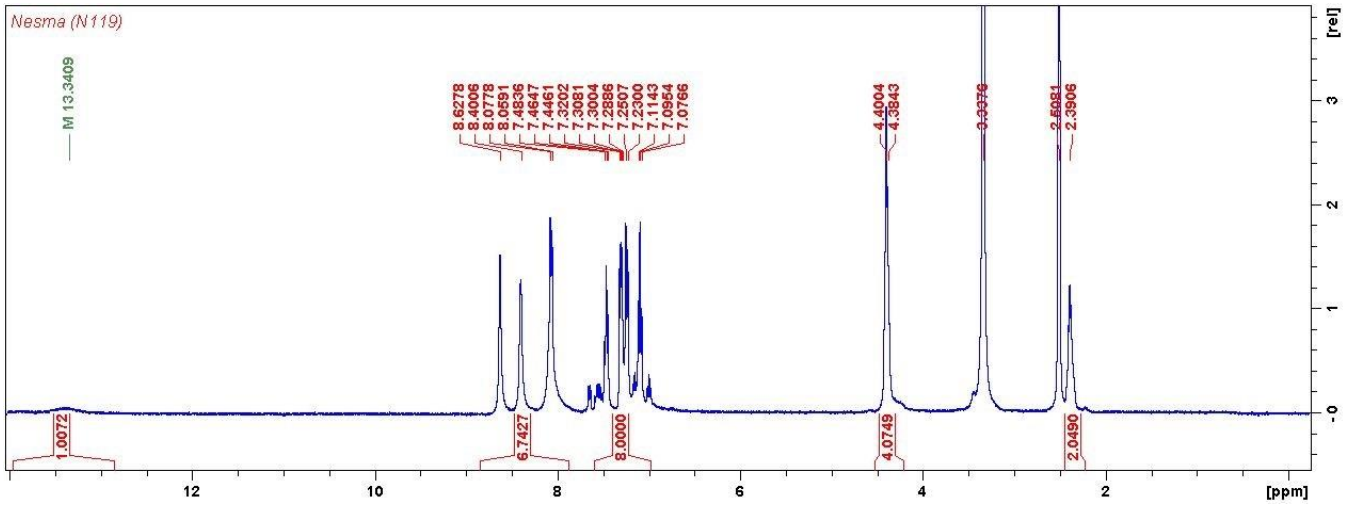
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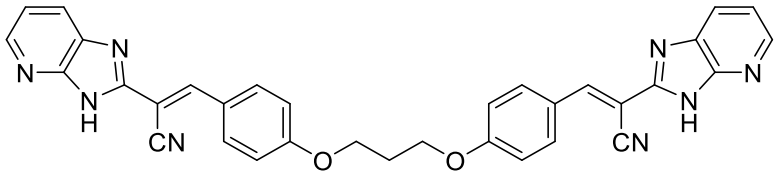

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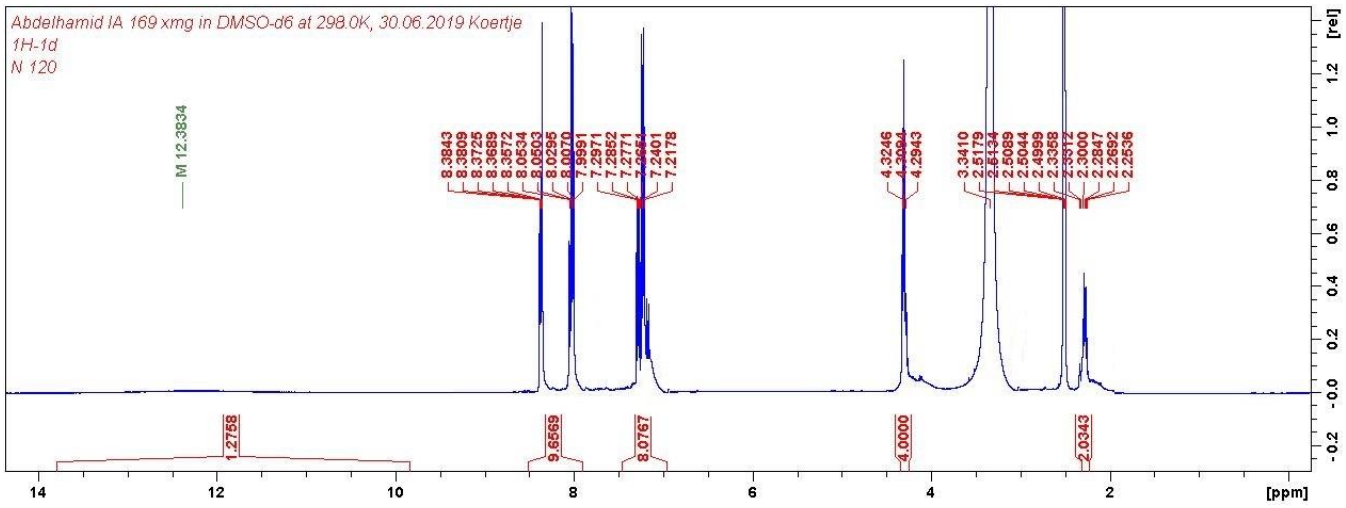
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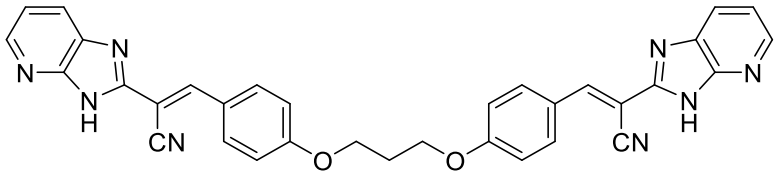

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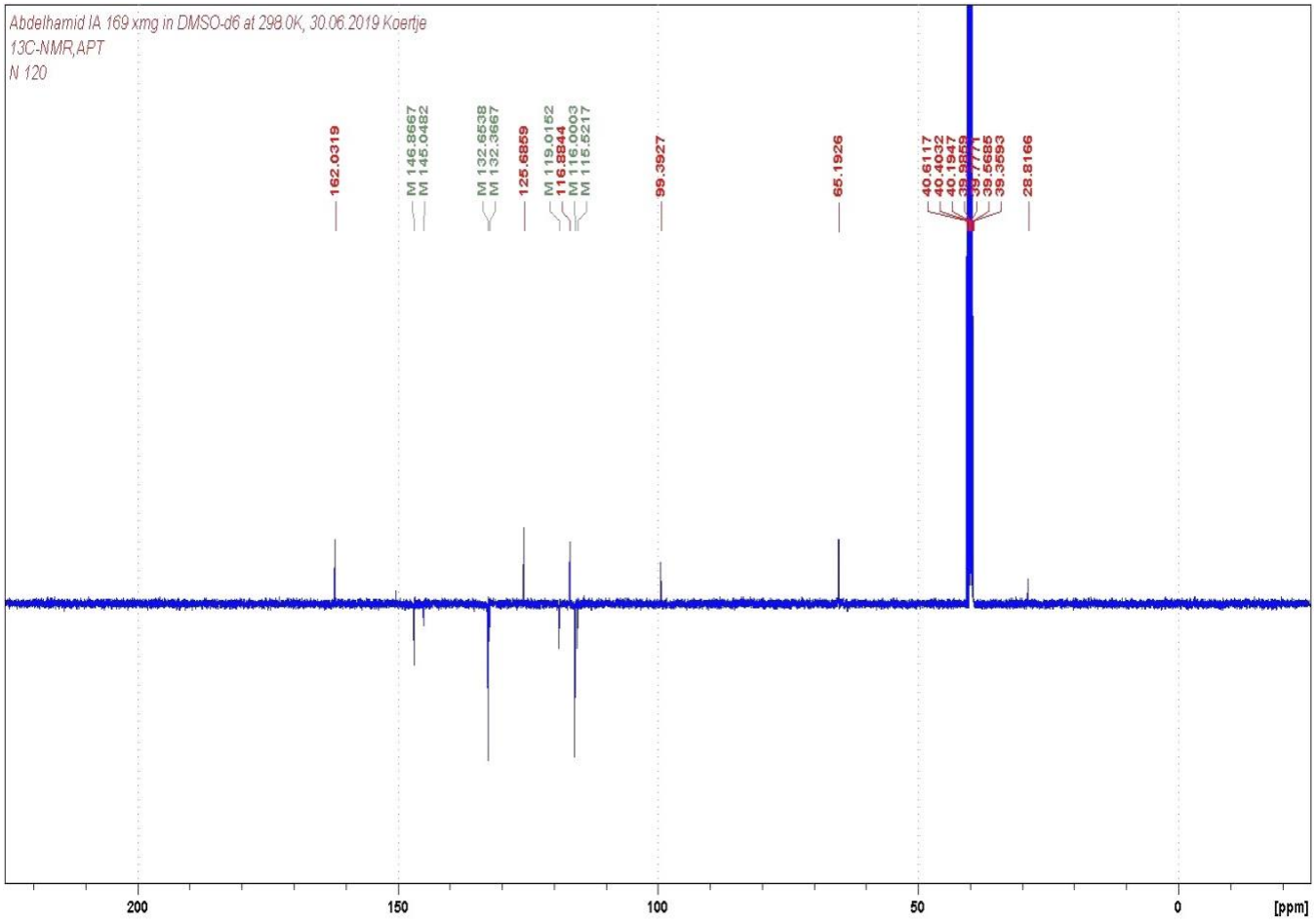
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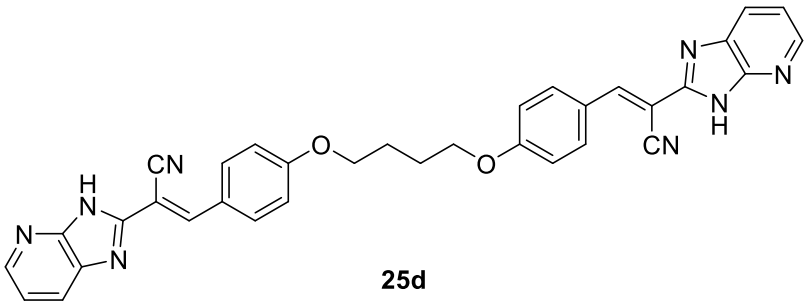

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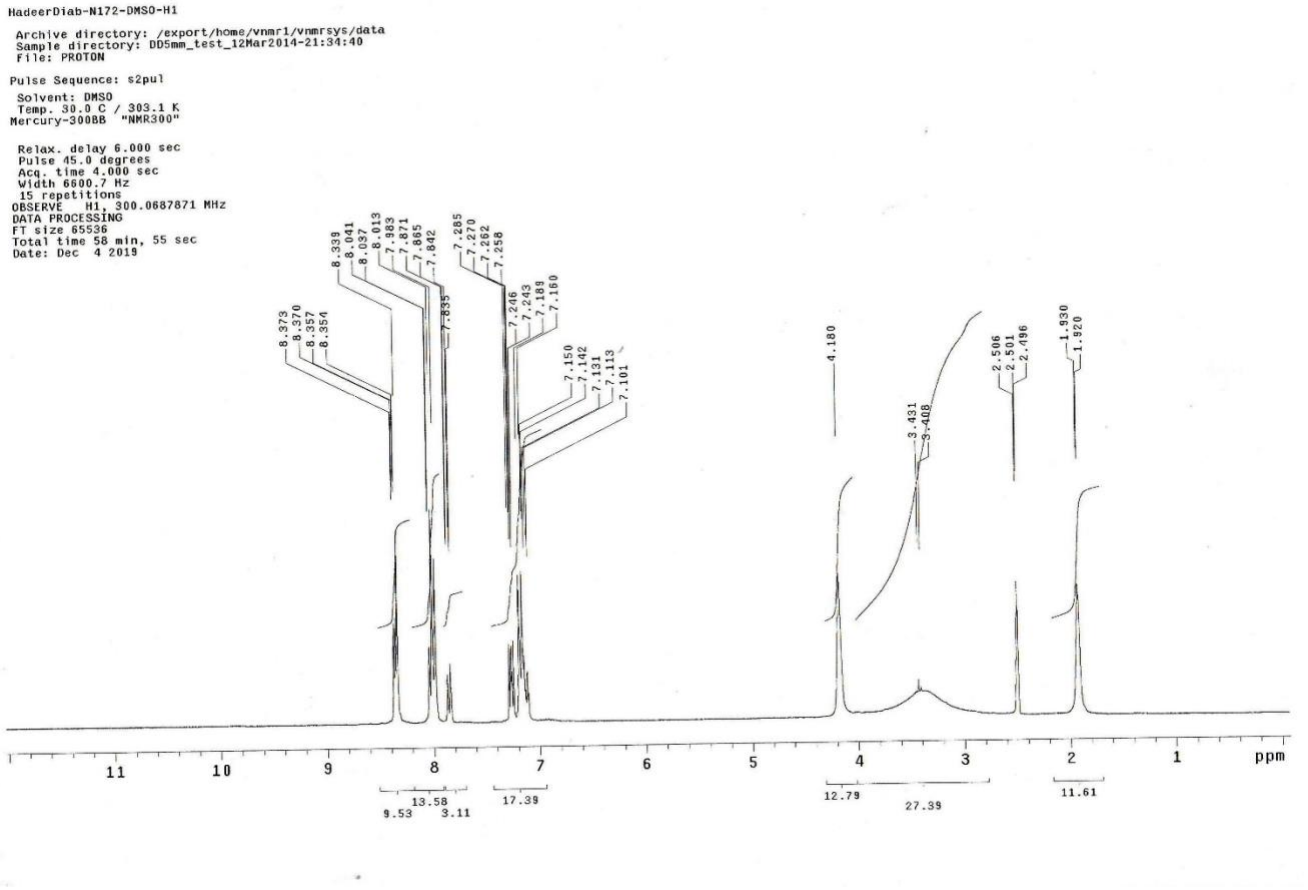
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Theoretical calculation

Different quantum chemical parameters such as, bond lengths, bond angles, electronic dipole moment (μ) as well as first-order hyperpolarizability (β) were calculated using DFT-B3LYP/6-311G** level of calculation. Quantum mechanical calculations of geometries and energies were attained using the density functional theory with Becke's three parameter exchange functional method, the Lee-Yang-Parr correlation functional approach (B3LYP/DFT) combined with 6.31G(d,p) basis set.

Tables 1-3

Table 1 Selected geometric bond lengths, bond angles and dihedral angles of the optimized **10**, **11, 12**, **14** and **16** using B3LYP/6-311G**

Compound	Bond lengths (Å)		Bond angles		Dihedral angles	
10	N10-C12	1.304	N10-C12-N11	113.552	C3-C10-C12-N11	0.027
	N11-C12	1.380	N11-C12-C14	120.609	N10-C12-C14-C15	0.072
	C12-C14	1.504	C12-C14-C15	113.535	C12-C14-C15-N18	-179.973
11	C12-C13	1.363	C2-C12-C13	131.674	C2-C12-C13-C14	180.000
	C13-C14	1.432	C12-C13-C14	119.212	C2-C12-C13-C15	0.000
	C14-N14	1.552	C13-C14-C16	179.700	C12-C13-C15-N17	-179.998
	C13-C15	1.428	C13-C15-N17	179.019	N17C15-C13-C14	0.002
12	C9-C11	1.428	C9-C11-C12	117.369	C13-C11-C12-N17	-176.879
	C11-C12	1.424	C11-C12-N17	179.059	C9-C11-C13-C14	-0.148
	C12-N17	1.555	C14-C13-C24	119.117	C11-C13-C14-C16	177.419
	C11-C13	1.392	C11-C13-C24	121.021	C13-C14-C16-N18	-179.389
	N10-C15	1.368	C11-C13-C14	119.862	C13-C14-C15-N21	179.799
	C14-C15	1.406	C13-C14-C15	121.211	C11-C13-C24-C29	123.976
14	C12-C14	1.517	N10-C12-C14	124.055	N10-C12-C14-C15	-99.885
	C14-C15	1.470	C12-C14-15	108.551	C12-C14-C15-N34	-41.891
	C15-N34	1.152	C14-15-N34	177.192	C14-15-C16-C29	82.874
	C14-C16	1.565	C12-C14-16	110.790	C14-C16-C29-C31	-163.236
	C16-C29	1.577	C14-C16-C29	110.728	C16-C29-C31-N36	-17.300
	C29-C31	1.468	C16-C29-C31	110.121	C16-C29-C32-N35	110.651

10	C12-C13	1.508	C12-C13-C14	112.639	C12-C13-C14-N17	155.210
	C13-C14	1.461	C13-C14-N17	177.024	C12-N11-C18-C19	-54.336
	C14-N17	1.151	C12-N11-C18	133.957	C18-C19-C32-N35	88.241
	C12-N11	1.395	N11-C18-C19	110.996	C18-C19-C33-N36	118.941

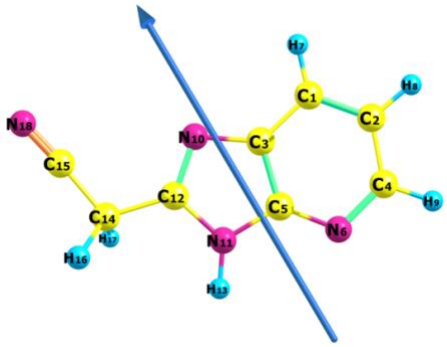
Table 2 Total energy, energy of HOMO and LUMO, energy gap, ionization energy (I, eV), electron affinity (A, eV), absolute electronegativities, (χ, eV), absolute hardness (η, eV), global softness (S, eV^{-1}) chemical potential (π, eV^{-1}) global electrophilicity ($\boldsymbol{\omega}$, eV), additional electronic charge, $\Delta N_{max,}$ of **10**, **11, 12, 13, 14** and **16** usingB3LYP/6-311G**

Parameter	**10**	**11**	**12**	**13**	**14**	**16**
E_T, eV	-14350	-13436	-27762	-27744	-27771	-27771
E_{HOMO}, eV	-6.7891	-7.3929	-6.1690	-5.9867	-6.8653	-6.9795
E_{LUMO}, eV	-1.5150	-3.0926	-2.8478	-3.2776	-1.7789	-1.8170
E_g, eV	5.2741	4.3003	3.3212	2.7091	5.0864	5.1625
I, eV	6.7920	7.3958	6.1713	5.9867	6.8653	6.9795
A, eV	1.5162	3.0937	2.8480	3.2776	1.7789	1.8170
χ, eV	4.1541	5.2448	4.5096	4.6322	4.2160	4.3983
η, eV	2.6379	4.3540	3.0018	1.3546	2.5432	2.5813
S, eV	0.1895	0.2324	0.3009	0.3691	0.1966	0.1937
π, eV	-4.1541	-5.2448	-4.5096	-4.6322	-4.2160	-4.3983
ω, eV	3.2709	3.1589	3.3874	7.9444	3.4945	3.7472
$\Delta N_{max.}$	1.5748	1.205	1.5023	3.4196	3.4196	1.6980

Table 3 Calculated total static dipole moment (μ), the mean polarizability <α>, anisotropy of the polarizability Δα and the first-order hyperpolarizability <β > configuration for the studied **10, 11** and **12** compounds usingB3LYP/6-311G**

Property	Urea	**10**	**11**	**12**
μ, D	1.3197	4.4076	6.6808	5.3942
αxx, a.u.	-	-78.3987	-78.8622	-104.9788
αyy	-	-64.3772	-71.7942	-159.5939
αzz	-	-69.0925	-71.2991	-135.1699
αxy	-	19.7622	-1.1918	6.1289
αxz	-	-0.0081	0	-0.6286
αyz	-	-0.0032	0	5.923
<α> esu	-	-1.046610^{-23}	-1.0965×10^{-23}	-1.9747×10^{-23}
Δα, esu	-	1.8315×10^{-24}	1.0860×10^{-24}	7.0226×10^{-24}
βxxx	-	107.9435	137.5982	68.0475
βxxy	-	-35.7904	23.0194	-29.3381
βxyy	-	3.8275	41.3742	86.8542
βyyy	-	-13.2108	-27.6441	60.184
βxxz	-	0.0317	0.0003	4.4649
βxyz	-	-0.0067	0.0002	-23.092
βyyz	-	0.0142	0	-4.7334
βxzz	-	-8.1671	-6.8291	-13.2092
βyzz	-	-4.5171	0.9181	1.243
βzzz	-	0.004	0	-0.2449
<β>, esu	0.1947×10^{-30}	1.0074×10^{-30}	1.4875×10^{-30}	1.2551×10^{-30}

Figures 2-5



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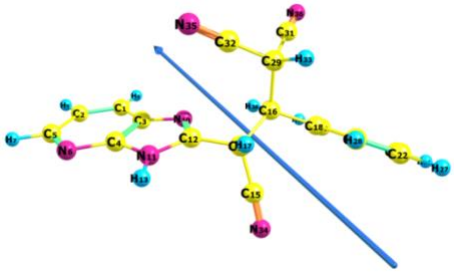

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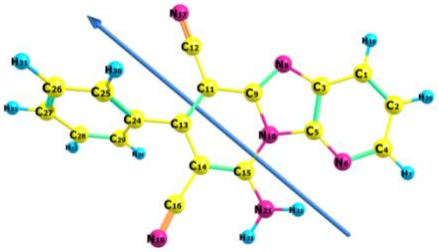

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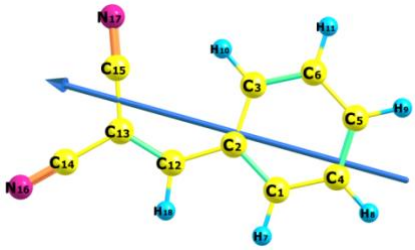

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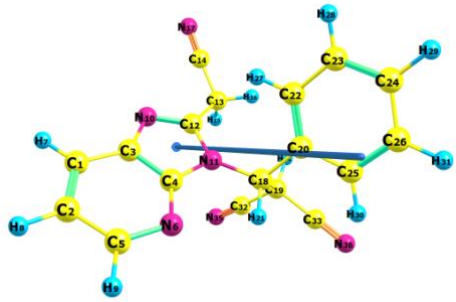

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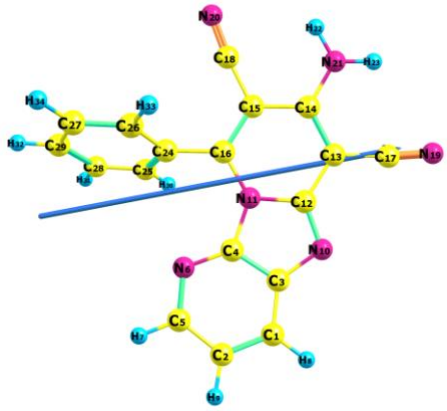


13

Fig. 2. Optimized geometry, numbering system and vector of dipole moment of **10, 11, 12** and **13, 14** and **16** using B3LYP/ 6-311G**.

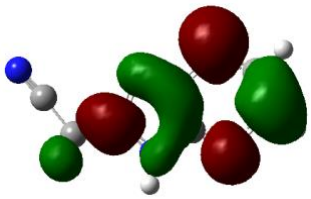
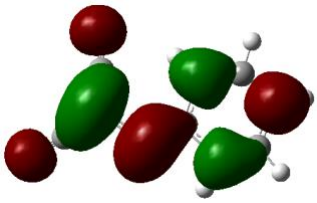
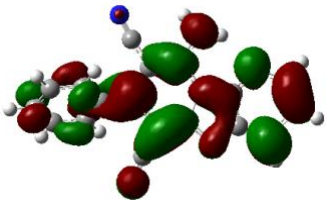
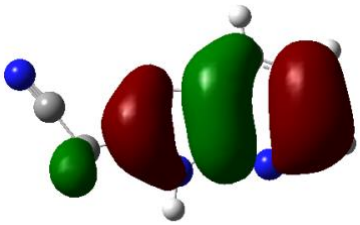
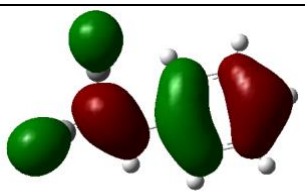
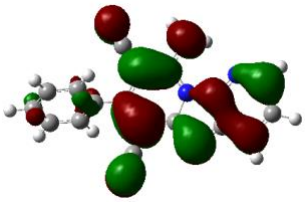
 LUMO -1.5150 eV	 LUMO -3.0926 eV	 LUMO -2.8478 eV	
 **10** HOMO -6.7891 eV	 **11** HOMO -7.3929 eV	 **12** HOMO -6.1689 eV	

Fig. 3. HOMO and LUMO molecular orbital maps of the studied **10, 11** and **12** using B3LYP/6-311G** level.

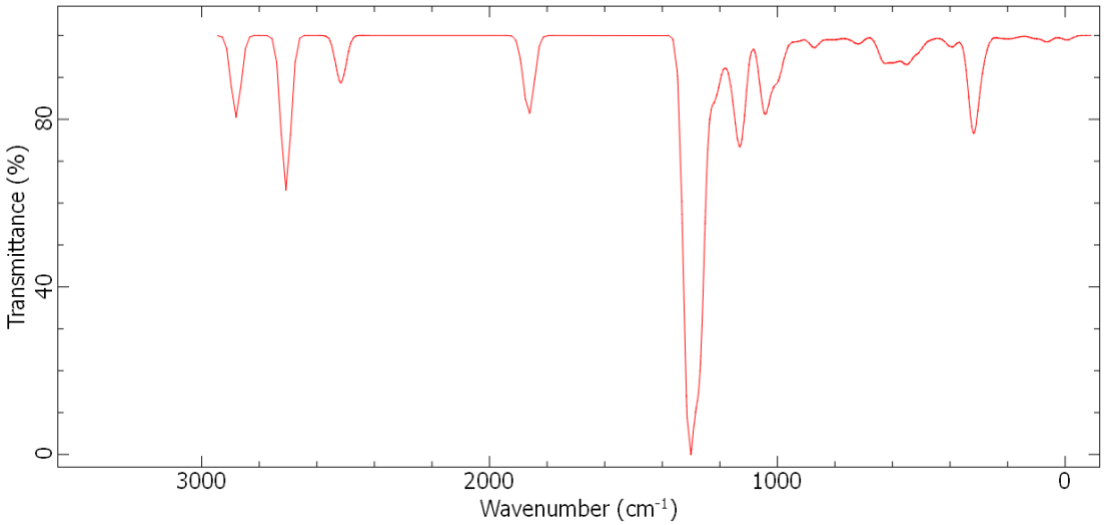


Fig. 4 Theoretical IR spectrum of 6a using B3LYP6-31G(d,p)

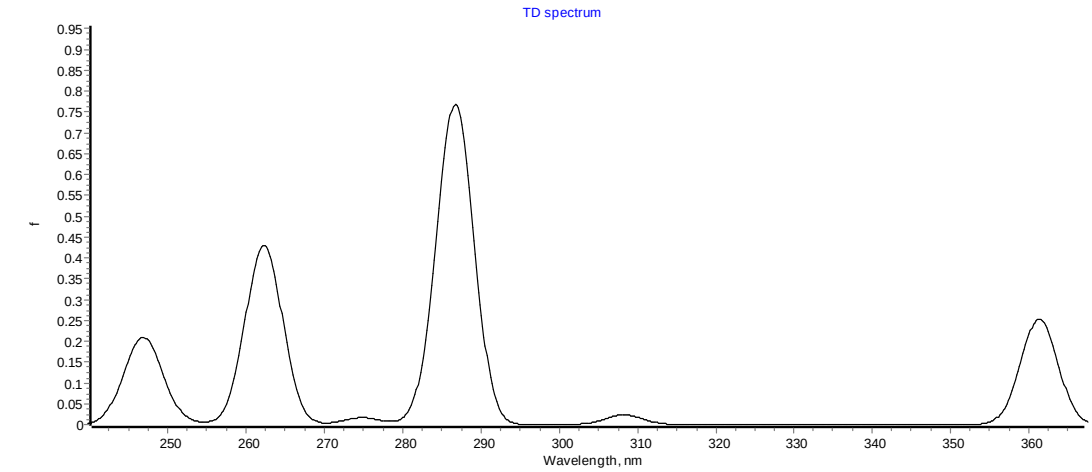


Fig. 5 Theoretical UV spectrum of 6a using B3LYP6-31G(d,p)