

Synthesis of 1,5-Functionalized 1,2,3-Triazoles Using Ionic Liquid/Iron(III) Chloride as an Efficient and Reusable Homogeneous Catalyst

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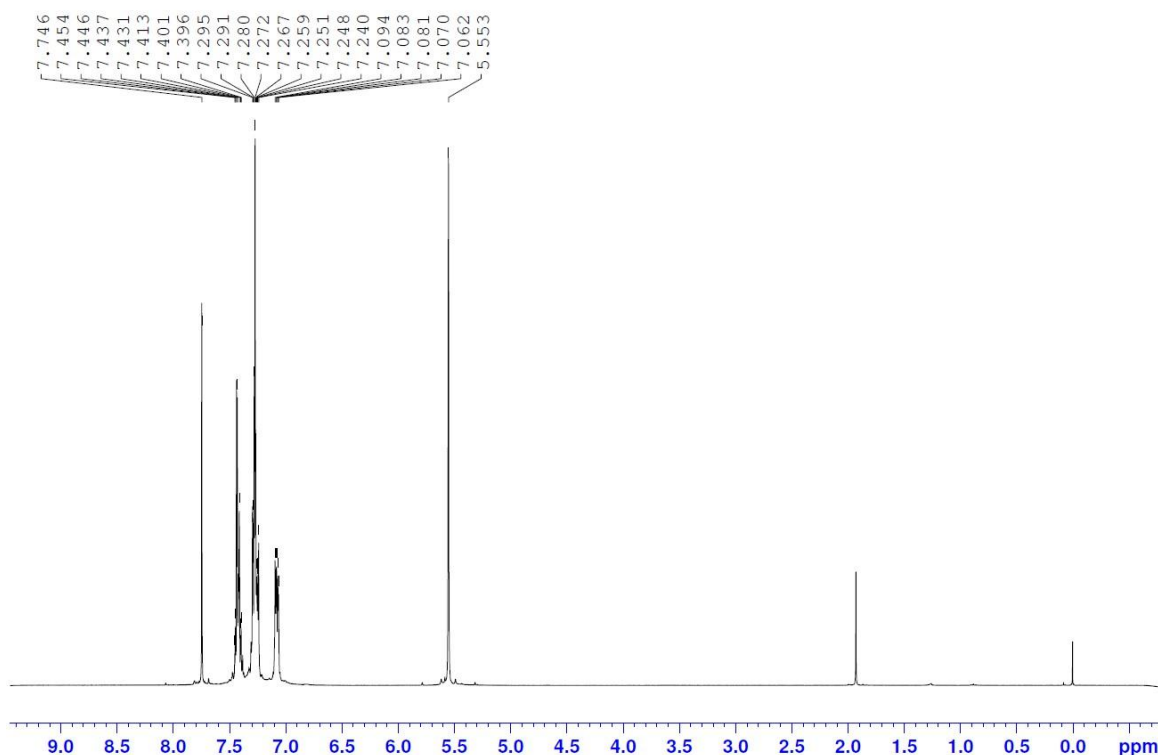
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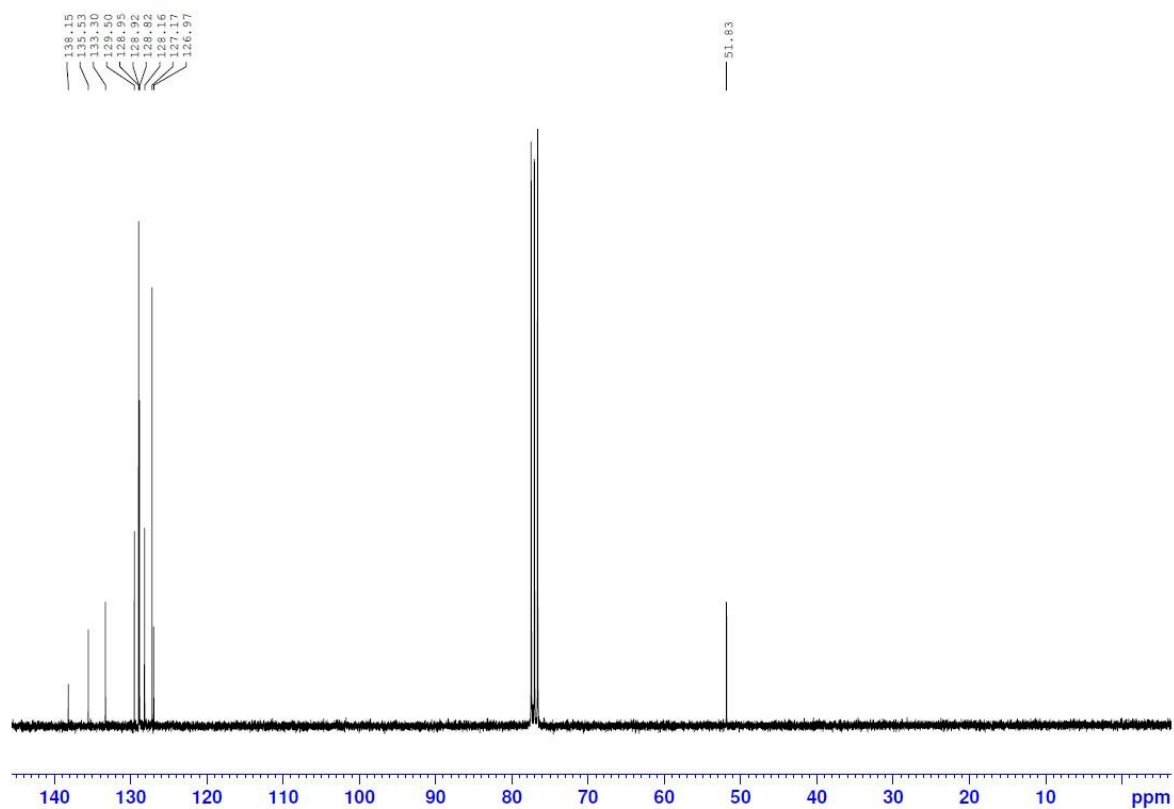
1. ¹H NMR, ¹³C NMR, and ESI(+)-MS spectra

1-benzyl-5-phenyl-1,2,3-triazole (3a)

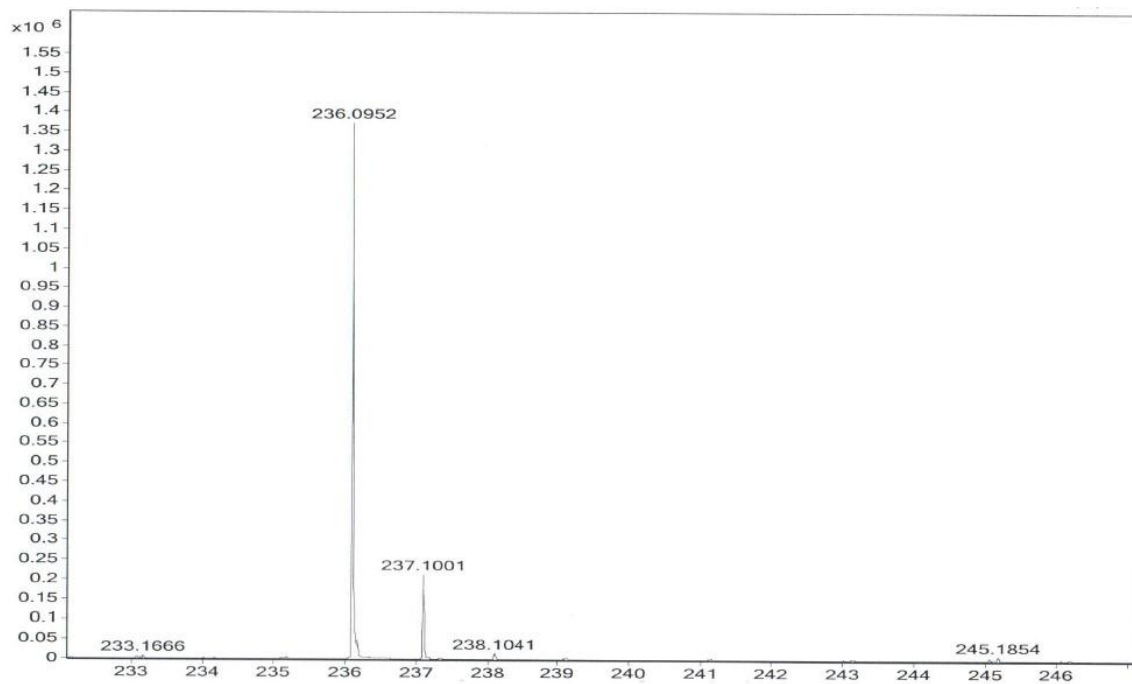
¹H-NMR



^{13}C -NMR

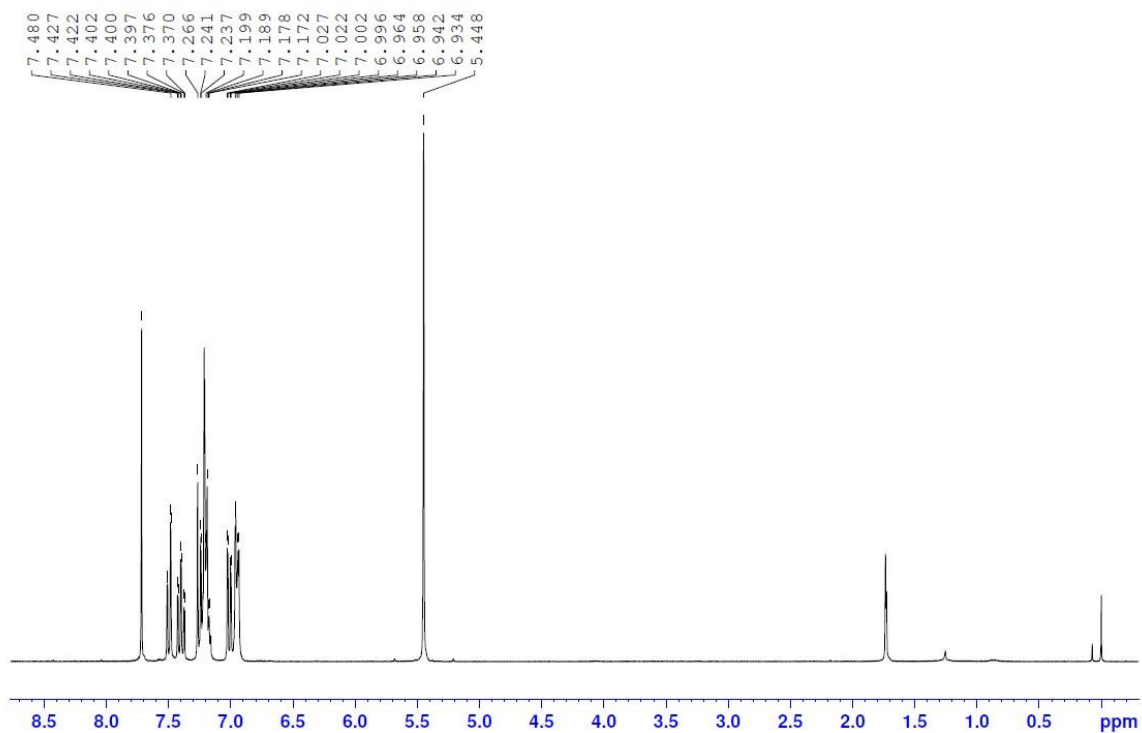


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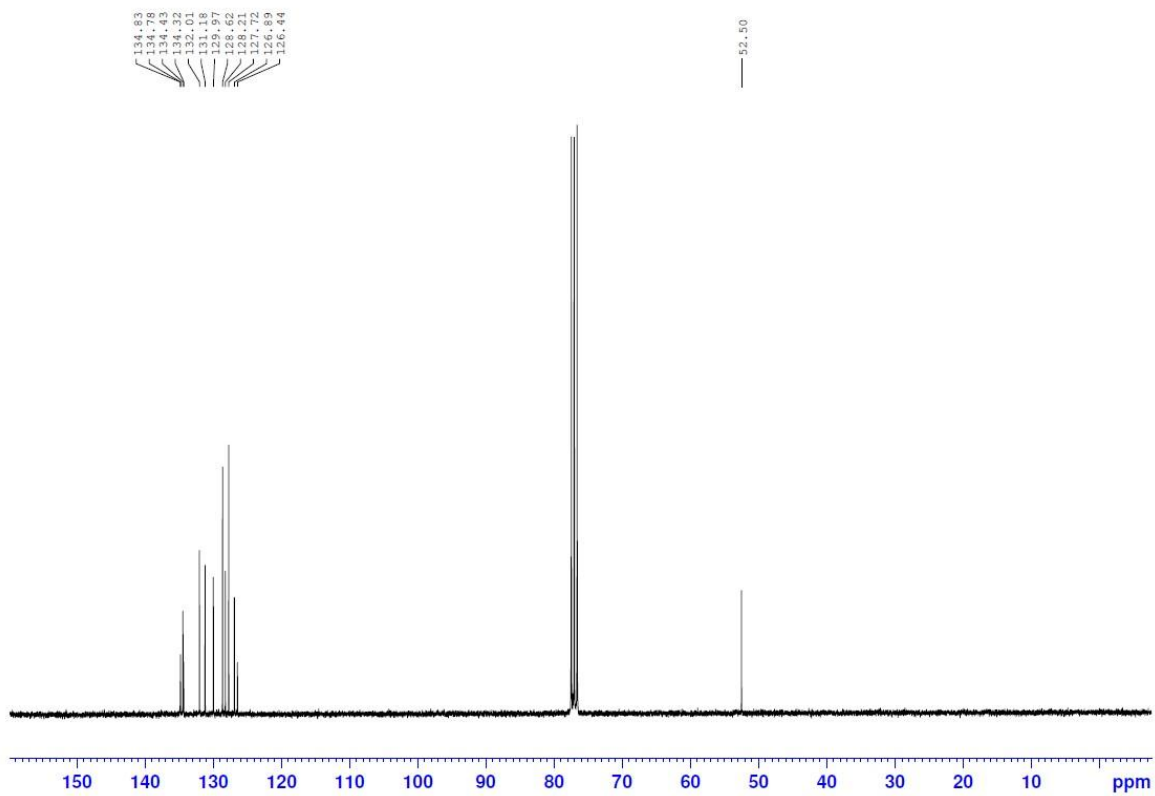


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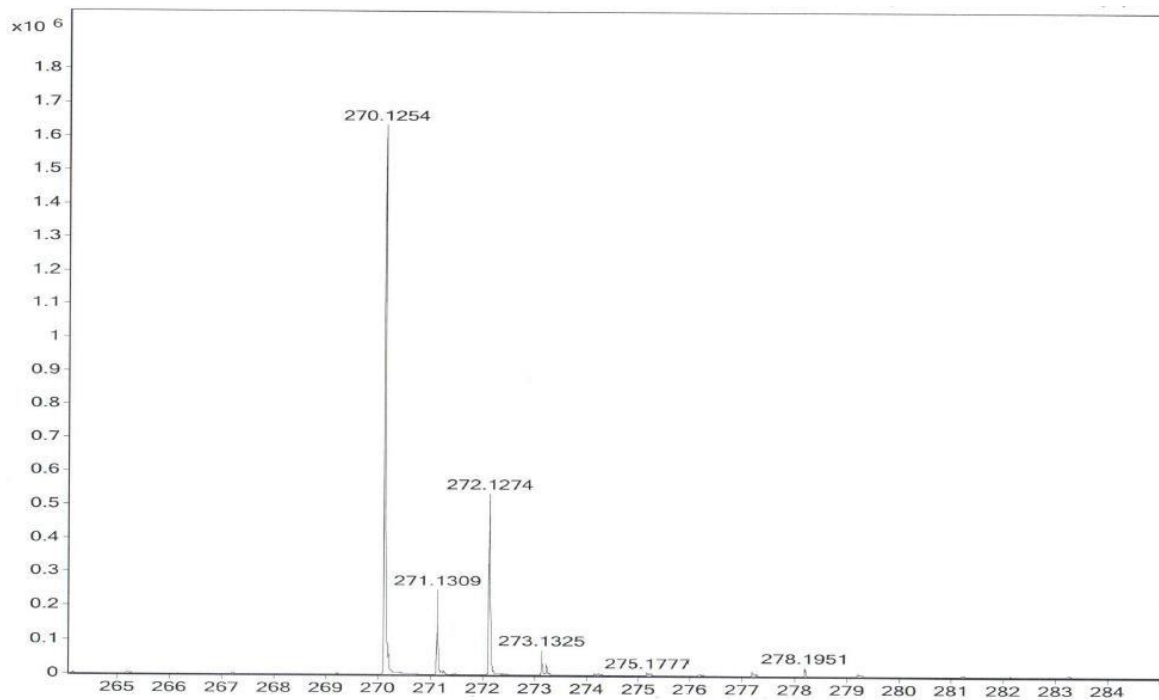
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¹³C-NMR

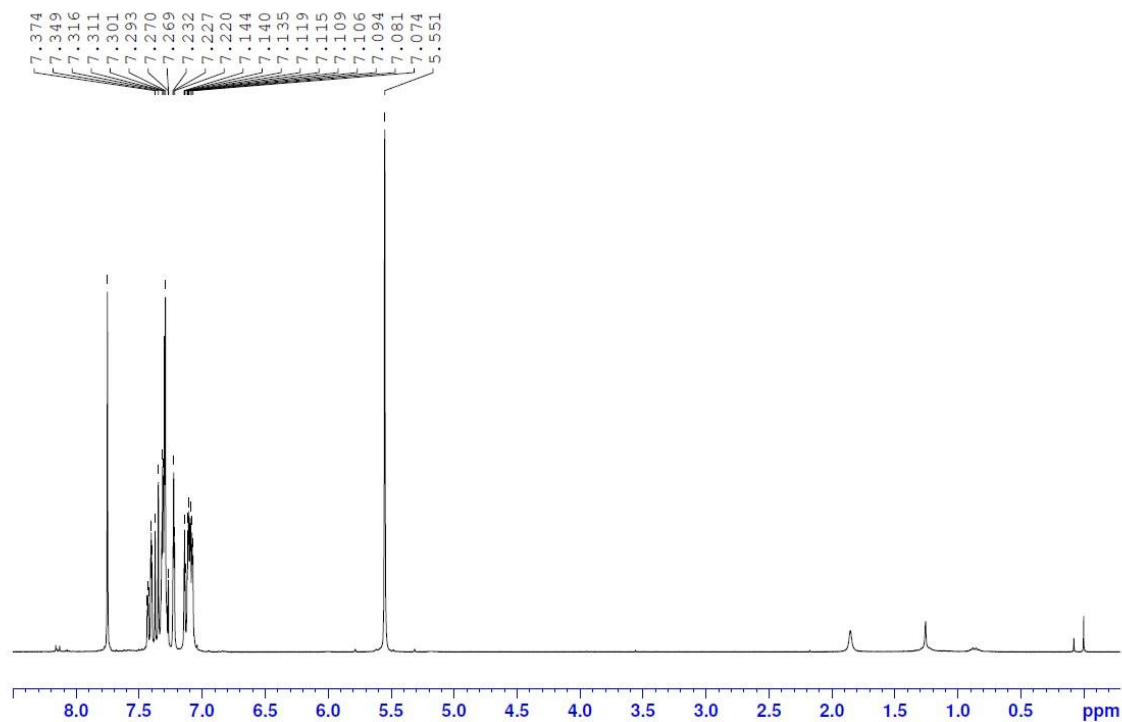


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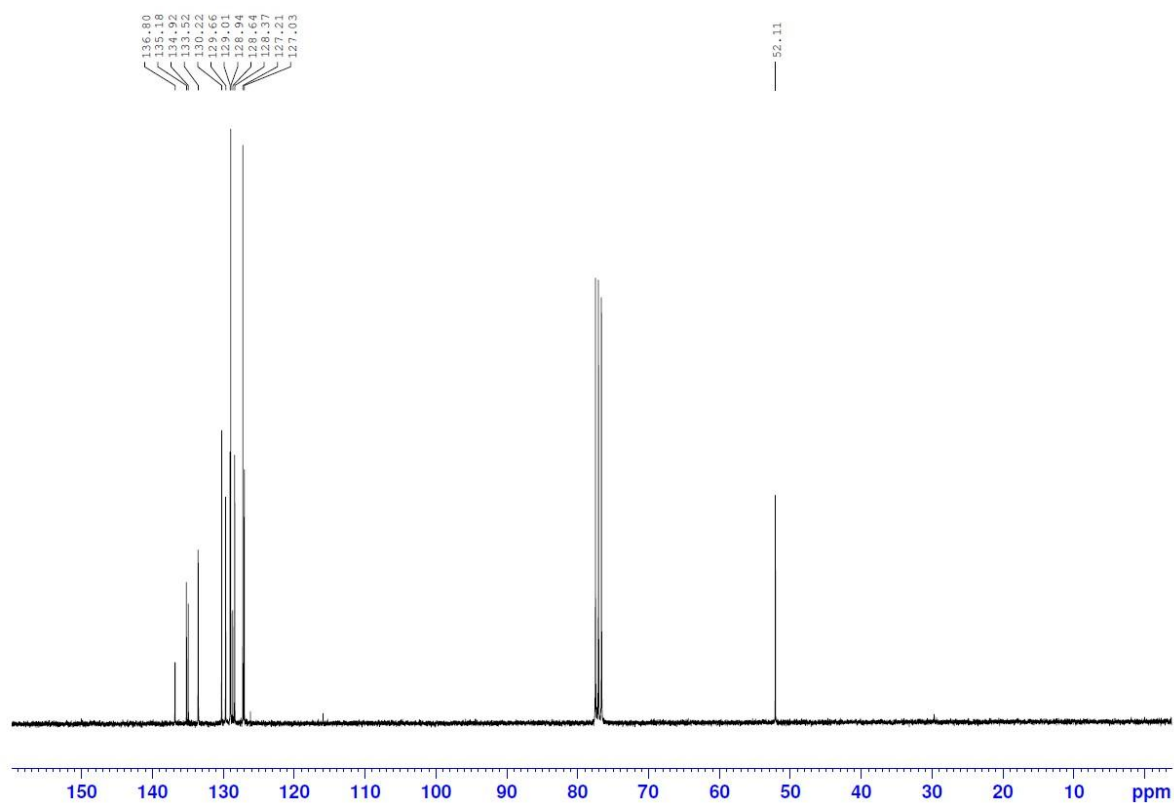


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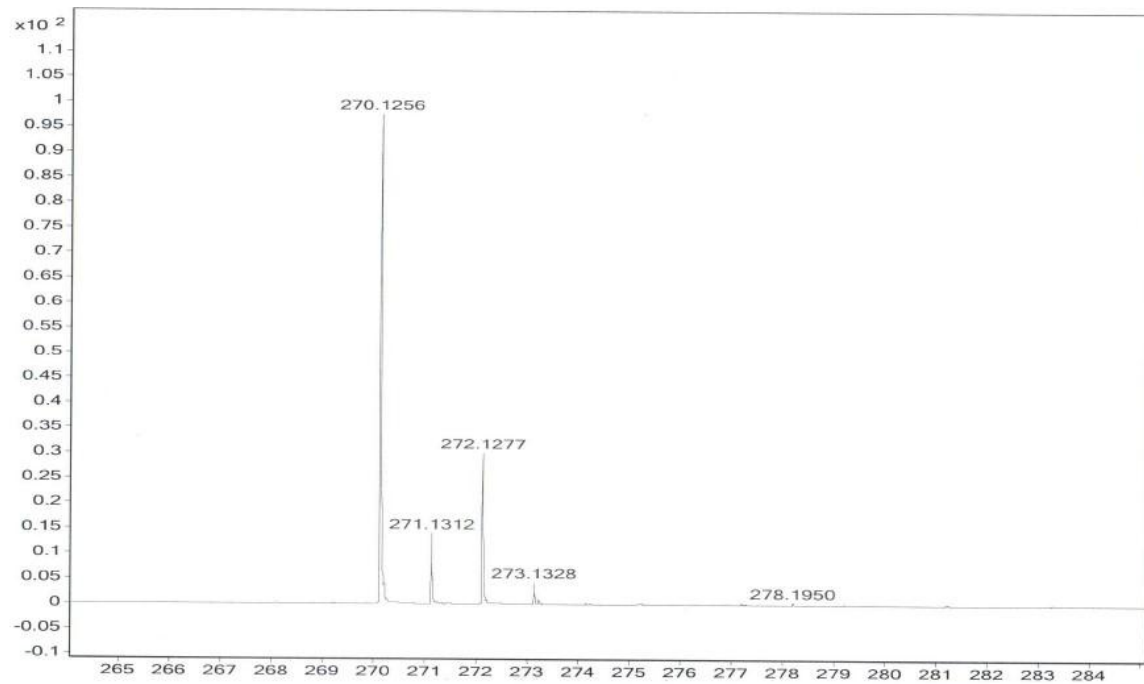
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^{13}C -NMR

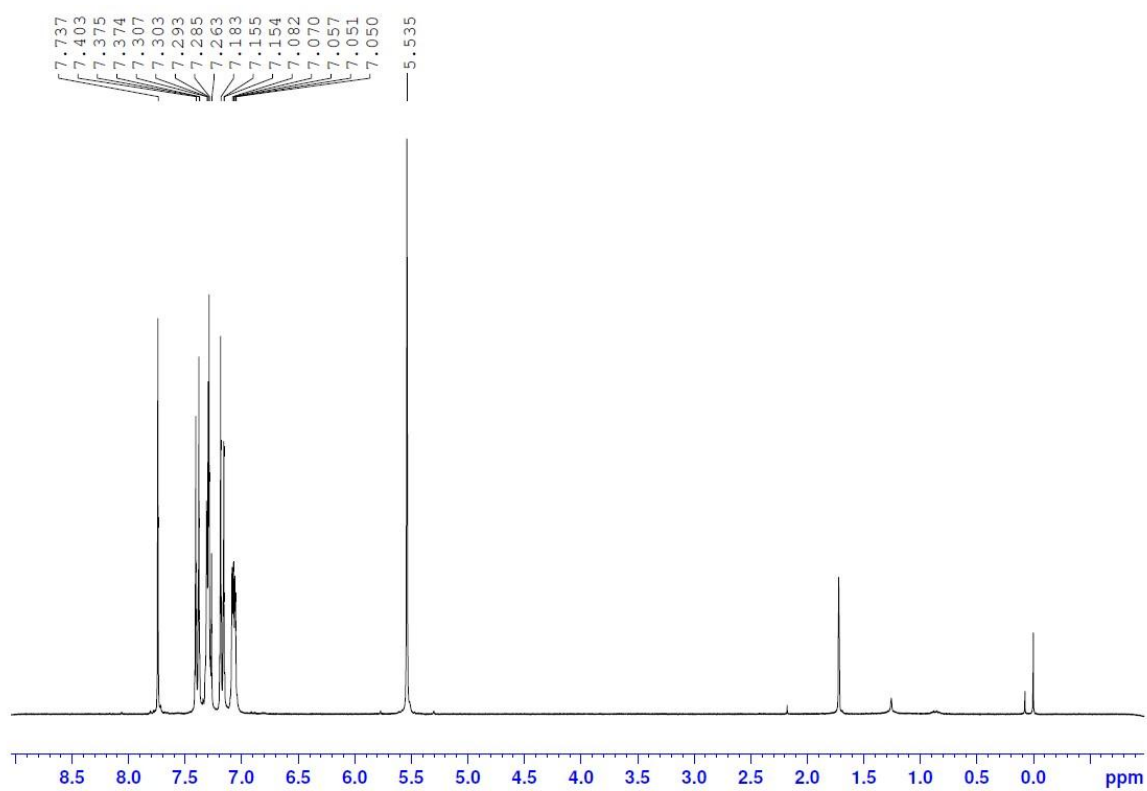


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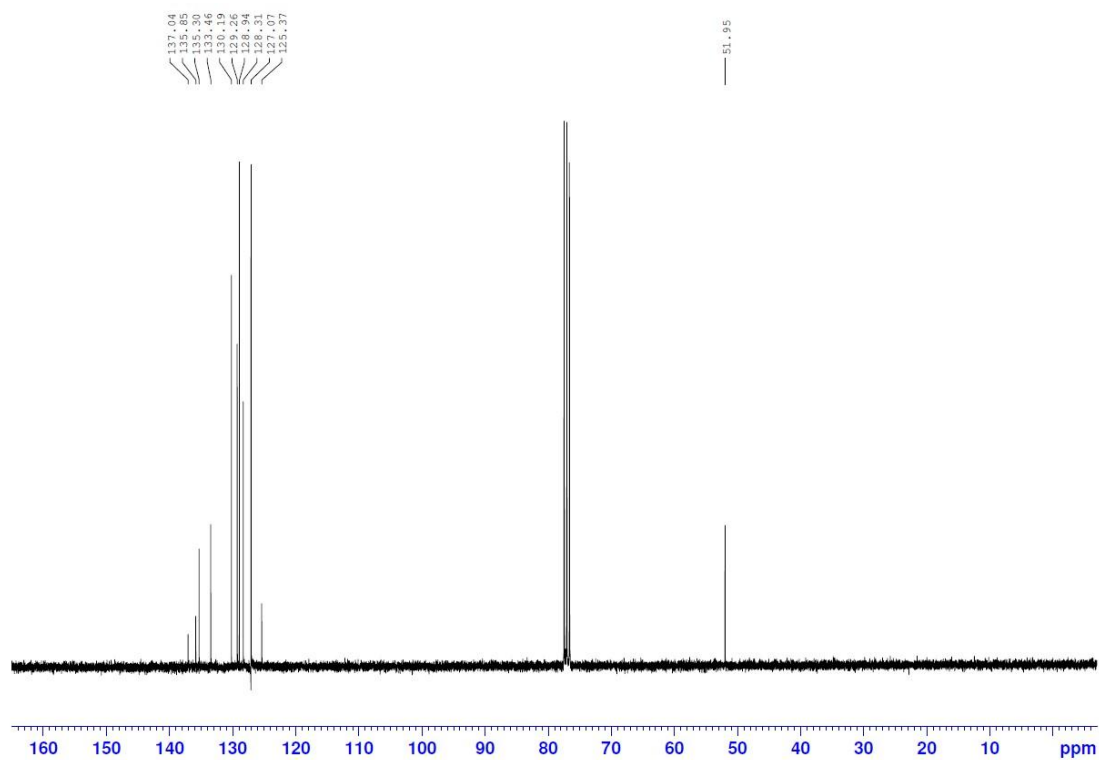


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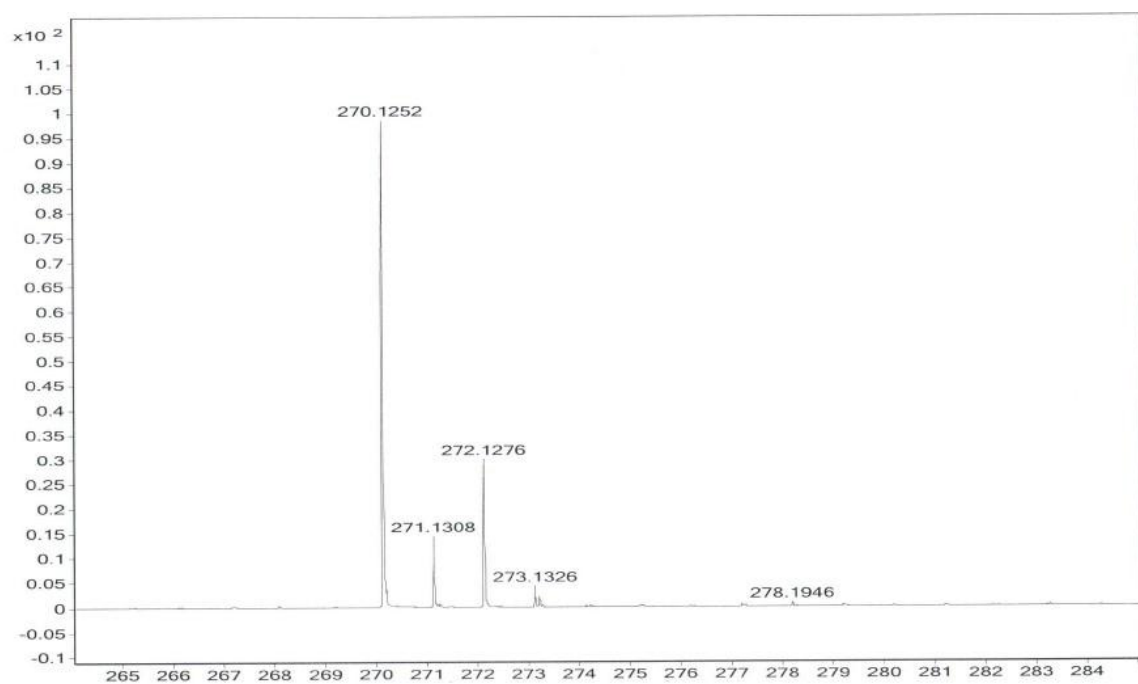
$^1\text{H-NMR}$



$^{13}\text{C-NMR}$

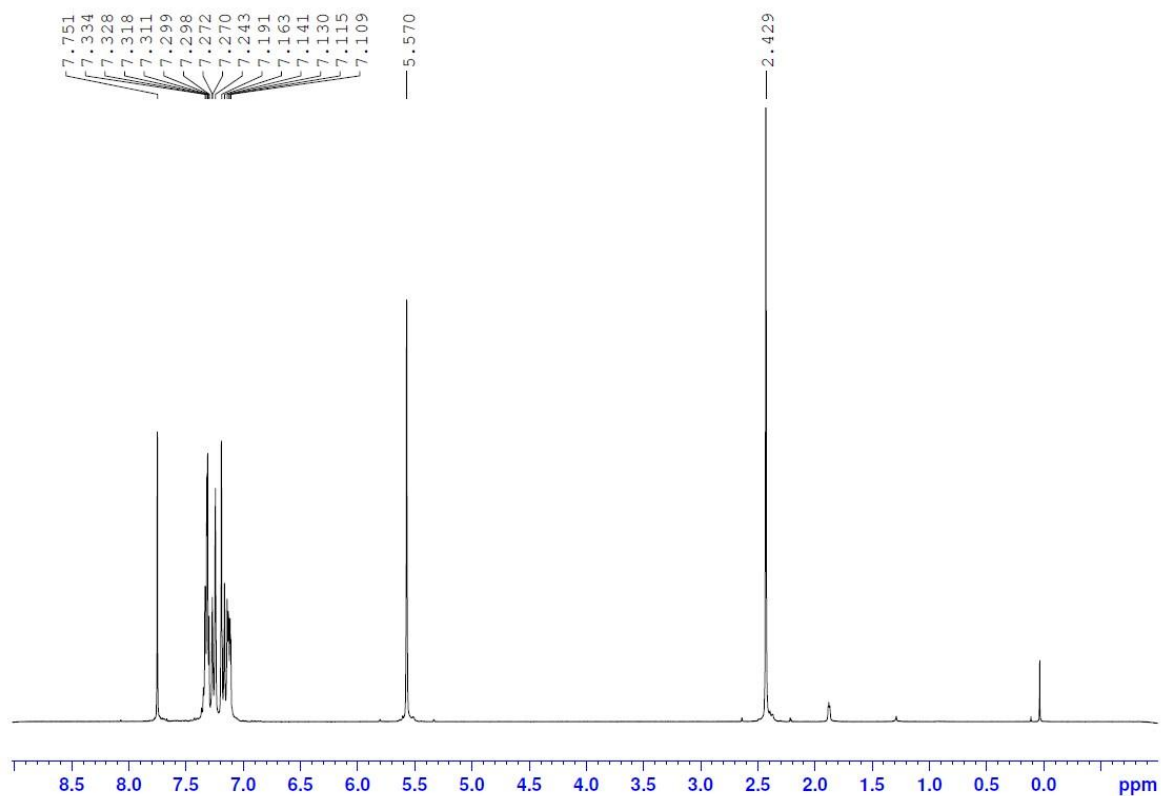


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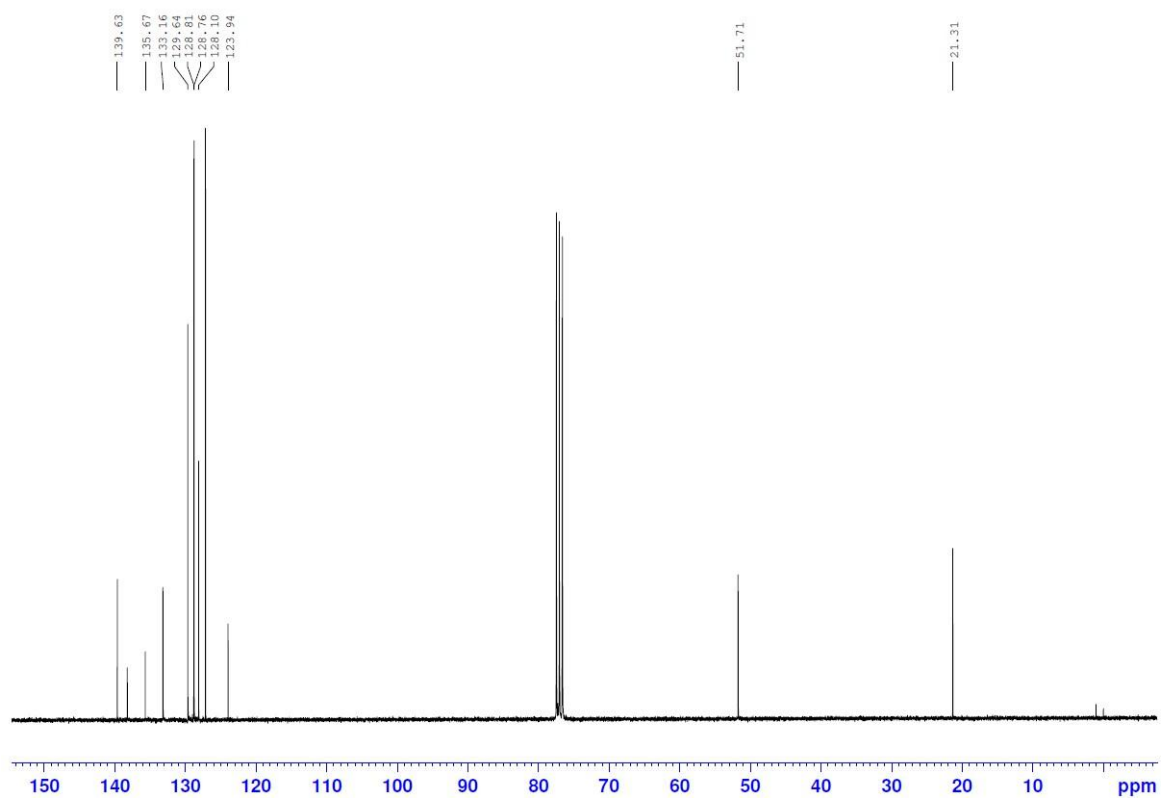


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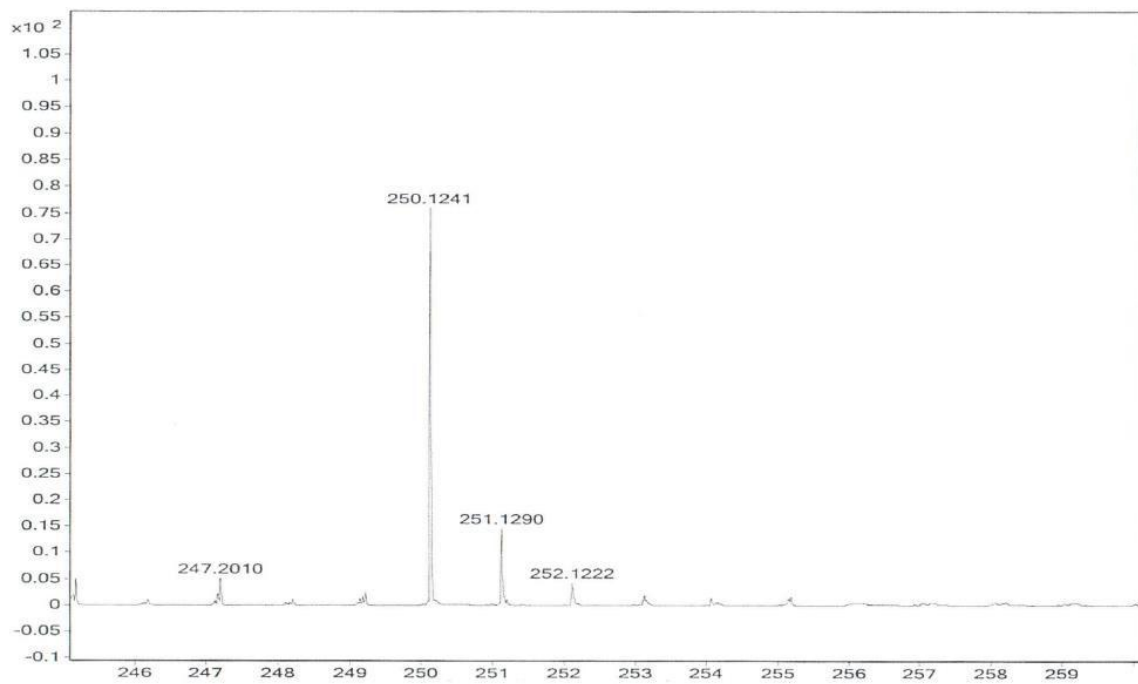
$^1\text{H-NMR}$



¹³C-NMR

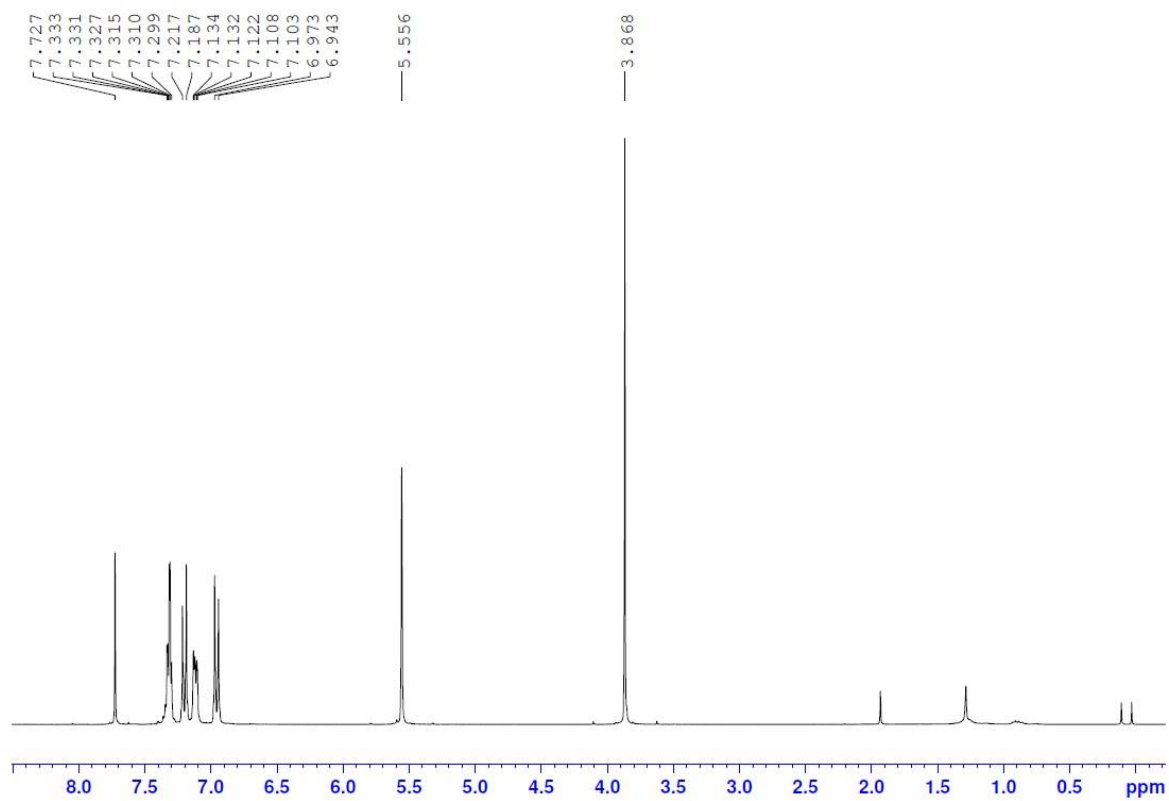


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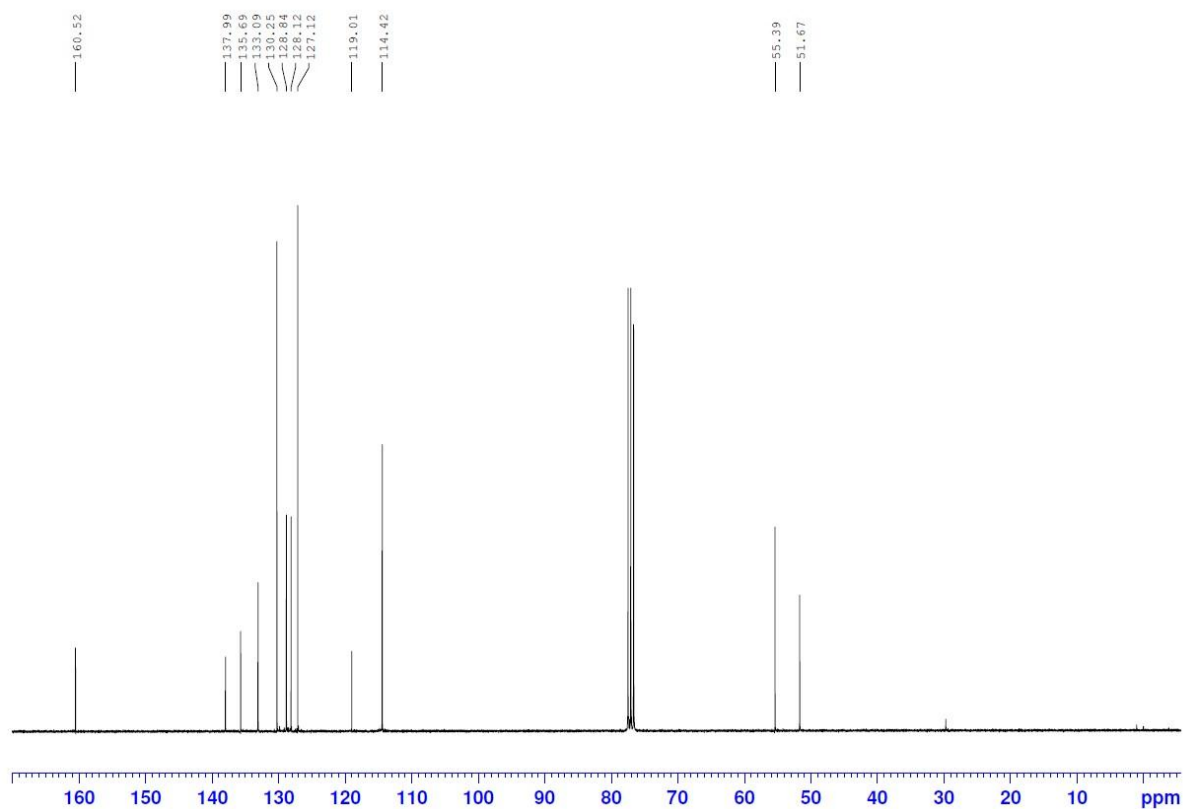


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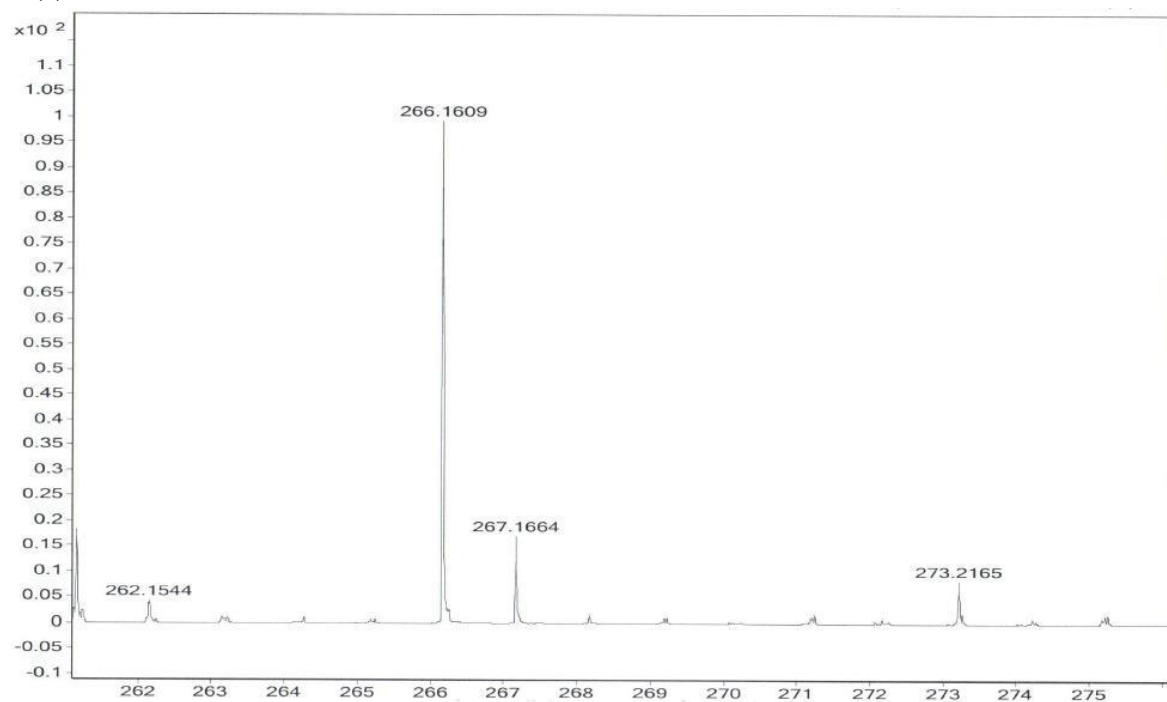
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¹³C-NMR

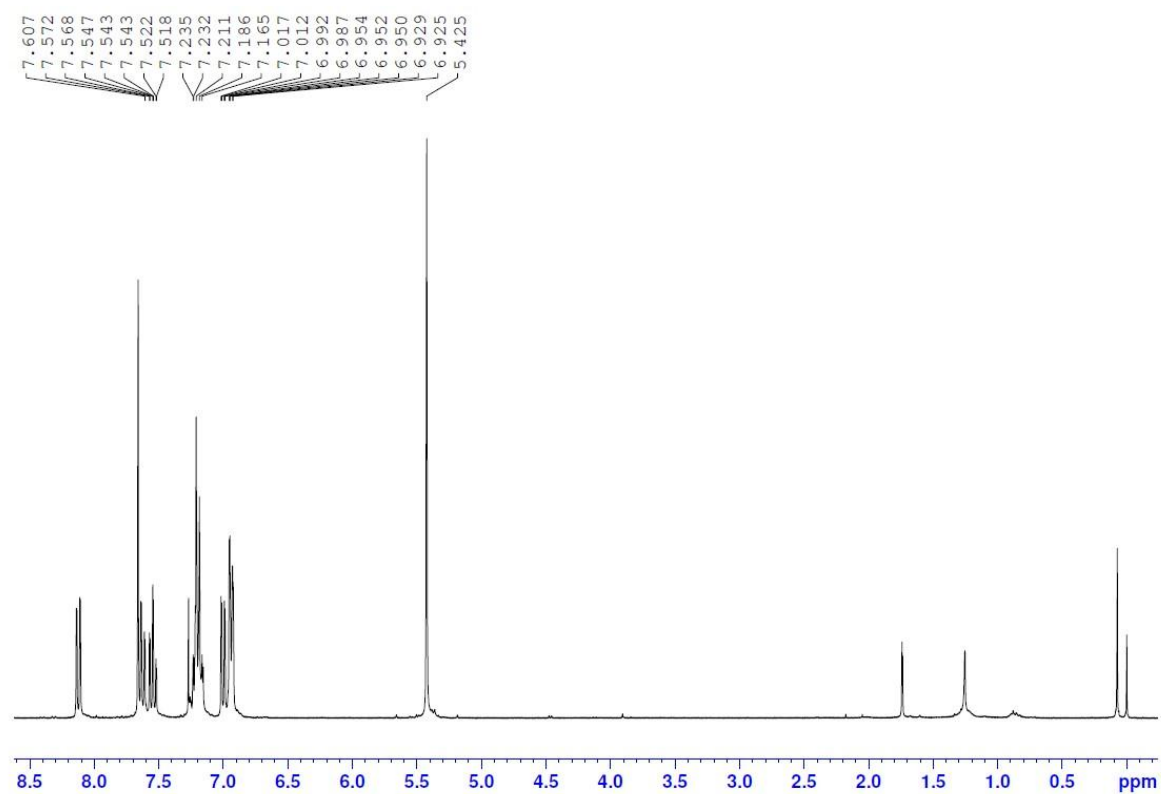


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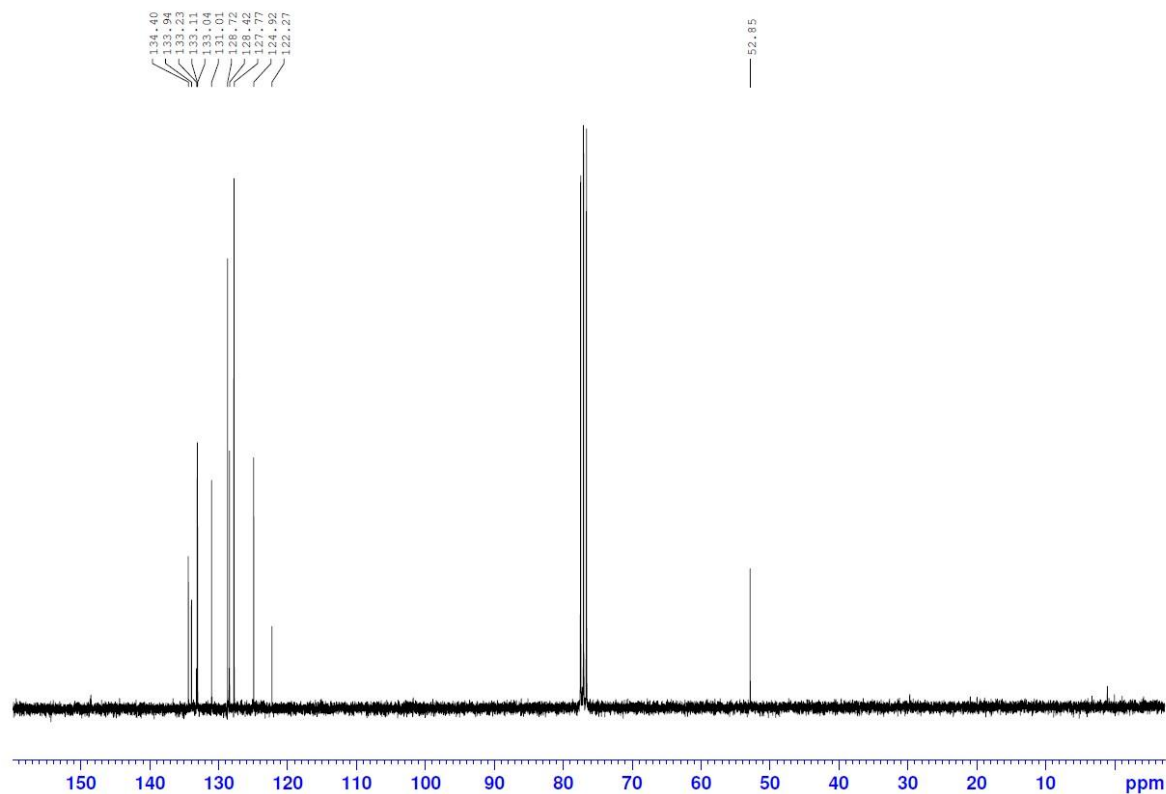


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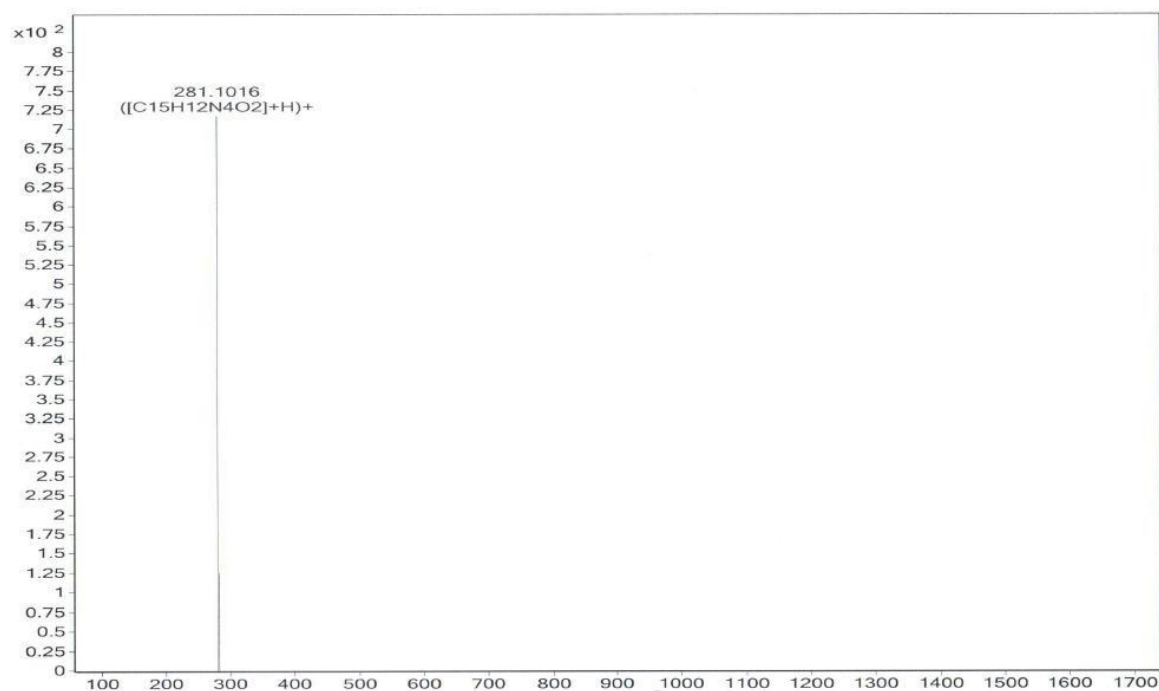
$^1\text{H-NMR}$



^{13}C -NMR

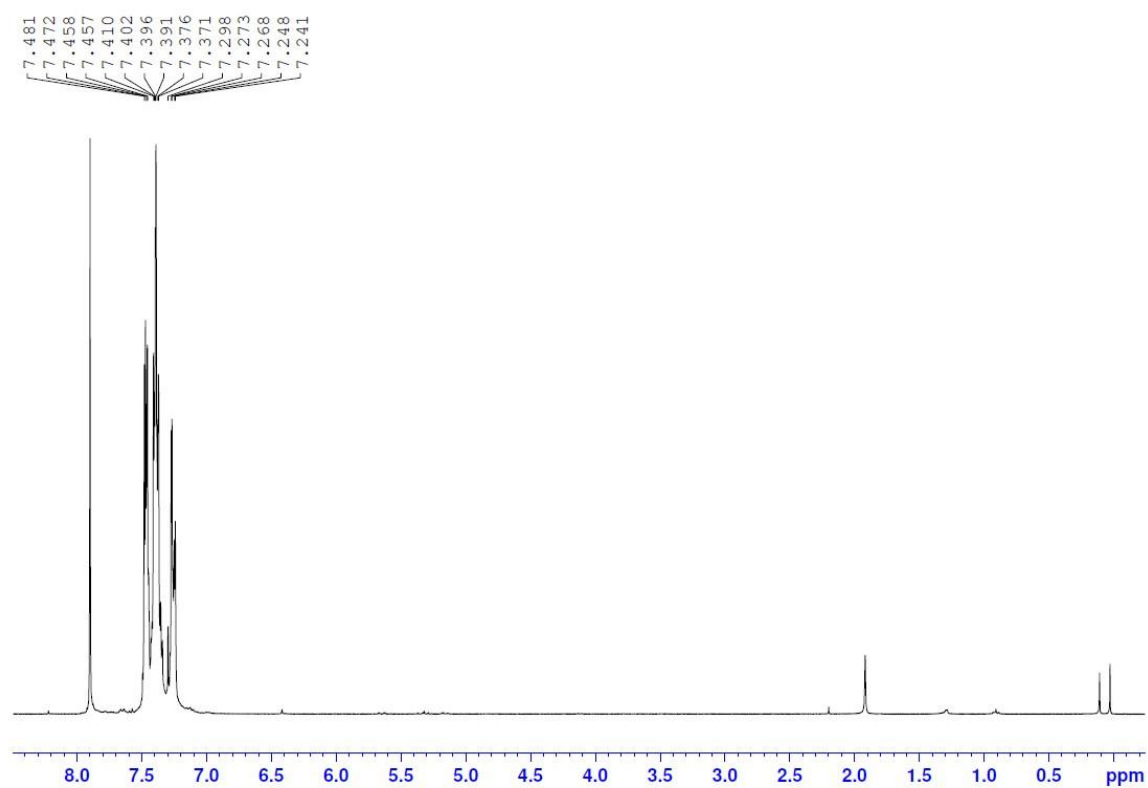


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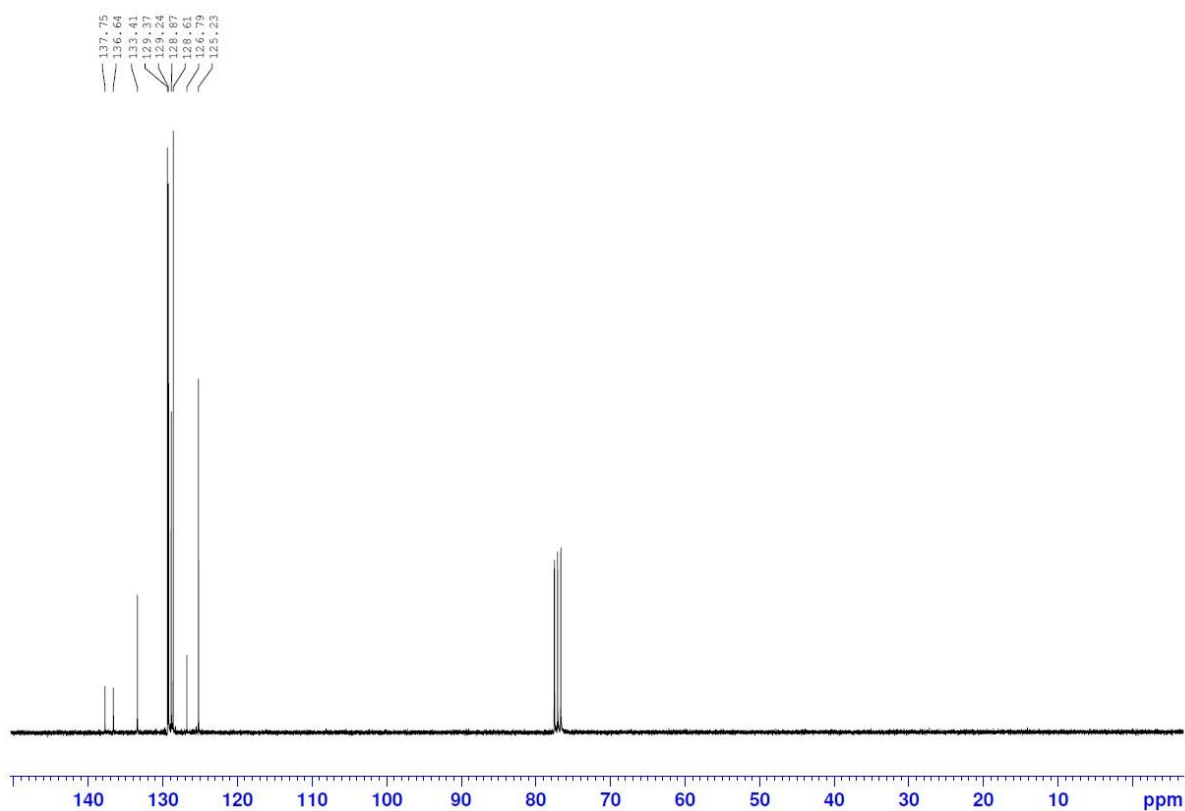


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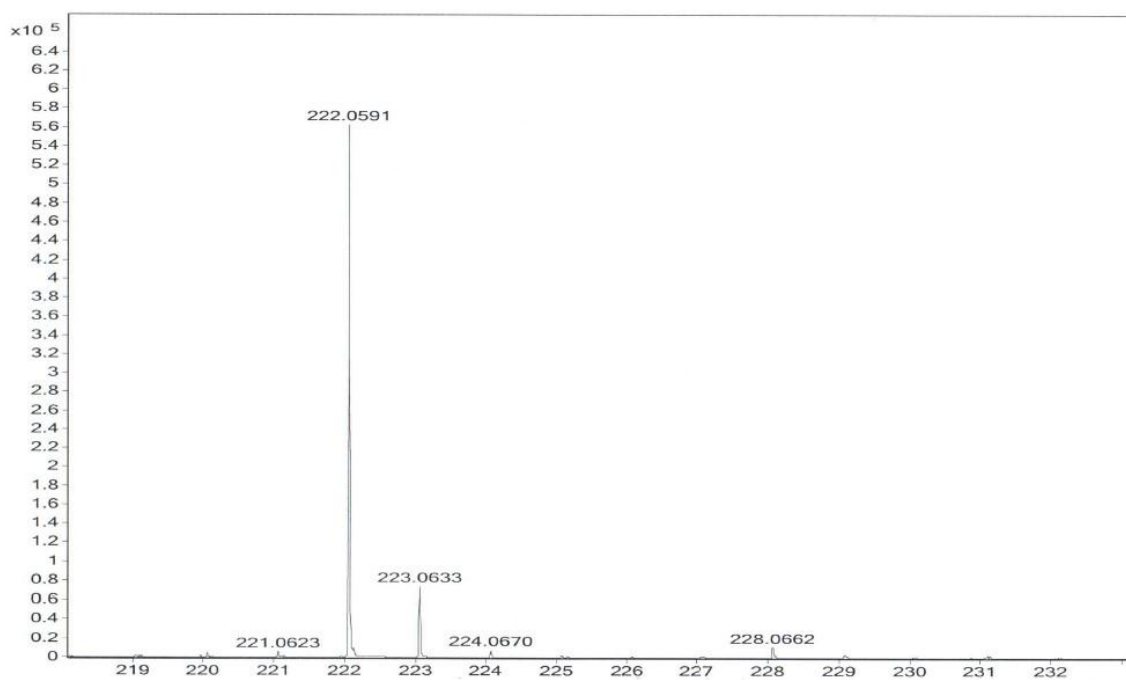
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¹³C-NMR

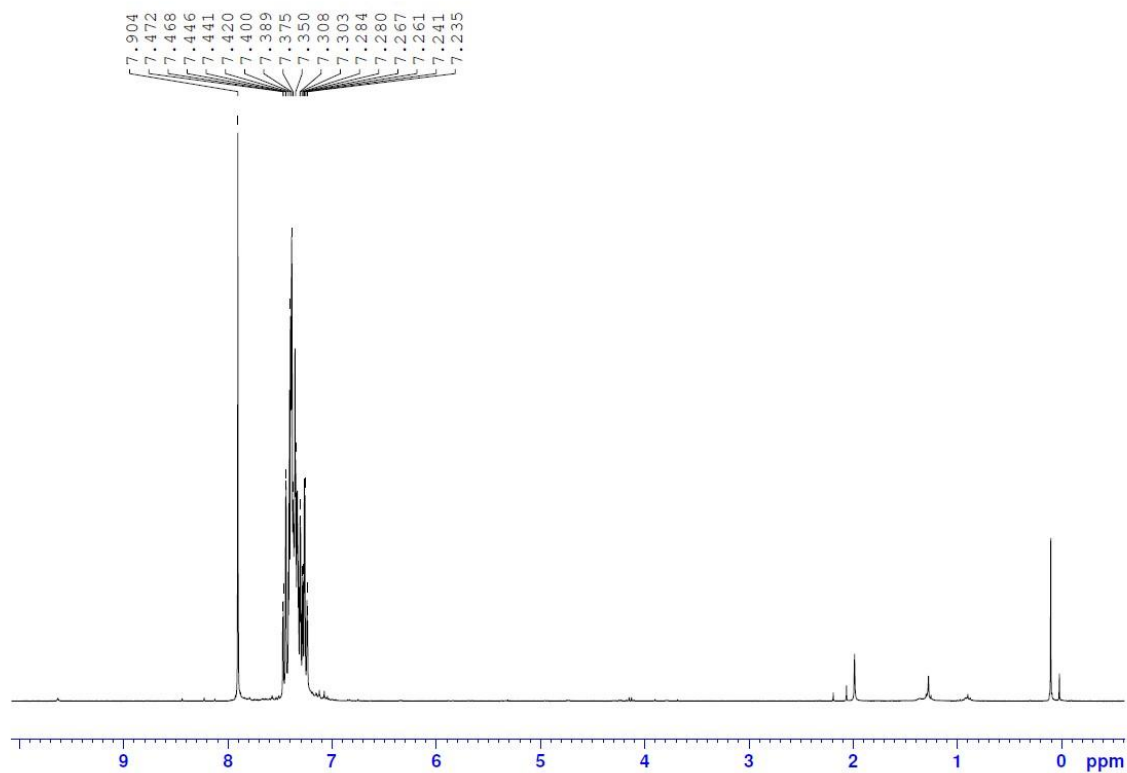


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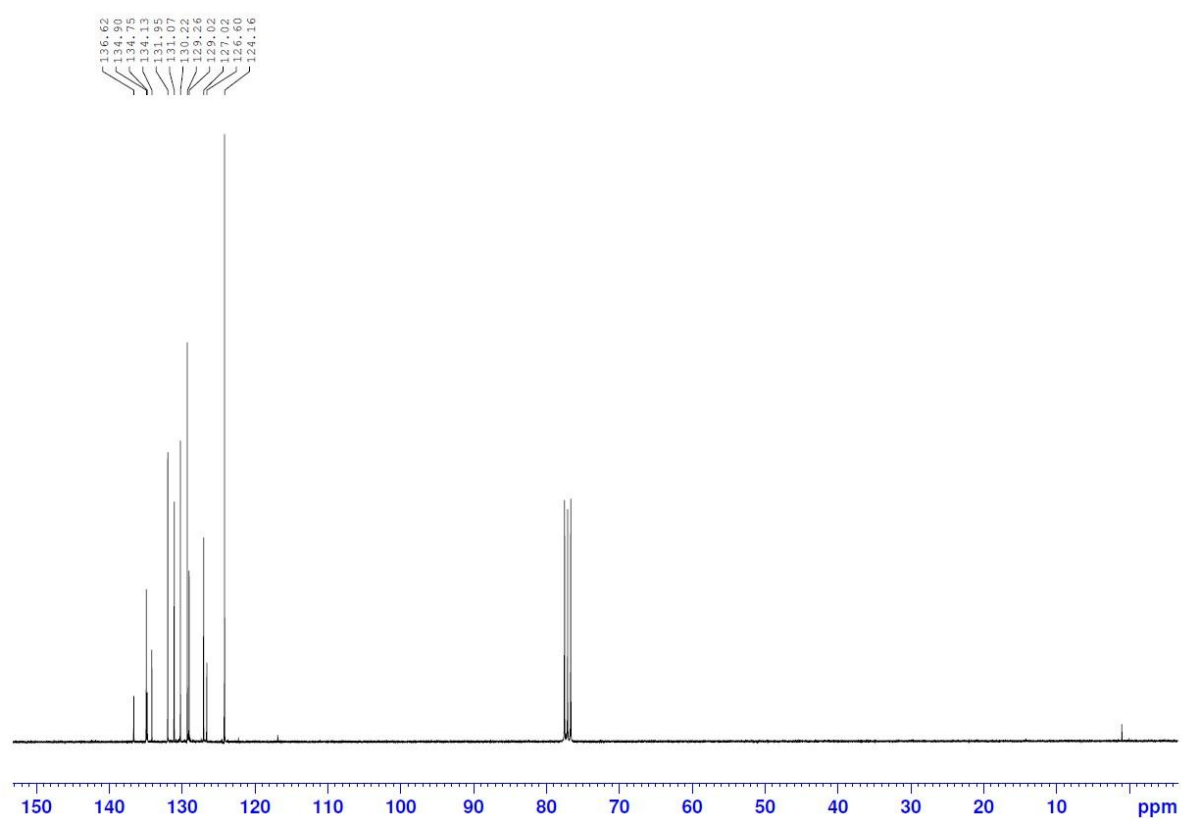


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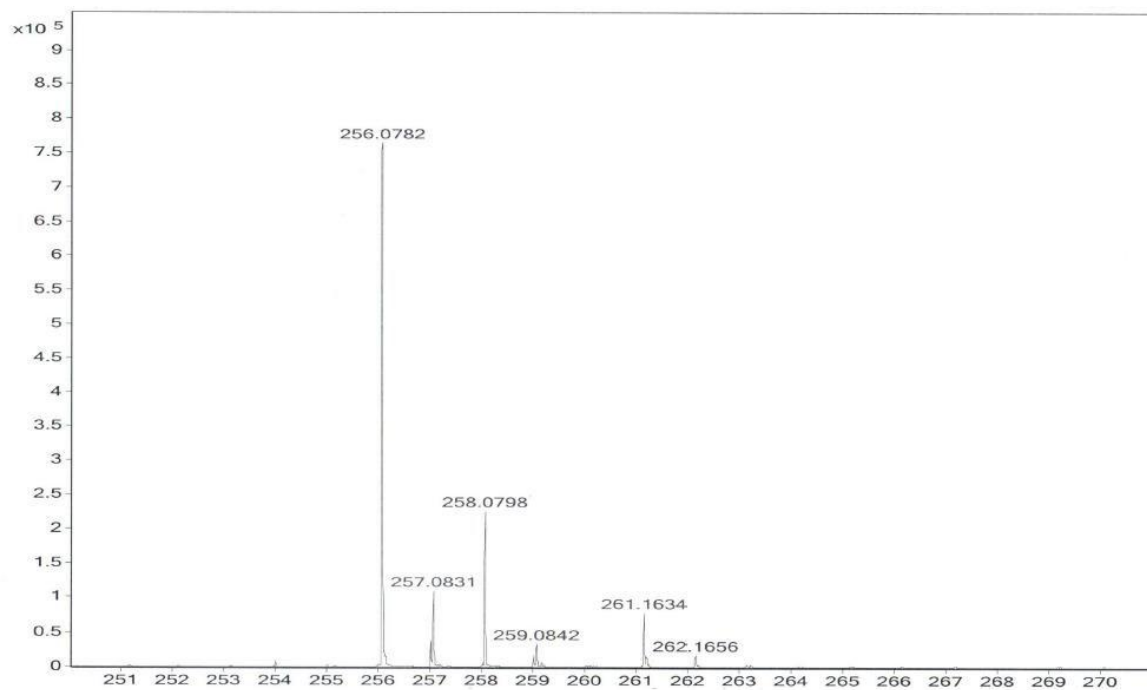
¹H-NMR



^{13}C -NMR

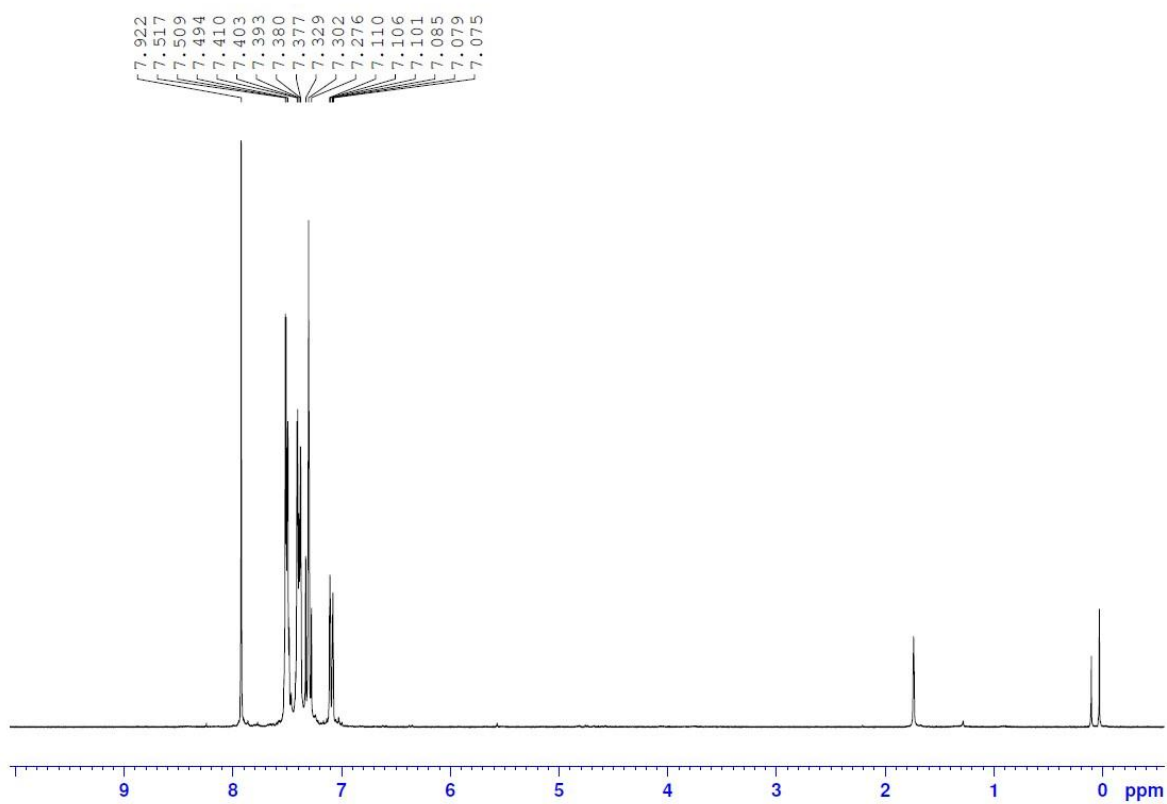


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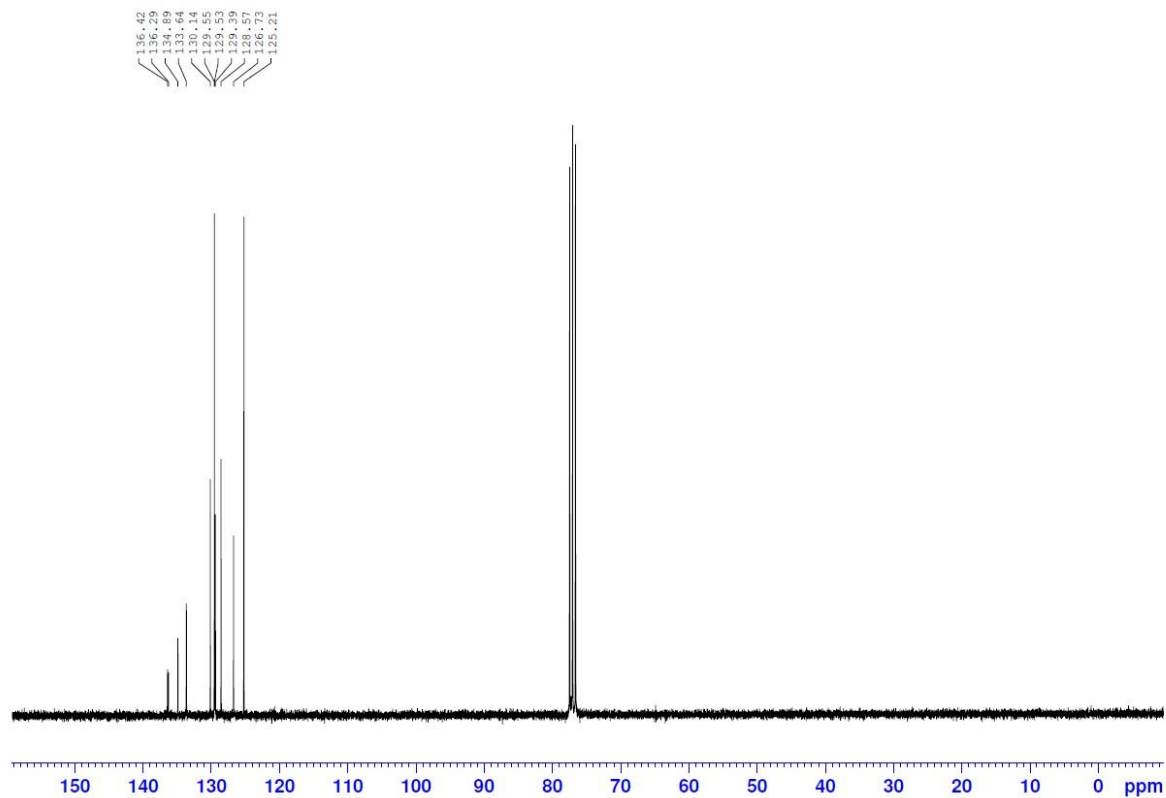


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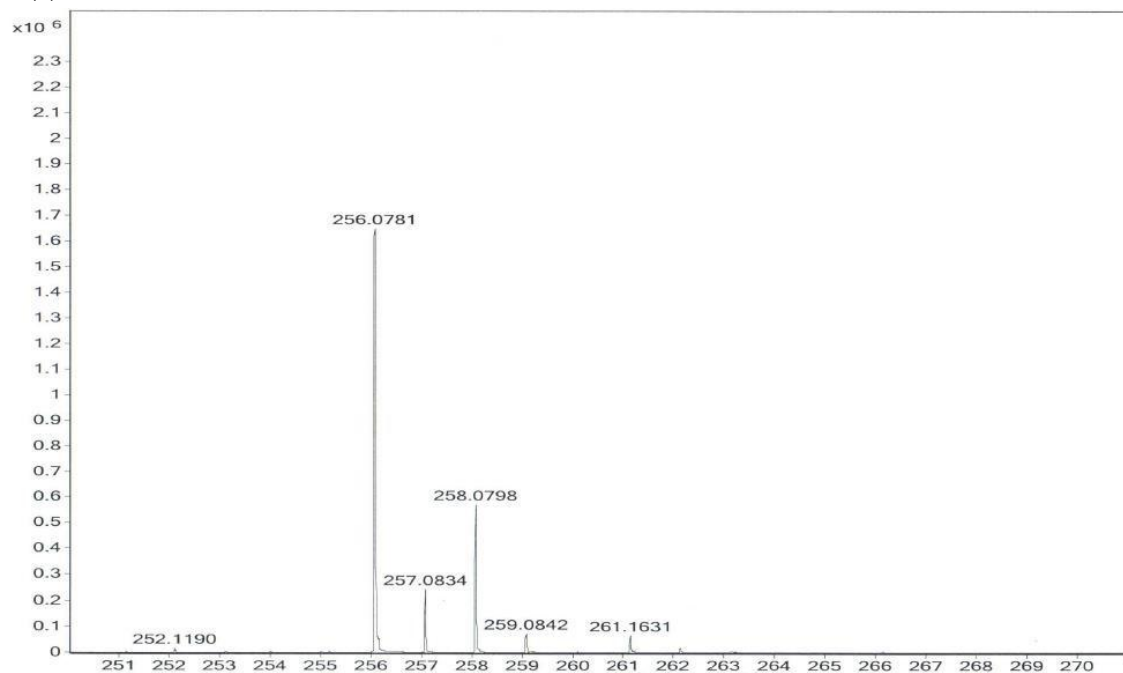
¹H-NMR



¹³C-NMR

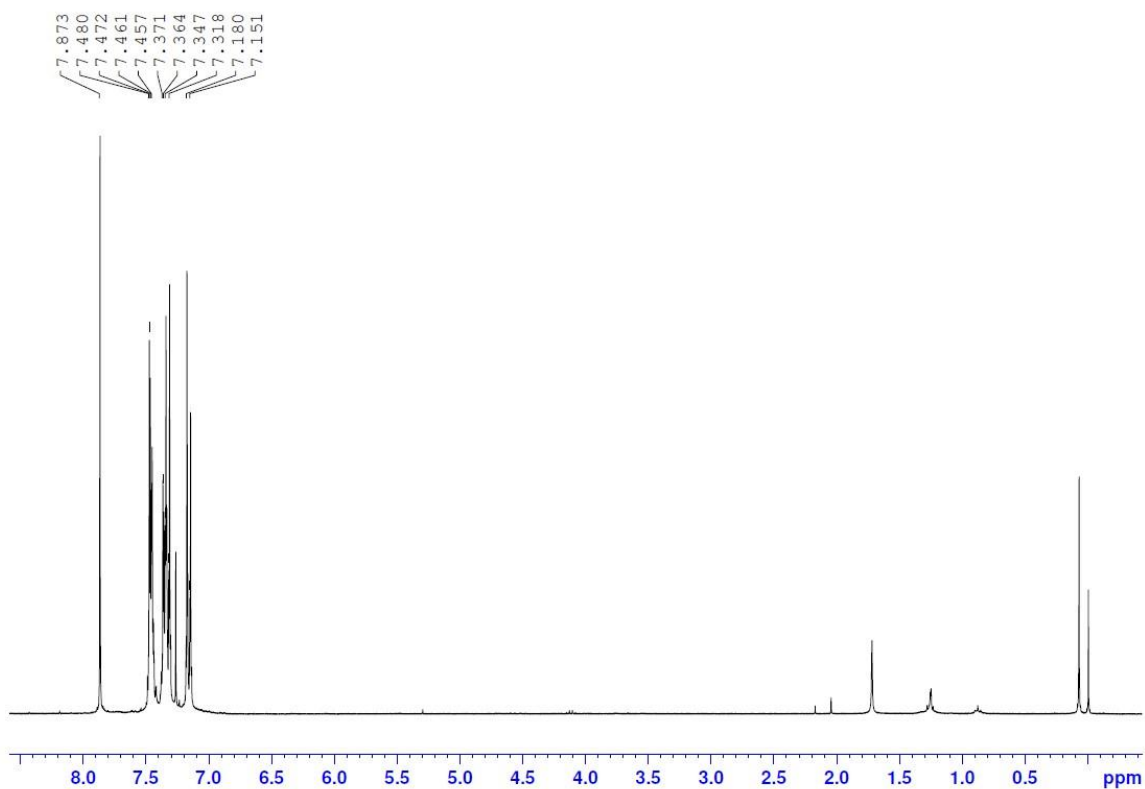


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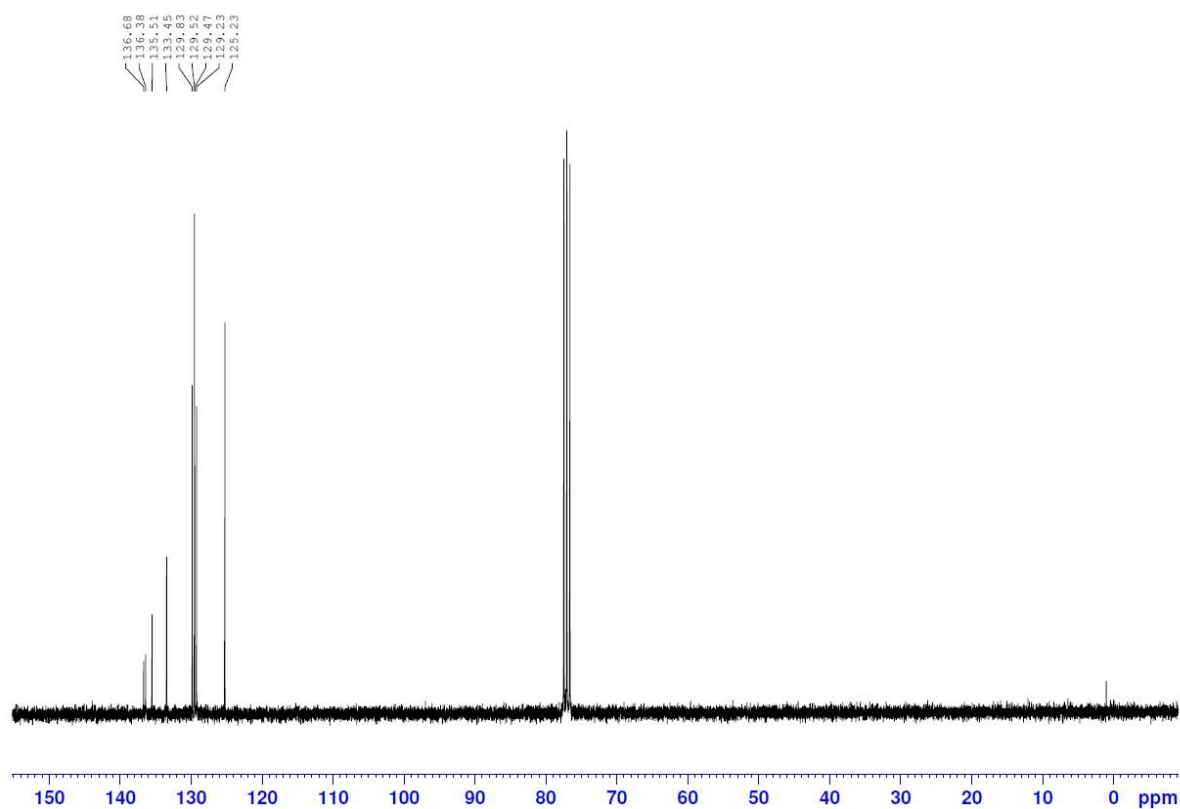


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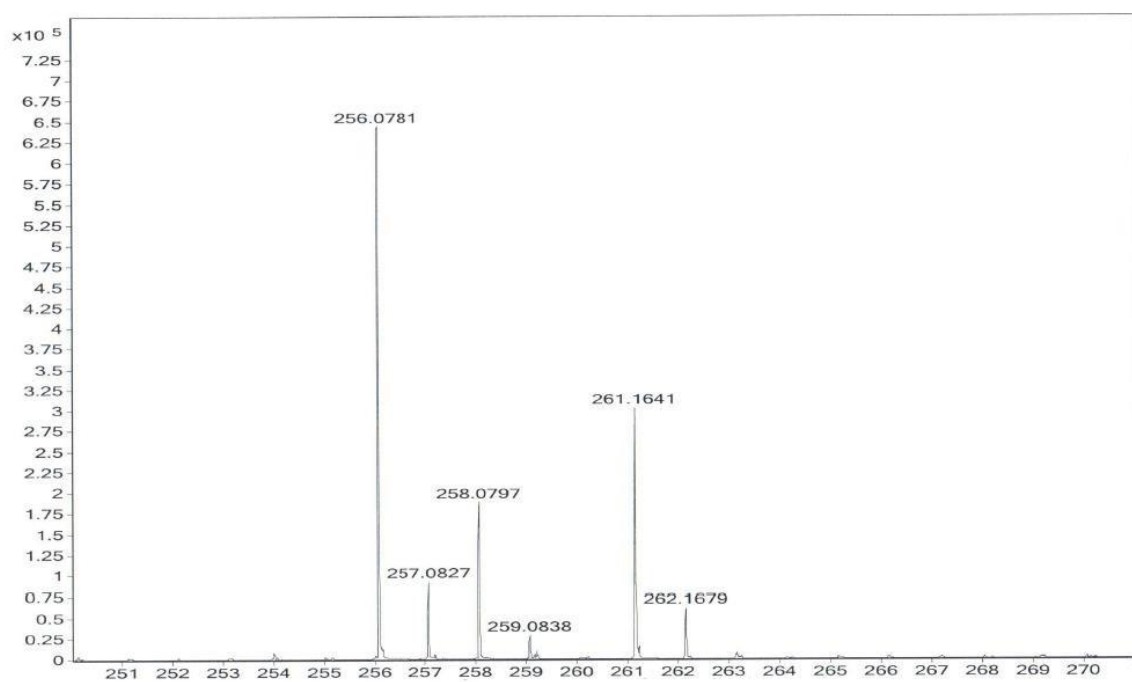
¹H-NMR



¹³C-NMR

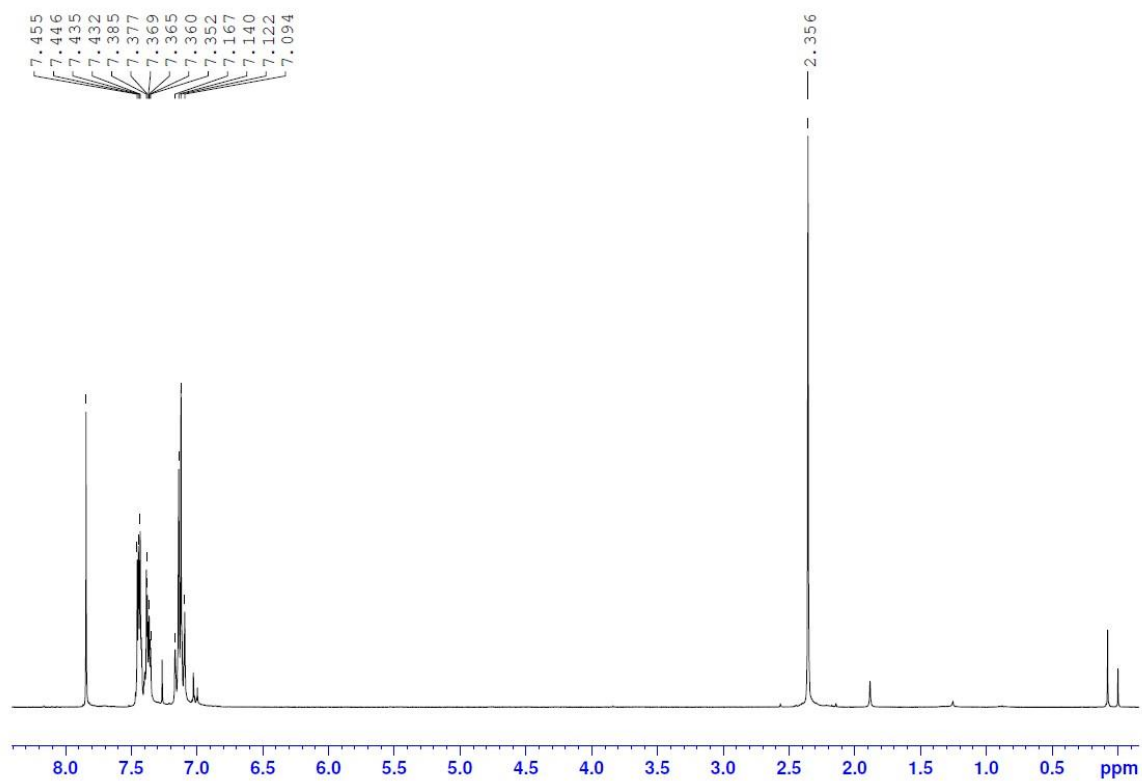


ESI(+)-MS

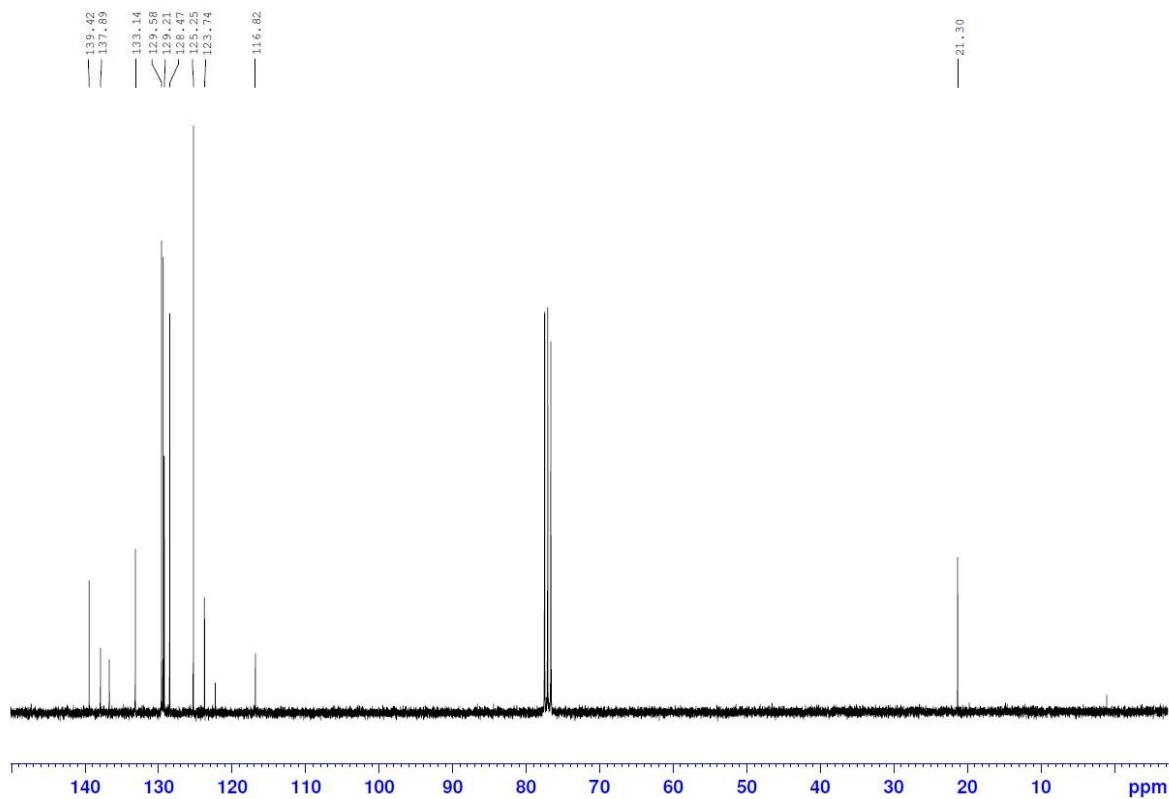


5-(4-methylphenyl)-1-phenyl-1,2,3-triazole (31)

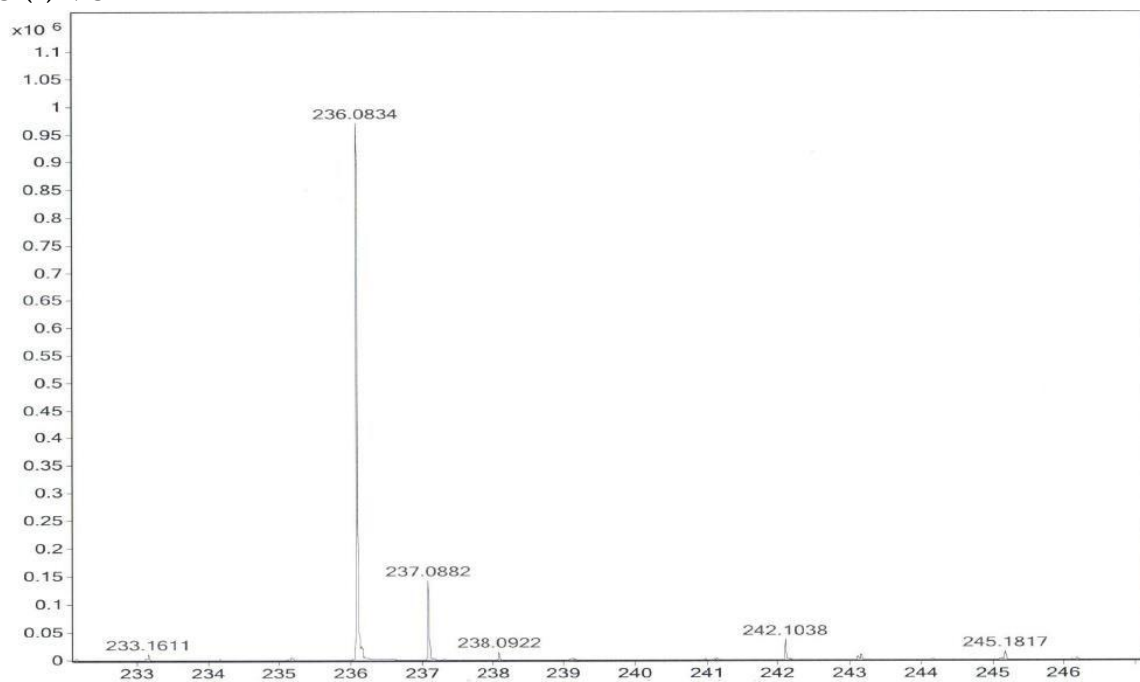
$^1\text{H-NMR}$



$^{13}\text{C-NMR}$

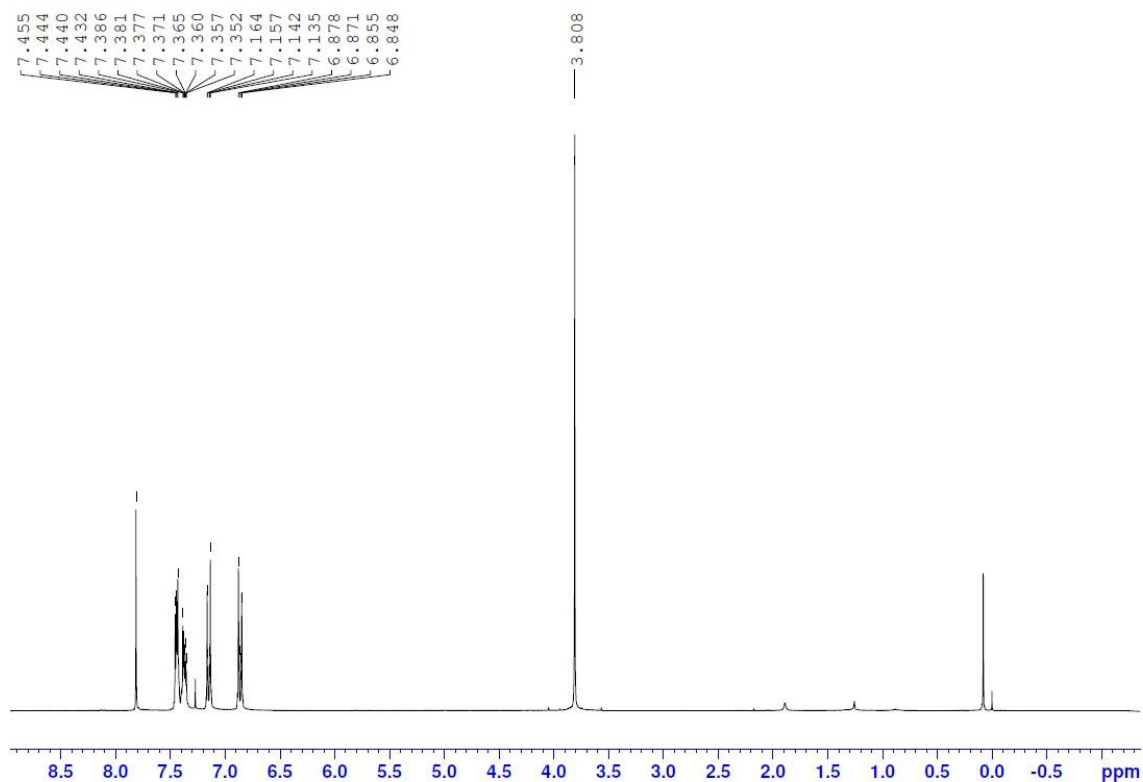


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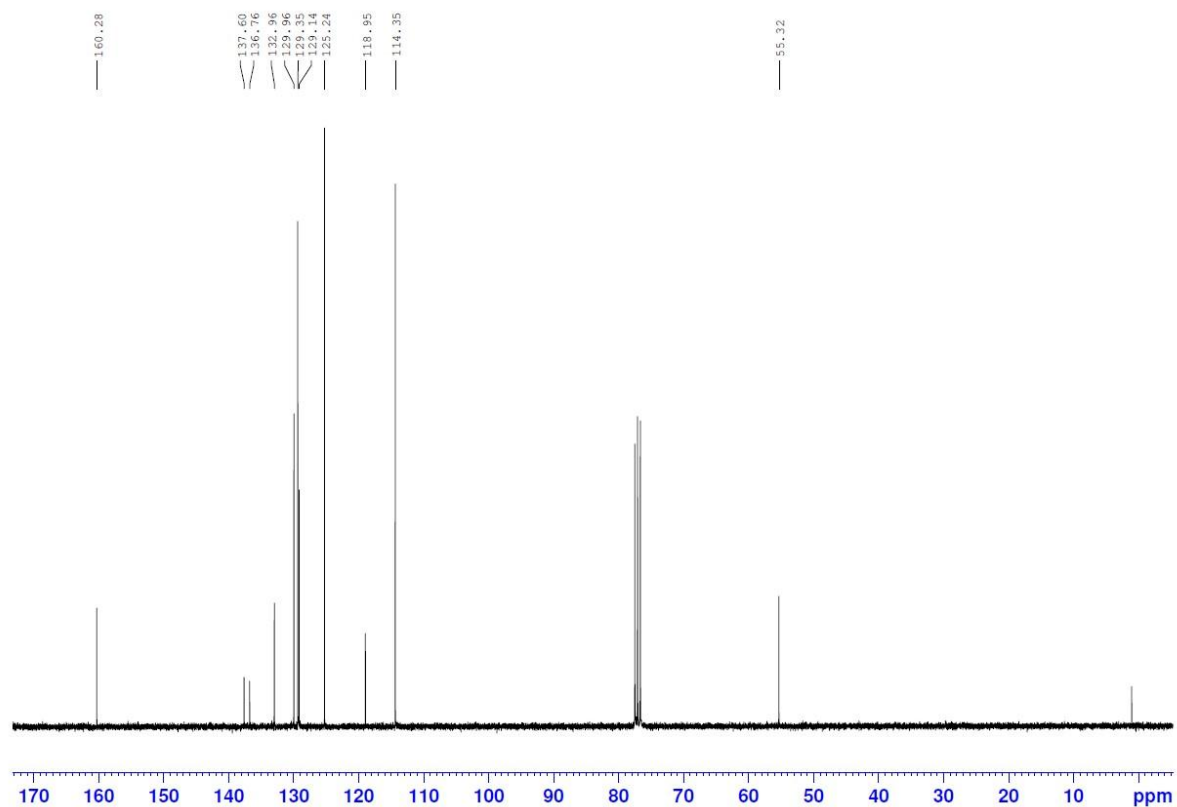


5-(4-methoxyphenyl)-1-phenyl-1,2,3-triazole (3m)

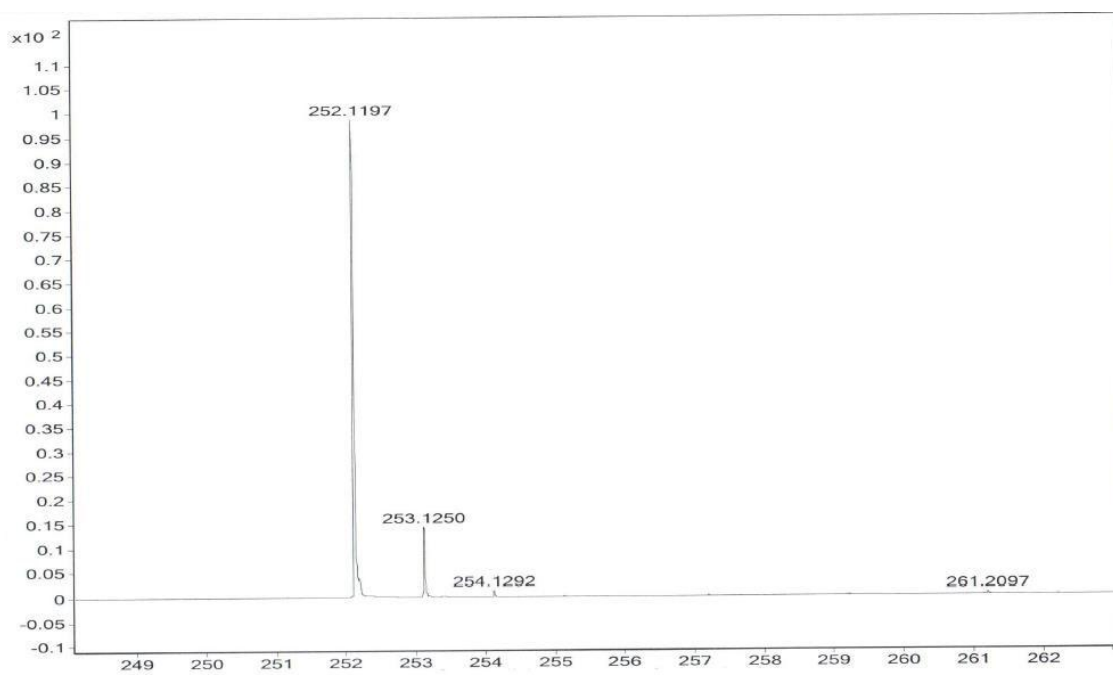
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¹³C-NMR

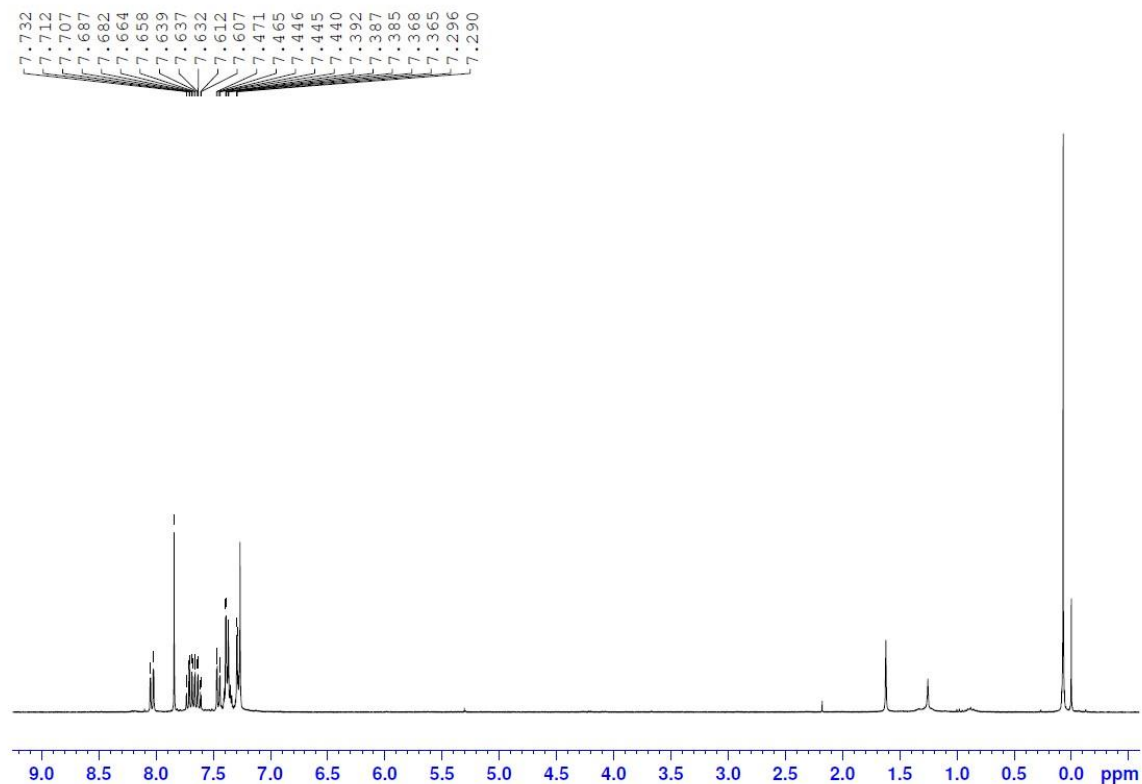


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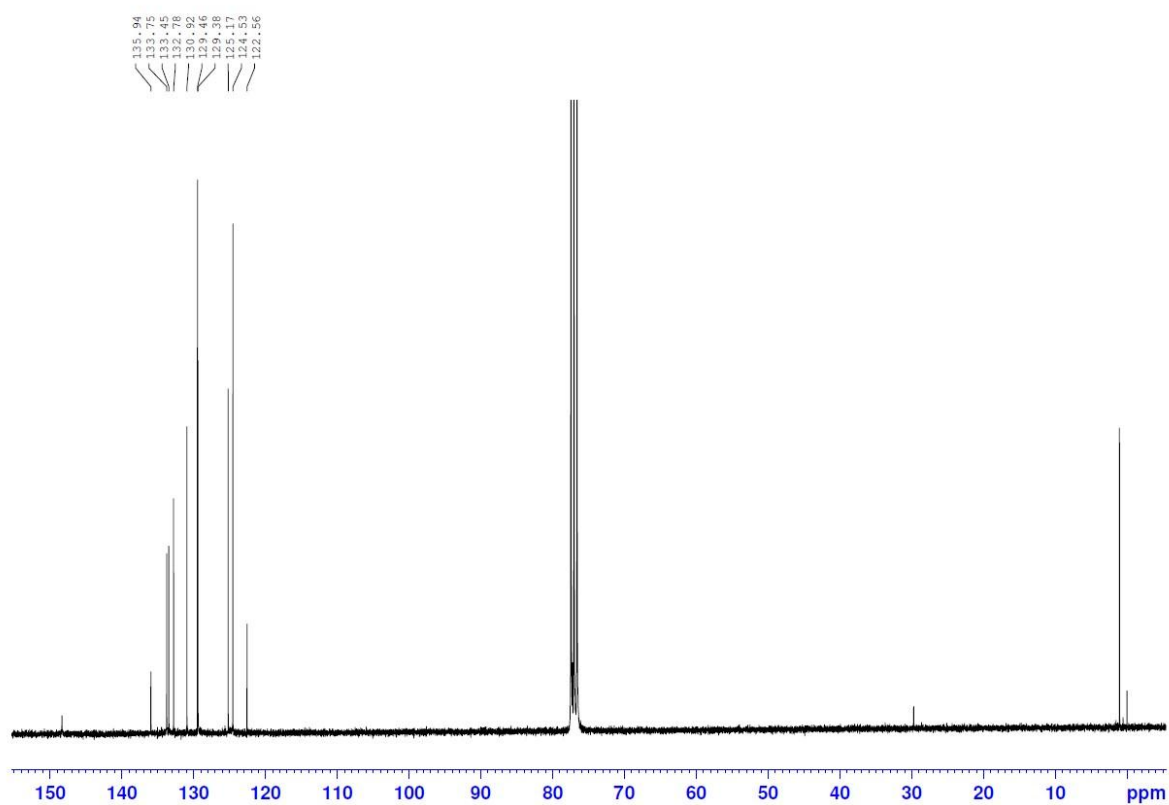


5-(2-nitrophenyl)-1-phenyl-1,2,3-triazole (3n)

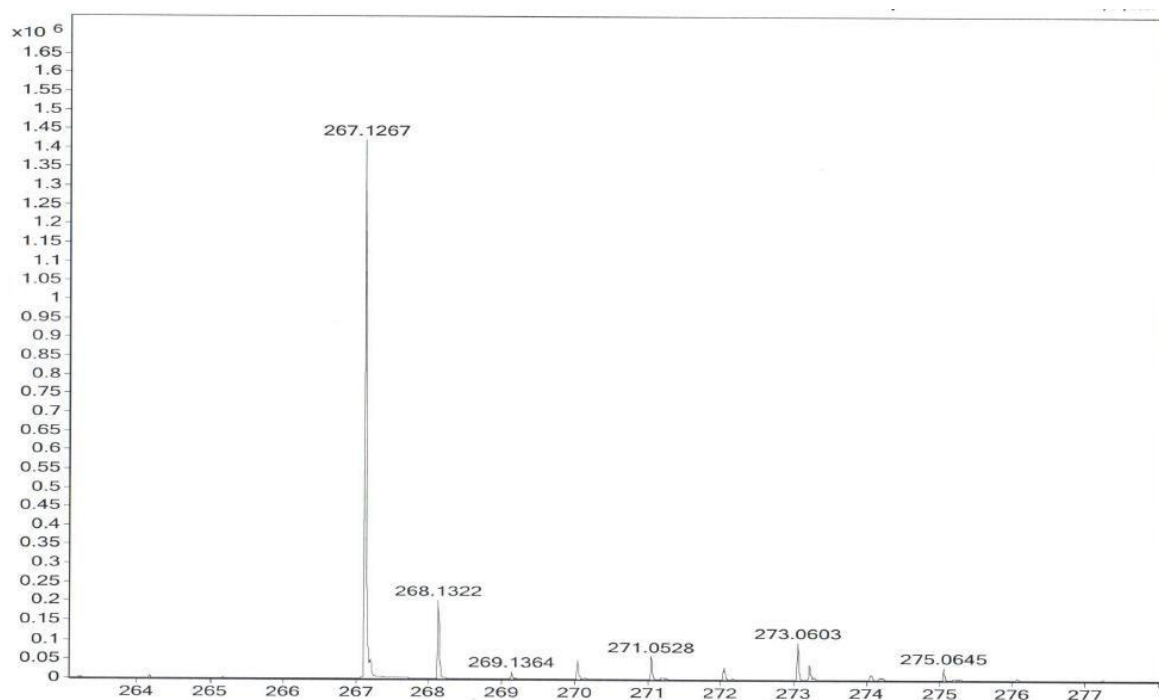
¹H-NMR



¹³C-NMR



ESI(+)-MS



2. Theoretical Calculations

2.1. Computational Details

All of the calculations were performed using the Gaussian09 program [1]. Computations were done using B3LYP functional [2,3] in conjunction with Grimme's dispersion correction [4,5]. Standard basis sets def2SVP and def2TZVP were employed [6,7]. Geometry full optimizations were made at the B3LYPD3BJ/def2SVP level and then single point calculations at the B3LYP-D3BJ/def2TZVP level were carried out in order to obtain more accurate values of the energies. The nature of stationary points was defined on the basis of calculations of normal vibrational frequencies (force constant Hessian matrix). The optimizations were carried out using the Berny analytical gradient optimization method [8,9]. Minimum energy pathways for the reactions studied were found by gradient descent of transition states in the forward and backward direction of the transition vector (IRC analysis), [10,11] using the Hratchian-Schlegel algorithm [12]. Structural representations were generated using CYLView [13].

2.2. Uncatalyzed Cycloaddition

Table S1. Absolute (hartrees) and relative (kcal/mol) energies (B3LYP-D3BJ/Def2TZVP/CPCM = water// B3LYPD3BJ/Def2SVP) corresponding to the reaction between **NS** and **PA**.

	E(0)	G	im. freq	$\Delta E(0)^a$	ΔG^a
NS	-514.252731	-514.288493			
PA	-395.912133	-395.943985			
TS1n	-910.135865	-910.182470	-417.7	18.2	31.4
TS1x	-910.135466	-910.182158	-413.2	18.4	31.6
TS2n	-910.139710	-910.185391	-386.2	15.8	29.5
TS2x	-910.138710	-910.185861	-393.0	16.4	29.3
P14	-910.185874	-910.233083		-13.2	-0.4
P15	-910.185728	-910.232347		-13.1	0.1

^a Related to **PA** + **NS**.

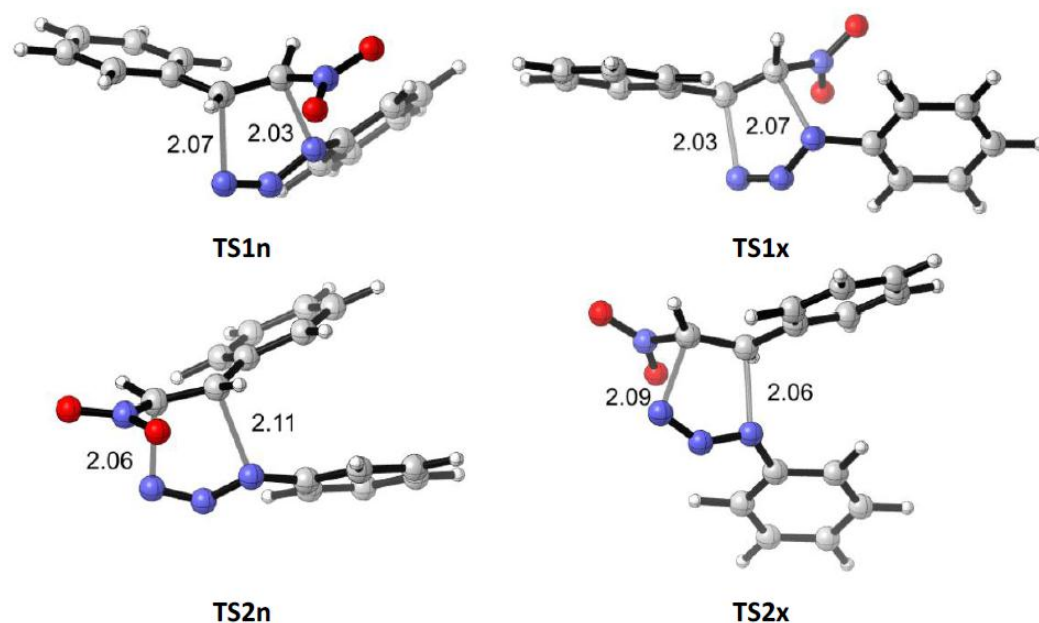


Figure S1. Optimized geometries of transition structures.

2.3. Iron(III) Chloride-Catalyzed Cycloaddition

Table S2. Absolute (hartrees) and relative (kcal/mol) energies (B3LYP-D3BJ/Def2TZVP/CPCM = water// B3LYPD3BJ/Def2SVP) corresponding to the reaction between **NS** and **PA** catalyzed by FeCl_3 .

Title	E(0)	G	im. freq	$\Delta E(0)^a$	ΔG^a
FeCl₃	-2644.511597	-2644.545020			
NS-Fe	-2644.511597	-3158.780212			
PA	-395.912133	-395.943985			
TS1n-Fe	-3554.676414	-3554.735544	-448.2	20.6	34.8
TS1x-Fe	-3554.689750	-3554.748587	-373.8	12.2	26.7
TS2n-Fe	-3554.682053	-3554.744016	-457.8	17.1	29.5
TS2x-Fe	-3554.694012	-3554.753395	-418.2	9.5	23.6
P14-Fe	-3554.720810	-3554.783938		-7.3	4.5
P15-Fe	-3554.722309	-3554.783128		-8.2	5.0

^a Related to **PA** + **NS-Fe**.

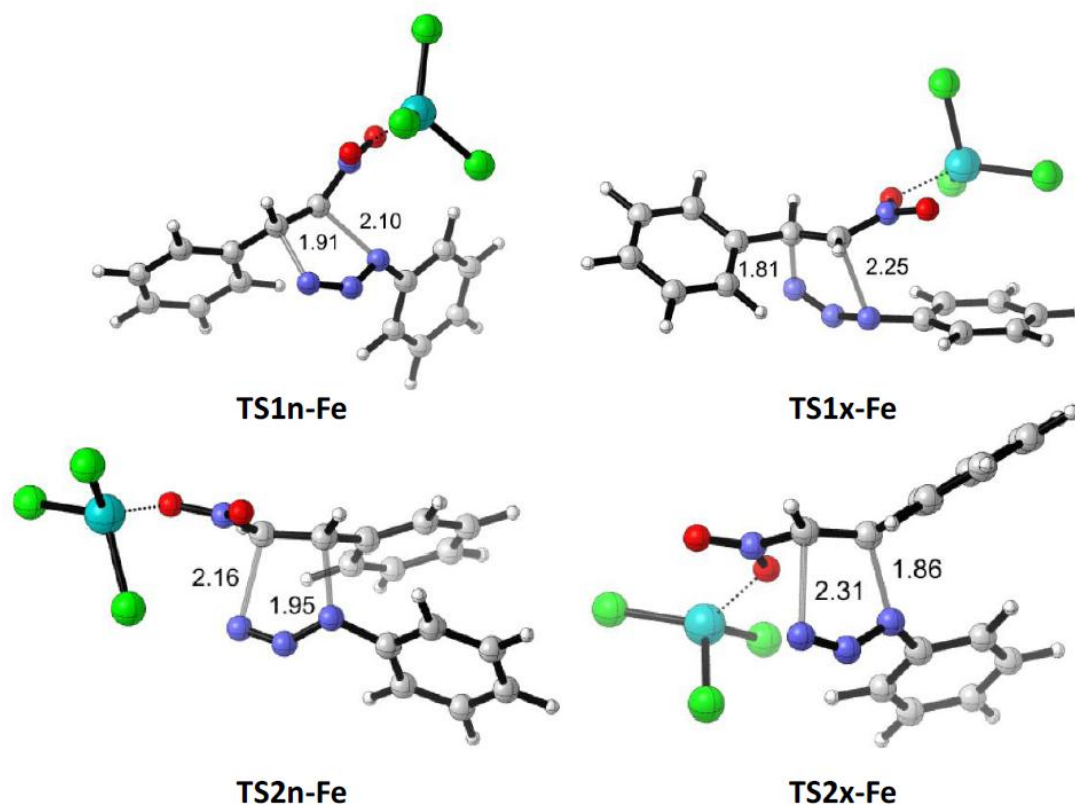


Figure S2. Optimized geometries of transition structures.

2.4. Denitration Reaction

Table S3. Absolute (hartrees) and relative (kcal/mol) energies (B3LYP-D3BJ/Def2TZVP/CPCM = water// B3LYPD3BJ/Def2SVP) corresponding to the denitration of **P15**.

Title	E(0)	G	im. freq	$\Delta E(0)^a$	ΔG^a
FeCl₃	-2644.511597	-2644.545020			
HNO₂	-205.777067	-205.801027			
P15	-910.185728	-910.232347			
TS3	-910.151094	-910.196560	-584.8	21.7	22.5
3h	-704.430619	-704.471295		-13.8	-25.1

^a Related to **P15**.

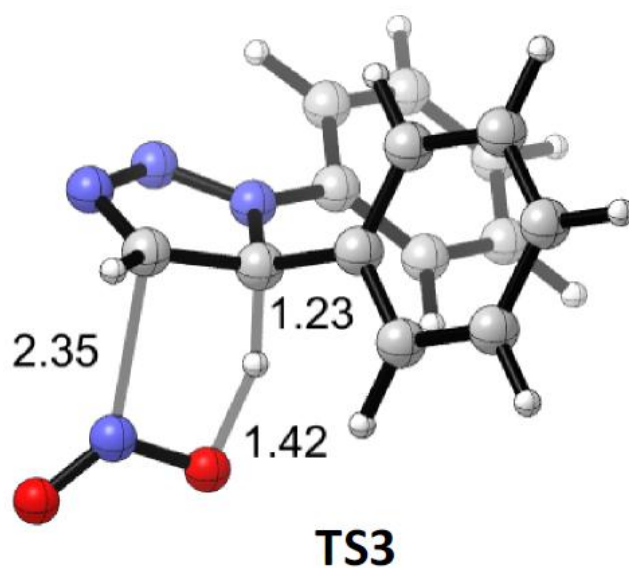


Figure S3. Optimized geometry of transition structure.

3. Cartesian Coordinates

FeCl3

0 2

Fe	4.9770894696	-0.5574901401	2.3293904510
Cl	4.5773932593	1.5031354156	2.6118550302
Cl	4.6360608156	-1.9173369620	3.9168686898
Cl	6.0197002956	-1.2005695448	0.6016544602

HNO2

0 1

N	3.4285475983	-1.8826535475	-0.5405215606
O	4.3040760833	-2.7258254914	0.1647044200
O	3.2474361569	-2.2692252712	-1.6302646322
H	4.3636822115	-2.2950458499	1.0344774328

NS-FeCl3

0 2

C	0.6157774704	-0.4905080346	0.0235914490
H	0.7182722320	-1.0935557023	0.9301482778
C	1.7527486831	0.0505136135	-0.4634977986
H	1.8656348771	0.6889236850	-1.3364864472
C	-0.7189070095	-0.3481654050	-0.5281930410
C	-1.7871129916	-0.9818877138	0.1402316134
C	-0.9931709558	0.3939874751	-1.6981305577
C	-3.0899357713	-0.8785531333	-0.3429289742
H	-1.5825388673	-1.5572520667	1.0462096703
C	-2.2938822357	0.4949625073	-2.1776293059
H	-0.1839621388	0.8935856303	-2.2337582651
C	-3.3451492432	-0.1403997911	-1.5018997773

H	-3.9079008302	-1.3735875881	0.1843524825
H	-2.4960657169	1.0711426807	-3.0828975817
H	-4.3655183025	-0.0575113735	-1.8829813421
N	2.9981648631	-0.1658489987	0.2000653691
O	3.9878105870	0.3964453089	-0.2133593648
O	3.0085561494	-0.9345300508	1.1935907800
Fe	4.5293078006	-0.8136414608	2.6091532474
Cl	4.3888291101	1.2900234697	3.0301884609
Cl	3.6198383447	-2.0724436962	4.0884576674
Cl	6.4683677253	-1.5451611355	2.0871290979

NS

0 1

C	0.6158600000	-0.4434960000	0.0002310000
H	0.9292150000	-1.4915870000	0.0005870000
C	1.6062000000	0.4611900000	-0.0002710000
H	1.5181740000	1.5453130000	-0.0006020000
C	-0.8191830000	-0.1752190000	0.0000870000
C	-1.7067250000	-1.2684470000	-0.0000310000
C	-1.3567840000	1.1285480000	0.0001620000
C	-3.0872700000	-1.0696150000	-0.0001070000
H	-1.3006340000	-2.2829260000	-0.0000950000
C	-2.7342480000	1.3257690000	0.0000480000
H	-0.6911520000	1.9936850000	0.0003640000
C	-3.6045440000	0.2279880000	-0.0000850000
H	-3.7610240000	-1.9292530000	-0.0002040000
H	-3.1364280000	2.3413170000	0.0000920000
H	-4.6852530000	0.3874920000	-0.0001570000
N	2.9976000000	0.0303580000	-0.0000520000
O	3.8299730000	0.9280350000	-0.0000170000
O	3.2530340000	-1.1651410000	0.0000400000

PA

0 1

C	-0.8839960000	-1.3125230000	-0.0000100000
C	0.1509470000	-0.3660890000	0.0000900000
C	-0.1527110000	1.0050300000	0.0001210000
C	-1.4859060000	1.4171300000	0.0000320000
C	-2.5203470000	0.4767560000	-0.0000780000
C	-2.2117060000	-0.8876880000	-0.0000940000
H	-0.6251500000	-2.3725020000	-0.0000290000
H	0.6509040000	1.7453110000	0.0002120000
H	-1.7161960000	2.4852320000	0.0000580000
H	-3.5616680000	0.8055790000	-0.0001490000
H	-3.0133280000	-1.6300280000	-0.0001840000
N	1.4718110000	-0.8690780000	0.0001920000
N	2.4206200000	-0.0891630000	-0.0000240000

N	3.3772490000	0.5254850000	-0.0002070000
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C3h

0 1

C	3.4144058173	-0.8238443147	-0.1943157408
C	4.6621573598	-1.2379753057	-0.6715010021
C	5.7372051175	-1.3301381711	0.2137881078
C	5.5710572327	-1.0021486006	1.5626498328
C	4.3180309382	-0.5948946794	2.0303269134
C	3.2324320299	-0.5128599581	1.1575266560
H	4.7695372441	-1.4891262270	-1.7269158995
H	6.7122275609	-1.6558757865	-0.1554567777
H	6.4166223522	-1.0691289574	2.2508011888
H	4.1792141206	-0.3488550916	3.0854239991
H	2.2491147801	-0.2117976150	1.5191810547
N	2.3228509309	-0.7446762590	-1.1026047535
N	2.1058830661	-1.7635571557	-1.9734933134
N	1.0319010431	-1.4930780832	-2.6405661684
C	1.3440809070	0.2093841935	-1.2240093852
C	0.5252893935	-0.3050083367	-2.2182047049
C	1.2814836805	1.4851719414	-0.4999508681
C	0.0409340693	1.9599083080	-0.0398956249
C	2.4298318321	2.2701490808	-0.2893195331
C	-0.0487683190	3.1863728520	0.6204307606
H	-0.8530396875	1.3512697453	-0.1915616092
C	2.3366435780	3.4926429810	0.3746919765
H	3.3971556304	1.9236737975	-0.6560564707
C	1.0988804115	3.9546638513	0.8333142703
H	-1.0194044363	3.5401728761	0.9757172364
H	3.2365149096	4.0924400498	0.5296361624
H	1.0295080588	4.9128017229	1.3535114882
H	-0.3639665914	0.1382721322	-2.6603867955

C3hi

0 1

C	3.3760869828	-0.8121376706	-0.0546911931
C	4.4779116063	-1.4112385273	-0.6784532102
C	5.7175760933	-1.3925528410	-0.0403173094
C	5.8681625262	-0.7753191840	1.2055793864
C	4.7627444232	-0.1817964768	1.8198555847
C	3.5128529310	-0.2032691897	1.1983226546
H	4.3427207606	-1.8836561409	-1.6505426999
H	6.5764325615	-1.8605018443	-0.5267105872
H	6.8431468185	-0.7599209863	1.6972460992
H	4.8671321922	0.2940912585	2.7974478825
H	2.6480155717	0.2359281691	1.6971165292
N	2.1157918141	-0.8291456223	-0.7069611188

N	1.8470906891	-1.7464524708	-1.6649673974
N	0.6463298850	-1.5383461404	-2.0871581017
C	1.0395176287	-0.0134064928	-0.5221366645
C	0.0903871063	-0.4774952932	-1.4185259675
C	-1.2710193262	-0.0063268478	-1.6944962398
C	-2.0412790967	-0.6411316833	-2.6846075110
C	-1.8303529843	1.0730557202	-0.9891163287
C	-3.3367974058	-0.2042623431	-2.9593049654
H	-1.6028134151	-1.4785674127	-3.2288397934
C	-3.1262665348	1.5078801036	-1.2667884033
H	-1.2496643177	1.5789908953	-0.2141587312
C	-3.8853161625	0.8709980148	-2.2533554898
H	-3.9239907074	-0.7072268813	-3.7315171082
H	-3.5465475779	2.3484860392	-0.7094138795
H	-4.9004566937	1.2116684477	-2.4703274445
H	1.0433090817	0.8134509501	0.1786852780

P14-Fe

0 2

C	2.3195870879	-0.5536535831	0.0239776650
C	3.1451703344	-1.2914083507	0.8871368068
C	4.3887080160	-1.7290475189	0.4364948084
C	4.8234337030	-1.4451798426	-0.8628344061
C	3.9974722446	-0.7106945749	-1.7139544481
C	2.7482195555	-0.2605422265	-1.2793401031
H	2.8034817617	-1.5092560245	1.8977736523
H	5.0273254236	-2.3007370823	1.1137679020
H	5.8002077026	-1.7914933142	-1.2059810344
H	4.3226183832	-0.4762011561	-2.7299165695
H	2.1261294918	0.3184761898	-1.9631882749
N	1.0592043429	-0.1028509448	0.4634829825
N	0.6016008085	-0.3489176249	1.7386403318
N	-0.5467413074	0.0740982325	1.9176575876
C	0.1121219178	0.6194982900	-0.3013749807
C	-1.0773955299	0.7243669842	0.7033191970
C	-2.3475167373	0.0943295166	0.1893003862
C	-3.2674478918	0.8891967016	-0.5078885276
C	-2.5899702669	-1.2755932215	0.3496897464
C	-4.4195138300	0.3139242663	-1.0473566322
H	-3.0777696635	1.9594533168	-0.6236000143
C	-3.7458485424	-1.8465126881	-0.1871868037
H	-1.8812964982	-1.8901121788	0.9088330659
C	-4.6599301387	-1.0540572905	-0.8878072098
H	-5.1349076837	0.9377289900	-1.5878813730
H	-3.9353928532	-2.9140657857	-0.0542153120

H	-5.5640616704	-1.5025354947	-1.3059528403
H	-0.1342686276	0.1931507243	-1.2815072339
H	-1.2651521373	1.7802094934	0.9531836461
N	0.5930888262	2.0329711619	-0.6261469102
O	0.3543854549	2.4889694701	-1.7119929718
O	1.1143160917	2.6552915799	0.3119664369
Fe	0.6630529398	4.7116499609	0.5552444550
Cl	-1.4785242948	4.4343674894	0.3486894502
Cl	1.2583064183	5.1384731539	2.5535677976
Cl	1.6312961086	5.9481595210	-0.8810626421

P14

0 1

C	0.3837474471	1.3218398116	0.3865178374
C	1.0500509141	1.5226043862	-0.8332041350
C	2.2175584307	2.2822163393	-0.8602391523
C	2.7336792639	2.8489290831	0.3103052912
C	2.0666455449	2.6437808748	1.5185587843
C	0.8962743522	1.8827917991	1.5663160482
H	0.6446525090	1.0800343557	-1.7417111108
H	2.7309177305	2.4328665135	-1.8128368605
H	3.6497317325	3.4421508525	0.2793782461
H	2.4579078015	3.0742767591	2.4430957496
H	0.4006615320	1.7288952146	2.5256594236
N	-0.8001109702	0.5635806373	0.4319041002
N	-1.3218805030	-0.0300000551	-0.6845350333
N	-2.3901283137	-0.6169632809	-0.4553062376
C	-1.5826634799	0.2957471004	1.5884724718
C	-2.7652561220	-0.4909487408	0.9675950150
C	-4.1143566225	0.1671127718	1.1775689481
C	-4.5624846918	0.3797464403	2.4898563202
C	-4.9138924413	0.5636354399	0.1006743984
C	-5.7966154271	0.9878518717	2.7210752601
H	-3.9381239834	0.0717028627	3.3336253441
C	-6.1510035692	1.1714247624	0.3364410359
H	-4.5640168263	0.3901375943	-0.9176150362
C	-6.5948050338	1.3849046214	1.6430150037
H	-6.1374307585	1.1504224790	3.7461927670
H	-6.7699800351	1.4800924046	-0.5092821545
H	-7.5616063757	1.8604888698	1.8235373240
N	-0.8308106015	-0.5977934195	2.5885649524
O	-1.0546471967	-0.3794588793	3.7659380251
O	-0.1226206082	-1.4674900829	2.1308853180
H	-1.8670491505	1.1822603183	2.1671261421
H	-2.7903141877	-1.5140389946	1.3773805737

P15-Fe

0 2

C	-1.8888050498	-0.6672036669	0.2479774828
C	-3.0218451063	-0.9554327630	1.0256298324
C	-4.2865323976	-0.6354515658	0.5367305444
C	-4.4388307755	-0.0302755933	-0.7156814883
C	-3.3066328712	0.2522206315	-1.4813388876
C	-2.0305690869	-0.0616410121	-1.0087916226
H	-2.8973270141	-1.4298314950	1.9980563263
H	-5.1649963997	-0.8633452577	1.1448340513
H	-5.4337891501	0.2180284059	-1.0904673909
H	-3.4088950105	0.7228236506	-2.4616293277
H	-1.1579490305	0.1700306829	-1.6185259344
N	-0.6003070714	-0.9833717249	0.7263298357
N	-0.4137920580	-1.7031414735	1.8284739557
N	0.7935672796	-1.9709496615	2.0671246611
C	0.6624624903	-0.6615208581	0.0512588843
C	1.6232692370	-1.4149104398	1.0120375786
C	0.9760117117	0.8099791560	-0.0619452926
C	1.8172557726	1.2384982894	-1.0975071349
C	0.4964397624	1.7317979750	0.8761377896
C	2.1794612345	2.5836840172	-1.1888863069
H	2.1973167251	0.5229973654	-1.8290616633
C	0.8546317828	3.0776858312	0.7759003006
H	-0.1666090906	1.3985043151	1.6776649126
C	1.6976492684	3.5051210704	-0.2546474108
H	2.8401677426	2.9082470425	-1.9956812374
H	0.4727682112	3.7956889914	1.5051720286
H	1.9774884766	4.5583643862	-0.3301612260
H	2.4498104298	-0.8017124996	1.3885978146
H	0.6754028645	-1.1227384507	-0.9481461282
N	2.2880309965	-2.5183771894	0.2146212254
O	3.3278780834	-2.1538320267	-0.3744695843
O	1.7651402448	-3.5847538552	0.0907865830
Fe	3.6723773796	-2.3845033521	-2.4150267715
Cl	4.6640621453	-0.5634857532	-2.9429141562
Cl	4.7994135170	-4.0953974138	-2.9778917400
Cl	1.5999232767	-2.2986014085	-3.0463815034

P15

0 1

C	1.1298225558	-1.4391481881	-0.5262040891
C	1.5760899869	-2.2860134969	-1.5553196462
C	2.8231229654	-2.8975234384	-1.4500083015
C	3.6381847363	-2.6793326734	-0.3336176397
C	3.1880570113	-1.8377693627	0.6845635140
C	1.9404624461	-1.2163921716	0.5971235171
H	0.9371043073	-2.4565444480	-2.4204898672

H	3.1614743942	-3.5556417605	-2.2538181358
H	4.6146593118	-3.1622476529	-0.2599404356
H	3.8113175432	-1.6562214592	1.5631680493
H	1.6107875576	-0.5554152015	1.3973545512
N	-0.1268246585	-0.8147981243	-0.6155015798
N	-0.9677003942	-1.0679734889	-1.6218233757
N	-2.0649654383	-0.4677961762	-1.5307483050
C	-0.6944627217	0.1392046689	0.3460468769
C	-2.0891243527	0.3070352820	-0.2771839334
C	0.0826703605	1.4323815608	0.4437379562
C	0.1842492210	2.0926809893	1.6739721088
C	0.6704034021	2.0007707348	-0.6936583439
C	0.8615802443	3.3110218806	1.7671032546
H	-0.2669134777	1.6487229483	2.5657057987
C	1.3495101865	3.2166039949	-0.6000979062
H	0.6057962003	1.4824191844	-1.6531824210
C	1.4456788652	3.8748321770	0.6298292863
H	0.9373887384	3.8180464218	2.7317255624
H	1.8086453801	3.6508013305	-1.4911067126
H	1.9795163721	4.8251042989	0.7021839843
N	-3.1962631741	-0.2944874705	0.5877468334
O	-4.2930272040	0.2091105341	0.4727972193
O	-2.9057118542	-1.2491538836	1.2850282081
H	-2.4034377431	1.3409493277	-0.4576253078
H	-0.7906167381	-0.3411923273	1.3306962801

TS1n-Fe

0 2

C	1.2370610623	2.2777229878	0.4709096561
C	2.5036052548	2.7391885526	0.8719242591
C	2.9209340613	4.0088414038	0.4796953941
C	2.0954620614	4.8061355935	-0.3235860257
C	0.8405678589	4.3365627178	-0.7240828764
C	0.3981347624	3.0767156118	-0.3217021254
H	3.1391225682	2.1070649960	1.4959600776
H	3.8970768204	4.3797942393	0.8000011559
H	2.4309629058	5.7989238762	-0.6311348268
H	0.1927072452	4.9617766500	-1.3419667817
H	-0.5872019655	2.6980459682	-0.5964760992
N	0.7732327087	0.9870746243	0.7753929910
N	1.2504557722	0.2883427886	1.7166594209
N	1.5612183203	-0.8476712826	1.8297795151
C	0.9600736229	-0.4833989069	-0.7098465918
C	1.5375974784	-1.5320203947	0.0465235132
C	2.9641301156	-1.8744209751	-0.1557167396
C	3.3854839816	-3.2043130067	-0.0026682062
C	3.9189573810	-0.8902738054	-0.4680751484

C	4.7273907855	-3.5475978569	-0.1741582710
H	2.6524079680	-3.9739727719	0.2504411738
C	5.2589614922	-1.2344001168	-0.6390432814
H	3.6195092775	0.1566937359	-0.5640352128
C	5.6672109806	-2.5647292033	-0.4949715400
H	5.0401149432	-4.5874568932	-0.0560580187
H	5.9905671072	-0.4602265217	-0.8811927130
H	6.7176880485	-2.8327136699	-0.6281851265
H	1.4984909239	0.0906360927	-1.4608919782
H	0.8665390616	-2.3598827179	0.2866448037
N	-0.4423804229	-0.4811984986	-0.9688271022
O	-0.8802496591	0.1980480543	-1.8723200840
O	-1.1750066294	-1.1484459136	-0.1971442949
Fe	-3.1626652120	-0.5453289694	-0.0298728257
Cl	-4.4862946531	-0.9028898115	-1.6675496681
Cl	-3.7387758728	-1.7581172222	1.6358303130
Cl	-2.8522361549	1.5286936451	0.4950562645

TS1n

0 1

C	2.0875301191	-0.3296066772	0.4672039275
C	2.1399335427	-1.6334226816	0.9884328208
C	3.1008755657	-2.5245094992	0.5118750025
C	3.9929876121	-2.1356183682	-0.4929563298
C	3.9260518679	-0.8403063796	-1.0163212768
C	2.9858511614	0.0700988704	-0.5350127099
H	1.4372442425	-1.9328353422	1.7683558765
H	3.1487416480	-3.5341324791	0.9265450912
H	4.7395077250	-2.8403517557	-0.8652375221
H	4.6198750078	-0.5296886167	-1.8006762418
H	2.9215996666	1.0853327490	-0.9297823814
N	1.1237344447	0.6144202258	0.8718621263
N	0.3402874092	0.3886133915	1.8500804589
N	-0.7976698502	0.5995190374	2.0587714312
C	-0.2168851268	1.3310111337	-0.4759094086
C	-1.4445364013	1.1523696006	0.1751935814
C	-2.3054579336	-0.0072248625	-0.1189489313
C	-3.6908007945	0.0849364794	0.0970754280
C	-1.7764399930	-1.2248837690	-0.5873116842
C	-4.5272405549	-1.0010924183	-0.1628475877
H	-4.1114019133	1.0216086981	0.4708913023
C	-2.6132646170	-2.3092643332	-0.8463500498
H	-0.6992971979	-1.3348439715	-0.7354485876
C	-3.9923227941	-2.2015840962	-0.6378748162
H	-5.6025718879	-0.9096951889	0.0071055827
H	-2.1859820045	-3.2473283891	-1.2084738789
H	-4.6462308237	-3.0528687846	-0.8403423300

N	0.3474857855	2.6847248189	-0.5436708715
O	1.2023279579	2.8707318771	-1.3994472674
O	-0.0457499882	3.5192043709	0.2525466747
H	0.1158330166	0.7258472856	-1.3169699559
H	-1.9193228919	2.0573220746	0.5577265272

TS1x-Fe

0 2

C	-0.2981981524	2.3801256924	-0.2477187678
C	-1.2308599683	1.9399694356	-1.2109744234
C	-2.5784264455	2.2255931890	-1.0330704600
C	-3.0065782680	2.9282920903	0.1007244529
C	-2.0833986541	3.3524777179	1.0606527006
C	-0.7277515920	3.0832797909	0.8925340603
H	-0.8964315873	1.3625462180	-2.0737387472
H	-3.3030004200	1.8561207232	-1.7594861778
H	-4.0705081243	3.1240389588	0.2436474729
H	-2.4235042851	3.8858370076	1.9502187669
H	0.0122445506	3.3946429831	1.6310598483
N	1.0561261537	2.0470937774	-0.3100981832
N	1.5792167091	1.6173815897	-1.3813095274
N	2.2657108825	0.6992532689	-1.6843577290
C	1.6072603273	0.1573119321	0.7739253229
C	2.4194595809	-0.4037379720	-0.2532833062
H	1.9916512805	-1.2874424121	-0.7331499990
H	1.9857469050	0.6166878819	1.6826386006
C	3.8916656926	-0.4398775155	-0.0450064390
C	4.6237330222	-1.5631072586	-0.4561453191
C	4.5699558519	0.6457929445	0.5344591527
C	6.0063474643	-1.6113602664	-0.2709316687
H	4.1034822997	-2.4051855245	-0.9188207431
C	5.9514546168	0.5972854911	0.7163697081
H	4.0170800253	1.5410218747	0.8304049610
C	6.6726214501	-0.5329294874	0.3172004802
H	6.5654659347	-2.4942383523	-0.5885138159
H	6.4696880262	1.4469507625	1.1664309159
H	7.7549305526	-0.5697341979	0.4599757202
N	0.2589653440	-0.1919267186	0.8664566076
O	-0.4011143020	0.1118027926	1.8462134113
O	-0.2771067769	-0.7173508436	-0.1585092142
Fe	-2.2489685256	-1.1432810517	0.0418163805
Cl	-3.9534593770	-0.2507697442	0.9893716167
Cl	-2.6146879992	-1.2049159602	-2.0909504941
Cl	-1.9712801921	-3.0091428177	1.0665738354

TS1x

0 1

C	-2.1943366459	-0.6958485642	0.3693715031
C	-3.0061086350	0.0409966117	1.2477679884
C	-4.3831701059	0.0772630364	1.0413110081
C	-4.9529341271	-0.5911470135	-0.0480057639
C	-4.1385473575	-1.3043492235	-0.9325061236
C	-2.7615577539	-1.3641271453	-0.7249881462
H	-2.5498796268	0.5749032426	2.0831048183
H	-5.0160667960	0.6415917268	1.7297820120
H	-6.0323965238	-0.5516700168	-0.2090717876
H	-4.5787438868	-1.8213557282	-1.7878057008
H	-2.1110116476	-1.9187845488	-1.4028144173
N	-0.7900767231	-0.7224701587	0.4856262113
N	-0.2215399527	-0.4264515338	1.5901293724
N	0.7465412262	0.1765247954	1.8818367669
C	0.2946648128	0.5396418538	-0.7385624075
C	1.3665842938	0.9016382912	0.0954760555
H	1.3559051214	1.9301623077	0.4589689002
H	0.3860267867	-0.1454520792	-1.5773745353
N	-0.7781471708	1.5026166619	-0.9479501110
O	-1.4546189899	1.3525255195	-1.9555949556
O	-0.9686942495	2.3538155276	-0.0882252222
C	2.6794732849	0.2355796797	-0.0203065455
C	3.8472730496	0.9380746875	0.3197992827
C	2.7947495411	-1.1024322738	-0.4401699562
C	5.0989271659	0.3287757218	0.2234422028
H	3.7680954680	1.9736138771	0.6596922698
C	4.0457819121	-1.7104240839	-0.5350861010
H	1.8961379810	-1.6779042714	-0.6749591778
C	5.2031770201	-0.9965947902	-0.2071530673
H	5.9974678785	0.8915730157	0.4870671052
H	4.1186103119	-2.7507539190	-0.8608283088
H	6.1824693380	-1.4749542060	-0.2812471692

TS2n-Fe

0 2

C	2.9561297603	-1.4448016679	-0.2427010394
C	3.8365394629	-1.2112394601	-1.3089634940
C	5.1660749047	-1.6146011724	-1.2005640900
C	5.6246184384	-2.2281907754	-0.0295314902
C	4.7439430040	-2.4516807838	1.0326921478
C	3.4068446209	-2.0671904242	0.9278318711
H	3.4742629961	-0.7139459733	-2.2106475471
H	5.8519245267	-1.4397851021	-2.0323632938
H	6.6692973602	-2.5356593348	0.0522957559
H	5.0967022768	-2.9380000887	1.9446921019
H	2.7008972701	-2.2445726664	1.7412043812
N	1.6267370935	-0.9699093853	-0.2503588941

N	0.9603434003	-0.8370034075	-1.3286116209
N	0.1005757717	-0.1382983188	-1.6975207751
C	1.2645476226	0.6964130624	0.6908795859
C	0.0610197017	1.1116913023	0.0653524571
C	2.5178616975	1.4414971121	0.4807518191
C	3.5452467371	1.3370539771	1.4332599591
C	2.7515740998	2.1789715835	-0.6950009191
C	4.7742134465	1.9618375140	1.2233952471
H	3.3769463029	0.7548600778	2.3415411585
C	3.9799308789	2.8035786180	-0.9023176437
H	1.9770085740	2.2508454032	-1.4613193106
C	4.9943211712	2.6962941156	0.0554346475
H	5.5637959638	1.8718587356	1.9723683493
H	4.1497811060	3.3738839596	-1.8181543012
H	5.9572072386	3.1842624729	-0.1113630061
H	-0.0719406231	2.0372414119	-0.4861750178
H	1.1436216451	0.1993040850	1.6550213577
N	-1.1533725447	0.5908265949	0.5758163976
O	-1.1694602257	-0.3447724085	1.3491898394
O	-2.2070632723	1.1276380059	0.1350735078
Fe	-3.8906721885	-0.0178102141	0.1326642549
Cl	-5.0153392163	-0.8747770159	1.7386356449
Cl	-5.1306554466	1.3541508732	-0.9592531361
Cl	-3.0185025552	-1.6303927057	-1.0085569046

TS2n

0 1

C	0.9391741544	-1.4767206791	-0.1862753968
C	1.7363571777	-1.1102803160	-1.2831564117
C	3.1243622712	-1.1468475050	-1.1696791272
C	3.7265855628	-1.5308154729	0.0338390834
C	2.9309796015	-1.8914728935	1.1251875660
C	1.5407134867	-1.8699315776	1.0180700424
H	1.2590000613	-0.7943848989	-2.2126128322
H	3.7423239848	-0.8635491086	-2.0248011874
H	4.8152523822	-1.5510241313	0.1184958215
H	3.3960295046	-2.1972870283	2.0650894727
H	0.9022673517	-2.1506220131	1.8576333746
N	-0.4586019526	-1.3505483560	-0.1918597446
N	-1.1280758129	-1.3718841745	-1.2720108024
N	-2.0958392087	-0.8273572542	-1.6618023969
C	-1.2530999450	0.4127372501	0.6399826628
C	-2.4289070570	0.4943916681	-0.1231306672
C	-0.1080163903	1.3023971982	0.4191282685
C	0.8880925219	1.3984146069	1.4070967076
C	0.0787693855	1.9925571341	-0.7944139978

C	2.0338016759	2.1639470532	1.1942887889
H	0.7605706898	0.8567308014	2.3465058924
C	1.2225249513	2.7601231138	-1.0042999184
H	-0.6666558035	1.9127789875	-1.5881183426
C	2.2050335939	2.8474169089	-0.0121031000
H	2.7990558190	2.2224315195	1.9713684324
H	1.3531769127	3.2885487779	-1.9514485669
H	3.1036355672	3.4448713083	-0.1817801988
N	-3.6367298625	-0.1240818548	0.4216805960
O	-4.6991683302	0.2690139093	-0.0334845159
O	-3.5083772151	-1.0003587283	1.2662496213
H	-2.6734351222	1.3348880347	-0.7674077289
H	-1.3433259561	-0.0720482799	1.6122256053

TS2x-Fe

0 2

C	-1.2123005136	1.7455930594	0.7480139567
C	0.0911171460	2.2533259412	0.8065904485
C	0.3201489997	3.5714912122	0.4154174211
C	-0.7362421860	4.3660124152	-0.0415965772
C	-2.0330365404	3.8449846553	-0.1038961584
C	-2.2798268907	2.5309268744	0.2959229038
H	0.9144069312	1.6179697419	1.1356465937
H	1.3383234510	3.9632685890	0.4437536499
H	-0.5471711340	5.3947379366	-0.3561449142
H	-2.8580483884	4.4667054831	-0.4583978315
H	-3.2843132407	2.1063306001	0.2655887570
N	-1.4829451441	0.3837409203	1.0543629193
N	-0.8609223896	-0.2391841907	1.9689655369
N	-0.4840179324	-1.3079865303	2.2035609965
C	-1.7003874296	-0.8253135531	-0.3406710121
H	-1.2316859716	-0.1754405724	-1.0830989203
C	-0.9203306580	-1.9541210411	0.0281072193
H	-1.3070051282	-2.9405447455	0.2679181753
C	-3.1716731869	-0.9626760965	-0.4541836349
C	-3.8480170415	-0.2708465245	-1.4707822703
C	-3.9091473189	-1.7459296878	0.4498806276
C	-5.2353696610	-0.3706779006	-1.5919153683
H	-3.2794466570	0.3461007614	-2.1706885197
C	-5.2945141959	-1.8416165510	0.3297184334
H	-3.3993051340	-2.2698739167	1.2617429075
C	-5.9607764630	-1.1561468017	-0.6924777911
H	-5.7509061619	0.1666461579	-2.3909651017
H	-5.8596570372	-2.4507387836	1.0386171261
H	-7.0464395645	-1.2332852209	-0.7847913257
N	0.4523232836	-1.9435087756	-0.2486306813
O	0.9380346139	-0.8368788930	-0.6674881860

O	1.1446435760	-2.9233879398	-0.0758651189
Fe	2.8690330299	-0.4056603305	-0.3459934505
Cl	2.7433536701	-0.2928599085	1.8127037716
Cl	4.6541778289	-1.4615868324	-0.8458760878
Cl	2.8129874386	1.5316104480	-1.2989034943

TS2x

0 1

C	-1.6933635822	-0.6907007713	0.5571111380
C	-2.9494735228	-0.1023810119	0.3382271961
C	-4.0048757959	-0.8909159147	-0.1158598901
C	-3.8093269858	-2.2520300372	-0.3786882663
C	-2.5507207300	-2.8275493648	-0.1799040892
C	-1.4912104767	-2.0534773407	0.2951042074
H	-3.0780432933	0.9681177113	0.5084172048
H	-4.9848283742	-0.4369383524	-0.2796868624
H	-4.6390446658	-2.8625514999	-0.7416679416
H	-2.3952724985	-3.8892570049	-0.3845665051
H	-0.5044457977	-2.4846565773	0.4709597009
N	-0.5726412089	0.0644559912	0.9522386258
N	-0.6825638968	1.1213471919	1.6449960756
N	-0.1451142695	2.1643412538	1.6777160265
C	0.7541601589	0.6825356520	-0.4927183237
H	0.0274777719	0.4890876325	-1.2840300094
C	0.9037663410	2.0289534321	-0.1295168793
H	1.8390565157	2.4729842749	0.2028908208
C	1.8257229648	-0.3128366537	-0.3176474884
C	1.8658983984	-1.4315287044	-1.1670372611
C	2.7955803780	-0.1955052952	0.6941095208
C	2.8574720845	-2.4029600959	-1.0188780111
H	1.1114823118	-1.5342204915	-1.9507914393
C	3.7843407390	-1.1663069426	0.8415852525
H	2.7641102483	0.6522484954	1.3820975362
C	3.8203029360	-2.2727235243	-0.0149255425
H	2.8786181498	-3.2641588258	-1.6907570373
H	4.5300114513	-1.0637705778	1.6333599787
H	4.5963493600	-3.0323494675	0.1035308975
N	0.0386095112	2.9999138174	-0.7880423994
O	0.4381931504	4.1514467024	-0.8362262593
O	-1.0405683728	2.6072972988	-1.2208879763

TS3

0 1

C	3.3949515791	-1.2942476227	-0.1073251141
C	4.3911990439	-2.1485933397	-0.6008629581
C	5.4188128155	-2.5568693824	0.2471157352
C	5.4637118428	-2.1148848255	1.5738485143

C	4.4655080898	-1.2636279354	2.0544327899
C	3.4250579152	-0.8513357105	1.2213066726
H	4.3435179669	-2.4813325435	-1.6371999559
H	6.1951441682	-3.2233146427	-0.1350513568
H	6.2744294781	-2.4353114339	2.2314994263
H	4.4883400190	-0.9195328079	3.0905626040
H	2.6420898102	-0.1980806895	1.6044926641
N	2.3502772462	-0.8729635556	-0.9641294319
N	2.0306821396	-1.5559029141	-2.0443852337
N	1.0336759020	-0.9852827092	-2.6672668700
C	1.4622802626	0.2385086406	-0.7687354250
C	0.6242881832	0.0832615470	-1.9519568091
C	2.0374512550	1.5677432325	-0.3648924006
C	1.3052013707	2.4079514487	0.4845492630
C	3.2841718828	1.9875536608	-0.8491131612
C	1.8133940040	3.6599800617	0.8393024216
H	0.3385686967	2.0746811394	0.8686197482
C	3.7937134368	3.2340214230	-0.4828447558
H	3.8577990439	1.3341733592	-1.5101737260
C	3.0589310418	4.0737967282	0.3600038233
H	1.2360379341	4.3107129357	1.4999948662
H	4.7675752495	3.5531404008	-0.8613228479
H	3.4584856060	5.0501102207	0.6436735372
H	-0.0682441064	0.8116256557	-2.3652303390
H	0.6399264799	-0.0845198466	0.0903929564
N	-1.1499844496	-0.5754189788	-0.5657610487
O	-2.2914219406	-0.9170326632	-0.7091274834
O	-0.6388489669	-0.4428908530	0.5822608949

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