Synthesis of New Heterocyclic Compounds Derived From 5,10-dihydrophenophosphazine

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Abstract:

This work comprises the synthesis of 18 new N- substituted 5,10-dihydrophenophosphazine.The diphenylamine was chosen as the starting material , which was reacted with phosphorus trichloride at elevated temperature (200-220)^{0}C for 6 hrs, followed by treating the reaction mixture with water to yield 5,10-dihydrophenophosphazine-10-oxide(1), this was reacted with ethylchloroacetat to obtain ethyl(5,10-dihydrophenophosphazine-10- oxide)acetate(2). Compound (2) was converted to acid hydrazide by treating with hydrazine hydrate(98%) to obtain 5-(5,10-dihydrophenophosphazine) acetohydrazide-10-oxide (3). The acid hydrazid was used to react with phenylisocyanat , phenylthioisocyanat to give (4,7) respectively which were used to prepare different heterocyclic compounds. Compound (5) was performed by the intramolecular cyclization of (4) in the presence of NaOH(2N).Compound (8) was synthesized by interaction of (7) with NaOH(2N).Compound (6) and (9) were obtaind upon the reaction of semicarbazide (4) and thiosemicarbazide (7) with phosphoric acid at 120^{0}C.

Compound (3) undergoes the character condensation reaction with different aromatic aldehyde in ethanol gave the shiff bases (10-18).

Keywords: 5, 10-dihydrophenophosphazine, Semicarbazide, Thiosemicarbazide, diphenylamine

تحضير مركبات حلقية غير متجانسة جديدة مشتقة من 10,5- ثنائي هايدروفينوفوسفازين

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الخلاصة:

يتضمن البحث تحضير 18 مشتقا جديد، من مشتقات 10،5-ثنائي هيدروفينوفوسفازين المعوض على ذرة النيتروجين اختير المركب ثنائي فنيل امين ليكون المادة الاولية والذي يتفاعل مع ثلاثي كلوروفسفور بدرجة حرارة (200-220)م^0 لمدة ستة ساعات ثم تم معاملة المزيج مع الماء حيث اعطى 10،5- ثنائي هيدروفينوفوسفازين 10-اوكسيد(1)والذي بدوره تفاعل مع اثيل كلورواسيتيت للحصول على اثيل 10،5- ثنائي هيدروفينوفوسفازين 10-اوكسيداسيتيت (2) وعند معاملة المركب (2) مع الهايدرازين المائي (98%) وكون المركب 5(10،5-ثنائي هيدروفينوفوسفازين) اسيتوهيدرازايد-10-اوكسيد (3) وبمفاعلة هذا المركب مع فنيل ايزوسينات و فنيل ثايوايزوسينات اعطى المركبين (4،7) ،والذين تفاعلا مع2N هيدروكسيدالصوديوم لينتج مركبات حلقية (5) و(8) وعند مفاعلة (4،7) مع حامض الفسفوريك بدرجة حرارة 120 م^{0}اعطى المركبين

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(6)و(9)على التوالي . عند مفاعلة المركب (3) مع الديهيدات مختلفه في كحول الايثانول اعطى قواعد شيف (10-18).

Introduction

Heterocyclic compounds are cyclic compounds in which the ring atoms are of carbon and some other element ،containing nitrogen, oxygen and sulfur are by far the most common, but other atoms such as boron phosphorous, or silicon compound also are members of heterocyclic ring. Some non-aromatic heterocyclic and some aromatic heterocyclic [1-5] examples thiadiazole , 1,2,3-oxadiazole, furane , thiophene , 1,2,3-triazole , dioxane , pyridine , phenothiazine [6,7]. The numerous derivatives of 5,10-dihydrophenophosphazine have been described in recent years[8]. Phenophosphazine have been reported to be both biologically and industrially versatile compounds [9]. In industry field, most of alkylated phenophosphazine have been used as additives for lubricating oils, greases ,and hydraulic fluids[10] . The application of 5,10-dihydrophenophosphazine[9] derivatives used for the determination of titanium and uranium dioxide.

Experimental: Material and Instrument

FT-IR spectra were Recoreded on [SHIMADZU] FT-IR 8400s Spectrophotometer; solid samples were run as KBr disk, liquid were run as smears. ^{1}H-NMR spectra were recorded on ultra shield 300 MHz,with tetra methyl silane as internal standerd and DMSO and methanol as solvents. Melting points were determined in a[Gallen Kamp] melting point apparatus with sample contained in open capillary glass tube in an electrically heated metal block apparatus. Thin layer chromatography [TLC] was performed on pre-coated plastic sheet with 0.25 mm layer of silica gel F 254. Spots were detected with iodine vapour using (CCl_4: EtOH) (3:1) as eluent. All chemicalls were supplied from BDH,Merck,Fluka and used without further purification.

N-sub derivative of 5,10-dihydrophenophosphazine-10-oxide(1).

A mixture of diphenylamine (12g, 0.72 mol) and PCl_3 (7ml, 0.78 mol) was stirred at room temperature for 20 min and then heated at 210-220^{0}C for 6 h. The viscous oil was cooled to 150^{0}C and water (20 ml) was added and kept overnight, the resultant brown solid was dissolved in hot ethanol and filtered to remove insoluble components. The filtrate was concentrated to give a white solid precipitate .The product was checked by (T.L.C) and
recrystallized from hot glacial acetic acid .

5-N-Ethyl (5, 10-dihydrophenophosphazine-10-oxide) acetate (2)

Amixture of 5,10-dihydrophenophosphazine-10-oxide(1),(5g,0.027mol) ethylchloroacetate (3.5ml,0.027 mol) in dry acetone (5 ml) and anhydrous K_2CO_3 (0.5 g) was refluxed for 24 h, then cooled ,filtered and solvent removed under reduced pressure. The resulting solid was monitored by (T.L.C) and recrystallized from ethanol.

5-N- acetohydrazide -(5,10-dihydrophenophosphazine) -10-oxide (3)

To a solution of compound (2) (2.5g,0.009 mol) in ethanol (50 ml), hydrazine hydrate (0.5ml,0.009 mol) was added and the reaction mixture was refluxed on a water bath for 2-3 h .Reaction and purity of the final product was checked by (T.L.C) ,then cooled . The resulting solid was filtered and recrystallized from ethanol.

5-N-(acetylphenylsemicarbazid)-5,10-dihydrophenophosphazine-10-oxide(4)

Amixture of (3) (2.5g,0.001 mol) and phenyl isocyanate (1.5ml,0.001mol) was refluxed in ethanol (20 ml) for 4 h . The reaction progress was monitored by (T.L.C), then cooled and filtered. The formed solid was recrystallized from ethanol.

5-N-[(4-Phenyl-1, 2, 4-triazole-5-one)-3-N-methylene]-(5,10 dihydrophenophosphazine)-10-oxide (5)

The compound (4), (0.5g, 0.001 mol) was refluxed with 2N NaOH (2 ml) for 3 h, then cooled and filtered. The filterate was neutralized by glacial acetic acid to give a solid, which was checked by (T.L.C), and recrystallized from ethanol**.**

5-N-[(phenylamine)-1, 3, 4-oxadiazole-2-N-methylene]-5,10-dihydrophenophosphazine-10-oxide) (6)

Compound (5) (0.5g,0.001 mol) was dissolved in syrapy phosphoric acid (5 ml) ,heated at 120^{0}C for 50 min , kept overnight and then poured in to ice-cold water. The resulting solid was checked by (T.L.C), filtered and recrystallized from ethanol**.**

5-N-(acetylphenylthiosemicarbazide)-5,10-dihydrophenophosphazine-10-oxide(7)

Compound (7) was prepared by the same method described for the preparation of semicarbazide (4) using phenylisothiocyanate (1g, 0.001mol).

5-N-[(4-phenyl-1,2,4-triazole-5-thiono-3-methylene)-5,10-dihydrophenophosphazine-10-oxide](8)

Compound (7) (0.5 g , 0.001 mol) was refluxed with 2N NaOH (2ml) for 3h . Cooled and filtered, the filtrate acidified with glacial acetic acid give a solid, which was checked by (T.L.C) and recrystallized from ethanol**.**

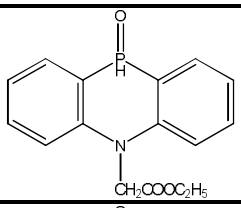
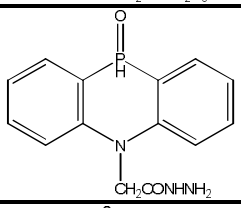
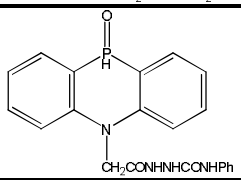
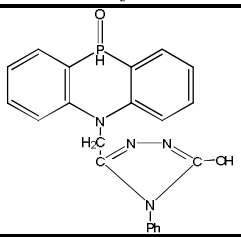
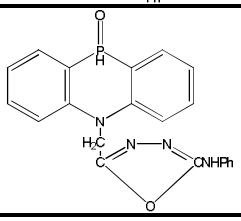
5-N-[(phenylamine)-1,3,4-thiadiazole-2-methylene]-5,10-dihydrophenophosphazine-10-oxide (9)

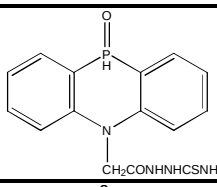
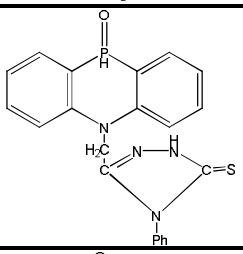
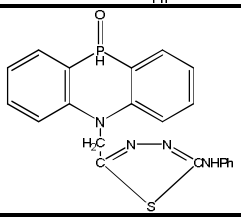
Compound (7) (0.5g, 0.001 mol) was dissolved in syrapy phosphoric acid (5 ml) , then heated at 120^0C for 50 min ,kept overnight , and poured in to ice-water.The resulting solid was filtered.The product was checked by (T.L.C) and recrystallized from ethanol see table1**.**

N-(phenylmethylene)-2-(5,10-dihydrophenphoshazine-10-oxid)acetohydrazide(10-18)

The compound (3) (0.25g, 0.001 mol) in 40 ml of ethanol was heated 10 min the aromatic aldehyed ArCHO (0.001 mol) was added and the reaction mixture was refluxed for 2 h. The reaction progress was monitored by (T.L.C). The precipitate was filtered and recrystallized from ethanol.

Table 1- Physical properties of compounds (2-9)

Comp. No.	Compound structure	Color	Melting Points °C	Yield %	Recrystallization Solvent
2		green	**182**	**71**	Ethanol
3		Yellow-reddish	**238**	**54**	Ethanol
4		white	**244**	**64**	Ethanol
5		orange	**236**	**62**	Ethanol
6		yellow	**174**	**57**	Ethanol

7		yellow	**172**	**83**	Ethanol
8		yellow	**248**	**70**	Ethanol
9		green	**373**	**74**	Ethanol

Result and discussion

5,10-dihydrophenophosphazine-10-oxide(1) was prepared by the reaction of diphenylamine and phosphorus trichloride at 220^0C followed by hydrolysis of the mixture with hot water [11] show figure 1.Compound(1) was treated with ethylchloroacetate to give N- ethyl(5,10dihydrophenophosphazine-10-oxide)acetate(2)which was characterized by T.L.C, m.p , ^{1}HNMR and FTIR spectrum figure 2 showed stretching bands at (3186- 3093) cm^{-1} for aromatic (C-H)., 2977 $cm^{-1}$for aliphatic (C-H) ., 2322 cm^{-1} (P-H).,1751cm^{-1} for ester(C=O).,(1612-1591-1520) $cm^{-1}$for (C=C) aromatic and bending band at 1465 cm^{-1} for (N-H) [12-14] see table2.

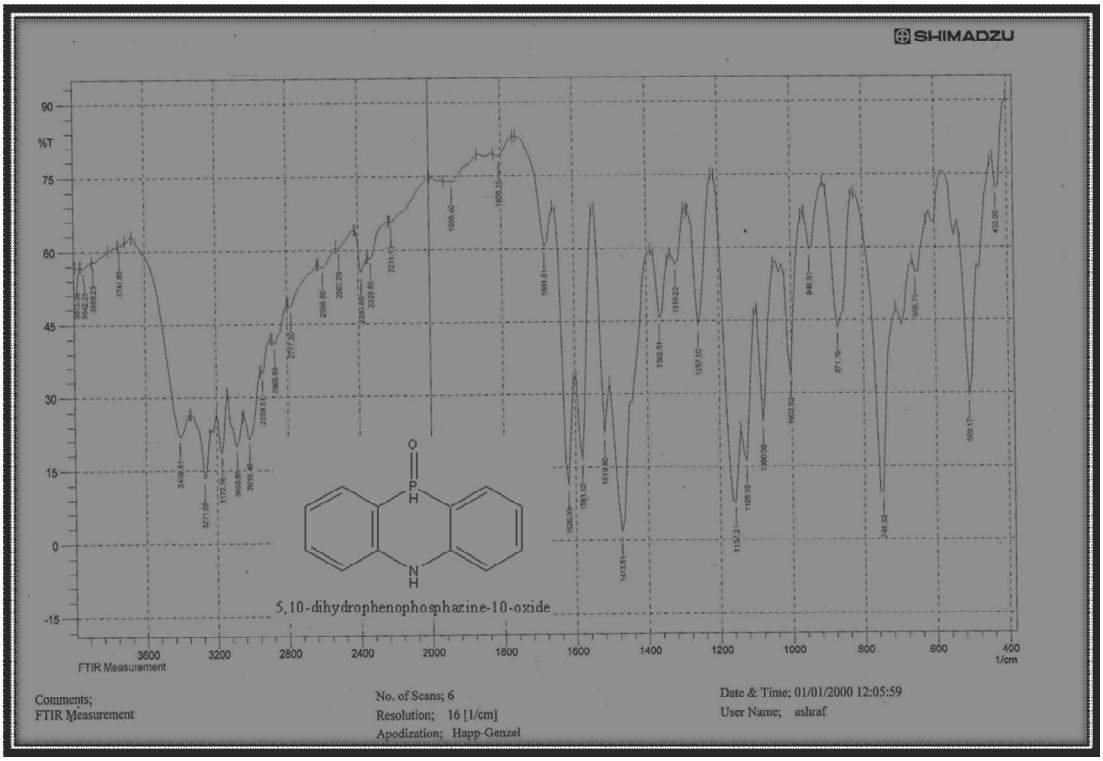


Figure 1-FTIR spectrum of compound (1)

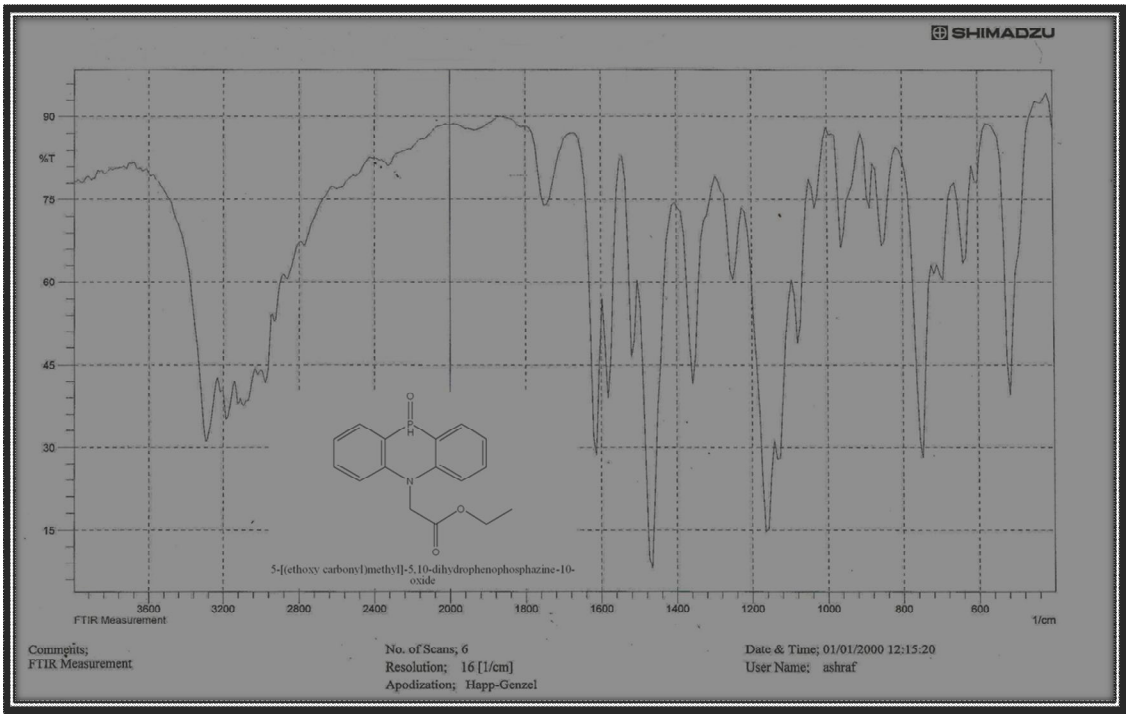


Figure 2-FTIR spectrum of compound (2)

Table 2-Characteristic FTIR absorption bands (cm^{-1}) of compounds (1-9)

Comp. No.	**υ(N-H)**	**υ(P-H)**	**υ(C=O)**	**υ(C=N)**	**υ(C=C)aromatic**	**υ(P=O)**	**(C-H) aromatic**	**others**
1	3271	2336			1581, 1519, 1612	1257, 1157	3085, 3015	
2	3249	2322	1751 ester		1581, 1612, 1520	1249, 1164	3093	2977 Aliphatic (CH_2),
3	3283	2345	1674 amide		1581, 1612, 1473	1249, 1164	3085, 3016	2931 aliphatic (CH_2)
4	3294	2391	1674 amide		1550 1604 1473	1242, 1165	3093	2930 aliphatic (CH_2)
5	3271	2395	1700 amide	1610	1573, 1610, 1520	1257, 1149	3093	3410, (OH) group
6	3278	2337		1620	1581, 1512	1249, 1144	3070	1118,1180 C-O-C
7	3210,	2352	1680 amide	1612	1545, 1512	1342, 1240	3008	1118 (C=S)
8	3230	2335		1697	1558, 1480, 1643	1243, 1157	3178	1018 (C=S)
9	3210	2329		1600	1566, 1500	1296, 1218	3029	694 (C-S)

The ^{1}HNMR spectrum figure 3 showed a singlet signal at (δ=1.3)ppm assigned to protons of CH_2 , multiplet signal at (δ=3.3)ppm C_2H_5 protons ,signal at (δ=4.9)ppm for MeOD solvent , multiplet

signals between (δ=7-7.9) ppm assingned to aromatic protons and singlet signal at (δ=9.7) ppm(P-H), as shown in table 3.

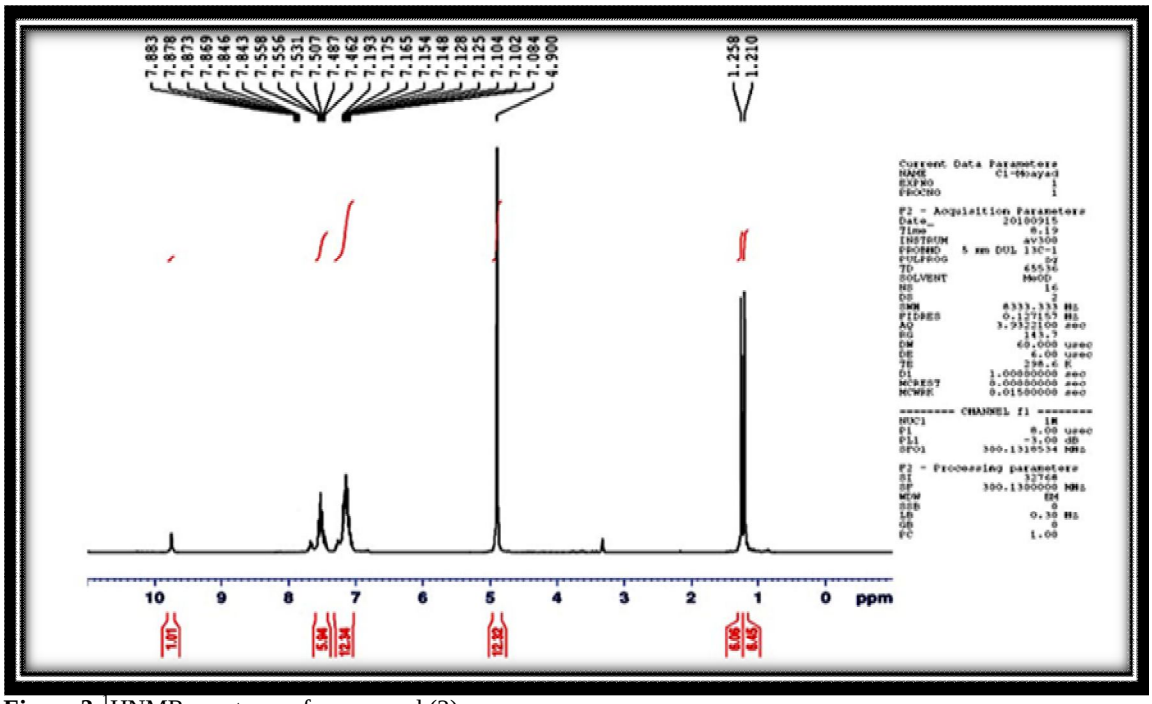
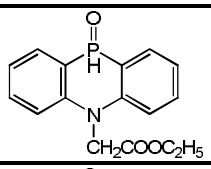
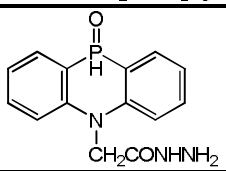
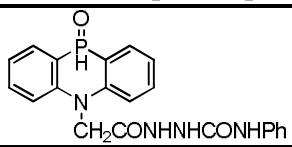
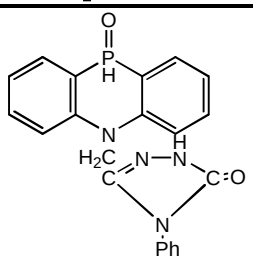
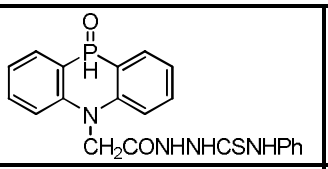
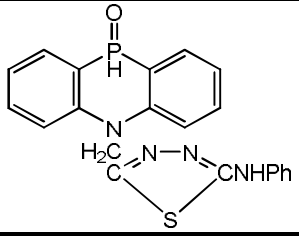


Figure 3-[1]HNMR spectrum of compound (2)

Table 3-[1]H-NMR spectral data(ppm)of compounds (2,3,4,5,7,9)

Comp. No.	Compound structure	aromatic	(P-H)	(NH)	aliphatic	other
2		m(δ=7-7.9)	s(δ=9.7)		m(δ=3.3) C_2H_5, s(δ=1.3) CH_2	
3		m(δ=7-7.1)	s(δ=9.7)	s(δ=3.3)	s(δ=1.2)	
4		m(δ=7-7.6)	s(δ=9.7)	m(δ=7.9)	s(δ=2.0)	
5		m(δ=7-7.8)	s(δ=9.7)	s(δ=10.1)	s (δ=1.3)	s(δ=10.4) (OH)

7		m(δ=7.2-7.6)	s(δ=9.7),	s(δ=3.3), s(δ=7.9)	s(δ=1.4)	
9		m(δ=7-7.5)	s(δ=9.7)	s(δ=3.3)	s(δ=2)CH_2	

Compound (3) was obtained by the interaction of (2) with hydrazine hydrate the product was characterized by T.L.C , m.p ,FT-IR and ^{1}HNMR. FTIR spectrum figure 4 showed stretching bands at (3283 - 3178) cm^{-1} for (NH-NH_2)., (3085 -3016) cm^{-1} aromatic (C-H) ., 2931 cm^{-1} aliphatic (C-H) ., 2345 cm^{-1} (P-H) ., strong band at 1674 cm^{-1} for amide (C=O) ., 1473cm^{-1} (N-H) bending ., stretching bands at (1612,1581,1522) cm^{-1} aromatic (C=C) ., 1357 cm^{-1} (C-N) .^{1}HNMR spectrum showed singlet signals at (δ=1.2) ppm assigned to aliphatic protons ., (δ=3.3) ppm assigned to (NH_2) ., (δ=4.9) ppm for (CH_3OD) ., multiplet signals (δ=7-7.1) ppm for aromatic protons while pH and NH protons showed singlet signals at(δ=9.7) and (δ=7.9) ppm respectively as shown in table 3.

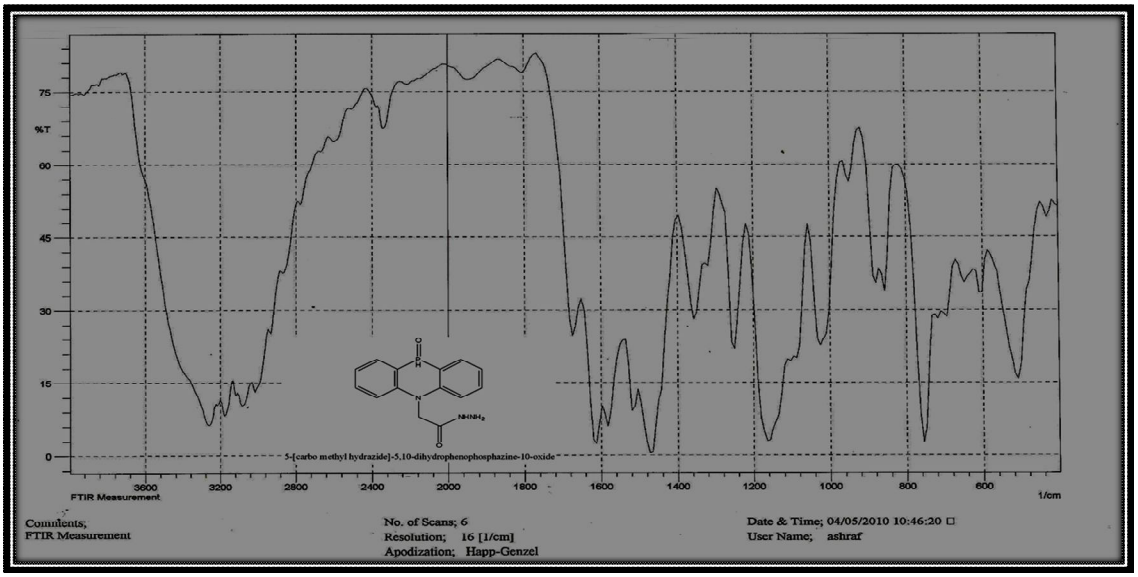


Figure 4-FTIR spectrum of compound (3)

The compound (3) was reacted with phenyl isocyanate to give 5-[N-phenyl acetyl- semicarbazid]-5,10-dihydrophenophosphazine-10-oxide(4). This compound was characterized by T.L.C , m.p ,FTIR, and ^{1}HNMR. The FTIR spectrum figure 5 showed the structure of (4) confirmed by the presence of two amidic carbonyl stretching bands at (3294- 3224) cm^{-1} (NH) ., 3093 cm^{-1} (C-H) aromatic ., 2930 cm^{-1} (C-H) aliphatic ., 2391 cm^{-1} (P-H)., strong band at 1674 cm^{-1} for (C=O) amid I and II ., 1450cm^{-1} (NH) bending ., (1604,1550,1473) cm^{-1} aromatic (C=C) ., 1334 cm^{-1} (C-N) ., (1314- 1292) cm^{-1} (P=O) .

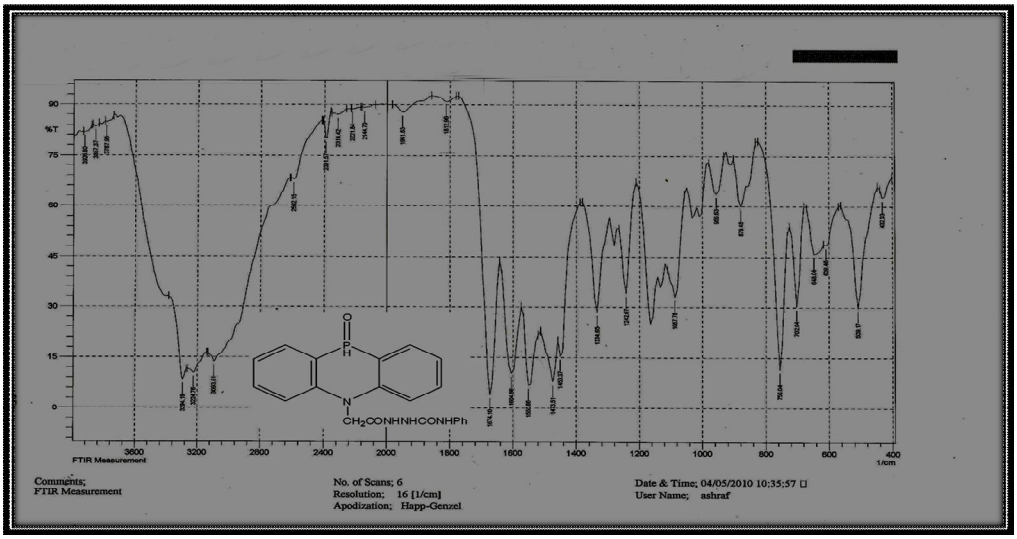


Figure 5-FTIR spectrum of compound (4)

The ^{1}HNMR spectrum figure 6 showed singlet signals at (δ=2.0) ppm assigned to aliphatic two protons., (δ=3.3) ppm assigned to (NH) ., (δ=7.9) ppm assigned to (NH) amide ., (δ=4.8) ppm (CH_3OD) ., multiplet signals at (δ=7-7.6) ppm for aromatic protons and singlet signal (δ=9.7) ppm assigned to (P-H) proton .

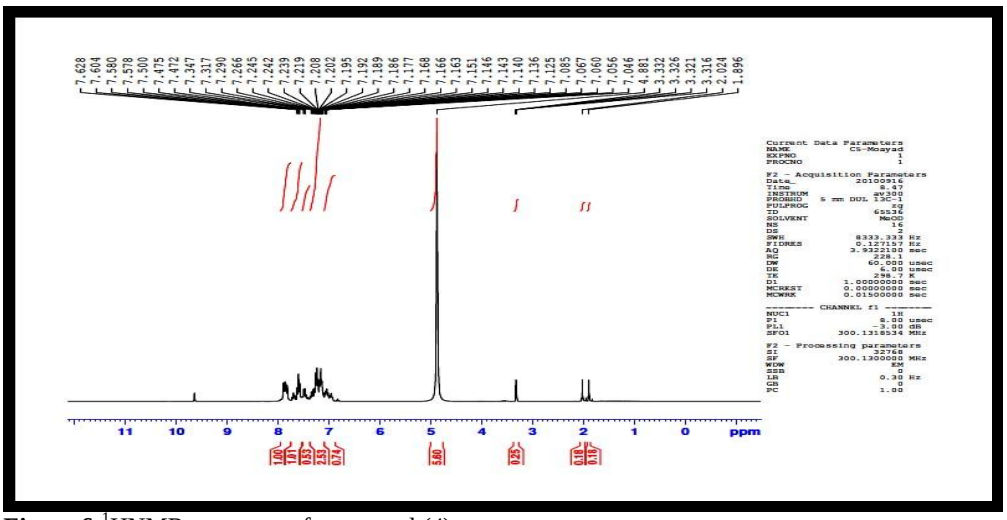


Figure 6-^{1}HNMR spectrum ofcompound (4)

The reaction of compound (4) with 2N NaOH to give compound (5), which exists one-ol tautomeric form as indicated by the IR spectrum .The structure(5) was confirmed by T.L.C , m.p , FTIR and ^{1}HNMR spectra . FTIR spectra showed stretching bands at 3410 cm^{-1} due to OH (tautomerism) ., 3271 cm^{-1} (NH) ., 3093 cm^{-1} (C-H) aromatic ., 2920 cm^{-1} (C-H) aliphatic ., 1700 cm^{-1} (C=O) ., (1610,1573,1520)cm^{-1}(C=C) aromatic., 1473 cm^{-1} (NH) bending ., 1350 cm^{-1} (C-N) ., (1149- 1257) cm^{-1} (P=O) See table 2 . The ^{1}HNMR spectrum figure 7 showed singlet signals at (δ=1.3) ppm assigned to (CH_2) ., (δ=2.5) ppm (DMSO) ., multiplet (δ=7-7.8) ppm aromatic protons ., singlet signal at (δ=10.1) ppm assigned to (NH) ., singlet(δ=9.7) ppm (PH) and singlet (δ=10.4) ppm (OH).

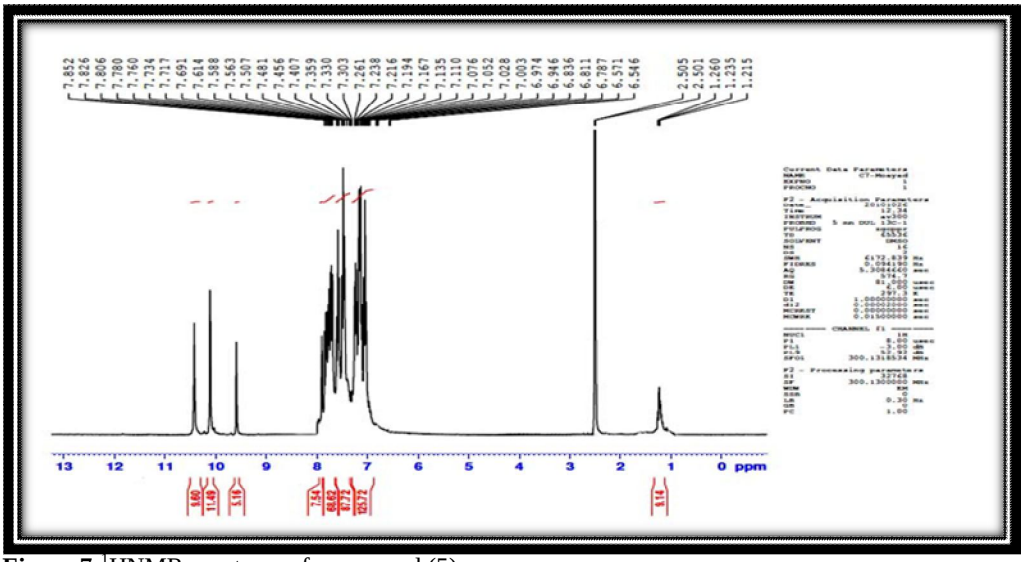


Figure 7-^{1}HNMR spectrum of compound (5)

Compound (6) was prepared by the reaction of compound (4) with phosphoric acid at 120^{0}C . It was affected by intramolecular cyclization through the loss of H_2O , to give the expected compound(6). The purity and structure of compound (6) were studied by T.L.C , m.p and FT-IR . FTIR spectrum of compound (6) showed weak stretching band at 3278 cm^{-1} assigned to the (N-H) ., 3070 cm^{-1} aromatic (C-H) ., 2993 cm^{-1} aliphatic (C-H) ., 2337 cm^{-1} due to (P-H) group ., 1620 $cm^{-1}$for (C=N) .,(1581 ,1512)cm^{-1} aromatic system (C=C) ., (1144 ,1249) cm^{-1} (P=O).,stretching bands at 1180 cm^{-1} and 1118 cm^{-1} which were attributed to the (asym and sym) of (C-O-C) See table 2.

Compound (7) was prepared by the reaction of hydrazide (3) with phenylisothiocyanate in ethanol to give the thiosemicarbazide. The structure of compound (7) was confirmed by T.L.C, m.p and FTIR spectrum. FTIR spectrum figure 8 showed stretching bands at 3417 cm^{-1} ,3210cm^{-1} and 3116 cm^{-1} assigned to (N-H) groups ., 3008 cm^{-1} for (C-H) aromatic ., 2939 cm^{-1} aliphatic (C-H)., 2352 cm^{-1} (P-H) ., 1680 cm^{-1} (C=O) ., (1612 ,1545 ,1512)cm^{-1} for (C=C) aromatic ., NH bending appeared at 1465 cm^{-1}, while (P=O) and (C=S) appeared at (1342 ,1240) cm^{-1} , 1118 cm^{-1} respectively. ^{1}HNMR spectrum showed singlet signals at (δ=1.4) ppm assigned to (CH_2) ., (δ=3.3)ppm(NH)for secondary amine.,(δ=4.4)ppm(MeOD)., m (δ=7.2-7.6) ppm aromatic protons., singlet (δ=7.9) ppm (NH)and singlet signal at (δ=9.7) ppm assigned to (PH) see table 3.

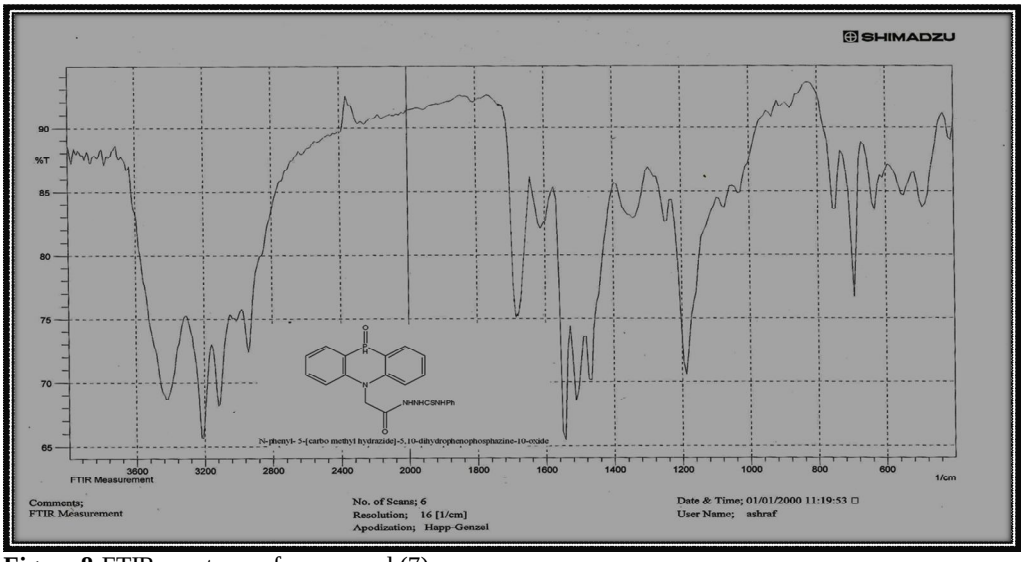


Figure 8-FTIR spectrum of compound (7)

The reaction of compound (7) with 2N NaOH under reflux give 5-[4-phenyl-1,2,4-triazole-5-thiono]-3-methylene- (5,10-dihydrophenophosphazine-10-oxide)(8).The purity and the structure of compound (8) was confirmed by T.L.C , m.p and FTIR spectrum. FTIR spectrum showed streching bands at 3230 cm^{-1} (N-H) ., 3178 (C-H) aromatic ., 2987 cm^{-1} (C-H) aliphatic., 2355 cm^{-1} (P-H) ., 1697 cm^{-1} (C=N).,(1643, 1558,1480)cm^{-1} (C=C) aromatic., 1342 cm^{-1} (C-N) and(1242 , 1157) cm^{-1} (P=O) , bending band at 1411 cm^{-1} for (N-H) See table 2.

Compound (9) was obtained by the reaction of compound (7) with phosphoric acid at 120^0C by intramolecular cyclization through the loss of H_2O give 2-[5-(N-phenylamino)-1,2.3-thia diazole-2-methylene]-5,10-dihydrophenophosphazine]-10-oxide (9) . FTIR spectrum showed figure 9 stretching bands 3210 cm^{-1} (N-H)., 3029 cm^{-1} (C-H) aromatic ., 2939 cm^{-1} (C-H) aliphatic ., 2329 cm^{-1}(P-H) ., 1596 cm^{-1} (C=N) ., (1566 -1500) cm^{-1} (C=C) aromatic .,1357 cm^{-1} (C-N) ., (1296 – 1218) cm^{-1} (P=O) and 694 cm^{-1} (C-S) See table 2.

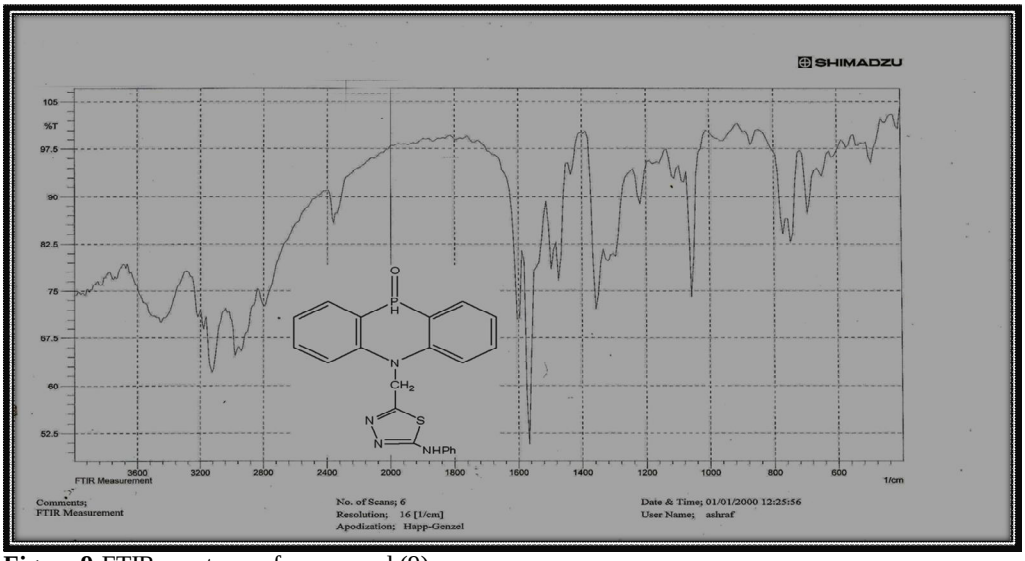


Figure 9-FTIR spectrum of compound (9)

The ^{1}HNMR spectrum figure 10 showed singlet signals at (δ=2.1) ppm (CH_2) ., (δ=3.3) ppm (NH) ., (δ=4.8) ppm (MeOD) solvent ., multiplet (δ=7-7.5) ppm aromatic protons and singlet (PH) at (δ=9.7) ppm See table 3 and scheme (1).

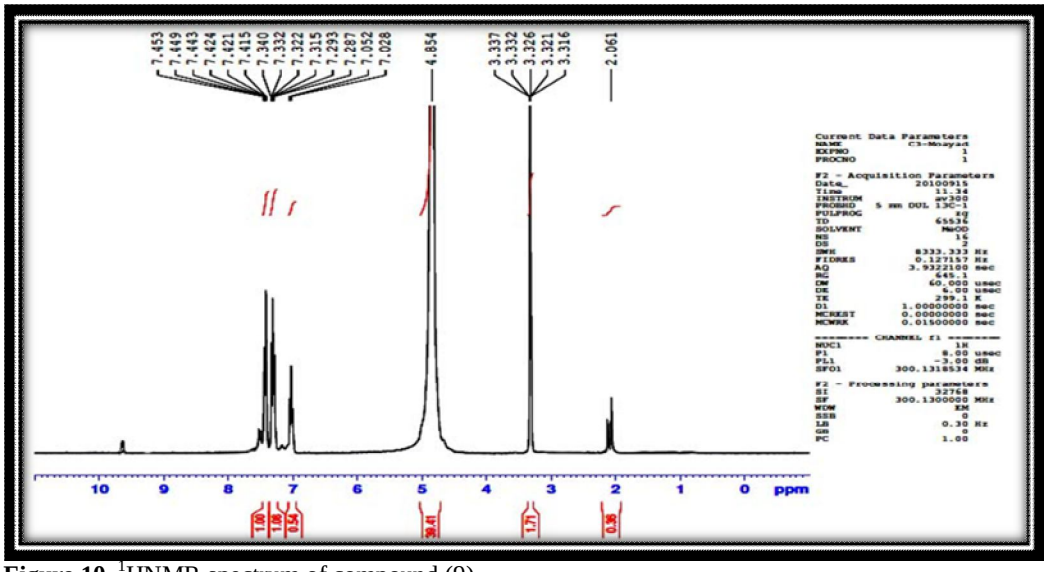
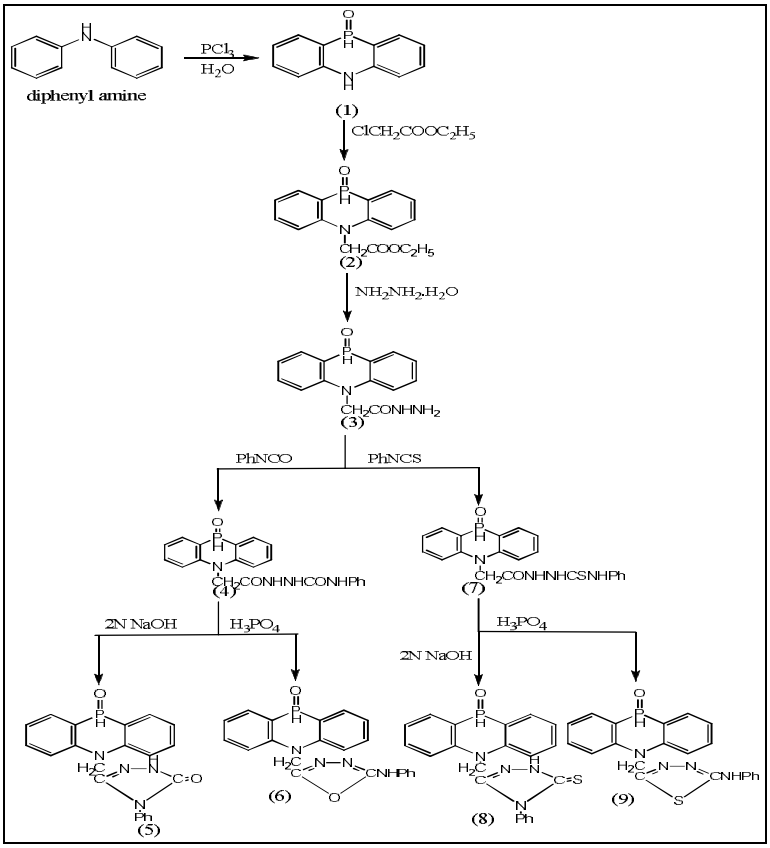


Figure 10- ^{1}HNMR spectrum of compound (9)

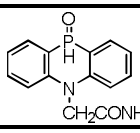
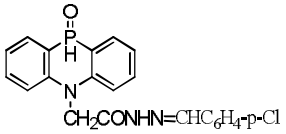
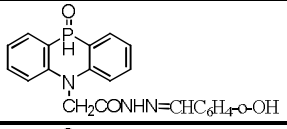
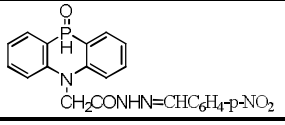


Scheme (1) Synthesis of N-sub phenophosphazine derivatives

Schiff bases derivatives

Compound (3) undergoes the character condensation reaction with different aromatic aldehydes in absolute ethanol gave the Schiff bases (10-18)[15] . The formation of these Schiff bases was indicated by the disappearance of the NH_2 stretching bands in FTIR spectra See table 4 and 5.

Table 4-Physical properties of the schiff base derivatives (10-18)

Comp No.	Compound structure	aldehyde	Color	Melting Points °C	Yield %	Recrystallization Solvent
10		benzaldehyde	green	146	46	Ethanol
11		4-chlorobenzaldehyde	Yellow	186	55	Ethanol
12		2-hydroxybenzaldehyde	Yellow-reddish	158	44	Ethanol
13		4-nitrobenzaldehyd	orange	244	66	Ethanol

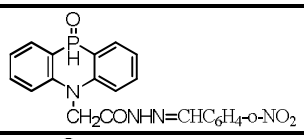
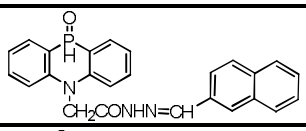
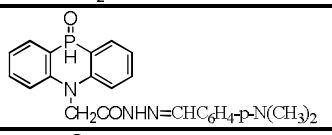
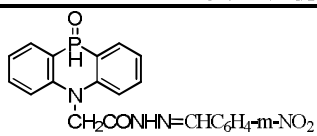
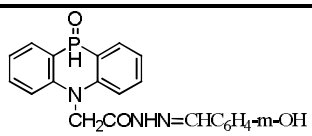
14		2-nitrobenzaldehyd	Yellow	204	61	Ethanol
15		2-naphthylaldehyde	orange	242	89	Ethanol
16		4-N,Ndimethylaminobenzalde-hyde	red	142	47	Ethanol
17		3-nitrobenzaldehyd	orange	198	41	Ethanol
18		3-hydroxybenzaldehyde	red	123	39	Ethanol

Table 5-Characteristic FTIR absorption bands (cm^{-1}) of Schiff-base derivatives(10-18)

Comp. No.	**υ(N-H)**	**υ(P-H)**	**υ(C=O) amide**	**υ(C=N)**	**υ(C=C)aromatic**	**υ(P=O)**	**(=CH) imine**	**others**
10	3283	2322	1697	1620	1581, 1522	1249, 1377	3170	
11	3271	2322	1697	1612	1589, 1520	1247, 1357	3178	702(Cl)
12	3263	2365	1697	1620	1581, 1522	1265, 1357	3178	3410(OH)
13	3278	2365	1710	1610	1581, 1522	1253, 1330	3178	1342,1518(NO_2)
14	3402	2386	1720	1610	1580, 1522	1220, 1345	3178	1355,1533(NO_2)
15	3263	2380	1715	1620	1581, 1520	1242, 1319	3178	
16	3283	2368	1670	1596	1550, 1596	1234, 1157	3170	
17	3271	2337	1697	1612	1581, 1520	1243, 1157	3178	1350,1530(NO_2)
18	3278	2322	1681	1620	1589, 1522	1249, 1155	3178	3410(OH)

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