Supporting information for

Unprecedented Ring Transformation of α-Active 2,4,5-Triphenylpyrylium Salt with η^3-Phosphines: Efficient Synthesis of Aryl- and Alkylphosphonium Triphenylcyclopentadienylides

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Ⅰ. Characterization of phosphonium salts 3, 4, 8 and phosphonium ylides 5.

Ⅱ. X-ray crystallographic data of 3a, 4a and 5c.

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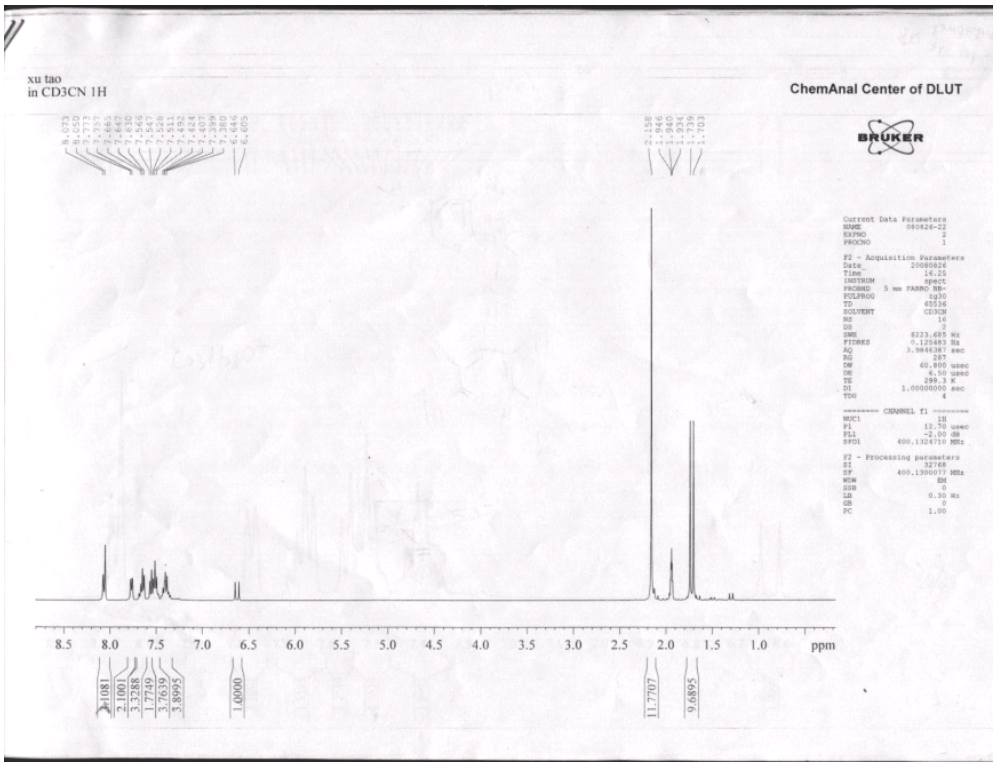
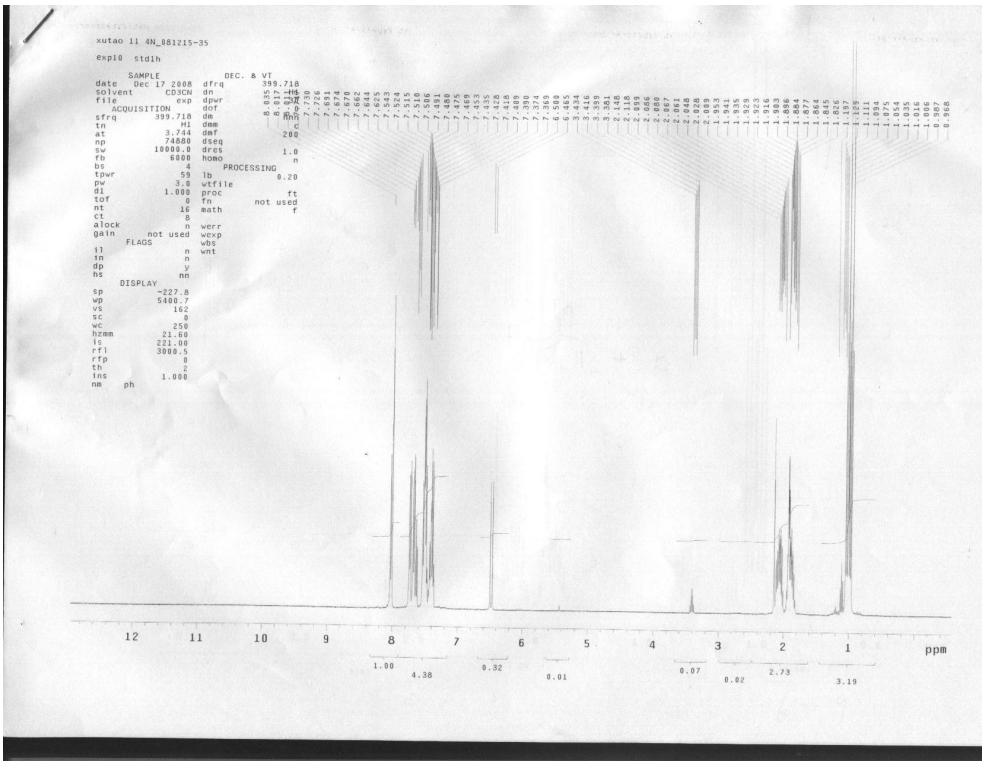


^{1}H NMR spectra of 3a



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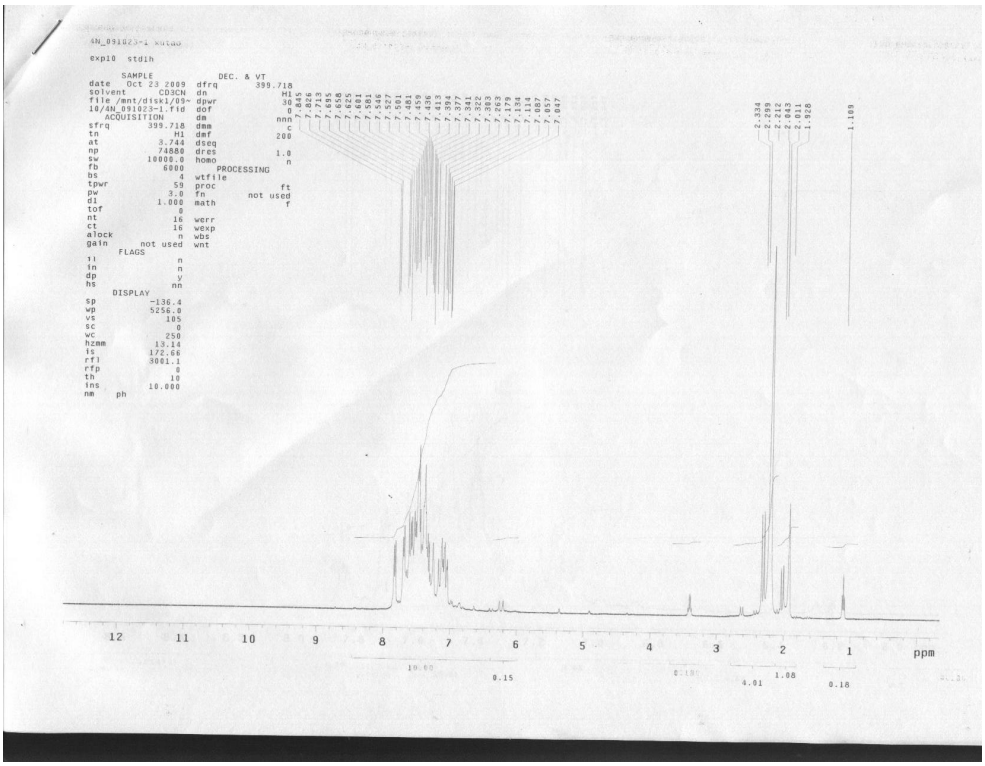
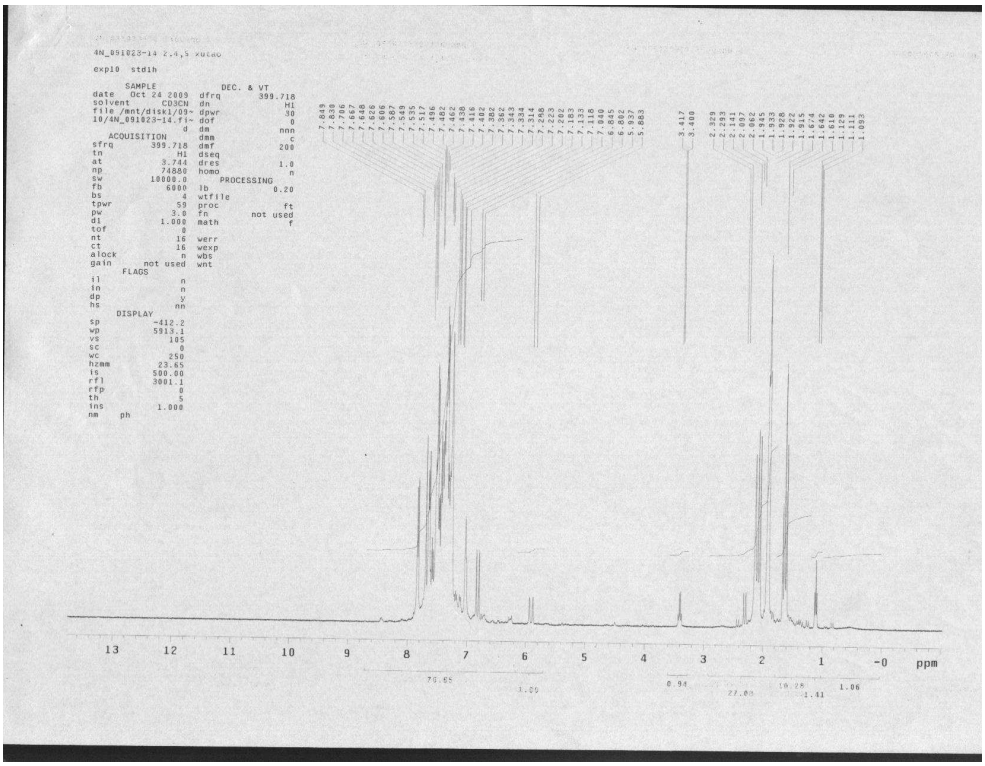
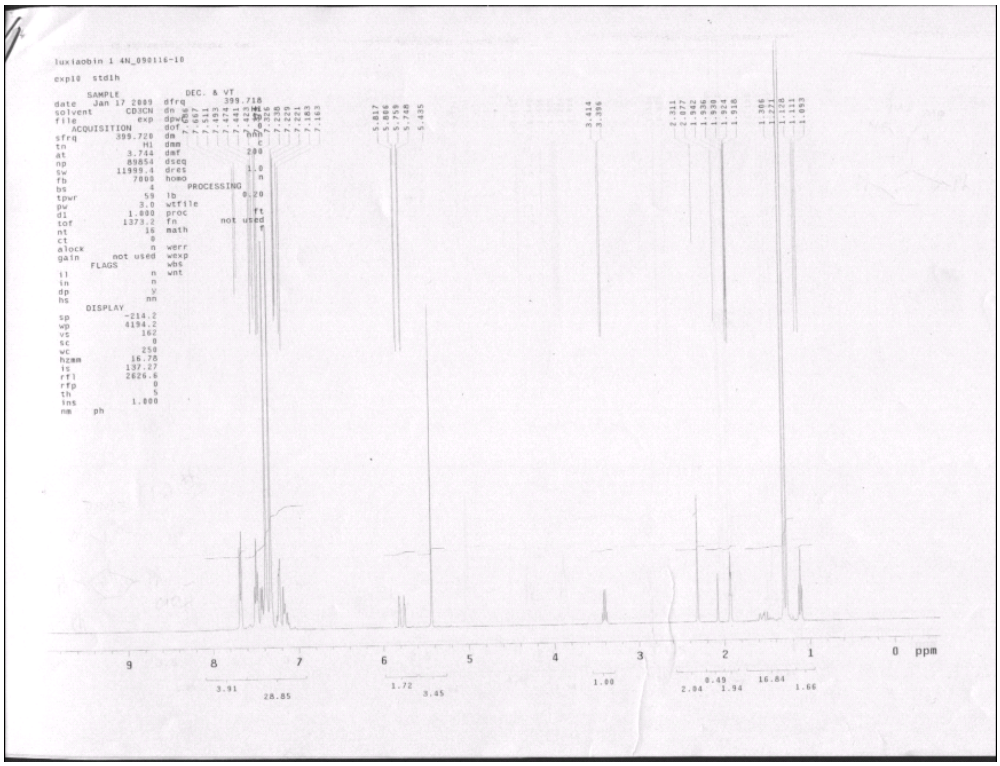


^{1}H NMR spectra of 3c



^{1}H NMR spectra of 3d



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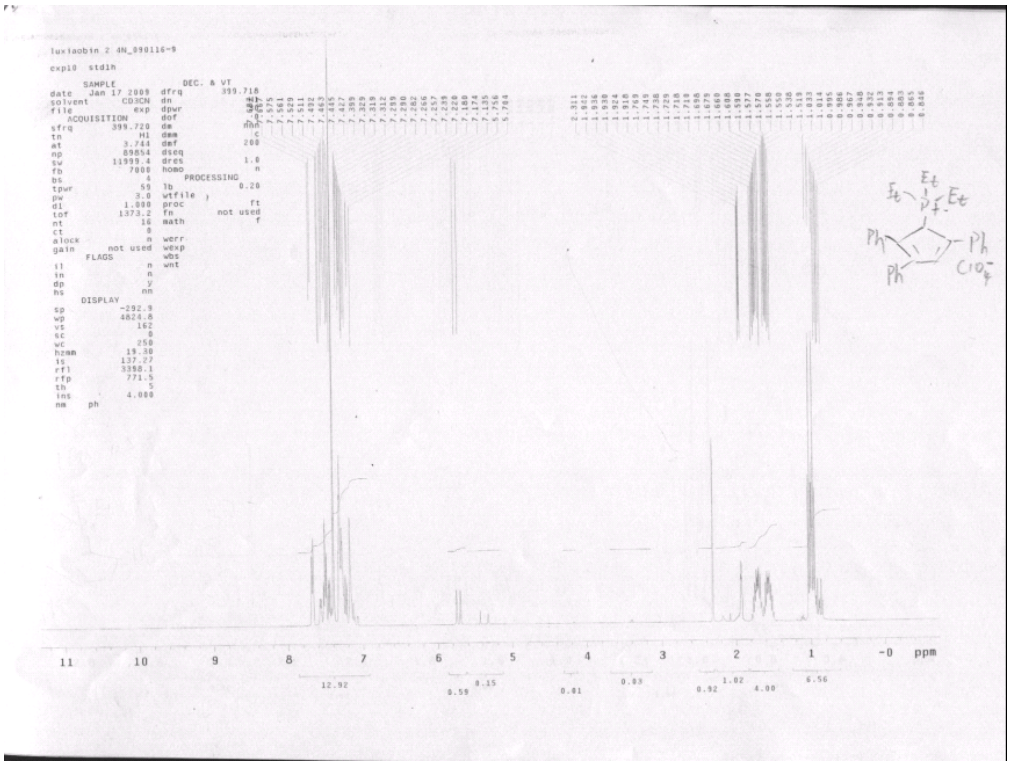
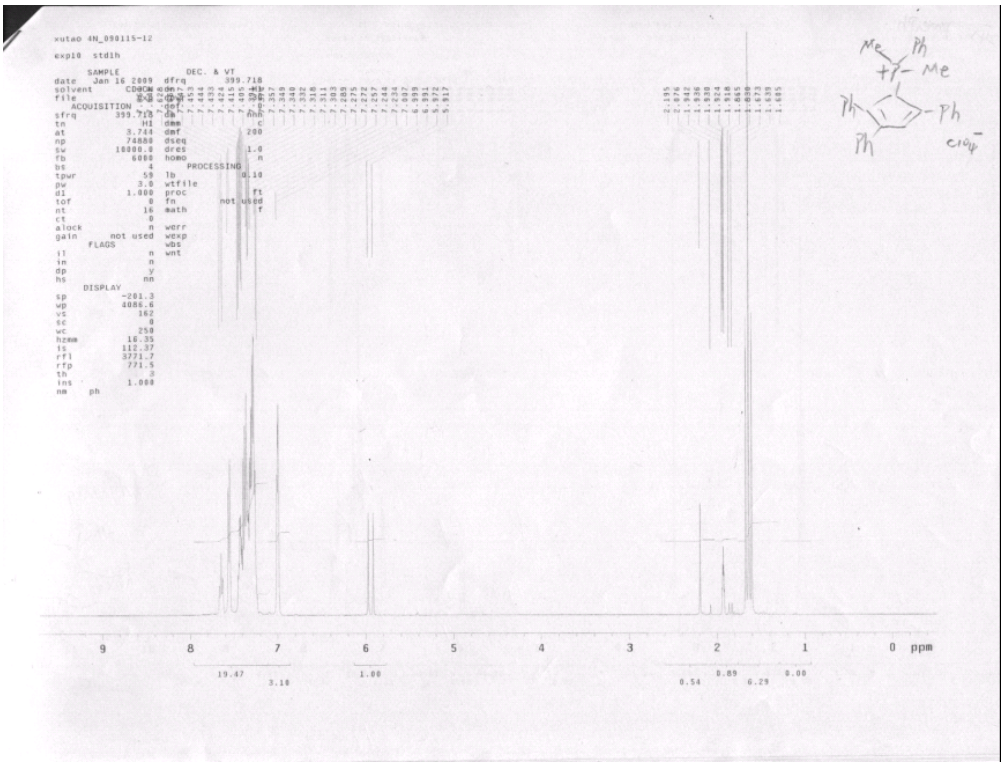
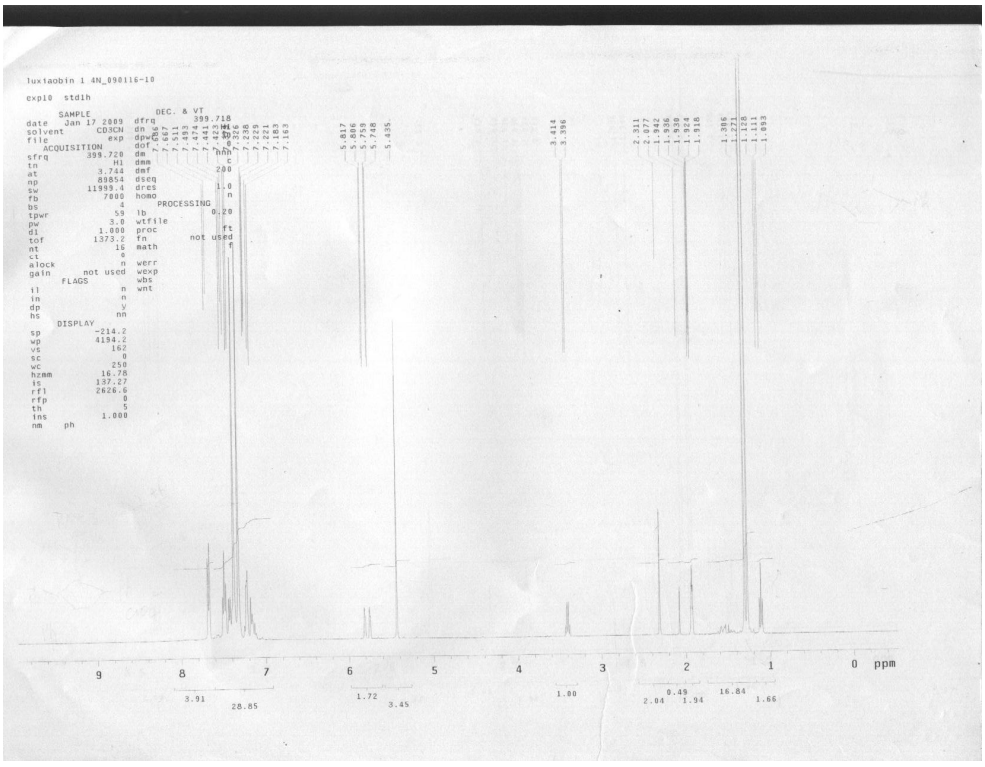


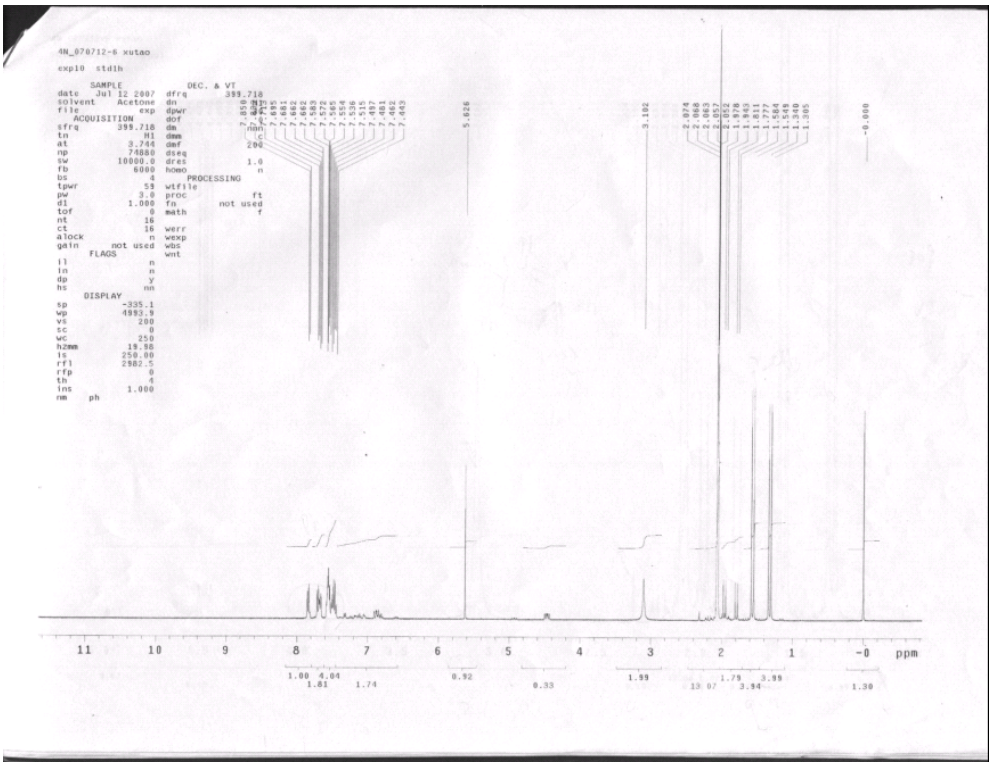
^{1}H NMR spectra of 4b



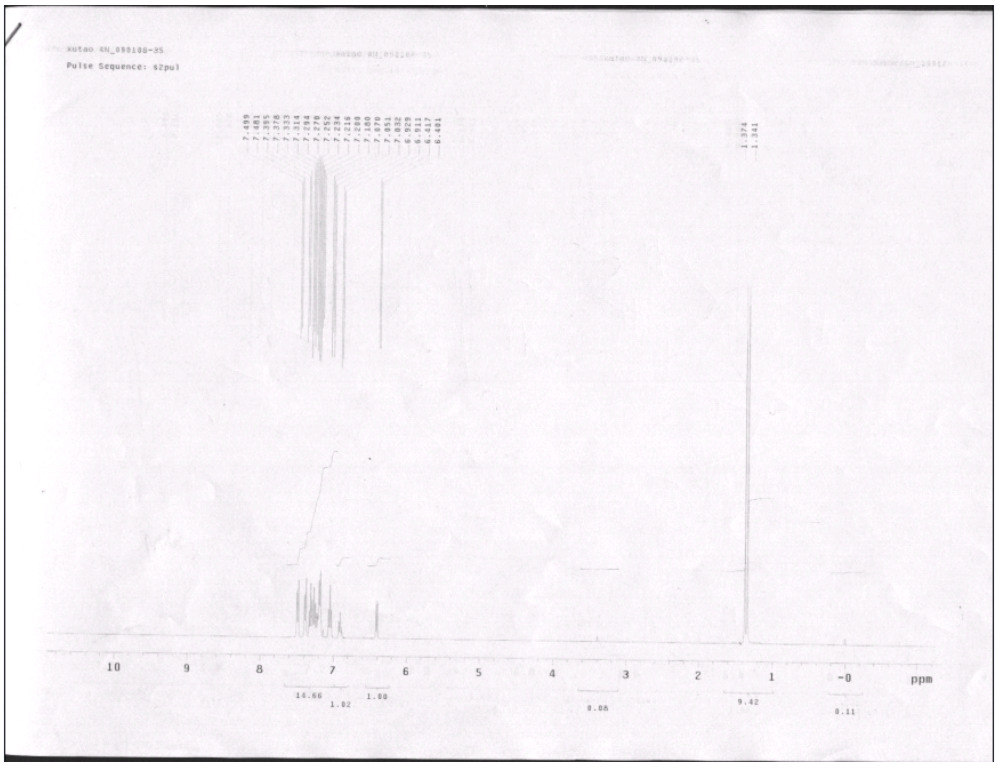
^{1}H NMR spectra of 4c



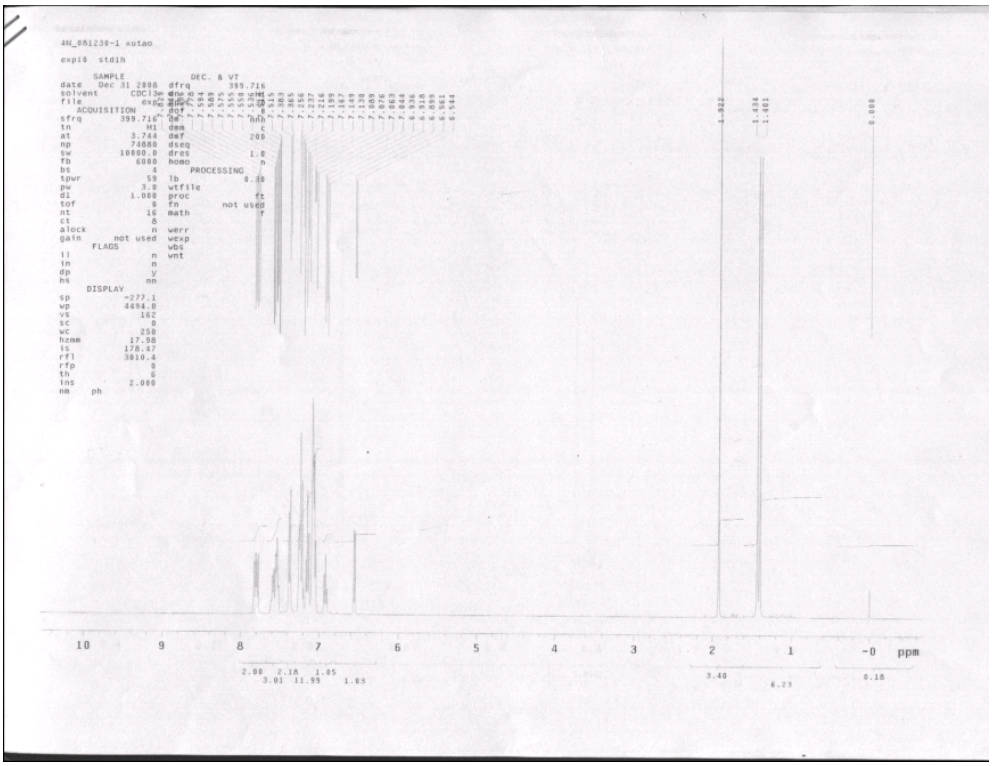
^{1}H NMR spectra of 4d



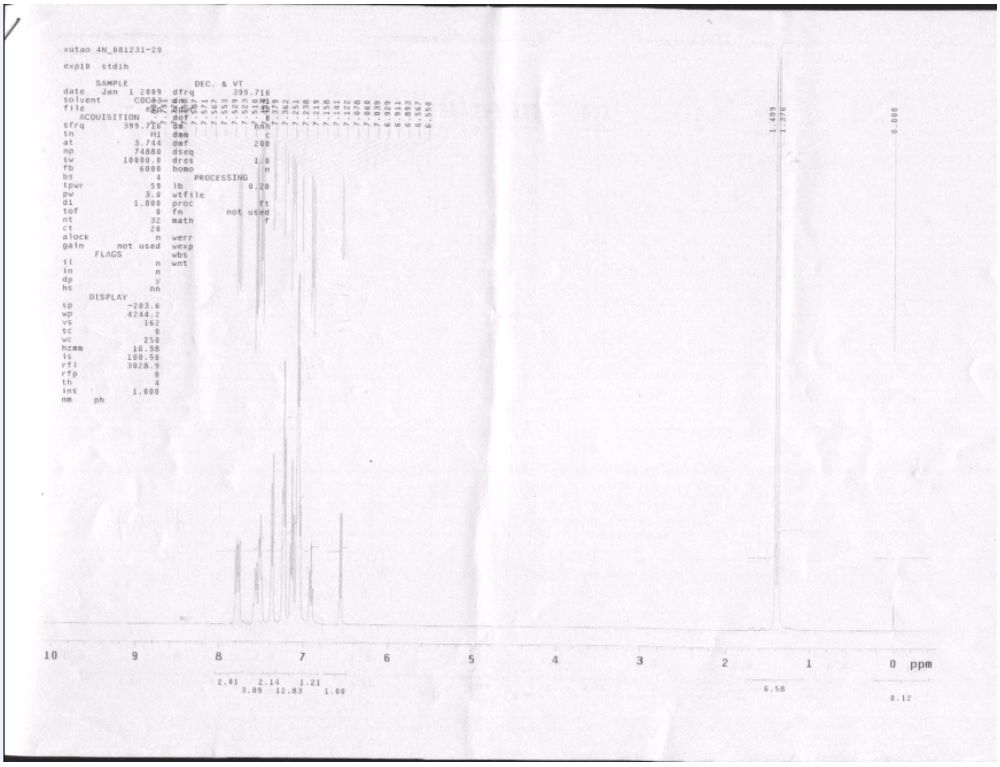
^{1}H NMR spectra of 8



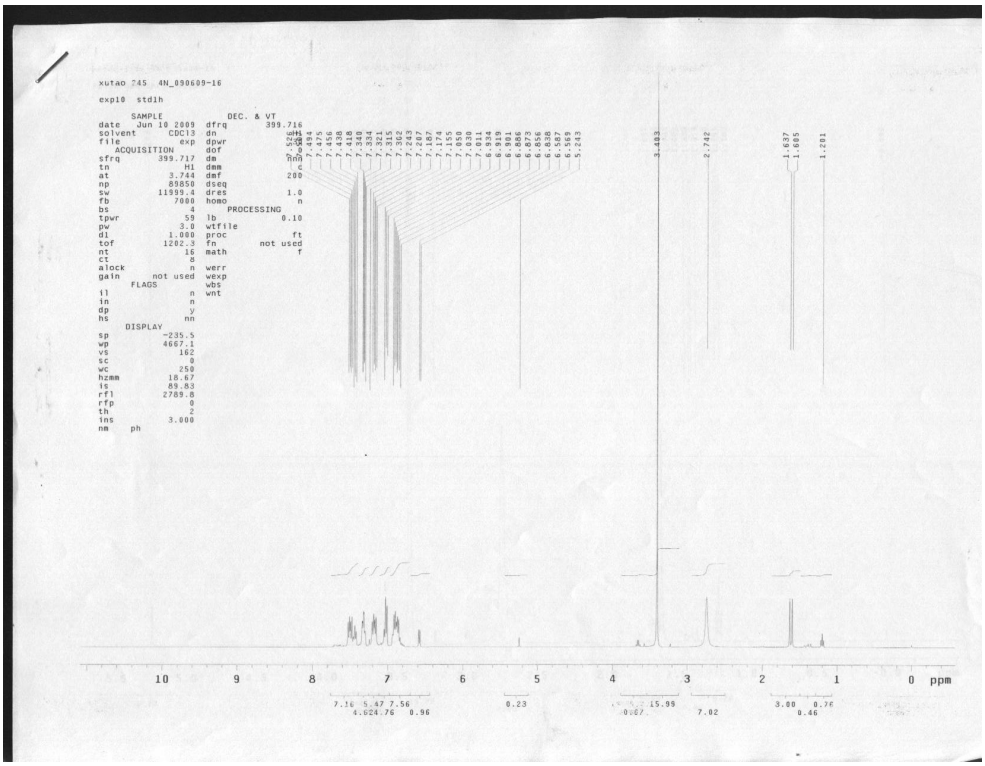
^{1}H NMR spectra of 5a



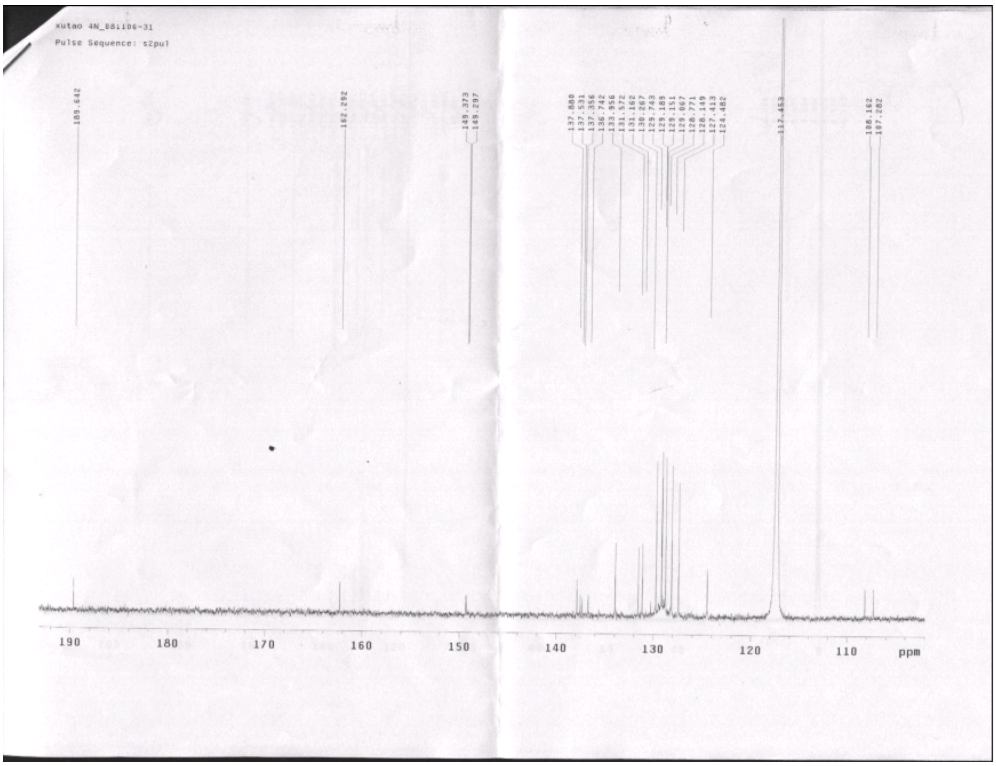
^{1}H NMR spectra of 5b



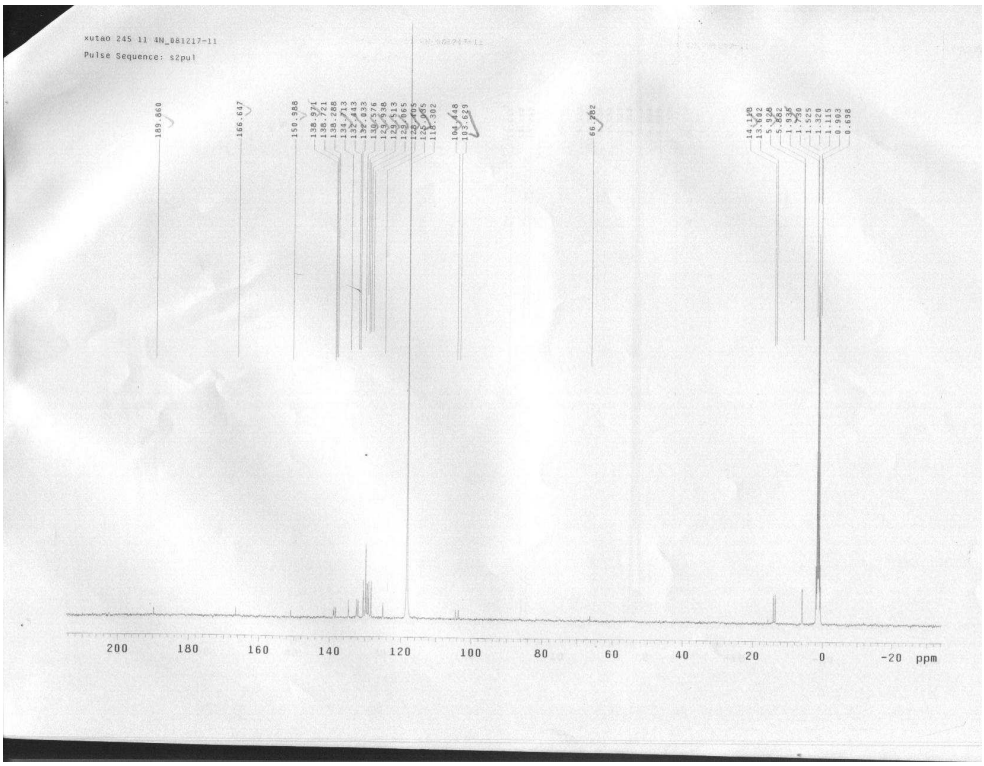
^{1}H NMR spectra of 5c



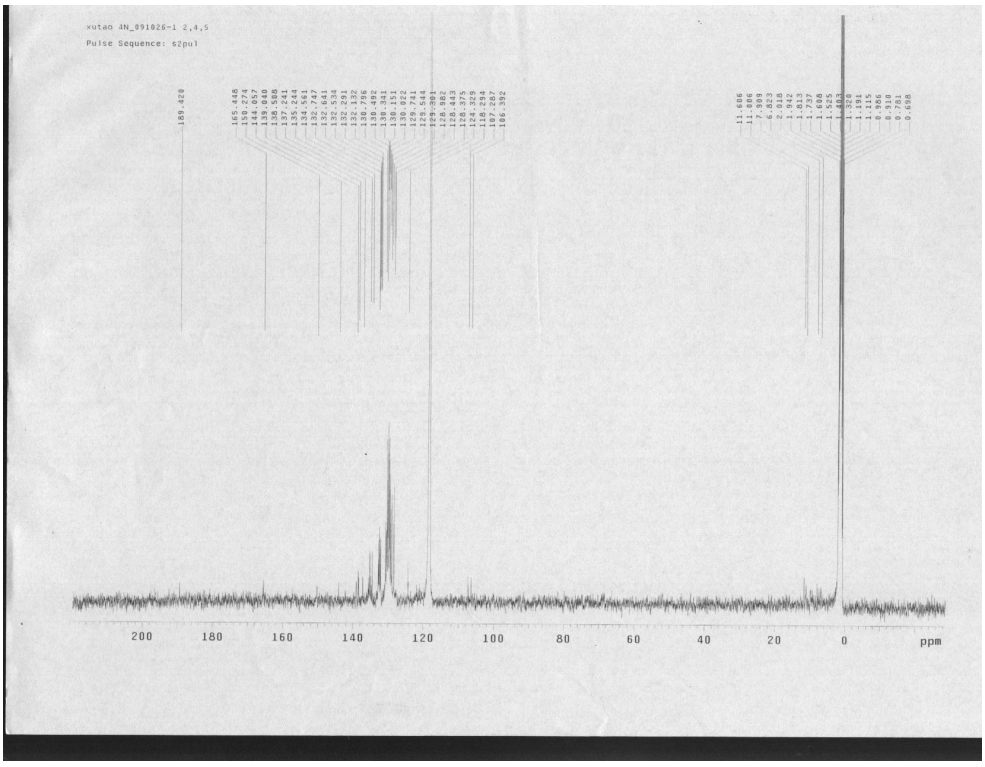
^{1}H NMR spectra of 5d



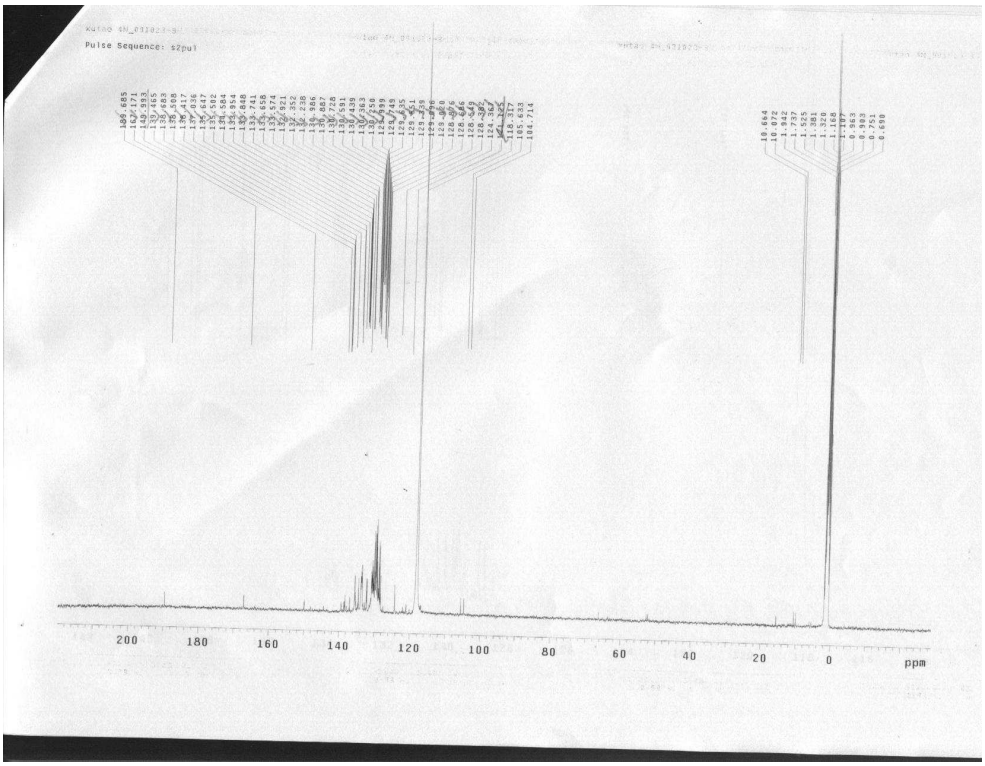
^{13}C NMR spectra of 3a



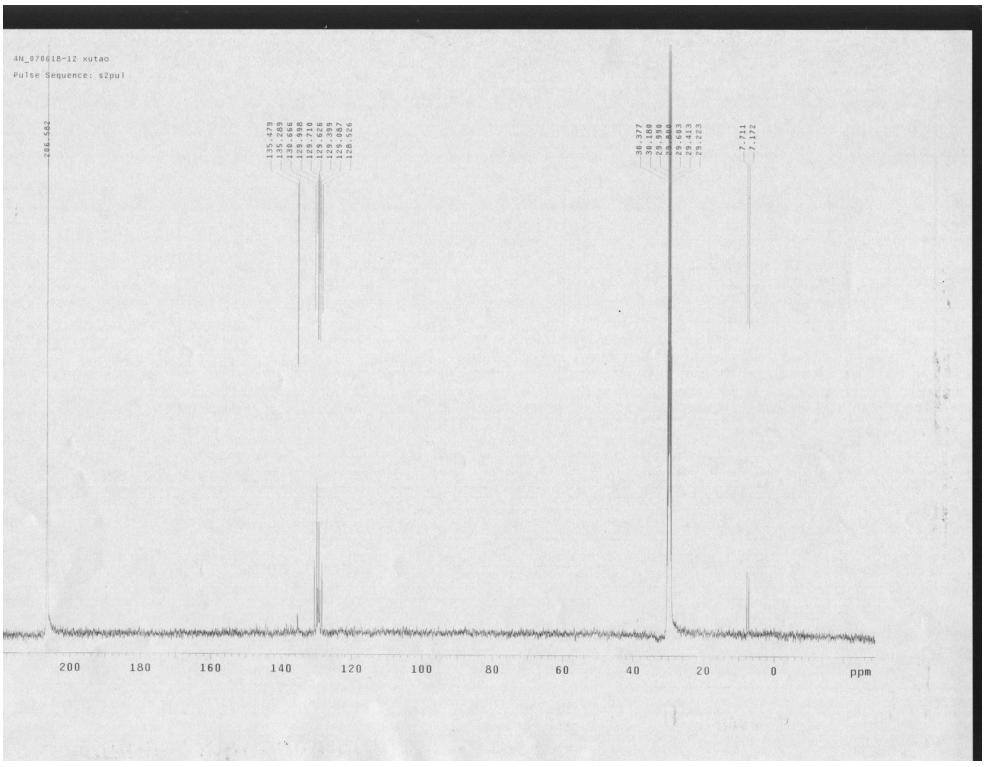
^{13}C NMR spectra of 3b



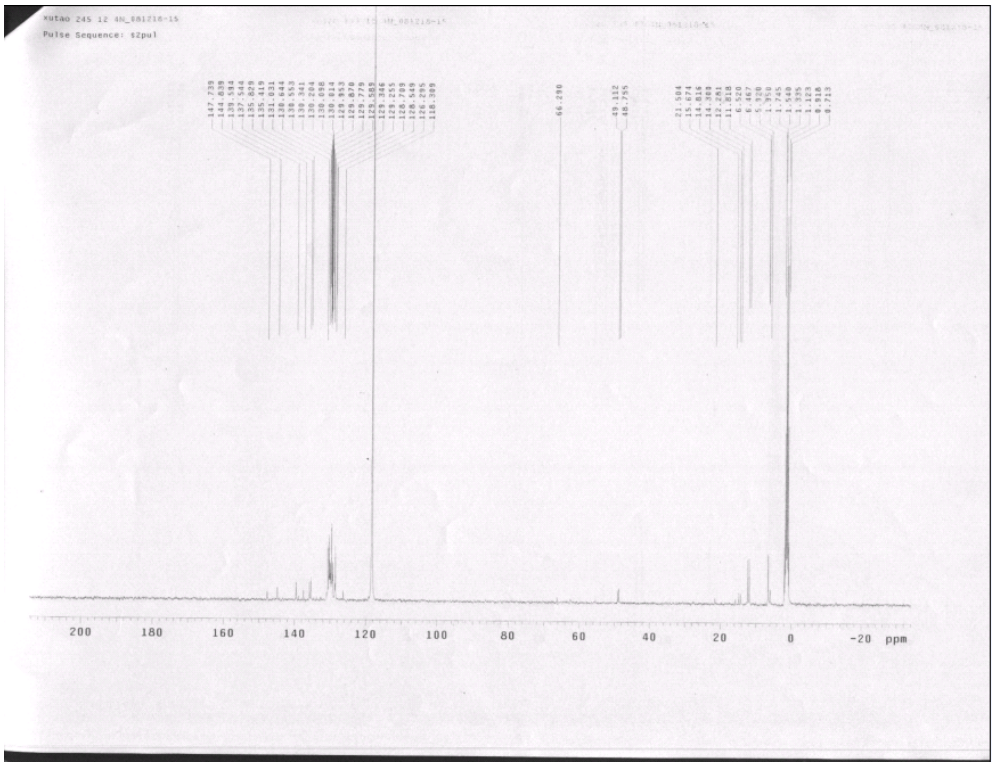
^{13}C NMR spectra of 3c



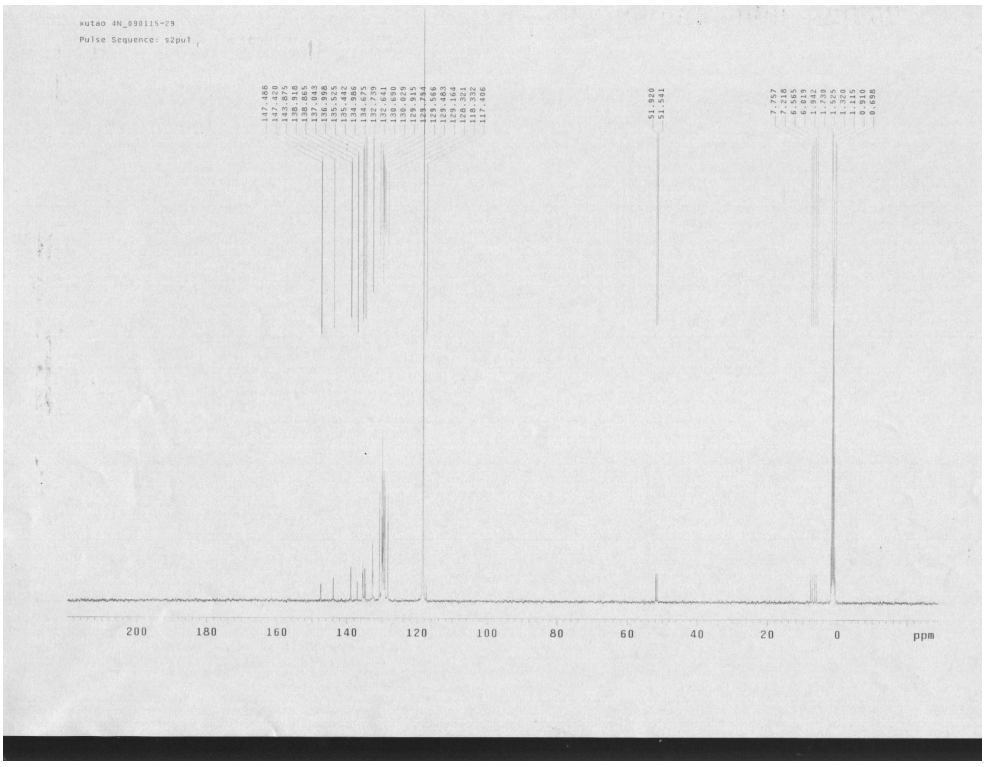
^{13}C NMR spectra of 3d



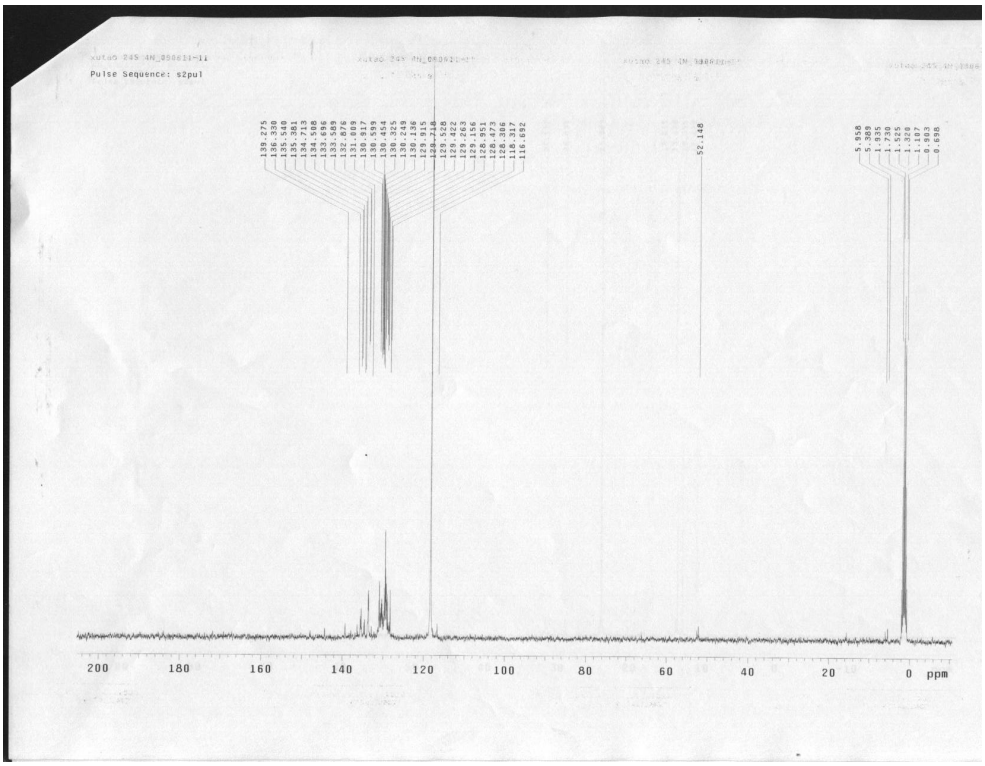
^{13}C NMR spectra of 4a



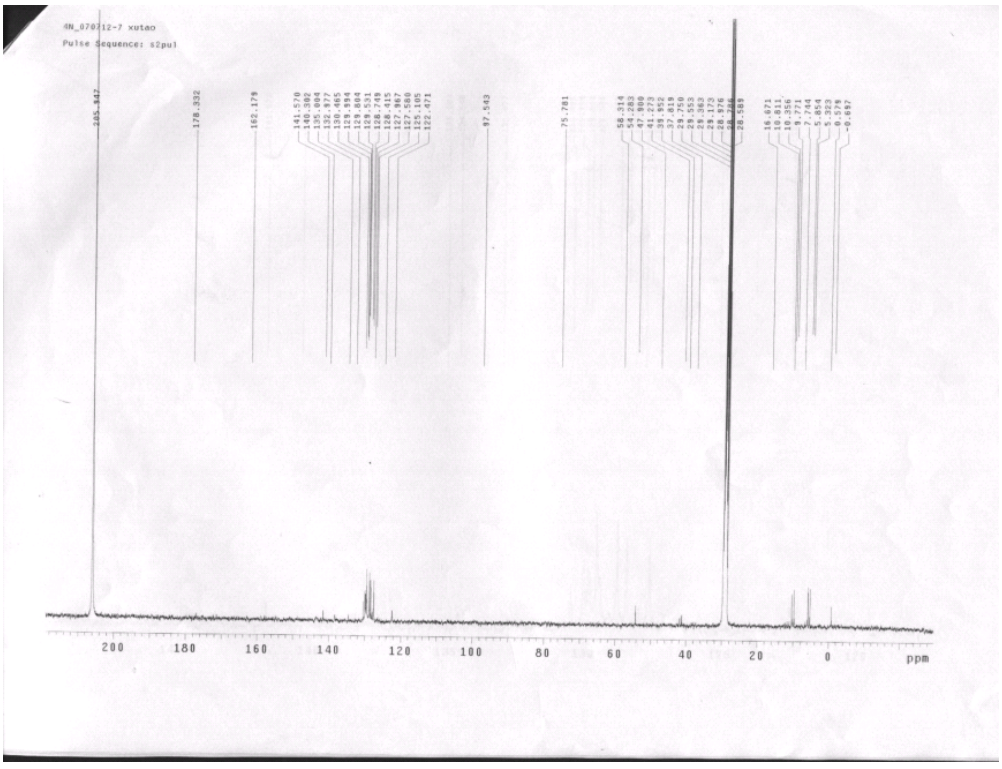
^{13}C NMR spectra of 4b



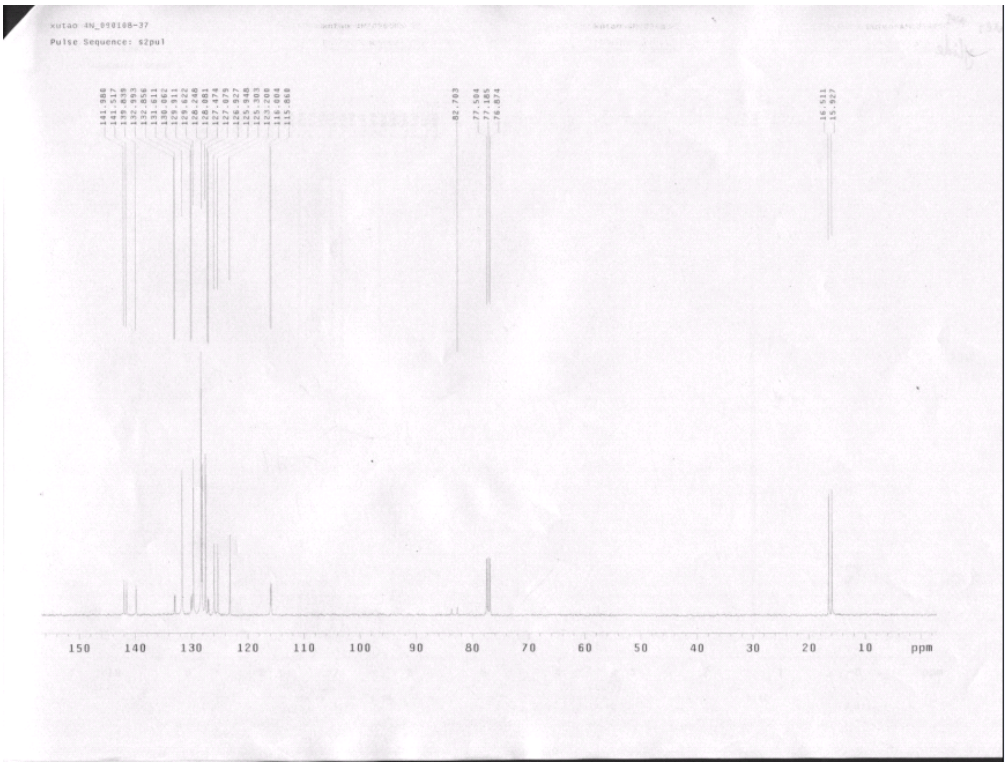
^{13}C NMR spectra of 4c



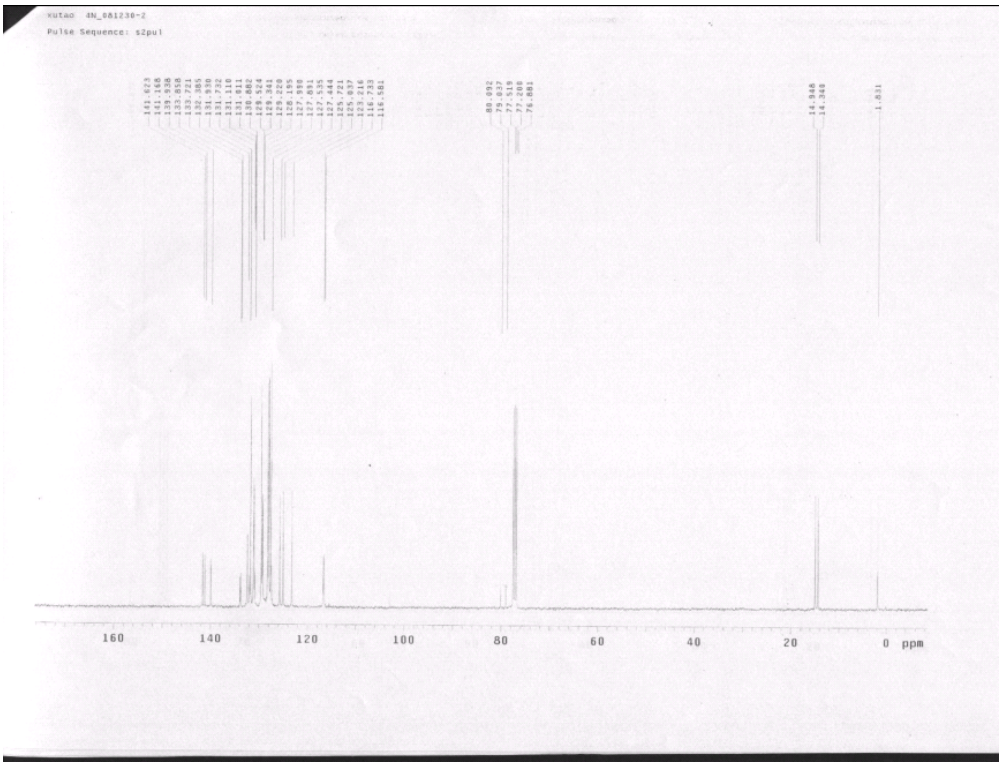
^{13}C NMR spectra of 4d



^{13}C NMR spectra of 8



^{13}C NMR spectra of 5a



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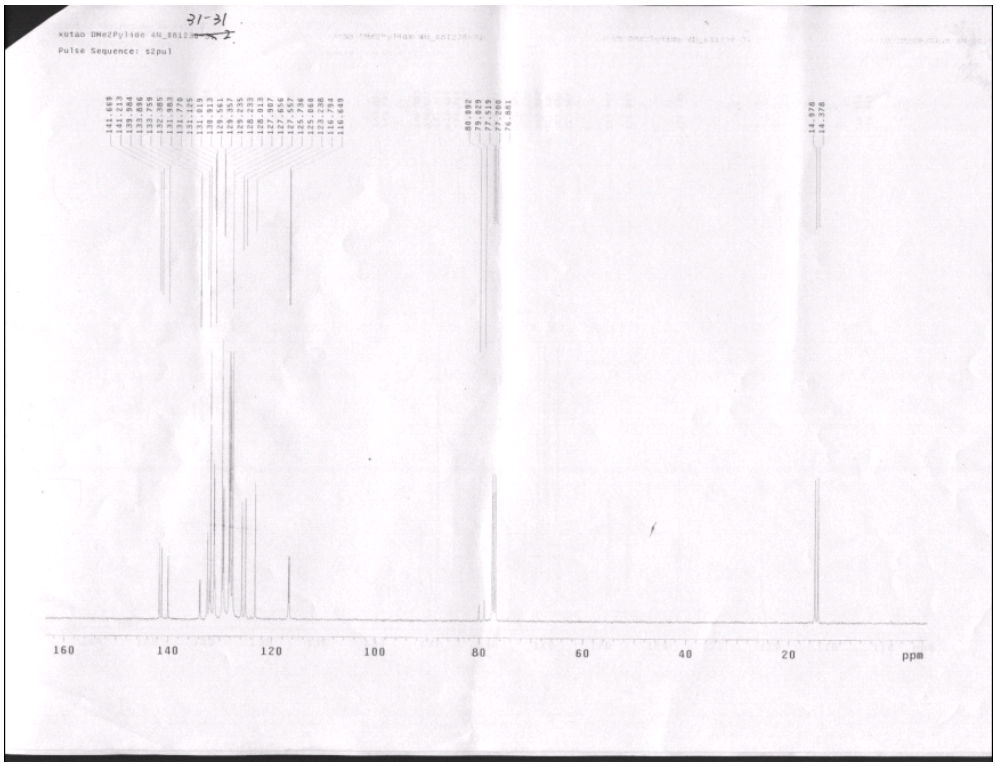
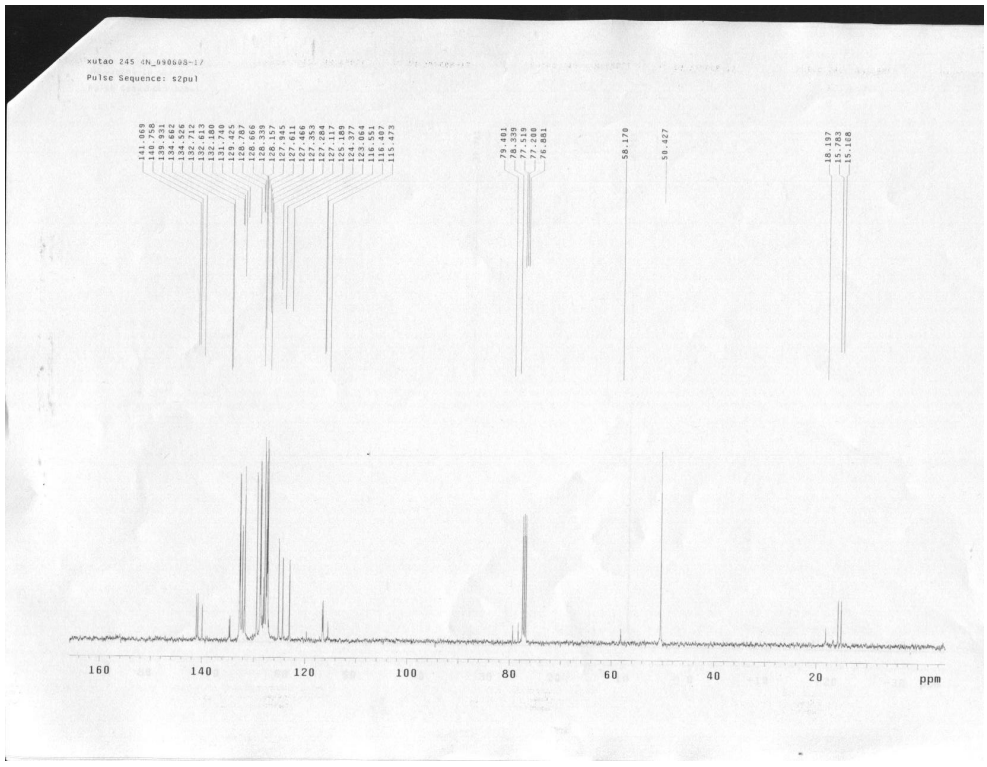
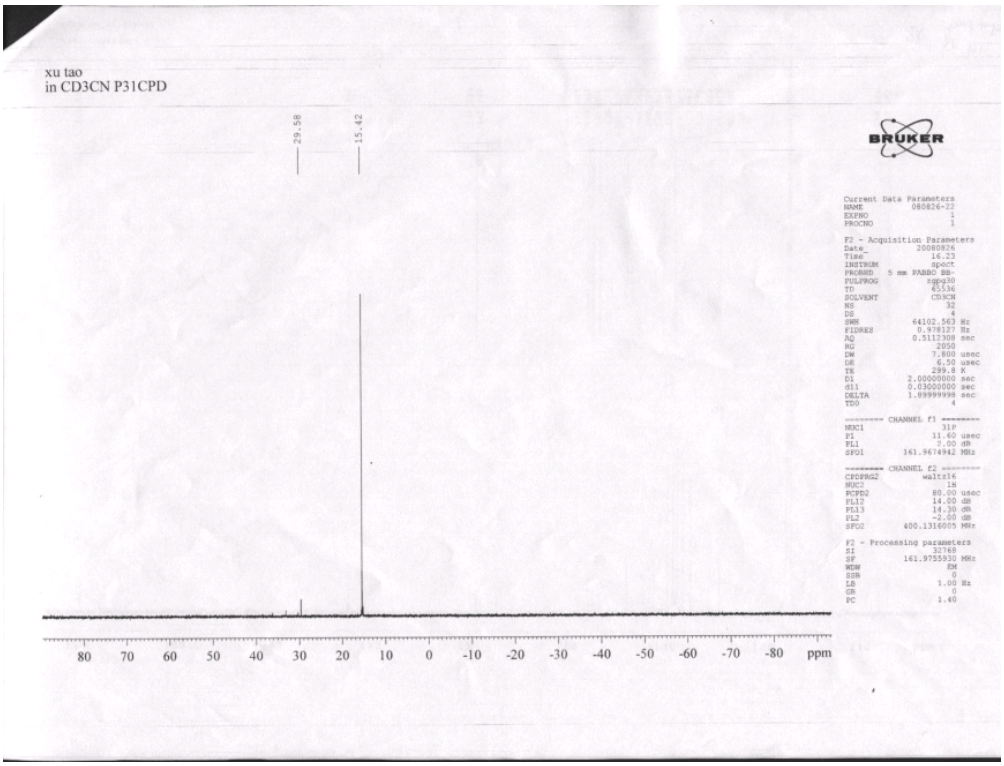


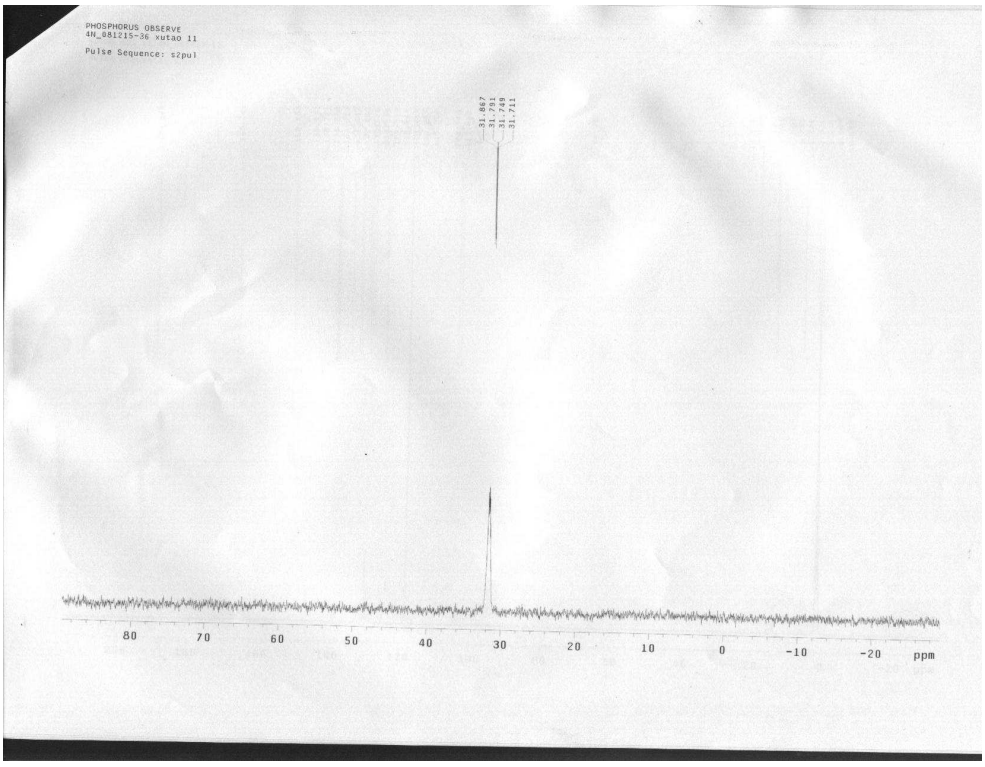
^{13}C NMR spectra of 5c



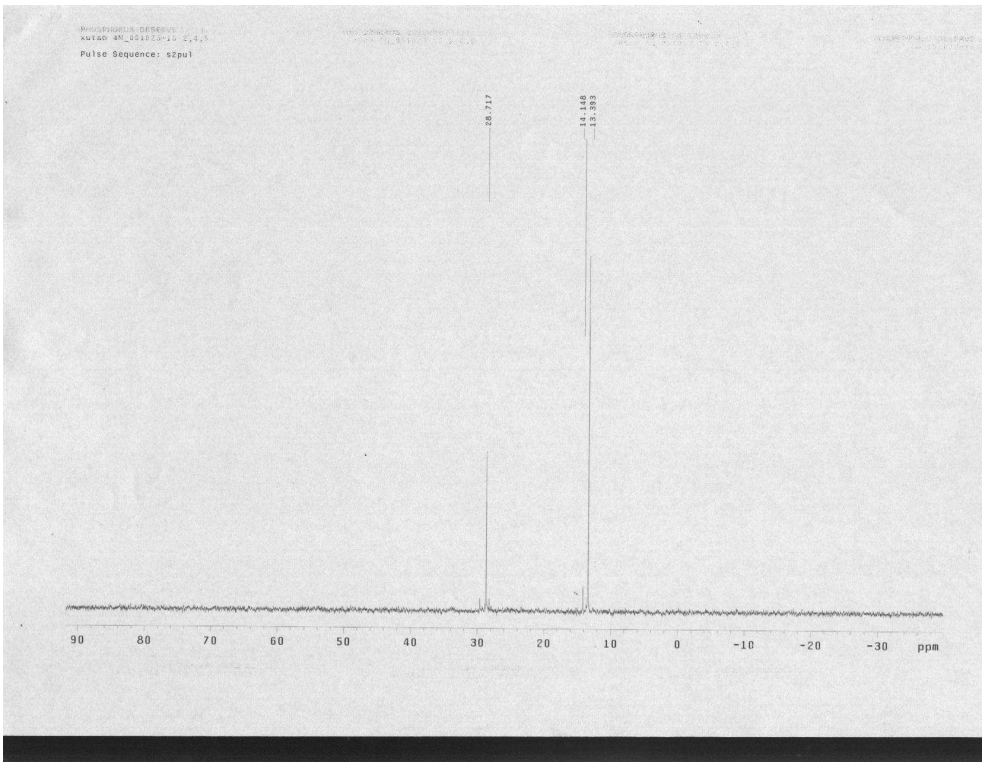
^{13}C NMR spectra of 5d



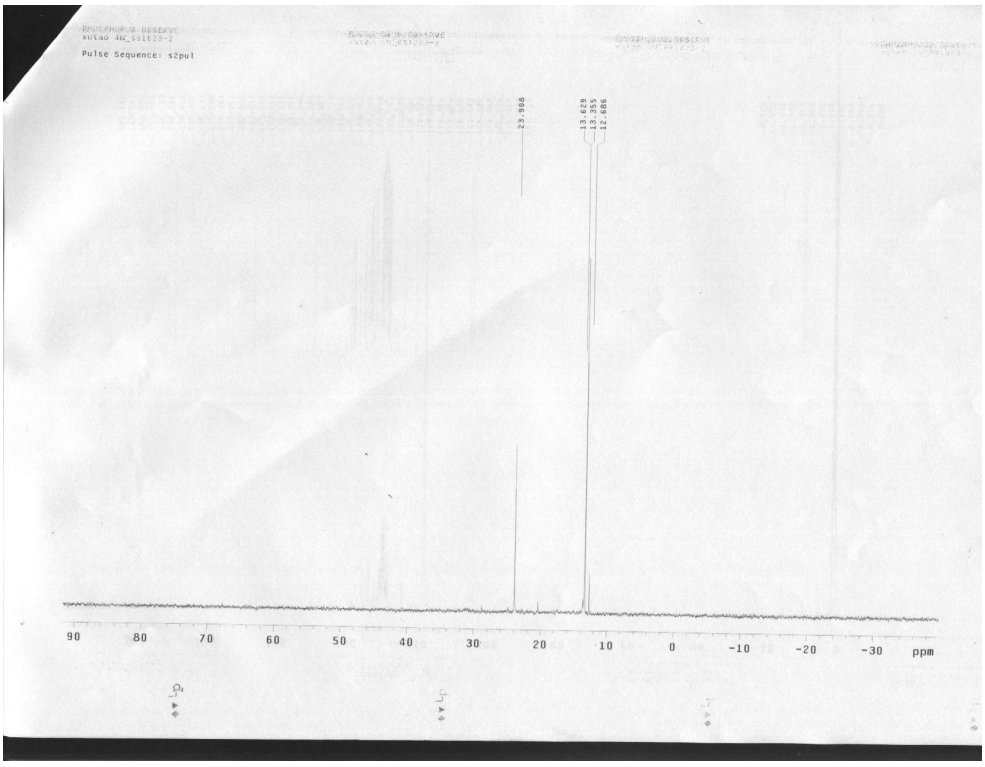
^{31}P NMR spectra of 3a



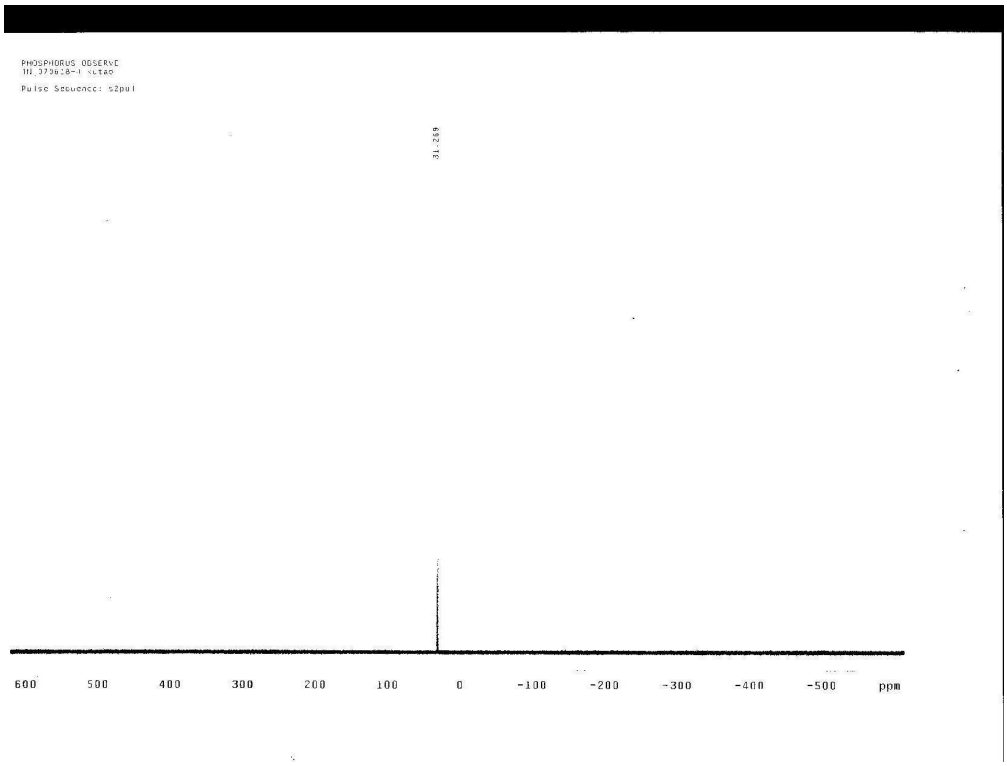
^{31}P NMR spectra of 3b



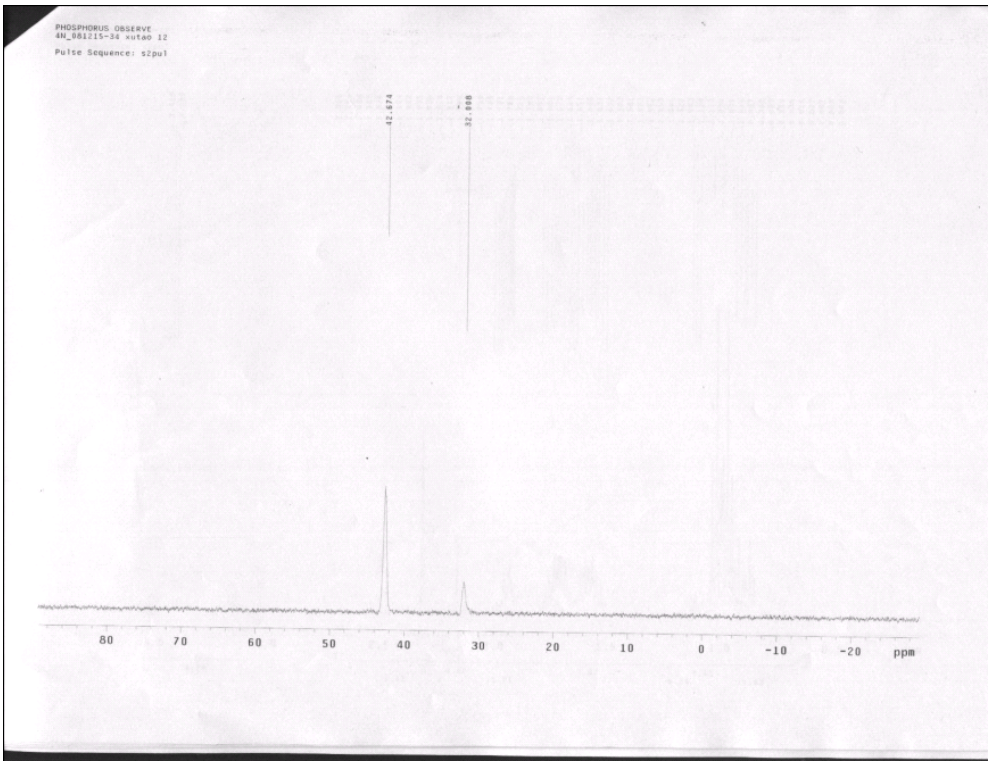
^{31}P NMR spectra of 3c



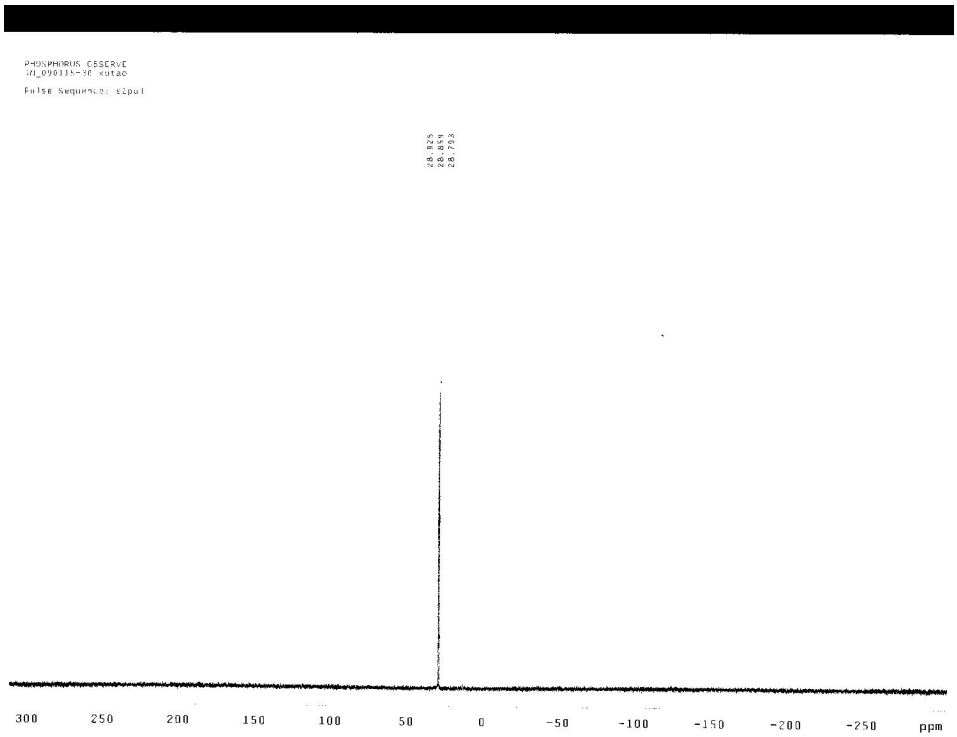
^{31}P NMR spectra of 3d



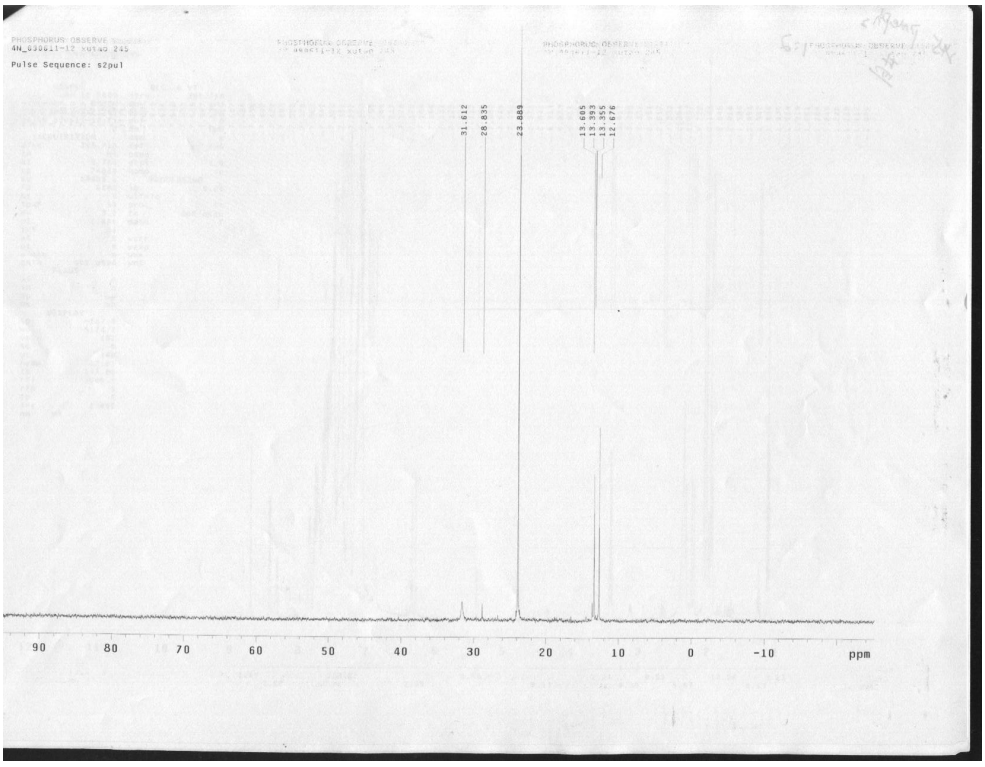
^{31}P NMR spectra of 4a



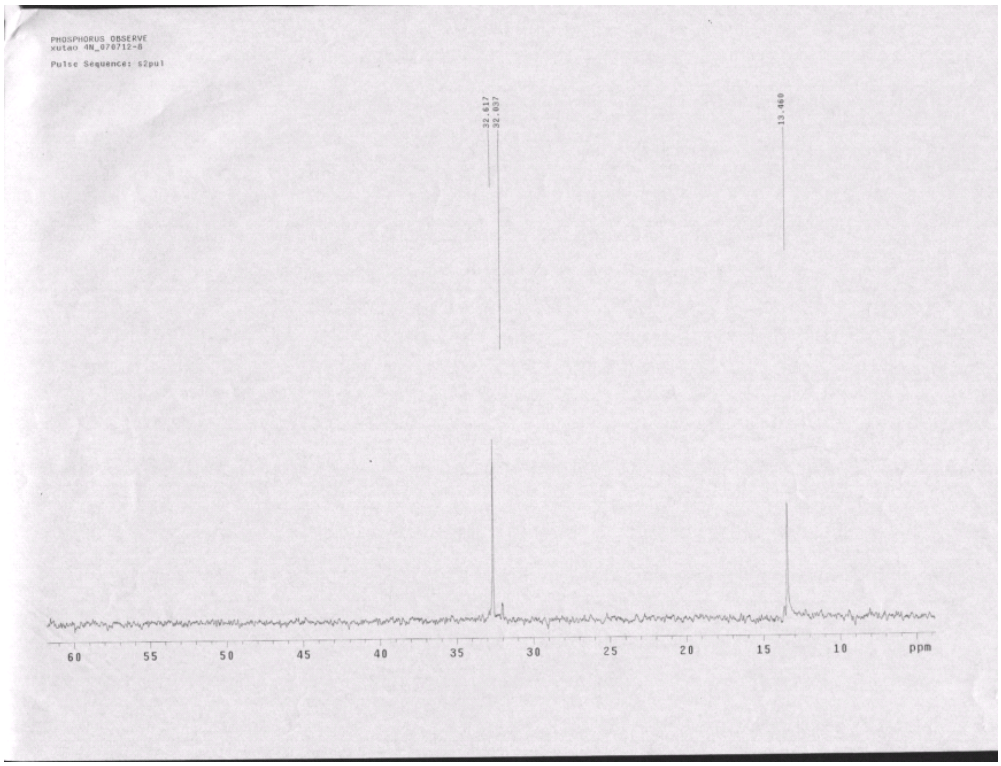
^{31}P NMR spectra of 4b



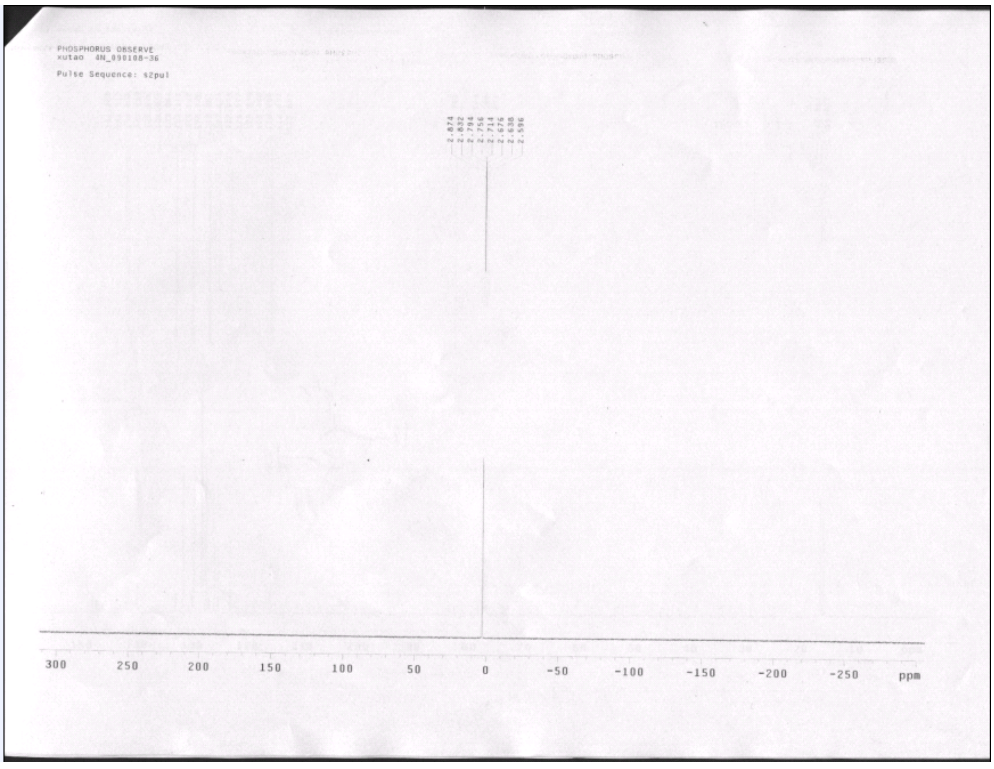
^{31}P NMR spectra of 4c



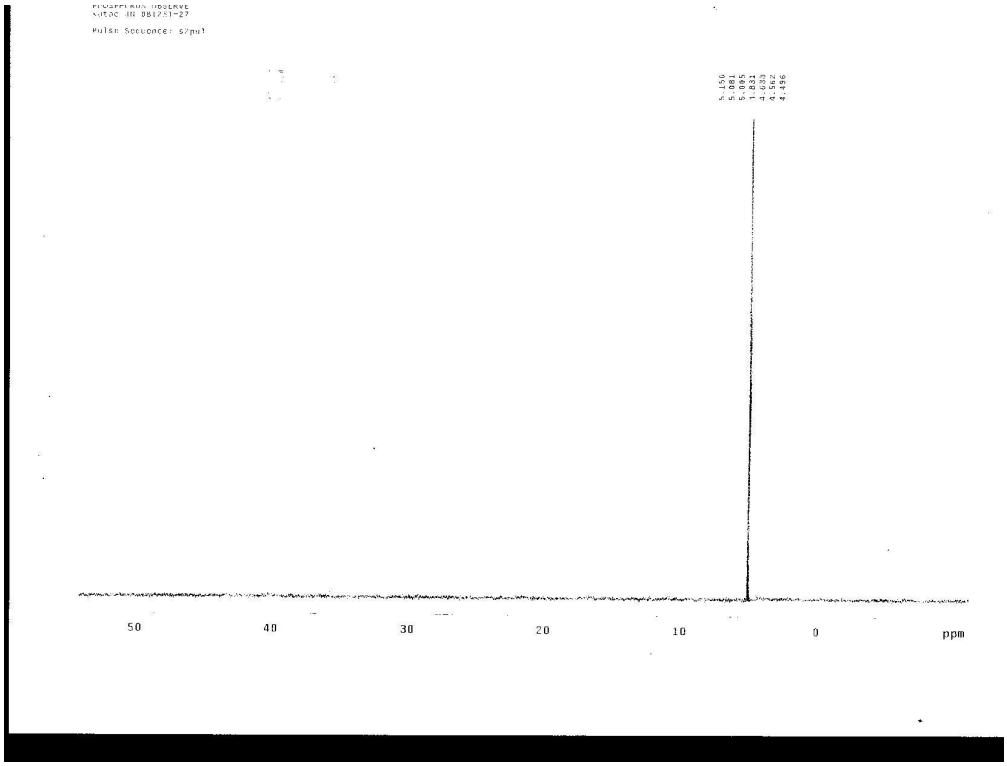
^{31}P NMR spectra of 4d



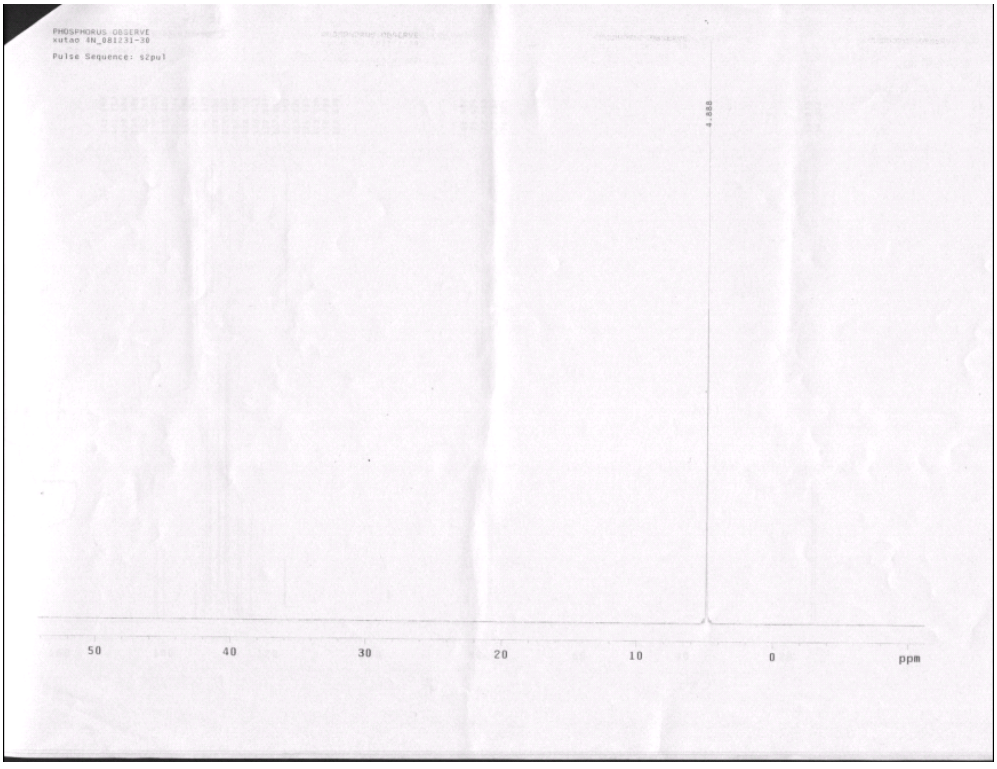
^{31}P NMR spectra of 8



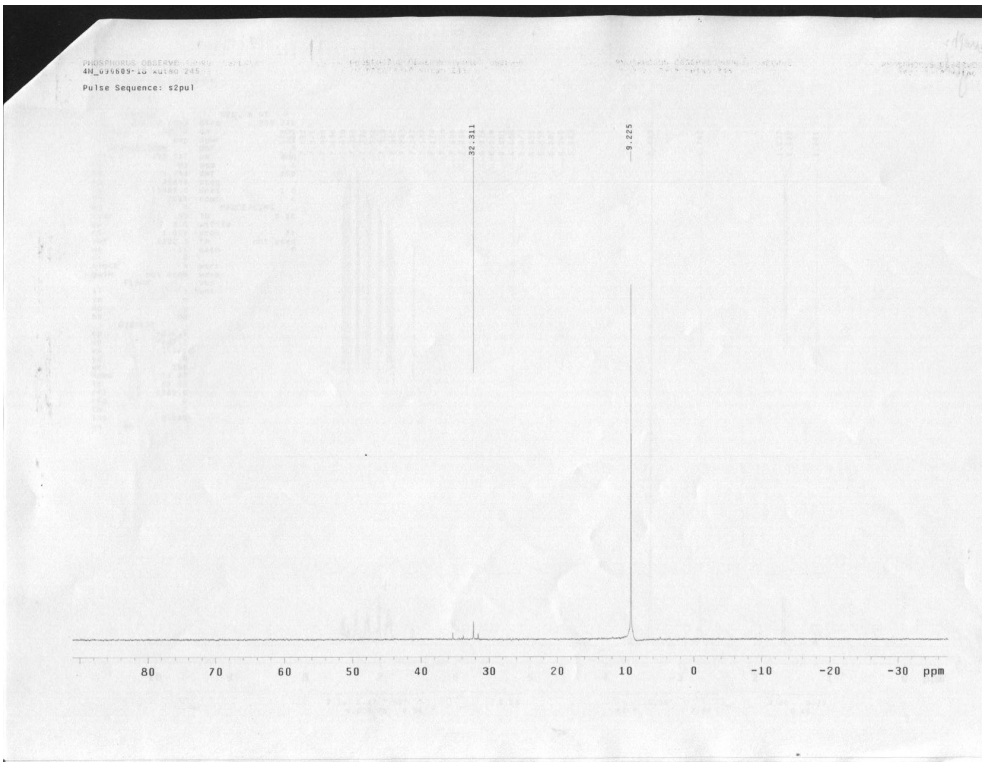
^{31}P NMR spectra of 5a



^{31}P NMR spectra of 5b



^{31}P NMR spectra of 5c



^{31}P NMR spectra of 5d

Ⅱ. X-ray crystallographic data of 3a, 4a and 5c.

1. X-ray crystallographic data of compound 5c.

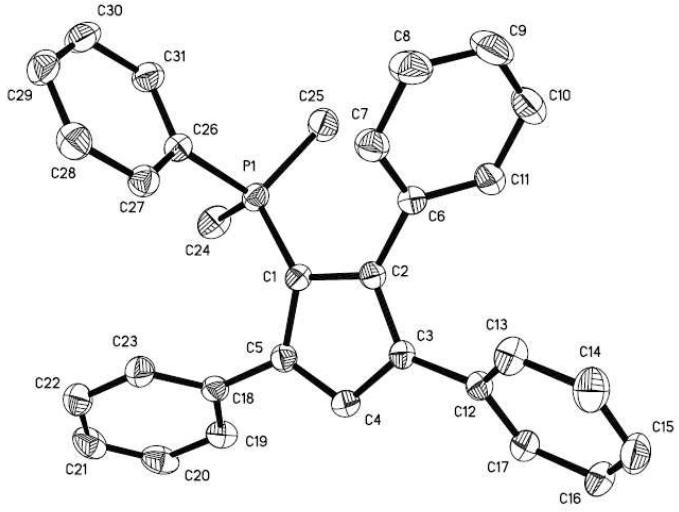


Table S1. **Crystal data and structure refinement for complex 5c.**

Identification code	5c
Empirical formula	$C_{31}H_{27}P.\ CH_2Cl_2$
Formula weight	515.42
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
space group	*P2(1)/c*
a (Å)	16.5447(5)
b (Å)	9.0530(3)
c (Å)	18.7979(5)
β (º)	125.869(2)
Volume ($Å^3$)	2746.96(14)
Z	4
D_{Calc} (mg/m^{-3})	1.246
μ (mm^{-1})	0.313
$F_{(000)}$	1080
Data / restraints / parameters	6219 / 0 / 316
Goodness-of-fit on F^2	1.051
R_1 [I>2σ(I)] [a]	0.0770
wR_2 [I>2σ(I)] [a]	0.2682
R_1 (all data) [a]	0.1065
wR_2 (all data) [a]	0.3067

[a] R1 = Σ| | Fo| –| Fc| | /Σ| Fo| ; wR2 = {Σ[w(Fo2–Fc2)2]/Σ[w(Fo2)]2}1/

Table S2. **Selected bond lengths [A] and angles [deg] for complex 5c.**

P(1)-C(1)	1.741(3)	C(2)-C(1)-P(1)	124.1(2)
P(1)-C(26)	1.806(3)	C(5)-C(1)-P(1)	126.6(2)
P(1)-C(25)	1.805(4)	C(3)-C(2)-C(1)	107.8(2)
P(1)-C(24)	1.805(4)	C(3)-C(2)-C(6)	126.8(3)
C(1)-C(2)	1.437(4)	C(1)-C(2)-C(6)	125.4(3)
C(1)-C(5)	1.444(4)	C(2)-C(3)-C(4)	108.0(2)
C(2)-C(3)	1.395(4)	C(2)-C(3)-C(12)	127.3(3)
C(2)-C(6)	1.478(4)	C(4)-C(3)-C(12)	124.5(3)
C(3)-C(4)	1.419(4)	C(5)-C(4)-C(3)	109.8(3)
C(3)-C(12)	1.482(4)	C(4)-C(5)-C(1)	107.1(2)
C(4)-C(5)	1.383(4)	C(4)-C(5)-C(18)	124.9(3)
C(5)-C(18)	1.478(4)	C(1)-C(5)-C(18)	127.5(3)
C(6)-C(7)	1.388(4)	C(7)-C(6)-C(11)	117.7(3)
C(6)-C(11)	1.399(4)	C(7)-C(6)-C(2)	121.6(3)
C(7)-C(8)	1.385(5)	C(11)-C(6)-C(2)	120.7(3)
C(8)-C(9)	1.386(6)	C(8)-C(7)-C(6)	121.2(3)
C(9)-C(10)	1.374(6)	C(7)-C(8)-C(9)	120.2(4)
C(10)-C(11)	1.382(5)	C(10)-C(9)-C(8)	119.3(4)
C(12)-C(17)	1.388(4)	C(9)-C(10)-C(11)	120.6(4)
C(12)-C(13)	1.391(5)	C(10)-C(11)-C(6)	121.0(3)
C(13)-C(14)	1.389(5)	C(17)-C(12)-C(13)	117.4(3)
C(14)-C(15)	1.370(6)	C(17)-C(12)-C(3)	120.8(3)
C(15)-C(16)	1.363(6)	C(13)-C(12)-C(3)	121.9(3)
C(16)-C(17)	1.386(5)	C(12)-C(13)-C(14)	121.0(3)
C(18)-C(19)	1.387(5)	C(15)-C(14)-C(13)	120.3(4)
C(18)-C(23)	1.398(5)	C(14)-C(15)-C(16)	119.7(3)
C(19)-C(20)	1.395(5)	C(15)-C(16)-C(17)	120.5(3)
C(20)-C(21)	1.376(6)	C(12)-C(17)-C(16)	121.2(3)
C(21)-C(22)	1.359(6)	C(19)-C(18)-C(23)	117.6(3)
C(22)-C(23)	1.381(5)	C(19)-C(18)-C(5)	121.7(3)
C(26)-C(27)	1.383(4)	C(23)-C(18)-C(5)	120.7(3)
C(26)-C(31)	1.390(4)	C(18)-C(19)-C(20)	120.1(3)
C(27)-C(28)	1.385(5)	C(21)-C(20)-C(19)	121.1(4)
C(28)-C(29)	1.369(5)	C(22)-C(21)-C(20)	119.2(3)
C(29)-C(30)	1.369(6)	C(21)-C(22)-C(23)	120.8(4)
C(30)-C(31)	1.386(5)	C(22)-C(23)-C(18)	121.2(3)
C(32)-Cl(2)	1.635(7)	C(27)-C(26)-C(31)	119.1(3)
C(32)-Cl(1)	1.685(7)	C(27)-C(26)-P(1)	120.5(2)
C(1)-P(1)-C(26)	114.74(14)	C(31)-C(26)-P(1)	120.4(2)
C(1)-P(1)-C(25)	112.72(16)	C(26)-C(27)-C(28)	120.4(3)
C(26)-P(1)-C(25)	106.10(17)	C(29)-C(28)-C(27)	120.2(3)
C(1)-P(1)-C(24)	112.24(16)	C(30)-C(29)-C(28)	120.0(3)
C(26)-P(1)-C(24)	105.67(16)	C(29)-C(30)-C(31)	120.6(3)
C(25)-P(1)-C(24)	104.57(19)	C(26)-C(31)-C(30)	119.7(3)
C(2)-C(1)-C(5)	107.2(2)	Cl(2)-C(32)-Cl(1)	117.1(4)

2. X-ray crystallographic data of compound 4a

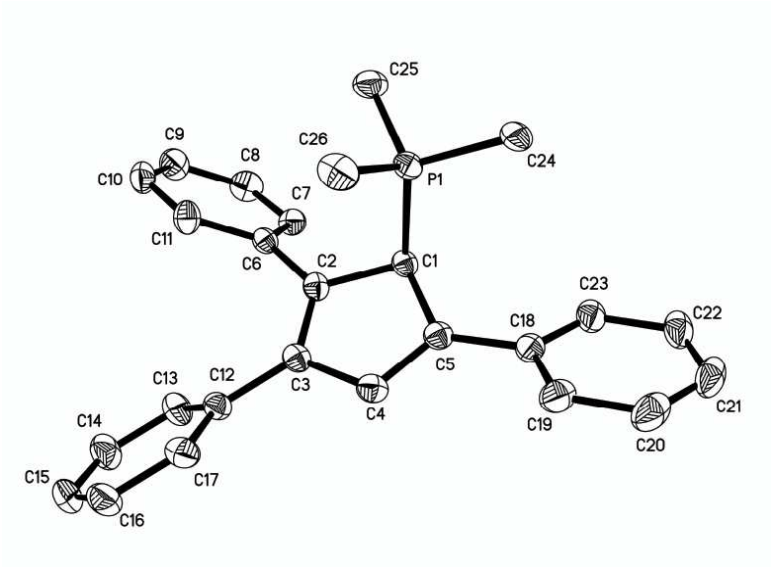


Fig. S1 **Crystal structure of compound 4a. The anion has been omitted for clarity.**

Table S3. **Crystal data and structure refinement for complex 4a.**

Identification code	4a
Empirical formula	$C_{26}H_{26}ClO_4P$
Formula weight	468.89
Temperature (K)	273(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
space group	*C*2/*c*
a (Å)	27.352(4)
b (Å)	10.2322(17)
c (Å)	20.664(6)
β (º)	125.869(2)
Volume ($Å^3$)	4686.5(17)
Z	8
D_{Calc} (mg/m^{-3})	1.329
μ (mm^{-1})	0.262
$F_{(000)}$	1968
Data / restraints / parameters	5310 / 0 / 292
Goodness-of-fit on F^2	1.043
R_1 [I>2σ(I)] [a]	0.0464
wR_2 [I>2σ(I)] [a]	0.0898
R_1 (all data) [a]	0.0616
wR_2 (all data) [a]	0.0966

[a] R1 = Σ| | Fo| –| Fc| | /Σ| Fo| ; wR2 = {Σ[w(Fo2–Fc2)2]/Σ[w(Fo2)]2}

Table S4. **Selected bond lengths [A] and angles [deg] for complex 4a.**

Cl(1)-O(3)	1.387(2)	C(1)-C(2)	1.518(3)
Cl(1)-O(4)	1.397(2)	C(2)-C(3)	1.358(3)
Cl(1)-O(1)	1.396(2)	C(2)-C(6)	1.474(3)
Cl(1)-O(2)	1.400(2)	C(3)-C(4)	1.460(3)
P(1)-C(26)	1.780(2)	C(3)-C(12)	1.482(3)
P(1)-C(24)	1.783(2)	C(4)-C(5)	1.347(3)
P(1)-C(25)	1.783(2)	C(5)-C(18)	1.472(3)
P(1)-C(1)	1.828(2)	C(6)-C(11)	1.392(3)
C(1)-C(5)	1.513(3)	C(6)-C(7)	1.387(3)
C(1)-C(2)	1.518(3)	C(7)-C(8)	1.384(3)
C(2)-C(3)	1.358(3)	C(8)-C(9)	1.380(3)
C(2)-C(6)	1.474(3)	C(9)-C(10)	1.366(4)
C(3)-C(4)	1.460(3)	C(10)-C(11)	1.381(3)
C(3)-C(12)	1.482(3)	C(2)-C(3)-C(4)	109.11(18)
C(4)-C(5)	1.347(3)	C(2)-C(3)-C(12)	128.12(19)
C(5)-C(18)	1.472(3)	C(4)-C(3)-C(12)	122.59(19)
C(6)-C(11)	1.392(3)	C(5)-C(4)-C(3)	110.70(19)
C(6)-C(7)	1.387(3)	C(4)-C(5)-C(18)	127.2(2)
C(7)-C(8)	1.384(3)	C(4)-C(5)-C(1)	108.04(18)
C(8)-C(9)	1.380(3)	C(18)-C(5)-C(1)	124.77(19)
C(9)-C(10)	1.366(4)	C(11)-C(6)-C(7)	117.9(2)
C(10)-C(11)	1.381(3)	C(11)-C(6)-C(2)	120.92(19)
C(12)-C(13)	1.391(3)	C(7)-C(6)-C(2)	121.19(19)
C(12)-C(17)	1.389(3)	C(8)-C(7)-C(6)	120.4(2)
C(13)-C(14)	1.383(3)	C(7)-C(8)-C(9)	120.6(2)
C(14)-C(15)	1.368(4)	C(10)-C(9)-C(8)	119.6(2)
C(15)-C(16)	1.372(4)	C(9)-C(10)-C(11)	120.0(2)
C(16)-C(17)	1.392(3)	C(10)-C(11)-C(6)	121.4(2)
C(18)-C(19)	1.391(3)	C(13)-C(12)-C(17)	118.4(2)
C(18)-C(23)	1.394(3)	C(13)-C(12)-C(3)	121.4(2)
C(19)-C(20)	1.379(3)	C(17)-C(12)-C(3)	120.2(2)
C(20)-C(21)	1.369(5)	C(12)-C(13)-C(14)	120.7(2)
C(21)-C(22)	1.383(4)	C(15)-C(14)-C(13)	120.3(3)
O(3)-Cl(1)-O(4)	110.49(19)	C(14)-C(15)-C(16)	119.9(2)
O(3)-Cl(1)-O(1)	108.6(2)	C(15)-C(16)-C(17)	120.4(3)
O(4)-Cl(1)-O(1)	111.43(14)	C(12)-C(17)-C(16)	120.2(2)
O(3)-Cl(1)-O(2)	107.0(2)	C(19)-C(18)-C(23)	119.4(2)
O(4)-Cl(1)-O(2)	108.79(16)	C(19)-C(18)-C(5)	119.9(2)
O(1)-Cl(1)-O(2)	110.38(19)	C(23)-C(18)-C(5)	120.7(2)
C(26)-P(1)-C(24)	108.56(12)	C(20)-C(19)-C(18)	120.0(3)
C(26)-P(1)-C(25)	108.39(13)	C(19)-C(20)-C(21)	120.5(3)
C(24)-P(1)-C(25)	106.96(12)	C(20)-C(21)-C(22)	120.6(2)

C(26)-P(1)-C(1)	109.12(11)	C(21)-C(22)-C(23)	119.5(3)
C(24)-P(1)-C(1)	112.21(10)	C(22)-C(23)-C(18)	120.0(3)
C(25)-P(1)-C(1)	111.48(11)	C(2)-C(3)-C(4)	109.11(18)
C(5)-C(1)-C(2)	103.56(16)	C(2)-C(3)-C(12)	128.12(19)
C(5)-C(1)-P(1)	108.76(13)	C(4)-C(3)-C(12)	122.59(19)
C(2)-C(1)-P(1)	108.78(14)	C(5)-C(4)-C(3)	110.70(19)
C(3)-C(2)-C(6)	128.40(19)	C(4)-C(5)-C(18)	127.2(2)
C(3)-C(2)-C(1)	108.38(18)	C(4)-C(5)-C(1)	108.04(18)
C(6)-C(2)-C(1)	123.22(18)	C(18)-C(5)-C(1)	124.77(19)
Cl(1)-O(3)	1.387(2)	C(11)-C(6)-C(7)	117.9(2)
Cl(1)-O(4)	1.397(2)	C(11)-C(6)-C(2)	120.92(19)
Cl(1)-O(1)	1.396(2)	C(7)-C(6)-C(2)	121.19(19)
Cl(1)-O(2)	1.400(2)	C(8)-C(7)-C(6)	120.4(2)
P(1)-C(26)	1.780(2)	C(7)-C(8)-C(9)	120.6(2)
P(1)-C(24)	1.783(2)	C(10)-C(9)-C(8)	119.6(2)
P(1)-C(25)	1.783(2)	C(9)-C(10)-C(11)	120.0(2)
P(1)-C(1)	1.828(2)	C(10)-C(11)-C(6)	121.4(2)
C(1)-C(5)	1.513(3)		

3. X-ray crystallographic data of compound 3a.

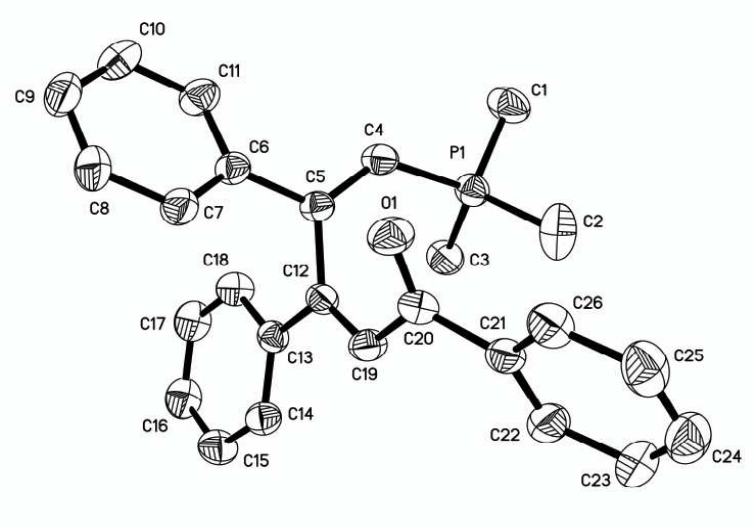


Fig. 2 **Crystal structure of compound 3a. The anion has been omitted for clarity.**

Table S5. **Crystal data and structure refinement for complex 3a.**

Identification code	3a
Empirical formula	$C_{26}H_{26}ClO_5P$
Formula weight	484.89
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
space group	$P2_1/n$
a (Å)	10.6802(5)
b (Å)	22.1133(10)
c (Å)	11.5904(5)
β (º)	114.767(3)
Volume ($Å^3$)	2485.57(19)
Z	4
D_{Calc} (mg/m^{-3})	1.296
μ (mm^{-1})	0.252
$F_{(000)}$	1016
Data / restraints / parameters	5696 / 0 / 298
Goodness-of-fit on F^2	0.998
R_1 [I>2σ(I)] [a]	0.0736,
wR_2 [I>2σ(I)] [a]	0.2385
R_1 (all data) [a]	0.1128,
wR_2 (all data) [a]	0.2833

[a] R1 = Σ| | Fo| –| Fc| | /Σ| Fo| ; wR2 = {Σ[w(Fo2–Fc2)2]/Σ[w(Fo2)]2}1/

Table S6. **Selected bond lengths [A] and angles [deg] for 3a.**

P(1)-C(1)	1.772(4)	C(7)-C(6)-C(11)	117.8(3)
P(1)-C(4)	1.779(3)	C(7)-C(6)-C(5)	120.8(3)
P(1)-C(3)	1.786(3)	C(11)-C(6)-C(5)	121.4(3)
P(1)-C(2)	1.791(4)	C(6)-C(7)-C(8)	120.2(3)
C(4)-C(5)	1.345(4)	C(9)-C(8)-C(7)	121.8(3)
C(5)-C(6)	1.481(3)	C(8)-C(9)-C(10)	118.9(3)
C(5)-C(12)	1.494(4)	C(11)-C(10)-C(9)	120.0(3)
C(6)-C(7)	1.380(4)	C(10)-C(11)-C(6)	121.3(3)
C(6)-C(11)	1.394(4)	C(19)-C(12)-C(13)	123.1(2)
C(7)-C(8)	1.387(4)	C(4)-C(5)-C(6)	120.7(2)
C(8)-C(9)	1.339(5)	C(4)-C(5)-C(12)	122.8(2)
C(9)-C(10)	1.401(5)	C(6)-C(5)-C(12)	116.4(2)
C(10)-C(11)	1.364(4)	C(19)-C(12)-C(5)	121.5(2)
C(12)-C(19)	1.343(4)	C(13)-C(12)-C(5)	115.3(2)
C(12)-C(13)	1.486(3)	C(14)-C(13)-C(18)	117.2(3)
C(13)-C(14)	1.392(4)	C(14)-C(13)-C(12)	122.1(2)
C(13)-C(18)	1.396(4)	C(18)-C(13)-C(12)	120.7(3)
C(14)-C(15)	1.367(4)	C(15)-C(14)-C(13)	121.8(3)
C(15)-C(16)	1.378(5)	C(14)-C(15)-C(16)	120.2(3)
C(16)-C(17)	1.390(5)	C(15)-C(16)-C(17)	119.3(3)
C(17)-C(18)	1.371(4)	C(18)-C(17)-C(16)	120.1(3)
C(19)-C(20)	1.493(4)	C(17)-C(18)-C(13)	121.4(3)
C(20)-O(1)	1.218(3)	C(12)-C(19)-C(20)	124.3(3)
C(20)-C(21)	1.489(4)	O(1)-C(20)-C(21)	120.2(2)
C(21)-C(26)	1.388(4)	O(1)-C(20)-C(19)	120.3(3)
C(21)-C(22)	1.389(4)	C(21)-C(20)-C(19)	119.5(2)
C(22)-C(23)	1.402(4)	C(26)-C(21)-C(22)	119.6(3)
C(23)-C(24)	1.348(5)	C(26)-C(21)-C(20)	117.8(3)
C(24)-C(25)	1.385(6)	C(22)-C(21)-C(20)	122.5(2)
C(25)-C(26)	1.390(5)	C(21)-C(22)-C(23)	119.9(3)
Cl(1)-O(2)	1.295(5)	C(24)-C(23)-C(22)	120.2(4)
Cl(1)-O(3)	1.373(3)	C(23)-C(24)-C(25)	120.4(3)
Cl(1)-O(5)	1.377(4)	C(24)-C(25)-C(26)	120.4(3)
Cl(1)-O(4)	1.398(4)	C(21)-C(26)-C(25)	119.4(3)
C(1)-P(1)-C(4)	105.57(15)	O(2)-Cl(1)-O(3)	111.1(3)
C(1)-P(1)-C(3)	109.37(17)	O(2)-Cl(1)-O(5)	116.3(4)
C(4)-P(1)-C(3)	111.33(14)	O(3)-Cl(1)-O(5)	114.7(3)
C(1)-P(1)-C(2)	108.4(2)	O(2)-Cl(1)-O(4)	109.7(4)
C(4)-P(1)-C(2)	113.33(15)	O(3)-Cl(1)-O(4)	100.1(3)
C(3)-P(1)-C(2)	108.67(19)	O(5)-Cl(1)-O(4)	103.2(3)
C(5)-C(4)-P(1)	128.8(2)		