

Reactivity of sp² nitrogen and phosphorus in a stable imidazolophosphinine

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General information and materials:

All reactions were routinely performed under an inert atmosphere of nitrogen by using standard Schlenk techniques and dry deoxygenated solvents. Dry THF was obtained by distillation from Na/benzophenone. Dry toluene was obtained by distillation from P₄O₁₀. n-butyl lithium (1.6 M in hexane) were purchased from J&K Scientific Ltd. Aluminum oxide neutral for TLC (100-200 mesh) were purchased from Kermel Co. Ltd.. And silica gel (200-300 mesh) purchased from Qingdao Hai Yang Chemical Industry Co. Ltd. was used for chromatographic separations. Nuclear magnetic resonance spectra were recorded on a Bruker 300 MHz spectrometer operating at 300.13 MHz for ¹H, 75.468 MHz for ¹³C, 121.495 MHz for ³¹P. Chemical shifts are expressed from internal TMS (¹H and ¹³C). All coupling constants (*J* values) are reported in hertz (Hz). HRMS were obtained on an Agilent 1290-6540 Q-Tof spectrometer by electrospray ionization (ESI). Given the high sensitivity of the new compounds, the small scale of their syntheses, the formation of clear solutions for NMR analysis, the excellent agreement of the NMR spectra with the crystal structures, and the general purity of the compounds based on NMR spectroscopy are acceptable.

X-ray crystal of 8, 9 and 11:

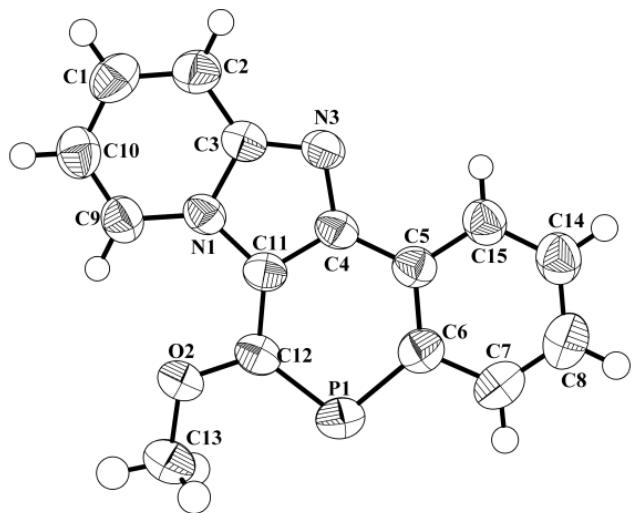


Figure S1: Crystal data and structure refinement for 8.

CCDC reference number: 1470402.

Table S1: Crystal data and structure refinement for 8.

Identification code	a-auto
Empirical formula	C ₁₅ H ₁₁ N ₂ OP
Formula weight	266.23
Temperature/K	293.15
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	17.1432(5)
b/Å	8.2411(2)
c/Å	17.8465(5)
α/°	90
β/°	95.7360(10)
γ/°	90
Volume/Å ³	2508.71(12)
Z	8
ρ _{calc} g/cm ³	1.410
μ/mm ⁻¹	1.877
F(000)	1104.0
Crystal size/mm ³	0.48 × 0.32 × 0.26
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	5.18 to 137.03
Index ranges	-18 ≤ h ≤ 20, -9 ≤ k ≤ 9, -21 ≤ l ≤ 21
Reflections collected	33411

Independent reflections	4567 [R _{int} = 0.0327, R _{sigma} = 0.0184]
Data/restraints/parameters	4567/0/345
Goodness-of-fit on F ²	1.061
Final R indexes [I>=2σ (I)]	R ₁ = 0.0879, wR ₂ = 0.2571
Final R indexes [all data]	R ₁ = 0.0958, wR ₂ = 0.2668
Largest diff. peak/hole / e Å ⁻³	1.90/-0.38

Table S2: Bond Lengths for 8.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.366(6)	C16	C17	1.341(8)
C1	C10	1.399(6)	C16	C25	1.384(8)
C2	C3	1.408(5)	C17	C18	1.416(7)
C3	N1	1.399(4)	C18	C19	1.399(6)
C3	N3	1.320(5)	C18	P2	1.792(5)
C4	C5	1.434(5)	C19	C20	1.457(6)
C4	C11	1.396(5)	C19	C26	1.398(6)
C4	N3	1.366(5)	C20	C29	1.396(5)
C5	C6	1.424(5)	C20	N2	1.345(5)
C5	C15	1.399(5)	C21	C22	1.429(6)
C6	C7	1.417(6)	C21	N2	1.329(5)
C6	P1	1.780(4)	C21	N4	1.383(5)
C7	C8	1.351(7)	C22	C23	1.372(7)
C8	C14	1.399(7)	C23	C24	1.379(8)
C9	C10	1.339(6)	C24	C30	1.335(7)
C9	N1	1.367(5)	C25	C26	1.355(7)
C11	C12	1.417(5)	C27	C29	1.391(5)
C11	N1	1.397(5)	C27	O3	1.365(5)
C12	O2	1.366(4)	C27	P2	1.744(5)
C12	P1	1.733(4)	C28	O3	1.444(6)
C13	O2	1.415(5)	C29	N4	1.404(5)
C14	C15	1.367(6)	C30	N4	1.371(6)

Table S3: Bond Angles for 8.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C10	120.2(4)	C26	C19	C18	120.3(4)
C1	C2	C3	119.2(4)	C26	C19	C20	120.2(4)
N1	C3	C2	118.0(3)	C29	C20	C19	123.2(4)
N3	C3	C2	129.7(3)	N2	C20	C19	124.7(3)
N3	C3	N1	112.3(3)	N2	C20	C29	112.1(4)
C11	C4	C5	123.0(3)	N2	C21	C22	128.5(4)
N3	C4	C5	125.1(3)	N2	C21	N4	113.1(4)

N3	C4	C11	111.8(3)	N4	C21	C22	118.5(4)
C6	C5	C4	120.0(3)	C23	C22	C21	118.1(4)
C15	C5	C4	120.8(3)	C22	C23	C24	120.3(5)
C15	C5	C6	119.1(4)	C30	C24	C23	122.5(5)
C5	C6	P1	126.3(3)	C26	C25	C16	120.3(5)
C7	C6	C5	117.8(4)	C25	C26	C19	120.0(5)
C7	C6	P1	115.9(3)	C29	C27	P2	122.6(3)
C8	C7	C6	121.9(4)	O3	C27	C29	115.3(4)
C7	C8	C14	119.7(4)	O3	C27	P2	122.0(3)
C10	C9	N1	118.8(4)	C20	C29	N4	104.8(3)
C9	C10	C1	121.7(4)	C27	C29	C20	126.7(4)
C4	C11	C12	126.1(3)	C27	C29	N4	128.5(4)
C4	C11	N1	104.6(3)	C24	C30	N4	118.7(5)
N1	C11	C12	129.2(3)	C9	N1	C3	122.1(3)
C11	C12	P1	123.0(3)	C9	N1	C11	131.9(3)
O2	C12	C11	114.4(3)	C11	N1	C3	106.0(3)
O2	C12	P1	122.6(3)	C21	N2	C20	104.9(3)
C15	C14	C8	120.7(4)	C3	N3	C4	105.2(3)
C14	C15	C5	120.8(4)	C21	N4	C29	105.1(3)
C17	C16	C25	121.0(5)	C30	N4	C21	121.8(4)
C16	C17	C18	121.0(5)	C30	N4	C29	133.1(4)
C17	C18	P2	116.2(4)	C12	O2	C13	117.5(3)
C19	C18	C17	117.4(4)	C27	O3	C28	116.3(4)
C19	C18	P2	126.4(3)	C12	P1	C6	101.37(18)
C18	C19	C20	119.5(4)	C27	P2	C18	101.50(19)

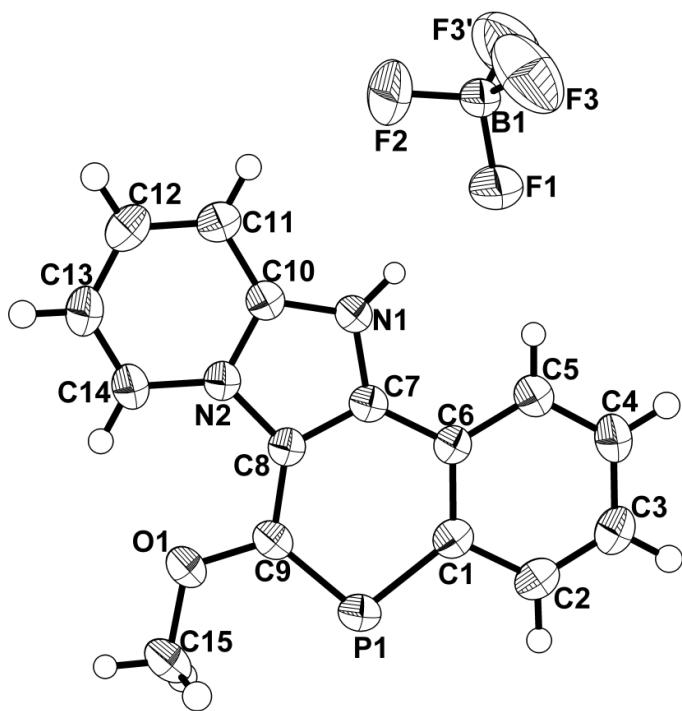


Figure S2: Crystal data and structure refinement for 9.

CCDC reference number: 1575426.

Table S4: Crystal data and structure refinement for 9.

Identification code	mo_170606a_0m
Empirical formula	C ₁₅ H ₁₂ N ₂ OPBF ₄
Formula weight	103.81
Temperature/K	273.15
Crystal system	monoclinic
Space group	P2 ₁ /m
a/Å	10.6527(14)
b/Å	6.8400(9)
c/Å	10.8254(14)
α/°	90
β/°	106.533(5)
γ/°	90
Volume/Å ³	756.18(17)
Z	2
ρ _{calc} g/cm ³	1.824
μ/mm ⁻¹	0.563
F(000)	408.0
Crystal size/mm ³	0.21 × 0.012 × 0.008
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.734 to 55.11

Index ranges	-13 ≤ h ≤ 13, -8 ≤ k ≤ 8, -14 ≤ l ≤ 13
Reflections collected	10413
Independent reflections	1885 [$R_{\text{int}} = 0.0252$, $R_{\text{sigma}} = 0.0191$]
Data/restraints/parameters	1885/18/149
Goodness-of-fit on F^2	1.097
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0491$, $wR_2 = 0.1488$
Final R indexes [all data]	$R_1 = 0.0589$, $wR_2 = 0.1651$
Largest diff. peak/hole / e Å ⁻³	0.45/-0.36

Table S5: Bond Lengths for 9.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C1	1.773(3)	C6	C1	1.417(4)
P1	C9	1.726(3)	C6	C5	1.408(4)
O1	C9	1.351(3)	C1	C2	1.419(4)
O1	C15	1.434(4)	F3	B1	1.352(3)
N1	C7	1.379(3)	C10	C11	1.396(4)
N1	C10	1.345(4)	F2	B1	1.354(4)
F1	B1	1.384(4)	C5	C4	1.372(4)
N2	C8	1.413(3)	C2	C3	1.362(5)
N2	C10	1.365(4)	C14	C13	1.351(5)
N2	C14	1.376(4)	C11	C12	1.363(5)
C7	C8	1.377(4)	C12	C13	1.402(5)
C7	C6	1.426(4)	C4	C3	1.394(5)
C8	C9	1.418(4)	B1	F3 ¹	1.352(3)

Table S6: Bond Angles for 9.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	P1	C1	101.37(13)	N1	C10	C11	130.5(3)
C9	O1	C15	116.9(3)	N2	C10	C11	121.4(3)
C10	N1	C7	109.7(2)	O1	C9	P1	123.1(2)
C10	N2	C8	108.2(2)	O1	C9	C8	114.5(2)
C10	N2	C14	120.5(3)	C8	C9	P1	122.4(2)
C14	N2	C8	131.3(3)	C4	C5	C6	120.2(3)
N1	C7	C6	126.8(2)	C3	C2	C1	121.7(3)
C8	C7	N1	107.6(2)	C13	C14	N2	118.7(3)
C8	C7	C6	125.5(2)	C12	C11	C10	117.9(3)
N2	C8	C9	128.1(2)	C11	C12	C13	120.0(3)
C7	C8	N2	106.4(2)	C5	C4	C3	120.4(3)
C7	C8	C9	125.5(2)	C14	C13	C12	121.6(3)
C1	C6	C7	117.7(2)	F3 ¹	B1	F1	109.3(2)
C5	C6	C7	122.2(2)	F3	B1	F1	109.3(2)

C5	C6	C1	120.1(2)	F3 ¹	B1	F3	108.8(3)
C6	C1	P1	127.5(2)	F3 ¹	B1	F2	112.1(2)
C6	C1	C2	117.3(3)	F3	B1	F2	112.1(2)
C2	C1	P1	115.2(2)	F2	B1	F1	105.0(3)
N1	C10	N2	108.1(2)	C2	C3	C4	120.3(3)

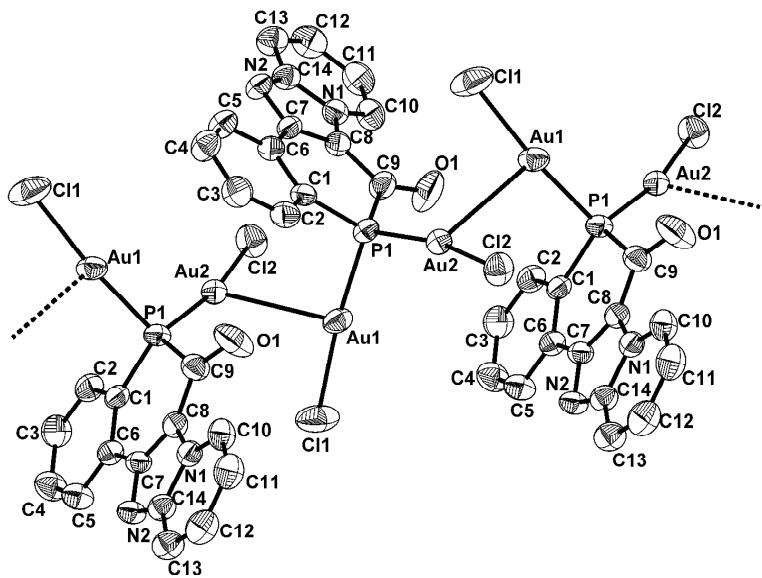


Figure S3: Crystal data and structure refinement for 11.

CCDC reference number: 1587250.

Table S7: Crystal data and structure refinement for 11.

Identification code	mo_170329b1_0m
Empirical formula	C ₁₇ H ₁₅ Au ₂ Cl ₂ NO ₂ PS
Formula weight	793.16
Temperature/K	296.31
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	9.1286(3)
b/Å	10.3643(3)
c/Å	21.2648(5)
α/°	90
β/°	99.2870(10)
γ/°	90
Volume/Å ³	1985.52(10)
Z	4
ρ _{calc} g/cm ³	2.653
μ/mm ⁻¹	15.228
F(000)	1452.0
Crystal size/mm ³	0.028 × 0.022 × 0.021

Radiation MoK α ($\lambda = 0.71073$)
 2 Θ range for data collection/ $^{\circ}$ 4.384 to 55.04
 Index ranges -11 \leq h \leq 11, -13 \leq k \leq 13, -23 \leq l \leq 27
 Reflections collected 32027
 Independent reflections 4551 [$R_{\text{int}} = 0.0452$, $R_{\text{sigma}} = 0.0263$]
 Data/restraints/parameters 4551/186/244
 Goodness-of-fit on F² 1.041
 Final R indexes [$I \geq 2\sigma(I)$] $R_1 = 0.0257$, $wR_2 = 0.0506$
 Final R indexes [all data] $R_1 = 0.0393$, $wR_2 = 0.0546$
 Largest diff. peak/hole / e Å⁻³ 0.96/-1.09

Table S8: Bond Lengths for 11.

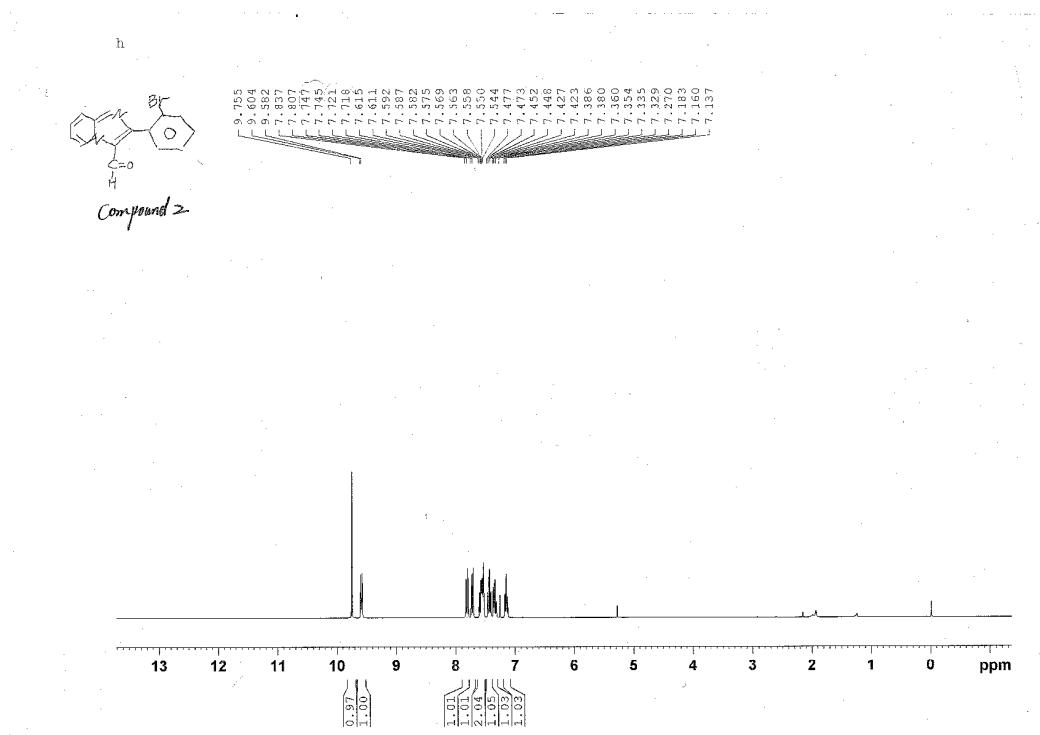
Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au2	Au1 ¹	3.0143(3)	C10	C11	1.360(8)
Au2	Cl2	2.3110(14)	C14	C13	1.386(8)
Au2	P1	2.2465(14)	C11	C12	1.398(9)
Au1	Au2 ²	3.0144(3)	C12	C13	1.361(8)
Au1	P1	2.2509(13)	C2	C3	1.362(8)
Au1	Cl1	2.3107(15)	C2	C1	1.386(7)
P1	C9	1.847(6)	C8	C7	1.373(7)
P1	C1	1.814(5)	C8	C9	1.432(7)
S1	O2	1.481(5)	O2	S2	1.437(16)
S1	C16	1.773(6)	C5	C6	1.389(7)
S1	C15	1.770(6)	C5	C4	1.382(8)
N1	C10	1.363(6)	C7	C6	1.452(7)
N1	C14	1.369(7)	C3	C4	1.382(8)
N1	C8	1.405(6)	C16	S2	1.883(11)
N2	C14	1.349(7)	C1	C6	1.413(7)
N2	C7	1.364(6)	C15	S2	1.801(13)
O1	C9	1.221(6)			

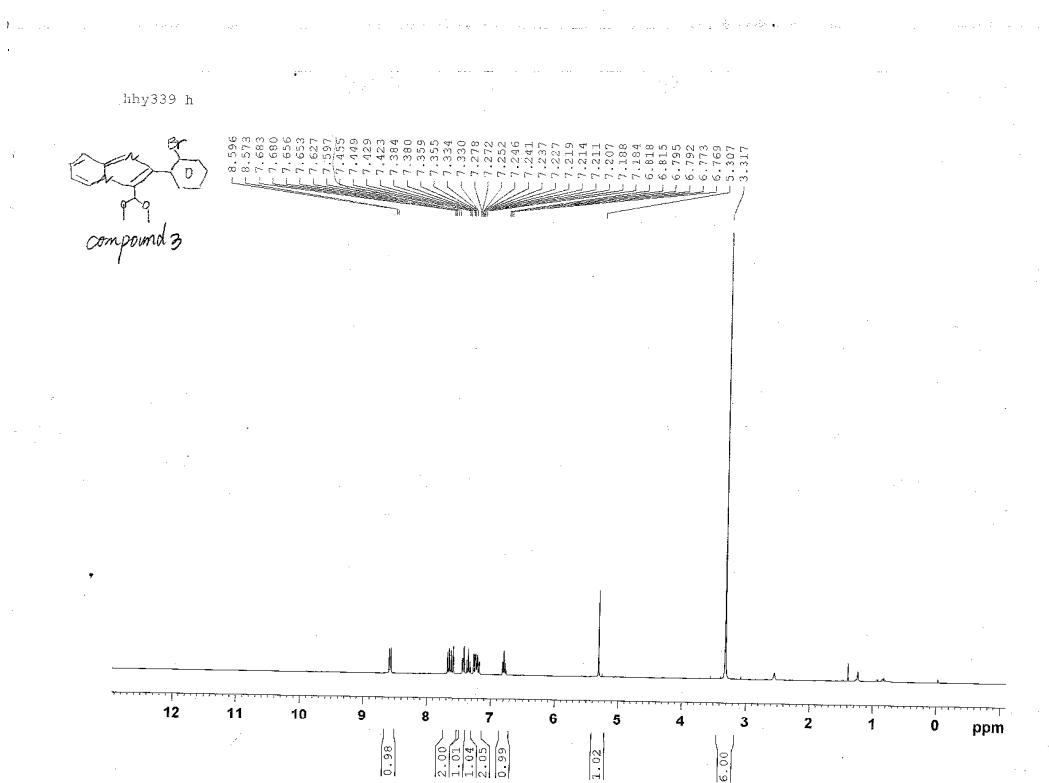
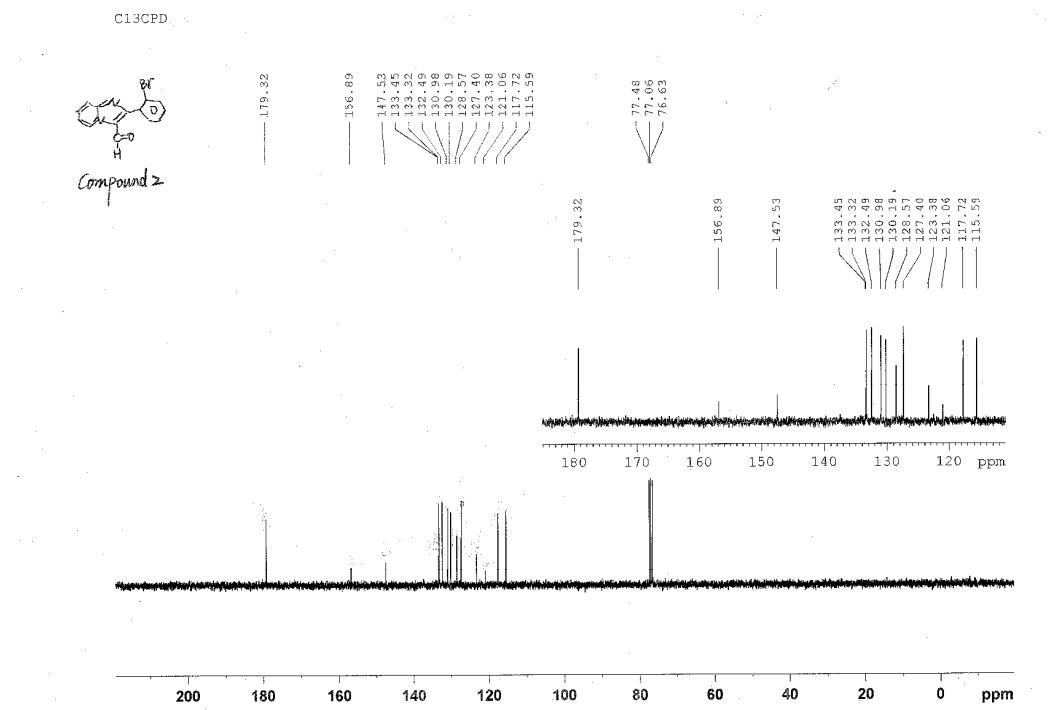
Table S9: Bond Angles for 11.

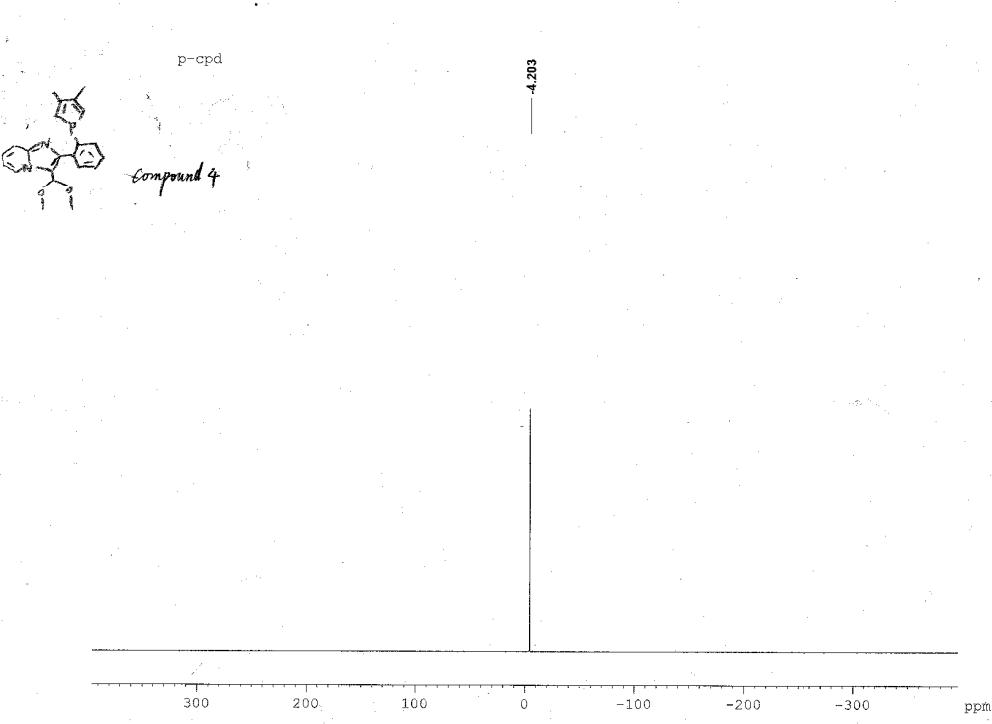
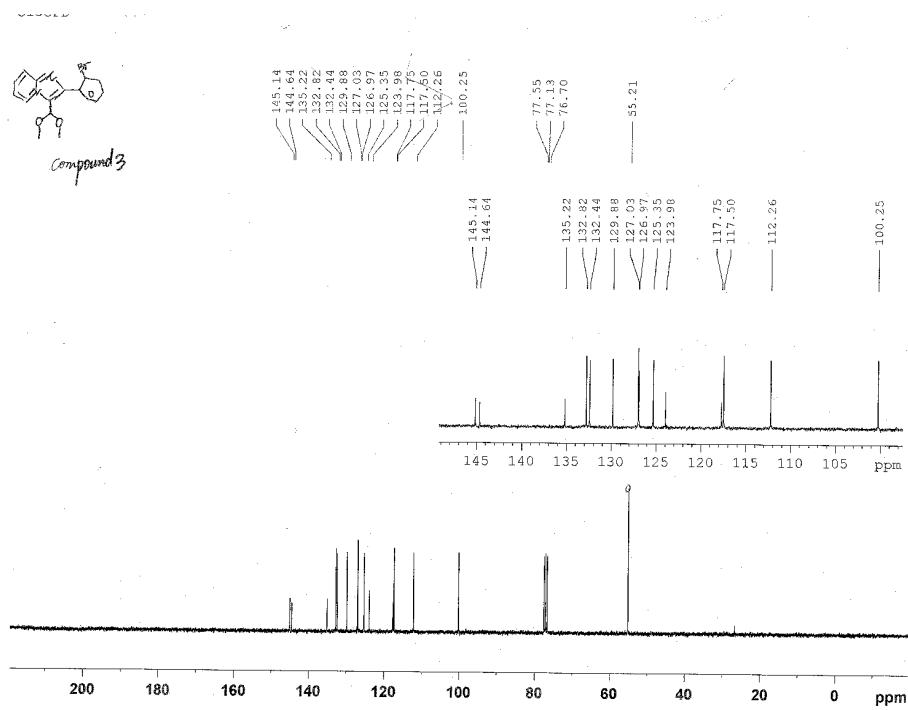
Atom	Atom	Atom	Angle/ $^{\circ}$	Atom	Atom	Atom	Angle/ $^{\circ}$
Cl2	Au2	Au1 ¹	89.50(4)	C13	C12	C11	121.3(6)
P1	Au2	Au1 ¹	104.22(4)	C3	C2	C1	121.5(5)
P1	Au2	Cl2	166.28(5)	C12	C13	C14	117.5(6)
P1	Au1	Au2 ²	99.44(3)	N1	C8	C9	126.1(5)
P1	Au1	Cl1	171.71(5)	C7	C8	N1	106.4(4)
Cl1	Au1	Au2 ²	87.62(5)	C7	C8	C9	127.6(5)
Au2	P1	Au1	108.66(5)	C4	C5	C6	120.5(5)
C9	P1	Au2	116.50(19)	N2	C7	C8	107.8(4)

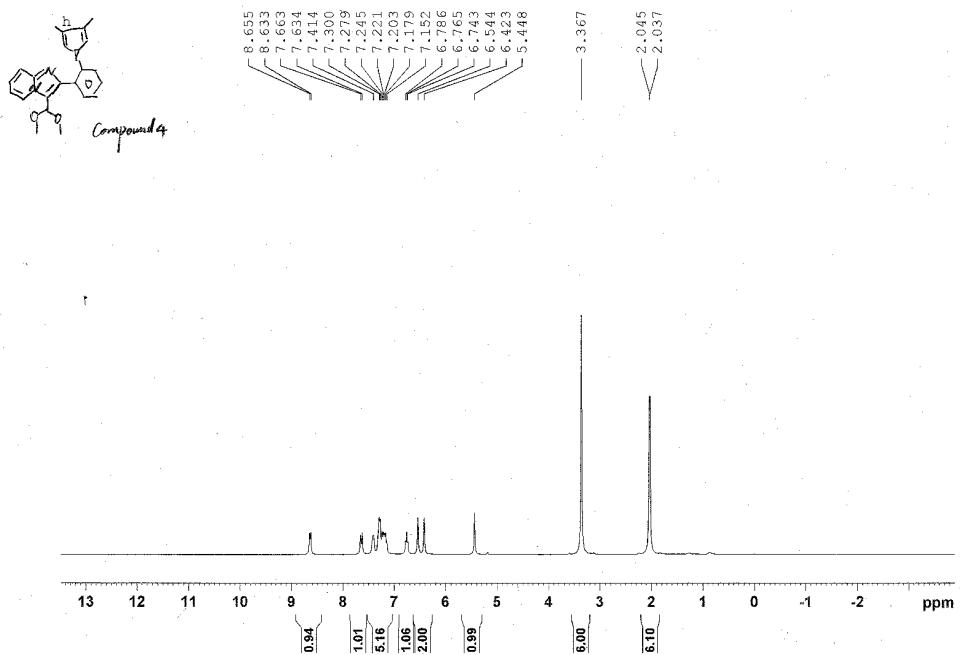
C9	P1	Au1	108.19(19)	N2	C7	C6	124.2(4)
C1	P1	Au2	110.48(17)	C8	C7	C6	128.0(4)
C1	P1	Au1	108.32(17)	O1	C9	P1	121.8(4)
C1	P1	C9	104.4(2)	O1	C9	C8	122.5(5)
O2	S1	C16	106.4(4)	C8	C9	P14	115.6(4)
O2	S1	C15	105.5(4)	C2	C3	C4	121.1(5)
C15	S1	C16	99.3(4)	C2	C1	P1	117.9(4)
C10	N1	C14	121.0(5)	C2	C1	C6	117.8(5)
C10	N1	C8	130.4(5)	C6	C1	P1	124.3(4)
C14	N1	C8	108.5(4)	C5	C6	C7	121.5(5)
C14	N2	C7	110.2(4)	C5	C6	C1	120.1(5)
C11	C10	N1	118.9(6)	C1	C6	C7	118.4(4)
N1	C14	C13	121.1(5)	C5	C4	C3	119.0(5)
N2	C14	N1	107.1(4)	O2	S2	C16	102.9(9)
N2	C14	C13	131.8(5)	O2	S2	C15	105.9(10)
C10	C11	C12	120.2(6)	C15	S2	C16	94.3(8)

¹H, ¹³C, ³¹P NMR and ¹⁹F NMR Spectra for Compounds 2, 3, 4, 5, 7, 8, 9, 10 and 11:

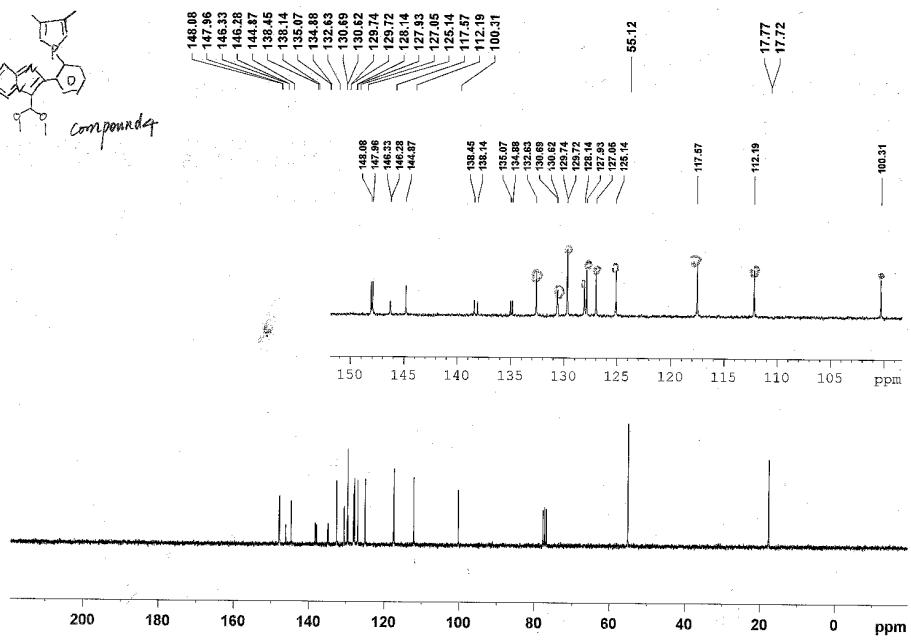


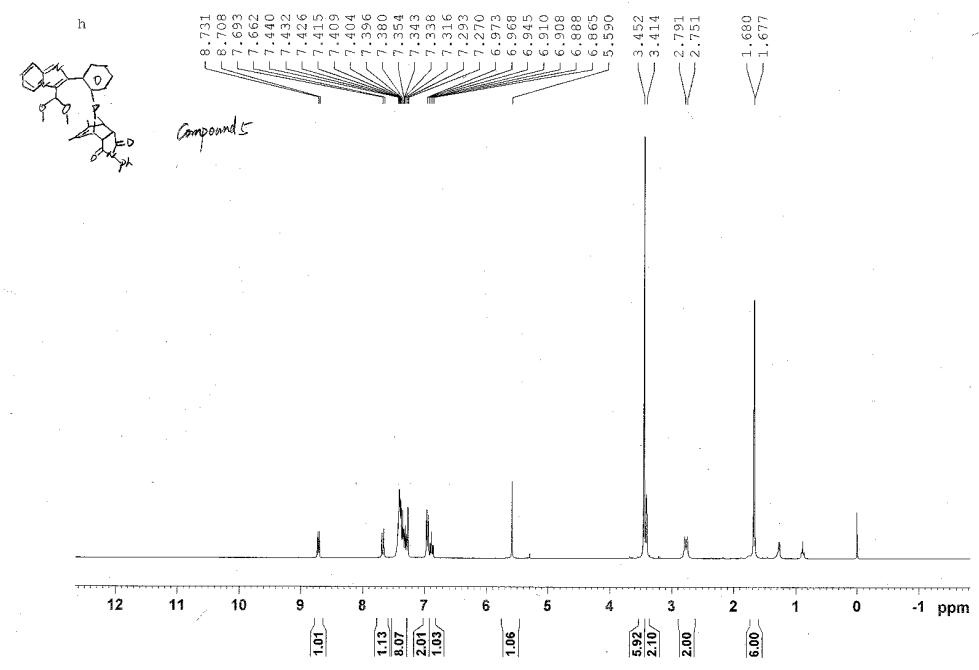
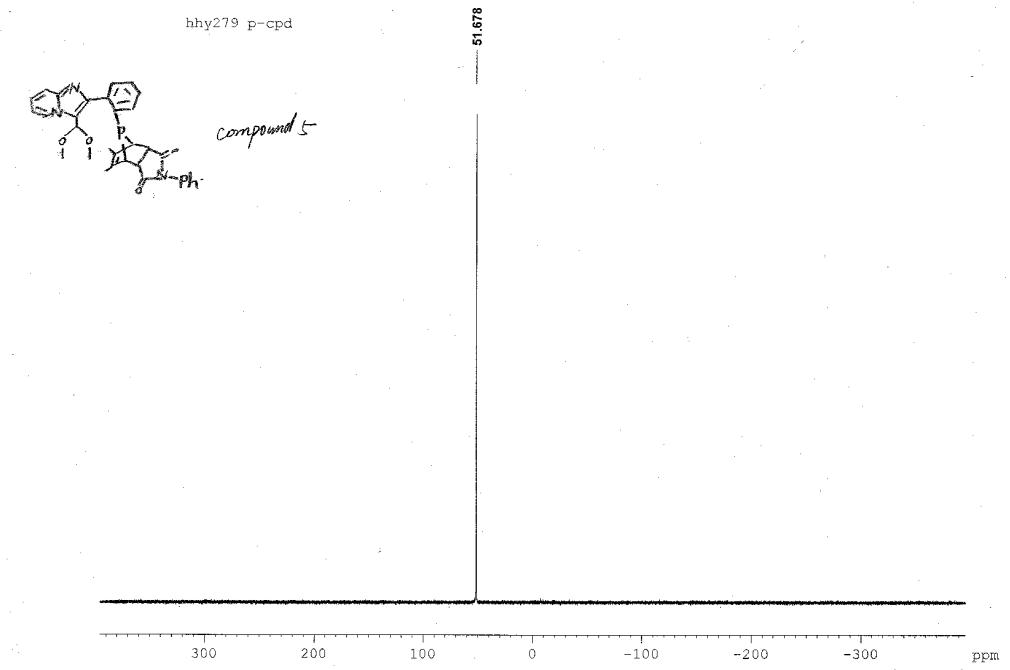


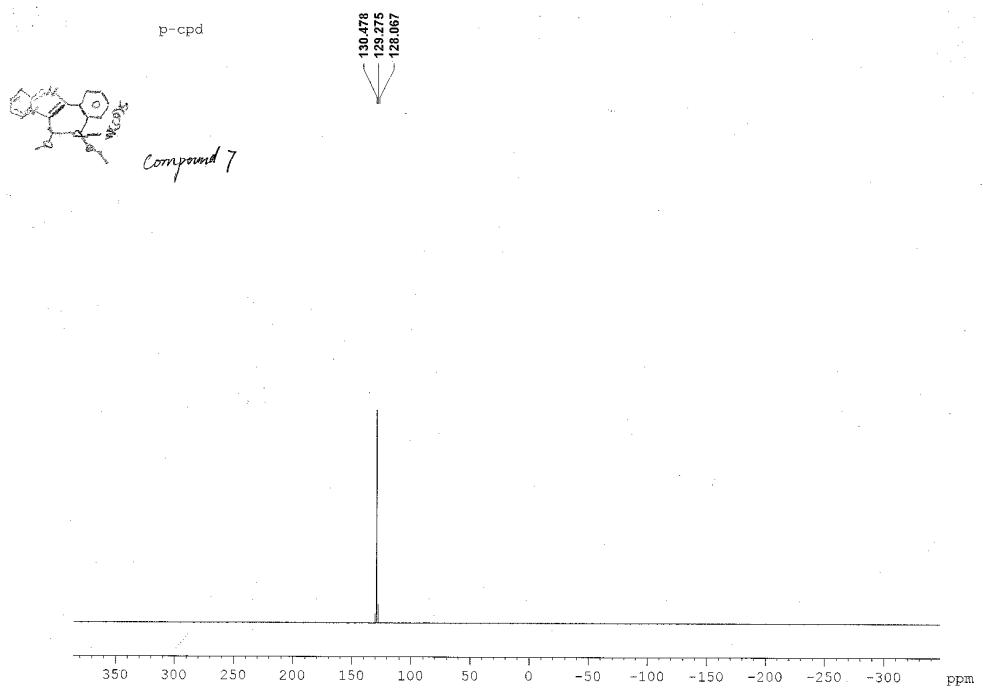
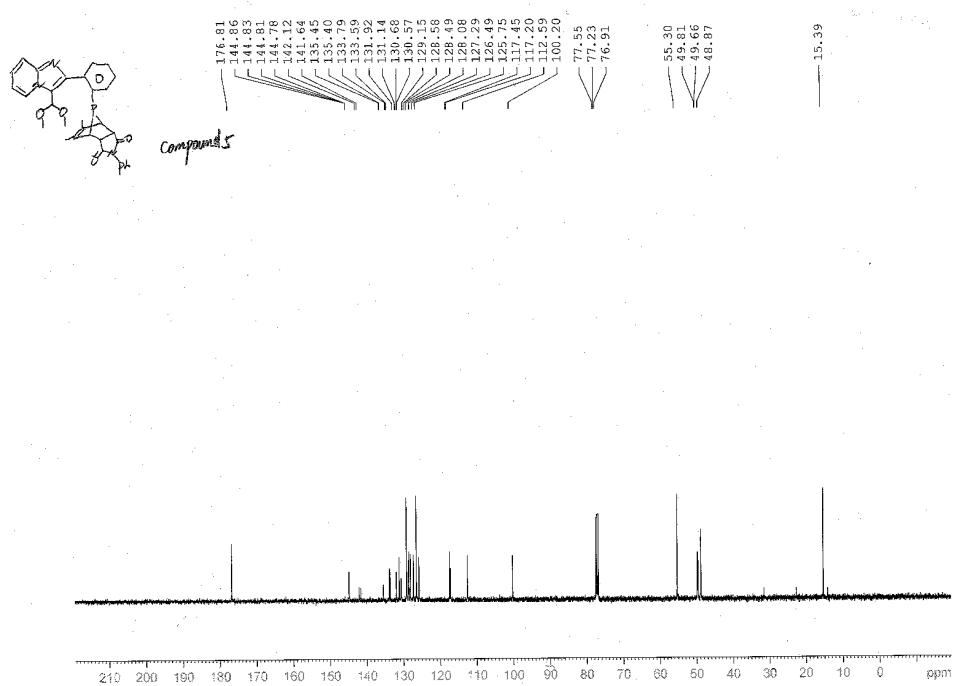


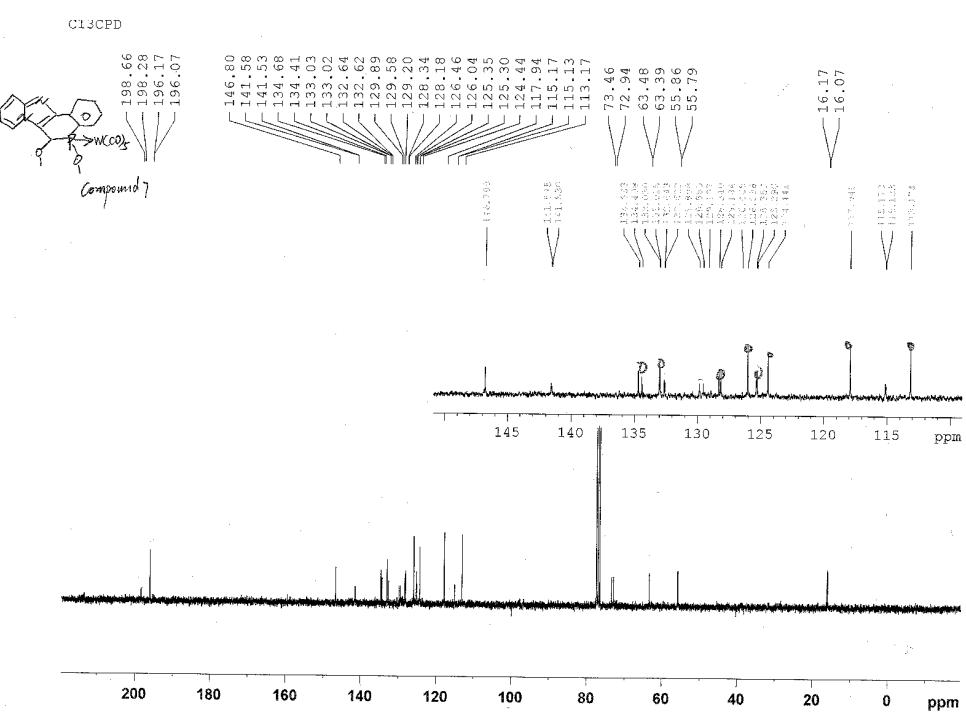
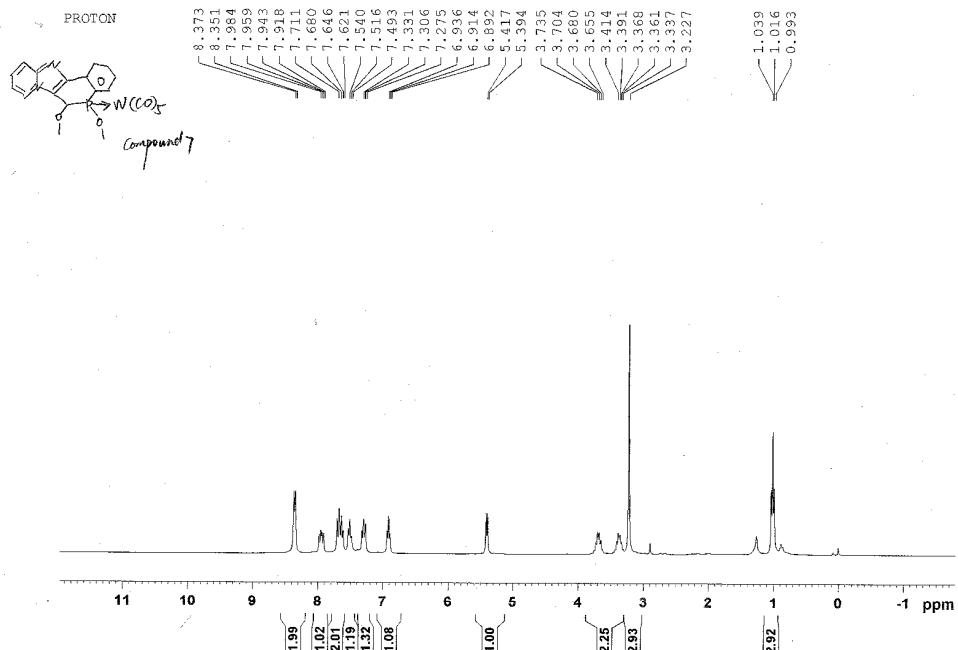


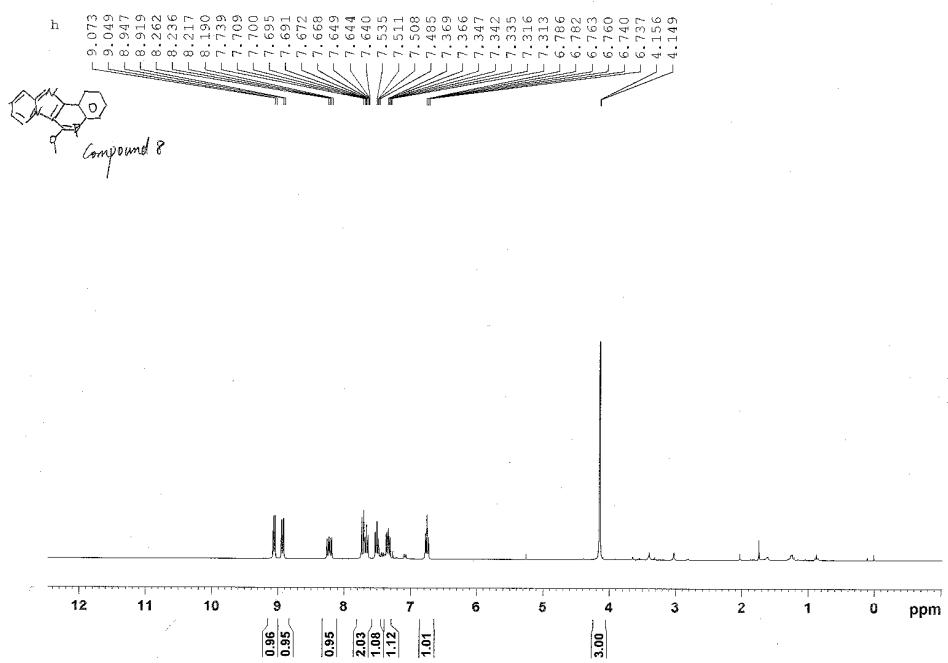
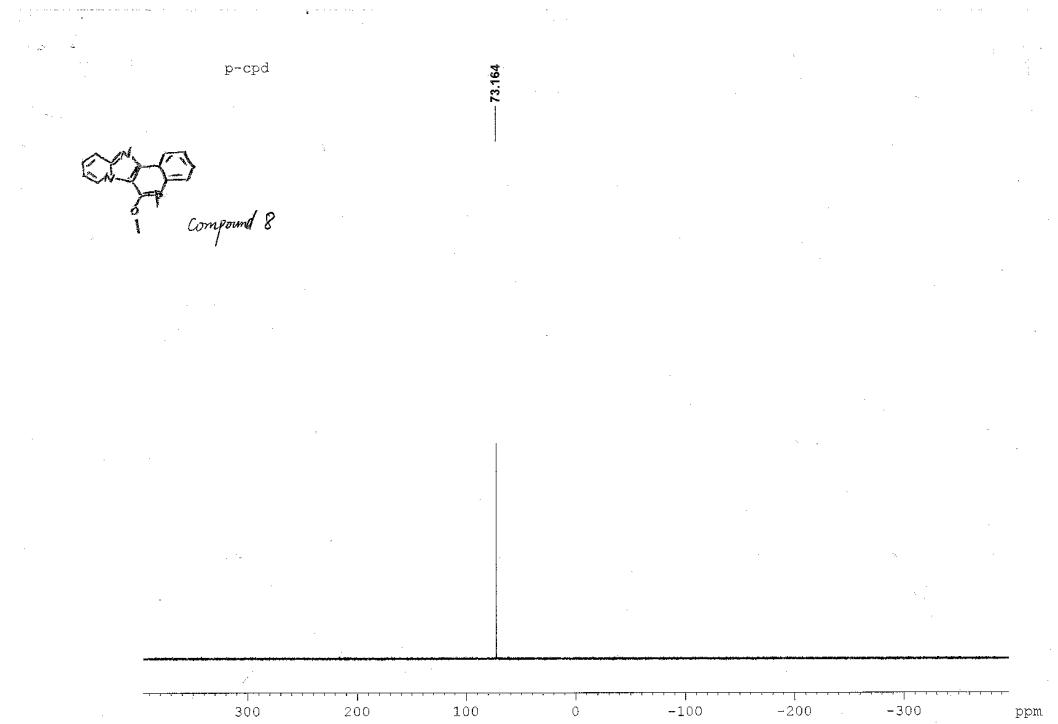
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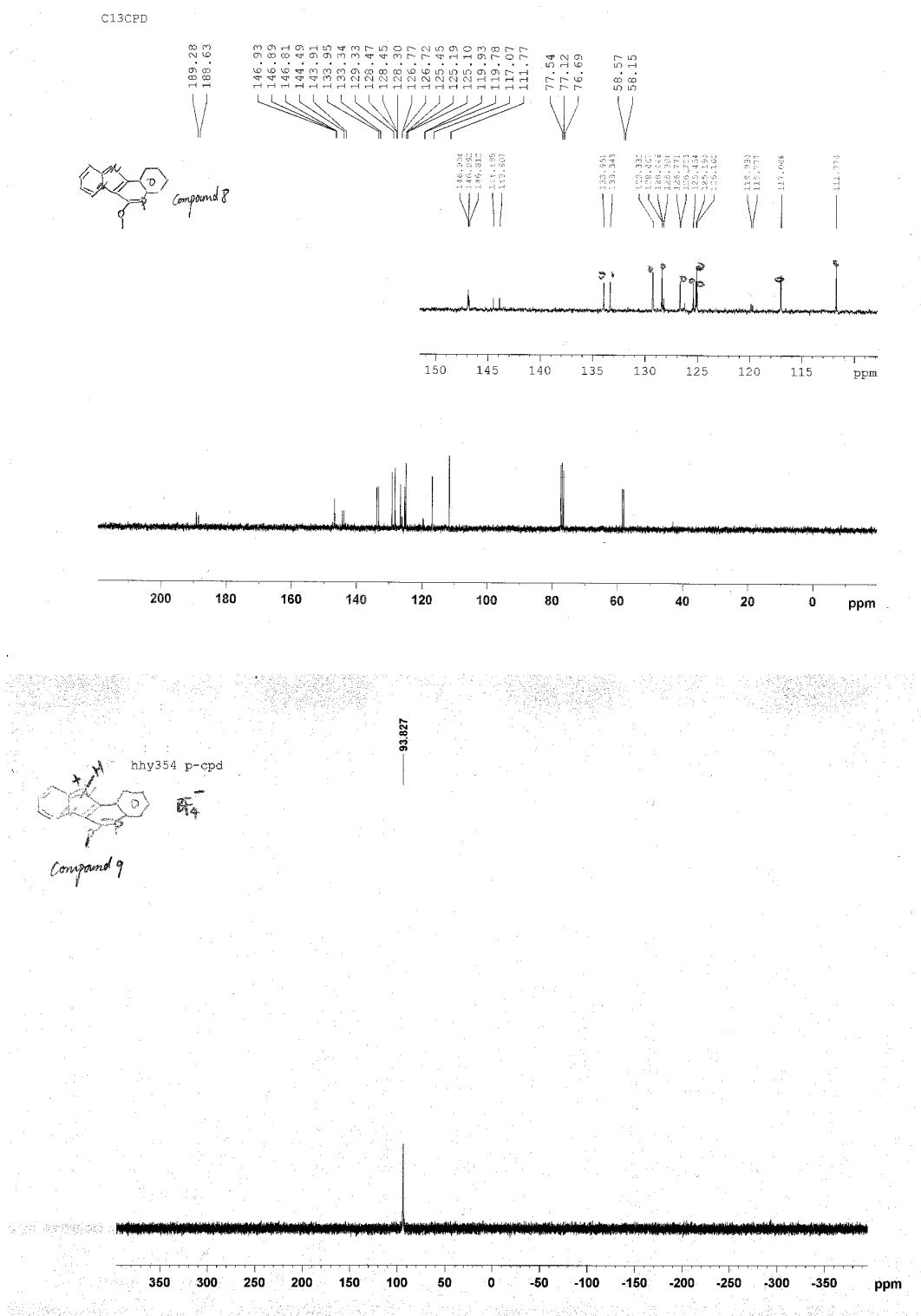


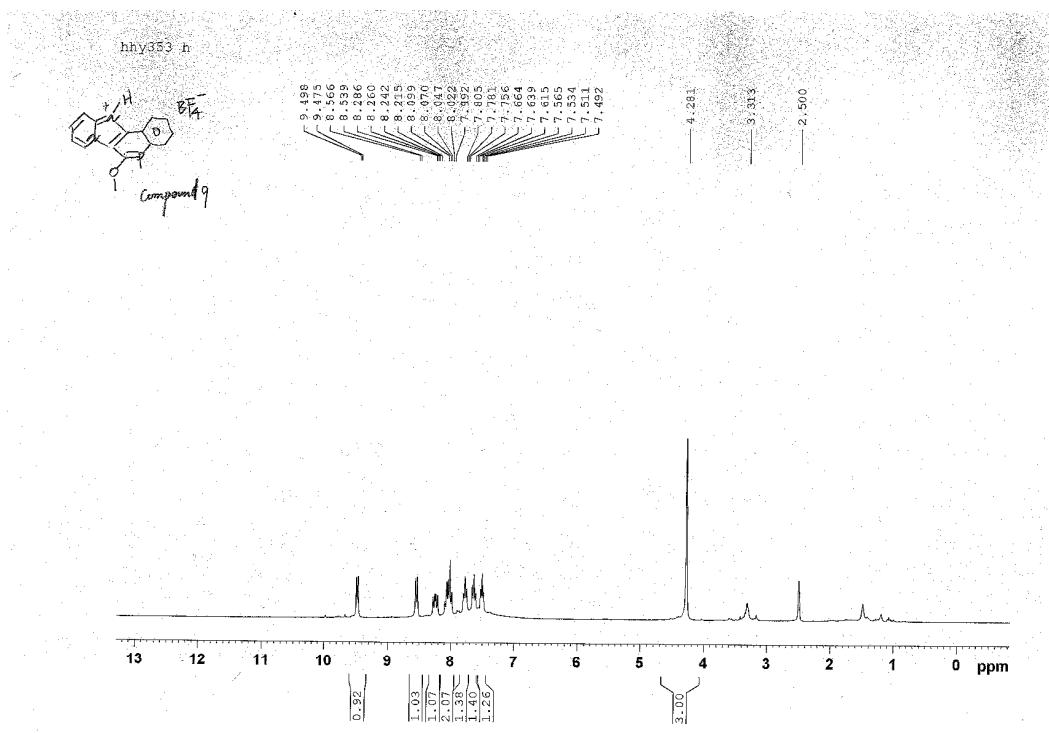
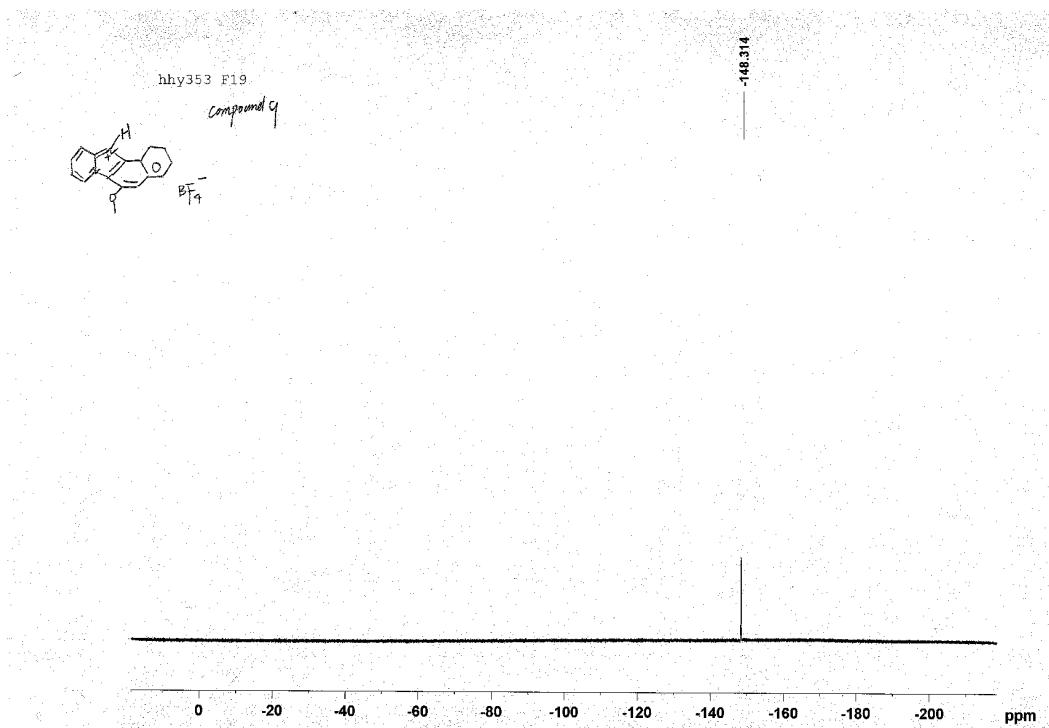


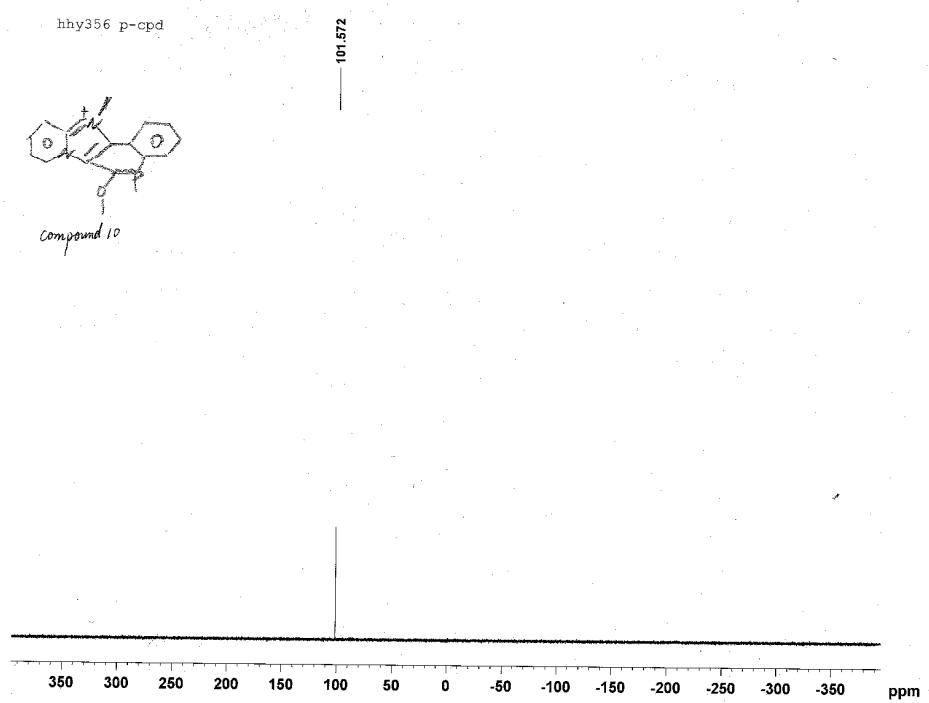
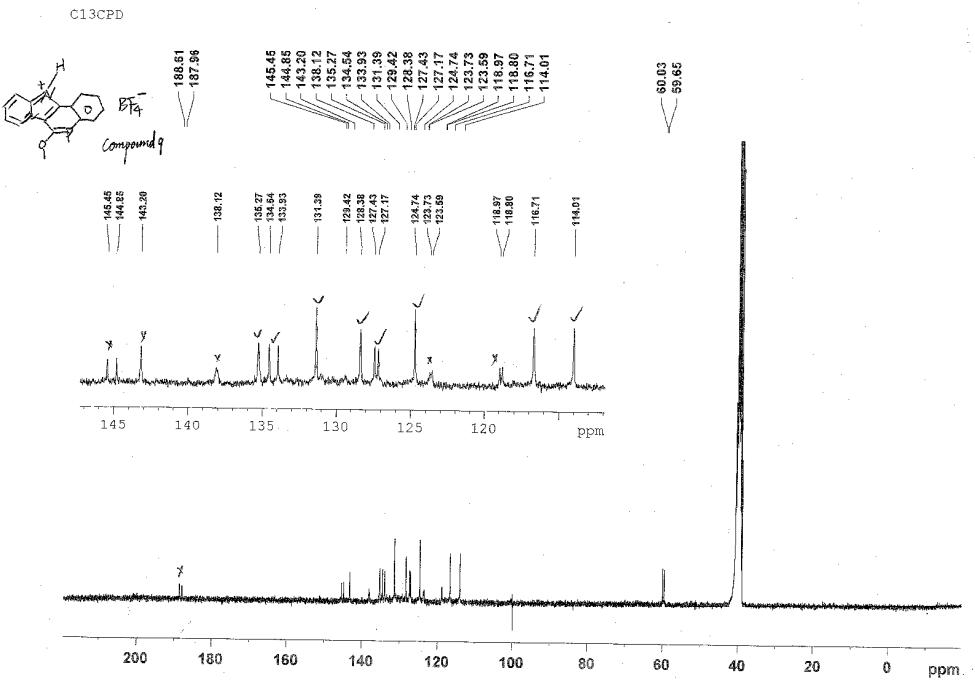




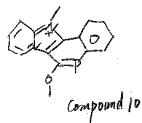




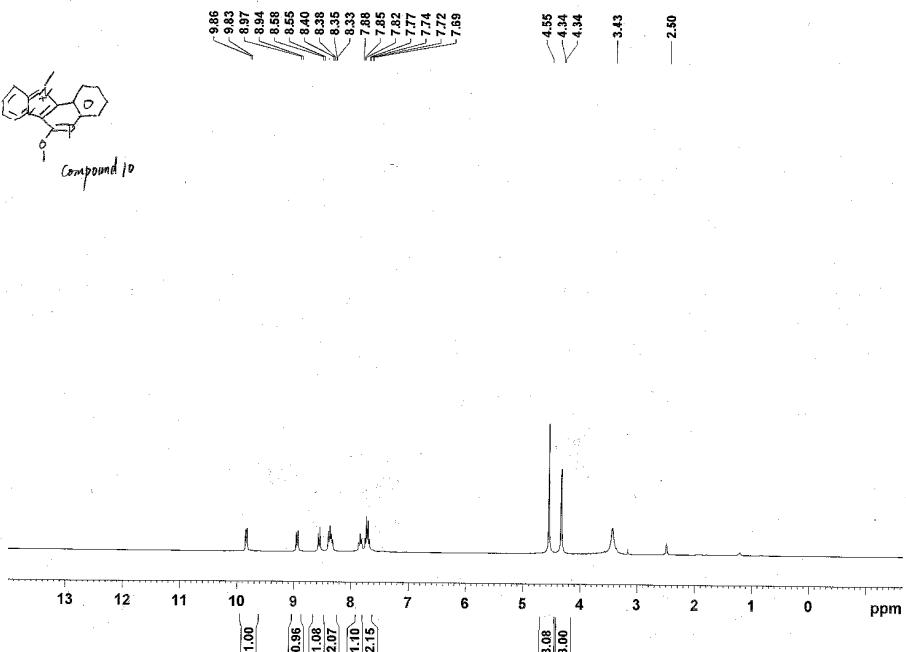




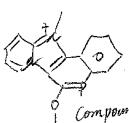
hhy356 h



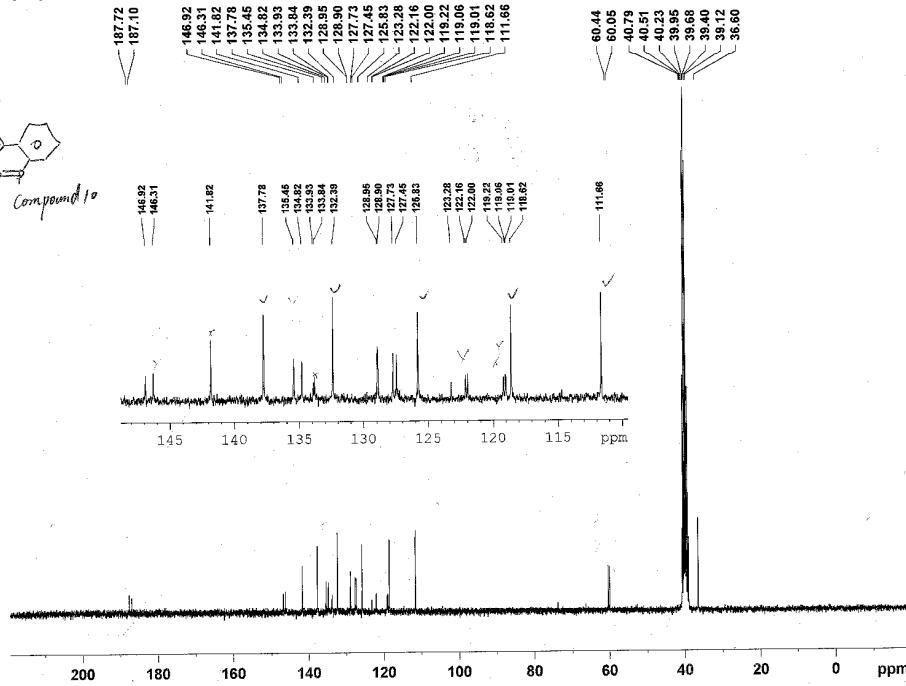
Compound 10



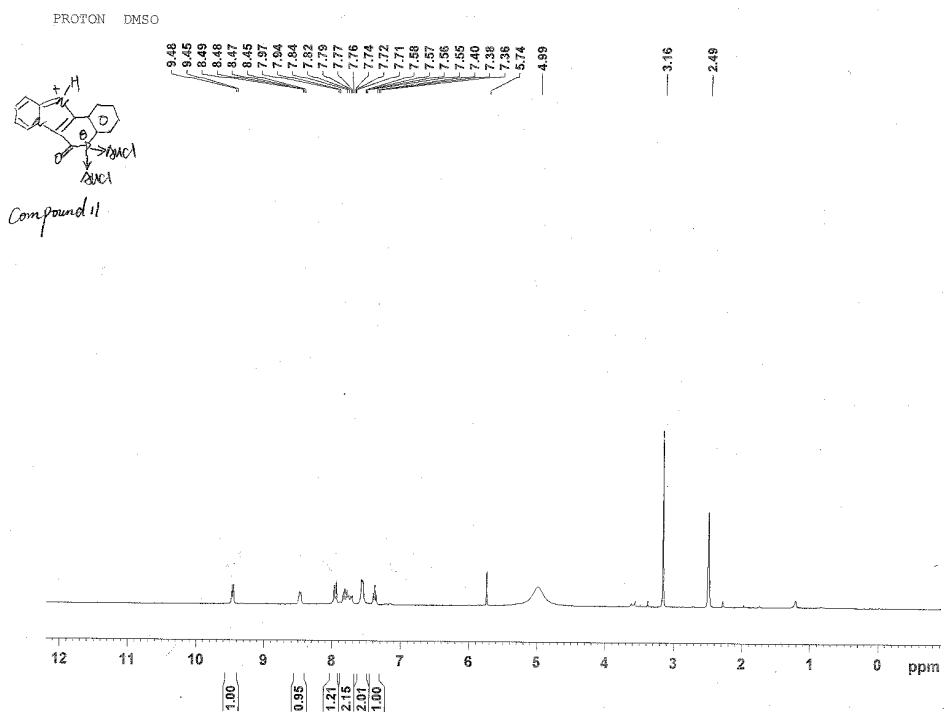
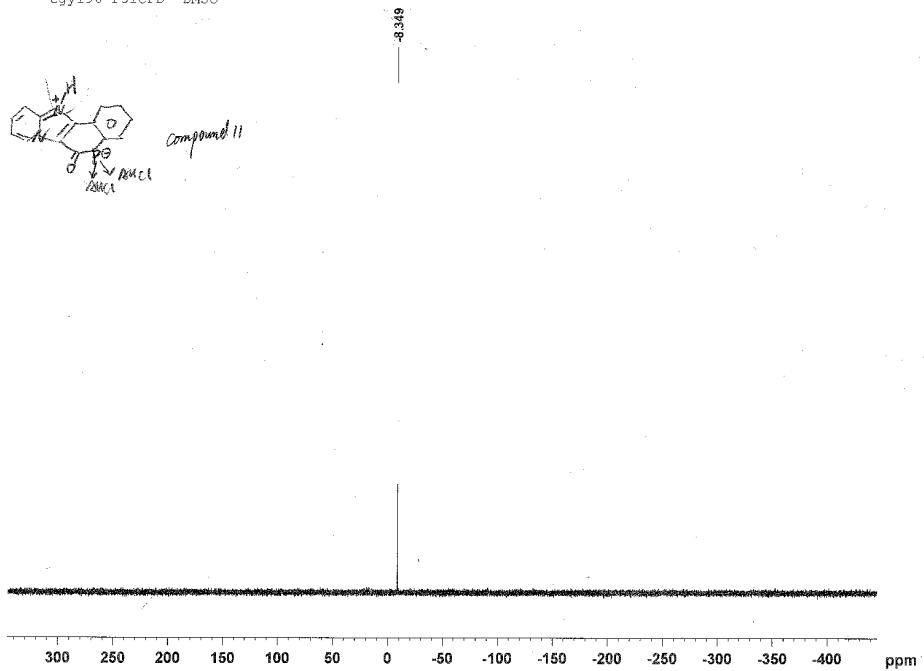
C13CPD



Compound 10



tgy196 P31CPD DMSO



TGY 196 C13CPD DMSO
ADD AuCl

