Supporting Information

Acid Promoted Selective Carbon-fluorine Bond Activation and Functionalization of Hexafluoropropene by Nickel Complexes Supported with Phosphine Ligands

Wengang Xu, Hongjian Sun, Zichang Xiong and Xiaoyan Li*

School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, 250100 Jinan, People's Republic of China

(1) Crystallographic Data of Complexes **2-3**, **5** and **7** – **11**

(2) Stick/ball representation and Cartesian coordinates of complex **1**

(3) IR, ^{31}P-NMR, ^{1}H-NMR and ^{19}F-NMR spectra of Complexes **1 - 11**

(4) GC-MS for confirmation of the formation of styrene

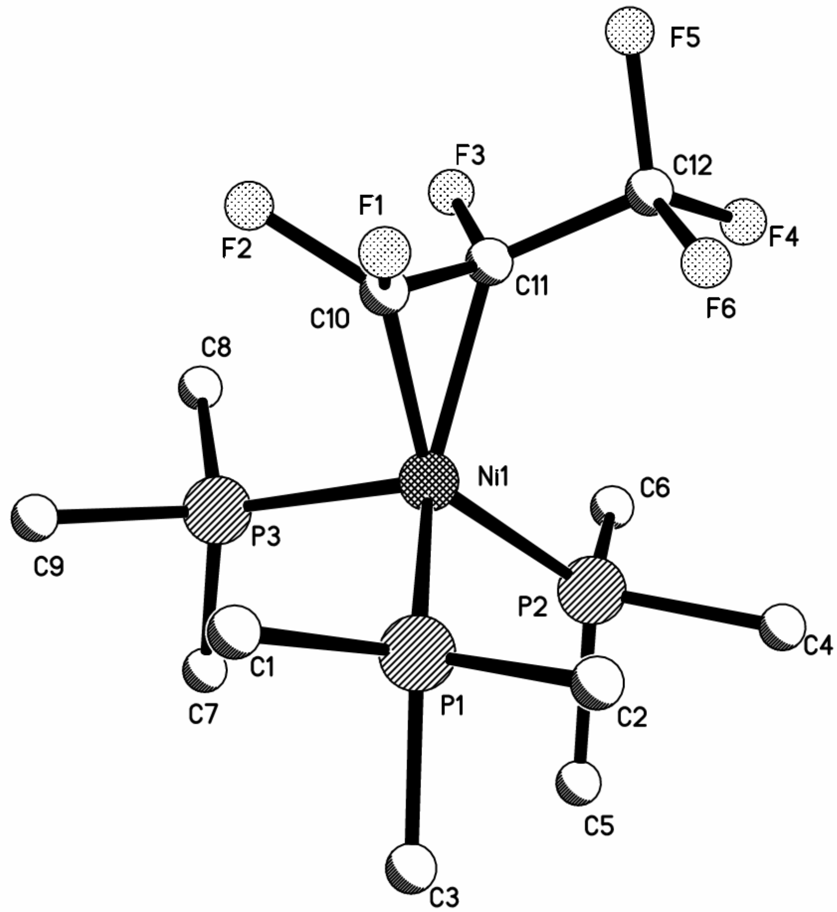
(5) The hydrido signal in the *in situ* ^{1}H NMR of the reaction in **Scheme 5**

(1) Crystallographic Data of Complexes **2-3**, **5** and **7 – 11**

complex	**2**	**3**	**5**	**7**	**8**	**9**	**10**	**11**
formula	$C_9H_{18}ClF_5NiP_2$	$C_9H_{18}BrF_5NiP_2$	$C_{11}H_{22}F_6NiO_2P_2$	$C_{11}H_{18}F_8NiO_2P_2$	$C_{15}H_{23}F_5NiP_2$	$C_{16}H_{25}F_5NiOP_2$	$C_{17}H_{23}F_5NiP_2$	$C_{17}H_{28}BrF_3NiP_2$
Fw, g/mol	377.33	421.79	420.94	454.9	418.98	449.01	443.00	489.95
temp, K	153(2)	153(2)	273(2)	153(2)	273(2)	153(2)	153(2)	273(2)
system	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	Pnma	Pnma	P21/c	P2(1)/c	P2(1)/n	P-1	Cc	P-1
a, Å	9.636(2)	9.373(2)	12.831(1)	11.481(2)	6.541(1)	13.386(3)	13.489(3)	8.903(2)
b, Å	10.862(2)	10.857(2)	11.955(1)	13.336(3)	22.222(5)	13.468(3)	14.090(3)	9.578(2)
c, Å	15.977(3)	16.181(3)	11.534(1)	12.547(3)	13.555(3)	13.612(3)	12.095(2)	13.003(3)
α, deg	90	90	90	90	90	83.04(3)	90	83.961(3)
β, deg	90	90	98.398(2)	104.37(3)	103.96	77.79(3)	114.75(3)	83.339(4)
γ, deg	90	90	90	90	90	61.22(3)	90	83.622(4)
V, Å^3	1672.3(6)	1646.7(6)	1750.3(3)	1861.0(6)	1911.9(7)	2101.5(7)	2087.5(7)	1089.8(4)
Z	4	4	4	4	4	4	4	2
d_{calc}, Mg/m^3	1.499	1.701	1.597	1.624	1.456	1.419	1.41	1.493
abs coeff, mm^{-1}	1.54	3.829	1.349	1.291	1.221	1.119	1.122	2.892

F(000)		768	840	864	920	864	928	912	500
cryst dimens, mm		0.20x0.19x0.18	0.19x0.18x0.16	0.20x0.18x0.16	0.21x0.20x0.18	0.20x0.19x0.16	0.21x0.18x0.16	0.21x0.20x0.18	0.18x0.16x0.15
θ range for data collection, deg		2.27 - 27.40	2.26 - 27.36	1.60 - 27.40	1.83 - 27.72	1.80 - 27.44	1.53 - 25.00	2.20 - 27.57	2.15 - 25.00
no. of reflns		9152	9117	9981	10746	11030	10483	5382	5471
no. of indep obs reflns		1990	1946	3916	4199	4230	7313	2686	3809
	R(int)	0.0401	0.031	0.1209	0.0305	0.0515	0.0185	0.0226	0.0303
$I > 2\sigma(I)$	R1	0.0679	0.0554	0.0476	0.0398	0.0351	0.0534	0.0291	0.0438
	wR2	0.1845	0.1305	0.1220	0.0966	0.0805	0.1669	0.0736	0.1017
	GoF on F^2	1.075	1.044	0.994	1.038	0.933	1.09	1.041	0.954

(2) Stick and ball representation of the structure of complex **1**



Atomic coordinates (x 10^4) of complex **1**

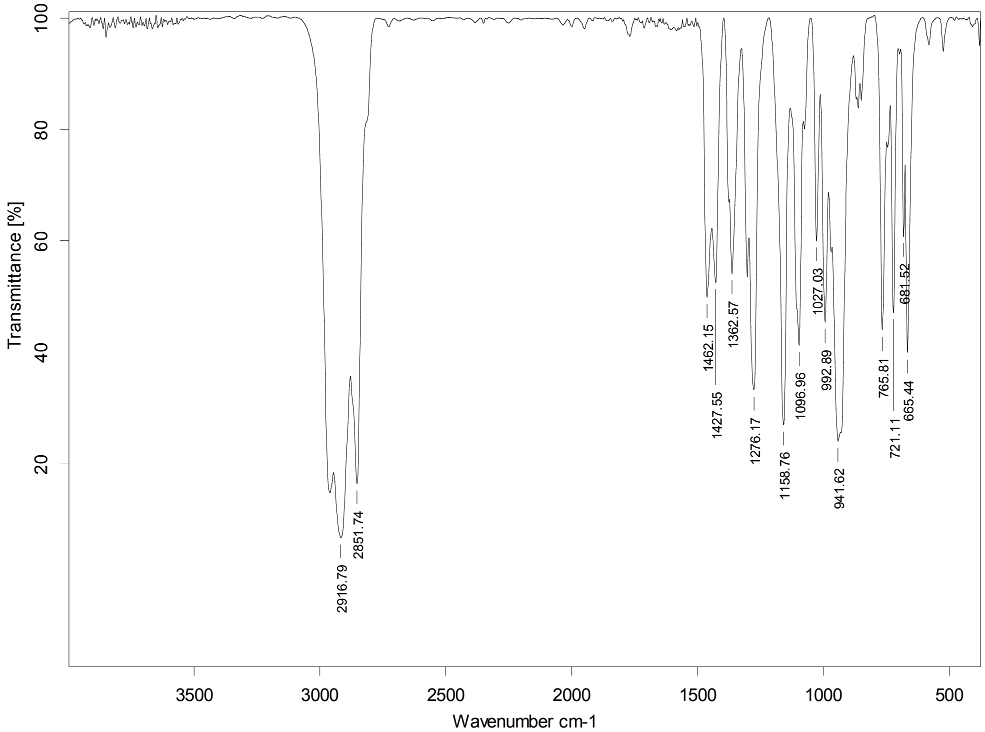
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

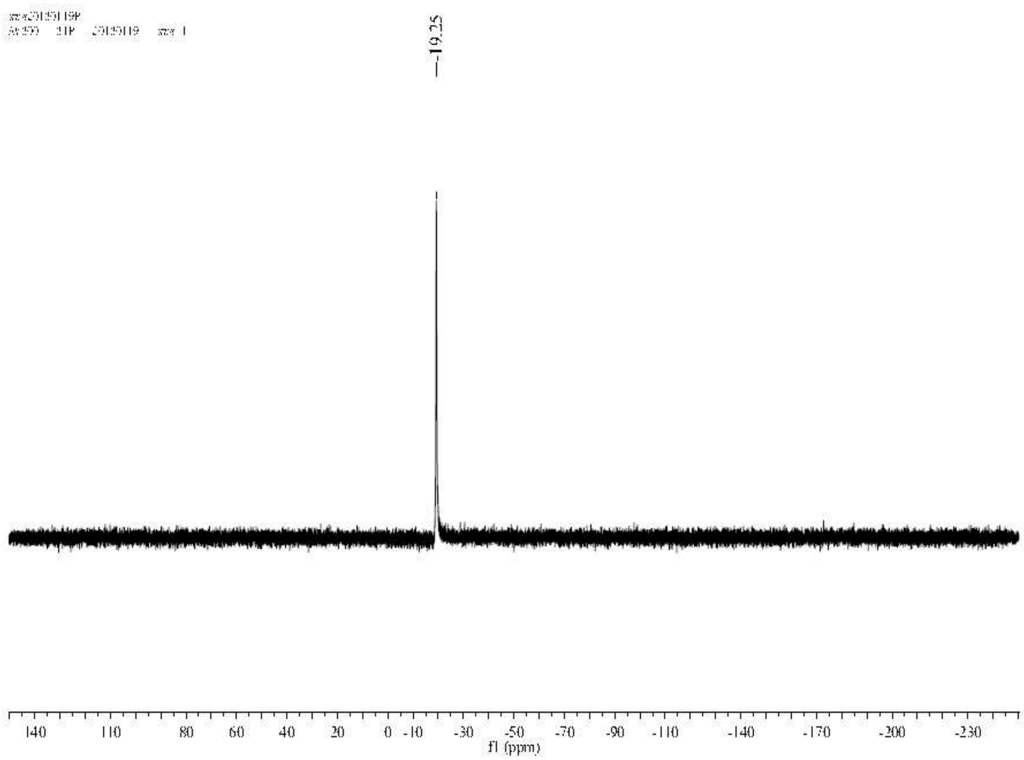
	x	**y**	**z**	**U(eq)**
Ni(1)	2619(2)	1230(1)	5312(2)	66(1)
Ni(2)	1945(3)	3779(1)	258(2)	83(1)
F(1)	670(20)	475(6)	3320(20)	172(7)
F(2)	1830(20)	260(6)	5630(20)	169(6)
F(3)	4890(20)	402(5)	6373(19)	167(6)
F(4)	5700(20)	728(6)	4170(20)	160(6)
F(5)	4190(20)	47(6)	3572(19)	159(6)
F(6)	3020(30)	763(7)	2450(20)	178(7)
F(7)	-250(20)	3420(7)	1530(20)	165(6)
F(8)	2080(20)	3068(6)	2520(20)	177(7)
F(9)	1910(20)	2740(7)	90(30)	195(8)
F(10)	-1470(30)	2646(8)	-960(30)	237(12)
F(11)	-670(30)	2917(9)	-2730(30)	231(12)
F(12)	-1830(20)	3411(8)	-1700(20)	198(9)
P(1)	334(7)	1620(2)	3714(7)	95(2)
P(2)	4509(7)	1766(2)	5659(7)	90(2)
P(3)	2721(8)	1197(3)	7740(6)	105(2)
P(4)	1995(8)	3974(2)	-1987(7)	107(2)
P(5)	959(8)	4453(2)	787(7)	103(2)
P(6)	4602(6)	3740(2)	2029(7)	103(2)
C(1)	-1640(30)	1357(9)	3430(30)	136(9)
C(2)	-120(30)	1754(11)	1710(30)	156(11)
C(3)	60(30)	2233(9)	4070(30)	145(10)
C(4)	4730(30)	1998(10)	4010(30)	134(9)
C(5)	4410(30)	2393(8)	6250(30)	126(8)
C(6)	6590(30)	1611(9)	7040(30)	141(9)
C(7)	3270(30)	1746(10)	8940(30)	145(9)
C(8)	4400(30)	841(10)	9250(20)	145(10)
C(9)	1020(30)	1039(10)	7980(30)	140(9)
C(10)	2010(30)	609(9)	4670(30)	114(7)
C(11)	3660(40)	628(9)	5060(30)	122(8)
C(12)	4200(40)	539(10)	3780(40)	131(10)
C(13)	2890(40)	3450(13)	-2590(40)	183(13)
C(14)	190(40)	3974(12)	-3690(30)	174(13)
C(15)	3030(30)	4488(11)	-2220(30)	150(10)
C(16)	-1300(30)	4538(10)	-250(30)	155(11)
C(17)	1380(30)	4521(11)	2880(30)	142(9)

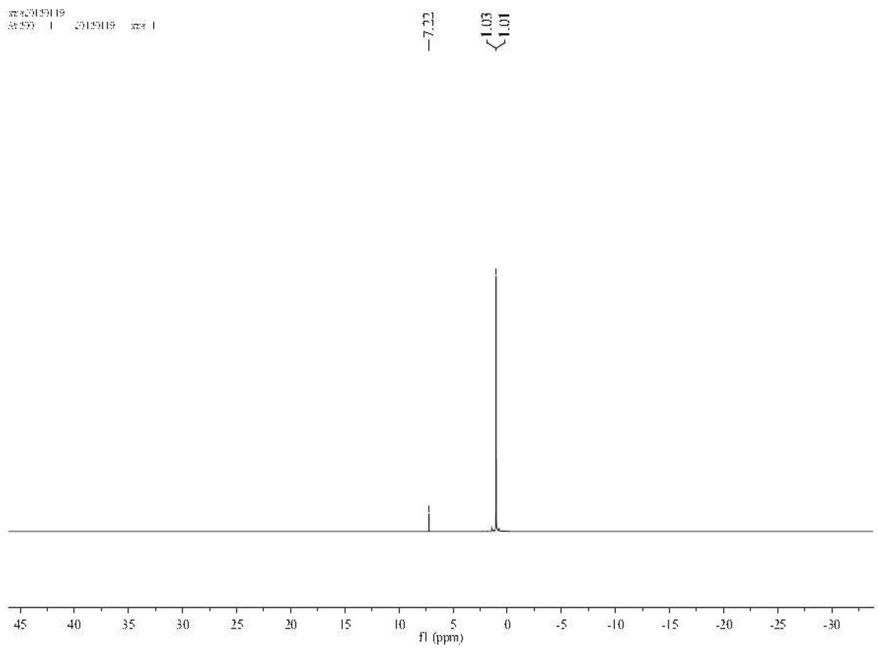
C(18)	1640(30)	5046(8)	460(30)	121(8)
C(19)	5990(30)	4190(9)	2020(30)	135(10)
C(20)	4990(30)	3621(11)	3990(30)	164(11)
C(21)	5550(30)	3131(10)	1870(40)	165(12)
C(22)	1010(40)	3304(11)	1150(50)	140(10)
C(23)	960(40)	3153(12)	-190(40)	138(10)
C(24)	-780(50)	3026(16)	-137 0(50)	168(14)

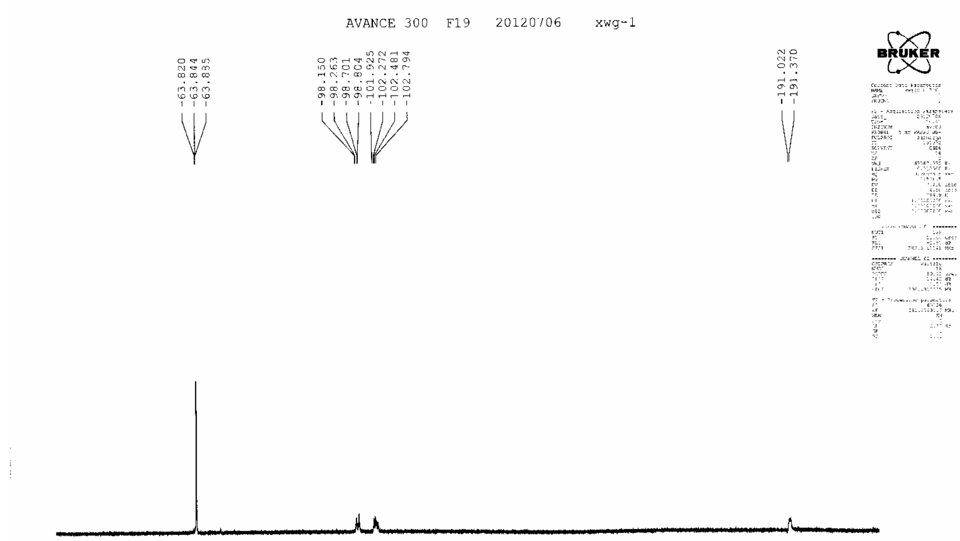
(3) IR, ^{31}P NMR, ^{1}H NMR and ^{19}F NMR spectra of complexes **1 - 11**

Complex **1**: IR, ^{31}P NMR, ^{1}H NMR and ^{19}F NMR

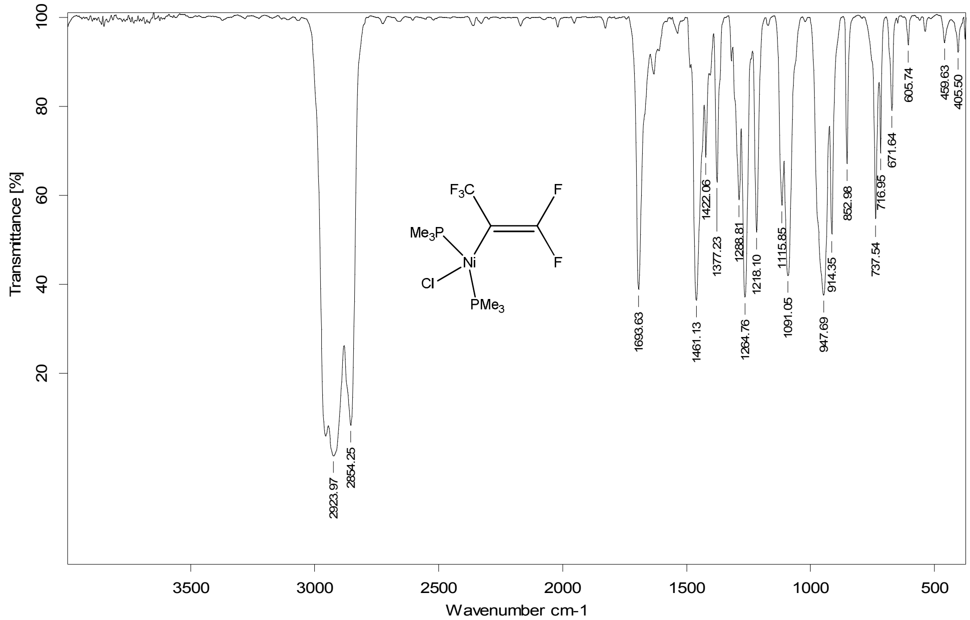


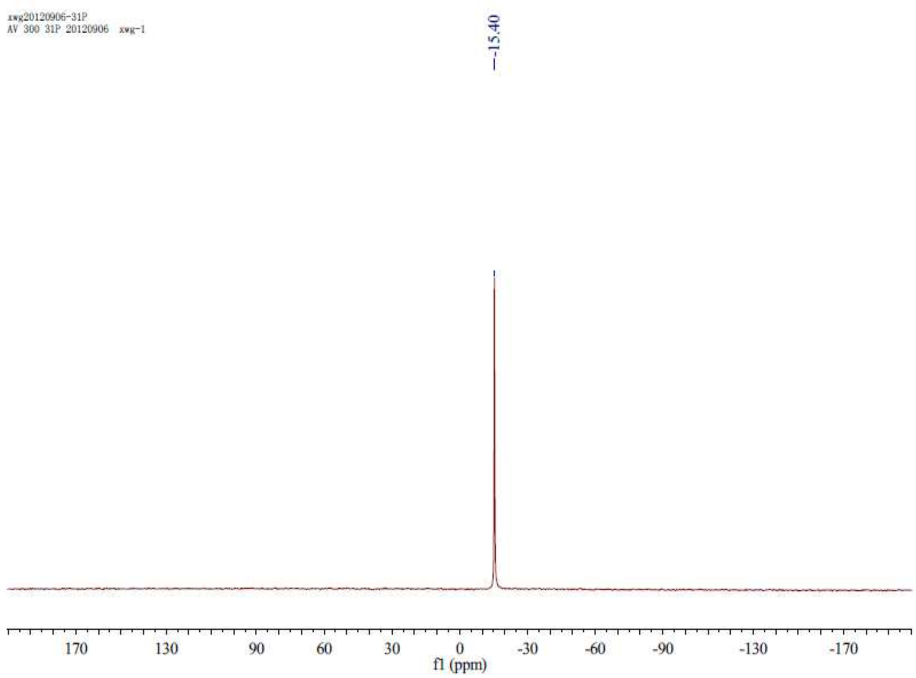


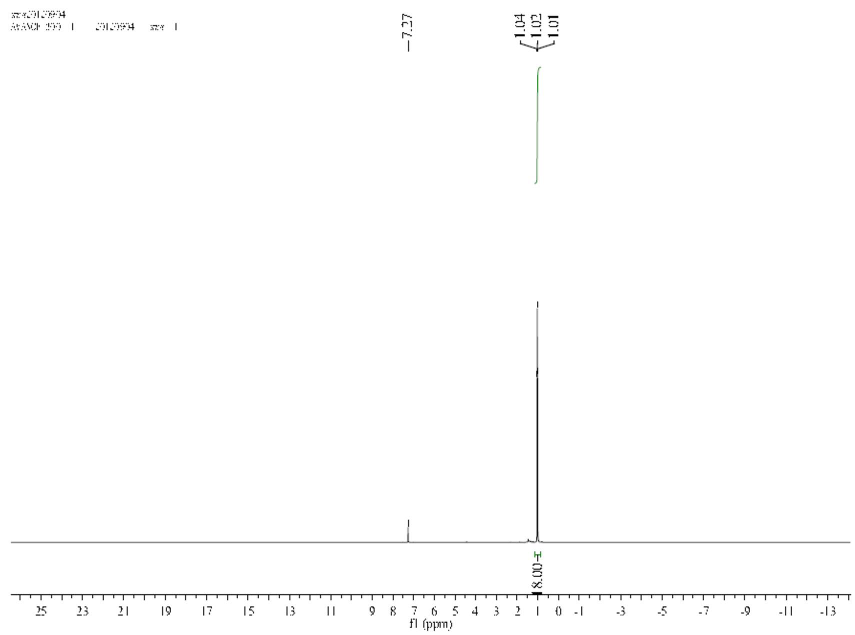


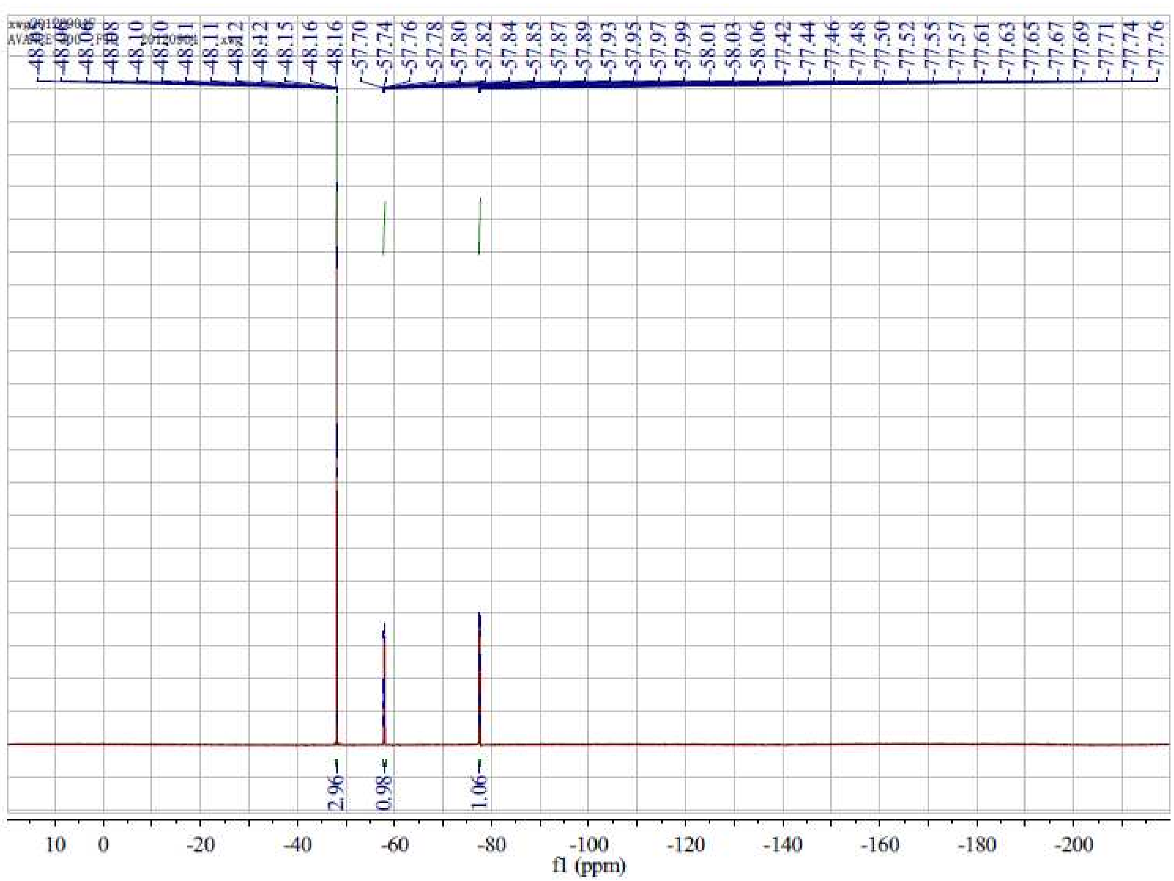


Complex **2**: IR, ^{31}P NMR, ^{1}H NMR and ^{19}F NMR

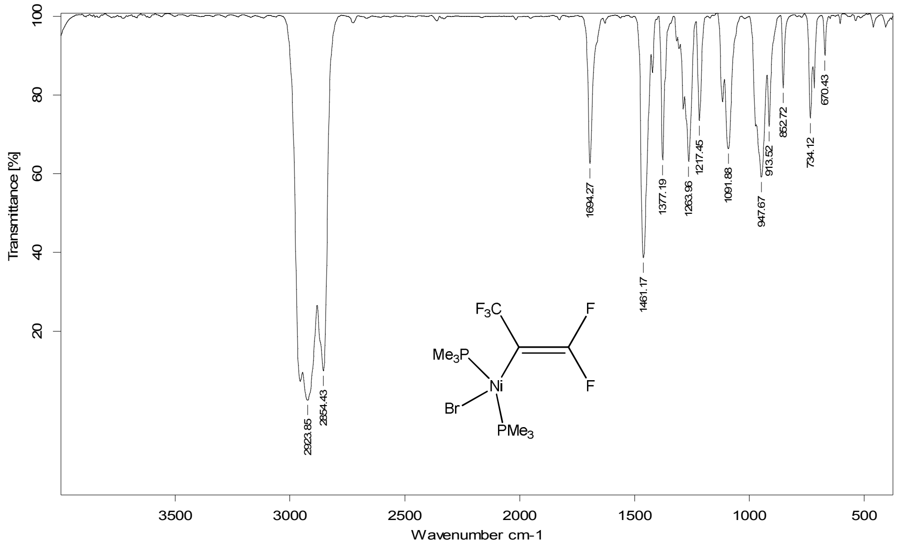


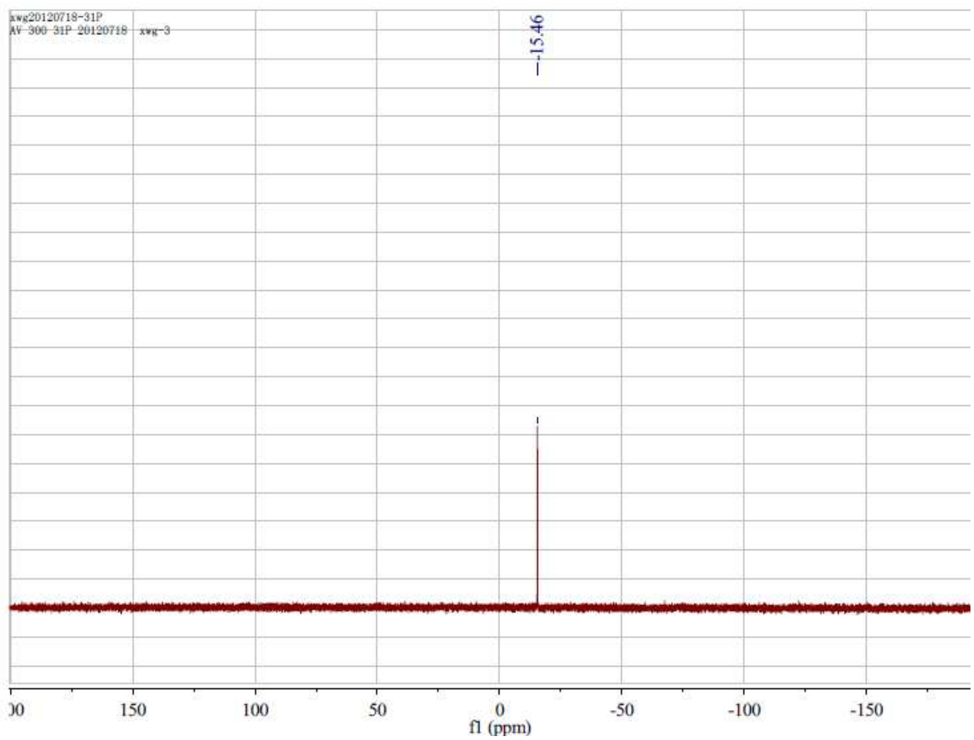


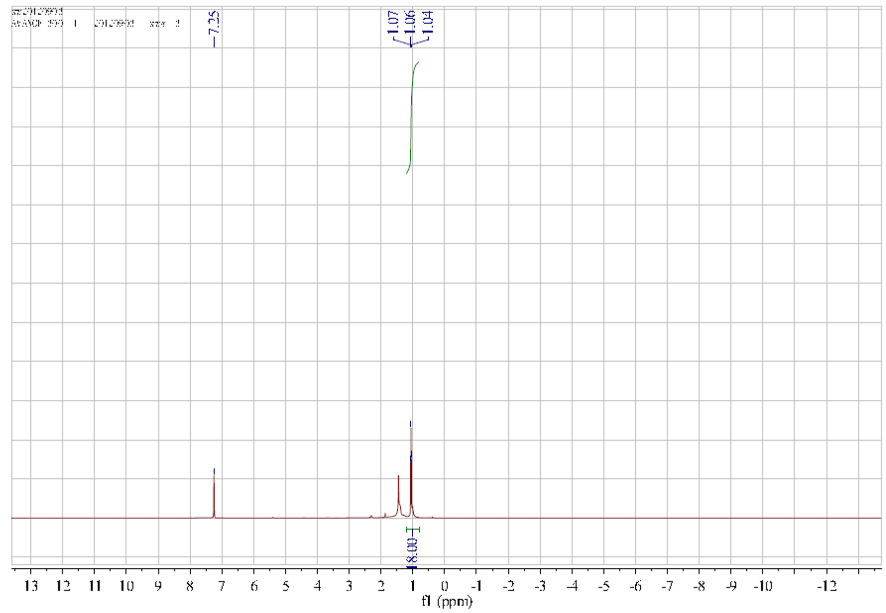


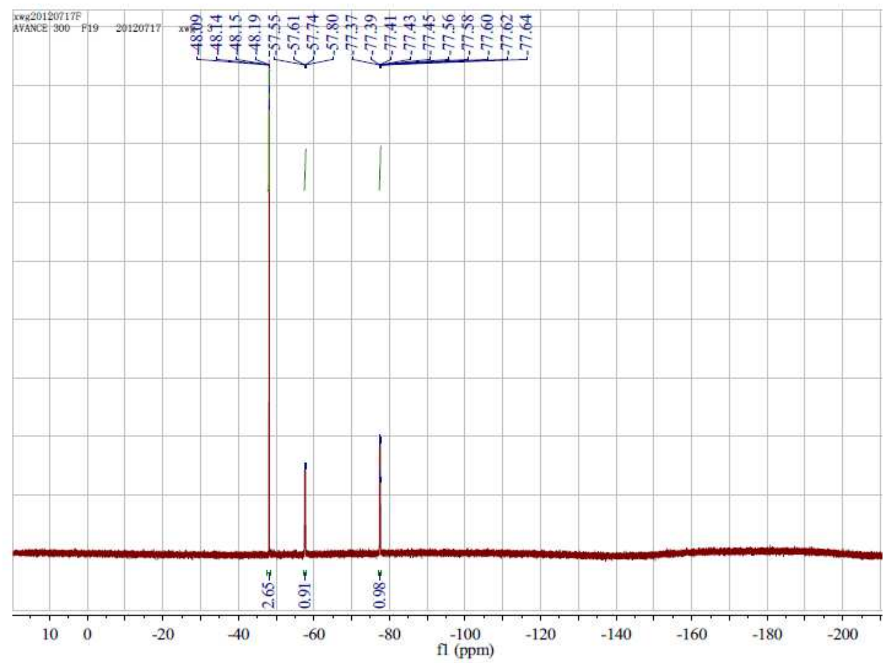


Complex **3**: IR, ^{31}P NMR, ^{1}H NMR and ^{19}F NMR

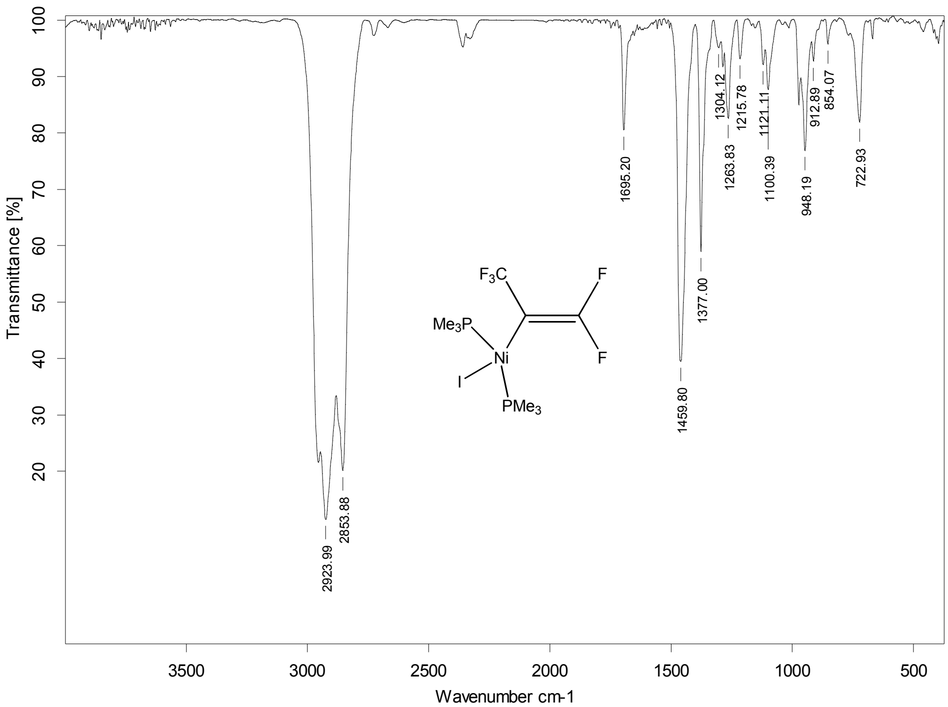


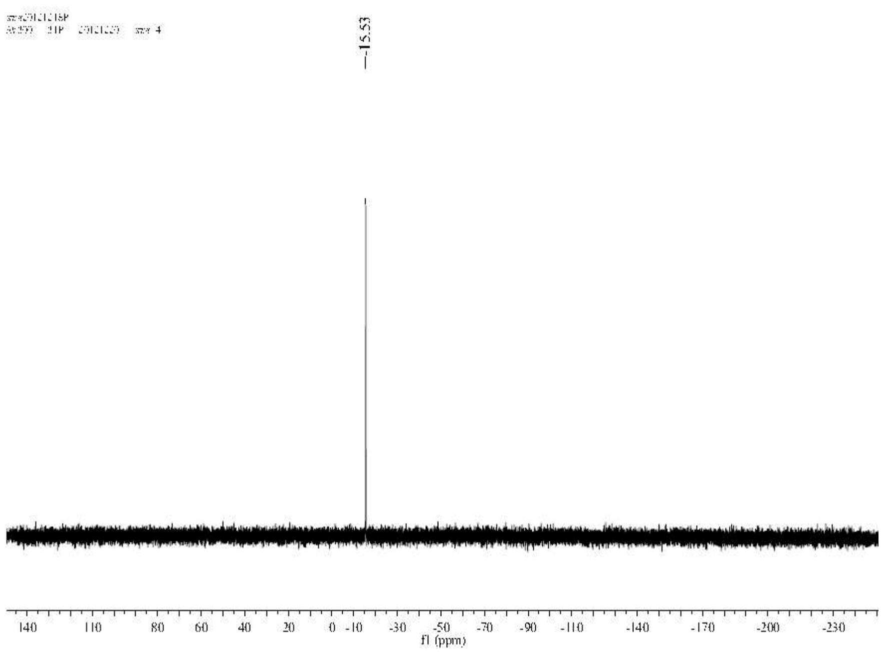


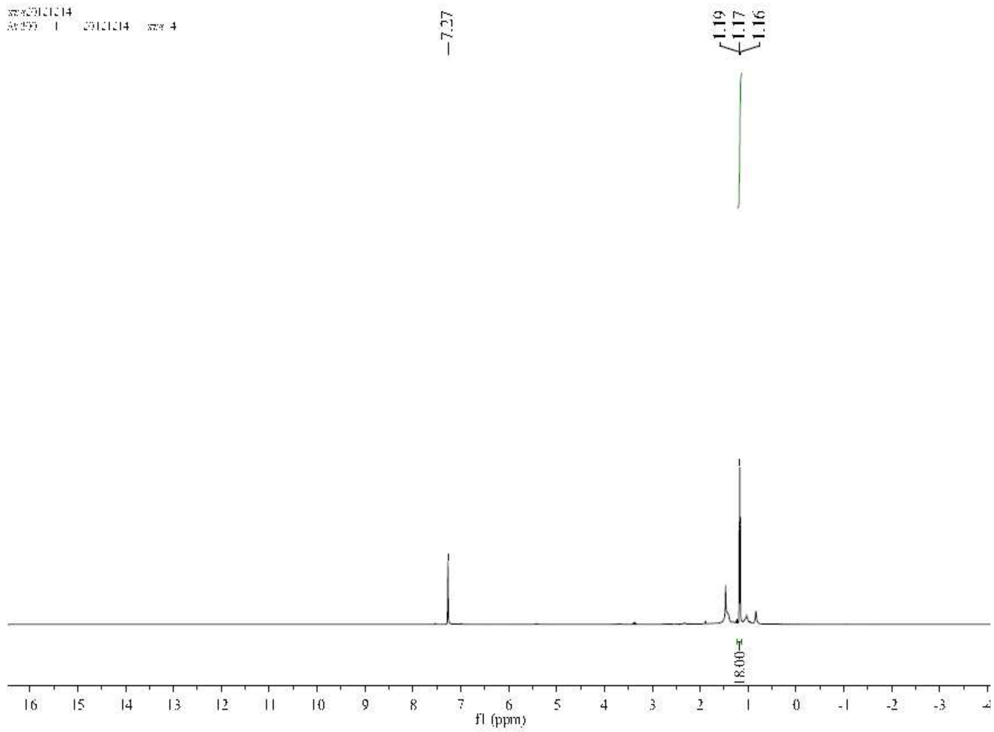


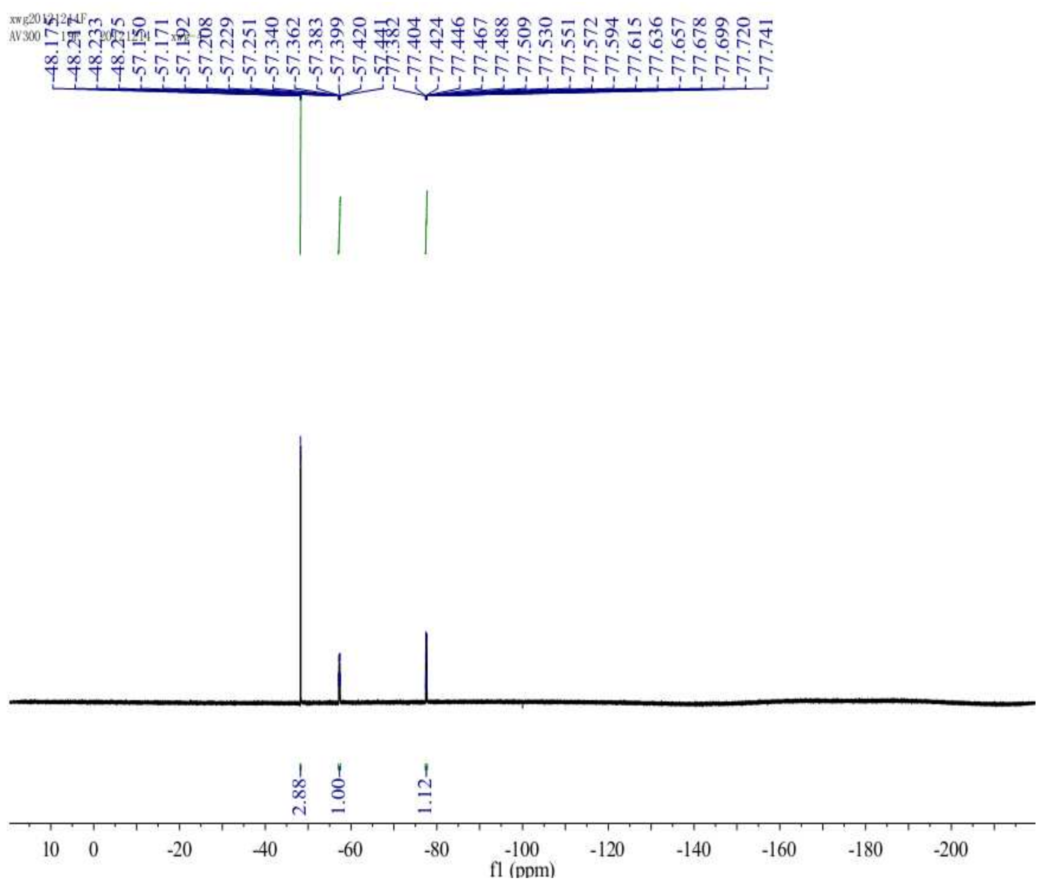


Complex **4**: IR, ^{31}P NMR, ^{1}H NMR and ^{19}F-NMR

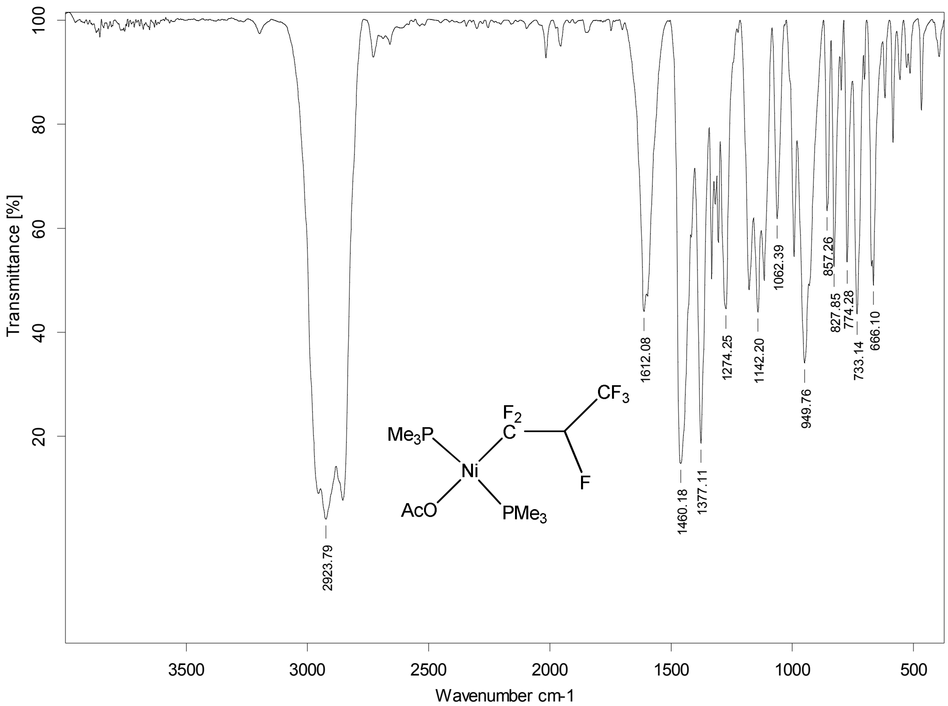


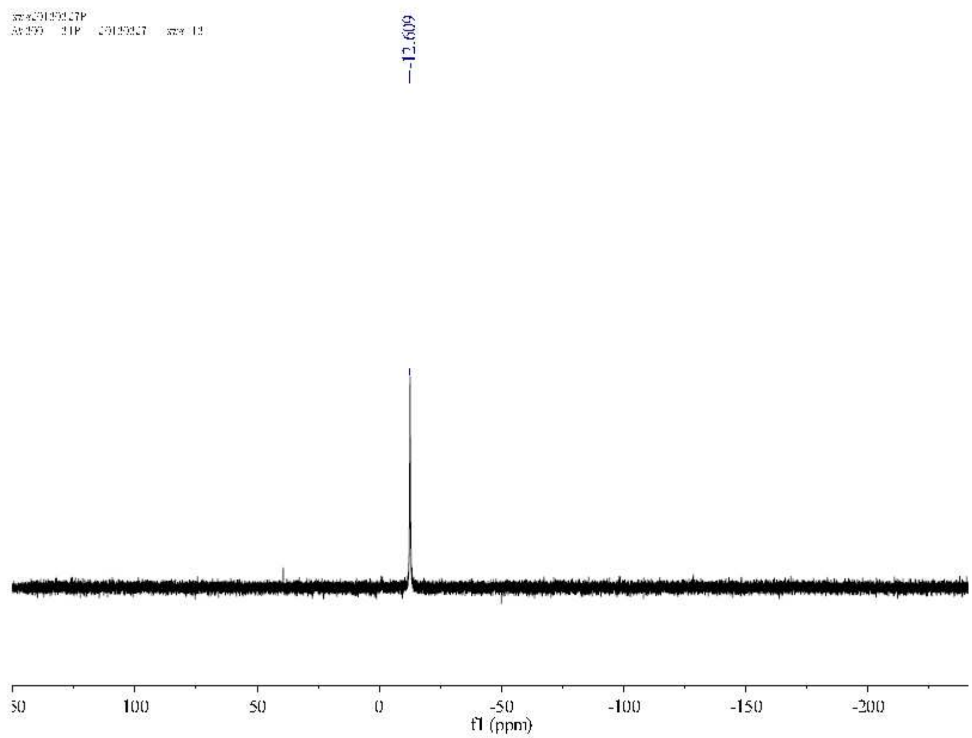


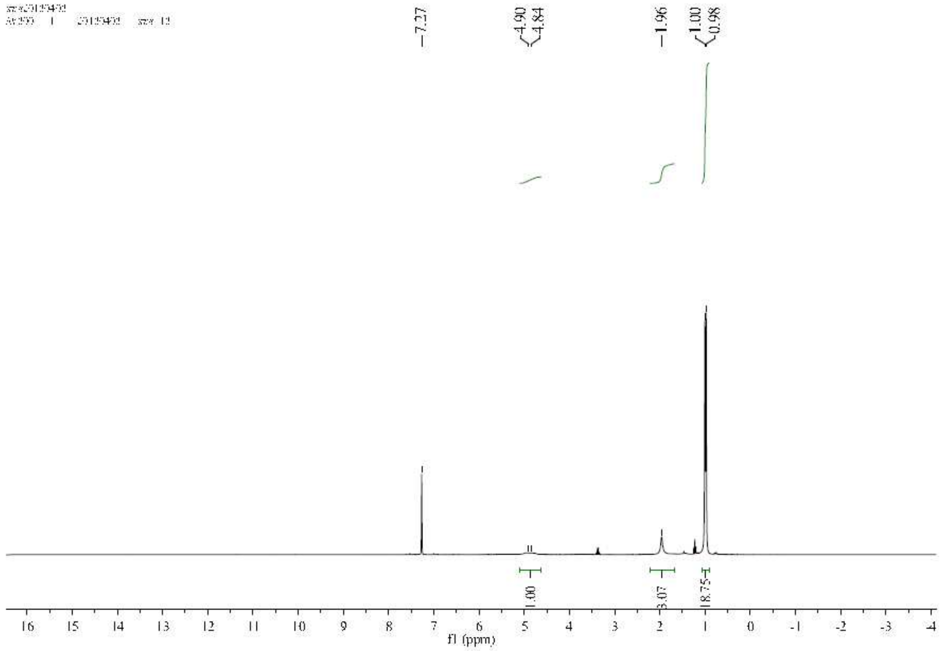

7.27
1.19
1.17
1.16
18.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

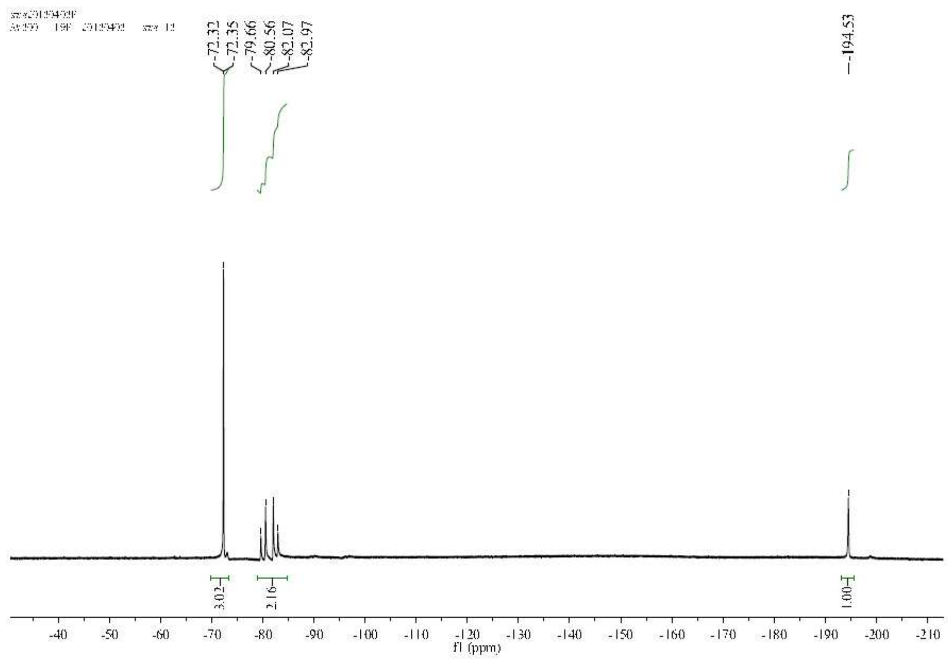

AV300
-57.150
-57.171
-57.208
-57.229
-57.251
-57.340
-57.362
-57.383
-57.399
-57.420
-77.404
-77.424
-77.446
-77.467
-77.488
-77.509
-77.530
-77.551
-77.572
-77.594
-77.615
-77.636
-77.657
-77.678
-77.699
-77.720
-77.741
2.88
1.00
1.12
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

Complex **5**: IR, ^{31}P NMR, ^{1}H-NMR and ^{19}F-NMR

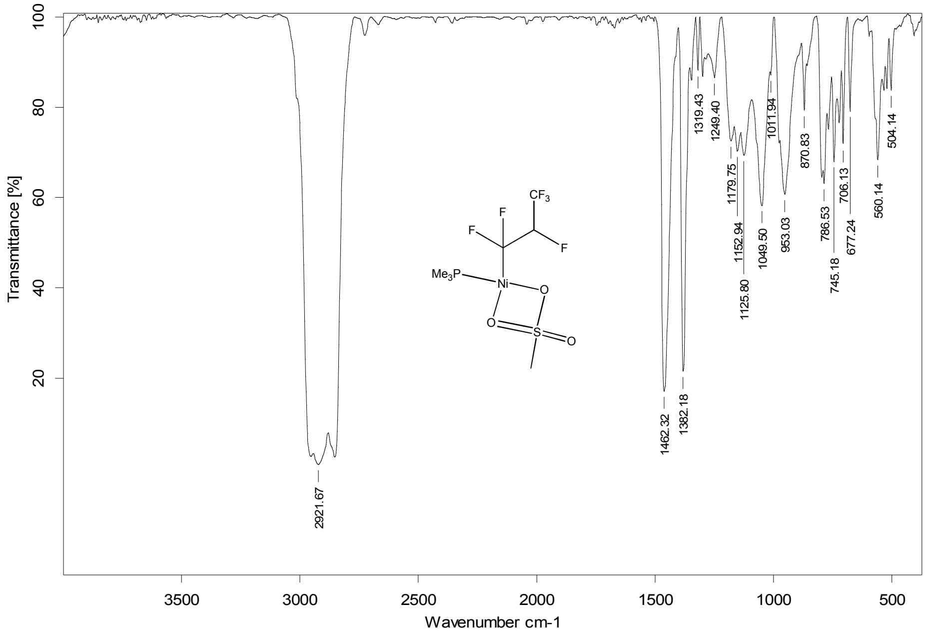


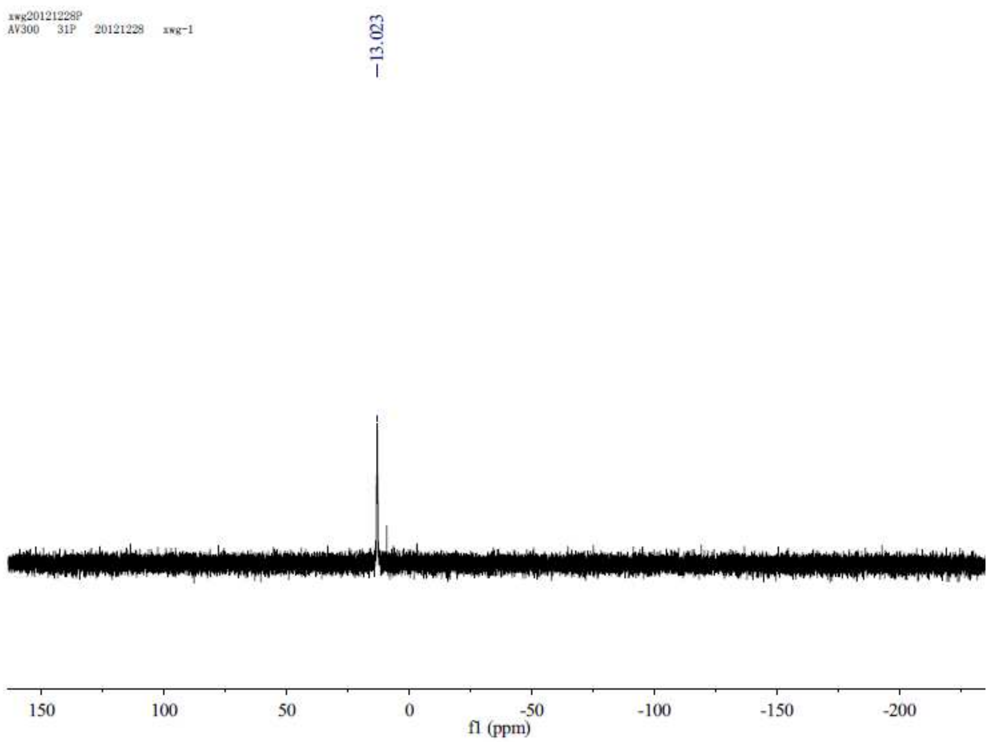


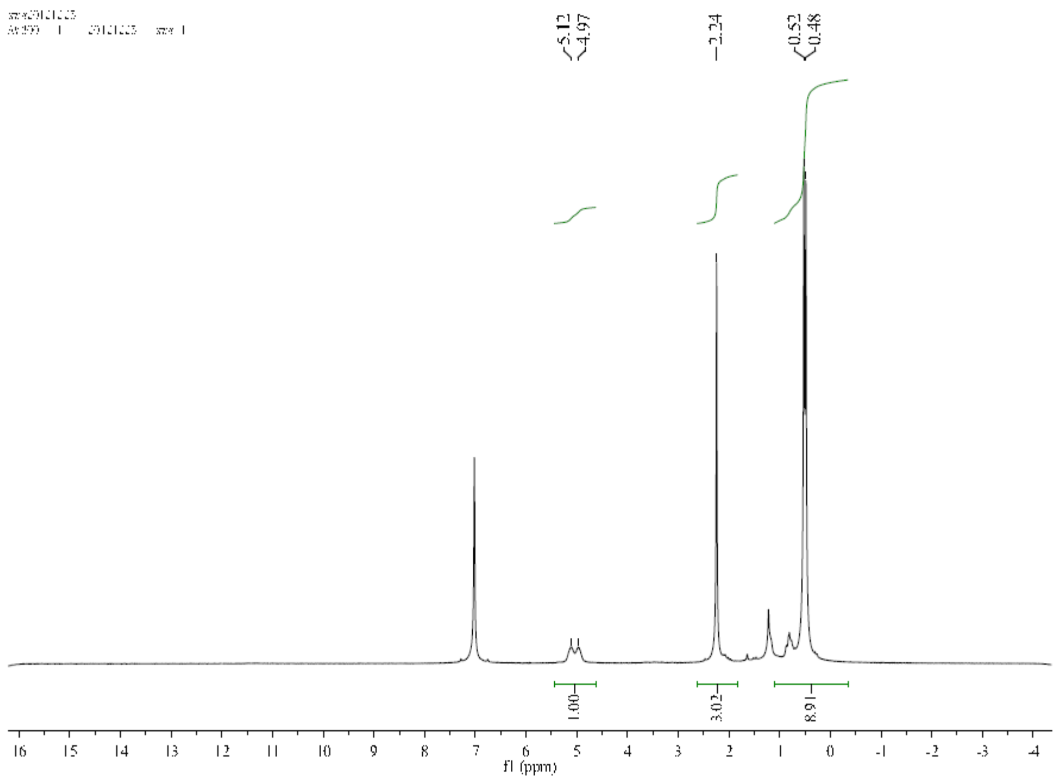

7.27
4.90
4.84
1.96
1.00
0.98
1.00
3.07
18.75
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


-72.32
-72.35
-79.66
-80.56
-82.07
-82.97
-194.53
3.02
2.16
1.00
-40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

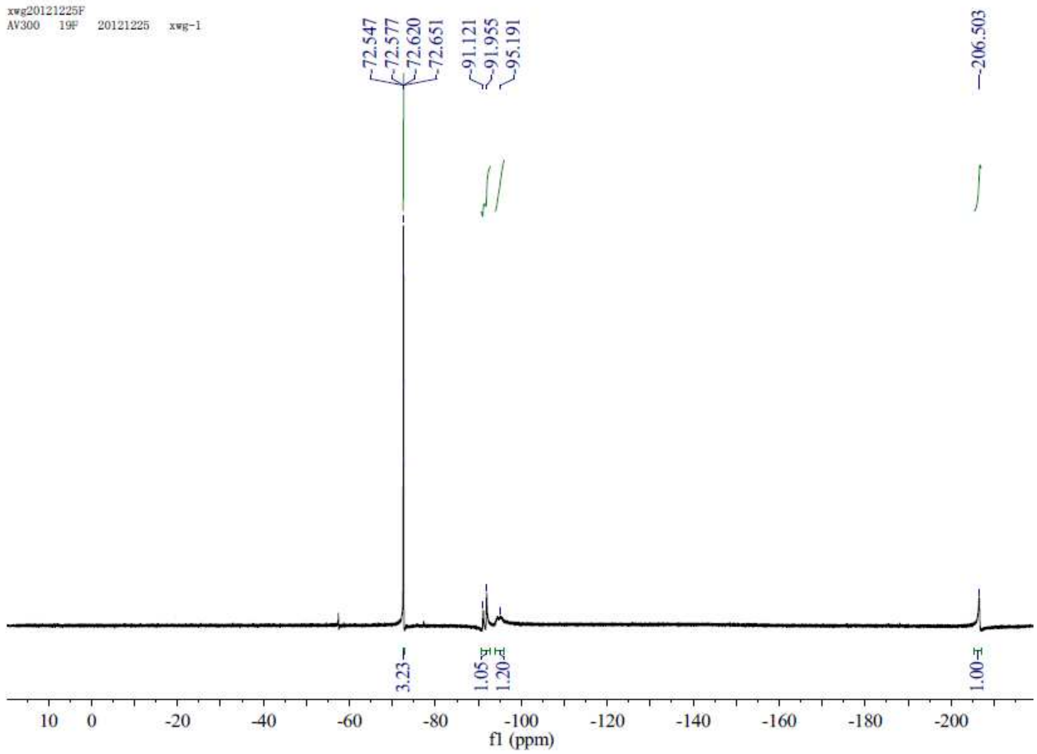
Complex **6**: IR, ^{31}P NMR, ^{1}H NMR and ^{19}F NMR





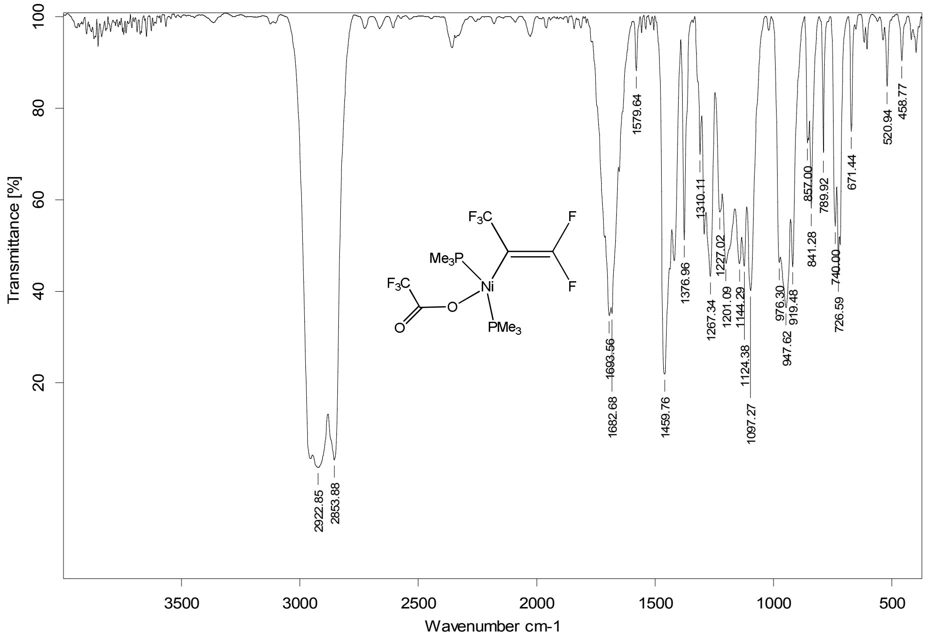


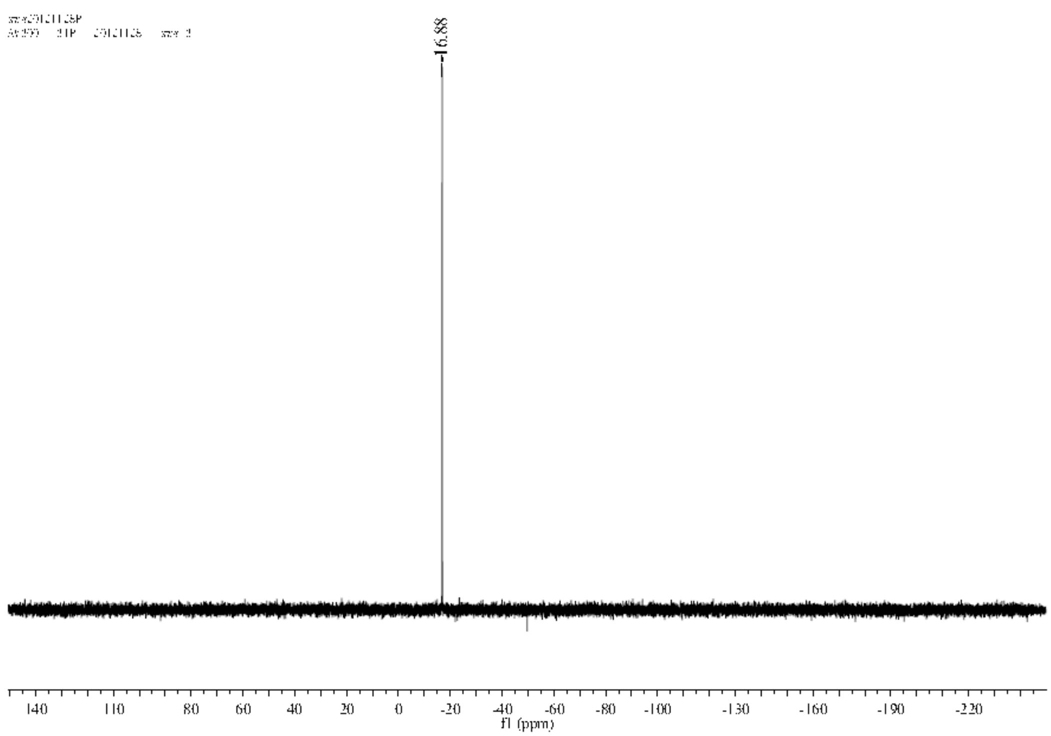
5.12
4.97
2.24
0.52
0.48
1.00
3.02
8.91
f1 (ppm)

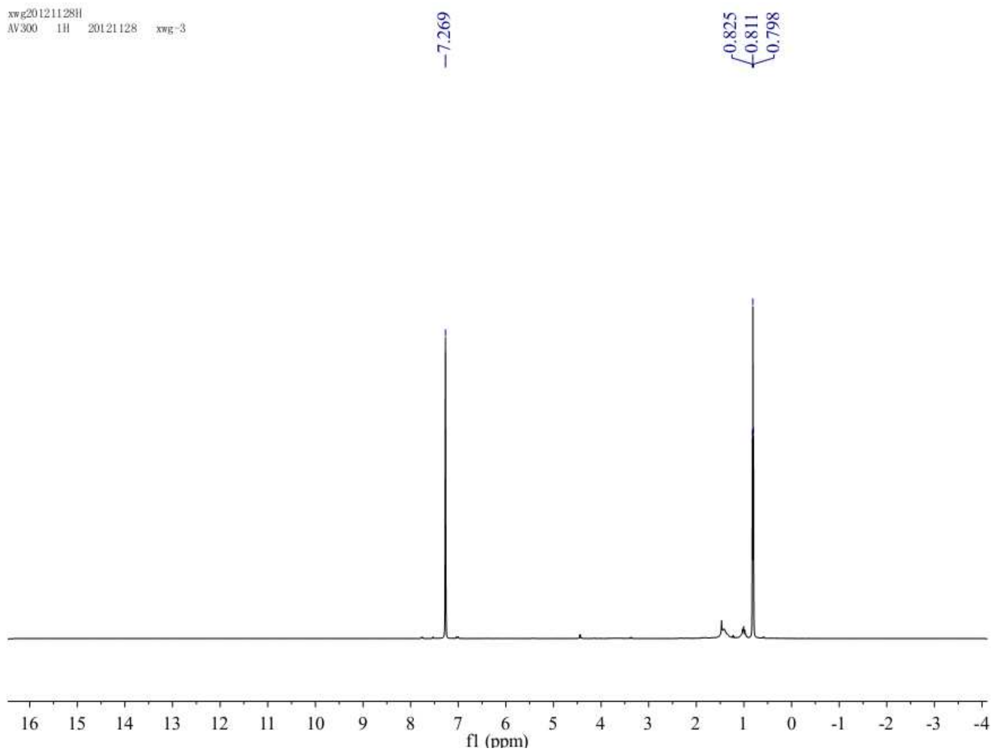


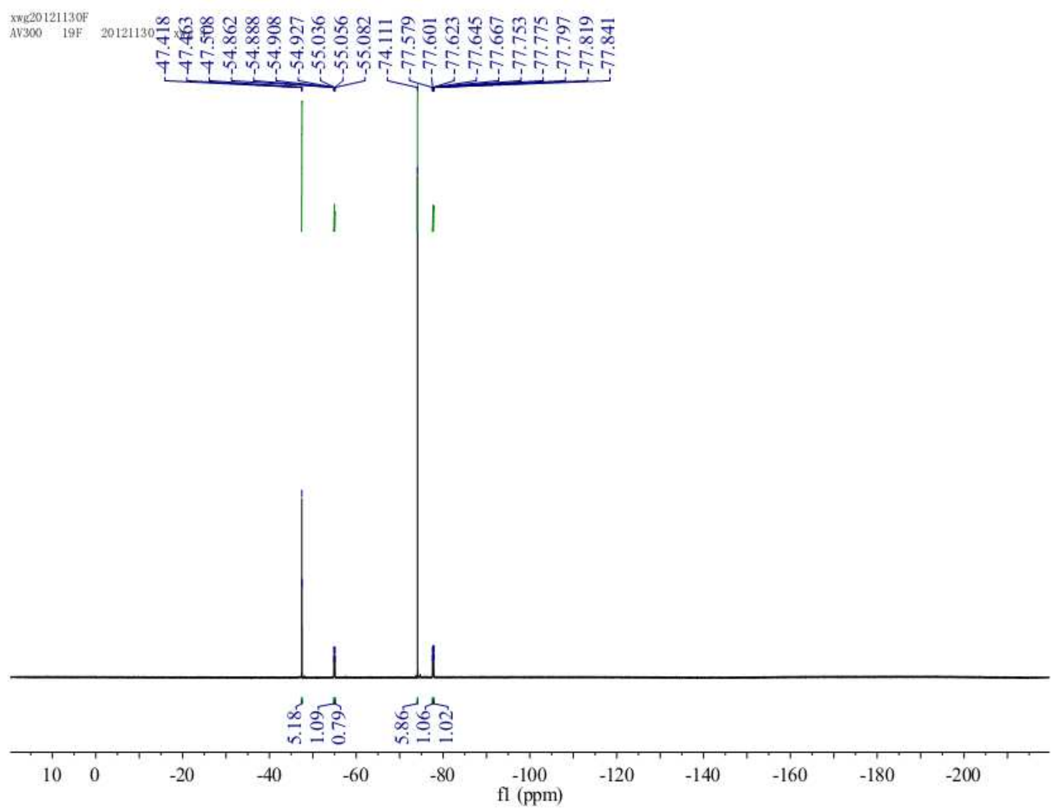
xwg20121225F
AV300 19F 20121225 xwg-1
-72.547
-72.577
-72.620
-72.651
-91.121
-91.955
-95.191
-206.503
3.23
1.05
1.20
1.00
f1 (ppm)

Complex **7**: IR, ^{31}P NMR, ^{1}H NMR and ^{19}F NMR

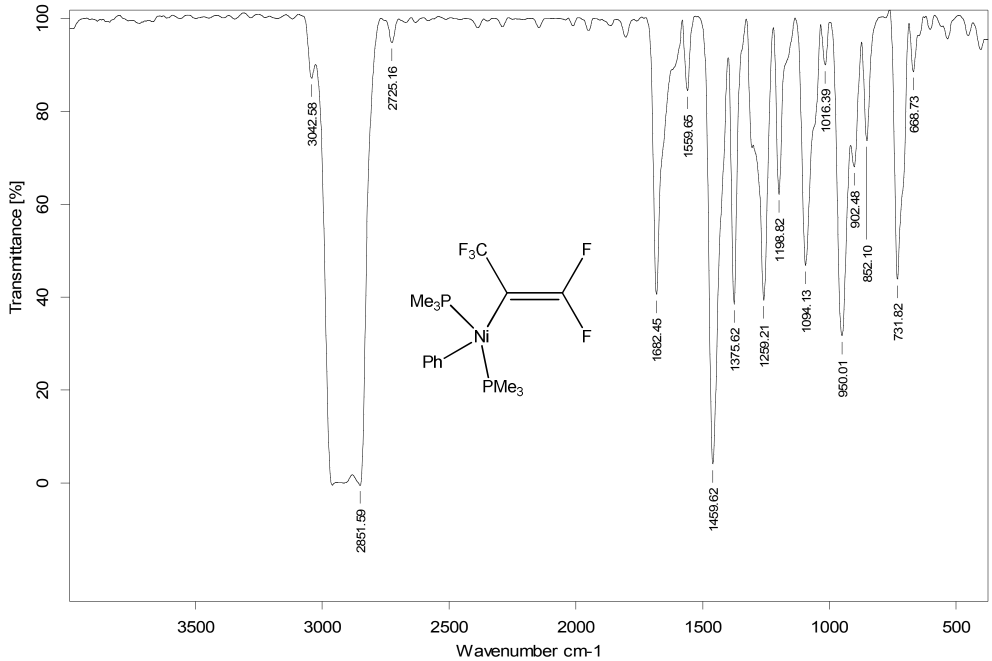


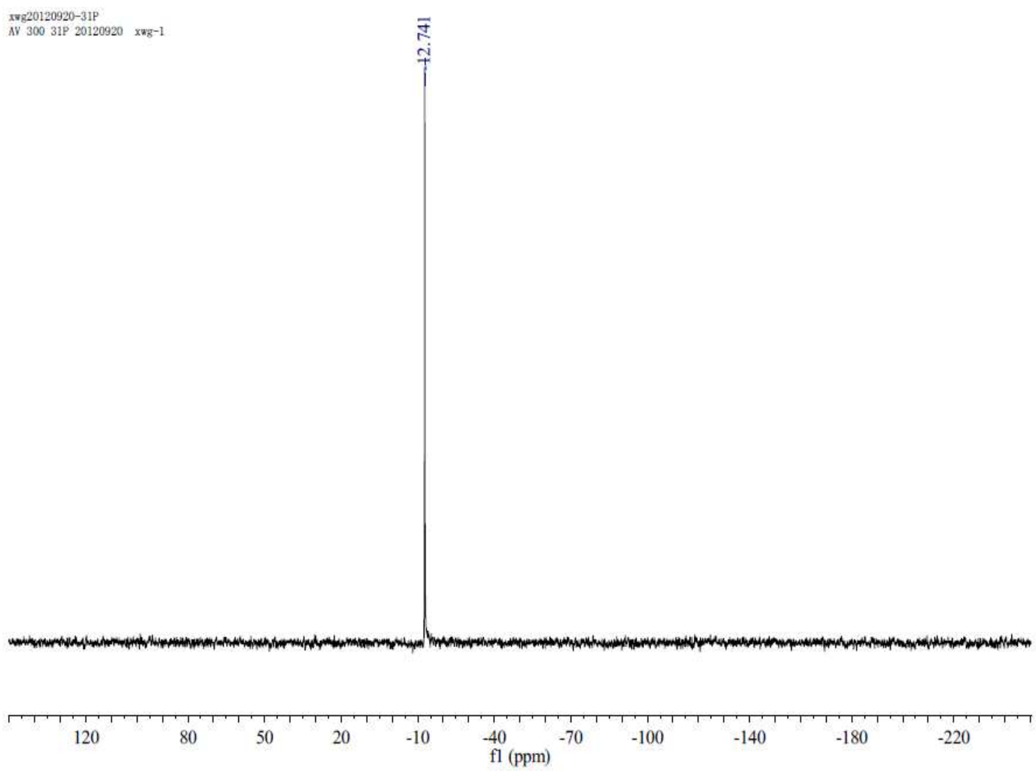


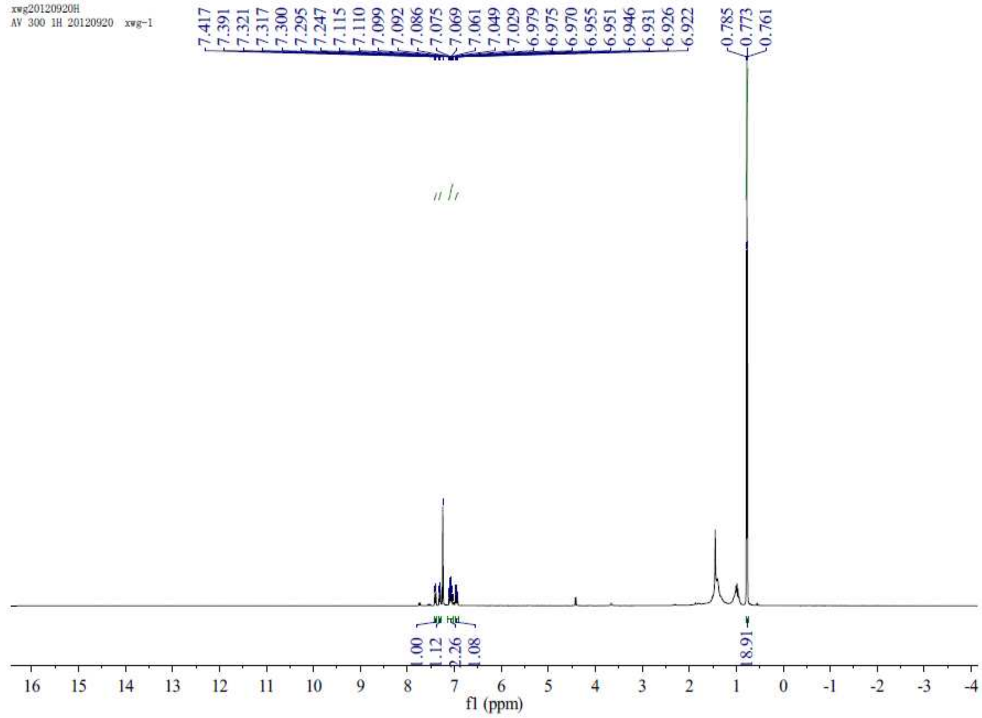

xwg20121128H
AV300 1H 20121128 xwg-3
7.269
0.825
0.811
0.798
fl (ppm)

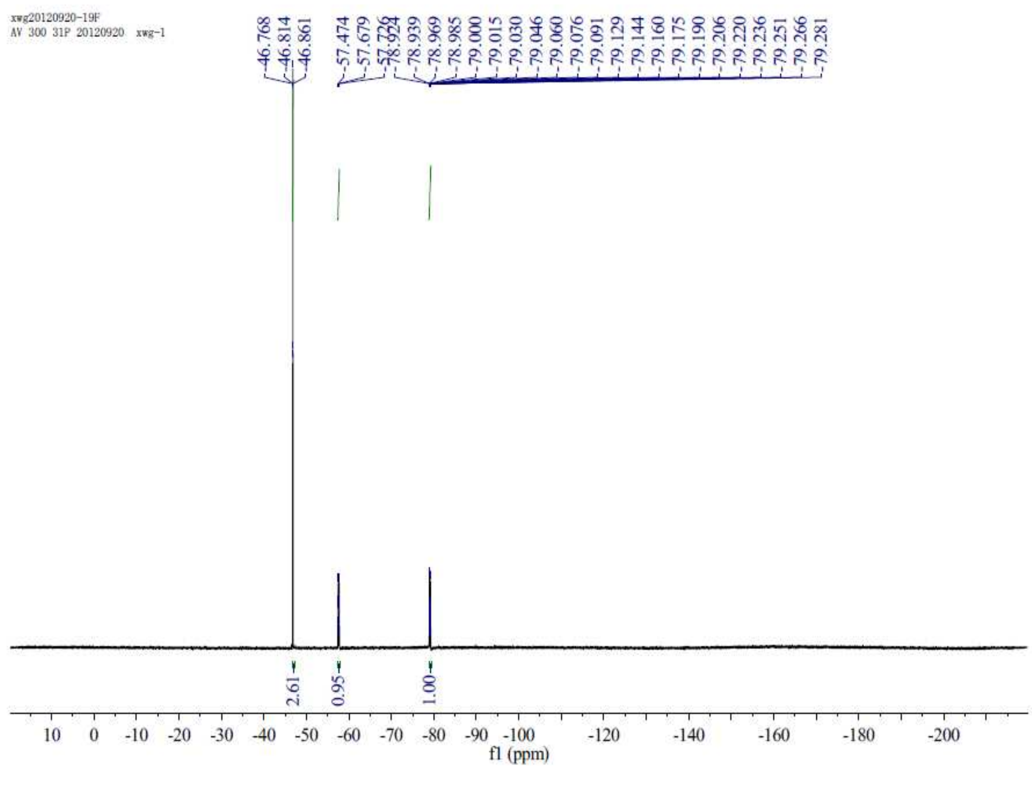

xwg20121130F
AV300 19F 20121130
-47.418
-47.463
-47.508
-54.862
-54.888
-54.908
-54.927
-55.036
-55.056
-55.082
-74.111
-77.579
-77.601
-77.623
-77.645
-77.667
-77.753
-77.775
-77.797
-77.819
-77.841
5.18
1.09
0.79
5.86
1.06
1.02
fl (ppm)

Complex **8**: IR, ^{31}P NMR, ^{1}H NMR and ^{19}F NMR

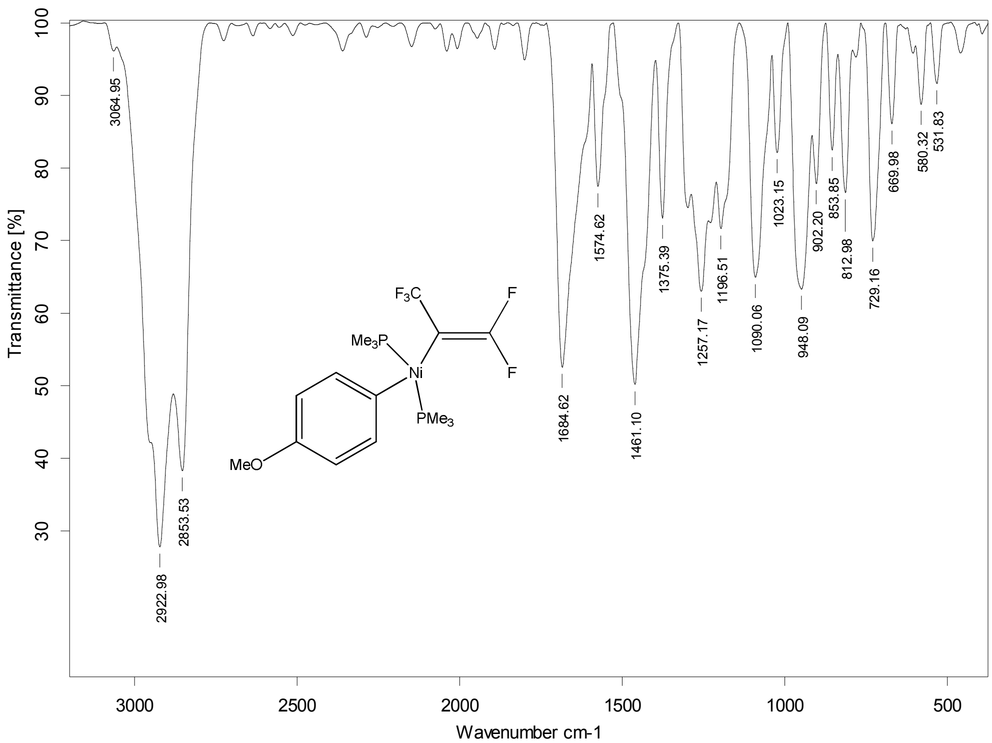


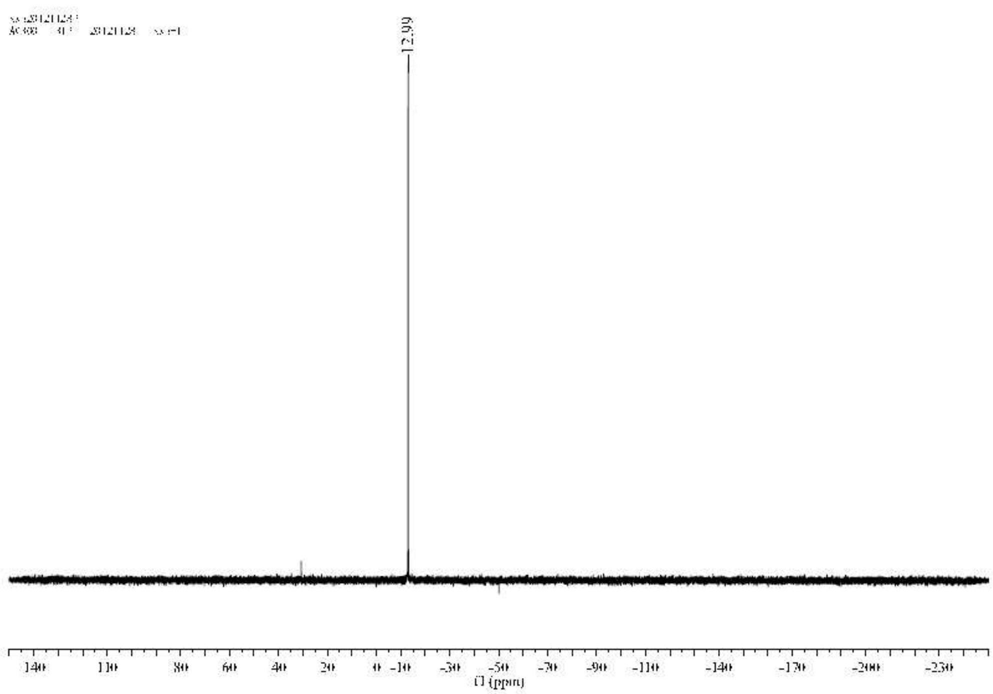


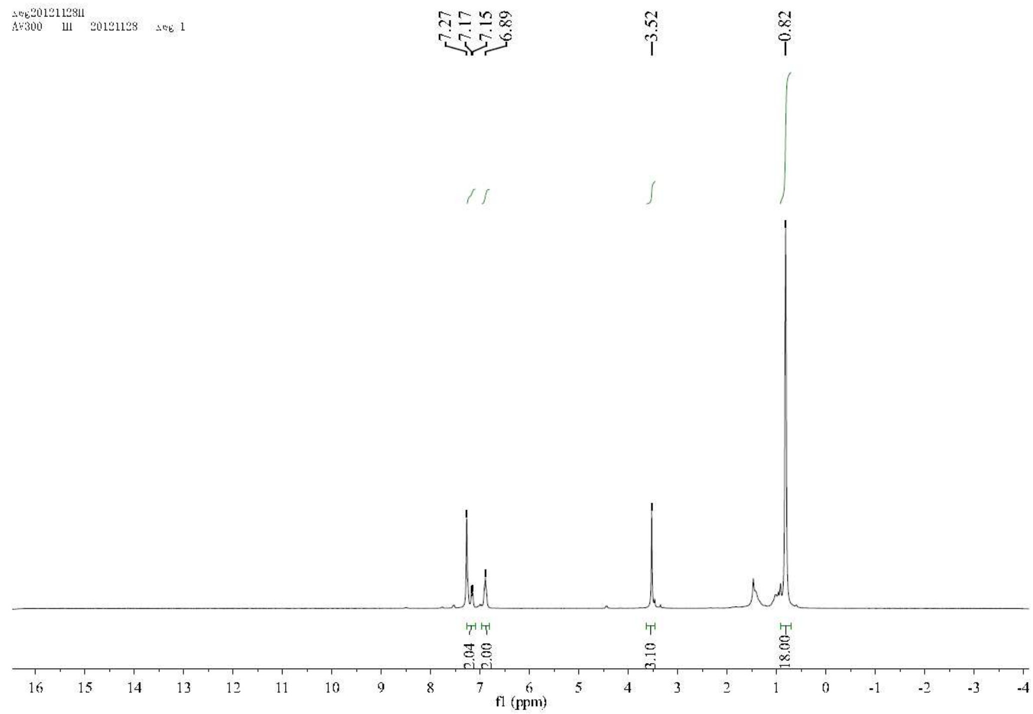


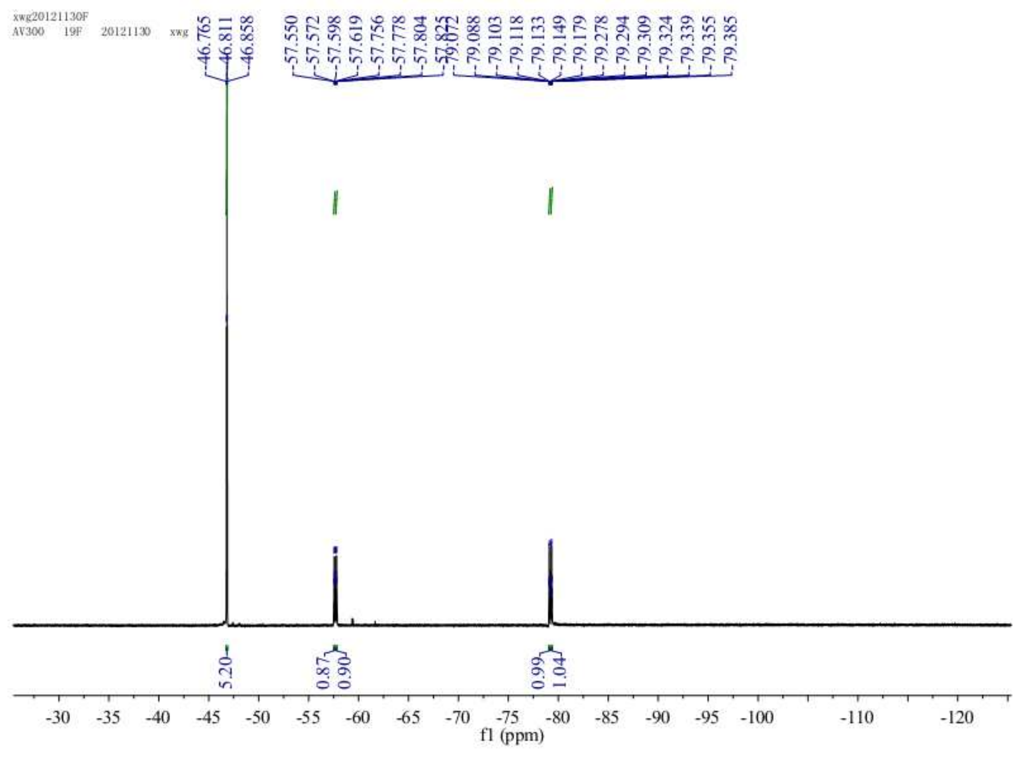


Complex **9**: IR, ^{31}P NMR, ^{1}H NMR and ^{19}F NMR

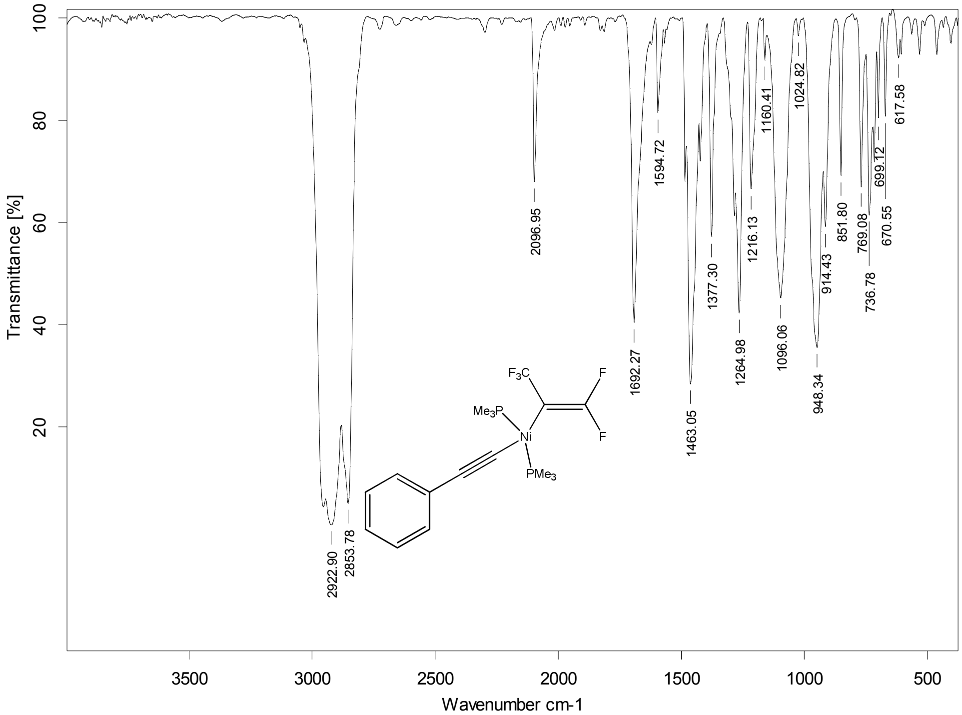


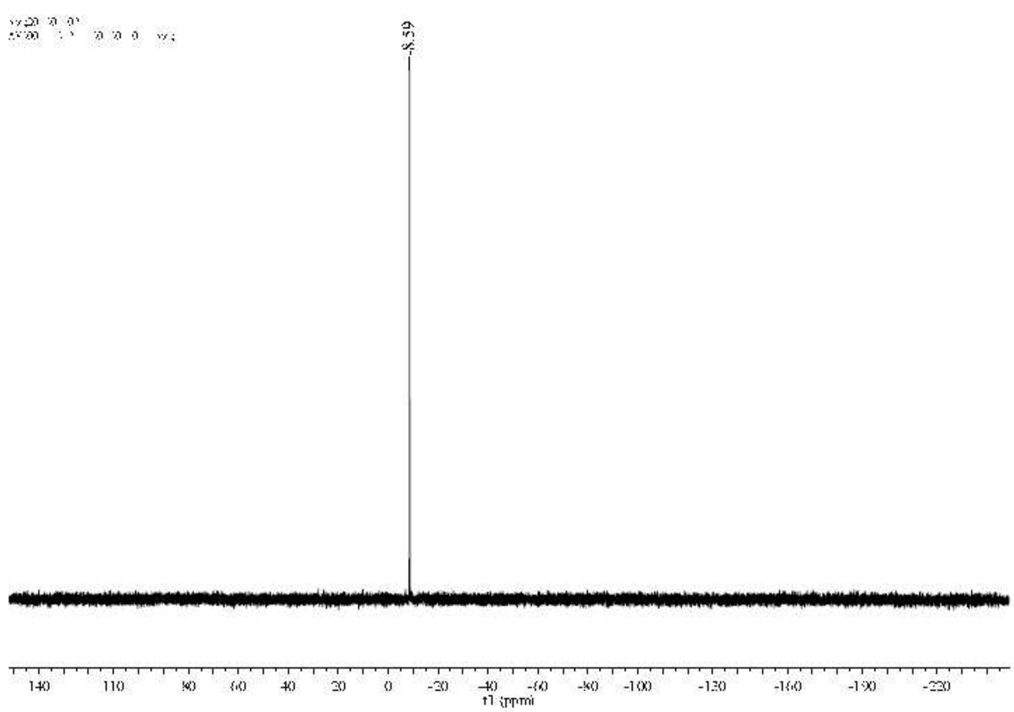


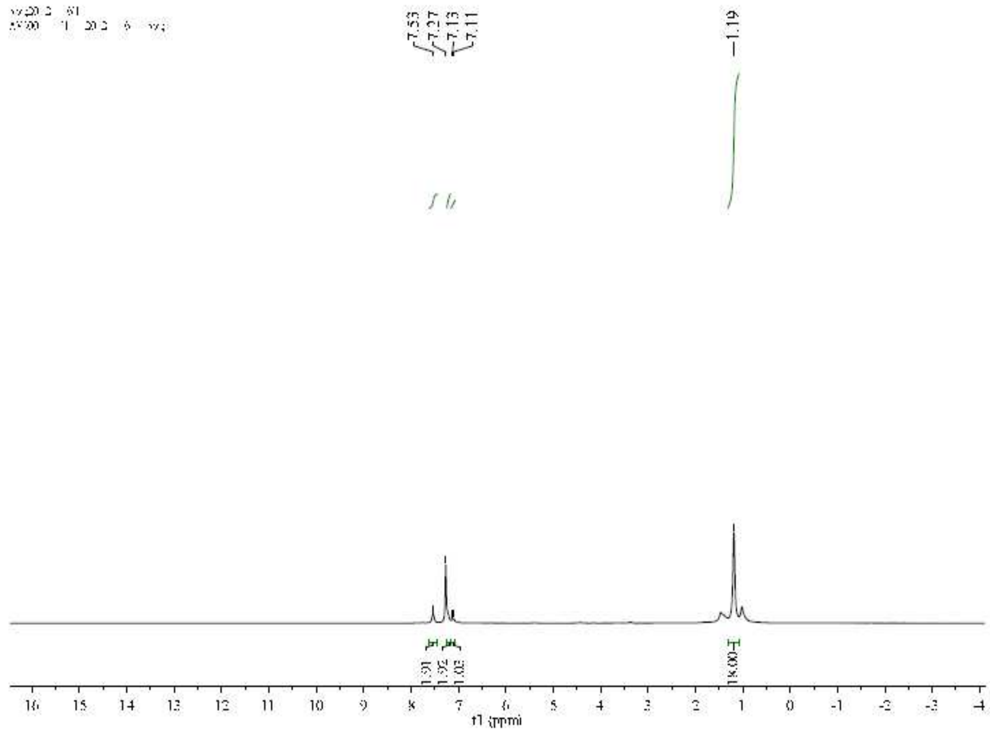

xwg20121128H
AV300 1H 20121128 xwg 1
7.27
7.17
7.15
6.89
3.52
0.82
2.04
2.00
3.10
18.00
f1 (ppm)

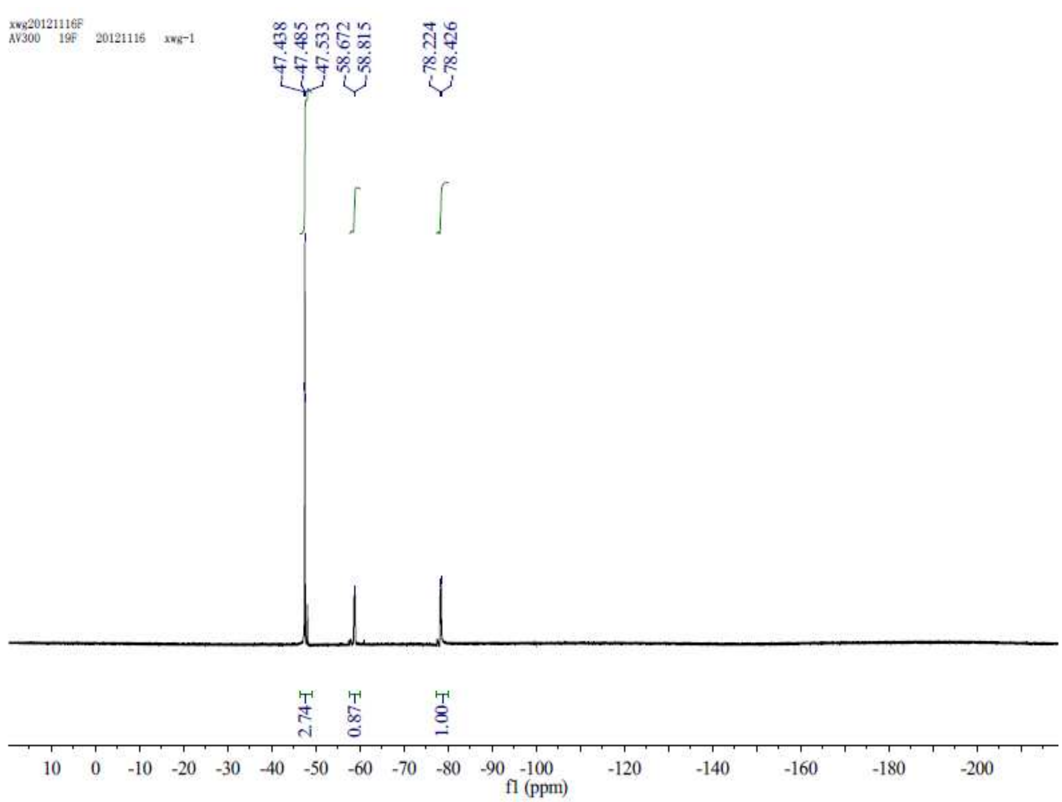

xwg20121130F
AV300 19F 20121130 xwg
-46.765
-46.811
-46.858
-57.550
-57.572
-57.598
-57.619
-57.756
-57.778
-57.804
-57.825
-79.072
-79.088
-79.103
-79.118
-79.133
-79.149
-79.179
-79.278
-79.294
-79.309
-79.324
-79.339
-79.355
-79.385
5.20
0.87
0.90
0.99
1.04
f1 (ppm)

Complex **10**: IR, ^{31}P NMR, ^{1}H NMR and ^{19}F NMR

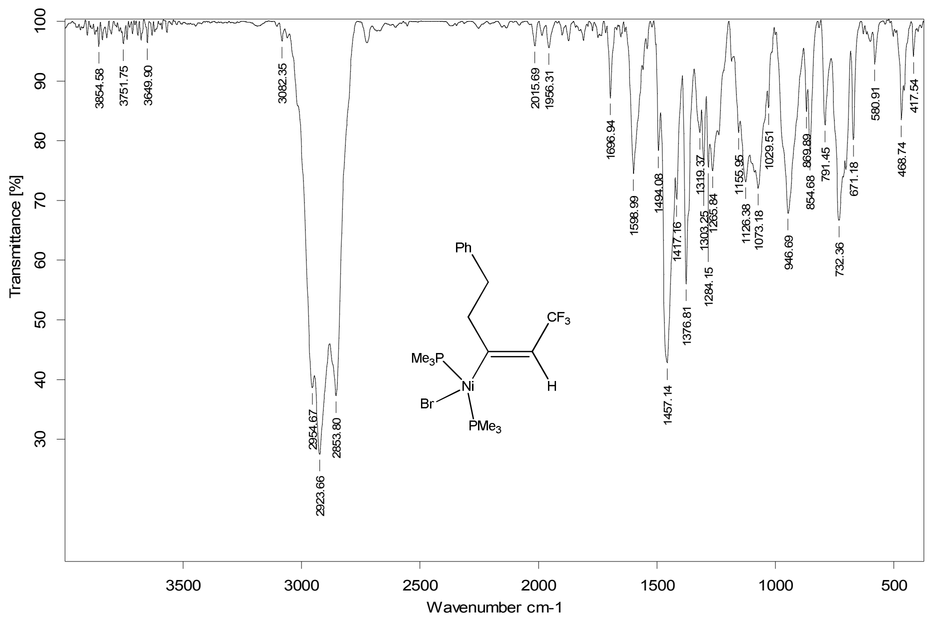


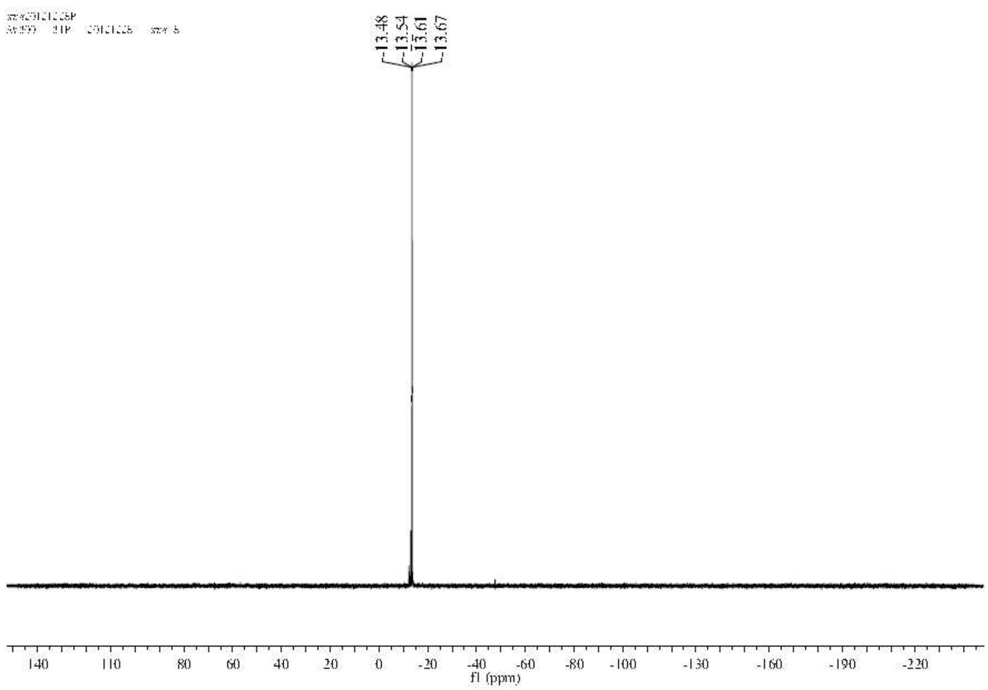


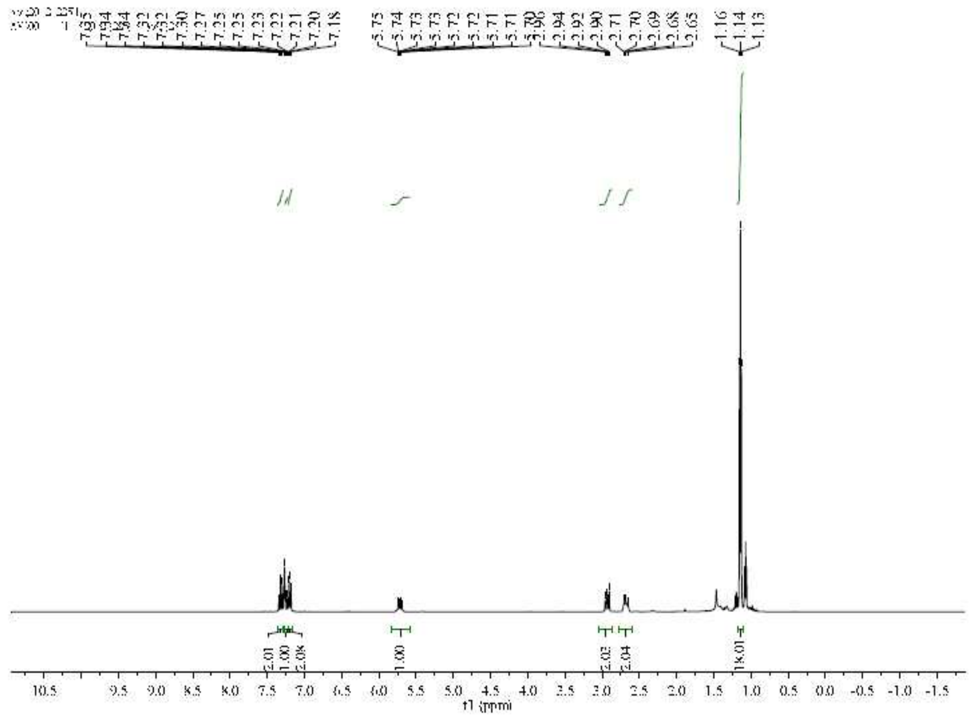

7.53
7.27
7.13
7.11
1.19
1.91
1.92
1.03
18.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


xwg20121116F
AV300 19F 20121116 xwg-1
-47.438
-47.485
-47.533
-58.672
-58.815
-78.224
-78.426
2.74
0.87
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

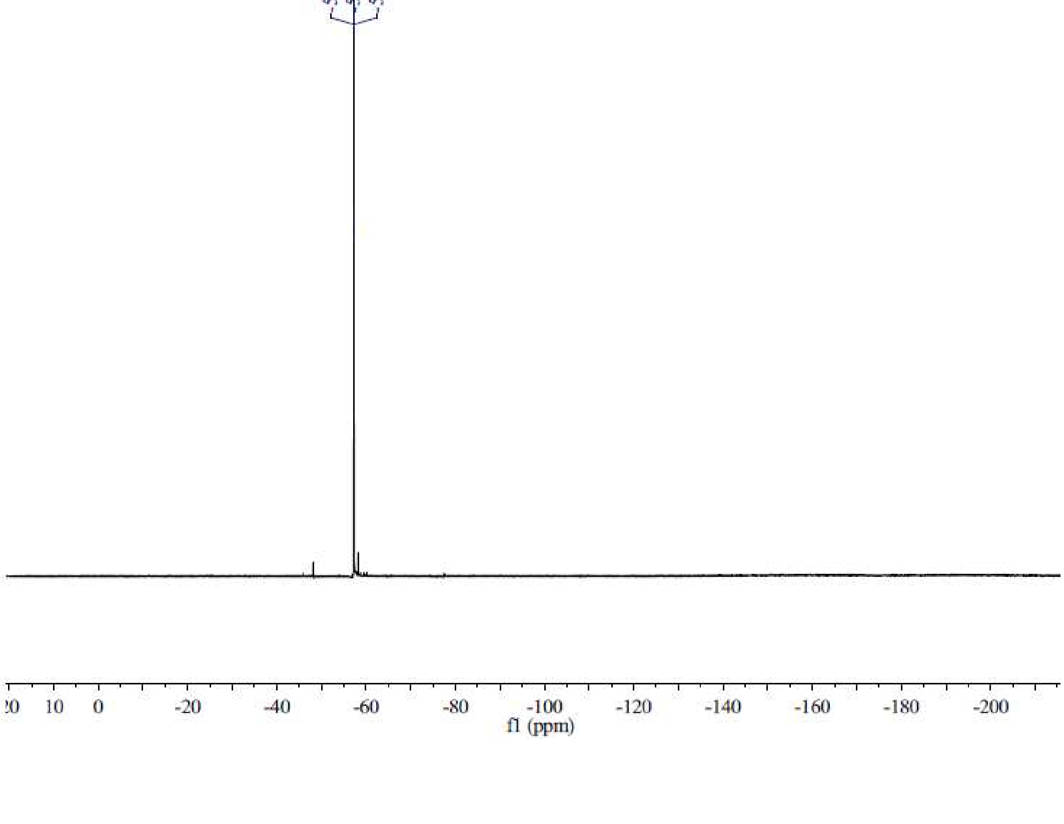
Complex **11**: IR, ^{31}P NMR, ^{1}H NMR, ^{19}F NMR and ^{13}C NMR

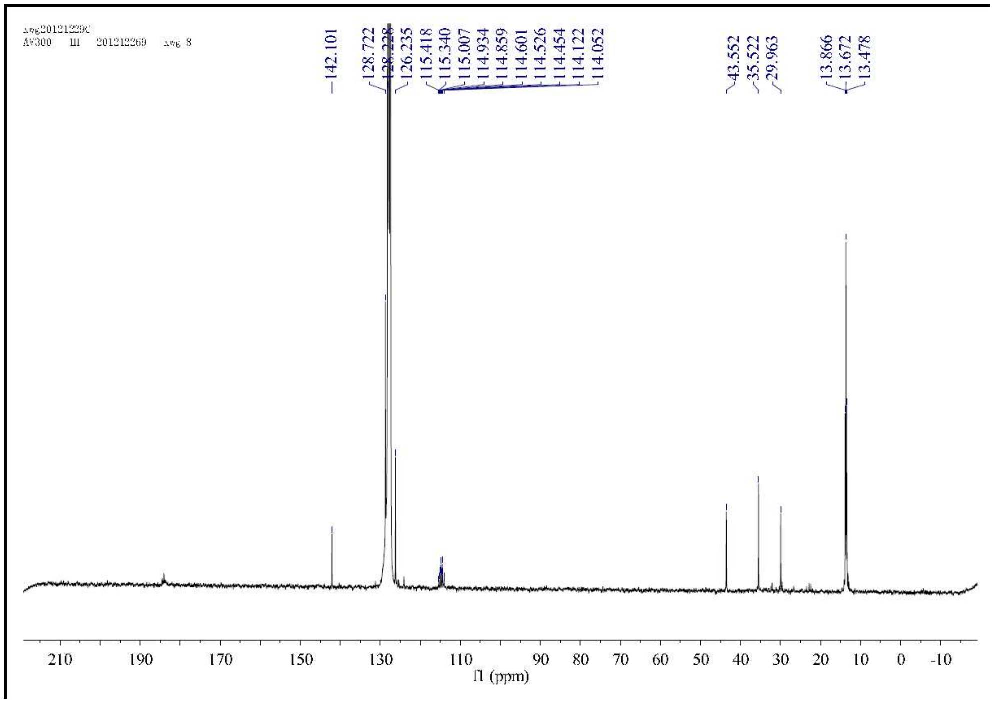




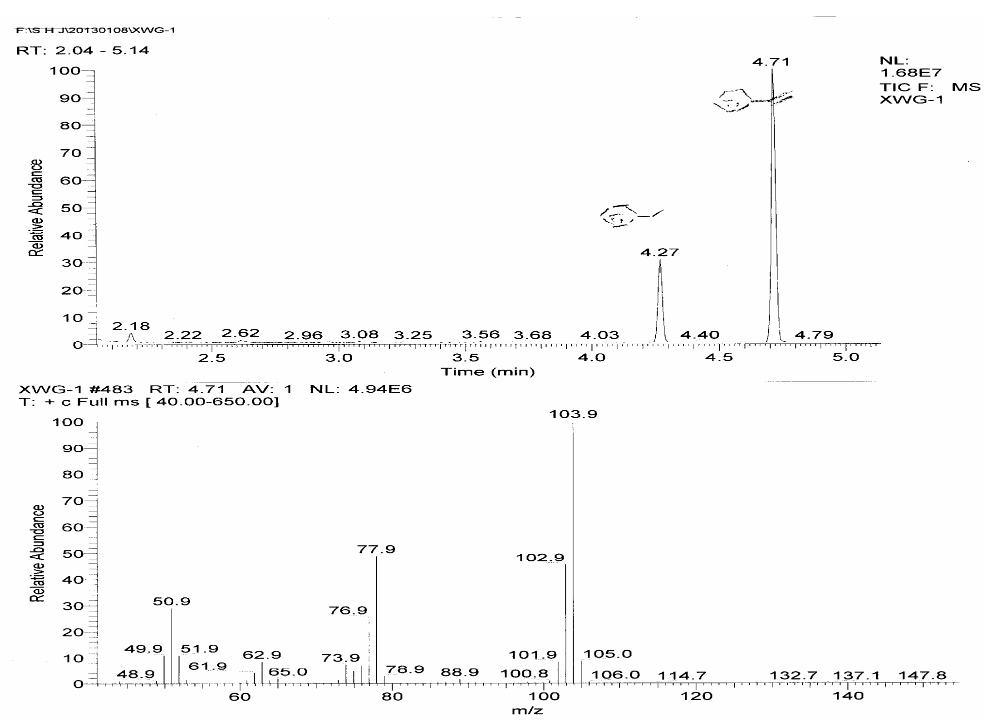


xwg20121030-19F
AV 300 31P 20121030 xwg 3





(4) GC-MS for confirmation of the formation of styrene



(5) The hydrido signal in the *in situ* ^{1}H NMR of the reaction in **Scheme 5**