

Synthesis and Catalytic Activity of N-Heterocyclic Silylene (NHSi) Cobalt Hydride for Kumada Coupling Reactions

Xinghao Qi,^a Hongjian Sun,^{a,*} Xiaoyan Li,^{a,*} Olaf Fuhr,^b Dieter Fenske^b

^a School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, 250199 Jinan, People's Republic of China

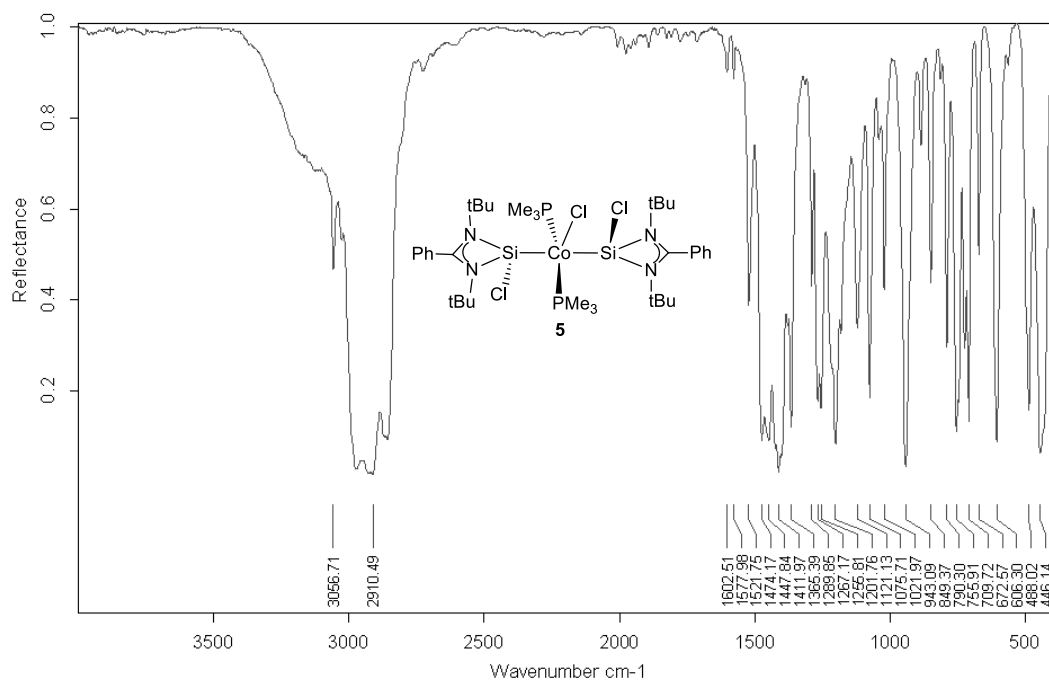
^b Institut für Nanotechnologie (INT) und Karlsruher Nano-Micro-Facility (KNMF), Karlsruher Institut für Technologie (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

SI The table of selected crystallographic data	2
SII IR, ¹ H, ³¹ P, ¹³ C NMR, HH COSY, HMQC, HSQC and ²⁹ Si NMR spectra of complexes 5 , 6 and 6d	3
SIII ¹ H and ¹³ C NMR spectra of coupling products	12
SIV MS of study on the catalytic reaction mechanism	27

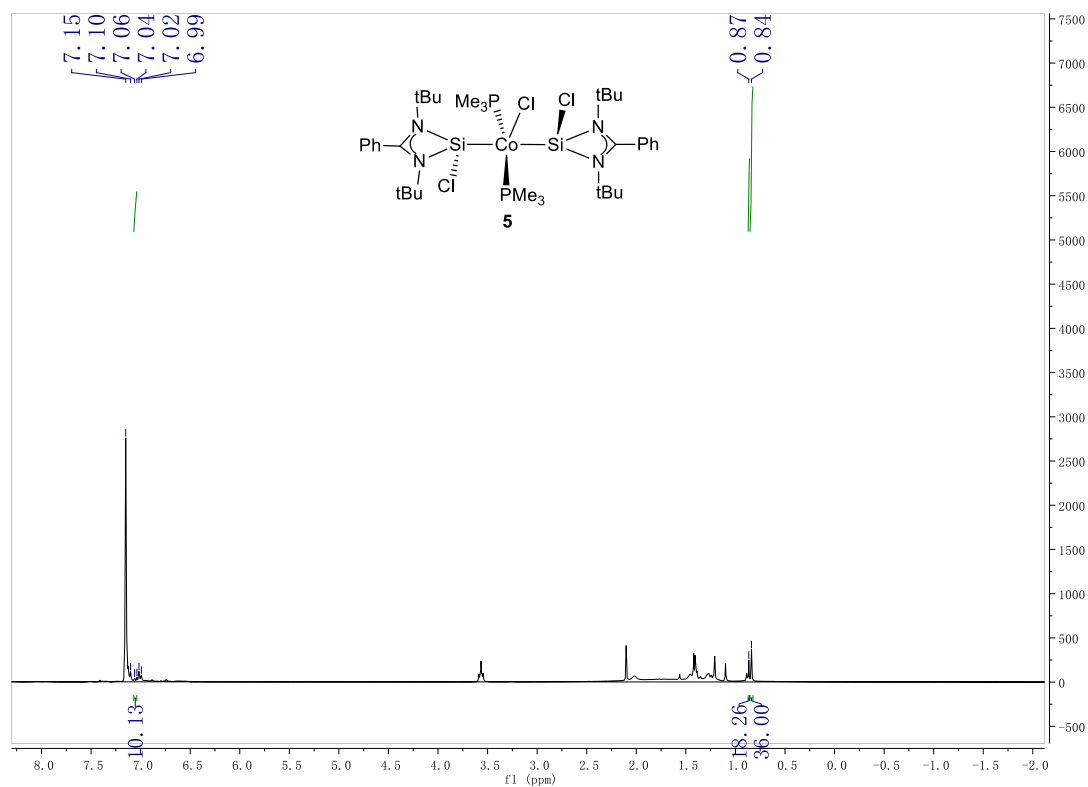
SI The table of selected crystallographic data

	5	6	6d
formula	C ₄₁ H ₇₆ Cl ₃ CoN ₄ P ₂ Si ₂	C ₁₀₆ H ₁₃₈ Cl ₄ Co ₂ N ₈ OP ₆ Si ₄	C ₅₅ H ₇₃ Cl ₂ CoN ₄ OP ₃ Si ₂
M_z	908.45	2098.08	1085.09
crystal system	Monoclinic	Triclinic	Triclinic
space group	P2 ₁ /c	P-1	P-1
a [Å]	13.8468(3)	13.9433(5)	13.9845(14)
b [Å]	19.5827(5)	17.2555(7)	17.415(2)
c [Å]	18.5459(4)	24.5173(10)	24.858(3)
α [°]	90	99.180(3)	98.767(9)
β [°]	103.406(2)	99.723(3)	101.053(8)
γ [°]	90	103.830(3)	103.860(8)
V [Å ³]	4891.8(2)	5521.0(4)	5642.2(11)
T [K]	150.15	150.15	173.15
Z	4	2	4
μ [mm ⁻¹]	5.581	4.862	0.568
total reflns	22857	49093	56456
unique reflns	7980	17989	30063
R _{int}	0.0674	0.1348	0.0696
R ₁ [I>2 σ (I)]	0.0466	0.0949	0.0838
wR(F ²)[I>2 σ (I)]	0.0988	0.2452	0.2208
R ₁ (all data)	0.0827	0.1749	0.1409
wR(F ²)(all data)	0.1097	0.3026	0.2695
GOF on F ²	0.875	0.847	0.951

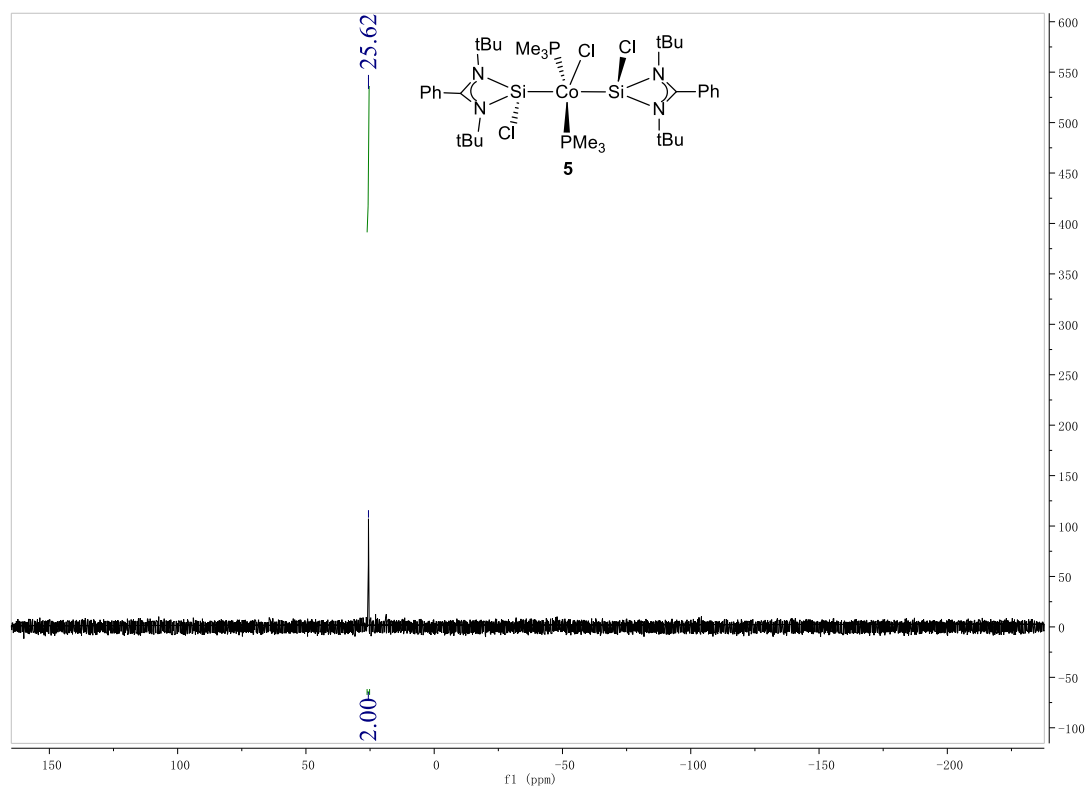
S II IR, ¹H, ³¹P and ¹³C NMR and ²⁹Si NMR spectra of complexes 5, 6 and 6d



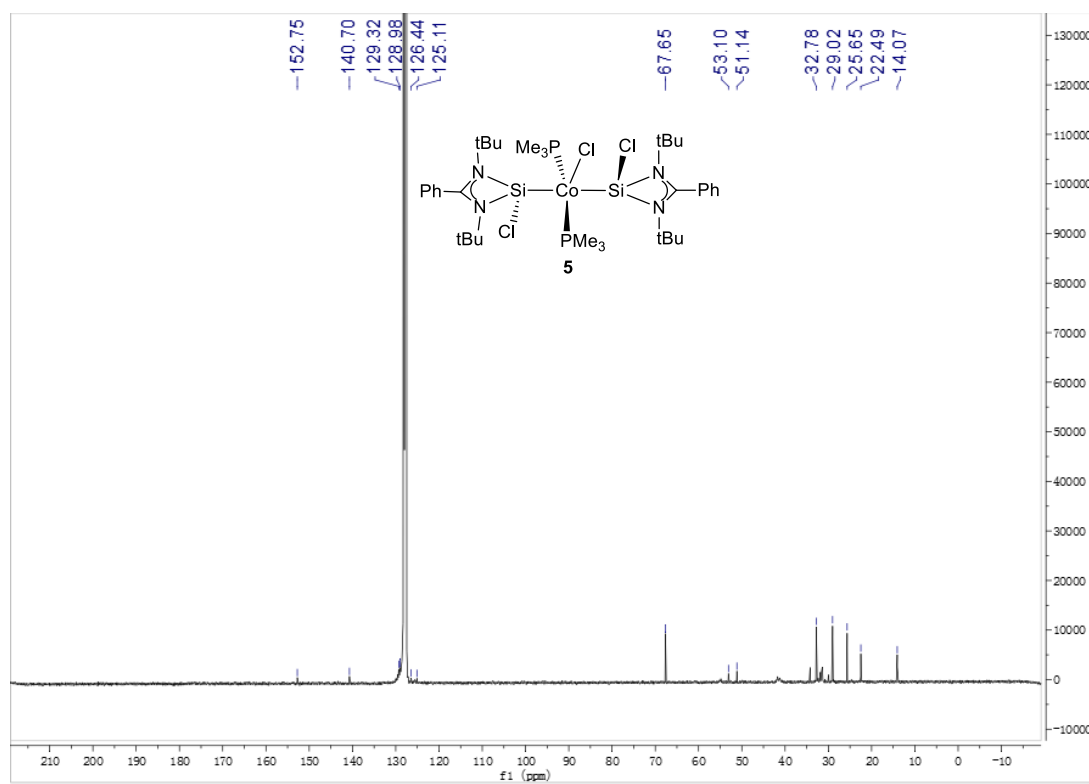
IR spectrum of complex 5



¹H NMR of complex 5

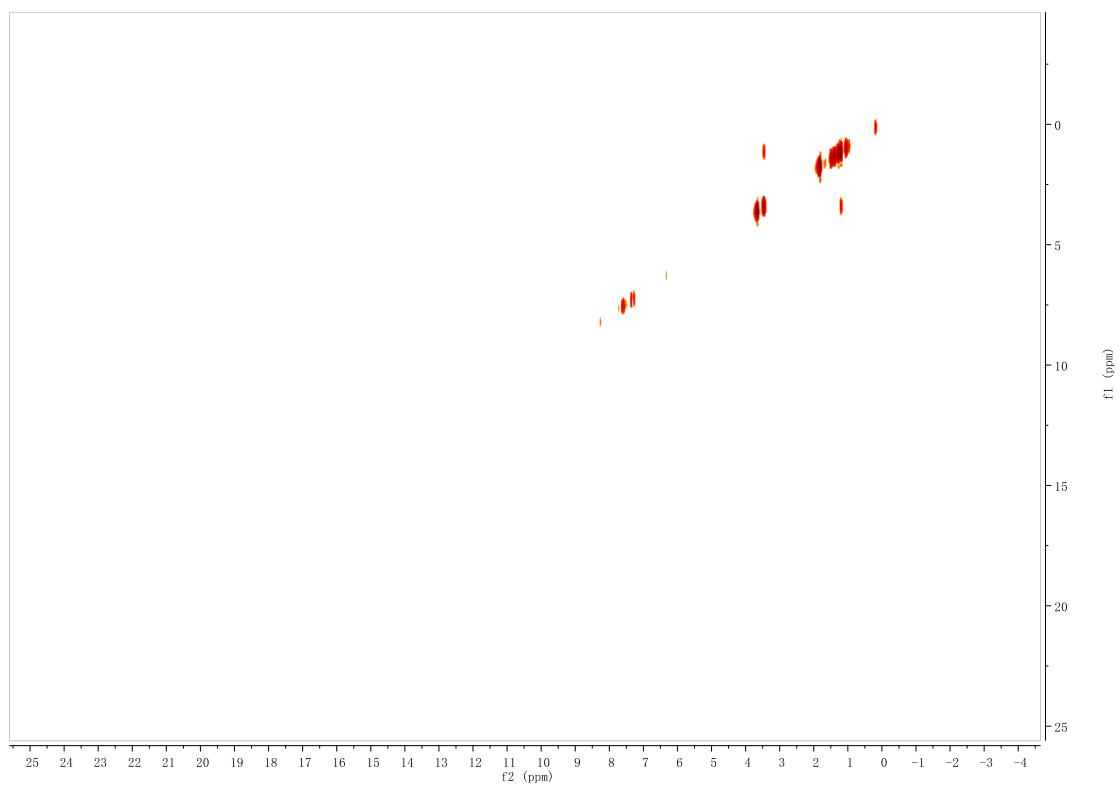


³¹P NMR of complex **5**

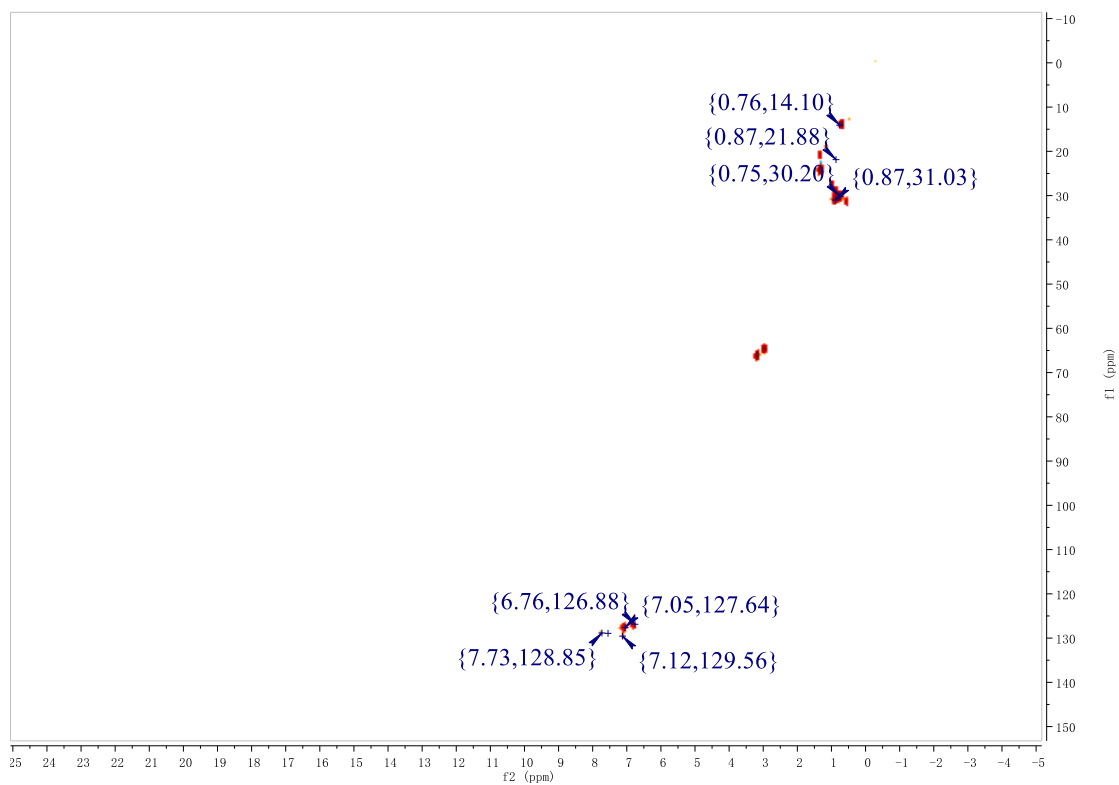


¹³C NMR of complex **5**

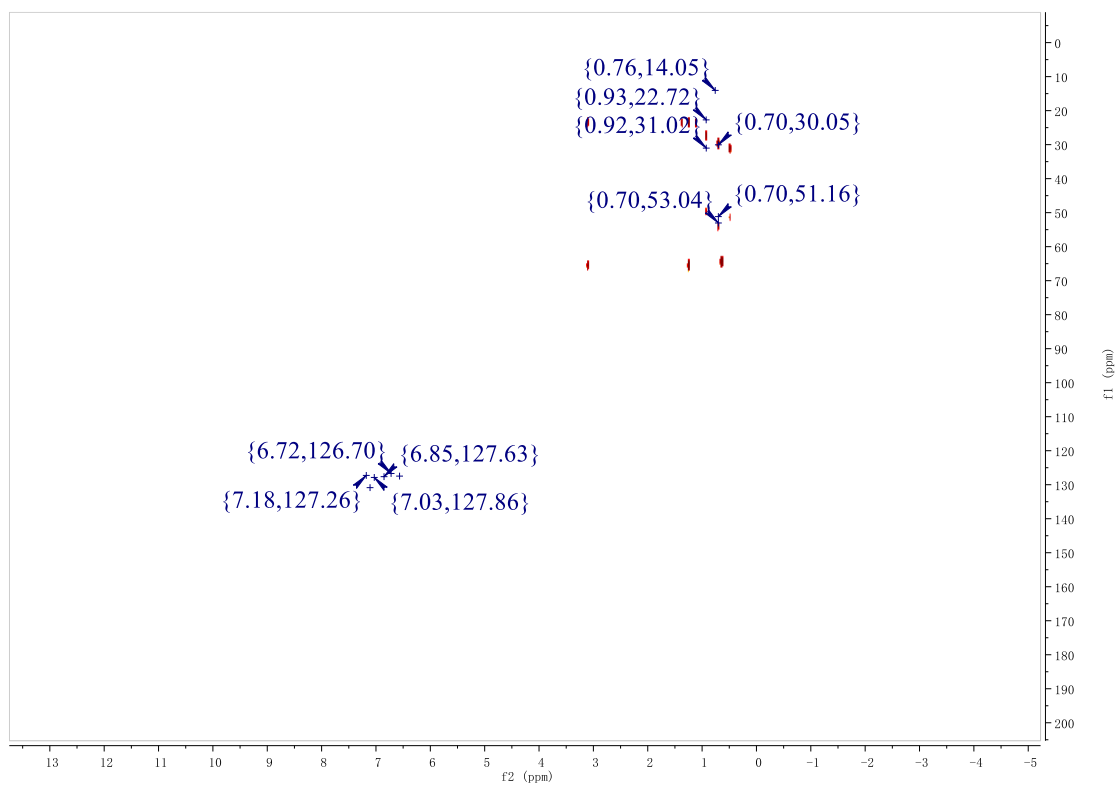
Note: The peaks at 67.65 and 25.65 ppm belong to THF.



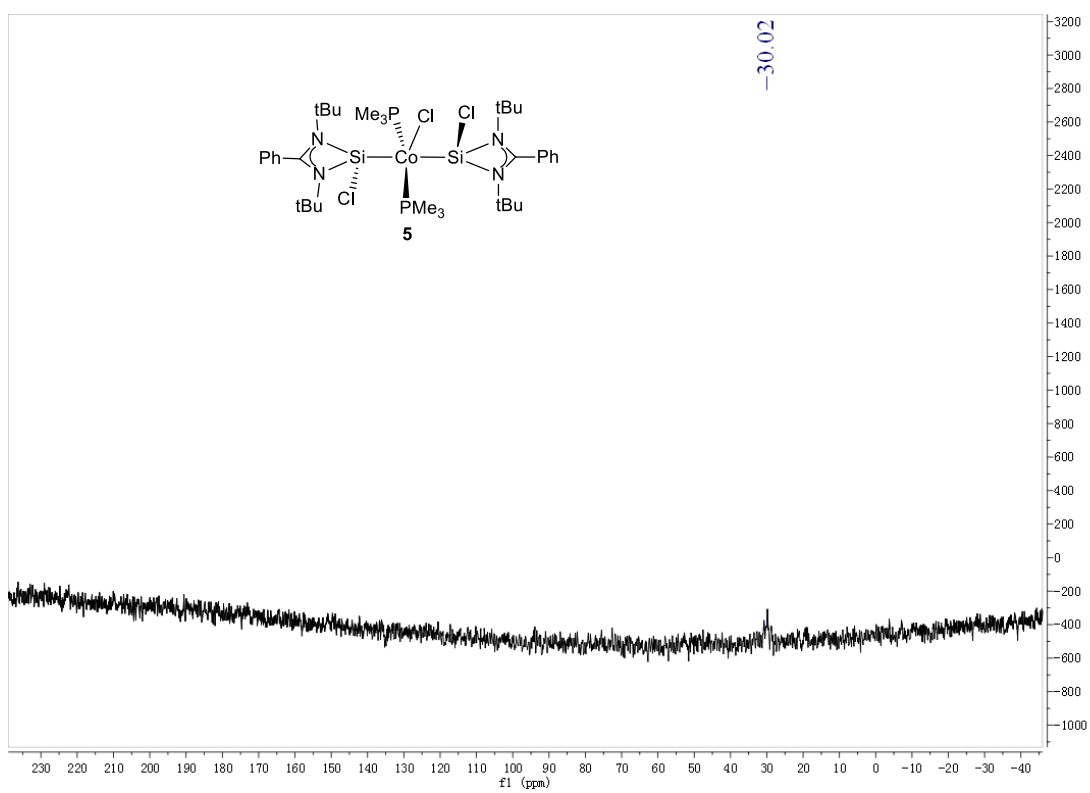
HH COSY of complex 5



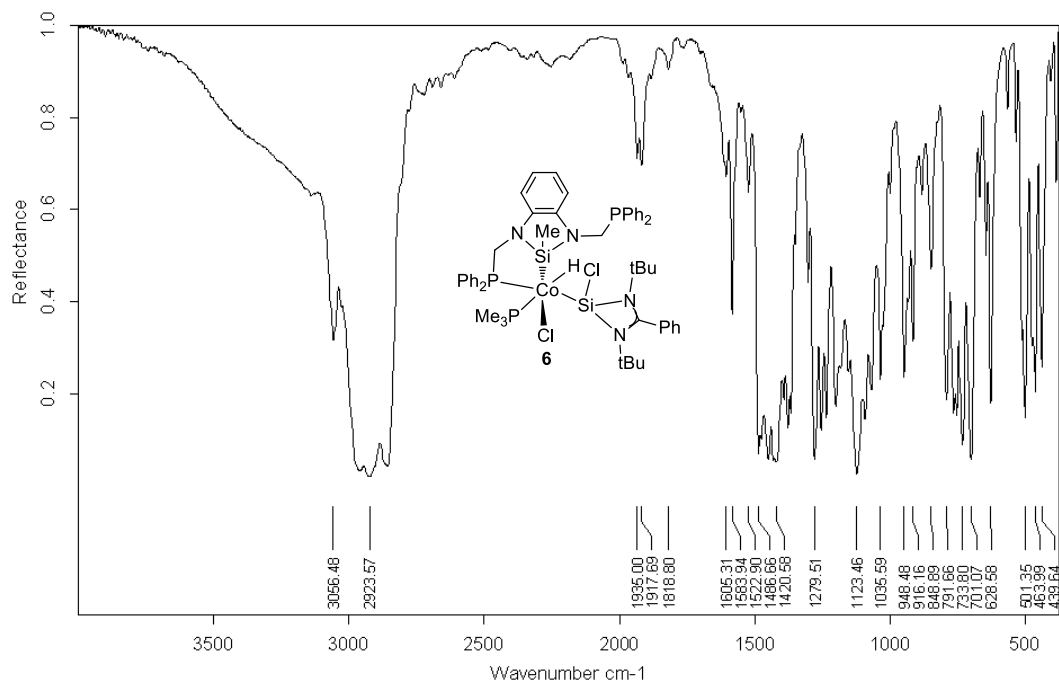
HSQC of complex 5



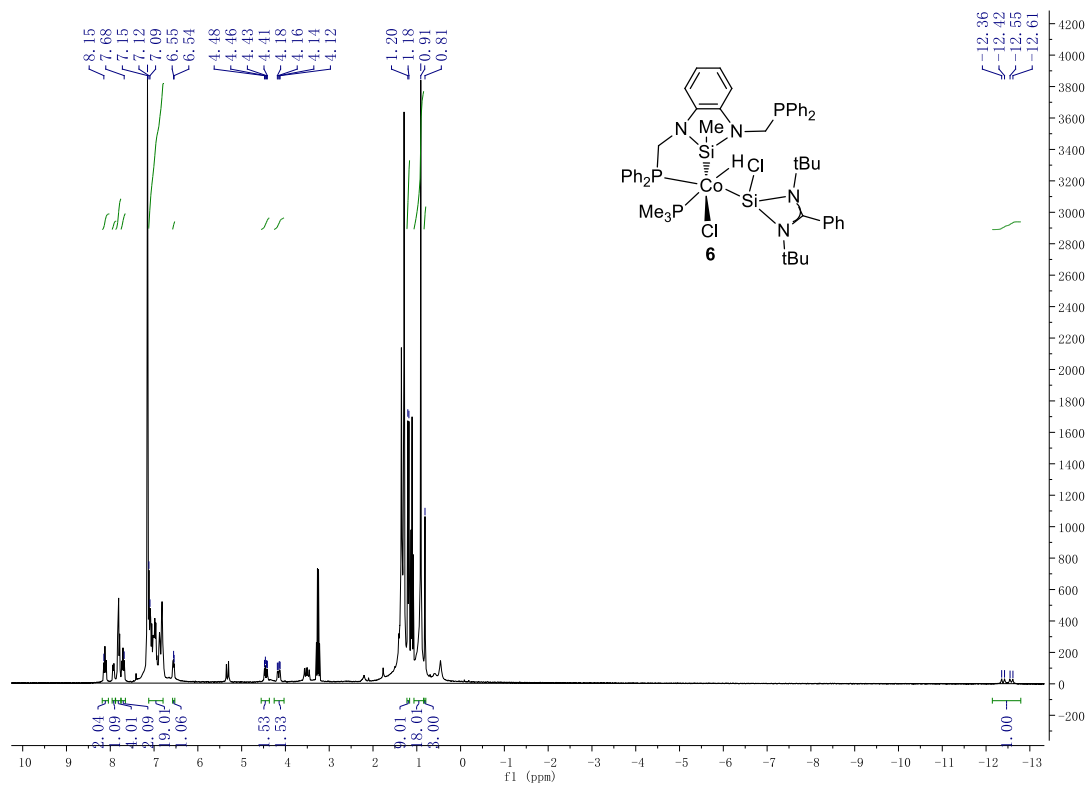
HMQC of complex **5**



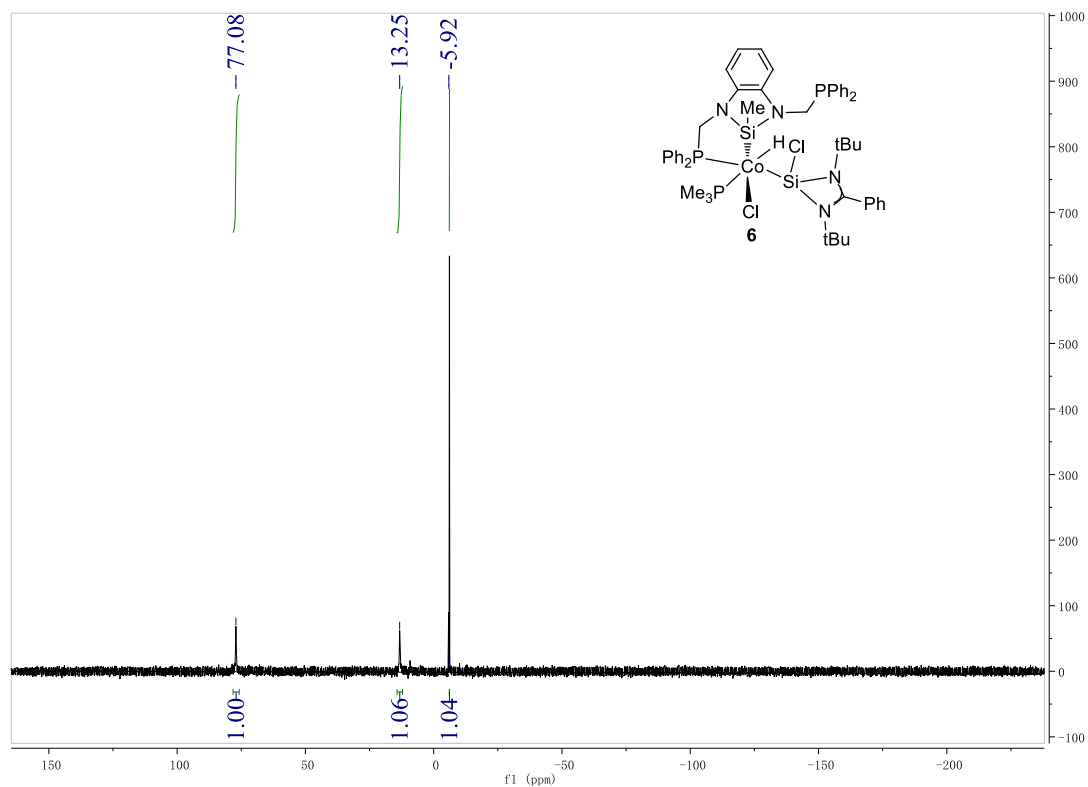
^{29}Si NMR of complex **5**



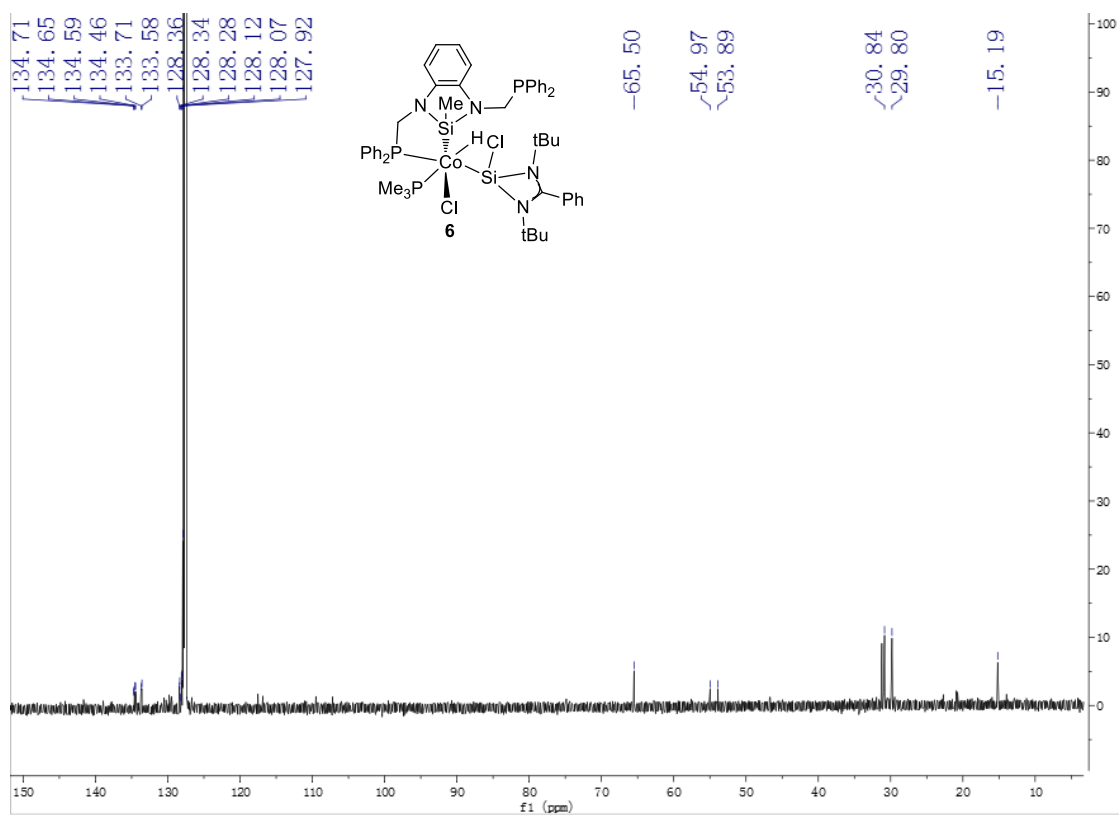
IR spectrum of complex **6**



¹H NMR of complex **6**

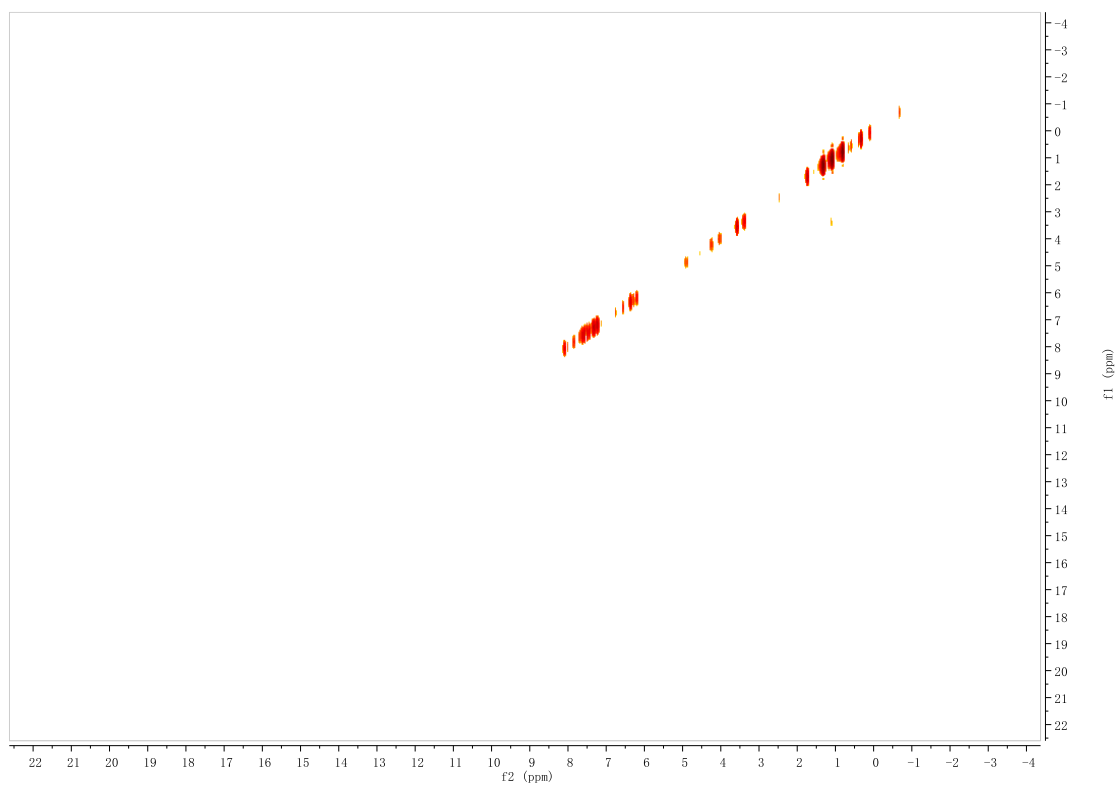


³¹P NMR of complex 6

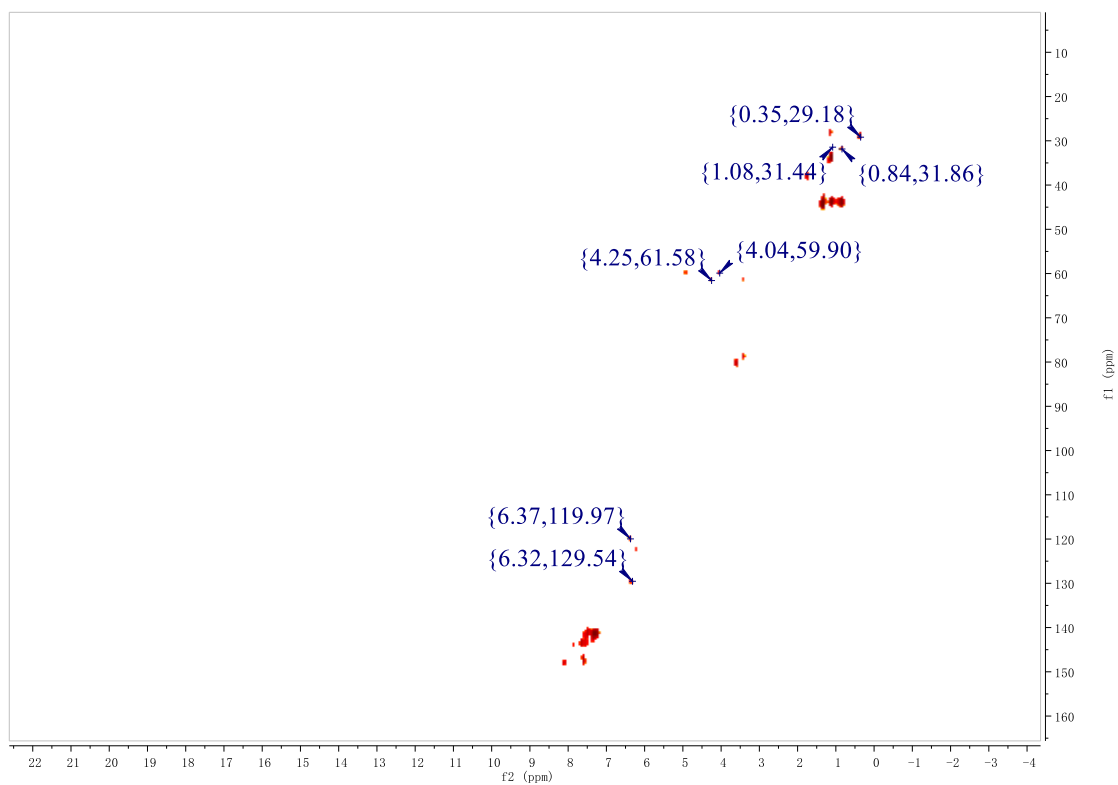


¹³C NMR of complex 6

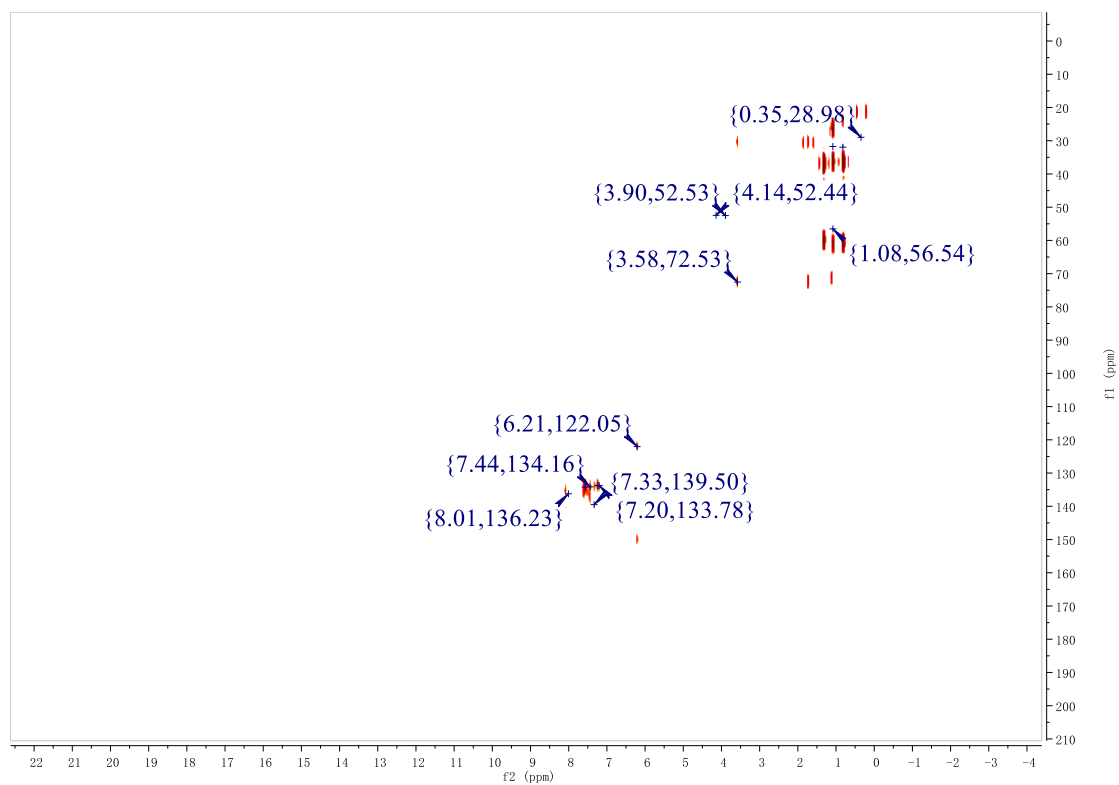
Note: The peaks at 65.50 and 15.19 ppm belong to Et₂O.



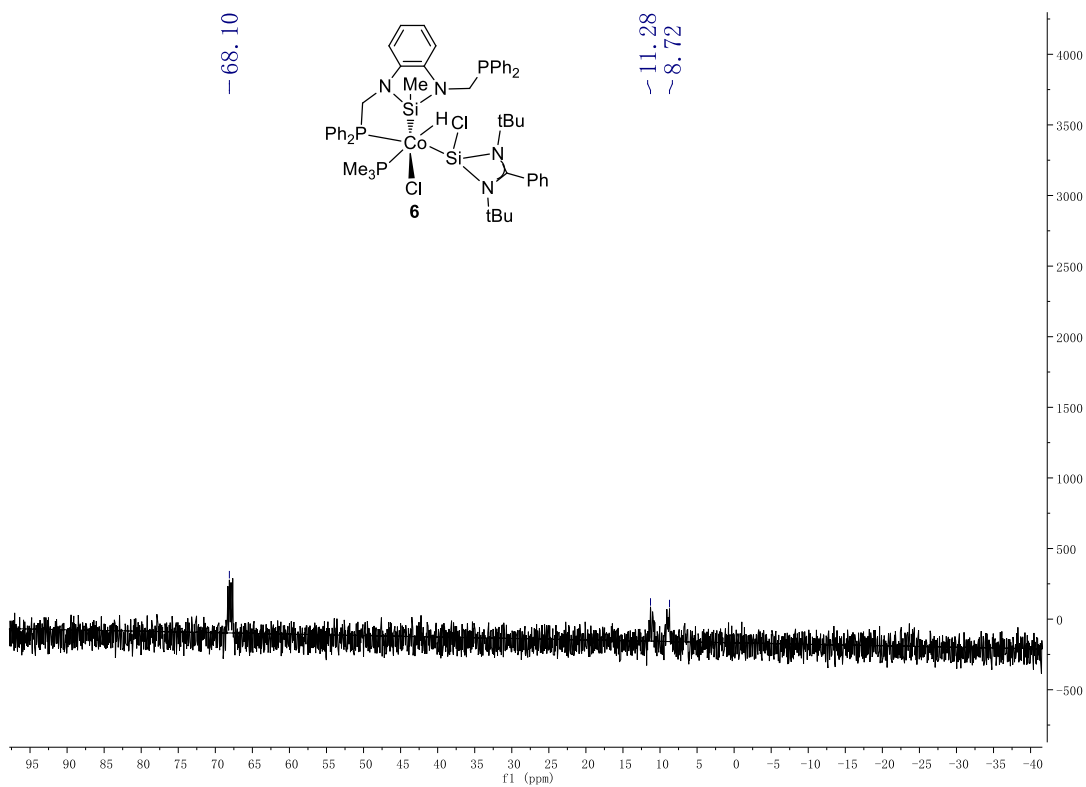
HH COSY of complex 6



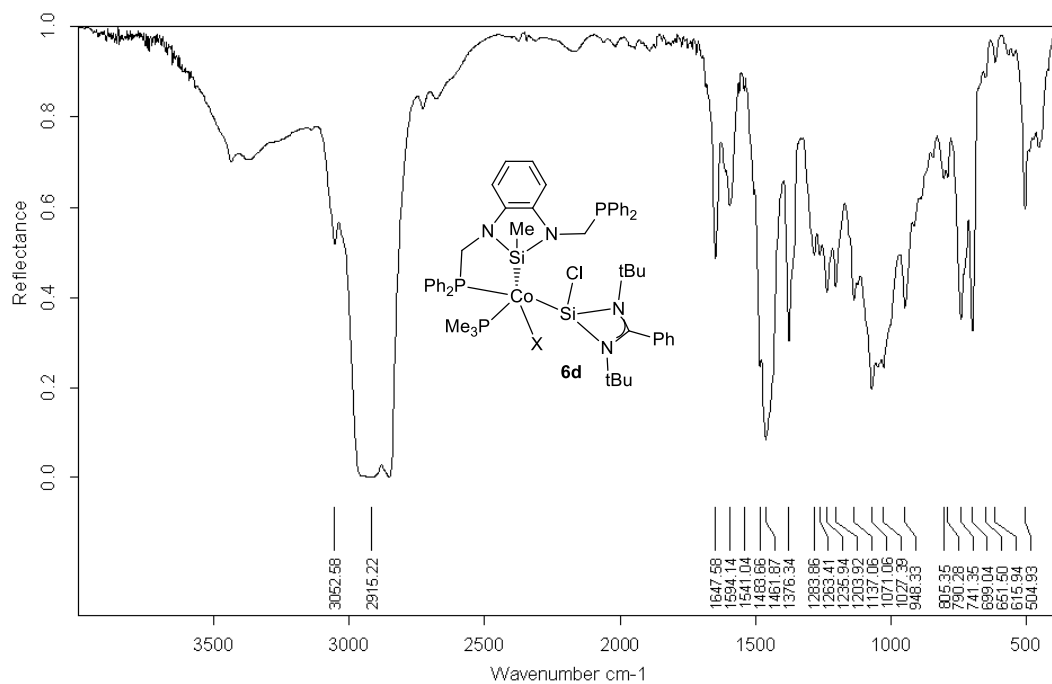
HSQC of complex 6



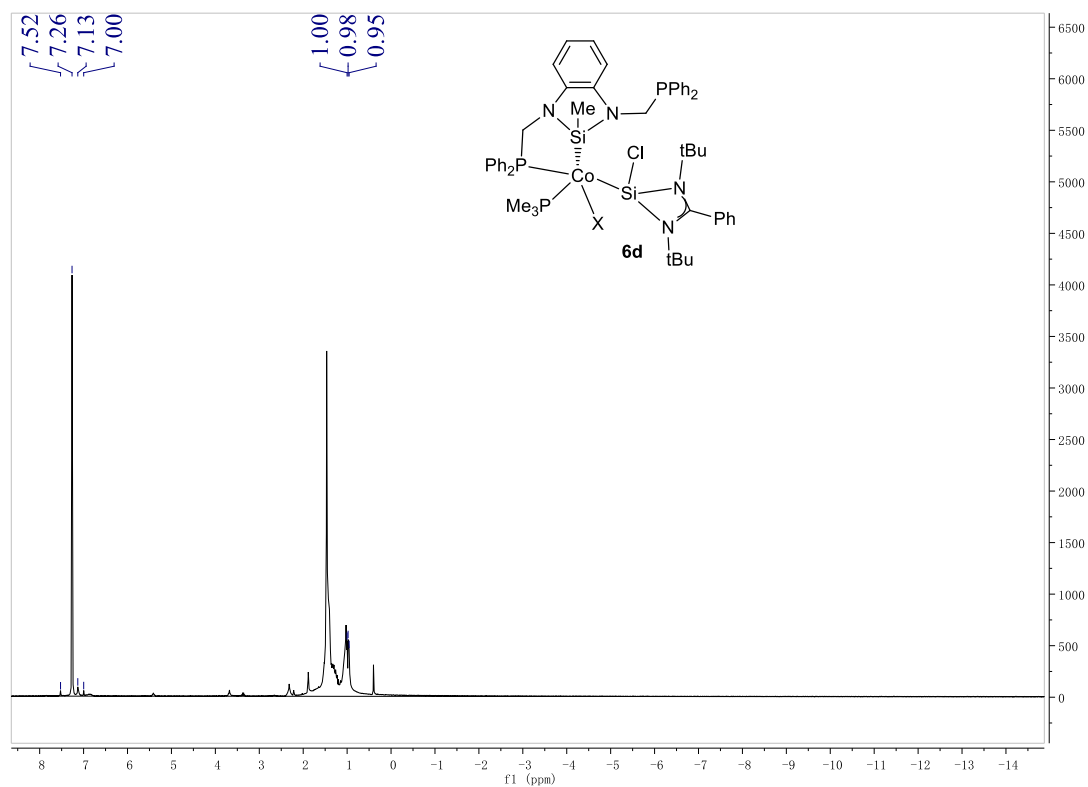
HMQC of complex **6**



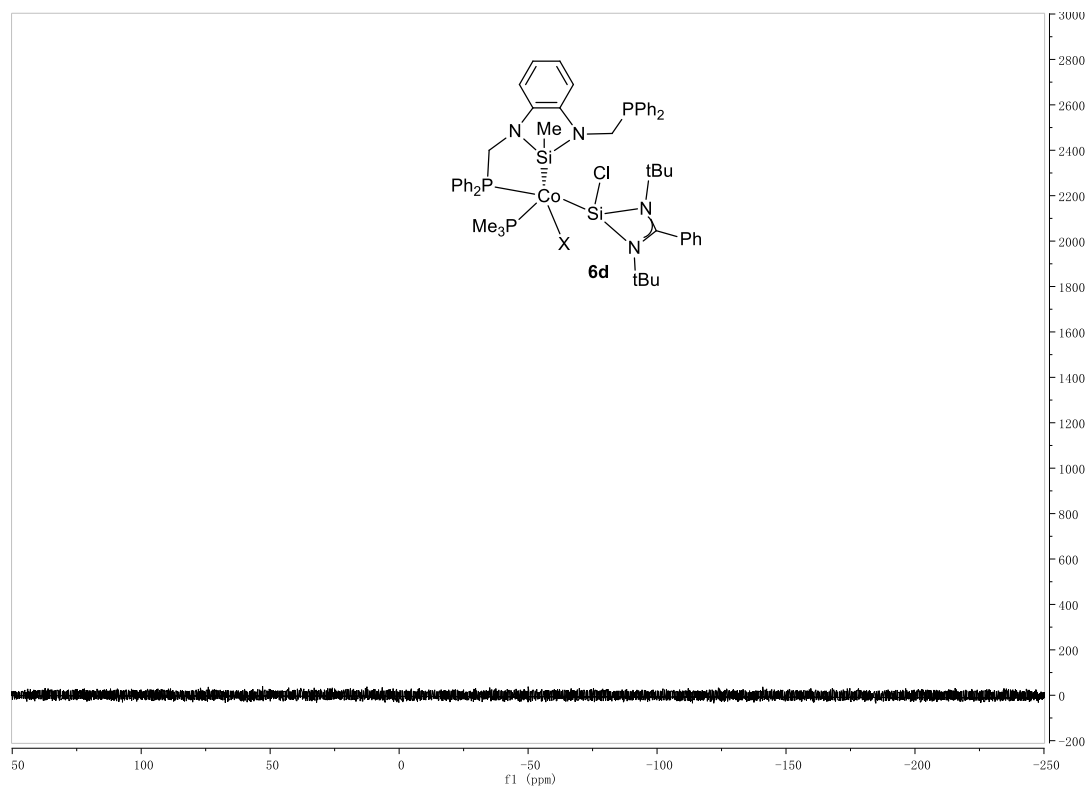
^{29}Si NMR of complex **6**



IR spectrum of complex **6d**

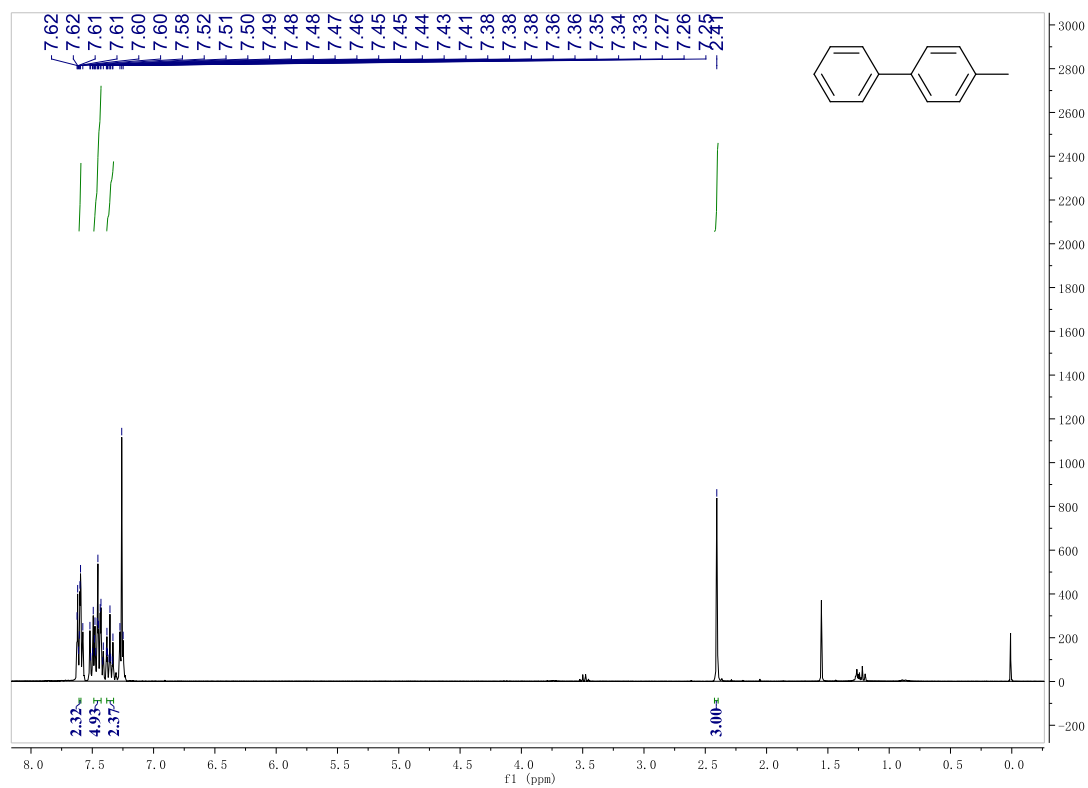


¹H NMR of complex **6d**

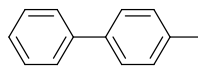


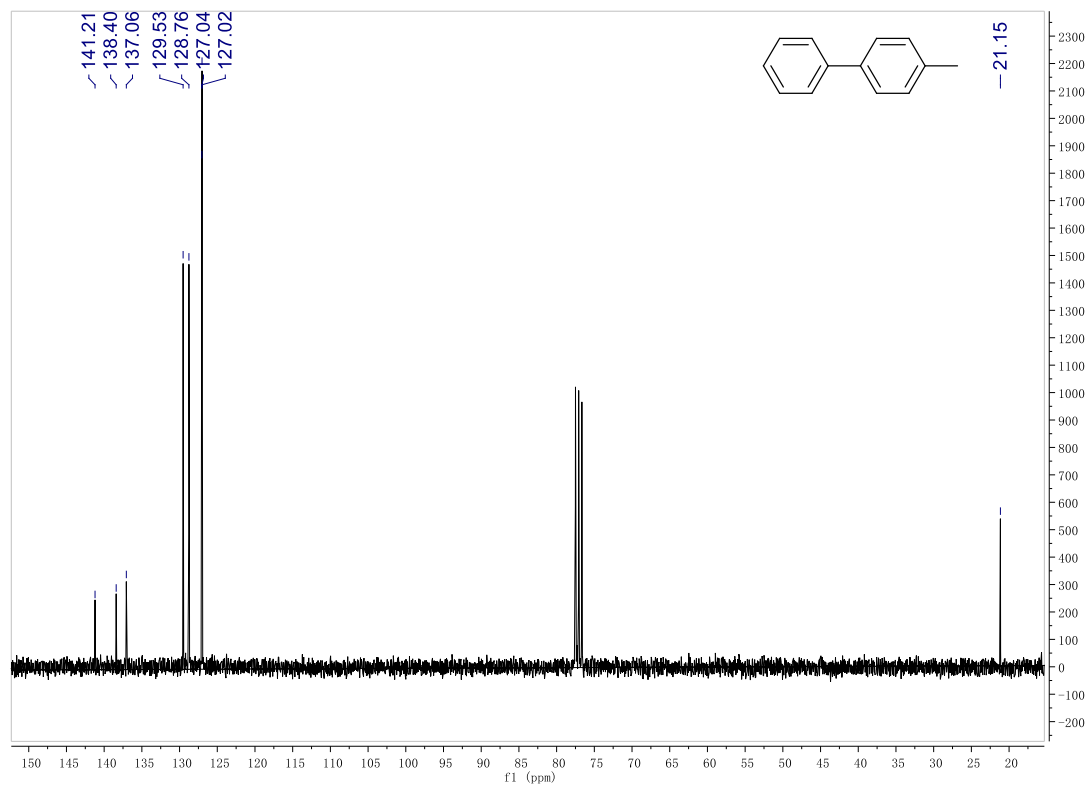
^{31}P NMR of complex **6d**

SIII ^1H and ^{13}C NMR spectra of coupling products

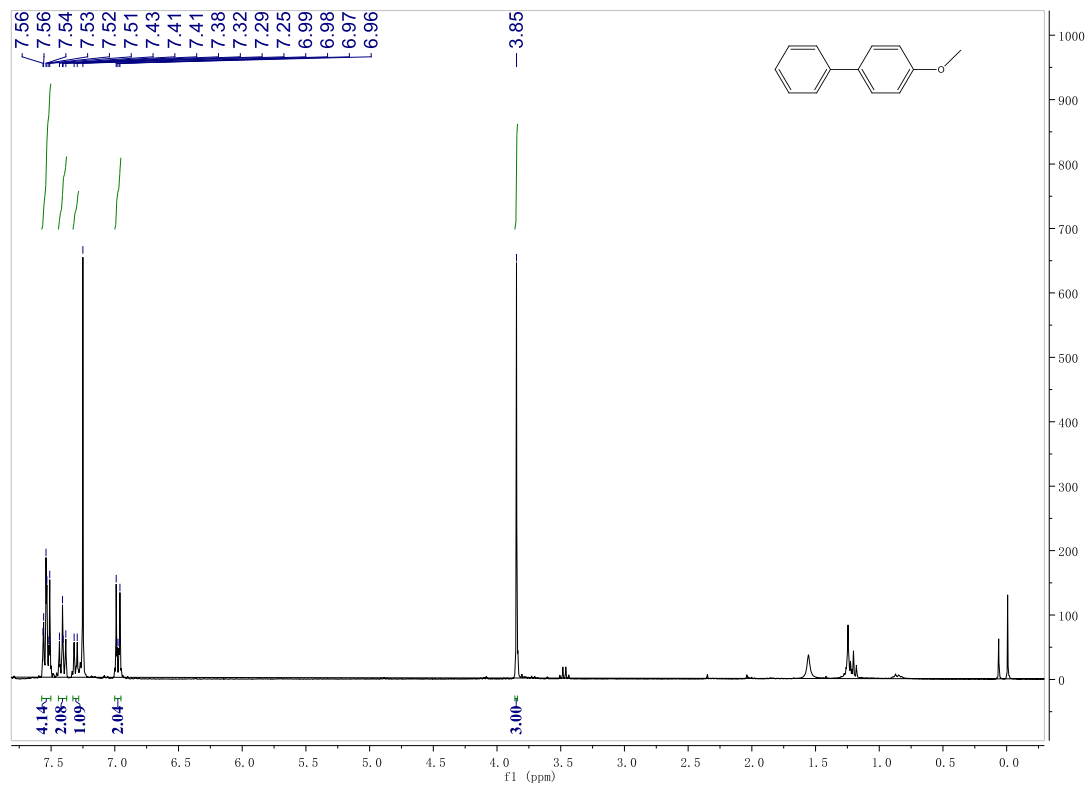
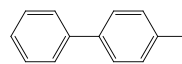


^1H NMR of compound

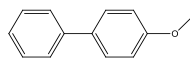


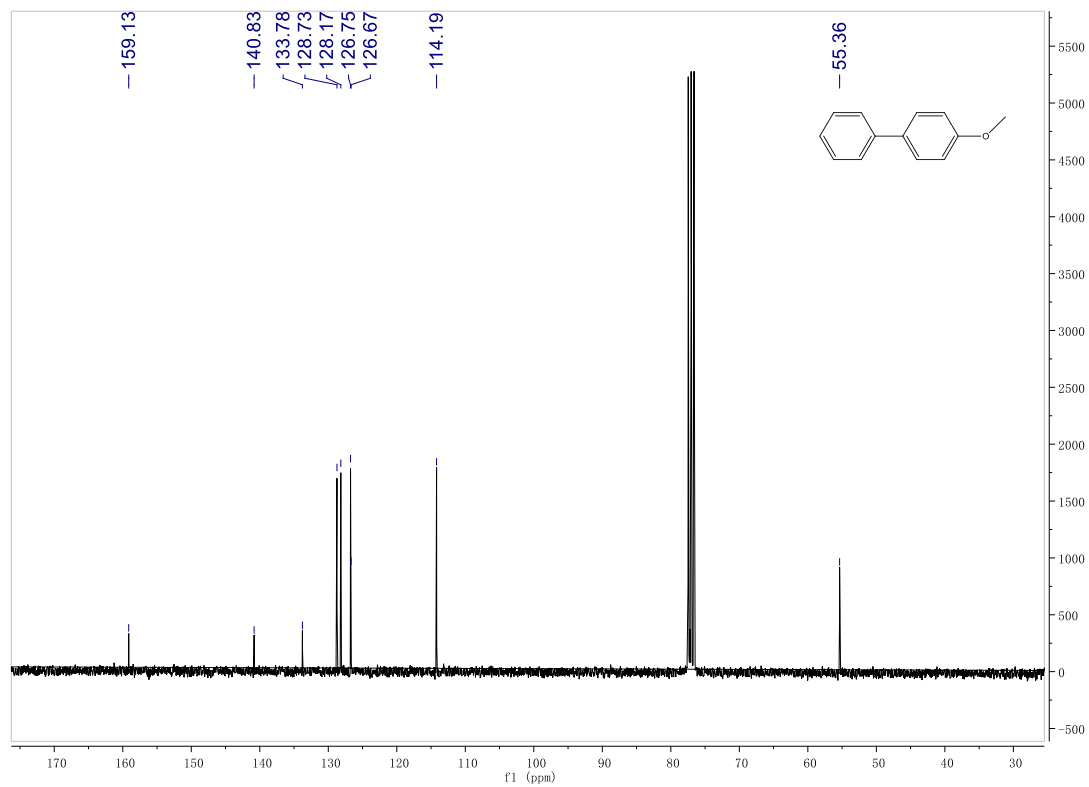


¹³C NMR of compound

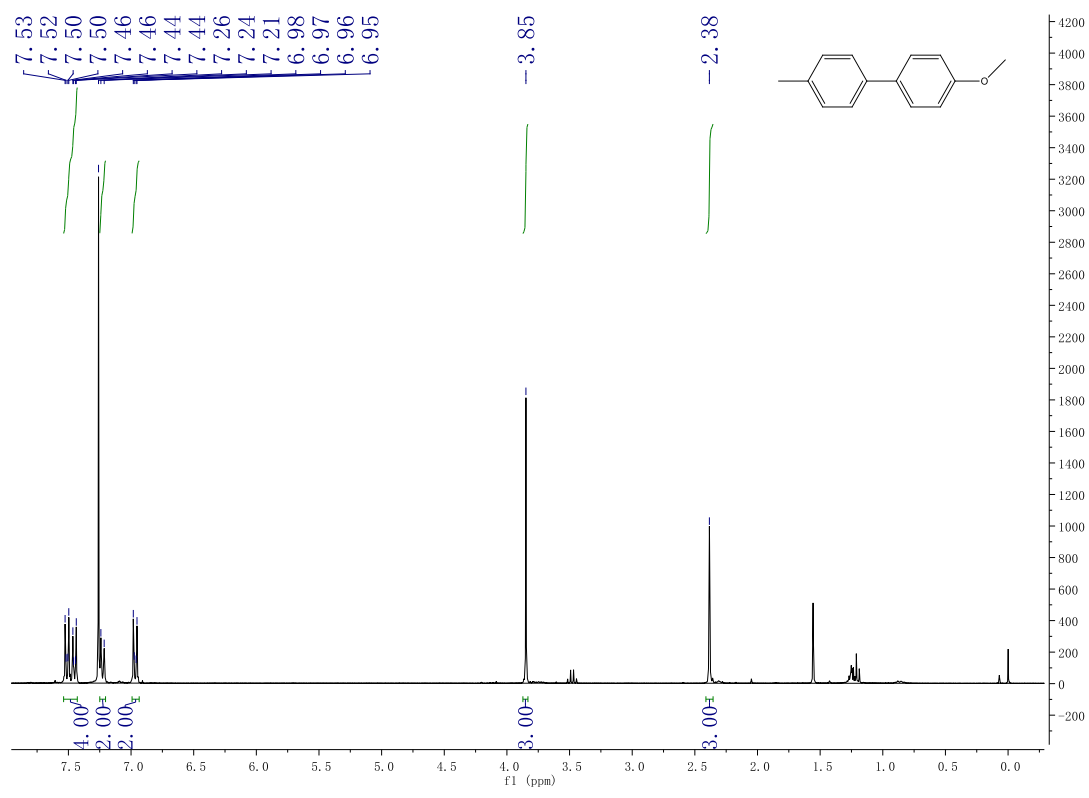


¹H NMR of compound

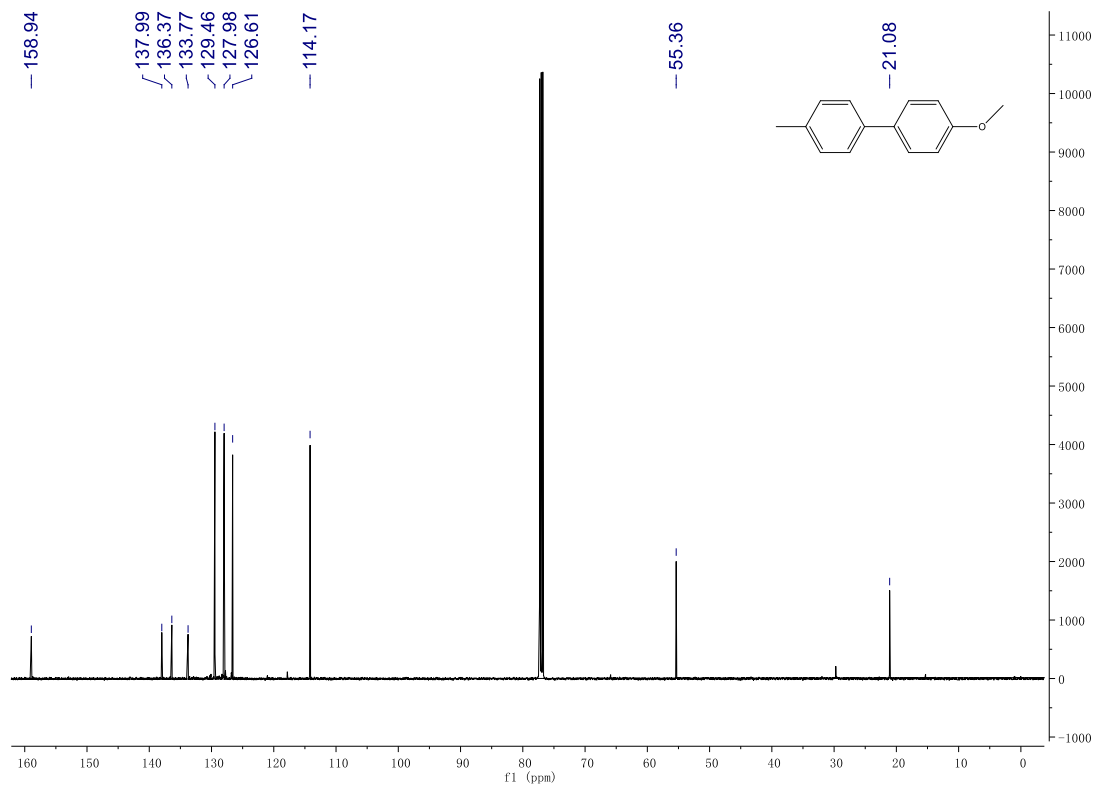




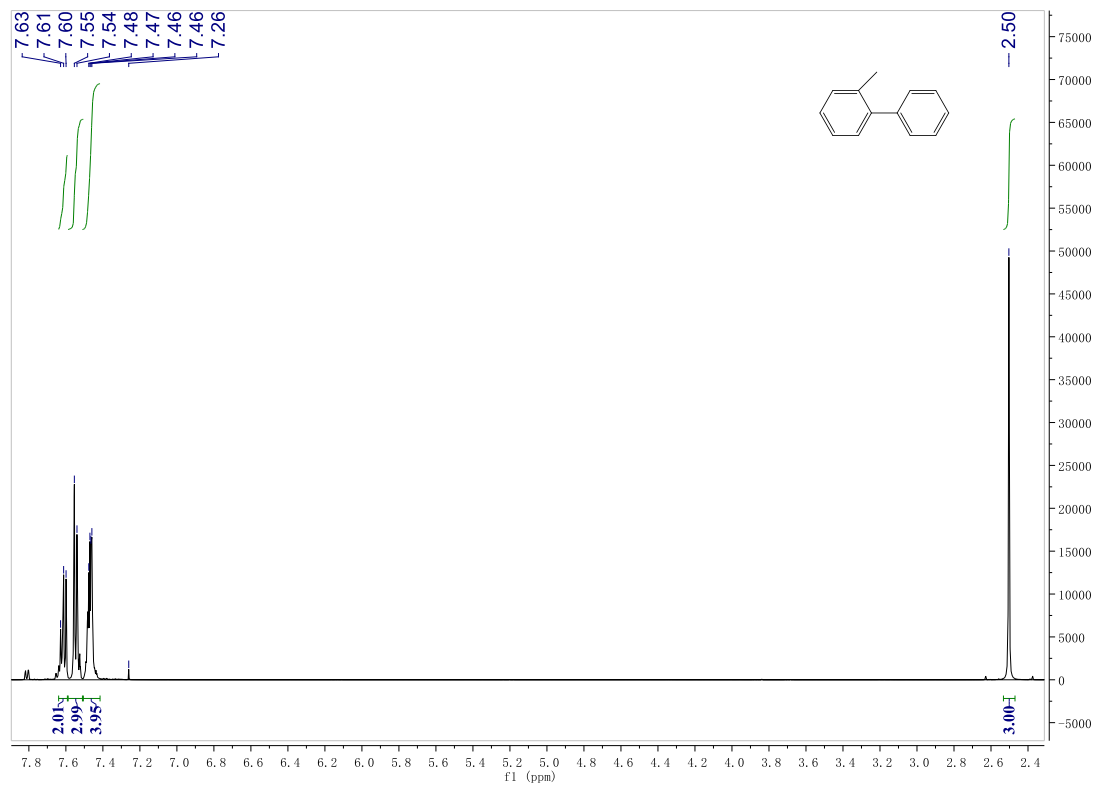
¹³C NMR of compound COc1ccc(cc1)-c2ccccc2



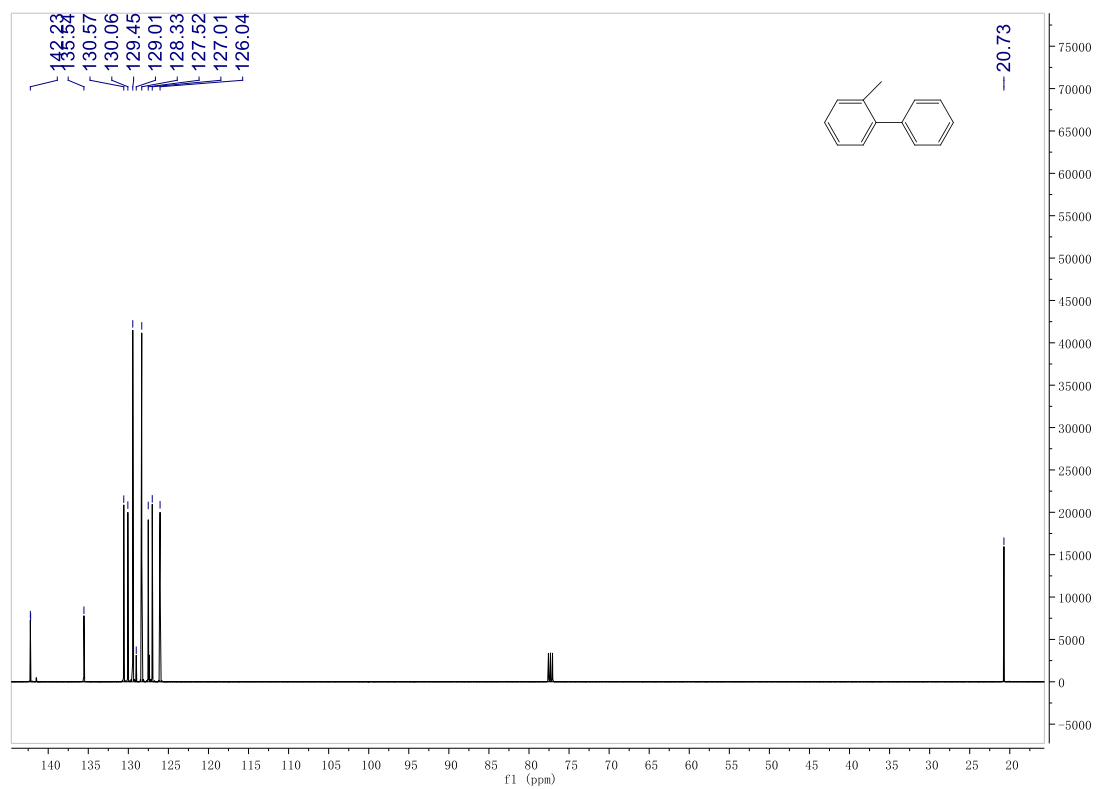
¹H NMR of compound COc1ccc(cc1)-c2ccccc2



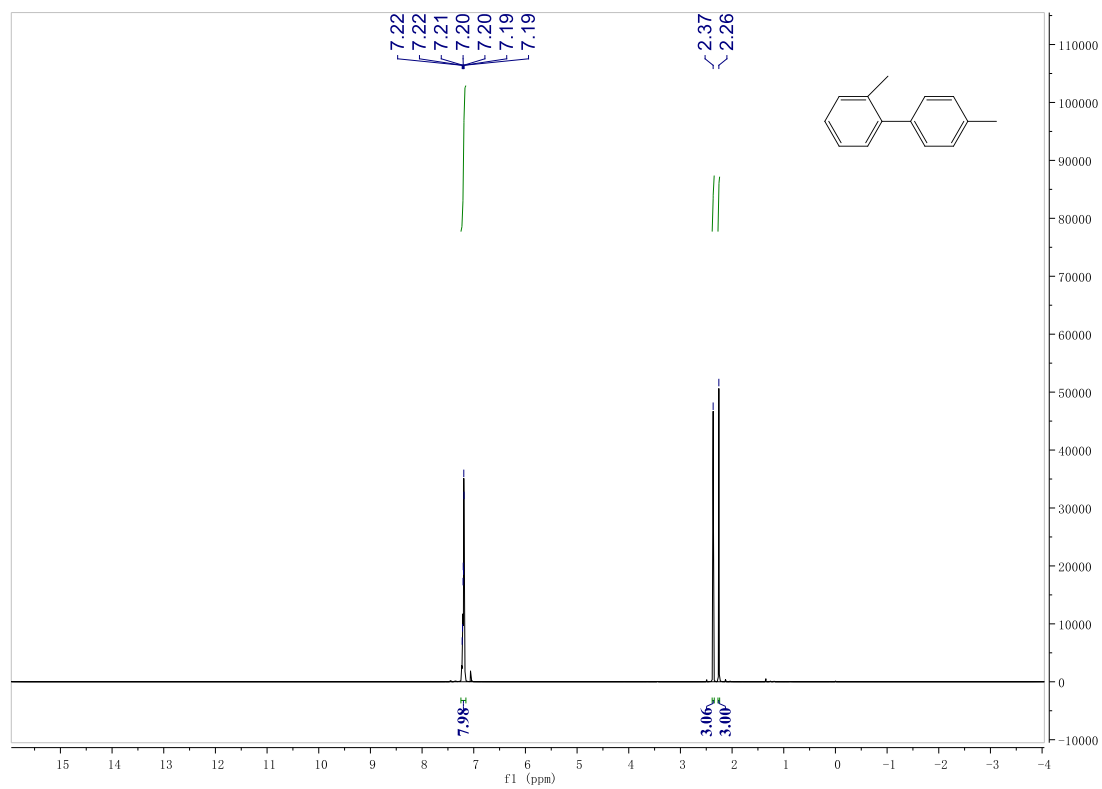
¹³C NMR of compound



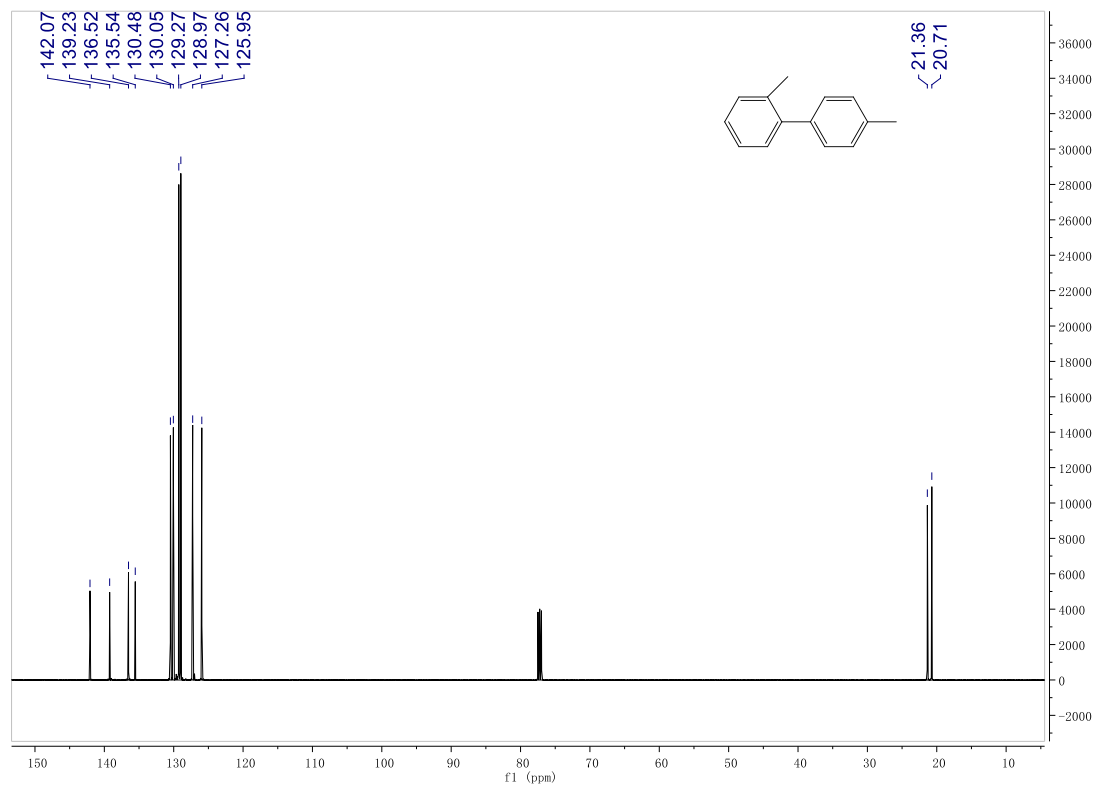
¹H NMR of compound



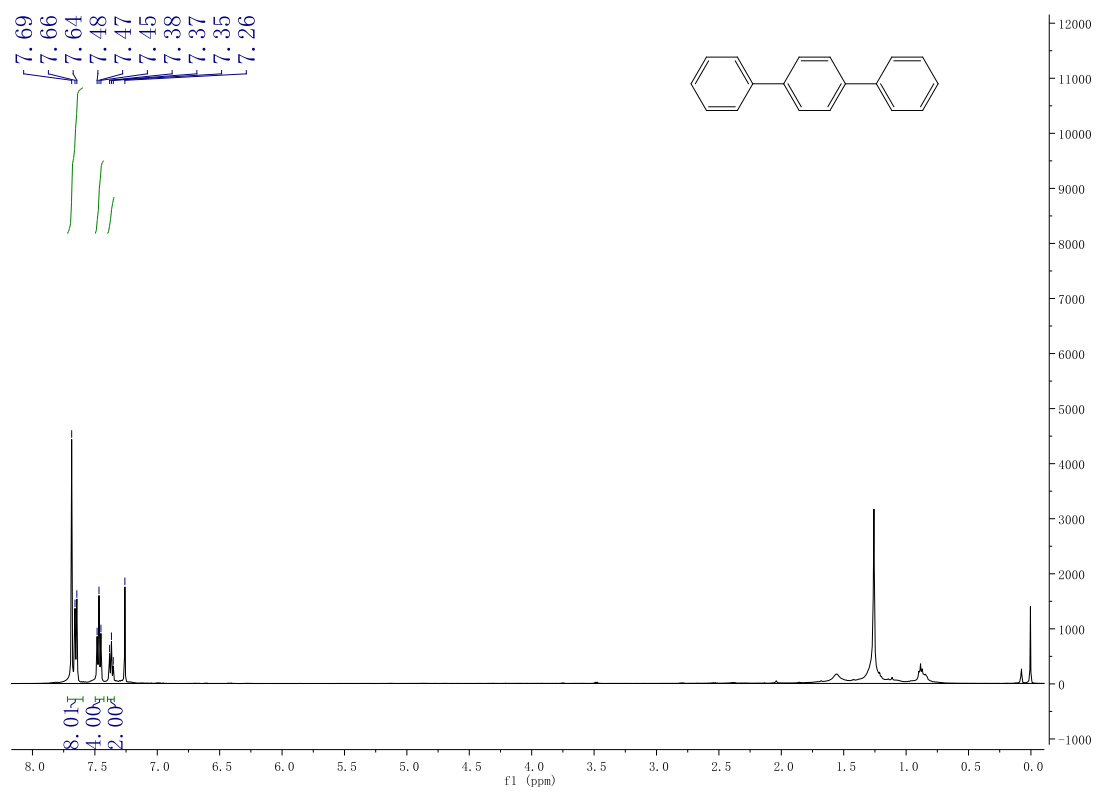
¹³C NMR of compound Cc1ccccc1-c2ccccc2



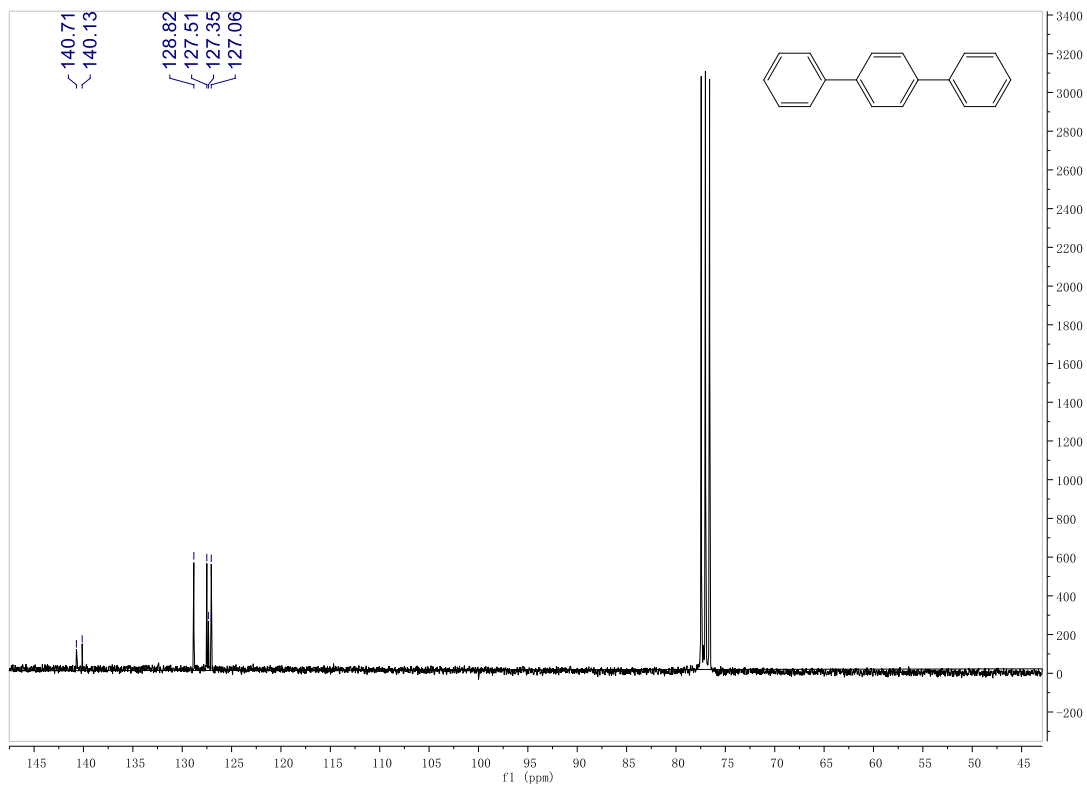
¹H NMR of compound Cc1ccccc1-c2ccc(C)cc2



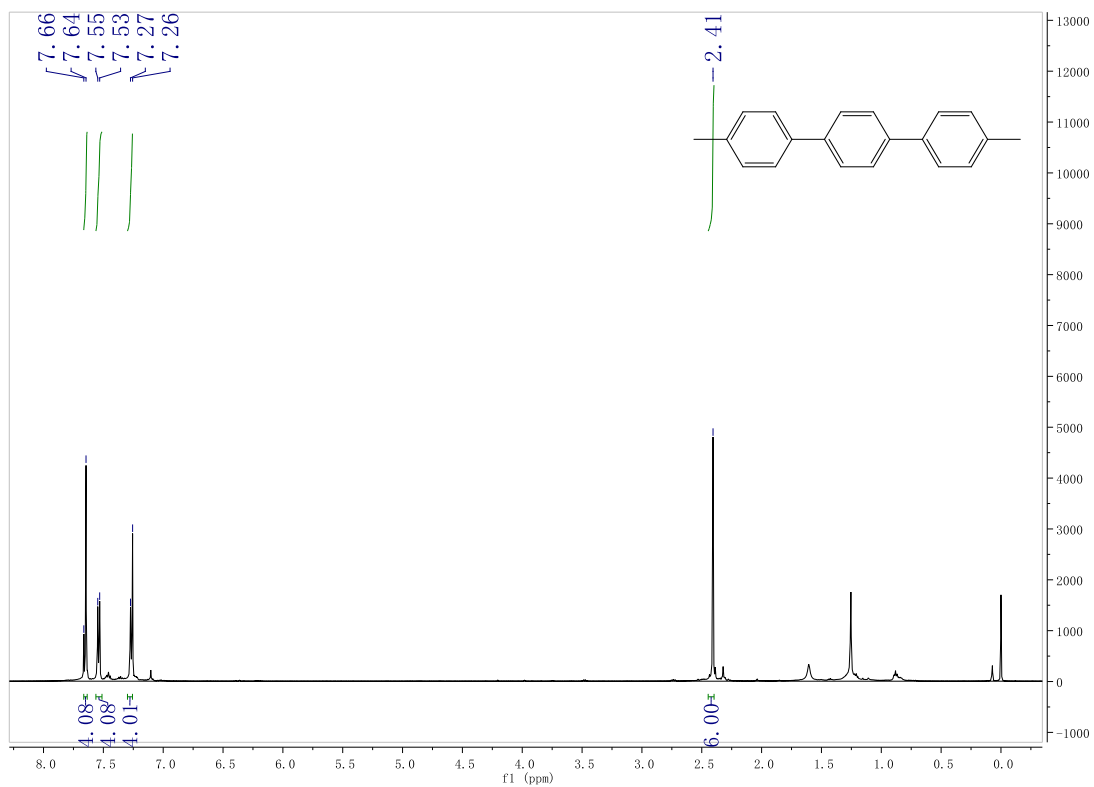
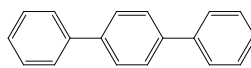
¹³C NMR of compound Cc1ccccc1-c2ccc(C)cc2



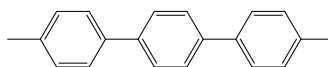
¹H NMR of compound c1ccc(cc1)-c2ccc(cc2)-c3ccccc3

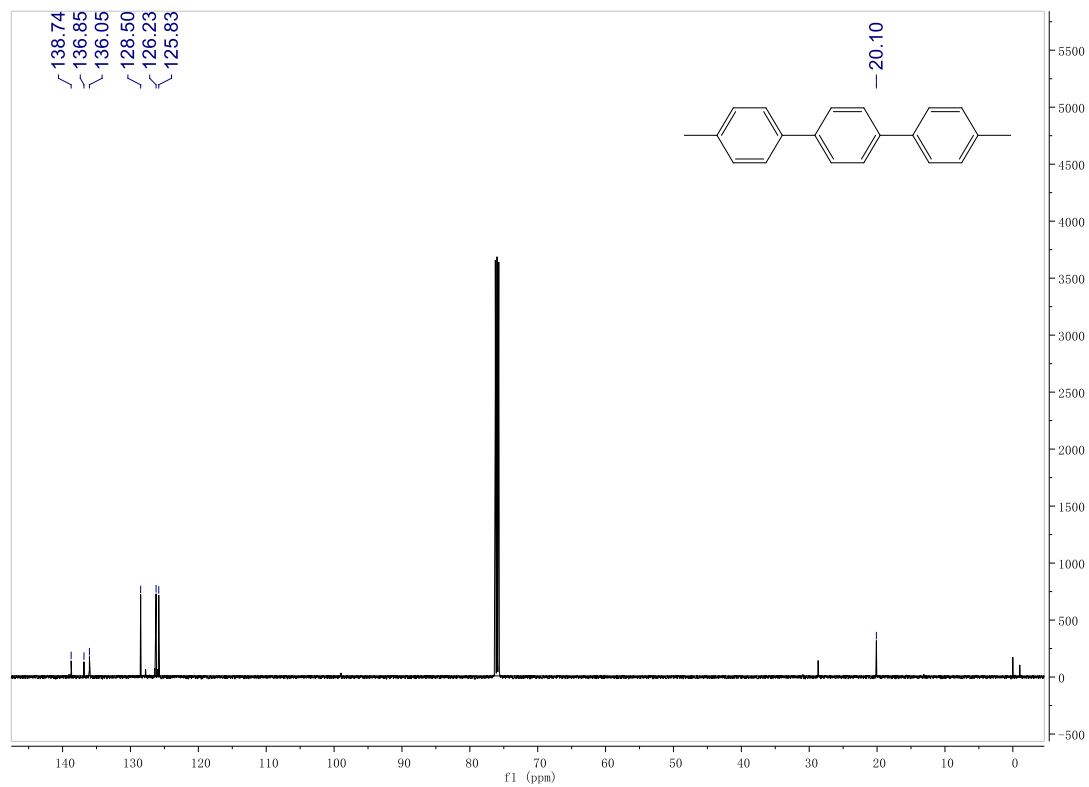


¹³C NMR of compound

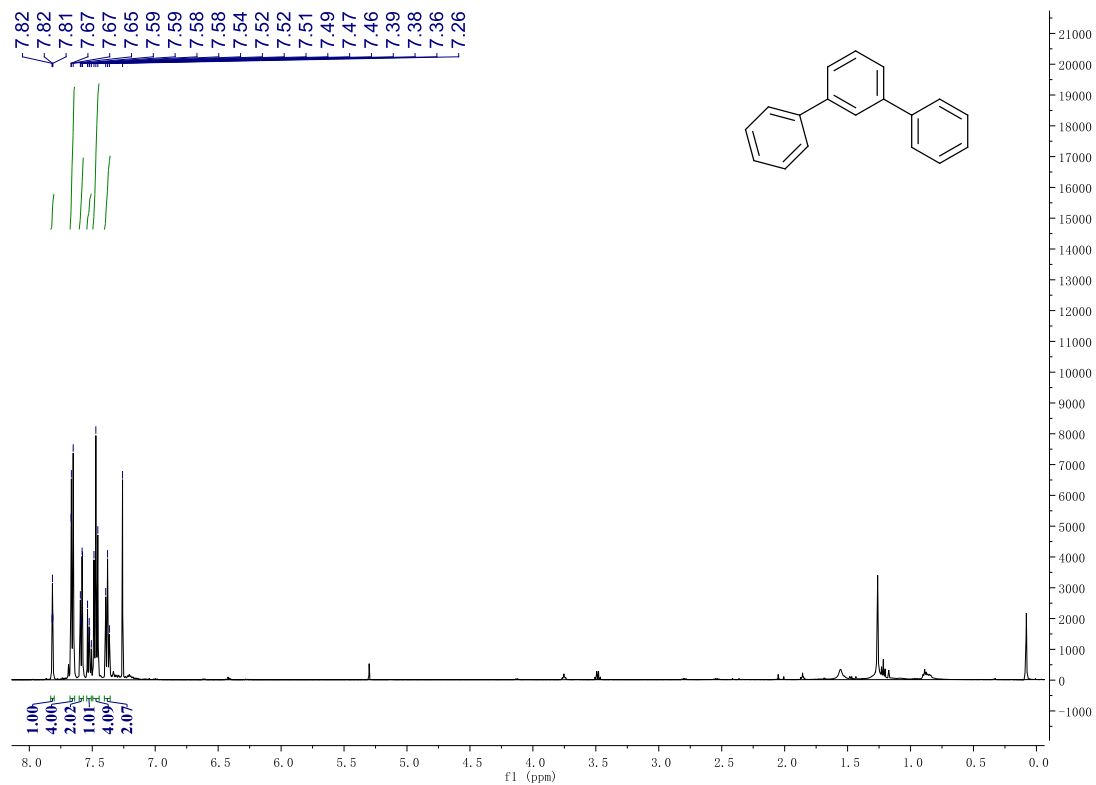
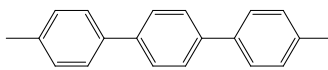


¹H NMR of compound

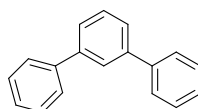


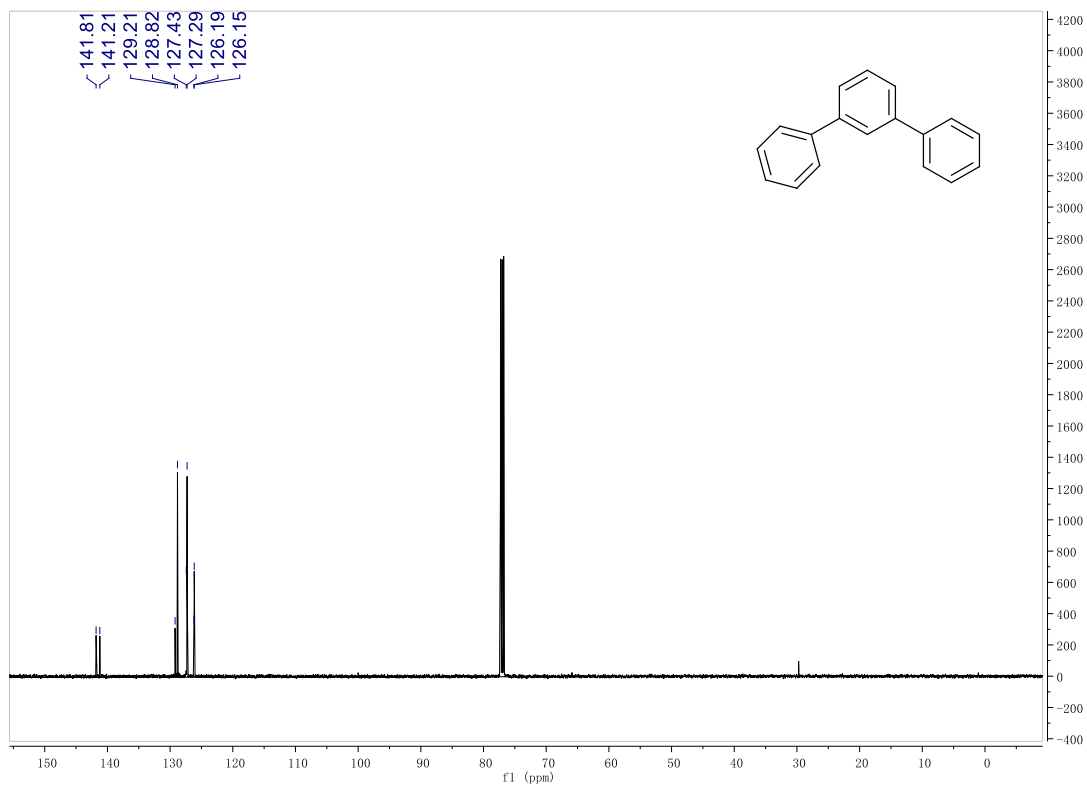


¹³C NMR of compound

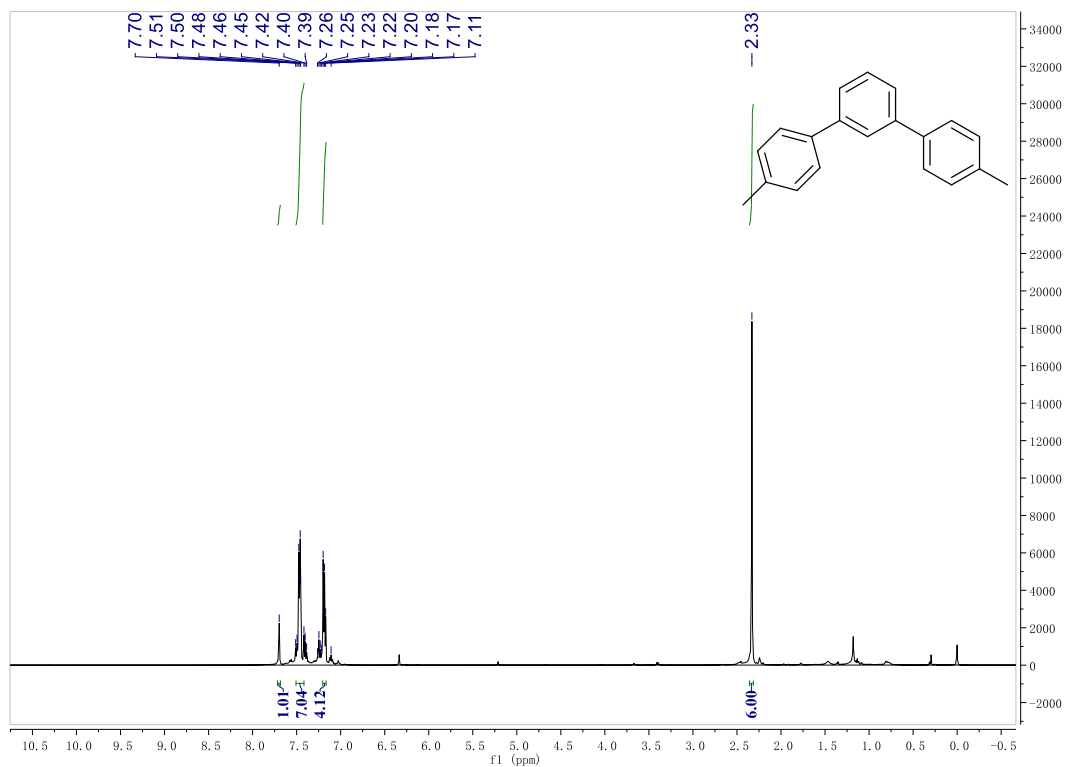
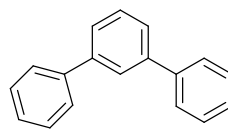


¹H NMR of compound

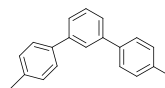


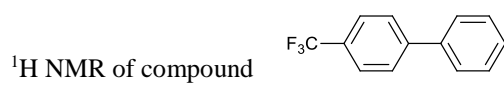
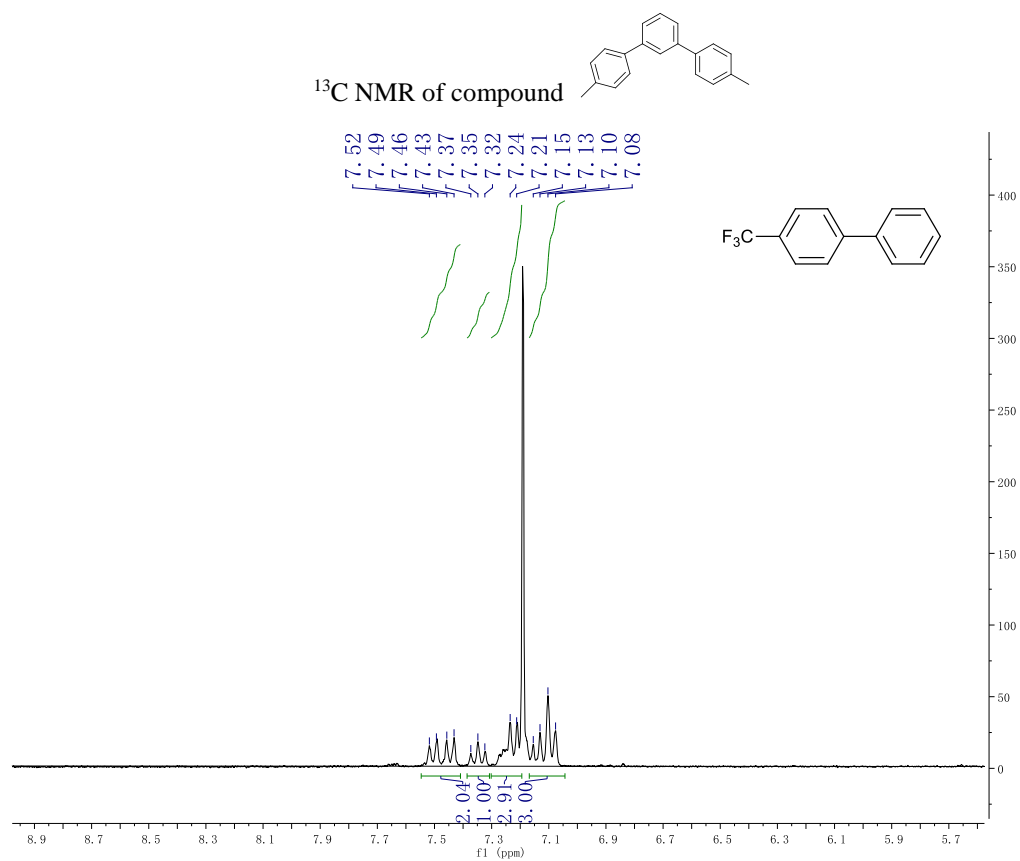
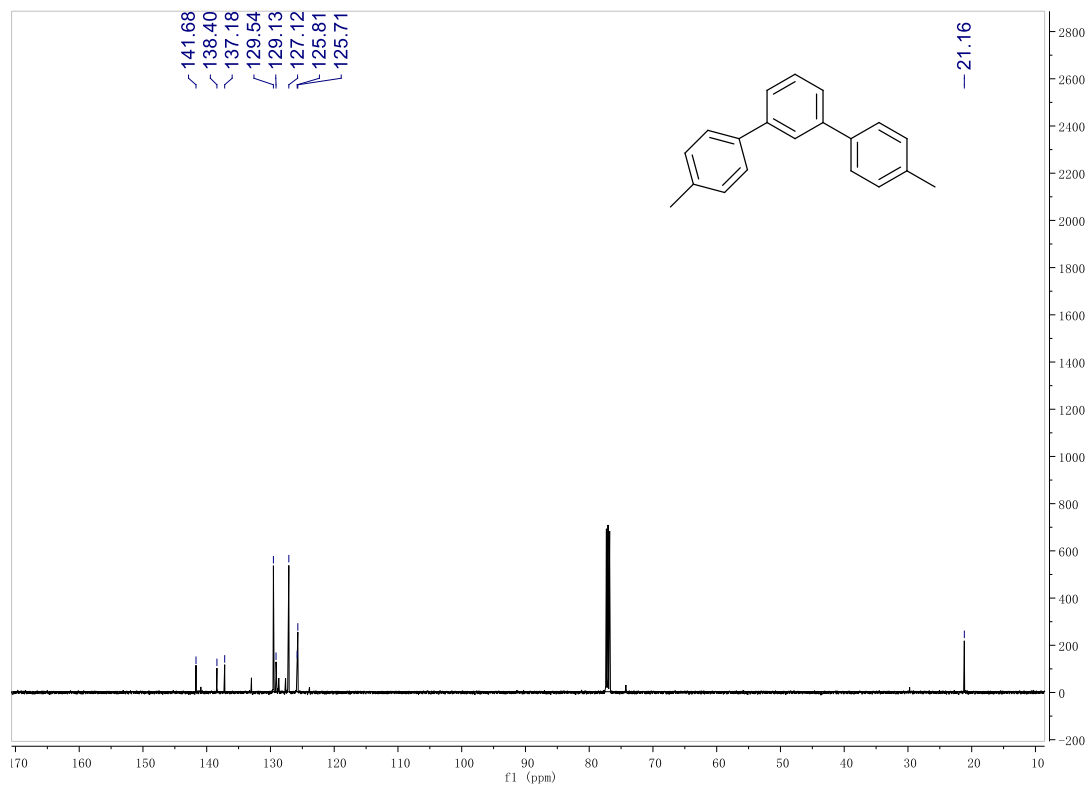


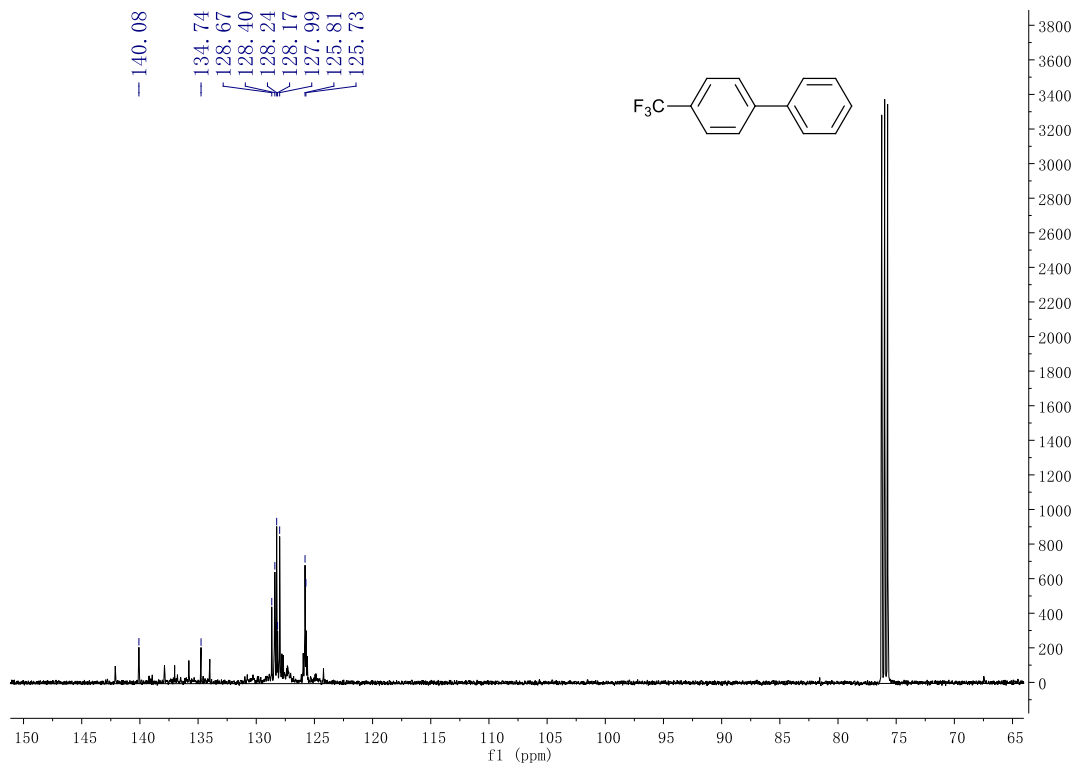
¹³C NMR of compound



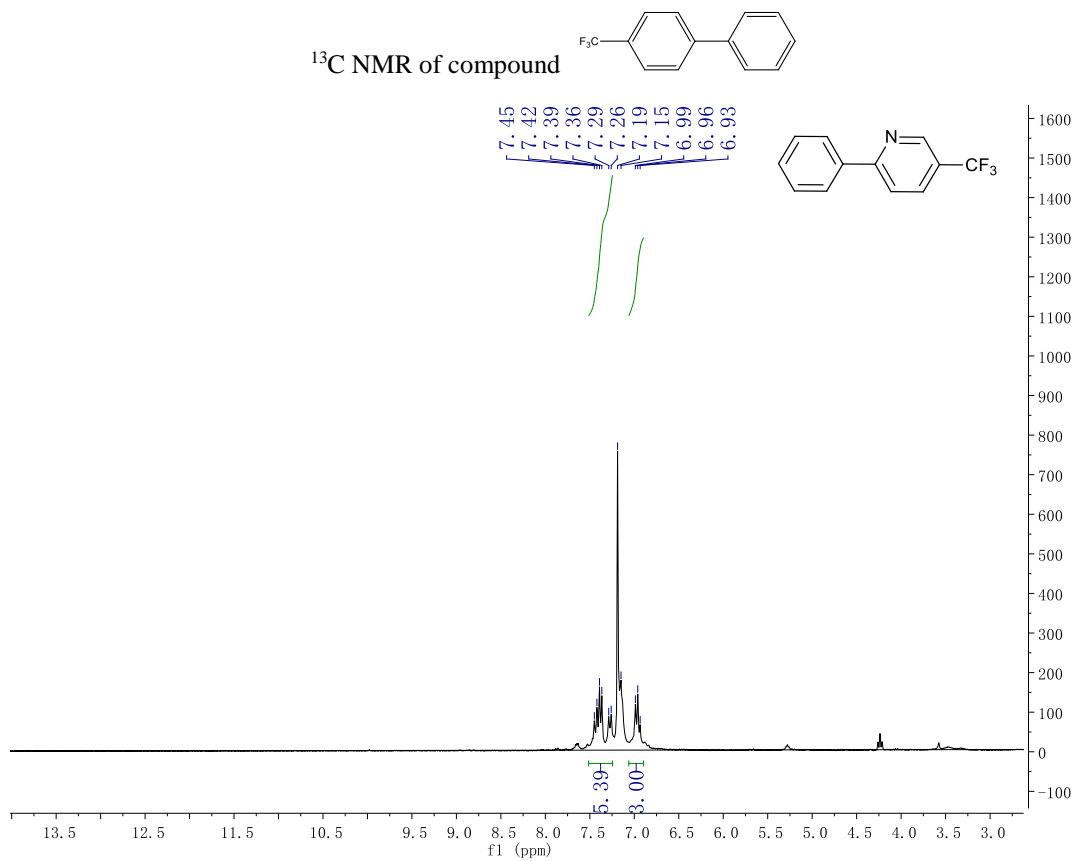
¹H NMR of compound



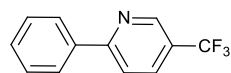


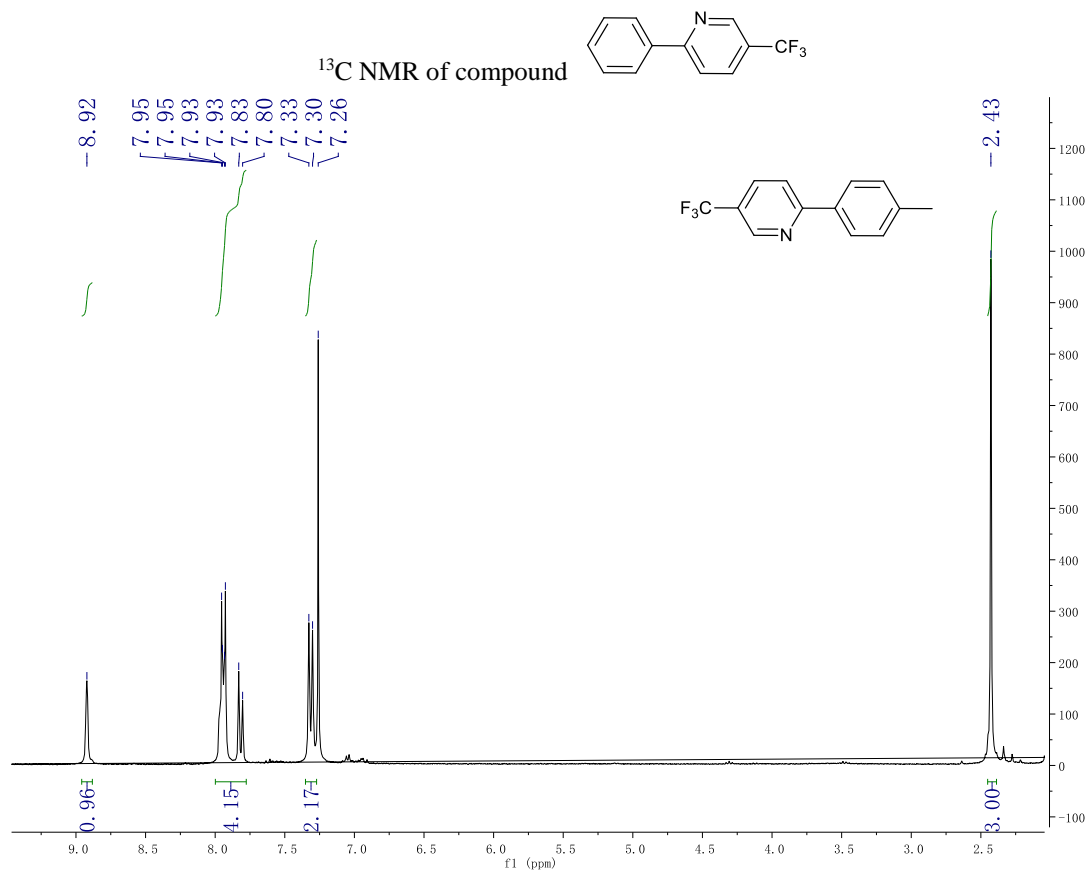
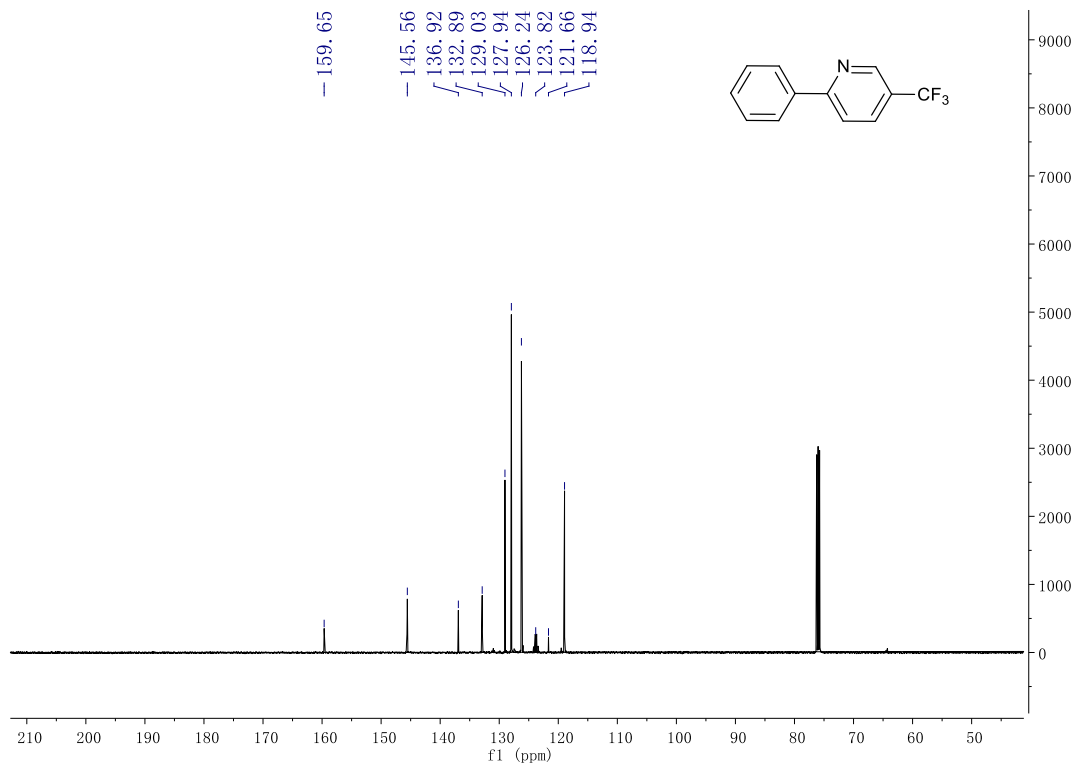


¹³C NMR of compound

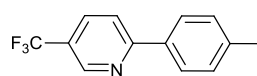


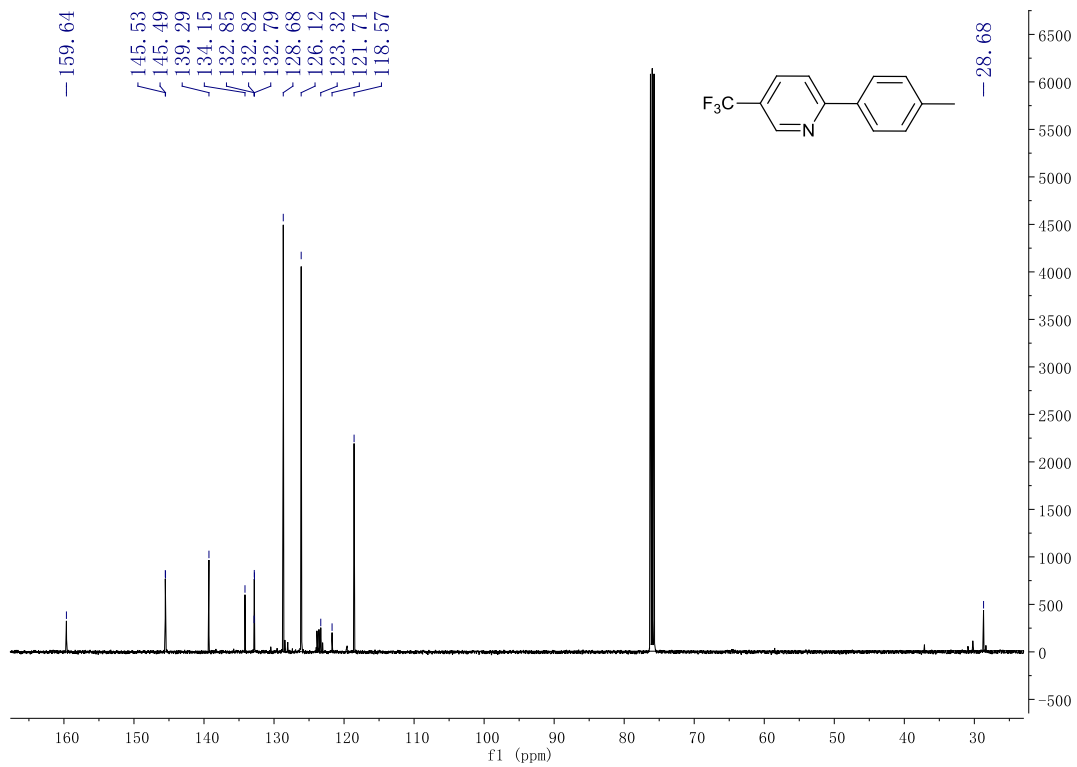
¹H NMR of compound



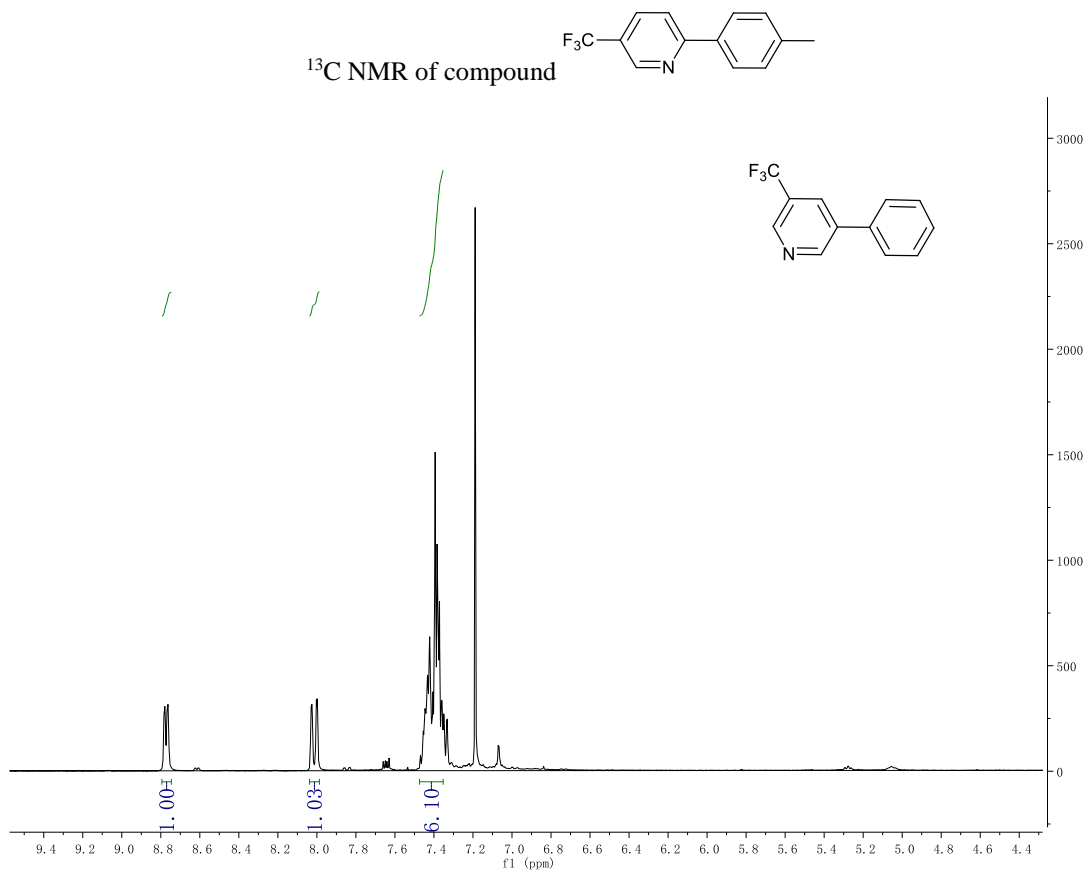


¹H NMR of compound

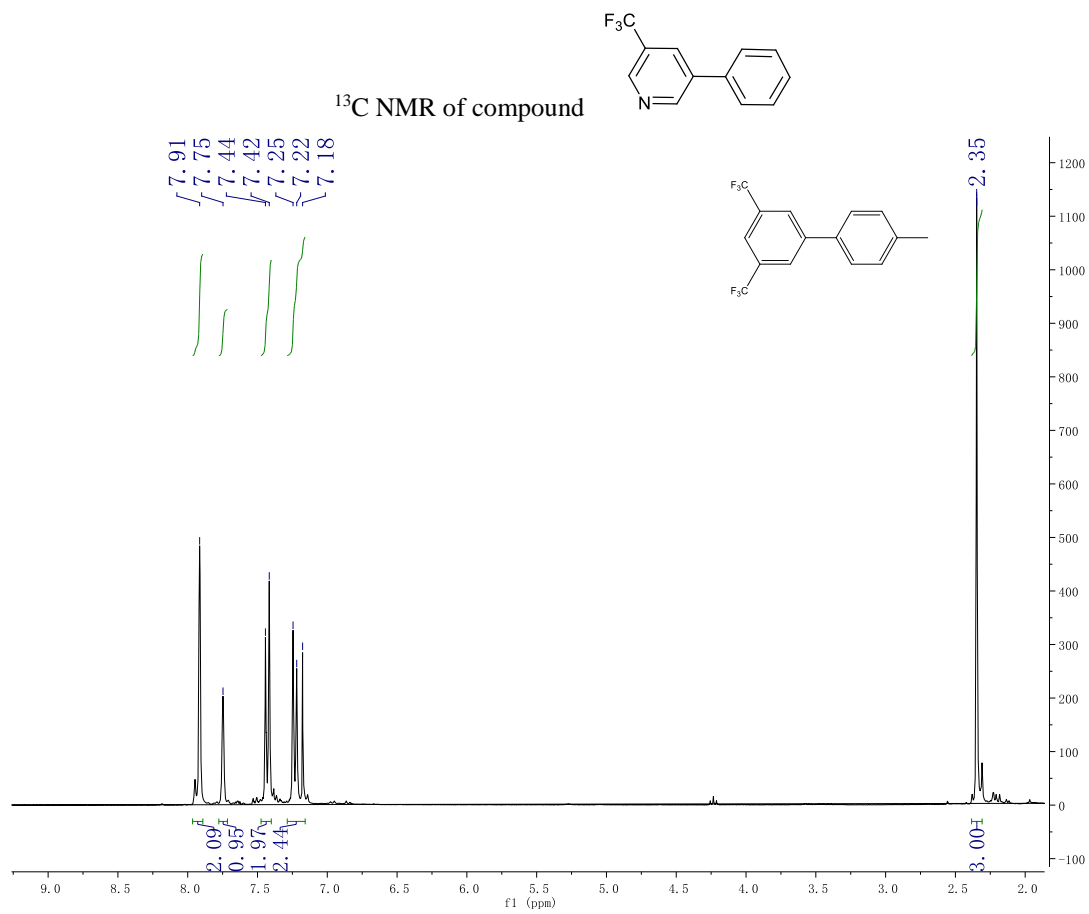
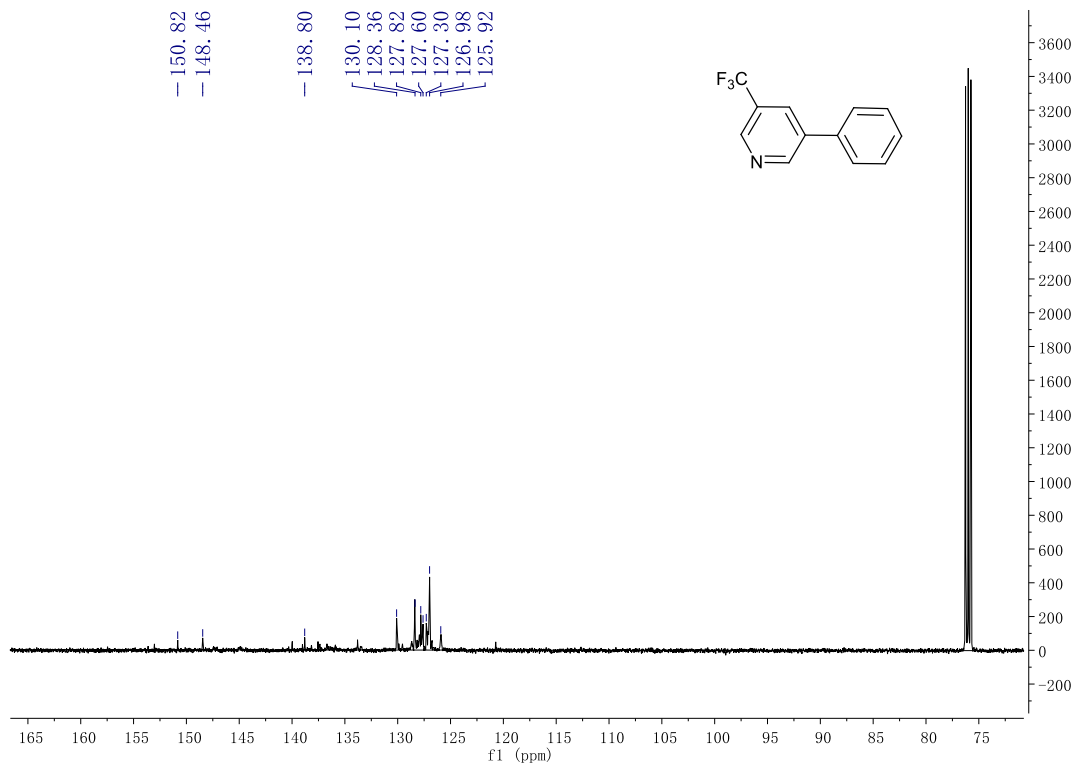




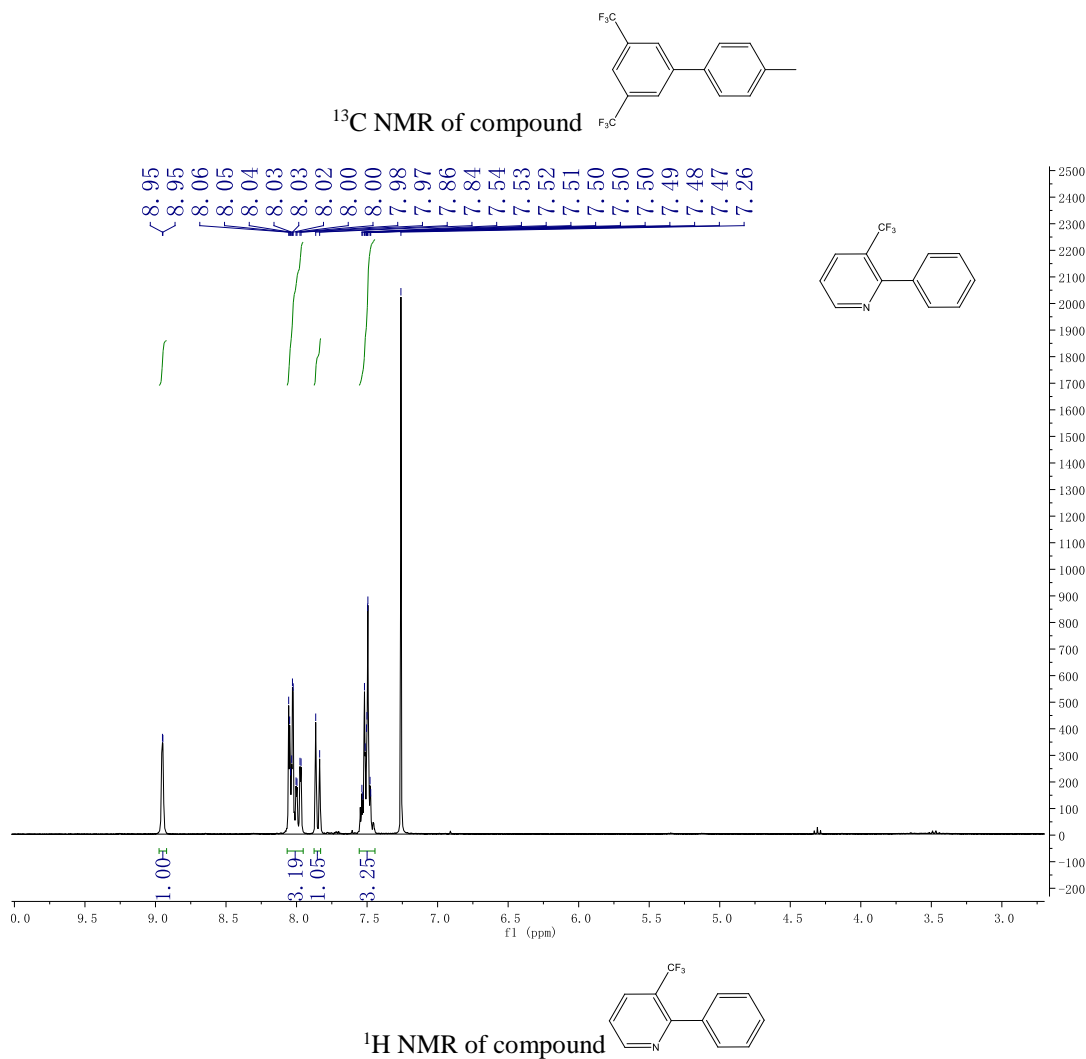
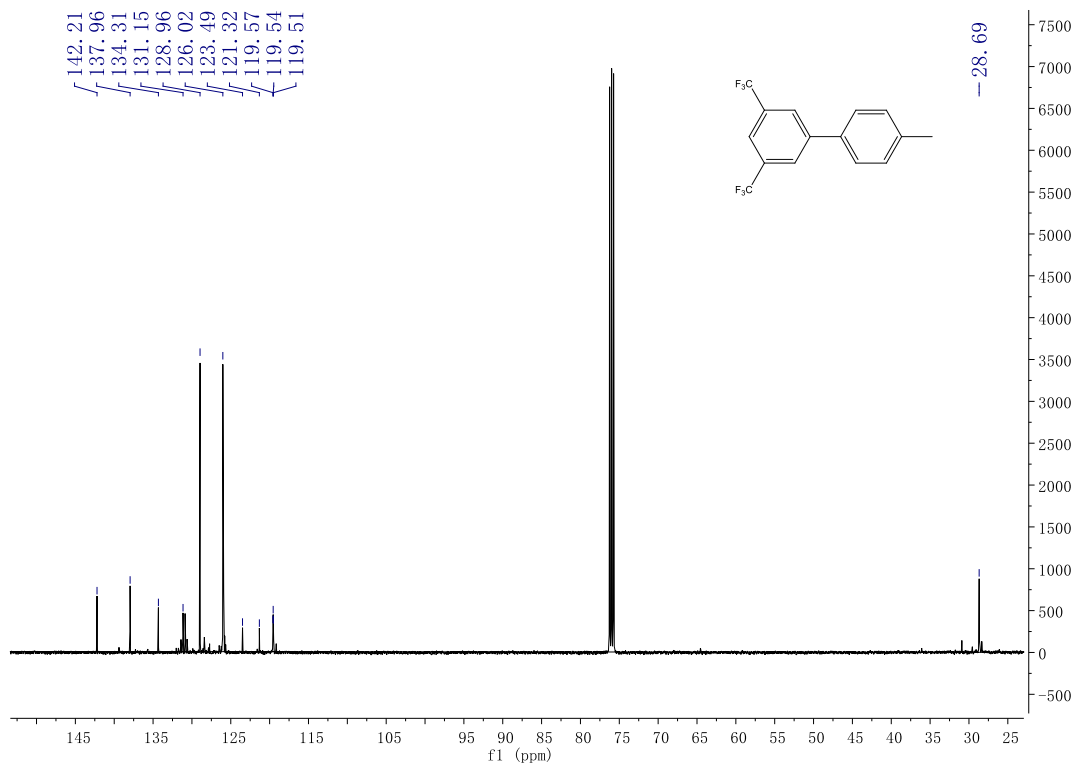
^{13}C NMR of compound

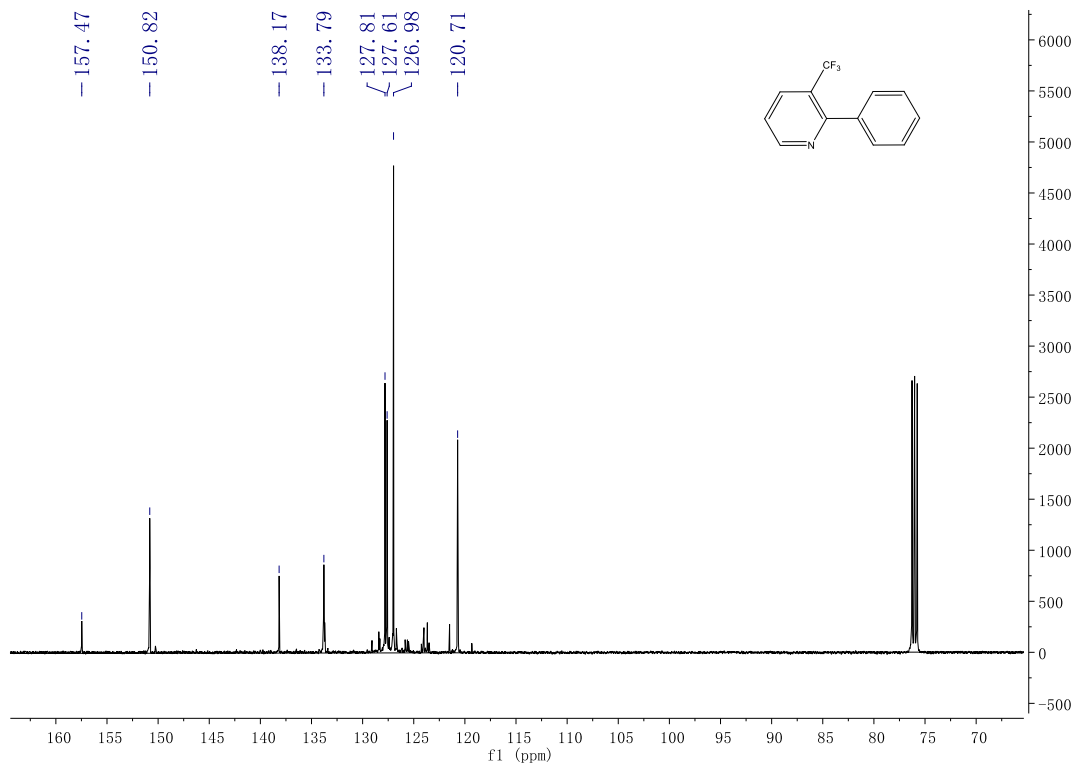


^1H NMR of compound



^1H NMR of compound

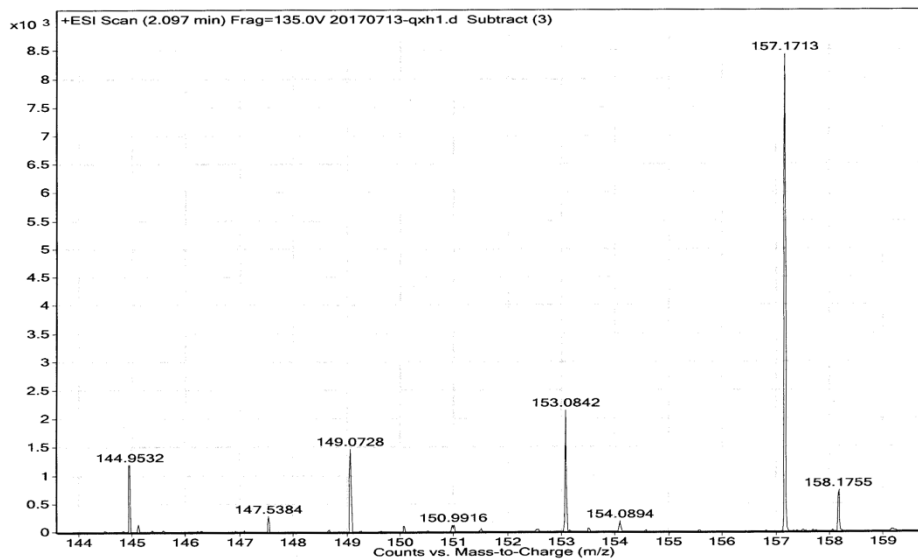




¹³C NMR of compound Cc1ccc(cc1)-c2ccccc2C(F)(F)F

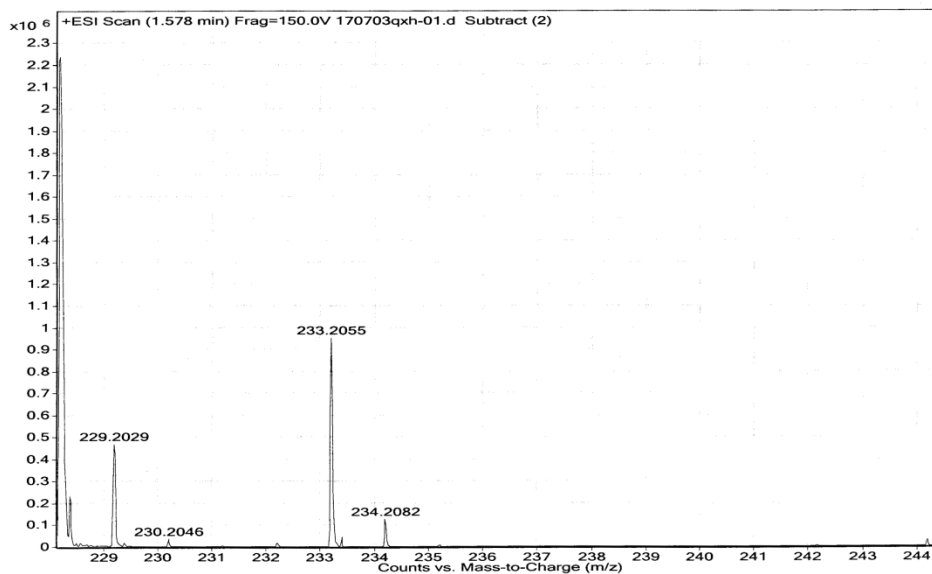
SIV MS of study on the catalytic reaction mechanism

Sample Name	20170713-qxh1	Position	P1-F7	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	20170713-qxh1.d	ACQ Method	0103.m	Comment		Acquired Time	7/13/2017 11:12:45 AM



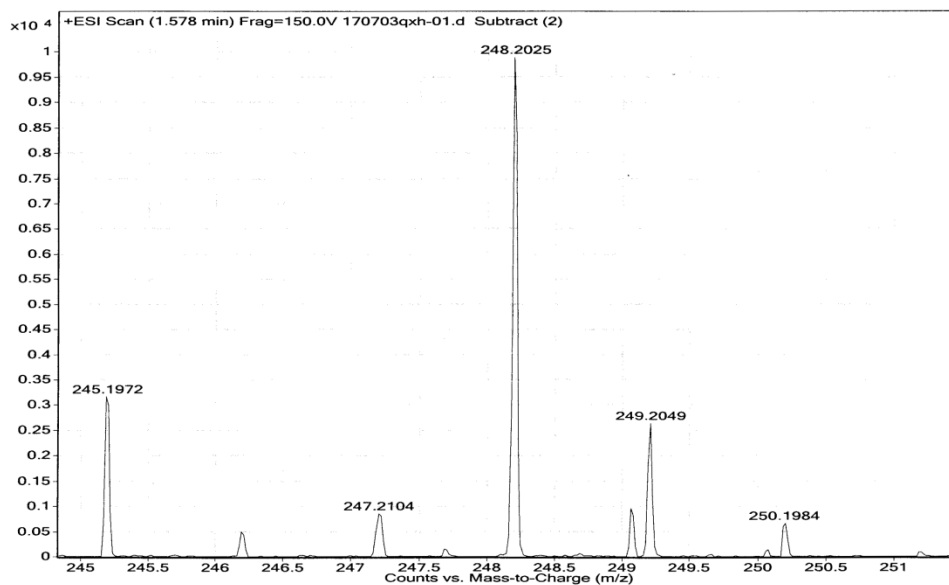
MS of biphenyl

Sample Name	qxh-01	Position	P1-F2	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	170703qxh-01.d	ACQ Method	0103.m	Comment		Acquired Time	7/3/2017 3:38:33 PM



MS of the TEMPO capture product of phenyl radical

Sample Name	qxh-01	Position	P1-F2	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	170703qxh-01.d	ACQ Method	0103.m	Comment		Acquired Time	7/3/2017 3:38:33 PM



MS of the TEMPO capture product of 4-methyl-phenyl radical