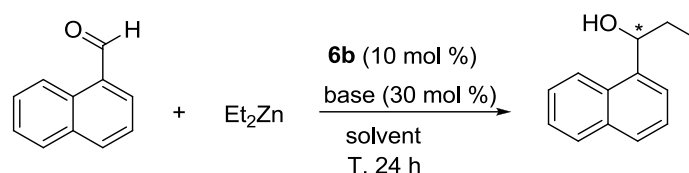


Supplementary Materials: Synthesis of New C₂-symmetric Six-Membered NHCs and Their Application for Asymmetric Diethylzinc Addition of Arylaldehydes

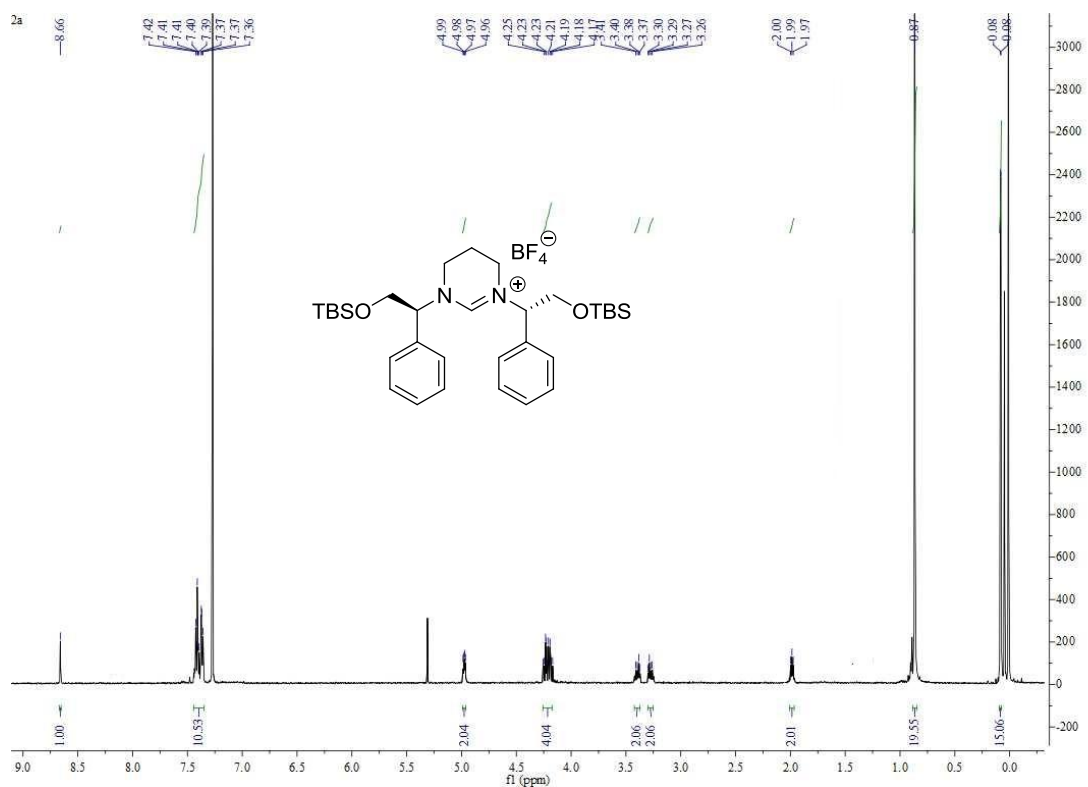
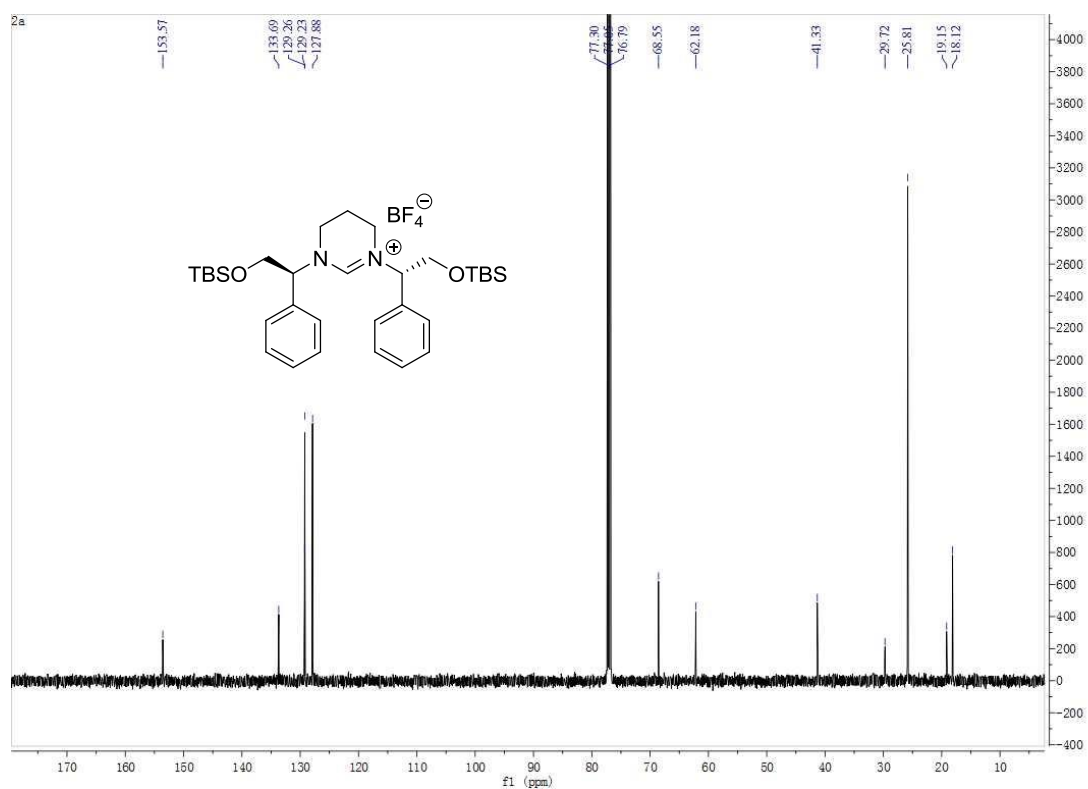
Jie Li ¹, Bihui Zhou ¹, Yajie Jiang ¹ and Xiaoming Liu ^{2,*}

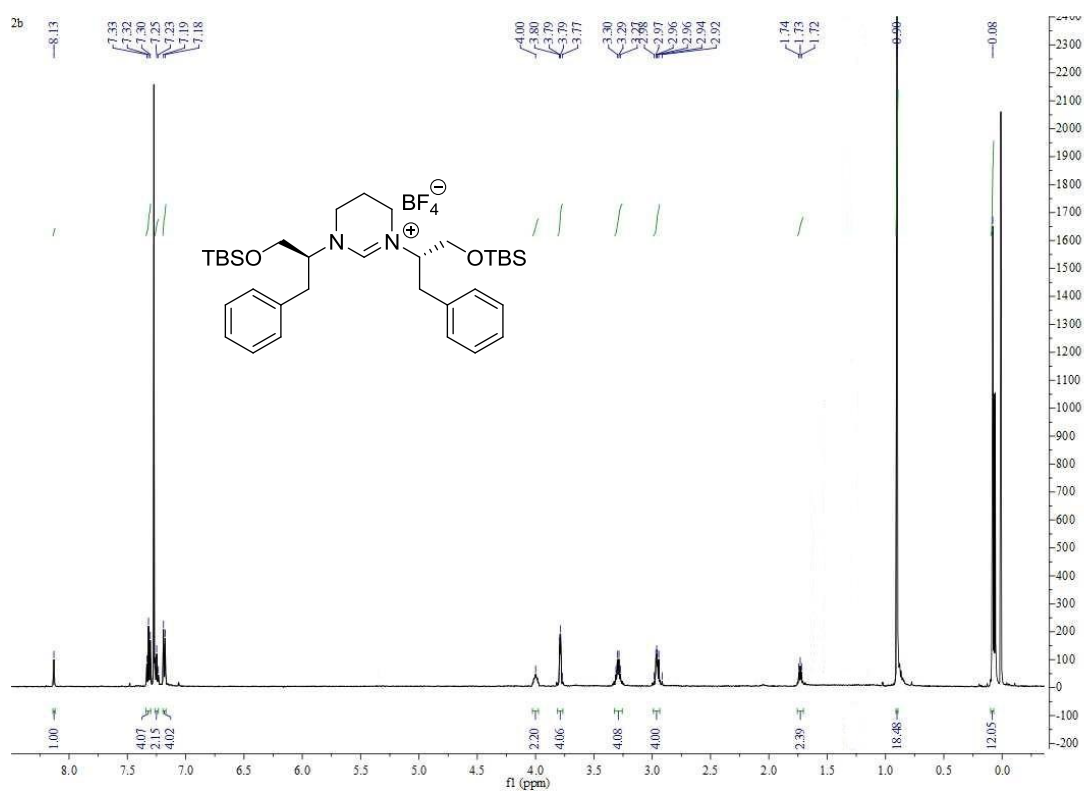
Table S1. Optimization of the reaction conditions.



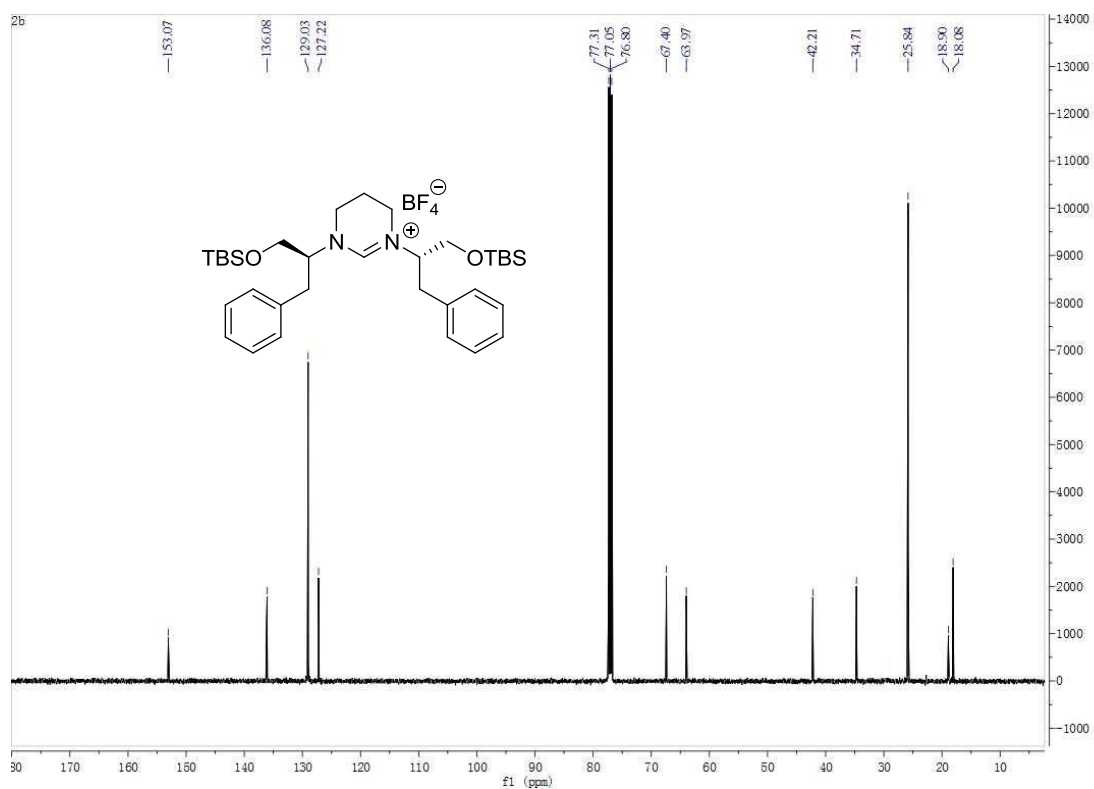
Entry ^a	Solvent	Base	Temperature	Yield (%) ^b	ee (%) ^c
1	xylene	LiO ^t Bu	rt	–	–
2	xylene	NaO ^t Bu	rt	61	4
3	xylene	KO ^t Bu	rt	93	29
4	xylene	K ₂ CO ₃	rt	–	–
5	xylene	KOH	rt	82	0
6	xylene	CS ₂ CO ₃	rt	–	–
7	xylene	Pyridin	rt	–	–
8	xylene	K ₃ PO ₄	rt	–	–
9	xylene	Et ₃ N	rt	–	–
10	xylene	LiOH	rt	–	–
11	xylene	LiHMDS	rt	68	11
12	xylene	NaHMDS	rt	79	13
13	xylene	KF	rt	28	0
14	xylene	10%KHMDS	rt	48	18
15	xylene	20%KHMDS	rt	75	29
16	xylene	50%KHMDS	rt	90	38
17	xylene	1eqKHMDS	rt	66	15
18	xylene	2eqKHMDS	rt	52	8
19	THF	KHMDS	rt	–	–
20	CH ₂ Cl ₂	KHMDS	rt	–	–
21	1,4-dioxane	KHMDS	rt	–	–
22	DME	KHMDS	rt	–	–
23	^t BuOH	KHMDS	rt	–	–
24	CH ₃ OH	KHMDS	rt	–	–
25	toluene	KHMDS	rt	56	11
26	Mesitylene	KHMDS	rt	95	1
27	xylene	KHMDS	100 °C	97	5
28	xylene	KHMDS	50°C	89	20
29	xylene	KHMDS	0°C	90	16
30	xylene	KHMDS	–20°C	61	0
31	xylene	KHMDS	–40°C	28	11
32	xylene	KHMDS	–80°C	–	–

^a Reaction condition: **6b** (10 mol %), base (30 mol %), Et₂Zn (2 equiv), N₂, xylene, rt, 24 h. ^b Isolated yield. ^c Determined by chiral HPLC (CHIRALCEL OD Column) analysis.

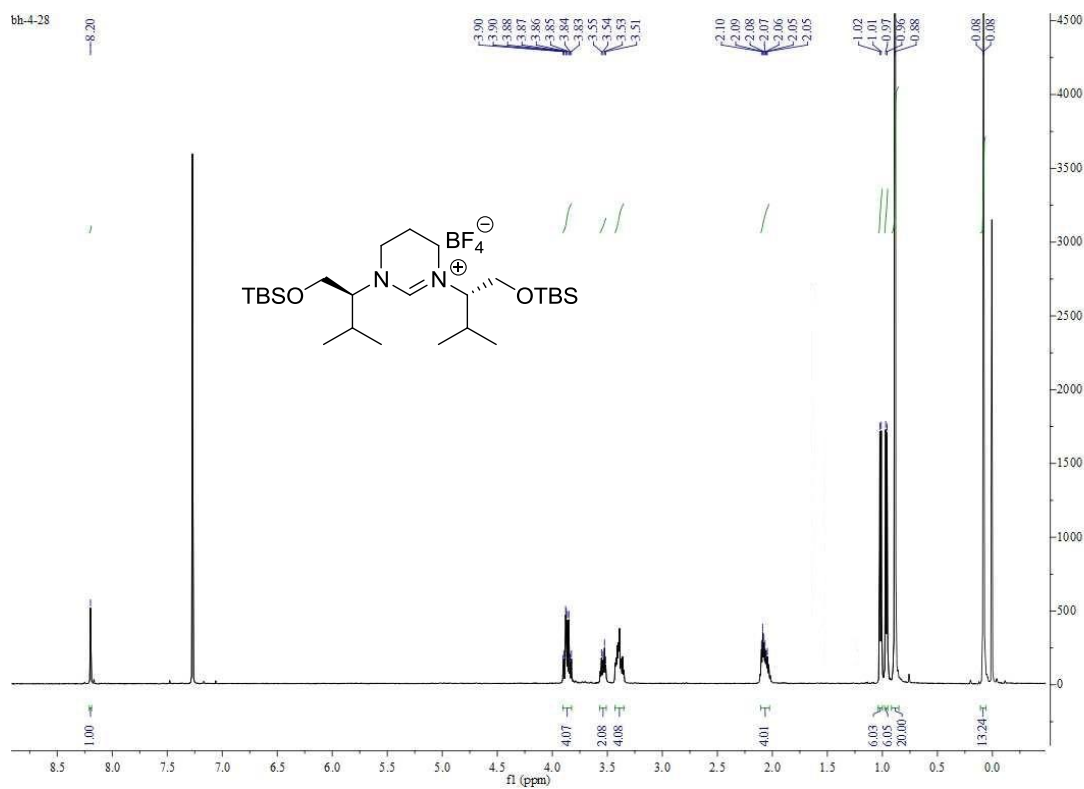
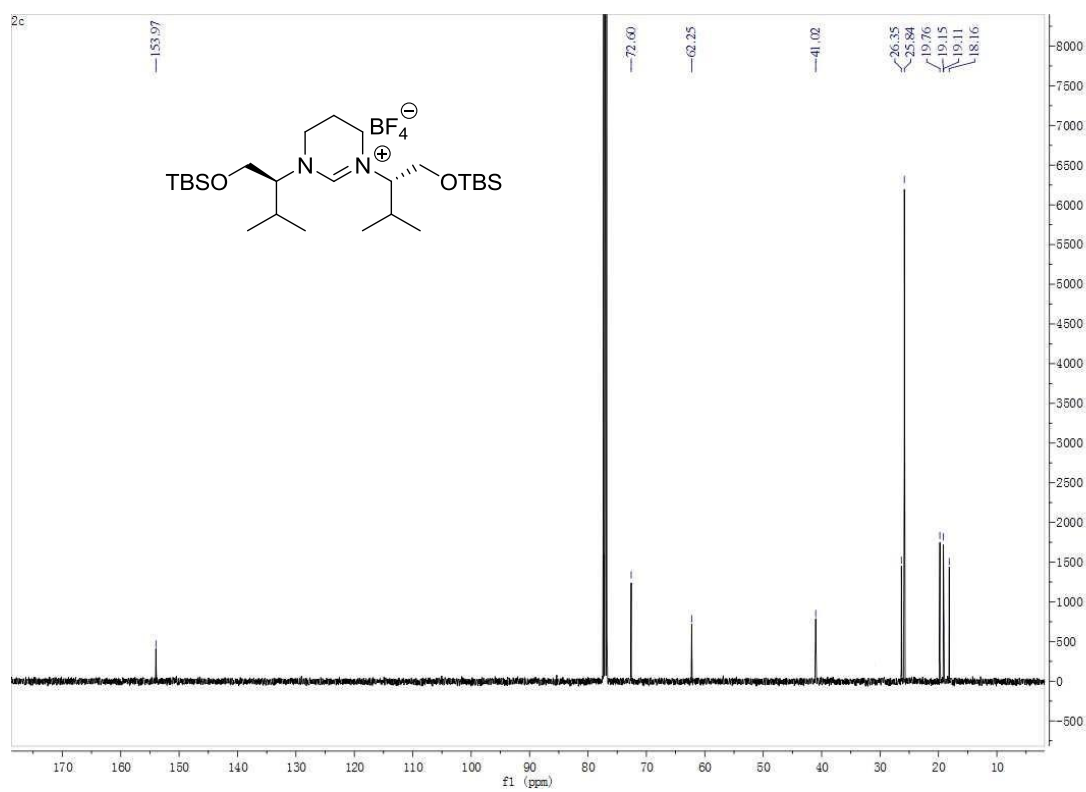
 ^1H NMR Spectra of Compound 2a ^{13}C NMR Spectra of Compound 2a

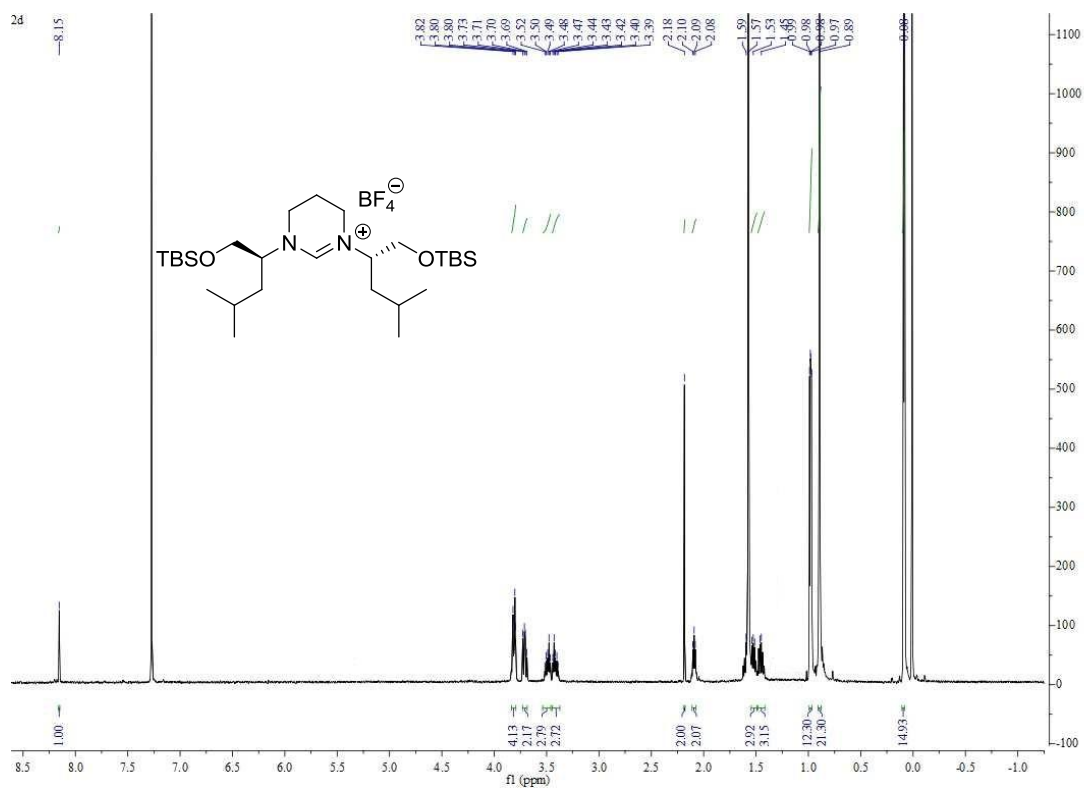
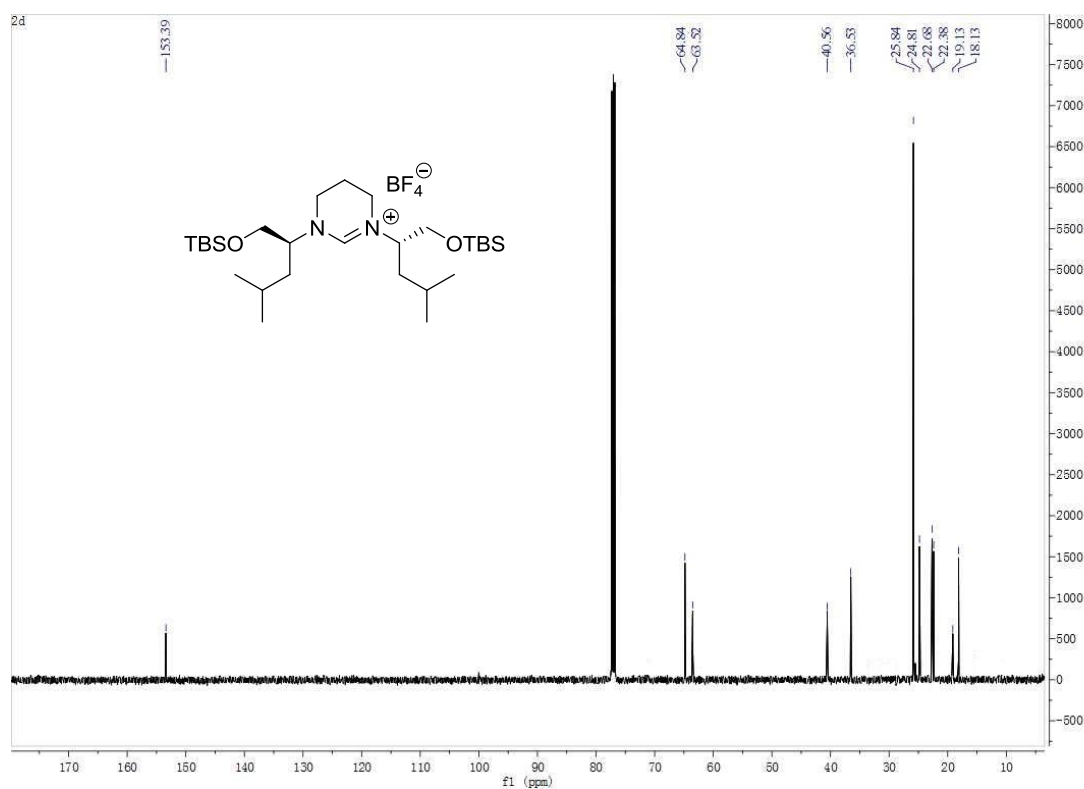


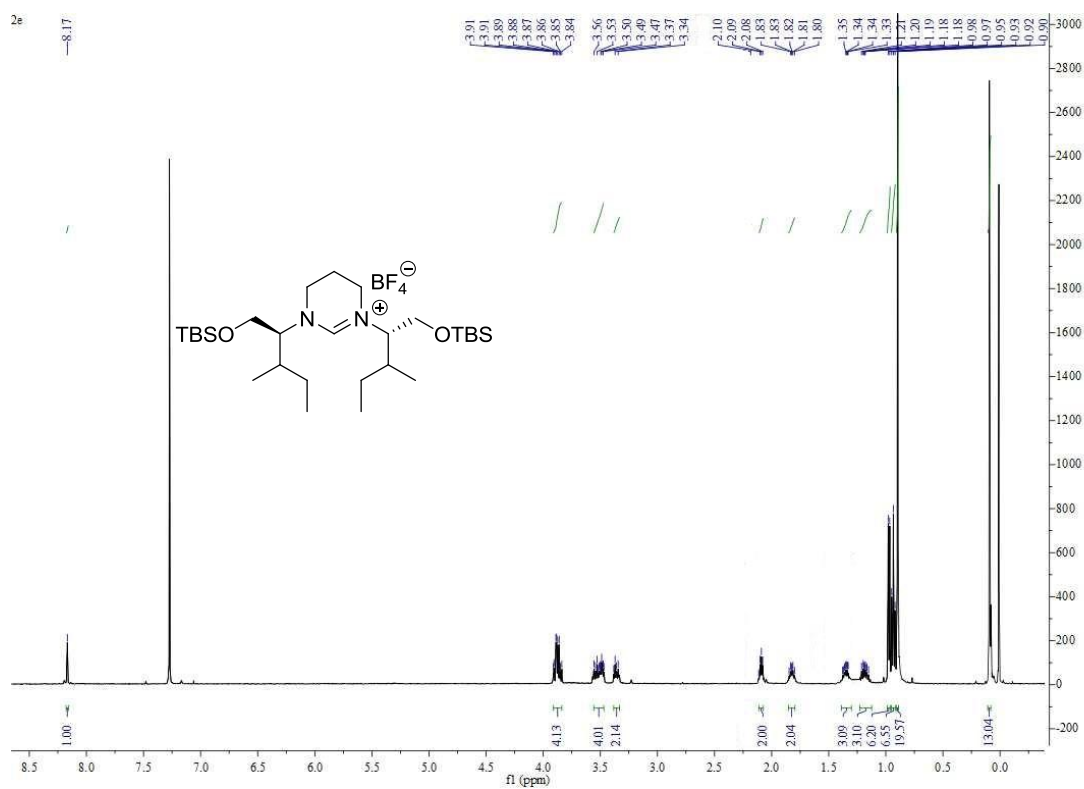
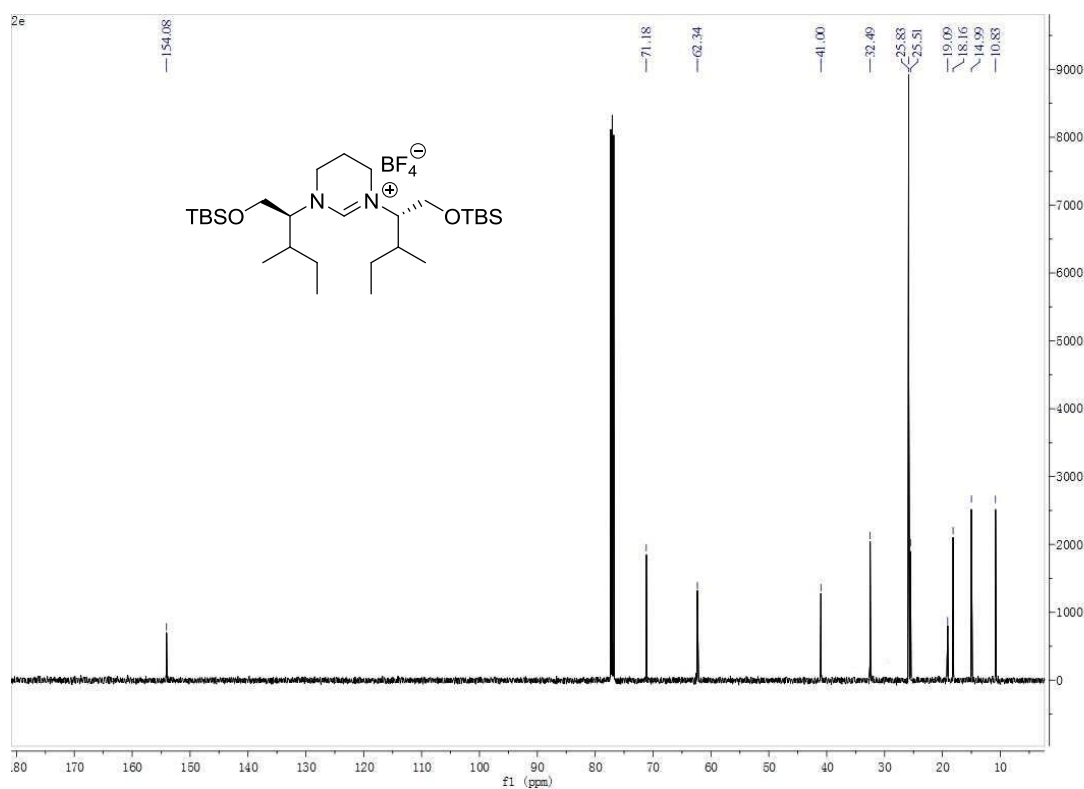
¹H NMR Spectra of Compound 2b

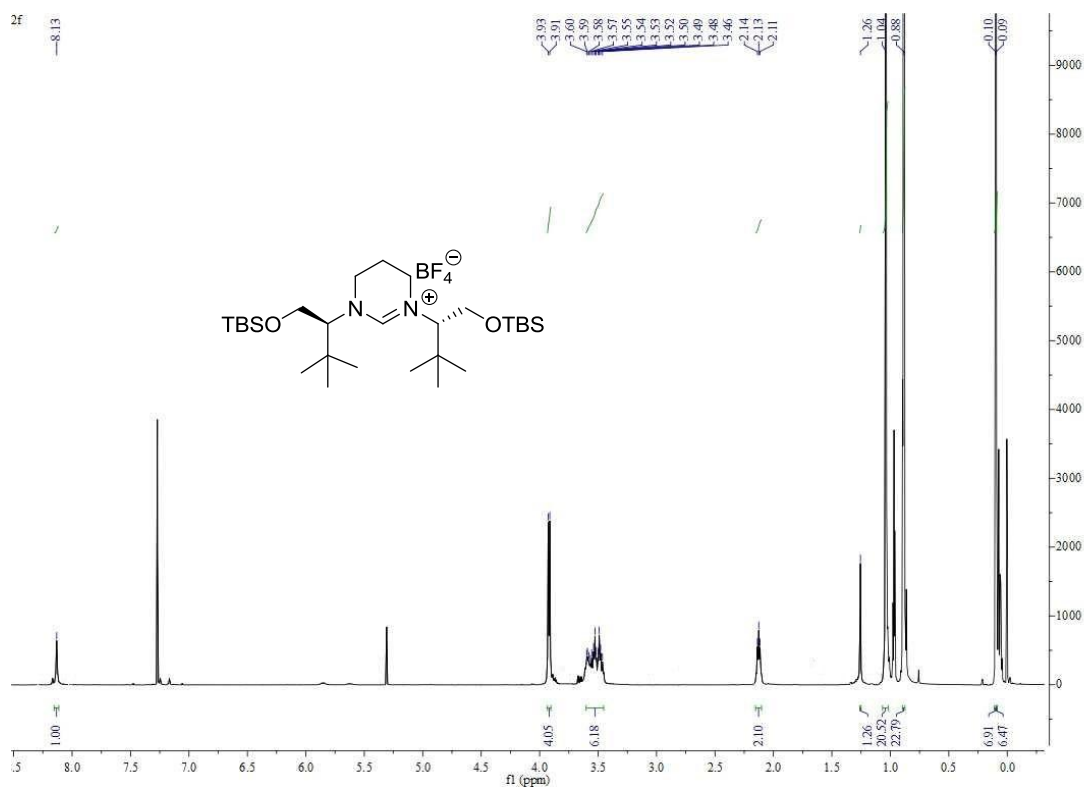
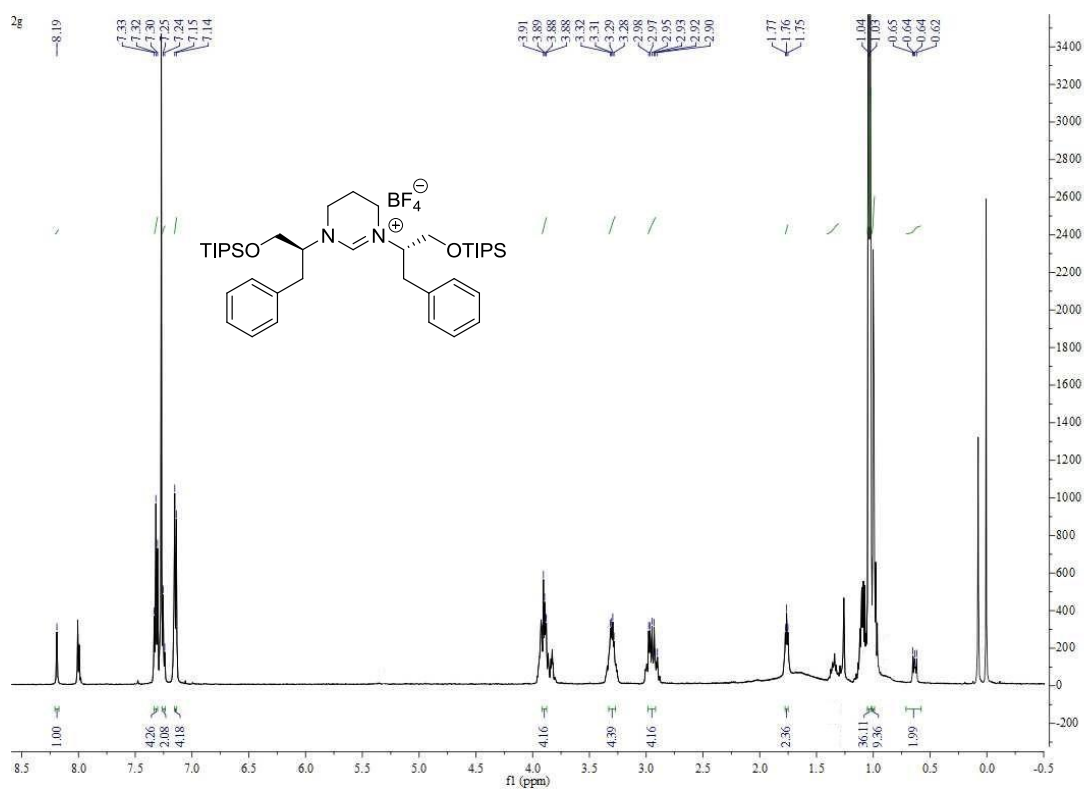


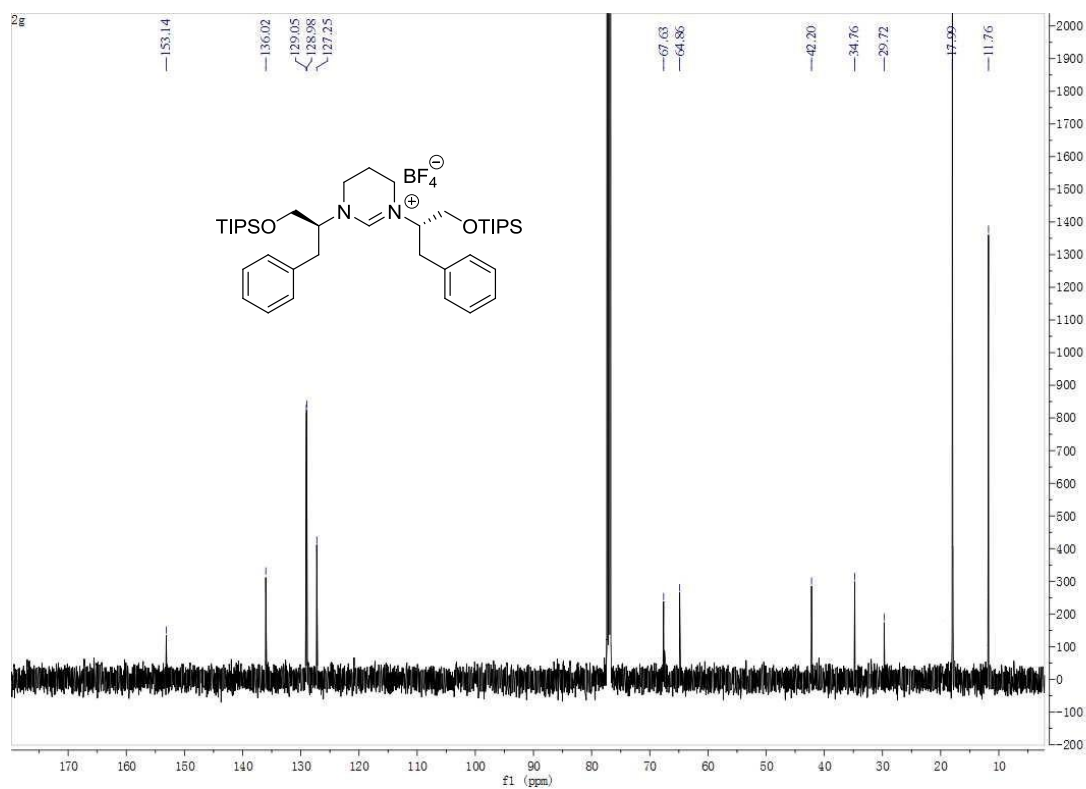
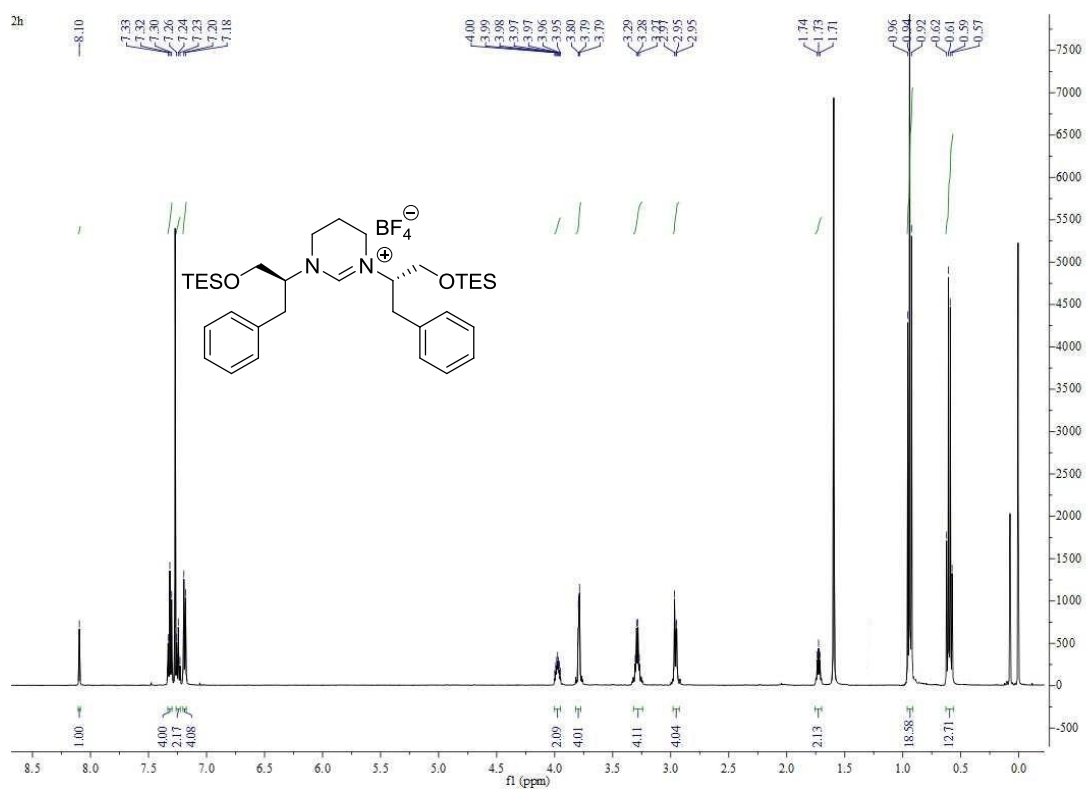
¹³C NMR Spectra of Compound 2b

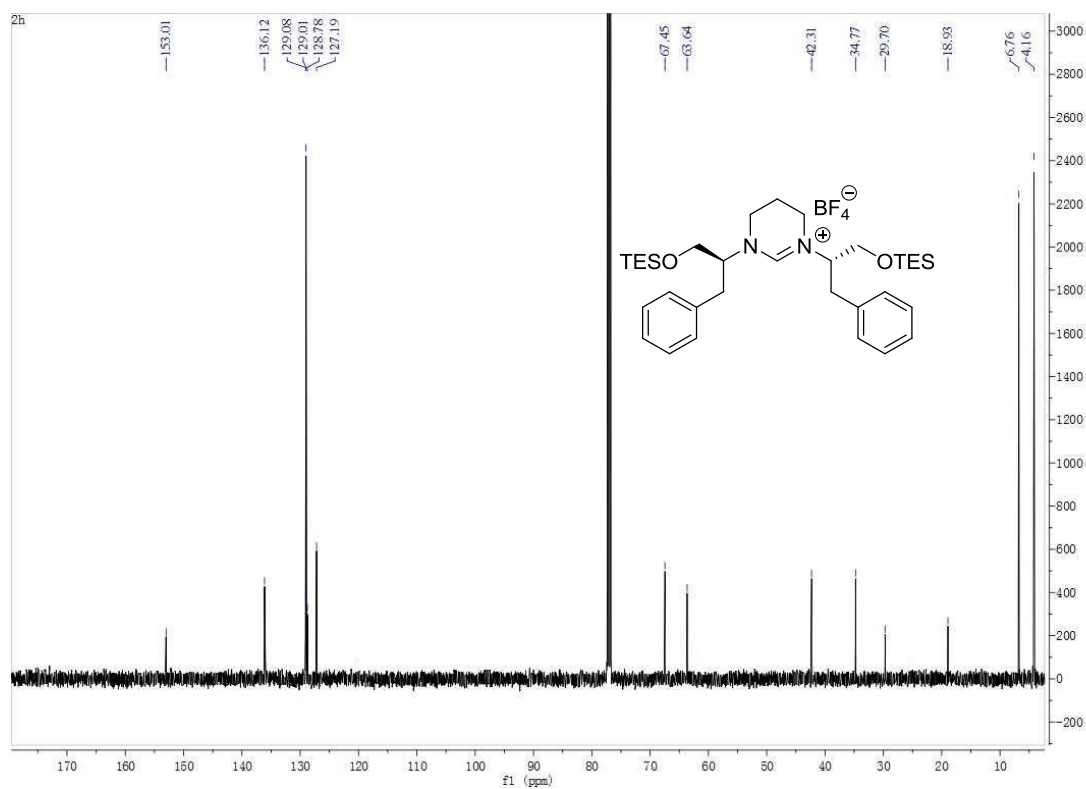
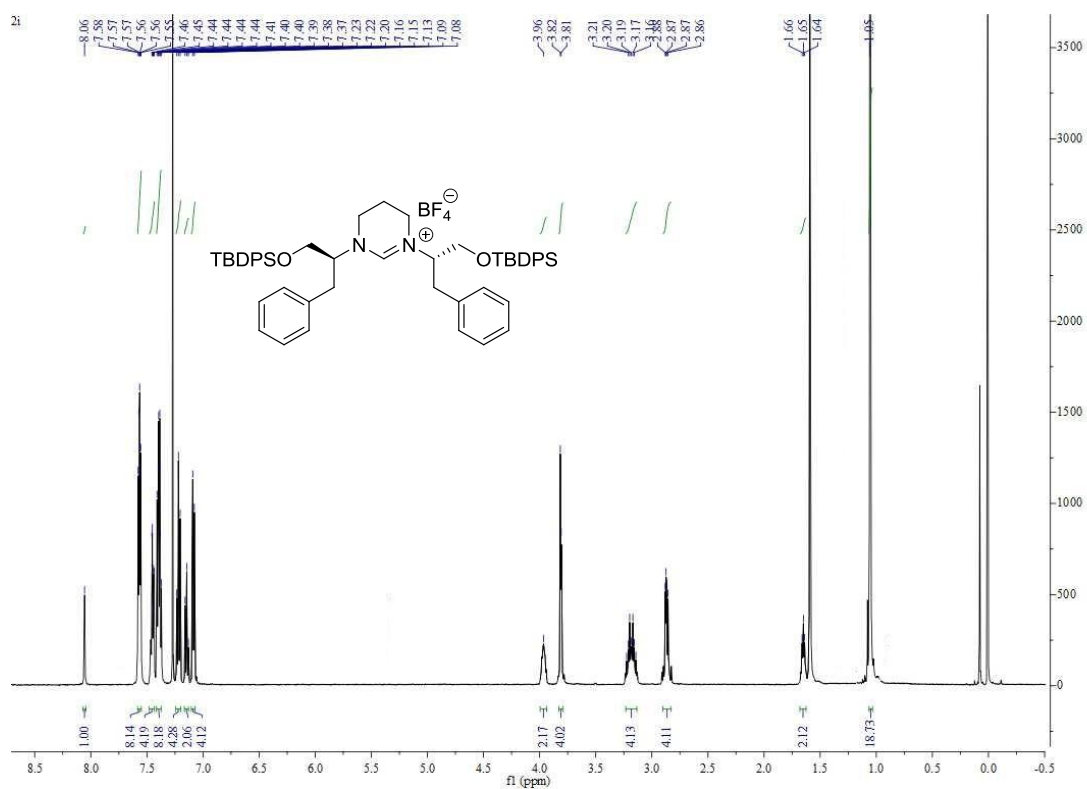
 ^1H NMR Spectra of Compound 2c ^{13}C NMR Spectra of Compound 2c

 ^1H NMR Spectra of Compound 2d ^{13}C NMR Spectra of Compound 2d

 ^1H NMR Spectra of Compound 2e ^{13}C NMR Spectra of Compound 2e

 ^1H NMR Spectra of Compound 2f ^1H Spectra of Compound 2g

**¹³C NMR Spectra of Compound 2g****¹H Spectra of Compound 2h**

 ^{13}C NMR Spectra of Compound 2h ^1H Spectra of Compound 2i

