

Supplementary Material

New C₂-symmetric six-membered carbene ligands for asymmetric diethylzinc addition of arylaldehydes

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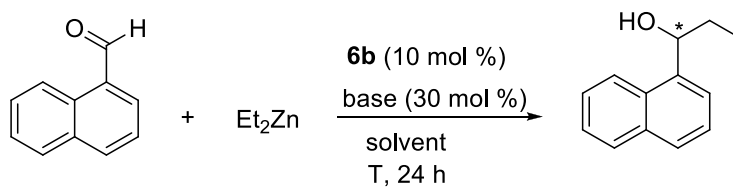
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1. Optimization of the reaction conditions

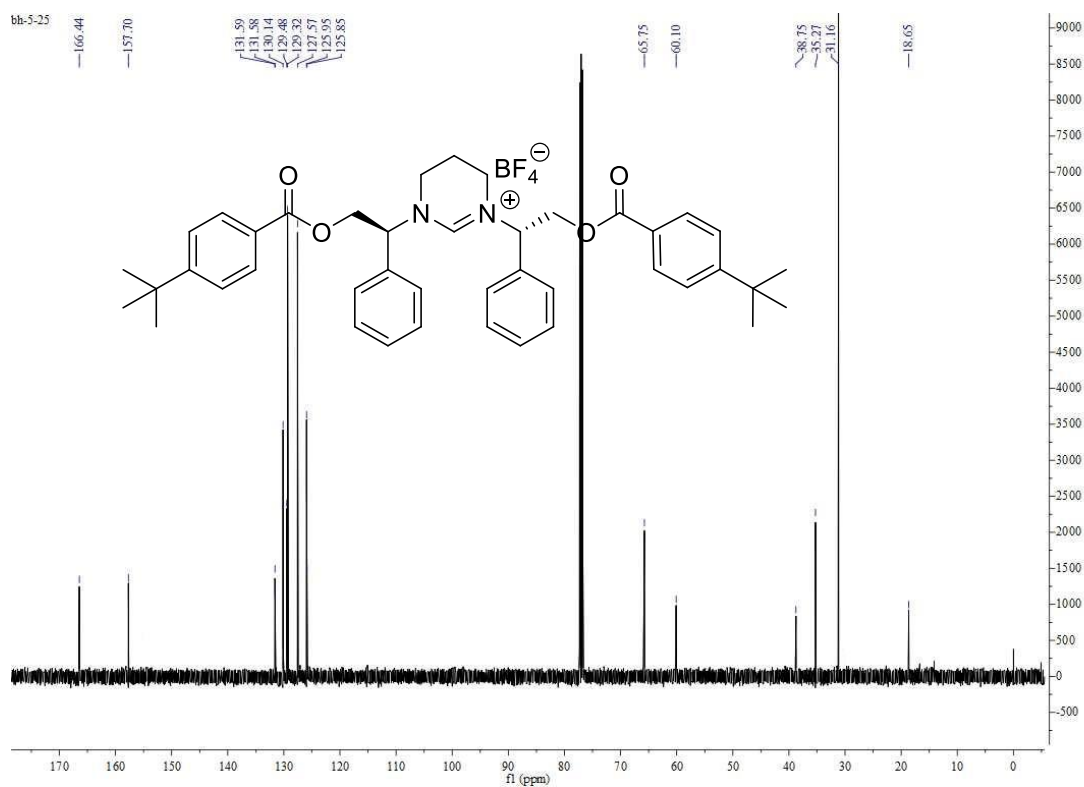
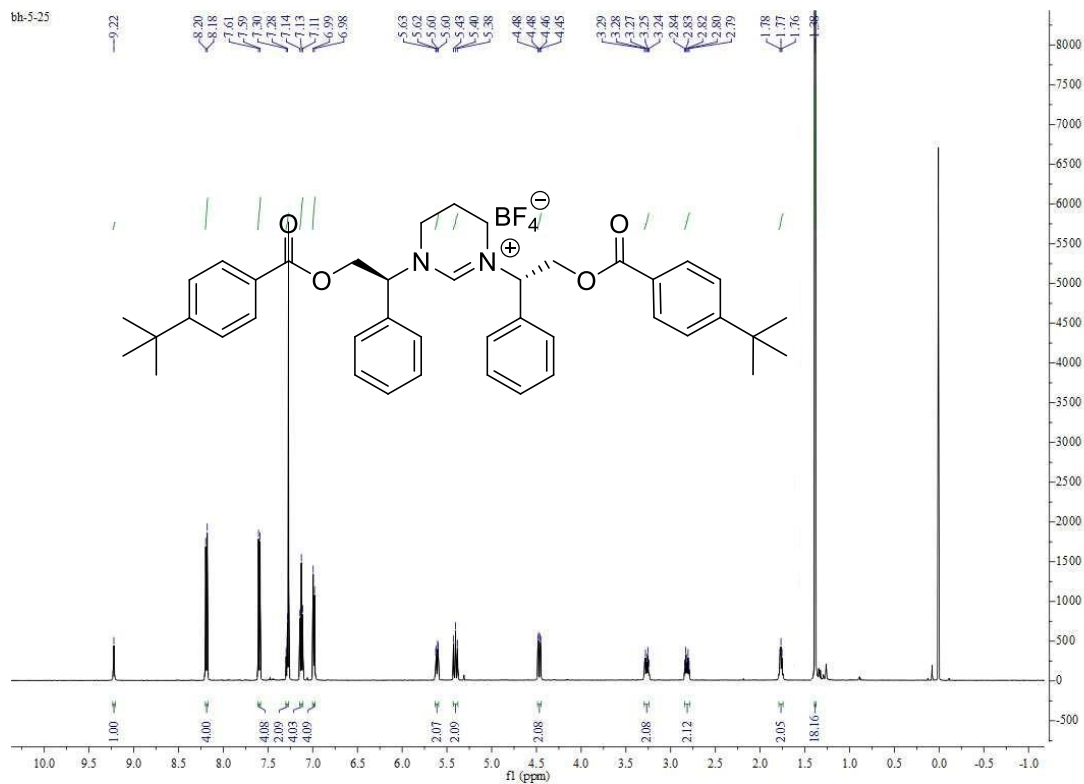


Entry ^a	Solvent	Base	Temperature	Yield (%) ^b	ee (%) ^c
1	xylene	LiO ^t Bu	rt	54	2
2	xylene	NaO ^t Bu	rt	92	11
3	xylene	KO ^t Bu	rt	93	29
4	xylene	K ₂ CO ₃	rt	46	2
5	xylene	KOH	rt	85	3
6	xylene	Cs ₂ CO ₃	rt	50	0
7	xylene	Pyridine	rt	44	2
8	xylene	K ₃ PO ₄	rt	35	8
9	xylene	Et ₃ N	rt	42	3
10	xylene	LiOH	rt	48	6
11	xylene	LiHMDS	rt	46	2
12	xylene	NaHMDS	rt	88	32
13	xylene	KF	rt	23	1
14	xylene	10%KHMDs	rt	44	13
15	xylene	20%KHMDs	rt	67	33
16	xylene	50%KHMDs	rt	90	41
17	xylene	1eqKHMDs	rt	93	20
18	xylene	2eqKHMDs	rt	92	28
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	86	28
25	mesitylene	KHMDs	rt	51	17
26	xylene	KHMDs	100 °C	99	20
27	xylene	KHMDs	50°C	96	17
28	xylene	KHMDs	0°C	43	32
29	xylene	KHMDs	−20°C	31	4

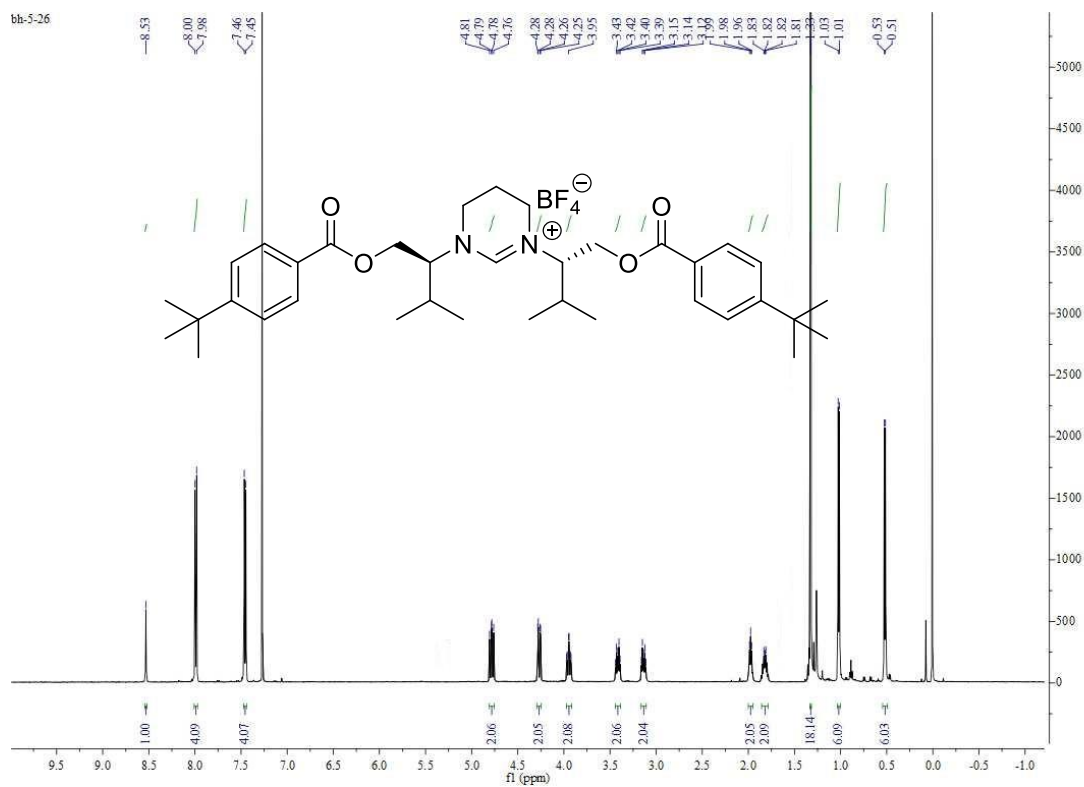
^aReaction condition: **6b** (10 mol %), base (30 mol %), Et_2Zn (2 equiv), N_2 , xylene, rt, 24 h.

^b Isolated yield.

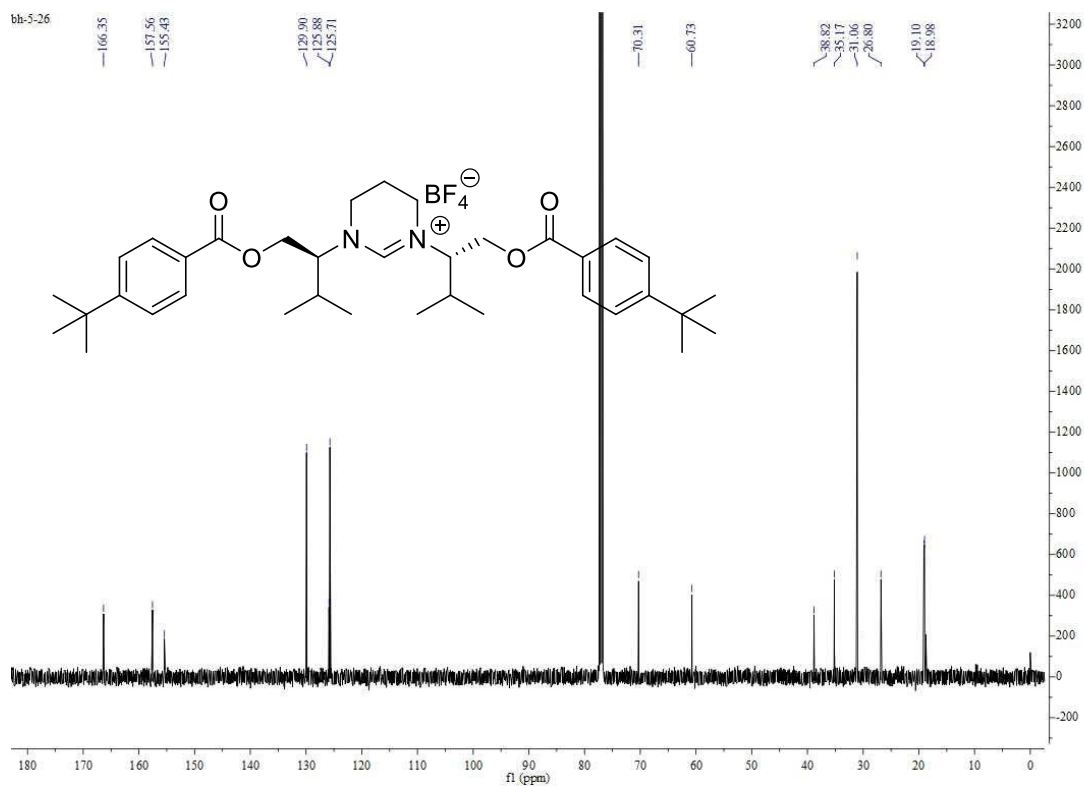
^c Determined by chiral HPLC (CHIRALCEL OD Column) analysis.

2. ^1H and ^{13}C NMR Spectra of Compounds 6a–6i

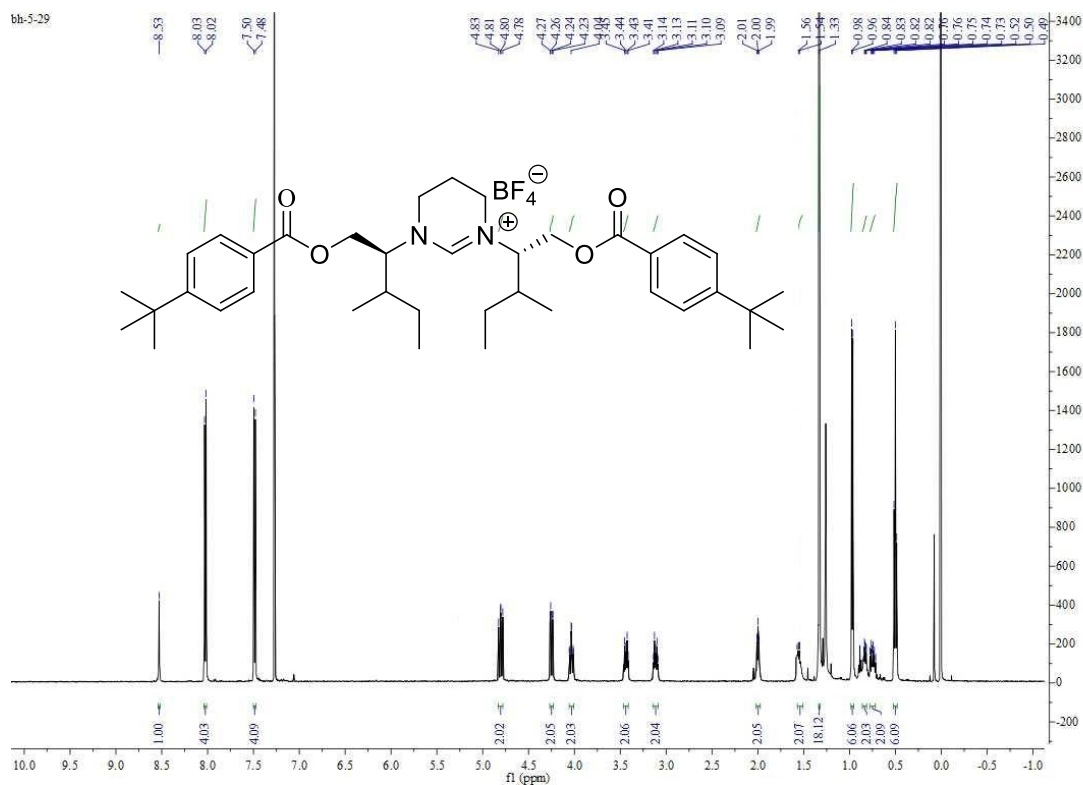
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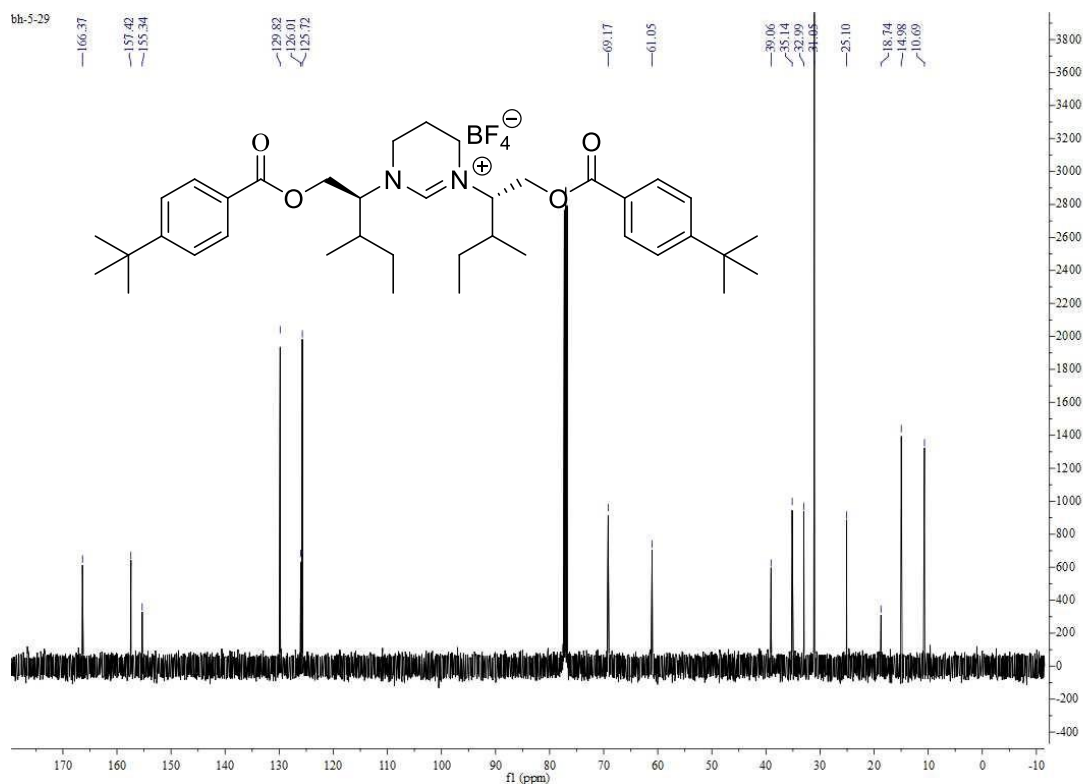
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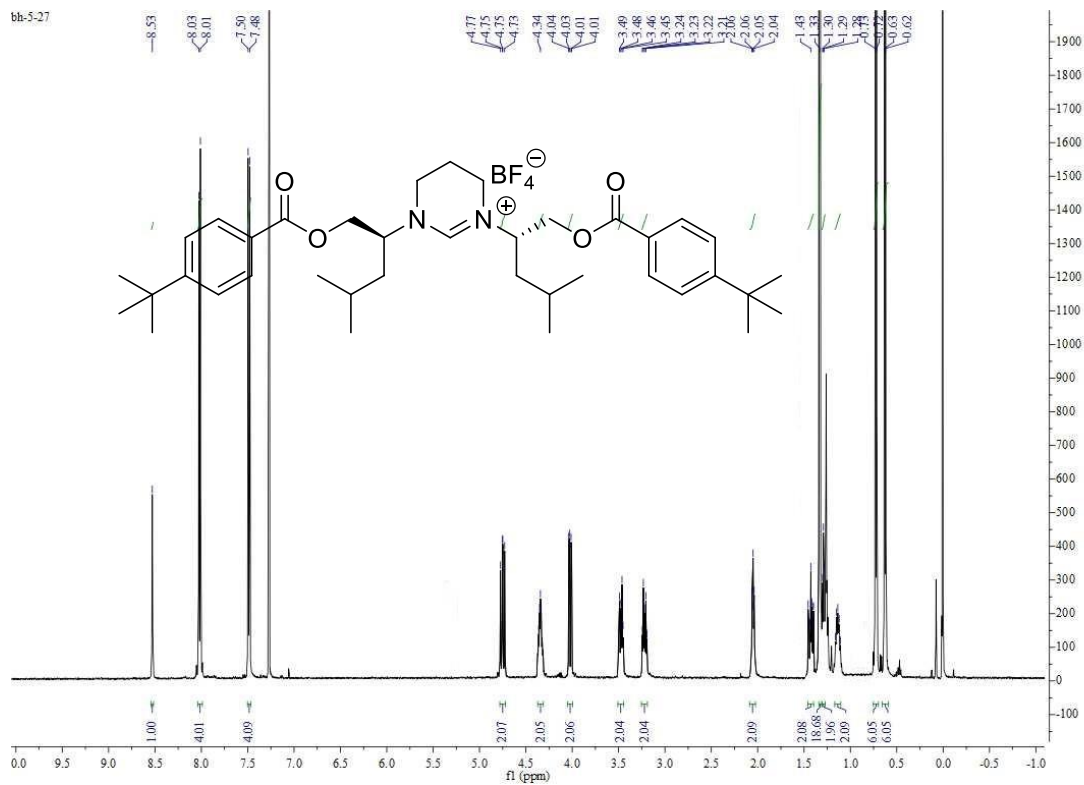
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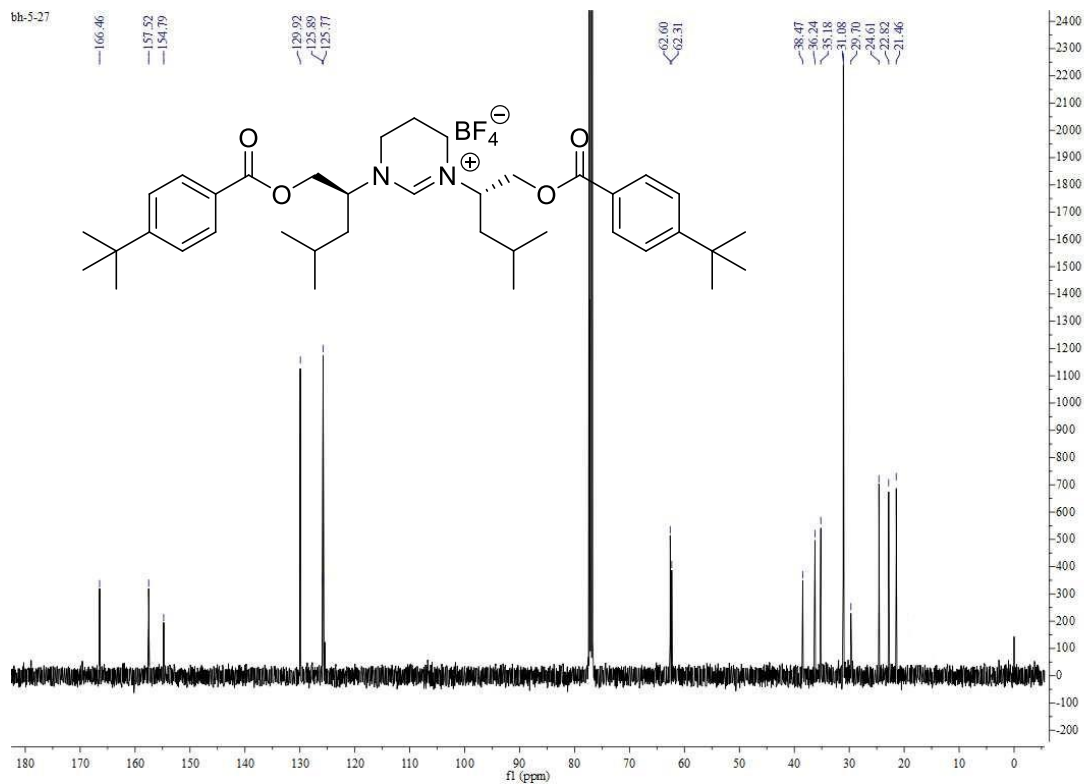
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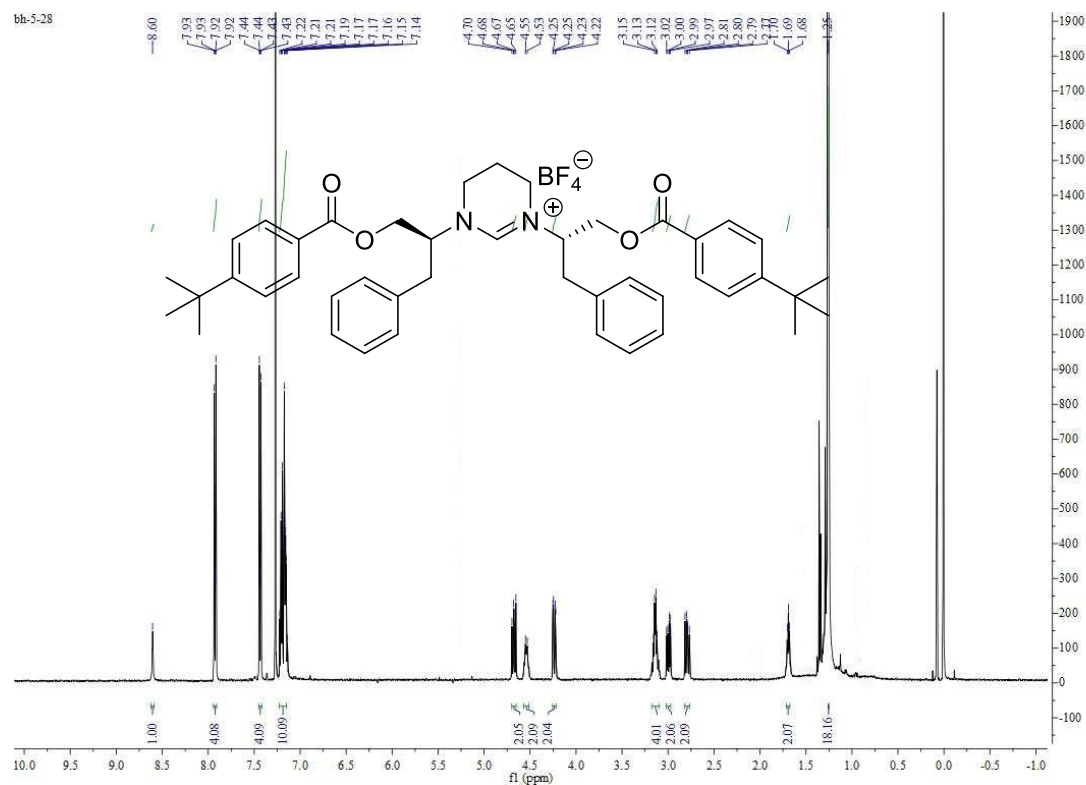
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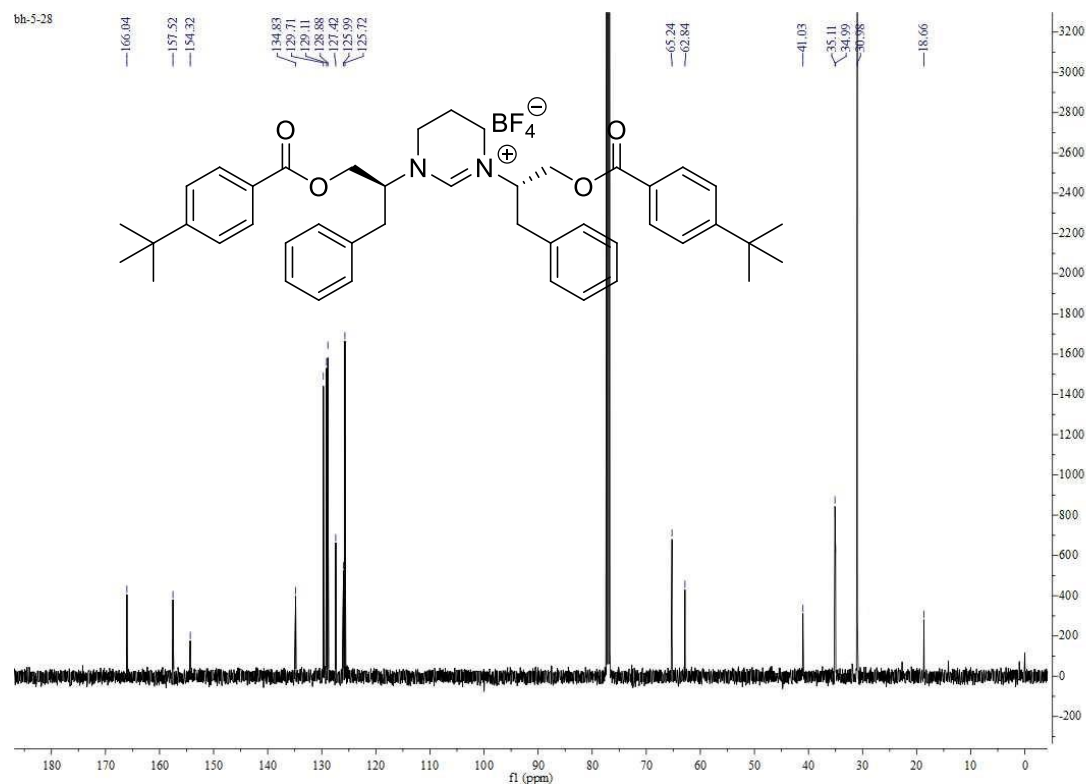
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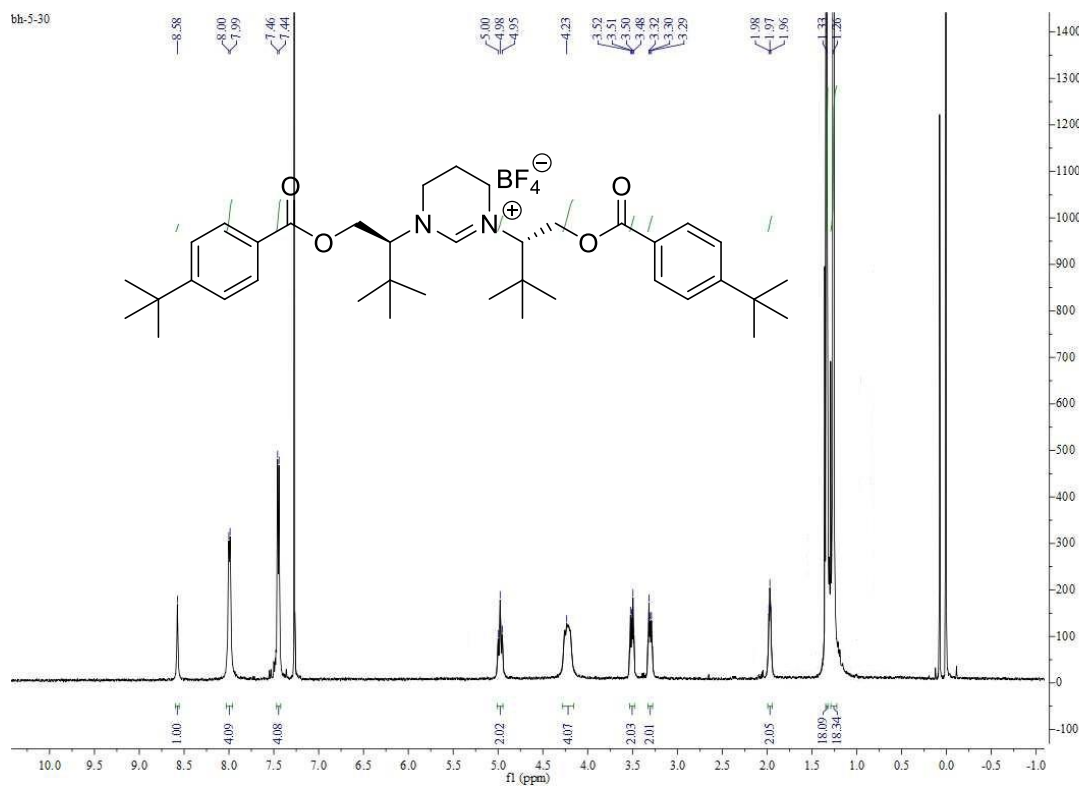
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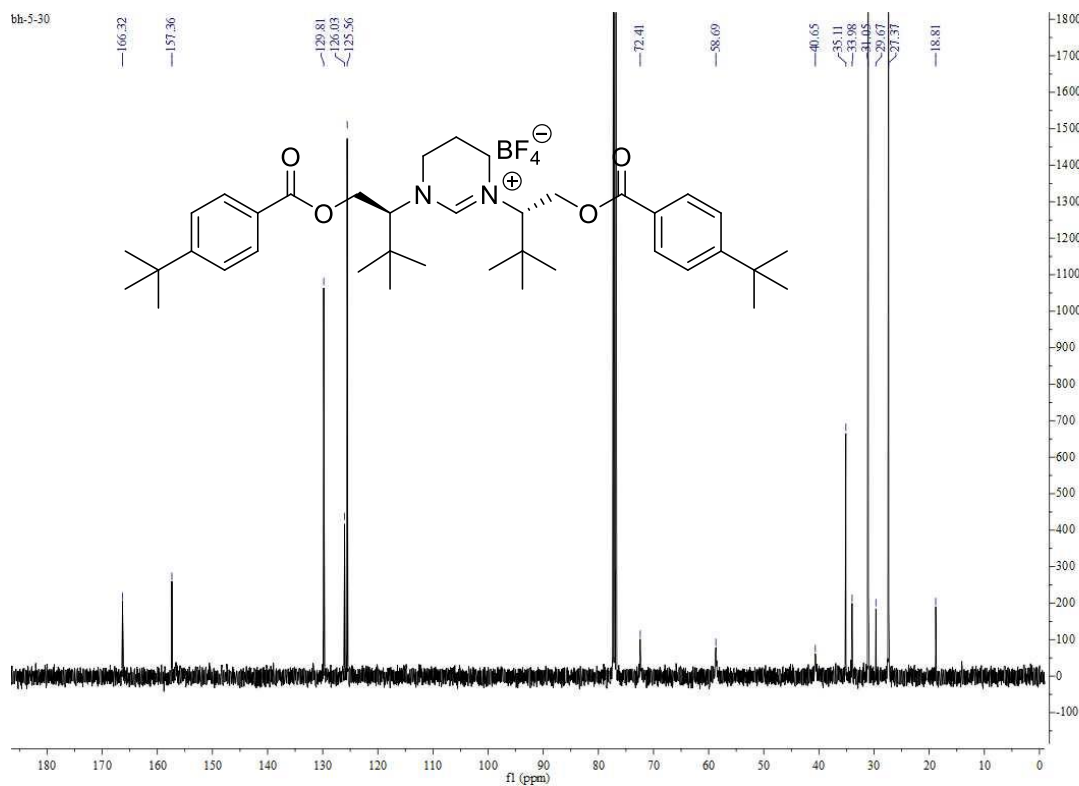
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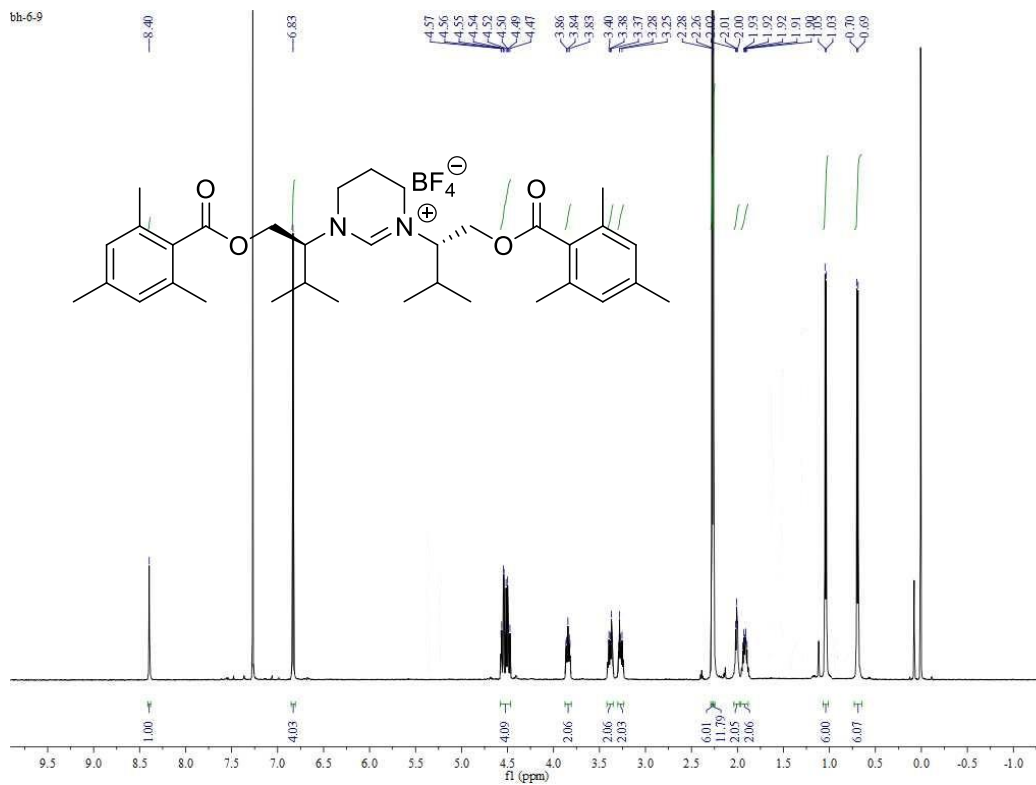
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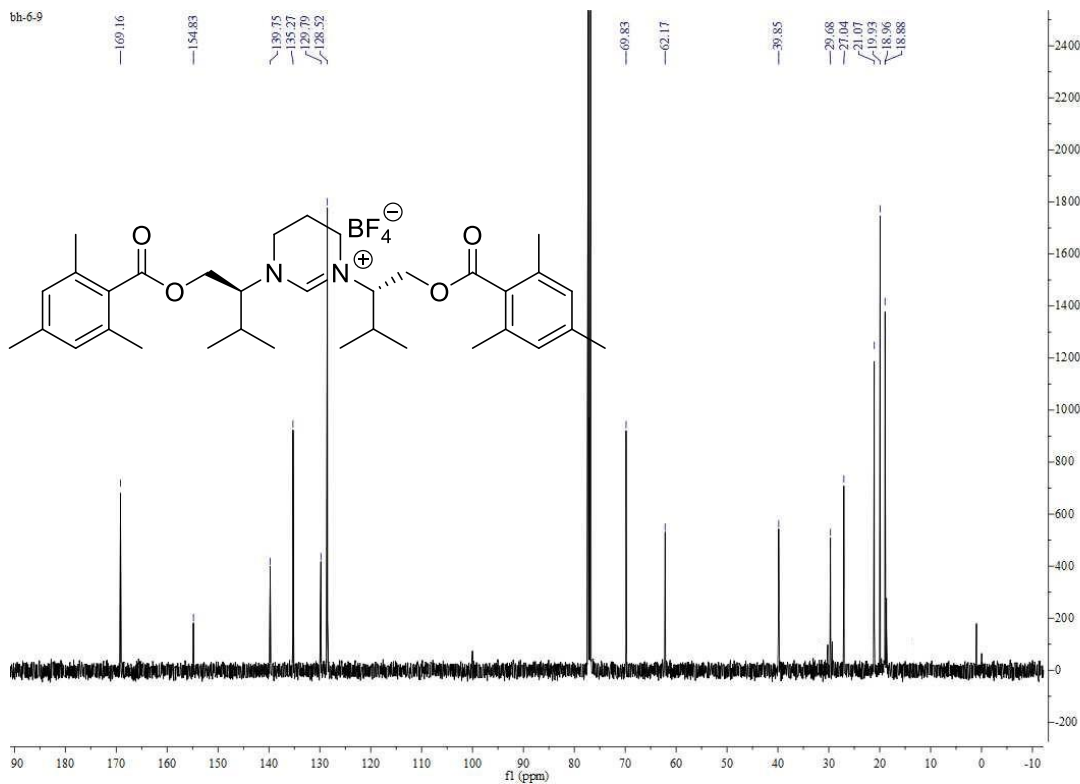
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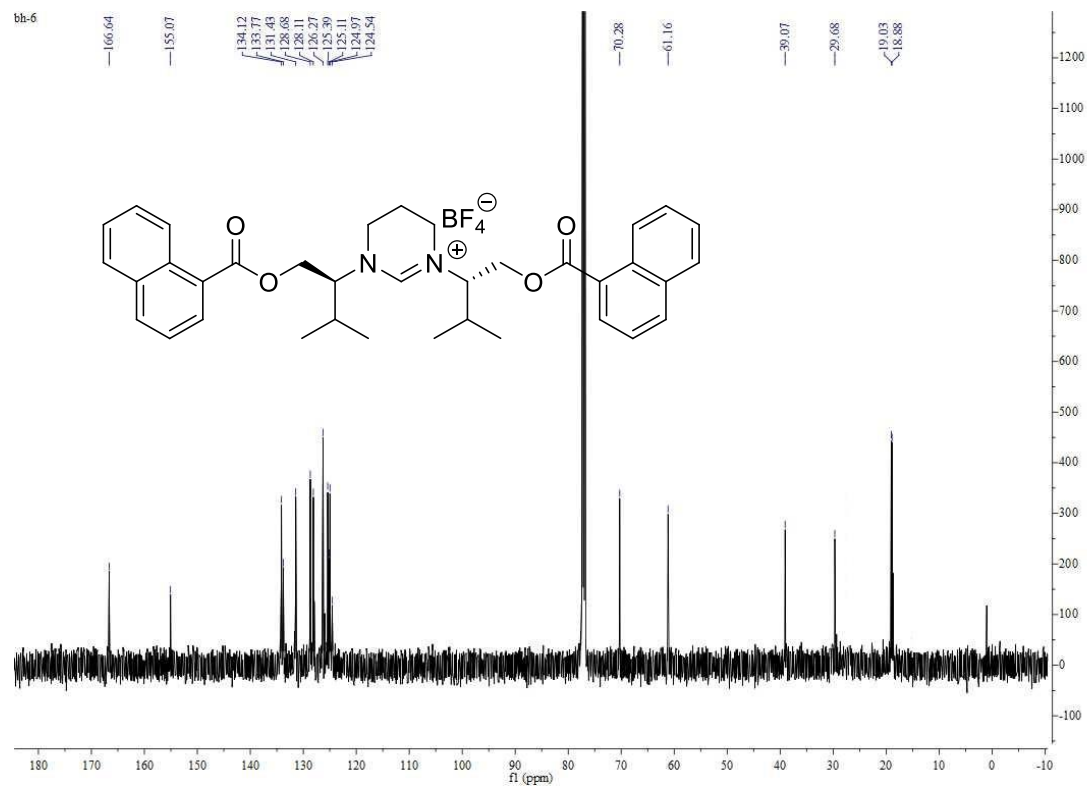
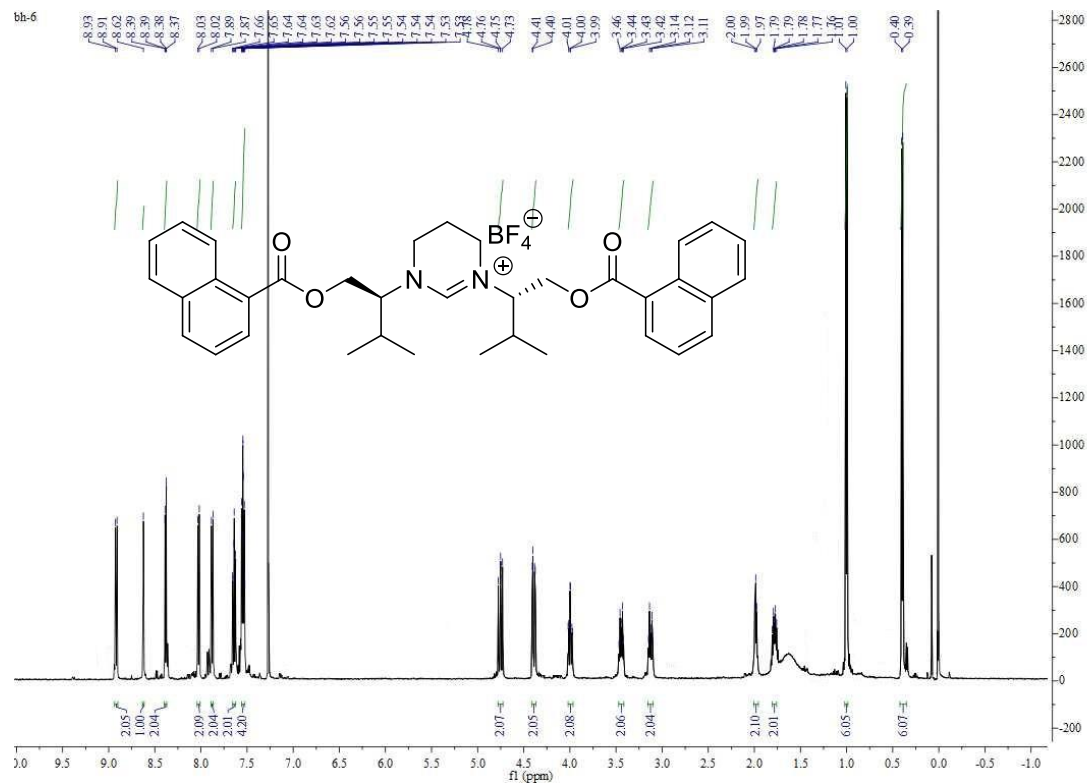


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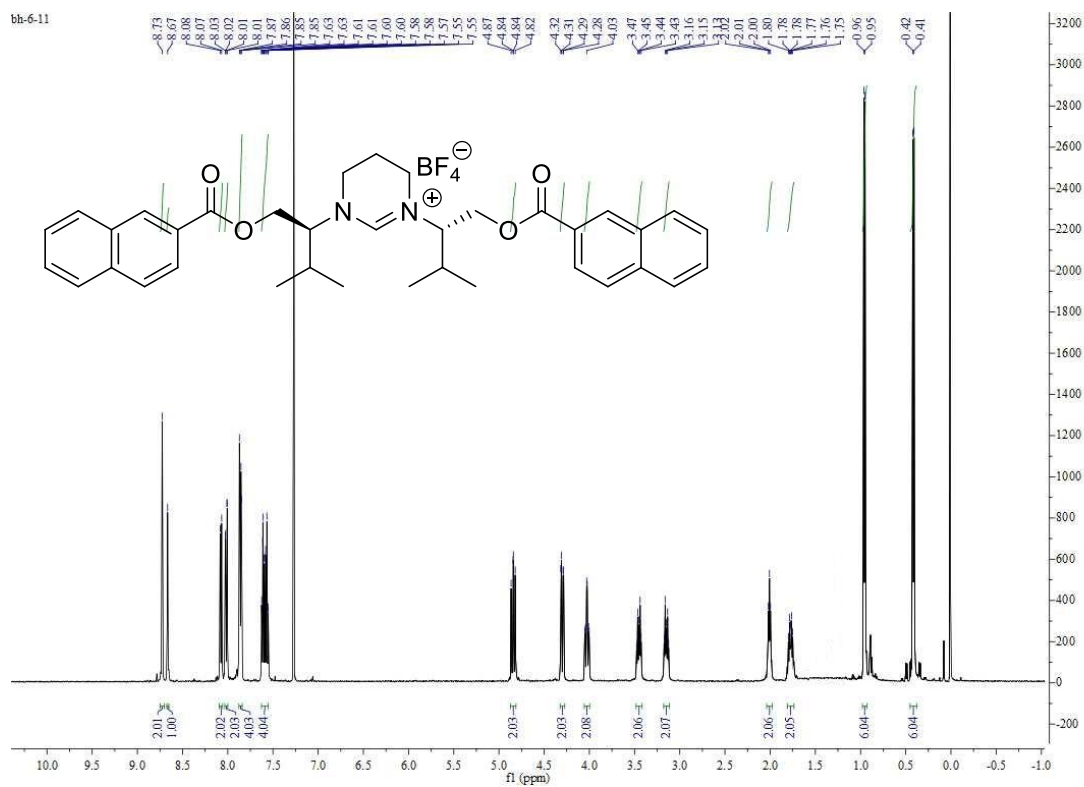


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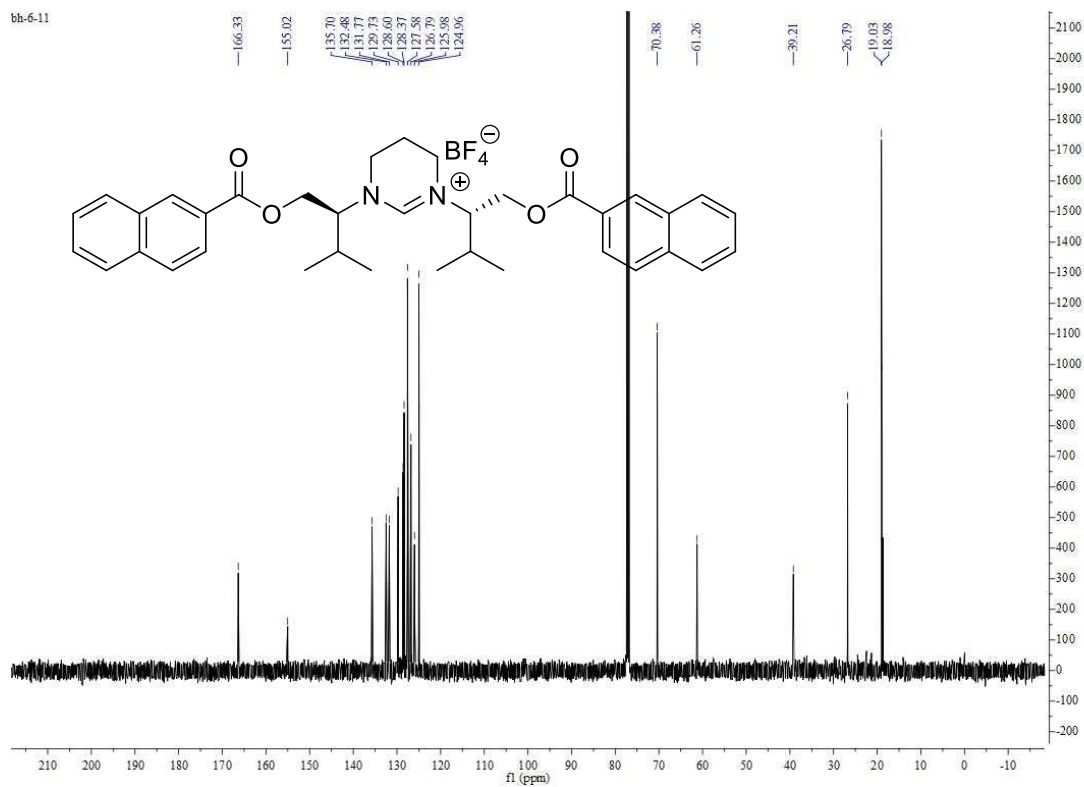




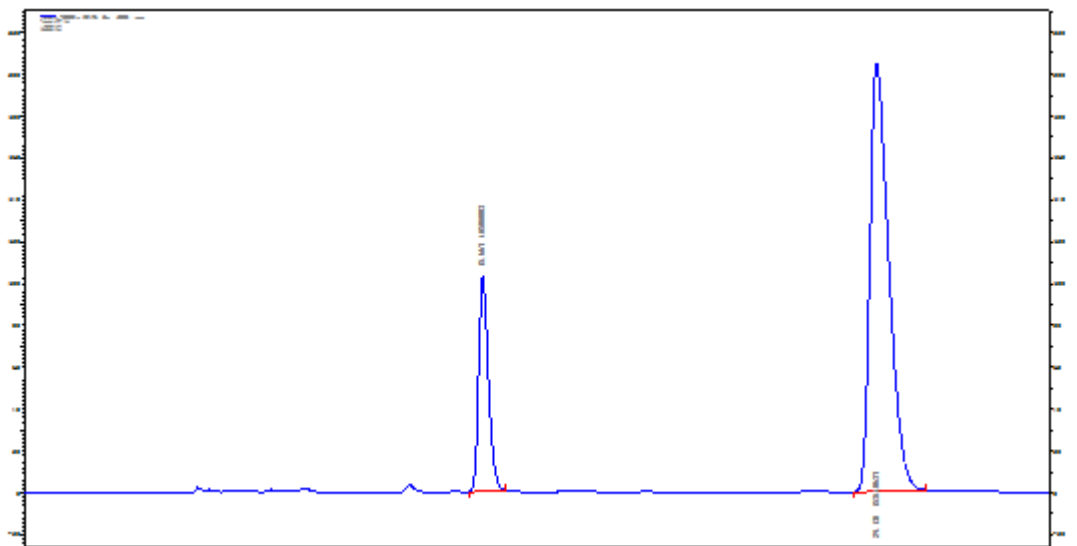
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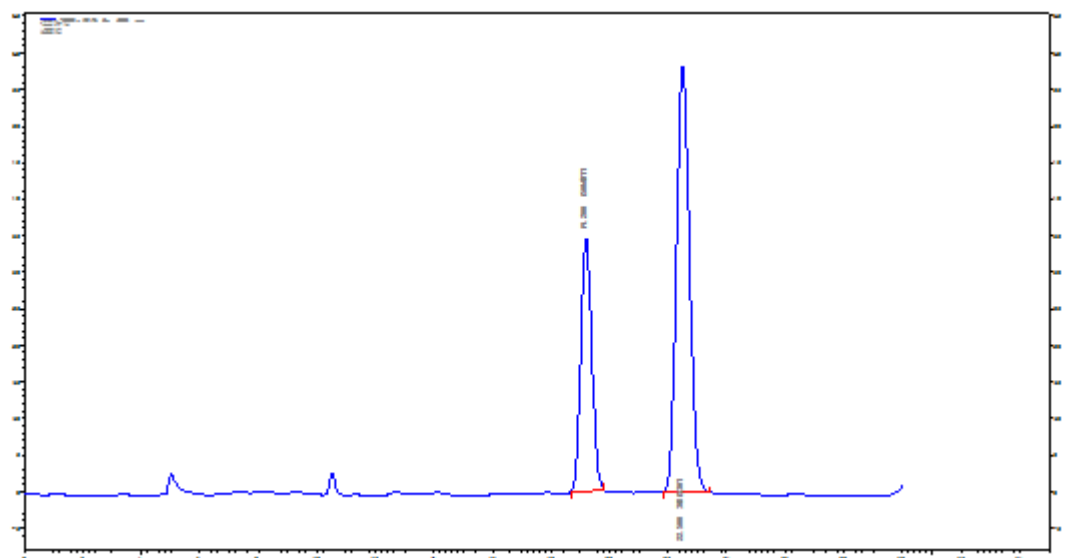
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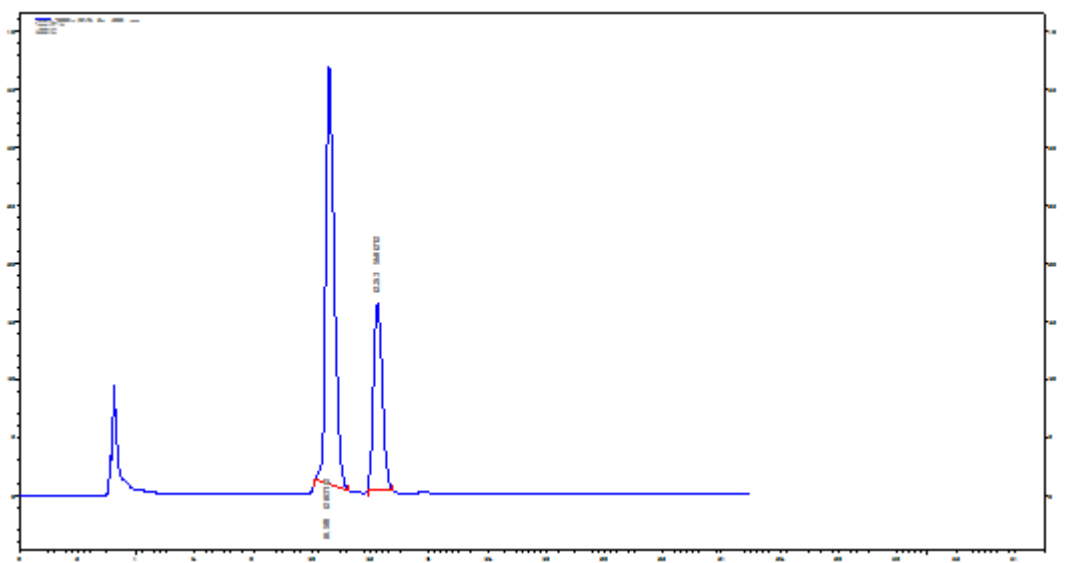
3. HPLC data of 8.



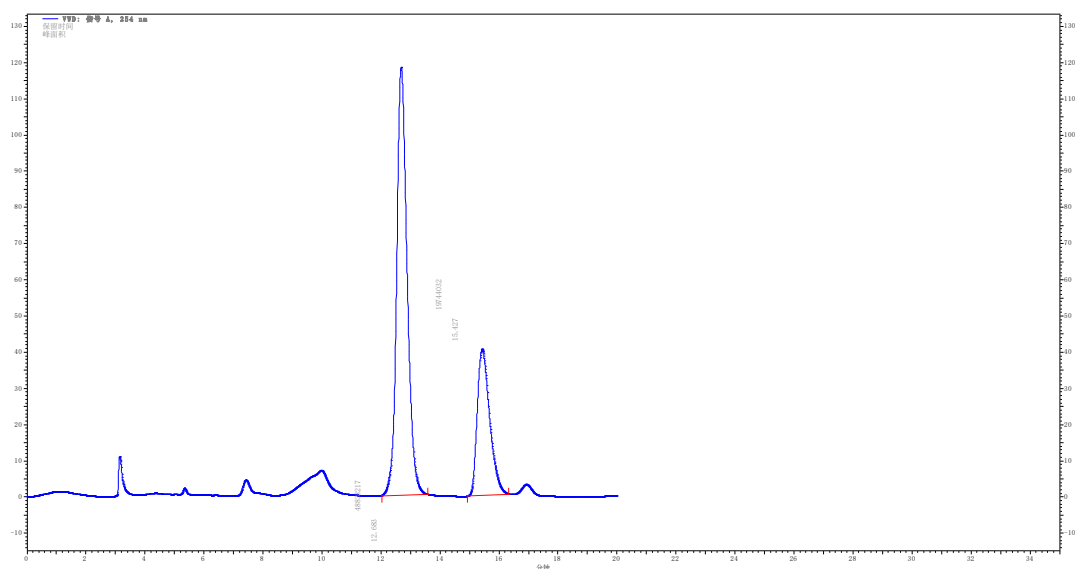
8a	Peak#	Time(min)	Area(%)
	1	15.667	20.91
	2	29.130	79.09



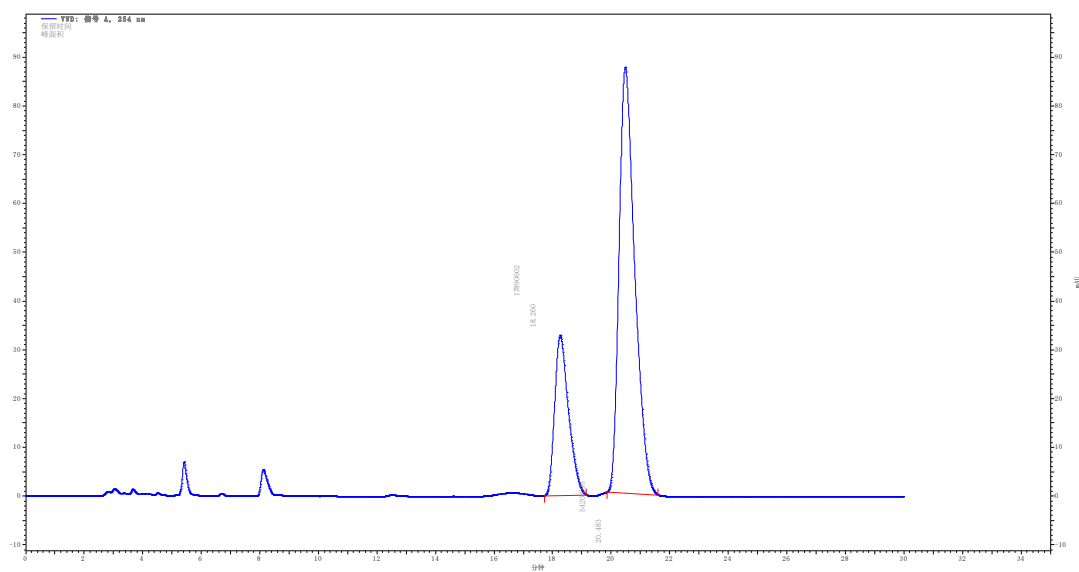
8b	Peak#	Time(min)	Area(%)
	1	19.200	33.20
	2	22.500	66.80



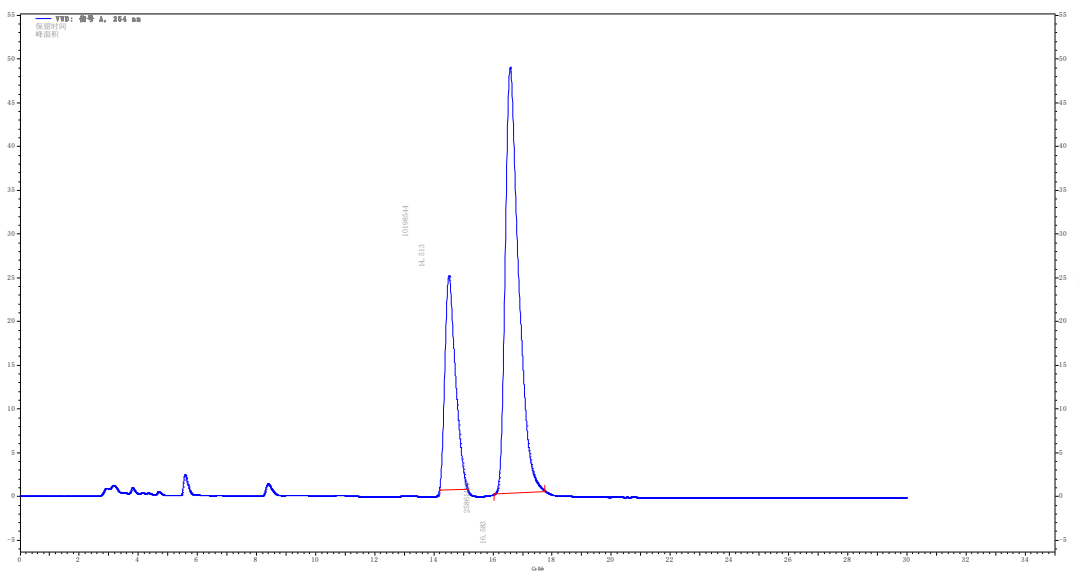
8c	Peak#	Time(min)	Area(%)
	1	10.587	68.06
	2	12.243	31.94



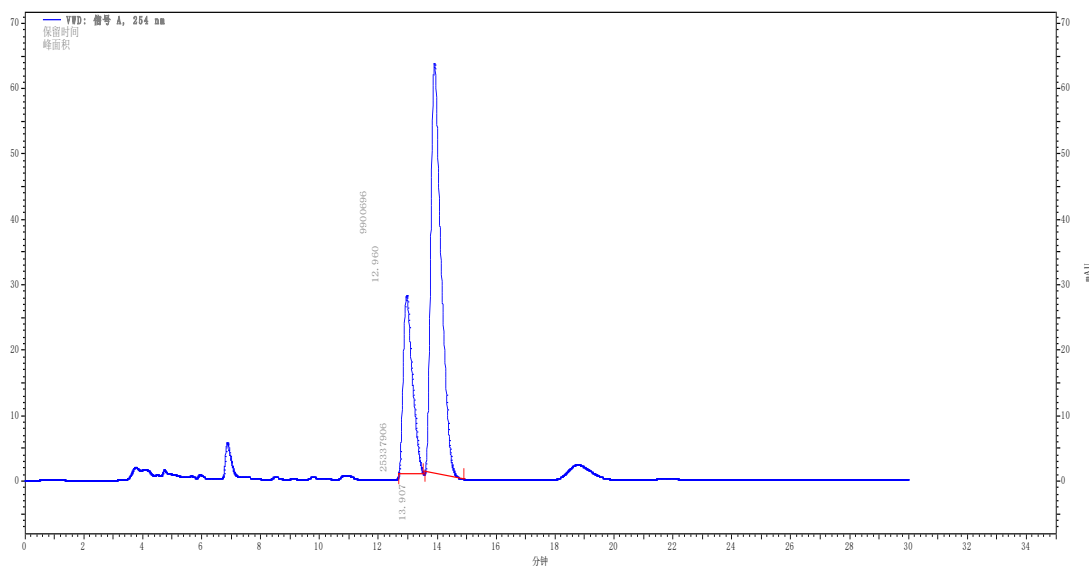
8d	Peak#	Time(min)	Area(%)
	1	12.683	71.21
	2	15.427	28.79



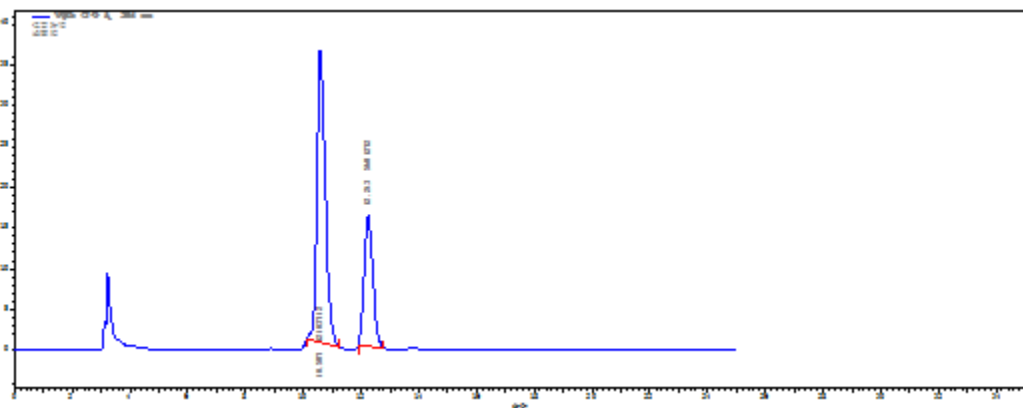
8e	Peak#	Time(min)	Area(%)
	1	18.260	24.81
	2	20.483	75.19



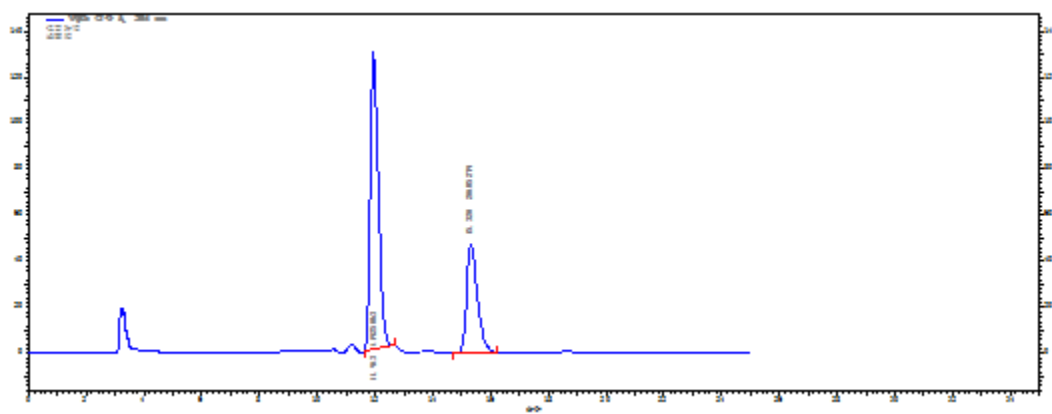
8f	Peak#	Time(min)	Area(%)
	1	14.513	28.28
	2	16.583	71.72



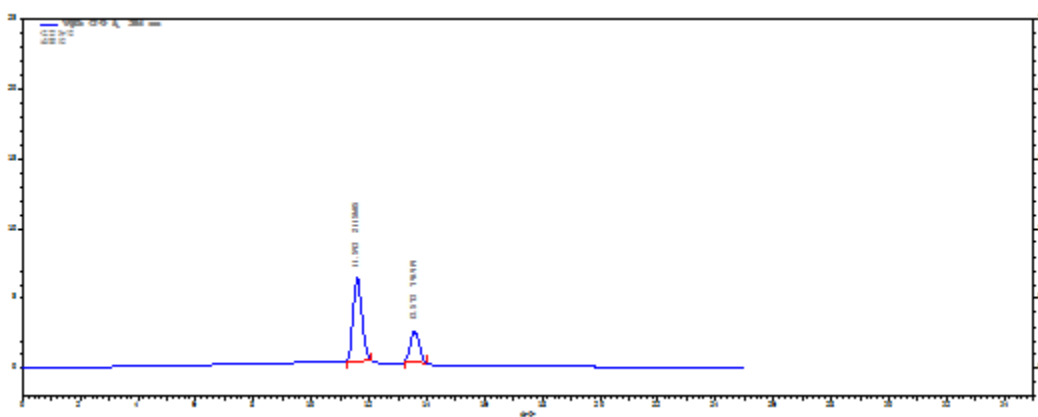
8g	Peak#	Time(min)	Area(%)
	1	12.960	28.10
	2	13.907	71.90



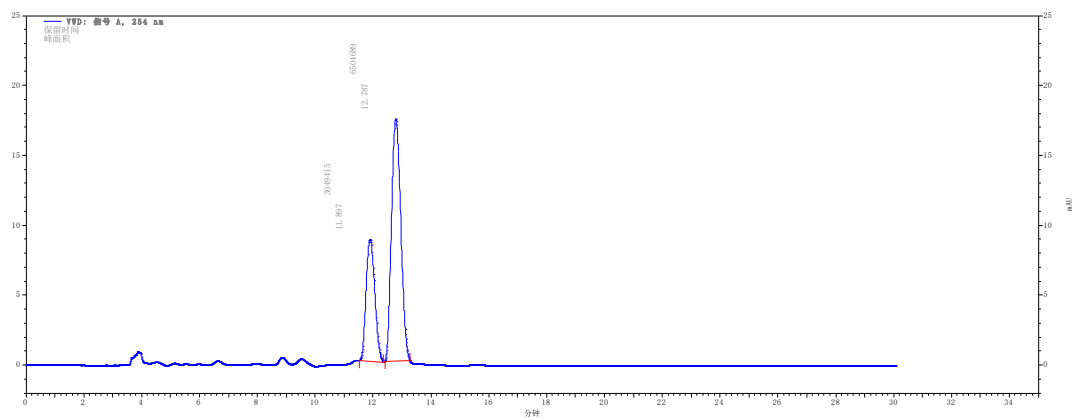
8h	Peak#	Time(min)	Area(%)
	1	10.587	68.06
	2	12.243	31.94



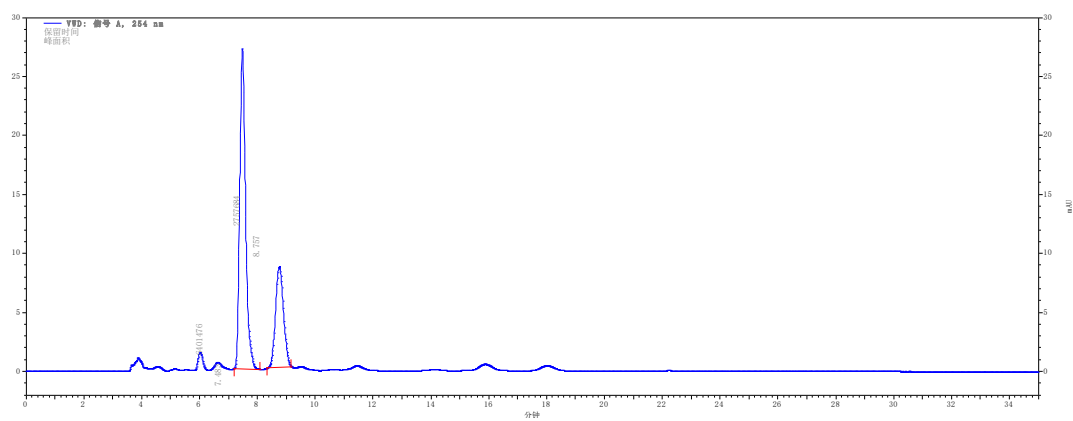
8i	Peak#	Time(min)	Area(%)
	1	11.943	67.18
	2	15.320	32.82



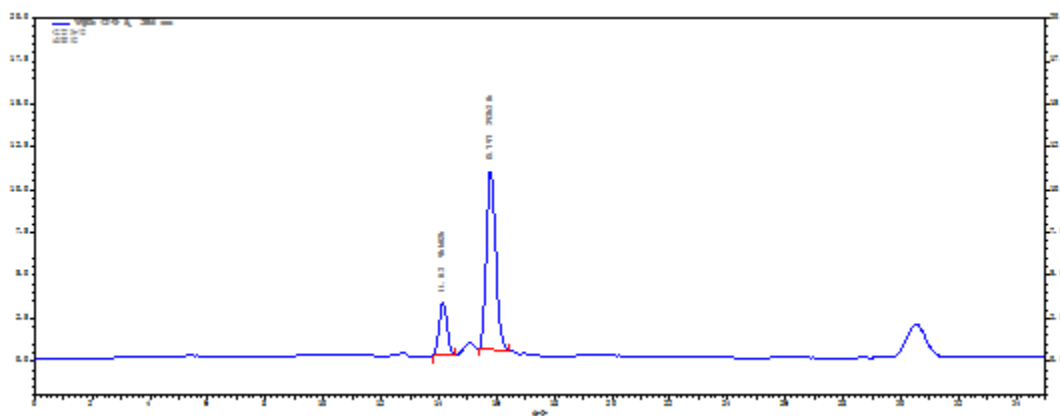
8j	Peak#	Time(min)	Area(%)
	1	11.593	72.69
	2	13.573	27.31



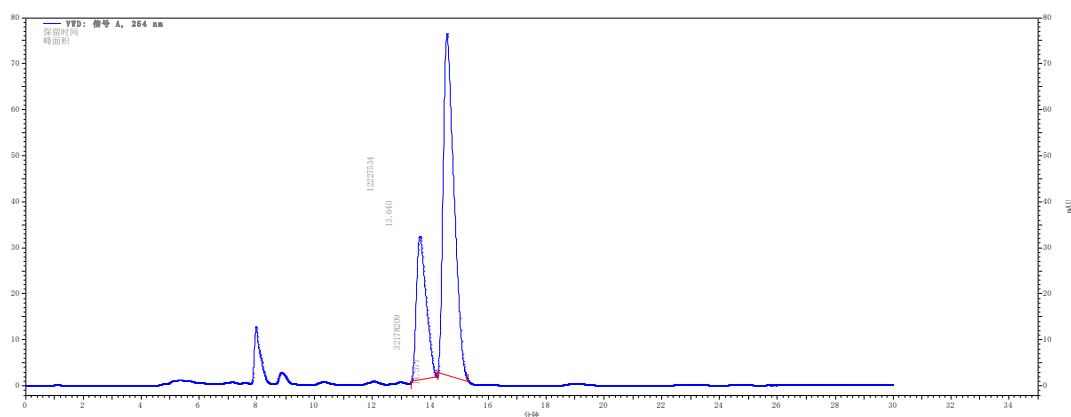
8k	Peak#	Time(min)	Area(%)
	1	11.897	31.92
	2	12.787	68.08



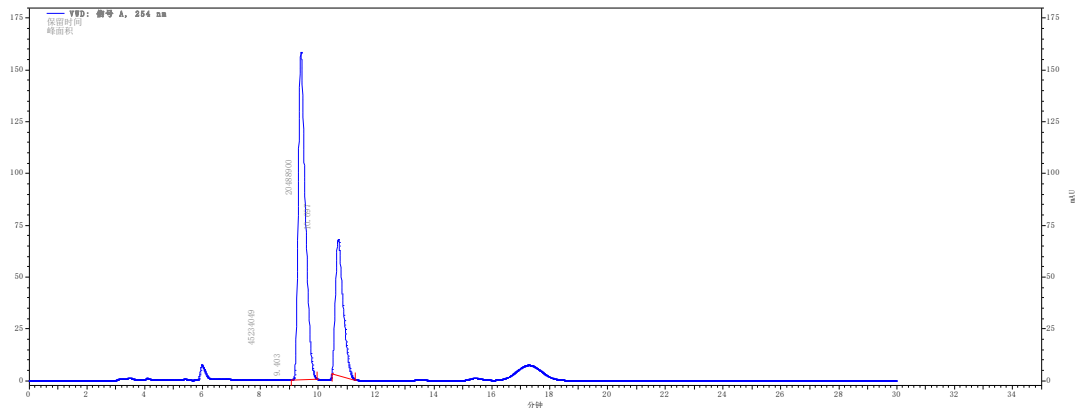
8l	Peak#	Time(min)	Area(%)
	1	7.483	69.89
	2	8.757	30.11



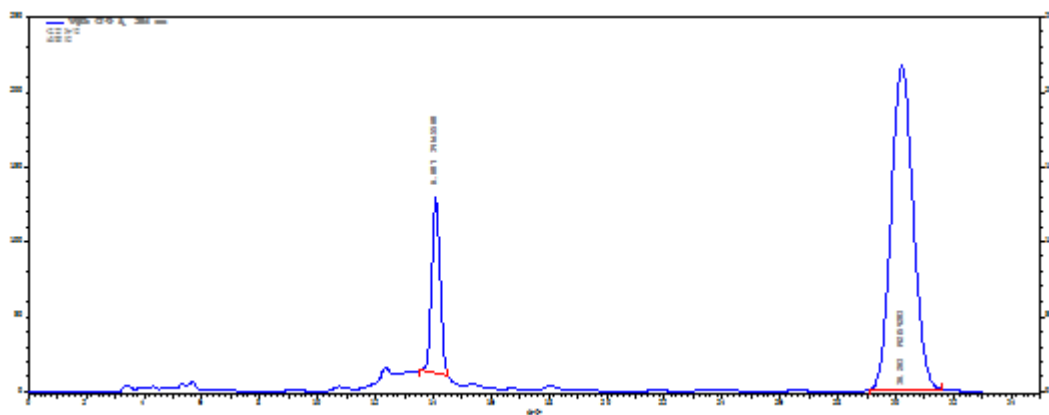
8m	Peak#	Time(min)	Area(%)
	1	14.143	19.71
	2	15.797	80.29



8n	Peak#	Time(min)	Area(%)
	1	13.640	27.54
	2	14.577	72.46



8o	Peak#	Time(min)	Area(%)
	1	9.403	68.83
	2	10.697	31.17



8p	Peak#	Time(min)	Area(%)
	1	14.087	17.10
	2	30.203	82.90