Supporting Information

Simple synthesis of [Ru(CO_3)(NHC)(*p*-cymene)] complexes and their use in transfer hydrogenation catalysis

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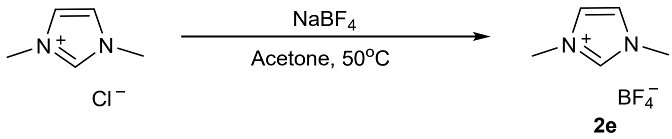
Synthesis of IMe·HBF$_4$

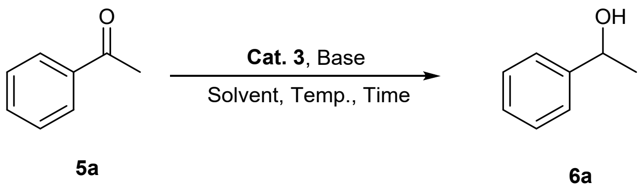


The synthesis process is similar to the literature.[1] In a 20 mL vial, 132.6 mg of IMe·HCl (1 mmol, 1 eq.) and 164.6 mg of $NaBF_4$ (1.2 mmol, 1.2 eq.) were stirred in 2 mL of acetone at 50 °C for 6 hours. The mixture was allowed to cool down to room temperature, filtered the suspension and washed the solid by 2 mL of acetone. The filtrate was collected and added extra 82.4 mg of $NaBF_4$ (0.75 mmol, 0.75 eq.) to the solvent, stirred at 50 °C for 3h. Filtered through a microfilter and washed with 6 mL of acetone (3 x 2 mL), and concentrated under reduced pressure. The product was dried in high vacuum overnight. Yield of product is 81 %.

^{1}H NMR (300 MHz, Acetone) δ 8.90 (s, 1H, N=C*H*N), 7.66 (d, *J* = 1.6 Hz, 2H, C*H*=C*H*), 4.02 (d, *J* = 0.5 Hz, 7H, NCH_3). ^{19}F NMR: δ -153.24 (s, 4F, BF_4).

Selected Optimization of the Reaction Conditions

Table S1 Optimization of the reaction conditions for hydrogenation.

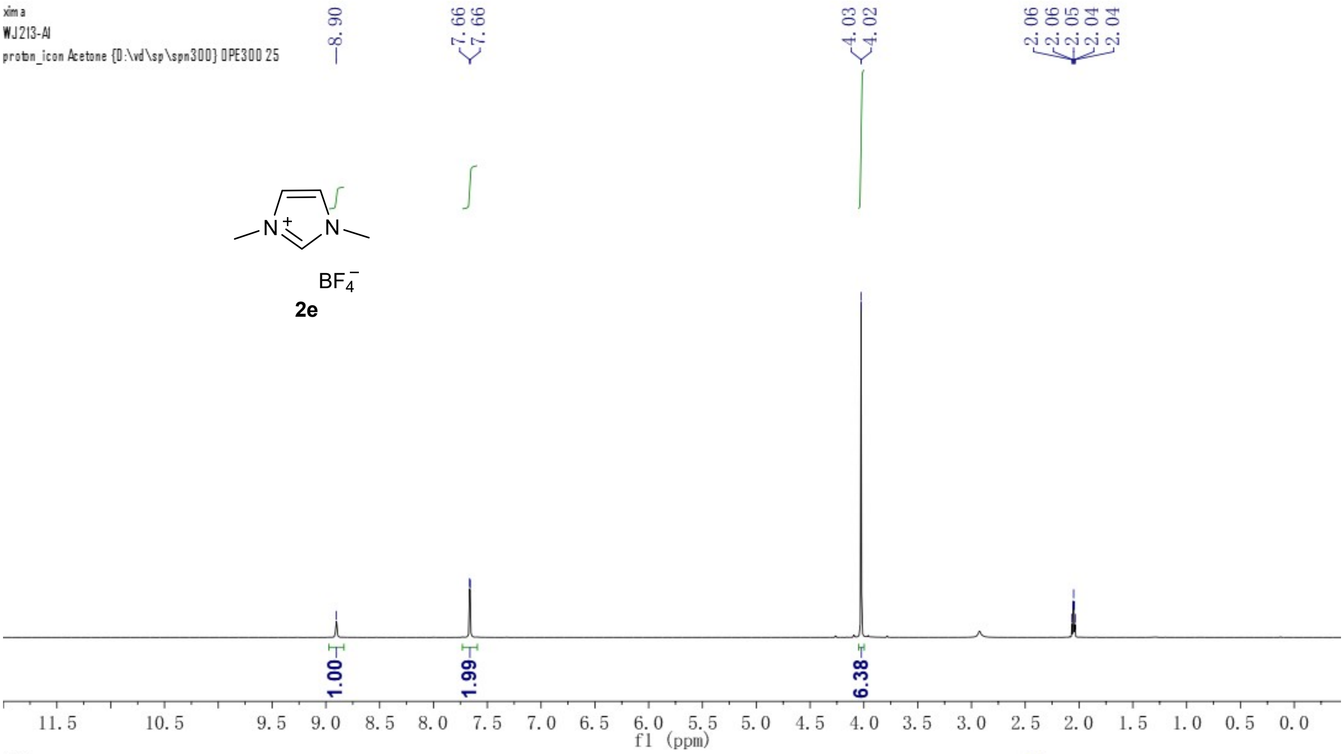


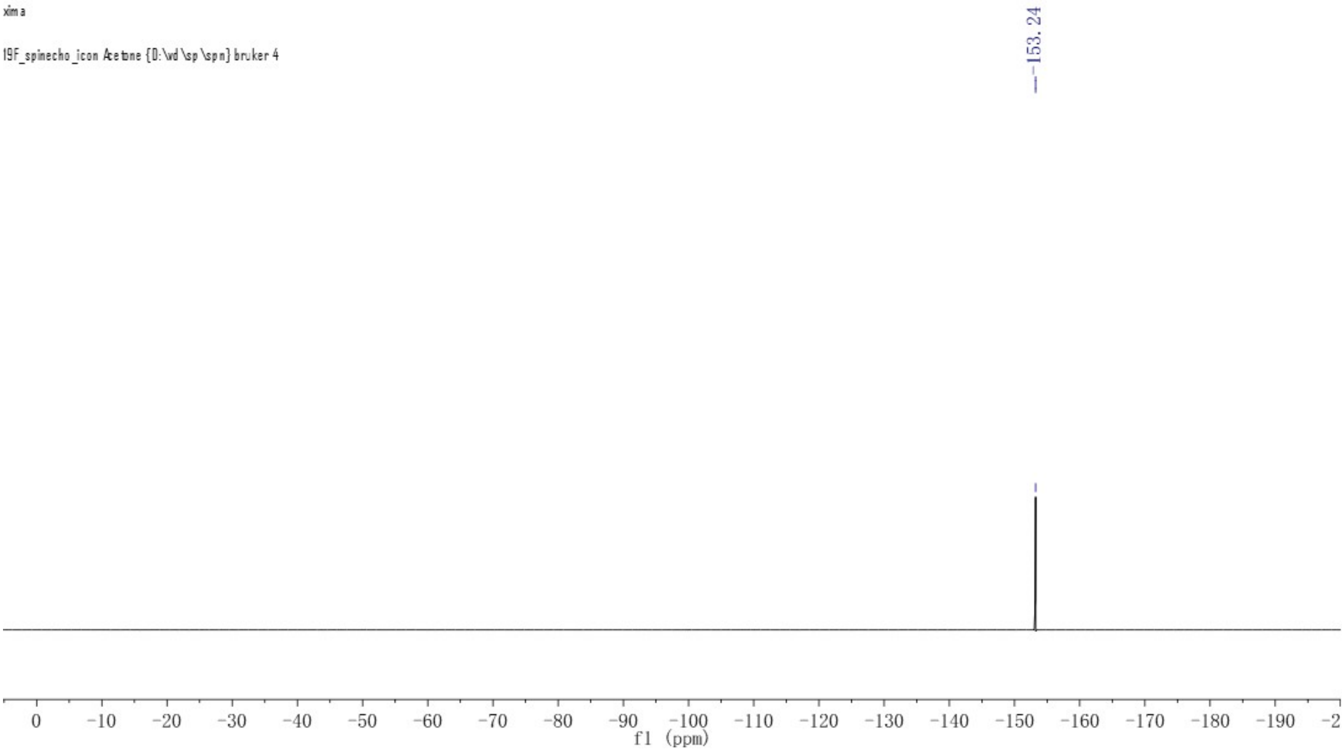
Entry	Ru-NHC	Base	Solvent	T(ºC)	Time (h)	Yield (%)[b]
1	**3a**	NaOH (20%)	^{i}PrOH	100	16	84
2	**3a**	K^{t}BuO (20%)	^{i}PrOH	100	16	91
3	**3a**	K_3PO_4 (20 %)	^{i}PrOH	100	16	trace
4	**3a**	K_2CO_3 (20%)	^{i}PrOH	100	16	47
5	**3a**	KOH (10%)	^{i}PrOH	100	16	93
6	**3a**	KOH (5%)	^{i}PrOH	100	16	76
7	**3a**	KOH (5%)	^{i}PrOH	100	36	83
8	**3a**	KOH (2.5%)	^{i}PrOH	100	16	56
9	-	KOH (10%)	^{i}PrOH	80	4	25
10	**3e**	KOH (10%)	EtOH	80	4	-
11	**3e**	KOH (10%)	MeOH	80	4	-
12	**3e**	KOH (10%)	H_2O	80	4	-
13	**3e(2 mol%)**	KOH (10%)	^{i}PrOH	80	2	94
14	**3e(0.5 mol%)**	KOH (10%)	^{i}PrOH	80	2	61

[a] Reaction conditions: **5a** (0.5 mmol, 1 eq.), **3** (1 mol%), Base, Solvent (1.5 mL) in a 4 mL vial. [b] NMR yields using 1,3,5-trimethoxybenzene as internal standard.

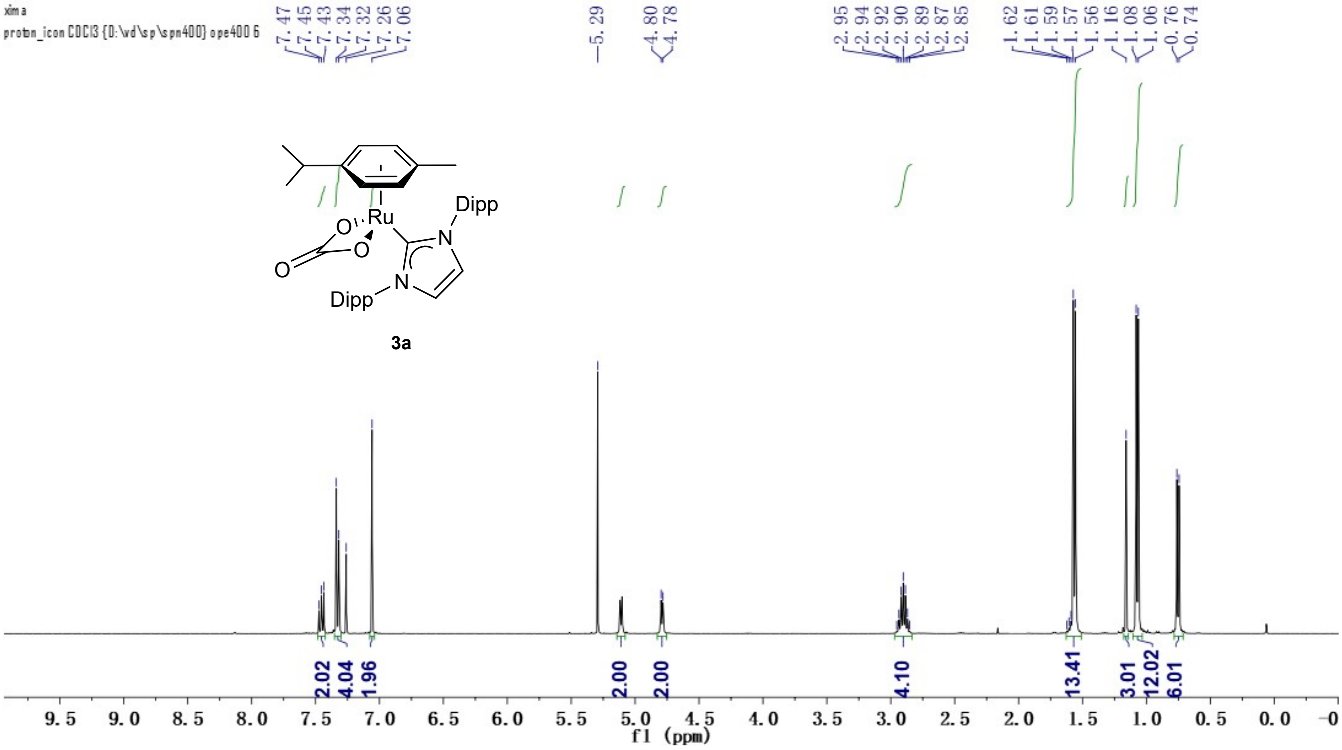
NMR spectra

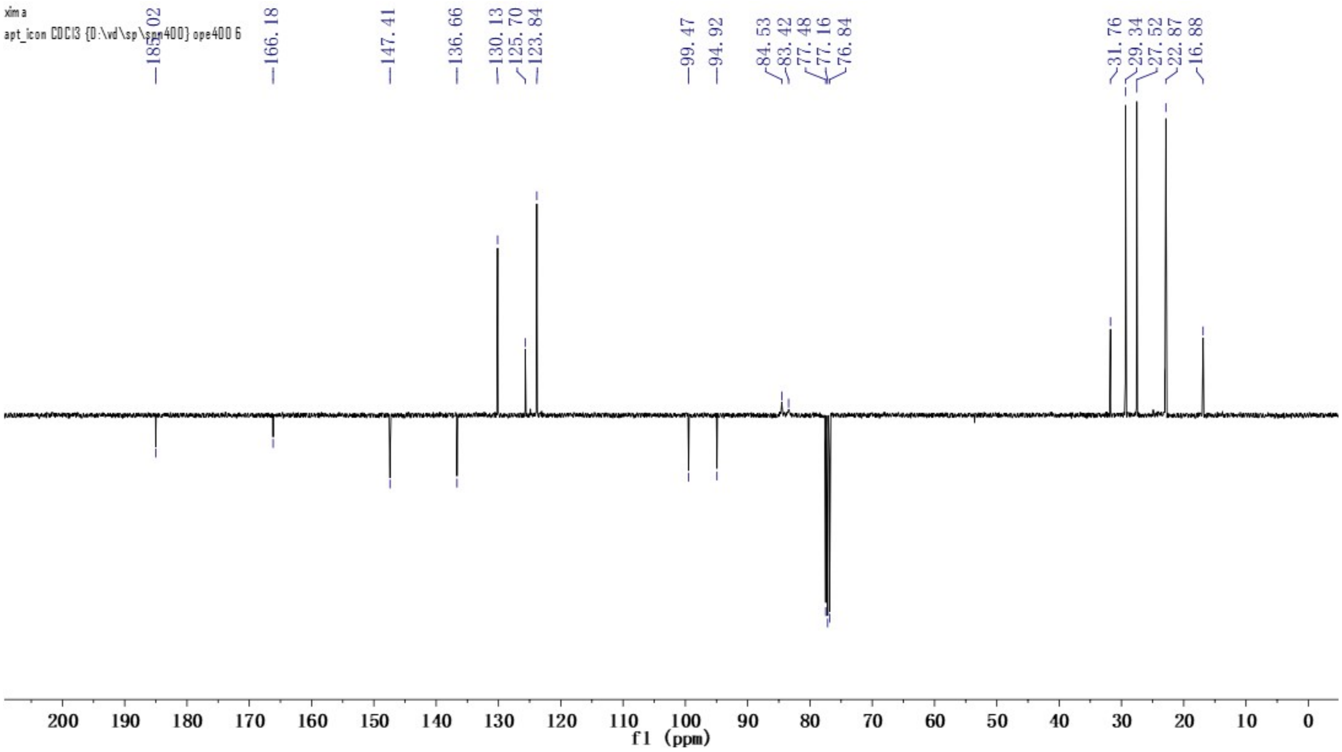
^{1}H and ^{19}F NMR of IMe·HBF_4 (**2e**)



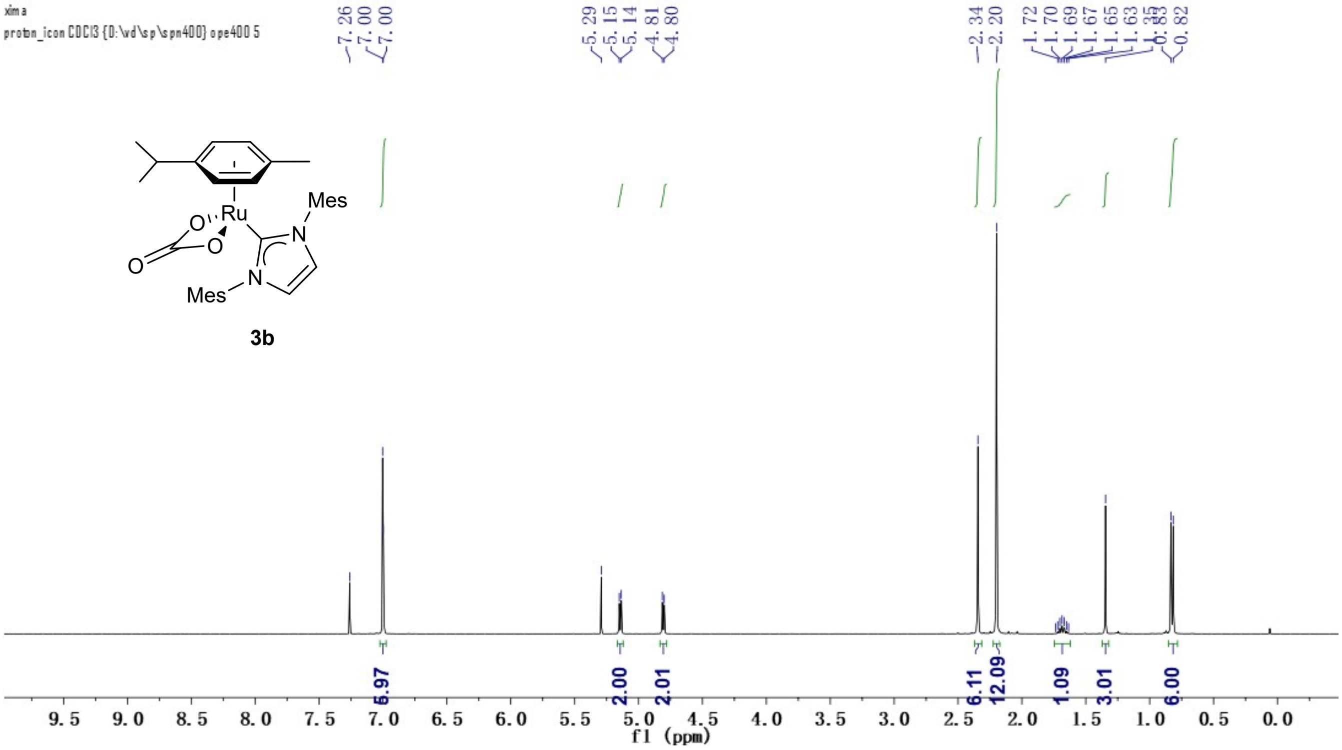


^{1}H and ^{13}C {1H} apt NMR of [Ru(CO_3)(IPr)(*p*-cymene)] (**3a**)





^{1}H and ^{13}C {1H} apt NMR of [Ru(CO_3)(IMes)(*p*-cymene)] (**3b**)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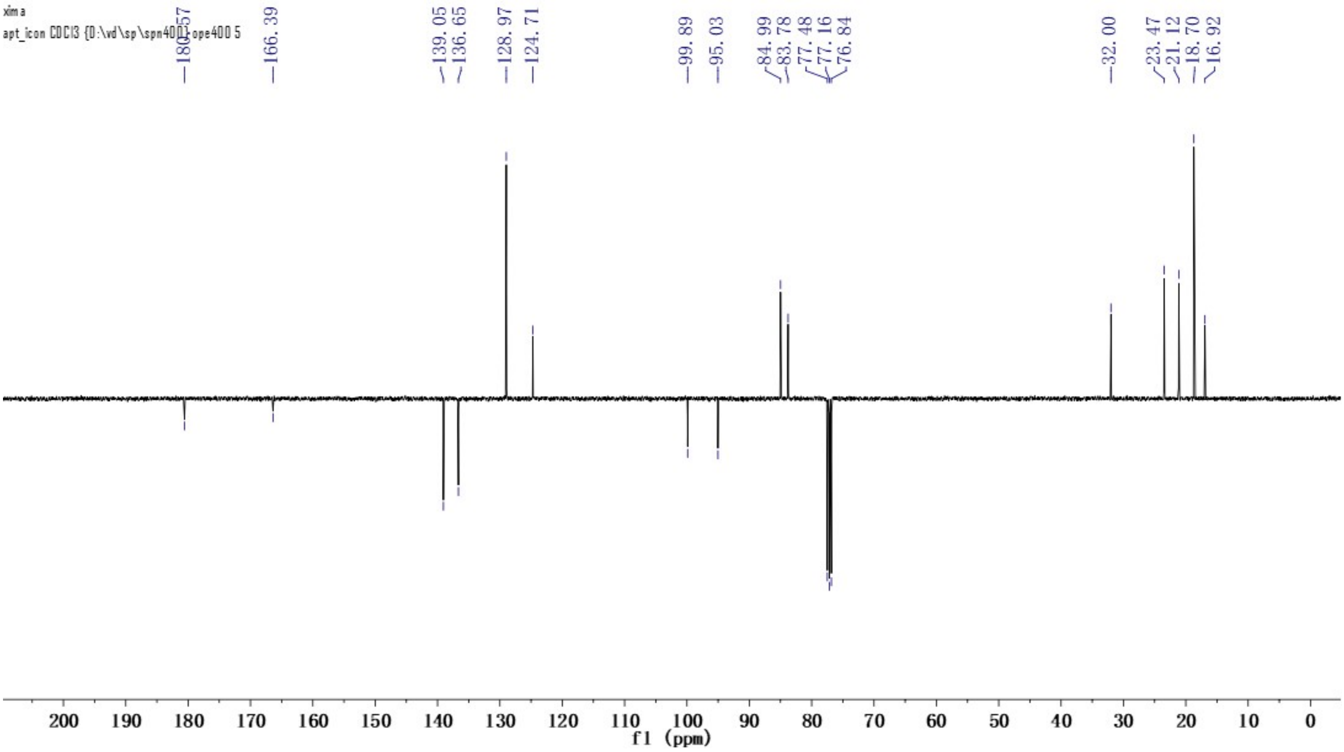
4.80
2.34
2.20
1.72
1.70
1.69
1.67
1.65
1.63
1.35
0.83
0.82
Mes
Ru
O
O
O
N
N
Mes
3b
6.97
2.00
2.01
6.11
12.09
1.09
3.01
6.00
f1 (ppm)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95.03
84.99
83.78
77.48
77.16
76.84
32.00
23.47
21.12
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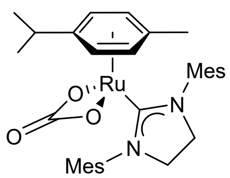
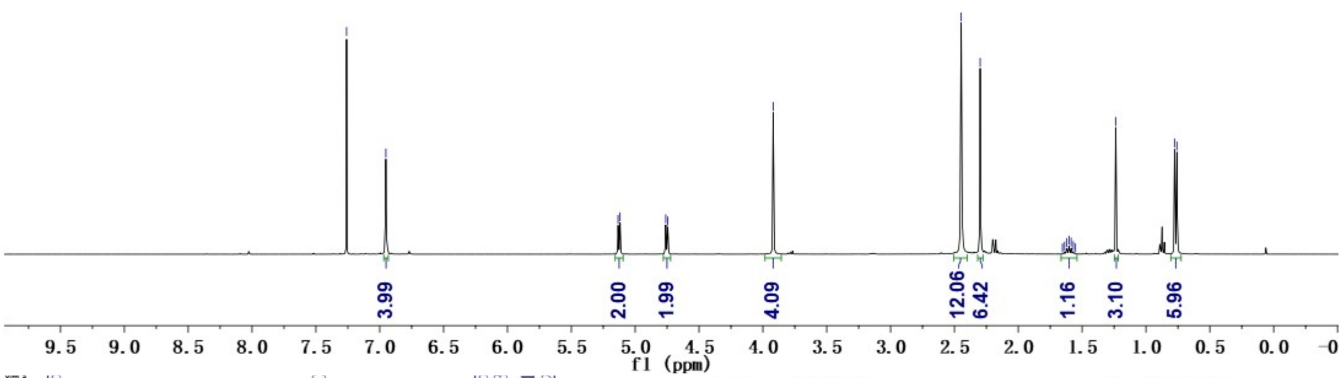
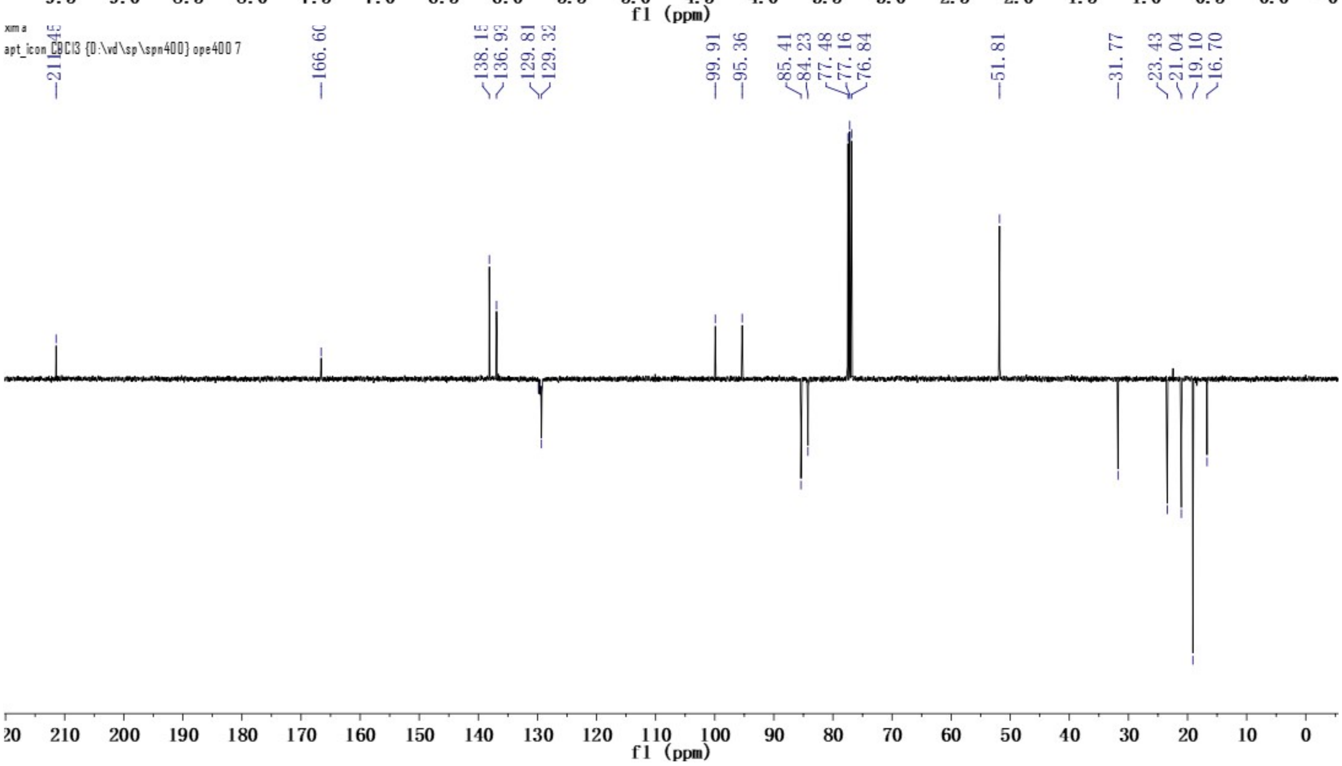
16.92
f1 (ppm)

^{1}H and ^{13}C {1H} apt NMR of [Ru(CO_3)(SIMes)(*p*-cymene)] (**3c**)

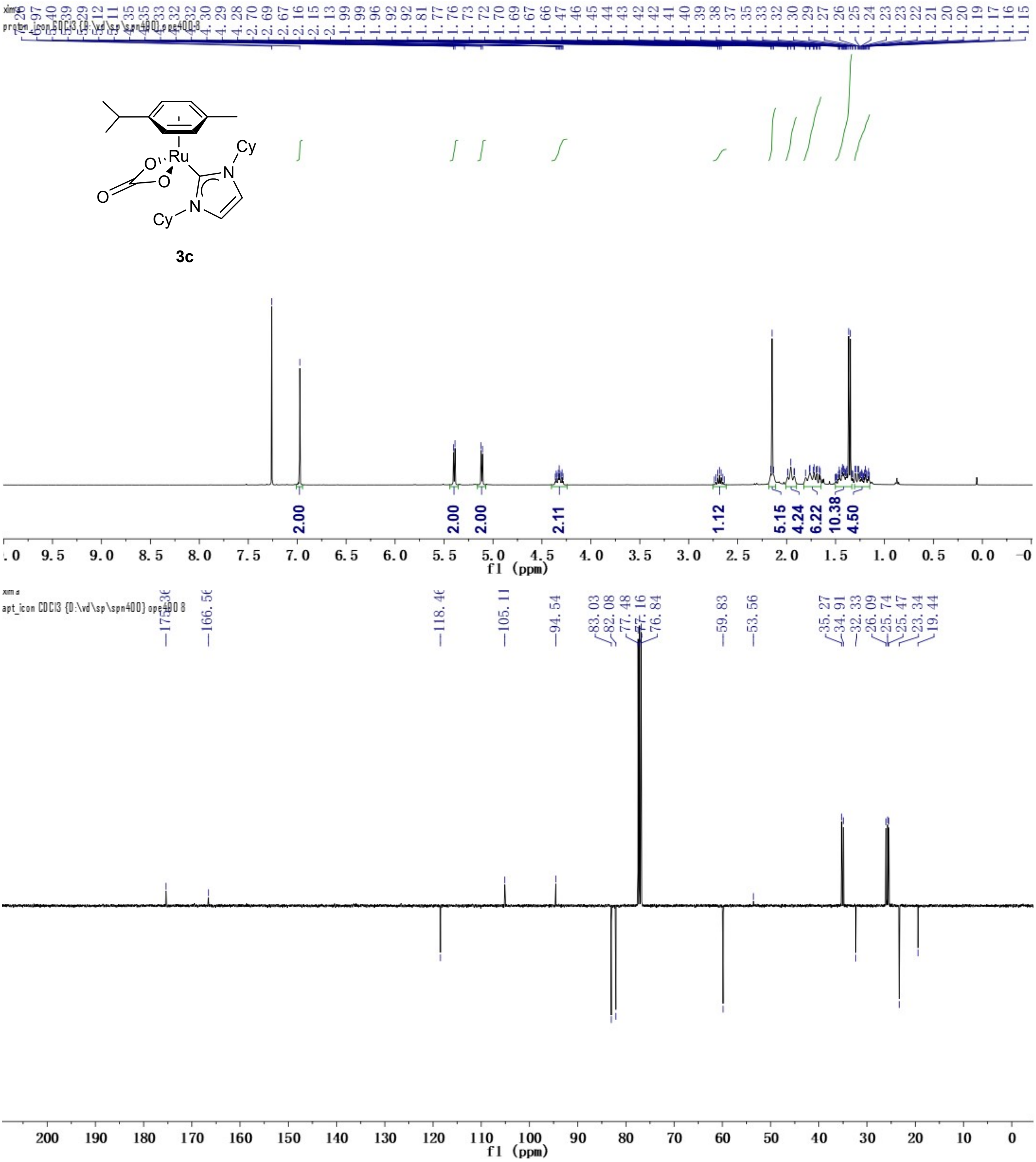


3e

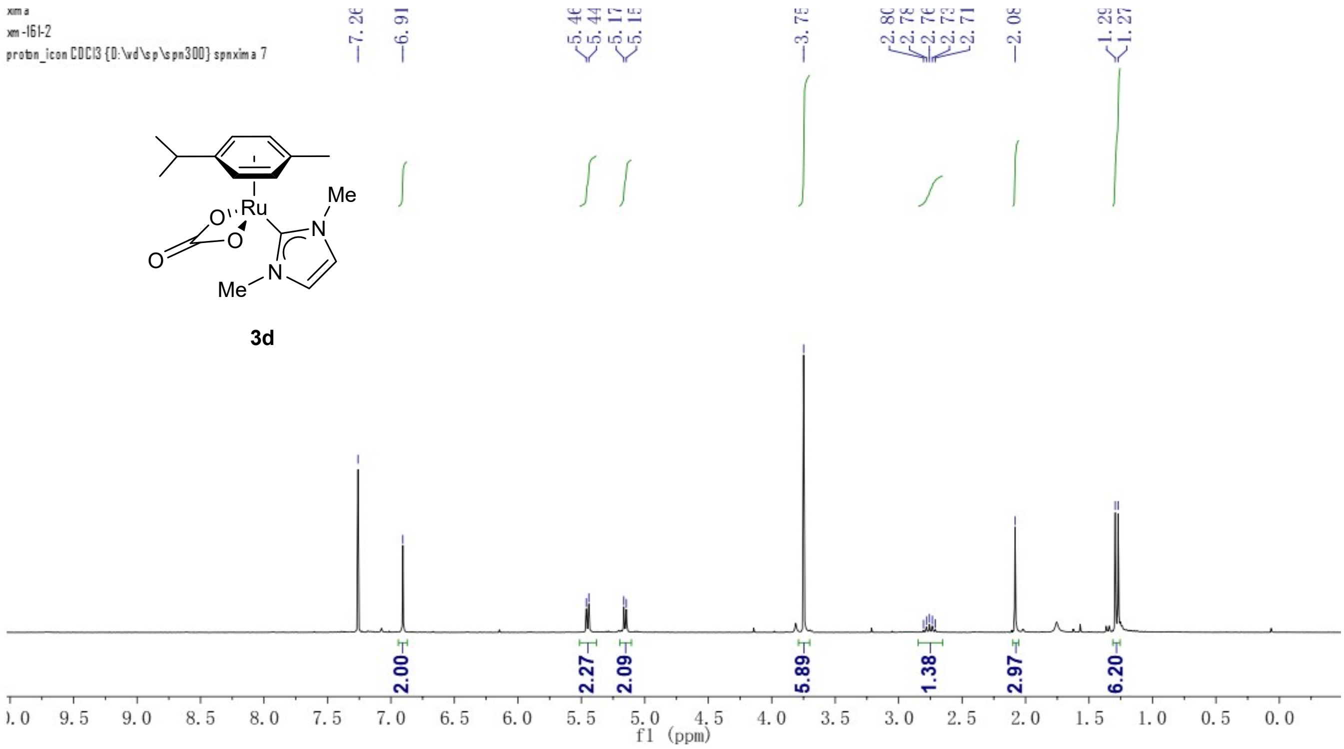


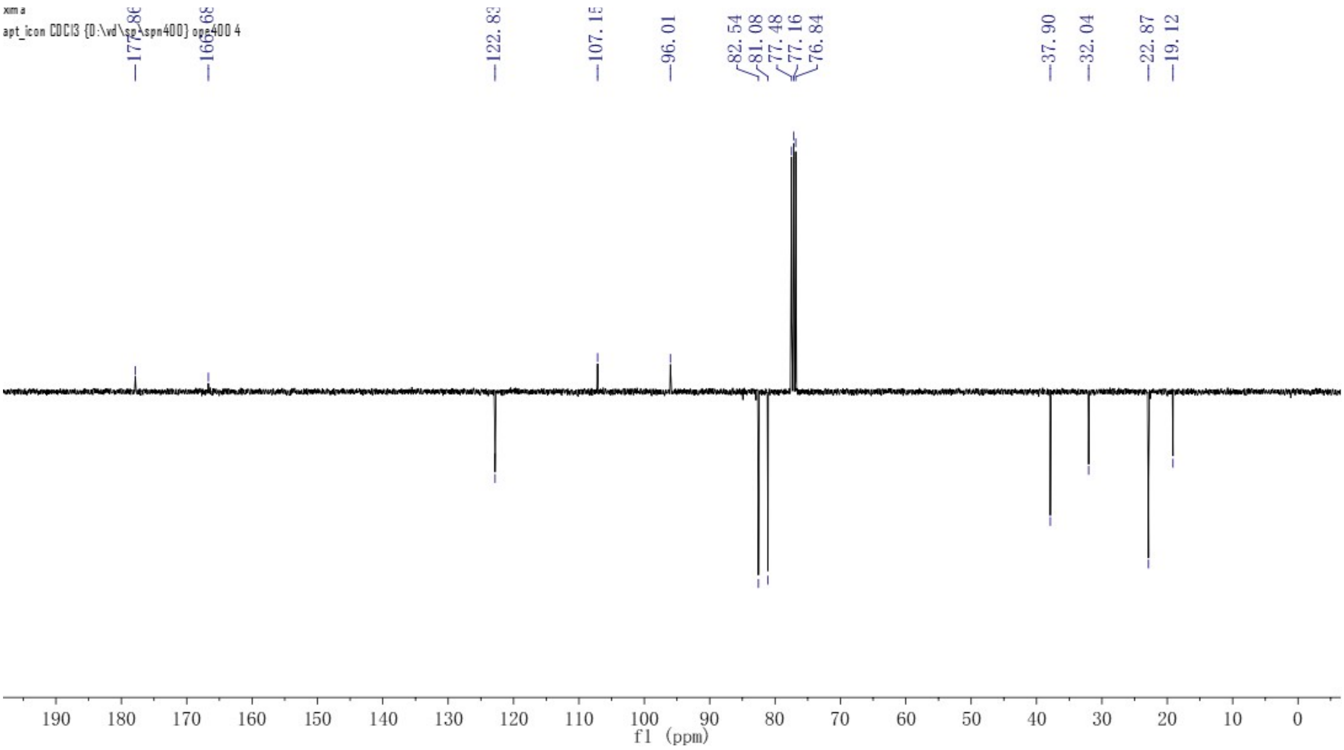


^{1}H and ^{13}C {1H} apt NMR of [Ru(CO_3)(ICy)(*p*-cymene)] (**3d**)

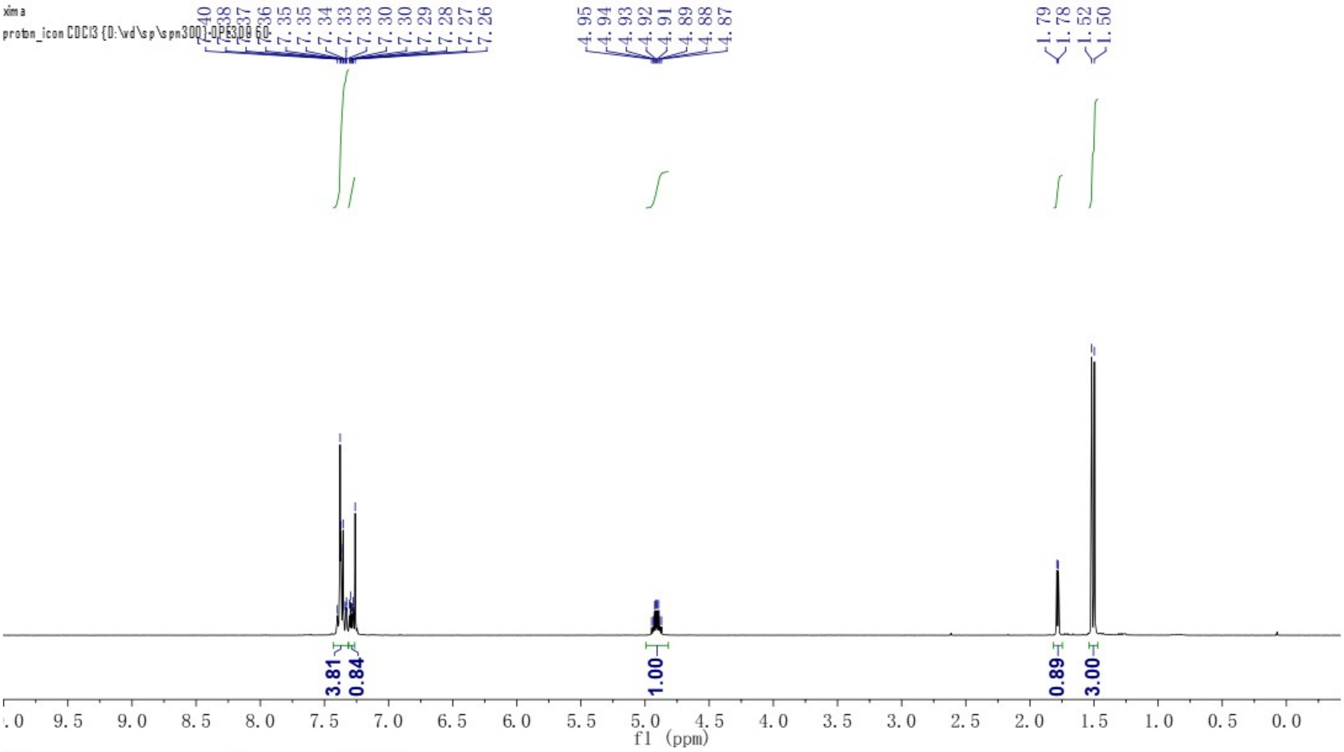


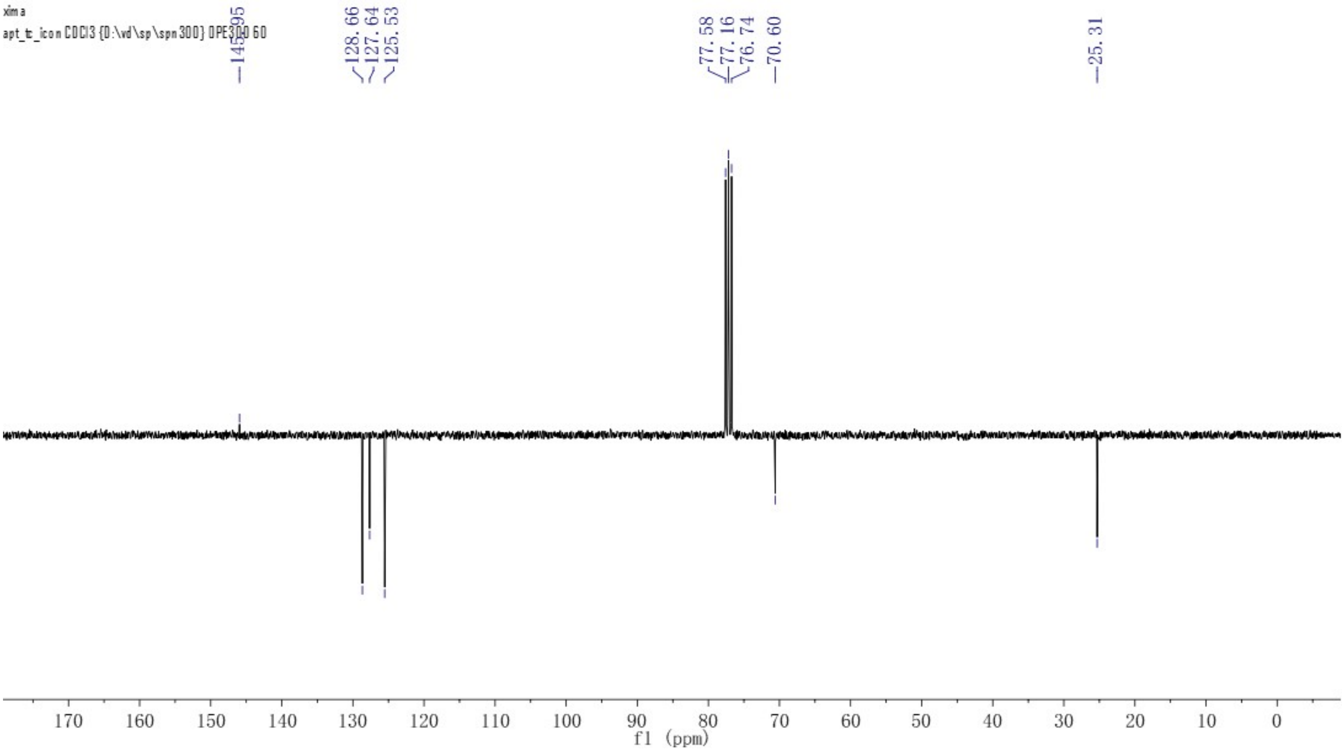
^{1}H and ^{13}C {1H} apt NMR of [Ru(CO_3)(IMe)(*p*-cymene)] (**3e**)



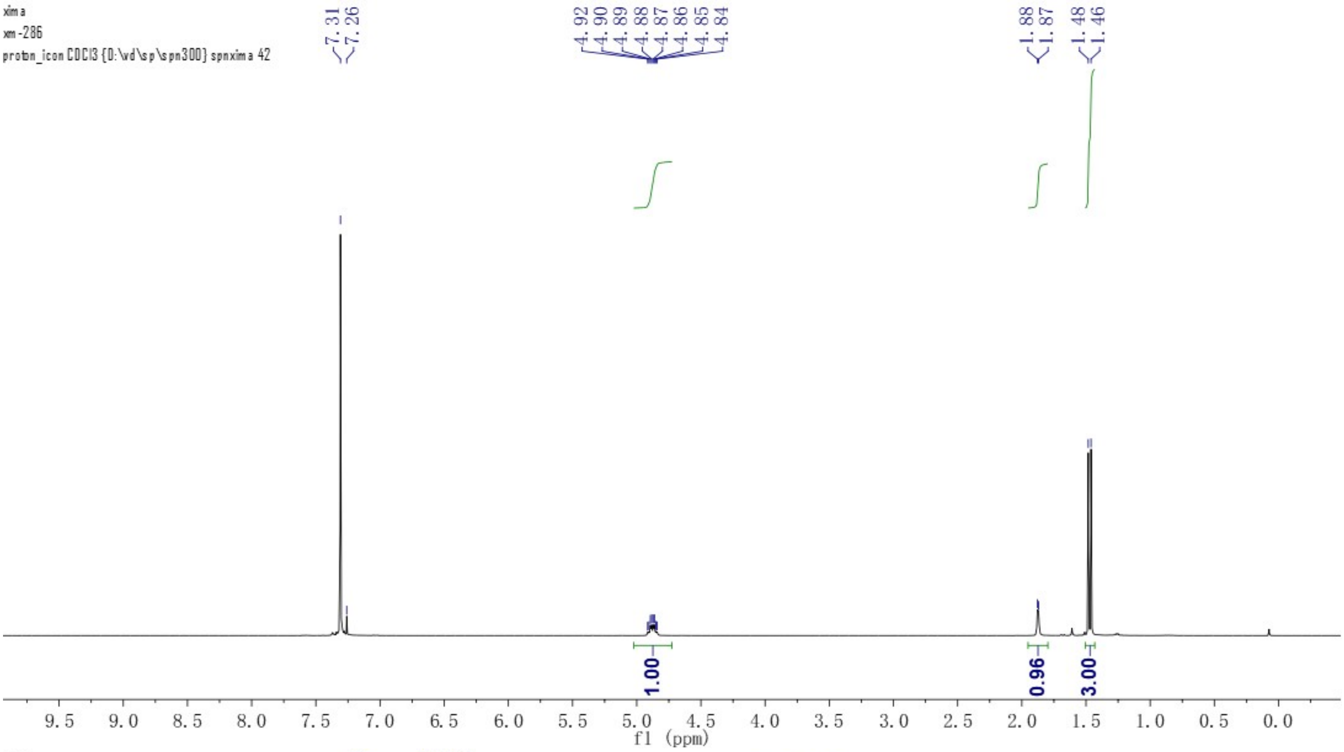


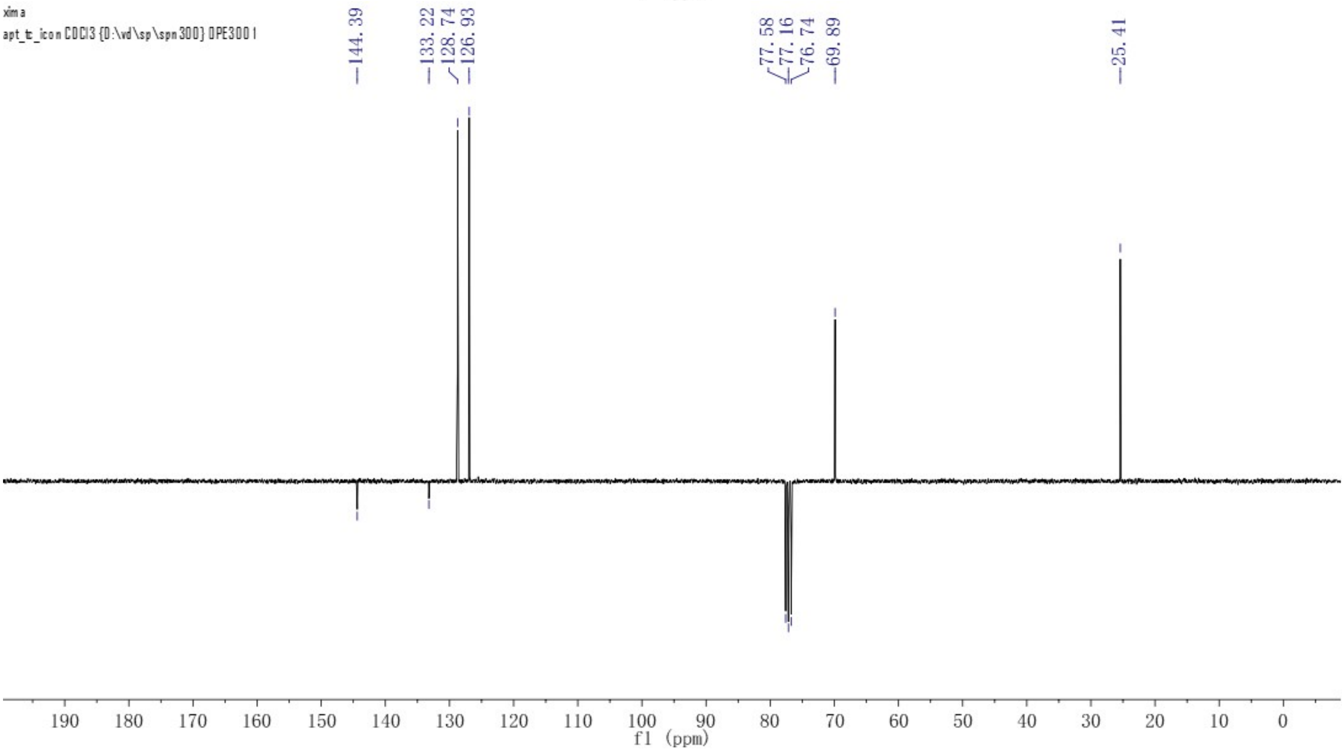
[1]H and [13]C {1H} apt NMR of *α*-Methylbenzenemethanol (**6a**)



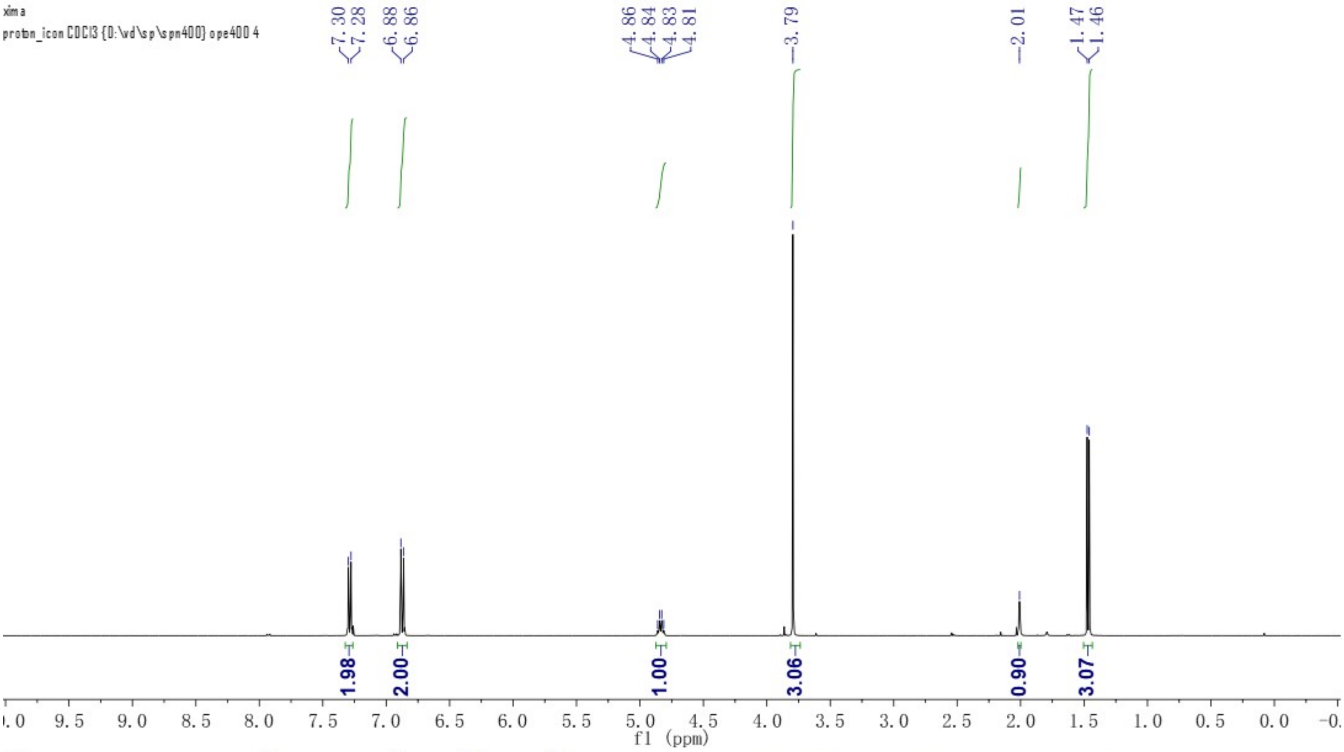


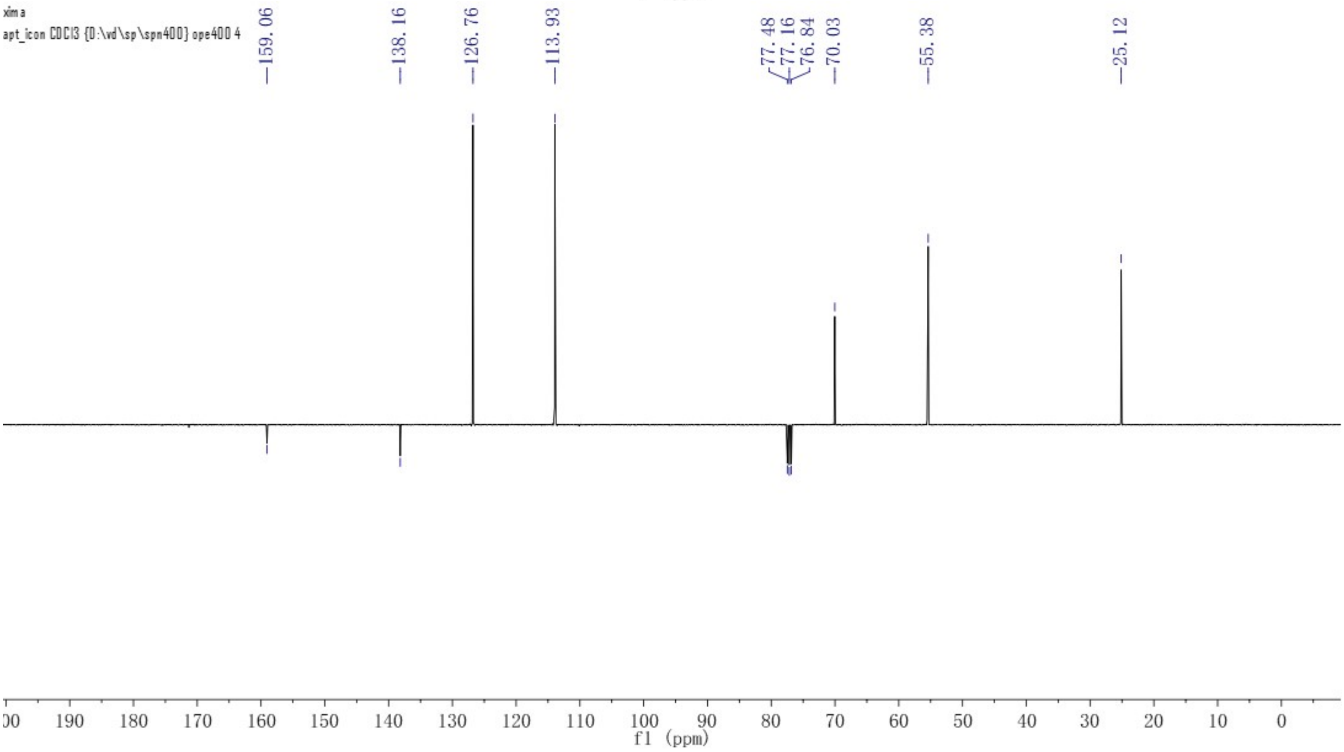
^{1}H and ^{13}C {1H} apt NMR of 4-chlorobenzenemethanol (**6b**)



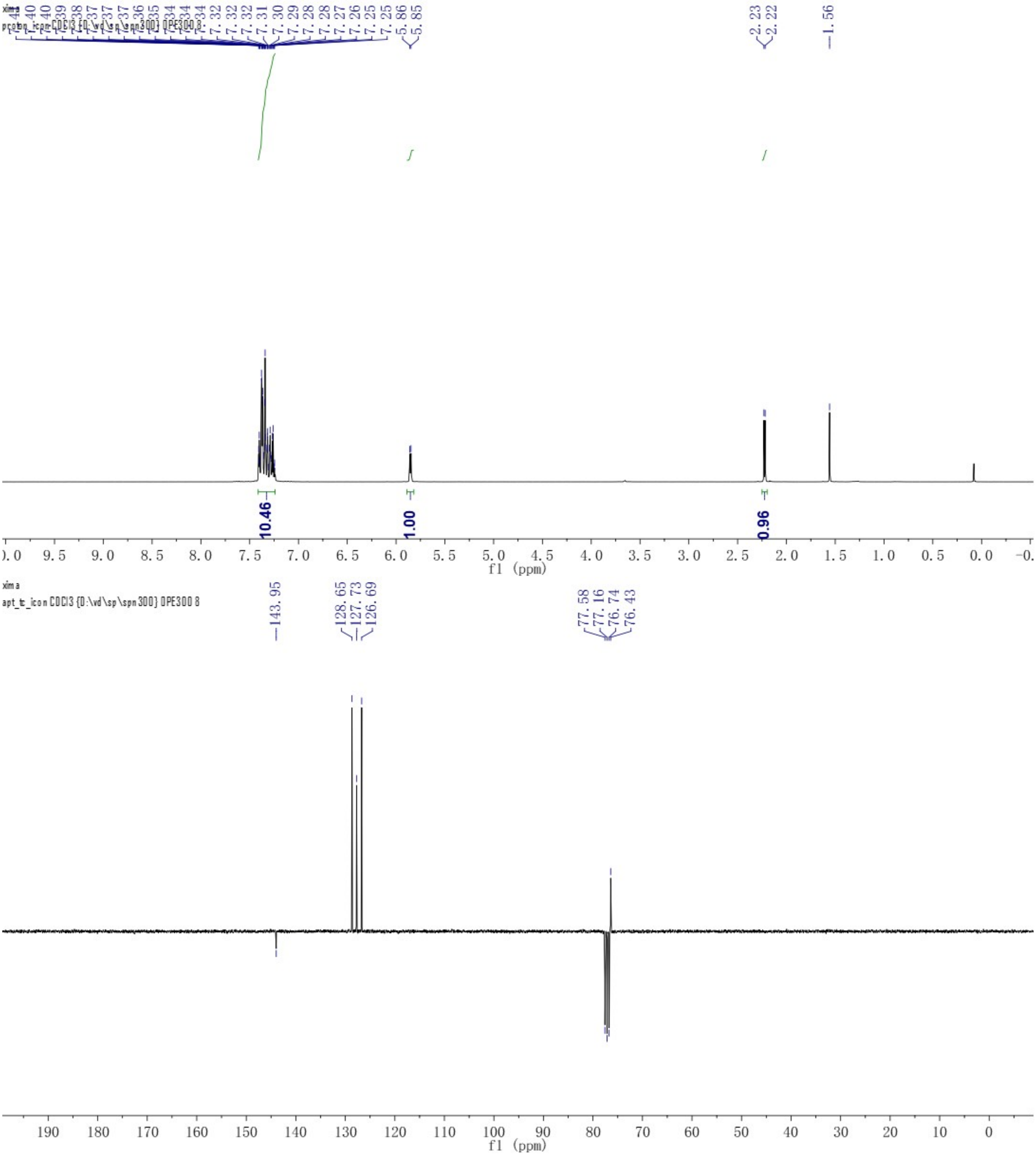


[1]H and [13]C {1H} apt NMR of 4-Methoxy-*α*-methylbenzyl alcohol (**6c**)

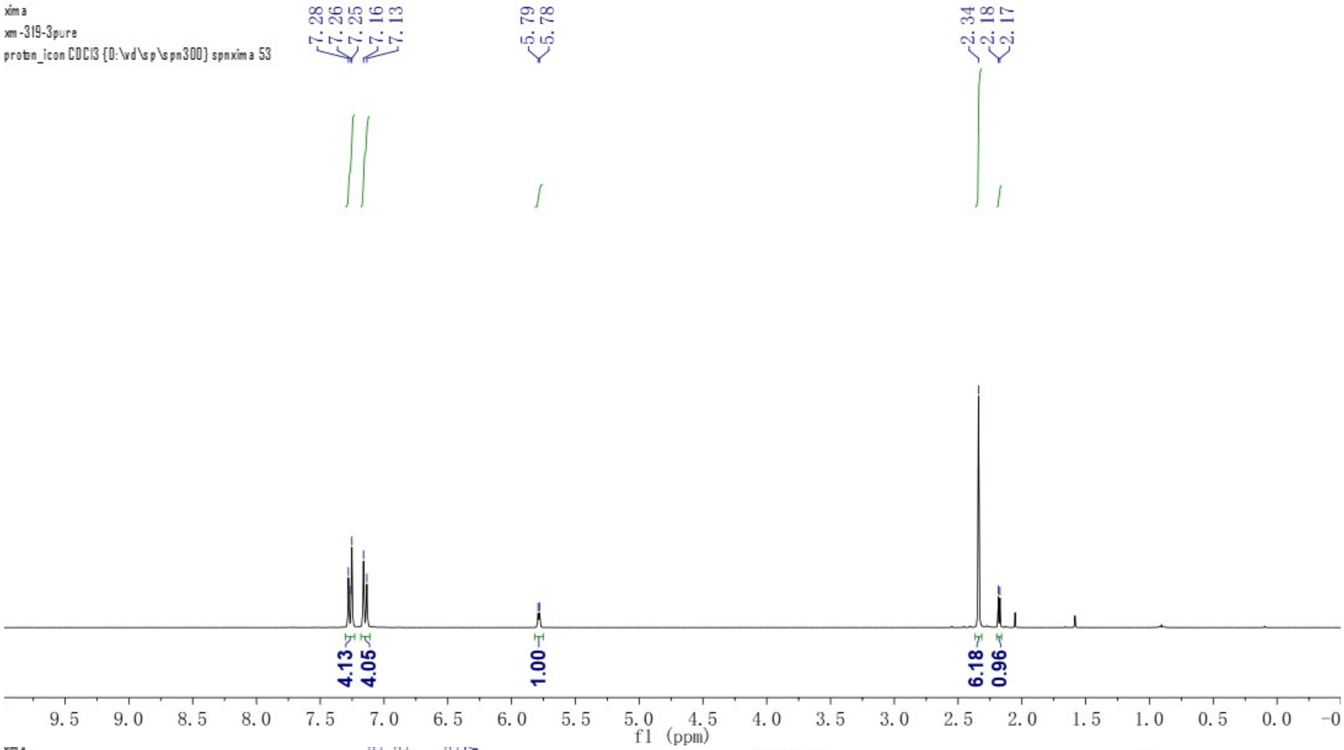


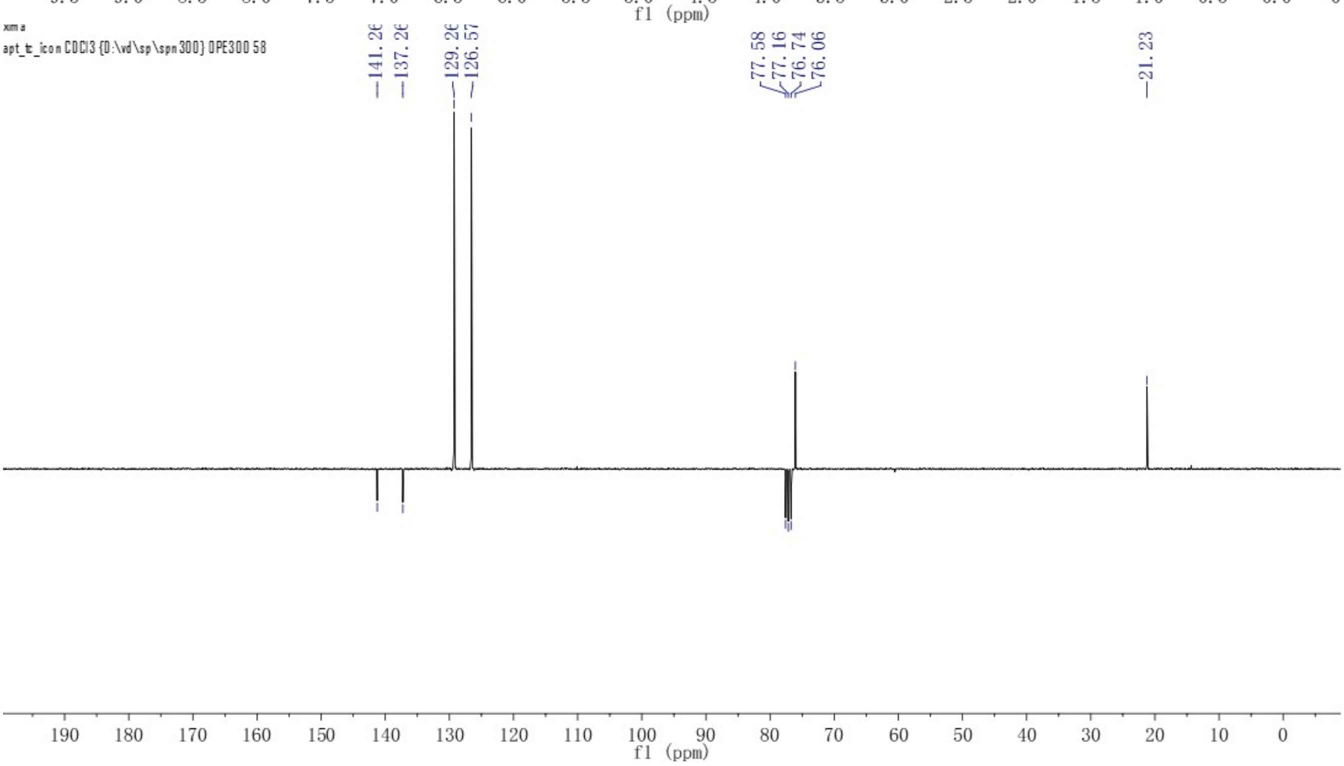


^{1}H and ^{13}C {1H} apt NMR of Diphenylmethanol (**6d**)

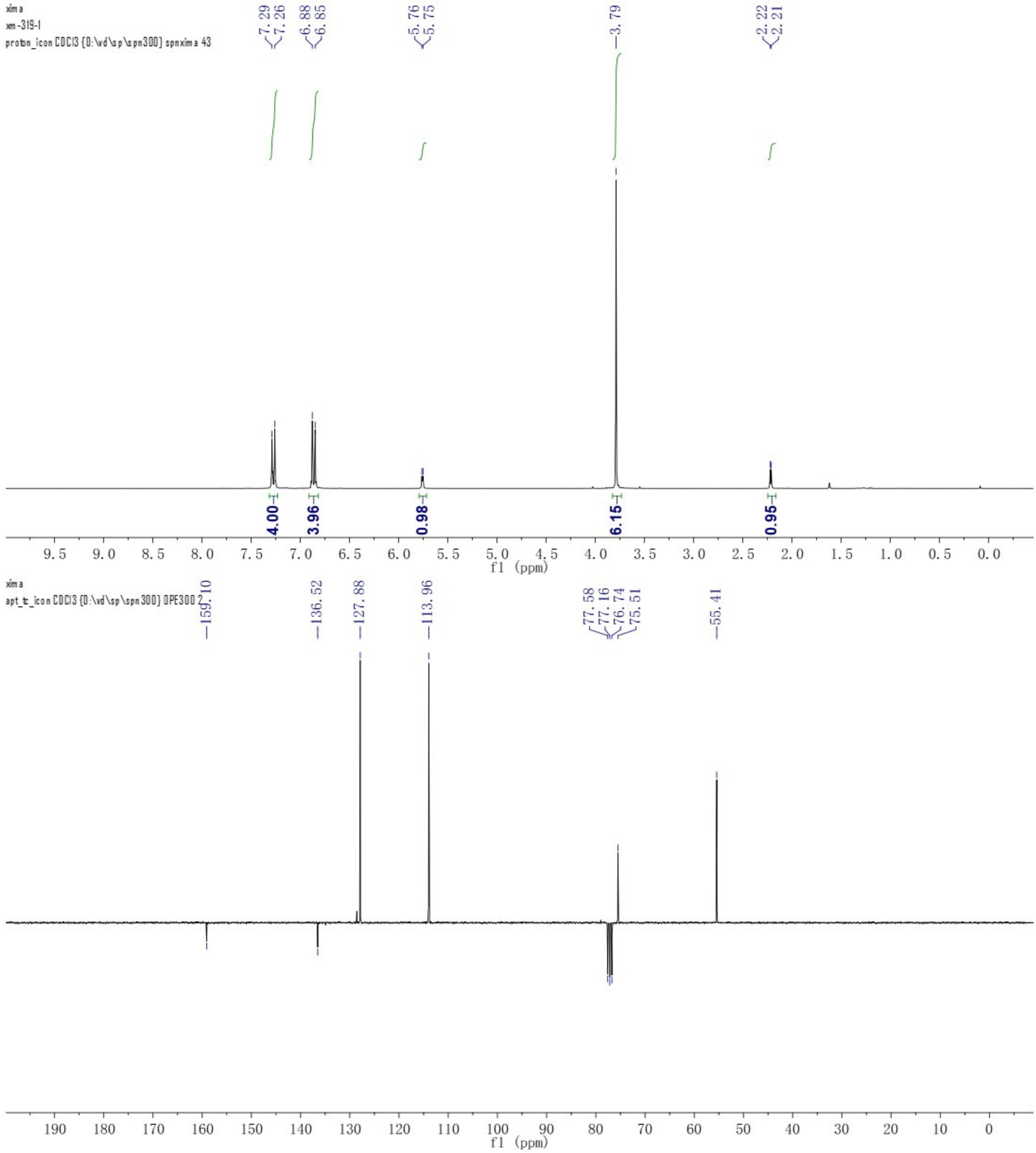


[1]H and [13]C {1H} apt NMR of 4,4'-Dimethylbenzhydrol (**6e**)

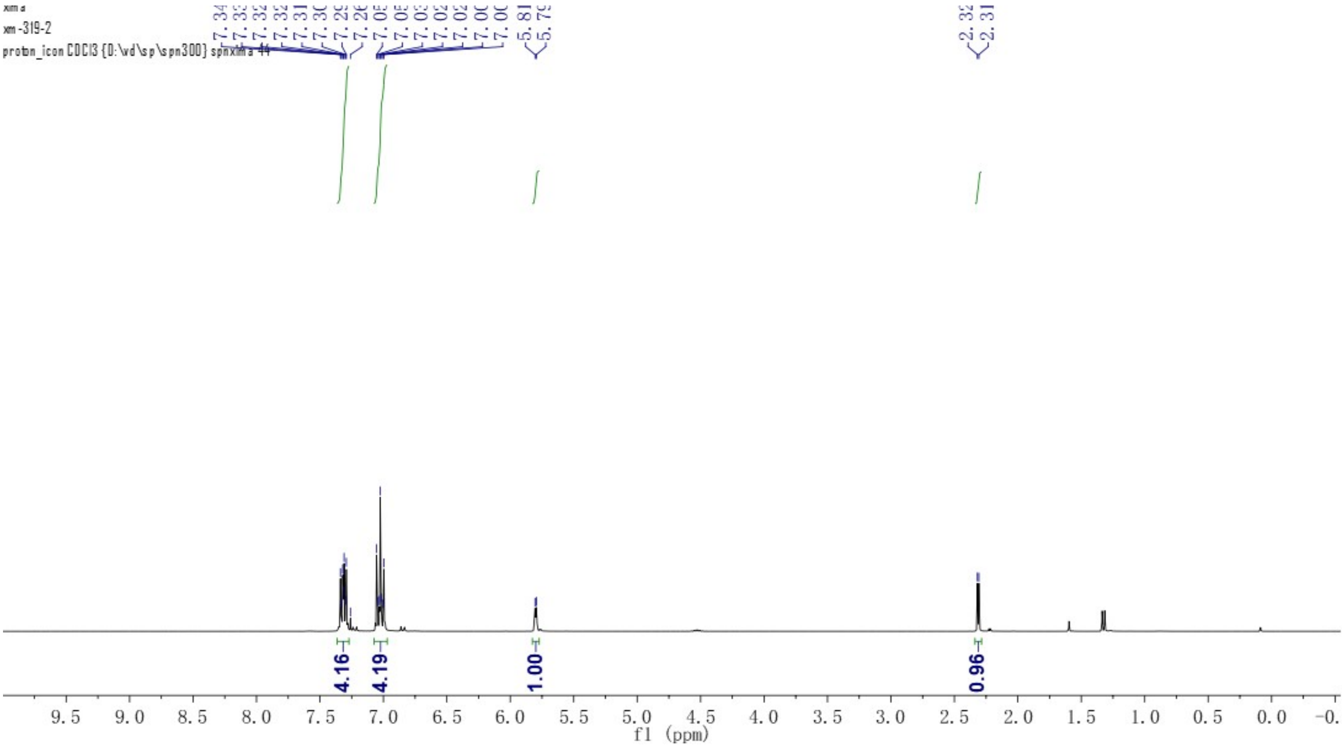


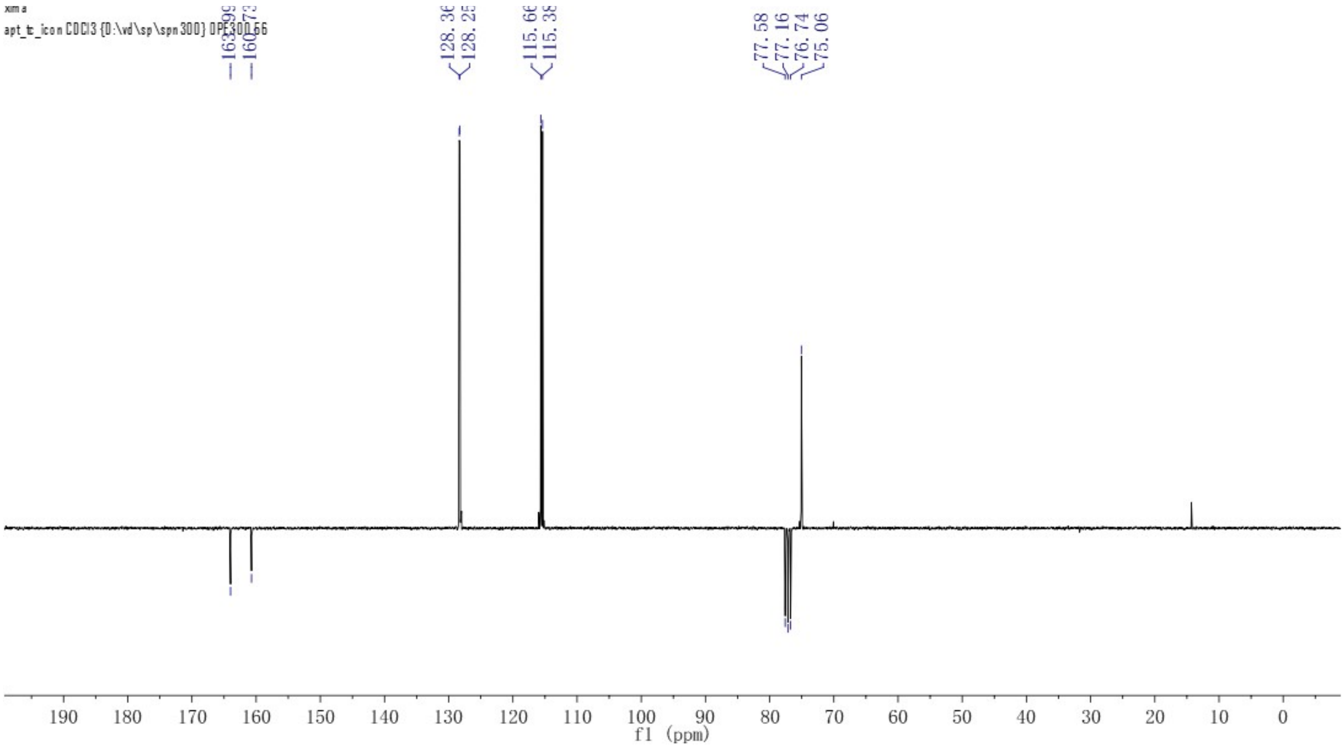


^{1}H and ^{13}C {1H} apt NMR of 4,4'-Dimethoxylbenzhydrol (**6f**)



^{1}H and ^{13}C {1H} apt NMR of 4, 4’-Difluorobenzhydrol (**6g**)





References

1. O. D. Bakulina, M. Yu. Ivanov, S. A. Prikhod'ko, S. Pylaeva, I. V. Zaytseva, N. V. Surovtsev, N. Y. Adonin and M. V. Fedin, *Nanoscale*, **2020**, *12*, 19982–19991.